

Engineering Circularly Polarized Light Emission in Nanostructured Oligodimethylsiloxane-Helicene Chiral Materials

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1. Materials and Methods

Chemicals were purchased from Sigma-Aldrich, Alfa Aesar or TCI Europe, abcr and used as received. Bis-phosphonium salt **1** was prepared according to the literature.¹ The discrete length oligodimethylsiloxanes (*o*DMS) dihydride with a length of 7, 12 repeating units were synthesized according to literature procedure.² Siloxane with a length of 3 repeating unit and Karstedt's catalyst was purchased and use without any further purification. Thin-layer chromatography (TLC) was performed on aluminum sheets precoated with Merck 5735 Kieselgel 60F254. Column chromatography was carried out with Merck 5735 Kieselgel 60F (0.040-0.063 mm mesh). Chemicals were purchased from Sigma-Aldrich, Alfa Aesar or TCI Europe and used as received. ¹H and ¹³C NMR spectra were recorded at room temperature on an *AVANCE III 400 BRUKER* at Centre Régional de Mesures Physiques de l'Ouest (CRMPO), Université de Rennes. Chemical shifts δ are given in ppm and coupling constants J in Hz. Chemical shifts for ¹H NMR spectra are referenced relative to residual proton in the deuterated solvent ($\delta = 7.26$ ppm, CDCl₃). ¹³C shifts are referenced to CDCl₃ peaks at $\delta = 77.16$ ppm.

High-resolution mass (HR-MS) determinations were performed at CRMPO on a Bruker MaXis 4G by ASAP (+ or -) Experimental and calculated masses are given with consideration of the mass of the electron.

Size Exclusion Chromatography (SEC) purification was performed on a LC-9160 II NEXT system from the Japan Analytical Industry Co., Ltd. (JAI) equipped with coupled UV-vis 4Ch NEXT through a set of two JAIGEL-2H columns at an elution rate of chloroform of 10 mL.min⁻¹ (CHCl₃).

Chromatography on chiral support was performed with an Agilent 1260 Infinity II unit for preparative separations (pump G7161A, autosampler G7157A, UV G17165A and collection valve G7166A), and with an Agilent 1260 Infinity unit for the determinations of enantiomeric excesses (pump G1311B, autosampler G1329B, DAD G1315D, OR-4090 and CD-2095 Jasco detector). Columns used are Chiralpak ID (250 x 4.6 mm, 5 μ m) and (250 x 10 mm, 5 μ m), amylose tris(3-chloro-phenylcarbamate) immobilized on silica, from Chiral Technologies Europe (Illkirch, France). Heptane, hexane and dichloromethane were HPLC grade. Retention times R_t in minutes, retention factors $k_i = (R_{t_i} - R_{t_0})/R_{t_0}$ and enantioselectivity factor $\alpha = k_2/k_1$ and resolution $R_s = 1.18 (R_{t_2} - R_{t_1}) / (w_1 + w_2)$ are given. R_{t_0} was determined by injection of tri-tertio-butyl benzene and w_i was the peak width at half-height.

Differential Scanning Calorimetry (DSC) was recorded on a Q2000 from TA Instruments. 2–8 mg samples were used in an aluminum pan. Thermal history was erased by heating the materials with 40 K min⁻¹ to 140 °C. A constant heating and cooling rate of 20 K min⁻¹ was used to ramp from 140 °C to 25 °C for two cooling and heating cycles. Enthalpies of fusion (in kJ mol⁻¹) were obtained by taking the area under the graph and subsequently multiplying that value with the respective molar mass of the compound.

Bulk Small Angle X-ray Scattering (SAXS) was performed on a Ganesha instrument from SAXSlab. The flight tube and sample holder are all under vacuum in a single housing, with a GeniX-Cu ultra-low divergence X-ray generator. The source produces X-rays with a wavelength (λ) of 0.154 nm and a flux of 1×10^8 ph s⁻¹. Scattered X-rays were captured on a 2-dimensional Pilatus 300K detector with 487 x 619-pixel resolution. The sample-to-detector distance was 0.084 m (WAXS mode) or 0.48 m (MAXS mode). The instrument was calibrated with diffraction patterns from silver behenate.

Polarized Optical Microscopy (POM) samples were placed on glass substrates and imaged using Nikon Xfinity1 Lumenera microscope with 4x, 25x, 32x magnification. Differential scanning calorimetry (DSC) data were collected on a DSC Q2000 from TA instruments, calibrated with an indium standard. The samples (4–8 mg) were weighed directly into aluminium pans and hermetically sealed.

Electronic circular dichroism (ECD, in M⁻¹ cm⁻¹) was measured on a Jasco J-815 Circular Dichroism Spectrometer IFR140 facility. Part of this work has been performed using the PRISM core facility (Biogenouest©, UMS Biosit, Université de Rennes - Campus de Villejean-35043 Rennes Cedex, France).

Circularly polarized luminescence (CPL) measurements were performed using a home-built CPL spectrofluoropolarimeter (constructed with the help of the JASCO Company). The samples were excited using a 90° geometry with a xenon ozone-free lamp 150 W LS. The absolute quantum yields (AQYs) were measured with a C9920-03 Hamamatsu system equipped with a 150 W xenon lamp, a monochromator, an integrating sphere.

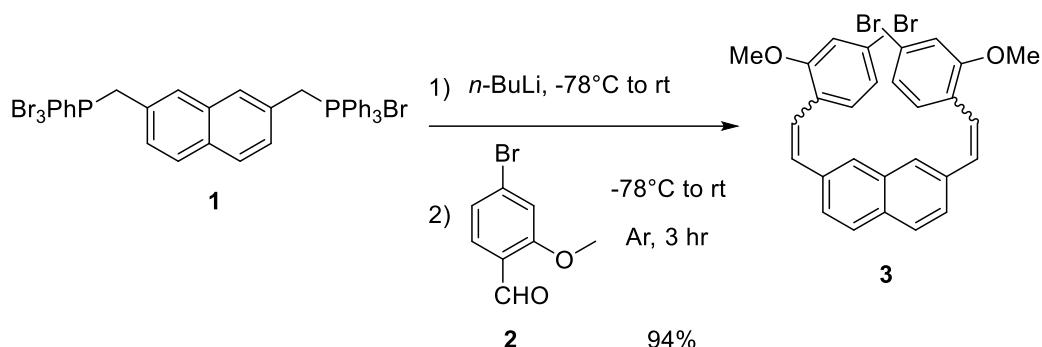
CPL measurements in solid state (thin films) were performed using home-built CPL measurement setup employing a photoelastic modulator and a 16-channel photomultiplier array involving a photon counting detection scheme (Figure SS19). Excitation light at 365 nm was selected from a Hg lamp using appropriate interference and bandpass filters. The direction of the excitation light was under a 90° angle with the direction of emission collection and in order to minimize artefacts the excitation light was polarized in the horizontal plane.

Fluorescence measurements were performed on an Edinburgh Instruments LifeSpec-PS spectrometer using a 405 nm (3.06 eV) pulsed laser (PicoQuant PDL 800B) operated at 2.5 MHz with a pulse duration of 59 ps. For detection a Peltier-cooled Hamamatsu microchannel plate photomultiplier (R3809U-50) was used.

All the compounds for the solid-state emission and absorption analysis (ECD, CPL, time delayed fluorescence) were prepared by dropcasting deposition on a quartz glass, after the deposition all the samples were annealed three times. During the first two cycles, the temperature was raised fast above the melting point and then the sample was quickly cooled down, in the third cycle the compound was melted, and the temperature was slowly decreased to a rate of 2°C/min. All the samples were analysed by polarized optical microscopy prior to perform the optical analysis, and all the sample presented diffraction structures due to self-organization.

2. Synthetic procedures

Bis-olefine 3



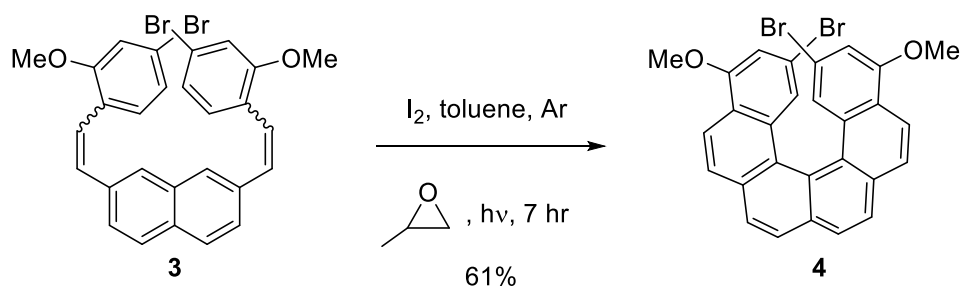
The phosphonium salt **1** (2,7-naphthalenedimethylene)-bis[triphenylphosphonium-bromide]¹ (1.41 g, 1.68 mmol) was placed in a flame-dried Schlenk under argon atmosphere. Freshly distilled THF (50 mL) was added, and the reaction mixture was cooled to -78°C; *n*-BuLi (1.5 mL, 3.7 mmol) was then added slowly, the cooling bath was removed, and the solution was stirred at room temperature for 30 minutes, slowly, the solution turned deep red. The solution was cooled again to -78°C, 4-bromo-2-methoxy-benzaldehyde **2** (815 mg, 3.79 mmol) was dissolved in a minimum amount of dry THF and then was slowly added to the reaction mixture. The solution was left stirring for 3 hours at room temperature. The crude was directly purified by column chromatography over silica gel (Heptane/Ethyl acetate 8:2) to afford a foamy light-yellow product **3** (876mg, 1.58 mmol, 94%) as a mixture of (*Z,Z*), (*Z,E*) and (*E,E*) isomers.

¹H NMR (400 MHz, CDCl₃) δ 8.62 – 6.33 (m, 18H), 3.93 (d, *J* = 4.7 Hz, 3H), 3.87 (d, *J* = 5.0 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 157.97, 157.44, 137.93, 135.70, 135.49, 135.23, 134.96, 133.81, 133.52, 132.24, 131.78, 131.33, 131.29, 130.78, 130.74, 129.62, 129.16, 128.34, 128.23, 128.17, 128.13, 128.05, 127.47, 127.39, 127.27, 126.92, 126.85, 125.62, 125.43, 125.31, 125.16, 123.95, 123.80, 123.43, 123.39, 122.92, 122.88, 121.97, 121.95, 121.92, 114.56, 114.43, 55.84, 55.80.

Mass spectrometry: Maldi ⁺C₂₈H₂₂O₂⁷⁹Br₂ Theoretical mass: 547.9981 m/z; Measured: 547.997 m/z.

2,15-Dibromo-4,13-dimethoxy-carbo[6]helicene 4



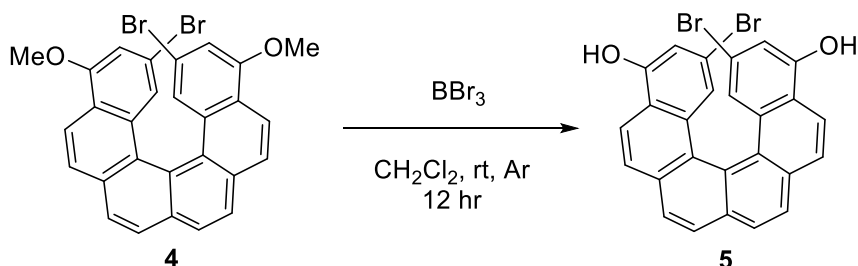
The olefine **3** (353mg, 0.641 mmol) was placed in a reactor (2.2 L) filled with toluene, the solution was bubbled with argon for 40 minutes. Propylene oxide (3.6 mL, 51 mmol) and I₂ (173 mg, 0.682 mmol) were added to the reactor, the solution was irradiated with UV light (mercury lamp, 500 W) for 7 hours. The toluene was evaporated, the crude product was washed with a minimum amount of dichloromethane, and with hot isopropyl alcohol. The pre-treated crude product was then dissolved with hot dichloromethane and after slowly addition of methanol, the 2,15-dibromo-4,13-dimethoxy-carbo[6]helicene **4** crystallized at room temperature as a yellow solid. The crystallization was then repeated using the mother liquor two more times. (214 mg, 0.392 mmol, 61%).

¹H NMR (400 MHz, DMSO) δ 8.30 (dd, *J* = 8.8, 0.8 Hz, 2H), 8.20 (d, *J* = 8.3 Hz, 2H), 8.16 (d, *J* = 8.3 Hz, 2H), 8.10 (d, *J* = 8.9 Hz, 2H), 7.09 (d, *J* = 1.1 Hz, 2H), 6.99 (d, *J* = 1.7 Hz, 2H), 3.99 (s, 6H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 156.37, 133.57, 132.60, 132.08, 128.05, 127.68, 126.50, 126.31, 124.57, 122.91, 122.82, 121.66, 119.31, 108.92, 56.61.

Mass spectrometry: Maldi $^{+}\text{C}_{28}\text{H}_{18}\text{O}_2^{79}\text{Br}_2$ Theoretical mass: 543.9668 m/z; Measured: 543.965 m/z.

2,15-Dibromo-4,13-dihydroxy-carbo[6]helicene **5**

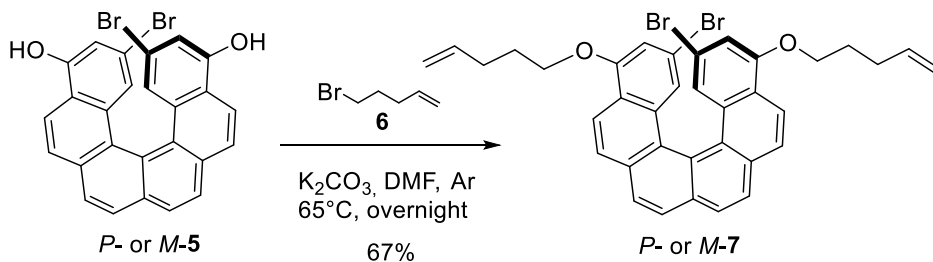


The helicene derivative **4** (31 mg, 0.0567 mmol) was placed in a flame dried Schlenk under argon atmosphere, and dry dichloromethane (1 mL) was added. BBr_3 (600 μL , 0.600 mmol) was added slowly at room temperature and the mixture was stirred overnight. The crude product was diluted with dichloromethane and was washed three times with a saturated solution of NaHCO_3 . The solution was dried over MgSO_4 and the solvent was evaporated. The crude 2,15-dibromo-4,13-dihydroxy-carbo[6]helicene **5** was directly used in the next step without further purification. Due to the fast degradation, the compound was kept in solution.

^1H NMR (400 MHz, DMSO) δ 10.65 (s, 2H), 8.29 (d, $J = 8.7$ Hz, 2H), 8.16 (d, $J = 8.2$ Hz, 2H), 8.11 (d, $J = 8.2$ Hz, 2H), 8.03 (d, $J = 8.8$ Hz, 2H), 7.02 (d, $J = 1.7$ Hz, 2H), 6.84 (d, $J = 1.8$ Hz, 2H).

^{13}C -NMR and mass spectroscopy were not recorded due to the instability of the product.

2,15-Dibromo-4,13-di-pentenyl-oxy-carbo[6]helicene **7**



The helicene derivative **5** (30 mg, 0.0580 mmol) was placed in a flame-dried Schlenk filled with argon, DMF (5 mL) and K_2CO_3 (36 mg, 0.40 mmol) were added to the solution. The solution was stirred for 15 minutes and heated to 65°C , then was added 5-bromo-1-pentene **6** (30 μL , 0.254 mmol); the reaction mixture was stirred at 65°C overnight. Dichloromethane was added to the Schlenk, and the solution was washed three times with brine, the solution was dried over MgSO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel (Heptane/Toluene 6:4), affording compound **7** as a crystalline yellow solid (25 mg, 0.0382 mmol, 67%).

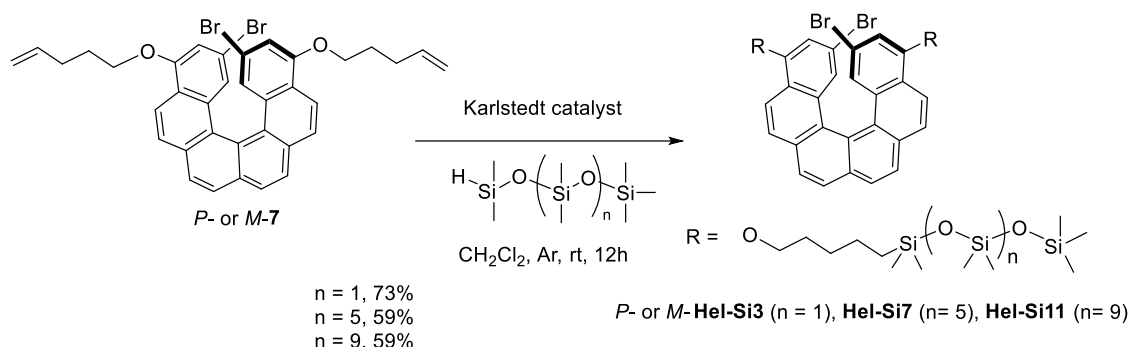
The same procedure applied to *M*- and *P*-**5** yielded enantiopure *M*- and *P*-**7**.

^1H NMR (400 MHz, CDCl_3) δ 8.39 (d, $J = 8.8$ Hz, 2H), 8.01 (d, $J = 8.1$ Hz, 2H), 7.98 (d, $J = 8.2$ Hz, 2H), 7.93 (d, $J = 8.8$ Hz, 2H), 7.24 (s, 2H), 6.78 (d, $J = 1.7$ Hz, 2H), 5.93 (ddt, $J = 17.0, 10.2, 6.6$ Hz, 4H), 5.21 – 4.99 (m, 4H), 4.30 – 4.02 (m, 4H), 2.48 – 2.29 (m, 4H), 2.19 – 1.95 (m, 4H).

^{13}C NMR (101 MHz, CDCl_3) δ 155.14, 137.72, 133.02, 132.07, 131.69, 127.54, 127.20, 126.13, 125.72, 124.27, 122.59, 121.48, 118.90, 115.51, 109.43, 68.01, 30.33, 28.41.

Mass spectrometry: Maldi $^{+}C_{36}H_{30}O_2^{79}Br_2$ Theoretical mass: 652.0607 m/z; Measured: 652.060 m/z.

General procedure for hydrosilylation



The compound **7** (58 mg, 0.0886 mmol) was placed in a flame-dried Schlenk filled with argon, a minimum amount of dry dichloromethane was added (800 μ L), and the solvent was degassed by three cycles of freeze-pump-thaw. The siloxane was added to the solution ($n=1$, 51 mg, 0.229 mmol,) and was added 1 drop of catalyst, the solution was stirred overnight. The solution was filtered over Celite, and the solvent was evaporated. Then, the crude product was purified by column chromatography over silica gel using a gradient of solvents (Heptane/Dichloromethane 9:1 to 8:2). For siloxane $n = 5$, 10 the use of GPC is mandatory after the first chromatographic column to obtain a pure product.

Molecule **Hel-Si₃** was obtained as a green/yellow wax (71 mg, 0.064 mmol, 73%).

Molecule **Hel-Si₇** was obtained as a light-yellow wax (43 mg, 0.026 mmol, 59%).

Molecule **Hel-Si₁₁** was obtained as a light-yellow wax (116 mg, 0.0507 mmol, 59%).

Similar procedures were used for the *P* and *M* enantiomers with similar yields obtained.

1H NMR **Hel-Si₃** (400 MHz, CD_2Cl_2) δ 8.41 (d, $J = 8.8$ Hz, 2H), 8.05 (d, $J = 8.2$ Hz, 2H), 8.01 (d, $J = 8.2$ Hz, 2H), 7.97 (d, $J = 8.8$ Hz, 2H), 7.23 (d, $J = 1.0$ Hz, 2H), 6.82 (d, $J = 1.7$ Hz, 2H), 4.35 – 3.93 (m, 4H), 2.09 – 1.88 (m, 4H), 1.75 – 1.43 (m, 8H), 0.77 – 0.56 (m, 4H), 0.29 – -0.14 (m, 40H).

^{13}C NMR **Hel-Si₃** (400 MHz, CD_2Cl_2) δ 155.86, 133.55, 132.60, 132.11, 128.00, 127.66, 126.54, 126.14, 124.62, 123.02, 122.69, 121.89, 119.34, 109.77, 69.57, 30.40, 29.43, 23.58, 18.69, 1.93, 1.42, 0.35.

1H NMR **Hel-Si₇** (300 MHz, $CDCl_3$) δ 8.40 (dd, $J = 8.8, 0.8$ Hz, 2H), 8.01 (d, $J = 8.3$ Hz, 2H), 7.97 (d, $J = 8.3$ Hz, 2H), 7.92 (d, $J = 8.8$ Hz, 2H), 7.24 (d, $J = 0.9$ Hz, 2H), 6.79 (d, $J = 1.7$ Hz, 2H), 4.34 – 3.94 (m, 4H), 1.97 (dt, $J = 8.6, 6.3$ Hz, 4H), 1.76 – 1.39 (m, 10H), 0.86 – 0.50 (m, 4H), 0.25 – -0.02 (m, 86H).

^{13}C NMR **Hel-Si₇** (101 MHz, CD_2Cl_2) δ 155.86, 132.61, 132.11, 128.00, 127.66, 126.55, 126.14, 123.02, 122.69, 121.89, 119.34, 109.75, 69.57, 54.38, 54.31, 54.11, 54.04, 53.84, 53.77, 53.57, 53.30, 30.41, 29.44, 23.58, 18.67, 1.87, 1.35, 1.28, 1.25, 1.24, 1.21, 0.34.

1H NMR **Hel-Si₁₁** (101 MHz, CD_2Cl_2) δ 8.41 (d, $J = 8.8$ Hz, 2H), 8.05 (d, $J = 8.2$ Hz, 2H), 8.01 (d, $J = 8.3$ Hz, 2H), 7.96 (d, $J = 8.9$ Hz, 2H), 7.22 (d, $J = 0.9$ Hz, 2H), 6.81 (d, $J = 1.7$ Hz, 2H), 4.39 – 4.00 (m, 4H), 2.09 – 1.89 (m, 4H), 1.76 – 1.39 (m, 20H), 0.79 – 0.49 (m, 4H), 0.33 – -0.03 (m, 151H).

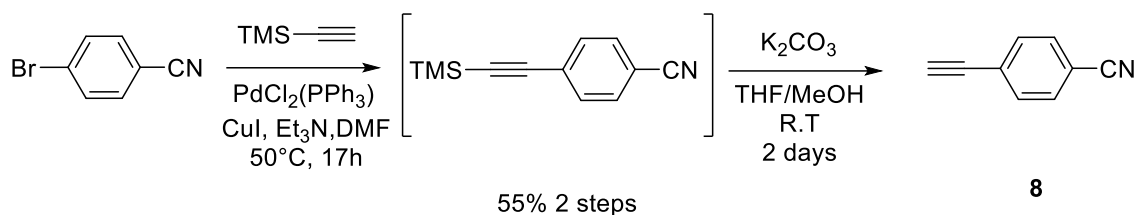
^{13}C NMR **Hel-Si₁₁** (101 MHz, CH_2Cl_2) δ 155.81, 132.56, 132.06, 127.98, 127.64, 126.11, 121.85, 119.30, 109.67, 69.50, 30.39, 29.40, 23.55, 18.63, 1.84, 1.32, 1.24, 1.19, 0.31.

Hel-Si₃ Mass spectrometry: Maldi $^{+}C_{50}H_{76}O_6^{79}Br_2Si_6$ Theoretical mass: 1096.24623 m/z; Measured: 1096.242 m/z.

Hel-Si₇ Mass spectrometry: Maldi $^{+}C_{50}H_{76}O_{14}^{79}Br_2Si_{14}$ Theoretical mass: 1692.68600 m/z; Measured: 1692.34 m/z.

Hel-Si₁₁ Mass spectrometry: Maldi $^{+}C_{50}H_{76}O_{22}^{79}Br_2Si_{22}$ Theoretical mass: 2285.9180 m/z; Measured: 2285.549 m/z.

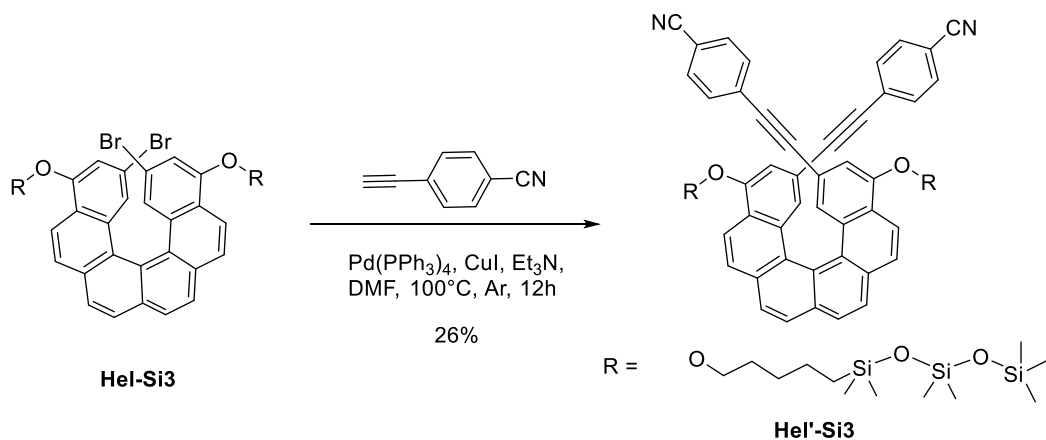
4-Ethynyl benzonitrile ³



The mixture of 4-bromo benzonitrile (1.05 g, 5.77 mmol) and 4-ethynylbenzonitrile (1.2 mL, 17.2 mmol) were placed in an oven-dried Schlenk under argon. Then 5.5 mL of dry DMF and 550 μ L of dry Et₃N were added and the resulting solution was deoxygenated by bubbling argon for 1 hour. Pd(PPh₃)₄ (464 mg, 0.661 mmol) and CuI (220 mg, 1.154 mmol) were added, the temperature was increased to 50°C and the solution was stirred for 17h. Then, 50 mL of dichloromethane was added to the reaction mixture and the solution was washed three times with brine, the solvent was evaporated, and the crude product was filtered over a short silica plug with a mixture of heptane/ethyl acetate 95:5. The crude product appeared as a yellow/brown crystalline solid, and it was used for the next step without any further purification. The crude product was placed in round bottom flask, and it was dissolved with 50 mL of tetrahydrofuran, 100 mL of methanol was added to the flask. Potassium carbonate was added to the reaction mixture (8g, 57.7 mmol) and the solution was stirred for 2 days. The solvent was then evaporated, the crude product was dissolved with dichloromethane and the solution was washed three times with brine. The crude product was purified by chromatographic column (heptane/ethyl acetate 9:1) the product was then recrystallized in heptane, affording a needle-like crystalline solid (405 mg, 3.18 mmol, 55%). The complete characterization is described in the paper of Michael Valasek et al.³

¹H NMR (300 MHz, CDCl₃) δ 7.65 – 7.60 (m, 2H), 7.59 – 7.54 (m, 2H), 3.30 (s, 1H).

General procedure for Sonogashira coupling reaction.



The mixture of *rac-5* (50 mg, 0.045 mmol) and 4-ethynylbenzonitrile (19 mg, 0.149 mmol) were placed in an oven-dried Schlenk under argon. Then 5.5 mL of dry DMF and 550 μ L of dry Et₃N were added and the resulting solution was deoxygenated by bubbling argon for 1 hour. Then, Pd(PPh₃)₄ (6 mg, 0.0050 mmol) and CuI (2 mg, 0.0105 mmol) were added, the temperature was increased to 100°C, the solution was stirred overnight, after which 50 mL of dichloromethane was added to the flask and the solvent was filtered through Celite; the solution was then washed three times with brine. The crude product was purified by column chromatography (Heptane/Ethyl acetate 9:1) the product was further purified by size exclusion chromatography.

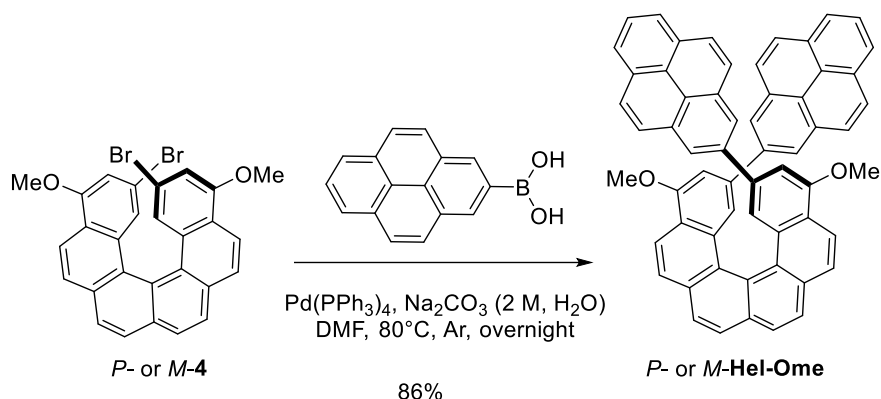
Affording the pure product as a yellow wax (14 mg, 0.0118 mmol, 26%).

¹H NMR **Hel'-Si3** (400 MHz, CD₂Cl₂) δ 8.48 (d, *J* = 8.8 Hz, 2H), 8.07 (dt, *J* = 16.7, 8.4 Hz, 6H), 7.63 (d, *J* = 8.3 Hz, 4H), 7.44 (d, *J* = 8.3 Hz, 4H), 7.37 (s, 2H), 6.76 (d, *J* = 1.3 Hz, 2H), 4.31 – 3.85 (m, 4H), 1.90 – 1.73 (m, 4H), 1.52 – 1.42 (m, 8H), 0.65 – 0.57 (m, 4H), 0.41 – -0.10 (m, 44H).

^{13}C NMR **Hel³-Si₃** (101 MHz, CD_2Cl_2) δ 155.26, 132.53, 132.43, 132.28, 130.82, 128.58, 128.09, 127.75, 127.38, 127.27, 125.78, 124.69, 121.68, 118.85, 118.46, 111.74, 107.44, 94.76, 87.24, 69.23, 30.36, 30.11, 29.47, 23.59, 18.67, 1.92, 1.87, 1.42, 1.36, 1.28, 1.26, 1.24, 1.21, 1.19, 0.34.

Hel³-Si₃ Mass spectrometry: Maldi $^+\text{C}_{68}\text{H}_{82}\text{N}_2\text{O}_6\text{Si}_6$ Theoretical mass: 1191.9220 m/z; Measured: 1191.46 m/z

Hel-Ome



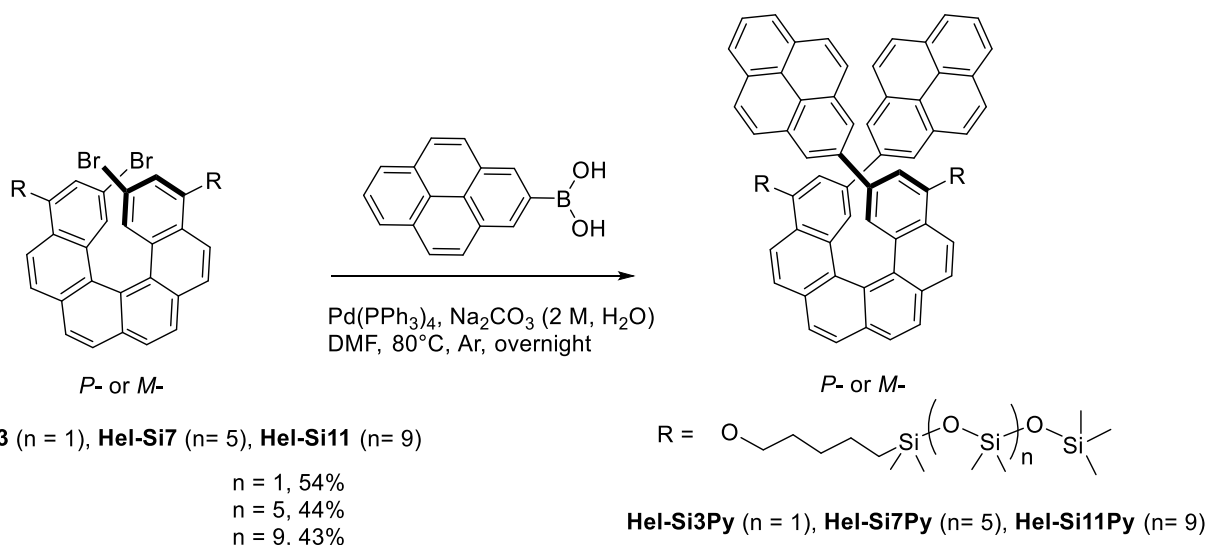
The compound **4** (20 mg, 0.0366 mmol) was added to a Schlenk flask, and was dissolved with DMF (1 mL) an aqueous solution of Na_2CO_3 2M (150 μL) was added to the reaction mixture, the solution was bubbled with argon for 15 minutes. 2-Pyrenylboronic acid (33 mg, 0.134 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (4mg, 0.0346 mmol) were added to the flask, the temperature was raised to 80°C and the solution was stirred overnight. Dichloromethane was added to the flask and the solution was washed three times with brine, the crude product was purified by chromatographic column (petroleum ether/ dichloromethane/ toluene 8:1:1).

Molecule **Hel-Ome** was obtained as a yellow solid (25 mg, 0.0317 mmol, 86%).

^1H NMR (400 MHz, CD_2Cl_2) δ 8.46 (d, $J = 8.9$ Hz, 2H), 8.18 (dd, $J = 7.6, 1.2$ Hz, 2H), 8.13 – 8.04 (m, 8H), 8.04 – 7.94 (m, 6H), 7.91 (d, $J = 8.9$ Hz, 2H), 7.85 (d, $J = 9.3$ Hz, 2H), 7.78 – 7.63 (m, 4H), 7.15 (s, 4H), 4.12 (s, 6H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 155.46, 139.13, 138.62, 132.36, 132.02, 131.83, 131.28, 130.88, 128.69, 128.59, 128.32, 127.75, 127.66, 127.60, 126.38, 126.28, 125.69, 125.44, 125.14, 125.07, 124.88, 124.42, 123.33, 122.72, 121.67, 108.52, 56.39, 54.38, 54.11, 53.84, 53.57, 53.30.

General procedure for Suzuki coupling reaction.



The compound **Heli-Si₃** (49 mg, 0.0446 mmol) was added to a Schlenk flask, the compound was dissolved with DMF (2 mL) an aqueous solution of Na_2CO_3 2M (200 μL) was added to the flask and the solution was

bubbled with argon for 15 minutes. 2-Pyrenylboronic acid (29 mg, 0.118 mmol) and Pd(PPh₃)₄ (5 mg, 0.00433 mmol) were added to the Schlenk, the temperature was raised to 80°C and the solution was stirred overnight. Dichloromethane was added to the flask and the solution was washed three times with brine, the crude product was purified by chromatographic column (petroleum ether/ dichloromethane/ toluene 8:1:1).

Molecule **Hel-Si₃** was obtained as a green/yellow wax (33 mg, 0.0243 mmol, 54%).

For siloxane n= 5, 10 the use of GPC is mandatory for separate the crude mixture after the first purification step.

Molecule **Hel-Si₇** was obtained as a light-yellow wax (30 mg, 0.0154 mmol, 44%).

Molecule **Hel-Si₁₁** was obtained as a light-yellow wax (19 mg, 0.00747 mmol, 43%).

Similar procedures were used for the *P* and *M* enantiomers with similar yields obtained.

¹H NMR **Hel-Si₃** (400 MHz, CD₂Cl₂) δ 8.49 (s, 2H), 8.18 (d, *J* = 6.4 Hz, 2H), 8.14 – 8.03 (m, 8H), 8.03 – 7.94 (m, 6H), 7.90 (d, *J* = 8.9 Hz, 2H), 7.84 (d, *J* = 9.3 Hz, 2H), 7.75 (d, *J* = 9.3 Hz, 2H), 7.67 (s, 2H), 7.17 (s, 2H), 7.10 (s, 2H), 4.18 (s, 4H), 1.96 (s, 4H), 1.52 (s, 8H), 0.69 (s, 4H), 0.41 – -0.27 (m, 43H).

¹³C NMR **Hel-Si₃** (101 MHz, CD₂Cl₂) δ 154.89, 139.06, 138.72, 133.66, 132.34, 132.03, 131.87, 131.30, 130.82, 128.58, 128.36, 127.78, 127.71, 127.63, 127.56, 127.51, 126.37, 126.10, 125.77, 125.42, 125.12, 125.04, 124.91, 124.51, 123.45, 122.58, 121.86, 109.32, 69.30, 54.38, 54.31, 54.11, 54.04, 53.84, 53.77, 53.57, 53.30, 30.68, 30.12, 29.82, 23.79, 18.79, 1.92, 1.44, 1.20, 0.36.

¹H NMR **Hel-Si₇** (400 MHz, CDCl₃) δ 8.50 (s, 2H), 8.16 (dd, *J* = 7.6, 1.2 Hz, 2H), 8.10 – 8.01 (m, 8H), 8.01 – 7.92 (m, 6H), 7.89 (d, *J* = 8.9 Hz, 2H), 7.83 (d, *J* = 9.3 Hz, 2H), 7.78 (d, *J* = 9.3 Hz, 2H), 7.74 (s, 2H), 7.18 (s, 2H), 7.08 (s, 2H), 4.15 (s, 4H), 1.96 (s, 4H), 1.54 (s, 8H), 0.69 (s, 4H), 0.51 – -0.19 (m, 91H).

¹³C NMR **Hel-Si₇** (101 MHz, CD₂Cl₂) δ 154.89, 139.06, 138.72, 133.67, 132.34, 132.04, 131.87, 131.31, 130.83, 128.58, 128.36, 127.78, 127.71, 127.63, 127.57, 127.52, 126.37, 126.11, 125.78, 125.42, 125.12, 125.04, 124.92, 124.52, 123.46, 122.60, 121.86, 109.32, 69.30, 54.38, 54.31, 54.11, 54.04, 53.84, 53.77, 53.57, 53.30, 30.69, 30.13, 29.82, 23.80, 23.13, 18.77, 14.31, 1.87, 1.39, 1.29, 1.26, 1.23, 1.20, 0.37.

¹H NMR **Hel-Si₁₁** (400 MHz, CD₂Cl₂) δ 8.50 (s, 2H), 8.18 (dd, *J* = 7.6, 1.2 Hz, 2H), 8.07 (d, *J* = 3.4 Hz, 8H), 7.97 (dd, *J* = 9.6, 7.8 Hz, 6H), 7.91 (d, *J* = 8.9 Hz, 2H), 7.85 (d, *J* = 9.3 Hz, 2H), 7.76 (d, *J* = 9.3 Hz, 2H), 7.68 (s, 2H), 7.17 (s, 2H), 7.11 (s, 2H), 4.19 (s, 4H), 1.97 (s, 4H), 1.54 (s, 8H), 0.70 (s, 4H), 0.24 – 0.00 (m, 138H).

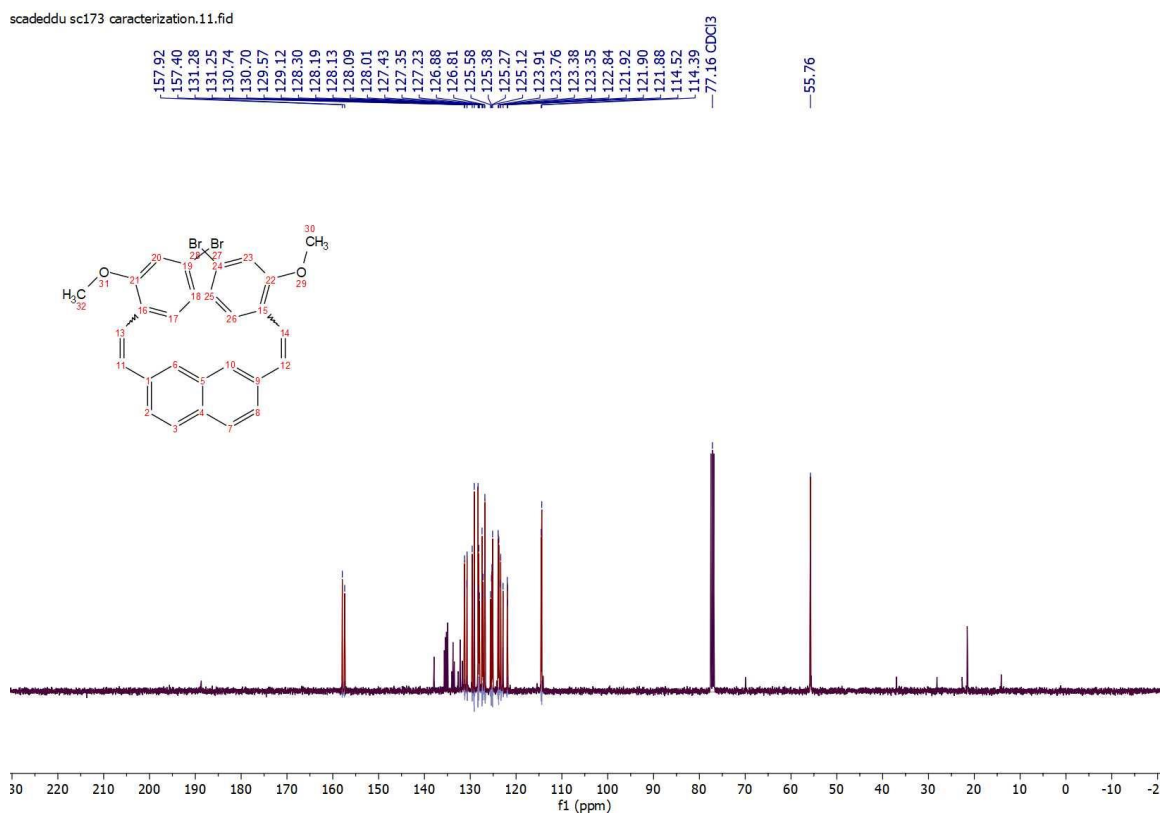
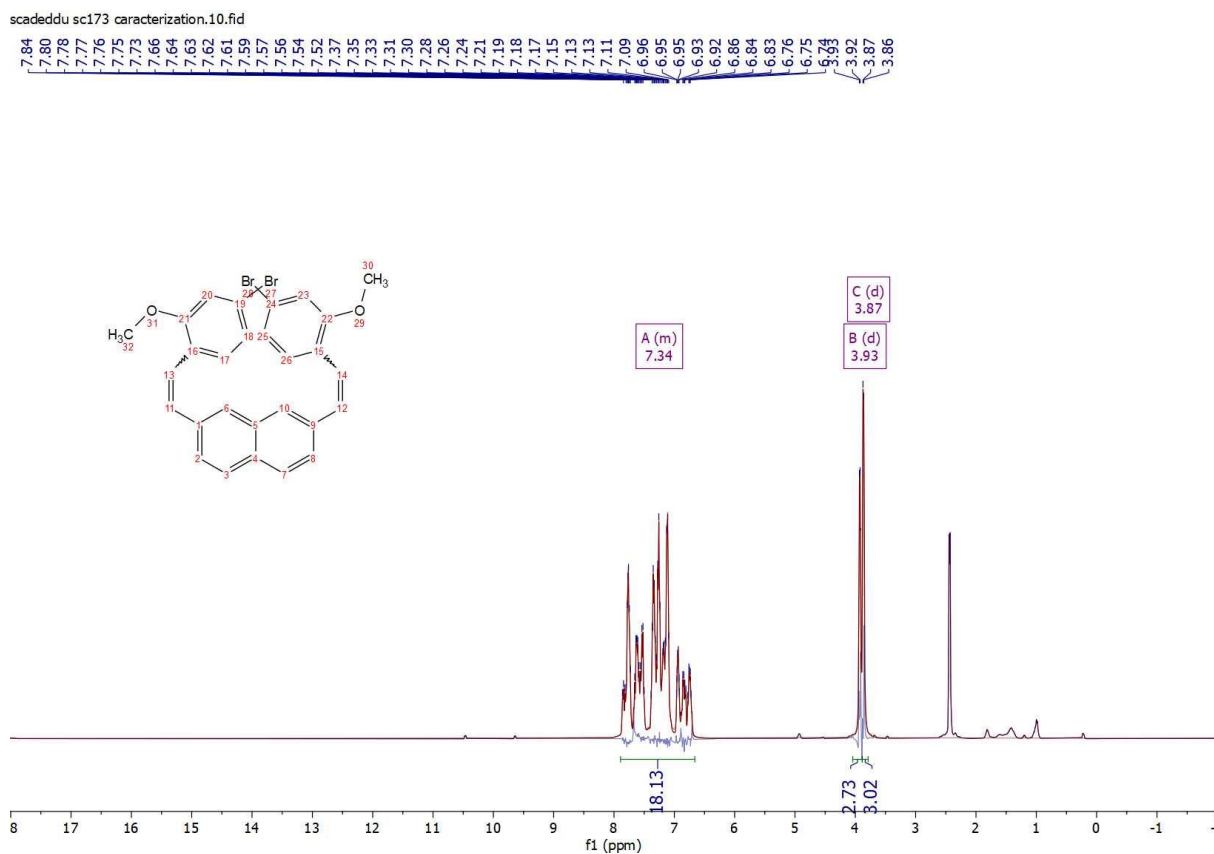
¹³C NMR **Hel-Si₁₁** (101 MHz, CD₂Cl₂) δ 154.85, 139.03, 138.69, 133.63, 132.31, 132.00, 131.83, 131.27, 130.79, 128.54, 128.32, 127.76, 127.70, 127.62, 127.55, 127.51, 126.35, 126.09, 125.75, 125.41, 125.11, 125.08, 125.00, 124.88, 124.49, 123.40, 122.56, 121.83, 109.25, 69.25, 30.69, 29.81, 23.79, 18.75, 1.86, 1.39, 1.27, 1.25, 1.23, 1.22, 1.20, 0.36.

Hel-Si₃ Mass spectrometry: Maldi ⁺C₈₃H₉₂O₆Si₆ Theoretical mass: 1342.1420 m/z; Measured: 1341.54 m/z

Hel-Si₇ Mass spectrometry: Maldi ⁺C₉₈H₁₄₀O₁₄Si₁₄ Theoretical mass: 1935.3740 m/z; Measured: 1934.68 m/z

Hel-Si₁₁ Mass spectrometry: Maldi ⁺C₁₁₄H₁₈₈O₂₂Si₂₂ Theoretical mass: 2528.6060 m/z; Measured: 2527.81 m/z

3. NMR spectra



scadeddu sc57 pur.10.fid

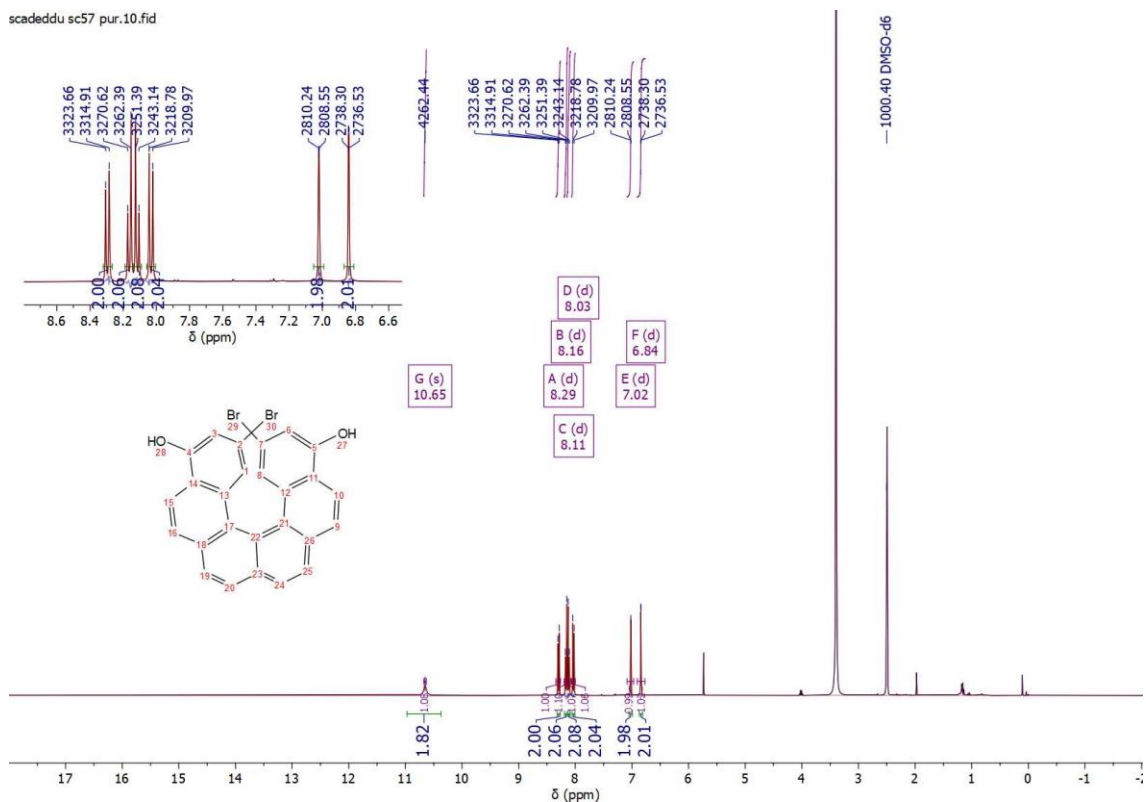


Figure S5: $^1\text{H-NMR}$ molecule 5 (400 MHz, DMSO-d_6).

scadeddu sc176 pure.10.fid

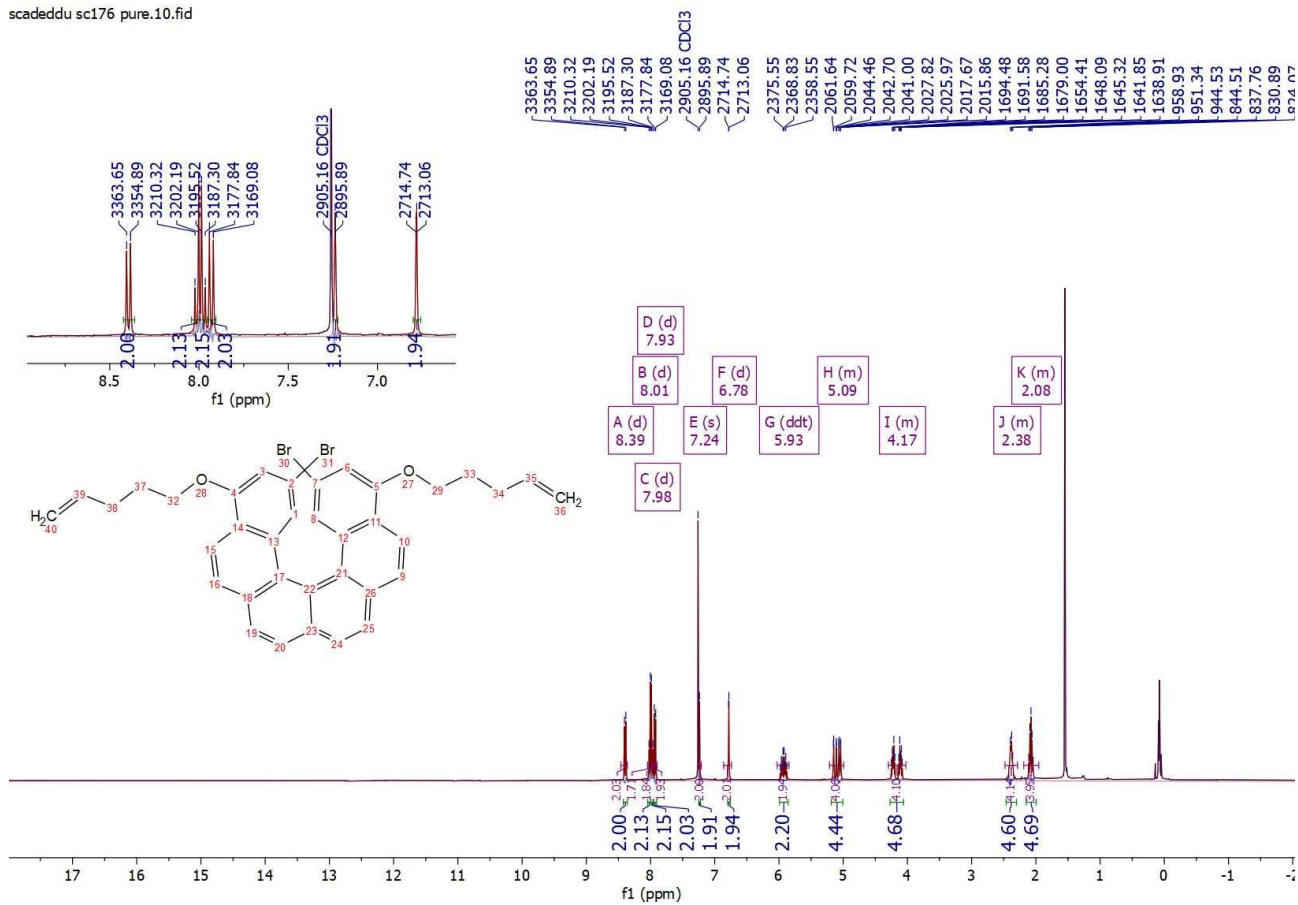


Figure S6: $^1\text{H-NMR}$ molecule 7 (400 MHz, CDCl_3).

scadeddu sc211 carac.10.fid

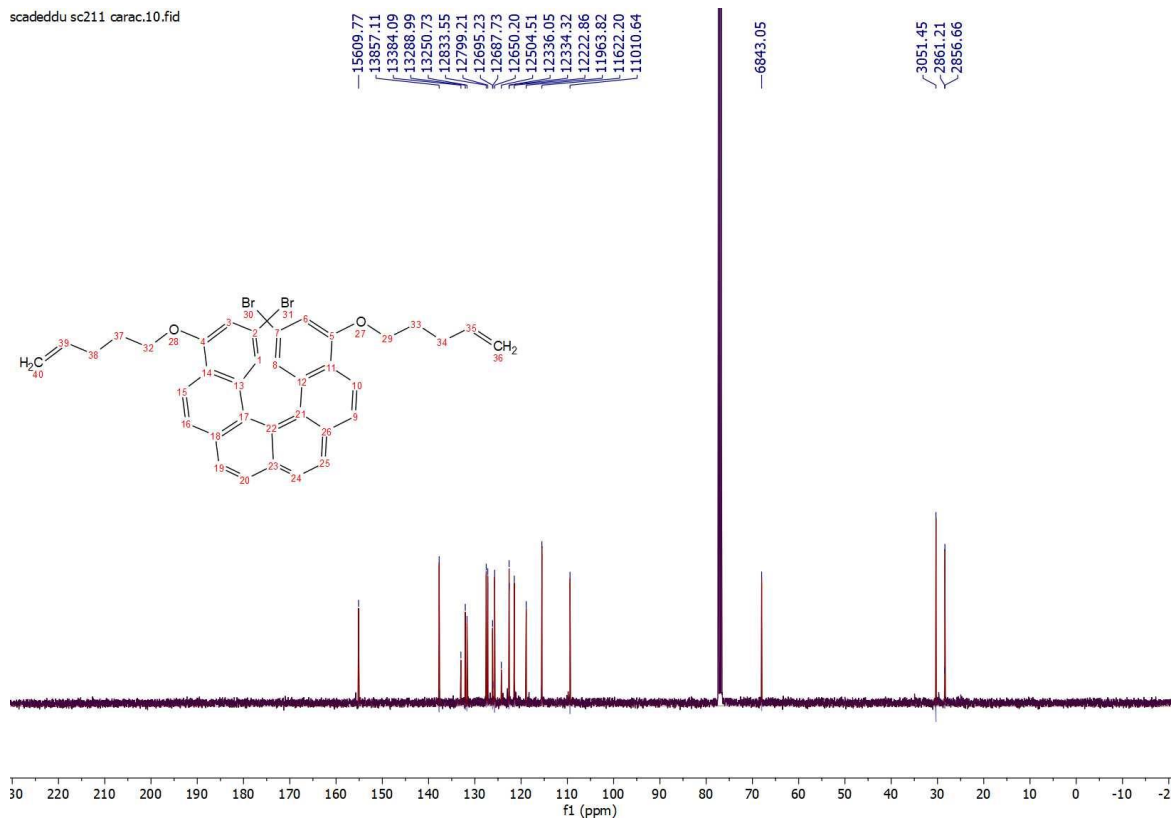


Figure S7: ¹³C NMR molecule 7 (101 MHz, CDCl₃)

scadeddu sc223 1st caract.10.fid

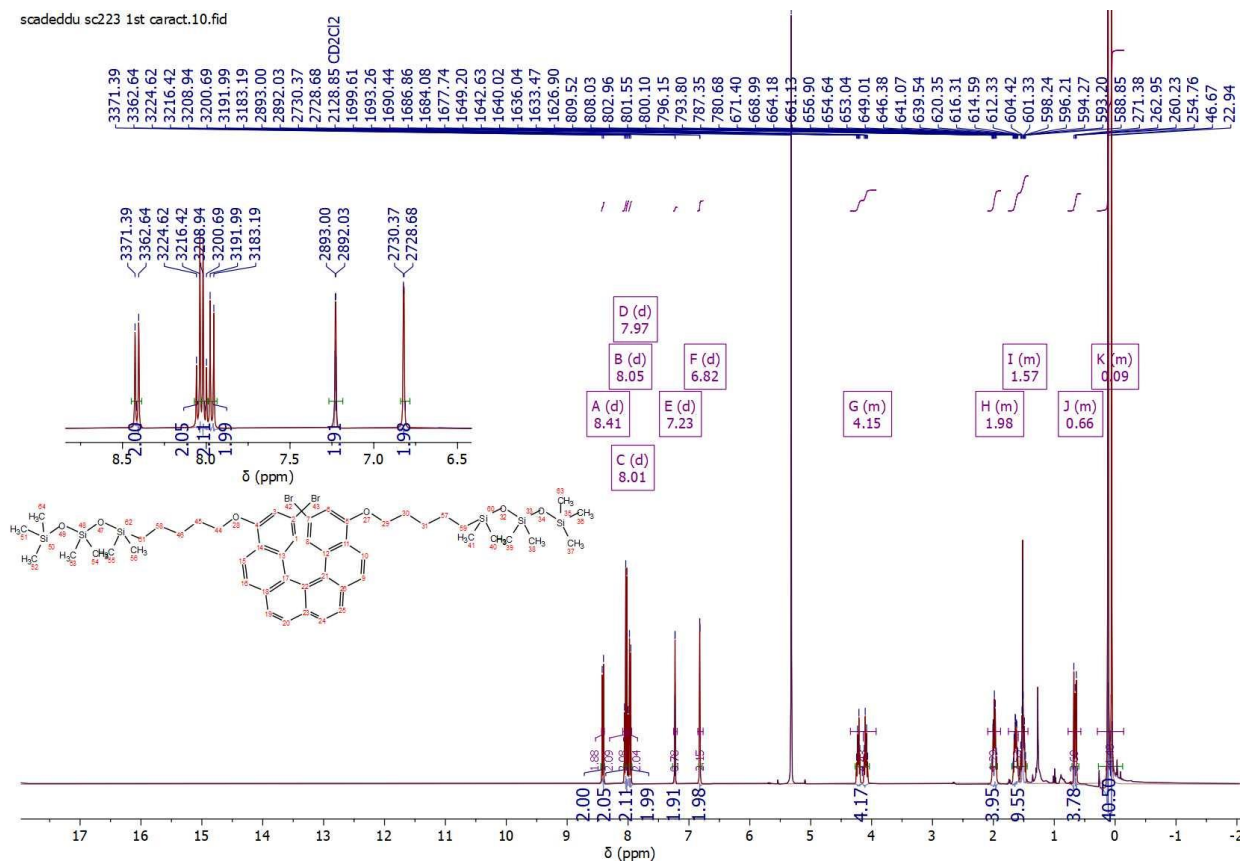


Figure S8: ¹H NMR molecule Hel-Si₃ (400 MHz, CDCl₃).

scadeddu sc223 1st caract.11.fid

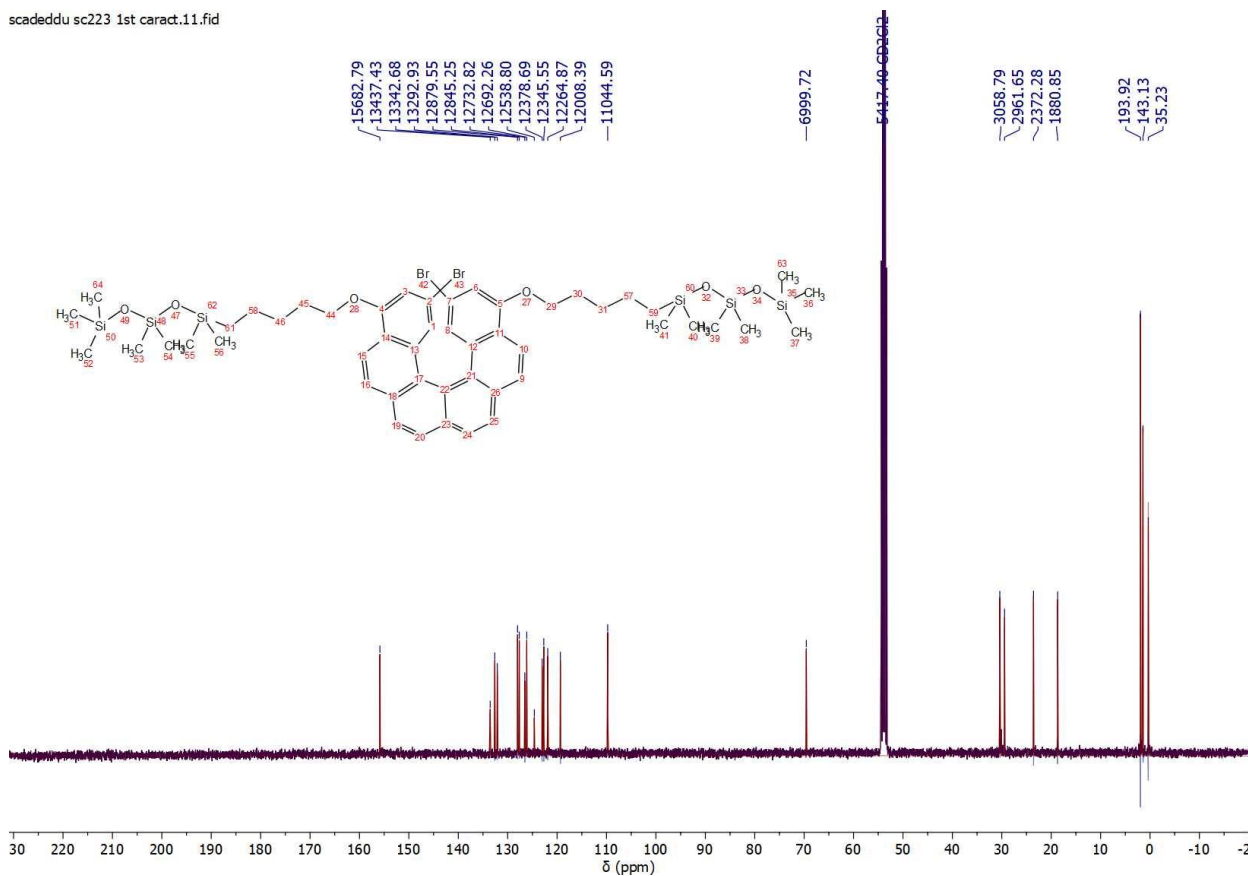


Figure S9: ^{13}C -NMR molecule **Hel-Si₃** (101 MHz, CDCl_3).

scadeddu sc134 pur.10.fid

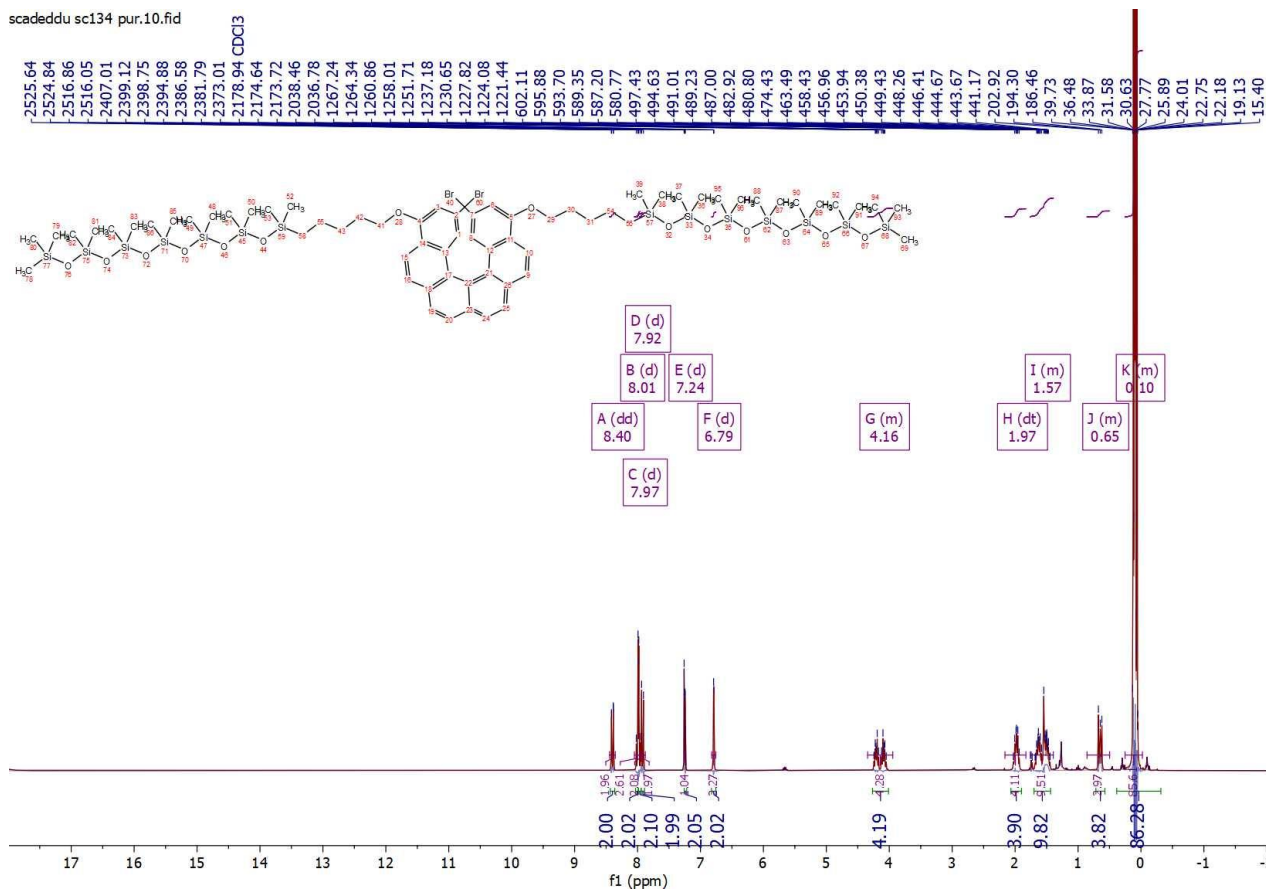


Figure S10: ^1H -NMR molecule **Hel-Si₇** (400 MHz, CDCl_3).

scadeddu sc226 1st caract.11.fid

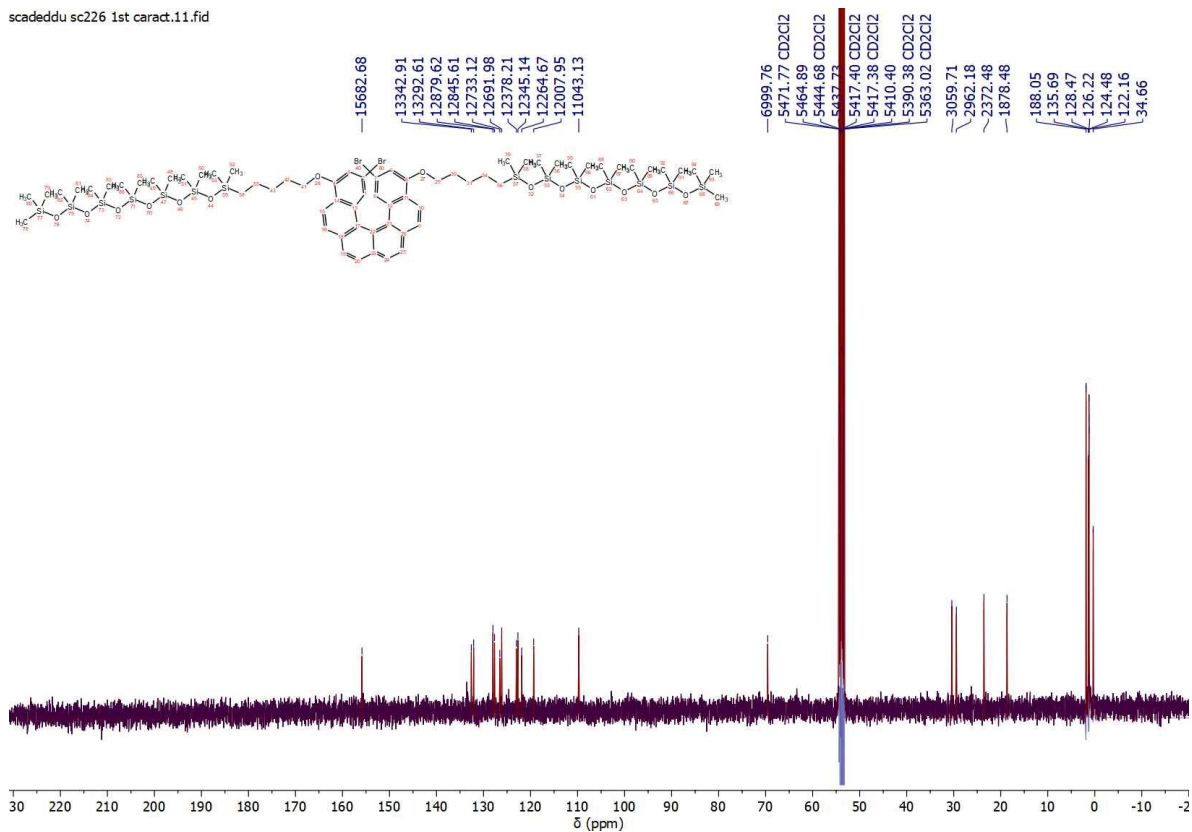


Figure S11 ¹³C-NMR molecule **Hel-Si₇** (101 MHz, CD₂Cl₂).

scadeddu sc227 1st caract.10.fid

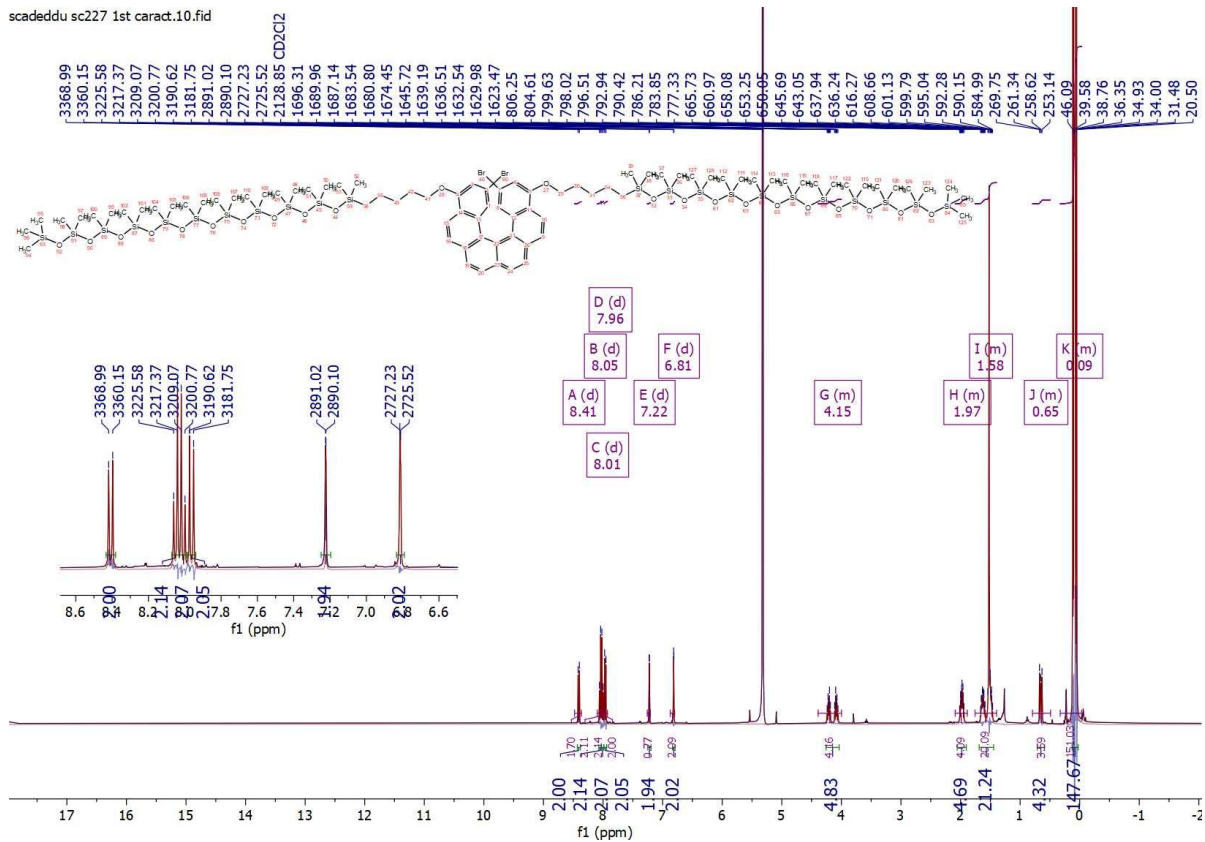


Figure S12: ¹H-NMR molecule **Hel-Si₁₁** (400 MHz, CD₂Cl₂).

scadeddu sc227 2nd caract.11.fid

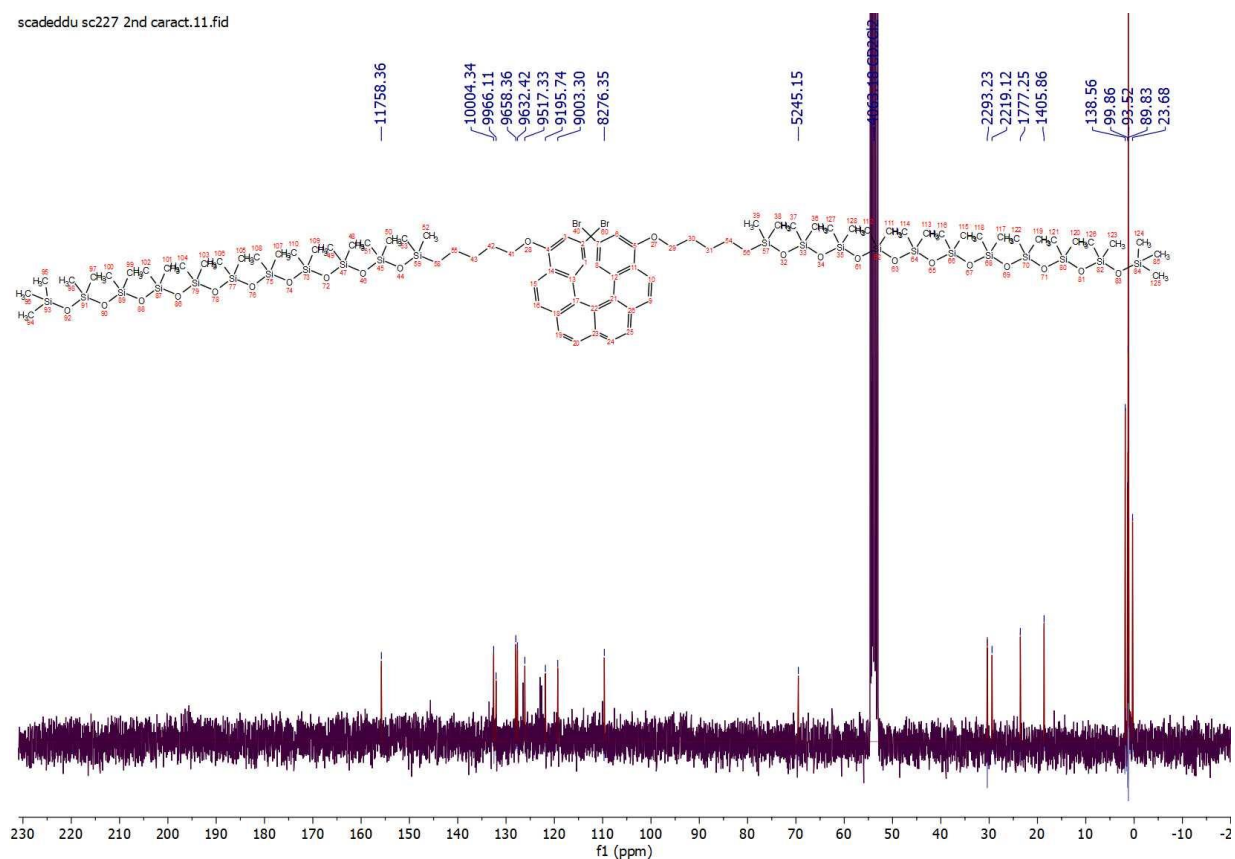


Figure S13: ^{13}C -NMR molecule **Hel-Si₁₁** (101 MHz, CD_2Cl_2).

scadeddu sc272 caract.11.fid

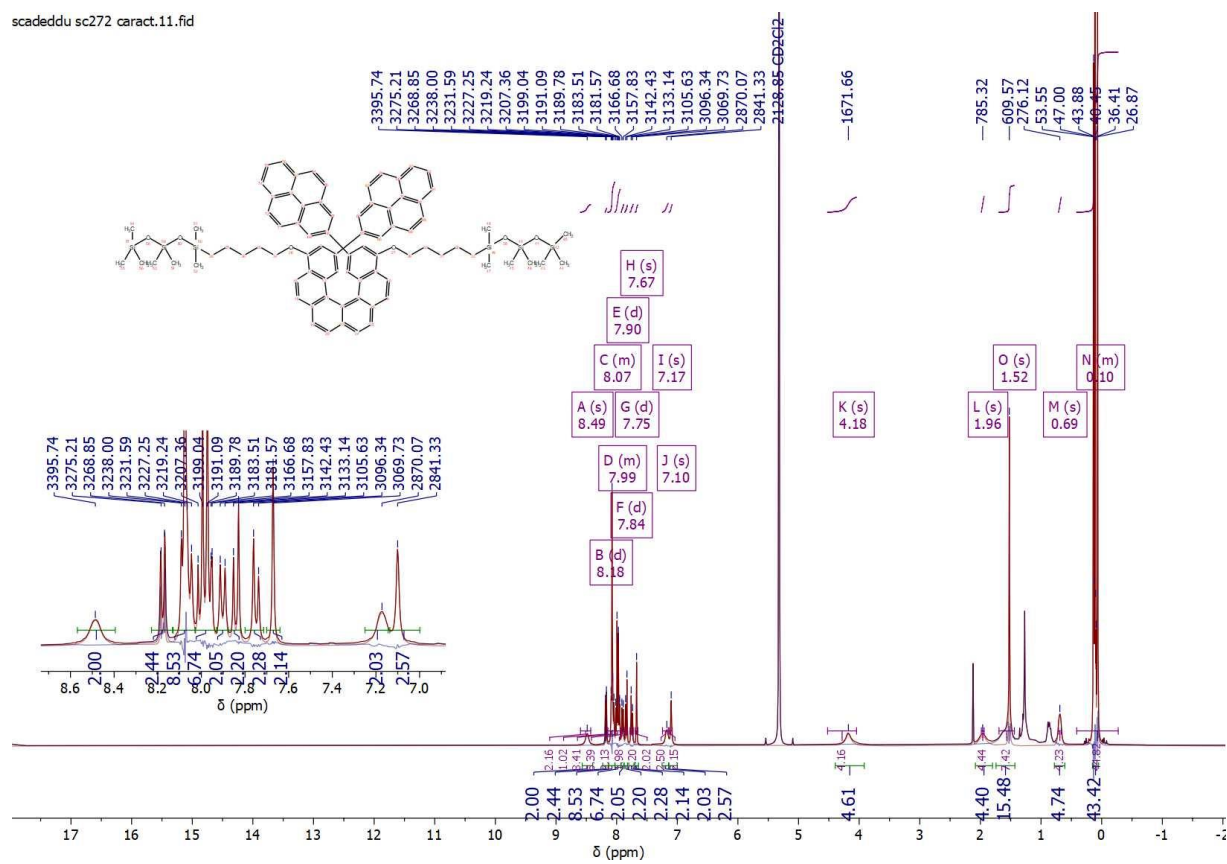


Figure S14: ^1H -NMR molecule **Hel-Si₃** (400 MHz, CD_2Cl_2).

scadeddu sc272 caract.10.fid

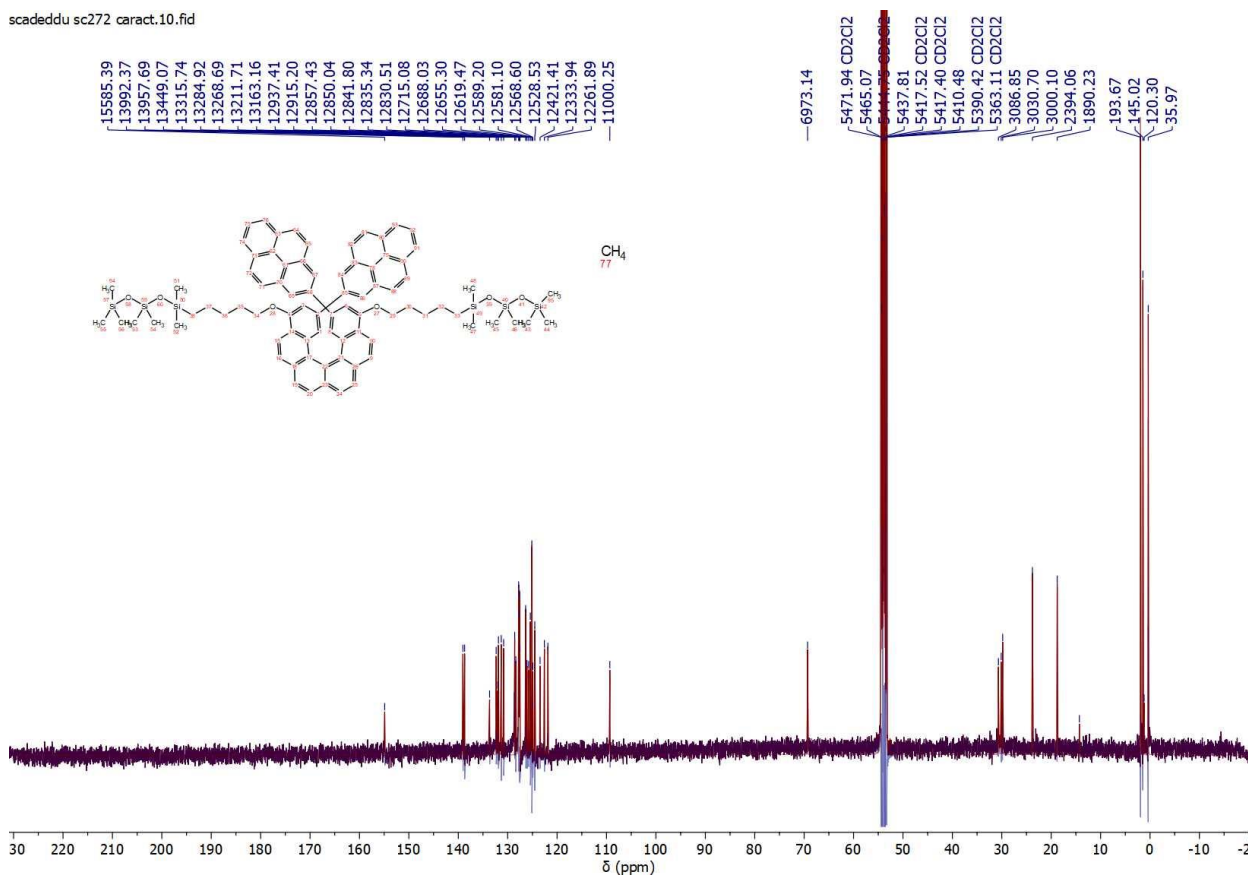


Figure S15: ¹³C-NMR molecule **Hel-Si₃** (101 MHz, CD₂Cl₂).

scadeddu sc236 1st eluted.10.fid

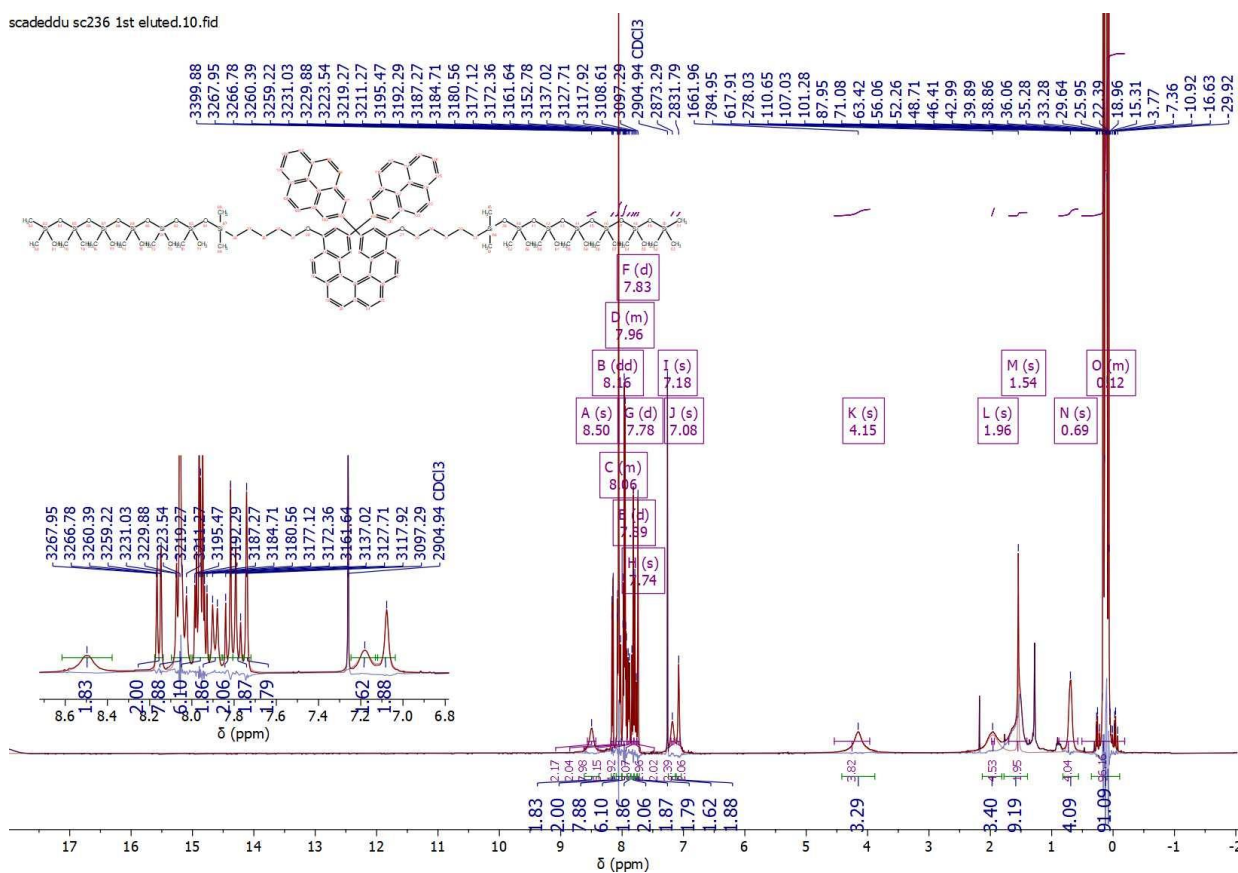


Figure S16: ¹H-NMR molecule **Hel-Si₇** (400 MHz, CDCl₃).

scadeddu sc276 caract.11.fid

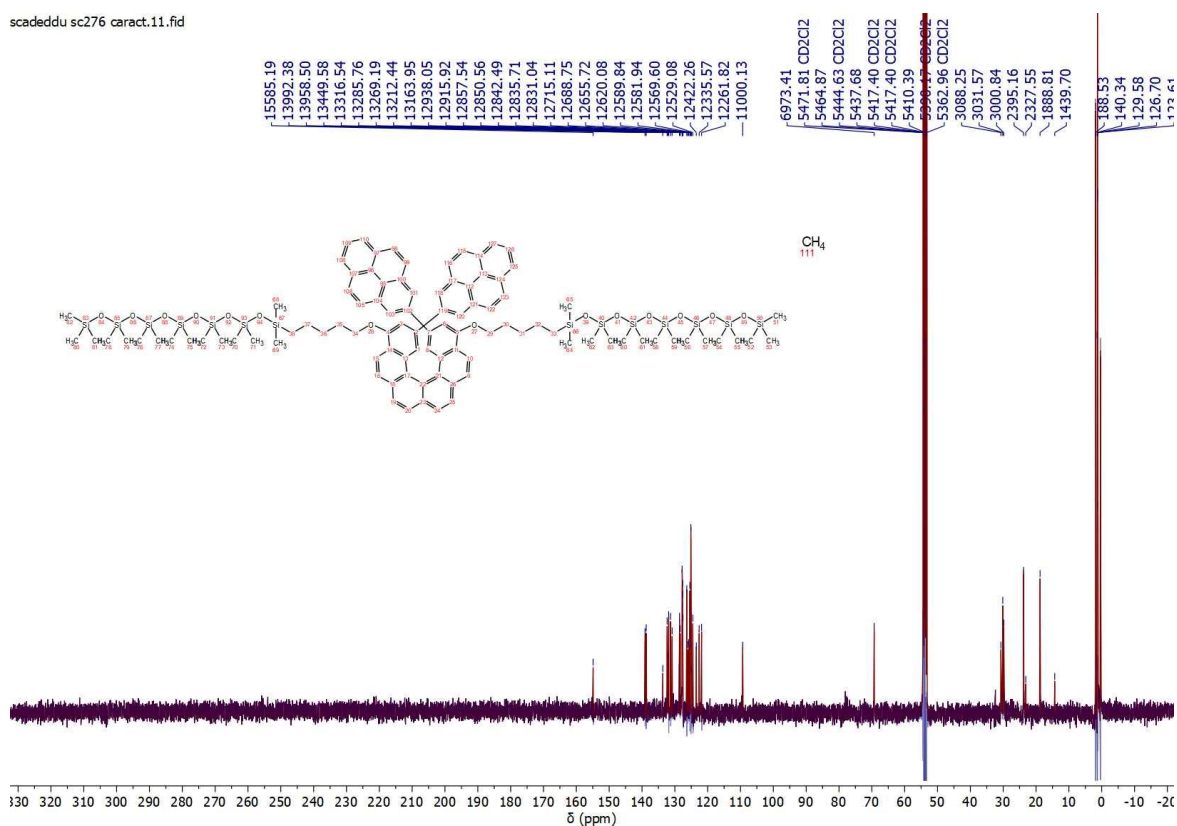


Figure S17: ¹³C-NMR molecule **Hel-Si₇** (101 MHz, CD₂Cl₂).

scadeddu sc307 carbon.10.fid

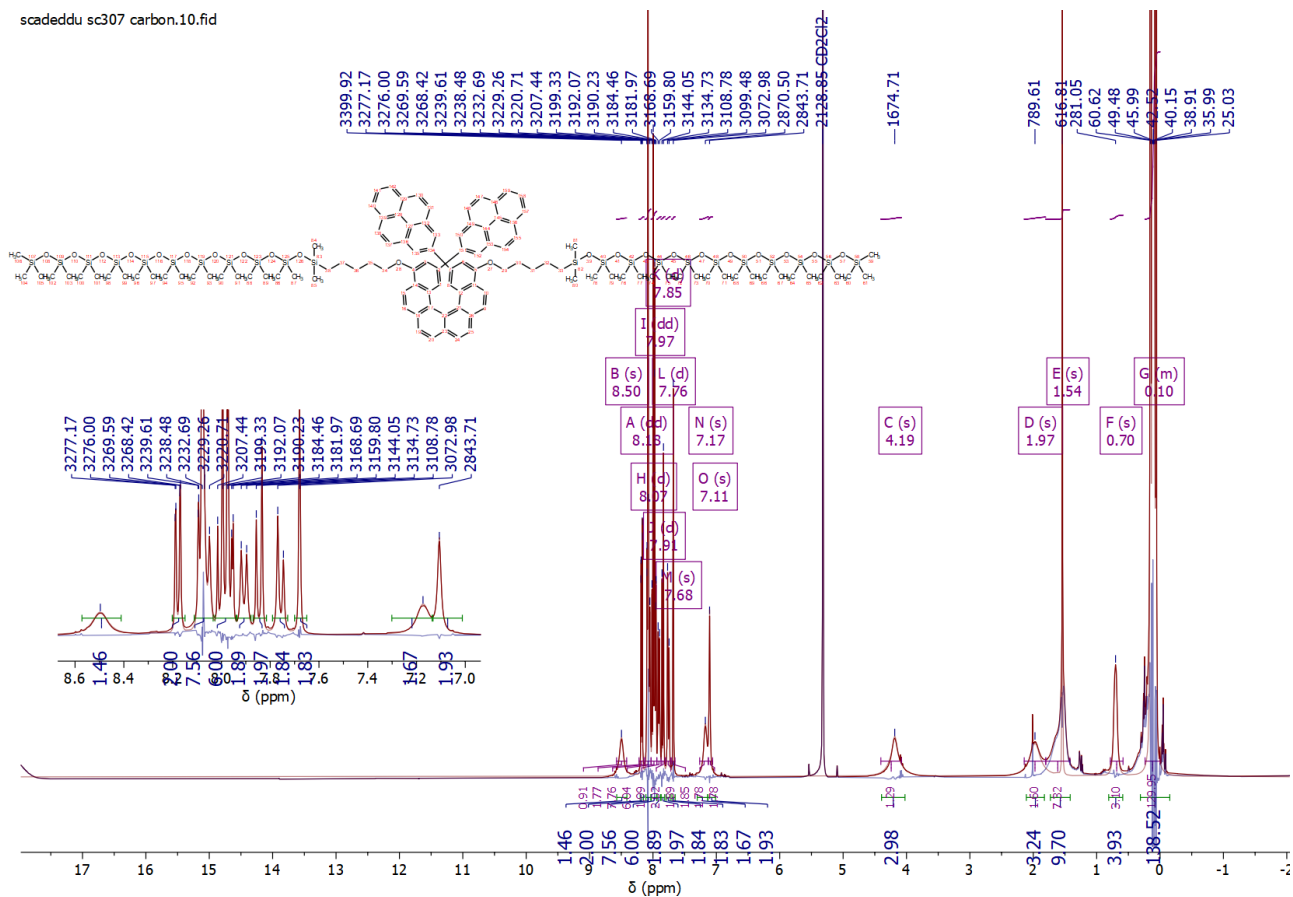


Figure S18: ¹H-NMR molecule **Hel-Si₁₁** (400 MHz, CD₂Cl₂).

scadeddu sc307 carbon.11.fid

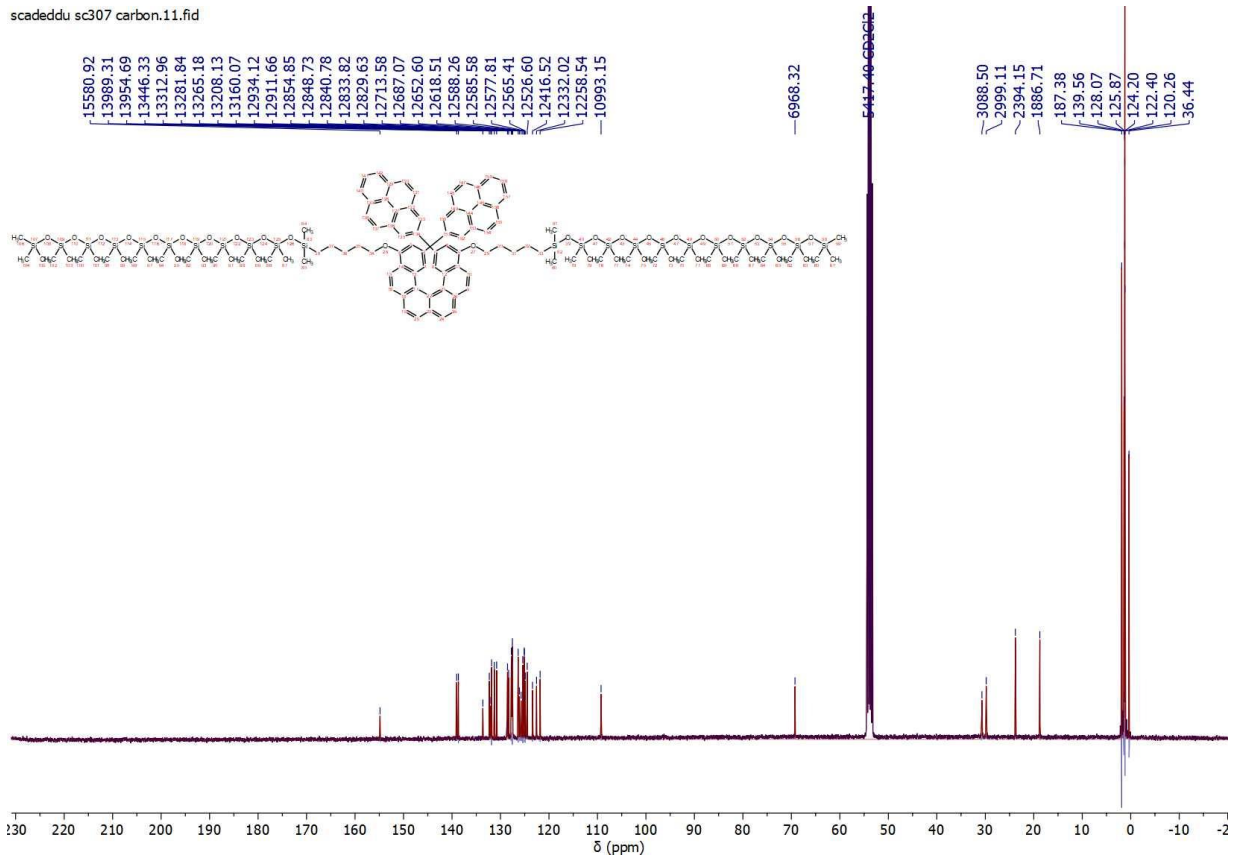


Figure S19: ¹³C-NMR molecule **Hel-Si₁₁** (101 MHz, CD₂Cl₂).

scadeddu sc121 caract.10.fid

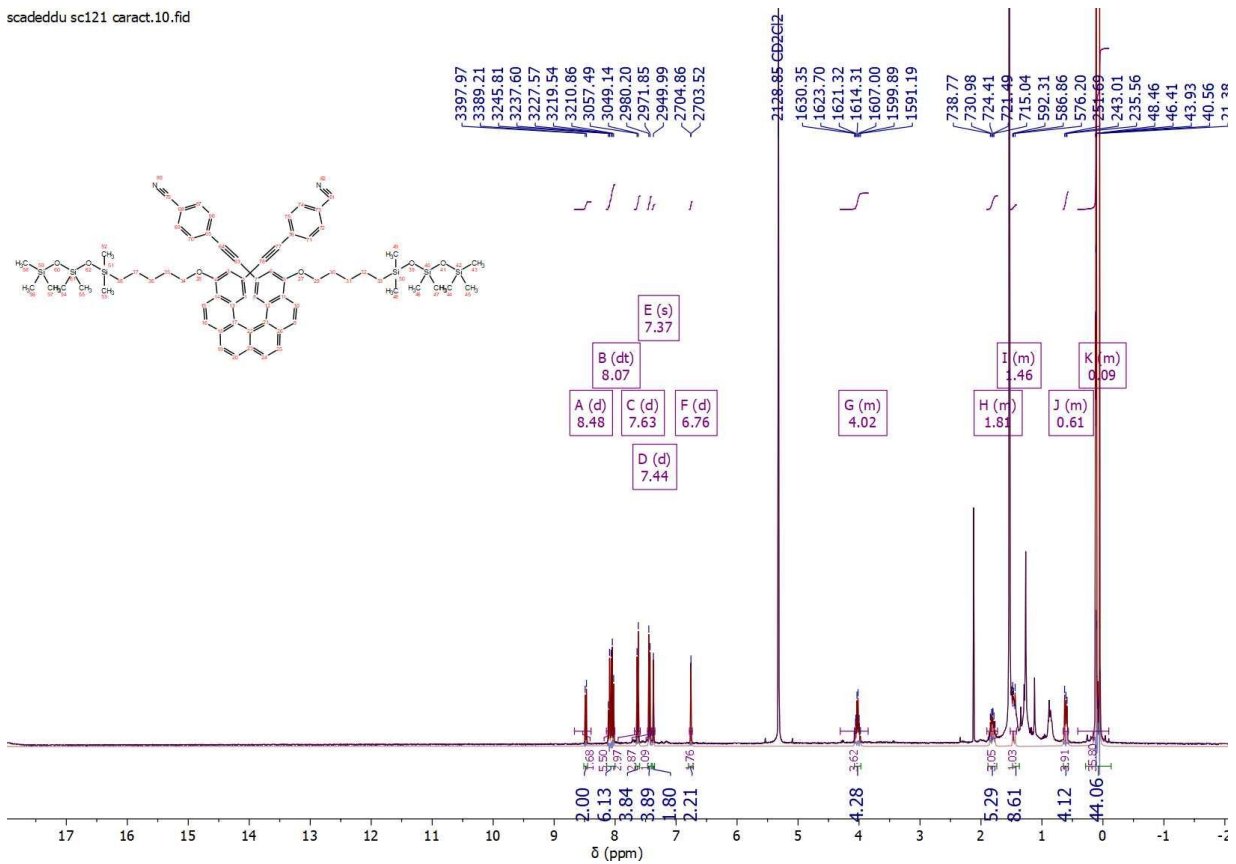


Figure S20: ¹H-NMR molecule **Hel'-Si₃** (400 MHz, CD₂Cl₂).

scadeddu sc121 caract.21.fid

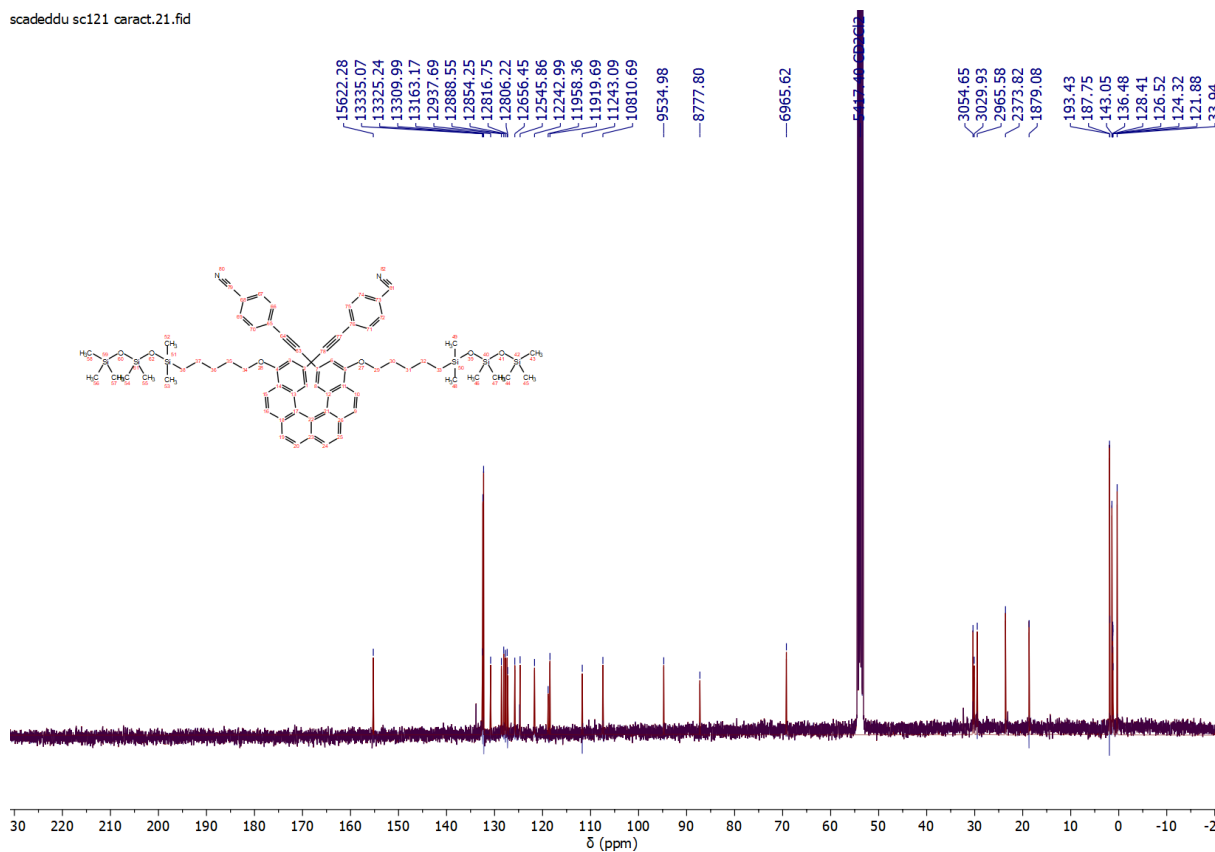


Figure S21: ¹³C-NMR molecule *Hel'*-Si₃ (101 MHz, CD₂Cl₂).

scadeddu sc149.11.fid

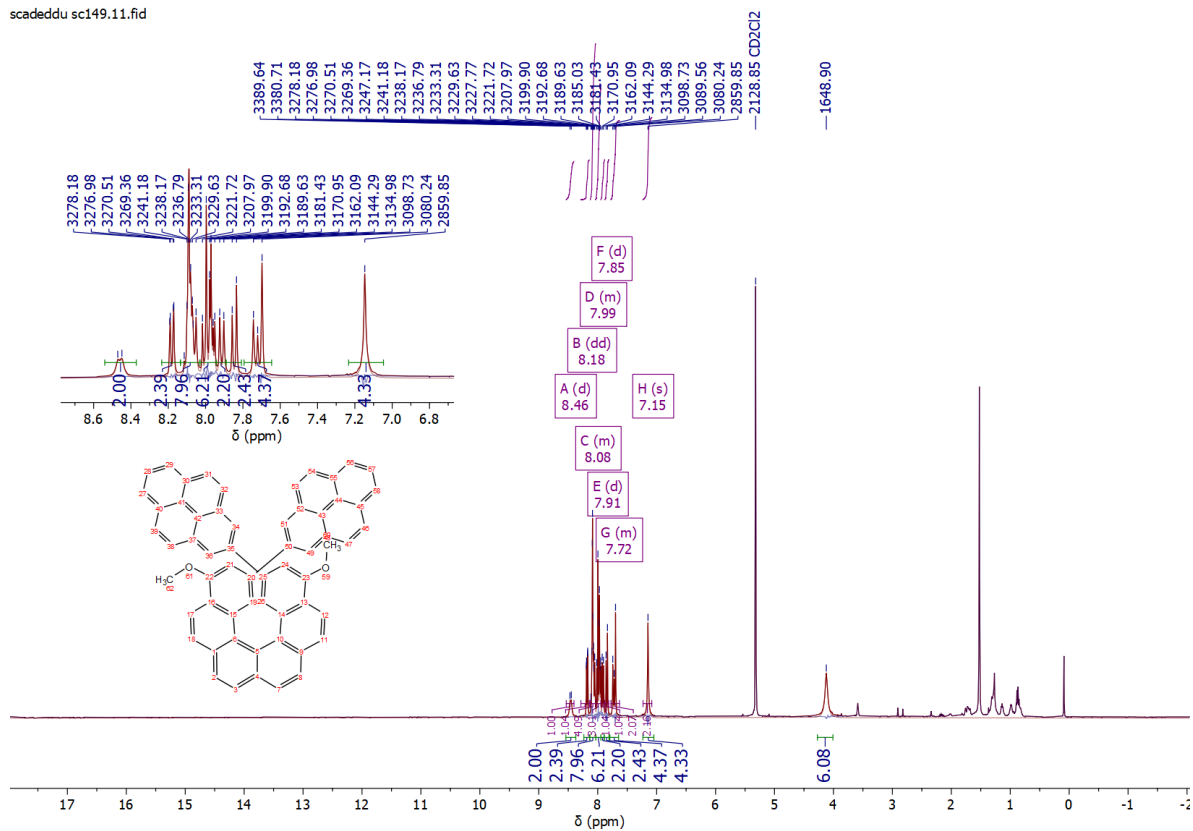


Figure S22: ¹H-NMR molecule *Hel-Ome* (400 MHz, CD₂Cl₂).

scadeddu sc149.10.fid

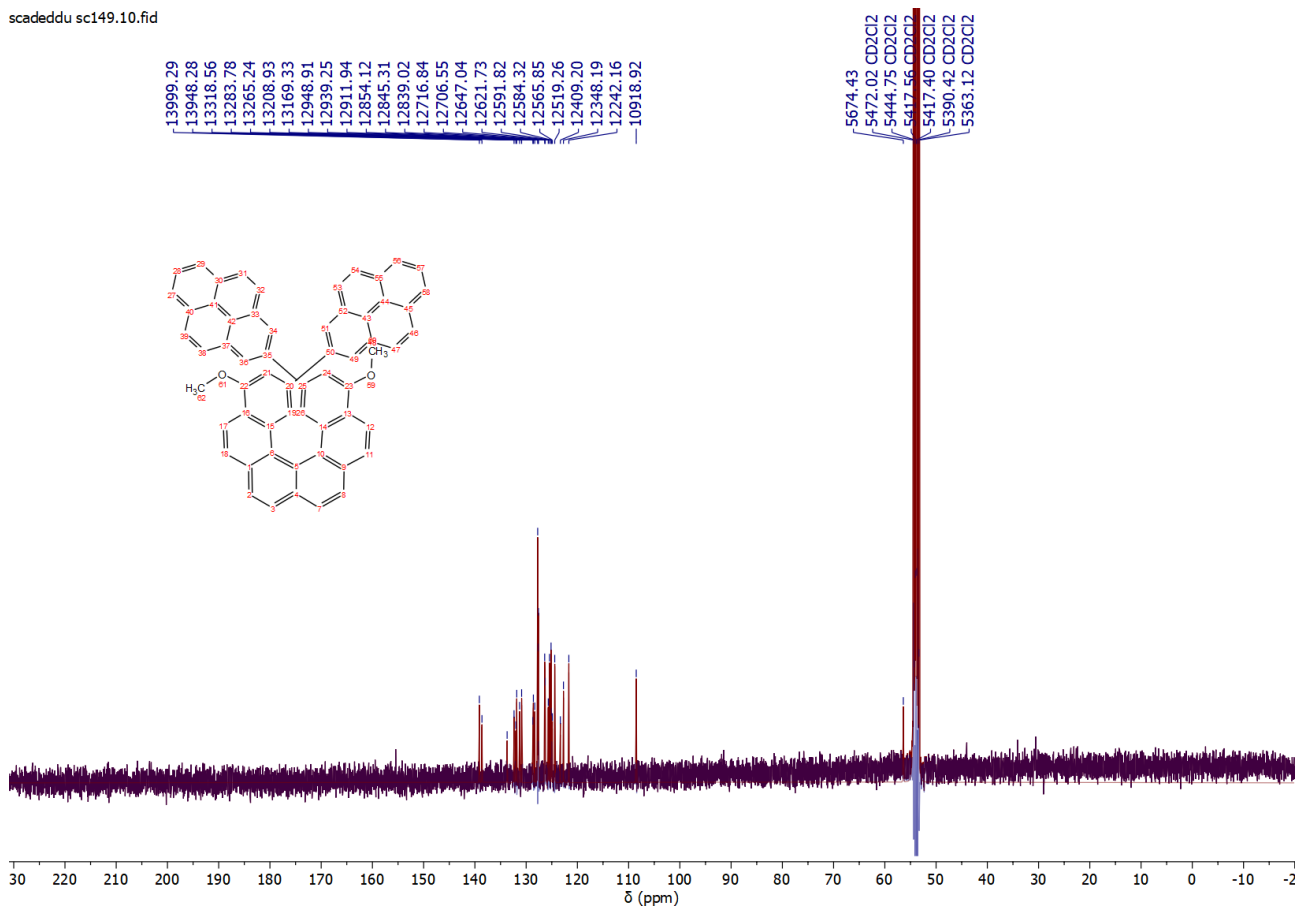


Figure S23: ¹³C-NMR molecule **Hel-Ome** (101 MHz, CD₂Cl₂).

scadeddu sc126.10.fid

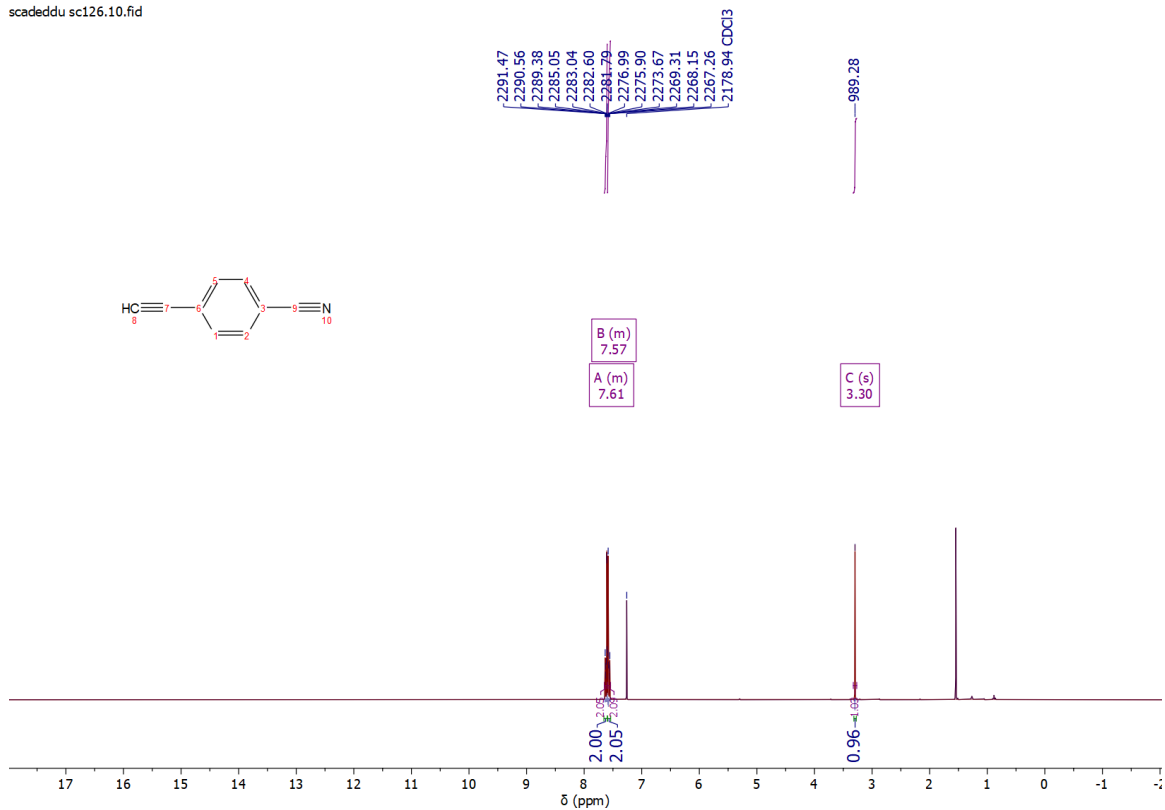


Figure S24: ¹H-NMR molecule **8** (400 MHz, CD₂Cl₂).

4. Mass spectroscopy analysis

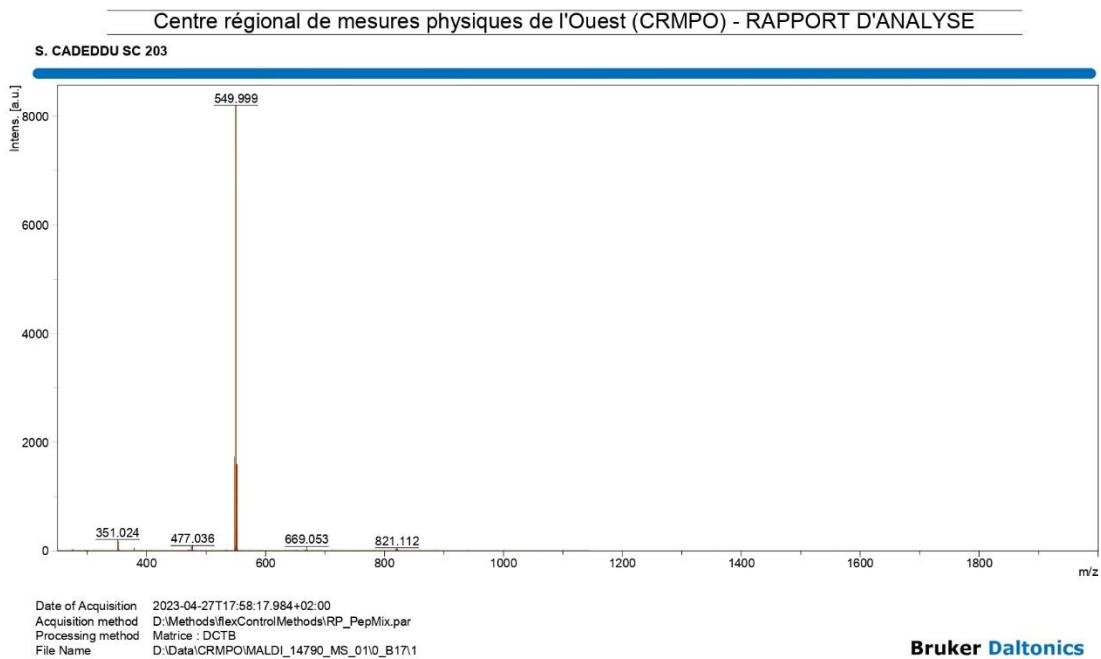


Figure S25: Maldi-ToF mass spectrum of molecule 3.

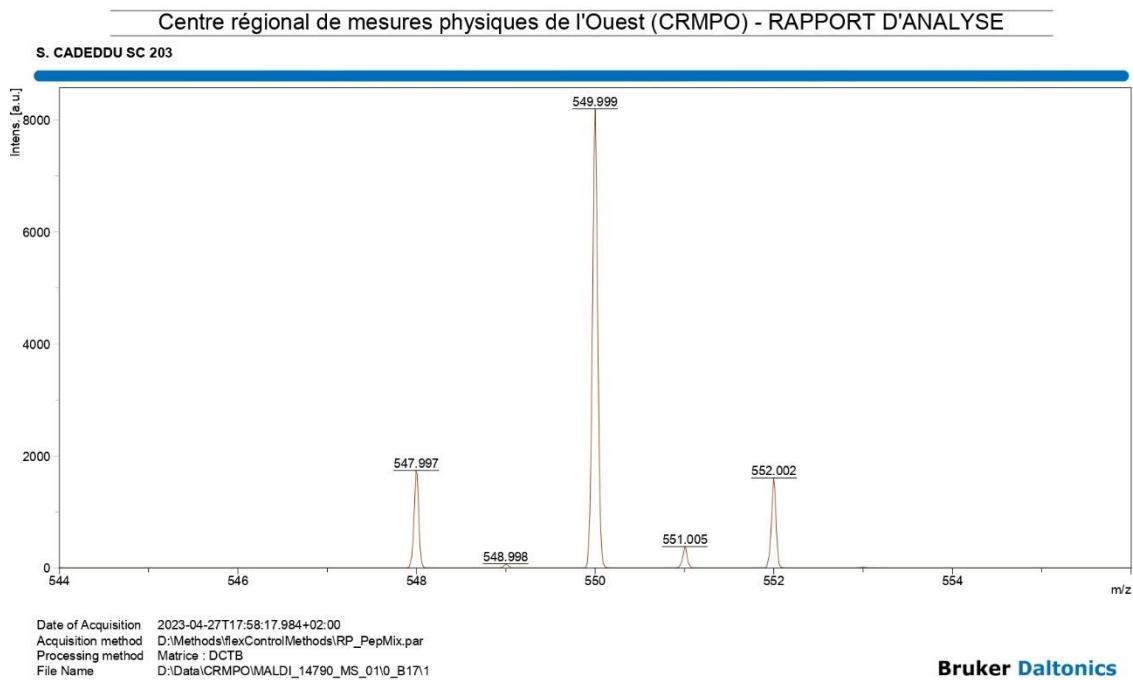
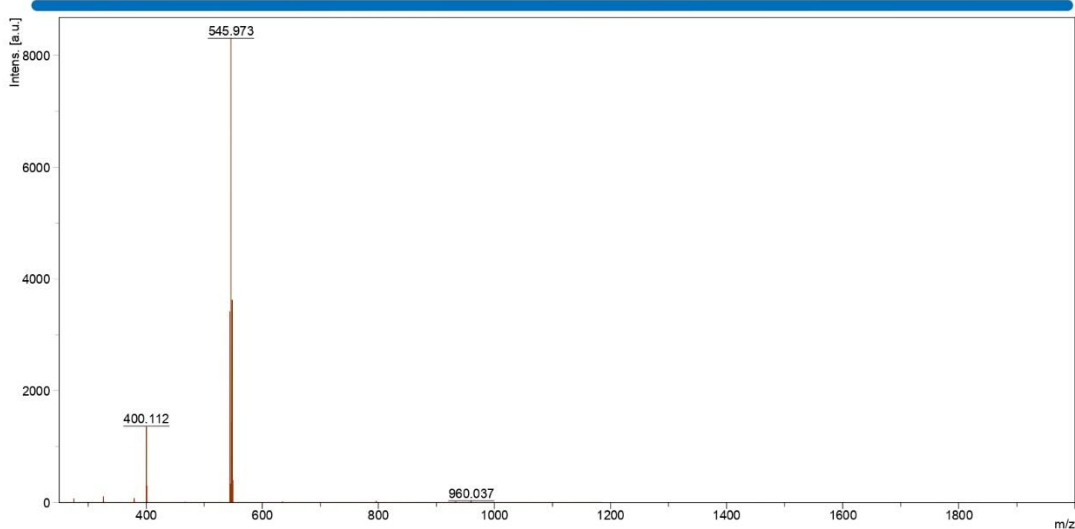


Figure S26: Maldi-ToF mass spectrum of molecule 3, zoom of the molecular peak.

Centre régional de mesures physiques de l'Ouest (CRMPO) - RAPPORT D'ANALYSE

S. CAEDDU SC 42



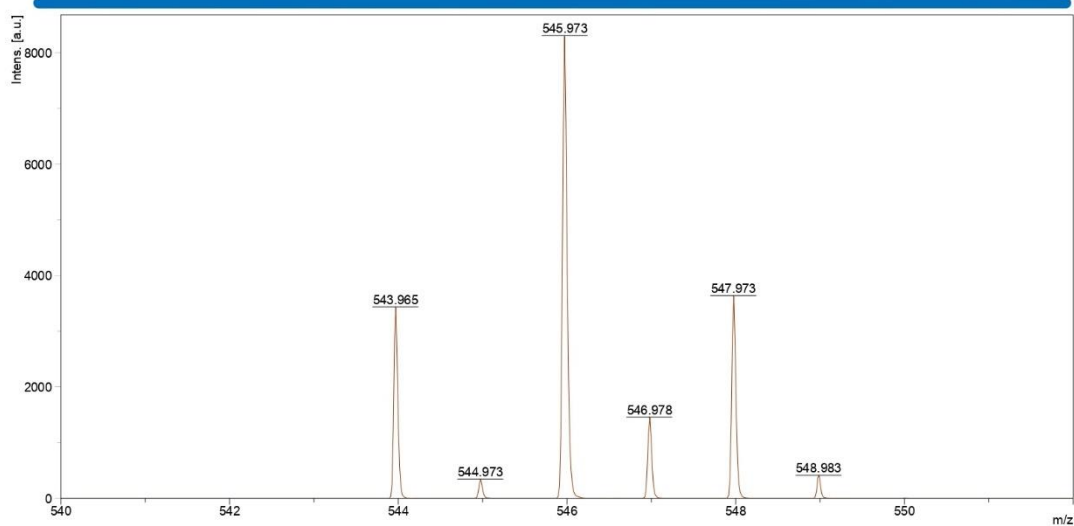
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Processing method Matrice : DCTB
File Name D:\Data\CRMPO\MALDI_14788_MS_0110_B1511

Bruker Daltonics

Figure S27: Maldi-Tof mass spectrum of molecule 4.

Centre régional de mesures physiques de l'Ouest (CRMPO) - RAPPORT D'ANALYSE

S. CAEDDU SC 42



Date of Acquisition 2023-04-27T19:03:36.850+02:00
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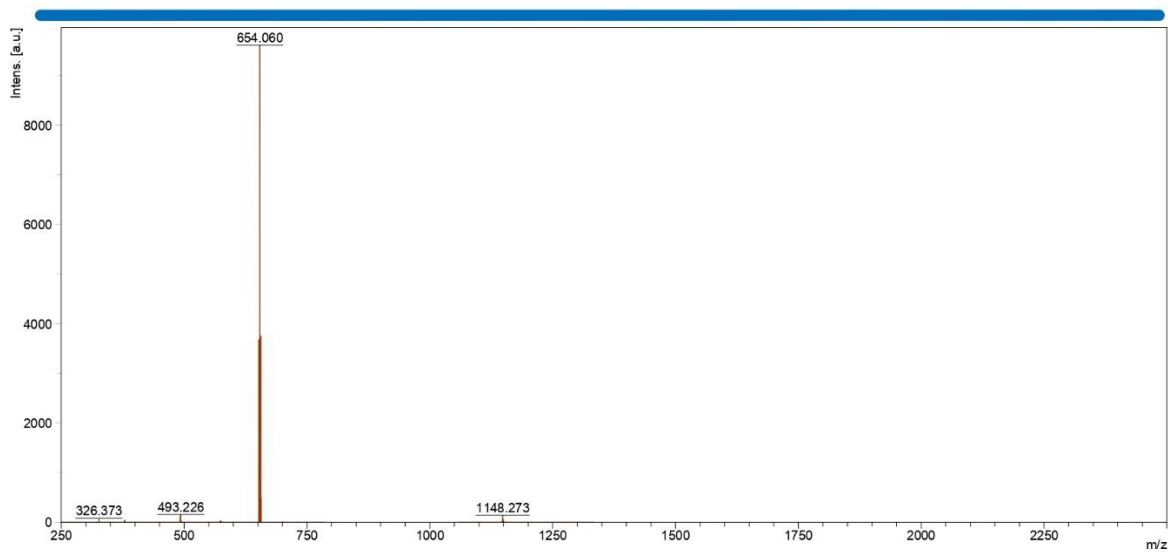
Bruker Daltonics

a

Figure S28: Maldi-Tof mass spectrum of molecule 4, zoom of the molecular peak.

Centre régional de mesures physiques de l'Ouest (CRMPO) - RAPPORT D'ANALYSE

S. CADEDDU SC 247



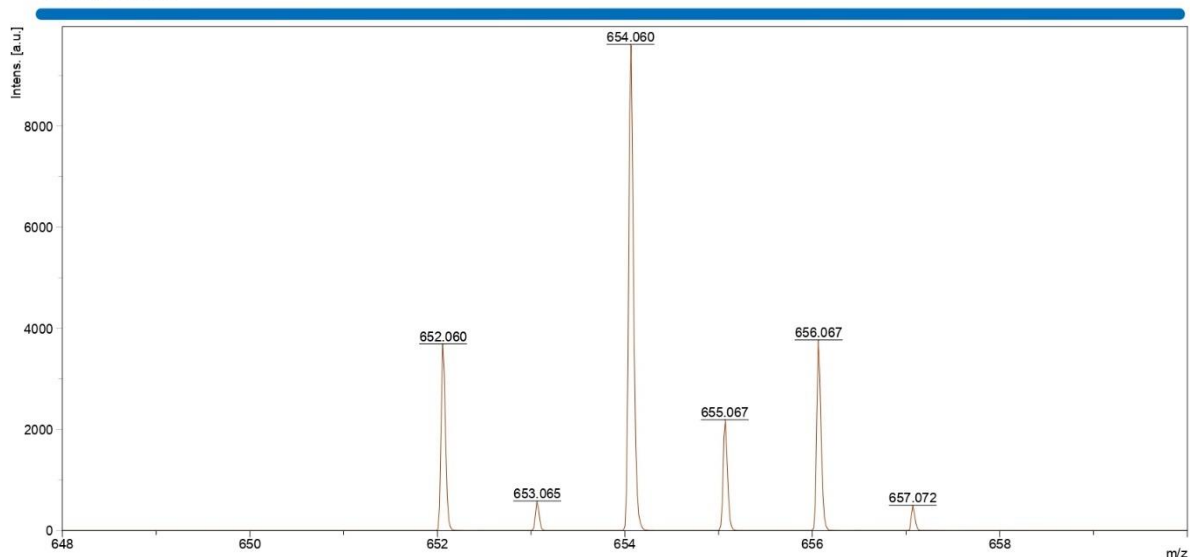
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Processing method Matrice : DCTB
File Name D:\Data\CRMPO\MALDI_14793_MS_0110_B20\1

Bruker Daltonics

Figure S29: Maldi-Tof mass spectrum of molecule 7.

Centre régional de mesures physiques de l'Ouest (CRMPO) - RAPPORT D'ANALYSE

S. CADEDDU SC 247



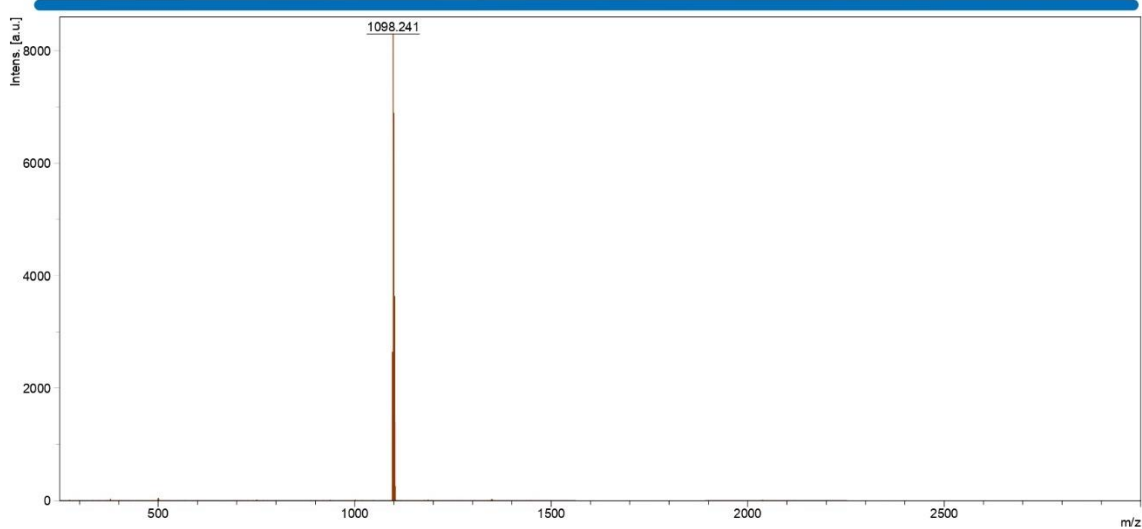
Date of Acquisition 2023-04-27T17:16:47.095+02:00
Acquisition method D:\Methods\flexControlMethods\RP_PepMix.par
Processing method Matrice : DCTB
File Name D:\Data\CRMPO\MALDI_14793_MS_0110_B20\1

Bruker Daltonics

Figure S30: Maldi-Tof mass spectrum of molecule 7, zoom of the molecular peak.

Centre régional de mesures physiques de l'Ouest (CRMPO) - RAPPORT D'ANALYSE

S. CAEDDU SC 133



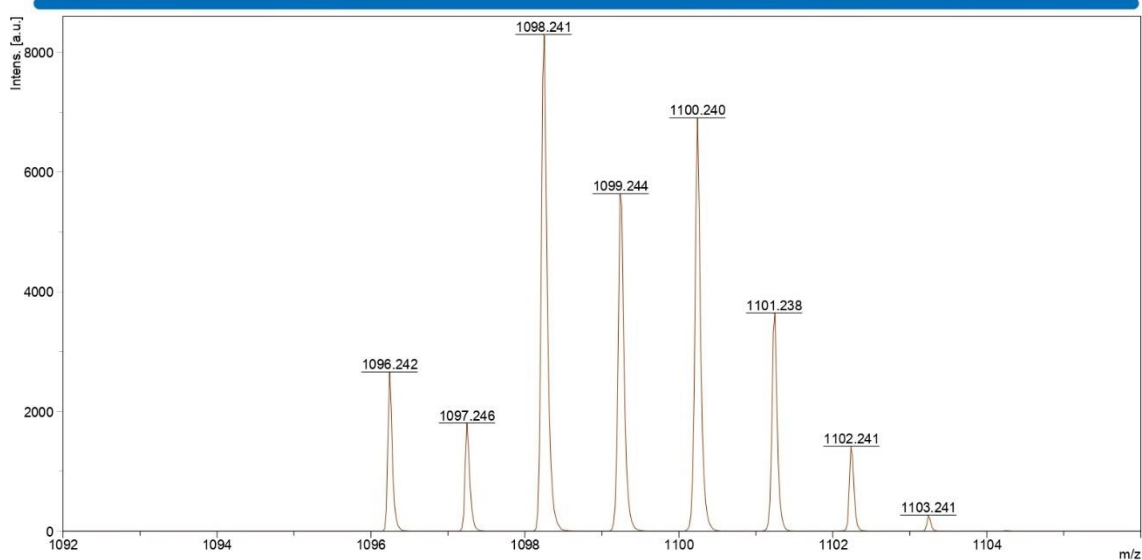
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File Name D:\Data\CRMPO\MALDI_14789_MS_02\0_F13\1

Bruker Daltonics

Figure S31: Maldi-ToF mass spectrum of molecule *Hel-Si₃*.

Centre régional de mesures physiques de l'Ouest (CRMPO) - RAPPORT D'ANALYSE

S. CAEDDU SC 133



Date of Acquisition 2023-10-23T14:41:57.806+02:00
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Bruker Daltonics

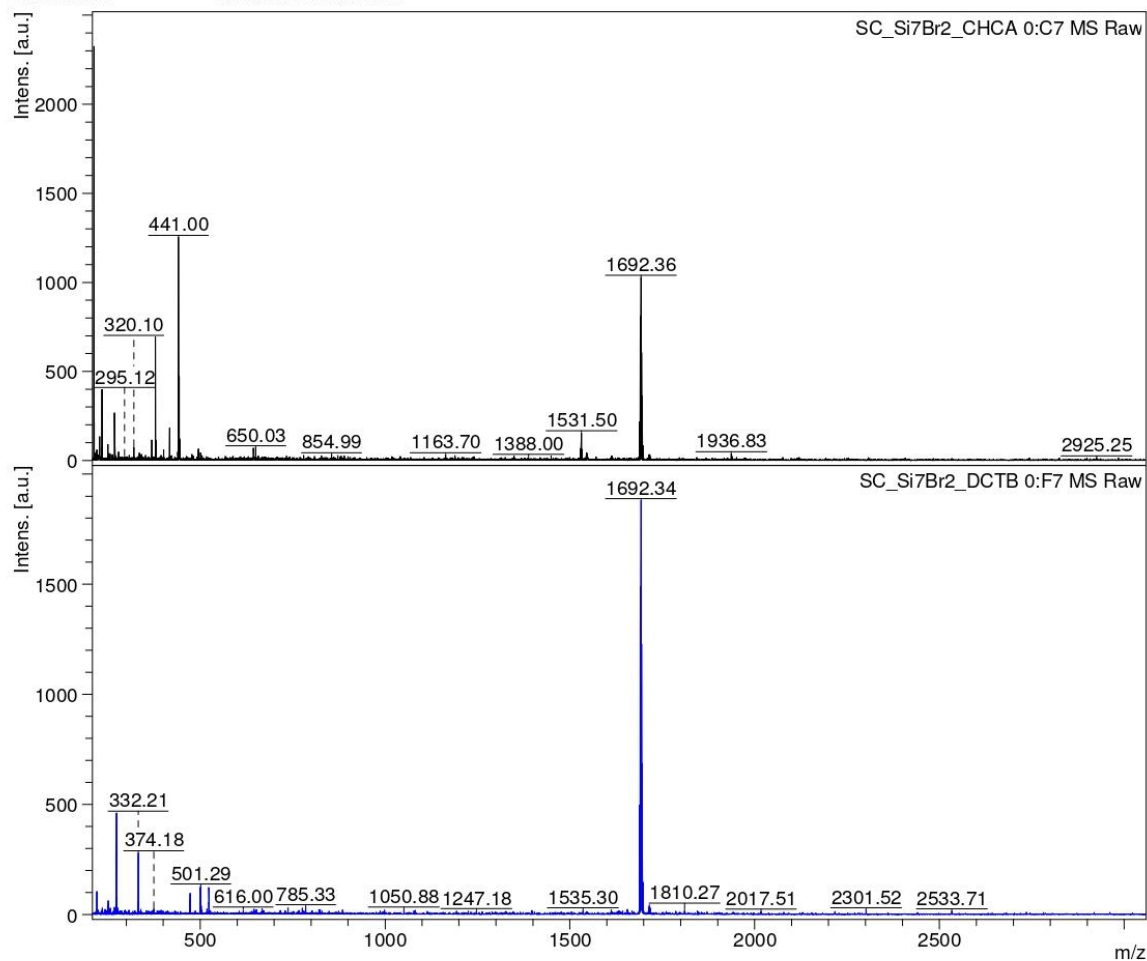
Figure S32: Maldi-ToF mass spectrum of molecule *Hel-Si₃*.

Comment 1

CHCA/DCTB in THF

Comment 2

Calibration in d:\..Bart



Acquisition Parameter

Date of acquisition 2024-01-26T15:21:16.787+01:00
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 Acquisition operation mode Reflector
 Voltage polarity POS
 Number of shots 500
 Name of spectrum used for calibration
 Calibration reference list used Cesium tri iodide positive mode

Instrument Info

User smo379
 Instrument ST-A2130
 Instrument type autoflex

Figure S33: Maldi-Tof mass spectrum of molecule *Hel-Si₇*.

S. CAEDDU SC 219

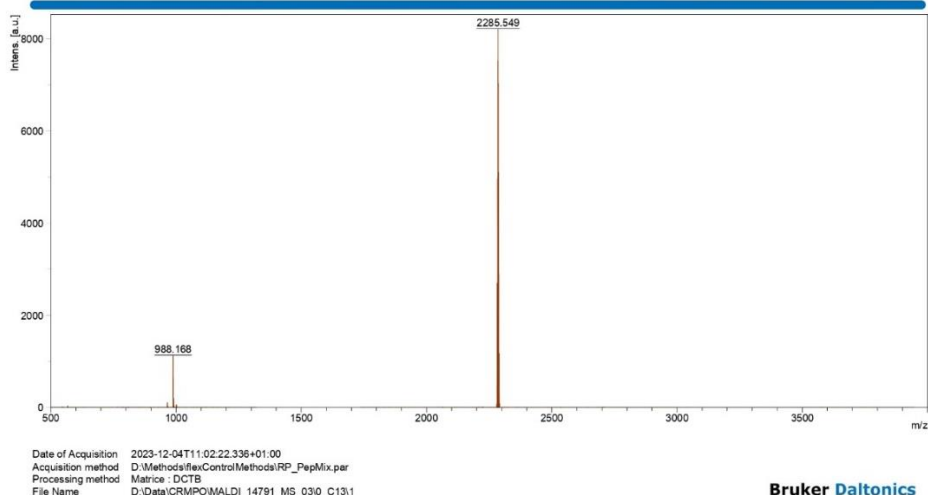
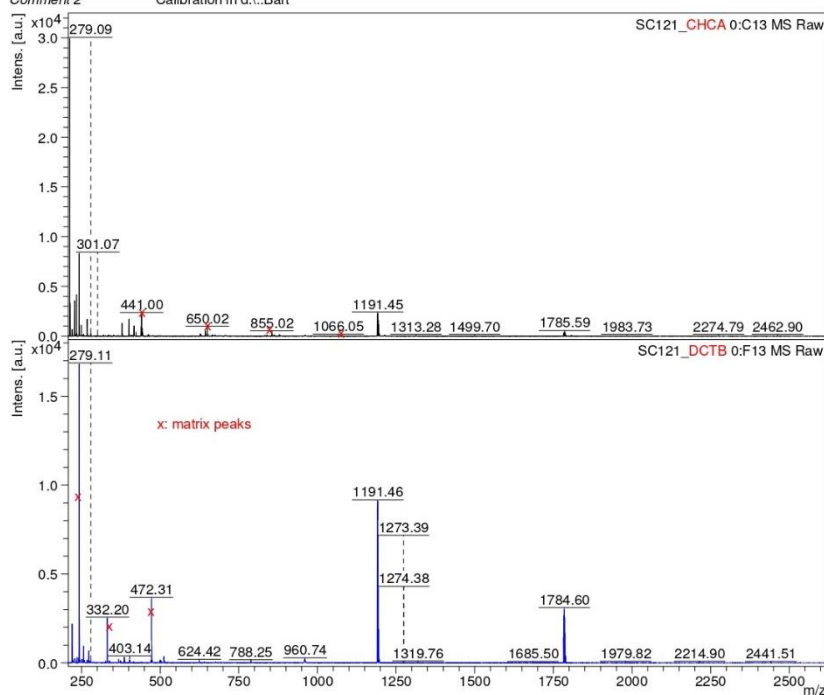


Figure S34: Maldi-ToF mass spectrum of molecule *Hel-Si₁₁*.

D:\Data\Users 2024January\Jan2624\Bart\SC121_DCTB\0_F13\1\1Ref

Comment 1 CHCA/DCTB in THF
 Comment 2 Calibration in d:\.Bart



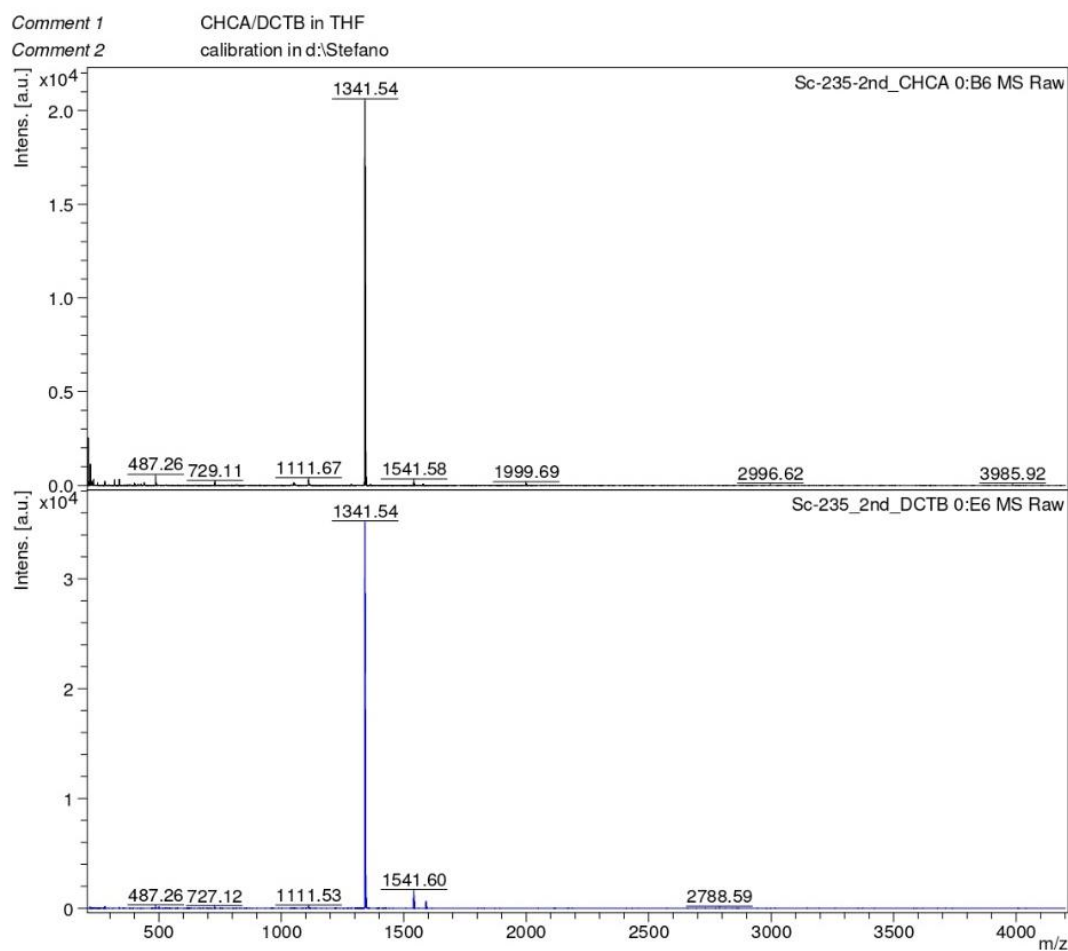
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 Number of shots: 500
 Name of spectrum used for calibration:
 Calibration reference list used: Cesium tri jodide positive mode

Instrument Info

User: smo379
 Instrument: ST-A2130
 Instrument type: autoflex

Figure S35: Maldi-ToF mass spectrum of molecule *Hel'-Si₃*



Acquisition Parameter

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Instrument Info

User smo379
 Instrument ST-A2130
 Instrument type autoflex

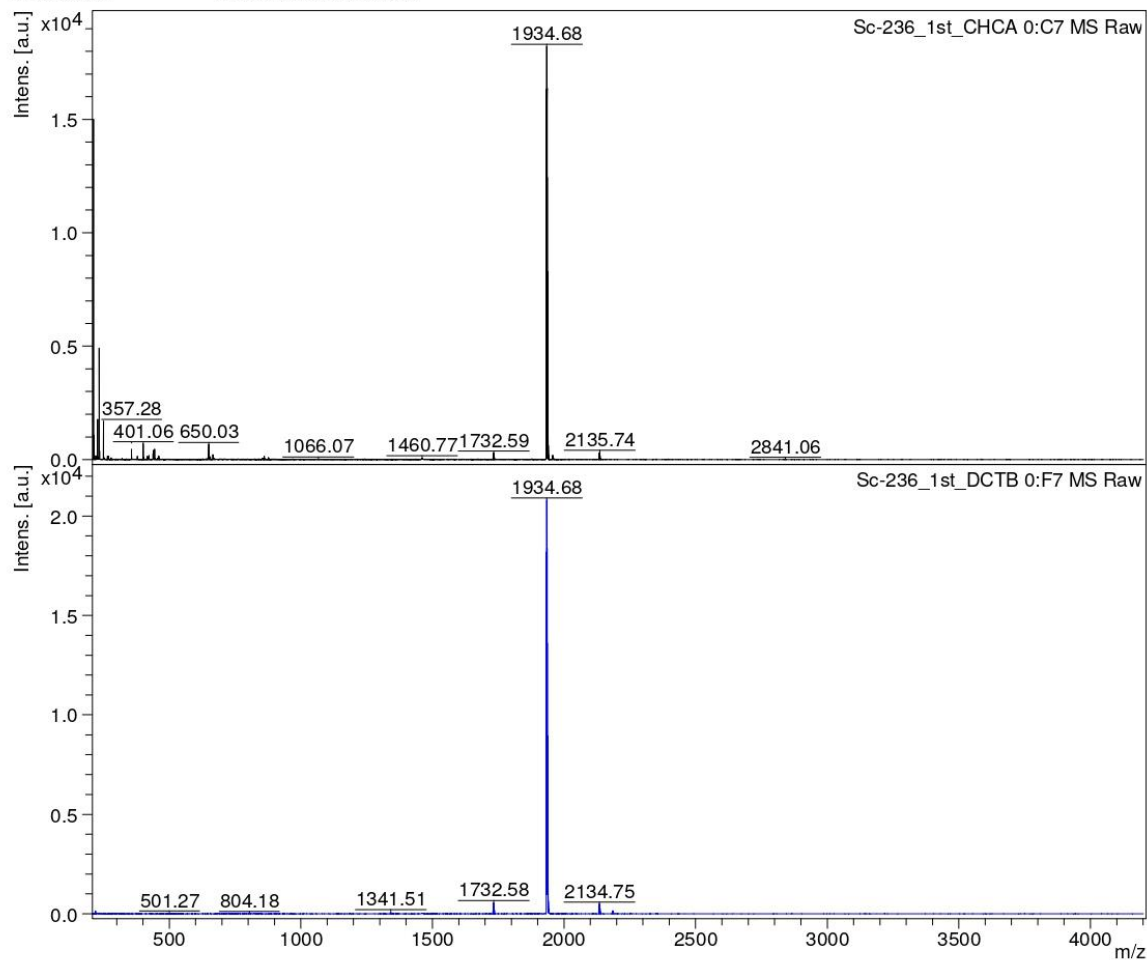
Figure S36: Maldi-Tof mass spectrum of molecule *Hel-Si₃*.

Comment 1

CHCA/DCTB in THF

Comment 2

calibration in d:\Stefano



Acquisition Parameter

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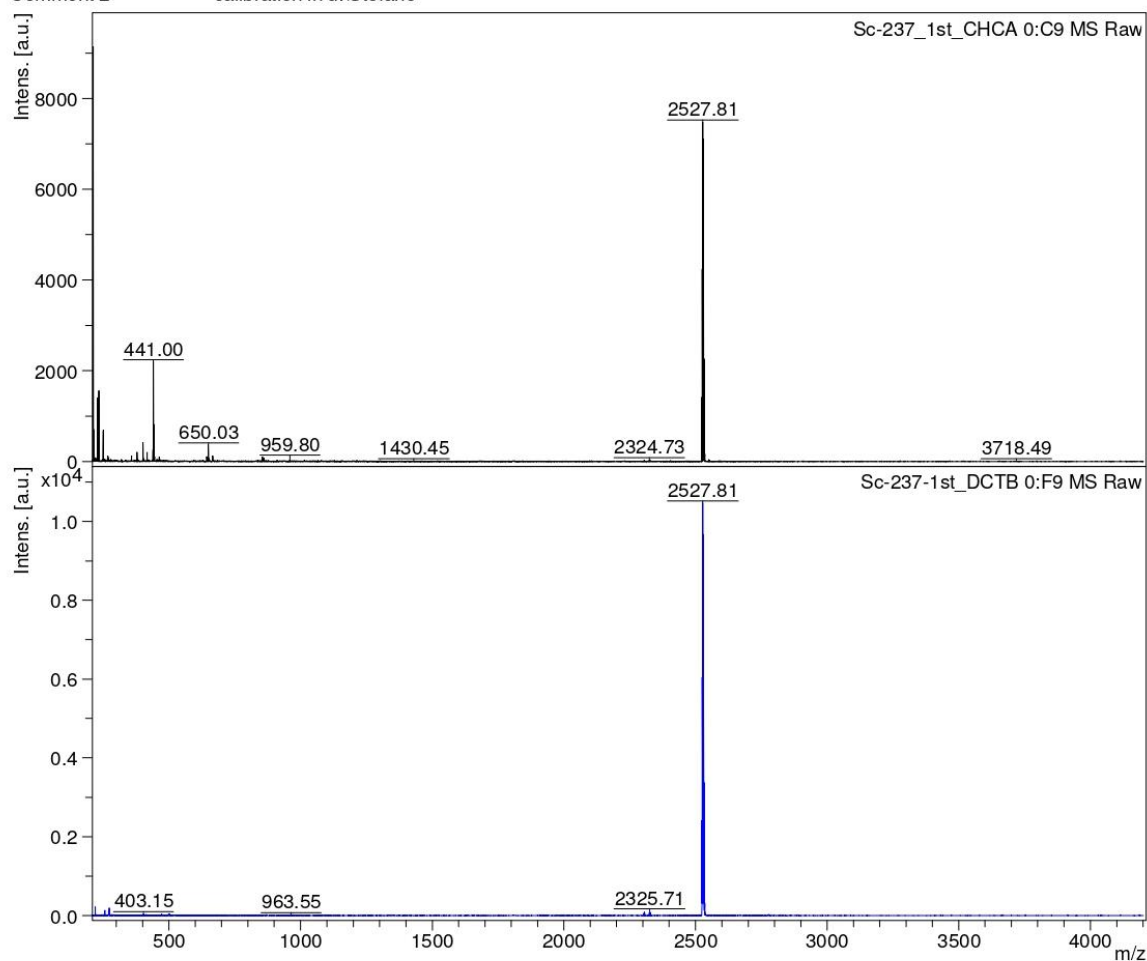
Instrument Info

User smo379
 Instrument ST-A2130
 Instrument type autoflex

Figure S37: Maldi-Tof mass spectrum of molecule **Hel-Si₇**.

Comment 1
Comment 2

CHCA/DCTB in THF
calibration in d:\Stefano



Acquisition Parameter

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 Name of spectrum used for calibration
 Calibration reference list used Csl_T6_9_12 positive mode

Instrument Info

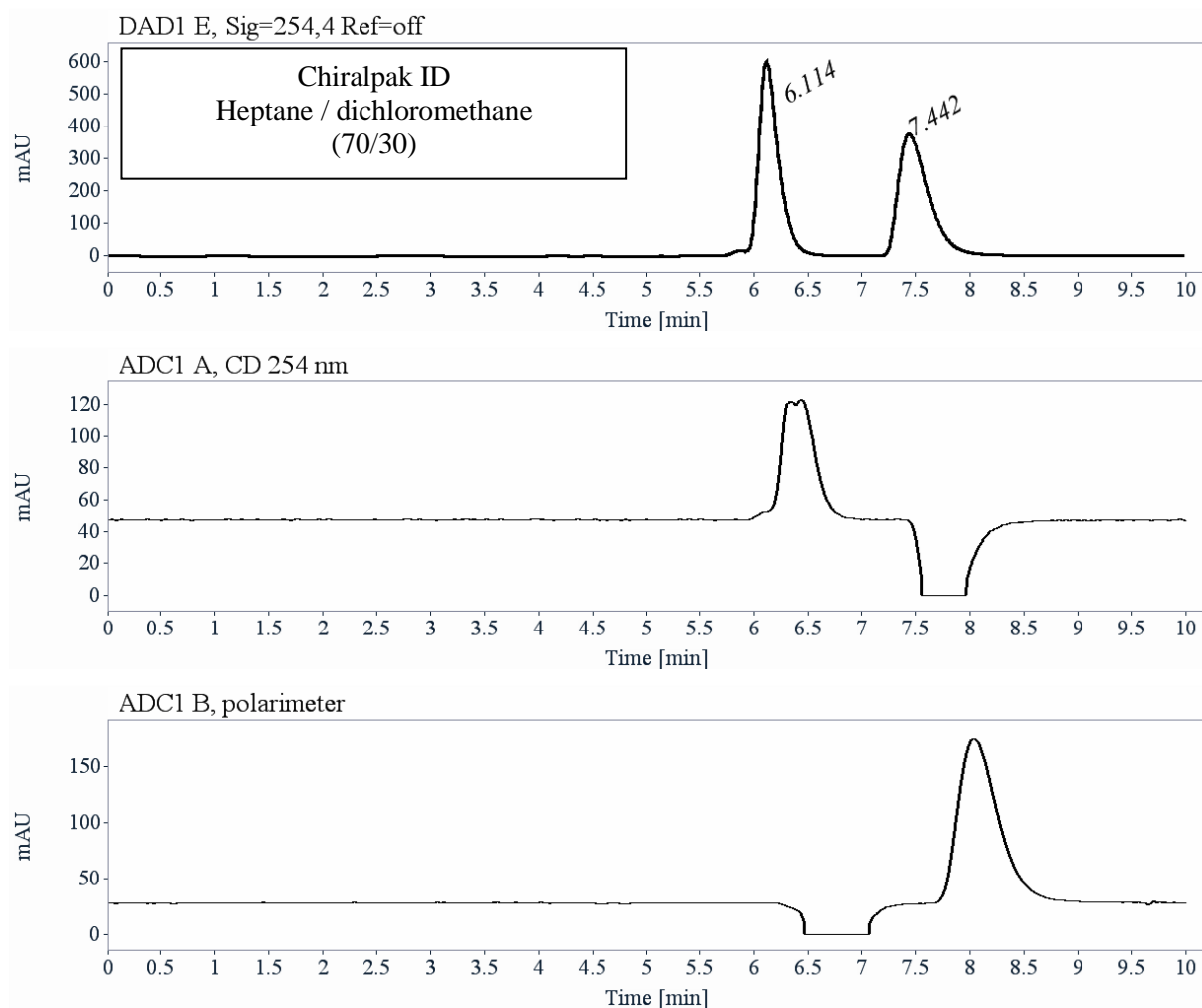
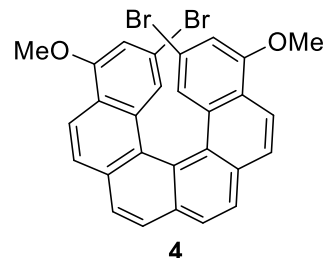
User smo379
 Instrument ST-A2130
 Instrument type autoflex

Figure S38: MalDI-ToF mass spectrum of molecule *Hel-Si₁₁*.

5. Enantiomeric resolution using chiral HPLC.

Analytical chiral HPLC separation for *rac-4*

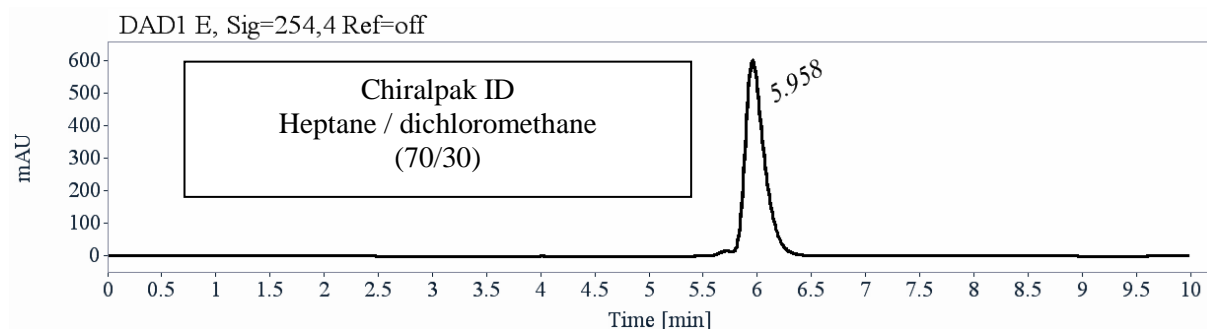
• *rac-4* is dissolved in dichloromethane, injected on the chiral column, Chiralpak ID (250 x 4.6 mm, 5 μ m, amylose tris(3-chloro-phenylcarbamate) immobilized on silica), and detected with an UV detector at 254 nm, a circular dichroism detector at 254 nm and a polarimetric detector. *M*-(**4**) is the first eluted enantiomer in these chromatographic conditions.



RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.11	7659	51.62	1.07		
7.44	7179	48.38	1.52	1.42	3.22
Sum	14838	100.00			

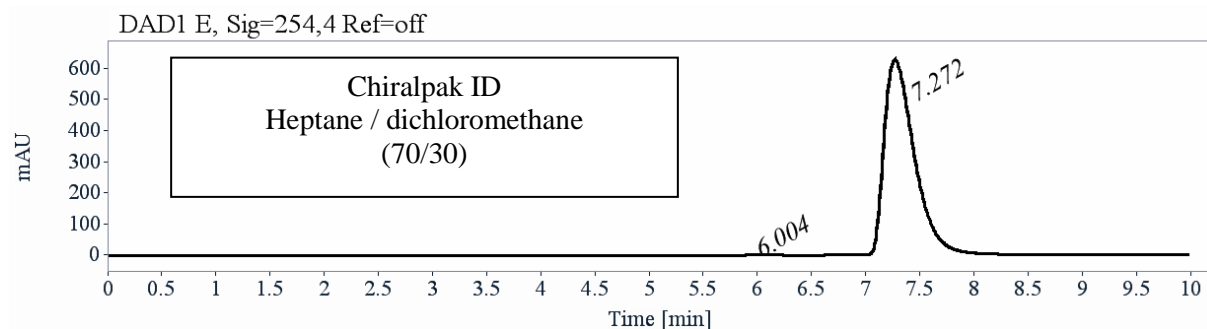
Preparative separation for *rac*-4:

- Sample preparation: About 350 mg of *rac*-4 are dissolved in 65 mL of dichloromethane.
- Chromatographic conditions: Chiralpak ID (250 x 10 mm, 5 μ m), hexane / dichloromethane (70/30) as mobile phase, flow-rate = 5 mL/min, UV detection at 330 nm.
- Injections (stacked): 380 times 170 μ L, every 4 minutes.
- First fraction: 162 mg of *M*-(4) with ee > 99.5 %



RT [min]	Area	Area%
5.96	7409	100.00
Sum	7409	100.00

- Second fraction: 142 mg of *P*-(4) with ee > 99.5 %



RT [min]	Area	Area%
6.00	12	0.10
7.27	12081	99.90
Sum	12094	100.00

6. Differential Scanning Calorimetry

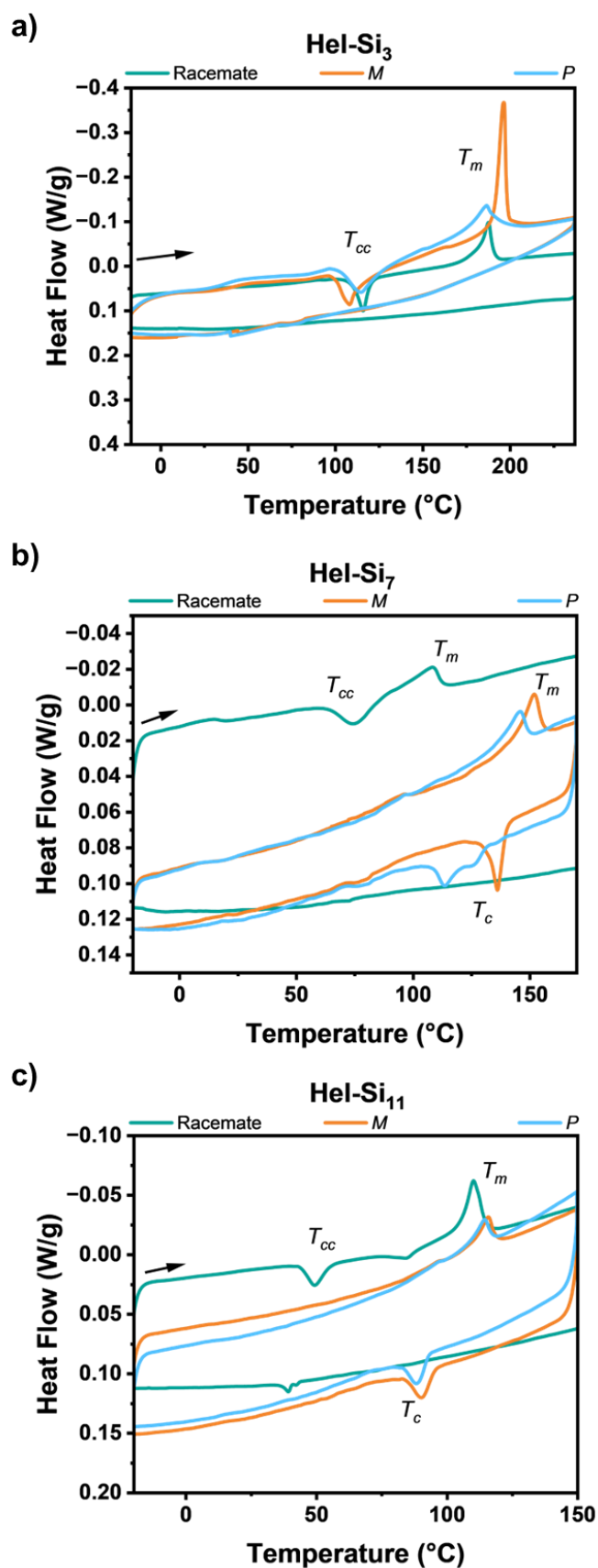


Figure S39: DSC thermograms of **Hel-Si_n**. Endothermic transitions are shown up. The 2nd heating and cooling run are shown, with a heating/cooling rate of 10 K min^{-1} .

7. Polarized Optical Microscopy

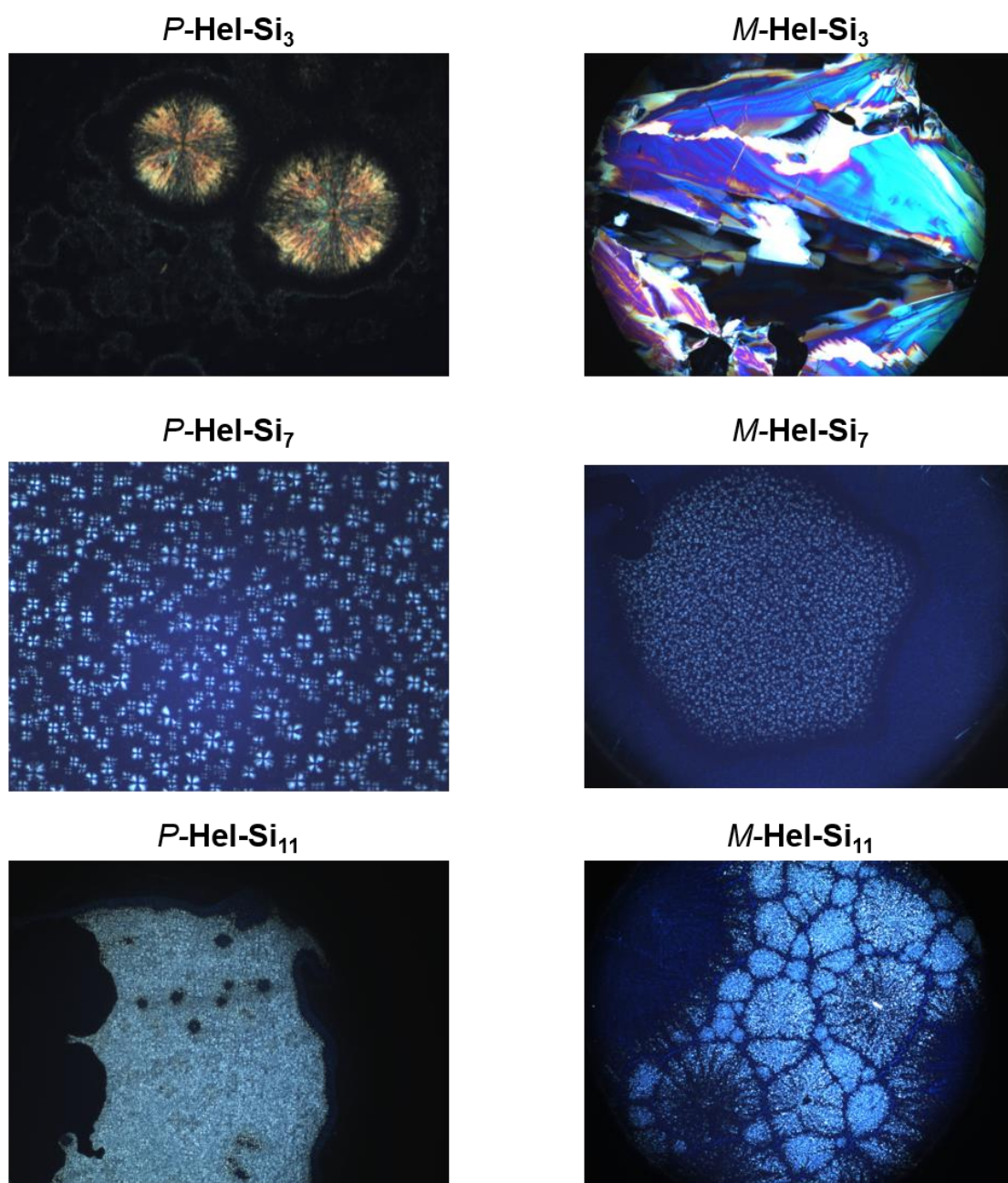


Figure S40: POM images of the different *P* and *M* enantiomers of *Hel-Si*_{3,7,11} highlighting their crystalline character in the solid state.

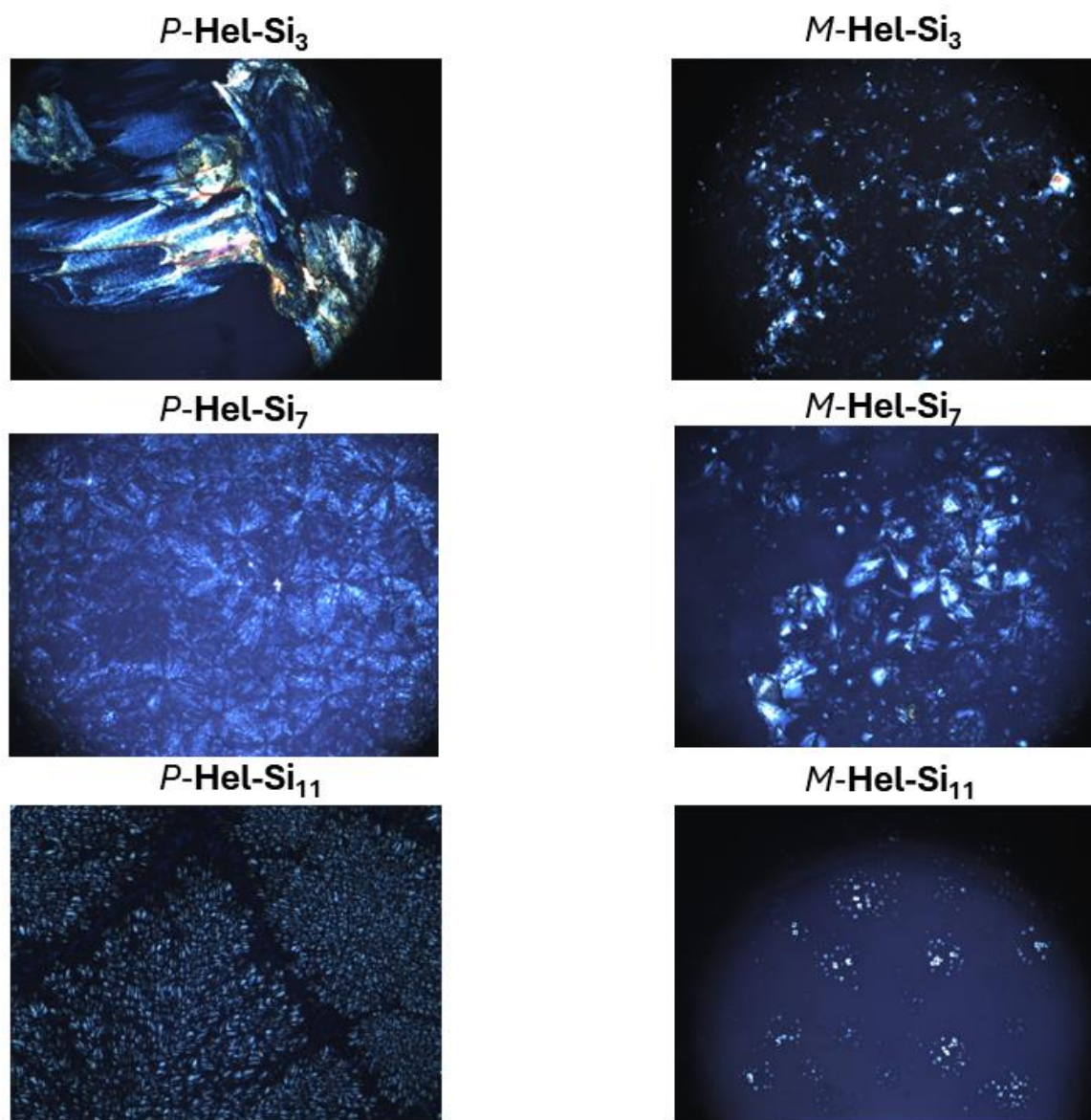


Figure S41: POM images of the different *P* and *M* enantiomers of **Hel-Si_n**, the different samples were drop casted on a quartz plate and analysed before performing ECD and CPL in solid state.

8. SAXS

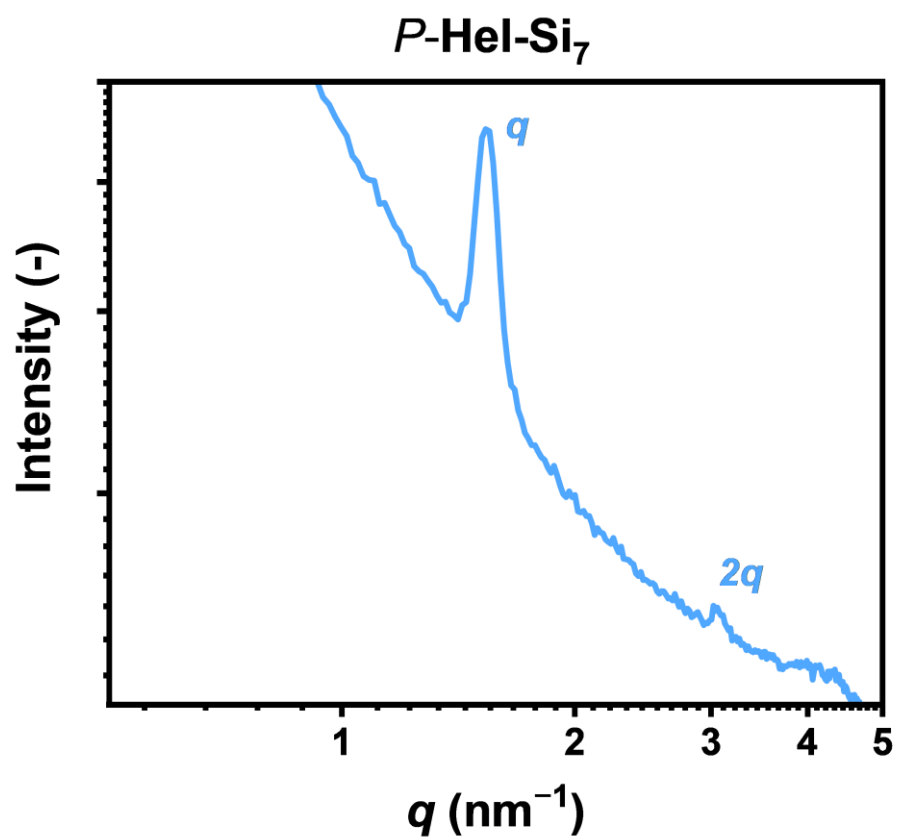


Figure S42: Zoom-in of the MAXS region of *P*-HelSi₇, clearly showing the lamellar pattern in the low intensity peaks

9. X-Ray crystallographic analyses

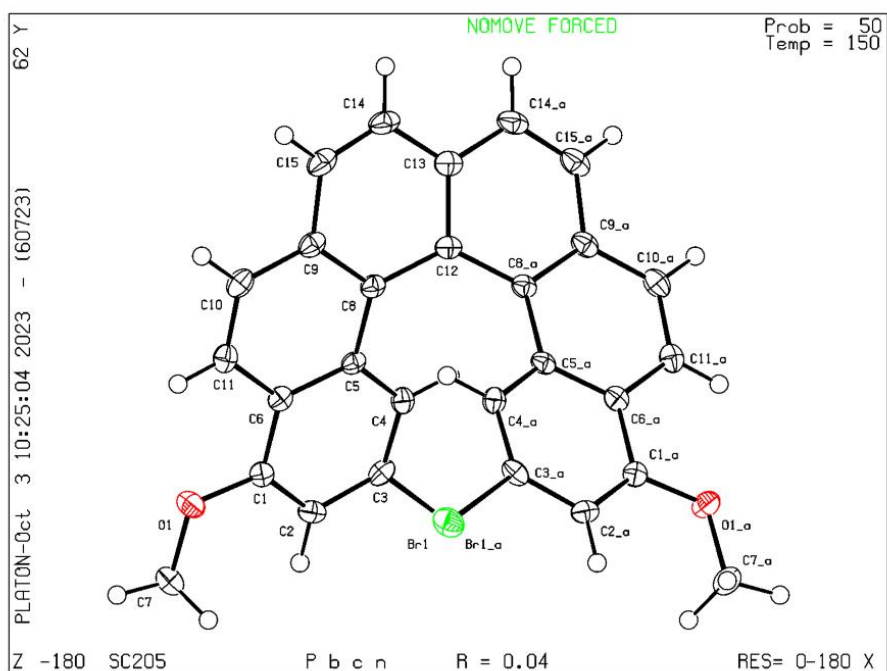


Figure S43: ORTEP structure of *rac-4*.

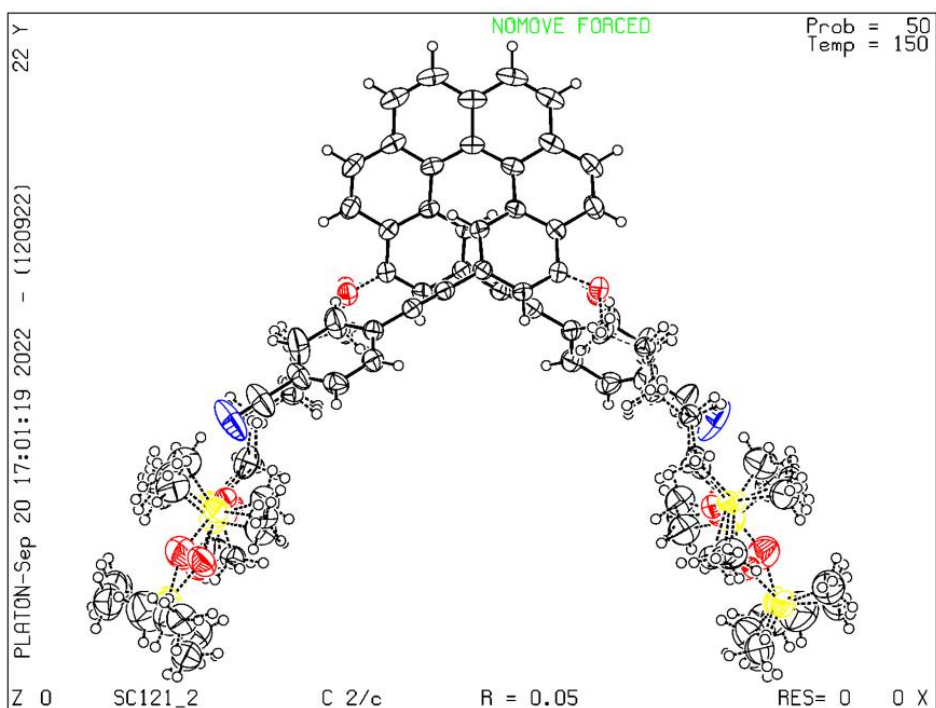


Figure S44: ORTEP structure of *rac-Hel'-Si₃*

Table S1: Crystallographic data *rac-4* and *rac-Hel⁺-Si₃*.

	<i>rac-4</i>	<i>rac-Hel⁺-Si₃</i>
Empirical formula	C ₂₈ H ₁₈ Br ₂ O ₂	C ₆₈ H ₈₂ N ₂ O ₆ Si ₆
CCDC number	2368946	2368947
Formula weight	546.24 g/mol	1191.89 g/mol
Temperature	150(2) K	150(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	orthorhombic, Pbcn	monoclinic, C2/c
a	14.9838(13) Å	38.94(7) Å
b	9.3761(9) Å	9.5940(16) Å
c	15.4285(15) Å	19.295(2) Å
α	90°	90°
β	90°	102.551(6)°
γ	90°	90°
Volume	2167.5(4) Å ³	7036.5(19) Å ³
Z, Calculated density	4, 1.674 g·cm ⁻³	4, 1.125 g·cm ⁻³
Absorption coefficient	3.764 mm ⁻¹	0.166 mm ⁻¹
F(000)	1088	2544
Crystal size	0.300 x 0.150 x 0.100 mm	0.680 x 0.210 x 0.090 mm
Crystal color	yellow	yellow
Crystal description	prism	stick
Theta range for data collection	2.563 to 27.496°	2.143 to 26.372°
(sinθ/λ) _{max}	0.650 Å ⁻¹	0.625 Å ⁻¹
h_min, h_max	-18, 19	-48, 48
k_min, k_max	-12, 11	-11, 11
l_min, l_max	-20, 20	-23, 24
Reflections collected / unique	15024 / 2487 [R(int) = 0.0365]	36759 / 7171 [R(int) = 0.0515]
Reflections [I>2σ]	2157	5564
Completeness to theta_max	1.000	0.999
Absorption correction type	multi-scan	multi-scan
Max. and min. transmission	0.686, 0.493	0.985, 0.892
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	2487 / 0 / 147	7171 / 295 / 683
S (Goodness-of-fit)	1.182	1.056
Final R indices [I>2σ]	R1 = 0.0352, wR2 = 0.0627	R1 = 0.0509, wR2 = 0.1249
R indices (all data)	R1 = 0.0443, wR2 = 0.0656	R1 = 0.0687, wR2 = 0.1352
Largest diff. peak and hole	0.414 and -0.422 e·Å ⁻³	0.249 and -0.244 e·Å ⁻³

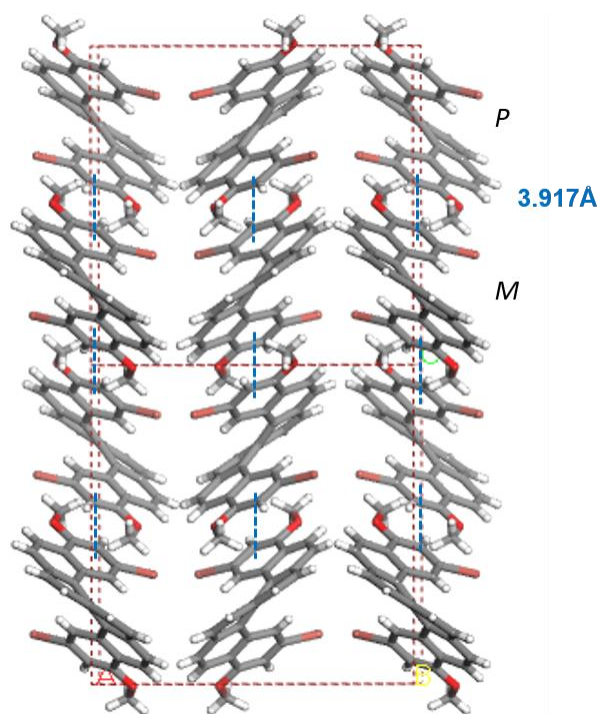


Figure S45: Supramolecular organisation of rac-4 in the solid state, through π stacking between P and M helices.

10. Electronic circular dichroism (ECD)

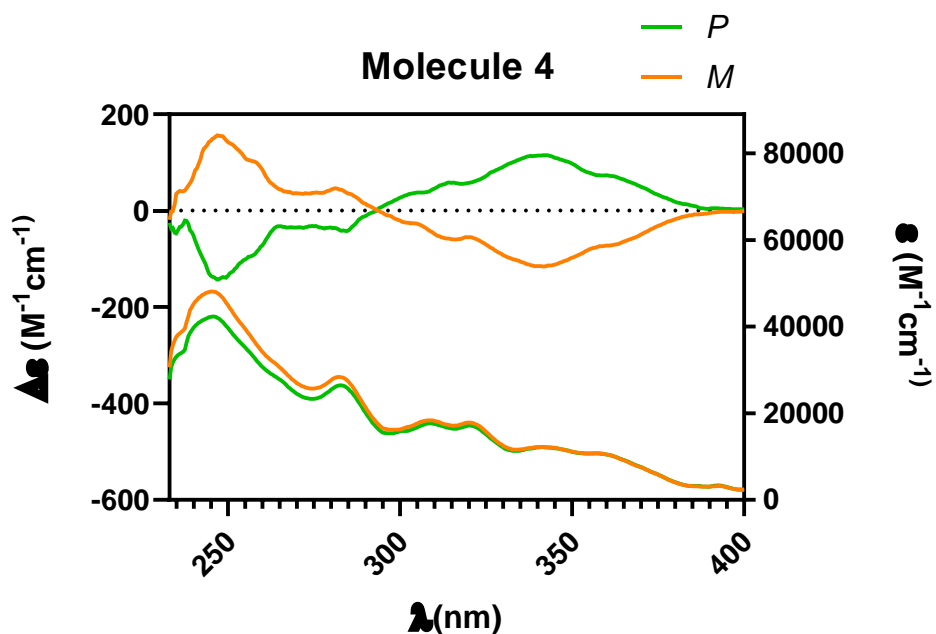


Figure S46: UV-Vis and ECD spectra of **4** enantiomers (DCM, $c = 2.4 \times 10^{-5} M$, $l = 0.2$ cm)

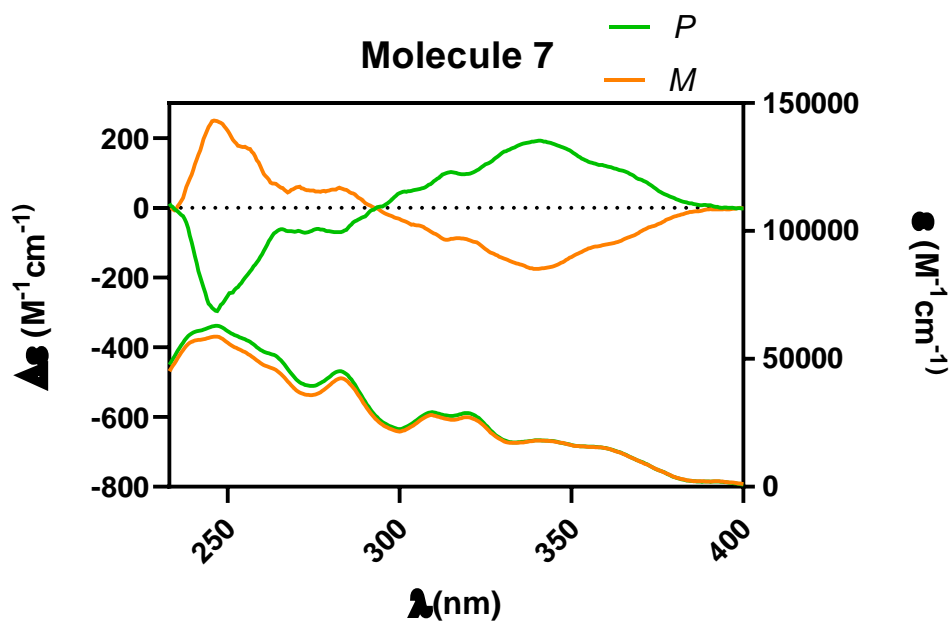


Figure S47: UV-Vis and ECD spectra of **7** enantiomers (DCM, $c = 1.8 \times 10^{-5} M$, $l = 0.2$ cm)

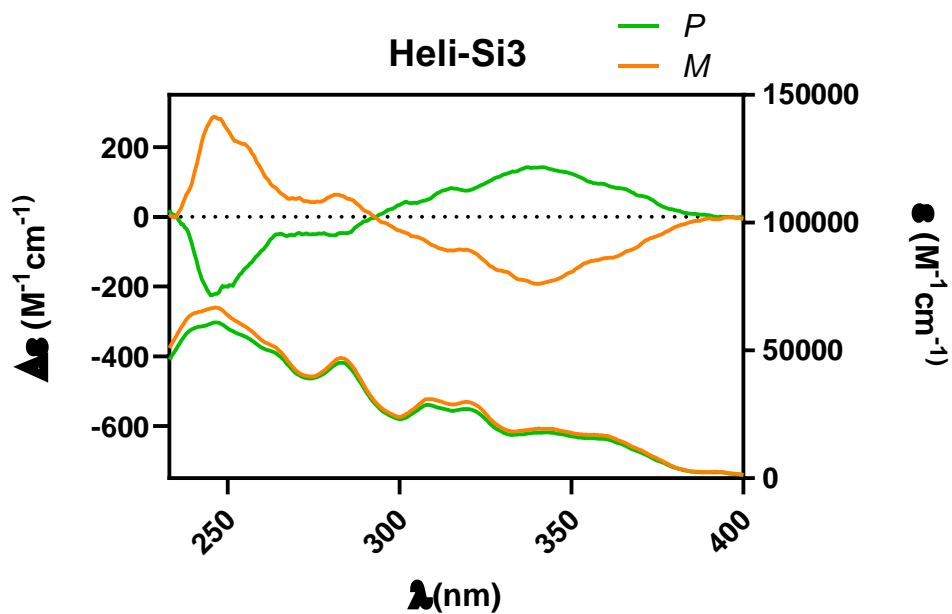


Figure S48: UV-Vis and ECD spectra of **Heli-Si₃** enantiomers (DCM, $c = 1.4 \times 10^{-5} M$, $l = 0.2 \text{ cm}$)

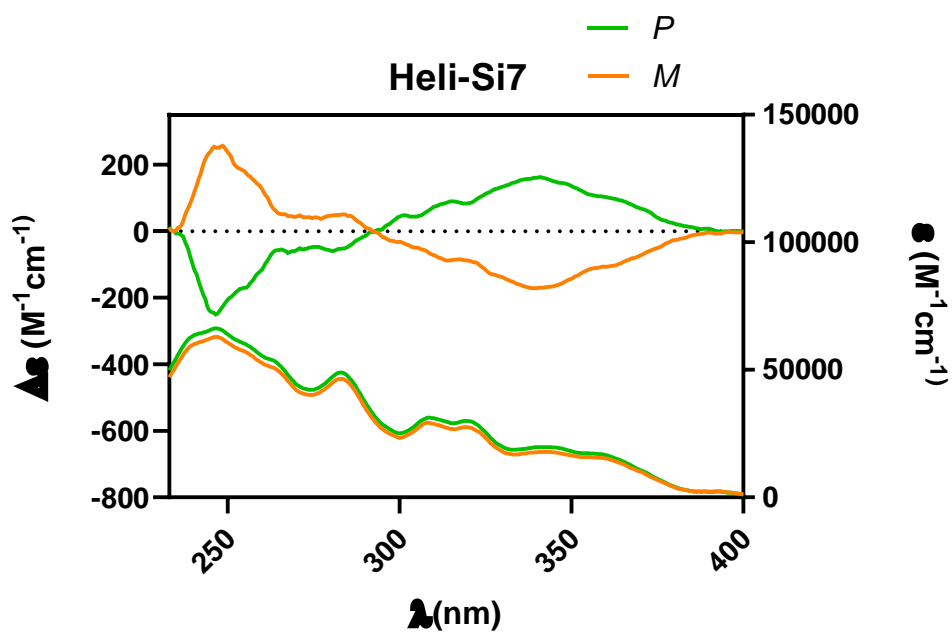


Figure S49: UV-Vis and ECD spectra of molecule **Heli-Si₇** enantiomers (DCM, $c = 1.5 \times 10^{-5} M$, $l = 0.2 \text{ cm}$)

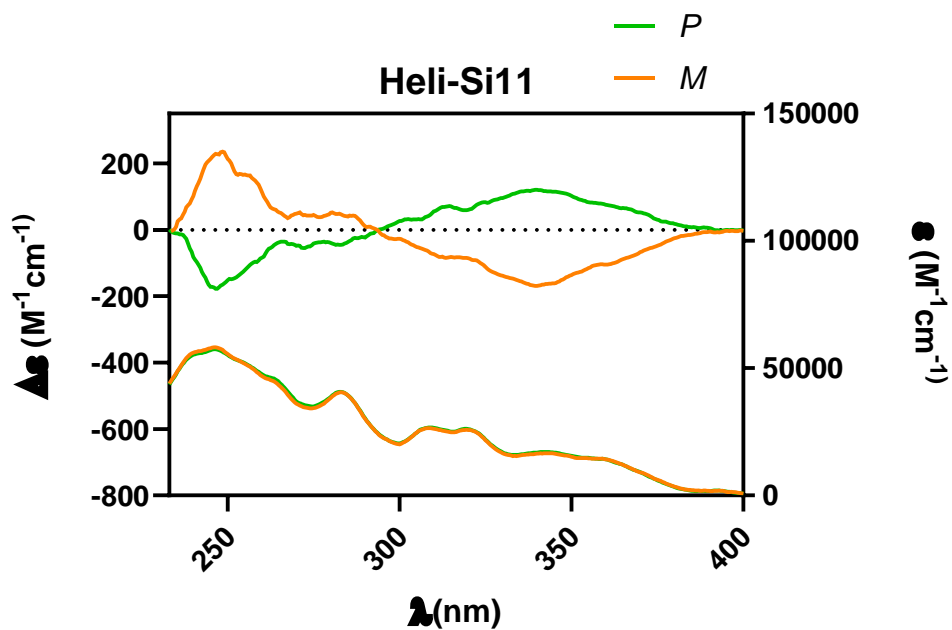


Figure S50: UV-Vis and ECD spectra of *Heli-Si11* enantiomers, (DCM, $c = 1.2 \times 10^{-5} M$, $l = 0.2 cm$)

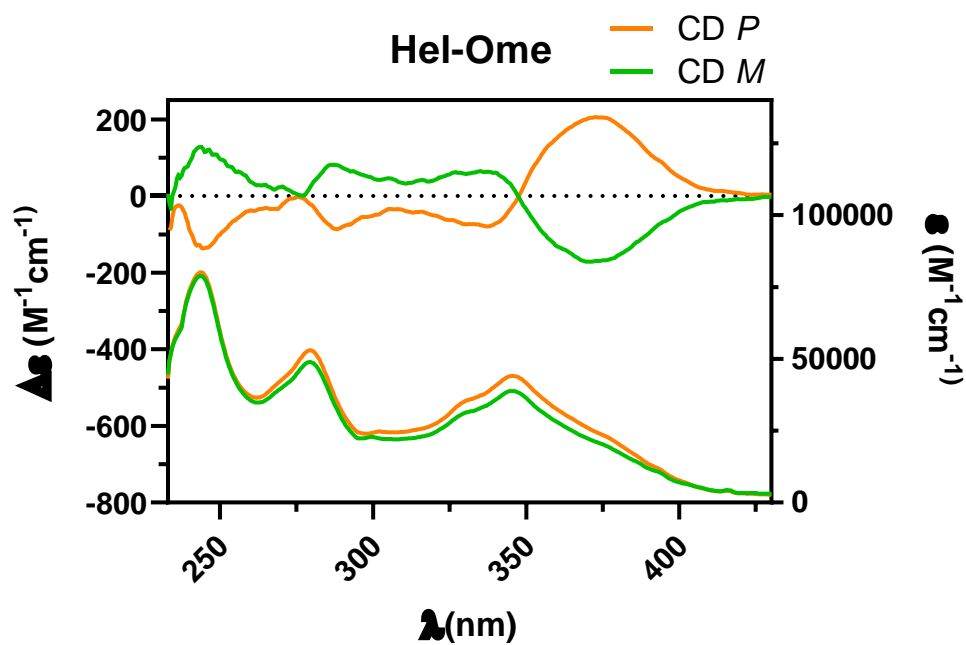


Figure S51: UV-Vis and ECD spectra of *Hel-Ome* enantiomers (DCM, $c = 1.2 \times 10^{-5} M$, $l = 0.2 cm$)

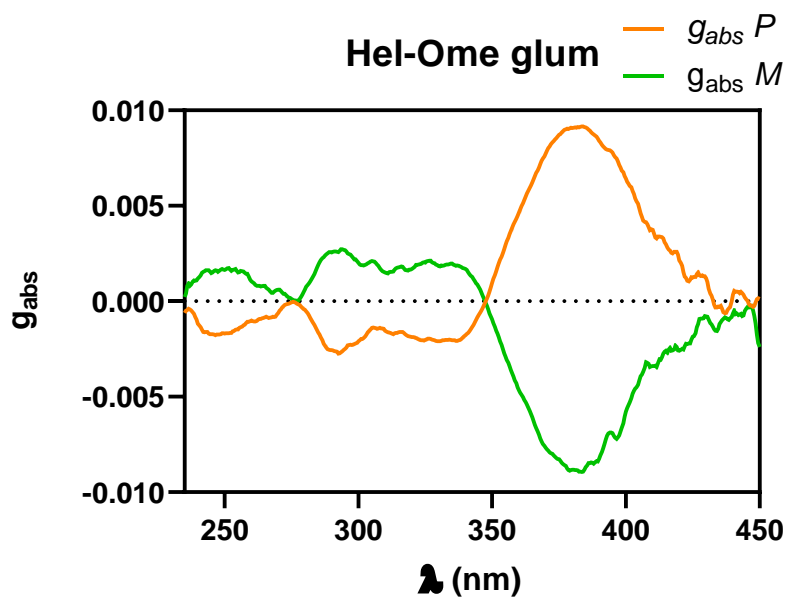


Figure S52: g_{abs} plot of molecule Hel-Ome enantiomers, g_{abs} at 380 nm = $8.83 \cdot 10^{-3}$.

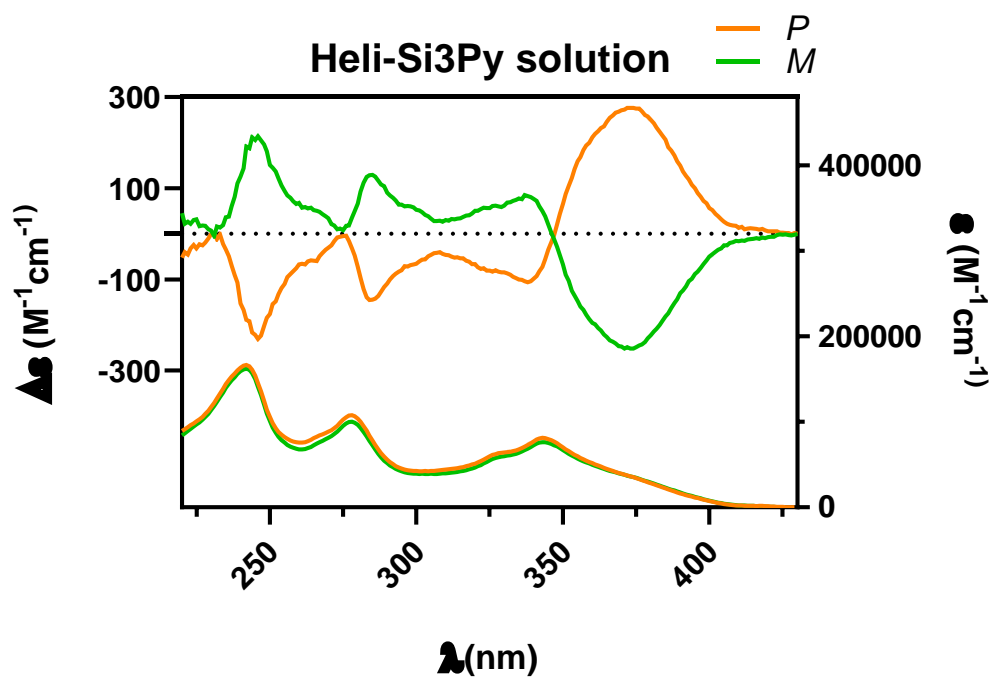


Figure S53: UV-Vis and ECD spectra of Heli-Si₃Py enantiomers (MCH, $c = 1.1 \times 10^{-5} M$, $l = 0.2$ cm)

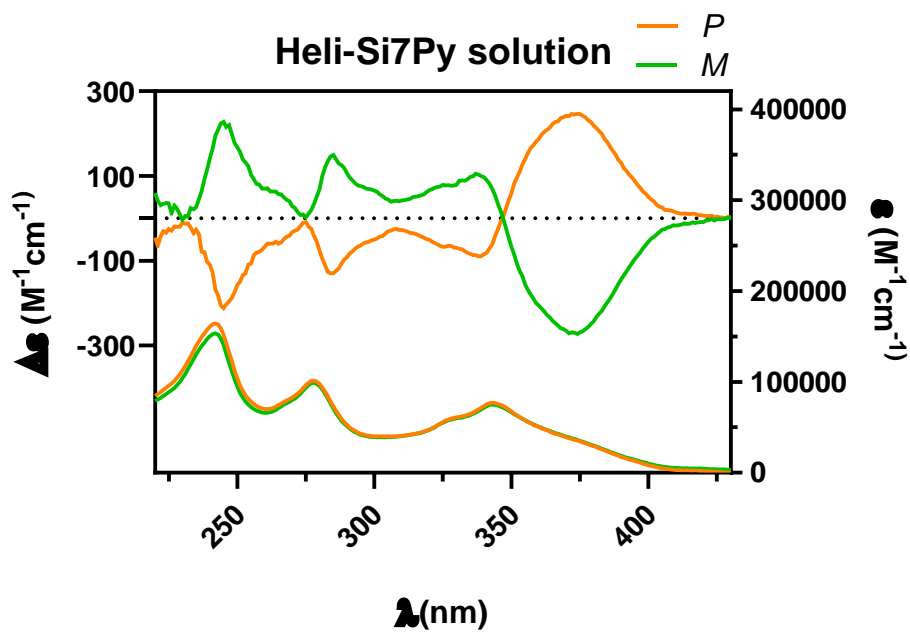


Figure S54: UV-Vis and ECD spectra of **Heli-Si₇Py** enantiomers (MCH, $c_M = 1.2 \times 10^{-5} M$, $c_P = 1.5 \times 10^{-5} M$, $l = 0.2$ cm)

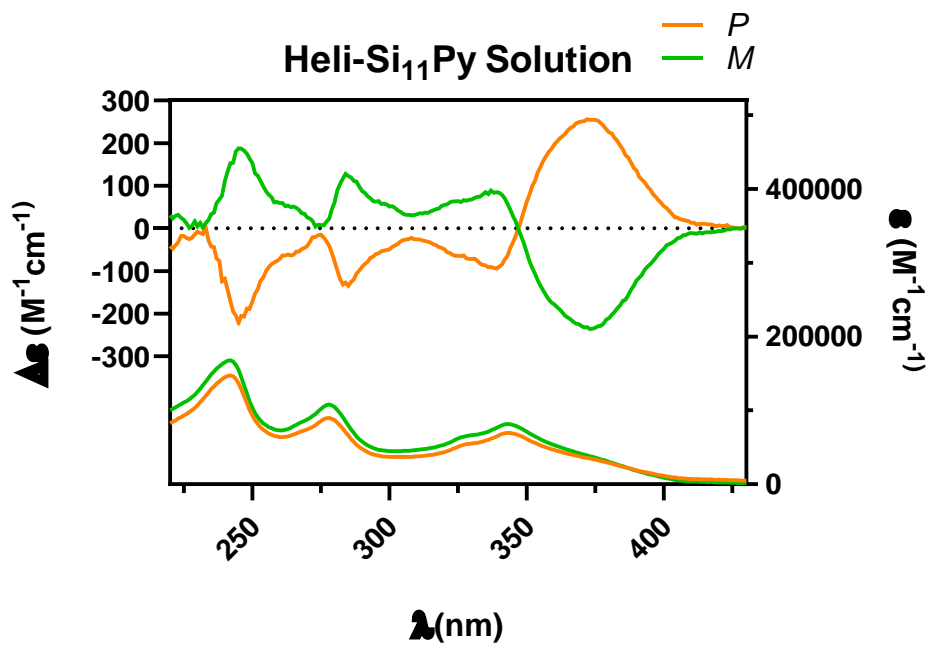


Figure S55: UV-Vis and ECD spectra of **Heli-Si₁₁Py** enantiomers (MCH, $c_M = 1.2 \times 10^{-5} M$, $c_P = 1.0 \times 10^{-5} M$, $l = 0.2$ cm)

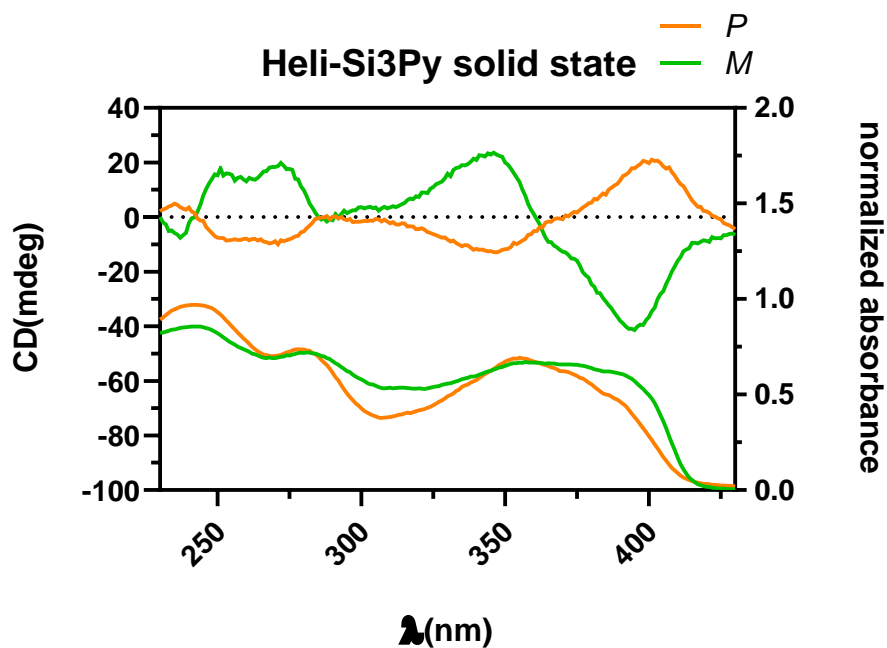


Figure S56: UV-Vis and ECD spectra in thin-film of **Heli-Si₃Py** enantiomers, support quartz, deposition by drop-casting.

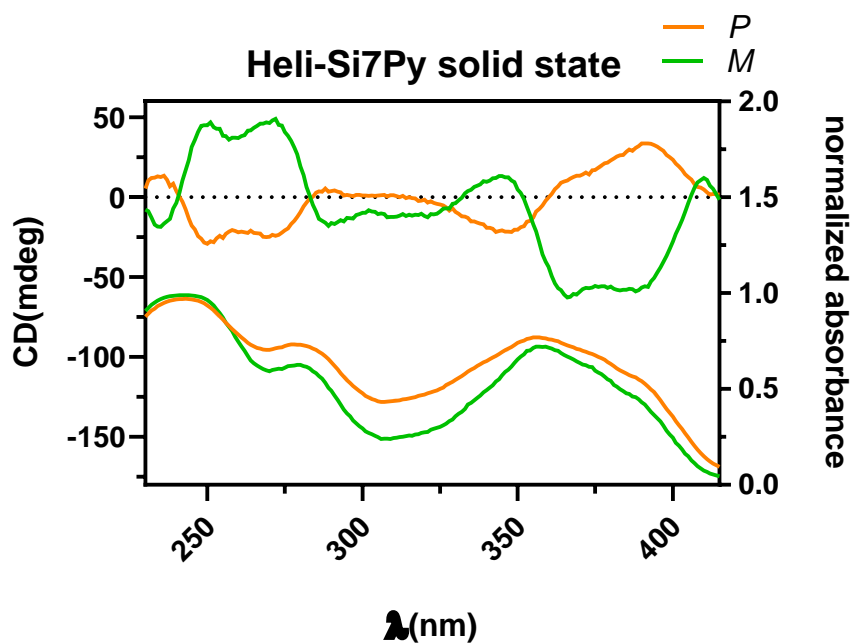


Figure S57: UV-Vis and ECD spectra in thin-film of **Heli-Si₇Py** enantiomers, support quartz, deposition by drop-casting.

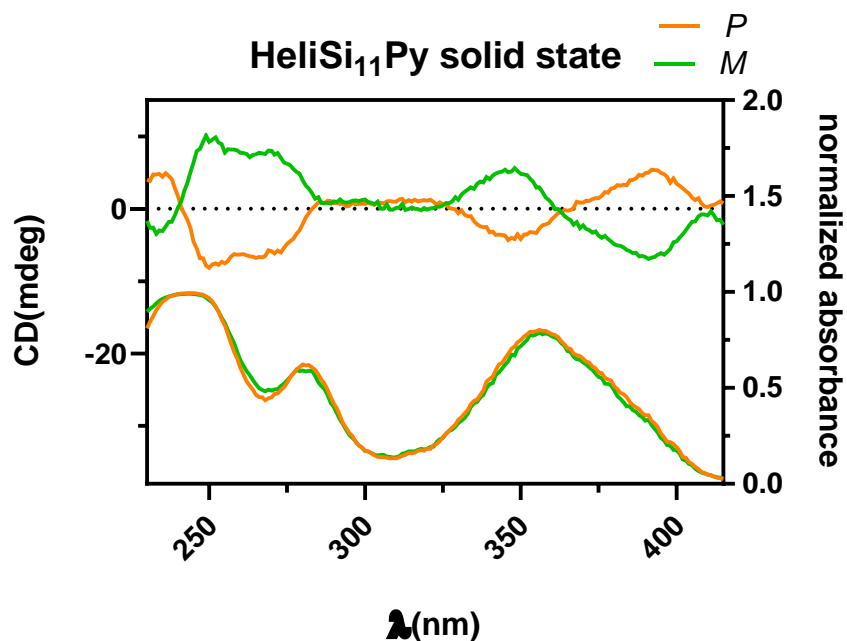


Figure S58: UV-Vis and ECD spectra in thin-film of **Hel-Si₁₁** enantiomers, support quartz, deposition by drop-casting.

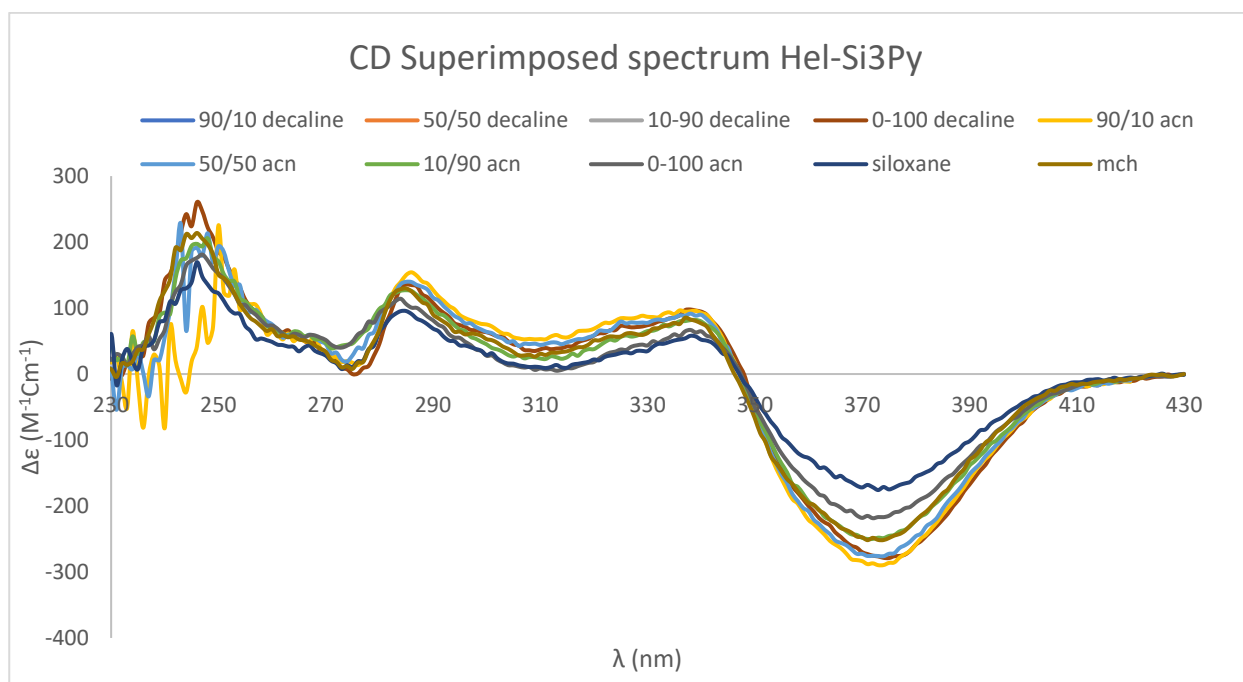


Figure S59: ECD spectra showing an attempt to form self-assembly structures in solution for the molecule **Hel-Si₃**, Tetrahydrofuran (THF) was used as a main solvent in combination with decaline, or acetonitrile as antisolvents at different percentage (THF-antisolvent), methyl cyclohexane and siloxanes were used as pure solvents. Only one enantiomer was analysed to decrease the number of experiments needed to observe self assembly.

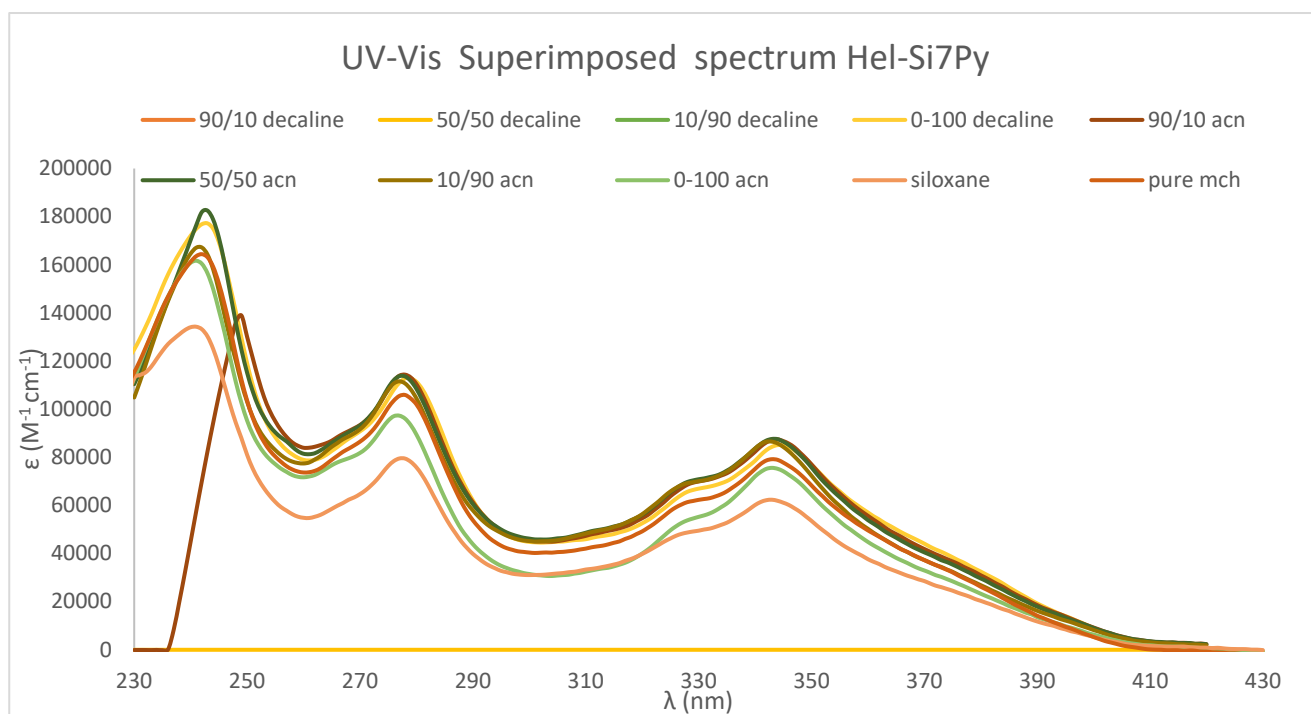


Figure S60: UV-Vis spectra showing an attempt to form self-assembly structures in solution of the molecule **Hel-Si₃** (see description of Figure S56 for further details).

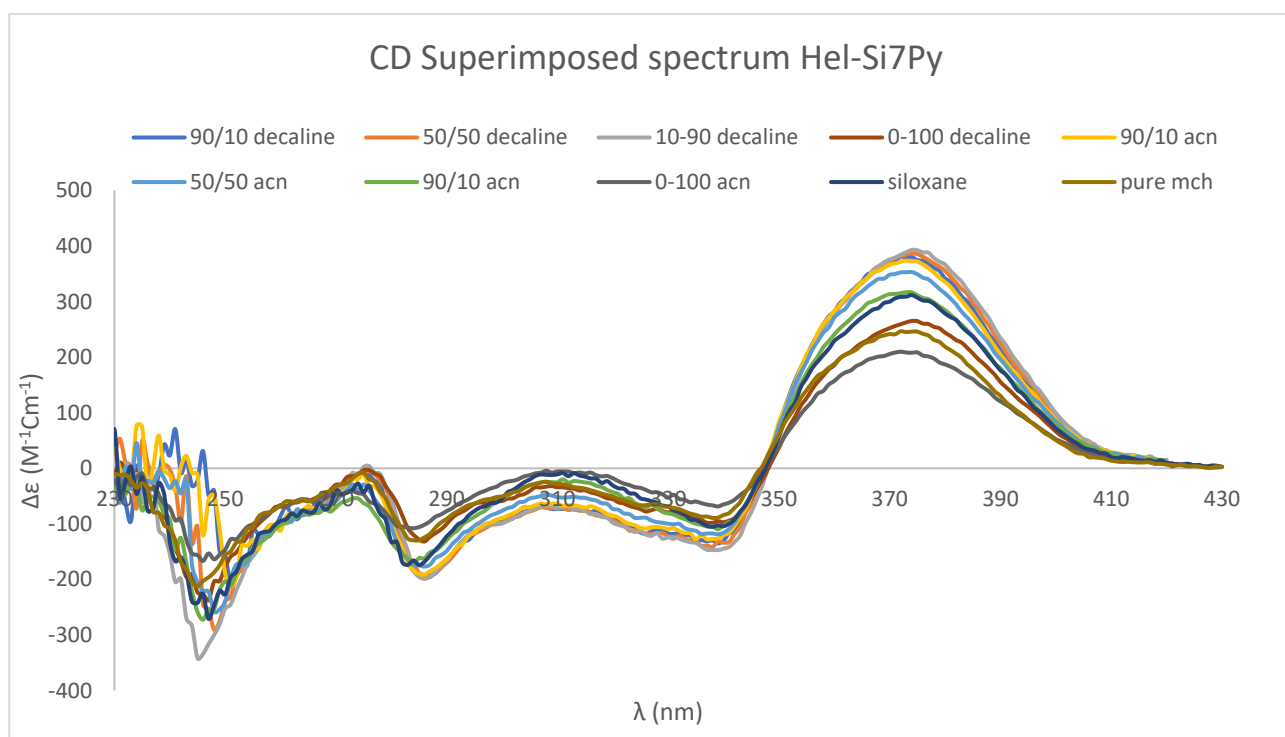


Figure S61: ECD spectra showing an attempt to form self-assembly structures in solution of the molecule **Hel-Si₇**. (see description of Figure S56 for further details).

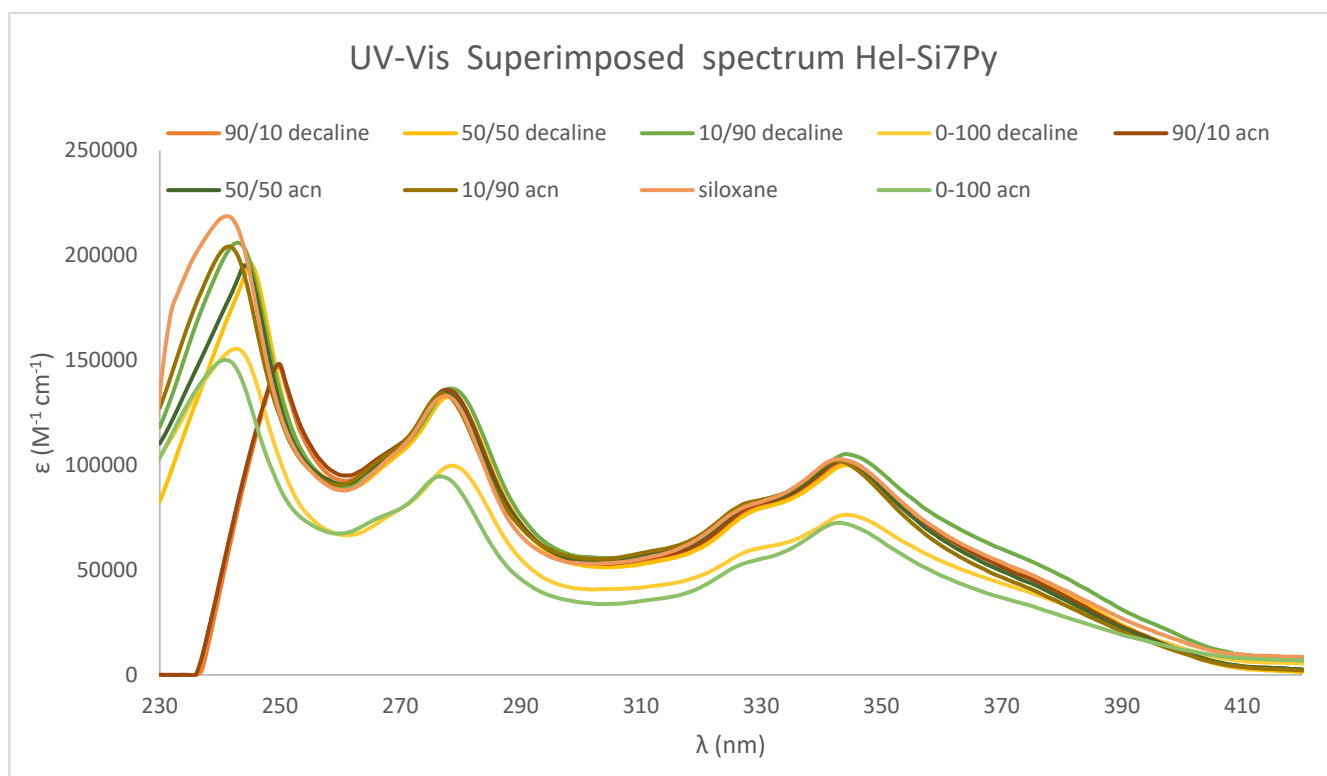


Figure S62: UV-Vis spectra showing an attempt to form self-assembly structures in solution of the molecule **Hel-Si7**. (see description of Figure S56 for further details).

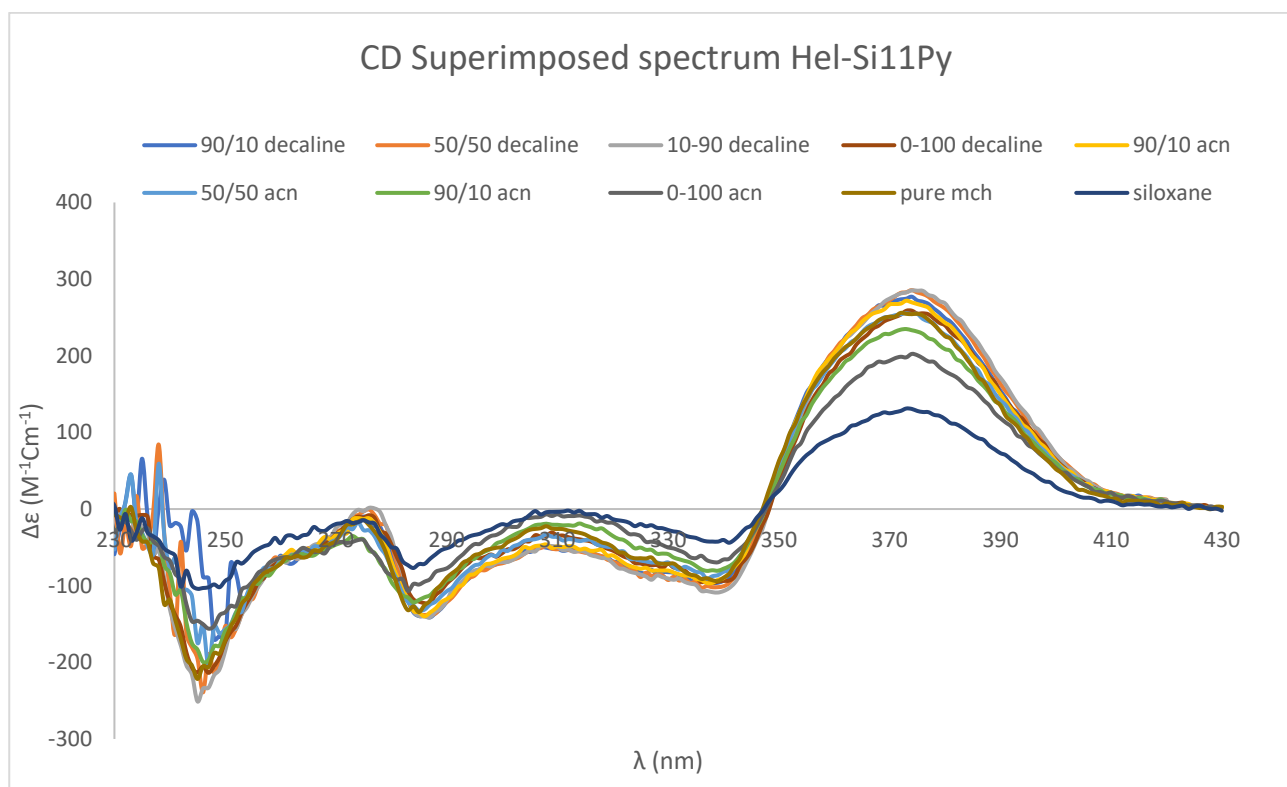


Figure S63: ECD spectra showing an attempt to form self-assembly structures in solution of the molecule **Hel-Si11**. (see description of Figure S56 for further details).

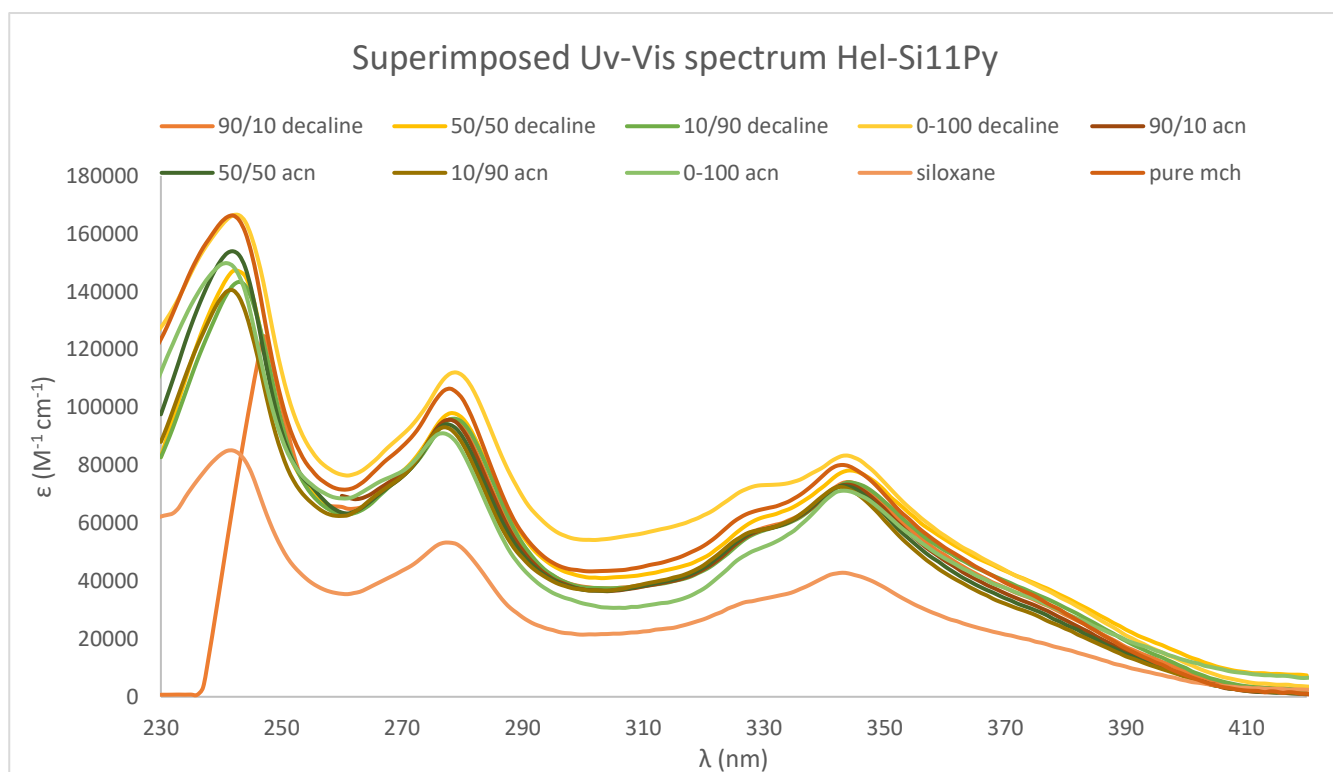


Figure S64: Uv-vis spectra showing an attempt to form self-assembly structures in solution of the molecule **Hel-Si₁₁**. (see description of Figure S56 for further details).

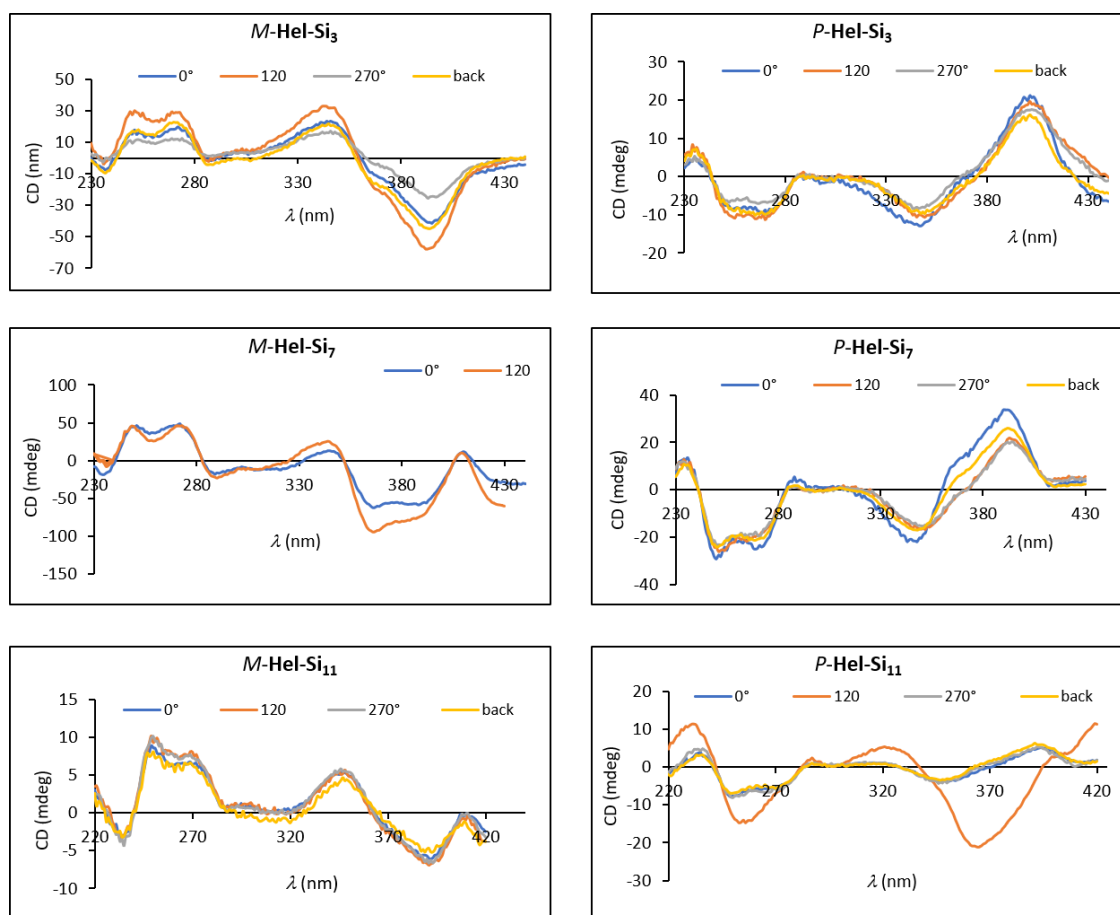


Figure S65: Evolution of the solid-state ECD spectra of **P- and M-Hel-Si_{3,7,11}** upon rotation and face flipping.

11. CPL and Fluorescence

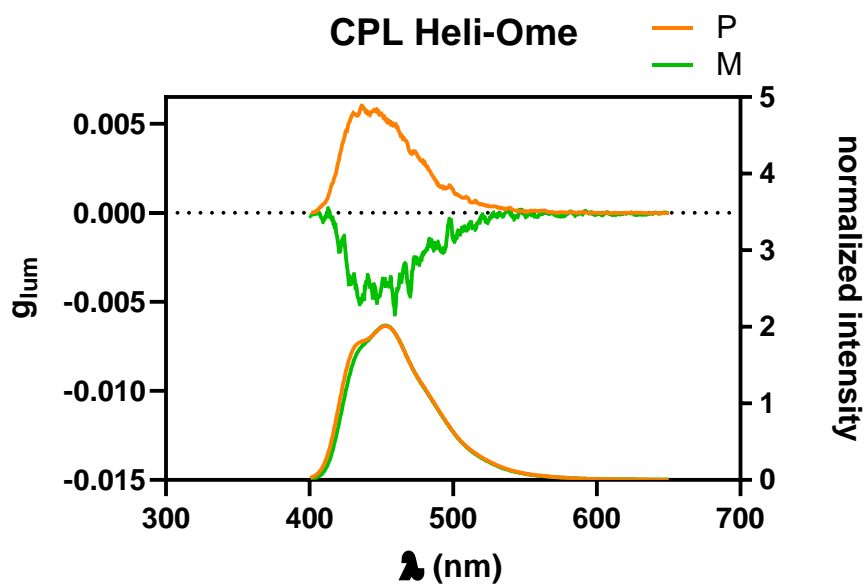


Figure S66: CPL spectra of **Heli-Ome**, excitation wavelength: 380 nm, g_{lum} at 438nm = $5.86 \cdot 10^{-3}$.

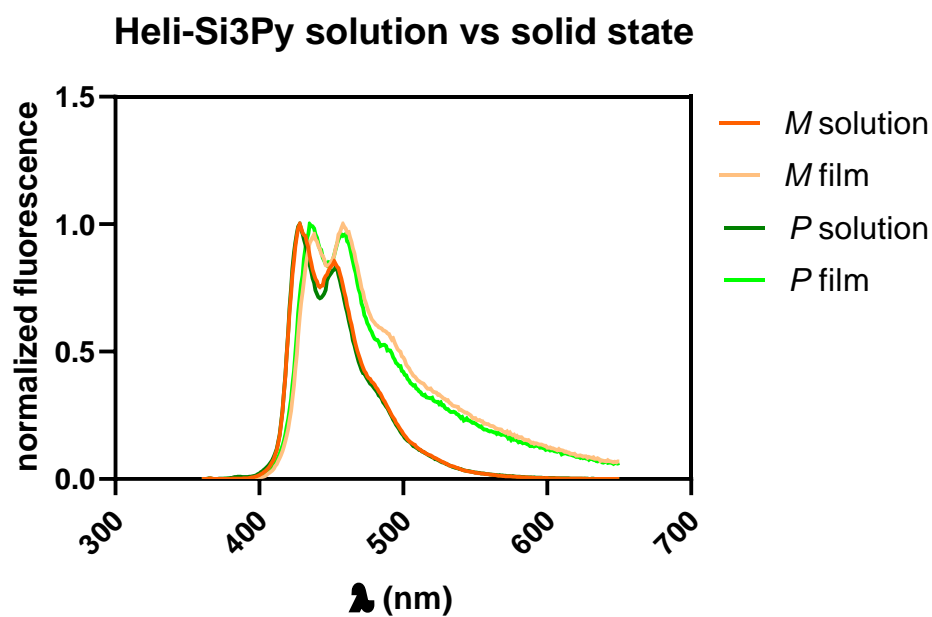


Figure S67: Fluorescence spectra of the compound **Heli-Si₃**, emission analysed in solution and in thin film. excitation wavelength: 380 nm.

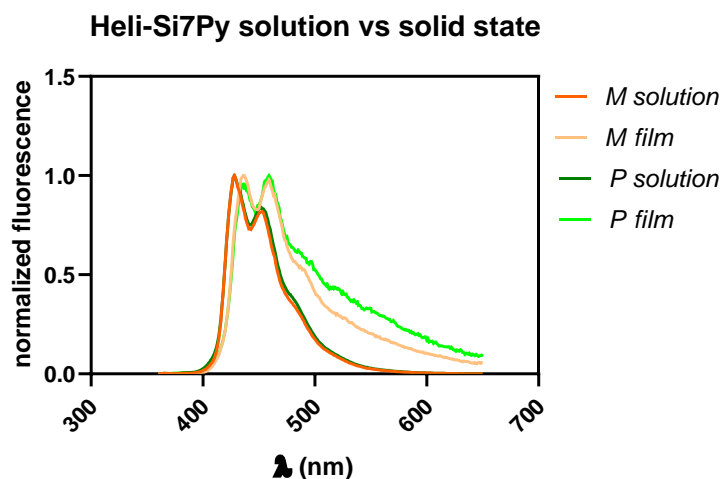


Figure S68: Fluorescence spectra of the compound **Hel-Si₇**, emission analysed in solution and in thin film. excitation wavelength: 380 nm

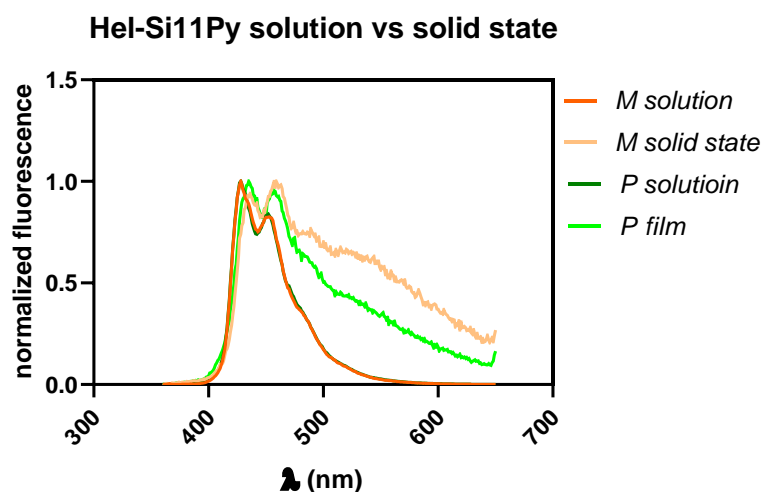


Figure S69: Fluorescence spectra of the compound **Hel-Si₁₁**, emission analysed in solution and in thin film. excitation wavelength: 380 nm

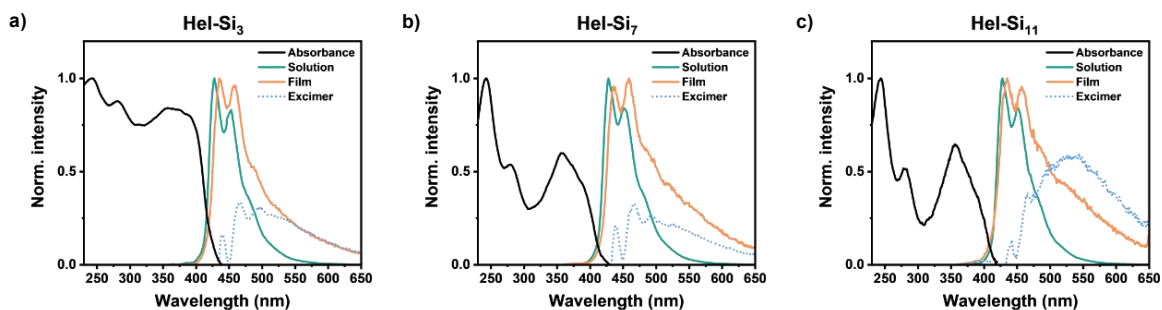


Figure S70: Absorption and emission spectra of **P-Hel-Si_n** in 10^{-5} M THF solution and in the solid state in thin film.

12. References

- (1) Schaack, C.; Sidler, E.; Ils Trapp, N.; Diederich, F.; Schaack, J C; Sidler, E.; Trapp, N.; Diederich, F. Helical Threads: Enantiomerically Pure Carbo[6]Helicene Oligomers. *Chem. – A Eur. J.* **2017**, *23* (57), 14153–14157. <https://doi.org/10.1002/CHEM.201703024>.
- (2) Lamers, B. A. G.; Waal, B. F. M.; Meijer, E. W. The Iterative Synthesis of Discrete Dimethylsiloxane Oligomers: A Practical Guide. *J. Polym. Sci.* **2020**, pol.20200649. <https://doi.org/10.1002/pol.20200649>.
- (3) Valášek, M.; Edelman, K.; Gerhard, L.; Fuhr, O.; Lukas, M.; Mayor, M. Synthesis of Molecular Tripods Based on a Rigid 9,9'-Spirobifluorene Scaffold. *J. Org. Chem.* **2014**, *79* (16), 7342–7357. https://doi.org/10.1021/JO501029T/SUPPL_FILE/JO501029T_SI_002.CIF.