Supplementary information

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(i) General considerations

All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of dry argon or dinitrogen. Solvents were degassed by sparging with argon and dried by passing through a column of the appropriate drying agent using a commercially available Braun SPS and stored over potassium. Diethyl ether and THF were dried over and distilled from sodium and benzophenone/potassium (respectively) and stored over a potassium mirror or sodium mirror, respectively. Solvents employed in the preparation of/reactions of **1**-E_2 and **2**-E_2 were degassed by three freeze-pump-thaw cycles and stored over activated 4 Å molecular sieves. Hexamethyldisiloxane was dried over CaH_2, distilled, degassed by three freeze-pump-thaw cycles and stored over activated 4 Å molecular sieves. NMR spectra were measured in benzene-d_6 or toluene-d_8 which were dried over CaH_2, with the solvent then being distilled under reduced pressure, degassed by three freeze-pump-thaw cycles 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. NMR spectra were measured on a Bruker Avance III HD Nanobay 400 MHz NMR spectrometer equipped with a 9.4 T magnet, Bruker Avance III 500 MHz NMR spectrometer equipped with a 11.75 T magnet or a Bruker Avance III NMR 500 MHz NMR spectrometer equipped with a 11.75 T magnet and a ^{13}C detect cryoprobe. ^{1}H and ^{13}C NMR spectra were referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). ^{119}Sn NMR spectra were referenced with respect to $SnMe_4$ in C_6D_6. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Infra-red spectra were measured on a Nicolet 500 FT-IR spectrometer. Elemental analyses were carried out by Elemental Microanalysis Ltd., Okehampton, Devon.

(ii) Starting Materials

The syntheses of 2,6-$(Et_2NCH_2)_2C_6H_3Br$,[s1] and $(Ar^{NEt2}Ge)_2$[s2] were carried out as per literature methods. CO_2 was dried over P_2O_5 for > 48 h, prior to use. All other reagents were used as received.

(iii) Novel Compounds

Synthesis of [2,6-(Et_2NCH_2)$_2$$C_6H_3$]SnCl ($Ar^{NEt2}$SnCl): To a solution of 2,6-(Et_2NCH_2)$_2$$C_6H_3$Br (3.92 g, 12.0 mmol) in diethyl ether (25 mL) at 0°C was added dropwise ^{n}BuLi (9.0 mL, 14.4 mmol, 1.6 M in *n*-hexane). The resulting solution was allowed to warm to room temperature and stirred for 30 min during which time the solution became pale yellow in colour and precipitated crystalline 1-lithio-2,6-bis[(diethylamino)methyl])benzene. Volatiles were subsequently removed *in vacuo* and the resulting crystalline material was dissolved in tetrahydrofuran (30 mL). The solution was then added dropwise to a slurry of $SnCl_2$ (2.72 g, 14.3 mmol), also in THF (20 mL), at –78°C before being allowed to warm to room temperature and stirred for 20 min. Volatiles were then removed *in vacuo* and the resulting oily residue treated with *n*-hexane (100 mL), filtered and concentrated to *ca.* 20 mL. Storage of the solution overnight at –30°C yielded a yellow oil, from which colourless crystals, which were suitable for X-ray crystallography, grew over the course of *ca.* 10 days. Yield: 3.86 g (80%). **Spectroscopic data: ^{1}H NMR** (400 MHz, benzene-d_6, 298 K): δ_H 0.82 (12H, t, $^3J_{HH}$ = 7.2 Hz, CH_3 of Et), 1.96 – 3.22 (8H, br m, overlapping CH_2 of Et), 3.40 and 3.72 (4H, AB system, $^2J_{HH}$ = 14.2 Hz, CH_2N), 6.98 (2H, d, $^3J_{HH}$ = 7.4 Hz, *m*-C*H* of Ar), 7.18 (1H, t, $^3J_{HH}$ = 7.4 Hz, *p*-C*H* of Ar). **^{13}C{^{1}H} NMR** (101 MHz, benzene-d_6, 298 K): δ_C 9.6 (br., *C*H_3 of Et), 44.6 (*C*H_2 of Et), 59.4 (*C*H_2N), 124.5 (*m*-Ar*C*), 146.4 (*o*-Ar*C*), 168.8 (*ipso*-Ar*C*). The resonance for *p*-ArC is obscured by the solvent peak. **^{119}Sn{^{1}H} NMR** (149 MHz, benzene-d_6, 298K): δ_{Sn} 162.4. The ^{119}Sn{^{1}H} NMR spectrum of the crystalline product shows a minor resonance at δ_{Sn} = 187.0 ppm. It is assumed, based on the reported behaviour of Ar^{NiPr2}SnCl,[s3] that this resonance corresponds to the tin centre of Ar^{NEt2}SnBr, formed by halogen exchange. The presence of Ar^{NiPr2}SnBr in the product showed no impact on its reactivity and no further purification was undertaken.

Synthesis of [2,6-(Et_2NCH_2)$_2$$C_6H_3$]SnI ($Ar^{NEt2}$SnI): Method A: To a solution of 2,6-(Et_2NCH_2)$_2$$C_6H_3$Br (3.36 g, 10.3 mmol) in diethyl ether (20 mL) at 0°C was added dropwise ^{n}BuLi (7.7 mL, 12.32 mmol, 1.6 M in *n*-hexane). The resulting solution was allowed to warm to room temperature and stirred for 30 min during which time the solution became pale yellow in colour and precipitated crystalline 1-lithio-2,6-bis[(diethylamino)methyl])benzene. Volatiles were subsequently removed *in vacuo* and the resulting crystalline material was dissolved in tetrahydrofuran (25 mL). The solution was then added dropwise to a slurry of $SnCl_2$ (2.36 g, 12.6 mmol), also in THF (20 mL), at –78°C before being allowed to warm to room temperature and stirred for 20 min. Volatiles were then removed *in vacuo* and the resulting oily residue treated with *n*-hexane (100 mL), filtered and concentrated to *ca.* 25 mL. Neat trimethylsilyliodide (1.75 mL, 12.3 mmol) was added dropwise to the solution which, after stirring for 10 min, began to precipitate bright yellow crystalline material. The resulting slurry was stirred for 1 h at room temperature before being concentrated to *ca.* 10 mL. The crude product was isolated by filtration, dried *in vacuo*, extracted into hot hexane (120 mL, 60°C) and filtered whilst hot. The solution was allowed to slowly cool to room temperature, producing large yellow crystals of Ar^{NEt2}SnI, which were suitable for X-ray crystallography. Storage of the solution at 6°C overnight yielded more crystals, which were isolated and dried *in vacuo*. Further concentration of the supernatant solution, followed by storage at –30°C, yielded a second crop of crystals. Combined yield: 3.29 g (65%). Method B: To a

Schlenk tube containing $Ar^{NEt2}SnCl$ (1.5 g, 3.74 mmol) and NaI (0.67 g, 4.47 mmol) was added THF (10 mL). The resulting slurry was stirred for 18 h at room temperature during which time the colourless solution evolved a bright yellow colour. The slurry was subsequently filtered and volatiles were removed *in vacuo* to yield a sticky yellow residue which was extracted into *n*-hexane (50 mL). The resulting slurry was filtered and concentrated to the point of incipient crystallisation. Storage of this solution at –30°C overnight yielded large yellow crystals of $Ar^{NEt2}SnI$, which were isolated and dried *in vacuo*. Yield: 1.64 g (89%). **Spectroscopic data: ^{1}H NMR** (400 MHz, benzene-d_6, 298 K): δ_H 0.77 (12H, t, $^{3}J_{HH}$ = 7.2 Hz, C*H*$_3$ of Et), 2.0 – 3.25 (8H, m (br.), C*H*$_2$ of Et), 3.37 and 3.73 (4H, AB system, $^{2}J_{HH}$ = 14.2 Hz, C*H*$_2$N), 6.95 (2H, d, $^{3}J_{HH}$ = 7.4 Hz, *m*-C*H* of Ar), 7.14 (1H, t, $^{3}J_{HH}$ = 7.4 Hz, *p*-C*H* of Ar). **^{13}C{^{1}H} NMR** (101 MHz, benzene-d_6, 298 K): δ_C 9.9 (*C*H$_3$ of Et), 45.0 (br., *C*H$_2$ of Et), 59.6 (*C*H$_2$N), 124.4 (*m*-Ar*C*), 128.4 (*p*-ArC), 146.7 (*o*-Ar*C*), 164.8 (*ipso*-Ar*C*). **^{119}Sn{^{1}H} NMR** (149 MHz, benzene-d_6, 298K): δ_{Sn} 212.2. **Elemental microanalysis**: calc. for $C_{16}H_{27}N_2SnI$ C 38.98%, H 5.52%, N 5.68%, meas. C 39.25%, H 5.58%, N 5.75%.

Synthesis of [{2,6-(Et$_2$NCH$_2$)$_2$C$_6$H$_3$}Sn]$_2$ ((Ar^{NEt2}Sn)$_2$, 1-Sn$_2$): A rapidly stirred mixture of $Ar^{NEt2}SnI$ (2 g, 4.06 mmol) and KC_8 (0.6 g, 4.47 mmol) was cooled to –78 °C and to it was added tetrahydrofuran (12 mL). The resulting slurry was stirred for 5 min at –78 °C before being allowed to warm to room temperature and stirred for a further 20 min. Following this, volatiles were removed *in vacuo* and the resulting deep red residue was treated with *n*-hexane (30 mL). The resulting red solution was filtered and concentrated until red oil was deposited onto the walls of the Schlenk tube. The oil was redissolved and the solution stored at –30 °C overnight, yielding clusters of dark red crystals, which were suitable for X-ray crystallography. The crystals were isolated and dried *in vacuo* and the supernatant solution was concentrated further and stored at –30 °C overnight, producing a second crop of crystals. Combined yield: 1.07 g (72%). **Spectroscopic data: ^{1}H NMR** (400 MHz, benzene-d_6, 298 K): δ_H 0.90 (24H, t, $^{3}J_{HH}$ = 7.2 Hz, C*H*$_3$ of Et), 2.68 – 2.75 (16H, br m, overlapping C*H*$_2$ of Et), 3.61 – 3.71 (8H, m, C*H*$_2$N), 6.97 – 7.04 (6H, m, *m*- and *p*-C*H* of Ar). **^{13}C{^{1}H} NMR** (101 MHz, benzene-d_6, 298 K): δ_C 10.3 (*C*H$_3$ of Et), 46.2 (*C*H$_2$ of Et), 62.6 (*C*H$_2$N), 123.3 (*m*-Ar*C*), 124.3 (*p*-Ar*C*), 144.6 (*o*-Ar*C*), 173.1 (*ipso*-Ar*C*). **^{119}Sn{^{1}H} NMR** (149 MHz, benzene-d_6, 298 K): δ_{Sn} 639.6 ($^{1}J_{119Sn\text{-}117Sn}$ = 1900 Hz). **Elemental microanalysis**: calc. for $C_{32}H_{54}N_4Sn_2$ C 52.49%, H 7.43%, N 7.65%, meas. C 52.57%, H 7.52%, N 7.66%.

Synthesis of [{2,6-(Et$_2$NCH$_2$)$_2$C$_6$H$_3$}Sn]$_2$(μ-CO$_2$) ((Ar^{NEt2}Sn)$_2$(μ-CO$_2$), 2-Sn$_2$): To a two-section crystallisation tube fitted with a J. Young's valve was added **1**-Sn$_2$ (160 mg, 0.22 mmol) and *n*-hexane (2 mL). The resulting slurry was degassed by three freeze-pump-thaw cycles, cooled to –30°C and back-filled with carbon dioxide (*ca*. 1 bar). The reaction mixture was allowed to stand at –30°C for *ca.* 5 min, during which time the crystalline distannyne dissolved and the resulting deep red solution decolourised, and was then degassed by three further freeze-pump-thaw cycles (whilst ensuring that the solution temperature did not rise above –30°C). The solution was then concentrated (at –30°C) by condensing the solvent into the second section of the crystallisation tube until small colourless crystals began to grow. The solution was then stored at –30°C for *ca.* 7 h, yielding clusters of colourless crystals, which were suitable for X-ray crystallography. The crystals were isolated and

dried *in vacuo*. Yield: 95 mg (56%). **Spectroscopic data: ^{1}H NMR** (400 MHz, benzene-d_6, 298 K): δ_H 0.84 (12H, t, $^{3}J_{HH}$ = 7.2 Hz, CH_3 of Et), 0.94 (12H, t, $^{3}J_{HH}$ = 7.2 Hz, CH_3 of Et), 2.63 (8H, q, $^{3}J_{HH}$ = 7.2 Hz, CH_2 of Et), 2.76 (8H, q, $^{3}J_{HH}$ = 7.2 Hz, CH_2 of Et), 3.44 and 4.03 (4H, AB system, $^{2}J_{HH}$ = 13.7 Hz, CH_2N), 3.49 and 3.77 (4H, AB system, $^{2}J_{HH}$ = 13.7 Hz, CH_2N), 6.98 – 7.02 (4H, m, *m*-C*H* of Ar), 7.11 – 7.18 (2H, m, *p*-C*H* of Ar). **^{13}C{^{1}H} NMR** (101 MHz, benzene-d_6, 298 K): δ_C 9.8, 9.9 (*C*H$_3$ of Et), 44.4, 44.9 (*C*H$_2$ of Et), 60.6, 60.7 (*C*H$_2$N), 123.7, 124.3 (*m*-Ar*C*), 126.6, 127.0 (*p*-ArC), 146.3, 147.3 (*o*-Ar*C*), 167.4, 170.3 (*ipso*-Ar*C*), 220.6 (*C*O$_2$). **^{119}Sn NMR** (149 MHz, benzene-d_6, 298 K): δ_{Sn} 80.9, 95.4. **IR** (cm^{-1}): 1520, 1399 cm^{-1} (ν(CO)). **Elemental microanalysis**: calc. for $C_{33}H_{54}N_4O_2Sn_2$ C 51.06%, H 7.01%, N 7.22%, meas. C 51.17%, H 6.89%, 7.05%.

Synthesis of [{2,6-(Et$_2$NCH$_2$)$_2$C$_6$H$_3$}Ge]$_2$(μ-CO$_2$) ((Ar^{NEt2}Ge)$_2$(μ-CO$_2$), 2-Ge$_2$): To a two-section crystallisation tube fitted with a J. Young's valve was added **1**-Ge$_2$ (134 mg, 0.21 mmol) and *n*-hexane (1 mL). The resulting solution was degassed by three freeze-pump-thaw cycles, cooled to –30°C and back-filled with carbon dioxide (*ca*. 1 bar). The reaction mixture was allowed to stand at –30°C for *ca.* 5 min, during which time the solution colour changed from pale orange to bright yellow, and was then degassed by three further freeze-pump-thaw cycles (whilst ensuring that the solution temperature did not rise above –30°C). The solution was then concentrated (at –30°C) by condensing the solvent into the second section of the crystallisation tube until small yellow crystals began to grow. The solution was then stored at –30°C for *ca.* 7 h, yielding small yellow crystals, which were suitable for X-ray crystallography. The crystals were isolated and dried *in vacuo*. Yield: 98 mg (69%). **Spectroscopic data: ^{1}H NMR** (400 MHz, benzene-d_6, 298 K): δ_H 0.89 (12H, t, $^{3}J_{HH}$ = 7.2 Hz, CH_3 of Et), 0.93 (12H, t, $^{3}J_{HH}$ = 7.2 Hz, CH_3 of Et), 2.42 – 2.93 (8H, m, CH_2 of Et), 3.44 and 3.94 (4H, AB system, $^{2}J_{HH}$ = 14.0 Hz, CH_2N), 3.45 and 3.89 (4H, AB system, $^{2}J_{HH}$ = 14.0 Hz, CH_2N), 7.00 – 7.01 (4H, m, *m*-C*H* of Ar), 7.07 – 7.15 (2H, m, *p*-C*H* of Ar). **^{13}C{^{1}H} NMR** (101 MHz, benzene-d_6, 298 K): δ_C 9.8 (2 x overlapping *C*H$_3$ of Et), 44.8, 45.2 (*C*H$_2$ of Et), 59.8, 60.0 (*C*H$_2$N), 123.1, 124.6 (*m*-Ar*C*), 126.3, 127.4 (*p*-ArC), 144.4, 146.0 (*o*-Ar*C*), 158.4, 159.2 (*ipso*-Ar*C*), 206.0 (*C*O$_2$). **IR** (cm^{-1}): 1604 cm^{-1} (ν(CO)). **Elemental microanalysis**: calc. for $C_{33}H_{54}N_4O_2Ge_2$ C 57.94%, H 7.96%, N 8.19%, meas. C 58.17%, H 8.02%, 8.16%.

Synthesis of [{2,6-(Et$_2$NCH$_2$)$_2$C$_6$H$_3$}Sn]$_2$(μ-CO$_3$) ((Ar^{NEt2}Sn)$_2$(μ-CO$_3$), 3-Sn$_2$): A solution of Ar^{NEt2}SnCl (0.3 g, 0.75 mmol) in THF (5 mL) was added dropwise to a slurry of Cs_2CO_3 (0.73 g, 2.24 mmol) in THF (2 mL) and the resulting reaction mixture was stirred at room temperature for 72 h. The colourless solution was filtered and volatiles were removed *in vacuo* to give a sticky colourless oil, which was extracted into *n*-hexane (10 mL). The solution was subsequently filtered and concentrated until oil was deposited onto the sides of the Schlenk tube. The oil was redissolved by gentle heating of the solution, which was subsequently left to cool to room temperature and stand for 72 h, producing colourless acicular crystals, which were suitable for X-ray crystallography. Yield: 0.12 g (41%). **Spectroscopic data: ^{1}H NMR** (400 MHz, benzene-d_6, 298 K): δ_H 0.89 (24H, t, $^{3}J_{HH}$ = 7.2 Hz, CH_3 of Et), 2.70 (16H, q, $^{3}J_{HH}$ = 7.2 Hz, CH_2 of Et), 3.44 and 3.99 (8H, AB system, $^{2}J_{HH}$ = 13.9 Hz, CH_2N), 7.02 (4H, d, $^{3}J_{HH}$ = 7.4 Hz, *m*-C*H* of Ar), 7.19 (2H, t, $^{3}J_{HH}$ = 7.4 Hz, *p*-C*H* of Ar). **^{13}C{^{1}H} NMR** (126 MHz, benzene-d_6, 298 K): δ_C 9.6 (*C*H$_3$ of Et), 44.5 (*C*H$_2$ of Et), 60.1 (*C*H$_2$N), 124.3 (*m*-Ar*C*), 127.5 (*p*-

ArC), 147.6 (*o*-Ar*C*), 168.2 (O_2C(O)), 170.2 (*ipso*-Ar*C*). **^{119}Sn NMR** (186 MHz, benzene-d_6, 298 K): δ_{Sn} –34.0. **Elemental microanalysis**: calc. for $C_{33}H_{54}N_4O_3Sn_2$ C 50.03%, H 6.87%, N 7.07%, meas. C 50.21%, H 6.92%, 7.03%.

Synthesis of [{2,6-(Et_2NCH_2)$_2$$C_6H_3$}Sn]$_2$(μ-O) ((Ar^{NEt2}Sn)$_2$(μ-O), 4-$Sn_2$): To a rapidly stirred mixture of **1**-Sn_2 (300 mg, 0.41 mmol) and pyridine-N-oxide (41 mg, 0.43 mmol) was added benzene (2.5 mL). The resulting deep red solution was stirred for 3 h at room temperature and volatiles were subsequently removed *in vacuo* to yield a sticky orange oil. The oil was extracted into minimal HMDSO, filtered and concentrated until microcrystalline solid grew from oil deposited on the walls of the Schlenk tube. The solid was redissolved by gentle heating and the solution was then allowed to cool to room temperature. Storage of the solution at –30°C for 1 week yielded small, orange crystals, which were suitable for X-ray crystallography. Yield: 83 mg (25%). **Spectroscopic data: ^{1}H NMR** (400 MHz, benzene-d_6, 298 K): δ_H 0.95 (24H, t, $^3J_{HH}$ = 7.2 Hz, C*H*$_3$ of Et), 2.67 – 2.80 (16H, m, C*H*$_2$ of Et), 3.56 and 3.83 (8H, AB system, $^2J_{HH}$ = 13.6 Hz, C*H*$_2$N), 7.05 (4H, d, $^3J_{HH}$ = 7.3 Hz, *m*-C*H* of Ar), 7.17 (2H, t, $^3J_{HH}$ = 7.3 Hz, *p*-C*H* of Ar). **^{13}C{^{1}H} NMR** (101 MHz, benzene-d_6, 298 K): δ_C 9.7 (*C*H$_3$ of Et), 44.6 (*C*H$_2$ of Et), 59.7 (*C*H$_2$N), 124.1 (*m*-Ar*C*), 126.6 (*p*-ArC), 146.2 (*o*-Ar*C*), 175.0 (*ipso*-Ar*C*). **^{119}Sn NMR** (149 MHz, benzene-d_6, 298 K): δ_{Sn} 177.1. **Elemental microanalysis**: calc. for $C_{32}H_{54}N_4OSn_2$ C 51.37%, H 7.27%, N 7.49%, meas. C 51.16%, H 7.27%, 7.45%.

***In situ* synthesis of [{2,6-(Et_2NCH_2)$_2$$C_6H_3$}Ge]$_2$(O) ((Ar^{NEt2}Ge)$_2$(O), 4-$Ge_2$):** To an NMR tube fitted with a J. Young's valve was added **1**-Ge_2 (30 mg, 0.047 mmol), pyridine-N-oxide (5 mg, 0.053 mmol) and benzene-d_6 (0.5 mL). The resulting solution was shaken vigorously and monitored regularly by ^{1}H NMR spectroscopy until the reaction reached completion (*ca.* 24 h). The reaction was shown to be quantitative by ^{1}H NMR spectroscopy, but repeated attempts to isolate **4**-Ge_2 as crystals or in the solid state by increasing the scale of the reaction were unsuccessful. ***In situ* spectroscopic data: ^{1}H NMR** (400 MHz, benzene-d_6, 298 K): δ_H 0.95 (24H, t, $^3J_{HH}$ = 7.2 Hz, C*H*$_3$ of Et), 2.66 – 2.72 (16H, m, C*H*$_2$ of Et), 3.51 and 3.91 (8H, AB system, $^2J_{HH}$ = 13.8 Hz, C*H*$_2$N), 7.10 (4H, d, $^3J_{HH}$ = 6.4 Hz, *m*-C*H* of Ar), 7.17 (2H, t, $^3J_{HH}$ = 6.4 Hz, *p*-C*H* of Ar). **^{13}C{^{1}H} NMR** (101 MHz, benzene-d_6, 298 K): δ_C 10.0 (*C*H$_3$ of Et), 45.0 (*C*H$_2$ of Et), 59.3 (*C*H$_2$N), 123.8 (*m*-Ar*C*), 127.0 (*p*-ArC), 145.1 (*o*-Ar*C*), 163.9 (*ipso*-Ar*C*).

***In situ* preparation of [{2,6-(Et_2NCH_2)$_2$$C_6H_3$}Ge](μ-$CO_2$)Sn[{2,6-($Et_2NCH_2$)$_2$$C_6H_3$}] ((Ar^{NEt2}Ge)(μ-$CO_2$)(SnAr^{NEt2}), 2-GeSn):** To an NMR tube fitted with a J. Young's valve was added **2**-Ge_2 (9 mg, 0.013 mmol), **2**-Sn_2 (10 mg, 0.013 mmol) and benzene-d_6 (0.5 mL). The solution was shaken vigorously and monitored at regular intervals by ^{1}H NMR spectroscopy until the reaction reached completion (*ca.* 4 h). **Preparation of single crystals of 2-GeSn:** To an NMR tube fitted with a J. Young's valve was added **2**-Ge_2 (25 mg, 0.037 mmol), **2**-Sn_2 (29 mg, 0.037 mmol) and *n*-hexane (0.7 mL). The resulting solution was shaken vigorously and analysed at regular intervals by ^{119}Sn NMR spectroscopy until the reaction reached completion (based on consumption of **2**-Sn_2). The resulting yellow solution was transferred to a two-section crystallisation tube fitted with a J. Young's valve and was cooled to –30°C. The solution was then concentrated (at –30°C) by condensing the solvent into the second section of the crystallisation tube until an oily residue remained. The *n*-hexane solvent

was decanted from the second section of the tube and the oily residue was stored at –30°C for 48 h, yielding a small number of colourless single crystals, which were suitable for X-ray crystallography. Repeated attempts to isolate pure bulk samples of ($Ar^{NEt2}Ge$)(CO_2)($SnAr^{NEt2}$) were unsuccessful. ***In situ* spectroscopic data: ^{1}H NMR** (400 MHz, benzene-d_6, 298 K): δ_H 0.89 (12H, t, $^3J_{HH}$ = 7.2 Hz, CH_3 of Et), 0.94 (12H, t, $^3J_{HH}$ = 7.2 Hz, CH_3 of Et), 2.53 – 2.78 (8H, m, CH_2 of Et), 3.43 and 4.04 (4H, AB system, $^2J_{HH}$ = 13.7 Hz, CH_2N), 3.48 and 3.85 (4H, AB system, $^2J_{HH}$ = 13.8 Hz, CH_2N), 6.97 – 6.99 (4H, m, *m*-C*H* of Ar), 7.12 (2H, t, $^3J_{HH}$ = 7.4 *p*-C*H* of Ar). **^{13}C{^{1}H} NMR** (101 MHz, benzene-d_6, 298 K): δ_C 9.6 (*C*H_3 of Et), 9.8 (*C*H_3 of Et (br)), 44.4 (*C*H_2 of Et (br)), 45.1 (*C*H_2 of Et), 59.6, 60.7 (*C*H_2N), 123.0, 124.3 (*m*-Ar*C*), 126.4, 127.1 (*p*-ArC), 144.2, 147.5 (*o*-Ar*C*), 158.7, 169.8 (*ipso*-Ar*C*), 210.4 (*C*O_2). **^{119}Sn NMR** (149 MHz, benzene-d_6, 298 K): δ_{Sn} 51.2.

Method for monitoring loss of CO from 2-E_2: E = Sn: To an NMR tube fitted with a J. Young's valve was added **2**-Sn_2 (20 mg, 0.026 mmol) and benzene-d_6 (0.5 mL). The resulting solution was stored at room temperature and regularly monitored by ^{1}H NMR spectroscopy until **2**-Sn_2 was consumed. The ^{1}H, ^{13}C and ^{119}Sn{^{1}H} NMR spectra of the product mixture show that **3**-Sn_2 and **1**-Sn_2 are formed in a 1:1 ratio; the data are consistent with those obtained for the compounds when prepared by independent methods (see above). E = Ge: **2**-Ge_2 (18 mg, 0.026 mmol) and benzene-d_6 (0.5 mL) were added to an NMR tube fitted with a J. Young's valve and the resulting yellow solution was heated to 70°C for 28 h. After this time, the ^{1}H NMR spectrum of the resulting colourless solution showed > 95% conversion of **2**-Ge_2 to **4**-Ge_2; the NMR spectra of the product are consistent with those of **4**-Ge_2 prepared independently from the reaction of **1**-Ge_2 and pyridine-N-oxide (see above).

Method for monitoring the reaction of 2-Sn_2 with 4-Sn_2: To an NMR tube fitted with a J. Young's valve was added **2**-Sn_2 (10 mg, 0.013 mmol), **4**-Sn_2 (10 mg, 0.013 mmol) and benzene-d_6 (0.5 mL). The resulting pale orange solution was shaken vigorously (where the solution colour changed immediately to dark red) and was analysed (within 5 min) by ^{1}H NMR spectroscopy. The resulting spectrum shows that the reaction yields a 1:1 mixture of **3**-Sn_2 and **1**-Sn_2. NMR data are consistent with those obtained for the compounds prepared independently (see above).

Method for monitoring the reaction of 2-E_2 with CO_2: E = Sn: To an NMR tube fitted with a J. Young's valve was added **2**-Sn_2 (20 mg, 0.026 mmol) and benzene-d_6 (0.5 mL). The resulting solution was degassed by three freeze-pump-thaw cycles, back-filled with carbon dioxide (*ca*. 1 bar) and shaken vigorously. The reaction solution was kept at room temperature and monitored by ^{1}H NMR spectroscopy until the reaction reached > 95% completion; the ^{1}H NMR spectrum of the product was consistent with that of **3**-Sn_2 when independently prepared by the metathesis route (see above). E = Ge: **2**-Ge_2 (18 mg, 0.026 mmol) and benzene-d_6 (0.5 mL) were added to an NMR tube fitted with a J. Young's valve. The resulting yellow solution was degassed by three freeze-pump-thaw cycles, back-filled with carbon dioxide (*ca.* 1 bar), shaken vigorously and heated to 70°C. The reaction solution was monitored at regular intervals by ^{1}H NMR spectroscopy until the reaction reached > 95% completion. ***In situ* spectroscopic data: ^{1}H NMR** (400 MHz, benzene-d_6, 298 K): δ_H 0.96 (24H, t, $^3J_{HH}$ = 7.2 Hz, CH_3 of Et), 2.70 – 2.79 (16H, m, CH_2 of Et), 3.43 and 3.85 (8H, AB system, $^2J_{HH}$ = 14.1 Hz, CH_2N),

6.98 (4H, d, $^3J_{HH}$ = 6.4 Hz, *m*-C*H* of Ar), 7.17 (2H, t, $^3J_{HH}$ = 6.4 Hz, *p*-C*H* of Ar). **^{13}C{^{1}H} NMR** (101 MHz, benzene-d_6, 298 K): δ_C 9.5 (*C*H_3 of Et), 44.6 (*C*H_2 of Et), 58.9 (*C*H_2N), 123.7 (*m*-Ar*C*), 145.9 (*o*-Ar*C*), 158.2 (*ipso*-Ar*C*) 163.5 (O_2*C*(O)). Resonance for *p*-ArC is obscured by the solvent resonance.

Reaction of 4-E_2 with CO_2: E = Sn**:** To an NMR tube fitted with a J. Young's valve was added 4-Sn_2 (10 mg, 0.013 mmol) and benzene-d_6 (0.5 mL). The resulting solution was degassed by three freeze-pump-thaw cycles, back-filled with carbon dioxide (*ca*. 1 bar) and shaken vigorously. The pale orange solution immediately decolorised, and the reaction was shown to be quantitative by ^{1}H NMR spectroscopy (within 5 min); the ^{1}H NMR spectrum of the product was consistent with that of **3**-Sn_2 prepared independently (see above). E = Ge**:** **4**-Ge_2 was generated *in situ* in an NMR tube fitted with a J. Young's valve from the reaction of **1**-Ge_2 (30 mg, 0.047 mmol) and pyridine-N-oxide (5 mg, 0.053 mmol) in benzene-d_6 (0.5 mL) (see above). The resulting solution of **4**-Ge_2 was degassed by three freeze-pump-thaw cycles, back-filled with carbon dioxide (*ca*. 1 bar) and shaken vigorously. The reaction was shown to be quantitative by ^{1}H NMR spectroscopy and the ^{1}H NMR spectrum of the product consistent with that of **3**-Ge_2 prepared by Method A above.

Reaction of 2-E_2 with 1-E′$_2$ (E = Ge, E′ = Sn; E = Sn, E′ = Ge): General method: To an NMR tube fitted with a J. Young's valve was added **2**-E_2 (0.01 mmol), **1**-E′$_2$ (0.012 mmol) and benzene-d_6 (0.5 mL). The resulting solution was shaken vigorously and analysed (within 5 min) by ^{1}H NMR spectroscopy. The solution was then analysed at regular intervals until no further change to the product distribution was observed. **E = Ge, E′ = Sn:** Upon shaking the solution, the deep red solution changed colour to bright orange. Analysis of the solution by ^{1}H NMR spectroscopy identifies the major products of the reaction as **2**-Sn_2 and **1**-Ge_2. **E = Sn, E′ = Ge:** Upon shaking the solution, the solution remains a bright orange colour. The ^{1}H NMR spectrum of the resulting solution shows unreacted **2**-Sn_2 and **1**-Ge_2. In both cases, over the course of *ca.* 1 h, the colour of the solution changes to deep red and the ^{1}H NMR spectra of both reaction solutions show that **2**-Sn_2 and **1**-Ge_2 (0.5 equiv. relative to **2**-Sn_2) are consumed to form **2**-GeSn and **1**-Sn_2. The resonances for one further species are also observed (accounting for < 10% of the product distribution); the identity of this species is proposed to be the unsymmetrical dimetallyne **1**-GeSn.

Reaction of 2-Ge_2 with $^{13}CO_2$: To an NMR tube fitted with a J. Young's valve was added **2**-Ge_2 (30 mg, 0.044 mmol) and benzene-d_6 (0.5 mL). The resulting yellow solution was degassed by three freeze-pump-thaw cycles and backfilled with $^{13}CO_2$. The reaction solution was monitored (within 10 min) by ^{13}C NMR spectroscopy and was further analysed by ^{13}C NMR spectroscopy at 15 min intervals for the following 12 h.

(iv) Representative ^{1}H and ^{13}C NMR spectra of novel compounds

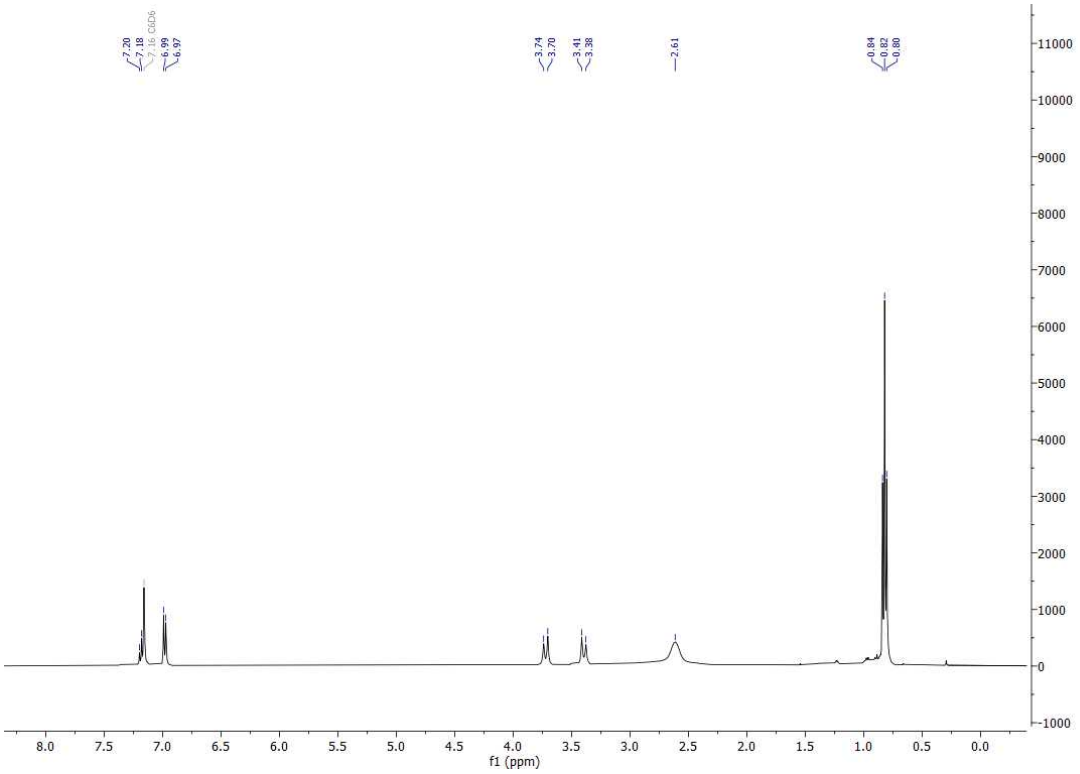


Figure s1. ^{1}H NMR spectrum of $Ar^{NEt2}SnCl$ measured in benzene-d_6 at 298 K.

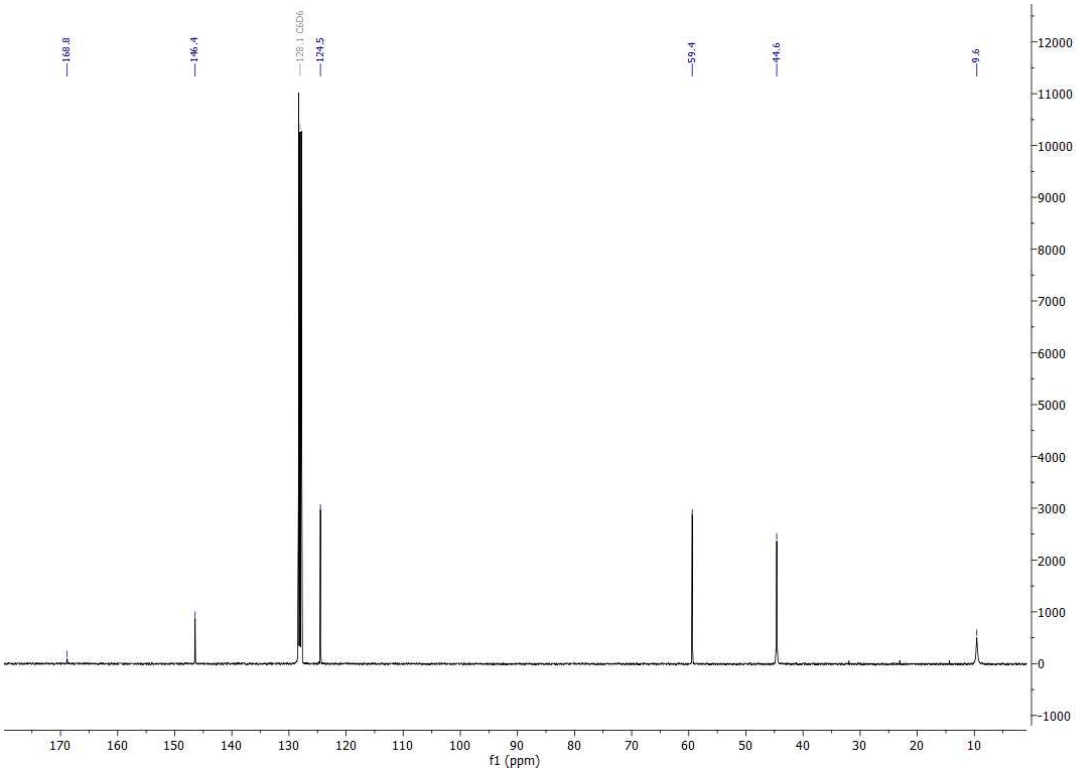


Figure s2. ^{13}C NMR spectrum of $Ar^{NEt2}SnCl$ measured in benzene-d_6 at 298 K.

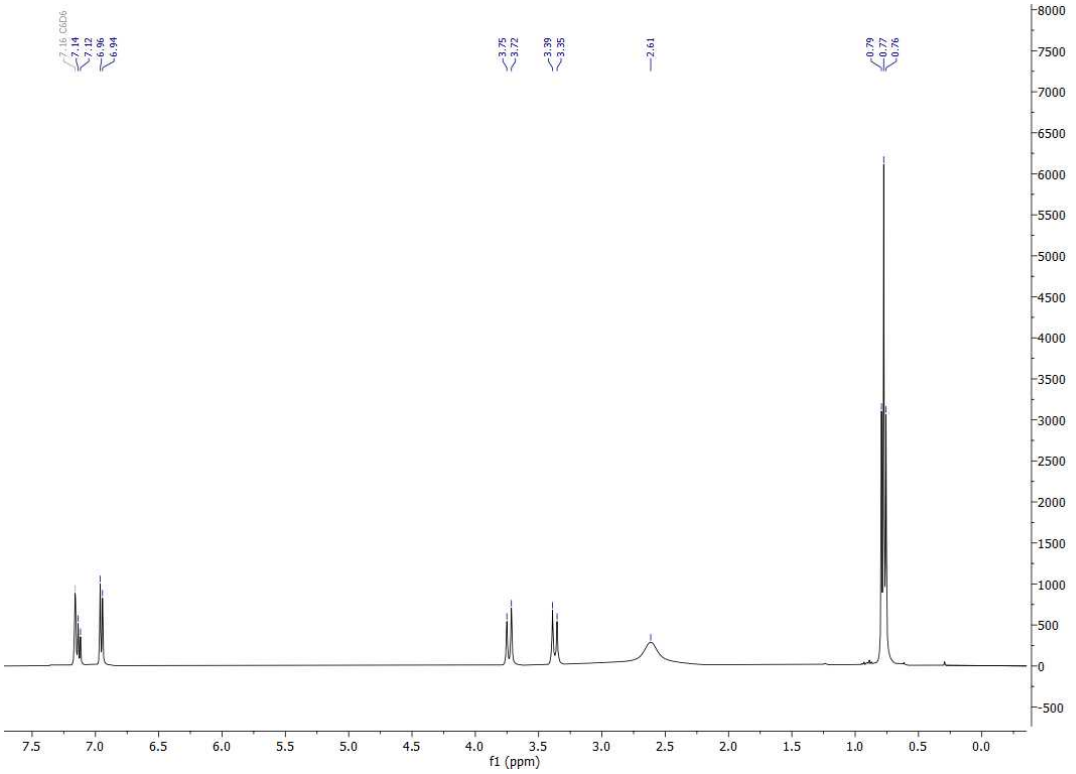


Figure s3. ^{1}H NMR spectrum of $Ar^{NEt2}SnI$ measured in benzene-d_6 at 298 K.

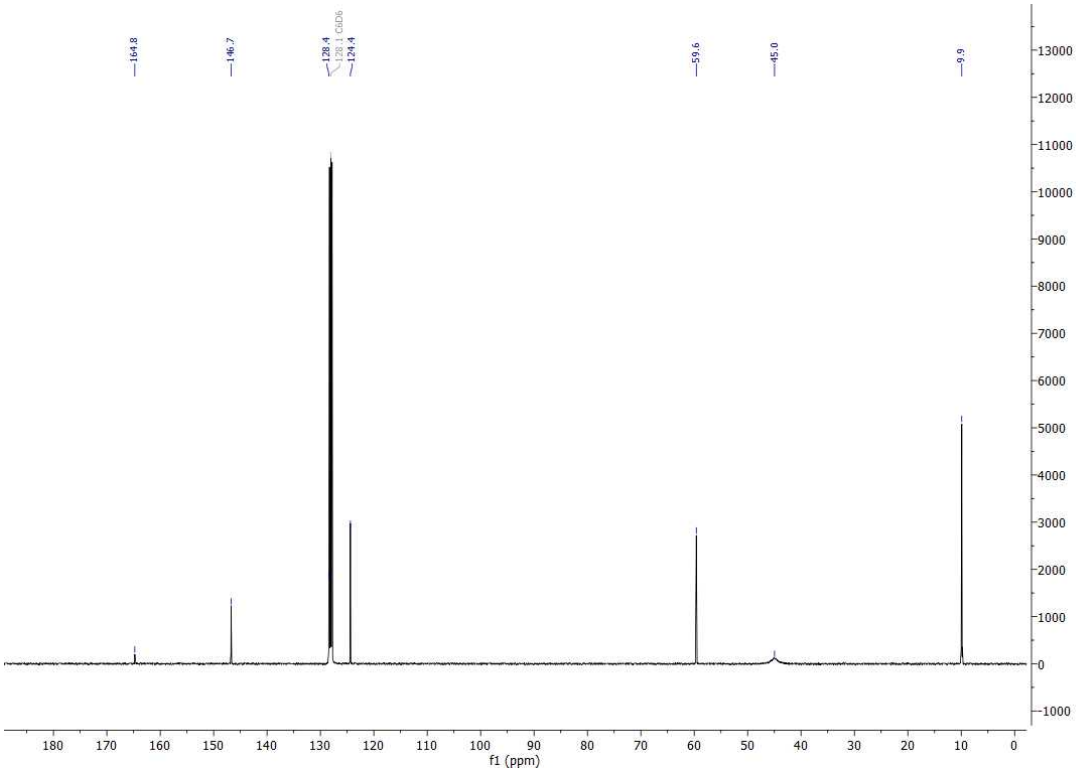


Figure s4. ^{13}C NMR spectrum of $Ar^{NEt2}SnI$ measured in benzene-d_6 at 298 K.

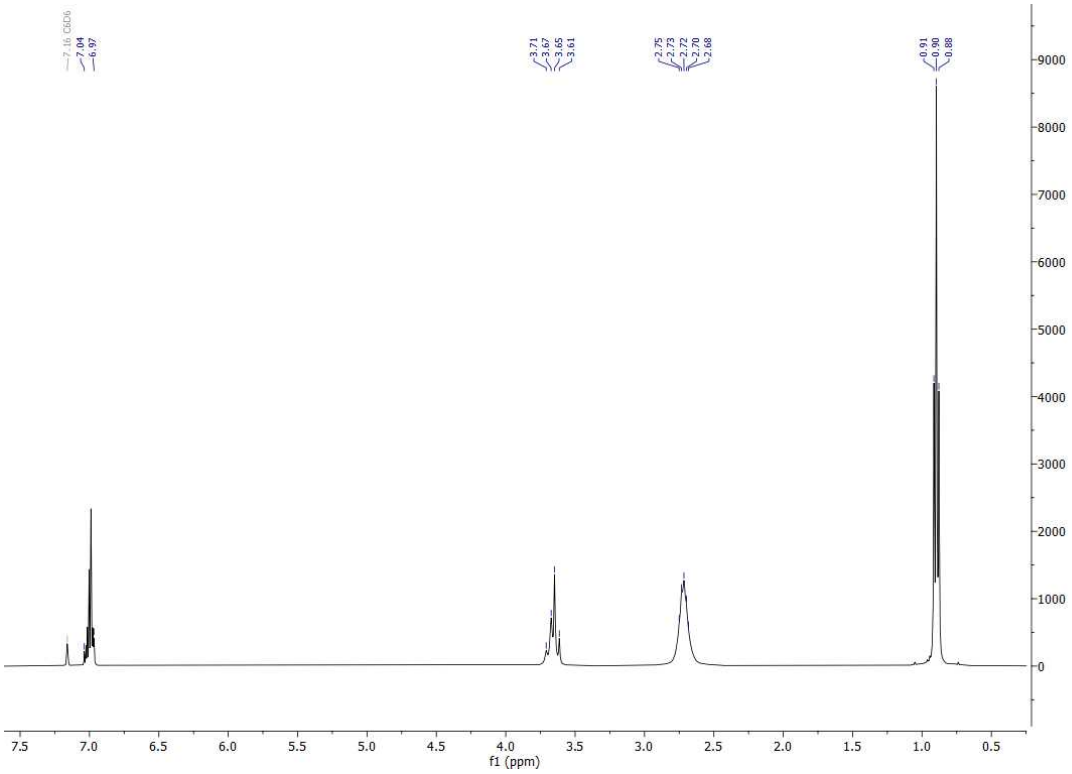


Figure s5. ^{1}H NMR spectrum of **1**-Sn_2 measured in benzene-d_6 at 298 K.

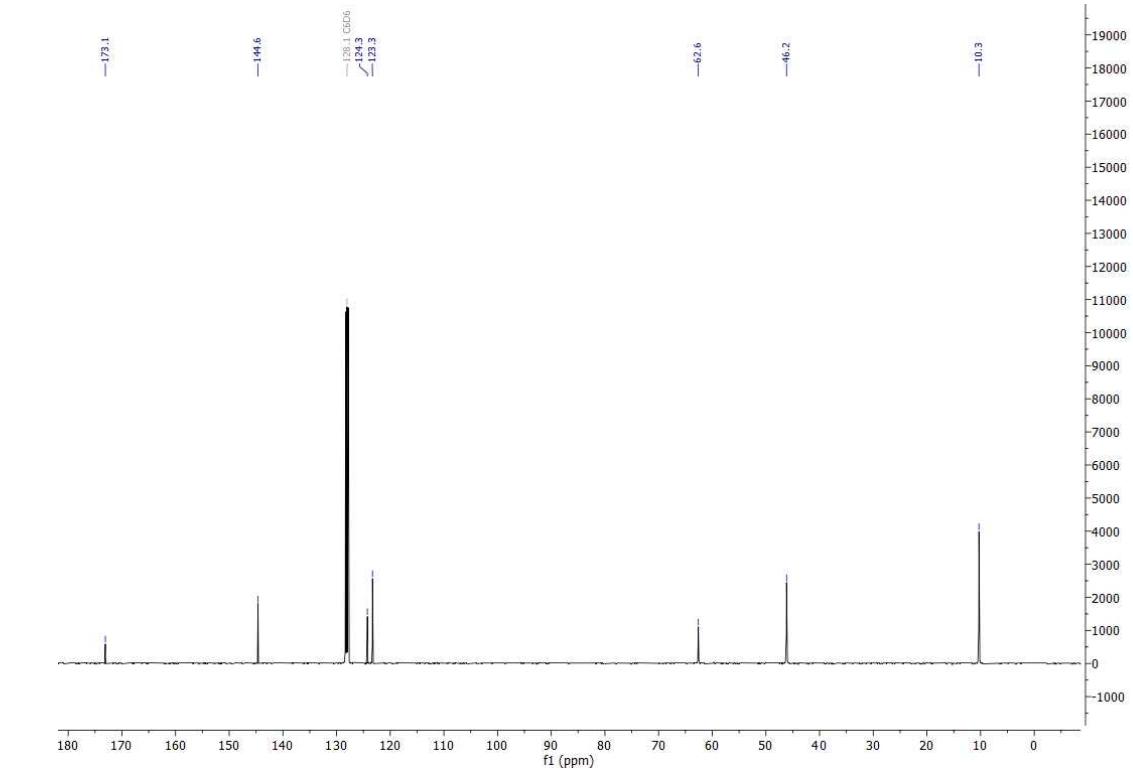


Figure s6. ^{13}C NMR spectrum of **1**-Sn_2 measured in benzene-d_6 at 298 K.

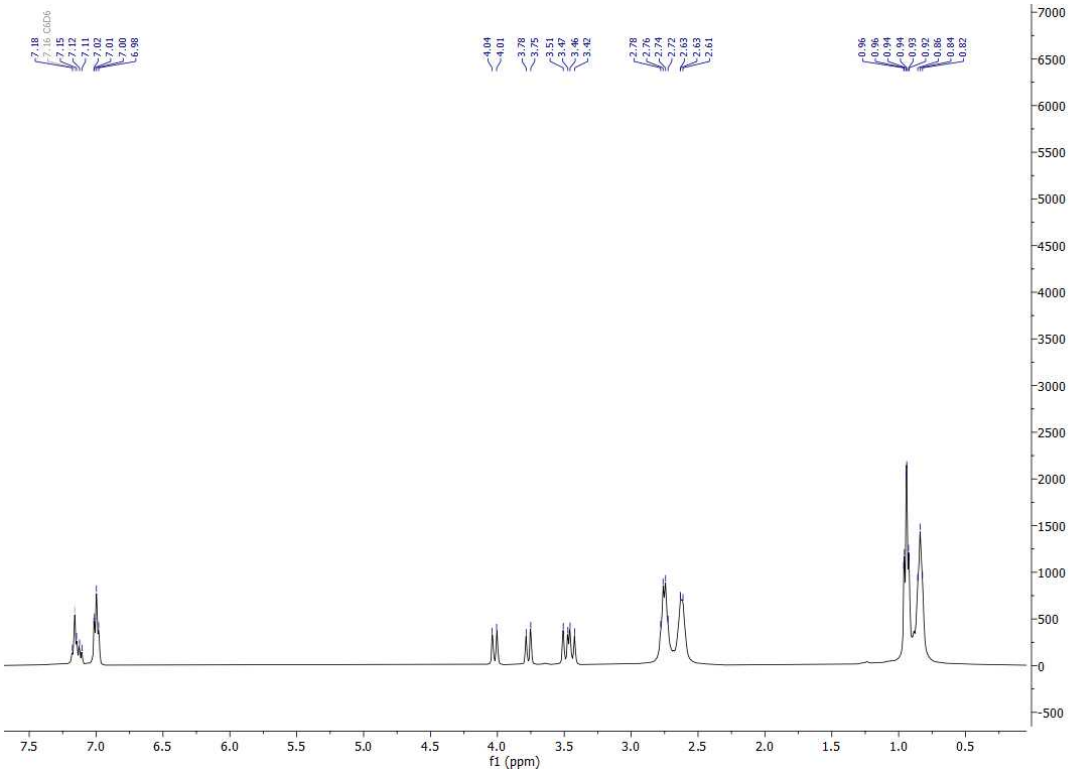


Figure s7. ^{1}H NMR spectrum of **2**-Sn_2 measured in benzene-d_6 at 298 K.

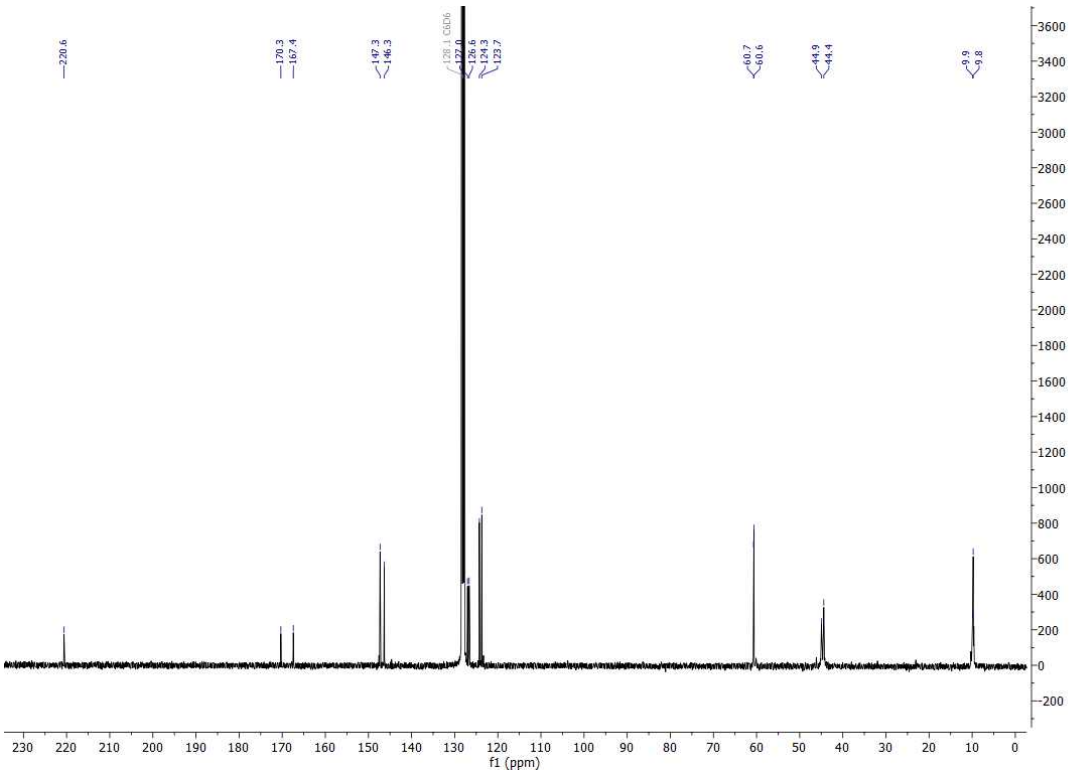


Figure s8. ^{13}C NMR spectrum of **2**-Sn_2 measured in benzene-d_6 at 298 K.

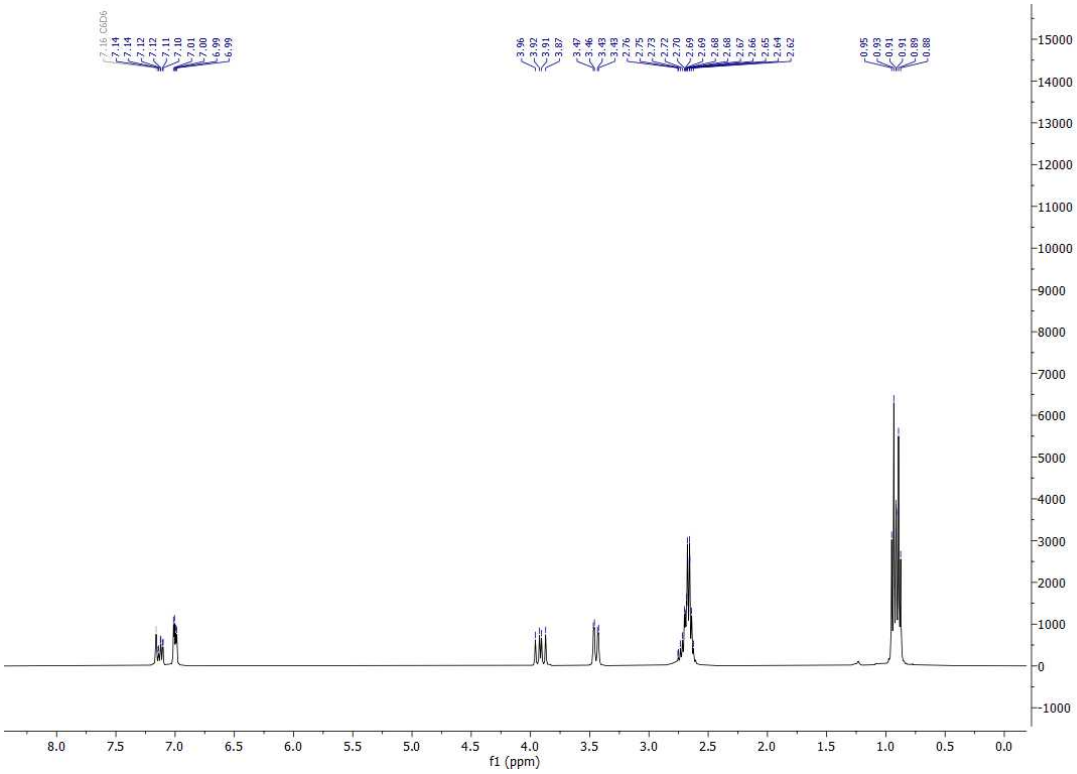


Figure s9. ^{1}H NMR spectrum of **2**-Ge_2 measured in benzene-d_6 at 298 K.

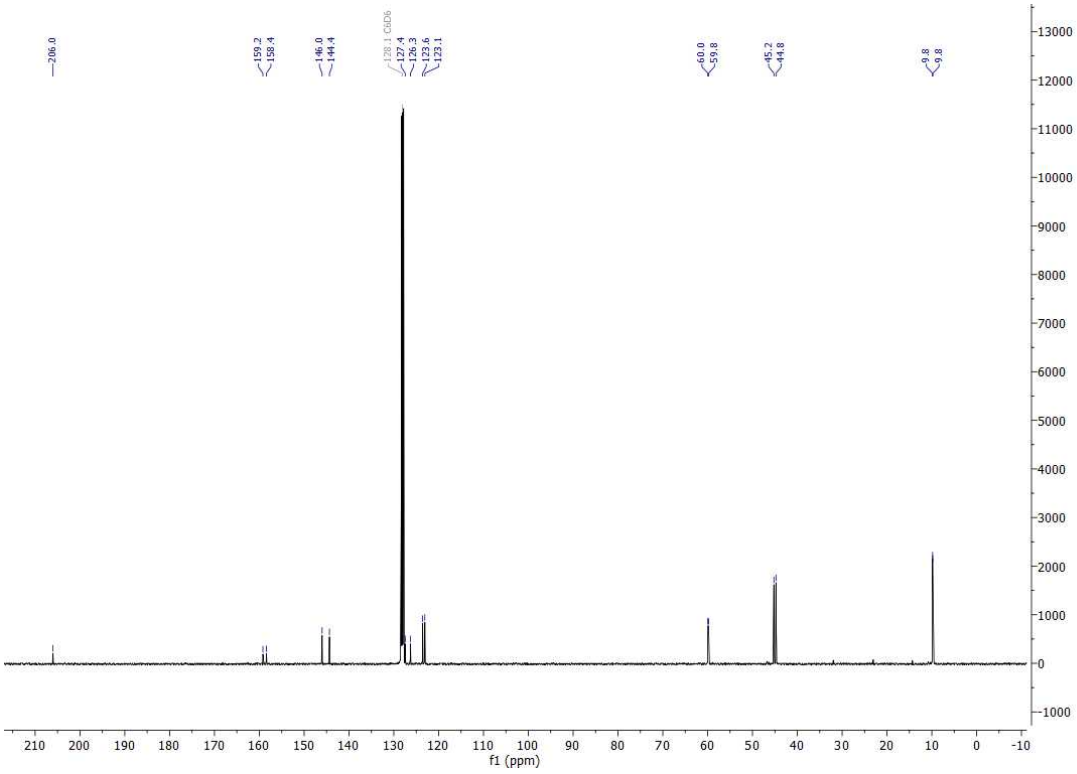


Figure s10. ^{13}C NMR spectrum of **2**-Ge_2 measured in benzene-d_6 at 298 K.

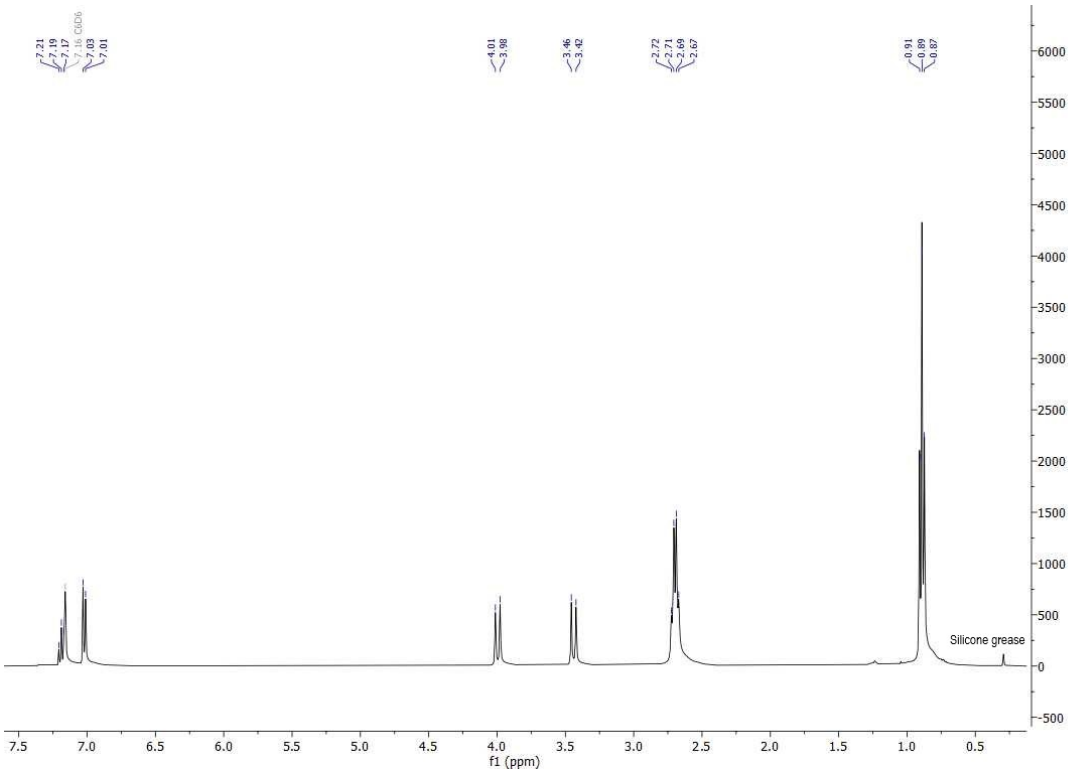


Figure s11. ^{1}H NMR spectrum of **3**-Sn_2 measured in benzene-d_6 at 298 K. Silicone grease impurity has been labelled.

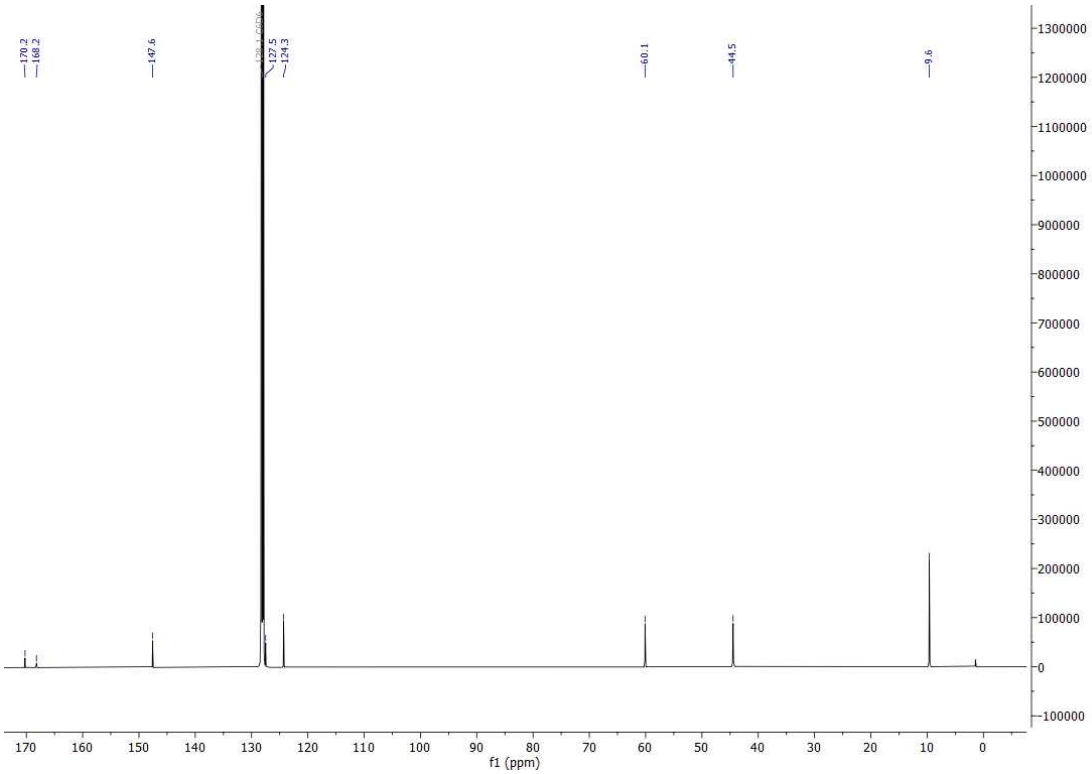


Figure s12. ^{13}C NMR spectrum of **3**-Sn_2 measured in benzene-d_6 at 298 K.

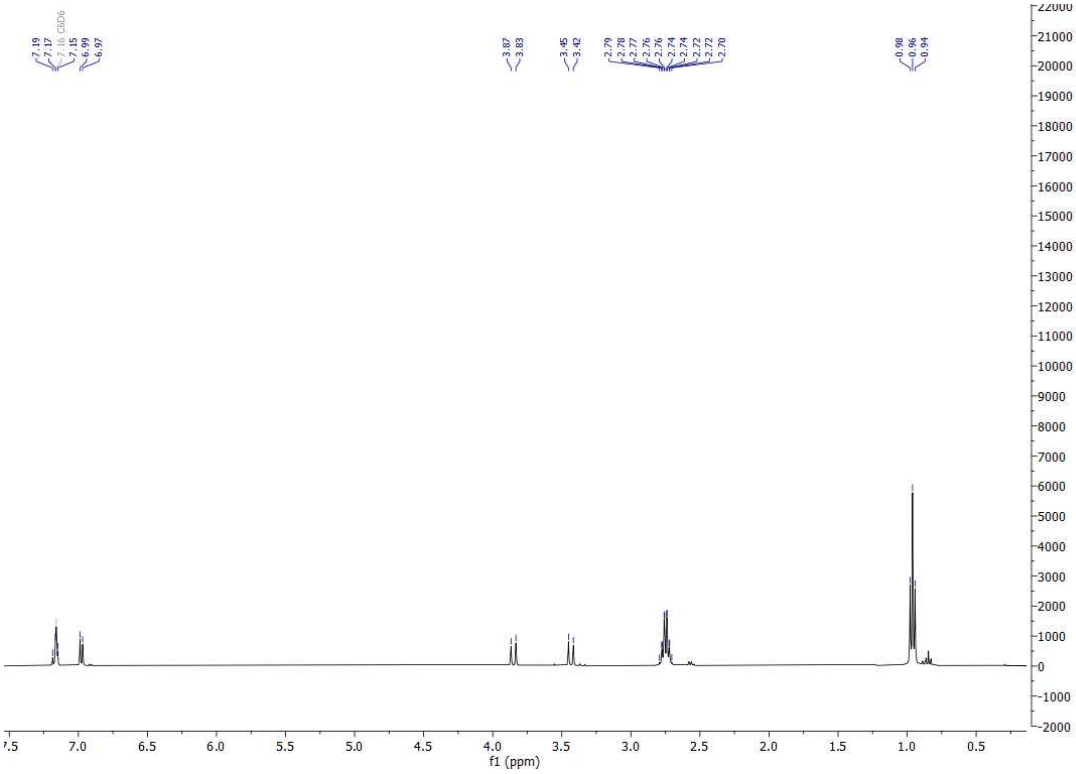


Figure s13. *In situ* ^{1}H NMR spectrum of **3**-Ge_2 measured in benzene-d_6 at 298 K.

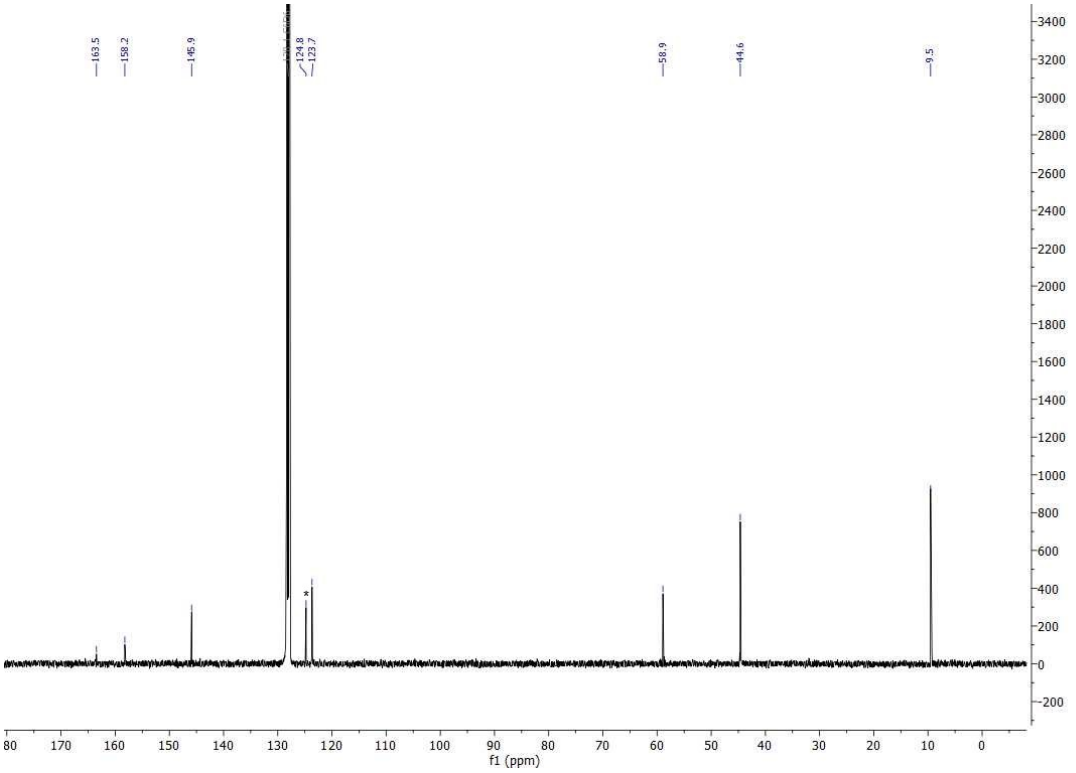


Figure s14. *In situ* ^{13}C NMR spectrum of **3**-Ge_2 measured in benzene-d_6 at 298 K. Resonance marked with * is for C-centre of CO_2.

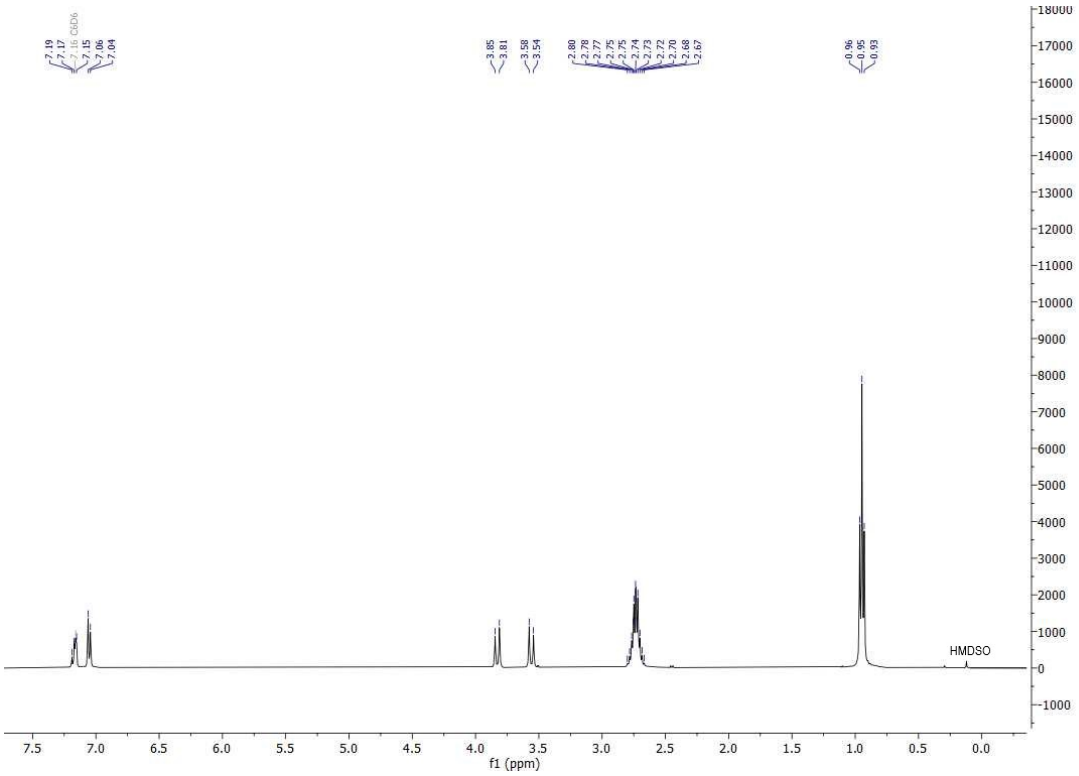


Figure s15. ^{1}H NMR spectrum of **4**-Sn_2 measured in benzene-d_6 at 298 K. Hexamethyldisiloxane impurity has been labelled.

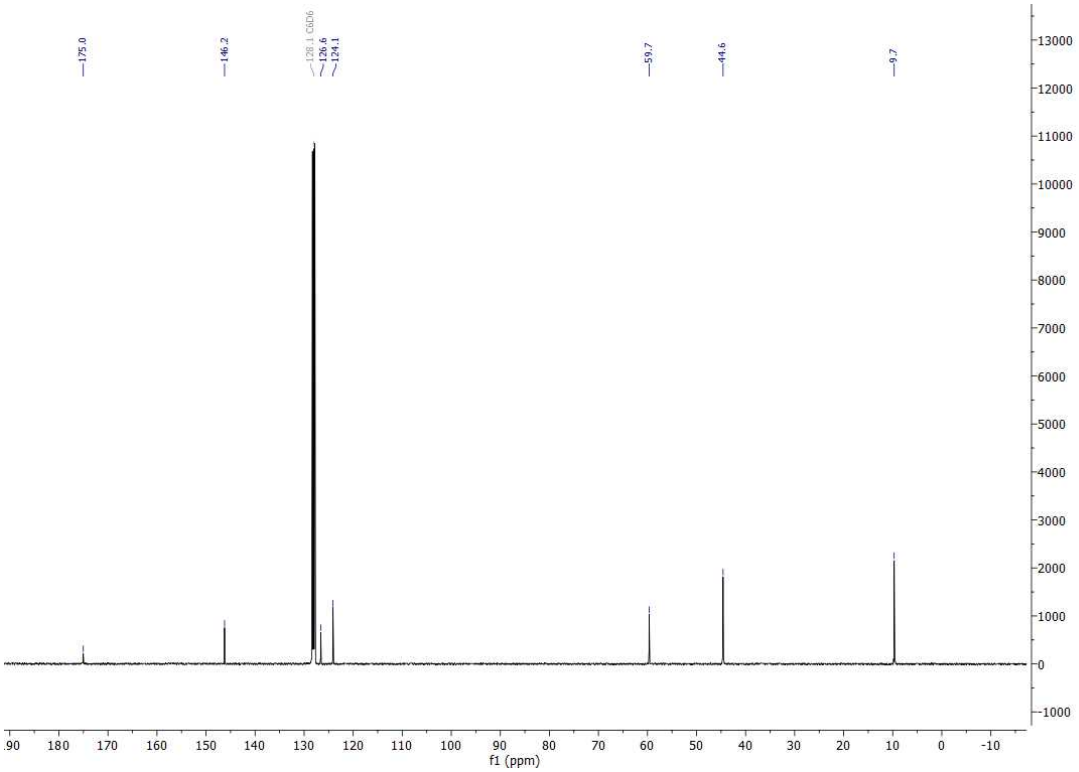


Figure s16. ^{13}C NMR spectrum of **4**-Sn_2 measured in benzene-d_6 at 298 K.

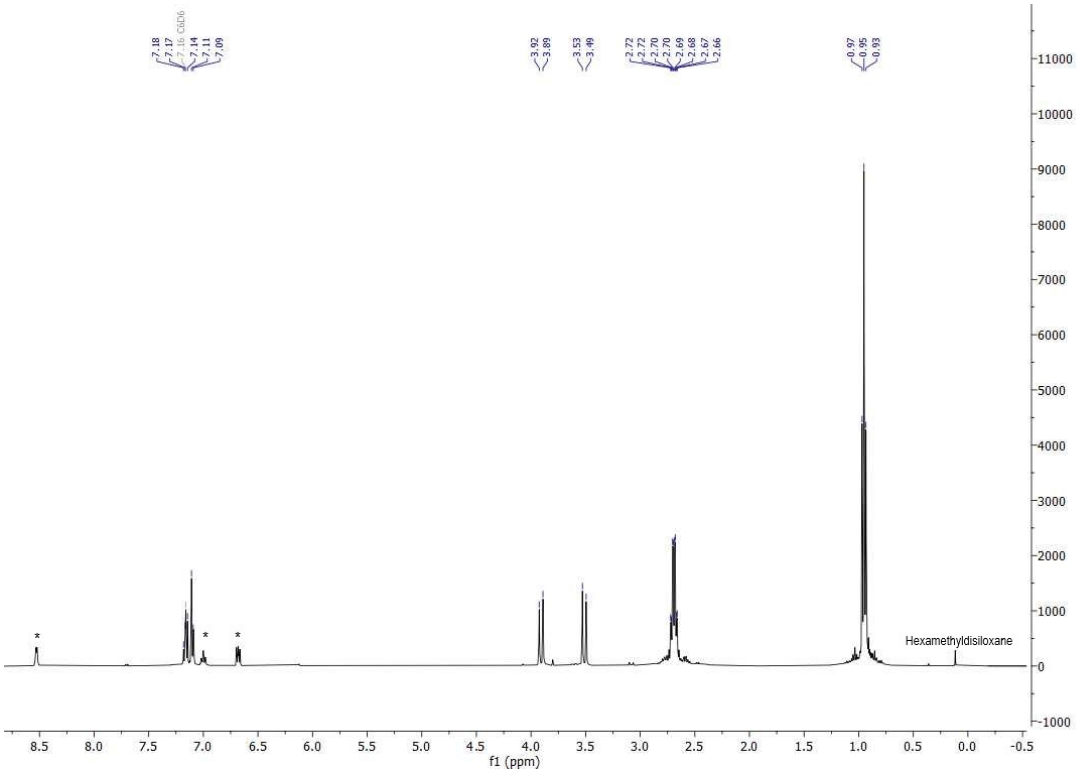


Figure s17. *In situ* ^{1}H NMR spectrum of **4**-Ge_2, generated from the reaction of **1**-Ge_2 and pyridine-N-oxide, measured in benzene-d_6 at 298 K. Hexamethyldisiloxane impurity has been labelled, resonances for pyridine by-product are marked with *.

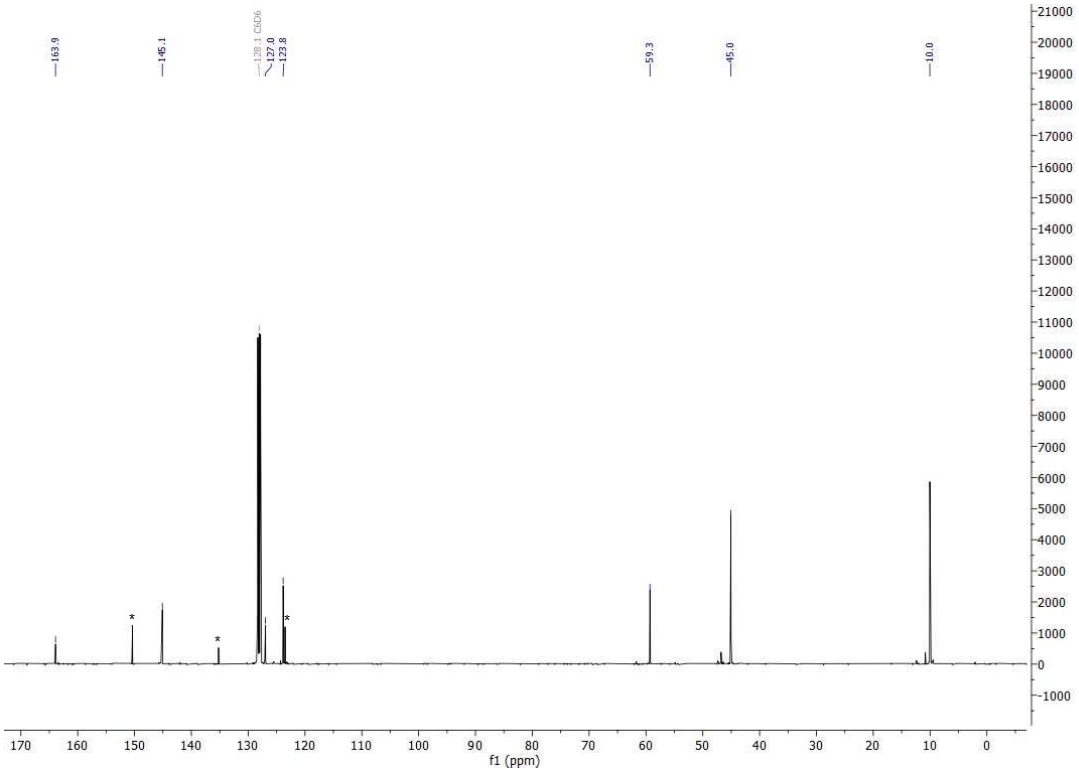


Figure s18. *In situ* ^{13}C NMR spectrum of **4**-Ge_2, generated from the reaction of **1**-Ge_2 and pyridine-N-oxide, measured in benzene-d_6 at 298 K. Resonances for pyridine by-product are marked with *.

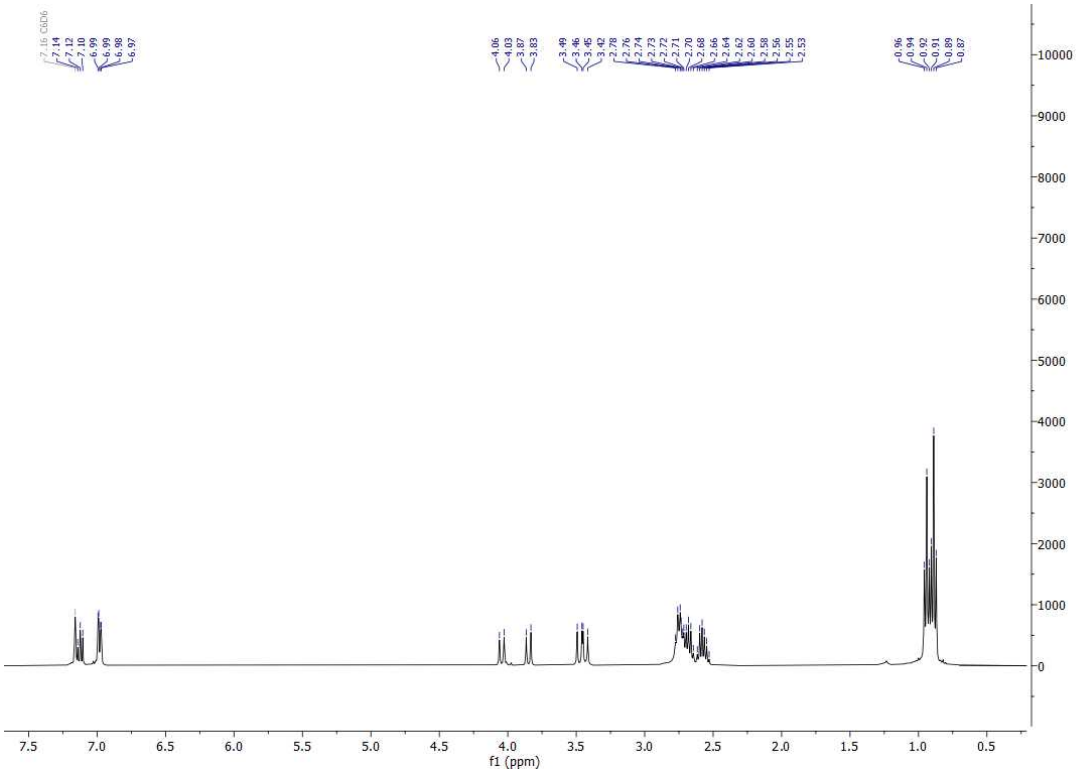


Figure s19. *In situ* ^{1}H NMR spectrum of **2**-GeSn, generated from the reaction of **2**-Ge_2 and **2**-Sn_2, measured in benzene-d_6 at 298 K.

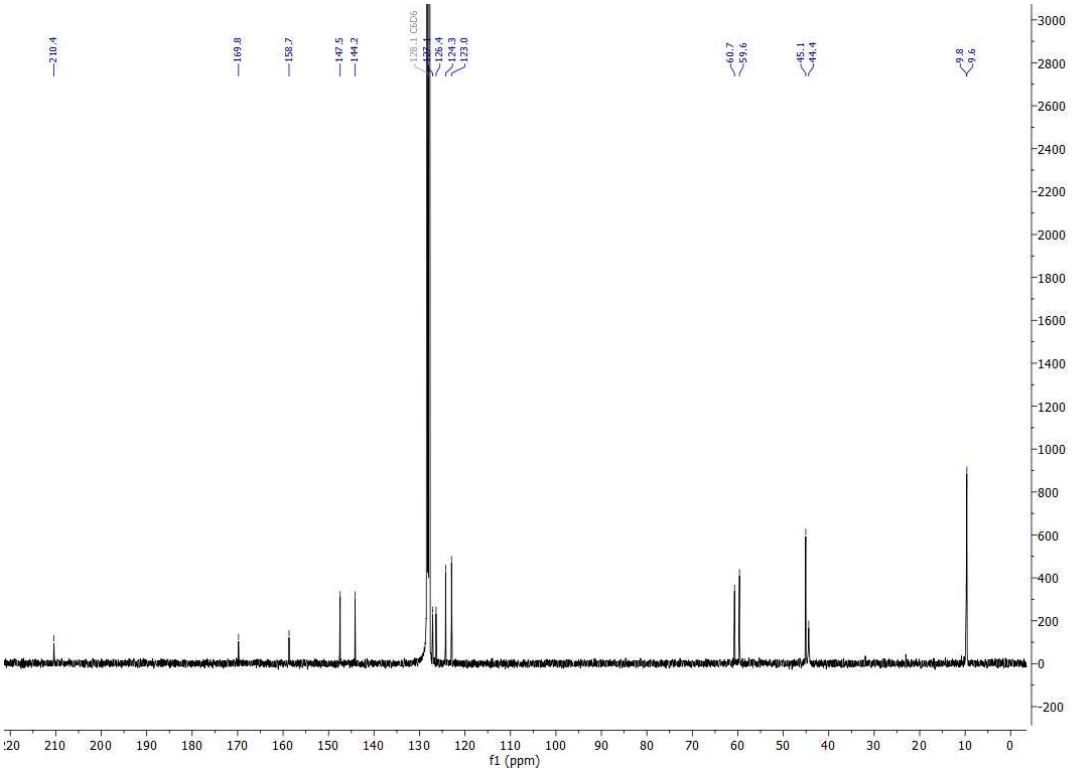


Figure s20. *In situ* ^{13}C NMR spectrum of **2**-GeSn, generated from the reaction of **2**-Ge_2 and **2**-$Sn)_2$, measured in benzene-d_6 at 298 K.

(v) Crystallographic details

Single-crystal X-ray diffraction data for all compounds were collected at 150 K on an Oxford Diffraction/Agilent SuperNova diffractometer using Cu-K_α radiation (λ = 1.54184 Å) or Mo-K_α (λ = 0.71073 Å), and equipped with a nitrogen gas Oxford Cryosystems cooling unit.[s4] Raw frame data were reduced using CrysAlisPro.[s5] The structures were solved using SHELXT[s6] and refined to convergence on F^2 by full-matrix least-squares using SHELXL[s7] in combination with OLEX2.[s8] Distances and angles were calculated using the full covariance matrix. Restraints were used to maintain sensible geometries for the disordered groups and approximate the displacement parameters to typical values. Selected crystallographic data are summarized in Table s1 and full details are given in the supplementary deposited CIF files (CCDC 2129770-2129777). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Table s1. Selected X-ray data collection and refinement parameters

	$Ar^{NEt2}SnCl$	$Ar^{NEt2}SnI$	**1**-Sn_2
Formula	$C_{16}H_{27}ClN_2Sn$	$C_{16}H_{27}IN_2Sn$	$C_{32}H_{54}N_4Sn_2$
Fw (g mol^{-1})	401.53	492.98	732.17
Cell setting	Orthorhombic	Orthorhombic	Monoclinic
Space group	*P n a* 2_1	*P b c a*	C 1 c 1
a (Å)	22.0134(3)	9.6717(2)	10.3809(5)
b (Å)	9.0306(2)	13.5551(2)	18.0521(9)
c (Å)	9.24480(10)	28.5197(6)	18.7802(12)
α (°)	90	90	90
β (°)	90	90	104.894(5)
γ (°)	90	90	90
V (Å^3)	1837.81(5)	3738.96(12)	3401.1(3)
Z	4	8	4
ρ_{calc} (g cm^{-3})	1.451	1.752	1.430
Radiation, λ (Å)	Cu K_α 1.54184	Mo K_α 0.71073	Cu K_α 1.54184
μ (mm^{-1})	12.328	3.013	11.855
Reflections collected	15437	28539	10660
Independent reflections	3258	4553	5397
$R_{(int)}$	0.0333	0.0463	0.0644
Parameters	185	185	351
R_1 (all data/$I > 2\sigma(I)$)	0.0271/0.0250	0.0527/0.0320	0.0884/0.0812
ωR_2 (all data/$I > 2\sigma(I)$)	0.0691/0.0672	0.0644/0.0565	0.2175/0.2027
GooF	1.080	1.044	1.074
T/K	150.00(10)	150.01(10)	150.01(10)
CCDC Deposition No.	2129770	2129776	2129774

Table s1 (cont). Selected X-ray data collection and refinement parameters

	2-Sn_2	**2**-Ge_2	**3**-Sn_2
Formula	$C_{33}H_{54}N_4O_2Sn_2$	$C_{33}H_{54}Ge_2N_4O_2$	$C_{33}H_{54}N_4O_3Sn_2$
Fw (g mol^{-1})	776.18	683.98	792.18
Cell setting	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1	*P* $2_1/n$	*P* $2_1/c$
a (Å)	8.4813(4)	10.9547(3)	10.31300(10)
b (Å)	11.7017(5)	18.2949(5)	36.5163(2)
c (Å)	18.4993(9)	17.8483(5)	19.35910(10)
α (°)	87.138(4)	90	90
β (°)	79.785(4)	107.229(3)	93.4930(10)
γ (°)	78.212(4)	90	90
V ($Å^3$)	1768.59(15)	3416.56(17)	7276.95(9)
Z	2	4	8
ρ_{calc} (g cm^{-3})	1.458	1.330	1.446
Radiation, λ (Å)	Cu K_α 1.54184	Cu K_α 1.54184	Cu K_α 1.54184
μ (mm^{-1})	11.478	2.421	11.192
Reflections collected	17327	22552	53833
Independent reflections	7315	7083	15042
$R_{(int)}$	0.0568	0.0381	0.0523
Parameters	378	397	773
R_1 (all data/$I > 2\sigma(I)$)	0.0496/0.0432	0.0490/0.0450	0.0394/0.0309
ωR_2 (all data/$I > 2\sigma(I)$)	0.1158/0.1090	0.1175/0.1143	0.0752/0.0709
GooF	1.050	1.126	1.018
T/K	150.00(10)	150.00(10)	150.0(2)
CCDC Deposition No.	2129772	2129771	2129777

Table s1 (cont). Selected X-ray data collection and refinement parameters

	4-Sn_2	**2**-GeSn
Formula	$C_{32}H_{54}N_4OSn_2$	$C_{33}H_{54}GeN_4O_2Sn$
Fw (g mol^{-1})	748.17	730.08
Cell setting	Orthorhombic	Triclinic
Space group	$P\,2_1\,2_1\,2_1$	P -1
a (Å)	10.96710(10)	8.5331(3)
b (Å)	16.1827(2)	11.7151(4)
c (Å)	19.4843(2)	18.3397(5)
α (°)	90	85.292(2)
β (°)	90	78.772(2)
γ (°)	90	76.746(3)
V ($Å^3$)	3458.02(6)	1749.01(10)
Z	4	2
ρ_{calc} (g cm^{-3})	1.437	1.386
Radiation, λ (Å)	Cu K_α 1.54184	Cu K_α 1.54184
μ (mm^{-1})	11.695	6.986
Reflections collected	20582	43357
Independent reflections	7231	7259
$R_{(int)}$	0.0415	0.0859
Parameters	360	378
R_1 (all data/$I > 2\sigma(I)$)	0.0368/0.0313	0.0586/0.0461
ωR_2 (all data/$I > 2\sigma(I)$)	0.0738/0.0700	0.1243/0.1135
GooF	1.038	1.016
T/K	150.01(10)	150.01(10)
CCDC Deposition No.	2129775	2129773

(vi) References

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