

# Supporting Information for

## Modular Silacyclopropenes: Synthesis and Application for Si-H containing Substrate Functionalization

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### A. Experimental Section

#### a) General Considerations:

All experiments and manipulations were carried out under dry oxygen-free argon atmosphere (Ar 4.6) using standard Schlenk techniques or in a LABmaster sp glovebox from MBraun. Glassware was heat-dried under vacuum prior to use. Solvents were dried by standard methods and freshly distilled prior to use. Dry pentane, Et<sub>2</sub>O, THF and toluene were obtained from a *M. Braun* MB-SPS 800 solvent purification system. Commercially available reagents were purchased from *Sigma-Aldrich*, *Acros*, *Alfa-Aesar*, *abcr* or *TCI* and used as received. The solution NMR spectra were recorded on Bruker Spectrometers AVHD 400 or AVHD 500 cryo with residual solvent signals as internal reference (<sup>1</sup>H NMR: C<sub>6</sub>D<sub>6</sub>, 7.16 ppm. <sup>13</sup>C NMR: C<sub>6</sub>D<sub>6</sub> 128.06 ppm) or an external standard (<sup>29</sup>Si NMR: SiMe<sub>4</sub>, 0.0 ppm). The following abbreviations were used to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet.

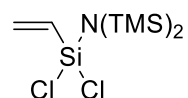
Liquid Injection Field Desorption Ionization Mass Spectrometry (LIFDI-MS) was measured directly from an inert atmosphere glovebox with a Thermo Fisher Scientific Exactive Plus Orbitrap equipped with an ion source from *Linden CMS*.<sup>(S1)</sup>

Elemental analyses were conducted with a Vario EL instrument from *Elementar*. Air-sensitive substances were placed into tin or aluminum boats and kept under argon atmosphere.

UV-Vis spectra were recorded on a Cary 50Scan UV-Visible spectrophotometer from *Varian* with 10·10 mm diameter UV quartz cuvette from *Hellma Analytics*.

## b) Synthesis and Characterization of New Compounds

### Synthesis of dichlorosilane **1**



Synthesis of dichlorosilane **1** was based on the synthesis procedure reported in literature.<sup>(S2)</sup> Modification of the described preparation were the substitution of the lithium-salt with the respective potassium-salt as well as a change of solvent from hexane to THF.

A solution of Trichlorovinylsilane (12.0 g, 74.3 mmol, 1.00 eq) in THF (250 mL) was cooled to 0 °C with an ice-bath. In a second flask a solution of potassium bis(trimethylsilyl)amide (KHMDS) (15.5 g, 78.1 mmol, 1.00 eq) in THF (50 mL) was prepared and cooled to 0 °C as well. The potassium-salt solution was added dropwise to the reaction flask and a rapid formation of the respective KCl-salt occurred. After stirring the solution for 20 min at 0 °C, the reaction was allowed to warm up to room temperature again and was stirred for additional 12 h. After the reaction was completed, the solvent was removed *in vacuo*. The crude product was resolved in 100 ml pentane and the precipitate was removed by filtration through a microfiber glass filter and washed twice with 25 mL pentane. The product was then dried *in vacuo* and further purification was performed by sublimation ( $2 \cdot 10^{-2}$  mbar, 100°C) to yield dichlorosilane **1** (18.6 g, 64.9 mmol, 87,4 %) as clear colourless crystals.

<sup>1</sup>H-NMR: (300 K, 500 MHz, C<sub>6</sub>D<sub>6</sub>) δ [ppm] = 0.28 (s, 18 H, Si-(CH<sub>3</sub>)<sub>3</sub>), 5.74 (dd, 1 H, <sup>2</sup>J<sub>HH</sub> = 3.0 Hz, <sup>3</sup>J<sub>HH</sub> = 14.0 Hz, SiCH-CH<sub>2</sub>), 5.98 (dd, 1 H, <sup>2</sup>J<sub>HH</sub> = 3.0 Hz, <sup>3</sup>J<sub>HH</sub> = 20.0 Hz, SiCH-CH<sub>2</sub>), 6.11 (dd, 1 H, <sup>3</sup>J<sub>HH</sub> = 14.0 Hz, <sup>3</sup>J<sub>HH</sub> = 20.0 Hz, Si-CH-CH<sub>2</sub>).

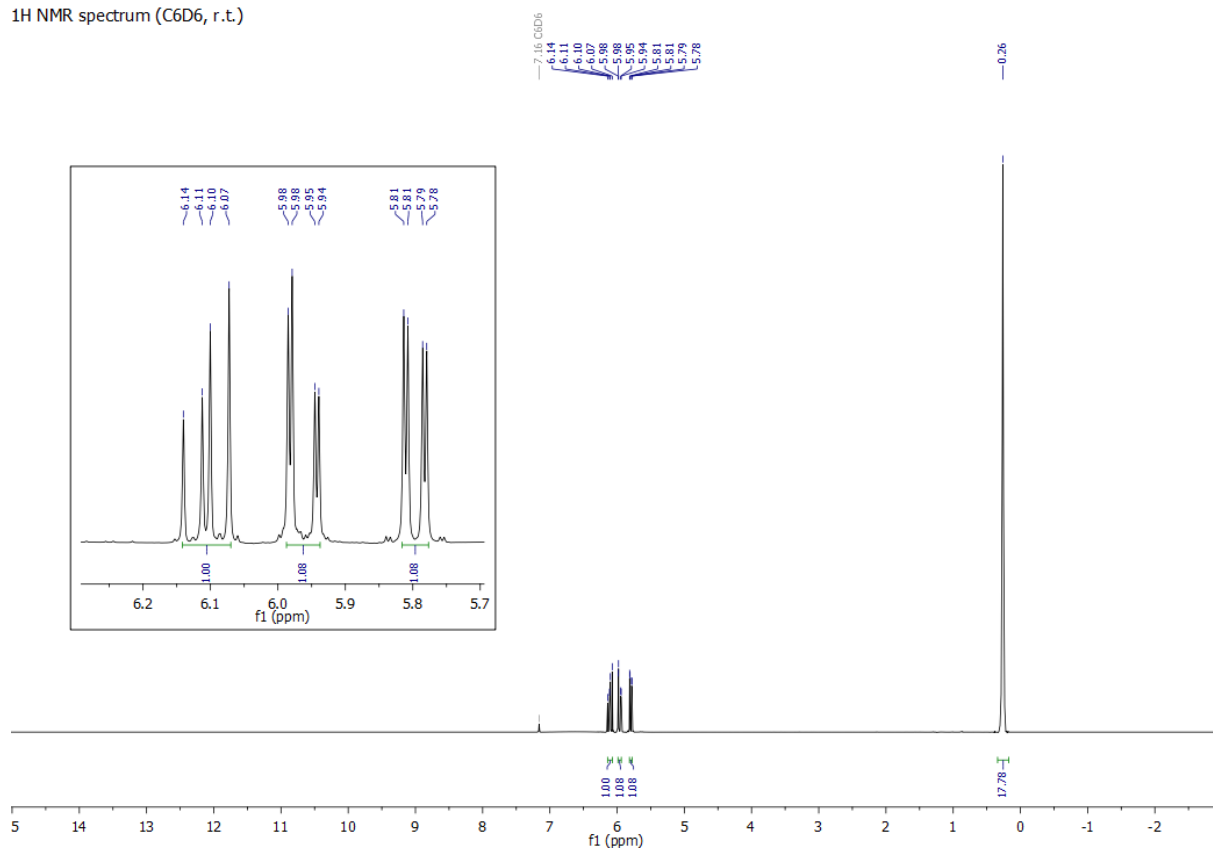
<sup>13</sup>C-NMR: (300 K, 125 MHz, C<sub>6</sub>D<sub>6</sub>) δ [ppm] = 5.09 (Si-(CH<sub>3</sub>)<sub>3</sub>), 135.95 (Si-CH-CH<sub>2</sub>), 136.79 (SiCH-CH<sub>2</sub>).

<sup>29</sup>Si-NMR: (300 K, 100 MHz, C<sub>6</sub>D<sub>6</sub>) δ [ppm] = -14.82 (Si-Cl<sub>2</sub>), 7.03 (Si-(CH<sub>3</sub>)<sub>3</sub>).

EA: calc. [%] for C<sub>8</sub>H<sub>21</sub>Cl<sub>2</sub>NSi<sub>3</sub> = C 33.55, H 7.39, N 4.89; found C 33.73, H 7.41, N 4.84.

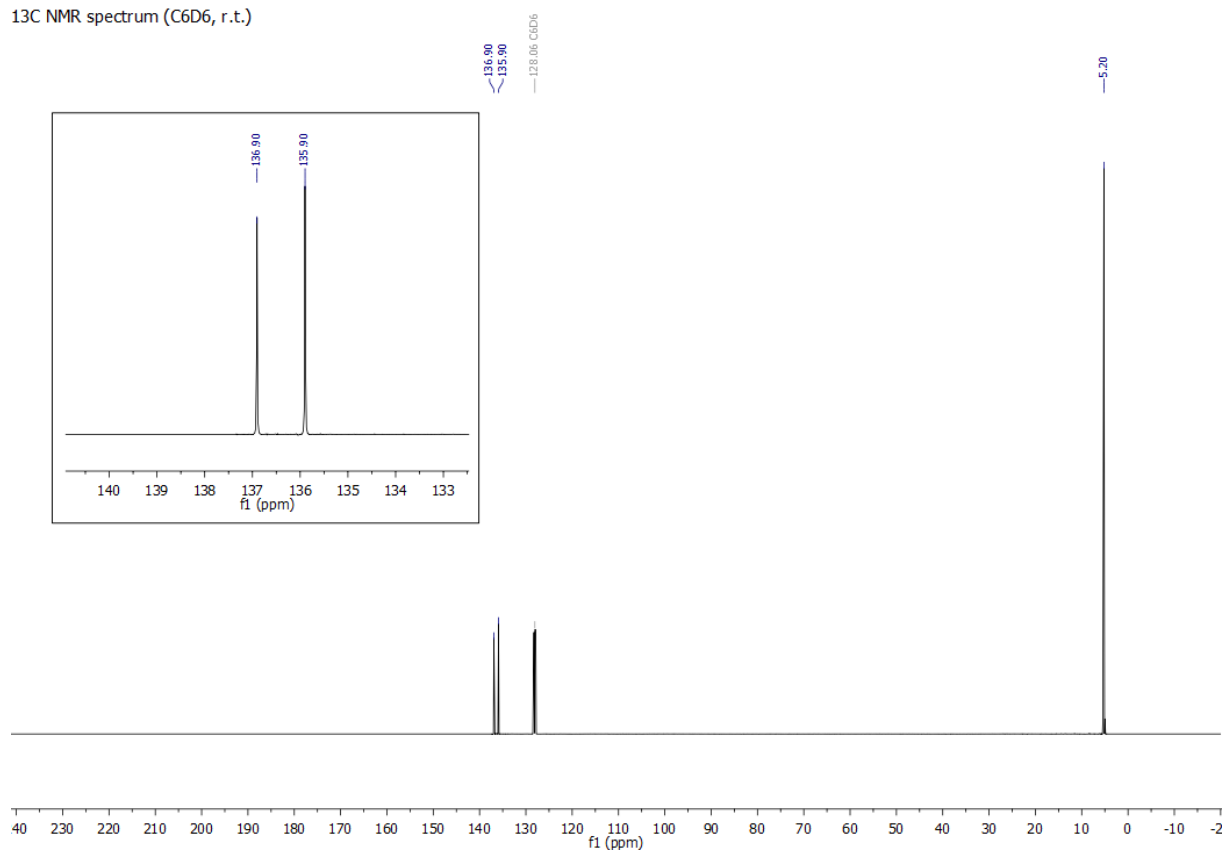
LIFDI-MS: m/z = calc. for [C<sub>8</sub>H<sub>21</sub>Cl<sub>2</sub>NSi<sub>3</sub>]<sup>+</sup> = 285.0359 [M]<sup>+</sup>, found 285.0107.

$^1\text{H}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , r.t.)



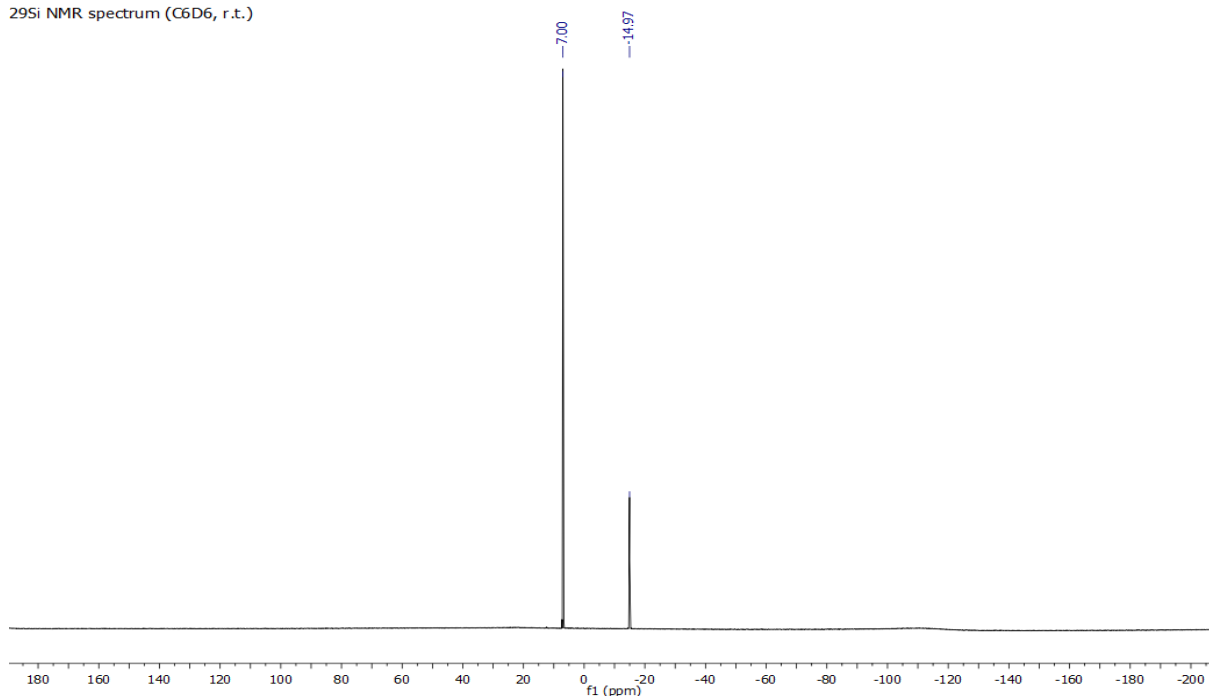
**Figure S1:**  $^1\text{H}$  NMR spectrum of dichlorosilane **1** ( $\text{C}_6\text{D}_6$ , r.t.).

$^{13}\text{C}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , r.t.)



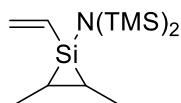
**Figure S2:**  $^{13}\text{C}$  NMR spectrum of dichlorosilane **1** ( $\text{C}_6\text{D}_6$ , r.t.).

<sup>29</sup>Si NMR spectrum (C<sub>6</sub>D<sub>6</sub>, r.t.)



**Figure S3:** <sup>29</sup>Si-ig NMR spectrum of dichlorosilane **1** (C<sub>6</sub>D<sub>6</sub>, r.t.).

### Synthesis of silacyclopropane **2**



A solution of dichlorosilane **1** (4.00 g, 14.0 mmol, 1.00 eq) in THF (10 mL) was prepared in an autoclave and cooled down to -30 °C. *Trans*-but-2-ene (21.9 g, 391 mmol, 28 eq) was condensed to the cold reaction and stirred for 5 min. After letting it warm up to -10 °C, freshly cut pieces of a Lithium/Sodium alloy (969 mg, 137 mmol, 10 eq, 2.5 mol% Na) were added to the reaction mixture. After sealing the autoclave, the reaction was heated to 50 °C and stirred for 72 h. Remaining but-2-ene gas was removed and the reaction mixture filtered and washed twice with 10 ml pentane through a glass frit to remove formed lithium salt. The solvent was then removed *in vacuo* and the crude product was purified by a sublimation (3·10<sup>-2</sup> mbar, 70°C) to yield silacyclopropane **2** (2.57 g, 9.50 mmol, 68.0 %) as clear colourless crystals.

**<sup>1</sup>H-NMR:** (300 K, 500 MHz, C<sub>6</sub>D<sub>6</sub>) δ [ppm] = 0.24 (s, 18 H, Si-(CH<sub>3</sub>)<sub>3</sub>), 0.27 (dq, 1 H, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, Si-CH-CH<sub>3</sub>), 0.69 (dq, 1 H, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, Si-CH-CH<sub>3</sub>), 1.28 (d, 3 H, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, Si-CH-CH<sub>3</sub>), 1.38 (d, 3 H, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, Si-CH-CH<sub>3</sub>), 5.93 (m, 1 H, SiCH-CH<sub>2</sub>), 5.95 (m, 1 H, SiCH-CH<sub>2</sub>), 6.08-6.11 (m, 1 H, Si-CH-CH<sub>2</sub>).

**<sup>13</sup>C-NMR:** (300 K, 125 MHz, C<sub>6</sub>D<sub>6</sub>) δ [ppm] = 3.60 (NSi-(CH<sub>3</sub>)<sub>3</sub>), 16.16 (SiCH-CH<sub>3</sub>), 16.35 (SiCH-CH<sub>3</sub>), 18.99 (Si-CH-CH<sub>3</sub>), 20.22 (Si-CH-CH<sub>3</sub>), 135.56 (Si-CH-CH<sub>2</sub>), 136.42 (SiCH-CH<sub>2</sub>).

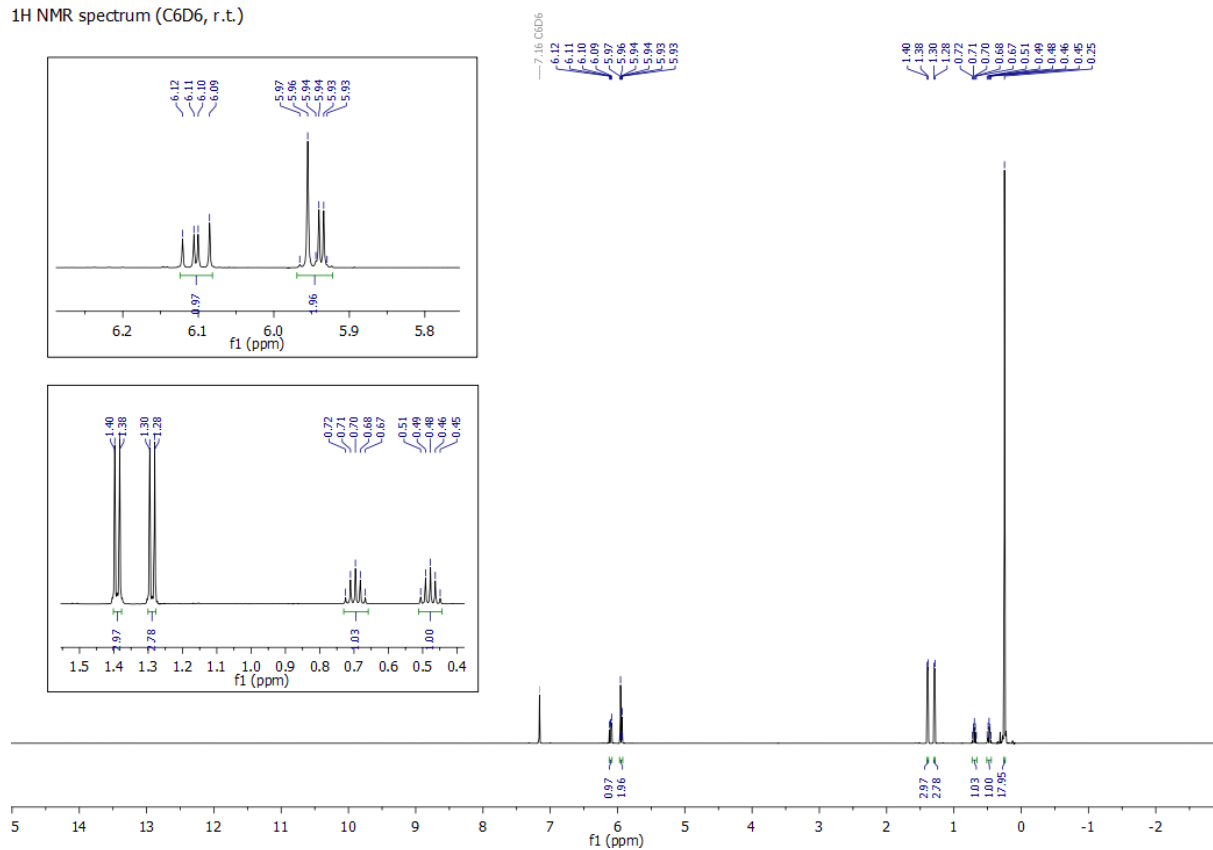
**<sup>29</sup>Si-NMR:** (300 K, 100 MHz, C<sub>6</sub>D<sub>6</sub>) δ [ppm] = -53.79 (Si-central), 5.71 (Si-(CH<sub>3</sub>)<sub>3</sub>).

**EA:** calc. [%] for C<sub>12</sub>H<sub>29</sub>NSi<sub>3</sub> = C 53.06, H 10.76, N 5.16; found C 52.73, H 10.66, N 5.18.

**LIFDI-MS:** m/z = calc. for [C<sub>12</sub>H<sub>29</sub>NSi<sub>3</sub>]<sup>+</sup>: 271.1608 [M]<sup>+</sup>, found 271.1604.

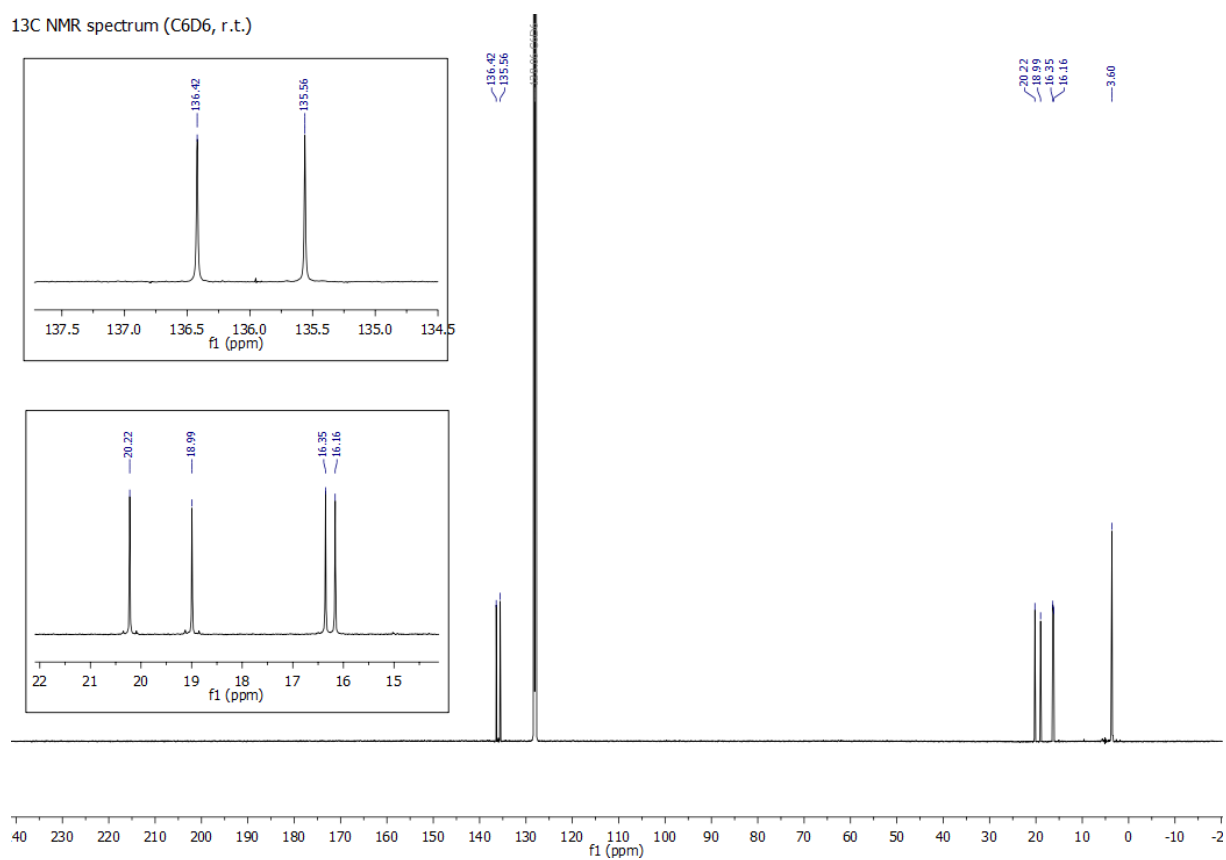
**UV-Vis:** (n-hexane), λ<sub>max</sub> [nm] (ε [Lmol<sup>-1</sup>cm<sup>-1</sup>]): 256 (3902).

$^1\text{H}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , r.t.)



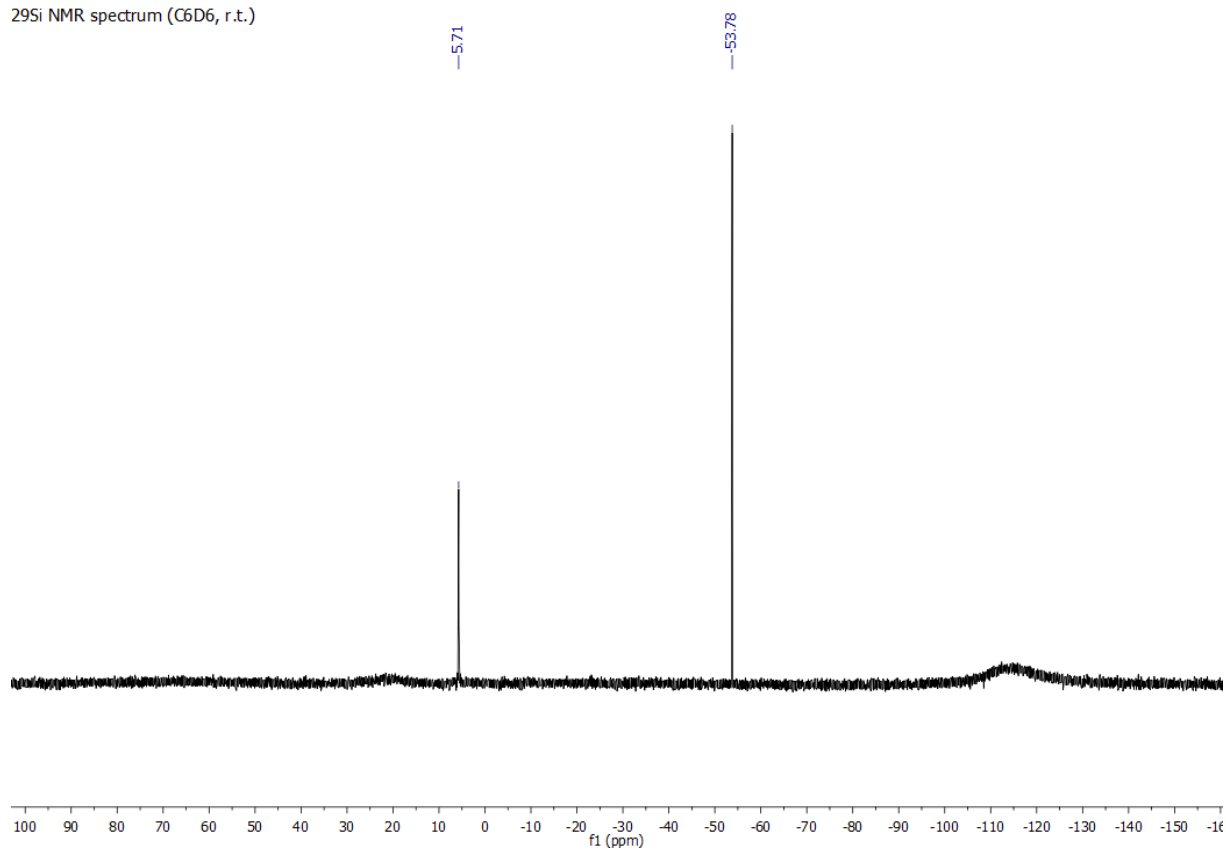
**Figure S4:**  $^1\text{H}$  NMR spectrum of silacyclopropane **2** ( $\text{C}_6\text{D}_6$ , r.t.).

$^{13}\text{C}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , r.t.)

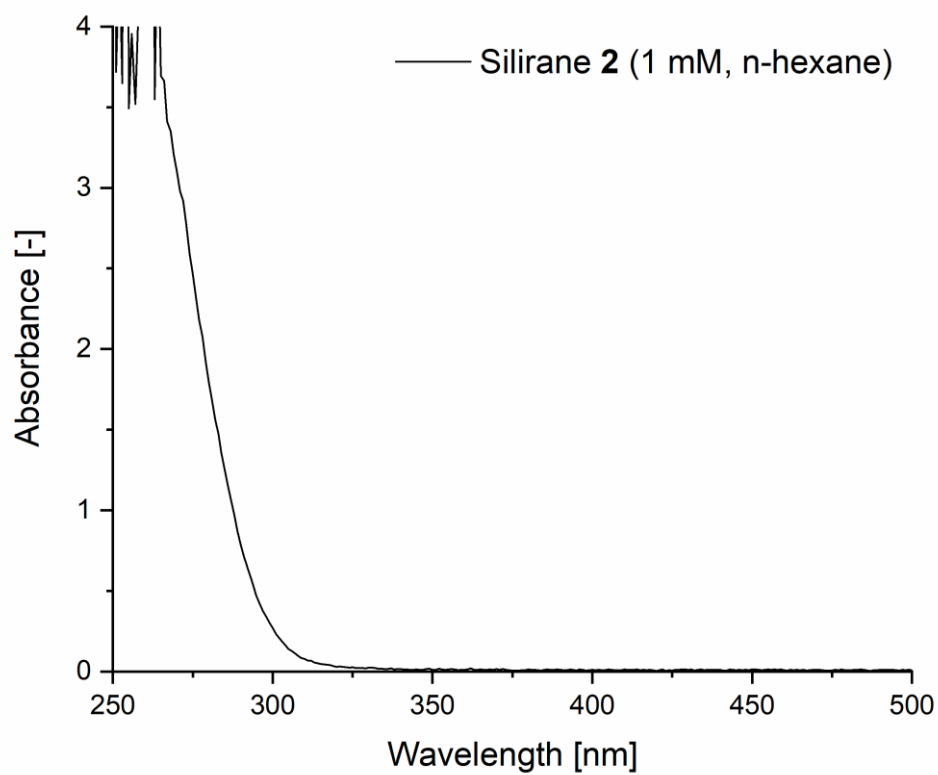


**Figure S5:**  $^{13}\text{C}$  NMR spectrum of silacyclopropane **2** ( $\text{C}_6\text{D}_6$ , r.t.).

$^{29}\text{Si}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , r.t.)

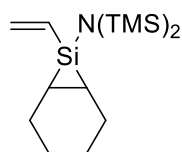


**Figure S6:**  $^{29}\text{Si}$  NMR spectrum of silacyclopropane **2** ( $\text{C}_6\text{D}_6$ , r.t.).



**Figure S7:** UV-VIS spectrum of silacyclopropane **2** (r.t., n-hexane,  $1.0 \times 10^{-3}$  M).

### Synthesis of silacyclopropane 3



Cyclohexene (4.30 g, 52.4 mmol, 30 eq.) was added to a solution of dichlorosilane **1** (500 mg, 1.75 mmol, 1 eq.) in THF (2 mL) at room temperature. The reaction was cooled down to -10 °C and freshly cut pieces of a Lithium/Sodium alloy (969 mg, 137 mmol, 10 eq, 2.5 mol% Na) were added. The mixture was stirred and immediately heated up to 55 °C for 48 h. After completion the solvent was removed *in vacuo* and the crude was resolved in pentane (20 mL). Additional filtration through a microfiber glass filter and a distillation ( $5 \cdot 10^{-2}$  mbar, 120°C), yielded silacyclopropane **3** (180 mg, 0.61 mmol, 35 %) as a colourless liquid. A small portion of not reacted reagent **1** could not be separated by distillation and remained in the product.

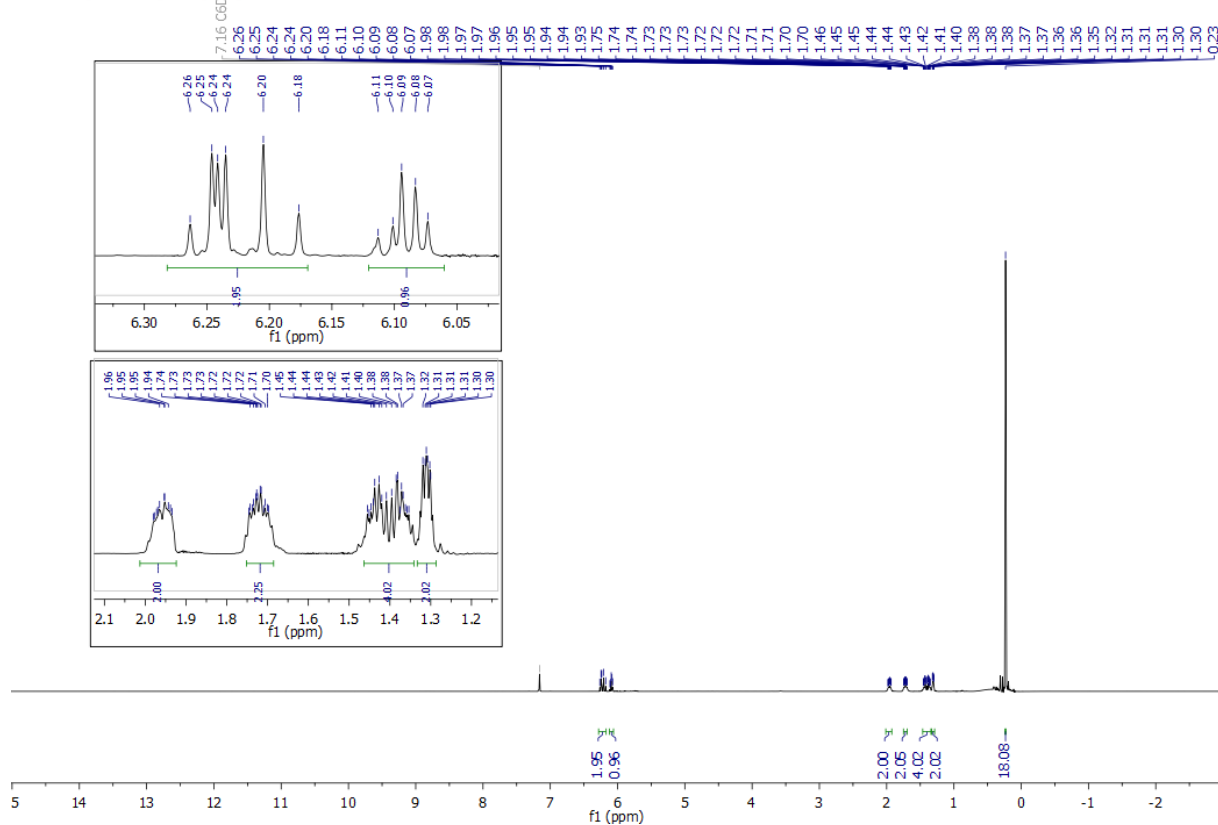
**<sup>1</sup>H-NMR:** (300 K, 500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  [ppm] = 0.23 (s, 18 H, Si-(CH<sub>3</sub>)<sub>3</sub>), 1.30-1.32 (m, 2 H, Si-CH<sub>cyclo</sub>), 1.35-1.46 (m, 4 H, SiCHCH<sub>2</sub>-CH<sub>2</sub>), 1.70-1.75 (m, 2 H, SiCH-CH<sub>2</sub>-CH<sub>2</sub>), 1.93-1.98 (m, 2 H, SiCH-CH<sub>2</sub>-CH<sub>2</sub>), 6.05-6.11 (m, 1 H, Si-CH<sub>vinyl</sub>), 6.18-6.26 (m, 2 H, SiCH-CH<sub>2, vinyl</sub>).

**<sup>13</sup>C-NMR:** (300 K, 125 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  [ppm] = 3.73 (SiNSi-(CH<sub>3</sub>)<sub>3</sub>), 15.83 (Si-CH-CH<sub>2</sub>CH<sub>2</sub>), 21.69 (SiCH-CH<sub>2</sub>-CH<sub>2</sub>), 24.50 (SiCHCH<sub>2</sub>-CH<sub>2</sub>), 134.59 (Si-CH-CH<sub>2, vinyl</sub>), 138.33 (SiCH-CH<sub>2, vinyl</sub>).

**<sup>29</sup>Si-NMR:** (300 K, 100 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  [ppm] = -60.45 (Si<sub>central</sub>), 5.55 (N-Si-(CH<sub>3</sub>)<sub>3</sub>).

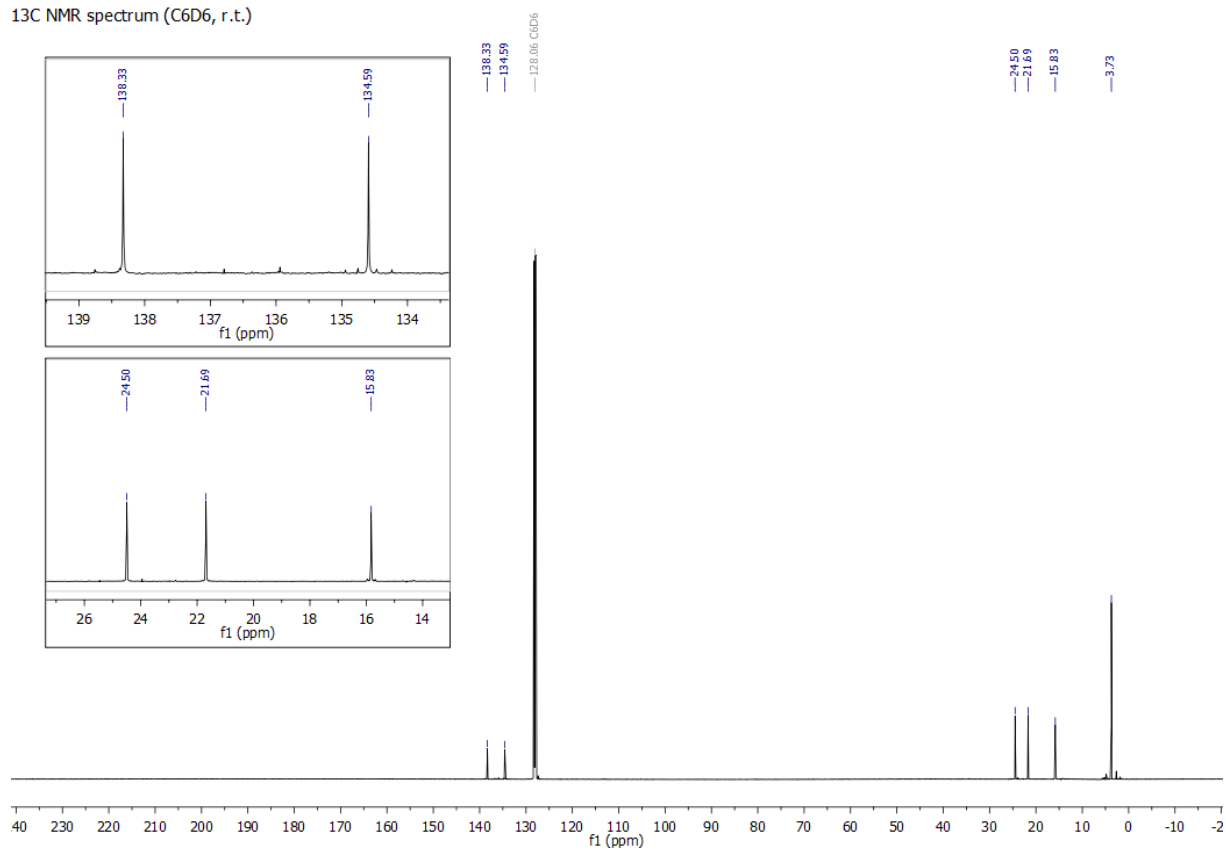
**EA:** calc. [%] for C<sub>12</sub>H<sub>29</sub>NSi<sub>3</sub> = C 56.49, H 10.50, N 4.71; found C 56.03, H 10.86, N 4.99.

<sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>, r.t.)



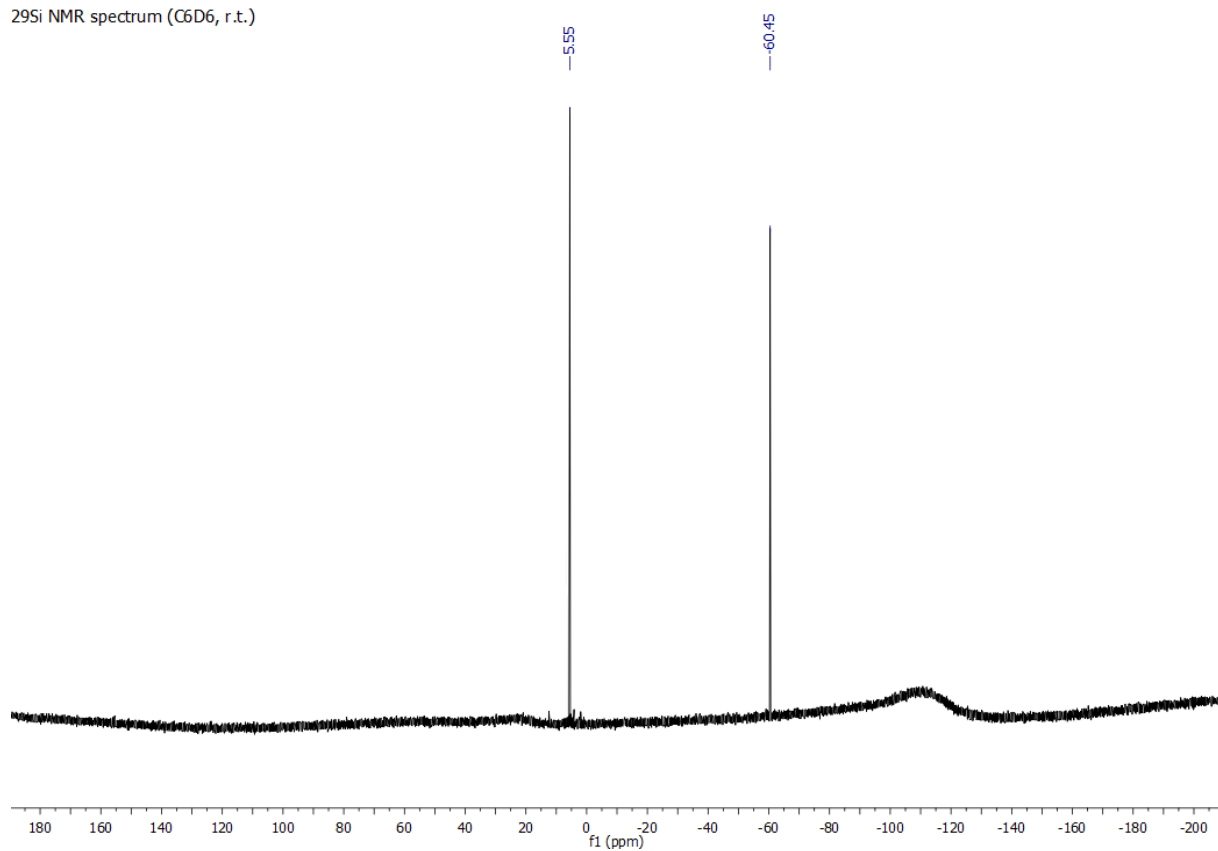
**Figure S8:** <sup>1</sup>H NMR spectrum of silacyclopropane **3** (C<sub>6</sub>D<sub>6</sub>, r.t.).

<sup>13</sup>C NMR spectrum (C<sub>6</sub>D<sub>6</sub>, r.t.)



**Figure S9:** <sup>13</sup>C NMR spectrum of silacyclopropane **3** (C<sub>6</sub>D<sub>6</sub>, r.t.).

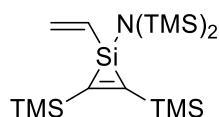
<sup>29</sup>Si NMR spectrum (C<sub>6</sub>D<sub>6</sub>, r.t.)



**Figure S10:** <sup>29</sup>Si NMR spectrum of silacyclopropane **3** (C<sub>6</sub>D<sub>6</sub>, r.t.).



## Synthesis of silacyclopropene 4



Bis-(trimethylsilyl)-acetylene (69.0 mg, 405  $\mu\text{mol}$ , 1.1 eq) was added to a solution of silacyclopropane **2** (100 mg, 368  $\mu\text{mol}$ , 1 eq) in toluene (10 mL). Then 1 mL of a silver-trifluoromethanesulfonate solution (1 mM in toluene) was added as a catalyst. The reaction was stirred at 60 °C for 48 h, while changing to a bright yellow color. The solution was filtrated through an appropriate amount of aluminium oxide ( $\text{Al}_2\text{O}_3$ ) and a syringe filter (PP, 0.5  $\mu\text{m}$ ). Then all volatiles were removed under vacuum, to give silacyclopropene **4** (42.0 mg, 109  $\mu\text{mol}$ , 30 %) as a colourless liquid.

$^1\text{H-NMR}$ : (300 K, 500 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  [ppm] = 0.30 (s, 18H,  $\text{SiNSi}-(\text{CH}_3)_3$ ), 0.31 (s, 18 H,  $\text{SiCSi}-(\text{CH}_3)_3$ ), 5.85-5.87 (m, 1 H,  $\text{Si-CH-CH}_2$ ), 6.03-6.08 (m, 2 H,  $\text{SiCH-CH}_2$ ).

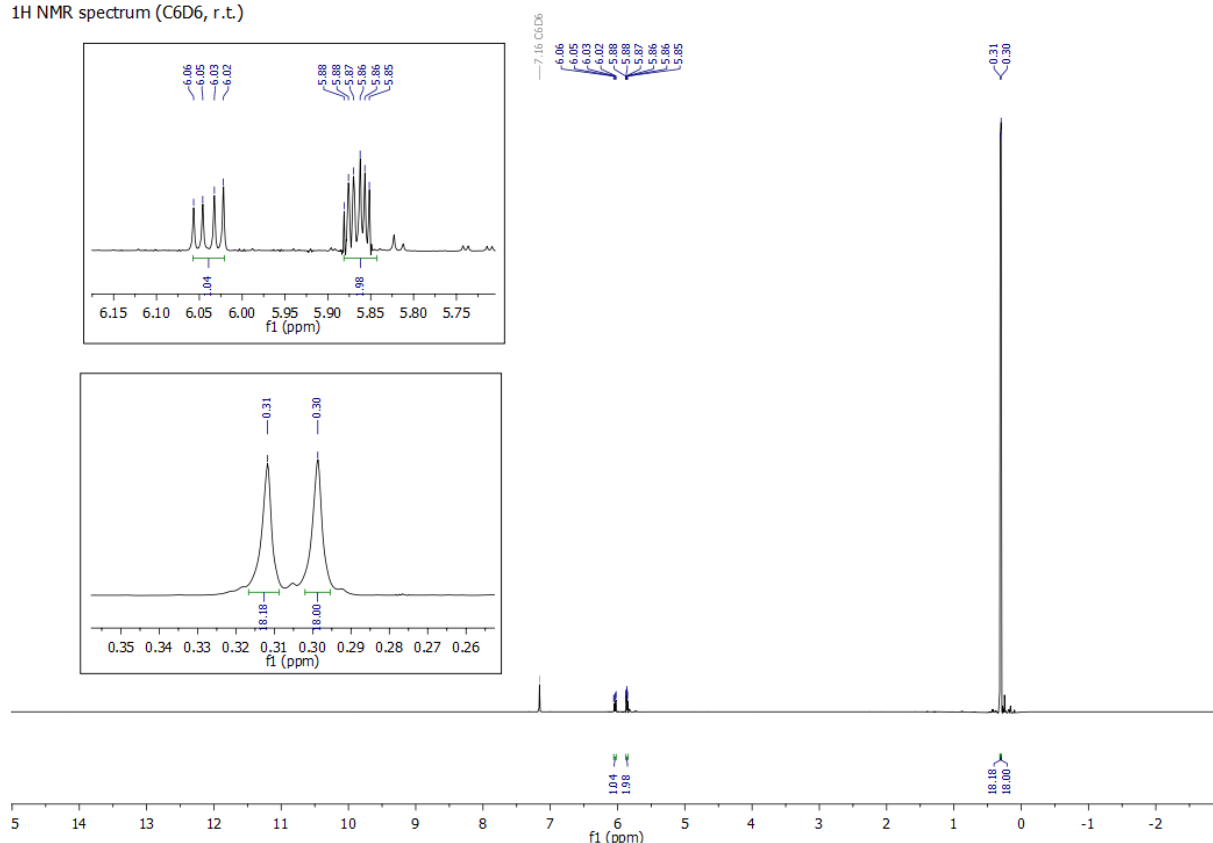
$^{13}\text{C-NMR}$ : (300 K, 125 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  [ppm] = 0.57 (s,  $\text{SiCSi}-(\text{CH}_3)_3$ ), 3.89 (,  $\text{SiNSi}-(\text{CH}_3)_3$ ), 135.64 ( $\text{Si-CH-CH}_2$ ), 140.42 ( $\text{SiCH-CH}_2$ ), 193.94 ( $\text{Si-C-Si}$ ).

$^{29}\text{Si-NMR}$ : (300 K, 100 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  [ppm] = -107.54 ( $\text{Si}_{\text{central}}$ ), -12.47 ( $\text{SiC-Si}-(\text{CH}_3)_3$ ), 4.53 ( $\text{SiN-Si}-(\text{CH}_3)_3$ ).

**LIFDI-MS**:  $m/z$  = calc. for  $[\text{H}_{12}\text{C}_2\text{Si}_1]^+ = 385.1929$  [M] $^+$ , found 385.1916.

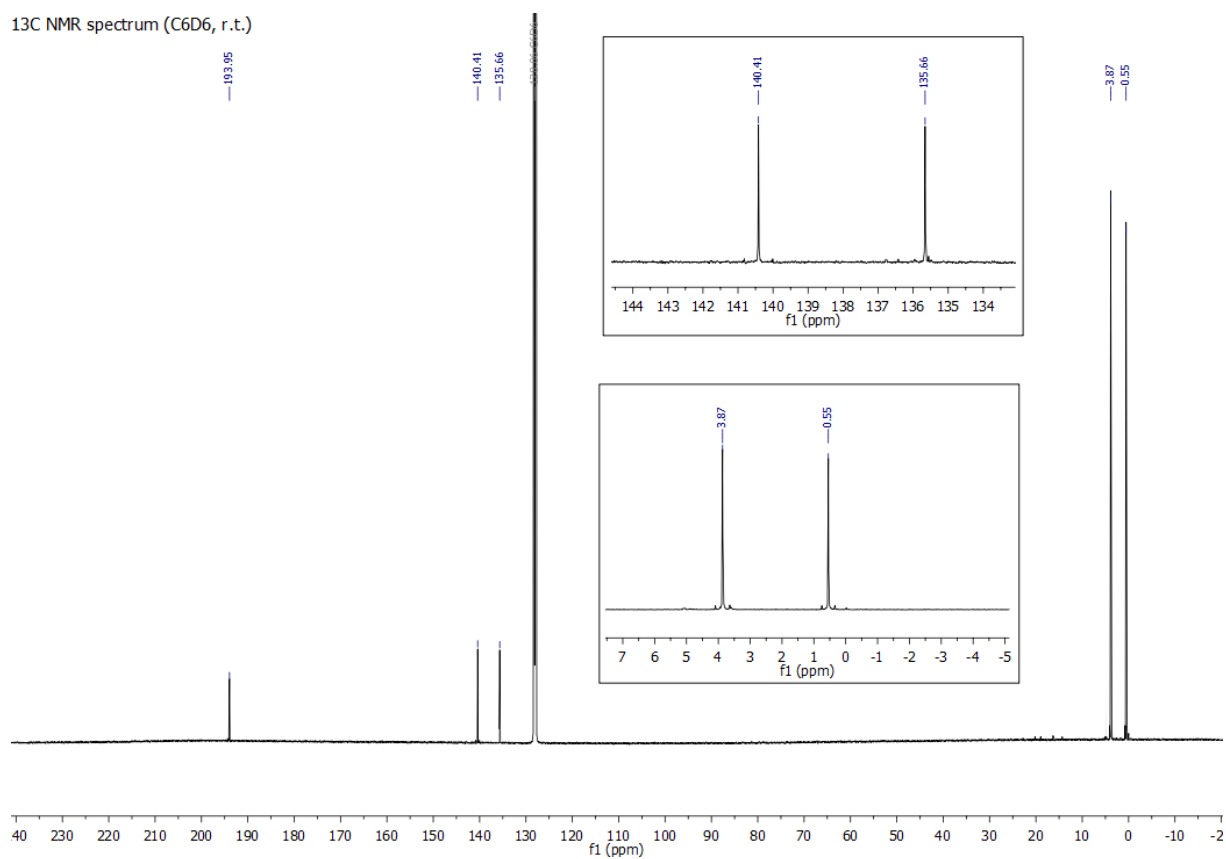
**UV-Vis**: (n-hexane),  $\lambda_{\text{max}}$  [nm] ( $\epsilon$  [ $\text{Lmol}^{-1}\text{cm}^{-1}$ ]): 356 (350).

$^1\text{H NMR}$  spectrum ( $\text{C}_6\text{D}_6$ , r.t.)



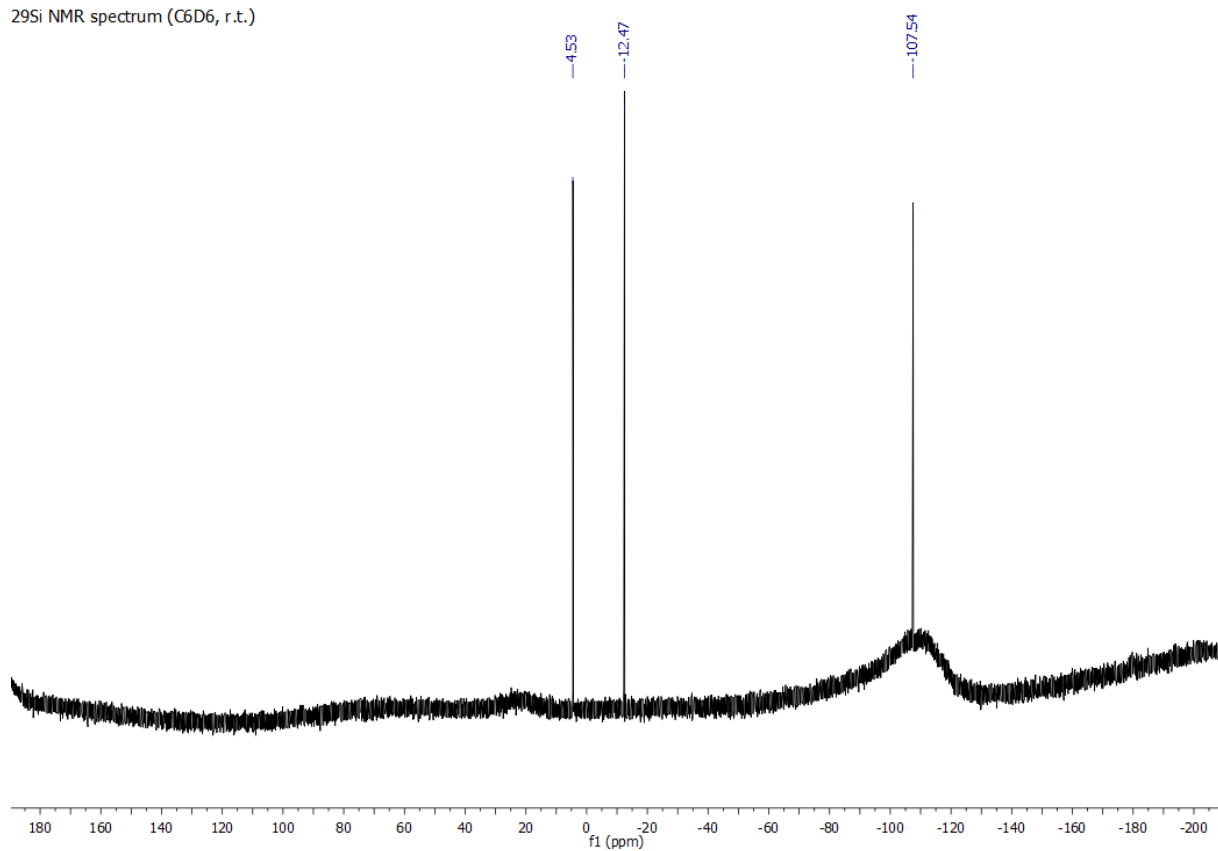
**Figure S11**:  $^1\text{H NMR}$  spectrum of silacyclopropene **4** ( $\text{C}_6\text{D}_6$ , r.t.).

$^{13}\text{C}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , r.t.)

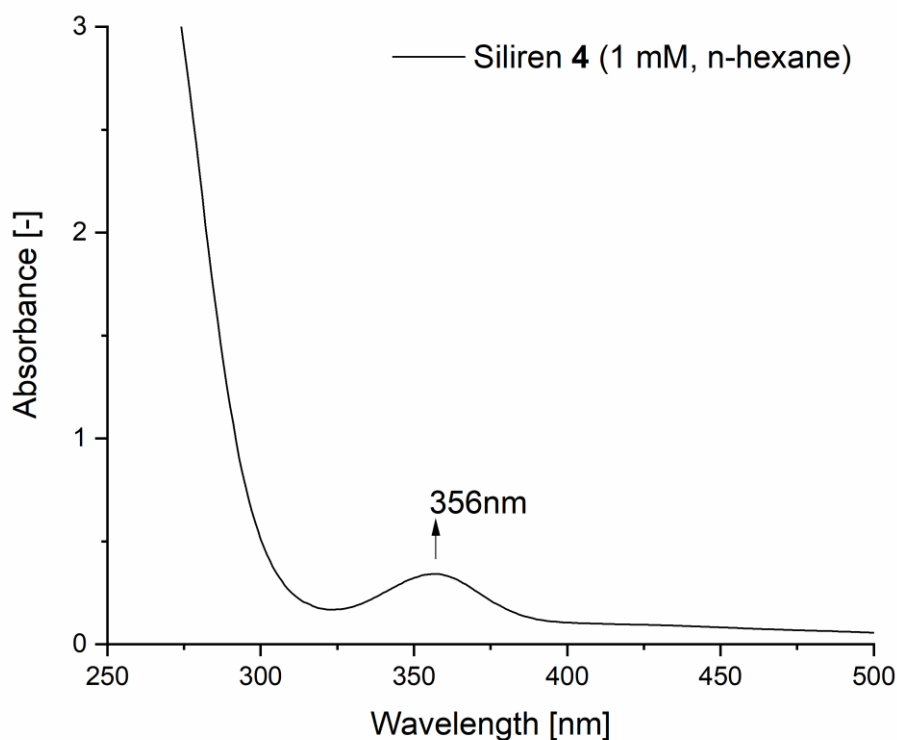


**Figure S12:**  $^{13}\text{C}$  NMR spectrum of silacyclopropene **4** ( $\text{C}_6\text{D}_6$ , r.t.).

$^{29}\text{Si}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , r.t.)

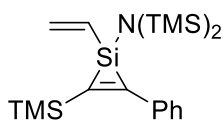


**Figure S13:**  $^{29}\text{Si}$  NMR spectrum of silacyclopropene **4** ( $\text{C}_6\text{D}_6$ , r.t.).



**Figure S14:** UV-VIS spectrum of silacyclopropene **4** (r.t., n-hexane,  $1.0 \times 10^{-3}$  M).

### Synthesis of silacyclopropene **5**



1-Phenyl-2-trimethyl-silylacetylene (1.11 g, 6.36 mmol, 1.2 eq) was added to a solution of silacyclopropane **2** (1.44 g, 5.30 mmol, 1 eq) in 20 mL toluene. After stirring for 16 h at 100 °C, the reaction was filter through a syringe filter (PP, 0.5  $\mu$ m). The volatiles were removed under vacuum. Then the residue was purified by a distillation under high vacuum ( $5 \cdot 10^{-5}$  mbar, 120 °C) to yield silacyclopropene **5** (1.50 g, 78 mmol, 72.5 %) as a colourless liquid.

**$^1\text{H-NMR}$ :** (300 K, 500 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  [ppm] = 0.27 (s, 18 H,  $\text{NSi}-(\text{CH}_3)_3$ ), 0.31 (s, 9 H,  $\text{SiCSi}-(\text{CH}_3)_3$ ), 6.00-6.08 (m, 2 H,  $\text{SiCH-CH}_2$ ), 6.10-6.14 (m, 1 H,  $\text{Si-CH-CH}_2$ ), 7.04-7.07 (m, 1 H,  $\text{CH}_{\text{arm}/\text{para}}$ ), 7.19-7.23 (m, 2 H,  $\text{CH}_{\text{arm}/\text{meta}}$ ), 7.47-7.50 (m, 2 H,  $\text{CH}_{\text{arm}/\text{ortho}}$ ).

**$^{13}\text{C-NMR}$ :** (300 K, 125 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  [ppm] = 0.50 ( $\text{SiCSi}-(\text{CH}_3)_3$ ), 3.63 ( $\text{NSi}-(\text{CH}_3)_3$ ), 128.16 ( $\text{CH}_{\text{arm}/\text{ortho}}$ ), 128.35 ( $\text{CH}_{\text{arm}/\text{meta}}$ ), 128.57 ( $\text{SiC-C}_{\text{arm}}-\text{CH}$ ), 136.96 ( $\text{Si-CH-CH}_2$ ), 138.22 ( $\text{CH}_{\text{arm}/\text{para}}$ ), 139.09 ( $\text{SiCH-CH}_2$ ), 167.22 ( $\text{Si-C-Si}(\text{CH}_3)_3$ ), 182.36 ( $\text{Si-C-C}_{\text{arm}}$ ).

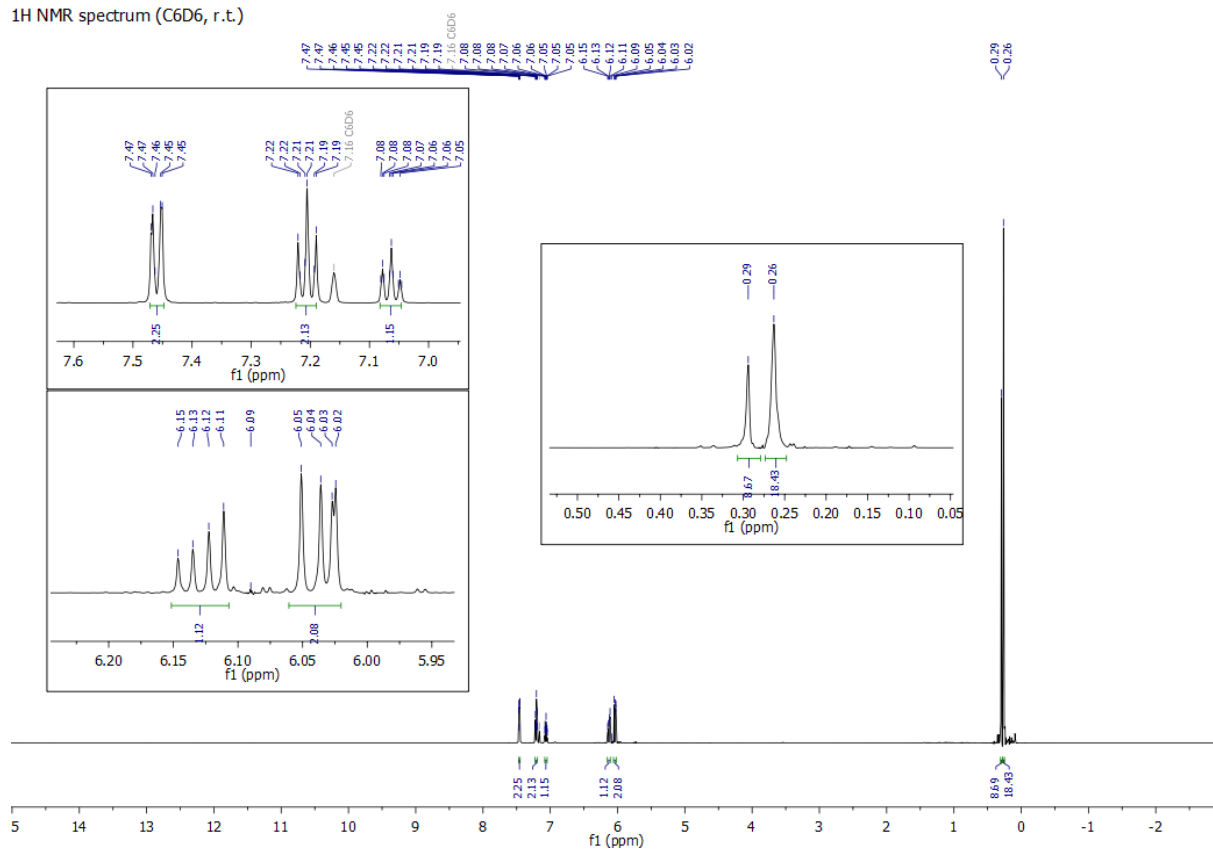
**$^{29}\text{Si-NMR}$ :** (300 K, 100 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  [ppm] = -97.51 (*Si*-central), -12.74 ( $\text{SiC-Si}-(\text{CH}_3)_3$ ), 4.44 (*N-Si*- $(\text{CH}_3)_3$ ).

**EA:** calc. [%] for  $\text{C}_{19}\text{H}_{35}\text{NSi}_4$  = C 58.54, H 9.05, N 3.59; found C 58.54, H 9.09, N 3.74.

**LIFDI-MS:**  $m/z$  = calc. for  $[\text{C}_8\text{H}_{21}\text{Cl}_2\text{NSi}_3]^+ = 389.1847$  [M] $^+$ , found 389.1859.

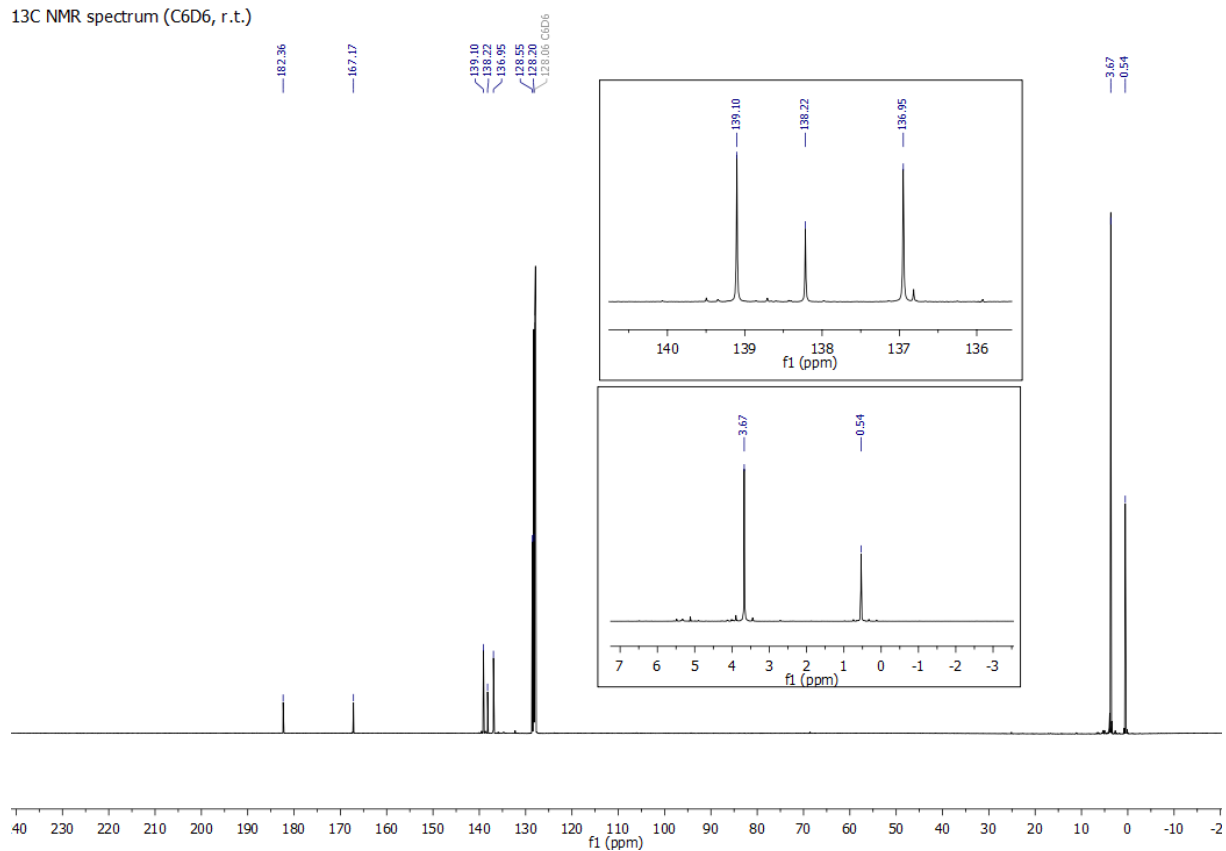
**UV-Vis:** (n-hexane),  $\lambda_{\text{max}}$  [nm] ( $\epsilon$  [ $\text{Lmol}^{-1}\text{cm}^{-1}$ ]): 323 (1850).

$^1\text{H}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , r.t.)



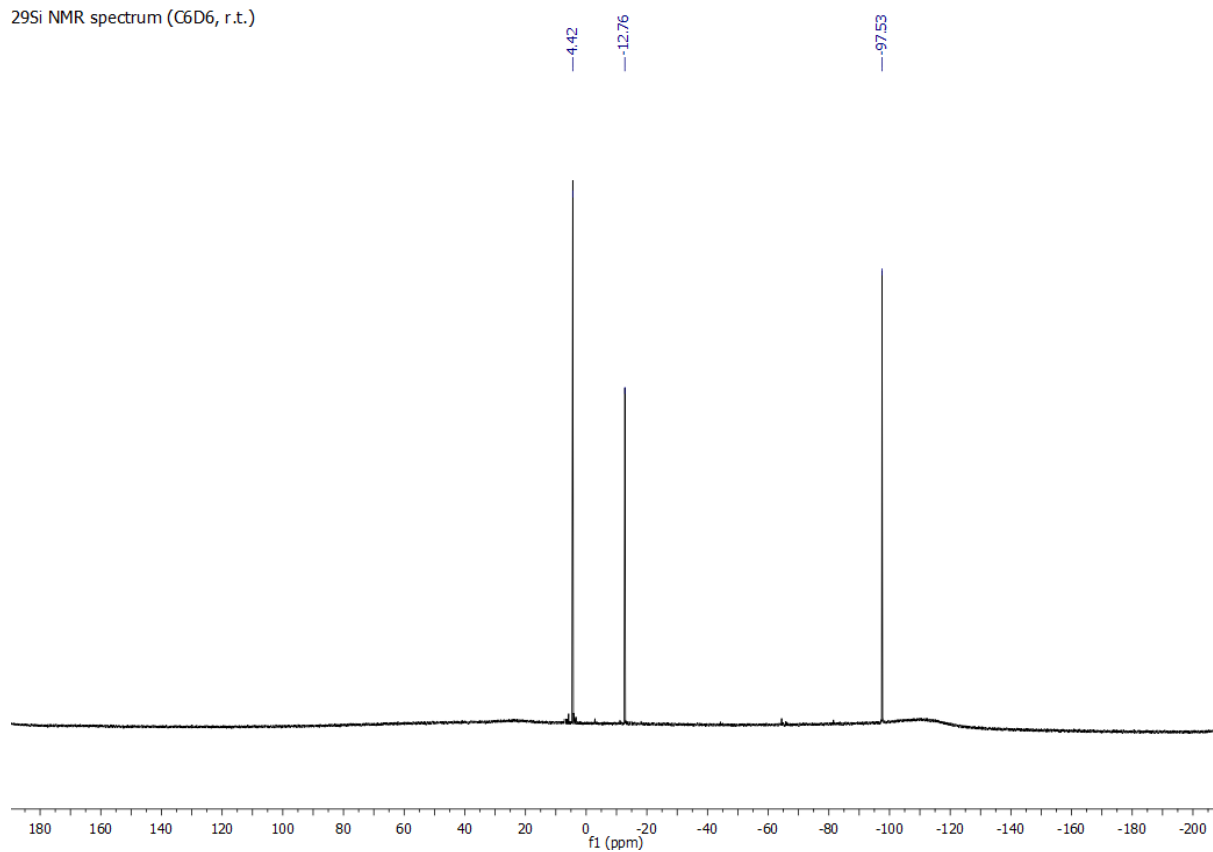
**Figure S15:**  $^1\text{H}$  NMR spectrum of silacyclopropene **5** ( $\text{C}_6\text{D}_6$ , r.t.).

$^{13}\text{C}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , r.t.)

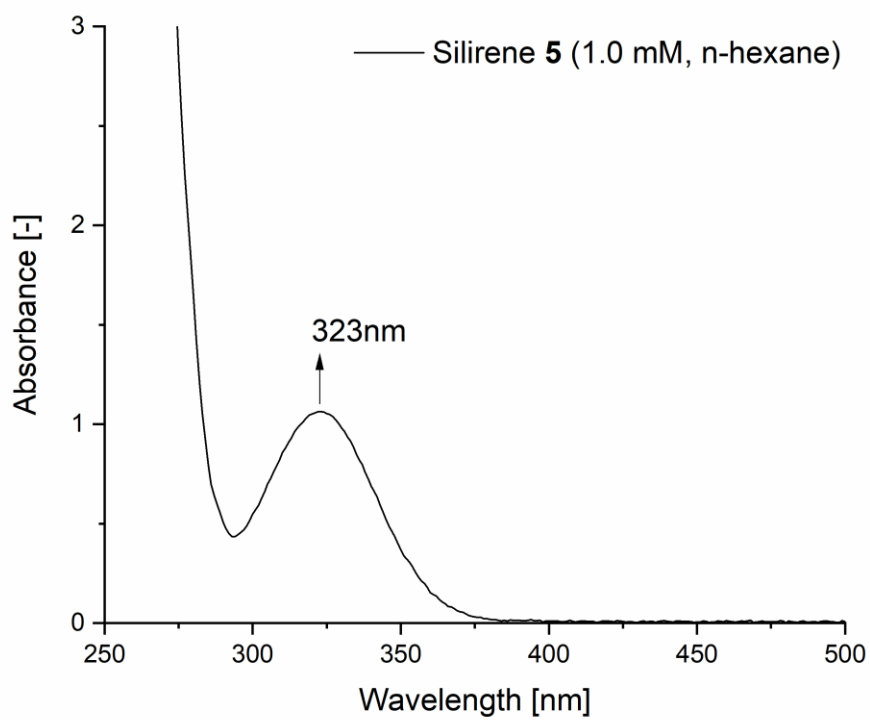


**Figure S16:**  $^{13}\text{C}$  NMR spectrum of silacyclopropene **5** ( $\text{C}_6\text{D}_6$ , r.t.).

$^{29}\text{Si}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , r.t.)

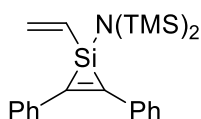


**Figure S17:**  $^{29}\text{Si}$ -ig NMR spectrum of silacyclopropene **5** ( $\text{C}_6\text{D}_6$ , r.t.).



**Figure S18:** UV-VIS spectrum of silacyclopropene **4** (r.t., n-hexane,  $1.0 \times 10^{-3}$  M).

## Synthesis of silacyclopropene 6



Diphenylacetylene (72.2 mg, 405  $\mu\text{mol}$ , 1.1 eq) was added to a solution of silacyclopropane **2** (100 mg, 368  $\mu\text{mol}$ , 1 eq) in toluene (10 mL). The reaction was stirred at 100 °C for 24 h, while changing to a yellowish color. The solution was filtrated through an appropriate amount of aluminium oxide ( $\text{Al}_2\text{O}_3$ ) and a syringe filter (PP, 0.5  $\mu\text{m}$ ). Then all volatiles were removed under vacuum, to give silacyclopropene **6** (79.1 mg, 200  $\mu\text{mol}$ , 55 %) as colourless crystals.

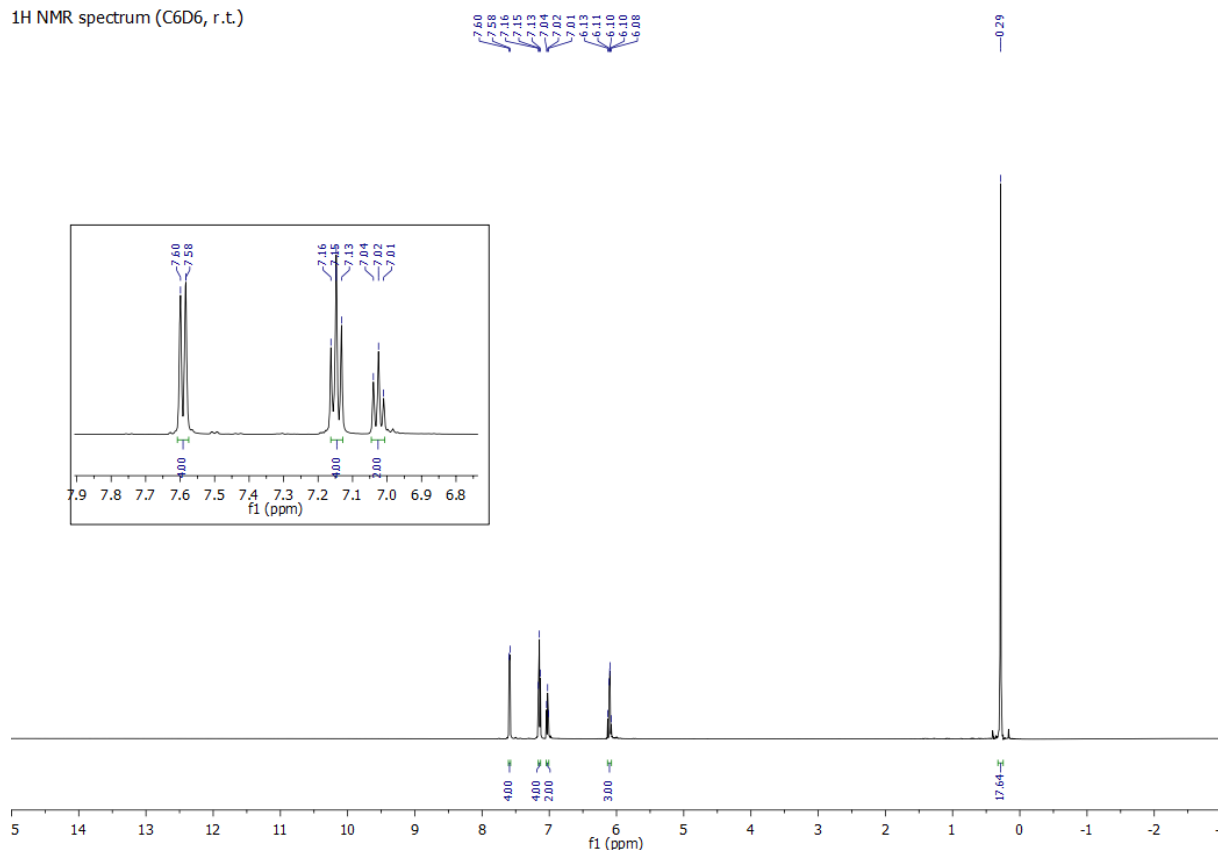
**$^1\text{H-NMR}$ :** (300 K, 500 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  [ppm] = 0.29 (s, 18H,  $\text{SiNSi}-(\text{CH}_3)_3$ ), 6.08-6.10 (m, 2 H,  $\text{SiCH-CH}_{2,\text{vinyl}}$ ), 6.12-6.13 (m, 1 H,  $\text{Si-CH-CH}_2$ ), 7.01-7.04 (m, 2 H,  $\text{CH}_{\text{arm}/\text{para}}$ ), 7.15 (t, 4 H,  $^3J_{\text{HH}} = 7.7$   $\text{CH}_{\text{arm}/\text{meta}}$ ), 7.58 (d, 4 H,  $^3J_{\text{HH}} = 7.7$  Hz,  $\text{CH}_{\text{arm}/\text{ortho}}$ ).

**$^{13}\text{C-NMR}$ :** (300 K, 125 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  [ppm] = 3.62 ( $\text{SiNSi}-(\text{CH}_3)_3$ ), 123.88 ( $\text{CH}_{\text{arm}/\text{para}}$ ), 127.73 ( $\text{CH}_{\text{arm}/\text{meta}}$ ), 128.82 ( $\text{CH}_{\text{arm}/\text{ortho}}$ ), 136.32 ( $\text{SiC-C}_{\text{arm}}-\text{CH}_{\text{arm}}$ ), 137.82 ( $\text{Si-CH-CH}_2$ ), 137.99 ( $\text{SiCH-CH}_2$ ), 159.24 ( $\text{Si-C-C}_{\text{arm}}$ ).

**$^{29}\text{Si-NMR}$ :** (300 K, 100 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  [ppm] = -96.18 ( $\text{Si}_{\text{central}}$ ), 4.41 ( $\text{SiN-Si}-(\text{CH}_3)_3$ )

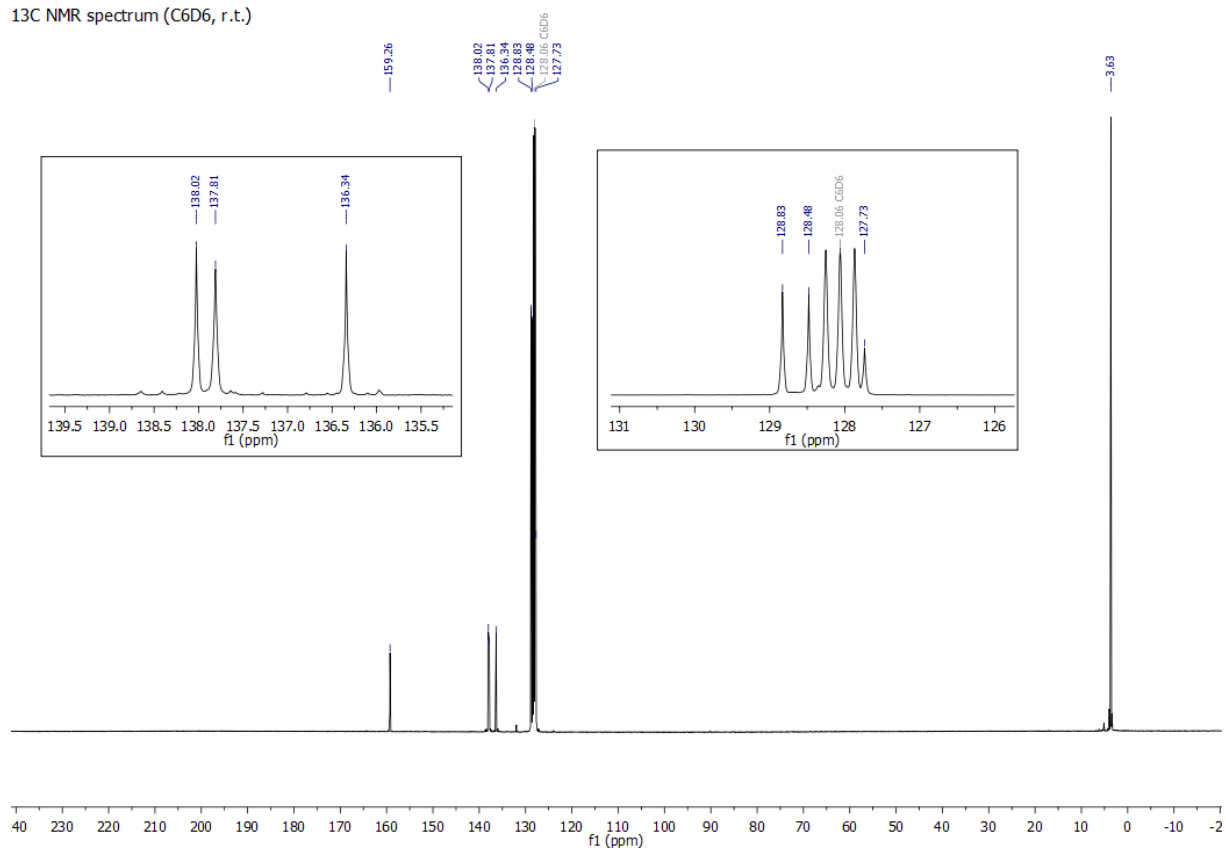
**LIFDI-MS:**  $m/z = \text{calc. for } [\text{H}_{12}\text{C}_2\text{Si}_1]^+ = 393.1764$  [M] $^+$ , found 393.1757.

$^1\text{H NMR}$  spectrum ( $\text{C}_6\text{D}_6$ , r.t.)



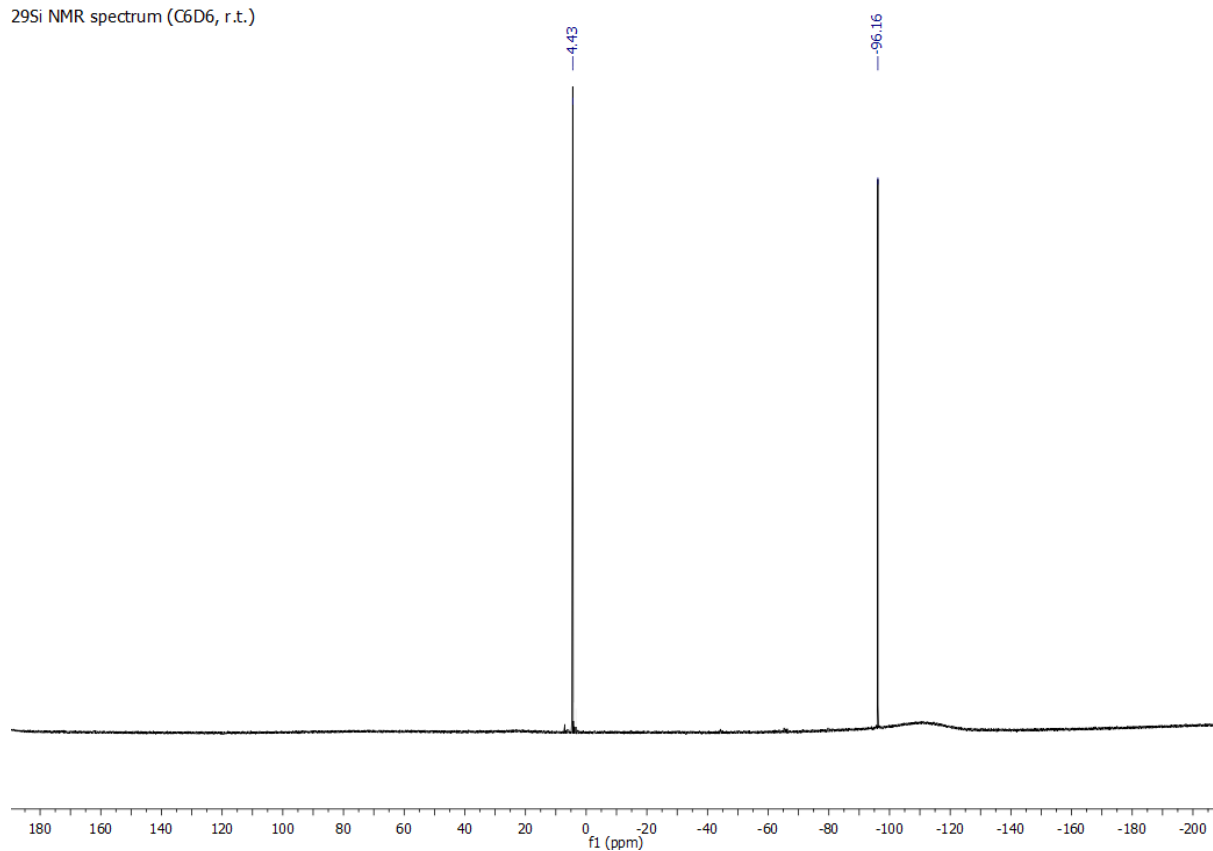
**Figure S19:**  $^1\text{H NMR}$  spectrum of silacyclopropene **6** ( $\text{C}_6\text{D}_6$ , r.t.).

$^{13}\text{C}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , r.t.)



**Figure S20:**  $^{13}\text{C}$  NMR spectrum of silacyclopropene **6** ( $\text{C}_6\text{D}_6$ , r.t.).

$^{29}\text{Si}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , r.t.)

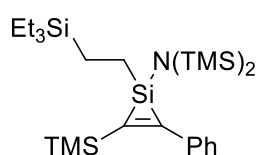


**Figure S21:**  $^{29}\text{Si}$ -ig NMR spectrum of silacyclopropene **6** ( $\text{C}_6\text{D}_6$ , r.t.).

### c) Substrate Functionalization

**Procedure for the hydrosilylation of silacyclopropene 5 with triethylsilane with catalysts of I – IV**  
Silacyclopropene **5** (100 mg, 256  $\mu\text{mol}$ , 1 eq) was added to a solution of triethylsilane (30.6 mg, 256  $\mu\text{mol}$ , 1 eq) in benzene (5 mL). Then 0.13  $\mu\text{mol}$  of the respective catalyst (**I-IV**)<sup>(53)</sup> was added, and the mixture was stirred at RT or 65 °C for 24 h. All volatiles were removed under vacuum and the residue was redissolved in pentane (5 mL). The reaction was monitored by  $^1\text{H-NMR}$  and  $^{29}\text{Si-NMR}$ . The product was purified by filtration through an appropriate amount of aluminium oxide ( $\text{Al}_2\text{O}_3$ ) and a syringe filter (PP, 0.5  $\mu\text{m}$ ) to remove the applied catalyst.

#### Functionalization of triethylsilane and characterization of **7**



Silacyclopropene **5** (100 mg, 256  $\mu\text{mol}$ , 1 eq) was added to a solution of triethylsilane (30.6 mg, 256  $\mu\text{mol}$ , 1 eq) in benzene (5 mL). Then 2.0 mg (0.24  $\mu\text{mol}$ ) of a Karstead-catalyst solution (2.25 wt.% Pt in xylene) was added, and the mixture was stirred at 65 °C for 12 h. The colour of the reaction changes from a bright yellow to a dark gold/brown over the time. All volatiles were removed under vacuum and the residue was redissolved in pentane (5 mL). The product was purified by filtration through an appropriate amount of aluminium oxide ( $\text{Al}_2\text{O}_3$ ) and a syringe filter (PP, 0.5  $\mu\text{m}$ ) to remove the applied catalyst. Further distillation under high vacuum ( $3 \cdot 10^{-5}$  mbar, 140 °C) result in the functionalized compound **7** (90.8 mg, 179  $\mu\text{mol}$ , 70 %) as a colourless liquid.

**$^1\text{H-NMR}$ :** (300 K, 500 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  [ppm] = 0.28 (s, 18 H,  $\text{NSi}-(\text{CH}_3)_3$ ), 0.33 (s, 9 H,  $\text{SiCSi}-(\text{CH}_3)_3$ ), 0.55 (q, 6 H,  $^3J_{\text{HH}} = 7.9$  Hz,  $\text{Si}(\text{CH}_2-\text{CH}_3)_3$ ), 0.59-0.60 (m, 2 H,  $\text{NSi}-\text{CH}_2-\text{CH}_2\text{Si}$ ), 0.93-0.96 (m, 2 H,  $\text{NSi}-\text{CH}_2-\text{CH}_2\text{Si}$ ), 0.99 (t, 9 H,  $^3J_{\text{HH}} = 7.9$  Hz,  $\text{Si}(\text{CH}_2-\text{CH}_3)_3$ ), 7.00-7.04 (m, 2 H,  $\text{CH}_{\text{arm/meta}}$ ), 7.10-7.15 (m, 2 H,  $\text{CH}_{\text{arm/ortho}}$ ), 7.21-7.28 (m, 1 H,  $\text{CH}_{\text{arm/para}}$ ).

**$^{13}\text{C-NMR}$ :** (300 K, 125 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  [ppm] = 0.7 ( $\text{SiCSi}-(\text{CH}_3)_3$ ), 3.33 ( $\text{Si}(\text{CH}_2-\text{CH}_3)_3$ ), 3.78 ( $\text{NSi}-(\text{CH}_3)_3$ ), 5.22 ( $\text{NSi}-\text{CH}_2-\text{CH}_2\text{Si}$ ), 7.83 ( $\text{Si}(\text{CH}_2-\text{CH}_3)_3$ ), 10.71 ( $\text{NSi}-\text{CH}_2-\text{CH}_2\text{Si}$ ), 127.6 ( $\text{CH}_{\text{arm/para}}$ ), 128.4 ( $\text{CH}_{\text{arm/meta}}$ ), 128.6 ( $\text{CH}_{\text{arm/ortho}}$ ), 139.2 ( $\text{SiC}-\text{C}_{\text{arm}}$ ), 168.2 ( $\text{Si}-\text{C}-\text{C}_{\text{arm}}$ ), 183.2 ( $\text{Si}-\text{C}-\text{Si}$ ).

**$^{29}\text{Si-NMR}$ :** (300 K, 100 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  [ppm] = -80.98 ( $\text{Si}_{\text{silirene}}$ ), -13.21 ( $\text{SiC}-\text{Si}-(\text{CH}_3)_3$ ), 3.35 ( $\text{N}-\text{Si}-(\text{CH}_3)_3$ ), 7.84 ( $\text{CH}_2-\text{Si}-(\text{CH}_2\text{CH}_3)_3$ ).

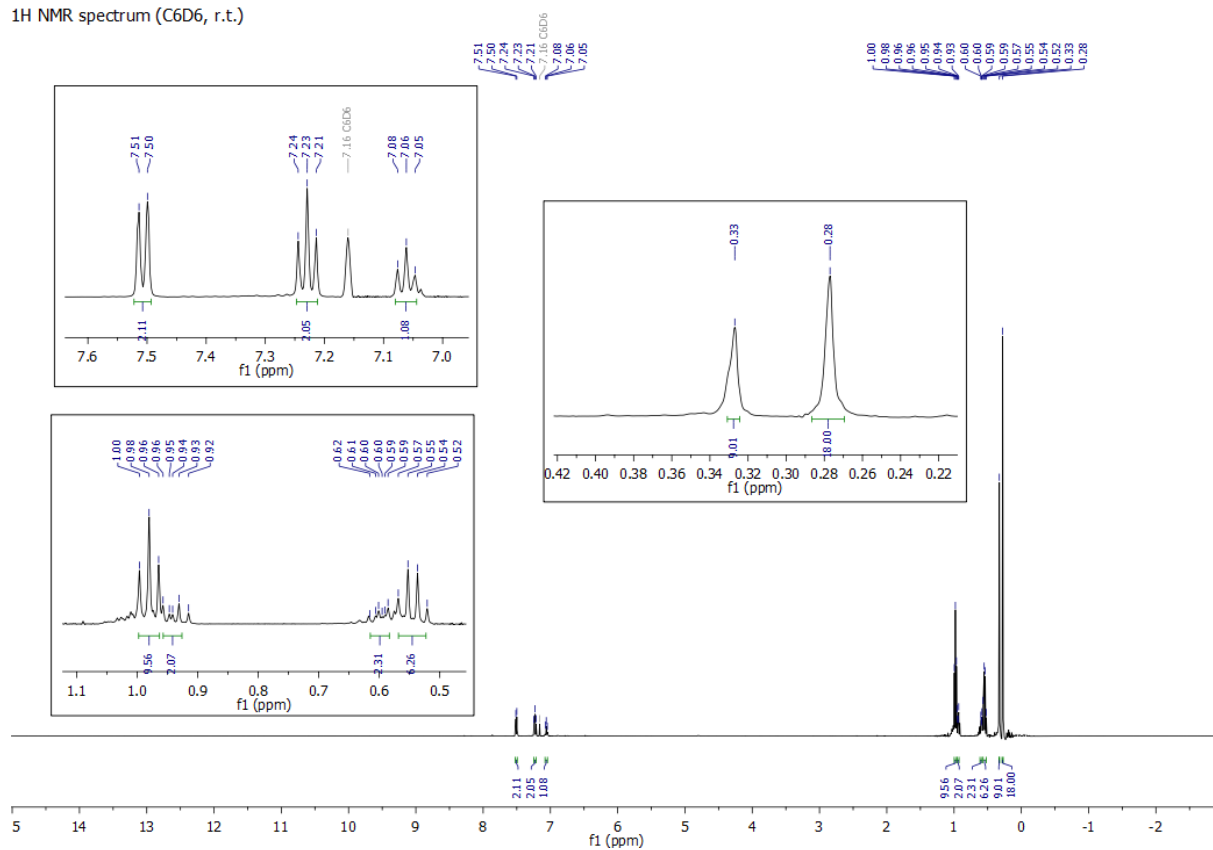
**EA:** calc. [%] for  $\text{C}_{25}\text{H}_{51}\text{NSi}_5$  = C 59.33, H 10.16, N 2.77; found C 59.01, H 10.31, N 2.79.

**LIFDI-MS:**  $m/z$  = calc. for  $[\text{C}_{25}\text{H}_{51}\text{NSi}_5]^+$ : 505.2868 [M]<sup>+</sup>, found 505.2867.

**UV-Vis:** (n-hexane),  $\lambda_{\text{max}}$  [nm] ( $\epsilon$  [ $\text{Lmol}^{-1}\text{cm}^{-1}$ ]): 316 (1862).

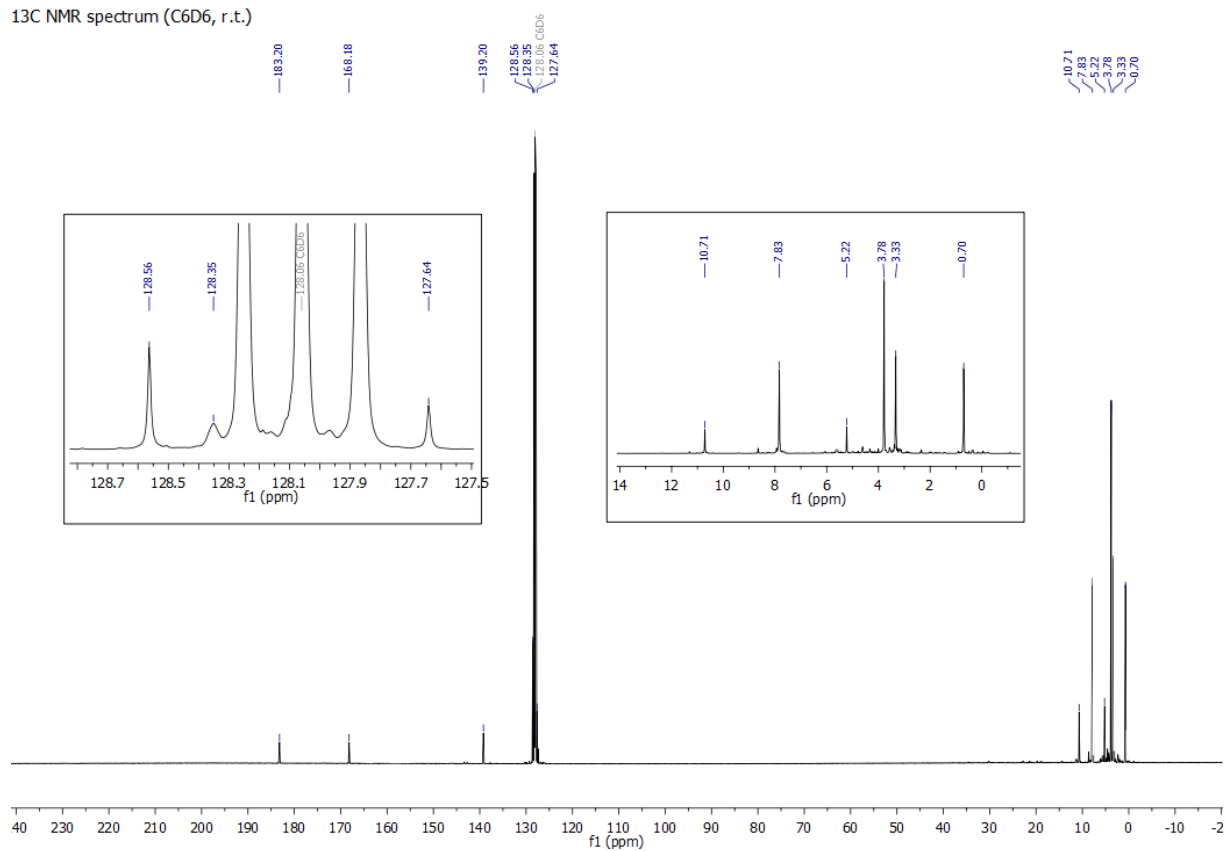


**1H NMR spectrum (C6D6, r.t.)**



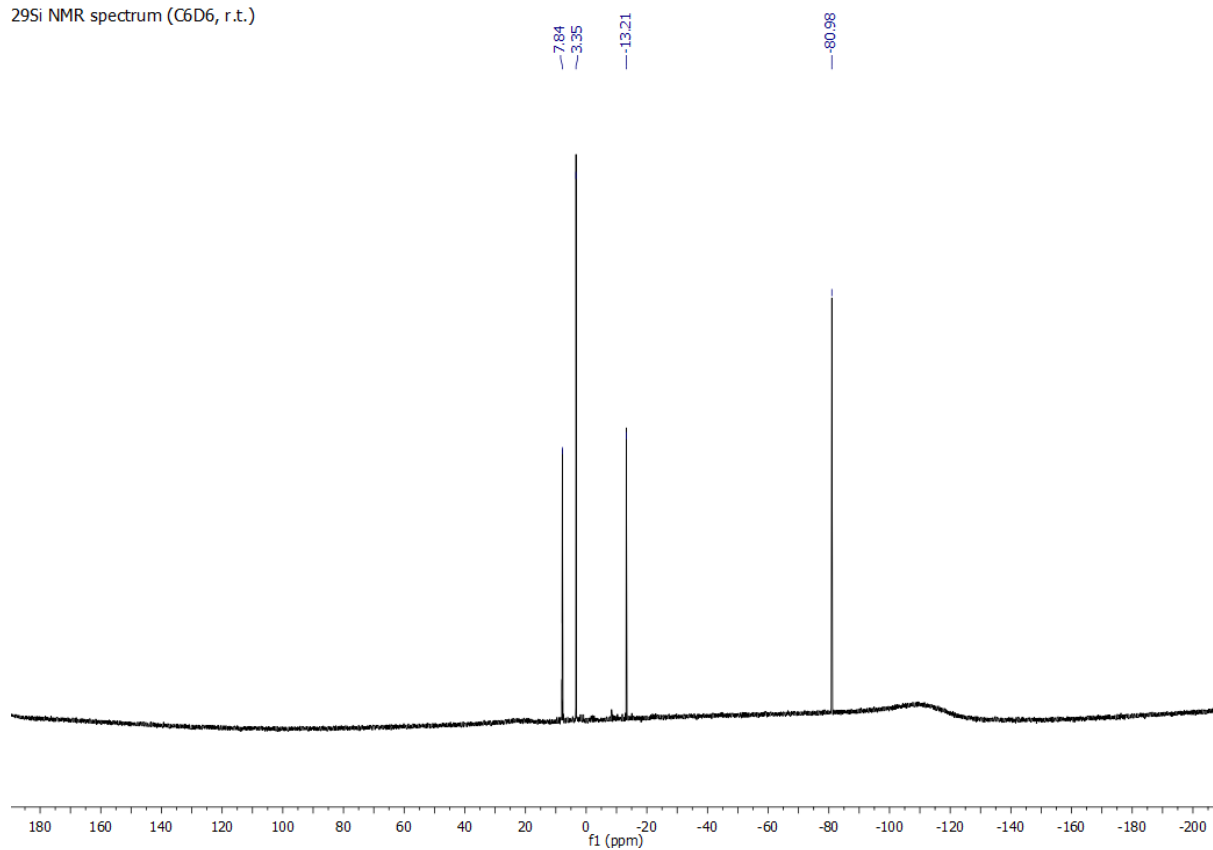
**Figure S22:** <sup>1</sup>H-NMR spectrum of silacyclopropene **7** (C<sub>6</sub>D<sub>6</sub>, r.t.).

**<sup>13</sup>C NMR spectrum (C6D6, r.t.)**

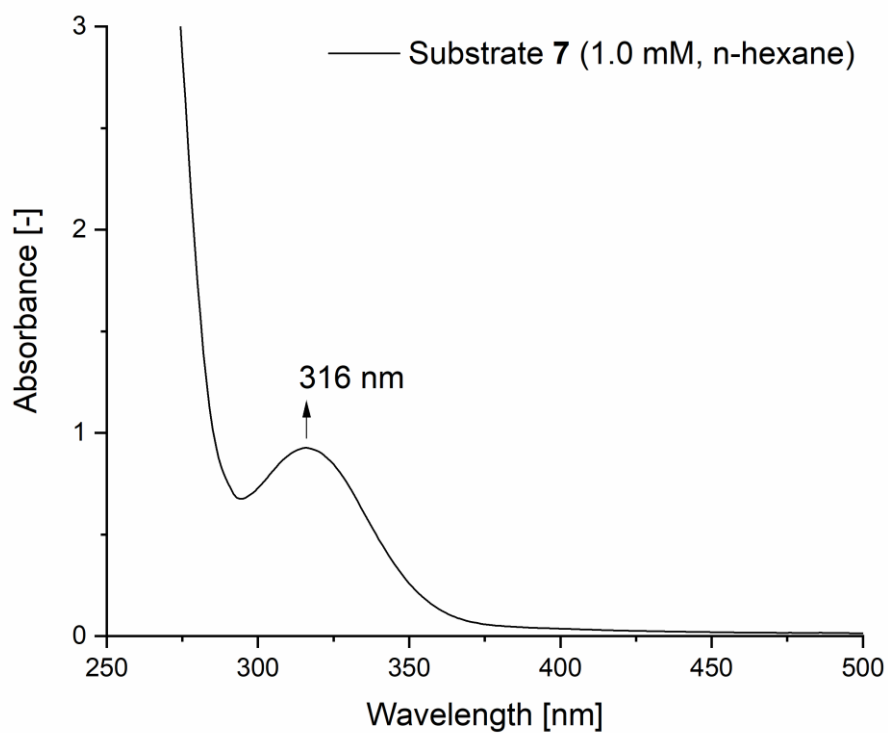


**Figure S23:** <sup>13</sup>C-NMR spectrum of silacyclopropene **7** (C<sub>6</sub>D<sub>6</sub>, r.t.).

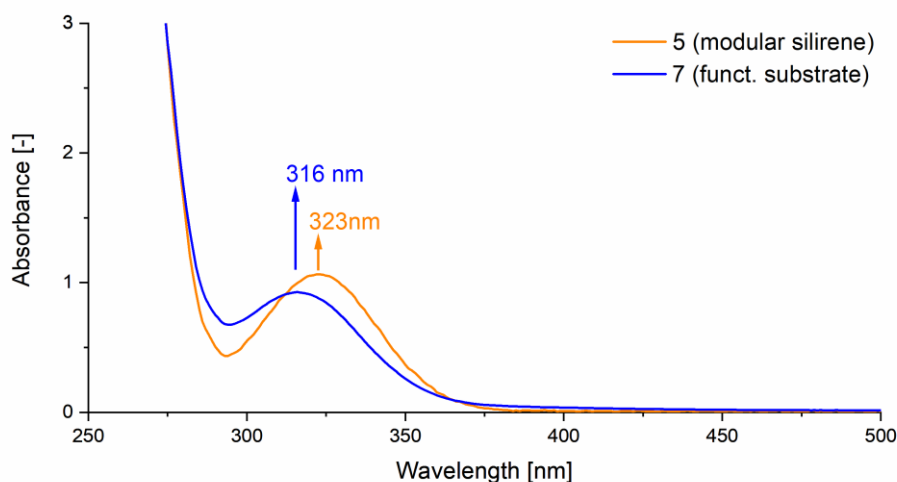
$^{29}\text{Si}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , r.t.)



**Figure S24:**  $^{29}\text{Si}$ -ig NMR spectrum of silacyclopropene **7** ( $\text{C}_6\text{D}_6$ , r.t.).

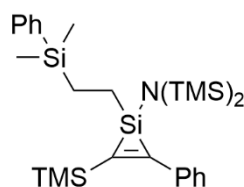


**Figure S25:** UV-VIS spectrum of silacyclopropene **7** (r.t., n-hexane,  $1.0 \times 10^{-3}$  M).



**Figure S26:** UV-VIS spectra of modular silacyclopropene **5** (orange) and functionalized substrate **7** (blue), (r.t., n-hexane,  $1.0 \times 10^{-3}$  M).

### Functionalization of dimethylphenylsilane and characterization of **8**



Silacyclopropene **5** (100 mg, 256  $\mu\text{mol}$ , 1 eq) was added to a solution of dimethylphenylsilane (35.0 mg, 256  $\mu\text{mol}$ , 1 eq) in benzene (5 mL). Then 2.0 mg (0.24  $\mu\text{mol}$ ) of a Karstead-catalyst solution (2.25 wt.% Pt in xylene) was added, and the mixture was stirred at 65  $^{\circ}\text{C}$  for 12 h. The colour of the reaction changes from a bright yellow to a dark gold/brown over the time. All volatiles were removed under vacuum and the residue was redissolved in pentane (5 mL). The product was purified by filtration through an appropriate amount of aluminium oxide ( $\text{Al}_2\text{O}_3$ ) and a syringe filter (PP, 0.5  $\mu\text{m}$ ) to remove the applied catalyst. Further distillation under high vacuum ( $3 \cdot 10^{-5}$  mbar, 110  $^{\circ}\text{C}$ ) result in the functionalized compound **8** (112 mg, 212  $\mu\text{mol}$ , 83 %) as a colourless liquid.

**$^1\text{H-NMR}$ :** (300 K, 500 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  [ppm] = 0.23 (s, 18 H,  $\text{NSi}-(\text{CH}_3)_3$ ), 0.26 (s, 6 H,  $\text{PhSi}-(\text{CH}_3)_2$ ), 0.32 (s, 9 H,  $\text{SiCSi}-(\text{CH}_3)_3$ ), 0.78-0.83 (m, 2 H,  $\text{NSi-CH}_2-\text{CH}_2\text{Si}$ ), 1.10-1.17 (m, 1 H,  $\text{NSi-CH}_2-\text{CH}_2\text{Si}$ ), 1.24-1.31 (m, 1 H,  $\text{NSi-CH}_2-\text{CH}_2\text{Si}$ ), 7.19-7.24 (m, 6 H,  $\text{CH}_{\text{arm}}$ ), 7.48-7.52 (m, 4 H,  $\text{CH}_{\text{arm}}$ ).

**$^{13}\text{C-NMR}$ :** (300 K, 125 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  [ppm] = -3.8 ( $\text{PhSi}-(\text{CH}_3)_2$ ), 0.3 ( $\text{SiCSi}-(\text{CH}_3)_3$ ), 3.8 ( $\text{NSi}-(\text{CH}_3)_3$ ), 9.6 ( $\text{NSi-CH}_2-\text{CH}_2\text{Si}$ ), 10.3 ( $\text{NSi-CH}_2-\text{CH}_2\text{Si}$ ), 127.3 ( $\text{CH}_{\text{arm}}$ ), 127.8 ( $\text{CH}_{\text{arm}}$ ), 127.9 ( $\text{CH}_{\text{arm}}$ ), 128.0 ( $\text{CH}_{\text{arm}}$ ), 128.2 ( $\text{CH}_{\text{arm}}$ ), 128.9 ( $\text{CH}_{\text{arm}}$ ), 138.6 ( $\text{C}_{\text{arm}}$ ), 138.7 ( $\text{C}_{\text{arm}}$ ), 167.9 ( $\text{Si-C-C}_{\text{arm}}$ ), 182.6 ( $\text{Si-C-Si}$ ).

**$^{29}\text{Si-NMR}$ :** (300 K, 100 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  [ppm] = -81.09 ( $\text{Si}_{\text{silirene}}$ ), -13.24 ( $\text{SiC-Si}-(\text{CH}_3)_3$ ), -1.88 ( $\text{Si-PhMe}_2$ ), 3.35 ( $\text{N-Si}-(\text{CH}_3)_3$ ).

**EA:** calc. [%] for  $\text{C}_{25}\text{H}_{51}\text{NSi}_5$  = C 61.64, H 9.01, N 2.66; found C 61.27, H 8.65, N 3.01.

**LIFDI-MS:** m/z = calc. for  $[\text{C}_{25}\text{H}_{51}\text{NSi}_5]^+$ : 525.2555[M] $^+$ , found 525.2560.

$^{29}\text{Si}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , r.t.)

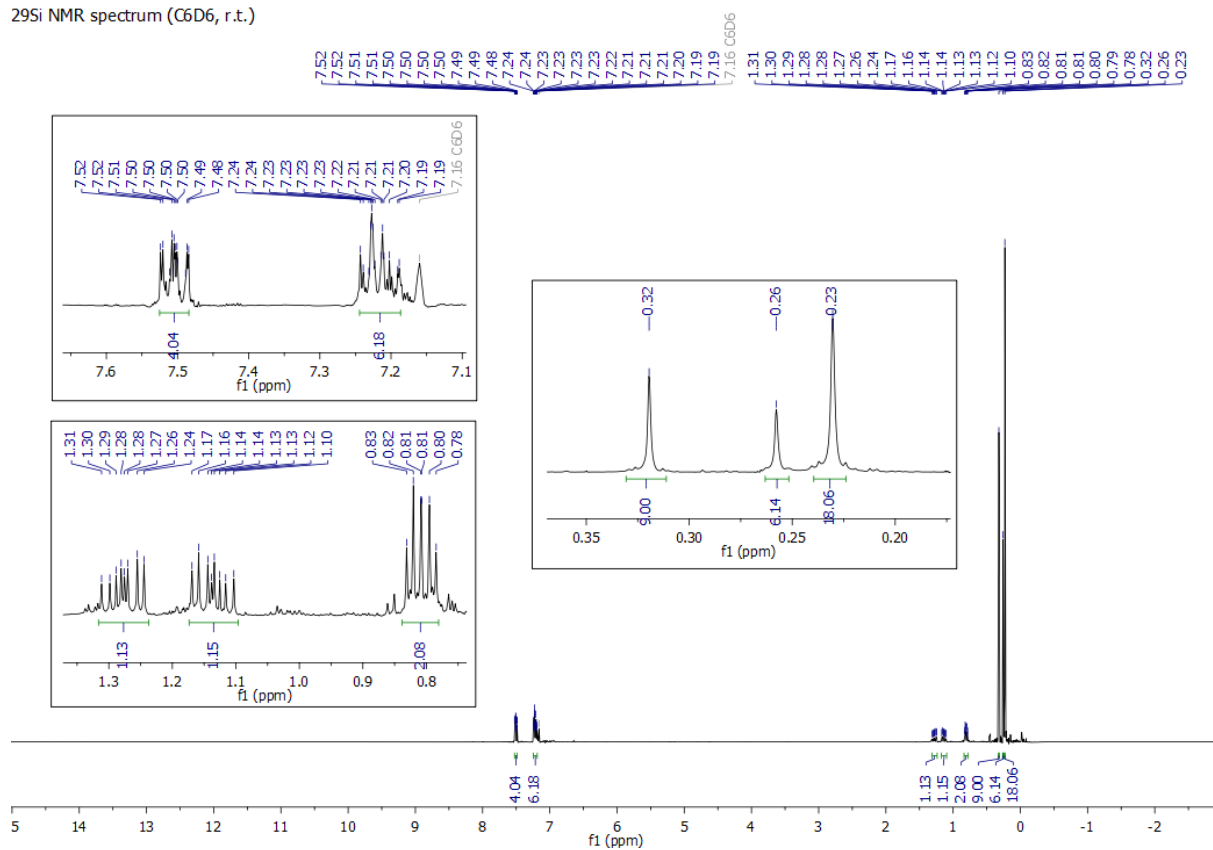


Figure S27:  $^1\text{H}$ -NMR spectrum of silacyclopropene **8** ( $\text{C}_6\text{D}_6$ , r.t.).

$^{13}\text{C}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , r.t.)

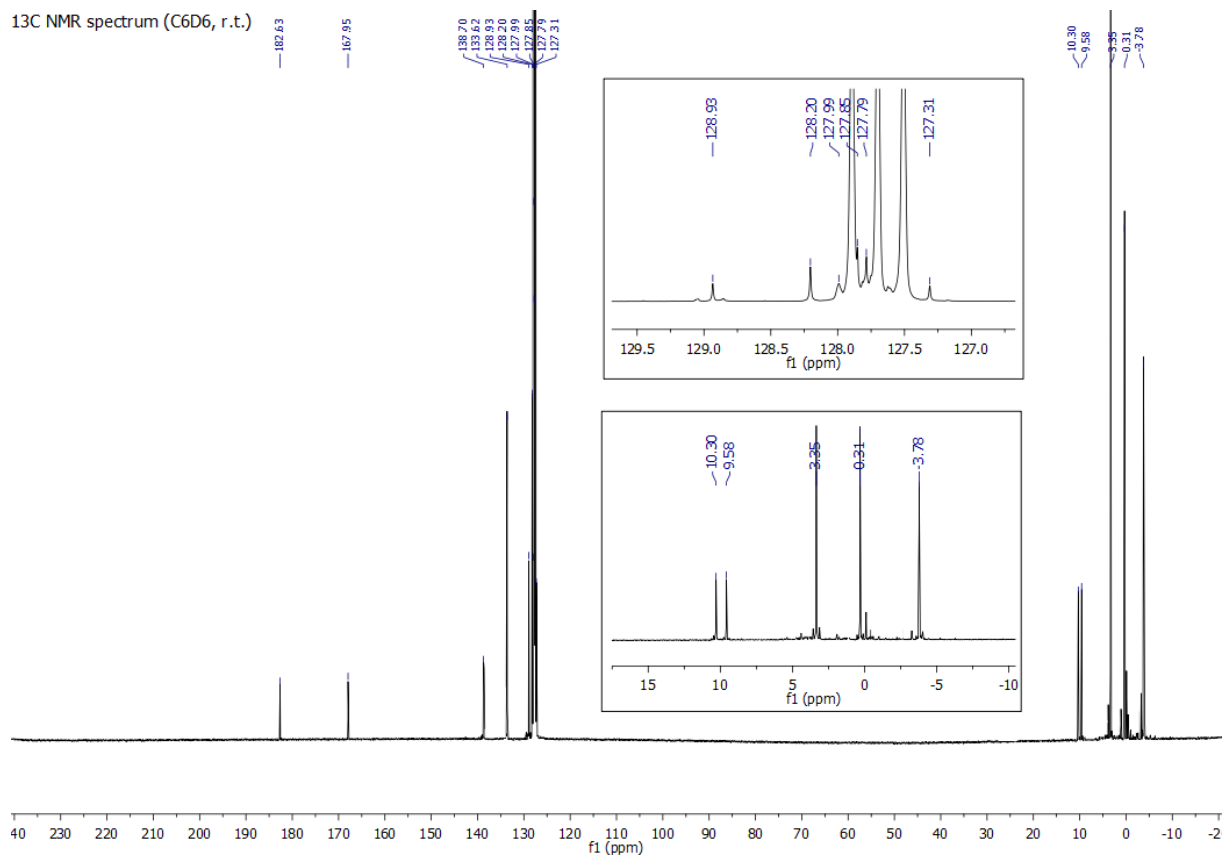


Figure S28:  $^{13}\text{C}$ -NMR spectrum of silacyclopropene **8** ( $\text{C}_6\text{D}_6$ , r.t.).

<sup>29</sup>Si NMR spectrum (C<sub>6</sub>D<sub>6</sub>, r.t.)

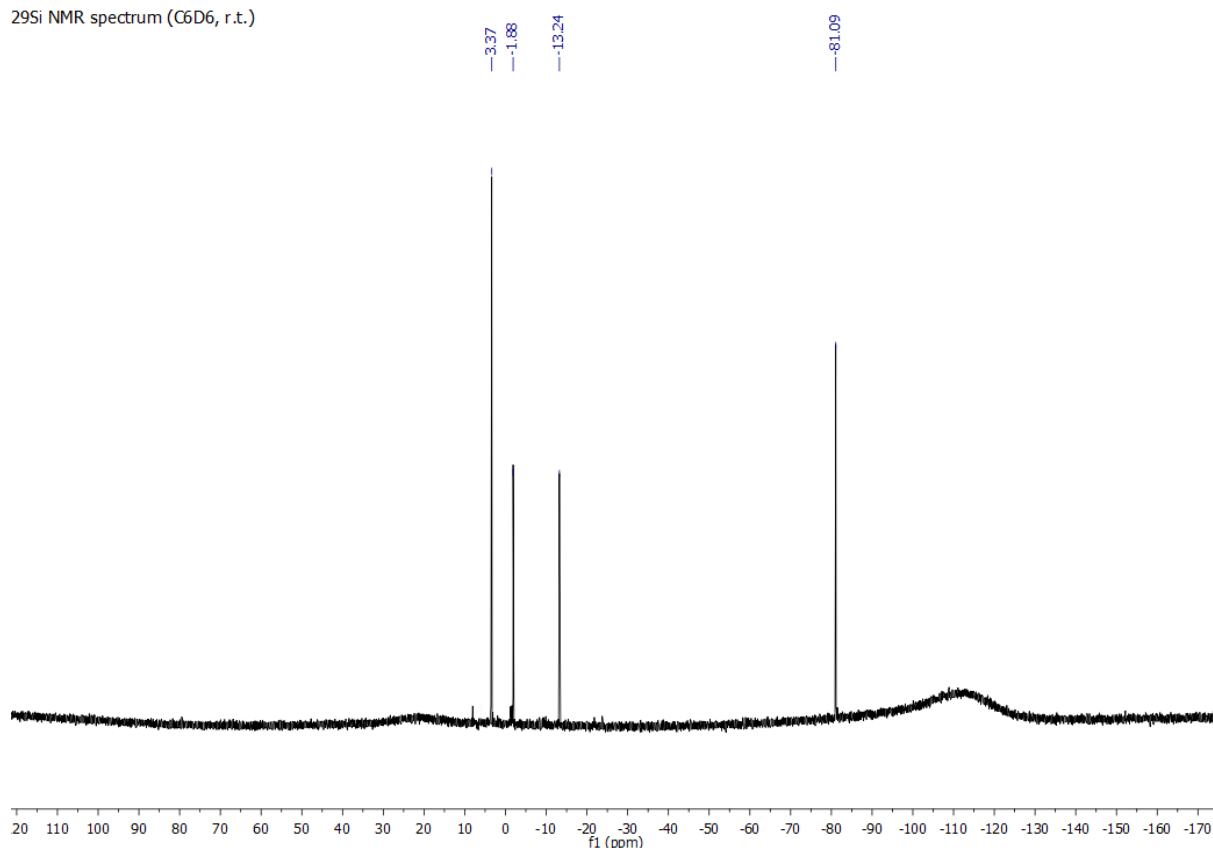
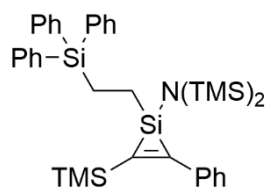


Figure S29: <sup>29</sup>Si-ig NMR spectrum of silacyclopropene **8** (C<sub>6</sub>D<sub>6</sub>, r.t.).

### Functionalization of dimethylphenylsilane and characterization of **9**



Silacyclopropene **5** (60.0 mg, 154  $\mu$ mol, 1 eq) was added to a solution of triphenylsilane (40.8 mg, 154  $\mu$ mol, 1 eq) in benzene (5 mL). Then 6.4 mg (0.77  $\mu$ mol) of a Karstead-catalyst solution (2.25 wt.% Pt in xylene) was added, and the mixture was stirred at 65 °C for 12 h. The colour of the reaction changes from a bright yellow to a dark gold/brown over the time. All volatiles were removed under vacuum and the residue was redissolved in pentane (5 mL). The product was purified by filtration through an appropriate amount of aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) and a syringe filter (PP, 0.5  $\mu$ m) to remove the applied catalyst. Further distillation under high vacuum (3·10<sup>-5</sup> mbar, 130 °C) result in the functionalized compound **9** (69.1 mg, 106  $\mu$ mol, 69 %) as a colourless liquid.

<sup>1</sup>H-NMR: (300 K, 500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  [ppm] = 0.19 (s, 18 H, NSi-(CH<sub>3</sub>)<sub>3</sub>), 0.32 (s, 9 H, SiCSi-(CH<sub>3</sub>)<sub>3</sub>), 0.81-0.87 (m, 2 H, NSi-CH<sub>2</sub>-CH<sub>2</sub>Si), 1.48-1.51 (m, 2 H, NSi-CH<sub>2</sub>-CH<sub>2</sub>Si), 7.11-7.13 (m, 3 H, CH<sub>arm</sub>), 7.52-7.54 (m, 2 H, CH<sub>arm</sub>), 7.58-7.60 (m, 6 H, CH<sub>arm</sub>), 7.62-7.64 (m, 3 H, CH<sub>arm</sub>), 7.65-7.68 (m, 6 H, CH<sub>arm</sub>).

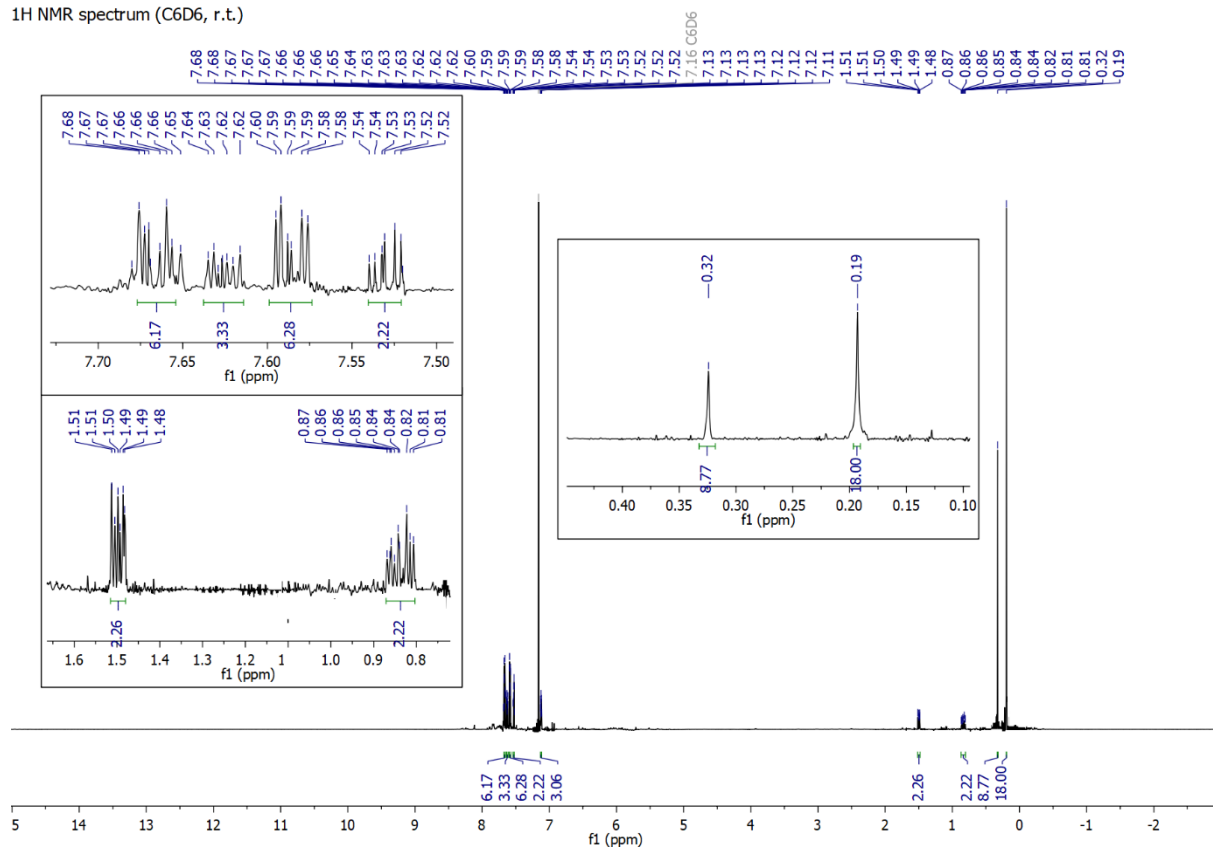
<sup>13</sup>C-NMR: (300 K, 125 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  [ppm] = 0.7 (SiCSi-(CH<sub>3</sub>)<sub>3</sub>), 3.7 (NSi-(CH<sub>3</sub>)<sub>3</sub>), 7.6 (NSi-CH<sub>2</sub>-CH<sub>2</sub>Si), 10.3 (NSiCH<sub>2</sub>-CH<sub>2</sub>-Si), 128.2 (CH<sub>arm</sub>), 128.4 (CH<sub>arm</sub>), 136.0 (CH<sub>arm</sub>), 136.2 (CH<sub>arm</sub>), 136.9 (CH<sub>arm</sub>), 139.1 (CH<sub>arm</sub>), 145.2 (C<sub>arm</sub>), 151.7 (C<sub>arm</sub>), 168.5 (Si-C-C<sub>arm</sub>), 182.8 (Si-C-Si).

$^{29}\text{Si-NMR}$ : (300 K, 100 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  [ppm] = -81.17 ( $\text{Si}_{\text{silirene}}$ ), -13.19 ( $\text{SiC-Si-(CH}_3)_3$ ), -9.53 ( $\text{Si-Ph}_3$ ), 3.50 ( $\text{N-Si-(CH}_3)_3$ ).

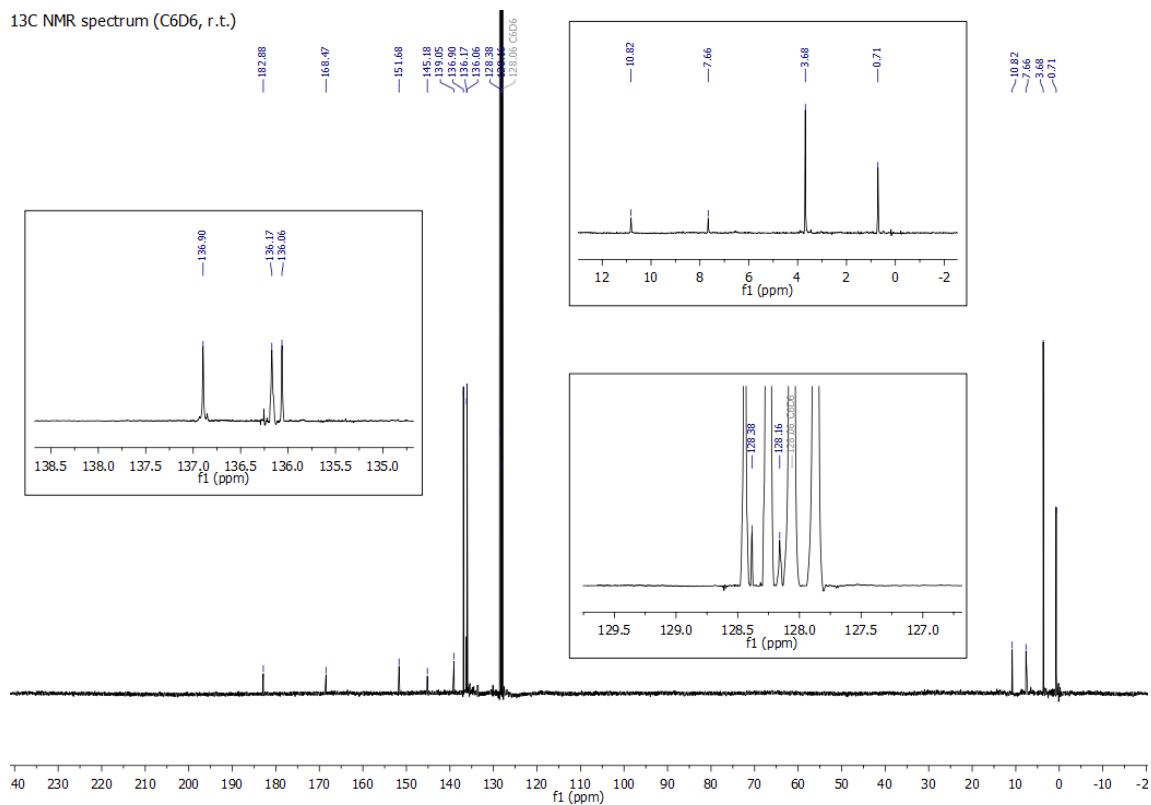
**EA**: calc. [%] for  $\text{C}_{37}\text{H}_{51}\text{NSi}_5$  = C 68.34, H 7.91, N 2.15; found C 61.99, H 7.73, N 2.68.

**LIFDI-MS**:  $m/z$  = calc. for  $[\text{C}_{37}\text{H}_{51}\text{NSi}_5]^+$ : 649.2868[M] $^+$ , found 649.2864.

$^1\text{H-NMR}$  spectrum ( $\text{C}_6\text{D}_6$ , r.t.)

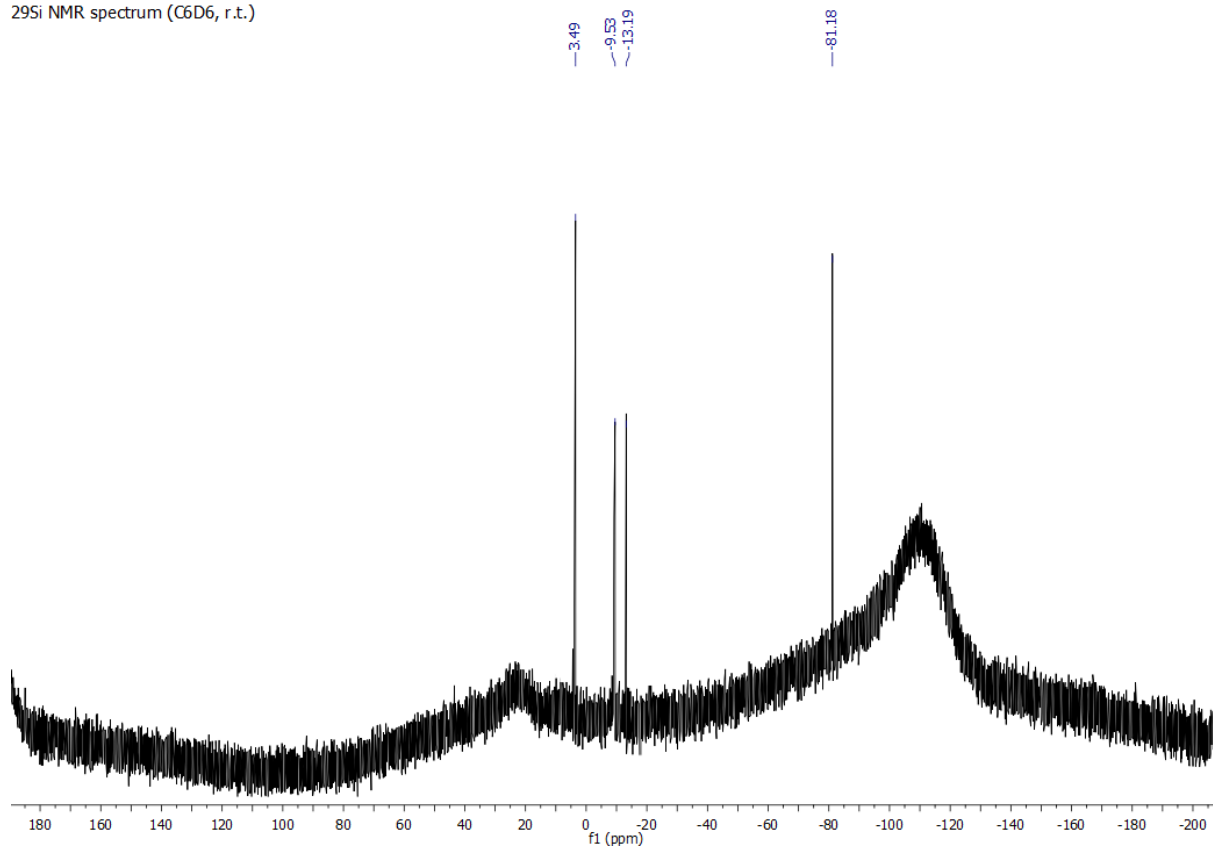


**Figure S30**:  $^1\text{H-NMR}$  spectrum of silacyclopropene **9** ( $\text{C}_6\text{D}_6$ , r.t.).



**Figure S31:**  $^{13}\text{C}$ -NMR spectrum of silacyclopropene **9** ( $\text{C}_6\text{D}_6$ , r.t.).

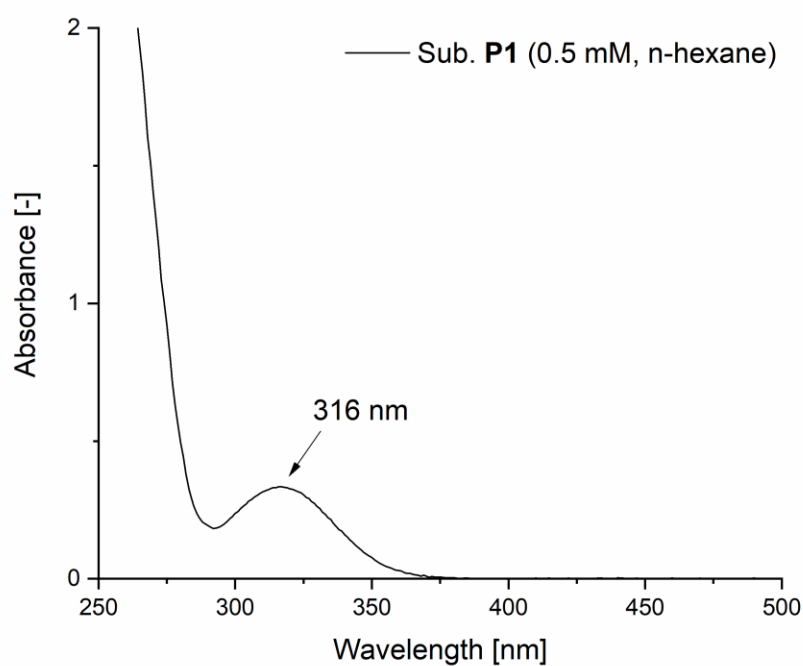
$^{29}\text{Si}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , r.t.)



**Figure S32:**  $^{29}\text{Si}$ -ig NMR spectrum of silacyclopropene **9** ( $\text{C}_6\text{D}_6$ , r.t.).

### Functionalization of Tetrakis(dimethylsilyoxy)silane **P1**

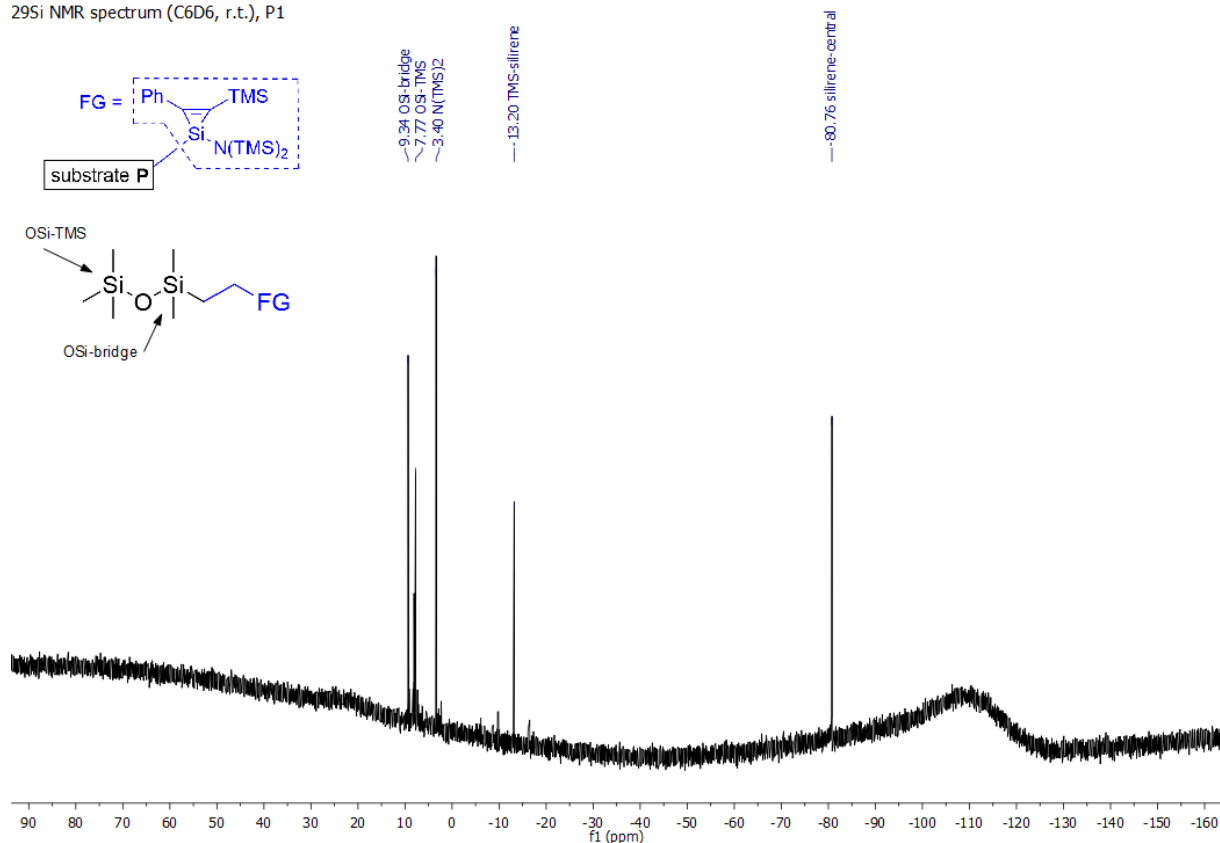
A solution of substrate **S1** (368  $\mu\text{mol}$ , 81.9 mg, 1 eq) in toluene (10 mL) was added to a solution of silacyclopropene **5** (404  $\mu\text{mol}$ , 109 mg, 1.1 eq) in toluene (5 mL). 16.8 mg (2.05  $\mu\text{mol}$ ) of a Karstead-catalyst solution (2.25 wt.% Pt in xylene) was added, and the mixture was stirred at 65 °C for 12 h. Over the reaction time the colour changed from a bright yellow to a dark orange. All volatiles were removed under vacuum and the obtained residue was redissolved in *n*-hexane (10 mL). The crude was purified by filtration through an appropriate amount of aluminium oxide ( $\text{Al}_2\text{O}_3$ ) and a syringe filter (PP, 0.5  $\mu\text{m}$ ) to remove the applied catalyst. The filter was further washed with *n*-hexane (2 mL). At last, the solvent was removed under vacuum to obtain the functionalized substrate **P1** (105.2 mg, 68 %).



**Figure S33:** UV-VIS spectrum of functionalized substrate **P1** (r.t., *n*-hexane,  $0.5 \times 10^{-3}$  M).



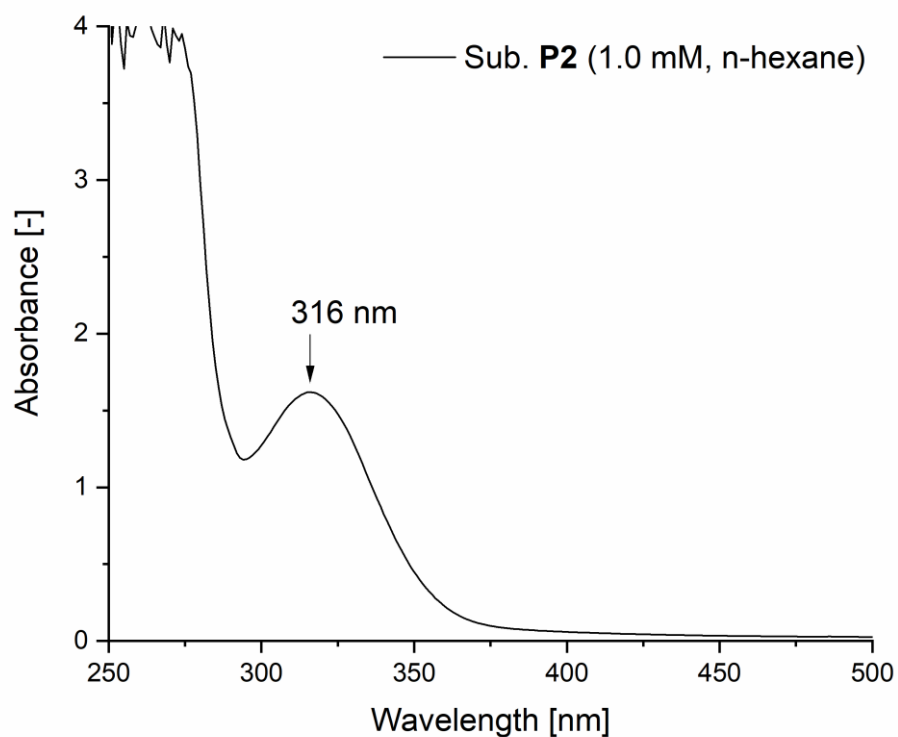
$^{29}\text{Si}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , r.t.), P1



**Figure S34:**  $^{29}\text{Si}$ -ig NMR spectrum of functionalized substrate **P1** ( $\text{C}_6\text{D}_6$ , r.t.).

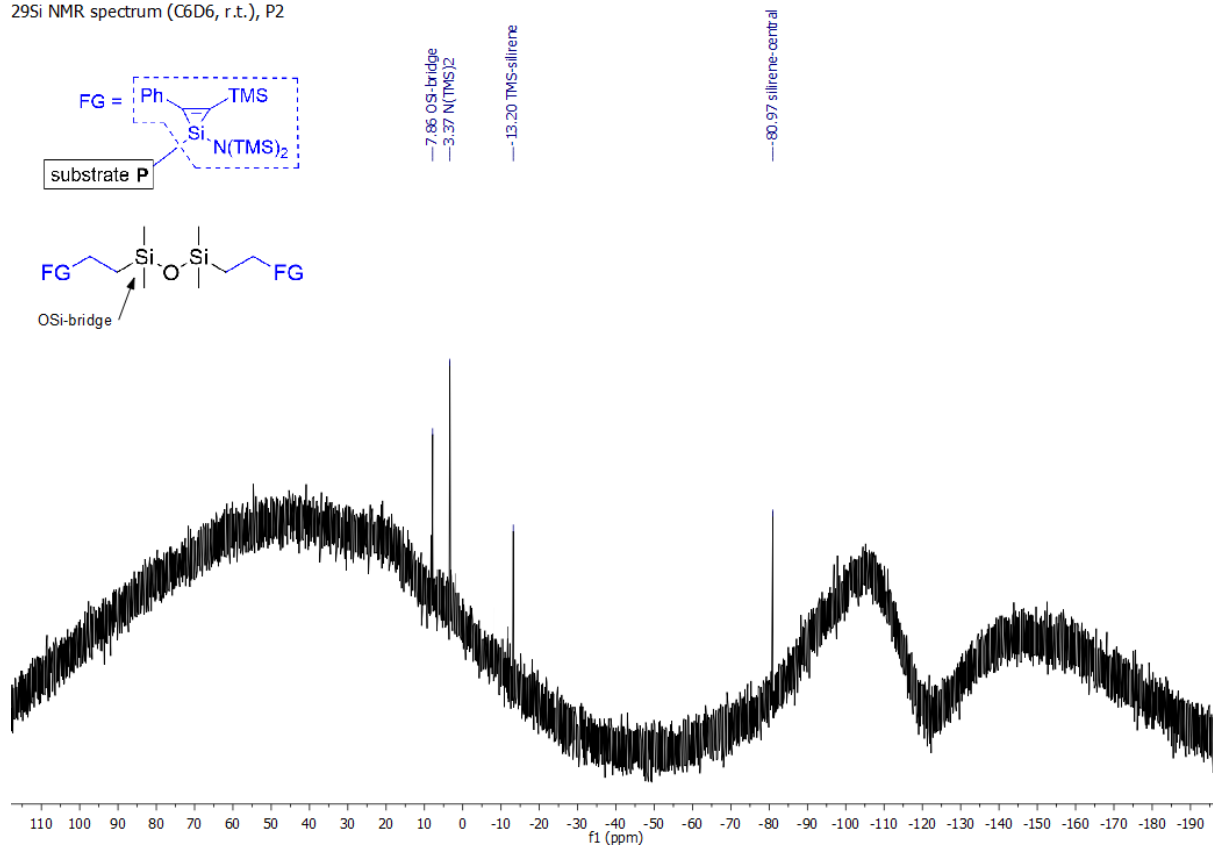
### Functionalization of Tetrakis(dimethylsilyloxy)silane **P2**

A solution of substrate **S2** (184  $\mu\text{mol}$ , 24.7 mg, 0.5 eq) in toluene (10 mL) was added to a solution of silacyclopropene **5** (404  $\mu\text{mol}$ , 109 mg, 1.1 eq) in toluene (5 mL). 16.8 mg (2.05  $\mu\text{mol}$ ) of a Karstead-catalyst solution (2.25 wt.% Pt in xylene) was added, and the mixture was stirred at 65  $^\circ\text{C}$  for 12 h. Over the reaction time the colour changed from a bright yellow to a dark orange. All volatiles were removed under vacuum and the obtained residue was redissolved in *n*-hexane (10 mL). The crude was purified by filtration through an appropriate amount of aluminium oxide ( $\text{Al}_2\text{O}_3$ ) and a syringe filter (PP, 0.5  $\mu\text{m}$ ) to remove the applied catalyst. The filter was further washed with *n*-hexane (2 mL). At last, the solvent was removed under vacuum to obtain the functionalized substrate **P2** (79.8 mg, 64 %).



**Figure S35:** UV-VIS spectrum of functionalized substrate **P2** (r.t., n-hexane,  $1.0 \times 10^{-3}$  M).

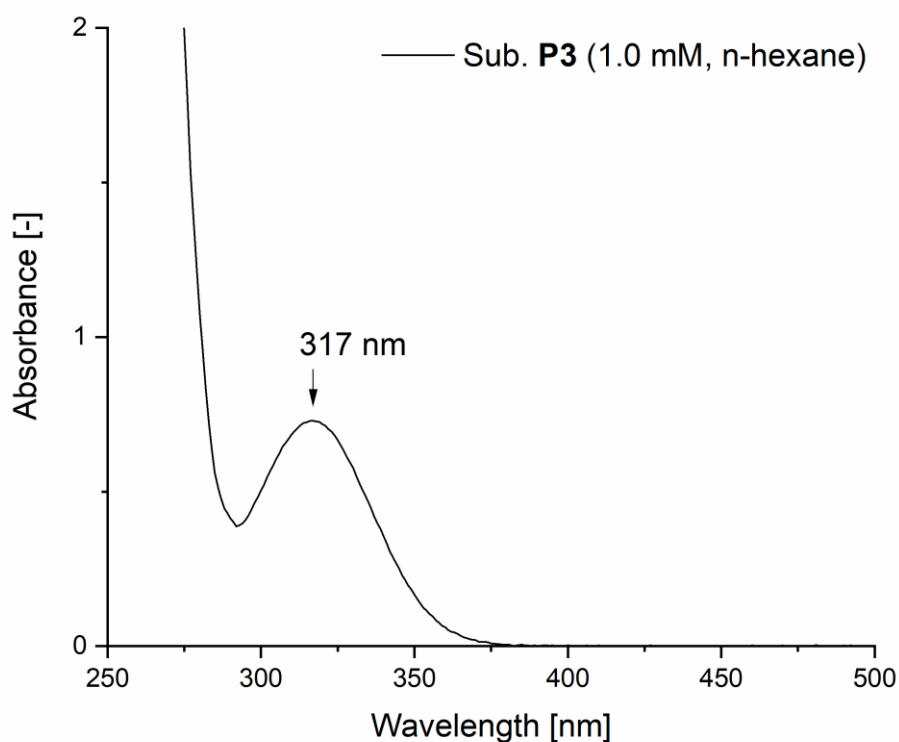
$^{29}\text{Si}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , r.t.), **P2**



**Figure S36:**  $^{29}\text{Si}$ -ig NMR spectrum of functionalized substrate **P2** ( $\text{C}_6\text{D}_6$ , r.t.).

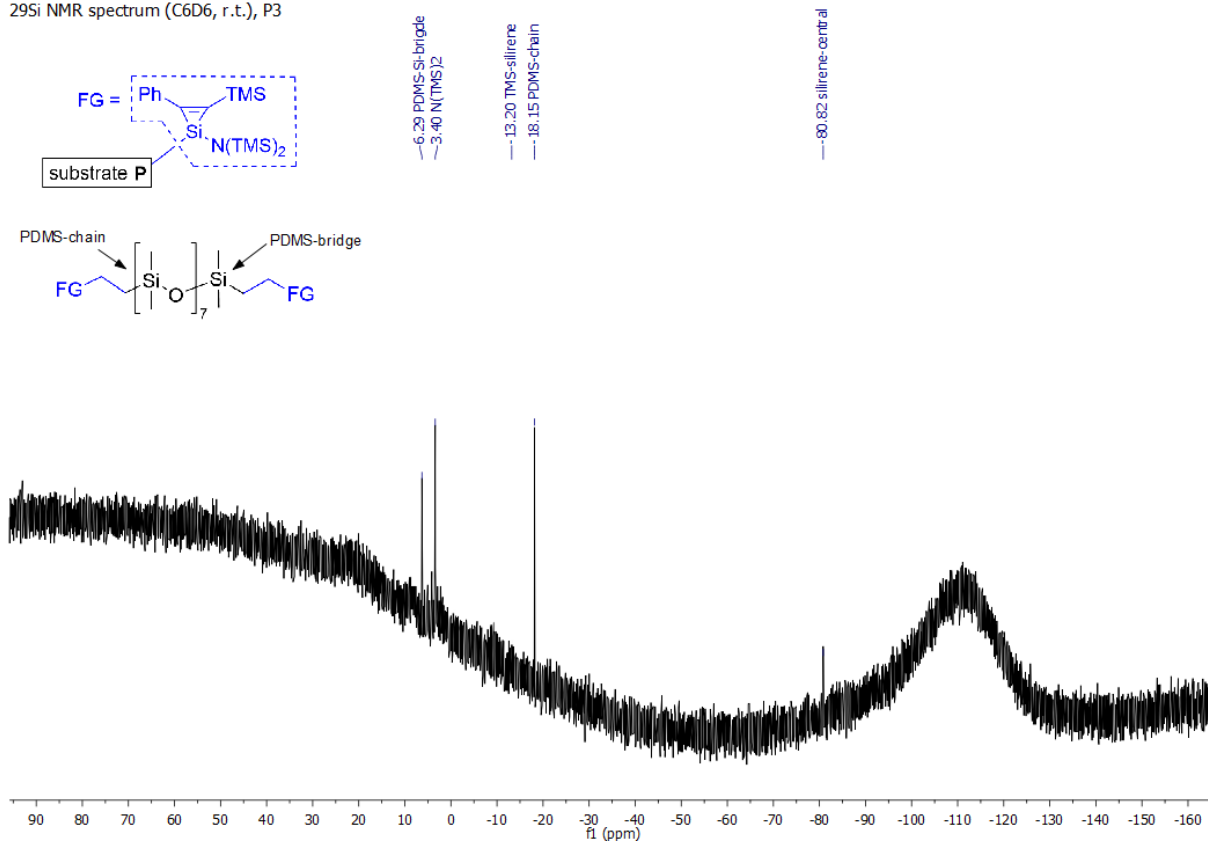
### Functionalization of Tetrakis(dimethylsilyoxy)silane **P3**

A solution of substrate PMHS **S3** ( $M = 580$  g/mol, hydrid-terminated,  $92 \mu\text{mol}$ ,  $59.5$  mg,  $0.5$  eq.) in toluene ( $10$  mL) was added to a solution of silacyclopene **5** ( $202 \mu\text{mol}$ ,  $54.5$  mg,  $1.1$  eq) in toluene ( $5$  mL).  $8.4$  mg ( $1.02 \mu\text{mol}$ ) of a Karstead-catalyst solution ( $2.25$  wt.% Pt in xylene) was added, and the mixture was stirred at  $65$  °C for  $12$  h. Over the reaction time the colour changed from a bright yellow to a dark orange. All volatiles were removed under vacuum and the obtained residue was redissolved in *n*-hexane ( $10$  mL). The crude was purified by filtration through an appropriate amount of aluminium oxide ( $\text{Al}_2\text{O}_3$ ) and a syringe filter (PP,  $0.5 \mu\text{m}$ ) to remove the applied catalyst. The filter was further washed with *n*-hexane ( $2$  mL). At last, the solvent was removed under vacuum to obtain the functionalized substrate **P3** ( $68.6$  mg,  $57$  %).



**Figure S37:** UV-VIS spectrum of functionalized substrate **P3** (r.t., *n*-hexane,  $1.0 \times 10^{-3}$  M).

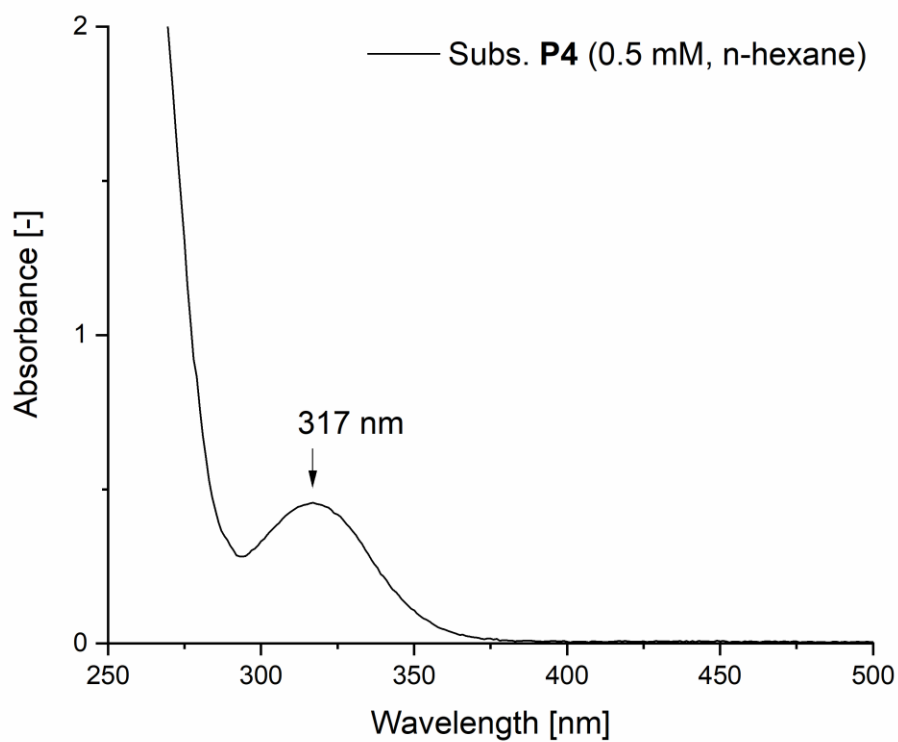
$^{29}\text{Si}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , r.t.), P3



**Figure S38:**  $^{29}\text{Si}$  NMR spectrum of functionalized substrate P3 ( $\text{C}_6\text{D}_6$ , r.t.).

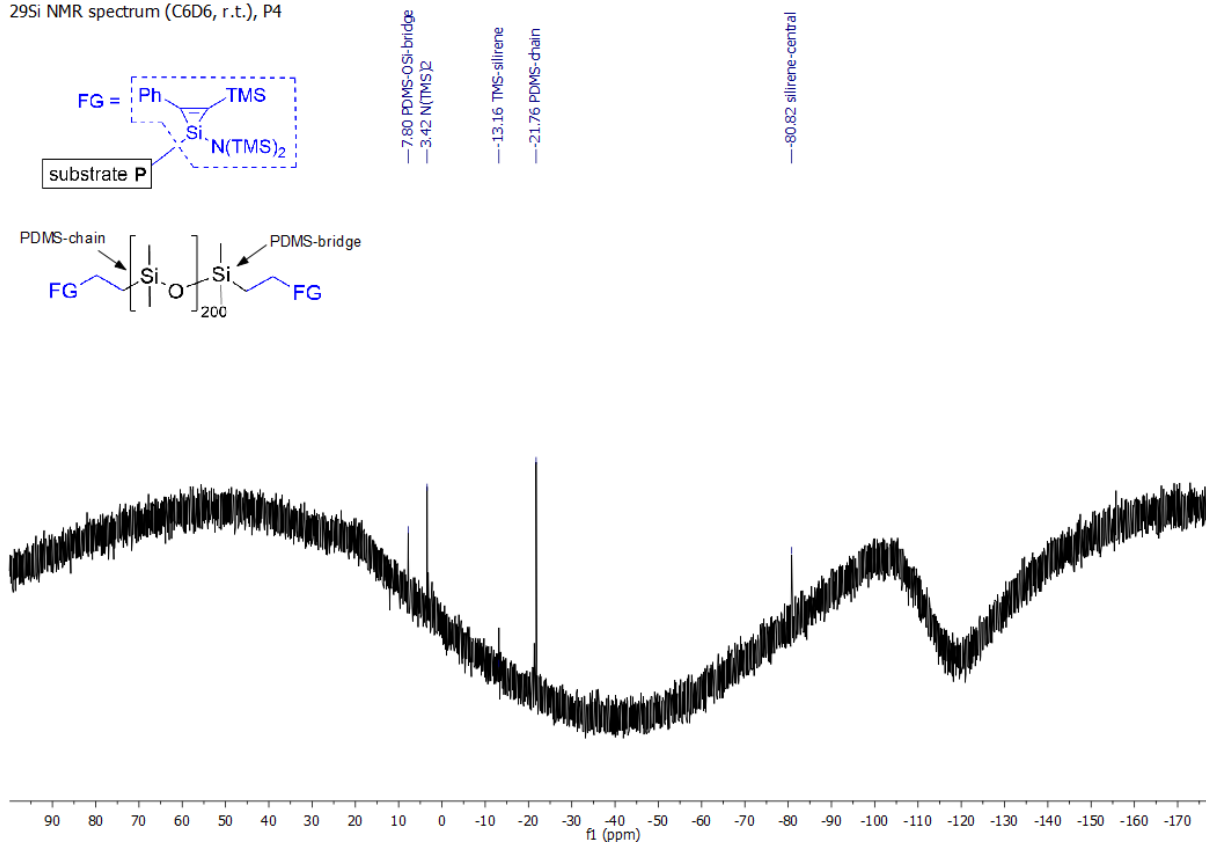
#### Functionalization of Tetrakis(dimethylsilyloxy)silane P4

A solution of substrate PMHS **S3** ( $M = 15000$  g/mol, hydrid-terminated,  $92 \mu\text{mol}$ ,  $1.38$  g,  $0.5$  eq.) in toluene ( $10$  mL) was added to a solution of silacyclopropene **5** ( $202 \mu\text{mol}$ ,  $54.5$  mg,  $1.1$  eq.) in toluene ( $5$  mL).  $8.4$  mg ( $1.02 \mu\text{mol}$ ) of a Karstead-catalyst solution ( $2.25$  wt.% Pt in xylene) was added, and the mixture was stirred at  $65$  °C for  $24$  h. Over the reaction time the colour changed from a bright yellow to a dark orange. All volatiles were removed under vacuum and the obtained residue was redissolved in *n*-hexane ( $10$  mL). The crude was purified by filtration through an appropriate amount of aluminium oxide ( $\text{Al}_2\text{O}_3$ ) and a syringe filter (PP,  $0.5 \mu\text{m}$ ) to remove the applied catalyst. The filter was further washed with *n*-hexane ( $2$  mL). At last, the solvent was removed under vacuum to obtain the functionalized substrate **P3** ( $677.7$  mg,  $47$  %).



**Figure S39:** UV-VIS spectrum of functionalized substrate **P4** (r.t., n-hexane,  $0.5 \times 10^{-3}$  M).

$^{29}\text{Si}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , r.t.), **P4**



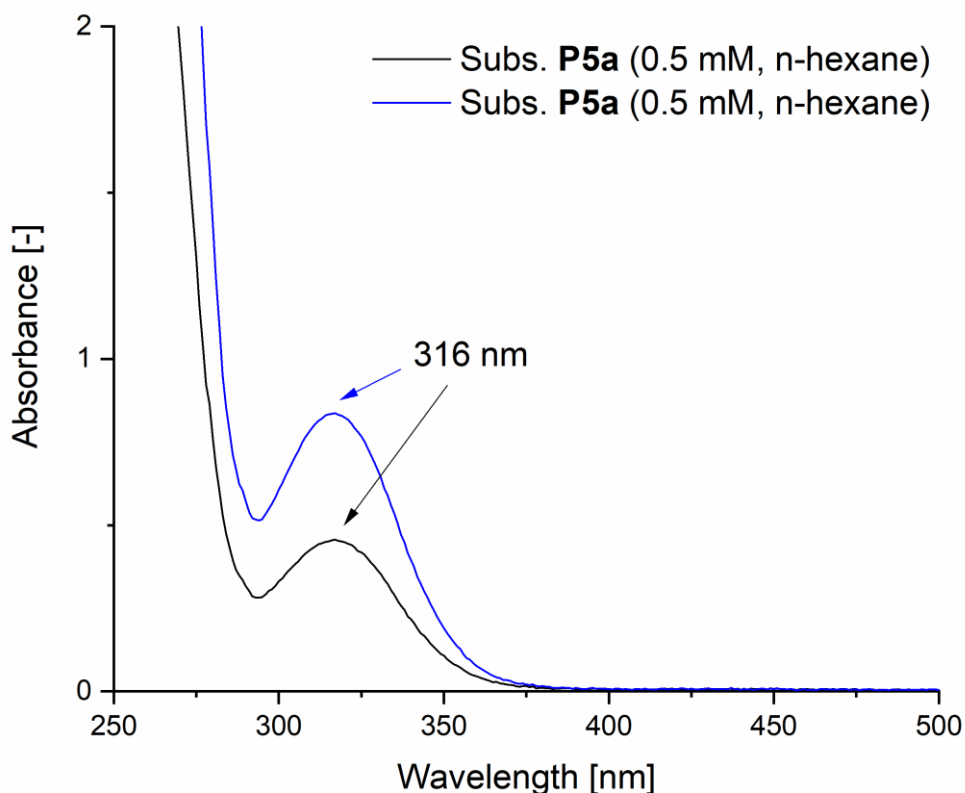
**Figure S40:**  $^{29}\text{Si}$ -ig NMR spectrum of functionalized substrate **P4** ( $\text{C}_6\text{D}_6$ , r.t.).

### Partial functionalization of Tetrakis(dimethylsilyoxy)silane **S5**

Silacyclopropene **5** (100 mg, 256  $\mu\text{mol}$ , 1 eq) was added to a solution of tetrakis-(dimethylsilyoxy)silane **S5** (44.2 mg, 134.6  $\mu\text{mol}$ , 0.5 eq) in toluene (5 mL). Then 5.6 mg (0.67  $\mu\text{mol}$ ) of a Karstead-catalyst solution (2.25 wt.% Pt in xylene) was added, and the mixture was stirred at 60 °C for 48 h. The colour of the reaction changes from a bright yellow to a dark gold/brown over the time. All volatiles were removed under vacuum and the residue was redissolved in pentane (5 mL). The product was purified by filtration through an appropriate amount of aluminium oxide ( $\text{Al}_2\text{O}_3$ ) and a syringe filter (PP, 0.5  $\mu\text{m}$ ) to remove the applied catalyst and give the compound **P5a** as a colourless, viscous oil. (79.3 mg, 48 %).

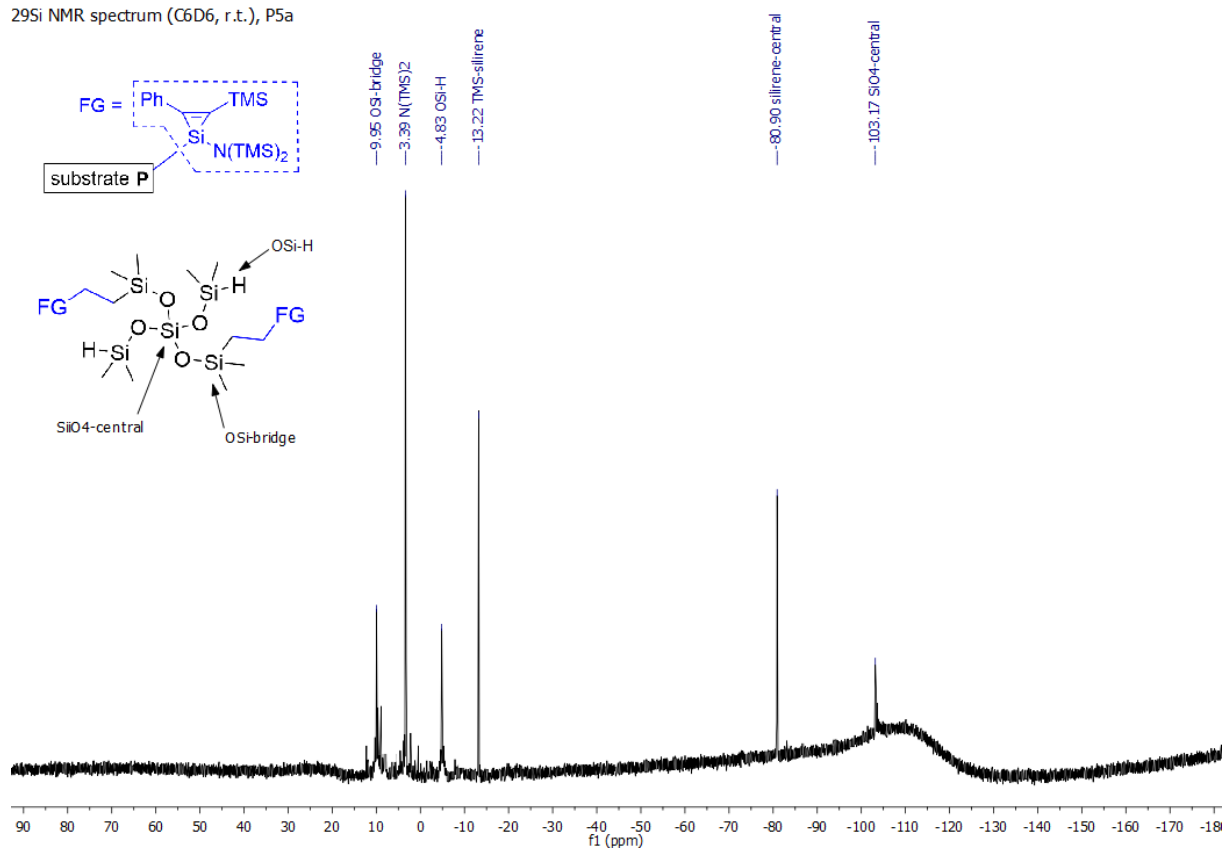
### Full functionalization of Tetrakis(dimethylsilyoxy)silane **S5**

Silacyclopropene **5** (100 mg, 256  $\mu\text{mol}$ , 1 eq) was added to a solution of tetrakis-(dimethylsilyoxy)silane **S5** (22.1 mg, 67.3  $\mu\text{mol}$ , 0.25 eq) in toluene (5 mL). 2.8 mg (0.34  $\mu\text{mol}$ ) of a Karstead-catalyst solution (2.25 wt.% Pt in xylene) was added, and the mixture was stirred at 60 °C for 48 h. The colour of the reaction changes from a bright yellow to a dark gold/brown over the time. All volatiles were removed under vacuum and the residue was redissolved in pentane (5 mL). The product was purified by filtration through an appropriate amount of aluminium oxide ( $\text{Al}_2\text{O}_3$ ) and a syringe filter (PP, 0.5  $\mu\text{m}$ ) to remove the applied catalyst and give the compound **P5b** as a colourless, viscous oil. (61.7 mg, 51 %).



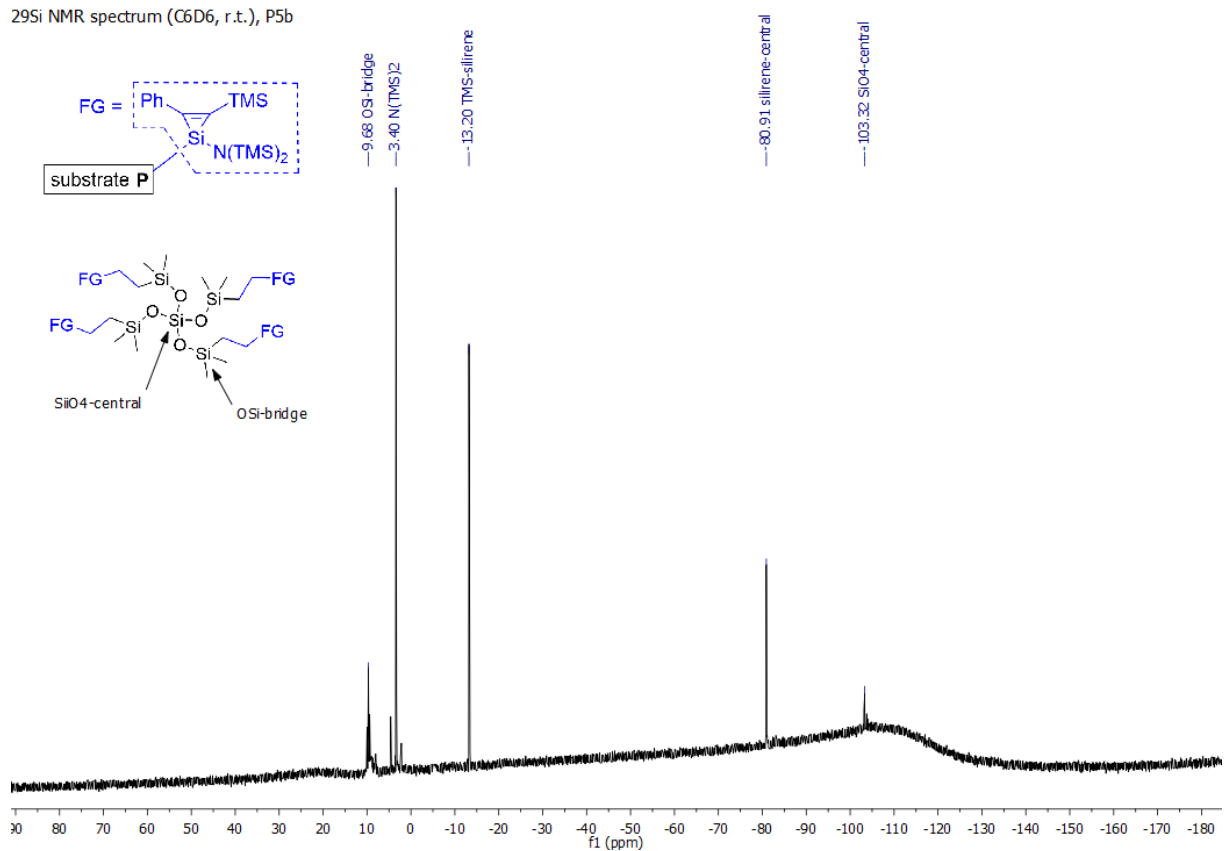
**Figure S41:** UV-VIS spectra of partial modified substrate **P5a** (black) and full modified substrate **P5b** (blue) (r.t., n-hexane,  $0.5 \times 10^{-3}$  M).

$^{29}\text{Si}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , r.t.), P5a



**Figure S42:**  $^{29}\text{Si}$ -ig NMR spectrum of functionalized substrate **P5a** ( $\text{C}_6\text{D}_6$ , r.t.).

$^{29}\text{Si}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , r.t.), P5b



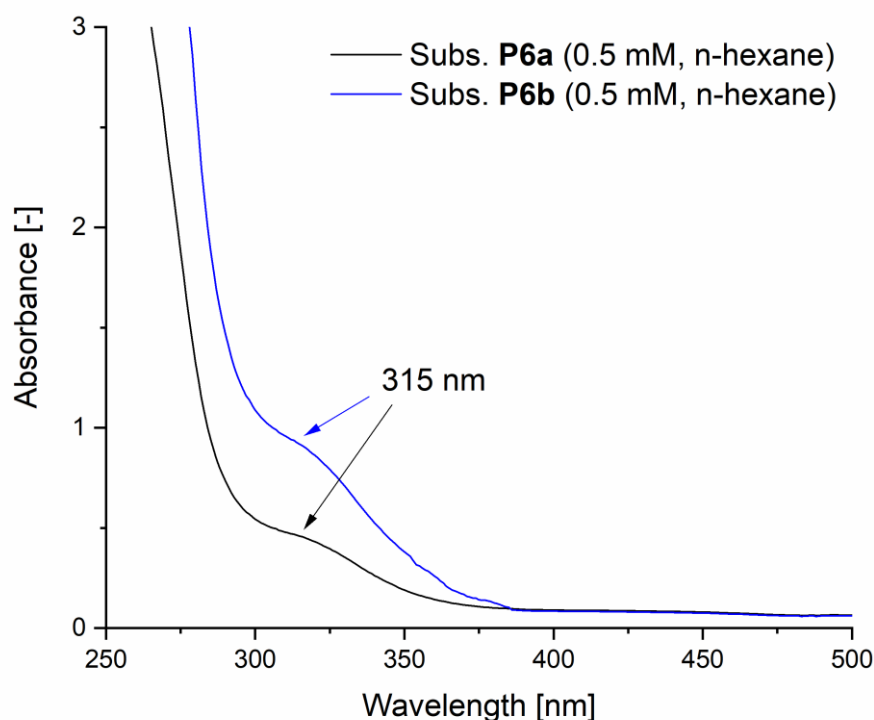
**Figure S43:**  $^{29}\text{Si}$ -ig NMR spectrum of functionalized substrate **P5b** ( $\text{C}_6\text{D}_6$ , r.t.).

### Partial functionalization of lateral polymethylhydrosiloxane (PMHS) S6

A solution of PMHS (520 mg,  $M = 4900$  g/mol, 4.9 mmol/g Si-H moiety, statistical copolymer of dimethylsiloxane and hydridomethylsiloxane) in toluene (10 mL) was added to a solution of silacyclopropene **5** (500 mg, 1.28 mmol, 0.5 eq per Si-H moiety) in toluene (5 mL). 53.5 mg (6.40  $\mu\text{mol}$ ) of a Karstead-catalyst solution (2.25 wt.% Pt in xylene) was added, and the mixture was stirred at 65 °C for 24 h. Over the reaction time the colour changed from a bright yellow to a dark orange. All volatiles were removed under vacuum and the obtained residue was redissolved in *n*-hexane (10 mL). The crude was purified by filtration through an appropriate amount of aluminium oxide ( $\text{Al}_2\text{O}_3$ ) and a syringe filter (PP, 0.5  $\mu\text{m}$ ) to remove the applied catalyst. The filter was further washed with *n*-hexane (2 mL). At last, the solvent was removed under vacuum to obtain the functionalized PDMS **P6a** as yellowish viscous fluid (530 mg, 51 %).

### Full functionalization of lateral polymethylhydrosiloxane (PMHS) S6

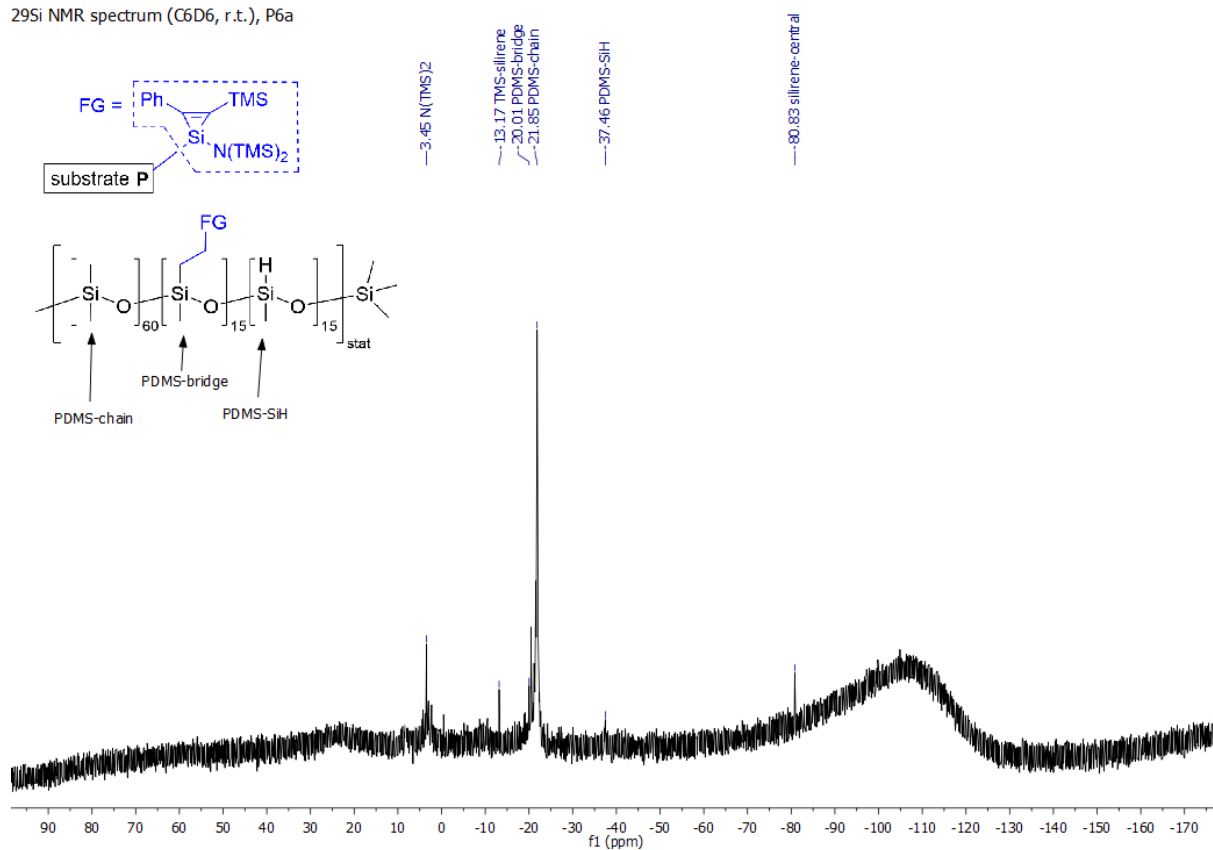
A solution of PMHS (260 mg,  $M = 4900$  g/mol, 4.9 mmol/g Si-H moiety, statistical copolymer of dimethylsiloxane and hydridomethylsiloxane) in toluene (5 mL) was added to a solution of silacyclopropene **5** (500 mg, 1.28 mmol, 1.0 eq per Si-H moiety) in toluene (5 mL). Then 53.5 mg (6.40  $\mu\text{mol}$ ) of a Karstead-catalyst solution (2.25 wt.% Pt in xylene) was added, and the mixture was stirred at 65 °C for 24 h. Over the reaction time the colour changed from a bright yellow to a dark orange. All volatiles were removed under vacuum and the obtained residue was redissolved in *n*-hexane (10 mL). The crude was purified by filtration through an appropriate amount of aluminium oxide ( $\text{Al}_2\text{O}_3$ ) and a syringe filter (PP, 0.5  $\mu\text{m}$ ) to remove the applied catalyst. The filter was further washed with *n*-hexane (2 mL). At last, the solvent was removed under vacuum to obtain the functionalized PDMS **P6b** as yellowish viscous fluid (378 mg, 48%).



**Figure S44:** UV-VIS spectra of partial modified polysiloxane **P6a** (black) and full modified polysiloxane **P6b** (blue), (r.t., *n*-hexane,  $0.5 \times 10^{-3}$  M).

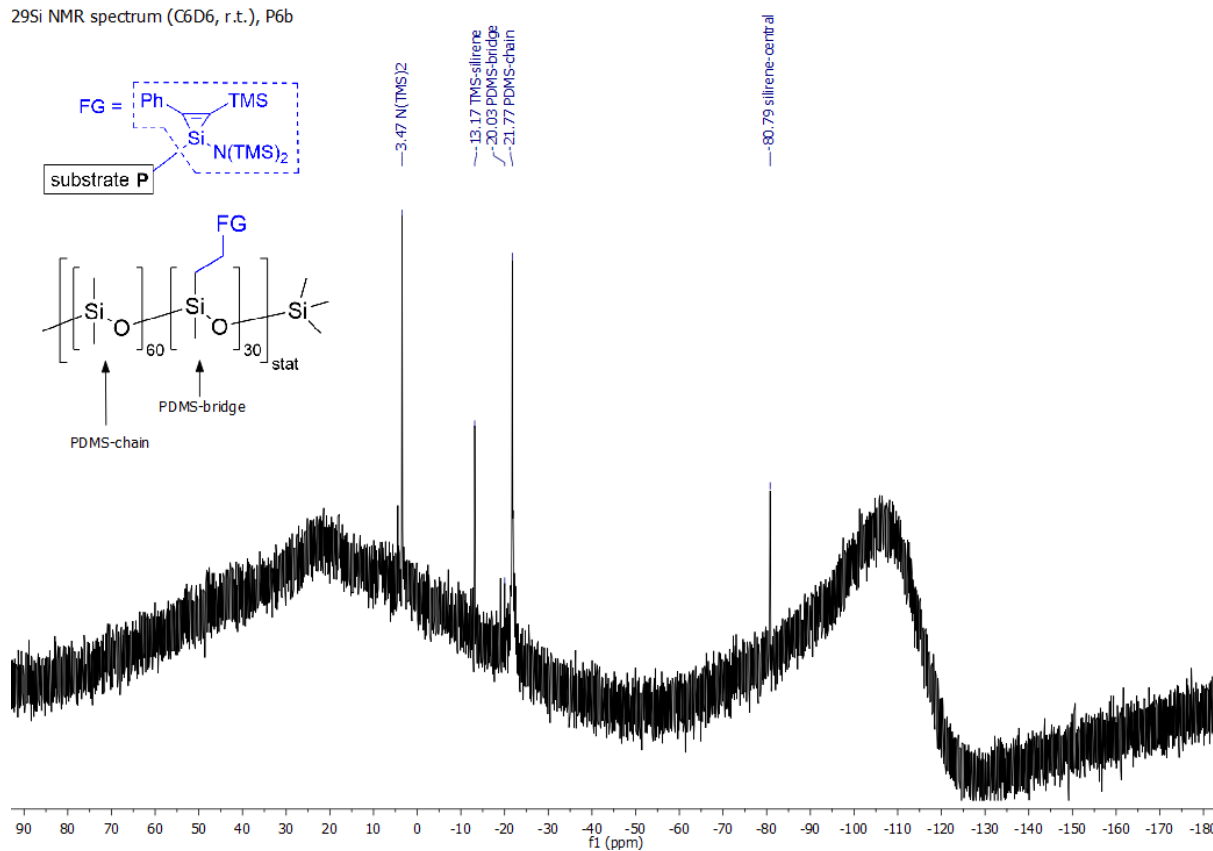


$^{29}\text{Si}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , r.t.), P6a

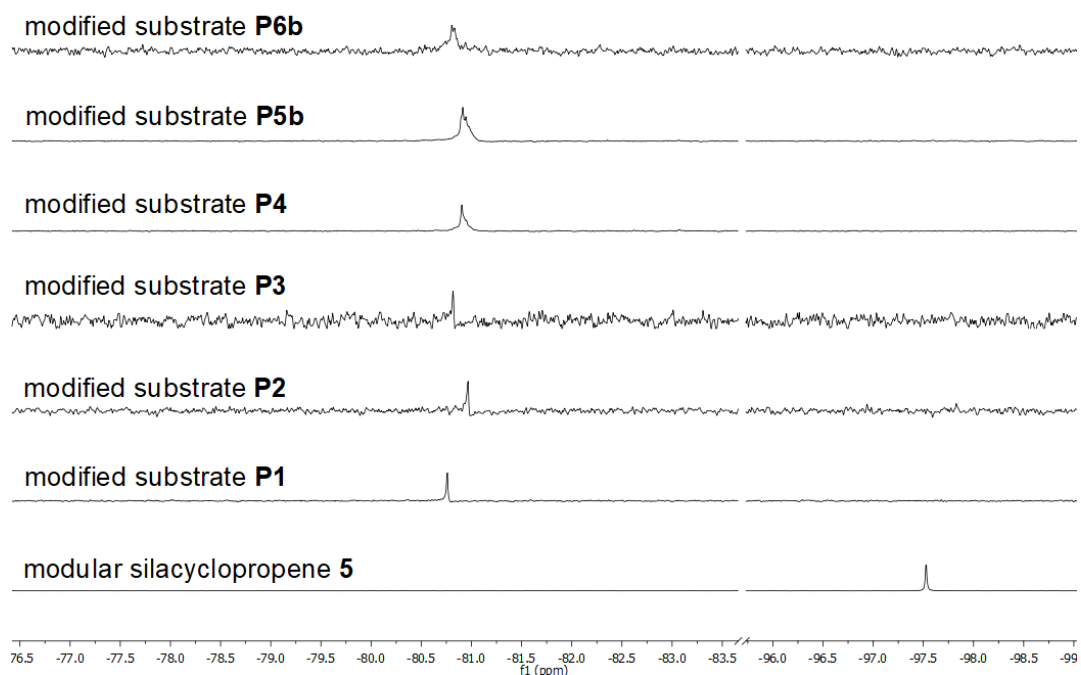


**Figure S45:**  $^{29}\text{Si}$ -ig NMR spectrum of functionalized substrate P6a ( $\text{C}_6\text{D}_6$ , r.t.).

$^{29}\text{Si}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , r.t.), P6b



**Figure S46:**  $^{29}\text{Si}$ -ig NMR spectrum of functionalized substrate P6b ( $\text{C}_6\text{D}_6$ , r.t.).



**Figure S47:** Overview of different  $^{29}\text{Si}$  NMR spectra of modified substrates **P1-P6** in comparison to silacyclopropene **5** ( $\text{C}_6\text{D}_6$ , r.t.) after reaction finalization.

## B. References

- (S1) M. Muhr, P. Hei, M. Schtz, R. Bhler, C. Gemel, M. H. Linden, H. B. Linden and R. A. Fischer, *Dalton Transactions*, 2021, **50**, 9031.
- (S2) a) U. Wannagat and H. Brger, *Z. anorg. allg. Chem.*, 1964, **326**, 309; b) N. Auner, A. W. Weingartner and E. Herdtweck, *Zeitschrift fr Naturforschung B*, 1993, **48**, 318;
- (S3) a) I. E. Mark, S. Strin, O. Buisine, G. Berthon, G. Michaud, B. Tinant and J.-P. Declercq, *Adv. Synth. Catal.*, 2004, **346**, 1429; b) B. D. Karstedt, General Electric, *US Patent*, US 3715334A, **1973**; c) P. B. Hitchcock, M. F. Lappert and N. J. W. Warhurst, *Angew. Chem. Int. Ed. Engl.*, 1991, **30**, 438; d) J. A. Osborn, F. H. Jardine, J. F. Young and G. Wilkinson, *J. Chem. Soc., A*, 1966, 1711;