Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for:

N—H cleavage vs. Werner complex formation: reactivity of cationic Group 14 tetrelenes towards amines

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Contents (33 pages total):

1. Synthetic and characterizing data for new compounds

General considerations: All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of Ar or N_2. Solvents were degassed by sparging with argon and dried by passing through a column of the appropriate drying agent. NMR spectra were measured in bromobenzene-d_5 or dichloromethane-d_2. Each deuteriated solvent was dried over CaH_2 and then distilled under reduced pressure, and stored under argon in Teflon valve ampoules. NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H}, ^{27}Al{^{1}H}, ^{29}Si{^{1}H}, and ^{119}Sn{^{1}H} NMR spectra were measured on Bruker Avance III HD nanobay 400 MHz, Bruker Avance III 500 MHz or Bruker AVII 500 MHz spectrometer at ambient temperature. ^{1}H and ^{13}C{^{1}H} resonances are referenced internally to residual protio-solvent signals. ^{19}F{^{1}H}, ^{27}Al{^{1}H}, ^{29}Si{^{1}H}, and ^{119}Sn{^{1}H}, NMR resonances are referenced externally to $CFCl_3$, $[Al(H_2O)_6]^{3+}$, tetramethylsilane, and Me_4Sn respectively. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Elemental analyses were carried out by London Metropolitan University. The chlorotetrelene starting materials (*N*-nacnac)^{Dipp}ECl ((**1-Dipp**)ECl, E = Si, Ge, Sn)[S1] and Li[Al(OR^F)$_4$] (R^F = C(CF$_3$)$_3$)[S2] were synthesised according to literature methods. ^{t}BuNH$_2$ was distilled over potassium metal.

Syntheses of novel compounds

***General synthetic scheme for the N-nacnac-stabilised cationic tetrelenes**:* A fluorobenzene solution (10 mL) of (**1-Dipp**)ECl (0.2 mmol) was slowly added to a solution of $Li[Al(OR^F)_4]$ (1.1 equiv.), also in fluorobenzene (5 mL), at room temperature. The reaction mixture was stirred for an additional 15 h, filtered and concentrated to *ca.* 2 mL. Layering with hexane and storage for several days produced crystals which were suitable for X-ray crystallography.

[(**1-Dipp**)Si][$Al(OR^F)_4$]: Yield 0.182 g (as light yellow crystals), 62 %. **^{1}H NMR** (500 MHz, C_6D_5Br): δ_H 0.96 (d, 12H, $(C\underline{H}_3)_2CH$, $^3J_{HH}$ = 6.9 Hz), 1.03 (d, 12H, $(C\underline{H}_3)_2CH$, $^3J_{HH}$ = 6.8 Hz), 2.29 (s, 12H, $(C\underline{H}_3)_2N$), 2.63 (sept, 4H, $(CH_3)_2C\underline{H}$, $^3J_{HH}$ = 6.8 Hz), 4.62 (s, 1H, methine H), 6.99 (d, 4H, *m*-H of Dipp, $^3J_{HH}$ = 7.8 Hz), 7.17 (t, 2H, *p*-H of Dipp, $^3J_{HH}$ = 7.8 Hz). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_5Br): δ_C 22.7, 25.3 ($(\underline{C}H_3)_2CH$), 29.1 ($(CH_3)_2\underline{C}H$), 41.4 ($(\underline{C}H_3)_2N$), 79.6 ($(CF_3)_3\underline{C}$), 83.7 (methine CH), 121.9 (q, $(\underline{C}F_3)_3C$, $^1J_{CF}$ = 293 Hz), 125.6, 133.0, 145.7 (aromatic carbons), 161.6 (imine quaternary C). **^{29}Si{^{1}H} NMR** (99 MHz, C_6D_5Br): δ_{Si} 80.5 ppm. **^{19}F{^{1}H} NMR** (470.6 MHz, C_6D_5Br): δ_F -74 ppm. **^{27}Al{^{1}H} NMR** (130 MHz, C_6D_5Br): δ_{Al} 36 ppm. **Elemental microanalysis**: calc. for $C_{47}H_{47}AlF_{36}N_4O_4Si$: C 38.38, H 3.22, N 3.81 %, meas. C 38.36, H 3.06, N 3.72 %.

[(**1-Dipp**)Ge][$Al(OR^F)_4$] (E = Ge): Yield 0.069 g, 23 % (as light yellow crystals); crude yield by washing with hexane after solvent evaporation 0.137 g, 45 %. **^{1}H NMR** (400 MHz, CD_2Cl_2): δ_H 1.16 (d, $^3J_{HH}$ = 6.9 Hz, 12H, $(C\underline{H}_3)_2CH$), 1.30 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $(C\underline{H}_3)_2CH$), 2.73 (is, 12H, $(C\underline{H}_3)_2N$), 2.86 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, $(CH_3)_2C\underline{H}$), 5.01 (s, 1H, methine CH), 7.35 (d, $^3J_{HH}$ = 7.7 Hz, 4H, *m*-H of Dipp), 7.47 (t, $^3J_{HH}$ = 7.7 Hz, 2H, *p*-H of Dipp) ppm. **^{13}C{^{1}H} NMR** (125 MHz, CD_2Cl_2): δ_C 23.2, 26.4 ($(\underline{C}H_3)_2CH$), 29.4 ($(CH_3)_2\underline{C}H$), 42.4 ($(\underline{C}H_3)_2N$), 85.0 (methine CH), 121.8 (q, $^1J_{CF}$ = 291 Hz, $C(\underline{C}F_3)_3$), 126.1 (*m*-C of Dipp), 130.5 (*p*-C of Dipp), 134.9 (*o*-C of Dipp), 145.4 (*ipso*-C of Dipp), 163.6 (imine quaternary C) ppm. **^{19}F{^{1}H} NMR** (376 MHz, CD_2Cl_2): δ_F -76 ppm. **^{27}Al{^{1}H} NMR** (104 MHz, CD_2Cl_2): δ_{Al} 35 ppm. **Elemental microanalysis**: calc. for $C_{47}H_{47}AlF_{36}GeN_4O_4$: C 37.25, H 3.13, N 3.70 %, meas. C 37.15, H 3.01, N 3.64%.

[(**1-Dipp**)Sn][$Al(OR^F)_4$] (E = Sn): Yield 0.151 g (as orange crystals), 48%. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ_H 1.14 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $(C\underline{H}_3)_2CH$), 1.21 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $(C\underline{H}_3)_2CH$), 2.88 (m, 4H, $(CH_3)_2C\underline{H}$), 2.93 (s, 12H, $(C\underline{H}_3)_2N$), 3.83 (s, 1H, methine CH), 7.20-7.23 (m, 6H, aromatic protons) ppm.**^{13}C{^{1}H} NMR** (125 MHz, CD_2Cl_2): δ_C 23.3, 26.4 ($(\underline{C}H_3)_2CH$), 29.5 ($(CH_3)_2\underline{C}H$), 41.2 ($(\underline{C}H_3)_2N$), 49.9 (methine CH), 121.8 (q, $^1J_{CF}$ = 292 Hz, $C(\underline{C}F_3)_3$), 125.0, 127.5,

139.1, 141.6 (aromatic carbons), 163.8 (imine quaternary C) ppm. **^{19}F{^{1}H} NMR** (376 MHz, CD_2Cl_2): δ_F -76 ppm. **^{27}Al{^{1}H} NMR** (104 MHz, CD_2Cl_2): δ_{Al} 35 ppm. **^{119}Sn{^{1}H} NMR** (186 MHz, CD_2Cl_2): δ_{Sn} -313 ppm. **Elemental microanalysis**: calc. for $C_{47}H_{47}AlF_{36}N_4O_4Sn$: C 36.15, H 3.03, N 3.59 %, meas. C 36.22, H 2.88, N 3.64%.

Reaction between the cationic tetrelenes [(1-Dipp)E][Al(OR^F)$_4$] and ^{t}BuNH$_2$:

E = Si: To a solution of [(**1-Dipp**)Si][Al(OR^F)$_4$] (99 mg, 0.067 mmol) in fluorobenzene (2 mL), a 0.232 M solution of ^{t}BuNH$_2$ in the same solvent (0.29 mL, *ca.* 1 equiv.) was added at room temperature. The mixture was left to react for 15 h, after which the solution was filtered and concentrated to *ca.* 1 mL. Layering with hexane at room temperature for 2 days, and subsequently at -26°C for 2 days yielded the pure product in the form of colourless crystals. Yield 56 mg, 53 %.

E = Ge : To a solution of [(**1-Dipp**)Ge][Al(OR^F)$_4$] (100 mg, 0.066 mmol) in dichloromethane (2 mL), a 0.232 M solution of ^{t}BuNH$_2$ in fluorobenzene (0.29 mL, *ca.* 1 equiv.) was added at room temperature. The mixture was left to react for 15 h, after which the solution was filtered and concentrated to ca. 1 mL. Layering with hexane at room temperature for 2 days, and subsequently at -26°C for 2 days yielded the pure product in the form of colourless crystals. Yield 69 mg, 66 %.

E = Sn: To a solution of [(**1-Dipp**)Sn][Al(OR^F)$_4$] (100 mg, 0.064 mmol) in dichloromethane (2 mL), a 0.232 M solution of ^{t}BuNH$_2$ in fluorobenzene (0.28 mL, *ca.* 1 equiv.) was added at room temperature, during which time the orange colour of the cation solution disappeared. The mixture was left to react for 15 h, after which the solution was filtered and concentrated to *ca.* 1 mL. Layering with hexane at room temperature for 2 days, and subsequently at -26°C for 2 days yielded the pure product in the form of colourless crystals. Yield 64 mg, 61 %.

[(**1-Dipp**)Si(H)(NH^{t}Bu)][Al(OR^F)$_4$]: **^{1}H NMR** (400 MHz, THF-d$_8$): δ_H 0.44 (s, 9H, (C$\underline{H}_3$)$_3$C), 0.97 (d, 1H, N$\underline{H}$, $^3J_{HH}$ = 7.6 Hz), 1.22 (d, $^3J_{HH}$ = 6.7 Hz, 6H, (C$\underline{H}_3$)$_2$CH), 1.28 (d, $^3J_{HH}$ = 6.7 Hz, 6H, (C$\underline{H}_3$)$_2$CH), 1.35 (d, $^3J_{HH}$ = 6.8 Hz, 6H, (C$\underline{H}_3$)$_2$CH), 1.44 (d, $^3J_{HH}$ = 6.7 Hz, 6H, (C$\underline{H}_3$)$_2$CH), 2.69 (sept, $^3J_{HH}$ = 6.7 Hz, 2H, (CH$_3$)$_2$C$\underline{H}$), 2.80 (s, 12H, (C$\underline{H}_3$)$_2$N), 3.37 (sept, $^3J_{HH}$ = 6.7 Hz, 2H, (CH$_3$)$_2$C$\underline{H}$), 4.55 (s, 1H, methine CH), 5.50 (d, 1H, Si$\underline{H}$, $^3J_{HH}$ = 7.6 Hz, Si satellites, $^1J_{SiH}$ = 285 Hz), 7.37-7.46 (6H, aromatic protons) ppm. **^{13}C{^{1}H} NMR** (101 MHz, THF-d$_8$): 24.6, 25.9 (($\underline{C}$H$_3$)$_2$CH, two other signals are overlapped with residual peak of THF-d$_8$), 29.8 (overlapping

signals, $(CH_3)_2\underline{C}H$), 32.9 ($(\underline{C}H_3)_3C$), 42.5 ($(\underline{C}H_3)_2N$), 51.8 ($(CH_3)_3\underline{C}$), 76.6 (methine C), 121.8 (q, $^1J_{CF}$ = 292 Hz, $C(\underline{C}F_3)_3$), 127.0, 127.4, 130.5, 134.8, 146.4, 147.2 (aromatic carbons), 165.3 (imine quaternary C) ppm. **^{29}Si{^{1}H} NMR** (80 MHz, THF-d_8): δ_{Si} -44.5 ppm. **^{19}F{^{1}H} NMR** (376 MHz, THF-d_8): δ_F -76 ppm. **^{27}Al{^{1}H} NMR** (104 MHz, THF-d_8): δ_{Al} 35 ppm. **Elemental microanalysis**: calc. for $C_{51}H_{58}AlF_{36}N_5O_4Si$: C 39.67, H 3.79, N 4.54 %, meas. C 39.55, H 3.84, N 4.40 %.

[(**1-Dipp**)Ge·(NH_2*t*Bu)][Al(OR^F)$_4$]: **^{1}H NMR** (400 MHz, CD_2Cl_2): δ_H 0.44 (s, 9H, $(C\underline{H}_3)_3C$), 1.21 (d, $^3J_{HH}$ = 6.6 Hz, 12H, $(C\underline{H}_3)_2CH$), 1.36 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $(C\underline{H}_3)_2CH$), 2.30 (br s, 2H, $N\underline{H}_2$), 2.71 (s, 12H, $(C\underline{H}_3)_2N$), 3.05 (br m, 4H, $(CH_3)_2C\underline{H}$), 4.15 (s, 1H, methine CH), 7.31-7.37 (m, 6H, aromatic protons) ppm. **^{13}C{^{1}H} NMR** (125 MHz, CD_2Cl_2): δ_C 25.1, 26.3 ($(\underline{C}H_3)_2CH$), 29.3 ($(CH_3)_2\underline{C}H$), 29.6 ($(\underline{C}H_3)_3C$), 42.0 ($(\underline{C}H_3)_2N$), 52.6 ($(CH_3)_3\underline{C}$), 75.2 (methine CH), 121.8 (q, $^1J_{CF}$ = 292 Hz, $C(\underline{C}F_3)_3$), 127.4, 128.9, 136.9, 144.9 (aromatic carbons), 164.2 (imine quaternary C) ppm. **^{19}F{^{1}H} NMR** (376 MHz, CD_2Cl_2): δ_F -76 ppm. **^{27}Al{^{1}H} NMR** (104 MHz, CD_2Cl_2): δ_{Al} 35 ppm. **Elemental microanalysis**: calc. for $C_{51}H_{58}AlF_{36}GeN_5O_4$: C 38.56, H 3.68, N 4.41 %, meas. C 38.42, H 3.52, N 4.33 %.

[(**1-Dipp**)Sn·(NH_2*t*Bu)][Al(OR^F)$_4$]: **^{1}H NMR** (400 MHz, CD_2Cl_2): δ_H 0.56 (s, 9H, $(C\underline{H}_3)_3C$), 1.21 (d, $^3J_{HH}$ = 6.5 Hz, 12H, $(C\underline{H}_3)_2CH$), 1.37 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $(C\underline{H}_3)_2CH$), 1.97 (br s, 2H, $N\underline{H}_2$), 2.72 (s, 12H, $(C\underline{H}_3)_2N$), 3.08 (br, 4H, $(CH_3)_2C\underline{H}$), 3.93 (s, 1H, methine CH), 7.29-7.33 (m, 6H, aromatic protons) ppm. **^{13}C{^{1}H} NMR** (125 MHz, CD_2Cl_2): δ_C 25.2, 27.0 ($(\underline{C}H_3)_2CH$), 29.1 ($(CH_3)_2\underline{C}H$), 30.4 ($(\underline{C}H_3)_3C$), 42.0 ($(\underline{C}H_3)_2N$), 51.8 ($(CH_3)_3\underline{C}$), 75.0 (methine CH), 121.8 (q, $^1J_{CF}$ = 292 Hz, $C(\underline{C}F_3)_3$), 127.2, 127.7, 138.8, 143.8 (aromatic carbons), 164.8 (imine quaternary C) ppm. **^{19}F{^{1}H} NMR** (376 MHz, CD_2Cl_2): δ_F -76 ppm. **^{27}Al{^{1}H} NMR** (104 MHz, CD_2Cl_2): δ_{Al} 35 ppm.**^{119}Sn{^{1}H} NMR** (186 MHz, CD_2Cl_2): δ_{Sn} -282 ppm. **Elemental microanalysis**: calc. for $C_{51}H_{58}AlF_{36}N_5O_4Sn$: C 37.47, H 3.58, N 4.28 %, meas. C 37.32, H 3.66, N 4.04 %.

[(**1-Dipp**)Si(H)(NH_2)][Al(OR^F)$_4$] and [(**1-Dipp**)Si(Cl)(CH_2Cl)][Al(OR^F)$_4$] were isolated in very low yields from the reactions of [(**1-Dipp**)Si][Al(OR^F)$_4$] with ammonia gas and dichloromethane, respectively and are characterized solely by X-ray crystallography.

2. NMR spectra of novel compounds

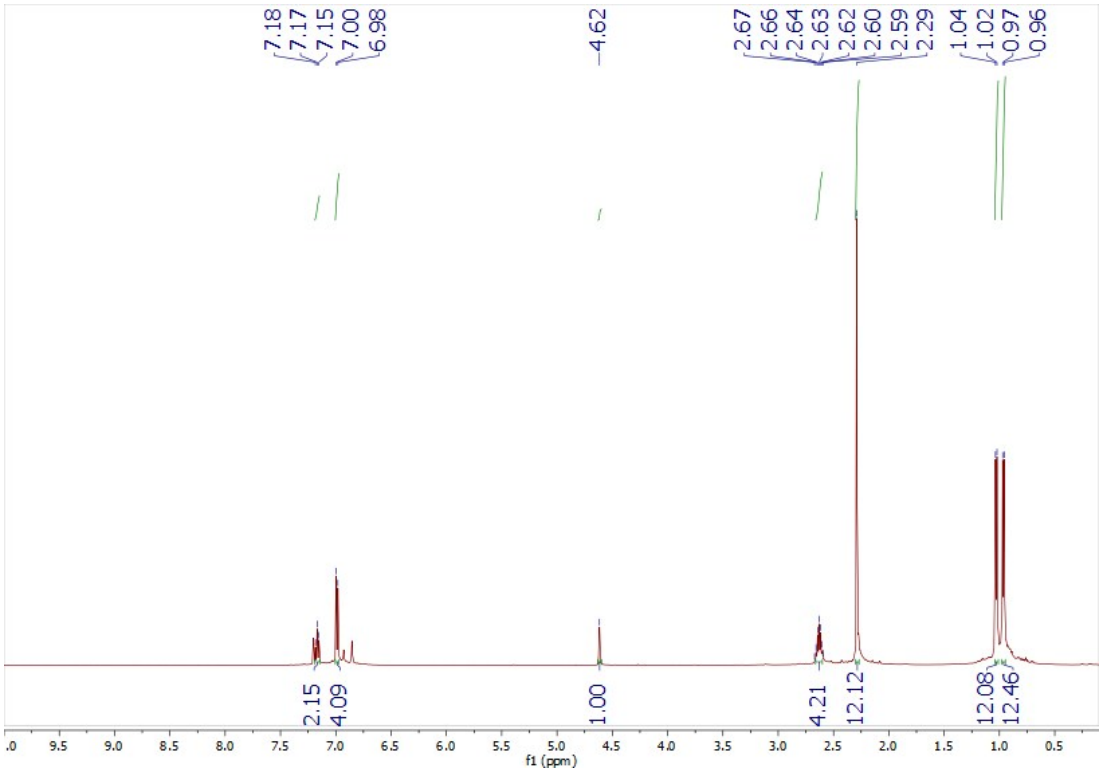

Figure s1: ^{1}H NMR spectrum of [(**1-Dipp**)Si][Al(OR^{F})$_4$]

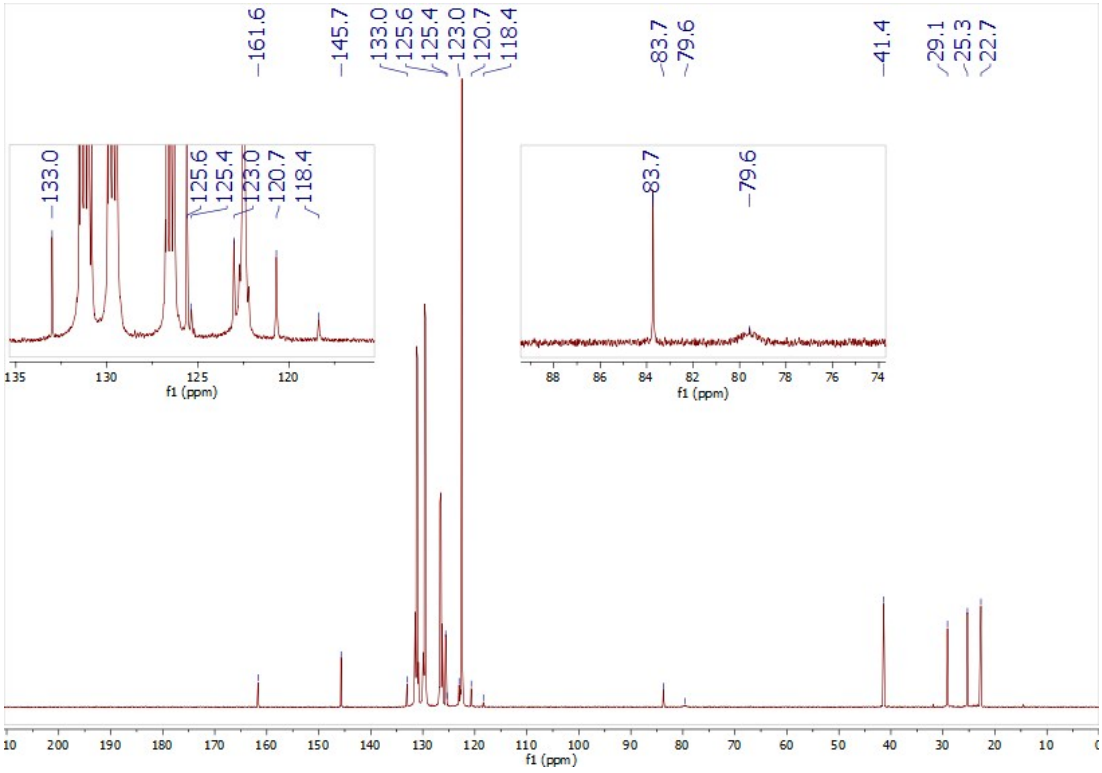

Figure s2: ^{13}C{^{1}H} NMR spectrum of [(**1-Dipp**)Si][Al(OR^{F})$_4$]

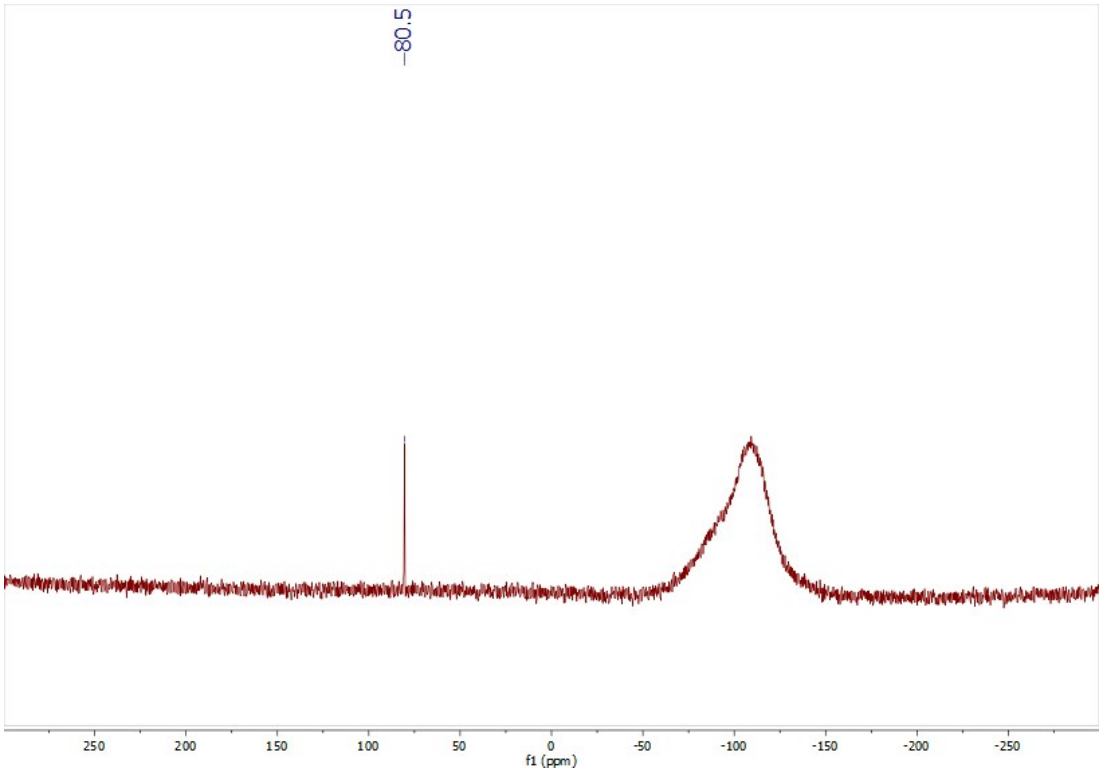

Figure s3: $^{29}Si\{^{1}H\}$ NMR spectrum of [(**1-Dipp**)Si][Al(OR^{F})$_4$]

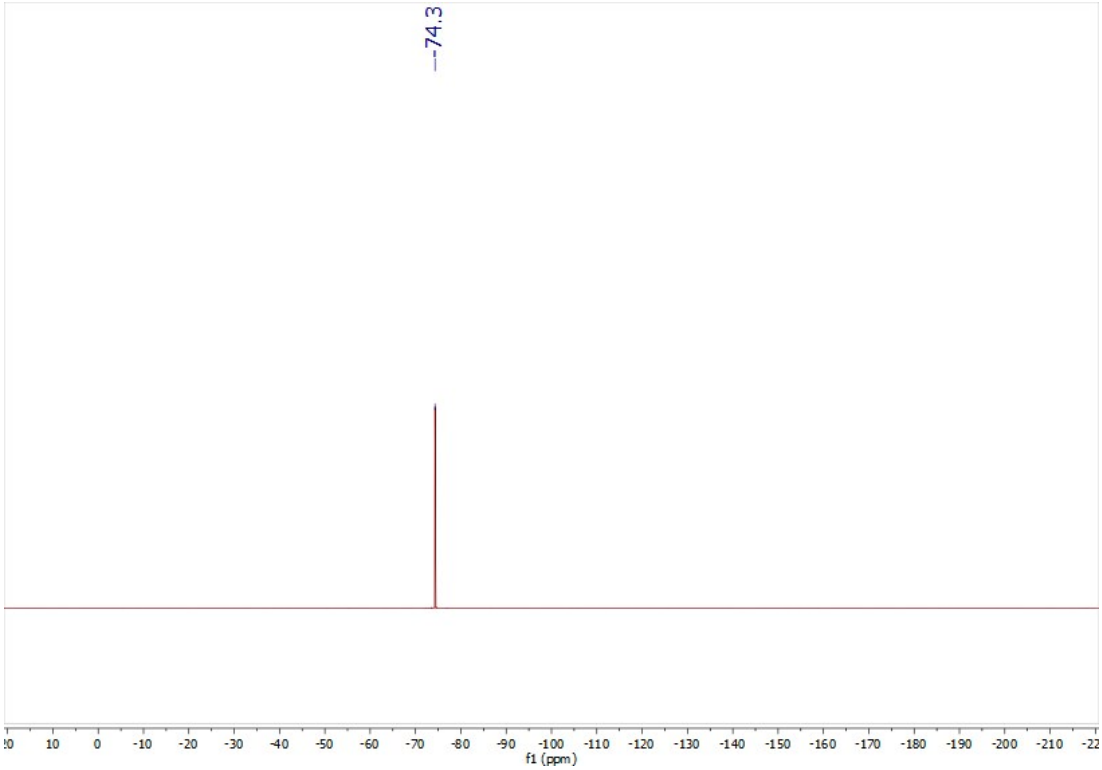

Figure s4: $^{19}F\{^{1}H\}$ NMR spectrum of [(**1-Dipp**)Si][Al(OR^{F})$_4$]

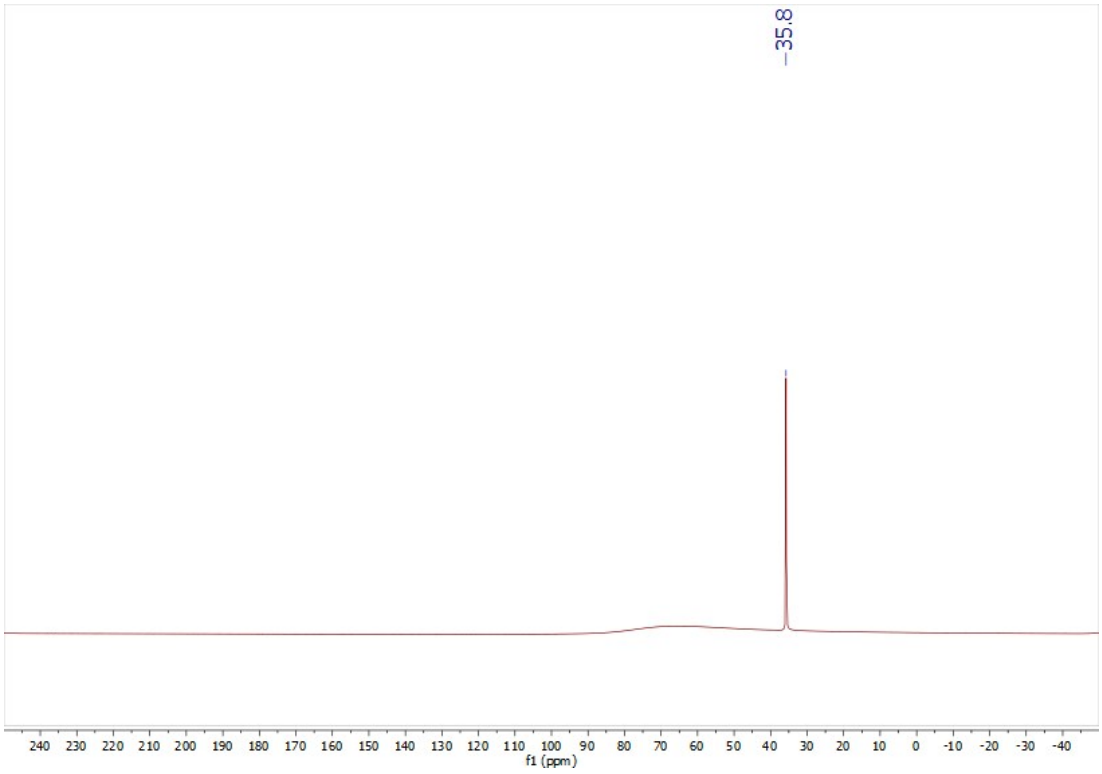

Figure s5: $^{27}Al\{^{1}H\}$ NMR spectrum of [(**1-Dipp**)Si][Al(OR^F)$_4$]

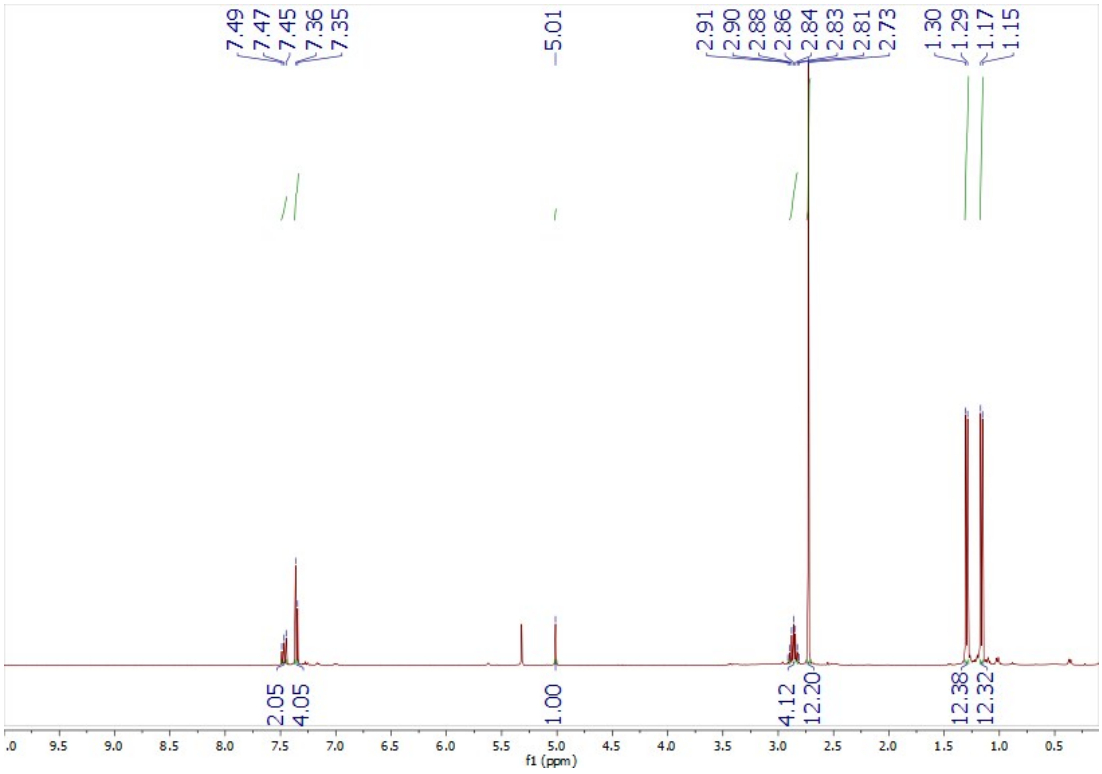

Figure s6: ^{1}H NMR spectrum of [(**1-Dipp**)Ge][Al(OR^{F})$_4$]

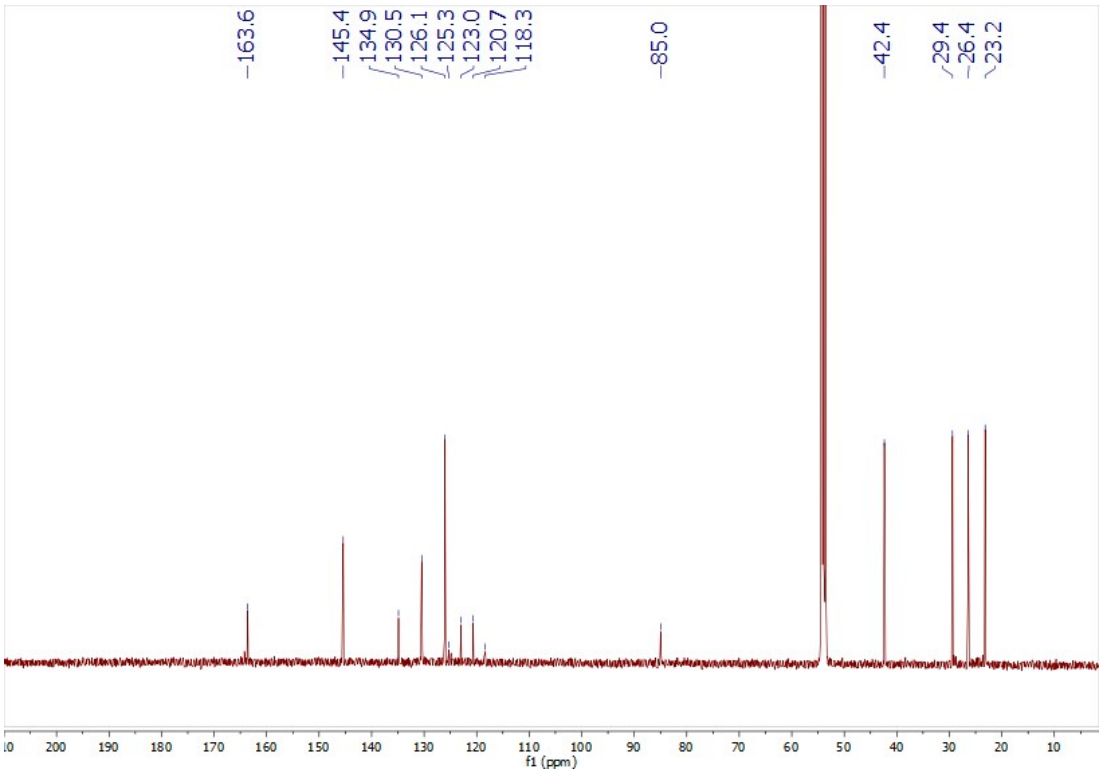

Figure s7: ^{13}C{^{1}H} NMR spectrum of [(**1-Dipp**)Ge][Al(OR^{F})$_4$]

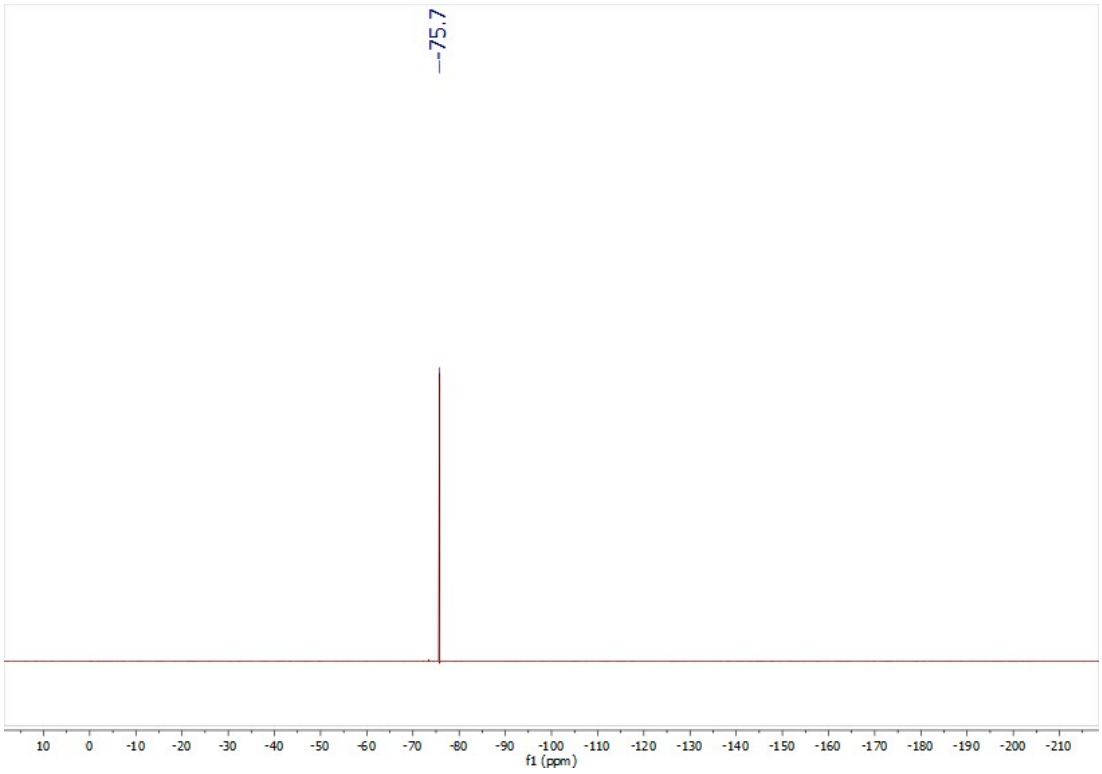

Figure s8: $^{19}F\{^{1}H\}$ NMR spectrum of [(**1-Dipp**)Ge][Al(OR^{F})$_4$]

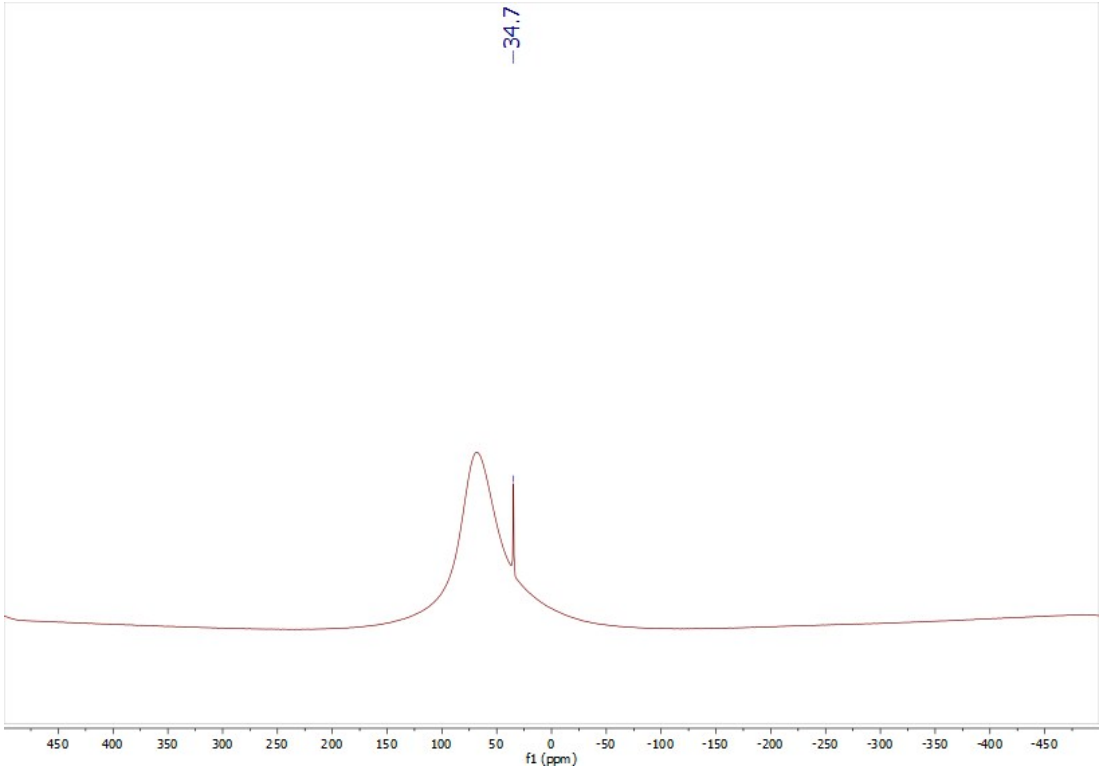

Figure s9: $^{27}Al\{^{1}H\}$ NMR spectrum of [(**1-Dipp**)Ge][Al(OR^{F})$_4$] (*with probe background at ca. 70 ppm*)

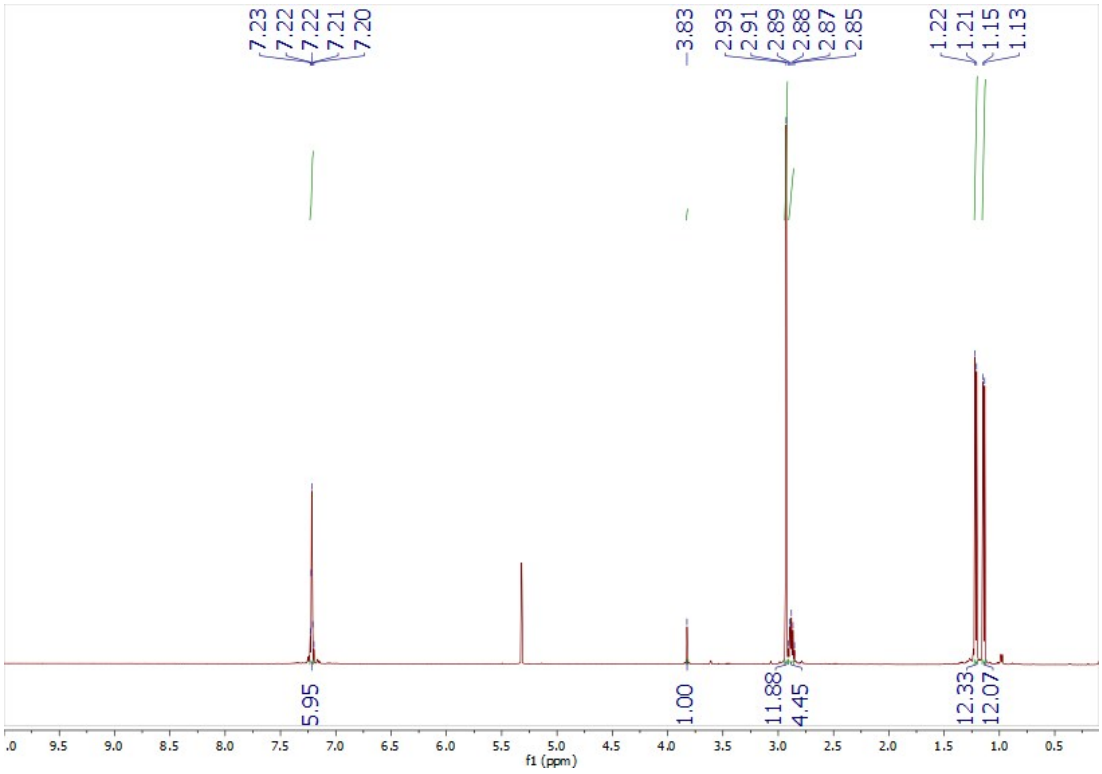

Figure s10: ^{1}H NMR spectrum of [(**1-Dipp**)Sn][Al(OR^{F})$_4$]

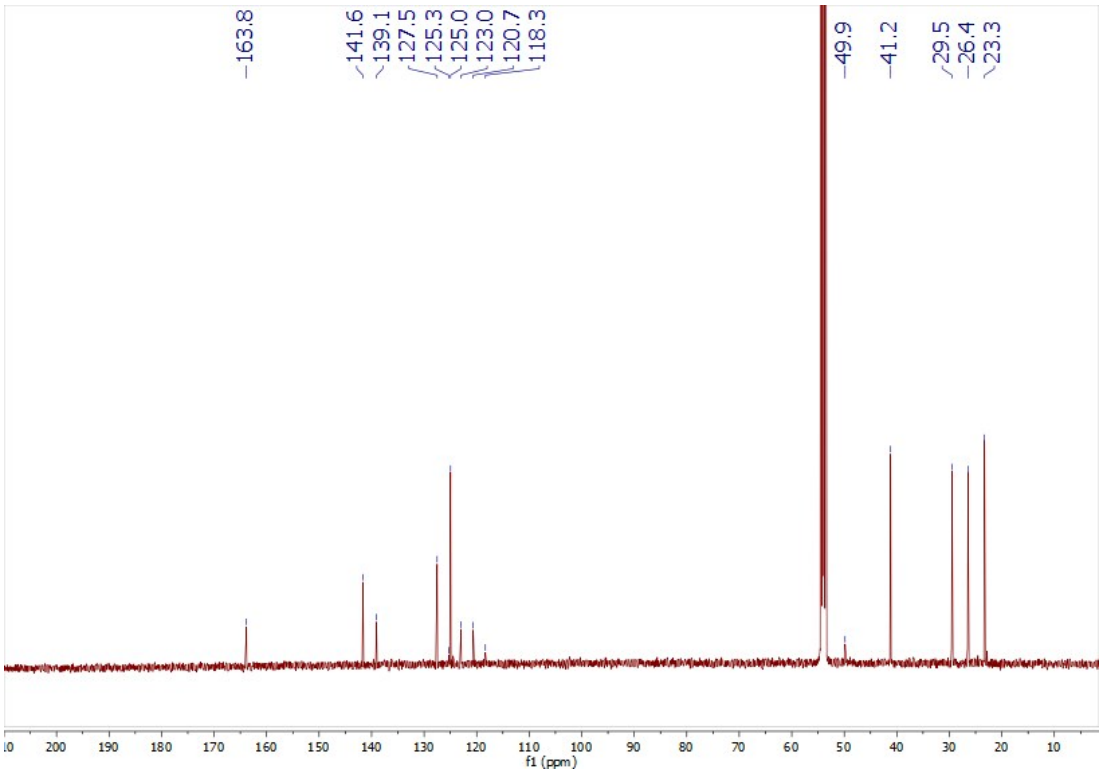

Figure s11: ^{13}C{^{1}H} NMR spectrum of [(**1-Dipp**)Sn][Al(OR^{F})$_4$]

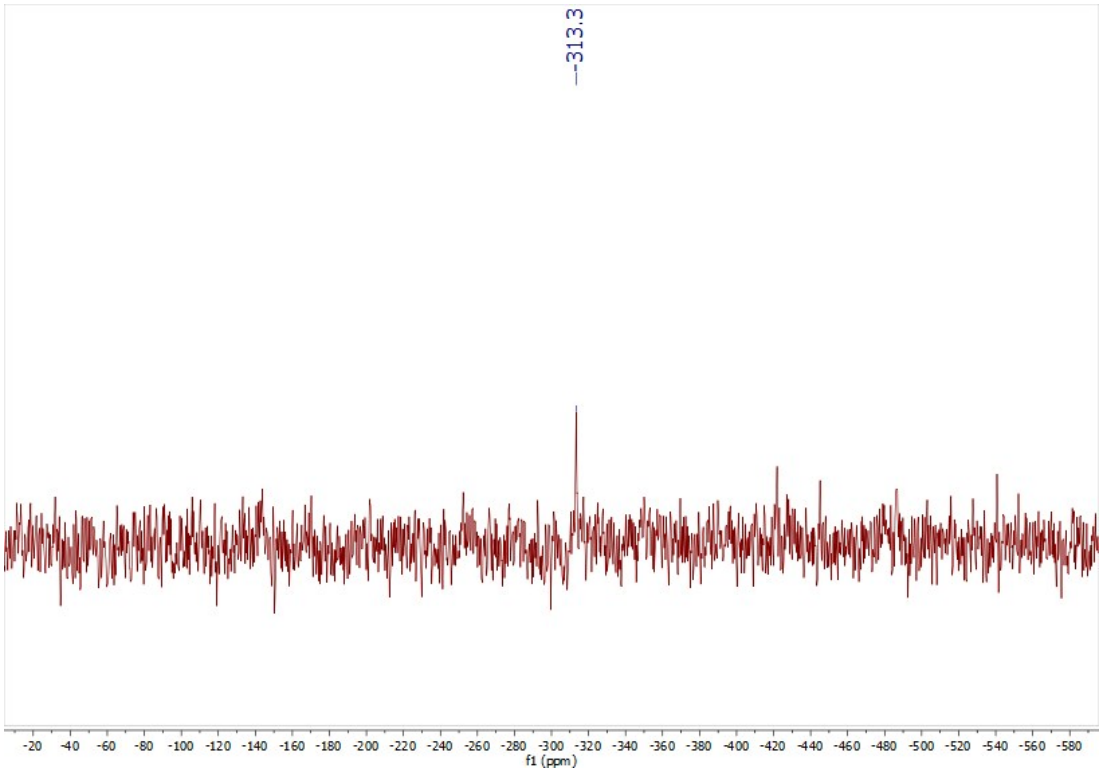

Figure s12: $^{119}Sn\{^{1}H\}$ NMR spectrum of [(**1-Dipp**)Sn][Al(OR^{F})$_4$]

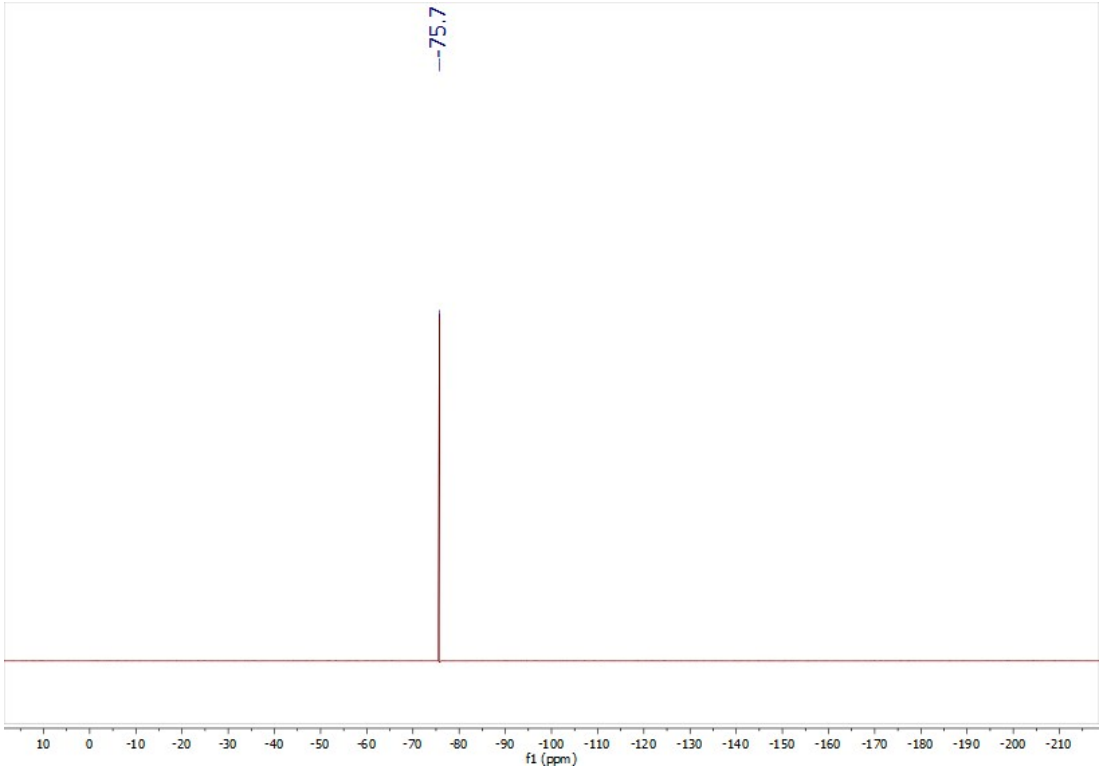

Figure s13: $^{19}F\{^{1}H\}$ NMR spectrum of [(**1-Dipp**)Sn][Al(OR^{F})$_4$]

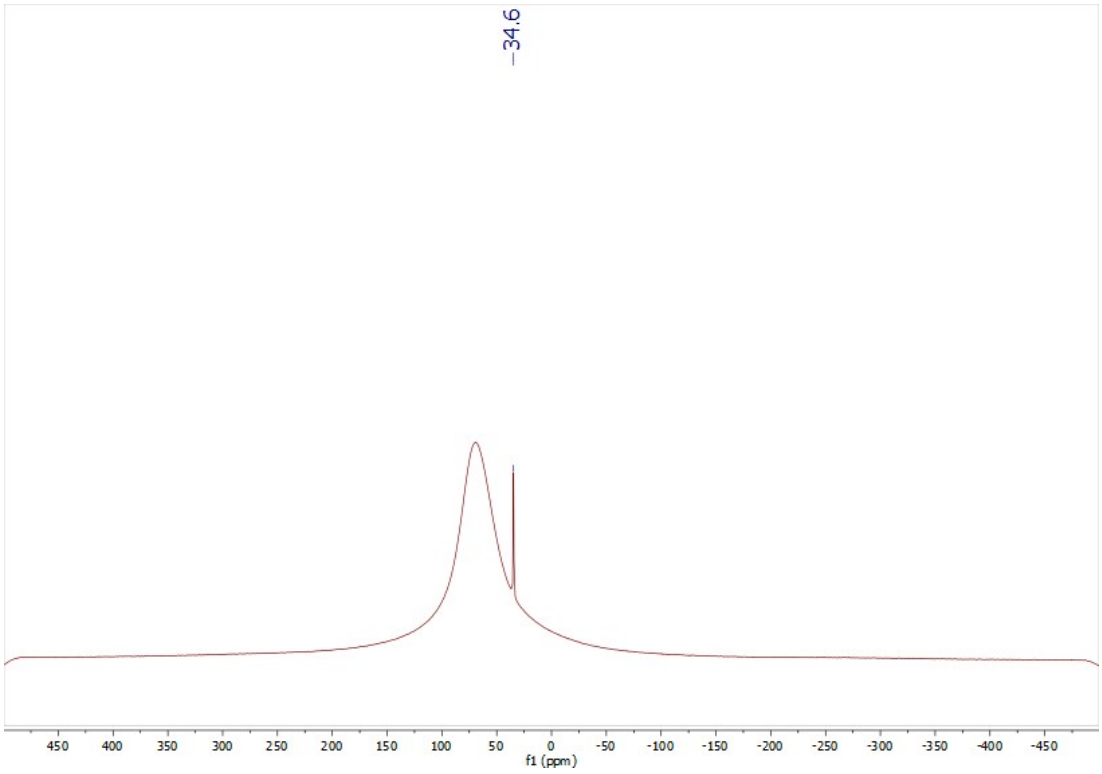

Figure s14: $^{27}Al\{^{1}H\}$ NMR spectrum of [(**1-Dipp**)Sn][Al(OR^{F})$_4$] (*with probe background at ca. 70 ppm*)

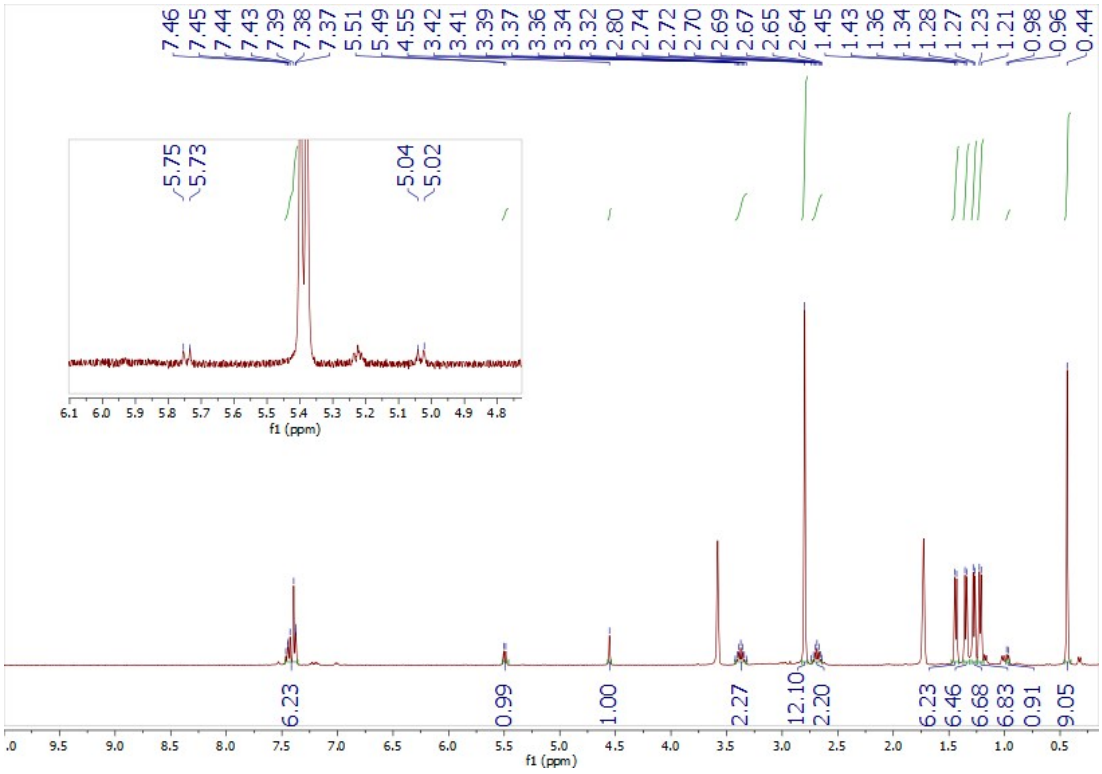

Figure s15: ^{1}H NMR spectrum of [(**1-Dipp**)Si(H)(NH^{t}Bu)][Al(OR^{F})$_4$]

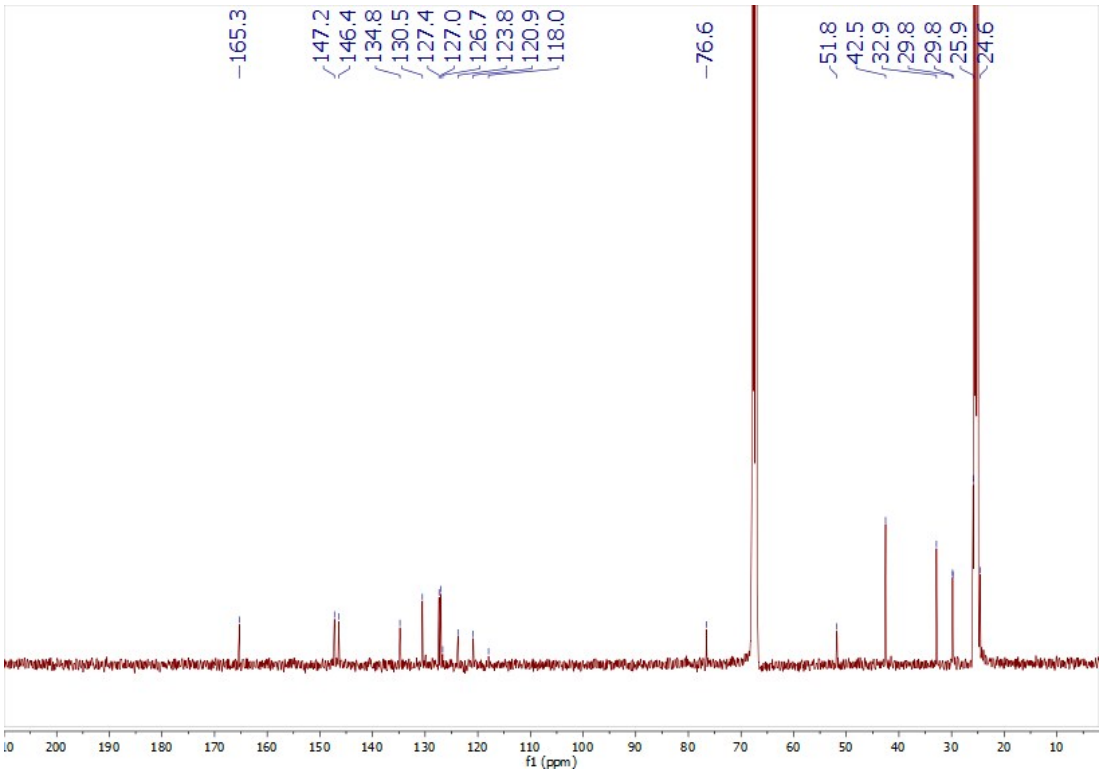

Figure s16: ^{13}C{^{1}H} NMR spectrum of [(**1-Dipp**)Si(H)(NH^{t}Bu)][Al(OR^{F})$_4$]

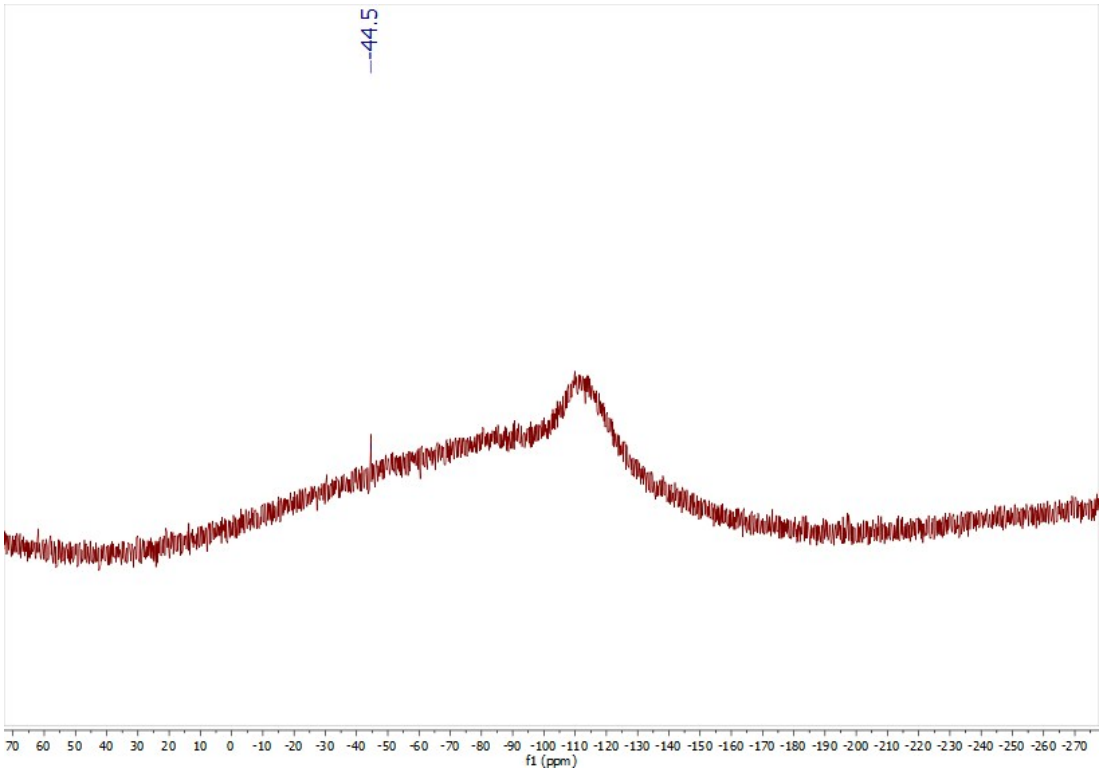

Figure s17: $^{29}Si\{^{1}H\}$ NMR spectrum of [(**1-Dipp**)Si(H)(NH^{t}Bu)][Al(OR^{F})$_4$]

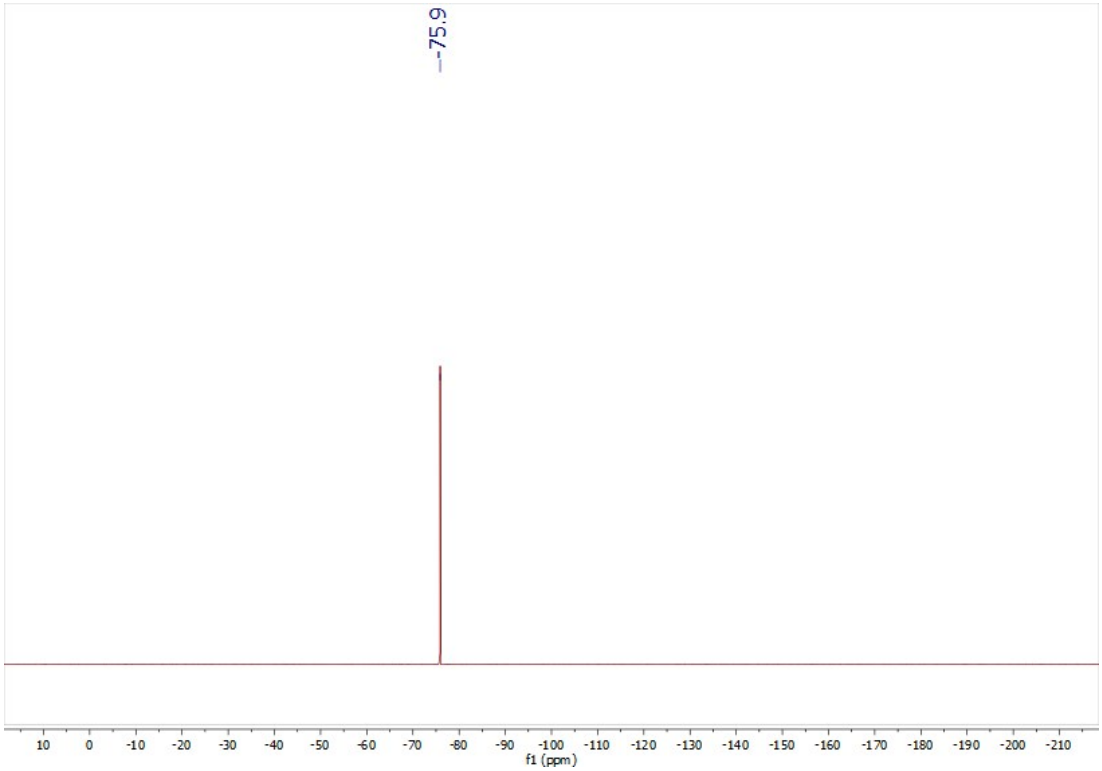

Figure s18: $^{19}F\{^{1}H\}$ NMR spectrum of [(**1-Dipp**)Si(H)(NH^{t}Bu)][Al(OR^{F})$_4$]

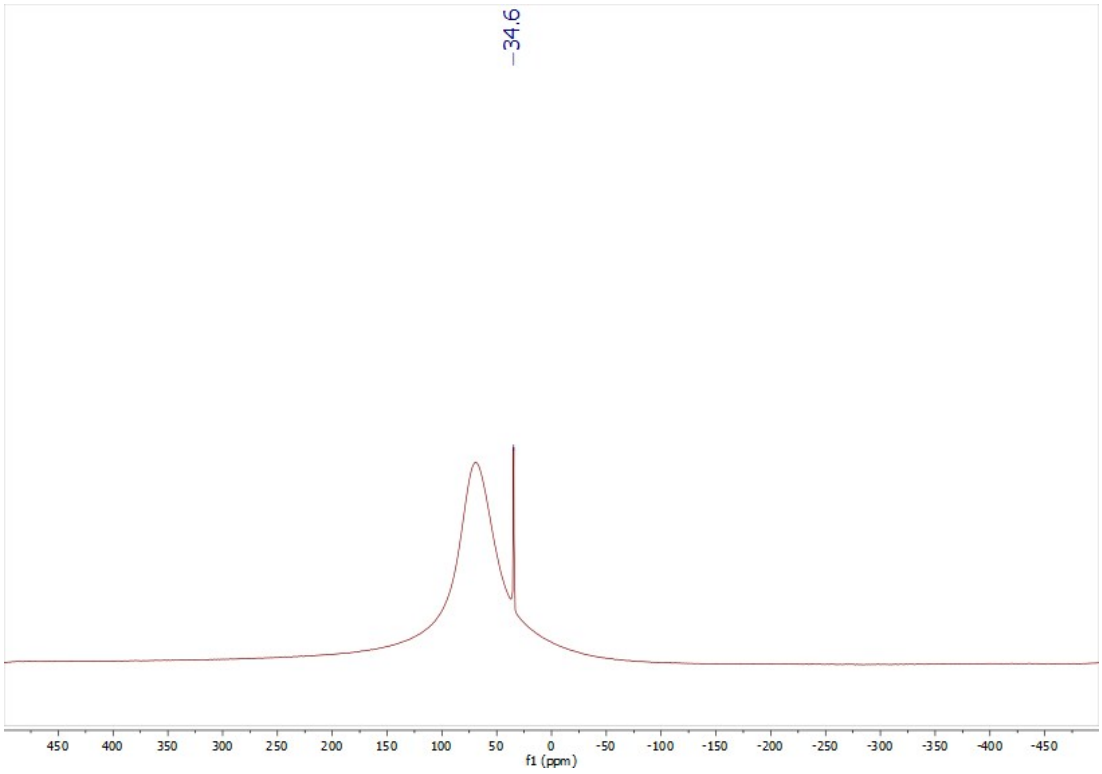

Figure s19: $^{27}Al\{^{1}H\}$ NMR spectrum of [(**1-Dipp**)Si(H)(NH^{t}Bu)][Al(OR^{F})$_4$]

(*with probe background at ca. 70 ppm*)

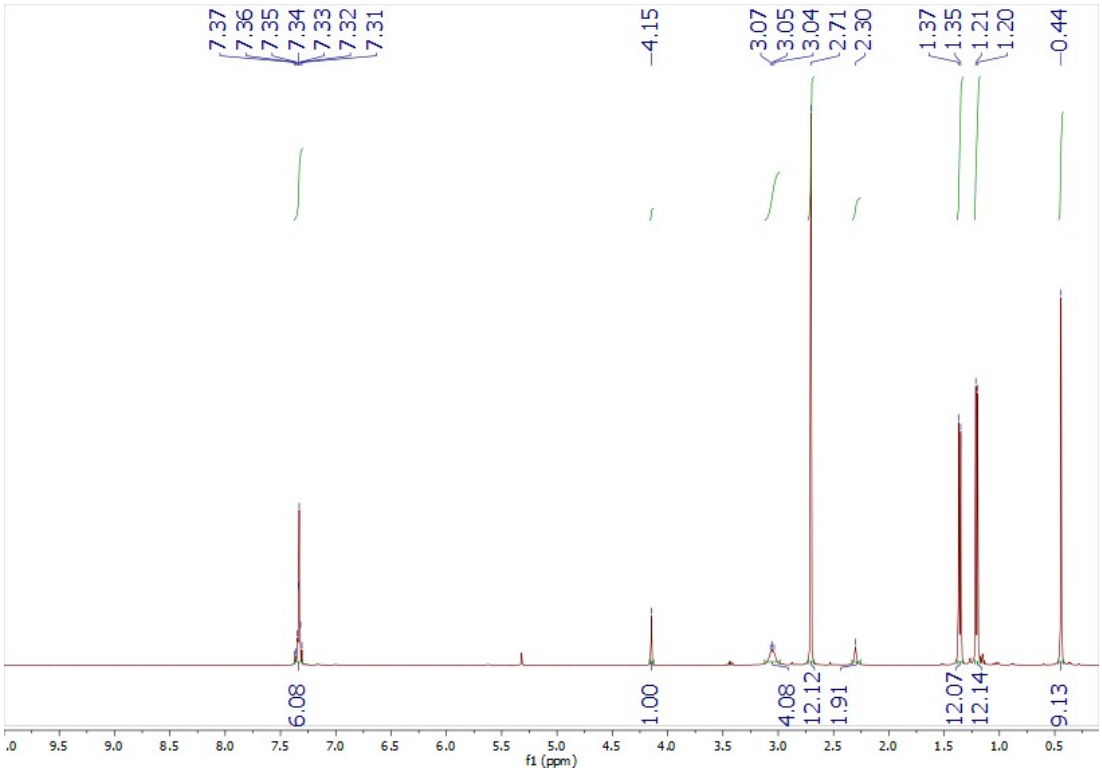

Figure s20: ^{1}H NMR spectrum of [(**1-Dipp**)Ge·($NH_2{}^{t}Bu$)][$Al(OR^F)_4$]

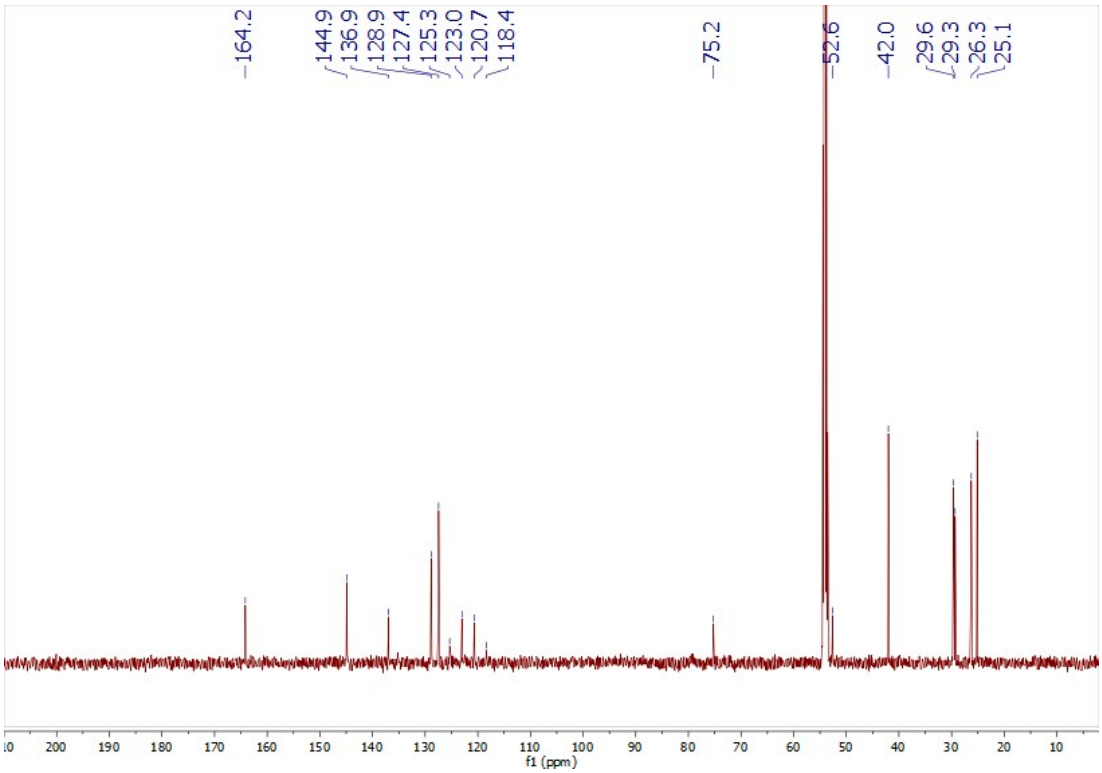

Figure s21: $^{13}C\{^{1}H\}$ NMR spectrum of [(**1-Dipp**)Ge·($NH_2{}^{t}Bu$)][$Al(OR^F)_4$]

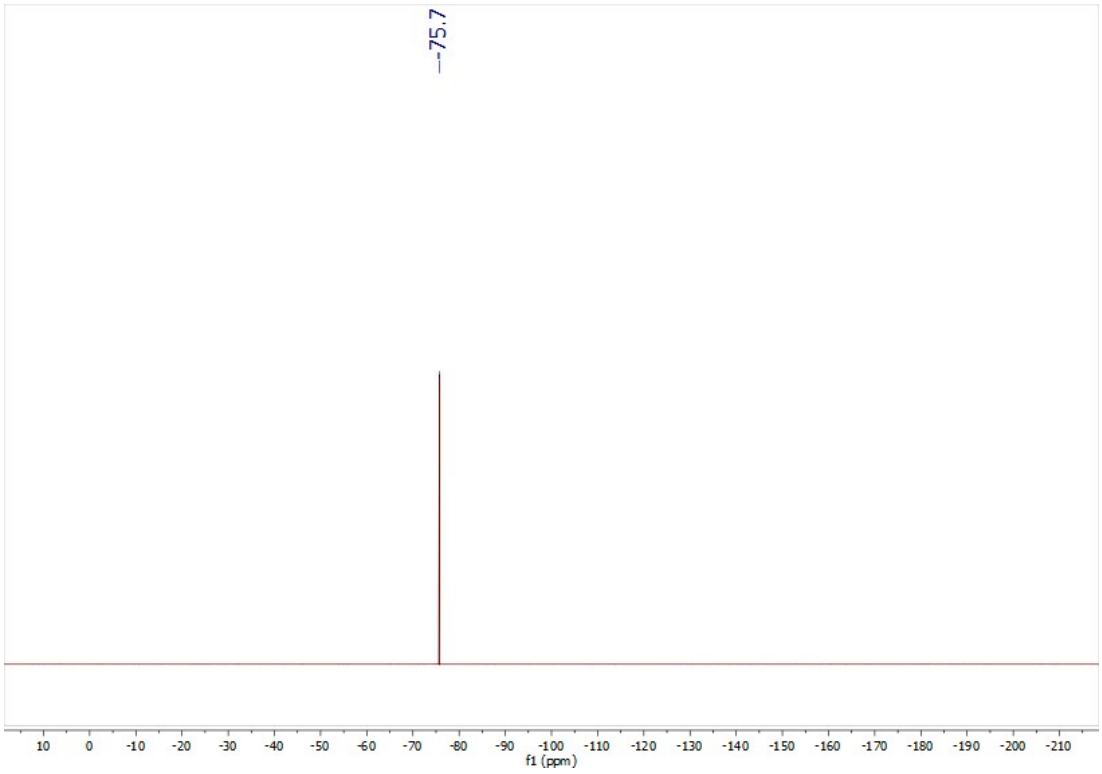

Figure s22: $^{19}F\{^{1}H\}$ NMR spectrum of [(**1-Dipp**)Ge·($NH_2{}^tBu$)][$Al(OR^F)_4$]

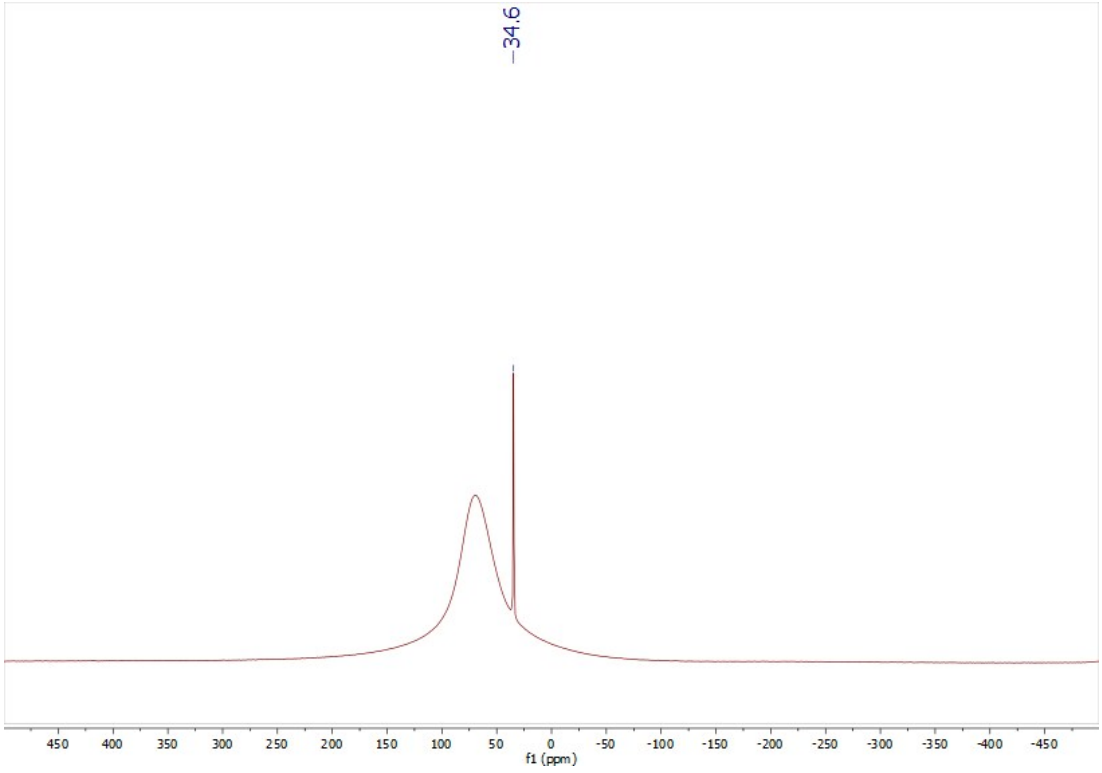

Figure s23: $^{27}Al\{^{1}H\}$ NMR spectrum of [(**1-Dipp**)Ge·($NH_2{}^tBu$)][$Al(OR^F)_4$]

(*with probe background at ca. 70 ppm*)

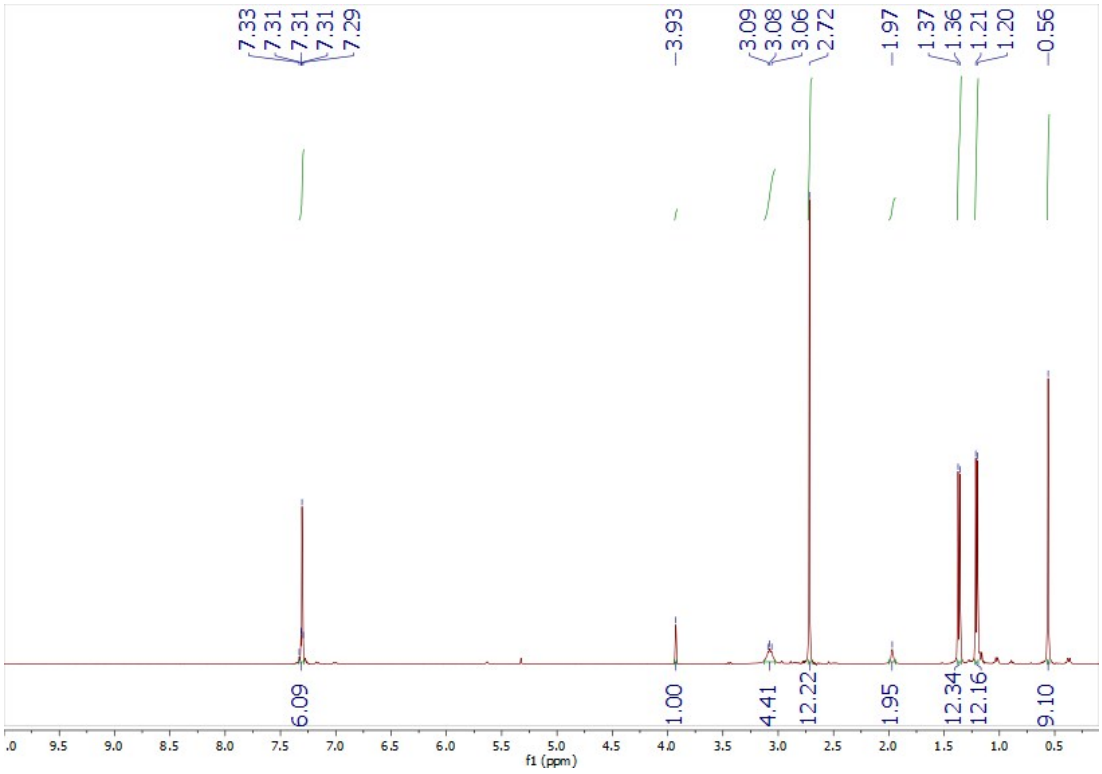

Figure s24: ^{1}H NMR spectrum of [(**1-Dipp**)Sn·($NH_2{}^{t}Bu$)][$Al(OR^F)_4$]

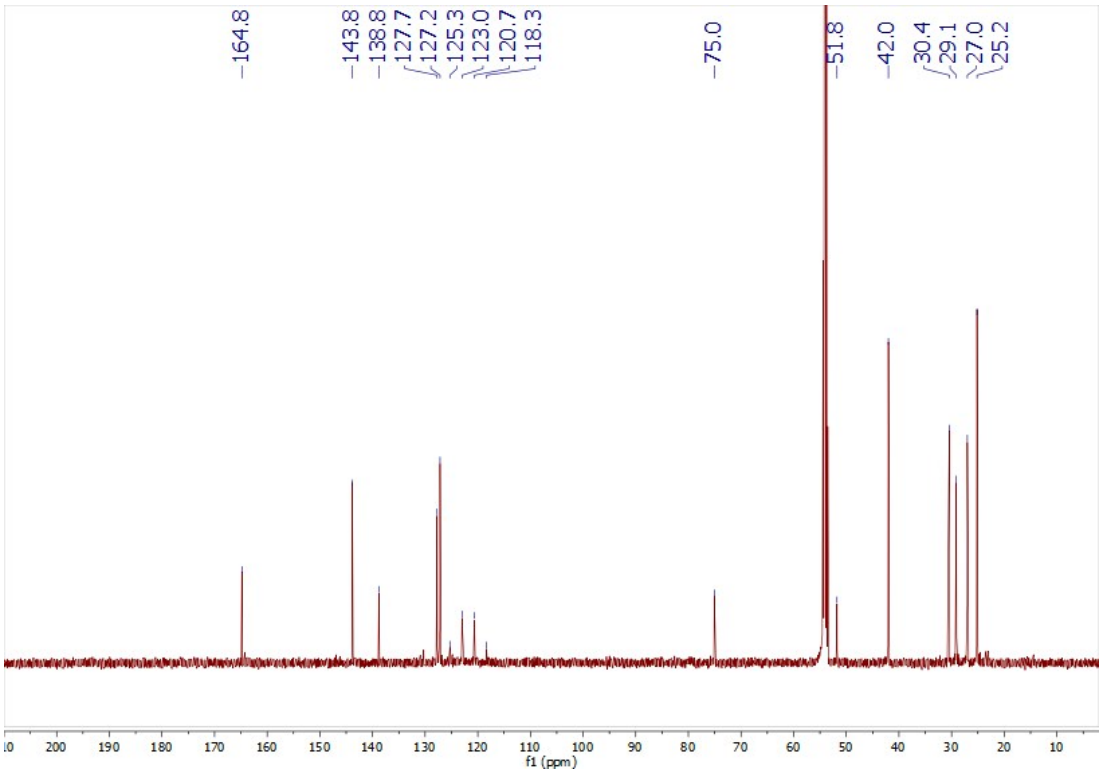

Figure s25: $^{13}C\{^{1}H\}$ NMR spectrum of [(**1-Dipp**)Sn·($NH_2{}^{t}Bu$)][$Al(OR^F)_4$]

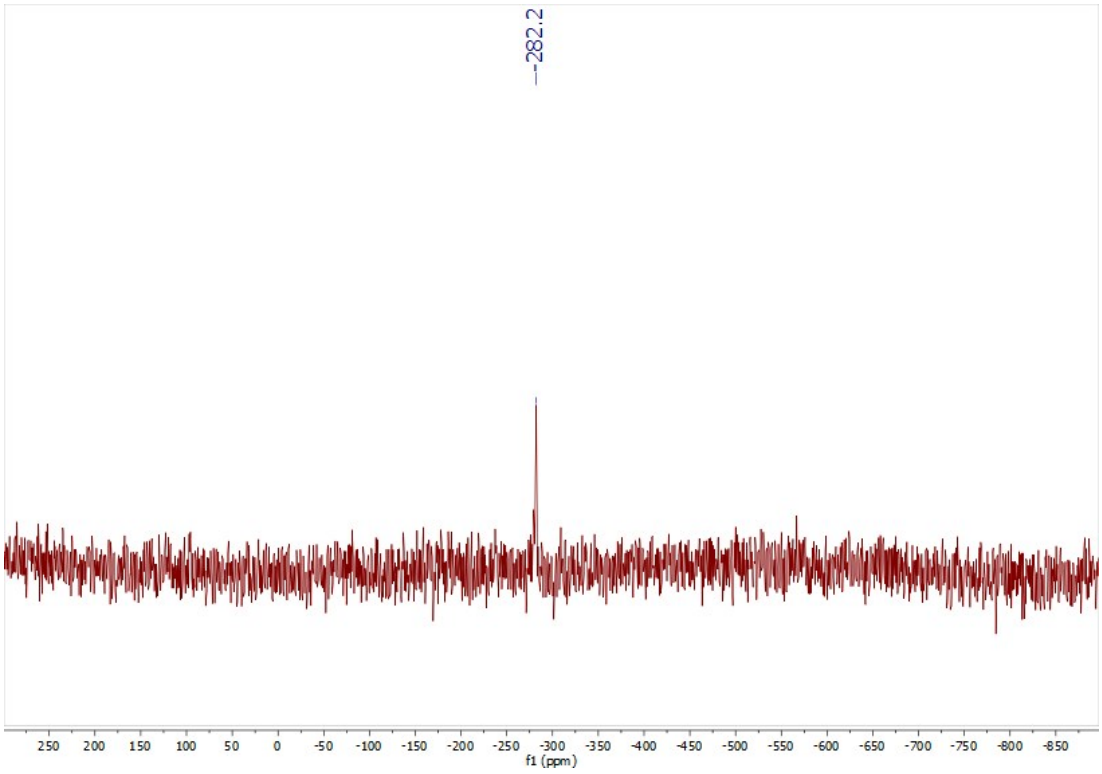

Figure s26: $^{119}Sn\{^{1}H\}$ NMR spectrum of [(**1-Dipp**)Sn·($NH_2{}^tBu$)][$Al(OR^F)_4$]

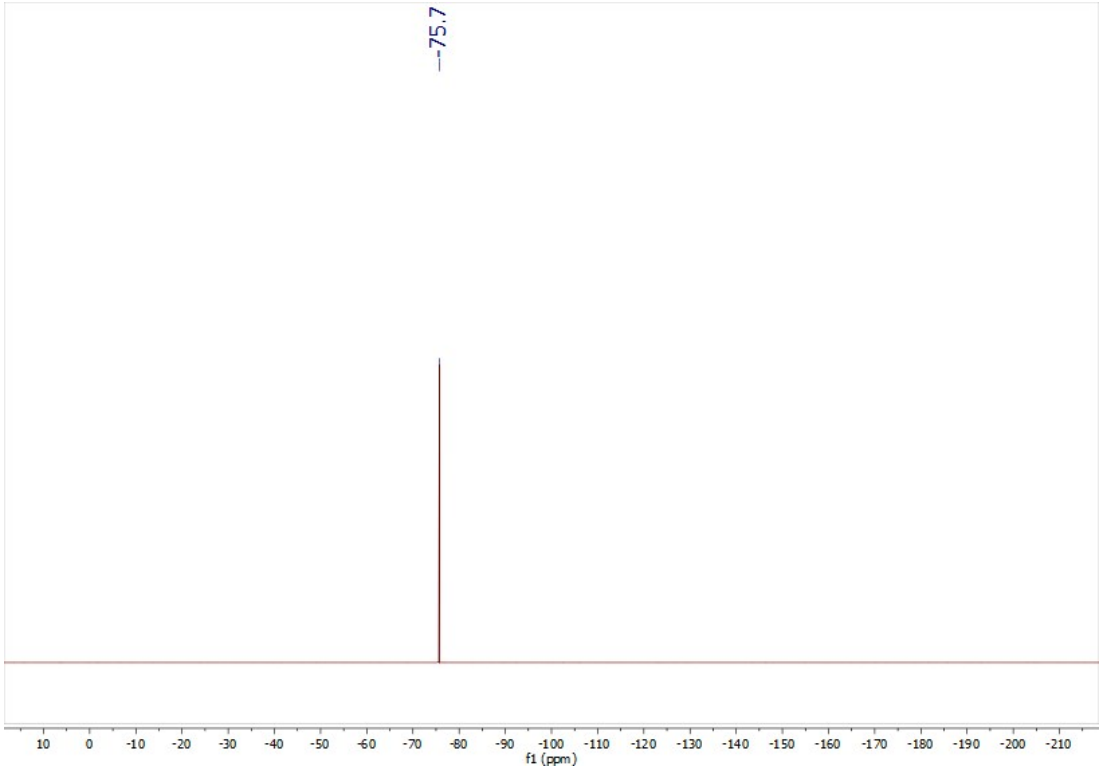

Figure s27: $^{19}F\{^{1}H\}$ NMR spectrum of [(**1-Dipp**)Sn·($NH_2{}^tBu$)][$Al(OR^F)_4$]

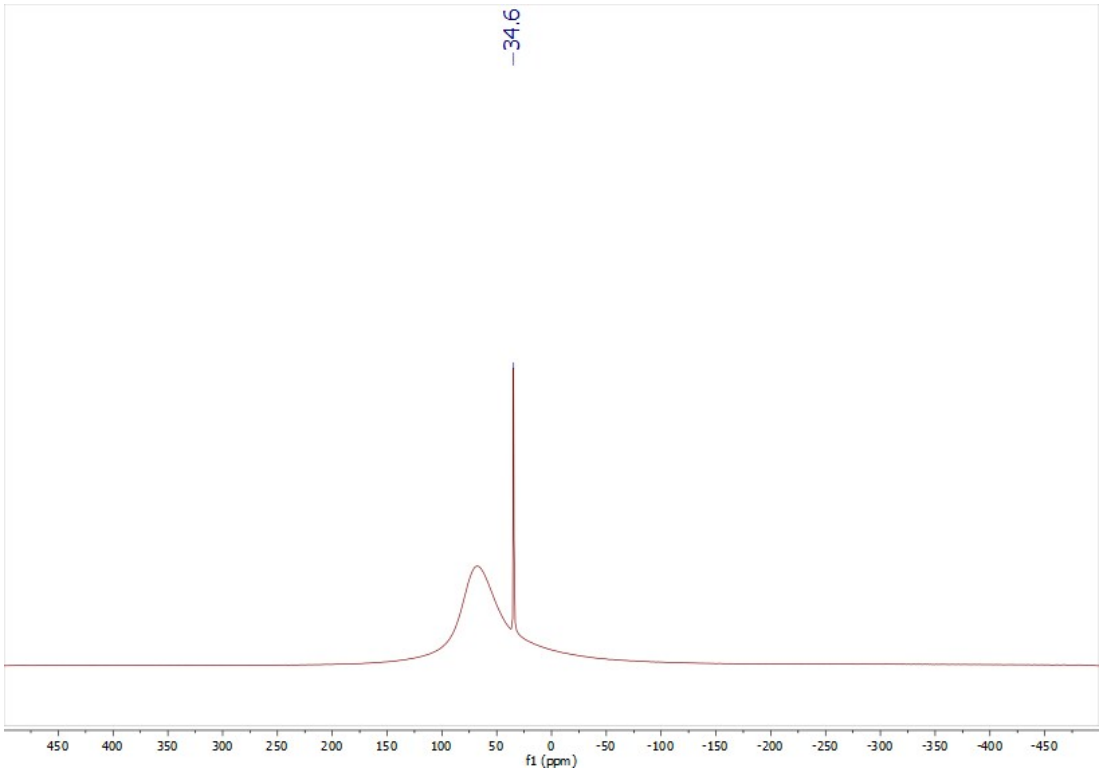

Figure s28: $^{27}Al\{^{1}H\}$ NMR spectrum of [(**1-Dipp**)Sn·($NH_2{}^{t}Bu$)][$Al(OR^F)_4$]

(*with probe background at ca. 70 ppm*)

3. X-ray crystallographic studies

Single-crystal X-ray diffraction data were collected using an Oxford Diffraction Supernova dual-source diffractometer equipped with a 135 mm Atlas CCD area detector. Crystals were selected under Paratone-N oil, mounted on Micromount loops and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device.[S3] Data were collected at 150 K using mirror monochromated Cu K_α radiation (λ = 1.5418 Å; Oxford Diffraction Supernova) (unless otherwise stated). Data collected were processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro).[S4] Equivalent reflections were merged and diffraction patterns processed with the CrysAlisPro suite. Structures were subsequently solved using ShelXT 2014 and refined on F^2 using the ShelXL 2014 package and ShelXle or XSeed.[S5]

Table S1. Summary of crystallographic parameters for [(**1-Dipp**)E][Al(OR^F)$_4$] (E = Si, Ge, Sn)

Compound	[(**1-Dipp**)Si][Al(OR^F)$_4$]	[(**1-Dipp**)Ge][Al(OR^F)$_4$]	[(**1-Dipp**)Sn][Al(OR^F)$_4$]
Empirical formula	$C_{47}H_{47}AlF_{36}N_4O_4Si$	$C_{47}H_{47}AlF_{36}N_4O_4Ge$	$C_{47}H_{47}AlF_{36}N_4O_4Sn$
Formula weight	1470.95	1515.45	1561.55
Temperature (K)	150(2)	150(2)	110(2)
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
Crystal system	Monoclinic	Monoclinic	Monoclinic
a (Å)	13.99300(10)	13.9314(3)	16.26100(10)
b (Å)	19.5525(2)	19.6837(3)	19.80550(10)
c (Å)	21.6682(2)	21.7403(4)	18.81110(10)
α (°)	90	90	90
β (°)	98.0120(10)	98.072(2)	103.1710(10)
γ (°)	90	90	90
Volume (Å^3)	5870.51(9)	5902.59(19)	5898.88(6)
Z	4	4	4
ρ_{calc} (g.cm^{-3})	1.664	1.705	1.758
μ (mm^{-1})	1.995	2.338	5.080
F(000)	2960.0	3032.0	3104.0
Crystal size (mm^3)	0.580 × 0.350 × 0.080	0.18 x 0.10 x 0.10	0.18 × 0.18 × 0.1
Radiation	Cu Kα (λ = 1.5418)	Cu Kα (λ = 1.5418)	Cu Kα (λ = 1.5418)
2Θ range for data collection (°)	6.116 to 152.498	7.826 to 148.994	7.148 to 152.608
Index ranges	-17 ≤ h ≤ 17, -24 ≤ k ≤ 23, -18 ≤ l ≤ 27	-17 ≤ h ≤ 17, -24 ≤ k ≤ 24, -24 ≤ l ≤ 27	-20 ≤ h ≤ 19, -24 ≤ k ≤ 23, -22 ≤ l ≤ 23
Reflections collected	69419	74075	93156
Independent reflections	12227 [R_{int} = 0.0708]	12073 [R_{int} = 0.0316]	12311 [R_{int} = 0.0421]
Data/restraints /parameters	12227/75/892	12073/3263/1319	12311/2790/1261
Goodness-of-fit on F^2	1.051	1.480	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0852, wR_2 = 0.2387	R_1 = 0.0916, wR_2 = 0.2927	R_1 = 0.0451, wR_2 = 0.1257
Final R indexes [all data]	R_1 = 0.0965, wR_2 = 0.2547	R_1 = 0.0975, wR_2 = 0.3088	R_1 = 0.0470, wR_2 = 0.1278
Largest diff. peak/hole (e Å^{-3})	1.32/-1.23	4.82/-0.72	1.30/-0.72

Table S2. Summary of crystallographic parameters of amine adducts.

Compound	[(**1-Dipp**)Ge·($NH_2{}^tBu$)][$Al(OR^F)_4$]	[(**1-Dipp**)Sn·($NH_2{}^tBu$)][$Al(OR^F)_4$]
Empirical formula	$C_{51}H_{58}AlF_{36}GeN_5O_4$	$C_{57}H_{72}AlF_{36}N_5O_4Sn$
Formula weight	1588.59	1720.86
Temperature (K)	150(2)	150(2)
Space group	P-1	$P2_1$
Crystal system	Triclinic	Monoclinic
a (Å)	11.2303(3)	11.02790(10)
b (Å)	14.7524(5)	19.9344(2)
c (Å)	20.0867(5)	17.9479(2)
α (°)	80.757(3)	90
β (°)	87.515(2)	107.2930(10)
γ (°)	86.337(3)	90
Volume ($Å^3$)	3276.07(17)	3767.22(7)
Z	2	2
ρ_{calc} ($g.cm^{-3}$)	1.610	1.517
μ (mm^{-1})	2.139	4.035
F(000)	1600.0	1736.0
Crystal size (mm^3)	0.250 × 0.090 × 0.050	0.07 × 0.07 × 0.04
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection (°)	6.948 to 152.502	6.802 to 152.498
Index ranges	13 ≤ h ≤ 14, -18 ≤ k ≤ 18, -25 ≤ l ≤ 21	-13 ≤ h ≤ 13, -24 ≤ k ≤ 24, -22 ≤ l ≤ 22
Reflections collected	35392	57095
Independent reflections	13531 [R_{int} = 0.0393]	15603 [R_{int} = 0.0352]
Data/restraints /parameters	13531/0/898	15603/3548/1529
Goodness-of-fit on F^2	1.022	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0456, wR_2 = 0.1209	R_1 = 0.0490, wR_2 = 0.1353
Final R indexes [all data]	R_1 = 0.0553, wR_2 = 0.1313	R_1 = 0.0522, wR_2 = 0.1408
Largest diff. peak/hole (e $Å^{-3}$)	0.78/-0.41	1.53/-0.49

Table S3. Summary of crystallographic parameters of N—H and C—Cl activation products.

Compound	[(**1-Dipp**)Si(H)(NH_2)] [$Al(OR^F)_4$]	[(**1-Dipp**)Si(H)(^{t}BuNH)] [$Al(OR^F)_4$]	[(**1-Dipp**)Si(Cl)(CH_2Cl)] [$Al(OR^F)_4$]
Empirical formula	$C_{47}H_{50}AlF_{36}N_5O_4Si$	$C_{51}H_{58}AlF_{36}N_5O_4Si$	$C_{48}H_{49}AlCl_2F_{36}N_4O_4Si$
Formula weight	1487.99	1544.09	1555.88
Temperature (K)	150(2)	150(2)	150(2)
Space group	$P2_1/m$	P-1	$P2_1$
Crystal system	Monoclinic	Triclinic	Monoclinic
a (Å)	10.8558(3)	11.1801(6)	10.8096(2)
b (Å)	19.5631(5)	14.7647(9)	36.2399(5)
c (Å)	14.1328(5)	20.0683(8)	15.9889(3)
α (°)	90	82.558(4)	90
β (°)	97.318(3)	87.937(4)	92.324(2)
γ (°)	90	85.473(5)	90
Volume (Å^3)	2976.99(14)	3273.4(3)	6258.32(19)
Z	2	2	4
ρ_{calc} (g.cm^{-3})	1.660	1.567	1.651
μ (mm^{-1})	1.979	1.822	2.675
F(000)	1500.0	1564.0	3128
Crystal size (mm^3)	0.20 × 0.13 × 0.09	0.280 × 0.120 × 0.030	0.180 × 0.160 × 0.060
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection (°)	7.758 to 139.988	4.442 to 154.77	7.378 to 152.804
Index ranges	-13 ≤ h ≤ 12, -23 ≤ k ≤ 23, -16 ≤ l ≤ 17	-13 ≤ h ≤ 14, -18 ≤ k ≤ 18, -15 ≤ l ≤ 25	-13 ≤ h ≤ 12, -37 ≤ k ≤ 45, -20 ≤ l ≤ 19
Reflections collected	15891	27682	37746
Independent reflections	5823 [R_{int} = 0.0538]	13555 [R_{int} = 0.0722]	21239 [Rint = 0.0339]
Data/restraints/parameters	5823/249/650	13555/0/901	21239/763/1854
Goodness-of-fit on F^2	1.021	1.021	1.723
Final R indexes [I>=2σ (I)]	R_1 = 0.0671, wR_2 = 0.1790	R_1 = 0.0747, wR_2 = 0.2003	R_1 = 0.1471, wR_2 = 0.3855
Final R indexes [all data]	R_1 = 0.0833, wR_2 = 0.1983	R_1 = 0.1273, wR_2 = 0.2381	R_1 = 0.1566, wR_2 = 0.4004
Largest diff. peak/hole (e Å^{-3})	0.70/-0.46	0.52/-0.38	1.49/-0.81

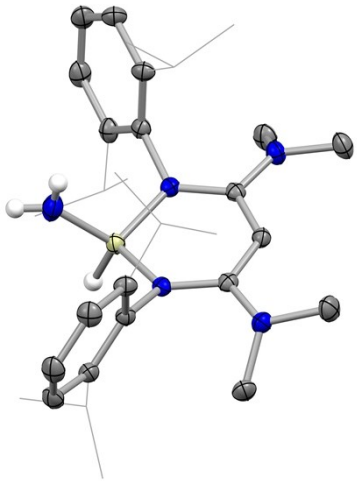

Figure s29: Molecular structure of [(**1-Dipp**)Si(H)(NH_2)][Al(OR^F)$_4$] in the solid state as determined by X-ray crystallography. [Al(OR^F)$_4$]$^-$ anion and most hydrogen atoms omitted, and isopropyl groups shown in wireframe format for clarity.

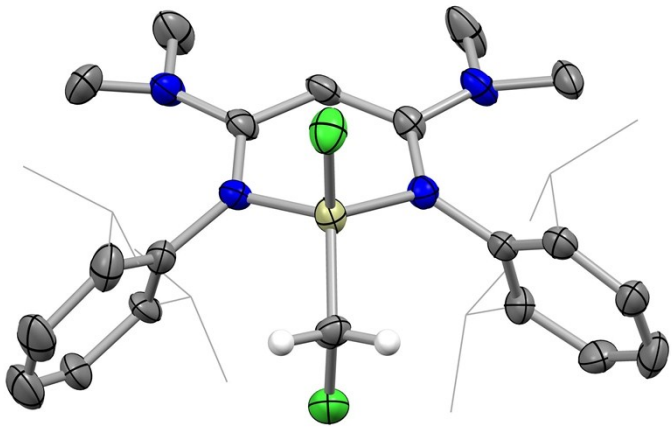

Figure s30: Molecular structure of [(**1-Dipp**)Si(Cl)(CH_2Cl)][$Al(OR^F)_4$] in the solid state as determined by X-ray crystallography. $[Al(OR^F)_4]^-$ anion, most hydrogen atoms and second component of asymmetric unit omitted, and isopropyl groups shown in wireframe format for clarity.

4. Computational details:

DFT calculations were performed using Gaussian09 (Revision D.01) programme package.[S6] Geometry optimisations were performed with the PBE1PBE hybrid exchange-correlation functional[S7], in conjunction with the Def2-TZVPP basis set for Sn, and the Def2-TZVP basis set for all other elements,[S8] with an ultrafine integration grid. For Sn, an effective core potential (ECP) was also employed, taking into account scalar relativistic effects. Structural optimisations were carried out for the full ligand systems, and were reported as Gibbs free energies in the gas phase. To confirm the nature of the stationary points found (minima with no imaginary frequencies), full frequency calculations were performed for optimised geometries. Graphics were created with the GaussView programme.[S9]

Cartesian coordinates of optimized structures

[(1-Dipp)Si]$^+$

83

Si	-0.000100	0.725700	-0.604400
N	1.346100	0.083900	0.348700
N	-1.346300	0.083400	0.348600
N	2.357800	-1.184000	2.074600
N	-2.357500	-1.187500	2.072500
C	1.252400	-0.722700	1.451100
C	0.000100	-1.087500	1.952600
H	0.000000	-1.587800	2.905200
C	-1.252300	-0.724000	1.450300
C	3.123400	-0.801100	-1.105300
C	2.589000	0.274800	-0.378600
C	-3.176800	1.551100	-0.405100
C	-3.122700	-0.800600	-1.107000
C	3.175800	1.551600	-0.407000
C	-2.589100	0.274600	-0.378600
C	2.468300	-2.164600	-1.187800
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C	4.898500	0.661800	-1.852100
H	5.805800	0.811800	-2.425400
C	4.334200	1.715800	-1.159200
H	4.805700	2.690700	-1.198600
C	4.293500	-0.580800	-1.824200
H	4.728700	-1.396700	-2.389600
C	-4.292800	-0.579800	-1.825900
H	-4.727400	-1.395100	-2.392600
C	-3.596600	-0.437600	2.202500
H	-3.451100	0.604200	1.942300
H	-3.908000	-0.481000	3.249000
H	-4.393700	-0.850200	1.579600
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H	1.777100	2.414600	0.950200
C	-4.335100	1.715700	-1.157300
H	-4.807200	2.690400	-1.195300
C	-2.466800	-2.163600	-1.191200

H	-1.582800	-2.168000	-0.549000
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H	-5.805700	0.812800	-2.425400
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H	-1.779500	2.412200	0.954600
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H	4.393500	-0.845000	1.580900
H	3.907700	-0.474700	3.250100
H	3.449400	0.608600	1.942400
C	3.392200	-3.278100	-0.699000
H	4.277500	-3.368500	-1.332200
H	2.874100	-4.239600	-0.723500
H	3.732500	-3.101300	0.323500
C	2.271600	-2.326500	2.961000
H	1.961900	-2.047300	3.975600
H	3.260900	-2.780700	3.025600
H	1.582400	-3.071000	2.564600
C	-2.270500	-2.331100	2.957500
H	-1.579800	-3.073900	2.560800
H	-3.259200	-2.786800	3.020500
H	-1.962300	-2.052700	3.972700
C	3.640400	3.389500	1.271800
H	4.044000	2.679600	1.997000
H	3.178200	4.208000	1.827900
H	4.483000	3.807100	0.716800
C	-2.087200	3.798500	-0.641900
H	-1.333400	3.381500	-1.313000
H	-1.641000	4.635700	-0.099900
H	-2.895600	4.195500	-1.260500
C	2.086100	3.798500	-0.648200
H	2.895000	4.195000	-1.266400
H	1.639100	4.636400	-0.107700
H	1.333100	3.380300	-1.319400
C	1.994000	-2.444500	-2.614000
H	1.319800	-1.663900	-2.973900
H	1.467600	-3.400700	-2.661100
H	2.837000	-2.495300	-3.306900
C	-3.390100	-3.278100	-0.703600
H	-3.730300	-3.102700	0.319100
H	-2.871600	-4.239400	-0.729500
H	-4.275500	-3.368100	-1.336900
C	-3.643200	3.386400	1.275900
H	-4.485200	3.805000	0.720800
H	-3.181500	4.203900	1.834000
H	-4.047500	2.675300	1.999500
C	-1.992300	-2.441500	-2.617700
H	-2.835100	-2.491700	-3.310700
H	-1.465500	-3.397400	-2.665900
H	-1.318300	-1.660200	-2.976500

[(1-Dipp)Ge]$^{+}$

83

Ge	0.000100	0.773500	-0.659900
N	-1.408600	0.064100	0.381600
N	1.408700	0.064000	0.381600
N	-2.352500	-1.241600	2.105300
N	2.352400	-1.242300	2.105000
C	-1.264800	-0.747200	1.466700
C	-0.000000	-1.092600	1.957400

H	-0.000000	-1.592100	2.910700
C	1.264800	-0.747500	1.466600
C	2.235500	-2.399600	2.966700
H	1.538700	-3.124000	2.547000
H	1.917600	-2.137100	3.983600
H	3.215900	-2.872800	3.034800
C	3.589900	-0.500600	2.280500
H	3.876500	-0.563200	3.333300
H	3.452700	0.546900	2.037100
H	4.402200	-0.902300	1.669900
C	-2.235800	-2.398700	2.967300
H	-3.216400	-2.871500	3.035700
H	-1.917600	-2.136100	3.984000
H	-1.539400	-3.123500	2.547600
C	-3.589500	-0.499100	2.281100
H	-4.402300	-0.900600	1.671000
H	-3.451800	0.548200	2.037300
H	-3.875700	-0.561200	3.334100
C	-2.658300	0.224500	-0.328100
C	-3.172200	-0.855000	-1.065600
C	-4.343500	-0.650900	-1.787700
H	-4.761000	-1.470800	-2.360800
C	-4.972300	0.579800	-1.808900
H	-5.879300	0.717100	-2.385800
C	-4.433300	1.637500	-1.101400
H	-4.926100	2.602200	-1.130900
C	-3.275700	1.488000	-0.345200
C	-2.746900	2.685700	0.421800
H	-1.927400	2.345100	1.062600
C	-3.804700	3.307200	1.334100
H	-4.238300	2.581600	2.025400
H	-4.623900	3.741100	0.757100
H	-3.361900	4.111100	1.926300
C	-2.194000	3.749500	-0.527800
H	-1.410500	3.354000	-1.178900
H	-1.779400	4.588300	0.036400
H	-2.984200	4.139900	-1.173500
C	-2.493200	-2.206500	-1.152600
H	-1.612500	-2.198200	-0.506000
C	-3.400500	-3.336600	-0.670900
H	-2.866300	-4.289400	-0.694600
H	-4.281200	-3.440400	-1.308400
H	-3.748200	-3.166700	0.350100
C	-2.008500	-2.474600	-2.577500
H	-1.469200	-3.423500	-2.626300
H	-1.342200	-1.684600	-2.932900
H	-2.846800	-2.533000	-3.275400
C	2.658300	0.224500	-0.328100
C	3.275800	1.488000	-0.344700
C	4.433400	1.637600	-1.100900
H	4.926300	2.602300	-1.130100
C	4.972300	0.580200	-1.808900
H	5.879200	0.717700	-2.385800
C	4.343300	-0.650500	-1.788200
H	4.760700	-1.470100	-2.361700
C	3.172000	-0.854800	-1.066100
C	2.492900	-2.206100	-1.153500
H	1.612200	-2.197900	-0.507000
C	3.400100	-3.336500	-0.672200

H	2.865900	-4.289200	-0.696300
H	3.747600	-3.166900	0.348900
H	4.280900	-3.440000	-1.309600
C	2.008300	-2.473700	-2.578600
H	2.846600	-2.532100	-3.276400
H	1.342100	-1.683600	-2.933700
H	1.468800	-3.422600	-2.627700
C	2.747200	2.685300	0.422900
H	1.927800	2.344400	1.063700
C	3.805100	3.306400	1.335300
H	4.239000	2.580500	2.026100
H	3.362400	4.109900	1.928000
H	4.624200	3.740700	0.758400
C	2.194100	3.749500	-0.526100
H	2.984200	4.140100	-1.171900
H	1.779600	4.588100	0.038500
H	1.410400	3.354300	-1.177100

[(1-Dipp)Sn]$^{+}$

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Sn	-0.000000	0.883300	-0.786000
N	1.490500	0.055600	0.432800
N	-1.490500	0.055600	0.432900
N	2.341400	-1.321300	2.139600
N	-2.341400	-1.321100	2.139900
C	1.281600	-0.770900	1.487900
C	0.000000	-1.091000	1.963400
H	0.000000	-1.593700	2.915500
C	-1.281600	-0.770800	1.488000
C	3.583600	-0.608200	2.377700
H	4.412000	-1.009500	1.788100
H	3.832800	-0.697800	3.438500
H	3.472200	0.446900	2.154000
C	2.178400	-2.501700	2.959500
H	1.852100	-2.266300	3.980800
H	3.143800	-3.005800	3.026700
H	1.467400	-3.190900	2.505800
C	-2.178400	-2.501400	2.959900
H	-1.467600	-3.190800	2.506200
H	-3.143900	-3.005300	3.027400
H	-1.851900	-2.265900	3.981100
C	-3.583700	-0.608000	2.377700
H	-3.472300	0.447100	2.153700
H	-3.832900	-0.697300	3.438600
H	-4.412000	-1.009600	1.788300
C	2.752000	0.164300	-0.254200
C	3.226800	-0.917900	-1.016700
C	4.401400	-0.743400	-1.741400
H	4.785400	-1.567600	-2.331800
C	5.077300	0.462200	-1.742900
H	5.985400	0.576700	-2.322800
C	4.584600	1.523000	-1.006600
H	5.117300	2.466900	-1.013900
C	3.426800	1.400600	-0.246100
C	2.956900	2.592100	0.568100
H	2.145100	2.254200	1.220100
C	2.413900	3.705500	-0.328200
H	3.193100	4.081200	-0.995800
H	2.054200	4.544000	0.272900

H	1.590100	3.367500	-0.964800
C	4.058600	3.152500	1.468300
H	4.497100	2.387700	2.112200
H	3.655100	3.940400	2.108300
H	4.868400	3.591900	0.882300
C	2.501400	-2.243900	-1.121300
H	1.620300	-2.210900	-0.476100
C	3.368700	-3.407800	-0.646300
H	4.247700	-3.535400	-1.282000
H	2.803500	-4.342300	-0.678400
H	3.718100	-3.255900	0.376800
C	2.013400	-2.485700	-2.549600
H	1.371500	-1.673900	-2.903200
H	1.445100	-3.417000	-2.608700
H	2.850600	-2.563000	-3.246900
C	-2.752000	0.164300	-0.254200
C	-3.226800	-0.918000	-1.016600
C	-4.401400	-0.743400	-1.741400
H	-4.785400	-1.567600	-2.331800
C	-5.077200	0.462300	-1.743000
H	-5.985300	0.576800	-2.323000
C	-4.584500	1.523100	-1.006700
H	-5.117200	2.467000	-1.014100
C	-3.426700	1.400600	-0.246200
C	-2.956800	2.592200	0.568000
H	-2.145000	2.254300	1.219900
C	-4.058400	3.152600	1.468200
H	-4.868300	3.592000	0.882200
H	-3.654900	3.940500	2.108100
H	-4.496900	2.387800	2.112100
C	-2.413800	3.705600	-0.328400
H	-1.590000	3.367500	-0.965000
H	-2.054000	4.544000	0.272700
H	-3.193000	4.081300	-0.996000
C	-2.501500	-2.244000	-1.121100
H	-1.620400	-2.210900	-0.476000
C	-3.368900	-3.407800	-0.646000
H	-3.718200	-3.255800	0.377000
H	-2.803700	-4.342400	-0.678100
H	-4.247900	-3.535300	-1.281700
C	-2.013500	-2.486000	-2.549500
H	-2.850800	-2.563200	-3.246700
H	-1.445400	-3.417300	-2.608500
H	-1.371600	-1.674300	-2.903200

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