Facile Activation of Inert Small Molecules using a 1,2-Disilylene

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Supplementary Information (26 pages)

Contents

1. Experimental

General considerations.

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Pentane was distilled over Na/K alloy (50:50), while hexane and toluene were distilled over molten potassium. ^{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 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 $[\{ArC(NDip)_2\}E]_2$ (E = Si or Ge) were prepared by literature procedures.[1] Gaseous reagents were dried over P_2O_5 prior to use. All other reagents were used as received.

Synthesis of $[\{ArC(NDip)_2\}Si(\mu\text{-}CNBu^t)]_2$, 3. To a solution of **1** (100 mg, 0.10 mmol) in pentane (10 mL), was added Bu^tNC (23 μL, 0.20 mmol) at room temperature. The reaction mixture was stirred for 30 minutes and then concentrated to ~5 mL. Storage of the mixture at room temperature for 2 days led to the deposition of **3** as dark red colored crystals (58 mg, 50 %). M.p. 130-134 °C (decomp.); ^{1}H NMR (400 MHz, toluene-d_8, 233 K) δ = -0.18 (d, $^3J_{HH}$ = 6.3 Hz, 6H, CH(CH_3)$_2$), -0.10 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH(CH_3)$_2$), 0.56 (d, $^3J_{HH}$ = 6.7 Hz, 6H, CH(CH_3)$_2$), 0.77 (s, 18H, C(CH_3)$_3$), 1.31 (d, $^3J_{HH}$ = 6.5 Hz, 6H, CH(CH_3)$_2$), 1.39 (2 overlapping d, 12H, CH(CH_3)$_2$), 1.49 (s, 18H, CNC(CH_3)$_3$), 1.57 (d, $^3J_{HH}$ = 6.7 Hz, 6H, CH(CH_3)$_2$), 1.74 d, $^3J_{HH}$ = 6.4 Hz, 6H, CH(CH_3)$_2$), 2.98 (m, 2H, CH(CH$_3$)$_2$), 3.37 (m, 2H, CH(CH$_3$)$_2$), 4.01 (m, 2H, CH(CH$_3$)$_2$), 4.72 (m, 2H, CH(CH$_3$)$_2$), 6.51 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar-H), 6.56 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar-H), 6.82 (d, $^3J_{HH}$ = 7.8 Hz, 4H, Ar-H), 6.88 (d, $^3J_{HH}$ = 8.2 Hz, 4H, Ar-H), 7.03-7.27 (m, 7H, Ar-H), 7.60 (d, $^3J_{HH}$ = 8.1 Hz, 1H, Ar-H); $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6, 298 K) δ = 28.1, 29.1 (CH(CH$_3$)$_2$), 30.3, 30.7 (CH(CH$_3$)$_2$), 30.8 (C(CH$_3$)$_3$), 31.0 (CNC(CH$_3$)$_3$), 34.8 (C(CH$_3$)$_3$), 55.3 (CNC(CH$_3$)$_3$), 124.1, 125.7, 127.7, 128.4, 128.5, 130.9, 146.3, 152.7 (Ar-C), 155.8 (NCN), 172.0 (CNC(CH$_3$)$_3$); $^{29}Si\{^{1}H\}$ NMR (80 MHz, C_6D_6, 298 K), δ = -46.3; IR ν/cm^{-1} (Nujol): 1606 (w), 1565 (w), 1267 (w), 1226 (w), 1183 (s), 1132 (w), 1115 (w), 1072 (w), 1020 (m), 982 (m), 933 (m), 840 (vs), 801 (w), 777 (vs),751 (m), 696 (s), 676 (s); anal. calc. for $C_{80}H_{112}N_6Si_2$·: C 79.15 %, H 9.30 %, N 6.92 %, found: C 79.50 %, H 9.07 %, N 6.30 %.

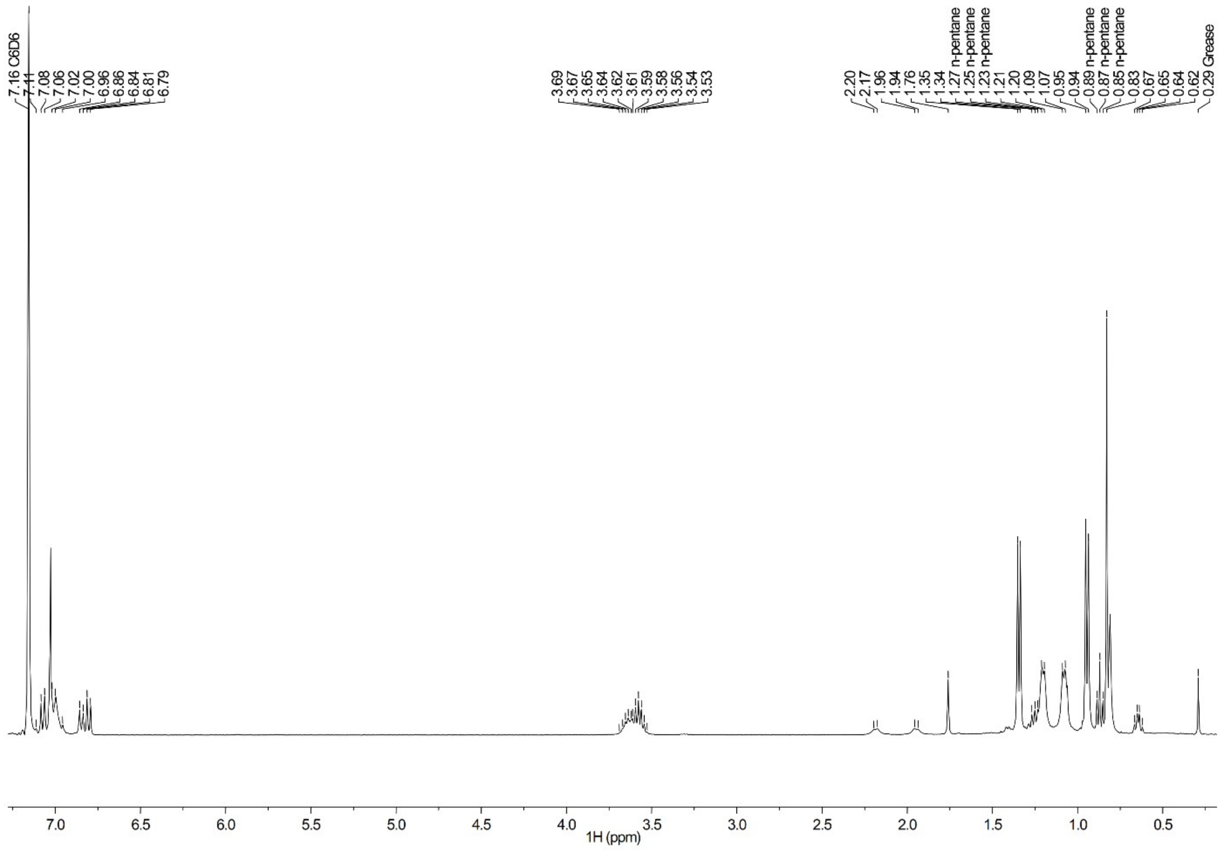


Figure S1. ^{1}H NMR spectrum (400 MHz, 233 K, toluene-d_8) of **3** (LH = ArC(NDip){N(H)Dip}).

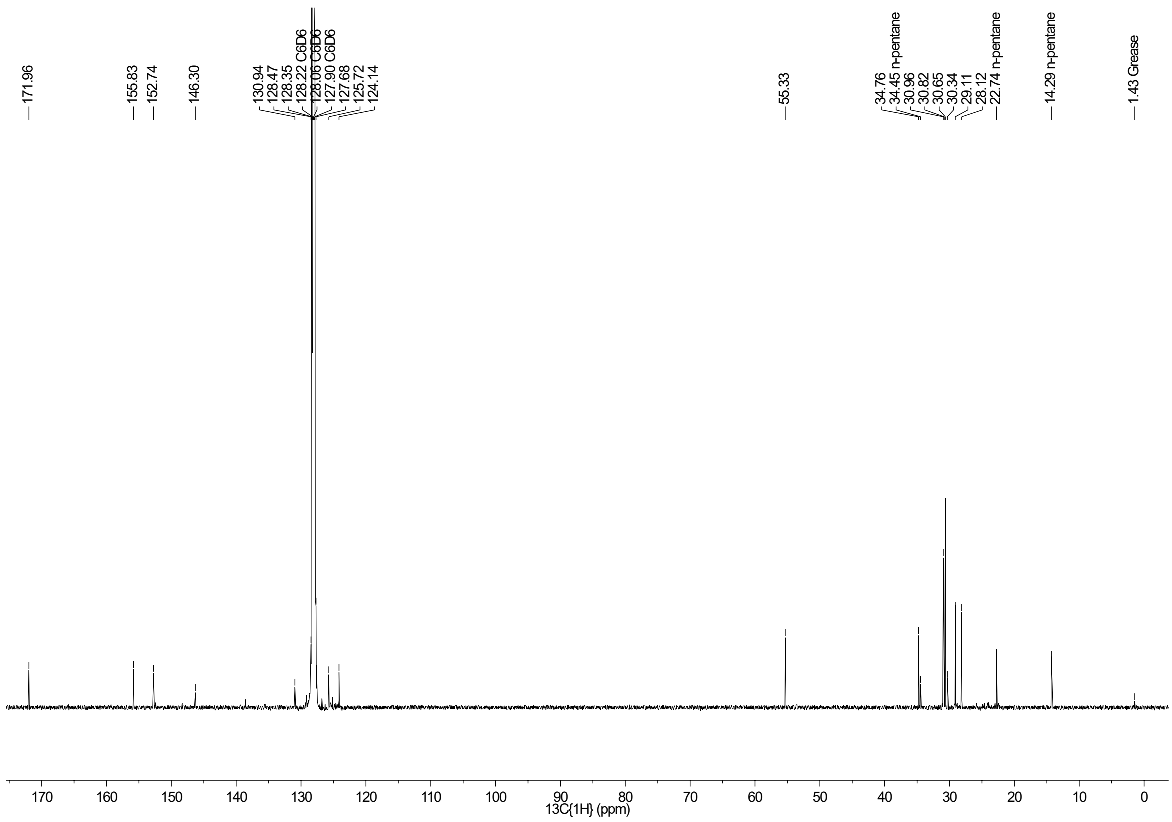


Figure S2. $^{13}C\{^1H\}$ NMR spectrum (151 MHz, 298 K, C_6D_6) of **3**.

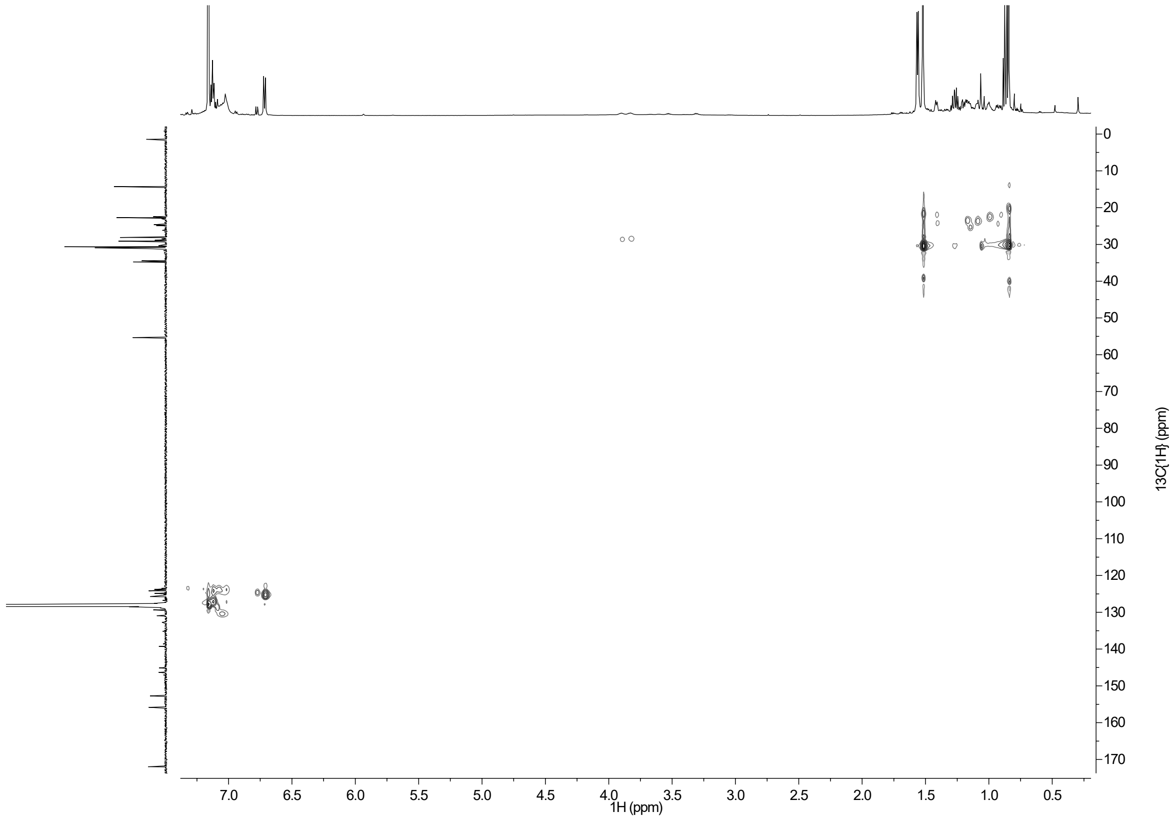


Figure S3. HSQC spectrum ([1]H: 600 MHz; [13]C: 151 MHz, 298 K, C_6D_6) of **3**.

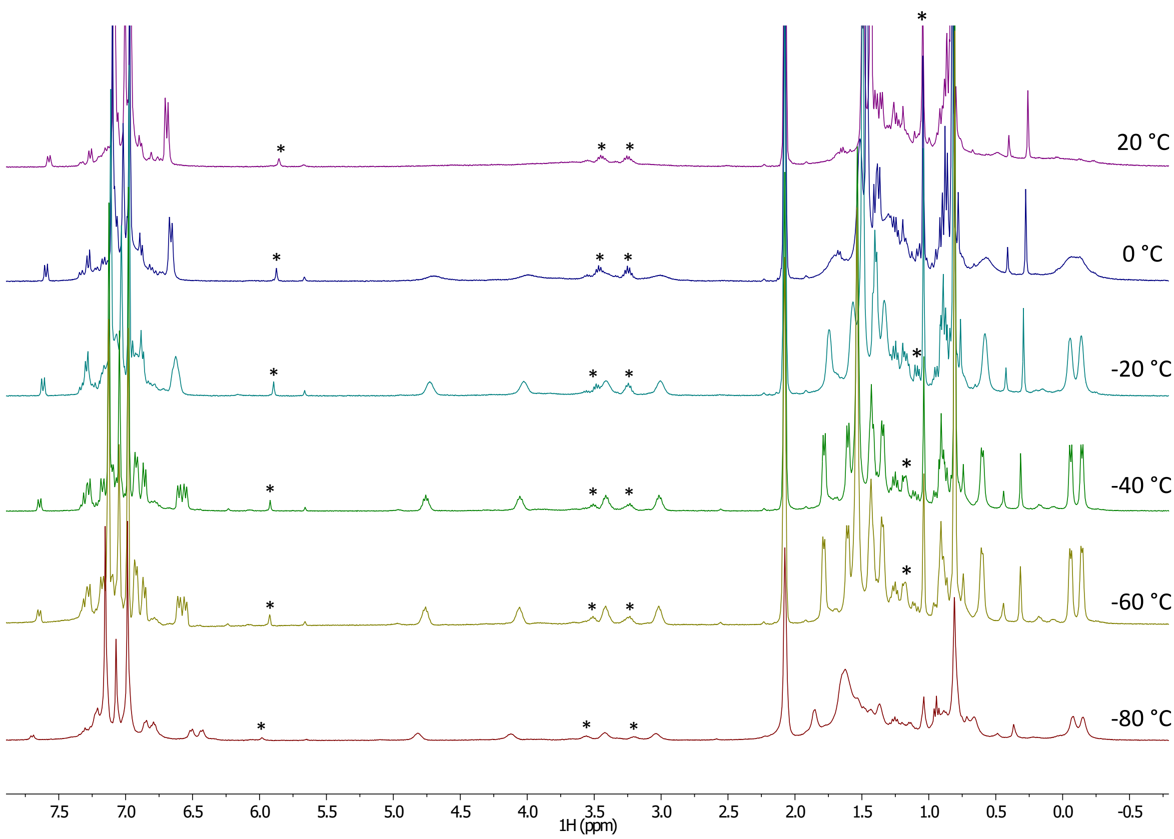


Figure S4. Variable temperature [1]H NMR spectrum (400 MHz, toluene-d_8) of **3** (* = ArC(NDip){N(H)Dip}).

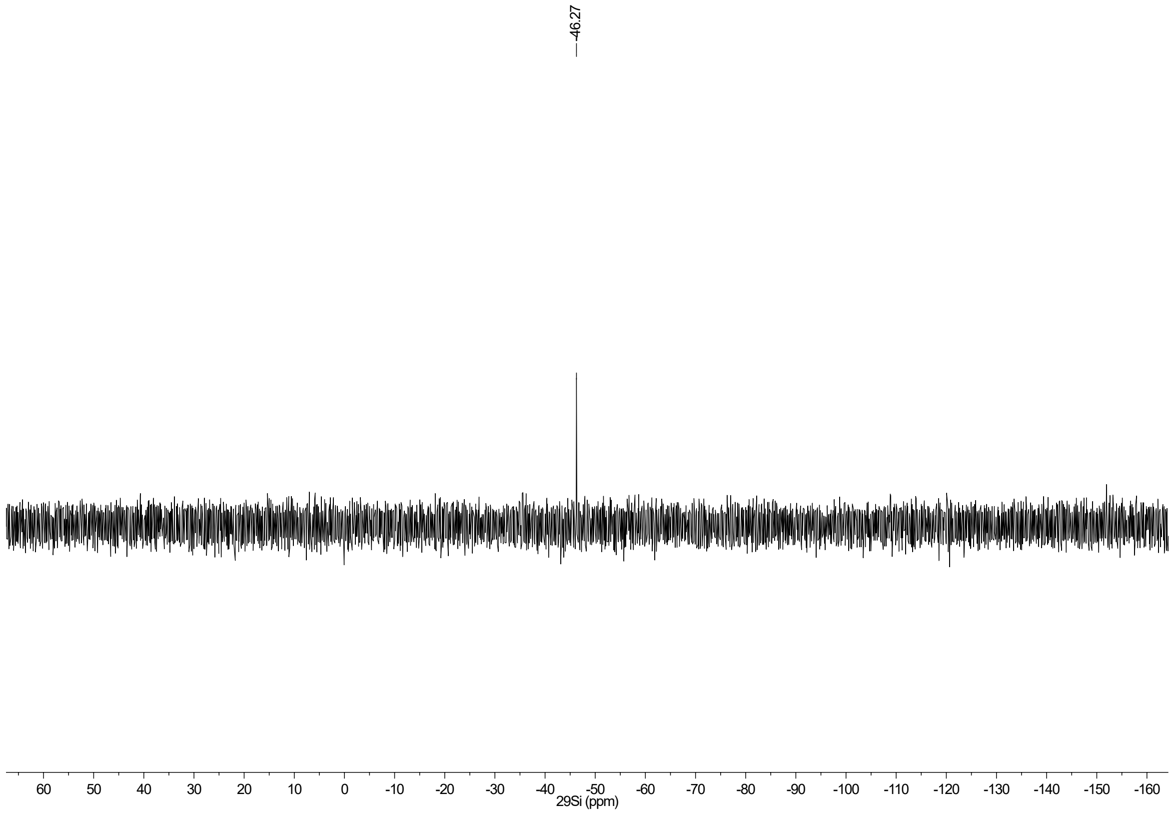


Figure S5. $^{29}Si\{^1H\}$ NMR spectrum (80 MHz, 298 K, C_6D_6) of **3**.

Synthesis of [{ArC(NDip)$_2$}(Br)Si(μ-CNBu^t)]$_2$, 4. To a solution of **1** (80 mg, 0.08 mmol) in toluene (15 mL) was added Bu^{t}NC (18 μL, 0.16 mmol) at room temperature and the mixture stirred for 30 minutes. The mixture was then cooled to -30 °C and 1,2-dibromoethane (8 μL, 0.09 mmol) was added. The mixture was warmed to room temperature, stirred for 1.5 h, then filtered. The filtrate was concentrated to *ca*. 5mL and layered with pentane. Storage at room temperature for 5 days led to the deposition of **4** as yellow-orange crystals (65 mg, 62 %). M.p. 170-175 °C (decomp.); ^1H NMR (600 MHz, C_6D_6, 298 K) δ = 0.07 (d, $^3J_{HH}$ = 5.5 Hz, 3H, CH(CH_3)$_2$), 0.22 (br, 6H, CH(CH_3)$_2$), 0.25 (d, $^3J_{HH}$ = 6.1 Hz, 3H, CH(CH_3)$_2$), 0.78 (s, 9H, C(CH_3)$_3$), 0.88 (s, 9H, C(CH_3)$_3$), 1.15 (d, $^3J_{HH}$ = 5.1 Hz, 3H, CH(CH_3)$_2$), 1.24 (d, $^3J_{HH}$ = 5.3 Hz, 3H, CH(CH_3)$_2$), 1.28 (d, $^3J_{HH}$ = 5.5 Hz, 3H, CH(CH_3)$_2$), 1.31 (d, $^3J_{HH}$ = 6.0 Hz, 3H, CH(CH_3)$_2$), 1.33 (s, 9H, CNC(CH_3)$_3$), 1.40 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CH(CH_3)$_2$), 1.43 (d, $^3J_{HH}$ = 5.6 Hz, 3H, CH(CH_3)$_2$), 1.46 (d, $^3J_{HH}$ = 5.8 Hz, 3H, CH(CH_3)$_2$), 1.51 (d, $^3J_{HH}$ = 6.0 Hz, 3H, CH(CH_3)$_2$), 1.53 (d, $^3J_{HH}$ = 5.1 Hz, 3H, CH(CH_3)$_2$), 1.62-1.65 (2 br overlapping d, 6H, CH(CH_3)$_2$), 1.76 (br., 12H, CH(CH_3)$_2$, CNC(CH_3)$_3$), 3.06 (br m, 1H, CH(CH$_3$)$_2$), 3.10-3.16 (2 br overlapping m, 2H, CH(CH$_3$)$_2$), 3.22 (br m, 1H, CH(CH$_3$)$_2$), 3.79 (br m, 1H, CH(CH$_3$)$_2$), 4.19 (br m, 1H, CH(CH$_3$)$_2$), 4.47 (br m, 1H, CH(CH$_3$)$_2$), 4.75 (br m, 1H, CH(CH$_3$)$_2$), 6.77 (d, $^3J_{HH}$ = 8.5 Hz, 4H, Ar-H), 6.89-7.29 (m, 15H, Ar-H), 7.43 (d, $^3J_{HH}$ = 7.7 Hz, 1H, Ar-H); $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6, 298 K) δ = 22.5, 22.7, 23.1, 23.5, 24.0, 24.1, 24.7, 24.9, 25.0, 25.1, 2×25.3, 25.7, 26.2, 27.3, 27.6

(CH(CH_3)$_2$), 27.9, 28.1, 28.2, 28.4, 28.6, 28.7, 28.9, 29.1 (*C*H(CH_3)$_2$), 30.5, 30.9 (C(*C*H_3)$_3$), 2×31.1 (CNC(*C*H_3)$_3$), 34.3, 34.7 (*C*(CH_3)$_3$), 60.3, 61.6 (CN*C*(CH_3)$_3$), 123.5, 123.6, 2×123.9, 124.0, 124.4, 2×124.6, 124.9, 125.0, 125.3, 125.9, 127.3, 127.5, 2×127.6, 128.4, 2×128.5, 128.8, 129.1, 132.3, 136.0, 137.6, 139.7, 141.7, 142.0, 144.5, 144.7, 145.6, 145.9, 146.3, 149.2, 149.3, 151.7, 156.2 (Ar-*C*), 160.3, 171.1 (N*C*N), 185.7, 192.3 (*C*NC(CH_3)$_3$); ^{29}Si{^{1}H} NMR (80 MHz, C_6D_6, 298 K)*:* no signal observed due to the low solubility of the compound in common non-coordinating deuterated solvents; IR ν/cm^{-1} (Nujol): 1609 (s), 1262 (s), 1239 (m), 1206 (m), 1168 (w), 1136 (w), 1117 (m), 1095 (w), 1076 (vs), 1046 (w), 1017 (m), 981 (m), 950 (m), 934 (m), 865 (m), 835 (s), 802 (s), 785 (vs), 777 (s), 767 (s), 755 (m), 743 (w), 728 (s), 700 (s), 688 (m), 663 (s); a reproducible microanalysis for the compound could not be obtained due to the persistent presence of the protonated amidinate, ArC(NDip){N(H)Dip}, which could not be removed bt recrystallisation.

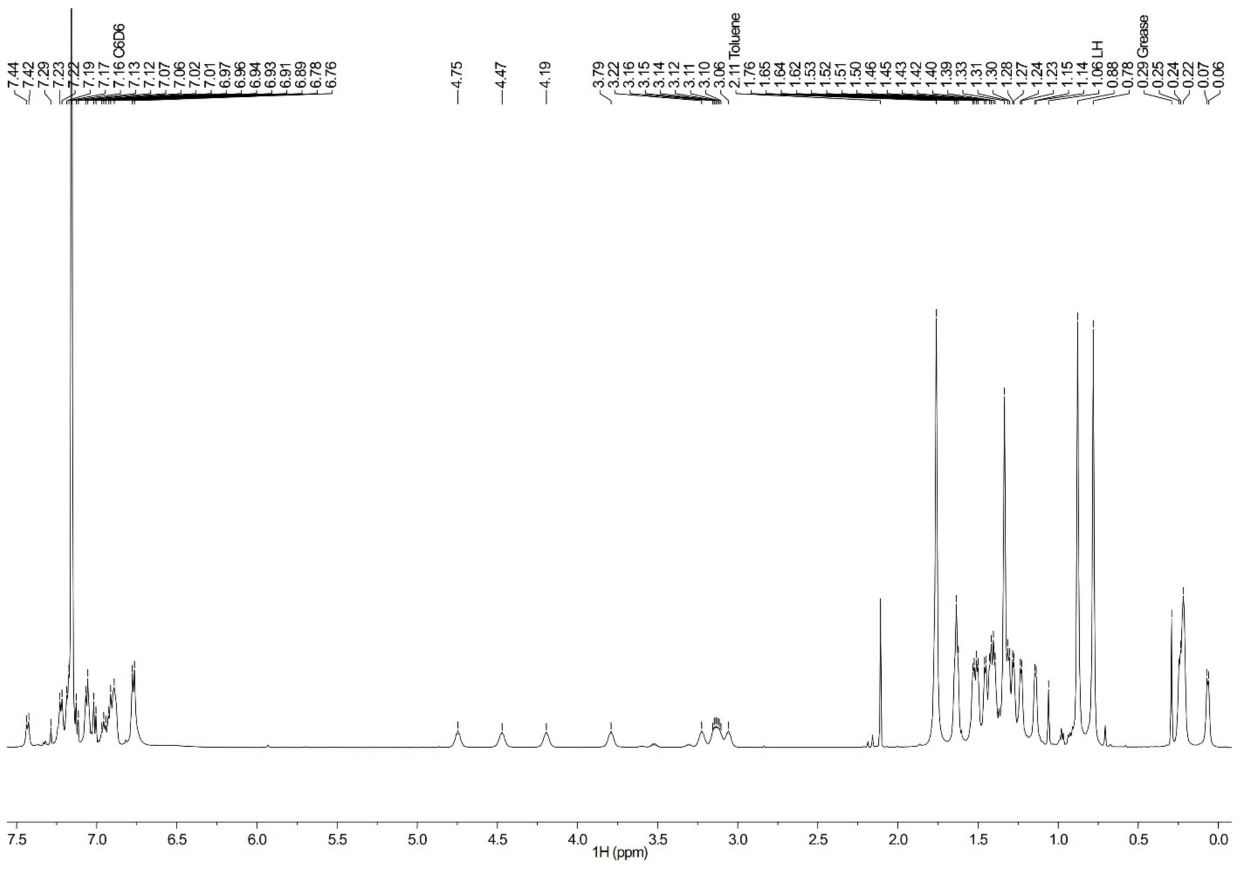


Figure S6. ^{1}H NMR spectrum (600 MHz, 298 K, C_6D_6) of **4** (LH = ArC(NDip){N(H)Dip}).

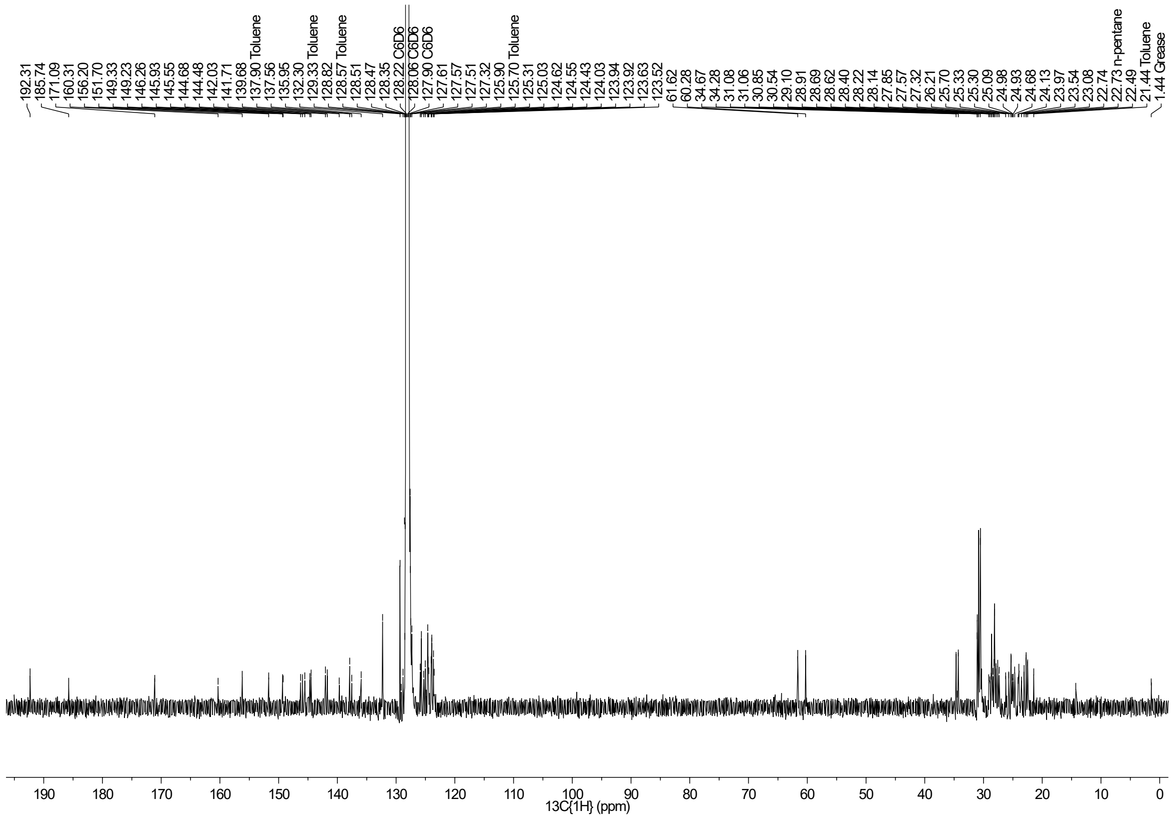


Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, 298 K, C_6D_6) of **4**.

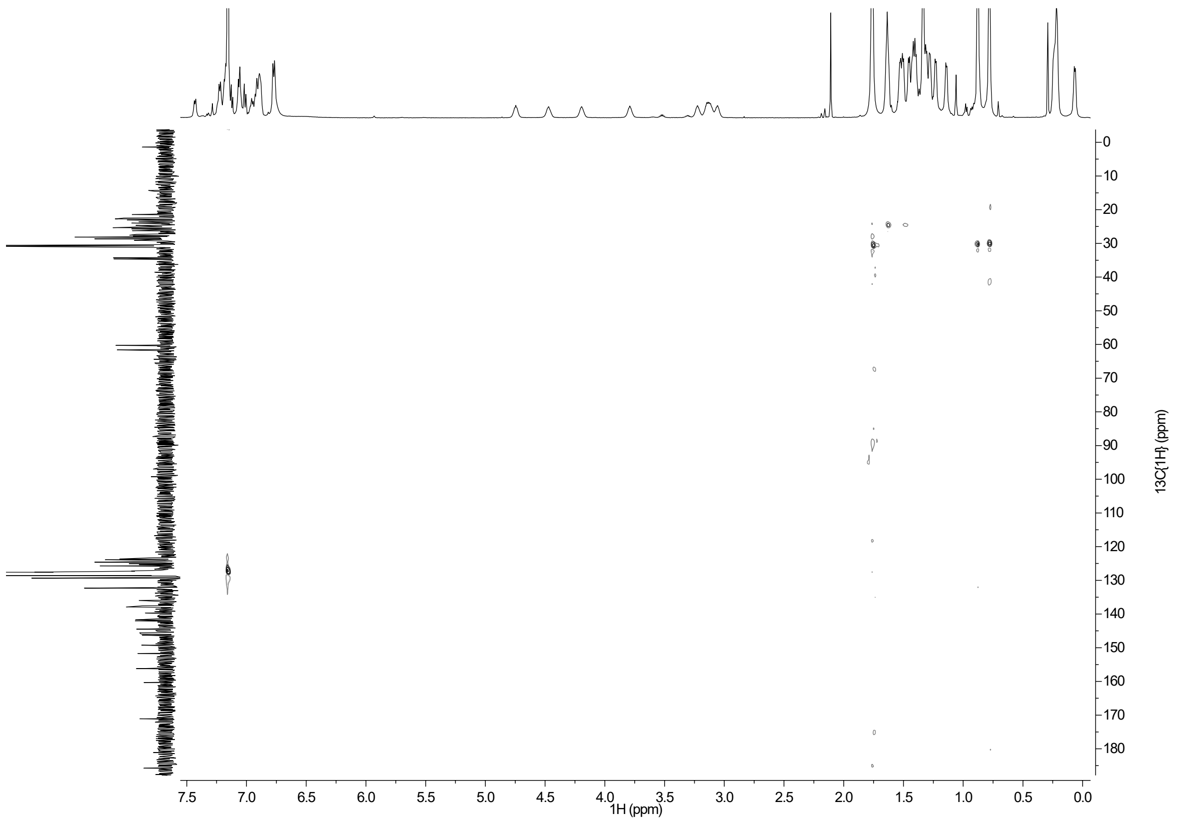


Figure S8. HSQC spectrum (^{1}H: 600 MHz; ^{13}C: 151 MHz, 298 K, C_6D_6) of **4**.

Synthesis of [{ArC(NDip)$_2$}Si(μ-C$_2$H$_4$)]$_2$, 5. A solution of **1** (150 mg, 0.14 mmol) in hexane (10 mL) was stirred under an atmosphere of dry C_2H_4 at room temperature for 1.5 h. All the volatiles were subsequently removed from the reaction mixture *in vacuo* and the residue was extracted in pentane (10 mL). The extract was filtered and the filtrate was concentrated to *ca.* 8 mL. Storage at room temperature for 1 day led to the deposition of **5** as light orange colored crystals. These were isolated and a second crop was obtained from the mother liquor (95 mg, 60 %). M.p. 122-126 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6, 298 K) δ 0.81 (s, 18H, C(C*H*$_3$)$_3$), 1.08 (d, br, $^3J_{HH}$ = 6.6 Hz, 24H, CH(C*H*$_3$)$_2$), 1.21 (d, br, $^3J_{HH}$ = 6.2 Hz, 24H, CH(C*H*$_3$)$_2$), 1.95 (br, 4H, SiC*H*$_2$), 2.19 (br, 4H, SiC*H*$_2$), 3.64 (sept, $^3J_{HH}$ = 6.2 Hz, 8H, C*H*(CH$_3$)$_2$), 6.83-7.14 (m, 20H, Ar-*H*); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K) δ = 17.2 (Si*C*H$_2$), 23.4, 25.5 (CH(*C*H$_3$)$_2$), 28.7 (*C*H(CH$_3$)$_2$), 30.8 (C(*C*H$_3$)$_2$), 31.0 (*C*(CH$_3$)$_3$), 123.7, 124.0, 124.5, 124.9, 125.9, 130.0. 130.4, 140.5, 143.7, 146.9 (Ar-*C*), N*C*N signal not observed; ^{29}Si{^{1}H} NMR (80 MHz, C_6D_6, 298 K) δ = 30.0; IR ν/cm^{-1} (Nujol): 1583 (vs), 1513 (m), 1200 (w), 1178 (m), 1129 (s), 1095 (s), 1056 (s), 1022 (w), 978 (m), 961 (s), 932 (w), 862 (w), 837 (vs), 788 (s), 766 (m), 747 (s), 723 (w), 701 (w), 663 (s); anal. calc. for $C_{74}H_{102}N_4Si_2$: C 80.52 %, H 9.31 %, N 5.08 %, found: C 79.53 %, H 9.21 %, N 4.89 %.

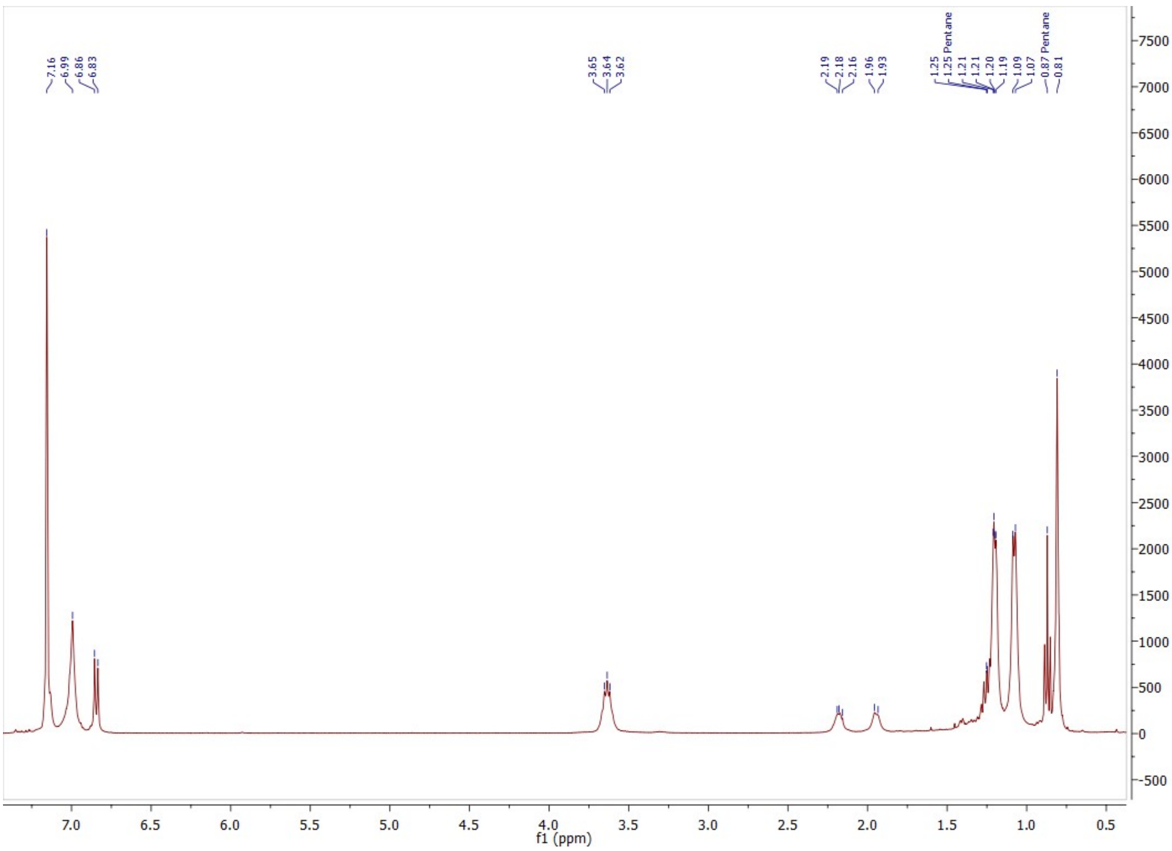


Figure S9. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of **5**.

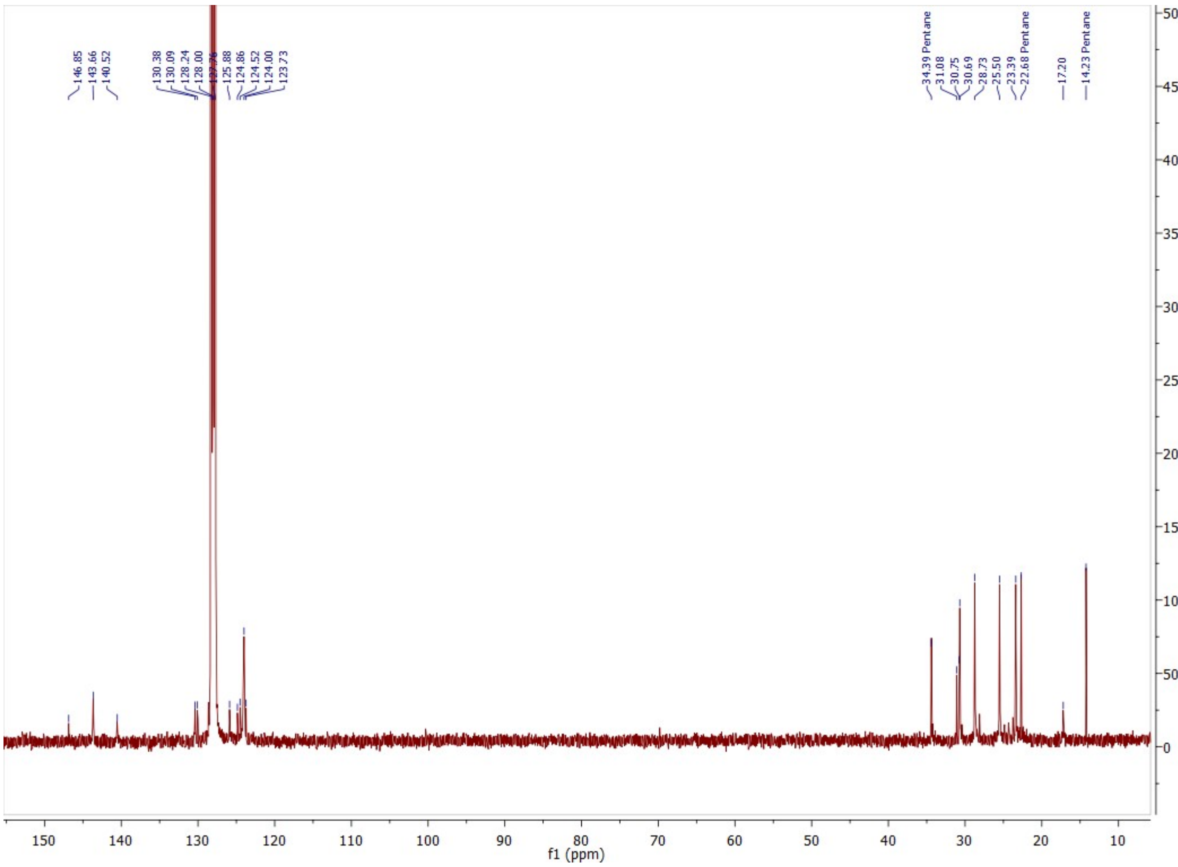


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of **5**.

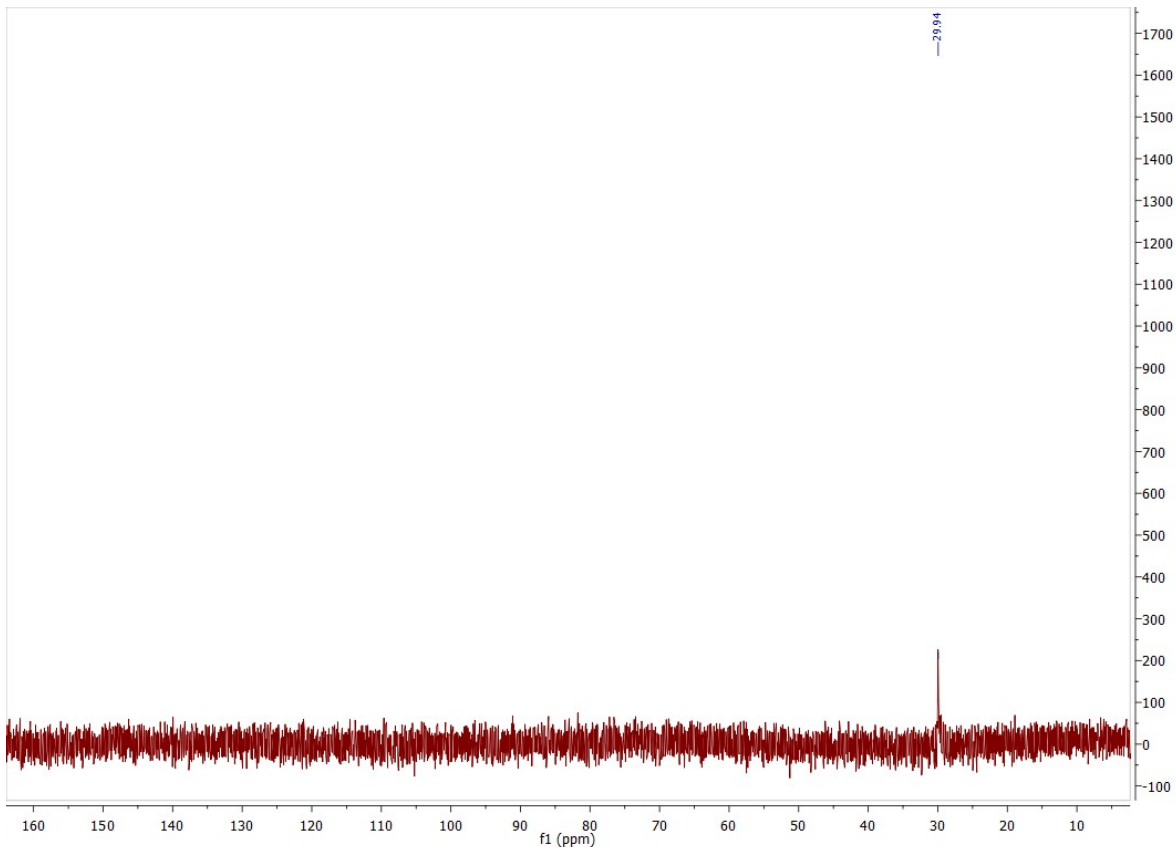


Figure S11. $^{29}Si\{^{1}H\}$ NMR spectrum (80 MHz, 298 K, C_6D_6) of **5**.

Synthesis of [{ArC(NDip)$_2$}Ge]$_2$(μ-C_2H_4), 7. A solution of **6** (80 mg, 0.07 mmol) in toluene (15 mL) was stirred under an atmosphere of dry C_2H_4 at room temperature for 1 h. All the volatiles were subsequently removed from the reaction mixture *in vacuo*. The residue was extracted in toluene (5 mL), filtered, the filtrate concentrated to *ca.*3 mL and layered with hexane. Storage at room temperature for 6-7 days led to the deposition of **7** as light orange crystals (45 mg, 55 %); M.p. 172-177 °C (decomp.); ^{1}H NMR (600 MHz, C_6D_6, 298 K) δ = 0.84 (s, 18H, C(CH_3)$_3$), 0.93 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.08 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(CH_3)$_2$), 1.18 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.44 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.67 (s, 4H, GeCH_2), 3.71 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, CH(CH$_3$)$_2$), 4.01 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, CH(CH$_3$)$_2$), 6.83 (d, $^3J_{HH}$ = 8.7 Hz, 4H, Ar-H), 7.00-7.06 (m, 12H, Ar-H), 7.18 (d, $^3J_{HH}$ = 8.6 Hz, 4H, Ar-H); ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K) δ = 2×23.1 (CH(CH$_3$)$_2$), 26.1 (CH(CH$_3$)$_2$), 26.2 (GeCH$_2$), 26.5 (CH(CH$_3$)$_2$), 28.8, 28.9 (CH(CH$_3$)$_2$), 30.8 (C(CH$_3$)$_3$), 34.6 (C(CH$_3$)$_3$), 124.0, 124.1, 125.1, 126.1, 127.6, 128.4, 128.5, 130.1, 139.4, 143.9, 144.4, 153.7, (Ar-C), 163.3 (NCN); IR ν/cm^{-1} (Nujol): 1617 (s), 1512(w), 1192 (m), 1096 (s), 1019 (s), 965 (w), 800 (vs), 778 (s), 691 (s); a reproducible microanalysis could not be obtained for the compound due to the persistent presence of trace impurities, which could not be removed.

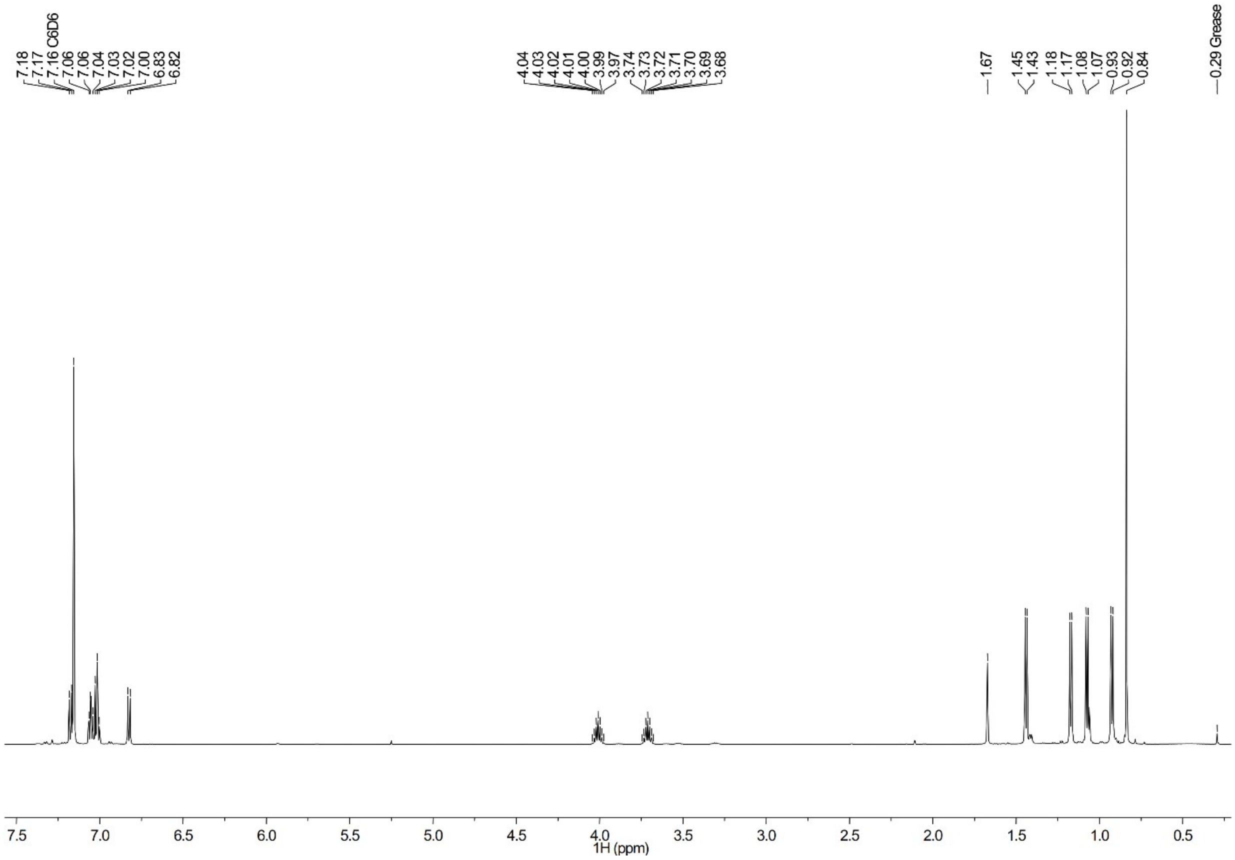


Figure S12. ^{1}H NMR spectrum (600 MHz, 298 K, C_6D_6) of **7**.

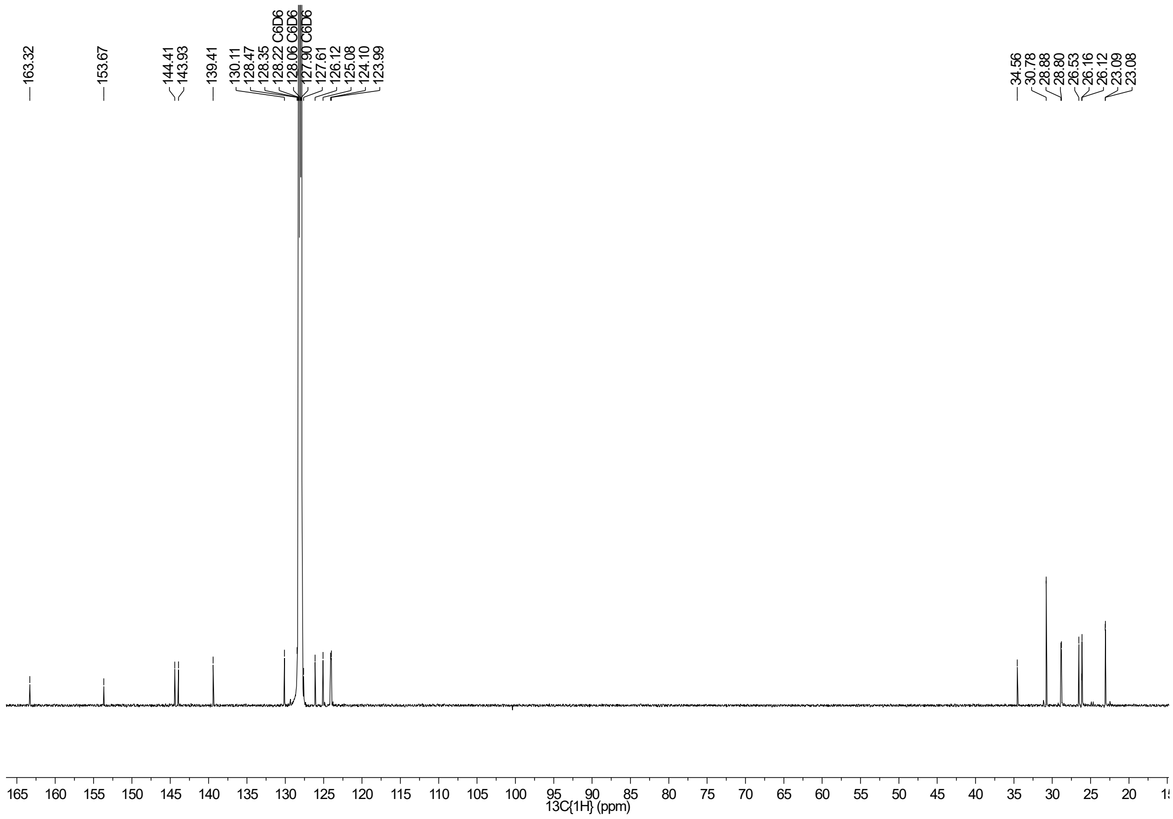


Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, 298 K, C_6D_6) of **7**.

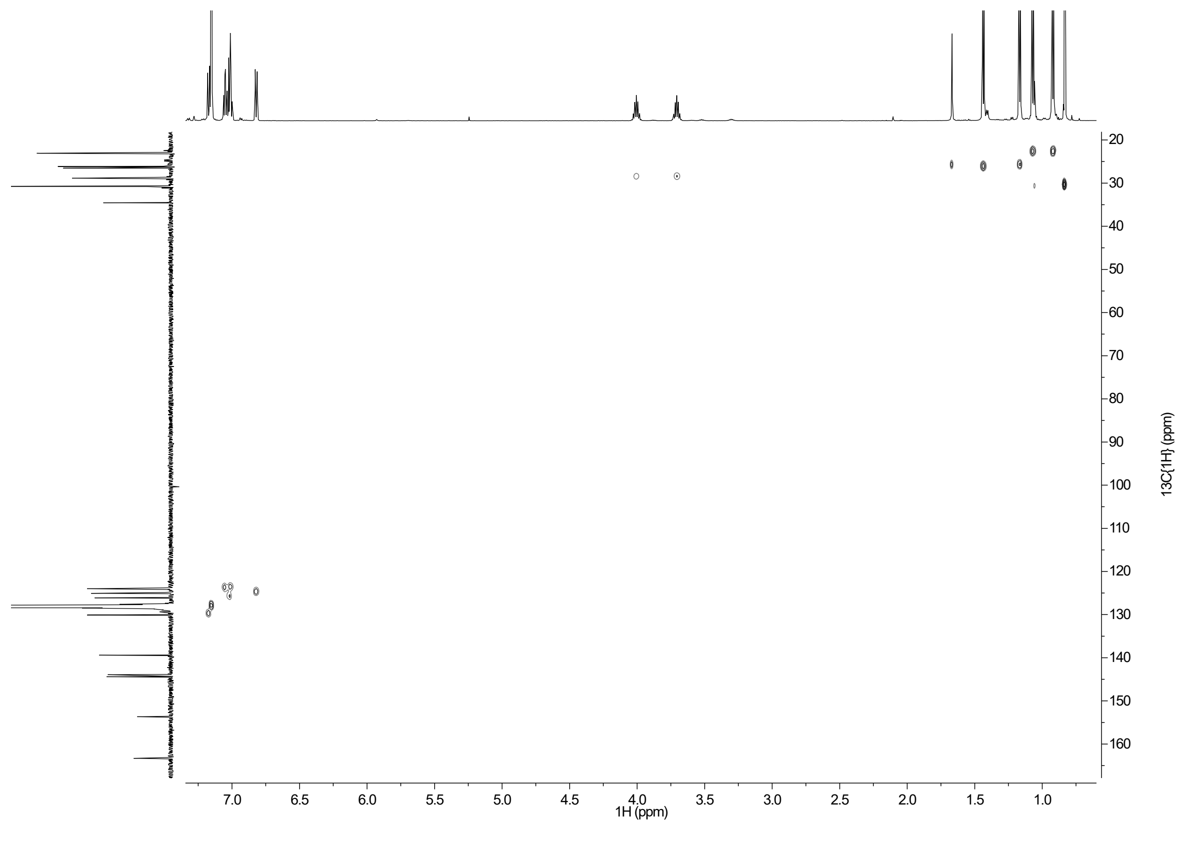


Figure S14. HSQC spectrum (^{1}H: 600 MHz; ^{13}C: 151 MHz, 298 K, C_6D_6) of **7**.

Synthesis of {ArC(NDip)$_2$}Si(μ-CO_3)$_2$(μ-O)Si{(NDip)$_2$CAr}, 10. A solution of **1** (100 mg, 0.10 mmol) in toluene (10 mL) was stirred under an atmosphere of dry CO_2 at room temperature for 1.5 h. All the volatiles were subsequently removed from the reaction mixture *in vacuo* and the residue was extracted in hexane (10 mL). The extract was filtered and the filtrate was concentrated to *ca.* 8 mL. Storage at -30 ºC for two days led to the deposition of **10** as colourless crystals. These were isolated and a second crop obtained from the mother liquor (75 mg, 66 %). M.p. > 260 °C; ^{1}H NMR (400 MHz, C_6D_6, 298 K) δ = 0.74 (s, 18H, C(CH_3)$_3$), 0.99 (d, $^3J_{HH}$ = 6.8 Hz, 24H, CH(CH_3)$_2$), 1.33 (d, $^3J_{HH}$ = 6.7 Hz, 24H, CH(CH_3)$_2$), 3.79 (sept, $^3J_{HH}$ = 6.8 Hz, 8H, CH(CH$_3$)$_2$), 6.80 (d, $^3J_{HH}$ = 8.7 Hz, 4H, Ar-H), 6.99-7.09 (m, 12H, Ar-H), 7.28 (d, $^3J_{HH}$ = 8.7 Hz, 4H, Ar-H); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K) δ = 23.7, 25.3 (CH(CH$_3$)$_2$), 29.1 (CH(CH$_3$)$_2$), 30.5 (C(CH$_3$)$_3$), 34.8 (C(CH$_3$)$_3$), 122.6, 124.7, 125.3, 128.2, 131.3, 135.4, 146.0, 147.8 (Ar-C), 157.3 (NCN), 173.6 (CO$_3$); ^{29}Si{^{1}H} NMR (80 MHz, C_6D_6, 298 K) δ = -121.1; IR ν/cm^{-1} (Nujol): 1756 (vs), 1581 (s), 1133 (m), 1099 (w), 1072 (s), 992 (m), 933 (w), 880 (vs), 822 (m), 785 (s), 755 (m), 726 (s); anal. calc. for $C_{72}H_{94}N_4O_7Si_2$: C 73.06 %, H 8.00 %, N 4.73 %, found: C 72.67 %, H 8.20 %, N 4.66 %.

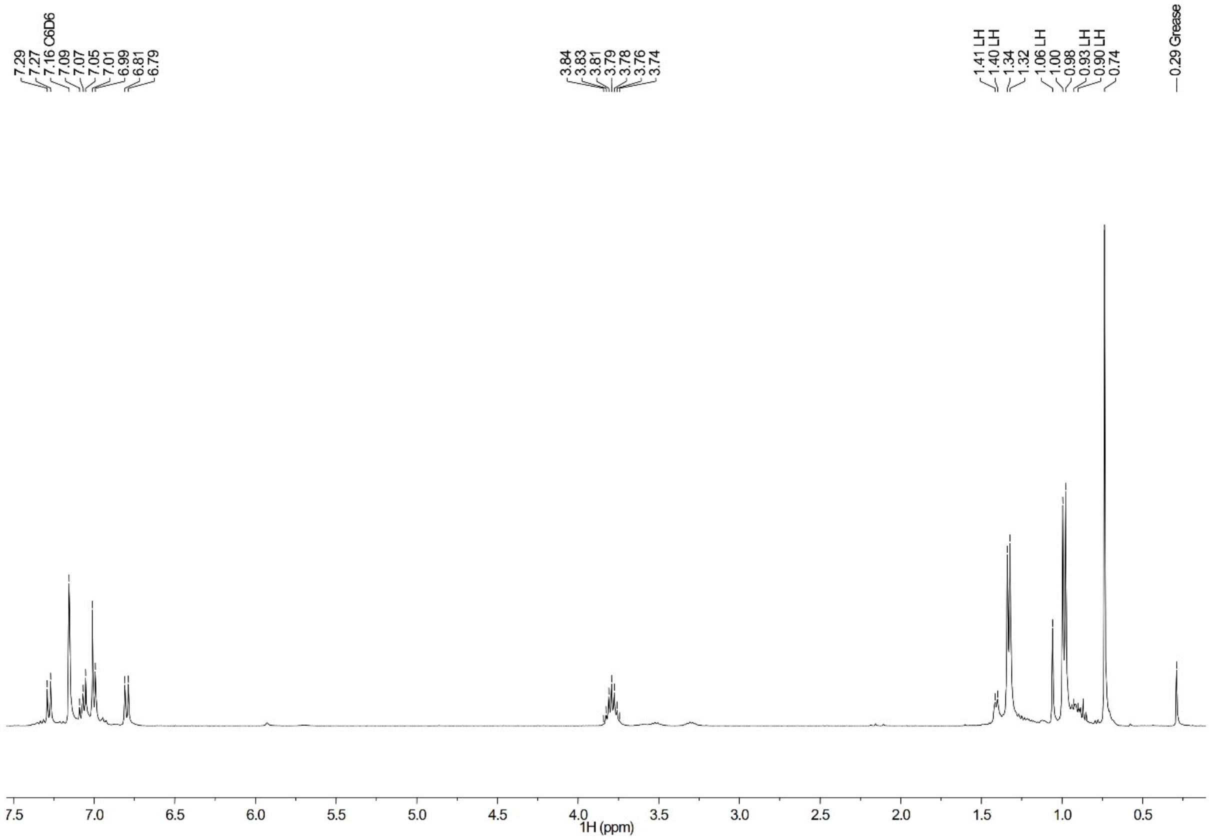


Figure S15. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of **10** (LH = ArC(NDip){N(H)Dip}).

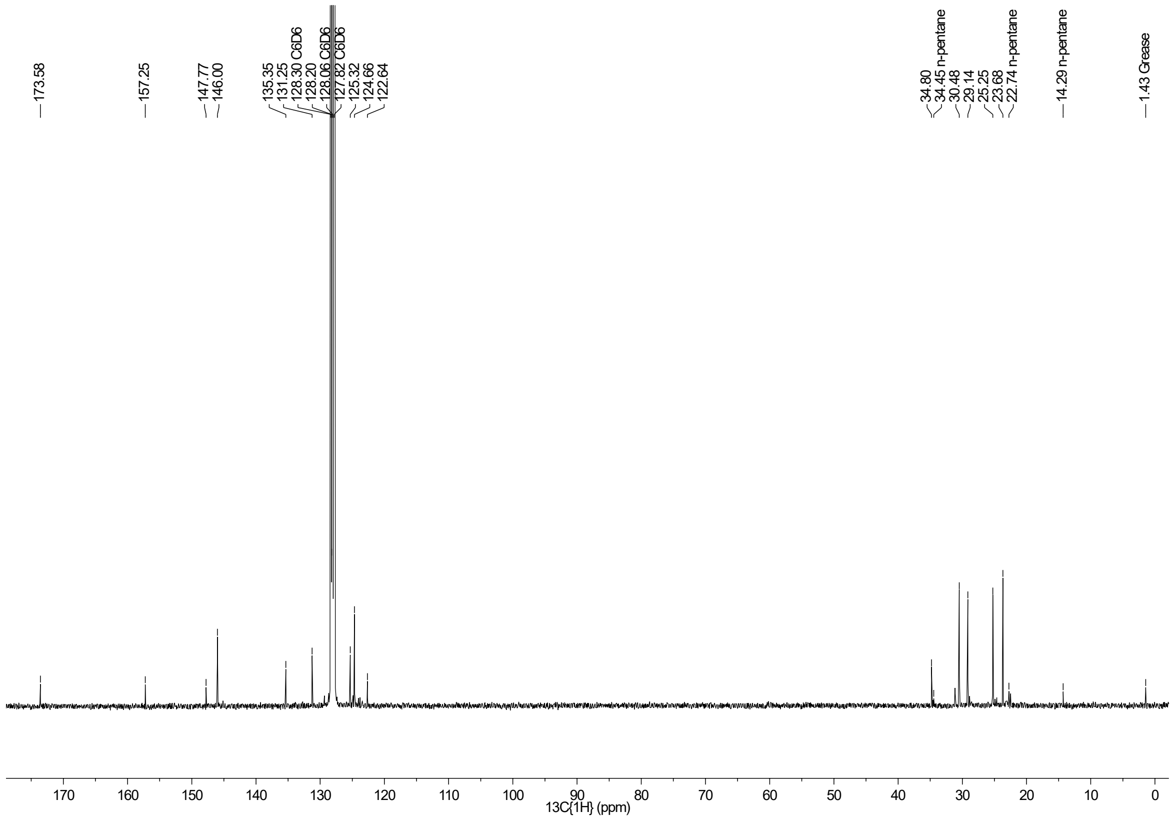


Figure S16. $^{13}C\{^1H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of **10**.

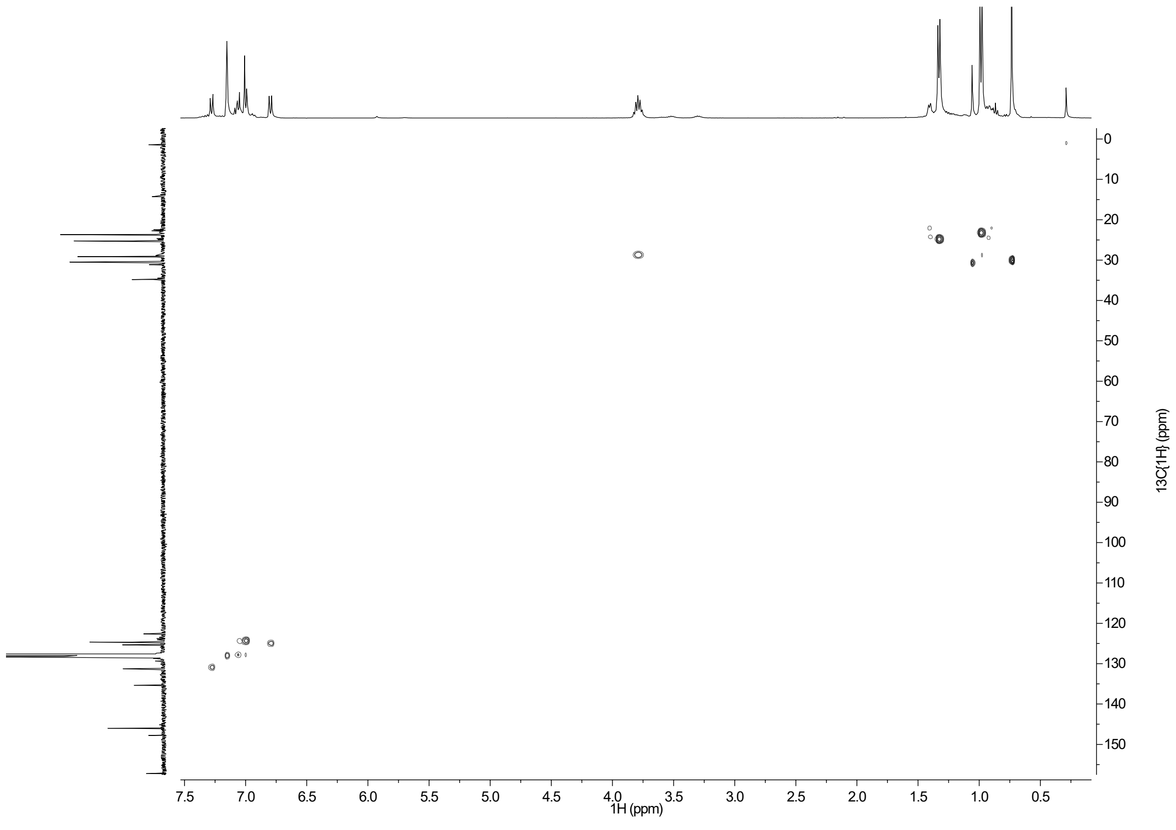


Figure S17. HSQC spectrum (^1H: 400 MHz; ^{13}C: 101 MHz, 298 K, C_6D_6) of **10**.

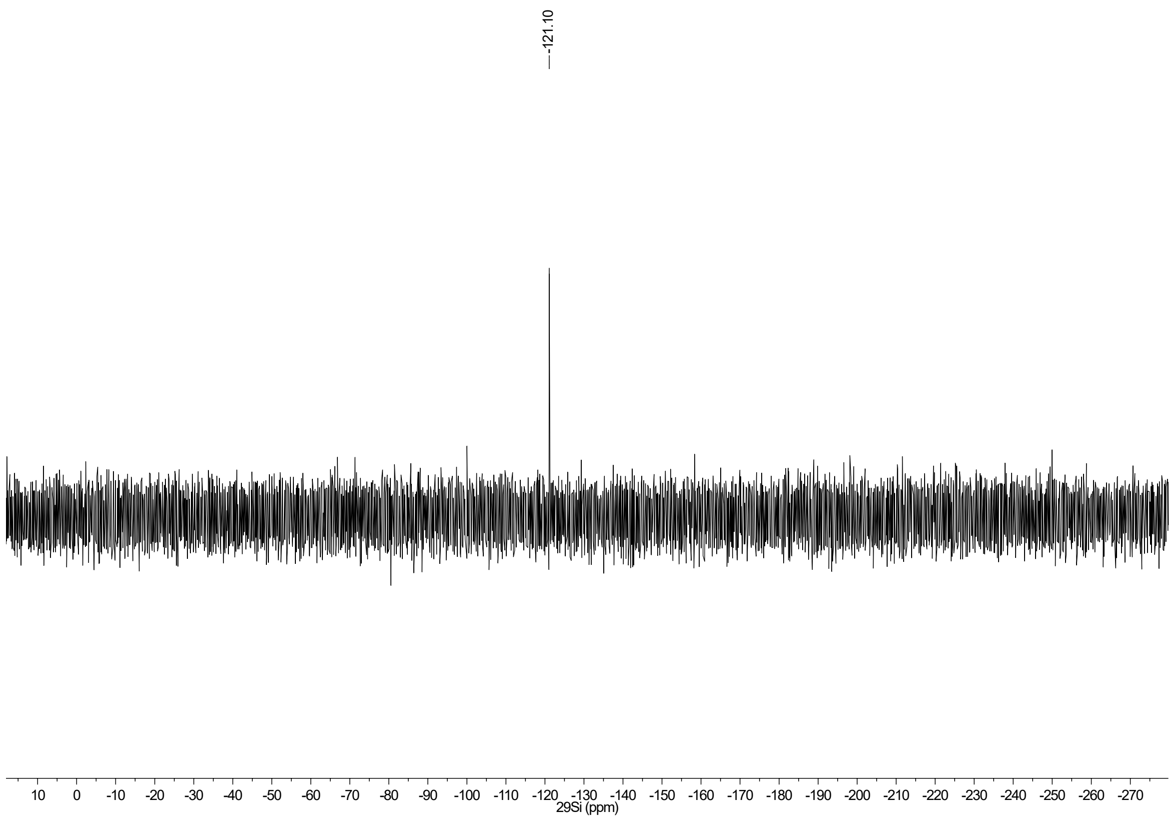


Figure S18. $^{29}Si\{^1H\}$ NMR spectrum (80 MHz, 298 K, C_6D_6) of **10**.

Synthesis of [{ArC(NDip)$_2$}(HO)Si(μ-O)]$_2$, 11. A solution of **1** (100 mg, 0.10 mmol) in hexane (15 mL) was stirred under an atmosphere of dry N_2O at room temperature for 2 h. The reaction mixture was filtered and the filtrate was concentrated to *ca.* 8 mL. Storage at -30 ºC for 2 days led to the deposition of **11** as colourless crystals (50 mg, 47 %). M.P. 198-201 °C (decomp.); ^1H NMR (400 MHz, C_6D_6, 298 K) δ = 0.80 (s, 18H, C(C*H*$_3$)$_3$), 1.00 (d, $^3J_{HH}$ = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 1.32 (d, $^3J_{HH}$ = 6.7 Hz, 24H, CH(C*H*$_3$)$_2$), 2.64 (s, 2H, O*H*), 3.89 (sept, $^3J_{HH}$ = 6.8 Hz, 8H, C*H*(CH$_3$)$_2$), 6.77 (d, $^3J_{HH}$ = 8.7 Hz, 4H, Ar-*H*), 7.08-7.14 (m, 12H, Ar-*H*), 7.33 (d, $^3J_{HH}$ = 8.6 Hz, 4H, Ar-*H*); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K), δ = 23.8, 25.1 (CH(*C*H$_3$)$_2$), 28.8 (*C*H(CH$_3$)$_2$), 30.7 (C(*C*H$_3$)$_3$), 34.7 (*C*(CH$_3$)$_3$), 124.2, 124.8, 125.2, 126.9, 130.9, 137.2, 145.4, 155.6 (Ar-*C*), 170.6 (N*C*N); $^{29}Si\{^1H\}$ NMR (80 MHz, C_6D_6, 298 K), δ = -102.4; IR ν/cm^{-1} (Nujol): 3653 (br m, OH), 1609 (m), 1573 (s), 1542 (w), 1175 (w), 1132 (w), 1099 (m), 1052 (m), 985 (m), 932 (m), 865 (s), 835 (s), 804 (vs), 781 (s), 750 (s), 725 (vs), 696 (s); anal. calc. for $C_{70}H_{96}N_4O_4Si_2$: C 75.49 %, H 8.69 %, N 5.03 %, found: C 74.97 %, H 8.65 %, N 5.01 %.

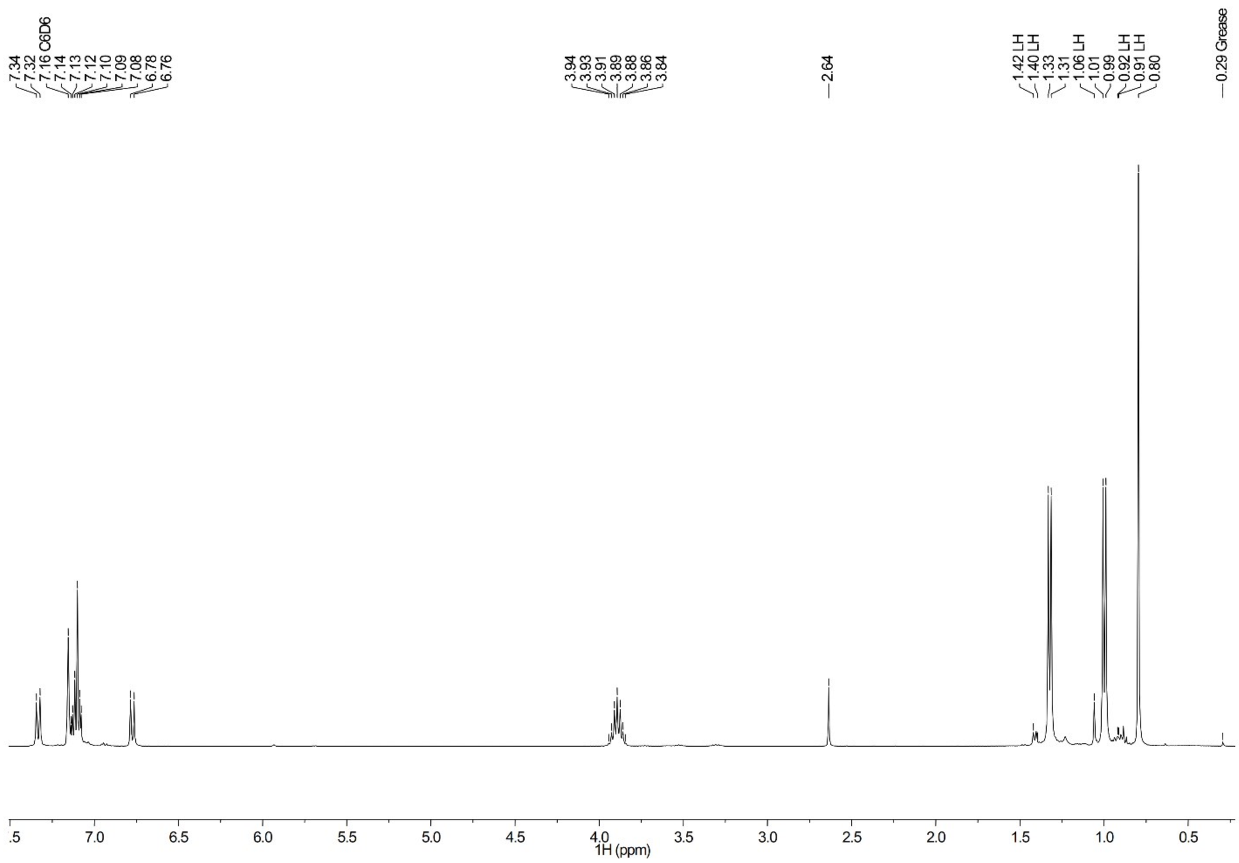


Figure S19. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of **11** (LH = ArC(NDip){N(H)Dip}).

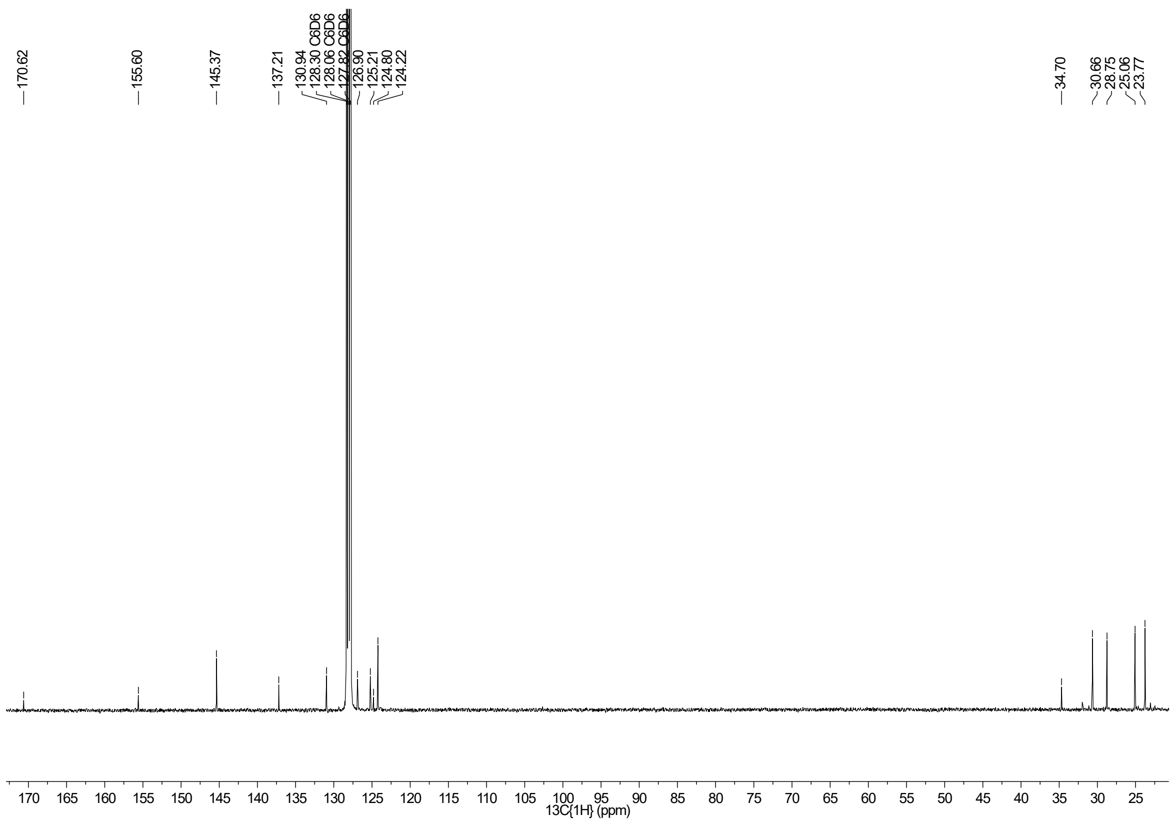


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of **11**.

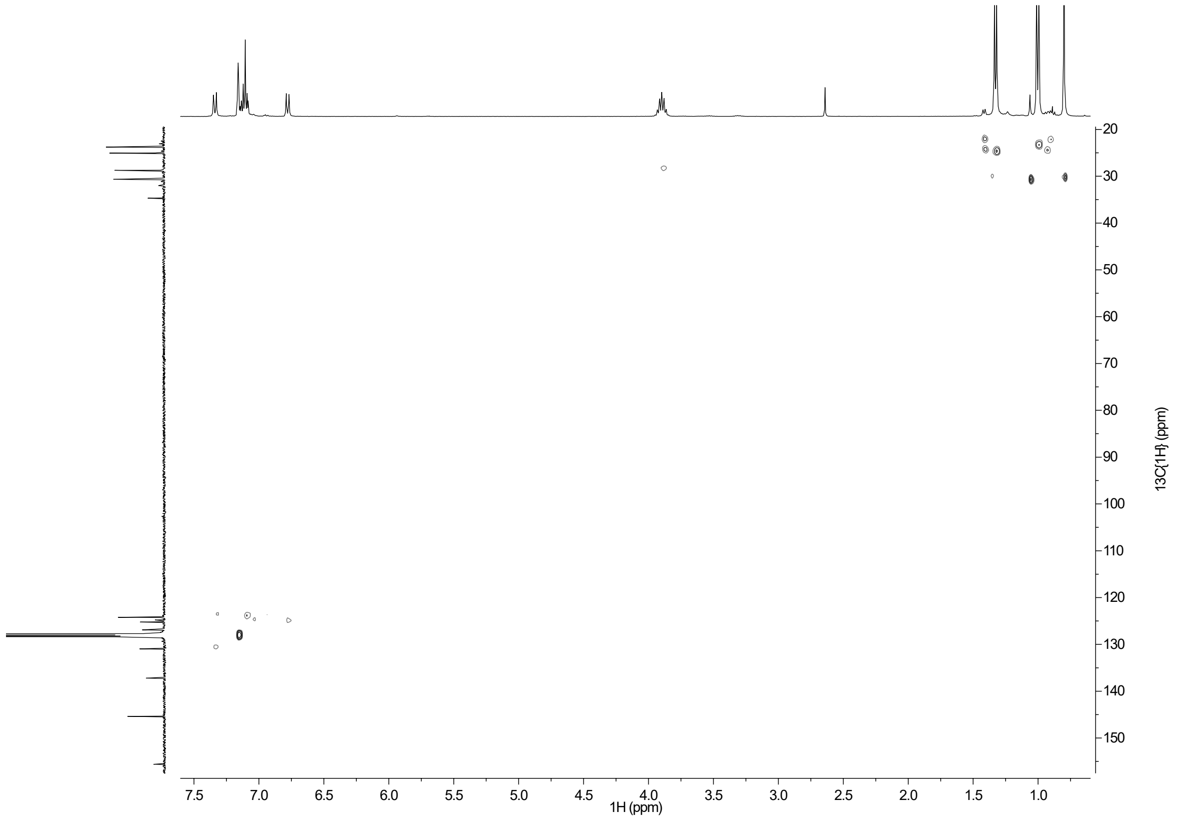
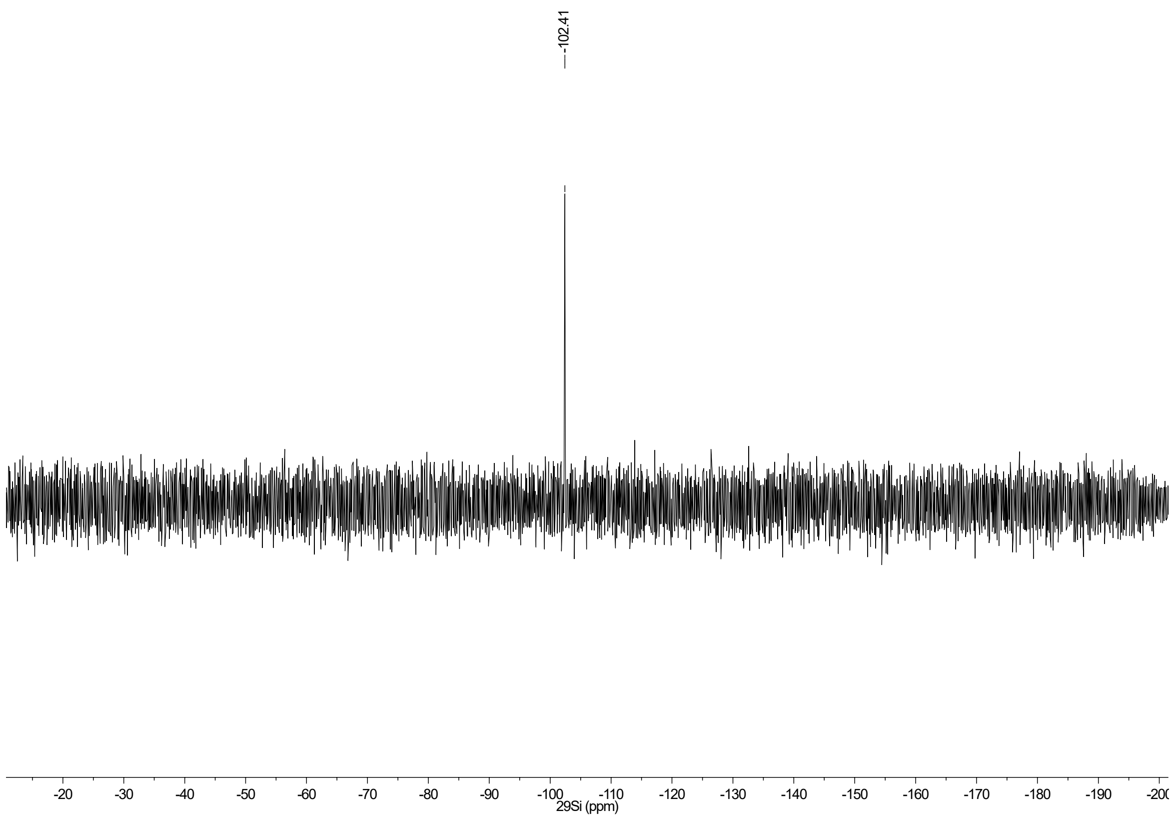


Figure S21. HSQC spectrum (^{1}H: 600 MHz; ^{13}C: 101 MHz, 298 K, C_6D_6) of **11**.



Figur

e S22. ^{29}Si{^{1}H} NMR spectrum (80 MHz, 298 K, C_6D_6) of **11**.

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[2]) using all unique data. Hydrogen atoms are typically included in calculated positions (riding model). 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 **3**, **4**, **5**, **7**, **10** and **11**.

	3·(pentane)$_{0.5}$	**4**	**5**·(pentane)$_{0.5}$	**7**
empirical formula	$C_{82.5}H_{118}N_6Si_2$	$C_{80}H_{112}Br_2N_6Si_2$	$C_{76.5}H_{108}N_4Si_2$	$C_{72}H_{98}Ge_2N_4$
formula weight	1250.0	1373.75	1139.84	1164.72
crystal system	monoclinic	monoclinic	monoclinic	triclinic
space group	*Cc*	*P*2$_1$/*n*	*P*2$_1$/*c*	*P*-1
a (Å)	18.1257(1)	18.1298(2)	21.7199(2)	9.4999(2)
b (Å)	23.6945(1)	23.3553(2)	18.5462(1)	11.1632(2)
c (Å)	35.2661(1)	18.3185(1)	19.8655(2)	16.1816(4)
α (º)	90	90	90	90.716(2)
β (º)	91.410(1)	105.822(1)	111.551(1)	94.053(2)
γ (º)	90	90	90	101.225(2)
V (Å^3)	15141.48(11)	7462.67(12)	7442.82(12)	1678.41(6)
Z	8	4	4	1
T (K)	123(2)	123(2)	123(2)	123(2)
ρ_{calcd} (g·cm^3)	1.097	1.223	1.017	1.152
μ (mm^{-1})	0.765	2.028	0.730	0.937
F(000)	5464	2928	2492	622
reflns collected	290456	59857	76386	21351
unique reflns	28055	13843	13804	6590
R_{int}	0.0427	0.0587	0.0481	0.0978
R1 [I > 2σ(I)]	0.0387	0.0400	0.0658	0.0370
wR2 (all data)	0.1054	0.1048	0.2048	0.0998
largest peak and hole (e·Å^{-3})	0.63, -0.39	0.80, -0.42	0.94, -0.48	0.99, -0.34
CCDC no.	2154627	2154626	2154625	2154622

	10	**11**
empirical formula	$C_{72}H_{94}N_4O_7Si_2$	$C_{70}H_{96}N_4O_4Si_2$
formula weight	1183.69	1113.68
crystal system	orthorhombic	triclinic
space group	$Pna2_1$	*P*-1
a (Å)	30.0835(4)	13.0014(4)
b (Å)	11.3217(1)	15.9395(4)
c (Å)	19.9786(2)	17.9934(4)
α (º)	90	82.276(2)
β (º)	90	70.961(2)
γ (º)	90	68.515(3)
V ($Å^3$)	6804.64(13)	3279.49(17)
Z	4	2
T (K)	123(2)	123(2)
ρ_{calcd} ($g{\cdot}cm^3$)	1.155	1.128
μ (mm^{-1})	0.899	0.866
F(000)	2552	1208
reflns collected	46900	62830
unique reflns	8409	12160
R_{int}	0.0522	0.0580
R1 [I > 2σ(I)]	0.0790	0.0487
wR2 (all data)	0.2014	0.1363
largest peak and hole ($e{\cdot}Å^{-3}$)	0.77, -0.32	0.49, -0.49
CCDC no.	2154624	2154623

3. Computational Studies

All calculations were performed using Gaussian16 suite of programs[3] using the Becke's 3-parameter hybrid functional[4] combined with the non-local correlation functional provided by Perdew/Wang(B3PW91)[5]. The 6-311+G(d) all-electron basis set was used for the Si atoms and the 6-31G(d,p) for the remaining atoms[6]. The molecular orbital diagram was obtained using Multiwfn suite of programs[7] and VMD[8].

Table S2. Cartesian coordinates for the geometry optimised structures of compound **3** in the singlet and triplet states.

200
singlet

Si	1.19627600	0.49785900	0.22962500
N	0.69205100	0.99393300	-2.52996600
C	-0.26588400	1.33994900	-3.58613800
Si	-1.22558600	0.47304400	-0.28268400
N	-0.77575800	0.86587500	2.47721600
C	0.53088300	1.55491100	-4.87492200
H	1.27765700	2.34121100	-4.73175600
H	-0.12757200	1.85032300	-5.69936300
H	1.05539300	0.64061600	-5.16113500
N	2.94434900	1.17705700	0.47872200
C	-0.99200700	2.64476600	-3.23464400
H	-1.62663100	2.52578100	-2.35373100
H	-1.62414800	2.98916600	-4.05999700
H	-0.26001800	3.42762300	-3.01848900
N	2.46781500	-0.87790300	0.07835200
C	-1.27639200	0.21348600	-3.81036900
H	-0.74997900	-0.72444800	-4.00748300
H	-1.93334100	0.42226500	-4.65946500
H	-1.91181500	0.06937900	-2.93042200
N	-2.48438800	-0.92055500	-0.14332100
C	0.25300900	0.77069200	-1.32500000
N	-2.97364000	1.14755600	-0.46047000
C	-0.29385700	0.70418700	1.27808300
C	0.13255700	1.18037000	3.58534800
C	0.84734100	2.51208100	3.32506500
H	1.46850100	2.46631000	2.42692500
H	1.48781800	2.79490800	4.16666400
H	0.10963700	3.30637800	3.18642400
C	1.15344700	0.06025100	3.79299200
H	0.63835900	-0.89545800	3.92145800
H	1.77350300	0.23510700	4.67655700
H	1.82137700	-0.02780100	2.92992000
C	-0.72455700	1.32882800	4.84417300
H	-1.51042800	2.07012700	4.67112800
H	-0.11892500	1.65050400	5.69879100
H	-1.20554800	0.38217600	5.09926600
C	3.61491300	2.35089200	0.89772500
C	3.37691000	3.53115100	0.15783400
C	4.01913500	4.70350000	0.55620100
H	3.84536900	5.61869400	0.00145600
C	4.88893500	4.71658600	1.64073900

H	5.38854500	5.63708300	1.92890300
C	5.10922200	3.54960100	2.35643400
H	5.77950000	3.56494300	3.21088200
C	4.47170400	2.35144200	2.02142400
C	4.72382600	1.14741100	2.91246100
H	4.10424800	0.31693200	2.56152900
C	6.19203700	0.70176200	2.88755300
H	6.83049400	1.47101100	3.33553300
H	6.55504000	0.51527300	1.87744100
H	6.31805900	-0.21468700	3.47311500
C	4.31685900	1.44242300	4.36120100
H	4.98449900	2.18387900	4.81208900
H	4.37773300	0.53107600	4.96502000
H	3.29992800	1.82851200	4.41968500
C	2.51647500	3.50514000	-1.09036400
H	1.66826000	2.83387000	-0.92043700
C	3.31363700	2.92224000	-2.26252600
H	4.21699600	3.51666200	-2.44753300
H	2.69977100	2.90841600	-3.16456300
H	3.60141500	1.88667000	-2.07094000
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H	1.42622000	5.33709000	-0.62003000
H	1.22882300	4.75798300	-2.27964500
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C	7.08984400	0.33606200	-0.77343200
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C	7.62795900	-0.90532400	-0.41786300
C	6.76217000	-1.84790000	0.15927500
H	7.14115500	-2.82307600	0.44809800
C	5.41950000	-1.57390700	0.36157800
H	4.77268200	-2.32949000	0.78994500
C	9.09572200	-1.26330100	-0.63606500
C	9.88454400	-0.11515400	-1.27277500
H	9.87857300	0.77982200	-0.64228800
H	9.48801000	0.15224200	-2.25751600
H	10.92736000	-0.41804600	-1.40753500
C	9.73611600	-1.59978600	0.72221900
H	10.79162200	-1.85972100	0.58837300
H	9.24184700	-2.44723800	1.20560900
H	9.67664400	-0.74430000	1.40227800
C	9.17839500	-2.48633300	-1.56658500
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C	2.04642600	-3.21991700	0.44753400
C	1.54179700	-2.87849500	1.83489500
H	1.04875600	-1.90252900	1.77463700
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H	3.40680000	-1.94995500	2.50047600
H	3.29794200	-3.68961100	2.82600100

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H	-0.30548700	-4.01049400	1.65792000
H	0.08600200	-3.49425600	3.30147000
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C	3.38255600	-1.42993000	-2.70895700
H	3.23605200	-0.44497500	-2.25798100
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C	-2.51390300	-2.27370700	0.26492700
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H	-5.51988900	-1.82551500	2.28762600
H	-5.06339900	-1.05627100	3.81625700
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C	-4.90783400	-0.35466100	0.05417000
C	-5.69916000	0.56909900	0.74942400
H	-5.26561100	1.50357200	1.08677900
C	-7.02828800	0.27930000	1.01204600
H	-7.61905800	1.00526900	1.56151100
C	-7.61933800	-0.91945900	0.58157200
C	-6.81364200	-1.82851800	-0.11290200
H	-7.22649300	-2.76771000	-0.46089400
C	-5.47251000	-1.56188100	-0.36443600
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C	-9.09107400	-1.18634300	0.88719300
C	-9.94442400	-0.07860700	0.24464900
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H	-9.68266500	0.91080400	0.63006400
C	-9.29379100	-1.17966900	2.41276600
H	-9.01952000	-0.21765300	2.85467500
H	-8.68319300	-1.95308500	2.88894800
H	-10.34428000	-1.37251100	2.65547400

C	-9.56129900	-2.53821800	0.34192700
H	-9.00428300	-3.37026400	0.78457800
H	-9.46027200	-2.59385200	-0.74680000
H	-10.61871000	-2.68253200	0.58366400
C	-3.67524000	2.33648200	-0.77690900
C	-3.38952900	3.49267300	-0.01996800
C	-4.08225800	4.66819500	-0.31349900
H	-3.86519700	5.56382500	0.25998700
C	-5.04480000	4.70877400	-1.31387000
H	-5.58512300	5.62869200	-1.51820600
C	-5.30005400	3.56754300	-2.06135000
H	-6.03630700	3.60471900	-2.85901800
C	-4.61711600	2.37086200	-1.83098300
C	-4.89919300	1.20821800	-2.76585200
H	-4.26959100	0.36290900	-2.47429000
C	-4.52755000	1.57487500	-4.20776300
H	-5.19380200	2.35143300	-4.59762000
H	-4.61848700	0.69917900	-4.85901000
H	-3.50559400	1.94862600	-4.27107100
C	-6.36524500	0.76077900	-2.71250200
H	-6.69757000	0.55424400	-1.69513200
H	-6.50795400	-0.14398100	-3.31217500
H	-7.01788500	1.53718100	-3.12625000
C	-2.31776400	3.49945500	1.04847800
H	-2.10166300	2.47096100	1.35092800
C	-1.03082600	4.09791300	0.46595100
H	-0.70469300	3.54273300	-0.41653200
H	-0.21863900	4.05727800	1.19579700
H	-1.18718400	5.14293400	0.17356600
C	-2.74744700	4.23654600	2.31810700
H	-2.86480800	5.31412200	2.15851900
H	-1.98959600	4.10147800	3.09505100
H	-3.69467000	3.84549600	2.70306600

200
Triplet

Si	1.28732700	0.52959500	0.22437200
N	0.64165900	1.06476300	-2.49128800
C	-0.31457700	1.41231700	-3.55419500
Si	-1.29739600	0.50752800	-0.27246400
N	-0.71905500	0.95447600	2.44034700
C	0.49399500	1.66485100	-4.82800400
H	1.21323000	2.47304900	-4.66988500
H	-0.16600200	1.94768300	-5.65466800
H	1.04798600	0.76988400	-5.11831800
N	2.95387700	1.20822500	0.41414000
C	-1.04710300	2.70188500	-3.16676200
H	-1.72984300	2.54332600	-2.32976900
H	-1.63307900	3.08327900	-4.00831900
H	-0.32629100	3.47171000	-2.87950000
N	2.42224200	-0.87308200	0.18241800
C	-1.30636000	0.27651700	-3.79922600
H	-0.77176000	-0.64906200	-4.02693500
H	-1.96113400	0.50680900	-4.64283200
H	-1.93994100	0.10146600	-2.92517100
N	-2.44793700	-0.90083800	-0.21914700
C	0.22795400	0.74985200	-1.30147200
N	-2.98121900	1.18426300	-0.38186900
C	-0.25735400	0.70043600	1.25336300
C	0.18584500	1.28169600	3.55272300
C	0.90156600	2.60276000	3.25284000
H	1.54975300	2.52416800	2.37720300
H	1.51758500	2.91061900	4.10223100

H	0.16843900	3.39196900	3.07131600
C	1.19173900	0.15506300	3.78280900
H	0.66947800	-0.79150700	3.94038400
H	1.80484900	0.35387500	4.66443900
H	1.86177900	0.03777200	2.92686800
C	-0.68414400	1.46577000	4.79757300
H	-1.45666000	2.21653500	4.60761900
H	-0.07905300	1.79243100	5.64968900
H	-1.18014200	0.53091100	5.06625500
C	3.61259700	2.38076600	0.85396800
C	3.38811500	3.56438100	0.11293000
C	4.02172300	4.73855400	0.51767000
H	3.85319600	5.65392700	-0.03856800
C	4.88561700	4.75054700	1.60710200
H	5.38520000	5.66984400	1.89891000
C	5.10090300	3.58131300	2.32035000
H	5.76795800	3.59477400	3.17733300
C	4.46199100	2.38353300	1.98524700
C	4.69813700	1.18757100	2.89329100
H	4.06131300	0.36550900	2.55521200
C	6.15515300	0.70604900	2.87322200
H	6.81662700	1.47969900	3.27899000
H	6.50078200	0.46096700	1.87042500
H	6.26273300	-0.18453900	3.50099000
C	4.31354500	1.51613100	4.34186500
H	5.01819500	2.22883300	4.78265300
H	4.33832800	0.60862700	4.95408900
H	3.31699700	1.95145200	4.40804400
C	2.55235700	3.53250000	-1.15192300
H	1.68737500	2.88301900	-0.98500000
C	3.36629600	2.90941900	-2.29201300
H	4.27054600	3.49993900	-2.48037300
H	2.77194100	2.86758000	-3.20676500
H	3.65964000	1.88520000	-2.05455400
C	2.01080100	4.89859600	-1.56565500
H	1.46373200	5.38278400	-0.75129000
H	1.32707400	4.78240100	-2.41129800
H	2.80925500	5.57376800	-1.89283900
C	3.51492300	-0.03831800	0.23211600
C	4.88404000	-0.36389500	0.02014000
C	5.78609100	0.59664400	-0.49183400
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C	7.11011700	0.26664100	-0.73341600
H	7.76068400	1.03236400	-1.14055500
C	7.61484800	-1.01415900	-0.46527500
C	6.71253500	-1.96101000	0.05581300
H	7.05956200	-2.96491300	0.28286300
C	5.38420600	-1.66168100	0.28593700
H	4.72433500	-2.42451800	0.67948900
C	9.06718900	-1.40771800	-0.71504600
C	9.89093000	-0.24945100	-1.28611500
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H	10.92288100	-0.57620100	-1.44876500
C	9.70783300	-1.84937000	0.61293400
H	10.75169900	-2.14291000	0.45494000
H	9.18257500	-2.70325100	1.05050800
H	9.68641900	-1.03385700	1.34269100
C	9.10928500	-2.57358000	-1.71923700
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H	10.14491500	-2.87608200	-1.91108500
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C	2.87378400	-2.48541200	-1.62762400
C	2.95381000	-3.82867400	-2.00792400
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C	1.53592200	-2.88260500	1.95050300
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C	2.77310200	-2.67942100	2.83519400
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H	-1.91637500	4.28426000	3.05817300
H	-3.64245600	4.11791700	2.70520200

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