Electronic Supplementary Material (ESI) for Dalton Transactions.

Bulky Arene-Bridged Bis(amide) and Bis(amidinate) Complexes of Germanium(II) and Tin(II)

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Supplementary Information (31 pages)

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1. Experimental

General considerations.

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Diethyl ether was distilled over Na/K alloy (50:50), while hexane, toluene and THF were distilled over molten potassium. Dichloromethane was distilled over CaH_2. ^{1}H, ^{13}C{^{1}H}and ^{29}Si{^{1}H} NMR spectra were recorded on either Bruker Avance III 400 or Bruker Avance III 600 spectrometers and were referenced to the resonances of the solvent used or external $SiMe_4$. The chemical shifts δ are reported in ppm. Mass spectra were collected using an Agilent Technologies 5975D inert MSD with a solid-state probe. FTIR spectra were recorded as Nujol mulls, using an Agilent Cary 630 spectrometer operating in attenuated total reflectance (ATR) or transmission modes, and the wavenumbers ν are reported in cm^{-1}. Microanalyses were carried out at the Science Centre, London Metropolitan University or using a PerkinElmer- 2400 CHNS/O Series II System. Melting points were determined in sealed glass capillaries under dinitrogen, and are uncorrected. The starting materials C(=NDip)$_2$,[1] {ClC(Bu^t)=N}$_2$(μ-C_6H_4),[2] and Ar†NH$_2$[3] were prepared by literature procedures. All other reagents were used as received.

Synthesis of 1,4-{N(H)(SiPr^i$_3$)}$_2$(μ-C_6H_4), L^{1}H$_2$. A solution of *p*-phenylenediamine (2.00 g, 18.5 mmol) in THF (50 mL) was cooled to -80 °C, and LiBu^n (24.3 mL of a 1.6 M solution in hexane, 38.9 mmol) was added to this over 10 minutes. After the addition, the reaction mixture was warmed to room temperature and stirred for 3 hours. To the reaction mixture a solution of Pr^i$_3$SiCl (7.9 mL, 37.0 mmol) in THF (20 mL) was then added at -80 °C. The reaction mixture was warmed to room temperature, stirred for 12 h, filtered, and volatiles removed from the filtrate *in vacuo* to give the title compound as a red-brown coloured powder (3.80 g, 49 %). M.p. 101-104 °C; ^{1}H NMR (400 MHz, C_6D_6, 298 K) δ = 1.10 (d, $^3J_{HH}$ = 6.4 Hz, 36H, CH(C*H*$_3$)$_2$), 1.13-1.20 (m, 6H, C*H*(CH$_3$)$_2$), 2.82 (s, 2H, N*H*), 6.61 (s, 4H, Ar-*H*); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K) δ = 12.9 (*C*H(CH$_3$)$_2$), 18.7 (CH(*C*H$_3$)$_2$), 118.9, 139.6 (Ar-*C*); ^{29}Si{^{1}H} NMR (80 MHz, C_6D_6, 298 K) δ = 4.6; IR ν/cm^{-1} (ATR): 3398 (m, NH), 1605 (w), 1506 (vs), 1013 (s), 994 (s), 883 (vs), 813 (vs), 711 (vs), 657 (vs); acc. mass calc. for $C_{24}H_{49}N_2Si_2$ (MH$^+$): 421.3434; found: 421.3459.

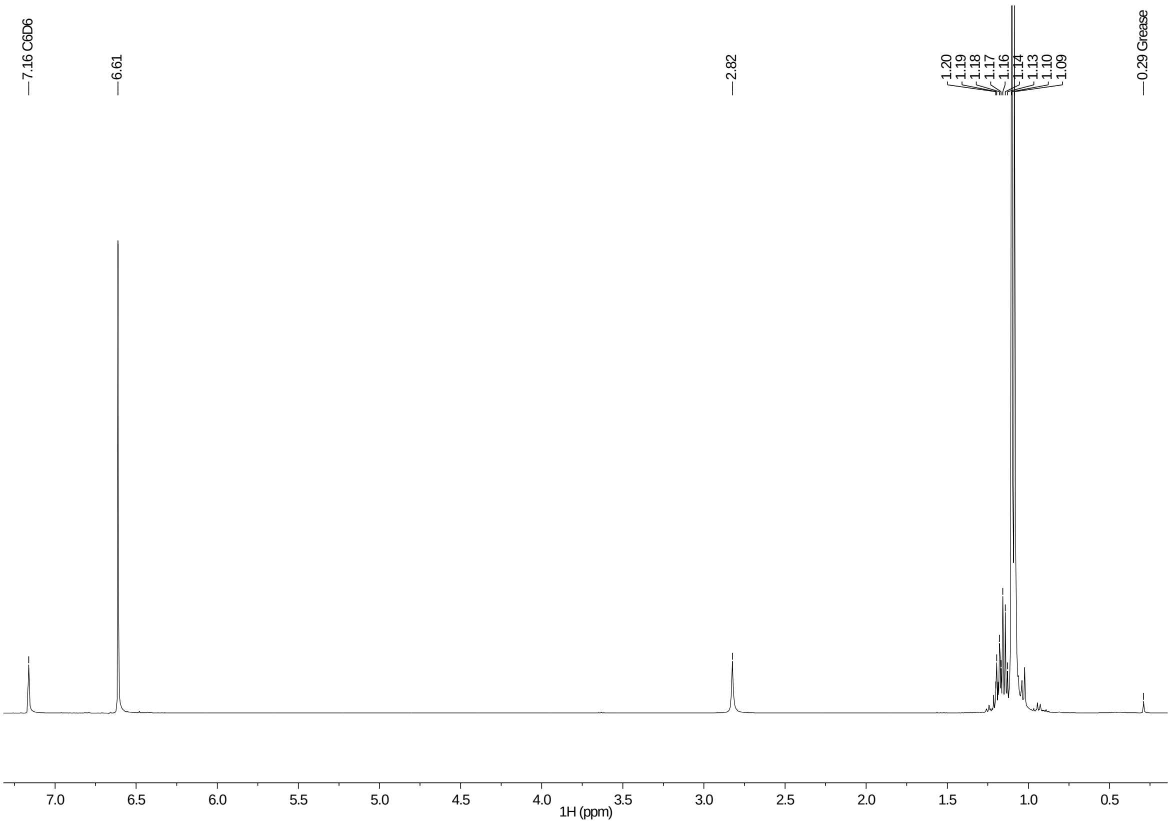

Figure S1. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of L^1H_2.

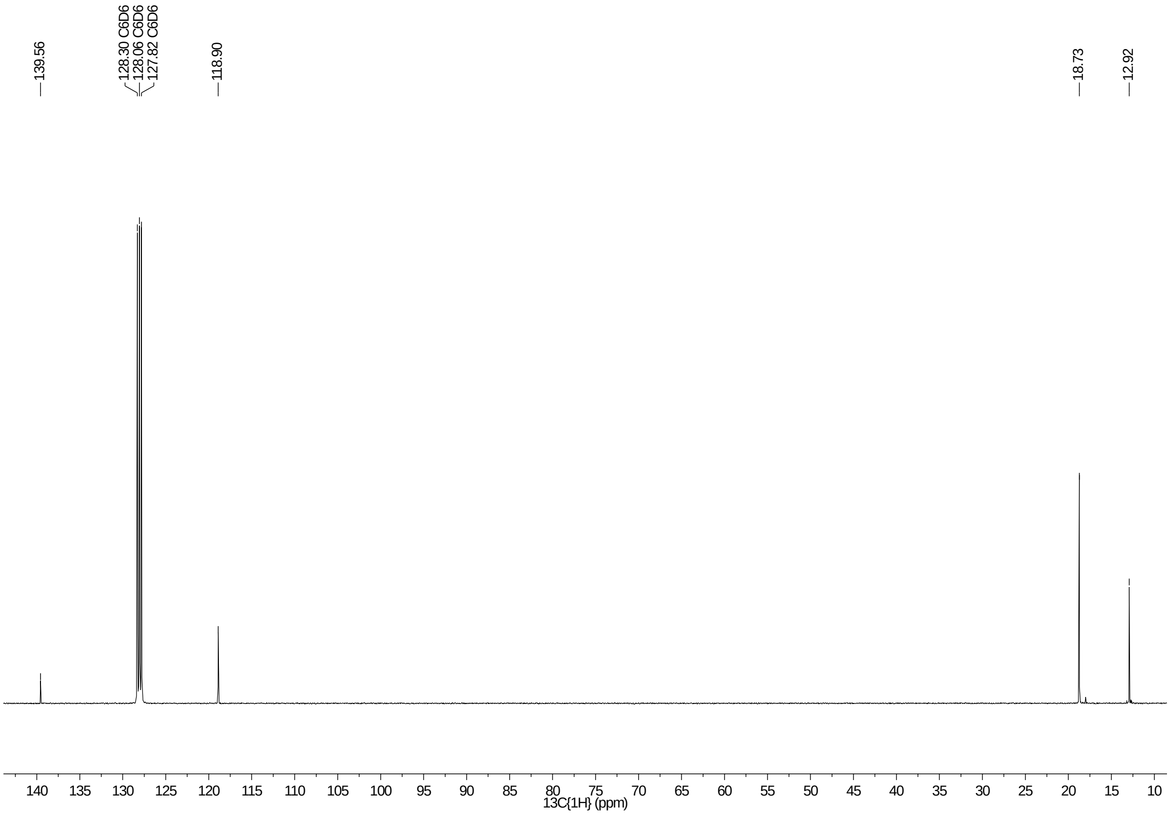

Figure S2. $^{13}C\{^1H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of L^1H_2.

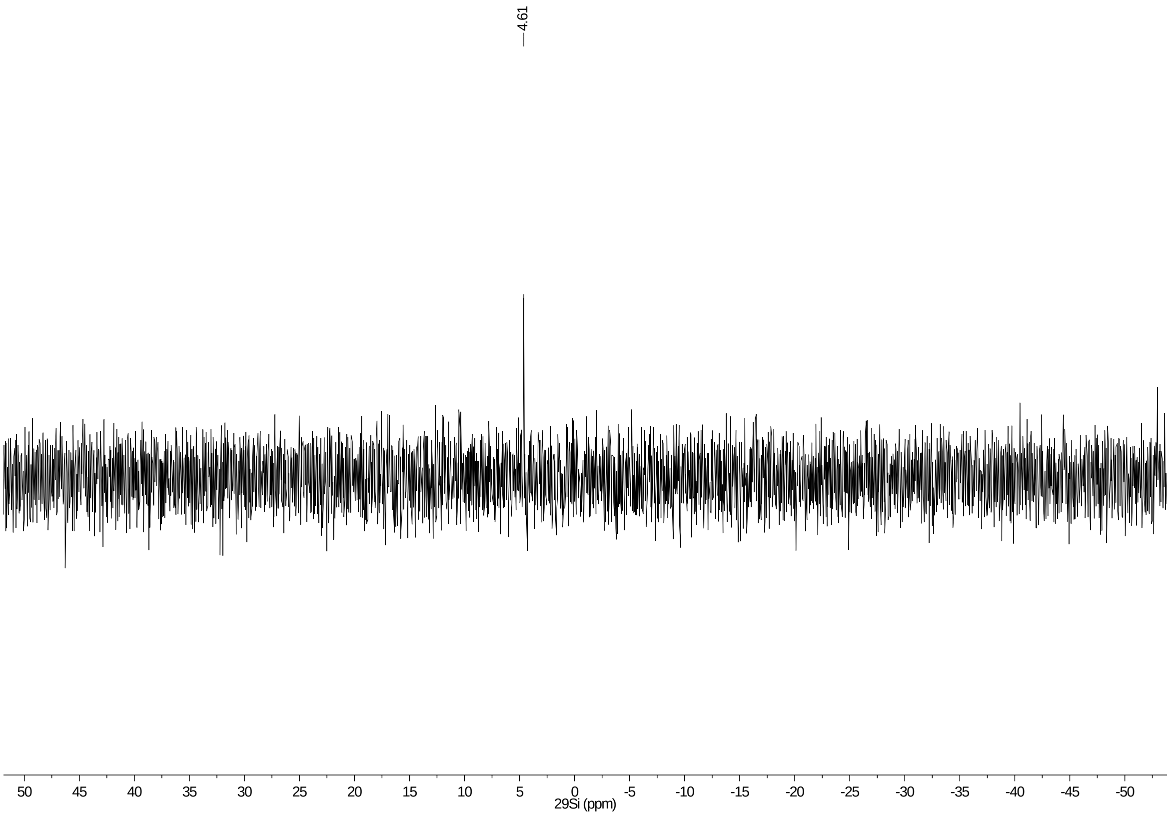

Figure S3. ^{29}Si{^{1}H} NMR spectrum (80 MHz, 298 K, C_6D_6) of L^1H_2.

Synthesis of 1,3-{N(H)(SiPr$^{i}_{3}$)}$_2$(μ-C_6H_4), L^2H_2. A solution of *m*-phenylenediamine (2.00 g, 18.5 mmol) in THF (50 mL) was cooled to -80 °C, and LiBu^{n} (24.3 mL of a 1.6 M solution in hexane, 38.9 mmol) was added to this over 10 minutes. After the addition, the reaction mixture was warmed to room temperature and stirred for 3 hours. To the reaction mixture a solution of Pr$^{i}_{3}$SiCl (7.9 mL, 37.0 mmol) in THF (20 mL) was then added at -80 °C. The reaction mixture was warmed to room temperature, stirred for 12 h, filtered, and volatiles removed from the filtrate *in vacuo* to give the title compound as a brown oil (4.10 g, 53 %). ^{1}H NMR (400 MHz, C_6D_6, 298 K) δ = 1.11 (d, $^{3}J_{HH}$ = 7.1 Hz, 36H, CH(C*H*$_3$)$_2$), 1.19-1.26 (m, 6H, C*H*(CH$_3$)$_2$), 3.01 (s, 2H, N*H*), 6.05 (s, 1H, Ar-*H*), 6.23 (d, $^{3}J_{HH}$ = 7.9 Hz, 2H, Ar-*H*), 7.02 (t, $^{3}J_{HH}$ = 7.9 Hz, 1H, Ar-*H*); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K) δ = 13.1 (*C*H(CH$_3$)$_2$), 18.7 (CH(*C*H$_3$)$_2$), 106.3, 108.0, 130.2, 149.1 (Ar-*C*); ^{29}Si{^{1}H} NMR (80 MHz, C_6D_6, 298 K) δ = 5.1; IR ν/cm^{-1} (ATR): 3402 (br w, NH), 1606 (vs), 1589 (m), 1164 (m), 1072 (m), 993 (vs), 920 (m), 882 (vs), 826 (m), 758 (m), 732 (w), 709 (w), 677 (vs); acc. mass calc. for $C_{24}H_{49}N_2Si_2$ (MH^{+}): 421.3434; found: 421.3445.

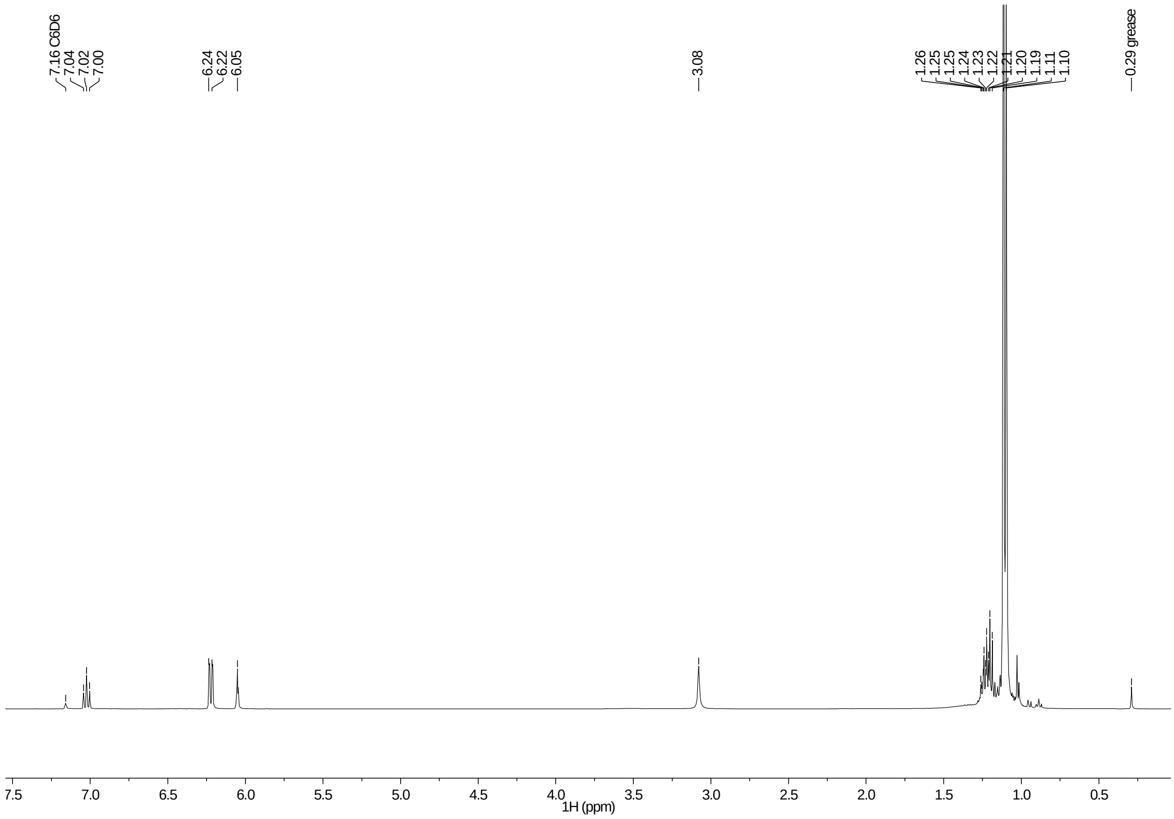

Figure S4. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of L^2H_2.

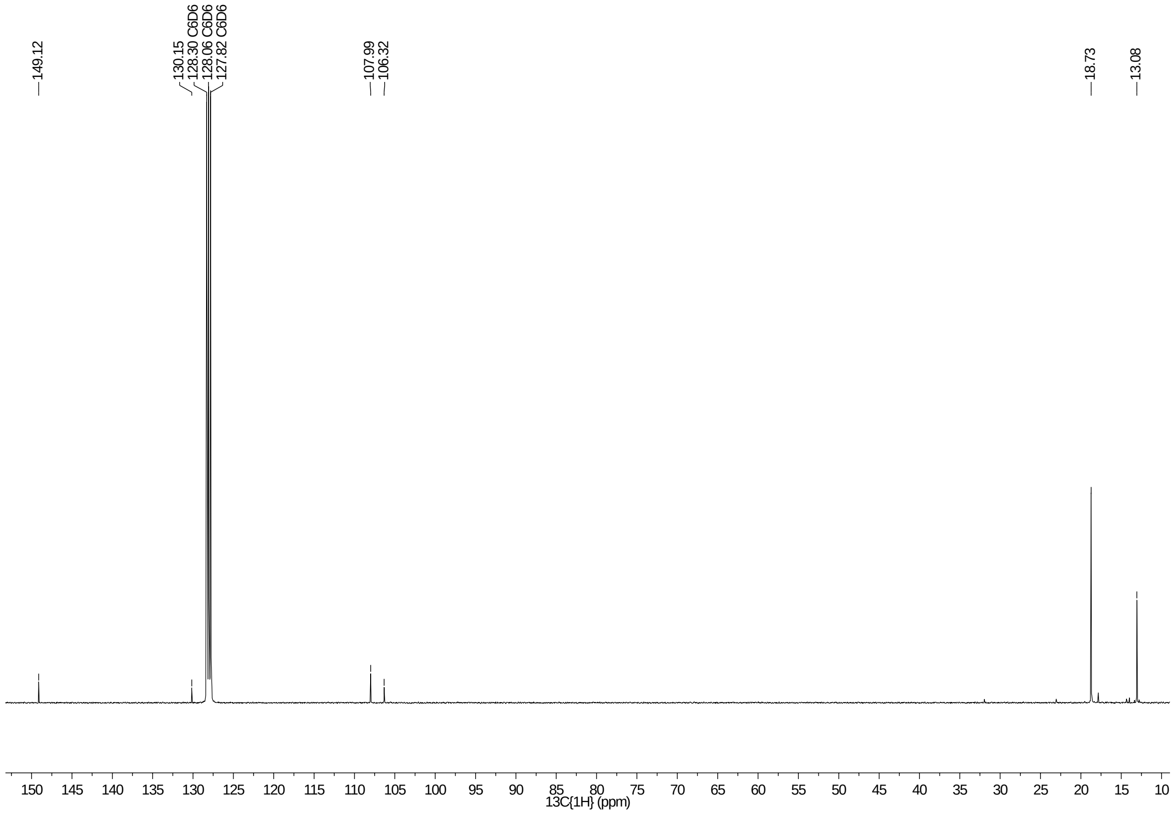

Figure S5. $^{13}C\{^1H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of L^2H_2.

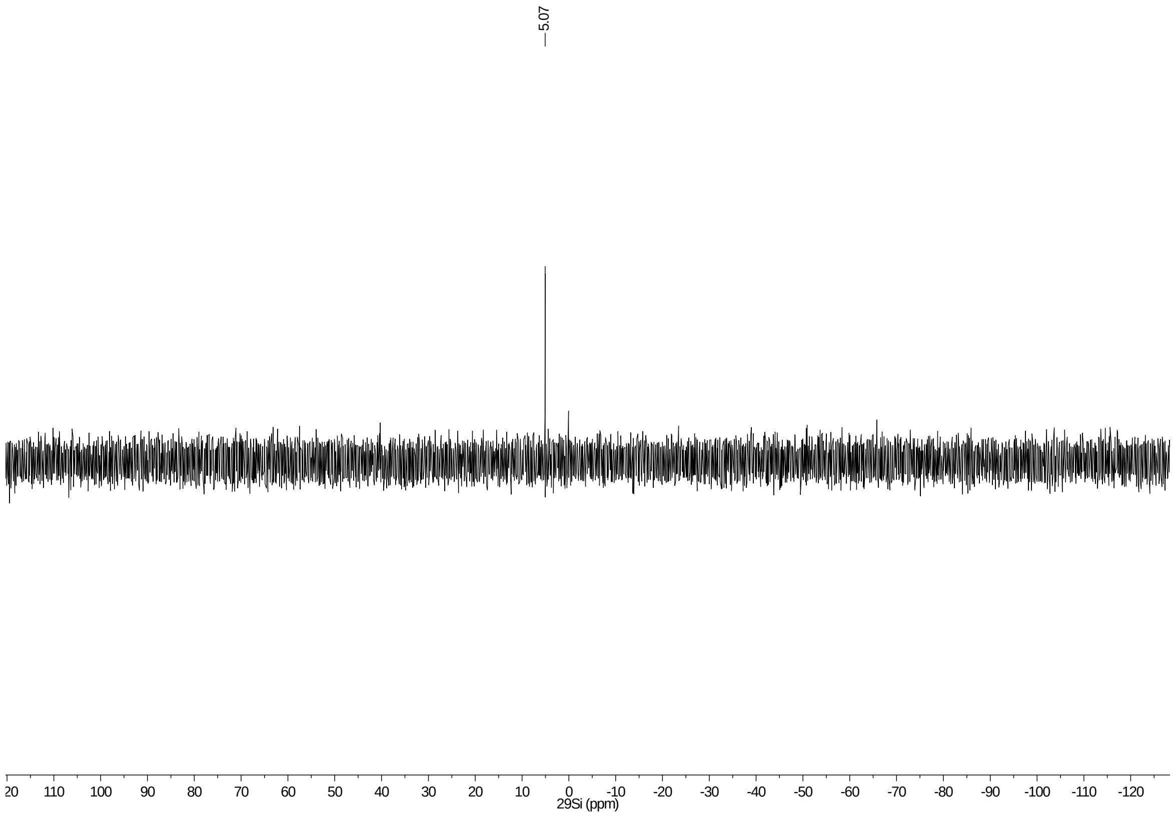

Figure S6. $^{29}Si\{^1H\}$ NMR spectrum (80 MHz, 298 K, C_6D_6) of L^2H_2.

Synthesis of 1,4-$\{N(H)(SiMe_2Ph)\}_2(\mu\text{-}C_6H_4)$. A solution of *p*-phenylenediamine (2.00 g, 18.5 mmol) in THF (50 mL) was cooled to -80 °C, and LiBu^n (24.3 mL of a 1.6 M solution in hexane, 38.9 mmol) was added to this over 10 minutes. After the addition, the reaction mixture was warmed to room temperature and stirred for 3 hours. To the reaction mixture a solution of $PhMe_2SiCl$ (6.2 mL, 37.01 mmol) in THF (20 mL) was then added at -80 °C. The reaction mixture was warmed to room temperature, stirred for 12 h, filtered, and volatiles removed from the filtrate *in vacuo*. The residue was extracted into hexane (30 mL), the extract concentrated to *ca.* 20 mL *in vacuo* and stored overnight at -30 °C to give the title compound as a dark red microcrystalline material (3.60 g, 52 %). M.p. 198-200 °C; ^1H NMR (400 MHz, C_6D_6, 298 K) $\delta = 0.31$ (s, 12H, CH_3), 3.00 (s, 2H, N*H*), 6.45 (s, 4H, Ar-*H*), 7.18-7.20 (m, 6H, Ar-*H*), 7.56-7.59 (m, 4H, Ar-*H*); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K) $\delta = -1.1$ (CH_3), 118.2, 129.6, 133.4, 134.1, 138.8, 139.2 (Ar-*C*); $^{29}Si\{^1H\}$ NMR (80 MHz, C_6D_6, 298 K) $\delta = -1.2$; IR ν/cm^{-1} (ATR): 3305 (br w, NH), 1597 (m), 1499 (m), 1044 (s), 826 (vs), 784 (vs), 723 (s), 696 (s); acc. mass calc. for $C_{22}H_{29}N_2Si_2$ (MH^+): 377.1869; found: 377.1873.

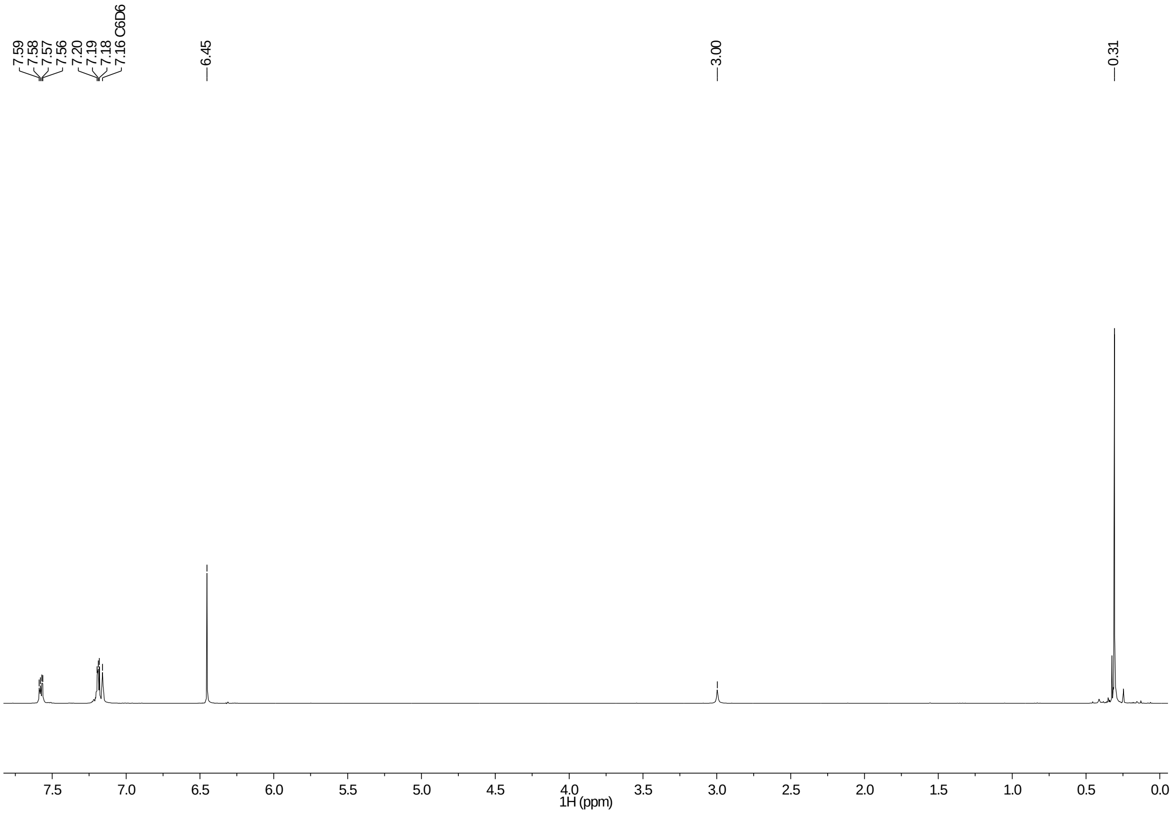

Figure S7. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of 1,4-{N(H)(SiMe$_2$Ph)}$_2$(μ-C_6H_4).

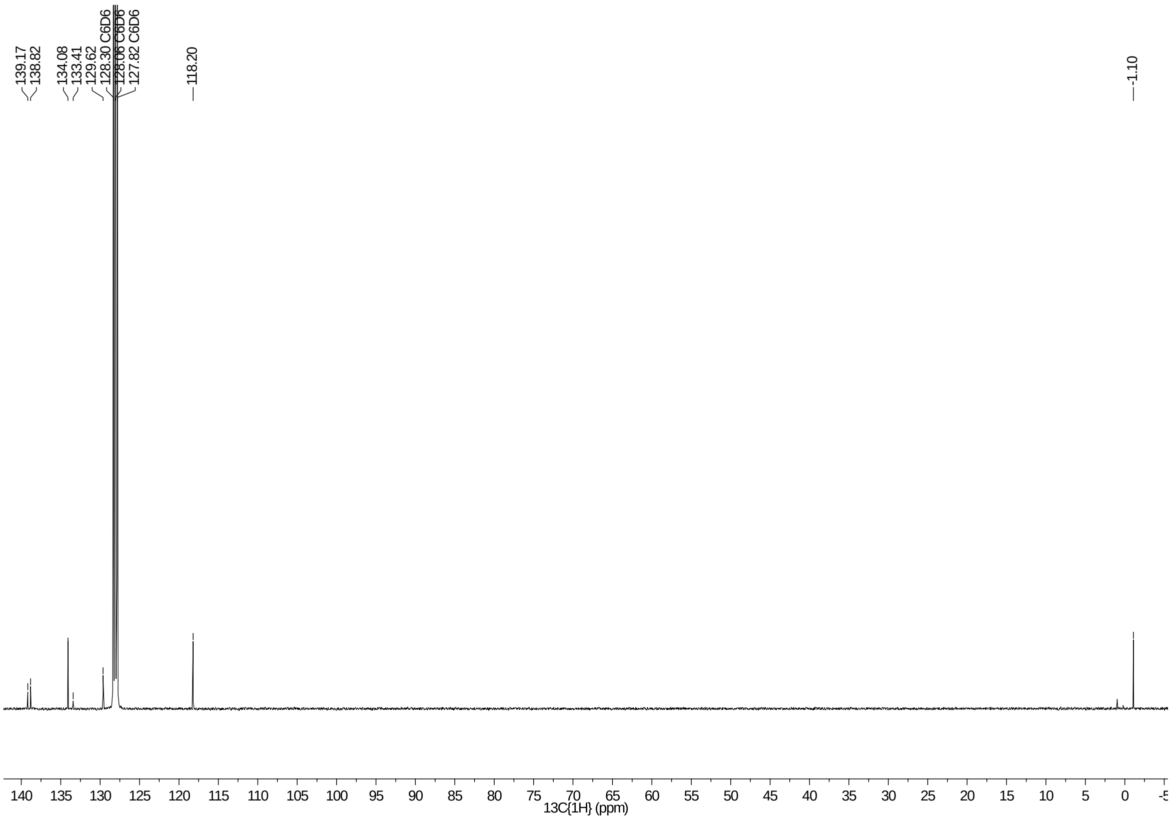

Figure S8. ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K, C_6D_6) of 1,4-{N(H)(SiMe$_2$Ph)}$_2$(μ-C_6H_4).

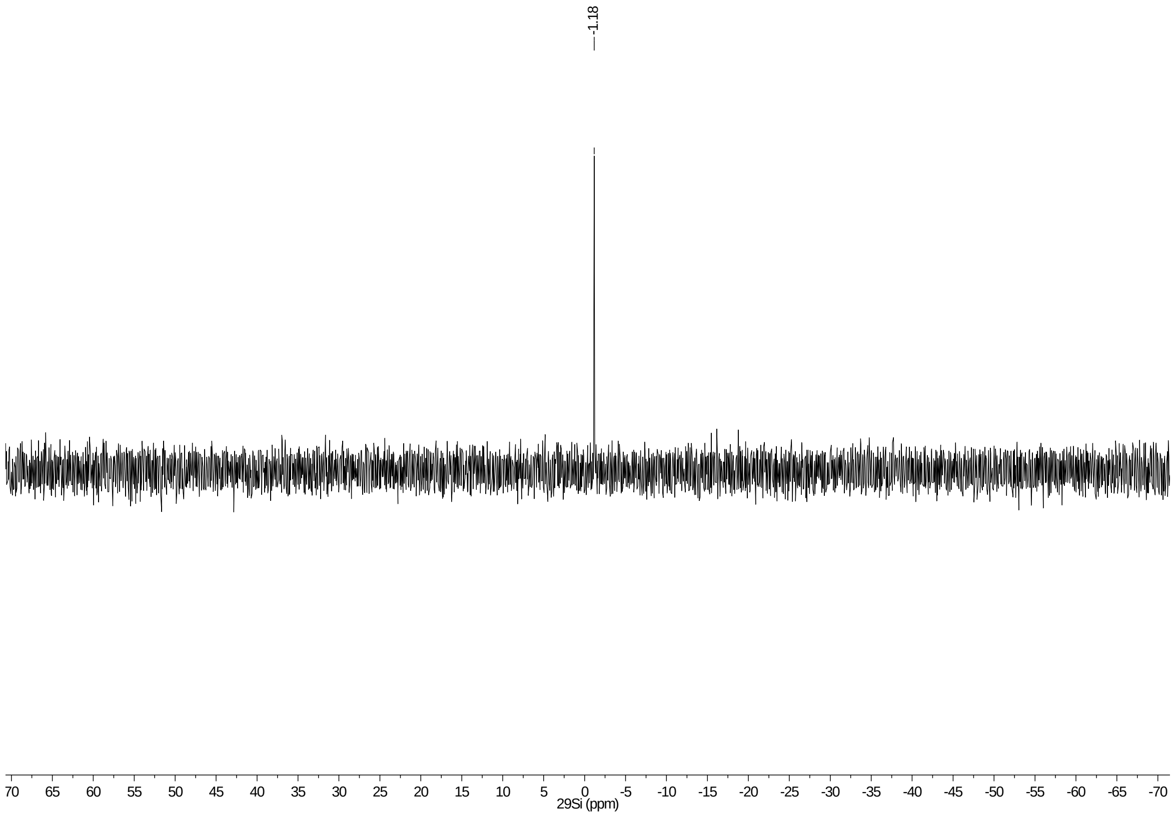

Figure S9. $^{29}Si\{^1H\}$ NMR spectrum (80 MHz, 298 K, C_6D_6) of 1,4-$\{N(H)(SiMe_2Ph)\}_2(\mu\text{-}C_6H_4)$.

Synthesis of 1,3-$\{N(H)(SiMe_2Ph)\}_2(\mu\text{-}C_6H_4)$. A solution of *p*-phenylenediamine (2.00 g, 18.5 mmol) in THF (50 mL) was cooled to -80 °C, and LiBu^n (24.3 mL of a 1.6 M solution in hexane, 38.9 mmol) was added to this over 10 minutes. After the addition, the reaction mixture was warmed to room temperature and stirred for 3 hours. To the reaction mixture a solution of $PhMe_2SiCl$ (6.2 mL, 37.01 mmol) in THF (20 mL) was then added at -80 °C. The reaction mixture was warmed to room temperature, stirred for 12 h, filtered, and volatiles removed from the filtrate *in vacuo*. The residue was extracted into hexane (30 mL), the extract concentrated to *ca.* 20 mL *in vacuo* and stored overnight at -30 °C to give the title compound as a dark red crystals (3.20 g, 46 %). M.p. 75-78 °C; ^1H NMR (400 MHz, C_6D_6, 298 K) δ = 0.17 (s, 12H, C*H*$_3$), 3.22 (s, 2H, N*H*), 5.97 (s, 1H, Ar-*H*), 6.05 (d, $^3J_{HH}$ = 7.9 Hz, 2H, Ar-*H*), 6.90 (t, $^3J_{HH}$ = 7.9 Hz, 1H, Ar-*H*), 7.13-7.15 (m, 6H, Ar-*H*), 7.47-7.50 (m, 4H, Ar-*H*); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K) δ = -1.3 (*C*H$_3$), 104.9, 108.2, 127.9, 129.7, 130.2, 134.1, 138.6, 148.2 (Ar-*C*); $^{29}Si\{^1H\}$ NMR (80 MHz, C_6D_6, 298 K) δ = -5.9; IR ν/cm^{-1} (ATR): 3384 (m, NH), 1604 (s), 1585 (s), 1165 (m), 1112 (vs), 1000 (vs), 890 (w), 827 (s), 814 (s), 785 (s), 751 (m), 727 (s), 698 (s), 682 (s); acc. mass calc. for $C_{22}H_{29}N_2Si_2$ (MH^+): 377.1869; found: 377.1986.

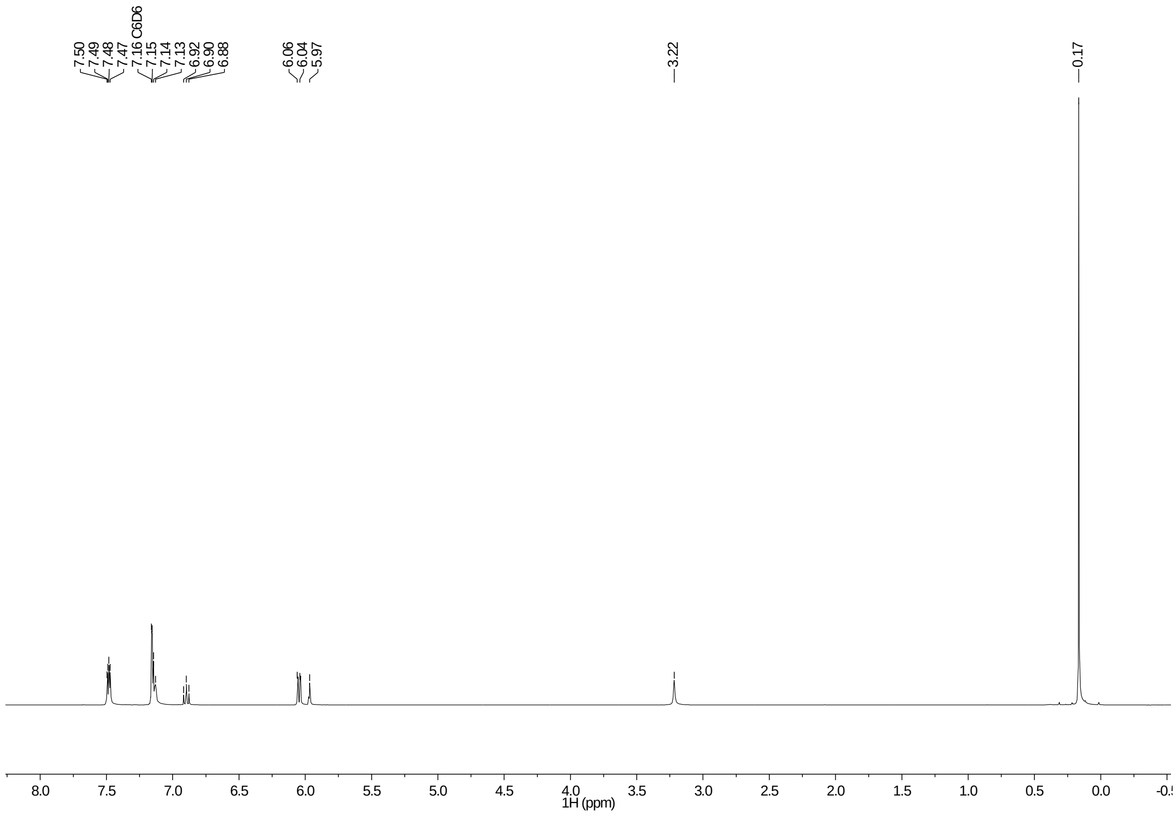

Figure S10. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of 1,3-{N(H)(SiMe$_2$Ph)}$_2$(μ-C_6H_4).

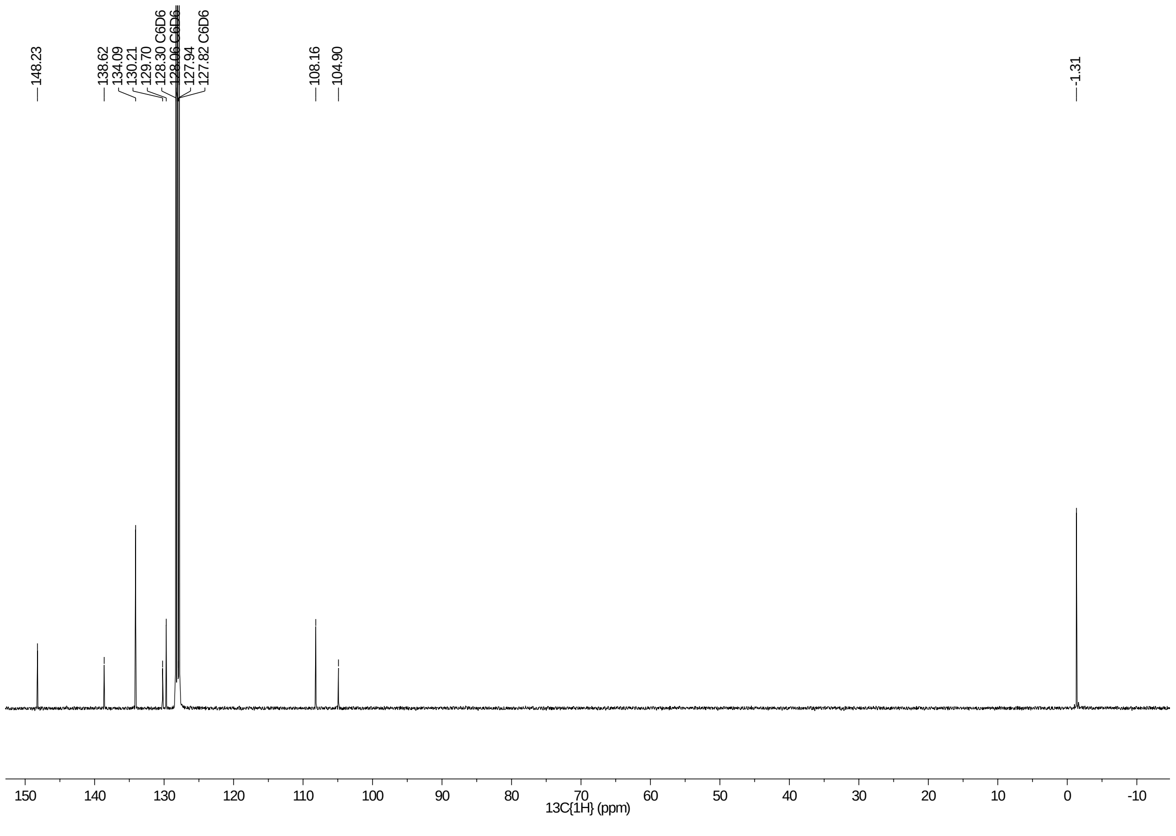

Figure S11. ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K, C_6D_6) of 1,3-{N(H)(SiMe$_2$Ph)}$_2$(μ-C_6H_4).

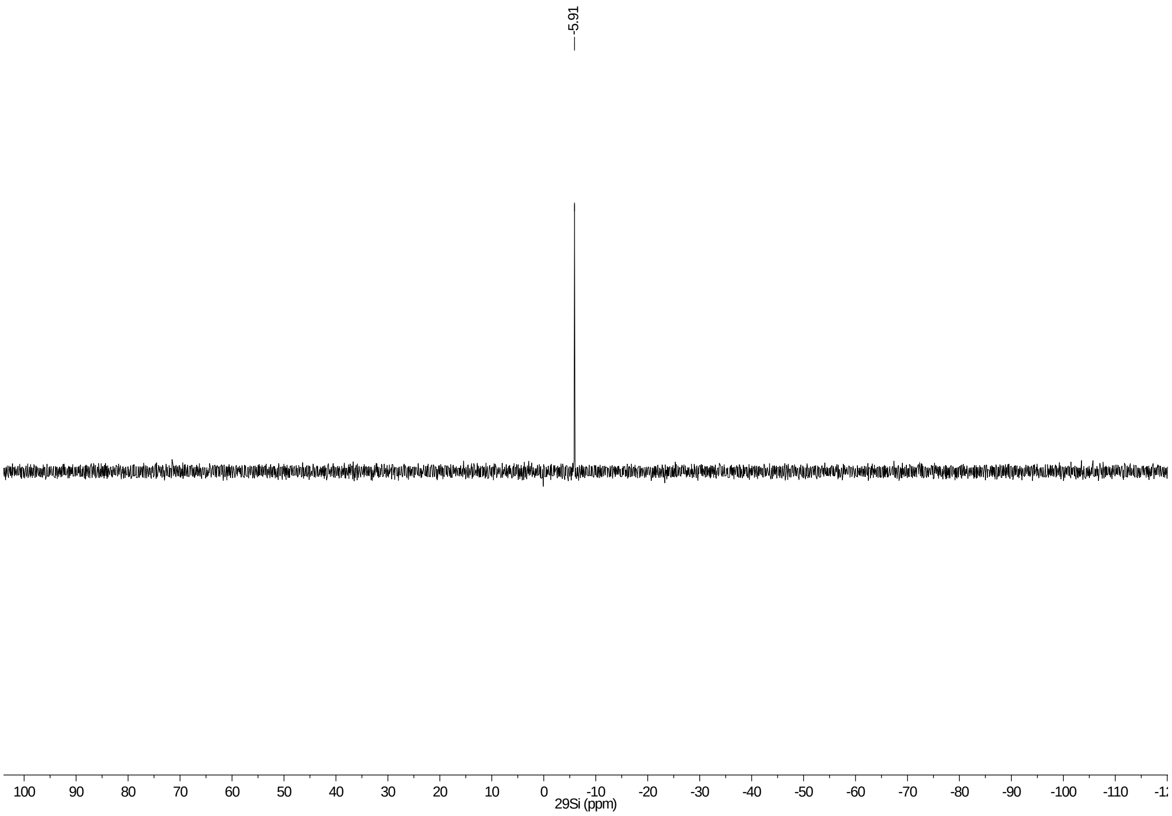

Figure S12. $^{29}Si\{^1H\}$ NMR spectrum (80 MHz, 298 K, C_6D_6) of 1,3-$\{N(H)(SiMe_2Ph)\}_2(\mu\text{-}C_6H_4)$.

Synthesis of 4,6-$\{[Dip(H)N](DipN)C\}_2$(μ-DBF), L^3H_2. $LiBu^n$ (26.8 mL, 42.8 mmol, 1.6 M solution in hexane) was added to a solution of dibenzofuran (3.00 g, 17.9 mmol) in hexane (20 mL) and tmeda (6.4 mL, 42.8 mmol). The resultant suspension was stirred under reflux for 3 h. A solution of bis(2,6-diisopropylphenyl)carbodiimide (13.90 g, 38.3 mmol) in hexane (20 mL) was added to the reaction mixture and stirred overnight at room temperature. The resultant suspension was hydrolysed using water (40 mL) and stirred for 30 min at room temperature. The formed precipitate was filtered, washed with water and hexane, and then dried under vacuum at 70 °C for 2 h, giving the title compound as a yellow powder. Crystals suitable for an X-ray diffraction study were obtained from toluene at room temperature (8.20 g, 52 %). M.p. > 260 °C; ^1H NMR (400 MHz, C_6D_6, 298 K) δ = 0.80 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $CH(CH_3)_2$), 0.90 (br, 12H, $CH(CH_3)_2$), 1.03 (d, $^3J_{HH}$ = 6.7 Hz, 12H, $CH(CH_3)_2$), 1.17 (br, 12H, $CH(CH_3)_2$), 3.12 (br, 4H, $CH(CH_3)_2$), 3.40 (br, 4H, $CH(CH_3)_2$), 6.59 (t, $^3J_{HH}$ = 7.7 Hz, 2H, Ar-*H*), 6.97-7.09 (m, 14H, Ar-*H*), 7.23 (d, $^3J_{HH}$ = 7.7 Hz, 2H, Ar-*H*), 7.39 (br, 2H, Ar-*H*); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K) δ = 22.9, 23.7 (x2), 24.2 ($CH(CH_3)_2$), 28.9, 29.7 ($CH(CH_3)_2$), 118.3, 122.3, 122.8, 123.6, 123.8, 123.9, 125.4, 127.7, 129.7, 135.3, 137.7, 145.3, 145.9, 147.7 (Ar-*C*), 152.8 (N*C*N); IR ν/cm^{-1} (ATR): 3458 (m, NH), 1083 (m), 1059 (m), 935 (m), 852 (m), 791 (vs), 758 (vs), 684 (m); acc. mass calc. for $C_{62}H_{77}N_4O$ (MH^+): 893.6097; found: 893.6190.

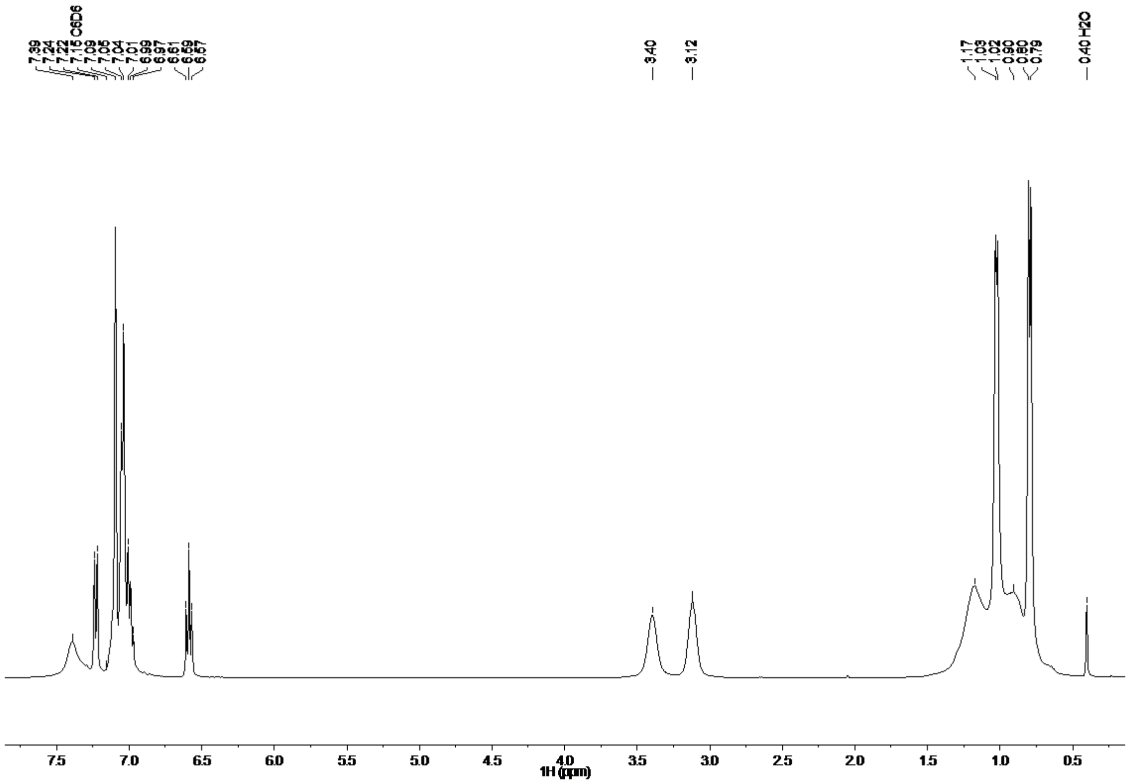

Figure S13. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of 4,6-{[Dip(H)N](DipN)C}$_2$(μ-DBF), L^3H_2.

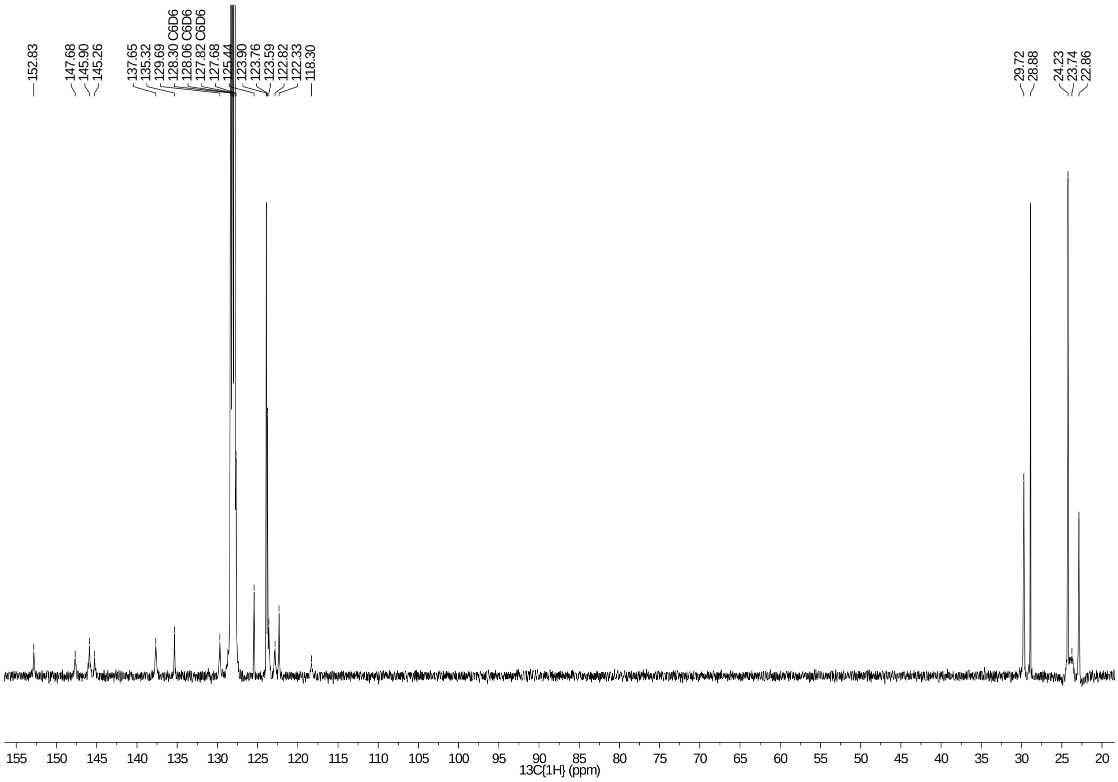

Figure S14. $^{13}C\{^1H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of 4,6-{[Dip(H)N](DipN)C}$_2$(μ-DBF), L^3H_2.

1,3-{Ar†N(H)C(Bu^t)N}$_2$(μ-C$_6$H$_4$), L^{4}H$_2$. {ClC(Bu^t)=N}$_2$(μ-C$_6$H$_4$) (4.53 g, 14.5 mmol) was dissolved in toluene (50 mL) and Ar†NH$_2$ (13.6 g, 29.1 mmol) and NEt$_3$ (4.0 mL, 29.0 mmol) added to the solution. The mixture was then heated at reflux for 3 d. Volatiles were then removed under reduced pressure, the solid residue was suspended in diethyl ether (100 mL) and a 1 M solution of Na$_2$CO$_3$ (30 mL) added. The mixture was transferred to a separating funnel, the organic layer was washed with water (2×60 mL) and dried over MgSO$_4$. The organic layer was separated and volatiles were removed under vacuum to give a solid residue which was washed with toluene (3×30 mL), yielding the title compound as white powder (14.10 g, 83 %). The X-ray quality crystals were grown by layering a dilute THF solution of the compound with hexane. M.p. > 260 °C; Meaningful solution state NMR spectroscopic data could not be obtained on the compound as it had very poor solubility in normal deutrated solvents; IR ν/cm^{-1} (ATR): 3461 (m, NH), 1648 (vs), 1600 (m), 1578 (m),1076 (s), 1030 (m), 1005 (w), 966 (w), 895 (m), 863 (m), 841 (w), 743 (s), 698 (vs); acc. mass calc. for C$_{86}$H$_{87}$N$_4$ (MH$^+$): 1175.6930; found: 1175.7098.

Synthesis of :Ge(μ-L^1)$_2$Ge:, 1. A solution of L^{1}H$_2$ (1.0 g, 2.38 mmol) in hexane (30 mL) was cooled to -80 °C and LiBu^n (3.1 mL of a 1.6 M solution in hexane, 5.00 mmol) added to it over 10 min. The reaction mixture was then warmed to room temperature and stirred for 3 h. It was then added to a suspension of GeCl$_2$.dioxane (0.61 g, 2.61 mmol) in hexane (20 mL) at -80 °C. The resultant solution was warmed to room temperature and stirred for 12 h. It was then filtered and concentrated to *ca.* 10 mL. The solution was stored at -30 °C for 2 d resulting in deposition of **1** as yellow crystals (0.55 g, 47 %). M.p. 247-250 °C; ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K) δ = 1.16 (d, $^3J_{HH}$ = 7.4 Hz, 72H, CH(C*H*$_3$)$_2$), 1.37 (sept, $^3J_{HH}$ = 7.4 Hz, 12H, C*H*(CH$_3$)$_2$), 6.27 (s, 8H, Ar-*H*); ^{13}C{^{1}H} NMR (101 MHz, C$_6$D$_6$, 298 K) δ = 13.4 (*C*H(CH$_3$)$_2$), 19.2 (CH(*C*H$_3$)$_2$), 128.7, 141.3 (Ar-*C*); ^{29}Si{^{1}H} NMR (80 MHz, C$_6$D$_6$, 298 K) δ = 9.4; IR ν/cm^{-1} (Nujol): 1489(s), 1012 (s), 1000 (m), 938 (s), 917 (m), 876 (s), 862 (vs), 824 (vs), 739 (vs), 717 (s), 677 (m), 664 (s); anal. calc. for C$_{48}$H$_{92}$Ge$_2$N$_4$Si$_4$: C 58.66 %, H 9.44 %, N 5.70 %, found: C 58.64 %, H 9.60 %, N 5.58 %.

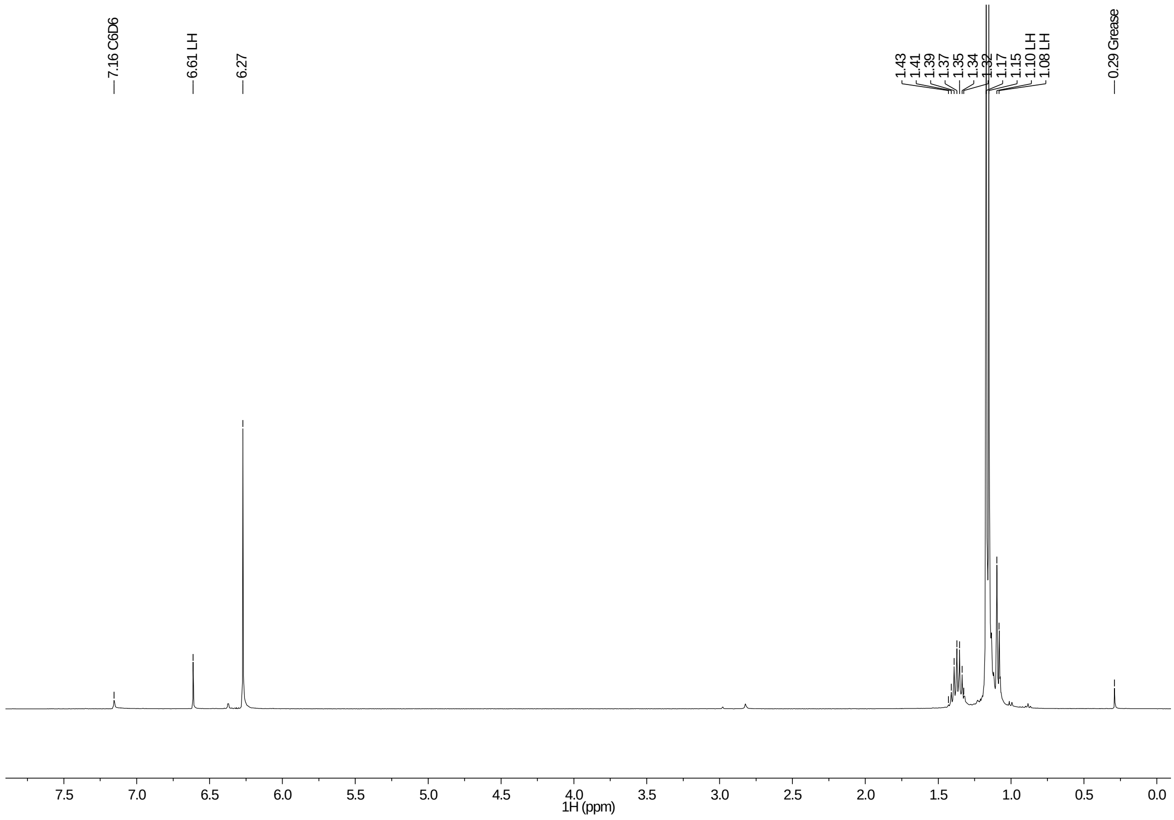

Figure S15. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of :Ge(μ-L^1)$_2$Ge:, **1** (LH = L^{1}H$_2$).

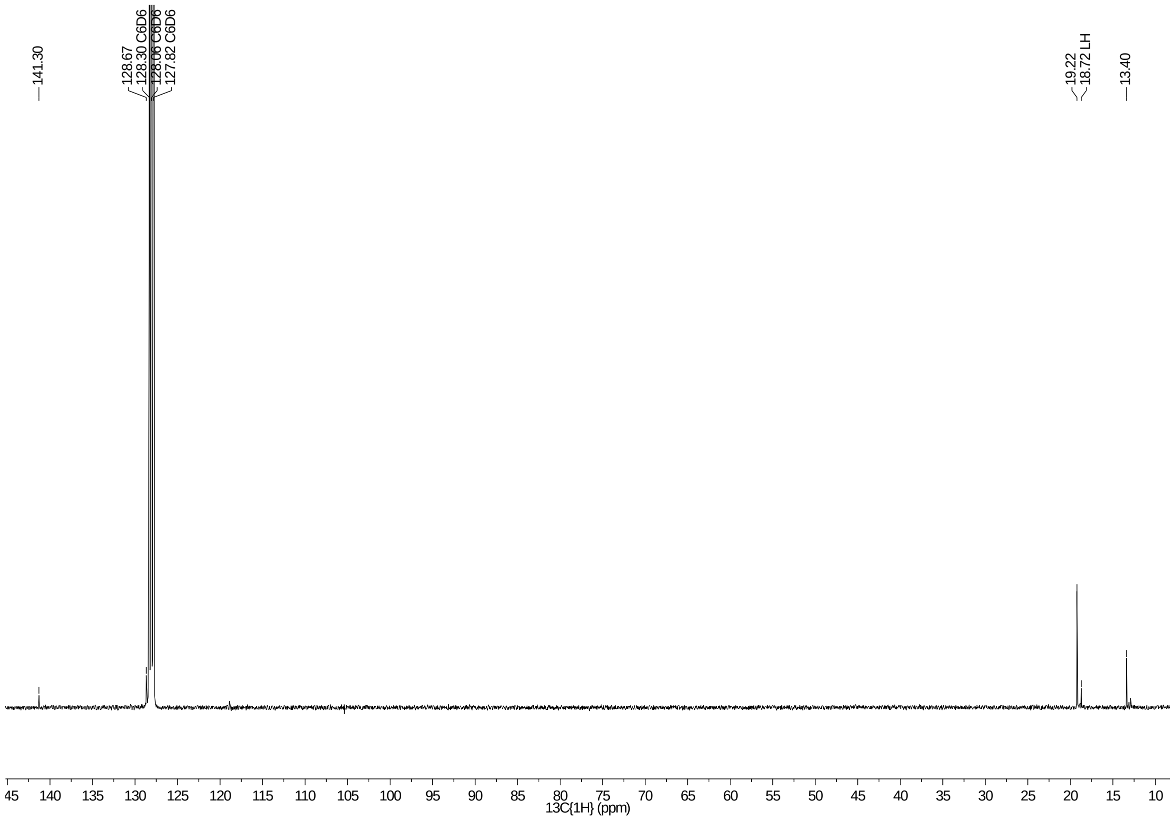

Figure S16. ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K, C_6D_6) of :Ge(μ-L^1)$_2$Ge:, **1** (LH = L^{1}H$_2$).

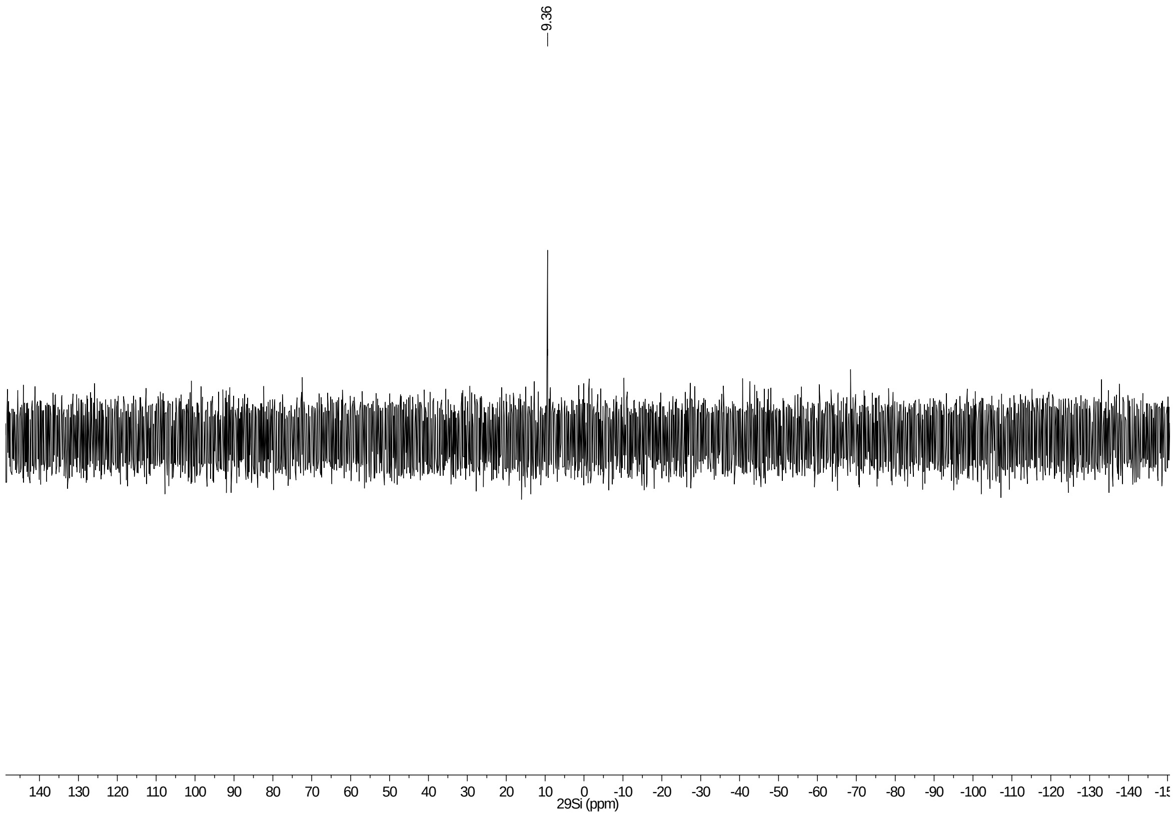

Figure S17. ^{29}Si{^{1}H} NMR spectrum (80 MHz, 298 K, C_6D_6) of :Ge(μ-L^{1})$_2$Ge:, **1**.

Synthesis of :Sn(μ-L^{1})$_2$Sn:, 2. A solution of L^1H_2 (1.0 g, 2.38 mmol) in hexane (30 mL) was cooled to -80 °C and LiBu^{n} (3.1 mL of a 1.6 M solution in hexane, 5.00 mmol) added to it over 10 min. The reaction mixture was then warmed to room temperature and stirred for 3 h. It was then added to a suspension of $SnBr_2$ (0.73 g, 2.61 mmol) in toluene (20 mL) at -80 °C. The resultant solution was warmed to room temperature and stirred for 12 h. It was then filtered and concentrated to *ca.* 10 mL. The solution was stored at -30 °C for 2 d resulting in deposition of **2** as dark red crystals (0.38 g, 30 %). M.p. 180-185 °C; ^{1}H NMR (400 MHz, C_6D_6, 298 K) δ = 1.15 (d, $^{3}J_{HH}$ = 7.4 Hz, 72H, CH(C*H*$_3$)$_2$), 1.34 (sept, $^{3}J_{HH}$ = 7.3 Hz, 12H, *C*H(CH$_3$)$_2$), 6.27 (s, 8H, Ar-*H*); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K) δ = 13.4 (*C*H(CH$_3$)$_2$), 19.2 (CH(*C*H$_3$)$_2$), 127.4, 144.5 (Ar-*C*); ^{29}Si{^{1}H} NMR (80 MHz, C_6D_6, 298 K) δ = 8.6; ^{119}Sn{^{1}H} NMR (149 MHz, C_6D_6, 298 K): no signal observed; IR ν/cm^{-1} (Nujol): 1459 (vs), 1011 (m), 876 (s), 857 (s), 798 (w), 739 (vs), 660 (s); anal. calc. for $C_{48}H_{92}Sn_2N_4Si_4$: C 53.63 %, H 8.63 %, N 5.21 %, found: C 53.37 %, H 8.40 %, N 5.11 %.

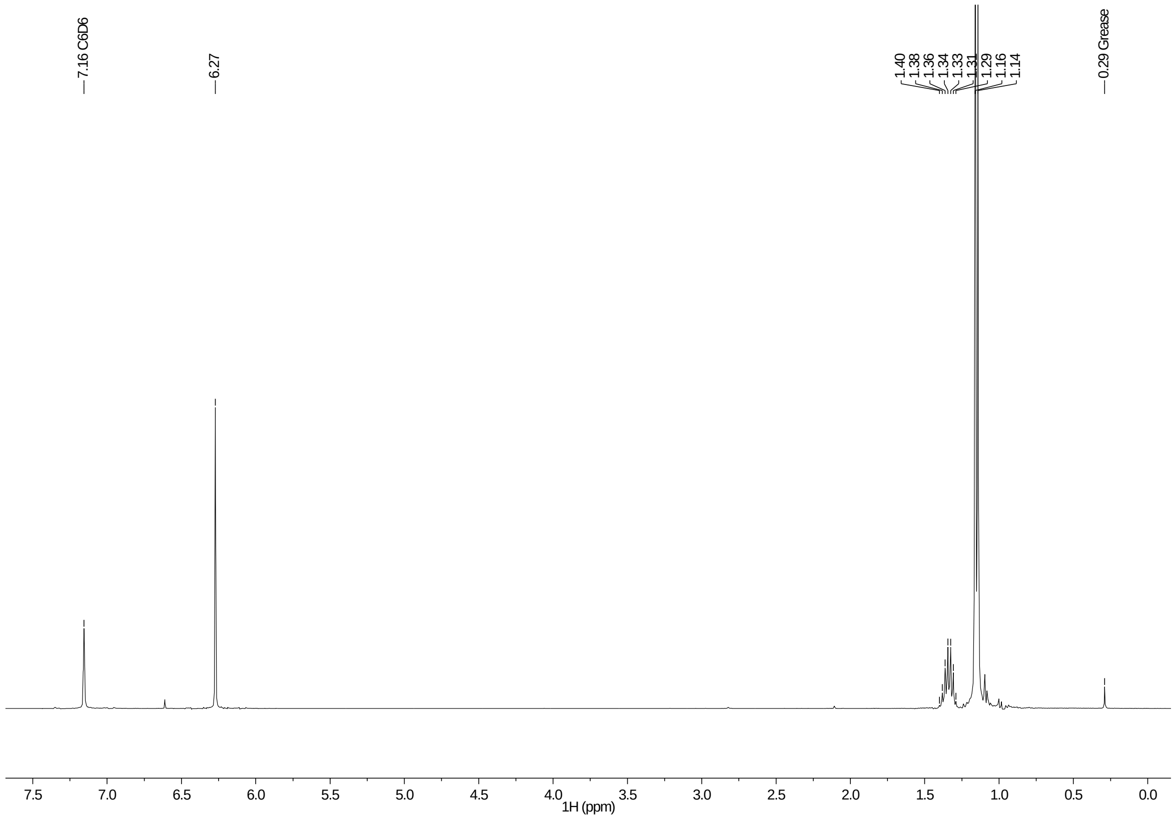

Figure S18. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of :Sn(μ-L^1)$_2$Sn:, **2**.

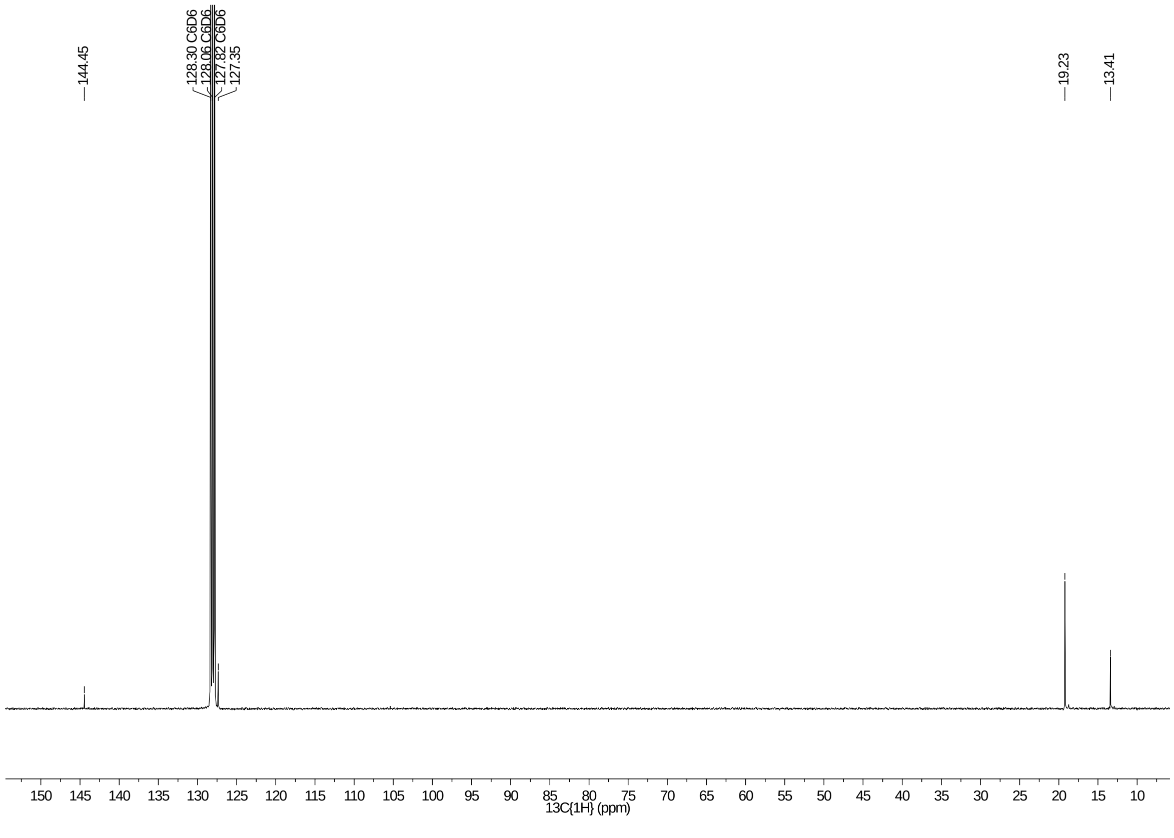

Figure S19. ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K, C_6D_6) of :Sn(μ-L^1)$_2$Sn:, **2**.

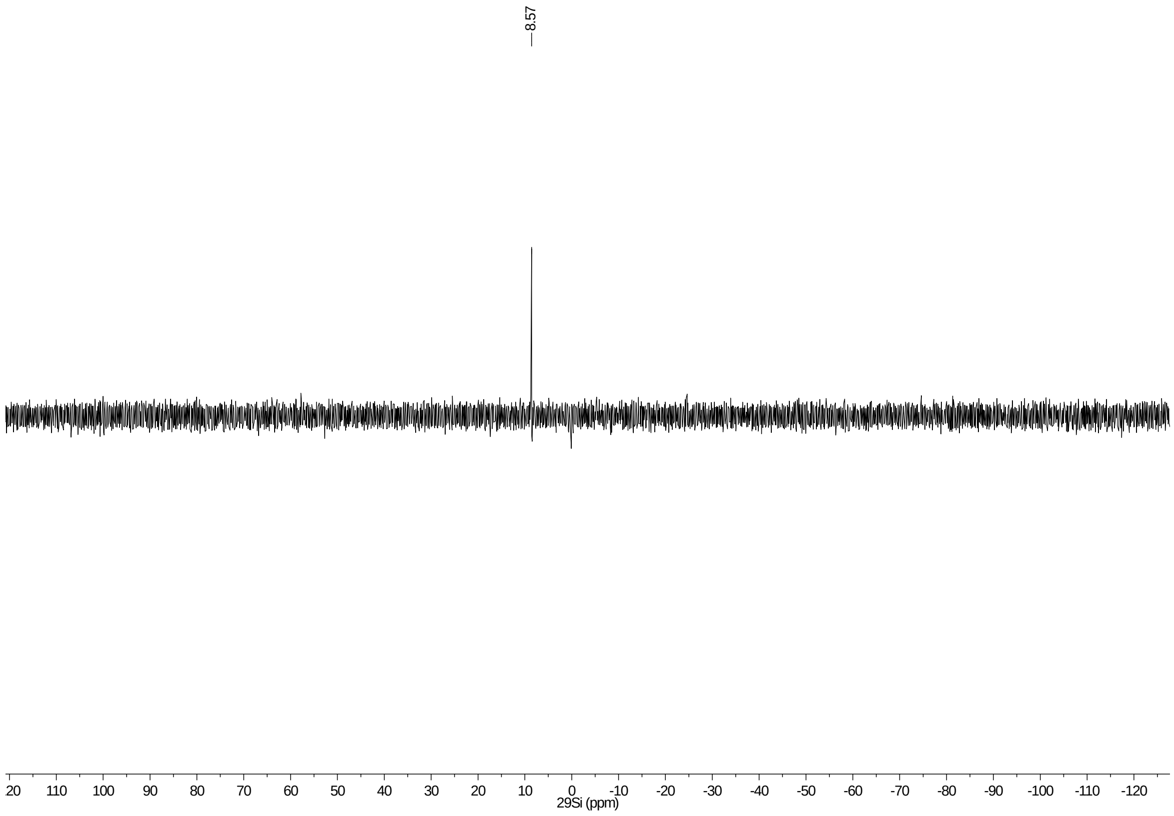

Figure S20. ^{29}Si{^{1}H} NMR spectrum (80 MHz, 298 K, C_6D_6) of :Sn(μ-L^{1})$_2$Sn:, **2**.

Synthesis of :Ge(μ-L^{2})$_2$Ge:, 3. A solution of L^2H_2 (1.0 g, 2.38 mmol) in hexane (30 mL) was cooled to -80 °C and LiBu^{n} (3.1 mL of a 1.6 M solution in hexane, 5.00 mmol) added to it over 10 min. The reaction mixture was then warmed to room temperature and stirred for 3 h. It was then added to a suspension of $GeCl_2$.dioxane (0.61 g, 2.61 mmol) in hexane (20 mL) at -80 °C. The resultant solution was warmed to room temperature and stirred for 12 h. It was then filtered and concentrated to *ca.* 10 mL. The solution was stored at -30 °C for 2 d resulting in deposition of **3** as dark yellow crystals (0.49 g, 42 %). M.p. > 260 °C; ^{1}H NMR (400 MHz, C_6D_6, 298 K) δ = 1.17-1.20 (overlapping doublets, 72H, CH(C*H*$_3$)$_2$), 1.45 (sept, $^{3}J_{HH}$ = 7.4 Hz, 12H, C*H*(CH$_3$)$_2$), 6.30 (d, $^{3}J_{HH}$ = 7.8 Hz, 4H, Ar-*H*), 6.36 (s, 2H, Ar-*H*), 6.52 (t, $^{3}J_{HH}$ = 7.9 Hz, 2H, Ar-*H*); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K) δ = 13.1 (*C*H(CH$_3$)$_2$), 19.0, 19.1 (CH(*C*H$_3$)$_2$), 122.8, 128.5, 129.0, 146.7 (Ar-*C*); ^{29}Si{^{1}H} NMR (80 MHz, C_6D_6, 298 K) δ = 15.6; IR ν/cm^{-1} (Nujol): 1576 (vs), 1017 (m), 984 (vs), 917 (w), 880 (vs), 789 (vs), 728 (vs), 687 (vs); anal. calc. for $C_{48}H_{92}Ge_2N_4Si_4$: C 58.66 %, H 9.44 %, N 5.70 %, found: C 58.12 %, H 9.69 %, N 5.66 %.

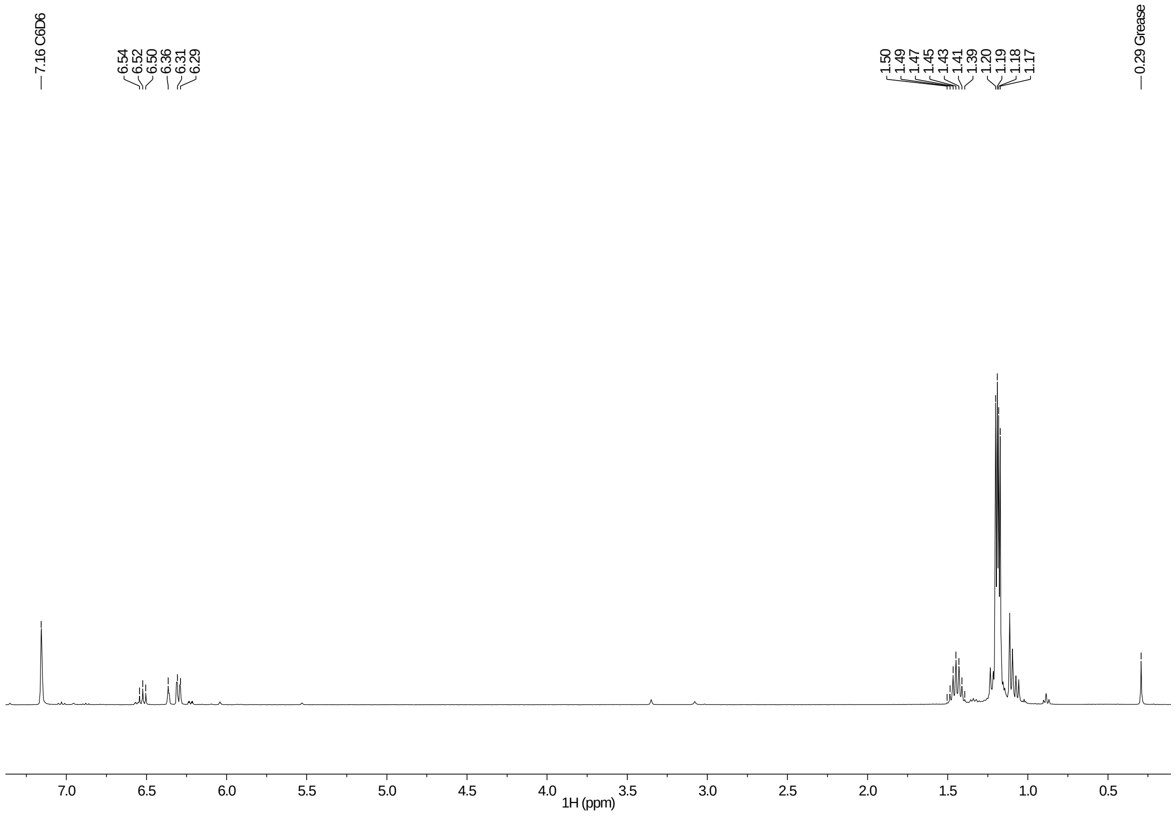

Figure S21. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of :Ge(μ-L^{2})$_2$Ge:, **3**.

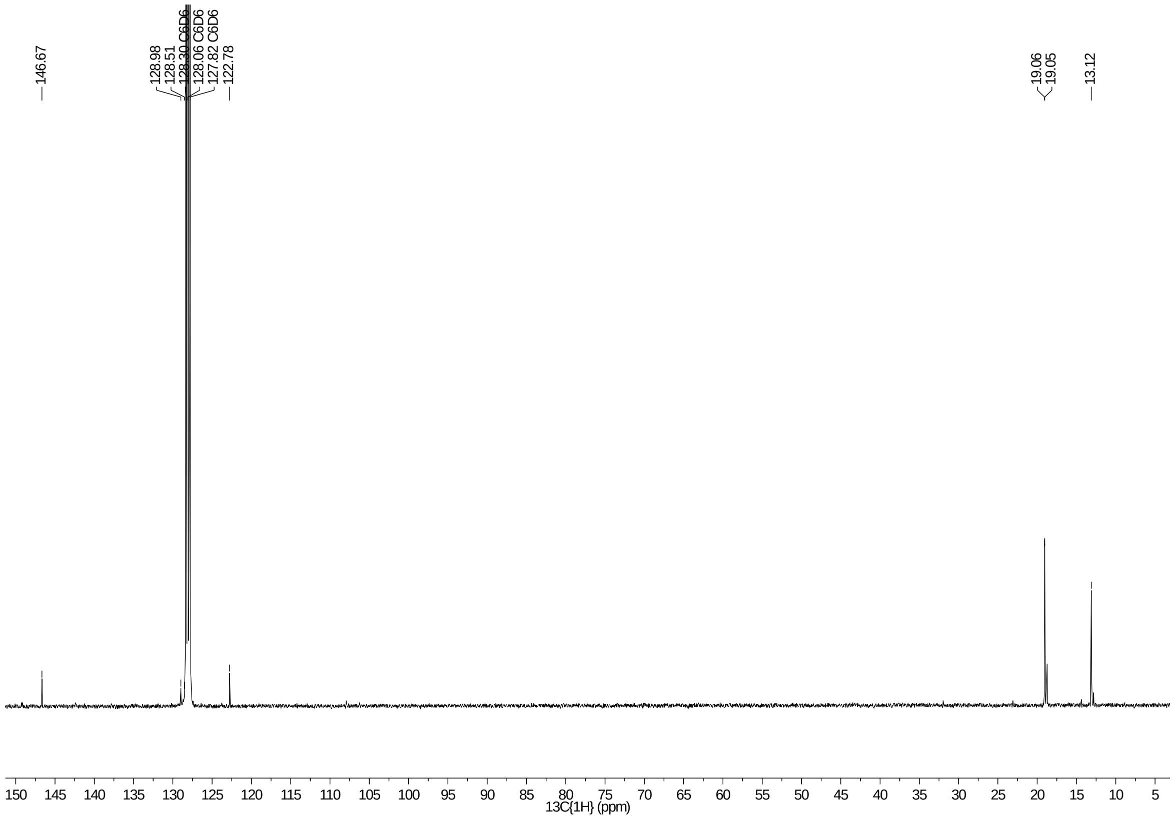

Figure S22. ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K, C_6D_6) of :Ge(μ-L^{2})$_2$Ge:, **3**.

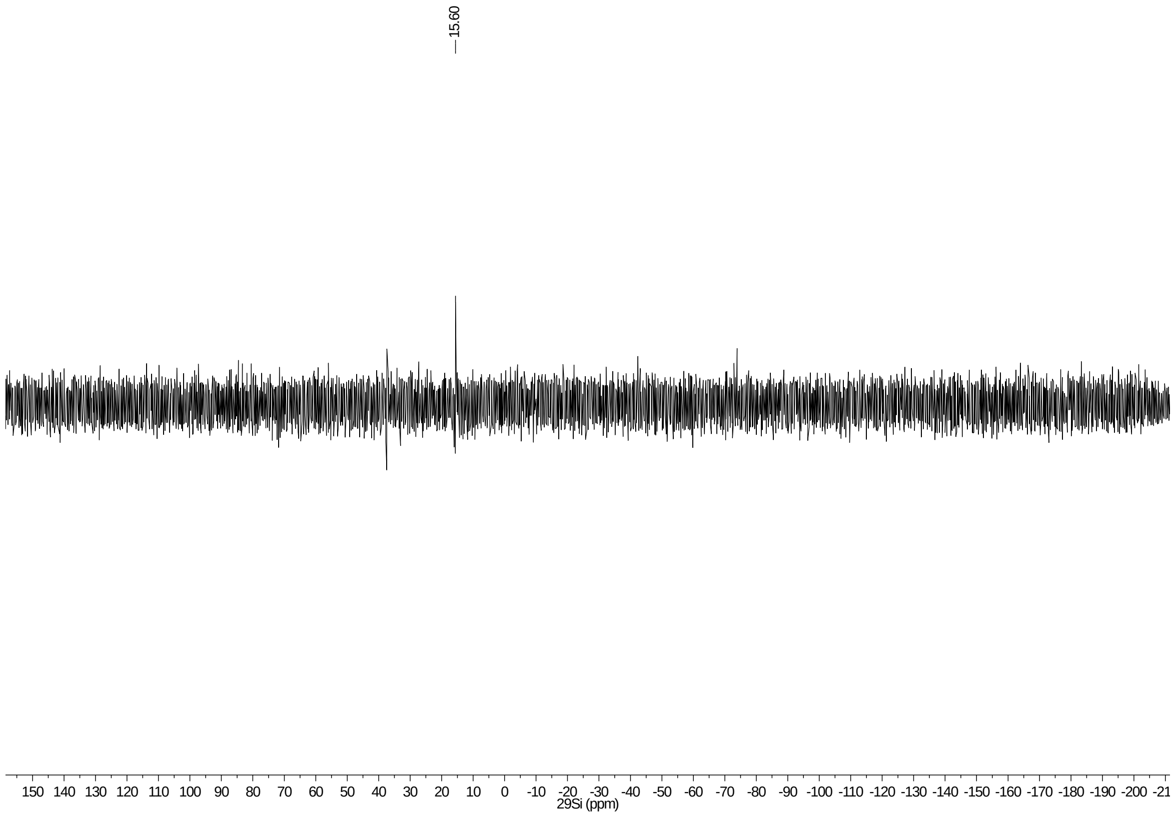

Figure S23. ^{29}Si{^{1}H} NMR spectrum (80 MHz, 298 K, C_6D_6) of :Ge(μ-L^{2})$_2$Ge:, **3**.

Synthesis of :Sn(μ-L^{2})$_2$Sn:, 4. A solution of L^{2}H$_2$ (1.0 g, 2.38 mmol) in hexane (30 mL) was cooled to -80 °C and LiBu^{n} (3.1 mL of a 1.6 M solution in hexane, 5.00 mmol) added to it over 10 min. The reaction mixture was then warmed to room temperature and stirred for 3 h. It was then added to a suspension of $SnBr_2$ (0.73 g, 2.61 mmol) in toluene (20 mL) at -80 °C. The resultant solution was warmed to room temperature and stirred for 12 h. It was then filtered and concentrated to *ca.* 10 mL. The solution was stored at -30 °C for 2 d resulting in deposition of **4** as dark red crystals (0.35 g, 27 %). M.p. 200-206 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6, 298 K) δ = 1.07 (d, $^{3}J_{HH}$ = 6.4 Hz, 36H, CH(C*H*$_3$)$_2$), 1.18-1.31 (m, 48H, C*H*(CH$_3$)$_2$, CH(C*H*$_3$)$_2$), 5.52 (s, 2H, Ar-*H*), 6.41 (d, $^{3}J_{HH}$ = 7.7 Hz, 4H, Ar-*H*), 6.86 (t, $^{3}J_{HH}$ = 7.7 Hz, 2H, Ar-*H*); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K) δ = 13.3 (*C*H(CH$_3$)$_2$), 19.0, 19.1 (CH(*C*H$_3$)$_2$), 123.2, 125.7, 127.5, 151.7 (Ar-*C*); ^{29}Si{^{1}H} NMR (80 MHz, C_6D_6, 298 K) δ = 6.7; ^{119}Sn{^{1}H} NMR (149 MHz, C_6D_6, 298 K): no signal observed; IR ν/cm^{-1} (Nujol): 1529 (s), 1019 (s), 933 (s), 845 (w), 764 (vs), 722 (s), 689 (vs), 664 (s); a reproducible microanalysis could not be obtained for the compound as it consistently co-crystallised with small amounts of the pro-ligand L^{2}H$_2$, which could not be separated after several recrystallisations.

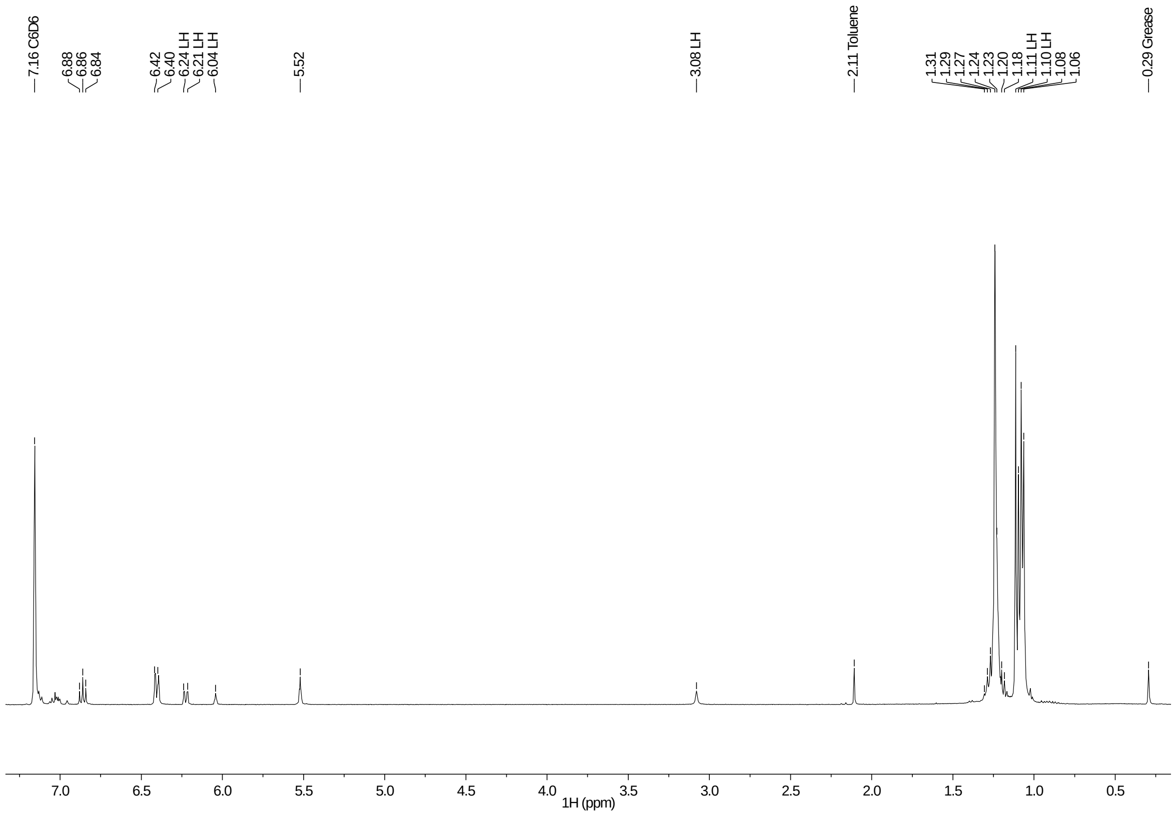

Figure S24. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of :Sn(μ-L^{2})$_2$Sn:, **4** (LH = L^{2}H$_2$).

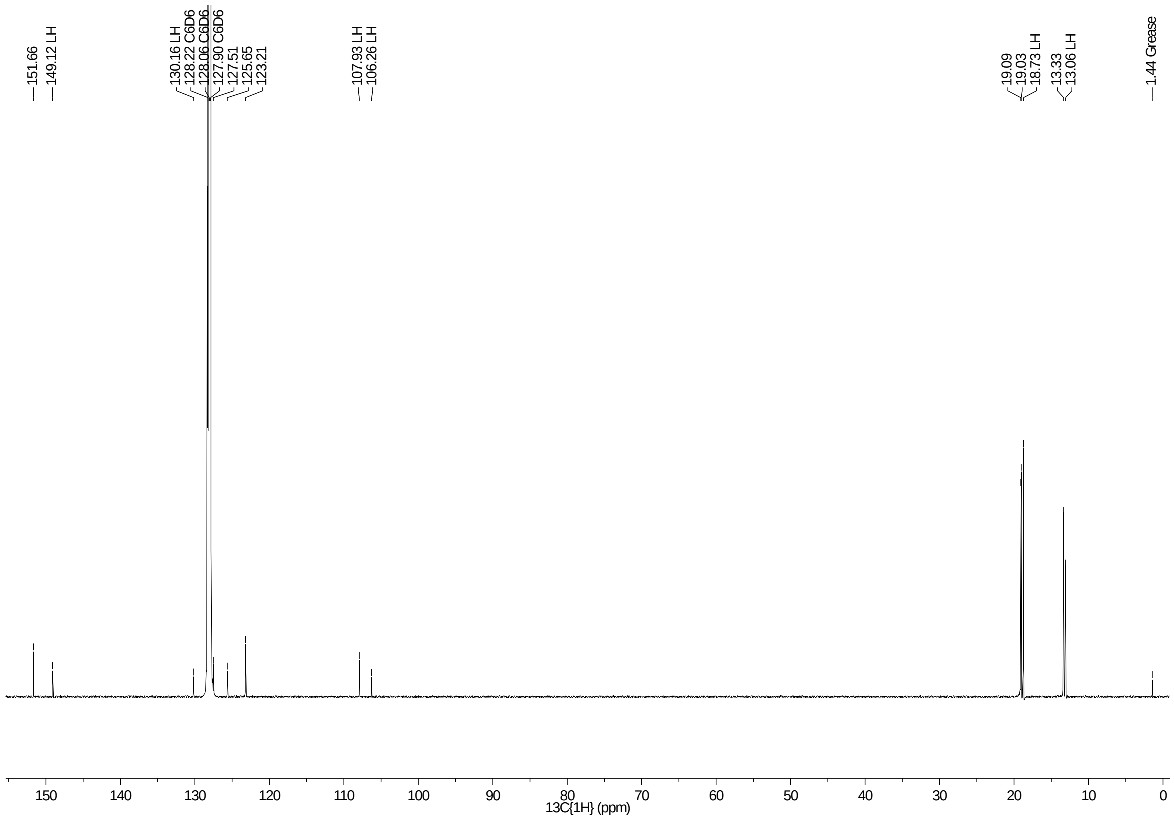

Figure S25. ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K, C_6D_6) of :Sn(μ-L^{2})$_2$Sn:, **4** (LH = L^{2}H$_2$).

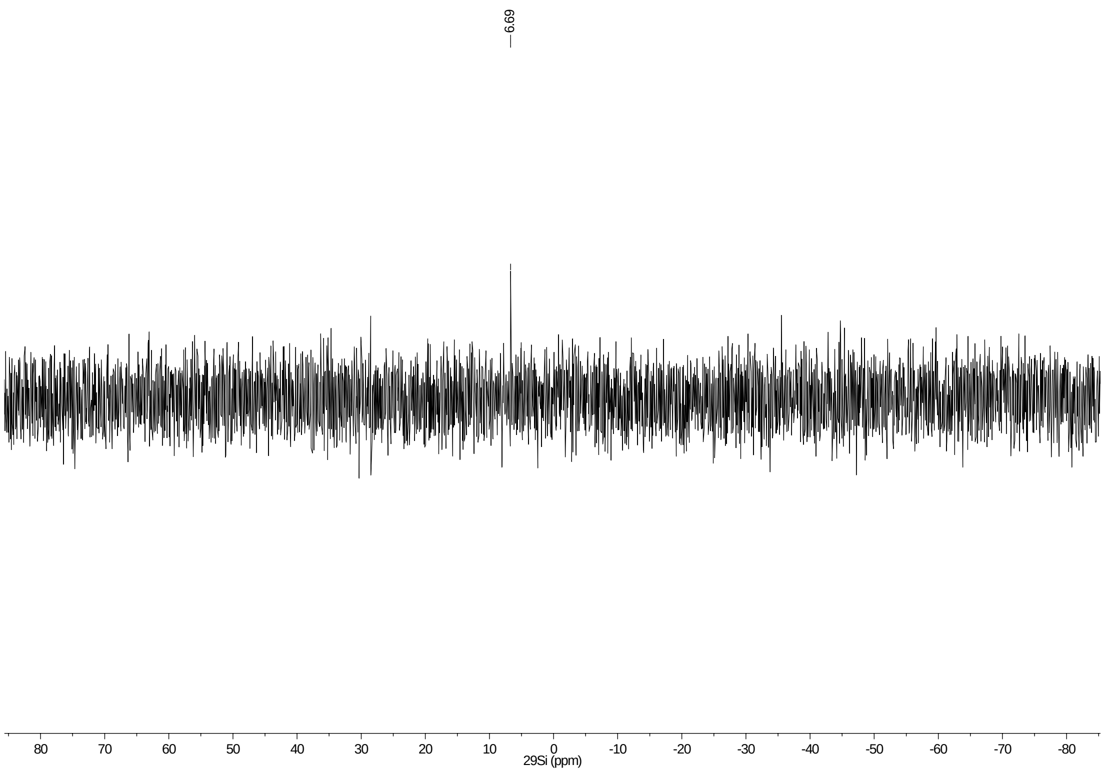

Figure S26. $^{29}Si\{^1H\}$ NMR spectrum (80 MHz, 298 K, C_6D_6) of :Sn(μ-L^2)$_2$Sn:, **4.**

Synthesis of :Ge(Cl)(μ-L^3)(Cl)Ge:, 5. A solution of L^3H_2 (1.00 g, 1.12 mmol) in THF (50 mL) was cooled to -80 °C and LiBu^n (1.5 mL, 2.46 mmol, 1.6 M solution in hexane) added to this over 10 min. After the addition, the reaction mixture was warmed to room temperature, and stirred for 4 h. This was then added to a solution of $GeCl_2$.dioxane (0.56 g, 2.41 mmol) in THF (20 mL) at -80 °C. The reaction mixture was stirred for 12 h at room temperature. Volatiles were subsequently removed *in vacuo,* and the residue extracted into hot toluene (30 mL). The extract was filtered and dried under vacuum. It was then extracted into hexane (15 mL) and stored at -30 ºC overnight to yield colourless crystals of **5** (0.68 g, 55 %). M.p. > 260 °C; ^1H NMR (600 MHz, C_6D_6, 298 K) δ = -0.66 (br, 6H, CH(C*H*$_3$)$_2$), 0.38 (br, 6H, CH(C*H*$_3$)$_2$), 0.95 (br, 6H, CH(C*H*$_3$)$_2$), 1.45-1.55 (m, 24H, CH(C*H*$_3$)$_2$), 1.78 (br, 6H, CH(C*H*$_3$)$_2$), 2.82 (br, 2H, C*H*(CH$_3$)$_2$), 3.51 (br, 2H, C*H*(CH$_3$)$_2$), 4.24 (br, 2H, C*H*(CH$_3$)$_2$), 4.42 (br, 2H, C*H*(CH$_3$)$_2$), 6.57 (m, 2H, Ar-*H*), 6.60 (br, 2H, Ar-*H*), 6.91-6.98 (m, 8H, Ar-*H*), 7.07 (m, 2H, Ar-*H*), 7.11 (br, 2H, Ar-*H*), 7.29 (m, 2H, Ar-*H*); $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6, 298 K) δ = 20.0, 24.3, 25.2, 27.3 (CH(*C*H$_3$)$_2$), 28.3, 29.0, 29.2, 29.4 (*C*H(CH$_3$)$_2$), 115.8, 122.5, 122.8, 123.8, 125.0, 125.1, 125.5, 126.0, 127.4, 127.6, 128.5, 134.7, 135.8, 142.3, 143.5, 144.7, 147.9, 152.8 (Ar-*C*), 168.4 (N*C*N); IR ν/cm^{-1} (Nujol): 1639 (w), 1611 (w),1586 (w), 1501 (w), 1020 (m), 990 (w), 968 (m), 936 (m), 915 (m), 884 (w), 852 (s), 799 (vs), 790 (vs), 765 (s), 756 (vs), 743 (vs), 743 (vs), 715 (w), 683 (w); anal. calc. for $C_{62}H_{74}Cl_2Ge_2N_4O$: C 67.24 %, H 6.74 %, N 5.06 %; found: C 67.35 %, H 6.89 %, N 4.92 %.

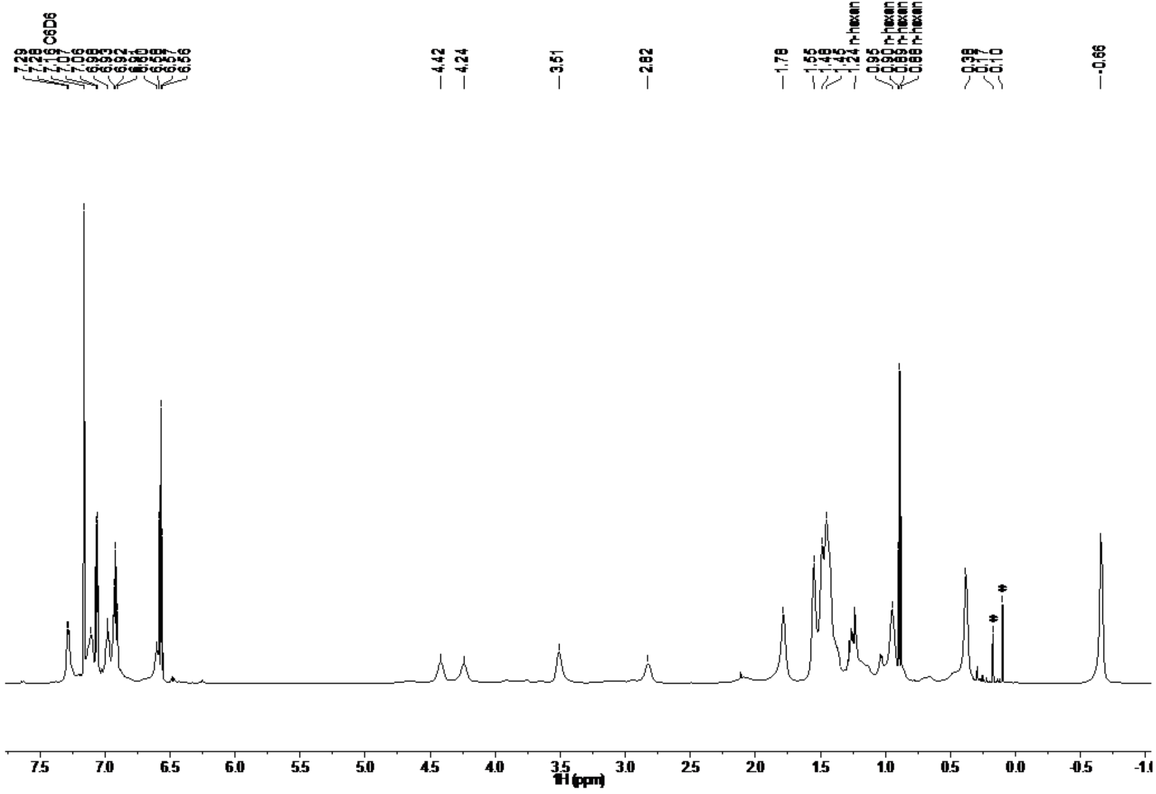

Figure S27. ^{1}H NMR spectrum (600 MHz, 298 K, C_6D_6) of :Ge(Cl)(μ-L^3)(Cl)Ge:, **5** (* = unknown impurity).

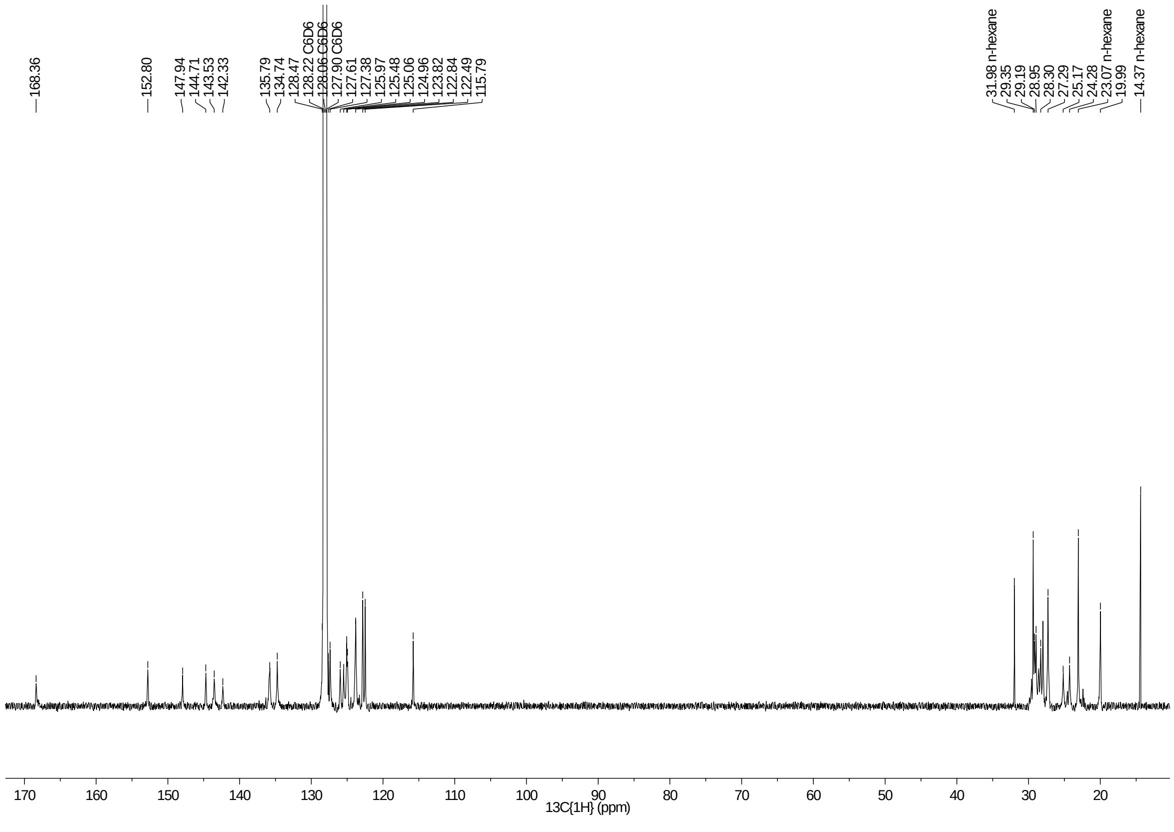

Figure S28. ^{13}C{^{1}H} NMR spectrum (151 MHz, 298 K, C_6D_6) of :Ge(Cl)(μ-L^3)(Cl)Ge:, **5**.

Synthesis of :Sn(Br)(μ-L^3)(Br)Sn:, 6. A solution of L^{3}H$_2$ (1.00 g, 1.12 mmol) in THF (50 mL) was cooled to -80 °C and LiBu^n (1.5 mL, 2.46 mmol, 1.6 M solution in hexane) added to this over 10 min. After the addition, the reaction mixture was warmed to room temperature, and stirred for 4 h. This was then added to a solution of SnBr$_2$ (0.67 g, 2.41 mmol) in THF (20 mL) at -80 °C. The reaction mixture was stirred for 12 h at room temperature. Volatiles were subsequently removed *in vacuo,* and the residue extracted into hot toluene (30 mL). The extract was filtered and dried under vacuum. It was then extracted into hexane (15 mL) and stored at -30 ºC overnight yield colourless crystals of **6** (0.40 g, 27.7 %). M.p. 220-224 °C (decomp.); ^{1}H NMR (600 MHz, C$_6$D$_6$, 298 K) δ = -0.73 (d, $^3J_{HH}$ = 6.7 Hz, 6H, CH(CH_3)$_2$), 0.44 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH(CH_3)$_2$), 0.89 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.29 (br, 6H, CH(CH_3)$_2$), 1.46 (br, 6H, CH(CH_3)$_2$), 1.58 (br, 12H, CH(CH_3)$_2$), 1.70 (br, 6H, CH(CH_3)$_2$), 2.72 (br, 2H, C*H*(CH$_3$)$_2$), 3.56 (m, 2H, C*H*(CH$_3$)$_2$), 4.11 (br, 2H, C*H*(CH$_3$)$_2$), 4.41 (br, 2H, C*H*(CH$_3$)$_2$), 6.55-6.57 (m, 4H, Ar-*H*), 6.87 (m, 2H, Ar-*H*), 6.94-7.09 (m, 10H, Ar-*H*), 7.25 (m, 2H, Ar-*H*); ^{13}C{^{1}H} NMR (151 MHz, C$_6$D$_6$, 298 K) δ = 19.6, 22.9, 24.6, 25.9, 27.4, 28.1, 28.3, 28.8 (CH(*C*H$_3$)$_2$), 28.6, 28.9, 2×29.1, (*C*H(CH$_3$)$_2$), 118.5, 122.1, 123.5, 123.9, 124.6, 125.0, 125.5, 126.7, 127.6, 128.4, 128.5, 134.8, 137.0, 137.3, 143.4, 144.4, 147.2, 152.7 (Ar-*C*), 169.8 (N*C*N); ^{119}Sn{^{1}H} NMR (149 MHz, C$_6$D$_6$, 298 K): no signal observed; IR ν/cm^{-1} (Nujol): 1643 (w), 1608 (w), 1584 (w), 11083 (m), 1050 (w), 963 (w), 934 (w), 910 (w), 849 (m), 794 (s), 740 (m), 699 (w); a reproducible microanalysis could not be obtained as it consistently co-crystallised with small amounts of the pro-ligand L^{3}H$_2$, which could not be separated after several recrystallisations.

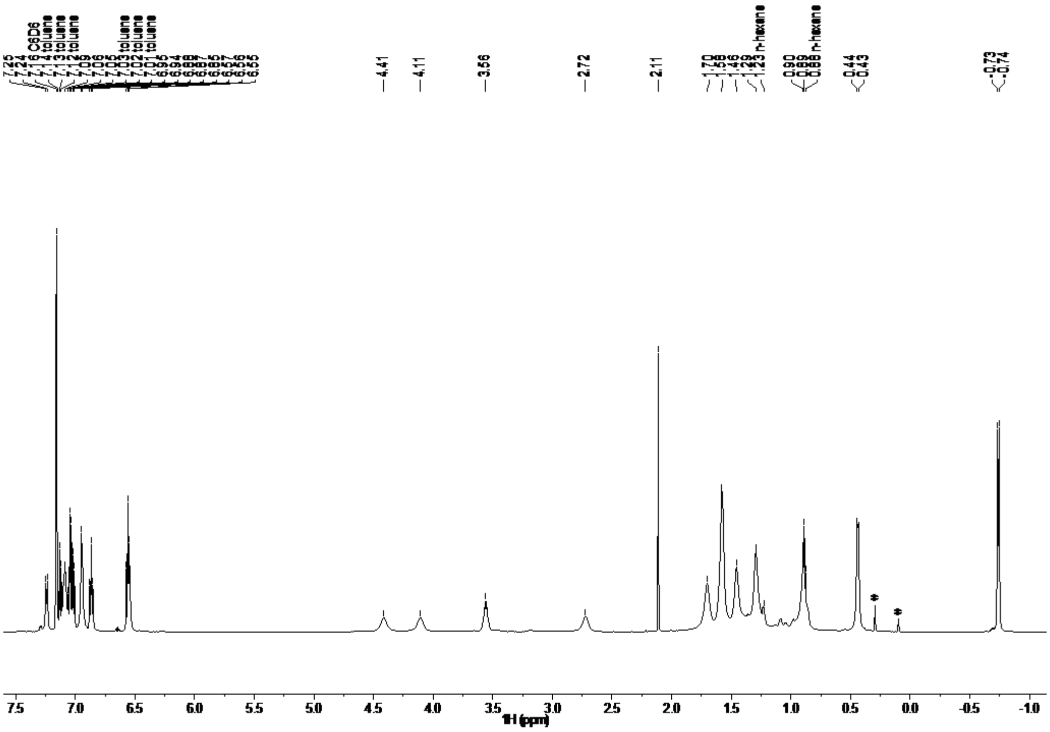

Figure S29. ^{1}H NMR spectrum (400 MHz, 298 K, C$_6$D$_6$) of :Sn(Br)(μ-L^3)(Br)Sn:, **6** (* = impurity).

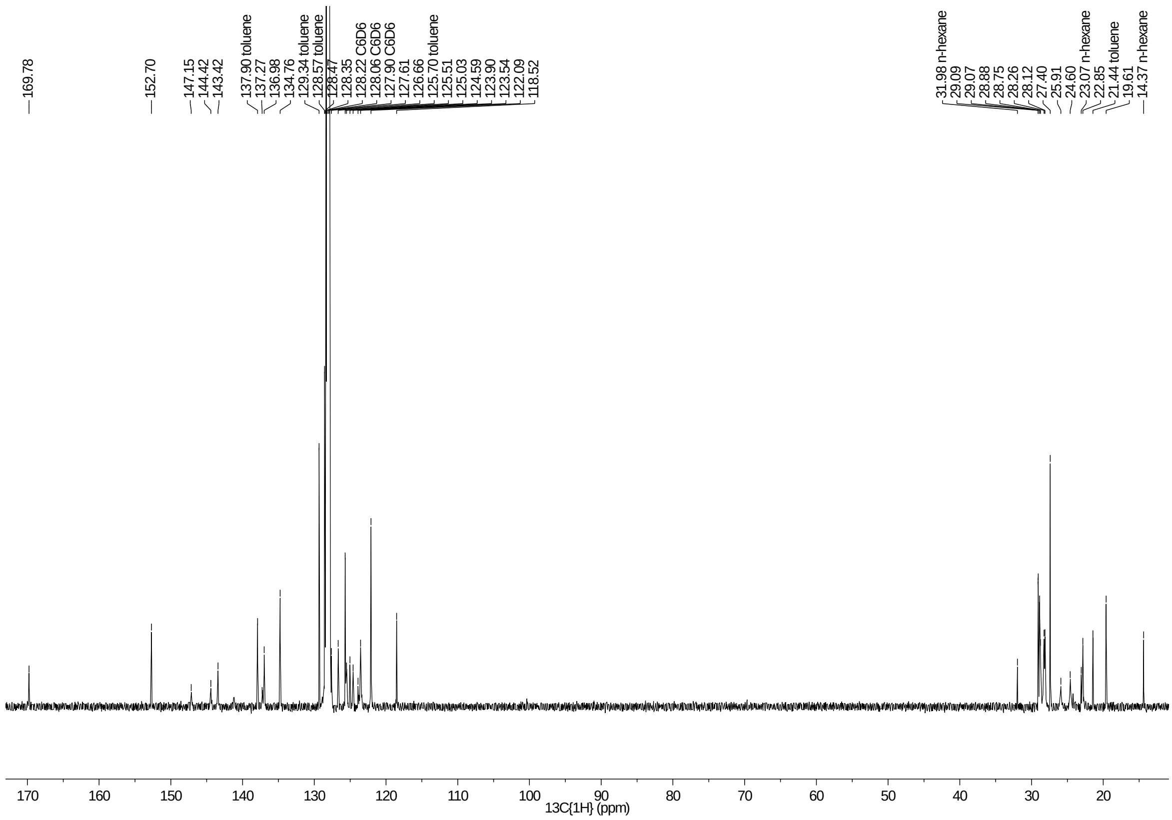

Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, 298 K, C_6D_6) of :Sn(Br)(μ-L^3)(Br)Sn: **6**.

Synthesis of :Ge(Cl)(μ-L^4)(Cl)Ge:, 7. A solution of L^4H_2 (1.0 g, 0.85 mmol) in THF (50 mL) was cooled to -80 °C and LiBu^n (1.1 mL, 1.79 mmol, 1.6 M solution in hexane) added over 10 min. After the addition, the reaction mixture was warmed to room temperature, and stirred for 4 h. The mixture was then added to a solution of $GeCl_2$.dioxane (0.414 g, 1.79 mmol) in THF (20 mL) at -80 °C. The resultant solution was warmed to room temperature and stirred for 12 h. Volatiles were subsequently removed *in vacuo* and the residue extracted into hot toluene (50 mL). The extract was filtered, concentrated to *ca.* 20 mL and stored at -30 °C overnight to yield **7** as a white precipitate (0.68 g, 58 %). M.p. 208-214 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6, 298 K) δ = 0.88 (s, 18H, $C(CH_3)_3$), 0.93 (d, 12H, $^{3}J_{HH}$ = 6.8 Hz, 12H, $CH(CH_3)_2$), 2.46 (sept, $^{3}J_{HH}$ = 6.9 Hz, 2H, $CH(CH_3)_2$), 5.96 (br s, 4H, Ph_2CH), 6.86-7.79 (m, 48 H, Ar-*H*); $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298 K) δ = 23.9 ($CH(CH_3)_2$), 28.9 ($C(CH_3)_3$), 33.8 ($CH(CH_3)_2$), 42.3 ($C(CH_3)_3$), 51.3 (Ph_2CH), 127.1, 128.4, 128.7, 128.8, 128.9, 129.0, 129.5, 130.1, 131.0, 139.9, 143.4, 145.8 (Ar-*C*), N*C*N resonance not observed; IR ν/cm^{-1} (Nujol): 1593 (vs), 1029 (s), 963 (w), 896 (w), 868 (w), 844 (w), 807 (w), 763 (w), 742 (w), 697 (vs); a reproducible microanalysis could not be obtained for the compound as it consistently crystallised with a small amount of an unknown impurity which could not be separated by repeated recrystallisations.

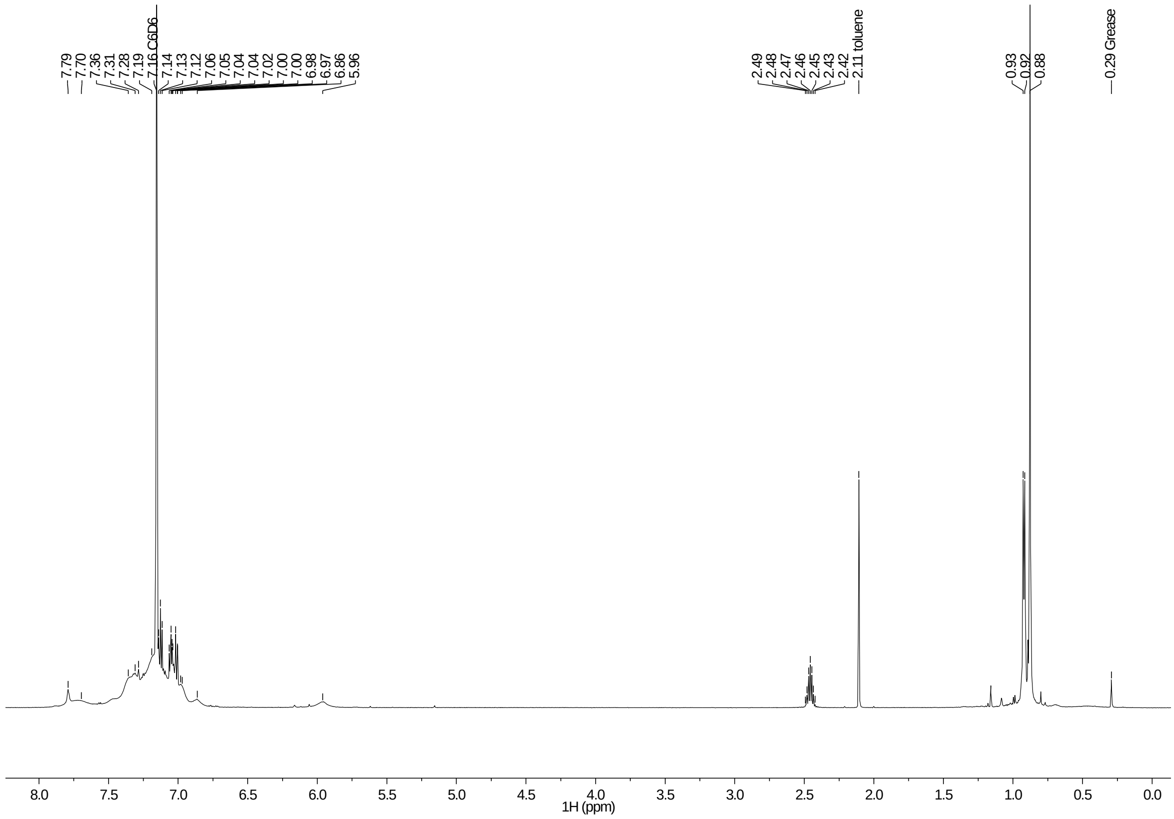

Figure S31. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of :Ge(Cl)(μ-L^{4})(Cl)Ge:, **7**.

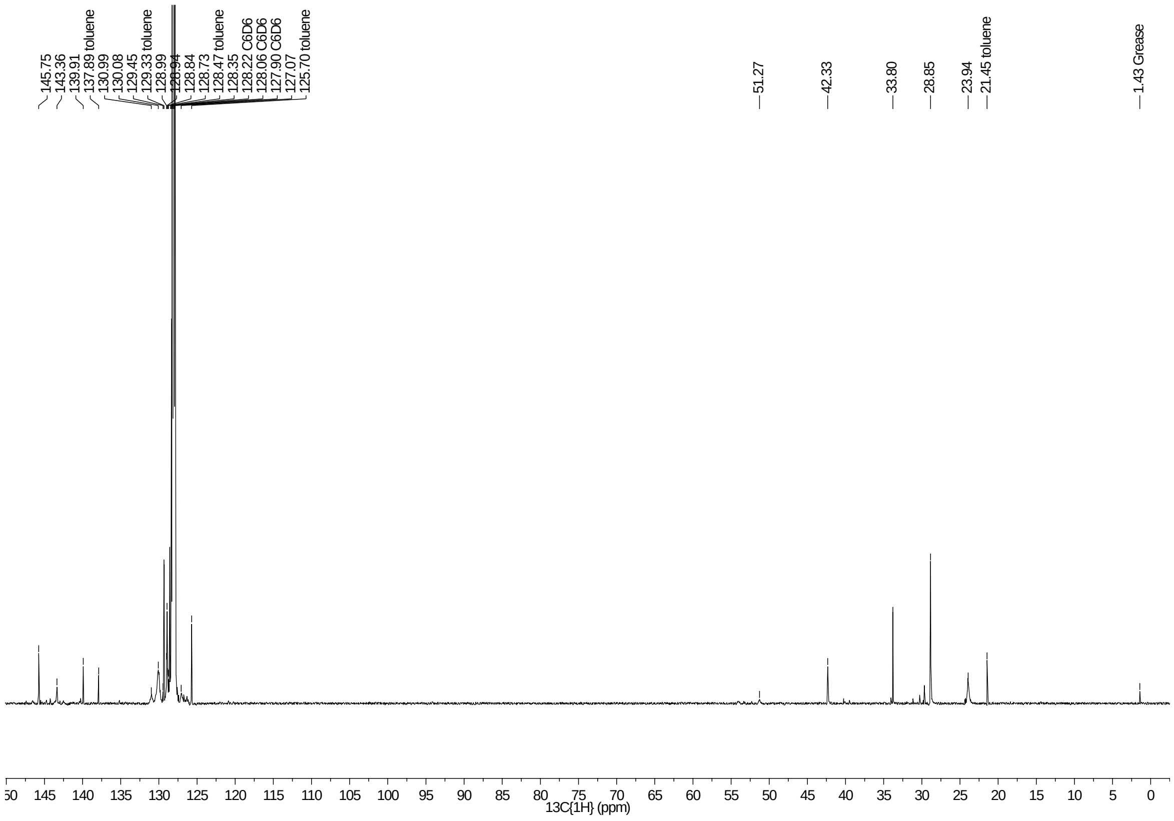

Figure S32. ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K, C_6D_6) of :Ge(Cl)(μ-L^{4})(Cl)Ge:, **7**.

Synthesis of :Ge(μ-L^4)$_2$Ge:, 8. A solution of **7** (0.60 g, 0.43 mmol) in toluene (20 mL) was added to a slurry of KC_8 (0.13 g, 0.95 mmol) in toluene (10 mL) at -80 °C. The mixture was warmed to room temperature and stirred for 4 h. Volatiles were then removed *in vacuo* and residue was extracted into hot toluene (20 mL). The extract was filtered, concentrated to *ca.* 10 mL and placed at room temperature overnight to yield yellow crystals of **8** (0.21 g, 39 %). M.p. 208-211 °C (decomp.); meaningful solution state spectroscopic data for the compound could not be obtained for the compound as it shows negligible solubility in normal non-coordinating deuterated solvents once crystallised; IR ν/cm^{-1} (Nujol): 1647 (s), 1579 (m), 1029 (s), 1016 (s), 895 (w), 864 (w), 798 (vs), 762 (w), 744 (w), 698 (vs); A reproducible microanalysis could not be obtained for this compound as its negligible solubility in common organic solvents precluded it being purified from minor by-products by recrystallisation.

2. Crystallography

Crystals suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made with a Rigaku Xtalab Synergy Dualflex diffractometer using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å) or Cu Kα radiation (λ = 1.54184 Å). All structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX-16[4]) using all unique data. Hydrogen atoms are typically included in calculated positions (riding model), except for amine protons, the positional and isotropic displacement parameters of which are freely refined. Crystal data, details of data collections and refinements for all structures can be found in their CIF files and are summarized in Table S1.

Table S1. Crystal data for compounds **1-6**, **8**, L^3H_2, L^4H_2 and 1,3-{N(H)(SiMe$_2$Ph)}$_2$(μ-C_6H_4) **1S**.

	1	**2**	**3**	**4**
empirical formula	$C_{48}H_{92}Ge_2N_4Si_4$	$C_{48}H_{92}N_4Si_4Sn_2$	$C_{48}H_{92}Ge_2N_4Si_4$	$C_{48}H_{92}N_4Si_4Sn_2$
formula weight	982.79	1074.99	982.79	1074.99
crystal system	triclinic	triclinic	monoclinic	monoclinic
space group	*P*-1	*P*-1	$P2_1/n$	$P2_1/n$
a (Å)	7.9765(10)	7.9922(4)	14.8934(7)	14.8476(6)
b (Å)	12.1182(16)	12.3215(6)	9.6017(4)	9.5319(3)
c (Å)	15.3472(2)	15.2347(8)	18.8362(8)	19.2672(6)
α (°)	111.399(5)	111.3240(10)	90	90
β (°)	103.493(5)	104.1690(10)	96.359(4)	97.133(3)
γ (°)	91.681(5)	90.3260(10)	90	90
V (Å^3)	1332.3(3)	1347.56(12)	2677.0(2)	2705.70(16)
Z	1	1	2	2
T (K)	123(2)	123(2)	123(2)	123(2)
ρ_{calcd} (g·cm^3)	1.225	1.325	1.219	1.319
μ (mm^{-1})	1.253	1.050	1.247	1.046
F(000)	528	564	1056	1128
reflns collected	14091	15024	22553	25186
unique reflns	4854	5009	4981	5018
R_{int}	0.0494	0.0202	0.0625	0.0497
R1 [I > 2σ(I)]	0.0567	0.0205	0.0553	0.0781
wR2 (all data)	0.1493	0.0456	0.1504	0.2152
largest peak and hole (e·Å^{-3})	2.01 (near Ge1), -1.04	0.41, -0.37	2.08 (near Ge1), -0.51	3.90 (near Sn1), -1.82
CCDC no.	2084560	2084561	2084565	2084568

	5	**6**	**8**	L^3H_2
empirical formula	$C_{72.50}H_{98.50}Cl_2Ge_2N_4O$	$C_{80.75}H_{99}Br_2N_4OSn_2$	$C_{195.50}H_{196}Ge_2N_8$	$C_{62}H_{76}N_4O$
formula weight	1258.13	1538.83	2802.77	893.26
crystal system	monoclinic	triclinic	triclinic	monoclinic
space group	*C*2/*c*	*P*-1	*P*-1	$P2_1/n$
a (Å)	30.4822(13)	14.0460(5)	14.6822(4)	16.0278(2)
b (Å)	18.7316(3)	14.8866(4)	15.1015(3)	18.3288(2)
c (Å)	31.0548(10)	19.4437(5)	19.6211(4)	18.2050(2)
α (º)	90	74.136(2)	108.178(2)	90
β (º)	118.703(5)	87.081(2)	95.271(2)	91.2690(10)
γ (º)	90	79.413(3)	93.182(2)	90
V (Å^3)	15552.8(11)	3844.2(2)	4099.53(17)	5346.78(11)
Z	8	2	1	4
T (K)	123(2)	123(2)	123(2)	123(2)
ρ_{calcd} (g·cm^3)	1.075	1.329	1.135	1.110
μ (mm^{-1})	0.881	1.734	0.422	0.495
F(000)	5340	1579	1489	1936
reflns collected	39107	53732	58248	40806
unique reflns	13955	14267	15217	9685
R_{int}	0.0322	0.0741	0.0871	0.0629
R1 [I > 2σ(I)]	0.0598	0.0494	0.0763	0.0631
wR2 (all data)	0.1860	0.1288	0.2210	0.1737
largest peak and hole (e·Å^{-3})	1.26, -0.46	1.65, -0.74	1.17, -0.62	0.40, -0.35
CCDC no.	2084563	2084567	2084569	2084564

	L^4H_2	**1S**
empirical formula	$C_{86}H_{86}N_4$	$C_{22}H_{28}N_2Si_2$
formula weight	1175.58	376.64
crystal system	monoclinic	monoclinic
space group	*P*2/*n*	$P2_1/c$
a (Å)	11.3242(2)	8.50330(10)
b (Å)	15.1015(3)	24.7877(2)
c (Å)	19.8014(4)	10.00290(10)
α (º)	90	90
β (º)	95.415(2)	96.9600(10)
γ (º)	90	90
V (Å^3)	3371.17(11)	2092.85(4)
Z	2	4
T (K)	123(2)	123(2)
ρ_{calcd} (g·cm^3)	1.158	1.195
μ (mm^{-1})	0.503	1.583
F(000)	1260	808
reflns collected	33585	20480
unique reflns	6261	3887
R_{int}	0.0410	0.0347
R1 [I > 2σ(I)]	0.0661	0.0365
wR2 (all data)	0.1924	0.0996
largest peak and hole (e·Å^{-3})	0.414, -0.282	0.450, -0.344
CCDC no.	2084566	2084562

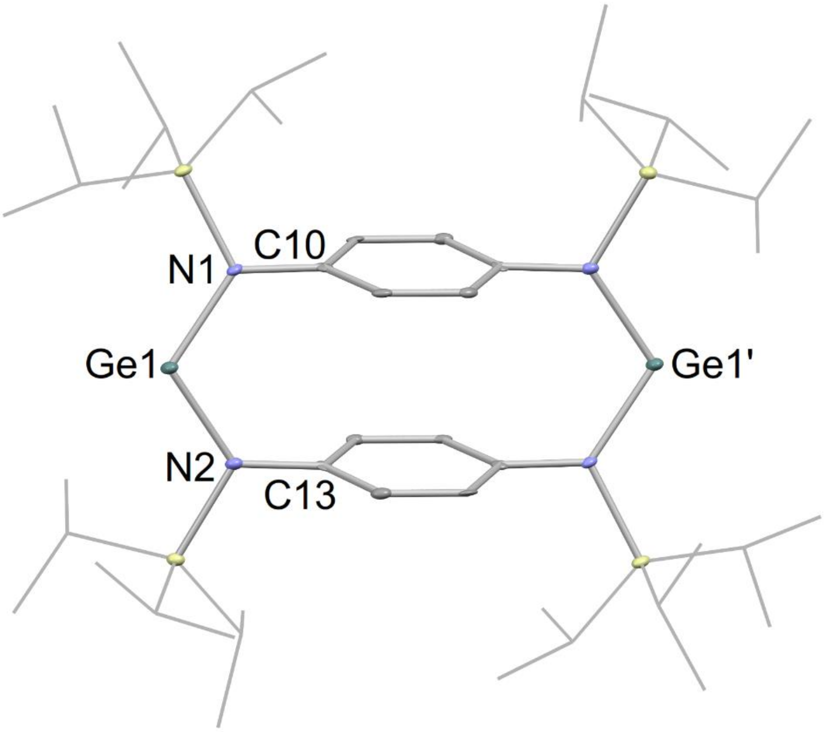

Figure S33. Molecular structure of :Ge(μ-L^1)$_2$Ge: **1**. Thermal ellipsoids drawn at the 25 % probability level. Hydrogen atoms omitted. Isopropyl groups displayed as wireframe for clarity (see main text for selected metrical parameters).

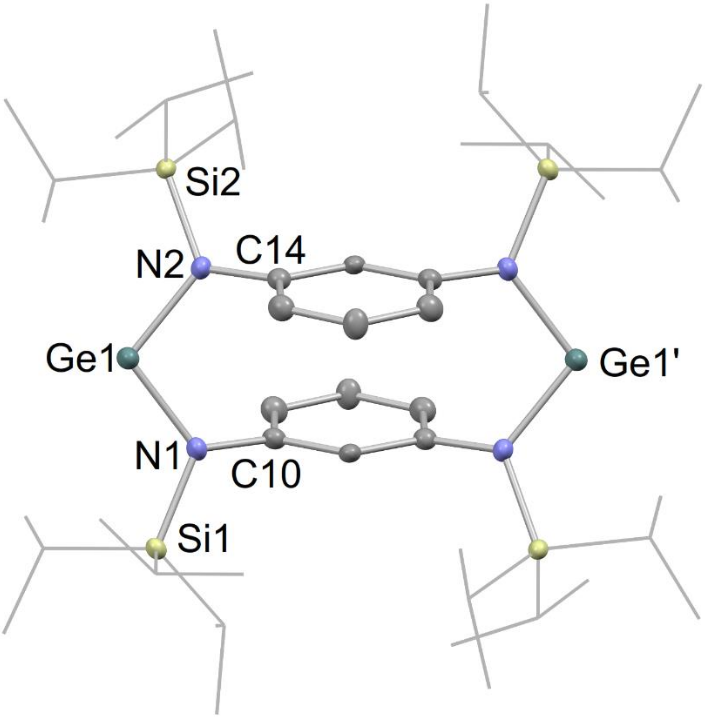

Figure S34. Molecular structure of :Ge(μ-L^2)$_2$Ge: **3**. Thermal ellipsoids drawn at the 25 % probability level. Hydrogen atoms omitted. Isopropyl groups displayed as wireframe for clarity (see main text for selected metrical parameters).

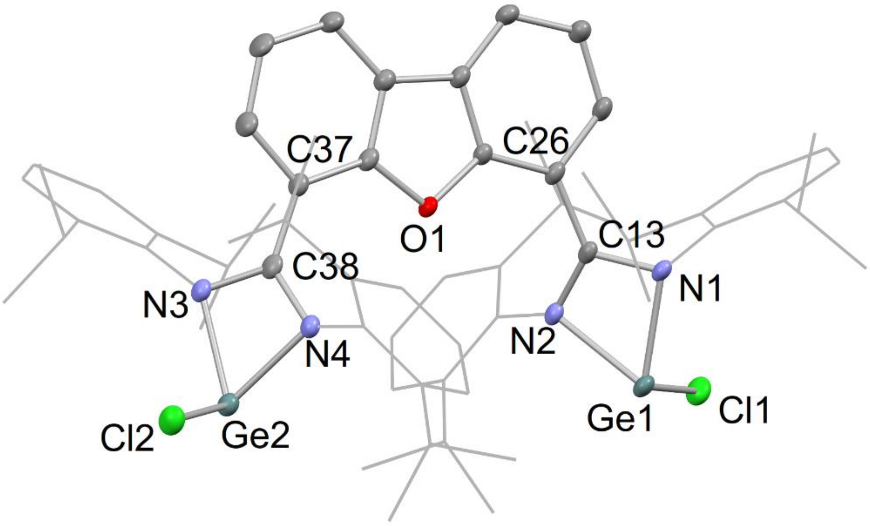

Figure S35. Molecular structure of :Ge(Cl)(μ-L^3)(Cl)Ge: **5**. Thermal ellipsoids drawn at the 25 % probability level. Hydrogen atoms omitted. Dip groups displayed as wireframe for clarity. Selected bond lengths (Å) and angles (°): Ge(1)-N(2) 2.030(3), Ge(1)-N(1) 2.036(3), Ge(1)-Cl(1) 2.2426(10), Ge(2)-N(4) 2.023(3), Ge(2)-N(3) 2.027(3), Ge(2)-Cl(2) 2.2512(10), N(2)-Ge(1)-N(1) 65.14(12), N(2)-Ge(1)-Cl(1) 95.97(8), N(1) Ge(1)-Cl(1) 99.36(8), N(4)-Ge(2)-N(3) 65.02(11), N(4)-Ge(2)-Cl(2) 95.93(8), N(3)-Ge(2)-Cl(2) 99.93(8).

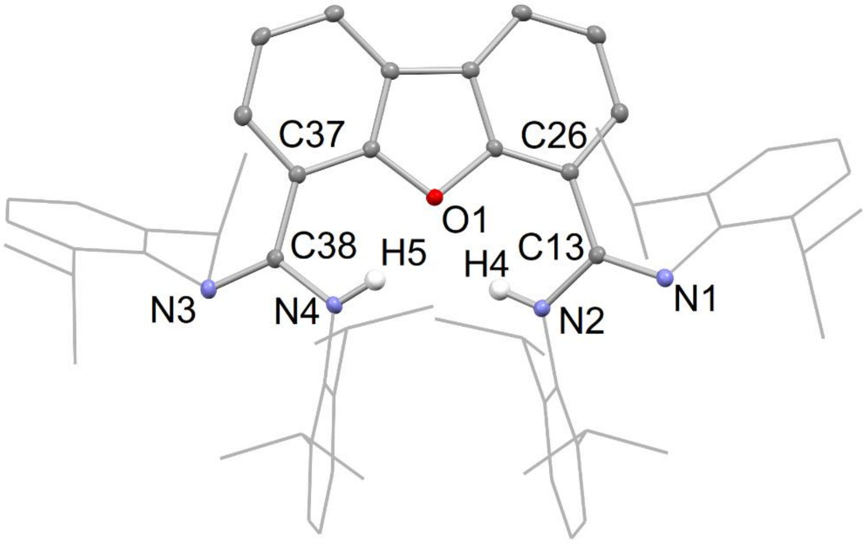

Figure S36. Molecular structure of 4,6-{[Dip(H)N](DipN)C}$_2$(μ-DBF), L^{3}H$_2$. Thermal ellipsoids drawn at the 25 % probability level. Hydrogen atoms, except amine protons, omitted. Dip groups displayed as wireframe for clarity. Selected bond lengths (Å) and angles (°): N(1)-C(13) 1.281(3), N(2)-C(13) 1.373(3), N(3)-C(38) 1.279(3), N(4)-C(38) 1.372(3), N(1)-C(13)-N(2) 120.24(19), N(3)-C(38)-N(4) 119.13(19).

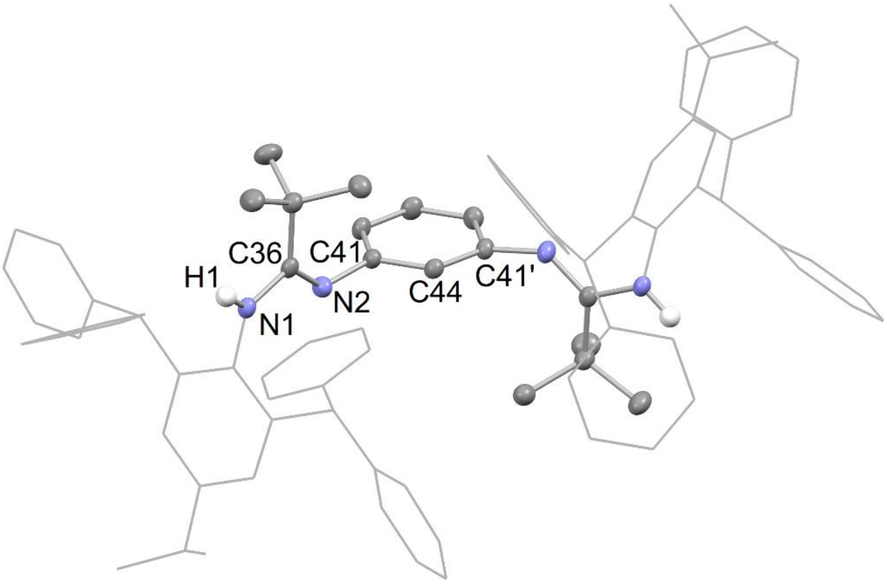

Figure S37. Molecular structure of 1,3-{Ar†N(H)C(Bu^{t})N}$_2$(μ-C$_6$H$_4$), L^{4}H$_2$. Thermal ellipsoids drawn at the 25 % probability level. Hydrogen atoms, except amine protons, omitted. Ar† groups displayed as wireframe for clarity. Selected bond lengths (Å) and angles (°): N(1)-C(36) 1.345(3), N(2)-C(36) 1.301(3), N(2)-C(41) 1.408(3), N(2)-C(36)-N(1) 116.82(19).

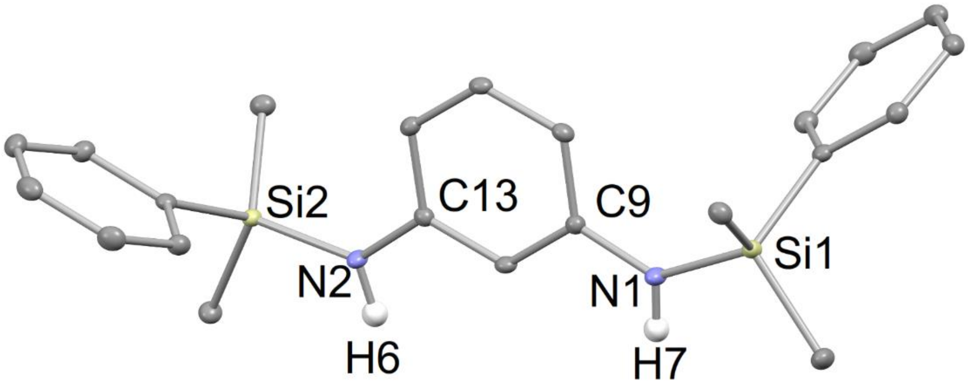

Figure S38. Molecular structure of 1,3-{N(H)(SiMe$_2$Ph)}$_2$(μ-C$_6$H$_4$), L^{4}H$_2$. Thermal ellipsoids drawn at the 25 % probability level. Hydrogen atoms, except amine protons, omitted. Selected bond lengths (Å) and angles (°): Si(1)-N(1) 1.7327(12), N(1)-C(9) 1.3986(18), Si(2)-N(2) 1.7328(12), N(2)-C(13) 1.3976(17), C(9)-N(1)-Si(1) 131.21(10), C(13)-N(2)-Si(2) 130.94(10).

3. References

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