

### Supplementary Information

#### **Towards the photodeposition of Si<sub>x</sub>Ge<sub>y</sub>-type materials *via* oligomers of cyclogermapentenes and cyclosilapentenes**

William Medroa del Pino,<sup>a</sup> Andres Forero Pico,<sup>b</sup> Abhishek V. Muralidharan,<sup>a</sup> Manisha Gupta,<sup>b</sup> and Eric Rivard<sup>\*,a</sup>

<sup>a</sup>Department of Chemistry, University of Alberta, 11227 Saskatchewan Dr., Edmonton, Alberta, Canada T6G 2G2. E-mail: erivard@ualberta.ca

<sup>b</sup>Department of Electrical Engineering, University of Alberta, 9211 116 St., Edmonton, Alberta, Canada T6G 2H5. E-mail: mgupta1@ualberta.ca

## Table of Contents

1. Experimental Procedures .....	S3
1.1. General information, materials, and instrumentation .....	S3
1.2. Synthetic procedures .....	S4
Synthesis of silaspiro-[4.4]-2,3,7,8-tetramethyl-2,7-nonadiene ( <b>SpiroSi</b> ): .....	S4
Synthesis of 2,3-dibutyl-1,3-butadiene ( <b>diene-<sup>n</sup>Bu</b> ): .....	S4
Synthesis of 1,1-dihydro-3,4-di- <i>iso</i> -propylsilacyclopent-3-ene ( <b>SiH<sub>2</sub>-<sup>i</sup>Pr</b> ) .....	S5
Synthesis of 1,1-dichloro-3,4-dibutylgermacyclopent-3-ene ( <b>GeCl<sub>2</sub>-<sup>n</sup>Bu</b> ): .....	S5
Synthesis of 1,1-dihydro-3,4-dibutylgermacyclopent-3-ene ( <b>GeH<sub>2</sub>-<sup>n</sup>Bu</b> ): .....	S5
Synthesis of oligo(3,4-di- <i>iso</i> -propylsilacyclopentene) ( <b>OligoSi</b> ): .....	S6
Synthesis of oligo(3,4-dibutylgermacyclopent-3-ene) ( <b>OligoGe</b> ): .....	S6
Synthesis of oligo(3,4-dibutylgermacyclopentene- <i>r</i> -3,4-di- <i>iso</i> -propylsilacyclopentene) ( <b>OligoSiGe</b> ): .....	S6
Photolysis attempt of oligo(3,4-di- <i>iso</i> -propylsilacyclopentene) ( <b>OligoSi</b> ): .....	S7
Photolysis attempt of oligo(3,4-dibutylgermacyclopentene- <i>r</i> -3,4-di- <i>iso</i> -propylsilacyclopentene) ( <b>OligoSiGe</b> ): .....	S7
Photolysis attempt of <b>SpiroSi</b> : .....	S7
2. NMR Spectra.....	S8
3. FT-IR and Raman Spectra.....	S19
4. Thermogravimetric Analyses (TGA) .....	S21
5. UV-vis Spectra .....	S23
6. Gel Permeation Chromatography (GPC) .....	S26
7. Characterization of Deposited Films/Powders.....	S28
8. Computational Details.....	S34
9. References .....	S36

## 1. Experimental Procedures

### 1.1. General information, materials, and instrumentation

All air- and moisture-sensitive reagents were handled using standard Schlenk techniques<sup>S1</sup> under an atmosphere of argon, nitrogen or in a nitrogen-filled glove box (Innovative Technology, Inc.). Solvents were dried using a Grubbs'-type solvent purification system<sup>S2</sup> manufactured by Innovative Technology, Inc., and stored under nitrogen before use. Silicon tetrachloride (99 %), anhydrous magnesium chloride (98 %), copper(I) bromide, hexylmagnesium bromide (2.0 M solution in THF), *iso*-propylmagnesium chloride-lithium chloride complex (1.3 M solution in THF), and *n*-butylmagnesium chloride (2.0 M solution in THF) were purchased from Sigma-Aldrich and used as received. Naphthalene was purchased from Northwest Laboratories Ltd. and was purified by sublimation before use. Germanium(II)dichloride-dioxane (Cl<sub>2</sub>Ge•diox) was purchased from Gelest and used as received. 1,4-Dichloro-2-butyne was purchased from TCI America and used as received. 2,3-Dimethyl-1,3-butadiene (**diene-Me**) was purchased from TCI America, and was distilled under nitrogen and stored over molecular sieves (4 Å) under nitrogen before use. Lithium bromide (solid) and lithium aluminum hydride (4.0 M solution in Et<sub>2</sub>O) were purchased by Thermo Fisher Scientific and Acros, respectively, and used as received. Lithium granules (99 %, 0.04-0.2 inches) were purchased by Thermo Fisher Scientific, stored under argon, and used as received. Cp<sub>2</sub>Zr(pyr)(Me<sub>3</sub>SiCCSiMe<sub>3</sub>),<sup>S3</sup> Pt(PCy<sub>3</sub>)<sub>2</sub>,<sup>S4</sup> and 2,3-di-*iso*-propyl-1,3-butadiene (**diene-<sup>i</sup>Pr**)<sup>S5</sup> were synthesized according to literature procedures.

<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on either 400, 500, 600 or 700 MHz Varian Inova spectrometers and referenced externally to Me<sub>4</sub>Si. <sup>29</sup>Si{<sup>1</sup>H} NMR spectra were recorded on a 400 MHz Varian Inova spectrometer and referenced externally to Me<sub>4</sub>Si. Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta using a Thermo Flash 2000 Elemental Analyzer. FT-IR spectra were collected using a Nicolet 8700 spectrometer (Thermo Fisher) and a Continuum microscope (Thermo Fisher) by the Analytical and Instrumentation Laboratory at the University of Alberta. Mass spectrometric (EI-MS) data were collected by the Mass Spectrometry Facility at the University of Alberta on either an Agilent 6220 Spectrometer or Kratos Analytical MS-50G instrument. Raman data were collected using a Renishaw inVia Raman Qontor Spectrometer (633 nm, 5 mW, 60 s collection). Gel permeation chromatography (GPC) studies were run in THF (flow rate = 0.5 mL min<sup>-1</sup>) using Viscotek T6000 M columns and a Viscotek VE 2001 autosampler. Absolute molecular weight determination was performed on all polymers using right- and low-angle light scattering, and a refractive index detector (GPC 270 Max dual detector + Viscotek VE 3580). Calibration of the GPC instrument was accomplished with 99 kDa and 1 kDa polystyrene standards supplied by Malvern. Photolysis studies on the synthesized oligomers were performed using a Coherent COMPex 102 KrF pulsed excimer laser (λ<sub>em</sub> = 248 nm, pulse width = 20 ns, max. pulse energy = 400 mJ, max. pulse frequency = 15 Hz). The exposed samples were contained in a N<sub>2</sub>-filled quartz reactor throughout the entire exposure process.<sup>S3</sup> The number of pulses ranged from 10000 to 20000, with the energy of each pulse ranging from 150 to 250 mJ. Scanning electron microscopy (SEM) images and energy-dispersive X-ray (EDX) spectroscopy maps were taken with a Zeiss Sigma 300-VP FESEM with a minimum resolution of 2 nm at an acceleration voltage of either 5, 10, and 15 kV for the imaging and EDX mapping; samples were mounted on aluminum stubs with carbon tape. Elemental analysis (CHN) were performed by the Analytical and Instrumentation Laboratory at the University of Alberta using a Thermo Flash 2000 Elemental Analyzer.

## 1.2. Synthetic procedures

**Synthesis of silaspiro-[4.4]-2,3,7,8-tetramethyl-2,7-nonadiene (SpiroSi):** To a Schlenk flask containing Li granules (0.55 g, 79 mmol) was added a solution of naphthalene (10.1 g, 78.5 mmol) dissolved in 60 mL of THF *via* cannula at room temperature; the mixture was then stirred for 18 hrs. The resultant dark-green solution was then transferred dropwise *via* cannula to a solution containing 2,3-dimethyl-1,3-butadiene (3.66 g, 41.9 mmol) and anhydrous MgCl<sub>2</sub> (4.06 g, 39.9 mmol) in 4 mL of THF at room temperature. The mixture was allowed to stir for 18 hrs affording a slightly turbid dark-red mixture. The mother liquor was then added dropwise to a Schlenk flask containing SiCl<sub>4</sub> (2.37 g, 14.0 mmol) in 20 mL of THF at -78 °C. After the addition was complete, the mixture was stirred at room temperature for 2 hrs. Ethanol (10 mL) was added dropwise to the reaction mixture (at 0 °C) and the resultant heterogeneous mixture was stirred for 10 minutes at room temperature. The organic fraction was then recovered by separate extractions with pentane (3 × 80 mL) with subsequent distilled water washes (3 × 20 mL) of the combined organic fractions. The organic layer was then dried over anhydrous MgSO<sub>4</sub>, the mixture filtered, and the volatiles were removed from the filtrate under vacuum to give a white solid. Pentane (15 mL) was then added to the solid, and the resulting solution was cooled down to -30 °C for 18 hours, leading to the partial precipitation of naphthalene. The supernatant was then recovered by decantation. Removal of volatiles from the soluble fraction *in vacuo* gave a viscous yellow liquid. Purification of this product by column chromatography (silica gel, hexanes) afforded **SpiroSi** as a white solid (0.547 g, 20 %). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz): δ 1.50 (s, 8H, Si(CH<sub>2</sub>)), 1.71 (s, 12H, CH<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 126 MHz): δ 19.6 (SiCH<sub>2</sub>), 24.6 (CCH<sub>3</sub>), 131.1 (CCH<sub>3</sub>). <sup>29</sup>Si {<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 79 MHz): δ 19.0 (s). Anal. Calcd. for C<sub>12</sub>H<sub>20</sub>Si: C, 74.92; H, 10.48 %. Found: C, 74.65; H, 10.38 %. HR-MS (EI): m/z calcd. for [C<sub>12</sub>H<sub>20</sub>Si]<sup>+</sup>: 192.13342; found: 192.13388 (Δppm = 2.0).

**Synthesis of 2,3-dibutyl-1,3-butadiene (diene-<sup>n</sup>Bu):** To a mixture of CuBr (6.85 g, 47.7 mmol) and LiBr (4.14 g, 47.7 mmol) in 65 mL of THF at -78 °C was added a solution of <sup>n</sup>BuMgCl (23.9 mL, 48 mmol, 2.0 M solution in THF), and the mixture was then stirred for 1 hr at -78 °C. A solution of 1,4-dichloro-2-butyne (2.42 g, 19.7 mmol) was then added, with cooling maintained at -78 °C. Once the addition of alkyne was complete, the cold bath was removed, and the reaction mixture was stirred at room temperature for 3 hrs. Distilled water (20 mL) was then added and the heterogeneous mixture was stirred for 10 minutes. The organic fraction was recovered by separate extractions with pentane (3 × 60 mL) with subsequent distilled water washes (3 × 20 mL) of the combined organic fractions. The organic layer was dried over anhydrous MgSO<sub>4</sub> and filtered. Removal of the volatiles from the filtrate *in vacuo* gave a yellow liquid. The product was then purified by distillation (0.2 Torr, 60 °C) affording **diene-<sup>n</sup>Bu** as a colorless liquid (2.23 g, 70 %). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz): δ 0.88 (t, 6H, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, CH<sub>2</sub>CH<sub>3</sub>), 1.27-1.31 (m, 4H, <sup>n</sup>Bu CH<sub>2</sub>), 1.43-1.47 (m, 4H, <sup>n</sup>Bu CH<sub>2</sub>), 2.24 (t, 4H, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, C(CH<sub>2</sub>)CH<sub>2</sub>), 5.13 (s, 2H, C=CH<sub>2</sub>), 4.94 (s, 2H, C=CH<sub>2</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 126 MHz): δ 14.3 (CH<sub>2</sub>CH<sub>3</sub>), 23.1 (<sup>n</sup>Bu CH<sub>2</sub>), 31.4 (<sup>n</sup>Bu CH<sub>2</sub>), 34.5 (<sup>n</sup>Bu CH<sub>2</sub>), 111.8 (C=CH<sub>2</sub>), 148.4 (C=CH<sub>2</sub>). HR-MS (EI): m/z calcd. for [C<sub>12</sub>H<sub>23</sub>]<sup>+</sup>: 167.1800; found: 167.1794 (Δppm = 3.6).

**Synthesis of 1,1-dihydro-3,4-di-*iso*-propylsilacyclopent-3-ene (SiH<sub>2</sub>-<sup>i</sup>Pr):** To a Schlenk flask containing an excess of Li granules (1.00 g, 145 mmol) was added a solution of naphthalene (10.6 g, 82.7 mmol) in 75 mL of THF *via* cannula at room temperature, and the mixture was stirred for 18 hrs under argon. The resultant dark-green solution was then transferred dropwise *via* cannula to a solution containing 2,3-di-*iso*-propyl-1,3-butadiene (**diene-<sup>i</sup>Pr**) (6.71 g, 48.3 mmol) and anhydrous MgCl<sub>2</sub> (3.99 g, 42.0 mmol) in 5 mL of THF at room temperature. The resulting mixture was allowed to stir for 16 hrs affording a slightly turbid dark-red mixture. The mother liquor from this mixture was added dropwise to a Schlenk flask containing SiCl<sub>4</sub> (14.3 g, 84.2 mmol) in THF (40 mL) at -78 °C *via* cannula. After the addition was completed, the cooling bath was removed and the mixture was stirred for 2 hrs at room temperature. The volatiles were removed under vacuum and then 40 mL of Et<sub>2</sub>O was added. The resulting mixture was cooled down to -78 °C and a solution of Li[AlH<sub>4</sub>] (12.2 mL, 49 mmol, 4.0 M solution in Et<sub>2</sub>O) diluted with 20 mL of Et<sub>2</sub>O was added dropwise *via* cannula. After the addition of Li[AlH<sub>4</sub>], the mixture was warmed to room temperature and stirred for 2 hrs. Distilled water (20 mL) was added carefully to the reaction mixture (0 °C) under a counterflow of N<sub>2</sub>, and the resulting heterogeneous mixture was left stirring for 10 minutes. The organic fraction was then recovered in air by separate extractions with pentane (3 × 60 mL) with subsequent distilled water washes (3 × 20 mL) of the combined organic fractions. Removal of the volatiles from the organic fraction *in vacuo* gave a slightly turbid yellow semi-solid. Addition of 100 mL of pentane to this semi-solid, followed by cooling to -78 °C for 10 minutes, allowed the partial precipitation of remanent naphthalene. The resulting supernatant was filtered by cannula and removal of the volatiles from the filtrate *in vacuo* gave a slightly-turbid yellow liquid. Purification of this product by column chromatography (silica gel, hexanes) afforded **SiH<sub>2</sub>-<sup>i</sup>Pr** as a colorless liquid (0.82 g, 12 %). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz): δ 0.92 (d, 12H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.44 (t, 4H, <sup>3</sup>J<sub>HH</sub> = 3.8 Hz, Si(CH<sub>2</sub>)), 2.83 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 4.10 (pentet, 2H, <sup>3</sup>J<sub>HH</sub> = 3.8 Hz, SiH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 126 MHz): δ 10.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 21.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 29.1 (Si(CH<sub>2</sub>)), 139.7 ((CH<sub>2</sub>)C(CH)). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 79 MHz): δ 29.8 (H<sub>2</sub>Si). HR-MS (EI): m/z calcd. for [C<sub>10</sub>H<sub>20</sub>Si]<sup>+</sup>: 168.13342; found: 168.13298 (Δppm = 2.6). IR (ATR, cm<sup>-1</sup>): 2144 (νSi-H).

**Synthesis of 1,1-dichloro-3,4-dibutylgermacyclopent-3-ene (GeCl<sub>2</sub>-<sup>n</sup>Bu):** In a glove box, a solution of **diene-<sup>n</sup>Bu** (2.00 g, 12.1 mmol) in 25 mL of toluene was added to a Schlenk flask containing Cl<sub>2</sub>Ge•dioxane (3.07 g, 13.3 mmol). The flask was heated to 90 °C in an oil bath for 2 hrs under constant stirring. The mixture was cooled down to 0 °C and the mixture was subjected to cannula filtration. Removal of the volatiles from the filtrate *in vacuo* afforded **GeCl<sub>2</sub>-<sup>n</sup>Bu** as a colorless liquid (2.76 g, 80 %). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz): δ 0.82 (t, 6H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, CH<sub>2</sub>CH<sub>3</sub>), 1.06-1.16 (m, 8H, <sup>n</sup>Bu CH<sub>2</sub>), 1.86-1.91 (br, 8H, C(CH<sub>2</sub>)CH<sub>2</sub> and Ge(CH<sub>2</sub>)C). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 126 MHz): δ 14.3 (CH<sub>2</sub>CH<sub>3</sub>), 22.9 (C(CH<sub>2</sub>)CH<sub>2</sub>), 30.3 (<sup>n</sup>Bu CH<sub>2</sub>), 30.4 (<sup>n</sup>Bu CH<sub>2</sub>), 32.2 (GeCH<sub>2</sub>), 133.7 (GeCH<sub>2</sub>C). Anal. Calcd. for C<sub>12</sub>H<sub>22</sub>Cl<sub>2</sub>Si: C, 46.52; H, 7.16 %. Found: C, 46.92; H, 7.30 %.

**Synthesis of 1,1-dihydro-3,4-dibutylgermacyclopent-3-ene (GeH<sub>2</sub>-<sup>n</sup>Bu):** A solution of **GeCl<sub>2</sub>-<sup>n</sup>Bu** (2.50 g, 8.75 mmol) in 20 mL of Et<sub>2</sub>O was added dropwise *via* cannula to a solution of Li[AlH<sub>4</sub>] (2.56 mL, 10 mmol, 4.0 M solution in Et<sub>2</sub>O) diluted in 3 mL of Et<sub>2</sub>O at -78 °C with constant stirring. During the addition, a white precipitate formed. The mixture was then stirred for 12 hrs at room temperature and filtered *via* cannula filtration. Distilled water (20 mL) was added dropwise to the cooled filtrate at 0 °C under N<sub>2</sub>. The organic fraction was then recovered by separate extractions with pentane (3 × 60 mL) and the combined organic fractions were washed

with distilled water (3 × 60 mL). The organic fraction was dried over anhydrous MgSO<sub>4</sub> and then filtered. The solvent was removed from the filtrate *in vacuo* at room temperature to give **GeH<sub>2</sub>-<sup>n</sup>Bu** as a colorless liquid (1.53 g, 81 %). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz): δ 0.89 (t, 6H, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, CH<sub>2</sub>CH<sub>3</sub>), 1.21-1.31 (m, 4H, CH<sub>2</sub>), 1.34-1.42 (m, 4H, CH<sub>2</sub>), 1.77 (t, 4H, <sup>3</sup>J<sub>HH</sub> = 3.4 Hz, GeCH<sub>2</sub>), 2.13 (t, 4H, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, CCH<sub>2</sub>), 4.12 (pentet, 2H, <sup>3</sup>J<sub>HH</sub> = 3.4 Hz, H<sub>2</sub>Ge). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 126 MHz): δ 14.5 (CH<sub>3</sub>), 18.4 (CH<sub>2</sub>CH<sub>3</sub>), 23.4 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 31.1 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 33.1 (Ge(CH<sub>2</sub>)C), 136.1 (Ge(CH<sub>2</sub>)C). HR-MS (EI): m/z calcd. for [C<sub>12</sub>H<sub>25</sub>Ge]<sup>+</sup>: 243.1168; found: 243.1163 (Δppm = 2.1).

**Synthesis of oligo(3,4-di-*iso*-propylsilacyclopentene) (OligoSi):** In a glove box, a solution of **SiH<sub>2</sub>-<sup>i</sup>Pr** (46.5 mg, 0.277 mmol) dissolved in 0.25 mL of toluene was added to a Schlenk flask containing Pt(PCy<sub>3</sub>)<sub>2</sub> (13 mg, 0.017 mmol) and 0.25 mL of toluene at room temperature. The reaction mixture was brought outside of the glovebox and was heated at 80 °C on a Schlenk line with constant stirring for 18 hrs. Bubbling and the progressive coloration of the solution to orange was observed overtime. The volatiles were then removed *in vacuo* affording a light-yellow semi-solid. Added purification by precipitation of the product dissolved in THF (100 μL) into 5 mL of cold MeCN (-30 °C) afforded **OligoSi** as a light-orange semi-solid (32 mg, 69 %). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz): δ 0.75-1.51 (br, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.52-2.25 (br, 4H, Si(CH<sub>2</sub>)), 2.81-3.26 (br, 2H, CH(CH<sub>3</sub>)<sub>2</sub>). Raman (cm<sup>-1</sup>): 2101 (νSi-H, end groups), 1622 (νC=C), 878 (δSi-H), 508 (νSi-Si). GPC (THF, absolute): M<sub>n</sub> = 1.0 kDa; PDI = 2.3.

**Synthesis of oligo(3,4-dibutylgermacyclopent-3-ene) (OligoGe):** In a glove box, a solution of **GeH<sub>2</sub>-<sup>n</sup>Bu** (50 mg, 0.23 mmol) dissolved in 0.5 mL of C<sub>6</sub>H<sub>6</sub> was added to a vial containing Pt(PCy<sub>3</sub>)<sub>2</sub> (11 mg, 0.014 mmol) at room temperature, followed by stirring for 18 hrs. Bubbling and the progressive coloration of the solution to light-yellow was observed overtime. The volatiles were then removed *in vacuo* affording a light-yellow semi-solid. Added purification by precipitation of the product dissolved in THF (100 μL) into 5 mL of cold MeCN (-30 °C) afforded **OligoGe-<sup>n</sup>Bu** as a light-yellow semi-solid (44 mg, 89 %). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz): δ 0.81-1.22 (br, 6H, CH<sub>2</sub>(CH<sub>3</sub>)), 1.25-1.591 (br, 8H, <sup>n</sup>Bu CH<sub>2</sub>), 1.93-2.73 (br, 8H, Ge(CH<sub>2</sub>) and C(CH<sub>2</sub>)). Raman (cm<sup>-1</sup>): 2021 (νGe-H, end groups), 1633 (νC=C), 300 (νGe-Ge). GPC (THF, absolute): M<sub>n</sub> = 1.4 kDa; PDI = 1.2. UV-vis (in THF): λ<sub>abs</sub> = 290 nm (shoulder).

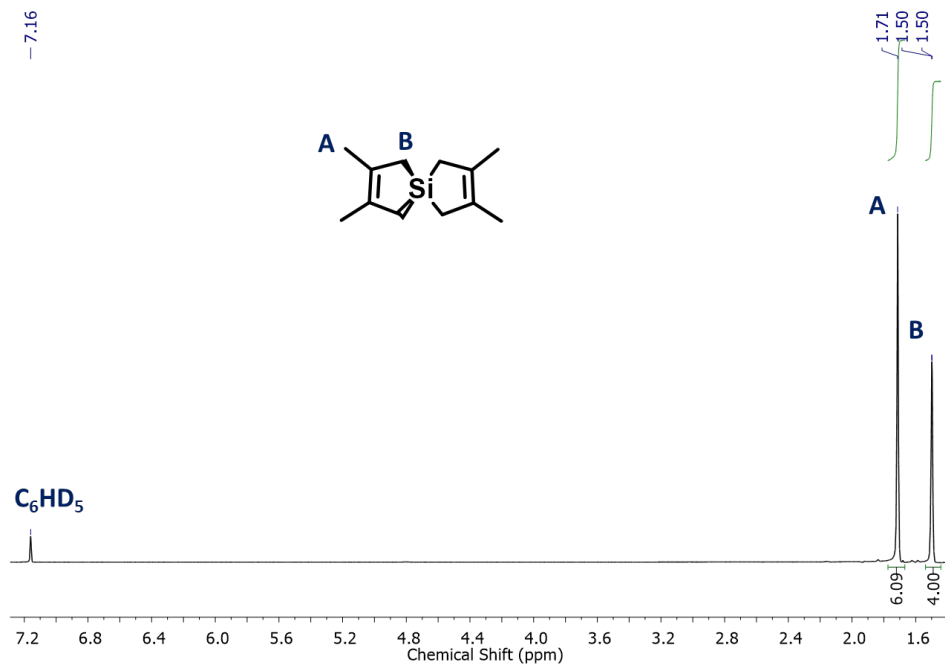
**Synthesis of oligo(3,4-dibutylgermacyclopentene-*r*-3,4-di-*iso*-propylsilacyclopentene) (OligoSiGe):** In a glove box, a solution of **GeH<sub>2</sub>-<sup>i</sup>Pr** (0.045 g, 0.21 mmol) and **SiH<sub>2</sub>-<sup>n</sup>Bu** (0.035 g, 0.21 mmol) dissolved in 0.5 mL of toluene was added to a vial containing Pt(PCy<sub>3</sub>)<sub>2</sub> (3.1 mg, 0.0043 mmol, 2 mol% with respect to the Si monomer). The solution was then transferred to a Schlenk flask and brought out of the glovebox and the mixture stirred for 18 hrs at 80 °C on a Schlenk line. Vigorous bubbling and the coloration of the solution to orange was observed overtime. The volatiles were then removed *in vacuo* and added purification by precipitation of the product dissolved in THF (100 μL) into 5 mL of cold MeCN (-30 °C) gave **OligoSiGe** as an orange-red colored semi-solid (66 mg, 81 % yield assuming a co-polymer is formed with a composition of 51 % of the Si monomer unit bearing *iso*-propyl repeating units, as estimated by <sup>1</sup>H NMR spectroscopy). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz): δ 0.65-1.12 (br, CH<sub>2</sub>CH<sub>3</sub> and CH(CH<sub>3</sub>)<sub>2</sub>), 1.15-2.23 (br, Si(CH<sub>2</sub>), Ge(CH<sub>2</sub>), C(CH<sub>2</sub>), C(CH<sub>2</sub>)(CH<sub>2</sub>), and CH<sub>2</sub>CH<sub>3</sub>), 2.81-3.05 (br, CH(CH<sub>3</sub>)<sub>2</sub>). Raman (cm<sup>-1</sup>): 2116 (νSi-H, end groups), 1997 (ν<sub>s</sub>Ge-H, end groups), 1622 (νC=C), 878 (δSi-H), 563 (νSi-Si), 463 (νSi-Ge), 304 (ν<sub>as</sub>Ge-Ge). GPC (THF, absolute): M<sub>n</sub> = 1.4 kDa; PDI = 1.2.

**Photolysis attempt of oligo(3,4-di-*iso*-propylsilacyclopentene) (OligoSi):** A solution of **OligoSi** (28 mg, 0.17 mmol per monomer unit) in 0.5 mL of dry THF in a custom-made,<sup>S3</sup> N<sub>2</sub>-filled, photolysis reactor was irradiated with a KrF laser of 248 nm. Once the irradiation period was complete, a brown-grey film formed on the inner wall of the reactor, along with a dark-grey precipitate at the bottom of the reactor. Inside a glove box, the light-yellow colored mother liquor was separated by decantation from the dark-grey powder. The volatiles were removed from the recovered mother liquor *in vacuo* affording a yellow oil; <sup>1</sup>H NMR analysis of the soluble fraction showed signals corresponding to 2,3-di-*iso*-propyl-1,3-butadiene (**diene-<sup>i</sup>Pr**; 3%) and unreacted **OligoSi**. The amount of recovered precipitate was too low to be measured by our laboratory balances.

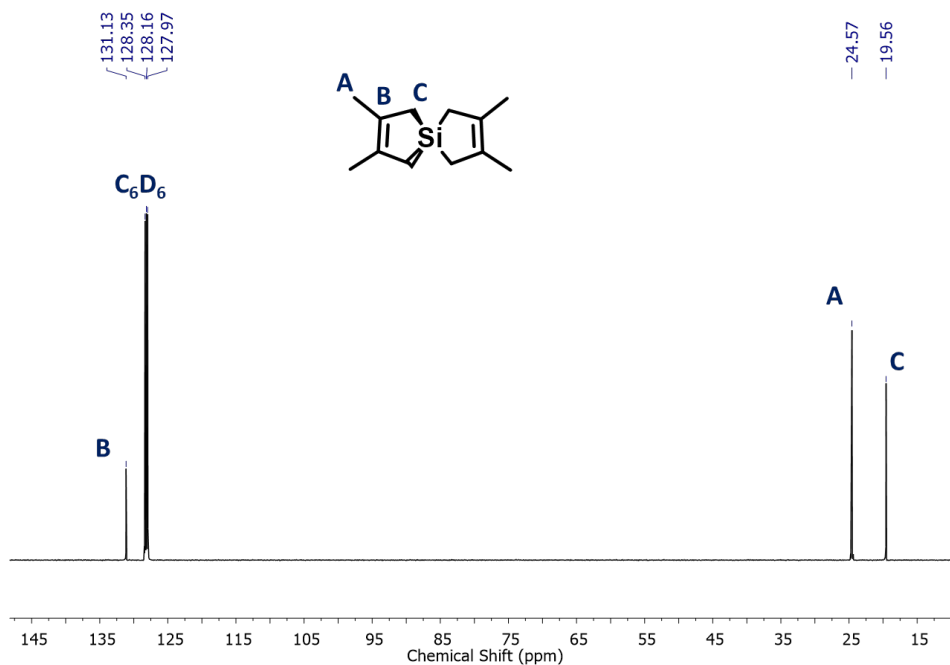
**Photolysis attempt of oligo(3,4-dibutylgermacyclopentene-r-3,4-di-*iso*-propylsilacyclopentene) (OligoSiGe):** A solution of **OligoSiGe** (55 mg, 0.28 mmol per monomer unit) in 0.5 mL of dry THF in a custom-made,<sup>S3</sup> N<sub>2</sub>-filled, photolysis reactor was irradiated with a KrF laser of 248 nm. Once the irradiation period was complete, a metallic-grey film formed on the inner wall of the reactor, along with a grey precipitate at the bottom of the reactor. Inside a glove box, the light-yellow colored mother liquor was separated by decantation from the dark-grey powder. The remaining precipitate was purified by washes with dry THF (20 mL total) followed by removal of volatiles *in vacuo* (3.2 mg, 23 % yield; yield based on a product composition of SiGe). <sup>1</sup>H NMR analysis of the reaction solution directly after photolysis shows the presence of released 2,3-di-*iso*-propyl-1,3-butadiene (**diene-<sup>i</sup>Pr**, 4 %) and 2,3-dibutyl-1,3-butadiene (**diene-<sup>n</sup>Bu**, 8 %).

**Photolysis attempt of SpiroSi:** A solution of **SpiroSi** (0.101 g, 0.459 mmol) in 0.5 mL of dry C<sub>6</sub>D<sub>12</sub> in a custom-made,<sup>S3</sup> N<sub>2</sub>-filled, photolysis reactor was irradiated with a KrF laser of 248 nm. Once the irradiation period was complete, a fine dark-grey precipitate film on the inner wall of the reactor was observed, along with a small amount of dark-grey powder at the bottom of the reactor. Inside a glove box, the mother liquor was separated by decantation from the dark-grey powder/film; <sup>1</sup>H NMR spectroscopic analysis of the mother liquor showed small signals corresponding to liberated 2,3-dimethyl-1,3-butadiene (3 %) as well as unreacted **SpiroSi**. The amount of recovered precipitate was too low to be measured by our laboratory balances.

## 2. NMR Spectra

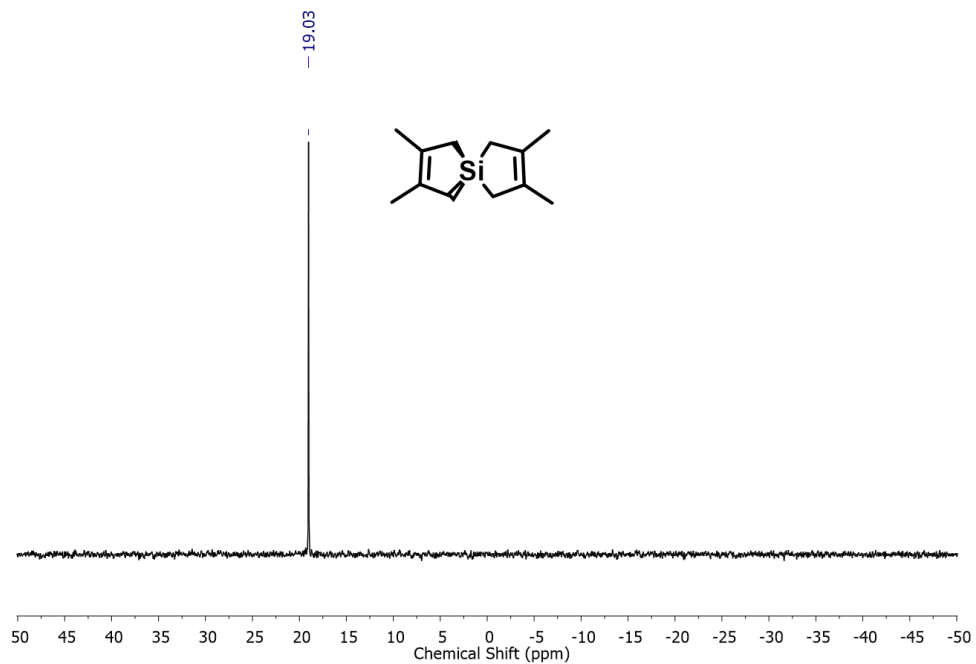


**Fig. S1.**  $^1\text{H}$  NMR spectrum of silaspiro-[4.4]-2,3,7,8-tetramethyl-2,7-nonadiene (**SpiroSi**) in  $\text{C}_6\text{D}_6$ .

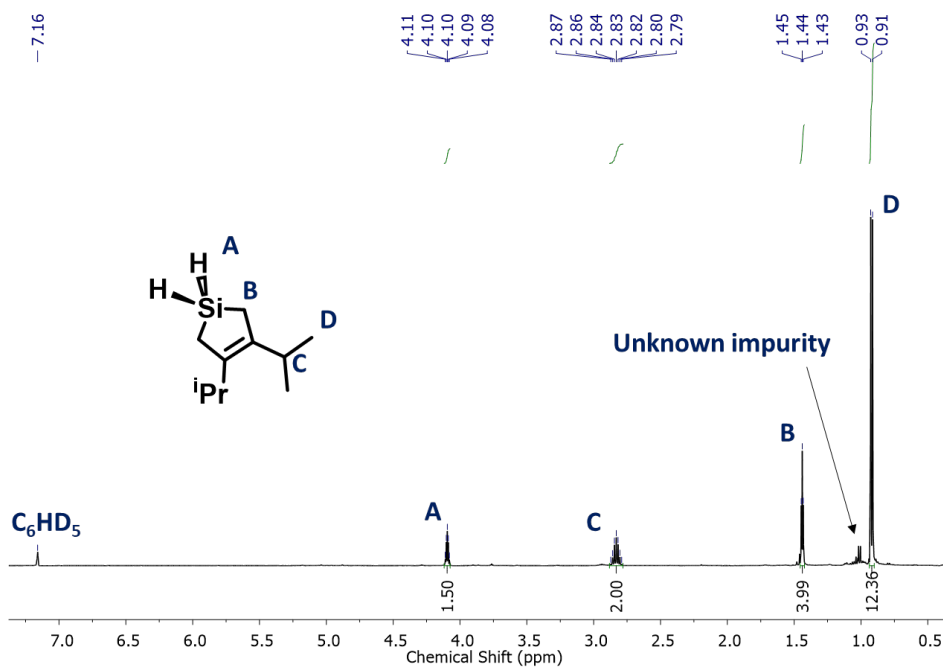


**Fig. S2.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of silaspiro-[4.4]-2,3,7,8-tetramethyl-2,7-nonadiene (**SpiroSi**) in  $\text{C}_6\text{D}_6$ .

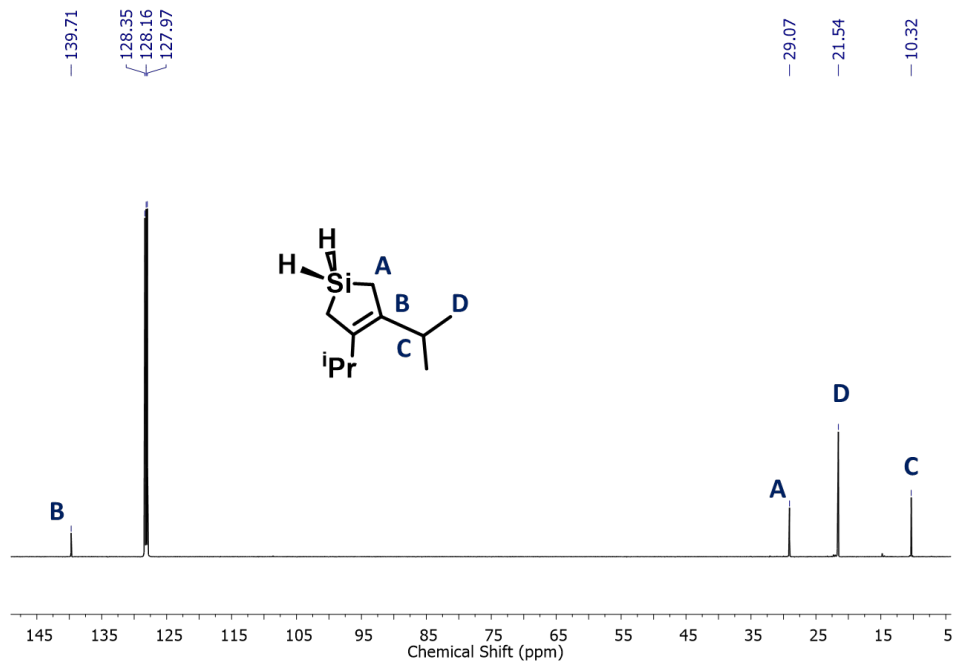




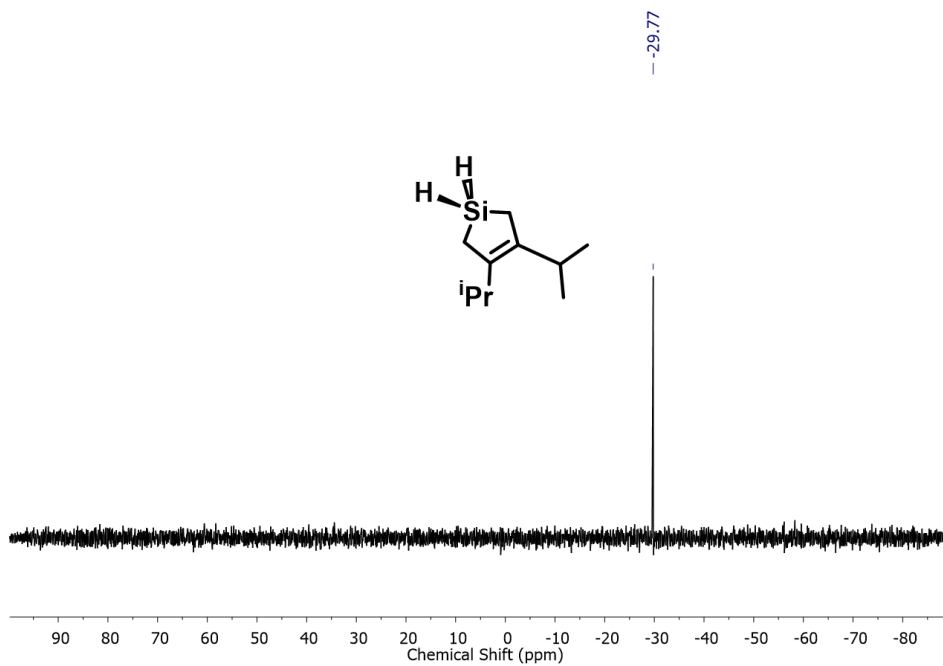
**Fig. S3.**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of silaspiro-[4.4]-2,3,7,8-tetramethyl-2,7-nonadiene (**SpiroSi**) in  $\text{C}_6\text{D}_6$ .



**Fig. S4.**  $^1\text{H}$  NMR spectrum of 1,1-dihydro-3,4-di-*iso*-propylsilacyclopent-3-ene ( $\text{SiH}_2\text{-iPr}$ ) in  $\text{C}_6\text{D}_6$ .



**Fig. S5.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 1,1-dihydro-3,4-di-*iso*-propylsilacyclopent-3-ene ( $\text{SiH}_2\text{-iPr}$ ) in  $\text{C}_6\text{D}_6$ .



**Fig. S6.**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of 1,1-dihydro-3,4-di-*iso*-propylsilacyclopent-3-ene ( $\text{SiH}_2\text{-iPr}$ ) in  $\text{C}_6\text{D}_6$ .

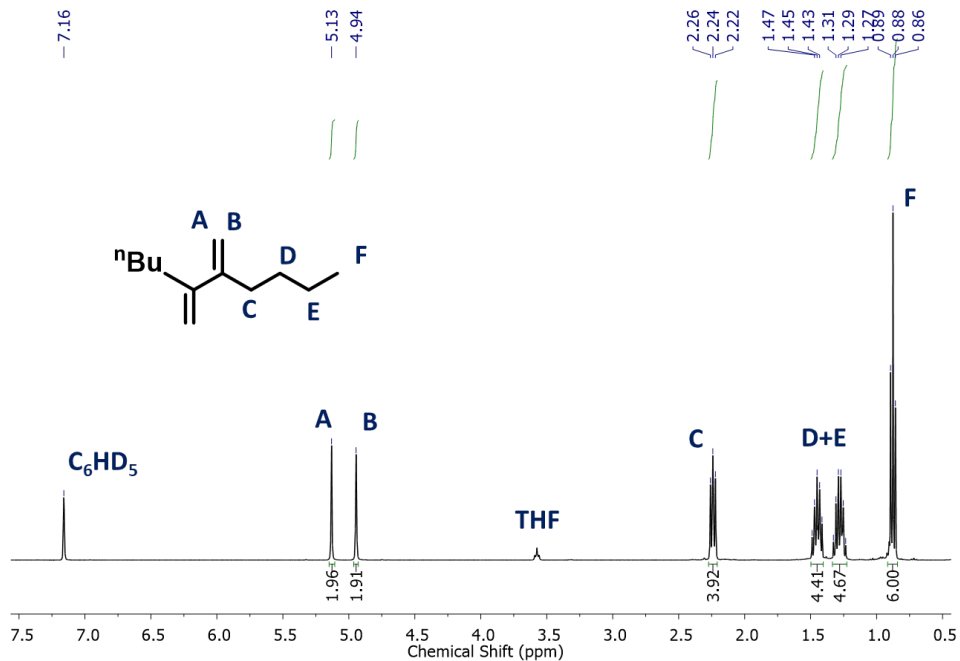


Fig. S7. <sup>1</sup>H NMR spectrum of 2,3-dibutyl-1,3-butadiene (**diene-nBu**) in C<sub>6</sub>D<sub>6</sub>.

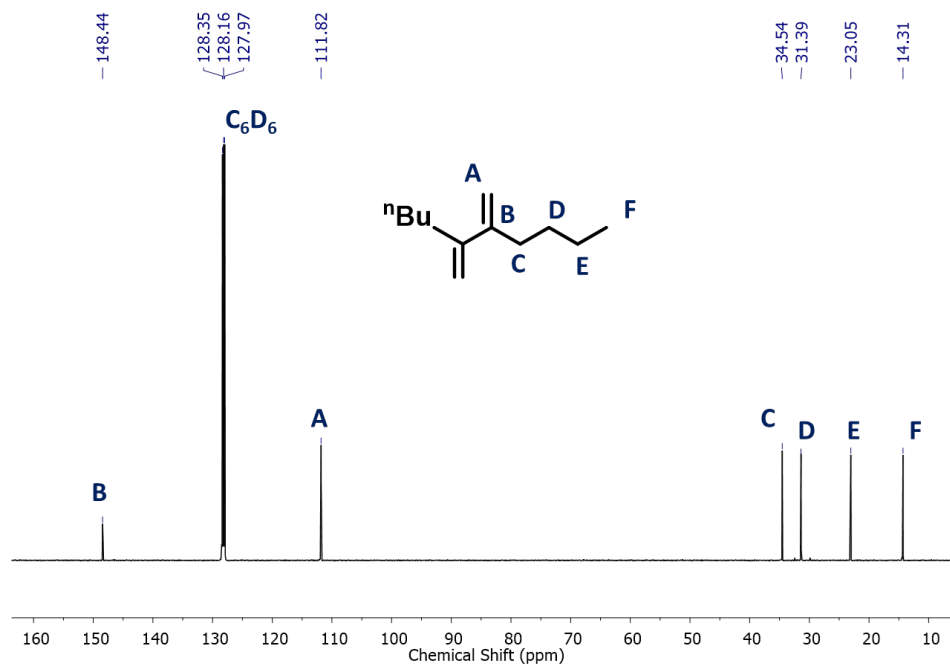
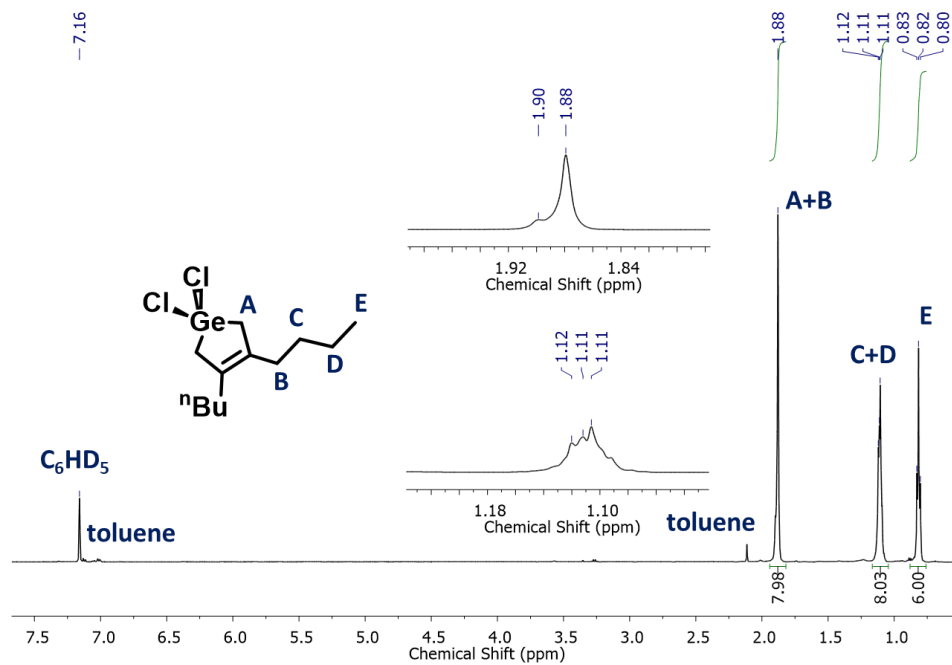
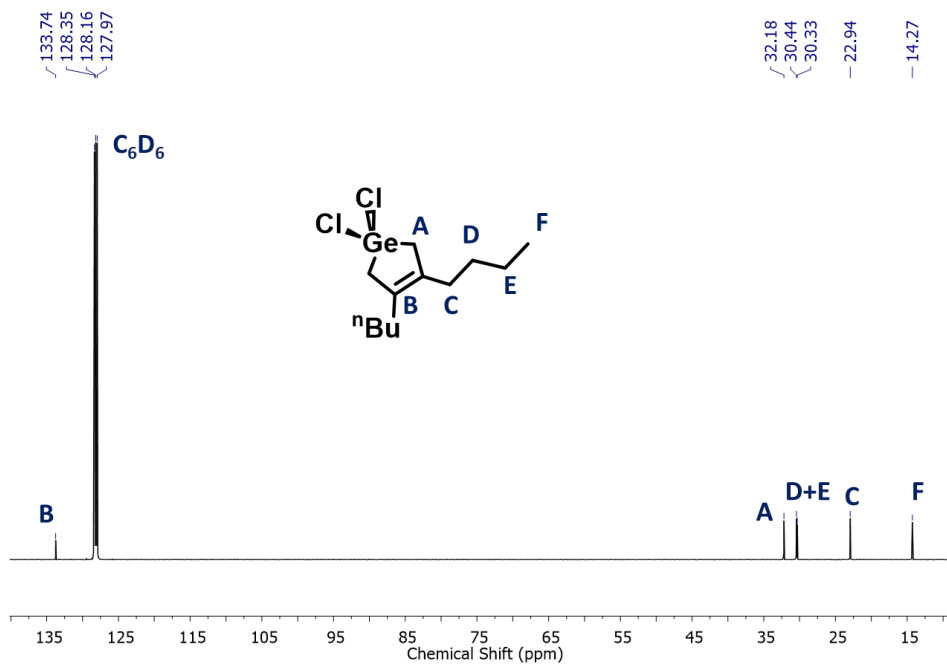


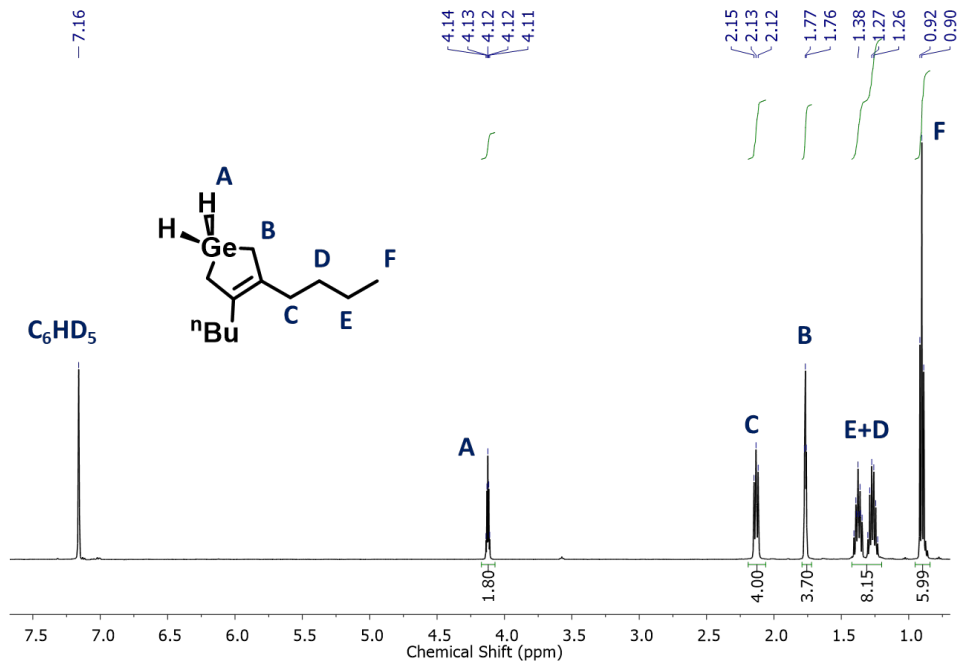
Fig. S8. <sup>13</sup>C {<sup>1</sup>H} NMR spectrum of 2,3-dibutyl-1,3-butadiene (**diene-nBu**) in C<sub>6</sub>D<sub>6</sub>.



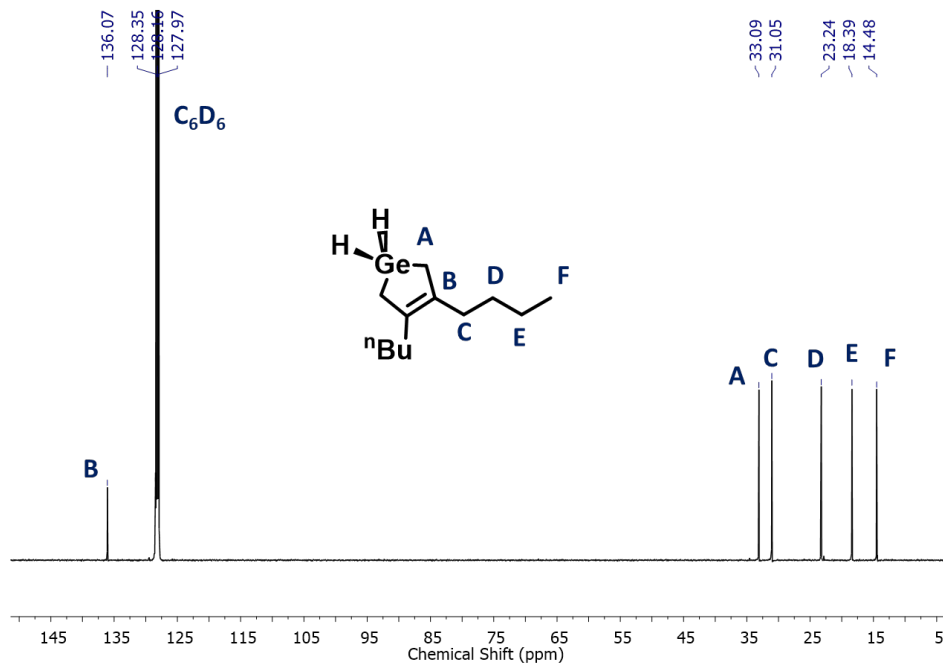
**Fig. S9.**  $^1\text{H}$  NMR spectrum of 1,1-dichloro-3,4-dibutylgermacyclopent-3-ene ( $\text{GeCl}_2\text{-}^n\text{Bu}$ ) in  $\text{C}_6\text{D}_6$ .



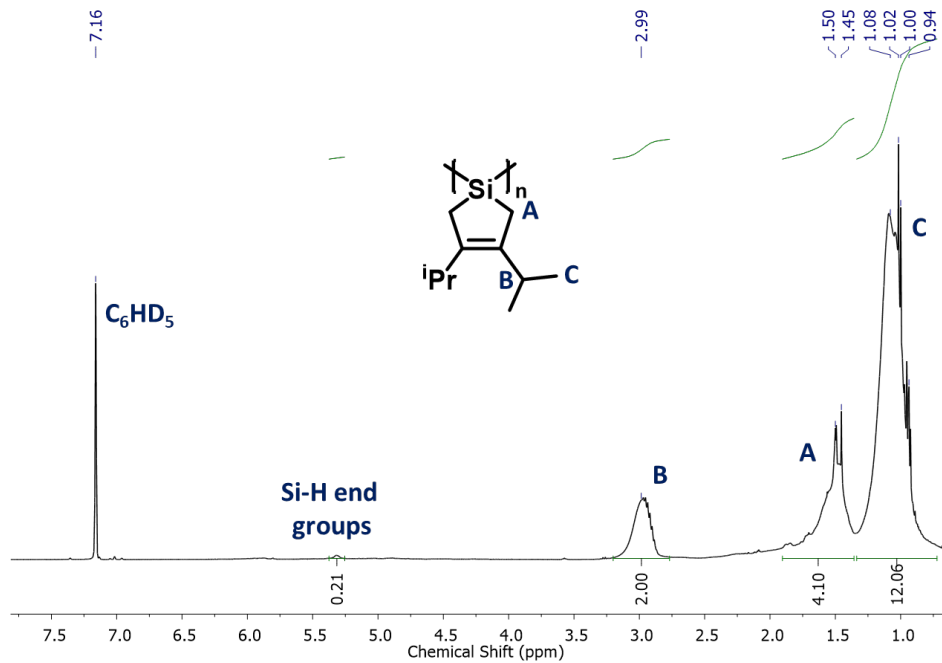
**Fig. S10.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 1,1-dichloro-3,4-dibutylgermacyclopent-3-ene ( $\text{GeCl}_2\text{-}^n\text{Bu}$ ) in  $\text{C}_6\text{D}_6$ .



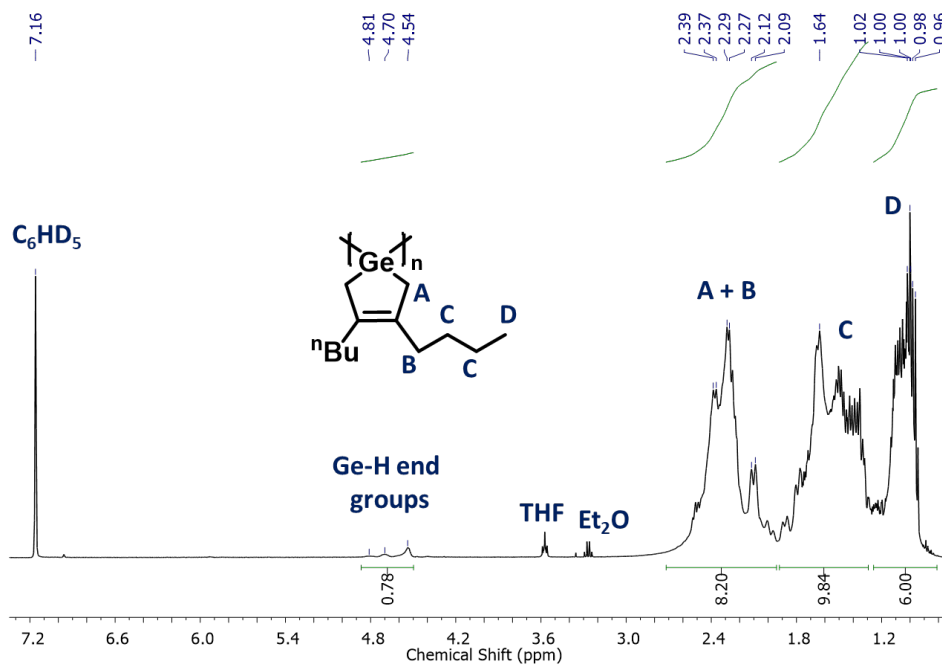
**Fig. S11.**  $^1\text{H}$  NMR spectrum of 1,1-dihydro-3,4-dibutylgermacyclopent-3-ene ( $\text{GeH}_2\text{-}^n\text{Bu}$ ) in  $\text{C}_6\text{D}_6$ .



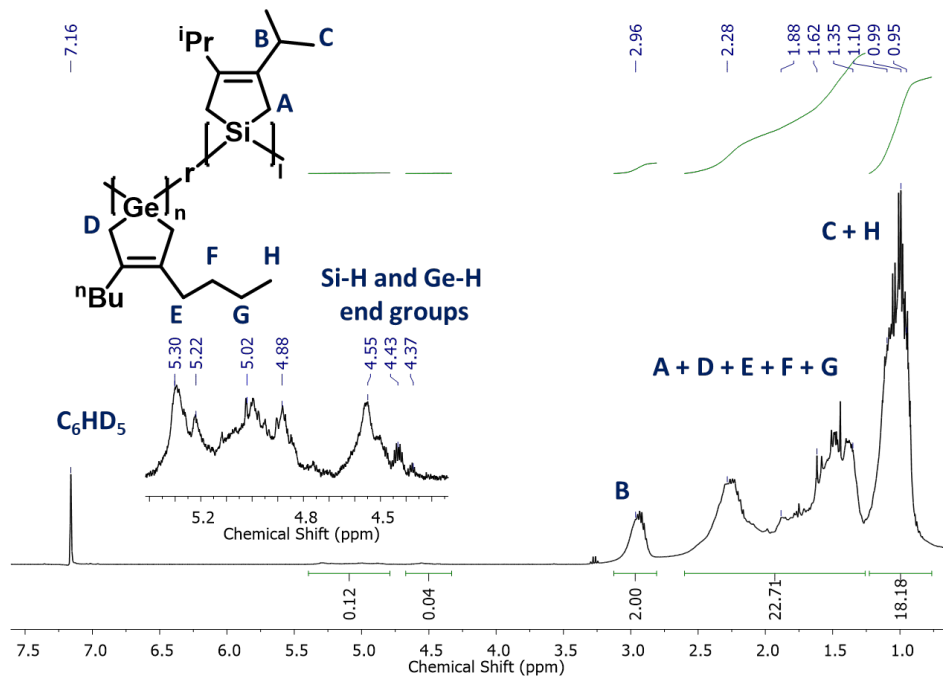
**Fig. S12.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 1,1-dihydro-3,4-dibutylgermacyclopent-3-ene ( $\text{GeH}_2\text{-}^n\text{Bu}$ ) in  $\text{C}_6\text{D}_6$ .



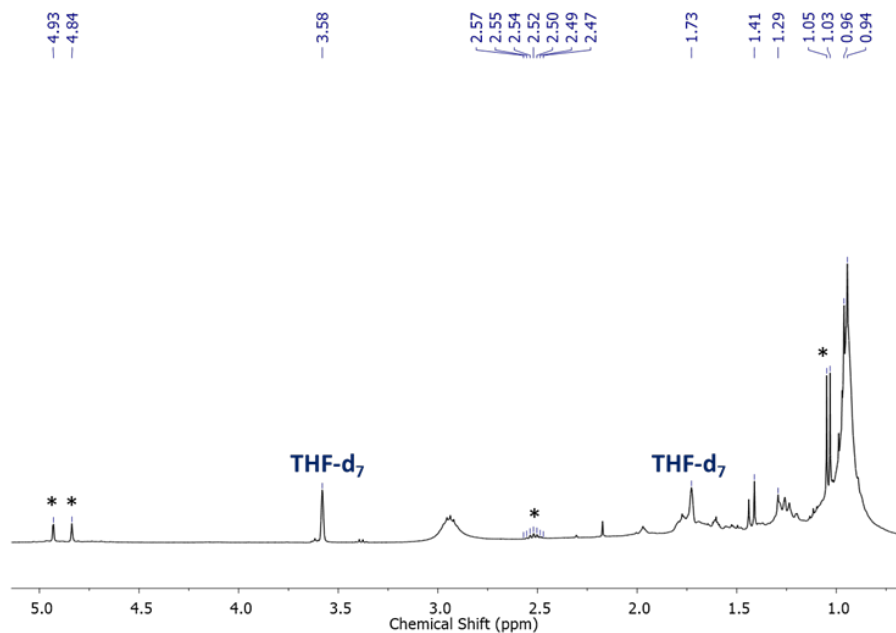
**Fig. S13.**  $^1\text{H}$  NMR spectrum of oligo(3,4-di-*iso*-propylsilacyclopentene) (**OligoSi**) in  $\text{C}_6\text{D}_6$ .



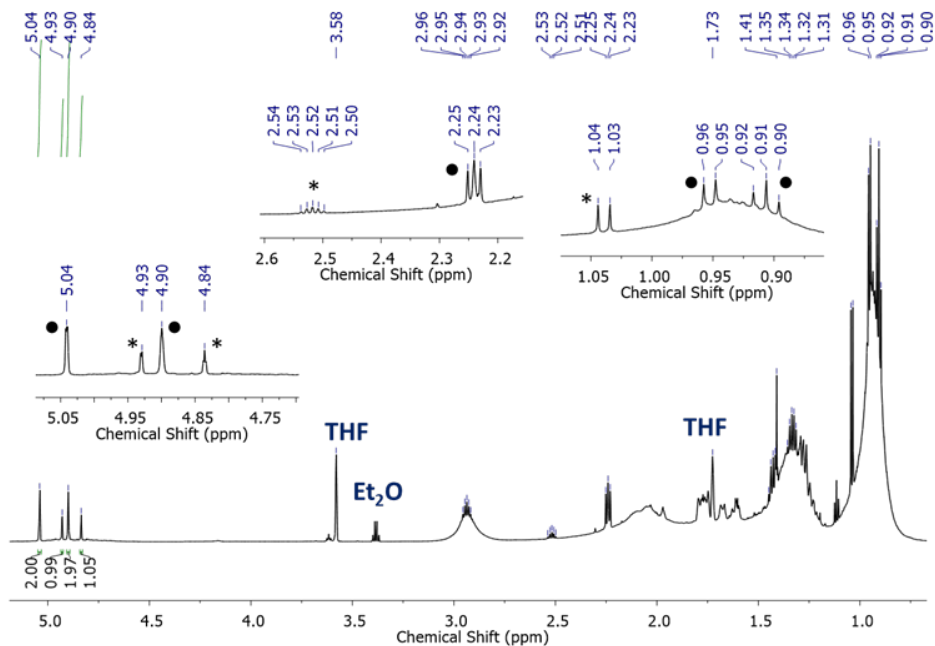
**Fig. S14.**  $^1\text{H}$  NMR spectrum of oligo(3,4-dibutylgermacyclopentene) (**OligoGe**) in  $\text{C}_6\text{D}_6$ .



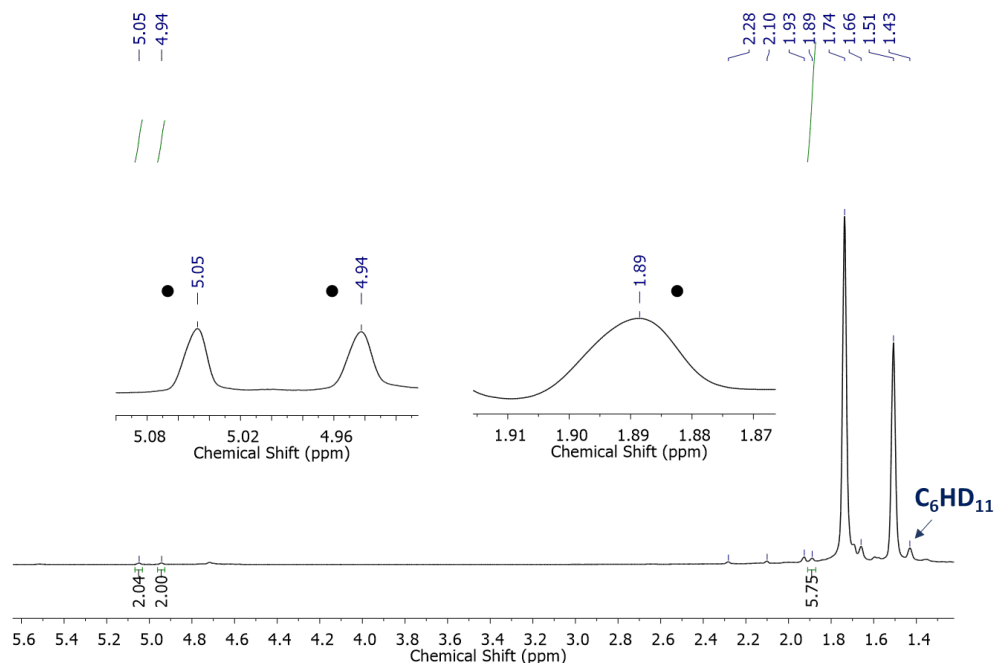
**Fig. S15.**  $^1\text{H}$  NMR spectrum of oligo(3,4-dibutylgermacyclopentene-*r*-3,4-di-*iso*-propylsilacyclopentene) (**OligoSiGe**) in  $\text{C}_6\text{D}_6$ .



**Fig. S16.**  $^1\text{H}$  NMR spectrum of the reaction mixture after photolysis of oligo(3,4-di-*iso*-propylsilacyclopentene) (**OligoSi**) in  $\text{THF-d}_8$ . Signals marked with (\*) at 4.93, 4.84, 2.52, and 1.04 ppm correspond to the free diene, 2,3-di-*iso*-propyl-1,3-butadiene.

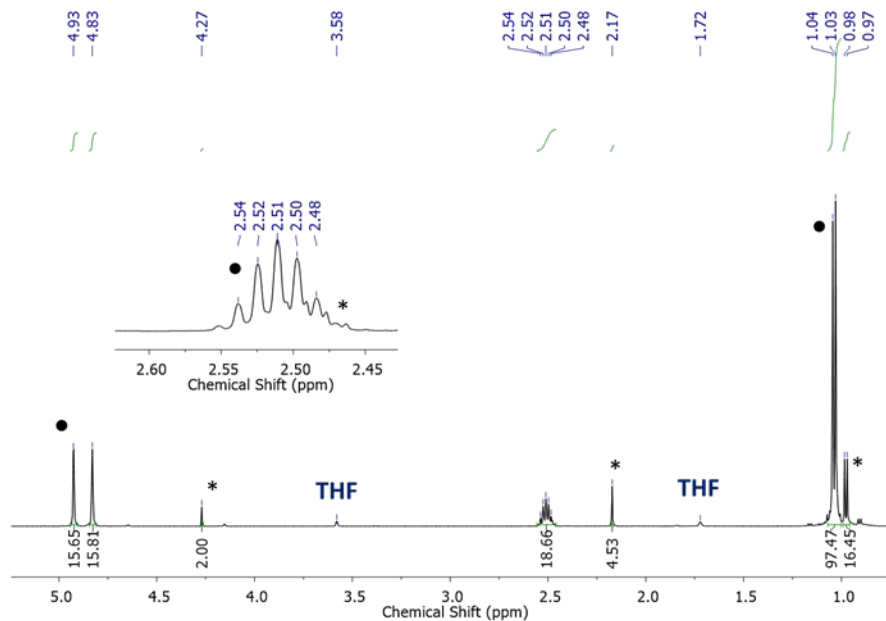


**Fig. S17.** <sup>1</sup>H NMR spectrum of the reaction solution after photolysis of oligo(3,4-dibutylgermacyclopentene-*r*-3,4-di-*iso*-propylsilacyclopentene) (**OligoSiGe**) in THF-*d*<sub>8</sub>. Signals (\*) at 4.93, 4.84, 2.52, and 1.04 ppm correspond to released 2,3-di-*iso*-propyl-1,3-butadiene. Signals (●) at 5.04, 4.90, 2.24, 0.96 and 0.91 ppm correspond to released 2,3-dibutyl-1,3-butadiene.

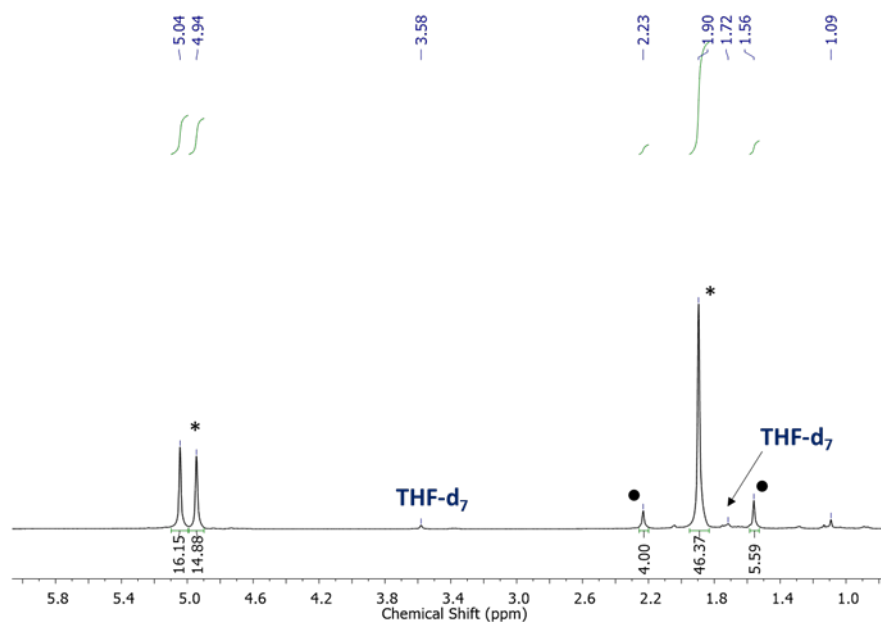


**Fig. S18.** <sup>1</sup>H NMR spectrum of the reaction mixture after photolysis of silaspiro-[4.4]-2,3,7,8-tetramethyl-2,7-nonadiene (**SpiroSi**) in cyclohexane-*d*<sub>12</sub>. Signals (●) at 5.05, 4.94, and 1.89 ppm correspond to 2,3-dimethyl-1,3-butadiene.

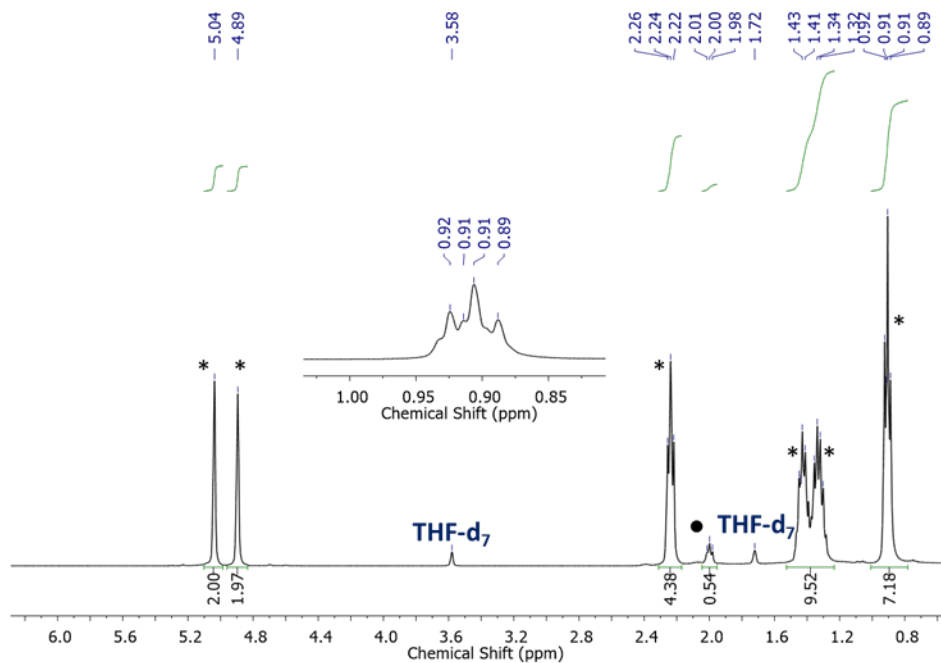




**Fig. S19.**  $^1\text{H}$  NMR spectrum of the reaction mixture after photolysis of 2,3-di-*iso*-propyl-1,3-butadiene (**diene-iPr**) in  $\text{THF-d}_8$ . Signals ( $\bullet$ ) at 4.93, 4.83, and 1.03 ppm correspond to 2,3-di-*iso*-propyl-1,3-butadiene (**diene-iPr**). Other signals ( $*$ ) correspond to the unknown decomposition product(s).

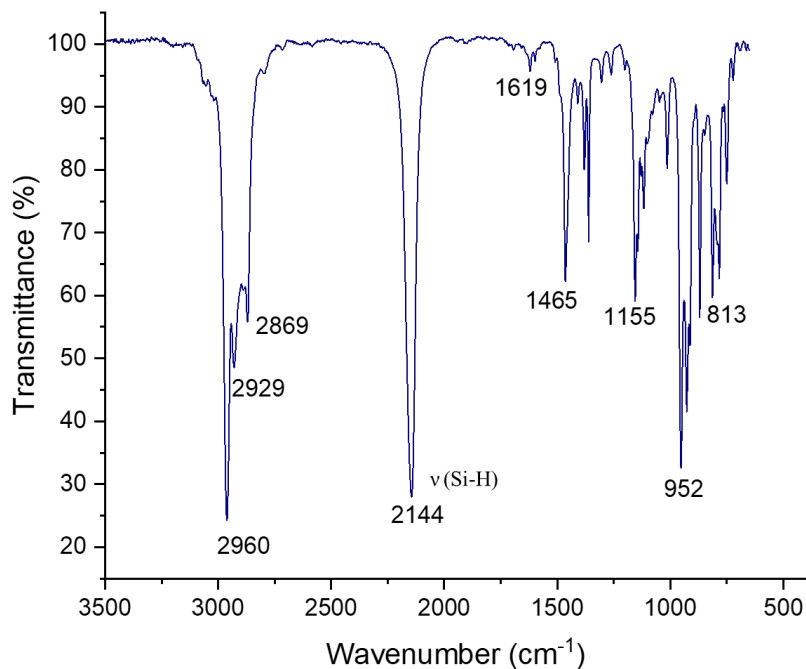


**Fig. S20.**  $^1\text{H}$  NMR spectrum of the reaction mixture after photolysis of 2,3-dimethyl-1,3-butadiene (**diene-Me**) in  $\text{THF-d}_8$ . Signals ( $*$ ) at 5.04 and 1.90 ppm correspond to 2,3-dimethyl-1,3-butadiene (**diene-Me**). Other signals ( $\bullet$ ) correspond to the unknown decomposition product(s).

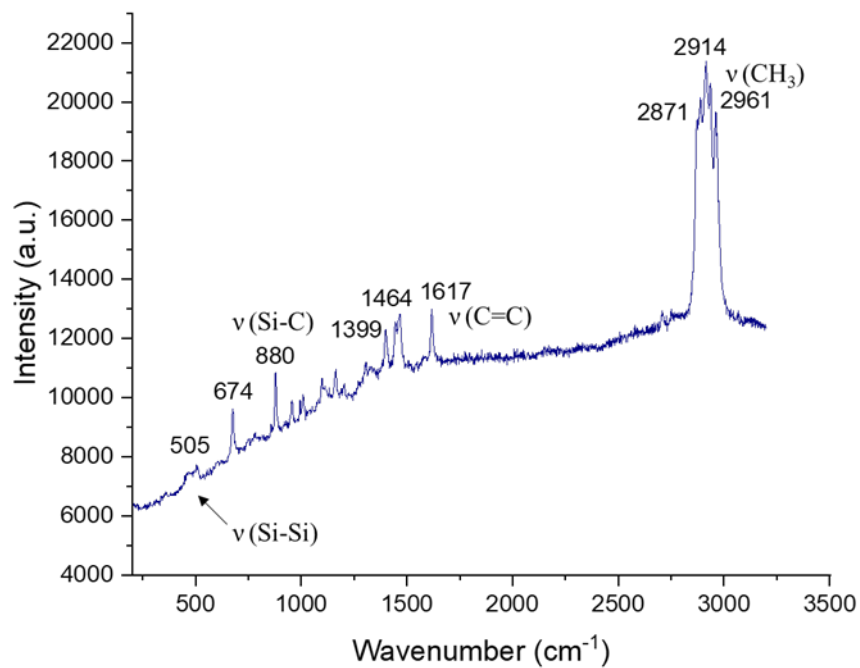


**Fig. S21.**  $^1\text{H}$  NMR spectrum of the reaction mixture after photolysis of 2,3-dimethyl-1,3-butadiene (**diene-nBu**) in THF-d<sub>8</sub>. Signals (\*) at 5.04, 4.89, 2.24, 1.41, 1.34, and 0.91 ppm correspond to 2,3-dibutyl-1,3-butadiene (**diene-nBu**). Other signals (•) correspond to the unknown decomposition product(s).

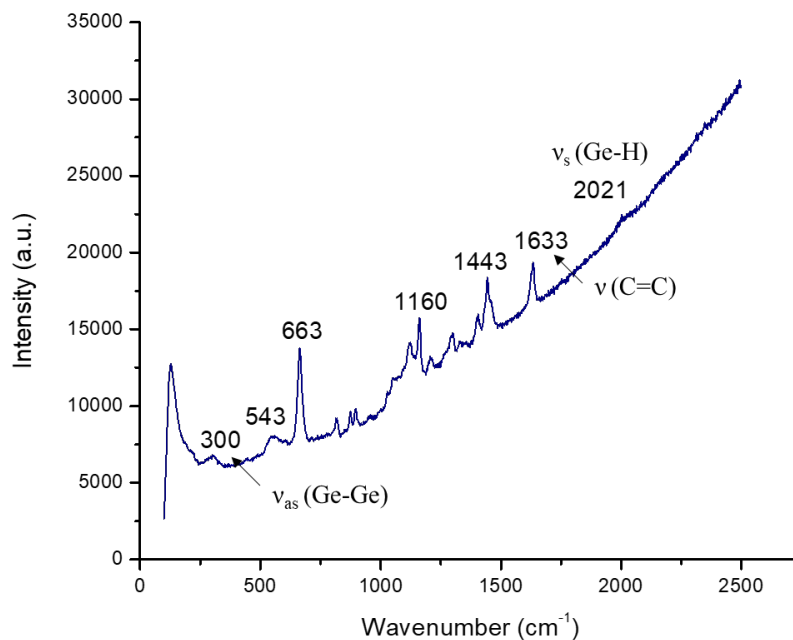
### 3. FT-IR and Raman Spectra



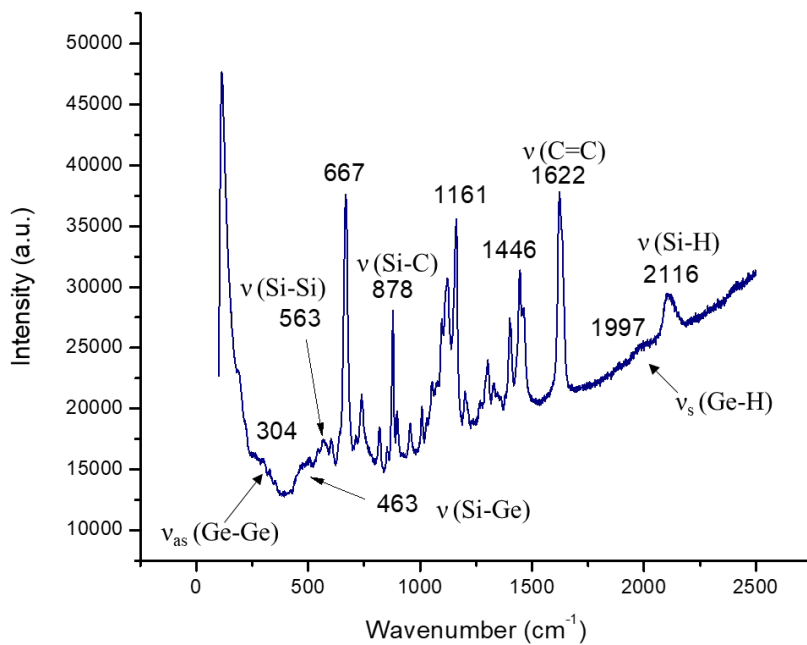
**Fig. S22.** FT-IR spectrum of 1,1-dihydro-2,3-di-*iso*-propylcyclosilapent-3-ene ( $\text{SiH}_2\text{-iPr}$ ); an intense Si-H stretch is observed at 2144  $\text{cm}^{-1}$ .



**Fig. S23.** Raman spectrum of oligo(3,4-di-*iso*-propylsilacyclopentene), **OligoSi**. Excitation wavelength: 633 nm.

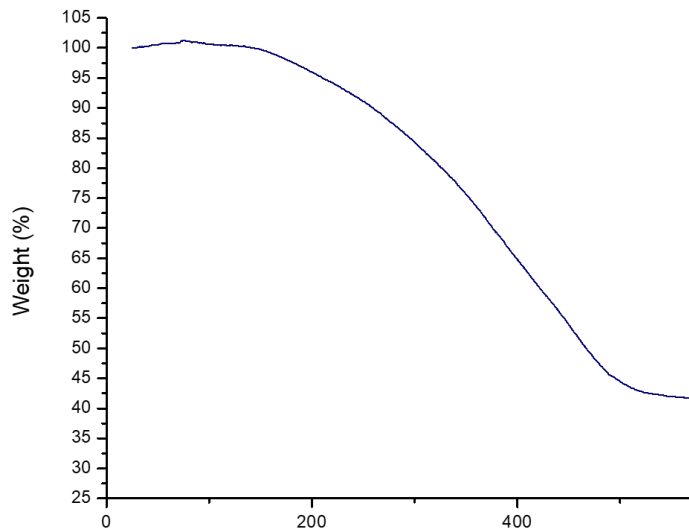


**Fig. S24.** Raman spectrum of oligo(3,4-dibutylgermacyclopentene) (**OligoGe**). Excitation wavelength: 633 nm.

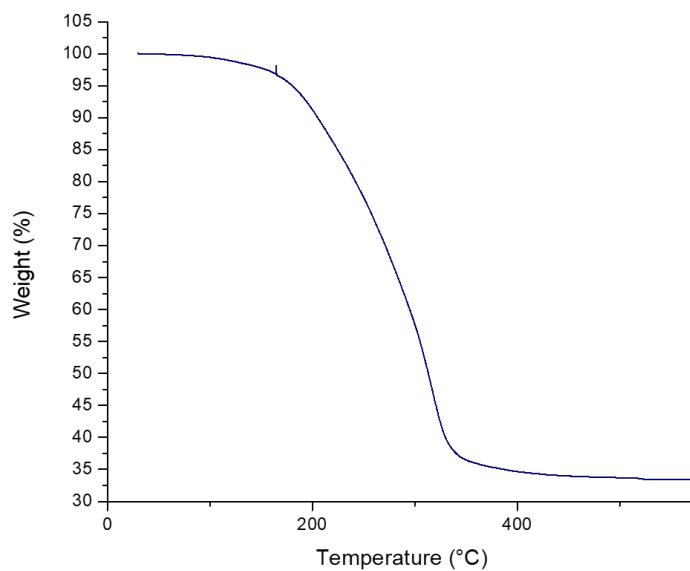


**Fig. S25.** Raman spectrum of oligo(3,4-dibutylgermacyclopentene-*r*-3,4-di-*iso*-propylsilacyclopentene) (**OligoSiGe**). Excitation wavelength: 633 nm.

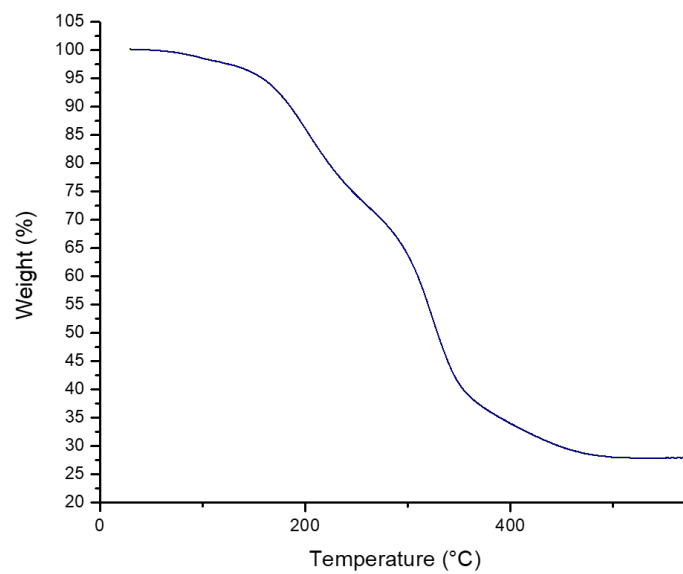
#### 4. Thermogravimetric Analyses (TGA)



**Fig. S26.** Thermogravimetric analysis (TGA) plot of oligo(3,4-di-*iso*-propylsilacyclopentene) (OligoSi). Scan rate: 10 °C min<sup>-1</sup> under Ar.

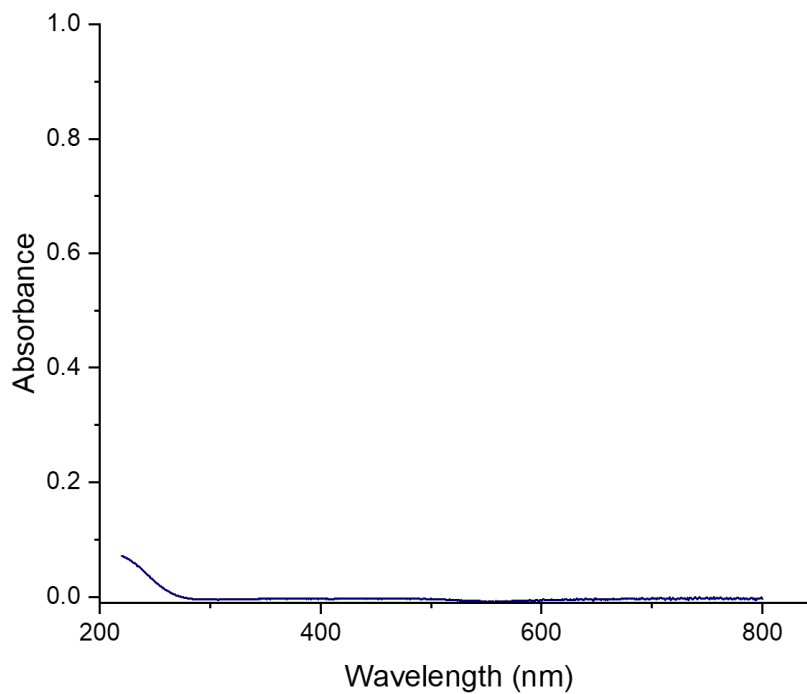


**Fig. S27.** Thermogravimetric analysis (TGA) plot of oligo(3,4-dibutylgermacyclopentene) (OligoGe). Scan rate: 10 °C min<sup>-1</sup> under Ar.

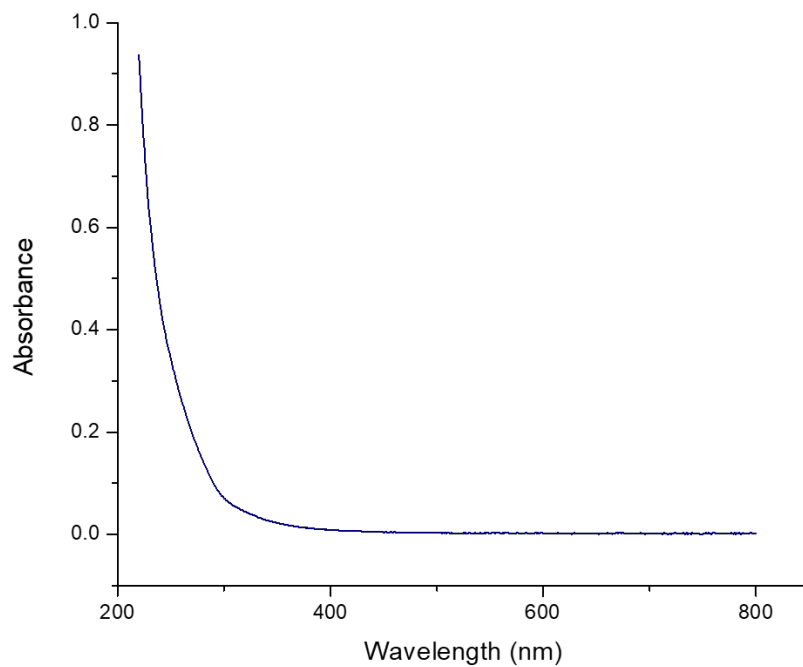


**Fig. S28.** Thermogravimetric analysis (TGA) plot of oligo(3,4-dibutylgermacyclopentene-*r*-3,4-di-*iso*-propylsilacyclopentene) (**OligoSiGe**). Scan rate: 10 °C min<sup>-1</sup> under Ar.

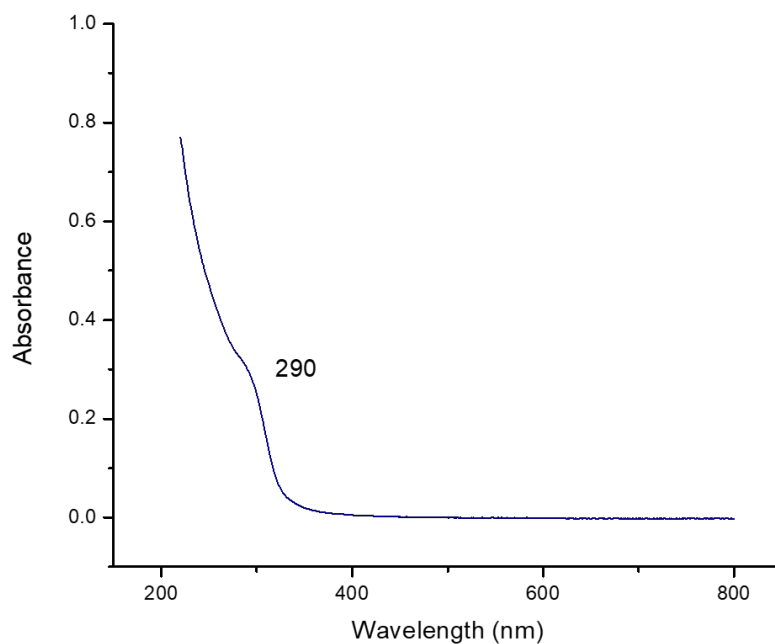
## 5. UV-vis Spectra



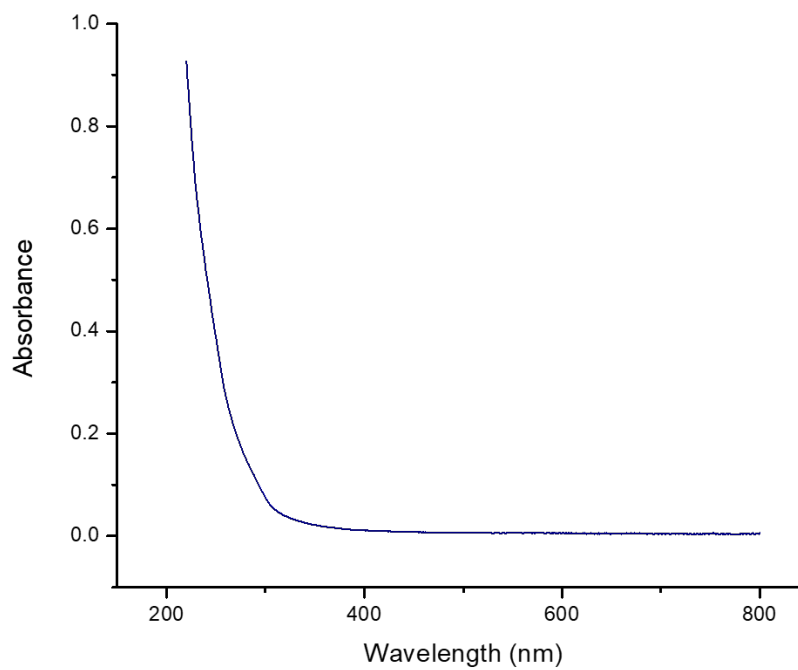
**Fig. S29.** UV-vis spectrum of THF.



**Fig. S30.** UV-vis spectrum of oligo(3,4-di-*iso*-propylsilacyclopentene) (**OligoSi**) in THF.

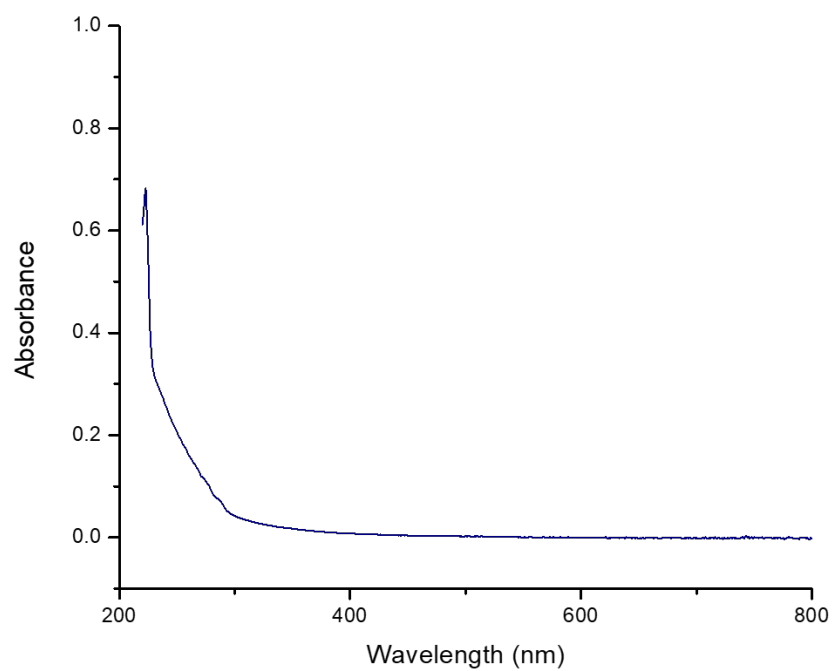


**Fig. S31.** UV-vis spectrum of oligo(3,4-dibutylgermacyclopentene) (**OligoGe**) in THF.



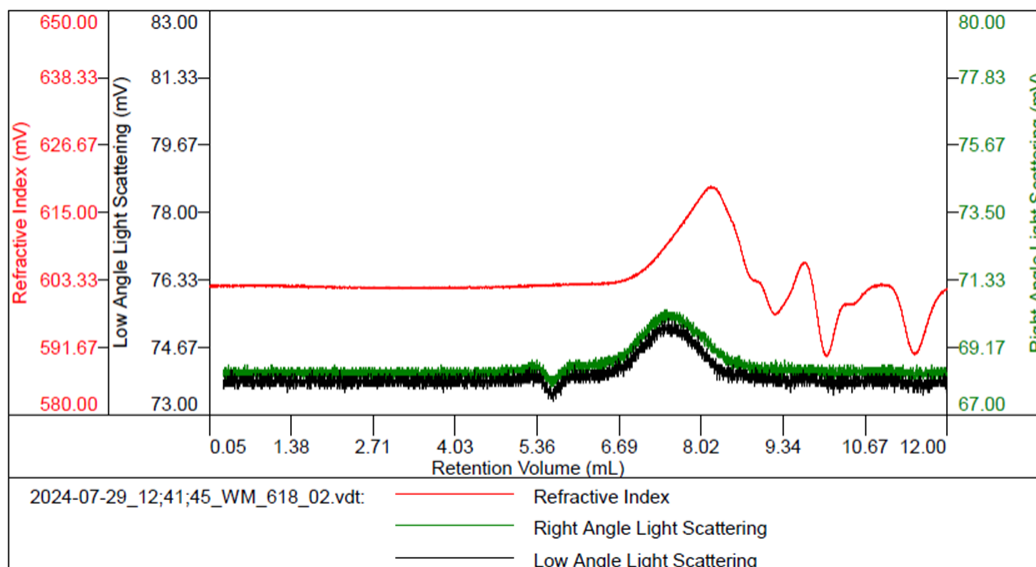
**Fig. S32.** UV-vis spectrum of oligo(3,4-dibutylgermacyclopentene-*r*-3,4-di-*iso*-propylsilacyclopentene), **OligoSiGe** in THF.



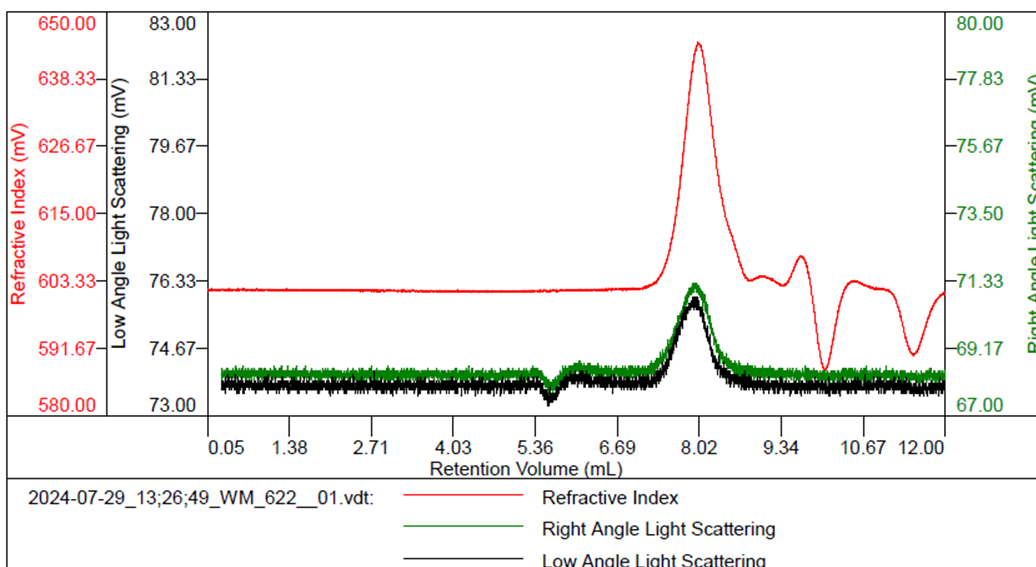


**Fig. S33.** UV-vis spectrum of silaspiro-[4.4]-2,3,7,8-tetramethyl-2,7-nonadiene (**SpiroSi**) in THF.

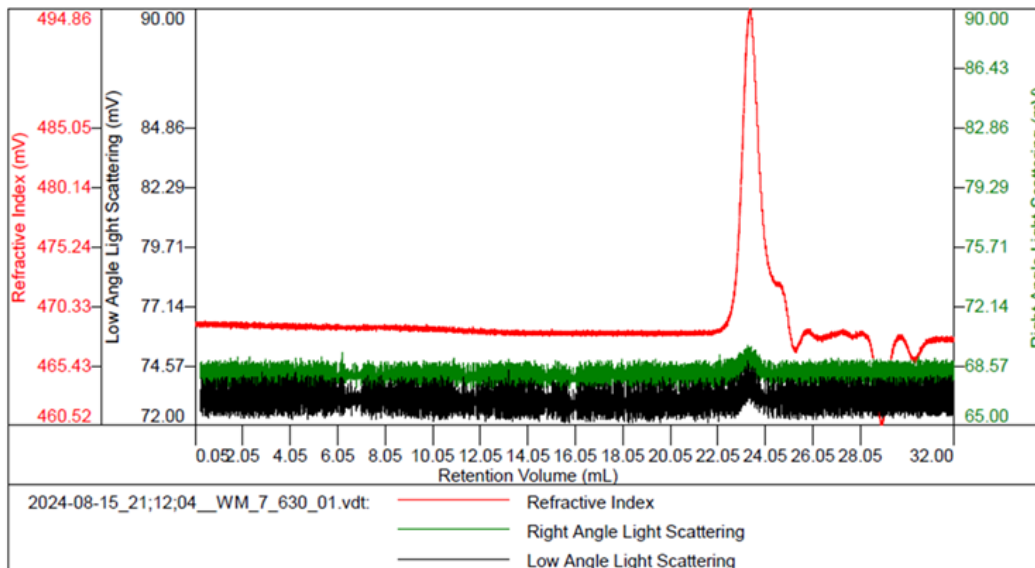
## 6. Gel Permeation Chromatography (GPC)



**Fig. S34.** GPC elution profile of oligo(3,4-di-*iso*-propylsilacyclopentene) (**OligoSi**) in THF. Negative peaks in the refractive index (RI) detector are artifacts of sample injection.

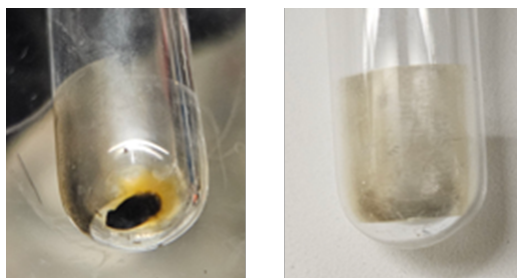


**Fig. S35.** GPC elution profile of oligo(3,4-dibutylgermacyclopentene) (**OligoGe**) in THF. Negative peaks in the refractive index (RI) detector are artifacts of sample injection.

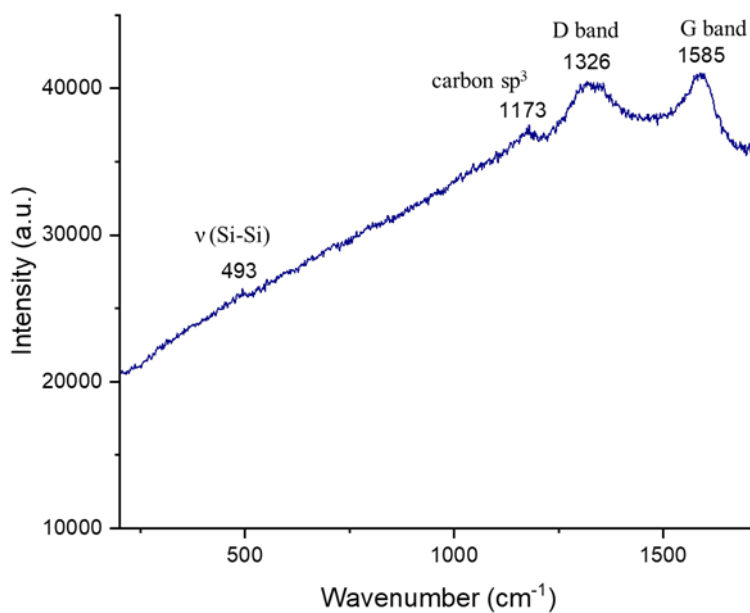


**Fig. S36.** GPC elution profile of oligo(3,4-dibutylgermacyclopentene-*r*-3,4-di-*iso*-propylsilacyclopentene) (**OligoSiGe**) in THF. Negative peaks in the refractive index (RI) detector are artifacts of sample injection.

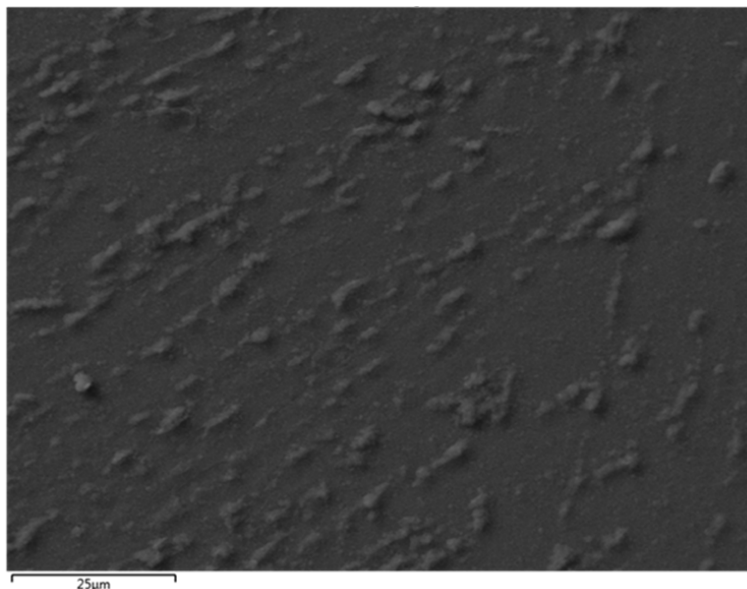
## 7. Characterization of Deposited Films/Powders



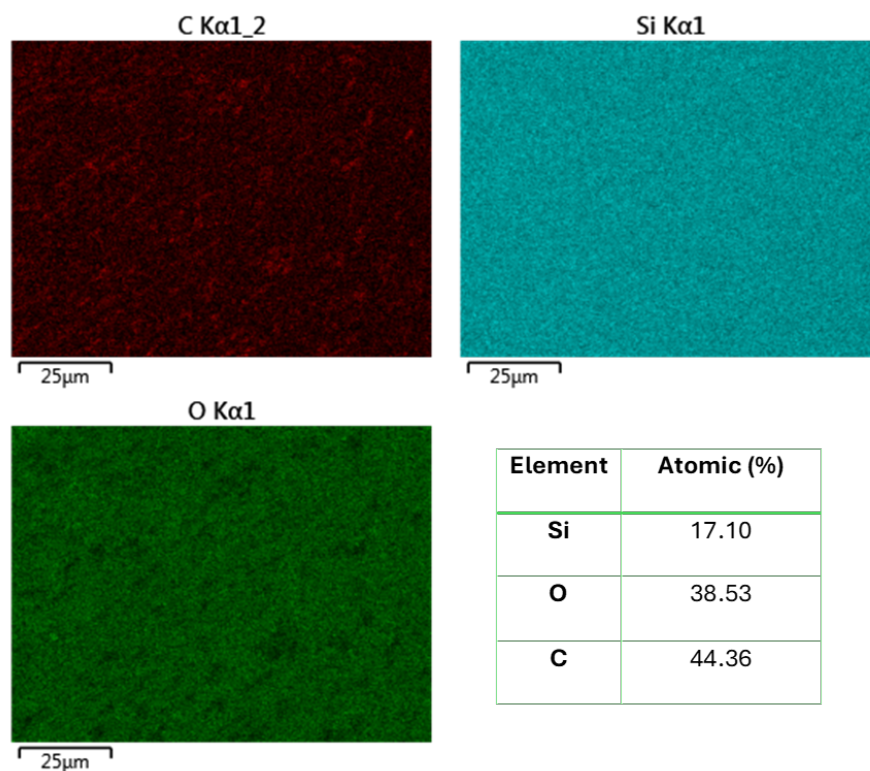
**Fig. S37.** Photograph of the deposited powder after photolysis of oligo(3,4-di-*iso*-propylsilacyclopentene) (**OligoSi**) in THF.



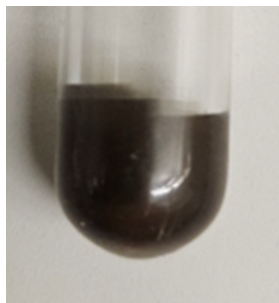
**Fig. S38.** Raman spectrum of the grey powder obtained from the photolysis of oligo(3,4-di-*iso*-propylsilacyclopentene), **OligoSi**.



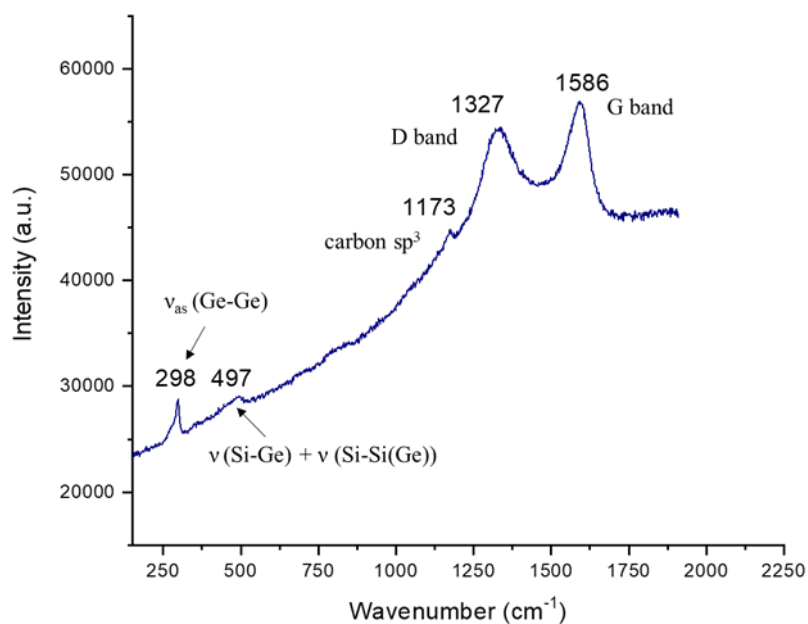
**Fig. S39.** SEM backscatter electron image for the deposited inner film obtained from the photolysis of oligo(3,4-di-*iso*-propylsilacyclopentene) **OligoSi** in THF. SEM data was collected at 15 keV.



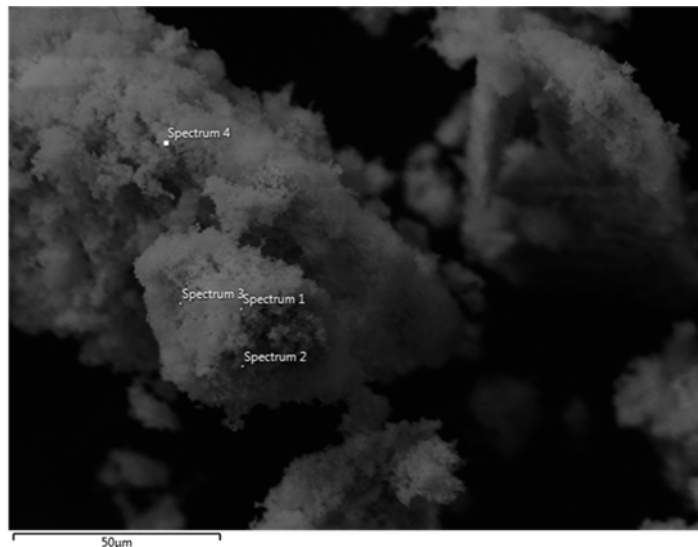
**Fig. S40.** EDX elemental mapping of deposited inner film obtained from the photolysis of oligo(3,4-di-*iso*-propylsilacyclopentene) **OligoSi**. Note: The missing 0.01 % corresponds to traces of Cu.



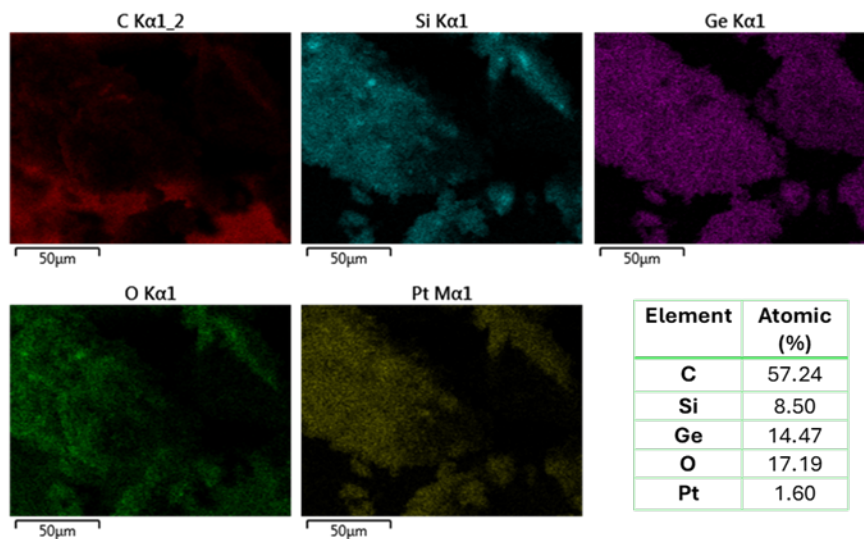
**Fig. S41.** Photograph of the deposited  $\text{Si}_x\text{Ge}_y$  film (and carbon) after photolysis of oligo(3,4-dibutylgermacyclopentene-*r*-3,4-di-*iso*-propylsilacyclopentene) (**OligoSiGe**) in THF.



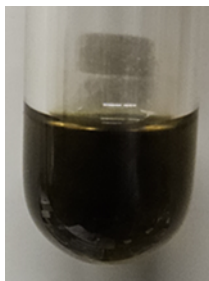
**Fig. S42.** Raman spectrum of the dark-grey film obtained from the photolysis of oligo(3,4-dibutylgermacyclopentene-*r*-3,4-di-*iso*-propylsilacyclopentene) (**OligoSiGe**).



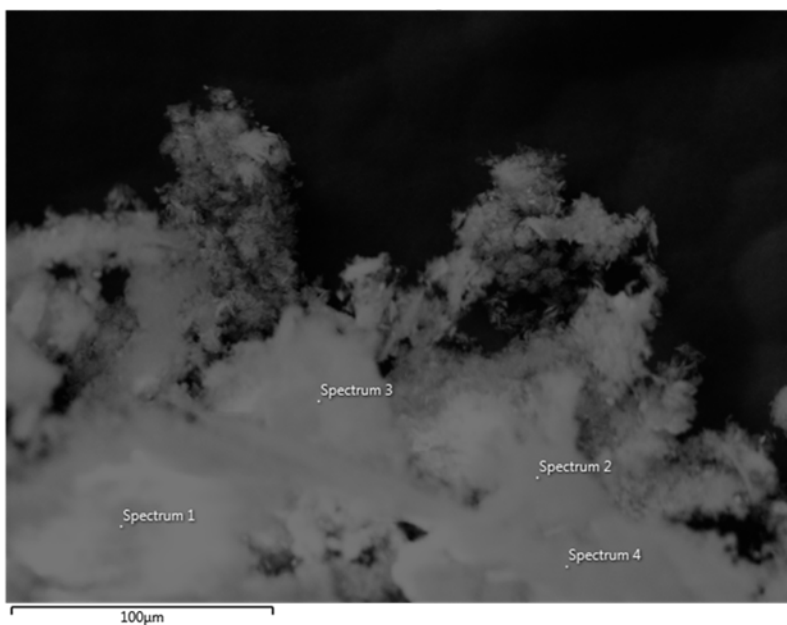
**Fig. S43.** SEM backscattered electron image for the dark-grey precipitate obtained from the photolysis of oligo(3,4-dibutylgermacyclopentene-*r*-3,4-di-*iso*-propylsilacyclopentene) (**OligoSiGe**). SEM data was collected at 15 keV.



**Fig. S44.** EDX elemental maps for the dark-grey precipitate obtained from the photolysis of oligo(3,4-dibutylgermacyclopentene-*r*-3,4-di-*iso*-propylsilacyclopentene) (**OligoSiGe**). Note: The missing 1 % corresponds to traces of Cl and P.

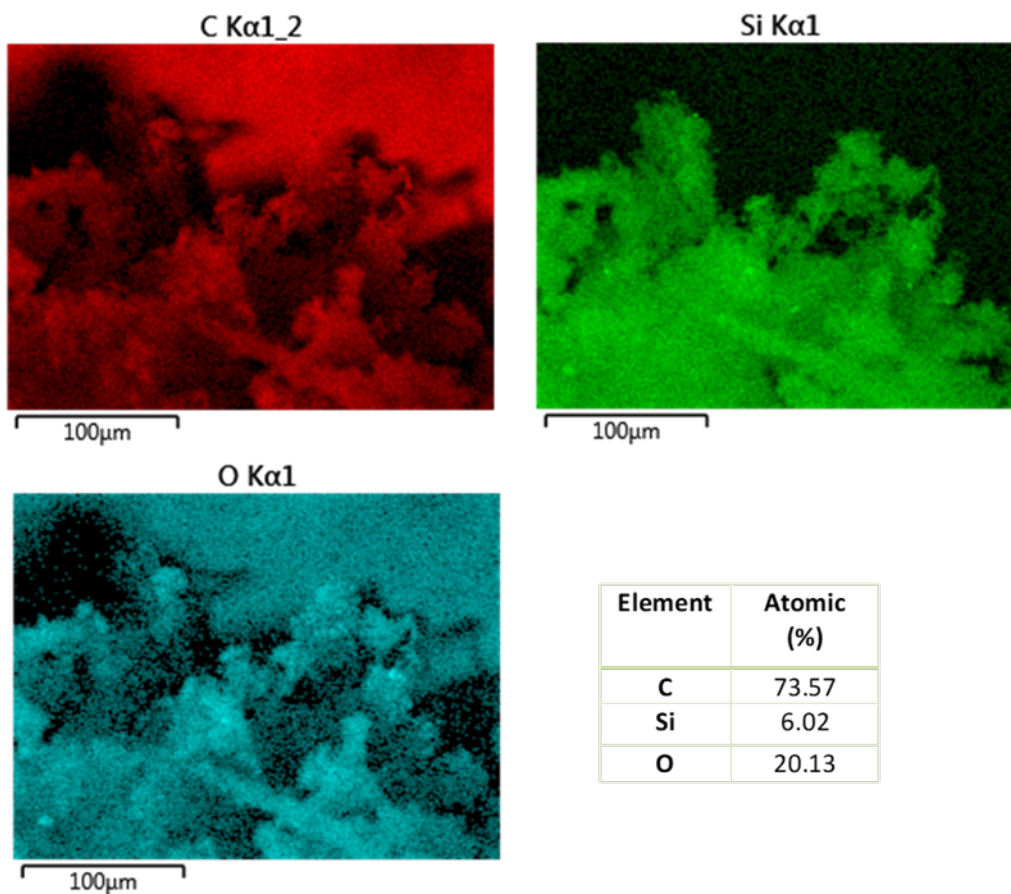


**Fig. S45.** Photograph of the reaction mixture after photolysis (248 nm, 15 Hz, 10000 pulses, 250 mJ/pulse) of silaspiro-[4.4]-2,3,7,8-tetramethyl-2,7-nonadiene (**SpiroSi**) in THF.



**Fig. S46.** SEM backscattered electron image for the dark-grey precipitate obtained from the photolysis of silaspiro-[4.4]-2,3,7,8-tetramethyl-2,7-nonadiene (**SpiroSi**). SEM data was collected at 15 keV.

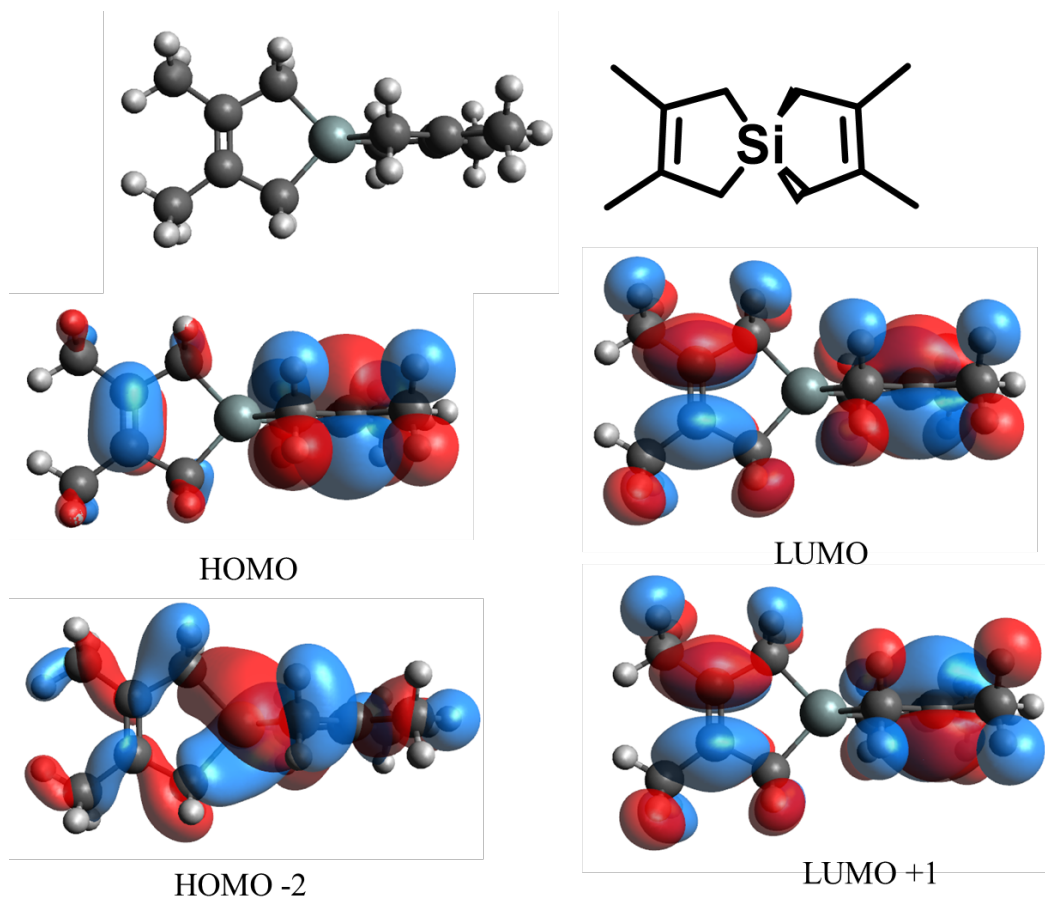




**Fig. S47.** EDX elemental maps for the dark-grey precipitate obtained from the photolysis of silaspiro-[4.4]-2,3,7,8-tetramethyl-2,7-nonadiene (**SpiroSi**) in THF. Note: The missing 0.28 % corresponds to traces of Na, Cl and Al (unknown sources).

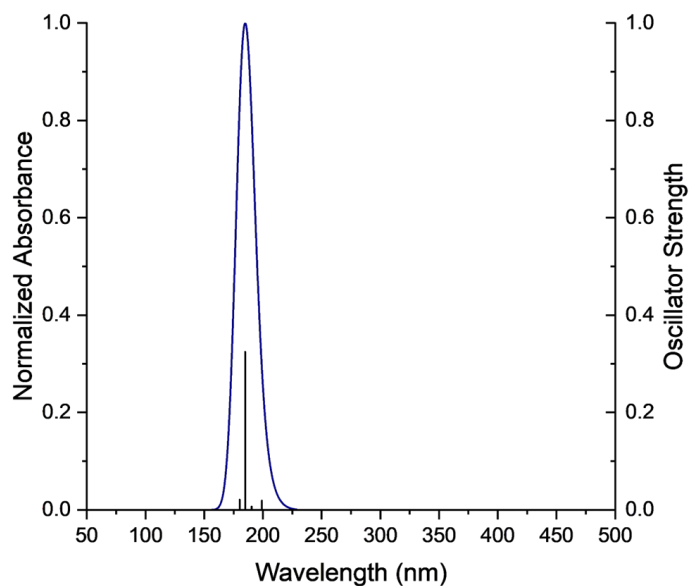
## 8. Computational Details

Calculations were performed using the Gaussian16 software package.<sup>S6</sup> All coordinates (xyz) for the optimized structure have been supplied as a separate .xyz file. Gas-phase structure optimization was performed by employing density functional theory (DFT) with the B3LYP functional and cc-pVDZ basis set.<sup>S7,S8</sup> Frequency analysis confirmed the optimized structure to be a local minima on the potential energy surface.



**Fig. S48.** Geometry optimization of  $\text{Si}\{\text{CH}_2\text{C}(\text{Me})=\text{C}(\text{Me})\text{CH}_2\}_2$  (**SpiroSi**) in the gas phase, and the computed frontier molecular orbitals at the B3LYP/cc-pVDZ level of theory.

Time dependent functional theory (TF-DFT) was used to compute the UV-vis spectrum of **SpiroSi**.<sup>S9</sup> The same functional/basis set was employed for the structure optimization and excited state calculations.



**Fig. S49.** Computed UV-vis spectrum for **SpiroSi** at the B3LYP/cc-pVDZ level of theory.

**Table S1.** Computed electronic transitions (from the ground state,  $S_0$ ) for **SpiroSi** at the B3LYP/cc-pVDZ level of theory.

Excited state	Energy (nm)	Oscillator strength	Main orbitals involved
$S_1$	199	0.0192	HOMO-1/LUMO HOMO-1/LUMO+1 HOMO/LUMO HOMO/LUMO+1
$S_9$	190	0.0073	HOMO-1/LUMO+2 HOMO/LUMO+2 HOMO-1/LUMO+2 HOMO/LUMO+3
$S_{11}$	185	0.3246	HOMO-1/LUMO HOMO-1/LUMO+1 HOMO/LUMO HOMO/LUMO+1
$S_{15}$	180	0.0214	HOMO-1/LUMO+2 HOMO-1/LUMO+3 HOMO/LUMO+2 HOMO/LUMO+3
$S_{19}$	176	<b>0.0002</b>	HOMO-2/LUMO HOMO-2/LUMO+1

## 9. References

- S1. A. M. Borys, *Organometallics*, 2023, **42**, 182.
- S2. A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518.
- S3. J. Linshoeft, E. J. Baum, A. Hussain, P. J. Gates, D. C. Nather and A. Staubitz, *Angew. Chem., Int. Ed.*, 2014, **53**, 12916.
- S4. M. Garcon, C. Bakewell, G. A. Sackman, A. J. P. White, R. I. Cooper, A. J. Edwards and M. R. Crimmin, *Nature*, 2019, **574**, 390.
- S5. W. Medroa del Pino, A. A. Forero Pico, M. Gupta and E. Rivard, *Chem. Commun.*, 2023, **59**, 6849.
- S6. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J.V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. J. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 16, Revision B.01, Gaussian, Inc., Wallingford CT.
- S7. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- S8. (a) T. H. Dunning Jr., *J. Chem. Phys.*, 1989, **90**, 1007; (b) A. K. Wilson, D. E. Woon, K. A. Peterson and T. H. Dunning Jr., *J. Chem. Phys.*, 1999, **110**, 7667.
- S9. (a) S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785; (c) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (d) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.