Supporting information:

Pentamethylcyclopentadienyl-substituted hypersilylsilylene: reversible and irreversible activation of C=C double bonds and dihydrogen

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General Methods

All manipulations were carried out under a protective atmosphere of argon (purity >99.999%), using Schlenk techniques or in a glovebox. Solvents (hexane, toluene, thf) were purified using a Pure Solv MD7 system from INERT or were refluxed over Na/benzophenone and distilled before use (pentane, benzene, Et_2O). Deuterated solvents (benzene-d_6, toluene-d_8) were dried over sodium/potassium alloy and then distilled under argon. UV/Vis spectra were acquired on a PerkinElmer Lambda 35 spectrometer or a Shimadzu UV-2600 spectrometer using quartz cells with a path length of 0.1 cm. NMR spectra in solution were recorded on a Bruker Avance III 300 MHz spectrometer or a Bruker Avance IV 400 NMR spectrometer. ^{1}H and ^{13}C NMR spectra were referenced to residual signals of the solvent; ^{29}Si NMR was referenced to external $SiMe_4$. NMR spectra in the solid state were recorded on a Bruker AV400 WB spectrometer: 100.6 MHz ^{13}C CP/MAS spectrum at 13 KHz MAS rate, 79.5 MHz ^{29}Si CP/MAS spectrum at 2 kHz, 3 kHz, 4 kHz, 5 kHz, 6 kHz, 8 kHz and 13 kHz MAS rate for compound **2** and 13 kHz MAS rate for compound **7**. Mass spectra were recorded on a Finnigan MAT950S spectrometer (CI) or on a Bruker Solarix 7.0T spectrometer (ESI). Elemental analysis was performed on an elementar vario MICRO cube analyzer. Pentamethylcyclopentadiene (Carbolution chemicals, 95%, distilled under reduced pressure before use), tetrabromosilane (Sigma-Adrich), tetrakis(trimethylsilyl)silane (ABCR, 98%), dihydrogen (Air Liquid 99,9%), ethylene (Air Liquid, 99,9%), deuterium (Aldrich, 99,8% D atom %) were purchased. Tribromo(pentamethylcyclopentadienyl)silane,[S1] potassium hypersilyl salt $(thf)_n[KSi(SiMe_3)_3]$,[S2] 1,3,4,5-(tetramethylimidazol)-2-ylidene,[S3] 1,3-di-tert-butyl-2,3-dihydro-1H-1,3,2-diazasilol-2-ylidene[S4] were prepared according to literature procedures.

(Hypersilyl)(pentamethylcyclopentadienyl)silylene **2**:

A precooled solution (0 °C) of potassium hypersilyl salt $(thf)_{1.5}[KSi(SiMe_3)_3]^{\#}$ (1.22 g, 3.09mmol) in hexane (~120 mL) was added via a cannula to a stirred and precooled (−78 °C) solution of tribromo(pentamethylcyclopentadienyl)silane (0.620 g, 1.54 mmol) in hexane (~50 mL) placed in a 250 mL Schlenk flask equipped with a magnetic stirrer. Immediately, a change of colour from pale yellow to purple and precipitation of a white solid were observed. The reaction mixture was stirred at low temperature for 0.5 h. Then the cooling bath was removed and stirring was continued for additional 2 h to afford a purple suspension. Filtration followed by concentration and crystallization from hexane (~4 mL) at −30 °C gave purple crystals of the target silylene which was recrystallized from hexane at −30 °C to remove traces of contamination by $BrSi(SiMe_3)_3$.* Yield 36% (0.230 g, 0.560 mmol).

$^{\#}$variable amounts of coordinated thf were observed depending on the batch
* After recrystallization traces of $BrSi(SiMe_3)_3$ (~3%) were still observed and could not be removed by repeated recrystallization. Deviations in EA are primarily ascribed to the highly air and moisture sensitive nature of silylene **2**.

^{1}H NMR (300.13 MHz, 300 K, benzene-d_6): δ = 0.40 (s, 27H, Si*Me*$_3$), 1.92 (s, 15H, Cp*-*Me*).

$^{13}C\{^{1}H\}$ NMR (75.47 MHz, 300 K, benzene-d_6): δ = 4.0 (s, Si*Me*), 11.2 (s, Cp*-*Me*), 121.5 (s, Cp*-*C*).

$^{29}Si\ \{^{1}H\}$ NMR (79.49 MHz, 300 K, benzene-d_6): δ =−110.0 (*Si*$(SiMe_3)_3$), −8.9 (*Si*Me_3), 207.2 (*Si*:).

^{13}C CP-MAS/NMR (100.65 MHz, 13 kHz, 300 K): δ = 5.4 (s, Si*Me*$_3)_3$, 12.7 (s, Cp*-*Me*), 122.3 (s, Cp*-*C*).

^{29}Si CP-MAS/NMR (79.53 MHz, 13 kHz, 300 K): δ = −108.3 (*Si*$(SiMe_3)$), −8.4 (Si(*Si*Me_3)), 203.1 (*Si*-Cp*).

M. p. 94-96 °C; **EA** (%): Calculated for $C_{19}H_{42}Si_5$ [410.97]: C 55.53, H 10.30; found C 54.76, H 9.94.

UV/Vis (hexane): $\lambda_{max}(\varepsilon)$ = 285 nm (22374 $M^{-1}cm^{-1}$), 525 nm (201 $M^{-1}cm^{-1}$).

HR-MS (ESI, m/z): $[M+H]^+$ calculated 411.2206, found 411.2210

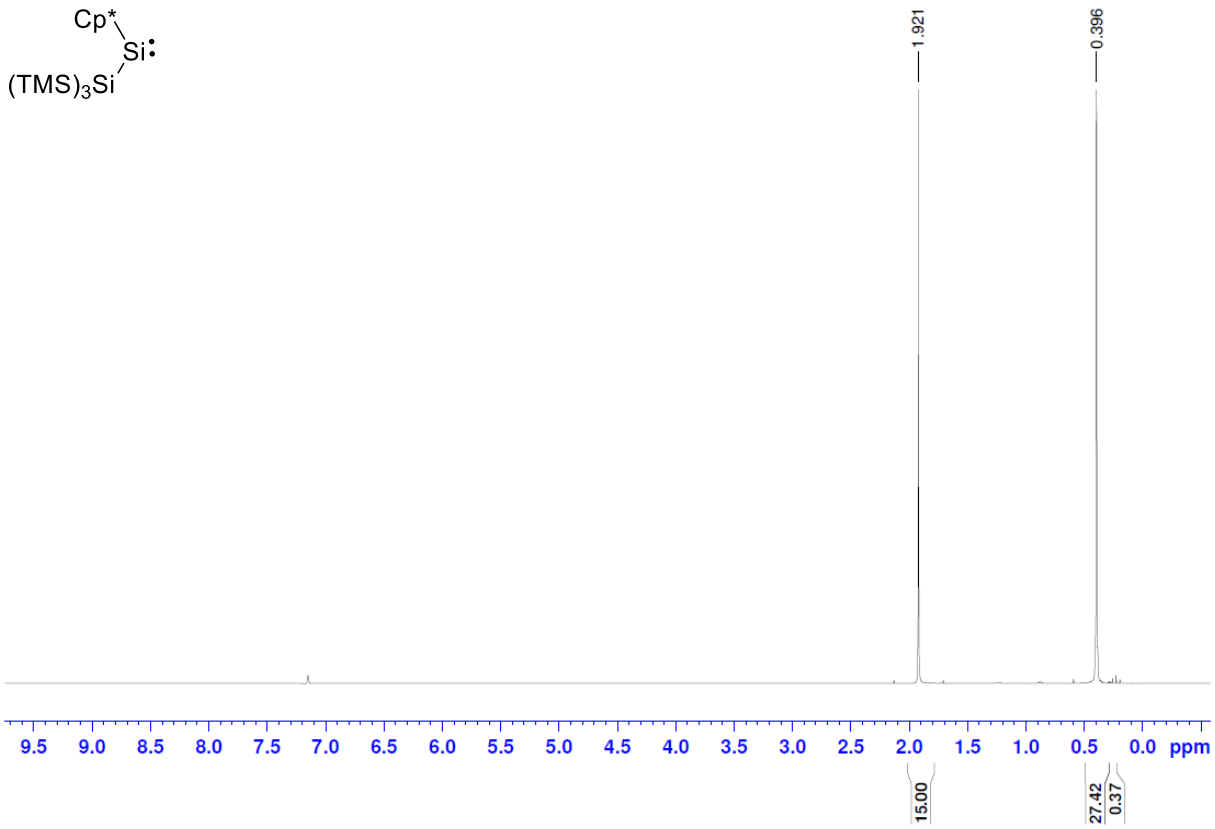

Fig. S1 ^{1}H NMR (300.13 MHz, 300 K, benzene-d_6) of compound **2**.

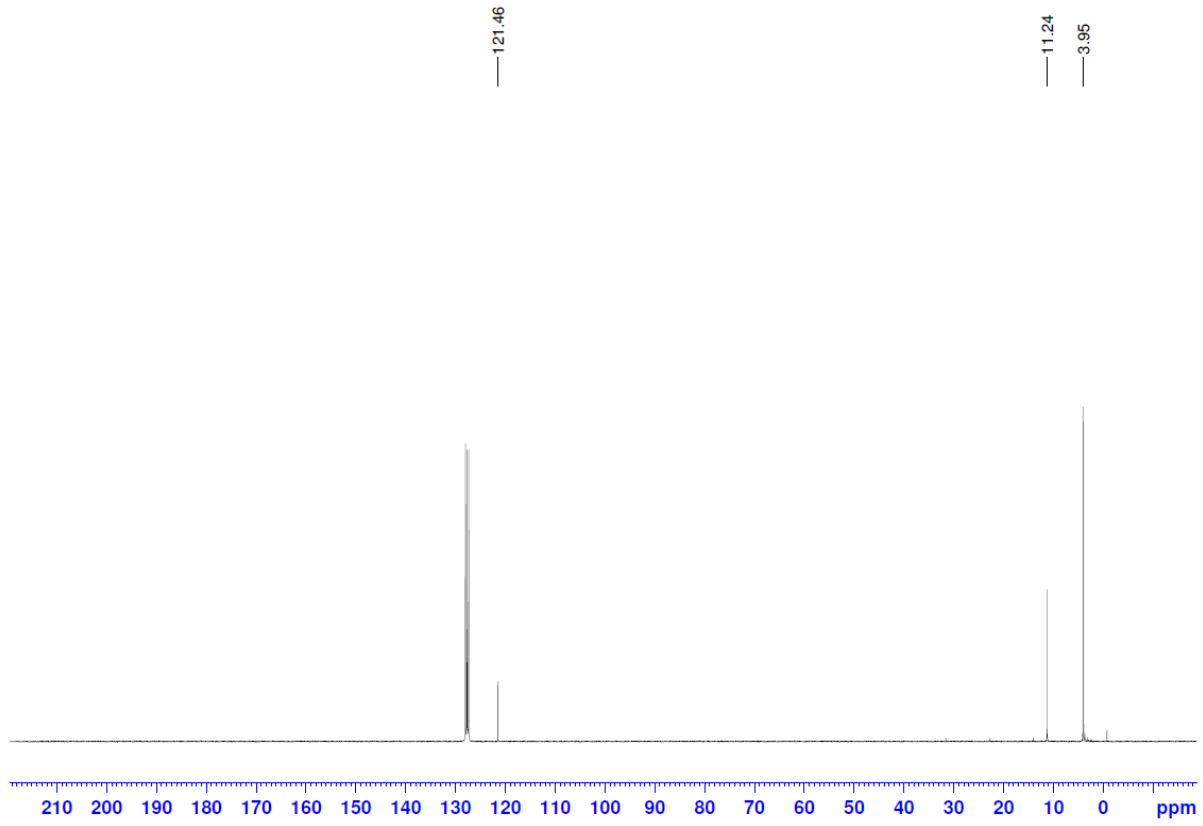

Fig. S2. ^{13}C{^{1}H} NMR (75.47 MHz, 300 K, benzene-d_6) of compound **2**.

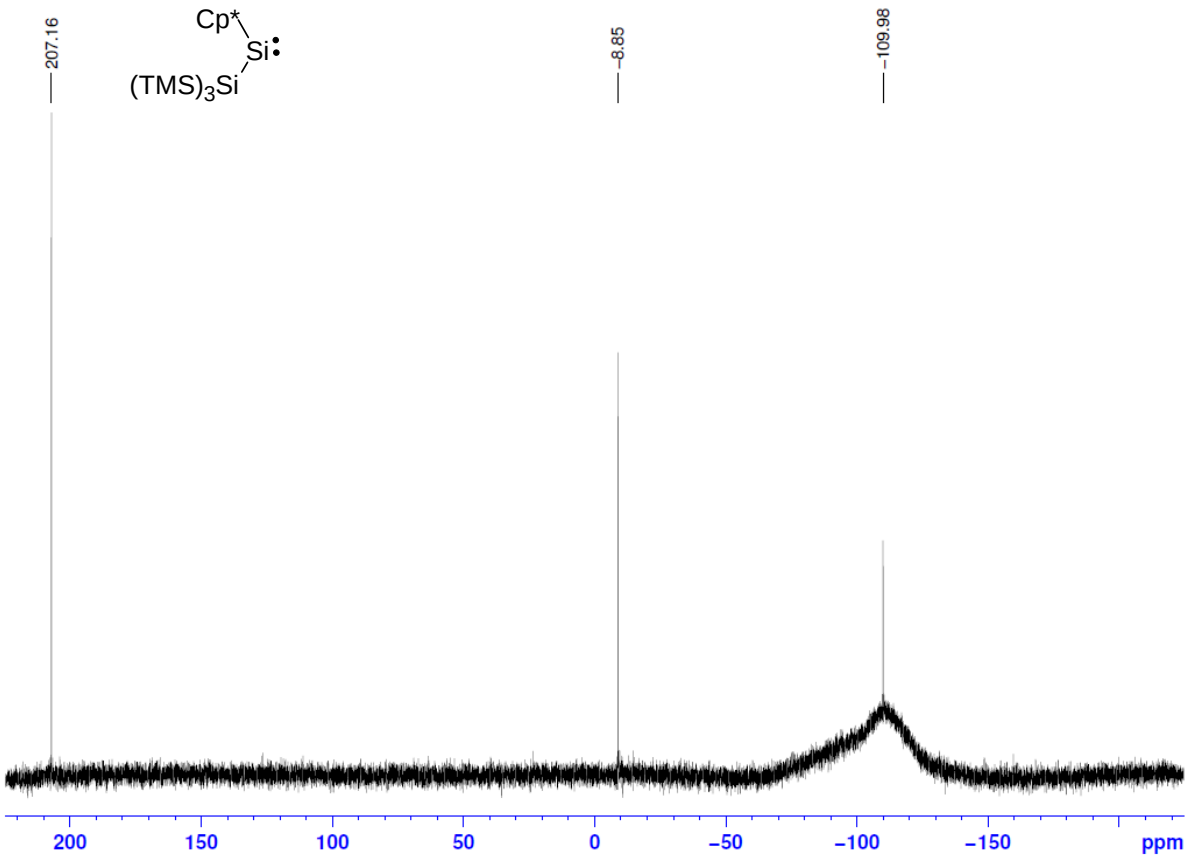

Fig. S3. $^{29}Si\{^{1}H\}$ NMR (79.49 MHz, 300 K, benzene-d_6) of compound **2**.

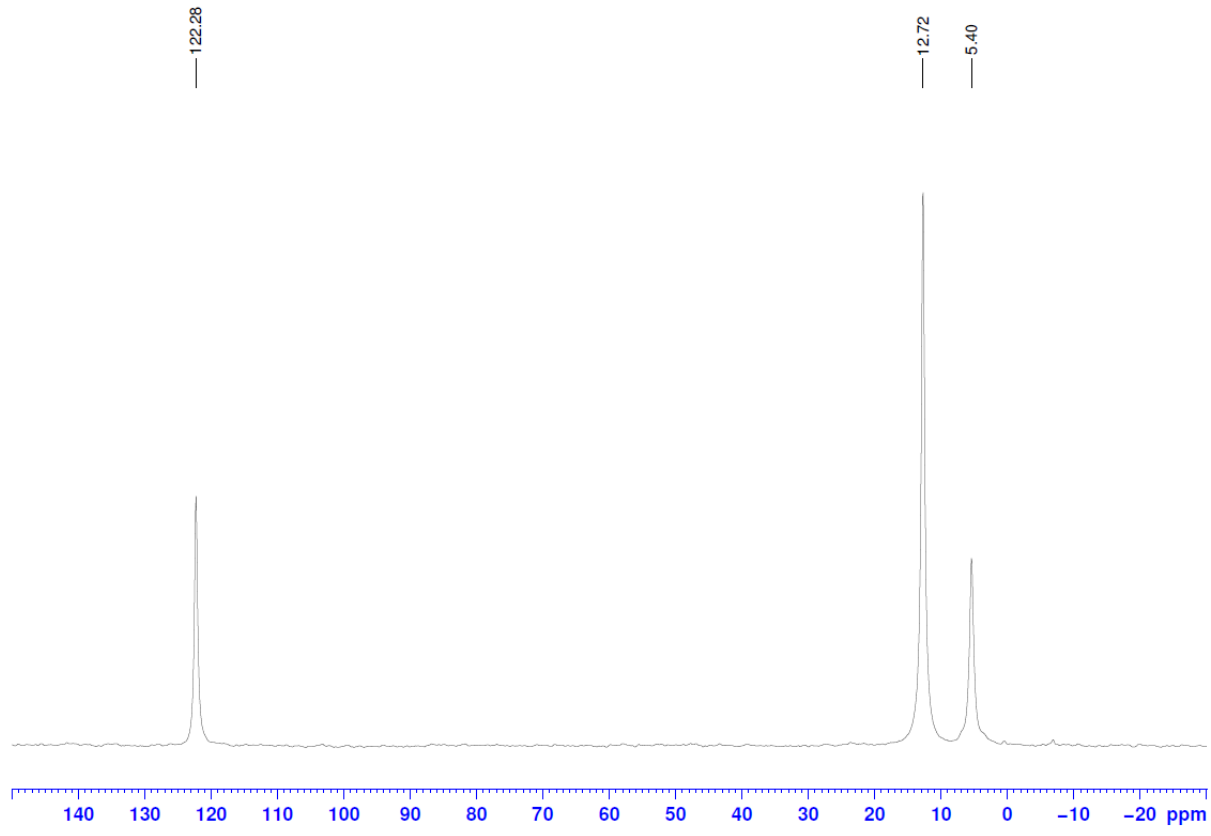

Fig. S4. ^{13}C CP-MAS/NMR (100.65 MHz, 13 kHz, 300K) of **2**.

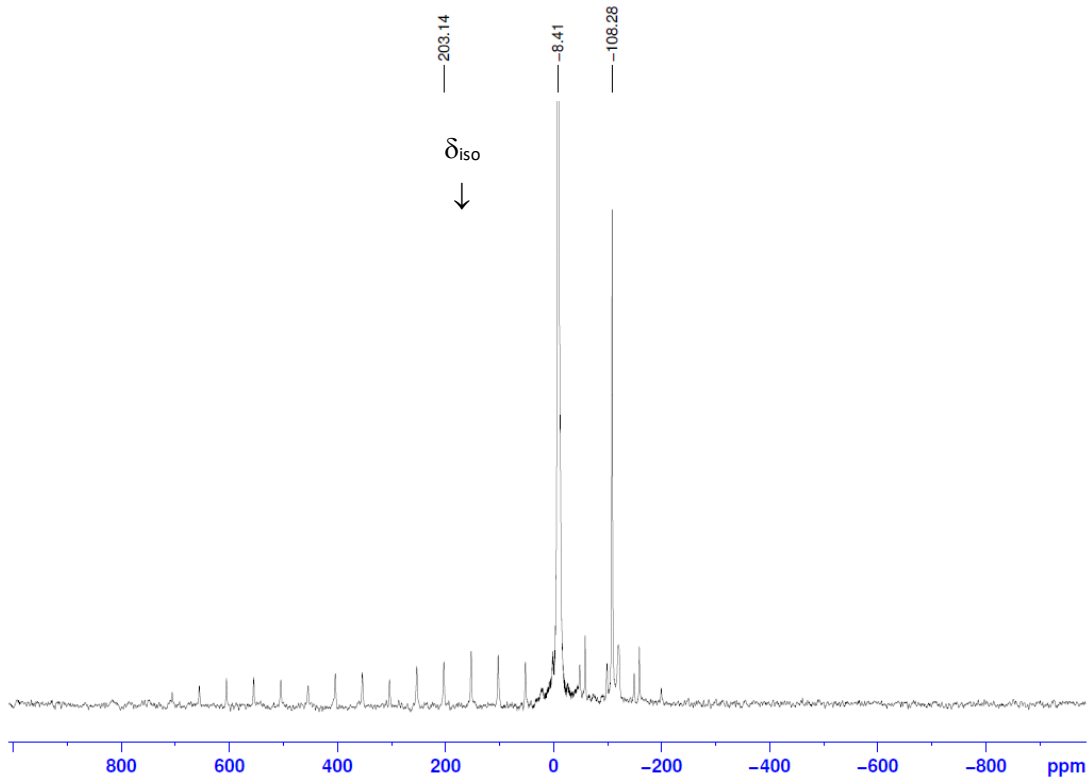

Fig. S5. ^{29}Si CP-MAS NMR (79.53 MHz, 13 kHz, 300 K) of compound **2**.

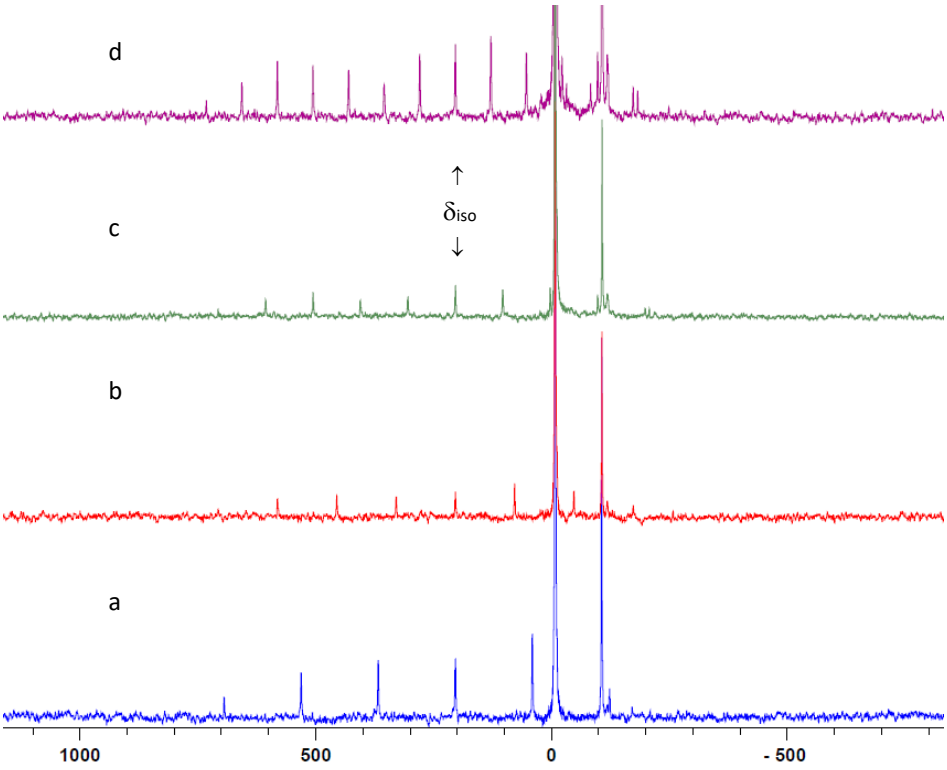

Fig. S6. ^{29}Si CP-MAS NMR (79.53 MHz, 300 K) of compound **2** at: 13 kHz (a), 10 kHz (b), 8 kHz (c), 6 kHz (d).

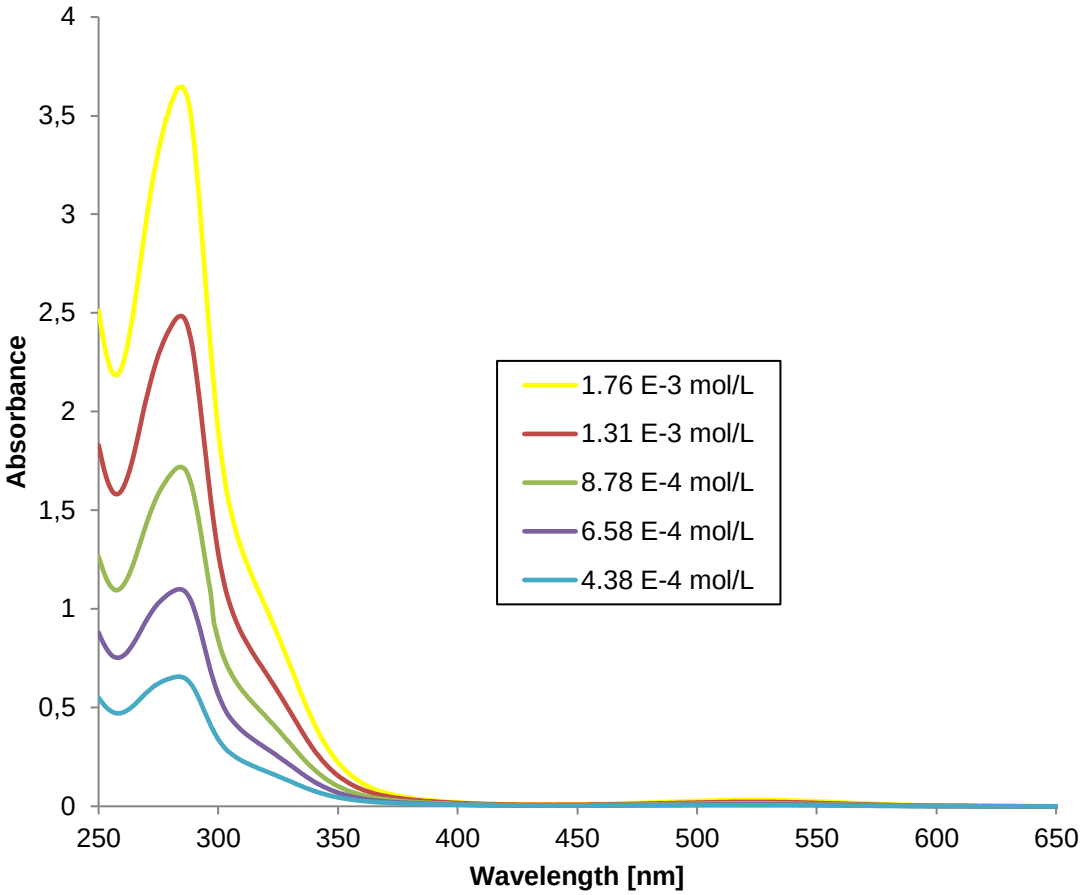

Fig. S7. UV/Vis spectrum of silylene **2** in hexane.

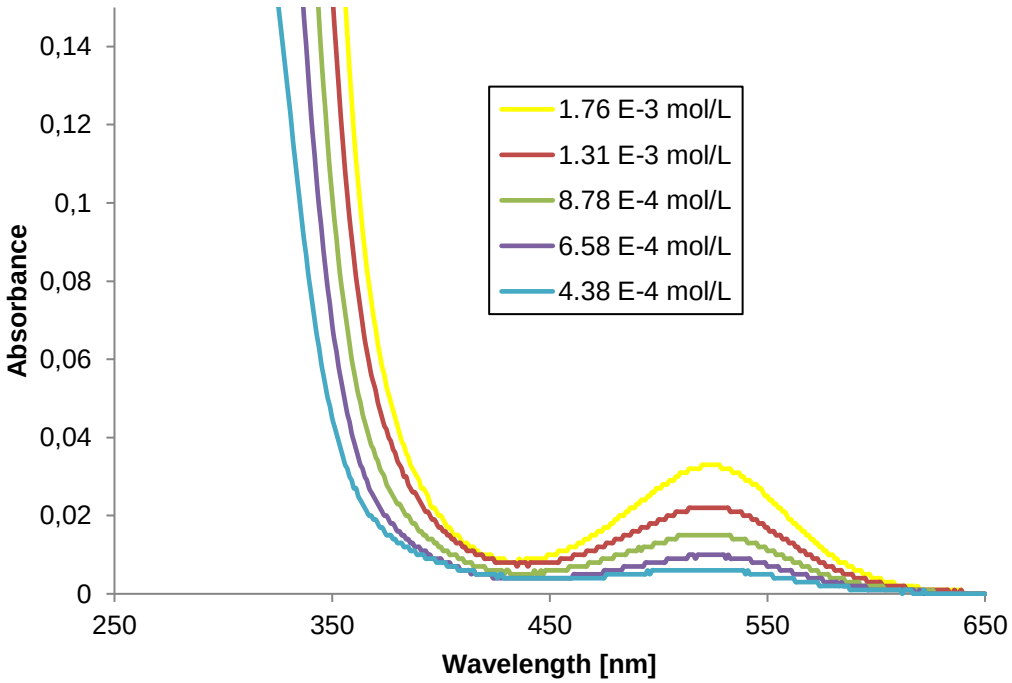

Fig. S8. UV/Vis spectrum of silylene **2** in hexane.

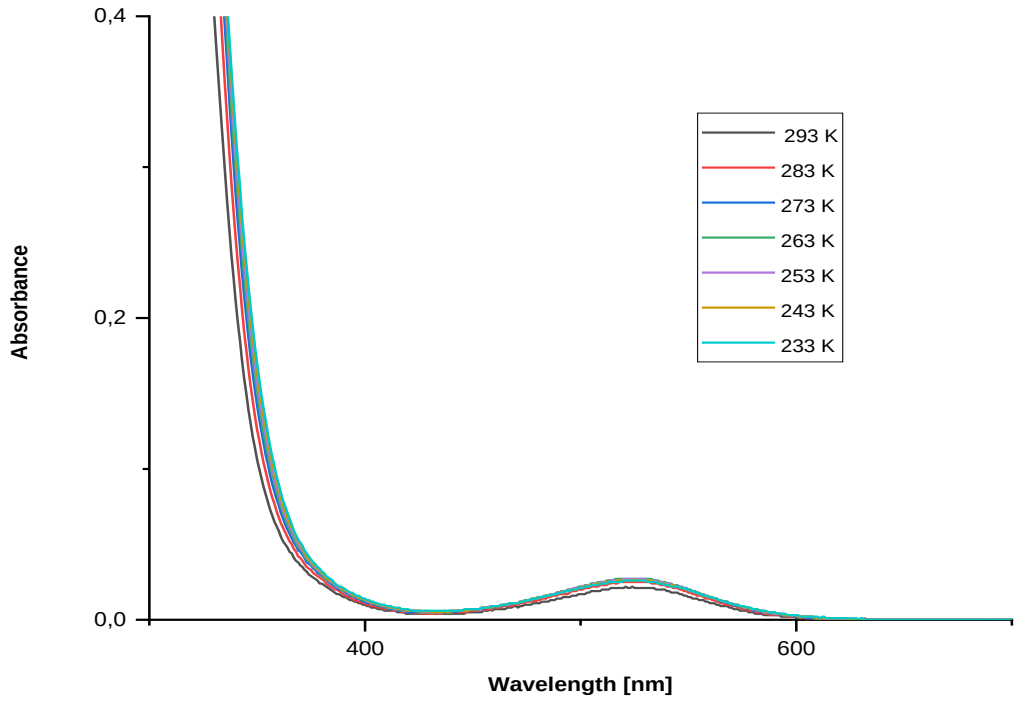

Fig. S9. VT UV/Vis spectrum of silylene **2** in hexane, concentration (at 298 K) 1.46 *10^{-3} mol/L.

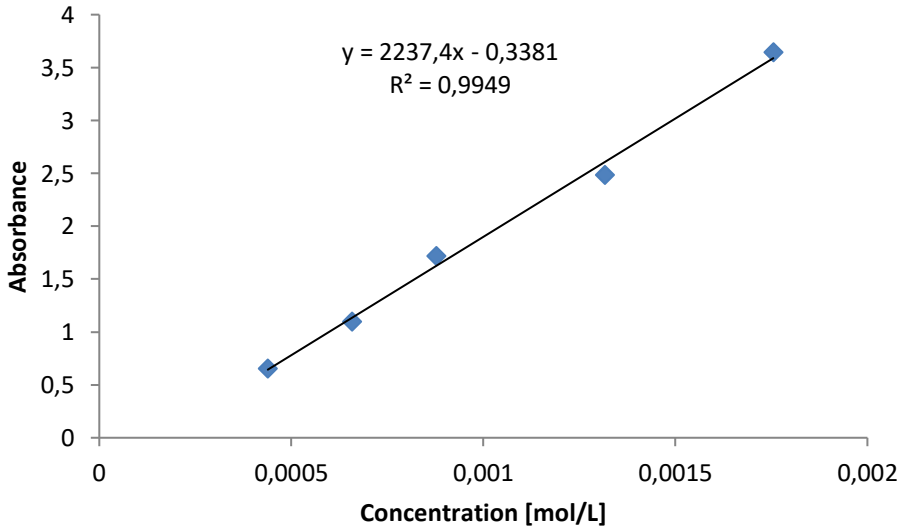

Fig. S10. Extinction coefficient ε =22374 $M^{-1}cm^{-1}$ (λ = 285 nm) for silylene **2**.

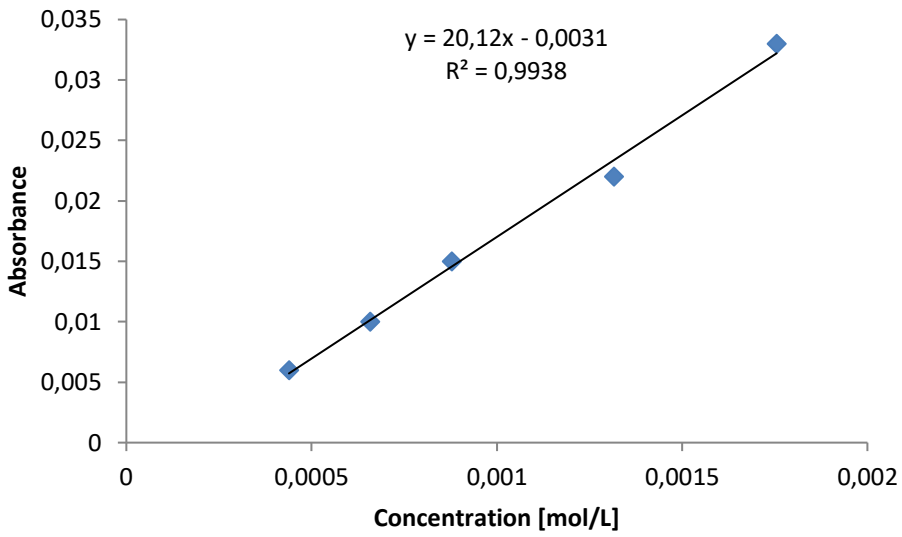

Fig. S11. Extinction coefficient ε =201 $M^{-1}cm^{-1}$ (λ = 525 nm) for silylene **2**.

Cp*[$(TMS)_3Si$]Si(CH_2CH_2) **3**

240 mg of (hypersilyl)(pentamethylcyclopentadienyl)silylene **2** (5.84 mmol) were dissolved in 2 mL of benzene-d_6 and placed in a 250mL Schlenk flask equipped with a magnetic stirrer. The flask was shortly evacuated and refilled with ethylene (pressure ~1 bar). Immediately, a change of colour from purple to pale yellow was observed. Stirring was continued for 15 minutes. The reaction mixture was analysed by multinuclear NMR to show quantitative conversion to silirane **3**. Overnight crystallization from benzene-d_6 at RT afforded colourless crystals of silirane **3** (150 mg, 3.64 mmol), yield 62.3%.

^{1}H NMR (300.13 MHz, 300 K, benzene-d_6): δ = 0.25 (s, 27H, ($SiMe_3$)$_3$), 0.46 (m, 2H, CH_2), 0.72 (m, 2H, CH_2), 0.79 (br, s, 3H, Cp*-*Me*), 1.84 (br, s, 6H, Cp*-*Me*), 2.00 (br, s, 6H, Cp*-*Me*).

^{13}C{^{1}H} NMR (75.47 MHz, 300 K, benzene-d_6): δ = –3.15 (s, *C*H_2), 3.47 ($SiMe_3$)$_3$, 12.28 (s, Cp*-*Me*), 12.92 (s, Cp*-*Me*), 17.59 (s, Cp*-*Me*), 52.02 (s, Cp*-*C*), 135.16 (s, Cp*-*C*), 140.90 (s, Cp*-*C*).

^{29}Si{^{1}H} NMR (59.63 MHz, 300 K, benzene-d_6): δ =–129.91 (*Si*($SiMe_3$)), –100.08 (*Si*(CH_2CH_2)), –8.69 (Si(*Si*Me_3)).

M. p. 125-127 °C

EA (%): Calculated for $C_{21}H_{46}Si_5$ [439.02]: C 57.45, H 10.56; found C 57.16, H 10.59.

Testing of possible reversibility of ethene addition to silylene **2**: 29 mg of the silirane **3** were placed in an NMR tube and heated (within ~1h) from RT to 140 °C under vacuum ($4*10^{-2}$ mbar). The remaining colourless residue was analysed by NMR (in benzene-d_6) to show pure substrate, silirane **3**.

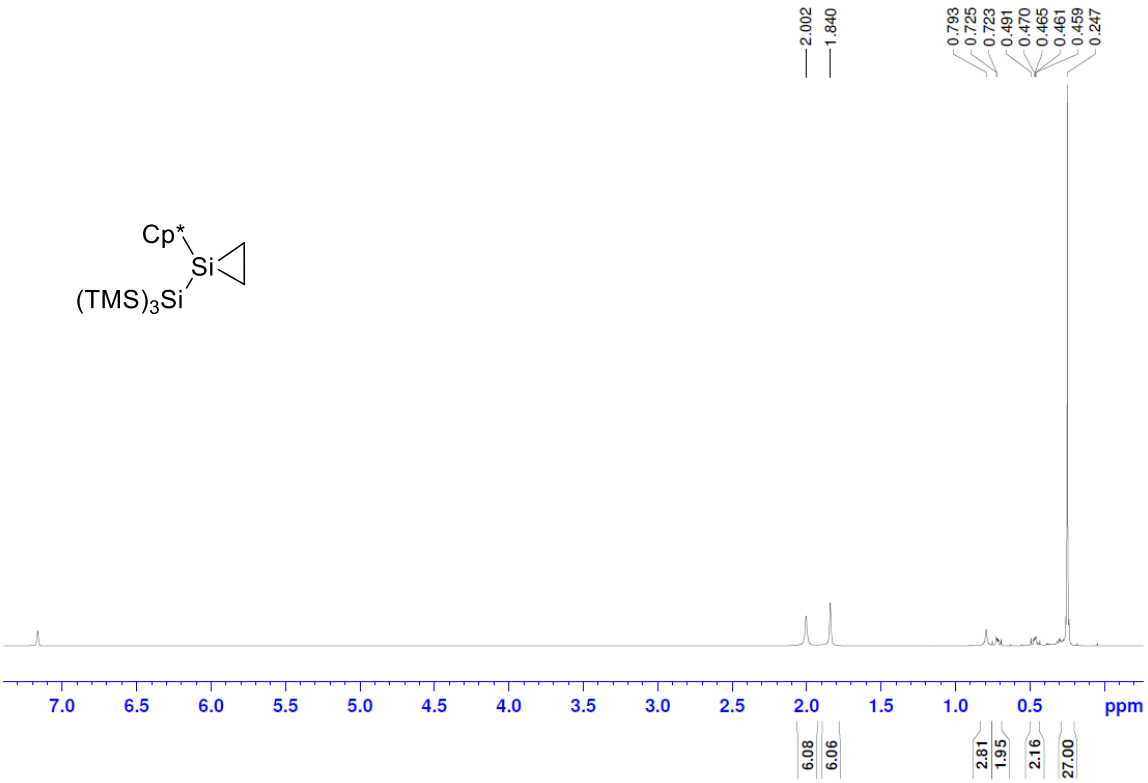

Fig. S12. ^{1}H NMR (300.13 MHz, 300 K, benzene-d_6) of **3**.

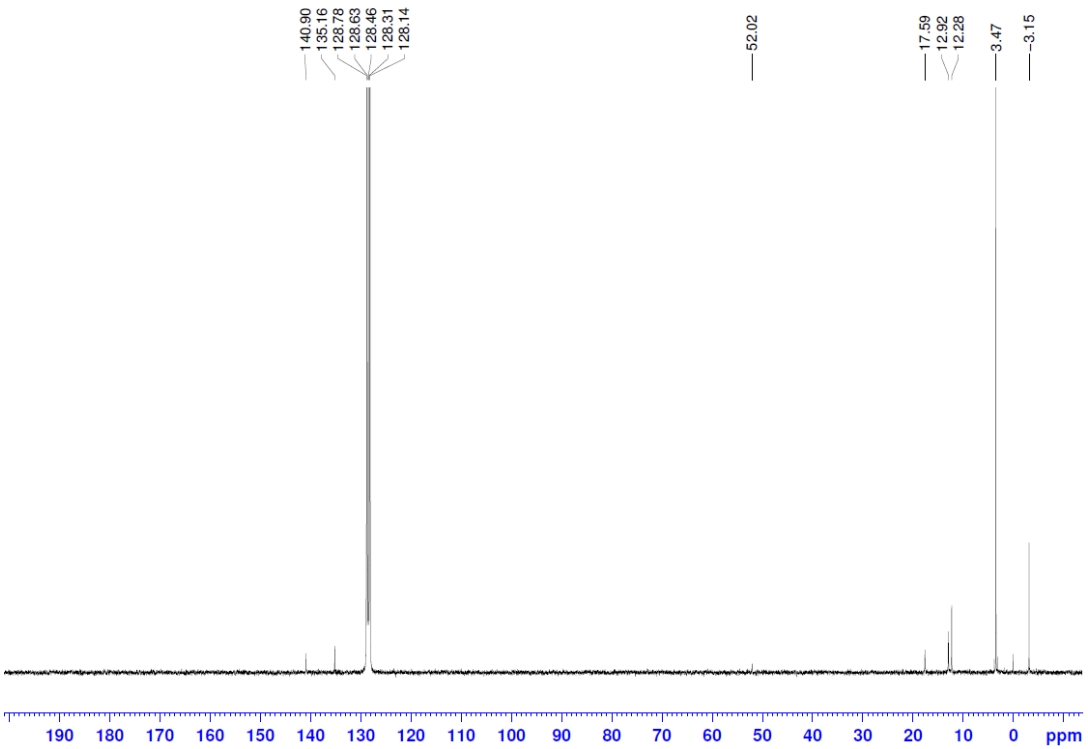

Fig. S13. ^{13}C {^{1}H} NMR (75.47 MHz, 300 K, benzene d_6) of **3**.

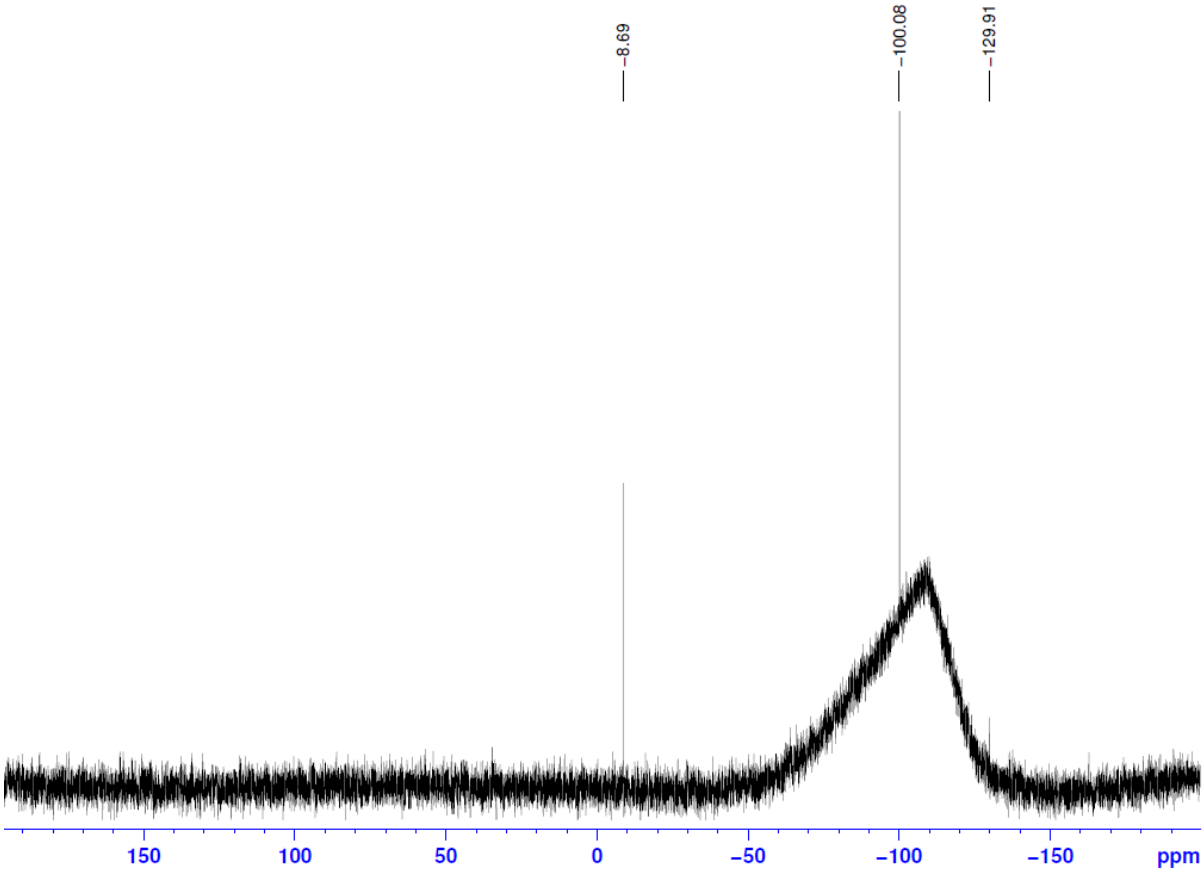

Fig. S14. $^{29}Si\{^{1}H\}$ NMR (59.63 MHz, 300 K, benzene-d_6) of compound **3**.

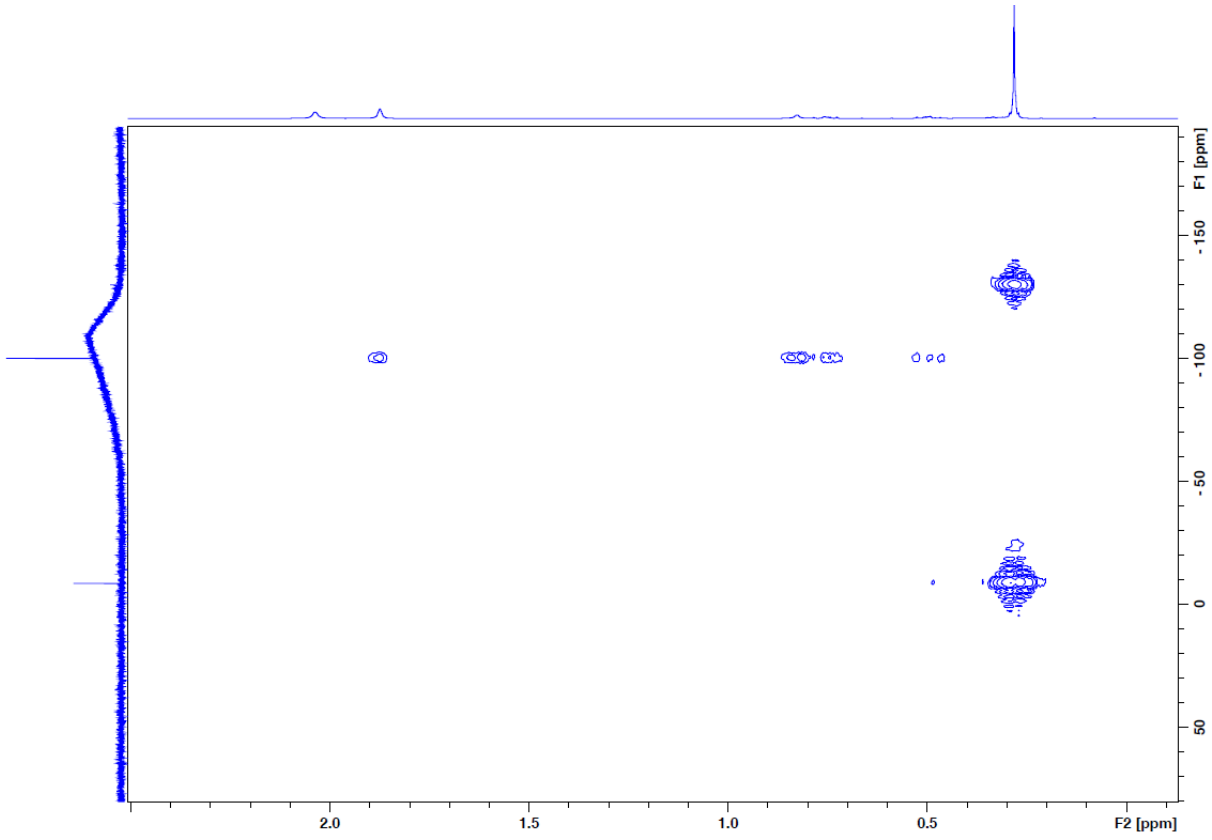

Fig. S15. $^{1}H/^{29}Si$ HMBC NMR (300 K, benzene-d_6) of compound **3**.

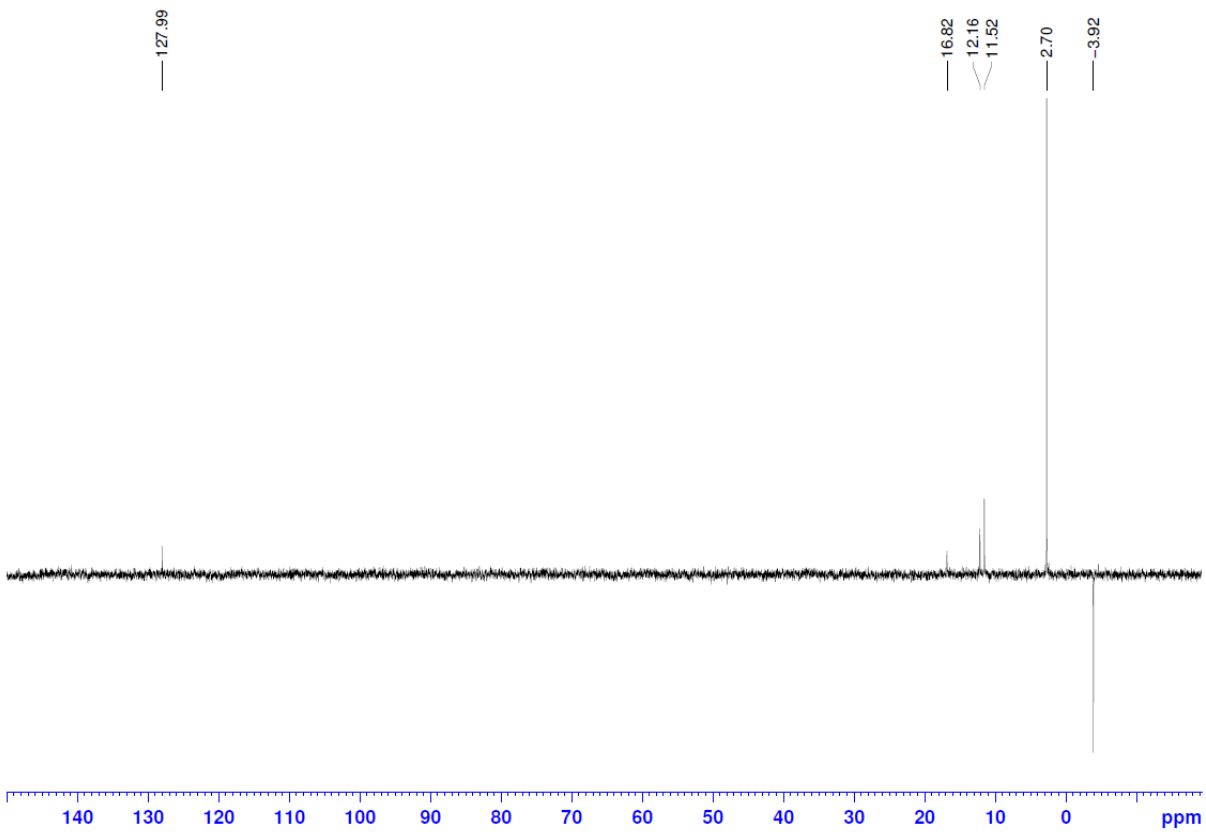

Fig. S16. $^{13}C\{^1H\}$ DEPT135 NMR (75.47 MHz, 300 K, benzene-d_6) of compound **3**.

Cp*[(TMS)$_3$Si]SiH$_2$ **4a**

A solution of 0.110 g (hypersilyl)(pentamethylcyclopentadienyl)silylene **2** in C_6D_6 (0.8 mL) was placed in a 50mL Schlenk flask equipped with a magnetic stirrer. The flask was shortly evacuated and refilled with dihydrogen (~1 bar). The reaction mixture was stirred at room temperature for 18h. Slowly a gradual change of colour from purple to colourless was observed. The post reaction mixture was analysed by MS and multinuclear NMR to show the conversion to dihydrido(hypersilyl)(pentamethylcyclopentadienyl)silane with a selectivity of ~95%. Efforts to crystallize this product were unsuccessful.

^{1}H NMR (300.13 MHz, 300 K, benzene-d_6): δ = 0.23 (s, 27H, (Si*Me*$_3$)$_3$), 1.29 (very br, 3H, Cp*-*Me*), 1.84 (br, s, 12H, Cp*-*Me*), 4.14 (s, $^1J_{Si-H}$ =180 Hz, 2H, Si-*H*).

$^{13}C\{^1H\}$ NMR (75.47 MHz, 300 K, benzene-d_6): δ = 2.19 (Si*Me*$_3$)$_3$, 11.47, 19.44 (br, Cp*-*Me*), 50.90, 134.05, 138.67 (br, Cp*-*C*).

$^{29}Si\{^1H\}$ NMR (59.63 MHz, 300 K, benzene-d_6): δ = –137.96 (*Si*(SiMe$_3$)), –36.31 (*Si*-H), –9.16 (Si(*Si*Me$_3$)).

HR MS (CI, m/z): $[M]^+$ found 412.2288, calculated for $C_{19}H_{44}Si_5$ 412.2289.

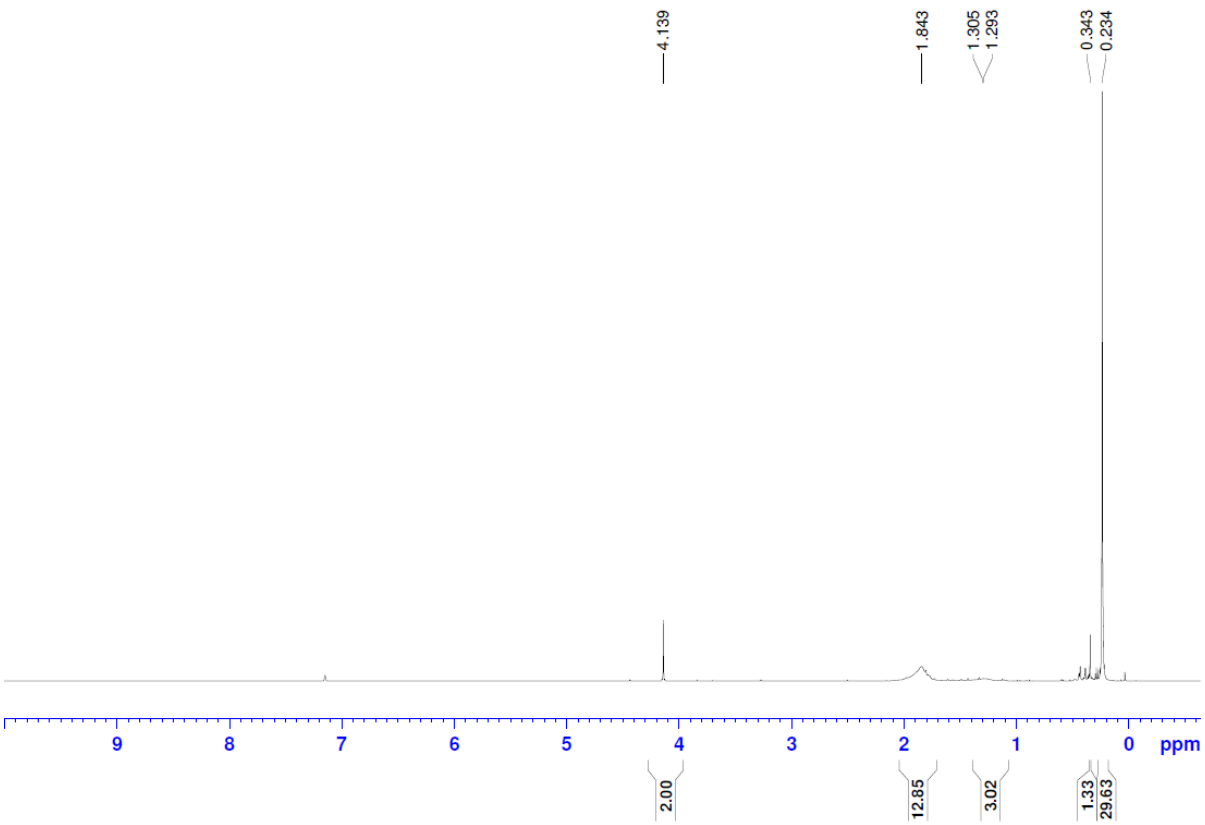

Fig. S17. ^{1}H NMR (300.13 MHz, 300 K, benzene-d_6). Post-reaction mixture **2** + H_2.

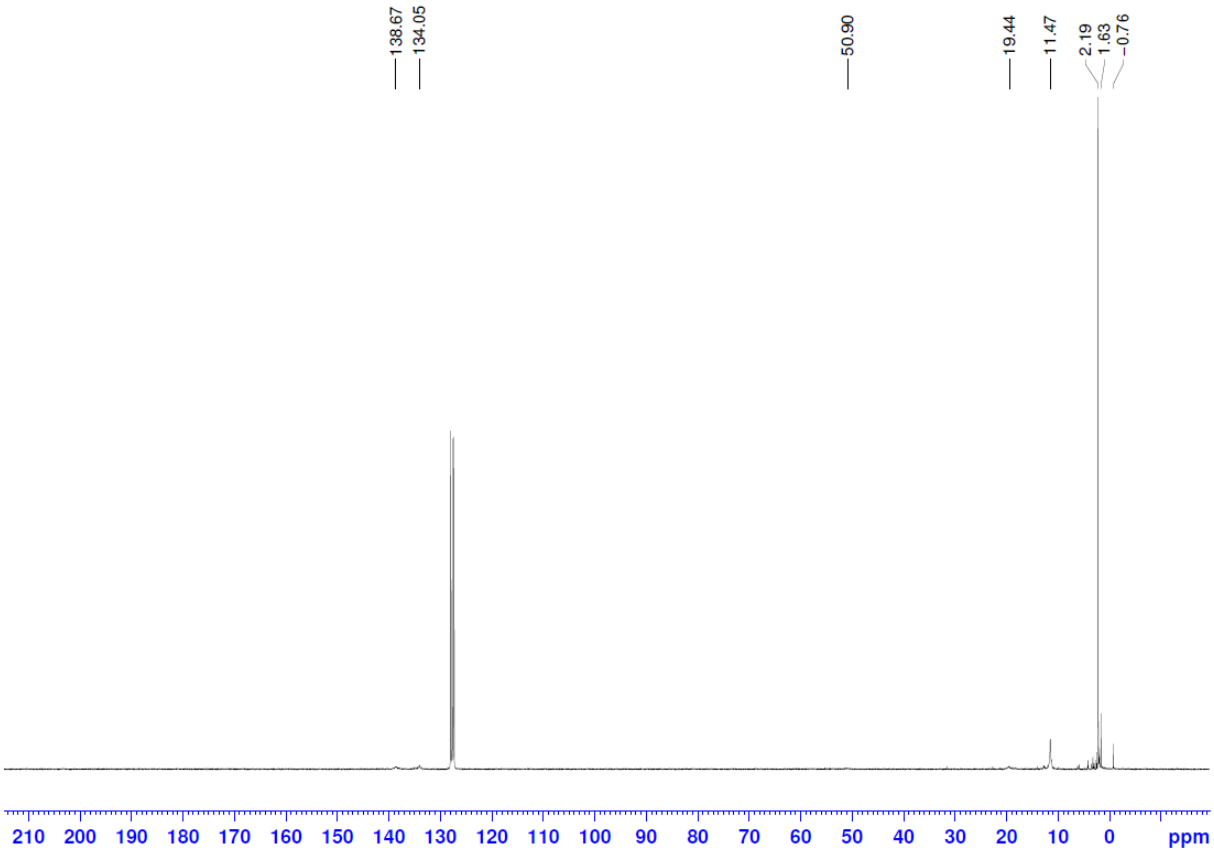

Fig. S18. ^{13}C {^{1}H} NMR (75.47 MHz, 300 K, benzene d_6). Post-reaction mixture **2** + H_2.

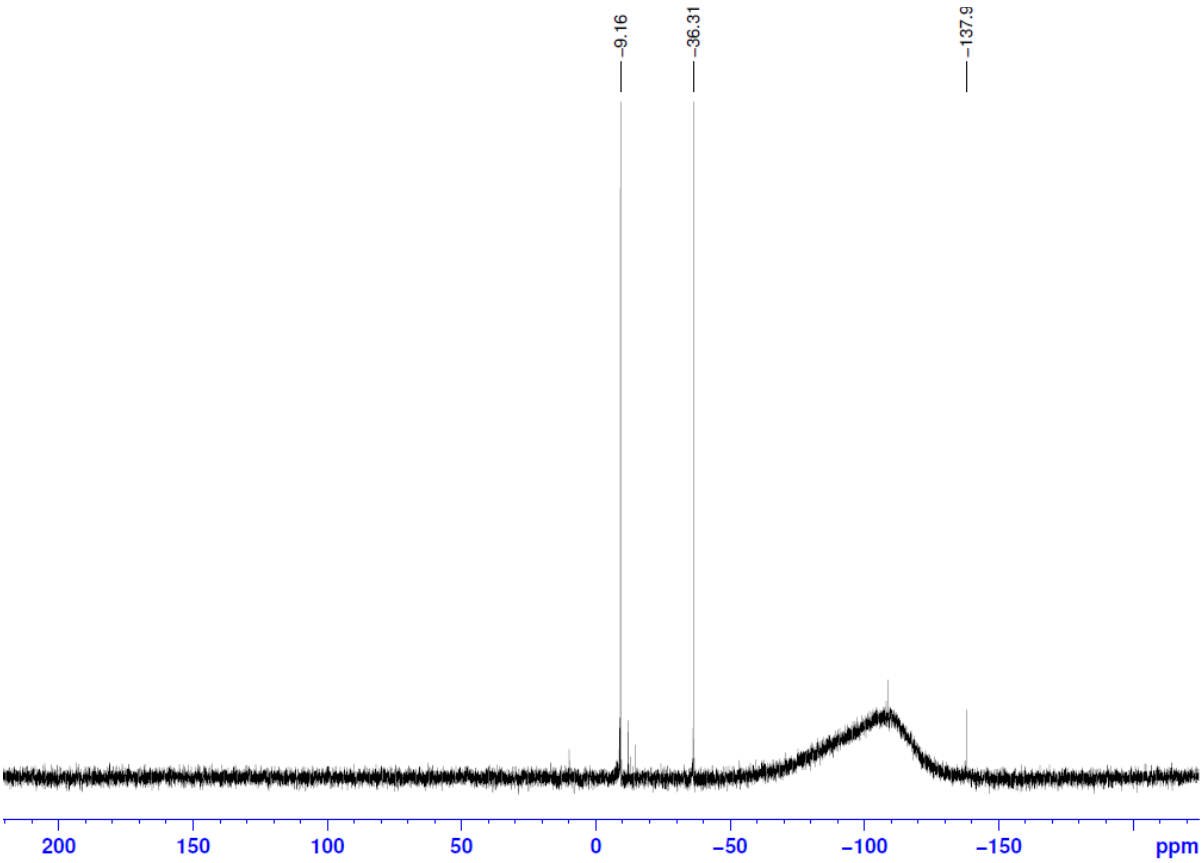

Fig. S19. $^{29}Si\{^{1}H\}$ NMR (59.63 MHz, 300 K, benzene-d_6). Post-reaction mixture **2** + H_2.

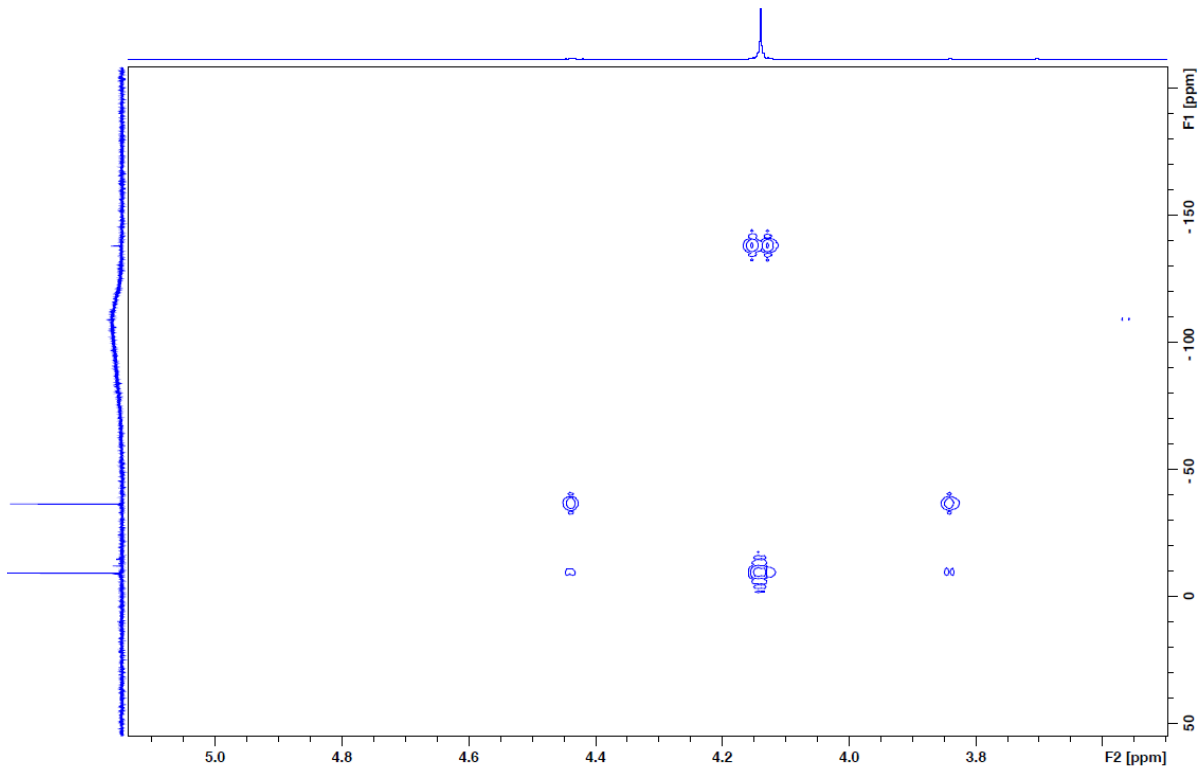

Fig. S20. $^{1}H/^{29}Si$ 2D NMR (300 K, benzene-d_6). Post-reaction mixture **2** + H_2.

Cp*[(TMS)$_3$Si]SiD$_2$ **4b**

A solution of a (hypersilyl)(pentamethylcyclopentadienyl)silylene **2** (0.098 g) in C_6D_6 (0.6 mL) was placed in a 50mL Schlenk flask equipped with a magnetic stirrer. The flask was shortly evacuated and refilled with deuterium (~1 bar). The reaction mixture was stirred at RT for 16h. Slowly a gradual change of colour from purple to colourless was observed. The post reaction mixture was analysed by MS and multinuclear NMR to show a conversion to dideuteride(hypersilyl)(pentamethylcyclopentadienyl)silane **4b** with a selectivity of ~95%. Efforts to crystallize this product were unsuccessful.

^{1}H NMR (300.13 MHz, 300 K, benzene-d_6): δ = 0.24 (s, 27H, (Si*Me*$_3$)$_3$), 1.29 (very br, 3H, Cp*-*Me*), 1.84 (br, s, 12H, Cp*-*Me*).

^{2}H NMR (46.07 MHz, 300 K, benzene-d_6): δ = 4.14 (s, Si-*D*).

^{13}C{^{1}H} NMR (75.47 MHz, 300 K, benzene-d_6): δ = 2.19 (Si*Me*$_3$)$_3$, 11.46, 19.44 (br, Cp*-*Me*), 50.84, 134.02, 138.60 (br, Cp*-*C*).

^{29}Si {^{1}H} NMR (59.63 MHz, 300 K, benzene-d_6): δ = −138.33 (*Si*(SiMe$_3$)), −37.01 (quint, $^1J_{Si-D}$ = 27 Hz, *Si*-D), −9.16 (Si(*Si*Me$_3$)).

HR MS (CI, m/z): [M]$^+$ found 414.2418, calculated for $C_{19}H_{42}D_2Si_5$ 414.2415.

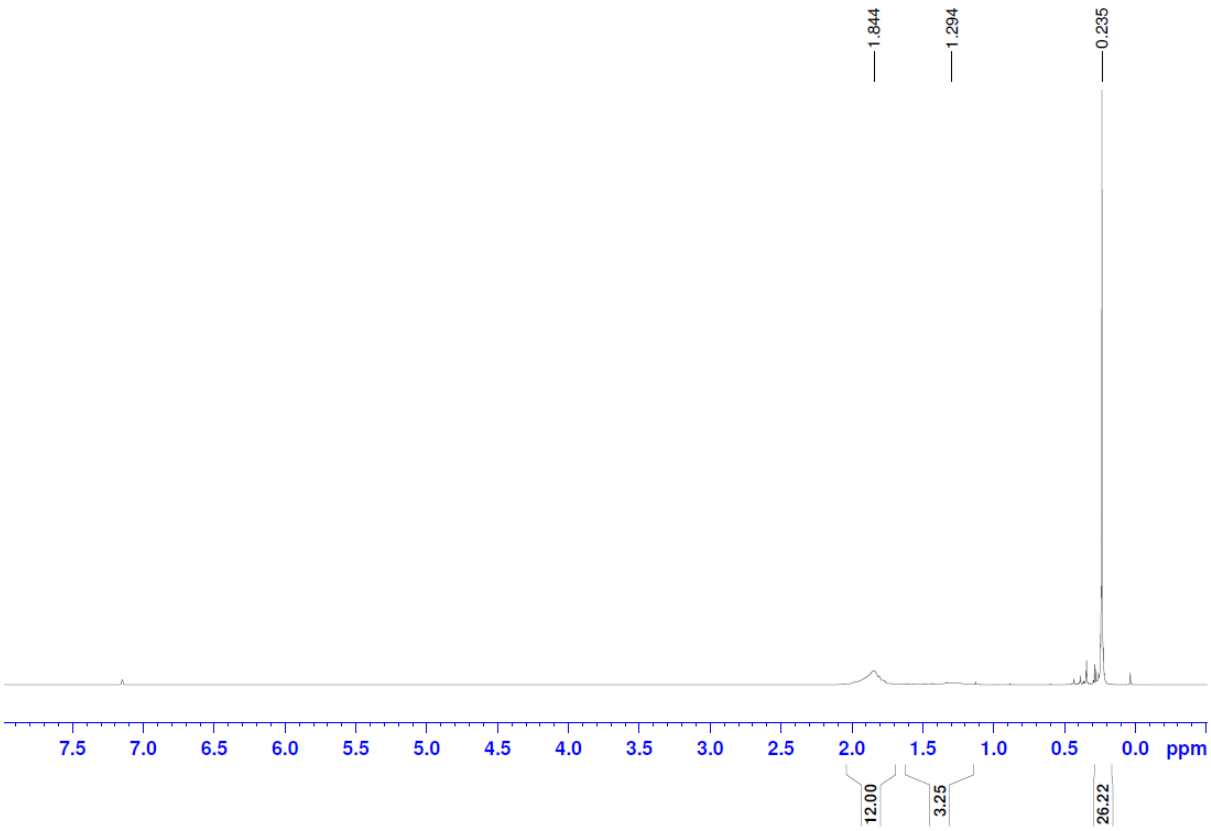

Fig. S21. ^{1}H NMR (300.13 MHz, 300 K, benzene-d_6). Post-reaction mixture **2** + D_2.

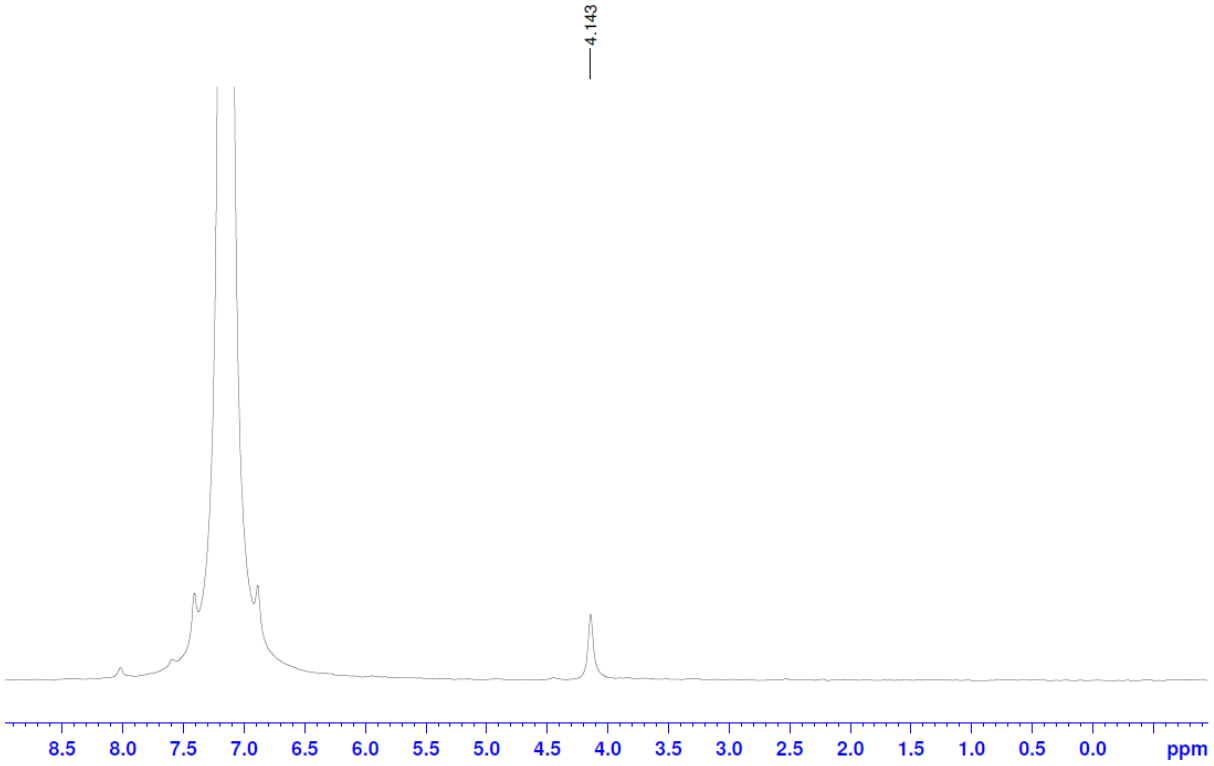

Fig. S22. ^{2}H NMR (46.07 MHz, 300 K, benzene-d_6). Post-reaction mixture **2** + D_2.

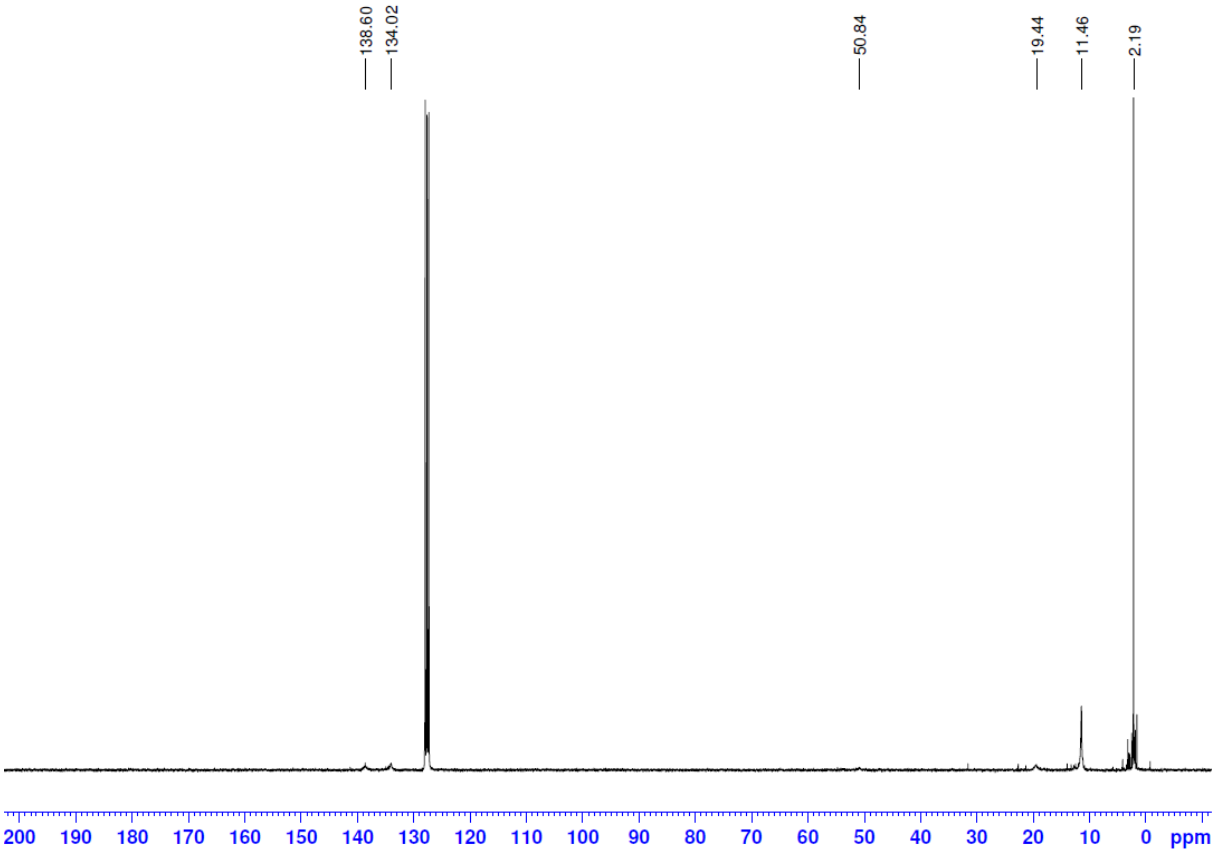

Fig. S23. ^{13}C {^{1}H} NMR (75.47 MHz, 300 K, benzene d_6). Post-reaction mixture **2** + D_2.

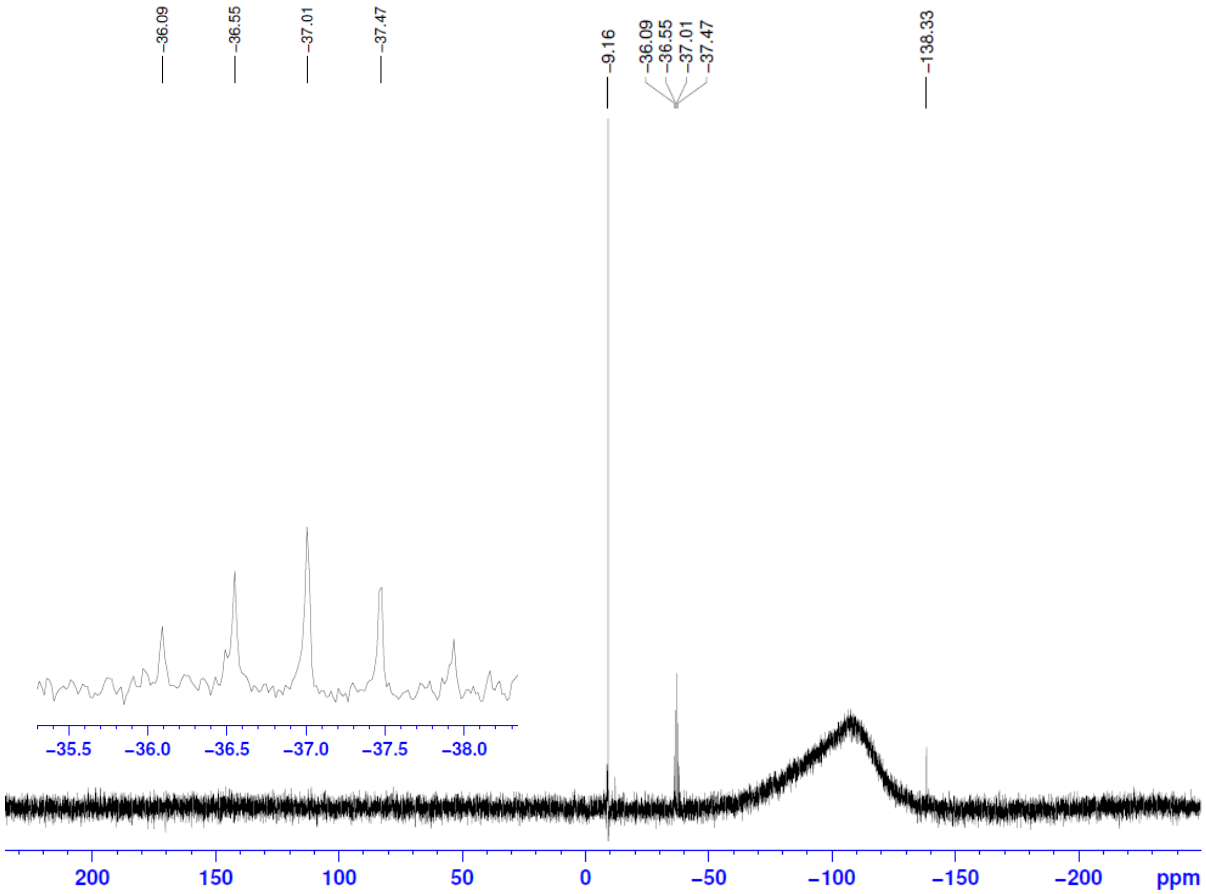

Fig. S24. $^{29}Si\{^{1}H\}$ NMR (59.63 MHz, 300 K, benzene-d_6). Post-reaction mixture **2** + D_2.

Cp*[(TMS)$_3$Si]SiH$_2$ **4a** + NHC (*in situ* formation of **5a**)

Solid 1,3,4,5-tetramethylimidazol-2-ylidene (31 mg, 0.25 mmol) was added to the crude product obtained from the reaction of silylene **2** (130 mg, 0.316 mmol) with H_2 in C_6D_6 (0.6 mL). The reaction mixture changed colour from colourless to orange. The sample was analysed by multinuclear NMR to show the formation of silylene-NHC adduct NHC[(TMS)$_3$Si](H)Si: **5a** under elimination of pentamethycyclopentadiene Cp*H with a selectivity of ~80%. Time dependent NMR shows complete decomposition of NHC stabilized silylene hydride **5a** within ~1 day in C_6D_6 solution. The formation of an orange solid insoluble in common organic solvents is observed and TMS_4Si is found as a byproduct soluble in C_6D_6. Decomposition of compound **5a** in solution prevented the isolation of analytically pure samples of compound **5a** and its further characterization.

^{1}H NMR (300.13 MHz, 300 K, benzene-d_6): NHC[(TMS)$_3$Si](H)Si: : δ = 0.36 (s, 27H, (Si*Me*$_3$)$_3$), 1.30 (s, 6H, NHC-*Me*), 3.20 (s, $^{1}J_{Si-H}$ = 94 Hz, 1H, Si-*H*), 3.21 (s, 6H, NHC-*Me*); Cp*H: δ = 0.98 (d, $^{3}J_{H-H}$ =7.6 Hz, 3H, Cp*H-*Me*), 1.72 (s, 6H, Cp*H-*Me*), 1.78 (s, 6H, Cp*H-*Me*),2.36 (br, 1H, Cp**H*); traces of TMS_4Si: 0.26 (s, 36H, Si(Si*Me*$_3$)$_4$) and traces of free NHC: δ = 1.61 (s, 6H, NHC-*Me*), 3.35 (s, 6H, NHC-*Me*).

^{13}C {^{1}H} NMR (100.61 MHz, 300 K, benzene-d_6): NHC[(TMS)$_3$Si](H)Si: : δ = 2.5 (Si*Me*$_3$)$_3$, 7.9 (NHC-*Me*), 33.5 (NHC-*Me*), 124.3 (NHC-*C*=C), 175.9 (NHC-*C*:); Cp*H: δ = 10.9, 11.4, 13.9 (Cp*H-*Me*), 51.4, 134.0, 137.1 (Cp*H-*C*); traces of TMS_4Si: δ = 2.5 Si(Si*Me*$_3$)$_4$ and traces of free NHC: δ = 8.5, 34.8 (NHC-*Me*),122.2 (NHC-*C*=C), 212.8 (NHC-*C*:).

^{29}Si{^{1}H} NMR (59.63 MHz, 300 K, benzene-d_6): NHC[(TMS)$_3$Si](H)Si: δ = −145.3 (*Si*-H), −130.3 (*Si*(SiMe$_3$)$_3$), −9.3 Si(*Si*Me$_3$)$_3$; TMS$_4$Si: δ = −135.9 (*Si*(SiMe$_3$)$_4$), −10.2 (Si(*Si*Me$_3$)$_4$).

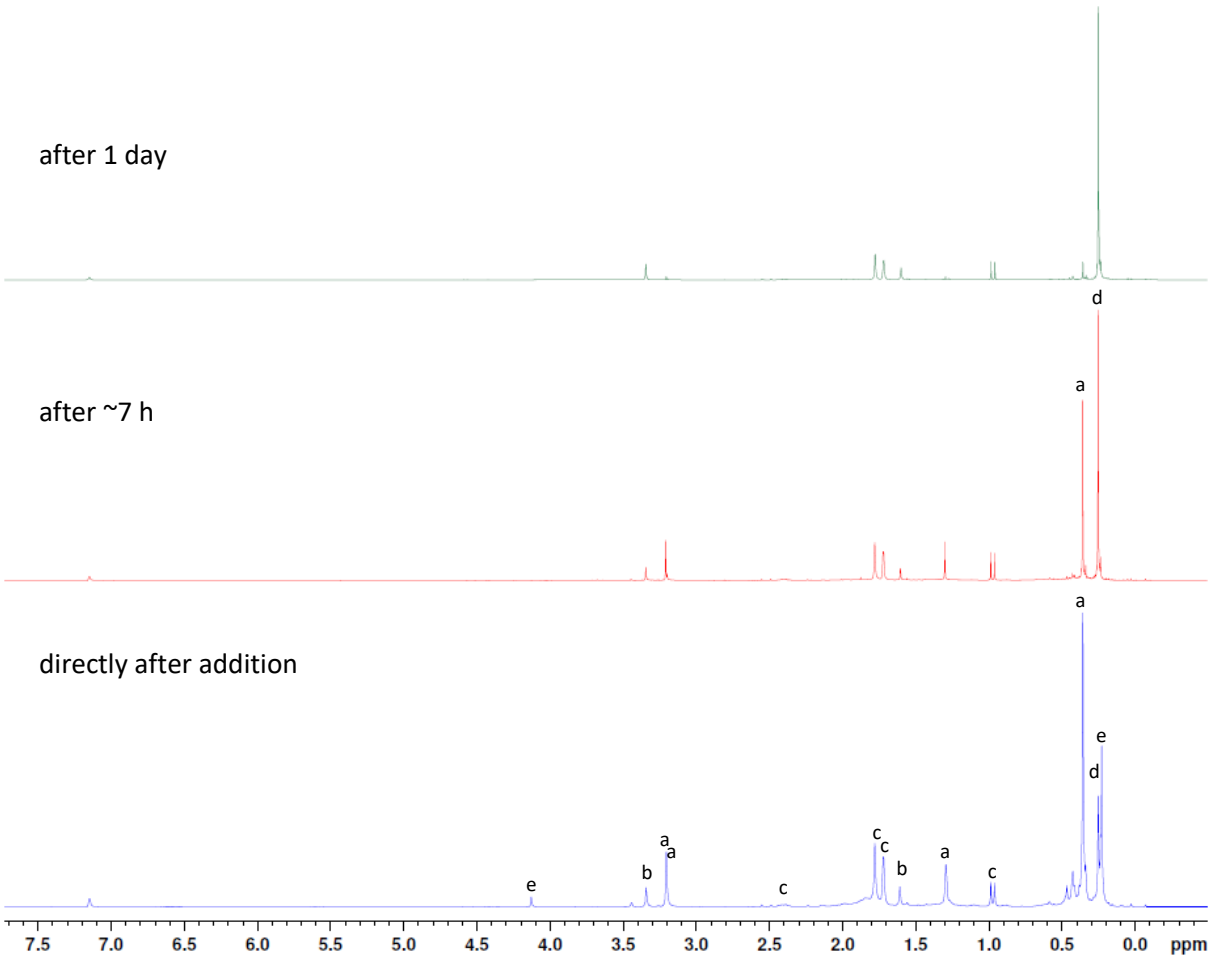

Fig. S25. ^{1}H NMR (300.13 MHz, 300 K, benzene-d_6). Crude Cp*[(TMS)$_3$Si]SiH$_2$ + NHC. NHC[(TMS)$_3$Si](H)Si: **5a** (a), free NHC (b), Cp*H (c), TMS$_4$Si (d), Cp*[(TMS)$_3$Si]Si**: 2** (e).

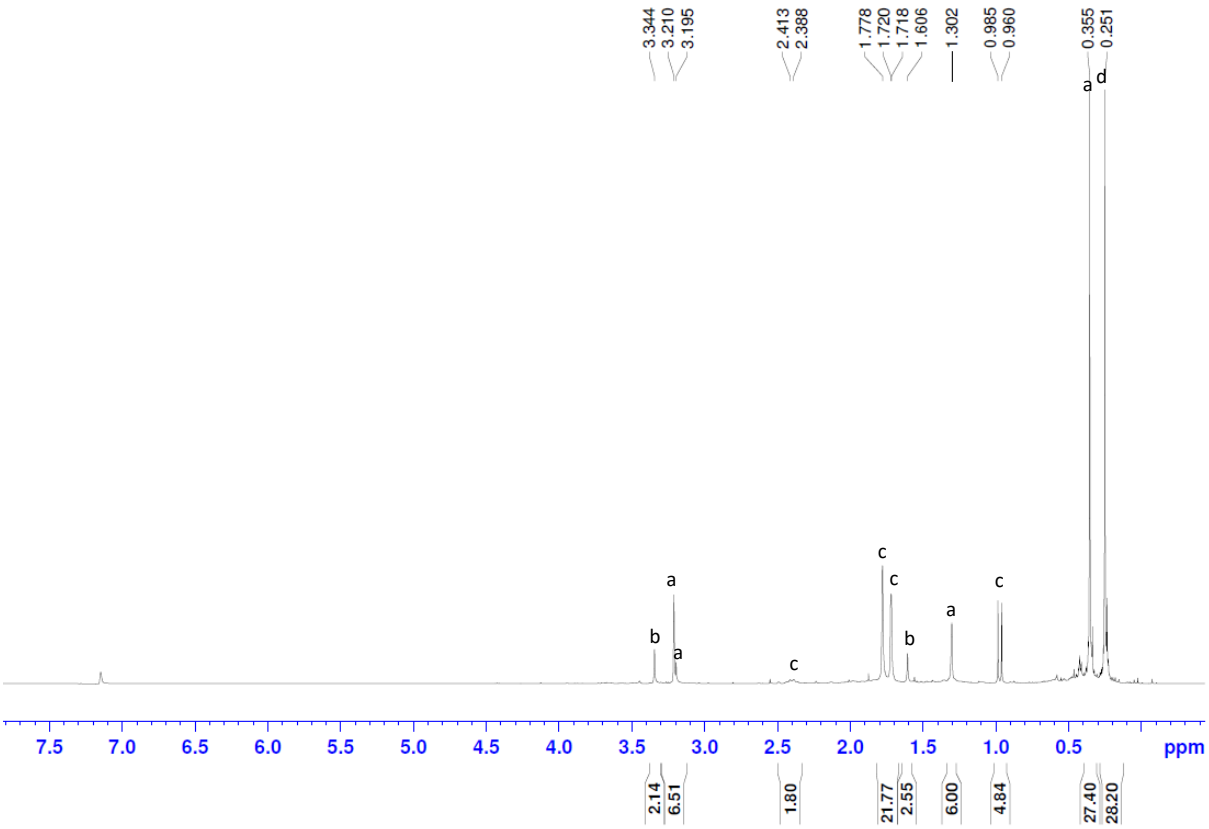

Fig. S26. ^{1}H NMR (300.13 MHz, 300 K, benzene-d_6). Crude Cp*[(TMS)$_3$Si]SiH$_2$ + NHC. Reaction mixture ~6.5 h after addition of carbene. NHC[(TMS)$_3$Si](H)Si: **5a** (a), free NHC (b), Cp*H (c), TMS$_4$Si (d).

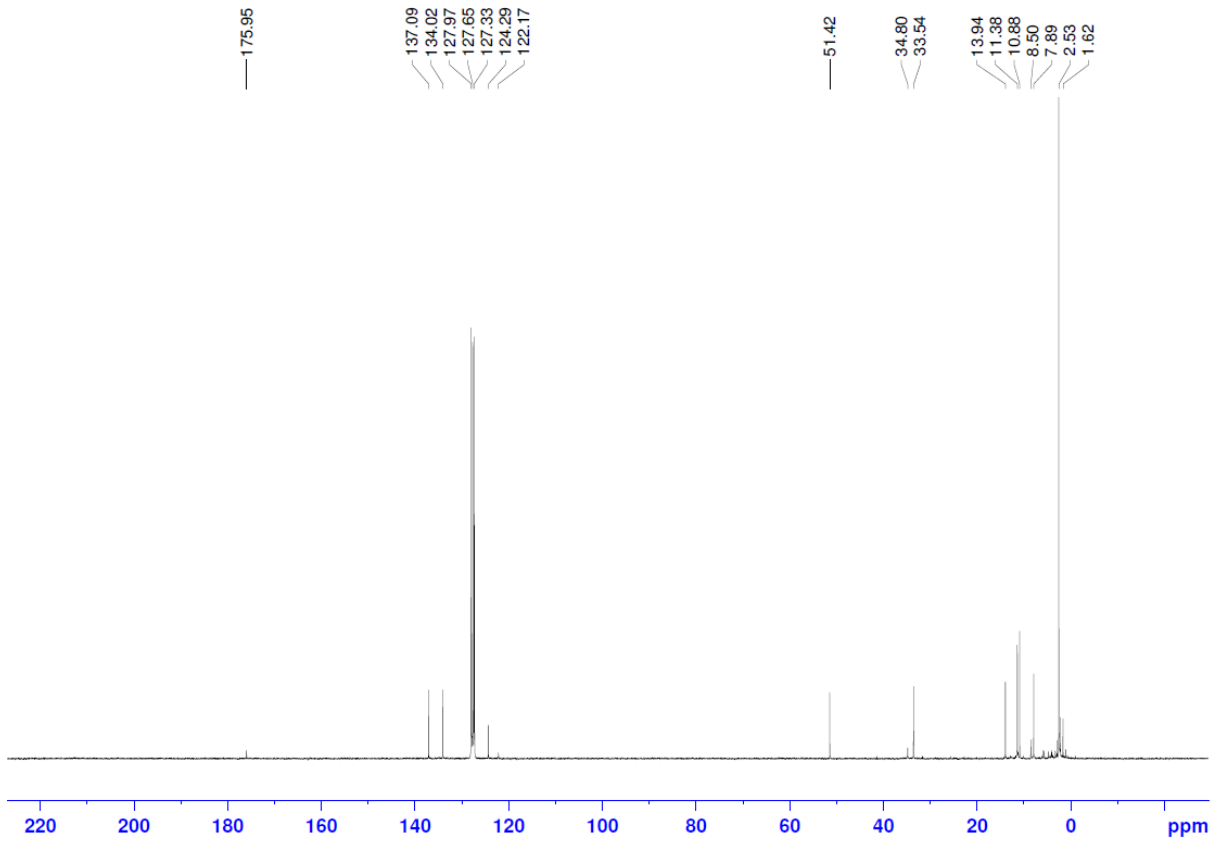

Fig. S27. ^{13}C{^{1}H} NMR (75.47 MHz, 300 K, benzene-d_6). Crude Cp*[(TMS)$_3$Si]SiH$_2$ + NHC.

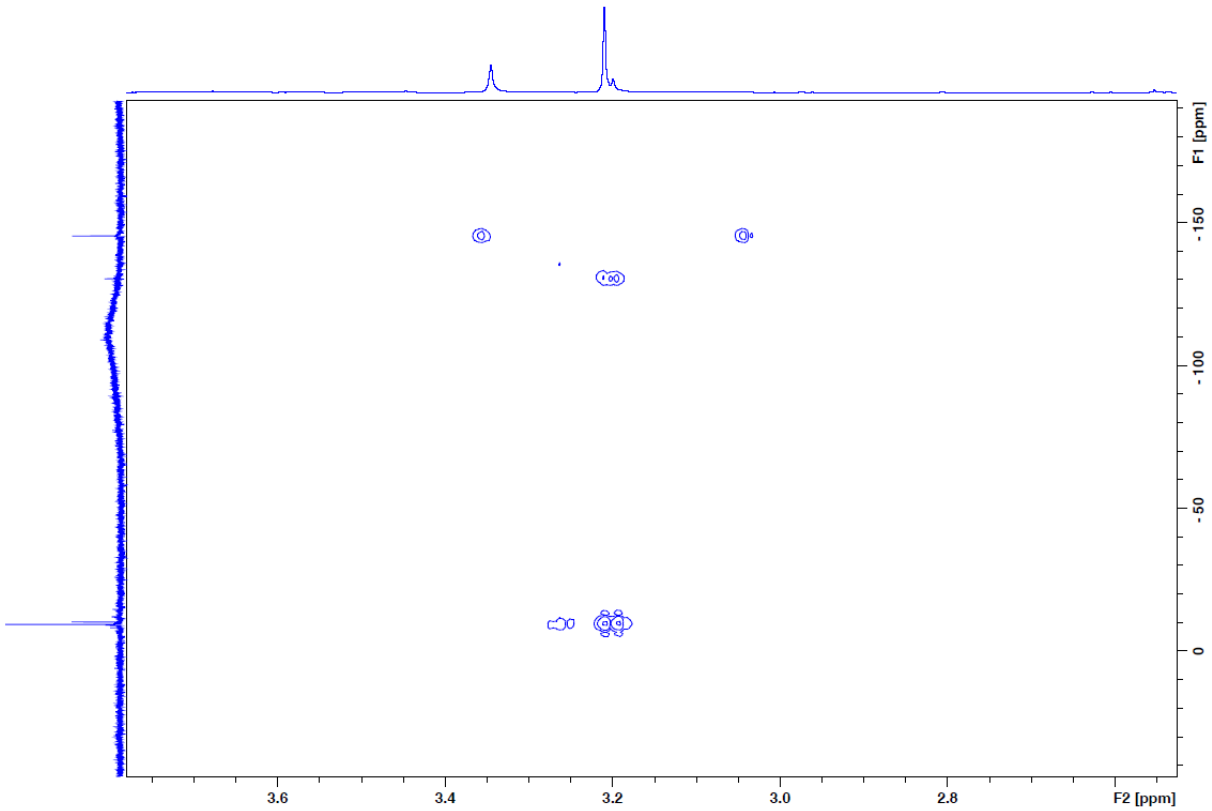

Fig. S28. $^{1}H/^{29}Si$ 2D NMR (300 K, benzene-d_6). Crude Cp*[(TMS)$_3$Si]SiH$_2$ + NHC.

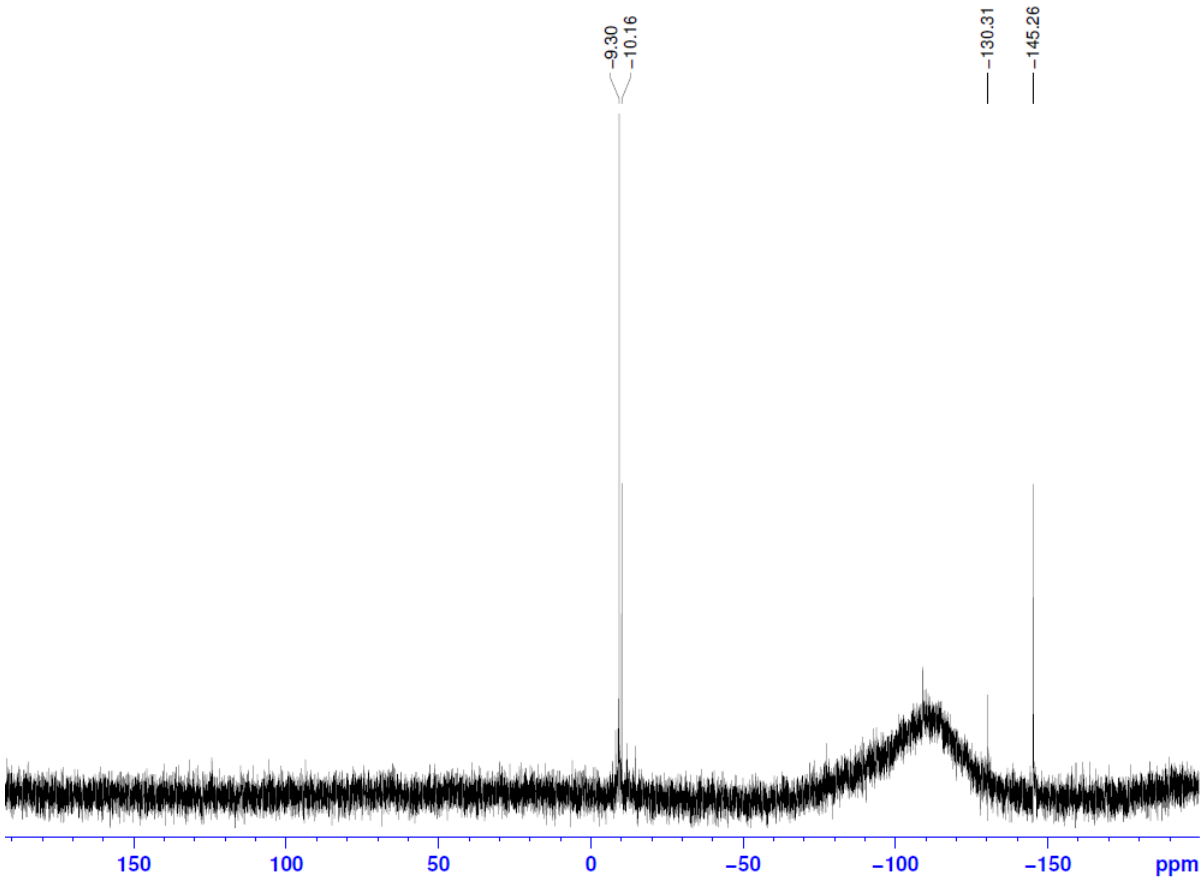

Fig. S29. $^{29}Si\{^{1}H\}$ NMR (59.63 MHz, 300 K, benzene-d_6). Cp*[(TMS)$_3$Si]SiH$_2$ + NHC.

Cp*[(TMS)$_3$Si]SiD$_2$ **4b** + NHC (*in situ* formation of **5b**)

Solid 1,3,4,5-tetramethylimidazol-2-ylidene (26 mg, 0.21 mmol) was added to the crude product obtained from the reaction of silylene **2** (88 mg, 0.238 mmol) with D_2 in C_6D_6 (0.6 mL). The reaction mixture changed colour from colourless to orange. The sample was analysed immediately by multinuclear NMR to show the formation of silylene NHC[(TMS)$_3$Si](D)Si: **5b** and deuterated pentamethycyclopentadiene Cp*D. Presence of Cp*D was also confirmed by HR_MS. While stored the sample changes colour to deep orange and a precipitation of plenty of an orange solid insoluble in common solvents is observed. Moreover, decomposition of the silylene NHC(TMS$_3$Si)(D)Si: and formation of TMS$_4$Si as a byproduct is found based on NMR and MS studies. Decomposition of compound **5b** in solution prevented the isolation of analytically pure samples of compound **5b** and its further characterization.

^{1}H NMR (300.13 MHz, 300 K, benzene-d_6): NHC[(TMS)$_3$Si](D)Si: : δ = 0.36 (s, 27H, (Si*Me*$_3$)$_3$), 1.31 (s, 6H, NHC-*Me*), 3.21 (s, 6H, NHC-*Me*); Cp*D: δ = 0.96 (br, Cp*D-*Me*), 1.72 (br, 6H, Cp*D-*Me*), 1.78 (br, 6H, Cp*D-*Me*); traces of TMS$_4$Si: 0.25 (s, 36H, Si(Si*Me*$_3$)$_4$) and traces of free NHC: δ = 1.61 (s, 6H, NHC-*Me*), 3.34 (s, 6H, NHC-*Me*). **^{2}H NMR** (46.07 MHz, 300 K, benzene-d_6): δ = 3.21 (Si-*D*), 2.35 (Cp**D*).

^{13}C {^{1}H} NMR (100.61 MHz, 300 K, benzene-d_6): NHC[(TMS)$_3$Si](D)Si: δ = 2.5 (Si*Me*$_3$)$_3$, 7.9 (NHC-*Me*), 33.5 (NHC-*Me*), 124.3 (NHC-*C*=C), 176.0 (NHC-*C*:); Cp*D: δ = 10.9, 11.4, 13.9 (Cp*D-*Me*), 51.0 (t, $^1J_{C\text{-}D}$ = 19 Hz, Cp*D-*C*D), 134.0, 137.1 (Cp*D-*C*); traces of TMS$_4$Si: δ = 2.5 Si(Si*Me*$_3$)$_4$ and traces of free NHC: δ = 8.5, 34.8 (NHC-*Me*), 122.2 (NHC-*C*=C), 212.8 (NHC-*C*:).

^{29}Si{^{1}H} NMR (59.63 MHz, 300 K, benzene-d_6): NHC[(TMS)$_3$Si](D)Si: δ = −146.0 (t, $^1J_{Si\text{-}D}$ = 14 Hz, *Si*-D), −130.5 (*Si*(SiMe$_3$)$_3$), −9.3 Si(*Si*Me$_3$)$_3$; TMS$_4$Si: δ = −135.9 (*Si*(SiMe$_3$)$_4$), −10.2 (Si(*Si*Me$_3$)$_4$).

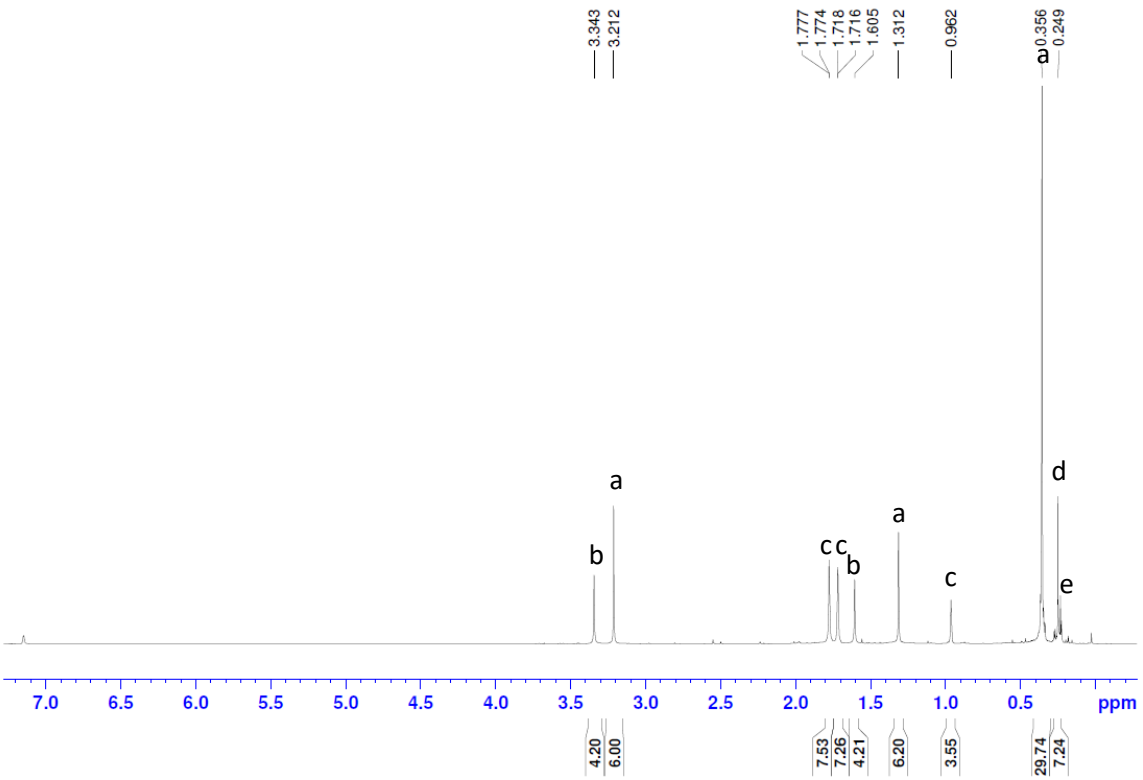

Fig. S30. ^{1}H NMR (300.13 MHz, 300 K, benzene-d_6). Crude Cp*[(TMS)$_3$Si]SiD$_2$ + NHC. The reaction mixture directly after addition of NHC. NHC[(TMS)$_3$Si](D)Si: **5b** (a), free NHC (b), Cp*D (c), TMS$_4$Si (d), Cp*[(TMS)$_3$Si]Si**:** **2** (e).

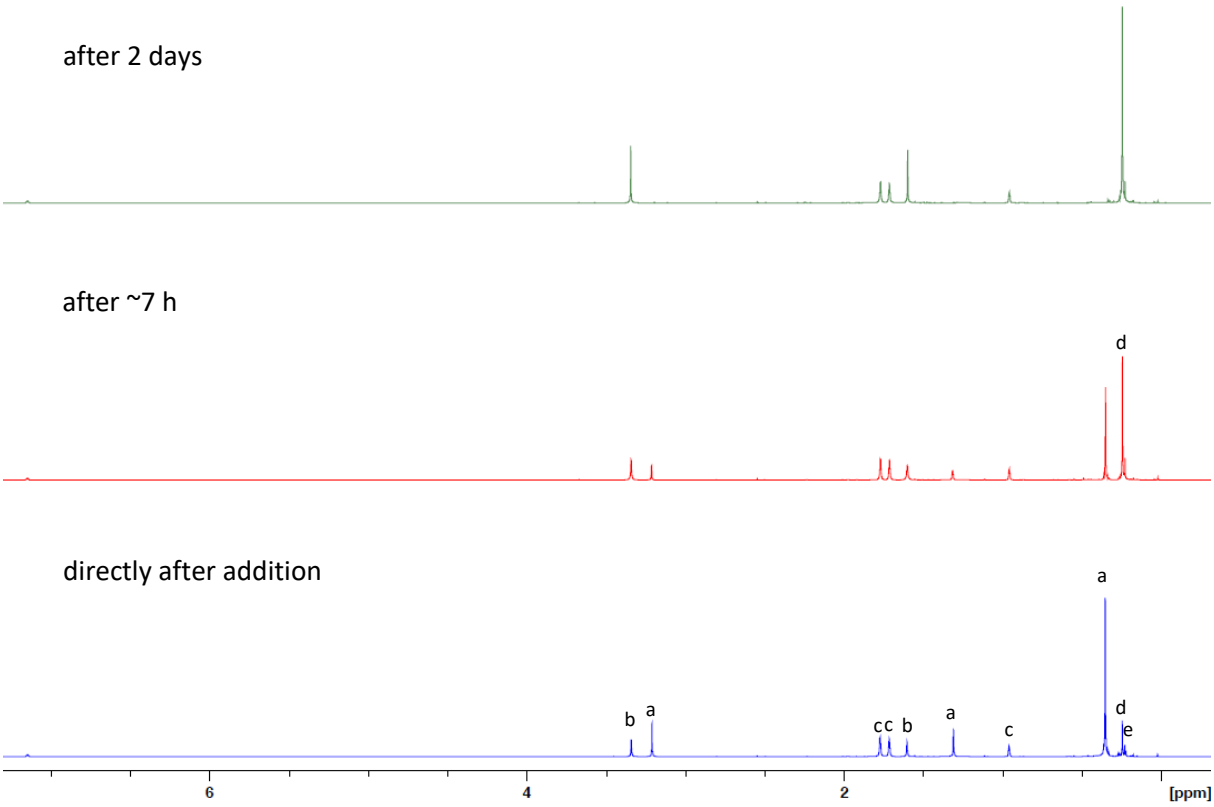

Fig. S31. ^{1}H NMR (300.13 MHz, 300 K, benzene-d_6). Crude Cp*[(TMS)$_3$Si]SiD$_2$ + NHC. NHC[(TMS)$_3$Si](D)Si: **5b** (a), free NHC (b), Cp*D (c), TMS$_4$Si (d), Cp*[(TMS)$_3$Si]Si**: 2** (e).

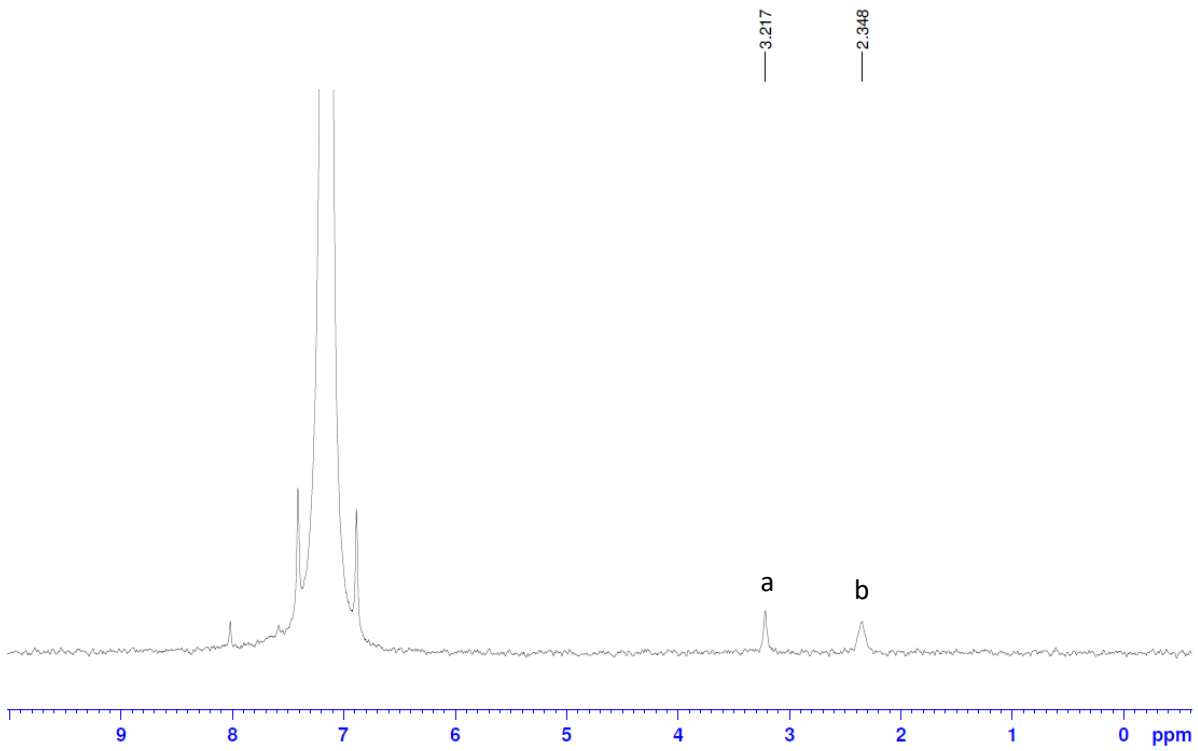

Fig. S32. ^{2}H NMR (46.07 MHz, 300 K, benzene-d_6). Crude Cp*[(TMS)$_3$Si]SiD$_2$ + NHC. NHC[(TMS)$_3$Si](D)Si: **5b** (a), Cp*D (b).

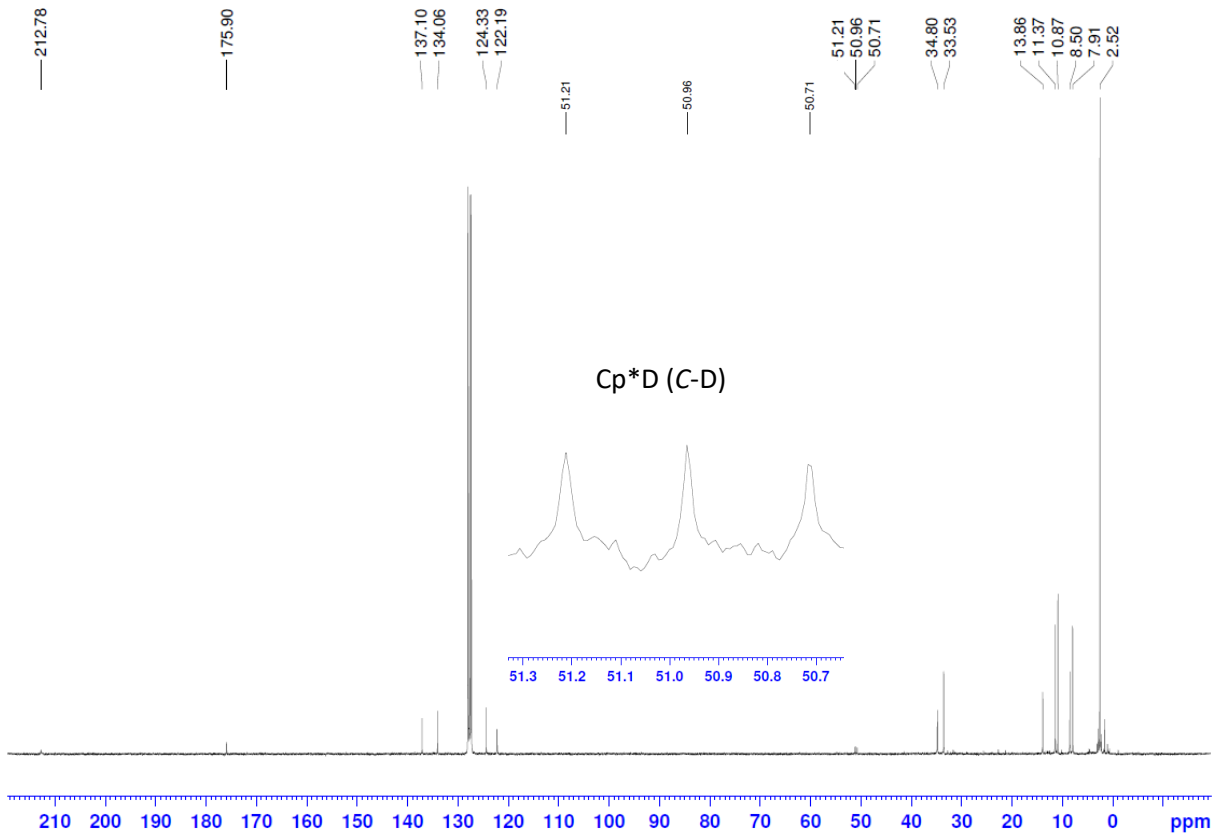

Fig. S33. ^{13}C{^{1}H} NMR (75.47 MHz, 300 K, benzene-d_6). Crude Cp*[(TMS)$_3$Si]SiD$_2$ + NHC.

NHC(TMS$_3$Si)(D)*Si*: **5b**

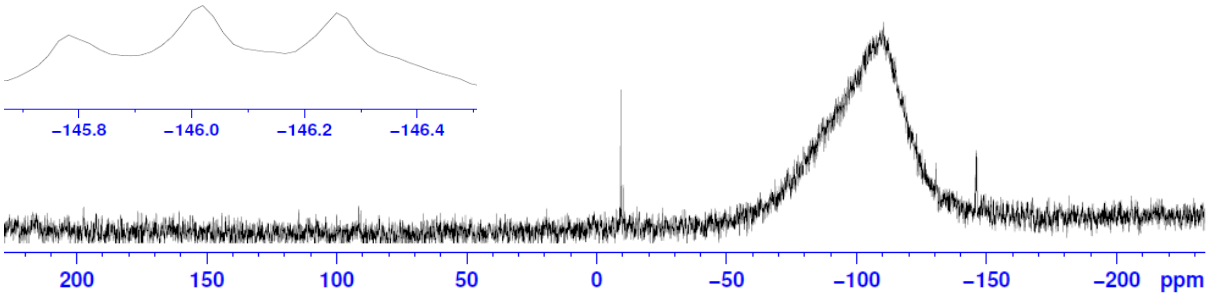

Fig. S34. ^{29}Si{^{1}H} NMR (59.63 MHz, 300 K, benzene-d_6). Crude Cp*[(TMS)$_3$Si]SiD$_2$ + NHC.

(NHC)[(Me$_3$Si)$_3$Si(Cp*)]Si: 6: Solid 1,3,4,5-tetramethylimidazol-2-ylidene (62 mg, 0.50 mmol) was added at room temperature to a solution of (hypersilyl)(pentamethylcyclopentadienyl)silylene **2** (210 mg, 0.511 mmol) in benzene (2 mL). Immediately, a change of colour from purple to orange was observed. Crystallization from benzene at room temperature afforded orange crystals of the adduct (210 mg, 0.392 mmol). Yield 78%.

^{1}H NMR (400.13 MHz, 298 K, benzene-d_6): δ = 0.47 (s, 27H, (Si*Me*$_3$)$_3$), 1.24 (s, 3H, NHC-*Me*), 1.38 (s, 3H, NHC-*Me*), 1.79 (br, 15H, Cp*-*Me*), 3.45 (s, 3H, NHC-*Me*), 3.47 (s, 3H, NHC-*Me*).

^{13}C {^{1}H} NMR (100.61 MHz, 300 K, benzene-d_6): δ = 4.0 (Si*Me*$_3$)$_3$, 7.8, 8.2 (NHC-*Me*), 13.2 (br, Cp*-*Me*), 34.2, 37.2 (NHC-*Me*), 123.8, 124.3 (NHC-C=C), 168.9 (NHC-C:).

^{29}Si{^{1}H} NMR (79.49 MHz, 300 K, benzene-d_6): δ = –134.2 (*Si*(SiMe$_3$)$_3$), –15.7 (Cp**Si*), –9.9 Si(*Si*Me$_3$)$_3$.

M.p. 132-135 °C (partial decomposition)

UV/Vis (hexane): $\lambda_{max}(\varepsilon)$ = 239 nm (33992 M^{-1}cm^{-1}), 277 nm (13477 M^{-1}cm^{-1}), 320 nm (10336 M^{-1}cm^{-1}), 450 nm (789 M^{-1}cm^{-1}).

EA (%): Calculated for $C_{26}H_{54}N_2Si_5$ [535.16]: C 58.35, H 10.17, N 5.23; found C 57.83, H 9.42, N 5.74.

HR-MS (ESI, m/z): calculated for [M+Na]$^+$ 557.3026, found 557.3036

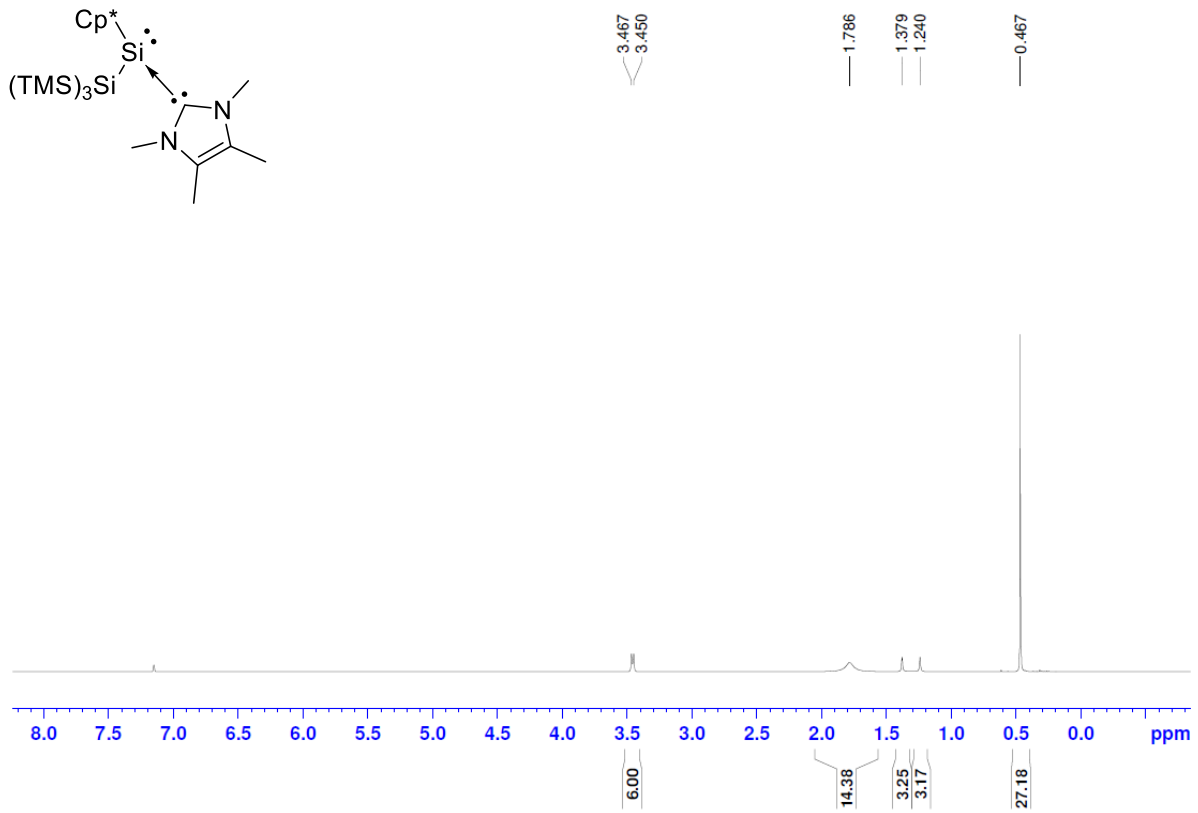

Fig. S35. ^{1}H NMR (400.13 MHz, 298 K, benzene- d_6) of compound **6**.

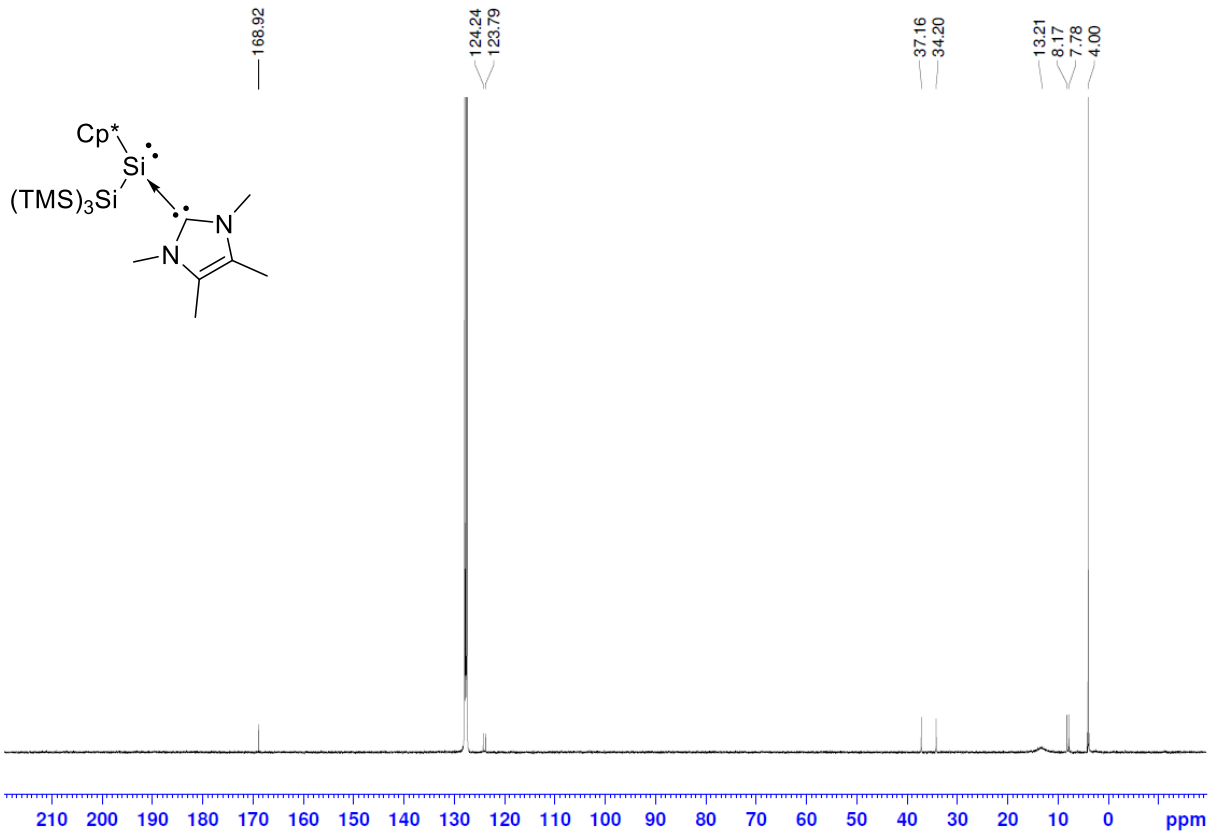

Fig. S36. ^{13}C{H} NMR (100.61 MHz, 300 K, benzene- d_6) of compound **6**.

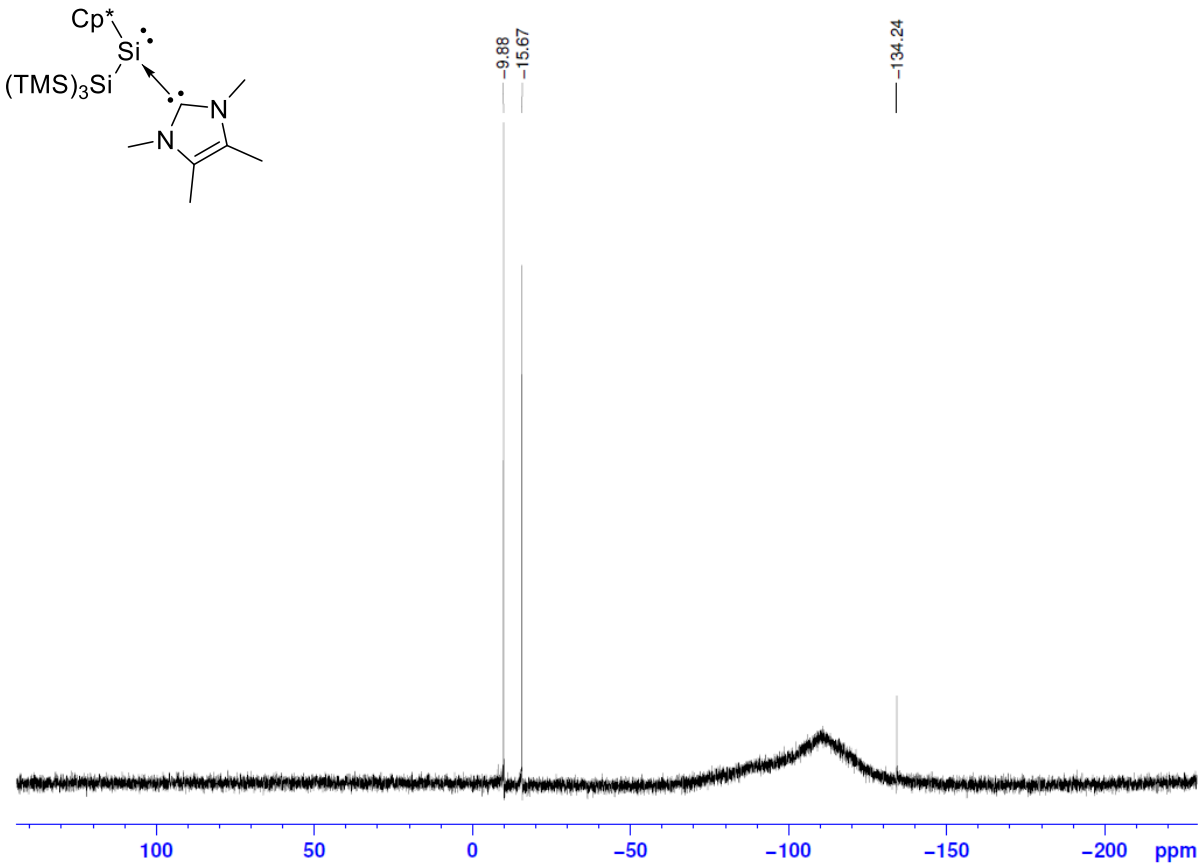

Fig. S37. ^{29}Si{H} NMR (79.49 MHz, 300 K, benzene-d_6) of compound **6**.

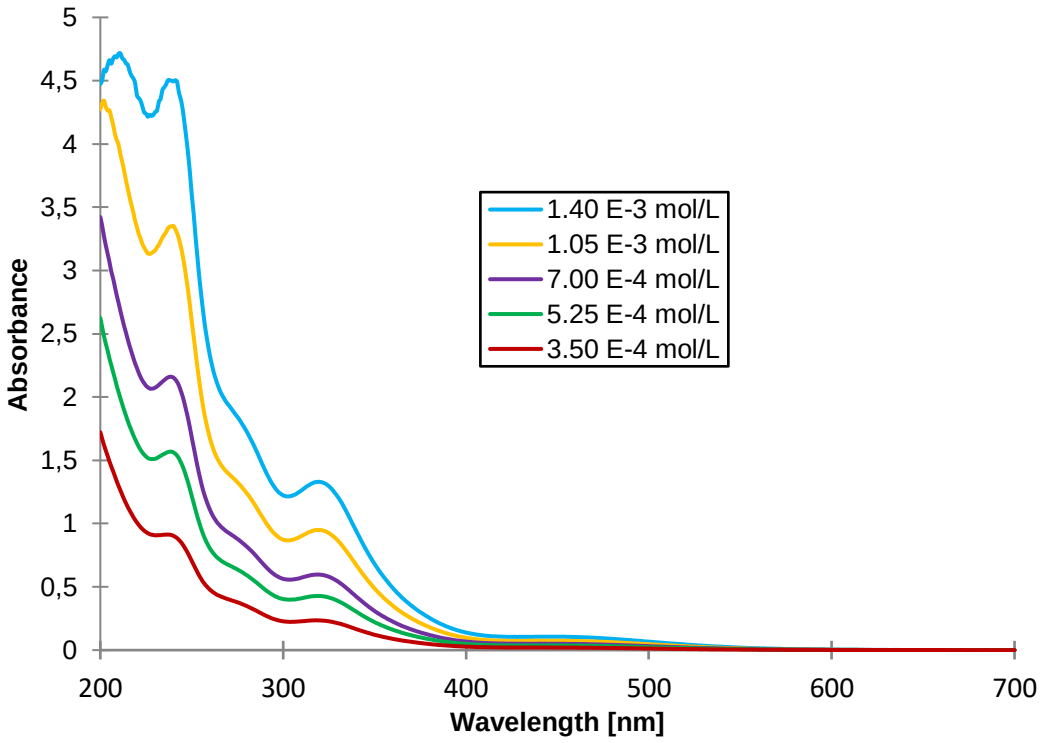

Fig. S38. UV/Vis spectrum of **6** in hexane.

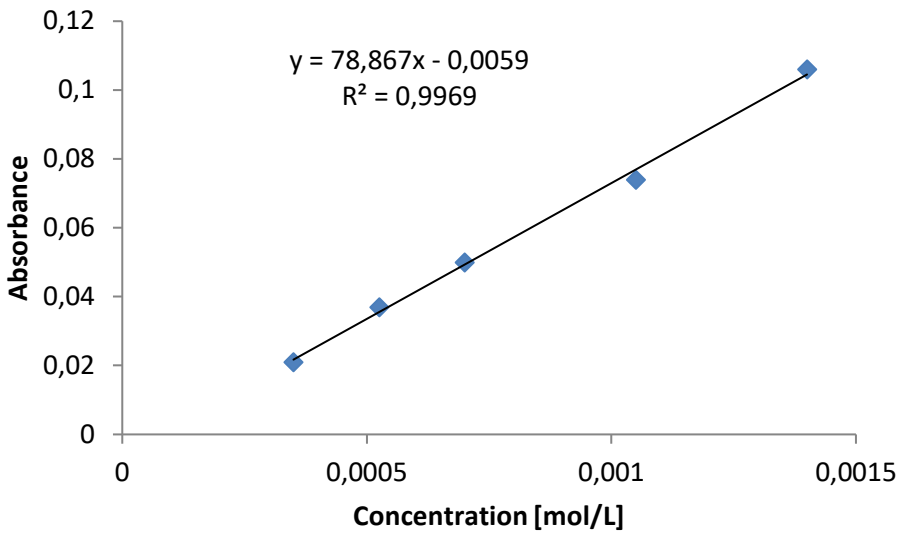

Fig. S39. Extinction coefficient ε =789 $M^{-1}cm^{-1}$ (λ = 450 nm) for **6**.

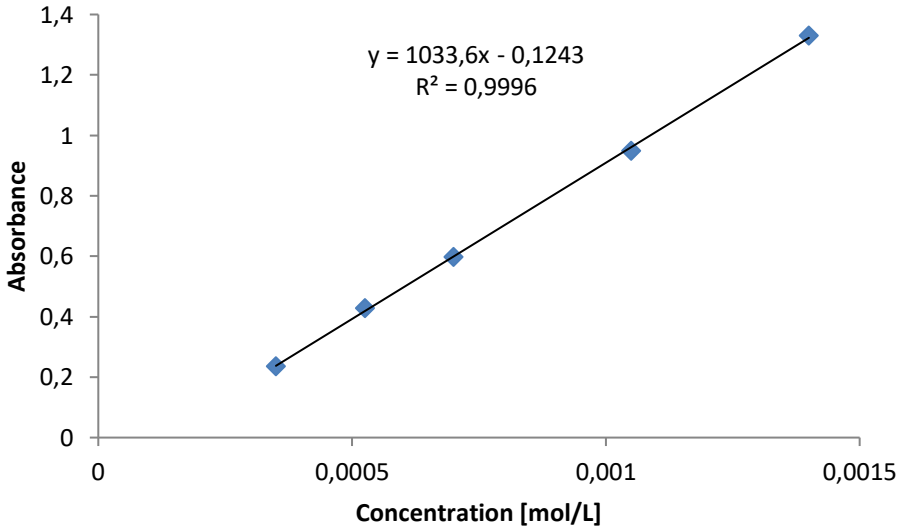

Fig. S40. Extinction coefficient ε =10336 $M^{-1}cm^{-1}$ (λ = 320 nm) for **6**.

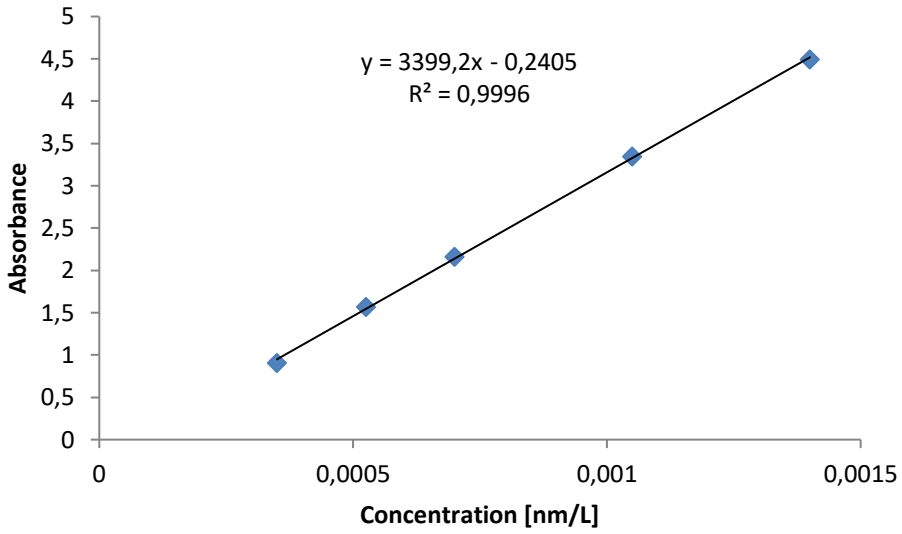

Fig. S41. Extinction coefficient ε =33992 $M^{-1}cm^{-1}$ (λ = 239 nm) for **6**.

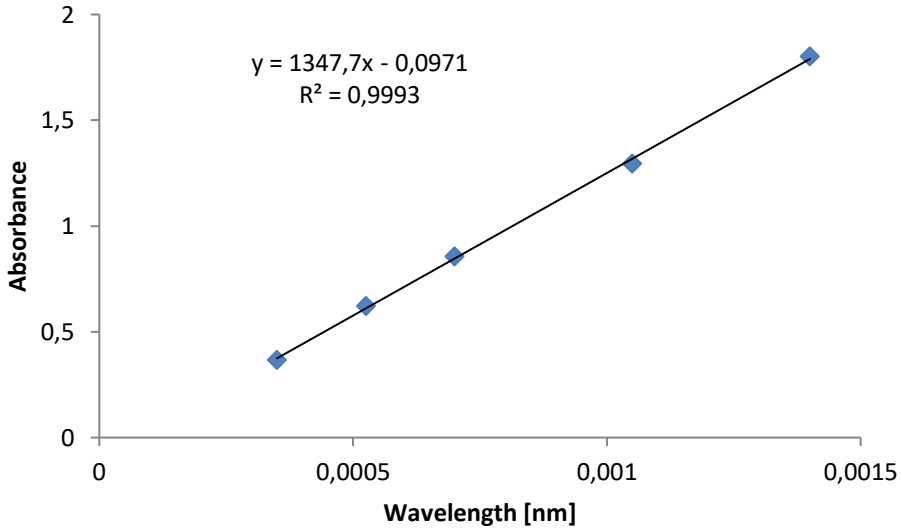

Fig. S42. Extinction coefficient ε = 13477 $M^{-1}cm^{-1}$ (λ = 277 nm) for **6**.

Synthesis of **7**:

1. A solution of potassium hypersilyl salt $(thf)_{1.85}[KSi(SiMe_3)_3]$ (1.20 g, 2.86 mmol) in hexane (~50 mL) was added via a cannula to a stirred solution of tribromo(pentamethylcyclopentadienyl)silane (0.568 g, 1.41 mmol) in hexane (~30 mL) placed in 100 mL Schlenk flask equipped with a stir bar. Immediately, a change of colour from pale yellow to purple and precipitation of a white solid were observed. The reaction mixture was stirred at room temperature for 2 h and then filtered. A solution of *N,N'*-di-tert-butyl-1,3-diaza-2-sila-2-ylidene (0.277 g, 1.41 mmol) in hexane (~10 mL) was added dropwise at room temperature to the stirred filtrate. A change in intensity of colour of the solution from intense purple to pink was observed. The reaction mixture was stirred 2h followed by solvent removal in vacuo. The solid residue was dissolved in hexane (~5 mL). Concentration of the hexane solution followed by storage at 5 ° afforded a yellow precipitate, which was washed with cold hexane. Further crystallization

from hexane at -30 °C followed by washing with a cold pentane afforded a second crop of yellow crystals, together 247 mg (yield: 41%).

Dissolving the yellow crystals of disilane **7** in toluene at room temperature results in a pinkish/purple solution which gradually reversibly changes the colour to yellow when cooled to 223 K.

Crystallization at 5 °C from hexane afforded crystals suitable for X-ray analysis.

2. Solid *N,N'*-di-tert-butyl-1,3-diaza-2-sila-2-ylidene (35 mg, 18 mmol) was added to a solution of **2** (72 mg, 18 mmol) in benzene-d_6 (0.6 mL) placed in an NMR tube. A change in intensity of colour of the solution from intense purple to pink/reddish was observed. NMR analysis gave the same results as for dissolved crystals of **7**. Crystallization from hexane at -30°C afforded **7** as yellow crystals 45 mg (yield 42%).

^{1}H NMR (300.13 MHz, 223 K, toluene-d_8):δ = 0.37 (s, 27H, (Si*Me*$_3$)$_3$), 1.28 (s, 3H, *Me*), 1.30 (s, 9H, *Me*$_3$C), 1.34 (s, 3H, *Me*), 1.51 (s, 9H, *Me*$_3$C), 1.55 (s, 3H, *Me*), 1.64 (s, 3H, *Me*), 1.89 (s, 3H, *Me*), 5.75 (d, $^3J_{H\text{-}H}$ = 3.9 Hz, 1H, C*H*=CH), 5.86 (d, $^3J_{H\text{-}H}$ = 3.9 Hz, 1H, C*H*=CH).

^{13}C{^{1}H} NMR (75.47 MHz, 223 K, toluene-d_8):δ = 2.81 (s, Si*Me*$_3$)$_3$, 12.34 (s, *Me*), 12.92 (s, *Me*), 13.71 (s, *Me*), 15.65 (s, *Me*), 19.40 (s, *Me*), 30.89 (s, *Me*$_3$C), 32.10 (s, *Me*$_3$C), 45.78 (s, cyclopentene), 51.22 (s, Me$_3$*C*), 51.93 (s, cyclopentene), 52.87 (s, Me$_3$*C*), 65.28 (s, cyclopentene), 113.24 (s, N*C*H=CHN), 115.02 (s, NCH=*C*HN), 130.31 (s, C=C-cyclopentene), 133.26 (s, C=C-cyclopentene).

^{29}Si {^{1}H} NMR (59.63 MHz, 223 K, toluene-d_8): δ = −135.95 (*Si*(SiMe$_3$)), −105.35(*Si*-SiN), −21.23 (Si-*Si*N), − 9.44(Si(*Si*Me$_3$)).

^{13}C CP-MAS/NMR (100.65 MHz, 13 kHz, 300K) : δ = 3.69 (s, Si*Me*$_3$)$_3$, 14.42 (s, *Me*), 15.11 (s, *Me*), 19.36 (s, *Me*), 32.31 (s, *Me*$_3$C), 33.80 (s, *Me*$_3$C), 46.78 (s, cyclopentene), 51.33 (s, Me$_3$*C*), 51.74 (s, cyclopentene), 53.54 (s, Me$_3$*C*), 64.08 (s, cyclopentene), 113.44 (s, N*C*H=CHN), 116.28 (s, NCH=*C*HN), 130.13 (s, C=C-cyclopentene), 134.54 (s, C=C-cyclopentene).

^{29}Si CP-MAS/NMR (79.53 MHz, 13 kHz, 300 K): δ = −131.80 (*Si*(SiMe$_3$)), −105.59 (*Si*-SiN), −21.23 (Si-*Si*N), −9.75(Si(*Si*Me$_3$)).

M.p. 117-120 °C (starts to change colour to red/purple from ~70 °C)

EA (%): Calculated for $C_{29}H_{62}N_2Si_6$ [607.34]: C 57.35, H 10.29, N 4.61; found C 56.45, H 9.73, N 4.34. Deviations in EA are primarily ascribed to the highly air and moisture sensitive nature of heterodimer **7**.

Addition of ethylene (~1bar) to dissolved crystals of **7** in benzene-d_6 gives quantitively compound **3** and free West silylene as confirmed by multinuclear NMR: 50 mg of compound **7** was dissolved in benzene-d_6 (0.7 mL) placed in 25mL Schlenk flask equipped with a stir bar. The Schlenk flask was shortly evacuated and refilled with ethylene (~1bar). The pink color of the reaction mixture disappeared and a colorless solution was formed. The reaction mixture was stirred for 10 minutes followed by NMR analysis.

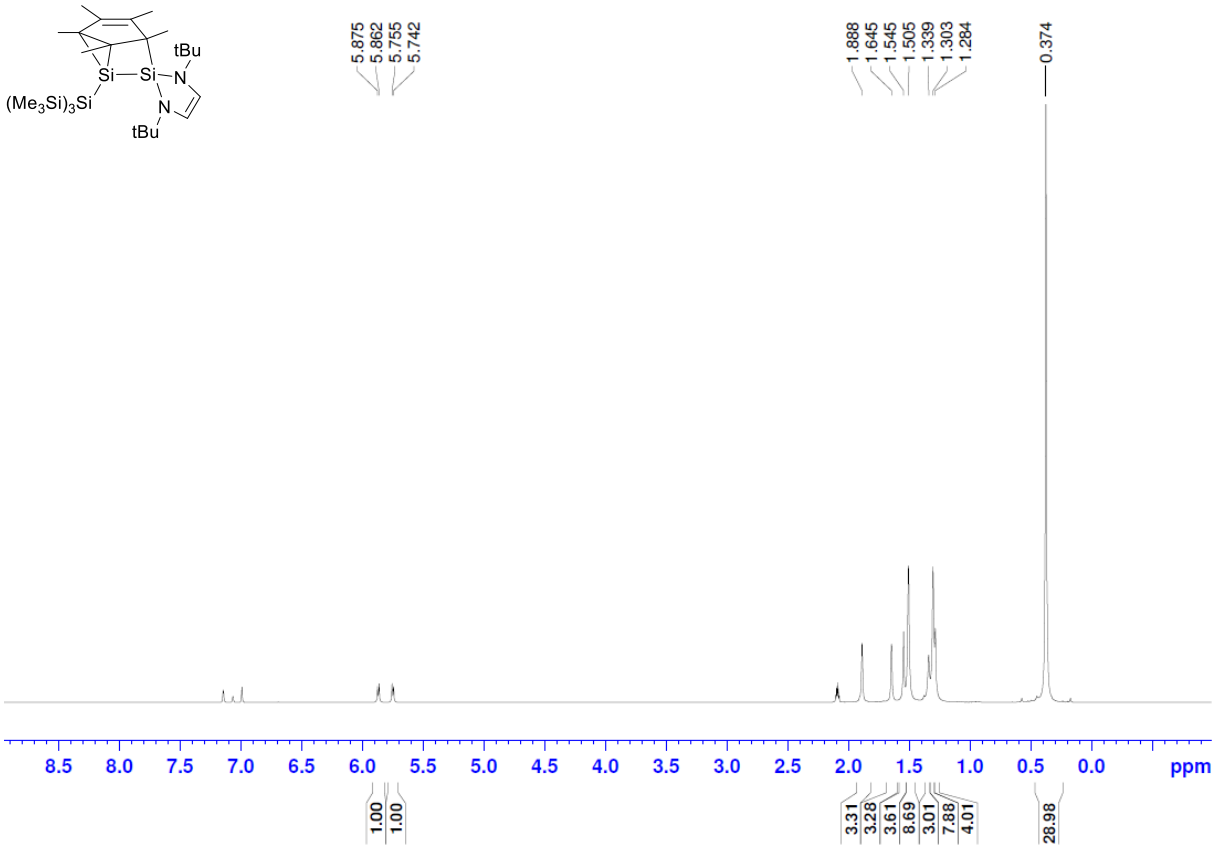

Fig. S43. ^{1}H NMR (300.13 MHz, 223 K, toluene- d_8) of **7**.

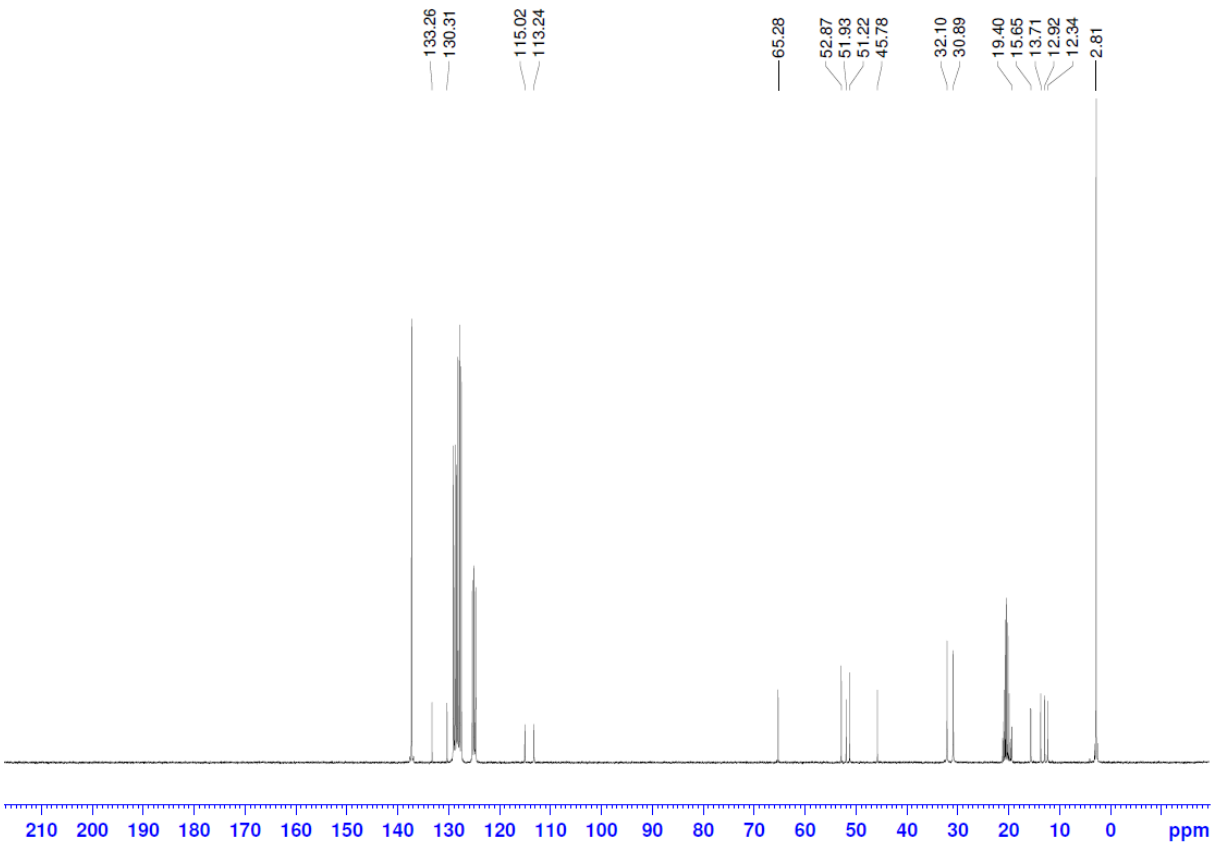

Fig. S44.[13]C NMR (75.47 MHz, 223 K, toluene- d_8) of **7**.

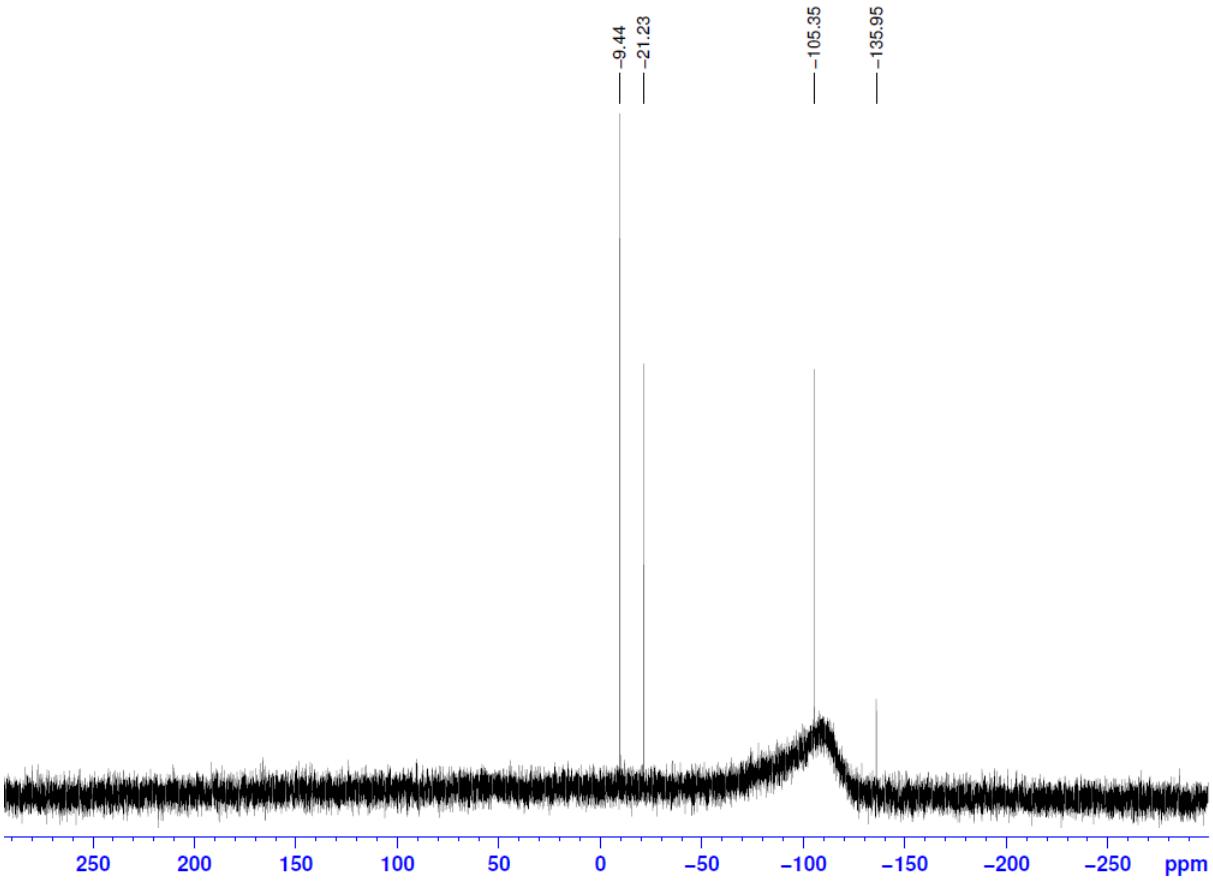

Fig. S45. [29]Si{[1]H} NMR (59.63 MHz, 223 K, toluene-d_8) of **7**.

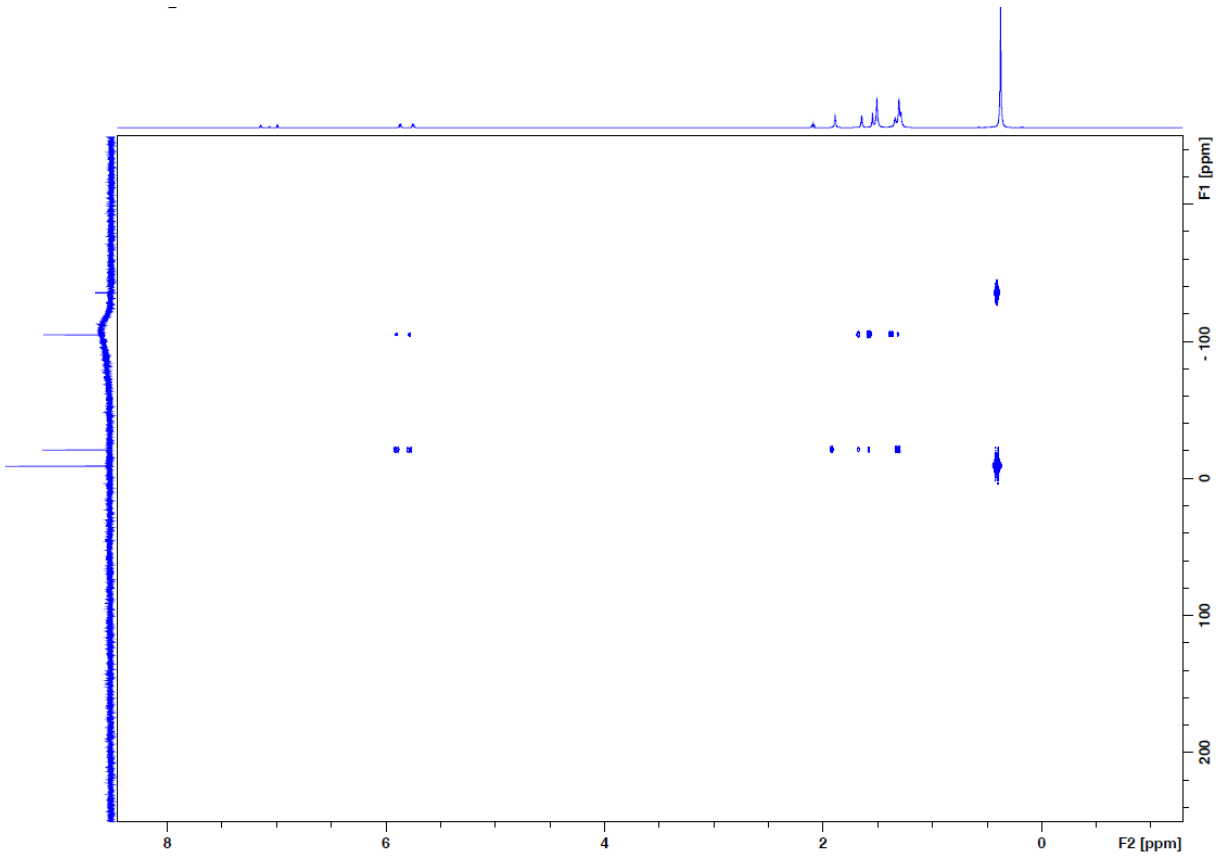

Fig. S46. $^{1}H/^{29}Si$ 2D NMR (223 K, toluene-d_8) of compound **7**.

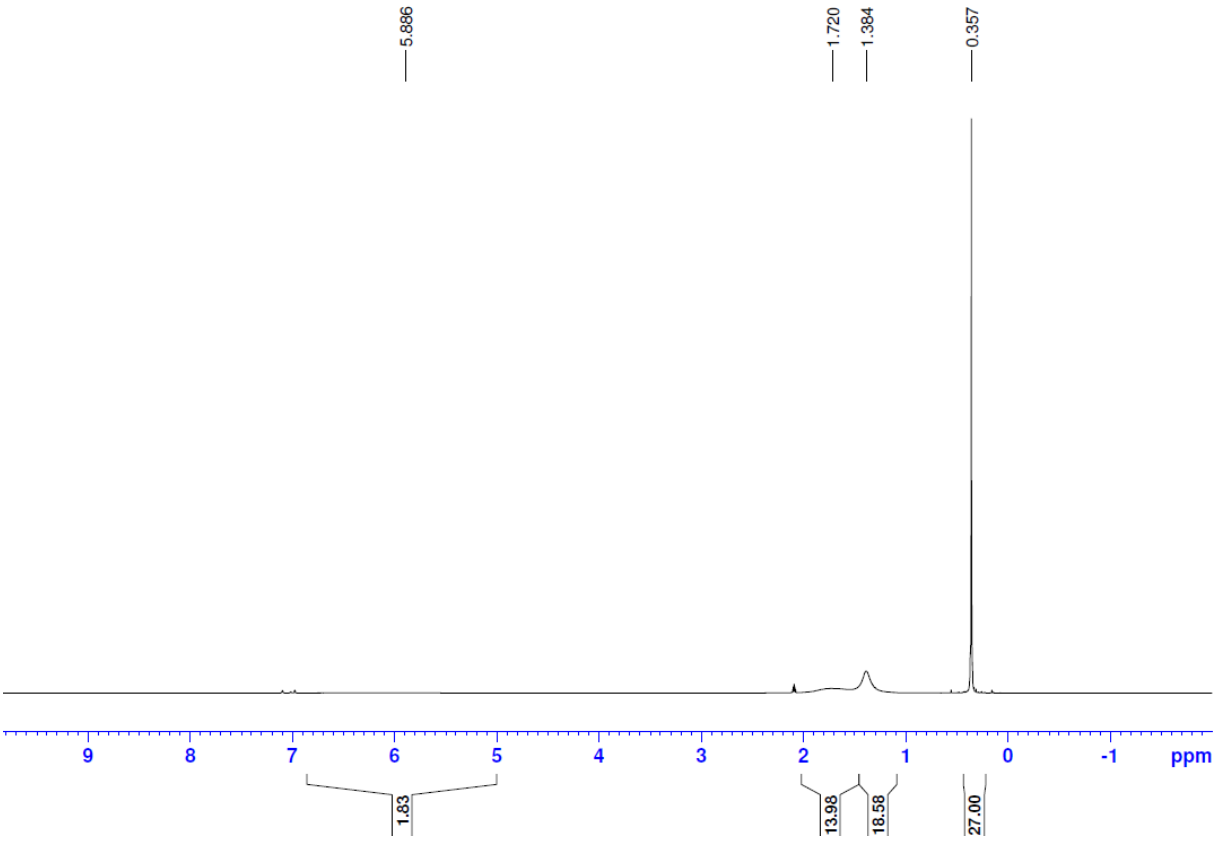

Fig. S47. ^{1}H NMR (300.13 MHz, 300 K, toluene-d_8) of compound **7**.

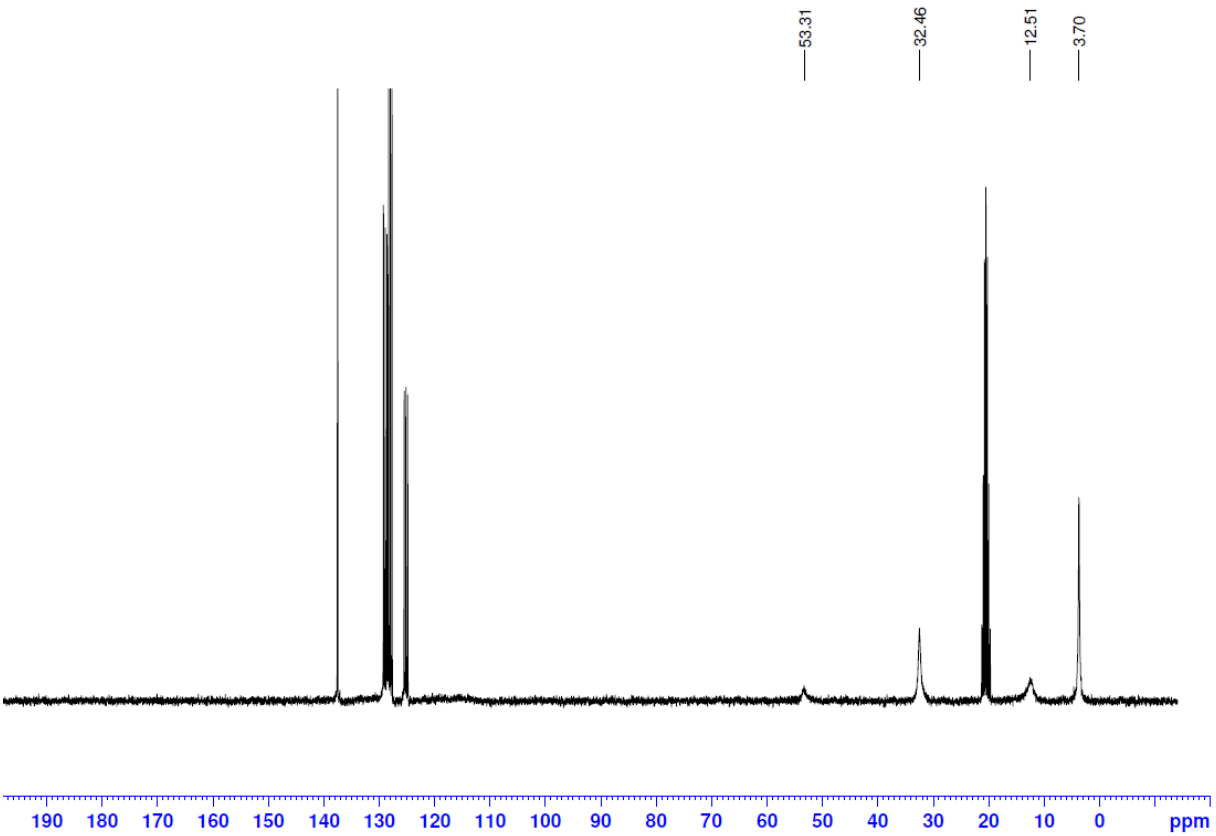

Fig. S48. $^{13}C\{^{1}H\}$ NMR (75.47 MHz, 300 K, toluene-d_8) of compound **7**.

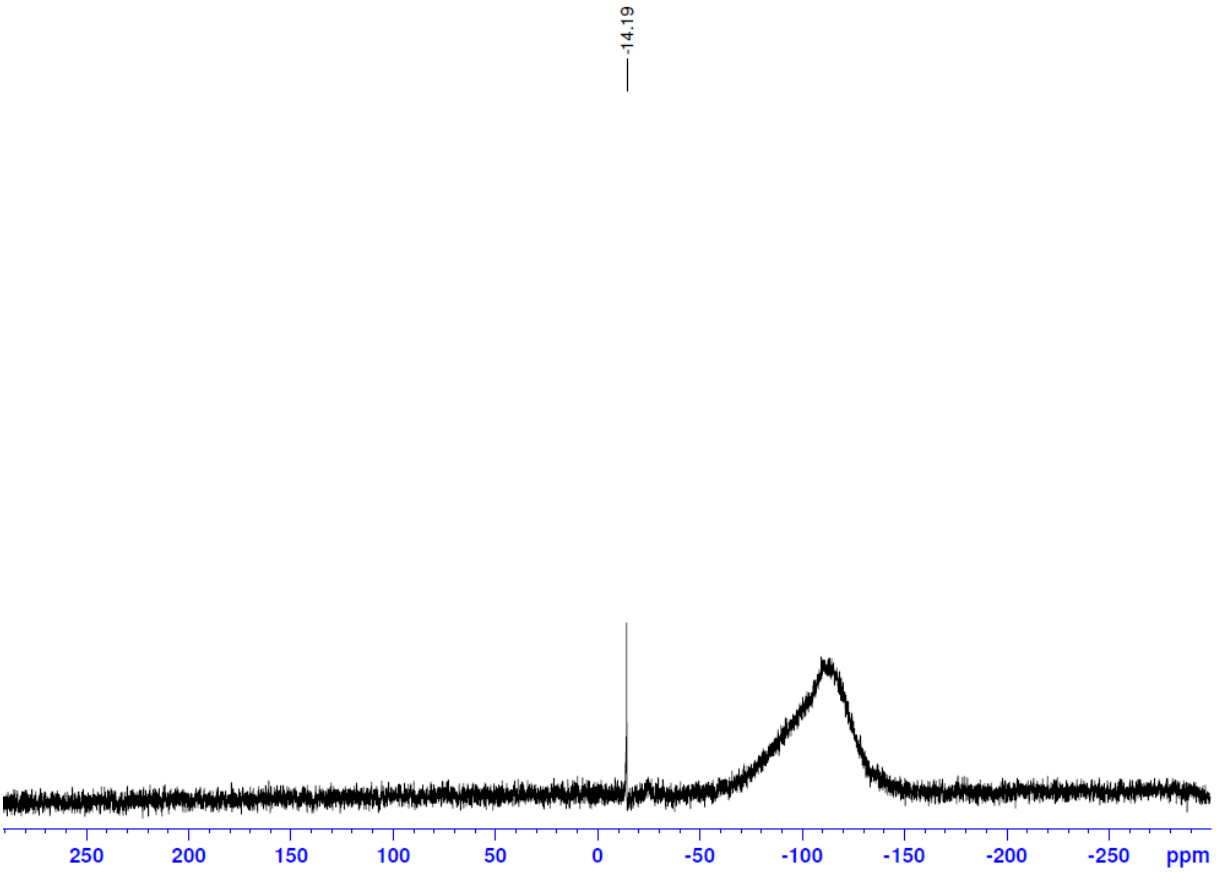

Fig. S49. $^{29}Si\{^{1}H\}$ NMR (59.63 MHz, 300 K, toluene- d_8) of **7**.

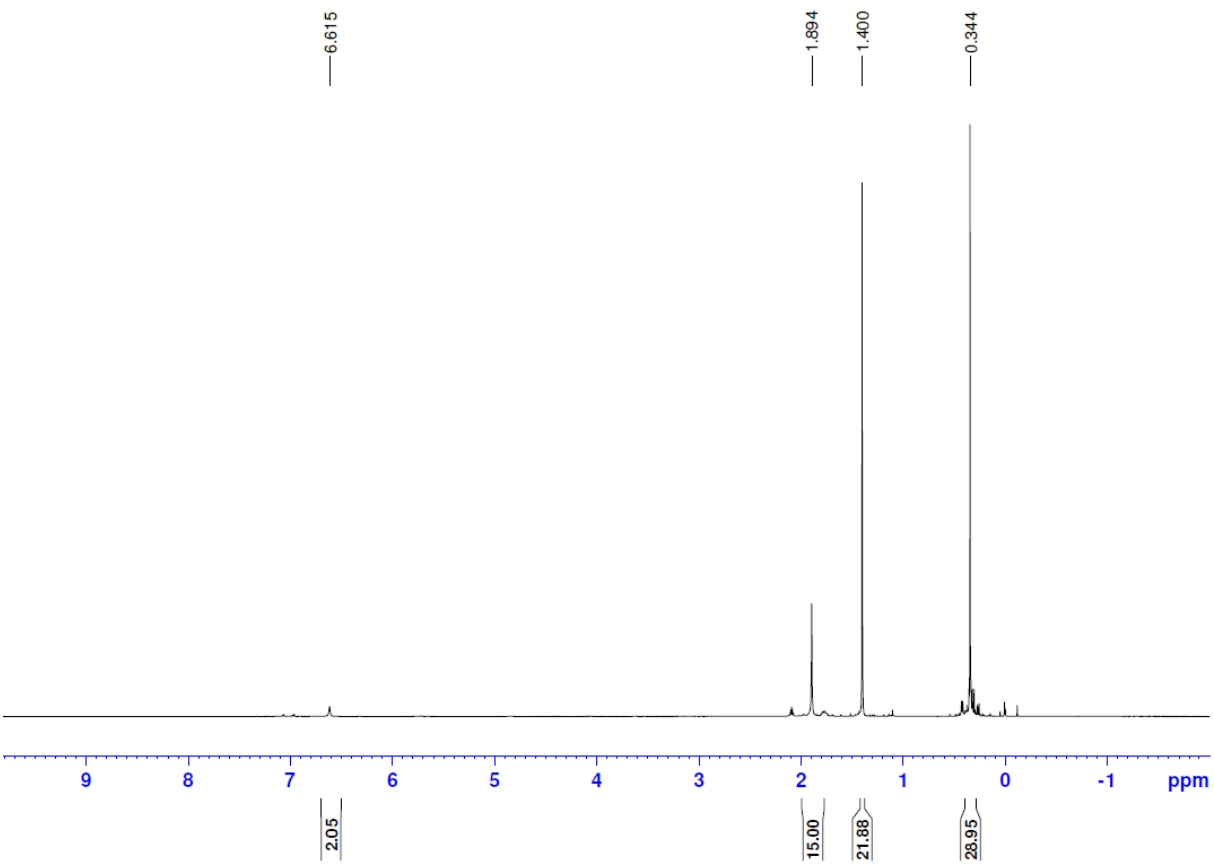

Fig. S50. ^{1}H NMR (300.13 MHz, 333 K, toluene-d_8) of **7**.

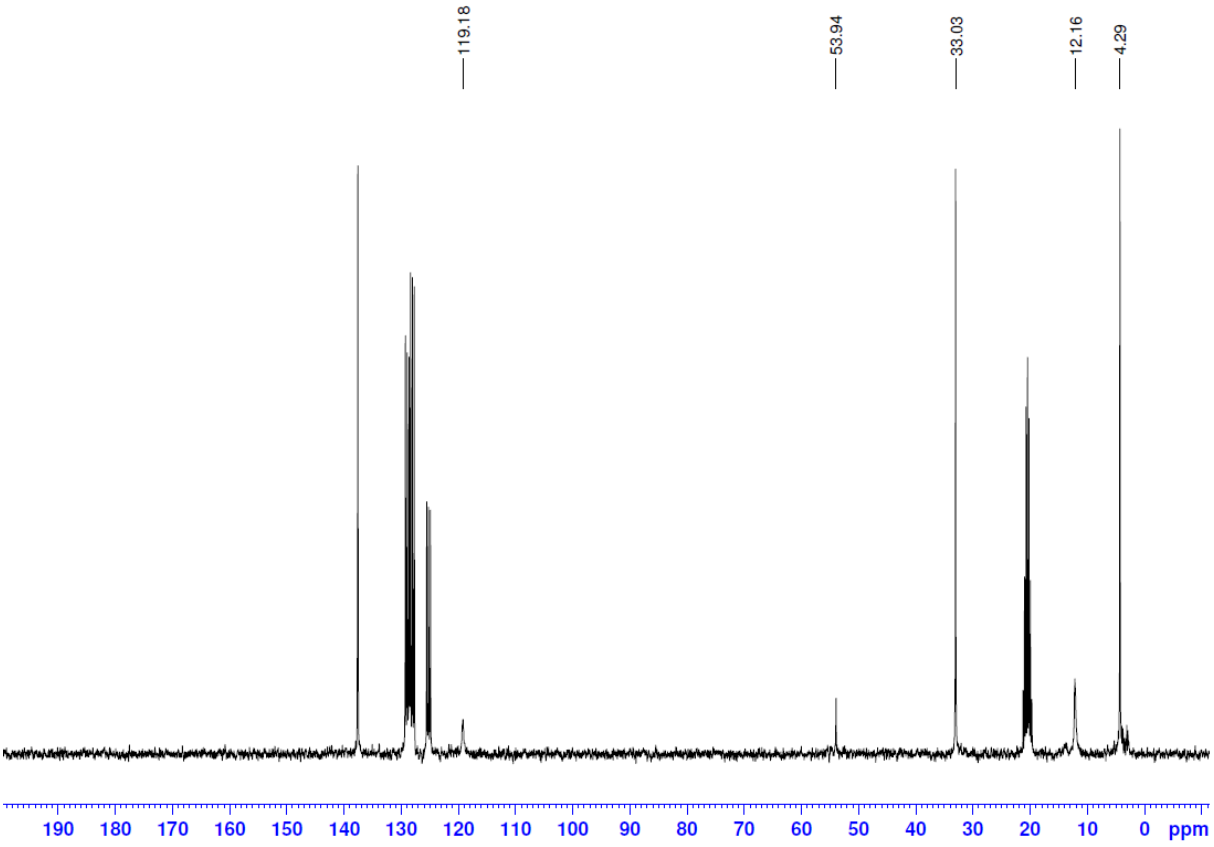

Fig. S51. ^{13}C{^{1}H} NMR (75.47 MHz, 300 K, toluene- d_8) of **7**.

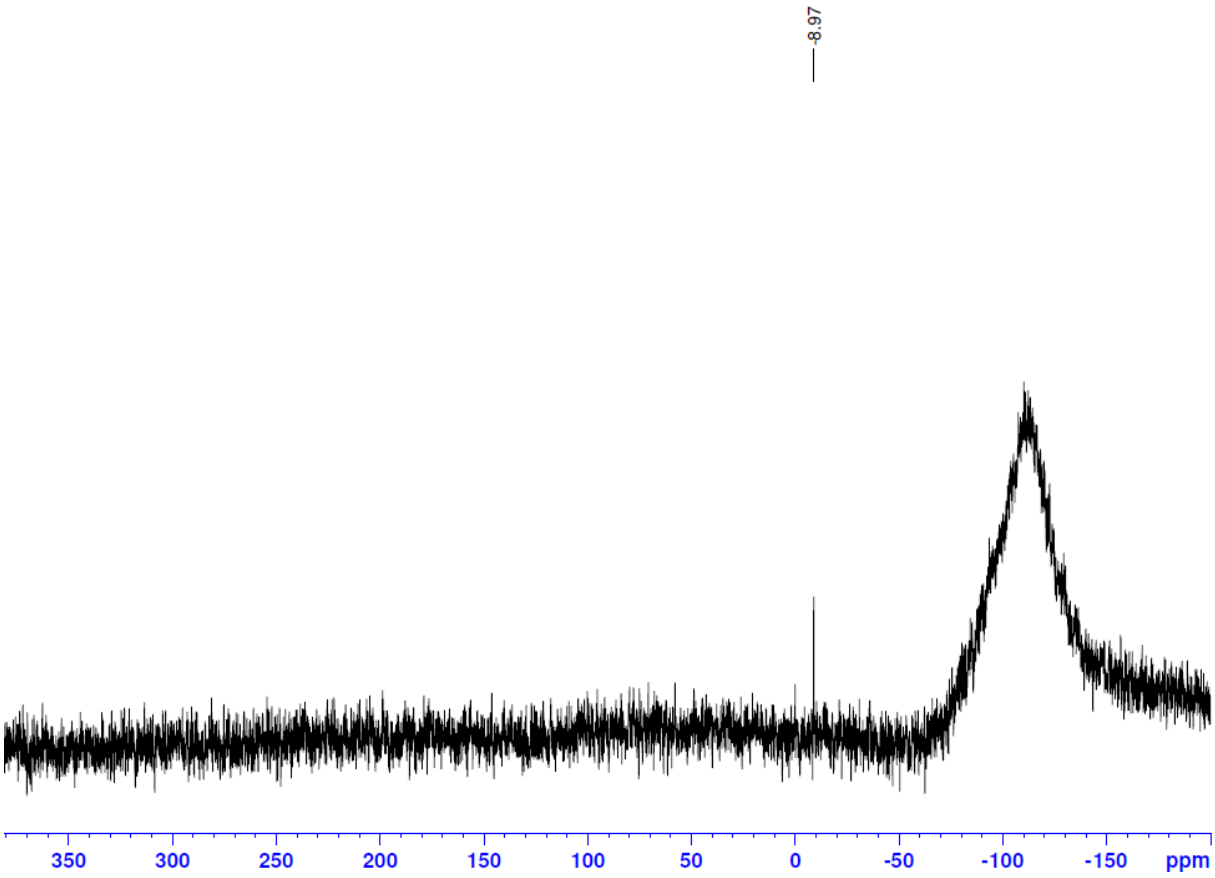

Fig. S52. $^{29}Si\{^{1}H\}$ NMR (59.63 MHz, 333 K, toluene- d_8) of **7**.

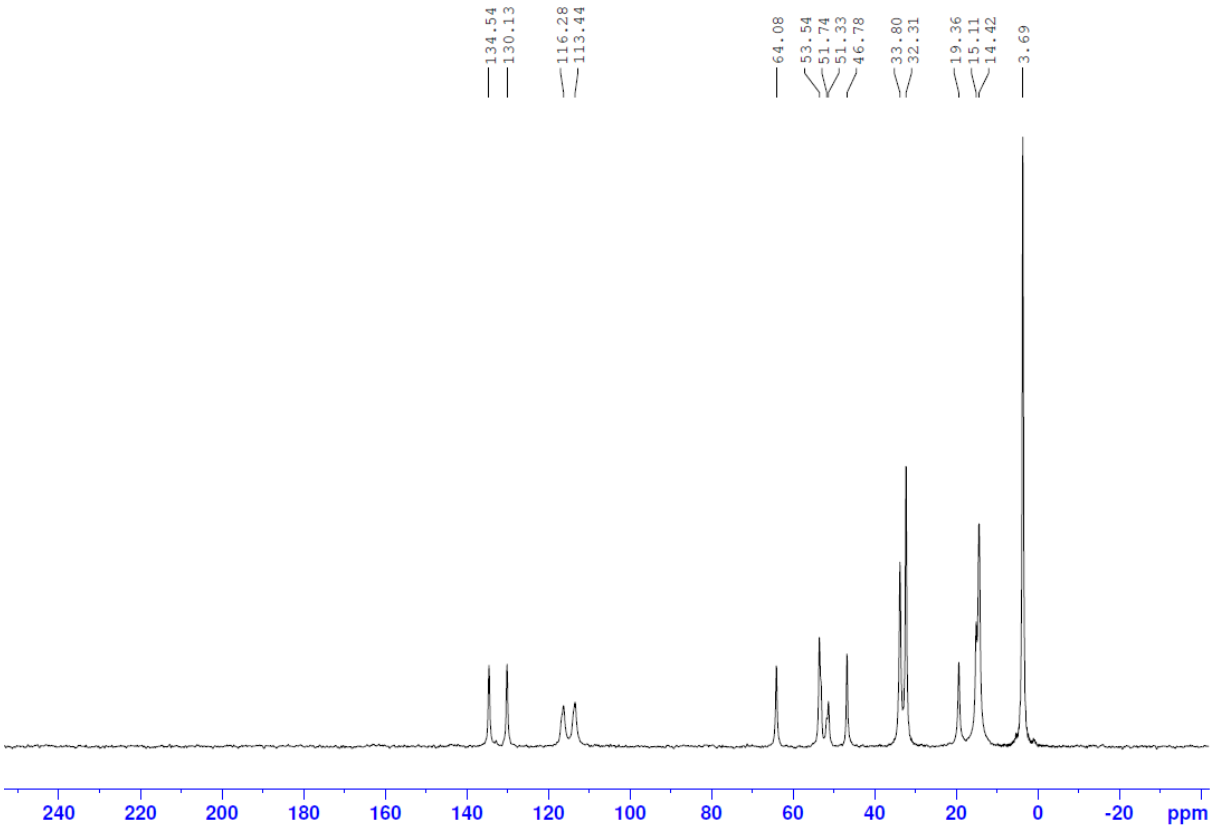

Fig. S53. ^{13}C CP-MAS/NMR (100.65 MHz, 13 kHz, 300K) of **7**.

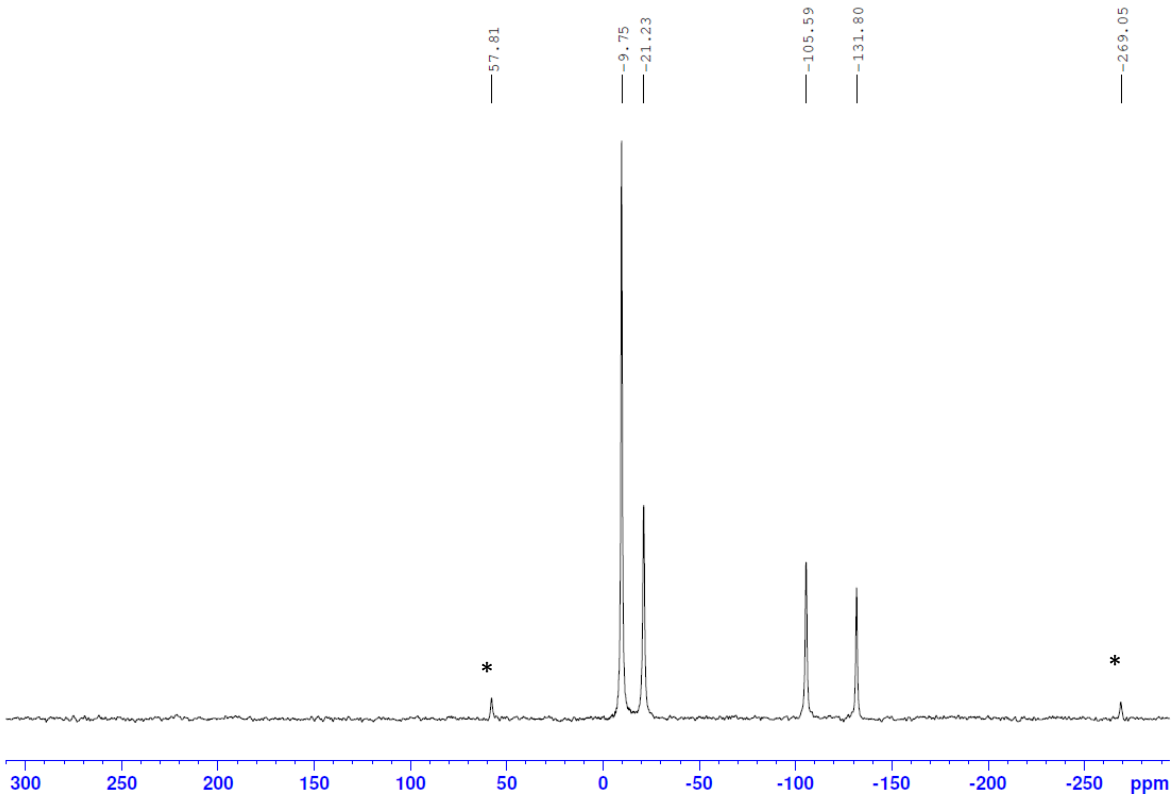

Fig. S54. ^{29}Si CP-MAS/NMR (79.53 MHz, 13 kHz, 300 K) **7**. * side bands.

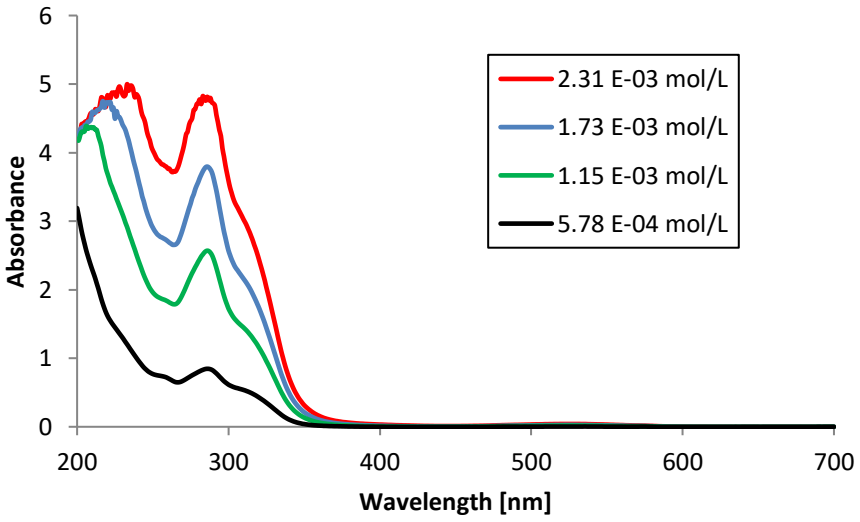

Fig. S55. UV/Vis of dissolved crystals of **7** in hexane at RT.

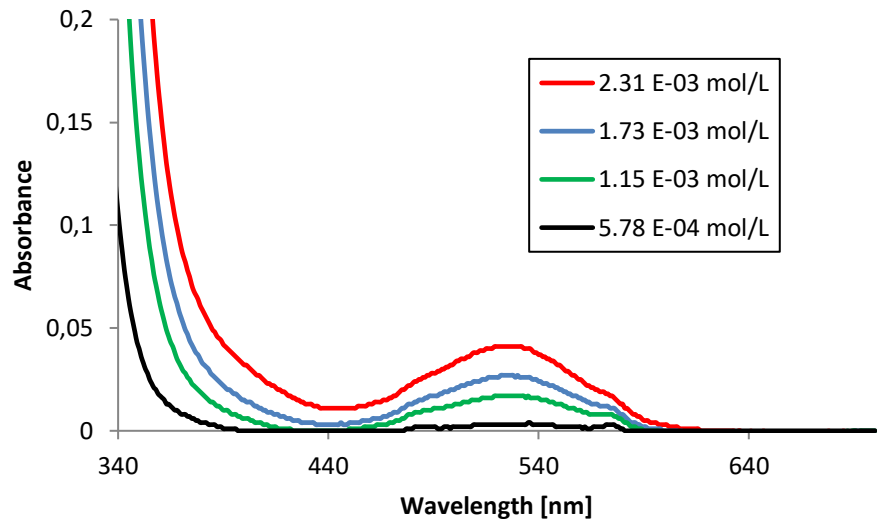

Fig. S56. UV/Vis of dissolved crystals of **7** in hexane at RT.

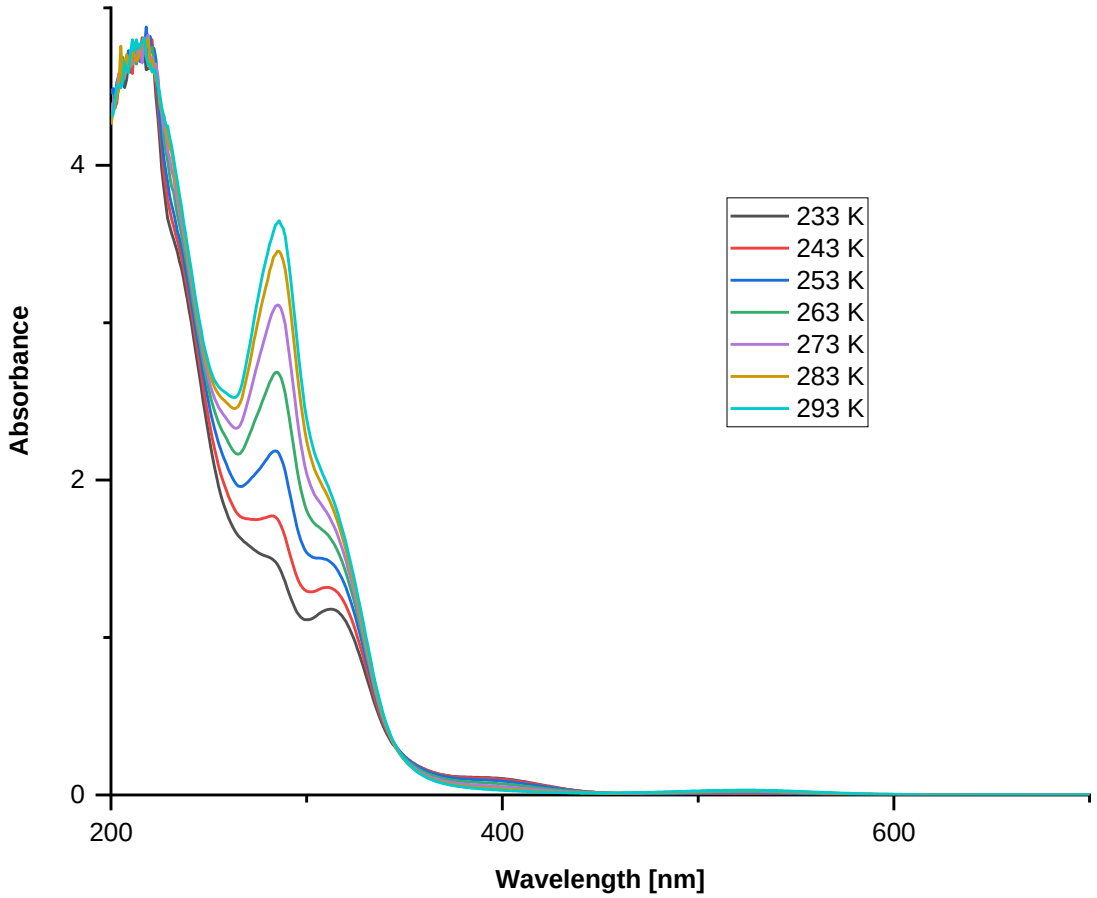

Fig. S57. VT UV/Vis spectra of dissolved crystals of **7** in hexane, concentration $1.50*10^{-3}$mol/L.

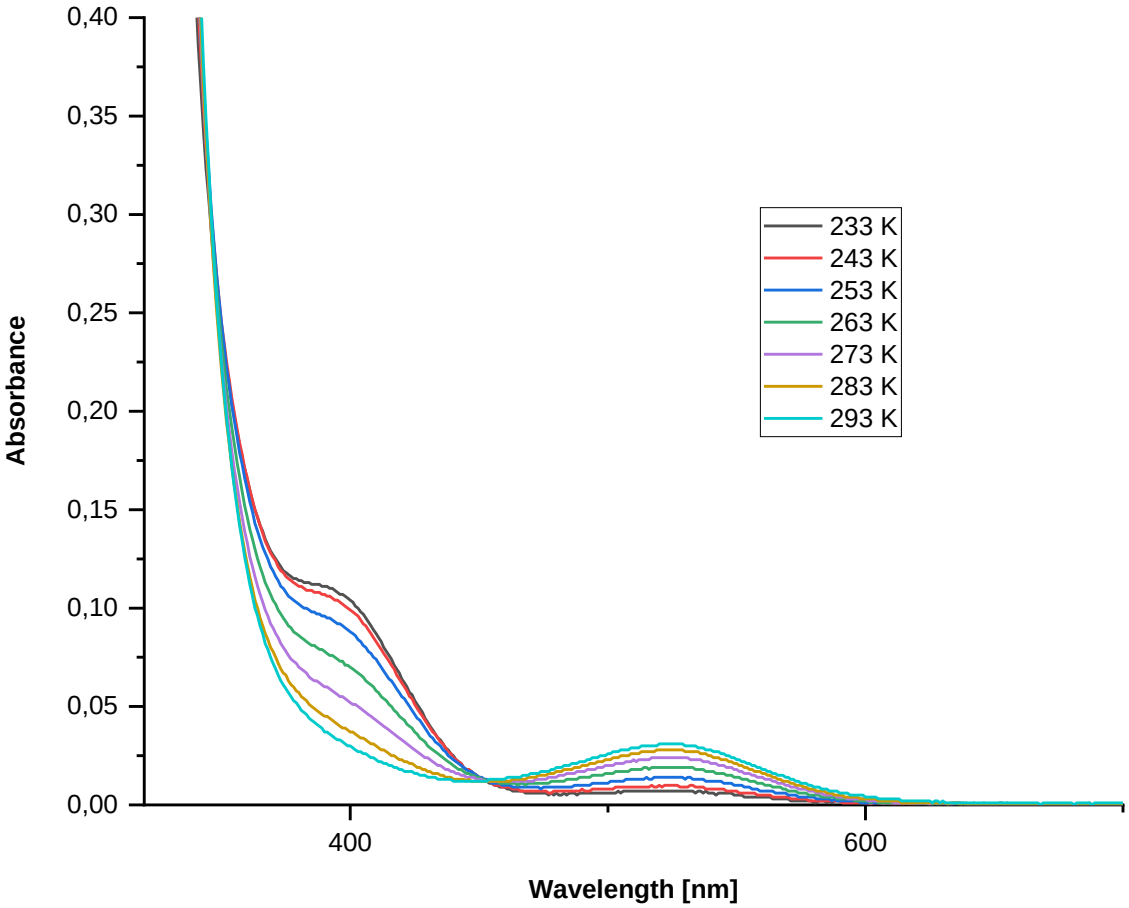

Fig. S58. VT UV/Vis spectra of dissolved crystals of **7** in hexane, concentration 1.50*10^{-3}mol/L.

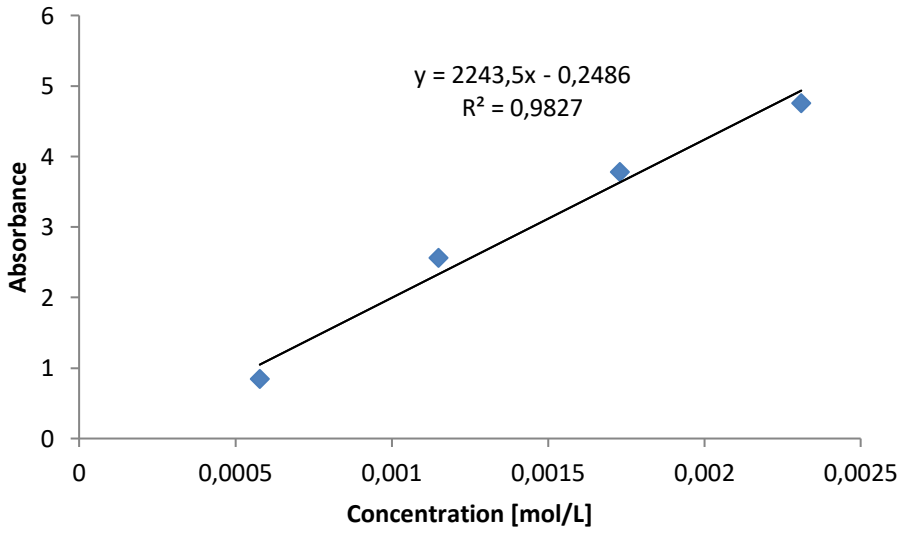

Fig. S59. Extinction coefficient ε =22435 M^{-1}cm^{-1} (λ = 285 nm) for **7** dissolved in hexane.

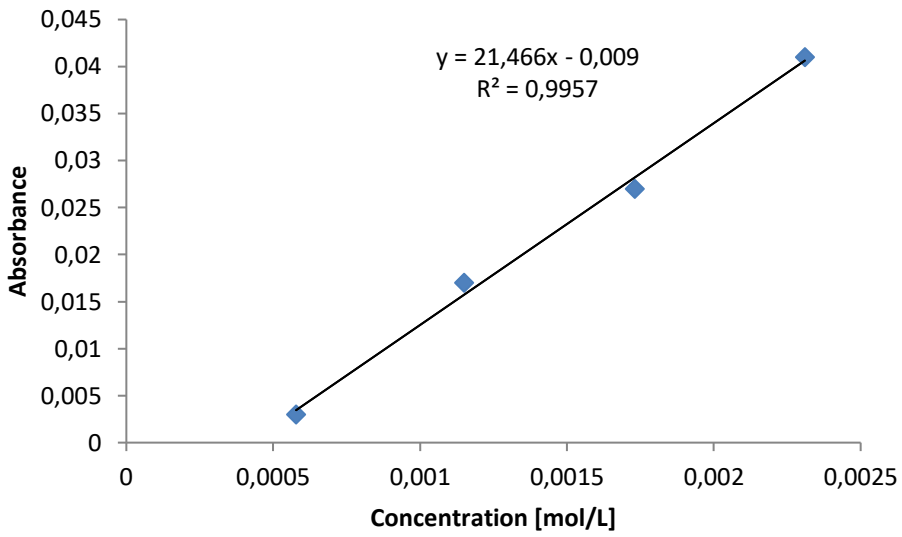

Fig. S60.Extinction coefficient ε =215 $M^{-1}cm^{-1}$ (λ = 525 nm) for **7** dissolved in hexane.

Details on X-ray diffraction studies

Table S1. Crystal data and structure refinement for (hypersilyl)(pentamethylcyclopentadienyl)silylene **2** (CCDC: 2002462).

Identification code	sh3832	
Empirical formula	C19 H42 Si5	
Formula weight	410.97	
Temperature	152(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.0809(7) Å	α = 89.447(2)°.
	b = 9.9667(9) Å	β = 89.918(2)°.
	c = 14.8247(13) Å	γ = 87.141(2)°.
Volume	1340.0(2) $Å^3$	
Z	2	
Density (calculated)	1.019 Mg/m^3	
Absorption coefficient	0.268 mm^{-1}	
F(000)	452	
Crystal size	0.603 x 0.404 x 0.188 mm^3	
Theta range for data collection	1.374 to 32.651°.	
Index ranges	-13<=h<=13, -15<=k<=15, -22<=l<=22	
Reflections collected	31861	
Independent reflections	9753 [R(int) = 0.0235]	
Completeness to theta = 25.242°	99.4 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7464 and 0.6930
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9753 / 0 / 231
Goodness-of-fit on F^2	1.135
Final R indices [I>2sigma(I)]	R1 = 0.0504, wR2 = 0.1361
R indices (all data)	R1 = 0.0593, wR2 = 0.1396
Extinction coefficient	n/a
Largest diff. peak and hole	0.690 and -0.307 e.$Å^{-3}$

Table S2. Crystal data and structure refinement for (hypersilyl)(pentamethylcyclopentadienyl) silirane **3** (CCDC: 2002464).

Identification code	sh4047	
Empirical formula	C21 H46 Si5	
Formula weight	439.03	
Temperature	142(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/m$	
Unit cell dimensions	a = 9.5450(4) Å	α = 90°.
	b = 14.1726(6) Å	β = 103.274(2)°.
	c = 10.4229(4) Å	γ = 90°.
Volume	1372.31(10) $Å^3$	
Z	2	
Density (calculated)	1.062 Mg/m^3	
Absorption coefficient	0.265 mm^{-1}	
F(000)	484	
Crystal size	0.449 x 0.341 x 0.210 mm^3	
Theta range for data collection	2.008 to 34.279°.	
Index ranges	-12<=h<=15, -22<=k<=18, -16<=l<=16	
Reflections collected	22047	
Independent reflections	5843 [R(int) = 0.0205]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7467 and 0.7229	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5843 / 0 / 221	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0269, wR2 = 0.0743	

R indices (all data)	R1 = 0.0349, wR2 = 0.0790
Extinction coefficient	n/a
Largest diff. peak and hole	0.453 and -0.253 e.Å^{-3}

Table S3. Crystal data and structure refinement for **6** (CCDC: 2002463)

Identification code	sh3854	
Empirical formula	C26 H54 N2 Si5	
Formula weight	535.16	
Temperature	142(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 40.367(13) Å	α = 90°.
	b = 9.976(3) Å	β = 99.403(19)°.
	c = 16.657(5) Å	γ = 90°.
Volume	6618(4) Å^3	
Z	8	
Density (calculated)	1.074 Mg/m^3	
Absorption coefficient	0.232 mm^{-1}	
F(000)	2352	
Crystal size	0.463 x 0.294 x 0.104 mm^3	
Theta range for data collection	2.045 to 33.367°.	
Index ranges	-62<=h<=59, -15<=k<=15, -25<=l<=25	
Reflections collected	91027	
Independent reflections	12649 [R(int) = 0.0481]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7465 and 0.6931	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12649 / 0 / 514	
Goodness-of-fit on F^2	1.019	
Final R indices [I>2sigma(I)]	R1 = 0.0329, wR2 = 0.0830	
R indices (all data)	R1 = 0.0505, wR2 = 0.0920	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.415 and -0.245 e.Å^{-3}	

Table S4. Crystal data and structure refinement for **7** (CCDC: 2002465).

Identification code	sh4217

Empirical formula	C29 H62 N2 Si6	
Formula weight	607.34	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.7576(4) Å	a= 90°.
	b = 34.3258(13) Å	b= 111.6700(10)°.
	c = 11.0315(4) Å	g = 90°.
Volume	3785.6(2) $Å^3$	
Z	4	
Density (calculated)	1.066 Mg/m^3	
Absorption coefficient	0.240 mm^{-1}	
F(000)	1336	
Crystal size	0.355 x 0.305 x 0.206 mm^3	
Theta range for data collection	2.122 to 35.694°.	
Index ranges	-17<=h<=16, -56<=k<=56, -18<=l<=18	
Reflections collected	116316	
Independent reflections	17503 [R(int) = 0.0413]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7470 and 0.7070	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	17503 / 75 / 582	
Goodness-of-fit on F^2	1.209	
Final R indices [I>2sigma(I)]	R1 = 0.0742, wR2 = 0.1632	
R indices (all data)	R1 = 0.0869, wR2 = 0.1683	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.495 and -0.671 $e.Å^{-3}$	

Computational part

Computational Details

All structures were optimized with the program package TURBOMOLE[S5] (version 7.2) at the B3-LYP level of theory[S6] including Grimme's dispersion correction[S7] (DFTD3 with BJ-damping) using a def-TZVP basis set[S8]. For more refined reactions thermodynamics (and kinetics, as well as for calculation of singlet-triplet-gaps), the same DFT method with the larger def2-TZVPD basis set[S9] was used. The same larger basis set was also used for computing electronic excitation spectra with TD-DFT, for deriving NBO partial charges and for obtaining orbital energies. Thermodynamic functions were computed assuming a gas phase at 25°C and 1 bar and applying the usual approximations for statistic thermodynamics (rigid rotor, harmonic oscillator).

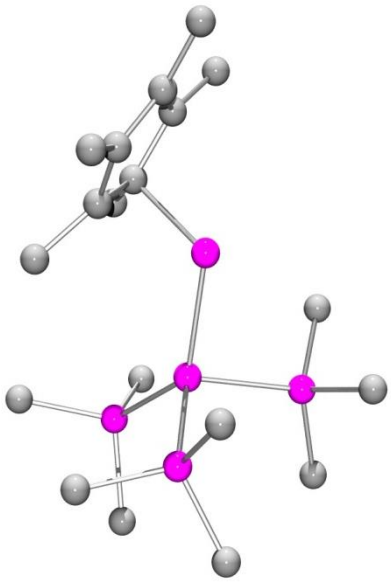

Fig. S61.Calculated structure of Cp*[$(Me_3Si)_3Si$]Si: **2'**.

Table 5. Coordinates of Cp*[$(Me_3Si)_3Si$]Si: **2'**.

```
66
Energy = -2196.566254722
Si    -0.9367176    1.0324927   -0.9033034
C     -2.9203429   -0.6931722   -1.4525603
C     -1.5466427   -0.8194506   -1.8453735
C     -1.3018477    0.2025453   -2.8517893
C     -2.5377615    0.9130005   -3.0283606
C     -3.5144414    0.3511935   -2.1859537
C     -3.5894937   -1.5278349   -0.4109212
H     -4.3176929   -0.9513078    0.1613265
H     -4.1269169   -2.3635050   -0.8718746
H     -2.8686691   -1.9497837    0.2893386
C     -4.9091604    0.8637375   -2.0006636
H     -5.2504443    0.7315993   -0.9722110
```

H	-4.9781839	1.9274998	-2.2341229
H	-5.6224498	0.3432567	-2.6478236
C	-0.6896417	-2.0261887	-1.5968941
H	0.3675251	-1.7951588	-1.6935897
H	-0.8449022	-2.4280235	-0.5945348
H	-0.9259996	-2.8214446	-2.3113889
C	-2.7272806	2.0680606	-3.9555602
H	-3.4063751	2.8138205	-3.5393403
H	-1.7812526	2.5612027	-4.1790214
H	-3.1561378	1.7335374	-4.9062740
C	-0.1702528	0.2060698	-3.8374910
H	0.1136533	1.2182041	-4.1297297
H	0.7123319	-0.2724041	-3.4233708
H	-0.4504062	-0.3366389	-4.7464412
Si	1.4804078	0.8268924	-0.5566635
Si	1.6366562	-0.0674257	1.6248685
Si	1.9313686	3.1392753	-0.3638170
Si	3.2604149	-0.0858595	-1.8210190
C	3.0649700	0.6963474	2.6198157
H	4.0229341	0.5525635	2.1174713
H	2.9178099	1.7689471	2.7594014
H	3.1281576	0.2343340	3.6095732
C	0.0223819	0.2379325	2.5816356
H	0.1020366	-0.1516038	3.6008216
H	-0.2085741	1.3030538	2.6422506
H	-0.8245519	-0.2532483	2.0968061
C	1.9172441	-1.9474652	1.5359809
H	1.9421168	-2.3795912	2.5405510
H	1.1185639	-2.4397590	0.9775088
H	2.8630614	-2.1871434	1.0457406
C	3.7710139	3.5365834	-0.0957120
H	4.1505944	3.0588243	0.8092154
H	4.3816174	3.1992353	-0.9353519
H	3.9111881	4.6166203	0.0072405
C	1.3618851	3.9916533	-1.9681513
H	1.5564745	5.0673438	-1.9333935
H	1.8793724	3.5820646	-2.8381221
H	0.2884341	3.8494162	-2.1185722
C	0.9447343	3.8843800	1.0798578
H	1.0885248	4.9679493	1.1236603
H	-0.1233864	3.6879322	0.9652417
H	1.2617691	3.4651071	2.0368005
C	4.8306149	-0.1087556	-0.7468535
H	5.0637945	0.8809494	-0.3531581
H	4.7212180	-0.7892648	0.0995645
H	5.6845569	-0.4481042	-1.3408631
C	2.9885489	-1.8778775	-2.4036343
H	3.9112132	-2.2498669	-2.8588169
H	2.7402708	-2.5355052	-1.5684586
H	2.1963082	-1.9654152	-3.1490269
C	3.6231048	0.9836608	-3.3512290
H	4.4618632	0.5644423	-3.9145145
H	2.7626059	1.0392334	-4.0198848
H	3.8895042	2.0028762	-3.0650849

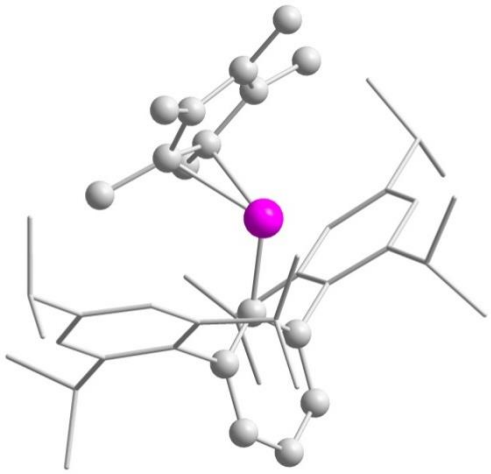

Fig. S62. Calculated structure of Cp*[$Tip_2(C_6H_3)$]Si: **1b'**.

Table S6. Coordinates of Cp*[$Tip_2(C_6H_3)$]Si: **1b'**.

```
111
Energy = -2080.526532292
Si    -1.2122395    -4.8799127     4.1486884
C     -3.3508002    -6.3686236     3.4452223
C     -2.0223599    -6.5305361     2.9298495
C     -1.7469888    -5.3815197     2.0893275
C     -2.9097669    -4.5458533     2.1346121
C     -3.8788045    -5.1636083     2.9531436
C     -4.0039911    -7.3260935     4.3883649
H     -4.7641085    -6.8401115     5.0006696
H     -4.4908818    -8.1430008     3.8445063
H     -3.2707580    -7.7750439     5.0583191
C     -5.1816648    -4.5368381     3.3465426
H     -5.8593686    -5.2663384     3.7901699
H     -5.0342980    -3.7350987     4.0779753
H     -5.6900002    -4.0994606     2.4842080
C     -1.2722547    -7.8223124     2.8667476
H     -0.2088553    -7.6498305     2.7207296
H     -1.3866669    -8.4063854     3.7768524
H     -1.6293051    -8.4293394     2.0267177
C     -3.0518038    -3.2260181     1.4500331
H     -3.6055039    -2.5122562     2.0629298
H     -2.0805615    -2.7877024     1.2285025
H     -3.5958188    -3.3346036     0.5050216
C     -0.6805578    -5.3401399     1.0420935
H     -0.4777005    -4.3217951     0.7197136
H      0.2541809    -5.7616577     1.4081074
H     -0.9869103    -5.9200170     0.1641827
C      0.7466929    -4.9946168     4.4021463
C      1.5215587    -3.8589485     4.0681543
C      2.7133813    -3.5878770     4.7406500
C      3.1752561    -4.4302909     5.7407646
```

C	2.4491831	-5.5687468	6.0560588
C	1.2537288	-5.8608855	5.3994877
C	1.0809053	-2.8880709	3.0128677
H	3.2698370	-2.6946233	4.4862722
H	4.0912888	-4.2001155	6.2712927
H	2.7992614	-6.2360086	6.8337077
C	0.5267452	-7.1118696	5.7917295
C	-0.5427833	-7.0575732	6.7086519
C	-1.2122878	-8.2345477	7.0367828
C	-0.8278773	-9.4692632	6.5215622
C	0.2655299	-9.5081710	5.6647163
C	0.9495088	-8.3548800	5.2821544
C	1.6103226	-2.9760565	1.7069257
C	1.2003584	-2.0531870	0.7492237
C	0.2873039	-1.0416558	1.0405818
C	-0.1962414	-0.9522525	2.3389674
C	0.1919520	-1.8466394	3.3380990
H	-2.0421690	-8.1880876	7.7301151
H	0.5796965	-10.4673732	5.2711199
H	1.6006884	-2.1263009	-0.2534924
H	-0.8897161	-0.1562979	2.5809487
C	-0.2685928	-1.6119021	4.7700231
H	-0.1268025	-2.5400992	5.3238264
C	2.6594340	-4.0209698	1.3452611
H	2.5285241	-4.8637333	2.0270420
C	-0.1614622	-0.0581614	-0.0232592
H	-0.8679676	0.6281652	0.4542660
C	-0.8928256	-5.7678824	7.4383755
H	-0.5208169	-4.9331298	6.8434287
C	2.1559318	-8.4692873	4.3592508
H	2.3098711	-7.4909839	3.8999027
C	-1.5759545	-10.7388405	6.8794333
H	-1.0559645	-11.5654296	6.3851507
C	3.4207030	-8.8128551	5.1646424
H	3.6209469	-8.0696096	5.9346174
H	3.3071236	-9.7836955	5.6539119
H	4.2925590	-8.8640408	4.5073162
C	1.9834925	-9.4936363	3.2297268
H	2.8271448	-9.4250967	2.5393319
H	1.9637769	-10.5161861	3.6127935
H	1.0679442	-9.3315943	2.6626022
C	-0.1559474	-5.7245506	8.7870952
H	-0.4809561	-6.5459328	9.4305935
H	0.9223841	-5.8114911	8.6472692
H	-0.3583903	-4.7838423	9.3054374
C	-2.3963754	-5.5519982	7.6299472
H	-2.5761230	-4.5672532	8.0668132
H	-2.9214914	-5.5955933	6.6759549
H	-2.8328854	-6.2917918	8.3049444
C	-3.0149772	-10.7095266	6.3460111
H	-3.5887101	-9.9056269	6.8130984
H	-3.0307368	-10.5460955	5.2667710
H	-3.5260258	-11.6521433	6.5570455
C	-1.5528393	-11.0120115	8.3890827
H	-2.0380029	-11.9645151	8.6161205

H	-0.5288307	-11.0498193	8.7652645
H	-2.0818284	-10.2300387	8.9388750
C	-1.7497473	-1.2388067	4.8829846
H	-1.9602431	-0.2625779	4.4404795
H	-2.3756237	-1.9867412	4.3953306
H	-2.0413377	-1.1905109	5.9344171
C	0.6183169	-0.5470326	5.4349659
H	0.3265187	-0.4018670	6.4782118
H	1.6684780	-0.8414028	5.4126425
H	0.5254975	0.4115971	4.9183652
C	2.5488707	-4.5531613	-0.0898373
H	1.5424630	-4.8910985	-0.3303771
H	2.8335234	-3.7945277	-0.8224001
H	3.2304124	-5.3963957	-0.2212582
C	4.0762796	-3.4604577	1.5597704
H	4.8272488	-4.2164598	1.3167496
H	4.2422021	-2.5959670	0.9119912
H	4.2353893	-3.1459813	2.5892577
C	1.0120575	0.7767042	-0.5533297
H	1.7420416	0.1459405	-1.0663881
H	0.6621457	1.5279074	-1.2656541
H	1.5275636	1.2888851	0.2611143
C	-0.8995057	-0.7614104	-1.1710860
H	-1.2520423	-0.0337118	-1.9059246
H	-0.2420376	-1.4654063	-1.6869695
H	-1.7613911	-1.3197623	-0.8018083

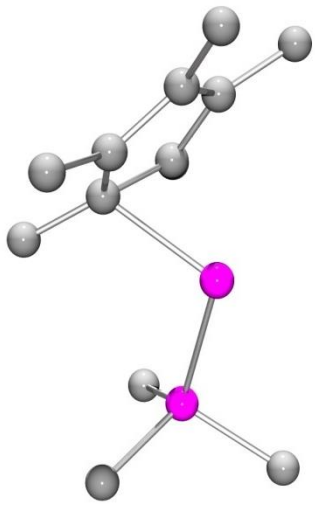

Fig. S63. Calculated structure of Cp*(TMS)Si: **1g'**.

Table S7. Coordinates of Cp*(TMS)Si: **1g'**.

39
Energy = -1088.631253927

Si	-1.1840408	1.3753210	-0.8138223
C	-2.9150702	-0.5781073	-1.3503649
C	-1.5076273	-0.5823729	-1.6310264
C	-1.2971571	0.3628169	-2.7187548
C	-2.5918673	0.8762366	-3.0751122

C	-3.5620847	0.2885425	-2.2525636
C	-3.5800305	-1.3678527	-0.2705209
H	-4.3310770	-0.7766478	0.2557683
H	-4.0892616	-2.2411261	-0.6921760
H	-2.8601676	-1.7291493	0.4632657
C	-5.0085070	0.6720609	-2.2033968
H	-5.6288159	-0.1492081	-1.8403374
H	-5.1711301	1.5262614	-1.5363389
H	-5.3802993	0.9524623	-3.1903081
C	-0.5698675	-1.6901166	-1.2426385
H	0.4694297	-1.4127927	-1.4030066
H	-0.6765546	-1.9653008	-0.1924223
H	-0.7691289	-2.5852472	-1.8408832
C	-2.8476597	1.9140767	-4.1189227
H	-3.5351783	2.6828442	-3.7609760
H	-1.9261182	2.4043781	-4.4313954
H	-3.2996387	1.4631846	-5.0087070
C	-0.0927529	0.4003437	-3.6170821
H	0.0982865	1.4037181	-4.0020780
H	0.8049081	0.0757296	-3.0981582
H	-0.2373997	-0.2604482	-4.4779611
Si	1.1571453	1.2520950	-0.0951616
C	1.6002470	3.0463096	0.3805918
H	2.5676391	3.0889055	0.8895260
H	1.6587947	3.6868443	-0.5033545
H	0.8492233	3.4749395	1.0486999
C	2.6018634	0.6210074	-1.1756844
H	3.5386041	0.7286903	-0.6200882
H	2.5015148	-0.4319349	-1.4465782
H	2.6956544	1.1995941	-2.0970964
C	1.1637418	0.2249660	1.5163344
H	2.1198572	0.3334272	2.0367410
H	0.3747743	0.5514314	2.1985355
H	1.0109811	-0.8370125	1.3130543

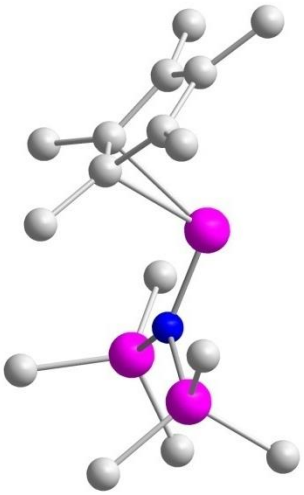

Fig. S64. Calculated structure of Cp*[$(Me_3Si)_2N$]Si: **1a'**.

Table S8. Coordinates of Cp*[$(Me_3Si)_2N$]Si: **1a'**.

```
53
Energy = -1552.688887347
Si    -0.5667112    1.2316177   -0.4530560
C     -2.6617211   -0.2461797   -1.0994229
C     -1.3470588   -0.7103698   -1.3763251
C     -0.8158352    0.1195316   -2.4308212
C     -1.8626932    1.0285553   -2.8264045
C     -2.9673634    0.8111901   -2.0048524
C     -3.6133099   -0.7858147   -0.0813470
H     -4.0036011    0.0039432    0.5652778
H     -4.4739936   -1.2509099   -0.5725641
H     -3.1502369   -1.5373640    0.5556030
C     -4.2405021    1.5997715   -1.9703738
H     -5.1156942    0.9441389   -1.9937043
H     -4.3148616    2.2040501   -1.0608585
H     -4.3180284    2.2753630   -2.8222565
C     -0.6941745   -1.9673840   -0.8920217
H      0.3199892   -1.7805223   -0.5321893
H     -1.2570499   -2.4248847   -0.0793039
H     -0.6286809   -2.7035298   -1.6994048
C     -1.7254139    2.0524520   -3.9081531
H     -2.4021708    2.8941131   -3.7581856
H     -0.7103953    2.4510794   -3.9509583
H     -1.9460568    1.6232448   -4.8916980
C      0.3407601   -0.2725569   -3.3000131
H      0.7184179    0.5677896   -3.8824517
H      1.1695963   -0.6814953   -2.7262043
H      0.0305594   -1.0445639   -4.0130698
N      0.9357003    0.6830710    0.3773467
Si     0.7808495    0.2024909    2.0821392
Si     2.5411449    0.9839198   -0.3076770
C      1.0704194    1.6655248    3.2448497
H      2.0926940    2.0400569    3.2032603
H      0.4001798    2.4882365    2.9828420
H      0.8584809    1.3764577    4.2779775
C     -0.9671874   -0.4278460    2.4314277
H     -1.0501968   -0.6558820    3.4978581
H     -1.7353607    0.3086292    2.1893438
H     -1.1864261   -1.3400037    1.8778981
C      1.9830115   -1.1975573    2.4962489
H      1.8242595   -1.5201633    3.5289530
H      1.8152543   -2.0581646    1.8452927
H      3.0285065   -0.9012451    2.4012716
C      3.7077689    1.8043590    0.9389413
H      3.3112635    2.7620871    1.2803547
H      3.9076956    1.1862918    1.8151585
H      4.6663049    1.9945459    0.4476172
C      3.3778663   -0.6182437   -0.8686649
H      4.3317114   -0.3952012   -1.3549347
H      3.5835489   -1.2641845   -0.0129964
H      2.7683895   -1.1869784   -1.5708057
C      2.3927873    2.2027224   -1.7466395
H      3.3792102    2.3645660   -2.1894919
```

H	1.7260546	1.8644597	-2.5374324
H	2.0272594	3.1678658	-1.3877795

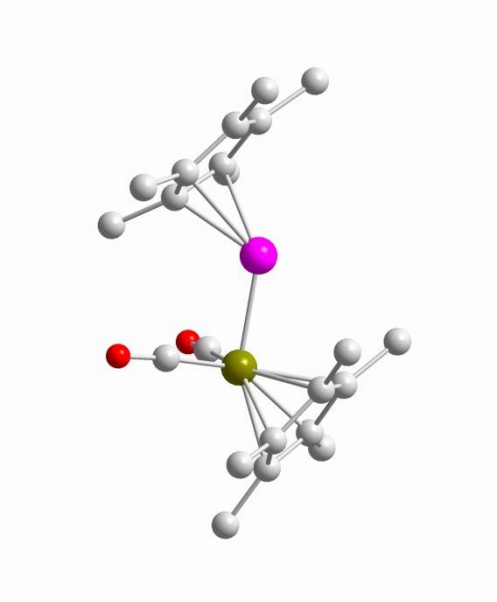

Fig. S65. Calculated structure of Cp*[Cp*$(CO)_2$Fe]Si: **1c'**.

Table S9. Coordinates of Cp*[Cp*$(CO)_2$Fe]Si: **1c'**.

56
Energy = -2559.837637589

Si	-1.1264974	0.8684753	0.2801429
C	-3.6688014	-0.3090262	-0.0385482
C	-3.0468721	-1.0912317	0.9484509
C	-1.7542611	-1.4568314	0.4937119
C	-1.5824986	-0.9195310	-0.8374878
C	-2.7804592	-0.1660761	-1.1353257
C	-4.9892041	0.3778127	0.1123128
H	-5.3919047	0.6933582	-0.8505494
H	-5.7248236	-0.2811500	0.5792947
H	-4.9074723	1.2679686	0.7454045
C	-3.0972915	0.4689137	-2.4548279
H	-3.6872829	1.3789723	-2.3346446
H	-2.1957006	0.7305574	-3.0060562
H	-3.6770604	-0.2173421	-3.0819434
C	-3.6044896	-1.3622399	2.3098141
H	-3.0959422	-2.1955233	2.7951505
H	-3.5073133	-0.4882833	2.9630180
H	-4.6678447	-1.6072092	2.2583767
C	-0.6675063	-1.5035660	-1.8755690
H	-0.4822187	-0.8148356	-2.6969076
H	0.2939956	-1.7970062	-1.4598310
H	-1.1267855	-2.4024141	-2.3008836
C	-0.8091489	-2.4005353	1.1726956
H	0.2115536	-2.2802403	0.8133908
H	-0.7994973	-2.2545499	2.2539391
H	-1.1018895	-3.4393808	0.9845053
Fe	0.9505044	1.7877206	-0.3275158
C	0.4834075	1.6343780	-2.0037866

```
C      1.6481553    0.1939505   -0.1689871
O      2.1866240   -0.8206296   -0.0386508
O      0.2270928    1.6083903   -3.1307629
C      2.5146135    3.2465985   -0.1809760
C      2.3202964    2.6210248    1.0870470
C      1.2891280    3.8880793   -0.5324653
C      0.3517241    3.6932118    0.5354700
C      0.9895123    2.9106110    1.5373074
C      3.7855367    3.2737213   -0.9689953
H      4.4021901    4.1345168   -0.6886584
H      4.3782603    2.3746521   -0.8009991
H      3.5898425    3.3426422   -2.0390031
C      1.0602482    4.7314210   -1.7467182
H      0.0192174    4.7017681   -2.0672026
H      1.3135856    5.7752542   -1.5370632
H      1.6734393    4.4037672   -2.5857262
C     -1.0108907    4.2958516    0.6434396
H     -1.7191444    3.5999974    1.0980837
H     -0.9848029    5.1972945    1.2635977
H     -1.4034258    4.5758949   -0.3340953
C      0.4037233    2.5596873    2.8656833
H     -0.6474911    2.2775127    2.7759236
H      0.9315609    1.7261017    3.3281231
H      0.4620219    3.4131272    3.5486278
C      3.3670079    1.8979052    1.8745357
H      2.9320690    1.1267931    2.5100525
H      4.0976392    1.4162080    1.2252467
H      3.9062811    2.5966025    2.5215044
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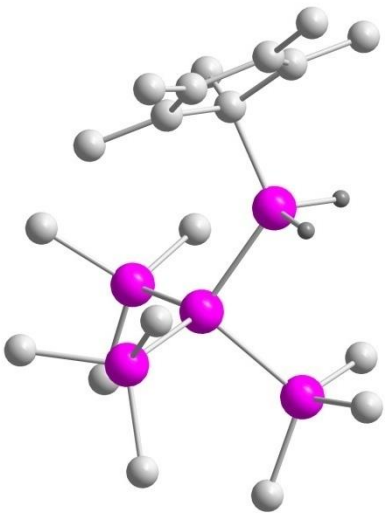

Fig. S66. Calculated structure of Cp*[$(Me_3Si)_3Si$]SiH_2 **4a'**.

Table S10. Coordinates of Cp*[$(Me_3Si)_3Si$]SiH_2 **4a'**.

```
68
Energy = -2197.803293823
Si    -0.4010352    1.5293538   -1.5399469
```

C	-2.9332446	-0.8809571	-1.2338975
C	-1.6367646	-0.9431093	-1.6282575
C	-1.3645194	0.1913498	-2.5760177
C	-2.7181307	0.8250438	-2.7708474
C	-3.6040563	0.2144622	-1.9428871
C	-3.6351303	-1.7596916	-0.2469085
H	-4.0528732	-1.1735210	0.5772802
H	-4.4705762	-2.2924723	-0.7112141
H	-2.9660507	-2.5048859	0.1828742
C	-5.0451159	0.5515820	-1.7239247
H	-5.2255599	0.8551952	-0.6876027
H	-5.3767345	1.3651926	-2.3680265
H	-5.6903797	-0.3109035	-1.9165969
C	-0.6096045	-1.9695736	-1.2859602
H	0.3552374	-1.5158605	-1.0564569
H	-0.9046471	-2.5735822	-0.4279900
H	-0.4379819	-2.6529397	-2.1247862
C	-2.9641144	1.9415356	-3.7330797
H	-4.0076809	2.2553601	-3.7221076
H	-2.3515239	2.8205597	-3.5114124
H	-2.7218307	1.6419059	-4.7582232
C	-0.6147176	-0.1794515	-3.8570546
H	-0.4301915	0.6959811	-4.4823035
H	0.3503650	-0.6367697	-3.6381420
H	-1.1999504	-0.8946598	-4.4413439
Si	1.7074606	1.0705002	-0.5814395
Si	1.4237740	-0.1046137	1.4621081
Si	2.4114529	3.2854804	-0.1103961
Si	3.2642961	0.0963053	-2.0651882
C	2.3702334	0.7485991	2.8712659
H	3.4448611	0.7629554	2.6810133
H	2.0383116	1.7775121	3.0196290
H	2.2020122	0.2044167	3.8052411
C	-0.4129092	-0.1300944	1.9333845
H	-0.5574294	-0.7001090	2.8555238
H	-0.7792789	0.8849109	2.1022784
H	-1.0302876	-0.5726138	1.1517223
C	2.0944899	-1.8800668	1.3655682
H	1.9712734	-2.3730857	2.3342842
H	1.5800951	-2.4799112	0.6155296
H	3.1602653	-1.8792924	1.1264365
C	4.0184528	3.3639756	0.8980113
H	3.8960431	2.9333108	1.8913315
H	4.8319184	2.8350917	0.3992990
H	4.3213300	4.4084001	1.0176495
C	2.7047913	4.2376280	-1.7273688
H	2.8660812	5.2982587	-1.5140744
H	3.5898062	3.8658628	-2.2478642
H	1.8534840	4.1532264	-2.4044249
C	1.0381335	4.1596330	0.8688713
H	1.3466145	5.1743373	1.1357158
H	0.1179886	4.2283948	0.2854338
H	0.8053129	3.6254664	1.7926986
C	5.0058493	0.3036297	-1.3335148
H	5.2954410	1.3550060	-1.2908961

H	5.0643845	-0.1001909	-0.3202229
H	5.7413924	-0.2226248	-1.9483579
C	2.9819584	-1.7599014	-2.3498535
H	3.7644052	-2.1449408	-3.0102733
H	3.0234666	-2.3213282	-1.4158833
H	2.0196185	-1.9629405	-2.8207327
C	3.2020103	0.9730152	-3.7474651
H	3.9500767	0.5468796	-4.4222073
H	2.2236346	0.8625381	-4.2176189
H	3.4049308	2.0399697	-3.6482492
H	-0.2073737	2.7001768	-2.4551049
H	-1.3131396	1.9730189	-0.4501665

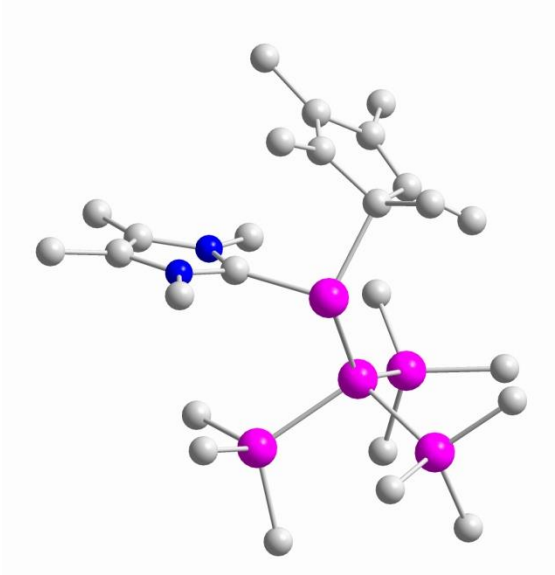

Fig. S67. Calculated structure of Cp*[(Me$_3$Si)$_3$Si]Si:← NHC **6'**.

Table S11. Coordinates of Cp*[(Me$_3$Si)$_3$Si]Si:← NHC **6'**.

87
Energy = -2579.978716004

Si	-0.1575924	1.5466370	-2.2231696
C	-2.9431015	-0.7309110	-0.9620563
C	-1.7297123	-0.8970186	-1.5560471
C	-1.5744025	0.1077893	-2.6460635
C	-2.8882323	0.8229845	-2.6575361
C	-3.6572257	0.3534348	-1.6391276
C	-3.5159884	-1.4920655	0.1913526
H	-3.7107585	-0.8443260	1.0546725
H	-4.4728783	-1.9543819	-0.0706902
H	-2.8489942	-2.2870440	0.5251595
C	-5.0136677	0.8333386	-1.2261386
H	-5.0286252	1.1558533	-0.1782141
H	-5.3462511	1.6751608	-1.8344910
H	-5.7678380	0.0446894	-1.3159954
C	-0.7255905	-1.9730260	-1.3205150
H	0.2896983	-1.5754042	-1.3226938
H	-0.8833678	-2.4830863	-0.3704277
H	-0.7671403	-2.7323273	-2.1101607

C	-3.2508713	1.8400502	-3.6924266
H	-3.9441645	2.5931181	-3.3091758
H	-2.3634994	2.3546542	-4.0652141
H	-3.7263824	1.3730624	-4.5621071
C	-1.1596323	-0.4966697	-3.9938044
H	-1.0868845	0.2702024	-4.7663216
H	-0.1842039	-0.9828423	-3.9302586
H	-1.8904060	-1.2470385	-4.3134732
Si	1.4196400	1.0165624	-0.4430168
Si	1.4802989	-0.5093360	1.3952600
Si	2.0109835	3.1342672	0.4555401
Si	3.3157600	0.4374412	-1.7368550
C	2.7450722	0.0975333	2.6854422
H	3.7442498	0.1660755	2.2528053
H	2.4860897	1.0758889	3.0927309
H	2.7873619	-0.6122139	3.5172909
C	-0.1648637	-0.7446489	2.3255661
H	-0.0433893	-1.5328248	3.0743557
H	-0.4622843	0.1651869	2.8505594
H	-0.9776960	-1.0350753	1.6600895
C	2.0806406	-2.2477440	0.8958064
H	2.2296080	-2.8415266	1.8028998
H	1.3675188	-2.7746347	0.2642109
H	3.0329577	-2.2099835	0.3661108
C	3.8322210	3.2074752	1.0031553
H	4.0807274	2.4310219	1.7255763
H	4.5010758	3.0987379	0.1477532
H	4.0356115	4.1789965	1.4638975
C	1.7867313	4.5503754	-0.7995156
H	2.3285650	5.4361707	-0.4549574
H	2.1601973	4.2823355	-1.7881580
H	0.7349867	4.8179950	-0.8948077
C	0.9513081	3.6145100	1.9700184
H	1.3752024	4.4996071	2.4530118
H	-0.0665828	3.8618911	1.6644390
H	0.9021868	2.8187312	2.7155391
C	4.8572576	0.0059800	-0.7042032
H	5.1639456	0.8426384	-0.0753221
H	4.6896694	-0.8549504	-0.0557046
H	5.6907749	-0.2365132	-1.3702716
C	2.9094469	-1.0665502	-2.8277593
H	3.7707599	-1.3373568	-3.4452612
H	2.6375731	-1.9365574	-2.2269181
H	2.0752064	-0.8418592	-3.4950181
C	3.7777191	1.8806572	-2.8842329
H	4.5706025	1.5832750	-3.5765882
H	2.9073639	2.1908582	-3.4655926
H	4.1334197	2.7435563	-2.3171746
C	-2.3635239	4.8357757	-0.8911575
N	-1.5776386	4.0921040	-1.7658790
C	-1.3035860	2.8588889	-1.2605171
N	-1.9229743	2.8461917	-0.0568451
C	-2.5823615	4.0438538	0.1932068
C	-1.9291240	1.7283147	0.8681030
H	-2.9508143	1.4038309	1.0536335

H	-1.3780081	0.9139845	0.4162986
H	-1.4594897	2.0204521	1.8053469
C	-3.3455980	4.2871227	1.4449319
H	-3.7723688	5.2887291	1.4388514
H	-4.1654567	3.5733711	1.5589585
H	-2.7064194	4.2010319	2.3271448
C	-2.8086298	6.2212233	-1.1936288
H	-3.4267711	6.6023624	-0.3822971
H	-1.9608389	6.9005431	-1.3140147
H	-3.3990002	6.2636352	-2.1122933
C	-1.0965078	4.6126494	-3.0393598
H	-0.5433784	5.5369005	-2.8748542
H	-0.4343761	3.8637006	-3.4720235
H	-1.9346791	4.7997275	-3.7100642

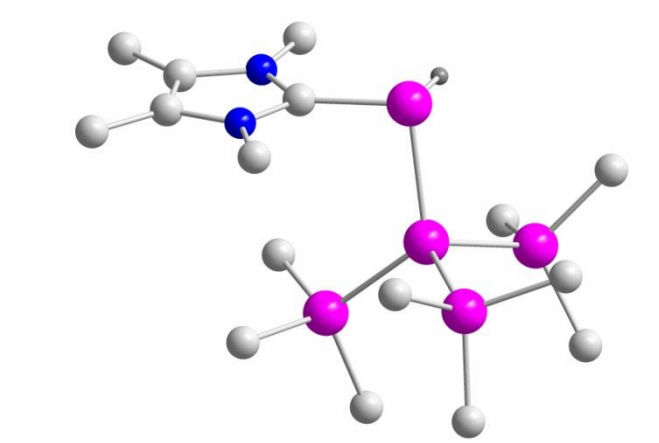

Fig. S68. Calculated structure of [(Me$_3$Si)$_3$Si](H)Si:← NHC **5a'**.

Table S12. Coordinates of [(Me$_3$Si)$_3$Si](H)Si:← NHC **5a'**.

63
Energy = -2190.574397474

Si	-2.1019046	0.2934684	-0.3690776
Si	-0.1820631	-0.0031158	1.0656819
Si	-0.4138507	-1.9070424	2.4330330
Si	-0.2763788	1.8557103	2.5137675
Si	1.9913090	0.0100263	0.1474094
C	1.1603827	-2.2459044	3.4480061
H	2.0009731	-2.4995407	2.7980271
H	1.4470687	-1.3763400	4.0415710
H	1.0009904	-3.0850687	4.1312601
C	-1.8641252	-1.6422172	3.6328109
H	-2.0511052	-2.5453887	4.2206112
H	-1.6606006	-0.8250689	4.3274554
H	-2.7767565	-1.3973752	3.0848917
C	-0.7892294	-3.4867115	1.4379289
H	-0.9347218	-4.3321511	2.1165897
H	-1.7010673	-3.3692098	0.8492170
H	0.0295540	-3.7414364	0.7613944
C	0.7040140	1.5959906	4.1248320
H	0.2858165	0.7757346	4.7117861

H	1.7523846	1.3652953	3.9284541
H	0.6655433	2.4998958	4.7398313
C	0.4264013	3.3923004	1.6372755
H	0.3006108	4.2816370	2.2613932
H	1.4908816	3.2806048	1.4215457
H	-0.0941587	3.5665101	0.6930529
C	-2.0799689	2.2222989	2.9830280
H	-2.1352099	3.0984290	3.6358293
H	-2.6801590	2.4217697	2.0934481
H	-2.5321159	1.3793617	3.5085220
C	3.2867155	0.3636304	1.4962326
H	3.1523759	1.3623821	1.9161003
H	3.2202191	-0.3532313	2.3159152
H	4.2957661	0.3087291	1.0767839
C	2.4579878	-1.6563585	-0.6553756
H	3.5149617	-1.6576585	-0.9370206
H	2.2917445	-2.4951742	0.0237779
H	1.8756495	-1.8306549	-1.5620178
C	2.2036169	1.3392793	-1.1996265
H	3.2640959	1.4716422	-1.4328987
H	1.6912234	1.0447773	-2.1156010
H	1.8036051	2.3022722	-0.8787134
H	-2.0787221	1.8130489	-0.3265004
C	-0.1345944	-0.8487494	-3.8251840
N	-0.7536903	-1.0298487	-2.5894236
C	-1.1221240	0.1595483	-2.0386842
N	-0.7542386	1.0891072	-2.9626929
C	-0.1427888	0.4883942	-4.0655397
C	-0.9188624	2.5250789	-2.8171688
H	0.0078214	3.0314470	-3.0839917
H	-1.7286491	2.8882539	-3.4524758
H	-1.1612239	2.7325598	-1.7793127
C	0.3832626	1.2757645	-5.2111855
H	0.7748504	0.6089480	-5.9777569
H	-0.3955077	1.8901813	-5.6703961
H	1.1937836	1.9427121	-4.9047286
C	0.3997705	-1.9788084	-4.6296031
H	0.8873346	-1.6016110	-5.5270641
H	1.1377968	-2.5567652	-4.0674292
H	-0.3902940	-2.6656069	-4.9454044
C	-0.9961124	-2.3092687	-1.9467495
H	-1.0698221	-3.0903879	-2.6997079
H	-0.1989581	-2.5530168	-1.2472484
H	-1.9343150	-2.2410573	-1.3948626

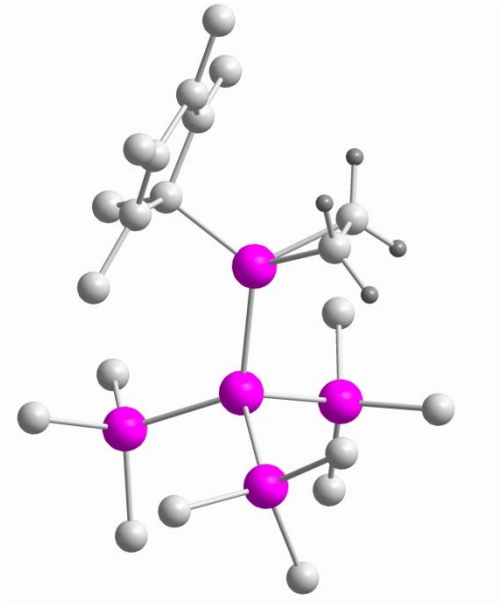

Fig. S69. Calculated structure of Cp*[$(Me_3Si)_3Si$]Si(H_2CCH_2) **3'**.

Table S13. Coordinates of Cp*[$(Me_3Si)_3Si$]Si(H_2CCH_2) **3'**.

```
72
Energy = -2275.175263875
Si    -0.6471972    1.3010348   -1.0635819
C     -3.1940563   -1.0288531   -1.7855684
C     -1.8411860   -1.0346222   -1.8497090
C     -1.3845499    0.2360345   -2.5238517
C     -2.6680400    0.8988983   -2.9394132
C     -3.7077881    0.1698635   -2.4672960
C     -4.0900341   -2.0348069   -1.1342897
H     -4.6880538   -1.5774846   -0.3396733
H     -4.7954289   -2.4654274   -1.8515912
H     -3.5255997   -2.8557502   -0.6929764
C     -5.1689095    0.4615389   -2.6029901
H     -5.6585367    0.4969166   -1.6248862
H     -5.3479524    1.4146316   -3.1000692
H     -5.6783089   -0.3154756   -3.1817554
C     -0.8875598   -2.0623533   -1.3369512
H     -0.0820660   -1.6115749   -0.7510134
H     -1.3847367   -2.7951020   -0.7013270
H     -0.4062348   -2.6088065   -2.1545926
C     -2.7005033    2.1111798   -3.8128994
H     -3.6572261    2.6312960   -3.7500737
H     -1.9160327    2.8214568   -3.5449396
H     -2.5433034    1.8437493   -4.8641213
C     -0.3778200    0.0589325   -3.6626063
H     -0.1049308    1.0182141   -4.1060460
H      0.5371003   -0.4161491   -3.3175127
H     -0.8081102   -0.5679010   -4.4483972
Si     1.6075080    1.1213476   -0.3960013
Si     1.8138898    0.1634547    1.7603383
Si     2.3238294    3.3745429   -0.2739746
Si     3.1406063   -0.0069477   -1.8055970
C      3.4145003    0.7998329    2.5650261
```

H	4.2911508	0.5829280	1.9537001
H	3.3756250	1.8787279	2.7254128
H	3.5562238	0.3227626	3.5390970
C	0.3650408	0.6231051	2.8925504
H	0.5453241	0.2362140	3.8996316
H	0.2410726	1.7052172	2.9643259
H	-0.5707468	0.1989486	2.5263502
C	1.9174473	-1.7311219	1.6642197
H	2.0214479	-2.1502170	2.6691419
H	1.0205993	-2.1602845	1.2140085
H	2.7780637	-2.0561606	1.0767186
C	4.2136966	3.5187940	-0.1382773
H	4.6028693	2.9665987	0.7182779
H	4.7092840	3.1461189	-1.0364537
H	4.4927805	4.5694195	-0.0162431
C	1.7825585	4.3061656	-1.8352550
H	2.0916941	5.3538883	-1.7820642
H	2.2379083	3.8657319	-2.7249247
H	0.7001974	4.2706493	-1.9608120
C	1.5790398	4.2013839	1.2676696
H	1.8236839	5.2672520	1.2825723
H	0.4933370	4.1050659	1.3042807
H	1.9823661	3.7542332	2.1785554
C	4.8032897	-0.0941169	-0.8862147
H	5.1549141	0.8838517	-0.5598947
H	4.7316752	-0.7386047	-0.0081256
H	5.5605399	-0.5219710	-1.5496423
C	2.7026827	-1.8115115	-2.2096278
H	3.5571627	-2.2704992	-2.7159635
H	2.5071129	-2.3831400	-1.3011654
H	1.8368764	-1.9153320	-2.8616072
C	3.4019232	0.9592208	-3.4188131
H	4.1103668	0.4344759	-4.0658945
H	2.4696635	1.0864606	-3.9707202
H	3.8080450	1.9516771	-3.2134856
C	-1.5210536	2.9376001	-0.6969437
C	-1.9000300	1.7819088	0.2464194
H	-0.9693651	3.7600254	-0.2573976
H	-2.2999264	3.2752122	-1.3693785
H	-1.5963757	1.8792414	1.2807855
H	-2.9033544	1.3854808	0.1308374

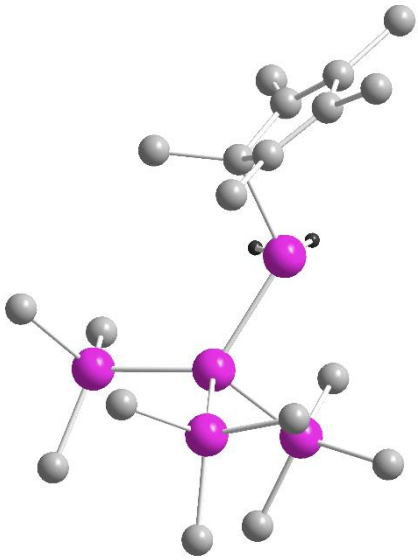

Fig. S70. Calculated structure of transition state for oxidative addition of H_2 to **2'**.

Table S14. Coordinates of transition state for oxidative addition of H_2 to **2'**.

```
68
Energy = -2197.547787407
Si    -1.0739619    0.5236584   -0.4277991
C     -4.3302371    0.3643169    0.5961482
C     -3.2074641   -0.2830590    1.0053876
C     -2.5017087   -0.8512545   -0.2036104
C     -3.4388381   -0.5316813   -1.3336319
C     -4.4746069    0.2092007   -0.8519229
C     -5.3082154    1.1307915    1.4347003
H     -5.3788837    2.1740446    1.1105295
H     -6.3155258    0.7087271    1.3605740
H     -5.0301028    1.1320590    2.4884815
C     -5.6180440    0.8016935   -1.6185758
H     -5.6433289    1.8910555   -1.5124679
H     -5.5594598    0.5767013   -2.6831004
H     -6.5799374    0.4275745   -1.2538543
C     -2.7276930   -0.5097485    2.4057206
H     -1.6544187   -0.3351450    2.5112959
H     -3.2338631    0.1406193    3.1196155
H     -2.9065811   -1.5440628    2.7224591
C     -3.2499039   -1.0456690   -2.7270091
H     -3.9801575   -0.6211787   -3.4159565
H     -2.2555825   -0.8241865   -3.1266043
H     -3.3610657   -2.1352870   -2.7655033
C     -2.0777618   -2.3141397   -0.0802036
H     -1.5873220   -2.6666600   -0.9883371
H     -1.3843893   -2.4668273    0.7476743
H     -2.9541300   -2.9465966    0.0992743
Si     1.2599069    0.1236100    0.0546504
Si     1.6514241    0.6340031    2.3638004
Si     2.2321886    1.9046257   -1.2424059
Si     2.3249593   -1.9478953   -0.5187071
```

C	3.4567801	1.1853976	2.6367134
H	4.1705882	0.4310739	2.2994968
H	3.6816800	2.1172677	2.1137201
H	3.6314055	1.3549322	3.7036540
C	0.5202727	2.0430395	2.9646718
H	0.7277700	2.2608479	4.0168819
H	0.6844879	2.9588876	2.3938654
H	-0.5374644	1.7879086	2.8788783
C	1.3633567	-0.8872155	3.4784467
H	1.4940788	-0.6075632	4.5282929
H	0.3593082	-1.3015056	3.3684534
H	2.0777060	-1.6838264	3.2582673
C	4.1308207	1.7472915	-1.3205309
H	4.5854934	1.7135921	-0.3287336
H	4.4415712	0.8525961	-1.8640884
H	4.5435167	2.6132106	-1.8475263
C	1.5979385	1.8996155	-3.0403765
H	2.1401044	2.6541875	-3.6184564
H	1.7489522	0.9346570	-3.5287339
H	0.5354962	2.1457942	-3.0960961
C	1.8142594	3.6028131	-0.4895295
H	2.2031472	4.3977652	-1.1332331
H	0.7355175	3.7424984	-0.3963912
H	2.2586500	3.7312386	0.4996933
C	4.1519119	-1.9269735	0.0327698
H	4.7008276	-1.0769590	-0.3749919
H	4.2415200	-1.8926778	1.1210100
H	4.6476697	-2.8409111	-0.3088197
C	1.5278587	-3.4700095	0.3035117
H	2.1324263	-4.3558606	0.0854735
H	1.4712133	-3.3656936	1.3889335
H	0.5202128	-3.6544276	-0.0695685
C	2.2758573	-2.2131899	-2.4049785
H	2.7262495	-3.1772430	-2.6598667
H	1.2508242	-2.2144842	-2.7827171
H	2.8282101	-1.4370618	-2.9392564
H	-0.5083525	-0.1491163	-1.8702438
H	-1.0208451	0.7417570	-1.9840699

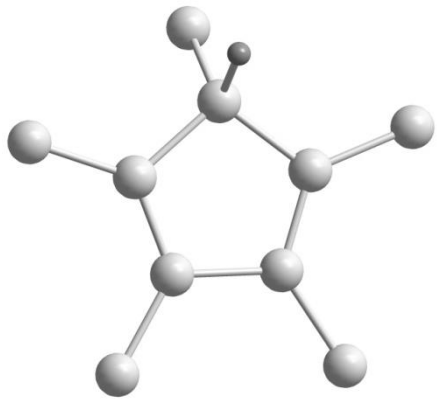

Fig. S71. Calculated structure of Cp*H.

Table S15. Coordinates of calculated structure of Cp*H.

```
26
Energy = -390.5903078578
H     -0.6416013    0.9010420   -2.1588606
C     -2.9167231   -0.8956710   -1.2552134
C     -1.6165579   -0.9253752   -1.6085794
C     -1.3535693    0.1877134   -2.5993712
C     -2.7018812    0.8592408   -2.7439708
C     -3.5937469    0.2177777   -1.9632623
C     -3.6391197   -1.7993379   -0.3067810
H     -4.0893570   -1.2345173    0.5152408
H     -4.4549639   -2.3291156   -0.8083021
H     -2.9761807   -2.5472818    0.1275181
C     -5.0469493    0.5195922   -1.7768068
H     -5.2733344    0.7512872   -0.7313148
H     -5.3676273    1.3672119   -2.3818083
H     -5.6685837   -0.3386440   -2.0504626
C     -0.5397101   -1.8571244   -1.1617339
H      0.3172894   -1.3096556   -0.7551205
H     -0.8885540   -2.5437343   -0.3900254
H     -0.1597049   -2.4619889   -1.9923941
C     -2.9068323    2.0382959   -3.6358675
H     -3.9253234    2.4228388   -3.5761102
H     -2.2275200    2.8571748   -3.3760579
H     -2.7108029    1.7894882   -4.6846667
C     -0.7766236   -0.3104239   -3.9319728
H     -0.6201744    0.5159017   -4.6281787
H      0.1844670   -0.8071331   -3.7847780
H     -1.4627052   -1.0231317   -4.3952895
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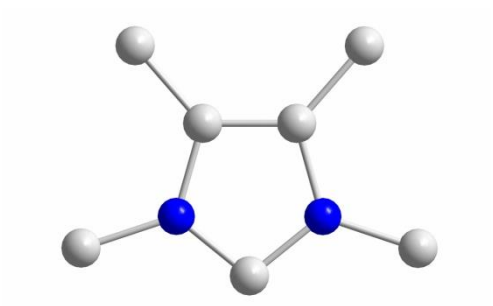


Fig. S72. Calculated structure of NHC.

Table S16. Coordinates of calculated structure of NHC.

```
21
Energy = -383.3476466815
C     -0.8882001    0.5446315    0.0246060
N     -0.0223329   -0.5539590    0.0215696
C      1.2937902   -0.2029565   -0.0189451
N      1.2217451    1.1580727   -0.0418650
C     -0.0904206    1.6431332   -0.0164872
C      2.4007287    2.0003541   -0.0876715
H      2.4534707    2.6520971    0.7877161
```

```
H     3.2661145    1.3433486   -0.0978862
H     2.4078090    2.6195343   -0.9878979
C    -0.4234114    3.0932225   -0.0352087
H    -1.5037295    3.2357391   -0.0119071
H    -0.0017739    3.6188050    0.8267233
H    -0.0444044    3.5861337   -0.9353963
C    -2.3697656    0.4136399    0.0642962
H    -2.8382098    1.3976465    0.0686026
H    -2.7537296   -0.1318542   -0.8028605
H    -2.7073854   -0.1173119    0.9592743
C    -0.4593537   -1.9355307    0.0630619
H    -1.0919444   -2.1743107   -0.7949971
H     0.4321588   -2.5561689    0.0362074
H    -1.0170356   -2.1449962    0.9790652
```

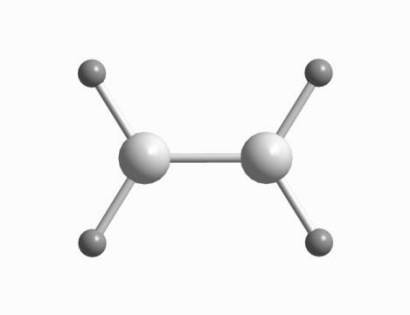


Fig. S73. Calculated structure of $H_2C=CH_2$.

Table 17. Coordinates of calculated structure of $H_2C=CH_2$.

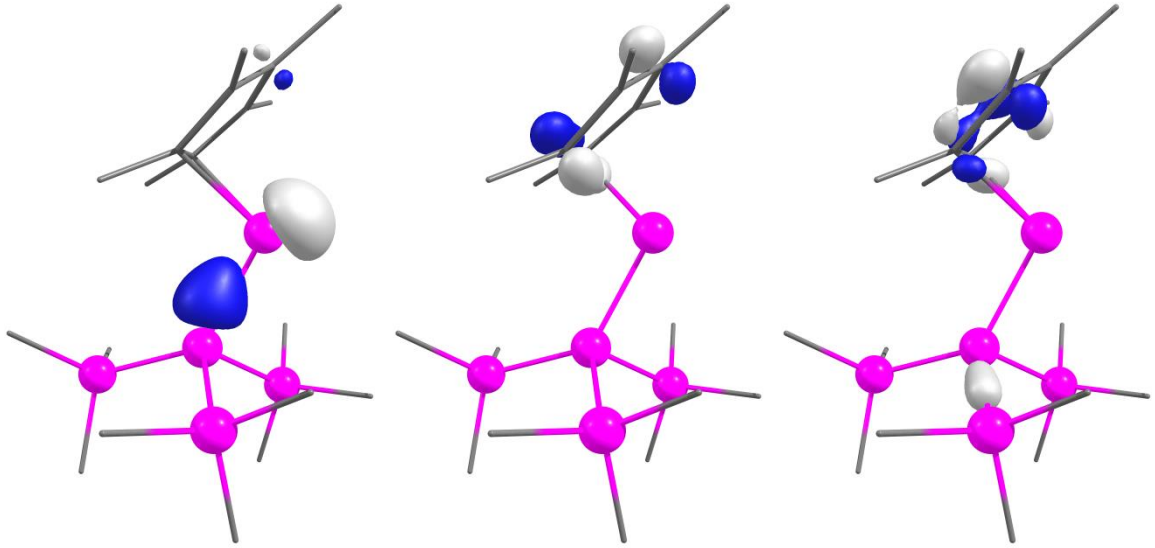
```
6
Energy = -78.56765304067
C    -1.5300266   -0.0906874    0.0000000
C    -0.2041034   -0.0873926    0.0000000
H    -2.0982969   -1.0139248   -0.0000000
H    -2.1028643    0.8297188   -0.0000000
H     0.3641669    0.8358448   -0.0000000
H     0.3687343   -1.0077988   -0.0000000
```

Fig. S74. Calculated structure of H_2.

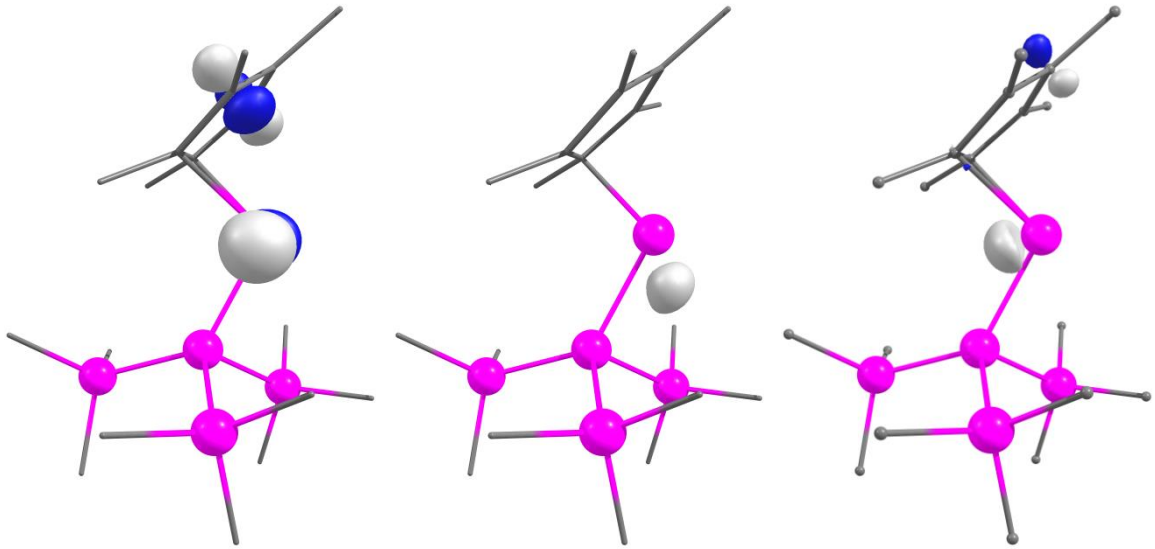
Table 18. Coordinates of calculated structure of H_2.

```
2
Energy = -1.173061500466
H    -1.0450400   -0.3213669    0.0000000
H    -0.3007200   -0.3155531    0.0000000
```

Fig. S75. Pictures of orbitals (isocontour value 0.09) of selected calculated Cp*-silylenes: $[(Me_3Si)_3Si](Cp^*)Si$: **2'**

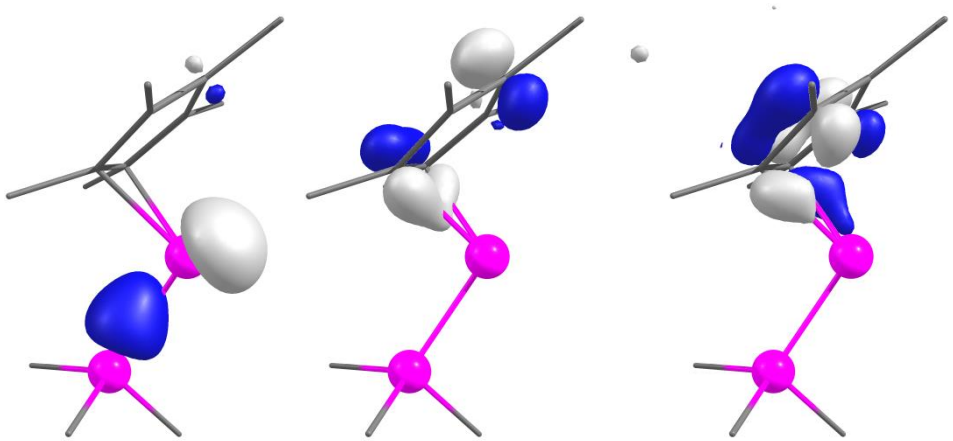


HOMO/HOMO-1/HOMO-2

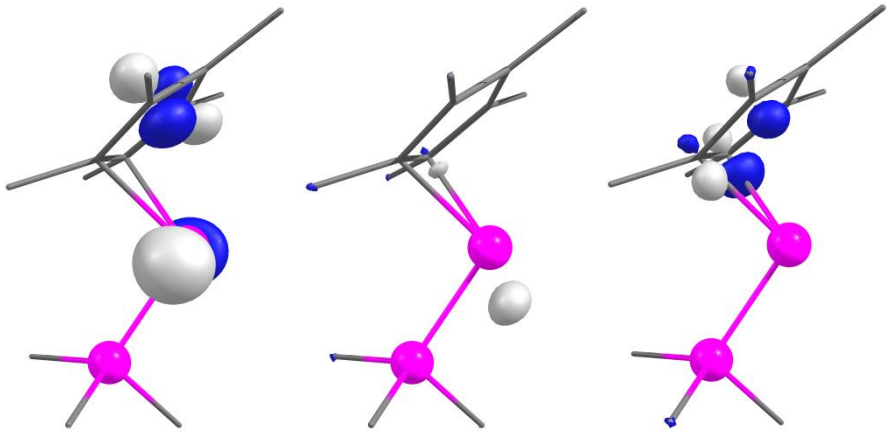


LUMO/LUMO+1/LUMO+2

(Me_3Si)(Cp*)Si: **1g'**

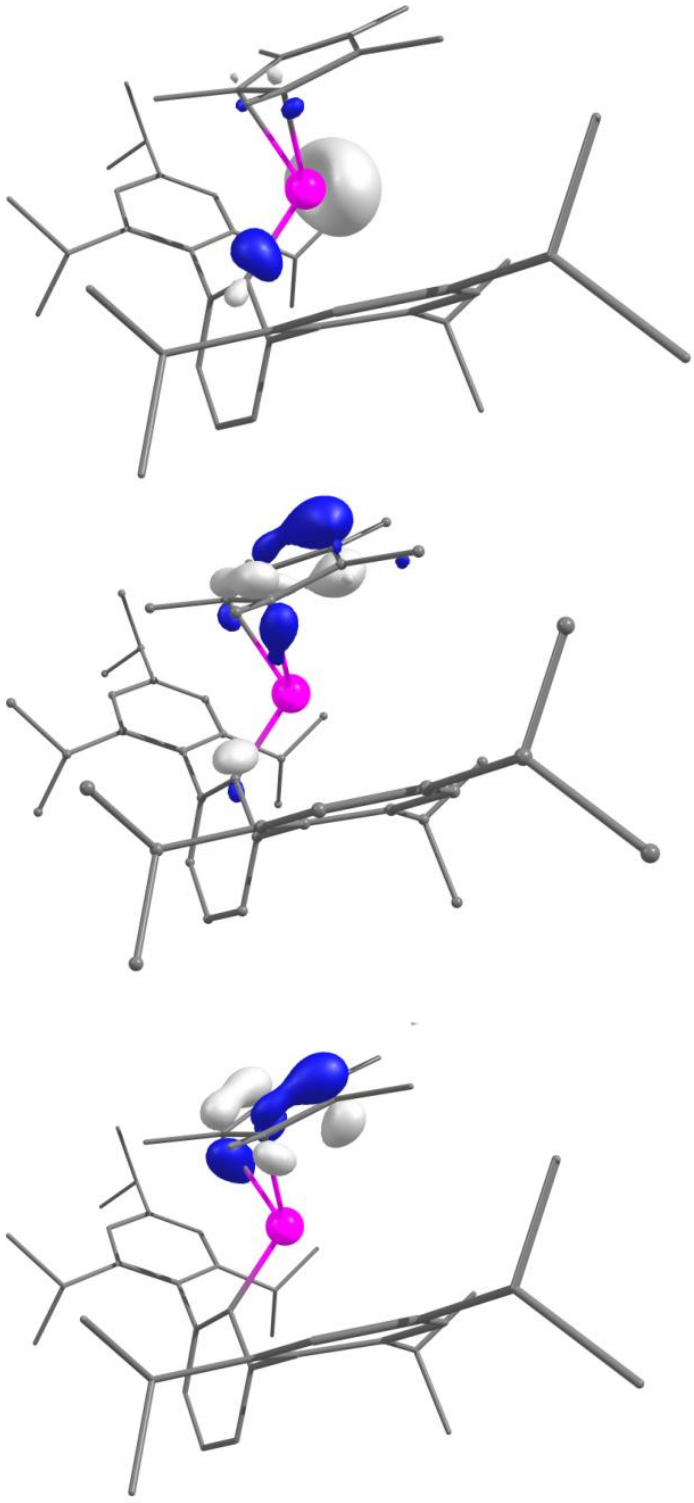


HOMO/HOMO-1/HOMO-2

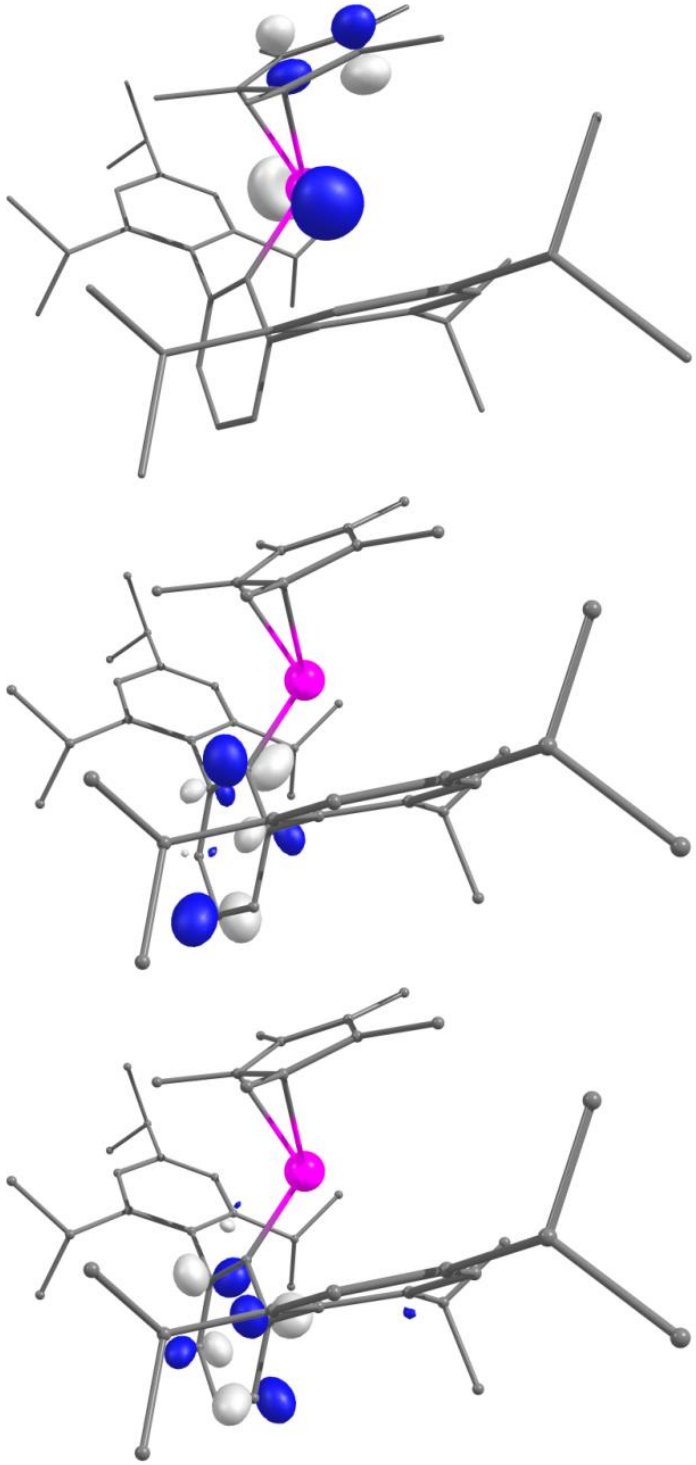


LUMO/LUMO+1/LUMO+2

[$Tip_2(C_6H_3)$](Cp*)Si: **1b'**

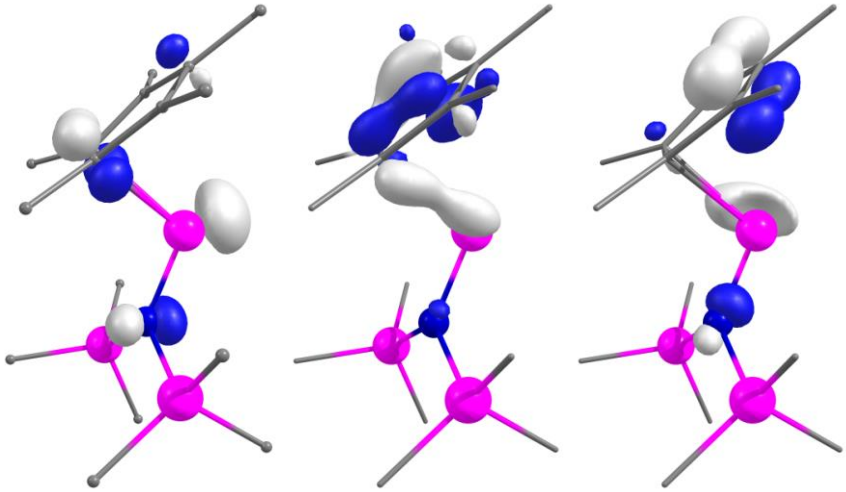


HOMO/HOMO-1/HOMO-2

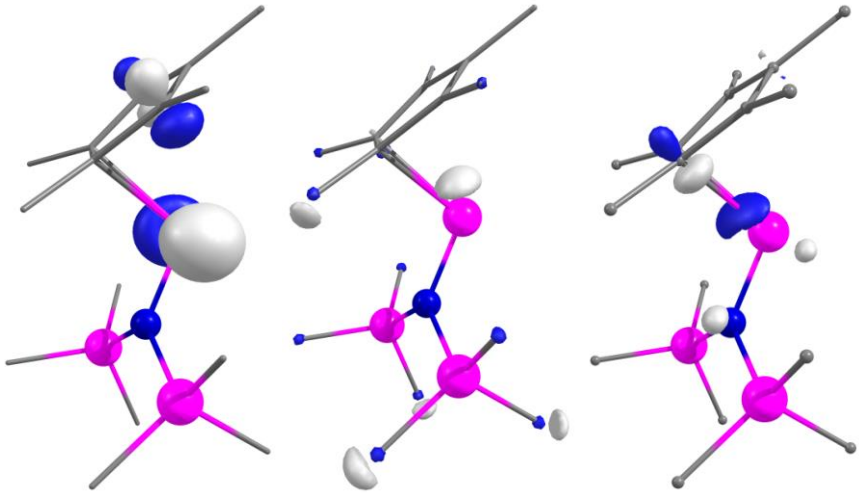


LUMO/LUMO+1/LUMO+2

[$(Me_3Si)_2N$](Cp*)Si: **1a'**

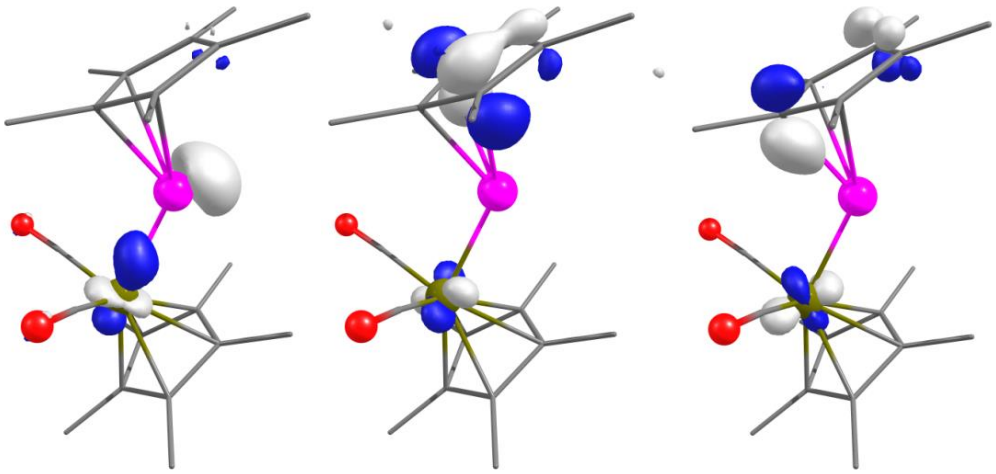


HOMO/HOMO-1/HOMO-2

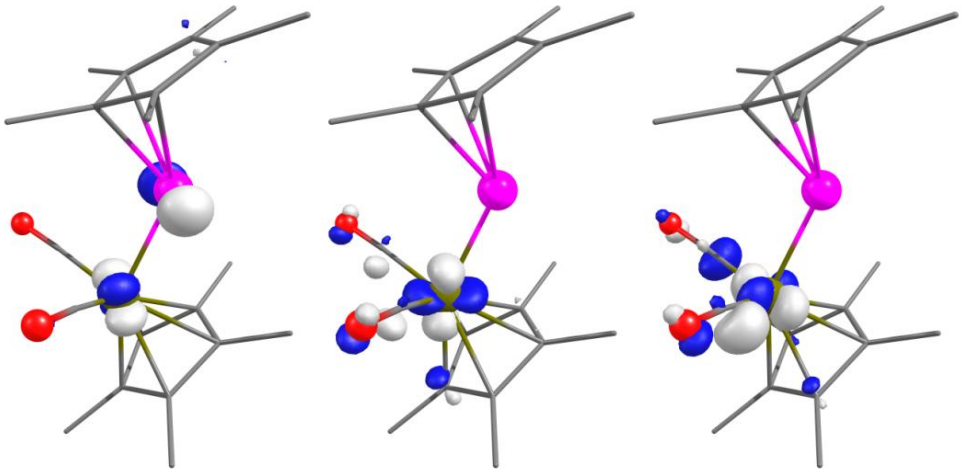


LUMO/LUMO+1/LUMO+2

[(Cp*)$(CO)_2$Fe](Cp*)Si: **1c'**



HOMO/HOMO-1/HOMO-2



LUMO/LUMO+1/LUMO+2

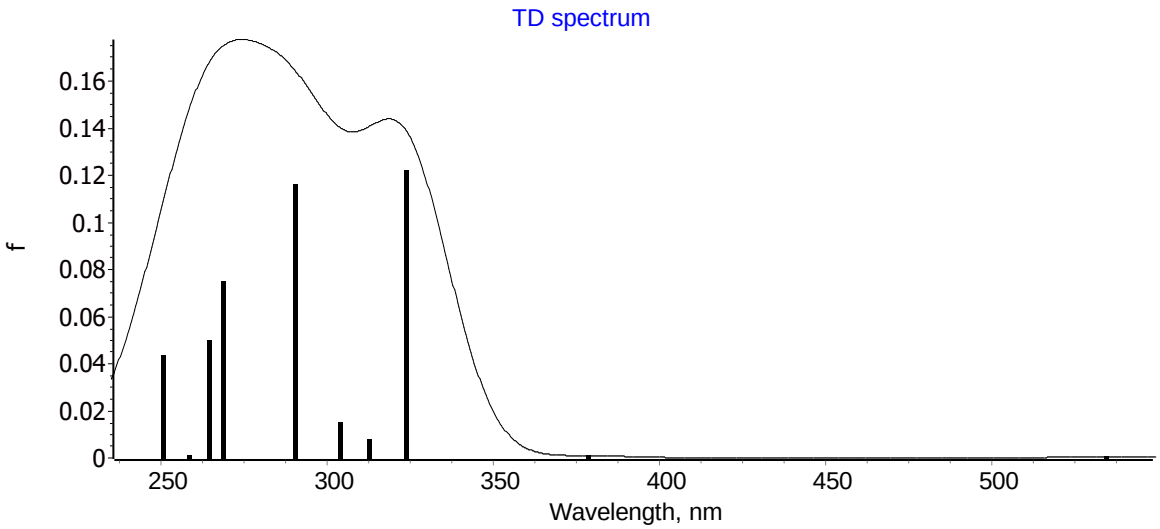


Fig. S76. Calculated transitions (vertical bars) and simulated UV/Vis absorption spectrum of **2'**.

excitation #	wavelength [nm]	oscillator strength
1	534.7	0.0006
2	378.6	0.0009
3	324.3	0.1058
4	313.0	0.0081
5	310.7	0.0398
6	291.5	0.1168
7	287.8	0.0010
8	274.6	0.1320
9	274.4	0.0114
10	267.9	0.0024

Table S19. Selected calculated transitions and optical parameters of **2'**.

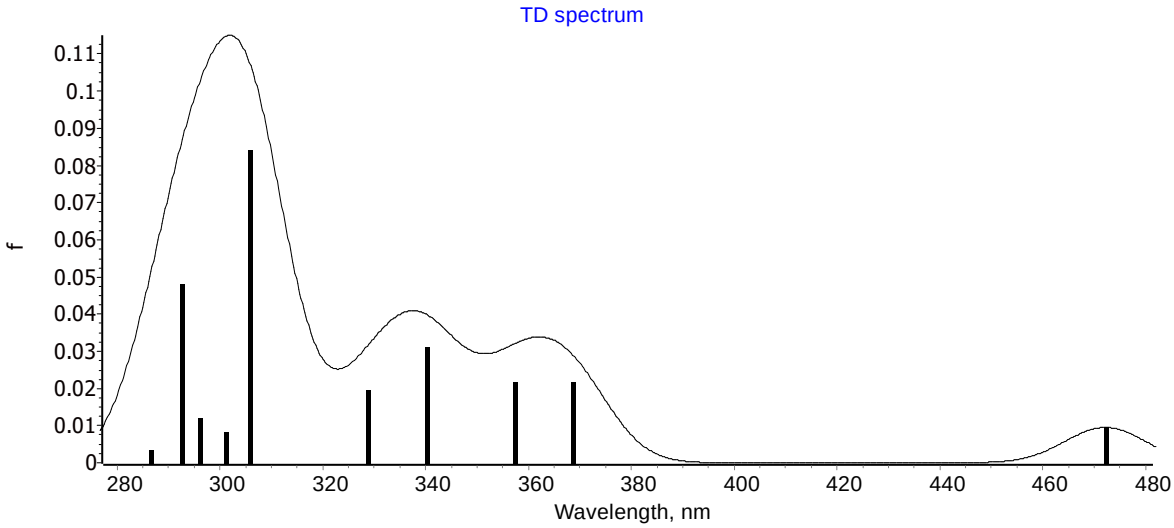


Fig. S77. Calculated transitions (vertical bars) and simulated UV/Vis absorption spectrum of **6'**.

excitation #	wavelength [nm]	oscillator strength
1	472.2	0.0095
2	368.4	0.0214
3	357.3	0.0215
4	340.0	0.0312
5	328.7	0.0195
6	305.7	0.0840
7	301.0	0.0081
8	295.9	0.0119
9	292.3	0.0481
10	286.5	0.0034

Table S20. Selected calculated transitions and optical parameters of **6'**.

Table S21. Comparison of the structural parameters for Cp*-substituted silylenes Cp*(X)Si:. Experimental data versus calculated structures. [S10]

COMPOUND/ SUBSTITUENT X	BOND LENGTH Si-C (Cp*)/Å	DISTANCE Si-C_g/Å	DISTANCE Si-C_f/Å	Angle/° X-Si-C1(Cp*) X-Si-C2(Cp*) X-Si-C_f X-Si-C_g	BOND LENGTH Si-X/Å	DISTANCE C_g-C_f	BONDING MODE
2/$Si(SiMe_3)_3$	2.100(2) 2.112(2) 2.544(2) 2.554(2) 2.806(2)	2.119(1)	1.965(1)	106.94(6) 106.15(8) 113.27(6) 135.24(4)	2.444(1)	0.793	η^2
2'/$Si(SiMe_3)_3$	2.1491 2.1655 2.6634 2.6860 2.9587	2.2357	2.0284	105.52 105.28 107.77 132.64	2.451	0.940	η^2
1a'/$N(SiMe_3)_2$	2.283 2.288 2.644 2.712 2.889	2.271	2.152	102.24 109.99 113.43 131.75	1.802	0.726	η^2
1b/$Tip_2(C_6H_3)$	2.096(2) 2.282(2) 2.268(2) 2.673(2) 2.682(2)	2.086(1)	1.976(1)	101.94(8) 120.52(7) 120.58(8) 117.45(8) 136.10(7)	1.973(2)	0.668	η^3
1b'/$Tip_2(C_6H_3)$	2.206 2.216 2.655 2.699 2.936	2.247	2.069	110.46 113.02 116.08 139.04	1.979	0.877	η^2
1c/$Fe(Cp^*)(CO)_2$	2.136(1) 2.210(2) 2.435(1) 2.583(2) 2.732(2)	2.108(1)	2.009(1)	112.77(5) 118.92(6) 126.85(6) 144.49(3)	2.368(1)	0.639	η^3
1c'/$Fe(Cp^*)(CO)_2$	2.157 2.410 2.418 2.824 2.820	2.230	2.092	112.14 128.91 124.30 144.60	2.351	0.754	η^1/η^3
1g'/$SiMe_3$	2.146 2.160 2.665 2.710 2.984	2.247	2.023	102.11 106.55 105.45 131.17	2.452	0.978	η^2

Table S22. Electronic properties computed at the B3-LYP-D/def2-TZVPD level of theory for Cp*-substituted silylenes Cp*(X)Si:. Triplet states: (v) = vertical, (a) = adiabatic.

electronic properties B3-LYP-D/ def2-TZVPD	unit	*COMPOUND/ SUBSTITUENT X*				
		***2'**/Si(SiMe$_3$)$_3$*	***1a'**/N(SiMe$_3$)$_2$*	***1b'**/ Tip$_2$(C$_6$H$_3$)*	***1c'**/Fe(Cp*)(CO)$_2$*	***1g'**/SiMe$_3$*
HOMO	eV	-4.959	-5.419	-5.189	-4.563	-4.844
LUMO	eV	-1.711	-1.042	-1.178	-1.194	-1.748
HOMO-LUMO gap	eV	+3.248	+4.377	+4.011	+3.369	+3.096
singlet-triplet gap (v)	kJ/mol	+180.4	+272.3	+236.8	+167.2	+159.5
singlet-triplet gap (a)	kJ/mol	+113.9	+163.6	+152.7	+110.3	+82.3
partial charge at Si(II)	e	+0.644	+1.123	+1.015	+0.728	+0.487

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