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Experimental data

General remarks

General information. All manipulations were carried out under an argon atmosphere using standard Schlenk techniques and gloveboxes. *n*-pentane and *n*-hexane were dried using a M. Braun – Solvent Purification System (SPS). 1,2-Difluorobenzene was distilled from CaH_2 and P_2O_5 and stored in a dry box. All other solvents were distilled from sodium or potassium. All solvents were subsequently degassed by 3 × freeze/pump/thaw. $[2,6\text{-}Trip_2C_6H_3SnH]_2$, $[2,6\text{-}Trip_2C_6H_3PbH]_2$, $[2,6\text{-}Trip_2C_6H_3Sn][Al(OC\{CF_3\}_3)_4]$, $[Ph_3C][Al(OC\{CF_3\}_3)_4]$, $[Cp_2TaH_3]$ and $[Cp_2ZrH_2]_2$, $[H(OEt_2)_2][B(3,5\text{-}\{CF_3\}_2C_6H_3)_4]$ (= $[H(OEt_2)_2][BAr^F]$), $[H(OEt_2)_2][Al(OC\{CF_3\}_3)_4]$, 1,3,4,5-tetramethylimidazol-2-ylidene (^{Me}NHC), $[Cp_2WHLi]_4$, $[Ar^*SnCl]_2$, $[Ar^*PbBr]_2$ were synthesized following literature procedures.[34, 43-46, 92-98] Further chemicals were purchased commercially and used as received. Elemental analyses were performed at the Institute of Inorganic Chemistry, University of Tübingen using a Vario MICRO EL analyzer.

NMR Spectroscopy

NMR spectra were recorded with either a Bruker Avance III HD 300 NanoBay spectrometer equipped with a 5 mm BBFO probe head and operating at 300.13 (^{1}H), 75.47 (^{13}C), 96.29 (^{11}B) and 111.92 (^{119}Sn) MHz, a Bruker AvanceII+400 NMR spectrometer equipped with a 5 mm QNP (quad nucleus probe) head and operating at 400.13 (^{1}H), 100.62 (^{13}C) and 376.48 (^{19}F) MHz, a Bruker AVII+ 500 NMR spectrometer with a variable temperature set up and a 5 mm TBO probe head and operating at 500.13 (^{1}H), 125.76 (^{13}C) and 104.63 MHz (^{207}Pb) MHz, a Bruker Avance III HDX 600 NMR spectrometer with a 5 mm Prodigy BBO cryo probe head operating at 600.13 (^{1}H) and 150.90 (^{13}C) MHz or a Bruker Avance III HDX 700 NMR spectrometer with a 5 mm Prodigy TCI cryo probe head operating at 700.29 (^{1}H) and 176.10 (^{13}C) MHz. Chemical shifts are reported in δ values in ppm relative to external TMS (^{1}H, ^{13}C), $SnMe_4$ (^{119}Sn) or $PbMe_4$ (^{207}Pb) referenced in most cases on the residual proton signal of the solvent C_6D_6 (^{1}H 7.15 ppm; ^{13}C 128.0 ppm). ^{19}F as well as ^{1}H and ^{13}C-spectra in toluene-d_8, benzene-d_6 were referenced using the chemical shift of the solvent ^{2}H resonance frequency and Ξ = 25.145020 % for ^{13}C, Ξ = 32.083974% for ^{11}B, Ξ = 94.094011 % for ^{19}F, Ξ = 37.290632 % for ^{119}Sn and Ξ = 20.920599 % for ^{207}Pb.[99] The multiplicity of the signals is abbreviated as s = singlet, d = doublet, t = triplet, quint = quintet, sept = septet and m = multiplet or unresolved. The proton and carbon signals were assigned by detailed analysis of ^{1}H, ^{13}C{^{1}H}, ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC and ^{13}C{^{1}H} DEPT-135 spectra. ^{1}H-^{183}W-HMQC NMR experiments were performed on a Bruker AVII+500 NMR spectrometer using 5 mm tubes with a 5 mm ATM probehead operating at 500.13 (^{1}H) and 20.84 MHz (^{183}W). In a first step, the ^{183}W resonance was located by monitoring the ^{1}H hydride multiplet and stepping the ^{183}W decoupler through the anticipated ^{183}W chemical shift range. In a second step, the exact ^{183}W chemical shift was established from a ^{1}H-^{183}W HMQC NMR experiment. For ^{183}W NMR the IUPAC reference standard with Ξ = 4.166387% has been used.[99]

Crystallography

X-ray data were collected with a Bruker Smart APEX II diffractometer with graphite-monochromated Mo Kα radiation or a Bruker APEX II Duo diffractometer with a Mo IμS microfocus tube. The programs used were Bruker's APEX2 v2011.8-0, including SAINT for data reduction. SADABS for absorption correction, and SHELXS for structure solution, as well as the WinGX suite of programs version 1.70.01 or the GUI ShelXle, including SHELXL for structure refinement.[100-104]

Synthesis

$[Ar^*Pb(C_6H_6)][Al(OC\{CF_3\}_3)_4]$ (**1b**). A solution of $[Ph_3C][Al(OC\{CF_3\}_3)_4]$ (29.2 mg, 24.2 µmol, 1.00 eq) in 1,2-difluorobenzene (1.0 mL) was added dropwise to a solution of $[Ar^*PbH]_2$ (20.0 mg, 14.5 µmol, 0.60 eq) in benzene (2.0 mL) at room temperature, upon which the reaction mixture turned red. All volatiles were removed *in vacuo* and the residue washed with pentane (3x 2.0 mL) to obtain **1b** as orange-brown powder (38.7 mg, 22.3 µmol, 92.4 %). Crystals suitable for X-ray analysis could be obtained from a concentrated benzene solution at room temperature after several days. **^{1}H-NMR** (600.13 MHz, C_6D_6 + 1,2-difluorobenzene): δ [ppm] 1.01 (d, 12H, *o*-CH(C$\underline{H}_3$)$_2$, $^3J_{HH}$= 6.8 Hz), 1.09 (d, 12H, *o*-CH(C$\underline{H}_3$)$_2$, $^3J_{HH}$= 7.0 Hz), 1.20 (d, 12H, *p*-CH(C$\underline{H}_3$)$_2$, $^3J_{HH}$= 7.0 Hz), 2.70 (sept, 4H, *o*-C$\underline{H}$(CH$_3$)$_2$, $^3J_{HH}$= 6.9 Hz), 2.83 (sept, 2H, *p*-C$\underline{H}$(CH$_3$)$_2$, $^3J_{HH}$= 6.9 Hz), 7.32 (s, 4H, *m*-C$_6\underline{H}_2$), 7.56 (t, 1H, *p*-C$_6\underline{H}_3$, $^3J_{HH}$= 7.5 Hz), 8.78 (d, 2H, *m*-C$_6\underline{H}_3$, $^3J_{HH}$= 7.5 Hz); **^{13}C-NMR** (150.90 MHz, C_6D_6 + 1,2-difluorobenzene): δ [ppm] 23.1 (*p*-CH(C$\underline{H}_3$)$_2$), 23.4 (*o*-CH(C$\underline{H}_3$)$_2$), 24.4 (*o*-CH(C$\underline{H}_3$)$_2$), 30.2 (*o*-C$\underline{H}$(C$\underline{H}_3$)$_2$), 34.3 (*p*-C$\underline{H}$(C$\underline{H}_3$)$_2$), 79.6 (br, Al[OC(CF$_3$)$_3$]$_4$), 121.8 (q, $^1J_{19F\text{-}13C}$ = 294 Hz, Al[OC(C$\underline{F}_3$)$_3$]$_4$), 122.4 (*m*-C$_6\underline{H}_2$), 128.9 (*p*-C$_6$H$_3$), 133.6 (*i*-C$_6\underline{H}_2$), 142.0 (*m*-C$_6$H$_3$), 144.9 (*o*-C$_6$H$_3$), 149.3 (*o*-C$_6\underline{H}_2$), 152.1 (*p*-C$_6\underline{H}_2$), 355.7 (Pb-*i*-C$_6$H$_3$);

^{19}F{^{1}H}-NMR (376.43 MHz, C_6D_6 + 1,2-difluorobenzene): δ [ppm] −75.1 (s). **^{207}Pb-NMR** (52.33 MHz, C_6D_6 + 1,2-difluorobenzene): δ [ppm] 8069.

[Cp_2TaH_2-Sn(H)Ar*][Al(OC{CF_3}$_3$)$_4$] (**2**). To a solution of [Ar*Sn(C_6H_6)][Al(OC{CF_3}$_3$)$_4$] **1a** (68.5 mg, 41.6 µmol, 1.00 eq) in 1,2-difluorobenzene (1.0 mL) was added at once a solution of Cp_2TaH_3 (13.1 mg, 41.6 µmol, 1.00 eq) in toluene (1.0 mL). The yellow-orange mixture was stirred for 1 h at rt and all volatiles were removed *in vacuo*. The resulting orange residue was redissolved in 1,2-difluorobenzene (0.4 mL) and layered with pentane (2.5 mL). After storing it for several days at −40 °C crystals suitable for X-ray analysis were obtained. Removal of the supernatant solution and drying *in vacuo* yields the product **2** as light orange powder (40.9 mg, 21.7 µmol, 52.2 %). **^{1}H-NMR** (500.13 MHz, C_6D_6 + 1,2-difluorobenzene): δ [ppm] −3.75 (d + satellites, 2H, $^{3}J_{HH}$ = ca. 1.4 Hz, $^{2}J_{119/117Sn-1H}$ = 300 Hz, Ta$\underline{H}_2$), 0.97 (d, 12H, $^{3}J_{HH}$ = 6.7 Hz, *o*-CH(C$\underline{H}_3$)$_2$), 1.18 (d, 12H, $^{3}J_{HH}$ = 6.9 Hz, *o*-CH(C$\underline{H}_3$)$_2$), 1.21 (d, 12H, $^{3}J_{HH}$ = 6.9 Hz, *p*-CH(C$\underline{H}_3$)$_2$), 2.80 (m, 6H, *p*/*o*-C$\underline{H}$(CH$_3$)$_2$), 4.46 (s, 10H, $C_5\underline{H}_5$), 7.12 (s, 4H, *m*-$C_6\underline{H}_2$), 7.29 (m, 2H, *m*-$C_6\underline{H}_3$), 7.33 (m, 1H, *p*-$C_6\underline{H}_3$), 15.55 (t + satellites, 1H, $^{3}J_{HH}$ = 1.7 Hz, $^{1}J_{119/117Sn-1H}$ = ca. 1040 Hz, Sn$\underline{H}$). **^{13}C{^{1}H}-NMR** (125.76 MHz, C_6D_6 + 1,2-difluorobenzene): δ [ppm] 21.7 (*o*-CH(C$\underline{H}_3$)$_2$), 23.5 (*p*-CH(C$\underline{H}_3$)$_2$), 25.7 (*o*-CH(C$\underline{H}_3$)$_2$), 30.6 (*o*-C$\underline{H}$(CH$_3$)$_2$), 34.4 (*p*-C$\underline{H}$(CH$_3$)$_2$), 88.4 ($\underline{C}_5H_5$), 121.9 (q, $^{1}J_{19F-13C}$ = 293 Hz, Al[OC($\underline{C}F_3$)$_3$]$_4$), 122.3 (*m*-$\underline{C}_6H_2$), 129.5 (*p*-$\underline{C}_6H_3$), 130.2 (*m*-$\underline{C}_6H_3$), 134.6 (*i*-$\underline{C}_6H_2$), 144.4 (*o*-$\underline{C}_6H_3$), 147.4 (*o*-$\underline{C}_6H_2$), 151.5 (*p*-$\underline{C}_6H_2$, superimposed by solvent signal), 159.1 (Sn-*ipso*-$\underline{C}_6H_3$). **^{19}F{^{1}H}-NMR** (376.48 MHz, C_6D_6 + 1,2-difluorobenzene): δ [ppm] −74.9 (s, $^{1}J_{19F-13C}$ = 291 Hz). **^{119}Sn-NMR** (111.92 MHz, C_6D_6 + 1,2-difluorobenzene): δ [ppm] 1161 (dt, $^{1}J_{119Sn-1H}$ = 1047 Hz, $^{2}J_{119Sn-1H}$ = 308 Hz). **IR** (KBr): 1818 cm^{-1}.

[(Cp_2WH_2)SnAr*][Al(OC{CF_3}$_3$)$_4$] (**3a**). A cold (−40 °C) solution of Cp_2WH_2 (7.0 mg, 22.3 µmol, 1.00 eq) in toluene (1.0 mL) was added dropwise to a cooled (−40 °C) solution of [Ar*Sn(C_6H_6)][Al(OC{CF_3}$_3$)$_4$] (36.7 mg, 22.3 µmol, 1.00 eq) in 1,2-difluorobenzene (1.0 mL). The solution turned deep pink and was allowed to warm to rt. After stirring for 15 min at rt all volatiles were removed *in vacuo* and the pink residue was washed with pentane (1x 2.0 mL). Crystallization is possible by layering a concentrated 1,2-difluorobenzene solution (0.3 mL) with pentane (2.5 mL) and storing it at −40 °C for several days (32.6 mg, 17.5 µmol, 78.5 %). However, the resulting plate-shaped pink crystals were not suitable for X-ray analysis. **^{1}H-NMR** (400.11 MHz, tol-d_8 + 1,2-difluorobenzene): δ [ppm] −10.83 (br, W$\underline{H}_2$), 1.00 (d, 12H, $^{3}J_{HH}$ = 6.6 Hz, *o*-CH(C$\underline{H}_3$)$_2$), 1.18 (d, 12H, $^{3}J_{HH}$ = 6.9 Hz, *p*-CH(C$\underline{H}_3$)$_2$), 1.22 (d, 12H, $^{3}J_{HH}$ = 6.9 Hz, *o*-CH(C$\underline{H}_3$)$_2$), 2.77 (sept, 2H, $^{3}J_{HH}$ = 6.9 Hz, *p*-C$\underline{H}$(CH$_3$)$_2$), 2.92 (sept, 4H, $^{3}J_{HH}$ = 6.7 Hz, *o*-C$\underline{H}$(CH$_3$)$_2$), 4.22 (br, 10H, $C_5\underline{H}_5$), 7.08 (s, 4H, *m*-$C_6\underline{H}_2$), 7.31 – 7.40 (m, 3H, *m*/*p*-$C_6\underline{H}_3$).

At lower temperature (< 0 °C) separation into two isomers is observable. A symmetric (main) and asymmetric (minor) isomer is present in a ratio of approximately 2:1 at −20 °C, determinable by integration of the C_5H_5 or hydride resonances. The terphenyl ligands show signal broadening and are indistinguishable for the two isomers. Both isomers are also observable in the ^{1}H-^{183}W-HMQC and ^{199}Sn NMR and show exchange at −20 °C in the ^{1}H-^{1}H-EXSY NMR. **^{1}H-NMR** (500.13 MHz, tol-d_8 + 1,2-difluorobenzene, −20 °C): δ [ppm] −11.13 (s + satellites, $^{1}J_{183W-1H}$ = 51 Hz, minor asymmetric isomer, W-$\underline{H}$), −10.86 (s + satellites, $^{1}J_{183W-1H}$ = 78 Hz, main symmetric isomer, W$\underline{H}_2$), −8.57 (s + satellites, $^{1}J_{183W-1H}$ = 77 Hz, minor asymmetric isomer, W(µ-$\underline{H}$)Sn), 3.99 (s, $C_5\underline{H}_5$, minor asymmetric isomer), 4.19 (s, $C_5\underline{H}_5$, main symmetric isomer). **^{13}C{^{1}H}-NMR** (125.76 MHz, tol-d_8 + 1,2-difluorobenzene, 0 °C): δ [ppm] 22.2 (br, *o*-CH(C$\underline{H}_3$)$_2$), 23.8 (*p*-CH(C$\underline{H}_3$)$_2$), 27.0 (br, *o*-CH(C$\underline{H}_3$)$_2$), 31.6 (br, *o*-C$\underline{H}$(CH$_3$)$_2$), 34.6 (*p*-C$\underline{H}$(CH$_3$)$_2$), 122.1 (br, *m*-$\underline{C}_6H_2$), 122.2 (q, $^{1}J_{19F-13C}$ = 293 Hz, Al[OC($\underline{C}F_3$)$_3$]$_4$), 128.7 (overlapped by solvent signal, *p*-$\underline{C}_6H_3$), 131.5 (*m*-$\underline{C}_6H_3$), 145.2 (*o*-$\underline{C}_6H_3$), 147.3 (br, *o*-$\underline{C}_6H_2$), 148.0 (*i*-$\underline{C}_6H_2$), 150.7 (*p*-$\underline{C}_6H_2$), 174.1 (Sn-*ipso*-$\underline{C}_6H_3$). **^{19}F{^{1}H}-NMR** (376.48 MHz, tol-d_8 + 1,2-difluorobenzene): δ [ppm] −80.0 (s, $^{1}J_{19F-13C}$ = 289 Hz). **^{119}Sn-NMR** (111.92 MHz, tol-d_8 + 1,2-difluorobenzene): δ [ppm] 1786 (t, $^{2}J_{119Sn-1H}$ = ca. 270 Hz, main symmetric isomer), 1735 (m, minor asymmetric isomer). **^{183}W-NMR** (20.84 MHz, tol-d_8 + 1,2-difluorobenzene, −40 °C): δ [ppm] −3910 (main symmetric isomer), −4309 (minor asymmetric isomer). **IR** (KBr): ν W-H not observed.

[(Cp_2WH_2)PbAr*][WCA] (**3b**). *Variant A* ([WCA]$^-$ = [Al(OC{CF_3}$_3$)$_4$]$^-$): To a solution of [Ar*Pb(C_6H_6)][Al(OC{CF_3}$_3$)$_4$] **1b** (37.6 mg, 21.7 µmol, 1.00 eq) in 1,2-difluorobenzene (1.0 mL) was added at once a solution of Cp_2WH_2 (7.5 mg, 23.9µmol, 1.10 eq)in toluene (1.0 mL). The solution turned immediately deep purple and was stirred for 15 min at rt. All volatiles were removed *in vacuo* and the residue was washed with pentane (3x 2.0 mL), to remove excess Cp_2WH_2. After drying *in vacuo,* the product **3b** was obtained as purple powder (41.3 mg, 20.9 µmol, 96.3 %). Crystallization is possible by layering a concentrated 1,2-difluorobenzene solution (0.3 mL) with pentane (2.5 mL) and storing it at −40 °C for several days (31.8 mg, 16.1 µmol, 74.3 %). However, the resulting plate-shaped purple crystals were not suitable for X-ray analysis. *Variant B* ([WCA]$^-$ = [BAr^F]$^-$): A cold (−40 °C) solution of [Cp_2W(H)-PbAr*] **5b** (32.7 mg, 32.6 µmol, 1.10 Eq.) in pentane (2.0 mL) was treated dropwise with a cold solution of [H(Et_2O)$_2$][BAr^F] (30.0 mg, 29.6 µmol, 1.00 Eq.) in 1,2-difluorobenzene (1.0 mL) and was stirred for 1 h without further cooling. All volatiles were removed *in vacuo* and the residue was washed with pentane (4 × 2.0 mL). The resulting residue was dried *in vacuo* to yield the product [(Cp_2WH_2)PbAr*][BAr^F] (**3b**) as lilac powder (47.4 mg, 25.4 µmol, 85.6 %). Analytical data for (**3b**)-[Al(OC{CF_3}$_3$)$_4$]: **^{1}H-NMR** (700.29 MHz, tol-d_8 + 1,2-difluorobenzene): δ [ppm] −7.55 (br, W$\underline{H}_2$), 1.03 (d, 12H,

$^3J_{HH}$ = 6.6 Hz, *o*-CH(C$\underline{H}_3$)$_2$), 1.23 (d, 12H, $^3J_{HH}$ = 6.9 Hz, *p*-CH(C$\underline{H}_3$)$_2$), 1.26 (d, 12H, $^3J_{HH}$ = 6.9 Hz, *o*-CH(C$\underline{H}_3$)$_2$), 2.82 (sept, 2H, $^3J_{HH}$ = 6.9 Hz, *p*-C$\underline{H}$(CH$_3$)$_2$), 2.94 (sept, 4H, $^3J_{HH}$ = 6.8 Hz, *o*-C$\underline{H}$(CH$_3$)$_2$), 4.21 (s, 10H, C$_5\underline{H}_5$), 7.01 (s, 4H, *m*-C$_6\underline{H}_2$), 7.54 (t, 1H, $^3J_{HH}$ = 7.6 Hz, *p*-C$_6\underline{H}_3$), 7.99 (d, 2H, $^3J_{HH}$ = 7.6 Hz, *m*-C$_6\underline{H}_3$).

At lower temperature (< −20 °C) separation into two isomers is observable. A symmetric (main) and asymmetric (minor) isomer is present in a ratio of approximately 3:1 at −40 °C, determinable by integration of the C_5H_5 or hydride resonances. The terphenyl ligands show signal broadening and are indistinguishable for the two isomers. Both isomers are also observable in the ^{1}H-^{183}W-HMQC NMR and show exchange at −40 °C in the ^{1}H-^{1}H-EXSY NMR. **^{1}H-NMR** (500.13 MHz, tol-d$_8$ + 1,2-difluorobenzene, −40 °C): δ [ppm] −12.31 (s +satellites, 1H, $^1J_{183W-1H}$ = ca. 52 Hz, minor asymmetric isomer, W-$\underline{H}$), −7.49 (s + satellites, 2H, $^1J_{183W-1H}$ = 75 Hz, main symmetric isomer, W$\underline{H}_2$), −4.30 (s +satellites, 1H, $^1J_{183W-1H}$ = ca. 76 Hz, minor asymmetric isomer, W(μ-$\underline{H}$)Pb), 1.04 (br, 12H, *o*/*p*-CH(C$\underline{H}_3$)$_2$), 1.26 (br m, 24H, *o*/*p*-CH(C$\underline{H}_3$)$_2$), 2.80 (m, 2H, *p*-C$\underline{H}$(CH$_3$)$_2$), 2.85 – 3.04 (m, 4H, *o*-C$\underline{H}$(CH$_3$)$_2$), 4.02 (s, C$_5\underline{H}_5$, minor isomer), 4.17 (s, C$_5\underline{H}_5$ main isomer), 7.17 (m, 4H, *m*-C$_6\underline{H}_2$), 7.52 (m, 1H, *p*-C$_6\underline{H}_3$), 7.98 (m, 2H, *m*-C$_6\underline{H}_3$) **^{13}C{^{1}H}-NMR** (176.09 MHz, tol-d$_8$ + 1,2-difluorobenzene): δ [ppm] 21.6 (*o*-CH(C$\underline{H}_3$)$_2$), 23.0 (*p*-CH(C$\underline{H}_3$)$_2$), 26.1 (*o*-CH(C$\underline{H}_3$)$_2$), 30.3 (*o*-C$\underline{H}$(CH$_3$)$_2$), 33.7 (*p*-C$\underline{H}$(CH$_3$)$_2$), 79.0 (br, Al[OC$\underline{(CF_3)_3}]_4$), 81.2 (C$_5\underline{H}_5$), 121.2 (*m*-C$_6\underline{H}_2$), 121.3 (q, $^1J_{19F-13C}$ = 293 Hz, Al[OC($\underline{C}$F$_3$)$_3$]$_4$), 125.6 (*p*-C$_6\underline{H}_3$), 132.8 (*i*-C$_6\underline{H}_2$), 138.9 (*m*-C$_6\underline{H}_3$), 145.2 (*o*-C$_6\underline{H}_3$), 146.3 (*o*-C$_6\underline{H}_2$), 149.6 (*p*-C$_6\underline{H}_2$), 267.8 (Pb-*ipso*-C$_6\underline{H}_3$). **^{19}F{^{1}H}-NMR** (376.48 MHz, tol-d$_8$ + 1,2-difluorobenzene): δ [ppm] −74.9 (s, $^1J_{19F-13C}$ = 291 Hz). **^{183}W-NMR** (20.84 MHz, tol-d$_8$ + 1,2-difluorobenzene, −40 °C): δ [ppm] −3994 (main isomer), −4259 (minor, asymmetric isomer). **^{207}Pb-NMR** (104.63 MHz, C$_6$D$_6$ + 1,2-difluorobenzene): δ [ppm] 7986 (s). **IR** (KBr): ν W-H not observed. Analytical data for (**3b**)-[BAr^F]: **^{1}H-NMR** (400.11 MHz, C$_6$D$_6$ + 1,2-difluorobenzene): δ [ppm] −7.76 (br, W$\underline{H}_2$), 1.03 (d, 12H, $^3J_{HH}$ = 6.6 Hz, *o*-CH(C$\underline{H}_3$)$_2$), 1.16 (d, 12H, $^3J_{HH}$ = 7.0 Hz, *p*-CH(C$\underline{H}_3$)$_2$), 1.18 (d, 12H, $^3J_{HH}$ = 7.0 Hz, *o*-CH(C$\underline{H}_3$)$_2$), 2.76 (sept, 2H, $^3J_{HH}$ = 6.9 Hz, *p*-C$\underline{H}$(CH$_3$)$_2$), 2.89 (sept, 4H, $^3J_{HH}$ = 6.8 Hz, *o*-C$\underline{H}$(CH$_3$)$_2$), 4.01 (s, 10H, C$_5\underline{H}_5$), 7.08 (s, 4H, *m*-C$_6\underline{H}_2$), 7.47 (t, 1H, $^3J_{HH}$ = 7.6 Hz, *p*-C$_6\underline{H}_3$), 7.63 (br s, 4H, *p*-[BAr^F]), 7.95 (d, 2H, $^3J_{HH}$ = 7.6 Hz, *m*-C$_6\underline{H}_3$), 8.31 (br s, 8H, *o*-[BAr^F]). **^{13}C{^{1}H}-NMR** (100.61 MHz, C$_6$D$_6$ + 1,2-difluorobenzene): δ [ppm] 22.1 (*o*-CH($\underline{C}$H$_3$)$_2$), 23.4 (*p*-CH($\underline{C}$H$_3$)$_2$), 26.7 (*o*-CH($\underline{C}$H$_3$)$_2$), 30.8 (*o*-$\underline{C}$H(CH$_3$)$_2$), 34.2 (*p*-$\underline{C}$H(CH$_3$)$_2$), 81.5 (C$_5\underline{H}_5$), 117.6 (br, *p*-[BAr^F]), 121.8 (*m*-C$_6\underline{H}_2$), 124.8 (q, $^1J_{F-C}$ = 272 Hz, [BAr^F-$\underline{C}$F$_3$]), 126.2 (*p*-C$_6\underline{H}_3$), 129.5 (br q, $^2J_{19F-13C}$ = ca. 32 Hz, *m*-[BAr^F]), 133.3 (*i*-C$_6\underline{H}_2$), 135.0 (br, *o*-[BAr^F]), 139.5 (*m*-C$_6\underline{H}_3$), 145.7 (*o*-C$_6\underline{H}_3$), 146.8 (*o*-C$_6\underline{H}_2$), 150.1 (*p*-C$_6\underline{H}_2$), 162.3 (q, $^1J_{13C-11B}$ = 50 Hz, *i*-[BAr^F]), 268.4 (Pb-*i*-C$_6\underline{H}_3$). **^{11}B-NMR** (96.29 MHz, C$_6$D$_6$ + 1,2-difluorobenzene): δ [ppm] −6.0 (s, [$\underline{B}$Ar^F]). **^{19}F{^{1}H}-NMR** (376.48 MHz, C$_6$D$_6$ + 1,2-difluorobenzene): δ [ppm] −62.2 (s, $^1J_{19F-13C}$ = 272 Hz, [BAr^F-$\underline{C}$F$_3$]). **^{207}Pb-NMR** (62.79 MHz, C$_6$D$_6$ + 1,2-difluorobenzene): δ [ppm] 7959 (s). **Elemental analysis** calcd (%) for $C_{78}H_{73}BF_{24}PbW$: C 50.15, H 3.94; found C 50.17, H 4.36.

[Cp$_2$W(H)=Sn(H)Ar*][WCA] (**4a**). *Variant A* ([WCA]$^-$ = [Al(OC{CF$_3$}$_3$)$_4$]$^-$): To a solution of [Ar*Sn(C$_6$H$_6$)][Al(OC{CF$_3$}$_3$)$_4$] **1a** (36.7 mg, 22.3 μmol, 1.00 eq) in 1,2-difluorobenzene (1.0 mL) was added at once a solution of Cp$_2$WH$_2$ (7.8 mg, 24.5 μmol, 1.10 eq) in toluene (1.0 mL) and NEt$_2$Me (ca. 55-80 μl, ca. 36 mg, ca. 0.450-0.670 mmol, ca. 20-30 eq). The pink solution turned orange after stirring the mixture for 1 h at rt. All volatiles were removed *in vacuo* and the orange residue was washed with pentane (3x 2.0 mL). After short drying *in vacuo* the product [Cp$_2$W(H)=Sn(H)Ar*][Al(OC{CF$_3$}$_3$)$_4$] **4a** was obtained as orange powder (40.6 mg, 21.7 μmol, 97.3 %). Crystals suitable for X-ray analysis were obtained by layering a concentrated 1,2-difluorobenzene solution (0.4 mL) with pentane (2.5 mL) and storing it at −40 °C for several days (29.2 mg, 15.5 μmol, 69.5 %). *Variant B* ([WCA]$^-$ = [BAr^F]$^-$): A cold (−40 °C) solution of [Cp$_2$W(H)-SnAr*] **5a** (22.1 mg, 24.2 μmol, 1.20 Eq.) in pentane (2.0 mL) was treated dropwise with a cold solution of [H(Et$_2$O)$_2$][BAr^F] (20.4 mg, 20.1 μmol, 1.00 Eq.) in 1,2-difluorobenzene (1.0 mL) and was stirred for 1 h without further cooling. All volatiles were removed *in vacuo* and the residue was washed with pentane (4 × 2.0 mL). The resulting residue was dried *in vacuo* to yield the product [Cp$_2$W(H)=Sn(H)Ar*][BAr^F] **4a** as orange powder (31.3 mg, 18.1 μmol, 90.0 %). Analytical data for (**4a**)-[Al(OC{CF$_3$}$_3$)$_4$]: **^{1}H-NMR** (600.13 MHz, C$_6$D$_6$ + 1,2-difluorobenzene): δ [ppm] −12.57 (s + satellites, 1H, $^1J_{183W-1H}$ = ca. 67 Hz, $^2J_{119/117Sn-1H}$ = ca. 120 Hz, Cp$_2$W$\underline{H}$), 0.98 (d, 12H, $^3J_{HH}$ = 6.7 Hz, *o*-CH(C$\underline{H}_3$)$_2$), 1.18 (d, 12H, $^3J_{HH}$ = 6.9 Hz, *p*-CH(C$\underline{H}_3$)$_2$), 1.18 (d, 12H, $^3J_{HH}$ = 6.9 Hz, *o*-CH(C$\underline{H}_3$)$_2$), 2.79 (m, 6H, *o*-/*p*-C$\underline{H}$(CH$_3$)$_2$), 4.03 (s, 10H, C$_5\underline{H}_5$), 7.08 (s, 4H, *m*-C$_6\underline{H}_2$), 7.27 – 7.30 (m, 2H, *m*-C$_6\underline{H}_3$), 7.33 (m, 1H, *p*-C$_6\underline{H}_3$), 15.13 (s + satellites, $^2J_{183W-1H}$ = ca. 32 Hz, $^1J_{119/117Sn-1H}$ = ca. 1165 Hz, Sn$\underline{H}$). At 300 MHz better distinguishable satellites: **^{1}H-NMR** (300.13 MHz, C$_6$D$_6$ + 1,2-difluorobenzene): δ [ppm] −12.57 (m + satellites, 1H, $^1J_{183W-1H}$ = ca. 67 Hz, $^2J_{119/117Sn-1H}$ = ca. 129 Hz, Cp$_2$W$\underline{H}$), 15.13 (d + satellites, $^3J_{HH}$ = 0.9 Hz, $^2J_{183W-1H}$ = ca. 32 Hz, $^1J_{119Sn-1H}$ = 1193 Hz, $^1J_{117Sn-1H}$ = 1141 Hz, Sn$\underline{H}$). **^{13}C{^{1}H}-NMR** (150.90 MHz, C$_6$D$_6$ + 1,2-difluorobenzene): δ [ppm] 21.8 (*o*-CH($\underline{C}$H$_3$)$_2$), 23.5 (*p*-CH($\underline{C}$H$_3$)$_2$), 25.9 (*o*-CH($\underline{C}$H$_3$)$_2$), 30.6 (*o*-$\underline{C}$H(CH$_3$)$_2$), 34.4 (*p*-$\underline{C}$H(CH$_3$)$_2$), 76.8 (C$_5\underline{H}_5$), 79.7 (br, Al[O$\underline{C}$(CF$_3$)$_3$]$_4$), 121.9 (q, $^1J_{19F-13C}$ = 293 Hz, Al[OC($\underline{C}$F$_3$)$_3$]$_4$), 122.0 (*m*-C$_6\underline{H}_2$), 129.3 (*p*-C$_6\underline{H}_3$), 130.3 (*m*-C$_6\underline{H}_3$), 134.5 (*i*-C$_6\underline{H}_2$), 144.5 (*o*-C$_6\underline{H}_3$), 147.7 (*o*-C$_6\underline{H}_2$), 151.2 (*p*-C$_6\underline{H}_2$), 157.9 (s + satellites, $^1J_{119/117Sn-13C}$ = ca. 16 Hz, Sn-*i*-C$_6\underline{H}_3$). **^{19}F{^{1}H}-NMR** (376.48 MHz, tol-d$_8$ + 1,2-difluorobenzene): δ [ppm] −74.9 (s, $^1J_{19F-13C}$ = 292 Hz). **^{119}Sn-NMR** (111.92 MHz, C$_6$D$_6$ + 1,2-difluorobenzene): δ [ppm] 1057 (dd, $^1J_{119Sn-1H}$ = 1199 Hz, $^2J_{119Sn-1H}$ = 131 Hz, $^1J_{183W-119Sn}$ = ca. 1350 Hz). **^{183}W-NMR** (20.84 MHz, C$_6$D$_6$ + 1,2-difluorobenzene): δ [ppm] −3629. **IR** (KBr): 1954, 1823 cm^{-1} (ν Sn-H, ν W-H).Analytical data for (**4a**)-[BAr^F]: **^{1}H-NMR** (400.11 MHz, C$_6$D$_6$ + 1,2-difluorobenzene): δ

[ppm] −12.66 (s + satellites, 1H, $^{1}J_{183W\text{-}1H}$ = ca. 67 Hz, $^{2}J_{119/117Sn\text{-}1H}$ = ca. 123 Hz, $Cp_2W\underline{H}$), 0.97 (d, 12H, $^{3}J_{HH}$ = 6.8 Hz, *o*-CH(C$\underline{H}_3$)$_2$), 1.14 (d, 24H, *o*+*p*-CH(C$\underline{H}_3$)$_2$), 2.70 – 2.82 (m, 6H, *o*+*p*-C$\underline{H}$(CH$_3$)$_2$), 3.93 (s, 10H, $C_5\underline{H}_5$), 7.05 (s, 4H, *m*-$C_6\underline{H}_2$), 7.25 – 7.33 (m, 3H, *m*+*p*-$C_6\underline{H}_3$), 7.63 (br s, 4H, *p*-[BAr^F]), 8.31 (br s, 8H, *o*-[BAr^F]), 15.10 (s + satellites, $^{2}J_{183W\text{-}1H}$ = ca. 32 Hz, $^{1}J_{119Sn\text{-}1H}$ = ca. 1195 Hz, $^{1}J_{117Sn\text{-}1H}$ = ca. 1149 Hz, Sn$\underline{H}$). **^{13}C{^{1}H}-NMR** (150.90 MHz, C_6D_6 + 1,2-difluorobenzene): δ [ppm] 21.8 (*o*-CH(C$\underline{H}_3$)$_2$), 23.5 (*p*-CH(C$\underline{H}_3$)$_2$), 25.9 (*o*-CH(C$\underline{H}_3$)$_2$), 30.6 (*o*-C$\underline{H}$(CH$_3$)$_2$), 34.4 (*p*-C$\underline{H}$(CH$_3$)$_2$), 76.7 ($C_5\underline{H}_5$), 117.6 (br, *p*-[BAr^F]), 122.0 (*m*-$C_6\underline{H}_2$), 124.9 (q, $^{1}J_{19F\text{-}13C}$ = 272 Hz, [BAr^F-$\underline{C}F_3$]) 129.4 (*p*-$C_6\underline{H}_3$), 129.5 (br q, $^{2}J_{19F\text{-}13C}$ = ca. 32 Hz, *m*-[BAr^F]), 130.3 (*m*-$C_6\underline{H}_3$), 134.5 (*i*-$C_6\underline{H}_2$), 135.0 (br, *o*-[BAr^F]), 144.5 (*o*-$C_6\underline{H}_3$), 147.7 (*o*-$C_6\underline{H}_2$), 151.2 (*p*-$C_6\underline{H}_2$), 157.7 (Sn-*i*-$C_6\underline{H}_3$), 162.4 (q, $^{1}J_{C\text{-}B}$ = 50 Hz, *i*-[BAr^F]). **^{11}B-NMR** (96.29 MHz, C_6D_6 + 1,2-difluorobenzene): δ [ppm] −6.0 (s, [$\underline{B}$Ar^F]). **^{19}F{^{1}H}-NMR** (376.48 MHz, C_6D_6 + 1,2-difluorobenzene): δ [ppm] −62.3 (s, $^{1}J_{19F\text{-}13C}$ = 272 Hz, [BAr^F-$\underline{C}F_3$]). **Elemental analysis** calcd (%) for $C_{78}H_{73}BF_{24}SnW$: C 52.64, H 4.13; found C 52.93, H 4.67.

[Cp_2W(H)-SnAr*] (**5a**). *Variant A*: A solution of [Cp_2WH=Sn(H)Ar*][Al(OC{CF_3}$_3$)$_4$] **4a** (155.7 mg, 82.6 µmol, 1.00 eq) in toluene/1,2-difluorobenzene (1:1, 3 mL) was treated with a solution of 1,3,4,5-tetramethylimidazol-2-ylidene (^{Me}NHC) (10.3 mg, 82.6 µmol, 1.00 eq) in toluene (1 mL). The orange solution turns yellow and was stirred for 3 days at 80 °C upon which a colourisation to dark green is visible. All volatiles were removed *in vacuo* and the dark green residue was extracted with pentane (4 mL). After filtration through a syringe filter the solvent was evaporated until incipient crystallisation and the solution stored at −40 °C. The product **5a** was obtained after removal of the supernatant solution and drying *in vacuo* as dark powder (33.8 mg, 36.9 µmol, 44.7 %). *Variant B*: A suspension of [Cp_2W(H)Li]$_4$ (25.0 mg, 19.4 µmol, 0.50 eq) in benzene (2 mL) was added dropwise to a solution of [Ar*SnCl]$_2$ (49.4 mg, 38.8 µmol, 1.00 eq) in benzene (2 mL) at room temperature. The mixture turns dark green and was stirred for 5 minutes. All volatiles were removed *in vacuo* and the residue was extracted with pentane (8 mL). Removing the solvent yields the product **5a** as dark-brown powder (68.2 mg, 74.5 µmol, 96.0 %). Crystals suitable for X-ray analysis could be obtained from a concentrated pentane (4.5 mL) solution at −40 °C. A second crop of crystals could be obtained by concentrating the mother liquor (43.8 + 13.8 mg, 62.9 µmol, 81.0 %). **^{1}H-NMR** (400.11 MHz, C_6D_6): δ [ppm] −12.37 (undecett + satellites, 1H, $^{1}J_{183W\text{-}1H}$ = 90 Hz, $^{3}J_{HH}$ = ca. 0.9 Hz, $Cp_2W\underline{H}$), 1.20 (d, 12H, $^{3}J_{HH}$ = 6.6 Hz, *o*-CH(C$\underline{H}_3$)$_2$), 1.22 (d, 12H, $^{3}J_{HH}$ = 7.0 Hz, *p*-CH(C$\underline{H}_3$)$_2$), 1.50 (d, 12H, $^{3}J_{HH}$ = 6.9 Hz, *o*-CH(C$\underline{H}_3$)$_2$), 2.78 (sept, 2H, $^{3}J_{HH}$ = 6.8 Hz, *p*-C$\underline{H}$(CH$_3$)$_2$), 3.41 (sept, 4H, $^{3}J_{HH}$ = 6.8 Hz, *o*-C$\underline{H}$(CH$_3$)$_2$), 3.87 (d, 10H, $^{3}J_{HH}$ = ca. 0.8 Hz, $C_5\underline{H}_5$), 7.13 (s, 4H, *m*-$C_6\underline{H}_2$), 7.37 (m, 3H, *m*/*p*-$C_6\underline{H}_3$). **^{13}C{^{1}H}-NMR** (75.47 MHz, C_6D_6): δ [ppm] 22.6 (*o*-CH(C$\underline{H}_3$)$_2$), 23.2 (*p*-CH(C$\underline{H}_3$)$_2$), 26.1 (*o*-CH(C$\underline{H}_3$)$_2$), 30.3 (*o*-C$\underline{H}$(CH$_3$)$_2$), 33.7 (*p*-C$\underline{H}$(CH$_3$)$_2$), 73.1 ($C_5\underline{H}_5$), 119.9 (*m*-$C_6\underline{H}_2$), 124.1 (*p*-$C_6\underline{H}_3$), 129.1 (*m*-$C_6\underline{H}_3$), 136.1 (*i*-$C_6\underline{H}_2$), 143.4 (*o*-$C_6\underline{H}_3$), 146.5 (*o*-$C_6\underline{H}_2$), 146.0 (*p*-$C_6\underline{H}_2$), 185.4 (Sn-*i*-$C_6\underline{H}_3$). **^{119}Sn-NMR** (111.92 MHz, C_6D_6): δ [ppm] 2883 (s, br). **^{183}W-NMR** (20.84 MHz, C_6D_6): δ [ppm] −4182. **IR** (KBr): ν W-H not observed. **Elemental analysis** calcd (%) for $C_{46}H_{60}SnW$: C 60.35, H 6.61; found C 60.43, H 6.73.

[Cp_2WH-PbAr*] (**5b**). *Variant A*: A solution of [(Cp_2WH_2)PbAr*][Al(OC{CF_3}$_3$)$_4$] **3b** (42.6 mg, 21.6 µmol, 1.00 eq) in toluene/1,2-difluorobenzene (1:1, 2 mL) was treated with a solution of 1,3,4,5-tetramethylimidazol-2-ylidene (^{Me}NHC) (2.5 mg, 20.1 µmol, 0.93 eq) in toluene (1 mL). The deep violet solution turns black and was stirred for 2 hours. All volatiles were removed *in vacuo* and the dark residue was extracted with pentane (4 mL). After filtration through a syringe filter the solvent was removed *in vacuo* to obtain the crude product **5b** (purity ca. 95 %, 17.4 mg, 17.3 µmol, 86.2 %) as black powder. Further purification is possible by crystallisation from pentane at −40 °C (9.8 mg, 9.8 µmol, 45 %). *Variant B*: A suspension of [Cp_2W(H)Li]$_4$ (25.0 mg, 19.4 µmol, 0.50 eq) in benzene (2 mL) was added dropwise to a solution of [Ar*PbBr]$_2$ (59.7 mg, 38.8 µmol, 1.00 eq) in benzene (2 mL) at room temperature. The mixture turns black and was stirred for 30 minutes. All volatiles were removed *in vacuo* and the residue was extracted with pentane (ca. 8 mL). Removing the solvent yields the crude product **5b** as black powder (purity > 98%, 74.7 mg, 74.4 µmol, 95.9 %). Crystals suitable for X-ray analysis could be obtained from a concentrated pentane solution at −40 °C. A second crop of crystals could be obtained by concentrating the mother liquor (26.7 +16.1 mg, 54.9 µmol, 54.9 %). **^{1}H-NMR** (400.11 MHz, C_6D_6): δ [ppm] −16.15 (undecett + satellites, 1H, $^{1}J_{183W\text{-}1H}$ = 91 Hz, $^{3}J_{HH}$ = ca. 0.9 Hz, $Cp_2W\underline{H}$), 1.19 (d, 12H, $^{3}J_{HH}$ = 6.8 Hz, *o*-CH(C$\underline{H}_3$)$_2$), 1.24 (d, 12H, $^{3}J_{HH}$ = 6.9 Hz, *p*-CH(C$\underline{H}_3$)$_2$), 1.50 (d, 12H, $^{3}J_{HH}$ = 6.9 Hz, *o*-CH(C$\underline{H}_3$)$_2$), 2.81 (sept, 2H, $^{3}J_{HH}$ = 6.9 Hz, *p*-C$\underline{H}$(CH$_3$)$_2$), 3.40 (sept, 4H, $^{3}J_{HH}$ = 6.8 Hz, *o*-C$\underline{H}$(CH$_3$)$_2$), 4.18 (d, 10H, $^{3}J_{HH}$ = ca. 0.9 Hz, $C_5\underline{H}_5$), 7.13 (s, 4H, *m*-$C_6\underline{H}_2$), 7.42 (t, 1H, $^{3}J_{HH}$ = 7.5 Hz, *p*-$C_6\underline{H}_3$), 7.66 (d, 2H, $^{3}J_{HH}$ = 7.5 Hz, *m*-$C_6\underline{H}_3$).**^{13}C{^{1}H}-NMR** (100.61 MHz, C_6D_6): δ [ppm] 24.0 (*o*-CH(C$\underline{H}_3$)$_2$), 24.1 (*p*-CH(C$\underline{H}_3$)$_2$), 26.8 (*o*-CH(C$\underline{H}_3$)$_2$), 31.2 (*o*-C$\underline{H}$(CH$_3$)$_2$), 34.5 ((*p*-C$\underline{H}$(CH$_3$)$_2$), 73.7 ($C_5\underline{H}_5$), 120.7 (*m*-$C_6\underline{H}_2$), 123.7 (*p*-$C_6\underline{H}_3$), 134.7 (*m*-$C_6\underline{H}_3$), 137.3 (*i*-$C_6\underline{H}_2$), 145.4 (*o*-$C_6\underline{H}_3$), 147.1 (*o*-$C_6\underline{H}_2$), 147.4 (*p*-$C_6\underline{H}_2$), 258.2 (Pb-*ipso*-$C_6\underline{H}_3$). **^{207}Pb-NMR** (104.63 MHz, C_6D_6): δ [ppm] 10534 (s, br). **^{183}W-NMR** (20.84 MHz, C_6D_6): δ [ppm] −2772. **IR** (KBr): ν W-H not observed. **Elemental analysis** calcd (%) for $C_{46}H_{60}PbW$: C 55.03, H 6.02; found C 55.18, H 6.07.

Protonation of [Cp_2WH-PbAr*] (**5b**): **3b** and [Cp_2W(H)=Pb(H)Ar*]$^+$ (**4b**). To a cold (−40 °C) solution [Cp_2WH-PbAr*] **5b** (15.0 mg, 14.9 µmol, 1.00 Eq.) in toluene-d_8 (0.2 mL), a cold solution of [H(Et_2O)$_2$][Al(OC{CF_3}$_3$)$_4$] (16.7 mg, 14.9 µmol, 1.00 Eq.) in toluene-d_8/1,2-difluorobenzene (1:1, 0.2 mL)was added dropwise. The resulting, deep purple reaction mixture was stirred for approximately 2 min at −40 °C and was transferred in a precooled Y. Joung NMR tube. The sample was stored in dry ice cooling (−78 °C) until nmr spectroscopic analysis (precooled nmr machine, −40 °C). Besides

starting material **5b** and product **3b**, the complex [$Cp_2W(H)$=Pb(H)Ar*][Al(OC{CF_3}$_3$)$_4$] **4b** can also be identified: **^{1}H-NMR** (500.13 MHz, tol-d_8 + 1,2-difluorobenzene, −40 °C): δ [ppm] −13.67 (s + satellites, $^1J_{183W\text{-}1H}$ = 66 Hz, W-H), 42.13 (s + satellites, $^1J_{207Pb\text{-}1H}$ = ca. 530 Hz, $^2J_{183W\text{-}1H}$ = 39 Hz, Pb-H).

[Cp_2WH-Sn(H)(^{Me}NHC)Ar*][Al(OC{CF_3}$_3$)$_4$] (**6**). A solution of [$Cp_2W(H)$=Sn(H)Ar*][Al(OC{CF_3}$_3$)$_4$] **4a** (36.0 mg, 19.1 µmol, 1.00 eq) in toluene/1,2-difluorobenzene (1:1, 1 mL) was treated dropwise with a solution of 1,3,4,5-tetramethylimidazol-2-ylidene (^{Me}NHC) (2.4 mg, 19.1 µmol, 1.00 eq) in toluene (1 mL). The orange solution turns yellow and all volatiles were removed *in vacuo*. The residue was washed with pentane (3x 2 mL) and dried *in vacuo* to obtain the product as yellow powder (35.8 mg, 17.8 µmol, 93.3 %). **^{1}H-NMR** (600.13 MHz, C_6D_6 + 1,2-difluorobenzene): δ [ppm] −13.82 (s + satellites, 1H, $^1J_{183W\text{-}1H}$ = 63 Hz, $^2J_{119/117Sn\text{-}1H}$ = 165 Hz, Cp_2WH), 0.94 (d, 6H, $^3J_{HH}$ = 6.7 Hz, *o*-CH(CH$_3$)$_2$), 0.98 (d, 6H, $^3J_{HH}$ = 6.7 Hz, *o*-CH(CH$_3$)$_2$), 1.03 (d, 6H, $^3J_{HH}$ = 6.7 Hz, *o*-CH(CH$_3$)$_2$), 1.11 (d, 6H, $^3J_{HH}$ = 6.9 Hz, *o*-CH(CH$_3$)$_2$), 1.28 (d, 6H, $^3J_{HH}$ = 6.9 Hz, *p*-CH(CH$_3$)$_2$), 1.28 (d, 6H, $^3J_{HH}$ = 6.9 Hz, *p*-CH(CH$_3$)$_2$), 1.56 (s, 6H, NHC-CH$_3$), 2.64 (m, 2H, *o*-CH(CH$_3$)$_2$), 2.78 (sept, 2H, $^3J_{HH}$ = 6.7 Hz, *o*-CH(CH$_3$)$_2$), 2.82 (s, 6H, N-CH$_3$), 2.87 (sept, 2H, $^3J_{HH}$ = 6.9 Hz, *p*-CH(CH$_3$)$_2$), 3.70 (s, 5H, C_5H_5), 4.01 (s, 5H, C_5H_5), 6.33 (s + satellites, 1H, $^1J_{119Sn\text{-}1H}$ = 1344 Hz, $^1J_{117Sn\text{-}1H}$ = 63 Hz $^2J_{183W\text{-}1H}$ = 1284 Hz, Sn-H), 7.03 – 7.08 (m, 4H, *m*-C_6H_2), 7.09 – 7.14 (m, 3H, *m*/*p*-C_6H_3). **^{13}C{^{1}H}-NMR** (150.90 MHz, C_6D_6 + 1,2-difluorobenzene): δ [ppm] 6.7 (NHC C-CH$_3$), 21.1 (*o*-CH(CH$_3$)$_2$), 21.4 (*o*-CH(CH$_3$)$_2$), 23.0 (*p*-CH(CH$_3$)$_2$), 23.2 (*p*-CH(CH$_3$)$_2$), 25.1 (*o*-CH(CH$_3$)$_2$), 25.1 (*o*-CH(CH$_3$)$_2$), 30.2 (*o*-CH(CH$_3$)$_2$), 30.2 (*o*-CH(CH$_3$)$_2$), 33.4 (NHC N-CH$_3$), 33.7 (*p*-CH(CH$_3$)$_2$), 73.6 (C_5H_5), 74.1 (C_5H_5), 78.9 (br, Al[OC(CF$_3$)$_3$]$_4$), 120.0 (*m*-C_6H_2), 120.2 (*m*-C_6H_2), 121.2 (q, $^1J_{19F\text{-}13C}$ = 293 Hz, Al[OC(CF$_3$)$_3$]$_4$), 126.2 (*p*-C_6H_3), 126.5 (NHC C-CH$_3$), 131.0 (s + satellites, $^3J_{119/117Sn\text{-}13C}$ = ca. 29 Hz, *m*-C_6H_3), 138.6 (*i*-C_6H_2), 141.2 (*o*-C_6H_3), 145.9 (*o*-C_6H_2), 146.3 (*o*-C_6H_2), 147.3 (s + satellites, *J* = ca. 34 Hz, Sn-*ipso*-C_6H_3), 148.4 (*p*-C_6H_2), 160.0 (s + satellites, $^1J_{119/117Sn\text{-}13C}$ = ca. 156 Hz, NHC C-Sn). **^{19}F{^{1}H}-NMR** (376.48 MHz, tol-d_8 + 1,2-difluorobenzene): δ [ppm] −75.0 (s, $^1J_{19F\text{-}13C}$ = 290 Hz). **^{119}Sn-NMR** (111.92 MHz, C_6D_6 + 1,2-difluorobenzene): δ [ppm] −230 (dd + satellites, $^1J_{119Sn\text{-}1H}$ = 1351 Hz, $^2J_{119Sn\text{-}1H}$ = 174 Hz, $^1J_{183W\text{-}119Sn}$ = ca. 1340 Hz). **^{119}Sn{^{1}H}-NMR** (111.92 MHz, C_6D_6/1,2-difluorobenzene): δ [ppm] −231 (s). **^{183}W-NMR** (20.84 MHz, C_6D_6 + 1,2-difluorobenzene): δ [ppm] −4378 (s +satellites, $^1J_{183W\text{-}119Sn}$ = 1332 Hz). **IR** (KBr): 1817 cm^{-1} (ν Sn-H / W-H).

[$Cp_2W(H)$-SnH_2Ar*] (**7**). To a mixture of [$Cp_2W(H)$=Sn(H)Ar*][Al(OC{CF_3}$_3$)$_4$] **4a** (60.3 mg, 32.0 µmol, 1.00 Eq.) and $LiAlH_4$ (1.2 mg, 32 µmol, 1.0 Eq.), Et_2O (1.0 mL) was added at once and the suspension stirred for approximately 1 min, upon which the solution quickly changes from orange to light yellow. All volatiles were removed under reduced pressure and the residue was resuspended in pentane (2.0 mL) and again dried *in vacuo* (2-3 times). The yellow residue was extracted with pentane (3.0 mL) and the filtered solution dried *in vacuo* to yield the product **7** as yellow powder (26.2 mg, 28.6 µmol, 89.3 %). Crystals suitable for X-ray analysis could be obtained from a concentrated hexane solution at −40 °C. **^{1}H-NMR** (400.11 MHz, C_6D_6): δ [ppm] −12.91 (br s + satellites, 1H, $^1J_{183W\text{-}1H}$ = 66 Hz, $^2J_{119/117Sn\text{-}1H}$ = ca. 134 Hz, Cp_2WH), 1.15 (d, 12H, $^3J_{HH}$ = 6.9 Hz, *o*-CH(CH$_3$)$_2$), 1.30 (d, 12H, $^3J_{HH}$ = 6.9 Hz, *p*-CH(CH$_3$)$_2$), 1.51 (d, 12H, $^3J_{HH}$ = 6.9 Hz, *o*-CH(CH$_3$)$_2$), 2.88 (sept, 2H, $^3J_{HH}$ = 6.9 Hz, *p*-CH(CH$_3$)$_2$), 3.10 (sept, 4H, $^3J_{HH}$ = 6.9 Hz, *o*-CH(CH$_3$)$_2$), 3.69 (s + satellites, 10H, $^2J_{183W\text{-}1H}$ = ca. 9 Hz, C_5H_5), 5.12 (d + satellites, $^3J_{HH}$ = ca. 1 Hz, $^1J_{119Sn\text{-}1H}$ = 1274 Hz, $^1J_{117Sn\text{-}1H}$ = 1216 Hz, $^2J_{183W\text{-}1H}$ = ca. 9 Hz, SnH_2), 7.23 (s, 4H, *m*-C_6H_2), 7.23 – 7.27 (m, 3H, *m*+*p*-C_6H_3). **^{13}C{^{1}H}-NMR** (100.61 MHz, C_6D_6): δ [ppm] 23.1 (*o*-CH(CH$_3$)$_2$), 24.7 (*p*-CH(CH$_3$)$_2$), 25.9 (*o*-CH(CH$_3$)$_2$), 30.8 (*o*-CH(CH$_3$)$_2$), 34.7 (*p*-CH(CH$_3$)$_2$), 73.6 (C_5H_5), 120.5 (*m*-C_6H_2), 125.5 (*p*-C_6H_3), 128.3 (*m*-C_6H_3), 141.2 (*i*-C_6H_2), 147.0 (*o*-C_6H_2), 147.3 (Sn-*i*-C_6H_3,), 147.8 (*p*-C_6H_2), 148.9 (*o*-C_6H_3). **^{119}Sn-NMR** (111.92 MHz, C_6D_6): δ [ppm] −236 (td + satellites, $^1J_{119Sn\text{-}1H}$ = 1273 Hz, $^2J_{119Sn\text{-}1H}$ = 134 Hz, $^1J_{183W\text{-}119Sn}$ = ca. 1110 Hz). **^{119}Sn{^{1}H}-NMR** (111.92 MHz, C_6D_6): δ [ppm] −236 (s). **^{183}W-NMR** (20.84 MHz, C_6D_6): δ [ppm] −3921. 1917 / 1772 cm^{-1} (Sn-H / W-H). **Elemental analysis** calcd (%) for $C_{46}H_{62}SnW$ C 60.22, H 6.81; found C 60.82, H 6.75.

[$Cp_2W(H)$=Sn(CH_2CH_2Ph)Ar*][Al(OC{CF_3}$_3$)$_4$] (**8**). To a solution of [$Cp_2W(H)$=Sn(H)Ar*][Al(OC{CF_3}$_3$)$_4$] **4a** (36.8 mg, 19.5 µmol, 1.00 Eq.) in 1,2-difluorobenzene (0.1 mL) and benzene (0.5 mL) styrene (ca. 50 mg, ca. 500 µmol, ca. 20 Eq.) was added and then heated to 75 °C for 24 h, upon which the initially orange solution turns red. All volatiles were removed *in vacuo* and the residue washed with pentane (4 × 1.5 mL). After drying *in vacuo* the product **8** was obtained as orange-red solid (32.5 mg, 16.4 µmol, 83.8 %). **^{1}H-NMR** (700.29 MHz, C_6D_6 + 1,2-difluorobenzene): δ [ppm] −12.51 (s + satellites, 1H, $^1J_{183W\text{-}1H}$ = ca. 68 Hz, $^2J_{119/117Sn\text{-}1H}$ = ca. 100 Hz, Cp_2WH), 0.97 (d, 12H, $^3J_{HH}$ = 6.7 Hz, *o*-CH(CH$_3$)$_2$), 1.01 – 1.20 (br, 12H, *o*-CH(CH$_3$)$_2$), 1.22 (d, 12H, $^3J_{HH}$ = 6.8 Hz, *p*-CH(CH$_3$)$_2$), 1.29 (m, 2H, SnCH$_2$CH$_2$Ph), 2.52 (m, 2H, SnCH$_2$CH$_2$Ph), 2.75 – 2.90 (m, 6H, *o*-/*p*-CH(CH$_3$)$_2$),4.13 (s, 10H, C_5H_5), 7.01 (d, 2H, $^3J_{HH}$ = 7.5 Hz, *o*-Ph), 7.10 (t, 1H, $^3J_{HH}$ = 7.4 Hz, *p*-Ph), 7.13 (s, 4H, *m*-C_6H_2), 7.22 (dd, 2H, $^3J_{HH}$ = 7.7 Hz, *m*-Ph), 7.29 – 7.36 (m, 3H, *m*+*p*-C_6H_3). **^{13}C{^{1}H}-NMR** (176.09 MHz, C_6D_6 + 1,2-difluorobenzene): δ [ppm] 20.9 (br, *o*-CH(CH$_3$)$_2$), 21.3 (br, *o*-CH(CH$_3$)$_2$), 22.8 (*p*-CH(CH$_3$)$_2$), 25.3 (br, *o*-CH(CH$_3$)$_2$), 25.8 (br, *o*-CH(CH$_3$)$_2$), 30.0 (br, *o*-CH(CH$_3$)$_2$), 30.9 (SnCH$_2$CH$_2$Ph), 33.7 (*p*-CH(CH$_3$)$_2$), 44.5 (SnCH$_2$CH$_2$Ph), 76.3 (C_5H_5), 78.9 (br, Al[OC(CF$_3$)$_3$]$_4$), 121.2 (q, $^1J_{19F\text{-}13C}$ = 293 Hz, Al[OC(CF$_3$)$_3$]$_4$), 121.5 (*m*-C_6H_2), 126.0 (*p*-Ph), 126.7 (*o*-Ph), 127.5 (*p*-C_6H_3), 128.1 (*m*-Ph), 130.7 (*m*-C_6H_3), 135.7 (*i*-C_6H_2), 142.3 (*i*-Ph), 142.9 (*o*-C_6H_3), 146.7 (br, *o*-C_6H_2), 147.2 (br, *o*-C_6H_2), 150.4 (*p*-C_6H_2), 161.8 (s + satellites, *J* = ca. 13 Hz, Sn-*i*-C_6H_3). **^{19}F{^{1}H}-NMR** (376.48 MHz, C_6D_6 + 1,2-difluorobenzene): δ [ppm] −74.9 (s, $^1J_{19F\text{-}13C}$ = 291 Hz). **^{119}Sn-NMR** (111.92 MHz, C_6D_6 + 1,2-difluorobenzene): δ [ppm] 1223 (d + satellites, $^2J_{119Sn\text{-}1H}$ = 132 Hz, $^1J_{183W\text{-}119Sn}$ = ca. 1250 Hz). **^{119}Sn{^{1}H}-NMR** (111.92 MHz, C_6D_6 + 1,2-

difluorobenzene): δ [ppm] 1233 (s + satellites, $^{1}J_{183W\text{-}119Sn}$ = ca. 1260 Hz). **^{183}W-NMR** (20.84 MHz, C_6D_6 + 1,2-difluorobenzene): δ [ppm] −3526. **IR** (KBr): ν W-H not observed.

[Cp_2W=Ge(H)Ar*] (**9**). To a suspension of[Cp_2W(H)Li]$_4$ (15.0 mg, 11.6 µmol, 0.50 eq) in benzene (1 mL) was added a solution of [Ar*GeCl]$_2$ (27.5 mg, 23.3 µmol, 1.00 eq) in benzene (3 mL) at once at room temperature. The mixture immediately turned green and was stirred for 24 hours. All volatiles were removed *in vacuo* and the residue was extracted with pentane (5 mL). Filtration through a syringe filter and storage at −40 °C yields the product **9** as green crystals, also suitable for X-ray analysis (21.4 mg, 24.6 µmol, 52.8 %). **^{1}H-NMR** (300.13 MHz, C_6D_6): δ [ppm] 1.15 (d, 12H, $^{3}J_{HH}$ = 6.8 Hz, *o*-CH(C$\underline{H}_3$)$_2$), 1.28 (d, 12H, $^{3}J_{HH}$ = 6.9 Hz, *p*-CH(C$\underline{H}_3$)$_2$), 1.44 (d, 12H, $^{3}J_{HH}$ = 6.9 Hz, *o*-CH(C$\underline{H}_3$)$_2$), 2.84 (sept, 2H, $^{3}J_{HH}$ = 6.9 Hz, *p*-C$\underline{H}$(CH$_3$)$_2$), 3.08 (sept, 4H, $^{3}J_{HH}$ = 6.8 Hz, *o*-C$\underline{H}$(CH$_3$)$_2$), 3.92 (d, 5H , $^{4}J_{HH}$ = ca. 0.5 Hz, $C_5\underline{H}_5$), 3.95 (s, 5H , $C_5\underline{H}_5$), 7.16 (s, 4H, *m*-$C_6\underline{H}_2$), 7.24 – 7.35 (m, 3H, *m*/*p*-$C_6\underline{H}_3$), 10.04 (m + satellites, $^{2}J_{183W\text{-}1H}$ = 35 Hz, Ge$\underline{H}$). **^{13}C{^{1}H}-NMR** (75.47 MHz, C_6D_6): δ [ppm] 22.6 (*o*-CH(C$\underline{H}_3$)$_2$), 24.0 (*p*-CH(C$\underline{H}_3$)$_2$), 26.3 (*o*-CH(C$\underline{H}_3$)$_2$), 30.5 (*o*-C$\underline{H}$(CH$_3$)$_2$), 34.6 (*p*-C$\underline{H}$(CH$_3$)$_2$), 69.3 ($\underline{C}_5H_5$), 70.3 ($\underline{C}_5H_5$), 120.7 (*m*-$\underline{C}_6H_2$), 126.5 (*p*-$\underline{C}_6H_3$), 129.4 (*m*-$\underline{C}_6H_3$), 137.5 (*i*-$\underline{C}_6H_2$), 142.8 (*o*-$\underline{C}_6H_3$), 147.0 (*o*-$\underline{C}_6H_2$), 148.4 (*p*-$\underline{C}_6H_2$), 157.8 (Ge-*i*-$\underline{C}_6H_3$). **^{183}W-NMR** (20.84 MHz, C_6D_6): δ [ppm] −3096. **IR** (KBr): 1862 cm^{-1} (ν Ge-H). **Elemental analysis** calcd (%) for $C_{46}H_{60}$GeW: C 63.55, H 6.96; found C 63.71, H 6.97.

Photochemically induced 1,2-H-Shift in **9**: [Cp_2W(H)-GeAr*] (**5c**). A solution of [Cp_2W=Ge(H)Ar*] **9** (15.0 mg, 17.3 µmol, 1.00 eq.) was dissolved in C_6D_6 (0.4 mL) and irradiated with a mercury vapor lamp for 16 h at rt. Via nmr spectroscopy, a mixture of [Cp_2W=Ge(H)Ar*] **9** and [Cp_2W(H)-GeAr*] **5c** can be identified (~ 60 : 40). Characteristic signals for **5c**: **^{1}H-NMR** (300.13 MHz, C_6D_6): δ [ppm] −11.03 (s + satellites, 1H, $^{1}J_{W\text{-}H}$ = 92 Hz, W$\underline{H}$), 1.22 (br d, 12H, $^{3}J_{HH}$ = 6.6 Hz, CH(C$\underline{H}_3$)$_2$), 1.23 (d, 12H, $^{3}J_{HH}$ = 6.9 Hz, CH(C$\underline{H}_3$)$_2$), 1.48 (d, 12H, $^{3}J_{HH}$ = 6.8 Hz, CH(C$\underline{H}_3$)$_2$), 2.80 (m, 2H, *p*-C$\underline{H}$(CH$_3$)$_2$), 3.27 (sept, 4H, $^{3}J_{HH}$ = 6.8 Hz, *o*-C$\underline{H}$(CH$_3$)$_2$), 4.01 (s, 10H, $C_5\underline{H}_5$)), 7.11 (s, 4H, *m*-$C_6\underline{H}_2$). **^{183}W-NMR** (20.84 MHz, C_6D_6): δ [ppm] −4079.

Protonation of [Cp_2W=Ge(H)Ar*] (**9**): [Cp_2W(H)=Ge(H)Ar*][BAr^F] (**4c**). A cold (−40 °C) solution of [Cp_2W=Ge(H)Ar*] **9** (21.8 mg, 25.1 µmol, 1.20 Eq.) in pentane (2.0 mL) was treated dropwise with a cold solution of [H(Et$_2$O)$_2$][BAr^F] (21.2 mg, 20.9 µmol, 1.00 Eq.) in 1,2-difluorobenzene (1.0 mL) and was stirred for 1 h without further cooling. All volatiles were removed *in vacuo* and the residue was washed with pentane (4 × 2.0 mL). The resulting residue was redissolved in 1,2-difluorobenzene (0.3 mL), filtered, layered with pentane and stored at −40 °C. After several days, the crystallization is completed and the supernatant solution is removed. Further washing with pentane (1 × 0.5 mL) and thoroughly drying *in vacuo* yields the product **4c** as yellow powder (24.6 mg, 14.2 µmol, 67.9 %). **^{1}H-NMR** (400.11 MHz, C_6D_6 + 1,2-difluorobenzene): δ [ppm] −11.08 (s + satellites, 1H, $^{1}J_{183W\text{-}1H}$ = ca. 69 Hz, Cp_2W$\underline{H}$), 0.96 (d, 12H, $^{3}J_{HH}$ = 6.7 Hz, *o*-CH(C$\underline{H}_3$)$_2$), 1.12 – 1.19 (m, 24H, *o*+*p*-CH(C$\underline{H}_3$)$_2$), 2.63 (sept, 4H, $^{3}J_{HH}$ = 6.8 Hz, *o*-C$\underline{H}$(CH$_3$)$_2$), 2.76 (sept, 2H, $^{3}J_{HH}$ = 6.9 Hz, *p*-C$\underline{H}$(CH$_3$)$_2$), 3.93 (s, 10H, $C_5\underline{H}_5$), 7.03 (s, 4H, *m*-$C_6\underline{H}_2$), 7.15 – 7.19 (m, 2H, *m*-$C_6\underline{H}_3$), 7.20 – 7.25 (m, 1H, *p*-$C_6\underline{H}_3$), 7.64 (br s, 4H, *p*-[BAr^F]), 8.31 (br s, 8H, *o*-[BAr^F]), 11.30 (s + satellites, $^{2}J_{183W\text{-}1H}$ = ca. 30 Hz, Ge$\underline{H}$). **^{13}C{^{1}H}-NMR** (100.61 MHz, C_6D_6 + 1,2-difluorobenzene): δ [ppm] 21.7 (*o*-CH(C$\underline{H}_3$)$_2$), 23.5 (*p*-CH(C$\underline{H}_3$)$_2$), 26.1 (*o*-CH(C$\underline{H}_3$)$_2$), 30.7 (*o*-C$\underline{H}$(CH$_3$)$_2$), 34.4 (*p*-C$\underline{H}$(CH$_3$)$_2$), 79.8 ($\underline{C}_5H_5$), 117.7 (br, *p*-[BAr^F]), 121.5 (*m*-$\underline{C}_6H_2$), 124.8 (q, $^{1}J_{19F\text{-}13C}$ = 273 Hz, [BAr^F-$\underline{C}$F$_3$]), 129.5 (br q, $^{2}J_{F\text{-}C}$ = ca. 32 Hz, *m*-[BAr^F]), 129.6 (*p*-$\underline{C}_6H_3$), 130.3 (*m*-$\underline{C}_6H_3$), 132.9 (*i*-$\underline{C}_6H_2$), 135.0 (br, *o*-[BAr^F]), 142.7 (*o*-$\underline{C}_6H_3$), 148.0 (*o*-$\underline{C}_6H_2$), 149.7 (Ge-*i*-$\underline{C}_6H_3$), 151.2 (*p*-$\underline{C}_6H_2$), 162.4 (q, $^{1}J_{13C\text{-}11B}$ = 50 Hz, *i*-[BAr^F]). **^{11}B-NMR** (96.29 MHz, C_6D_6 + 1,2-difluorobenzene): δ [ppm] −6.0 (s, [$\underline{B}$Ar^F]). **^{19}F{^{1}H}-NMR** (376.48 MHz, C_6D_6 + 1,2-difluorobenzene): δ [ppm] −62.3 (s, $^{1}J_{19F\text{-}13C}$ = 273 Hz, [BAr^F-$\underline{C}$F$_3$]). **^{183}W-NMR** (20.84 MHz, C_6D_6/1,2-difluorobenzene): δ [ppm] −3585. **IR** (KBr): 2005 cm^{-1} (ν Ge-H). **Elemental analysis** calcd (%) for $C_{78}H_{73}BF_{24}$GeW: C 54.04, H 4.24; found C 54.24, H 5.50.

[({Cp_2Zr}$_2$(µ-H})(µ-H)$_2$Sn(H)Ar*][WCA] (**10**). *Variant A* ([WCA]$^-$ = [Al(OC{CF$_3$}$_3$)$_4$]$^-$): A solution of [Ar*Sn(C_6H_6)][Al(OC{CF$_3$}$_3$)$_4$] **1a** (54.8 mg, 33.3 µmol, 1.00 eq) in 1,2-difluorobenzene (1.0 mL) was added at once to a suspension of [Cp_2ZrH_2]$_2$ (14.9 mg, 33.3 µmol, 1.00 eq) in toluene (1.0 mL). The resulting mixture was stirred for 1 h at rt upon which it turned to a dark yellow solution. All volatiles were removed *in vacuo* and the residue was washed with pentane (3x 2.0 mL). Drying *in vacuo* yields the product **10** as yellow powder (59.7 mg, 29.9 µmol, 89.8 %). Crystals suitable for X-ray analysis were obtained by layering a concentrated 1,2-difluorobenzene (0.3 mL) solution with pentane (2.5 mL) and storing it for several days at −40 °C (46.5 mg, 23.1 µmol, 69.4 %). *Variant B* ([WCA]$^-$ = [BAr^F]$^-$): A cold (−40 °C) solution of **11** (20 mg, 19.1 µmol, 1.20 Eq.) in pentane (2.0 mL) was treated dropwise with a cold solution of [H(Et$_2$O)$_2$][BAr^F] (16.1 mg, 15.9 µmol, 1.00 Eq.) in 1,2-difluorobenzene (1.0 mL) and was stirred for 1 h without further cooling. All volatiles were removed *in vacuo* and the residue was washed with pentane (4 × 2.0 mL). The resulting residue was dried *in vacuo* and afterwards redissolved in 1,2-difluorobenzene (0.3 mL), layered with pentane (2.5 mL) and stored for several days at −40 °C. After complete crystallization the supernatant solution was removed and the crystals were dried thoroughly *in vacuo* to obtain the product **10** as yellow powder (20.4 mg, 10.7 µmol, 67.3 %). Analytical data for **10**-[Al(OC{CF$_3$}$_3$)$_4$]: **^{1}H-NMR** (400.11 MHz, C_6D_6 + 1,2-difluorobenzene): δ [ppm] −6.24 (m + satellites, 1H, $^{3}J_{119/117Sn\text{-}1H}$ = ca. 32 Hz, Zr-(µ-$\underline{H}$)-Zr), −0.06 (dd +satellites, 2H, $^{2}J_{HH}$ = 2.6 Hz, $J_{119/117Sn\text{-}1H}$ = 199 Hz, Zr-(µ-$\underline{H}$)-Sn), 0.97 (d, 12H, $^{3}J_{HH}$ = 6.7 Hz, *o*-CH(C$\underline{H}_3$)$_2$), 1.20 (d, 12H, $^{3}J_{HH}$ = 6.9 Hz, *o*-CH(C$\underline{H}_3$)$_2$), 1.28 (d, 12H, $^{3}J_{HH}$ = 6.9 Hz, *p*-

CH(C<u>H</u>$_3$)$_2$), 2.68 (sept, 4H, $^3J_{HH}$ = 6.8 Hz, *o*-C<u>H</u>(CH$_3$)$_2$), 2.88 (sept, 2H, $^3J_{HH}$ = 6.9 Hz, *p*-C<u>H</u>(CH$_3$)$_2$), 5.38 (s, 10H, C$_5$<u>H</u>$_5$), 5.43 (s, 10H, C$_5$<u>H</u>$_5$), 6.95 (m, 2H, *m*-C$_6$<u>H</u>$_3$), 7.01 (m, 1H, *p*-C$_6$<u>H</u>$_3$), 7.17 (s, 4H, *m*-C$_6$<u>H</u>$_2$), 9.06 (t + satellites, 1H, $^2J_{HH}$ = 2.6 Hz, $^1J_{119/117Sn-1H}$ = 1344 Hz, Sn-<u>H</u>). **^{13}C{^{1}H}-NMR** (150.90 MHz, C$_6$D$_6$ + 1,2-difluorobenzene): δ [ppm] 22.5 (*o*-CH(<u>C</u>H$_3$)$_2$), 23.7 (*p*-CH(<u>C</u>H$_3$)$_2$), 25.2 (*o*-CH(<u>C</u>H$_3$)$_2$), 31.0 (*o*-<u>C</u>H(CH$_3$)$_2$), 34.5 (*p*-<u>C</u>H(CH$_3$)$_2$), 79.7 (br, Al[O<u>C</u>(CF$_3$)$_3$]$_4$), 104.9 (<u>C</u>$_5$H$_5$), 106.1 (<u>C</u>$_5$H$_5$), 121.4 (*m*-<u>C</u>$_6$H$_2$), 121.9 (q, $^1J_{19F-13C}$ = 292 Hz, Al[OC(<u>C</u>F$_3$)$_3$]$_4$), 127.9 (*p*-<u>C</u>$_6$H$_3$), 132.0 (*m*-<u>C</u>$_6$H$_3$), 138.9 (*i*-<u>C</u>$_6$H$_2$), 146.8 (*o*-<u>C</u>$_6$H$_2$), 147.0 (*o*-<u>C</u>$_6$H$_3$), 147.4 (Sn-*i*-<u>C</u>$_6$H$_3$), 149.9 (*p*-<u>C</u>$_6$H$_2$). **^{19}F{^{1}H}-NMR** (376.48 MHz, C$_6$D$_6$ + 1,2-difluorobenzene): δ [ppm] −74.8 (s, $^1J_{19F-13C}$ = 291 Hz). **^{119}Sn-NMR** (111.92 MHz, C$_6$D$_6$ + 1,2-difluorobenzene): δ [ppm] 440 (dt, $^1J_{119Sn-1H}$ = 1341 Hz, $^2J_{119Sn-1H}$ = 202 Hz). **IR** (KBr): 1868 cm^{-1} (ν Sn-H), 1541 cm^{-1} (ν Zr-H), 1457 cm^{-1} (ν Zr-H). Analytical data for **10**-[BAr^F]: **^{1}H-NMR** (300.13 MHz, C$_6$D$_6$ + 1,2-difluorobenzene): δ [ppm] −6.36 (m + satellites, 1H, $^3J_{119/117Sn-1H}$ = ca. 36 Hz, Zr-(μ-<u>H</u>)-Zr), 0.06 (dd +satellites, 2H, $^2J_{HH}$ = ca. 2 Hz, $J_{119/117Sn-1H}$ = 198 Hz, Zr-(μ-<u>H</u>)-Sn), 0.97 (d, 12H, $^3J_{HH}$ = 6.7 Hz, *o*-CH(C<u>H</u>$_3$)$_2$), 1.20 (d, 12H, $^3J_{HH}$ = 6.9 Hz, *o*-CH(C<u>H</u>$_3$)$_2$), 1.28 (d, 12H, $^3J_{HH}$ = 7.0 Hz, *p*-CH(C<u>H</u>$_3$)$_2$), 2.68 (sept, 4H, $^3J_{HH}$ = 6.8 Hz, *o*-C<u>H</u>(CH$_3$)$_2$), 2.88 (sept, 2H, $^3J_{HH}$ = 6.9 Hz, *p*-C<u>H</u>(CH$_3$)$_2$), 5.32 (s, 10H, C$_5$<u>H</u>$_5$), 5.38 (s, 10H, C$_5$<u>H</u>$_5$), 6.92 – 6.98 (m, 2H, *m*-C$_6$<u>H</u>$_3$), 6.98 – 7.06 (m, 1H, *p*-C$_6$<u>H</u>$_3$), 7.17 (s, 4H, *m*-C$_6$<u>H</u>$_2$), 7.64 (br s, 4H, *p*-[BAr^F]), 8.32 (br m, 8H, *o*-[BAr^F]), 9.07 (t + satellites, 1H, $^2J_{HH}$ = 2.7 Hz, $^1J_{119Sn-1H}$ = 1352 Hz, $^1J_{117Sn-1H}$ = 1292 Hz, Sn-<u>H</u>). **^{13}C{^{1}H}-NMR** (100.61 MHz, C$_6$D$_6$ + 1,2-difluorobenzene): δ [ppm] 22.4 (*o*-CH(<u>C</u>H$_3$)$_2$), 23.6 (*p*-CH(<u>C</u>H$_3$)$_2$), 25.1 (*o*-CH(<u>C</u>H$_3$)$_2$), 30.9 (*o*-<u>C</u>H(CH$_3$)$_2$), 34.5 (*p*-<u>C</u>H(CH$_3$)$_2$), 104.8 (<u>C</u>$_5$H$_5$), 106.0 (<u>C</u>$_5$H$_5$), 117.6 (br, *p*-[BAr^F]), 121.4 (*m*-<u>C</u>$_6$H$_2$), 124.9 (q, $^1J_{19F-13C}$ = 273 Hz, [BAr^F-<u>C</u>F$_3$]), 128.0 (*p*-<u>C</u>$_6$H$_3$, superimposed by solvent signal), 129.4 (br q, $^2J_{19F-13C}$ = ca. 32 Hz, *m*-[BAr^F]), 132.0 (*m*-<u>C</u>$_6$H$_3$), 135.0 (br, *o*-[BAr^F]), 138.8 (*i*-<u>C</u>$_6$H$_2$), 146.7 (*o*-<u>C</u>$_6$H$_2$), 146.9 (*o*-<u>C</u>$_6$H$_3$), 147.2 (Sn-*i*-<u>C</u>$_6$H$_3$), 149.8 (*p*-<u>C</u>$_6$H$_2$), 162.3 (q, $^1J_{13C-11B}$ = 50 Hz, *i*-[BAr^F]). **^{11}B-NMR** (96.29 MHz, C$_6$D$_6$ + 1,2-difluorobenzene): δ [ppm] −6.0 (s, [<u>B</u>Ar^F]). **^{19}F{^{1}H}-NMR** (376.48 MHz, C$_6$D$_6$ + 1,2-difluorobenzene): δ [ppm] −62.3 (s, $^1J_{19F-13C}$ = 273 Hz, [BAr^F-<u>C</u>F$_3$]). **^{119}Sn-NMR** (111.92 MHz, C$_6$D$_6$ + 1,2-difluorobenzene): δ [ppm] 441 (dt, $^1J_{119Sn-1H}$ = 1354 Hz, $J_{119Sn-1H}$ = 200 Hz). **^{119}Sn{^{1}H}-NMR** (111.92 MHz, C$_6$D$_6$ + 1,2-difluorobenzene): δ [ppm] 441 (s). **Elemental analysis** calcd (%) for $C_{88}H_{85}BF_{24}SnZr_2$: C 55.32, H 4.48; found C 55.94, H 5.11.

[({Cp$_2$Zr}$_2${μ-H})(μ-H)Sn(H)Ar*] (**11**). *Variant A*: A cold (−40 °C) solution of [({Cp$_2$Zr}$_2${μ-H})(μ-H)$_2$Sn(H)Ar*][Al(OC{CF$_3$}$_3$)$_4$] **10** (33.5 mg, 16.6 μmol, 1.00 eq) in 1,2-difluorobenzene (1.0 mL) was added to a cold (−40 °C) suspension of benzyl potassium (2.2 mg, 16.6 μmol, 1.00 eq) in toluene (1.0 mL). The suspension was stirred for 15 min at this temperature and was then allowed to warm to rt. The reaction mixture was then stirred for 2 days upon which it turned deep red brown. All volatiles were removed *in vacuo* and the dark residue was extracted with hexane (1.0 mL). Filtration and storage at −40 °C yields crystals of the product suitable for X-ray analysis. The supernatant solution was removed, and the crystals were dried *in vacuo* to obtain the product **11** as red-brown solid (13.4 mg, 12.8 μmol, 77.1 %). *Variant B*: Toluene (1.0 mL) was added to a mixture of [Ar*SnH]$_2$ (25.0 mg, 20.8 μmol, 1.00 eq) and [Cp$_2$ZrH$_2$]$_2$ (18.6 mg, 41.6 μmol, 2.00 eq) at rt. The suspension was stirred for 24 h upon which it turned dark brown, and all volatiles removed *in vacuo*. The residue was extracted with hexane (2.0 mL) and filtered. Removal of all volatiles *in vacuo* yields a crude product (purity >95 % by nmr, 40.2 mg, 38.4 μmol, 92.3 %). Alternatively, the solution can be stored at −40 °C for several days to yield the product as brown crystals suitable for X-ray analysis. The supernatant solution was removed, and the crystals were dried *in vacuo* to obtain the product as red-brown solid (14.8 mg, 14.1 μmol, 34.0 %). **^{1}H-NMR** (500.13 MHz, tol-d$_8$): δ [ppm] −12.90 (s, 1H, Zr-(μ-<u>H</u>)-Zr), −3.08 (br, 1H, Zr-(μ-<u>H</u>)-Sn), 1.09 (d, 12H, $^3J_{HH}$ = 6.8 Hz, *o*-CH(C<u>H</u>$_3$)$_2$), 1.34 (d, 12H, $^3J_{HH}$ = 6.9 Hz, *o*-CH(C<u>H</u>$_3$)$_2$) 1.38 (d, 12H, $^3J_{HH}$ = 6.9 Hz, *p*-CH(C<u>H</u>$_3$)$_2$), 2.94 (sept, 2H, $^3J_{HH}$ = 6.9 Hz, *p*-C<u>H</u>(CH$_3$)$_2$), 3.00 (sept, 4H, $^3J_{HH}$ = 6.8 Hz, *o*-C<u>H</u>(CH$_3$)$_2$), 5.32 (br, 20H, C$_5$<u>H</u>$_5$), 6.99 (m, 2H, *m*-C$_6$<u>H</u>$_3$), 7.06 (m, 1H, *p*-C$_6$<u>H</u>$_3$), 7.11-7.26 (br, 1H, $^1J_{119/117Sn-1H}$ = ca. 860 Hz, Sn-<u>H</u>), 7.22 (s, 4H, *m*-C$_6$<u>H</u>$_2$). **^{1}H-NMR** (500.13 MHz, tol-d$_8$, -20 °C): δ [ppm] −12.90 (s, 1H, Zr-(μ-<u>H</u>)-Zr), −3.08 (m, 1H, Zr-(μ-<u>H</u>)-Sn), 1.12 (d, 12H, $^3J_{HH}$ = 6.8 Hz, *o*-CH(C<u>H</u>$_3$)$_2$), 1.37 (m, 12H, *o*-CH(C<u>H</u>$_3$)$_2$) 1.41 (d, 12H, $^3J_{HH}$ = 6.9 Hz, *p*-CH(C<u>H</u>$_3$)$_2$), 2.95 (sept, 2H, $^3J_{HH}$ = 6.9 Hz, *o*-C<u>H</u>(CH$_3$)$_2$), 3.05 (m, 4H, *o*-C<u>H</u>(CH$_3$)$_2$), 5.21 (s, 5H, C$_5$<u>H</u>$_5$), 5.29 (s, 5H, C$_5$<u>H</u>$_5$), 5.34 (s, 5H, C$_5$<u>H</u>$_5$), 5.43 (s, 5H, C$_5$<u>H</u>$_5$), 7.03 (m, 2H, overlapped by solvent signal, *m*-C$_6$<u>H</u>$_3$), 7.07 (m, 1H, *p*-C$_6$<u>H</u>$_3$), 7.19 (d + satellites, $^2J_{HH}$ = 1.7 Hz, $^1J_{119/117Sn-1H}$ = ca. 860 Hz, Sn-<u>H</u>). **^{13}C{^{1}H}-NMR** (150.90 MHz, C$_6$D$_6$): δ [ppm] 22.3 (*o*-CH(<u>C</u>H$_3$)$_2$), 23.4 (*p*-CH(<u>C</u>H$_3$)$_2$), 24.7 (*o*-CH(<u>C</u>H$_3$)$_2$), 30.1 (*o*-<u>C</u>H(CH$_3$)$_2$), 33.9 (*p*-<u>C</u>H(CH$_3$)$_2$), 99.1 (<u>C</u>$_5$H$_5$), 99.4 (<u>C</u>$_5$H$_5$), 100.1 (<u>C</u>$_5$H$_5$), 100.6 (<u>C</u>$_5$H$_5$), 120.0 (*m*-<u>C</u>$_6$H$_2$), 124.3 (*p*-<u>C</u>$_6$H$_3$), 129.9 (*m*-<u>C</u>$_6$H$_3$), 140.9 (*i*-<u>C</u>$_6$H$_2$), 145.6 (*o*-<u>C</u>$_6$H$_2$), 146.8 (*p*-<u>C</u>$_6$H$_2$), 147.1 (*o*-<u>C</u>$_6$H$_3$), 156.6 (Sn-*i*-<u>C</u>$_6$H$_3$). **^{119}Sn-NMR** (111.92 MHz, C$_6$D$_6$): δ [ppm] 446 (d, $^1J_{119Sn-1H}$ = 872 Hz). **^{119}Sn{^{1}H}-NMR** (111.92 MHz, C$_6$D$_6$): δ [ppm] 444 (s). **IR** (KBr): 1763 cm^{-1} (ν Sn-H), 1460 cm^{-1} (ν Zr-H). **Elemental analysis** calcd (%) for $C_{56}H_{72}SnZr_2$: C 64.28, H 6.94; found C 64.42, H 7.28.

[Cp$_2$Zr(μ-H)(SnH$_2$Ar*)]$_2$ (**13**). To a mixture of [Ar*SnH]$_2$ (50.0 mg, 41.6 μmol, 1.05 eq) and [Cp$_2$ZrH$_2$]$_2$ (17.7 mg, 39.6 μmol, 1.00 eq) pentane (2.5 mL) was added at rt and stirred for approximately 2 h. The ochre suspension was filtered, and the solid was dried *in vacuo* to obtain the product **13** as yellow powder (53.4 mg, 32.4 μmol, 81.8 %). Crystals suitable for X-ray analysis were obtained from a concentrated Et$_2$O solution at −40 °C after several days. **^{1}H-NMR** (400.11 MHz, C$_6$D$_6$): δ [ppm] −5.16 (m + satellites*, 2H, $^2J_{1H-1H}$ = 13.5 Hz, $^2J_{119Sn-1H}$ = ca. 190 Hz, $^2J_{119Sn-1H}$ = 44 Hz, Zr-<u>H</u>-Zr), 1.17 (d, 24H, $^3J_{HH}$ = 6.8 Hz, *o*-CH(C<u>H</u>$_3$)$_2$), 1.28 (d, 24H, $^3J_{HH}$ = 7.0 Hz, *p*-CH(C<u>H</u>$_3$)$_2$), 1.41 (d, 24H, $^3J_{HH}$ = 6.9 Hz, *o*-CH(C<u>H</u>$_3$)$_2$), 2.88 (sept, 4H, $^3J_{HH}$ = 6.9 Hz, *p*-C<u>H</u>(CH$_3$)$_2$), 3.10 (sept, 8H, $^3J_{HH}$ = 6.9 Hz, *o*-C<u>H</u>(CH$_3$)$_2$), 4.55 (dd + satellites, 4H,

$^{1}J_{119Sn\text{-}1H}$ = 1023 Hz, Sn$\underline{H}_2$), 5.34 (s, 20H, $C_5\underline{H}_5$), 7.17 – 7.26 (m, 6H, *m*-/*p*-$C_6\underline{H}_3$), 7.24 (s, 8H, *m*-C_6H_2). **^{1}H-NMR** (600.13 MHz, tol-d_8, −40 °C): −5.36 (m + satellites*, 2H, Zr-$\underline{H}$-Zr), 1.19 (d, 24H, $^{3}J_{HH}$ = 6.7 Hz, *o*-CH(C$\underline{H}_3$)$_2$), 1.29 (d, 24H, $^{3}J_{HH}$ = 6.8 Hz, *p*-CH(C$\underline{H}_3$)$_2$), 1.41 (d, 24H, $^{3}J_{HH}$ = 6.8 Hz, *o*-CH(C$\underline{H}_3$)$_2$), 2.87 (sept, 4H, $^{3}J_{HH}$ = 6.9 Hz, *p*-C$\underline{H}$(CH$_3$)$_2$), 3.07 (sept, 8H, $^{3}J_{HH}$ = 6.9 Hz, *o*-C$\underline{H}$(CH$_3$)$_2$), 4.55 (m + satellites, 4H, $^{1}J_{119Sn\text{-}1H}$ = 1025 Hz, Sn$\underline{H}_2$), 5.27 (s, 20H, $C_5\underline{H}_5$), 7.24 (br, 6H, *m*-/*p*-$C_6\underline{H}_3$), 7.25 (s, 8H, *m*-C_6H_2). **^{13}C{^{1}H}-NMR** (150.90 MHz, tol-d_8, −40 °C): δ [ppm] 23.4 (*o*-CH(C$\underline{H}_3$)$_2$), 24.6 (*p*-CH(C$\underline{H}_3$)$_2$), 25.8 (*o*-CH(C$\underline{H}_3$)$_2$), 30.9 (*o*-C$\underline{H}$(CH$_3$)$_2$), 34.9 (*p*-C$\underline{H}$(CH$_3$)$_2$), 103.8 ($\underline{C}_5H_5$), 125.6 (*o*/*p*-$\underline{C}_6H_3$), 128.5 (*o*/*p*-$\underline{C}_6H_3$, overlapped by solvent signal), 142.0 (*i*-$\underline{C}_6H_2$), 146.7 (*o*-$\underline{C}_6H_2$), 147.9 (*p*-$\underline{C}_6H_2$), 149.0 (*o*-$\underline{C}_6H_3$), 152.4 (s + satellites, $^{1}J_{119Sn\text{-}13C}$ = 103 Hz, Sn-*ipso*-$\underline{C}_6H_3$). **^{119}Sn-NMR** (111.92 MHz, Tol-*d8*): δ [ppm] −230 (tdd, $^{1}J_{119Sn\text{-}1H}$ = 1534 Hz, $^{2}J_{119Sn\text{-}1H}$ = 196 Hz, $^{2}J_{119Sn\text{-}1H}$ = 44 Hz). **^{119}Sn{^{1}H}-NMR** (111.92 MHz, C_6D_6): δ [ppm] −229 (s). **IR** (KBr): ca. 1700 cm^{-1}. **Elemental analysis** calcd (%) for $C_{92}H_{124}Sn_2Zr_2$: C 66.98, H 7.58; found C 67.02, H 7.54.

* satellites can be interpreted as A part of a AA'X spin system (one nmr active tin nucleus) and A part of a AA'XX' spin system (two nmr active tin nuclei, corresponds to "satellites of satellites"), see SI for spectra simulation.

Crystallography

Table S1. Crystal structure refinement table of **1b**, **2**, **4a**, **5a**, **5b**, **7**, **9**.

	1b	**2·$C_6H_4F_2$**	**4a**	**5a**	**5b**	**7·0.5 C_6H_{14}**	**9**
Empirical formula	$C_{58}H_{55}AlF_{36}O_4Pb$	$C_{68}H_{66}AlF_{38}O_4SnTa$	$C_{62}H_{61}AlF_{36}O_4SnW$	$C_{46}H_{60}SnW$	$C_{46}H_{60}PbW$	$C_{49}H_{69}SnW$	$C_{46}H_{60}GeW$
M [g mol^{-1}]	1734.19	1995.85	1883.62	915.48	1003.98	960.59	869.38
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
T [K]	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
crystal system	monoclinic	triclinic	monoclinic	triclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
Z	4	2	4	4	4	4	2
a [Å]	18.2520(11)	10.8653(2)	22.4091(4)	11.0451(3)	11.3299(2)	14.5594(2)	8.3996(2)
b [Å]	18.8552(11)	18.1156(4)	15.2890(3)	15.3034(4)	15.3358(4)	11.4818(2)	11.9230(3)
c [Å]	18.9325(11)	19.7769(4)	23.2574(5)	24.1609(6)	23.0888(5)	30.5835(4)	21.0264(5)
α [°]	90	82.9010(10)	90	87.191(2)	90	90	76.7860(10)
β [°]	91.625(2)	76.5990(10)	117.3340(10)	83.206(2)	100.3500(10)	98.1790(10)	87.3990(10)
γ [°]	90	84.7840(10)	90	89.644(2)	90	90	74.3220(10)
V [Å^3]	6512.9(7)	3749.87(13)	7078.6(2)	4050.31(18)	3946.47(15)	5060.58(13)	1973.44(8)
D_c [g cm^{-3}]	1.769	1.768	1.767	1.501	1.690	1.261	1.463
μ [mm^{-1}]	2.752	1.944	2.129	3.484	7.203	2.792	3.704
F(000)	3416	1968	3704	1840	1968	1948	884
crystal size [mm]	0.22×0.16×0.13	0.20×0.12×0.11	0.20×0.18×0.17	0.30×0.11×0.06	0.26×0.15×0.11	0.279×0.194×0.115	0.202×0.161×0.122
θ range [°]	1.553 – 26.790	2.944 – 30.552	2.965 – 35.009	1.545 – 26.748	2.306 – 29.610	2.268 – 31.504	2.986 – 33.001

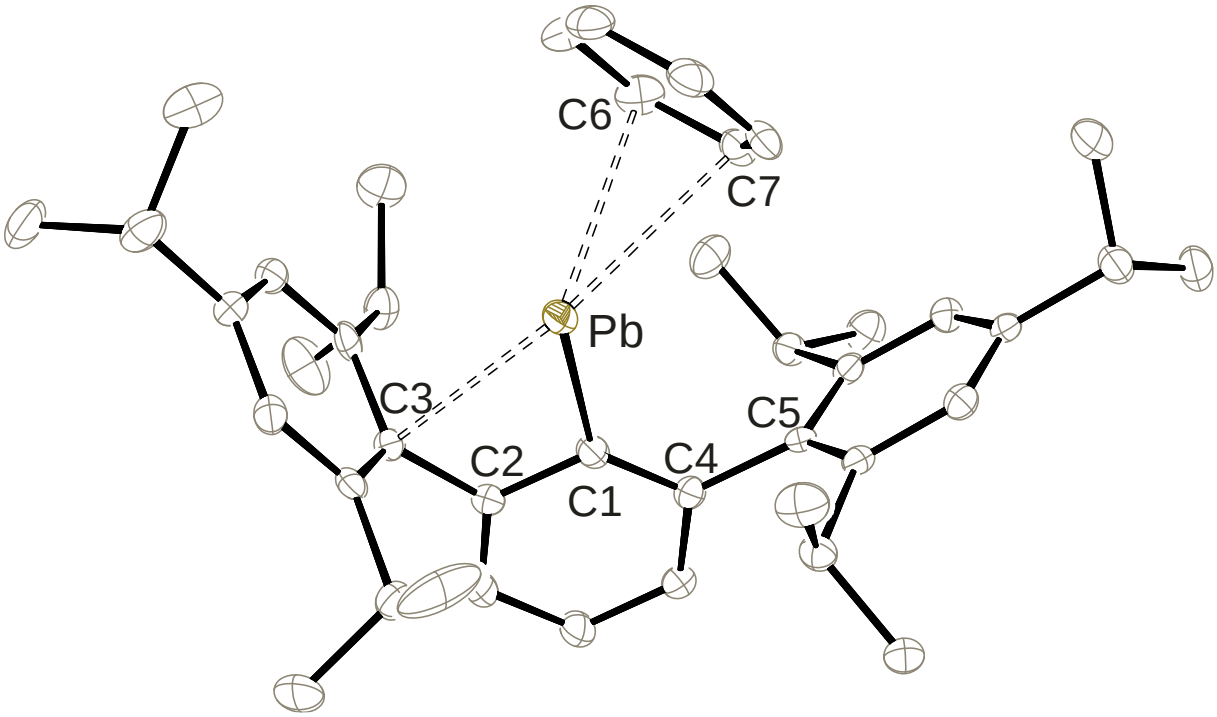
limiting indices	−23 ≤ h ≤ 23	−15 ≤ h ≤ 14	−35 ≤ h ≤ 36	−13 ≤ h ≤ 13	−15 ≤ h ≤ 15	−21 ≤ h ≤ 21	−12 ≤ h ≤ 12
	−23 ≤ k ≤ 23	−25 ≤ k ≤ 24	−24 ≤ k ≤ 23	−19 ≤ k ≤ 19	−21 ≤ k ≤ 19	−16 ≤ k ≤ 14	−17 ≤ k ≤ 17
	−23 ≤ l ≤ 23	−26 ≤ l ≤ 28	−37 ≤ l ≤ 36	−30 ≤ l ≤ 30	−32 ≤ l ≤ 32	−44 ≤ l ≤ 39	−32 ≤ l ≤ 31
refelctions collected	71919	73792	168222	66809	69279	87692	43725
independent reflections	13785	21769	31084	17031	11058	16739	13355
R_{int}	0.0498	0.0379	0.0483	0.0516	0.0560	0.0568	0.0275
completeness	99.2	94.7	99.6	99.0	99.4	99.4	89.7
absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	numerical	multi-scan	multi-scan
max., min. transmission	0.7454, 0.5035	0.7461, 0.6495	0.7469, 0.6714	0.7454, 0.5811	0.516, 0.253	0.7462, 0.6433	0.7465, 0.6948
parameters/restraints	968/0	1157/894	1375/10972	891/4	456/1	486/0	462/0
R_1, ωR_2 [I > 2σ(I)]	0.0487, 0.1157	0.0355, 0.0699	0.0461, 0.1106	0.0364, 0.0657	0.0265, 0.0497	0.0356, 0.0862	0.0262, 0.0473
R_1, ωR_2 (all data)	0.0657, 0.1277	0.0555, 0.0763	0.0623, 0.1206	0.0549, 0.0715	0.0427, 0.0544	0.0565, 0.0936	0.0341, 0.0491
GooF on F^2	1.032	1.036	1.016	1.008	1.017	1.034	1.025
$\Delta\rho_{max,min}$ [e·Å^{-3}]	2.450, −1.450	1.806, −1.181	2.928, −2.291	1.882, −2.589	1.250, −0.937	0.882, −1.070	0.646, −0.714
CCDC	2142088	2142080	2142081	2142086	2142085	2142087	2142084

Table S2. Crystal structure refinement table of **10**, **11**, **13**.

	10 ·$C_6H_4F_2$ ·0.5 C_5H_{12}	**11 ·C_6H_{14}**	**13·2 Et_2O**
Empirical formula	$C_{161}H_{166}Al_2F_{76}O_8Sn_2Zr_4$	$C_{56}H_{72}SnZ_{r2}$	$C_{100}H_{144}O_2Sn_2Zr_2$
M [g mol^{-1}]	4329.20	1046.29	1798.02
λ [Å]	0.71073	0.71073	0.71073
T [K]	100(2)	100(2)	100(2)
crystal system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	1	2	2
a [Å]	11.3131(3)	12.3457(3)	18.1709(6)
b [Å]	16.2812(4)	13.6478(3)	18.2757(6)
c [Å]	23.9753(6)	17.2813(4)	18.2781(6)
α [°]	88.1350(10)	78.6800(10)	104.494(2)
β [°]	81.3650(10)	75.6210(10)	118.338(2)
γ [°]	84.3120(10)	81.1780(10)	104.162(2)
V [$Å^3$]	4343.78(19)	2748.84(11)	4678.4(3)
D_c [g cm^{-3}]	1.655	1.264	1.276
μ [mm^{-1}]	0.660	0.854	0.789
F(000)	2166	1076	1880
crystal size [mm]	0.20×0.18×0.17	0.26×0.13×0.11	0.19×0.19×0.18
θ range [°]	2.133 – 34.443	3.361 – 30.550	3.182 – 29.660
limiting indices	−17 ≤ h ≤ 17	−17 ≤ h ≤ 17	−25 ≤ h ≤ 25
	−25 ≤ k ≤ 25	−19 ≤ k ≤ 19	−25 ≤ k ≤ 25
	−38 ≤ l ≤ 36	−24 ≤ l ≤ 24	−24 ≤ l ≤ 25
refelctions collected	164064	61372	72411
independent reflections	35825	16632	25141
R_{int}	0.0278	0.0318	0.0393
completeness	97.8	98.6	95.0
absorption correction	multi-scan	multi scan	multi scan
max., min. transmission	0.7468, 0.6881	0.7461, 0.7046	0.7459, 0.6879
parameters/restraints	1340/8	572/3	1032/0
R_1, ωR_2 [I > 2σ(I)]	0.0309, 0.0806	0.0327, 0.0874	0.0398, 0.0917
R_1, ωR_2 (all data)	0.0386, 0.0892	0.0421, 0.0928	0.0571, 0.1020
GooF on F^2	0.826	1.024	1.023

$\Delta\rho_{max,min}$ [e·Å^{-3}]	1.475, −1.354	1.915, −0.836	1.113, −0.937
CCDC	2142083	2142082	2142089

X-ray data were collected with a Bruker Smart APEX II diffractometer with graphite-monochromated Mo Kα radiation or a Bruker APEX II Duo diffractometer with a Mo IμS microfocus tube. The programs used were Bruker's APEX2 v2011.8-0, including SAINT for data reduction. SADABS for absorption correction, and SHELXS for structure solution, as well as the WinGX suite of programs version 1.70.01 or the GUI ShelXle, including SHELXL for structure refinement.[1-5]



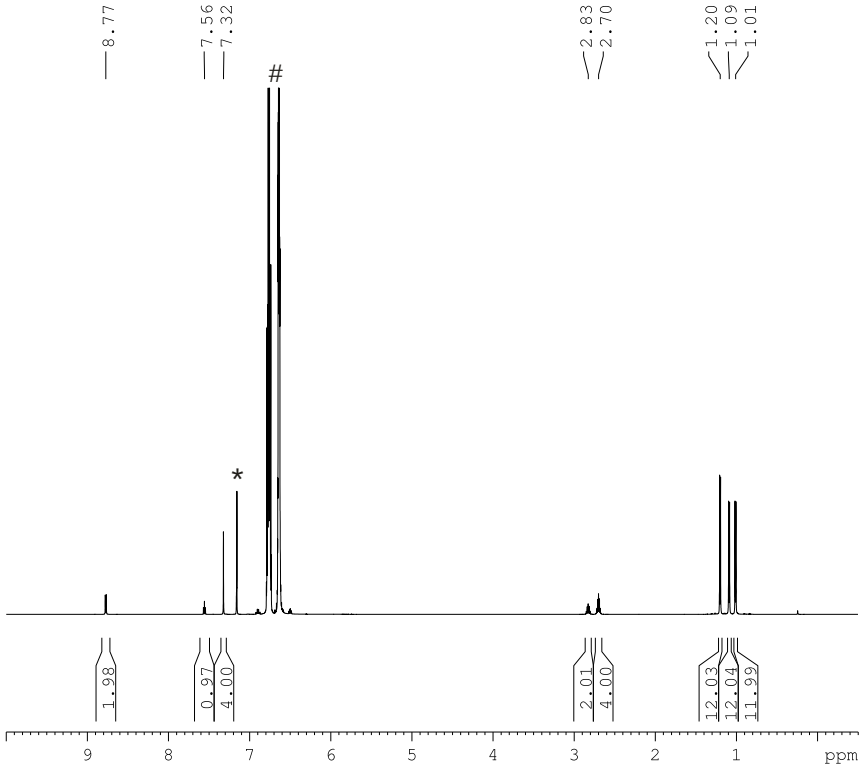
ORTEP of the molecular structure of the cation **1b** in the solid state. Thermal ellipsoids are shown at 50% probability level. Hydrogen atoms and anion $[Al(OC\{CF_3\}_3)_4]^-$ have been omitted for clarity. Selected interatomic distances [Å] and angles [°] are given: Pb-C1 2.277(5), Pb-C3 2.755(5), Pb-C5 3.722(5), Pb-C6 3.046(6), Pb-C7 2.964(5), Pb-C1-C2 105.3(4), Pb-C1-C4 133.0(4).

NMR Spectroscopy

NMR spectra

Compound **1b**

^{1}H NMR (C_6D_6 + 1,2-difluorobenzene, rt) of [Ar*Pb(C_6H_6)][Al(O^{t}Bu^F)$_4$] (**1b**)

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Current Data Parameters
NAME      [ArPb][Al(ORF4)]
EXPNO                   10
PROCNO                   1

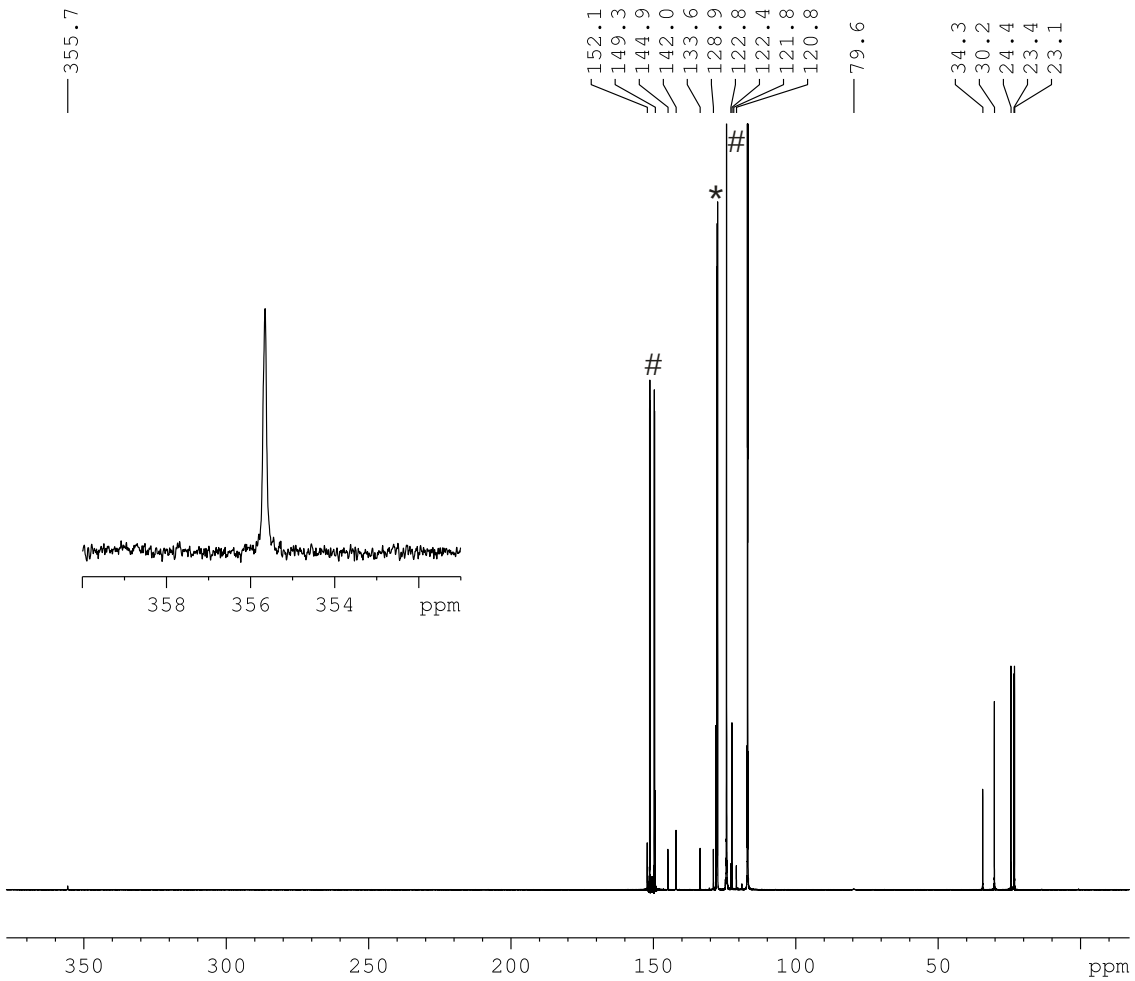
F2 - Acquisition Parameters
Date_           20210114
Time                8.52 h
INSTRUM             spect
PROBHD   Z126545_0027 (
PULPROG              zg30
TD                  65536
SOLVENT              C6D6
NS                     64
DS                      2
SWH            12019.230 Hz
FIDRES          0.366798 Hz
AQ             2.7262976 sec
RG                 10.18
DW                41.600 usec
DE                10.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                     1
SFO1         600.1337058 MHz
NUC1                   1H
P1                 12.00 usec
PLW1        23.41200066 W

F2 - Processing parameters
SI                  65536
SF           600.1299935 MHz
WDW                    EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

* C_6D_6
\# 1,2-$C_6H_4F_2$

Figure S1, ^{1}H NMR of compound **1b**.

$^{13}C\{^{1}H\}$ NMR (C_6D_6 + 1,2-difluorobenzene, rt) of [Ar*Pb(C_6H_6)][Al(O^tBu^F)$_4$] (**1b**)

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Current Data Parameters
NAME      [ArPb][Al(ORF4)]
EXPNO                   11
PROCNO                   1

F2 - Acquisition Parameters
Date_           20210114
Time               14.40 h
INSTRUM             spect
PROBHD   Z126545_0027 (
PULPROG             udeft
TD                  32768
SOLVENT              C6D6
NS                   4361
DS                      8
SWH            59523.809 Hz
FIDRES          3.633045 Hz
AQ             0.2752512 sec
RG                  189.6
DW                  8.400 usec
DE                 18.00 usec
TE                 298.0 K
D1            4.00000000 sec
D12           0.00002000 sec
D20          20.00000000 sec
TD0                     1
SFO1         150.9299710 MHz
NUC1                 13C
P1                 10.00 usec
P13              2000.00 usec
P26               500.00 usec
PLW1         57.02700043 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5  0 Hz
SPW5          8.71310043 W
SPNAM[8] Crp60,0.5,20.1
SPOAL8             0.500
SPOFFS8  0 Hz
SPW8          8.71310043 W
SFO2         600.1324005 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2              70.00 usec
PLW2         23.41200066 W
PLW12         0.68803000 W

F2 - Processing parameters
SI                 131072
SF           150.9028085 MHz
WDW                  EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 1.40
```
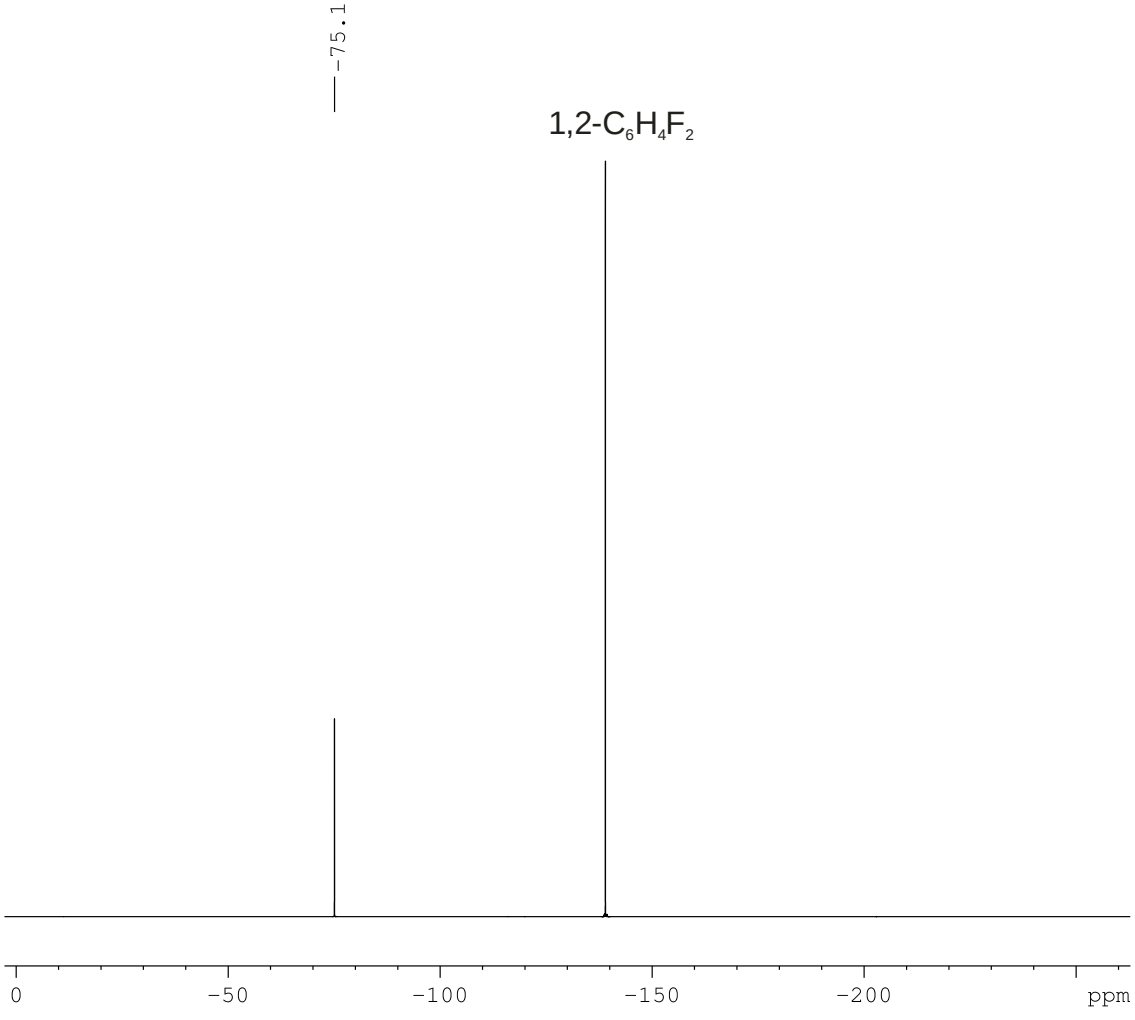

* C_6D_6
\# 1,2-$C_6H_4F_2$

Figure S2. $^{13}C\{^{1}H\}$ NMR of compound **1b**.

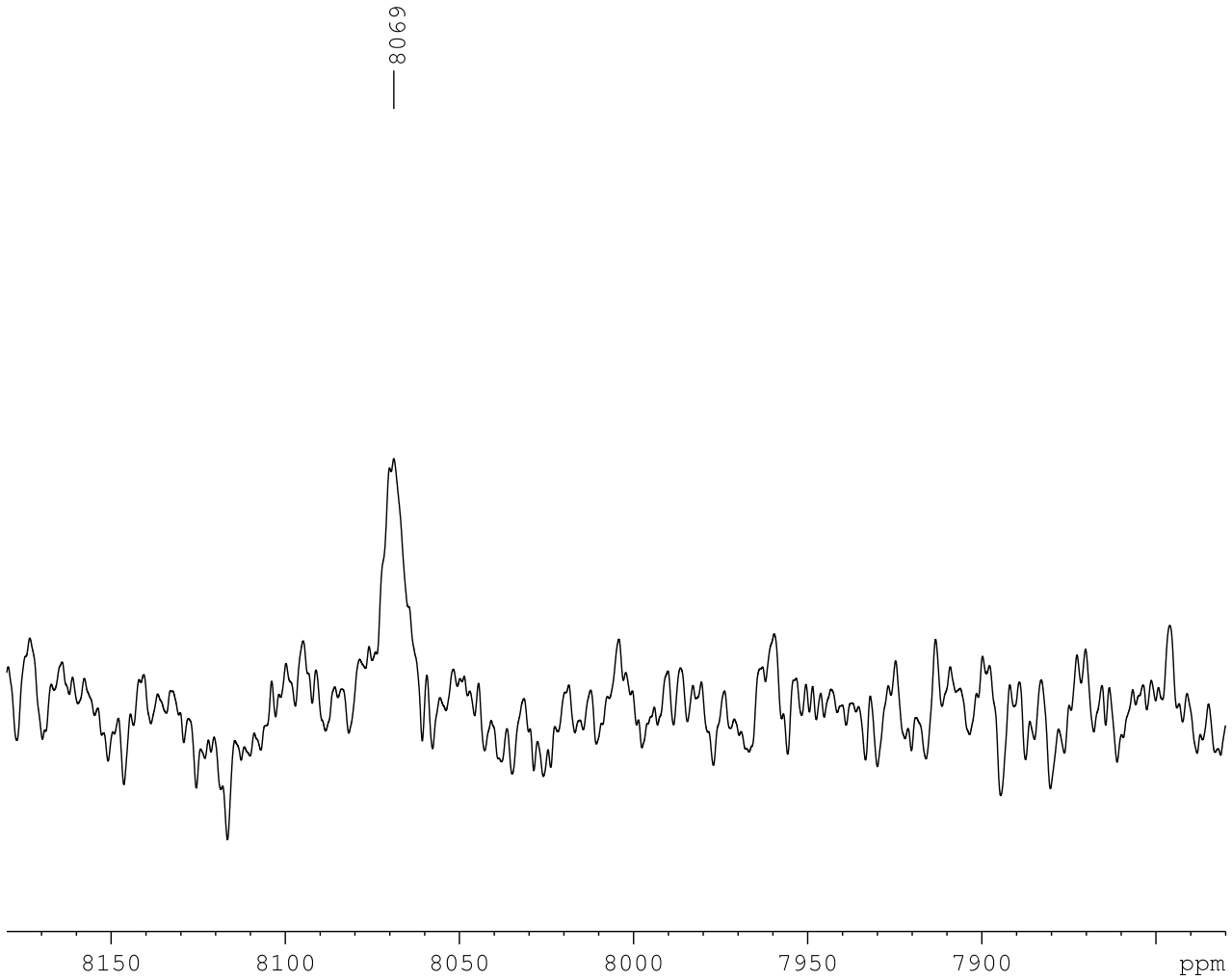
$^{19}F\{^{1}H\}$ NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Ar^*Pb(C_6H_6)][Al(O^tBu^F)_4]$ (**1b**)




```
Current Data Parameters
NAME           MW955_400
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210113
Time               14.27
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG         zgfhigqn
TD                131072
SOLVENT             C6D6
NS                    64
DS                     0
SWH           100000.000 Hz
FIDRES          0.762939 Hz
AQ             0.6553600 sec
RG                  4100
DW                 5.000 usec
DE                 6.00 usec
TE                299.2 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  19F
P1                 18.75 usec
PL1                -2.92 dB
PL1W         30.50645256 W
SFO1        376.4306030 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               11.77 dB
PL2W         16.03799057 W
PL12W         0.53474891 W
SFO2        400.1120007 MHz

F2 - Processing parameters
SI                262144
SF          376.4795470 MHz
WDW                   EM
SSB      0
LB                 2.00 Hz
GB       0
PC                 1.00
```

Figure S3. $^{19}F\{^{1}H\}$ NMR of compound **1b**.

^{207}Pb NMR (C_6D_6 + 1,2-difluorobenzene, rt) of [Ar*Pb(C_6H_6)][Al(O^tBu^F)$_4$] (**1b**)

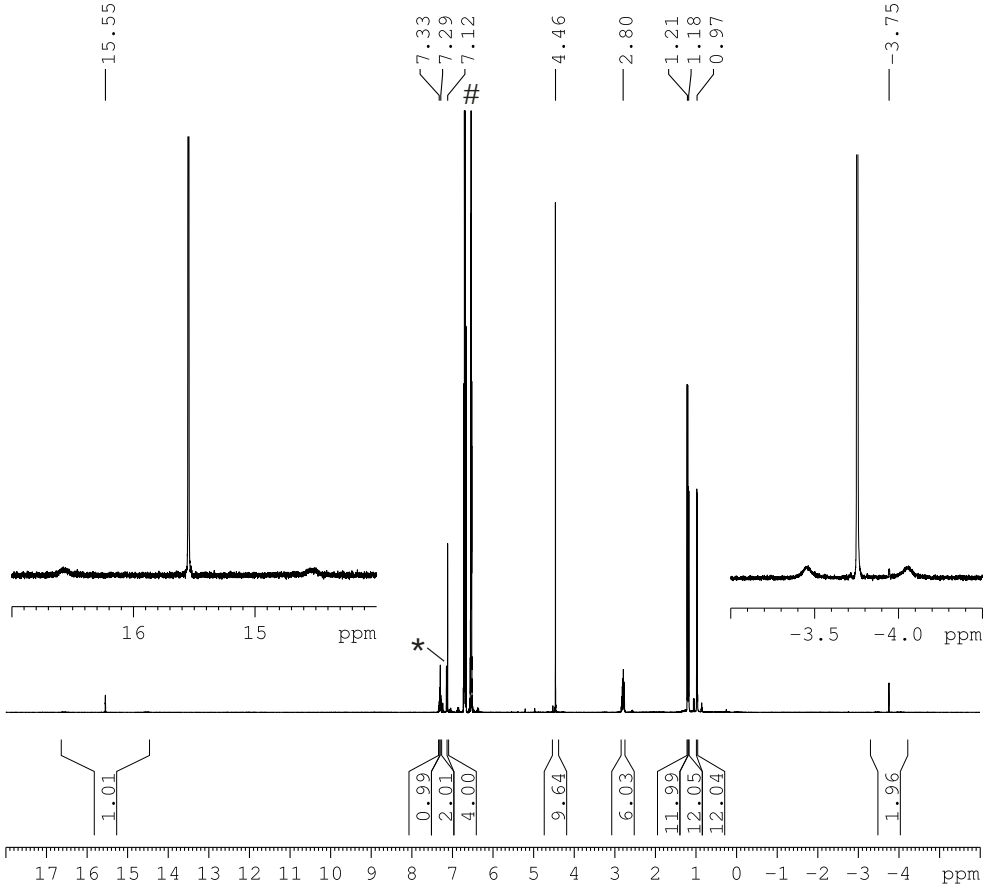



```
Current Data Parameters
NAME         RS25_300_Pb
EXPNO                 21
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191017
Time                1.07 h
INSTRUM            spect
PROBHD   Z104275_0338 (
PULPROG             zg30
TD                 14998
SOLVENT             C6D6
NS                 39936
DS                     0
SWH            25252.525 Hz
FIDRES          3.367452 Hz
AQ             0.2969604 sec
RG                 204.67
DW                 19.800 usec
DE                 10.00 usec
TE                 298.0 K
D1            0.20000000 sec
TD0                    1
SFO1           63.2913058 MHz
NUC1               207Pb
P1                 12.50 usec
PLW1         40.00000000 W

F2 - Processing parameters
SI                 65536
SF            62.7889938 MHz
WDW                   EM
SSB       0
LB                100.00 Hz
GB        0
PC                 3.00
```

Figure S4. ^{207}Pb NMR of compound **1b**.

Compound **2**

^{1}H NMR (C_6D_6 + 1,2-difluorobenzene, rt) of [Cp_2TaH_2-Sn(H)Ar*][Al(O^tBu^F)$_4$] (**2**)

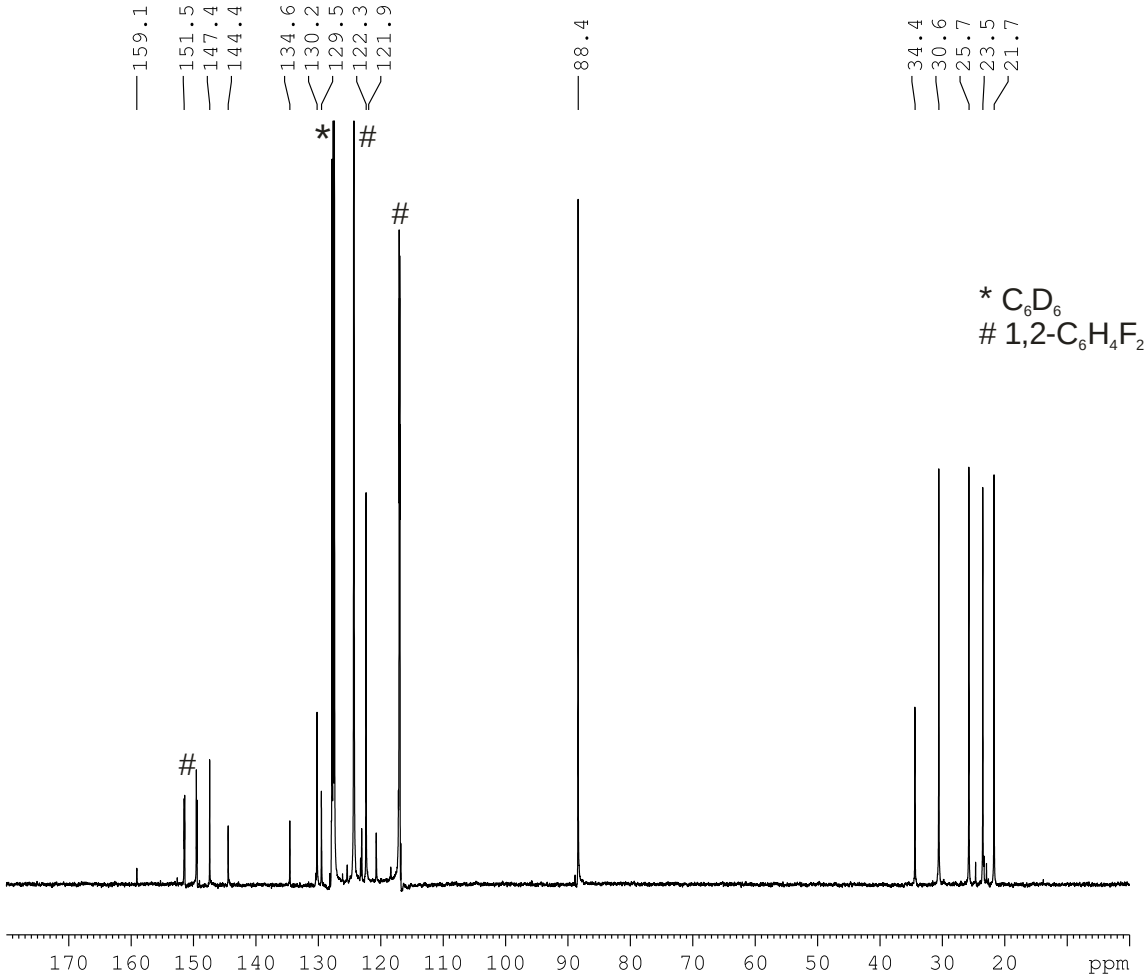



```
Current Data Parameters
NAME         MW_TP84_500
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200817
Time               15.58
INSTRUM            spect
PROBHD   5 mm TBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT             C6D6
NS                   256
DS                     0
SWH            15000.000 Hz
FIDRES          0.228882 Hz
AQ             2.1845334 sec
RG                     4
DW                33.333 usec
DE                 6.00 usec
TE                299.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                11.38 usec
PL1       0 dB
PL1W        21.60222244 W
SFO1        500.1325007 MHz

F2 - Processing parameters
SI                 65536
SF           500.1300000 MHz
WDW                   no
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```

* C_6D_6
\# 1,2-$C_6H_4F_2$

Figure S5, ^{1}H NMR of compound **2**.

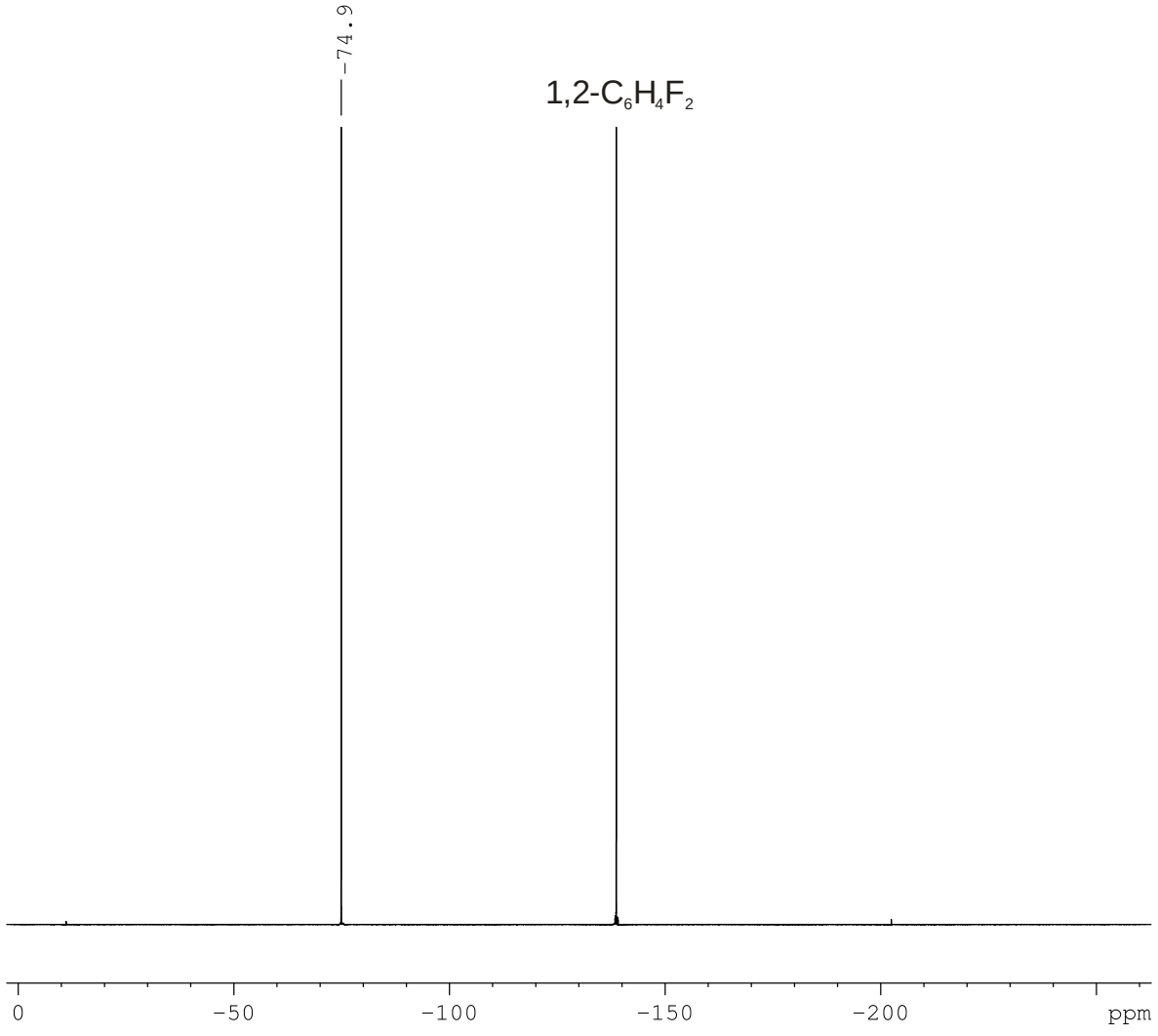
$^{13}C\{^{1}H\}$ NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2TaH_2\text{-}Sn(H)Ar^*][Al(O^tBu^F)_4]$ (**2**)




```
Current Data Parameters
NAME         MW_TP84_500
EXPNO                  6
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200818
Time                8.26
INSTRUM            spect
PROBHD   5 mm TBO BB-1H
PULPROG            udeft
TD                 27268
SOLVENT             C6D6
NS                 21044
DS                     0
SWH            37878.789 Hz
FIDRES         1.389130 Hz
AQ             0.3599376 sec
RG                  2050
DW                13.200 usec
DE                 6.00 usec
TE                299.2 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
D20         100.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 12.00 usec
P13              2000.00 usec
P26               500.00 usec
PL1       0 dB
PL1W         83.89700317 W
SFO1        125.7728799 MHz
SP8                6.58 dB
SP13               6.58 dB
SPNAM[8] Crp60,0.5,20.1
SPNAM[13    Crp60comp.4
SPOAL8             0.500
SPOAL13            0.500
SPOFFS8  0 Hz
SPOFFS13 0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2       0 dB
PL12               16.94 dB
PL2W         21.60222244 W
PL12W         0.43701705 W
SFO2        500.1325007 MHz

F2 - Processing parameters
SI                262144
SF          125.7577890 MHz
WDW                   EM
SSB       0
LB                 4.00 Hz
GB        0
PC                 1.40
```

Figure S6. $^{13}C\{^{1}H\}$ NMR of compound **2**.

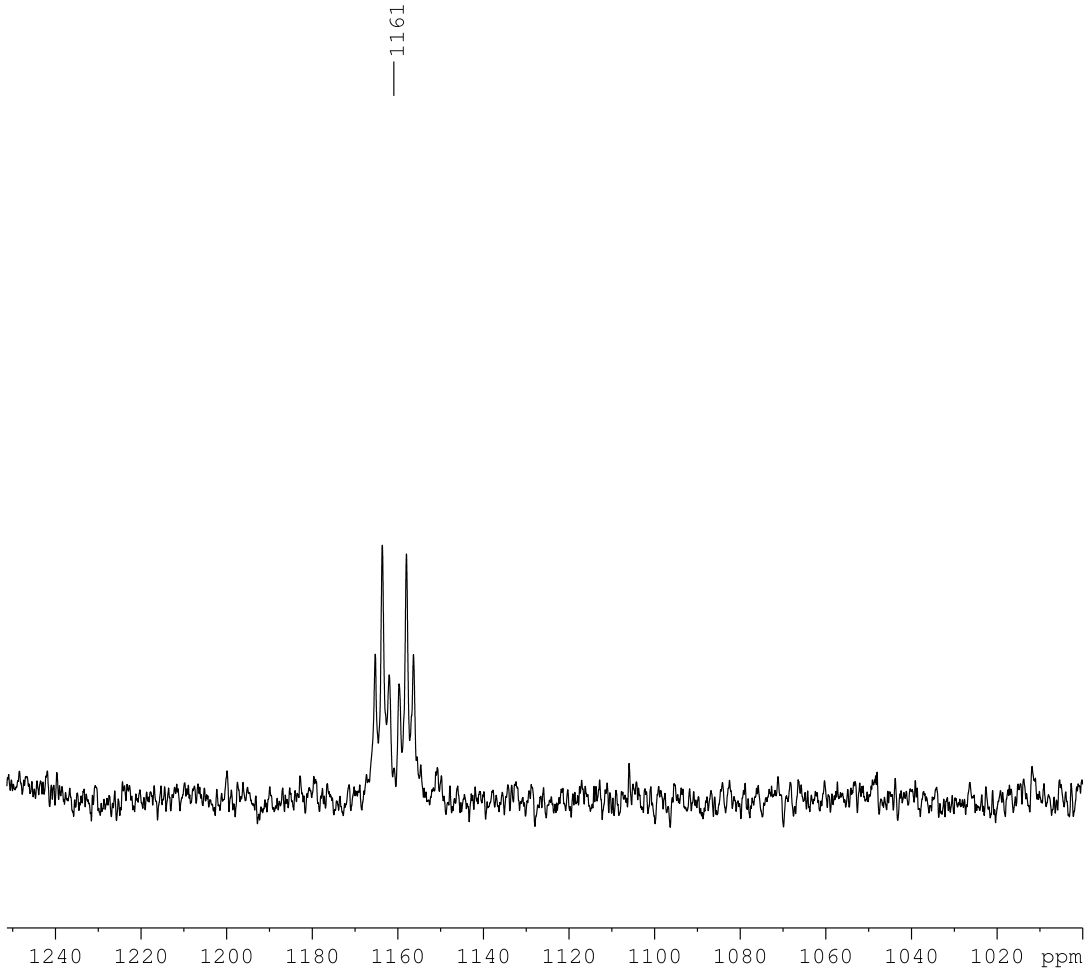
$^{19}F\{^{1}H\}$ NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2TaH_2\text{-}Sn(H)Ar^*][Al(O^tBu^F)_4]$ (**2**)




```
Current Data Parameters
NAME        MW_TP84_400
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20200818
Time              10.14
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG         zgfhigqn
TD               131072
SOLVENT             C6D6
NS                   128
DS                     0
SWH          100000.000 Hz
FIDRES         0.762939 Hz
AQ             0.6553600 sec
RG                  4100
DW                 5.000 usec
DE                 6.00 usec
TE                 300.2 K
D1           1.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 19F
P1                 18.75 usec
PL1                -2.92 dB
PL1W        30.50645256 W
SFO1        376.4306030 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               11.77 dB
PL2W        16.03799057 W
PL12W        0.53474891 W
SFO2        400.1120007 MHz

F2 - Processing parameters
SI                 262144
SF          376.4795470 MHz
WDW                    EM
SSB       0
LB                  2.00 Hz
GB        0
PC                  1.00
```

Figure S7. $^{19}F\{^{1}H\}$ NMR of compound **2**.

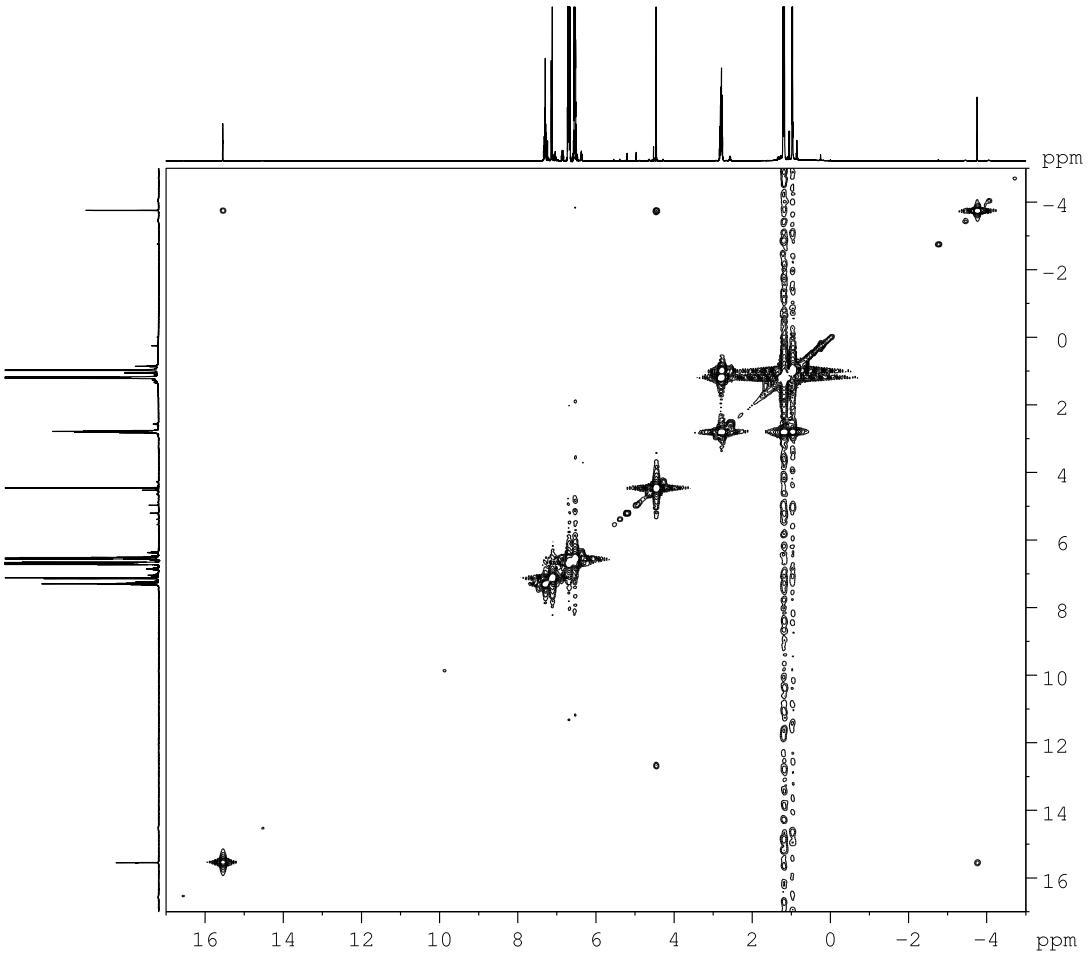
^{119}Sn NMR (C_6D_6 + 1,2-difluorobenzene, rt) of [Cp_2TaH_2-Sn(H)Ar*][Al(O^tBu^F)$_4$] (**2**)




```
Current Data Parameters
NAME          TP84_500Sn
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200806
Time               17.06
INSTRUM            spect
PROBHD   5 mm TBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT             C6D6
NS                 40960
DS                     0
SWH            93750.000 Hz
FIDRES          1.430511 Hz
AQ             0.3495253 sec
RG                  2050
DW                 5.333 usec
DE                  6.00 usec
TE                 299.3 K
D1            0.20000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1               119Sn
P1                11.93 usec
PL1                3.00 dB
PL1W         45.32131577 W
SFO1         186.6881396 MHz

F2 - Processing parameters
SI                131072
SF           186.5016380 MHz
WDW                  EM
SSB       0
LB                 50.00 Hz
GB        0
PC                  1.40
```

Figure S8. ^{119}Sn NMR of compound **2**.

$^{1}H,^{1}H$ COSY NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2TaH_2\text{-}Sn(H)Ar^*][Al(O^tBu^F)_4]$ (**2**)

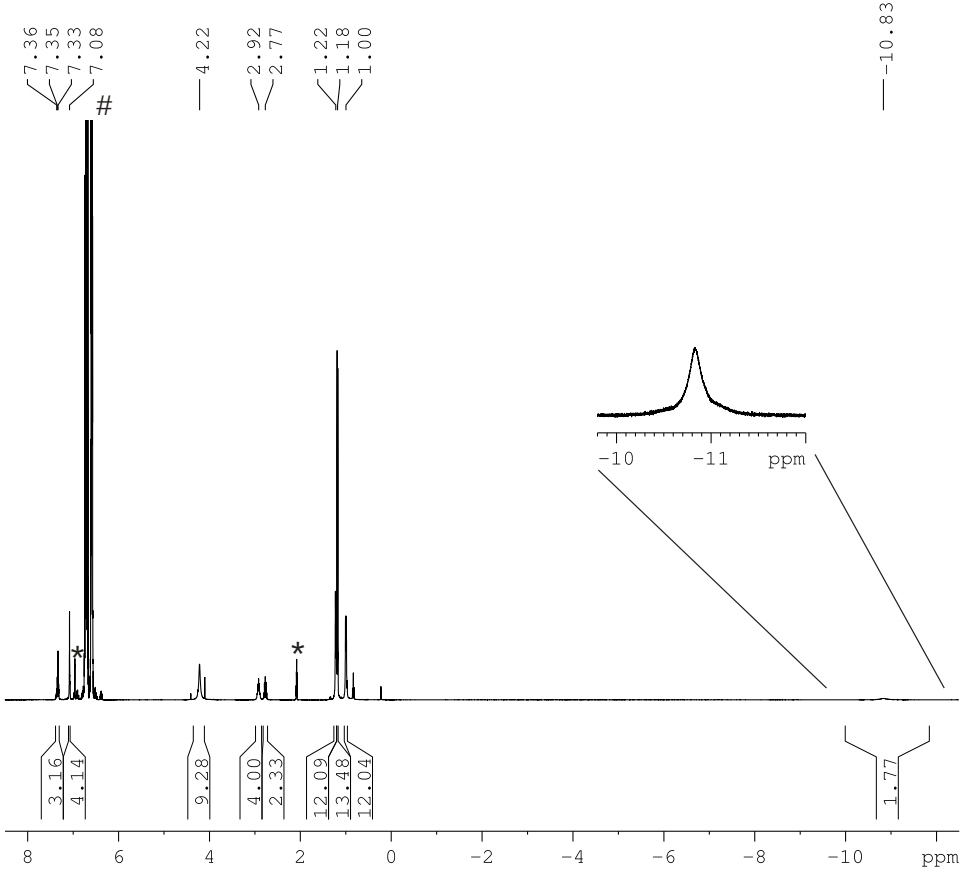



```
Current Data Parameters
NAME         MW_TP84_500
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200817
Time               15.58
INSTRUM            spect
PROBHD   5 mm TBO BB-1H
PULPROG         cosygpqf
TD                 1024
SOLVENT            C6D6
NS                    8
DS                    8
SWH           15000.000 Hz
FIDRES        14.648438 Hz
AQ            0.0341333 sec
RG                   64
DW               33.333 usec
DE                6.00 usec
TE               299.2 K
D0           0.00000300 sec
D1           1.00000000 sec
D13          0.00000400 sec
D16          0.00020000 sec
IN0          0.00006665 sec

======== CHANNEL f1 ========
NUC1                 1H
P0                11.38 usec
P1                11.38 usec
PL1       0 dB
PL1W        21.60222244 W
SFO1        500.1325007 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPZ1              10.00 %
P16             1000.00 usec

F1 - Acquisition parameters
TD                   256
SFO1            500.1325 MHz
FIDRES       117.218552 Hz
SW                30.000 ppm
FnMODE              QF

F2 - Processing parameters
SI                  1024
SF           500.1300000 MHz
WDW                 SINE
SSB       0
LB        0 Hz
GB        0
PC                  0.60

F1 - Processing parameters
SI                   512
MC2                   QF
SF           500.1300000 MHz
WDW                 SINE
SSB       0
LB        0 Hz
GB        0
```

Figure S9. $^{1}H\text{-}^{1}H$ Cosy NMR of compound **2**.

Compound **3a**

^{1}H NMR (tol-d_8 + 1,2-difluorobenzene, rt) of $[(Cp_2WH_2)SnAr^*][Al(O^tBu^F)_4]$ (**3a**)

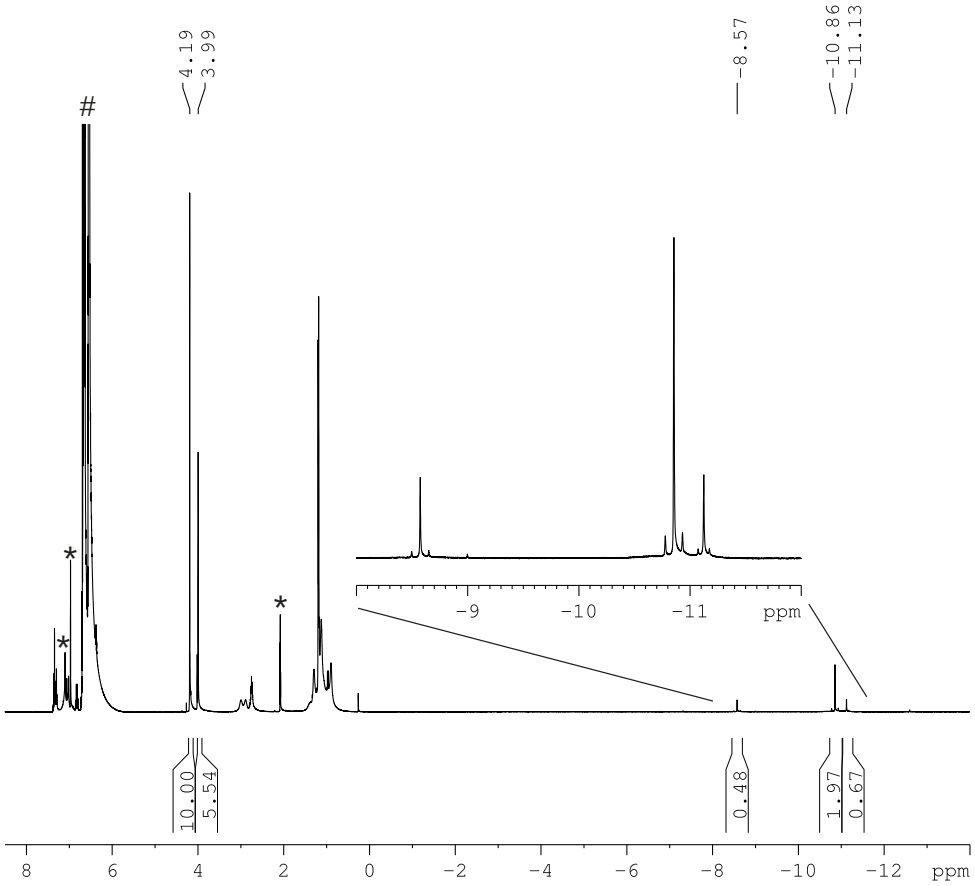



```
Current Data Parameters
NAME           MW920_400
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210113
Time               14.40
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 52656
SOLVENT              Tol
NS                   128
DS                     0
SWH            16025.641 Hz
FIDRES          0.304346 Hz
AQ             1.6428672 sec
RG                  45.2
DW                31.200 usec
DE                 6.00 usec
TE                299.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.60 usec
PL1                -3.00 dB
PL1W        16.03799057 W
SFO1        400.1100000 MHz

F2 - Processing parameters
SI                 65536
SF          400.1080006 MHz
WDW                   EM
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```

* tol-d_8
\# 1,2-$C_6H_4F_2$

Figure S10, ^{1}H NMR of compound **3a**.

^{1}H NMR (tol-d_8 + 1,2-difluorobenzene, −20 °C) of [(Cp_2WH_2)SnAr*][Al(O^{t}Bu^{F})$_4$] (**3a**)

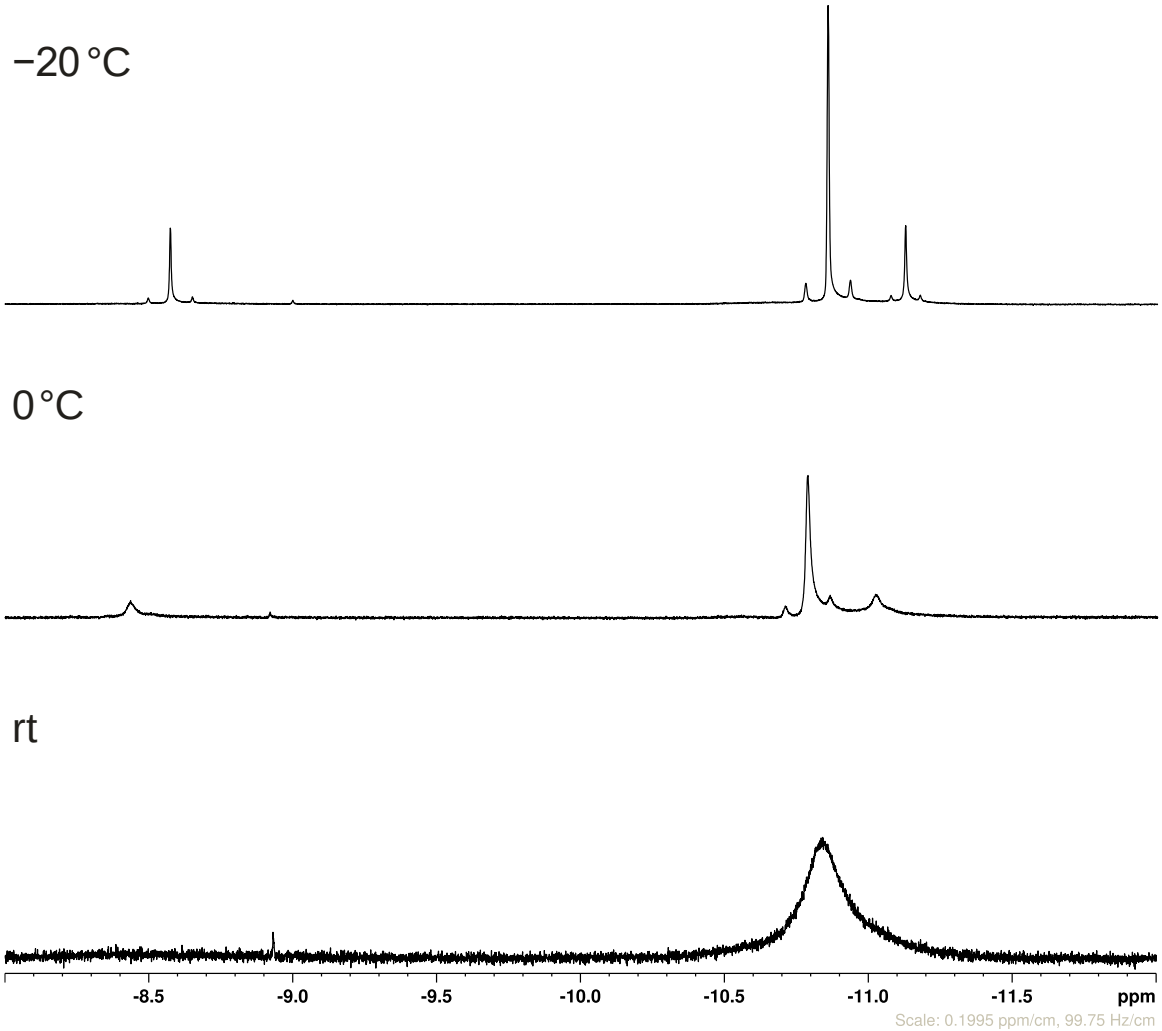



```
Current Data Parameters
NAME      MW957_500_[WH2Sn][Kr]_VT
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_           20210118
Time               14.22
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT              Tol
NS                    64
DS                     0
SWH            20000.000 Hz
FIDRES          0.305176 Hz
AQ             1.6384000 sec
RG                     4
DW                25.000 usec
DE                 6.00 usec
TE                251.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1       0 dB
PL1W        21.60222244 W
SFO1        500.1300000 MHz

F2 - Processing parameters
SI                 65536
SF          500.1300253 MHz
WDW                   no
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```

* tol-d_8
\# 1,2-$C_6H_4F_2$

Figure S11, ^{1}H NMR (-20°C) of compound **3a**.

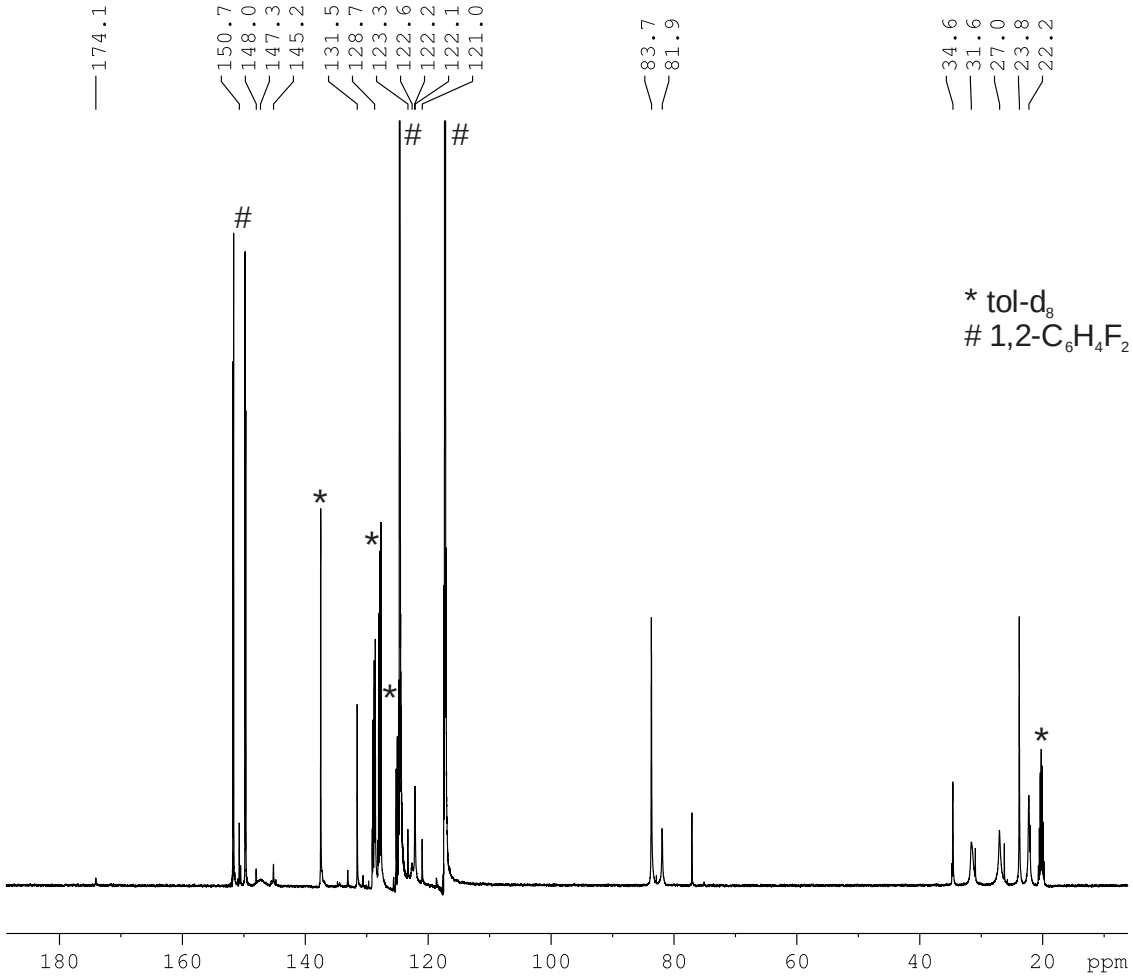
^{1}H-NMR (tol-d_8 + 1,2-difluorobenzene, VT) of $[(Cp_2WH_2)SnAr^*][Al(O^tBu^F)_4]$ (**3a**)




```
Current Data Parameters
NAME     MW957_500_[WH2Sn][Kr]_VT
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_           20210118
Time              13.57
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT             Tol
NS                   32
DS                    0
SWH           20000.000 Hz
FIDRES         0.305176 Hz
AQ            1.6384000 sec
RG                    4
DW               25.000 usec
DE                6.00 usec
TE               299.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                12.50 usec
PL1       0 dB
PL1W        21.60222244 W
SFO1        500.1300000 MHz

F2 - Processing parameters
SI                65536
SF          500.1300238 MHz
WDW                  no
SSB       0
LB        0 Hz
GB        0
PC                 1.00
```

Figure S12, ^{1}H NMR (VT) of compound **3a**.

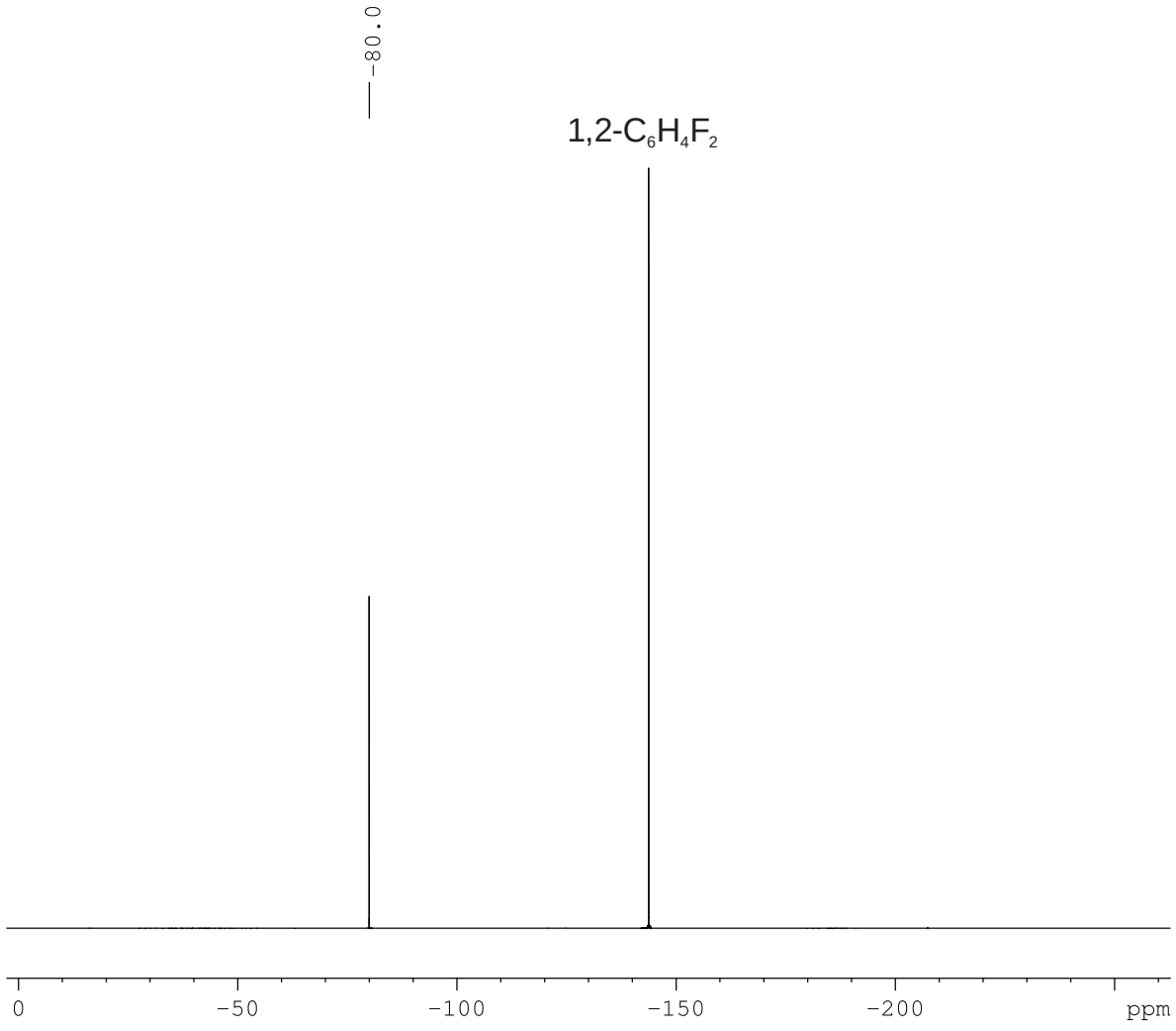
$^{13}C\{^{1}H\}$ NMR (tol-d_8 + 1,2-difluorobenzene, rt) of $[(Cp_2WH_2)SnAr^*][Al(O^tBu^F)_4]$ (**3a**)




```
Current Data Parameters
NAME      MW957_500_[WH2Sn][Kr]_VT
EXPNO                 21
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210119
Time                1.09
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             udeft
TD                  27268
SOLVENT               Tol
NS                  18432
DS                      0
SWH             37878.789 Hz
FIDRES          1.389130 Hz
AQ              0.3599376 sec
RG                   2050
DW                13.200 usec
DE                 6.00 usec
TE                273.2 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
D20         100.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 12.00 usec
P13              2000.00 usec
P26               500.00 usec
PL1       0 dB
PL1W         83.89700317 W
SFO1         125.7728799 MHz
SP8                 6.58 dB
SP13                6.58 dB
SPNAM[8] Crp60,0.5,20.1
SPNAM[13    Crp60comp.4
SPOAL8               0.500
SPOAL13              0.500
SPOFFS8   0 Hz
SPOFFS13  0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2       0 dB
PL12                16.12 dB
PL2W         21.60222244 W
PL12W         0.52783525 W
SFO2         500.1325007 MHz

F2 - Processing parameters
SI                  262144
SF           125.7577527 MHz
WDW                    EM
SSB       0
LB                  2.00 Hz
GB        0
PC                  1.40
```

Figure S13. $^{13}C\{^{1}H\}$ NMR of compound **3a**.

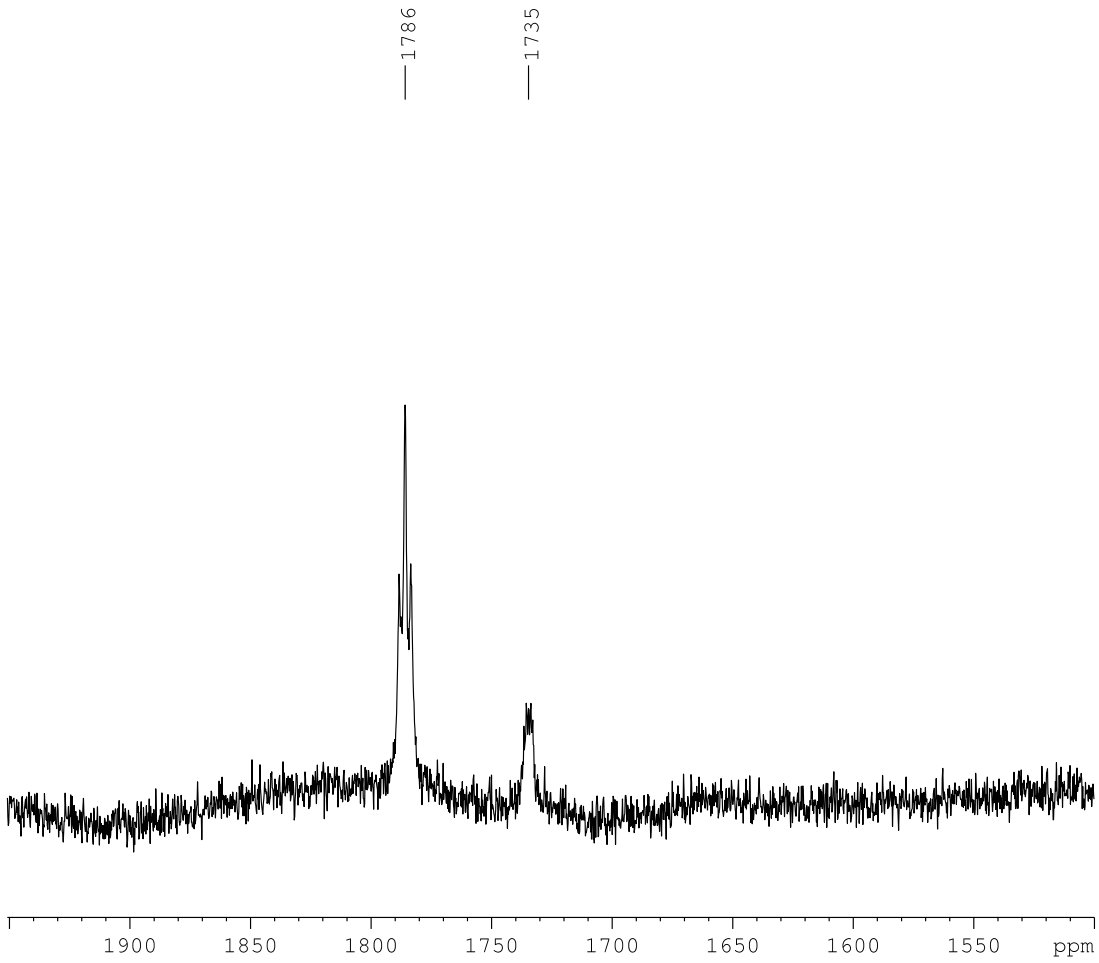
$^{19}F\{^{1}H\}$ NMR (tol-d_8 + 1,2-difluorobenzene, rt) of $[(Cp_2WH_2)SnAr^*][Al(O^tBu^F)_4]$ (**3a**)




```
Current Data Parameters
NAME          MW920_400
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20210113
Time              14.48
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG        zgfhigqn
TD               131072
SOLVENT             Tol
NS                  256
DS                    0
SWH          100000.000 Hz
FIDRES         0.762939 Hz
AQ             0.6553600 sec
RG                 4100
DW                5.000 usec
DE                6.00 usec
TE                299.2 K
D1           1.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 19F
P1                18.75 usec
PL1               -2.92 dB
PL1W        30.50645256 W
SFO1        376.4306030 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -3.00 dB
PL12              11.77 dB
PL2W        16.03799057 W
PL12W        0.53474891 W
SFO2        400.1120007 MHz

F2 - Processing parameters
SI                 262144
SF          376.4795470 MHz
WDW                   EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 1.00
```

Figure S14. $^{19}F\{^{1}H\}$ NMR of compound **3a**.

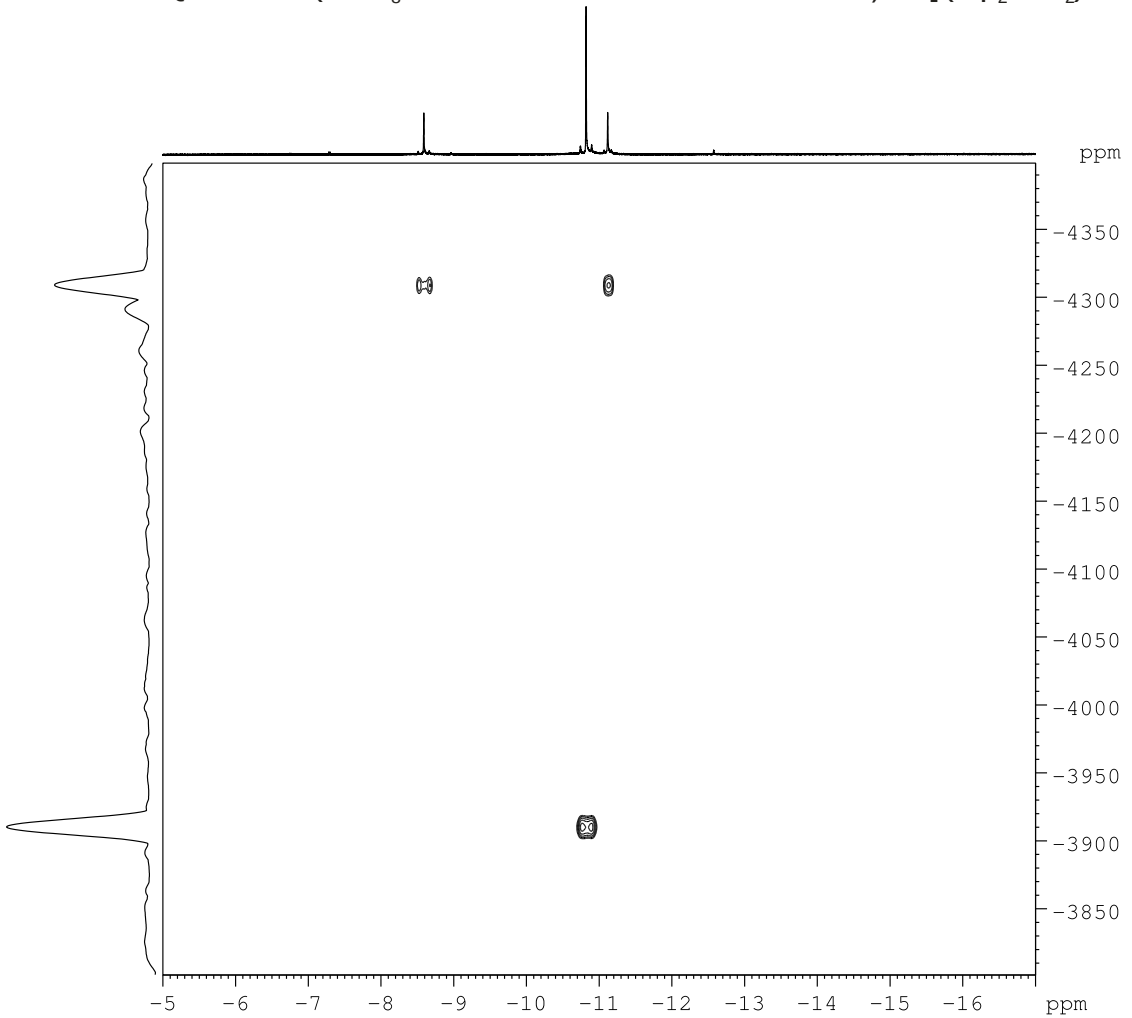
^{119}Sn NMR (tol-d_8 + 1,2-difluorobenzene, rt) of [(Cp_2WH_2)SnAr*][Al(O^tBu^F)$_4$] (**3a**)




```
Current Data Parameters
NAME       MW920_300_Sn
EXPNO                24
PROCNO                1

F2 - Acquisition Parameters
Date_          20210113
Time              22.05 h
INSTRUM            spect
PROBHD   Z104275_0338 (
PULPROG             zg30
TD                  8918
SOLVENT              Tol
NS                307200
DS                     1
SWH            89285.711 Hz
FIDRES         20.023708 Hz
AQ             0.0499408 sec
RG                204.67
DW                 5.600 usec
DE                 6.50 usec
TE                298.0 K
D1           0.02000000 sec
TD0                    1
SFO1         112.0994460 MHz
NUC1               119Sn
P0                 4.03 usec
P1                12.10 usec
PLW1         12.00000000 W

F2 - Processing parameters
SI                  4096
SF           111.9203740 MHz
WDW                   EM
SSB       0
LB                10.00 Hz
GB        0
PC                 1.40
```

Figure S15. ^{119}Sn NMR of compound **3a**.

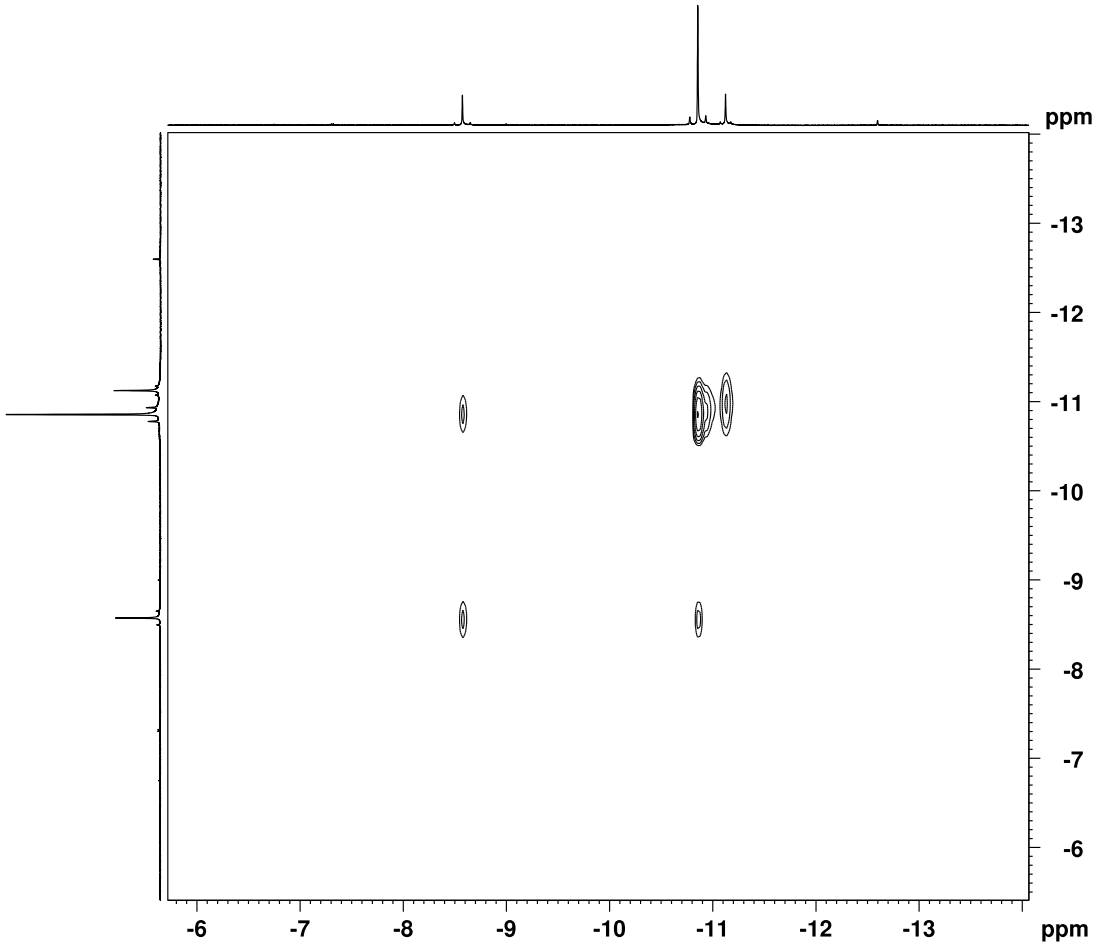
$^{1}H,^{183}W$ HMQC NMR (tol-d_8 + 1,2-difluorobenzene, −40 °C) of [$(Cp_2WH_2)SnAr^*$][$Al(O^tBu^F)_4$] (**3a**)




```
Current Data Parameters
NAME         MW920_500_W
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210112
Time               14.57
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG           hmqcph
TD                 1024
SOLVENT             Tol
NS                    4
DS                   16
SWH           10000.000 Hz
FIDRES         9.765625 Hz
AQ            0.0512000 sec
RG                    4
DW               50.000 usec
DE                6.00 usec
TE               232.2 K
CNST2         76.6999969
D0            0.00000300 sec
D1            2.00000000 sec
D2            0.00651891 sec
D11           0.03000000 sec
D13           0.00000400 sec
IN0           0.00004015 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                12.50 usec
P2                25.00 usec
PL1       0 dB
PL1W        21.60222244 W
SFO1       500.1249987 MHz

======== CHANNEL f2 ========
CPDPRG[2             garp
NUC2                 183W
P3                28.00 usec
PCPD2             400.00 usec
PL2       0 dB
PL12              23.10 dB
SFO2         20.7519179 MHz

F1 - Acquisition parameters
TD                    91
SFO1           20.75192 MHz
FIDRES        273.651672 Hz
SW               600.000 ppm
FnMODE       States-TPPI

F2 - Processing parameters
SI                  1024
SF           500.1300000 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
PC                  1.00

F1 - Processing parameters
SI                  1024
MC2          States-TPPI
SF           20.8373510 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
```

Figure S16. ^{1}H, ^{183}W HMQC NMR (-40°C) of compound **3a**.

$^{1}H,^{1}H$ EXSY NMR (tol-d_8 + 1,2-difluorobenzene, −20 °C) of $[(Cp_2WH_2)SnAr^*][Al(O^tBu^F)_4]$ (**3a**)

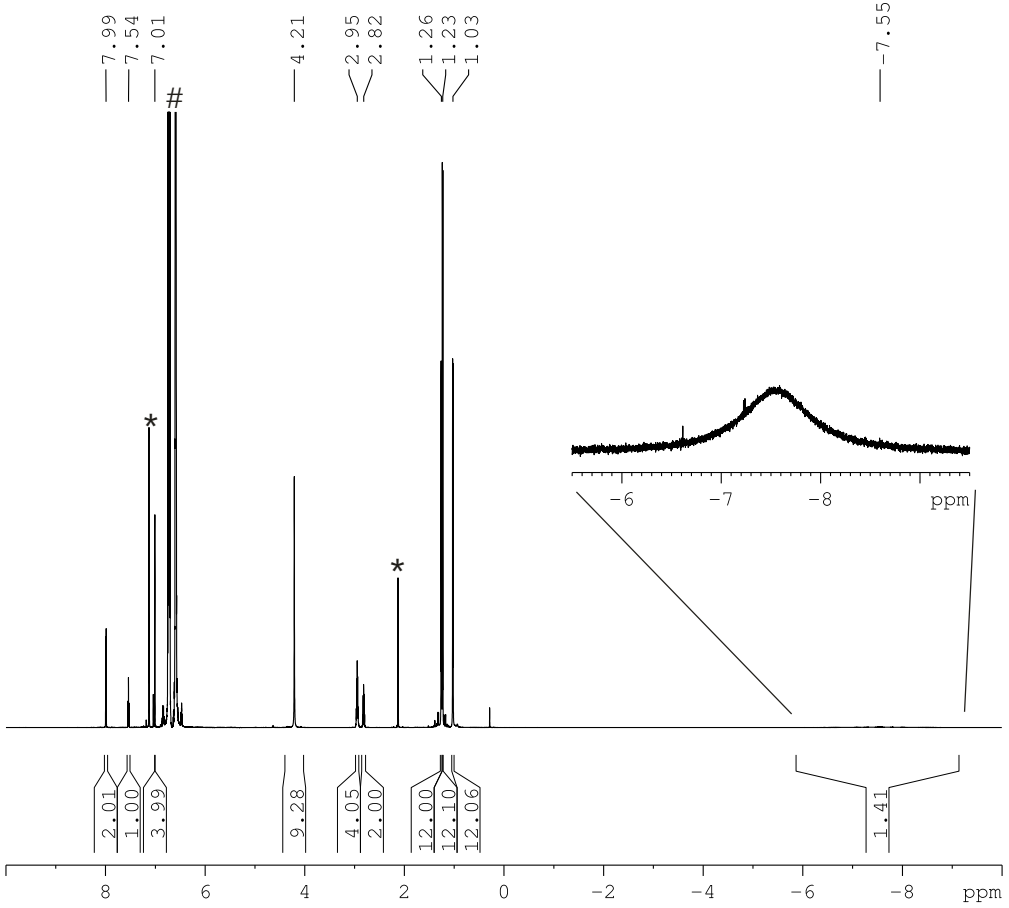



```
Current Data Parameters
NAME      MW957_500_[WH2Sn][Kr]_VT
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210118
Time              14.26
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG       noesygpph
TD                1024
SOLVENT            Tol
NS                  16
DS                  16
SWH           12019.230 Hz
FIDRES        11.737530 Hz
AQ            0.0425984 sec
RG                  64
DW               41.600 usec
DE                6.00 usec
TE               251.6 K
D0            0.00002717 sec
D1            1.50000000 sec
D8            0.30000001 sec
D16           0.00020000 sec
IN0           0.00008330 sec

======== CHANNEL f1 ========
NUC1                1H
P1                11.38 usec
P2                22.76 usec
PL1       0 dB
PL1W       21.60222244 W
SFO1       500.1289997 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPZ1              40.00 %
GPZ2             -40.00 %
P16             1000.00 usec

F1 - Acquisition parameters
TD                  130
SFO1            500.129 MHz
FIDRES       184.663010 Hz
SW               24.000 ppm
FnMODE      States-TPPI

F2 - Processing parameters
SI                1024
SF           500.1300242 MHz
WDW               QSINE
SSB                   2
LB        0 Hz
GB        0
PC                 1.00

F1 - Processing parameters
SI                1024
MC2         States-TPPI
SF           500.1300211 MHz
WDW               QSINE
SSB                   2
LB        0 Hz
GB        0
```

Figure S17. ^{1}H, ^{1}H EXSY NMR (-20°C) of compound **3a**.

Compound **3b**

^{1}H NMR (tol-d_8 + 1,2-difluorobenzene , rt) of [(Cp_2WH_2)PbAr*][Al(O^tBu^F)$_4$] (**3b**)




```
Current Data Parameters
NAME      MW820_700_13C
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_          20200921
Time             14.03 h
INSTRUM           spect
PROBHD   Z135421_0007 (
PULPROG           zg30
TD               65536
SOLVENT            Tol
NS                  32
DS                   2
SWH          21008.404 Hz
FIDRES        0.641126 Hz
AQ           1.5597568 sec
RG                6.77
DW              23.800 usec
DE              10.00 usec
TE              298.0 K
D1           1.00000000 sec
TD0                  1
SFO1        700.2900000 MHz
NUC1                1H
P1                8.00 usec
PLW1        14.67599964 W

F2 - Processing parameters
SI               65536
SF          700.2900000 MHz
WDW                 EM
SSB      0
LB               0.30 Hz
GB       0
PC               1.00
```

* tol-d_8
\# 1,2-$C_6H_4F_2$

Figure S18, ^{1}H NMR of compound **3b** {WCA = [Al(O^tBu^F)$_4$]}.

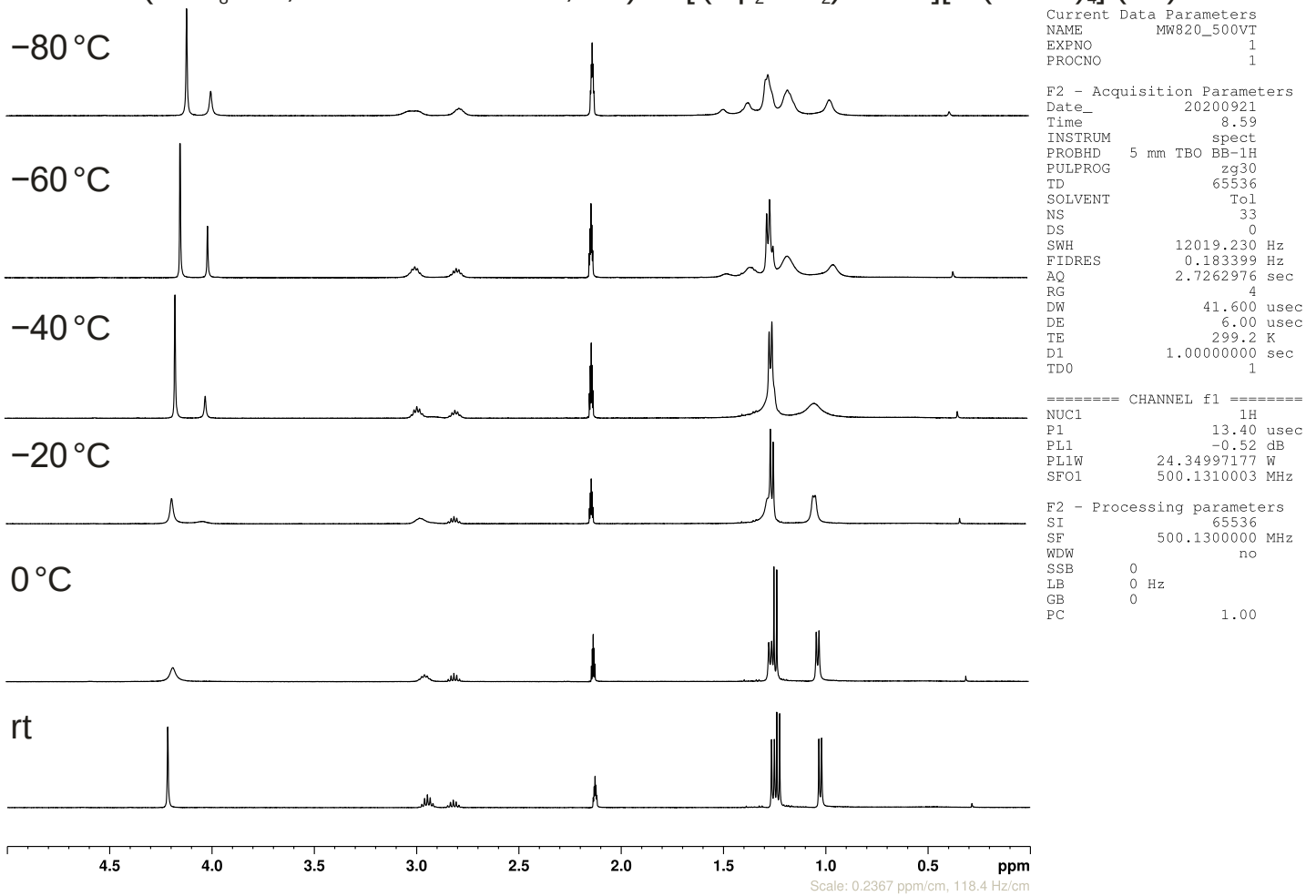


Figure S19, ^{1}H NMR (VT) of compound **3b** {WCA = [Al(O^{t}Bu^F)$_4$]} (5-0 ppm).

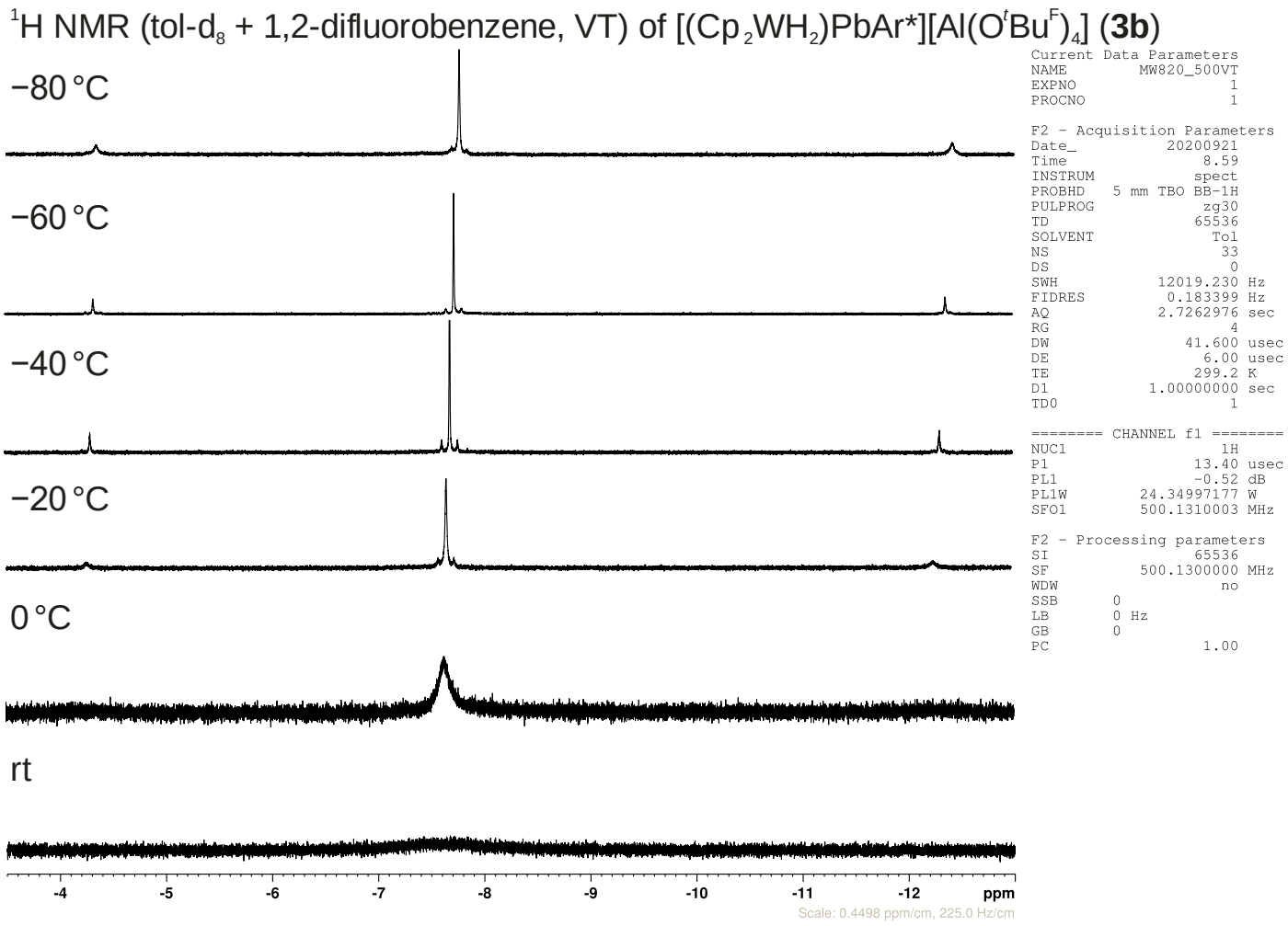
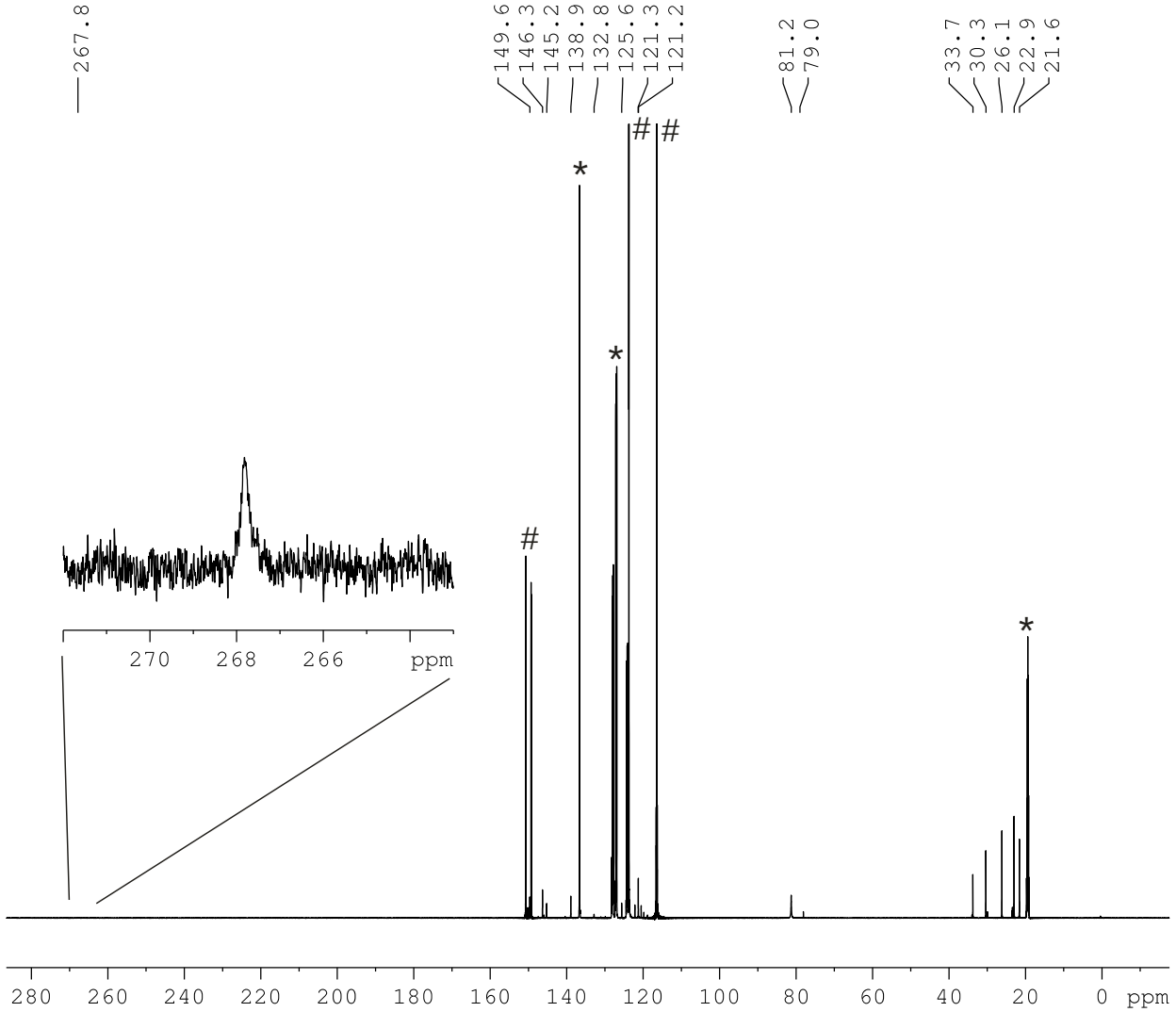


Figure S20, ^{1}H NMR (VT) of compound **3b** {WCA = [Al(O^{t}Bu^F)$_4$]} (-3.5- -13 ppm).

$^{13}C\{^{1}H\}$ NMR (tol-d_8 + 1,2-difluorobenzene, rt) of of $[(Cp_2WH_2)PbAr^*][Al(O^tBu^F)_4]$ (**3b**)

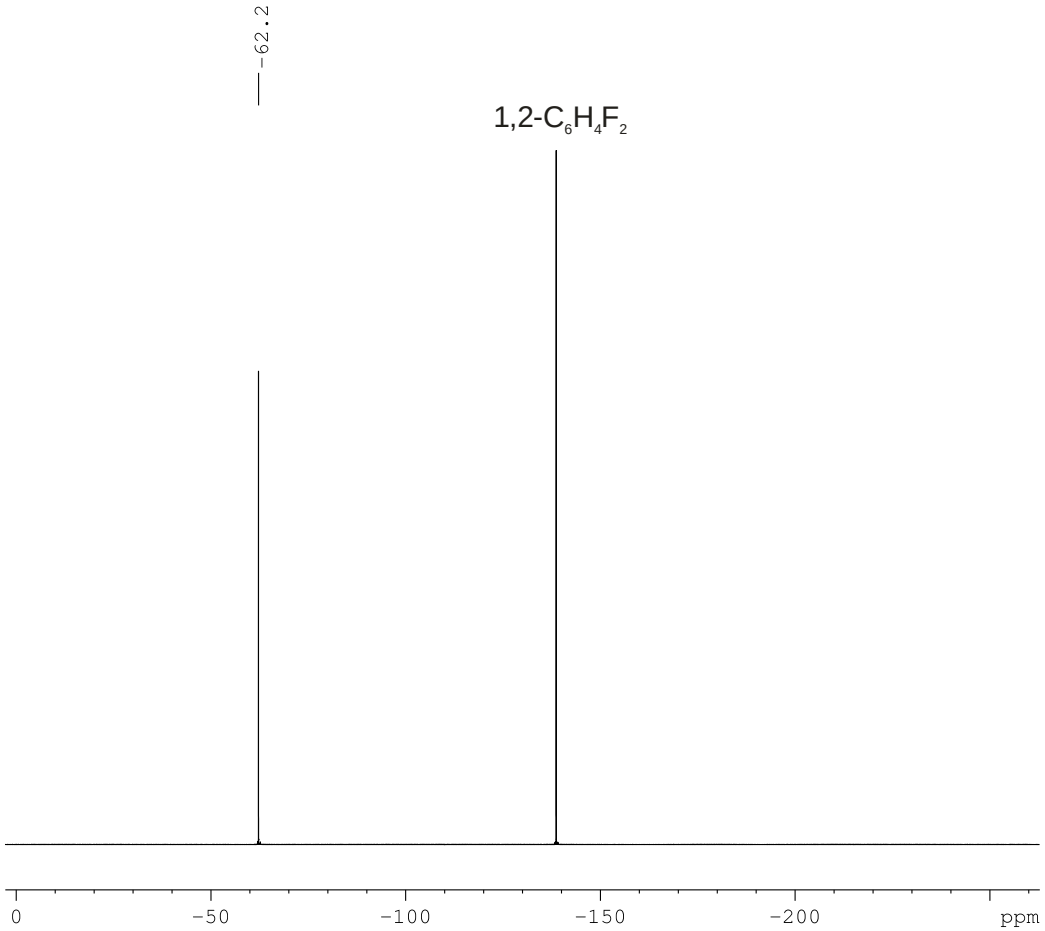



```
Current Data Parameters
NAME      MW820_700_13C
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_           20200922
Time               7.41 h
INSTRUM            spect
PROBHD   Z135421_0007 (
PULPROG            udeft
TD                 32768
SOLVENT              Tol
NS                 13312
DS                     0
SWH            53571.430 Hz
FIDRES          3.269741 Hz
AQ             0.3058347 sec
RG                179.42
DW                 9.333 usec
DE                18.00 usec
TE                298.0 K
D1           4.00000000 sec
D12          0.00002000 sec
D20        200.00000000 sec
TD0                    1
SFO1         176.1118324 MHz
NUC1                 13C
P1                12.00 usec
P13             2000.00 usec
P26              500.00 usec
PLW1        146.39999390 W
SPNAM[5]     Crp80comp.4
SPOAL5             0.500
SPOFFS5  0 Hz
SPW5         42.94699860 W
SPNAM[8] Crp80,0.5,20.1
SPOAL8             0.500
SPOFFS8  0 Hz
SPW8         42.94699860 W
SFO2         700.2928012 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2              65.00 usec
PLW2        14.67599964 W
PLW12        0.22231001 W

F2 - Processing parameters
SI                131072
SF           176.0881546 MHz
WDW                  EM
SSB      0
LB                2.00 Hz
GB       0
PC                1.40
```

* tol-d_8
\# 1,2-$C_6H_4F_2$

Figure S21. $^{13}C\{^{1}H\}$ NMR of compound **3b** {WCA = $[Al(O^tBu^F)_4]$}.

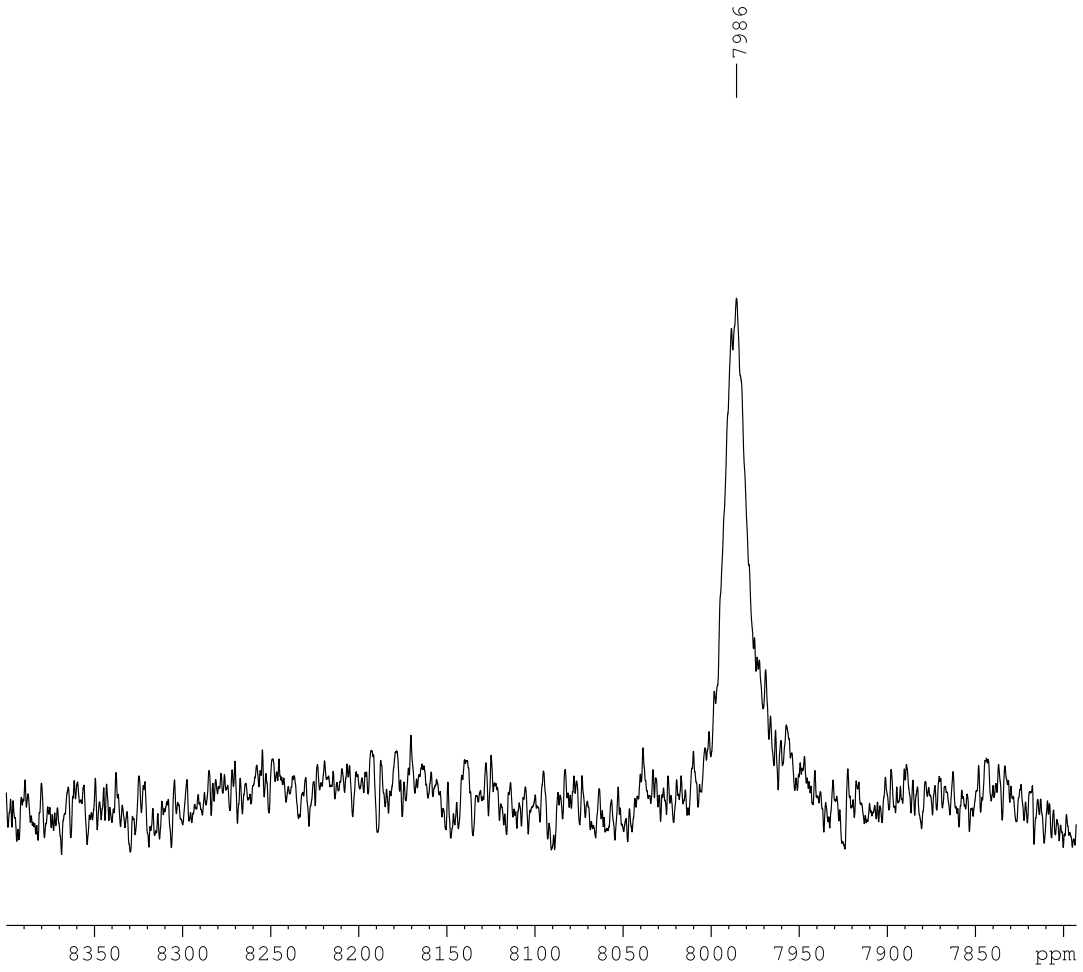
$^{19}F\{^{1}H\}$ NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[(Cp_2WH_2)PbAr^*][BAr^F{}_4]$ (**3b**)




```
Current Data Parameters
NAME       MW1054_400NM
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20210505
Time              17.51
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG         zgfhigqn
TD               131072
SOLVENT             C6D6
NS                   128
DS                     0
SWH          100000.000 Hz
FIDRES         0.762939 Hz
AQ             0.6553600 sec
RG                  4100
DW                 5.000 usec
DE                 6.00 usec
TE                299.2 K
D1           1.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 19F
P1                 18.75 usec
PL1                -2.92 dB
PL1W        30.50645256 W
SFO1        376.4306030 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               11.77 dB
PL2W        16.03799057 W
PL12W        0.53474891 W
SFO2        400.1120007 MHz

F2 - Processing parameters
SI                262144
SF          376.4795470 MHz
WDW                   EM
SSB      0
LB                 2.00 Hz
GB       0
PC                 1.00
```

Figure S22. $^{19}F\{^{1}H\}$ NMR of compound **3b** {WCA = $[Al(O^tBu^F)_4]$}.

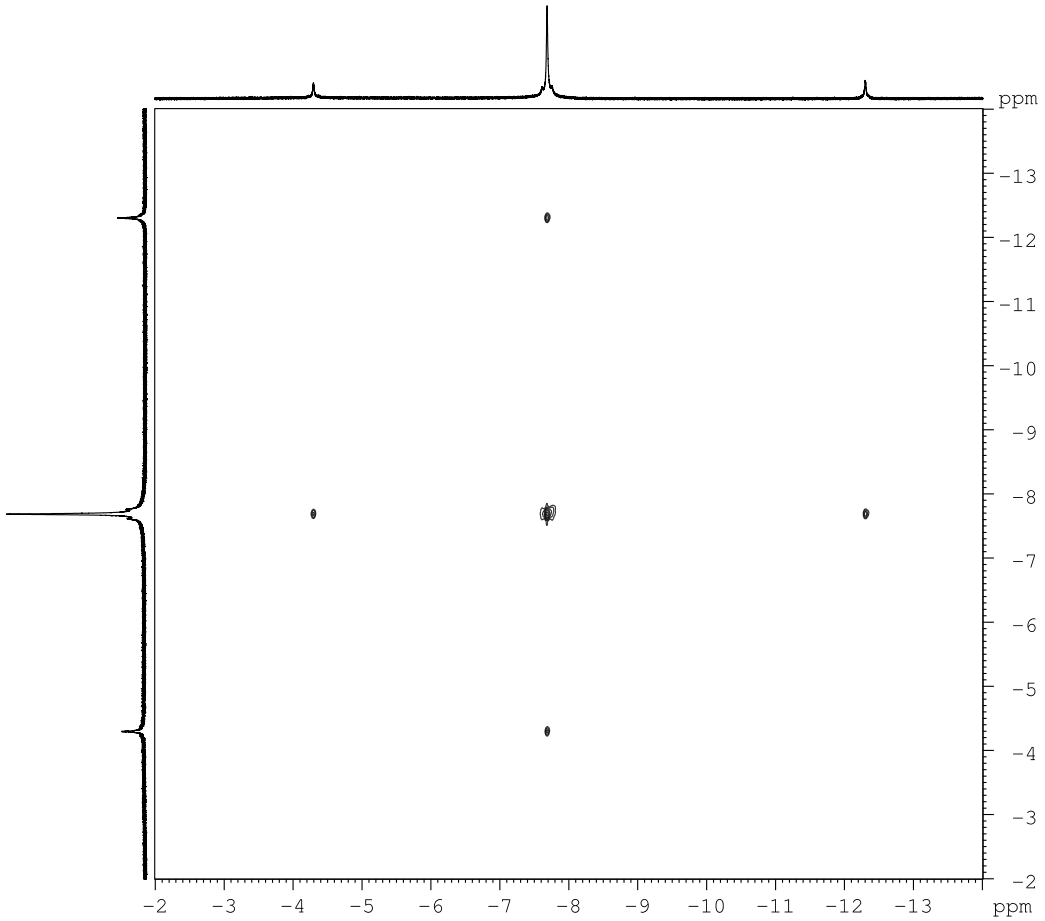
^{207}Pb NMR (C_6D_6 + 1,2-difluorobenzene, rt) of [(Cp_2WH_2)PbAr*][Al(O^tBu^F)$_4$] (**3b**)




```
Current Data Parameters
NAME         MW762_500Pb
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200803
Time               16.03
INSTRUM            spect
PROBHD   5 mm TBO BB-1H
PULPROG             zg30
TD                 15608
SOLVENT             C6D6
NS                307200
DS                     0
SWH            85227.273 Hz
FIDRES          5.460486 Hz
AQ             0.0915669 sec
RG                  2050
DW                 5.867 usec
DE                 17.40 usec
TE                 299.2 K
D1           0.05000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1               207Pb
P1                  9.50 usec
PL1       0 dB
SFO1        105.4881596 MHz

F2 - Processing parameters
SI                131072
SF          104.6301920 MHz
WDW                 EM
SSB       0
LB                100.00 Hz
GB        0
PC                  1.40
```

Figure S23. ^{207}Pb NMR of compound **3b** {WCA = [Al(O^tBu^F)$_4$]}.

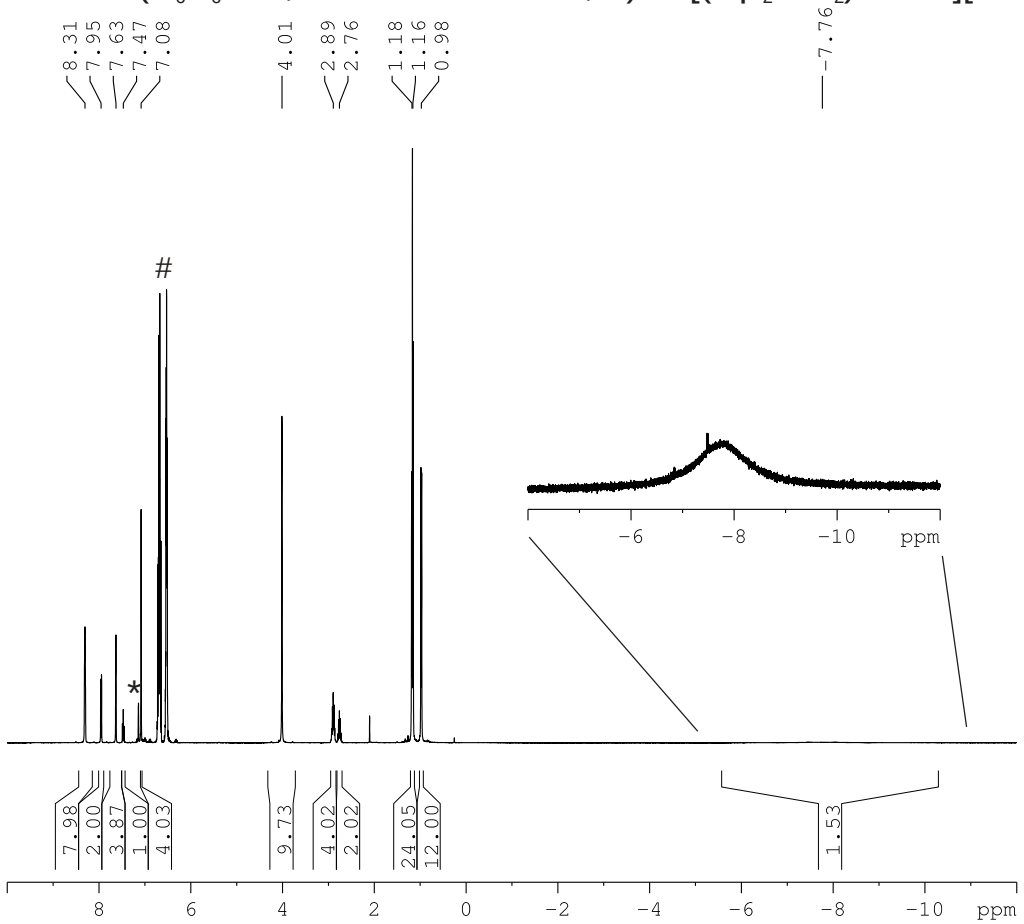
^{1}H,^{1}H EXSY NMR (tol-d$_8$ + 1,2-difluorobenzene, −40 °C) of [(Cp$_2$WH$_2$)PbAr*][Al(O^{t}Bu^F)$_4$] (**3b**)




```
Current Data Parameters
NAME          MW923_500_W
EXPNO                   7
PROCNO                  1

F2 - Acquisition Parameters
Date_           20210112
Time               13.53
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG        noesygpph
TD                  1024
SOLVENT              Tol
NS                     2
DS                    16
SWH             6009.615 Hz
FIDRES          5.868765 Hz
AQ             0.0851968 sec
RG                    64
DW               83.200 usec
DE                6.00 usec
TE                233.4 K
D0            0.00006729 sec
D1            1.50000000 sec
D8            0.30000001 sec
D16           0.00020000 sec
IN0           0.00016640 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                12.50 usec
P2                25.00 usec
PL1       0 dB
PL1W         21.60222244 W
SFO1        500.1259990 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPZ1               40.00 %
GPZ2              -40.00 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                    256
SFO1            500.126 MHz
FIDRES         46.949329 Hz
SW                12.016 ppm
FnMODE       States-TPPI

F2 - Processing parameters
SI                   1024
SF           500.1300000 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
PC                   1.00

F1 - Processing parameters
SI                   1024
MC2          States-TPPI
SF           500.1300000 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
```

Figure S24. EXSY NMR (-40°C) of compound **3b** {WCA = [Al(O^{t}Bu^F)$_4$]}.

^{1}H NMR (C_6D_6 + 1,2-difluorobenzene, rt) of [(Cp_2WH_2)PbAr*][BAr^F_4] (**3b**)

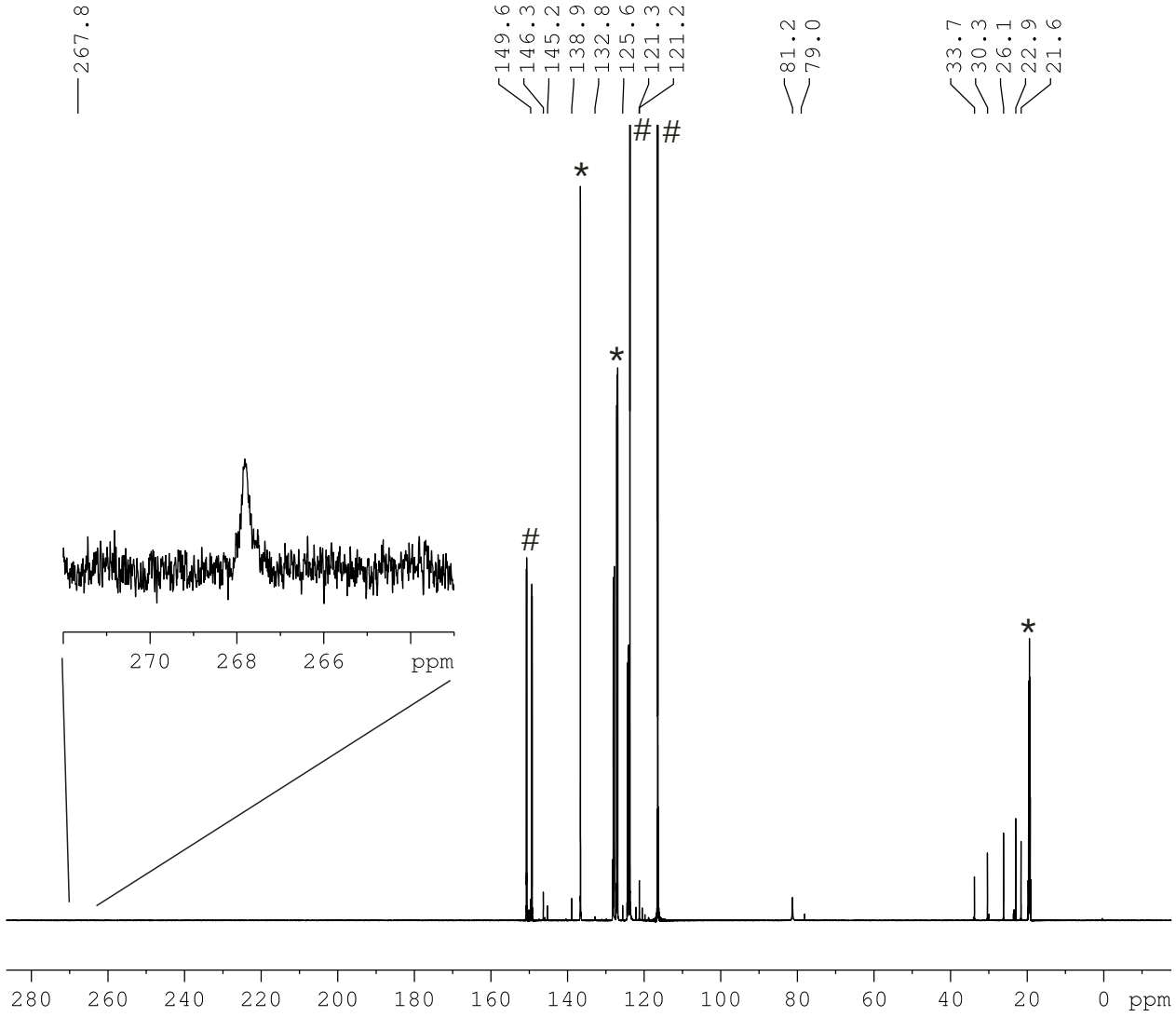



```
Current Data Parameters
NAME       MW1054_400NM
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210505
Time               17.47
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 52656
SOLVENT             C6D6
NS                    64
DS                     0
SWH            16025.641 Hz
FIDRES          0.304346 Hz
AQ             1.6428672 sec
RG                  50.8
DW                31.200 usec
DE                 6.00 usec
TE                299.2 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.60 usec
PL1                -3.00 dB
PL1W        16.03799057 W
SFO1        400.1100000 MHz

F2 - Processing parameters
SI                 65536
SF          400.1100000 MHz
WDW                   EM
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```

* C_6D_6
\# 1,2-$C_6H_4F_2$

Figure S25, ^{1}H NMR of compound **3b** {WCA = [BAr^F]}.

$^{13}C\{^{1}H\}$ NMR (tol-d_8 + 1,2-difluorobenzene, rt) of of $[(Cp_2WH_2)PbAr^*][Al(O^tBu^F)_4]$ (**3b**)

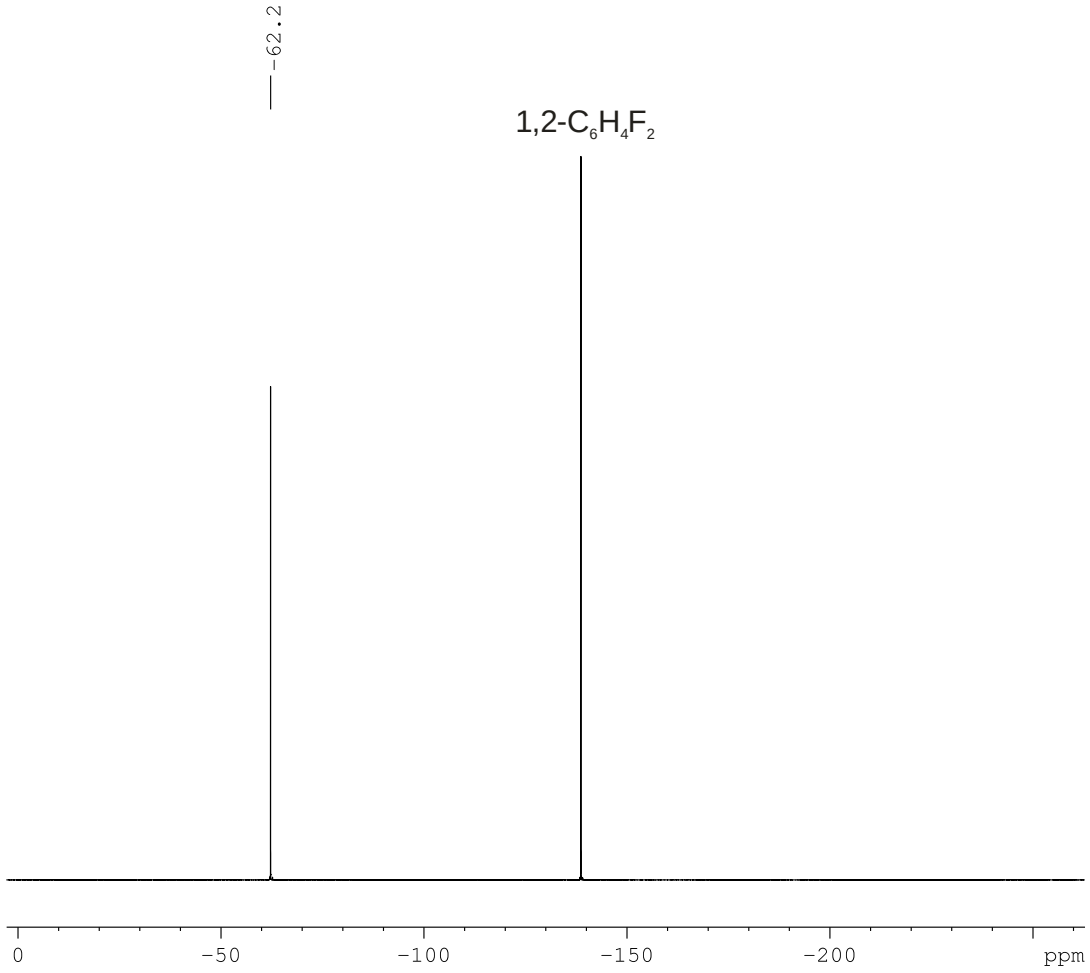



```
Current Data Parameters
NAME      MW820_700_13C
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20200922
Time               7.41 h
INSTRUM           spect
PROBHD   Z135421_0007 (
PULPROG           udeft
TD                32768
SOLVENT             Tol
NS                13312
DS                    0
SWH           53571.430 Hz
FIDRES         3.269741 Hz
AQ            0.3058347 sec
RG               179.42
DW                9.333 usec
DE                18.00 usec
TE                298.0 K
D1           4.00000000 sec
D12          0.00002000 sec
D20        200.00000000 sec
TD0                   1
SFO1        176.1118324 MHz
NUC1                13C
P1                12.00 usec
P13             2000.00 usec
P26              500.00 usec
PLW1       146.39999390 W
SPNAM[5]    Crp80comp.4
SPOAL5            0.500
SPOFFS5  0 Hz
SPW5        42.94699860 W
SPNAM[8] Crp80,0.5,20.1
SPOAL8            0.500
SPOFFS8  0 Hz
SPW8        42.94699860 W
SFO2        700.2928012 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             65.00 usec
PLW2        14.67599964 W
PLW12        0.22231001 W

F2 - Processing parameters
SI                131072
SF          176.0881546 MHz
WDW                 EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 1.40
```

* tol-d_8
\# 1,2-$C_6H_4F_2$

Figure S26. $^{13}C\{^{1}H\}$ NMR of compound **3b** {WCA = $[BAr^F]$}.

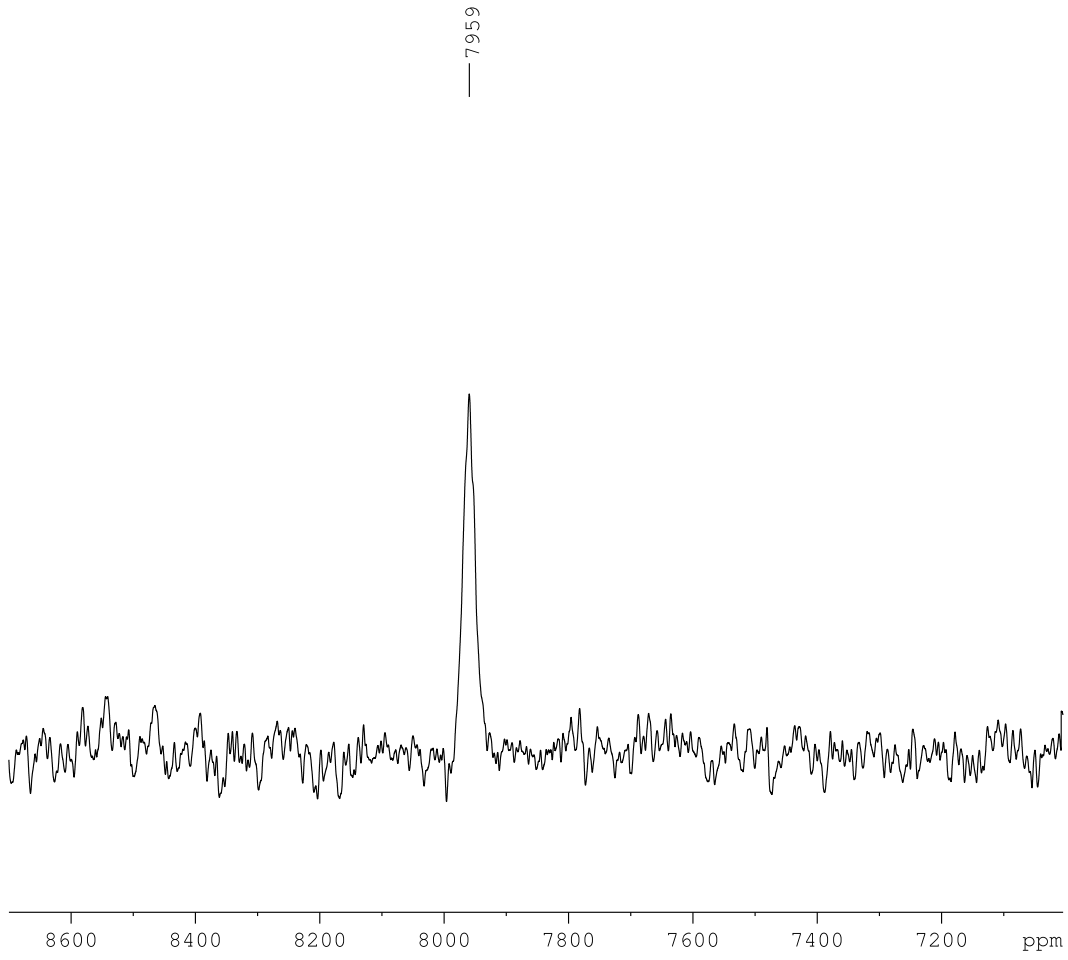
$^{19}F\{^{1}H\}$ NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[(Cp_2WH_2)PbAr^*][BAr^F_4]$ (**3b**)




```
Current Data Parameters
NAME       MW1054_400NM
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20210505
Time              17.51
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG         zgfhigqn
TD               131072
SOLVENT             C6D6
NS                   128
DS                     0
SWH           100000.000 Hz
FIDRES          0.762939 Hz
AQ              0.6553600 sec
RG                   4100
DW                5.000 usec
DE                6.00 usec
TE                299.2 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 19F
P1                18.75 usec
PL1               -2.92 dB
PL1W         30.50645256 W
SFO1         376.4306030 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -3.00 dB
PL12              11.77 dB
PL2W         16.03799057 W
PL12W         0.53474891 W
SFO2         400.1120007 MHz

F2 - Processing parameters
SI                 262144
SF           376.4795470 MHz
WDW                    EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 1.00
```

Figure S27. $^{19}F\{^{1}H\}$ NMR of compound **3b** {WCA = $[BAr^F]$}.

^{207}Pb NMR (C_6D_6 + 1,2-difluorobenzene, rt) of [(Cp_2WH_2)PbAr*][BAr^F_4] (**3b**)

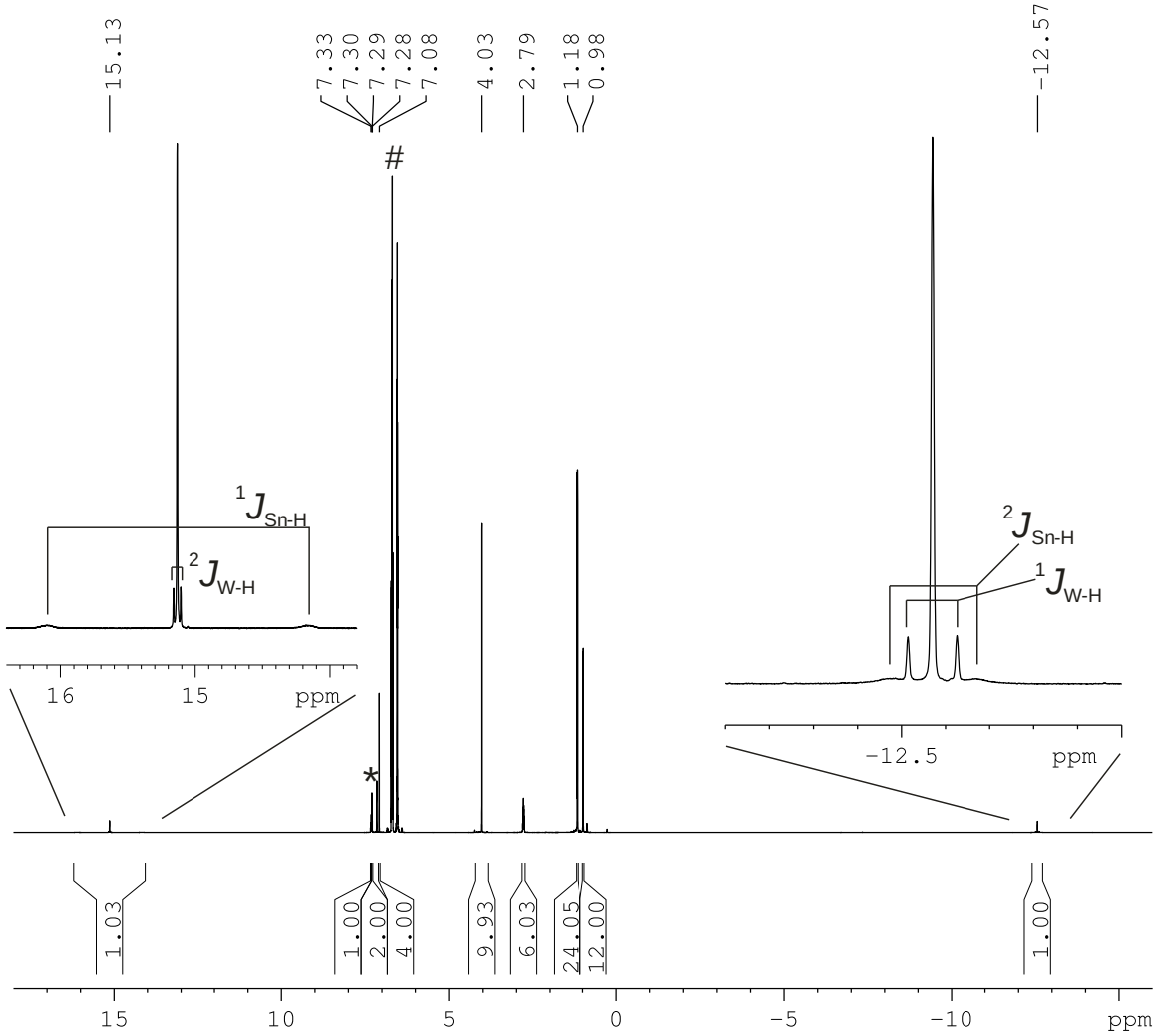



```
Current Data Parameters
NAME          MW1054_300
EXPNO                 21
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210508
Time                9.20 h
INSTRUM            spect
PROBHD   Z104275_0338 (
PULPROG             zg30
TD                 14998
SOLVENT             C6D6
NS                 25600
DS                     0
SWH           125000.000 Hz
FIDRES         16.668890 Hz
AQ              0.0599920 sec
RG                 204.67
DW                  4.000 usec
DE                 10.00 usec
TE                 298.0 K
D1            0.20000000 sec
TD0                    1
SFO1          63.2913058 MHz
NUC1               207Pb
P0                  4.17 usec
P1                 12.50 usec
PLW1         40.00000000 W

F2 - Processing parameters
SI                 65536
SF            62.7889938 MHz
WDW                   EM
SSB       0
LB                250.00 Hz
GB        0
PC                  3.00
```

Figure S28. ^{207}Pb NMR of compound **3b** {WCA = [BAr^F]}.

Compound **4a**

^{1}H NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2W(H)=Sn(H)Ar^*][Al(O^tBu^F)_4]$ (**4a**)

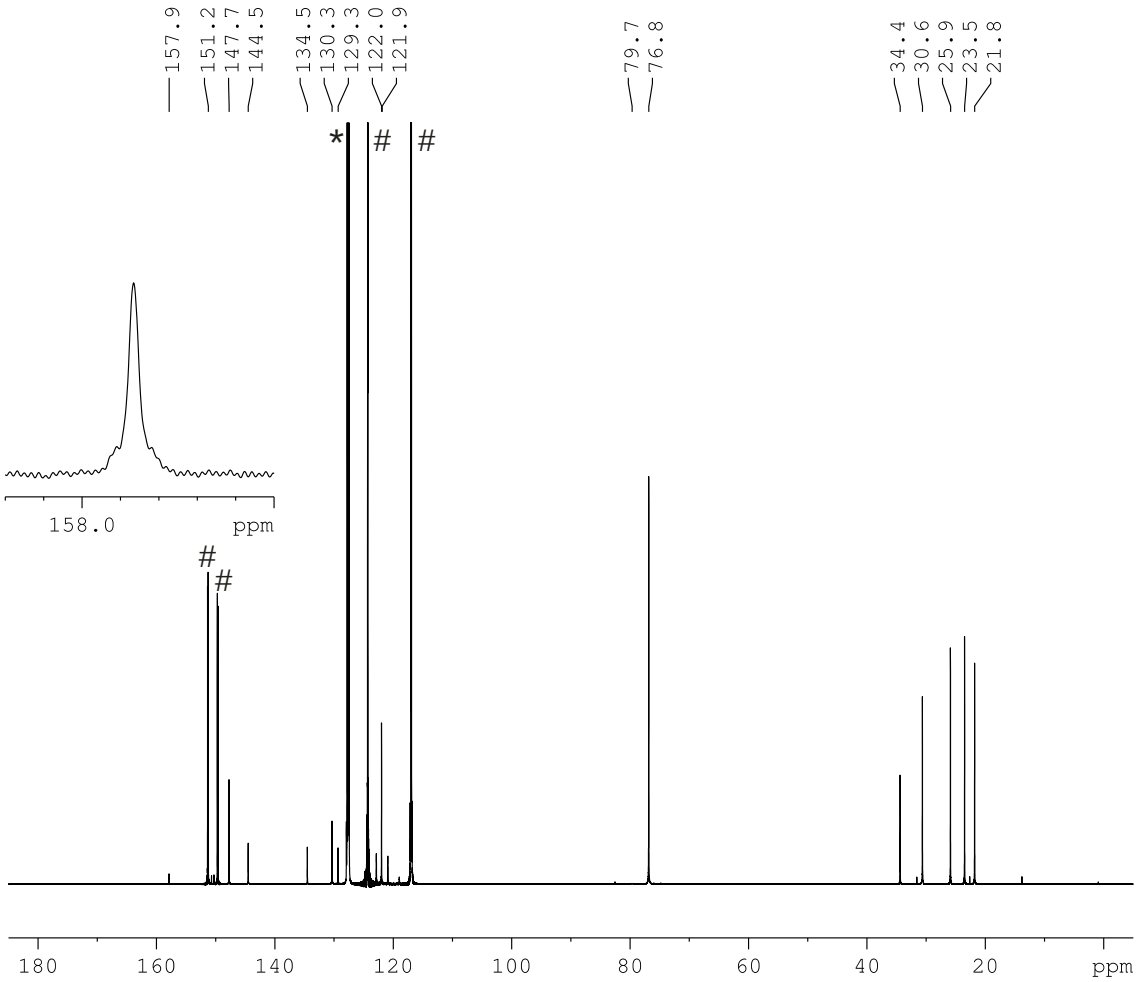



```
Current Data Parameters
NAME         MW830_600NM
EXPNO                 16
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201001
Time                8.44 h
INSTRUM            spect
PROBHD   Z126545_0027 (
PULPROG             zg30
TD                131072
SOLVENT             C6D6
NS                    19
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             2.7262976 sec
RG                 15.53
DW                20.800 usec
DE                10.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1
SFO1          600.1300000 MHz
NUC1                  1H
P1                 12.00 usec
PLW1          23.41200066 W

F2 - Processing parameters
SI                 65536
SF            600.1300000 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

* C_6D_6
\# 1,2-$C_6H_4F_2$

Figure S29. ^{1}H NMR of compound **4a** {WCA = $[Al(O^tBu^F)_4]$}.

$^{13}C\{^{1}H\}$ NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2W(H)=Sn(H)Ar^*][Al(O^tBu^F)_4]$ (**4a**)

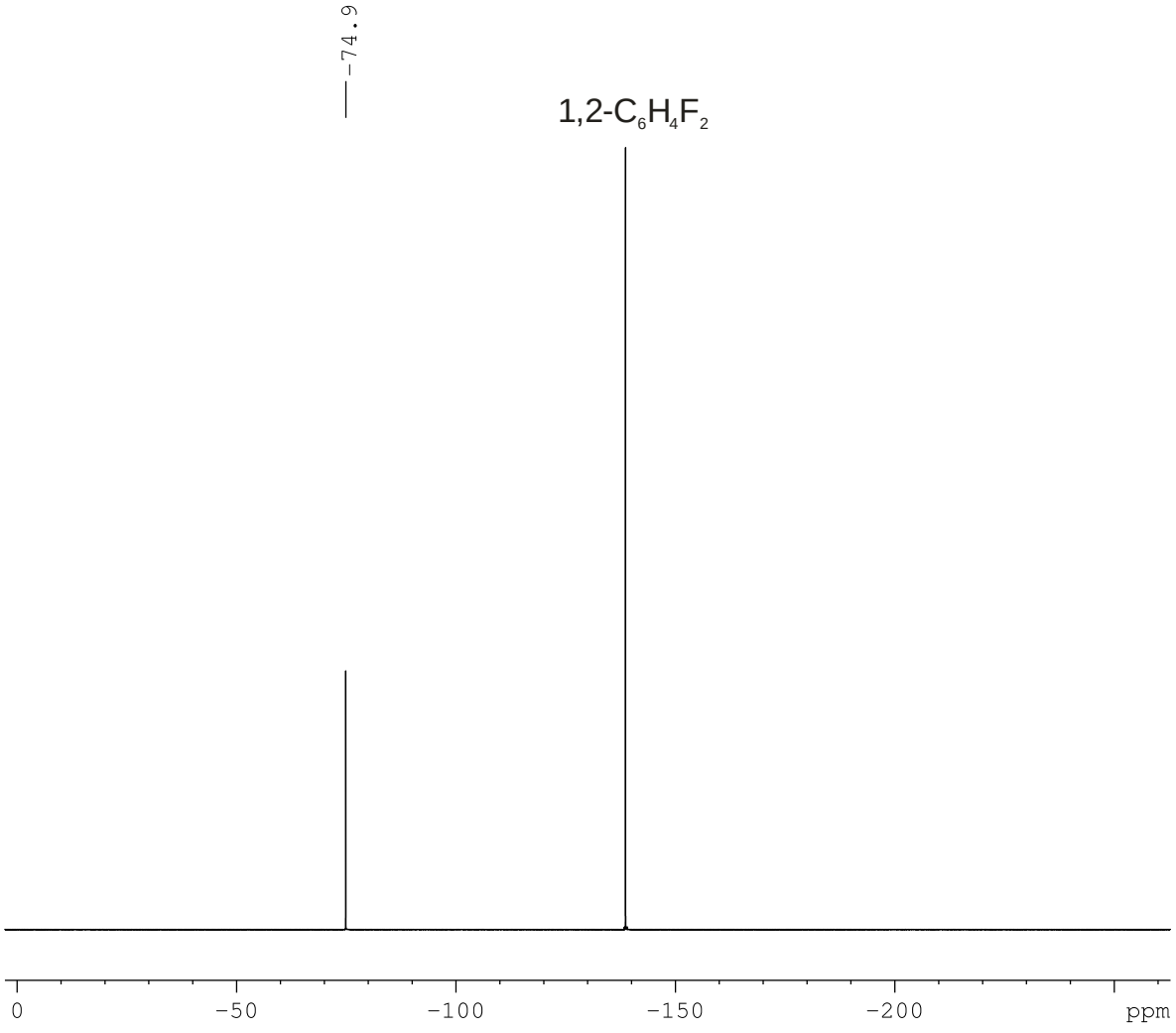



```
Current Data Parameters
NAME         MW830_600NM
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200930
Time              21.02 h
INSTRUM             spect
PROBHD   Z126545_0027 (
PULPROG             udeft
TD                  25902
SOLVENT              C6D6
NS                   4096
DS                      8
SWH           36231.883 Hz
FIDRES         2.797613 Hz
AQ            0.3574476 sec
RG                  189.6
DW                13.800 usec
DE                18.00 usec
TE                298.0 K
D1            4.00000000 sec
D12           0.00002000 sec
D20          20.00000000 sec
TD0                     1
SFO1         150.9178988 MHz
NUC1                  13C
P1                 10.00 usec
P13              2000.00 usec
P26               500.00 usec
PLW1         57.02700043 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5  0 Hz
SPW5          8.71310043 W
SPNAM[8] Crp60,0.5,20.1
SPOAL8             0.500
SPOFFS8  0 Hz
SPW8          8.71310043 W
SFO2         600.1324005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              70.00 usec
PLW2         23.41200066 W
PLW12         0.68803000 W

F2 - Processing parameters
SI                  131072
SF           150.9028085 MHz
WDW                   EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 1.40
```

* C_6D_6
\# 1,2-$C_6H_4F_2$

Figure S30. $^{13}C\{^{1}H\}$ NMR of compound **4a** {WCA = $[Al(O^tBu^F)_4]$}.

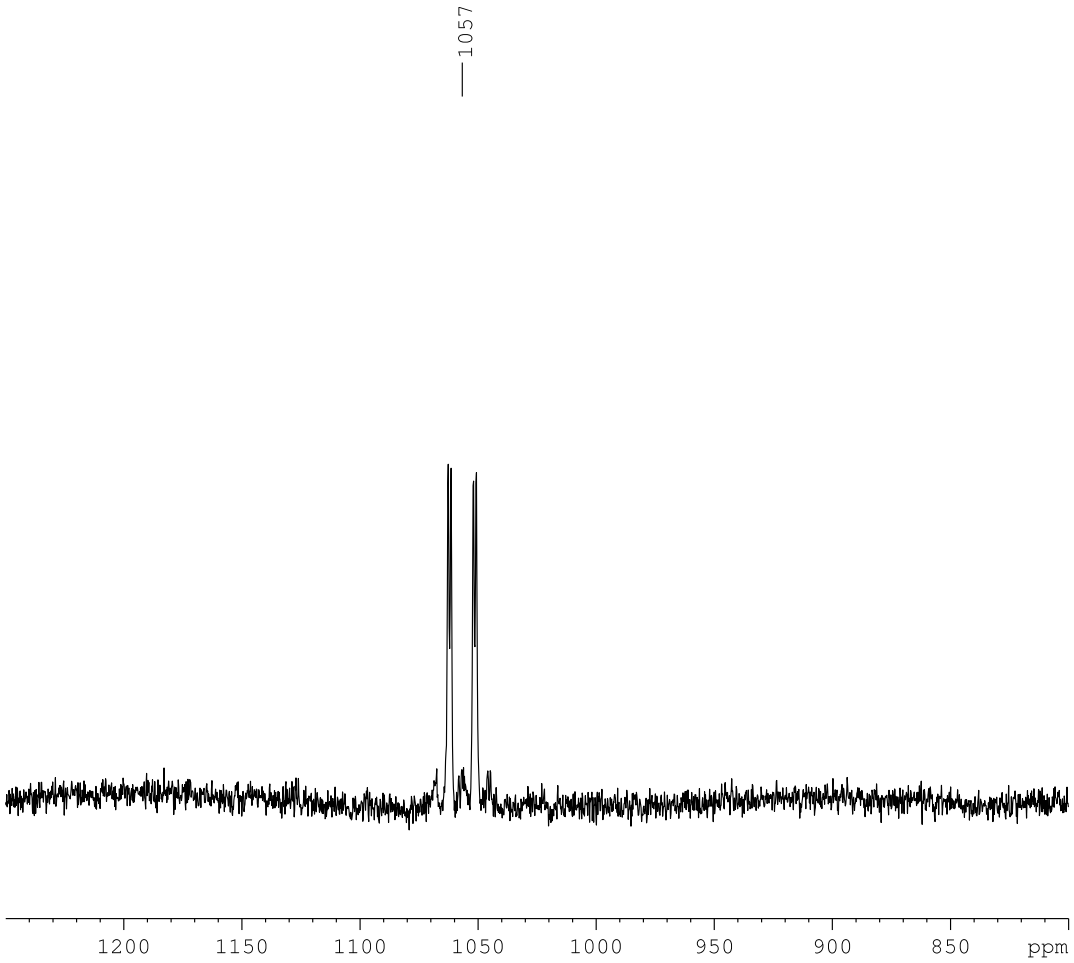
$^{19}F\{^{1}H\}$ NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2W(H)=Sn(H)Ar^*][Al(O^tBu^F)_4]$ (**4a**)




```
Current Data Parameters
NAME          MW830_400
EXPNO                21
PROCNO                1

F2 - Acquisition Parameters
Date_          20201001
Time               9.03
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG         zgfhigqn
TD                131072
SOLVENT             C6D6
NS                   128
DS                     0
SWH           100000.000 Hz
FIDRES          0.762939 Hz
AQ              0.6553600 sec
RG                  4100
DW                 5.000 usec
DE                 6.00 usec
TE                300.2 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 19F
P1                 18.75 usec
PL1                -2.92 dB
PL1W         30.50645256 W
SFO1         376.4306030 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               11.77 dB
PL2W         16.03799057 W
PL12W         0.53474891 W
SFO2         400.1120007 MHz

F2 - Processing parameters
SI                 262144
SF           376.4795470 MHz
WDW                  EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 1.00
```

Figure S31. $^{19}F\{^{1}H\}$ NMR of compound **4a** {WCA = $[Al(O^tBu^F)_4]$}.

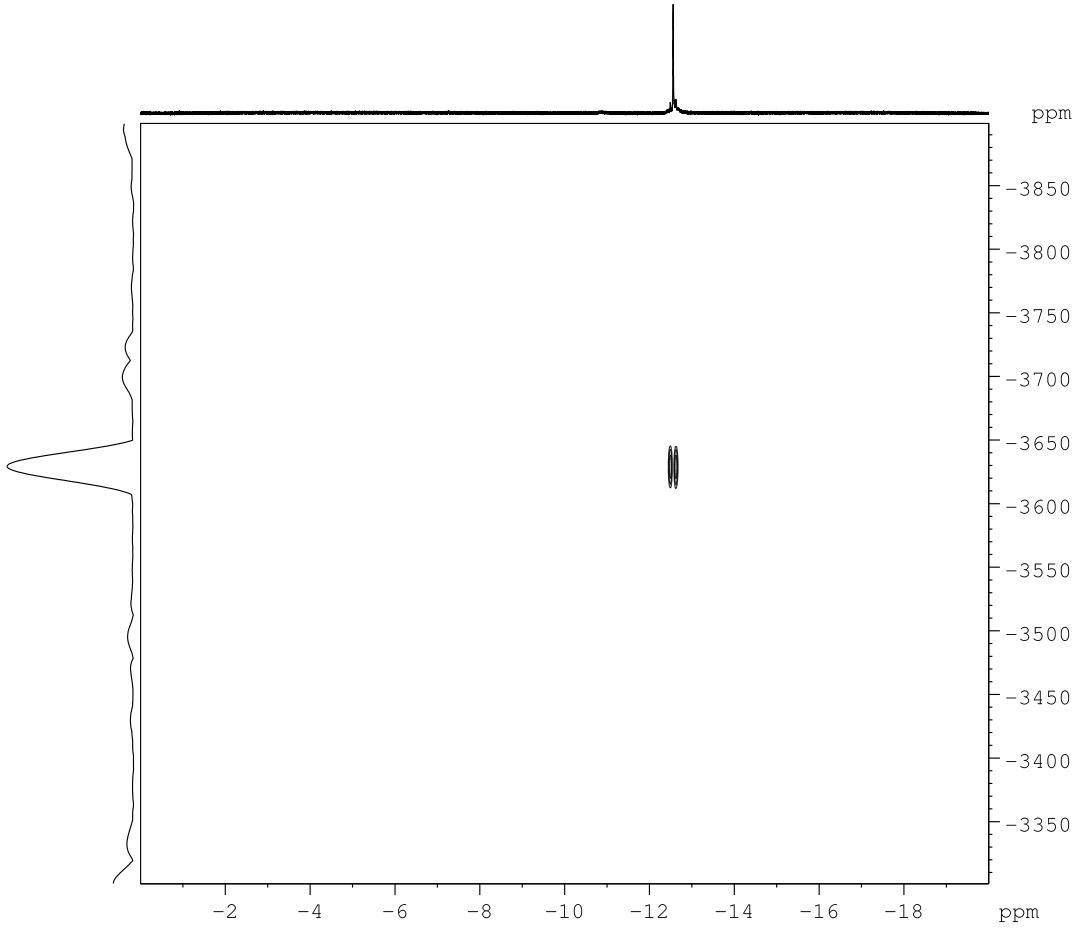
^{119}Sn NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2W(H)=Sn(H)Ar^*][Al(O^tBu^F)_4]$ (**4a**)




```
Current Data Parameters
NAME         MW750_300Sn
EXPNO                 25
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200716
Time               23.13 h
INSTRUM            spect
PROBHD   Z104275_0338 (
PULPROG             zg30
TD                  8918
SOLVENT             C6D6
NS                286720
DS                     1
SWH            89285.711 Hz
FIDRES         20.023708 Hz
AQ             0.0499408 sec
RG                204.67
DW                 5.600 usec
DE                 6.50 usec
TE                298.0 K
D1           0.02000000 sec
TD0                    1
SFO1         112.0322940 MHz
NUC1               119Sn
P0                 4.03 usec
P1                12.10 usec
PLW1         12.00000000 W

F2 - Processing parameters
SI                  4096
SF           111.9203740 MHz
WDW                   EM
SSB       0
LB                10.00 Hz
GB        0
PC                 1.40
```

Figure S32. ^{119}Sn NMR of compound **4a** {WCA = $[Al(O^tBu^F)_4]$}.

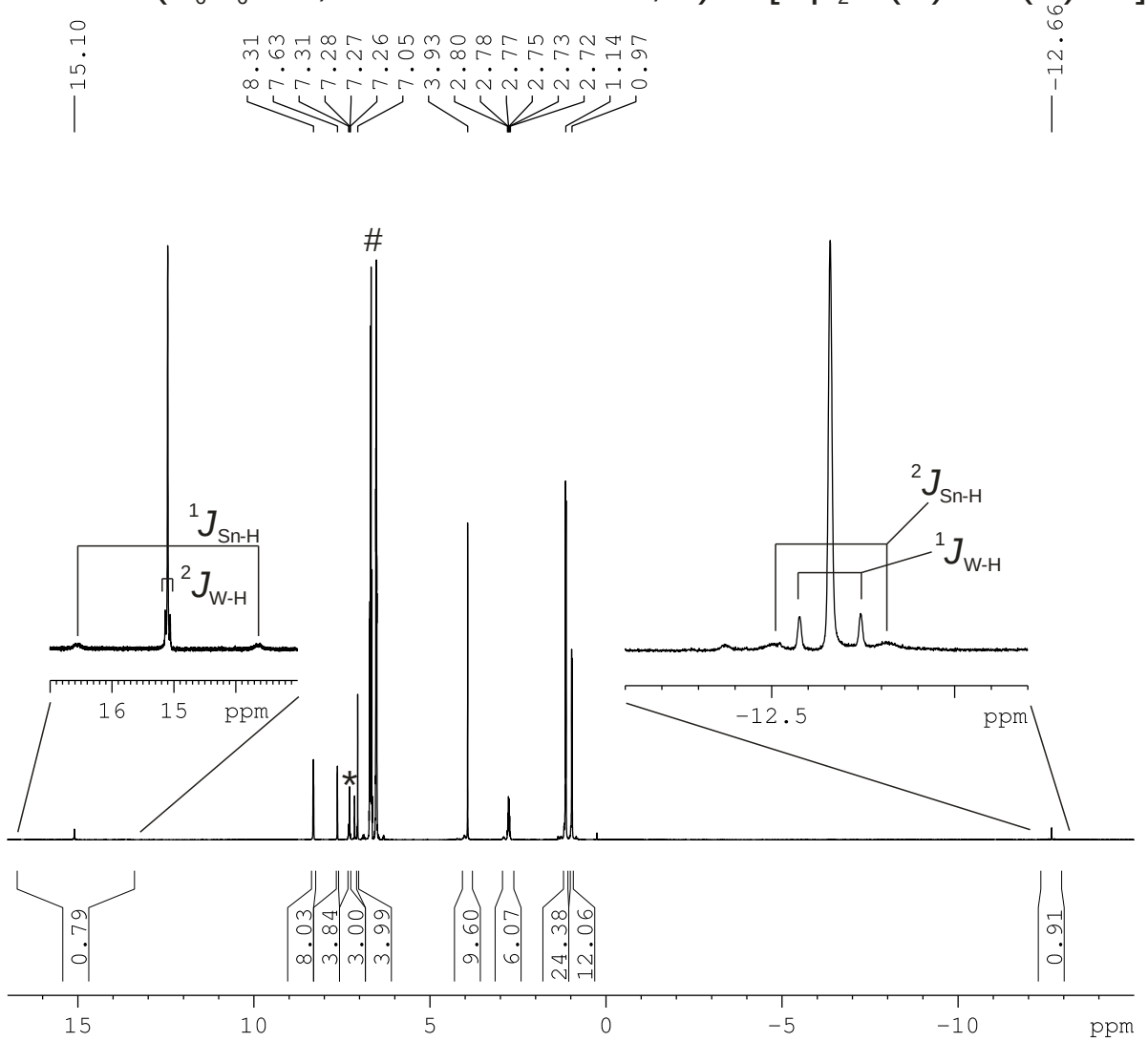
$^{1}H,^{183}W$ HMQC NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2W(H)=Sn(H)Ar^*][Al(O^tBu^F)_4]$ (**4a**)




```
Current Data Parameters
NAME         MW949_500_W
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210112
Time              10.30
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          hmqcph
TD                 1024
SOLVENT            C6D6
NS                    4
DS                   16
SWH           10000.000 Hz
FIDRES         9.765625 Hz
AQ            0.0512000 sec
RG                    4
DW               50.000 usec
DE                6.00 usec
TE                299.2 K
CNST2         67.0000000
D0            0.00000300 sec
D1            2.00000000 sec
D2            0.00746269 sec
D11           0.03000000 sec
D13           0.00000400 sec
IN0           0.00004015 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                12.50 usec
P2                25.00 usec
PL1       0 dB
PL1W        21.60222244 W
SFO1       500.1249987 MHz

======== CHANNEL f2 ========
CPDPRG[2             garp
NUC2                 183W
P3                28.00 usec
PCPD2             400.00 usec
PL2       0 dB
PL12                23.10 dB
SFO2         20.7623365 MHz

F1 - Acquisition parameters
TD                    48
SFO1           20.76234 MHz
FIDRES        519.058411 Hz
SW               600.000 ppm
FnMODE      States-TPPI

F2 - Processing parameters
SI                  1024
SF           500.1300000 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
PC                 1.00

F1 - Processing parameters
SI                  1024
MC2          States-TPPI
SF           20.8373510 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
```

Figure S33. ^{1}H, ^{183}W HMQC NMR of compound **4a** {WCA = $[Al(O^tBu^F)_4]$}.

^{1}H NMR (C_6D_6 + 1,2-difluorobenzene, rt) of [$Cp_2W(H)=Sn(H)Ar^*$][BAr^F] (**4a**)

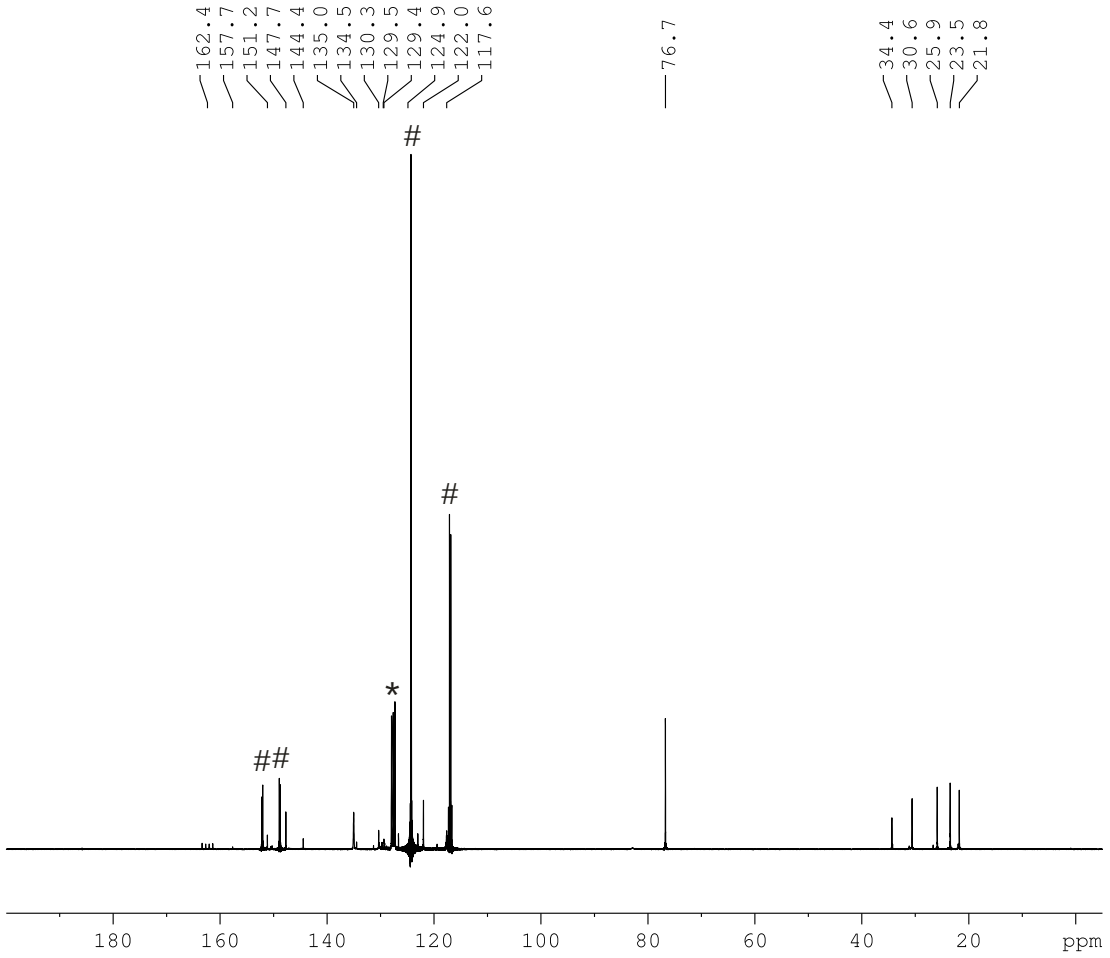



```
Current Data Parameters
NAME          MW1042_400
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210420
Time               15.48
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 52656
SOLVENT             C6D6
NS                    64
DS                     0
SWH            16025.641 Hz
FIDRES          0.304346 Hz
AQ             1.6428672 sec
RG                    57
DW                31.200 usec
DE                 6.00 usec
TE                299.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.60 usec
PL1                -3.00 dB
PL1W        16.03799057 W
SFO1        400.1100000 MHz

F2 - Processing parameters
SI                 65536
SF          400.1100000 MHz
WDW                   EM
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```

* C_6D_6
\# *o*-$C_6H_4F_2$

Figure S34. ^{1}H NMR of compound **4a** {WCA = [BAr^F]}.

$^{13}C\{^{1}H\}$ NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2W(H)=Sn(H)Ar^*][BAr^F]$ (**4a**)

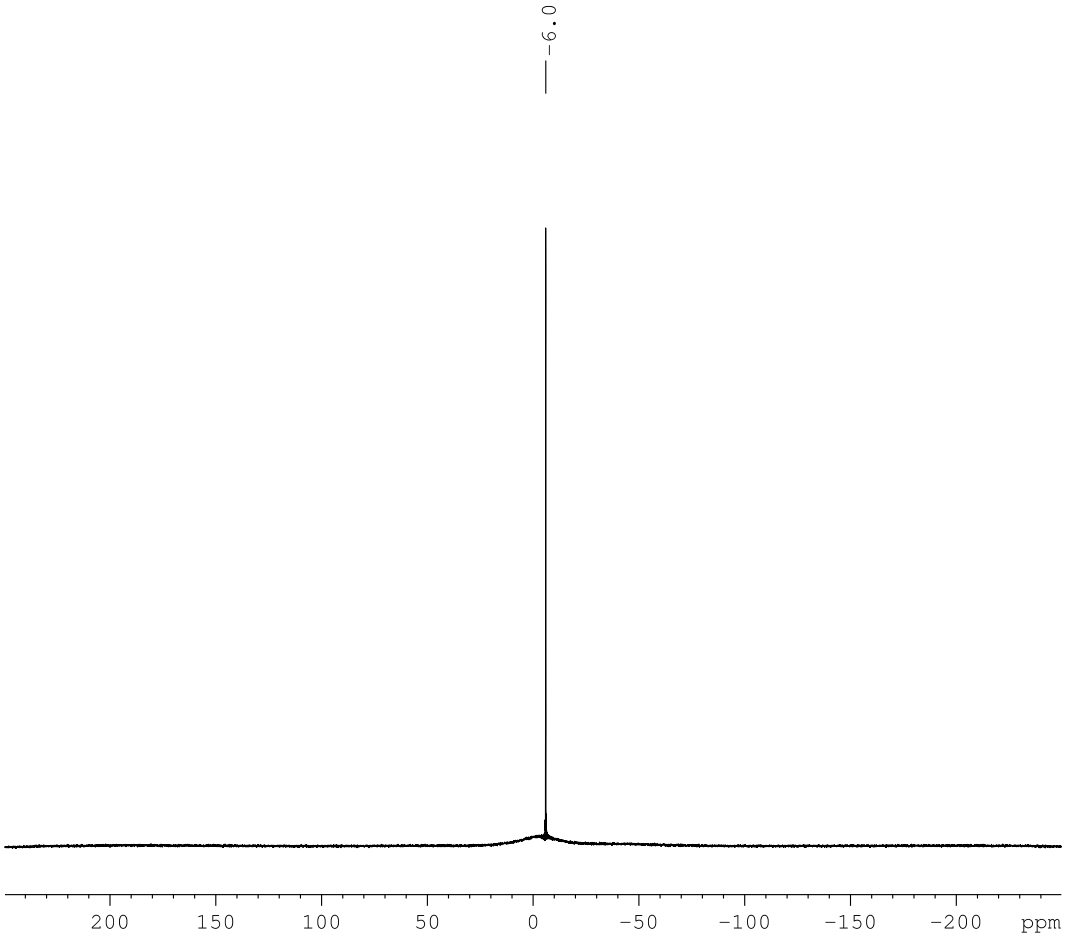



```
Current Data Parameters
NAME       MW1042_300NM
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20210420
Time              23.52 h
INSTRUM            spect
PROBHD   Z104275_0338 (
PULPROG           udeft
TD                13040
SOLVENT             C6D6
NS                  3584
DS                     4
SWH           18115.941 Hz
FIDRES         2.778519 Hz
AQ            0.3599040 sec
RG               204.67
DW               27.600 usec
DE                6.50 usec
TE                298.0 K
D1           4.00000000 sec
D12          0.00002000 sec
D20         20.00000000 sec
TD0                    1
SFO1          75.4752953 MHz
NUC1                 13C
P1                10.00 usec
P13             2000.00 usec
P26              500.00 usec
PLW1         33.55099869 W
SPNAM[5]    Crp60comp.4
SPOAL5             0.500
SPOFFS5  0 Hz
SPW5          5.12620020 W
SPNAM[8] Crp60,0.5,20.1
SPOAL8             0.500
SPOFFS8  0 Hz
SPW8          5.12620020 W
SFO2         300.1312005 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2          8.26509953 W
PLW12         0.20000000 W

F2 - Processing parameters
SI                 32768
SF            75.4677485 MHz
WDW                   EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

* C_6D_6
\# 1,2-$C_6H_4F_2$

Figure S35. $^{13}C\{^{1}H\}$ NMR of compound **4a** {WCA = $[BAr^F]$}.

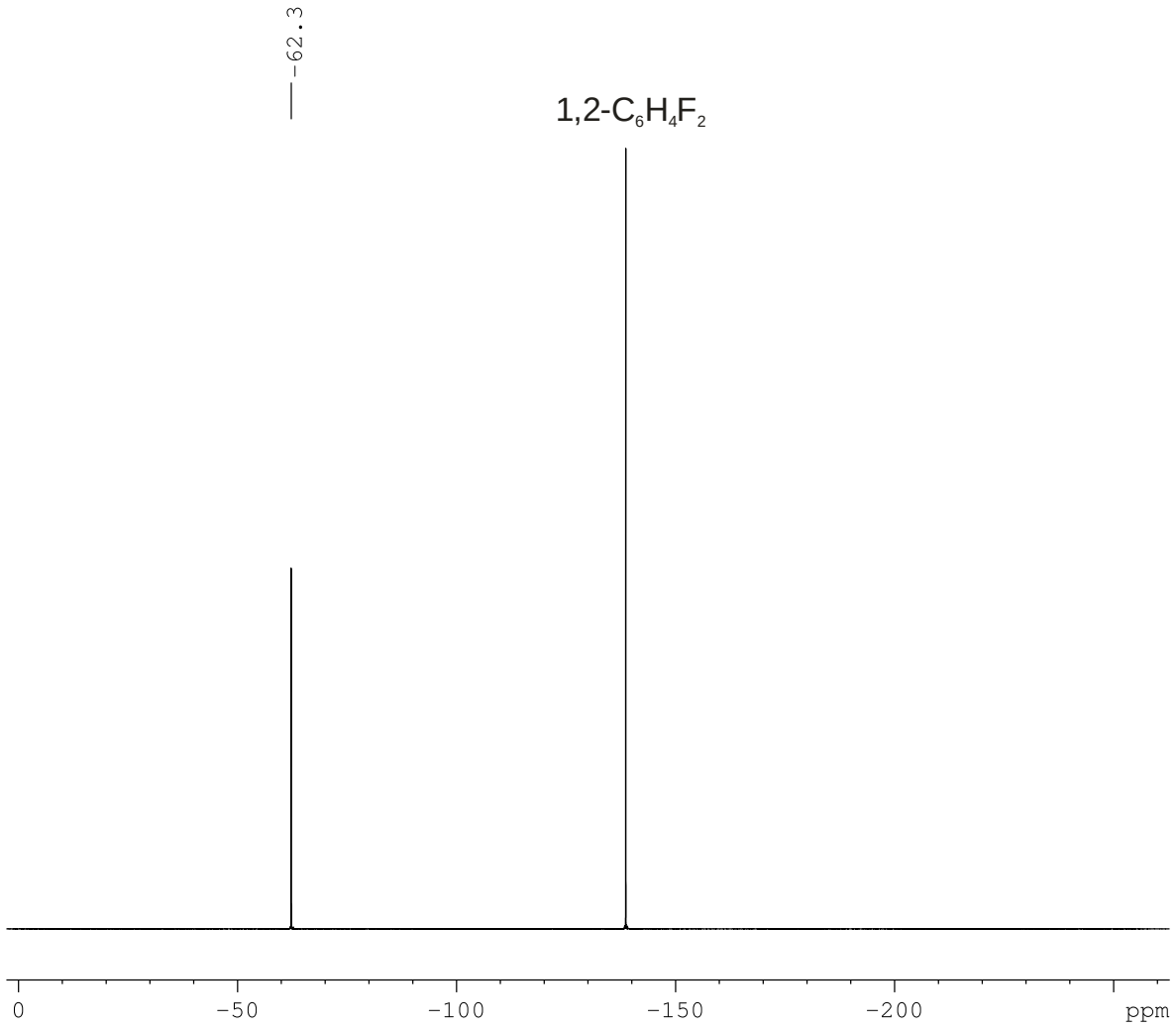
^{11}B NMR (C_6D_6 + 1,2-difluorobenzene, rt) of [Cp_2W(H)=Sn(H)Ar*][BAr^F] (**4a**)




```
Current Data Parameters
NAME         MW1042_300
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20210420
Time               16.22 h
INSTRUM            spect
PROBHD   Z104275_0338 (
PULPROG            zgbs
TD                 8192
SOLVENT            C6D6
NS                 2048
DS                    0
SWH            48076.922 Hz
FIDRES         11.737530 Hz
AQ             0.0851968 sec
RG                204.67
DW                10.400 usec
DE                 6.50 usec
TE                298.0 K
D1           0.10000000 sec
TD0                   1
SFO1          96.2936312 MHz
NUC1                 11B
P1                 5.75 usec
P2                11.50 usec
PLW1        70.00000000 W

F2 - Processing parameters
SI                32768
SF            96.2936312 MHz
WDW                  EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

Figure S36. ^{11}B NMR of compound **4a** {WCA = [BAr^F]}.

$^{19}F\{^{1}H\}$ NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2W(H)=Sn(H)Ar^*][BAr^F]$ (**4a**)

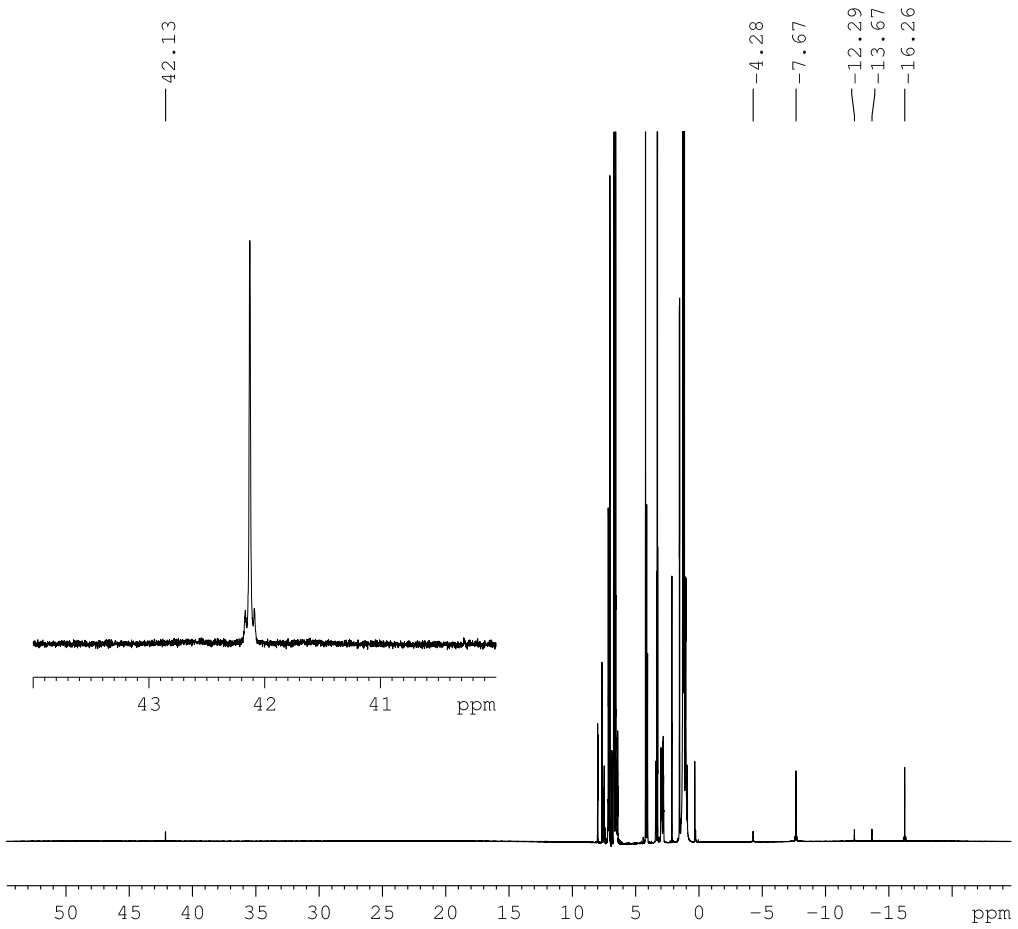



```
Current Data Parameters
NAME         MW1042_400
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20210420
Time              15.52
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG         zgfhigqn
TD               131072
SOLVENT             C6D6
NS                   128
DS                     0
SWH           100000.000 Hz
FIDRES          0.762939 Hz
AQ             0.6553600 sec
RG                  4100
DW                5.000 usec
DE                6.00 usec
TE                299.2 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 19F
P1                18.75 usec
PL1               -2.92 dB
PL1W        30.50645256 W
SFO1        376.4306030 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -3.00 dB
PL12              11.77 dB
PL2W        16.03799057 W
PL12W        0.53474891 W
SFO2        400.1120007 MHz

F2 - Processing parameters
SI                262144
SF          376.4795470 MHz
WDW                 EM
SSB       0
LB                2.00 Hz
GB        0
PC                1.00
```

Figure S37. $^{19}F\{^{1}H\}$ NMR of compound **4a** {WCA = $[BAr^F]$}.

Compound **4b**

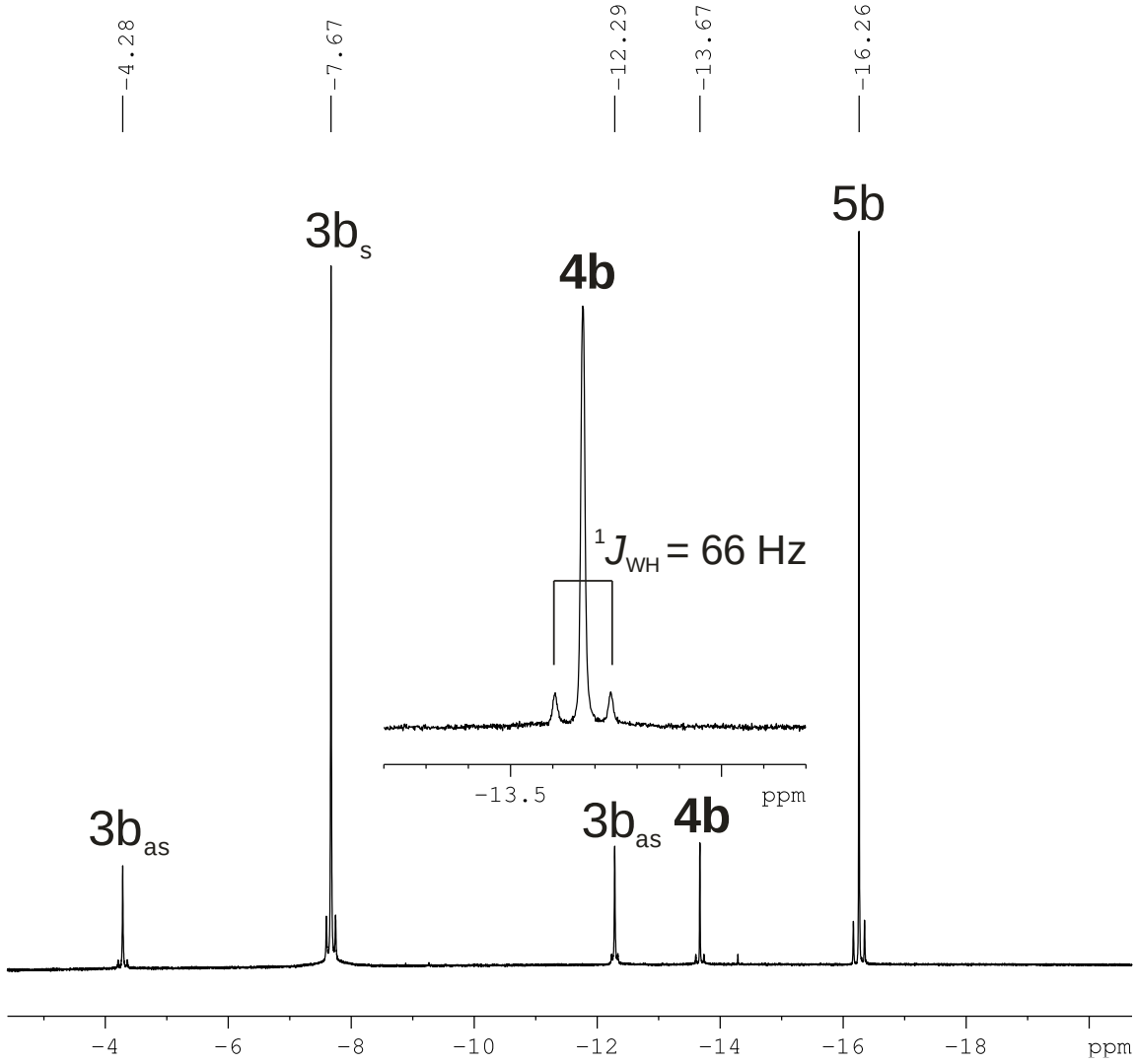
^{1}H NMR (C_6D_6 + 1,2-difluorobenzene, −40 °C) of **5b** + $[H(Et_2O)_2][Al(O^tBu^F)_4]$: **4b**




```
Current Data Parameters
NAME          MW1091_500
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210531
Time               13.41
INSTRUM            spect
PROBHD   5 mm TBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT              Tol
NS                  1892
DS                     0
SWH            39682.539 Hz
FIDRES          0.605507 Hz
AQ             0.8257536 sec
RG                     4
DW                12.600 usec
DE                 6.00 usec
TE                233.1 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.63 usec
PL1                -0.52 dB
PL1W        24.34997177 W
SFO1        500.1375020 MHz

F2 - Processing parameters
SI                 65536
SF          500.1300000 MHz
WDW                   EM
SSB       0
LB        0 Hz
GB        0
PC                 1.00
```

Figure S38. Protonation of **5b** complete spectrum to give **4b**.

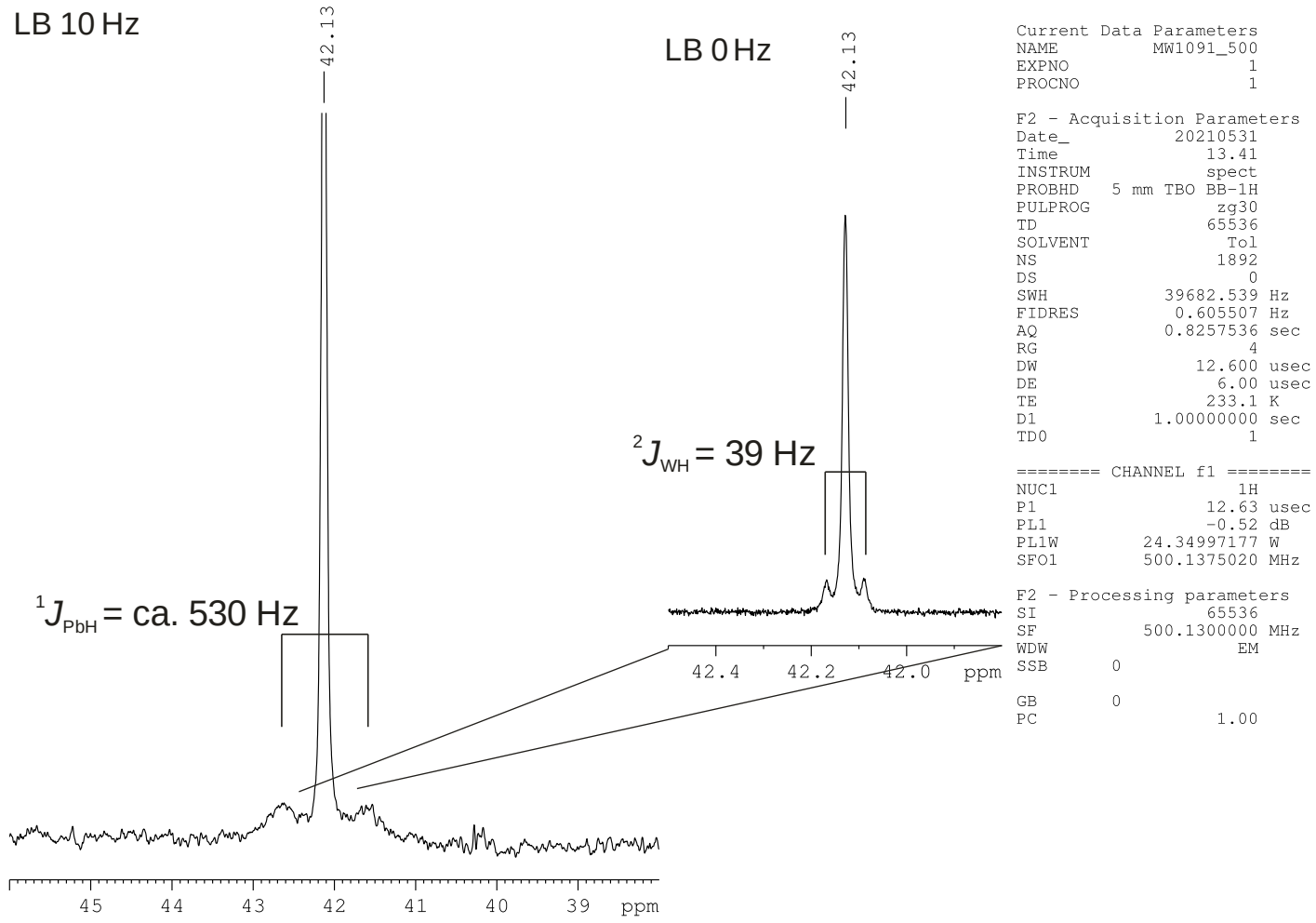
^{1}H NMR (C_6D_6 + 1,2-difluorobenzene, −40 °C) of**5b** + $[H(Et_2O)_2][Al(O^tBu^F)_4]$: **4b** high field




```
Current Data Parameters
NAME          MW1091_500
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210531
Time               13.41
INSTRUM            spect
PROBHD   5 mm TBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT              Tol
NS                  1892
DS                     0
SWH            39682.539 Hz
FIDRES          0.605507 Hz
AQ             0.8257536 sec
RG                     4
DW                12.600 usec
DE                 6.00 usec
TE                233.1 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.63 usec
PL1                -0.52 dB
PL1W        24.34997177 W
SFO1        500.1375020 MHz

F2 - Processing parameters
SI                 65536
SF          500.1300000 MHz
WDW                   EM
SSB       0
LB        0 Hz
GB        0
PC                 1.00
```

Figure S39. Protonation of **5b** hydride region, signals of **4b**.

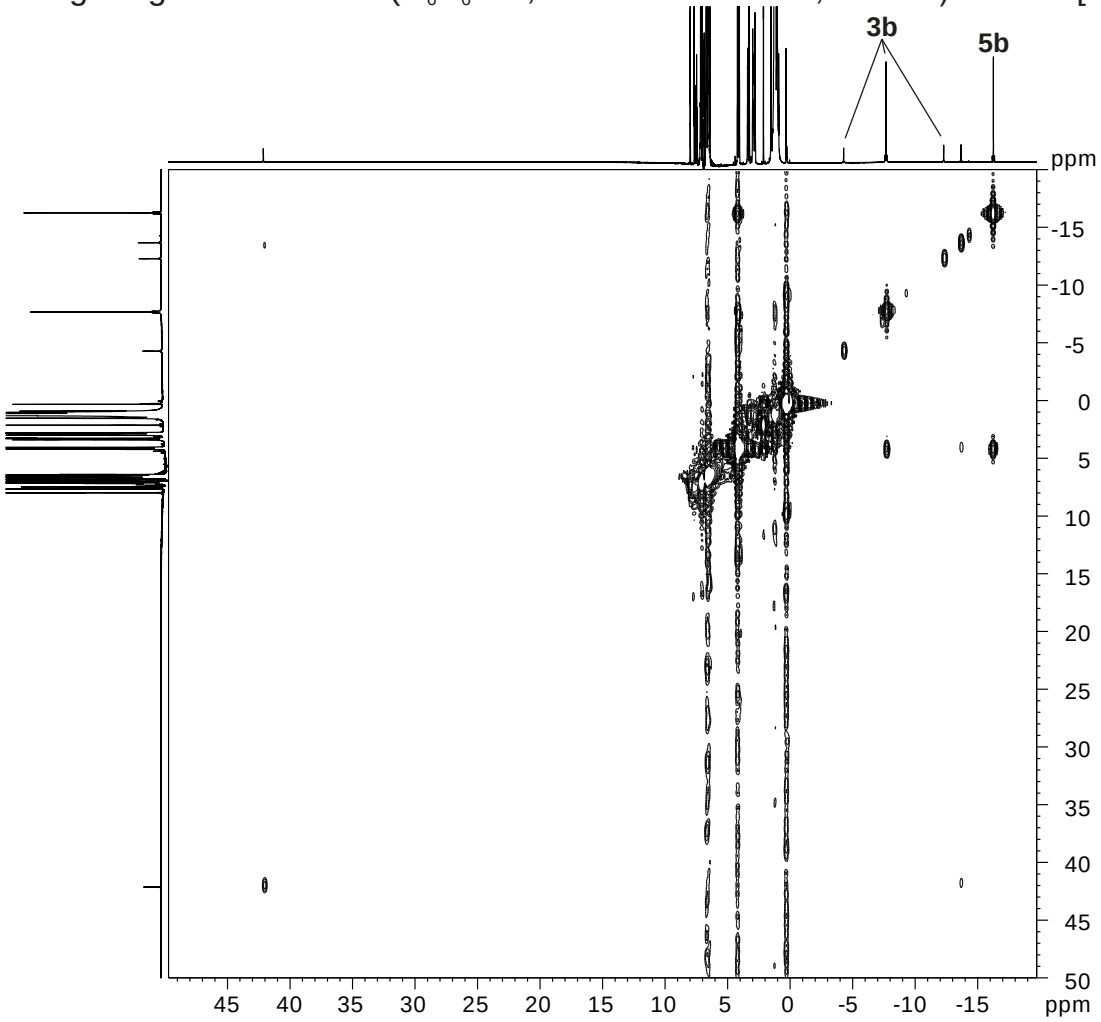
^{1}H NMR (C_6D_6 + 1,2-difluorobenzene, −40 °C) of **5b** + $[H(Et_2O)_2][Al(O^tBu^F)_4]$: **4b** low field




```
Current Data Parameters
NAME          MW1091_500
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210531
Time               13.41
INSTRUM            spect
PROBHD   5 mm TBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT              Tol
NS                  1892
DS                     0
SWH            39682.539 Hz
FIDRES          0.605507 Hz
AQ             0.8257536 sec
RG                     4
DW                12.600 usec
DE                 6.00 usec
TE                233.1 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.63 usec
PL1                -0.52 dB
PL1W        24.34997177 W
SFO1        500.1375020 MHz

F2 - Processing parameters
SI                 65536
SF          500.1300000 MHz
WDW                   EM
SSB       0

GB        0
PC                  1.00
```

Figure S40. Protonation of **5b** high frequency region, signals of **4b**.

$^{1}H,^{1}H$ long range COSY NMR (C_6D_6 + 1,2-difluorobenzene, −40 °C) of **5b** + $[H(Et_2O)_2][Al(O^tBu^F)_4]$: **4b**



Current Data Parameters
NAME MW1066_500_VT_WPb
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210504
Time 13.39
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG cosylrgpqf
TD 1024
SOLVENT Tol
NS 64
DS 16
SWH 34722.223 Hz
FIDRES 33.908421 Hz
AQ 0.0147456 sec
RG 575
DW 14.400 usec
DE 6.00 usec
TE 222.6 K
D0 0.00000300 sec
D1 1.00000000 sec
D6 0.05000000 sec
D13 0.00000400 sec
D16 0.00020000 sec
IN0 0.00002855 sec

======== CHANNEL f1 ========
NUC1 1H
P0 12.50 usec
P1 12.50 usec
PL1 0 dB
PL1W 21.60222244 W
SFO1 500.1375020 MHz

====== GRADIENT CHANNEL =====
GPNAM[1] SINE.100
GPZ1 10.00 %
P16 1000.00 usec

F1 - Acquisition parameters
TD 63
SFO1 500.1375 MHz
FIDRES 1111.416626 Hz
SW 70.000 ppm
FnMODE QF

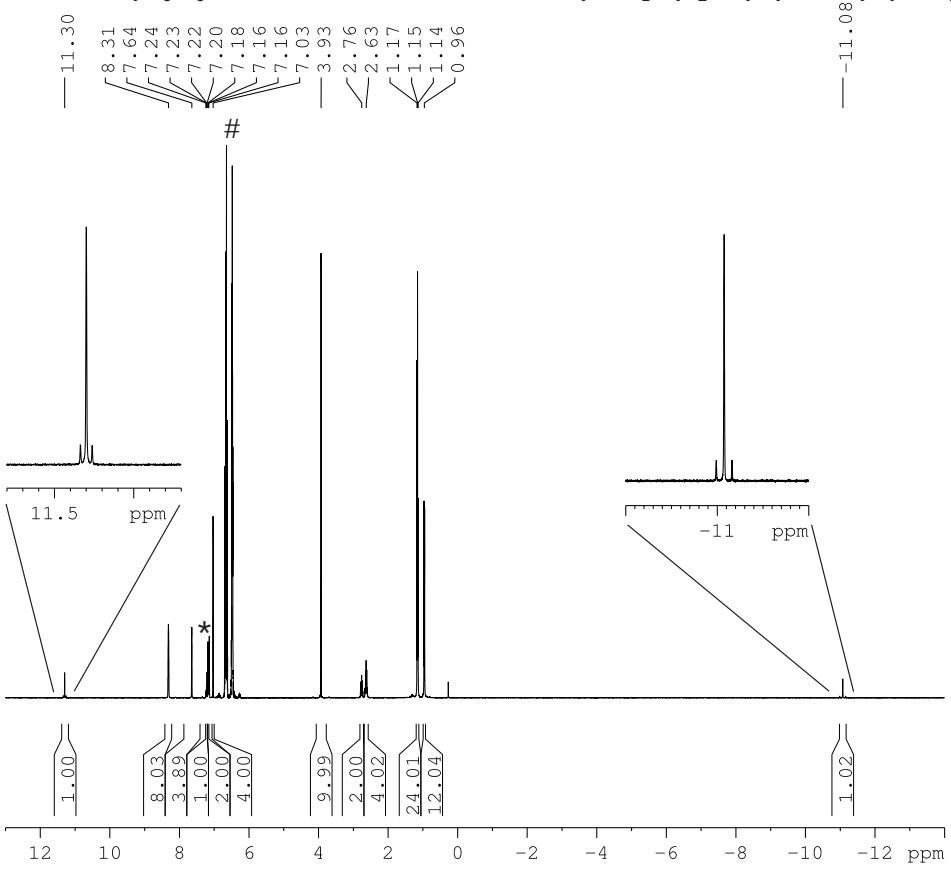
F2 - Processing parameters
SI 1024
SF 500.1300000 MHz
WDW SINE
SSB 0
LB 0 Hz
GB 0
PC 0.60

F1 - Processing parameters
SI 512
MC2 QF
SF 500.1300000 MHz
WDW SINE
SSB 0
LB 0 Hz
GB 0

Figure S41. Protonation of **5b**, ^{1}H, ^{1}H long range COSY NMR of **4b**.

Compound **4c**

^{1}H NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2W(H)=Ge(H)Ar^*][BAr^F]$ (**4c**)

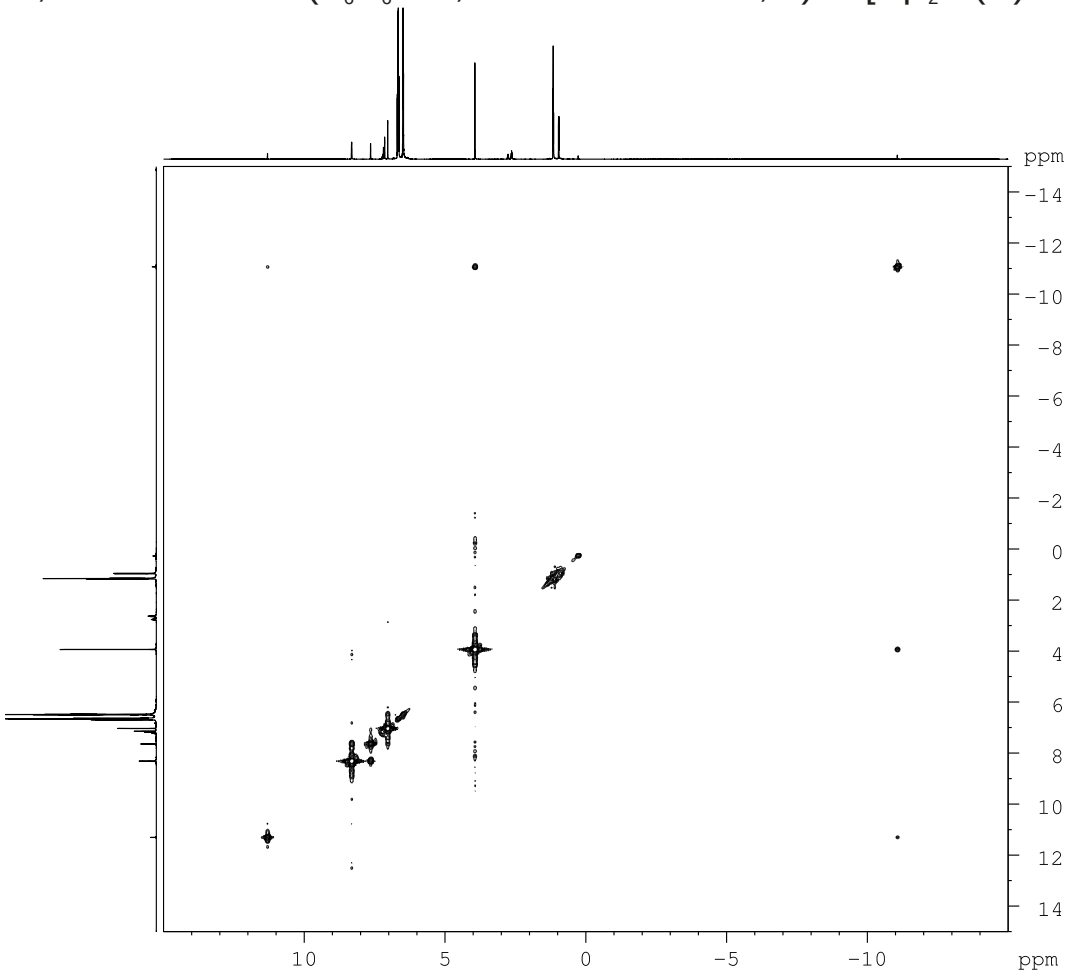



```
Current Data Parameters
NAME          MW1048_400
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210427
Time               12.17
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 52656
SOLVENT             C6D6
NS                    64
DS                     0
SWH            16025.641 Hz
FIDRES          0.304346 Hz
AQ             1.6428672 sec
RG                   161
DW                31.200 usec
DE                 6.00 usec
TE                299.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.60 usec
PL1                -3.00 dB
PL1W         16.03799057 W
SFO1         400.1100000 MHz

F2 - Processing parameters
SI                 65536
SF           400.1100000 MHz
WDW                   EM
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```

* C_6D_6
\# 1,2-$C_6H_4F_2$

Figure S42. ^{1}H NMR of compound **4c**.

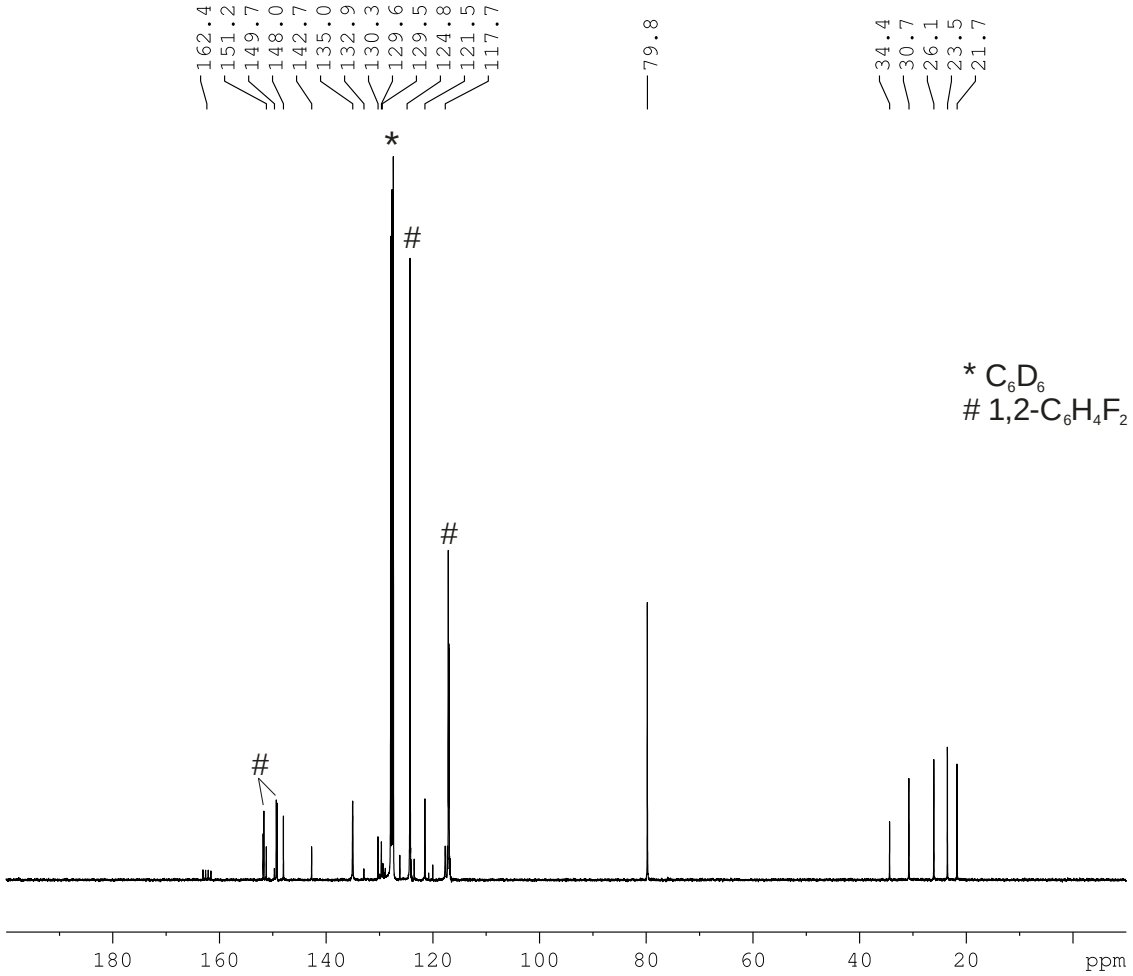
$^{1}H,^{1}H$ COSY NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2W(H)=Ge(H)Ar^*][BAr^F]$ (**4c**)




```
Current Data Parameters
NAME         MW1048_500W
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210504
Time               10.12
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG      cosylrgpqf
TD                 1024
SOLVENT            C6D6
NS                    6
DS                   16
SWH           15000.000 Hz
FIDRES        14.648438 Hz
AQ             0.0341333 sec
RG                   64
DW               33.333 usec
DE                6.00 usec
TE                299.2 K
D0            0.00000300 sec
D1            1.00000000 sec
D6            0.05000000 sec
D13           0.00000400 sec
D16           0.00020000 sec
IN0           0.00006665 sec

======== CHANNEL f1 ========
NUC1                  1H
P0                12.50 usec
P1                12.50 usec
PL1       0 dB
PL1W        21.60222244 W
SFO1         500.1300000 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPZ1               10.00 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                  256
SFO1             500.13 MHz
FIDRES        117.217972 Hz
SW                30.000 ppm
FnMODE               QF

F2 - Processing parameters
SI                 1024
SF           500.1300000 MHz
WDW                SINE
SSB       0
LB        0 Hz
GB        0
PC                 0.60

F1 - Processing parameters
SI                  512
MC2                  QF
SF           500.1300000 MHz
WDW                SINE
SSB       0
LB        0 Hz
GB        0
```

Figure S43. $^{1}H,^{1}H$ COSY NMR of compound **4c**.

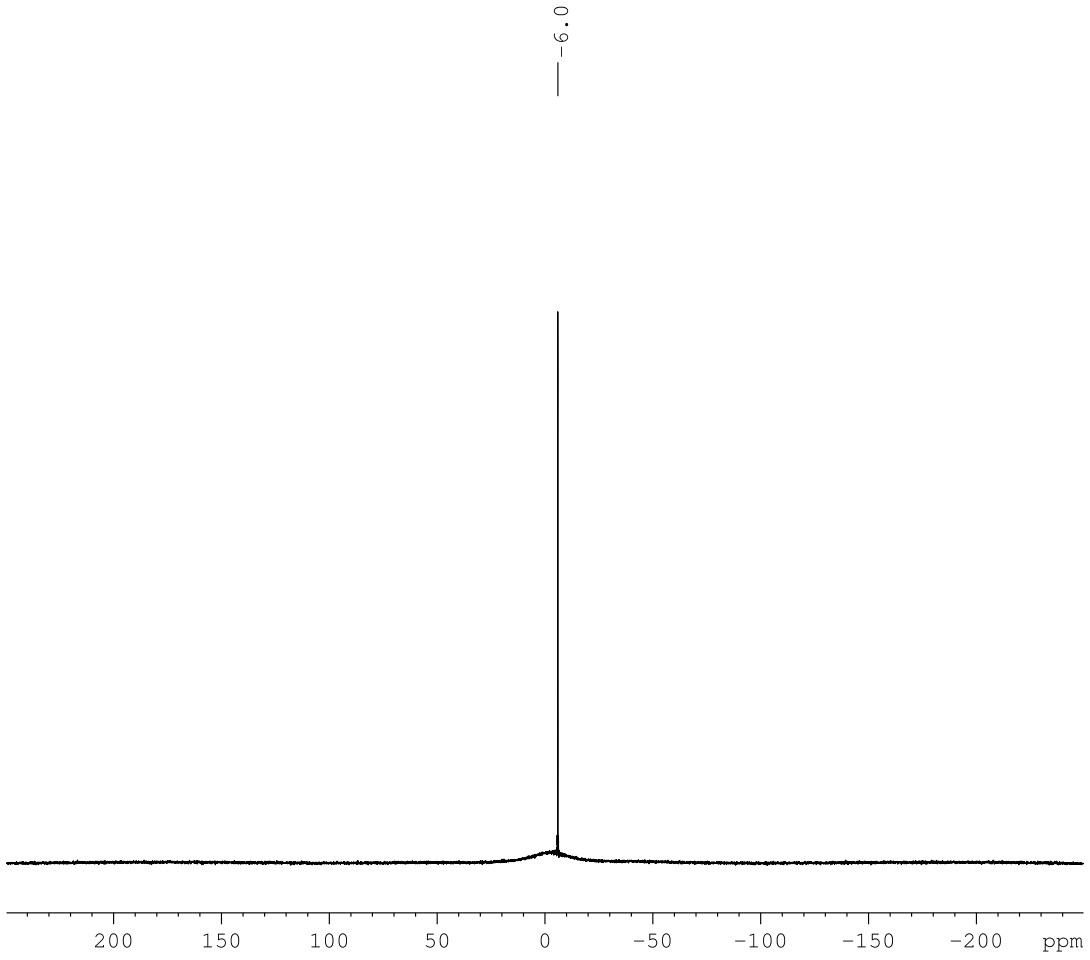
$^{13}C\{^{1}H\}$ NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2W(H)=Ge(H)Ar^*][BAr^F]$ (**4c**)




```
Current Data Parameters
NAME       MW1048_400NM
EXPNO                13
PROCNO                1

F2 - Acquisition Parameters
Date_          20210429
Time               2.13
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG           udeft
TD                22218
SOLVENT             C6D6
NS                 5900
DS                    0
SWH           30864.197 Hz
FIDRES         1.389153 Hz
AQ            0.3599316 sec
RG                32800
DW               16.200 usec
DE                6.00 usec
TE                299.2 K
D1           3.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
D20        100.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                13.50 usec
P13             2000.00 usec
P26              500.00 usec
PL1               -4.16 dB
PL1W        78.55633545 W
SFO1       100.6198135 MHz
SP8               1.39 dB
SP13              1.39 dB
SPNAM[8] Crp60,0.5,20.1
SPNAM[13    Crp60comp.4
SPOAL8             0.500
SPOAL13            0.500
SPOFFS8  0 Hz
SPOFFS13 0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                1H
PCPD2             80.00 usec
PL2               -3.00 dB
PL12              11.77 dB
PL2W        16.03799057 W
PL12W        0.53474891 W
SFO2       400.1120007 MHz

F2 - Processing parameters
SI                131072
SF          100.6077400 MHz
WDW                 EM
SSB      0
LB                2.00 Hz
GB       0
PC                1.40
```

Figure S44. $^{13}C\{^{1}H\}$ NMR of compound **4c**.

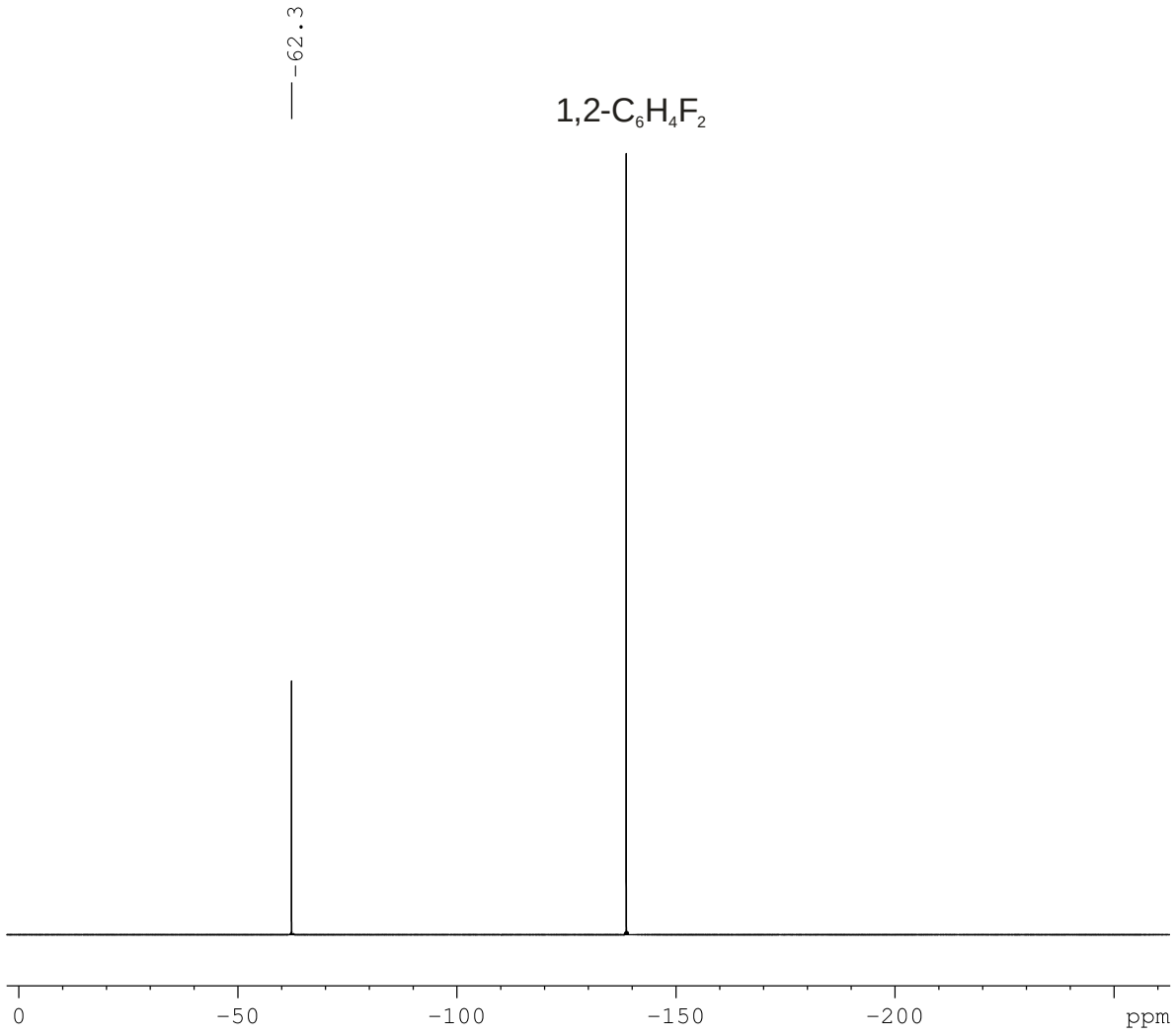
^{11}B NMR (C_6D_6 + 1,2-difluorobenzene, rt) of [$Cp_2W(H)=Ge(H)Ar^*$][BAr^F] (**4c**)




```
Current Data Parameters
NAME          MW1048_300
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210427
Time               11.56 h
INSTRUM            spect
PROBHD   Z104275_0338 (
PULPROG             zgbs
TD                  8192
SOLVENT             C6D6
NS                  1536
DS                     0
SWH            48076.922 Hz
FIDRES         11.737530 Hz
AQ             0.0851968 sec
RG                204.67
DW                10.400 usec
DE                 6.50 usec
TE                298.0 K
D1            0.10000000 sec
TD0                    1
SFO1          96.2936312 MHz
NUC1                11B
P1                 5.75 usec
P2                11.50 usec
PLW1         70.00000000 W

F2 - Processing parameters
SI                 32768
SF            96.2936312 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

Figure S45. ^{11}B NMR of compound **4c**.

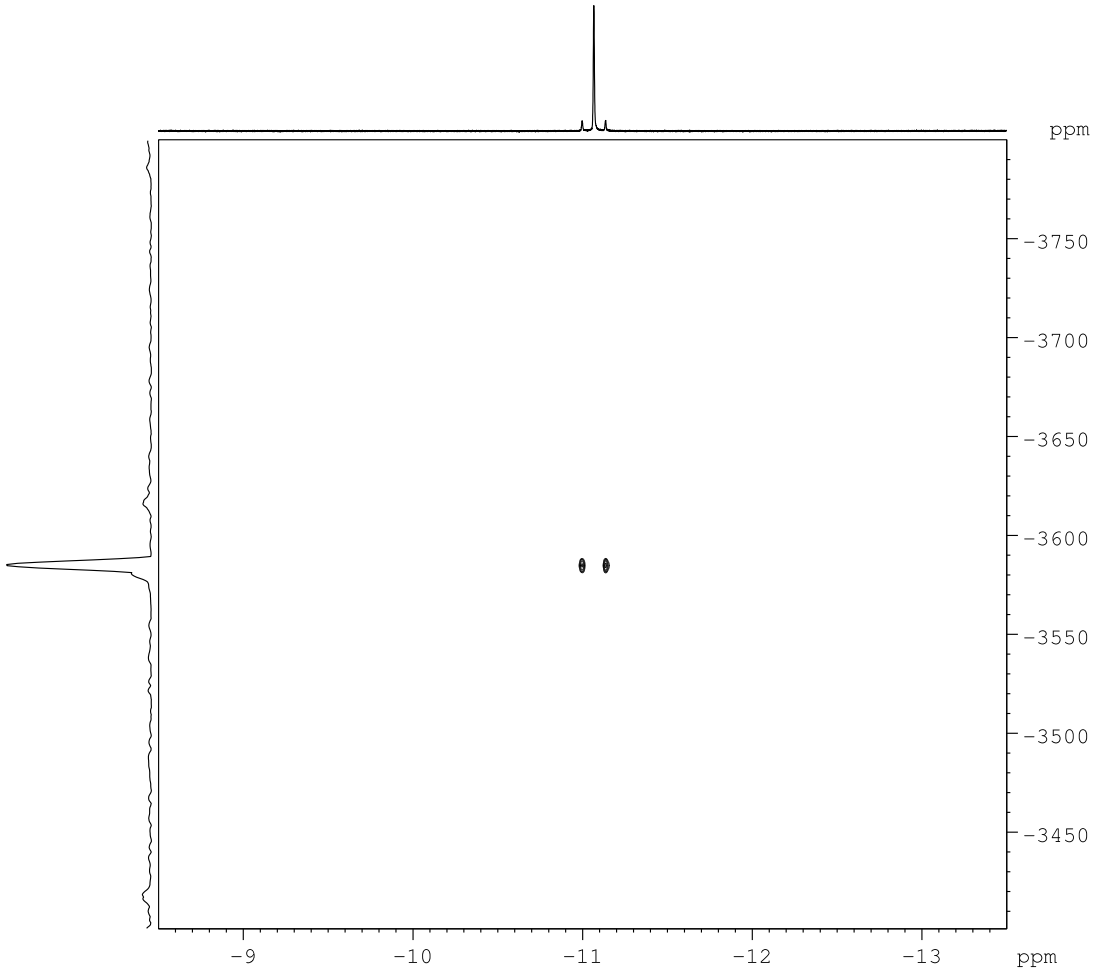
$^{19}F\{^{1}H\}$ NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2W(H)=Ge(H)Ar^*][BAr^F]$ (**4c**)




```
Current Data Parameters
NAME         MW1048_400
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20210422
Time              13.44
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG         zgfhigqn
TD               131072
SOLVENT             C6D6
NS                   128
DS                     0
SWH           100000.000 Hz
FIDRES          0.762939 Hz
AQ              0.6553600 sec
RG                   4100
DW                5.000 usec
DE                6.00 usec
TE                299.2 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 19F
P1                18.75 usec
PL1               -2.92 dB
PL1W        30.50645256 W
SFO1        376.4306030 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -3.00 dB
PL12              11.77 dB
PL2W        16.03799057 W
PL12W        0.53474891 W
SFO2        400.1120007 MHz

F2 - Processing parameters
SI                 262144
SF          376.4795470 MHz
WDW                  EM
SSB       0
LB                2.00 Hz
GB        0
PC                1.00
```

Figure S46. $^{19}F\{^{1}H\}$ NMR of compound **4c**.

$^{1}H,^{183}W$ HMQC NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2W(H)=Ge(H)Ar^*][BAr^F]$ (**4c**)

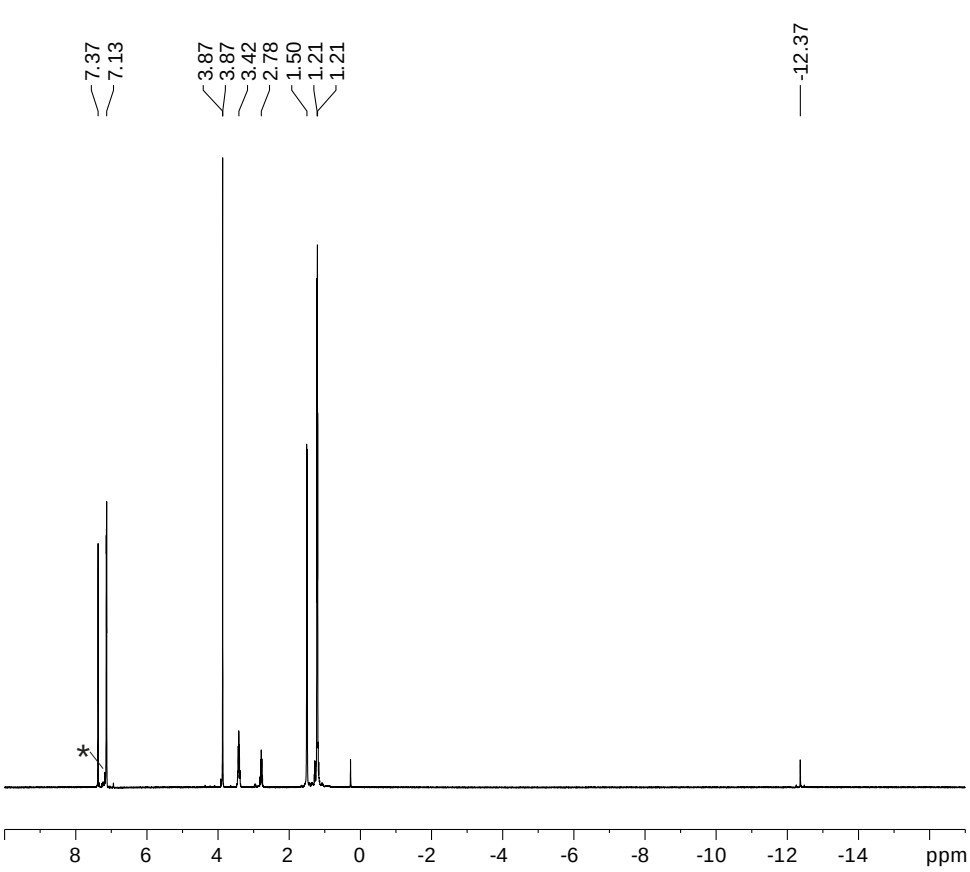



```
Current Data Parameters
NAME         MW1048_500W
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_             20210504
Time                10.43
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           hmqcph
TD                  1024
SOLVENT             C6D6
NS                     4
DS                    16
SWH             2500.000 Hz
FIDRES          2.441406 Hz
AQ             0.2048000 sec
RG                  90.5
DW               200.000 usec
DE                 6.00 usec
TE                299.3 K
CNST2          69.3000031
D0             0.00000300 sec
D1             2.00000000 sec
D2             0.00721501 sec
D11            0.03000000 sec
D13            0.00000400 sec
IN0            0.00004015 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.50 usec
P2                  25.00 usec
PL1       0 dB
PL1W         21.60222244 W
SFO1        500.1244986 MHz

======== CHANNEL f2 ========
CPDPRG[2              garp
NUC2                 183W
P3                  28.00 usec
PCPD2              400.00 usec
PL2       0 dB
PL12                23.10 dB
SFO2          20.7602528 MHz

F1 - Acquisition parameters
TD                    256
SFO1            20.76025 MHz
FIDRES          97.313683 Hz
SW                600.000 ppm
FnMODE       States-TPPI

F2 - Processing parameters
SI                   1024
SF           500.1300000 MHz
WDW                  QSINE
SSB                      2
LB        0 Hz
GB        0
PC                    1.00

F1 - Processing parameters
SI                   1024
MC2          States-TPPI
SF            20.8373510 MHz
WDW                  QSINE
SSB                      2
LB        0 Hz
GB        0
```

Figure S47. $^{1}H,\ ^{183}W$ HMQC NMR of compound **4c**.

Compound **5a**

^{1}H NMR (C_6D_6, rt) of 1/2$[Cp_2W(H)Li]_4$ + $[Ar^*SnCl]_2$: crude product **5a** of after pentane extraction



Current Data Parameters
NAME MW1124_400
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210827
Time 12.24
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 52656
SOLVENT C6D6
NS 64
DS 0
SWH 16025.641 Hz
FIDRES 0.304346 Hz
AQ 1.6428672 sec
RG 456
DW 31.200 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
TD0 1

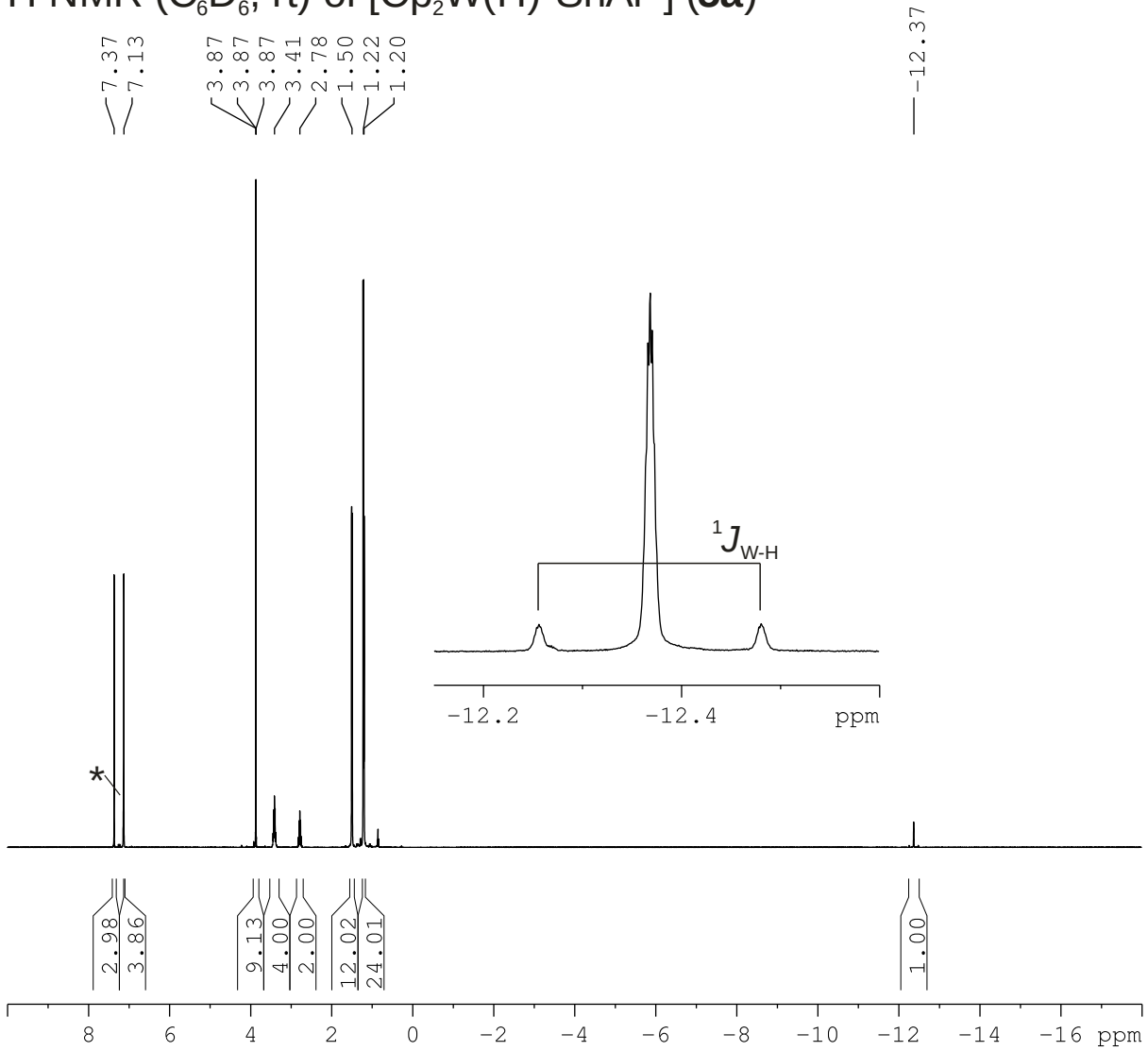
======== CHANNEL f1 ========
NUC1 1H
P1 14.60 usec
PL1 -3.00 dB
PL1W 16.03799057 W
SFO1 400.1100000 MHz

F2 - Processing parameters
SI 65536
SF 400.1100000 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

* C_6D_6

Figure S48. ^{1}H NMR of compound **5a** (crude product).

^{1}H NMR (C_6D_6, rt) of [$Cp_2W(H)$-SnAr*] (**5a**)

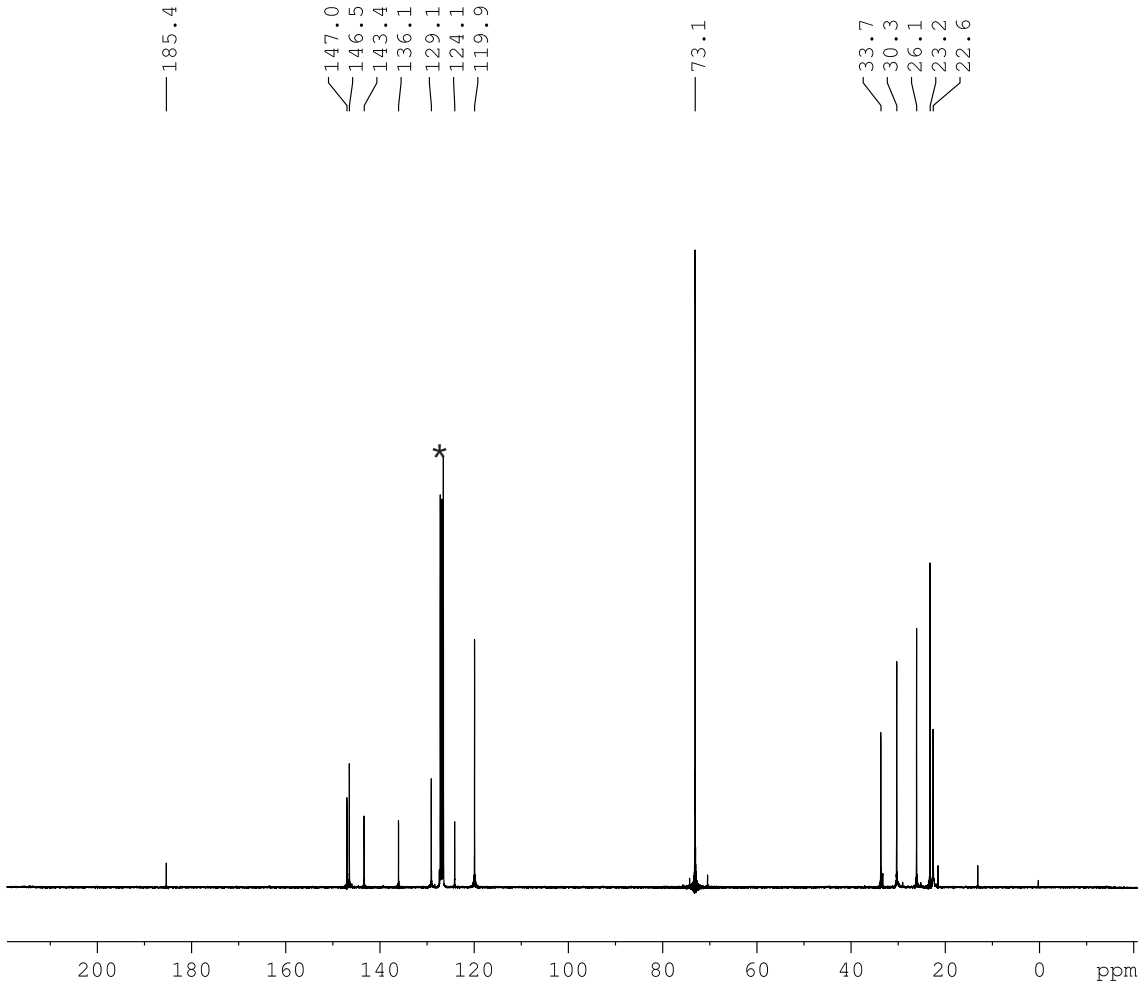



```
Current Data Parameters
NAME          MW974_400
EXPNO                20
PROCNO                1

F2 - Acquisition Parameters
Date_          20210202
Time              10.18
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG            zg30
TD                52656
SOLVENT            C6D6
NS                   64
DS                    0
SWH           16025.641 Hz
FIDRES         0.304346 Hz
AQ            1.6428672 sec
RG                  203
DW               31.200 usec
DE                6.00 usec
TE                299.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.60 usec
PL1               -3.00 dB
PL1W        16.03799057 W
SFO1       400.1100000 MHz

F2 - Processing parameters
SI                65536
SF         400.1100000 MHz
WDW                  EM
SSB       0
LB        0 Hz
GB        0
PC                 1.00
```

* C_6D_6

Figure S50. ^{1}H NMR of compound **5a**.

$^{13}C\{^{1}H\}$ NMR (C_6D_6, rt) of [$Cp_2W(H)$-SnAr*] (**5a**)

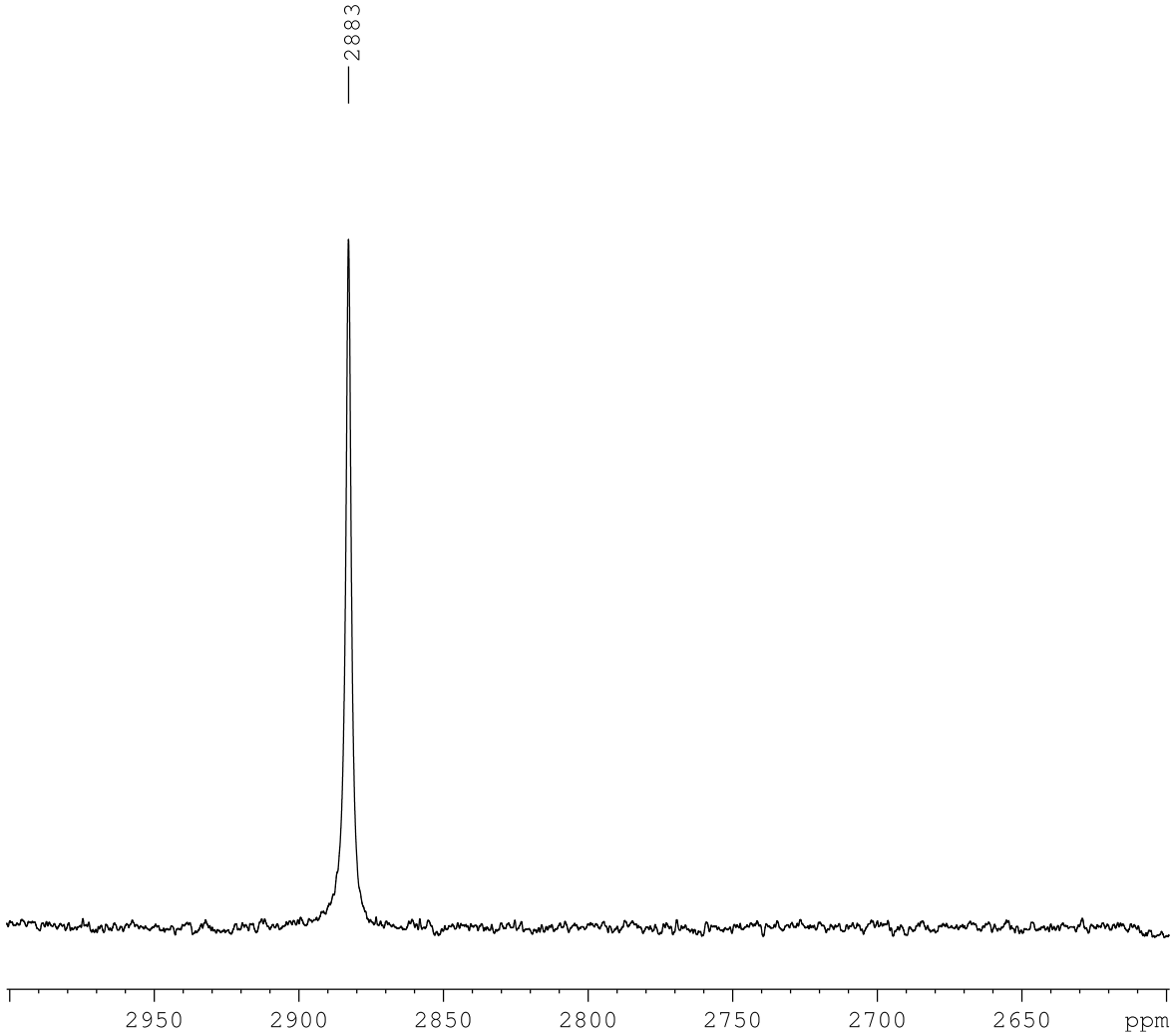



```
Current Data Parameters
NAME         MW974_300NM
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210120
Time                1.13 h
INSTRUM            spect
PROBHD   Z104275_0338 (
PULPROG            udeft
TD                 13040
SOLVENT              C6D6
NS                   4608
DS                      4
SWH            18115.941 Hz
FIDRES          2.778519 Hz
AQ             0.3599040 sec
RG                 204.67
DW                27.600 usec
DE                 6.50 usec
TE                298.0 K
D1            4.00000000 sec
D12           0.00002000 sec
D20          20.00000000 sec
TD0                    1
SFO1          75.4752953 MHz
NUC1                  13C
P1                 10.00 usec
P13              2000.00 usec
P26               500.00 usec
PLW1         33.55099869 W
SPNAM[5]     Crp60comp.4
SPOAL5               0.500
SPOFFS5  0 Hz
SPW5          5.12620020 W
SPNAM[8] Crp60,0.5,20.1
SPOAL8               0.500
SPOFFS8  0 Hz
SPW8          5.12620020 W
SFO2         300.1312005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2               90.00 usec
PLW2          8.26509953 W
PLW12         0.20000000 W

F2 - Processing parameters
SI                 32768
SF            75.4678110 MHz
WDW                   EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

* C_6D_6

Figure S51. $^{13}C\{^{1}H\}$ NMR of compound **5a**.

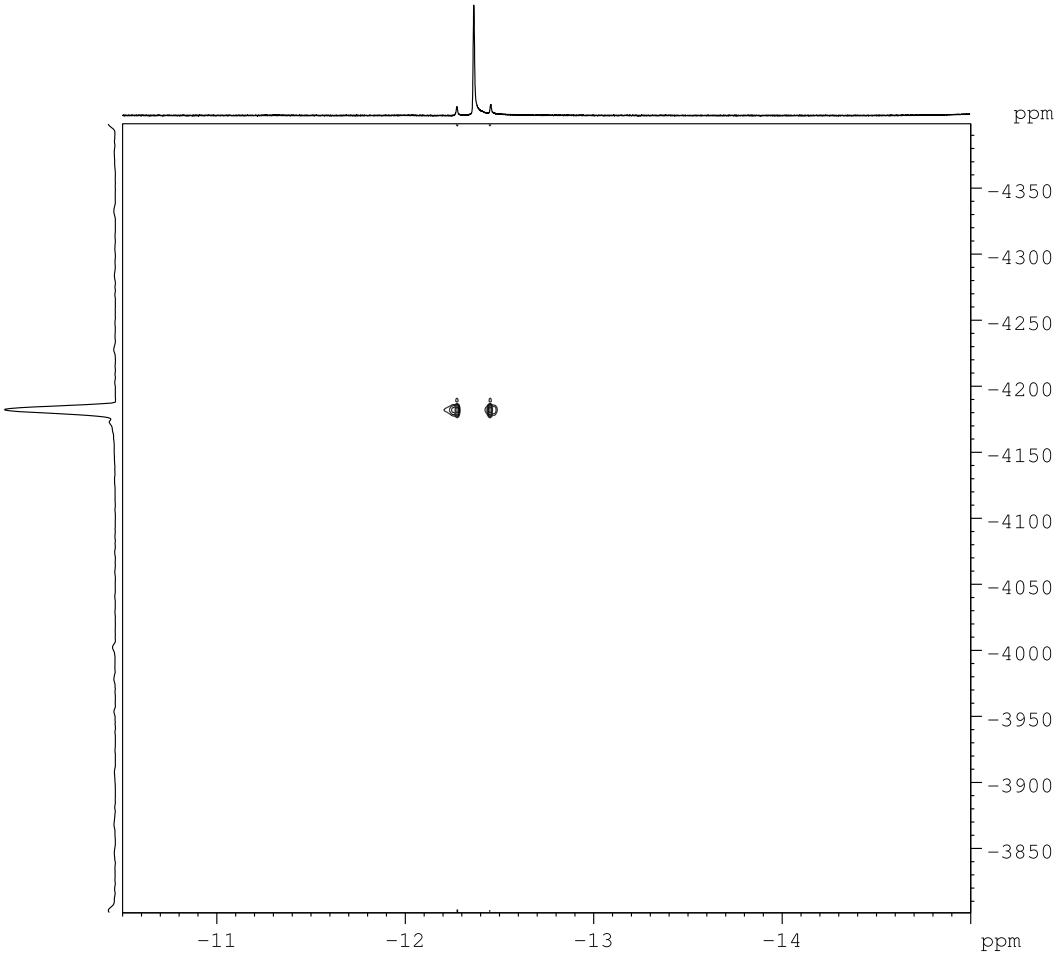
^{119}Sn NMR (C_6D_6, rt) of [$Cp_2W(H)$-SnAr*] (**5a**)




```
Current Data Parameters
NAME         MW974_500_W
EXPNO                 23
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210203
Time                7.31
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT             C6D6
NS                 81920
DS                     0
SWH            75000.000 Hz
FIDRES         1.144409 Hz
AQ             0.4369067 sec
RG                  2050
DW                 6.667 usec
DE                  6.00 usec
TE                 299.2 K
D1            0.20000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1               119Sn
P1                 13.00 usec
PL1       0 dB
PL1W         90.42790985 W
SFO1         187.0238426 MHz

F2 - Processing parameters
SI                131072
SF          186.5016380 MHz
WDW                 EM
SSB       0
LB                100.00 Hz
GB        0
PC                  1.40
```

Figure S52. ^{119}Sn{^{1}H} NMR of compound **5a**.

$^{1}H,^{183}W$ HMQC NMR (C_6D_6, rt) of [$Cp_2W(H)$-SnAr*] (**5a**)

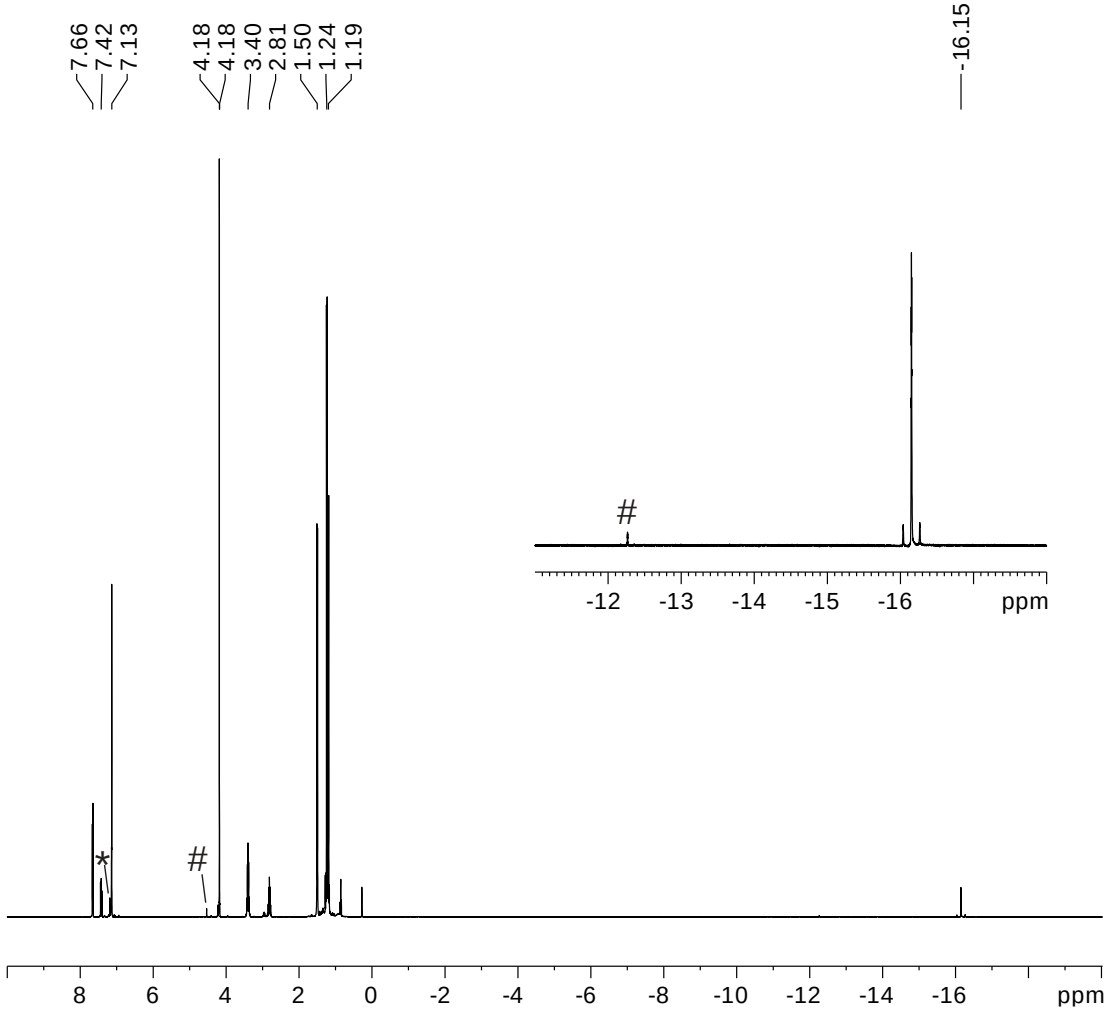



```
Current Data Parameters
NAME         MW974_500_W
EXPNO                 21
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210202
Time              11.38
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          hmqcph
TD                 1024
SOLVENT            C6D6
NS                   12
DS                   16
SWH           2500.000 Hz
FIDRES        2.441406 Hz
AQ           0.2048000 sec
RG                   4
DW             200.000 usec
DE               6.00 usec
TE              299.4 K
CNST2        89.0000000
D0           0.00000300 sec
D1           2.00000000 sec
D2           0.00561798 sec
D11          0.03000000 sec
D13          0.00000400 sec
IN0          0.00004015 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.50 usec
P2                25.00 usec
PL1       0 dB
PL1W        21.60222244 W
SFO1       500.1234983 MHz

======== CHANNEL f2 ========
CPDPRG[2             garp
NUC2                 183W
P3                28.00 usec
PCPD2             400.00 usec
PL2       0 dB
PL12                23.10 dB
SFO2         20.7519179 MHz

F1 - Acquisition parameters
TD                    199
SFO1           20.75192 MHz
FIDRES       125.137192 Hz
SW               600.000 ppm
FnMODE      States-TPPI

F2 - Processing parameters
SI                   1024
SF           500.1300000 MHz
WDW                  QSINE
SSB                      2
LB        0 Hz
GB        0
PC                    1.00

F1 - Processing parameters
SI                   1024
MC2         States-TPPI
SF           20.8373510 MHz
WDW                  QSINE
SSB                      2
LB        0 Hz
GB        0
```

Figure S53. $^{1}H,\ ^{183}W$ HMQC NMR of compound **5a**.

Compound **5b**

^{1}H NMR (C_6D_6, rt) of 1/2$[Cp_2W(H)Li]_4$ + $[Ar^*PbBr]_2$: crude product **5b** of after pentane extraction



Current Data Parameters
NAME MW1128_400
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20211004
Time 14.00
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 52656
SOLVENT C6D6
NS 64
DS 0
SWH 16025.641 Hz
FIDRES 0.304346 Hz
AQ 1.6428672 sec
RG 256
DW 31.200 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
TD0 1

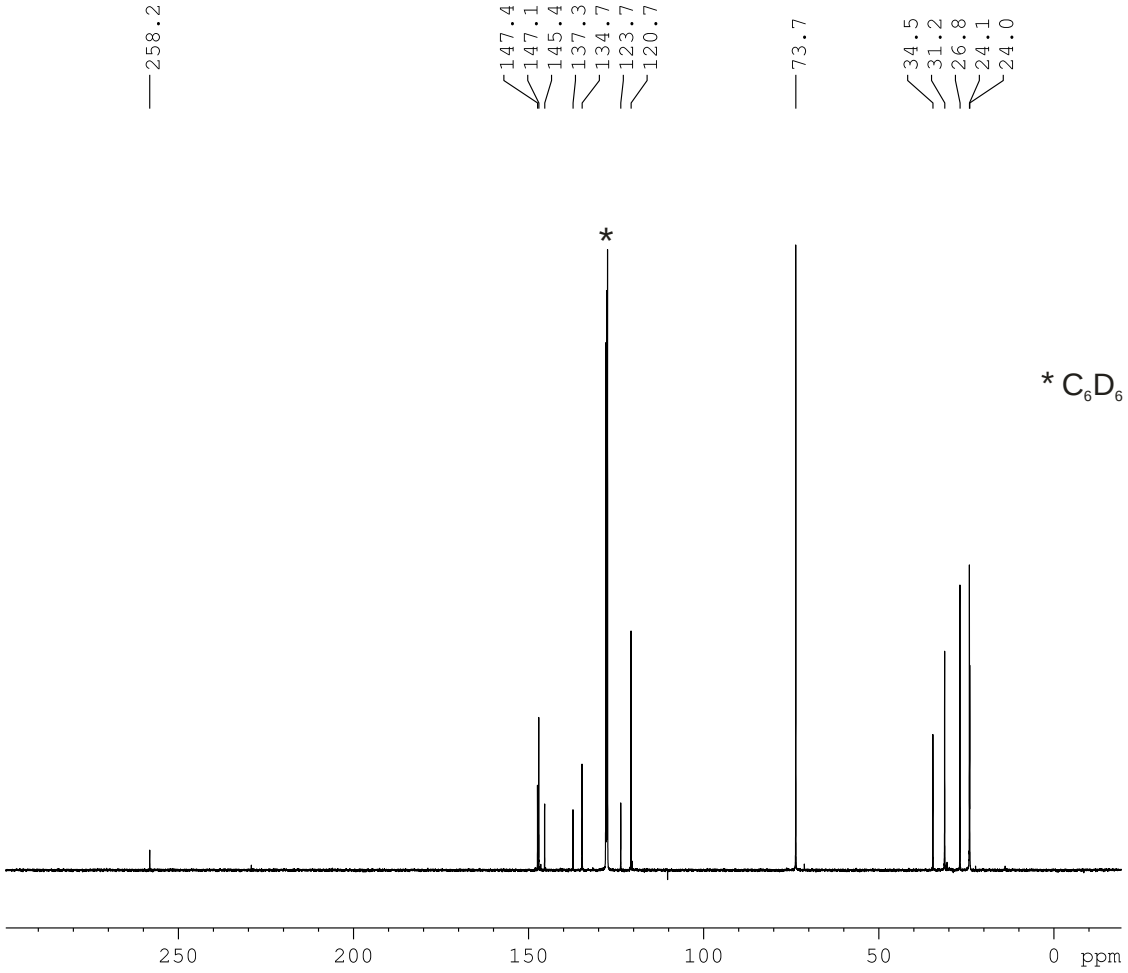
======== CHANNEL f1 ========
NUC1 1H
P1 14.60 usec
PL1 -3.00 dB
PL1W 16.03799057 W
SFO1 400.1100000 MHz

F2 - Processing parameters
SI 65536
SF 400.1100000 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

* C_6D_6
# Cp_2WH_2

Figure S54. ^{1}H NMR of compound **5b** (crude product).

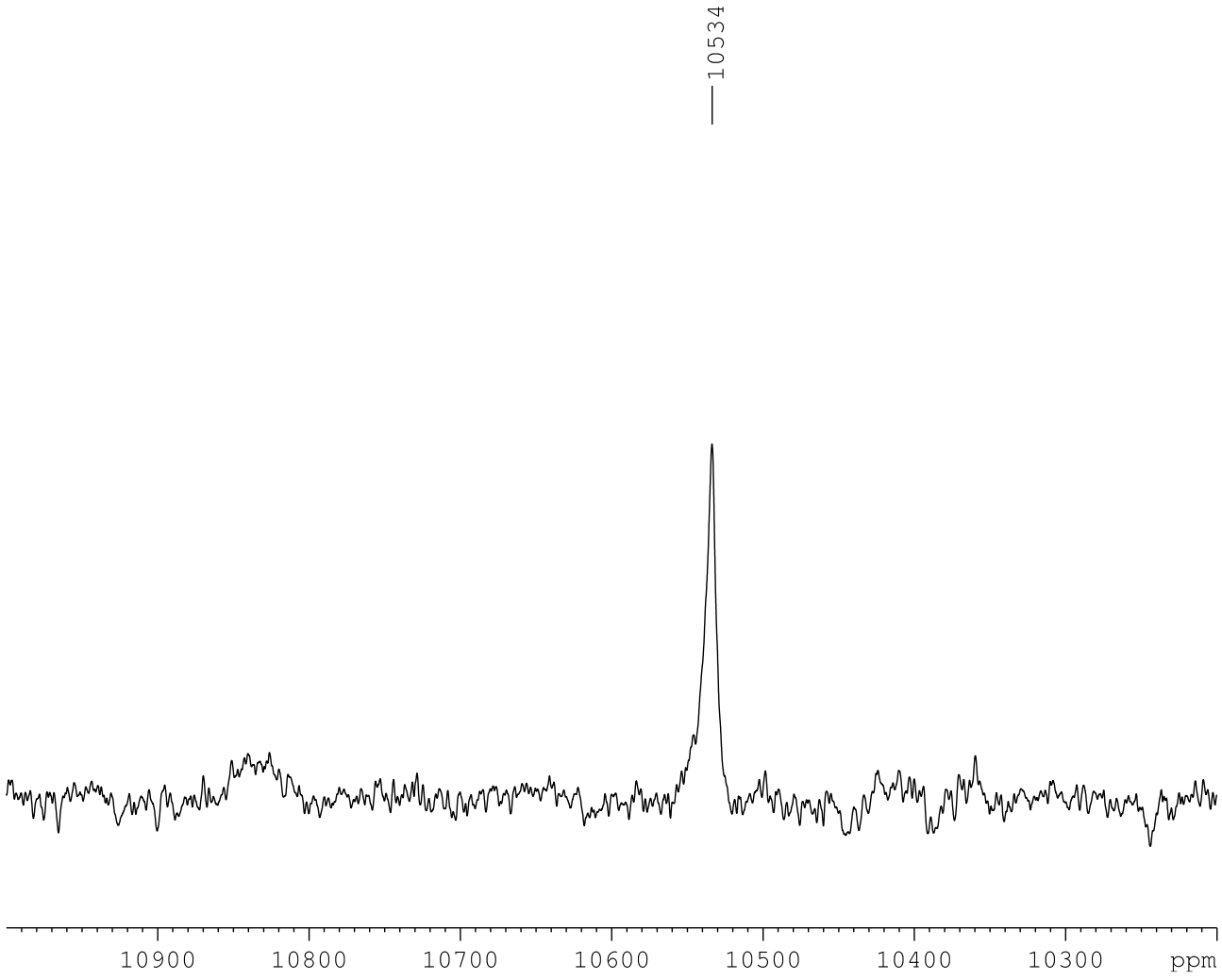
$^{13}C\{^{1}H\}$ NMR (C_6D_6, rt) of [$Cp_2W(H)$-PbAr*] (**5b**)




```
Current Data Parameters
NAME         MW982_400NM
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210203
Time                2.31
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG            udeft
TD                 22218
SOLVENT             C6D6
NS                  6144
DS                     0
SWH            32051.281 Hz
FIDRES          1.442582 Hz
AQ             0.3466008 sec
RG                 32800
DW                15.600 usec
DE                 6.00 usec
TE                299.2 K
D1            3.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
D20         100.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                13C
P1                13.50 usec
P13             2000.00 usec
P26              500.00 usec
PL1               -4.16 dB
PL1W         78.55633545 W
SFO1        100.6218251 MHz
SP8                1.39 dB
SP13               1.39 dB
SPNAM[8] Crp60,0.5,20.1
SPNAM[13    Crp60comp.4
SPOAL8             0.500
SPOAL13            0.500
SPOFFS8  0 Hz
SPOFFS13 0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               11.77 dB
PL2W         16.03799057 W
PL12W         0.53474891 W
SFO2        400.1120007 MHz

F2 - Processing parameters
SI                131072
SF          100.6077400 MHz
WDW                 EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 1.40
```

Figure S55. $^{13}C\{^{1}H\}$ NMR of compound **5b**.

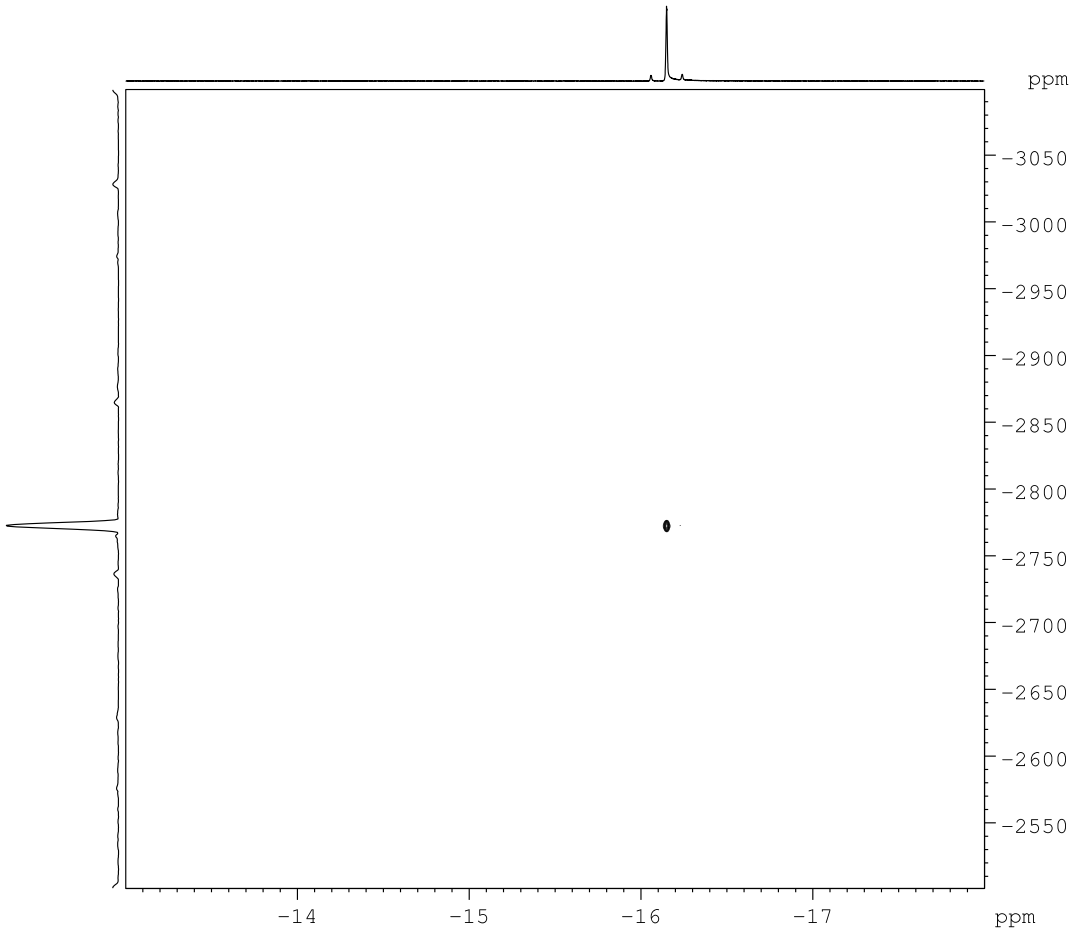
^{207}Pb NMR (C_6D_6, rt) of [$Cp_2W(H)$-PbAr*] (**5b**)




```
Current Data Parameters
NAME       MW966_300_Pb
EXPNO                15
PROCNO                1

F2 - Acquisition Parameters
Date_          20210116
Time              23.41 h
INSTRUM           spect
PROBHD   Z104275_0338 (
PULPROG            zg30
TD                14998
SOLVENT            C6D6
NS                81920
DS                    0
SWH          125000.000 Hz
FIDRES        16.668890 Hz
AQ             0.0599920 sec
RG                204.67
DW                4.000 usec
DE                10.00 usec
TE                298.0 K
D1           0.20000000 sec
TD0                   1
SFO1         63.4796728 MHz
NUC1               207Pb
P0                 4.17 usec
P1                12.50 usec
PLW1        40.00000000 W

F2 - Processing parameters
SI                65536
SF           62.7889938 MHz
WDW                  EM
SSB       0
LB              100.00 Hz
GB        0
PC                 3.00
```

Figure S56. ^{207}Pb NMR of compound **5b**.

$^{1}H,^{183}W$ HMQC NMR (C_6D_6, rt) of [$Cp_2W(H)$-PbAr*] (**5b**)

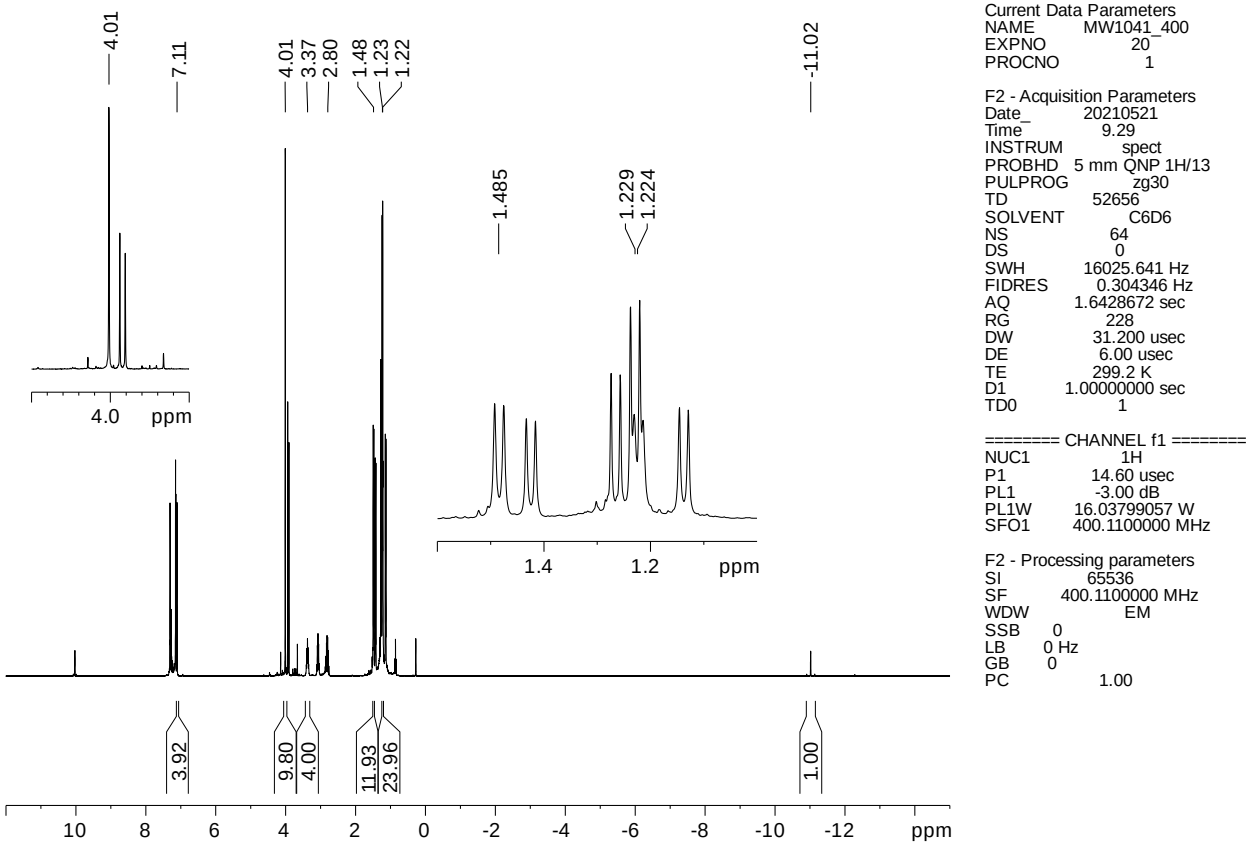



```
Current Data Parameters
NAME         MW982_500_W
EXPNO                 21
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210202
Time               13.40
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG          hmqcph
TD                 1024
SOLVENT            C6D6
NS                    4
DS                   16
SWH           2500.000 Hz
FIDRES        2.441406 Hz
AQ            0.2048000 sec
RG                    4
DW             200.000 usec
DE               6.00 usec
TE              299.3 K
CNST2         91.0000000
D0            0.00000300 sec
D1            2.00000000 sec
D2            0.00549451 sec
D11           0.03000000 sec
D13           0.00000400 sec
IN0           0.00004010 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                12.50 usec
P2                25.00 usec
PL1       0 dB
PL1W        21.60222244 W
SFO1        500.1222480 MHz

======== CHANNEL f2 ========
CPDPRG[2             garp
NUC2                 183W
P3                 28.00 usec
PCPD2             400.00 usec
PL2       0 dB
PL12              23.10 dB
SFO2         20.7790064 MHz

F1 - Acquisition parameters
TD                    256
SFO1            20.77901 MHz
FIDRES         97.401596 Hz
SW               600.000 ppm
FnMODE       States-TPPI

F2 - Processing parameters
SI                   1024
SF           500.1300000 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
PC                   1.00

F1 - Processing parameters
SI                   1024
MC2          States-TPPI
SF            20.8373510 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
```

Figure S57. ^{1}H, ^{183}W HMQC NMR of compound **5b**.

Compound **5c**

^{1}H NMR (C_6D_6, rt) of [$Cp_2W(H)$-GeAr*] (**5c**) (*in situ*), ca. 40 % **9** present



Current Data Parameters
NAME MW1041_400
EXPNO 20
PROCNO 1

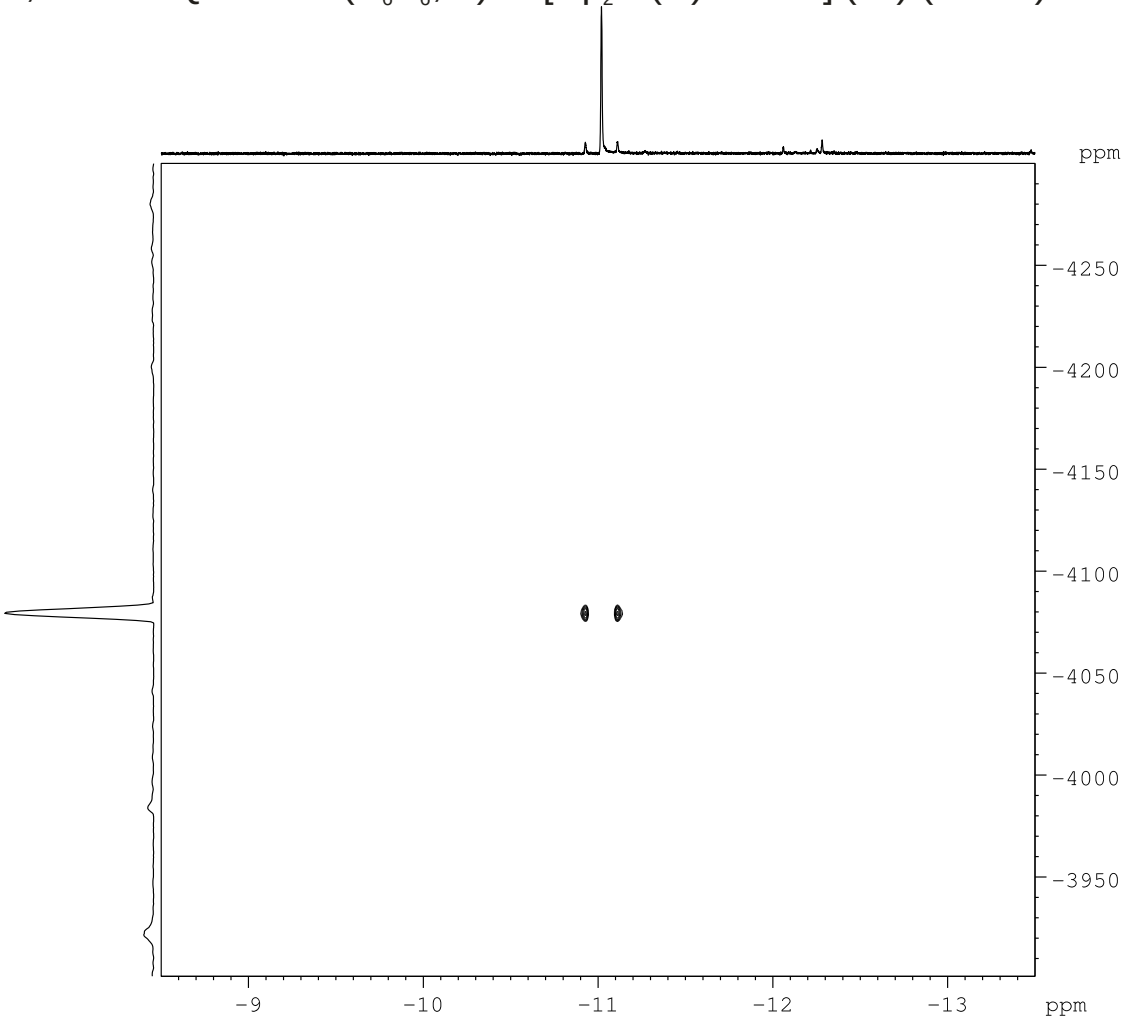
F2 - Acquisition Parameters
Date_ 20210521
Time 9.29
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 52656
SOLVENT C6D6
NS 64
DS 0
SWH 16025.641 Hz
FIDRES 0.304346 Hz
AQ 1.6428672 sec
RG 228
DW 31.200 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.60 usec
PL1 -3.00 dB
PL1W 16.03799057 W
SFO1 400.1100000 MHz

F2 - Processing parameters
SI 65536
SF 400.1100000 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

Figure S58. ^{1}H NMR of compound **5c** in situ after reaction under light.

$^{1}H,^{183}W$ HMQC NMR (C_6D_6, rt) of [$Cp_2W(H)$-GeAr*] (**5c**) (*in situ*)




```
Current Data Parameters
NAME       MW1041_500_W
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20210525
Time              10.26
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          hmqcph
TD                 1024
SOLVENT            C6D6
NS                    8
DS                   16
SWH            2500.000 Hz
FIDRES         2.441406 Hz
AQ           0.2048000 sec
RG                  101
DW             200.000 usec
DE               6.00 usec
TE              299.2 K
CNST2         92.5599976
D0           0.00000300 sec
D1           2.00000000 sec
D2           0.00540190 sec
D11          0.03000000 sec
D13          0.00000400 sec
IN0          0.00004015 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.50 usec
P2                25.00 usec
PL1       0 dB
PL1W        21.60222244 W
SFO1       500.1244986 MHz

======== CHANNEL f2 ========
CPDPRG[2            garp
NUC2                183W
P3                28.00 usec
PCPD2             400.00 usec
PL2       0 dB
PL12               23.10 dB
SFO2         20.7519179 MHz

F1 - Acquisition parameters
TD                   256
SFO1           20.75192 MHz
FIDRES        97.274612 Hz
SW              600.000 ppm
FnMODE      States-TPPI

F2 - Processing parameters
SI                  1024
SF           500.1300000 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
PC                  1.00

F1 - Processing parameters
SI                  1024
MC2          States-TPPI
SF           20.8373510 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
```

Figure S59. ^{1}H, ^{183}W HMQC NMR of compound **5c** in situ after reaction under light.

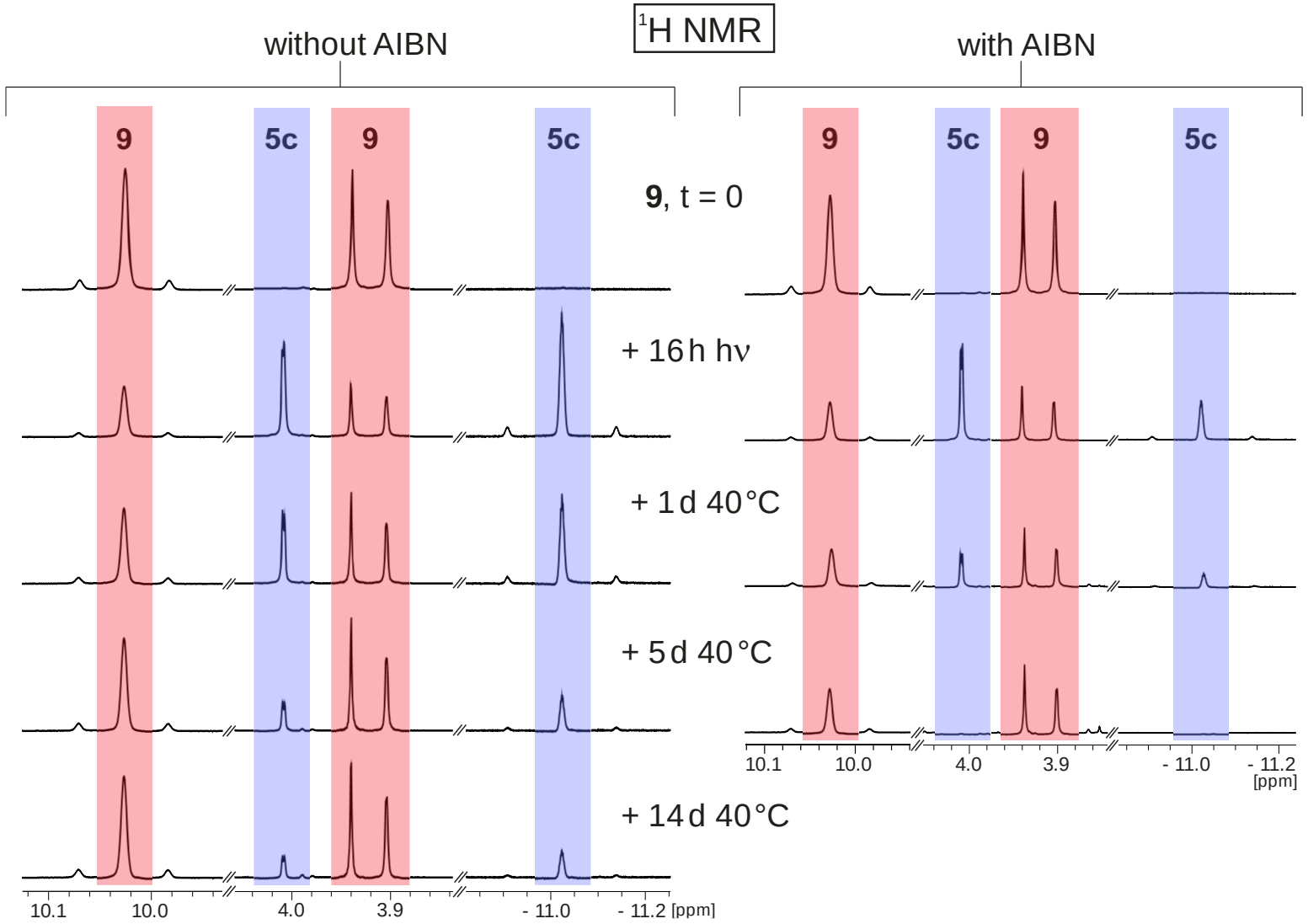


Figure S60. ^{1}H NMR: reversible 1-2-H shift of **9** to **5c** to give **9**.

^{1}H NMR (C_6D_6, rt) of [Cp_2W=Ge(H)Ar*] (**9**): reversible 1,2-H-Shift (**9** - **5c**), with AIBN

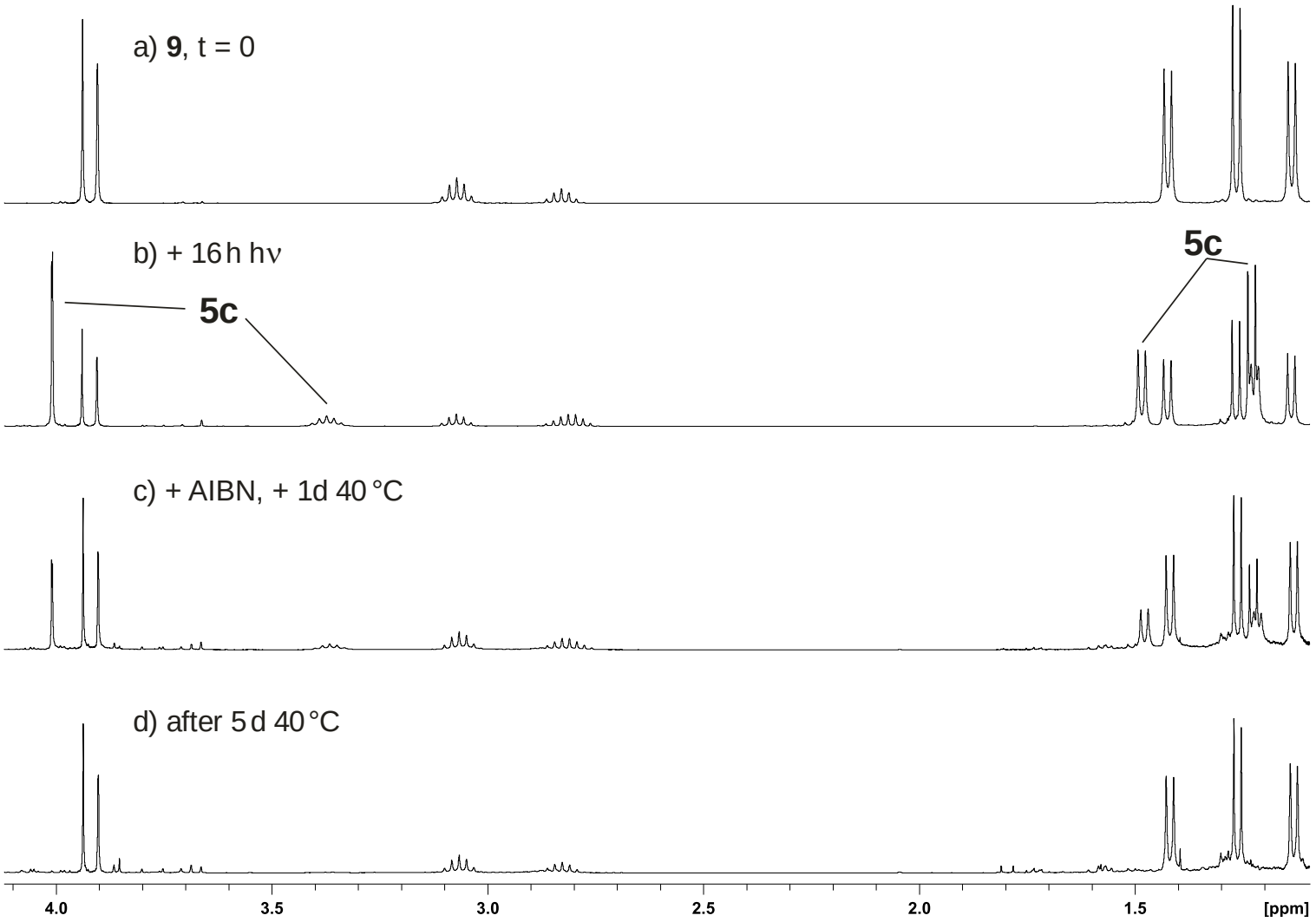
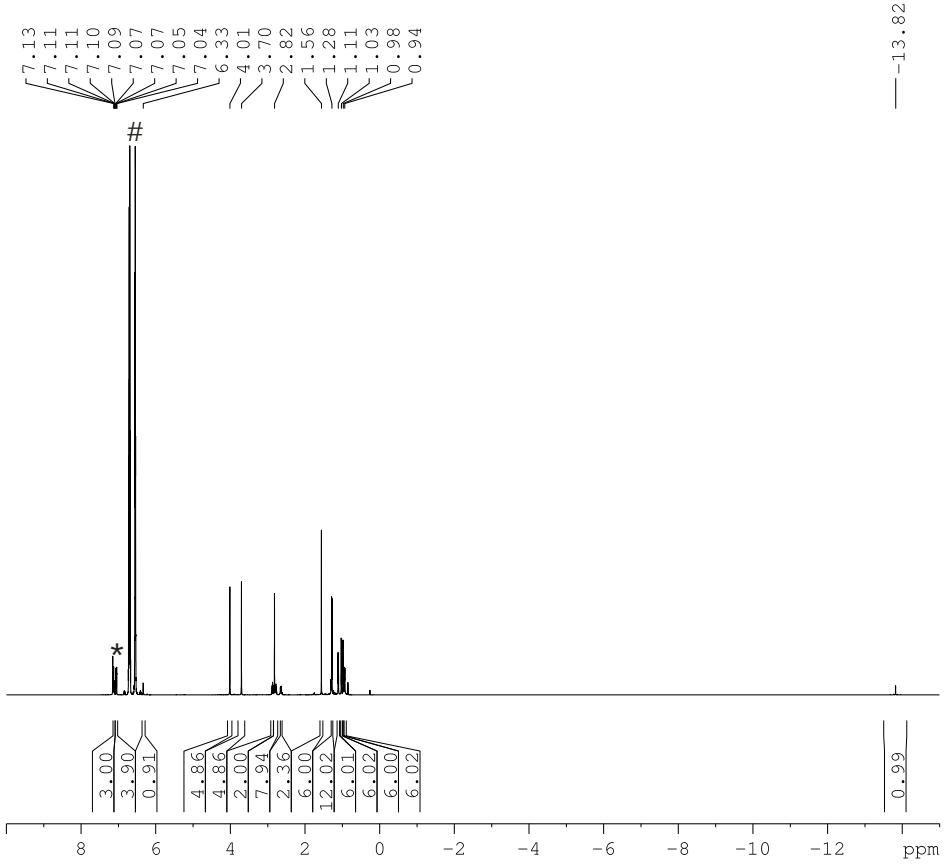


Figure S61. ^{1}H NMR: 1-2-H shift of **9** to give **5c**.

Compound **6**

^{1}H NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2W(H)=Sn(H)(^{Me}NHC)Ar^*][Al(O^tBu^F)_4]$ (**6**)

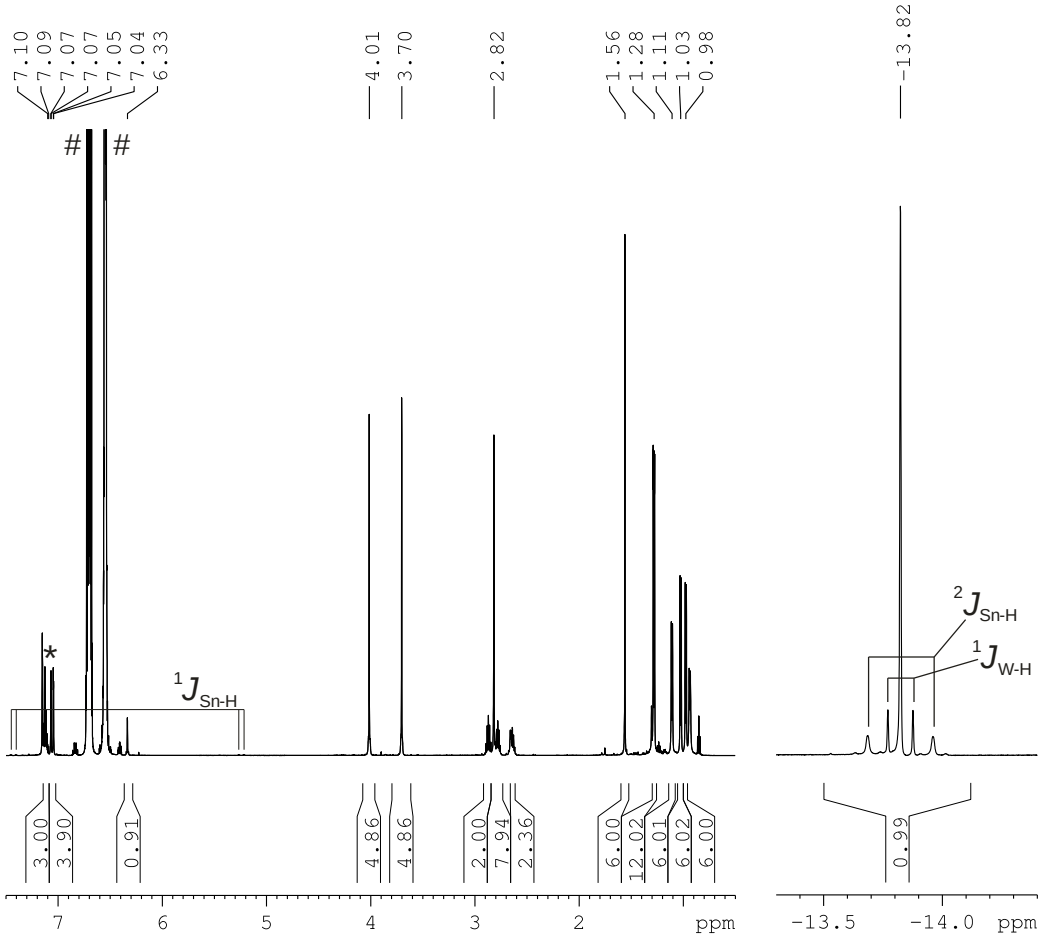



```
Current Data Parameters
NAME         MW980_600NM
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210121
Time               12.24 h
INSTRUM             spect
PROBHD   Z126545_0027 (
PULPROG             zg30
TD                131072
SOLVENT             C6D6
NS                    96
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             2.7262976 sec
RG                 14.03
DW                20.800 usec
DE                10.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1
SFO1         600.1300000 MHz
NUC1                  1H
P1                12.00 usec
PLW1         23.41200066 W

F2 - Processing parameters
SI                 65536
SF           600.1300000 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

* C_6D_6
\# 1,2-$C_6H_4F_2$

Figure S62. ^{1}H NMR of compound **6**.

^{1}H NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2W(H)=Sn(H)(^{Me}NHC)Ar^*][Al(O^tBu^F)_4]$ (**6**)

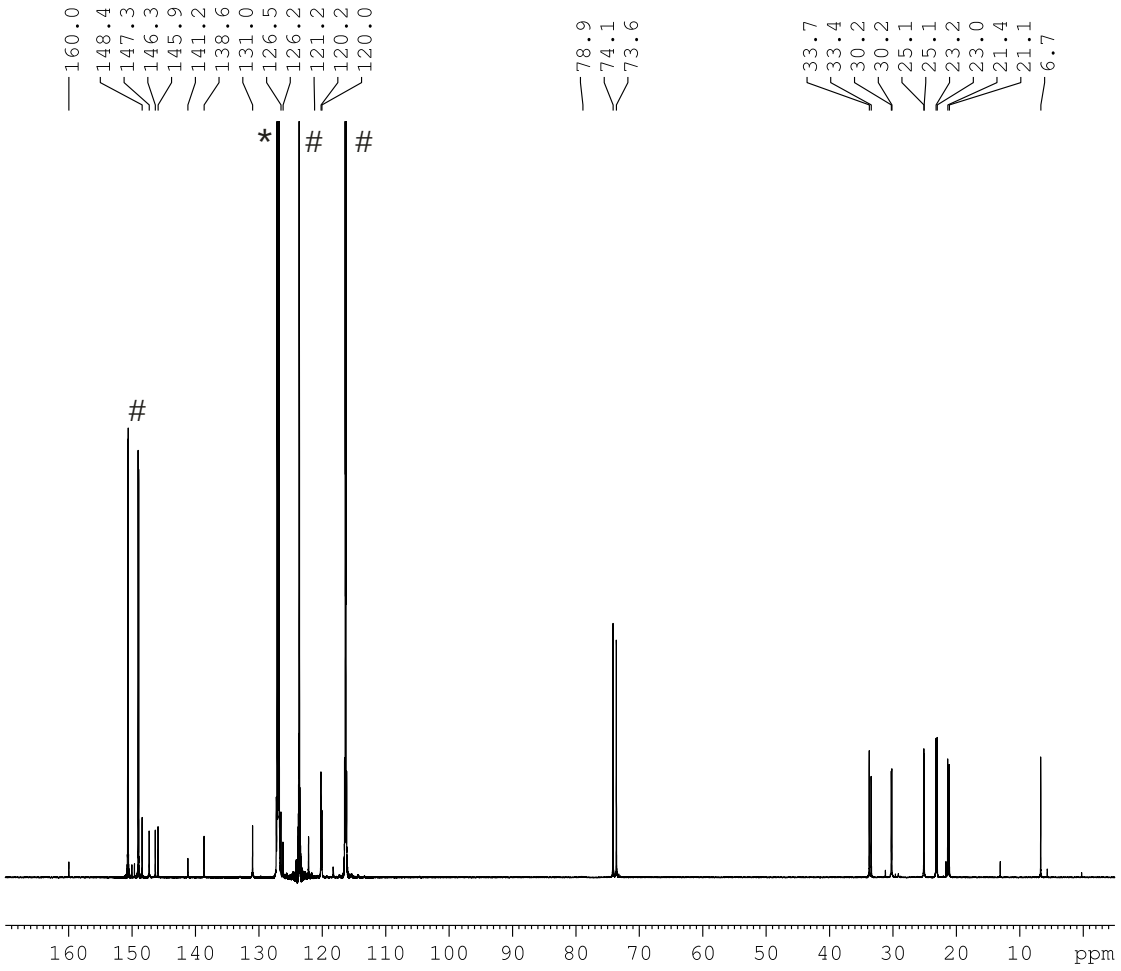



```
Current Data Parameters
NAME         MW980_600NM
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210121
Time              12.24 h
INSTRUM             spect
PROBHD   Z126545_0027 (
PULPROG             zg30
TD                131072
SOLVENT             C6D6
NS                    96
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             2.7262976 sec
RG                 14.03
DW                20.800 usec
DE                10.00 usec
TE                298.0 K
D1           1.00000000 sec
TD0                    1
SFO1         600.1300000 MHz
NUC1                  1H
P1                12.00 usec
PLW1         23.41200066 W

F2 - Processing parameters
SI                 65536
SF           600.1300000 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

* C_6D_6
\# 1,2-$C_6H_4F_2$

Figure S63. ^{1}H NMR of compound **6** (selected area).

$^{13}C\{^{1}H\}$ NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2W(H)=Sn(H)(^{Me}NHC)Ar^*][Al(O^tBu^F)_4]$ (**6**)

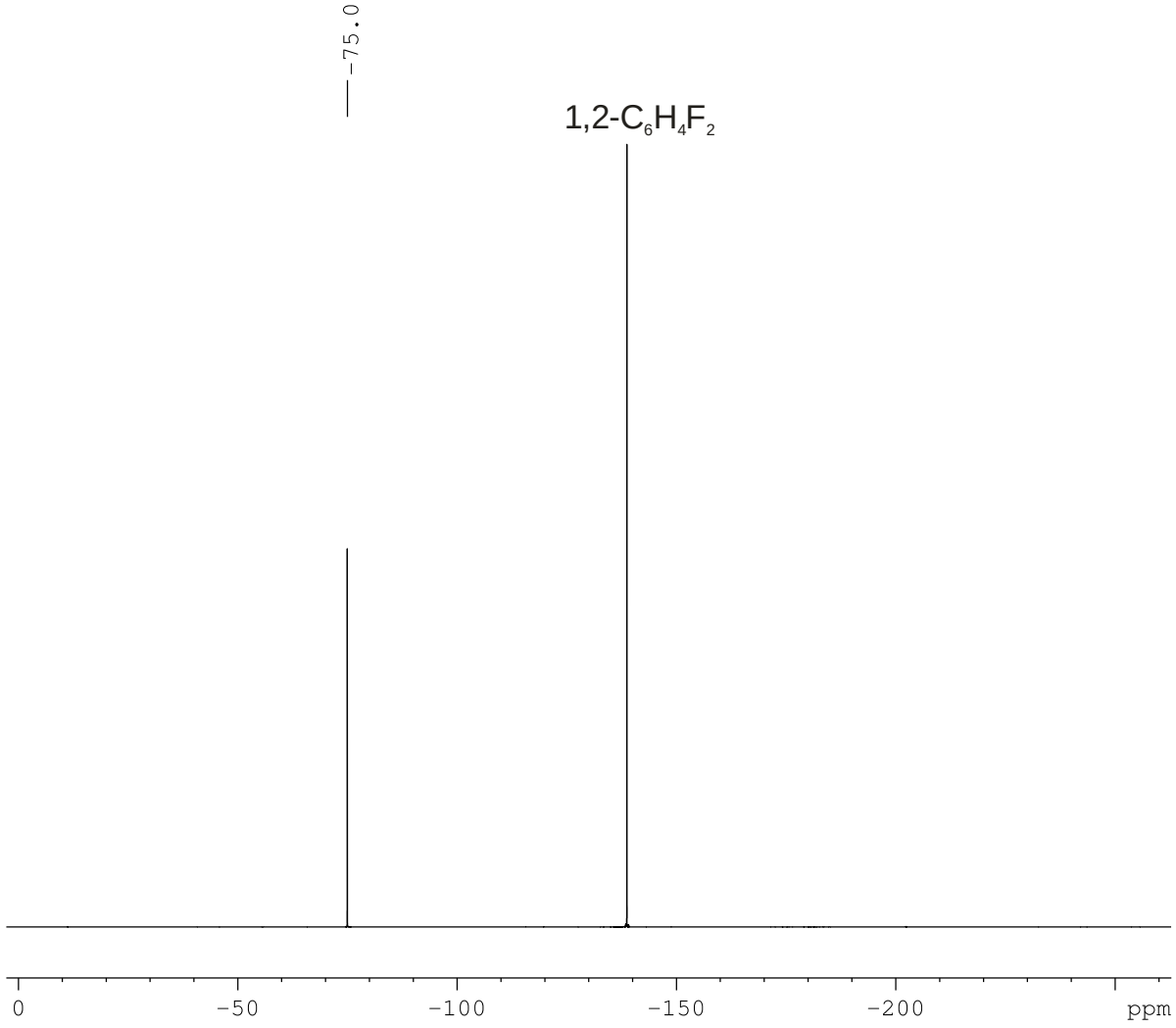



```
Current Data Parameters
NAME         MW980_600NM
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210121
Time              15.09 h
INSTRUM             spect
PROBHD    Z126545_0027 (
PULPROG             udeft
TD                  25902
SOLVENT               C6D6
NS                    2048
DS                       8
SWH             36231.883 Hz
FIDRES           2.797613 Hz
AQ              0.3574476 sec
RG                   189.6
DW                 13.800 usec
DE                 18.00 usec
TE                 298.0 K
D1            4.00000000 sec
D12           0.00002000 sec
D20          20.00000000 sec
TD0                    1
SFO1         150.9178988 MHz
NUC1                 13C
P1                 10.00 usec
P13              2000.00 usec
P26               500.00 usec
PLW1          57.02700043 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5   0 Hz
SPW5           8.71310043 W
SPNAM[8] Crp60,0.5,20.1
SPOAL8             0.500
SPOFFS8   0 Hz
SPW8           8.71310043 W
SFO2         600.1300000 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2              70.00 usec
PLW2          23.41200066 W
PLW12          0.68803000 W

F2 - Processing parameters
SI                 131072
SF           150.9029076 MHz
WDW                  EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 1.40
```

* C_6D_6
\# 1,2-$C_6H_4F_2$

Figure S64. $^{13}C\{^{1}H\}$ NMR of compound **6**.

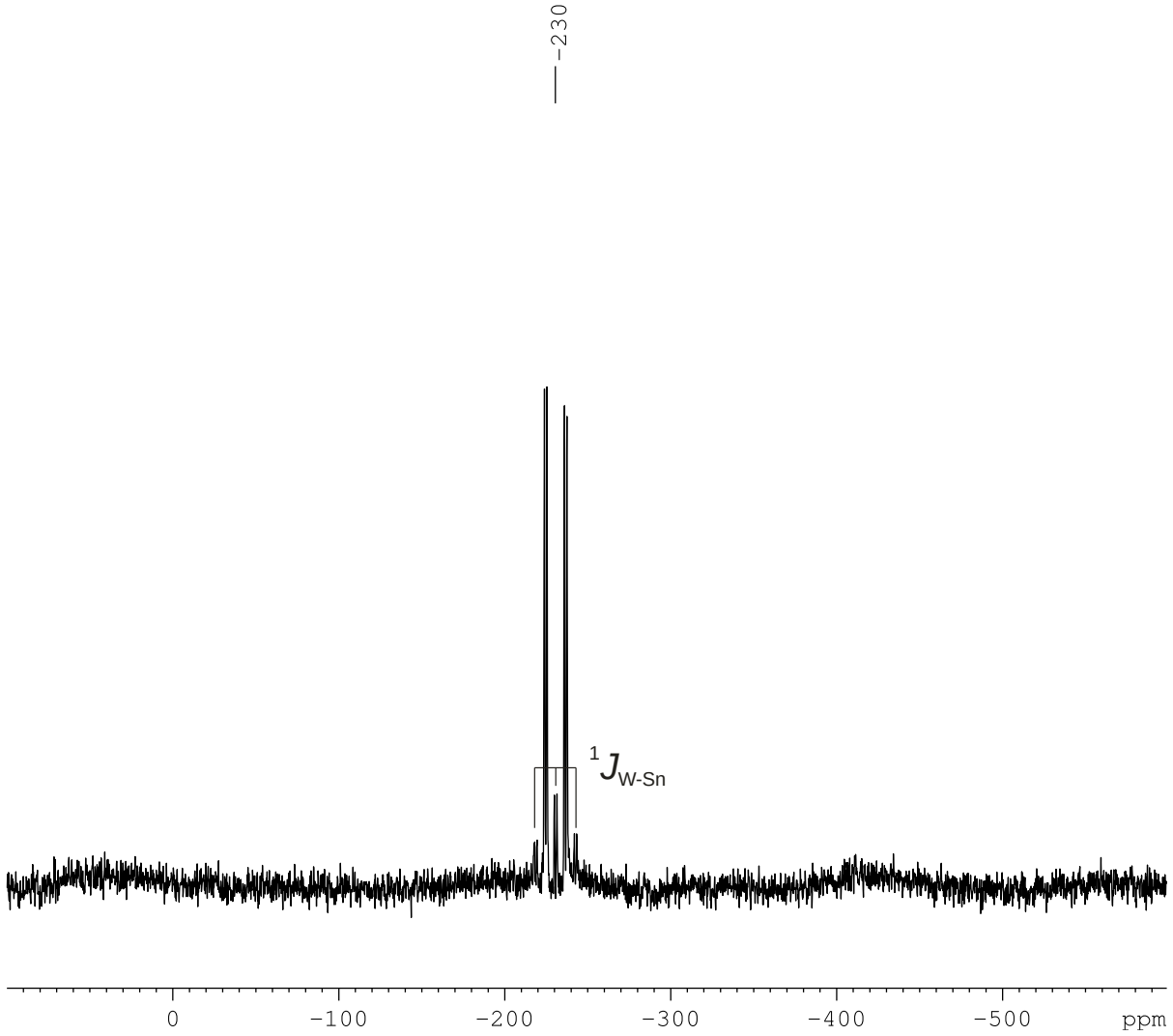
$^{19}F\{^{1}H\}$ NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2W(H)=Sn(H)(^{Me}NHC)Ar^*][Al(O^tBu^F)_4]$ (**6**)




```
Current Data Parameters
NAME          MW980_400
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20210121
Time               11.32
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG         zgfhigqn
TD                131072
SOLVENT             C6D6
NS                   128
DS                     0
SWH           100000.000 Hz
FIDRES          0.762939 Hz
AQ             0.6553600 sec
RG                  4100
DW                 5.000 usec
DE                 6.00 usec
TE                299.2 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  19F
P1                 18.75 usec
PL1                -2.92 dB
PL1W         30.50645256 W
SFO1         376.4306030 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               11.77 dB
PL2W         16.03799057 W
PL12W         0.53474891 W
SFO2         400.1120007 MHz

F2 - Processing parameters
SI                 262144
SF           376.4795470 MHz
WDW                    EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 1.00
```

Figure S65. $^{19}F\{^{1}H\}$ NMR of compound **6**.

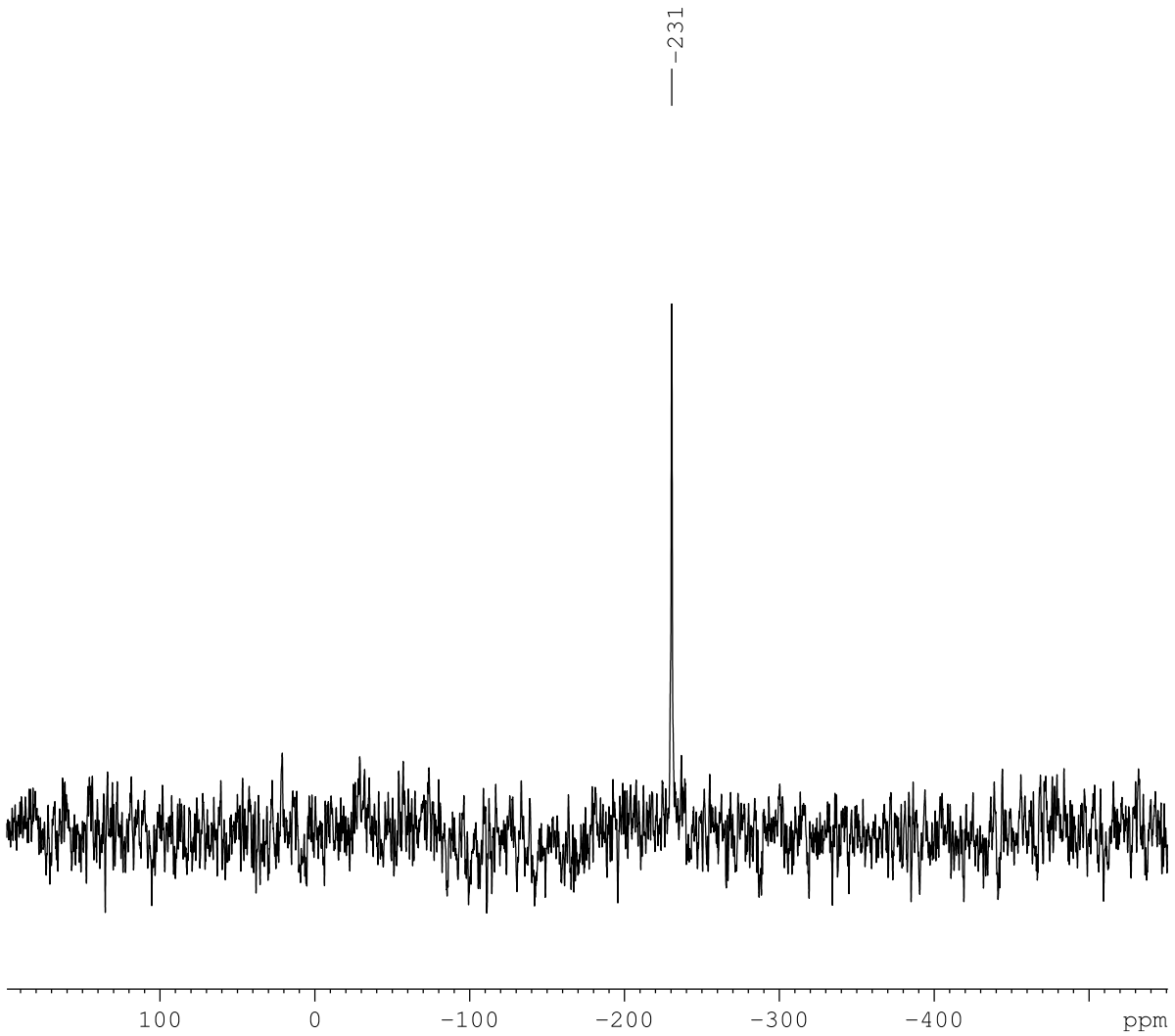
^{119}Sn NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2W(H)=Sn(H)(^{Me}NHC)Ar^*][Al(O^tBu^F)_4]$ (**6**)




```
Current Data Parameters
NAME         MW980_300Sn
EXPNO                 35
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210122
Time               22.04 h
INSTRUM            spect
PROBHD   Z104275_0338 (
PULPROG            zg30
TD                 8918
SOLVENT            C6D6
NS               307200
DS                    1
SWH            89285.711 Hz
FIDRES         20.023708 Hz
AQ             0.0499408 sec
RG                204.67
DW                 5.600 usec
DE                 6.50 usec
TE                298.0 K
D1            0.02000000 sec
TD0                   1
SFO1         111.8979900 MHz
NUC1               119Sn
P0                 4.03 usec
P1                12.10 usec
PLW1         12.00000000 W

F2 - Processing parameters
SI                 4096
SF           111.9203740 MHz
WDW                EM
SSB       0
LB                10.00 Hz
GB        0
PC                 1.40
```

Figure S66. ^{119}Sn NMR of compound **6**.

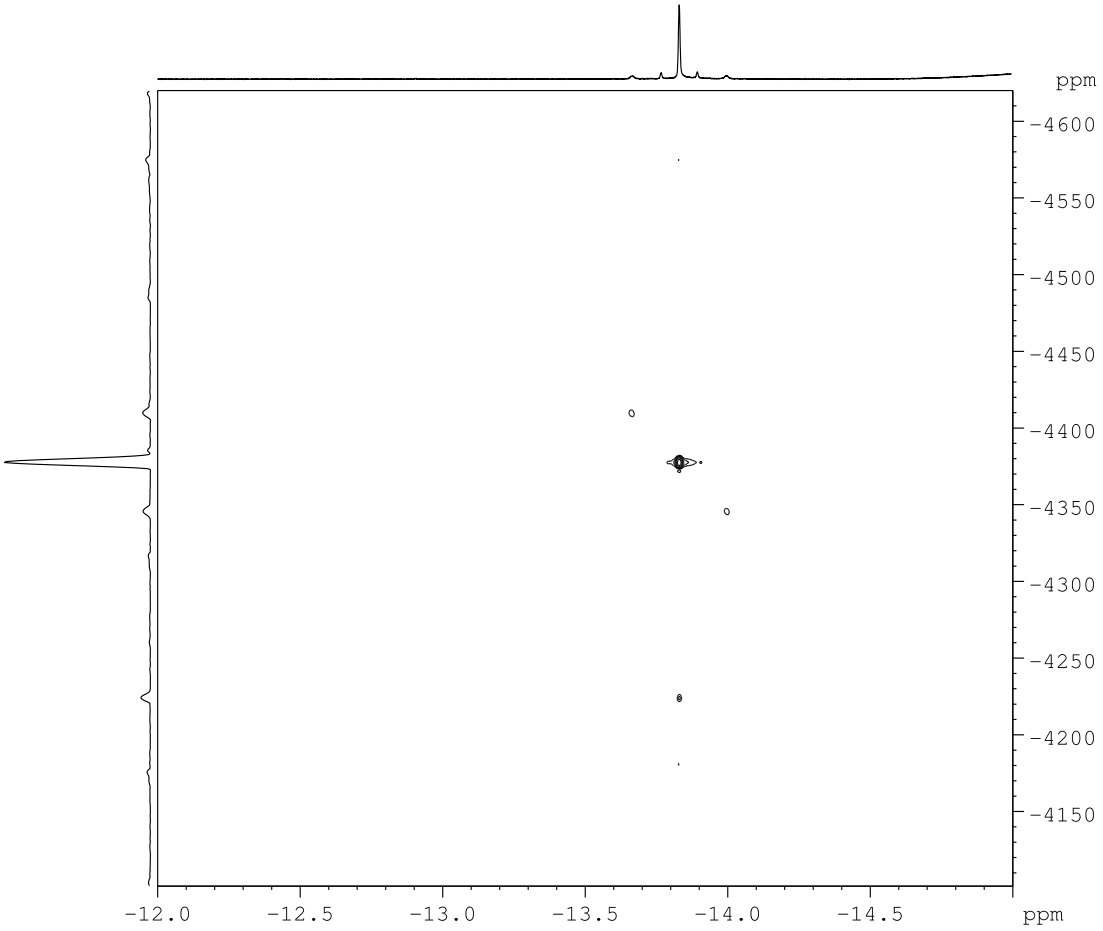
$^{119}Sn\{^{1}H\}$ NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2W(H)=Sn(H)(^{Me}NHC)Ar^*][Al(O^tBu^F)_4]$ (**6**)




```
Current Data Parameters
NAME         MW980_300Sn
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210122
Time               11.56 h
INSTRUM             spect
PROBHD   Z104275_0338 (
PULPROG           zgig30
TD                 39186
SOLVENT             C6D6
NS                  5000
DS                     4
SWH            89285.711 Hz
FIDRES          4.557021 Hz
AQ             0.2194416 sec
RG                204.67
DW                 5.600 usec
DE                 6.50 usec
TE                298.0 K
D1           0.10000000 sec
D11          0.03000000 sec
TD0                    1
SFO1         111.8979898 MHz
NUC1                119Sn
P0                 4.03 usec
P1                12.10 usec
PLW1         12.00000000 W
SFO2         300.1312005 MHz
NUC2                   1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2          8.26509953 W
PLW12         0.20000000 W

F2 - Processing parameters
SI                 65536
SF           111.9203738 MHz
WDW                   EM
SSB       0
LB                50.00 Hz
GB        0
PC                 1.40
```

Figure S67. $^{119}Sn\{^{1}H\}$ NMR of compound **6**.

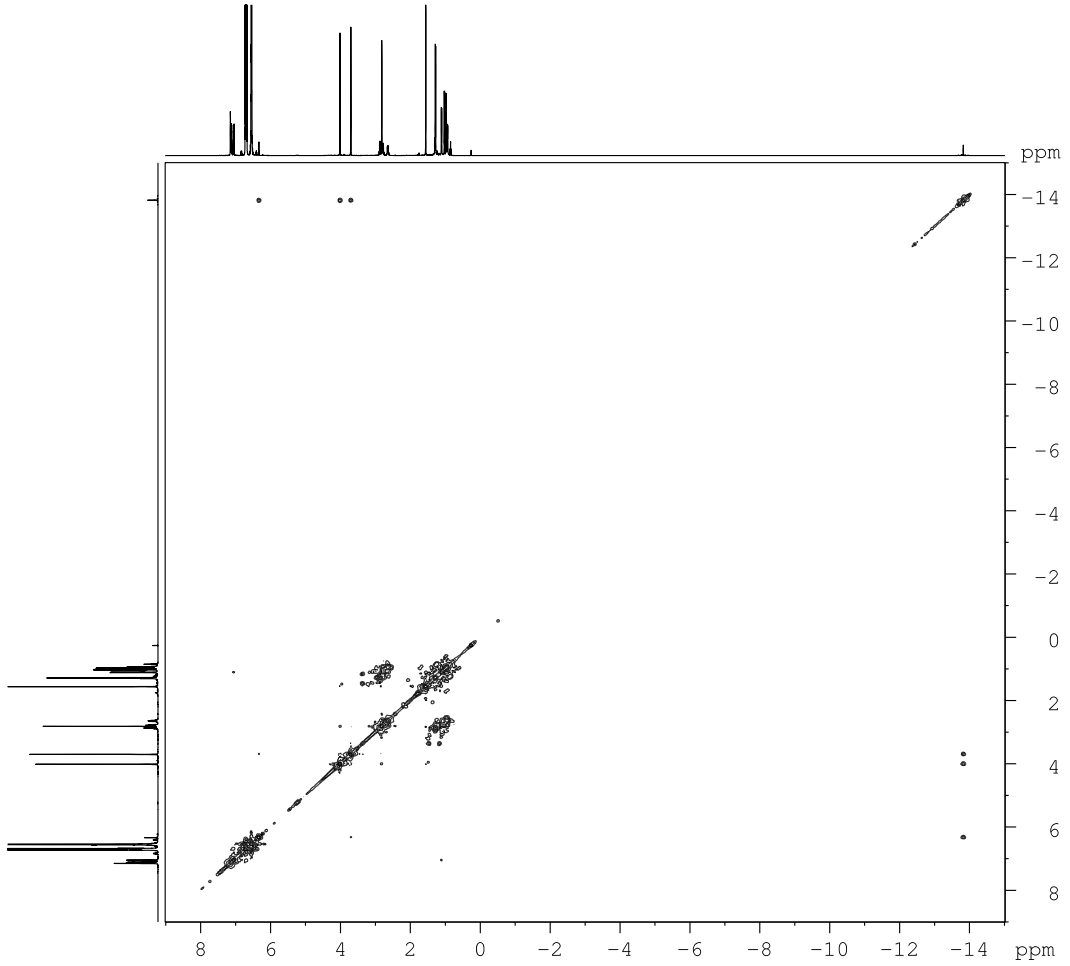
$^{1}H,^{183}W$ HMQC NMR (C_6D_6 + 1,2-difluorobenzene , rt) of $[Cp_2W(H)=Sn(H)(^{Me}NHC)Ar^*][Al(O^tBu^F)_4]$ (**6**)




```
Current Data Parameters
NAME         MW980_500_W
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210202
Time              14.56
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          hmqcph
TD                 1024
SOLVENT            C6D6
NS                    4
DS                   16
SWH           2500.000 Hz
FIDRES        2.441406 Hz
AQ           0.2048000 sec
RG                    4
DW             200.000 usec
DE               6.00 usec
TE              299.2 K
CNST2         63.2999992
D0           0.00000300 sec
D1           2.00000000 sec
D2           0.00789889 sec
D11          0.03000000 sec
D13          0.00000400 sec
IN0          0.00004015 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                12.50 usec
P2                25.00 usec
PL1      0 dB
PL1W       21.60222244 W
SFO1       500.1227481 MHz

======== CHANNEL f2 ========
CPDPRG[2           garp
NUC2               183W
P3                28.00 usec
PCPD2            400.00 usec
PL2      0 dB
PL12              23.10 dB
SFO2         20.7456667 MHz

F1 - Acquisition parameters
TD                   256
SFO1           20.74567 MHz
FIDRES        97.245316 Hz
SW              600.000 ppm
FnMODE      States-TPPI

F2 - Processing parameters
SI                  1024
SF           500.1300000 MHz
WDW                 QSINE
SSB                     2
LB       0 Hz
GB       0
PC                 1.00

F1 - Processing parameters
SI                  1024
MC2         States-TPPI
SF           20.8373510 MHz
WDW                 QSINE
SSB                     2
LB       0 Hz
GB       0
```

Figure S68. ^{1}H, ^{183}W HMQC NMR of compound **6**.

$^{1}H,^{1}H$ COSY NMR (C_6D_6 + 1,2-difluorobenzene , rt) of $[Cp_2W(H)=Sn(H)(^{Me}NHC)Ar^*][Al(O^tBu^F)_4]$ (**6**)

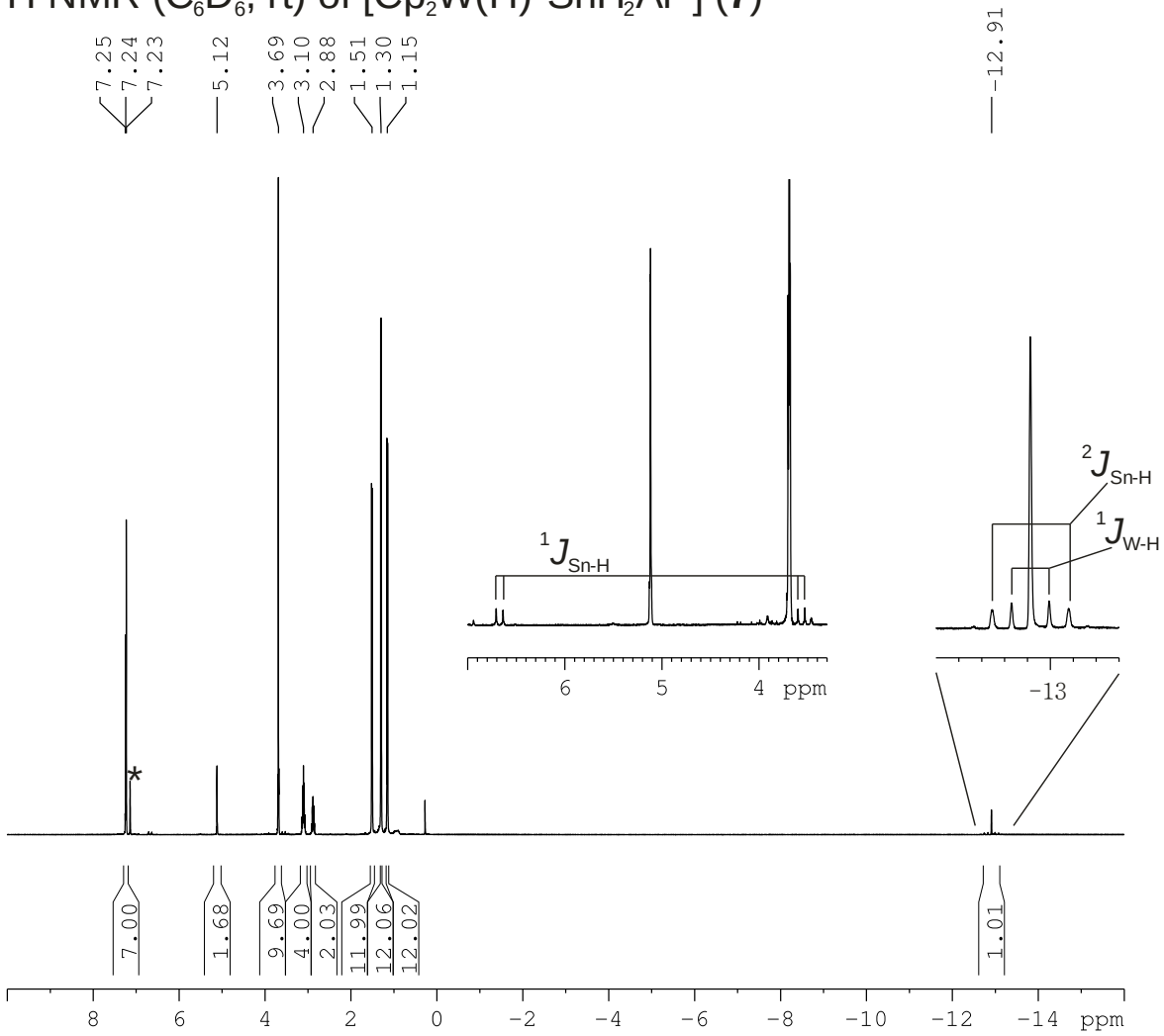



```
Current Data Parameters
NAME          MW980_600NM
EXPNO                  13
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210121
Time                16.39 h
INSTRUM             spect
PROBHD    Z126545_0027 (
PULPROG       cosygpppqf
TD                  4096
SOLVENT             C6D6
NS                     8
DS                    16
SWH             14423.077 Hz
FIDRES          7.042518 Hz
AQ              0.1419947 sec
RG                  19.61
DW                 34.667 usec
DE                 10.00 usec
TE                 298.0 K
D0             0.00000300 sec
D1             2.00000000 sec
D11            0.03000000 sec
D12            0.00002000 sec
D13            0.00000400 sec
D16            0.00020000 sec
IN0            0.00006940 sec
TDav                    1
SFO1          600.1281996 MHz
NUC1                   1H
P0                 12.00 usec
P1                 12.00 usec
P17              2500.00 usec
PLW1         23.41200066 W
PLW10         5.39410019 W
GPNAM[1]      SMSQ10.100
GPZ1               10.00 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                    512
SFO1            600.1282 MHz
FIDRES         56.286022 Hz
SW                24.010 ppm
FnMODE                 QF

F2 - Processing parameters
SI                    1024
SF            600.1300000 MHz
WDW                 QSINE
SSB       0
LB        0 Hz
GB        0
PC                  1.40

F1 - Processing parameters
SI                    1024
MC2                    QF
SF            600.1300000 MHz
WDW                 QSINE
SSB       0
LB        0 Hz
GB        0
```

Figure S69. ^{1}H, ^{1}H COSY NMR of compound **6**.

Compound **7**

^{1}H NMR (C_6D_6, rt) of [$Cp_2W(H)$-SnH_2Ar^*] (**7**)

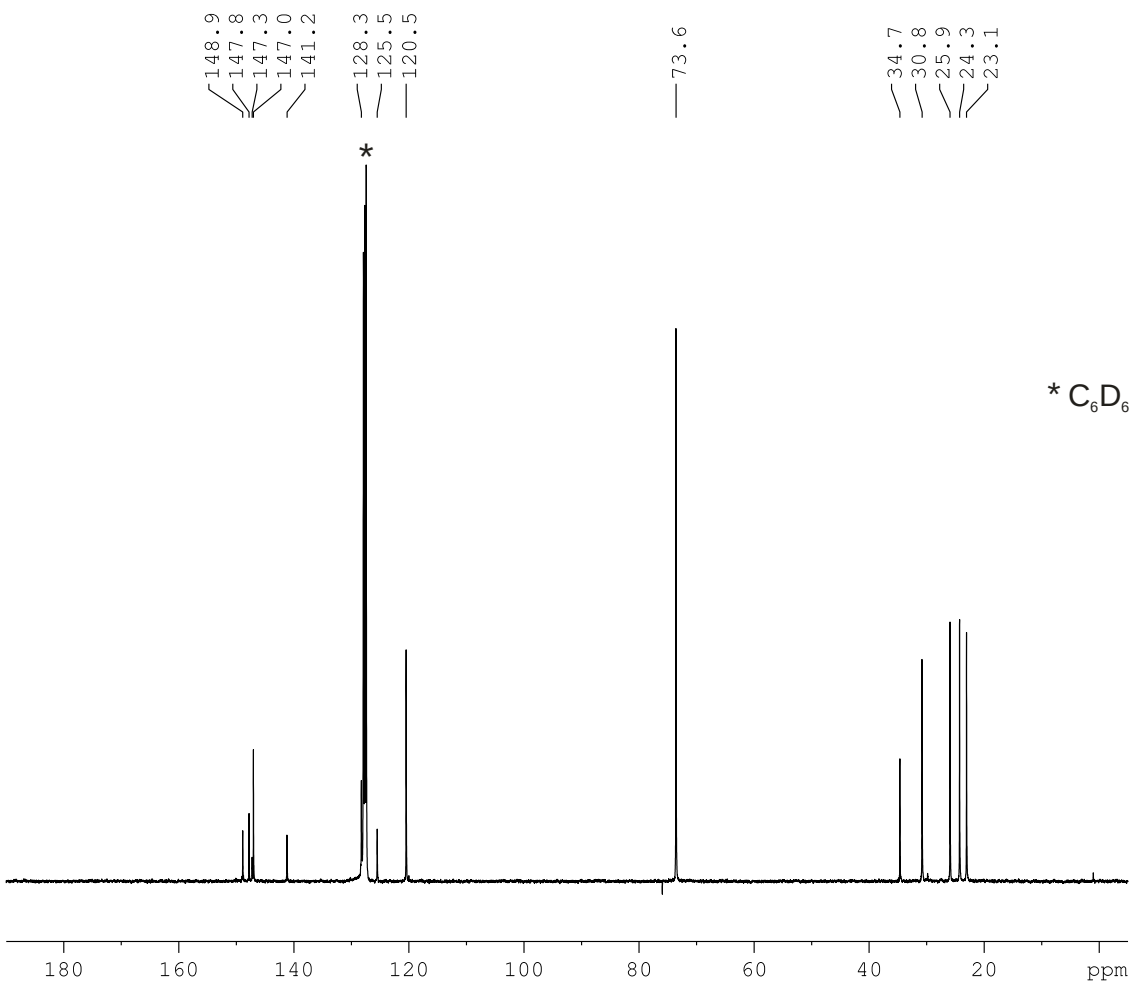



```
Current Data Parameters
NAME       MW1069_400NM
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_          20210508
Time              15.12
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG            zg30
TD                52656
SOLVENT            C6D6
NS                   64
DS                    0
SWH           16025.641 Hz
FIDRES         0.304346 Hz
AQ            1.6428672 sec
RG                  228
DW               31.200 usec
DE                6.00 usec
TE                299.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.60 usec
PL1               -3.00 dB
PL1W        16.03799057 W
SFO1        400.1100000 MHz

F2 - Processing parameters
SI                 65536
SF          400.1100000 MHz
WDW                   EM
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```

* C_6D_6

Figure S70. ^{1}H NMR of compound **7**.

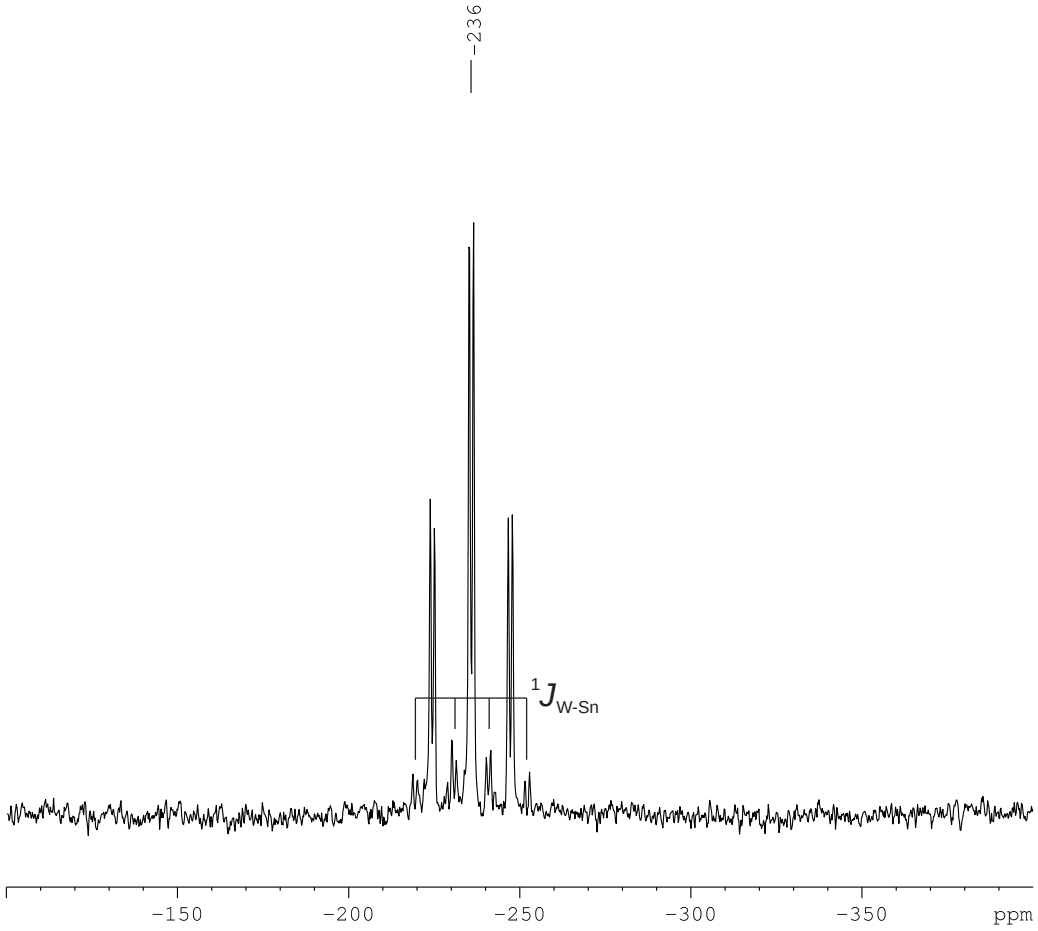
$^{13}C\{^{1}H\}$ NMR (C_6D_6, rt) of [$Cp_2W(H)$-SnH_2Ar^*] (**7**)




```
Current Data Parameters
NAME       MW1069_400NM
EXPNO                13
PROCNO                1

F2 - Acquisition Parameters
Date_          20210509
Time               2.26
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG           udeft
TD                22218
SOLVENT            C6D6
NS                 6144
DS                    0
SWH           30864.197 Hz
FIDRES         1.389153 Hz
AQ            0.3599316 sec
RG                32800
DW               16.200 usec
DE                6.00 usec
TE               299.2 K
D1            3.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
D20         100.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                 13.50 usec
P13              2000.00 usec
P26               500.00 usec
PL1                -4.16 dB
PL1W         78.55633545 W
SFO1        100.6198135 MHz
SP8                1.39 dB
SP13               1.39 dB
SPNAM[8] Crp60,0.5,20.1
SPNAM[13    Crp60comp.4
SPOAL8             0.500
SPOAL13            0.500
SPOFFS8  0 Hz
SPOFFS13 0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               11.77 dB
PL2W         16.03799057 W
PL12W         0.53474891 W
SFO2        400.1120007 MHz

F2 - Processing parameters
SI                131072
SF           100.6077400 MHz
WDW                  EM
SSB      0
LB                 2.00 Hz
GB       0
PC                 1.40
```

Figure S71. $^{13}C\{^{1}H\}$ NMR of compound **7**.

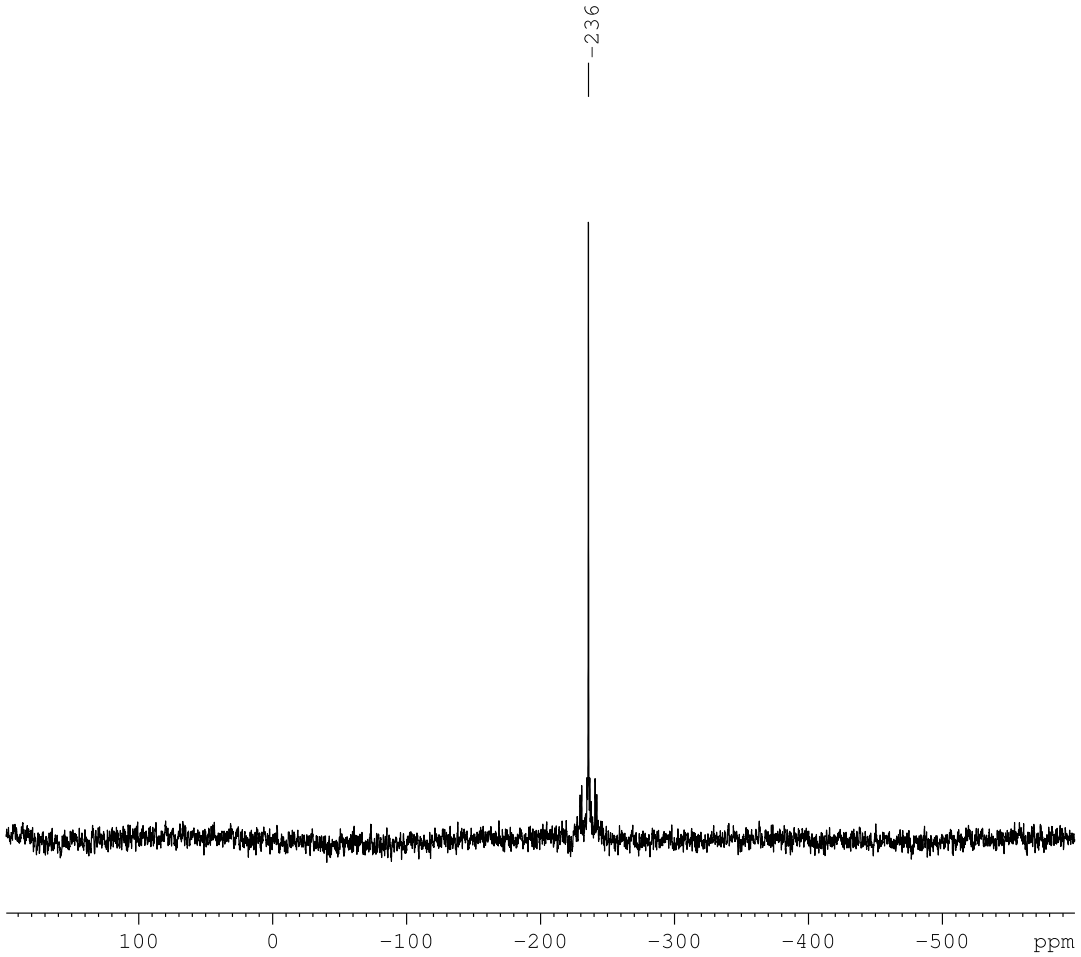
^{119}Sn NMR (C_6D_6, rt) of [$Cp_2W(H)$-SnH_2Ar^*] (**7**)




```
Current Data Parameters
NAME       MW1069_300NM
EXPNO                 14
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210510
Time              22.41 h
INSTRUM            spect
PROBHD   Z104275_0338 (
PULPROG             zg30
TD                  8918
SOLVENT             C6D6
NS                204800
DS                     1
SWH            89285.711 Hz
FIDRES         20.023708 Hz
AQ             0.0499408 sec
RG                204.67
DW                 5.600 usec
DE                 6.50 usec
TE                298.0 K
D1           0.02000000 sec
TD0                    1
SFO1        111.8979900 MHz
NUC1               119Sn
P0                 4.03 usec
P1                12.10 usec
PLW1        12.00000000 W

F2 - Processing parameters
SI                  4096
SF           111.9203740 MHz
WDW                 EM
SSB       0
LB                30.00 Hz
GB        0
PC                 1.40
```

Figure S72. ^{119}Sn NMR of compound **7**.

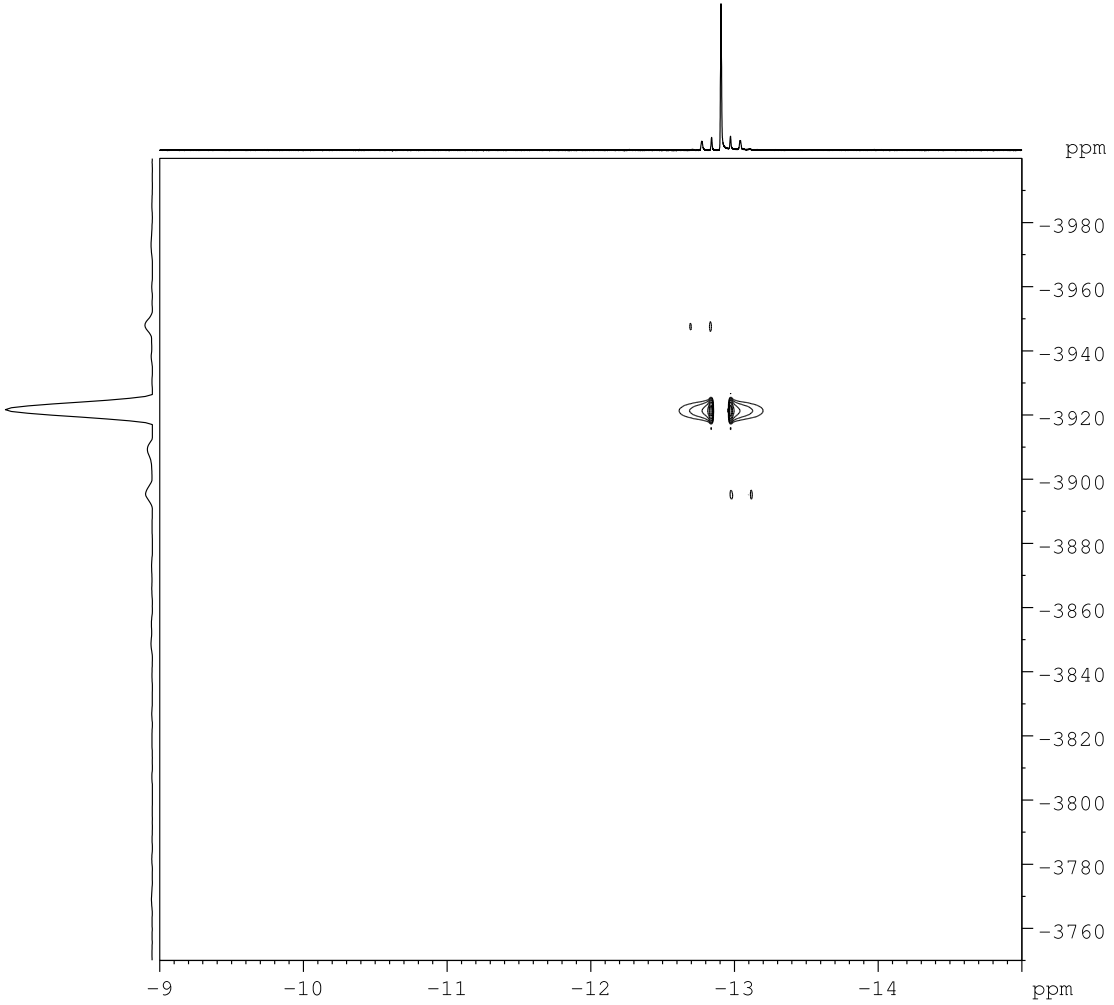
$^{119}Sn\{^{1}H\}$ NMR (C_6D_6, rt) of [$Cp_2W(H)$-SnH_2Ar^*] (**7**)




```
Current Data Parameters
NAME       MW1069_300NM
EXPNO                18
PROCNO                1

F2 - Acquisition Parameters
Date_          20210511
Time               3.08 h
INSTRUM            spect
PROBHD   Z104275_0338 (
PULPROG          zgig30
TD                39186
SOLVENT            C6D6
NS                35328
DS                    4
SWH           89285.711 Hz
FIDRES         4.557021 Hz
AQ            0.2194416 sec
RG               204.67
DW                5.600 usec
DE                6.50 usec
TE               298.0 K
D1           0.10000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        111.8979898 MHz
NUC1              119Sn
P0                4.03 usec
P1               12.10 usec
PLW1        12.00000000 W
SFO2        300.1312005 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2             90.00 usec
PLW2         8.26509953 W
PLW12        0.20000000 W

F2 - Processing parameters
SI                65536
SF          111.9203738 MHz
WDW                  EM
SSB       0
LB                25.00 Hz
GB        0
PC                 1.40
```

Figure S73. $^{119}Sn\{^{1}H\}$ NMR of compound **7**.

$^{1}H,^{183}W$ HMQC NMR (C_6D_6, rt) of [$Cp_2W(H)$-SnH_2Ar^*] (**7**)

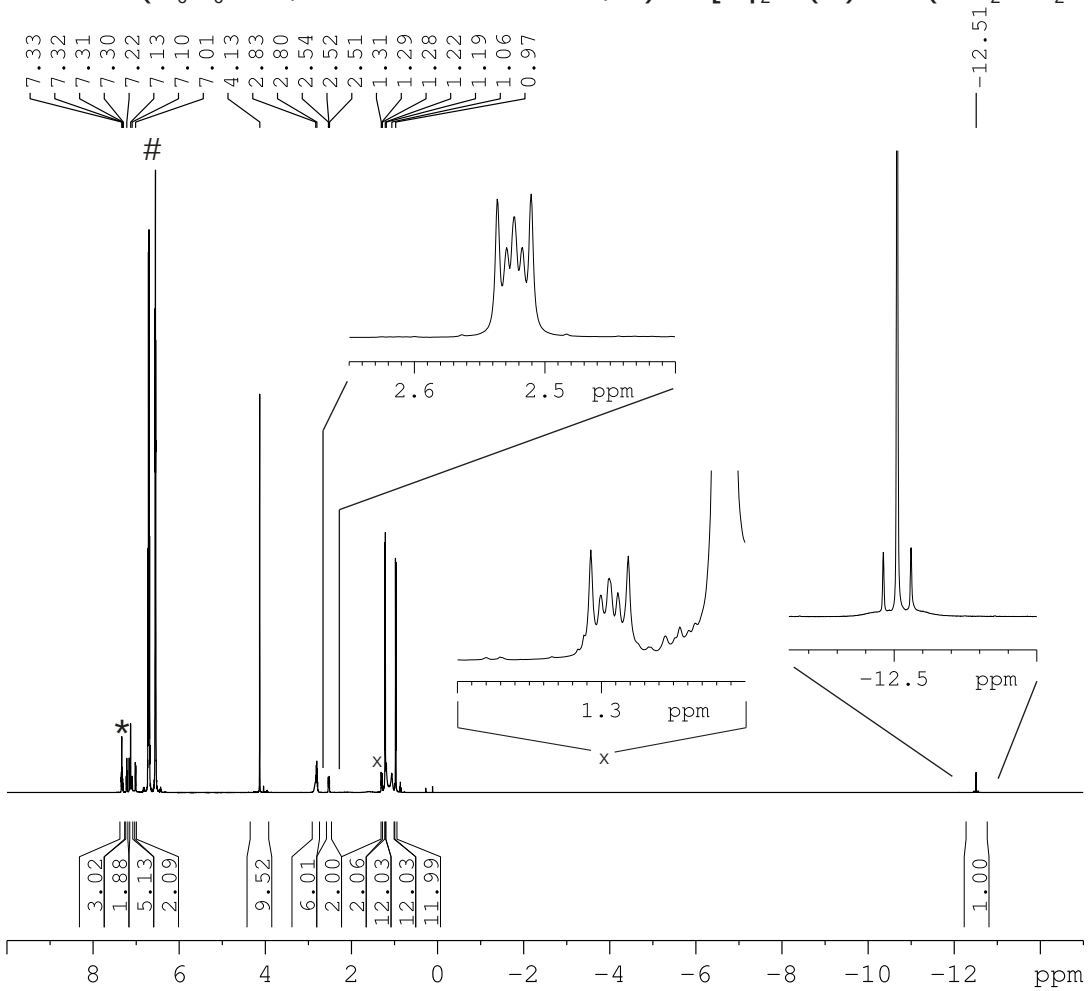



```
Current Data Parameters
NAME       MW1069_500_W
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20210514
Time              12.30
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           hmqcph
TD                  1024
SOLVENT             C6D6
NS                    12
DS                    16
SWH             3001.200 Hz
FIDRES          2.930860 Hz
AQ              0.1705984 sec
RG                 90.5
DW               166.600 usec
DE                 6.00 usec
TE                299.2 K
CNST2          66.0000000
D0             0.00000300 sec
D1             2.00000000 sec
D2             0.00757576 sec
D11            0.03000000 sec
D13            0.00000400 sec
IN0            0.00004015 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                12.50 usec
P2                25.00 usec
PL1       0 dB
PL1W         21.60222244 W
SFO1         500.1239984 MHz

======== CHANNEL f2 ========
CPDPRG[2              garp
NUC2                  183W
P3                 28.00 usec
PCPD2             400.00 usec
PL2       0 dB
PL12              23.10 dB
SFO2          20.7581691 MHz

F1 - Acquisition parameters
TD                   256
SFO1            20.75817 MHz
FIDRES          97.303917 Hz
SW                600.000 ppm
FnMODE       States-TPPI

F2 - Processing parameters
SI                   1024
SF           500.1300000 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
PC                   1.00

F1 - Processing parameters
SI                   1024
MC2          States-TPPI
SF            20.8373510 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
```

Figure S74. ^{1}H, ^{183}W HMQC NMR of compound **7**.

Compound **8**

^{1}H NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2W(H)=Sn(CH_2CH_2Ph)Ar^*][Al(O^tBu^F)_4]$ (**8**)



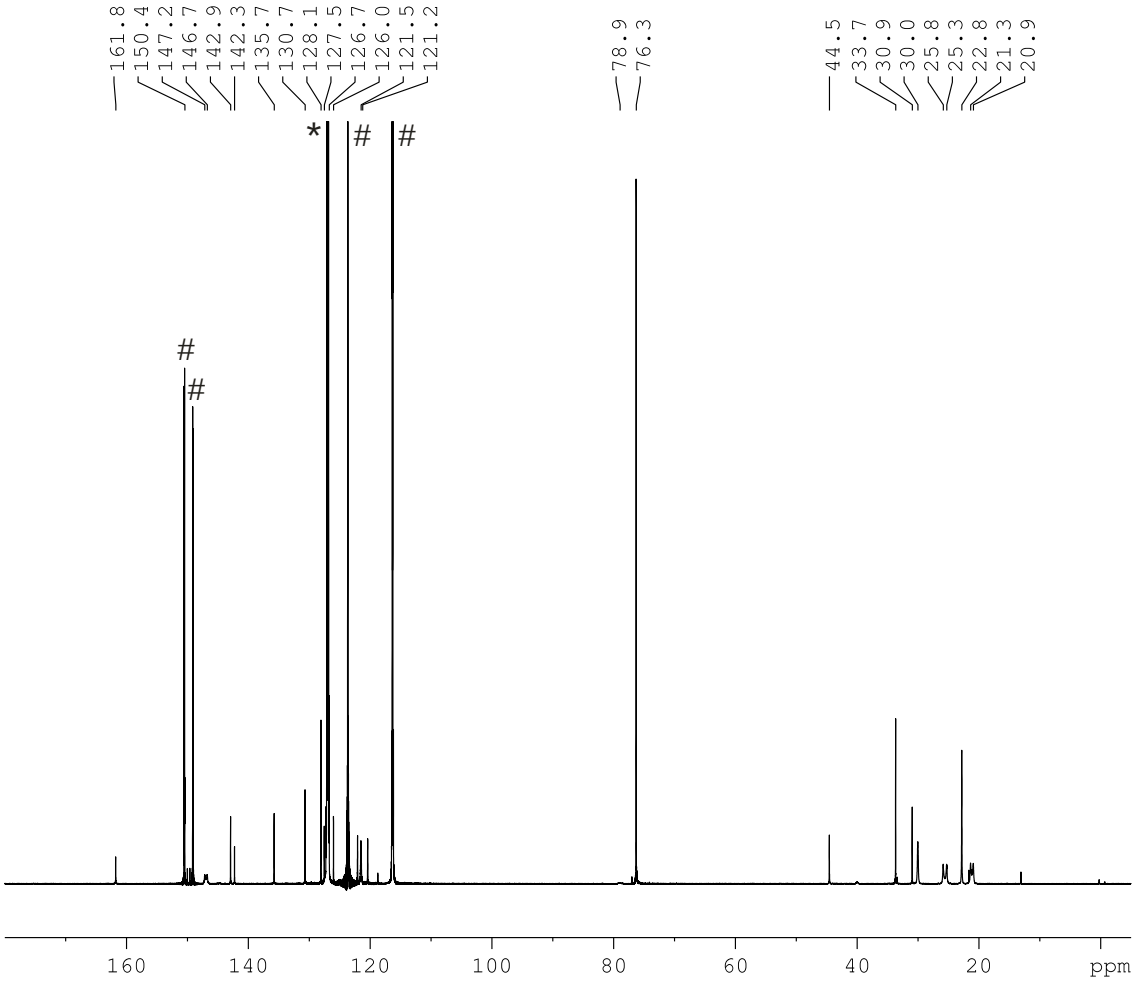

```
Current Data Parameters
NAME        MW1023_700NM
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210324
Time              11.12 h
INSTRUM            spect
PROBHD   Z135421_0007 (
PULPROG             zg30
TD                 65536
SOLVENT             C6D6
NS                    64
DS                     2
SWH            27777.777 Hz
FIDRES          0.847710 Hz
AQ              1.1796480 sec
RG                  5.49
DW                 18.000 usec
DE                 10.00 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1
SFO1         700.2900000 MHz
NUC1                  1H
P1                  8.00 usec
PLW1         14.67599964 W

F2 - Processing parameters
SI                 65536
SF           700.2899935 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

* C_6D_6

\# 1,2-$C_6H_4F_2$

Figure S75. ^{1}H NMR of compound **8**.

$^{13}C\{^{1}H\}$ NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2W(H)=Sn(CH_2CH_2Ph)Ar^*][Al(O^tBu^F)_4]$ (**8**)

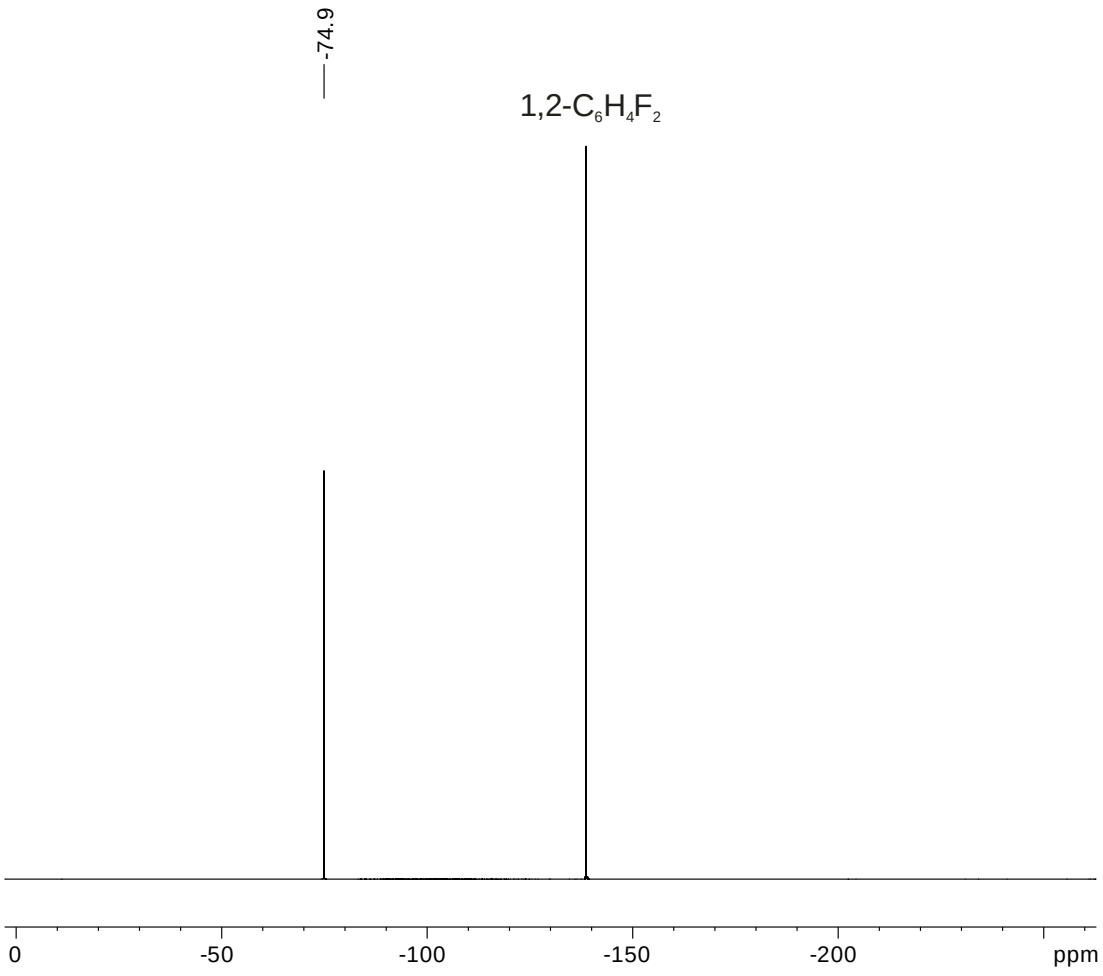



```
Current Data Parameters
NAME       MW1023_700NM
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20210324
Time               19.32 h
INSTRUM            spect
PROBHD   Z135421_0007 (
PULPROG            udeft
TD                 30496
SOLVENT             C6D6
NS                  6144
DS                     0
SWH            42613.637 Hz
FIDRES          2.794703 Hz
AQ             0.3578197 sec
RG                179.42
DW                11.733 usec
DE                18.00 usec
TE                298.0 K
D1             4.00000000 sec
D12            0.00002000 sec
D20          200.00000000 sec
TD0                    1
SFO1         176.1056694 MHz
NUC1                13C
P1                 12.00 usec
P13              2000.00 usec
P26               500.00 usec
PLW1         146.39999390 W
SPNAM[5]     Crp80comp.4
SPOAL5               0.500
SPOFFS5  0 Hz
SPW5          42.94699860 W
SPNAM[8] Crp80,0.5,20.1
SPOAL8               0.500
SPOFFS8  0 Hz
SPW8          42.94699860 W
SFO2         700.2928012 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2              65.00 usec
PLW2         14.67599964 W
PLW12         0.22231001 W

F2 - Processing parameters
SI                131072
SF           176.0881798 MHz
WDW                 EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 1.40
```

* C_6D_6
\# 1,2-$C_6H_4F_2$

Figure S76. $^{13}C\{^{1}H\}$ NMR of compound **8**.

$^{19}F\{^{1}H\}$ NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2W(H)=Sn(CH_2CH_2Ph)Ar^*][Al(O^tBu^F)_4]$ (**8**)



Current Data Parameters
NAME MW1023_400
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210325
Time 17.09
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgfhigqn
TD 131072
SOLVENT C6D6
NS 256
DS 0
SWH 100000.000 Hz
FIDRES 0.762939 Hz
AQ 0.6553600 sec
RG 4100
DW 5.000 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
TD0 1

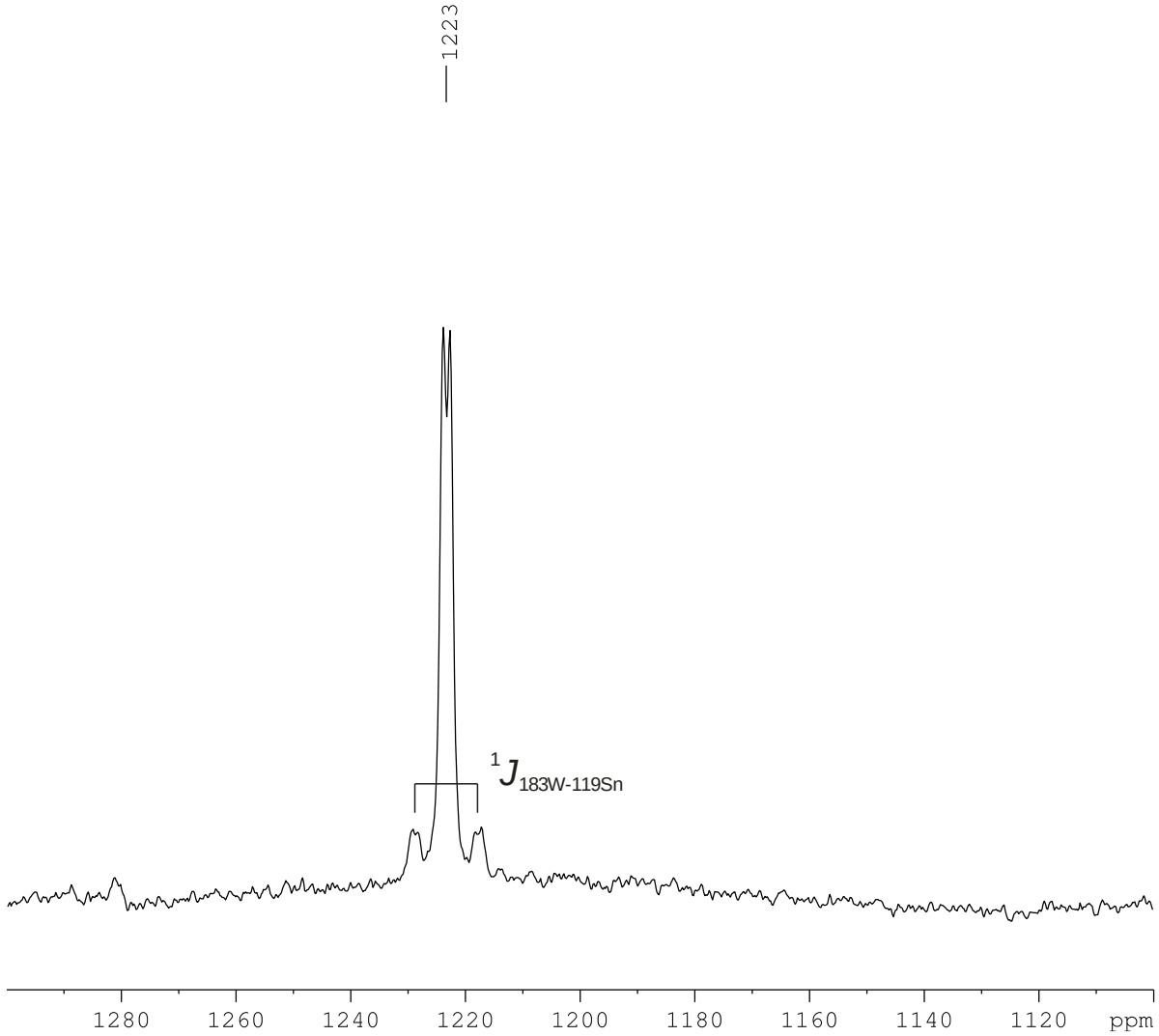
======== CHANNEL f1 ========
NUC1 19F
P1 18.75 usec
PL1 -2.92 dB
PL1W 30.50645256 W
SFO1 376.4306030 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 11.77 dB
PL2W 16.03799057 W
PL12W 0.53474891 W
SFO2 400.1120007 MHz

F2 - Processing parameters
SI 262144
SF 376.4795470 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

Figure S77. $^{19}F\{^{1}H\}$ NMR of compound **8**.

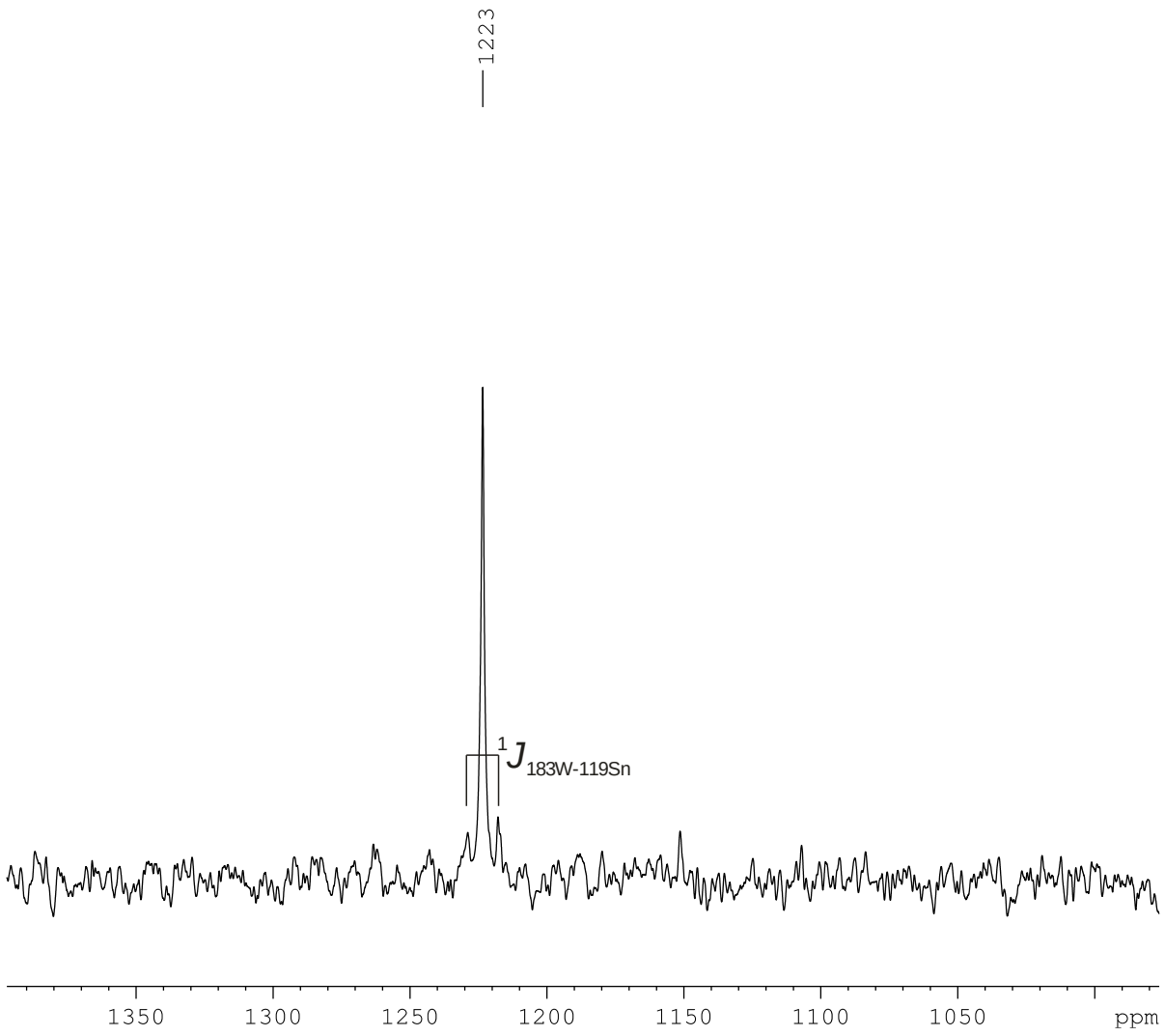
^{119}Sn NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2W(H)=Sn(CH_2CH_2Ph)Ar^*][Al(O^tBu^F)_4]$ (**8**)




```
Current Data Parameters
NAME      MW1023_300_NM
EXPNO                36
PROCNO                1

F2 - Acquisition Parameters
Date_          20210323
Time              22.27 h
INSTRUM           spect
PROBHD   Z104275_0338 (
PULPROG           zg30
TD                8918
SOLVENT           C6D6
NS              327680
DS                   1
SWH           89285.711 Hz
FIDRES        20.023708 Hz
AQ            0.0499408 sec
RG               204.67
DW                5.600 usec
DE                6.50 usec
TE               298.0 K
D1           0.02000000 sec
TD0                  1
SFO1        112.0546780 MHz
NUC1              119Sn
P0                4.03 usec
P1               12.10 usec
PLW1        12.00000000 W

F2 - Processing parameters
SI                4096
SF          111.9203740 MHz
WDW                EM
SSB      0
LB               50.00 Hz
GB       0
PC                1.40
```

Figure S78. ^{119}Sn NMR of compound **8**.

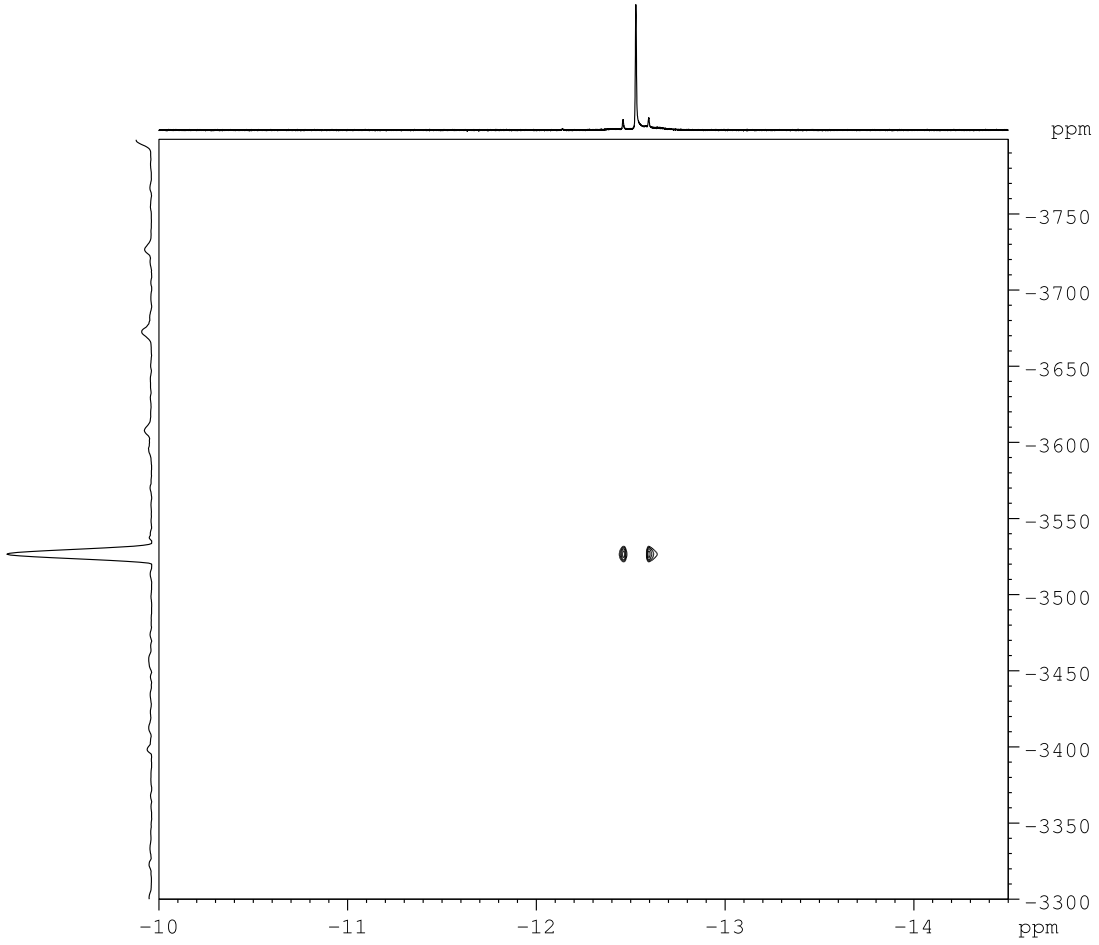
$^{119}Sn\{^{1}H\}$ NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2W(H)=Sn(CH_2CH_2Ph)Ar^*][Al(O^tBu^F)_4]$ (**8**)




```
Current Data Parameters
NAME      MW1023_300_NM
EXPNO                22
PROCNO                1

F2 - Acquisition Parameters
Date_          20210323
Time              11.23 h
INSTRUM            spect
PROBHD   Z104275_0338 (
PULPROG          zgig30
TD                39186
SOLVENT             C6D6
NS                  9000
DS                     4
SWH            89285.711 Hz
FIDRES          4.557021 Hz
AQ             0.2194416 sec
RG                204.67
DW                 5.600 usec
DE                 6.50 usec
TE                298.0 K
D1            0.10000000 sec
D11           0.03000000 sec
TD0                    1
SFO1         112.0546778 MHz
NUC1               119Sn
P0                 4.03 usec
P1                12.10 usec
PLW1         12.00000000 W
SFO2         300.1312005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2          8.26509953 W
PLW12         0.20000000 W

F2 - Processing parameters
SI                 65536
SF           111.9203738 MHz
WDW                   EM
SSB       0
LB              100.00 Hz
GB        0
PC                 1.40
```

Figure S79. $^{119}Sn\{^{1}H\}$ NMR of compound **8**.

$^{1}H,^{183}W$ HMQC NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[Cp_2W(H)=Sn(CH_2CH_2Ph)Ar^*][Al(O^tBu^F)_4]$ (**8**)

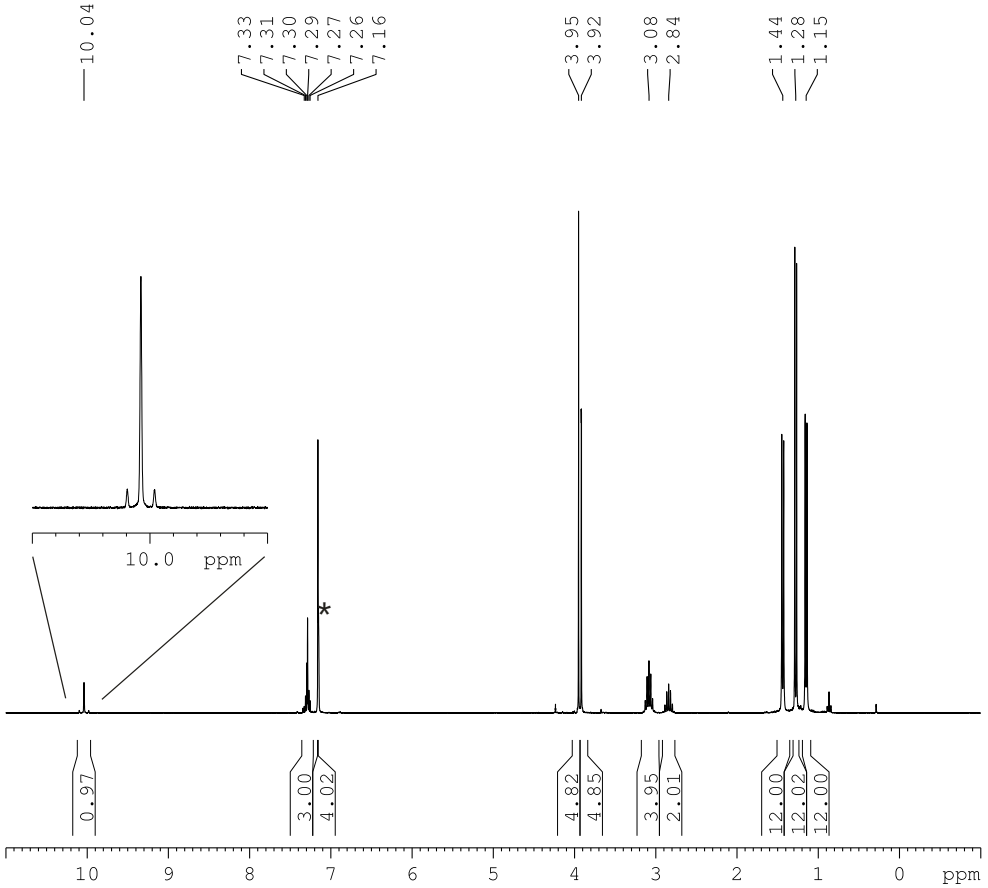



```
Current Data Parameters
NAME       MW1023_500_W
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20210330
Time               8.52
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         hmqcph
TD                1024
SOLVENT           C6D6
NS                   8
DS                  16
SWH           2500.000 Hz
FIDRES        2.441406 Hz
AQ           0.2048000 sec
RG                  57
DW             200.000 usec
DE               6.00 usec
TE              299.3 K
CNST2        68.0000000
D0          0.00000300 sec
D1          2.00000000 sec
D2          0.00735294 sec
D11         0.03000000 sec
D13         0.00000400 sec
IN0         0.00004015 sec

======== CHANNEL f1 ========
NUC1                1H
P1               12.50 usec
P2               25.00 usec
PL1       0 dB
PL1W       21.60222244 W
SFO1      500.1239984 MHz

======== CHANNEL f2 ========
CPDPRG[2            garp
NUC2               183W
P3               28.00 usec
PCPD2           400.00 usec
PL2       0 dB
PL12             23.10 dB
SFO2       20.7644203 MHz

F1 - Acquisition parameters
TD                  185
SFO1          20.76442 MHz
FIDRES      134.688126 Hz
SW             600.000 ppm
FnMODE      States-TPPI

F2 - Processing parameters
SI                 1024
SF          500.1300000 MHz
WDW                QSINE
SSB                    2
LB        0 Hz
GB        0
PC                  1.00

F1 - Processing parameters
SI                 1024
MC2         States-TPPI
SF          20.8373510 MHz
WDW                QSINE
SSB                    2
LB        0 Hz
GB        0
```

Figure S80. ^{1}H, ^{183}W HMQC NMR of compound **8**.

Compound **9**

^{1}H NMR (C_6D_6, rt) of [Cp_2W=Ge(H)Ar*] (**9**)

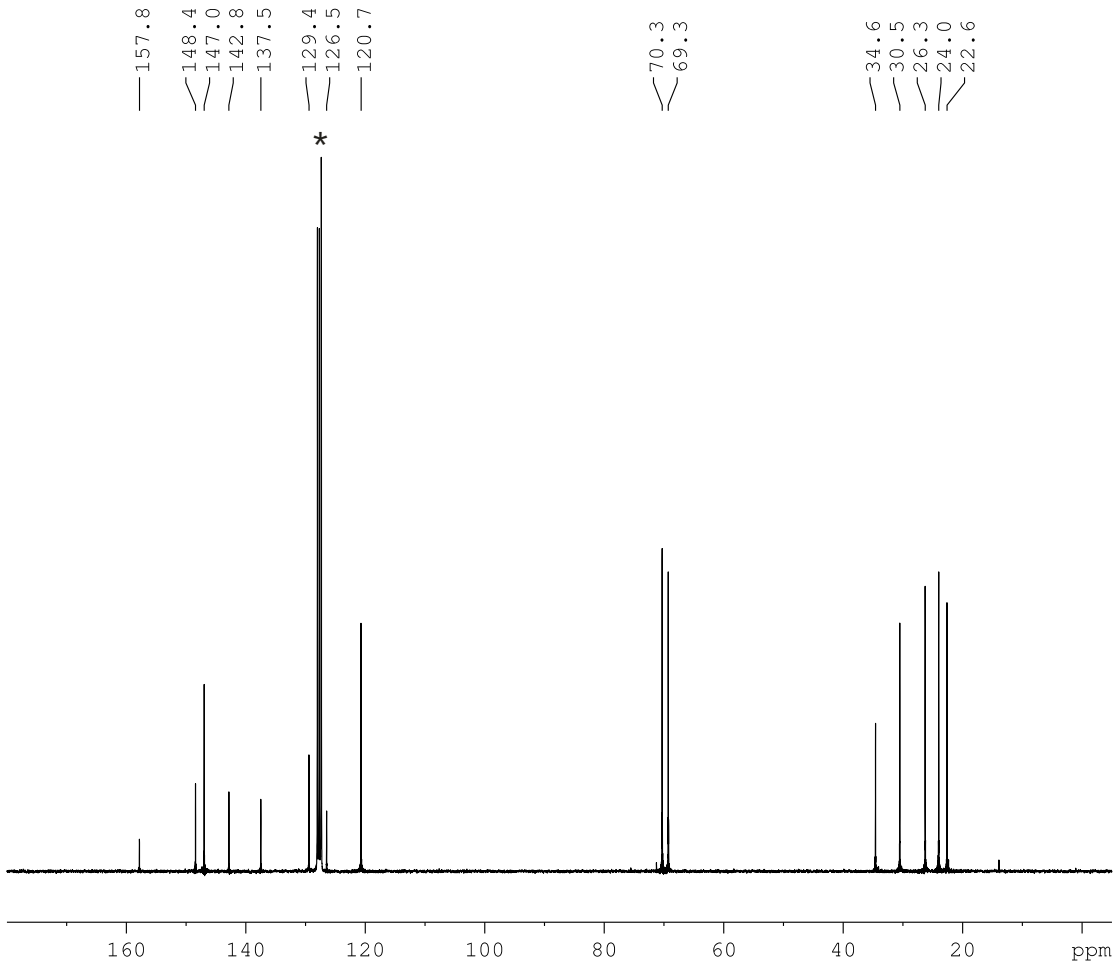



```
Current Data Parameters
NAME        MW1001_300NM
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210225
Time              19.06 h
INSTRUM             spect
PROBHD   Z104275_0338 (
PULPROG             zg30
TD                 38044
SOLVENT             C6D6
NS                    16
DS                     0
SWH             6009.615 Hz
FIDRES          0.315930 Hz
AQ              3.1652608 sec
RG                 204.67
DW                 83.200 usec
DE                  6.50 usec
TE                 298.0 K
D1            1.00000000 sec
TD0                    1
SFO1         300.1318533 MHz
NUC1                  1H
P0                  4.67 usec
P1                 14.00 usec
PLW1          8.26509953 W

F2 - Processing parameters
SI                 32768
SF           300.1300000 MHz
WDW                   EM
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```

* C_6D_6

Figure S81. ^{1}H NMR of compound **9**.

$^{13}C\{^{1}H\}$ NMR (C_6D_6, rt) of [Cp_2W=Ge(H)Ar*] (**9**)

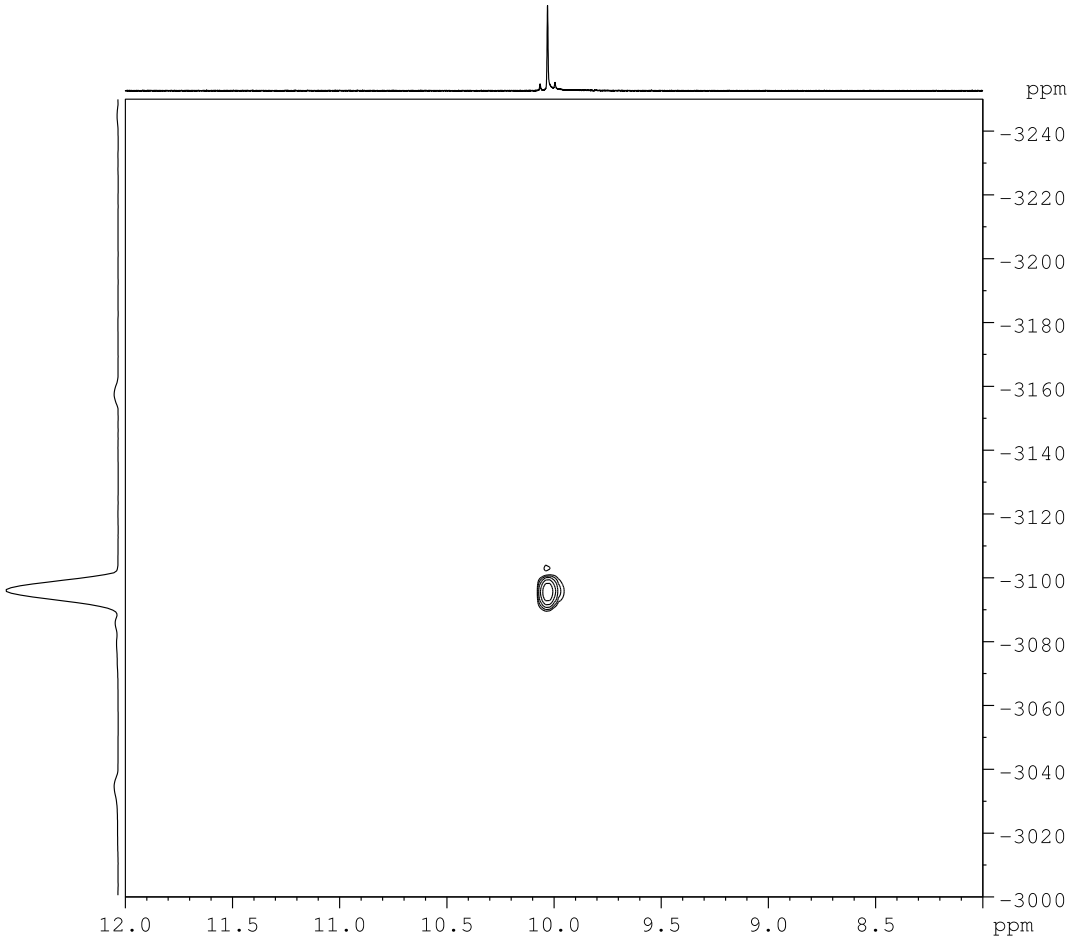



```
Current Data Parameters
NAME       MW1001_300NM
EXPNO                12
PROCNO                1

F2 - Acquisition Parameters
Date_          20210226
Time               1.04 h
INSTRUM           spect
PROBHD   Z104275_0338 (
PULPROG          udeft
TD               13040
SOLVENT           C6D6
NS                4500
DS                   4
SWH           18115.941 Hz
FIDRES         2.778519 Hz
AQ            0.3599040 sec
RG               204.67
DW               27.600 usec
DE                6.50 usec
TE               298.0 K
D1           4.00000000 sec
D12          0.00002000 sec
D20         20.00000000 sec
TD0                  1
SFO1          75.4752953 MHz
NUC1                13C
P1                10.00 usec
P13             2000.00 usec
P26              500.00 usec
PLW1        33.55099869 W
SPNAM[5]    Crp60comp.4
SPOAL5            0.500
SPOFFS5  0 Hz
SPW5         5.12620020 W
SPNAM[8] Crp60,0.5,20.1
SPOAL8            0.500
SPOFFS8  0 Hz
SPW8         5.12620020 W
SFO2        300.1312005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2         8.26509953 W
PLW12        0.20000000 W

F2 - Processing parameters
SI                32768
SF            75.4677485 MHz
WDW                  EM
SSB      0
LB                1.00 Hz
GB       0
PC                1.40
```

* C_6D_6

Figure S82. $^{13}C\{^{1}H\}$ NMR of compound **9**.

$^{1}H,^{183}W$ HSQC NMR (C_6D_6, rt) of [Cp_2W=Ge(H)Ar*] (**9**)

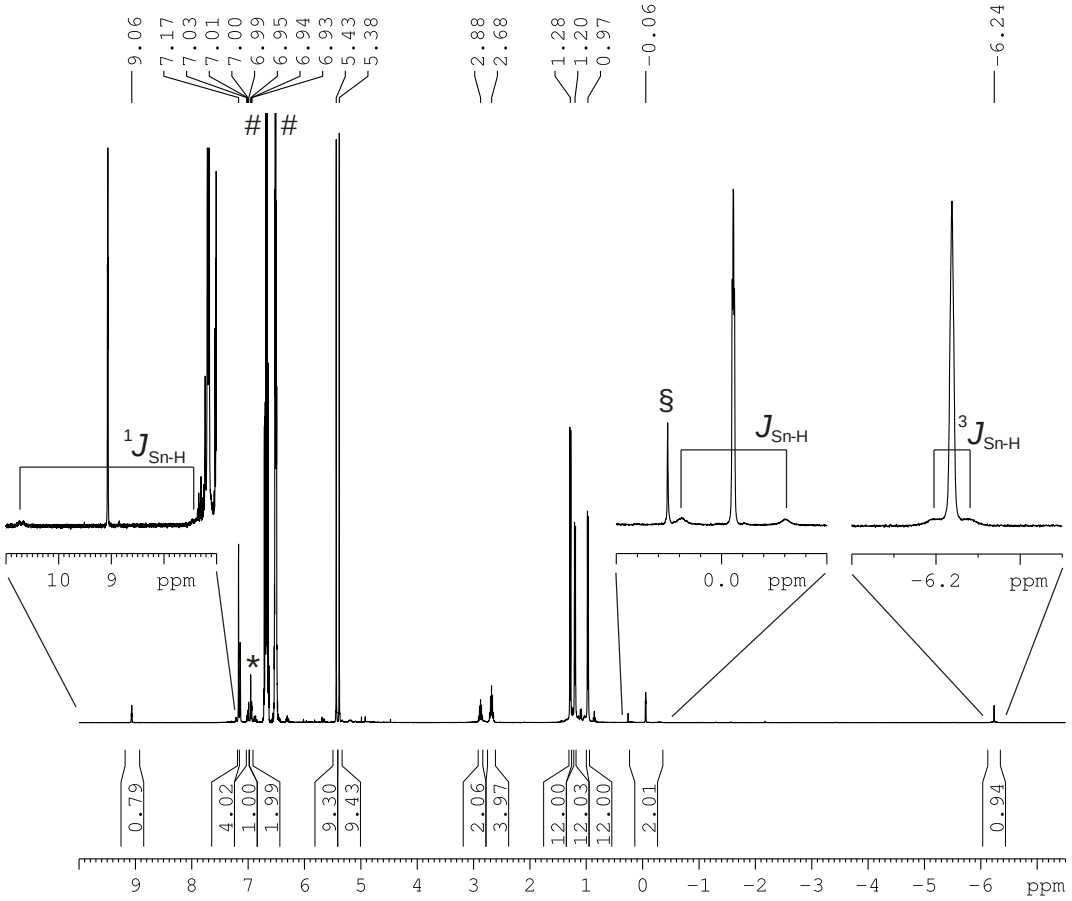



```
Current Data Parameters
NAME         MW1001_500W
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210302
Time               15.16
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG  hsqcetgpsi2.tue
TD                 1024
SOLVENT             C6D6
NS                    2
DS                   16
SWH           10000.000 Hz
FIDRES         9.765625 Hz
AQ            0.0512000 sec
RG                 2050
DW               50.000 usec
DE                6.00 usec
TE                299.3 K
CNST2         34.0000000
D0            0.00000300 sec
D1            1.50000000 sec
D4            0.00735294 sec
D11           0.03000000 sec
D13           0.00000400 sec
D16           0.00020000 sec
D24           0.00367647 sec
IN0           0.00004010 sec
ZGOPTNS

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.50 usec
P2                  25.00 usec
P28               1000.00 usec
PL1       0 dB
PL1W        21.60222244 W
SFO1         500.1325007 MHz

======== CHANNEL f2 ========
CPDPRG[2               garp
NUC2                 183W
P3                  28.00 usec
P4                  56.00 usec
PCPD2              400.00 usec
PL2       0 dB
PL12                23.10 dB
SFO2          20.7706715 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]         SINE.100
GPNAM[2]         SINE.100
GPNAM[3]         SINE.100
GPNAM[4]         SINE.100
GPZ1                80.00 %
GPZ2                 3.30 %
GPZ3                11.00 %
GPZ4                -5.00 %
P16               1000.00 usec
P19                600.00 usec

F1 - Acquisition parameters
TD                    256
SFO1            20.77067 MHz
FIDRES         97.362526 Hz
SW               600.000 ppm
FnMODE    Echo-Antiecho

F2 - Processing parameters
SI                   1024
SF           500.1300000 MHz
WDW                  QSINE
SSB                     2
LB        0 Hz
GB        0
PC                   1.40

F1 - Processing parameters
SI                   1024
MC2        echo-antiecho
SF           20.8373510 MHz
WDW                  QSINE
SSB                     2
LB        0 Hz
GB        0
```

Figure S83. ^{1}H, ^{183}W HMQC NMR of compound **9**.

Compound **10**

^{1}H NMR (C_6D_6 + 1,2-difluorobenzene, rt) of [({Cp_2Zr}$_2$H)(μ-H)$_2$Sn(H)Ar*][Al(O^{t}Bu^F)$_4$] (**10**)

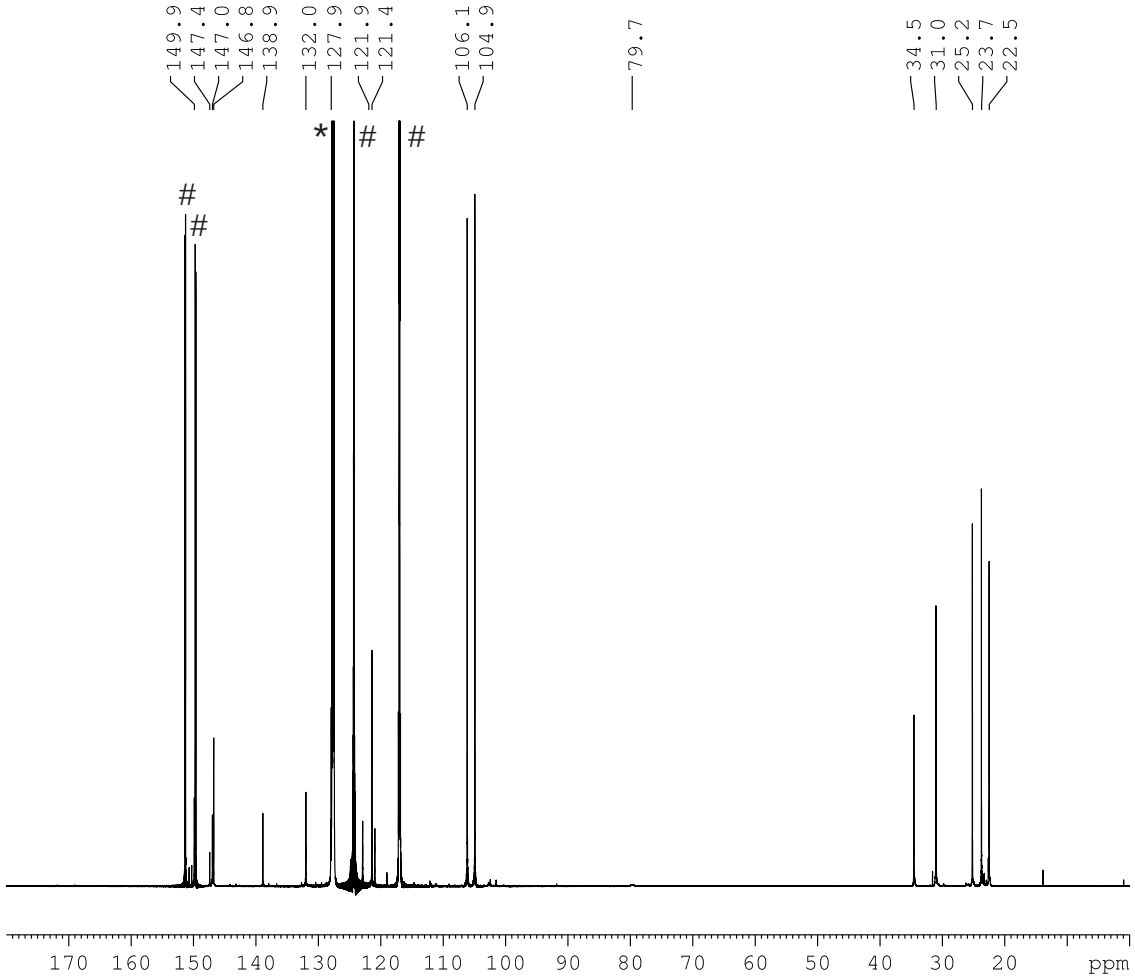



```
Current Data Parameters
NAME          MW814_400
EXPNO                50
PROCNO                1

F2 - Acquisition Parameters
Date_          20200922
Time              14.48
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG            zg30
TD                52656
SOLVENT            C6D6
NS                   64
DS                    0
SWH           16025.641 Hz
FIDRES         0.304346 Hz
AQ            1.6428672 sec
RG                  101
DW               31.200 usec
DE                6.00 usec
TE               300.2 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.60 usec
PL1               -3.00 dB
PL1W        16.03799057 W
SFO1        400.1100000 MHz

F2 - Processing parameters
SI                65536
SF          400.1100000 MHz
WDW                  EM
SSB       0
LB        0 Hz
GB        0
PC                1.00
```

* C_6D_6
# 1,2-$C_6H_4F_2$
§ silicone grease

Figure S84. ^{1}H NMR of compound **10** {WCA = [Al(O^{t}Bu^F)$_4$]}.

$^{13}C\{^{1}H\}$ NMR (C_6D_6 + 1,2-difluorobenzene, rt) of [({Cp_2Zr}$_2$H)(μ-H)$_2$Sn(H)Ar*][Al(O^{t}Bu^F)$_4$] (**10**)

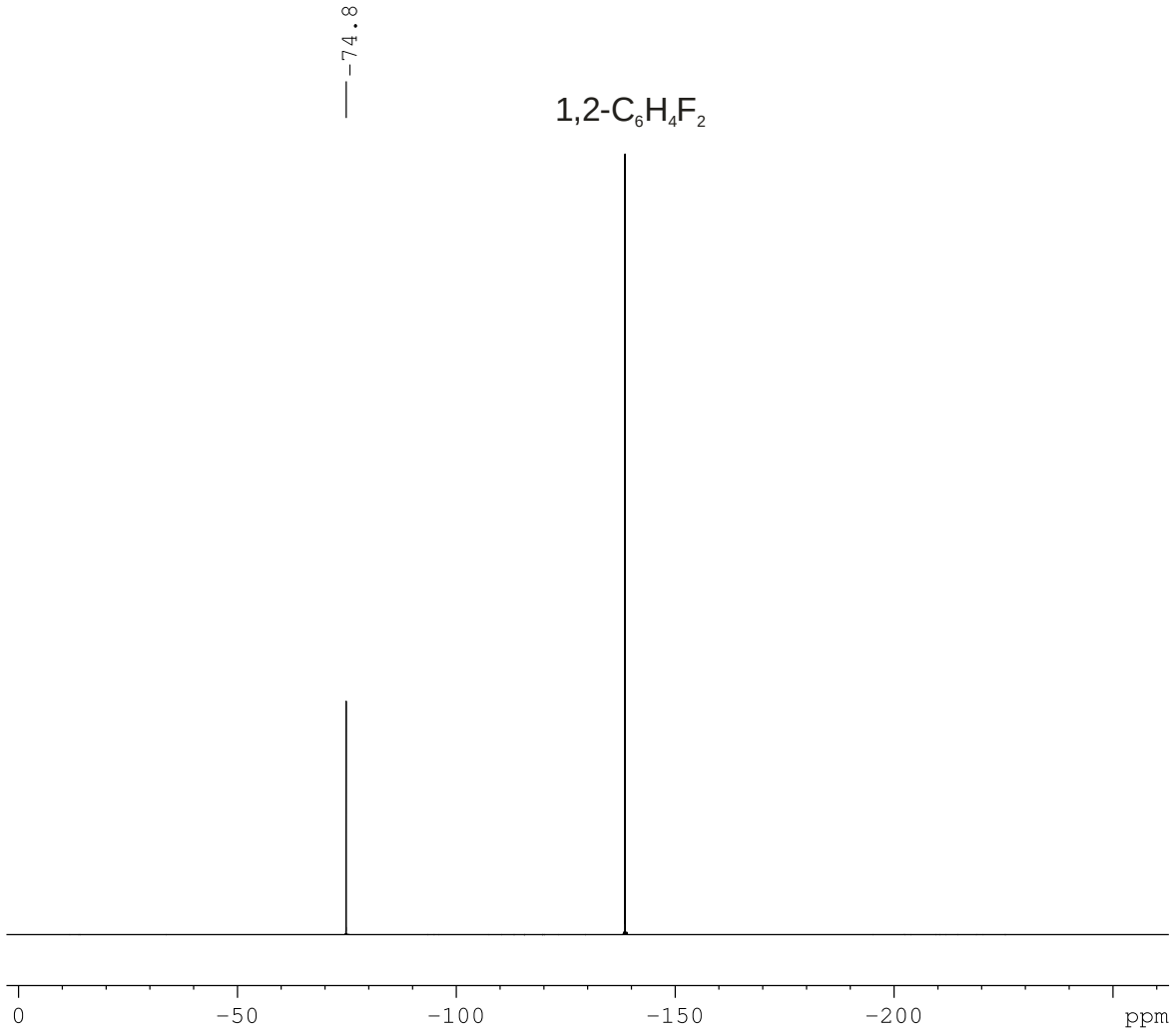



```
Current Data Parameters
NAME         MW814_600NM
EXPNO                 14
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200922
Time                7.43 h
INSTRUM            spect
PROBHD   Z126545_0027 (
PULPROG            udeft
TD                 25902
SOLVENT             C6D6
NS                  8192
DS                     8
SWH            36231.883 Hz
FIDRES          2.797613 Hz
AQ              0.3574476 sec
RG                 189.6
DW                13.800 usec
DE                18.00 usec
TE                298.0 K
D1             4.00000000 sec
D12            0.00002000 sec
D20           20.00000000 sec
TD0                    1
SFO1         150.9178988 MHz
NUC1                 13C
P1                10.00 usec
P13             2000.00 usec
P26              500.00 usec
PLW1         57.02700043 W
SPNAM[5]    Crp60comp.4
SPOAL5             0.500
SPOFFS5  0 Hz
SPW5          8.71310043 W
SPNAM[8] Crp60,0.5,20.1
SPOAL8             0.500
SPOFFS8  0 Hz
SPW8          8.71310043 W
SFO2         600.1324005 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             70.00 usec
PLW2         23.41200066 W
PLW12         0.68803000 W

F2 - Processing parameters
SI                131072
SF           150.9028085 MHz
WDW                  EM
SSB       0
LB                2.00 Hz
GB        0
PC                1.40
```

* C_6D_6
# 1,2-$C_6H_4F_2$

Figure S85. $^{13}C\{^{1}H\}$ NMR of compound **10** {WCA = [Al(O^{t}Bu^F)$_4$]}.

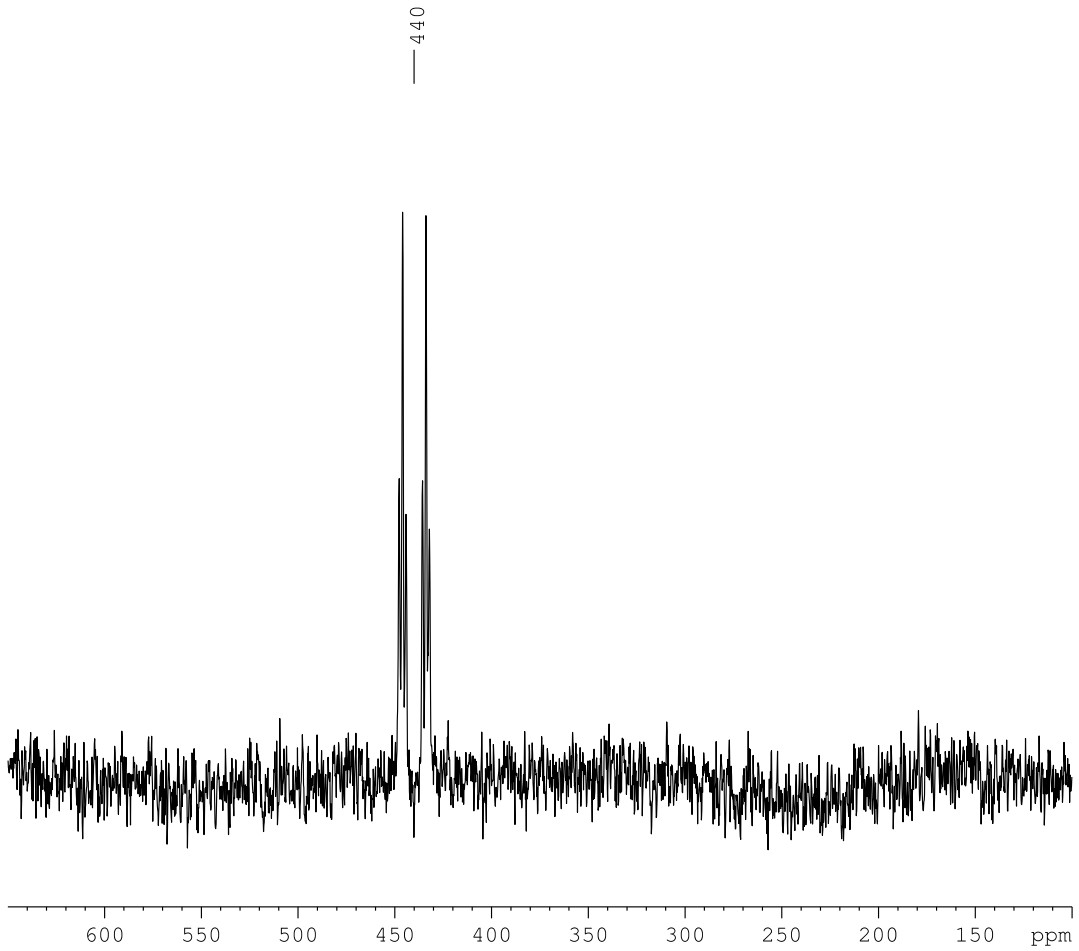
$^{19}F\{^{1}H\}$ NMR (C_6D_6 + 1,2-difluorobenzene, rt) of [({Cp_2Zr}$_2$H)(μ-H)$_2$Sn(H)Ar*][Al(O^{t}Bu^F)$_4$] (**10**)




```
Current Data Parameters
NAME          MW814_400
EXPNO                51
PROCNO                1

F2 - Acquisition Parameters
Date_          20200922
Time              14.56
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG         zgfhigqn
TD               131072
SOLVENT             C6D6
NS                   256
DS                     0
SWH           100000.000 Hz
FIDRES          0.762939 Hz
AQ             0.6553600 sec
RG                  4100
DW                 5.000 usec
DE                 6.00 usec
TE                300.2 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  19F
P1                 18.75 usec
PL1                -2.92 dB
PL1W         30.50645256 W
SFO1         376.4306030 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               11.77 dB
PL2W         16.03799057 W
PL12W         0.53474891 W
SFO2         400.1120007 MHz

F2 - Processing parameters
SI                262144
SF           376.4795470 MHz
WDW                   EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 1.00
```

Figure S86. $^{19}F\{^{1}H\}$ NMR of compound **10** {WCA = [Al(O^{t}Bu^F)$_4$]}.

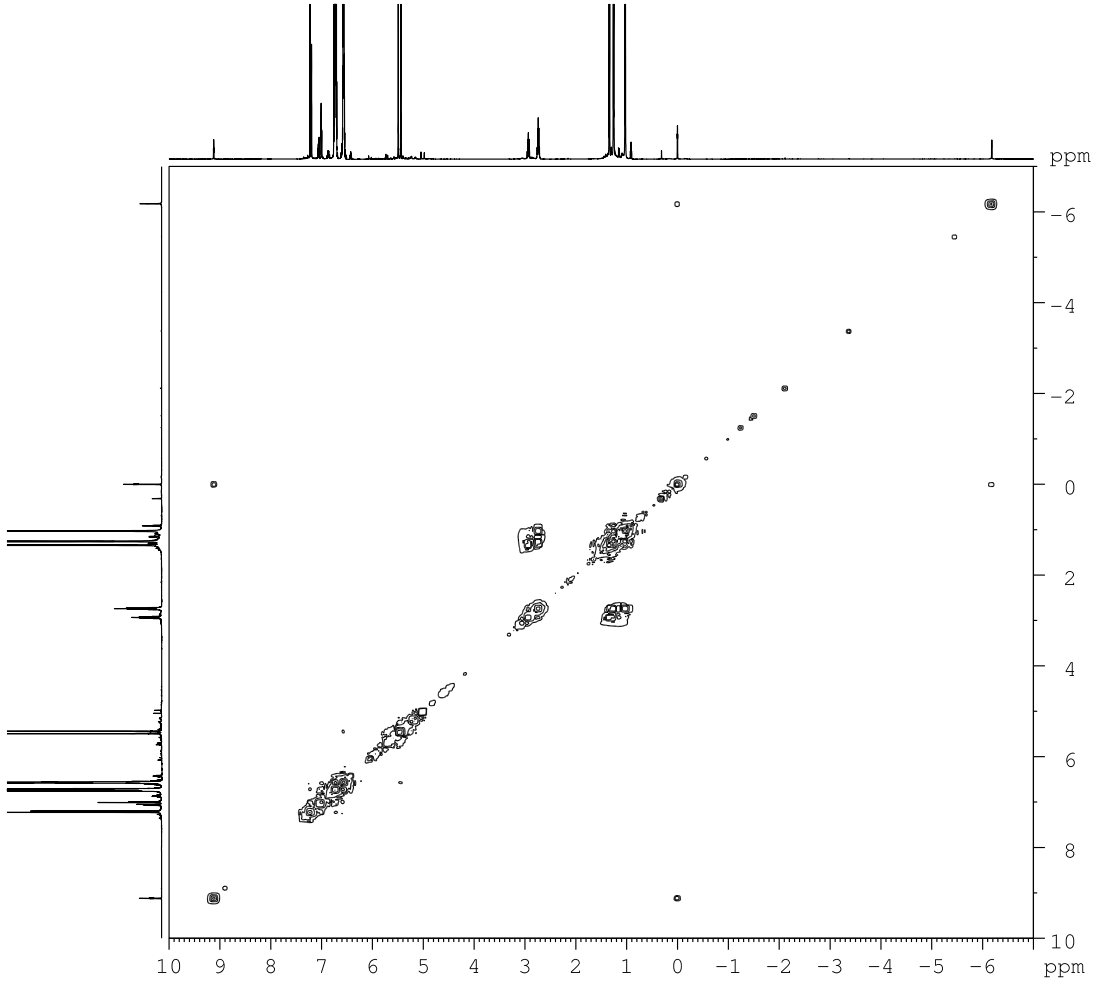
^{119}Sn NMR (C_6D_6 + 1,2-difluorobenzene, rt) of[({Cp_2Zr}$_2$H)(μ-H)$_2$Sn(H)Ar*][Al(O^{t}Bu^F)$_4$] (**10**)




```
Current Data Parameters
NAME         MW744_300Sn
EXPNO                 43
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200715
Time                1.25 h
INSTRUM            spect
PROBHD   Z104275_0338 (
PULPROG             zg30
TD                  8918
SOLVENT             C6D6
NS                 76800
DS                     1
SWH            89285.711 Hz
FIDRES         20.023708 Hz
AQ             0.0499408 sec
RG                204.67
DW                 5.600 usec
DE                 6.50 usec
TE                 298.0 K
D1            0.02000000 sec
TD0                    1
SFO1         111.9539501 MHz
NUC1               119Sn
P0                 4.03 usec
P1                12.10 usec
PLW1         12.00000000 W

F2 - Processing parameters
SI                  4096
SF           111.9203740 MHz
WDW                   EM
SSB       0
LB                25.00 Hz
GB        0
PC                 1.40
```

Figure S87. ^{119}Sn NMR of compound **10** {WCA = [Al(O^{t}Bu^F)$_4$]}.

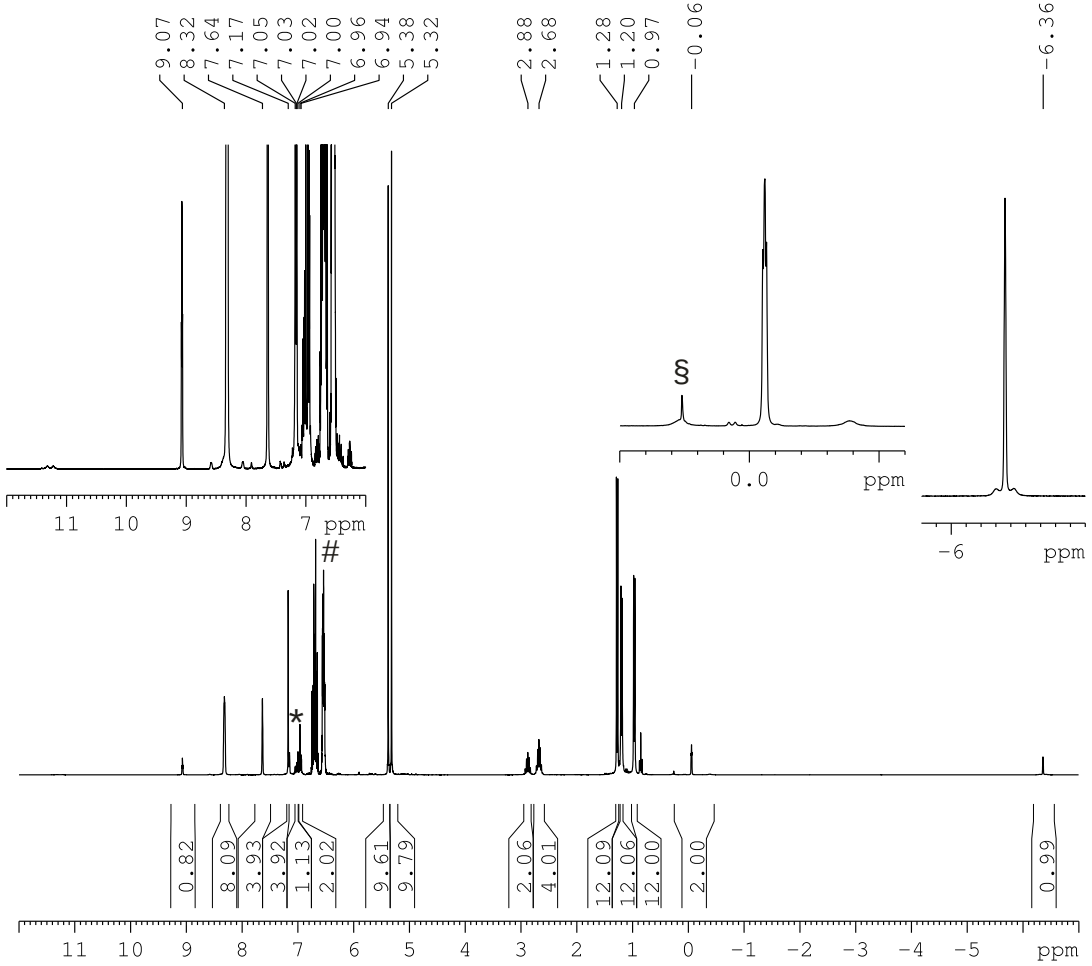
^{1}H,^{1}H COSY NMR (C_6D_6 + 1,2-difluorobenzene, rt) of [({Cp_2Zr}$_2$H)(μ-H)$_2$Sn(H)Ar*][Al(O^{t}Bu^F)$_4$] (**10**)




```
Current Data Parameters
NAME         MW814_600NM
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200921
Time              14.11 h
INSTRUM             spect
PROBHD   Z126545_0027 (
PULPROG       cosygpppqf
TD                  2048
SOLVENT             C6D6
NS                    16
DS                    16
SWH            14423.077 Hz
FIDRES         14.085036 Hz
AQ             0.0709973 sec
RG                 17.08
DW                34.667 usec
DE                10.00 usec
TE                298.0 K
D0            0.00000300 sec
D1            2.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
D13           0.00000400 sec
D16           0.00020000 sec
IN0           0.00006940 sec
TDav                   1
SFO1         600.1312003 MHz
NUC1                  1H
P0                12.00 usec
P1                12.00 usec
P17             2500.00 usec
PLW1         23.41200066 W
PLW10         5.39410019 W
GPNAM[1]      SMSQ10.100
GPZ1              10.00 %
P16             1000.00 usec

F1 - Acquisition parameters
TD                   128
SFO1            600.1312 MHz
FIDRES        225.144089 Hz
SW                24.010 ppm
FnMODE                QF

F2 - Processing parameters
SI                   1024
SF           600.1299695 MHz
WDW                 QSINE
SSB       0
LB        0 Hz
GB        0
PC                  1.40

F1 - Processing parameters
SI                   1024
MC2                   QF
SF           600.1299741 MHz
WDW                 QSINE
SSB       0
LB        0 Hz
GB        0
```

Figure S88. ^{1}H, ^{1}H COSY NMR of compound **10** {WCA = [Al(O^{t}Bu^F)$_4$]}.

^{1}H NMR (C_6D_6 + 1,2-difluorobenzene, rt) of [({Cp_2Zr}$_2$H)(μ-H)$_2$Sn(H)Ar*][BAr^F] (**10**)

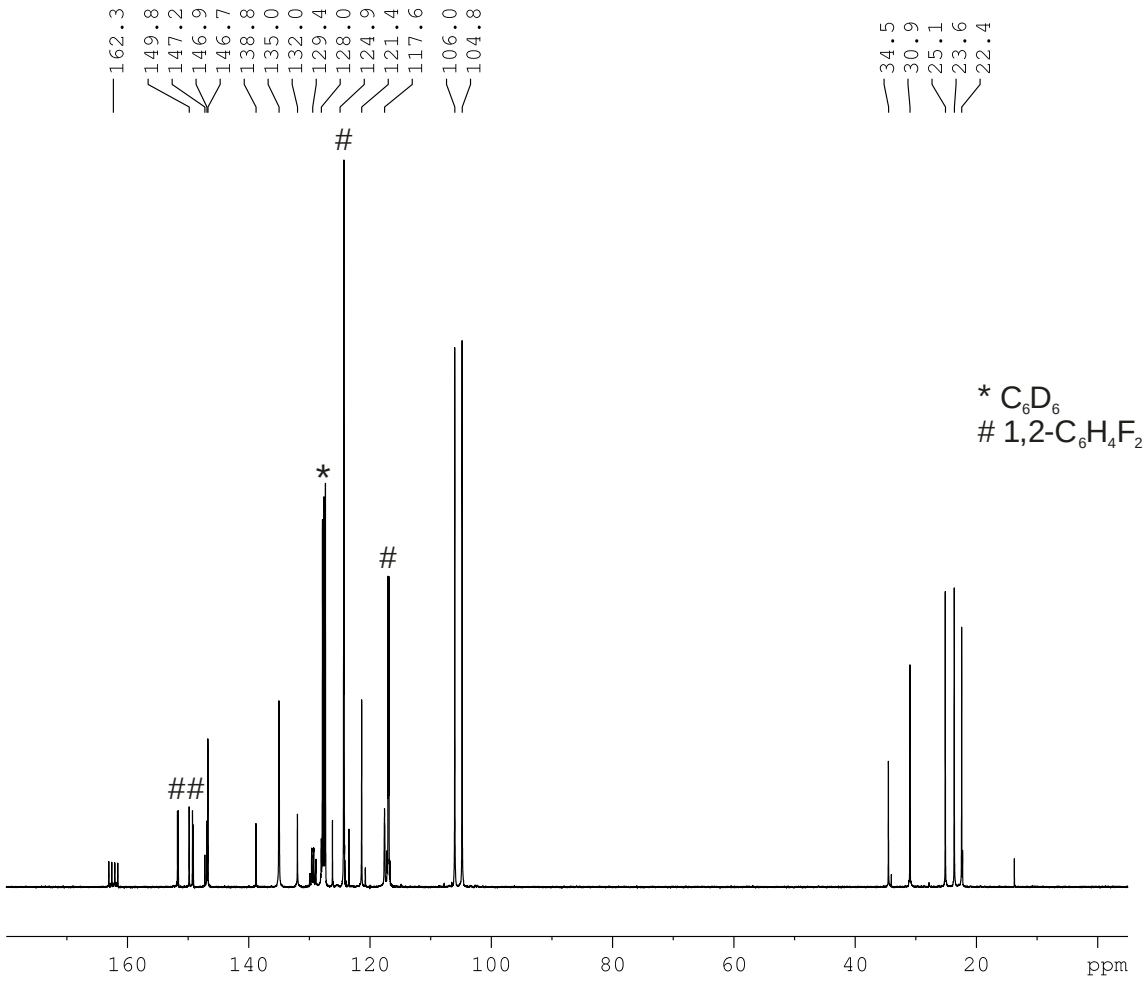



```
Current Data Parameters
NAME          MW1052_300
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210423
Time              16.02 h
INSTRUM            spect
PROBHD   Z104275_0338 (
PULPROG             zg30
TD                 38044
SOLVENT             C6D6
NS                   128
DS                     0
SWH            12019.230 Hz
FIDRES          0.631859 Hz
AQ             1.5826304 sec
RG                 49.23
DW                41.600 usec
DE                 6.50 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1
SFO1         300.1300000 MHz
NUC1                  1H
P0                 4.67 usec
P1                14.00 usec
PLW1           8.26509953 W

F2 - Processing parameters
SI                 32768
SF           300.1300001 MHz
WDW                   EM
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```

* C_6D_6
# 1,2-$C_6H_4F_2$
§ silicone grease

Figure S89. ^{1}H NMR of compound **10** {WCA = [BAr^F]}.

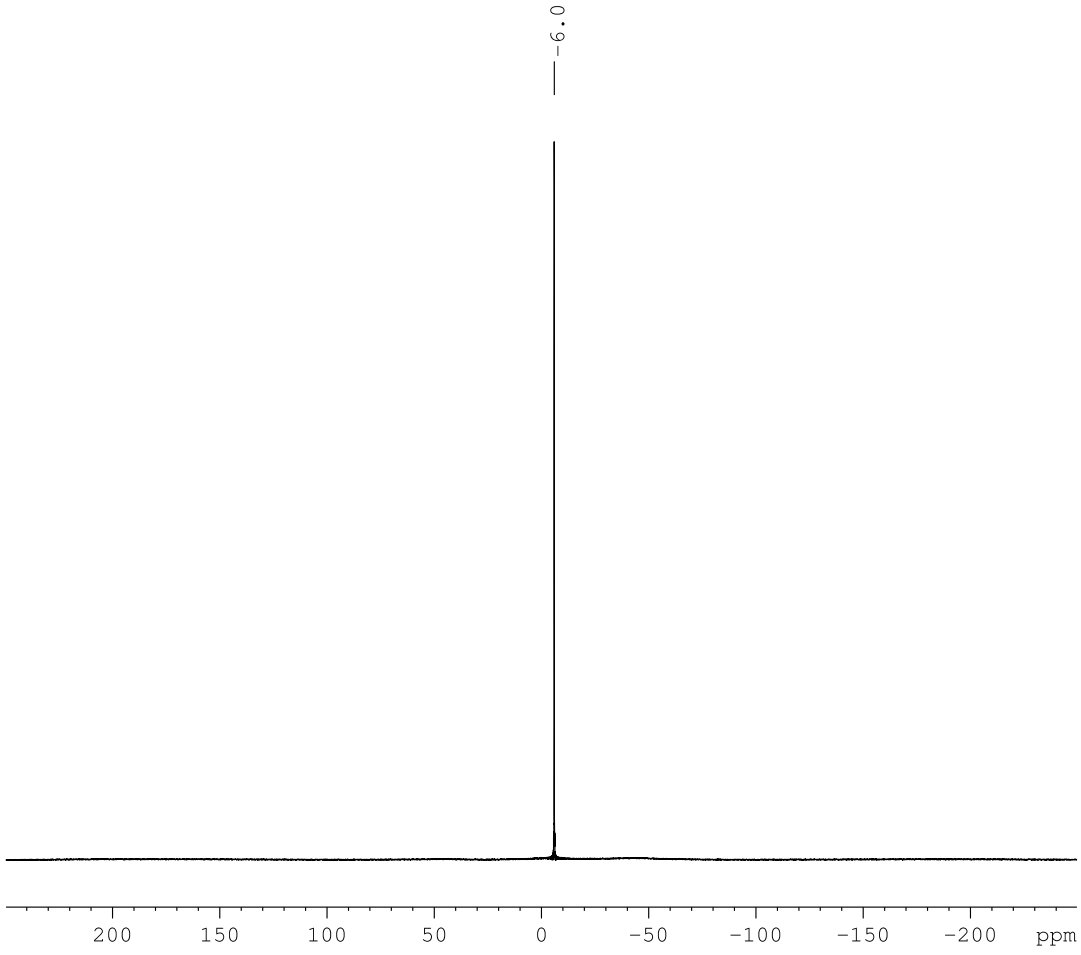
$^{13}C\{^{1}H\}$ NMR (C_6D_6 + 1,2-difluorobenzene, rt) of [({Cp_2Zr}$_2$H)(μ-H)$_2$Sn(H)Ar*][BAr^F] (**10**)




```
Current Data Parameters
NAME       MW1052_400NM
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20210424
Time               2.04
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG           udeft
TD                22218
SOLVENT            C6D6
NS                 5700
DS                    0
SWH           30864.197 Hz
FIDRES         1.389153 Hz
AQ            0.3599316 sec
RG                32800
DW               16.200 usec
DE                6.00 usec
TE                299.2 K
D1           3.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
D20        100.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                 13.50 usec
P13              2000.00 usec
P26               500.00 usec
PL1                -4.16 dB
PL1W         78.55633545 W
SFO1        100.6198135 MHz
SP8                1.39 dB
SP13               1.39 dB
SPNAM[8] Crp60,0.5,20.1
SPNAM[13    Crp60comp.4
SPOAL8              0.500
SPOAL13             0.500
SPOFFS8  0 Hz
SPOFFS13 0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -3.00 dB
PL12              11.77 dB
PL2W         16.03799057 W
PL12W         0.53474891 W
SFO2        400.1120007 MHz

F2 - Processing parameters
SI                131072
SF          100.6077412 MHz
WDW                 EM
SSB       0
LB                2.00 Hz
GB        0
PC                1.40
```

Figure S90. $^{13}C\{^{1}H\}$ NMR of compound **10** {WCA = [BAr^F]}.

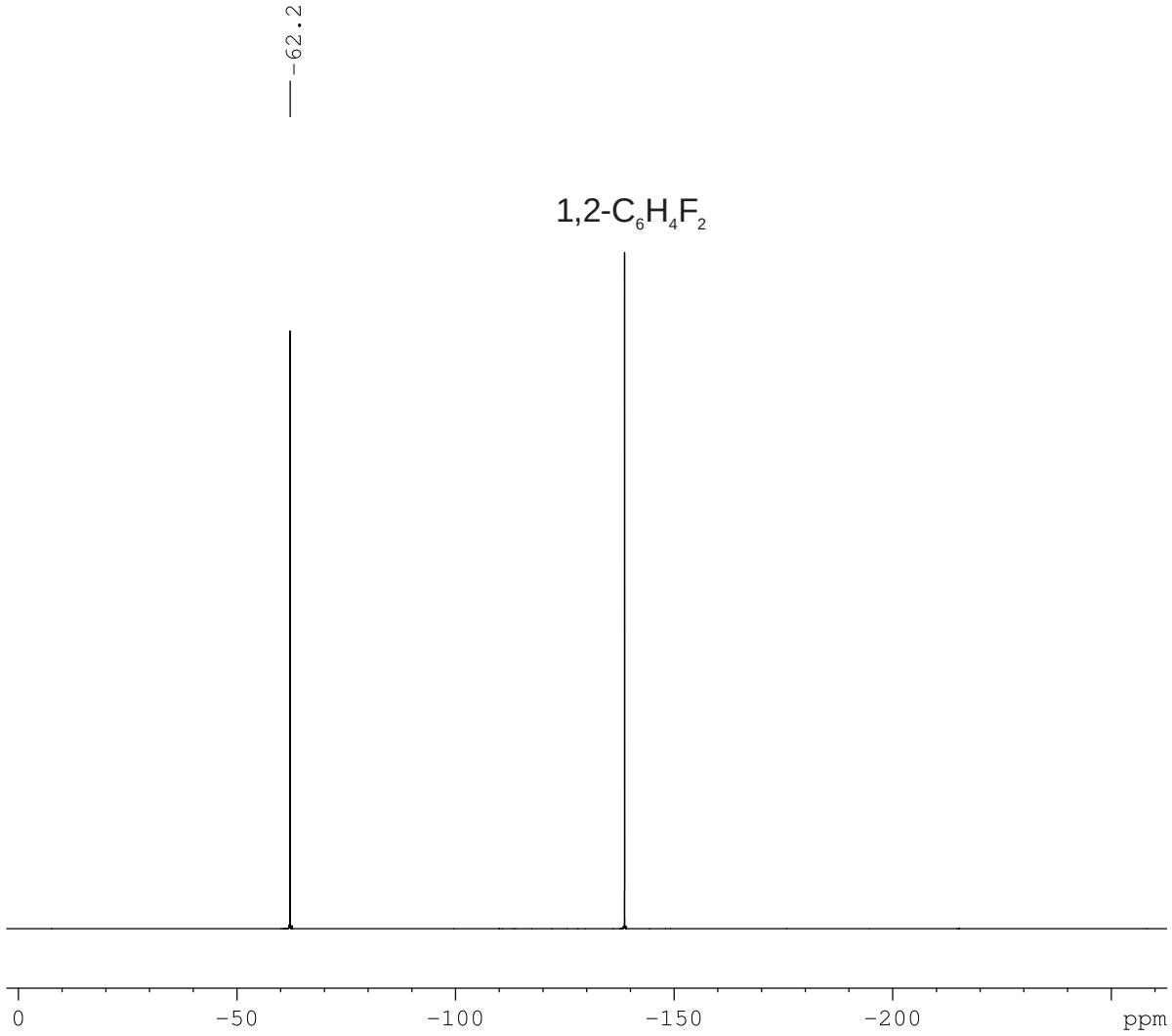
^{11}B NMR (C_6D_6 + 1,2-difluorobenzene, rt) of $[(\{Cp_2Zr\}_2H)(\mu\text{-}H)_2Sn(H)Ar^*][BAr^F]$ (**10**)




```
Current Data Parameters
NAME          MW1052_300
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210423
Time               16.10 h
INSTRUM            spect
PROBHD   Z104275_0338 (
PULPROG             zgbs
TD                  8192
SOLVENT             C6D6
NS                  2048
DS                     0
SWH            48076.922 Hz
FIDRES         11.737530 Hz
AQ             0.0851968 sec
RG                204.67
DW                10.400 usec
DE                 6.50 usec
TE                298.0 K
D1            0.10000000 sec
TD0                    1
SFO1          96.2936312 MHz
NUC1                 11B
P1                 5.75 usec
P2                11.50 usec
PLW1         70.00000000 W

F2 - Processing parameters
SI                 32768
SF            96.2936312 MHz
WDW                  EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

Figure S91. ^{11}B NMR of compound **10** {WCA = $[BAr^F]$}.

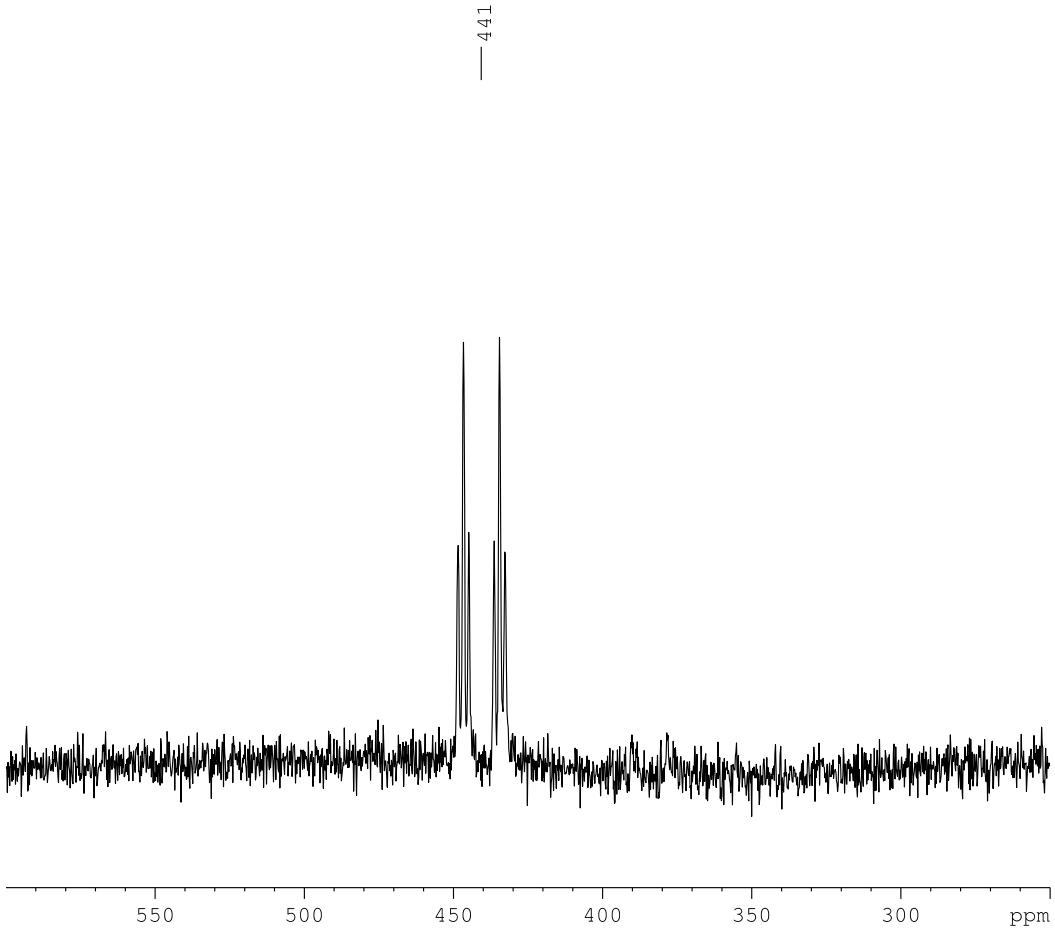
$^{19}F\{^{1}H\}$ NMR (C_6D_6 + 1,2-difluorobenzene, rt) of[({Cp_2Zr}$_2$H)(μ-H)$_2$Sn(H)Ar*][BAr^F] (**10**)




```
Current Data Parameters
NAME         MW1052_400
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20210423
Time              15.06
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG         zgfhigqn
TD                131072
SOLVENT             C6D6
NS                   128
DS                     0
SWH           100000.000 Hz
FIDRES          0.762939 Hz
AQ             0.6553600 sec
RG                  4100
DW                 5.000 usec
DE                 6.00 usec
TE                299.2 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  19F
P1                 18.75 usec
PL1                -2.92 dB
PL1W         30.50645256 W
SFO1         376.4306030 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               11.77 dB
PL2W         16.03799057 W
PL12W         0.53474891 W
SFO2         400.1120007 MHz

F2 - Processing parameters
SI                 262144
SF           376.4795470 MHz
WDW                   EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 1.00
```

Figure S92. $^{19}F\{^{1}H\}$ NMR of compound **10** {WCA = [BAr^F]}.

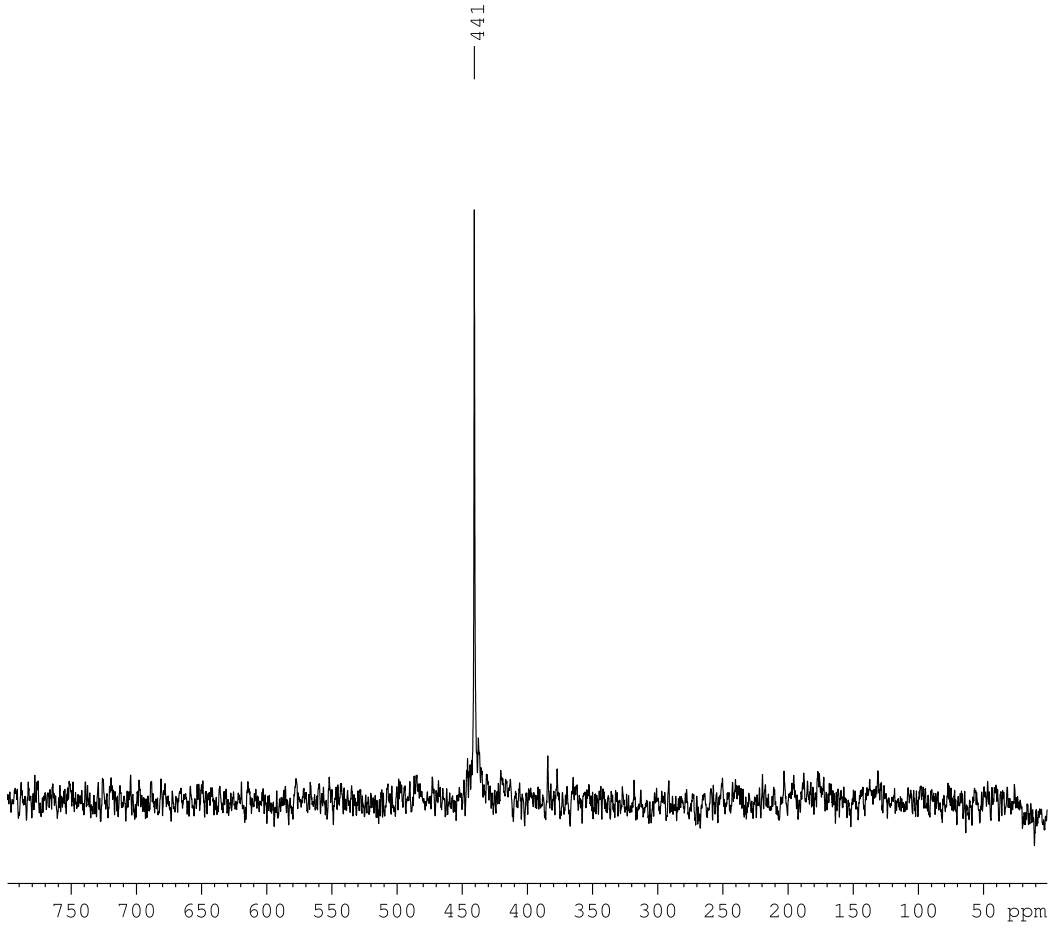
^{119}Sn NMR (C_6D_6 + 1,2-difluorobenzene, rt) of[({Cp_2Zr}$_2$H)(μ-H)$_2$Sn(H)Ar*][BAr^F] (**10**)




```
Current Data Parameters
NAME       MW1052_300NM
EXPNO                13
PROCNO                1

F2 - Acquisition Parameters
Date_          20210424
Time               19.42 h
INSTRUM            spect
PROBHD   Z104275_0338 (
PULPROG             zg30
TD                  8918
SOLVENT             C6D6
NS                102400
DS                     1
SWH            89285.711 Hz
FIDRES         20.023708 Hz
AQ             0.0499408 sec
RG                204.67
DW                 5.600 usec
DE                 6.50 usec
TE                298.0 K
D1           0.02000000 sec
TD0                    1
SFO1         111.9651420 MHz
NUC1               119Sn
P0                 4.03 usec
P1                12.10 usec
PLW1        12.00000000 W

F2 - Processing parameters
SI                  4096
SF           111.9203740 MHz
WDW                   EM
SSB       0
LB        0 Hz
GB        0
PC                 1.40
```

Figure S93. ^{119}Sn NMR of compound **10** {WCA = [BAr^F]}.

$^{119}Sn\{^{1}H\}$ NMR (C_6D_6 + 1,2-difluorobenzene, rt) of[({Cp_2Zr}$_2$H)(μ-H)$_2$Sn(H)Ar*][BAr^F] (**10**)

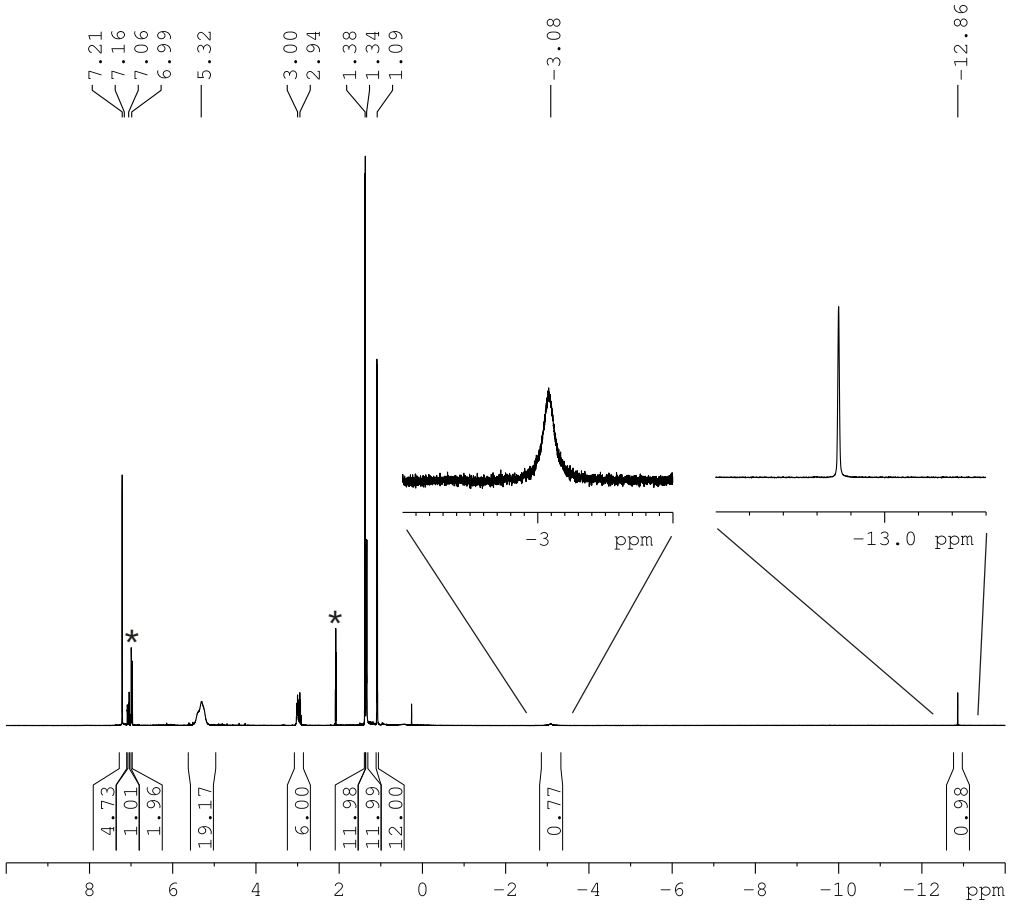



```
Current Data Parameters
NAME       MW1052_300NM
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_           20210424
Time               15.32 h
INSTRUM            spect
PROBHD   Z104275_0338 (
PULPROG          zgig30
TD                39186
SOLVENT             C6D6
NS                  5120
DS                     4
SWH            89285.711 Hz
FIDRES          4.557021 Hz
AQ             0.2194416 sec
RG                204.67
DW                 5.600 usec
DE                 6.50 usec
TE                298.0 K
D1           0.10000000 sec
D11          0.03000000 sec
TD0                    1
SFO1         111.9651418 MHz
NUC1               119Sn
P0                 4.03 usec
P1                12.10 usec
PLW1         12.00000000 W
SFO2         300.1312005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2          8.26509953 W
PLW12         0.20000000 W

F2 - Processing parameters
SI                 65536
SF           111.9203738 MHz
WDW                   EM
SSB      0
LB                50.00 Hz
GB       0
PC                 1.40
```

Figure S94. $^{119}Sn\{^{1}H\}$ NMR of compound **10** {WCA = [BAr^F]}.

Compound **11**

^{1}H NMR (tol-d_8, rt) of [({Cp_2Zr}$_2$H)(μ-H)Sn(H)Ar*] (**11**)

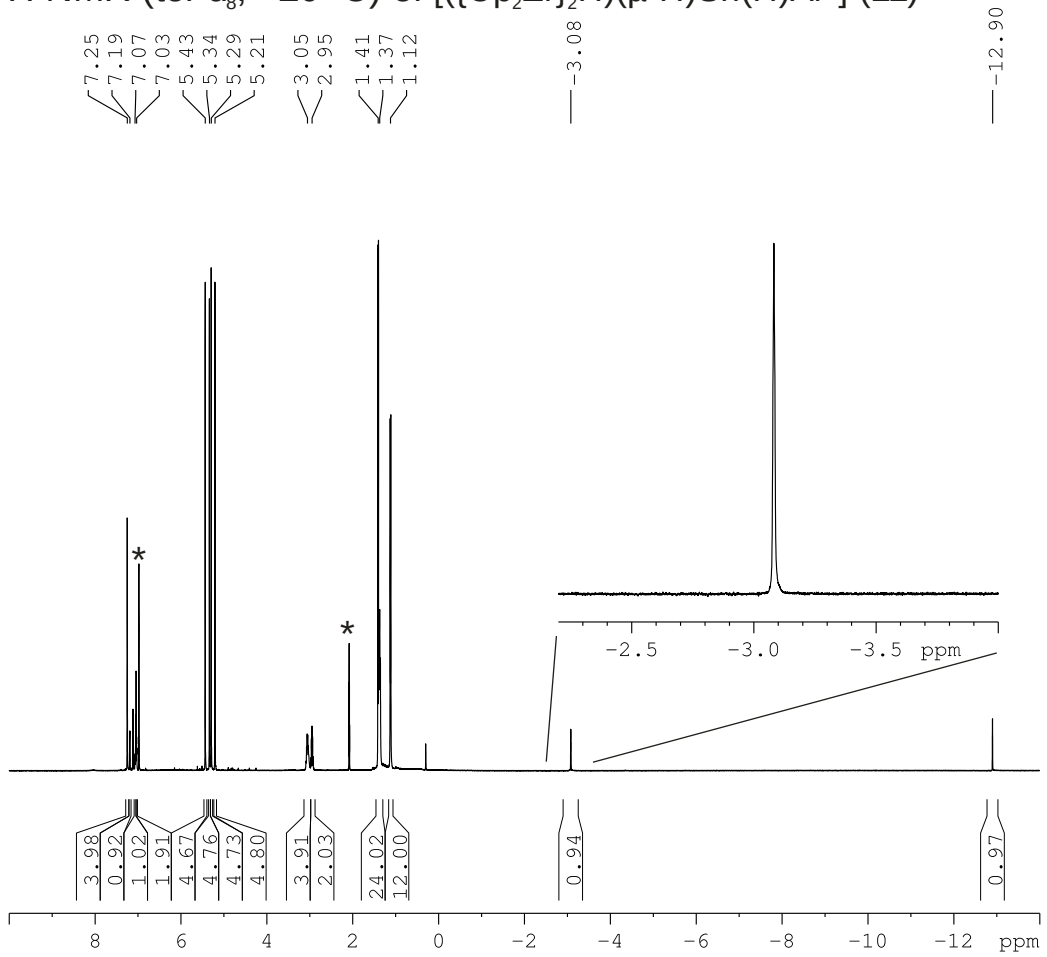



```
Current Data Parameters
NAME       MW866_500_VT
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_           20201028
Time               13.32
INSTRUM            spect
PROBHD   5 mm TBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT              Tol
NS                    64
DS                     0
SWH            20000.000 Hz
FIDRES         0.305176 Hz
AQ             1.6384000 sec
RG                     4
DW                25.000 usec
DE                 6.00 usec
TE                299.2 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 13.40 usec
PL1                -0.52 dB
PL1W         24.34997177 W
SFO1         500.1300000 MHz

F2 - Processing parameters
SI                 65536
SF           500.1300241 MHz
WDW                   no
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```

* tol-d_8

Figure S95. ^{1}H NMR of compound **11**.

^{1}H NMR (tol-d_8, −20 °C) of [({Cp_2Zr}$_2$H)(μ-H)Sn(H)Ar*] (**11**)

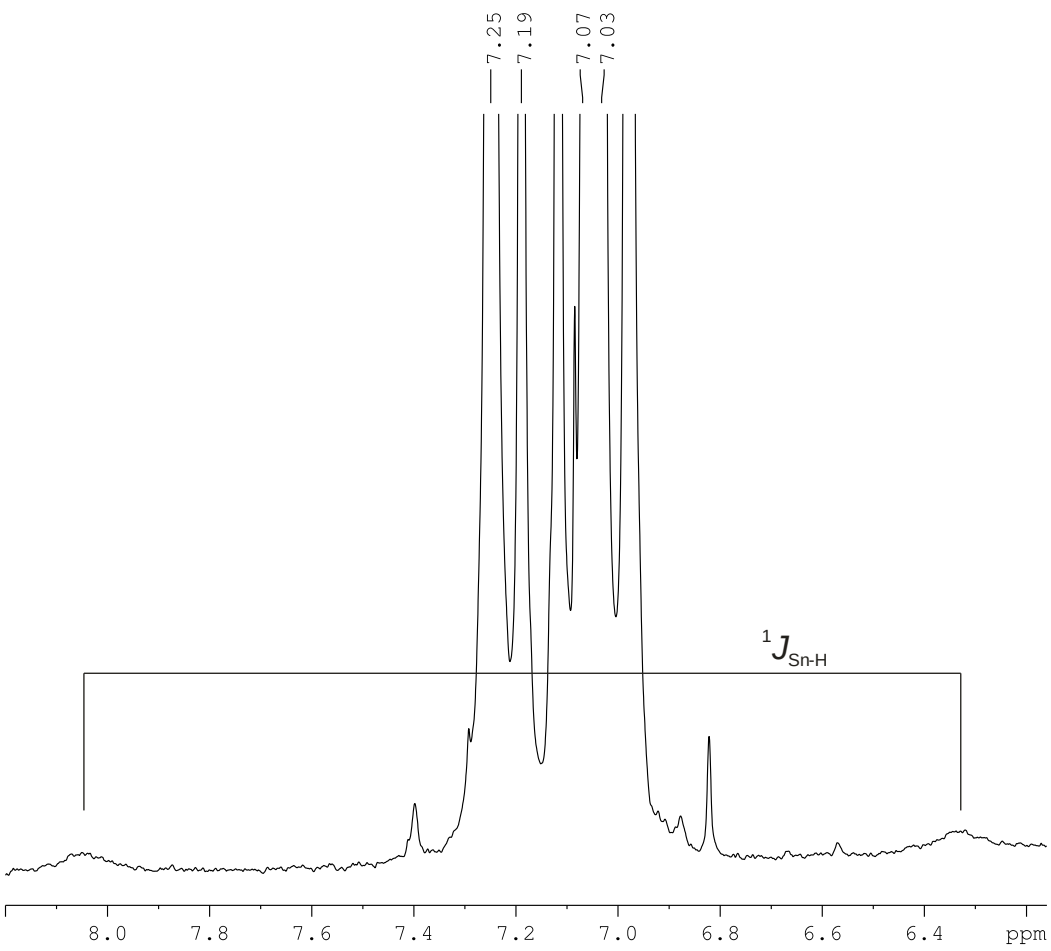



```
Current Data Parameters
NAME       MW866_500_VT
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20201028
Time              13.52
INSTRUM           spect
PROBHD   5 mm TBO BB-1H
PULPROG            zg30
TD                65536
SOLVENT             Tol
NS                   64
DS                    0
SWH           20000.000 Hz
FIDRES         0.305176 Hz
AQ            1.6384000 sec
RG                    4
DW               25.000 usec
DE                6.00 usec
TE               252.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                13.40 usec
PL1               -0.52 dB
PL1W        24.34997177 W
SFO1        500.1300000 MHz

F2 - Processing parameters
SI                65536
SF          500.1300258 MHz
WDW                  no
SSB       0
LB        0 Hz
GB        0
PC                1.00
```

* tol-d_8

Figure S96. ^{1}H NMR (-20°C) of compound **11**.

^{1}H NMR (tol-d_8, −20 °C) of [({Cp_2Zr}$_2$H)(μ-H)Sn(H)Ar*] (**11**)




```
Current Data Parameters
NAME       MW866_500_VT
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20201028
Time              13.52
INSTRUM           spect
PROBHD   5 mm TBO BB-1H
PULPROG            zg30
TD                65536
SOLVENT             Tol
NS                   64
DS                    0
SWH           20000.000 Hz
FIDRES         0.305176 Hz
AQ            1.6384000 sec
RG                    4
DW               25.000 usec
DE                6.00 usec
TE               252.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                13.40 usec
PL1               -0.52 dB
PL1W        24.34997177 W
SFO1       500.1300000 MHz

F2 - Processing parameters
SI                65536
SF         500.1300258 MHz
WDW                  EM
SSB       0
LB                2.00 Hz
GB        0
PC                1.00
```

Figure S97. ^{1}H NMR (-20°C) of compound **11** (hydride signal).

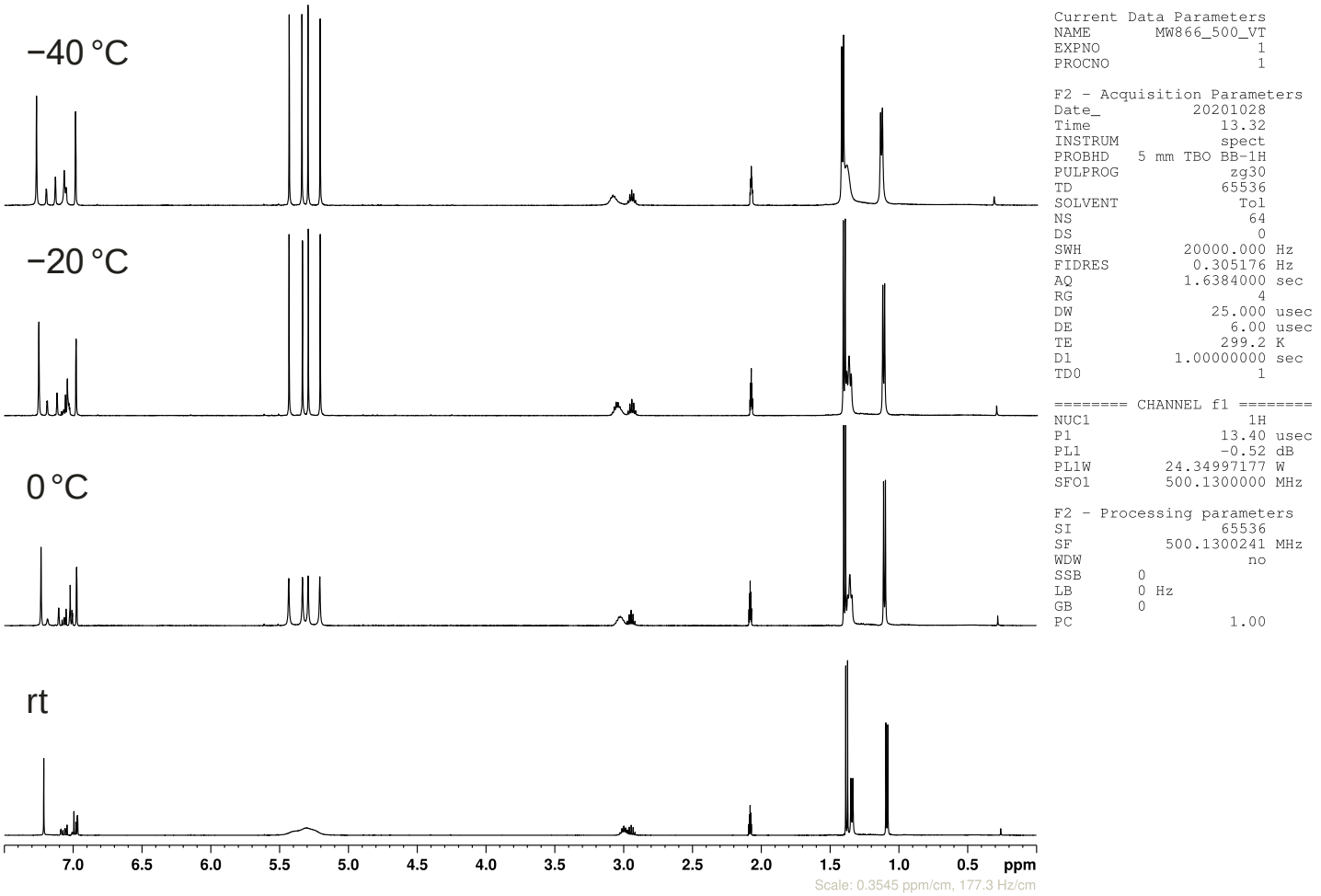


Figure S98. ^{1}H NMR (VT) of compound **11**.

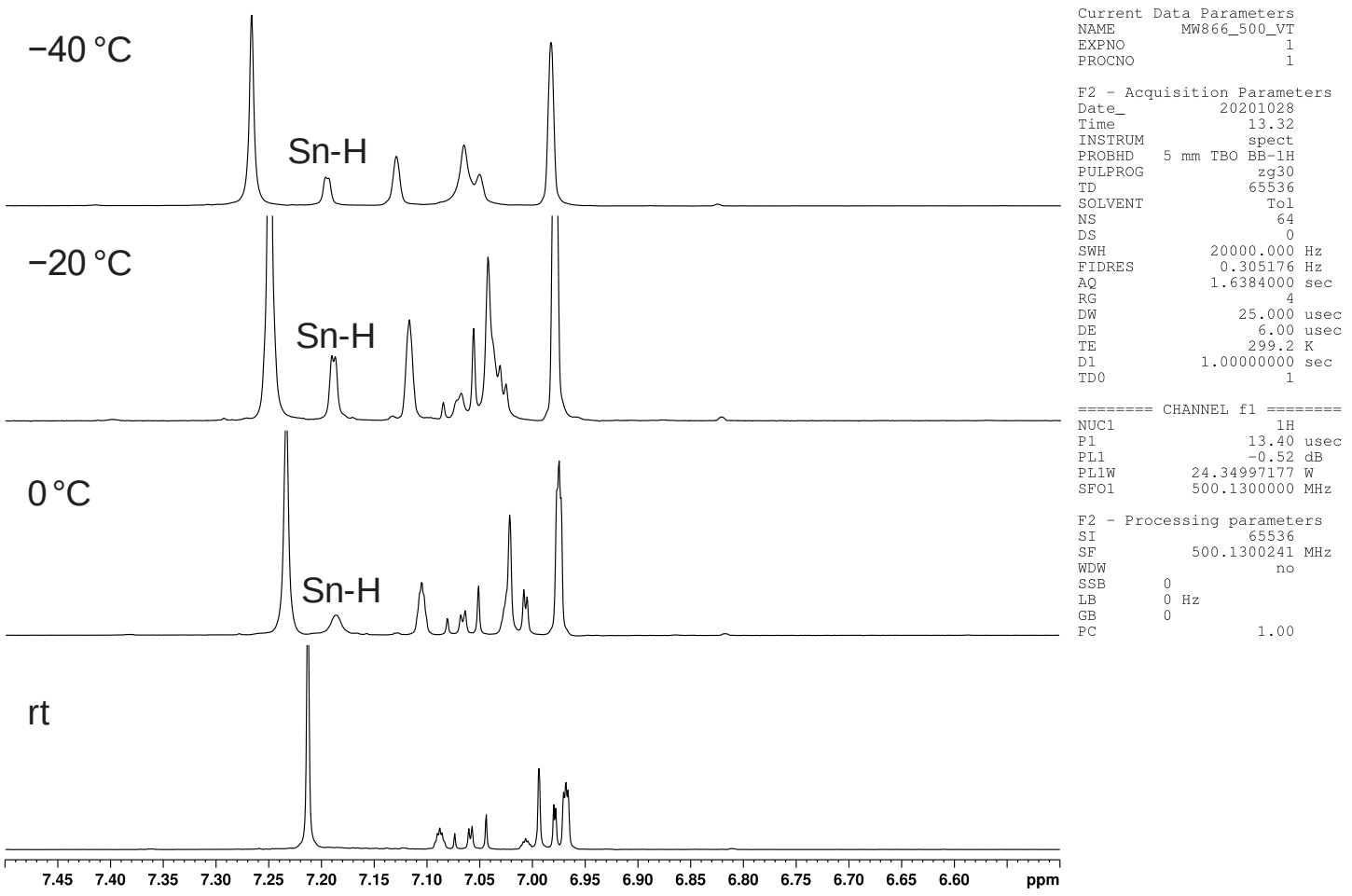
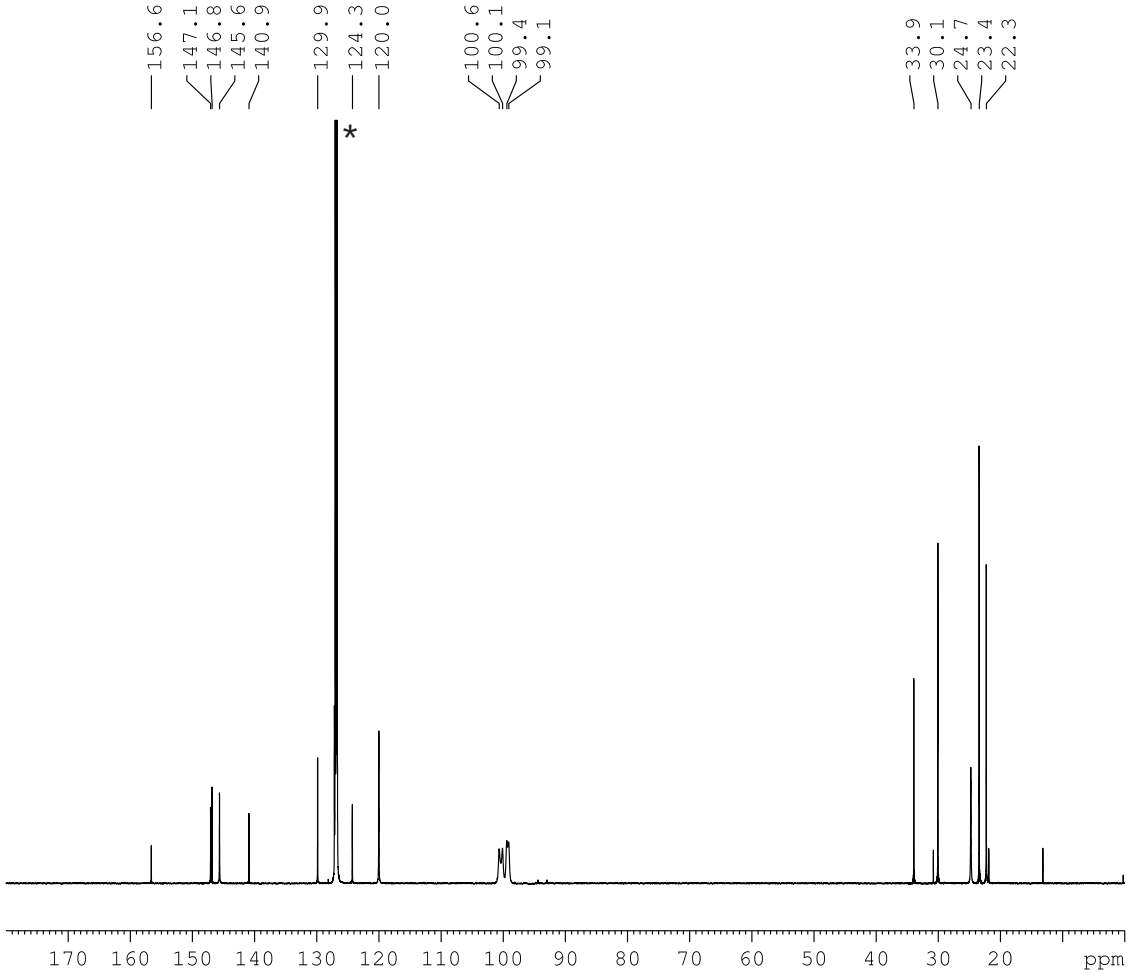


Figure S99. ^{1}H NMR (VT) of compound **11** (selected area).

$^{13}C\{^{1}H\}$ NMR (C_6D_6, rt) of [({Cp_2Zr}$_2$H)(μ-H)Sn(H)Ar*] (**11**)

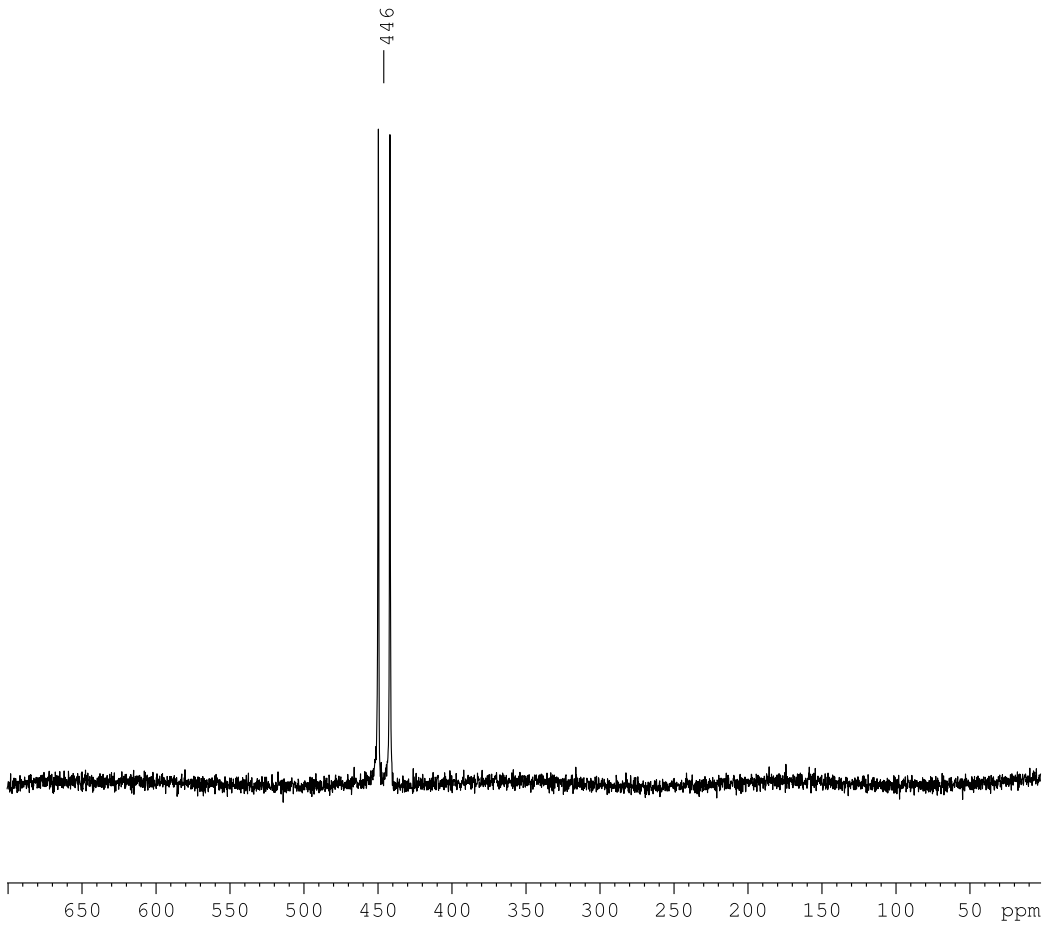



```
Current Data Parameters
NAME          MW847_600
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20201014
Time              19.59 h
INSTRUM            spect
PROBHD   Z126545_0027 (
PULPROG            udeft
TD                 25902
SOLVENT             C6D6
NS                  3072
DS                     8
SWH            36231.883 Hz
FIDRES          2.797613 Hz
AQ             0.3574476 sec
RG                 189.6
DW                13.800 usec
DE                 18.00 usec
TE                298.0 K
D1             4.00000000 sec
D12            0.00002000 sec
D20           20.00000000 sec
TD0                    1
SFO1         150.9178988 MHz
NUC1                 13C
P1                 10.00 usec
P13              2000.00 usec
P26               500.00 usec
PLW1         57.02700043 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5  0 Hz
SPW5          8.71310043 W
SPNAM[8] Crp60,0.5,20.1
SPOAL8             0.500
SPOFFS8  0 Hz
SPW8          8.71310043 W
SFO2         600.1324005 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2             70.00 usec
PLW2         23.41200066 W
PLW12         0.68803000 W

F2 - Processing parameters
SI                131072
SF           150.9029326 MHz
WDW                  EM
SSB       0
LB                2.00 Hz
GB        0
PC                1.40
```

* C_6D_6

Figure S100. $^{13}C\{^{1}H\}$ NMR of compound **11**.

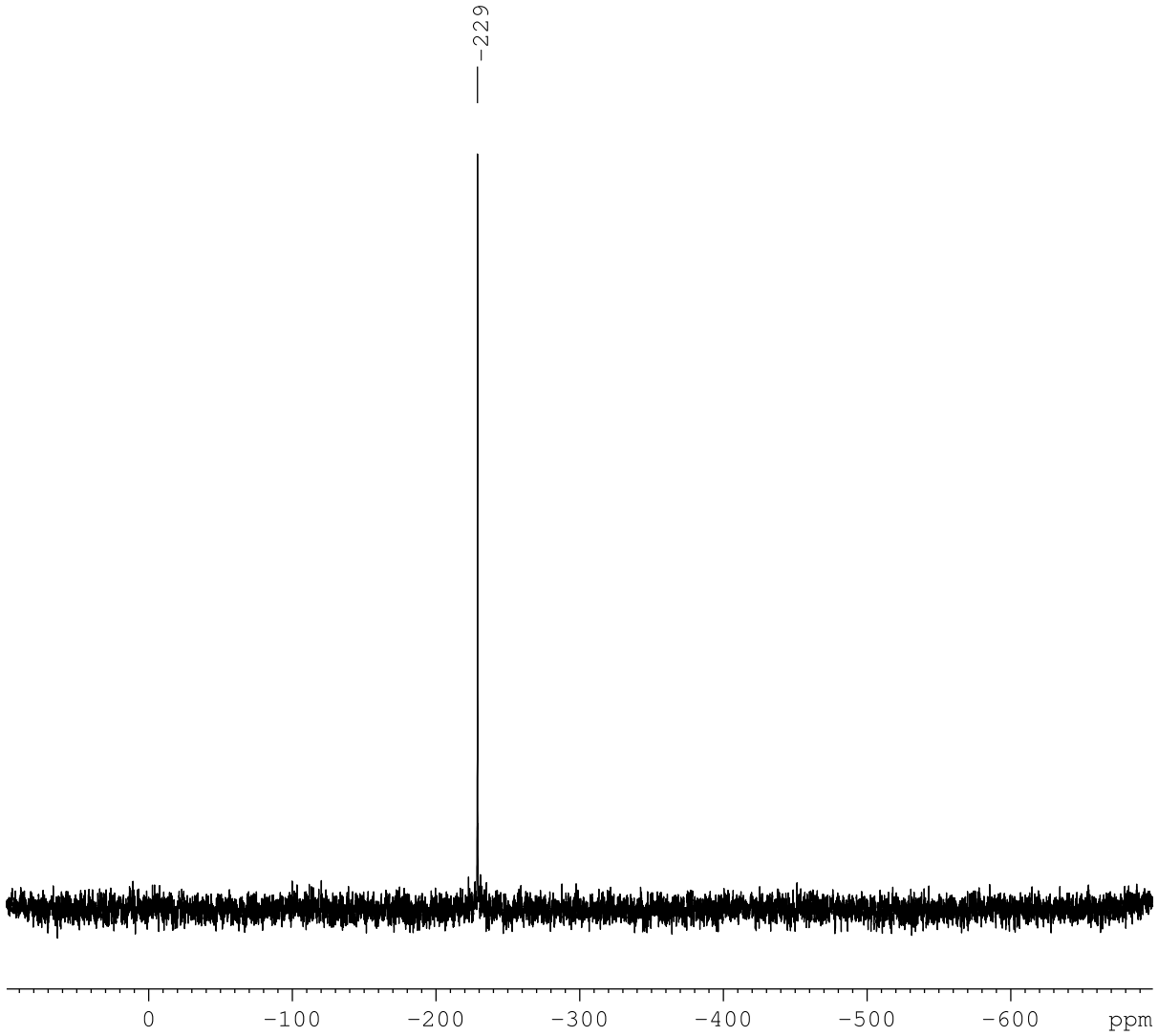
^{119}Sn NMR (C_6D_6, rt) of [({Cp_2Zr}$_2$H)(μ-H)Sn(H)Ar*] (**11**)




```
Current Data Parameters
NAME         MW852_300Sn
EXPNO                 23
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201016
Time               20.54 h
INSTRUM            spect
PROBHD   Z104275_0338 (
PULPROG             zg30
TD                  8918
SOLVENT             C6D6
NS                122880
DS                     1
SWH            89285.711 Hz
FIDRES         20.023708 Hz
AQ             0.0499408 sec
RG                204.67
DW                 5.600 usec
DE                 6.50 usec
TE                298.0 K
D1            0.02000000 sec
TD0                    1
SFO1         111.9651420 MHz
NUC1               119Sn
P0                 4.03 usec
P1                12.10 usec
PLW1         12.00000000 W

F2 - Processing parameters
SI                  4096
SF           111.9203740 MHz
WDW                   EM
SSB       0
LB        0 Hz
GB        0
PC                 1.40
```

Figure S101. ^{119}Sn NMR of compound **11**.

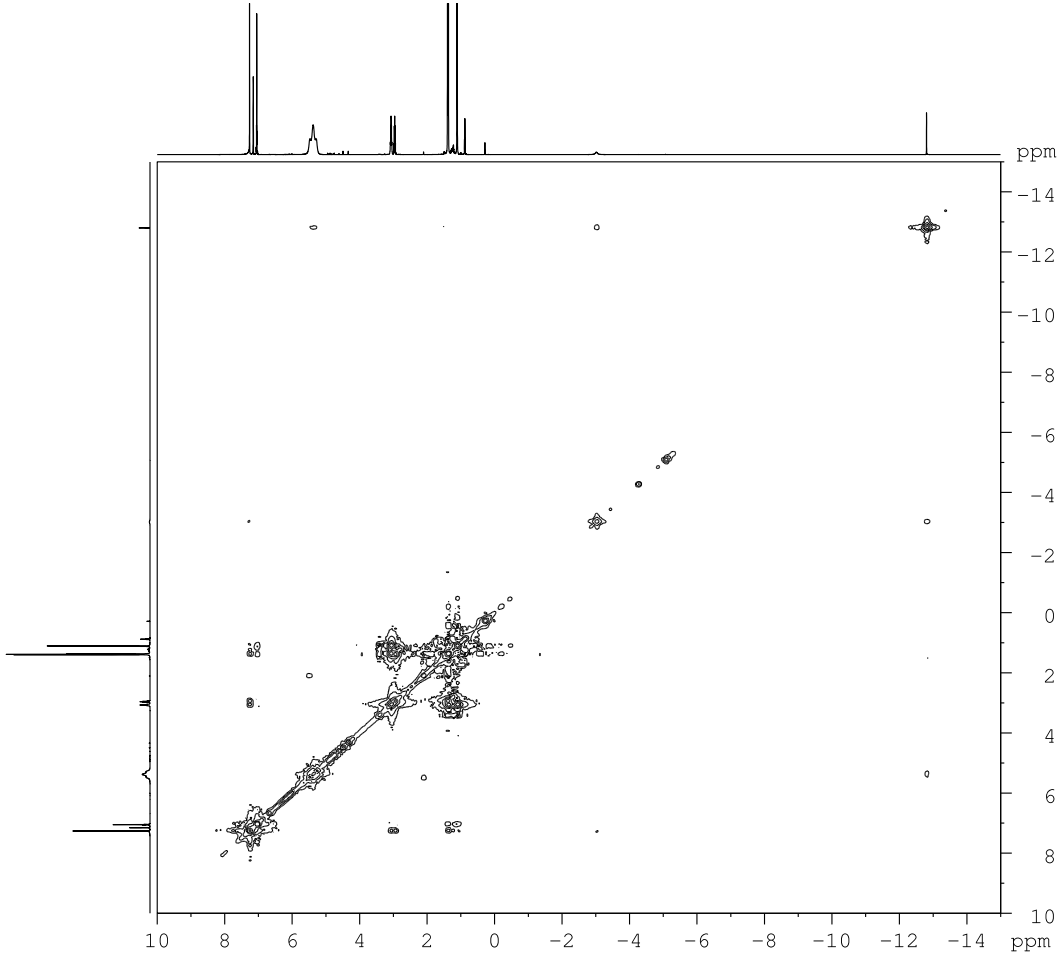
$^{119}Sn\{^{1}H\}$ NMR (tol-d_8, rt) of $[Cp_2Zr(\mu\text{-}H)(SnH_2Ar^*)]_2$ (**13**)




```
Current Data Parameters
NAME         MW898_300Sn
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201105
Time               18.26 h
INSTRUM            spect
PROBHD   Z104275_0338 (
PULPROG           zgig30
TD                 39186
SOLVENT              C6D6
NS                   5000
DS                      4
SWH            89285.711 Hz
FIDRES          4.557021 Hz
AQ             0.2194416 sec
RG                204.67
DW                 5.600 usec
DE                 6.50 usec
TE                 298.0 K
D1            0.10000000 sec
D11           0.03000000 sec
TD0                    1
SFO1         111.8867977 MHz
NUC1                119Sn
P0                 4.03 usec
P1                12.10 usec
PLW1         12.00000000 W
SFO2         300.1312005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2          8.26509953 W
PLW12         0.20000000 W

F2 - Processing parameters
SI                 65536
SF           111.9203738 MHz
WDW                   EM
SSB       0
LB                10.00 Hz
GB        0
PC                 1.40
```

Figure S102. $^{119}Sn\{^{1}H\}$ NMR of compound **11**.

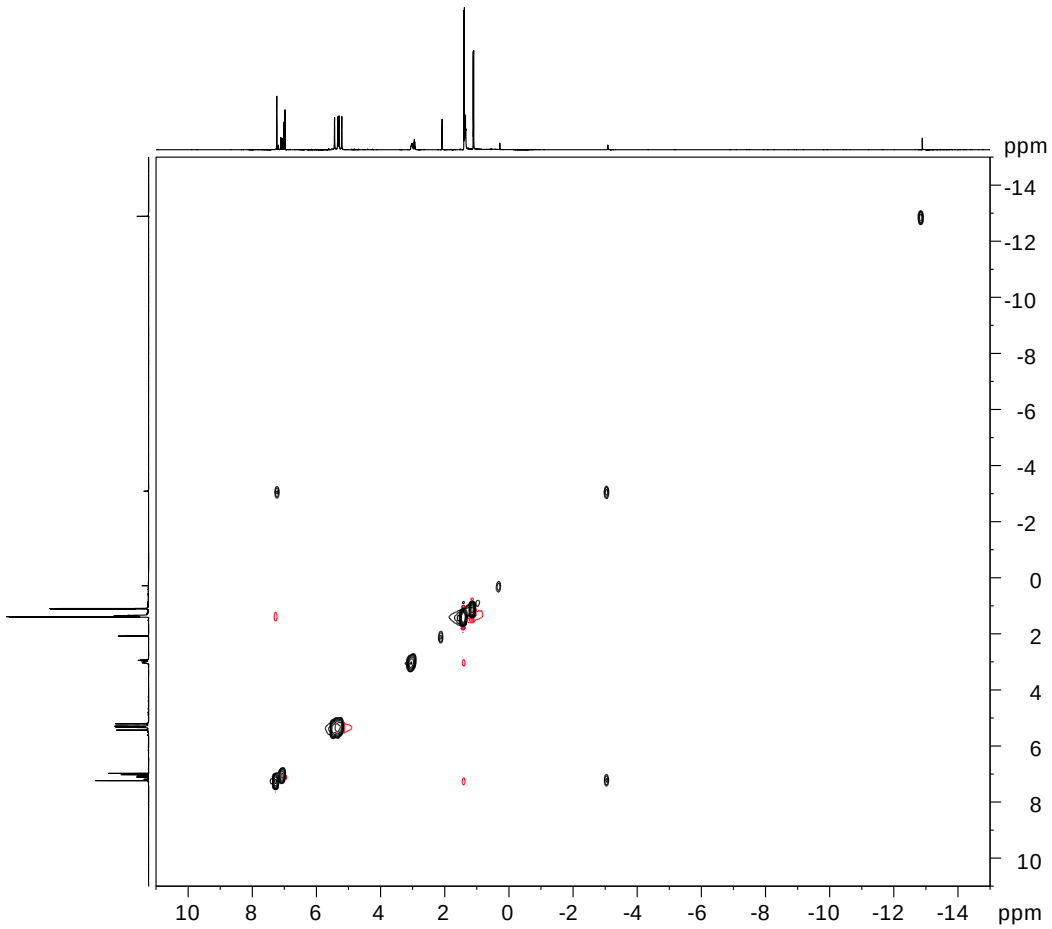
^{1}H,^{1}H COSY NMR (C_6D_6, rt) of [({Cp_2Zr}$_2$H)(μ-H)Sn(H)Ar*] (**11**)




```
Current Data Parameters
NAME            MW847_600
EXPNO                  13
PROCNO                  1

F2 - Acquisition Parameters
Date_            20201014
Time               21.59 h
INSTRUM             spect
PROBHD   Z126545_0027 (
PULPROG       cosygpppqf
TD                  2048
SOLVENT             C6D6
NS                    10
DS                    16
SWH            24038.461 Hz
FIDRES         23.475060 Hz
AQ             0.0425984 sec
RG                 34.14
DW                20.800 usec
DE                10.00 usec
TE                298.0 K
D0            0.00000300 sec
D1            2.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
D13           0.00000400 sec
D16           0.00020000 sec
IN0           0.00004160 sec
TDav                   1
SFO1          600.1300000 MHz
NUC1                  1H
P0                 12.00 usec
P1                 12.00 usec
P17              2500.00 usec
PLW1         23.41200066 W
PLW10         5.39410019 W
GPNAM[1]      SMSQ10.100
GPZ1              10.00 %
P16             1000.00 usec

F1 - Acquisition parameters
TD                   512
SFO1              600.13 MHz
FIDRES         93.900238 Hz
SW                40.055 ppm
FnMODE                QF

F2 - Processing parameters
SI                   1024
SF            600.1300000 MHz
WDW                 QSINE
SSB       0
LB        0 Hz
GB        0
PC                  1.40

F1 - Processing parameters
SI                   1024
MC2                   QF
SF            600.1300000 MHz
WDW                 QSINE
SSB       0
LB        0 Hz
GB        0
```

Figure S103. ^{1}H, ^{1}H COSY NMR of compound **11**.

$^{1}H,^{1}H$ EXSY NMR (tol-d_8, 0°C) of [({Cp_2Zr}$_2$H)(μ-H)Sn(H)Ar*] (**11**)



Current Data Parameters
NAME MW866_500_VT
EXPNO 7
PROCNO 1

F2 - Acquisition Parameters
Date_ 20201028
Time 21.16
INSTRUM spect
PROBHD 5 mm TBO BB-1H
PULPROG noesyph
TD 1024
SOLVENT Tol
NS 48
DS 16
SWH 20000.000 Hz
FIDRES 19.531250 Hz
AQ 0.0256000 sec
RG 64
DW 25.000 usec
DE 6.00 usec
TE 273.2 K
D0 0.00000793 sec
D1 2.00000000 sec
D8 0.30000001 sec
IN0 0.00005000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 13.40 usec
PL1 -0.52 dB
PL1W 24.34997177 W
SFO1 500.1300000 MHz

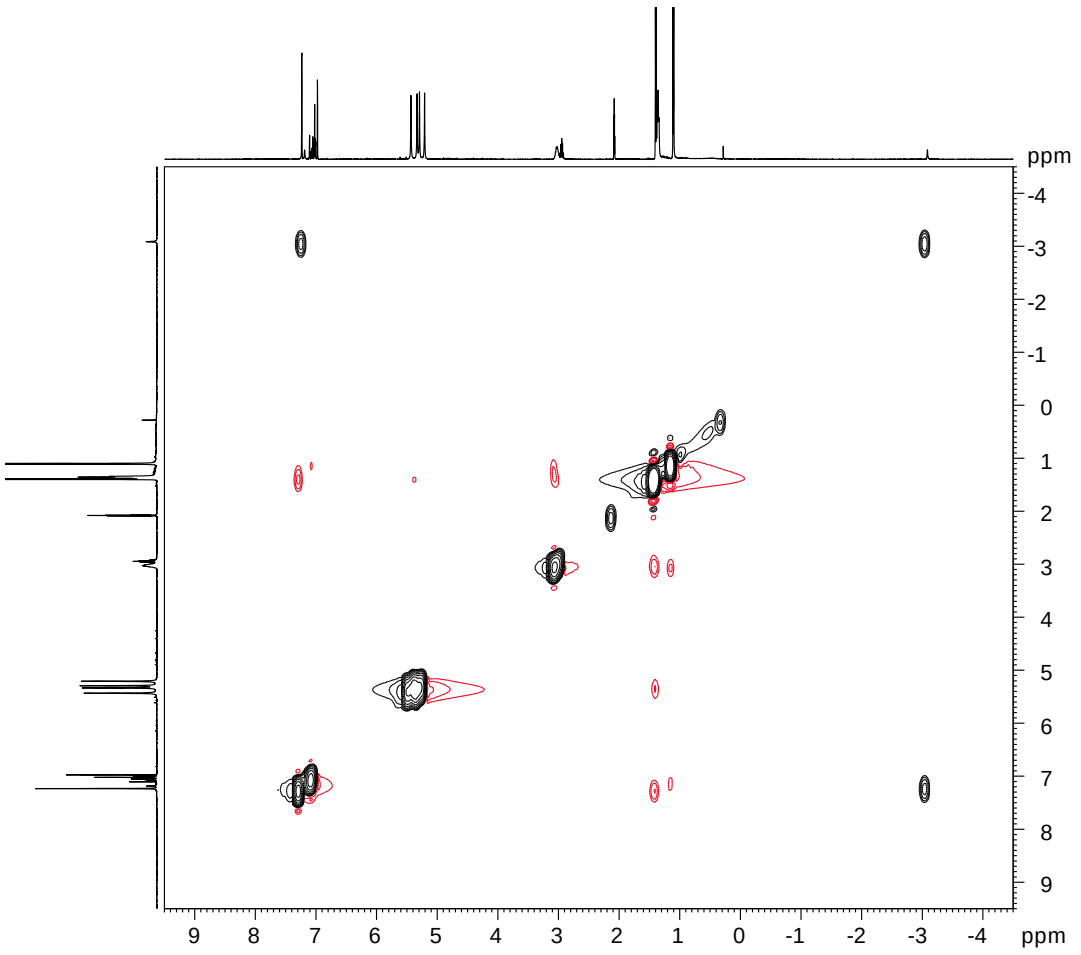
F1 - Acquisition parameters
TD 256
SFO1 500.13 MHz
FIDRES 156.290619 Hz
SW 40.000 ppm
FnMODE States-TPPI

F2 - Processing parameters
SI 1024
SF 500.1300000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 1.00

F1 - Processing parameters
SI 1024
MC2 States-TPPI
SF 500.1300000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0

Figure S104. $^{1}H,^{1}H$ EXSY NMR (0°C) of compound **11**.

$^{1}H,^{1}H$ EXSY NMR (tol-d_8, 0°C) of [({Cp_2Zr}$_2$H)(μ-H)Sn(H)Ar*] (**11**)



Current Data Parameters
NAME MW866_500_VT
EXPNO 7
PROCNO 1

F2 - Acquisition Parameters
Date_ 20201028
Time 21.16
INSTRUM spect
PROBHD 5 mm TBO BB-1H
PULPROG noesyph
TD 1024
SOLVENT Tol
NS 48
DS 16
SWH 20000.000 Hz
FIDRES 19.531250 Hz
AQ 0.0256000 sec
RG 64
DW 25.000 usec
DE 6.00 usec
TE 273.2 K
D0 0.00000793 sec
D1 2.00000000 sec
D8 0.30000001 sec
IN0 0.00005000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 13.40 usec
PL1 -0.52 dB
PL1W 24.34997177 W
SFO1 500.1300000 MHz

F1 - Acquisition parameters
TD 256
SFO1 500.13 MHz
FIDRES 156.290619 Hz
SW 40.000 ppm
FnMODE States-TPPI

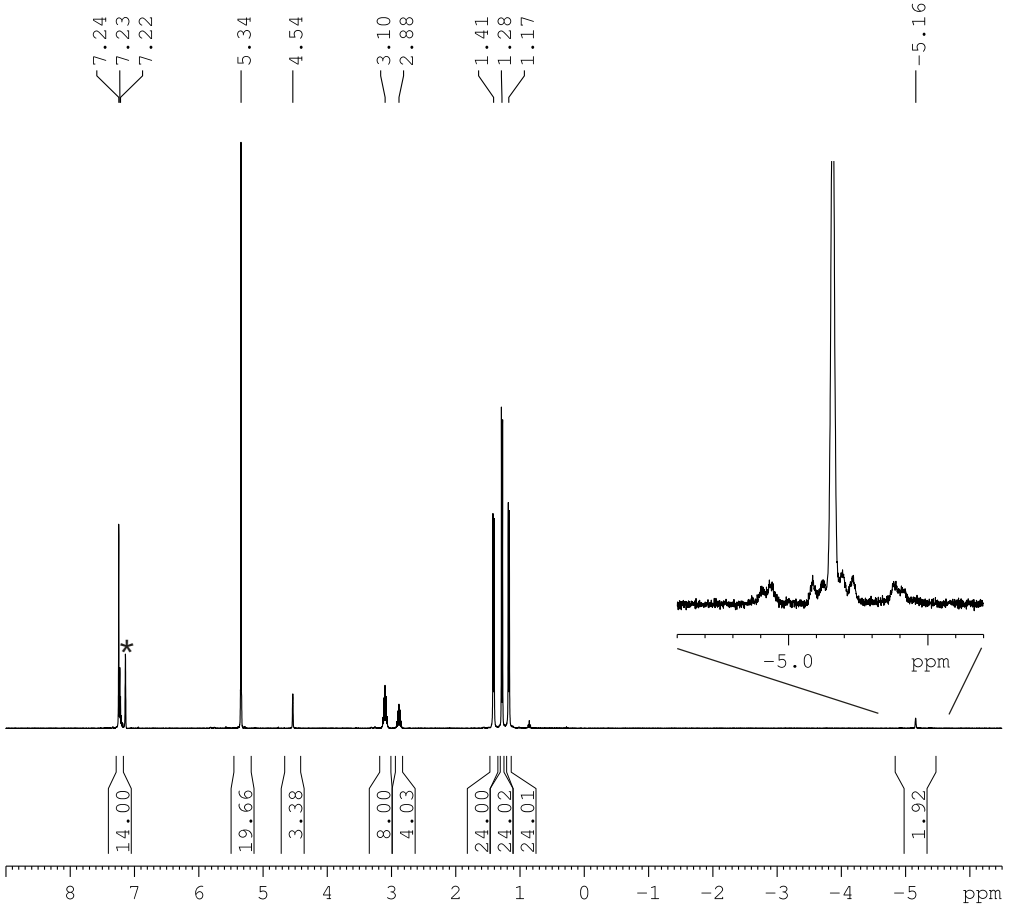
F2 - Processing parameters
SI 1024
SF 500.1300000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 1.00

F1 - Processing parameters
SI 1024
MC2 States-TPPI
SF 500.1300000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0

Figure S105. ^{1}H, ^{1}H EXSY NMR (0°C) of compound **11** (selected area).

Compound **13**

^{1}H NMR (C_6D_6, rt) of $[Cp_2Zr(\mu\text{-}H)(SnH_2Ar^*)]_2$ (**13**)

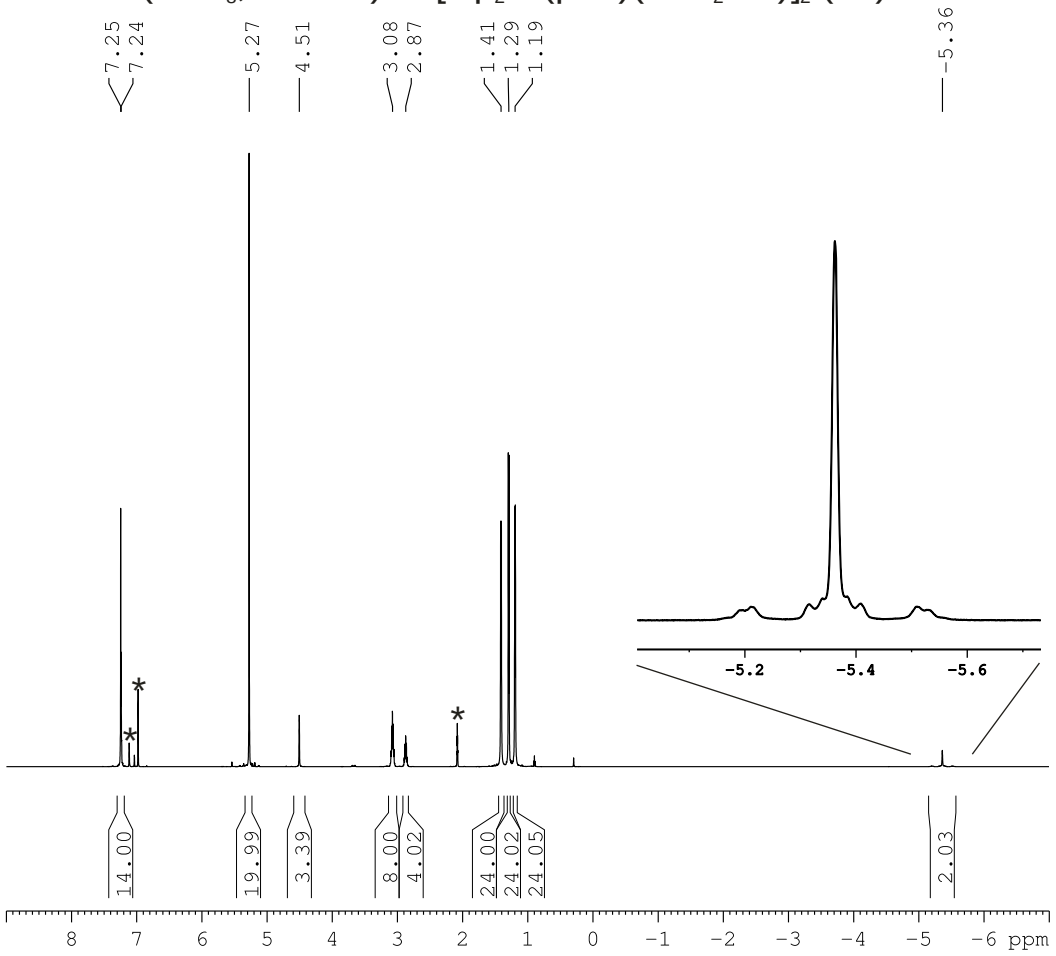



```
Current Data Parameters
NAME          MW919_400
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_          20201127
Time               9.17
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG            zg30
TD                52656
SOLVENT            C6D6
NS                   64
DS                    0
SWH           16025.641 Hz
FIDRES         0.304346 Hz
AQ            1.6428672 sec
RG                  322
DW               31.200 usec
DE                6.00 usec
TE                299.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.60 usec
PL1               -3.00 dB
PL1W        16.03799057 W
SFO1        400.1100000 MHz

F2 - Processing parameters
SI                65536
SF          400.1100000 MHz
WDW                  EM
SSB       0
LB        0 Hz
GB        0
PC                 1.00
```

* C_6D_6

Figure S106. ^{1}H NMR of compound **13**.

^{1}H NMR (tol-d_8, −40 °C) of [$Cp_2Zr(\mu\text{-}H)(SnH_2Ar^*)]_2$ (**13**)




```
Current Data Parameters
NAME           MW919_600
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201210
Time                8.34 h
INSTRUM            spect
PROBHD   Z126545_0027 (
PULPROG             zg30
TD                 65536
SOLVENT              Tol
NS                    34
DS                     0
SWH            18028.846 Hz
FIDRES          0.550197 Hz
AQ             1.8175317 sec
RG                 19.61
DW                27.733 usec
DE                10.00 usec
TE                253.0 K
D1            1.00000000 sec
TD0                    1
SFO1         600.1300000 MHz
NUC1                  1H
P1                 12.00 usec
PLW1         23.41200066 W

F2 - Processing parameters
SI                 65536
SF           600.1300301 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

* tol-d_8

Figure S107. ^{1}H NMR (-40°C) of compound **13**.

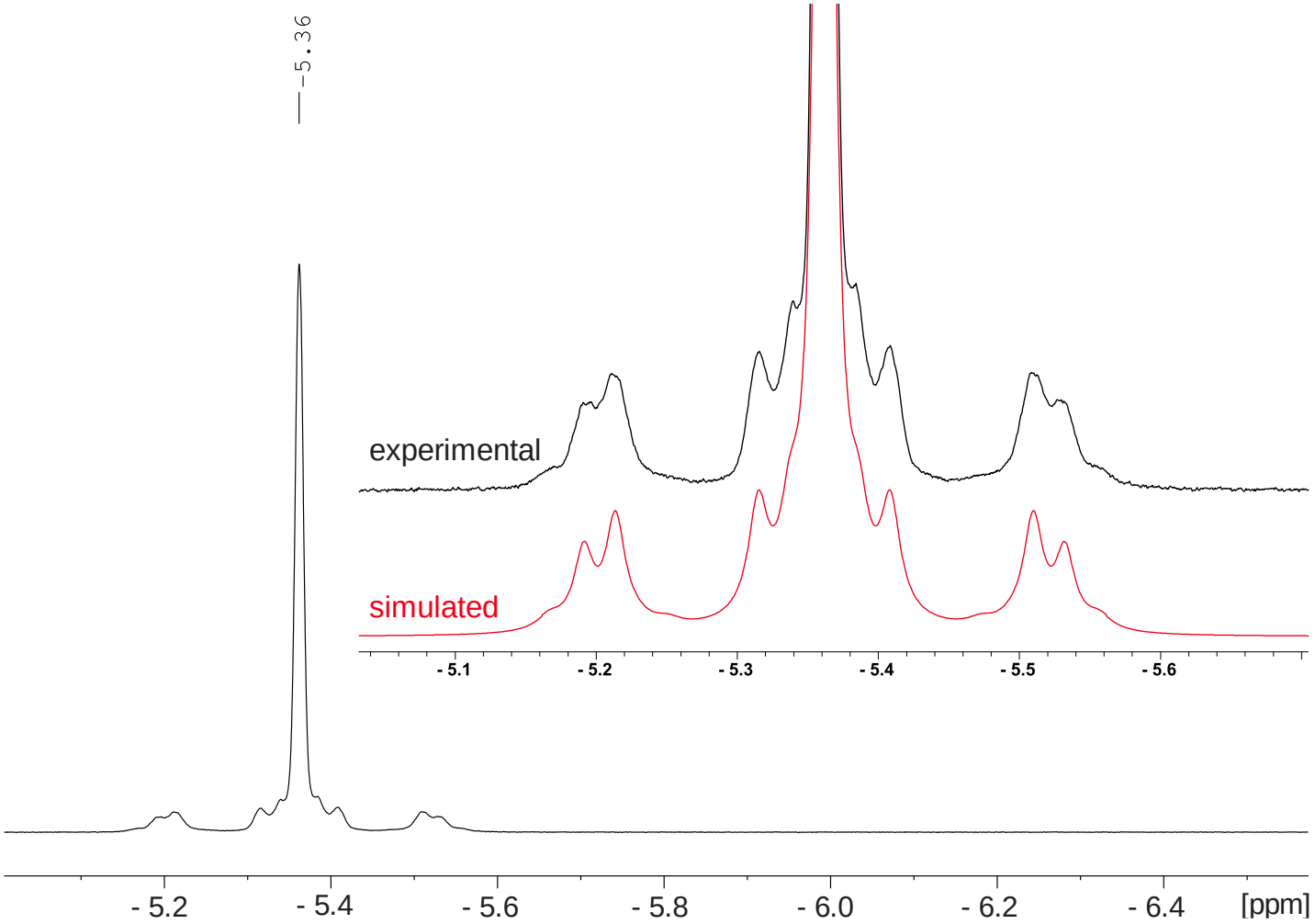
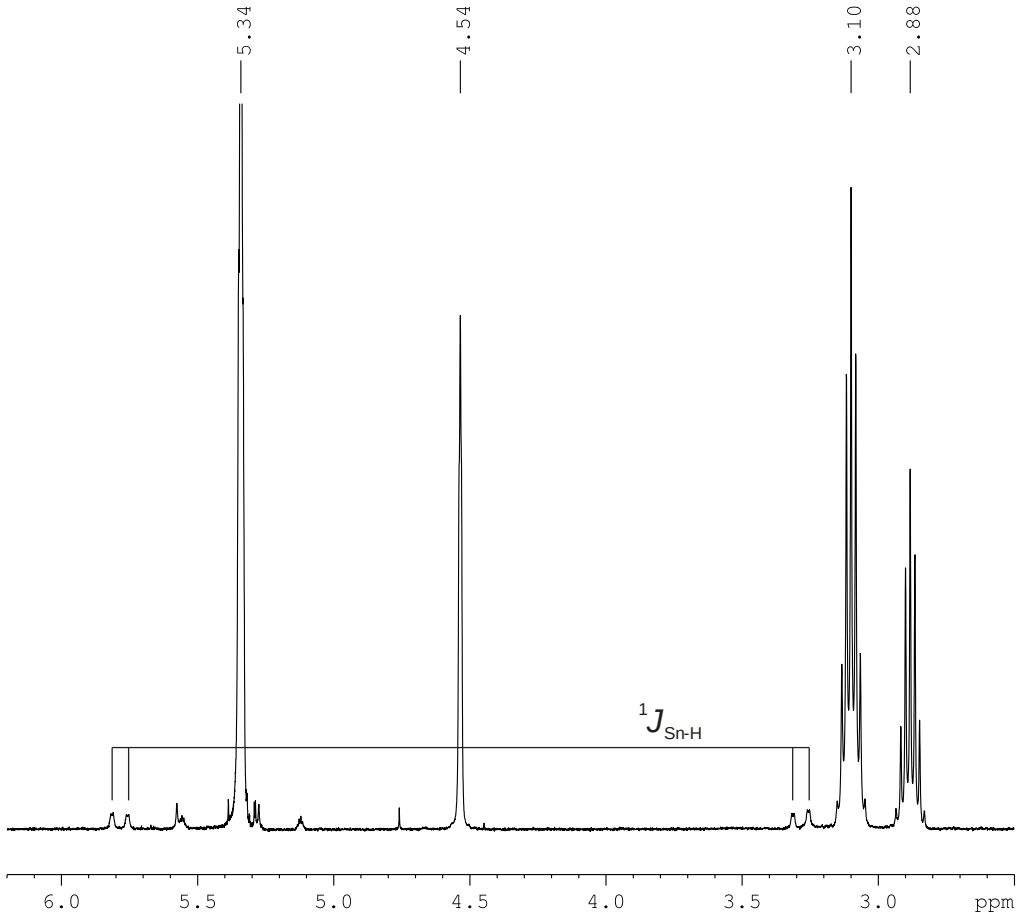


Figure S108: Part of the ^{1}H-NMR spectrum (600.13 MHz, Tol-$d_{8,}$ −40 °C) of **13** and simulation. The satellite spectra can be interpreted as A part of an AA'X spin system (one nmr active tin nucleus, $^{2}J_{H\text{-}H}$ = 13.5 Hz, $^{2}J_{Sn\text{-}H}$ = 190 Hz, $^{2}J_{Sn\text{-}H}$ = 44 Hz, LB 10.0 Hz) and A part of an AA'XX' spin system (two nmr active tin nuclei, same parameters, except LB 14.0 Hz). Statistical weight: Main signal (singulett) 0.70; AA'X spin system 0.27; AA'XX' spin system 0.03.

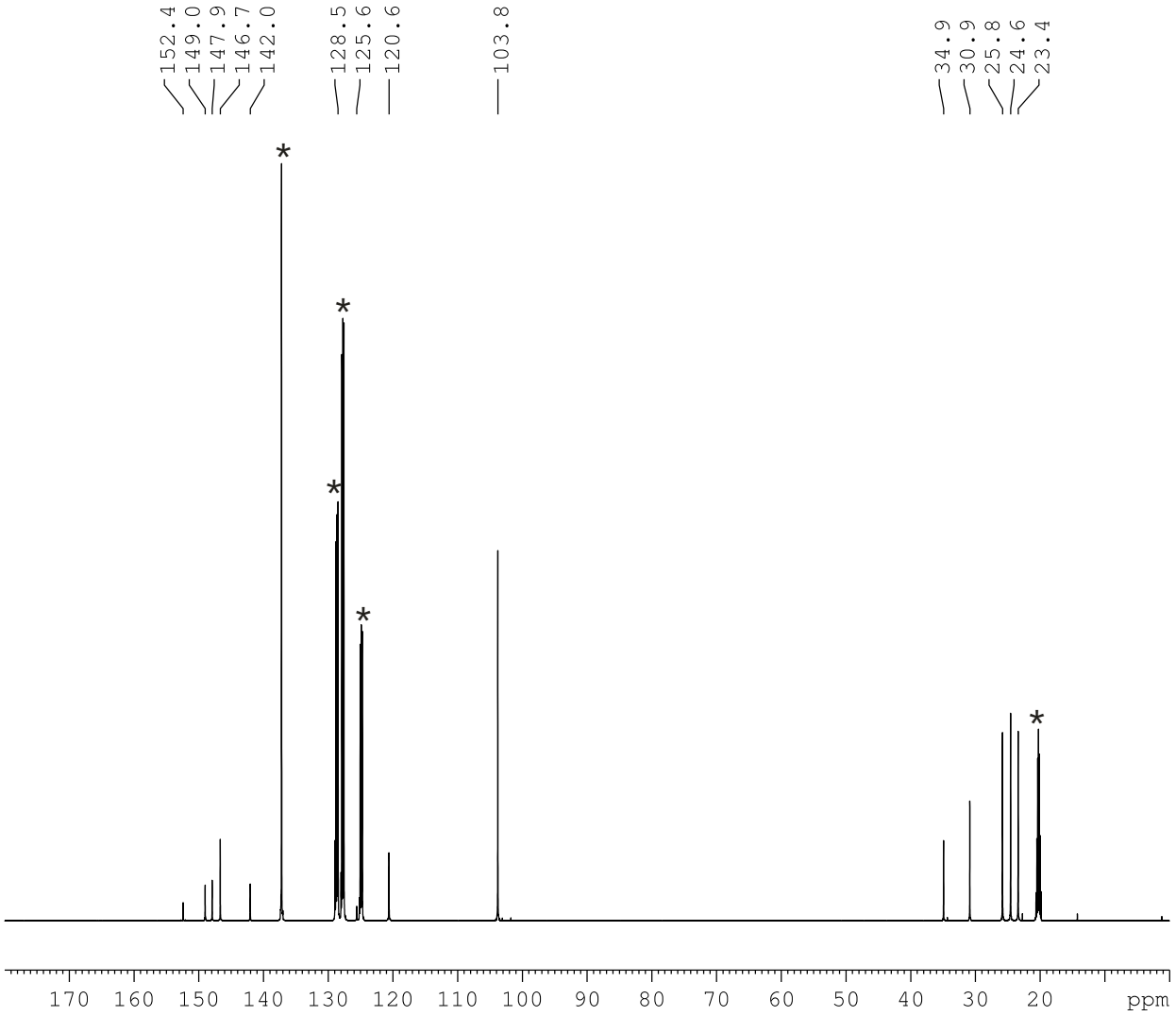
^{1}H NMR (tol-d_8, rt) of $[Cp_2Zr(\mu\text{-}H)(SnH_2Ar^*)]_2$ (**13**)




```
Current Data Parameters
NAME          MW919_400
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_           20201127
Time                9.17
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 52656
SOLVENT             C6D6
NS                    64
DS                     0
SWH            16025.641 Hz
FIDRES          0.304346 Hz
AQ             1.6428672 sec
RG                   322
DW                31.200 usec
DE                 6.00 usec
TE                299.2 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.60 usec
PL1                -3.00 dB
PL1W        16.03799057 W
SFO1        400.1100000 MHz

F2 - Processing parameters
SI                 65536
SF          400.1100000 MHz
WDW                   EM
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```

Figure S109. ^{1}H NMR of compound **13** (selected area).

$^{13}C\{^{1}H\}$ NMR (tol-d_8, −40 °C) of $[Cp_2Zr(\mu\text{-}H)(SnH_2Ar^*)]_2$ (**13**)

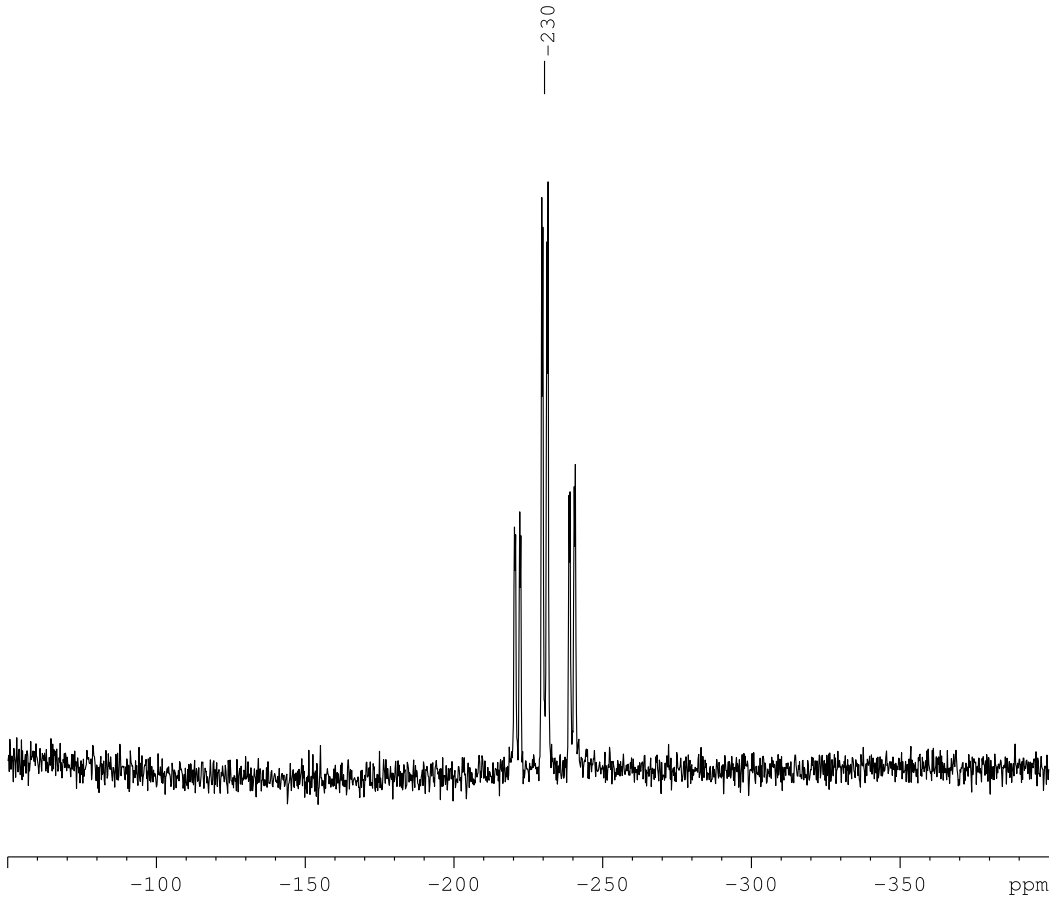



```
Current Data Parameters
NAME          MW919_600
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20201210
Time               10.46 h
INSTRUM            spect
PROBHD   Z126545_0027 (
PULPROG           udeft
TD                25902
SOLVENT             Tol
NS                 1536
DS                    0
SWH           36231.883 Hz
FIDRES         2.797613 Hz
AQ            0.3574476 sec
RG                189.6
DW               13.800 usec
DE               18.00 usec
TE               253.0 K
D1           4.00000000 sec
D12          0.00002000 sec
D20         20.00000000 sec
TD0                   1
SFO1        150.9178988 MHz
NUC1                13C
P1               10.00 usec
P13            2000.00 usec
P26             500.00 usec
PLW1         57.02700043 W
SPNAM[5]    Crp60comp.4
SPOAL5             0.500
SPOFFS5  0 Hz
SPW5          8.71310043 W
SPNAM[8] Crp60,0.5,20.1
SPOAL8             0.500
SPOFFS8  0 Hz
SPW8          8.71310043 W
SFO2         600.1300000 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2              70.00 usec
PLW2         23.41200066 W
PLW12         0.68803000 W

F2 - Processing parameters
SI                131072
SF           150.9028085 MHz
WDW                 EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 1.40
```

* tol-d_8

Figure S110. $^{13}C\{^{1}H\}$ NMR (-40°C) of compound **13**.

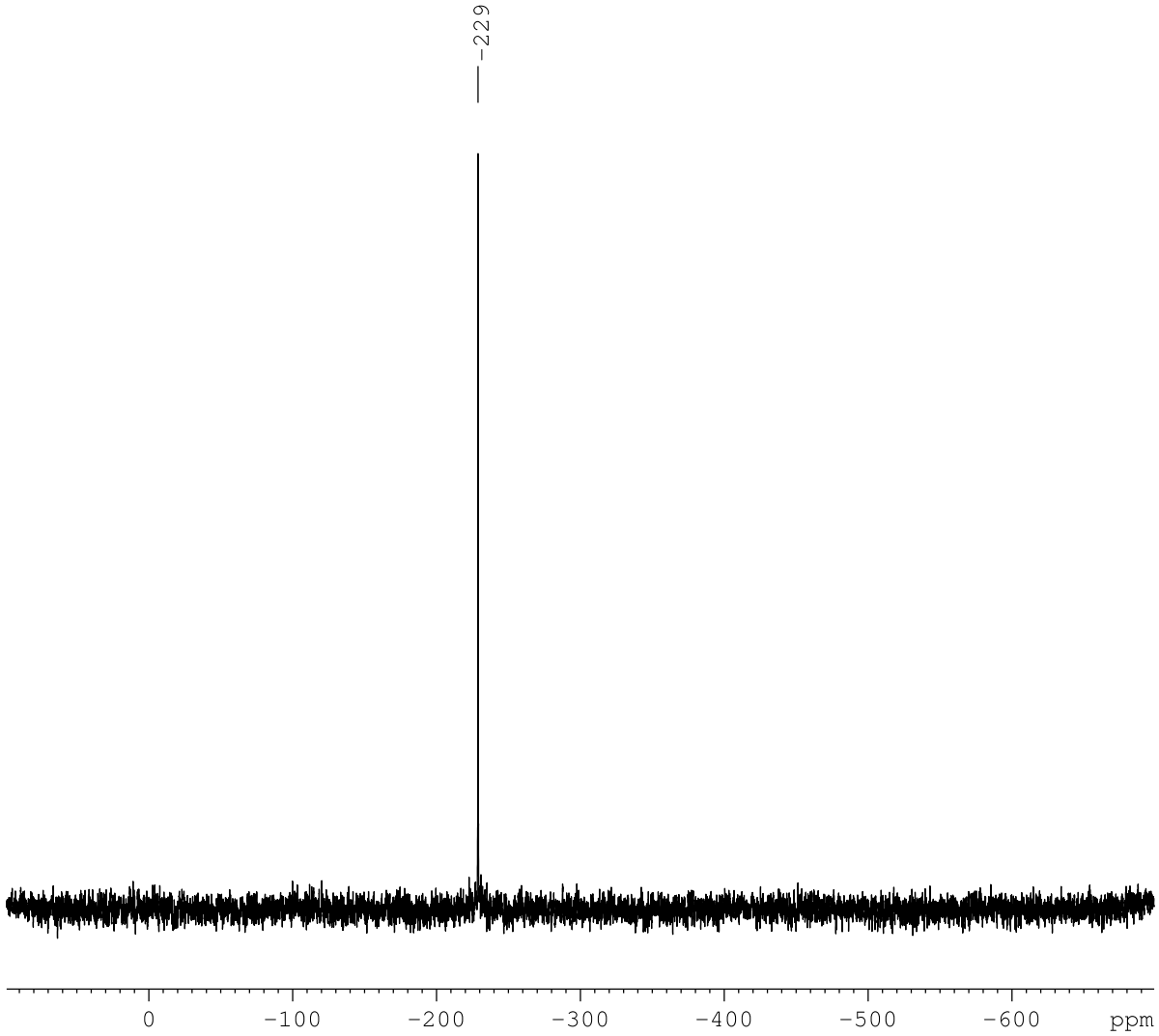
^{119}Sn NMR (tol-d_8, rt) of $[Cp_2Zr(\mu\text{-}H)(SnH_2Ar^*)]_2$ (**13**)




```
Current Data Parameters
NAME      MW919_300_Sn addiert
EXPNO                  16
PROCNO                  1

F2 - Acquisition Parameters
Date_            20201211
Time                19.11 h
INSTRUM             spect
PROBHD    Z104275_0338 (
PULPROG              zg30
TD                   8918
SOLVENT               Tol
NS                 384000
DS                      1
SWH             89285.711 Hz
FIDRES          20.023708 Hz
AQ              0.0499408 sec
RG                 204.67
DW                  5.600 usec
DE                  6.50 usec
TE                 298.0 K
D1            0.02000000 sec
TD0                     1
SFO1         111.8979900 MHz
NUC1                119Sn
P0                  4.03 usec
P1                 12.10 usec
PLW1         12.00000000 W

F2 - Processing parameters
SI                   4096
SF           111.9203740 MHz
WDW                    EM
SSB       0
LB        0 Hz
GB        0
PC                  1.40
```

Figure S111. ^{119}Sn NMR of compound **13**.

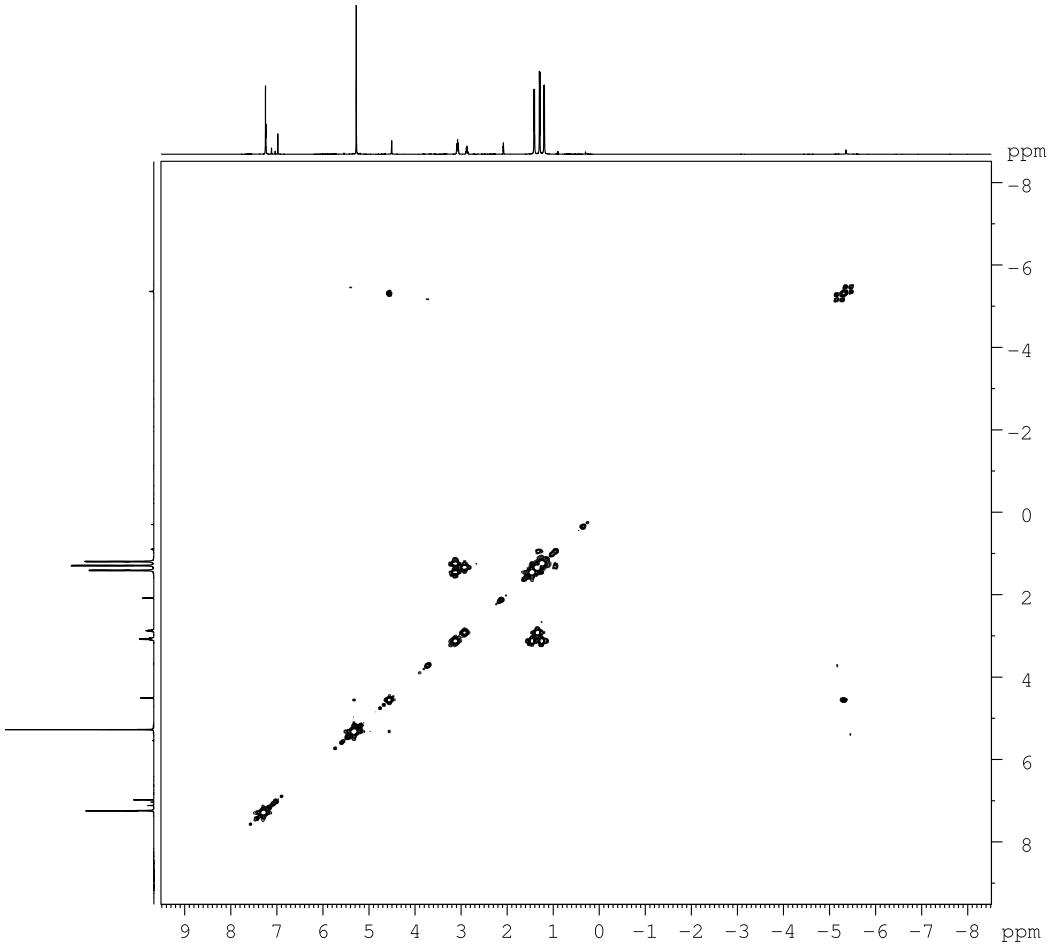
$^{119}Sn\{^{1}H\}$ NMR (tol-d_8, rt) of $[Cp_2Zr(\mu\text{-}H)(SnH_2Ar^*)]_2$ (**13**)




```
Current Data Parameters
NAME         MW898_300Sn
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201105
Time               18.26 h
INSTRUM             spect
PROBHD   Z104275_0338 (
PULPROG           zgig30
TD                 39186
SOLVENT             C6D6
NS                  5000
DS                     4
SWH            89285.711 Hz
FIDRES          4.557021 Hz
AQ             0.2194416 sec
RG                204.67
DW                 5.600 usec
DE                 6.50 usec
TE                298.0 K
D1           0.10000000 sec
D11          0.03000000 sec
TD0                    1
SFO1         111.8867977 MHz
NUC1                119Sn
P0                 4.03 usec
P1                12.10 usec
PLW1         12.00000000 W
SFO2         300.1312005 MHz
NUC2                   1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2          8.26509953 W
PLW12         0.20000000 W

F2 - Processing parameters
SI                 65536
SF           111.9203738 MHz
WDW                   EM
SSB       0
LB                10.00 Hz
GB        0
PC                 1.40
```

Figure S112. $^{119}Sn\{^{1}H\}$ NMR of compound **13**.

$^{1}H,^{1}H$ COSY NMR (tol-d_8, −40 °C) of $[Cp_2Zr(\mu\text{-}H)(SnH_2Ar^*)]_2$ (**13**)




```
Current Data Parameters
NAME         MW919_600NM
EXPNO                 13
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201210
Time              11.31 h
INSTRUM             spect
PROBHD   Z126545_0027 (
PULPROG       cosygpppqf
TD                  2048
SOLVENT              Tol
NS                     4
DS                    16
SWH           10822.511 Hz
FIDRES        10.568858 Hz
AQ            0.0946176 sec
RG                58.62
DW               46.200 usec
DE               10.00 usec
TE                253.0 K
D0           0.00000300 sec
D1           2.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
D13          0.00000400 sec
D16          0.00020000 sec
IN0          0.00009240 sec
TDav                   1
SFO1        600.1303001 MHz
NUC1                  1H
P0                12.00 usec
P1                12.00 usec
P17             2500.00 usec
PLW1        23.41200066 W
PLW10        5.39410019 W
GPNAM[1]     SMSQ10.100
GPZ1              10.00 %
P16             1000.00 usec

F1 - Acquisition parameters
TD                   256
SFO1            600.1303 MHz
FIDRES         84.550865 Hz
SW                18.034 ppm
FnMODE                QF

F2 - Processing parameters
SI                   1024
SF          600.1300000 MHz
WDW                 QSINE
SSB       0
LB        0 Hz
GB        0
PC                  1.00

F1 - Processing parameters
SI                   1024
MC2                    QF
SF          600.1300000 MHz
WDW                 QSINE
SSB       0
LB        0 Hz
GB        0
```

Figure S113. ^{1}H, ^{1}H COSY NMR (-40°C) of compound **13**.

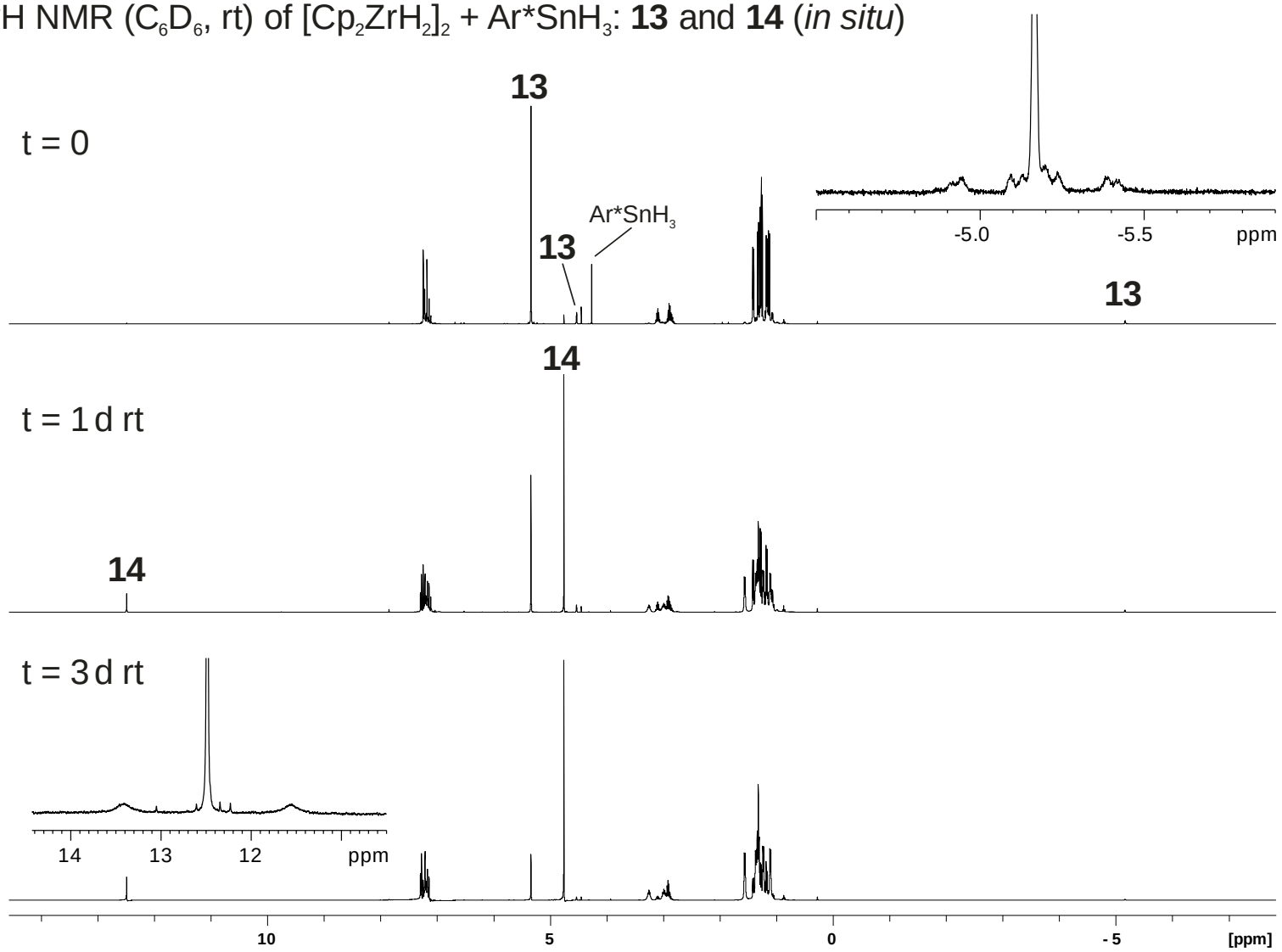


Figure S114. [1]H NMR: Formation of **14**, reaction between [$(Cp_2ZrH_2)_2$] and [Ar^*SnH_3], with intermediate **13**.

IR-Spectroscopy

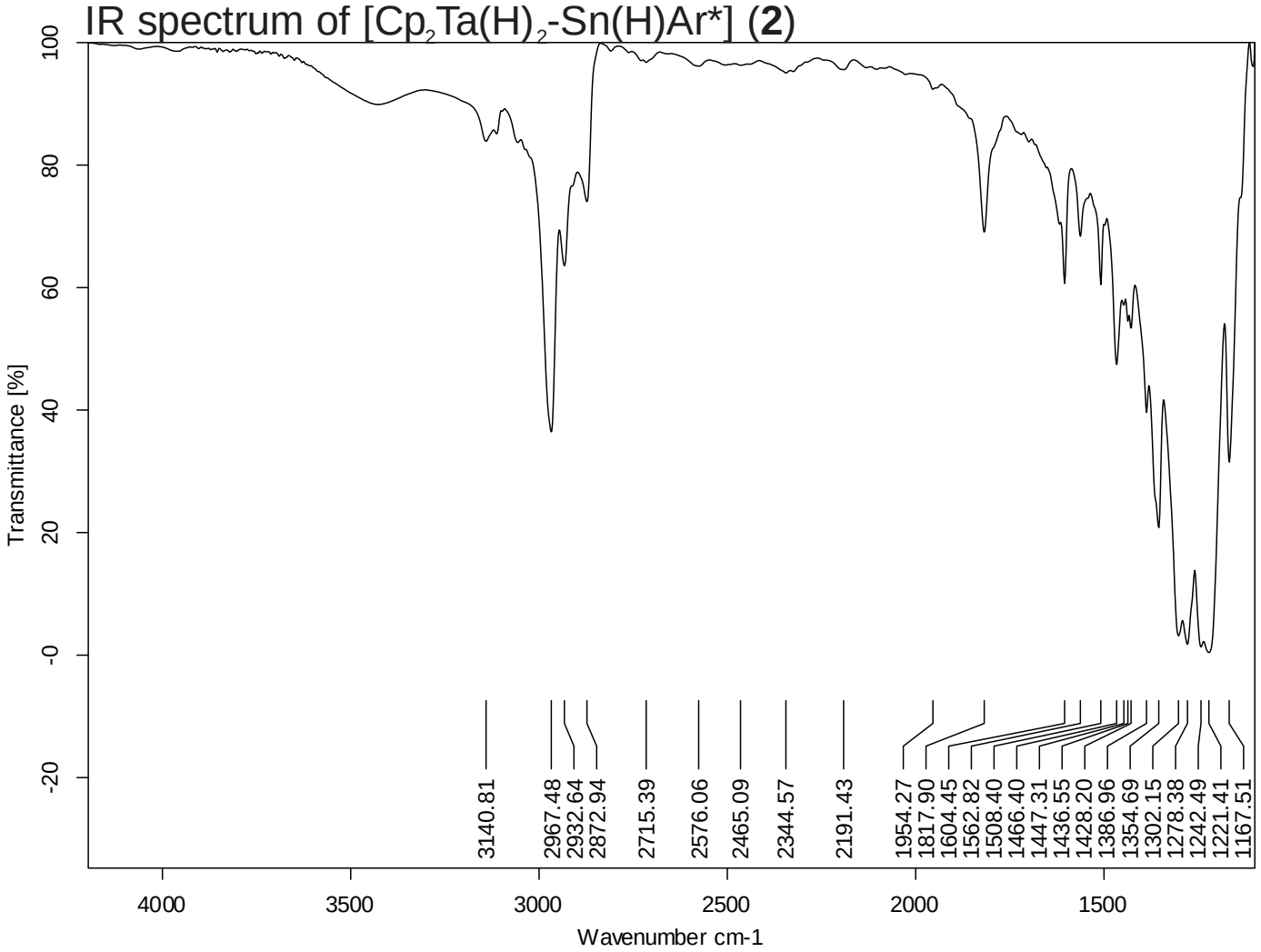


Figure S115. IR spectrum of compound **2**.

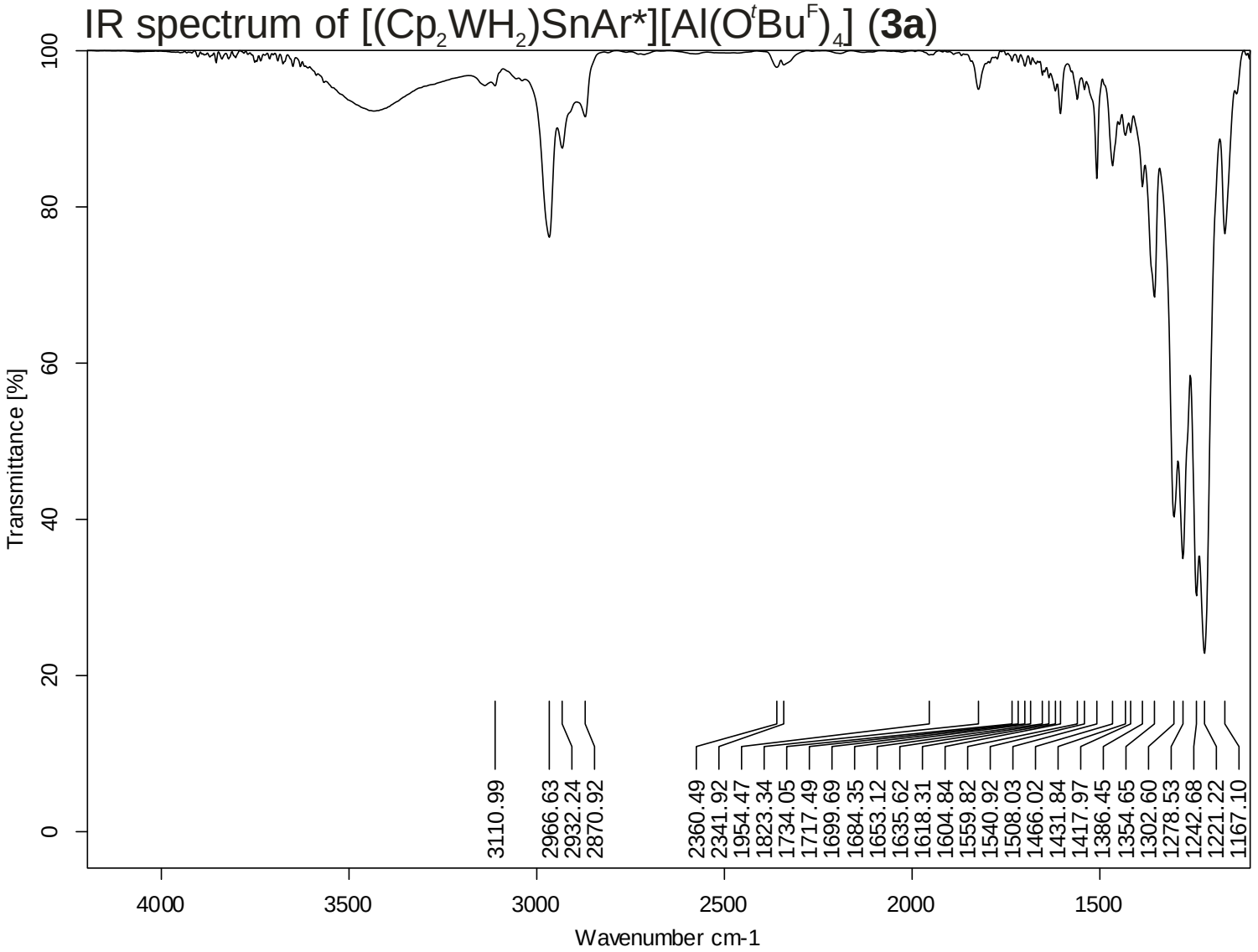


Figure S116. IR spectrum of compound **3a**.

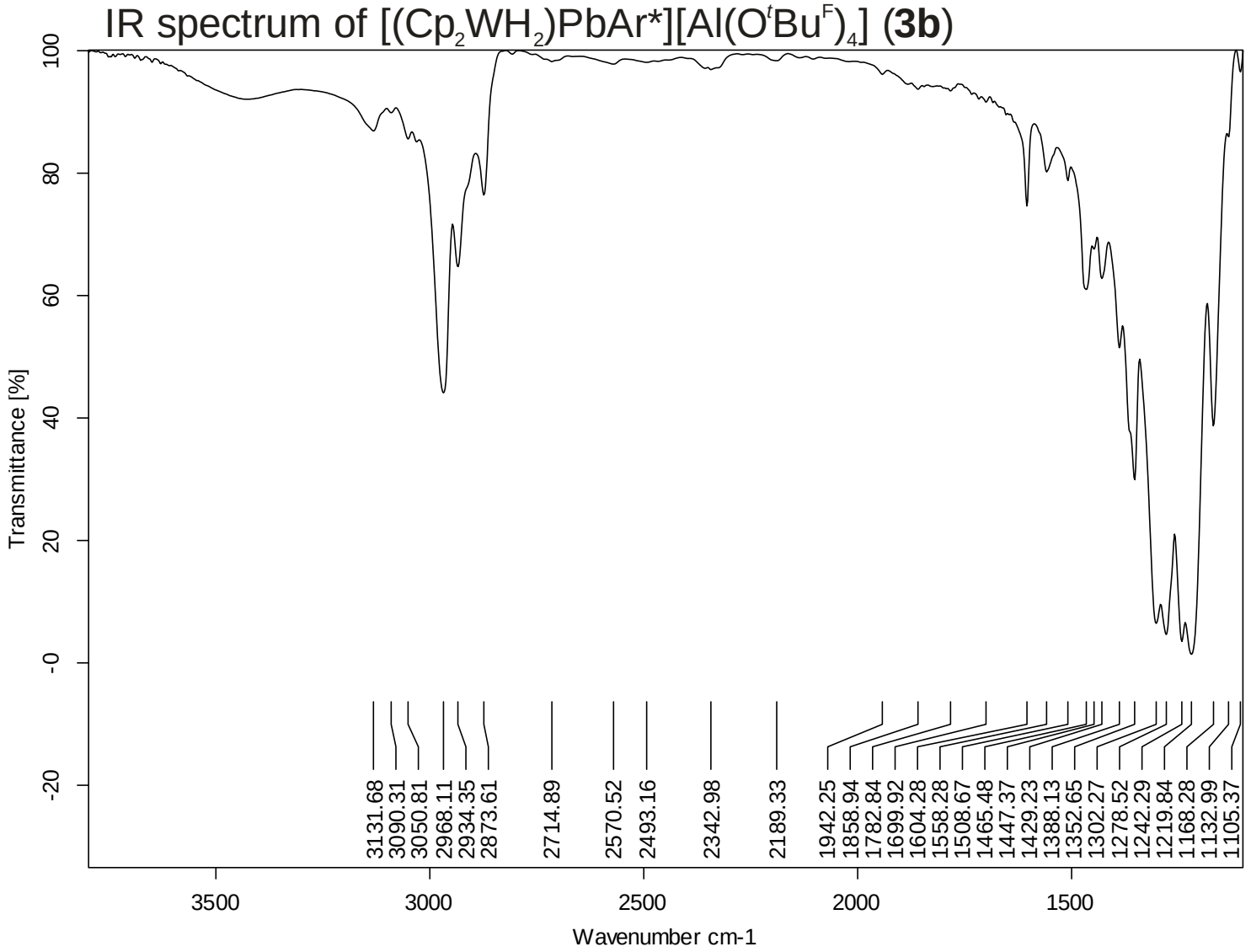


Figure S117. IR spectrum of compound **3b**.

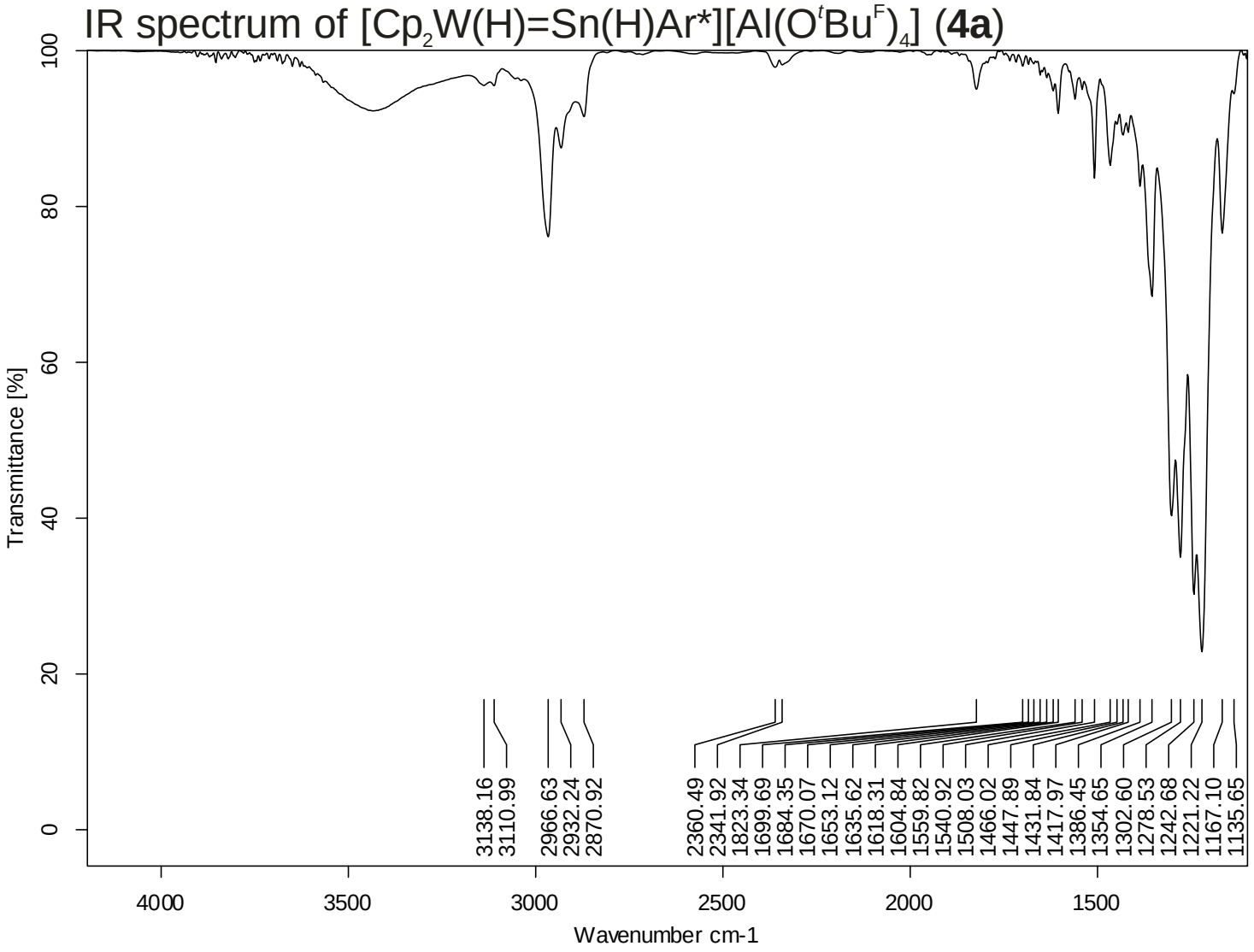


Figure S118. IR spectrum of compound **4a**.

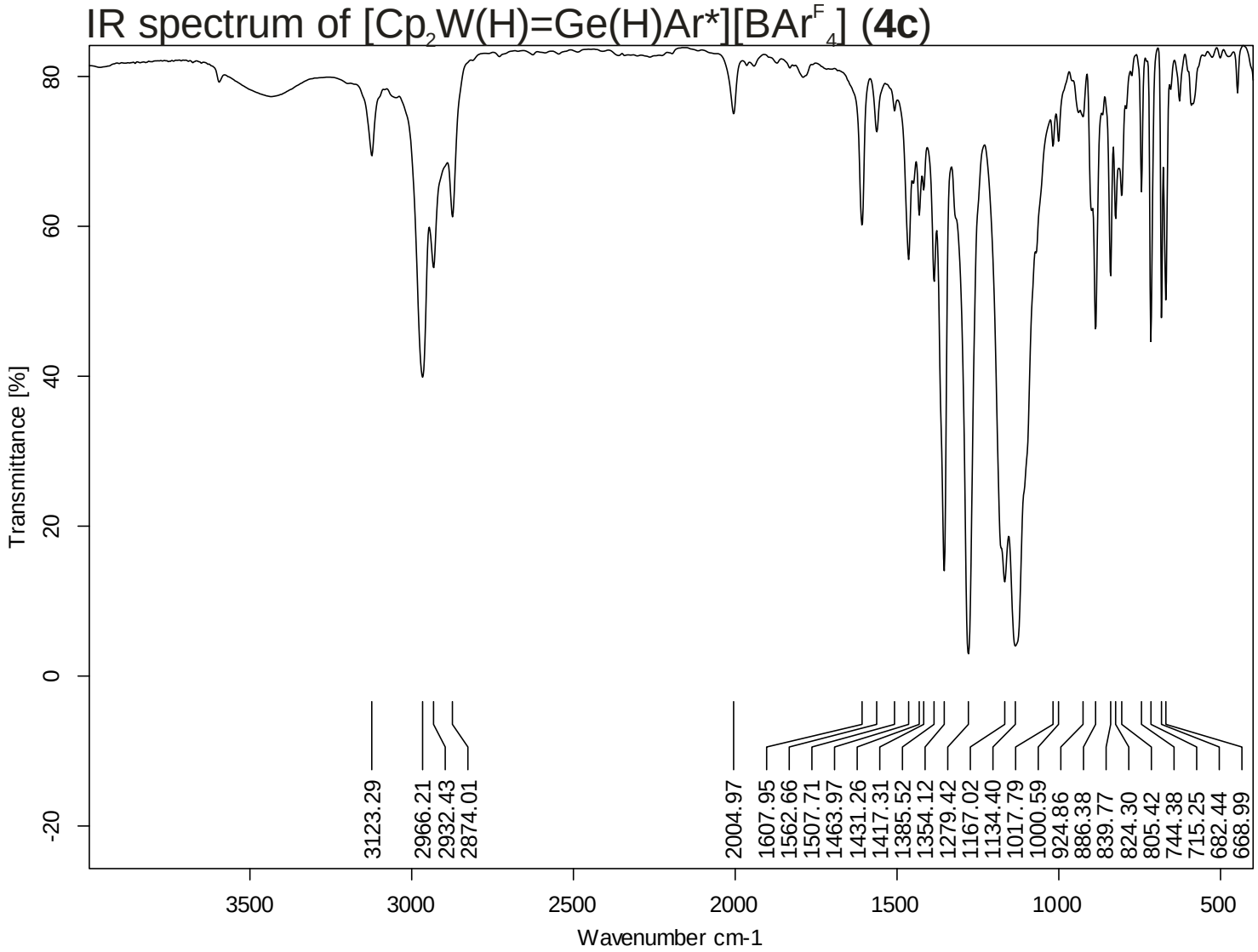


Figure S119. IR spectrum of compound **4c**.

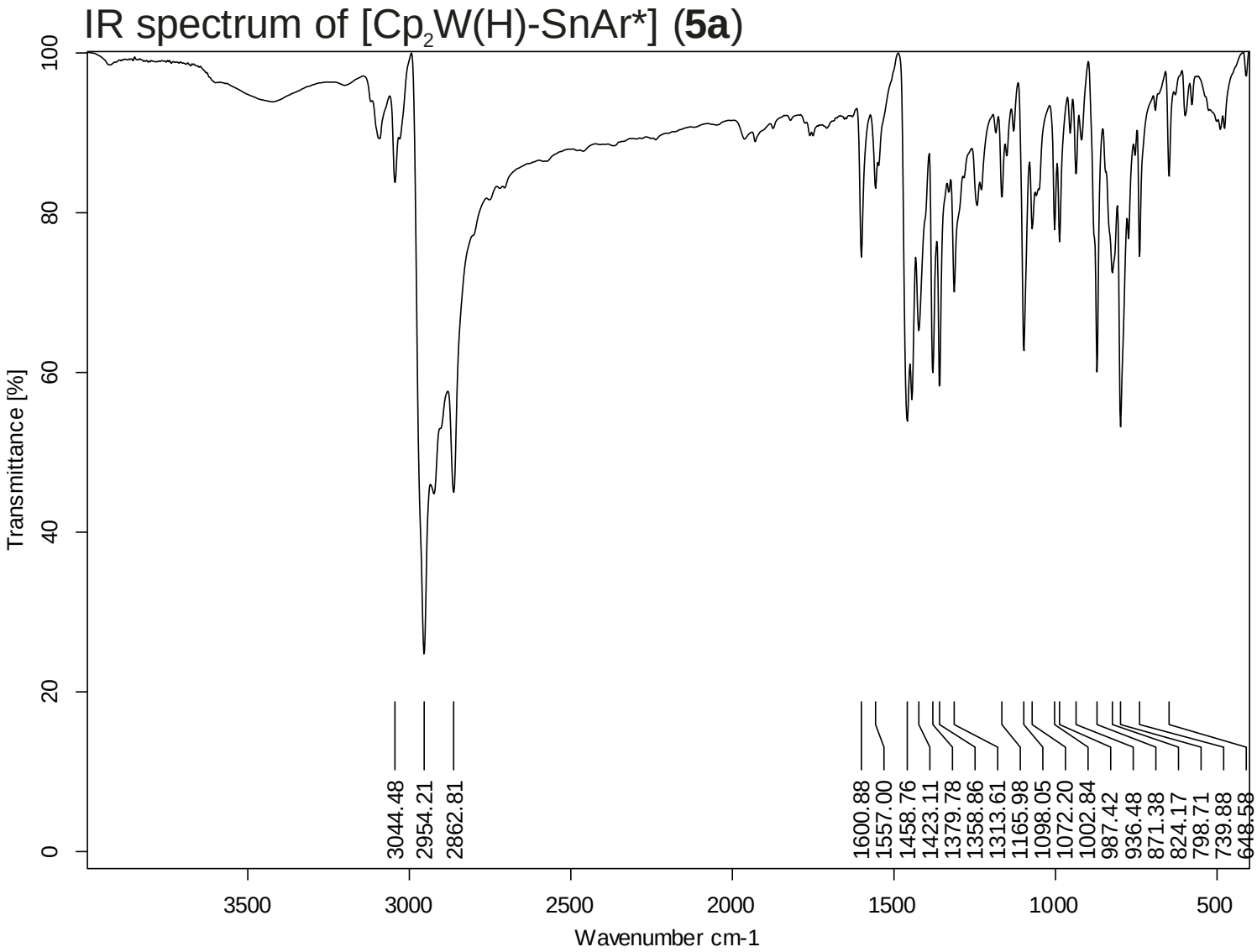


Figure S120. IR spectrum of compound **5a**.

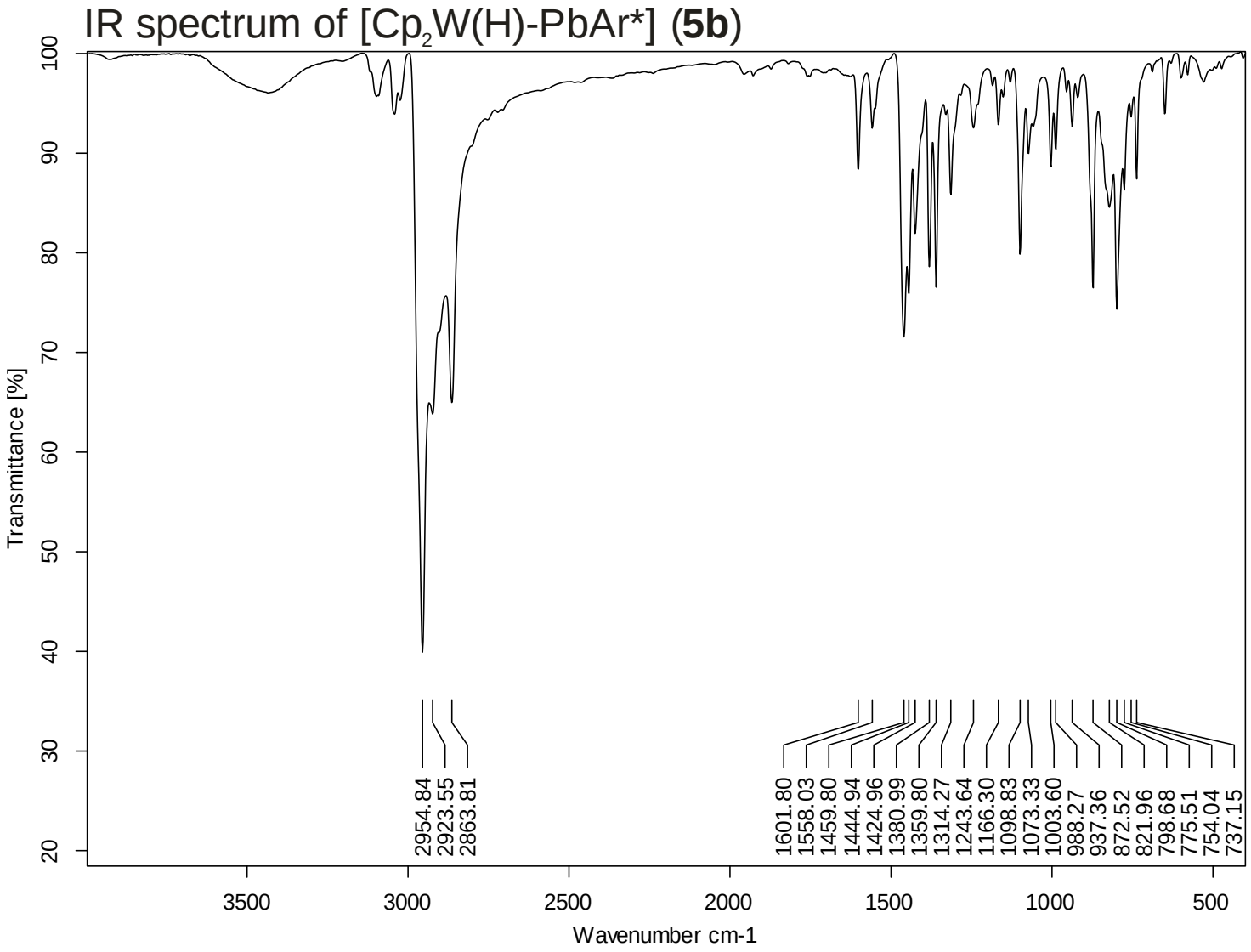


Figure S121. IR spectrum of compound **5b**.

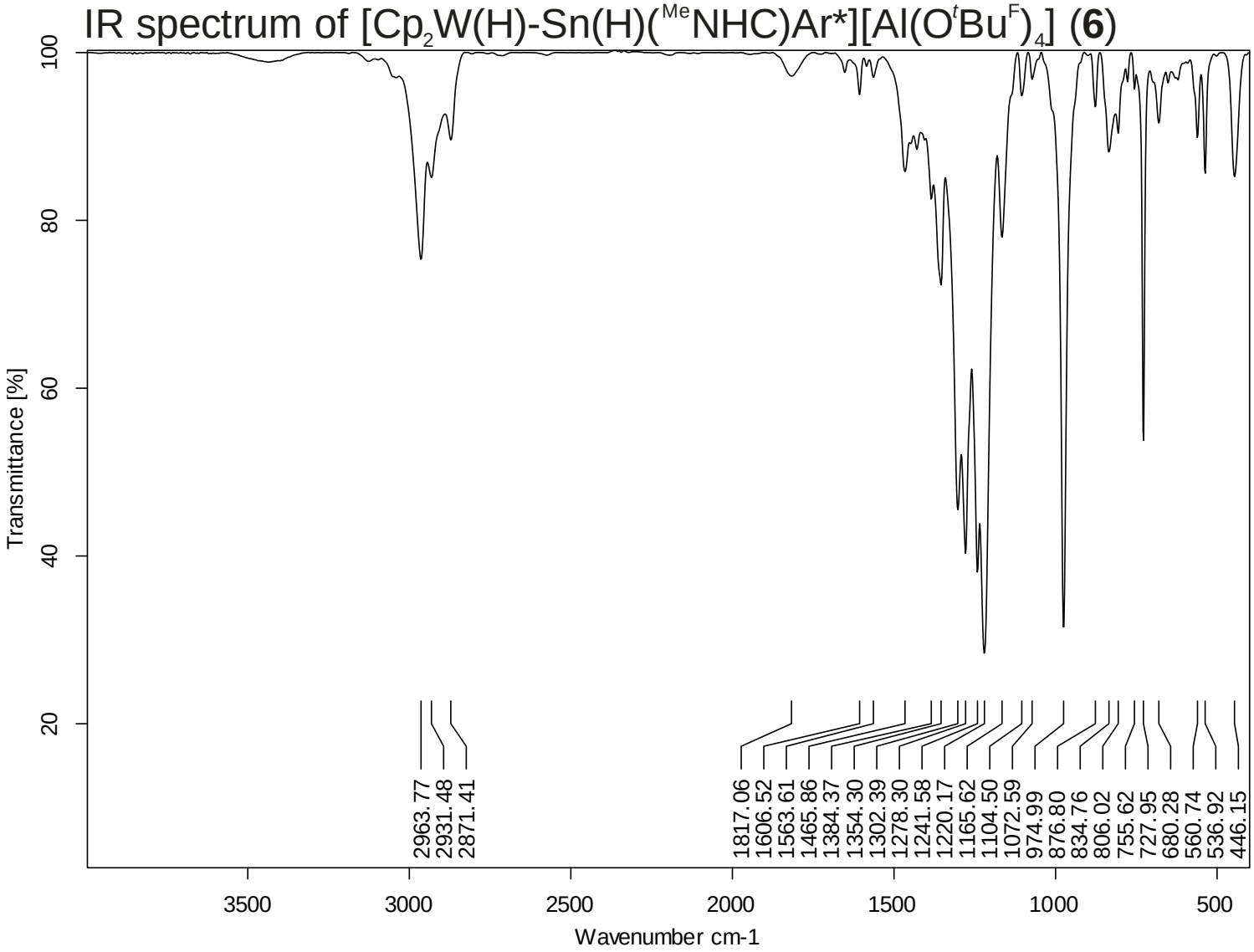


Figure S122. IR spectrum of compound **6**.

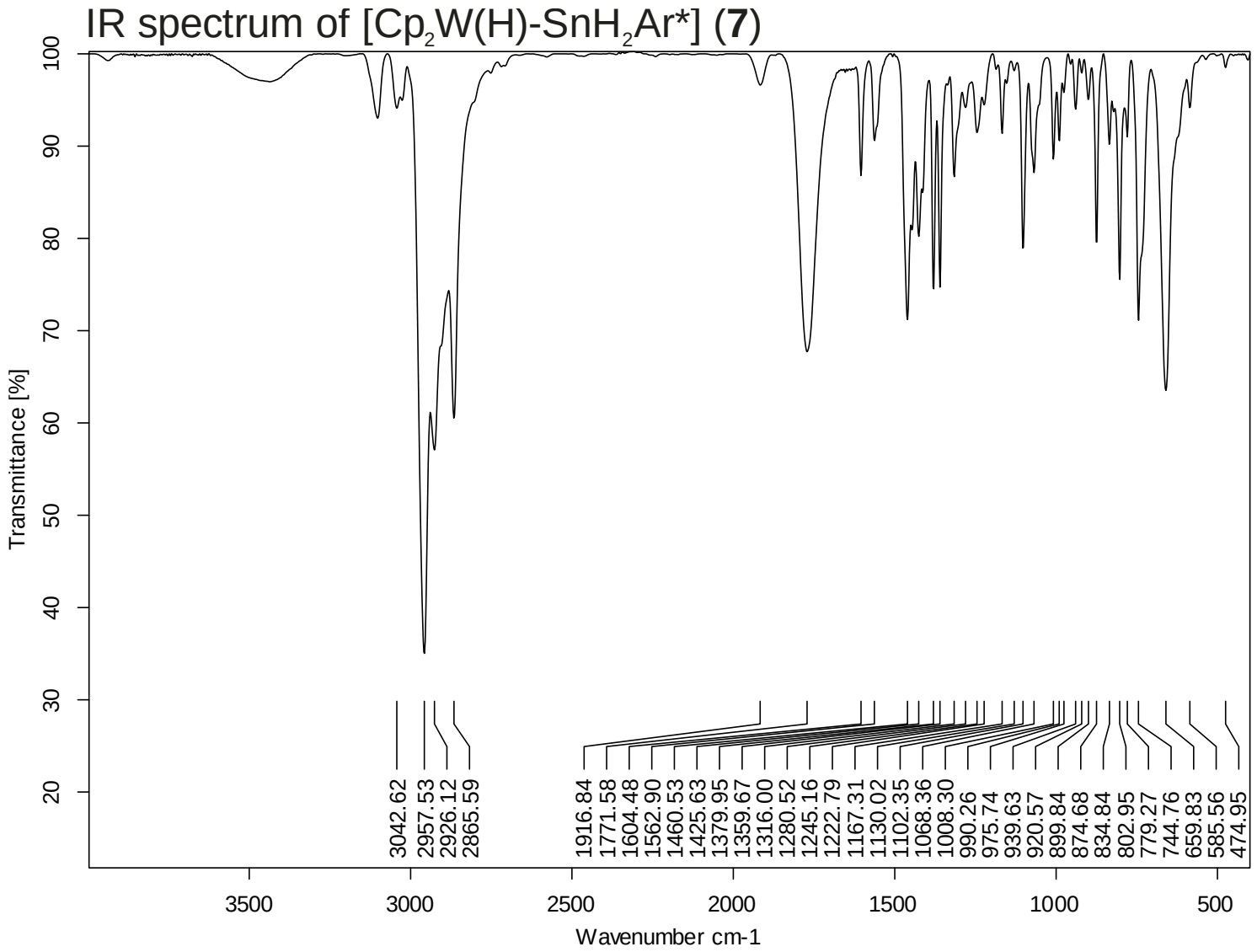


Figure S123. IR spectrum of compound **7**.

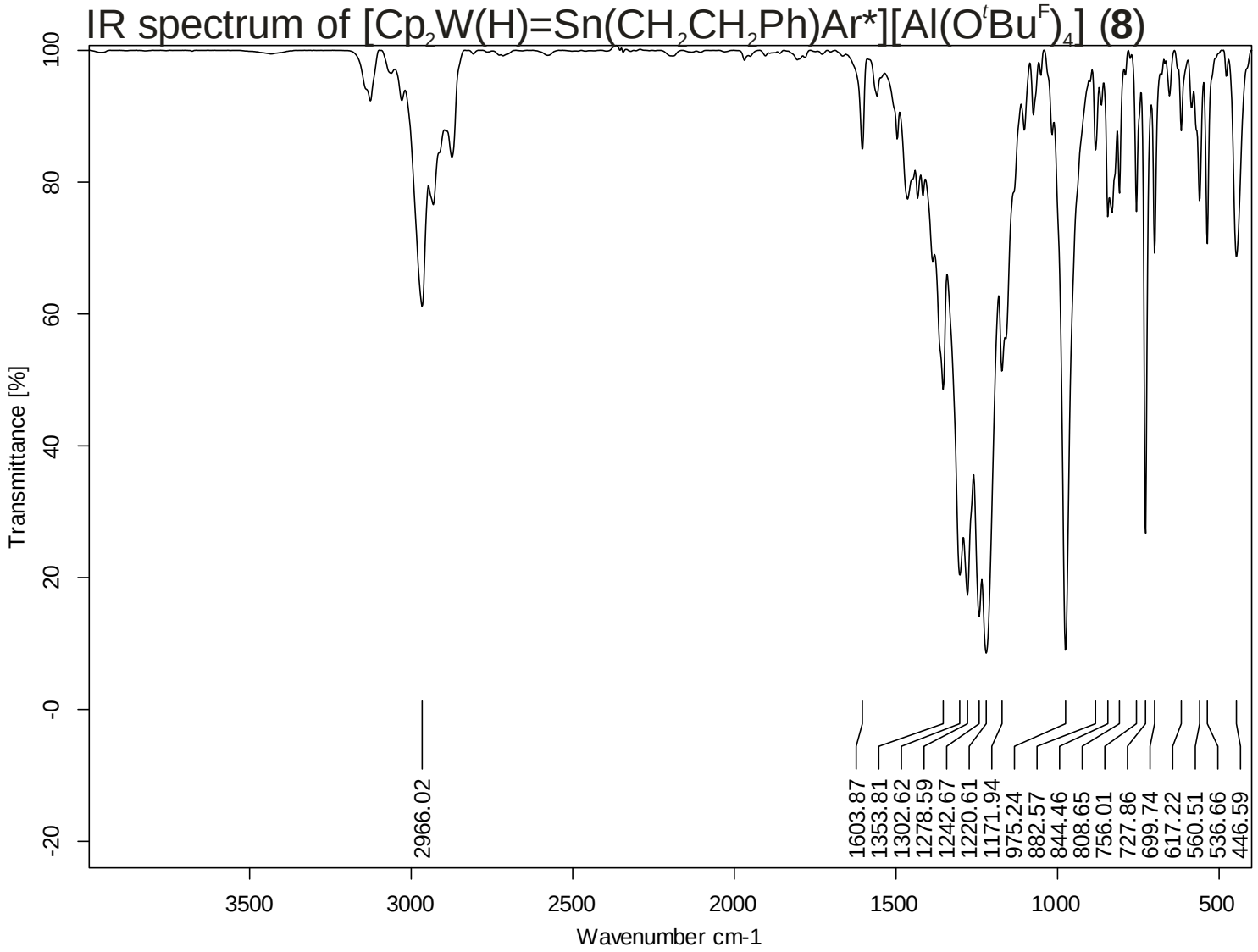


Figure S124. IR spectrum of compound **8**.

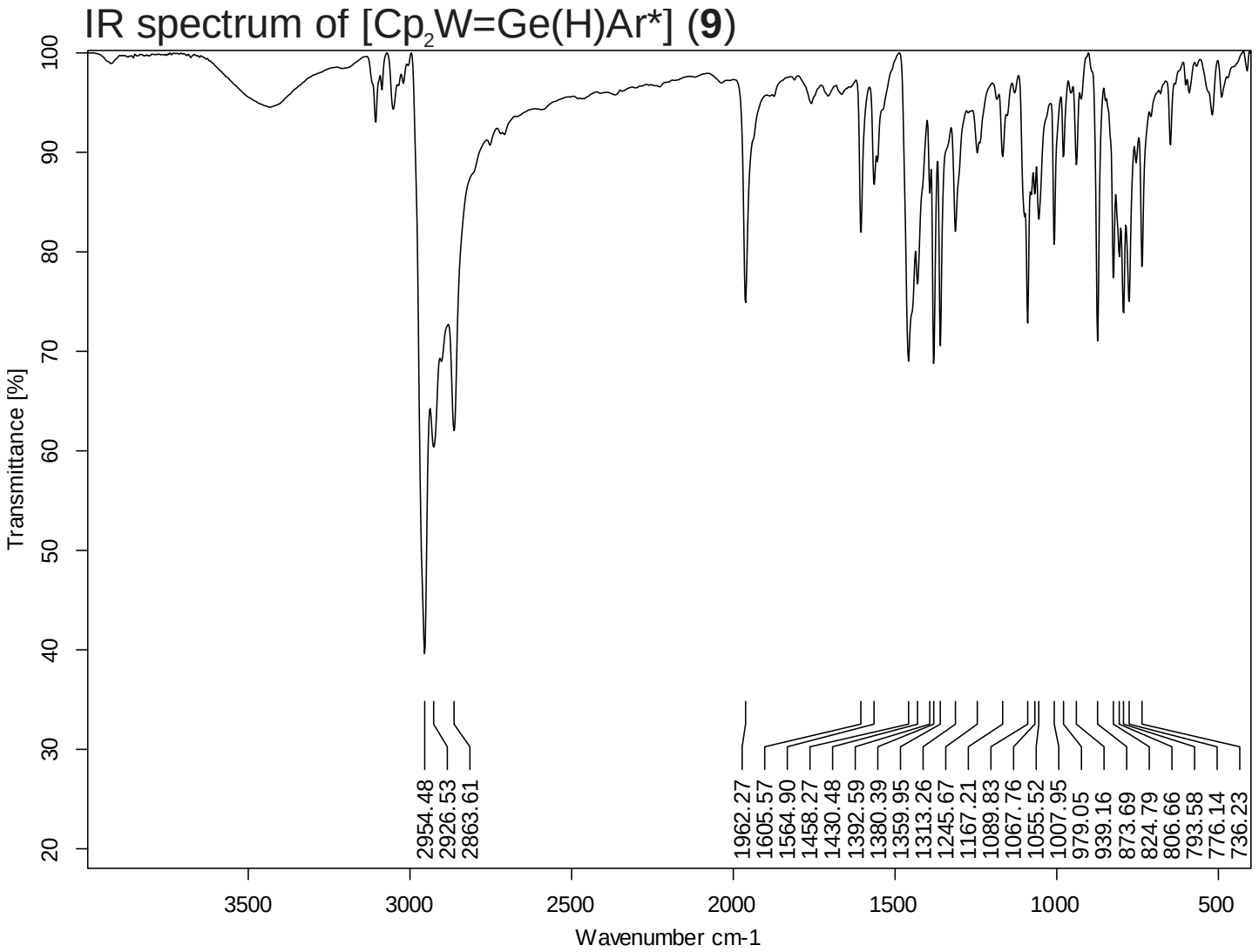


Figure S125. IR spectrum of compound **9**.

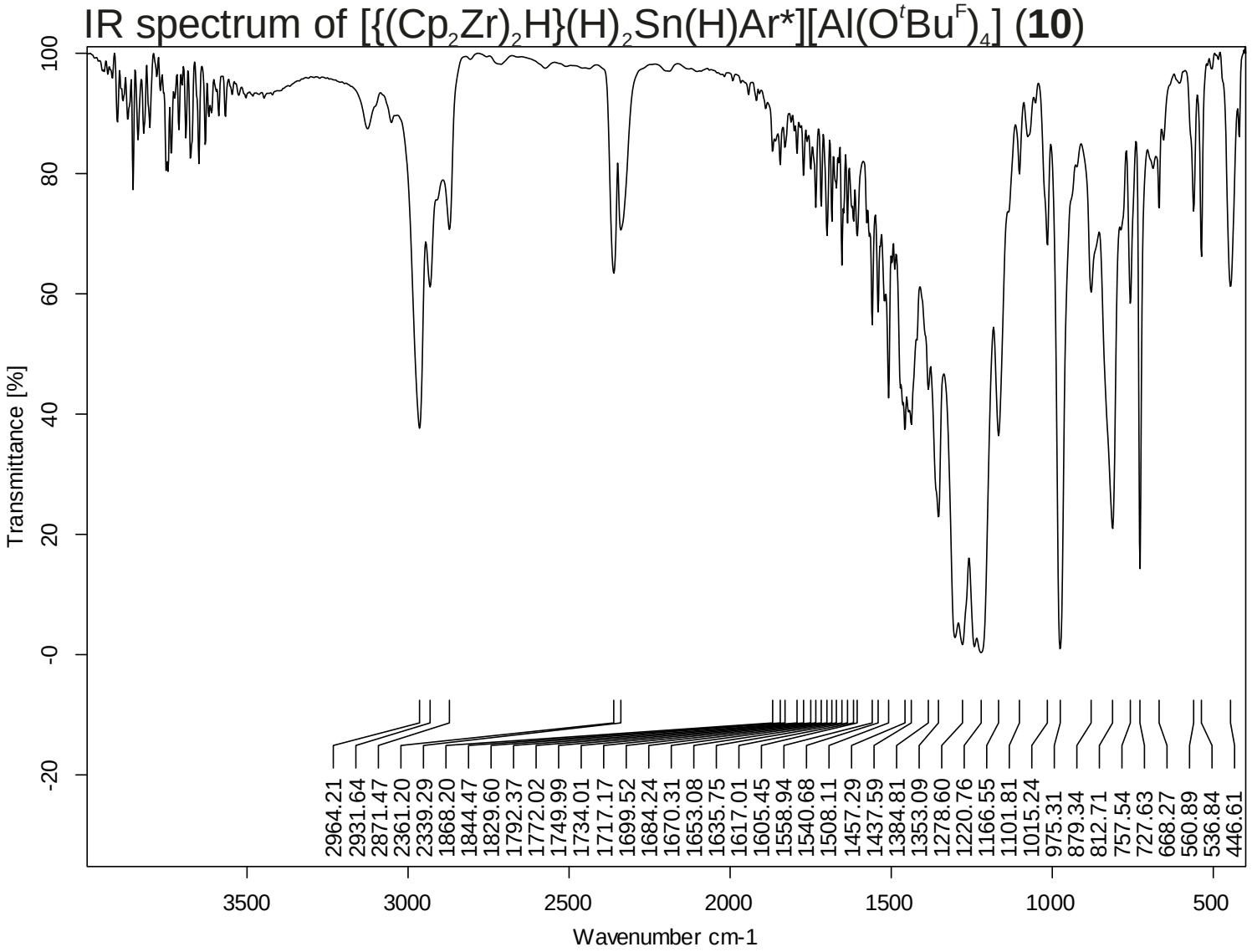


Figure S126. IR spectrum of compound **10**.

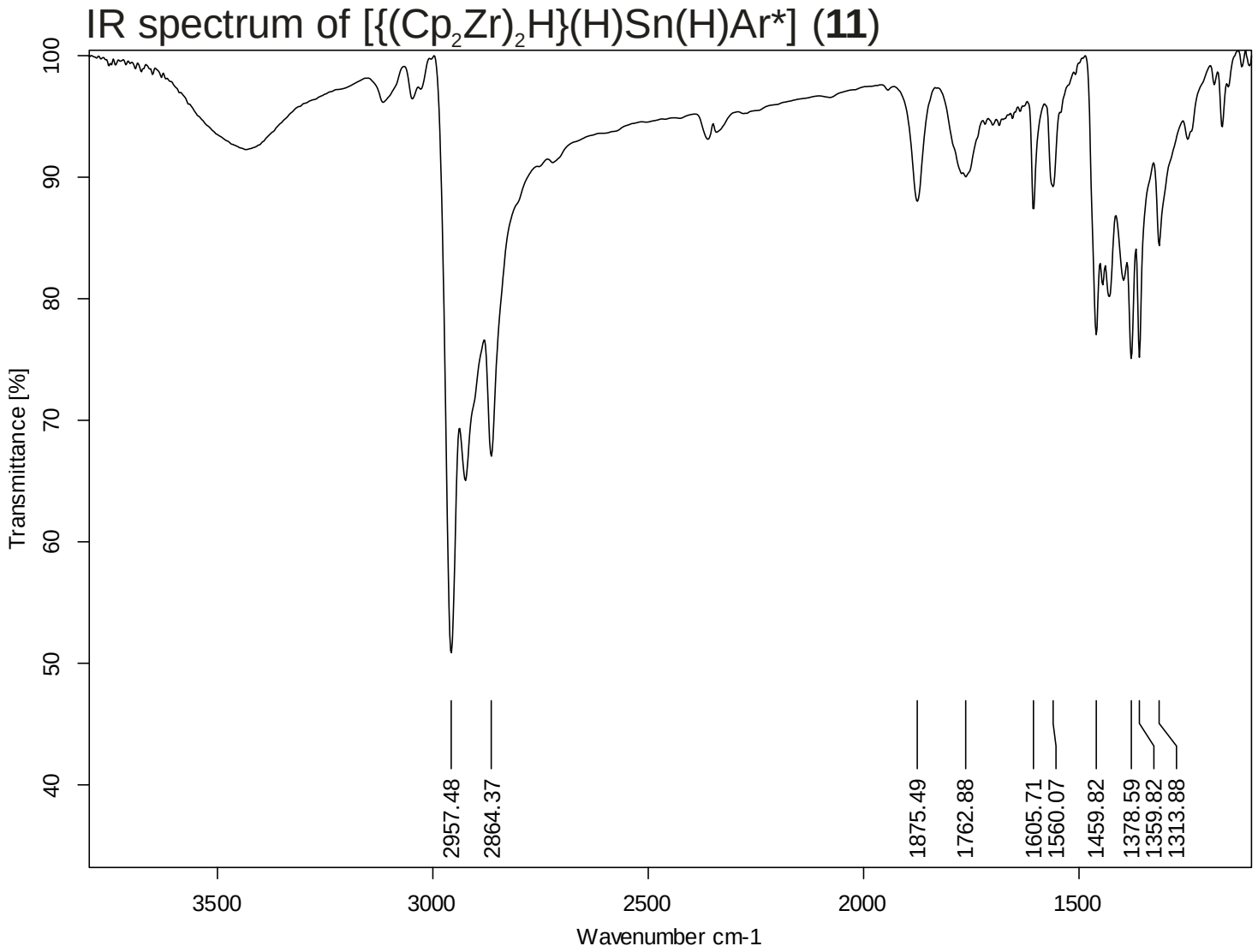


Figure S127. IR spectrum of compound **11**.

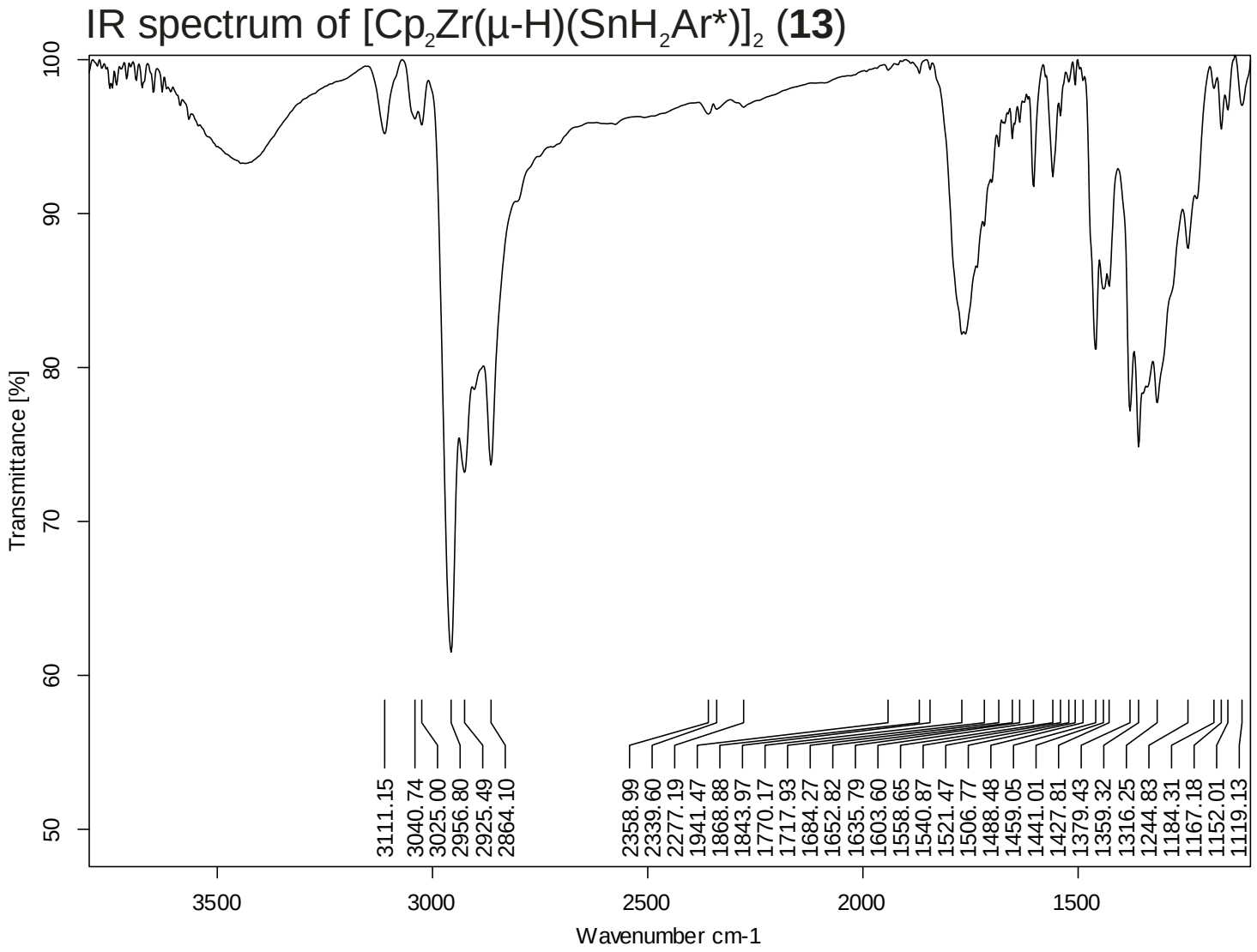


Figure S128. IR spectrum of compound **13**.

UV-Vis spectroscopy

UV-Vis spectrum of $[(Cp_2WH_2)SnAr^*][Al(O^tBu^F)4]$ (**3a**) in toluene at rt (1.1×10^{-4} mol/l)

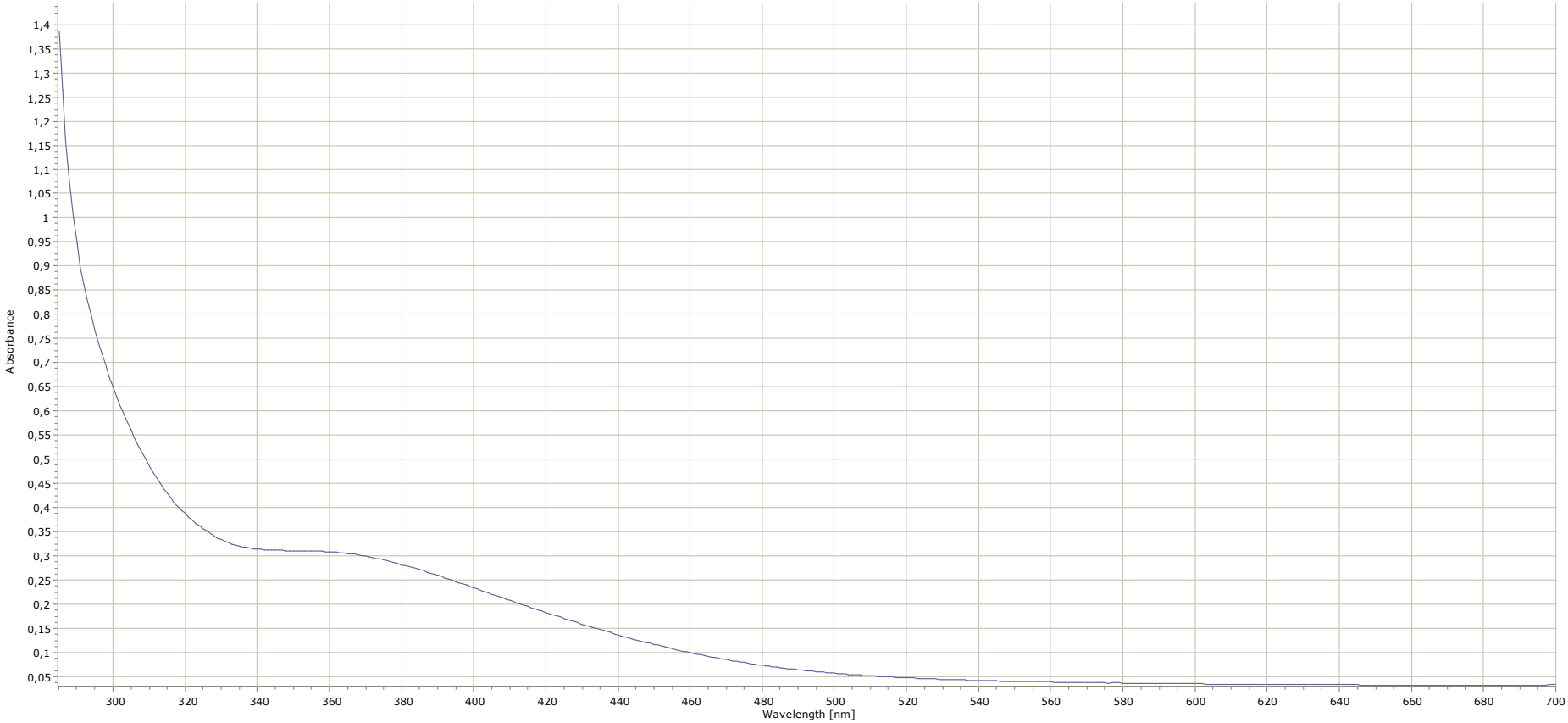


Figure S129. UV-Vis spectrum of compound **3a**.

UV-Vis spectrum of [(Cp_2WH_2)PbAr*][Al(O^tBu^F)4] (**3b**) in toluene at rt (1.0×10^{-4} mol/l)

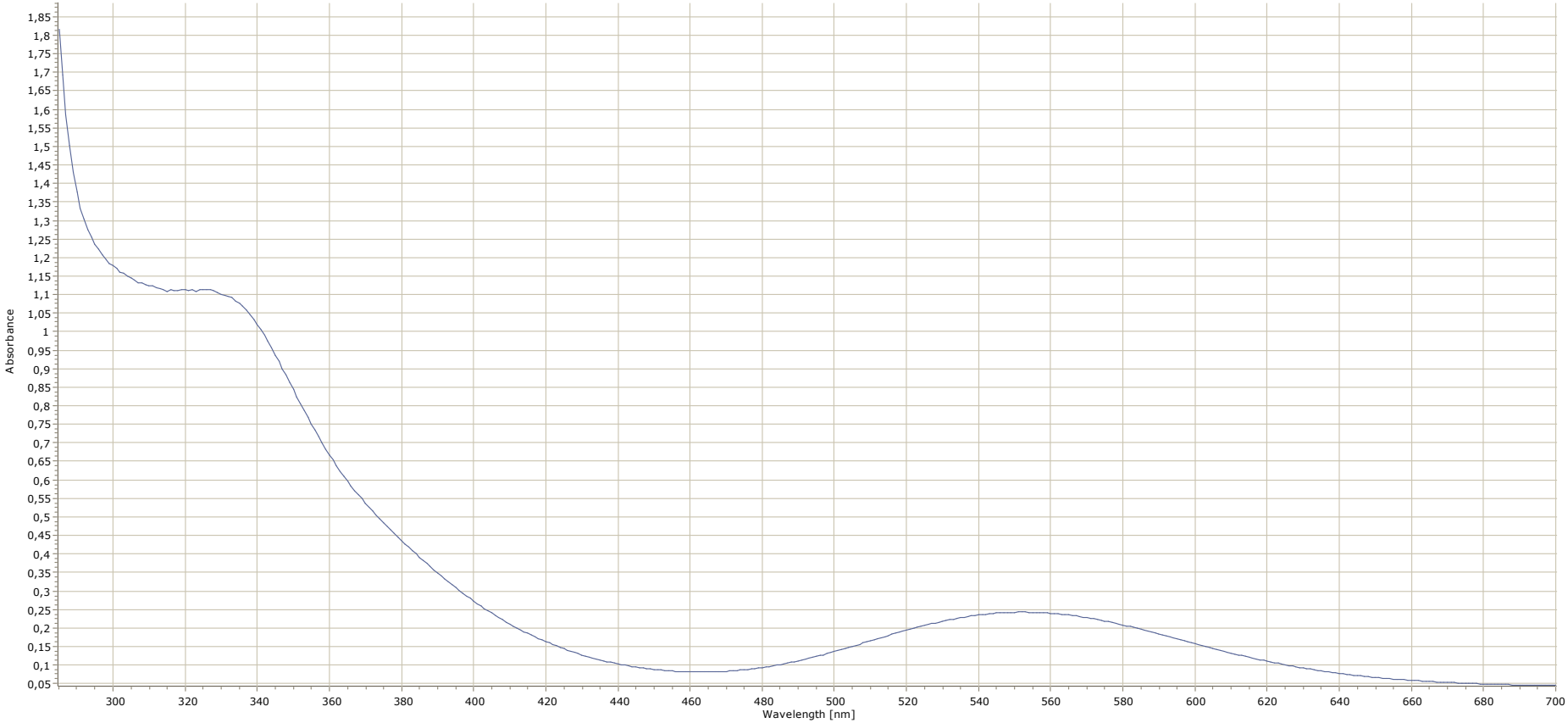


Figure S130. UV-Vis spectrum of compound **3b**.

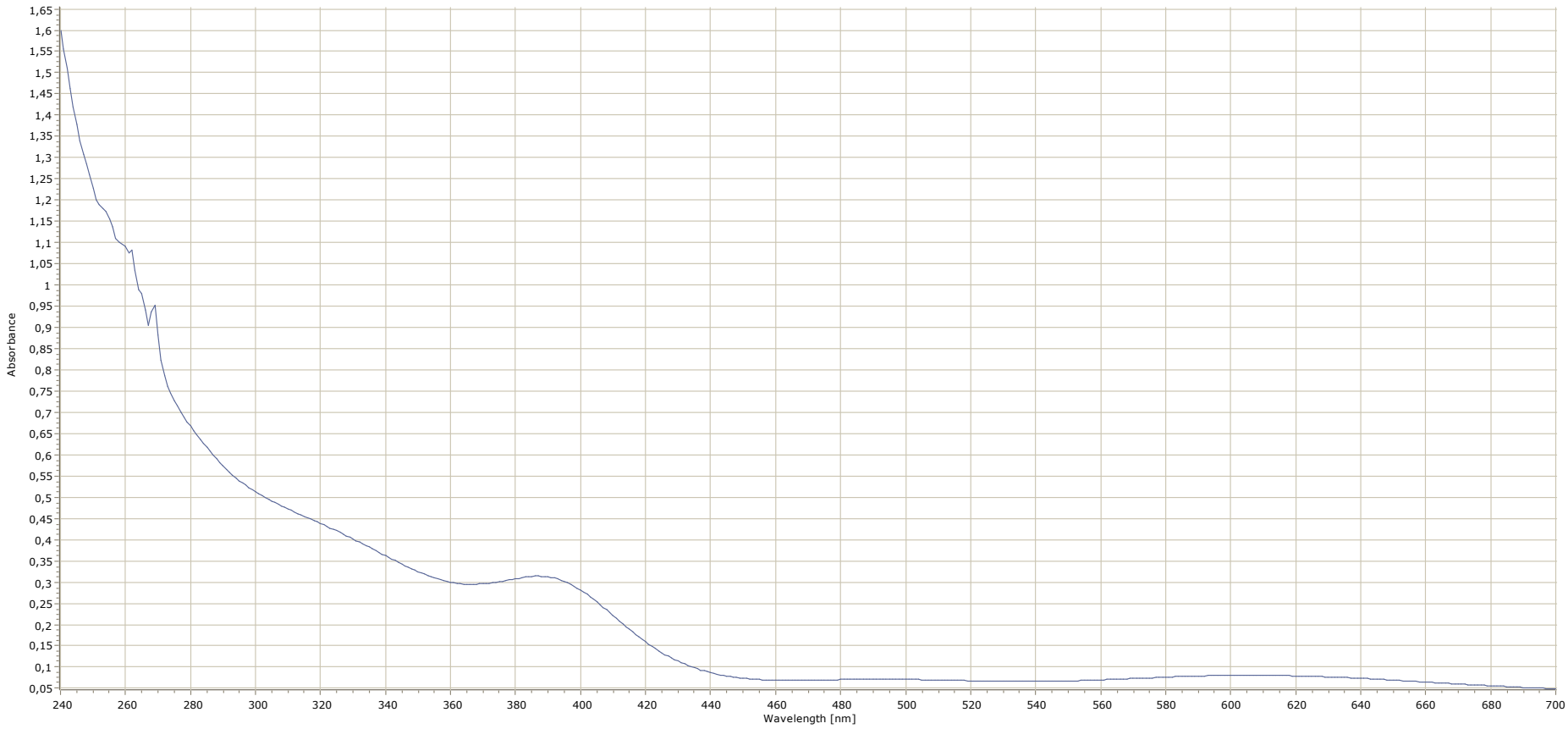


Figure S131. UV-Vis spectrum of compound **5a**.

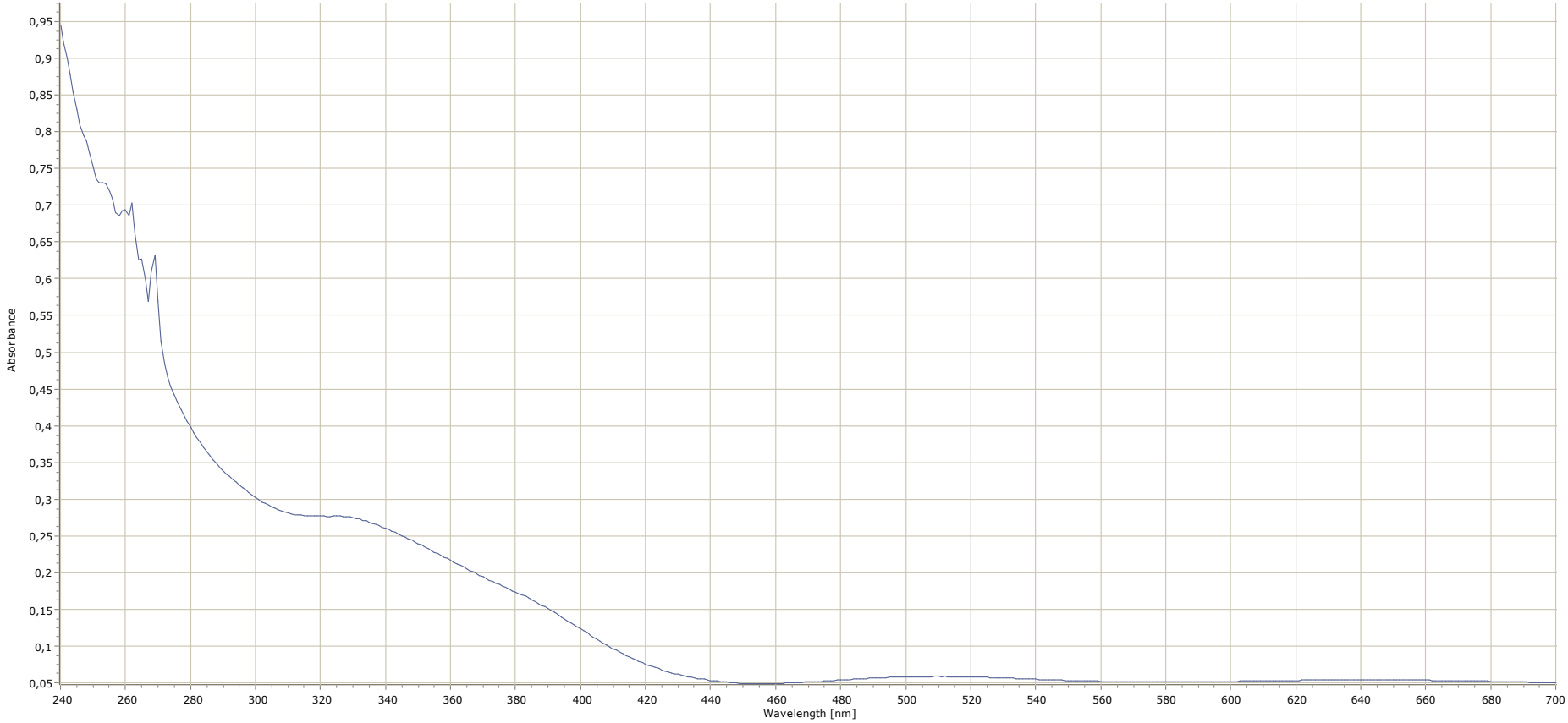


Figure S132. UV-Vis spectrum of compound **5b**.

UV-Vis spectrum of [Cp_2W=Ge(H)Ar*] (**9**) in hexane at rt (6.9×10^{-5} mol/l)

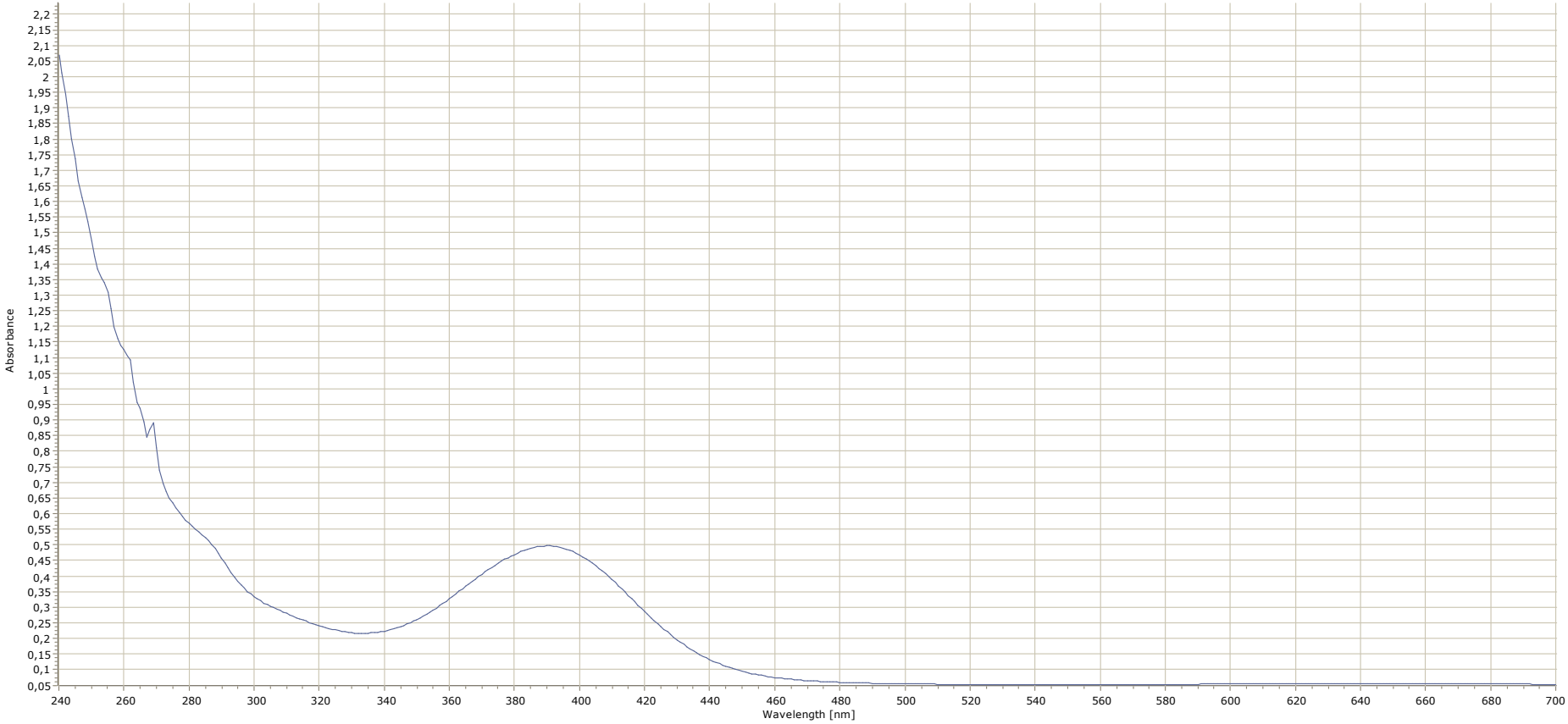


Figure S133. UV-Vis spectrum of compound **9**.

UV-Vis spectrum of [{(Cp$_2$Zr)$_2$H}(H)Sn(H)Ar*] (**11**) in hexane at rt (5.7 × 10^{-5} mol/l)

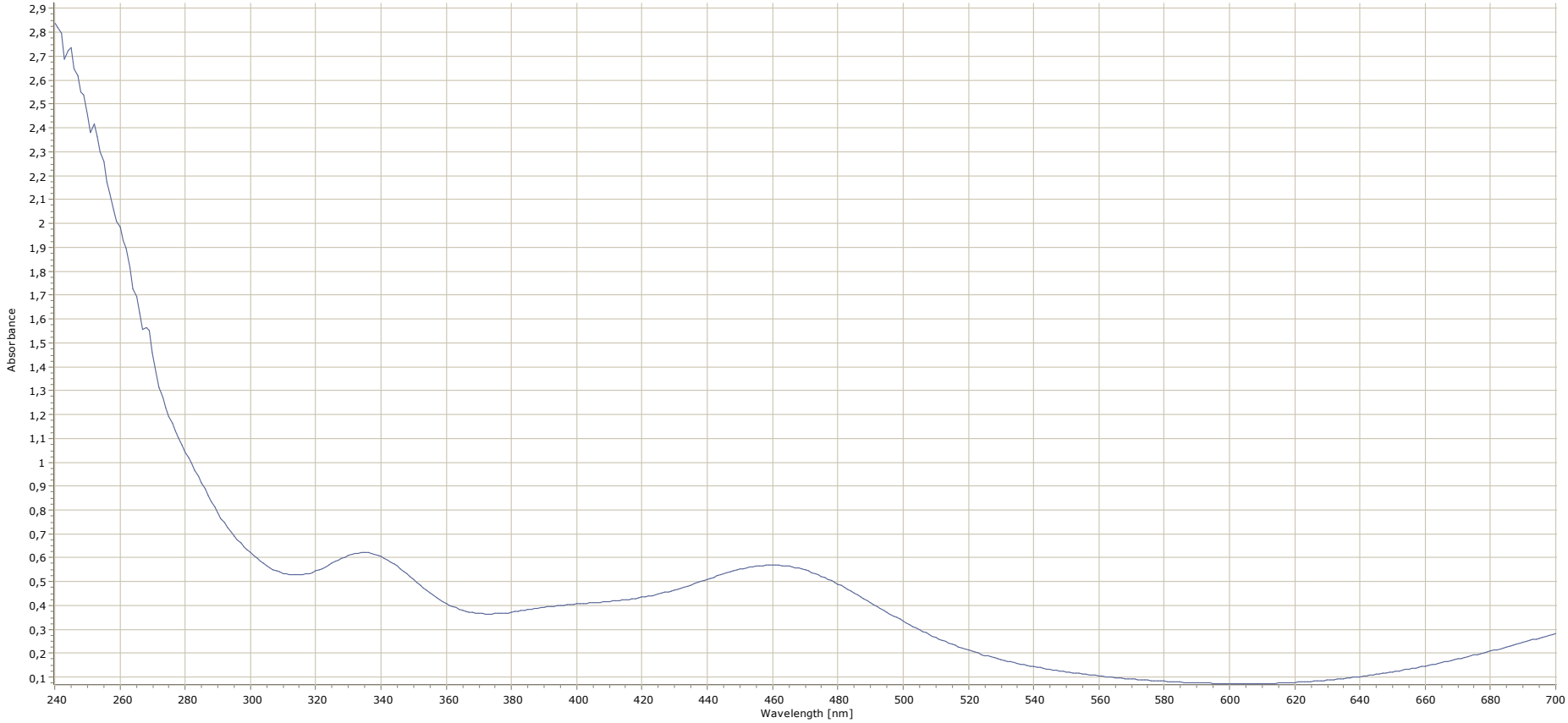


Figure S134. UV-Vis spectrum of compound **11**.

Quantum chemical calculations

On the basis of the molecular structures of **2**, **4a, 9**, **10**, **11** and in the case of **4b** based on the molecular structure of **4a** (Sn was exchanged against Pb) determined in the solid state the structures were optimized using the programme Orca4.2.1[6, 7] with BP86,[8, 9] Grimme´s dispersion correction and Becke-Johnson damping (D3BJ)[10] making use of the resolution of identity (RI) approximation. The basis set chosen was def2-TZVP for Sn, Pb, Zr, Ta, W and def2-SVP on all other elements as implemented in ORCA4.2.1.[11-14] For all calculations *tight* convergence criteria for optimisations and *verytight* for SCF convergence were applied with *grid6* and *finalgrid7* gridsizes. Absence of imaginary frequencies on this level of theory confirmed local minima on the PES for **10** one spurious frequencies (-3.62 cm^{-1}) was observed. Analyses of the electronic structure have been performed using NBO7.[15] On the basis of optimized structures NMR chemical shifts were computed for **2** and **4b** at SO-ZORA level with ADF,[16, 17, 18] including the crucial exchange correlation kernel (PBE density functional, basis sets: TZ2P for Ta, W, Pb and Sn and TZP for C, H).[19] The obtained ^{119}Sn and ^{1}H NMR shieldings were converted to chemical shifts (δ, in ppm) relative to the shieldings of $SnMe_4$ and $SiMe_4$ calculated at identical computational level.

Results of calculations of the cation of **2**

The LUMO of the cation of **2** is shown in the manuscript and the optimized structure was used for NMR calculation of the tin atom and SnH as well as TaH_2 protons.

NMR calculations

^{119}Sn: 981.2 ppm (exp. 1161 ppm), ^{1}H NMR TaH_2: -0.471 ppm (exp. -3.75 ppm), SnH: 14.67 ppm (exp. 15.55 ppm).

Results of calculation of **4a**

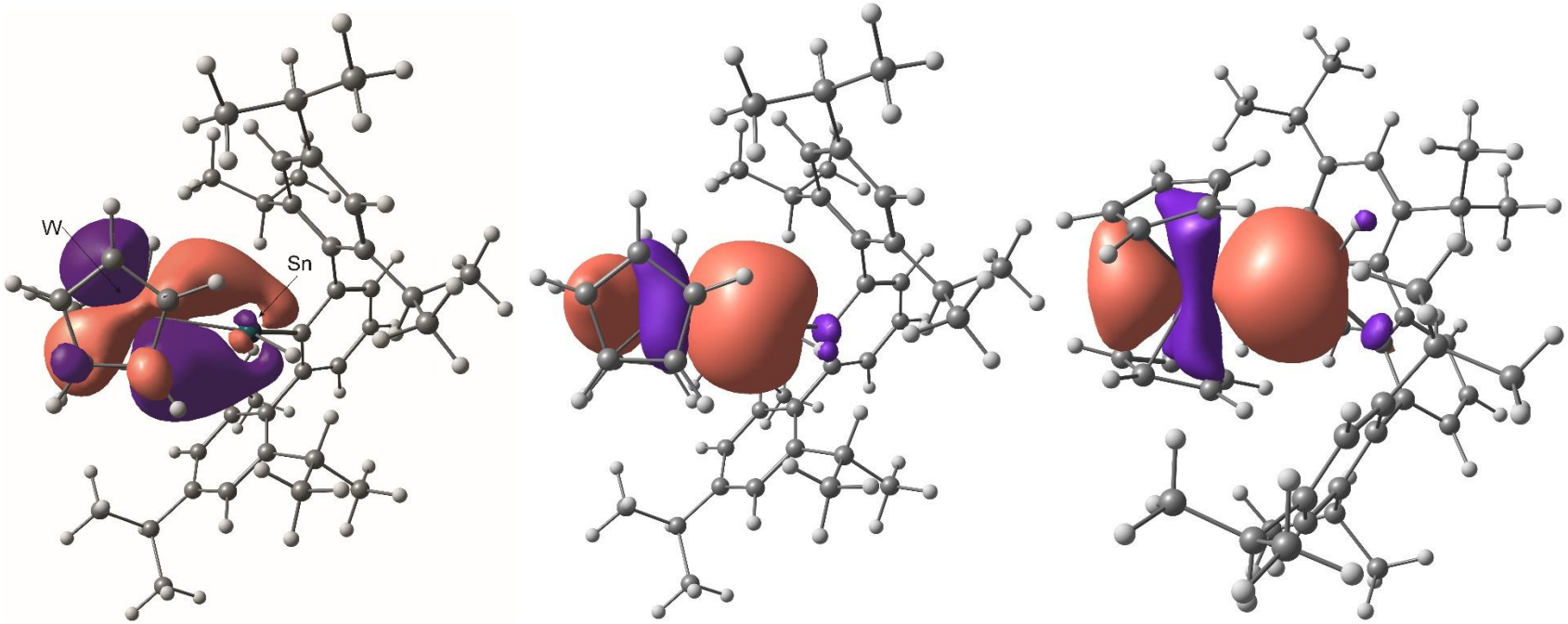


Figure S135. NLMO representing the W-Sn interaction.

Left NLMO: two electrons 76% W (d orbital), 6.5% Sn (p orbital), right NLMO: two electrons 41% Sn (71% s orbital, 29% p orbital), 54% W (d orbital)

Results of calculation of **4b**

The geometry of the optimized structure based on the molecular structure of **4a** after exchange of the tin against a lead atom was used for calculation of the NMR shieldings of the WH and PbH units using ADF.
NMR calculations ^{1}H NMR PbH 39.3 ppm (exp. 42.13 ppm), WH –11.5 ppm (exp. –13.67 ppm)

Results of calculation of **9**

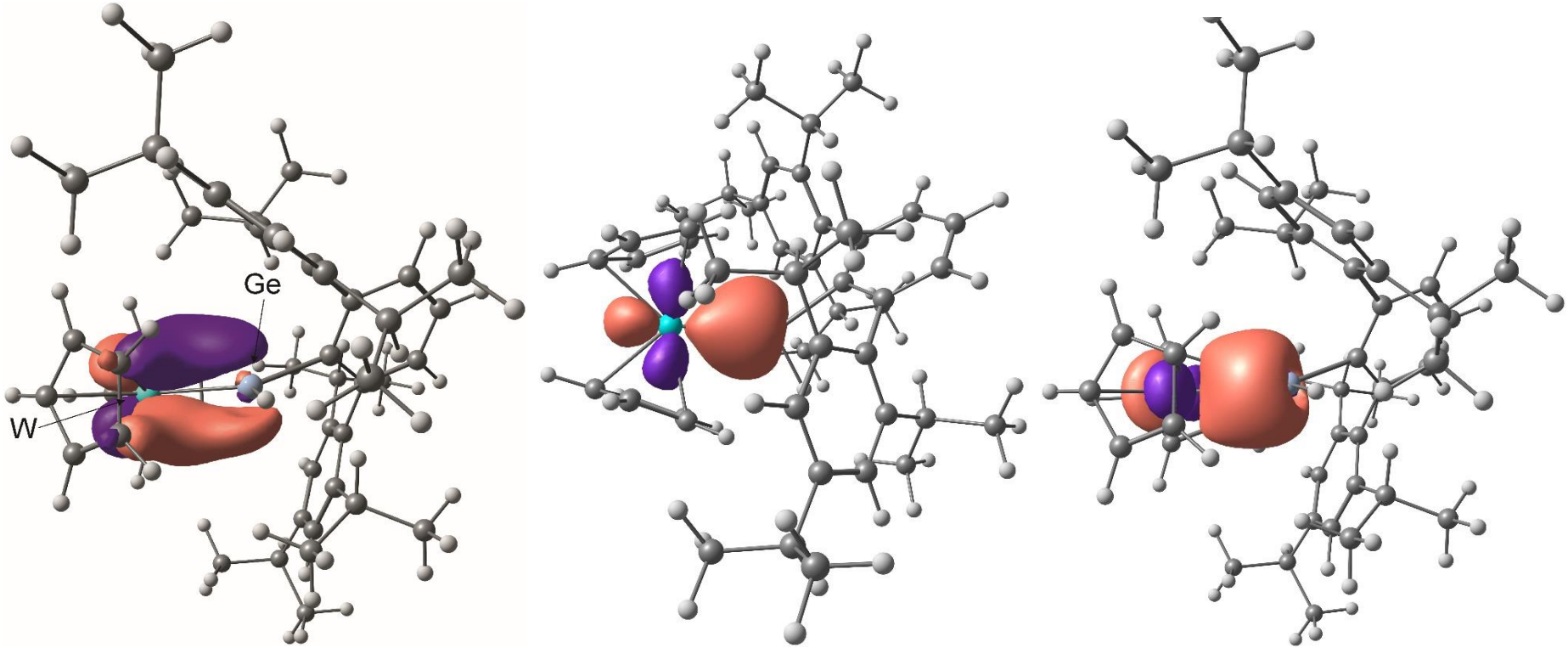


Figure S136. Two NLMOs representing the W-Ge interaction
Left NLMO: two electrons, 23% Ge (p-orbital), 57 % W (d-orbital), right NLMO: two electrons, 54% Ge (63% s orbital, 37% p orbital), 44% W 84% (d orbital)

Relative energies approximation of the isomers $Cp_2W(H)$-EAr* and Cp_2W=E(H)Ar*

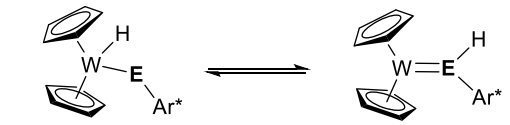
Gas phase structure optimizations followed by frequency calculations were performed in ORCA 4.2.1[6, 7] RI-BP86, Grimmes dispersion correction with Becke-Johnson damping (D3-BJ) and def2-SVP basis sets on all elements as well as default ECPs on heavy elements.[8-14] Input structures were taken from experimental X-ray structures were available (**9** and **5a**). Input structures for the experimentally not observed isomers were generated by simple replacement of the tetrele element in (**9** and **5a**). Structures were subsequently re-optimised using a def2-TZVP basis set on all elements. Thermal corrections were used from the def2-SVP frequency calculations.

SI-Table S3: Thermochemical data for compounds relevant for energetic approximations considered:

		RI-BP86-D3BJ-**def2TZVP/J** (gasphase structures); thermal corrections from **def2-SVP** frequency calculations in Hartree						
ENTRY	**MOLECULE**	**E(SCF)**	**$E(ZPV)_{corr}$**	**H_{corr}**	**G_{corr}**	**E(ZPV)**	**H**	**G**
1	Cp_2W=Ge(H)Ar* (**9**)	-3934,4659	0,90594504	0,96057308	0,82886508	-3933,56	-3933,5054	-3933,6371
2	Cp_2WH-GeAr* (**5c**)	-3934,4672	0,90653765	0,96111237	0,82975737	-3933,5606	-3933,5061	-3933,6374
3	Cp_2W=Sn(H)Ar*	-2071,6171	0,90409481	0,95922883	0,8261831	-2070,713	-2070,6579	-2070,7909
4	Cp_2WH-SnAr* (**5a**)	-2071,6390	0,90535758	0,96043767	0,82758633	-2070,7336	-2070,6785	-2070,8114

SI-Table S4: Thermochemical data summary for some considered reactions

			RI-BP86-D3BJ-**def2TZVP/J** (**gasphase**) in kcal mol^{-1}			
ENTRY	**Reactant Entries**	**Reaction Description**	**dE(SCF)**	**dE(ZPV)**	**dH**	**dG**
RXN1	1 ---> 2	Isomerisation W=GeHAr -> W(H)-GeAr*	-0,7758	-0,4039	-0,4373	-0,2158
RXN2	3 ---> 4	Isomerisation W=SnHAr -> W(H)-SnAr*	-13,7260	-12,9336	-12,9675	-12,8455



0

		$dE_{(ZVPE)}$	dH	dG
Ge	BP86-D3BJ/def2-SVP	0.183	0.216	-0.005
	BP86-D3BJ/def2-TZVP	0.404	0.437	0.216
Sn	BP86-D3BJ/def2-SVP	13.747	13.781	13.659
	BP86-D3BJ/def2-TZVP	12.934	12.968	12.846

in kcal mol^{-1}

Results of calculation of **10**

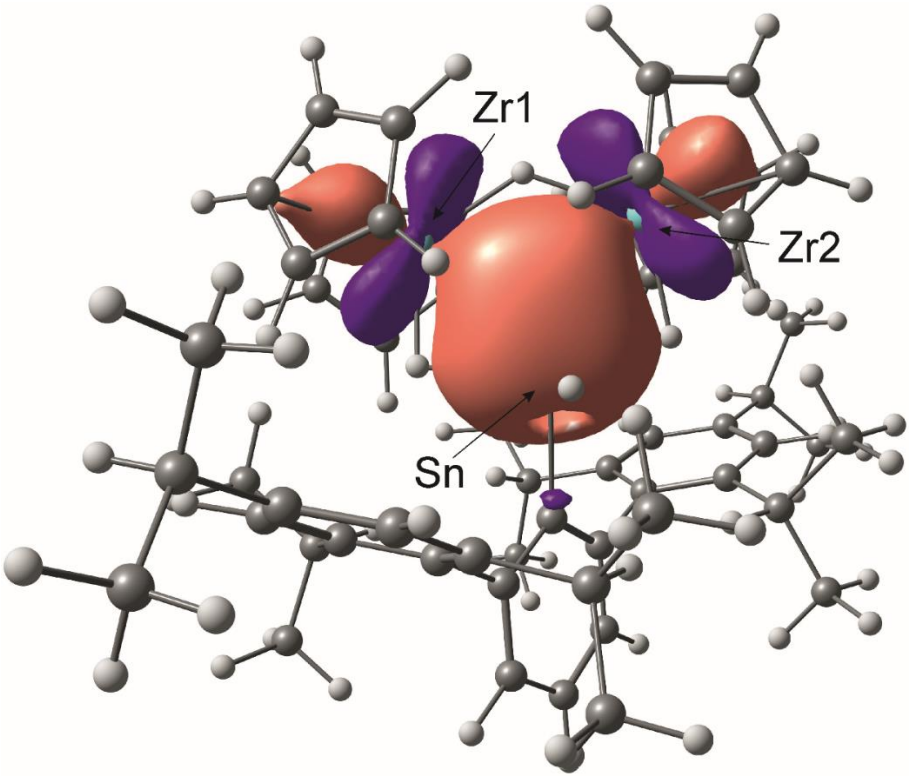


Figure S137. NLMO representing Zr_2Sn interaction.
NLMO two electrons: 48% Sn (68% s orbital, 32% p orbital), 24%, 23% Zr (d orbital)

Results of calculation of **11**

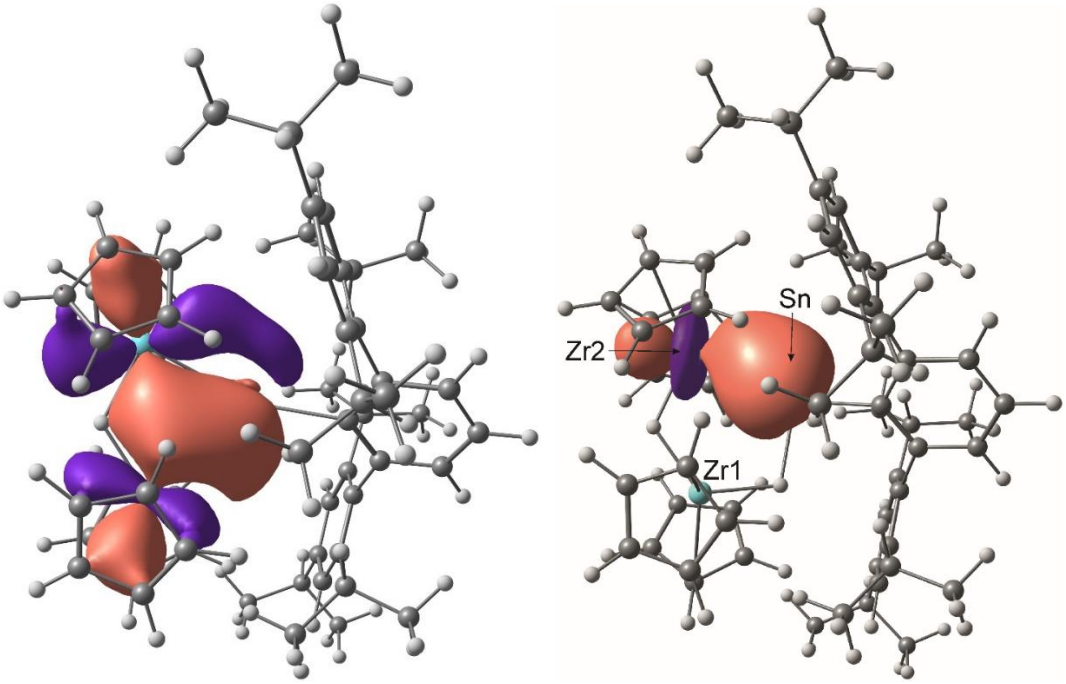


Figure S138. Left NLMO representing Zr_2Sn interaction, right representing the Zr2-Sn bond.
Left NLMO two electrons: 23% Sn (25% s orbital, 74% p orbital), 34% Zr2, 29% Zr1 (d orbital), right NLMO 35% Zr2 (d orbital), 58% Sn (65% s orbital, 34% p orbital)

Coordinates of optimized structures

Compound **2**

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110
Coordinates from ORCA-job bp86optfreq_hnumac
  C   0.24808607999935     -2.46141783243991     -7.90982307875426
  C   0.35553348150611     -3.98062669636268     -7.65652328431952
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  C   5.61010646365655     -3.85816430205527     -7.06583234834430
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Cation of Compound **4a**

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H	8.31214580778300	0.05737525192697	2.17036447599604
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H	8.16074315274613	1.57062929825954	3.09518833686011
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H	5.15145443462594	6.93542253884038	5.03349204334303
H	0.41198882926244	0.67867068830372	4.57837151387502

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  H   -0.38228260601243      5.60127021866936      6.19383321305926
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Cation of Compound **4b**

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109
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  C   4.79555100580672      -3.24646196859391     -1.89597959301706
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  C   4.77935648307611       1.13324283007604     -1.71091869144919
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  C   6.28681384634748       5.57385874713621     -1.32928763357120
  C   5.28474362628383      -2.54115894153562     -0.62406947032339
  C   5.46337838369035      -1.03595563542255     -0.77356687225993
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  C   6.39038334247521      -0.36803261023217      0.04850673823733
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  C   5.23844534854837       1.51828758757661      4.75258355892286
  C   0.44148723774741       4.89631926721402      5.23020992752560
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Molecular structure of $Cp_2W=Ge(H)Ar^*$ (9) // -3934.465940973379 H

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C	3.85375154746488	-3.45528189911918	-2.26206599332528
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C	2.46337798181709	-3.04606228693677	-1.74478753869221
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C	-2.31736214030034	4.13230082184018	-1.34171407284478
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C	-1.29003557043240	-2.23443914306322	-0.63468616730305
C	-1.14138947187780	4.49896898842221	-0.68425053067988
C	2.37732258530439	-0.30335462659037	-0.58752403870210
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C	1.23913262157786	0.53001997035447	-0.60669842312611
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C	2.45834853056443	-1.49214074390276	0.30957341653943
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C	2.54898235641175	-3.89565233133029	0.62185570594400
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C	-3.11105405802395	1.20795740938592	1.34810745024784
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C	2.48253053678806	-4.97223130973149	2.91056828396421
C	3.54670329448865	-4.93727165260035	4.01657697253928
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Ge	-0.32341065264777	0.43419647929385	0.64121628226742
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H	-1.84135934176074	1.16459944422384	3.20325273455822
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H	-3.31134604201443	-0.99245818788351	3.90092201256736
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Molecular structure of Cp_2WH-GeAr* (5c) // -3934.467177298875 H

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C	-3.45773742567405	-1.43320553829727	-2.17362053745042
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C	3.16381388212109	0.30620473881343	-0.98365093511758
C	4.33127707580622	4.38623113086872	0.33317958272469
C	-1.79924328328841	-2.03982234110561	-0.50482692807552
C	-1.64729174746048	3.21002976578258	-1.13146105043101
C	5.28089973910035	3.17895579517041	0.43066141559428
C	-2.60762877958539	2.13954346127779	-1.04754492344047
C	-4.04002532184174	-1.40192247374744	0.15368528545005
C	4.49645187582125	1.88404713891094	0.32694132567493
C	-0.37357920800178	-2.36820241451590	-0.17602341670882
C	0.53016401111333	-1.28229597200030	-0.09662143601500
C	0.07489560639154	-3.68674172659257	-0.04526145750320
C	-2.75354643892004	-1.81541483913702	0.51463562232114
C	2.87060543492761	-0.42647965768651	0.19622724530325
C	1.89952868733173	-1.56087665391739	0.12795764597060
C	1.42982722616493	-3.94936918001312	0.16955637634556
C	-1.93132624666931	4.11146852064407	-0.04988054746299

C	2.33297615199492	-2.88908521352830	0.25468071440208
C	-3.46736331151426	2.39448981990922	0.07089095943987
C	4.26981546595076	1.09909412976425	1.45768666433211
C	3.46126943495220	-0.04459604818900	1.42228870332135
C	-3.05827892745700	3.60894108717641	0.68109414284841
C	0.94225431200253	2.10362144183727	1.53025944956332
C	-2.44341523637858	-3.53285911427333	2.33271444397884
C	-2.38629814417450	-2.03584036374360	1.97453259844319
C	0.30890367144837	3.27466811471207	2.05815018719055
C	0.29215854845144	0.97072812298937	2.14372719802708
C	-3.25259989151824	-1.24682011977423	2.96299548274825
C	3.26069735873210	-0.85339852636148	2.69628073287775
C	4.46305674398591	-1.78763014402399	2.92643578788368
C	-0.70973035093428	2.86996860687017	2.98894180293658
C	-0.69797915775657	1.45251267926070	3.05268233518544
C	3.02714535512794	0.01054379038671	3.94484323950546
Ge	-0.25436785398721	0.45815550787475	-0.87045109196146
W	-1.26924416643961	2.11889018959531	0.86290055785939
H	-0.44239199178066	-1.46096938873541	-4.88681689222362
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H	2.11626758231403	0.39948191804875	-4.32243656773612
H	-6.13937973765962	-2.21134290248813	-3.13066626217846
H	-6.60969310209090	-2.80330752230327	-1.52349080756485
H	-2.42632485944155	-3.76265008912905	-3.86061751715702
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H	3.44078865625939	1.38243508231427	-3.67516040798400
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H	-1.30675864240919	-4.34795833496479	-2.60868500528150
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H	-0.16773123082647	-2.14230073933014	-2.55920466482783
H	6.00513081511002	3.30850414451412	-1.63144222285765
H	4.14659184609031	2.03683589669451	-1.79286074251391
H	1.80391790550163	-0.77229421102262	-2.22485074390641
H	-6.88482037463469	0.80098396160054	-2.61898547224652
H	-5.37522916149543	0.28688468447692	-3.39732923642867
H	-6.32365362132766	-0.50781308656300	-0.57946849439142
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H	3.91223844603825	-2.06768393671425	-2.10476764135200
H	6.99768854717699	4.19134608626844	-0.45572785228599
H	-0.90368316333950	3.33674061524899	-1.91014676758493
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H	4.88117800584931	5.33235400895335	0.44863866234688
H	-5.31630052769591	1.32720986161385	-1.96065235537684
H	3.55648785617038	4.33931389675133	1.11173229973029
H	-0.63562281744248	-4.51070749707605	-0.13823544792277
H	-4.78283993168087	-1.21759854722505	0.93194476117915
H	5.74280202822740	3.19491916682769	1.43248211084348
H	-1.39656890357255	5.03010574682462	0.16909792890910
H	1.78285188300279	-4.97773678615370	0.25773501216416
H	3.39488036841376	-3.09260822955677	0.40360018167024
H	1.81380730313261	2.07453597122034	0.88643689896694
H	-1.76274874466237	-4.12386926584604	1.70979489131897
H	-4.27985954939160	1.75392302547060	0.39538287888652
H	0.55835669462562	4.29919972656335	1.80049584113517
H	-3.46404615559664	-3.91875999204303	2.18890559902858
H	-2.25735912073362	0.81833624411154	1.32743442748805
H	4.71248824438440	1.41167684376371	2.40600224891562
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H	-4.28059699358483	-1.63816586578763	3.00100286905142
H	-2.16381535149036	-3.68819553367963	3.38568682566172
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H	-3.29811311047383	-0.18157107364749	2.69797755040473
H	2.37114178417289	-1.48485798579919	2.54795551845062
H	5.38081942464848	-1.19895336421095	3.07679705209918
H	-1.36143641746172	3.53208765073124	3.55039140149620
H	-2.83808735082714	-1.33847240140903	3.97777281925973

H	2.21637877343414	0.73410129086160	3.79210646452235
H	4.30652469752087	-2.41150752908536	3.81915642865630
H	3.93241766724811	0.56850534266986	4.22629275783120
H	-1.35792786036217	0.83805802286063	3.65434337931587
H	2.76192817938892	-0.62920465767830	4.79925463029621

Molecular structure of $Cp_2W=Sn(H)Ar^*$ // -2071.617105732283 H

C	-0.65987603444510	1.16124044708296	-4.38134623685548
C	-2.53137381661093	0.19972326480296	-2.96944913679693
C	-1.15764075859664	0.87440770964184	-2.95315756149395
C	-3.99413628815873	5.46507858052205	-2.58202795414328
C	3.51312522361855	1.09966809215482	-2.29753491222421
C	2.38365475231559	1.91627989209054	-2.36398358526103
C	3.84681791104912	-3.43193050216001	-2.24736814590154
C	-2.24646714001732	2.96145843407344	-2.01011054934792
C	-1.11365399009773	2.15079766407794	-2.12576853700714
C	1.40547725375578	-4.04603778194178	-2.16400242682632
C	2.45617885783690	-3.00545778731147	-1.74451690241448
C	-3.46281910164092	5.03935808276857	-1.20401674907645
C	3.54148000964415	0.02359978313899	-1.41125870826861
C	-2.21642661921428	4.18146274092621	-1.32522559437532
C	1.29104554612717	1.67468710559338	-1.52113902633506
C	0.09616573873375	2.57462023611365	-1.51833213880638
C	-2.79454518053399	-2.55113398970992	-0.70395996215759
C	-4.55309714790008	4.32894347387518	-0.38566467994380
C	-1.38867418228245	-2.29470462926022	-0.64608325990672
C	-1.01193575426083	4.58445134949525	-0.74703174227692
C	2.44105623112533	-0.26374677183223	-0.58587454846028
C	0.14537137888621	3.79984741922668	-0.81822192167073
C	1.31597130762635	0.58371964610523	-0.62529803530989
C	2.11815818141553	5.35307983414877	-0.96394019138112
C	-3.14265382925918	-3.21669512766946	0.52813399450289
C	2.47817937276425	-2.75926555212315	-0.24173711413262
C	-4.40442581061471	0.08042237135287	0.90153617164145
C	1.42001311042430	4.26500806018702	-0.13085184714230
C	2.47722322653753	-1.45605074004948	0.31071015343393
C	-0.88277777988010	-2.76343489257427	0.61547362404293
C	2.49298035070913	-3.86089562094081	0.62315891500405
C	-1.96812162003064	-3.31310546768784	1.36541969701194
C	-3.41675369240216	0.99152271158176	1.40153481995083
C	-4.55990181908301	-0.94873180060107	1.90541284753105
C	1.17674200666106	4.74341587891670	1.30773694962103
C	2.50046947139219	-1.28984576592320	1.71877821365391
C	2.47525514777015	-3.71847924603013	2.01059035924445
C	2.66170767348880	0.08753027261145	2.34968301962305
C	-2.93771293981689	0.50180563469882	2.66633728517827
C	-3.62225589974376	-0.71357409141387	2.97774091847651
C	4.15916945527457	0.39480174028103	2.53066131948816
C	2.48164162142111	-2.42258691729363	2.53736025303655
C	2.38904947393945	-4.93762298643472	2.90961730870952
C	3.42020472535409	-4.91311225305685	4.04651221457885
C	1.89396408057334	0.25622830688567	3.66614254964488
C	0.95938376050877	-5.09139442400975	3.45845781352529
Sn	-0.42619598362862	0.45878903925390	0.70725171764032
W	-2.48678552332542	-1.12164051220315	1.04216475708530
H	-0.65345158755564	0.23952539899732	-4.98220089338750
H	-1.31684609246126	1.89134463174550	-4.87768670021927
H	0.35913620904321	1.57110469656814	-4.37140194464019
H	-2.46330118264090	-0.77240026899453	-3.47936333644191
H	-4.31882124369074	4.59147924612042	-3.16668239244460
H	-3.27581376740454	0.79755380587914	-3.51642618018831
H	3.84002171267634	-3.57040423834455	-3.33877796407347
H	-3.21933452131589	5.98660751460479	-3.16112326443317
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H	-4.85872947487143	6.13687371254920	-2.47583454349015
H	-0.44529413909282	0.16868322520612	-2.49687338791181
H	2.34982710282432	2.75803917508782	-3.05797171084669
H	1.34219421467531	-4.09552726092778	-3.26094613766732
H	-3.18020834464320	2.63093427381560	-2.46625293693190
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H	4.61420659998041	-2.68625562833279	-2.00106995235554
H	-3.44277015028524	-2.38266619399909	-1.55623656182564
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H	4.14754064528441	-4.38436239715190	-1.78512925365604
H	-4.86596309884516	3.39464997776736	-0.87537715665269
H	4.42779952239543	-0.60927738816104	-1.35201783557223
H	-0.80222424239588	-1.82413294564482	-1.42814155368655
H	0.41075835871008	-3.80132336817786	-1.77090984928579
H	1.66766692994449	-5.05264657046794	-1.80652416905362
H	2.34933723446946	4.99249602536517	-1.97581230196640
H	-5.44248273062053	4.96774776475653	-0.28016505753159
H	-3.17256356288474	5.95259622664686	-0.65751486526959
H	-5.01298371031747	0.22200068552517	0.01517075186167
H	1.47365237910786	6.23975019946664	-1.06306293788157
H	-4.19280991271790	4.07484765732965	0.62089637357345
H	-4.12877292310915	-3.58830445015982	0.78440661863843
H	-0.98413587644166	5.53109998498465	-0.20246080908386
H	3.05880921012200	5.66622548054934	-0.48680692598134
H	2.48182935826937	-4.86893010765417	0.20244983412657
H	2.09677540971296	3.39931329268902	-0.07864057211188
H	-3.10571548599281	1.90771941785193	0.90971723115214
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H	-5.26581795118155	-1.77054258934627	1.85603007216115
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H	2.27240617576237	0.83419672407087	1.64227102823339
H	0.57889221139763	5.66643084936508	1.33636450199996
H	4.68780443151708	0.34557338360735	1.56844722856389
H	-1.89322249330003	-3.81024504316030	2.32599857242791
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H	2.13516068718098	4.95675562241927	1.80338064484552
H	2.60276595135692	-5.81693254916734	2.27845228142982
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H	4.30124248917465	1.40147696853726	2.95111235202103
H	-2.18096549133688	0.97736022851038	3.28187712186361
H	4.62384576900542	-0.33373680864871	3.21215924060551
H	-3.53030287553327	-1.28276686430641	3.89613327015324
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H	2.48047625162935	-2.28866705021945	3.61965647617905
H	1.92207314492153	1.30717632867252	3.98633063123080
H	3.22799822660505	-4.08422484404131	4.74367198213200
H	3.37824156216940	-5.84692554922008	4.62595591949925
H	0.23146448735305	-5.16729047299207	2.63872005254342
H	2.32987542488912	-0.34623604430490	4.47690346112061
H	0.87230378478093	-5.99169653846230	4.08496287892197
H	0.68539552926999	-4.21951067385887	4.07154389650473

Molecular structure of Cp_2WH-SnAr* (5a) // -2071.638979598401 H

C	-1.15000939351284	-1.12400239960876	-4.21992759923474
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C	-1.06702498471491	-2.04198593060823	-2.99669293449450
C	3.92613249933885	-1.56193283415521	-2.70792022916538
C	-3.36801078843949	-1.29375253863209	-2.23823086213404
C	2.89446908387581	-0.46245835335637	-2.39087868249398
C	-5.77257825583772	-0.70970294065835	-1.65990528237059
C	-2.07437126528474	-1.71327112882711	-1.90016362959284
C	-5.79108382031229	0.61088200107611	-2.44423671172382
C	-4.36658938176137	-1.13400964824078	-1.27397127190861
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C	4.01719455316132	1.35630025071587	-1.02272278648417
C	3.25661917221683	0.18286030083788	-1.05740462532441
C	4.25338151140915	4.35167368132506	0.14471450196763
C	-1.76387887250899	-1.95501059858752	-0.53585866628787
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C	-2.77143684515842	2.19097438309377	-0.76654364162077
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C	-0.35341414790576	-2.29673880190173	-0.16402515619949
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C	-2.76566595580045	-1.81249431302586	0.45112546727168
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C	1.94181801606877	-1.57961419115755	0.15403711293909
C	1.36870977308053	-3.93573757110799	0.32049606919700

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C	2.31766303029096	-2.91379679969064	0.36821499726151
C	-3.61105711552069	2.07945303324503	0.39740715762956
C	4.31366043112941	1.14025626237264	1.34569581799345
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C	-3.43714962236975	3.24779916414961	1.18174035507363
C	0.88102879195844	1.92685451054701	1.68631050220496
C	-2.75380794805647	-3.61365135793426	2.20346526359033
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C	0.08893440724141	0.99834607958410	2.43897281994807
C	-3.24214498250199	-1.25082035490564	2.90644044606843
C	3.32328285241167	-0.76204072358706	2.68245688736445
C	4.50846572120692	-1.71314709161932	2.93484681681271
C	-0.59873490580102	3.12269897639530	3.01153974750299
C	-0.82766352531894	1.73184763132225	3.26934627367260
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Sn	-0.10961741939086	0.74522220703911	-0.96980202957729
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H	-0.48157479150664	-3.78962470808811	-4.17019804385605
H	2.40427598275939	-0.01125420154673	-4.45087230875875
H	-5.96792041358545	-2.02017375327722	-3.39648502955854
H	-6.49550761874429	-2.76474574820556	-1.87255248186956
H	-2.22799486248139	-3.69925248616547	-3.82012674649418
H	-7.52232661346383	-1.54479128997740	-2.67249788171759
H	3.73591297745931	0.97247265869112	-3.82206952284752
H	-1.05838373577404	-0.06822117150496	-3.92537815606418
H	3.67053830637814	-2.07047758234782	-3.64946297454763
H	-3.60317475803241	-1.10374255352015	-3.28654070832487
H	2.05243302759747	1.31968216471402	-3.32830881907442
H	-1.08737045148978	-4.18332643658733	-2.54258247397417
H	4.93267835113856	-1.12900517940597	-2.81137899426458
H	-0.06091392600696	-1.93028115458249	-2.56473981994235
H	5.89808002352614	3.33835940502797	-1.87126440509511
H	4.22115977508650	1.87945738842189	-1.95710699862161
H	1.92050527018425	-0.95963715587099	-2.26872176811583
H	-6.82417087144638	0.90813167876896	-2.67715150704959
H	-5.25082097296347	0.51285407892567	-3.39755081702179
H	-6.32947990251722	-0.55260621131017	-0.72011677356894
H	3.70716244372189	4.32353833282359	-0.81023317745430
H	3.95775434612094	-2.31481883244813	-1.90905304518692
H	6.89834858886411	4.26948758969804	-0.74241488310318
H	-1.41401299888415	3.85782450459742	-1.46156040675464
H	-2.76576799579040	1.49028581270598	-1.59691950442584
H	7.05780152584108	2.49602640490509	-0.82035364127048
H	4.75901022758497	5.32593826750018	0.22210948853173
H	-5.32064629870200	1.42335467753191	-1.87420670814422
H	3.51511871209714	4.27884946233673	0.95606737578319
H	-0.70685260330500	-4.42408847489298	-0.01918377566926
H	-4.82938074607435	-1.30509166195840	0.81364515910871
H	5.76653296614644	3.25018572692392	1.20221970672290
H	-2.12686464564479	5.04637400277710	0.88148566694082
H	1.67124696413321	-4.97222059194106	0.47674854741585
H	3.36549864365440	-3.15530764284643	0.55479094601861
H	1.74209508325723	1.69619531651748	1.06767635214344
H	-2.16237729628426	-4.27342479211038	1.55734214242454
H	-4.25397592917829	1.23754109553730	0.62670550581030
H	0.82987197560038	4.16349530941088	1.61604387753253
H	-3.81798287608634	-3.83914549868887	2.03558042698565
H	-1.95051171287741	0.56173268464794	1.20227800650921
H	4.73960057031001	1.51601468947574	2.27848325738319
H	-1.39525988533680	-1.95161924248507	2.06158762269917
H	4.65330243081713	-2.41150279750792	2.10061199420693
H	-3.92362808638495	3.45609822542984	2.13005570564286
H	-4.31902832872449	-1.47772270313095	2.89993867059573
H	-2.51401039232306	-3.85409780821186	3.25011178122241
H	0.17376871212425	-0.08032451040340	2.37401079614498
H	-3.10652055387906	-0.18419615064515	2.68018230189626
H	2.41642199368730	-1.37635094871663	2.57262634099414
H	5.43944998527985	-1.13806517679516	3.05366780003172
H	-1.12730691713032	3.95059712324309	3.47474464049244

H	-2.88007345937654	-1.44133730101720	3.92746210668618
H	2.33368387841139	0.89182900634871	3.73195523080056
H	4.34890500273649	-2.29940511580623	3.85214103588626
H	4.05424672559406	0.70247886343448	4.14350411204261
H	-1.52130038633226	1.31386342528046	3.98953588377490
H	2.86585020396267	-0.44292630393002	4.78061539335103

Compound **10**

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Coordinates from ORCA-job bp86optfreq_hnumac

C	-9.93246035626268	0.38464471705587	-7.13793825359152
C	-8.62184353724760	-1.56959551685503	-6.16638885365211
C	-5.77373547223789	4.03592082924157	-5.95735241271738
C	-4.57880779164742	1.80326433833049	-5.96789969040807
C	-9.44167879516815	-0.30457544447304	-5.85026546256777
C	-7.44173863677833	1.21244584602252	-5.39252145608420
C	-5.44421097159784	2.76845105830251	-5.14227981793528
C	-8.66792845355608	0.66639469474297	-4.96882844034256
C	-6.72615363112245	2.13320354316467	-4.60859127393280
C	-9.16648967645140	1.05477605561452	-3.71352936828148
C	-7.24295097393009	2.49461141826930	-3.33211123815076
C	-6.82318560021507	4.85546722590360	-2.63357045587530
C	-8.47119366306210	1.94799719968243	-2.87448790555153
C	-6.49642850347069	-2.02253349516983	-2.87395122756694
C	-3.04851947858607	-1.66075302423430	-3.09129209254438
C	-2.08283336890580	-0.61204287954713	-3.16755561421795
C	-6.50913058367473	3.48940406135467	-2.48224393095107
C	-7.80476908146900	-1.80556373668256	-2.33558954335721
C	-6.16678867836360	5.83201767247236	-1.87392589849462
C	-5.94545593108550	-3.17377870057850	-2.24397816914096
C	-9.93506827151025	3.61450928228290	-1.65562300450377
C	-2.46847150318651	-2.74235154535864	-2.35358840183175
C	-0.92265200945349	-1.03055366067100	-2.45514592022711
C	-8.05129026690899	-2.81847576707143	-1.36765016846320
C	-9.05611962979040	2.35427136511629	-1.52346153825717
C	-6.89116994687858	-3.65497668176493	-1.28959676242679
C	-1.15842016906429	-2.35332670696489	-1.96189202722944
C	-5.51145982637817	3.10062651102937	-1.54393058087556
C	-1.73771904740640	5.53621945012960	-1.93612614745843
C	-0.92202064691283	3.13984863486924	-2.10952265366122
C	-5.19923937191743	5.44285052221916	-0.94146168808579
C	-2.06427390596263	4.05833682210623	-1.64427346521215
C	-9.84745900236475	1.22573813206671	-0.84503875762884
C	-4.86216602707626	4.08109372053907	-0.75831667156740
C	-2.42733436780312	3.87345068052914	-0.17057261472454
C	-3.78553264929270	3.80340534989258	0.24528986304471
C	-8.02706917781961	-1.06081984189941	1.23836884830995
C	-0.65159570008483	-0.74639727558570	0.63007194664789
C	-1.22983712965290	0.55197993506324	0.65433874619147
C	-7.20025126412702	0.09766293568882	1.29210756589636
C	-1.41735975472215	3.86019874861471	0.80884202588609
C	-7.25741346097353	-2.17924945003403	1.68509092291499
C	-4.10972684762766	3.66899173483398	1.62437072644660
C	-1.54244480278476	-1.64450633746099	1.29520916604885
C	-6.19651039157647	4.98034431220822	2.26031327322837
C	-5.56383518342730	3.58264680742162	2.09147228385572
C	-2.46737033492209	0.47265327401538	1.36977512669603
C	-5.90924243478663	-0.30553059925785	1.75288367386451
C	-5.95260092079995	-1.71490196348767	2.00779584778912
C	-2.64772733222174	-0.87735924784347	1.77601046082349
C	-1.71060749417873	3.76875597881470	2.18168587890399
C	-3.05928353617437	3.65564923208057	2.56315078357326
C	-5.73728688200697	2.79009919217586	3.39876674974504
C	0.28382627491744	2.52734978444849	3.13156793923855
C	-0.60468032143685	3.78203553423880	3.22829760998019
C	0.23231639833612	5.07216933045459	3.15144580573720
Zr	-6.21646202512583	-1.41352167937103	-0.44815462801486
Zr	-2.73075544999101	-0.84219779159456	-0.74633529922421
Sn	-4.93675825524068	1.02034180766476	-1.62147260133084
H	-10.55093774603311	-0.30759762183473	-7.74483066915709
H	-9.07867563847512	0.71120228105211	-7.76747126206171
H	-6.39902496950369	3.78265002999665	-6.83817432569030
H	-7.71048633000459	-1.32405899910367	-6.75060602359511

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  H   -10.54237269630416      1.28080285268377     -6.90741994198237
  H   -9.21834809030028     -2.28407650089043     -6.76928819033885
  H   -4.84593052640855      4.52182515118033     -6.32291624112082
  H   -5.05266064241710      1.54347653478849     -6.93657831091863
  H   -7.04060214574654      0.92567517802246     -6.37591404749139
  H   -3.59993655659045      2.26798016558003     -6.20298407395652
  H   -6.32961768307738      4.77611699759852     -5.35055805685404
  H   -8.30132232829680     -2.08932721151373     -5.24095105745469
  H   -10.33910015418991     -0.61925358584275     -5.27307764915910
  H   -4.38934991791020      0.85779633029957     -5.41868617521498
  H   -4.84534840971101      3.08819544417577     -4.26224406859038
  H   -7.58845217905955      5.14489986670107     -3.36904813353915
  H   -6.04585576849044     -1.40713145836395     -3.66141362119271
  H   -10.13628241100967      0.64789432743361     -3.38691765747837
  H   -4.02813938702603     -1.65042741786264     -3.57355617309589
  H   -2.20921085366809      0.33962681556582     -3.69502105569931
  H   -8.48236744519926     -1.00394487672479     -2.64928909501695
  H   -4.82341553458591      0.77838170134649     -3.32655418389784
  H   -10.78533540965146      3.42374660931586     -2.34234855686663
  H   -6.40996849223915      6.89655284355691     -2.00862664555721
  H   -9.36234637813319      4.47225132639378     -2.05471374097190
  H   -4.97173382827069     -3.62526226871371     -2.45109623874503
  H   -0.73922468021072      3.27137570620473     -3.19521364000469
  H   -1.51127165059063      5.68668515342773     -3.01153884244019
  H   -2.93259277393198     -3.71016667119872     -2.13205003095631
  H   -0.00180246477578     -0.44788418293086     -2.33426793159464
  H   -2.96237878953097      3.79463116808205     -2.24201108206849
  H   -10.81094468271087      1.03020543184146     -1.35812816715151
  H   -8.97612117579417     -2.94900625125293     -0.79456276104500
  H   -2.58645139374385      6.19571214418835     -1.67042103183539
  H   -10.34932023482160      3.91064002765018     -0.67003516637978
  H   -1.17011026522005      2.07401251978935     -1.93247199070871
  H   -6.77038790762164     -4.54009212096155     -0.65306201293094
  H   -0.45103878916503     -2.96839426412442     -1.39329102520871
  H   -6.75218978044211      0.25348170975685     -1.20700517568698
  H   -8.19720172977221      2.61357637440734     -0.86574458508290
  H   -2.95845142122398      0.98318972092587     -1.32996577805141
  H   -4.67517058328501      6.19965910991294     -0.33890669888377
  H   -9.26988423465869      0.28139089380274     -0.83712220595952
  H   0.03318535298918      3.36403027112230     -1.59124488925149
  H   -0.85573516787191      5.86825729212898     -1.35027176573744
  H   -10.09163031321488      1.49636483478880      0.20227732038644
  H   -4.30998008787502     -1.95509270240995     -0.29177276888052
  H   -9.07956806917236     -1.08121945362244      0.93590770246405
  H   0.31543891201317     -1.01024729515085      0.18795458840674
  H   -6.21467124638666      5.54502490966256      1.31067817620621
  H   -6.12509040501329      3.05850637461916      1.28524000907081
  H   -0.80336112411839      1.46786937069086      0.23753622027198
  H   -7.50219374320774      1.11980244386196      1.04002658576063
  H   -0.36611106163423      3.94756586583094      0.49130438354710
  H   -7.61434405982958     -3.21162672736866      1.78096046097513
  H   -1.38179703610867     -2.71754218343370      1.45785298010697
  H   -7.24099647455253      4.89275017387294      2.62345771955621
  H   -3.12135414400472      1.32755146939636      1.57740143556382
  H   -5.06579751327419      0.36554709127723      1.92653105093679
  H   -5.62522385682424      5.57378976253787      3.00350647297231
  H   -5.13952400324974     -2.34207176386787      2.38948910320384
  H   -3.47346955833542     -1.26885319180859      2.37342222049305
  H   -6.80780866524694      2.56333016211476      3.57495908826310
  H   0.82123863108371      2.48985555870553      2.16060448802120
  H   -5.18319736398808      1.83137704327819      3.39738377797729
  H   0.78298021111913      5.14072617905676      2.19007165827381
  H   -3.29195282487690      3.56529931234969      3.63475362407382
  H   -0.31343217954384      1.59813079782062      3.22241294659943
  H   -5.38354333627453      3.37227816107274      4.27396728678700
  H   -0.40673020442820      5.97342291722026      3.23861350504835
  H   1.04928262854673      2.52521495553855      3.93407010635426
  H   -1.10429689640921      3.76209217686372      4.22146616162308
  H   0.98368353265926      5.10194881673346      3.96648246382685
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Compound **11**

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Coordinates from ORCA-job bp86optfreq_hnumac
  C   -6.19806714775562     -2.05205479735750     -4.34765421383978
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C   -5.45045111801042     0.38007242005937    -4.36139155826927
C   -5.00455829874424    -1.08859846559706    -4.48685769783508
C   -0.23493338606960    -3.15125099599805    -5.03149580790163
C   -2.62107638881237    -1.81063475823064    -3.96056486666495
C   -3.89360669693639    -1.43107307814652    -3.50263913333467
C   -1.23213114470841     2.80330969133583    -3.11307853163046
C   0.79260295554317    -1.44040882406451    -3.47443529807505
C   -0.21530563457223    -2.59510890363109    -3.60151509558727
C   1.79609983384658     1.74381979159084    -2.76584390913065
C   -1.58386323940637    -2.16335713445331    -3.07681054665094
C   -1.78864279078979     1.53997656406799    -2.76821661831193
C   2.13563072992703     3.13529894765168    -2.80807572787463
C   -2.15502162443074     3.82782066907319    -2.72829376985798
C   -4.11043055808625    -1.38692456283662    -2.11374689973091
C   -3.06684410038032     1.77152851712890    -2.17744242817412
C   2.91065846486934     1.03408925340345    -2.21545146050094
C   -3.30308554223786     3.17722126894184    -2.17488688290000
C   3.44121160999941     3.28450345229234    -2.26720731218412
C   3.91998205804617     1.98745591875684    -1.90182859142205
C   -1.82153961848693    -2.09459307695087    -1.67590426604627
C   -3.09742670633797    -1.69927841036425    -1.18891073591081
C   4.79086759662858    -0.93564041043789     0.01160999702036
C   -0.80123229311966    -2.63198561156174    -0.71832331312039
C   -0.72329219925432    -4.04389954901909    -0.66122853649948
C   -3.40301953834949    -1.71349918796948     0.30797177545027
C   4.27509569023581    -3.36422447207638     0.46167573323992
C   -3.95213721317856    -3.08968013476240     0.73165346027342
C   -4.33420145121915    -0.57552962965829     0.74730717544956
C   3.70945305469019    -1.93013450894562     0.46102472278890
C   0.00571706815893    -1.82925318874872     0.13205917073932
C   -2.81329412446722     4.51456415171947     0.62285648707692
C   -3.39167578013703     3.23397439632434     0.89827634074364
C   0.13568115001715    -4.68316914153420     0.23718191964504
C   3.94112770517829     3.15231831635314     0.96423374148583
C   3.27569087031758     2.13289256721919     1.70645715613627
C   0.86569493947684    -2.49096087907965     1.05639290658160
C   -1.52692678589914     4.55353820990082     1.22373034913202
C   3.08570205263780     4.29911586865576     0.91223672219643
C   -2.46427483701206     2.47969116408873     1.67759040650217
C   0.91775780769124    -3.90243961302595     1.09597730923838
C   3.09865304954981    -1.57078460853951     1.81460707048395
C   -1.30076056292363     3.29611716806075     1.86761420083345
C   2.01253498851110     2.65528156762978     2.12676024164053
C   1.90429153051292     3.99194984840455     1.64882684384801
C   1.71970541902221    -1.78848296678219     2.07179860345111
C   3.90831562515663    -1.04896786125004     2.84113120382222
C   1.16891344568902    -1.45762530278008     3.33886733470938
C   3.38447311967726    -0.70617930327494     4.10109410364185
C   4.86591251677811     1.23176323479072     4.80290473111969
C   -0.29295331050167    -1.76068401683634     3.66130519958896
C   2.01167764246796    -0.90670812468873     4.32189744584839
C   4.27545123380128    -0.13492435067959     5.19711843058185
C   5.38074979296192    -1.12852578730797     5.60090475794270
C   -0.42323156463628    -3.15156466508707     4.31370030037687
C   -0.96496771524388    -0.68353116329760     4.52596191632731
Zr  -1.43996976486707     2.80352849277970    -0.58485513774557
Zr  1.97817787405874     2.47402462934686    -0.39405035224173
Sn  -0.26367064174860     0.36357171546020     0.26794386914040
H   -6.97357837126621    -1.83669779866540    -5.11184220579588
H   -6.21451222225410     0.62745013459577    -5.12737407261349
H   -4.58026830181586    -1.22340491555511    -5.50631020658006
H   -5.87910098747984    -3.10726908607199    -4.46535548257917
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