Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

Depolymerizable semi-fluorinated polymers for sustainable functional materials

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Materials and Instrumentation

1,5-cyclooctadiene (COD) and maleic anhydride were purchased from Acros. Potassium carbonate was purchased from Alfa Aesar. 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) was purchased from Chem-Impex. Thiophenol, Grubbs first- and second-generation catalysts (G1 and G2), Quadrapure TU, N,N-dimethylaminopyridine, *t*-butyldimethylsilylchloride, 2,3,4,5,6-pentafluoroaniline, 1-butanol, ethyl vinyl ether and succinic anhydride were purchased from Sigma Aldrich. Hexafluorobenzene and 2,2,3,3,4,4,4-heptafluorobutanol were purchased from SynQuest. Sodium acetate, polyethylene glycol monomethyl ether and aniline were purchased from TCI. Ethylene glycol was purchased from Fisher. Unless specified, all reagents were used as received without further purification.

LaboACE LC-5060 preparatory GPC with two JAIGEL-2HR columns was used for purification where specified, with HPLC grade chloroform containing 0.75% ethanol as the eluent.

Column chromatography was performed using Silicycle F60 silica gel.

^{1}H, ^{13}C and ^{19}F NMR were obtained on a Varian 500 MHz NMR using deuterated chloroform ($CDCl_3$) as the solvent. Single crystal data for all structures were collected on a Bruker CCD-based diffractometer with dual Cu/Mo ImuS microfocus optics (Cu Kα radiation, λ =1.54178 Å or Mo Kα radiation, λ = 0.71073). Crystals were mounted on a cryoloop using Paratone oil and placed under a steam of nitrogen at 100 K (Oxford Cryosystems). The data were corrected for absorption with the SADABS program. The structures were refined using Bruker SHELXTL Software Package (Version 6.1) and were solved using direct methods until the final anisotropic full-matrix least squares refinement of F2 converged. Electronic Supplementary Information (ESI) available: CCDC 2151352 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

High resolution mass spectra (HRMS) were performed on Waters Synapt HDMS Quadrupole/Time-of-Flight (Q-ToF) Mass Spectrometer (Waters, Beverly, MA) in positive ion mode.
Gel permeation chromatography (GPC) was performed on a Tosoh EcoSec HLC8320GPC Single Detector with two 17393 TSKgel columns (7.8 mm ID x 30 cm, 13 μm) and one 17367-TSKgel Guard Column (7.5 mm ID x 7.5 cm, 13 μm).

DLS was performed using a Brookhaven BI-200SM goniometer Brookhaven BI-9000AT digital autocorrelator

Water contact angle measurements were performed using a Rame-Hart contact angle goniometer.

Thermal testing was performed using a TA Discovery DSC 250 and TGA 550.

Depolymerization studies

Depolymerization experiments were performed with polymers **P1**, **P2** and **P3** at $[olefin]_0$ = 25 mM, 50 mM, 100 mM, 200 mM, and 400 mM. 1 mol% G2 was used for **P1** and **P2**. With 1 mol% G2, we observed an unexpectedly low extent of depolymerization of **P3**, possibly due to the poisoning of the catalyst in presence of trace fluoroolefin impurities before equilibrium was reached.[1] Thus, 2 mol% G2 was used for **P3**. Three parallel studies were conducted for each polymer at each concentration and the average extent of depolymerization was reported. Given below is a representative example of the depolymerization procedure.

In a 1-dram vial equipped with a stir bar, **P1** (30 mg, 0.051 mmol, 1 eq.) was dissolved in 1990 μL $CHCl_3$. To the polymer solution was added G2 (0.43 mg, 0.00051 mmol, 0.01 eq.) in 10 μL $CHCl_3$ from a stock solution. The amount of the stock solution to be added was determined such that initial olefin concentration $[olefin]_0$ = 25 mM. The solution was divided into three vials and the depolymerization was allowed to progress overnight (~16 h) at room temperature following which 100 μL EVE was added to each vial. After stirring for 30 min., the solvent was removed via a rotary evaporator and the extent of depolymerization was determined by ^{1}H NMR.

Water contact angle measurements

To prepare the polymer surface for contact angle measurements, polymer solutions were prepared in solvents where the polymers can dissolve well. **P3**, **P1-NF**, and **P2** were dissolved in toluene while **P1** was dissolved in chloroform and **P2-NF** in chlorobenzene. 200 µL of a 5 wt.% solution of each polymer was loaded onto a glass plate mounted on the spin coater, which was then rotated at 2000 rpm for 60 seconds. Residual solvent was allowed to evaporate overnight under ambient conditions before the measurement.

The static contact angle was measured for a 10 µL water droplet deposited on the coated glass slides using a Rame-Hart contact angle goniometer. DROPImage advanced was used to calculate the contact angle from the droplet profile shape. For each sample, the measurement was taken immediately after addition of the droplet and was repeated six times, and the average value was reported.

Self-assembly of amphiphilic diblock copolymer

3 mg of **P1-*b*-P4** was dissolved in 0.3 mL THF and sealed in a microwave vial. To this, 3 mL MiliQ water was added dropwise over a span of 2 h via an automated syringe pump. The solution was then dialyzed with DI water for 36 h (MW cutoff for dialysis tubing: 12 kDa), following which it was filtered with a 0.22 µm PTFE filter and stored at room temperature. Particle size of the micelles was measured via dynamic light scattering.

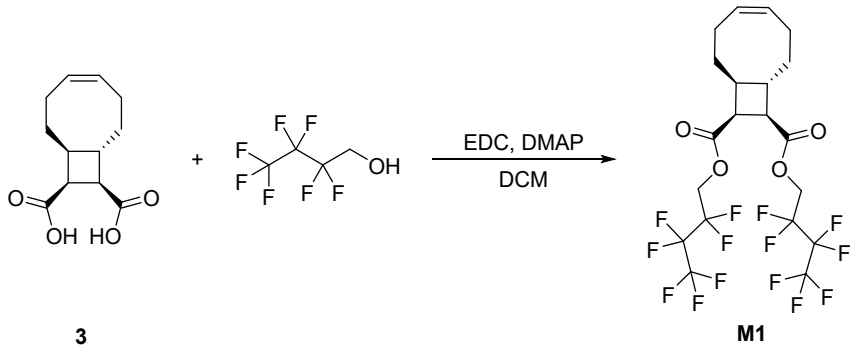
***Para*-fluoro-thiol S_NAr reaction**

In a 1-dram vial equipped with a stir bar, was dissolved **P2** (10 mg, 0.026 mmol, 1 eq.) in 2-butanone (200 µL). To the polymer solution were added thiophenol (3.01 mg, 0.027 mmol, 1.05 eq.) and K_2CO_3 (5.4 mg, 0.039 mmol, 1.5 eq.). The vial was placed in a preheated oil bath at 80 °C and allowed to stir for 4.5 h, after which the reaction mixture was filtered through a celite plug, and the filtrate was concentrated on a rotavap. After further drying under high vacuum, the product was analyzed vial ^{19}F NMR and GPC.

Synthesis

Small molecule synthesis

M1

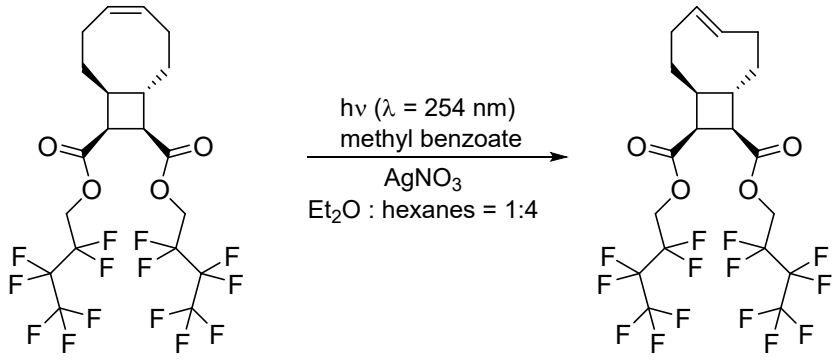


3 **M1**

To a round bottom flask equipped with a stir bar were added **3** (0.772 g, 3.45 mmol, 1 eq.) (prepared according to literature procedure)[2], 2,2,3,3,4,4,4-heptafluoro-1-butanol (0.94 mL, 7.25 mmol, 2.1 eq.), *N*,*N*-dimethylaminopyridine (0.084 g, 0.69 mmol, 0.2 eq.) and DCM (25 mL). To this solution was added EDC (2.639 g, 13.8 mmol, 4 eq.). The reaction was then allowed to proceed overnight at room temperature. The reaction mixture was diluted with DCM, washed with brine (× 3), and concentrated on a rotavap. The residue was purified via column chromatography with 5% EA/hexanes as eluent, affording **M1** as a colorless oil. Yield: 1.34 g (66.2%).

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.70 – 5.57 (m, 2H), 4.64 – 4.47 (m, 4H), 3.54 – 3.51 (m, 1H), 2.88 – 2.84 (m, 2H), 2.55 – 2.49 (m, 1H), 2.28 – 2.12 (m, 1H), 2.29 – 2.02 (m, 5H), 1.67 – 1.61 (m, 1H), 1.30 – 1.20 (m, 2H); ^{19}F NMR (470 MHz, $CDCl_3$, ppm): δ -81.00 (dt, *J* = 19.1 Hz, 9.2 Hz, 6F), -120.45 – -120.64 (m, 4F), -127.62 – -127.74 (m, 4F); ^{13}C NMR (125MHz, $CDCl_3$, ppm): δ 171.14, 170.47, 130.52, 129.61, 118.66, 116.37, 113.93, 111.89, 110.82, 108.73, 106.64, 59.46, 43.29, 42.28, 42.04, 39.53, 34.14, 28.79, 24.13, 23.47. HRMS-ESI (m/z): calcd. for $C_{20}H_{18}F_{14}NaO_4^+$ $[M+Na]^+$, 611.0874; found, 611.0918.

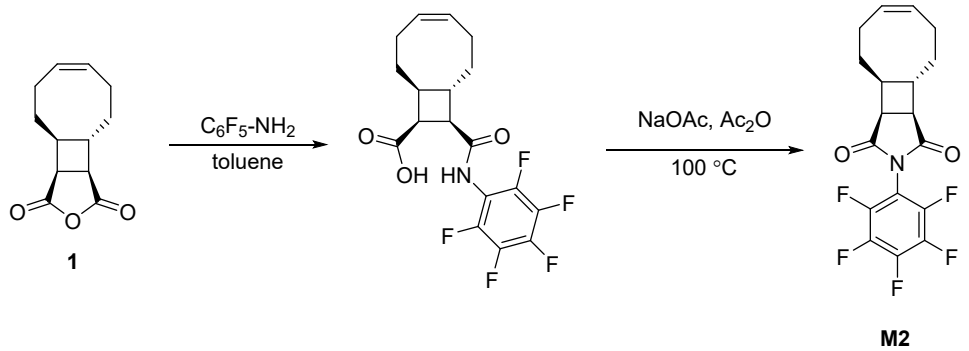
***E*-M1**



M1 ***E*-M1**

The photoisomerization was conducted following our recently reported procedure.[3] **M1** (235 mg, 0.4 mmol, 1.0 equiv) and methyl benzoate (109 mg, 0.8 mmol, 2.0 equiv) were dissolved in a 1:4 v/v Et_2O/hexane solvent mixture in a quartz tube. A column was first filled with a small amount of normal silica gel at the bottom to prevent silver leaking and then filled with 10 wt % $AgNO_3$-impregnated silica gel (136 mg $AgNO_3$, 0.8 mmol, 2.0 equiv). The reaction mixture was irradiated overnight with 254 nm UV light in a Rayonet photoreaction chamber with 16 RPR-2537A lamps, and meanwhile, it was circulated through the above-mentioned column using a metering pump. All substances in the column were loaded to a column packed with normal silica gel and $AgNO_3$-impregnated silica gel. The column was washed with 1:4 v/v Et_2O/hexanes to remove **M1** and methyl benzoate. Acetone was then used to wash the column to elute out Ag^+ coordinated ***E*-M1**. After the removal of acetone using rotary evaporator, DCM and aqueous ammonia solution were added, and the mixture was stirred for 30 min. The organic phase was collected, and the aqueous phase was further extracted with DCM for 3 times. The combined organic phase was washed with water and brine and dried over sodium sulfate. After filtration and removal of solvent, the resulting yellow oil was run through a short plug of silica gel, affording a white solid as the product (127 mg, yield = 54%). The product contained a mixture of two diastereomers and was used without further separation.
^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.87 – 5.73 (m, 0.4H), 5.56 – 5.43 (m, 1.6H), 4.65 – 4.39 (m, 4H), 3.51 (t, *J* = 9.1 Hz, 0.8H), 3.48 – 3.43 (m, 0.2H), 2.62 – 2.34 (m, 1.2H), 2.33 – 1.90 (m, 5.8H), 2.43 – 1.88 (m, 4H), 1.58 – 1.48 (m, 2H); ^{19}F NMR (470 MHz, $CDCl_3$, ppm): δ -81.01 (dt, *J* = 25.6 Hz, 9.2 Hz, 6F), -120.48 – -120.66 (m, 4F), -127.67 – -127.73 (m, 4F); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 171.1, 170.9, 170.3, 170.2, 136.6, 134.9, 134.4, 134.2, 118.6, 116.3, 113.9, 113.8, 111.8, 108.5, 59.6, 59.5, 59.4, 59.3, 59.2, 59.1, 46.4, 45.4, 44.6, 44.0, 43.2, 43.0, 42.4, 41.4, 40.9, 40.3, 35.7, 35.5, 33.0, 32.7, 25.7, 25.4. HRMS-ESI (m/z): calcd. for $C_{20}H_{18}F_{14}NaO_4^+$ $[M+Na]^+$, 611.0874; found, 611.0811.

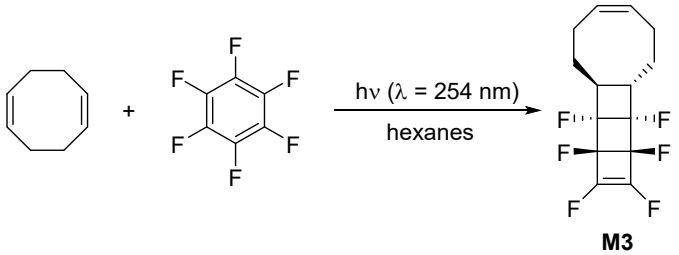
M2



Anhydride **1** (0.92 g, 4.46 mmol, 1 eq.) (prepared according to literature procedure)[2] and 2,3,4,5,6-pentafluoroaniline (1.68 g, 9.2 mmol, 2.06 eq.) were dissolved in toluene (10 mL), and the solution was heated at 90 °C overnight, during which an off-white precipitate emerged. The precipitate was filtered and dried to afford the amic-acid intermediate, which was used for the next step without further purification.

The amic-acid (726 mg, 1.87 mmol, 1 eq.) was then added into a round bottom flask together with sodium acetate (240 mg, 2.92 mmol, 1.6 eq.) and acetic anhydride (10 mL). The mixture was heated at 100 °C overnight, and then poured into cold water and stirred for 30 min. The resulting precipitate was filtered and purified via column chromatography using DCM to afford pure monomer **M2**. Yield: 546 mg (~78.9 %). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.68 – 5.60 (m, 2H), 3.48 – 3.45 (m, 1H), 3.11 (t, *J* = 6.4 Hz, 1H), 2.86 – 2.79 (m, 1H), 2.57 – 2.50 (m, 1H), 2.33 – 2.25 (m, 1H), 2.24 – 2.19 (m, 1H), 2.16 – 2.08 (m, 2H), 2.07 – 2.01 (m, 1H) 1.92 – 1.86 (m, 1H), 1.65 – 1.58 (m, 1H), 1.43 – 1.36 (m, 1H). ^{19}F NMR (470 MHz, $CDCl_3$, ppm): δ -142.9 (dtd, *J* = 22.0, 6.5, 2.1 Hz, 1F), -143.6 (dtd, *J* = 23.0, 6.5, 2.2 Hz, 1F), -152.1 – -152.2 (m, 1F), -160.7 – -160.8 (m, 1F), -161.0 – -161.1 (m, 1F) ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 175.98, 174.70, 144.67, 143.17, 142.36, 141.12, 138.89, 137.04, 136.92, 130.09, 129.75, 45.64, 42.41, 40.56, 40.34, 32.80, 29.25, 23.97, 23.81 HRMS-ESI (m/z): calcd for $C_{18}H_{15}F_5NO_2^+$ $[M+H]^+$, 372.1017; found, 372.1061.

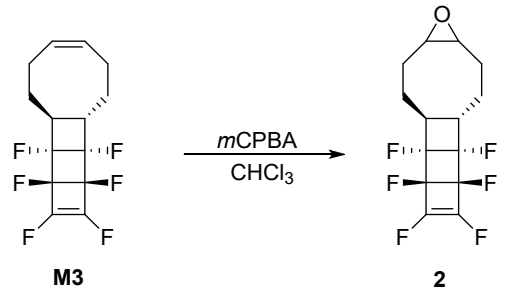
M3



To an oven-dried quartz flask was added a solution of cyclooctadiene (1.32 mL, 10.75 mmol, 1.0 equiv.) and hexafluorobenzene (1.24 mL, 10.75 mmol, 1.0 equiv.) in 100 mL hexanes. The reaction mixture was bubbled with N_2 for 30 min and then irradiated with 254 nm UV light in a Rayonet photoreaction chamber with 16 RPR-2537A lamps for 24 h. The mixture was washed with sat. $NaHCO_3$ (a.q.), extracted with hexanes and dried with Na_2SO_4. After filtration and solvent removal, the crude product was purified by column chromatography with hexanes as the eluent to obtain 1.01 g product as a colorless oil (yield: 31.8%, containing 5 ~ 7% of *cis*-isomer, when the reaction concentration was increased, the amount of *cis*-isomer was increased). The product was polymerized

by using 1 mol% G2 as initiator at 1 g/mL concentration in DCM and quenched with EVE. The polymerization solution was then precipitated in MeOH to obtain a white fibrous polymer. After drying on vacuum overnight, the polymer was depolymerized in $CHCl_3$ ($[olefin]_0$ = 0.1 M) in the presence of 1 mol% G2 at 50 °C for 2h and quenched with EVE. The pure *trans*-isomer was separated through flash column chromatography from the depolymerization mixture. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.76 – 5.61 (m, 2H), 2.93 – 2.79 (m, 1H), 2.72 – 2.61 (m, 1H), 2.43 – 2.32 (m, 1H), 2.26 – 2.09 (m, 3H), 1.95 – 1.86 (m, 1H), 1.84 – 1.67 (m, 3H); ^{19}F NMR (470 MHz, $CDCl_3$, ppm): δ -120.00 (tt, *J* = 11.6, 5.4 Hz), -120.46 (td, *J* = 11.6, 5.8 Hz), -154.06 (dddd, *J* = 24.1, 15.9, 12.2, 4.1 Hz), -182.14, -186.53 (qd, *J* = 10.6, 9.9, 4.8 Hz), -186.75 (ddt, *J* = 16.8, 11.0, 4.9 Hz);^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 130.8, 130.3, 130.2, 130.1, 100.9, 100.3, 95.6, 94.5, 47.4, 37.1, 26.3, 25.3, 25.0, 22.9. HMRS (ASAP) calcd. for $C_{14}H_{12}F_6^-$ $[M]^-$ 294.0849, found 294.0822.

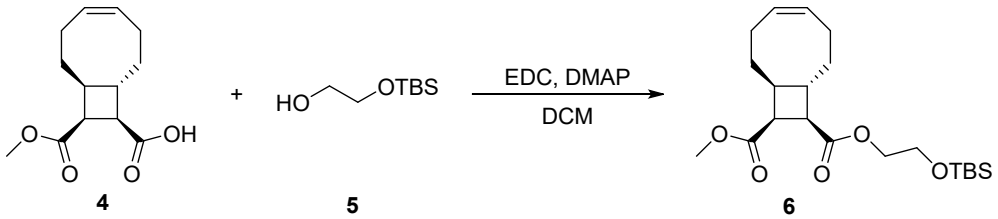
Fluorinated ladderane epoxide 2:



M3 **2**

To a round bottom flask was added a solution of **M3** (0.16 g, 0.53 mmol, 1.0 equiv.) in 5 mL $CHCl_3$, and the solution was cooled down in an ice bath. A solution of *m*CPBA (0.12 g, 0.53 mmol, 1.0 equiv. 75 wt%) in 5 mL $CHCl_3$ was added dropwise into the solution of **M3**. The reaction mixture was allowed to stir overnight and slowly warm to room temperature. The mixture was washed with sat. $NaHSO_3$ (a.q.) and sat. $NaHCO_3$ (a.q.), extracted with DCM and dried over Na_2SO_4. After filtration and concentration, the crude product was purified by column chromatography, affording 0.12 g product as a white solid (yield: 73.8%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 3.06 – 2.83 (m, 2H), 2.70 – 2.16 (m, 4H), 2.10 – 1.80 (m, 3H), 1.79 – 1.60 (m, 1H), 1.47 – 1.09 (m, 2H); ^{19}F NMR (470 MHz, $CDCl_3$, ppm): δ -119.6 – -119.9 (m), -120.0 – -120.2 (m), -153.3 – -154.2 (m), -182.4 – -184.8 (m), -185.7 – -187.2 (m); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 130.8, 130.2, 101.2, 100.0, 95.8, 94.6, 54.7(3C), 54.6 (3C), 48.0, 47.3, 37.6, 37.4, 27.8, 26.9, 24.0, 23.7, 23.6, 22.1, 21.7, 21.5. HMRS (ASAP) calcd. for $C_{14}H_{12}F_6^-$ $[M]^-$ 310.0792, found 310.0802.

6

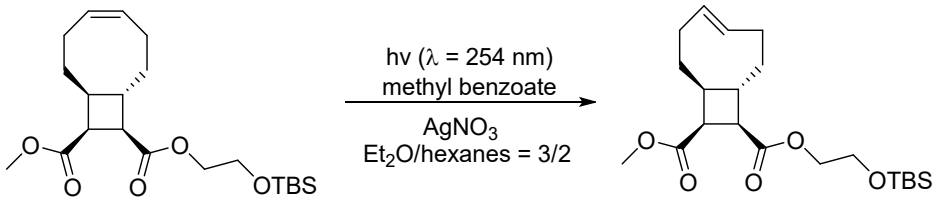


4 **5** **6**

To a 250 mL round bottom flask equipped with a stir bar were added **4** (prepared from previously reported procedure[2], 3727.6 mg, 15.6 mmol, 1 eq.), **5** (prepared from previously reported procedure[4], 3030.7 mg, 17.2 mmol, 1.1 eq.), *N*,*N*-dimethylaminopyridine (191.1 mg, 1.56 mmol, 0.1 eq.), EDC (6000 mg, 30.3 mmol, 2 eq.), and DCM (80 mL). The reaction was allowed to proceed for 18 h at room temperature, following which it was diluted with DCM, washed with water (2 × 200 mL) and concentrated on a rotavap. After column chromatography with 8% EA/hexanes as eluent, **6** was

obtained as a pale-yellow oil. Yield: 3.85 g (62%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.68 – 5.54 (m, 2H), 4.13 (td, *J* = 5.1 Hz, 3.1 Hz, 2H), 3.82 – 3.75 (m, 2H), 3.65 (s, 3H), 3.39 (t, *J* = 10 Hz, 1H), 2.82 (qd, *J* = 10.5 Hz, 4.5 Hz, H), 2.70 – 2.67 (m, 1H), 2.43 – 2.36 (m, 1H), 2.27 – 2.20 (m, 1H), 2.19 – 2.11 (m, 2H), 2.07 – 2.00 (m, 2H), 1.64 – 1.57 (m, 1H), 1.32 – 1.25 (m, 1H), 1.24 – 1.17 (m, 1H), 0.9 (s, 9H), 0.07 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 173.09, 172.74, 130.58, 129.76, 63.75, 63.15, 51.37, 43.71, 42.82, 42.00, 39.21, 34.48, 28.99, 25.83, 24.39, 23.67, 18.29, 5.34. calcd. for $C_{21}H_{36}NaO_5Si^+$ $[M+Na]^+$: 419.2224; found: 419.2206.

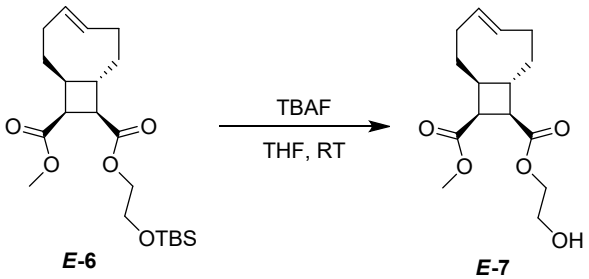
***E*-6**



6 ***E*-6**

The photoisomerization of **6** was based on a previously reported procedure.[3] **6** (3.85 g, 9.71 mmol, 1 eq.) and methyl benzoate (1.32 g, 9.71 mmol, 1 eq.) were dissolved in a 150 mL of 3:2 v/v Et_2O/hexanes solvent mixture in a quartz tube. A column was first filled with a small amount of normal silica gel at the bottom to prevent silver leaking and then filled with 10 wt % $AgNO_3$-impregnated silica gel (3.3 g $AgNO_3$, 19.4 mmol, 2 eq.). The reaction mixture was irradiated overnight with 254 nm UV light in a Rayonet photoreaction chamber with 16 RPR2537A lamps, and meanwhile, it was circulated through the column using a metering pump. After 17 h of irradiation, the contents of the column were collected and loaded onto another column with a normal silica gel layer at the bottom, and a fresh $AgNO_3$- impregnated silica gel layer (3.3 g AgNO3, 19.4 mmol, 2 eq.) at the top. First, **6** and methyl benzoate were eluted from the column using 750 mL of 3:2 v/v Et_2O/hexanes as eluent. Further, acetone was used to elute out the Ag^+ coordinated ***E*-6**. Acetone was removed via a rotary evaporator, and 50% aq. NH_4OH was added to the residue. The mixture was added to a separatory funnel and the aqueous layer was extracted with DCM (5 x 300 mL), dried over Na_2SO_4, filtered, and concentrated on a rotavap. The brown crude oil was purified via column chromatography using 8% EA/hexanes mixture as the eluent. After solvent removal, the product ***E*-6** was obtained as a pale-yellow oil. The product contained a mixture of 2 diastereomers and was used without further purification. Yield: 2.25 g (58%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.86 – 5.73 (m, 0.5H), 5.53 – 5.46 (m, 1.5 H), 4.15 – 4.08 (m, 2H), 3.81 – 3.76 (m, 2H), 3.63 (s, 3H), 3.38 (t, *J*=9.1 Hz, 0.75H), 3.31 (t, *J*=8,7 Hz, 0.25H), 2.75-2.68 (m, 0.25H), 2.65–2.51 (m, 1.75H), 2.4 – 1.89 (m, 6H), 1.86 – 1.75 (m, 1H), 1.70 – 1.58 (m, 1H), 1.58 – 1.47 (m, 1H), 0.9 (s, 9H), 0.07 (s, 6H). ^{13}C (125 MHz, $CDCl_3$, ppm): 173.0, 172.8, 134.5, 134.4, 65.8, 61.1, 51.4, 45.3, 43.7, 42.8, 41.2, 35.7, 33.2, 33.0, 25.8, 18.3, -5.3. calcd. for $C_{21}H_{36}NaO_5Si^+$ $[M+Na]^+$: 419.2224, found: 419.2192.

***E*-7**



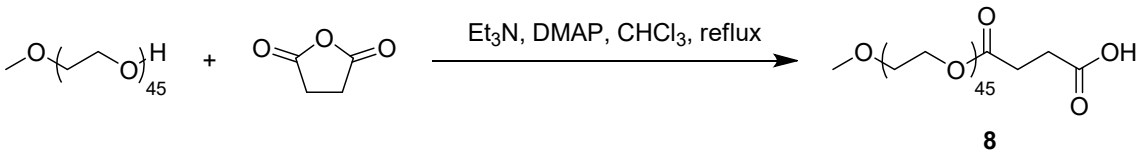
***E*-6** ***E*-7**

The desilylation of the photoisomerization product was carried out in the presence of a fluoride instead of a strong Brønsted acid (e.g. HCl), can lead to hydration of the olefin in *trans*-cyclooctene.[5] To a solution of the silyl ether ***E*-6** (2.25 g, 5.67 mmol) in THF (5.67 mL) was added TBAF (1 M solution in THF, 11.2 mL, 11.2 mmol, 2 eq.). The mixture was stirred at ambient conditions for 30 min, at which point TLC (1:1 v/v EA/hexanes) suggested full conversion. The reaction mixture was then diluted with EA, washed with D.I. H_2O three times and brine, and dried over Na_2SO_4. The solution was concentrated and directly loaded on a silica column. Flash column chromatography (EA/hexanes = 1:1) yielded a slightly yellow oil (1282 mg, 80%). The non-solid product was kept in a

dilute solution with a known amount of BHT to prevent radical-induced side reactions on *trans*-cyclooctene [6] and as internal reference for mass calculation.

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.86 – 5.74 (m, 0.25H), 5.53 – 5.46 (m, 1.75 H), 4.25 – 4.16 (m, 2H), 3.84 – 3.75 (m, 2H), 3.66 (s, 3H), 3.38 (td, *J*=9.2, 0.9, Hz, 0.87H), 3.35 (t, *J*=8.6 Hz, 0.13H), 2.74 – 2.62 (m, 1H), 2.58 – 2.52 (m, 1H), 2.39 – 1.99 (m, 6H), 1.82 – 1.79 (m, 1H), 1.69 – 1.59 (m, 1H), 1.56 – 1.49 (m, 1H); ^{13}C (125 MHz, $CDCl_3$, ppm):173.8, 172.7, 136.6, 135.0, 134.4, 134.4, 66.2, 65.8, 61.1, 51.6, 50.8, 46.4, 45.5, 45.3, 44.0, 43.6, 43.1, 43.0, 42.6, 42.1, 41.1, 40.4, 39.1, 36.1, 35.8, 33.2, 32.9, 15.2, 14.2 calcd. for $C_{15}H_{22}NaO_5^+$ $[M+Na]^+$: 305.1357, found: 305.1378.

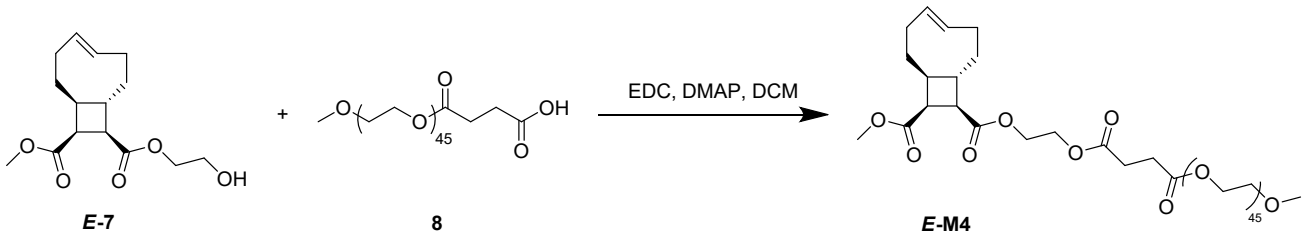
PEG succinate ester 7



8

Following reported procedures[7] with slight modifications, mPEG (3.8 g, 1.9 mmol, 1 eq.), succinic anhydride (0.95 g, 9.5 mmol, 5 eq.), Et_3N (0.96 g, 9.5 mmol, 5 eq.) and DMAP (232 mg, 1.9 mmol, 1 eq.) were dissolved in chloroform (amylene stabilized), and left to reflux for 24 h. The mixture was concentrated on a rotary evaporator and was redissolved in 1 N HCl. The aqueous solution was washed with 1:1 v/v EA/hexanes (3×) and extracted with DCM three times. The DCM solution was dried over Na_2SO_4, concentrated to around 10% (w/v) and precipitated into cold Et_2O (2 ×), affording a white powder. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 4.27 – 4.25 (m, 2H), 4.68 – 3.64 – 4.25 (m, 178H), 3.38 (s, 3H), 2.68 – 2.61 (m, 4H).

***E*-M4**

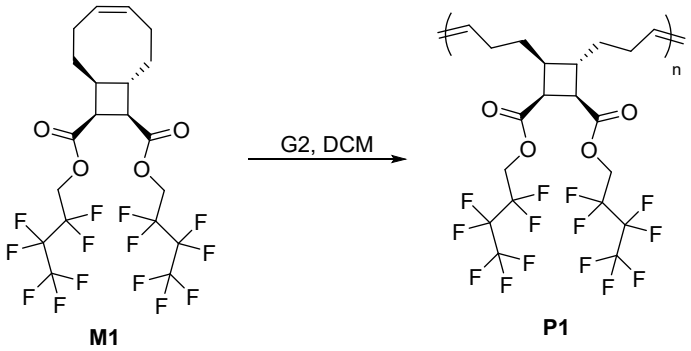


***E*-7** **8** ***E*-M4**

To a 25 mL round-bottom flask equipped with a stir bar were added ***E*-7** (100 mg, 0.35 mmol, 1.2 eq.), DMAP (3.7 mg, 0.035 mmol, 0.1 eq.), PEG succinate ester **8** (618 mg, 0.3 mmol, 1 eq.), EDC (115 mg, 0.6 mmol, 2 eq.), and DCM (10 mL), and the reaction mixture was allowed to stir at toom temperature overnight. The mixture was concentrated at a reduced pressure before 150 mL D.I. H_2O was added. The aqueous layer was washed with 1:1 v/v EA/hexanes mixture (3 × 200 mL), and the organic layer was discarded. The aqueous layer was extracted with DCM (6 × 200 mL). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated at a reduced pressure, and then precipitated into cold Et_2O (× 2). The product was obtained as a white solid (475 mg, yield: 67%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.85 – 5.74 (m, 0.5H), 5.52 – 5.45 (m, 1.5H), 4.29 – 4.23 (m, 6H), 3.64 (s, 183 H), 3.4 – 3.32 (m, 4H), 2.82 – 2.49(m, 6H), 2.41 – 1.47 (m, 9H).

Polymer Synthesis

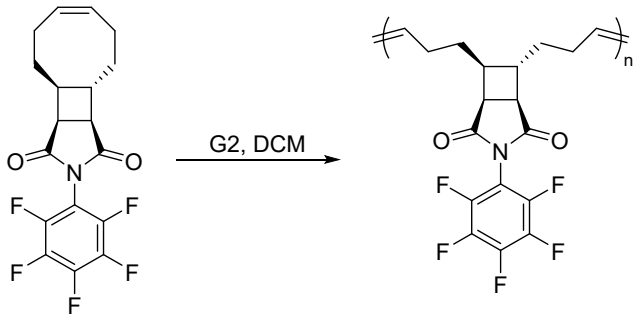
P1



M1 **P1**

To a 1-dram vial equipped with a stir bar, were added **M1** (250 mg, 0.42 mmol, 1 eq.) and DCM (30 µL). To the monomer solution was added G2 (0.72 mg, 0.00085 mmol, 0.002 eq.) in 20 µL DCM from a stock solution. The polymerization was allowed to proceed overnight at room temperature. The reaction was quenched with ethyl vinyl ether (100 µL) and stirred for 30 min. To the mixture were added Quadrapure TU microporous particles (100 mg) and DCM (1 mL). The mixture was stirred for 12 h and was then filtered through a celite plug and concentrated. Pure polymer was obtained by precipitation in hexanes (× 3). Yield: 110 mg (~44%). M_n=276 kDa, $Đ$=1.42. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.41 – 5.29 (m, 2H), 4.61 – 4.65 (m, 4H), 3.57 (t, 1H), 2.91 – 2.86 (s, 1H), 2.72 – 2.66 (m, 1H), 2.77 – 2.73 (m, 1H), 2.23 – 2.16 (m, 1H), 2.05 – 1.91 (m, 4H), 1.55 – 1.46 (m, 4H); ^{19}F NMR (470 MHz, $CDCl_3$, ppm): δ -81.17 (m, 4F), -120.72 (m, 2F), -127.84 (m, 2F).

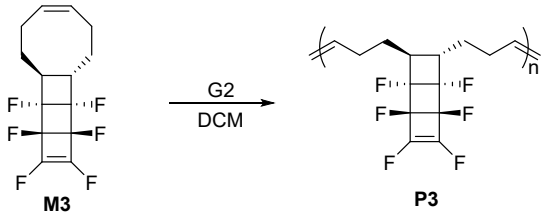
P2



M2 **P2**

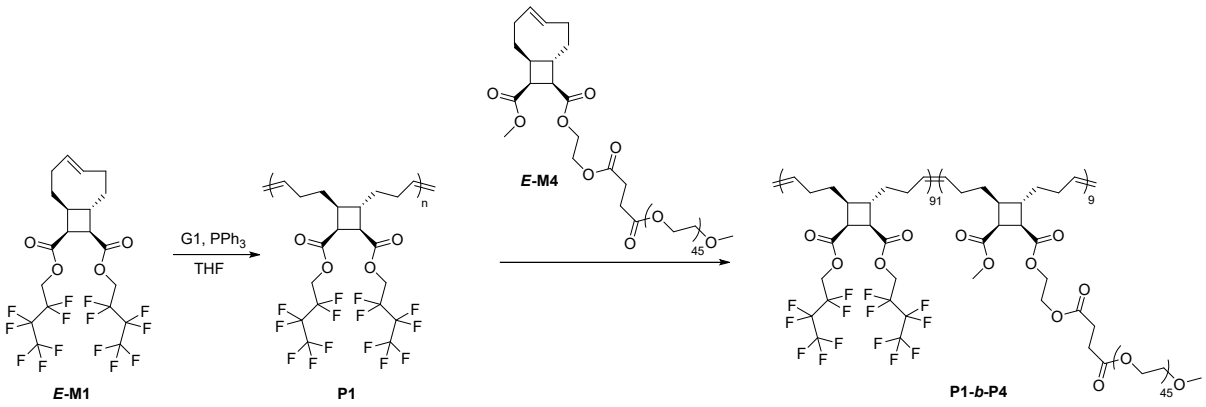
To a 1-dram vial equipped with a stir bar, was added **M2** (0.3 g, 0.81 mmol, 1 eq.) and DCM (300 µL). To the monomer solution was added a solution of G2 (1.37 mg, 0.00162 mmol, 0.002 eq.) in (20 µL) DCM from a stock solution, and the polymerization was allowed to proceed overnight at room temperature. It was quenched with ethyl vinyl ether (100 µL), and after stirring for 30 min., Quadrapure TU microporous particles (250 mg) and DCM (1 mL) were added. The mixture was stirred for 12 h, following which it was filtered through a celite plug and concentrated. Pure polymer was obtained by precipitation in methanol (× 3). Yield: 0.22 g (~73%). M_n = 147 kDa, $Đ$ = 1.75. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.44 – 5.33 (m, 2H), 3.55 – 3.50 (m, 1H), 3.06 (t, 1H), 2.51 – 2.46 (m, 1H), 2.23 (m, 1H), 2.09 – 2.04 (m, 4H), 1.74 – 1.64 (m, 3H), 1.47 (s, 1H). ^{19}F NMR (470 MHz, $CDCl_3$, ppm): δ -143.12 (2F, *ortho*), -151.1 (1F, *para*), -160.86 (2F, *meta*).

P3



To a 1-dram vial was added **M3** (0.50 g, 1.70 mmol, 1.0 equiv.). G2 (2.89 mg, 3.40 mmol, 0.002 equiv.) was weighed in another vial and dissolved in 0.85 mL DCM, and the solution was added to the vial containing monomer. The reaction mixture was allowed to stir at room temperature overnight. The polymerization was then quenched with 1.0 mL ethyl vinyl ether and stirred for 30 min, at which point, Quadrapure TU macroporous particles (150 mg) and 2.0 mL DCM were added. The mixture was stirred for 5 h, filtered through a Celite plug and concentrated under reduced pressure. The concentrated solution was precipitated in 200 mL cold methanol for three times and dried on vacuum, yielding **P3** as white fibers. Yield: 0.30 g (~60%). M_n = 108.3 kDa, $Đ$ = 1.63. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.50 – 5.33 (m, 2H), 2.68 – 2.52 (m, 1H), 2.47 – 2.37 (m, 1H), 2.16 – 1.97 (m, 4H), 1.89 – 1.74 (m, 2H), 1.75 – 1.64 (m, 1H), 1.64 – 1.54 (m, 1H); ^{19}F NMR (470 MHz, $CDCl_3$, ppm): δ -120.2 (2F), -153.0, -184.0, -186.9 (d, J = 85.1 Hz), -187.8.

P1-*b*-P4



To a vial were added ***E*-M1** (58.8 mg, 100 μmol, 1.0 equiv) and PPh_3 (7.89 mg, 30 μmol, 0.3 equiv). THF was added to reach a monomer concentration of 0.25 M. G1 (0.82296 mg, 1 μmol, 0.01 equiv) was added while vigorous stirring, and the mixture was stirred for 10 min. An aliquot was taken at this point for analysis of thefirst block. To the polymerization mixture was added 900 μL THF solution of ***E*-M4** (23.59 mg, 10 μmol, 0.1 equiv). The mixture was stirred for another 10 min before ethyl vinyl ether (1 mL) was added. After stirring for 30 min, solvent was removed under reduced pressure, and the polymer was purified with a prep GPC. The ratio of DP for the two blocks was determined to be approximately **P1**:**P4** = 91.2:8.8 from the integral at 4.67-4.40 (4H for **P1**) and 4.40-4.16 (6H for **P2**) in the ^{1}H NMR. The GPC trace of the first block (**P1**) showed M_n = 42.2 kDa and $Đ$ = 1.08. However, the GPC trace obtained after synthesis of the second block showed a higher retention time (lower M_n) than the first block, precluding the accurate determination of the M_n of **P1-*b*-P4** (Fig. S41). We therefore used the M_n obtained from the GPC trace of the first block and the ratio of the two blocks obtained from NMR to estimate the M_n.

M_n = 58.5 kDa. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 5.49 – 5.15 (m, 200H), 4.67 – 4.40 (m, 364H), 4.40 – 4.16 (m, 54H), 3.81 – 3.60 (m, 1629H), 3.59 – 3.52 (m, 100H), 2.94 – 2.73 (m, 100H), 2.73 – 2.58 (m, 136H), 2.26 – 2.14 (m, 91H), 2.14 – 1.83 (m, 409H), 1.72 – 1.33 (m, 400H).

Figures

Figure for crude product of cycloaddition between cyclooctadiene and hexafluorobenzene

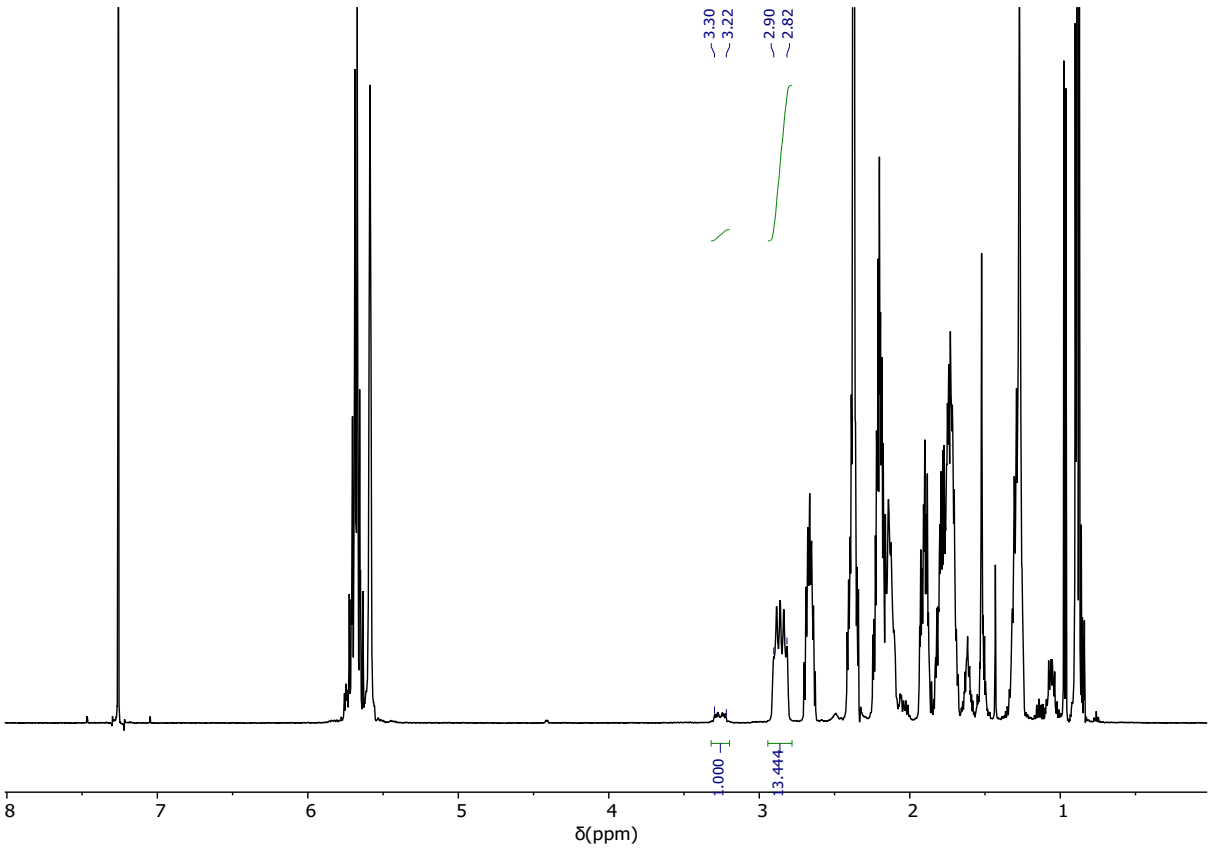
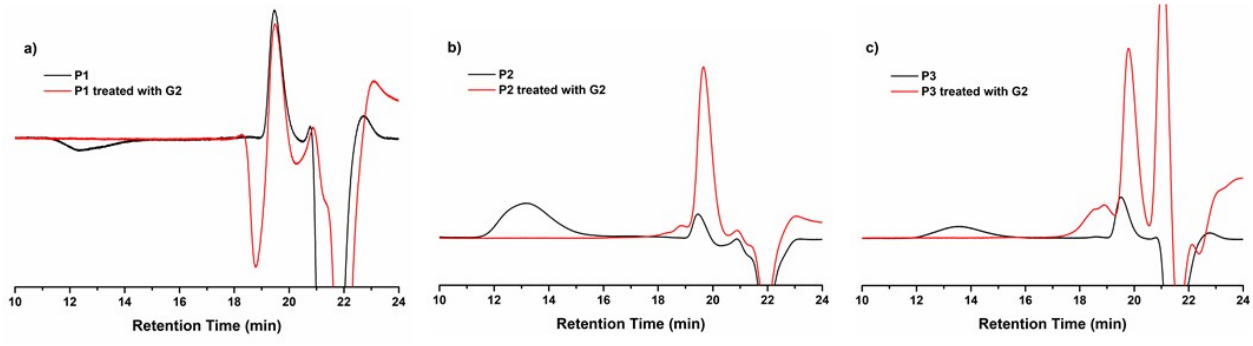


Figure S1 ^{1}H NMR spectrum (125 MHz, $CDCl_3$) for the crude product obtained from the photocycloaddition cyclooctadiene and hexafluorobenzene. The protons at 3.30-3.22 correspond to the *cis*-cyclobutane isomer of **M3** while those at 2.90-2.82 ppm correspond to the *trans*-cycobutane isomer.

Figures for depolymerization studies

Figure S2 GPC traces before (black) and after (red) depolymerization of a) **P1**, b) **P2** and c) **P3**.



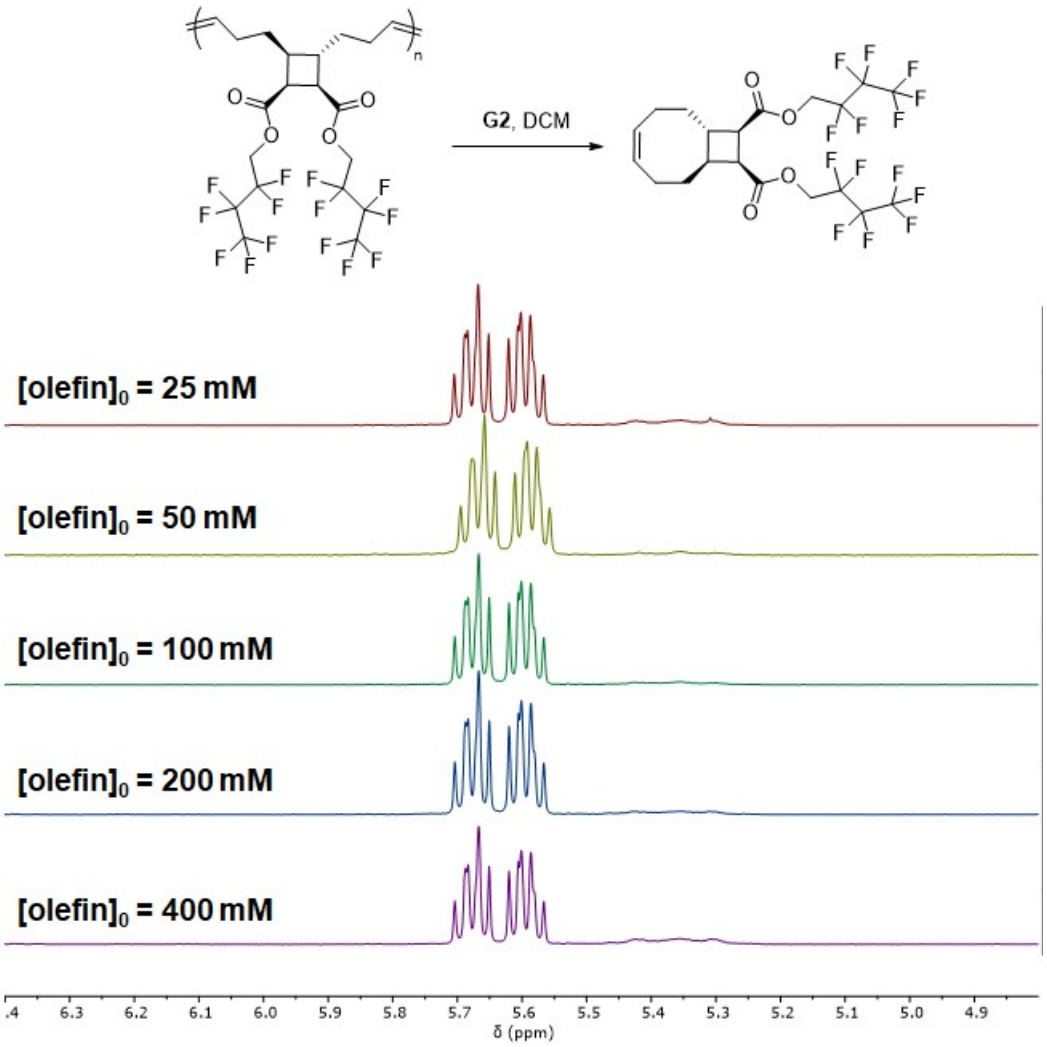


Figure S3 Partial ^{1}H NMR spectra (500 MHz, $CDCl_3$) corresponding to one of the three parallel depolymerization studies with **P1**.

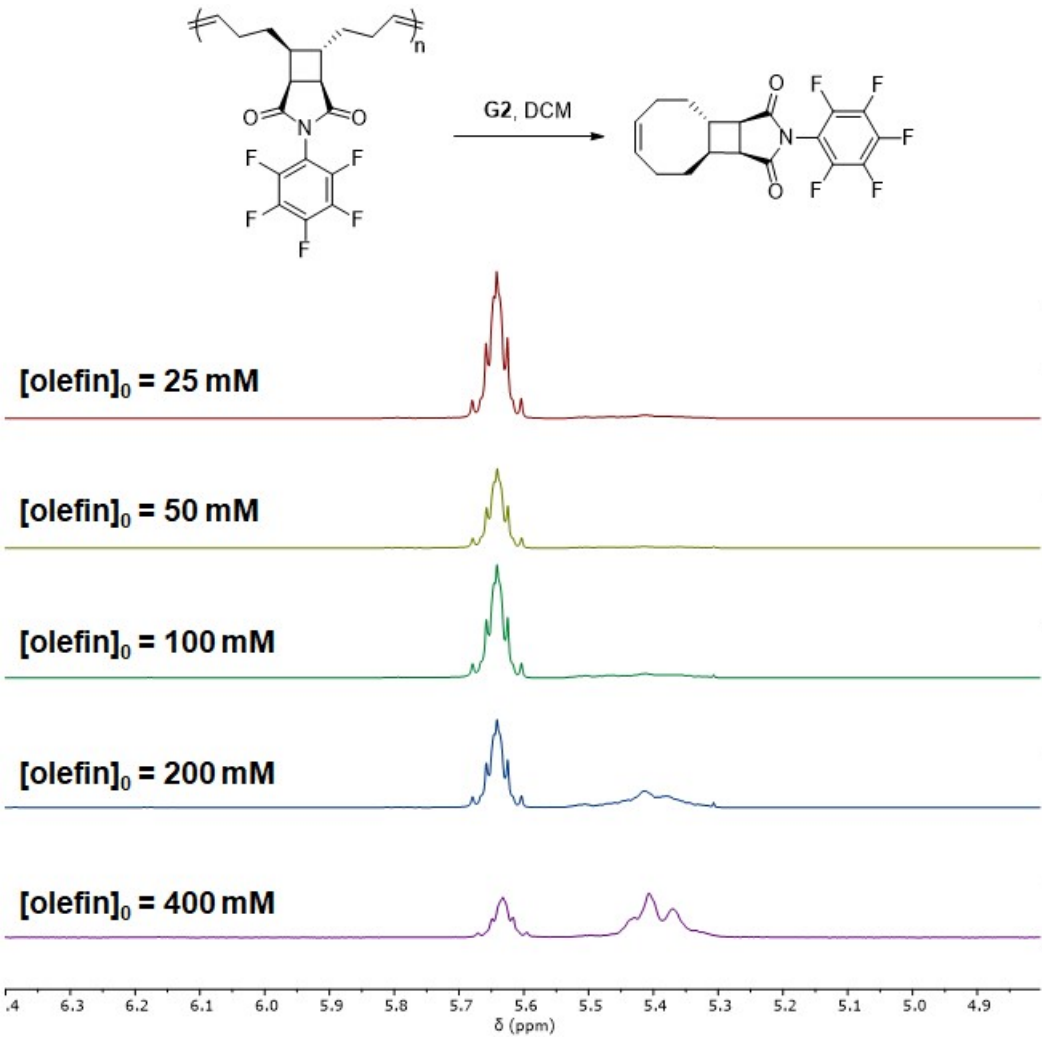


Figure S4 Partial ^{1}H NMR spectra (500 MHz, $CDCl_3$) corresponding to one of the three parallel depolymerization studies with **P2**.

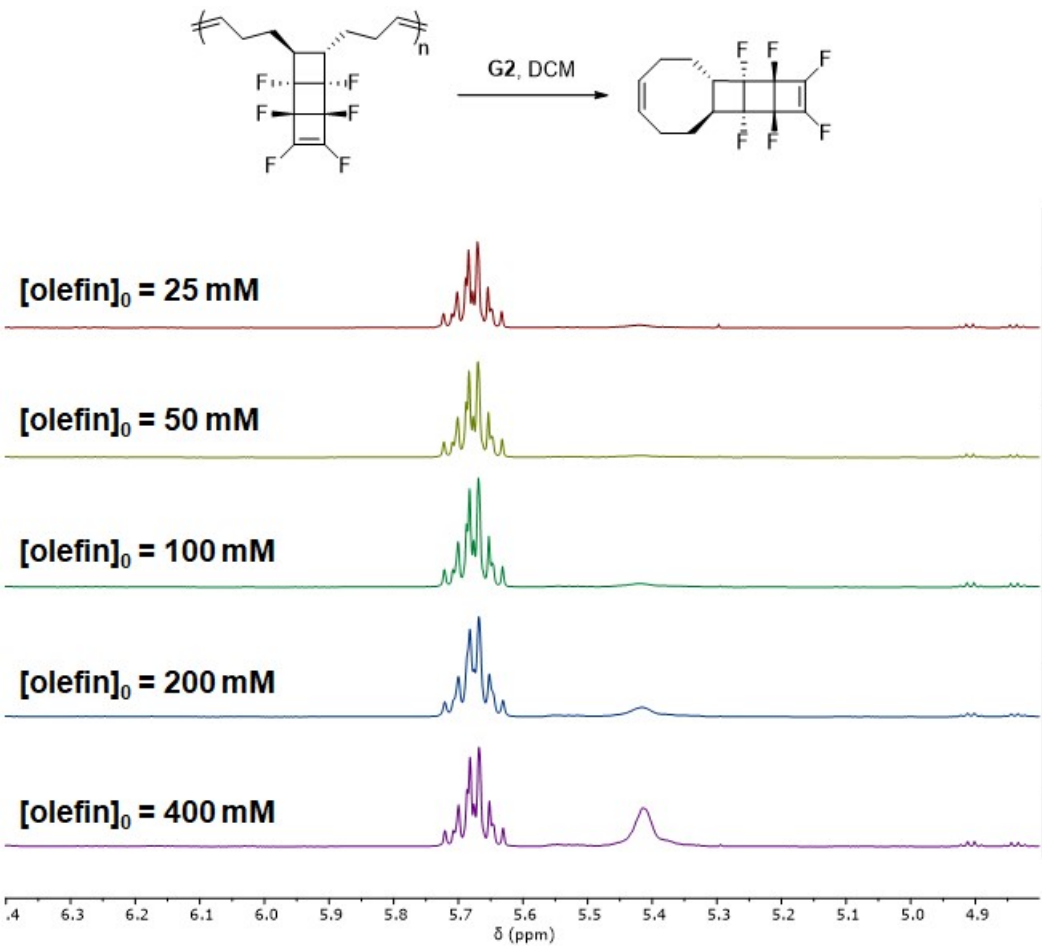


Figure S5 Partial ^{1}H NMR spectra (500 MHz, $CDCl_3$) corresponding to one of the three parallel depolymerization studies with **P3**.

Figures for small molecule characterization

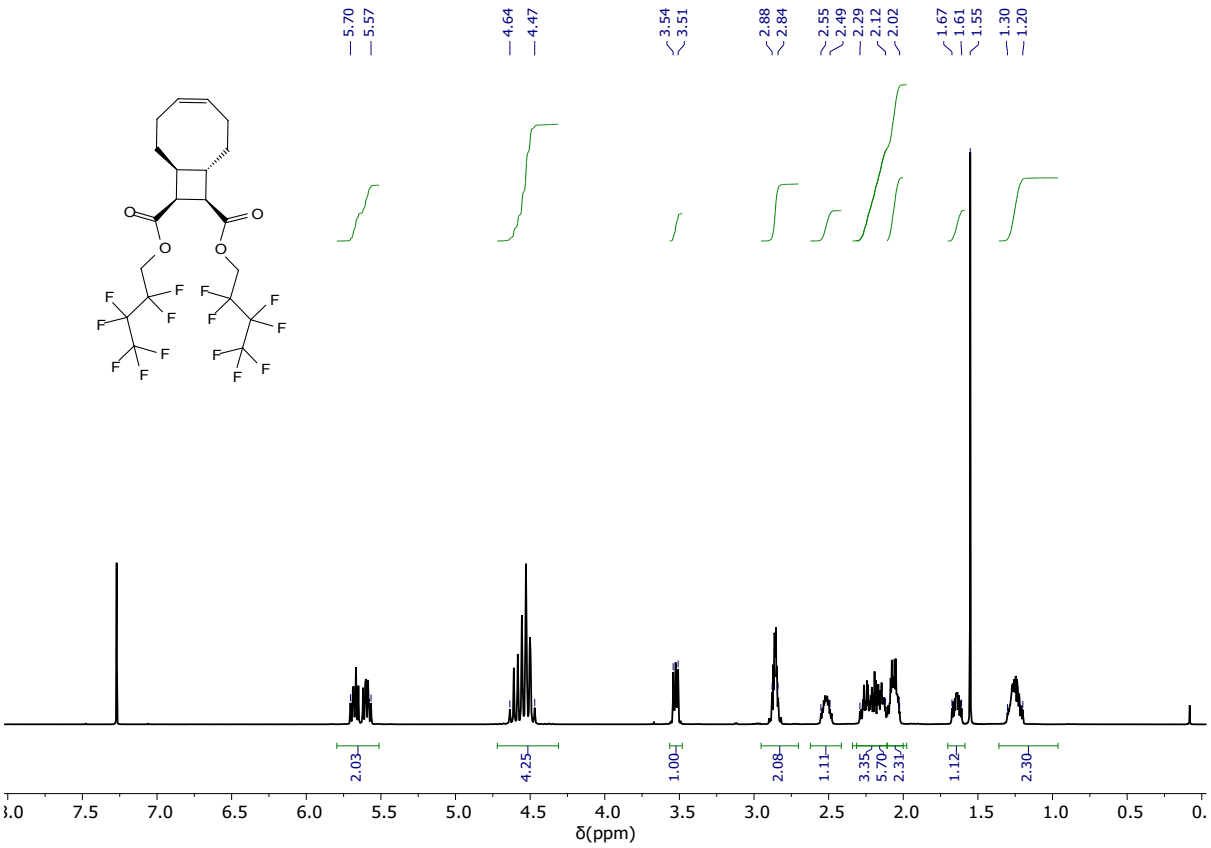


Figure S6 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) for the heptafluorobutyl diester **M1**.

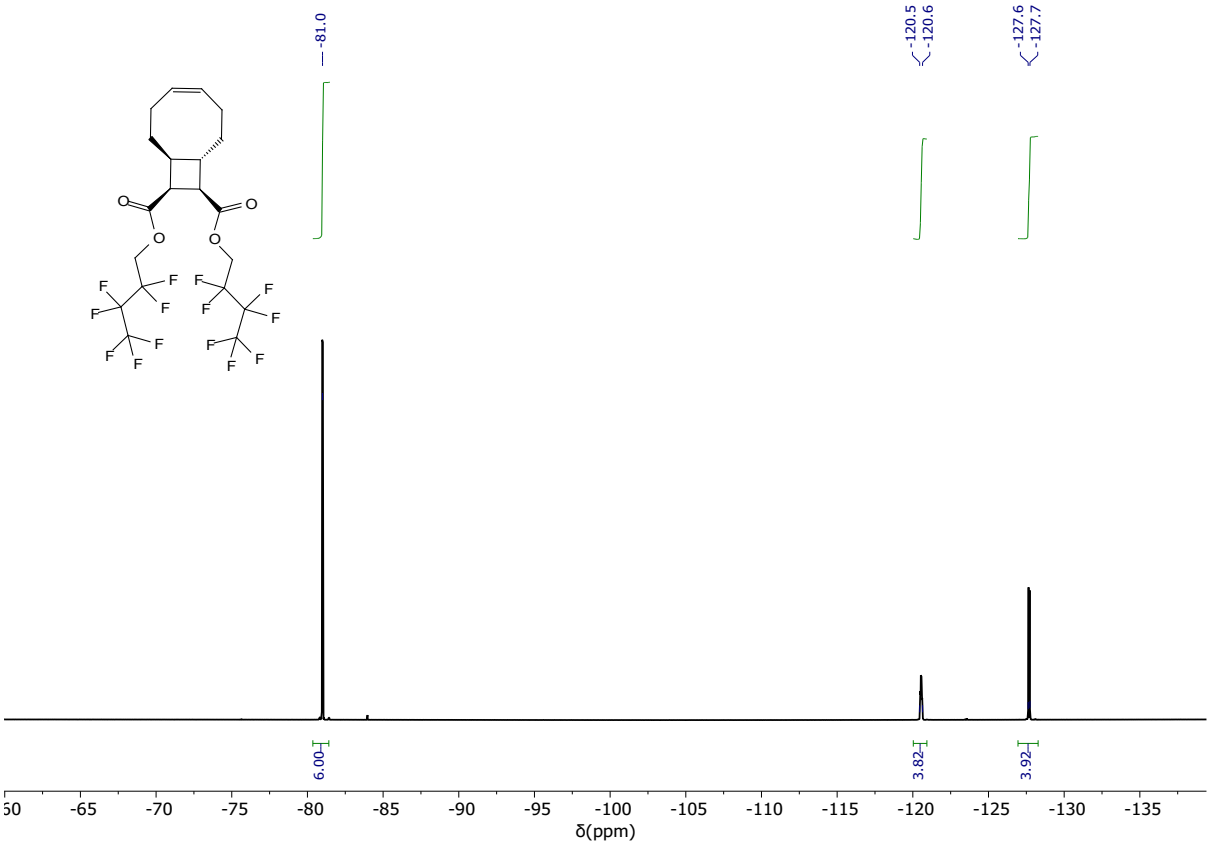


Figure S7 ^{19}F NMR spectrum (470 MHz, $CDCl_3$) for the heptafluorobutyl diester **M1**.

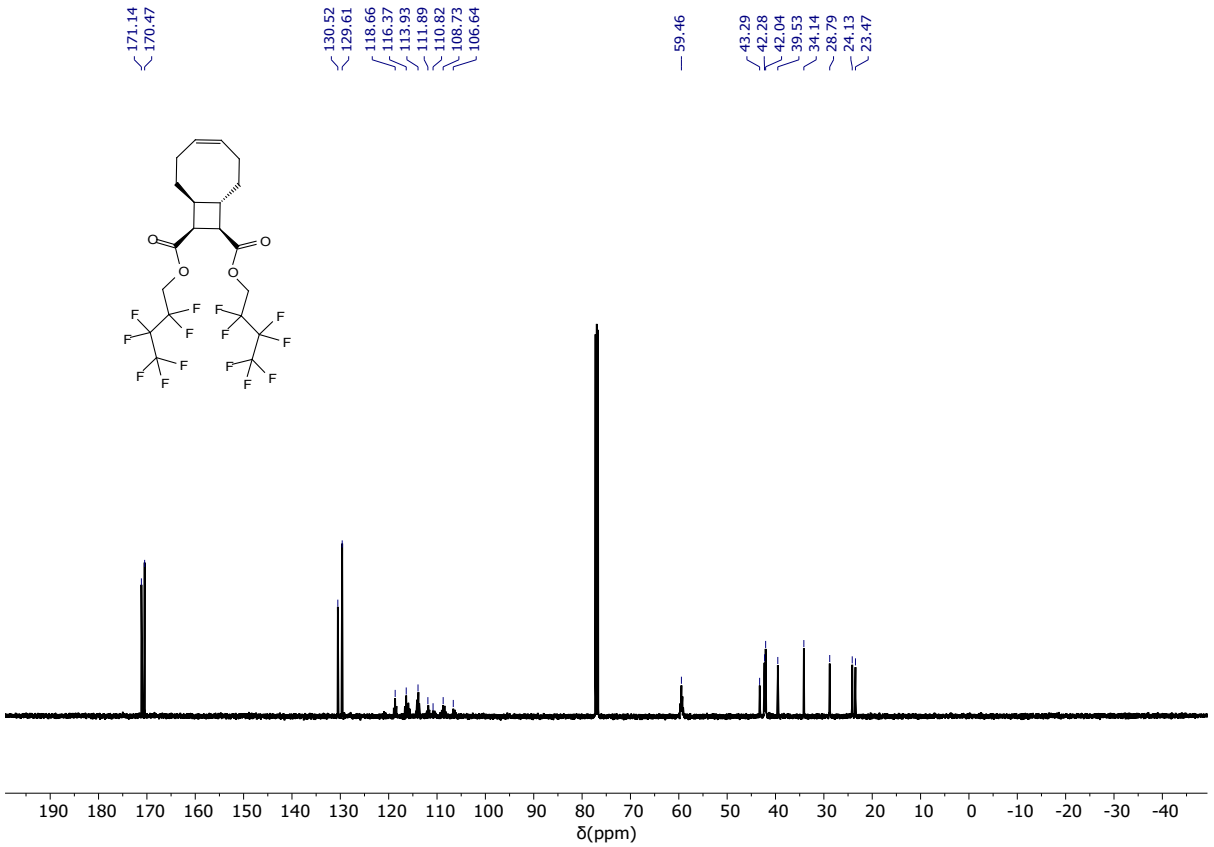


Figure S8 ^{13}C NMR spectrum (125 MHz, $CDCl_3$) for the heptafluorobutyl diester **M1**.

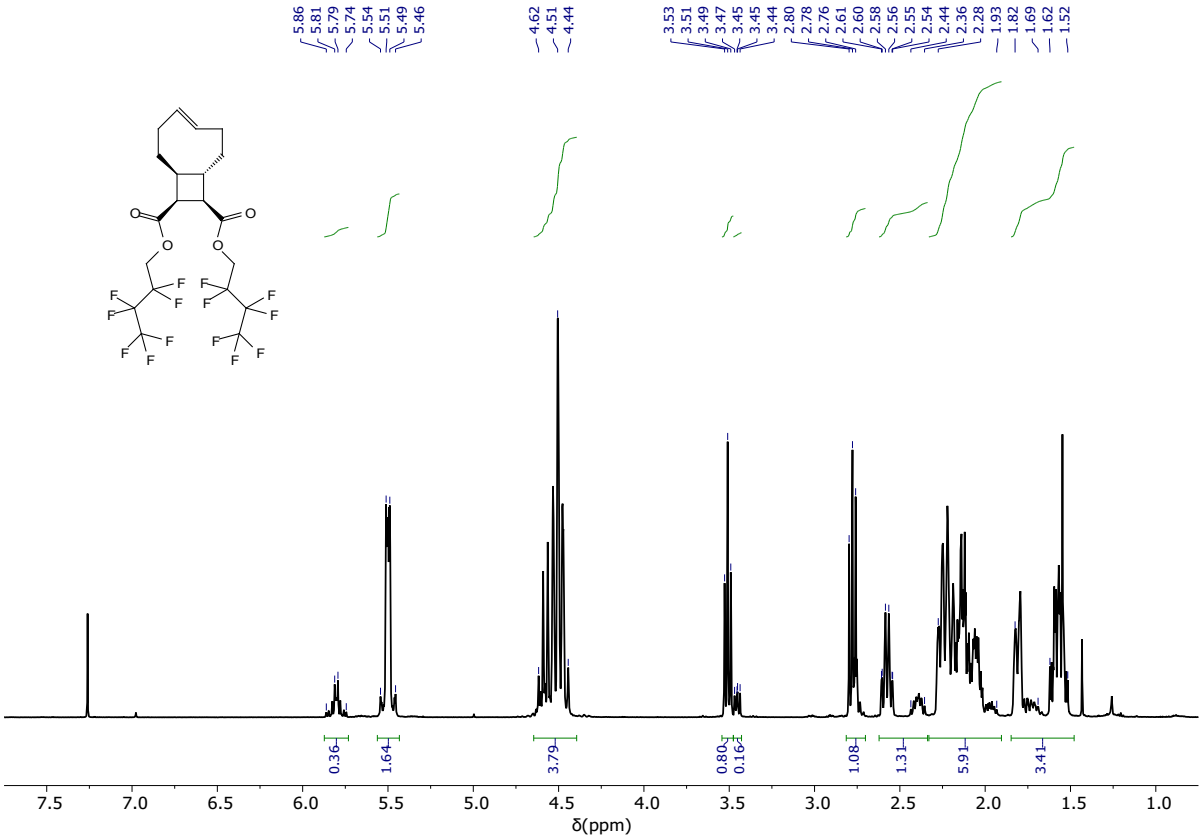


Figure S9 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) for the *E*-heptafluorobutyl diester ***E*-M1**.

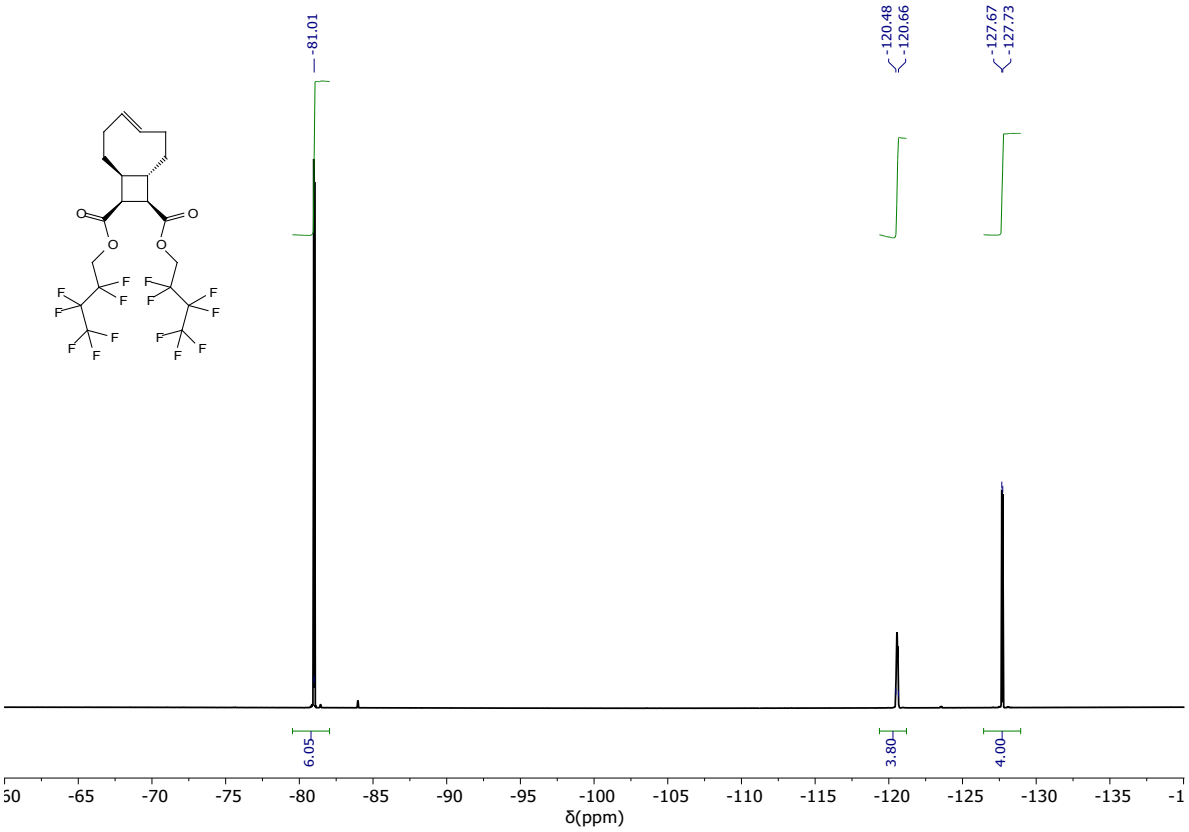


Figure S10 ^{19}F NMR spectrum (470 MHz, $CDCl_3$) for the *E*-heptafluorobutyl diester ***E*-M1**.

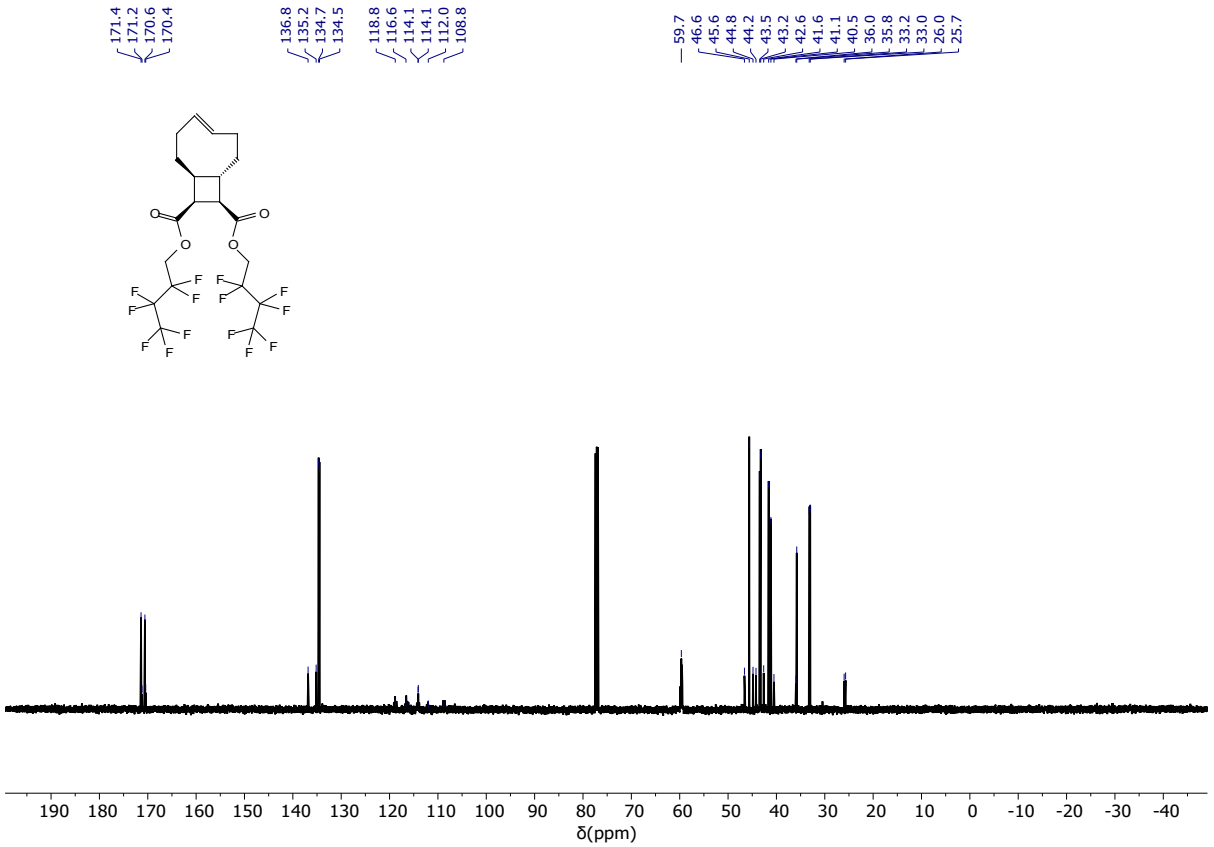


Figure S11 ^{13}C NMR spectrum (125 MHz, $CDCl_3$) for the *E*-heptafluorobutyl diester ***E*-M1**.

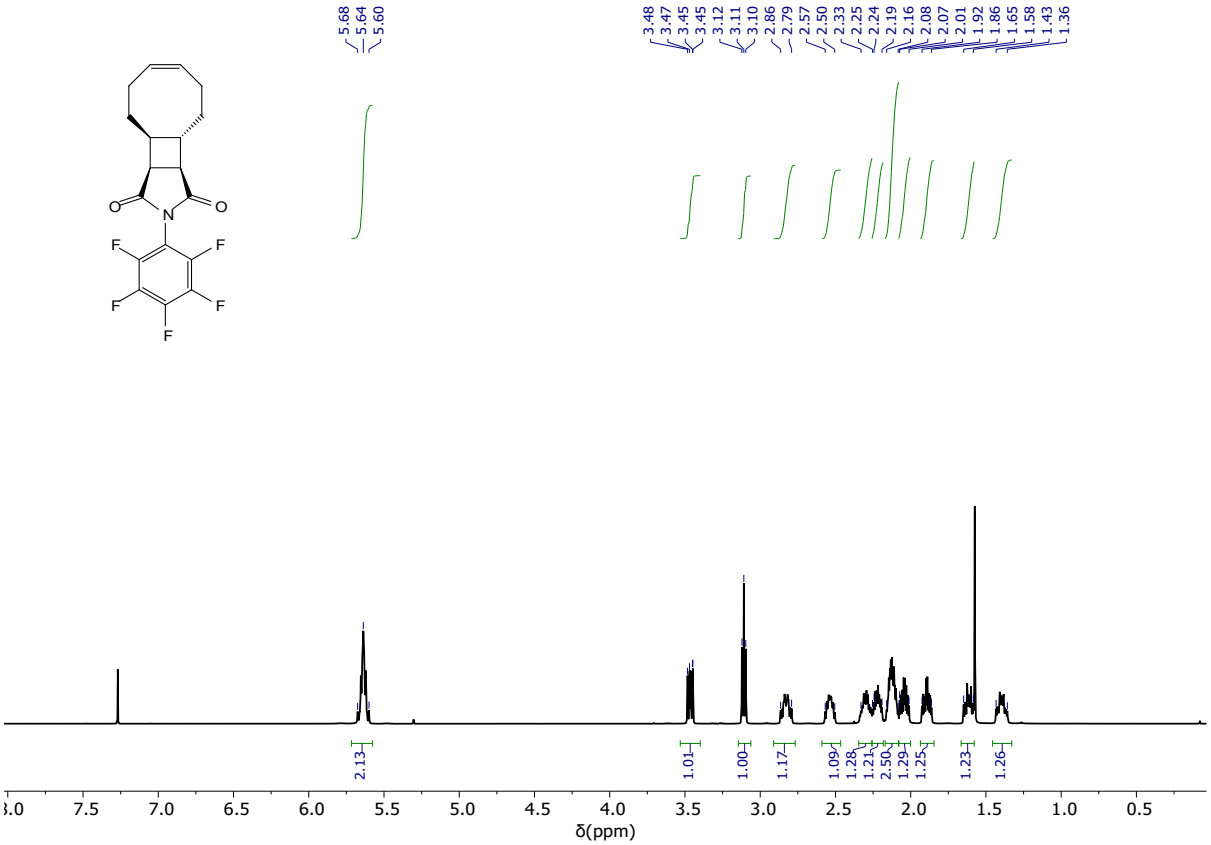


Figure S12 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) for the pentafluorophenyl imide **M2**.

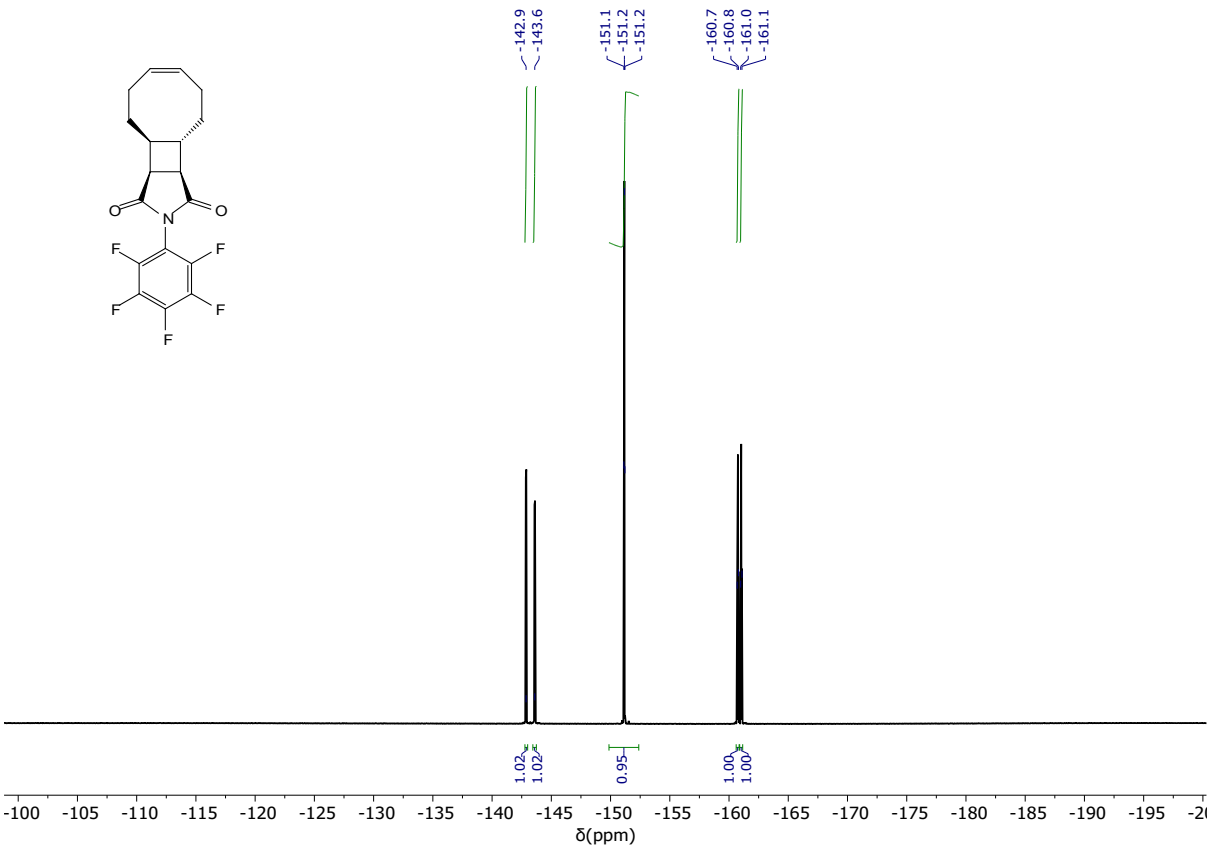


Figure S13 ^{19}F NMR spectrum (470 MHz, $CDCl_3$) for the pentafluorophenyl imide **M2**.

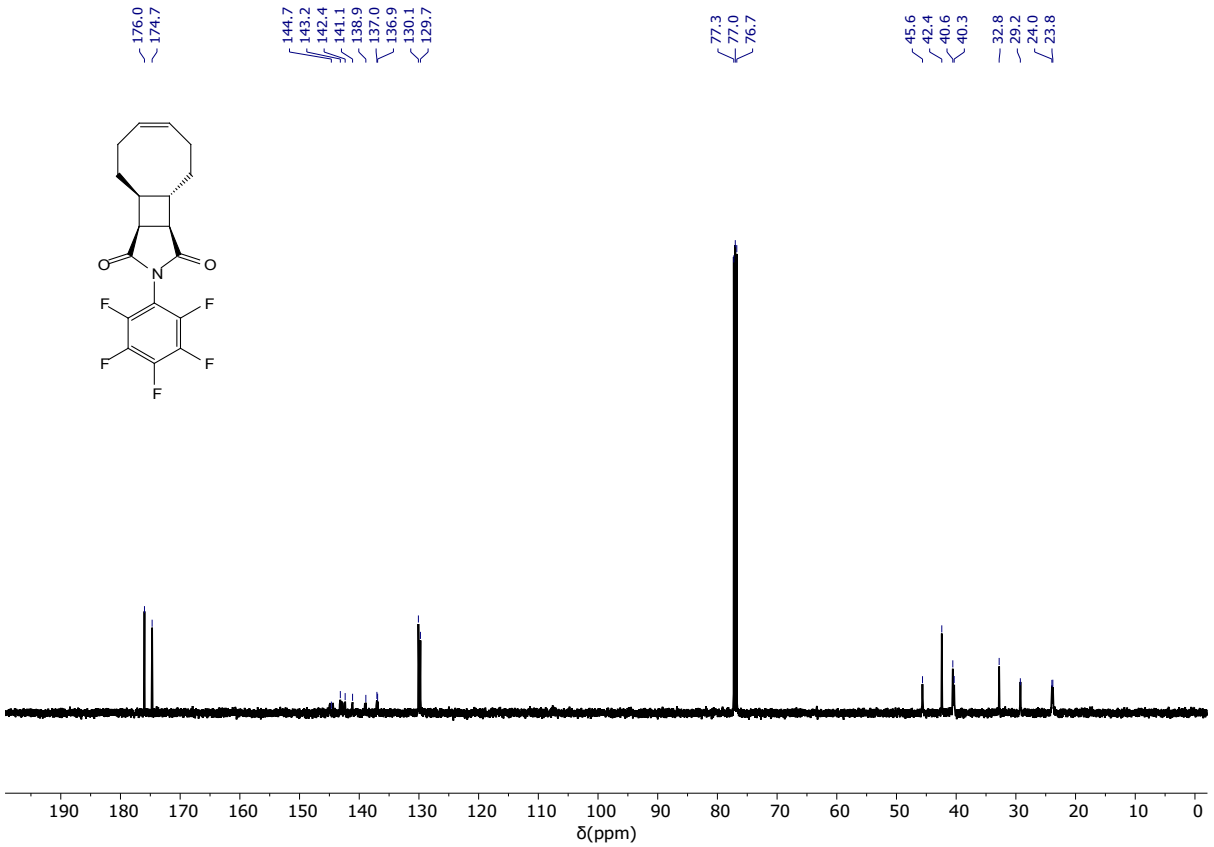


Figure S14 ^{13}C NMR spectrum (125 MHz, $CDCl_3$) for the pentafluorophenyl imide **M2**.

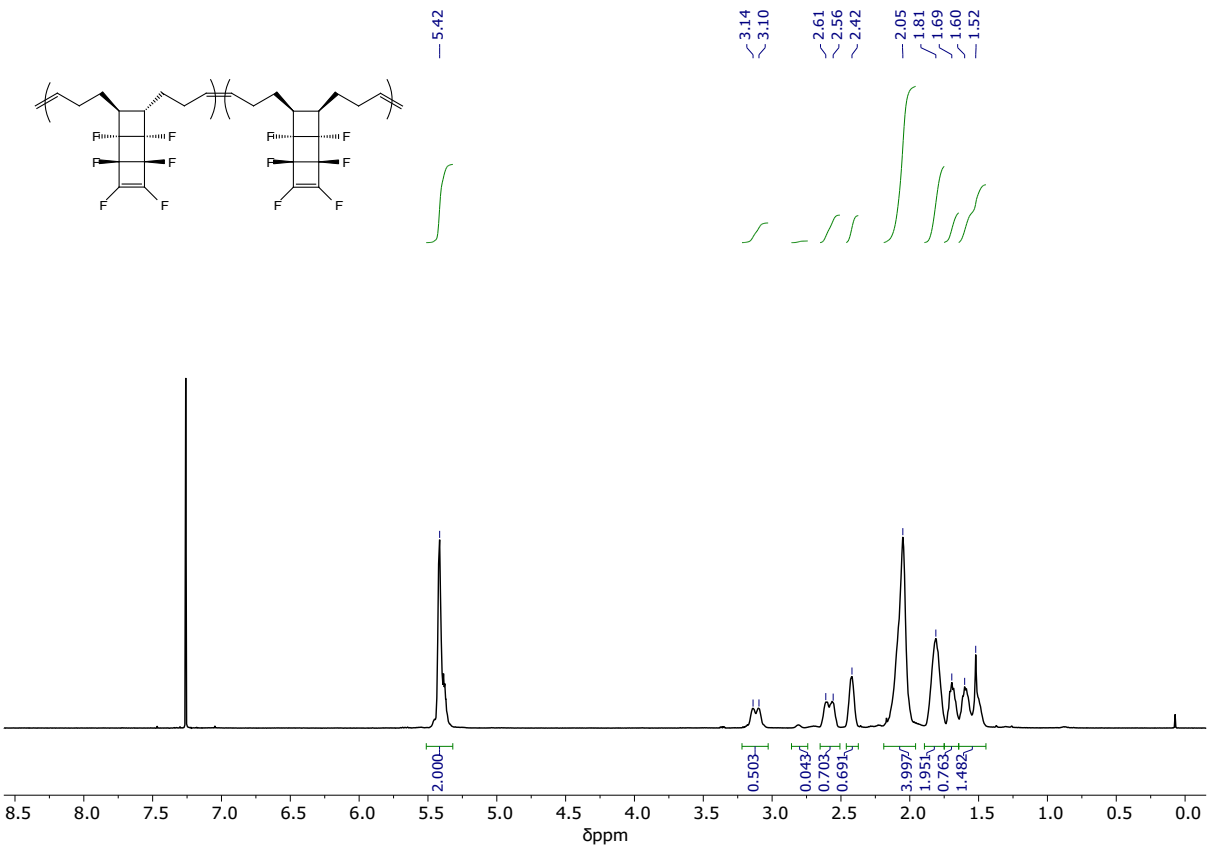


Figure S15 ^{1}H NMR spectrum (125 MHz, $CDCl_3$) for the polymerized mixture of *trans*- and *cis*-cyclobutane isomers of **M3**.

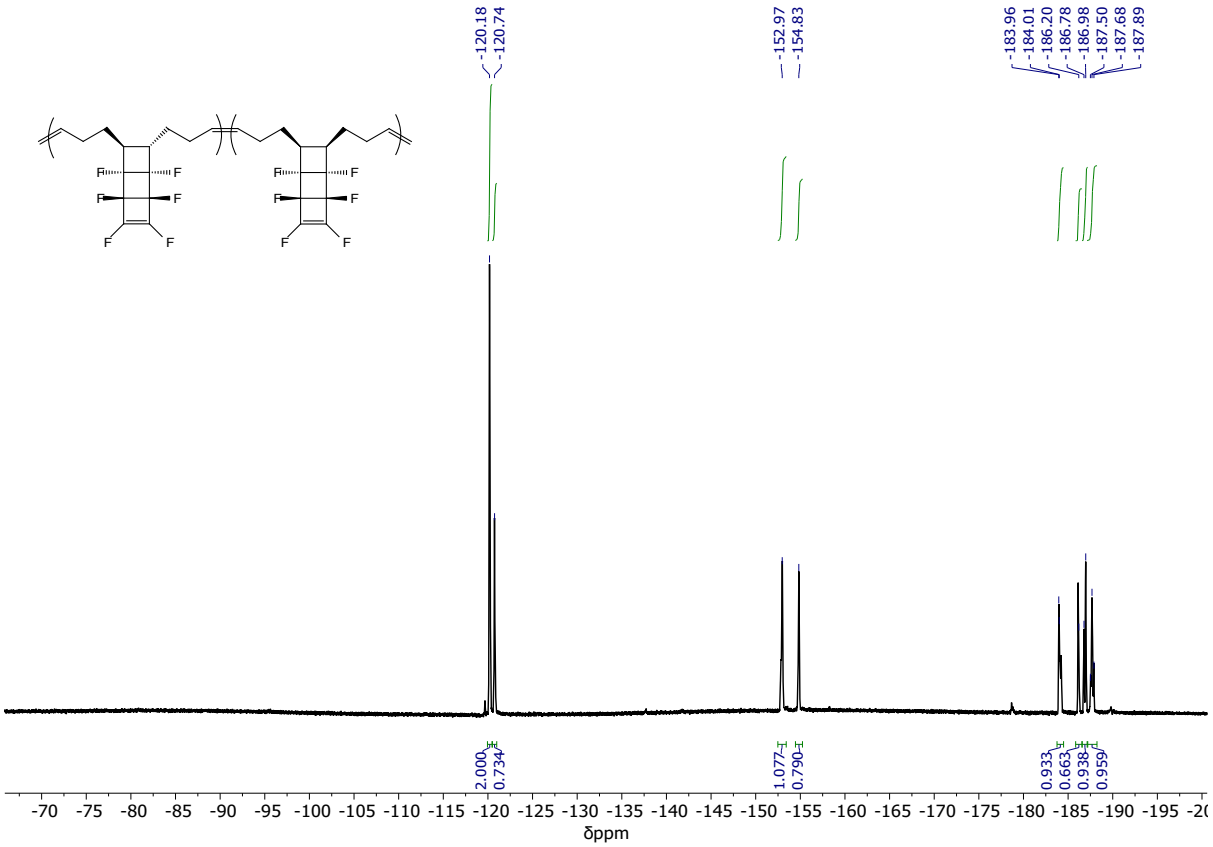


Figure S16 ^{19}F NMR spectrum (125 MHz, $CDCl_3$) for the polymerized mixture of *trans*- and *cis*-cyclobutane isomers of **M3**.

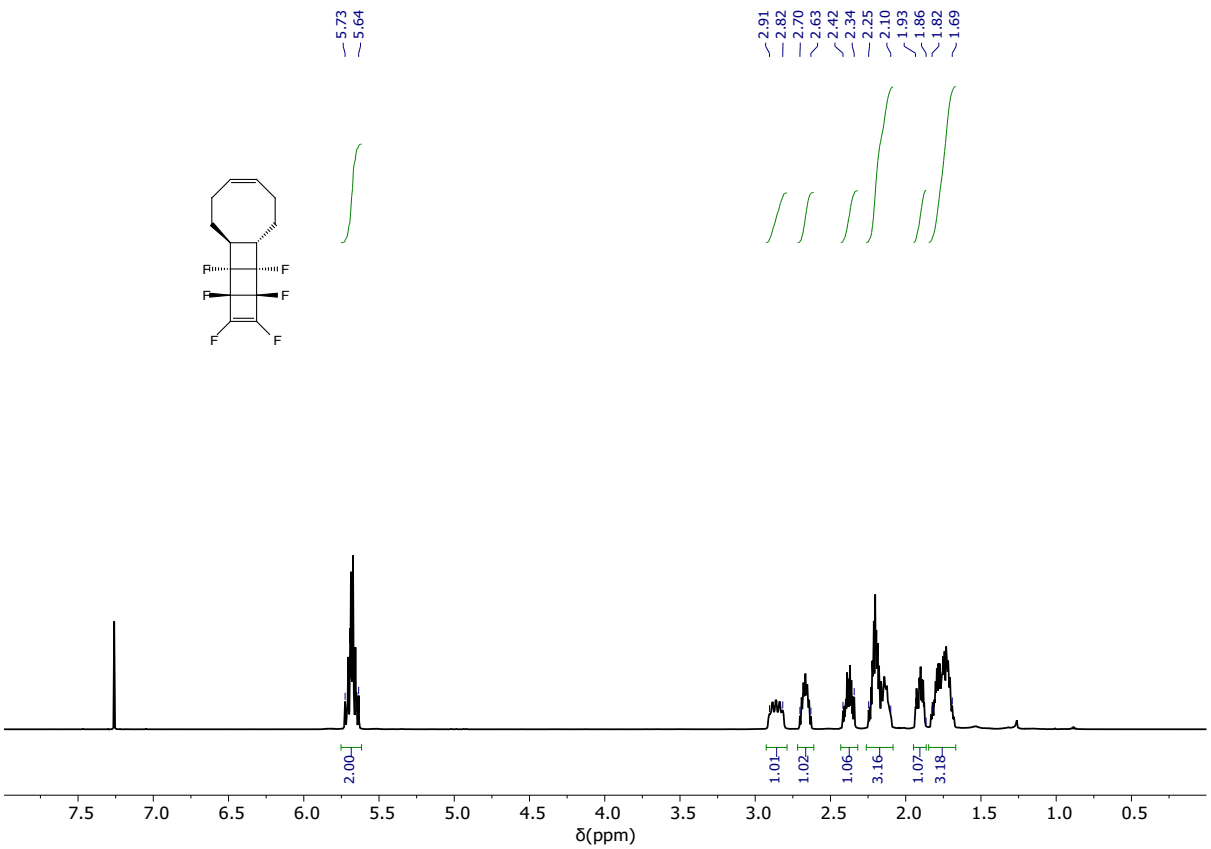


Figure S17 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) for the fluorinated ladderene **M3**.

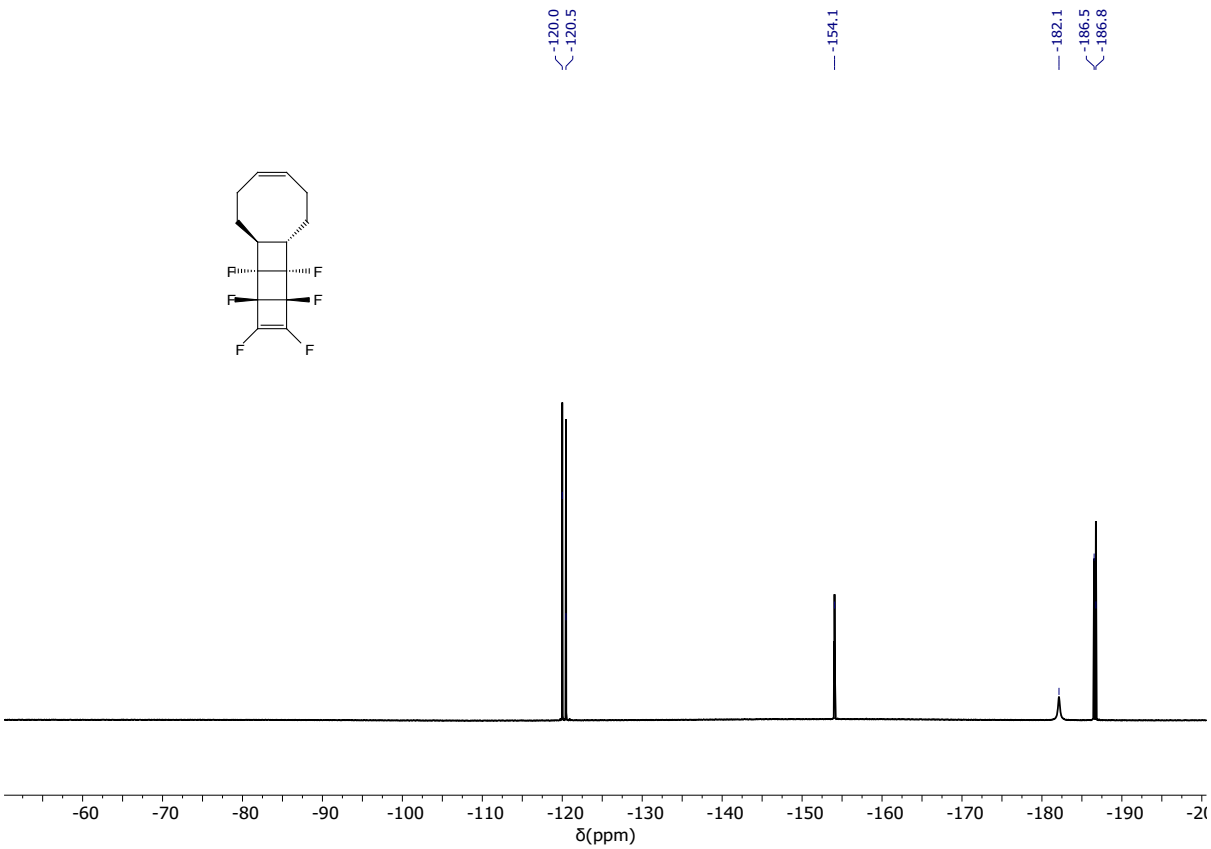


Figure S18 ^{19}F NMR spectrum (470 MHz, $CDCl_3$) for the fluorinated ladderene **M3**.

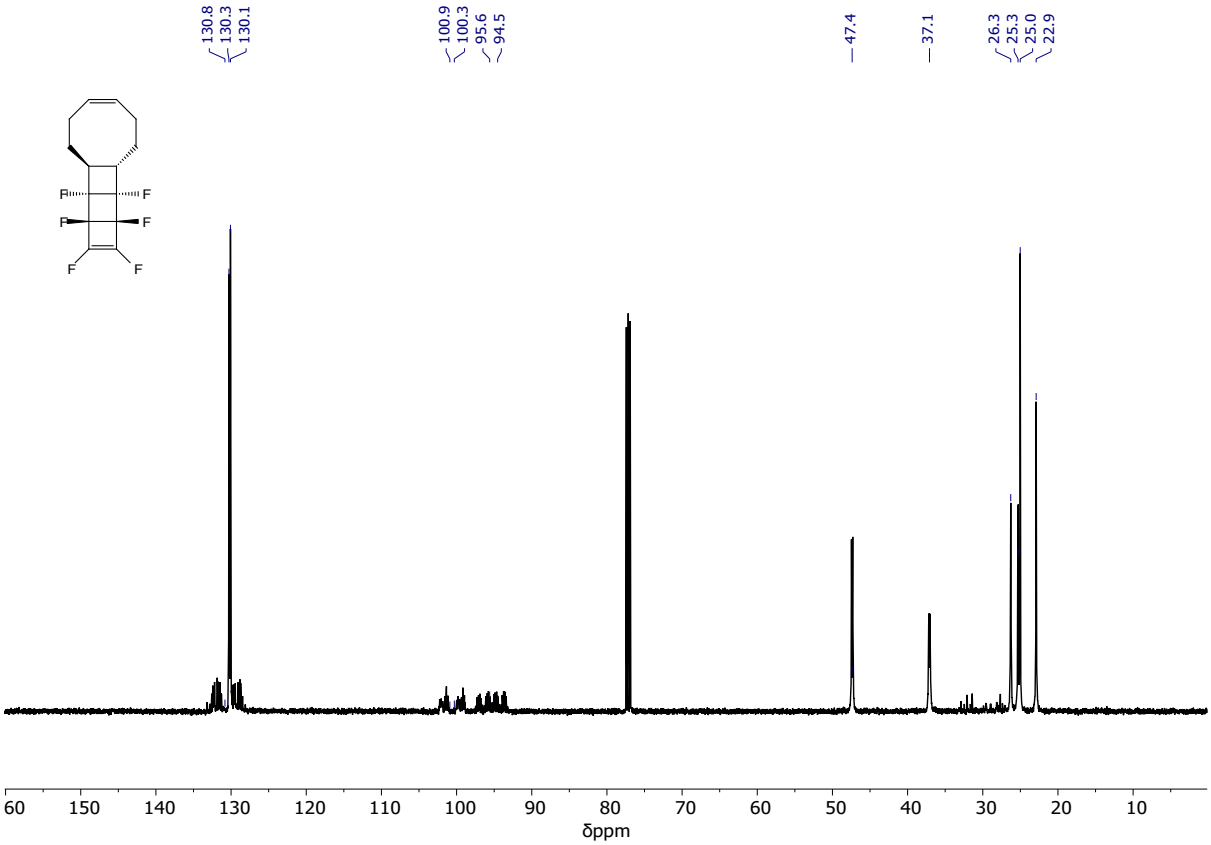


Figure S19 ^{13}C NMR spectrum (125 MHz, $CDCl_3$) for the fluorinated ladderene **M3**.

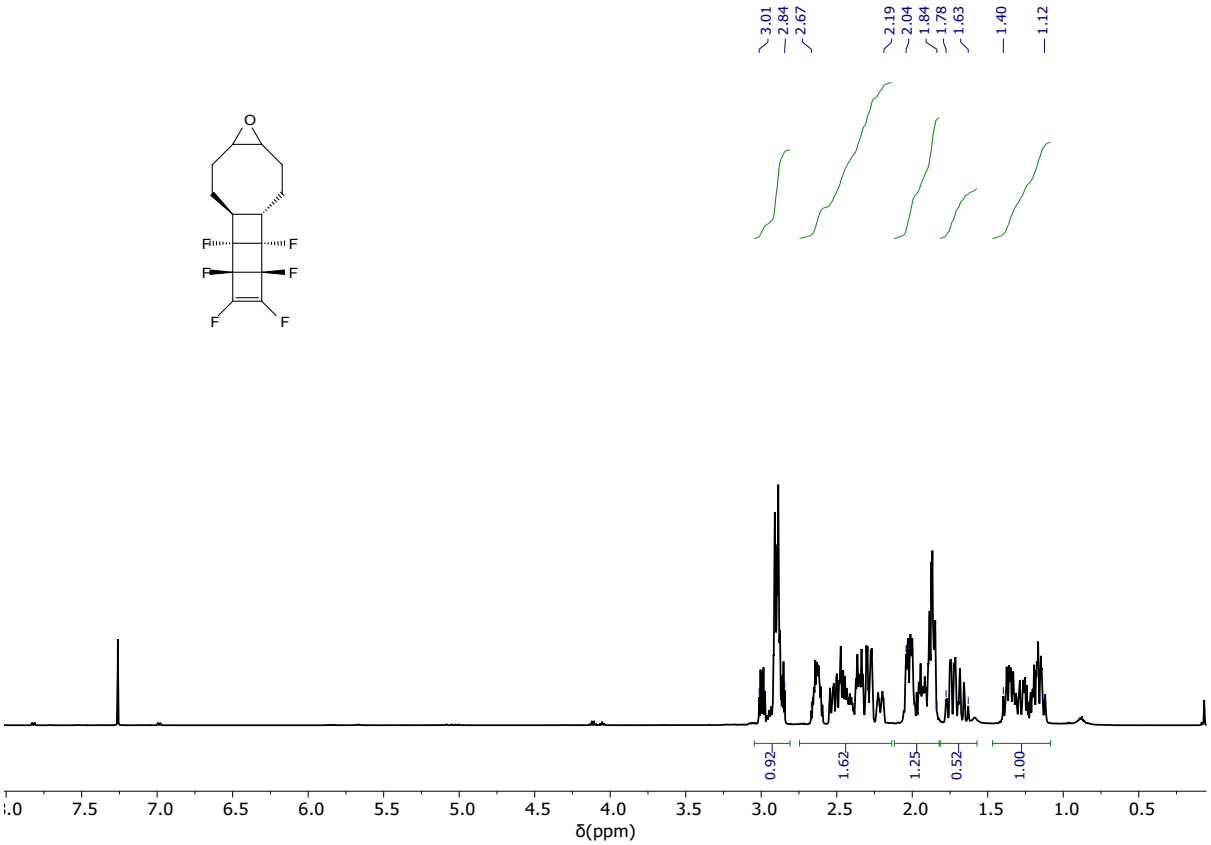


Figure S20 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) for the epoxide **2**.

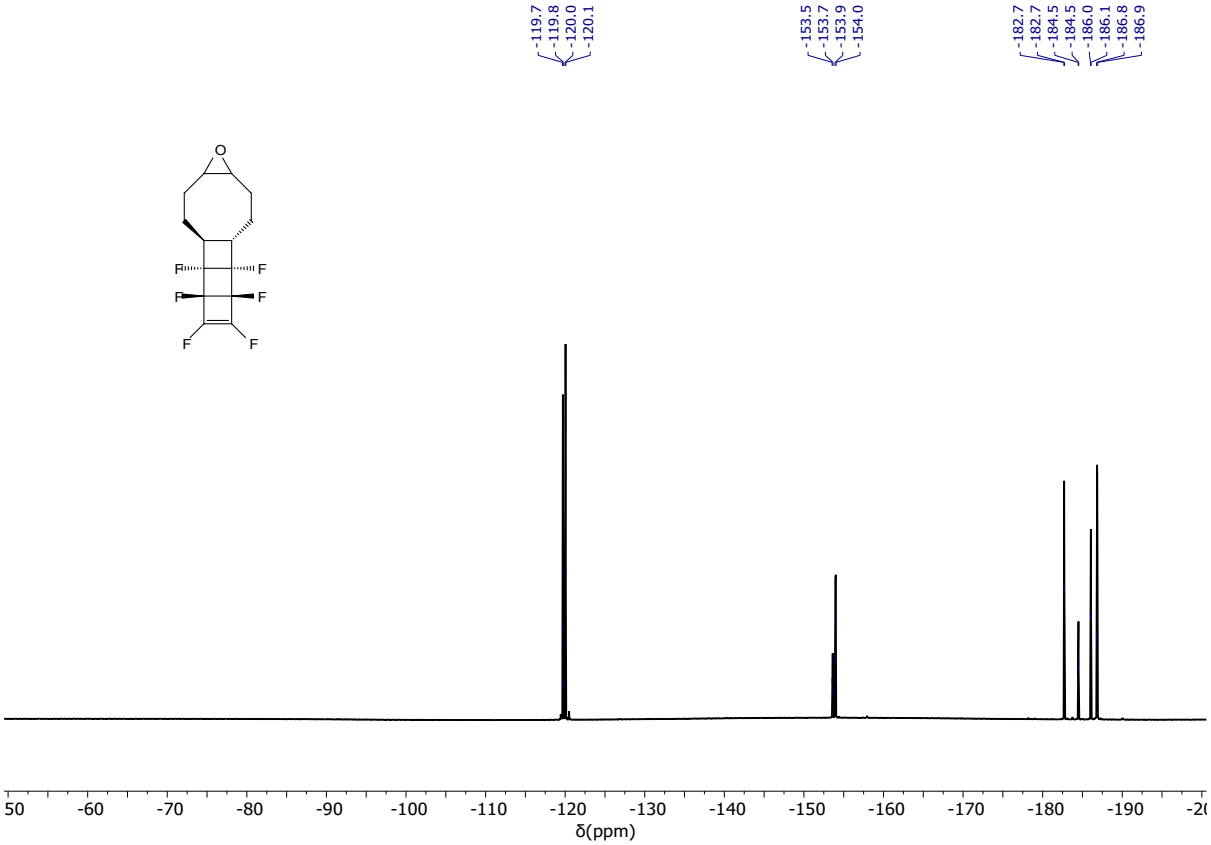


Figure S21 ^{19}F NMR spectrum (470 MHz, $CDCl_3$) for the epoxide **2**.

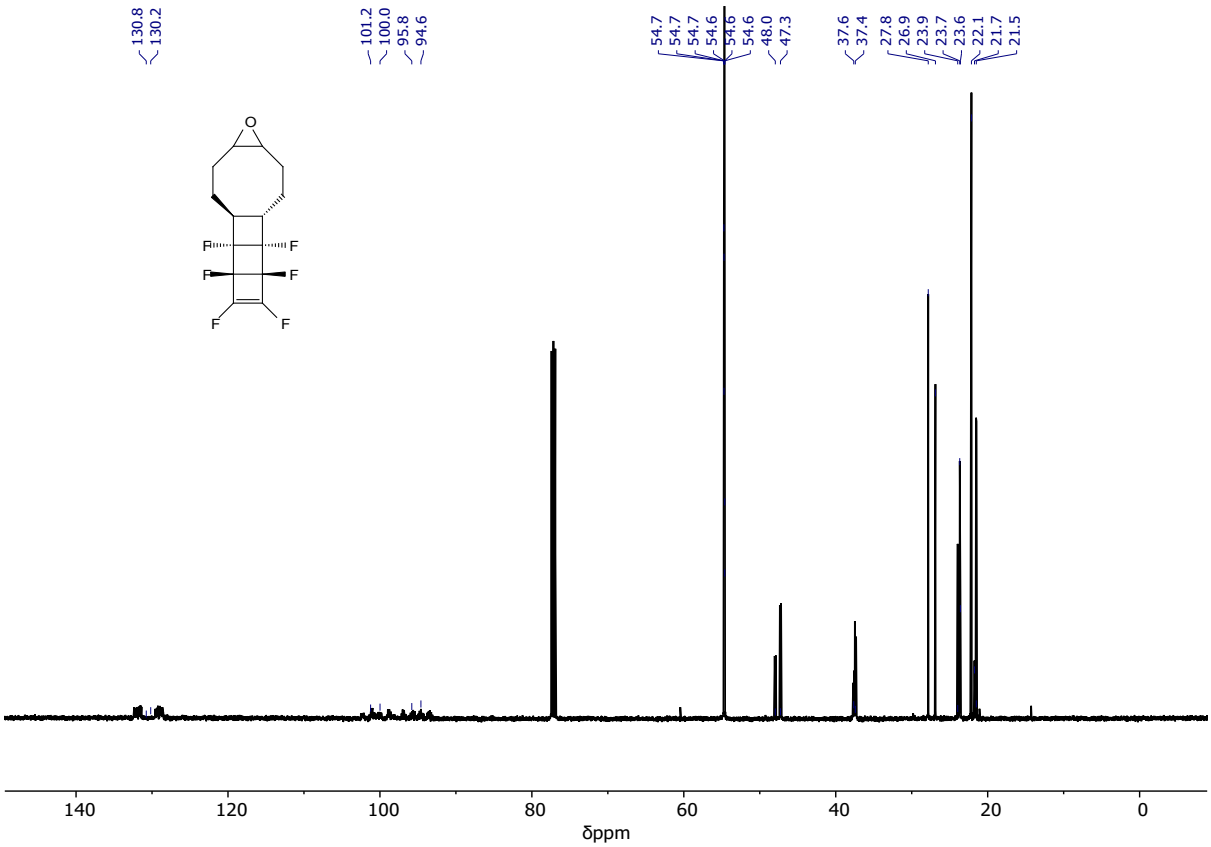


Figure S22 ^{13}C NMR spectrum (125 MHz, $CDCl_3$) for the epoxide **2**.

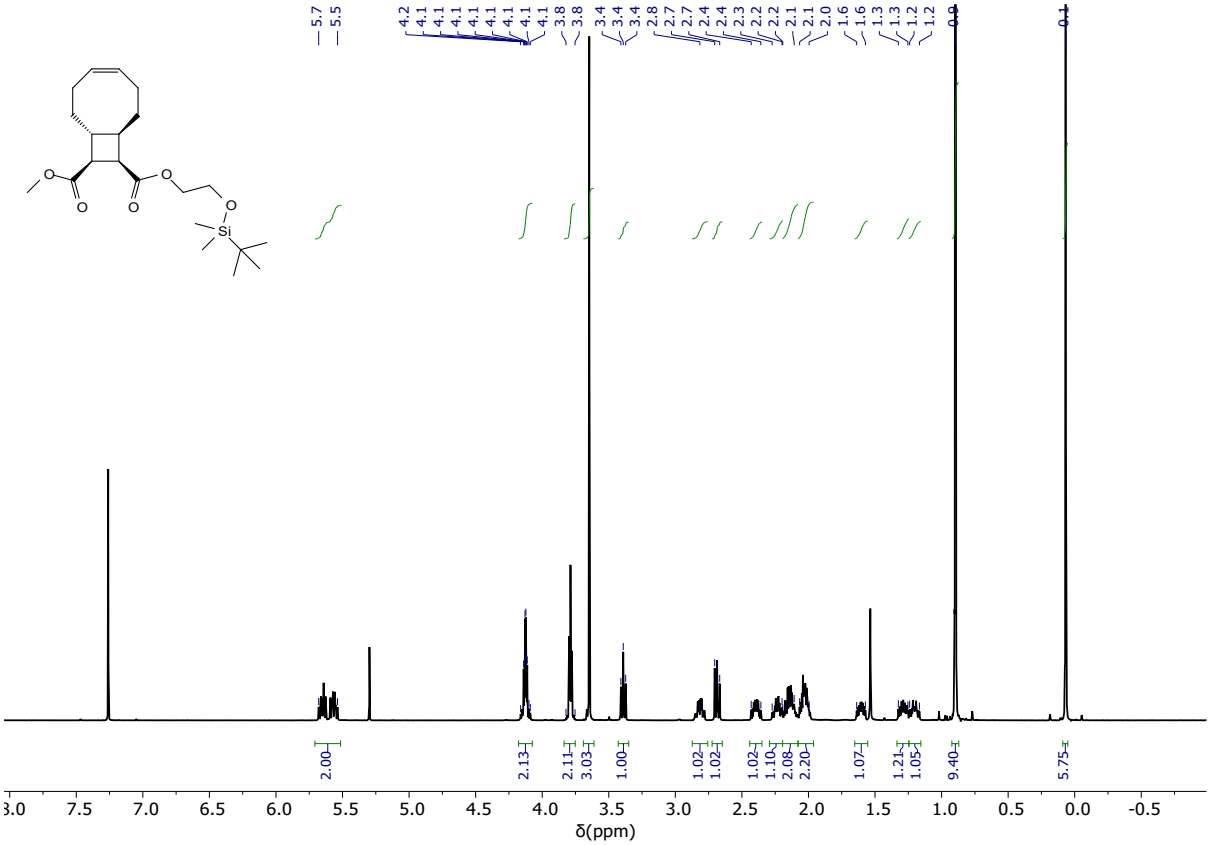


Figure S23 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) for the TBS-diester **6**.

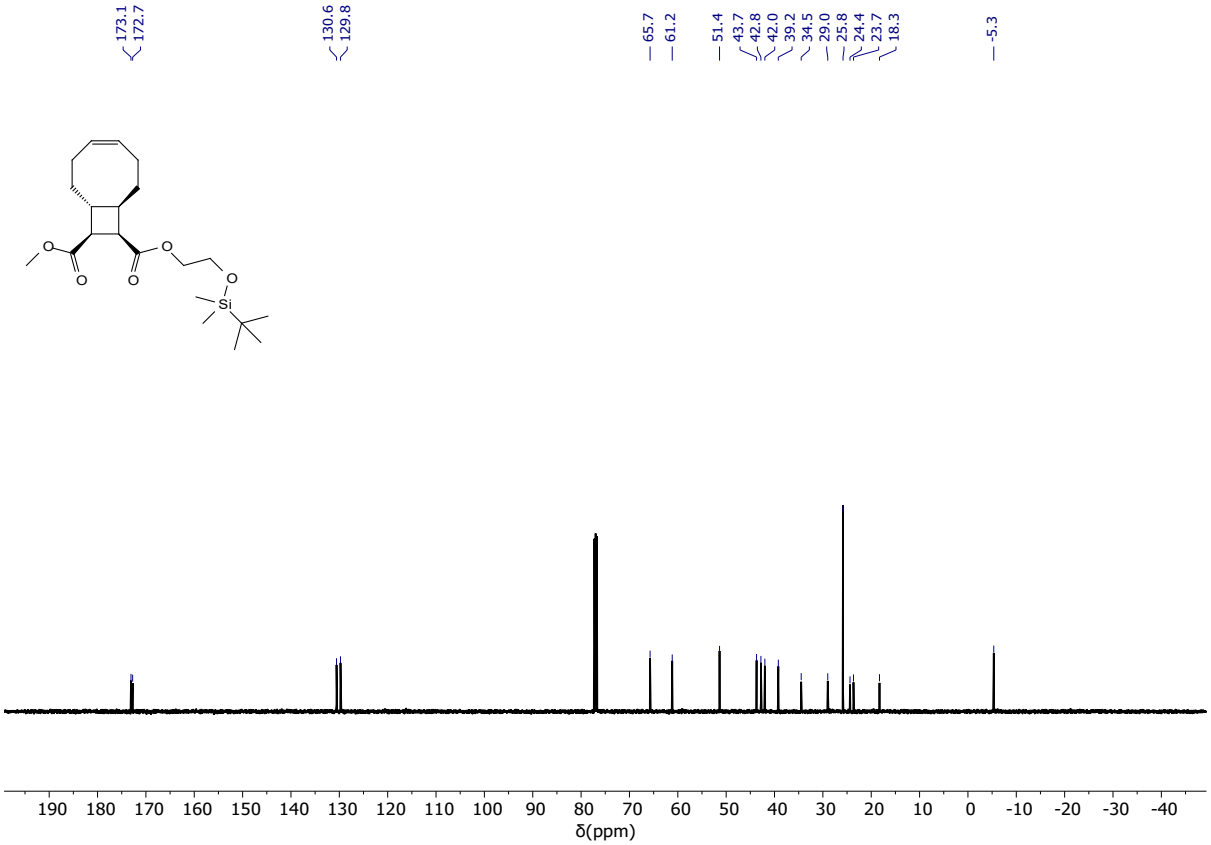


Figure S24 ^{13}C NMR spectrum (125 MHz, $CDCl_3$) for the TBS-diester **6**.

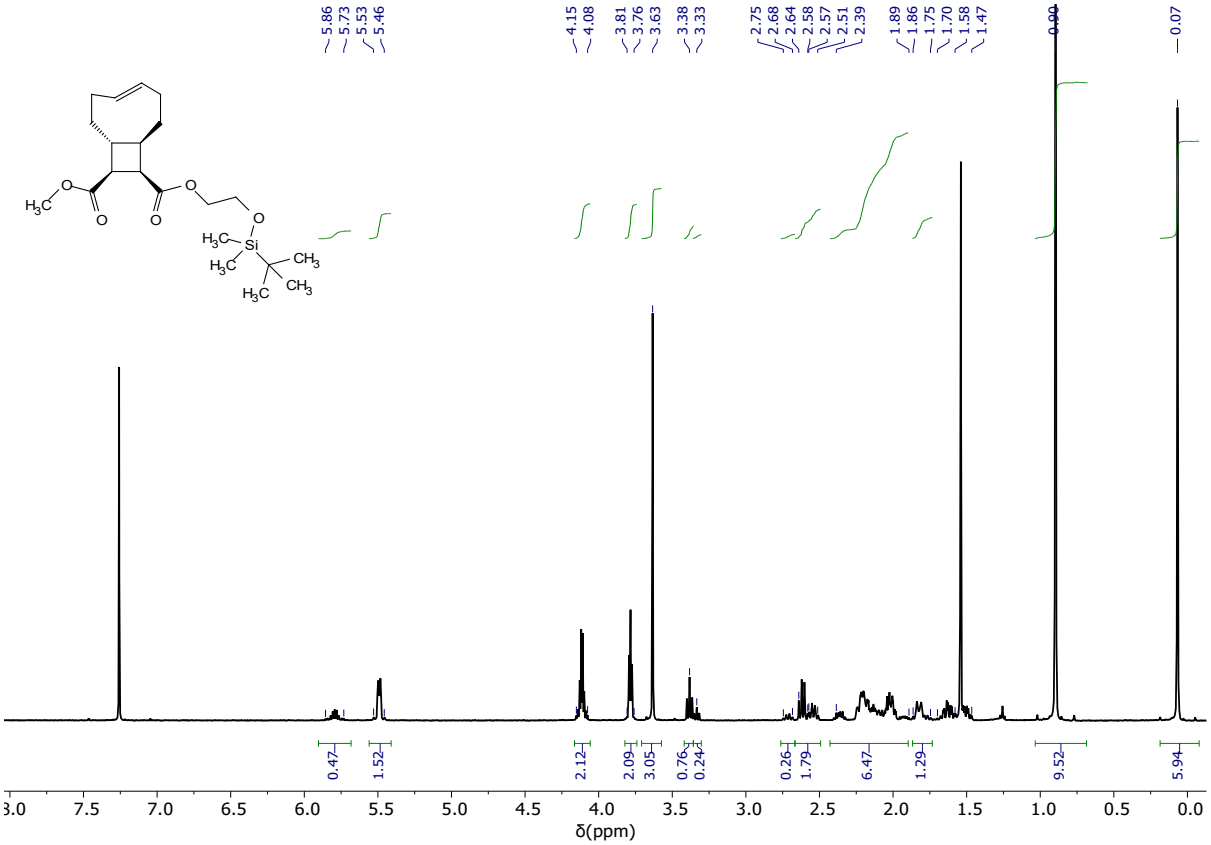


Figure S25 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) for the *E*-TBS diester ***E*-6**.

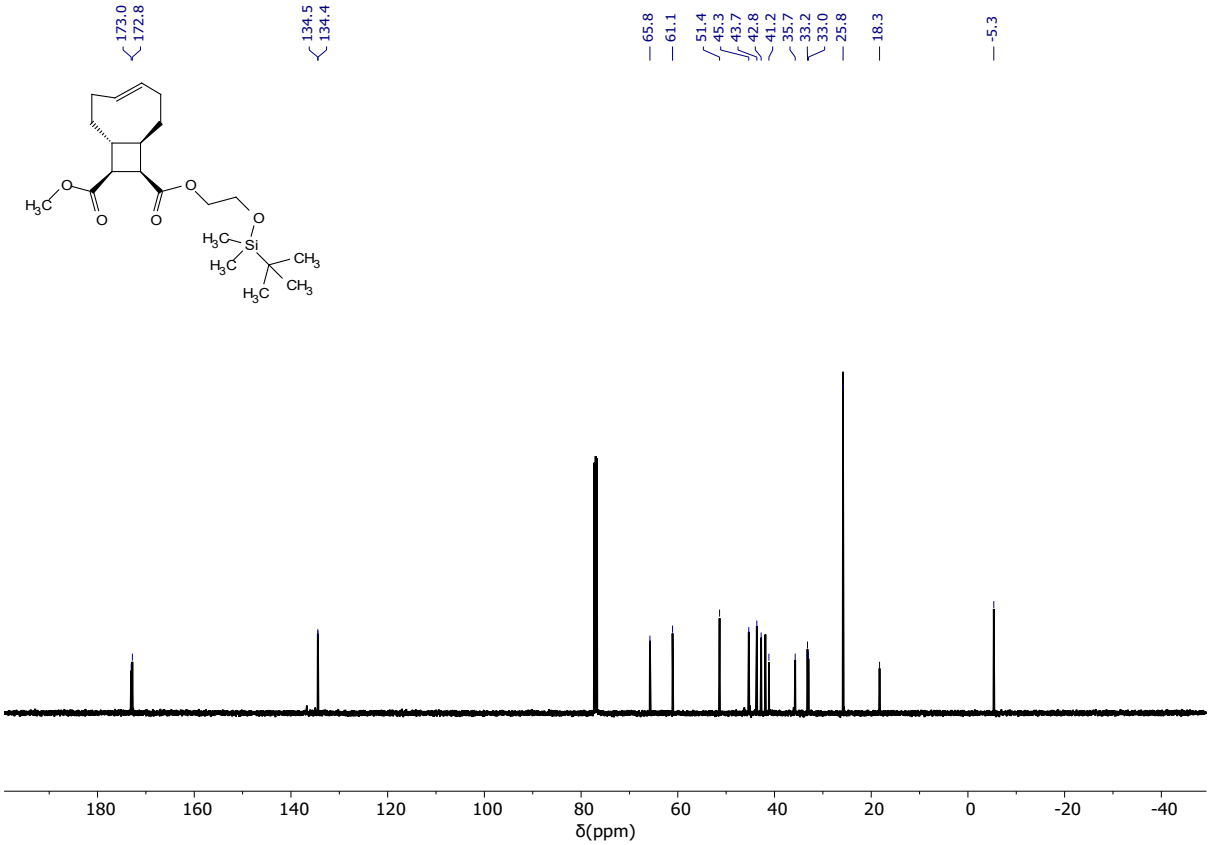


Figure S26 ^{13}C NMR spectrum (125 MHz, $CDCl_3$) for the *E*-TBS diester ***E*-6**.

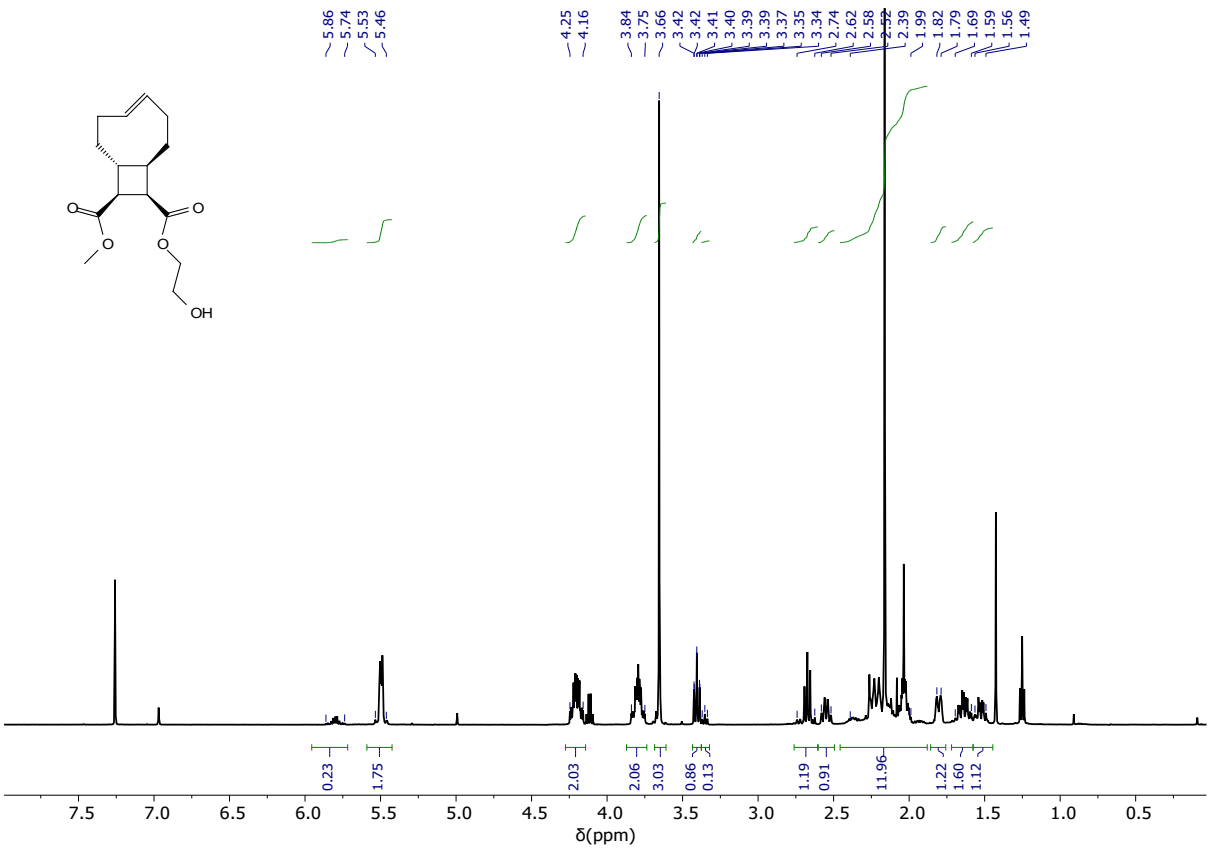


Figure S27 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) for the hydroxy ester ***E*-7**.

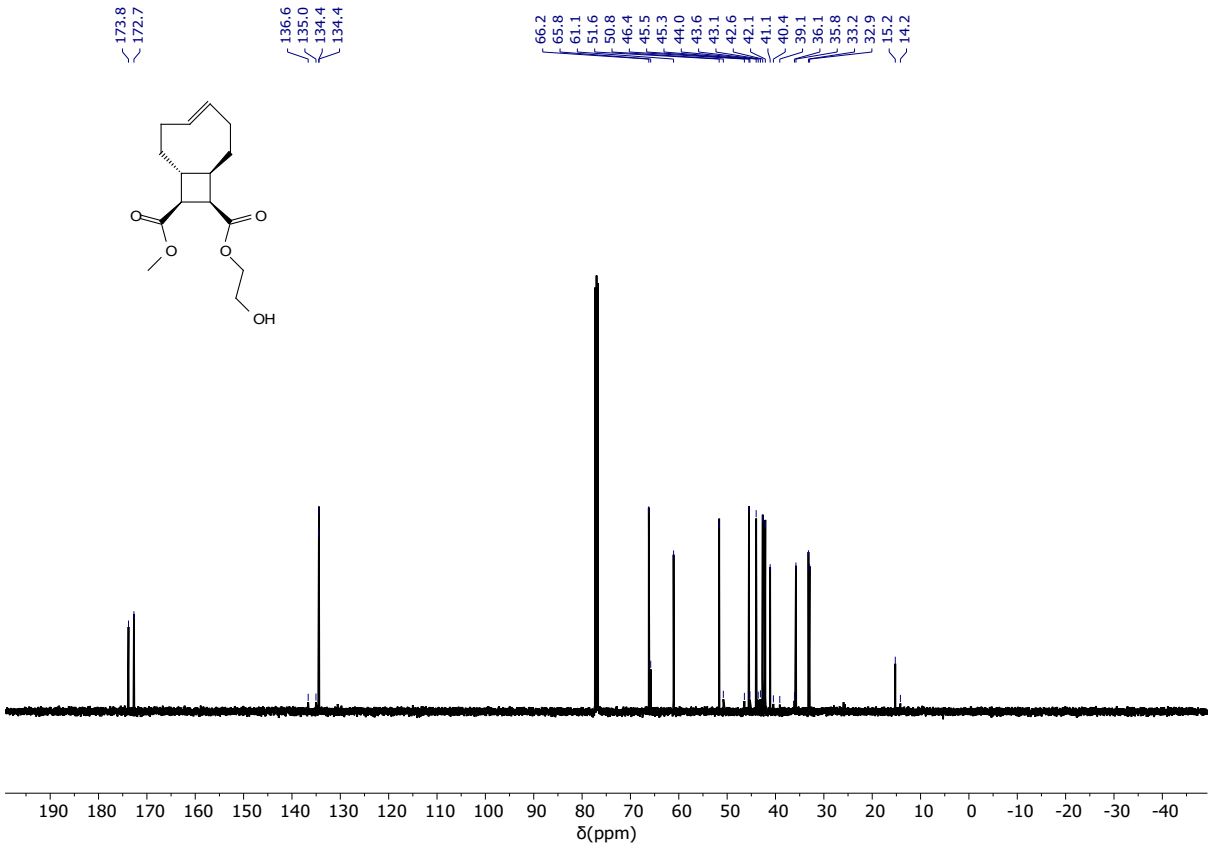


Figure S28 ^{13}C NMR spectrum (125 MHz, $CDCl_3$) for the hydroxy ester ***E*-7**.

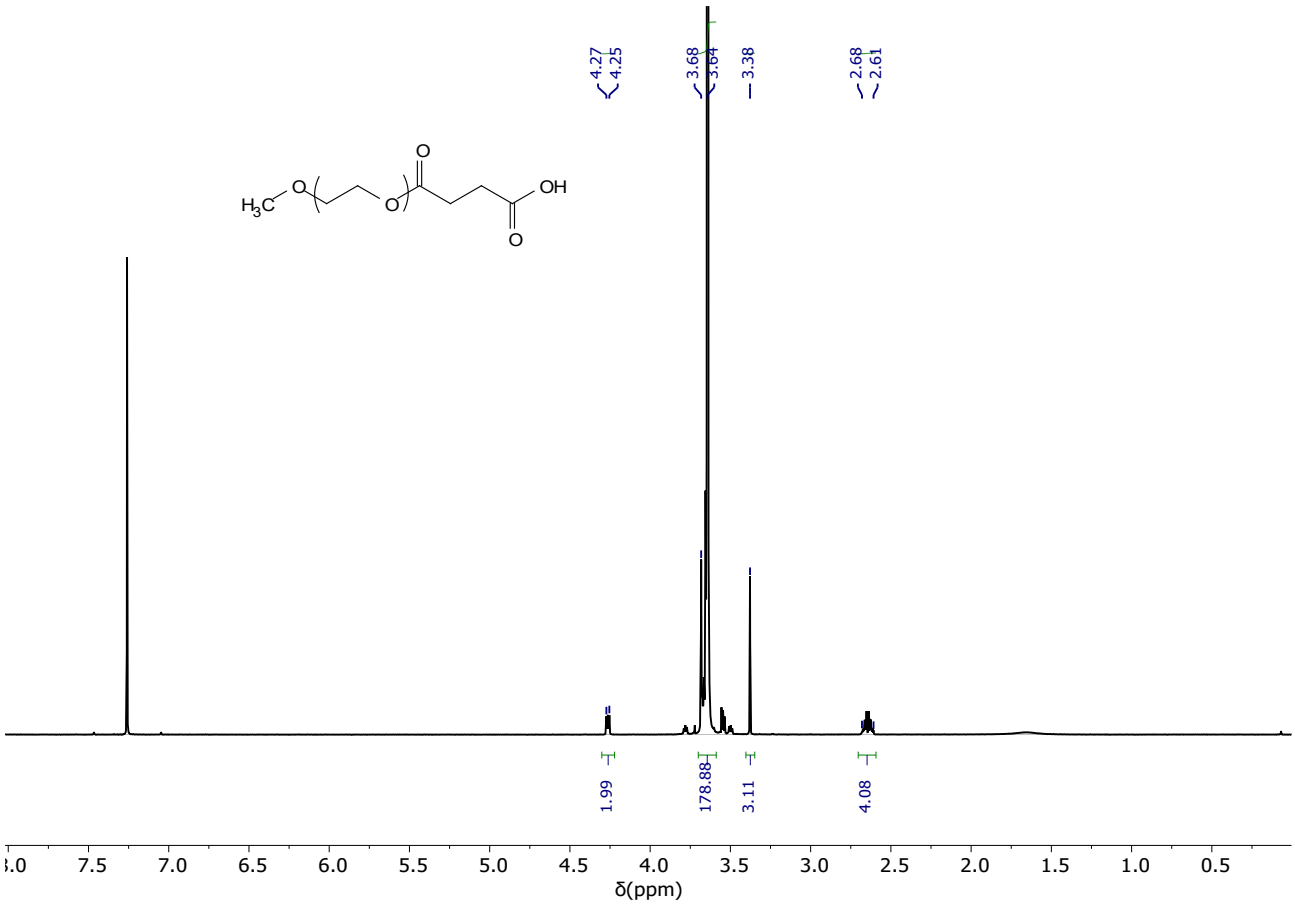


Figure S29 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) for the PEG succinate ester **8.**

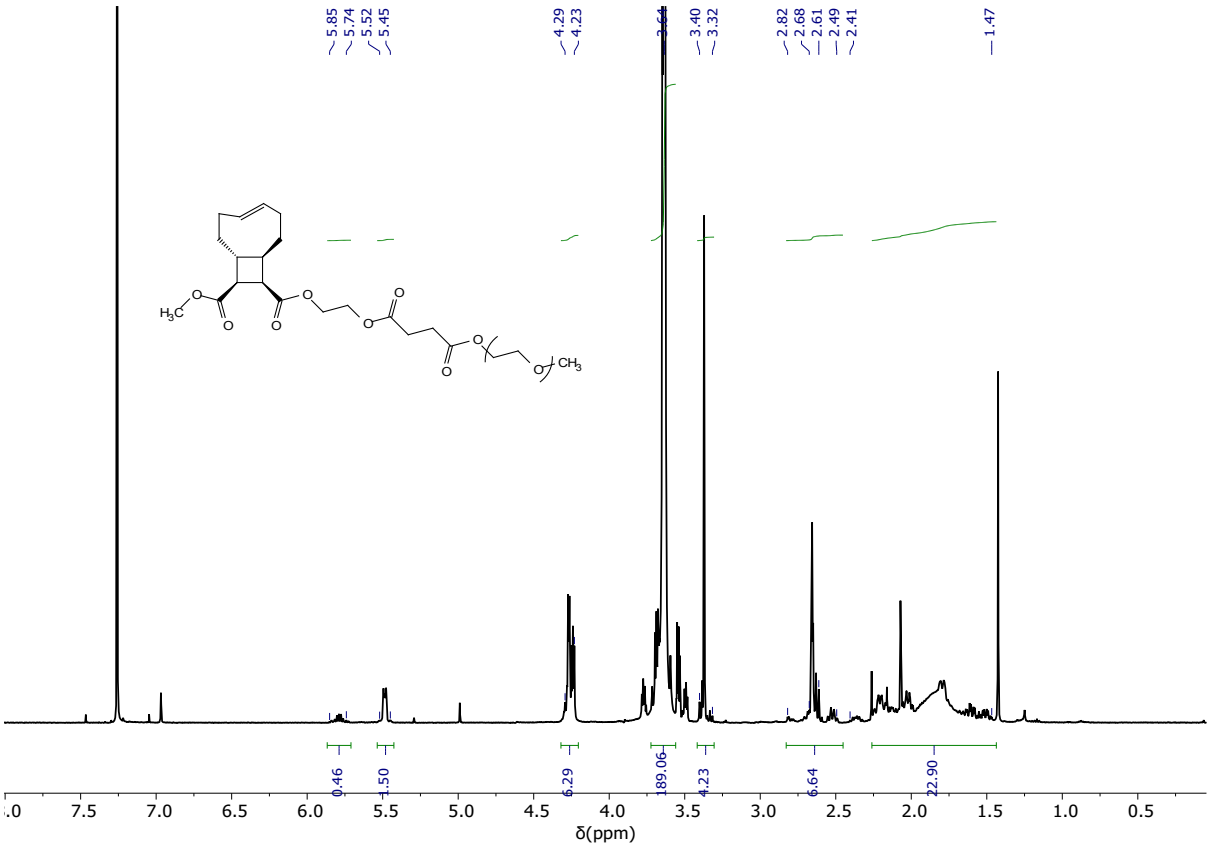


Figure S30 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) for the macromonomer ***E*-M4.**

Figures for polymer characterization

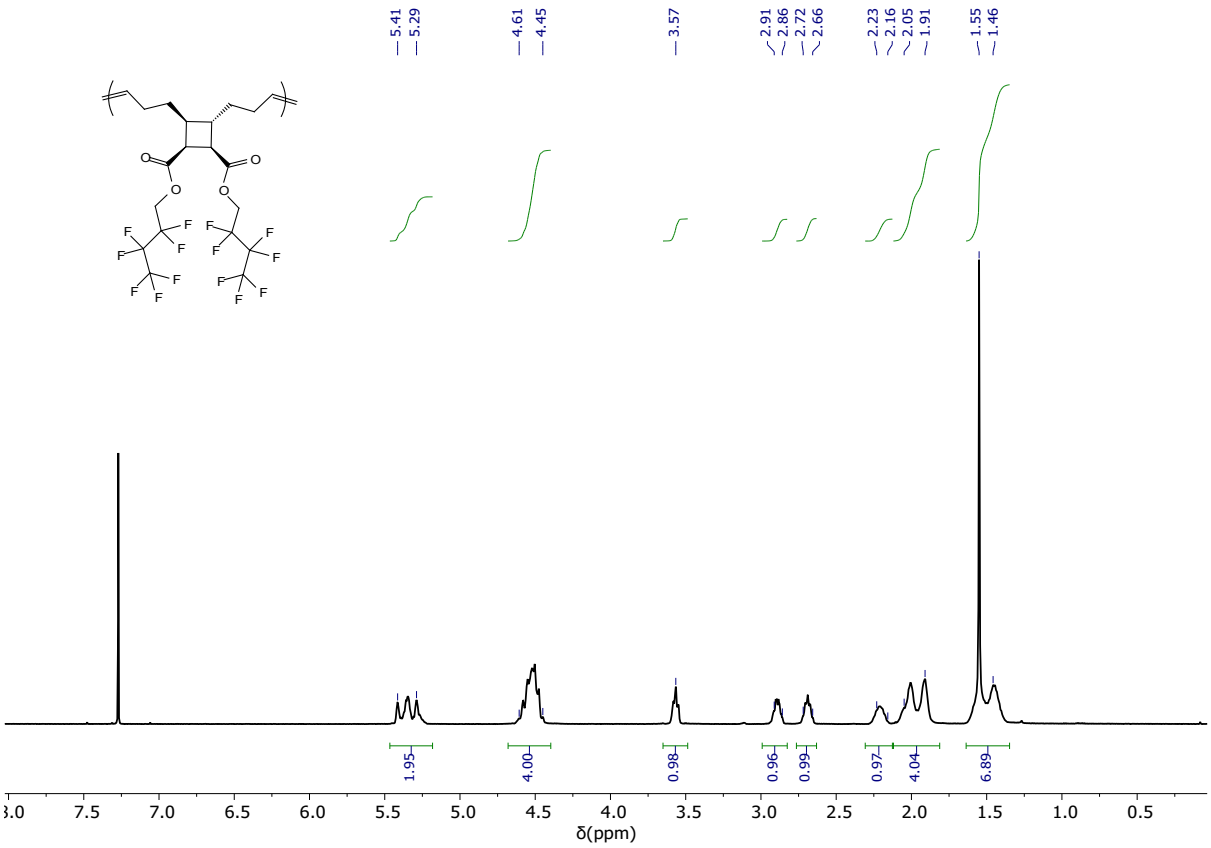


Figure S31 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) for the heptafluorobutyl diester polymer **P1**.

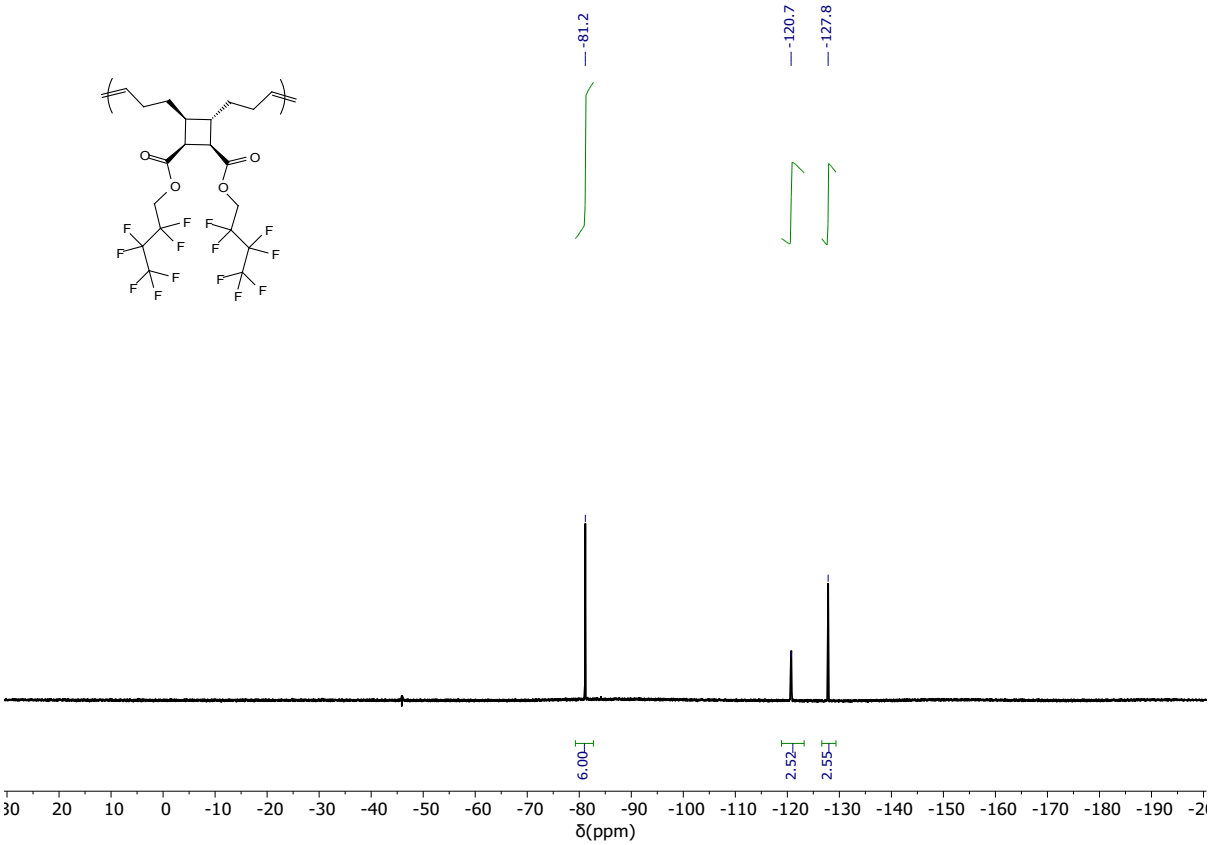


Figure S32 ^{19}F NMR spectrum (470 MHz, $CDCl_3$) for the heptafluorobutyl diester polymer **P1**.

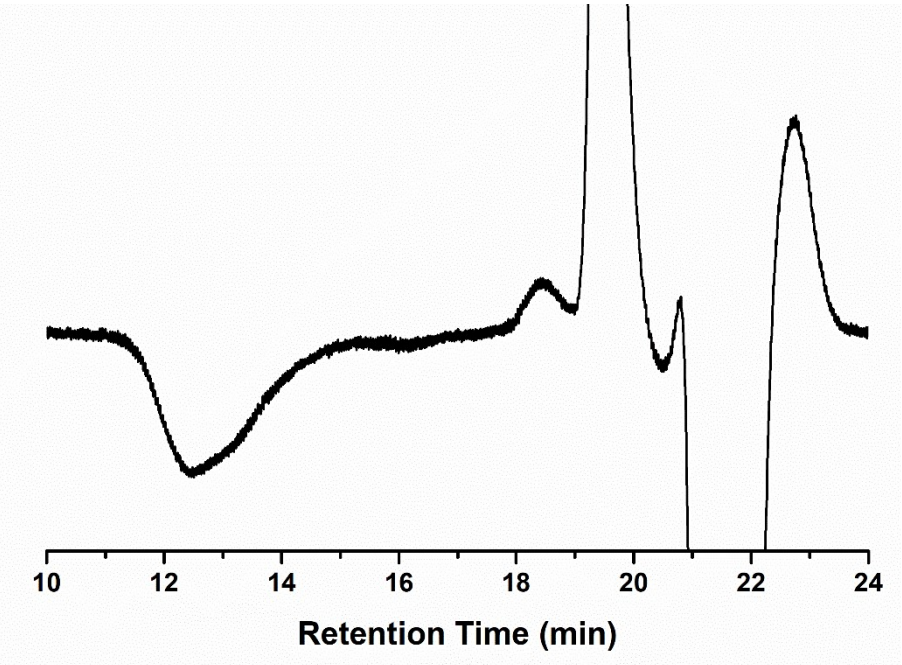


Figure S33 GPC trace for the heptafluorobutyl diester polymer **P1**.

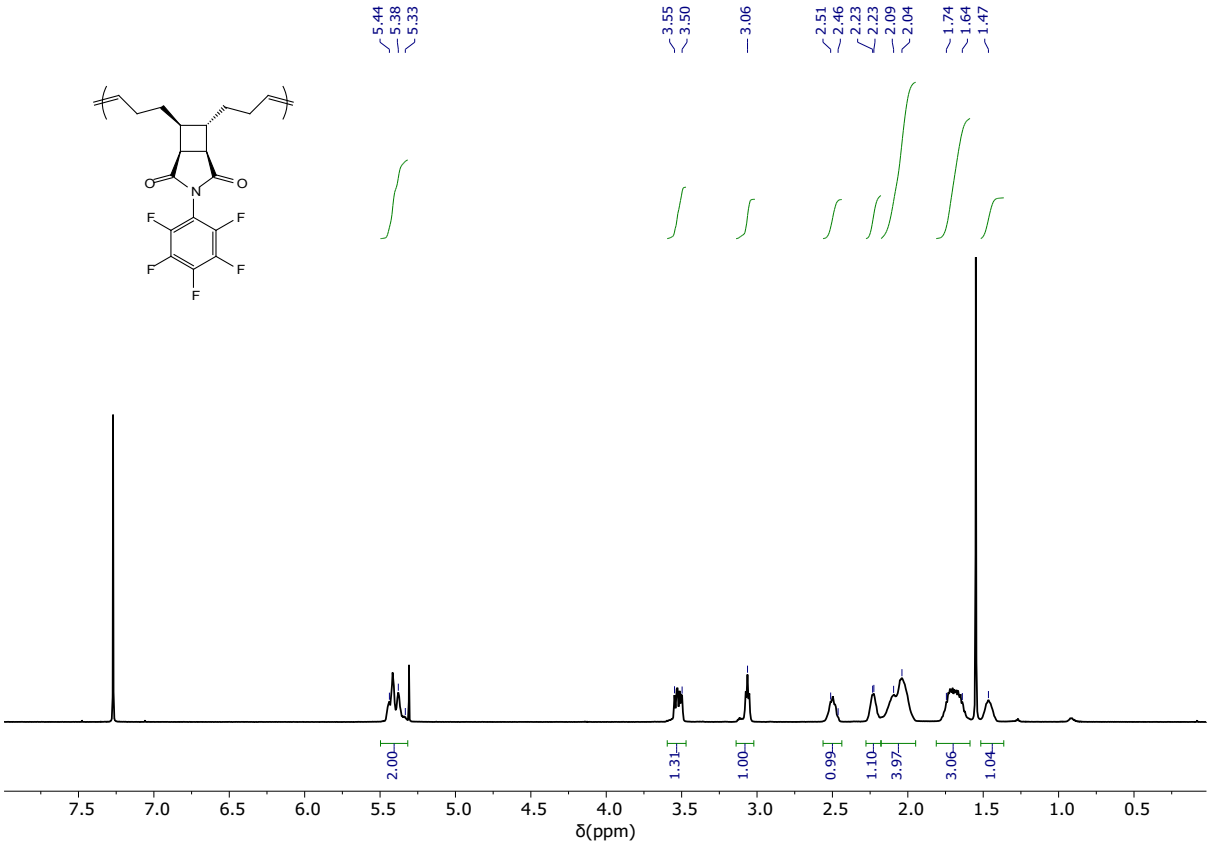


Figure S34 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) for the pentafluorophenyl imide polymer **P2**.

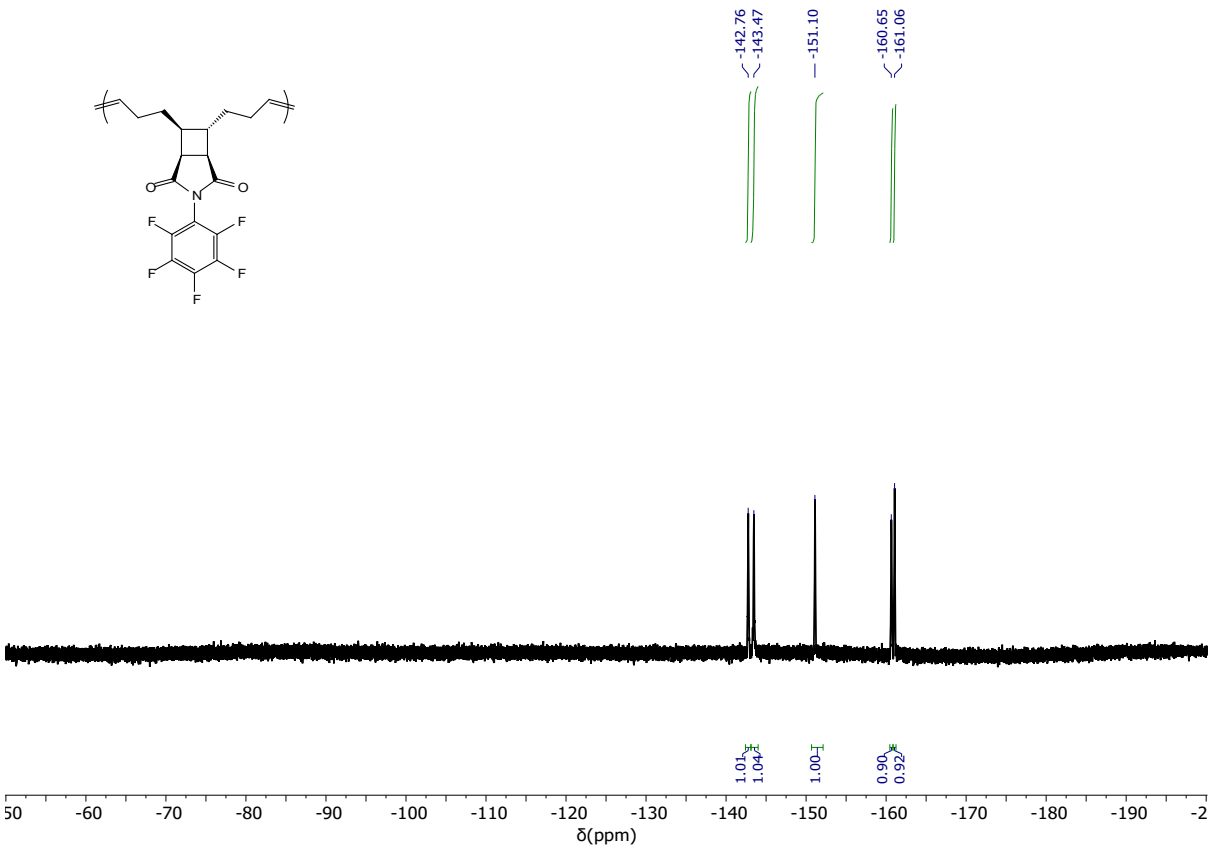


Figure S35 ^{19}F NMR spectrum (470 MHz, $CDCl_3$) for the pentafluorophenyl imide polymer **P2**.

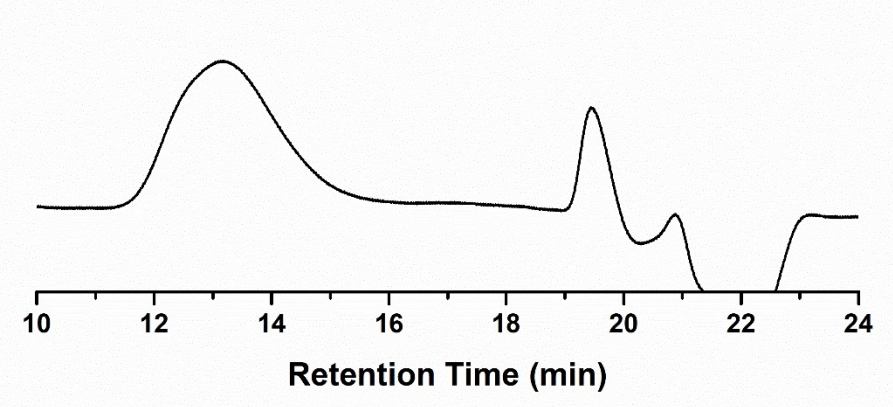


Figure S36 GPC trace for the pentafluorophenyl imide polymer **P2**.

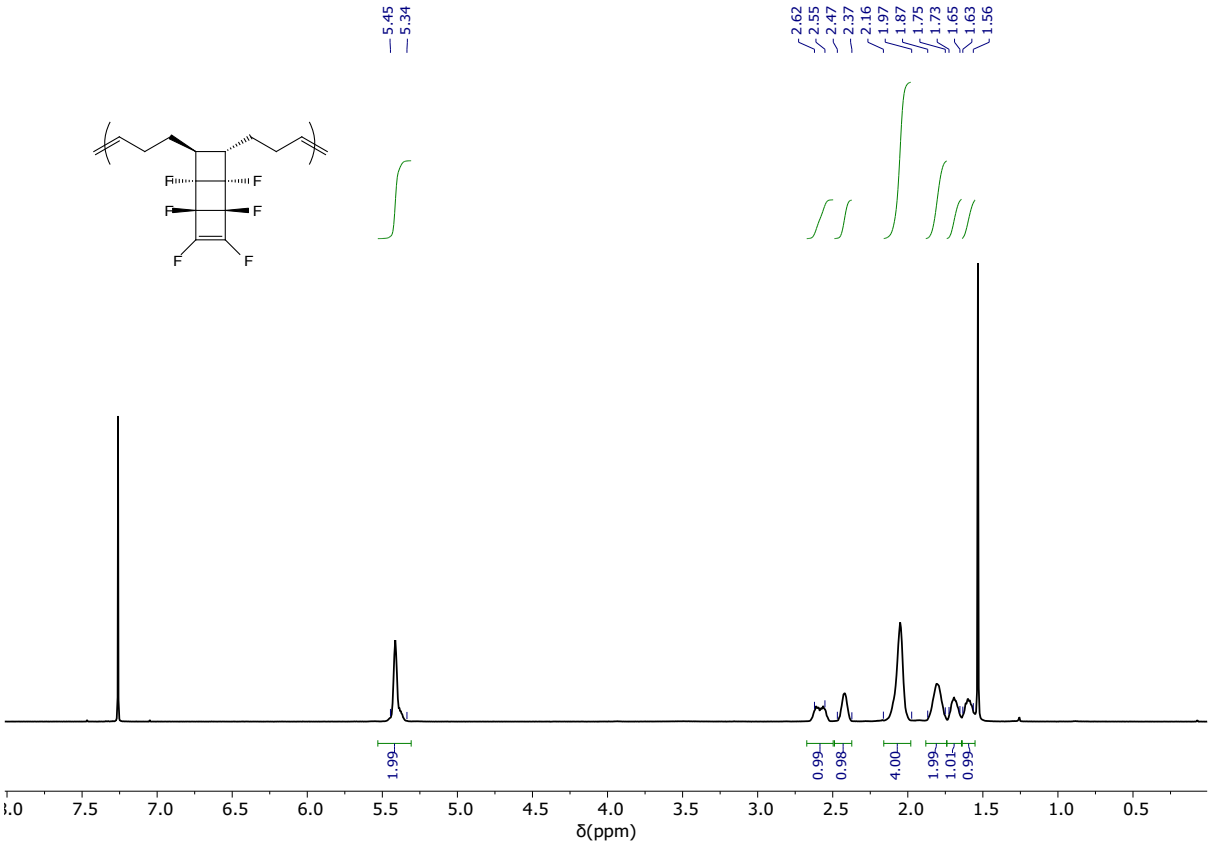


Figure S37 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) for the fluorinated ladderene polymer **P3**.

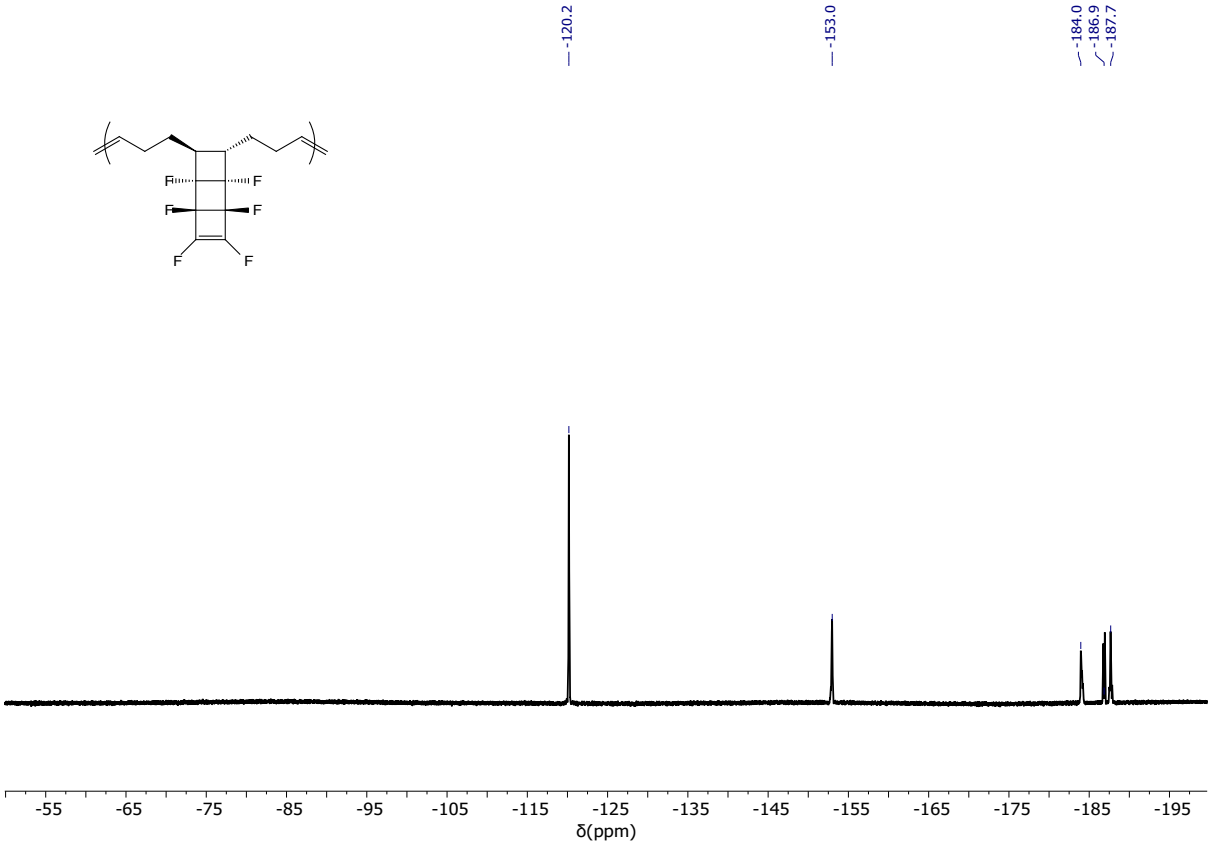


Figure S38 ^{19}F NMR spectrum (470 MHz, $CDCl_3$) for the fluorinated ladderene polymer **P3**.

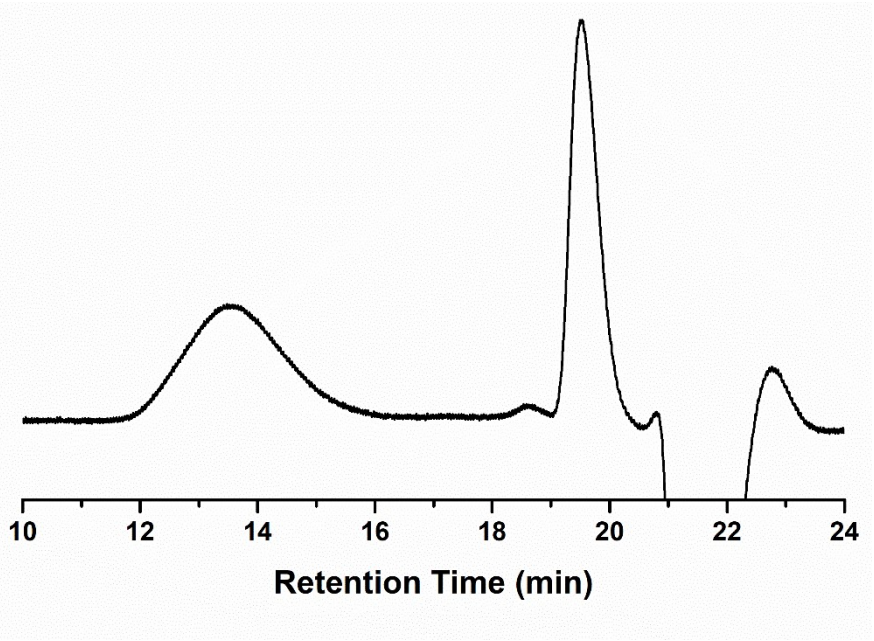


Figure S39 GPC trace for the fluorinated ladderene polymer **P3**.

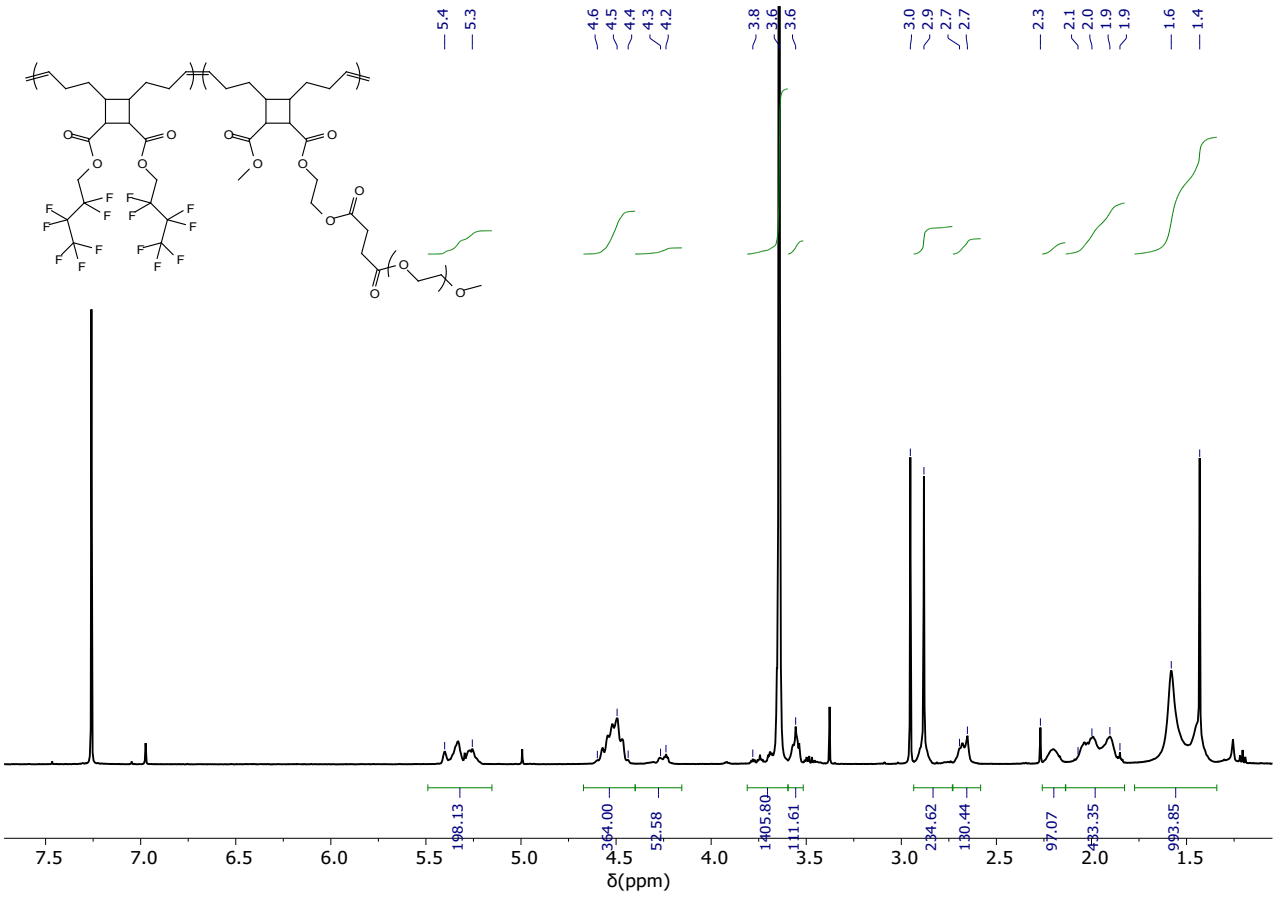


Figure S40 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) for the diblock copolymer **P1-*b*-P4**.

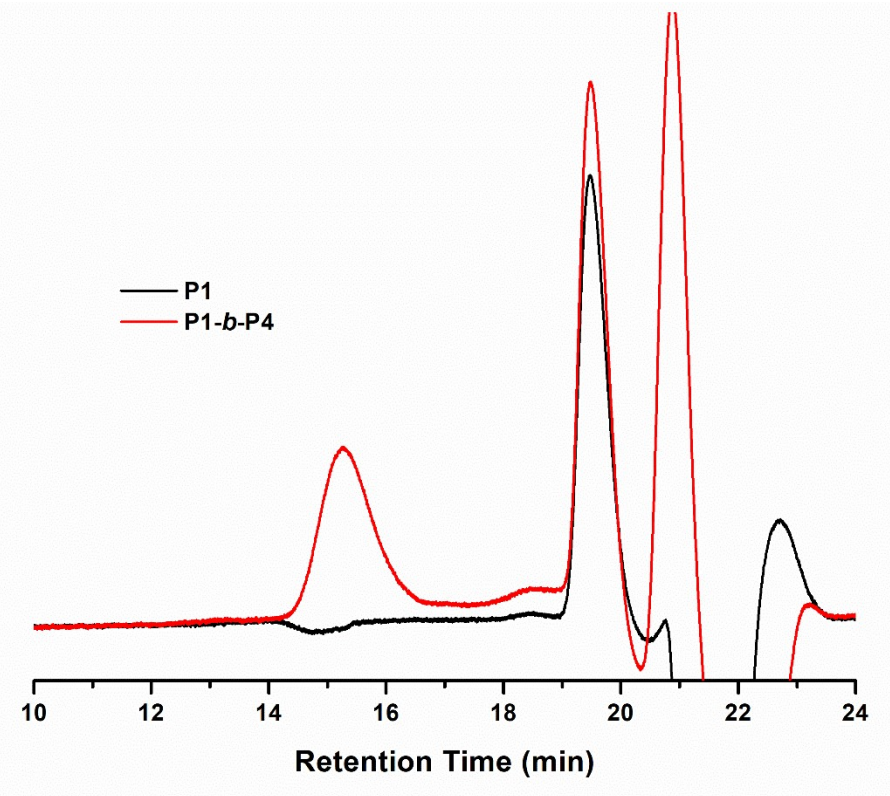


Figure S41 GPC for the first block (black) and second block (red) of the diblock copolymer **P1-*b*-P4**.

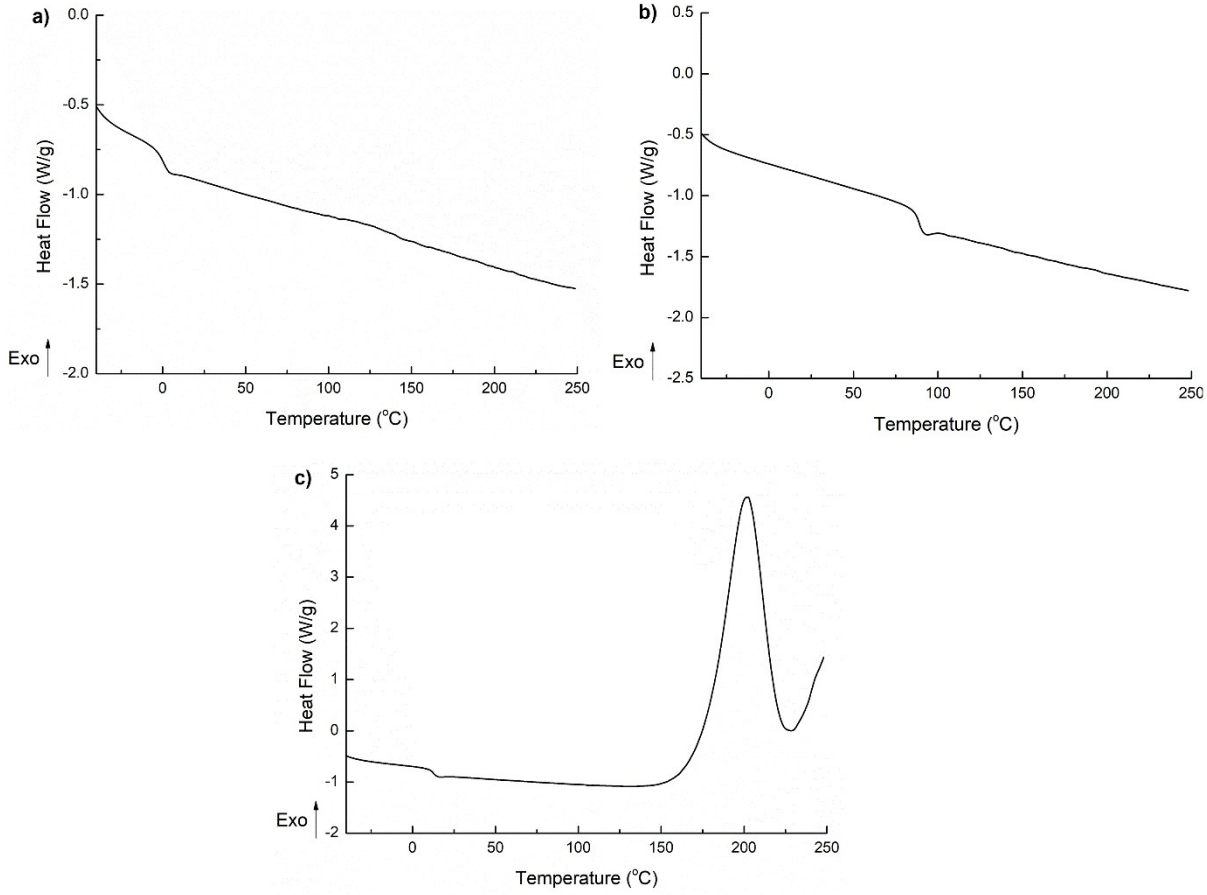


Figure S42 Extended DSC traces for polymers a) **P1**, b) **P2**, and c) **P3** (heating rate 10 °Cmin^{-1}).

Tables

Table S1 Extent of depolymerization for polymers P1, P2 and P3 at different $[olefin]_0$, as determined from ^1H NMR.

Concentration (mM)	Depolymerization (%)		
	P1	P2	P3
25	90±0.6	93±0.6	94±0
50	97±1.0	92±0.6	93±0.6
100	96±1.0	85±1	90±0.6
200	93±1.0	68±4.4	83±0
400	87±1.7	34±3	61±0.6

Table S2 X-ray crystal data and structure parameters for compound 2.

Compound	4
CCDC number	2151352
Empirical formula	$C_{14}H_{12}F_6O$
Formula weight	310.24
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/ Å	5.8199(8)
b/ Å	11.7062(14)
c/ Å	18.082(2)
α(°)	90
β(°)	90
γ(°)	90
Volume (Å^3)	1231.9(3)
Z	4
Dc (Mg/m^3)	1.673
μ (mm^{-1})	0.166
F(000)	632
reflns collected	11485
indep. reflns	2168
GOF on F^2	1.059
R1 (on F_o^2, I > 2σ(I))	0.0775
wR2 (on F_o^2, I > 2σ(I))	0.2021
R1 (all data)	0.0944
wR2 (all data)	0.2160

References:

1 M. L. Macnaughtan, M. J. A. Johnson, J. W. Kampf, *Organometallics*, 2007, **26**, 780-782.
2 D. Sathe, J. Zhou, H. Chen, H.-W. Su, W. Xie, T.-G. Hsu, B. R. Schrage, T. Smith, C. J. Ziegler and J. Wang, *Nat. Chem.*, 2021, **13**, 743–750.
3 H. Chen, Z. Shi, T. Hsu and J. Wang, *Angew Chem. Int. Ed.*, 2021, **60,** 25493–25498.
4 J. D. Lewicky, M. Ulanova and Z. H. Jiang, *Carbohydr. Res.*, 2011, **346**, 1705–1713.
5 Y. Chiang and A. J. Kresge, *J. Am. Chem. Soc.* 1985, **107**, 6363–6367.
6 Y. Fang, J. C. Judkins, S. J. Boyd, C. W. am Ende, K. Rohlfing, Z. Huang, Y. Xie, D. S. Johnson and J. M. Fox, *Tetrahedron*, 2019, **75**, 4307–4317.
7 J. Fu, J. Fiegel and J. Hanes, *Macromolecules*, 2004, **37**, 7174–7180.