

## Supplementary Information

### Germanium photopatterning via poly(cyclogermapentene)s

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## Table of Contents

1. Experimental Procedures .....	S4
1.1. General information, materials and instrumentation .....	S4
1.2. Compound syntheses .....	S5
Synthesis of 2,3-diisopropyl-1,3-butadiene ( <b>2</b> ):.....	S5
Synthesis of 2,3-di- <i>tert</i> -butyl-1,3-butadiene ( <b>3</b> ): .....	S5
Synthesis of 2,3-dihexyl-1,3-butadiene ( <b>4</b> ): .....	S6
Synthesis of 1,1-dichloro-3,4-dimethylgermacyclopent-3-ene ( <b>5</b> ): .....	S6
Synthesis of 1,1-dichloro-3,4-diisopropylgermacyclopent-3-ene ( <b>6</b> ): .....	S7
Attempted synthesis of 1,1-dichloro-3,4-di- <i>tert</i> -butylgermacyclopent-3-ene:.....	S7
Synthesis of 1,1-dichloro-3,4-dihexylgermacyclopent-3-ene ( <b>7</b> ):.....	S7
Synthesis of 1,1-dihydro-3,4-dimethylgermacyclopent-3-ene ( <b>8</b> ): .....	S8
Synthesis of 1,1-dihydro-3,4-diisopropylgermacyclopent-3-ene ( <b>9</b> ): .....	S8
Synthesis of 1,1-dihydro-3,4-dihexylgermacyclopent-3-ene ( <b>10</b> ):.....	S9
Synthesis of oligo(3,4-dimethylgermacyclopentene) ( <b>11</b> ) using [Rh(COD)Cl] <sub>2</sub> as a pre-catalyst:.....	S9
Synthesis of poly(3,4-diisopropylgermacyclopentene) ( <b>12</b> ) using [Rh(COD)Cl] <sub>2</sub> as a pre-catalyst:.....	S10
Attempted synthesis of poly(3,4-diisopropylgermacyclopentene) ( <b>12</b> ) using [ClRh(PPh <sub>3</sub> ) <sub>3</sub> ] as a pre-catalyst: .....	S10
Attempted synthesis of poly(3,4-dihexylgermacyclopentene) ( <b>13</b> ) using [Rh(COD)Cl] <sub>2</sub> as a pre-catalyst: .....	S11
Attempted synthesis of poly(3,4-dihexylgermacyclopentene) ( <b>13</b> ) using [ClRh(PPh <sub>3</sub> ) <sub>3</sub> ] as a pre-catalyst: .....	S11
Synthesis of poly(3,4-dihexylgermacyclopentene) ( <b>13</b> ) using Cp <sub>2</sub> Zr(pyr)(Me <sub>3</sub> SiCCSiMe <sub>3</sub> ) as a catalyst:.....	S11
Synthesis of poly(3,4-dihexylgermacyclopentene- <i>r</i> -3,4-diisopropylgermacyclopentene) ( <b>14</b> ) using Cp <sub>2</sub> Zr(pyr)(Me <sub>3</sub> SiCCSiMe <sub>3</sub> ) as catalyst: .....	S12
Photolysis of poly(3,4-dimethylgermacyclopentene) ( <b>11</b> ): .....	S13
Photolysis of poly(3,4-dihexylgermacyclopentene) ( <b>13</b> ): .....	S13
Photolysis of poly(3,4-dihexylgerma-3,4-diisopropylgermacyclopentene) ( <b>14</b> ): .....	S14
Deposition of <b>13</b> via spin-coating and photolysis .....	S14
Photopatterning of <b>14</b> from solution.....	S14
2. NMR spectra .....	S15
3. FT-IR and Raman spectra of the poly(cyclogermapentene)s.....	S27

4. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the poly(cyclogermapentene)s .....	S32
5. UV-vis spectra of the poly(cyclogermapentene)s .....	S35
6. Gel permeation chromatography (GPC) .....	S37
7. Characterization of deposited Ge .....	S38
8. Computational details .....	S46
9. References .....	S49

## 1. Experimental Procedures

### 1.1. General information, materials and instrumentation

All reactions were conducted employing standard Schlenk techniques under an atmosphere of nitrogen or in a nitrogen-filled glove box (Innovative Technology, Inc.). Solvents were dried using a Grubbs-type solvent purification system manufactured by Innovative Technology, Inc., and stored under nitrogen gas prior to use. Copper(I) bromide, *tert*-butylmagnesium chloride (1.0 M solution in THF), hexylmagnesium bromide (2.0 M solution in THF), isopropylmagnesium chloride lithium chloride (1.3 M solution in THF), bis(cyclopentadienyl)zirconium(IV) dichloride, and *n*-butyllithium (2.5 M solution in hexanes) were purchased from Sigma-Aldrich and used as received. 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 and used as received. Lithium bromide, lithium aluminum hydride (4.0 M solution in Et<sub>2</sub>O), chloro(1,5-cyclooctadiene)rhodium(I) dimer, and bis(trimethylsilyl)acetylene were purchased by Thermo Scientific, Acros, Pressure Chemical, and Matrix Scientific, respectively, and used as received. Cp<sub>2</sub>Zr(pyr)(Me<sub>3</sub>SiCCSiMe<sub>3</sub>) was synthesized according to a literature procedure.<sup>S1</sup> Pyridine was purchased from Caledon, was distilled under nitrogen, degassed, and then stored over molecular sieves (4 Å) under N<sub>2</sub> before use. 2,3-Dimethyl-1,3-butadiene (**1**) was purchased from TCI and was distilled under nitrogen, degassed, and stored over molecular sieves (4 Å) under N<sub>2</sub> before use.

<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on either 500 or 700 MHz Varian Inova spectrometers 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. 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. Scanning electron microscope (SEM) images and energy-dispersive X-ray (EDX) spectroscopy element 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 deposited over a <100> oriented – type Si wafer substrate (University Wafer, 4" size, 500 μm thickness with surface oxide). Raman data were collected using a Renishaw inVia Raman Qontor Spectrometer (532 nm, 5 mW, 60 s collection) or a Renishaw's inVia Raman Confocal Spectrometer (632 nm, 0.6 mW, 3 × 10 s collection). Gel permeation chromatography (GPC) studies were done 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 oligomers/polymers using a right and low angle light scattering, and a refractive index detector (GPC 270 Max dual detector + Viscotek VE 3580). This GPC instrument was calibrated with 99 kDa polystyrene standards (supplied by Malvern). Photolysis studies on the synthesized polymer/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 = 20 Hz). The exposed samples were contained in a N<sub>2</sub> filled quartz reactor throughout the entire exposure process. The pulse energy used was 100 mJ at a laser fluence of 130 mJ cm<sup>-2</sup> resulting in a UV light intensity of 1.95 W cm<sup>-2</sup>. The number of pulses was 10000, giving a total exposure dose of 1298 J cm<sup>-2</sup> per sample. The patterning mask was fabricated on a piranha cleaned 10 mm by 10 mm quartz substrate. Standard photolithography using AZ5214E photoresist was used to transfer a pre-defined pattern onto the quartz substrate, followed by e-beam evaporation of 100 nm Cr and liftoff to reveal the final pattern used.

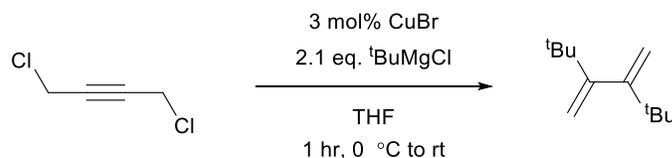
## 1.2. Compound syntheses

### Synthesis of 2,3-diisopropyl-1,3-butadiene (**2**):



To a mixture of <sup>i</sup>PrMgCl•LiBr (27.8 mL, 36 mmol, 1.3 M solution in THF) and CuBr (54 mg, 0.36 mmol) in 40 mL of THF at -60 °C was added a solution of 1,4-dichloro-2-butyne (2.2 g, 18 mmol) in 20 mL of THF. Once the addition was complete, the cold bath was removed, and the reaction mixture was left stirring at room temperature for 3 hrs. Distilled water (20 mL) was added to the reaction mixture and then the mixture was stirred for 10 minutes at room temperature. The organic fraction was recovered by separate extractions with pentane (3 × 40 mL) with subsequent distilled water washes (3 × 40 mL) of the combined organic extracts. The organic layer was dried over anhydrous MgSO<sub>4</sub> and then filtered. The volatiles were removed from the filtrate *in vacuo* to give a yellow liquid. Distillation of the yellow product *in vacuo* (0.3 Torr, 23 °C) afforded **1** as a colorless liquid (1.52 g, 61%); NMR data for **1** matched those found in the literature.<sup>S2</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 1.04 (d, 12H, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 2.51 (septet, 2H, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 4.84 (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 (CDCl<sub>3</sub>, 126 MHz): δ 22.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 30.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 108.1 (C=CH<sub>2</sub>), 156.9 (C=CH<sub>2</sub>).

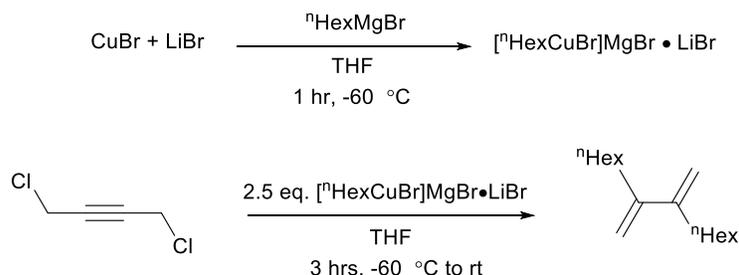
### Synthesis of 2,3-di-*tert*-butyl-1,3-butadiene (**3**):



To a mixture of <sup>t</sup>BuMgCl (12.6 mL, 25 mmol, 2.0 M solution in THF) and CuBr (60 mg, 0.36 mmol) at 0 °C was added a solution of 1,4-dichloro-2-butyne (1.5 g, 12 mmol) in 20 mL of THF. Once the addition was complete, the cold bath was removed, and the reaction mixture was left stirring at room temperature for 1 hr. Distilled water (20 mL) was added and the heterogeneous mixture was stirred for 10 minutes at room temperature. The organic fraction was recovered by separate extractions with pentane (3 × 40 mL), the extracts were combined and then washed with distilled water (3 × 40 mL). The organic fraction was dried over anhydrous MgSO<sub>4</sub> and filtered. Removal of the volatiles *in vacuo* yielded a yellow liquid. Distillation of the yellow product *in vacuo* (0.3 Torr, 60 °C) afforded **2** as a colorless liquid (1.1 g, 55%). <sup>1</sup>H NMR data for **2** matched those found in the literature.<sup>S2</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 1.11 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 4.73 (d, 2H, <sup>2</sup>J<sub>HH</sub> = 1.4 Hz, C=CH<sub>2</sub>), 5.10 (d, 2H, <sup>2</sup>J<sub>HH</sub> = 1.4 Hz, C=CH<sub>2</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 126 MHz): δ

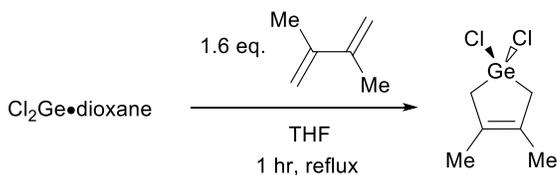
31.5 (C(CH<sub>3</sub>)<sub>3</sub>), 35.9 (C(CH<sub>3</sub>)<sub>3</sub>), 111.0 (C=CH<sub>2</sub>), 159.5 (C=CH<sub>2</sub>).

### Synthesis of 2,3-dihexyl-1,3-butadiene (4):



To a mixture of CuBr (1.6 g, 11 mmol) and LiBr (1.0 g, 11 mmol) in 30 mL of THF at -60 °C was added a solution of <sup>n</sup>HexMgBr (5.7 mL, 11 mmol, 2.0 M solution in THF) and the mixture was then stirred at 1 hr at -60 °C. A solution of 1,4-dichloro-2-butyne (0.56 g, 4.6 mmol) was then added, with cooling maintained at -60 °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 added to the reaction mixture and the heterogeneous mixture was stirred for 10 minutes. The organic fraction was recovered by separate extractions with pentane (3 × 20 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 *in vacuo* gave a yellow liquid. The product was then purified by fractional distillation (0.3 Torr) with the product fraction collected at 110 °C; an initial fraction with bp = 98 °C, consisting of dodecane, was collected and discarded. Compound **3** was obtained as a colorless liquid (0.51 g, 49%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 0.89 (t, 6H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, (CH<sub>2</sub>CH<sub>3</sub>)), 1.28-1.31 (m, 12H, <sup>n</sup>Hex CH<sub>2</sub>), 1.40-1.46 (m, 4H, <sup>n</sup>Hex CH<sub>2</sub>), 2.22 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, C(CH<sub>2</sub>)CH<sub>2</sub>), 4.91 (s, 2H, C=CH<sub>2</sub>), 5.04 (s, 2H, C=CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 126 MHz): δ 14.3 (CH<sub>2</sub>CH<sub>3</sub>), 22.8 (<sup>n</sup>Hex CH<sub>2</sub>), 28.8 (<sup>n</sup>Hex CH<sub>2</sub>), 29.4 (<sup>n</sup>Hex CH<sub>2</sub>), 31.9 (<sup>n</sup>Hex CH<sub>2</sub>), 34.5 (<sup>n</sup>Hex CH<sub>2</sub>), 111.4 (C=CH<sub>2</sub>), 148.3 (C=CH<sub>2</sub>). Anal. Calcd. for C<sub>16</sub>H<sub>30</sub>: C, 86.40; H, 13.60%. Found: C, 86.62; H, 13.26%.

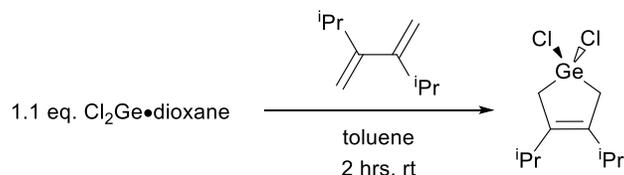
### Synthesis of 1,1-dichloro-3,4-dimethylgermacyclopent-3-ene (5):



A solution of **1** (1.1 g, 14 mmol) in 10 mL of THF was added dropwise to a flask containing Cl<sub>2</sub>Ge•dioxane (2.0 g, 8.5 mmol) in 30 mL of THF, and then the mixture was heated to reflux for 1 hr. The mixture was cooled to room temperature and the apparatus was adapted for distillation.

The solvent was first removed by heating at 80 °C under 1 atm of nitrogen, then continued distillation under vacuum (0.3 Torr, 80 °C) afforded **4** as a colorless liquid (1.6 g, 84%) with NMR data that matched those in the literature.<sup>S3</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 1.80 (s, 6H, CH<sub>3</sub>), 2.22 (s, 4H, GeCH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 126 MHz): δ 18.8 (CH<sub>3</sub>), 32.9 (Ge(CH<sub>2</sub>)), 129.2 (Ge(CH<sub>2</sub>)C).

### Synthesis of 1,1-dichloro-3,4-diisopropylgermacyclopent-3-ene (**6**):

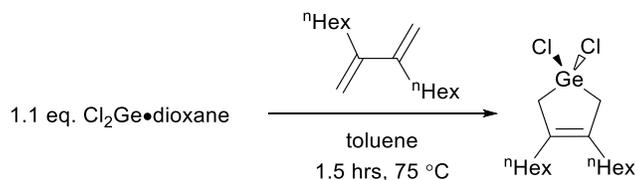


In a glove box, a solution of **2** (0.83 g, 6.1 mmol) in 4 mL of toluene was added to a vial containing Cl<sub>2</sub>Ge•dioxane (1.3 g, 5.5 mmol). The reaction mixture was left stirring at room temperature for 2 hrs. The precipitate was separated by centrifugation in a glove box (3150 rpm) and the mother liquor was collected. The mother liquor was cooled down to -30 °C and filtered through Celite. The volatiles were then removed from the filtrate *in vacuo* to give **5** as a colorless viscous liquid (1.4 g, 92%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 0.99 (d, 12H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 2.20 (s, 4H, GeCH<sub>2</sub>), 3.03 (septet, 2H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 126 MHz): δ 21.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.4 (GeCH<sub>2</sub>), 29.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 137.5 (Ge(CH<sub>2</sub>)C). Anal. Calcd. for C<sub>6</sub>H<sub>10</sub>Cl<sub>2</sub>Ge: C, 42.62; H, 6.44%. Found: C, 41.91; H, 6.25%.

### Attempted synthesis of 1,1-dichloro-3,4-di-*tert*-butylgermacyclopent-3-ene:

In a glove box, a solution of **3** (0.72 g, 4.3 mmol) in 4 mL of toluene was added to a microwave tube containing Cl<sub>2</sub>Ge•dioxane (1.1 g, 4.7 mmol). The sealed flask was heated to 80 °C in an oil bath for 2 hrs under constant stirring. The mixture was cooled down to room temperature and analysis of the product mixture by <sup>1</sup>H NMR spectroscopy [in 0.7 mL of CDCl<sub>3</sub>, with 20 μL of THF added] showed the presence of unreacted **2**.

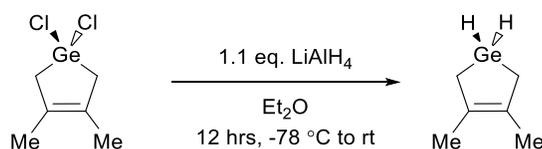
### Synthesis of 1,1-dichloro-3,4-dihexylgermacyclopent-3-ene (**7**):



In a glove box, a solution of **4** (1.0 g, 4.5 mmol) in 4 mL of toluene was added to a microwave tube containing Cl<sub>2</sub>Ge•dioxane (1.1 g, 4.8 mmol). The sealed flask was heated to 75 °C in an oil

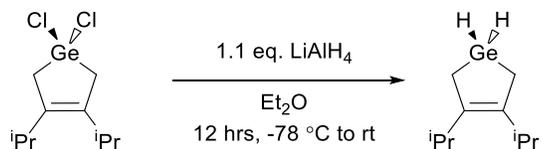
bath for 1.5 hrs under constant stirring. The mixture was cooled down to room temperature and the small amount of precipitate present was separated by centrifugation in a glove box (rpm = 3150). The mother liquor was then decanted/collected, cooled to -30 °C, and then filtered through Celite. Removal of the volatiles from the filtrate *in vacuo* afforded **7** as a colorless viscous oil (1.4 g, 84%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 0.89 (t, 6H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, CH<sub>2</sub>CH<sub>3</sub>), 1.26-1.33 (m, 12H, <sup>n</sup>Hex CH<sub>2</sub>), 1.36-1.42 (m, 4H, <sup>n</sup>Hex CH<sub>2</sub>), 2.18 (t, 4H, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, C(CH<sub>2</sub>)CH<sub>2</sub>), 2.23 (s, 4H, Ge(CH<sub>2</sub>)C). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 126 MHz): δ 14.2 (CH<sub>2</sub>CH<sub>3</sub>), 22.8 (<sup>n</sup>Hex CH<sub>2</sub>), 28.2 (<sup>n</sup>Hex CH<sub>2</sub>), 29.3 (<sup>n</sup>Hex internal CH<sub>2</sub>), 30.6 (GeCH<sub>2</sub>), 31.9 (<sup>n</sup>Hex CH<sub>2</sub>), 32.5 (C(CH<sub>2</sub>)CH<sub>2</sub>), 133.8 (GeCH<sub>2</sub>C). Anal. Calcd. for C<sub>16</sub>H<sub>30</sub>Cl<sub>2</sub>Ge: C, 52.51; H, 8.26%. Found: C, 52.12; H, 8.21%.

### Synthesis of 1,1-dihydro-3,4-dimethylgermacyclopent-3-ene (**8**):



A solution of **5** (1.9 g, 8.6 mmol) in 10 mL of Et<sub>2</sub>O was added dropwise *via* cannula to a solution of Li[AlH<sub>4</sub>] (2.4 mL, 9.6 mmol, 4.0 M solution in Et<sub>2</sub>O) diluted in 20 mL of Et<sub>2</sub>O at -78 °C under constant stirring; a white precipitate formed during the addition. The mixture was stirred for 12 hrs at room temperature and then filtered *via* cannula filtration. Distilled water (5 mL) was added carefully to the cooled filtrate at 0 °C. The organic fraction was then recovered by separate extractions with pentane (3 × 20 mL) and the combined organic fractions were washed with distilled water (3 × 20 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 **8** as a colorless liquid (0.76 g, 56%) with NMR data that matched those in the literature.<sup>S3</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 1.73 (s, 6H, CH<sub>3</sub>), 1.79 (br, 4H, GeCH<sub>2</sub>), 3.94 (pentet, 2H, <sup>3</sup>J<sub>HH</sub> = 3.5 Hz, GeH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 126 MHz): δ 19.2 (CH<sub>3</sub>), 20.9 (Ge(CH<sub>2</sub>)C), 131.3 (Ge(CH<sub>2</sub>)C).

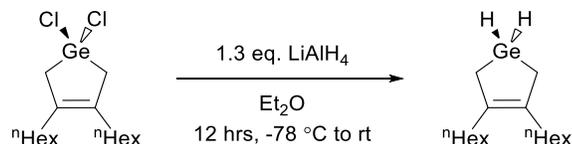
### Synthesis of 1,1-dihydro-3,4-diisopropylgermacyclopent-3-ene (**9**):



A solution of **6** (1.4 g, 5.0 mmol) in 10 mL of Et<sub>2</sub>O was added dropwise *via* cannula to a solution of Li[AlH<sub>4</sub>] (1.4 mL, 5.6 mmol, 4.0 M solution in Et<sub>2</sub>O) diluted in 20 mL of Et<sub>2</sub>O at -78 °C; a white precipitate formed during the addition. The mixture was stirred for 12 hrs at room temperature and then filtered *via* cannula filtration. Distilled water (5 mL) was then added carefully (dropwise) to the filtrate at 0 °C. The organic fraction was then recovered by separate extractions with pentane (3 × 20 mL) and the combined organic extracts were washed with distilled water (3 × 20 mL). The organic fraction was dried over anhydrous MgSO<sub>4</sub> and then filtered. The solvent

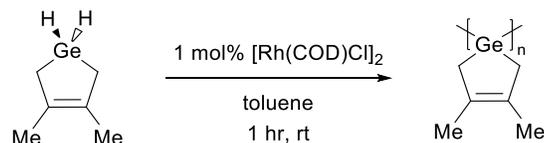
was removed from the filtrate *in vacuo* to give **9** as a colorless liquid (0.84 g, 80%).  $^1\text{H}$  NMR (THF- $d_8$ , 500 MHz):  $\delta$  0.98 (d, 12H,  $^3J_{\text{HH}} = 6.8$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.77 (t, 4H,  $^3J_{\text{HH}} = 3.5$  Hz,  $\text{Ge}(\text{CH}_2)\text{C}$ ), 2.95 (septet, 2H,  $^3J_{\text{HH}} = 6.8$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 3.93 (pentet, 2H,  $^3J_{\text{HH}} = 3.5$  Hz,  $\text{GeH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (THF- $d_8$ , 126 MHz):  $\delta$  12.2 ( $\text{CH}(\text{CH}_3)_2$ ), 21.7 ( $\text{CH}(\text{CH}_3)_2$ ), 29.9 ( $\text{Ge}(\text{CH}_2)\text{C}$ ), 140.3 ( $\text{Ge}(\text{CH}_2)\text{C}$ ). Anal. Calcd. for  $\text{C}_{10}\text{H}_{20}\text{Ge}$ : C, 56.96; H, 8.60%. Found: C, 56.07; H, 9.25%.

### Synthesis of 1,1-dihydro-3,4-dihexylgermacyclopent-3-ene (**10**):



A solution of **7** (0.56 g, 1.5 mmol) in 10 mL of  $\text{Et}_2\text{O}$  was added dropwise to a cold ( $-30$  °C) solution of  $\text{Li}[\text{AlH}_4]$  (0.49 mL, 2.0 mmol, 4.0 M solution in  $\text{Et}_2\text{O}$ ) that has been diluted in 10 mL of  $\text{Et}_2\text{O}$ ; a white precipitate formed during the addition. The mixture was stirred for 12 hrs at room temperature and then filtered through a pad of Celite on top of glass fiber filter paper (packed within a pipette); the remaining precipitate on the Celite was rinsed by passing more  $\text{Et}_2\text{O}$  through the filter pipette ( $2 \times 2$  mL). Distilled water (5 mL) at  $0$  °C was added carefully (dropwise) to the combined filtrates. The organic fraction was then recovered by separate extractions with pentane ( $3 \times 20$  mL) and the combined fractions were washed with distilled water ( $3 \times 20$  mL). The organic layer was dried over anhydrous  $\text{MgSO}_4$  and then filtered. The solvent was removed from the filtrate *in vacuo* to yield **10** as a colorless liquid (0.32 g, 73%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  0.89 (t, 6H,  $^3J_{\text{HH}} = 7.0$  Hz,  $\text{CH}_2(\text{CH}_3)$ ), 1.24-1.32 (m, 12H,  $^n\text{Hex CH}_2$ ), 1.34-1.40 (m, 4H,  $^n\text{Hex CH}_2$ ), 1.79 (t, 4H,  $^3J_{\text{HH}} = 3.5$  Hz,  $\text{Ge}(\text{CH}_2)$ ), 1.79 (t, 4H,  $^3J_{\text{HH}} = 7.5$  Hz,  $\text{C}(\text{CH}_2)\text{CH}_2$ ), 3.94 (pentet, 2H,  $^3J_{\text{HH}} = 3.5$  Hz,  $\text{H}_2\text{Ge}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 126 MHz):  $\delta$  14.3 ( $\text{CH}_2\text{CH}_3$ ), 18.2 ( $\text{Ge}(\text{CH}_2)$ ), 22.8 ( $^n\text{Hex CH}_2$ ), 28.5 ( $^n\text{Hex CH}_2$ ), 29.6 ( $^n\text{Hex CH}_2$ ), 32.0 ( $^n\text{Hex CH}_2$ ), 33.0 ( $\text{CH}_2\text{CH}_3$ ), 135.9 ( $\text{Ge}(\text{CH}_2)\text{C}$ ). HR-MS (EI):  $m/z$  calcd. for  $[\text{C}_{16}\text{H}_{33}\text{Ge}]^+$ : 299.1789. Found: 299.1794 ( $\Delta\text{ppm} = 0.4$ ). Anal. Calcd. for  $\text{C}_{16}\text{H}_{32}\text{Ge}$ : C, 64.69; H, 10.86%. Found: C, 64.87; H, 11.00%.

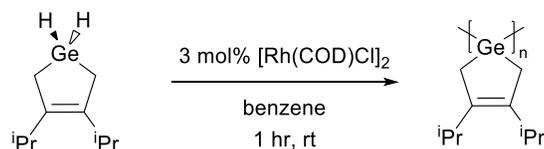
### Synthesis of oligo(3,4-dimethylgermacyclopentene) (**11**) using $[\text{Rh}(\text{COD})\text{Cl}]_2$ as a pre-catalyst:



A solution of  $[\text{Rh}(\text{COD})\text{Cl}]_2$  (3.1 mg, 0.0063 mmol) in 0.5 mL of toluene was added rapidly to a solution of **8** (0.10 g, 0.63 mmol) dissolved in 0.5 mL of toluene at room temperature, and the mixture was stirred for 1 hr. Vigorous bubbling was noted along with a progressive change in the color of the mixture to dark red, and the formation of a pink precipitate were observed. The

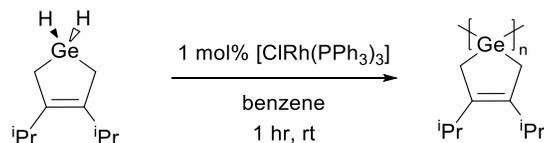
insoluble precipitate was separated by decantation followed by subsequent washes with hexanes (20 mL total). The soluble (organic) fractions were collected and combined, then the volatiles were removed *in vacuo* affording a dark-red viscous liquid (67 mg). This product was re-dissolved in 100  $\mu$ L of THF and oligomeric **11** was recovered as a pale pink solid after precipitation into 5 mL of rapidly stirring MeCN (31 mg yield after drying to constant weight, 32%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 700 MHz):  $\delta$  1.40-1.80 (br, 6H,  $\text{CH}_3$ ), 1.80-2.20 (br, 4H,  $\text{GeCH}_2$ ), 4.04 (s, Ge-H end group). IR (ATR,  $\text{cm}^{-1}$ ): 2906 ( $\nu\text{C-H}$ ), 2015 ( $\nu\text{Ge-H}$ , end group), 1648 ( $\nu\text{C=C}$ ). Raman ( $\text{cm}^{-1}$ ): 1641 ( $\nu\text{C=C}$ ), 1145 (H-C-H wag), 355 ( $\nu\text{Ge-Ge}$ , broad band). UV-vis (in THF):  $\lambda_{\text{max}} = 296$  and 243 nm (shoulders). Anal. Calcd. for  $\text{C}_6\text{H}_{10}\text{Ge}$ : C, 46.56; H, 6.51%. Found: C, 45.30; H, 6.45%; despite repeated attempts, elemental analysis values for carbon were consistently low. GPC (THF): The molecular weight of this material was too low to be detected reliably with our GPC columns/instrument (number average molecular weight,  $M_n$ , is likely below 2500  $\text{g mol}^{-1}$ ).

### Synthesis of poly(3,4-diisopropylgermacyclopentene) (**12**) using $[\text{Rh}(\text{COD})\text{Cl}]_2$ as a pre-catalyst:



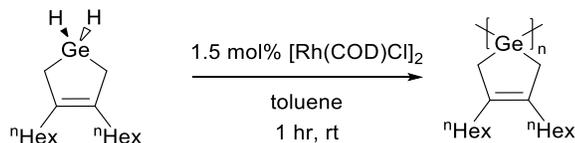
In a glove box, a solution of  $[\text{Rh}(\text{COD})\text{Cl}]_2$  (2.3 mg, 0.0047 mmol) in 0.5 mL of benzene was added rapidly to **9** (0.10 g, 0.47 mmol) dissolved in 0.5 mL of benzene, then the mixture was stirred for 1 hr at room temperature. Vigorous bubbling and the formation of a pink precipitate were observed. The precipitate was isolated and purified by washing with benzene (20 mL total) and dried to give **12** as a pale-pink solid (81 mg, 81%). IR (ATR,  $\text{cm}^{-1}$ ): 2960 ( $\nu\text{C-H}$ ), 2011 ( $\nu\text{Ge-H}$ , end group), 1618 ( $\nu\text{C=C}$ ). Raman ( $\text{cm}^{-1}$ ): 2015 ( $\nu\text{Ge-H}$ ), 1619 ( $\nu\text{C=C}$ ), 1150 (H-C-H wag), 301 (Ge-Ge). Anal. Calcd. for  $\text{C}_{10}\text{H}_{18}\text{Ge}$ : C, 56.96; H, 8.60%. Found: C, 56.91; H, 8.49%.

### Attempted synthesis of poly(3,4-diisopropylgermacyclopentene) (**12**) using $[\text{CIRh}(\text{PPh}_3)_3]$ as a catalyst:



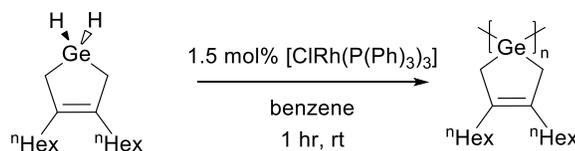
In a glove box, a solution of  $[\text{CIRh}(\text{PPh}_3)_3]$  (44 mg, 0.0047 mmol) in 0.5 mL of benzene was added rapidly to a solution of **9** (0.10 g, 0.47 mmol) dissolved in 0.5 mL of benzene. The mixture was stirred at room temperature for 1 hr; analysis of the mixture by  $^1\text{H}$  NMR spectroscopy in  $\text{C}_6\text{D}_6$  showed only unreacted **9**.

**Attempted synthesis of poly(3,4-dihexylgermacyclopentene) (13) using [Rh(COD)Cl]<sub>2</sub> as a pre-catalyst:**



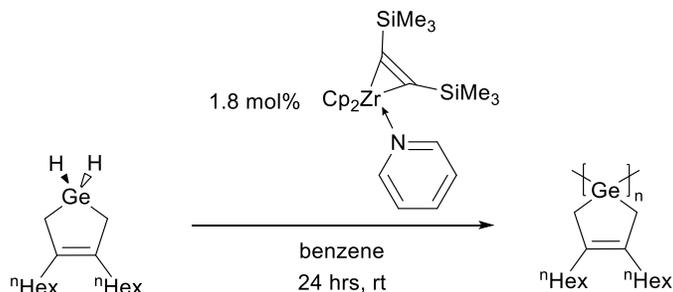
In a glove box, a solution of [Rh(COD)Cl]<sub>2</sub> (2.5 mg, 0.0051 mmol) in 0.5 mL of toluene was added rapidly to a solution of **10** (0.10 g, 0.34 mmol) dissolved in 0.5 mL of toluene. Slight bubbling and a progressive change of the color of the mixture to dark red were observed. The volatiles were removed *in vacuo* after a total reaction time of 1 hr, affording a dark-red liquid. <sup>1</sup>H NMR analysis of the recovered material showed unreacted **10**, with no sign of the target polymer **13**.

**Attempted synthesis of poly(3,4-dihexylgermacyclopentene) (13) using [ClRh(PPh<sub>3</sub>)<sub>3</sub>] as a catalyst:**



In a glove box, a solution of [ClRh(PPh<sub>3</sub>)<sub>3</sub>] (6.0 mg, 0.0065 mmol) in 0.5 mL of benzene was added rapidly to a solution of **10** (0.13 g, 0.43 mmol) dissolved in 0.5 mL of benzene, followed by stirring for 1 hr. Slight bubbling and a progressive change in the color of the mixture to light orange were observed. The volatiles were removed *in vacuo* affording an orange liquid. <sup>1</sup>H NMR analysis of the recovered material showed unreacted **10**, with no sign of the target polymer **13**.

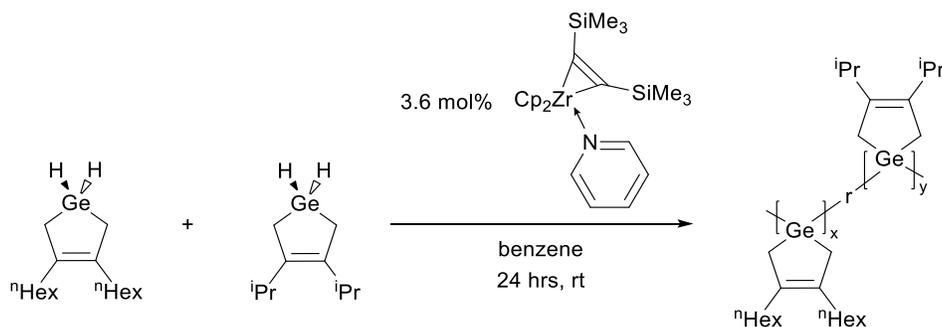
**Synthesis of poly(3,4-dihexylgermacyclopentene) (13) using Cp<sub>2</sub>Zr(pyr)(Me<sub>3</sub>SiCCSiMe<sub>3</sub>) as a catalyst:**



In a glove box, a solution of Cp<sub>2</sub>Zr(pyr)(Me<sub>3</sub>SiCCSiMe<sub>3</sub>) (4.0 mg, 0.0084 mmol) in 1 mL of benzene was added rapidly to neat **10** (0.14 g, 0.47 mmol) at room temperature, followed by

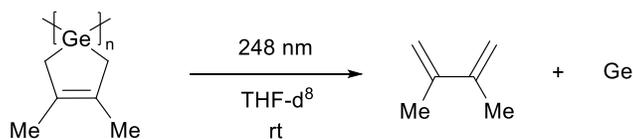
stirring for 24 hrs. Slight bubbling and progressive thickening of the mixture was observed overtime until a viscous red liquid remained. The volatiles were then removed *in vacuo* affording a dark-red viscous solid. Added purification by precipitation of the product dissolved in THF (100  $\mu\text{L}$ ) into 5 mL of MeCN afforded polymeric **13** as a light-yellow semi-solid (87 mg, 61%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  0.80-0.97 (br, 6H,  $\text{CH}_2(\text{CH}_3)$ ), 1.04-1.50 (br, 16H,  $^n\text{Hex CH}_2$ ), 1.66-1.89 (br, 4H,  $\text{Ge}(\text{CH}_2)$ ), 1.91-2.12 (br, 4H,  $^n\text{Hex CH}_2$ ). IR (ATR,  $\text{cm}^{-1}$ ): 2926 ( $\nu\text{C-H}$ ), 2025 ( $\nu\text{Ge-H}$ , end group), 1637 ( $\nu\text{C=C}$ ). Raman ( $\text{cm}^{-1}$ ): 1635 ( $\nu\text{C=C}$ ), 1160 (H-C-H wag), 307 ( $\nu\text{Ge-Ge}$ ). GPC (THF, absolute): Bimodal distribution:  $M_{w\text{-first-peak}} = 31$  kDa;  $\text{PDI}_{\text{first-peak}} = 1.1$ .  $M_{w\text{-second-peak}} = 6$  kDa;  $\text{PDI}_{\text{second-peak}} = 2.2$ . UV-vis (in THF):  $\lambda_{\text{max}} = 299$  nm ( $\epsilon = 7.60 \times 10^3$  L  $\text{mol}^{-1}$   $\text{cm}^{-1}$  per monomer unit).  $\text{dn/dc}$  (dl/g): 0.185. Anal. Calcd. for  $\text{C}_{16}\text{H}_{30}\text{Ge}$ : C, 65.13; H, 10.25%. Found: C, 65.49; H, 10.40%.

**Synthesis of poly(3,4-dihexylgermacyclopentene-*r*-3,4-diisopropylgermacyclopentene) (**14**) using  $\text{Cp}_2\text{Zr}(\text{pyr})(\text{Me}_3\text{SiCCSiMe}_3)$  as a catalyst:**



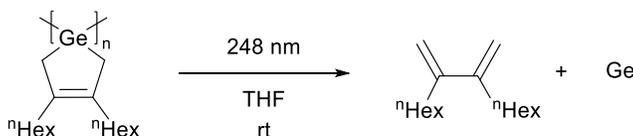
In a glove box, a solution of  $\text{Cp}_2\text{Zr}(\text{pyr})(\text{Me}_3\text{SiCCSiMe}_3)$  (8.0 mg, 0.017 mmol) in 1 mL of benzene was added rapidly to a neat mixture of **9** (0.099 g, 0.47 mmol) and **10** (0.14 g, 0.47 mmol) at room temperature, followed by stirring for 24 hrs. Slight bubbling and progressive thickening of the mixture was observed overtime until a viscous light-orange liquid remained. The volatiles were then removed *in vacuo* to give an orange semi-solid. Added purification by precipitation of the product dissolved in THF (100  $\mu\text{L}$ ) into 5 mL of MeCN gave polymeric **14** as a light-yellow gum (0.19 g, 75% yield assuming a copolymer is formed with a composition of 47% of the monomer unit bearing *n*-hexyl repeating units, as estimated by  $^1\text{H}$  NMR spectroscopy.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  0.67-1.09 (br,  $\text{CH}_2\text{CH}_3$  and  $\text{CH}(\text{CH}_3)_2$ ), 1.11-1.41 (br,  $^n\text{Hex CH}_2$ ), 1.65-2.17 (br,  $\text{Ge}(\text{CH}_2)$  and  $^n\text{Hex CH}_2$ ), 2.71-2.97 (br 2H,  $\text{CH}(\text{CH}_3)_2$ ). IR (ATR,  $\text{cm}^{-1}$ ): 2956 ( $\nu\text{C-H}$ ), 2031 ( $\nu\text{Ge-H}$ , end group), 1633 ( $\nu\text{C=C}$ ). Raman ( $\text{cm}^{-1}$ ): 1636 ( $\nu\text{C=C}$ ), 1150 (H-C-H wag), 306 ( $\nu\text{Ge-Ge}$ ). GPC (THF, absolute): Bimodal distribution:  $M_{w\text{-first-peak}} = 18$  kDa;  $\text{PDI}_{\text{first-peak}} = 1.3$ .  $M_{w\text{-second-peak}} = 15$  kDa;  $\text{PDI}_{\text{second-peak}} = 2.5$ .  $\text{dn/dc}$  (dl/g): 0.185. UV-vis (in THF):  $\lambda_{\text{max}} = 292$  nm ( $\epsilon = 6.72 \times 10^3$  L  $\text{mol}^{-1}$   $\text{cm}^{-1}$  per monomer unit).

### Photolysis of poly(3,4-dimethylgermacyclopentene) (**11**):



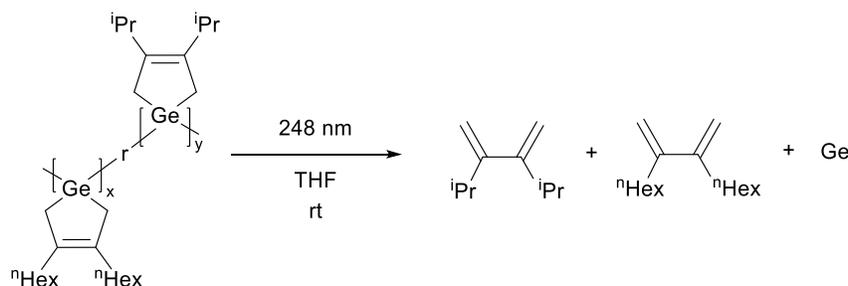
A red-colored solution of **11** (23 mg, 0.15 mmol per monomer unit) in 0.5 mL of dry THF-d<sub>8</sub> in a custom-made, N<sub>2</sub> filled, photolysis reactor was irradiated with a KrF laser of 248 nm (see conditions in the “General information, materials and instrumentation” section). Once the irradiation period was complete, a dark grey-brown precipitate film on the inner wall of the reactor, along with a grey powder at the bottom of the reactor. Inside a glove box, the mother liquor was separated by decantation from the dark-grey powder. The precipitate was purified by washes with dry THF (20 mL total) followed by removal of volatiles *in vacuo* (4.0 mg, 55% yield of Ge). <sup>1</sup>H NMR analysis of the mother liquor showed signals corresponding to 2,3-dimethyl-1,3-butadiene and unreacted **11**.

### Photolysis of poly(3,4-dihexylgermacyclopentene) (**13**):



A solution of **13** (57 mg, 0.20 mmol per monomer unit) in 0.5 mL of dry THF in a custom-made, N<sub>2</sub> filled, photolysis reactor was irradiated with a KrF laser of 248 nm (see conditions in the “General information, materials and instrumentation” section). Once the irradiation period was complete, a dark brown-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 precipitate was purified by washes with dry THF (20 mL total) followed by removal of volatiles *in vacuo* (8.5 mg, 59% yield of Ge). 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-dihexyl-1,3-butadiene and unreacted **13**.

### Photolysis of poly(3,4-dihexylgermacyclopentene-r-3,4-diisopropylgermacyclopentene) (**14**):



A solution of **14** (43 mg) in 0.5 mL of dry THF in a custom-made, N<sub>2</sub> filled, photolysis reactor was irradiated with a KrF laser of 248 nm (see conditions in the “General information, materials and instrumentation” section). Once the irradiation period was complete, a dark brown-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* (5.6 mg, 44% yield of Ge).

### Deposition of **13** via spin-coating and photolysis

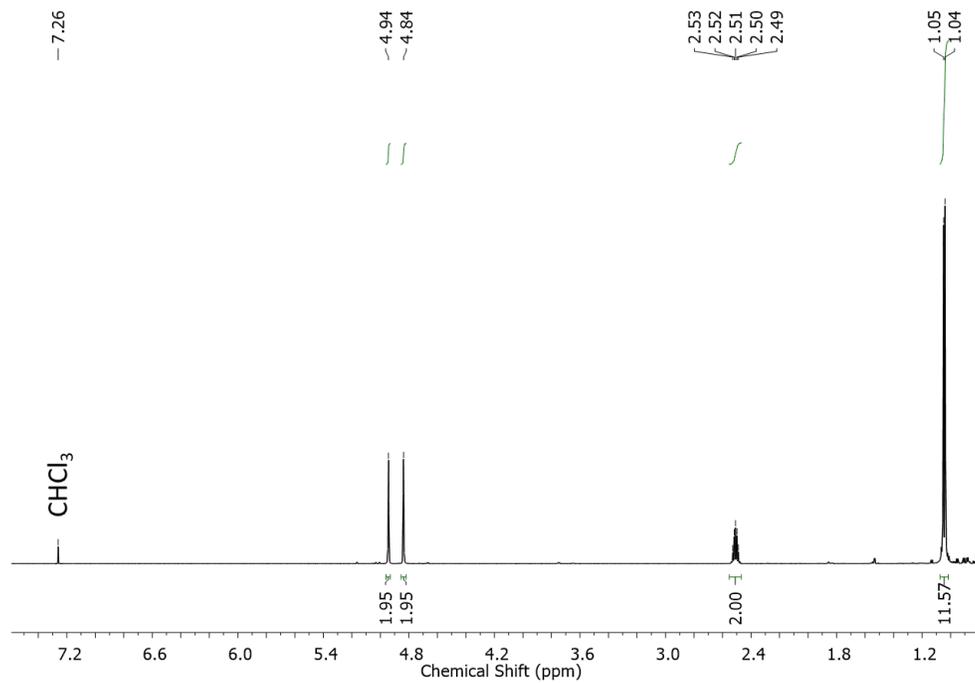
A 200  $\mu$ L of a solution of **13** in THF (0.031 mg mL<sup>-1</sup>) was prepared followed by filtration through a 0.45  $\mu$ m pore-sized glass fiber filter. Meanwhile, a Si wafer substrate was tapped onto a home-made spin coater and setup to rotate at 2200 rpm (measured by a Strobotac type 1531-A stroboscope, manufactured by General Radio Company). The prepared solution was then added dropwise to the Si wafer substrate (while in motion) affording a thin polymer film. The deposited sample was dried under vacuum until no change in mass was recorded. Film thickness characterization was attempted *via* contact profilometry, however, the softness of the material did not allow for an accurate measurement. Analysis *via* SEM-EDX also proved to be unsuccessful due to the high reflectivity and malleability of the polymer.

In a homemade and N<sub>2</sub> filled quartz photolysis reactor, the previously prepared polymer film of **13** on the Si substrate was irradiated with a KrF laser of 248 nm (see conditions in the “General information, materials and instrumentation” section). Once the irradiation period was complete, an uneven layer on the Si wafer composed of a dark-grey solid and a glue-like material remained. Additionally, a metallic film on the inner wall of the quartz reactor (opposite to the Si substrate) formed.

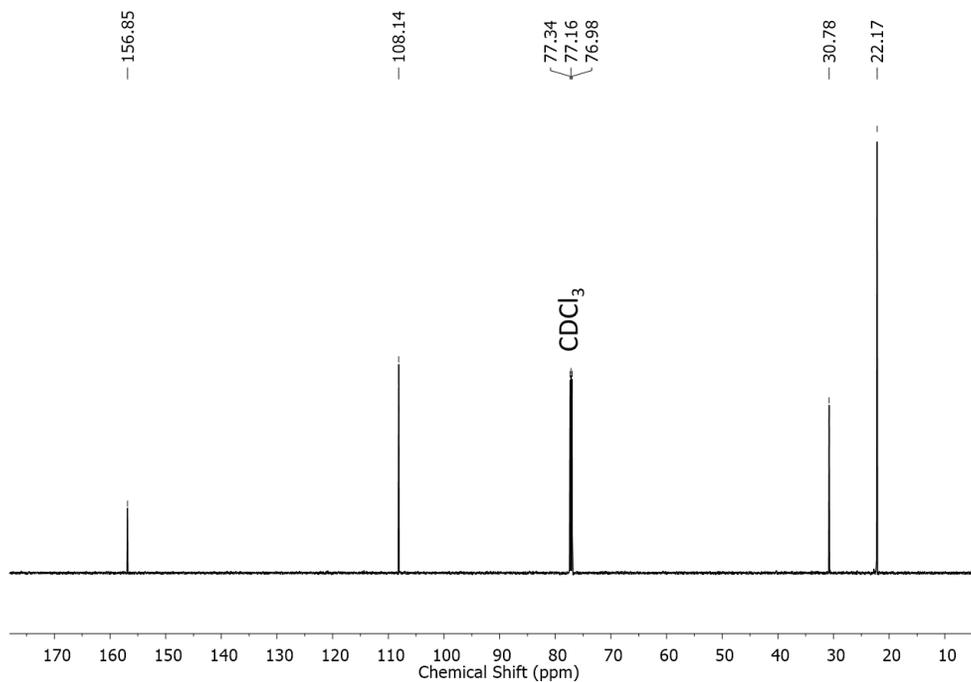
### Photopatterning of **14** from solution

A solution of **14** (41 mg) in 1 mL of dry THF in a custom-made, N<sub>2</sub> filled, photolysis reactor was irradiated with a KrF laser of 248 nm (see conditions in the “General information, materials and instrumentation” section). Prior to the irradiation, a mask made of a quartz substrate and chromium, metal forming predetermined patterns, was attached to the outside wall of the reactor. The mask was positioned so the laser beam would pass through it before hitting the quartz reactor.

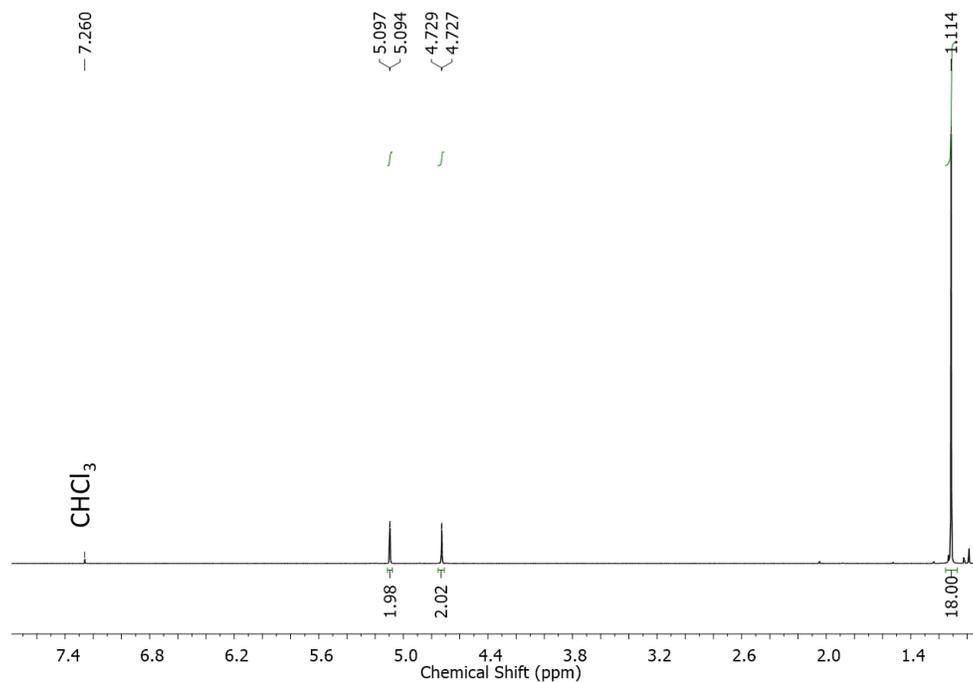
## 2. NMR spectra



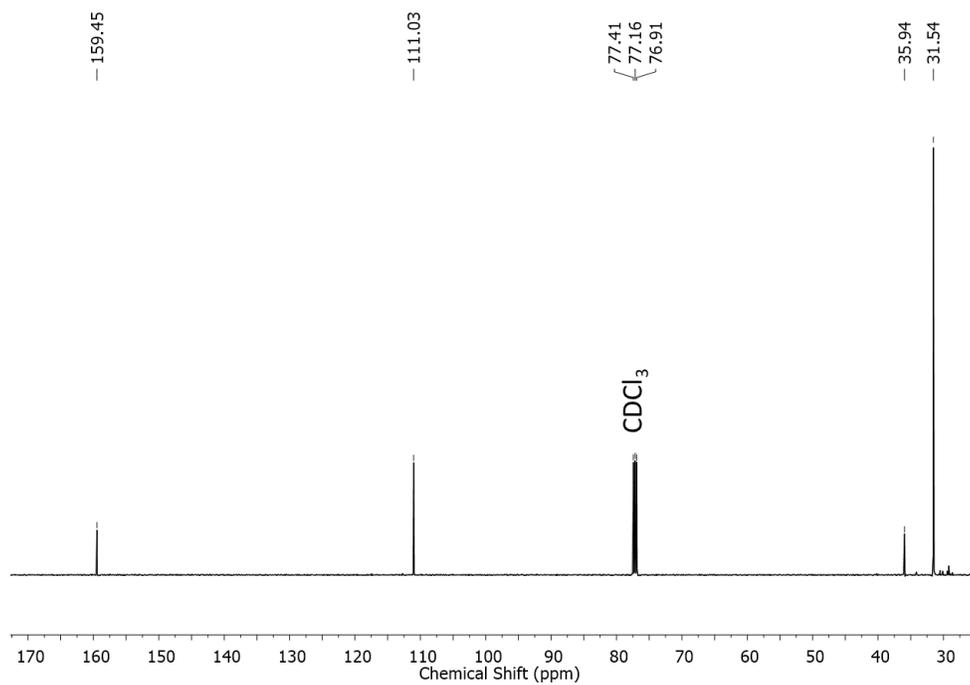
**Fig. S1.**  $^1\text{H}$  NMR spectrum of 2,3-diisopropyl-1,3-butadiene (**2**) in  $\text{CDCl}_3$ .



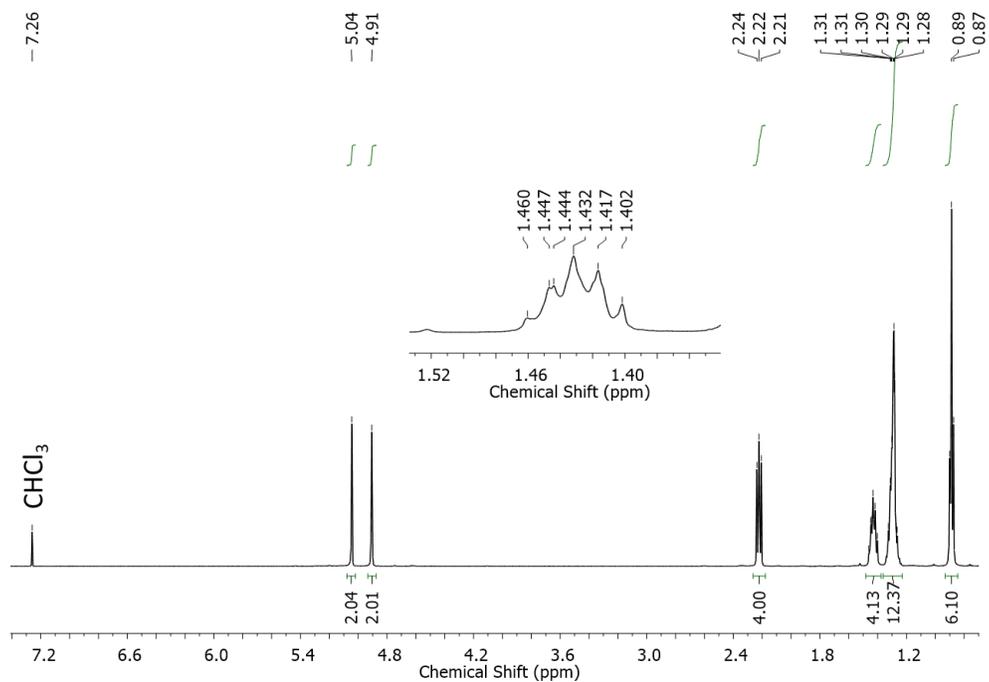
**Fig. S2.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 2,3-diisopropyl-1,3-butadiene (**2**) in  $\text{CDCl}_3$ .



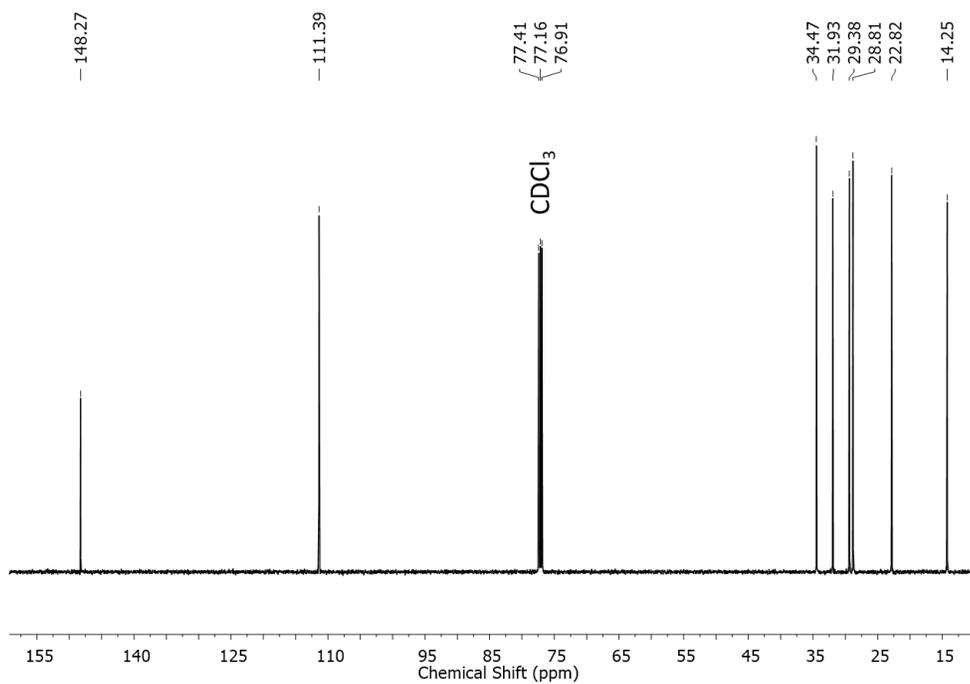
**Fig. S3.**  $^1\text{H}$  NMR spectrum of 2,3-di-*tert*-butyl-1,3-butadiene (**3**) in  $\text{CDCl}_3$ .



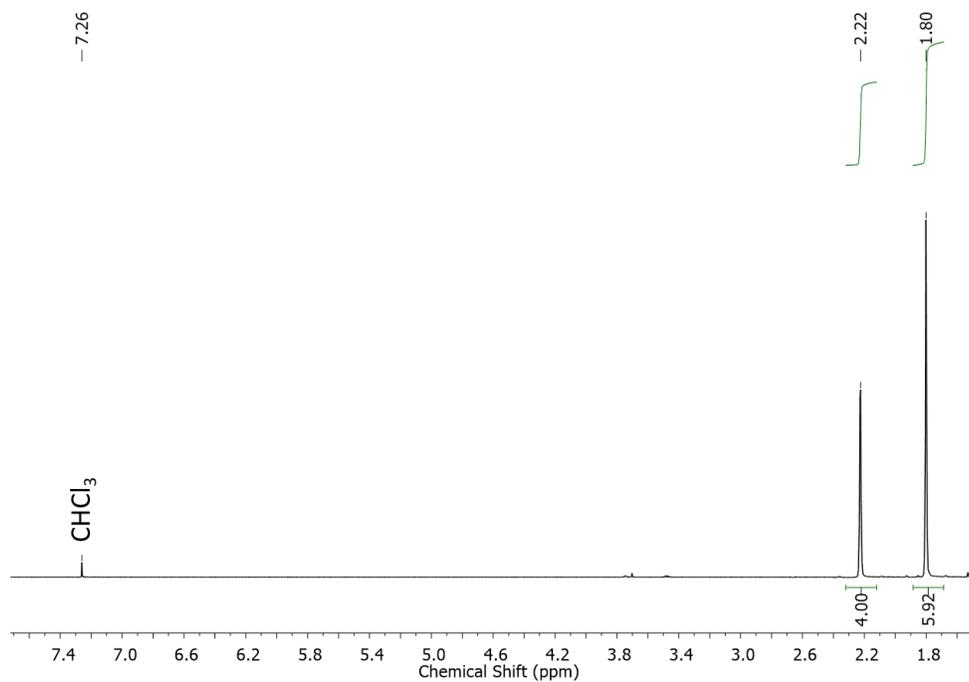
**Fig. S4.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 2,3-di-*tert*-butyl-1,3-butadiene (**3**) in  $\text{CDCl}_3$ .



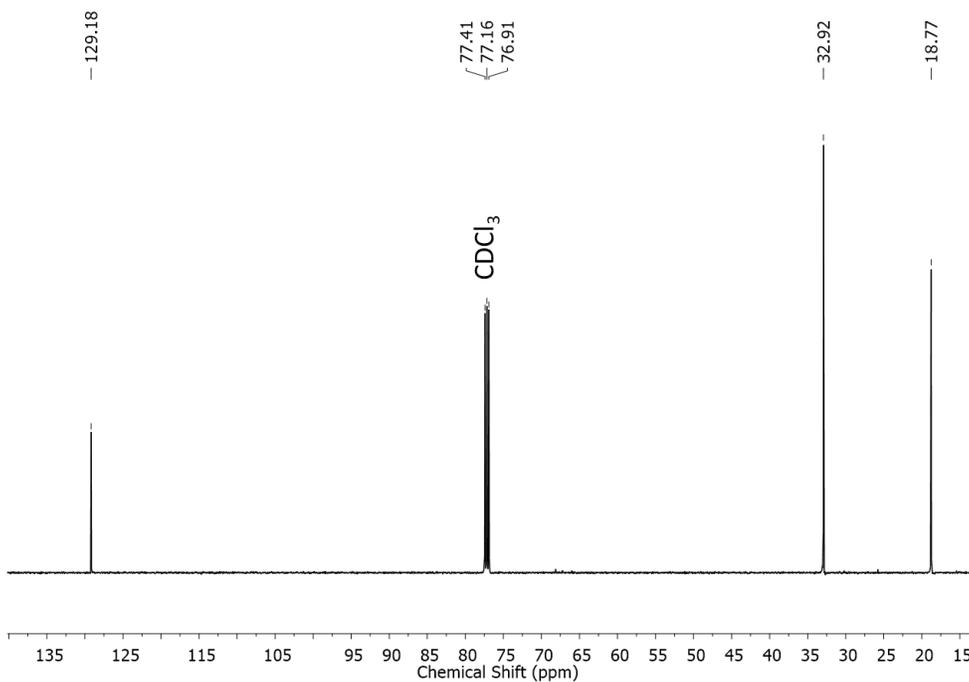
**Fig. S5.**  $^1\text{H}$  NMR spectrum of 2,3-dihexyl-1,3-butadiene (**4**) in  $\text{CDCl}_3$ .



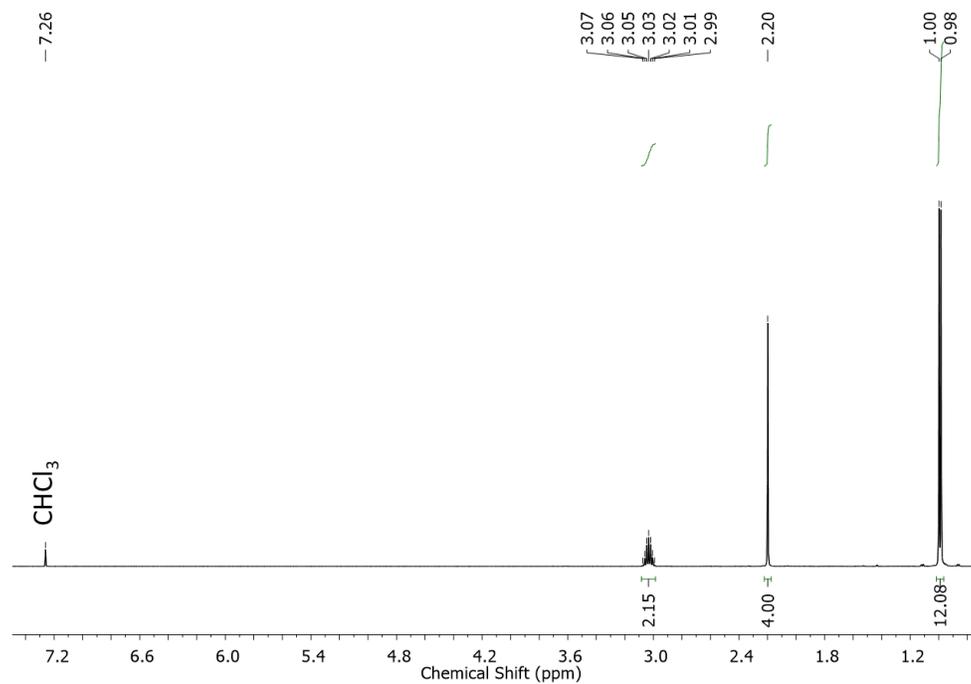
**Fig. S6.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 2,3-dihexyl-1,3-butadiene (**4**) in  $\text{CDCl}_3$ .



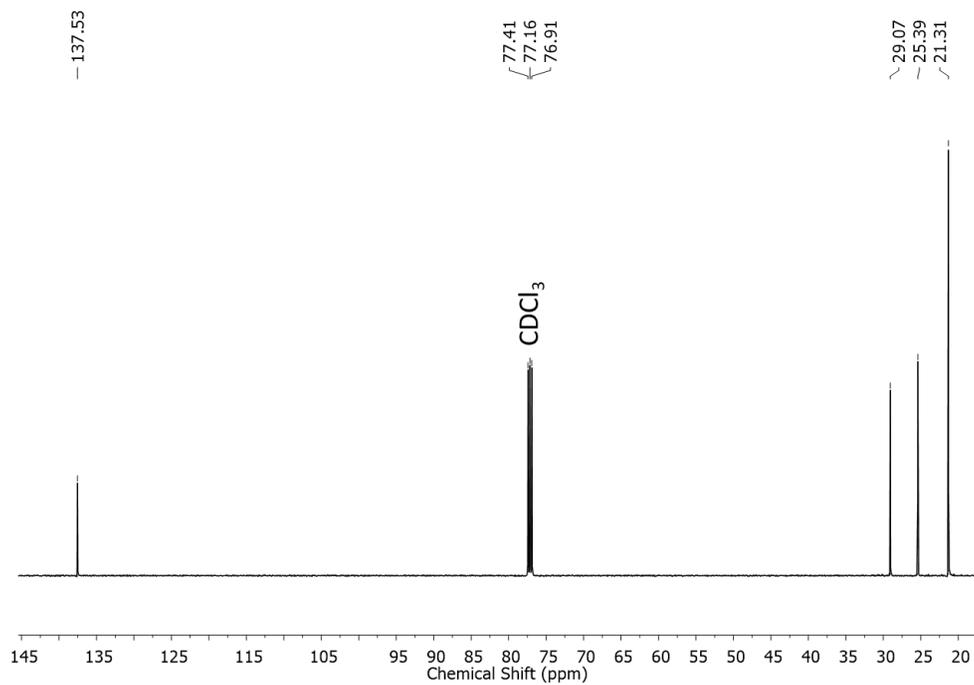
**Fig. S7.**  $^1\text{H}$  NMR spectrum of 1,1-dichloro-3,4-dimethylgermacyclopent-3-ene (**5**) in  $\text{CDCl}_3$ .



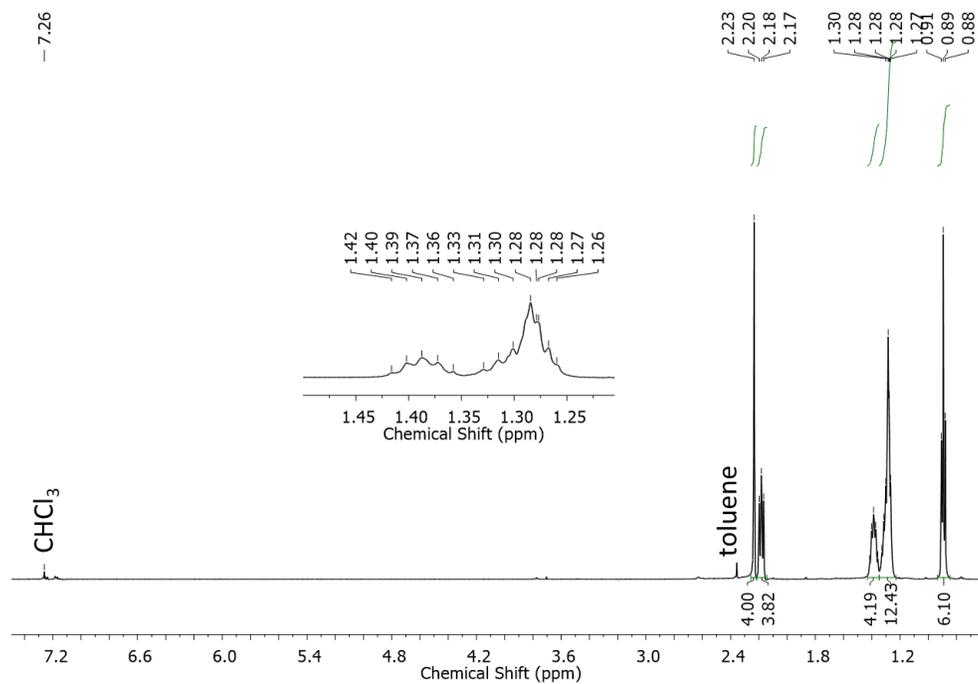
**Fig. S8.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 1,1-dichloro-3,4-dimethylgermacyclopent-3-ene (**5**) in  $\text{CDCl}_3$ .



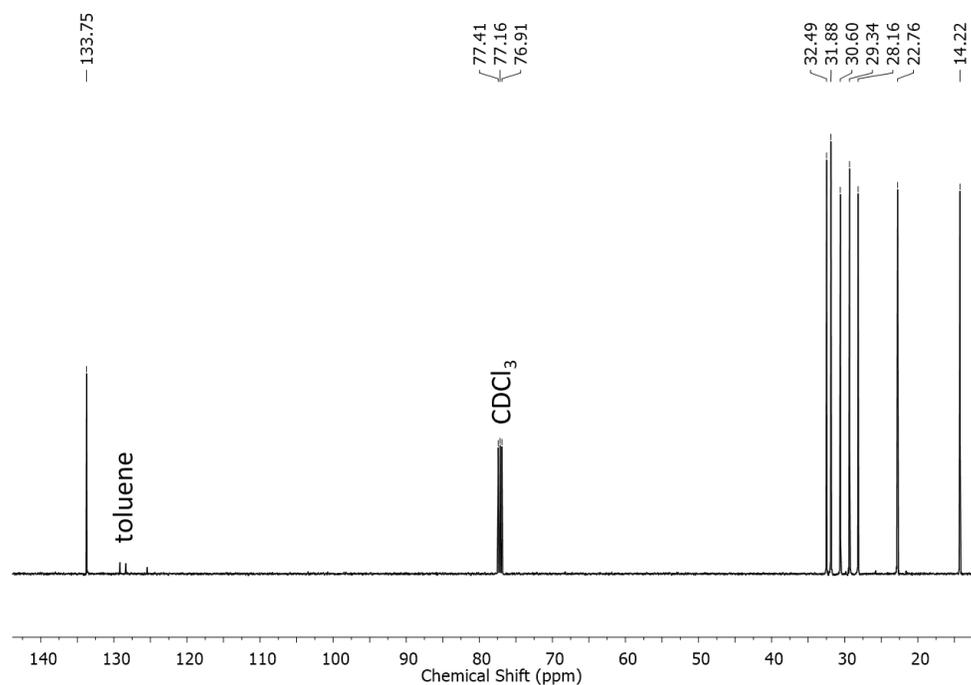
**Fig. S9.**  $^1\text{H}$  NMR spectrum of 1,1-dichloro-3,4-diisopropylgermacyclopent-3-ene (**6**) in  $\text{CDCl}_3$ .



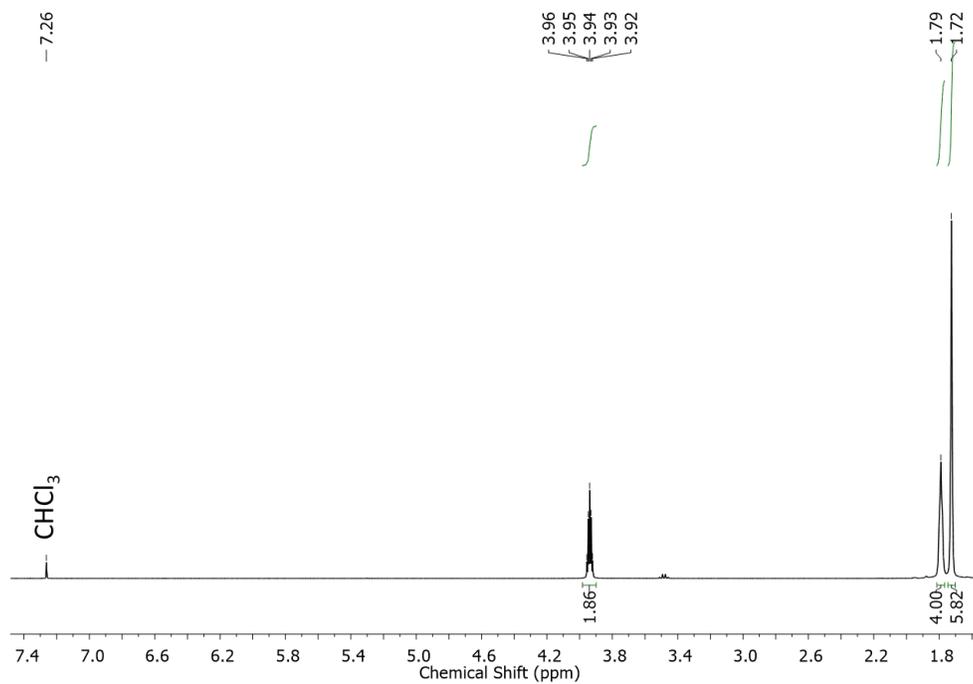
**Fig. S10.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 1,1-dichloro-3,4-diisopropylgermacyclopent-3-ene (**6**) in  $\text{CDCl}_3$ .



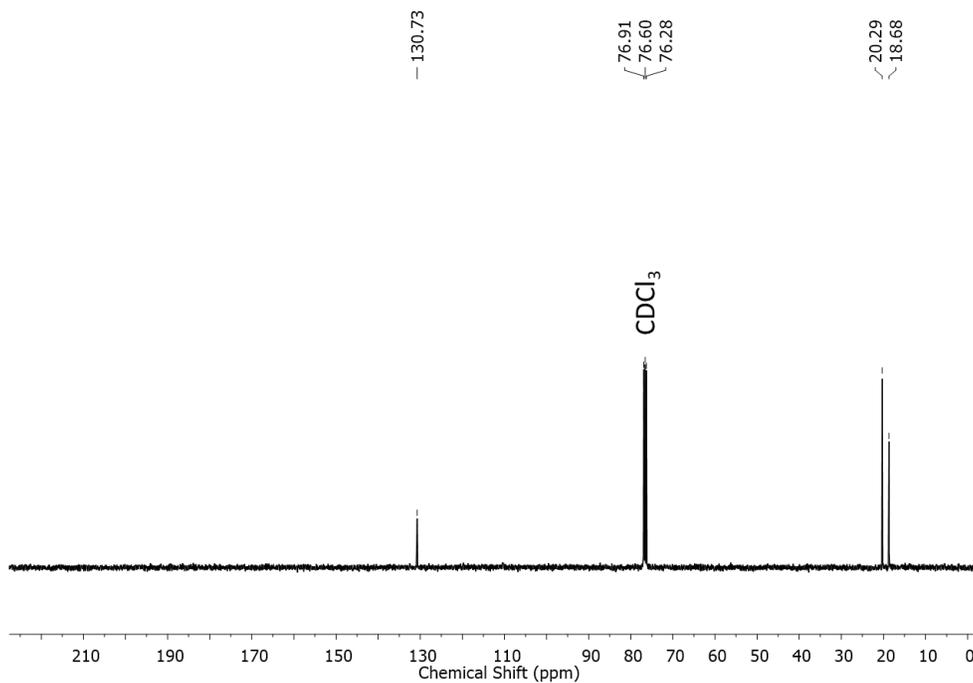
**Fig. S11.**  $^1\text{H}$  NMR spectrum of 1,1-dichloro-3,4-dihexylgermacycloprop-3-ene (**7**) in  $\text{CDCl}_3$ .



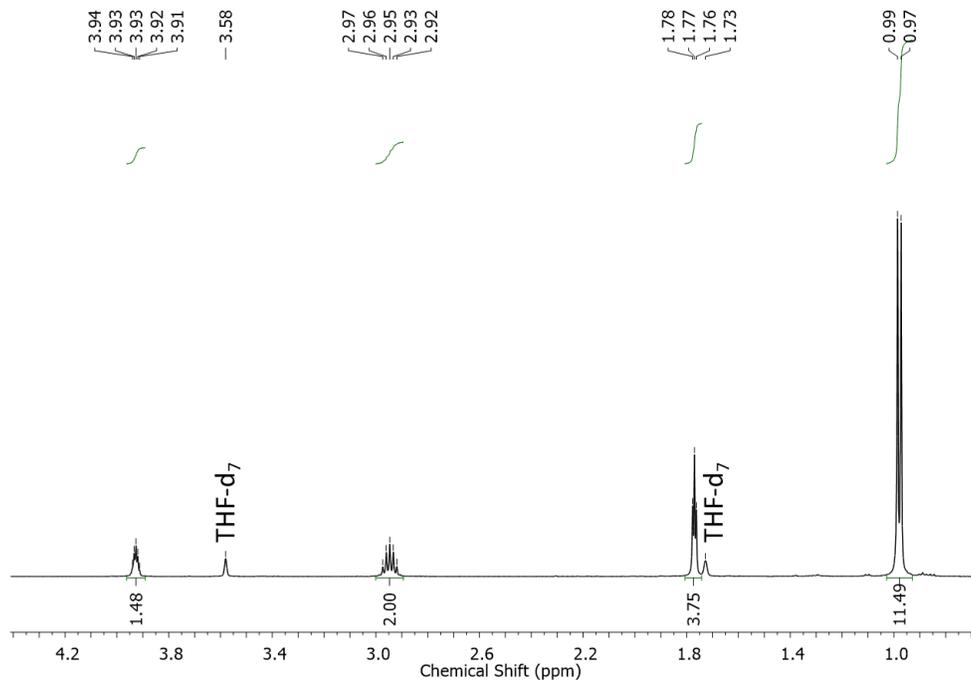
**Fig. S12.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 1,1-dichloro-3,4-dihexylgermacycloprop-3-ene (**7**) in  $\text{CDCl}_3$ .



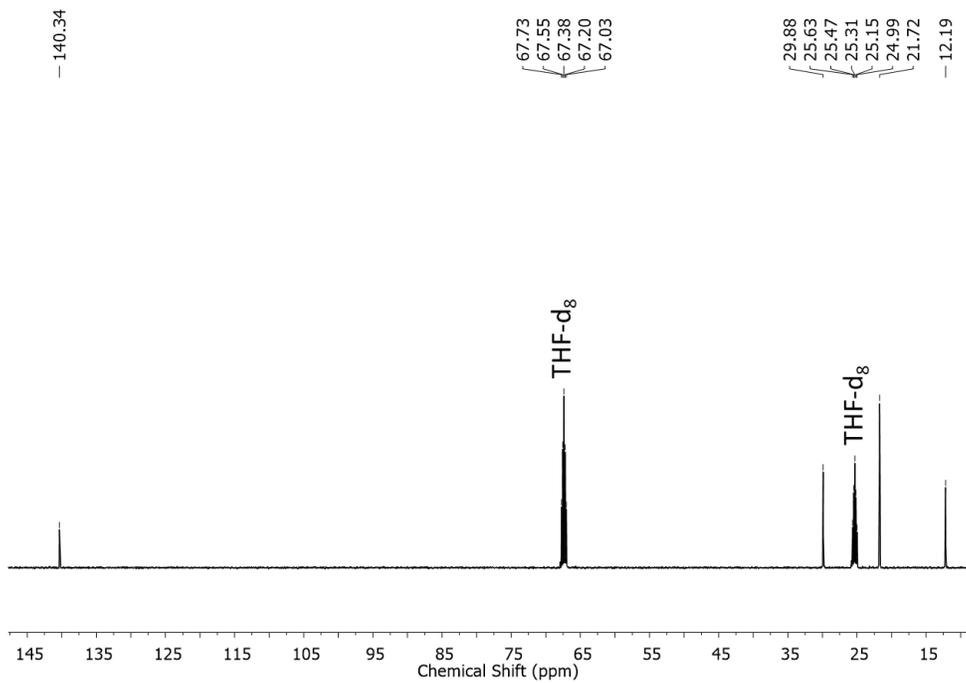
**Fig. S13.**  $^1\text{H}$  NMR spectrum of 1,1-dihydro-3,4-dimethylgermacyclopent-3-ene (**8**) in  $\text{CDCl}_3$ .



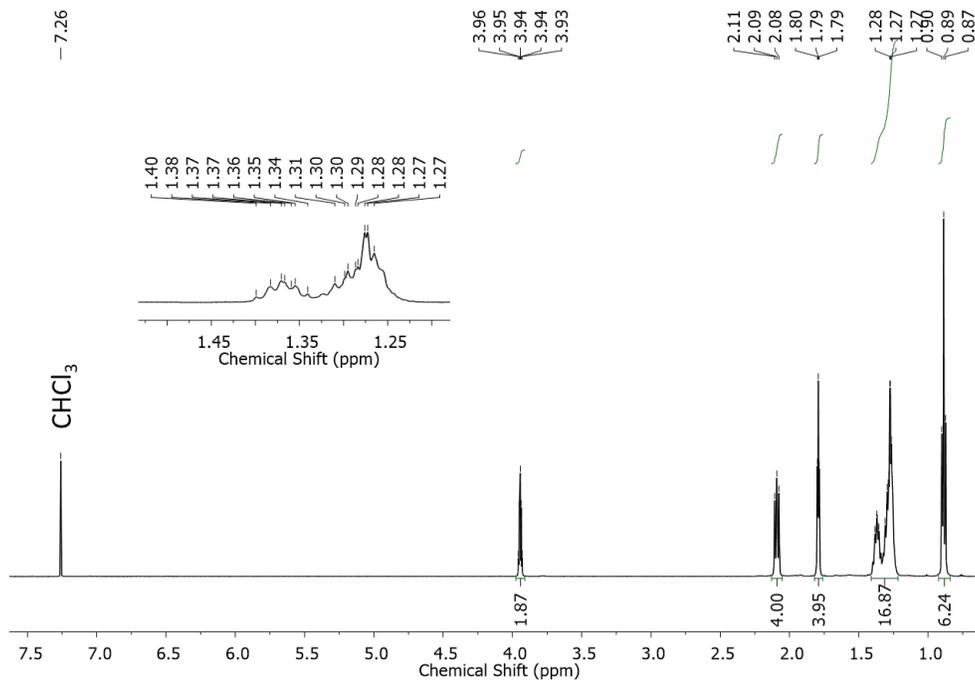
**Fig. S14.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 1,1-dihydro-3,4-dimethylgermacyclopent-3-ene (**8**) in  $\text{CDCl}_3$ .



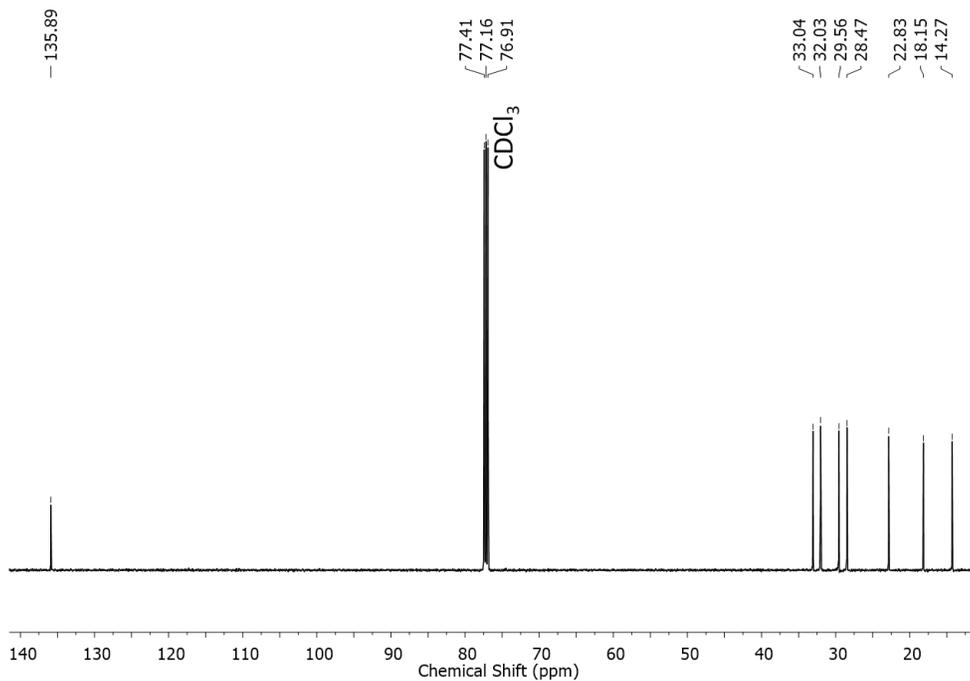
**Fig. S15.**  $^1\text{H}$  NMR spectrum of 1,1-dihydro-3,4-diisopropylgermacyclopent-3-ene (**9**) in THF-d<sub>7</sub>.



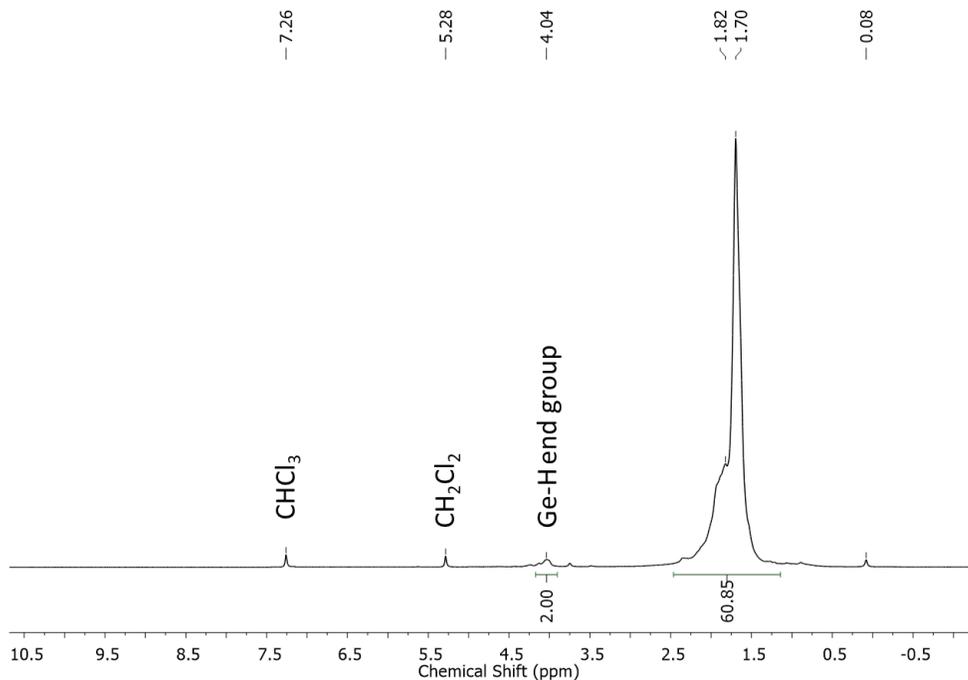
**Fig. S16.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 1,1-dihydro-3,4-diisopropylgermacyclopent-3-ene (**9**) in THF-d<sub>8</sub>.



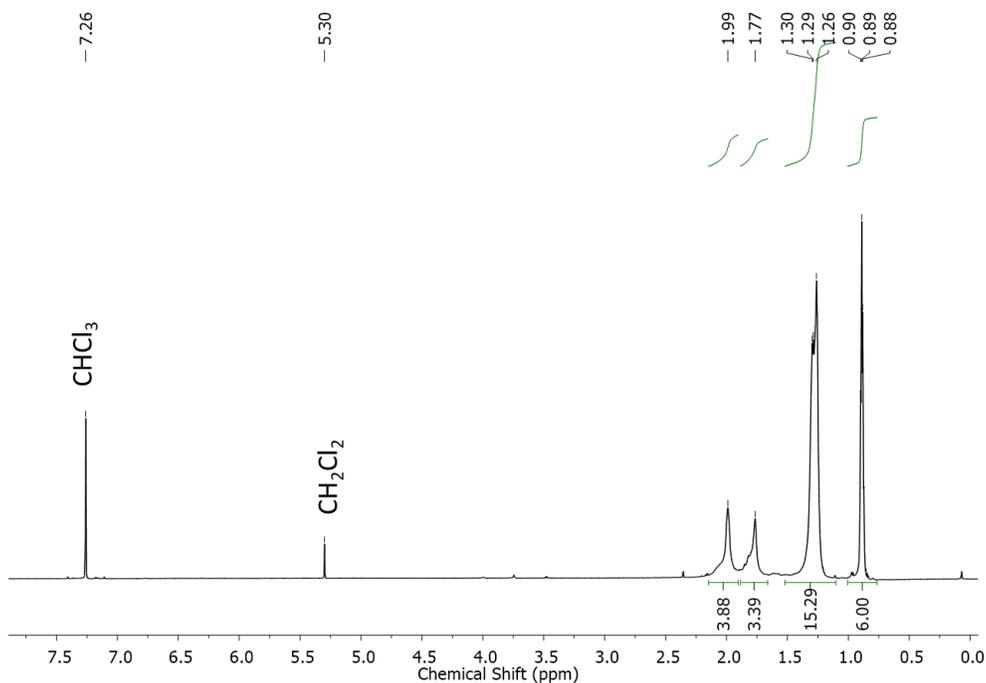
**Fig. S17.**  $^1\text{H}$  NMR spectrum of 1,1-dihydro-3,4-dihexylgermacycloprop-3-ene (**10**) in  $\text{CDCl}_3$ .



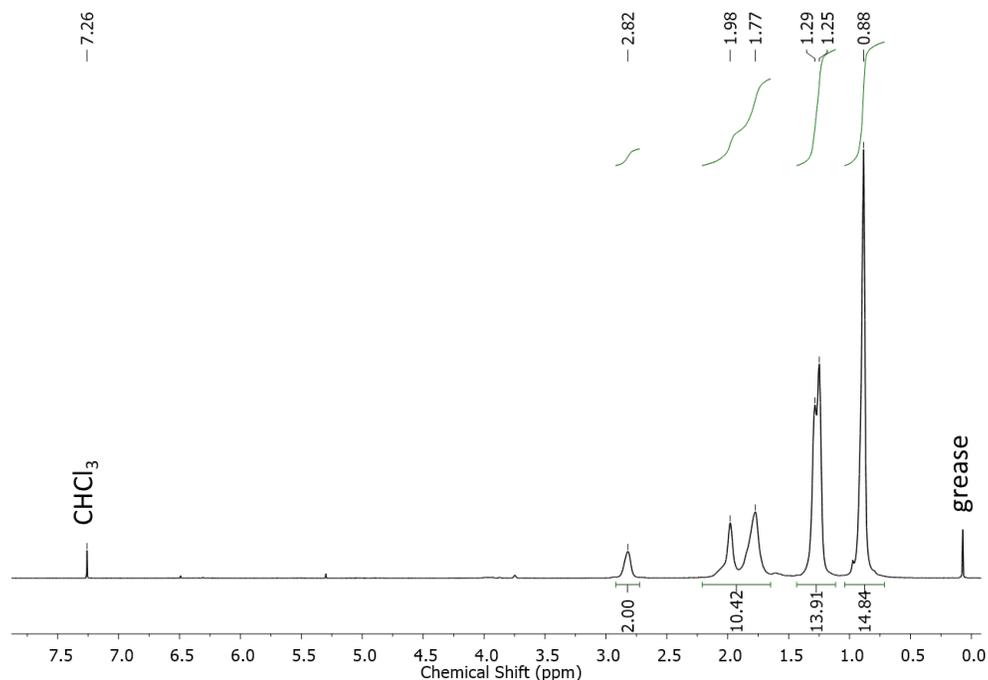
**Fig. S18.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 1,1-dihydro-3,4-dihexylgermacycloprop-3-ene (**10**) in  $\text{CDCl}_3$ .



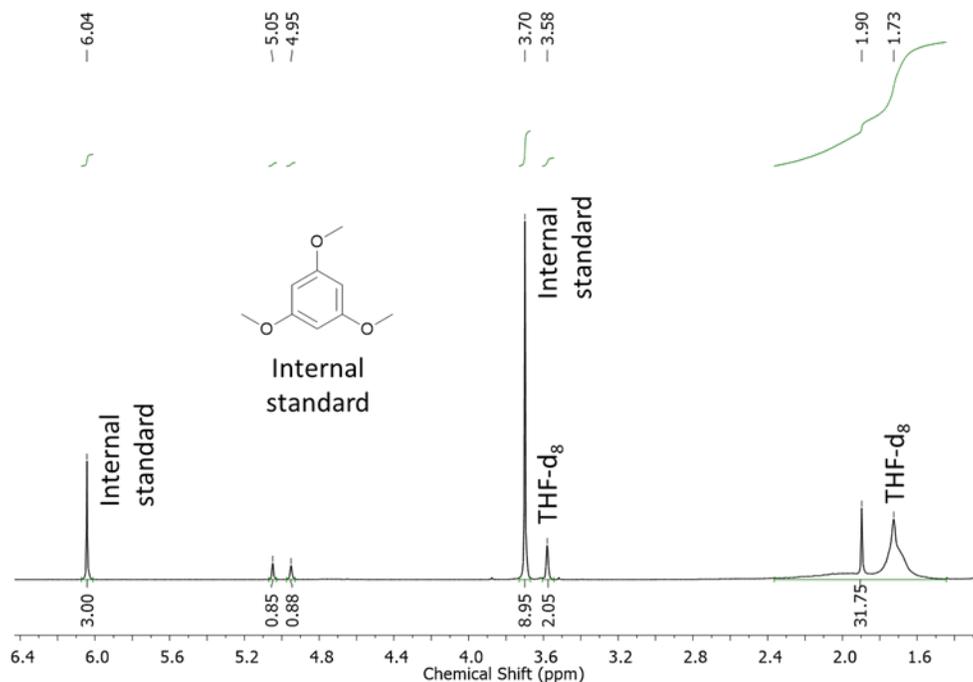
**Fig. S19.**  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  of poly(3,4-dimethylgermacyclopentene) (**11**), prepared with 1 mol% of  $[\text{Rh}(\text{COD})\text{Cl}]_2$  as a pre-catalyst.



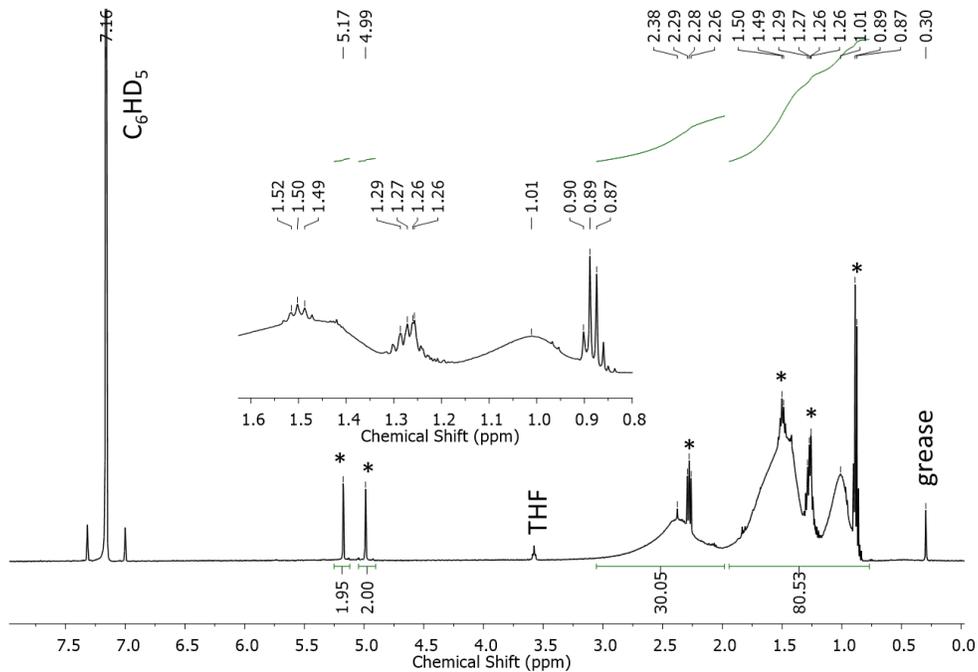
**Fig. S20.**  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  of poly(3,4-dihexylgermacyclopentene) (**13**), prepared with 1.8 mol% of  $\text{Cp}_2\text{Zr}(\text{pyr})(\text{Me}_3\text{SiCCSiMe}_3)$  as a catalyst.



**Fig. S21.**  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  of poly(3,4-dihexylgermacyclopentene-*r*-3,4-diisopropylgermacyclopentene) (**14**), prepared from 1.8 mol% of  $\text{Cp}_2\text{Zr}(\text{pyr})(\text{Me}_3\text{SiCCSiMe}_3)$  as a catalyst.

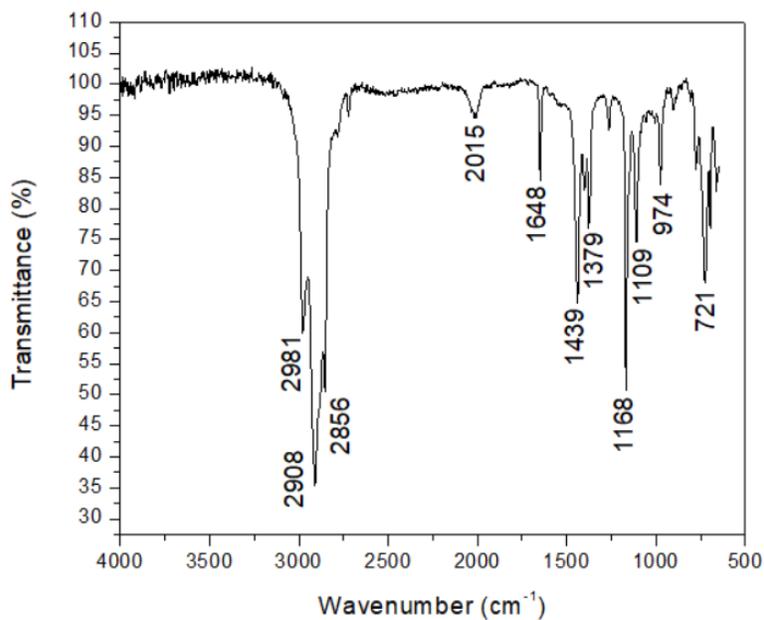


**Fig. S22.**  $^1\text{H}$  NMR spectrum of the mixture after photolysis of poly(3,4-dimethylgermacyclopentene) (**11**) in  $\text{THF-d}_8$ . Singlets at 5.05, 4.95, and 1.90 ppm correspond to 2,3-dimethyl-1,3-butadiene.

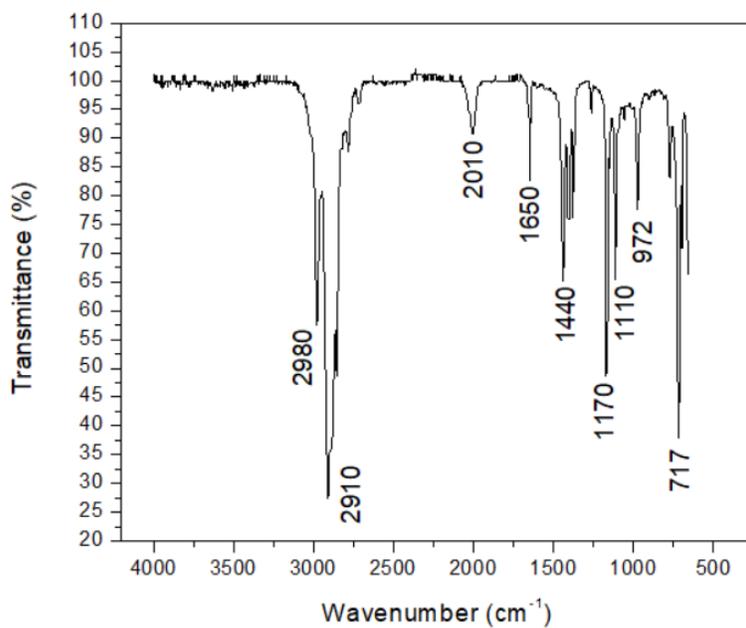


**Fig. S23.**  $^1\text{H}$  NMR spectrum of the mixture after photolysis of poly(3,4-dimethylgermacyclopentene) (**13**) in  $\text{C}_6\text{D}_6$ . Signals (\*) at 5.17, 4.99, 2.28, 1.50, 1.27, and 0.89 ppm correspond to 2,3-dihexyl-1,3-butadiene.

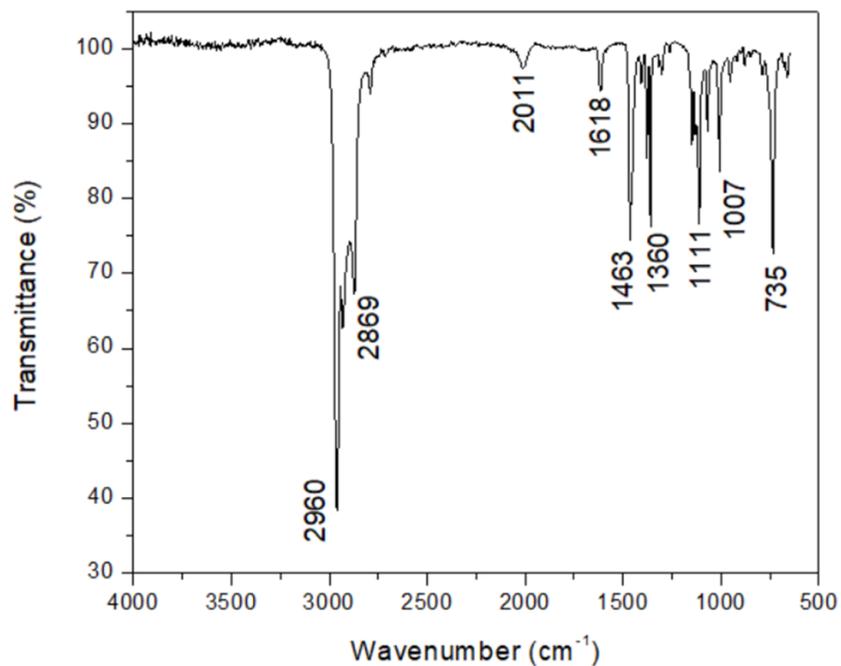
### 3. FT-IR and Raman spectra of the poly(cyclogermapentene)s



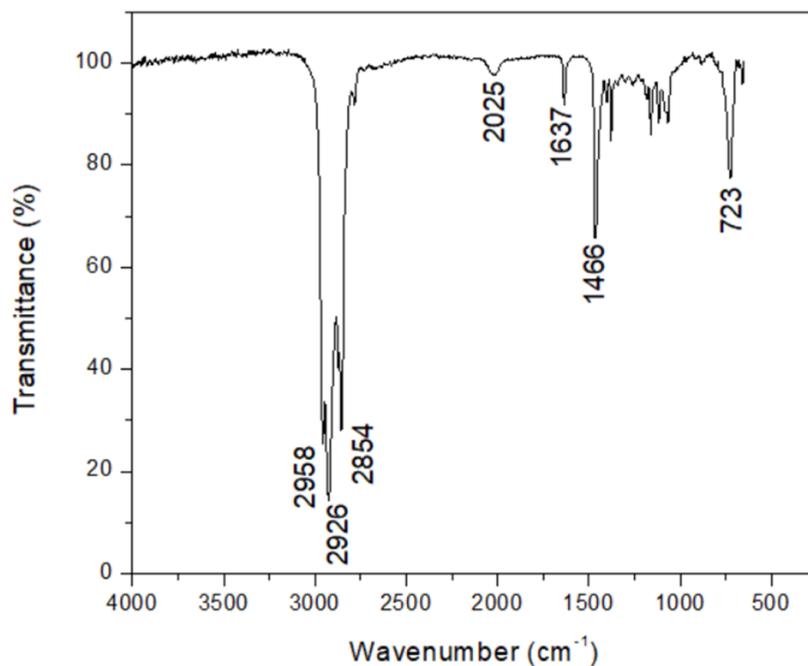
**Fig. S24.** FT-IR spectrum of oligo(3,4-dimethylgermacyclopentene) (**11**); a weak Ge-H stretch is observed at 2015 cm<sup>-1</sup> due to end groups.



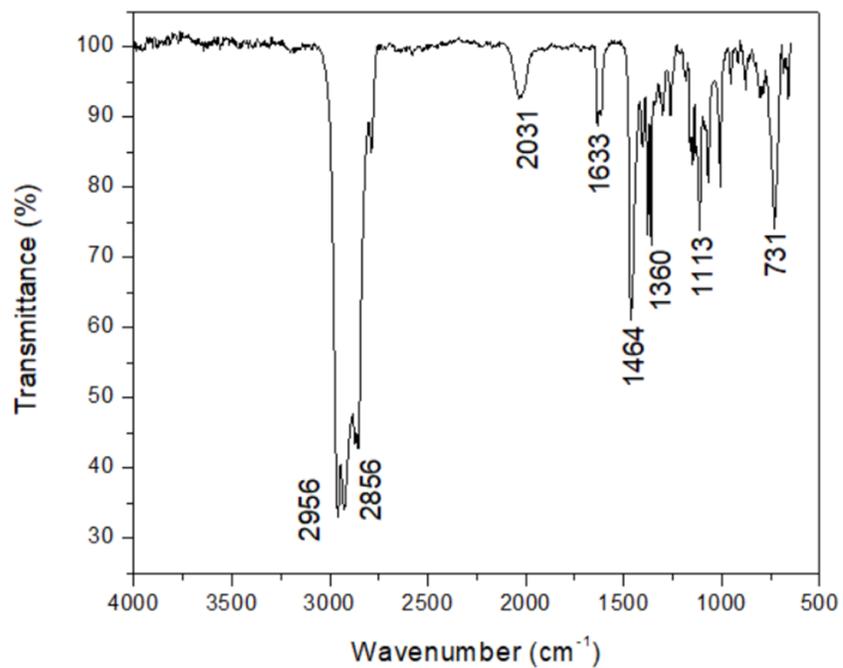
**Fig. S25.** FT-IR spectrum of insoluble poly(3,4-dimethylgermacyclopentene) (**11**). A weak Ge-H stretch is observed at 2010 cm<sup>-1</sup> due to end groups.



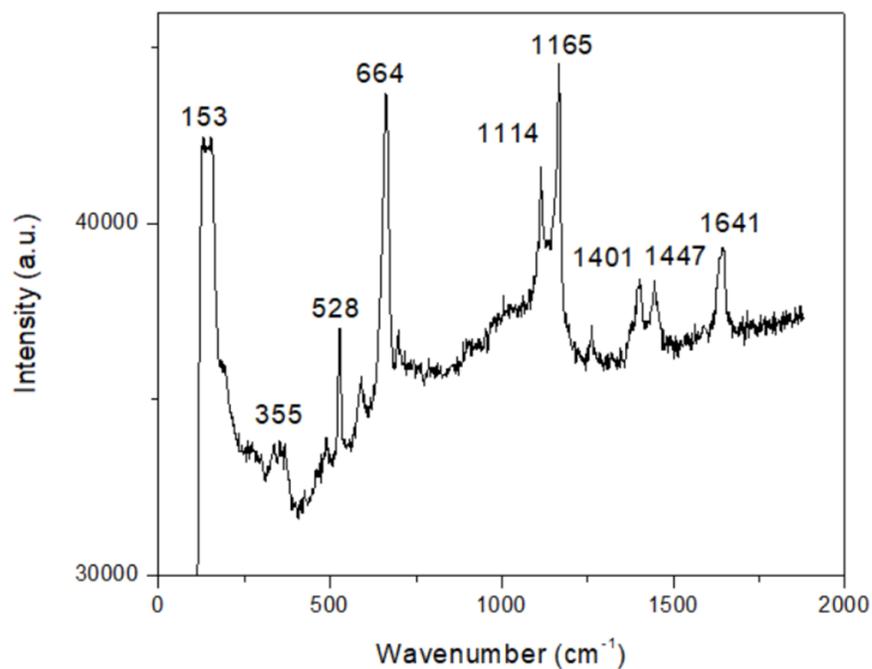
**Fig. S26.** FT-IR spectrum of poly(3,4-diisopropylgermacyclopentene) (**12**); a weak Ge-H stretch is observed at 2011 cm<sup>-1</sup> due to end groups.



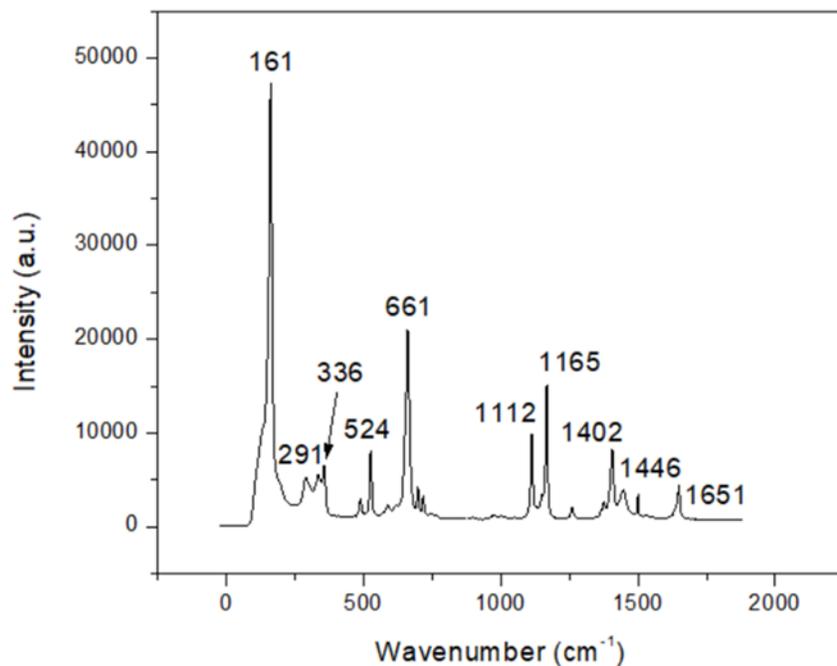
**Fig. S27.** FT-IR spectrum of poly(3,4-dihexylgermacyclopentene) (**13**); a weak Ge-H stretch is observed at 2025 cm<sup>-1</sup> due to end groups.



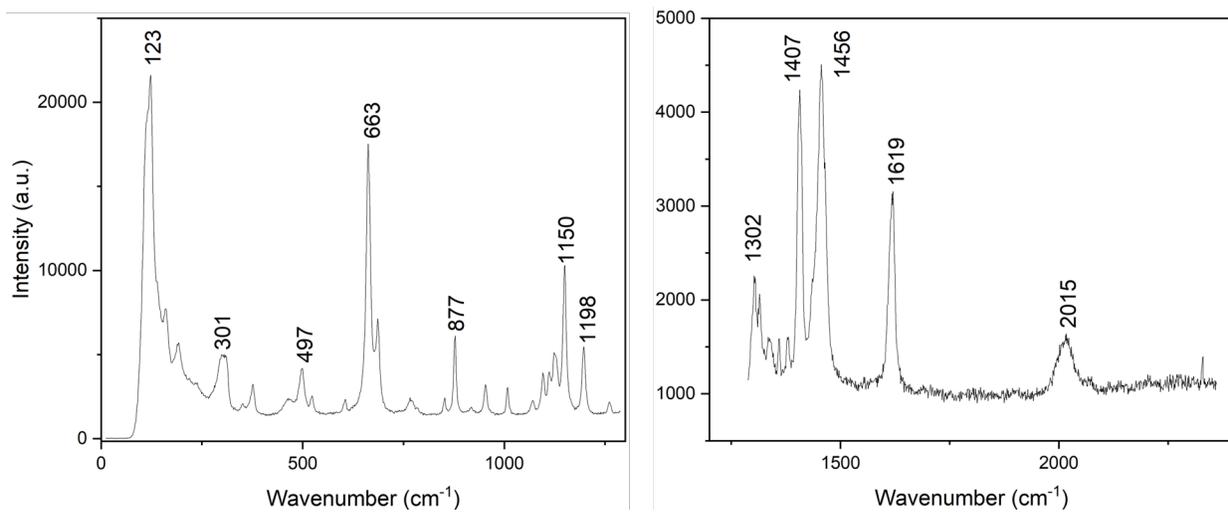
**Fig. S28.** FT-IR spectrum of poly(3,4-dihexylgermacyclopentene-*r*-3,4-diisopropylgermacyclopentene) (**14**); a weak Ge-H stretch is observed at 2031 cm<sup>-1</sup> due to end groups.



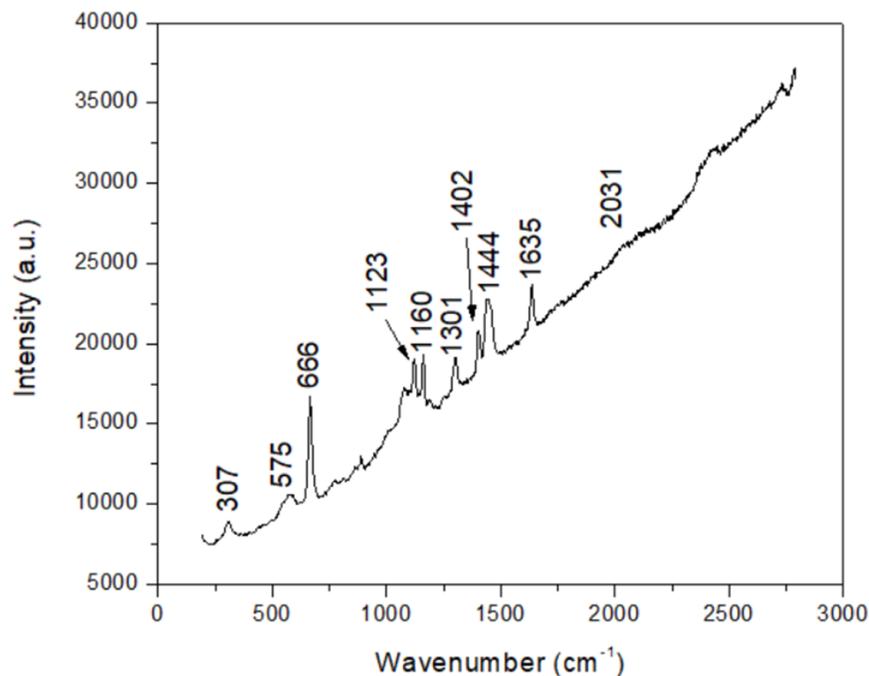
**Fig. S29.** Raman spectrum of soluble oligo(3,4-dimethylgermacyclopentene) (**11**). Ge-Ge and C=C stretches are found at 355 and 1641 cm<sup>-1</sup>, respectively. Excitation wavelength: 610 nm.



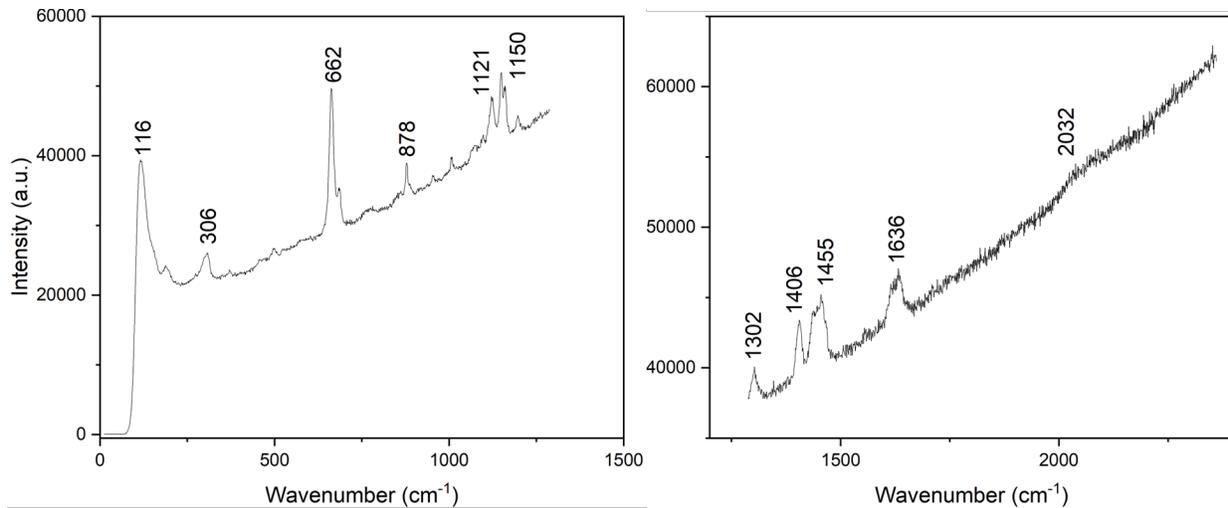
**Fig. S30.** Raman spectrum of insoluble poly(3,4-dimethylgermacyclopentene) (**11**). Ge-Ge and C=C stretches are found at 336 and 1651  $\text{cm}^{-1}$ , respectively. Excitation wavelength: 610 nm.



**Fig. S31.** Raman spectrum of poly(3,4-diisopropylgermacyclopentene) (**12**). Ge-Ge and C=C stretches are found at 301 and 1619  $\text{cm}^{-1}$ , respectively. A weak Ge-H stretch is observed at 2015  $\text{cm}^{-1}$  due to end groups. Excitation wavelength: 532 nm

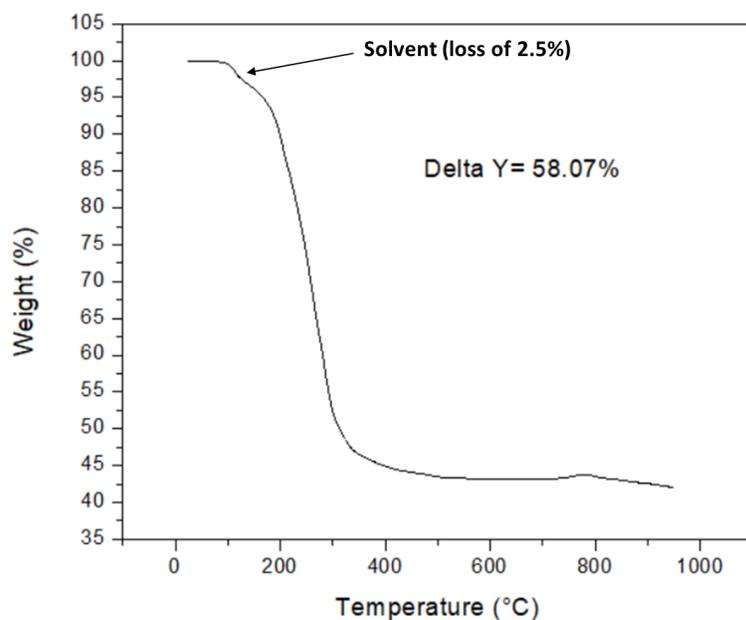


**Fig. S32.** Raman spectrum of poly(3,4-dihexylgermacyclopentene) (**13**); Ge-Ge and C=C stretches are found at 307 and 1635  $\text{cm}^{-1}$ , respectively. A weak Ge-H stretch is observed at 2031  $\text{cm}^{-1}$  due to end groups. Excitation wavelength: 532 nm.

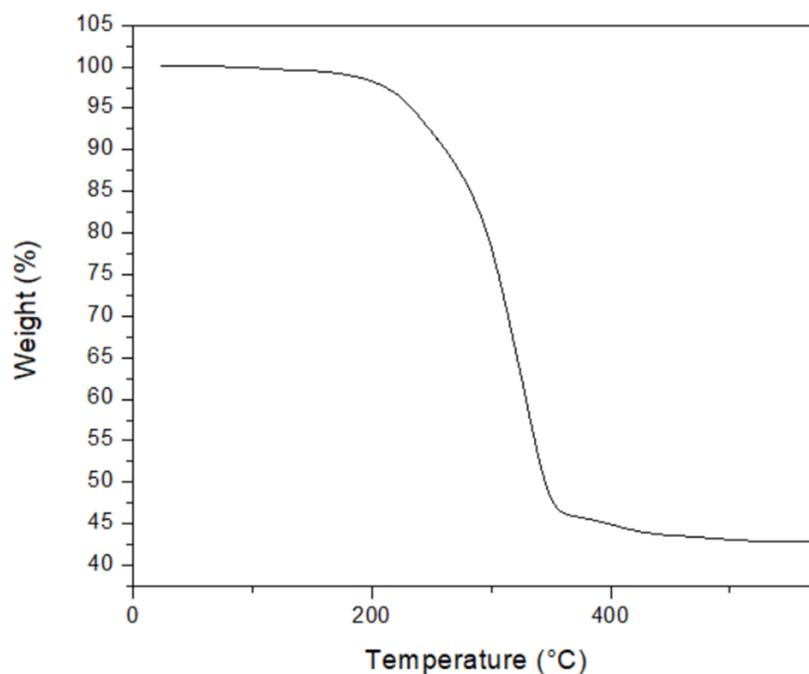


**Fig. S33.** Raman spectrum of poly(3,4-dihexylgermacyclopentene-*r*-3,4-diisopropylgermacyclopentene) (**14**). Ge-Ge and C=C stretches are found at 306 and 1636  $\text{cm}^{-1}$ , respectively. Excitation wavelength: 532 nm.

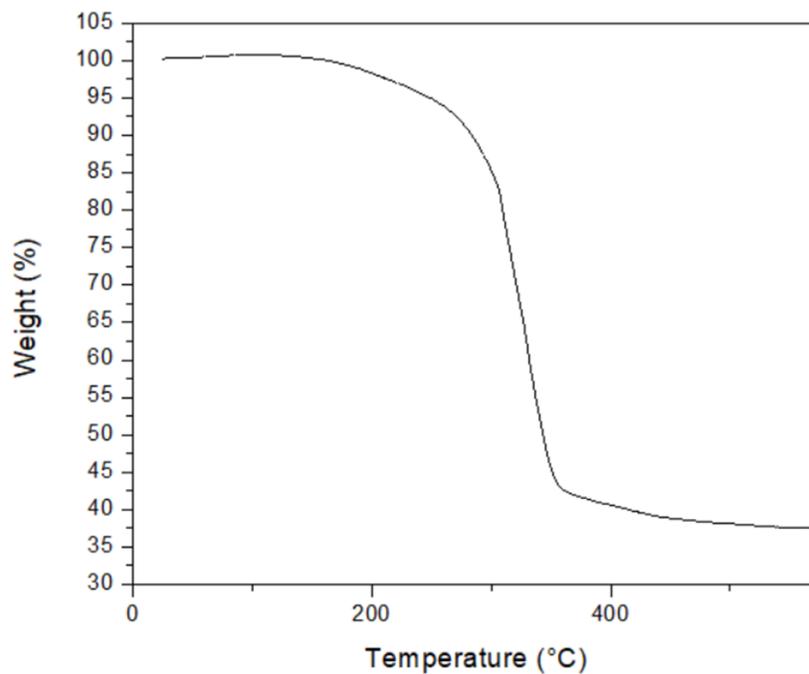
4. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of poly(cyclogermapentene)s



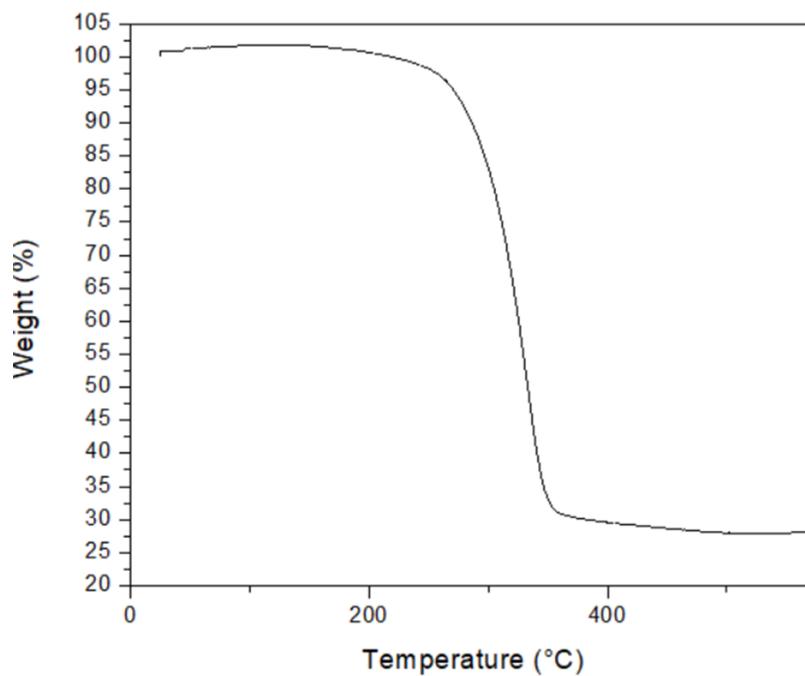
**Fig. S34.** Thermogravimetric analysis (TGA) plot of poly(3,4-dimethylgermacyclopentene) (11). Scan rate = 10 °C min<sup>-1</sup> under Ar.



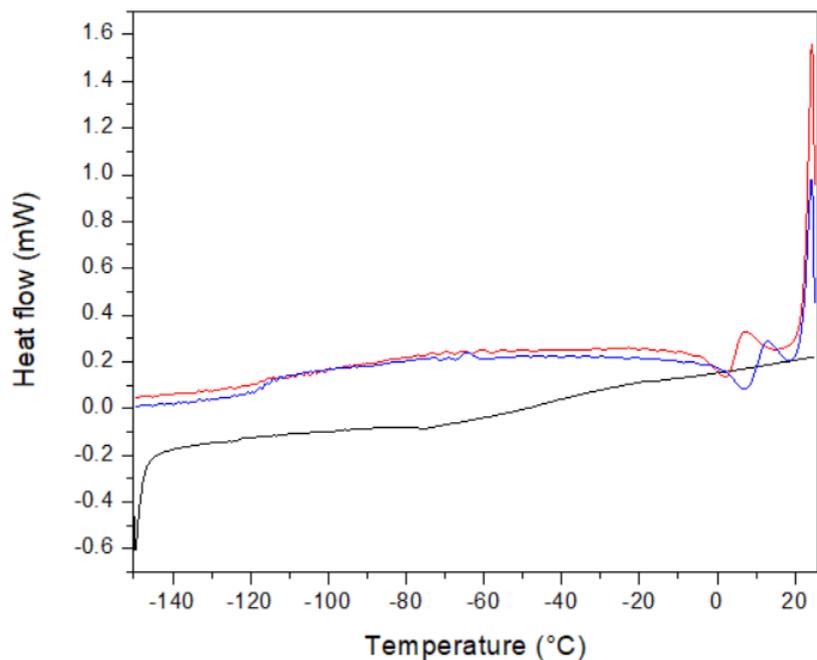
**Fig. S35.** Thermogravimetric analysis (TGA) plot of poly(3,4-diisopropylgermacyclopentene) (12). Scan rate = 10 °C min<sup>-1</sup> under Ar.



**Fig. S36.** Thermogravimetric analysis (TGA) plot of poly(3,4-dihexylgermacyclopentene) (**13**). Scan rate =  $10\text{ }^{\circ}\text{C min}^{-1}$  under Ar.

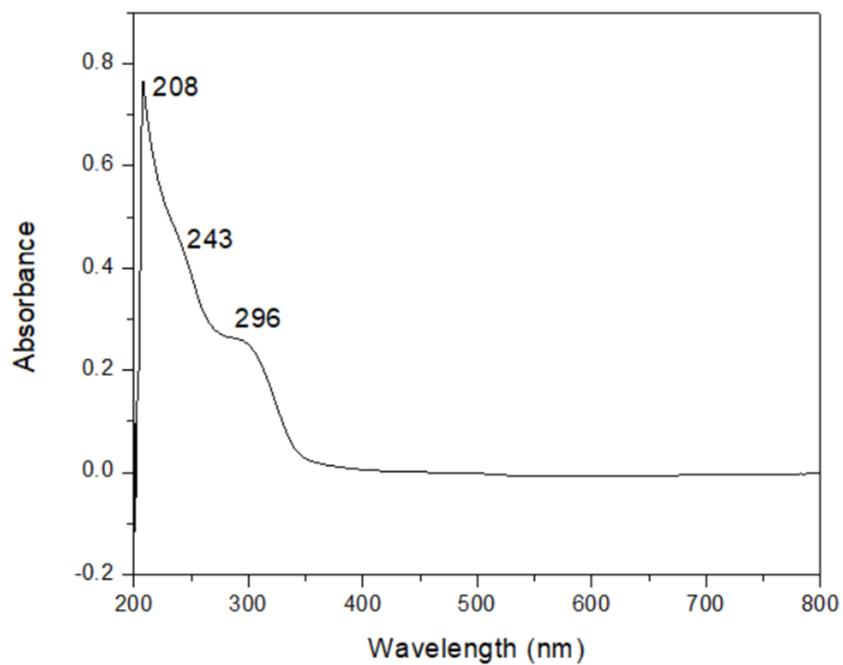


**Fig. S37.** Thermogravimetric analysis (TGA) plot of poly(3,4-dihexylgermacyclopentene-*r*-3,4-diisopropylgermacyclopentene) (**14**). Scan rate =  $10\text{ }^{\circ}\text{C min}^{-1}$  under Ar.

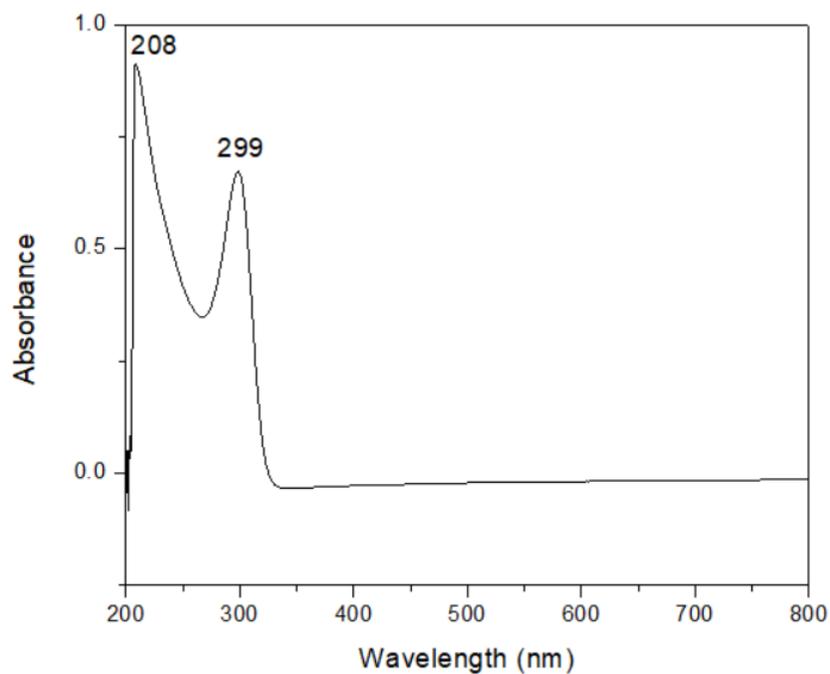


**Fig. S38.** Differential scanning calorimetry (DSC) of poly(3,4-dihexylgermacyclopentene) (**13**) obtained at  $10\text{ °C min}^{-1}$  under argon. The red and blue curves represent cooling cycles of the material. Signals at  $7\text{ °C}$  (red) and  $10\text{ °C}$  (blue) correspond to a monotropic solid-solid phase transition of the polymer.<sup>S4</sup> The black curve represent the heating cycles of the material. The intense exotherms ( $23\text{ °C}$ ) and endotherm ( $-150\text{ °C}$ ) are instrument artifacts owing to the exchange from a dynamic to a static step.

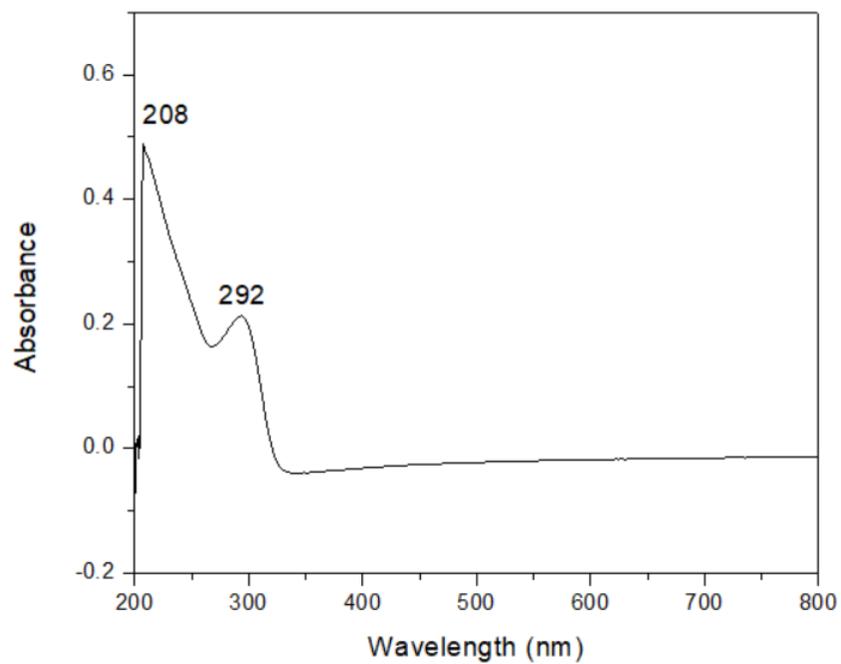
5. UV-vis spectra of the poly(cyclogermapentene)s



**Fig. S39.** UV-vis spectrum of oligo(3,4-dimethylgermacyclopentene) (**11**) in THF.

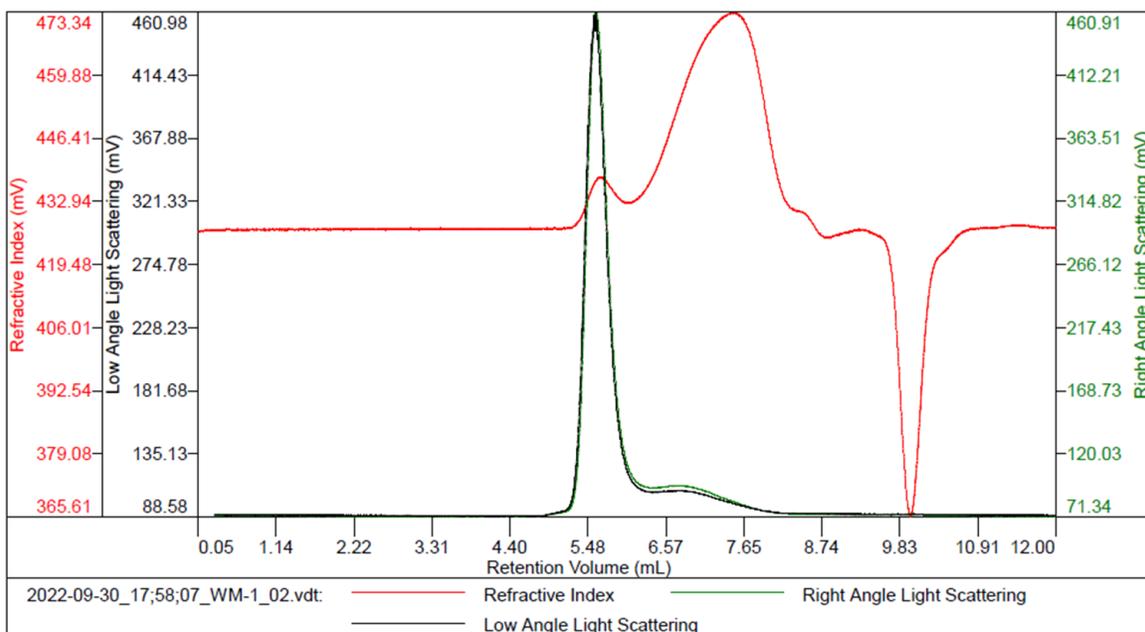


**Fig. S40.** UV-vis spectrum of poly(3,4-dihexylgermacyclopentene) (**13**) in THF.

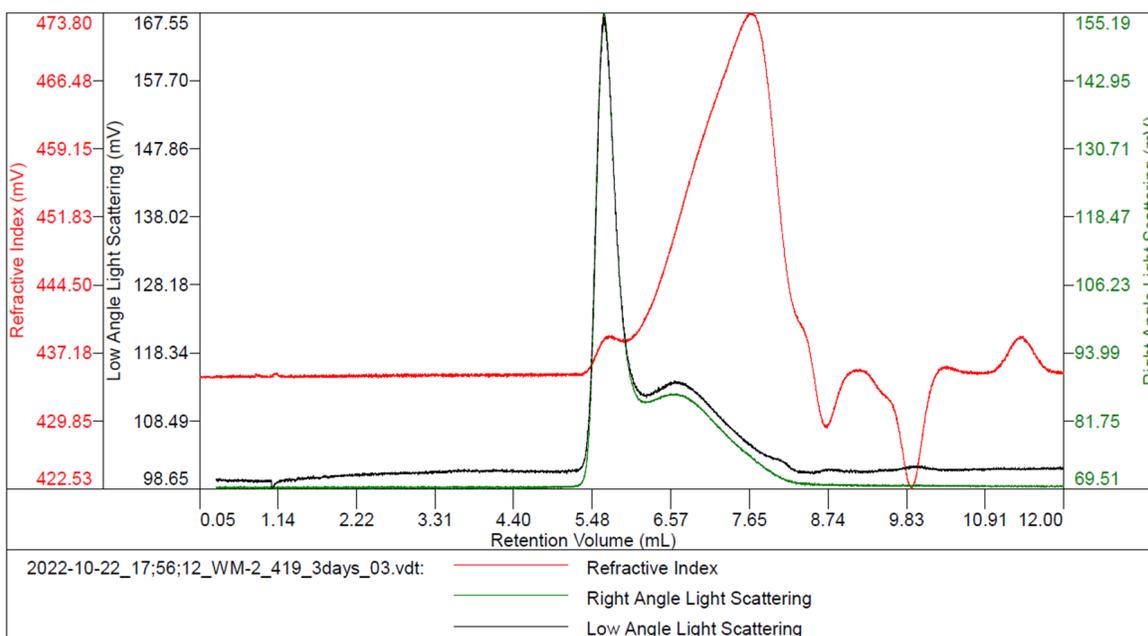


**Fig. S41.** UV-vis spectrum of poly(3,4-dihexylgermacyclopentene-*r*-3,4-diisopropylgermacyclopentene) (**14**) in THF.

## 6. Gel permeation chromatography (GPC)



**Fig. S42.** GPC elution profile of poly(3,4-dihexylgermacyclopentene) (**13**) in THF. Negative peaks in the refractive index (RI) detector are artifacts of sample injection.



**Fig. S43.** GPC elution profile of poly(3,4-dihexylgermacyclopentene-*r*-3,4-diisopropylgermacyclopentene) (**14**) in THF. Negative peaks in the RI detector are artifacts of sample injection.

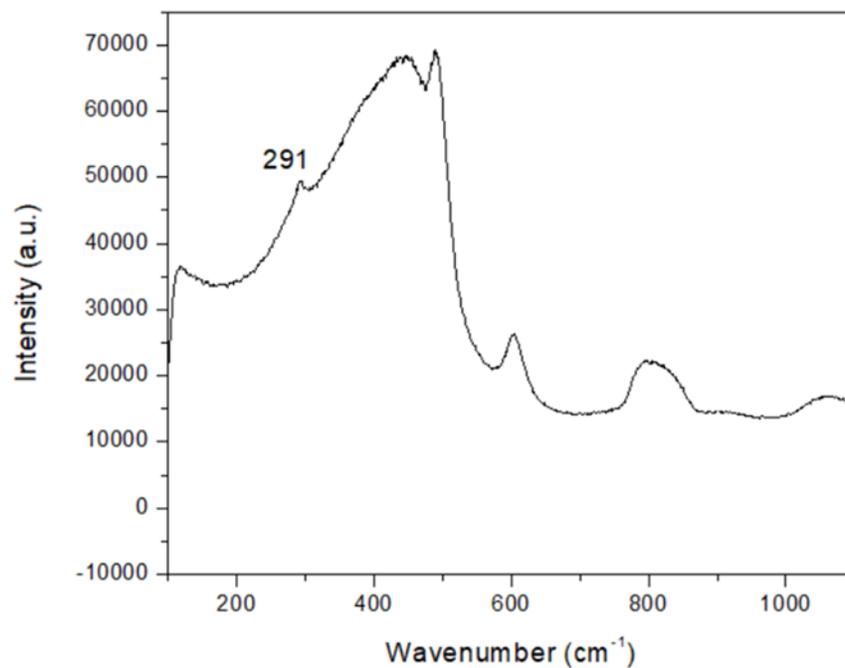
## 7. Characterization of deposited Ge



**Fig. S44.** Photograph of the quartz reactor employed for the photolysis of the polymers **11**, **13** and **14** under  $N_2$ .



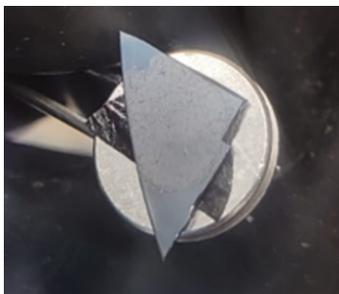
**Fig. S45.** Photograph of the Ge film deposited on the inner wall of the quartz reactor from photolysis of oligo(3,4-dimethylgermacyclopentene) (**11**) in  $THF-d^8$ .



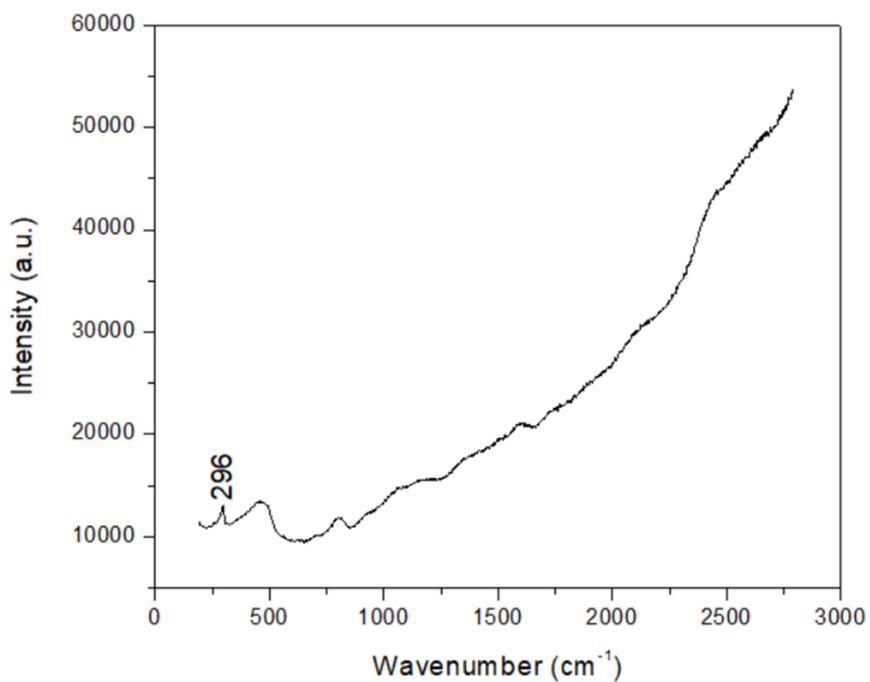
**Fig. S46.** Raman spectrum of the deposited Ge film, from the photolysis of oligo(3,4-dimethylgermacyclopentene) (**11**) in THF. The band at 291 cm<sup>-1</sup> corresponds to Ge-Ge stretches in Ge metal. Bands at other wavenumbers correspond to the quartz substrate.



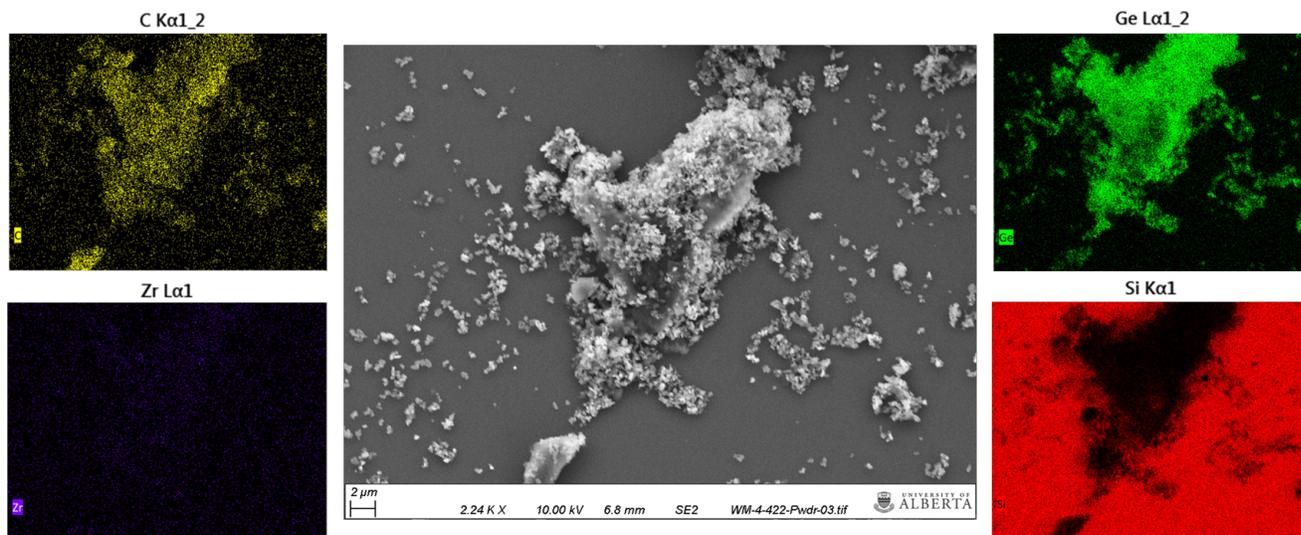
**Fig. S47.** Photograph of the Ge film deposited on the inner wall of the quartz reactor after photolysis of poly(3,4-dihexylgermacyclopentene) (**13**) in THF.



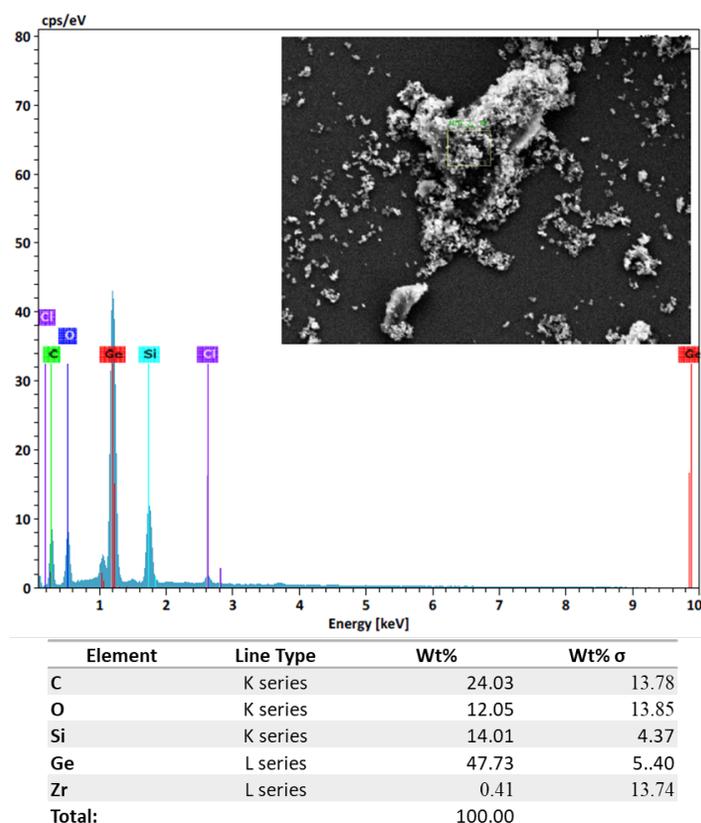
**Fig. S48.** Photograph of the Ge precipitate on a Si wafer for SEM/EDX analysis. The Ge powder was obtained from the photolysis of poly(3,4-dihexylgermacyclopentene) (**13**) in THF.



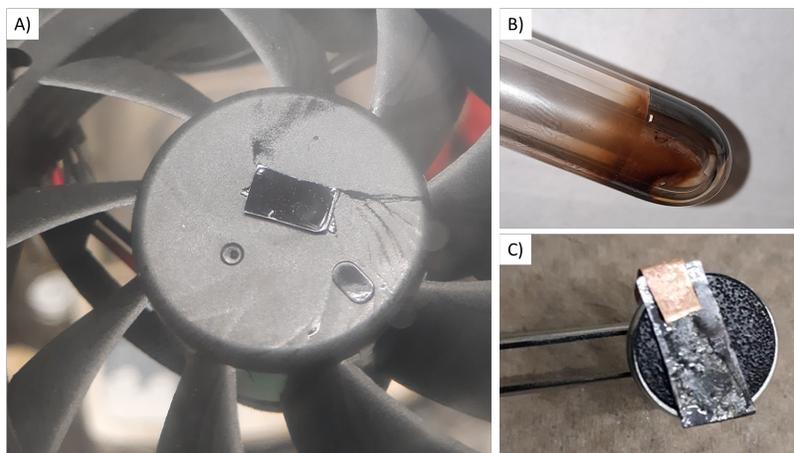
**Fig. S49.** Raman spectrum of the Ge precipitate from the photolysis of poly(3,4-dihexylgermacyclopentene) (**13**) in THF. The band at 296 cm<sup>-1</sup> corresponds to the Ge-Ge stretching frequency in Ge metal. Bands at other wavenumbers correspond to the quartz substrate.



**Fig. S50.** SEM backscatter electron image and EDX elemental mapping for the Ge precipitate (drop-casted from a toluene slurry onto a Si wafer) obtained from the photolysis of poly(3,4-dihexylgermacyclopentene) (**13**) in THF (See experimental section). SEM data was collected at 15 keV.



**Fig. S51.** Energy-dispersive X-ray (EDX) survey spectrum for the element mapping shown in Fig. S50.



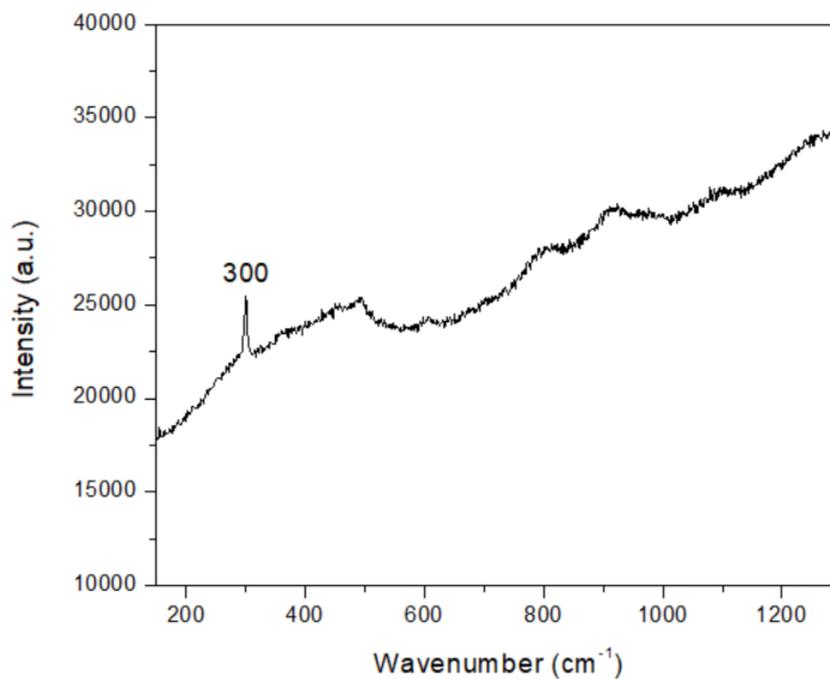
**Fig. S52.** (a) Photograph of the spin-coated polymer **13** onto a Si wafer substrate; (b) photograph of the quartz reactor after photolysis of the spin-coated polymer **13**, showing added film deposition on the walls of the reactor; (c) photograph of the spin-coated polymer **13** after photolysis.



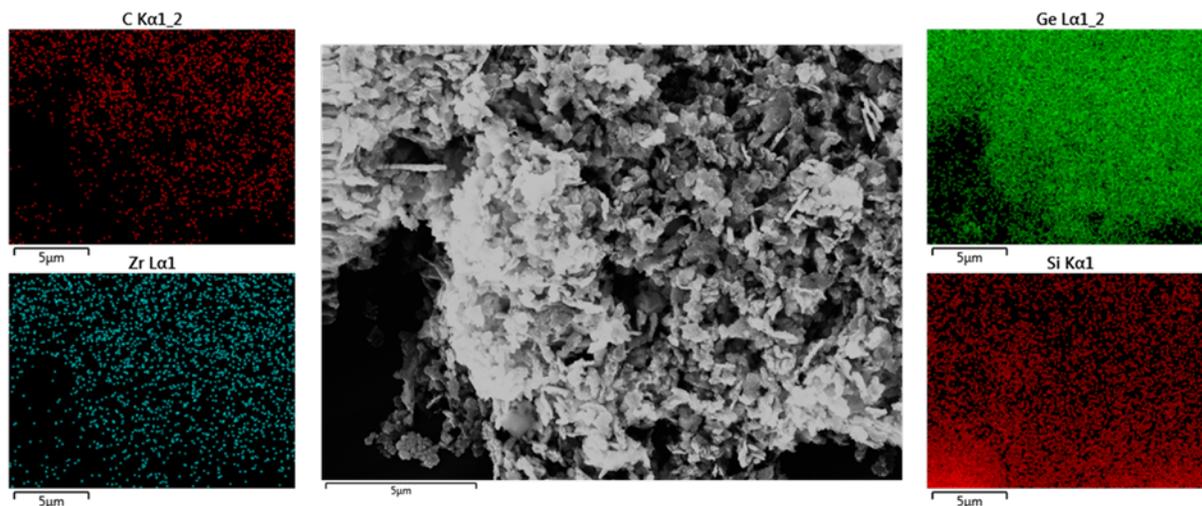
**Fig. S53.** Photograph of the Ge film deposited on the inner wall of the quartz reactor from the photolysis of poly(3,4-dihexylgermacyclopentene-*r*-3,4-diisopropylgermacyclopentene) (**14**) in THF.



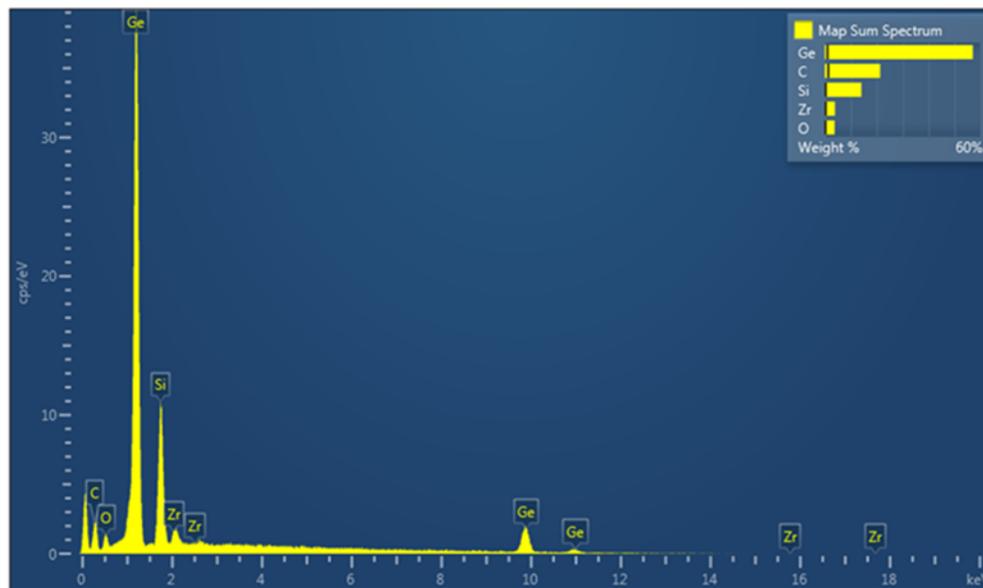
**Fig. S54.** Photograph of the Ge precipitate on a Si wafer for SEM/EDX analysis. The powder was obtained from the photolysis of poly(3,4-dihexylgermacyclopentene-*r*-3,4-diisopropylgermacyclopentene) (**14**) dissolved in THF.



**Fig. S55.** Raman spectrum of the deposited Ge film from the photolysis of poly(3,4-dihexylgermacyclopentene-*r*-3,4-diisopropylgermacyclopentene) (**14**) dissolved in THF. The band at 300 cm<sup>-1</sup> corresponds to the Ge-Ge stretching frequency in Ge metal. Bands at other wavenumbers correspond to the quartz substrate.



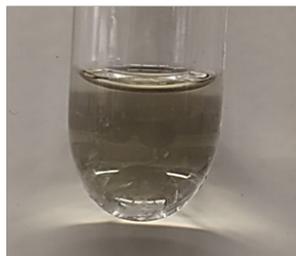
**Fig. S56.** SEM backscatter electron image and EDX elemental mapping for the Ge precipitate (drop-casted from a toluene slurry onto a Si wafer) from the photolysis of poly(3,4-dihexylgermacyclopentene-*r*-3,4-diisopropylgermacyclopentene) (**14**). SEM data was collected at 15 keV.



Element	Line Type	Wt%	Wt% $\sigma$
C	K series	21.31	1.27
O	K series	3.74	0.28
Si	K series	14.04	0.32
Ge	L series	57.06	0.98
Zr	L series	3.85	0.35
<b>Total:</b>		<b>100.00</b>	

**Fig. S57.** Energy-dispersive X-ray (EDX) survey spectrum for the element mapping shown in Fig. S56.

A)



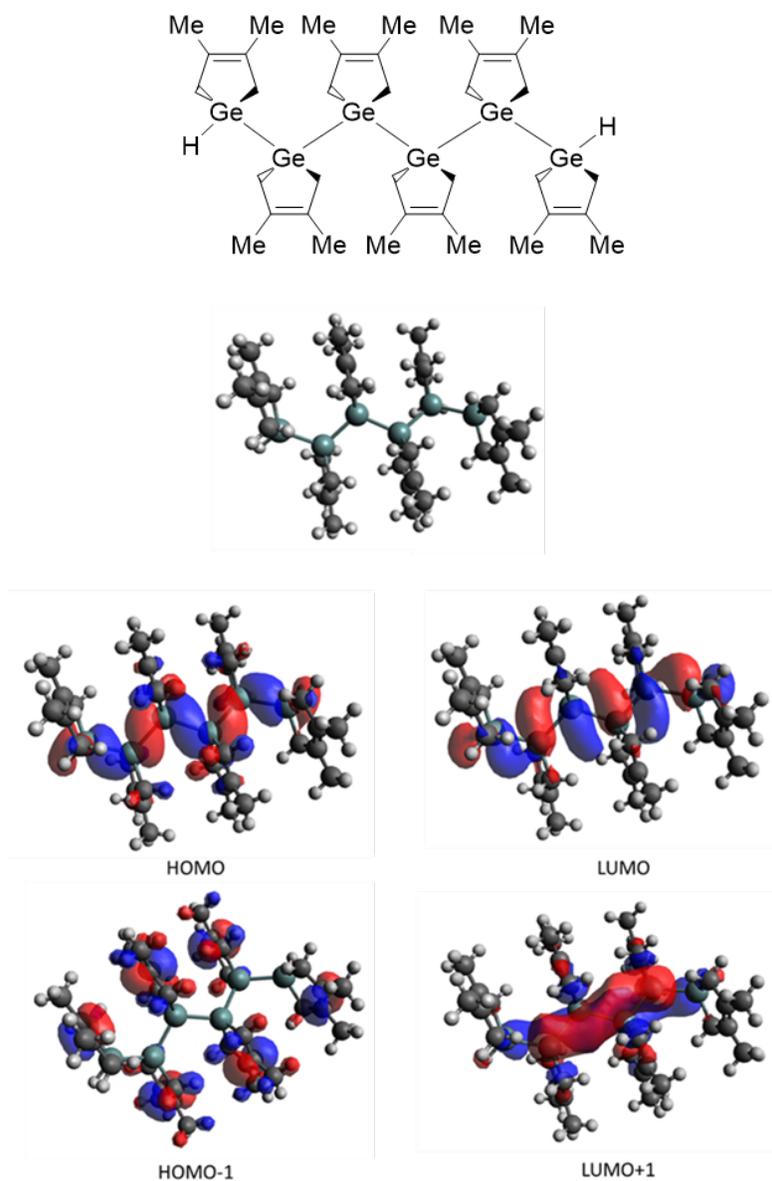
B)



**Fig. S58.** (a) Photograph of the photolysis reactor filled with a solution of poly(3,4-dihexylgerma-cyclopentene) (**13**) in THF pre-photolysis; (b) photograph of the photolysis reactor after photolysis and removal of the photopatterning mask. Deposited germanium shows a pattern on the inner wall of the reactor.

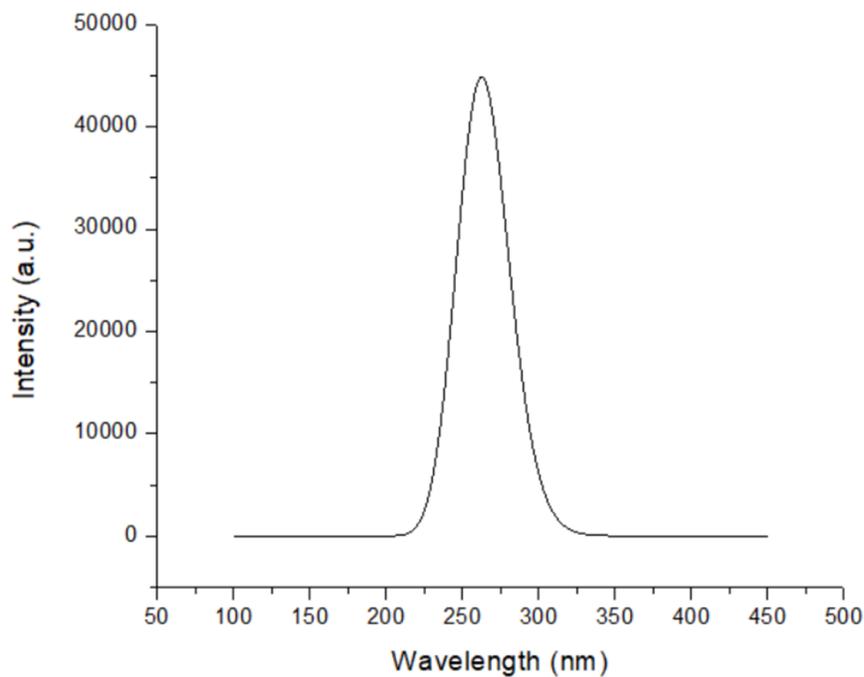
## 8. Computational details

Calculations were performed using the Gaussian16 software package.<sup>S5</sup> All xyz coordinates for the optimized structures have been supplied as a separate .xyz file. Gas phase structure optimization in the gas phase was performed using density functional theory (DFT) with the B3LYP functional and cc-pVDZ basis set.<sup>S6,S7</sup> Frequency analysis confirmed modeled structure to be local minima on the potential energy surface. Optimized structure was modeled to be an oligomer of **11** containing six repeating units: H-[Ge(CH<sub>2</sub>CMe)<sub>2</sub>]<sub>6</sub>-H (**11<sup>M</sup>**).



**Fig. S59.** Frontier molecular orbitals for H-[Ge(CH<sub>2</sub>CMe)<sub>2</sub>]<sub>6</sub>-H (**11<sup>M</sup>**) computed at the B3LYP/cc-pVDZ level of theory.

IR and Raman frequencies were obtained using DFT with the B3LYP functional and cc-pVDZ basis set. Time dependent functional theory (TF-DFT) was used to calculate the theoretical UV-vis spectrum of the oligomer, **11<sup>M</sup>** (see below).<sup>S8</sup> The same functional/basis set was employed for the structure optimization and excited state calculations.



**Fig. S60.** Computed UV-vis spectrum for H-[Ge(CH<sub>2</sub>CMe)<sub>2</sub>]<sub>6</sub>-H (**11<sup>M</sup>**) at the B3LYP/cc-pVDZ level of theory.

**Table S1.** Computed excited states for H-[Ge(CH<sub>2</sub>CMe)<sub>2</sub>]<sub>6</sub>-H (**11<sup>M</sup>**) (B3LYP/cc-pVDZ level).

Excited state	Energy (nm)	Oscillator strength	Main orbitals involved
<b>T1</b>	319	0.0000	
<b>T3</b>	319	0.0000	
<b>T5</b>	318	0.0000	
<b>T7</b>	306	0.0000	
<b>T8</b>	268	0.0000	
<b>S1</b>	265	0.9235	HOMO/LUMO
<b>T9</b>	265	0.0000	

<b>T10</b>	264	0.0000	
<b>S2</b>	263	0.0006	HOMO-5/LUMO HOMO-1/LUMO
<b>S3</b>	262	0.0356	HOMO-4/LUMO HOMO-2/LUMO HOMO/LUMO
<b>S4</b>	255	0.0000	
<b>S5</b>	253	0.0713	HOMO-6/LUMO HOMO-4/LUMO HOMO-2/LUMO
<b>S6</b>	253	0.0004	HOMO/LUMO+1
<b>S7</b>	250	0.0003	HOMO-5/LUMO HOMO-3/LUMO HOMO-1/LUMO
<b>S8</b>	248	0.1361	HOMO-6/LUMO HOMO-4/LUMO HOMO-2/LUMO
<b>S9</b>	242	0.0393	HOMO-5/LUMO+1 HOMO-3/LUMO+1 HOMO-1/LUMO+1 HOMO/LUMO+2
<b>S10</b>	241	0.0001	HOMO-6/LUMO+1 HOMO-4/LUMO+1 HOMO-3/LUMO+2 HOMO-2/LUMO+1

## 9. References

- S1. J. Linshoef, E. J. Baum, A. Hussain, P. J. Gates, D. C. Nather and A. Staubitz, *Angew. Chem., Int. Ed.*, 2014, **53**, 12916-12920.
- S2. H. Kleijin, H. Westmijze, J. Meijer and P. Vermeer, *Recl. Trav. Chim. Pays-Bas*, 1980, **99**, 340-343.
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