

Supporting Information

for

Bis(silylene)siloles – Synthesis, Properties and Reactivity

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Experimental Part

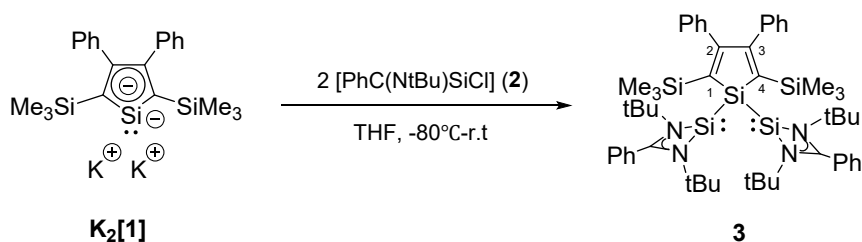
General. All manipulations of air- and moisture-sensitive compounds were carried out under an argon 5.0 or nitrogen 5.0 atmosphere using Schlenk techniques or a standard glove box (Braun Unilab). Glassware was dried in an oven at $T = 120\text{ }^{\circ}\text{C}$ and evacuated prior to use. The solvents THF, diethylether, toluene and *n*-hexane were dried over sodium/potassium alloy and distilled under a nitrogen atmosphere. Benzene- d_6 and CDCl_3 were first dried over sodium and then either condensed before use or stored over molecular sieves (4 Å). All used standard chemicals were obtained from commercial suppliers and used as delivered if not mentioned otherwise. Dipotassiumsilacyclopenta-dienediide $\text{K}_2[\mathbf{1}]^{[\text{S1}]}$ and $\text{PhC}(\text{NtBu})_2\text{SiCl}[\mathbf{2}]^{[\text{S2}]}$ were prepared according to modified literature procedures.

NMR spectroscopy. NMR spectra were recorded on Bruker Avance DRX 500 and Bruker Avance III 500 spectrometers. ^1H NMR spectra were calibrated against the residual proton signal of the solvent as internal reference (Benzene- d_6 : $\delta\ ^1\text{H}(\text{C}_6\text{D}_5\text{H}) = 7.20$; CDCl_3 : $\delta\ ^1\text{H}(\text{CHCl}_3) = 7.26$; and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra by using the central line of the solvent signal (Benzene- d_6 : $\delta\ ^{13}\text{C}(\text{C}_6\text{D}_6) = 128.0$; CDCl_3 : $\delta\ ^{13}\text{C}(\text{CDCl}_3) = 77.16$. ^{29}Si , ^{77}Se and ^{125}Te NMR spectra were calibrated against an external standard ($\delta\ ^{29}\text{Si}(\text{Me}_2\text{SiHCl}) = 11.1$ versus tetramethylsilane (TMS), $\delta\ ^{77}\text{Se}(\text{Me}_2\text{Se}) = 0.0$ and $\delta\ ^{125}\text{Te}(\text{Ph}_2\text{Te}_2) = 422.0$ versus dimethyltelluride (Me_2Te)). The $^{29}\text{Si}\{^1\text{H}\}$ NMR inverse gated spectra were recorded with a relaxation delay $D1 = 10\text{ s}$.

Mass spectrometry: Mass spectra were recorded on a Waters Q-ToF Premier (ESI-MS) and Thermo Scientific DFS (EI-MS). The used method for each compound is given in the experimental part.

UV/Vis spectroscopy: UV/Vis spectra were recorded in *n*-hexane at room temperature on an Agilent Cary60 spectrophotometer.

Synthesis of **3**:



Scheme S1

3. A solution of PhC(NtBu)₂SiCl (**2**) (178 mg, 0.6 mmol, 2 eq.) in THF (6 mL) was slowly added to a solution of K₂[**1**] (0.3 mmol) in THF (10 mL) at -80 °C. The reaction mixture was stirred for 0.5 h at -80 °C and was allowed to warm to room temperature over 4 hours. The solvent was removed under vacuum. The residue was re-dissolved in Et₂O (4 mL) and the filtrate was kept at +5 °C for one night to afford red crystals of the Silole bissilylene **3**. Yield: 183mg (0.19 mmol, 65%).

NMR spectra for **3** recorded in C₆D₆ at 305 K.

¹H NMR (499.9 MHz, 305.0 K, C₆D₆): δ = 0.48 (s, 18 H, Si-(CH₃)₃), 1.37 (s, 36 H, tBu), 6.92-7.19 (m, 18H, Ph), 7.79 (m, 2H, Ph).

¹³C{¹H} NMR (125.8 MHz, 305.0 K, C₆D₆): δ = 3.24 (Si-(CH₃)₃), 32.40, 53.66 (tBu), 15.61, 65.91 (Et₂O), 125.89, 127.12, 127.34, 129.18, 129.58, 130.47, 130.78 (C of Ph), 135.47 (C^{1/4}), 145.82(C of amidinate-phenyl), 151.49 (C^{2/3}), 151.85 (PhC(NtBu)₂), 163.95(C of silole-phenyl).

²⁹Si{¹H} NMR (99.4 MHz, 305.0 K, C₆D₆): δ = -10.57 (SiMe₃), 6.45 (¹J_{Si-Si} = 62 Hz, SiC₂), 65.64(¹J_{Si-Si} = 62 Hz, SiN₂).

EA: C/H/N [%] calculated for C₅₂H₇₄N₄Si₅: 69.74/8.33/6.26; found: 69.34/8.85/6.53.

HR-MS (EI): m/z calculated for C₅₂H₇₄N₄Si₅: 894.4760; found: 894.4806.

UV-vis (n-hexane): λ_{max} (ε) = 474 (10900 M⁻¹cm⁻¹) nm.

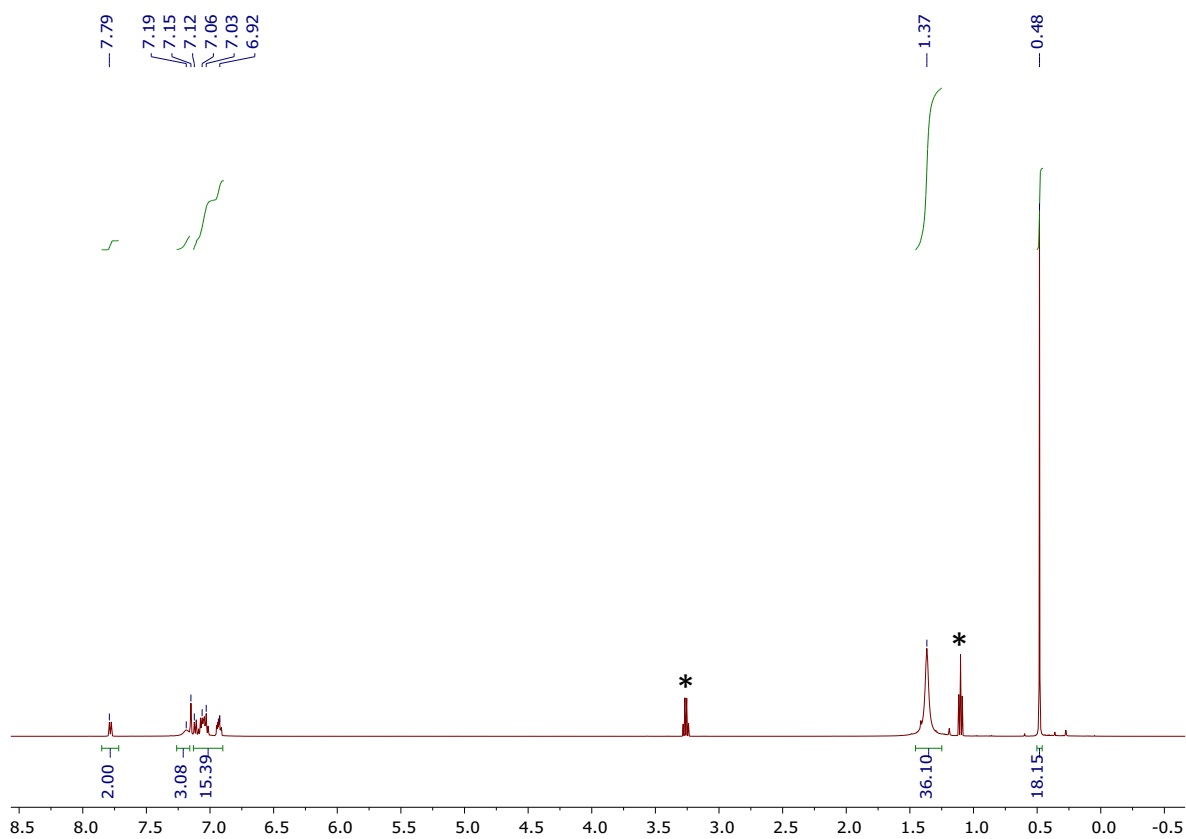


Figure S1a. ^1H NMR (499.9 MHz, 305.0 K, C_6D_6) spectrum of **3** ($^*\text{Et}_2\text{O}$).

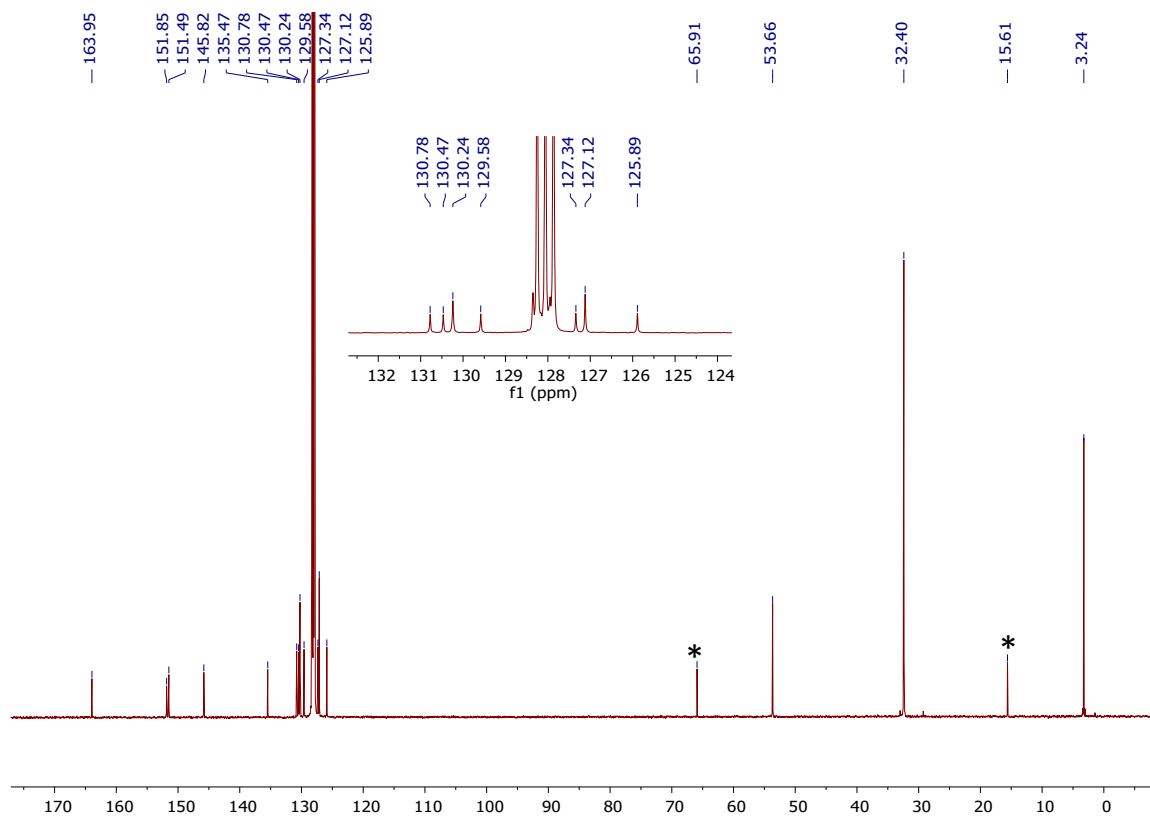


Figure S1b. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, 305.0 K, C_6D_6) spectrum of **3** ($^*\text{Et}_2\text{O}$).

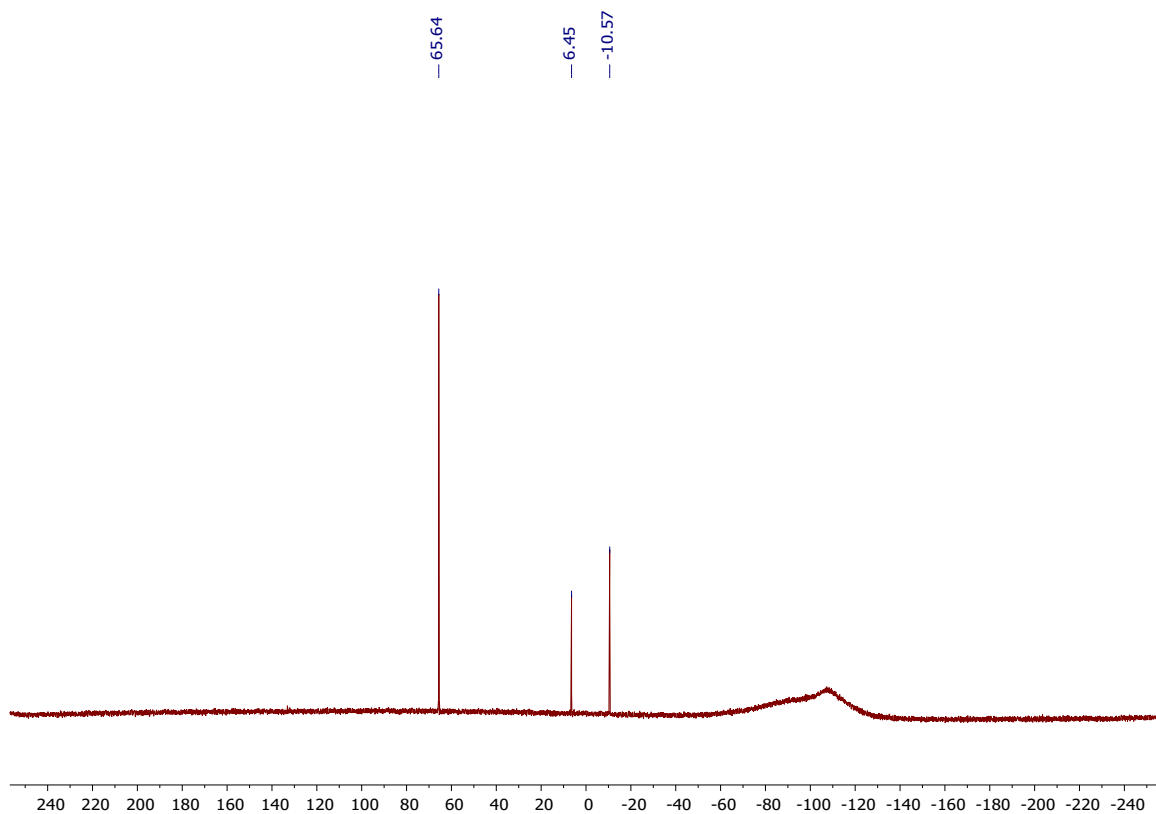


Figure S1c. $^{29}\text{Si}\{^1\text{H}\}$ NMR (99.4 MHz, 305.0 K, C_6D_6) spectrum of **3**.

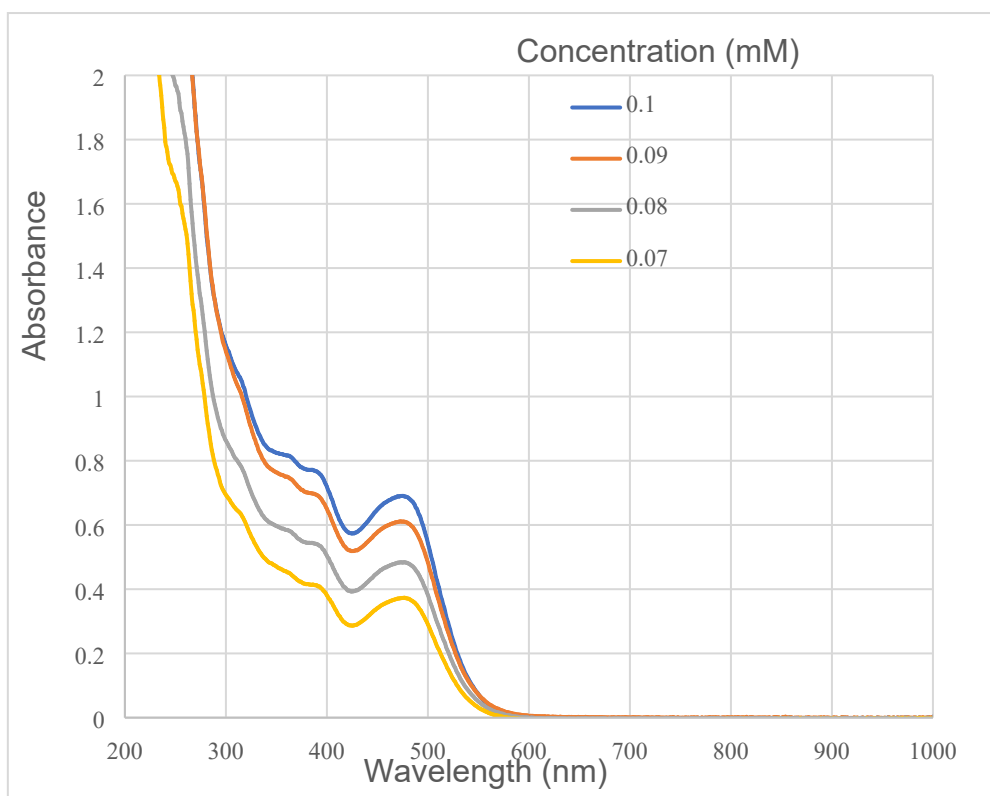


Figure S1d. UV/Vis absorption spectra of **3** at different concentrations (in *n*-hexane).

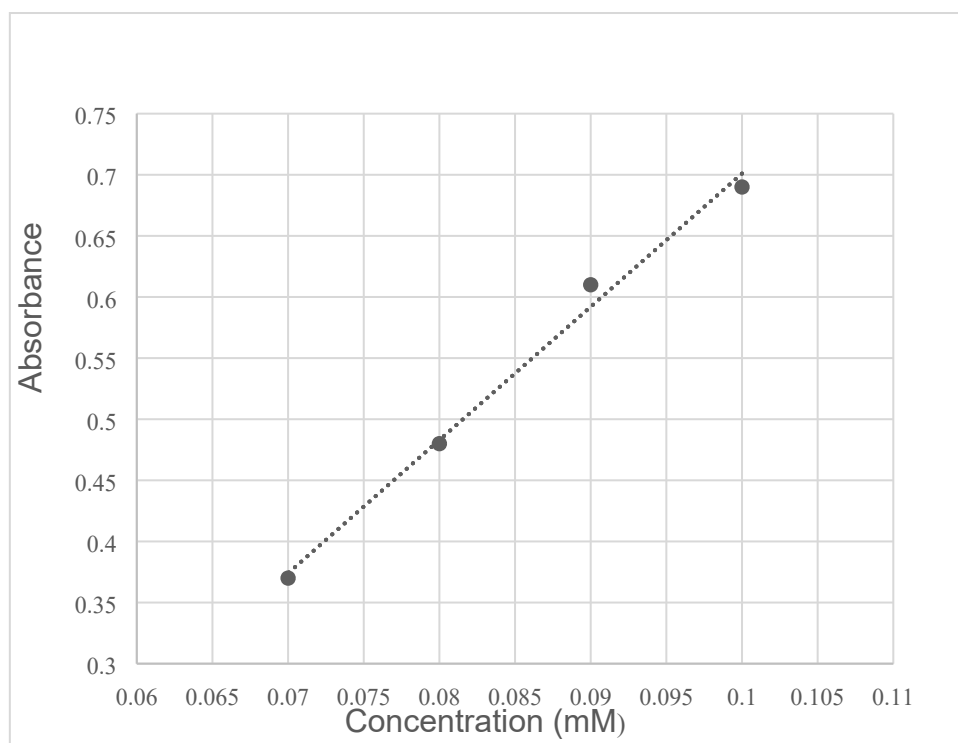


Figure S1e. Linear regression of the concentration dependence of absorbance of **3** at 474 nm.

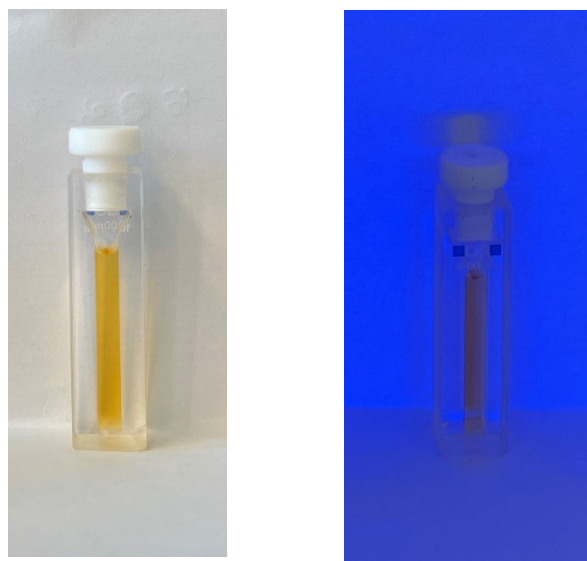
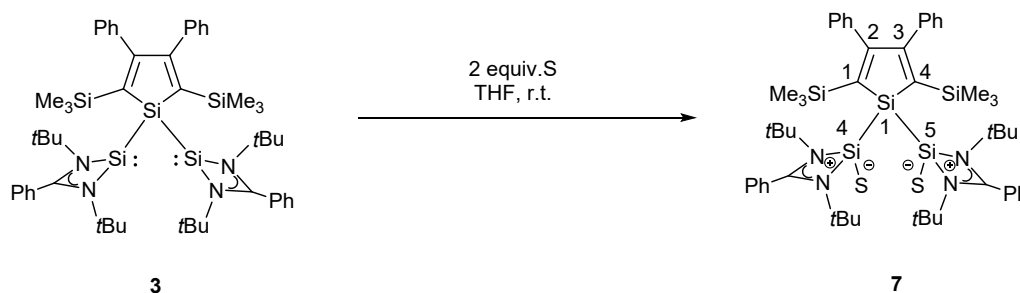


Figure S1f. UV sample of *bissilylene 3* in hexane at daylight (left) and at UV-light (right).

Synthesis of 7:



Scheme S2

7. THF (5 mL) was added to a mixture of **3** (179 mg, 0.20 mmol) and sulfur powder (13 mg, 0.40 mmol) at room temperature. The reaction was kept stirring for overnight. After that, the solvent was removed and the residue was extracted by Et₂O (8 mL). The solvent was removed and the residue was washed three times with *n*-hexane (3 x 4 mL) to afford an oil. Yellow single crystals suitable for XRD investigations were obtained by recrystallization from THF and *n*-hexane solution at room temperature. Yield: 157 mg (0.16 mmol, 79 %)

NMR spectra recorded in C₆D₆ at 305 K.

¹H NMR (499.9 MHz, 305.0 K, C₆D₆): δ = 0.61 (s, 18H, SiMe₃), 1.28 (s, 18H, tBu), 1.64 (s, 18H, tBu), 6.72-6.97(m, 13H, Ph), 7.18(m, 3H, Ph), 7.41-7.49(m, 4H, Ph).

¹³C{¹H} NMR (125.8 MHz, 305.0 K, C₆D₆): δ = 4.57 (Si-(CH₃)₃), 32.61, 32.33 (C(CH₃)₃), 56.46, 54.71 (C-Me₃), 126.81, 127.25, 128.63, 129.23, 129.61, 130.51 (C of Ph), 131.33 (C of amidinate-phenyl), 144.13 (C of silole-phenyl), 148.40 (C^{1/4}), 171.13 (PhC(NtBu)₂), 174.92 (C^{2/3}).

²⁹Si{¹H} NMR (99.4 MHz, 305.0 K, C₆D₆): δ = -18.87 (¹J_{Si-Si} = 86 Hz, SiC₂), -8.59 (SiMe₃), 19.71 (¹J_{Si-Si} = 86 Hz, SiN₂).

EA: C/H/N [%] calculated for C₅₂H₇₄N₄S₂Si₅: 65.08/7.77/5.84; found: 65.48/7.67/5.96

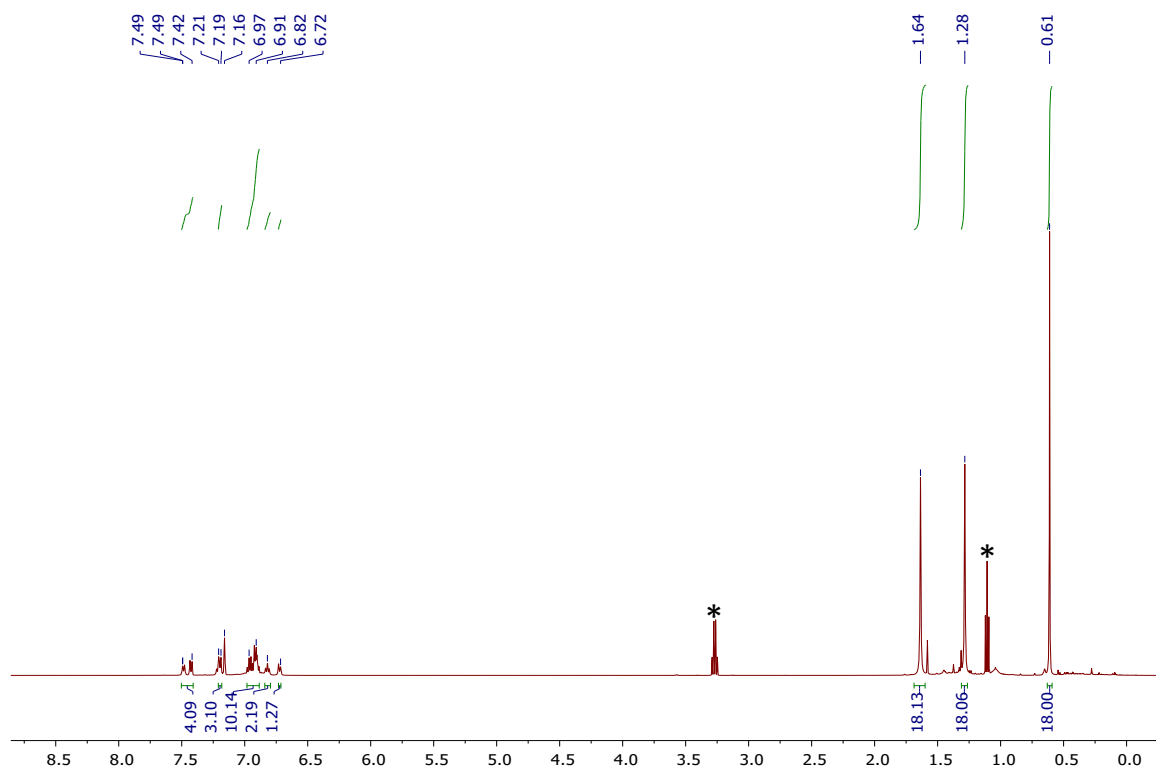


Figure S2a. ^1H NMR (499.0 MHz, 305.0 K, C_6D_6) spectrum of **7** (* Et_2O).

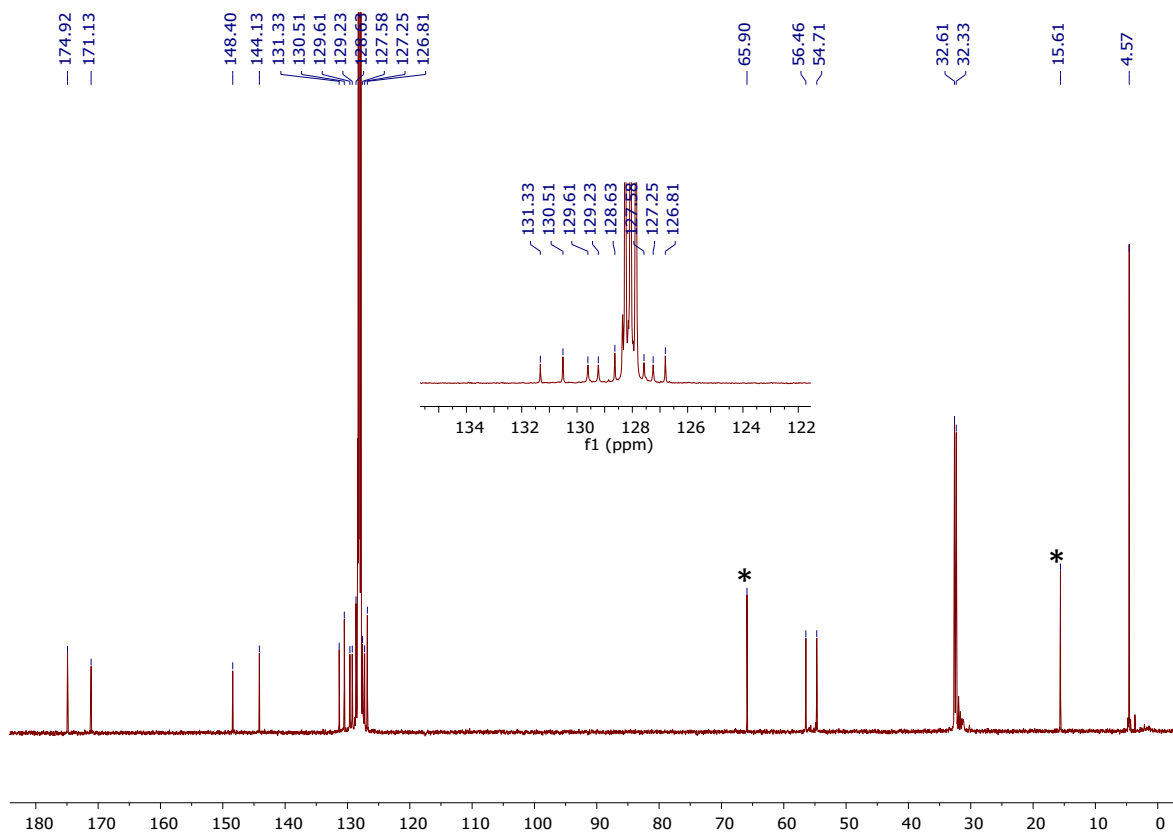


Figure S2b. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, 305.0 K, C_6D_6) spectrum of **7** (* Et_2O).

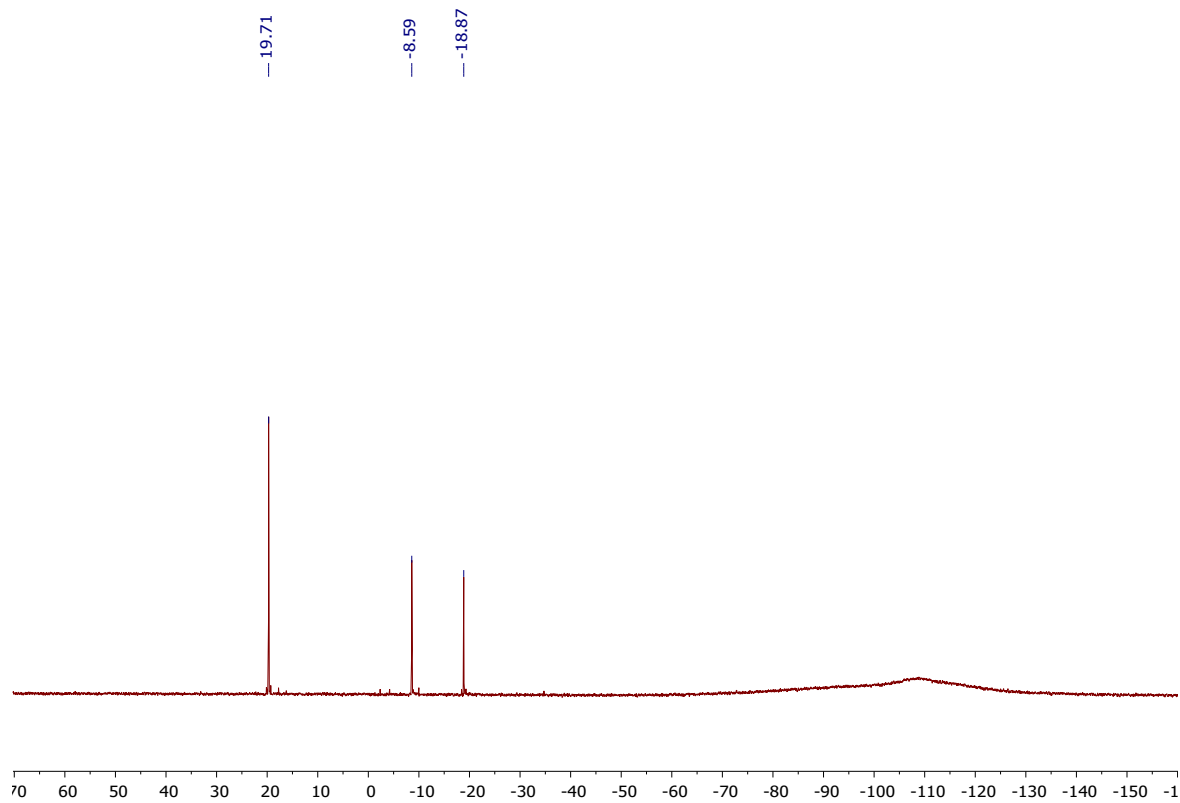
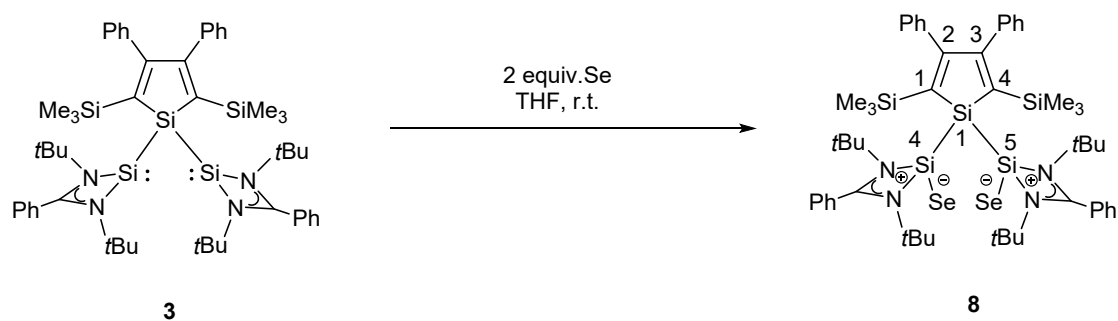


Figure S2c. $^{29}\text{Si}\{^1\text{H}\}$ NMR (99.4 MHz, 305.0 K, C_6D_6) spectrum of **7**.

Synthesis of 8:



Scheme S3

8. THF (5 mL) was added to a mixture of **3** (179 mg, 0.20 mmol) and Selenium powder (32 mg, 0.40 mmol) at room temperature. The reaction was kept stirring for overnight. After that, the solvent was removed and the residue was extracted by Et₂O (8 mL). The solvent was removed and the residue was washed three times with n-hexane (3 x 4 mL) to afford an oil. Yellow single crystals suitable for XRD investigations were obtained by recrystallization from Et₂O solution at room temperature. Yield: 179 mg (0.17 mmol, 83 %)

NMR spectra recorded in C₆D₆ at 305 K.

¹H NMR (499.9 MHz, 305.0 K, C₆D₆): δ = 0.63 (s, 18H, SiMe₃), 1.30 (s, 18H, tBu), 1.67 (s, 18H, tBu), 6.71-6.91(m, 12H, Ph), 7.19(m, 4H, Ph), 7.44(m, 4H, Ph).

¹³C{¹H} NMR (125.8 MHz, 305.0 K, C₆D₆): δ = 3.80, 4.85 (Si-(CH₃)₃), 29.24, 32.43, 32.59, 33.01 (C(CH₃)₃), 55.06, 56.86 (C-Me₃), 126.86, 127.26, 128.68, 129.25, 129.60, 131.50 (C of Ph), 131.56 (C of amidinate-phenyl), 144.08 (C of silole-phenyl), 147.90 (C^{1/4}), 171.19 (PhC(NtBu)₂), 174.45 (C^{2/3}).

²⁹Si{¹H} NMR (99.4 MHz, 305.0 K, C₆D₆): δ = -15.94 (¹J_{Si-Si} = 77 Hz, SiC₂), -8.48 (SiMe₃), 15.04 (¹J_{Si-Si} = 77 Hz, ¹J_{Si-Se} = 292 Hz, SiN₂).

⁷⁷Se{¹H} NMR (76 MHz, 305.0 K, C₆D₆): δ = -184.32 (¹J_{Si-Se} = 292 Hz).

EA: C/H/N [%] calculated for C₅₂H₇₄N₄Se₂Si₅: 59.28/7.08/5.32; found: 59.34/7.32/5.12.

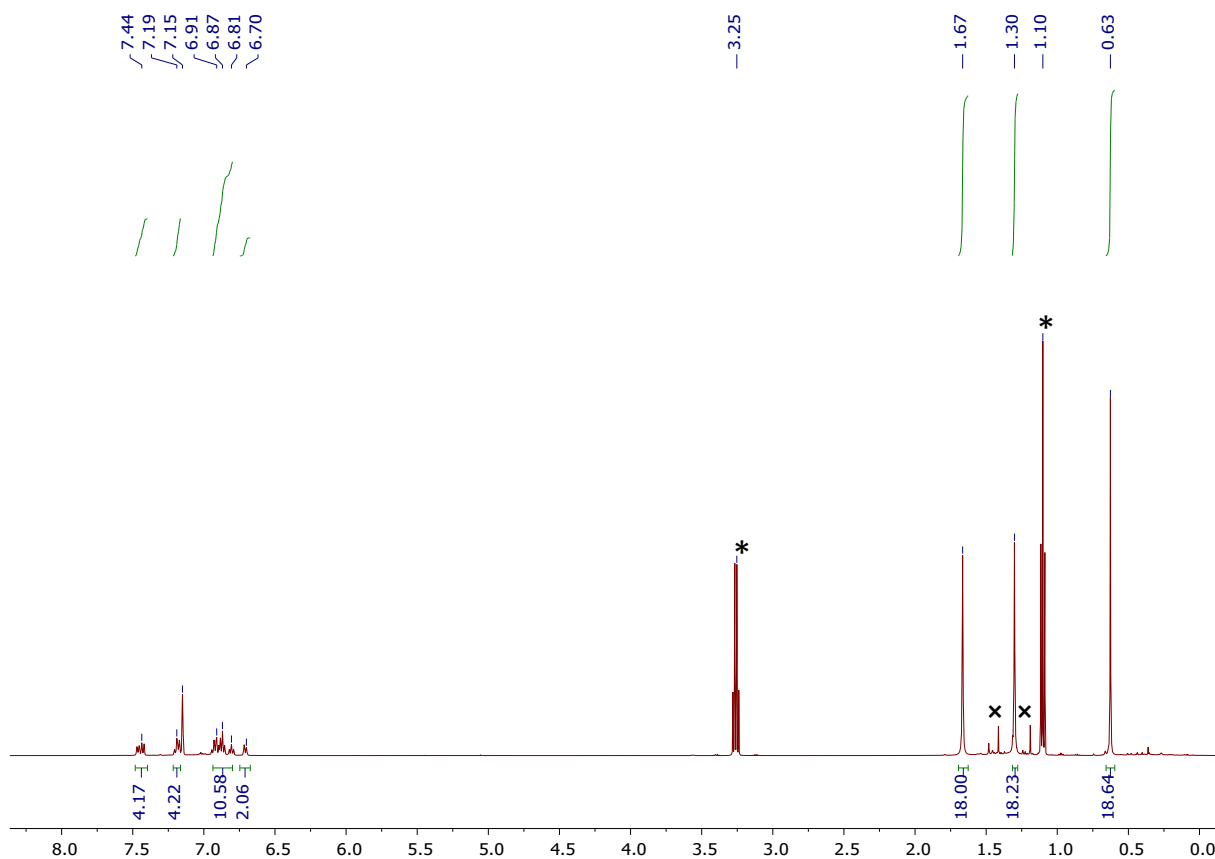


Figure S3a. ^1H NMR (499.9 MHz, 305.0 K, C_6D_6) spectrum of **8** (* Et_2O , \times unknown impurities).

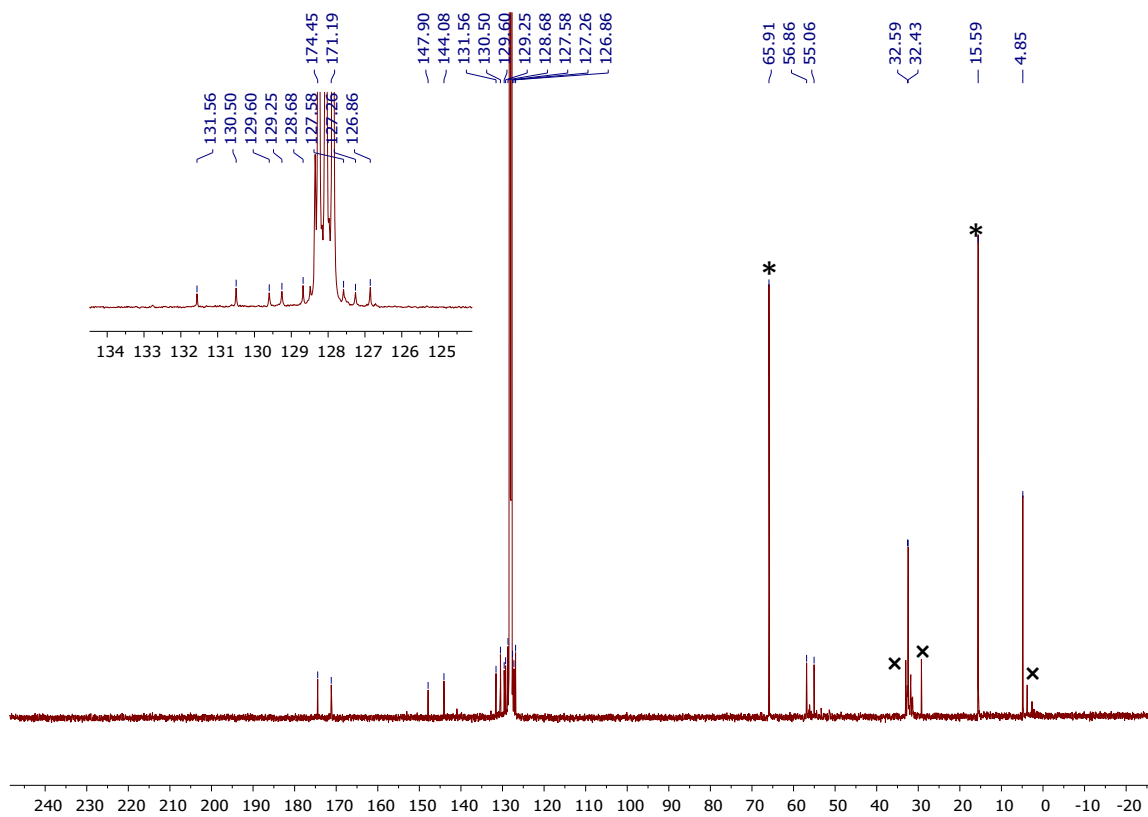


Figure S3b. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, 305.0 K, C_6D_6) spectrum of **8** (* Et_2O , \times unknown impurities).

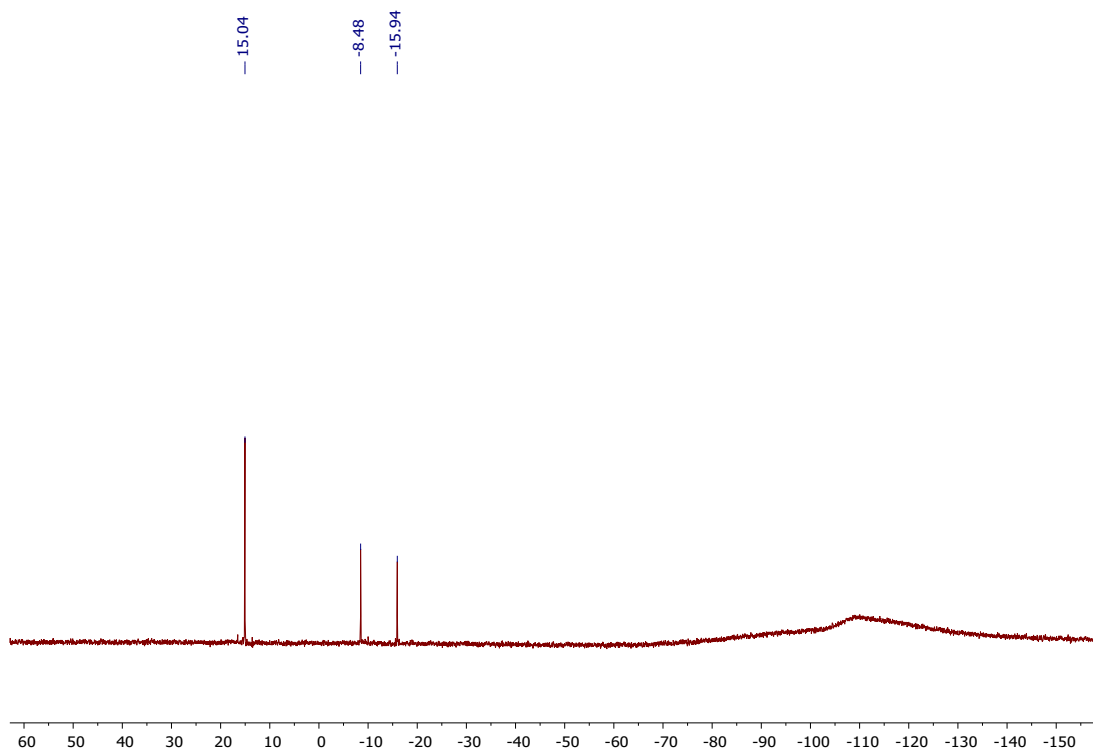


Figure S3c. $^{29}\text{Si}\{^1\text{H}\}$ NMR (99.4 MHz, 305.0 K, C_6D_6) spectrum of **8**.

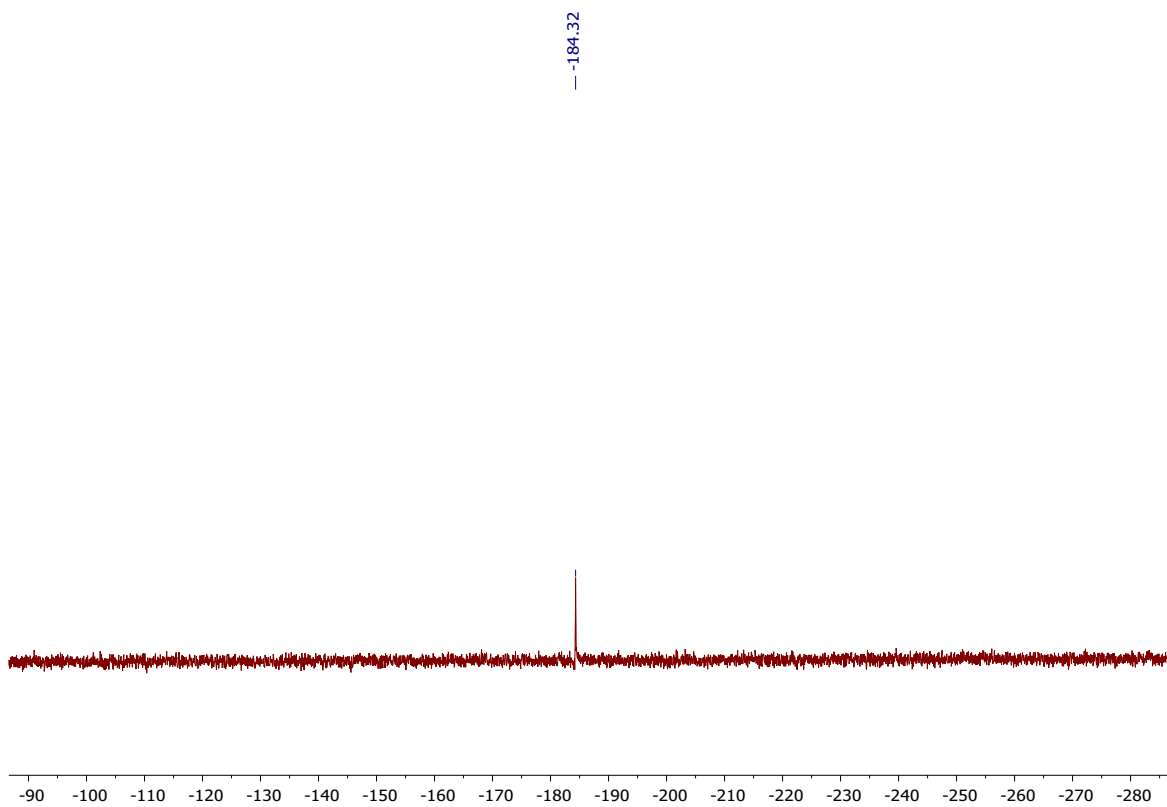
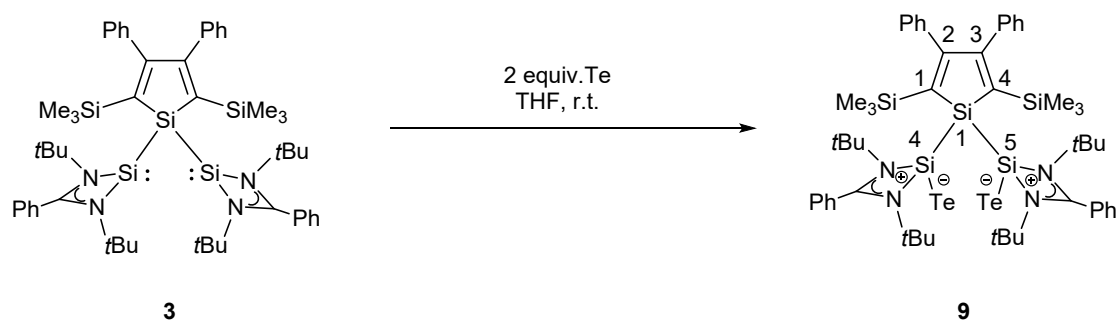


Figure S3d. $^{77}\text{Se}\{^1\text{H}\}$ NMR (76 MHz, 305.0 K, C_6D_6) spectrum of **8**.

Synthesis of 9:



Scheme S4

9. THF (5 mL) was added to a mixture of **3** (179 mg, 0.20 mmol) and Tellurium powder (51 mg, 0.40 mmol) at room temperature. The reaction was kept stirring for overnight. After that, the solvent was removed and the residue was extracted by Et₂O (8 mL). The solvent was removed and the residue was washed three times with *n*-hexane (3 x 4 mL) to afford a oil. Orange single crystals suitable for XRD investigations were obtained by recrystallization from THF and *n*-hexane solution at -30°C. Yield: 153 mg (0.13 mmol, 66 %)

NMR spectra recorded in C₆D₆ at 305 K.

¹H NMR (499.9 MHz, 305.0 K, C₆D₆): δ = 0.66 (s, 18H, SiMe₃), 1.34 (s, 18H, tBu), 1.73 (s, 18H, tBu), 6.69-6.94(m, 12H, Ph), 7.19(m, 4H, Ph), 7.44(m, 4H, Ph).

¹³C{¹H} NMR (125.8 MHz, 305.0 K, C₆D₆): δ = 5.47 (Si-Me₃), 32.66, 32.84 (C(CH₃)₃), 55.58, 57.48 (C-Me₃), 126.94, 127.26, 128.71, 129.29, 129.55, 130.59 (CH of Ph), 131.93 (C of amidinate-phenyl), 143.93 (C of silole-phenyl), 147.15 (C^{1/4}), 171.34 (PhC(NtBu)₂), 173.45 (C^{2/3}).

²⁹Si{¹H} NMR (99.4 MHz, 305.0 K, C₆D₆): δ = -14.19 (SiC₂), -11.71 (SiN₂), -8.45 (SiMe₃).

¹²⁵Te{¹H} NMR (76 MHz, 305.0 K, C₆D₆): δ = -692.48

EA: C/H/N [%] calculated for C₅₂H₇₄N₄Te₂Si₅: 54.27/6.48/4.87; found: 54.63/6.26/4.76

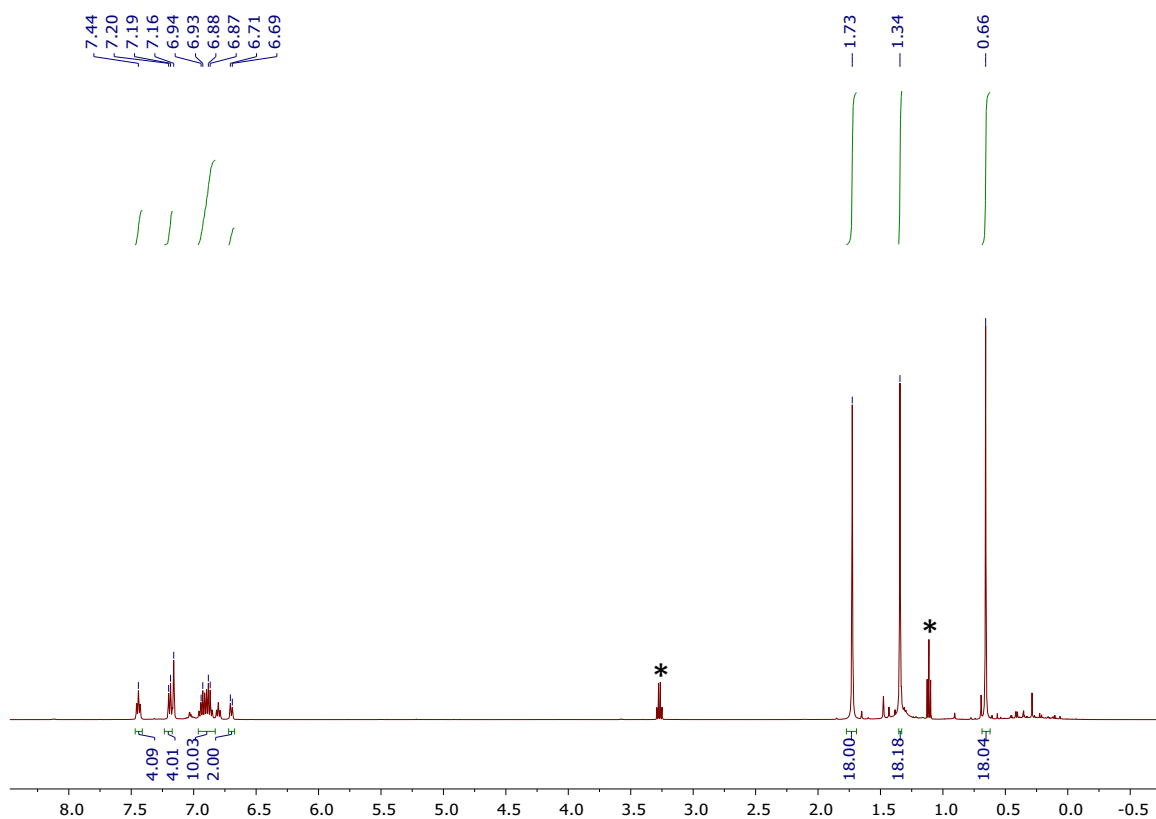


Figure S4a. ^1H NMR (499.9 MHz, 305.0 K, C_6D_6) spectrum of **9** ($^*\text{Et}_2\text{O}$).

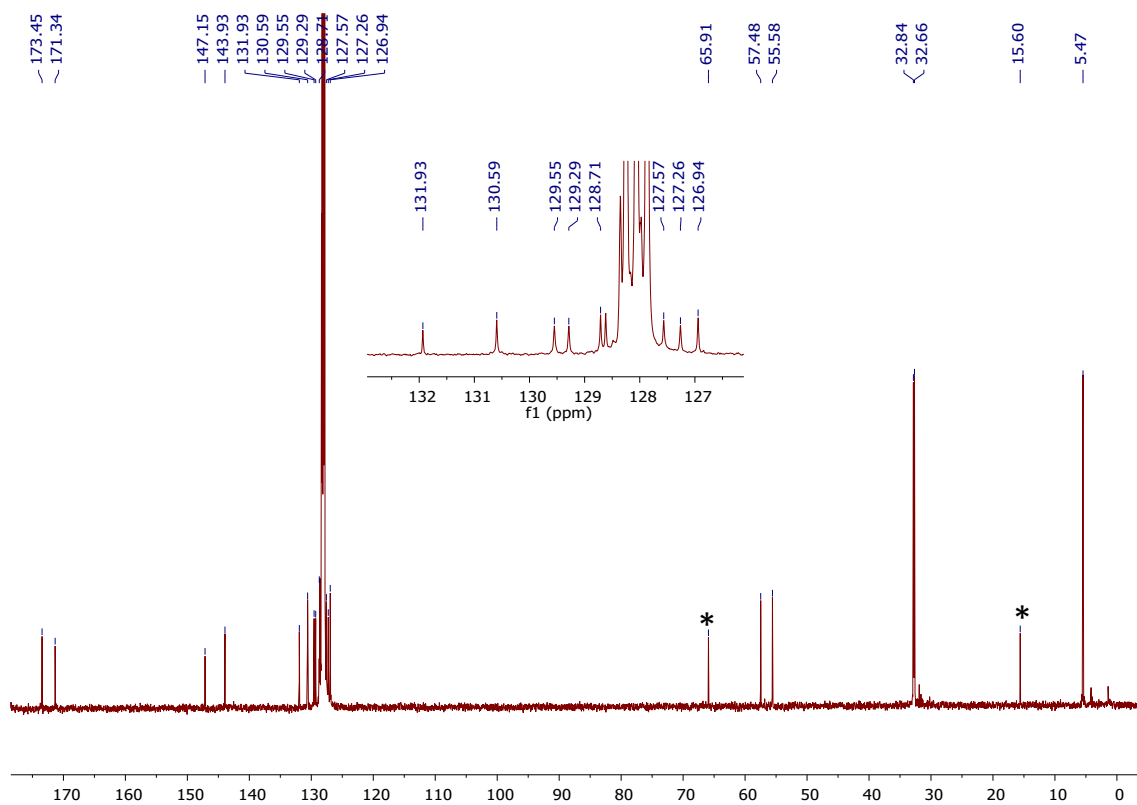


Figure S4b. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, 305.0 K, C_6D_6) spectrum of **9** ($^*\text{Et}_2\text{O}$).

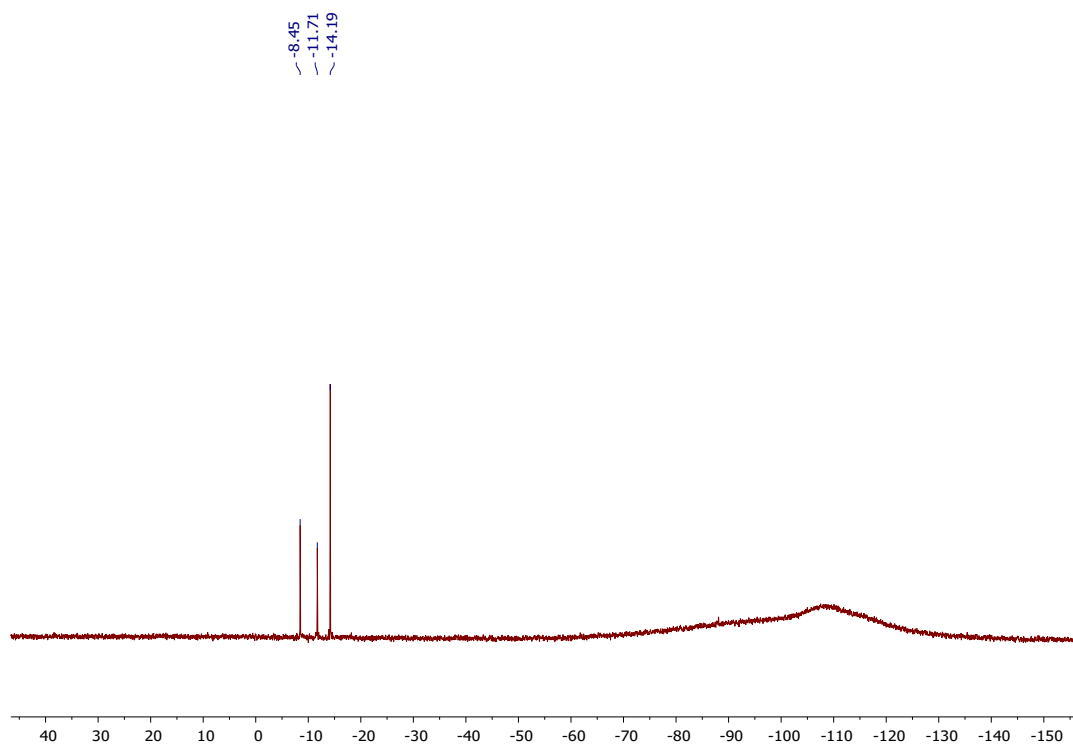


Figure S4c. $^{29}\text{Si}\{^1\text{H}\}$ NMR (99.314 MHz, 305.0 K, C_6D_6) spectrum of **9**.

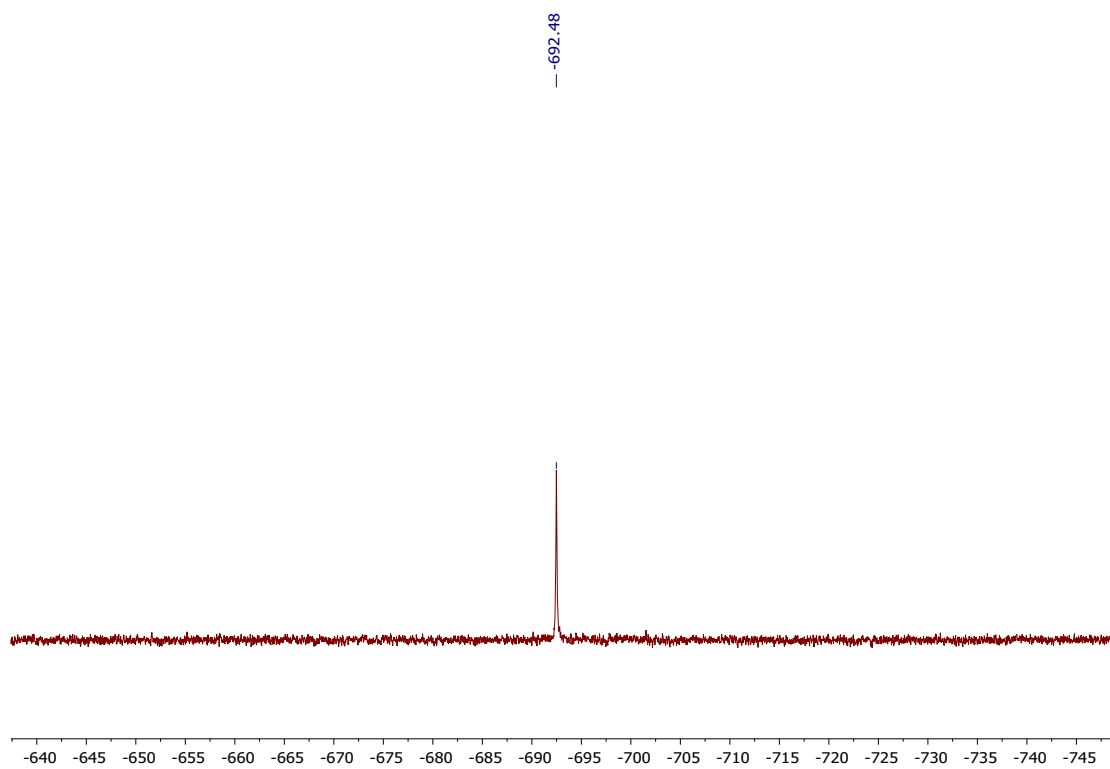
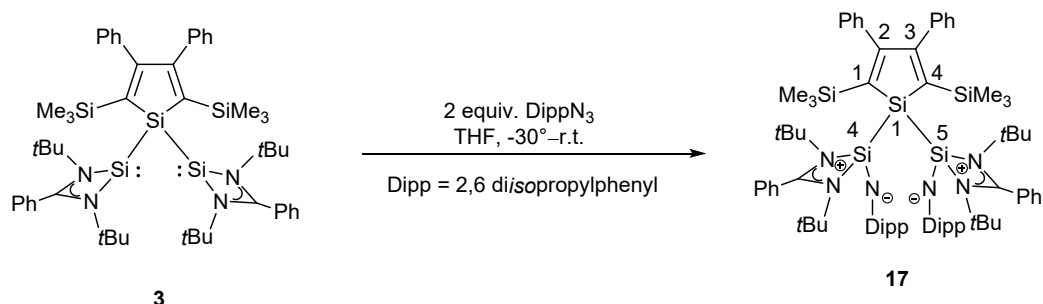


Figure S4d. $^{125}\text{Te}\{^1\text{H}\}$ NMR (157.8 MHz, 305.0 K, C_6D_6) spectrum of **9**.

Synthesis of 17:



Scheme S5

17. THF (5 mL) was added to the mixture of **3** (179 mg, 0.20 mmol) and Dipp-N₃ (83.7 mg, 0.40 mmol) at -30°C. The reaction was allowed to warm to room temperature and kept stirring for overnight. After that, the solvent was removed and the residue was extract by Toluene (8 mL). The filtrate was concentrated to 2 mL and put in room temperature to afford red crystalline solid. The red single crystals suitable for XRD investigations were obtained from C₆D₆ a few hours later. Yield: 174 mg (0.14 mmol, 71 %)

NMR spectra recorded in CDCl₃ at 305 K.

¹H NMR (499.9 MHz, 305.0 K, CDCl₃): δ = -1.16-0.75 (br, 18H, Si-(CH₃)₃), 1.09 (d, 6H, CH-(CH₃)₂), 1.27 (d, 6H, CH-(CH₃)₂), 1.28 (d, 6H, CH-(CH₃)₂), 1.29 (s, 18H, tBu), 1.31 (s, 18H, tBu), 1.37 (d, 6H, CH-(CH₃)₂), 3.89 (m, 2H, CH-(CH₃)₂), 4.20 (m, 2H, CH-(CH₃)₂), 6.49 (d, 2H, silole-Ph), 6.66 (t, 2H, silole-Ph), 6.82 (t, 2H, Dipp-Ph), 7.00-7.05 (m, 6H, silole-Ph), 7.21 (t, 2H, Dipp-Ph), 7.33 (d, 2H, Dipp-Ph), 7.38-7.51 (m, 10H, amidinate-Ph).

¹³C{¹H} NMR (125.8 MHz, 305.0 K, CDCl₃): δ = 1.18 (Si-(CH₃)₃), 23.60, 25.07 (C(CH₃)₂), 26.72, 26.80 (C(CH₃)₂), 27.68, 27.79 (C(CH₃)₂), 31.71, 32.71 (C-(CH₃)₃), 54.35, 54.72 (C-(CH₃)₃), 114.85 (pC of Dipp), 122.88, 123.09 (mC of Dipp), 126.41 (pC of silole-Ph), 126.79 (mC of silole-Ph), 127.45 (mC of PhC(NtBu)₂), 128.01 (mC of silole-Ph), 128.17, 128.23 (oC of Dipp), 128.71, 128.93 (oC of silole-Ph), 129.05 (oC of PhC(NtBu)₂), 130.55 (pC of PhC(NtBu)₂), 130.93 (N₂C-C-C₅H₅), 138.52, 140.15 (C-iPr of Dipp), 143.09 (C of silole-C-C₅H₅), 147.11 (C-N of Dipp), 151.36 (C^{1/4}), 170.47 (C^{2/3}), 176.08 (PhC(NtBu)₂).

²⁹Si{¹H} NMR (99.4 MHz, 305.0 K, CDCl₃): δ = -8.98 (Si-(CH₃)₃), -20.29 (SiC₂), -73.10 (SiN₂).

EA: C/H/N [%] calculated for C₇₆H₁₀₈N₆Si₅: 73.25/8.74/6.74; found: 73.55/8.63/6.93

HR-MS (ESI): m/z calculated for C₇₆H₁₀₈N₆Si₅: 1244.7482; found: 1244.7479.

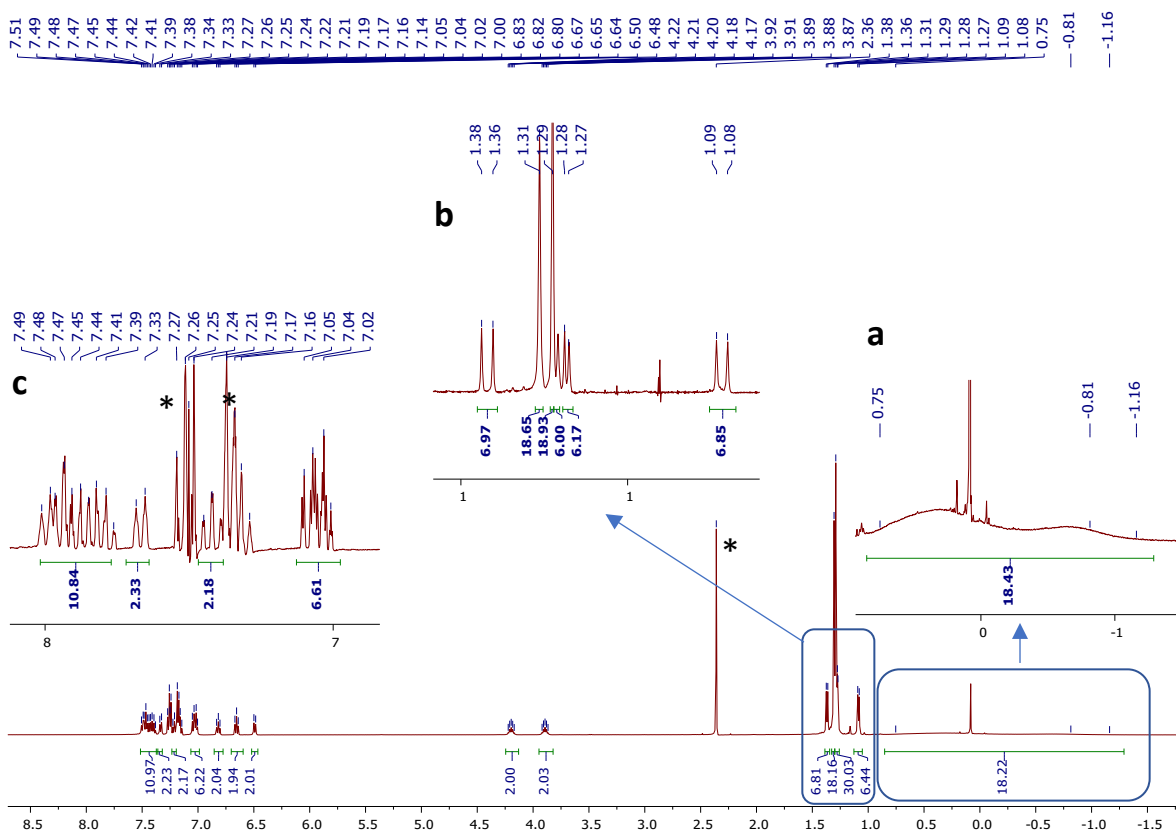


Figure S5a. ^1H NMR (499.9 MHz, 305.0 K, CDCl_3) spectrum of **17** (*Toluene), (Part a-c of the spectrum resolution enhanced by gaussian multiplication).

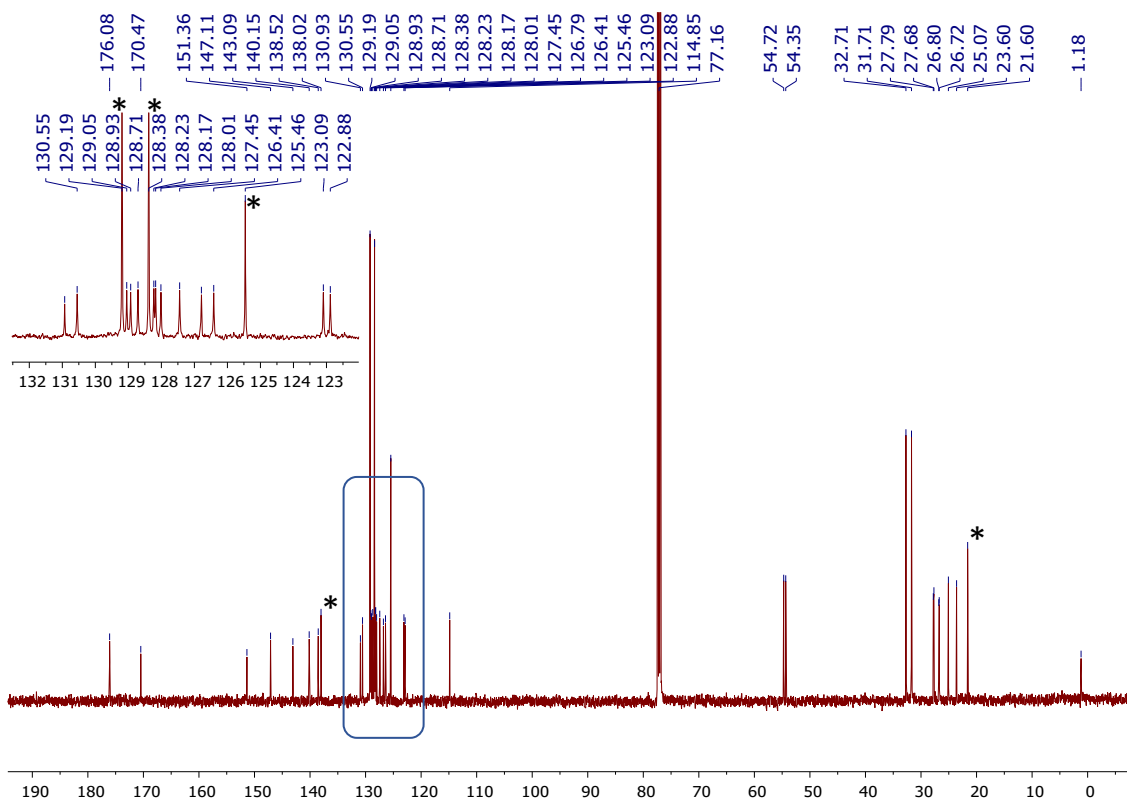


Figure S5b. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, 305.0 K, CDCl_3) spectrum of **17** (*Toluene).

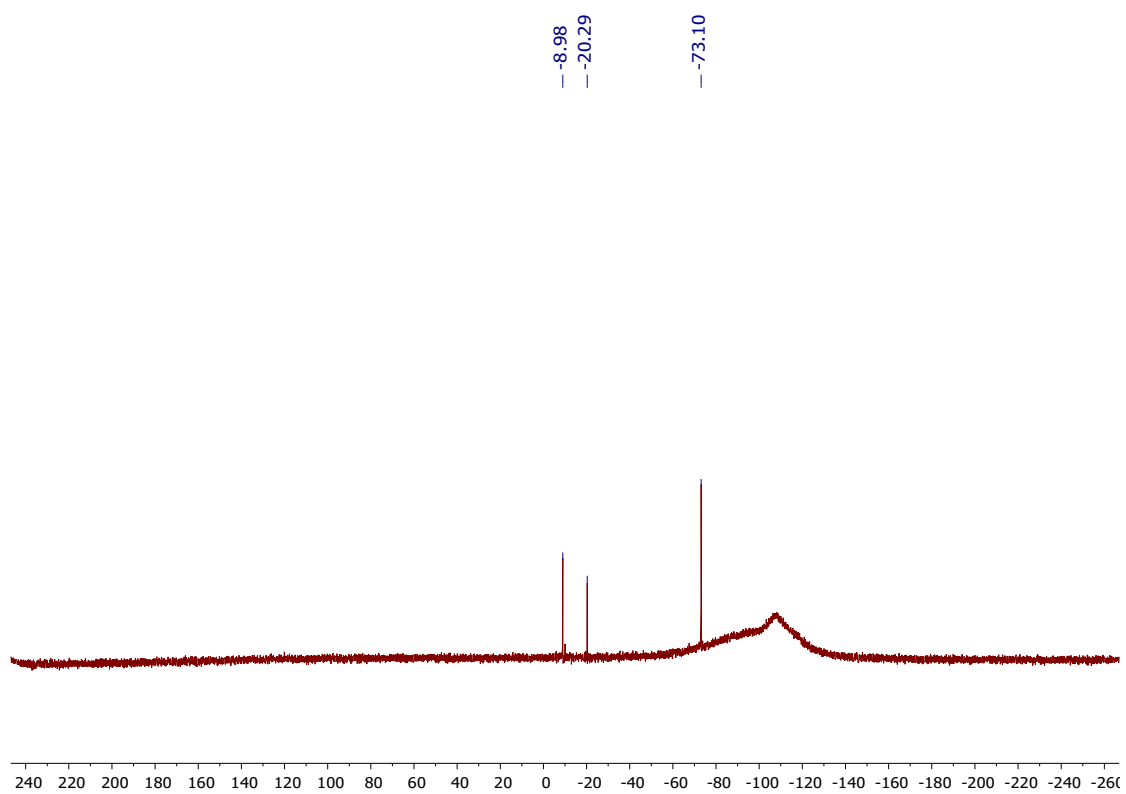


Figure S5c. $^{29}\text{Si}\{^1\text{H}\}$ NMR (99.314 MHz, 305.0 K, CDCl_3) spectrum of **17**.

^{77}Se and ^{125}Te NMR chemical shift of silicon(IV)selenides and tellurides.

An important feature in selenium and tellurium NMR spectroscopy is that tellurium and selenium shieldings run closely parallel in equivalent compounds. The plot of $\delta^{125}\text{Te}$ versus $\delta^{77}\text{Se}$ is linear with reported slopes between 1.6 and 1.8.^[S3] We found that for the limited group of known silicon(IV)selenides and tellurides also a linear correlation exists with a slope of 1.67 (see Figure 6). As the ^{77}Se and ^{125}Te NMR chemical shifts of chalcogenides **8** and **9** are significantly different from those reported for other amidinate-stabilized silicon chalcogenides such as **14-16**, the accordance of our data to this correlation further supports their validity.

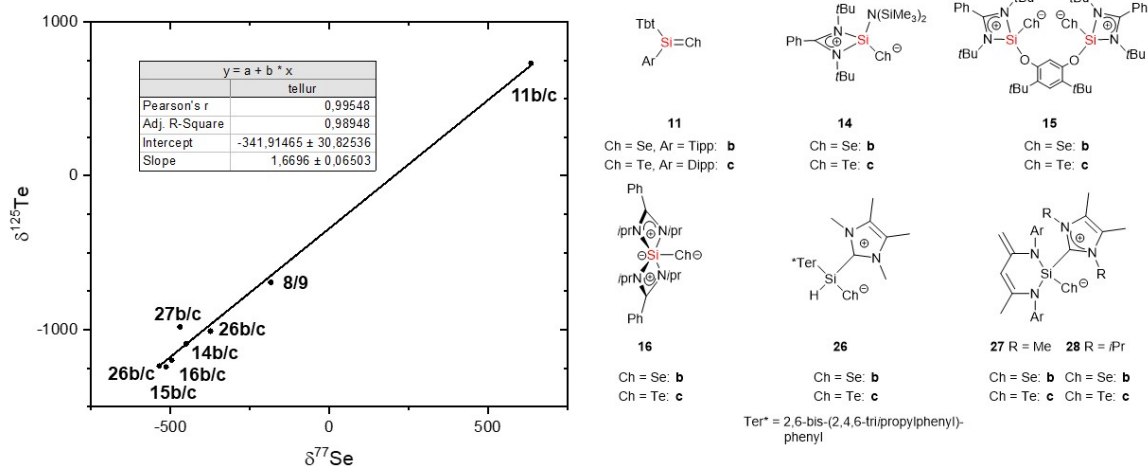
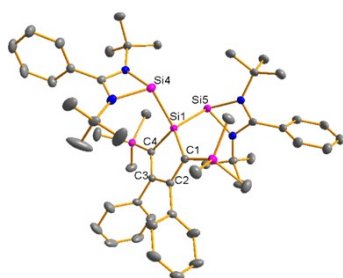
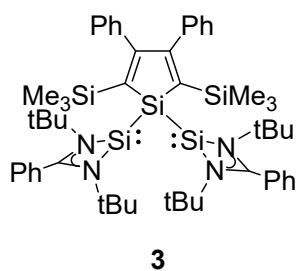


Figure S6. Plot of $\delta^{125}\text{Te}$ versus $\delta^{77}\text{Se}$ NMR chemical shifts for silicon tellurides and silicon selenides of equivalent compounds. The data for compounds **11, 14-16** and **26-28** are from references [S4-S11]).

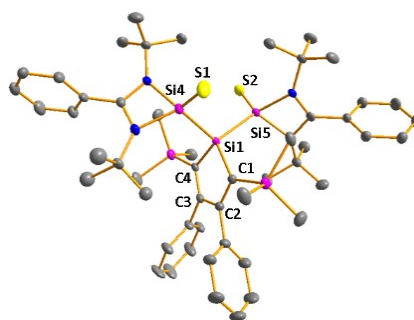
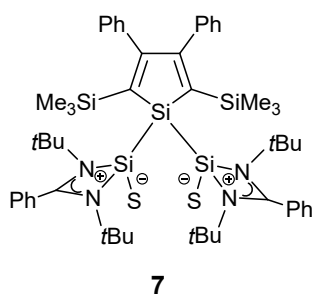
Details of X-ray Analysis

Single crystal X-ray data were measured on a Bruker AXS Apex II diffractometer (Mo-K α radiation, $\lambda = 0.71073\text{\AA}$, Kappa 4 circle goniometer, Bruker Apex II detector). The crystal was kept at 100.0 K during data collection. Absorption corrections based on symmetry-related measurements (multi-scan) were performed with the program SADABS.^[S12] The structures were solved with the program SHELXS and refined with SHELXL.^[S13] Pertinent data are summarized in Table S1-S5. CCDC-2345914 (**3**·1.5Et₂O), CCDC-2345913 (**7**·1.5Et₂O), CCDC-2345916 (**8**·4THF), CCDC-2345912 (**9**·Et₂O), CCDC-2345915 (**17**·2C₆D₆) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

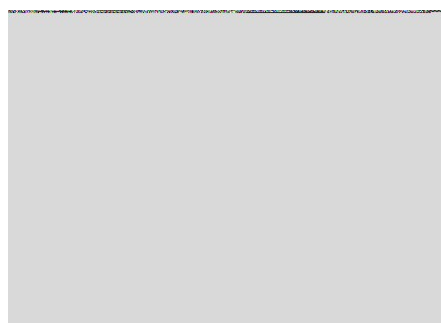
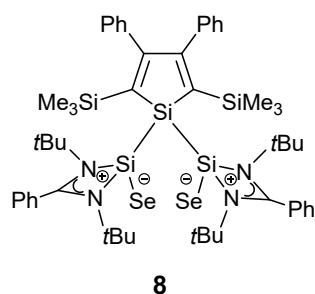
Table S1.

| | |
|--|---|
| Name | 3 ·1.5Et ₂ O |
| CCDC | 2345914 |
| Empirical formula | C ₅₈ H ₈₉ N ₄ O _{1.5} Si ₅ |
| Formula weight | 1006.78 |
| Temperature (K) | 100(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Triclinic |
| Space group | P-1 |
| a(Å) | 13.1877(4) |
| b(Å) | 15.3176(5) |
| c(Å) | 16.4228(5) |
| α (°) | 112.2626(12) |
| β (°) | 90.2282(11) |
| γ (°) | 95.8902(11) |
| V (Å ³) | 3050.65(17) |
| Z | 2 |
| D _{calc} (Mg/m ³) | 1.096 |
| μ (mm ⁻¹) | 0.157 |
| F (000) | 1094 |
| θ range (°) | 1.341 to 30.032 |
| Index ranges | -16,18; -21,21; -23,23 |
| Ref. collected | 178979 |
| Independent reflections | 17852 (R(int) = 0.0477) |
| Completeness to θ (°) | 30.032 (100%) |
| Goodness-of-fit on F ² | 1.098 |
| Final R indices (I > 2σ(I)) | R1 = 0.0503 wR2 = 0.1112 |
| R indices (all data) | R1 = 0.0599 wR2 = 0.1158 |
| Δρmax, min (e/Å ³) | 0.756, -0.421 |

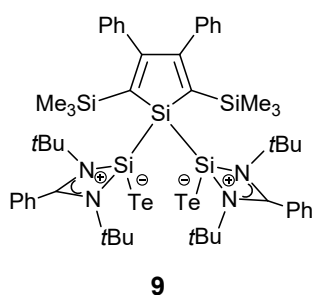
Table S2.



| | |
|--|--|
| Name | 7 ·1.5Et ₂ O |
| CCDC | 2345913 |
| Empirical formula | C ₅₈ H ₈₉ N ₄ O _{1.5} S ₂ Si ₅ |
| Formula weight | 1070.9 |
| Temperature (K) | 100(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Triclinic |
| Space group | P-1 |
| a(Å) | 13.6292(7) |
| b(Å) | 15.0182(8) |
| c(Å) | 15.9881(8) |
| α (°) | 82.885(2) |
| β (°) | 80.451(2) |
| γ (°) | 75.486(2) |
| V (Å ³) | 3112.6(3) |
| Z | 2 |
| D _{calc} (Mg/m ³) | 1.143 |
| μ (mm ⁻¹) | 0.223 |
| F (000) | 1158 |
| θ range (°) | 1.296 to 30.034 |
| Index ranges | -19,19; -21,21; -22,22 |
| Ref. collected | 151405 |
| Independent reflections | 18196 (R(int) = 0.0566) |
| Completeness to θ (°) | 30.034 (100%) |
| Goodness-of-fit on F ² | 1.098 |
| Final R indices (I>2σ(I)) | R1 = 0.0545 wR2 = 0.1314 |
| R indices (all data) | R1 = 0.0674 wR2 = 0.1383 |
| Δρmax, min (e/Å ³) | 0.746, -1.025 |

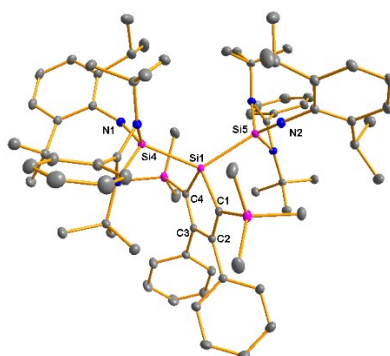
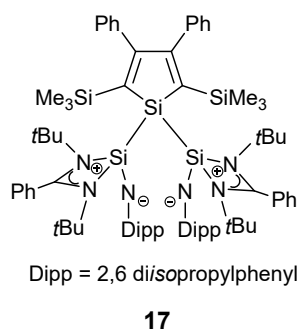
Table S3.

| | |
|--|--|
| Name | 8 ·4THF |
| CCDC | 2345916 |
| Empirical formula | C ₆₈ H ₁₀₆ N ₄ O ₄ Se ₂ Si ₅ |
| Formula weight | 1341.93 |
| Temperature (K) | 100(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Monoclinic |
| Space group | P2 ₁ /c |
| a(Å) | 13.3426(6) |
| b(Å) | 23.7190(10) |
| c(Å) | 22.8201(9) |
| α (°) | 90 |
| β (°) | 98.6421(15) |
| γ (°) | 90 |
| V (Å ³) | 7140.0(5) |
| Z | 4 |
| D _{calc} (Mg/m ³) | 1.248 |
| μ (mm ⁻¹) | 1.167 |
| F (000) | 2848 |
| θ range (°) | 1.246 to 32.032 |
| Index ranges | -19,19; -35,35; -30,34 |
| Ref. collected | 355149 |
| Independent reflections | 24852 (R(int) = 0.0416) |
| Completeness to θ (°) | 32.032 (100%) |
| Goodness-of-fit on F ² | 1.046 |
| Final R indices (I > 2σ(I)) | R1 = 0.0366 wR2 = 0.0944 |
| R indices (all data) | R1 = 0.0454 wR2 = 0.0996 |
| Δρmax, min (e/Å ³) | 1.372, -1.026 |

Table S4.

| | |
|--|---|
| Name | 9 ·Et ₂ O |
| CCDC | 2345912 |
| Empirical formula | C ₅₆ H ₈₄ N ₄ OSi ₅ Te ₂ |
| Formula weight | 1224.92 |
| Temperature (K) | 100(2) |
| Wavelength (Å) | 1.54178 |
| Crystal system | Orthorhombic |
| Space group | P2 ₁ 2 ₁ 2 ₁ |
| a(Å) | 13.3105(6) |
| b(Å) | 15.4573(6) |
| c(Å) | 30.3266(12) |
| α (°) | 90 |
| β (°) | 90 |
| γ (°) | 90 |
| V (Å ³) | 6239.5(4) |
| Z | 4 |
| D _{calc} (Mg/m ³) | 1.304 |
| μ (mm ⁻¹) | 8.586 |
| F (000) | 2520 |
| θ range (°) | 2.914 to 74.489 |
| Index ranges | -16,16; -17,19; -37,37 |
| Ref. collected | 103799 |
| Independent reflections | 12770 (R(int) = 0.0605) |
| Completeness to θ (°) | 74.489 (100%) |
| Goodness-of-fit on F ² | 1.065 |
| Final R indices (I > 2σ(I)) | R1 = 0.0269 wR2 = 0.0662 |
| R indices (all data) | R1 = 0.0282 wR2 = 0.0669 |
| Δρmax, min (e/Å ³) | 1.084, -0.324 |

Table S5.



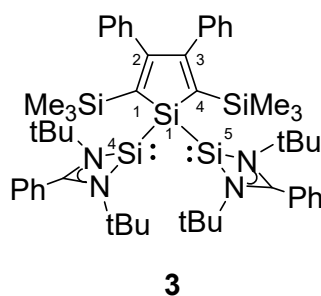
| | |
|--|---|
| Name | 17 ·2C ₆ D ₆ |
| CCDC | 2345915 |
| Empirical formula | C ₈₈ H ₁₀₈ D ₁₂ N ₆ Si ₅ |
| Formula weight | 1414.42 |
| Temperature (K) | 100(2) K |
| Wavelength (Å) | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P2/c |
| a(Å) | 12.3959(4) |
| b(Å) | 15.5019(6) |
| c(Å) | 21.2307(8) |
| α (°) | 90 |
| β (°) | 99.0856(12) |
| γ (°) | 90 |
| V (Å ³) | 4028.5(3) |
| Z | 2 |
| D _{calc} (Mg/m ³) | 1.166 |
| μ (mm ⁻¹) | 0.137 |
| F (000) | 1520 |
| θ range (°) | 1.314 to 34.971 |
| Index ranges | -19,19; -25,25; -34,34 |
| Ref. collected | 221628 |
| Independent reflections | 17685 (R(int) = 0.0368) |
| Completeness to θ (°) | 34.971 (100%) |
| Goodness-of-fit on F ² | 1.063 |
| Final R indices (I > 2σ(I)) | R1 = 0.0358 wR2 = 0.0944 |
| R indices (all data) | R1 = 0.0411 wR2 = 0.0978 |
| Δρmax, min (e/Å ³) | 0.545, -0.323 |

Computational Details

All quantum chemical calculations were carried out using the Gaussian16 package.^[S14] The molecular structure optimization were performed using the M06-2X functional^[S15] along with the 6-311+G(d,p) basis set. The level of theory is justified by the close agreement between calculated and experimentally determined structural parameter (see Table S6). TD-DFT computations were performed as implemented in Gaussian 16 and the M06-2X functional along with the 6-311+G(d,p) basis set for molecular structures obtained at the same level of theory. This level of theory has been shown to provide computational estimates for Wavelength, that are close to the experimental data.^[S16-17]

Natural bond analysis was performed with the NBO7 program integrated into the Gaussian16 package.^[S18]

Table S6. Comparison of structural parameter of compounds **3** and calculated structures **3**^{opt}.



| | 3 ^[a] | 3 ^{opt} ^[b] | Deviation |
|-------------|-------------------------|--|-----------|
| Si1-Si4 | 245.90 | 244.24 | 0.68 |
| Si1-Si5 | 246.35 | 245.80 | 0.22 |
| Si1-C1 | 189.11 | 189.30 | 0.10 |
| Si1-C4 | 189.48 | 189.96 | 0.25 |
| C1-C2 | 137.09 | 136.39 | 0.51 |
| C2-C3 | 147.64 | 148.60 | 0.65 |
| C3-C4 | 137.26 | 136.50 | 0.55 |
| Si4-Si1-Si5 | 108.91 | 110.29 | 1.27 |

[a] Experimental data from XRD. [b] M06-2X/6-311+G(d,p).

Figure S7. Simulated UV-Vis spectra of **3** at M06-2X/6-311+G(d,p)//M06-2X/6-311+G(d,p) level of theory.

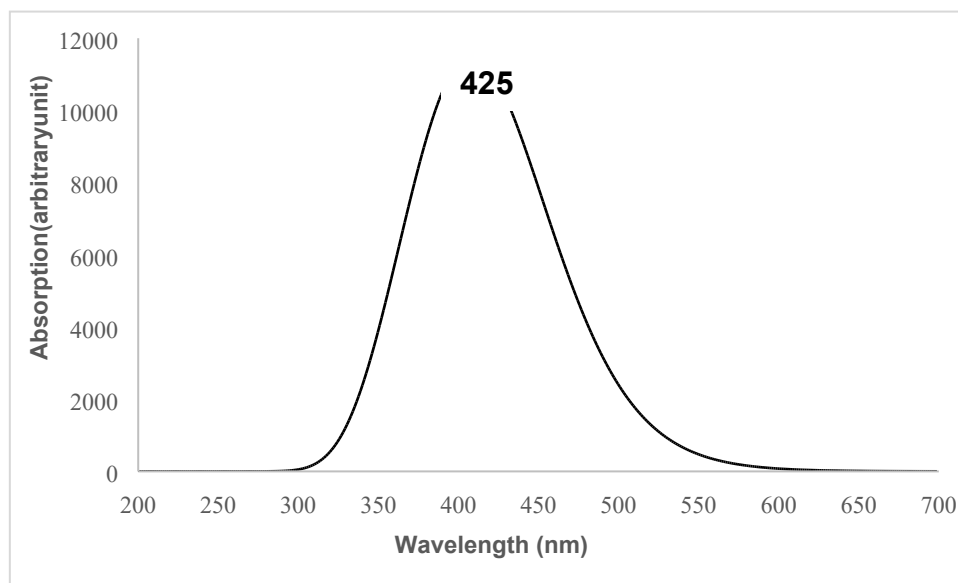
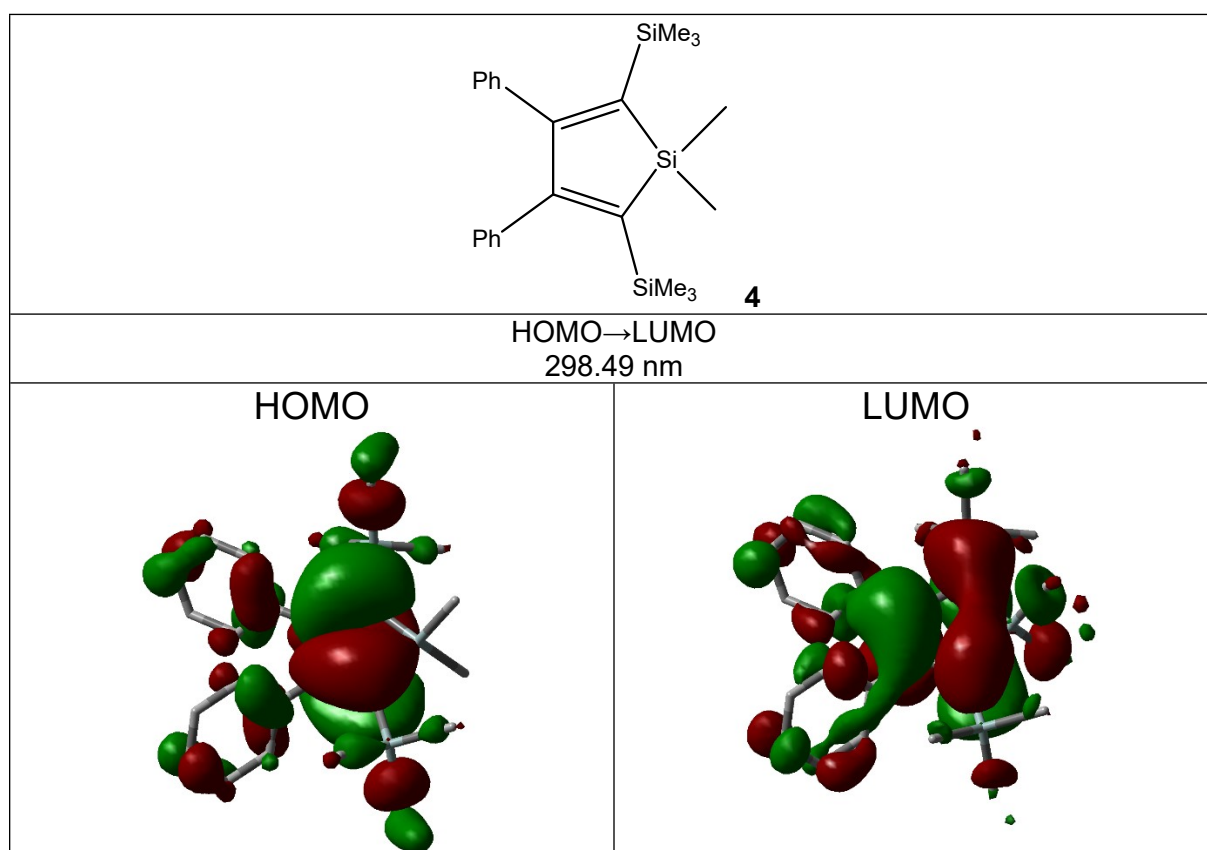
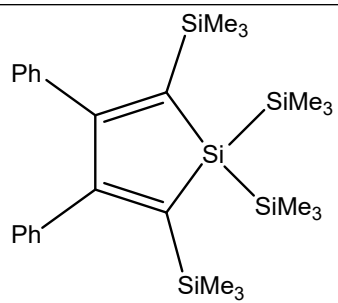


Figure S8. TD-DFT calculations of **4**, **5,6** and **J** at M06-2X/6-311+G(d,p)//M06-2X/6-311+G(d,p) level of theory.

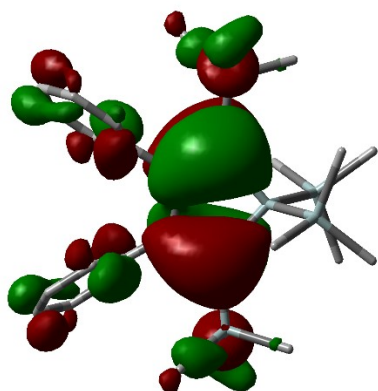




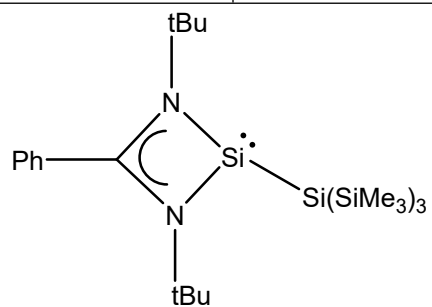
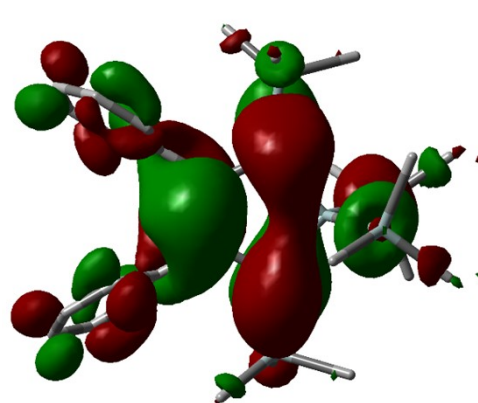
5

HOMO→LUMO
297.73 nm

HOMO



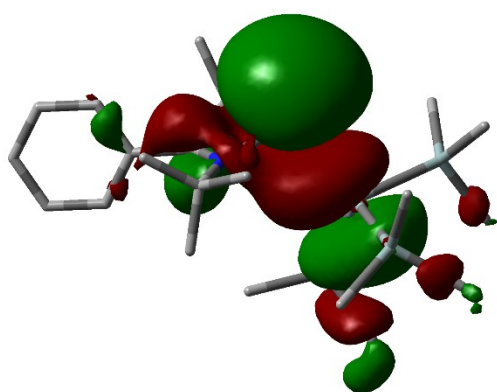
LUMO



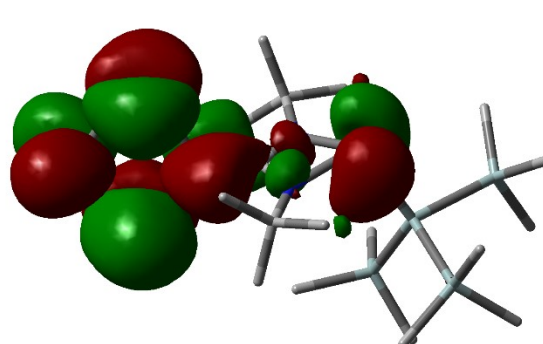
6

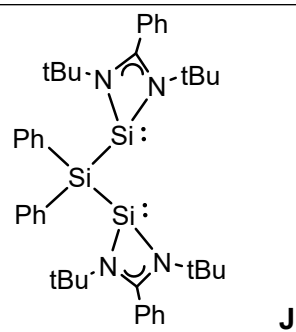
HOMO→LUMO
370.07 nm

HOMO



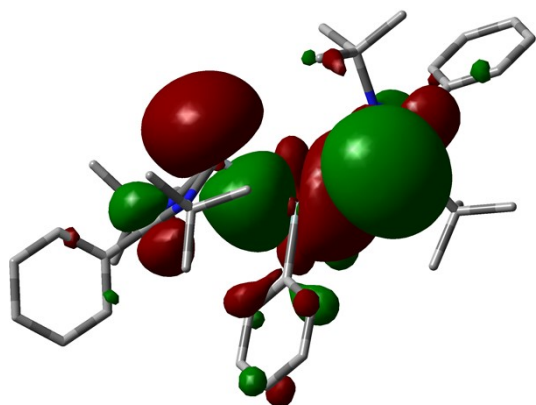
LUMO



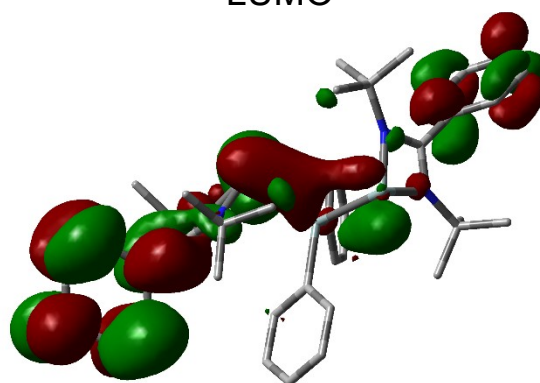


HOMO→LUMO
386.80 nm

HOMO



LUMO



Comparative NBO analysis for the tricoordinated silicon sulphide **10(S)** and amidinato-stabilized silicon sulphide **7**

For both silicon sulphides **10(S)** and **7** a NBO analysis based on the optimized structures at the M06-2X/6-311+G(d,p) level of theory was performed. The following analysis concentrates on the electronic situation around the Si-S linkage in both compounds. Only the results for one Si-S linkage of **7** are presented here. The NBO analysis indicates for the Si-S bond of the tricoordinated silicon sulphide **10(S)** a higher bond order than for the same linkage in the amidinate stabilized sulphide **7** (Wiberg bond indices (WBI) 1.75 (**10(S)**) vs. 1.49 (**7**), see Figure S8). The negative charge accumulation is higher at the sulphur atom of **7** while the electron deficiency at the silicon atom is reduced due the electron donation from the amidinate ligand. Based on the NBO analysis for **10(S)** a Lewis structure with a Si=S double bond is suggested, while for sulphide **7** Si-S single bond is indicated with three lone pairs at the sulphur atom (Figure S8). Figure S9 shows the surface diagrams of the two lone pairs at sulphur and the π -orbital of the Si=S bond of sulphide **10(S)**. The second order perturbation analysis indicates delocalization of one of the lone pairs at sulphur into the antibonding $\sigma^*(\text{Si-C})$ orbitals (negative hyperconjugation, Figure S10). In contrast, three lone pairs at each sulphur atoms in *bissulphide* **7** are located (see Figure S11) and the hyperconjugation with the Si-Si linkage and the amidinate ligand is much more pronounced (see Figures S12 and S13) resulting in the observed short Si-S separation.

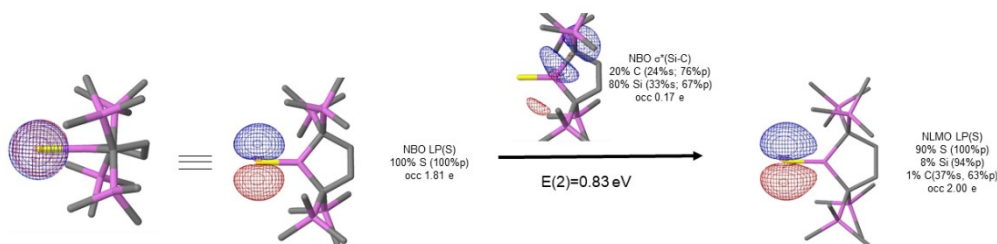


Figure S11. Results of the 2nd order perturbation analysis of sulphide **10(S)** indicating the LP(S) / $\sigma^*(\text{Si-C})$ hyperconjugation (at M06-2X/6-311+G(d,p)), isodensity value 0.05).

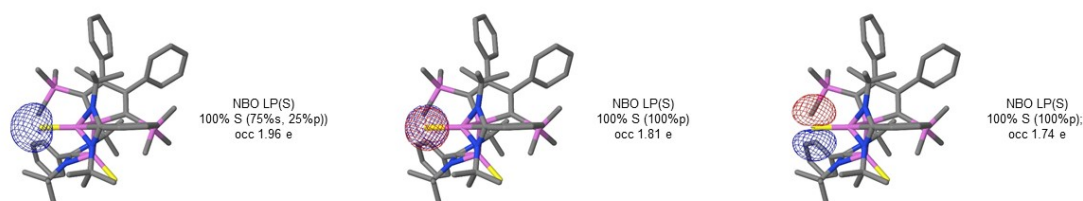


Figure S12. Surface diagrams of the NBOs representing the three sulphur lone pairs (LP(S)) of one of the C-S bond of *bisulphide 7* (M06-2X/6-311+G(d,p), isodensity value 0.05).

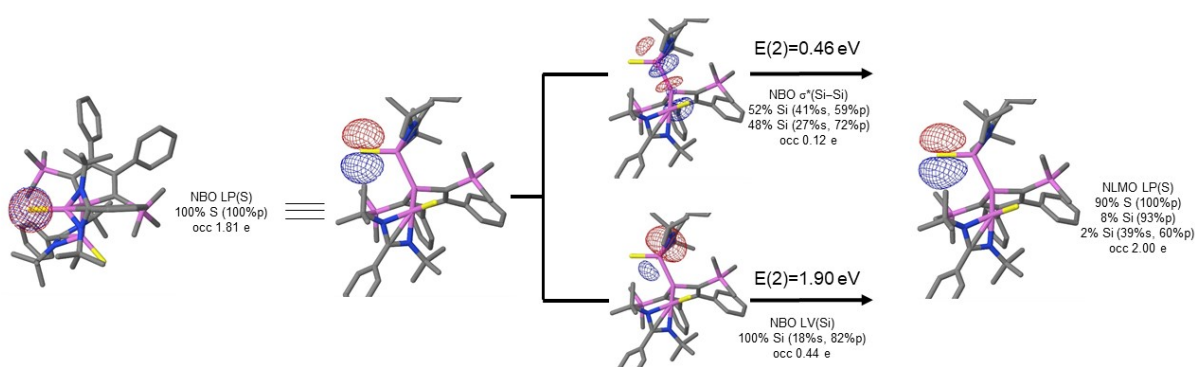


Figure S13. Results of the 2nd order perturbation analysis of *bisulphide 7* indicating the LP(S) / $\sigma^*(\text{Si-Si})$ and LP(S) / LV(Si) hyperconjugation (at M06-2X/6-311+G(d,p)), isodensity value 0.05).

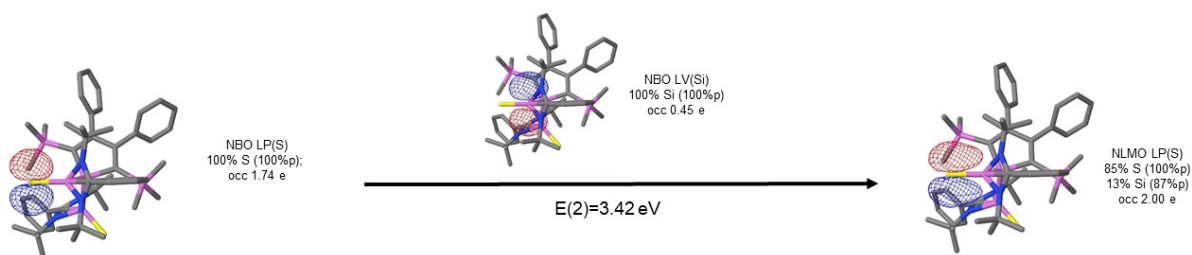


Figure S14. Results of the 2nd order perturbation analysis of *bisulphide 7* indicating the LP(S) / LV(Si) hyperconjugation (at M06-2X/6-311+G(d,p)), isodensity value 0.05).

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