Electronic Supplementary Material (ESI) for Chemical Science.

Supplementary information for

Metal-metal bonded alkaline-earth distannyls

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Experimental Procedures

General Considerations:

All manipulations were performed under an inert atmosphere by using standard Schlenk techniques or in a dry, solvent-free glovebox (Jacomex; O_2<1 ppm, H_2O<3 ppm). THF was distilled under argon from Na/benzophenone prior to use. Hexanes (petroleum ether), toluene, dichloromethane, and Et_2O were collected from MBraun SPS-800 purification alumina columns and thoroughly degassed with argon before being stored on 4 Å molecular sieves. Deuterated solvents (Eurisotop, Saclay, France) were stored in sealed ampoules over activated 4 Å molecular sieves and degassed by a minimum of three freeze–thaw cycles. Standard NMR spectra (see below for high-resolution data) were recorded with Bruker AM-400 or AM-500 spectrometers. All chemical shifts (δ) [ppm] were determined relative to the residual signal of the deuterated solvent or to an external standard in $[D_6]$benzene or $[D_8]$thf: $Si(SiMe_3)_4$ for $^{29}Si\{^1H\}$ NMR, $Sn(N(SiMe_3)_2$ for $^{119}Sn\{^1H\}$ NMR. Assignment of the signals was assisted by 1D (^1H, ^{13}C) and 2D (COSY, HMBC, and HMQC) NMR experiments. $[K(Si(SiMe_3)_3]$,[1] and $[Sn(SiMe_3)_4]$[2] were prepared following literature procedures. $[KSnPh_3]$[3] was prepared by an adaptation to the literature procedure. All other chemicals were provided by commercial suppliers and used as received. Melting points were measured in sealed glass capillaries loaded with ca. 3-5 mg of the complex. Satisfactory combustion analysis of the complexes could not be achieved, likely due to their extreme air- and moisture-sensitivity of the complexes.

Preparation of $[Ca(SnPh_3)_2.(thf)_4]$ (1')

To a Schlenk containing CaI_2 (346 mg, 1.17 mmol) in thf (10 mL) was added a solution of $KSnPh_3$ (914 mg, 2.35 mmol) in thf (20 mL) dropwise. The gold coloured solution was stirred at room temperature for 2 hours, by which time a suspension had developed. The solution was isolated from the white precipitate by cannula filtration, and hexanes (50 mL) was added, precipitating an off-white solid from the solution. The solid was isolated by filtration, washed with hexanes (20 mL) and dried under reduced pressure to give the desired compound as an off white solid. The collected washings were left at room temperature overnight, after which time a crop of large pale-yellow crystals suitable for an X-ray diffraction study had grown. Although the crystalline compound has the formula $[Ca(SnPh_3)_2.thf_4]$ (**1'**), one molecule of thf is easily removed under reduced pressure to give the trisolvate product. Yield: 814 mg (73%) of $[Ca(SnPh_3)_2.thf_3]$ (**1**).

^{1}H NMR (500.13 MHz, $[D_8]$thf, 300 K): δ 7.54-7.48 (m, 12H, *o*rtho-$C_6\mathbf{H_5}$); 7.04-7.00 (m,12H, *meta*-$C_6\mathbf{H_5}$); 6.99-6.94 (m, 6H, *para*-$C_6\mathbf{H_5}$); 3.62 (m, 12H, 2,5-C$\mathbf{H_2}$-thf); 1.77 (m, 12H, *3,4-C$\mathbf{H_2}$-thf*) ppm.

^{13}C{^{1}H} NMR (125.77 MHz, $[D_8]$thf, 300 K): δ 157.97 (*ipso*-**C**, $^1J_{13C\text{-}117/119Sn}$ = 88.9 Hz); 138.93 (*ortho*-**C,** $^2J_{13C\text{-}117/119Sn}$ = 43.5 Hz); 127.76 (*meta*-**C,** $^3J_{13C\text{-}117/119Sn}$ = 13.4 Hz); 125.87 (*para*-**C**); 68.38 (2,5-**C**H_2-thf) 26.51 (3,4-**C**H_2-thf) ppm.

^{119}Sn{^{1}H} NMR (149.18 MHz, $[D_8]$thf, 302 K): δ –133.4 ppm.

Melting point: 163.7-164.0 °C (decomposition).

Preparation of [Sr($SnPh_3$)$_2$.(thf)$_4$] (2')

To a Schlenk containing SrI_2 (402 mg, 1.17 mmol) in thf (10 mL) was added a solution of $KSnPh_3$ (914 mg, 2.35 mmol) in thf (20 mL) dropwise. The gold coloured solution was stirred at room temperature for 2 hours, by which time a suspension had developed. The solution was isolated from the white precipitate by cannula filtration, and hexanes (50 mL) was added, precipitating an off-white solid from the solution. The solid was isolated by filtration, washed with hexanes (20 mL) and dried under reduced pressure to give the desired compound as an off-white solid. The collected washings were left at room temperature overnight, after which time a crop of pale-yellow crystals suitable for an X-ray diffraction study had grown. Although the crystalline compound has the formula [Sr($SnPh_3$)$_2$.thf$_4$] (**2'**), one molecule of thf is easily removed under reduced pressure to give the trisolvate product. Yield: 680 mg (58%) of [Sr($SnPh_3$)$_2$.(thf)$_3$] (**2**).

^{1}H NMR (500.13 MHz, [D$_8$]thf, 298 K): δ 7.52-7.48 (m, 12H, *ortho*-C$_6$**H$_5$**); 7.03-6.97 (m,12H, *meta*-C$_6$**H$_5$**); 6.96-6.89 (m, 6H, *para*-C$_6$**H$_5$**); 3.62 (m, 12H, 2,5-C**H$_2$**-thf); 1.76 (m, 12H, *3,4-C**H$_2$**-thf*) ppm.

^{13}C{^{1}H} NMR (125.77 MHz, [D$_8$]thf, 298 K): δ 160.26 (*ipso*-C $^1J_{13C\text{-}117/119Sn}$ = 134.6 Hz); 139.01 (*ortho*-**C,** $^2J_{13C\text{-}117/119Sn}$ = 45.6 Hz); 127.52 (*meta*-**C,** $^3J_{13C\text{-}117/119Sn}$ = 10.9 Hz); 125.44 (*para*-**C**); 66.38 (2,5-**C**H$_2$-thf) 26.48 (3,4-**C**H$_2$-thf) ppm.

^{119}Sn{^{1}H} NMR (149.18 MHz, [D$_8$]thf, 302 K): δ –123.6 ppm.

Melting point: 152.1-152.5 °C (decomposition).

Preparation of [Ba($SnPh_3$)$_2$.(thf)$_5$] (3')

To a Schlenk containing BaI_2 (528 mg, 1.35 mmol) in thf (10 mL) was added a solution of $KSnPh_3$ (914 mg, 2.35 mmol) in thf (20 mL) dropwise. The gold coloured solution was stirred at room temperature for 2 hours, by which time a suspension had developed. The solution was isolated from the white precipitate by cannula filtration, and hexanes (50 mL) was added, precipitating an off-white solid from the solution. The solid was isolated by filtration, washed with hexanes (20 mL) and dried under reduced pressure to give the desired compound as an off-white solid. The collected washings were left at room temperature overnight, after which time a crop of yellow crystals suitable for an X-ray diffraction study had grown. Although the crystalline compound has the formula [Ba($SnPh_3$)$_2$.thf$_5$] (**3'**), two molecules of thf are easily removed under reduced pressure to give the tetrasolvate product. Yield: 768 mg (39%) of [Ba($SnPh_3$)$_2$.(thf)$_4$] (**3**).

^{1}H NMR (500.13 MHz, [D$_8$]thf, 298 K): δ 7.51-7.46 (m, 12H, *ortho*-C$_6$**H$_5$**); 7.02-6.98 (m,12H, *meta*-C$_6$**H$_5$**); 6.96-6.91 (m, 6H, *para*-C$_6$**H$_5$**); 3.62 (m, 16H, 2,5-C**H$_2$**-thf); 1.76 (m, 16H, 3,4-C**H$_2$**-thf) ppm.

^{13}C{^{1}H} NMR (125.77 MHz, [D$_8$]thf, 300 K): δ 160.78 (*ipso*-**C** $^1J_{13C\text{-}119Sn}$ = 143.1 Hz, $^1J_{13C\text{-}117Sn}$ = 138.9 Hz); 139.02 (*ortho*-**C,** $^2J_{13C\text{-}117/119Sn}$ = 46.1 Hz); 127.60 (*meta*-**C**, $^3J_{13C\text{-}117/119Sn}$= 10.0 Hz); 125.49 (*para*-**C**); 68.4 (2,5-**C**H$_2$-thf) 26.5 (3,4-**C**H$_2$-thf) ppm.

^{119}Sn{^{1}H} NMR (149.18 MHz, [D$_8$]thf, 300 K): δ –95.5 ppm.

Melting point: 112.0-112.2 °C (decomposition).

Preparation of [Ca{Sn(SiMe$_3$)$_3$}$_2$.(thf)$_4$] (4)

A Schlenk was loaded with Sn(SiMe$_3$)$_4$ (500 mg, 1.22 mmol) and KO^{t}Bu (137 mg, 1.22 mmol) and the contents were dissolved in thf (7 mL). The pale-yellow solution was left to stir for 1 hour, before it was added dropwise to a suspension of CaI$_2$ (240 mg, 0.82 mmol) in thf (15 mL) at room temperature. The suspension was left to stir overnight. The thf was removed under reduced pressure and the residue was extracted into hexanes (30 mL). The solution was isolated via cannula filtration, concentrated to 5 mL and transferred to a −30 °C freezer to give the compound as pale-yellow crystals which were isolated by filtration. Further concentration of the mother liquor gave a second crop of crystals suitable for an X-ray diffraction study. Yield: 252 mg (41%).

^{1}H NMR (500.13 MHz, [D$_6$]benzene, 298 K): δ 3.86 (m, 16H, 2,5-C**H$_2$**-thf); 1.49 (m, 16H, 3,4-C**H$_2$**-thf); 0.55 (s, $^{2}J_{\text{1H-29Si}}$ = 6.3 Hz, $^{3}J_{\text{1H-117/119Sn}}$ = 9.0 Hz, 54H, Sn(SiMe$_3$)$_3$) ppm.

^{13}C{^{1}H} NMR (125.77 MHz, [D$_6$]benzene, 298 K): δ 69.73 (2,5-**C**H$_2$-thf); 25.19 (3,4-**C**H$_2$-thf); 7.76 ($^{1}J_{\text{13C-29Si}}$ = 19.3 Hz, $^{2}J_{\text{13C-117/119Sn}}$ = 36.7 Hz (SiMe$_3$)$_3$)) ppm.

^{29}Si-DEPT NMR (99.36 MHz, [D$_6$]benzene, 298 K): δ –12.9 ($^{1}J_{\text{29Si-119Sn}}$ = 82.9 Hz, $^{1}J_{\text{29Si-117Sn}}$ = 79.0 Hz, $^{1}J_{\text{29Si-13C}}$ = 36.7, $^{3}J_{\text{29Si-117/119Sn}}$ = 2.7 Hz) ppm.

^{119}Sn{^{1}H} NMR (186.36 MHz, [D$_6$]benzene, 298 K): δ –856.8 ($^{1}J_{\text{119Sn-29Si}}$ = 82.1 Hz, $^{2}J_{\text{119Sn-117Sn}}$ = 455.0 Hz) ppm.

^{1}H NMR (400.13 MHz, [D$_8$]thf, 302 K): δ 3.62 (m, 8H, 2,5-C**H$_2$**-thf); 1.77 (m, 8H, 3,4-C**H$_2$**-thf); 0.21 (s, 54 H, Sn(SiMe$_3$)$_3$) ppm.

^{13}C{^{1}H} NMR (100.62 MHz, [D$_8$]thf, 302 K): δ 68.39 (2,5-**C**H$_2$-thf); 25.52 (3,4-**C**H$_2$-thf); 7.91 ($^{1}J_{\text{13C-29Si}}$ = 35.8 Hz, $^{2}J_{\text{13C-117/119Sn}}$ = 17.7 Hz (SiMe$_3$)$_3$)) ppm.

^{29}Si{^{1}H}-DEPT NMR (79.49 MHz, [D$_8$]thf, 302 K): δ –11.5 ppm.

^{119}Sn{^{1}H} NMR (149.12 MHz, [D$_8$]thf, 302 K): δ –861.5 ppm.

Melting point: 158.9-159.4 °C (decomposition).

Preparation of [Sr{Sn(SiMe$_3$)$_3$}$_2$.(thf)$_4$] (5)

A Schlenk was loaded with Sn(SiMe$_3$)$_4$ (411 mg, 1.70 mmol) and KO^{t}Bu (191 mg, 1.70 mmol) and the contents were dissolved in thf (10 mL). The pale-yellow solution was left to stir for 1 hour, before it was added dropwise to a suspension of SrI$_2$ (300 mg, 0.87 mmol) in thf (20 mL) at room temperature. The suspension was left to stir overnight. The thf was removed under reduced pressure and the residue was extracted into hexanes (30 mL). The solution was isolated via cannula filtration, concentrated to 3 mL and transferred to a −30 °C freezer to give the compound as pale-yellow crystals which were isolated by filtration. Further concentration of the mother liquor gave a second crop of crystals suitable for an X-ray diffraction study. Yield: 557 mg (62%).

^{1}H NMR (500.13 MHz, [D$_6$]benzene, 298 K): δ 3.85 (m, 16H, 2,5-C**H$_2$**-thf); 1.49 (m, 16H, 3,4-C**H$_2$**-thf); 0.57 (s, $^{2}J_{\text{1H-29Si}}$ = 6.3 Hz, $^{3}J_{\text{1H-117/119Sn}}$ = 9.2 Hz, 54H, Sn(SiMe$_3$)$_3$) ppm.

^{13}C{^{1}H} NMR (125.77 MHz, [D$_6$]benzene, 298 K): δ 69.34 (2,5-**C**H$_2$-thf); 25.23 (3,4-**C**H$_2$-thf); 7.88 ($^{1}J_{\text{13C-29Si}}$ = 36.7 Hz, $^{2}J_{\text{13C-117/119Sn}}$ = 20.8 Hz (SiMe$_3$)$_3$)) ppm.

^{29}Si{^{1}H}-DEPT NMR (99.36 MHz, [D$_6$]benzene, 298 K): δ –12.9 ($^{1}J_{\text{29Si-119Sn}}$ = 98.8 Hz, $^{1}J_{\text{29Si-117Sn}}$ = 94.4 Hz, $^{1}J_{\text{29Si-13C}}$ = 36.5, $^{3}J_{\text{29Si-117/119Sn}}$ = 3.6 Hz) ppm.

^{119}Sn{^{1}H} NMR (186.36 MHz, [D$_6$]benzene, 298 K): δ – 848.2 ($^{1}J_{\text{119Sn-29Si}}$ = 98.8 Hz, $^{2}J_{\text{119Sn-117Sn}}$ = 582.2 Hz) ppm.

^{1}H NMR (400.13 MHz, [D$_8$]thf, 300 K): δ 3.62 (m, 8H, 2,5-C**H$_2$**-thf); 1.77 (m, 8H, 3,4-C**H$_2$**-thf); 0.21 (s, 54 H, Sn(SiMe$_3$)$_3$) ppm.

^{13}C{^{1}H} NMR (100.62 MHz, [D$_8$]thf, 300 K): δ 68.39 (2,5-**C**H$_2$-thf); 25.52 (3,4-**C**H$_2$-thf); 8.22 ($^{1}J_{\text{13C-29Si}}$ = 35.7 Hz, $^{2}J_{\text{13C-117/119Sn}}$ = 18.7 Hz (SiMe$_3$)$_3$)) ppm.

^{29}Si{^{1}H}-DEPT NMR (79.49 MHz, [D$_8$]thf, 302 K): δ –12.8 ppm.

^{119}Sn{^{1}H} NMR (149.12 MHz, [D$_8$]thf, 302 K): δ –850.3 ppm.

Melting point: 140.8-141.1 °C (decomposition).

Preparation of [Ba{Sn(SiMe$_3$)$_3$}$_2$.(thf)$_5$] (6')

A Schlenk was loaded with Sn(SiMe$_3$)$_4$ (411 mg, 1.00 mmol) and KO^{t}Bu (112 mg, 1.00 mmol) and the contents were dissolved in thf (7 mL). The pale-yellow solution was left to stir for 1 hour, before it was added dropwise to a suspension of BaI$_2$ (200 mg, 0.51 mmol) in thf (15 mL) at room temperature. The resulting brown suspension was left to stir overnight. The thf was removed under reduced pressure and the residue extracted into hexanes (30 mL). The solution was isolated via cannula filtration, concentrated to 5 mL and transferred to a −30 °C freezer to give the compound as pale-yellow crystals which were isolated by filtration. Note that the crystals will slowly turn black at 4 °C (assumed to be the precipitation of Sn^{0}), and hence should be kept at –30 °C. Yield: 198 mg (34%). Crystals suitable for an X-ray diffraction study were grown from a saturated hexane solution with 2 drops of thf at −30 °C. Although the crystalline compound has the formula [Ba{Sn(SiMe$_3$)$_3$}$_2$.(thf$_5$], two molecules of thf are easily removed under reduced pressure to give the tetrasolvate product (**6**). Yield: 198 mg (31%).

^{1}H NMR (500.13 MHz, [D$_6$]benzene, 298 K): δ 3.79 (m, 16H, 2,5-C**H$_2$**-thf); 1.49 (m, 16H, 3,4-C**H$_2$**-thf); 0.59 (s, $^{2}J_{\text{1H-29Si}}$ = 6.2 Hz, $^{3}J_{\text{1H-117/119Sn}}$ = 9.1 Hz, 54H, Sn(SiMe$_3$)$_3$) ppm.

^{13}C{^{1}H} NMR (125.77 MHz, [D$_6$]benzene, 298 K): δ 68.90 (2,5-**C**H$_2$-thf); 25.26 (3,4-**C**H$_2$-thf); 8.06 ($^{1}J_{^{13}\text{C}-^{29}\text{Si}}$ = 36.7 Hz, $^{2}J_{^{13}\text{C}-^{117/119}\text{Sn}}$ = 20.8 Hz (SiMe$_3$)$_3$)) ppm.

^{29}Si{^{1}H}-DEPT NMR (99.36 MHz, [D$_6$]benzene, 298 K): δ –11.1 ($^{1}J_{^{29}\text{Si}-^{119}\text{Sn}}$ = 116.9 Hz, $^{1}J_{^{29}\text{Si}-^{117}\text{Sn}}$ = 111.8 Hz, $^{1}J_{^{29}\text{Si}-^{13}\text{C}}$ = 36.5) ppm.

^{119}Sn{^{1}H} NMR (186.35 MHz, [D$_6$]benzene, 298 K): δ –792.7 ($^{1}J_{^{119}\text{Sn}-^{29}\text{Si}}$ = 116.7 Hz, $^{2}J_{^{119}\text{Sn}-^{117}\text{Sn}}$ = 772.1 Hz) ppm.

^{1}H NMR (400.13 MHz, [D$_8$]thf, 302 K): δ 3.62 (m, 8H, 2,5-C**H$_2$**-thf); 1.77 (m, 8H, 3,4-C**H$_2$**-thf); 0.20 (s, 54 H, Sn(SiMe$_3$)$_3$) ppm.

^{13}C{^{1}H} NMR (100.62 MHz, [D$_8$]thf, 302 K): δ 68.38 (2,5-**C**H$_2$-thf); 26.33 (3,4-**C**H$_2$-thf); 7.96 ($^{1}J_{^{13}\text{C}-^{29}\text{Si}}$ = 36.3 Hz, $^{2}J_{^{13}\text{C}-^{117/119}\text{Sn}}$ = 19.6 Hz (SiMe$_3$)$_3$)) ppm.

^{29}Si{^{1}H}-DEPT NMR (79.49 MHz, [D$_8$]thf, 302 K): δ –11.9 ppm.

^{119}Sn{^{1}H} NMR (149.12 MHz, [D$_8$]thf, 302 K): δ –813.5 ppm.

Melting point: 126.8-127.1 °C (decomposition).

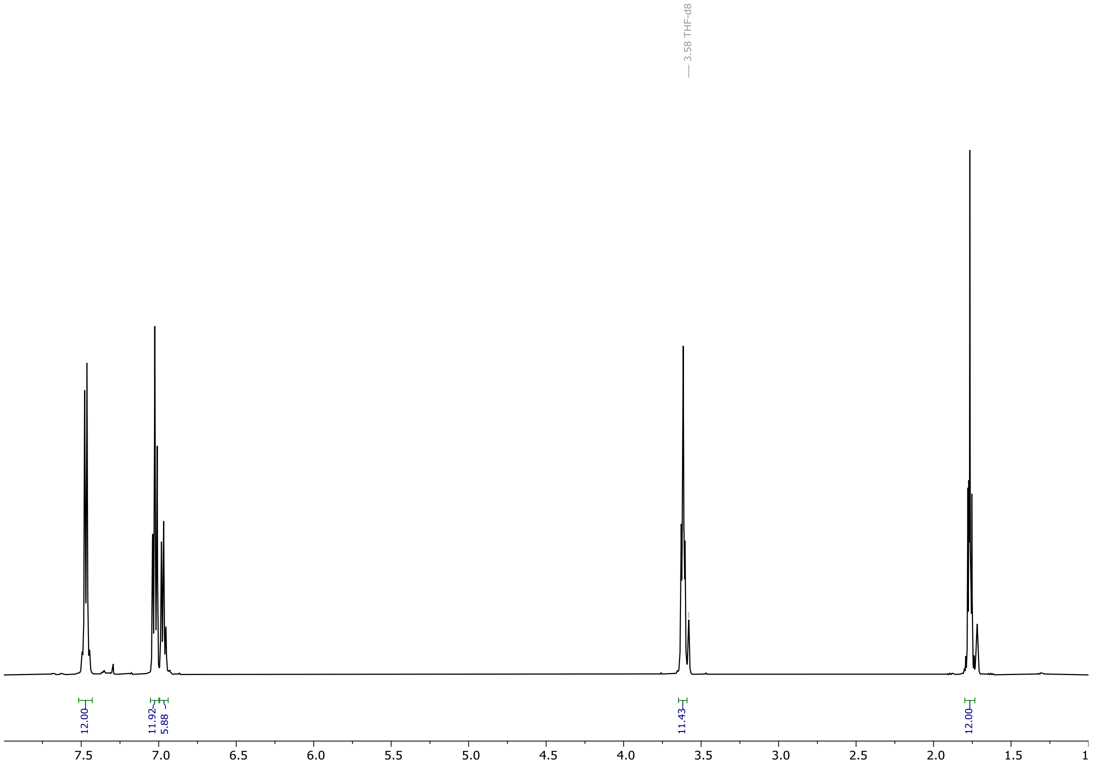

Figure S1. ^{1}H NMR spectrum (500.13 MHz, [D$_8$]thf, 298 K) of [Ca(SnPh$_3$)$_2$.(thf)$_3$] (**1**).

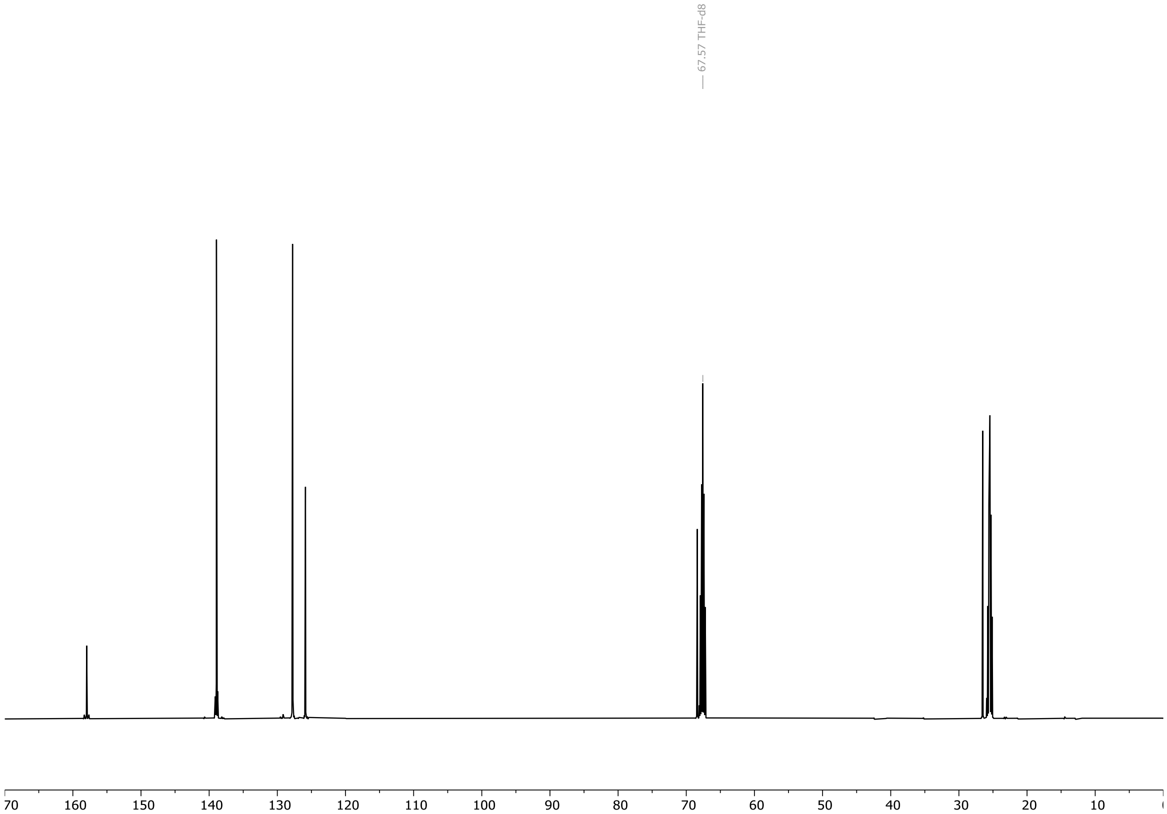

Figure S2. ^{13}C{^{1}H} NMR spectrum (125.77 MHz, [D$_8$]thf, 298 K) of [Ca(SnPh$_3$)$_2$.(thf)$_3$] (**1**).

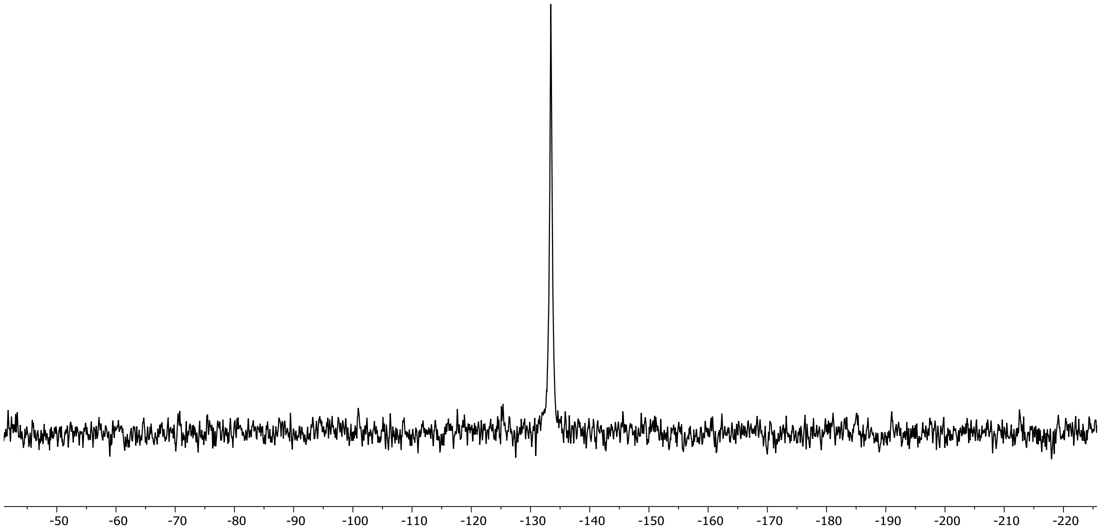

Figure S3. ^{119}Sn{^{1}H} NMR spectrum (149.18 MHz, [D$_8$]thf, 302 K) of [Ca(SnPh$_3$)$_2$.(thf)$_3$] (**1**).

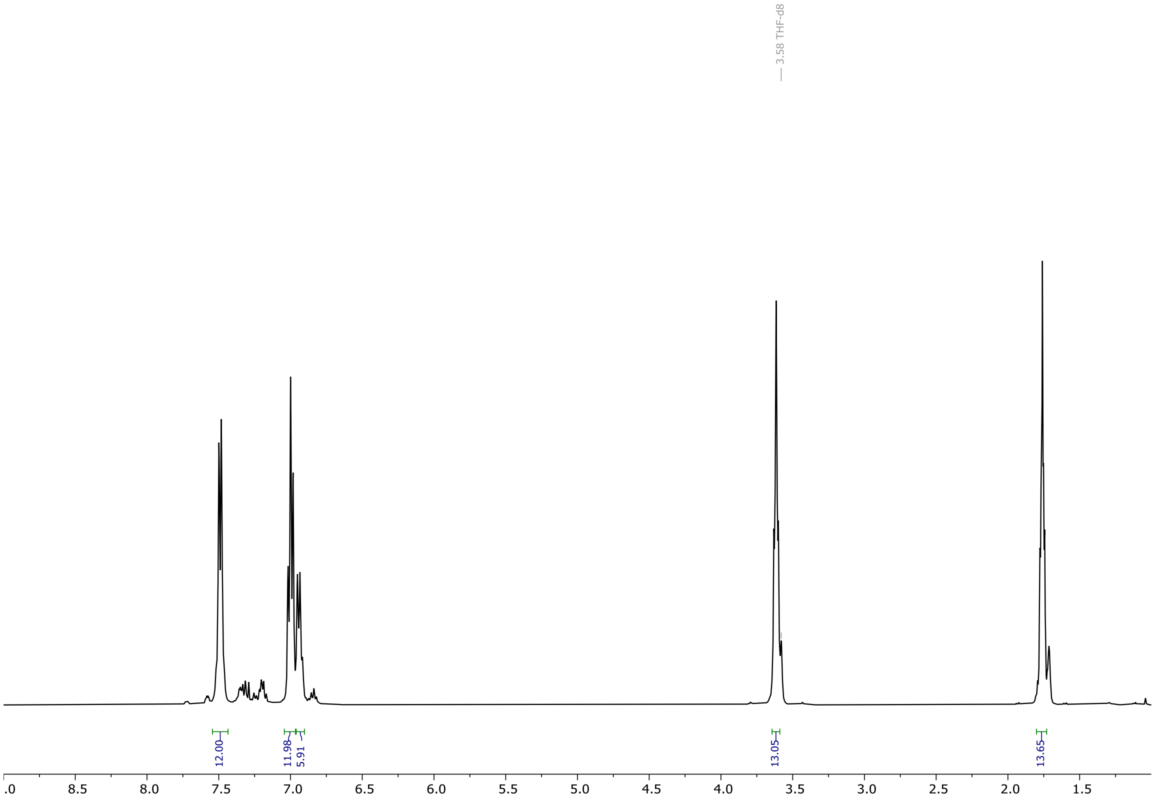

Figure S4. ^{1}H NMR spectrum (500.13 MHz, [D$_8$]thf, 298 K) of [Sr(SnPh$_3$)$_2$.(thf)$_3$] (**2**).

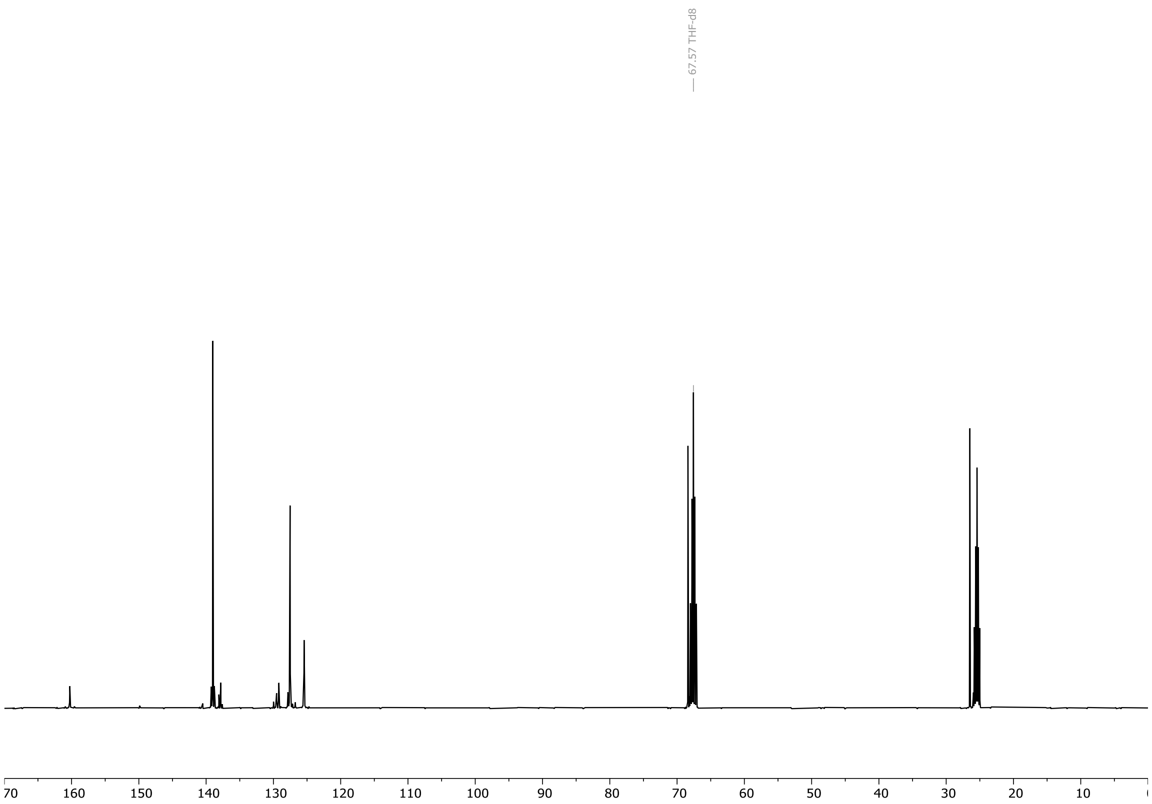

Figure S5. $^{13}C\{^1H\}$ NMR spectrum (125.77 MHz, [D$_8$]thf, 298 K) of [Sr(SnPh$_3$)$_2$.(thf)$_3$] (**2**).

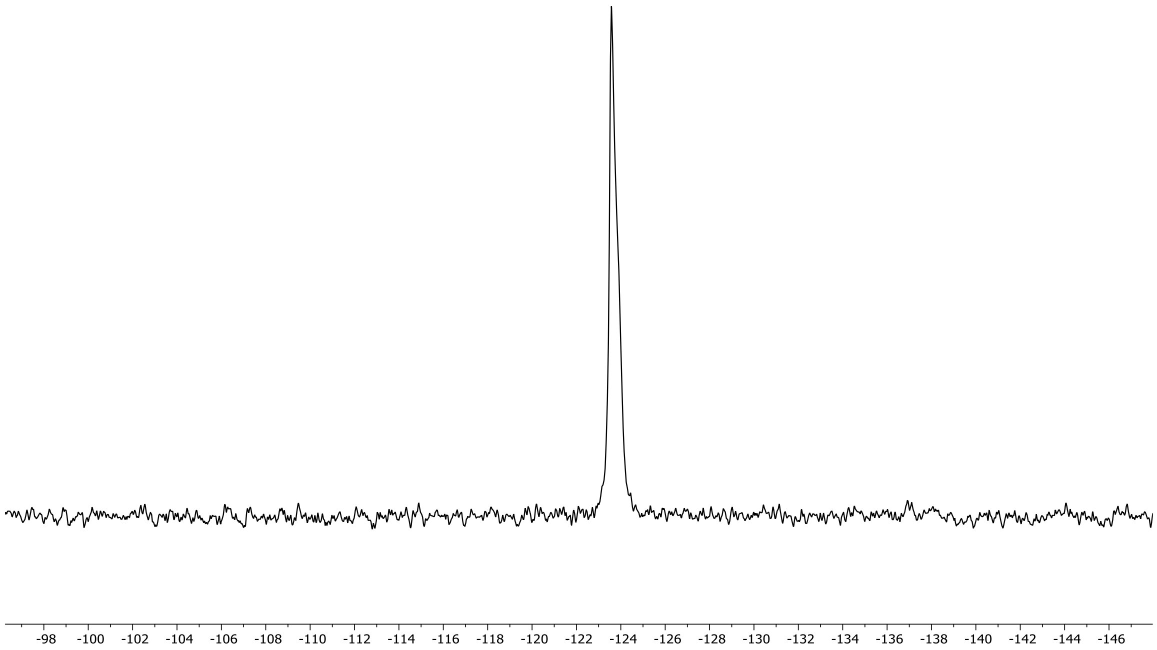

Figure S6. $^{119}Sn\{^1H\}$ NMR spectrum (149.18 MHz, [D$_8$]thf, 302 K) of [Sr(SnPh$_3$)$_2$.(thf)$_3$] (**2**).

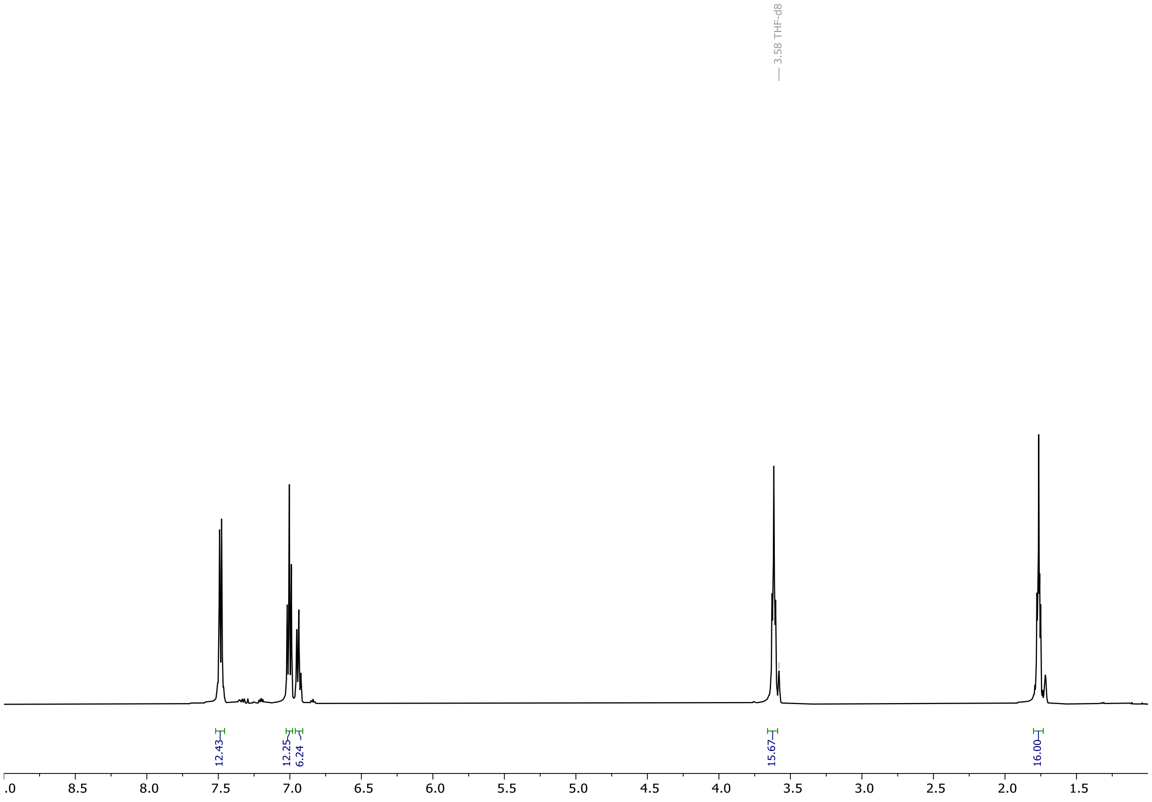

Figure S7. ^{1}H NMR spectrum (500.13 MHz, [D$_8$]thf, 298 K) of [Ba(SnPh$_3$)$_2$.(thf)$_4$] (**3**).

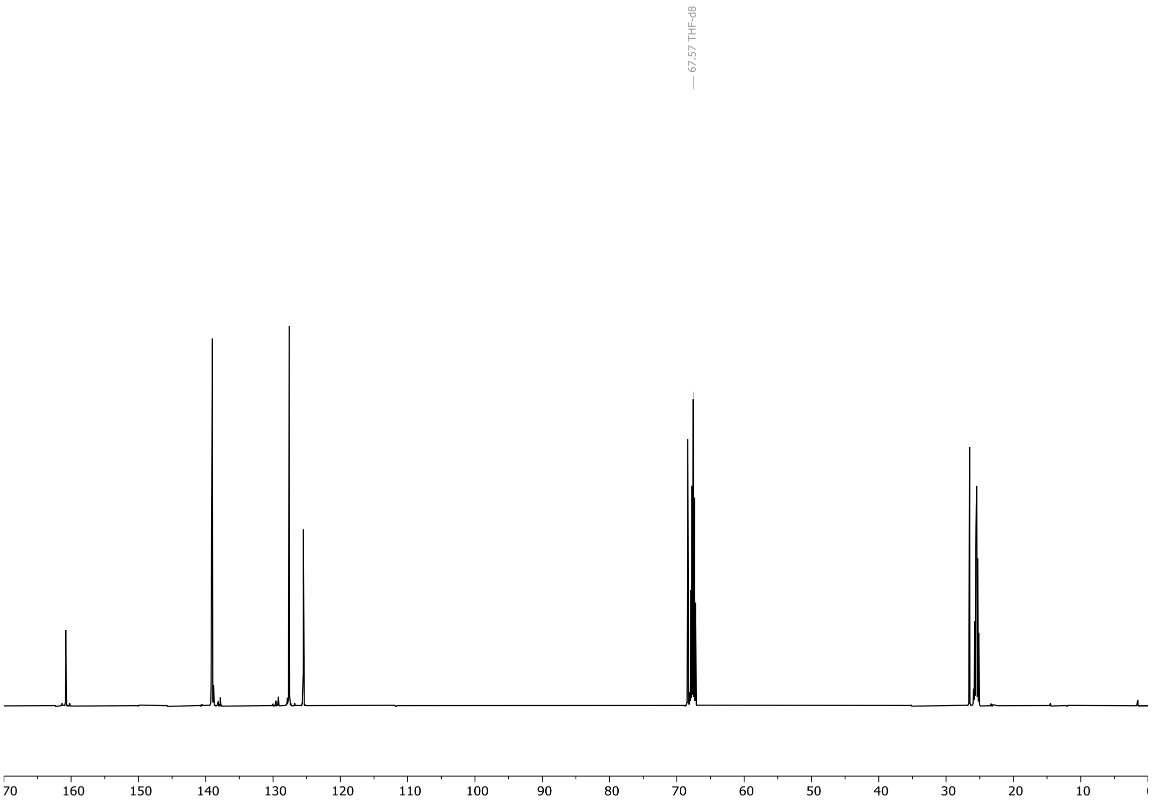

Figure S8. ^{13}C{^{1}H} NMR spectrum (125.77 MHz, [D$_8$]thf, 300 K) of [Ba(SnPh$_3$)$_2$.(thf)$_4$] (**3**).

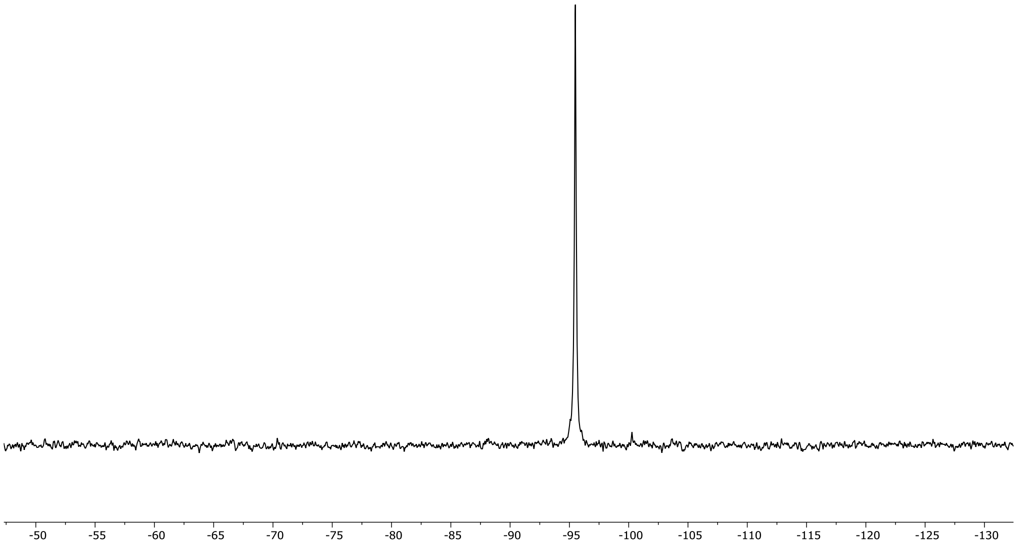

Figure S9. ^{119}Sn{^{1}H} NMR spectrum (149.18 MHz, [D$_8$]thf, 300 K) of [Ba(SnPh$_3$)$_2$.(thf)$_4$] (**3**).

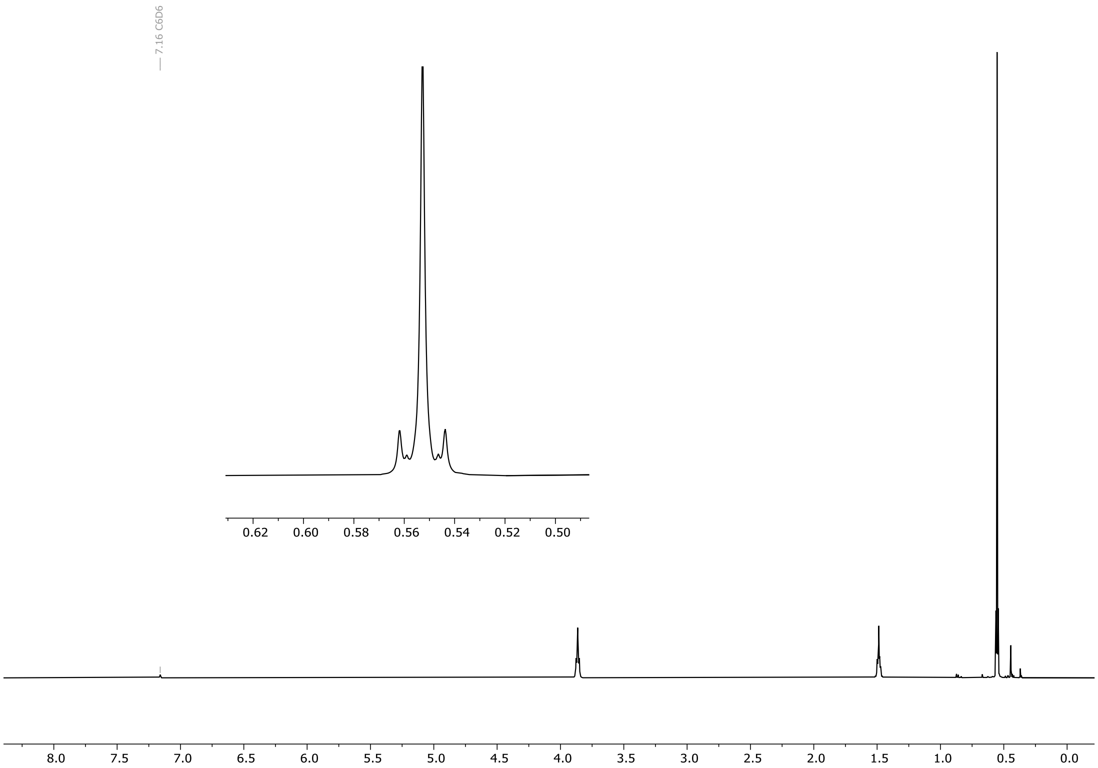

Figure S10. ^{1}H NMR spectrum (500.13 MHz, [D$_6$]benzene, 298 K) of [Ca(Sn(SiMe$_3$)$_3$)$_2$.(thf)$_4$] (**4**).

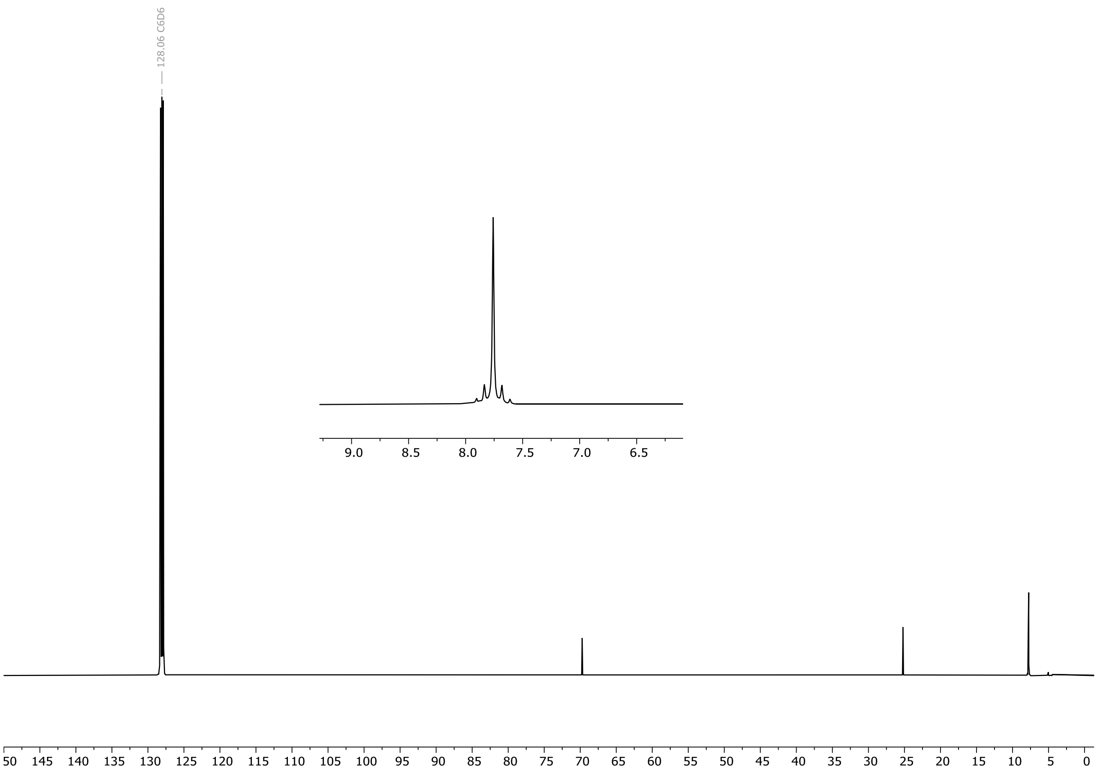

Figure S11. $^{13}C\{^1H\}$ NMR spectrum (125.77 MHz, [D$_6$]benzene, 298 K) of [Ca{Sn(SiMe$_3$)$_3$}$_2$.(thf)$_4$] (**4**).

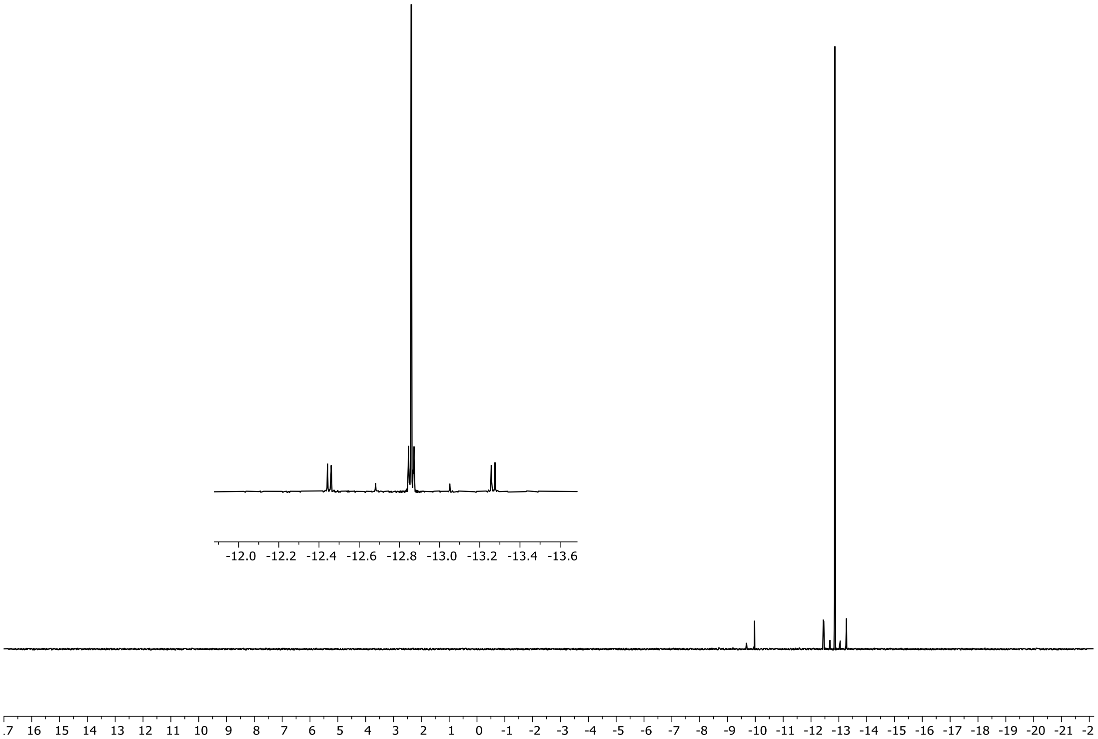

Figure S12 $^{29}Si\{^1H\}$-DEPT NMR spectrum (99.36 MHz, [D$_6$]benzene, 298 K) of [Ca{Sn(SiMe$_3$)$_3$}$_2$.(thf)$_4$] (**4**).

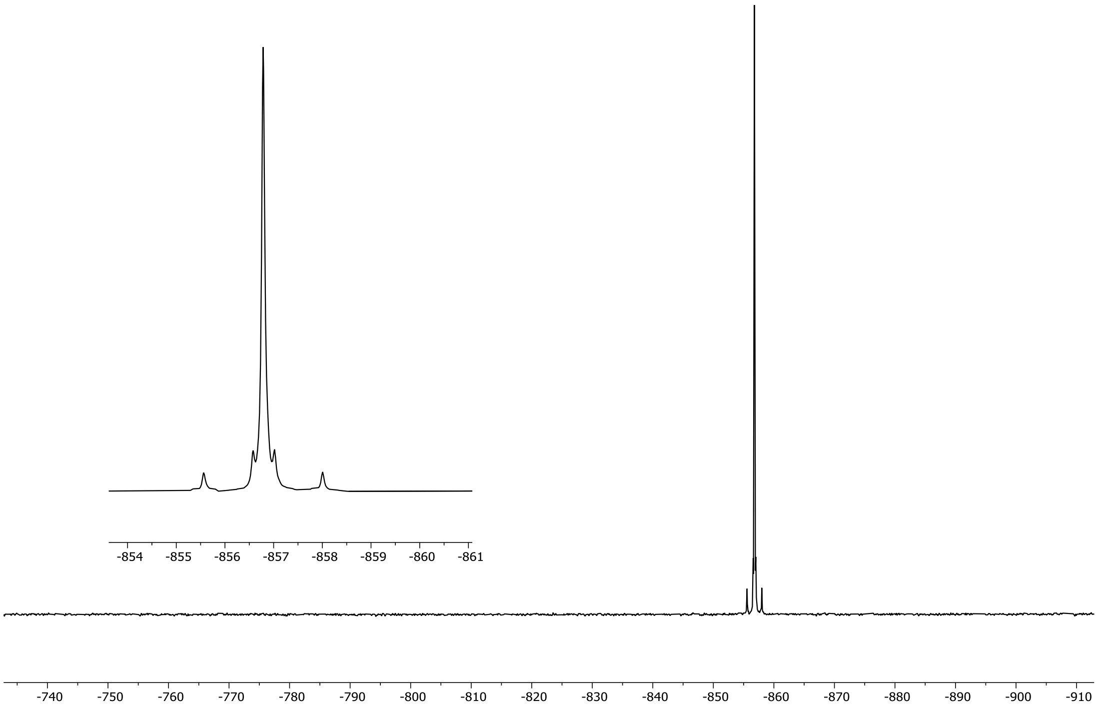

Figure S13. ^{119}Sn{^{1}H} NMR spectrum (186.36 MHz, [D$_6$]benzene, 298 K) of [Ca{Sn(SiMe$_3$)$_3$}$_2$.(thf)$_4$] (**4**).

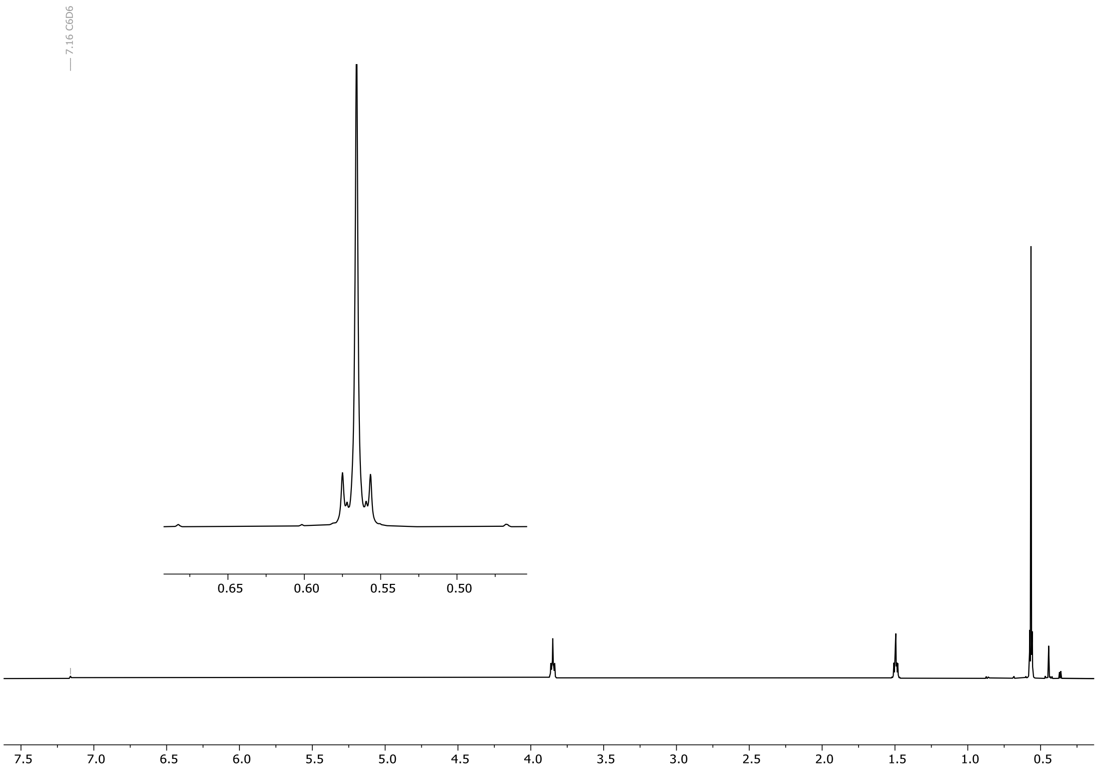

Figure S14. ^{1}H NMR spectrum (500.13 MHz, [D$_6$]benzene, 298 K) of [Sr{Sn(SiMe$_3$)$_3$}$_2$.(thf)$_4$] (**5**).

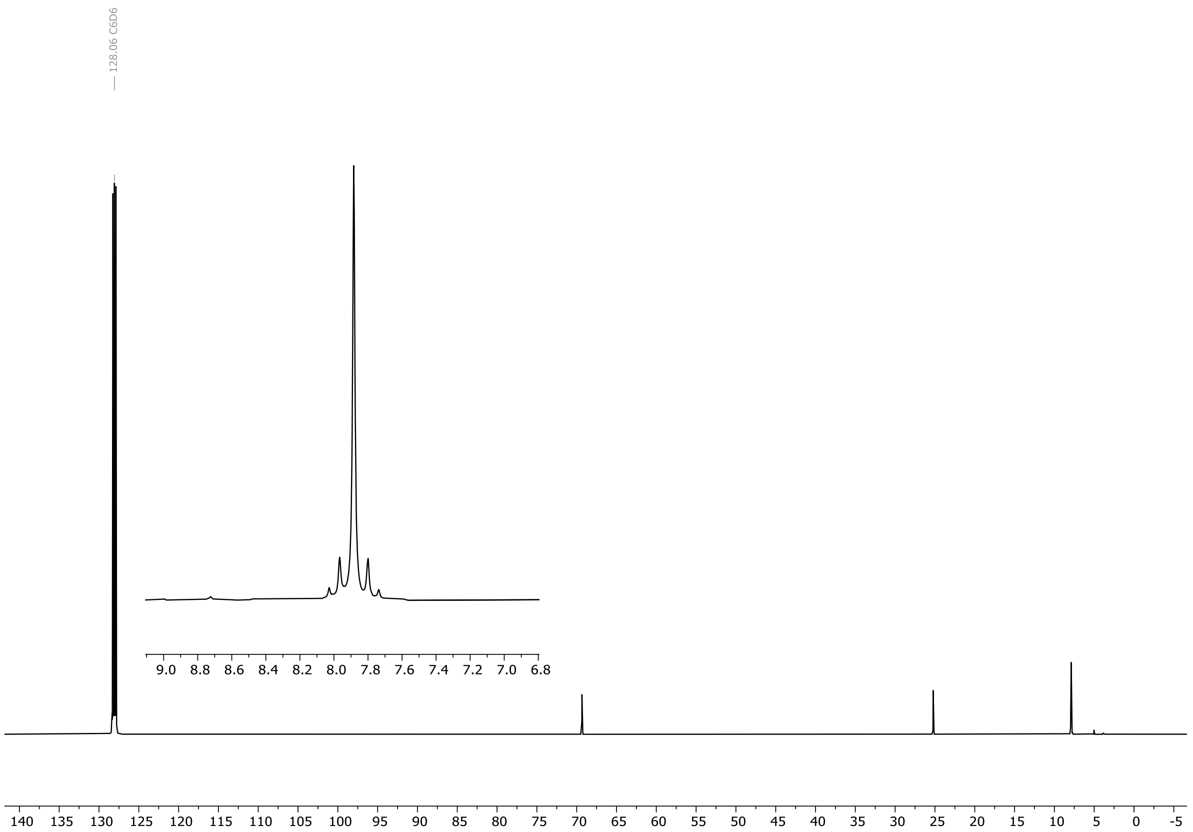

Figure S15. $^{13}C\{^1H\}$ NMR spectrum (125.77 MHz, [D$_6$]benzene, 298 K) of [Sr{Sn(SiMe$_3$)$_3$}$_2$.(thf)$_4$] (**5**).

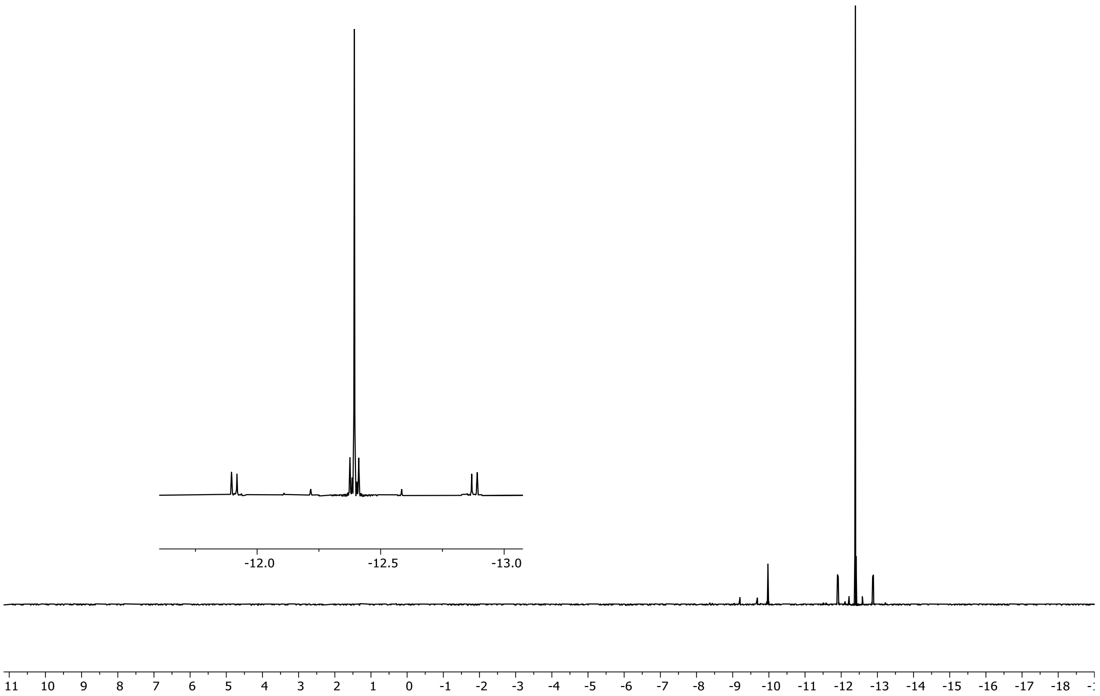

Figure S16. $^{29}Si\{^1H\}$-DEPT NMR spectrum (99.36 MHz, [D$_6$]benzene, 298 K) of [Sr{Sn(SiMe$_3$)$_3$}$_2$.(thf)$_4$] (**5**).

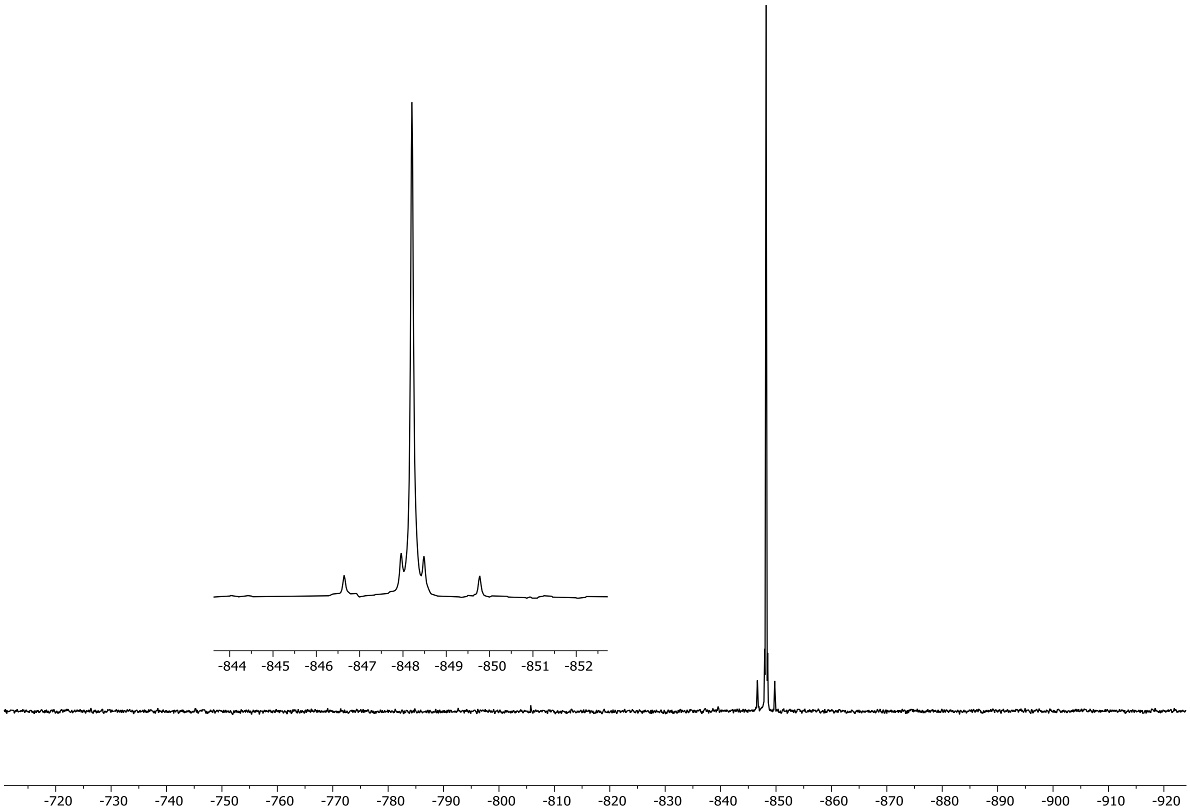

Figure S17. ^{119}Sn{^{1}H} NMR spectrum (186.36 MHz, [D$_6$]benzene, 298 K) of [Sr{Sn(SiMe$_3$)$_3$}$_2$.(thf)$_4$] (**5**).

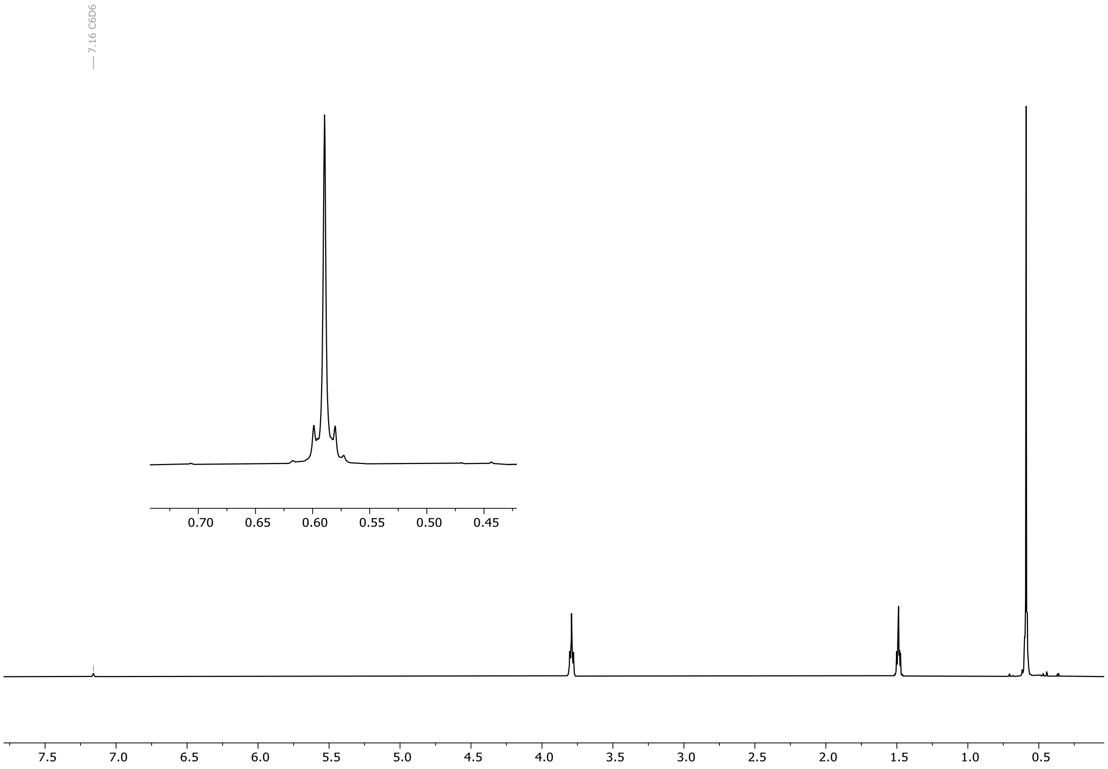

Figure S18. ^{1}H NMR spectrum (500.13 MHz, [D$_6$]benzene, 298 K) of [Ba{Sn(SiMe$_3$)$_3$}$_2$.(thf)$_4$] (**6**).

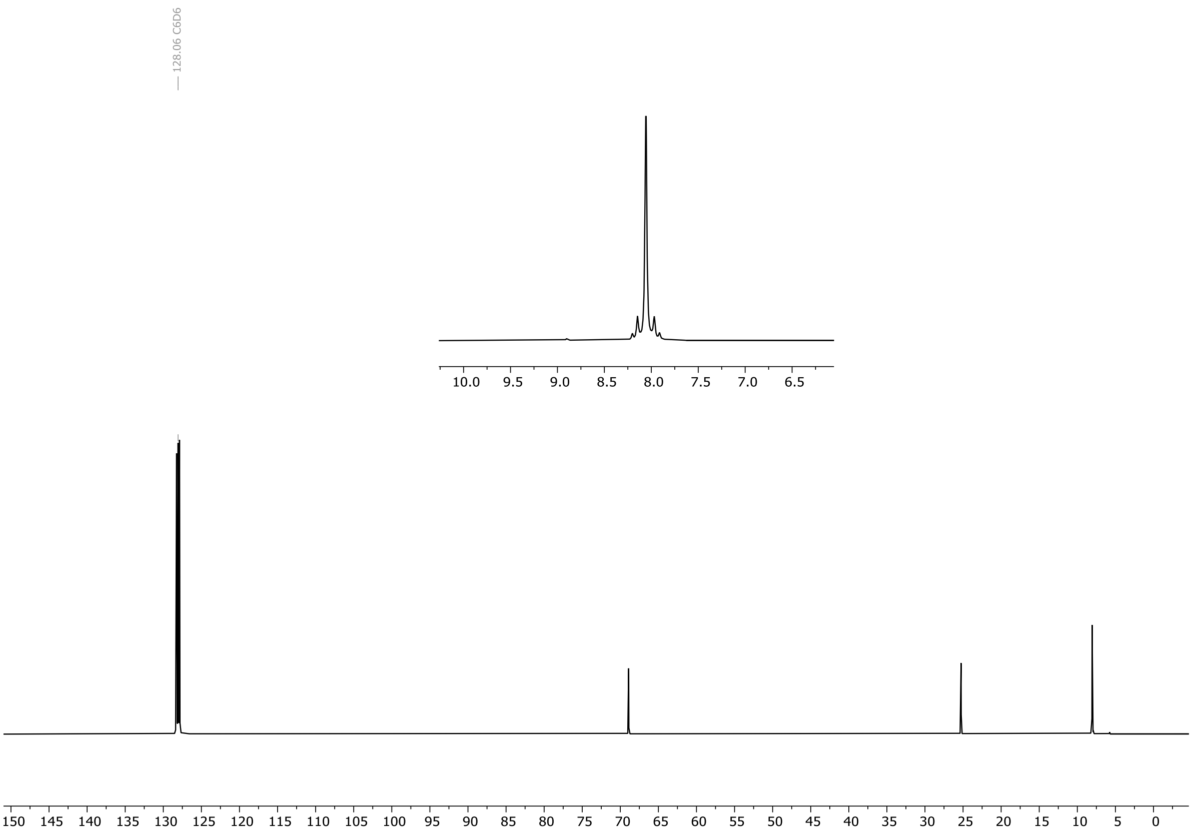

Figure S19. $^{13}C\{^1H\}$ NMR spectrum (125.77 MHz, [D$_6$]benzene, 298 K) of [Ba{Sn(SiMe$_3$)$_3$}$_2$.(thf)$_4$] (**6**).

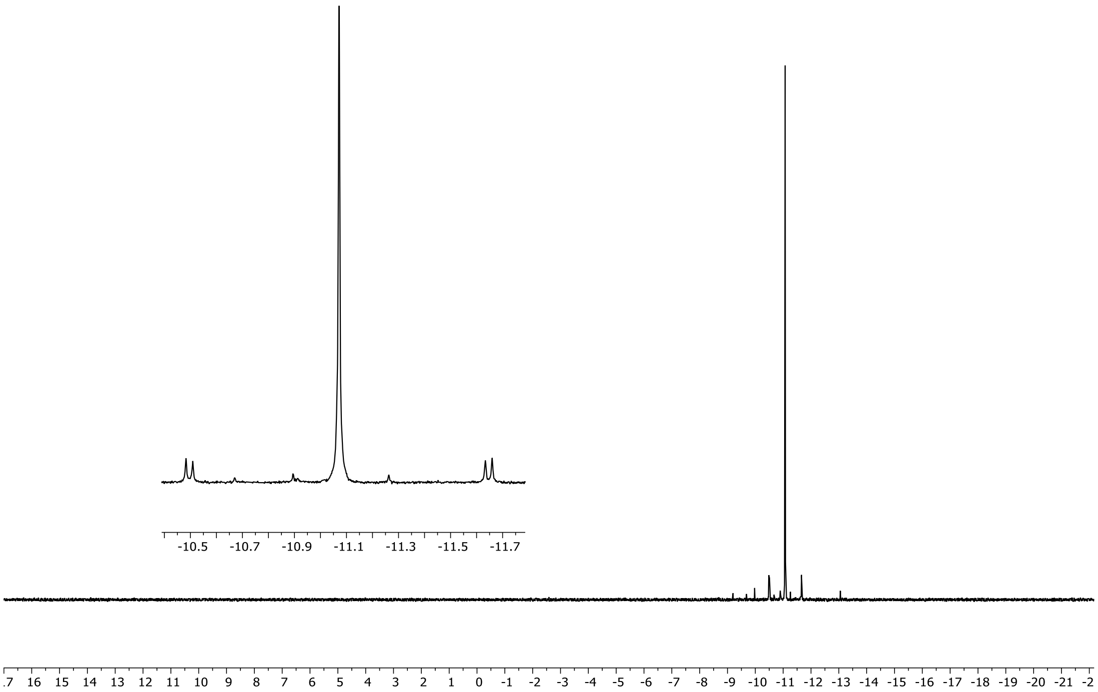

Figure S20. $^{29}Si\{^1H\}$-DEPT NMR spectrum (99.36 MHz, [D$_6$]benzene, 298 K) of [Ba{Sn(SiMe$_3$)$_3$}$_2$.(thf)$_4$] (**6**).

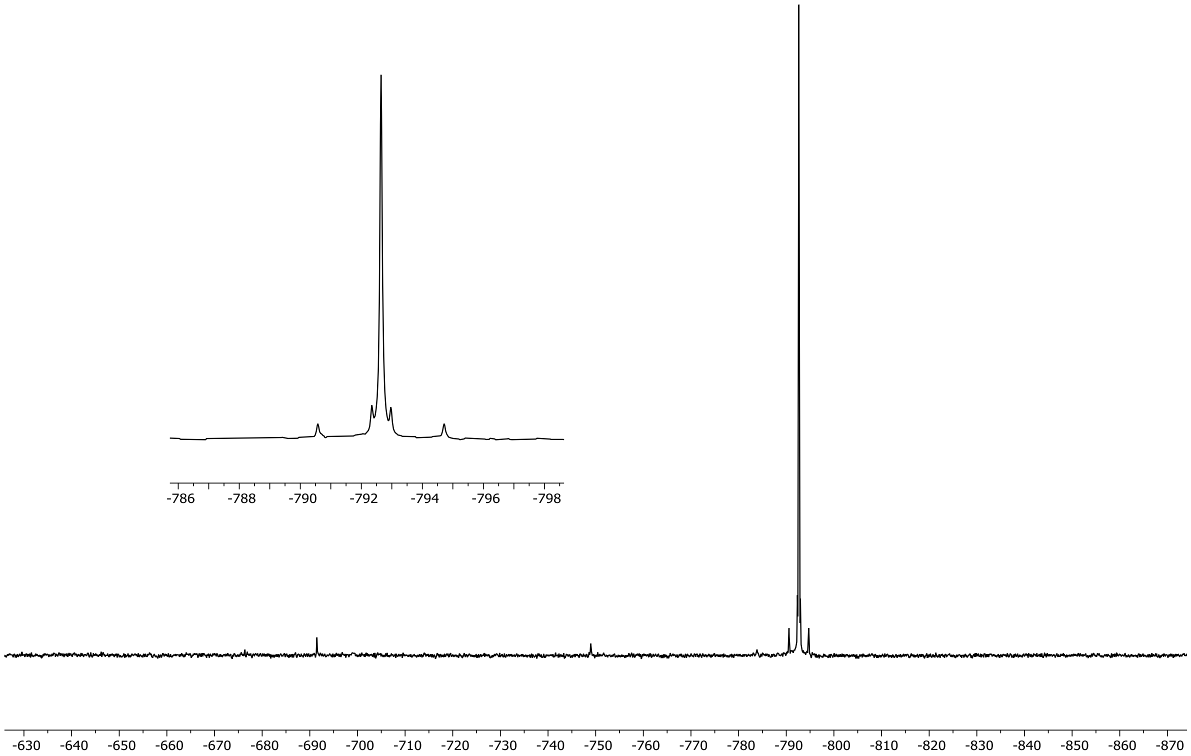

Figure S21. ^{119}Sn{^{1}H} NMR spectrum (186.36 MHz, [D$_6$]benzene, 298 K) of [Ba{Sn(SiMe$_3$)$_3$}$_3$)$_2$.(thf)$_4$] (**6**).

High-Resolution NMR Spectroscopy for Complexes 4-6

NMR experiments were carried out by using Bruker AVIII 500 spectrometers (Bruker, Wissembourg, France) equipped with a 10 A gradient amplifier giving a maximum gradient of 50 G.cm^{-1} and a 5 mm BBFO probe including shielded z-gradients. Measuring frequencies were 500 MHz for ^{1}H, 125 MHz for ^{13}C, 186 MHz for ^{119}Sn and 99 MHz for ^{29}Si. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm using the residual peak of C_6D_6 (7.16 ppm and 128.0 ppm) as internal standard. ^{29}Si and ^{119}Sn NMR spectra were referenced ($\delta = 0.0$ ppm) to calculated ^{29}Si and ^{119}Sn in Me_4Si and Me_4Sn references compounds, respectively.[4]

1D NMR Measurements.

1D ^{1}H. One-dimensional ^{1}H experiments were acquired with standard Bruker "zg" program. The spectra were acquired with sweep width of 10000 Hz and 59998 data points, using 256 scans and the relaxation delay (D1) was 30 s. Exponential window function (LB=0.3) was applied before Fourier Transformation.

1D ^{13}C. One-dimensional ^{13}C NMR spectra were recorded with standard Bruker "zgig" program with broadband proton decoupling in order to remove ^{13}C - ^{1}H coupling. The spectra were acquired with sweep width of 50505 Hz and 202014 data points, using 1340 scans and the relaxation delay (D1) was 30 s. Exponential window function (LB=1.5) was applied before Fourier Transformation.

1D ^{29}Si. One-dimensional ^{29}Si experiment were acquired with standard Bruker "dept45" program with broadband proton decoupling in order to remove ^{29}Si - ^{1}H coupling. The spectra were acquired width sweep with of 3894 and 36012 data points, using 1024 scans and the recycling delay was 5 s. Exponential window function (LB=0.2) was applied before Fourier Transformation.

1D ^{119}Sn. One-dimensional ^{119}Sn experiments were acquired with standard Bruker "zgig" program. The spectra were acquired with sweep width of 64935 Hz and 194798 data points, using 3072 scans and the recycling delay was 18 s. Exponential window function (LB=10) was applied before Fourier Transformation.

X-ray Diffraction Crystallography Details for Complexes 1’-6’.

Compound	Complex Number	Experiment Number	CCDC Number
[Ca(SnPh$_3$)$_2$.(thf)$_4$]	**1’**	PC0505	2051213
[Sr(SnPh$_3$)$_2$.(thf)$_4$]	**2’**	PC0506	2051214
[Ba(SnPh$_3$)$_2$.(thf)$_5$]	**3’**	PC0507	2051215
[Ca{Sn(SiMe$_3$)$_3$}$_2$.(thf)$_4$]	**4**	PC04068	2051216
[Sr{Sn(SiMe$_3$)$_3$}$_2$.(thf)$_4$]	**5**	PC04156x2	2051217
[Ba{Sn(SiMe$_3$)$_3$}$_2$.(thf)$_5$]]	**6’**	PC05035x3	2051218

[Ca{SnPh$_3$)$_2$.thf$_4$] (**1’**); $C_{52}H_{62}CaO_4Sn_2$; *M* = 1028.47. A suitable crystal for X-ray diffraction single crystal experiment (colourless prism, dimensions = 0.750 x 0.670 x 0.350 mm) was selected and mounted on the goniometer head of a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, using Mo-$K\alpha$ radiation (λ = 0.71073 Å, multilayer monochromator) at T = 150 K; the crystal structure has been described in monoclinic symmetry and $C2/c$ (I.T.#15) space group. Cell parameters have been refined as follows: a = 16.2273(12), b = 15.8447(9), c = 18.9351(14) Å, β = 98.715(3), V = 4812.3(6) Å^3. Number of formula unit Z is equal to 4 and calculated density d and absorption coefficient μ values are 1.420 g.cm^{-3} and 1.187 mm^{-1}, respectively. The structure was solved by dual-space algorithm using the *SHELXT* program,[5] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[6] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 5485 unique intensities and 268 parameters converged at ωR_F^2 = 0.0709 (R_F = 0.0336) for 4404 observed reflections with $I > 2\sigma(I)$.

[Sr(SnPh$_3$)$_2$.(thf)$_4$] (**2’**); $C_{52}H_{62}O_4Sn_2Sr$; *M* = 1076.01. A suitable crystal for X-ray diffraction single crystal experiment (colourless prism, dimensions = 0.390 x 0.210 x 0.170 mm) was selected and mounted on the goniometer head of a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, using Mo-$K\alpha$ radiation (λ = 0.71073 Å, multilayer monochromator) at T = 150 K; the crystal structure has been described in monoclinic symmetry and $C2/c$ (I.T.#15) space group. Cell parameters have been refined as follows: a = 16.3942(19), b = 15.9570(17), c = 19.010(2) Å, β = 99.049(5), V = 4911.2(9) Å^3. Number of formula unit Z is equal to 4 and calculated density d and absorption coefficient μ values are 1.455 g.cm^{-3} and 2.133 mm^{-1}, respectively. The structure was solved by dual-space algorithm using the *SHELXT* program,[5] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[6] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 5657 unique intensities and 268 parameters converged at ωR_F^2 = 0.0744 (R_F = 0.0331) for 4796 observed reflections with $I > 2\sigma(I)$.

[Ba{SnPh$_3$}$_2$.(thf)$_5$] (**3'**); $C_{116}H_{148}Ba_2O_{11}Sn_4$; *M* = 2467.78. A suitable crystal for X-ray diffraction single crystal experiment (colourless prism, dimensions = 0.750 x 0.400 x 0.080 mm) was selected and mounted on the goniometer head of a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, using Mo-*Kα* radiation (λ = 0.71073 Å, multilayer monochromator) at *T* = 150 K; the crystal structure has been described in orthorhombic symmetry and *P c a* 2_1 (I.T.#29) space group. Cell parameters have been refined as follows: *a* = 17.2099(9), *b* = 35.155(2), *c* = 18.6605(10) Å, *V* = 11289.9(11) Å^3. Number of formula unit *Z* is equal to 4 and calculated density *d* and absorption coefficient μ values are 1.452 g.cm^{-3} and 1.613 mm^{-1}, respectively. The structure was solved by dual-space algorithm using the *SHELXT* program,[5] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[6] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 20964 unique intensities and 1191 parameters converged at ωR_F^2 = 0.1355 (R_F = 0.0606) for 18131 observed reflections with $I > 2\sigma(I)$.

[Ca{Sn(SiMe$_3$)$_3$}$_2$.(thf)$_4$] (**4**); $C_{34}H_{86}CaO_4Si_6Sn_2$; *M* = 1005.02. A suitable crystal for X-ray diffraction single crystal experiment (colourless prism, dimensions = 0.500 x 0.450 x 0.400 mm) was selected and mounted on the goniometer head of a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-*Kα* radiation (λ = 0.71073 Å, multilayer monochromator), *T* = 150 K; monoclinic $P2_1/c$ (I.T.#14), *a* = 20.9784(13), *b* = 13.2370(8), *c* = 20.0226(16) Å, *β* = 105.698(4), *V* = 5352.7(6) Å^3. *Z* = 4, *d* = 1.247 g.cm^{-3}, *μ* = 1.192 mm^{-1}. The structure was solved by dual-space algorithm using the *SHELXT* program,[5] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[6] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 12033 unique intensities and 452 parameters converged at ωR_F^2 = 0.0830 (R_F = 0.0407) for 8673 observed reflections with $I > 2\sigma(I)$.

[Sr{Sn(SiMe$_3$)$_3$}$_2$.(thf)$_4$] (**5**); $C_{34}H_{86}O_4Si_6Sn_2Sr$; *M* = 1052.56. A suitable crystal for X-ray diffraction single crystal experiment (prism, dimensions = 0.440 x 0.420 x 0.280 mm) was selected and mounted on the goniometer head of a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, using Mo-*Kα* radiation (λ = 0.71073 Å, multilayer monochromator) at *T* = 150 K; the crystal structure has been described in monoclinic symmetry and $P2_1/c$ (I.T.#14) space group. Cell parameters have been refined as follows: *a* = 40.215(5), *b* = 13.1722(17), *c* = 20.520(3) Å, *β* = 93.183(4), *V* = 10853(2) Å^3. Number of formula unit *Z* is equal to 8 and calculated density *d* and absorption coefficient μ values are 1.288 g.cm^{-3} and 2.053 mm^{-1}, respectively. The structure was solved by dual-space algorithm using the *SHELXT* program,[5] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[6] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 24932 unique intensities and 788 parameters converged at $\omega R_F^2 = 0.2469$ ($R_F = 0.0812$) for 22195 observed reflections with $I > 2\sigma(I)$.

[Ba{Sn(SiMe$_3$)$_3$}$_2$.(thf)$_5$] (**6'**); $C_{38}H_{94}BaO_5Si_6Sn_2$; $M = 1174.39$. A suitable crystal for X-ray diffraction single crystal experiment (colourless prism, dimensions = 0.300 x 0.170 x 0.130 mm) was selected and mounted on the goniometer head of a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, using Mo-$K\alpha$ radiation (λ = 0.71073 Å, multilayer monochromator) at T = 150 K; the crystal structure has been described in monoclinic symmetry and $C2/c$ (I.T.#15) space group. Cell parameters have been refined as follows: a = 19.499(4), b = 17.117(3), c = 34.898(7) Å, β = 91.768(6), V = 11642(4) Å^3. Number of formula unit Z is equal to 8 and calculated density d and absorption coefficient μ values are 1.340 g.cm^{-3} and 1.676 mm^{-1}, respectively. The structure was solved by dual-space algorithm using the *SHELXT* program,[5] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[6] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 13389 unique intensities and 525 parameters converged at $\omega R_F^2 = 0.1231$ ($R_F = 0.0569$) for 11983 observed reflections with $I > 2\sigma(I)$.

Computational Details

Density functional theory (DFT) calculations were performed using the Amsterdam Density Functional ADF2019 code.[7] Scalar relativistic effects were taken into account via the Zeroth Order Regular Approximation (ZORA).[8] A triple-zeta basis set augmented with a polarisation function (STO-TZP)[9] was used together with the PBE0 functional[10] and Grimme's empirical DFT-D3 corrections[11] for geometry optimisation and analytical vibrational frequency computations. It has to be noted that D3 corrections were found to be responsible for underestimating the Ca-Sn bond lengths, when compared to their X-ray counterparts. However, the results discussed in our paper correspond to their inclusion in the calculations, not only for the obvious sake of homogeneity across the whole series of Ae complexes, but also because of the need to account for the many weak van der Waals interactions originating from the bulky substituents in the considered compounds. Natural atomic orbital (NAO) populations and Wiberg bond indices were computed with the NBO6.0 program.[12] Interaction energy between fragments were computed according to the Morokuma-Ziegler energy decomposition analysis (EDA) formalism[13] implemented in the ADF2019 program. The QTAIM analysis[14] was performed as implemented in the ADF2019 suite.[15] The NMR chemical shifts were computed according to the gauge-independent atomic orbitals (GIAO) method, as implemented in ADF2019.[16]

Table S1. Complementary DFT-computed metrical data (range and average in brackets) for the octahedral and the pentagonal bipyramidal complexes $[Ae(SnPh_3)_2.(thf)_x]$ and $[Ae\{Sn(SiMe_3)_3\}_2.(thf)_x]$ (Ae = Ca, Sr, Ba; x = 4, 5).

	$[Ca(SnPh_3)_2.(thf)_4]$ **1'**	$[Sr(SnPh_3)_2.(thf)_4]$ **2'**	$[Ba(SnPh_3)_2.(thf)_4]$ **3**	$[Ba(SnPh_3)_2.(thf)_5]$ **3'** (molecule 1)	$[Ba(SnPh_3)_2.(thf)_5]$ **3'**(molecule 2)
Sn-C /Å	2.189-2.200 [2.193]	2.188-2.202 [2.194]	2.189-2.238 [2.201]	2.184-2.215 [2.200]	2.192-2.210 [2.199]
∠ C-Sn-C/°	100-102 [101]	98-102 [100]	95-102 [98]	98-100 [98]	98-100 [99]

	$[Ca\{Sn(SiMe_3)_3\}_2.(thf)_4]$ **4**	$[Sr\{Sn(SiMe_3)_3\}_2.(thf)_4]$ **5**	$[Ba\{Sn(SiMe_3)_3\}_2.(thf)_4]$ **6**	$[Ba\{Sn(SiMe_3)_3\}_2.(thf)_5]$ **6'**	$[Mg\{Sn(SiMe_3)_3\}_2.(thf)_2]$
Sn-Si /Å	2.592-2.602 [2.600]	2.588-2.601 [2.595]	2.578-2.592 [2.586]	2.597-2.606 [2.602]	2.578-2.581 [2.579]
∠ Si-Sn-Si/°	96-99 [97]	97-99 [98]	97-100 [99]	95-99 [97]	101-103 [102]

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Author Contributions

P. M. Chapple performed synthetic experimental work and data analysis, and assisted in writing of the draft. M. Cordier performed the XRD analyses. JY. Saillard, J. Cartron and S. Kahlal carried out all computational work and took part to the writing of the draft. JF. Carpentier participated to the design of experiments and analysis of experimental data. H. Oulyadi and G. Hamdoun performed NMR analysis on compounds **4**, **5** and **6**. Y. Sarazin was the lead investigator; he participated to the design of experiments, analysis of experimental data and writing of the draft.