

*Supporting Information*

**Reactivity Studies of the Silylene [PhC(NtBu)<sub>2</sub>](C<sub>5</sub>Me<sub>5</sub>)Si -  
Reactions with [M(COD)Cl]<sub>2</sub> (M = Rh(I), Ir(I)), S, Se, Te, and BH<sub>3</sub>**

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# NMR-Spectra

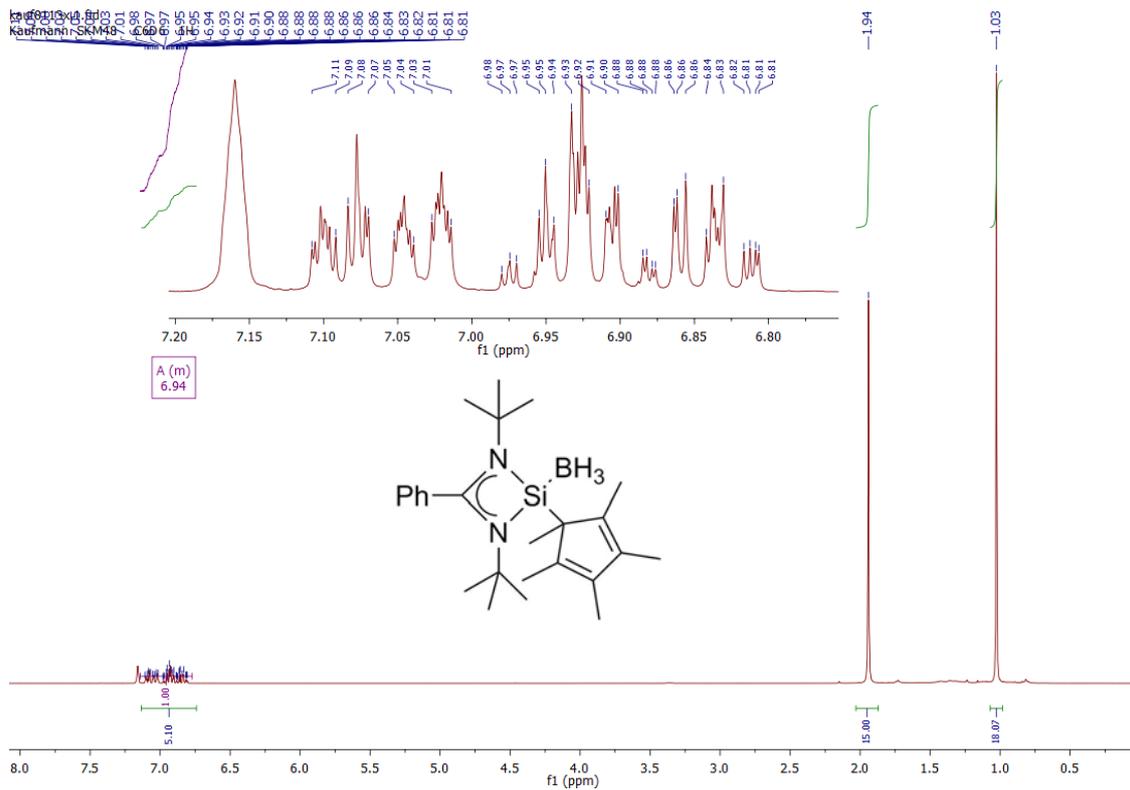


Figure S1:  $^1\text{H}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$ .

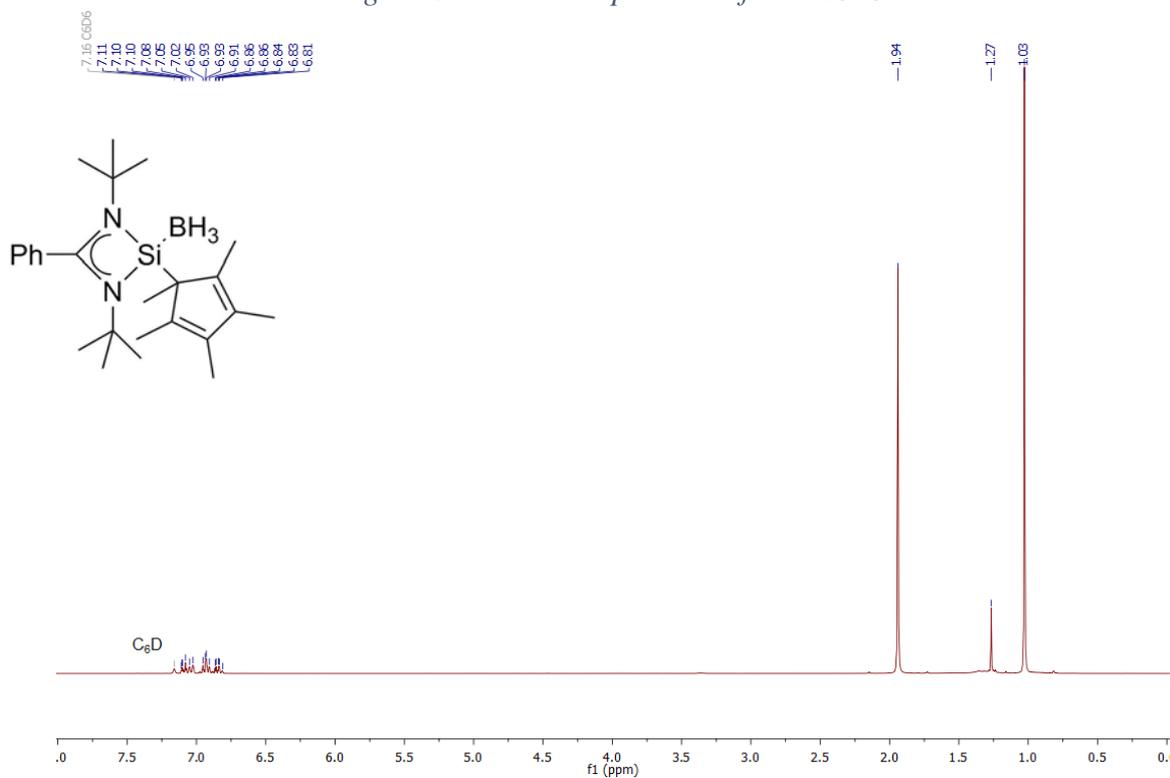


Figure S2:  $^1\text{H}\{^{11}\text{B}\}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$ .

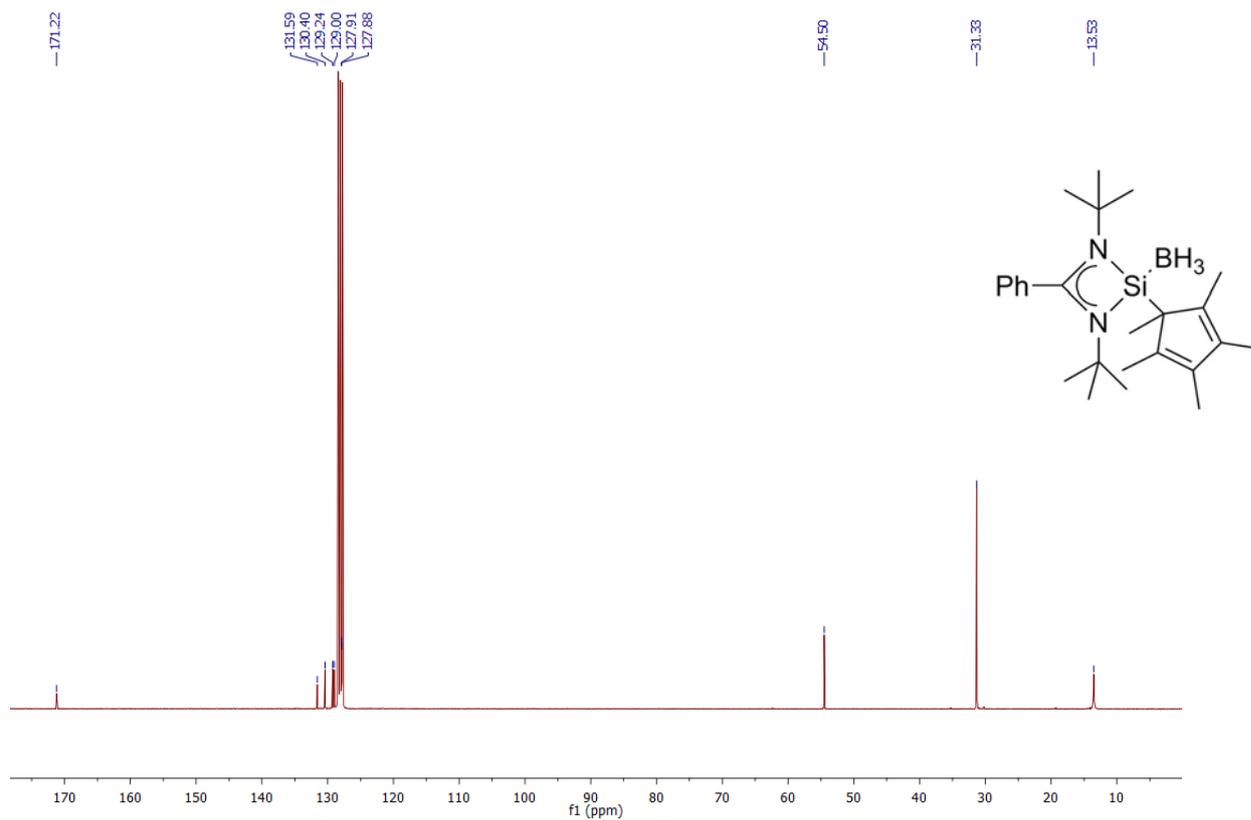


Figure S3:  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$ .

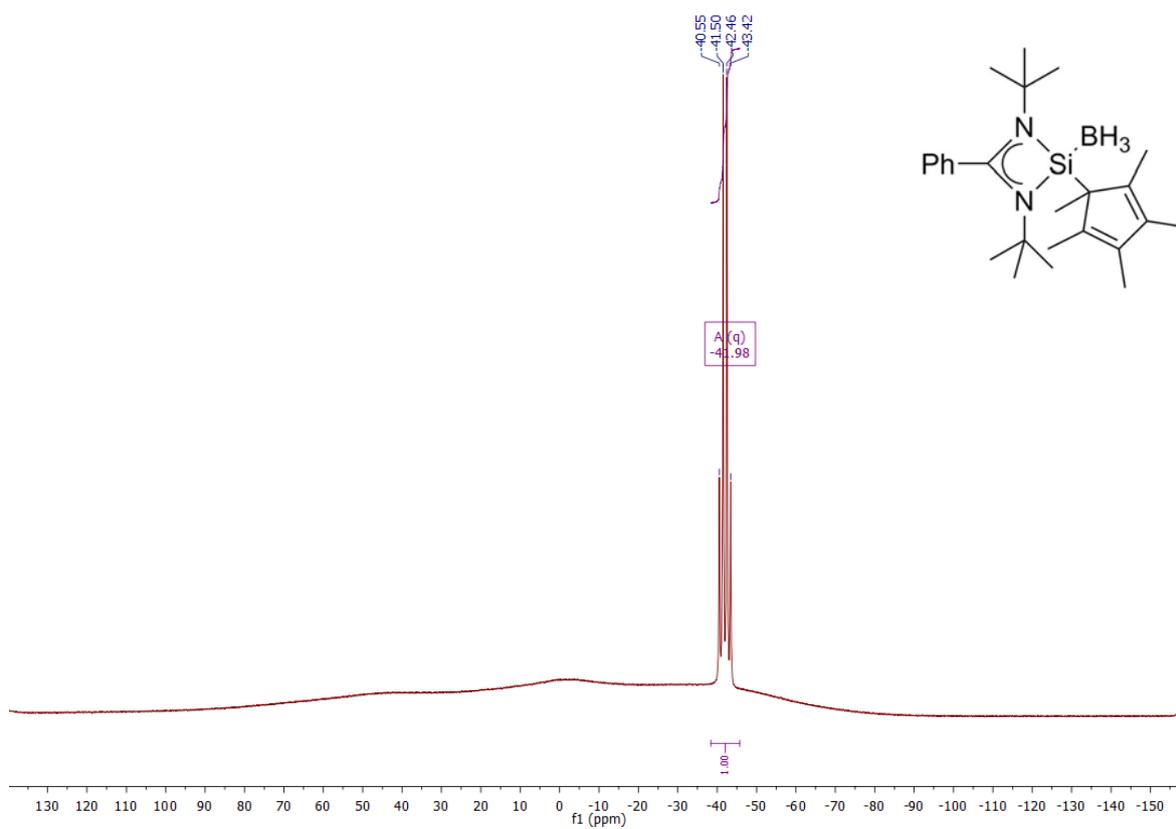


Figure S4:  $^{11}\text{B}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$ .

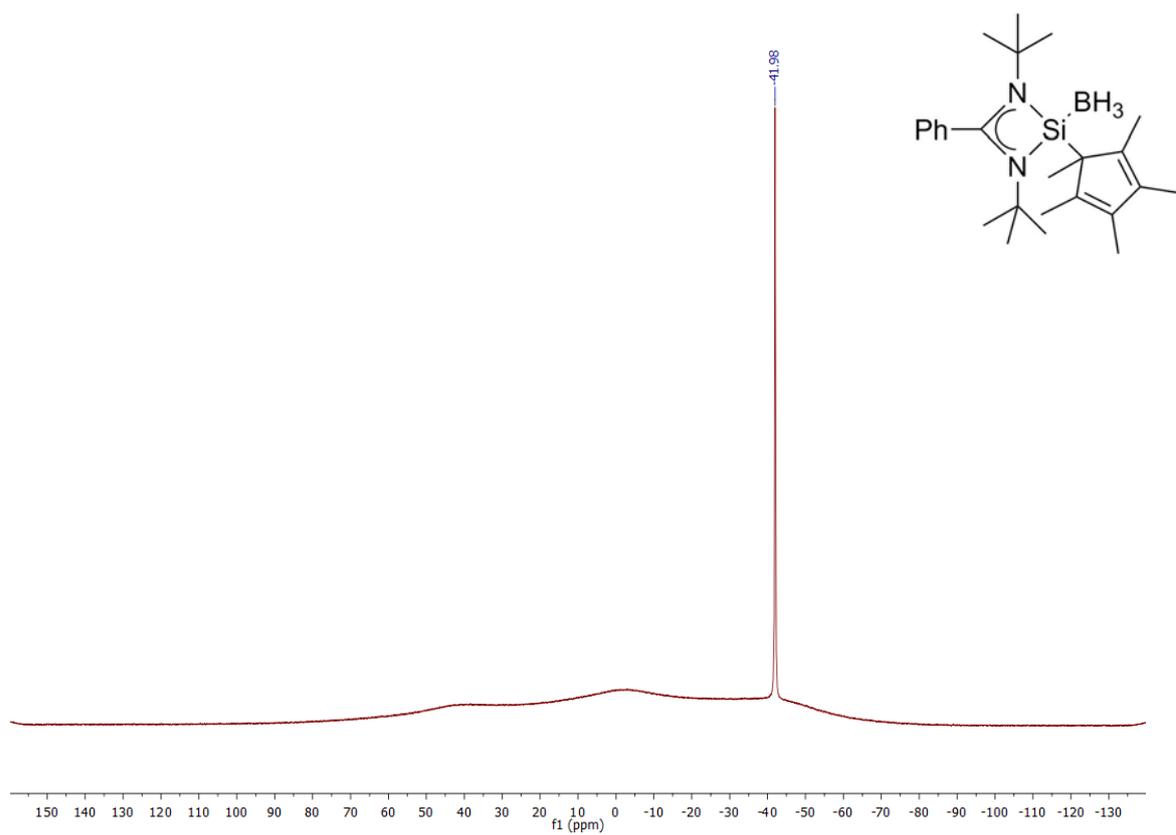


Figure S5:  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$ .

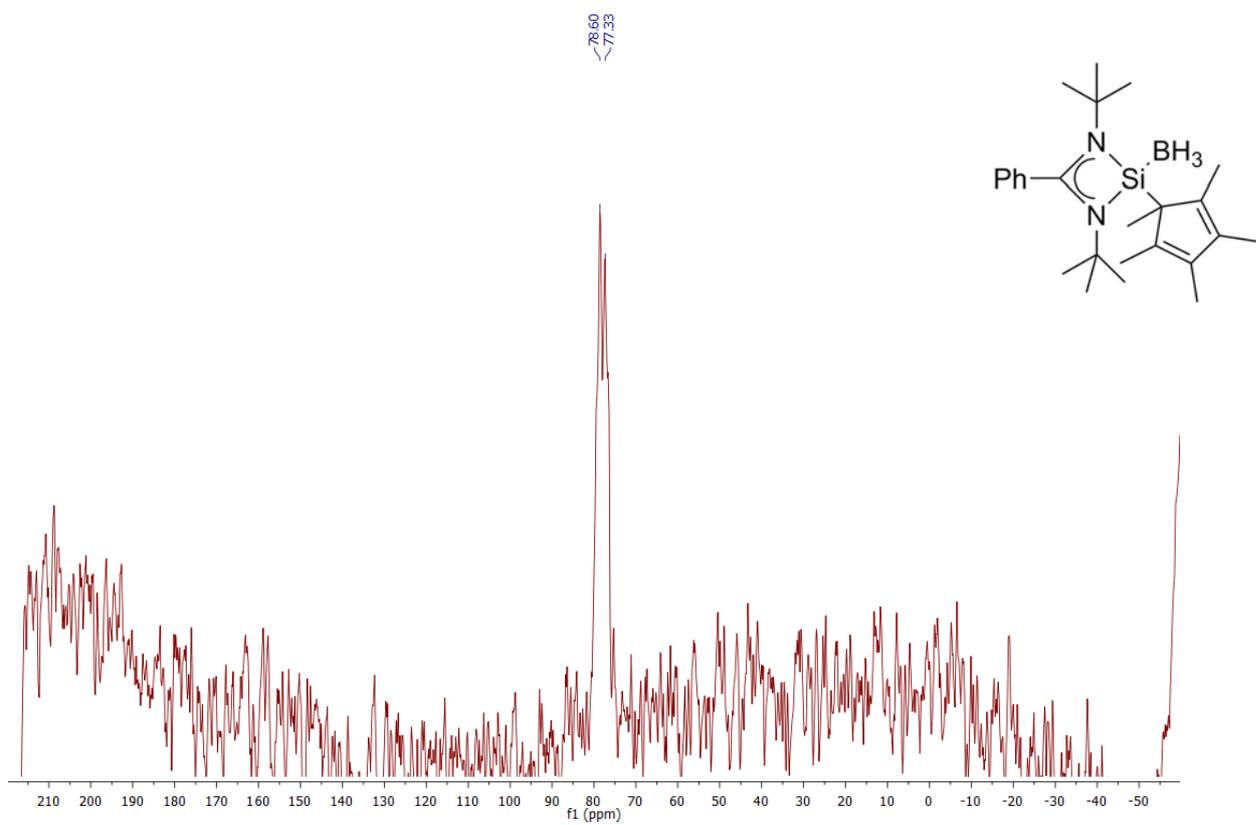


Figure S6:  $^{29}\text{Si}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$ .

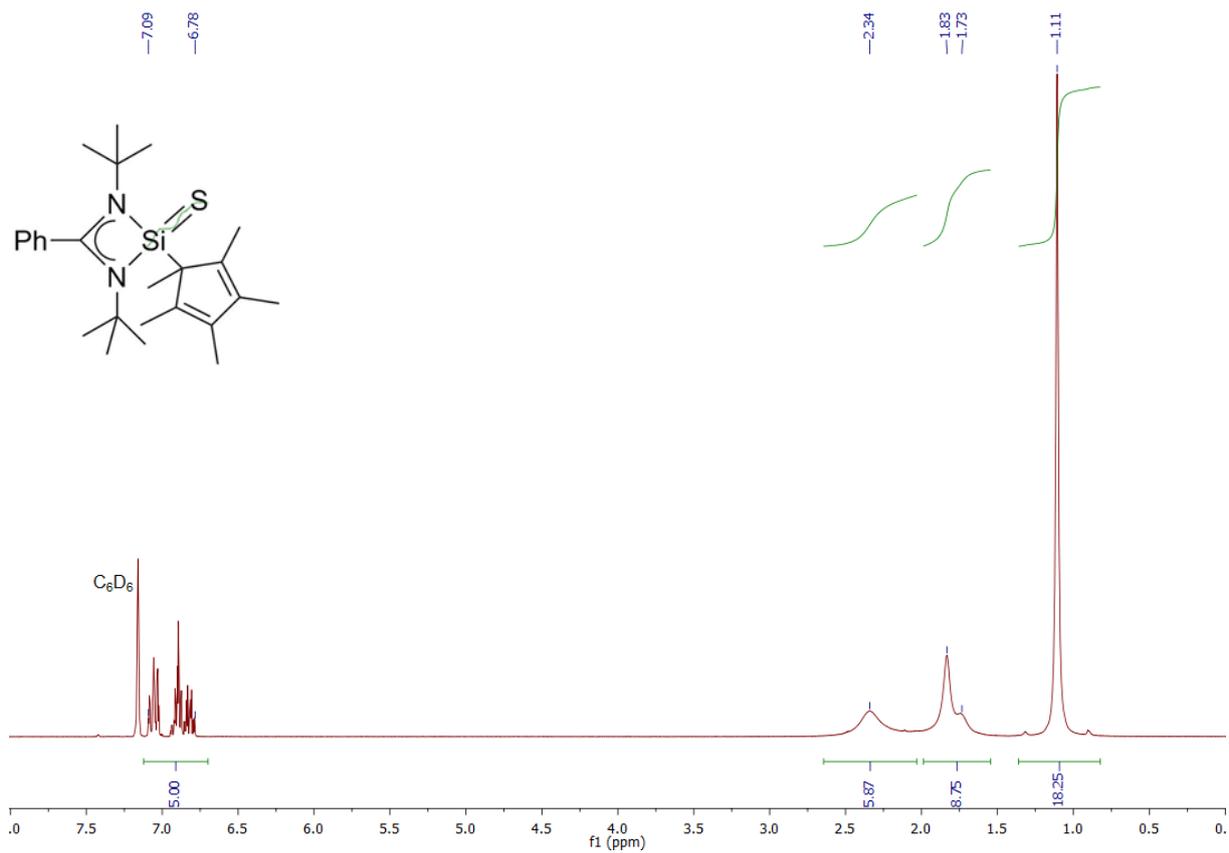


Figure S7: <sup>1</sup>H NMR spectrum of **2** in C<sub>6</sub>D<sub>6</sub>.

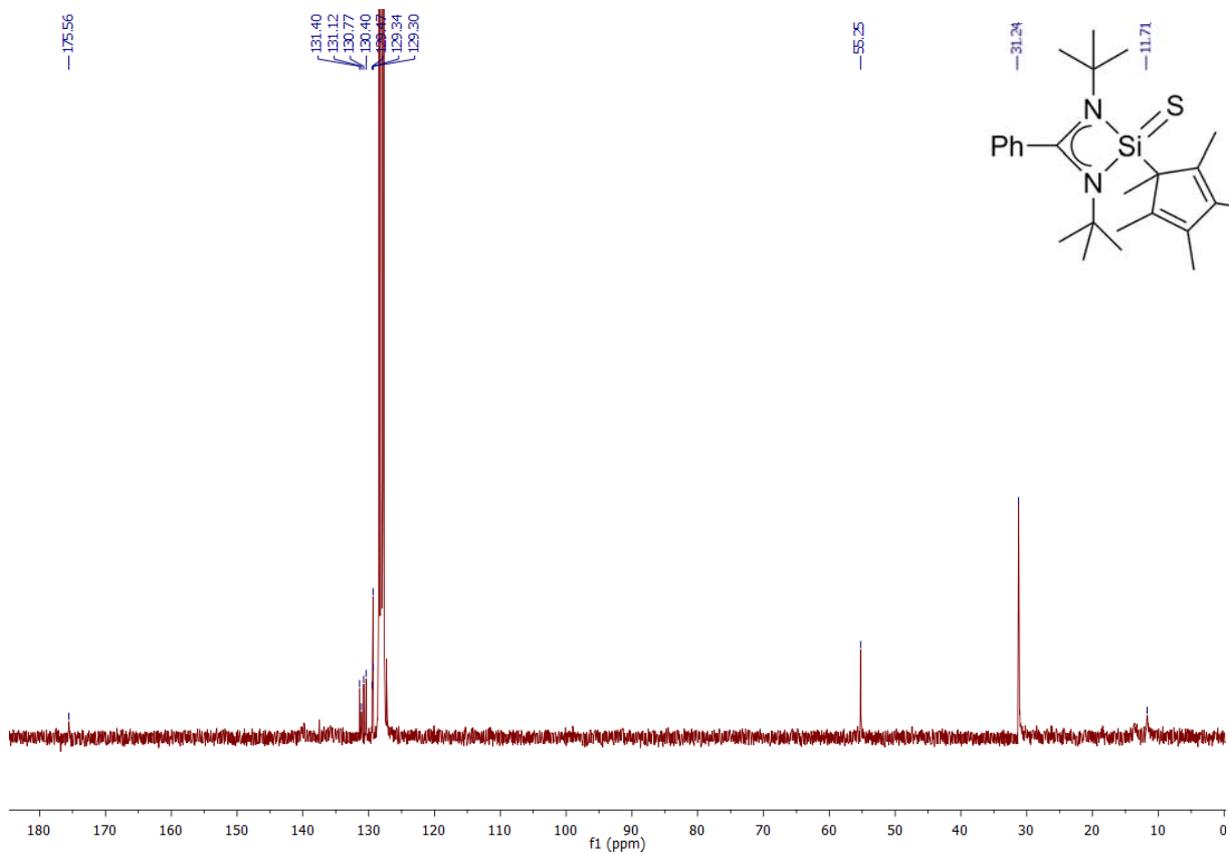


Figure S8: <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **2** in C<sub>6</sub>D<sub>6</sub>.

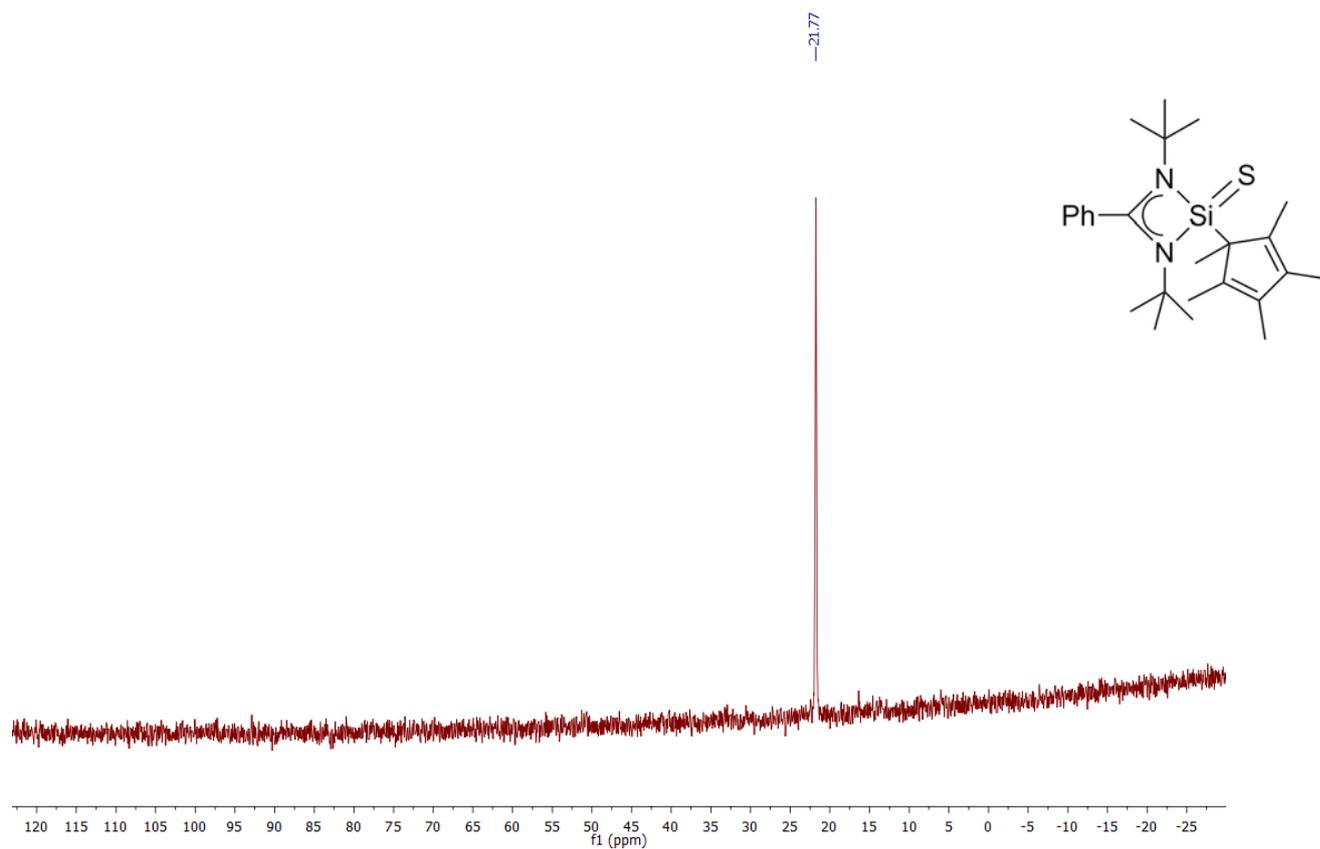


Figure S9:  $^{29}\text{Si}$  NMR spectrum of **2** in  $\text{C}_6\text{D}_6$ .

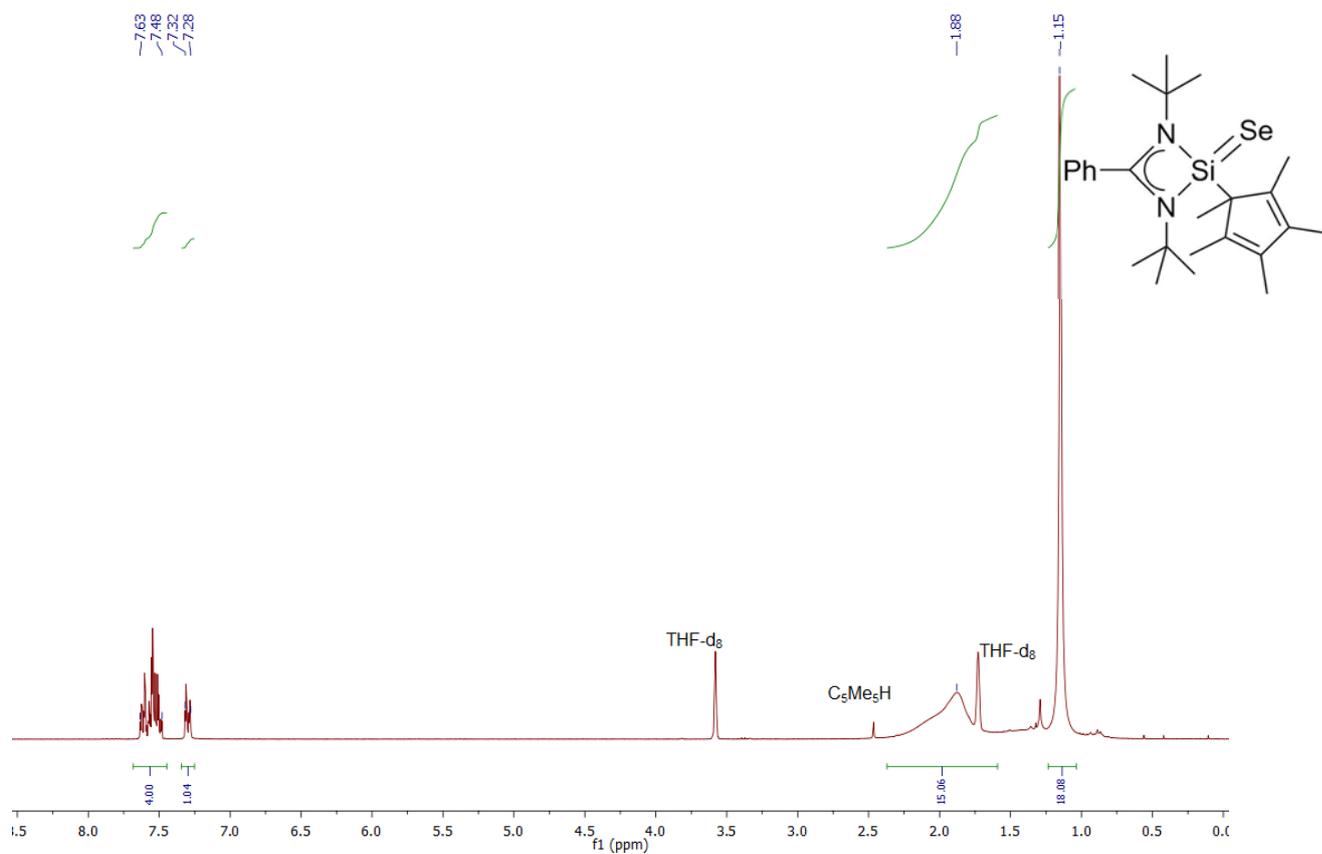


Figure S10:  $^1\text{H}$  NMR spectrum of **3** in  $\text{THF-d}_8$ .

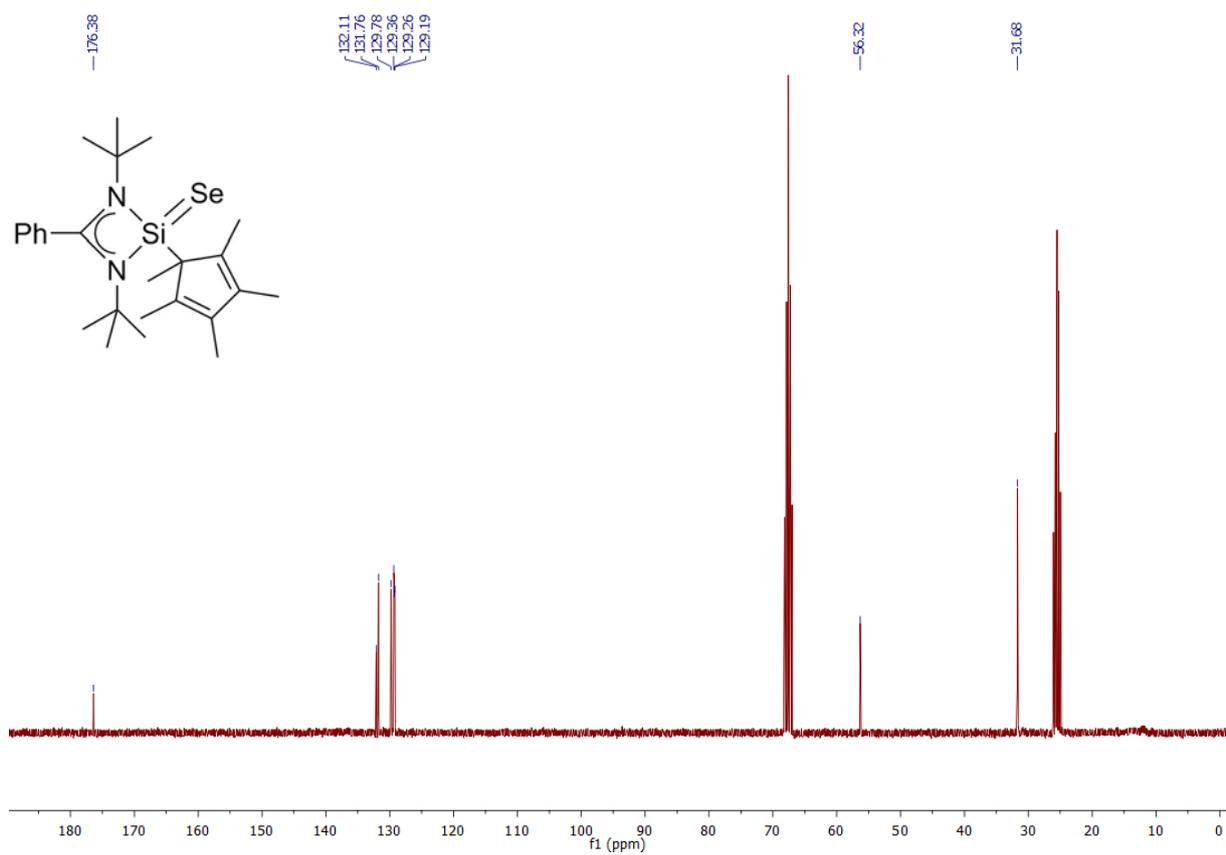


Figure S11:  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3** in  $\text{THF-}d_8$ .

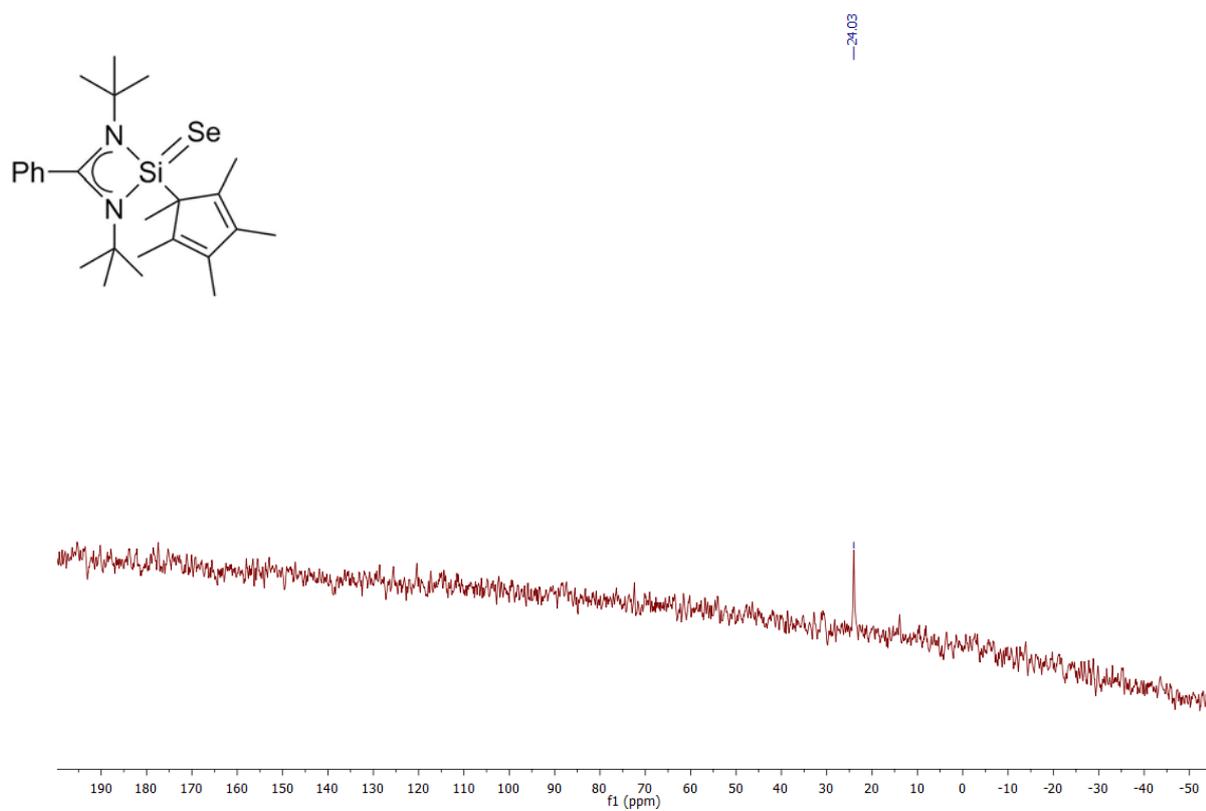


Figure S12:  $^{29}\text{Si}$  NMR spectrum of **3** in  $\text{THF-}d_8$ .

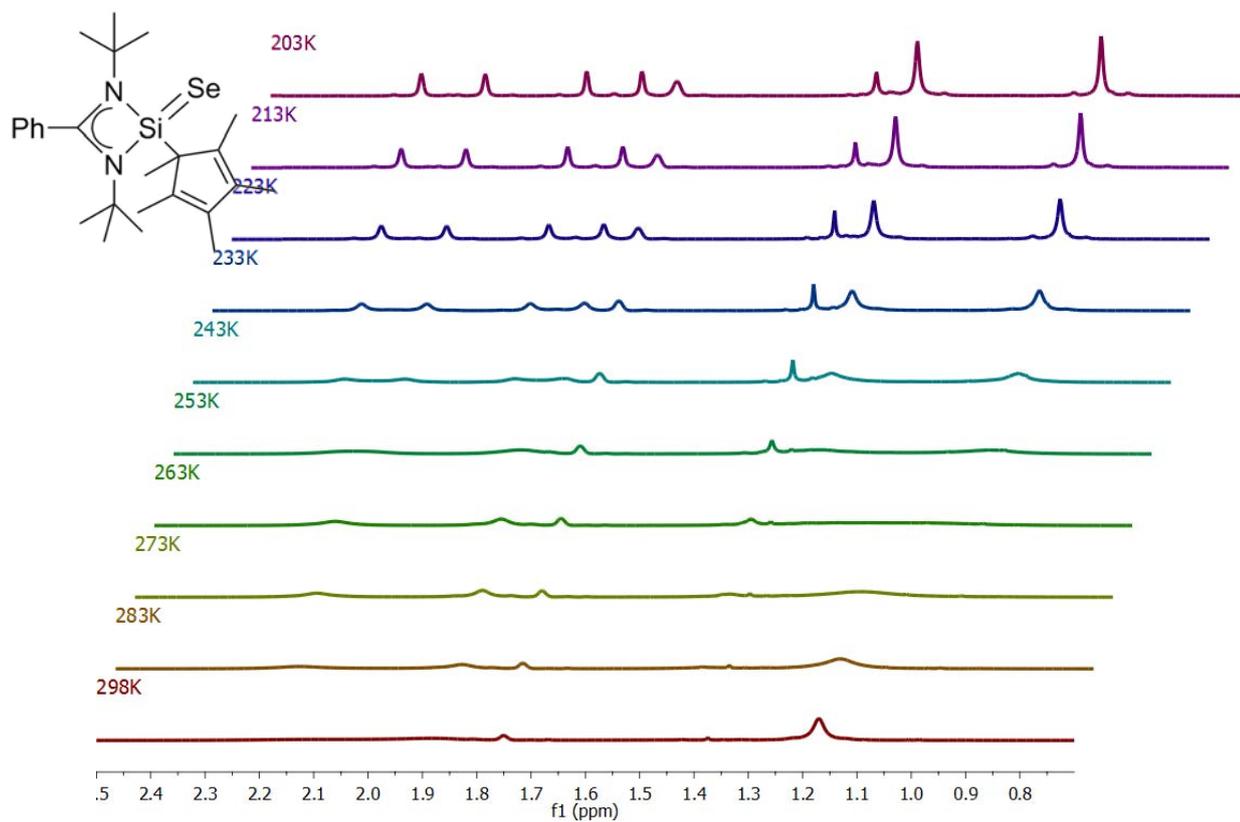


Figure S13: Low temperature VT  $^1\text{H}$  NMR spectra of compound **3** in  $\text{THF-d}_8$ .

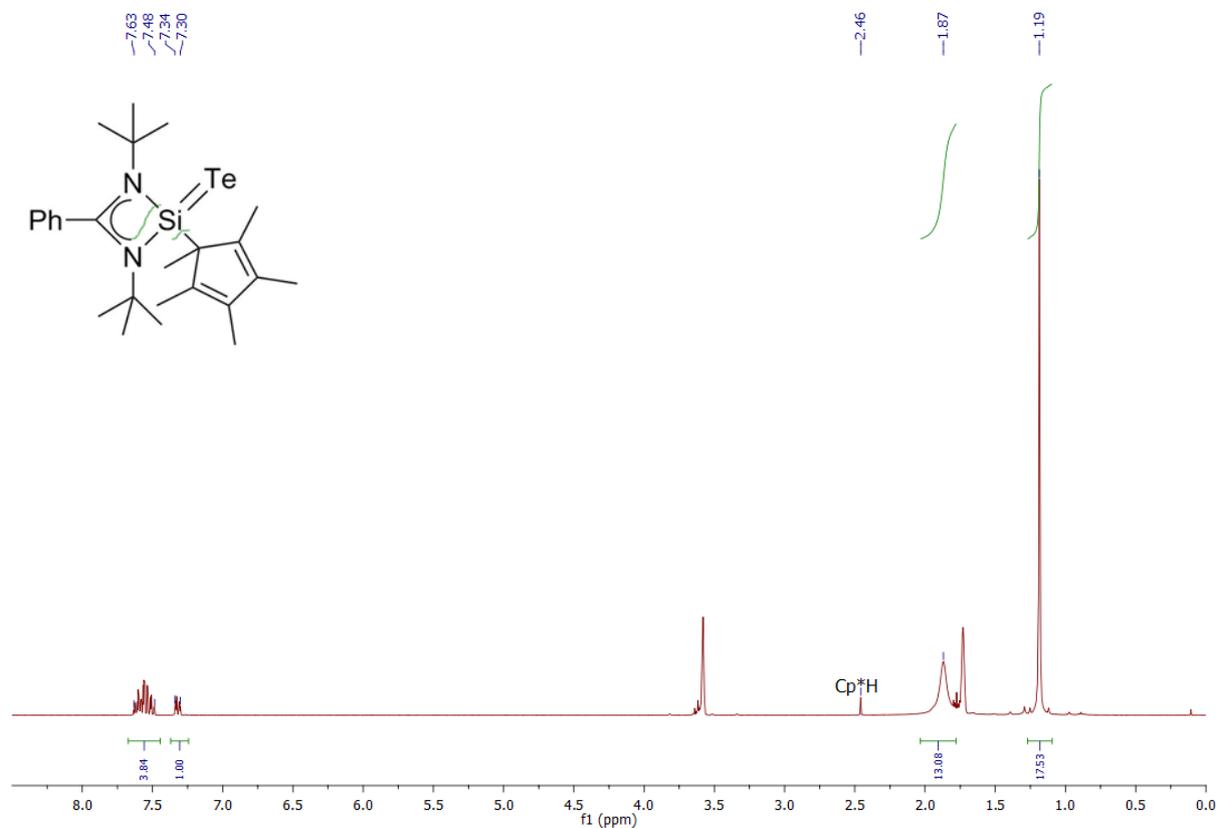


Figure S14:  $^1\text{H}$  NMR spectrum of **4** in  $\text{THF-d}_8$ .

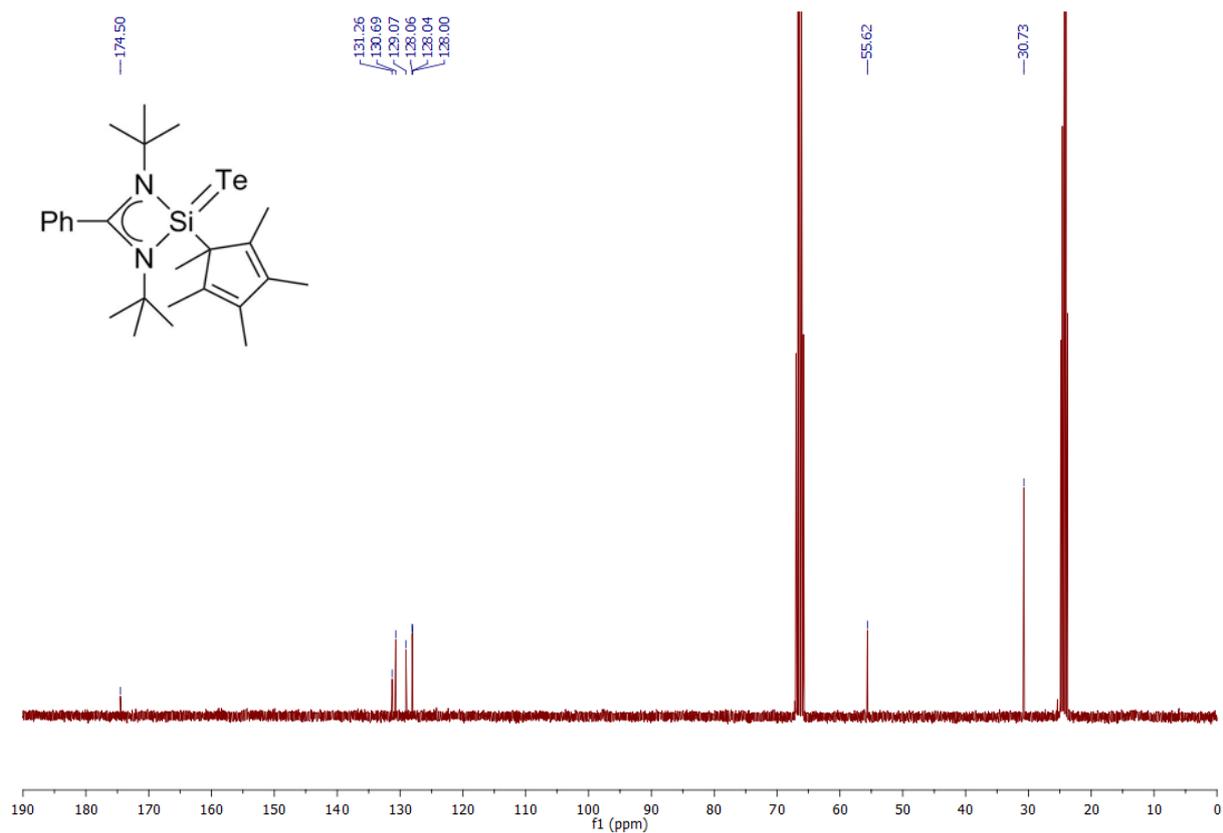


Figure S15:  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4** in THF-*d*<sub>8</sub>.

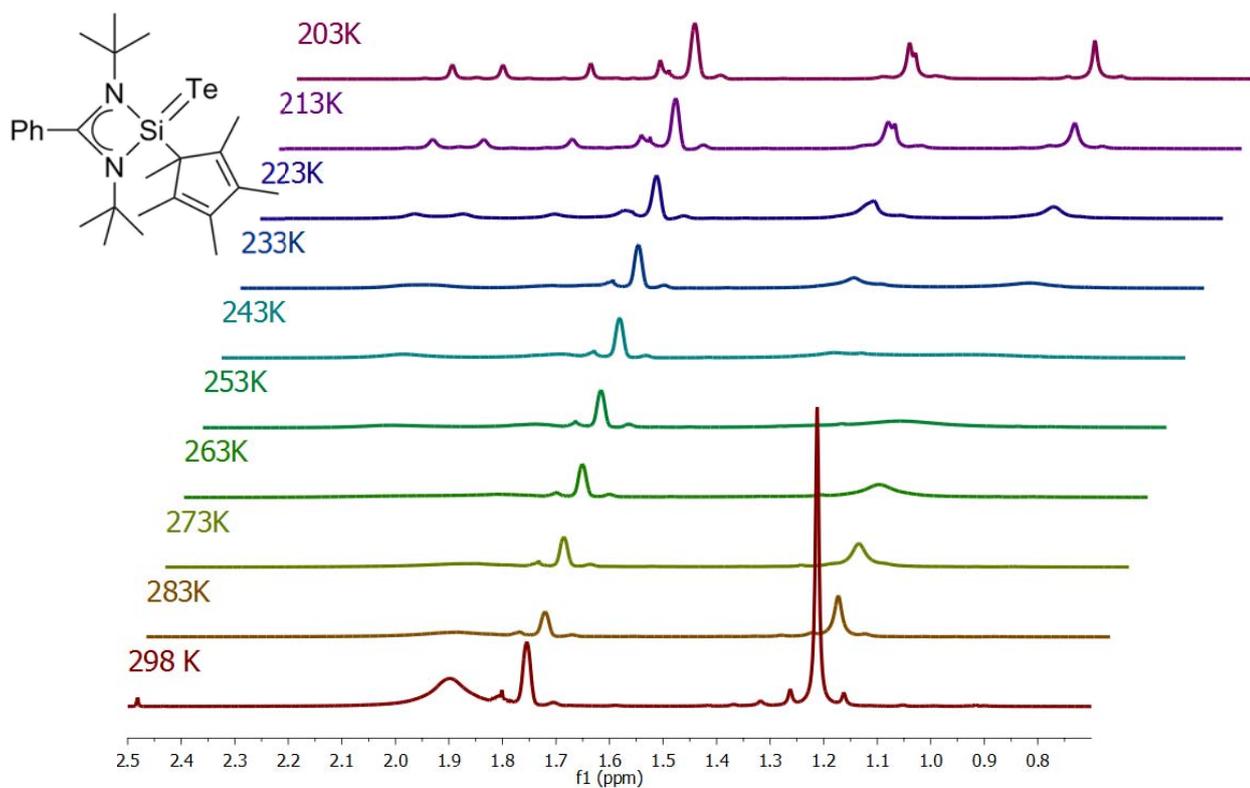


Figure S16: Low temperature VT  $^1\text{H}$  NMR spectra of compound **4** in THF-*d*<sub>8</sub>.

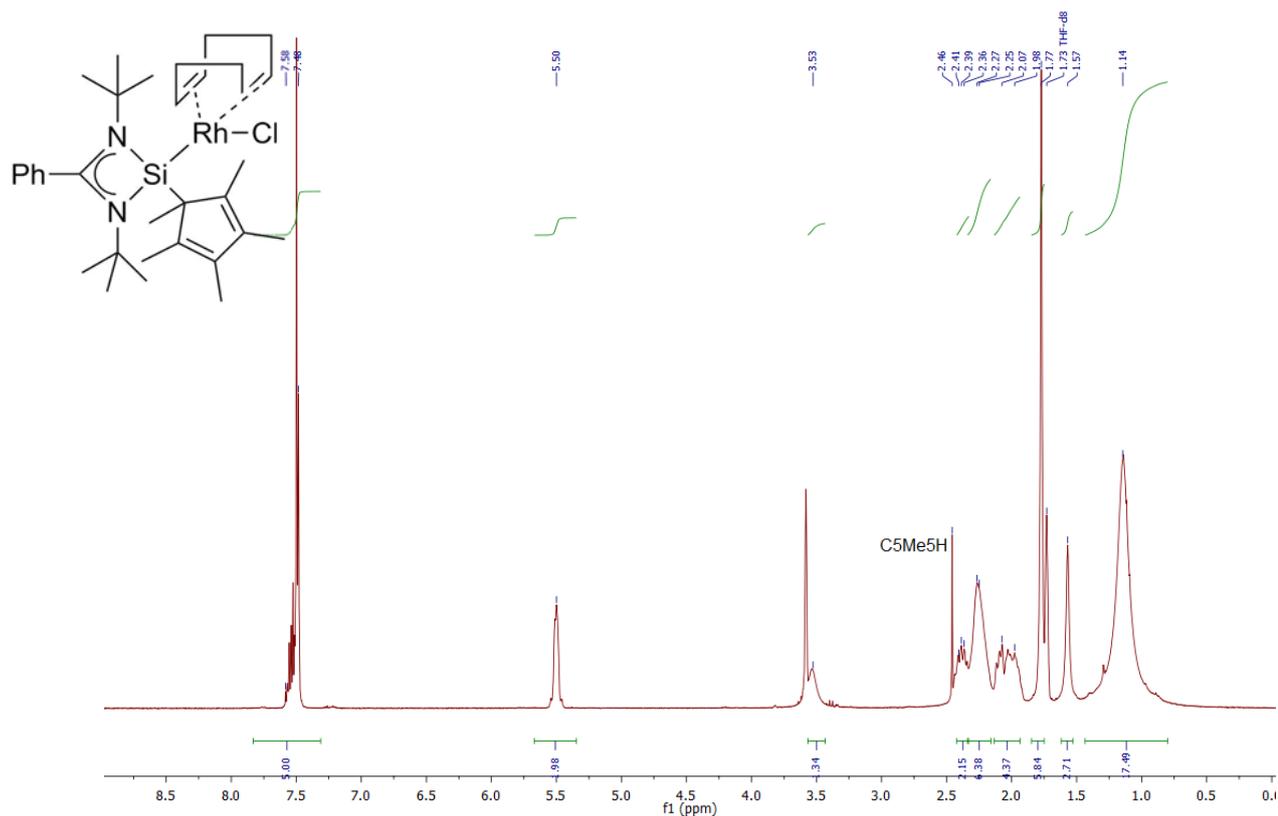


Figure S17:  $^1\text{H}$  NMR spectrum of **5** in  $\text{THF-d}_8$ .

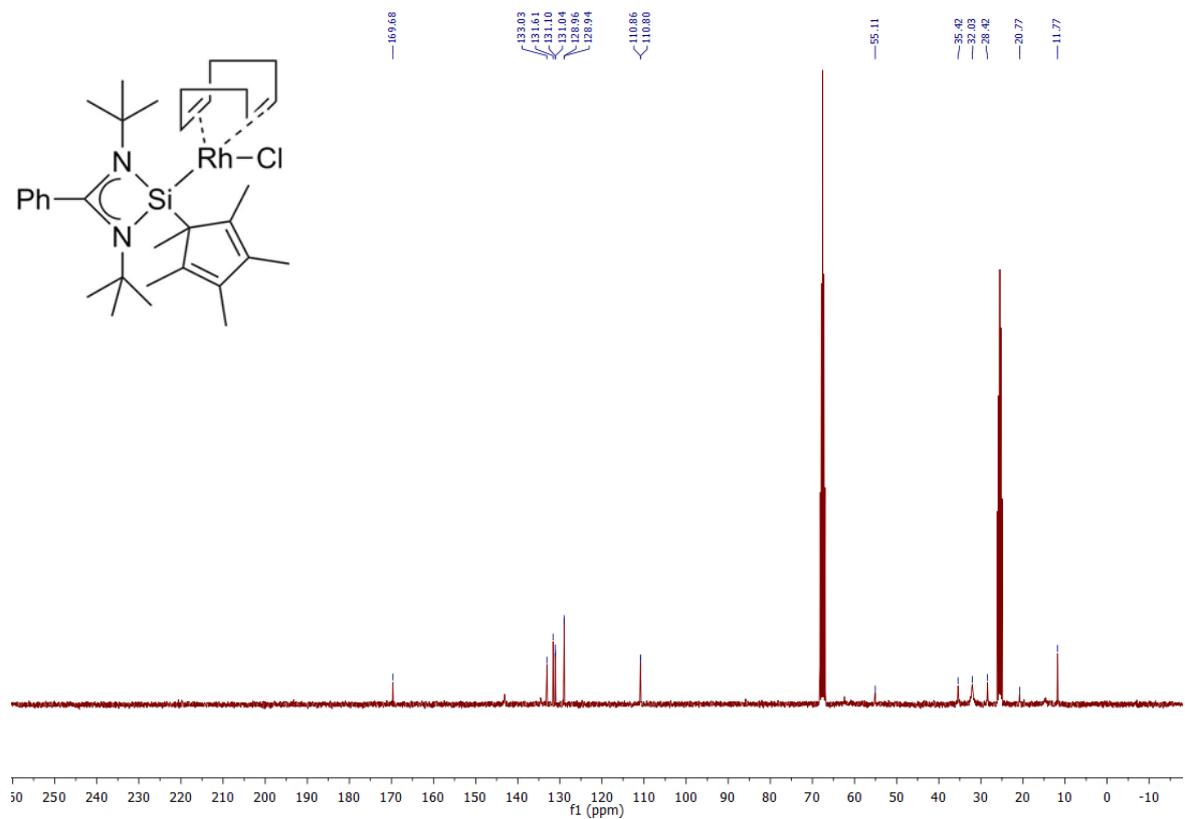


Figure S18:  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **5** in  $\text{THF-d}_8$ .

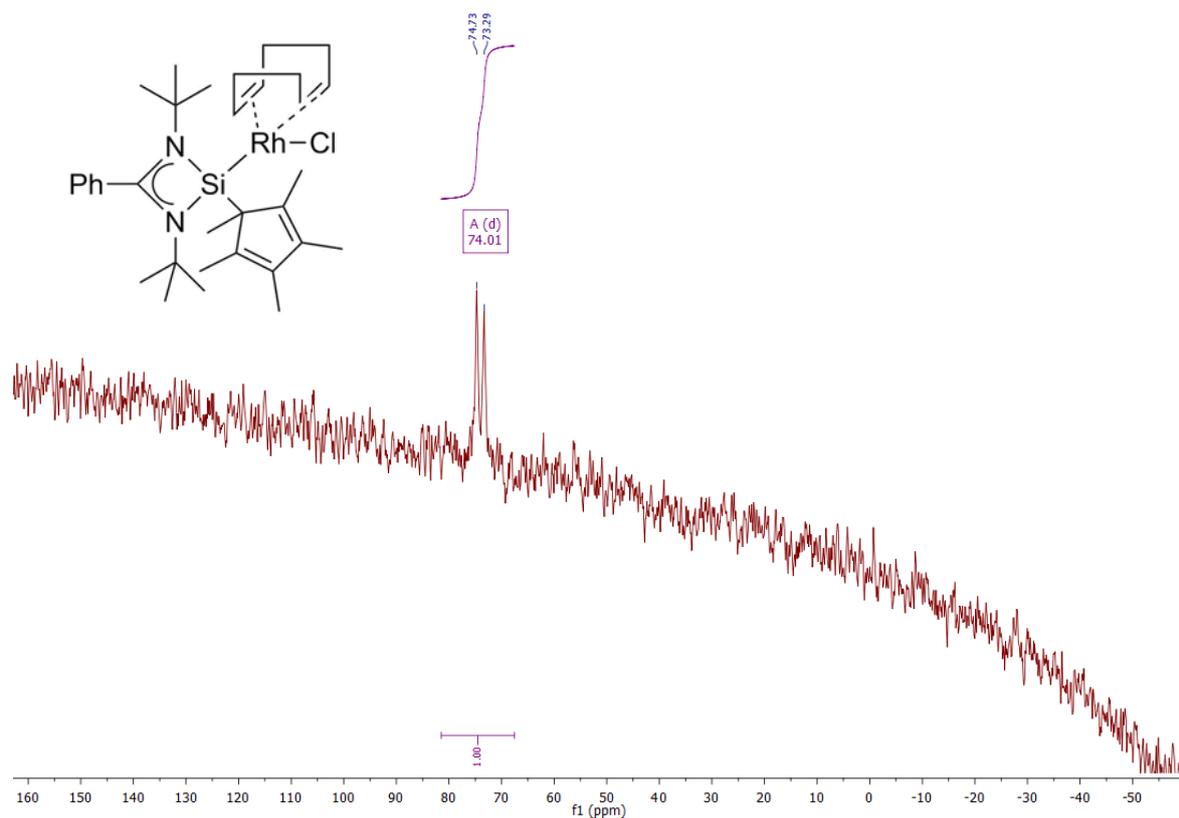


Figure S19:  $^{29}\text{Si}$  NMR spectrum of **5** in THF- $d_8$ .

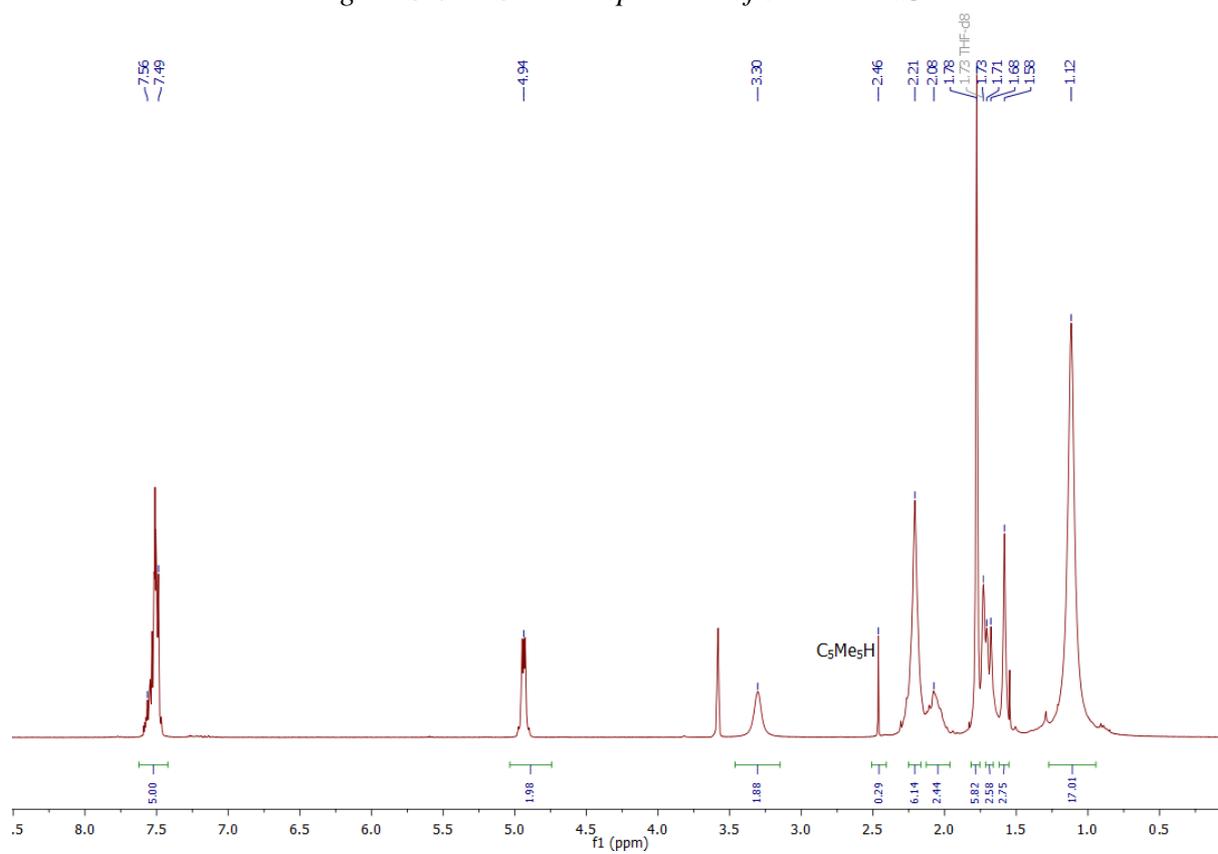


Figure S20:  $^1\text{H}$  NMR spectrum of **6** in THF- $d_8$ .

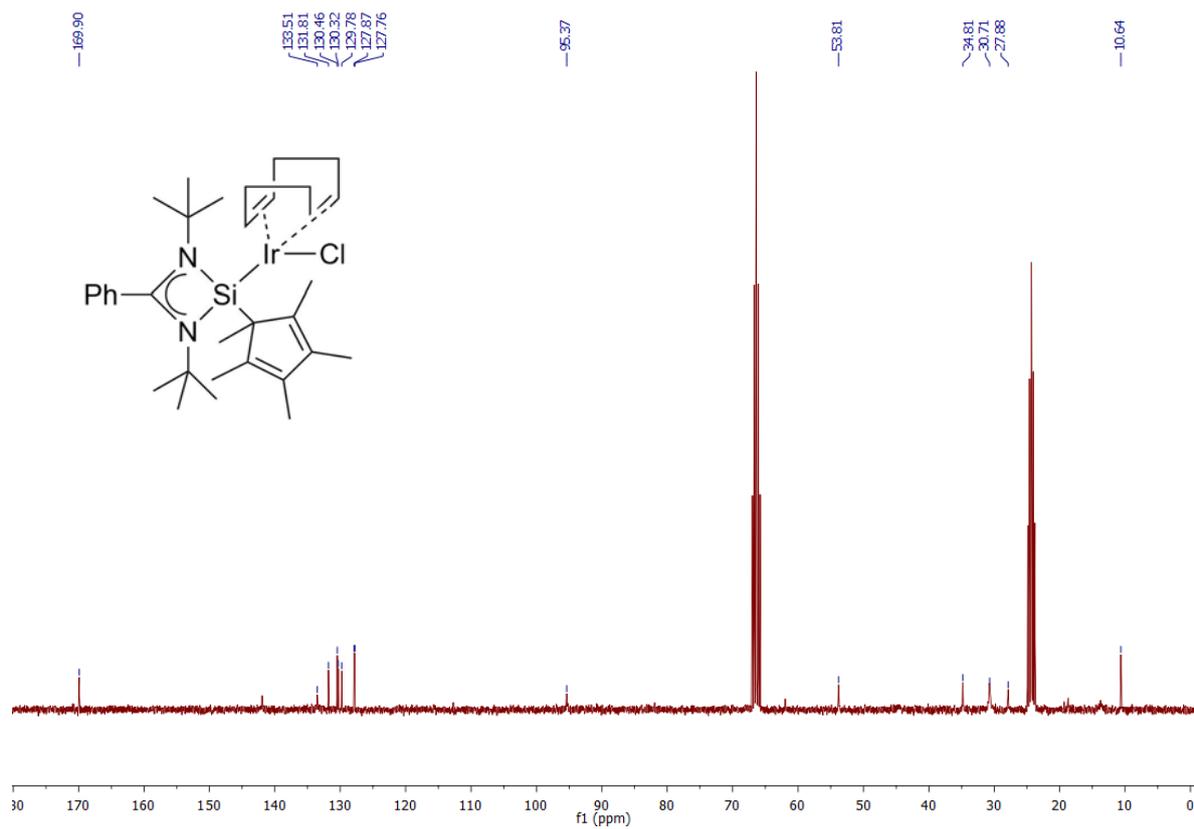


Figure S21:  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **6** in  $\text{THF-}d_8$ .

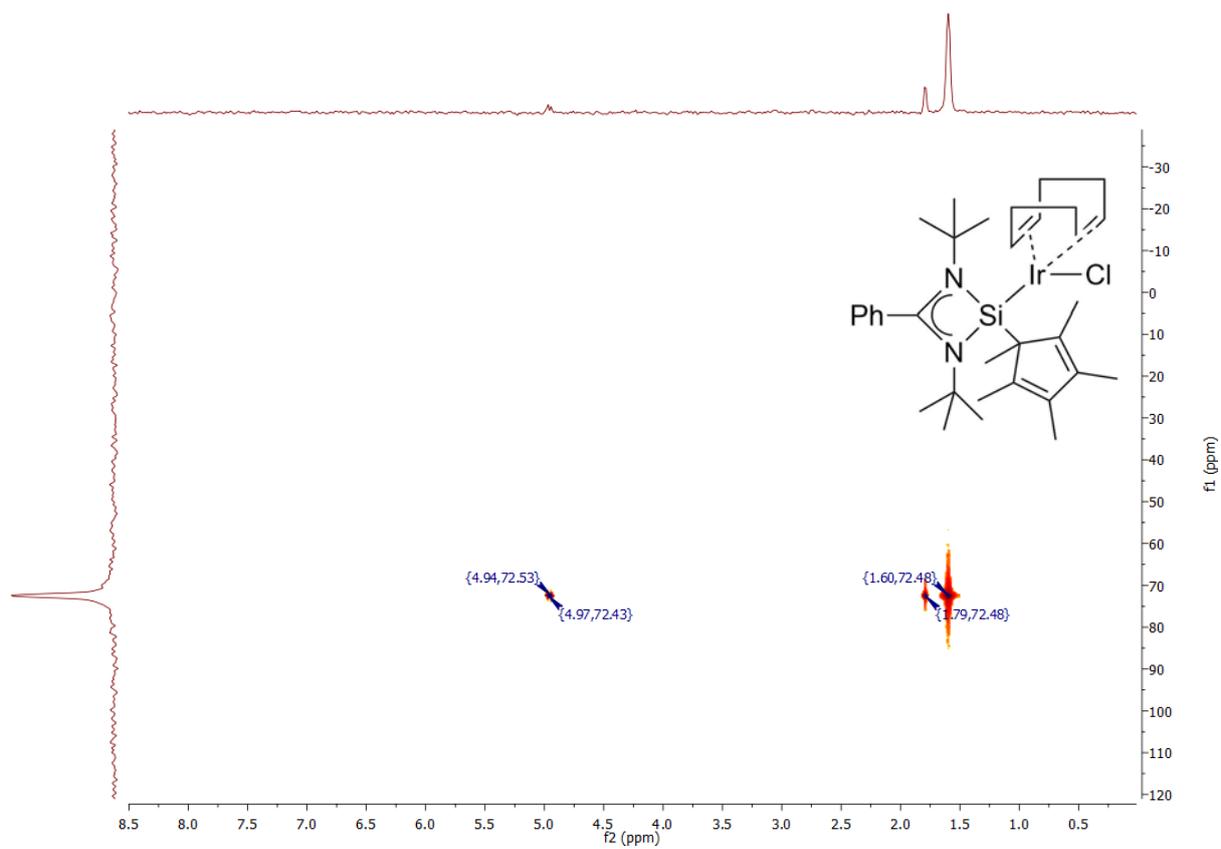
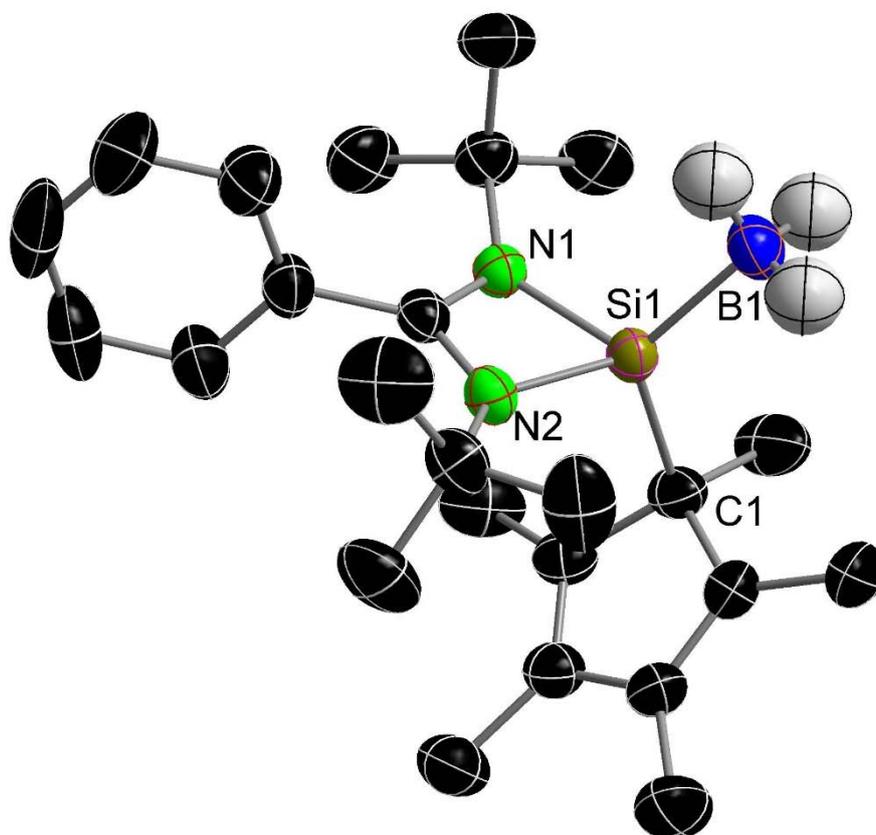
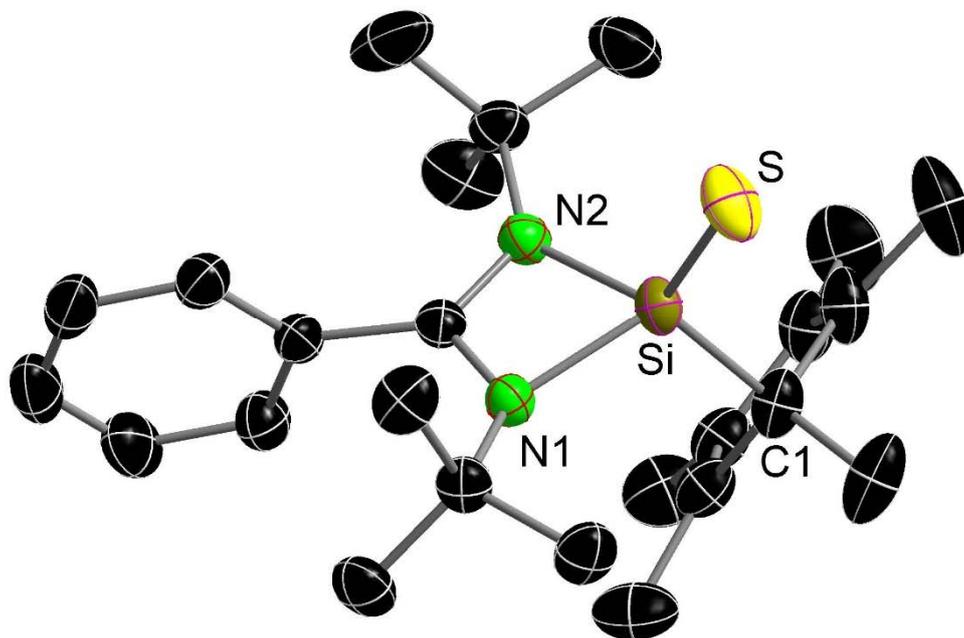


Figure S22:  $2\text{D } ^1\text{H } ^{29}\text{Si}$  NMR Spectrum of **6** in  $\text{THF-}d_8$ .

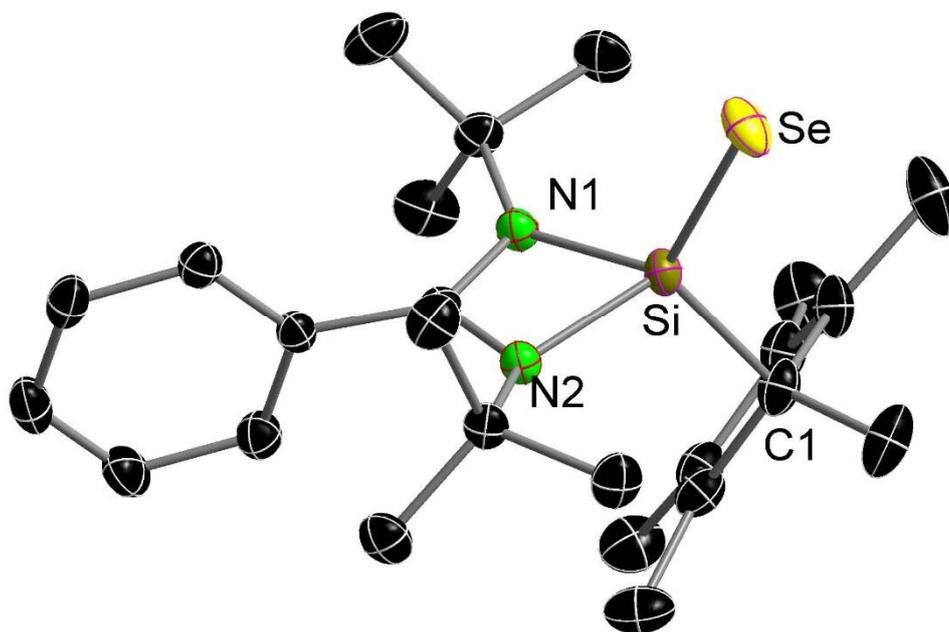
Plots showing thermal ellipsoids of all structures



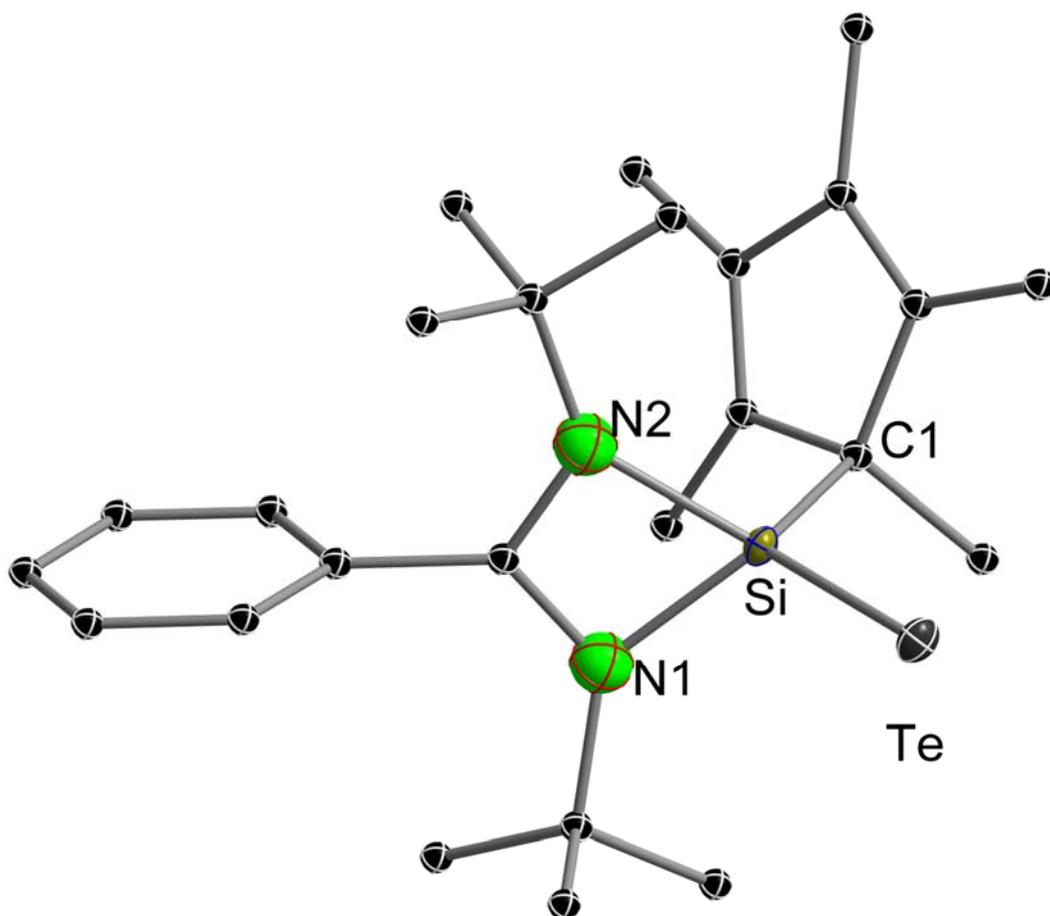
*Figure S23: Molecular structure of 1 in the solid-state. Hydrogen atoms (except BH<sub>3</sub>) are omitted for clarity. Ellipsoids displayed at 50% probability.*



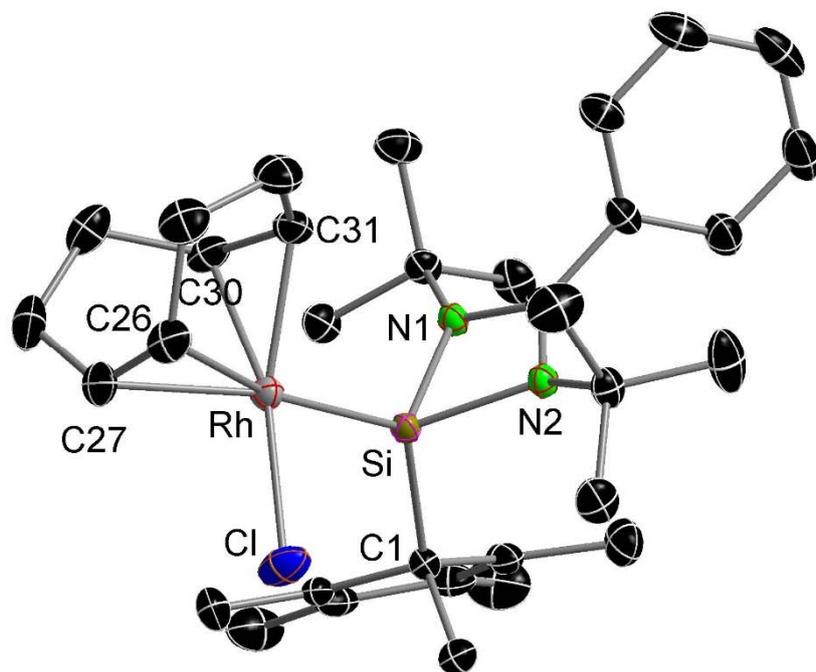
*Figure S24: Molecular structure of 2 in the solid-state. Hydrogen atoms are omitted for clarity. Ellipsoids displayed at 50% probability.*



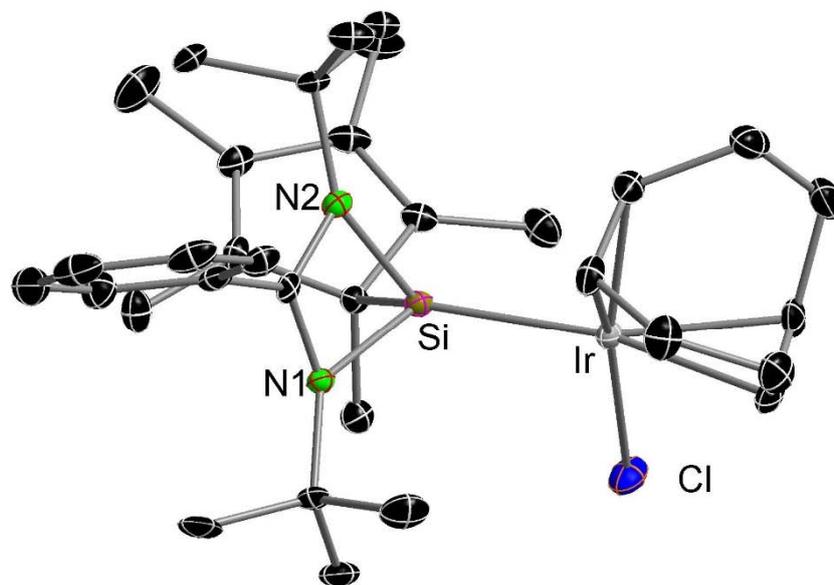
*Figure S25: Molecular structure of 3 in the solid-state. Hydrogen atoms are omitted for clarity. Ellipsoids displayed at 50% probability.*



*Figure S26: Molecular structure of 4 in the solid-state. Hydrogen atoms are omitted for clarity. Ellipsoids displayed at 50% probability.*



*Figure S27: Molecular structure of 5 in the solid-state. Hydrogen atoms are omitted for clarity. Ellipsoids displayed at 50% probability.*



*Figure S28: Molecular structure of 6 in the solid-state. Hydrogen atoms are omitted for clarity. Ellipsoids displayed at 50% probability.*