

Supporting Information

Synthesis of Recyclable Tire Additives via Equilibrium Ring Opening Metathesis Polymerization

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General information

All reactions were conducted under argon atmosphere in a glovebox. Ruthenium catalysts **G2**, **G3** and **HG2** (Materia), cyclopentene (Aldrich), ethyl vinyl ether (Aldrich), cyclopentene, 1-hydroxy-3-cyclopentene, 1,6-heptadiene-4-ol (Aldrich), palladium on carbon (Aldrich), THF-*d*₈, toluene-*d*₈ (Cambridge Isotope or Aldrich) and other solvents, were used as received. Chlorotrimethylsilane, triethoxychlorosilane and imidazole were purchased from Sigma-Aldrich.

NMR experiments were performed at 0 - 40 °C. All NMR samples were stabilized at the given temperature for 10 min before data collection. All the NMR tubes were flame dried. The ¹H and ¹³C NMR spectra were recorded on a Bruker Avance II 400 and Bruker Avance II 600 spectrometer in THF-*d*₈ and Toluene-*d*₈ and referenced to residual internal THF (δ = 1.73 ppm ¹H and 25.4 ppm ¹³C) and toluene (δ = 2.09 ppm ¹H and 20.4 ppm ¹³C).

GPC analyses were carried out using a Viscotek GPC Max VE 2001 instrument with a Viscotek TDA 302 triple array detector and Viscotek Org Guard column with three (in series) Mixed Medium columns (LT5000L) at 35 °C and a flow rate of 1.0 mL/min. A 12-point Universal Calibration Standard calibration curve was recorded.

Theoretical calculations

The ring strain energy of a series of substituted cyclopentene derivatives have been calculated with density functional theory studies performed using RB3LYP method at 6-31G (D) basis set using SPARTAN '10 MECHANICS PROGRAM: PC/x86 1.1.0.software.

Example for cyclopentene ΔE (kcal/mol) calculation:



Energy (Hartree):

A: -195.333677; B: -78.588104; C: -273.930443

$$\Delta E = E_c - (E_a + E_b)$$

$$\Delta E \text{ (Hartree)} = -273.930443 - (-195.333677 - 78.588104) = -0.008662 \text{ Hartree}$$

$$1 \text{ Hartree} = 627.5 \text{ kcal/mol}$$

$$\Delta E \text{ (kcal/mol)} = -0.008662 * 627.5 = \underline{\underline{-5.44 \text{ kcal/mol}}}$$

Table S1. Calculated ring strain energy and double bond orders for different cyclopentene derivatives. Solvation: toluene [SM8]. ($E_{\text{Ethylene}} = -78.588104$ Hartree; 1 Hartree = 627.5 kcal/mol)

<i>cyclopentene derivatives</i>	<i>Energy (Hartree)</i>	<i>Bond order</i>	<i>1,6-heptadiene derivatives</i>	<i>Energy (Hartree)</i>	<i>ΔH (kcal/mol)</i>
1	-195.333677	1.959	1-hd	-273.930443	-5.44
2	-604.005309	1.926	2-hd	-682.597818	-2.76
3	-604.004267	1.957	3-hd	-682.592563	-0.12
4	-270.54342	1.958	4-hd	-349.142307	-6.77
5	-679.263366	1.952	5-hd	-757.856631	-3.24
6	-905.007252	1.953	6-hd	-983.607012	-7.31
7	-864.487677	1.889	7-hd	-943.088634	-8.07
8	-949.85017	1.891	8-hd	-1028.451652	-8.39
9	-981.162554	1.942	9-hd	-1059.794265	-27.36
10	-1059.794265	1.909	10-hd	-1138.383366	-0.63
11	-1022.960649	1.953	11-hd	-1101.559076	-6.89

Table S2. Calculation report example for cyclopentene 1.

SPARTAN '10 MECHANICS PROGRAM: PC/x86 1.1.0
Frequency Calculation
Reason for exit: Successful completion
Mechanics CPU Time : .02
Mechanics Wall Time: .05
SPARTAN '10 Quantum Mechanics Program: (PC/x86) Release 1.1.0v4
Job type: Geometry optimization.
Method: RB3LYP
Basis set: 6-31G(D)
Number of shells: 36
Number of basis functions: 91
Multiplicity: 1
SCF model:
A restricted hybrid HF-DFT SCF calculation will be
performed using Pulay DIIS + Geometric Direct Minimization
Solvation: toluene [SM8]
Optimization:
Step Energy Max Grad. Max Dist.
1 -195.331799 0.021925 0.086707
2 -195.333632 0.004196 0.035797
3 -195.333677 0.000269 0.000540
Reason for exit: Successful completion
Quantum Calculation CPU Time : 38.00
Quantum Calculation Wall Time: 38.48
SPARTAN '10 Properties Program: (PC/x86) Release 1.1.0
Atomic Charges:
Electrostatic Mulliken Natural
1 C0 : -0.192 -0.121 -0.229
2 C1 : -0.017 -0.307 -0.488
3 C2 : -0.210 -0.286 -0.459
4 C3 : -0.017 -0.307 -0.488
5 C4 : -0.192 -0.121 -0.229
6 H1 : +0.124 +0.131 +0.232
7 H2 : +0.060 +0.147 +0.237
8 H3 : +0.050 +0.147 +0.241
9 H4 : +0.069 +0.144 +0.240
10 H5 : +0.093 +0.147 +0.235
11 H6 : +0.060 +0.147 +0.237
12 H7 : +0.050 +0.147 +0.241
13 H8 : +0.124 +0.131 +0.232
2 C0 C4 : 1.959
3 C0 H1 : 0.929
4 C1 C2 : 1.000
5 C1 H2 : 0.930
6 C1 H3 : 0.936
7 C2 C3 : 1.000
8 C2 H4 : 0.944
9 C2 H5 : 0.948
10 C3 C4 : 1.011
11 C3 H6 : 0.930
12 C3 H7 : 0.936
13 C4 H8 : 0.929
Reason for exit: Successful completion
Bond Orders Mulliken
1 C0 C1 : 1.011
Properties CPU Time: .22
Properties Wall Time: .22

ROMP of cyclopentene in neat

G2 catalyst (7.8 mg; 9.19×10^{-3} mmol) was dissolved in CH_2Cl_2 (1.0 mL) and added to cyclopentene (**1**; 8.10 mL; 91.70 mmol) at different reaction temperature (Monomer/Catalyst ratio = 10^4). (Some solvent was used to avoid the formation of extreme high local catalyst loading and create a homogenous mixture in the first couple of minutes). The first reaction was performed at room temperature without any temperature control. The reaction was very exothermic and mixture solidified within 20 minutes. Due to the violent reaction the mixture warmed up and started to boil. Thus, following the solidification gas bubbles could be observed in the polymer. When the reaction was repeated at controlled condition at 20 °C similar gas (**1** vapor) formation was observed, however the solidification took longer. After 15 min reaction time there was no gelation observed, however the mixture solidified after 40 minutes.

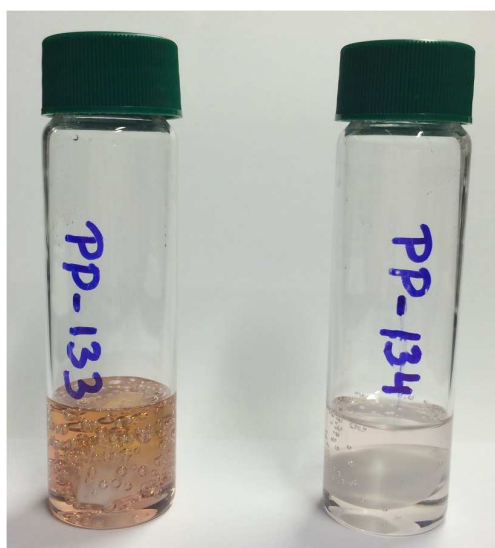
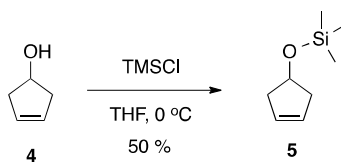


Figure S1. Solid polypentenamer synthesized in neat at 10^4 (PP - 133) and 10^5 (PP-134) monomer/catalyst loading at 20 °C

The test was reproduced at lower 10^5 monomer - catalyst loading. **G2** catalyst (0.78 mg; 9.19×10^{-4} mmol) as CH_2Cl_2 solution has been added to **1** (8.10 mL; 91.70 mmol), gelation was observed after 1h and the mixture solidified after 3h reaction

time. Some bubble formation was observed, however following the initiation period the reaction - as expected - was not as violent as at higher catalyst loading.

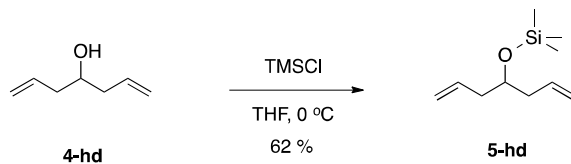
Synthesis of **5**



Scheme S1. Synthesis of **5**

In the glove box a vial (40 mL) was charged with imidazole (2.20 g, 32.30 mmol), THF (20 mL) and **4** (1.00 mL, 12.70 mmol). The vial was closed, brought out of the glovebox and cooled down to 0 °C. TMSCl (2.00 mL, 15.80 mmol) was added dropwise within 5 minutes. Immediate white precipitate formation was observed. The mixture was stirred for 3 hours and then water (40 mL) was added. The solution was transferred into a separation funnel and CH₂Cl₂ (40 mL) was added. The organic layer was separated and extracted with additional water (2 × 40 mL). Then it was collected and dried over MgSO₄. The supernatant was separated by filtration and concentrated by vacuum giving **5** (0.97 g, 50 %). ¹H NMR (benzene-*d*₆): δ 5.58 (s, 2H, =CH-), 4.39 (m, 1H, O-CH), 2.47 – 2.37 (br s, 4H, CH₂), 0.10 (s, 9H, (Si(CH₃)₃)). ¹³C{¹H}NMR (benzene-*d*₆): δ 128.6 (=CH-), 72.51 (O-CH), 42.88 (CH₂), 0.21 (Si(CH₃)₃).

Synthesis of 5-hd

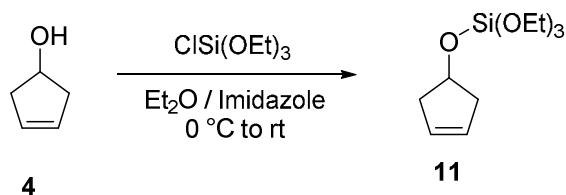


Scheme S2. Synthesis of **5-hd**

In the glove box a round bottom flask (100 mL) was charged with imidazole (2.60 g, 38.30 mmol), THF (30 mL) and **4-hd** (2.00 mL, 15.30 mmol). The vial was closed, brought out from the glovebox and cooled down to 0 °C. TMSCl (3.00 mL, 23.70 mmol) was added dropwise within 5 minutes. Immediately a white precipitate was observed. The mixture was stirred for 3 hours, then water (50 mL) was added. The solution was transferred into a separation funnel and CH₂Cl₂ (50 mL) was added. The organic layer was separated and extracted with additional water (2 x 40 mL). Then it was collected and dried over MgSO₄. The supernatant was separated by filtration and concentrated by vacuum giving **5-hd** (1.76 g, 62 %).

¹H NMR (benzene-*d*₆): δ 5.89 – 5.79 (m, 2H, =CH-), 5.07 – 5.02 (m, 4H, =CH₂), 3.64 (m, 1H, O-CH), 2.22 – 2.18 (br s, 4H, CH₂), 0.10 (s, 9H, (OSi(CH₃)₃)). ¹³C {¹H} NMR (benzene-*d*₆): δ 135.68 (=CH-), 117.0 (=CH₂), 72.17 (O-CH), 42.16 (CH₂), 0.53 (OSi(CH₃)₃).

Synthesis of 11

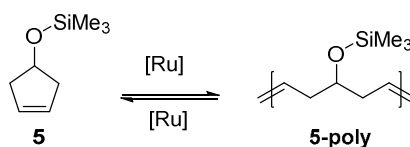


Scheme S3. Synthesis of **11**

An oven-dried round-bottom flask (100 mL) was charged with imidazole (3.24 g, 47.70 mmol), Et₂O (40 mL) and **4** (2.00 g, 23.70 mmol). The flask was cooled to 0 °C and then ClSi(OEt)₃ reagent (7.06 mL, 35.66 mmol) was added dropwise within 10 minutes. Immediately a white precipitate n was observed. The mixture was stirred for 3 hours at 0°C, then left to warm up to room temperature and stirred further 24 hours. After that water (50 mL) was added. The solution was transferred into a separation funnel and CH₂Cl₂ (50 mL) was added. The organic layer was separated and washed with water (2 x 40 mL), then with NH₄Cl solution (5%, 100 ml). Then it was collected and dried over Na₂SO₄. The supernatant was separated by filtration and concentrated by vacuum giving **11** (3.80g, 65%).

¹H NMR (benzene-*d*₆) δ: 5.57 (m, 2H, =CH-), 4.81 (m, 1H, O-CH), 3.83 (m, 6H, OCH₂), 2.51 (m, 4H, CH₂), 1.17 (m, 9H, (OCH₂CH₃)₃). ¹³C{¹H} NMR (benzene-*d*₆) δ: 128.11, 72.82, 58.87, 42.21, 18.00.

ROMP of **5**



Scheme S4. ROMP of **5**

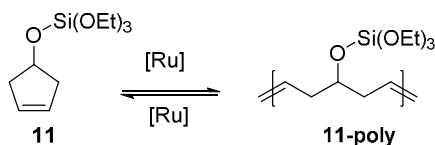
In toluene: A vial (4 mL) was charged with **5** (0.20 mL; 0.171 g; 1.09 mmol) and toluene-*d*₈ (0.4 mL). Another vial (4 mL) was charged with **HG2** catalyst (0.69 mol%, 4.70 mg; 7.50×10^{-3} mmol) and toluene-*d*₈ (0.4 mL). Then the catalyst solution was transferred to the **5** solution by a Pasteur pipet. Following the addition of the green **HG2** solution to **5** the color of the mixture gradually turned to orange. Although the color change may indicate some catalyst activity the ¹H NMR analysis revealed that after 4 hours the reaction mixture contained mainly the starting monomer, there was no polymer formation detected.

In neat: A vial (4 mL) was charged with **HG2** catalyst (0.75 mol%, 2.60 mg; 4.15×10^{-3} mmol), then **5** (0.1 mL; 0.55 mmol) was added by a syringe. Following the addition of compound **5** to the catalyst there was no immediate solidification observed. The color of the mixture gradually turned from green to orange within 15 minutes. The mixture became viscous after 30 min and solidified after 60 reaction time. After 3.5 h reaction time the solid polymer was dissolved in CD₂Cl₂ and ¹H NMR test was carried out. The ¹H NMR spectra showed a significant upshift of –CH= proton peaks. The magnitude of the chemical shifts and the shape (broad) of the peaks indicated the formation of **5-poly**. The polymer was dissolved in CH₂Cl₂ (3 mL) and the solution was added to MeOH (5 mL). Immediate polymer precipitation was observed, the milky mixture was placed into the centrifuge for 30 (4000 rpm, RT) and then the supernatant was removed by a syringe. The remaining semi solid material was dried under vacuum giving a colorless, glue like polymer (43.8 mg; 51.2%).

¹H NMR (CD₂Cl₂): δ 5.48 – 5.44 (br s, 2H, =CH-), 3.66 – 3.63 (br m, 1H, CH), 2.15 (br s, 4H, CH₂), 0.85 (br s, 9H, Si(CH₃)₃). ¹³C{¹H} NMR (CD₂Cl₂): δ 129.45 (*trans*,

=CH-), 128.03 (*cis*, =CH-), 73.00 (*trans*, O-CH), 72.85 (*cis*, O-CH), 40.89 (*trans*, CH₂), 35.65 (*cis*, CH₂).

ROMP of 11

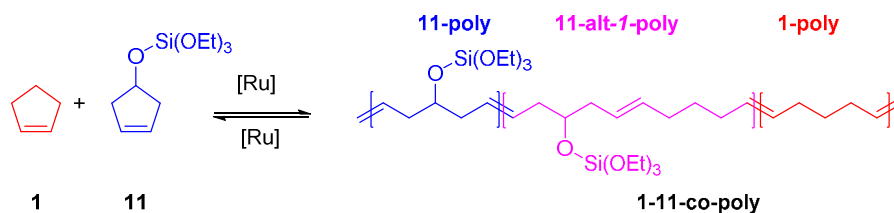


Scheme S5. ROMP of 11

Hoveyda-Grubbs 2nd generation catalyst **HG2** (6.0 mg, 9.58×10^{-3} mmol, 4.77 mM, 0.22 mol%) was weighed into a screw-cap fitted vial then dissolved in toluene-*d*₈ (0.900 mL) inside the glove-box. The vial was placed into ice bath outside of the glove-box and cooled to 0 °C. Monomer **11** was added in one portion (pre-cooled to 0°C prior to addition; 1.100 mL, 4.34 mmol) and the reaction was stirred at 0 °C for 3 hours. The green catalyst solution gradually turned orange. ¹H NMR spectra were recorded at 2h, and 3h reaction times. Then ethyl vinyl ether (0.1 mL) was added. The reaction mixture was poured into a vial (40 mL) containing methanol (15 mL, pre-cooled to 0 °C prior to usage) and placed into the freezer (-10 °C) for 30 minutes. The supernatant was removed by syringe and the remaining material was washed again with pre-cooled methanol (5 mL) and the remaining precipitate was dried in *vacuo* giving a 260 mg; (24%). Further fraction of product was isolated by evaporation the solvent (MeOH) in high vacuum yielding a brown oil (supposedly contains residues of Ru catalyst) 610 mg (57%). Total isolated yield: 81%. The monomer/polymer ratio in the equilibrium at 0 °C was determined by ¹H NMR spectroscopy and found to be 19.9%/80.1 %. The polymer was analyzed by GPC: *M*_w = 39.104 kDa, Đ = 2.05.

¹H NMR (toluene-*d*₈): δ 5.65 (m, 2H, =CH-), 4.09 (m, 1H, CH), 3.82 (m, 6H, OCH₂-), 2.36 (m, 4H, CH₂), 1.20 (m, 9 H, CH₃). ¹³C{¹H} NMR (toluene-*d*₈): δ 129.51, 129.39, 73.60, 59.32, 41.52, 35.32, 18.48.

Co-polymerization of monomers 1 and 11



Scheme S6. Co-polymerization of 1 and 11

Hoveyda-Grubbs 2nd generation catalyst (6 mg, 9.58 μmol , 4.77 mM, 0.22 mol%) was weighed into a screw-cap fitted vial then dissolved in toluene-*d*₈ (1.26 mL) inside the glove-box. The vial was placed into ice bath outside of the glove-box and cooled to 0 °C. Monomer **11** (pre-cooled prior to addition, 0.550 mL, 2.17 mmol) and monomer **1** (pre-cooled prior to addition, 0.192 mL, 2.17 mmol) were added in one portion and the reaction was stirred at 0 °C for 3 hours. The green catalyst solution gradually turned orange, ¹H NMR spectra were recorded after 2h, and after 3h reaction times. Then ethyl vinyl ether (0.10 mL) was added. The reaction mixture was poured into a vial (40 mL) containing methanol (15 mL, pre-cooled to 0°C prior to usage) with immediate polymer precipitation. The supernatant was removed by syringe and the remaining material was washed again with pre-cooled methanol (5 mL) and the remaining precipitate was dried in *vacuo* giving 287 mg product. Evaporating the solvent from the MeOH fraction gave further 208 mg brown oily product (which presumably contains residues of ruthenium catalyst). Total yield: 73%. $M_w = 25.739$ kDa, $\bar{D} = 2.52$

Depolymerisation of polymer 1-Poly

The preparation was carried out inside an Argon filled glove-box. A screw-cap fitted NMR tube was charged with of catalyst **HG2** (2 mg, 3.19×10^{-3} mmol, 0.4 mol%) and toluene- d_8 (0.40 mL) was added. **PP-134** (56.20 mg) was dissolved in toluene- d_8 (1.00 ml) and this polymer solution was added to the catalyst solution. ^1H NMR spectra were recorded after 5 minutes, after 10 and 40 minutes.

Depolymerisation of polymer 11-poly

The preparation was carried out inside an Argon filled glove-box. A screw-cap fitted NMR tube was charged with a toluene- d_8 solution of **11-poly** ((0.25 mmol) 62 mg/0.400 ml solvent). ^1H NMR spectrum was recorded then a toluene- d_8 solution of catalyst **HG2** ($(8 \times 10^{-3}$ mmol; 3 mol%) 5 mg/0.400 ml solvent) was added ^1H NMR spectra were recorded before adding the solution of the catalyst, then immediately after the addition then after 20 min, 45 min, 75 min, 120 min and 180 min. Approximately 99% depolymerization was observed after 180 minutes resulting in a formation of monomer **11**.

Depolymerisation of co-polymer 1-11-co-poly

The preparation was carried out inside an Argon filled glove-box. A screw-cap fitted NMR tube was charged with a toluene- d_8 solution of **1-11-poly** (32 mg/0.400 ml solvent),. ^1H NMR spectrum was recorded then a toluene- d_8 solution of catalyst **HG2** ($(8 \times 10^{-3}$ mmol); 5 mg/0.400 ml solvent) was added ^1H NMR spectra were recorded before adding the solution of the catalyst, then immediately after the addition then after 20 min, 45 min, 75 min, 120 min and 180 min. Approximately 99% depolymerization was observed after 75 minutes resulting in a formation of monomer **11** and monomer **1**.

PP-129.10.fid
 PP-129 isolated pale yellow liquid CP-OSiMe3
 PROTON C6D6 D:\ robert 44

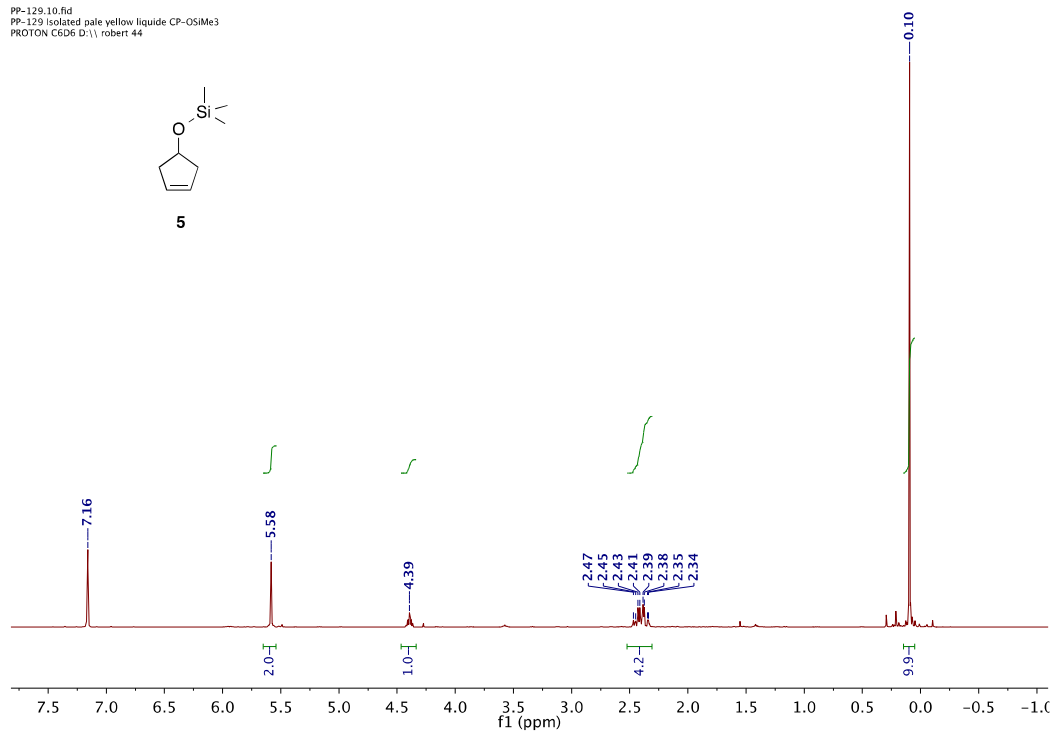


Figure S2. ¹H NMR spectra of 5 (benzene-*d*₆)

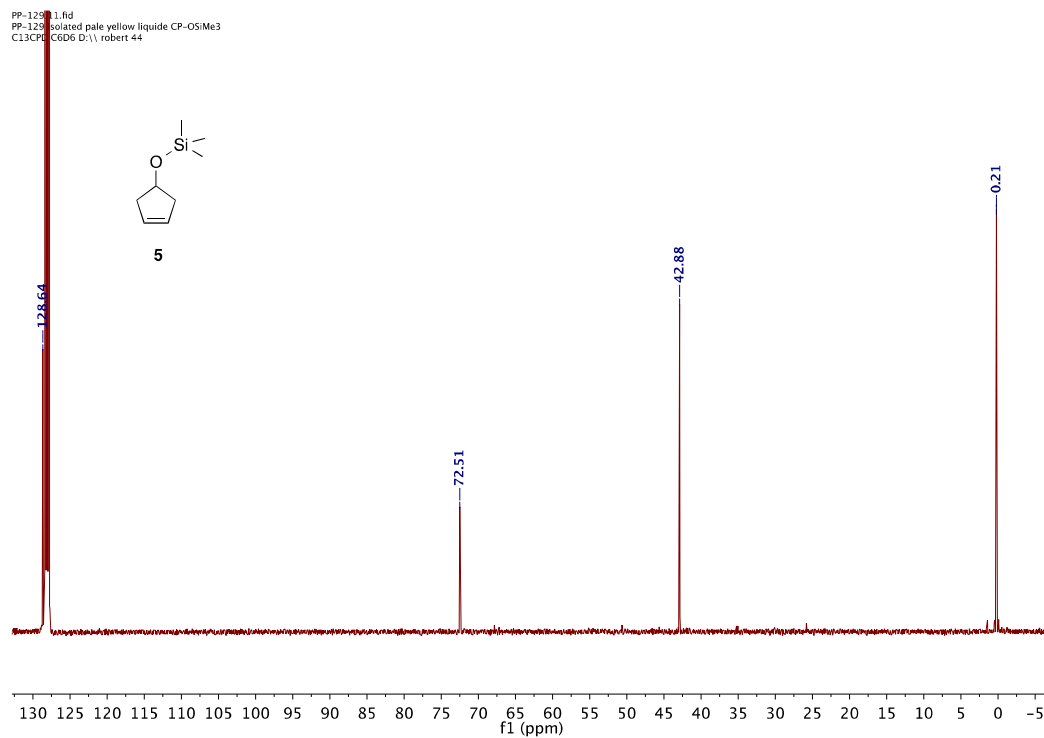
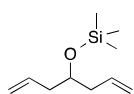


Figure S3. ^{13}C NMR spectra of **5** (benzene- d_6)

PP-126 10.Rd
PP-126 isolated colorless liquid
PROTON CGD6 D:\robert 35



5-hd

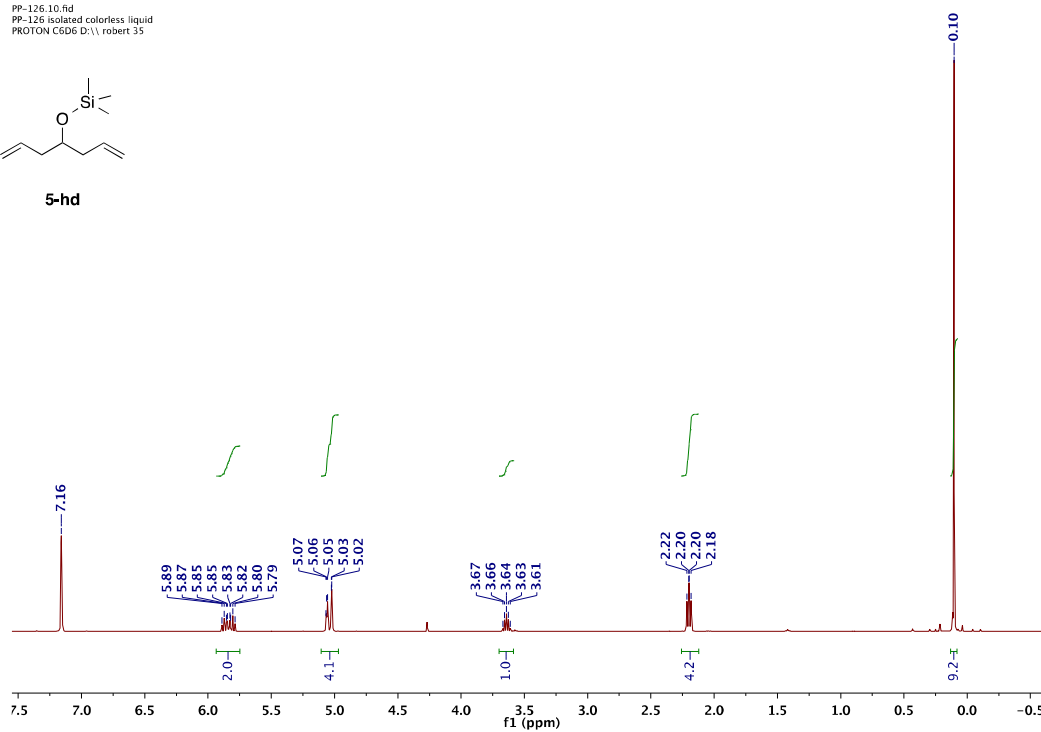


Figure S4. ¹H NMR spectra of 5-hd (benzene-*d*₆)

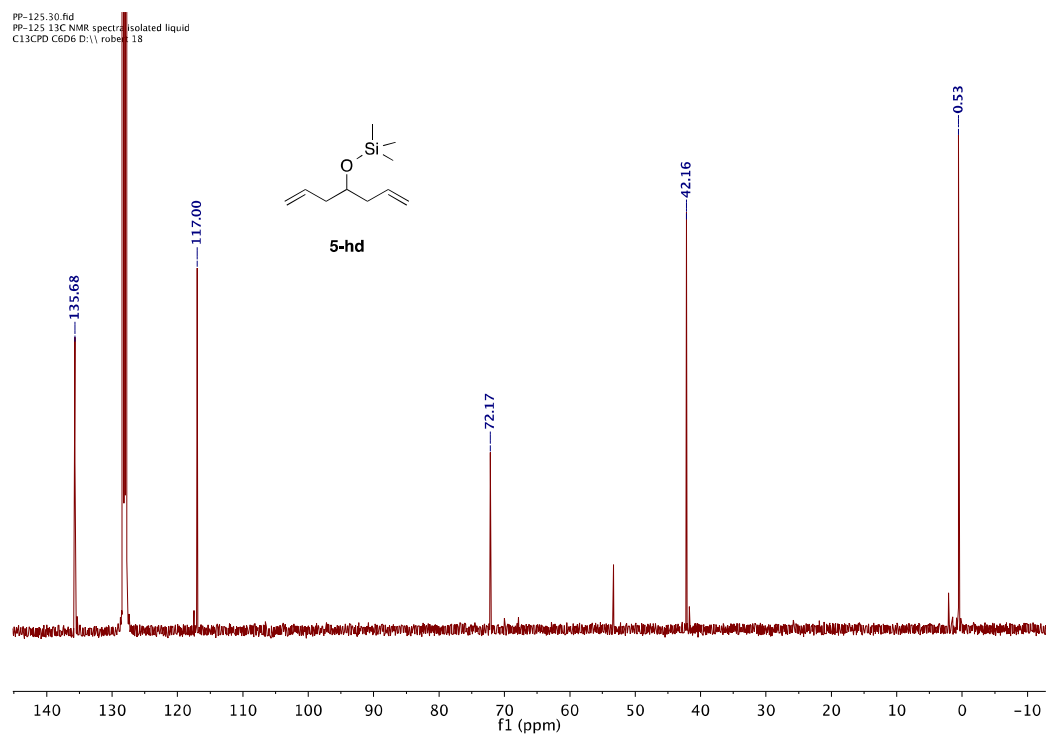


Figure S5. ^{13}C NMR spectra of 5-hd (benzene- d_6)

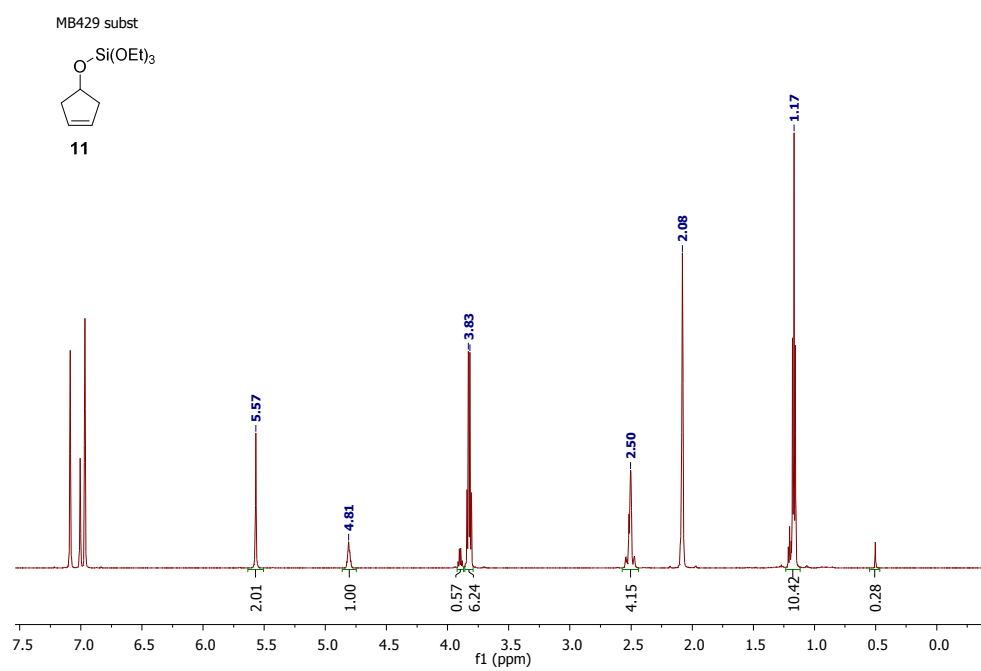


Figure S6. ^1H NMR spectrum of 11 (toluene- d_8)

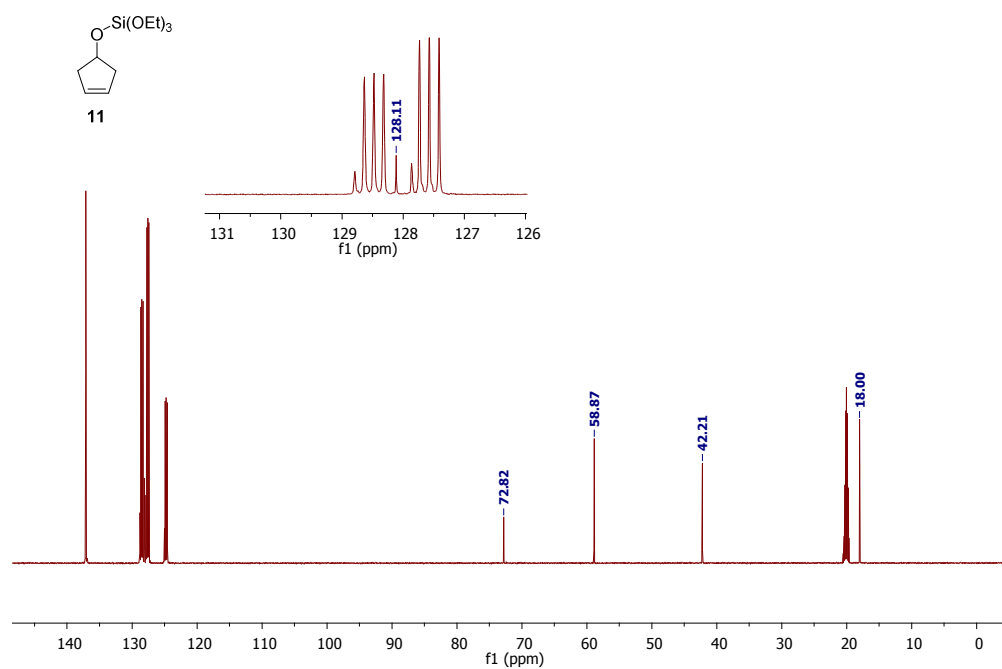


Figure S7. ^{13}C NMR spectrum of 11 (toluene- d_8)

PP-131.30.fid
PP-131 purified polymer
PROTON CD2Cl2 D:\robert 55

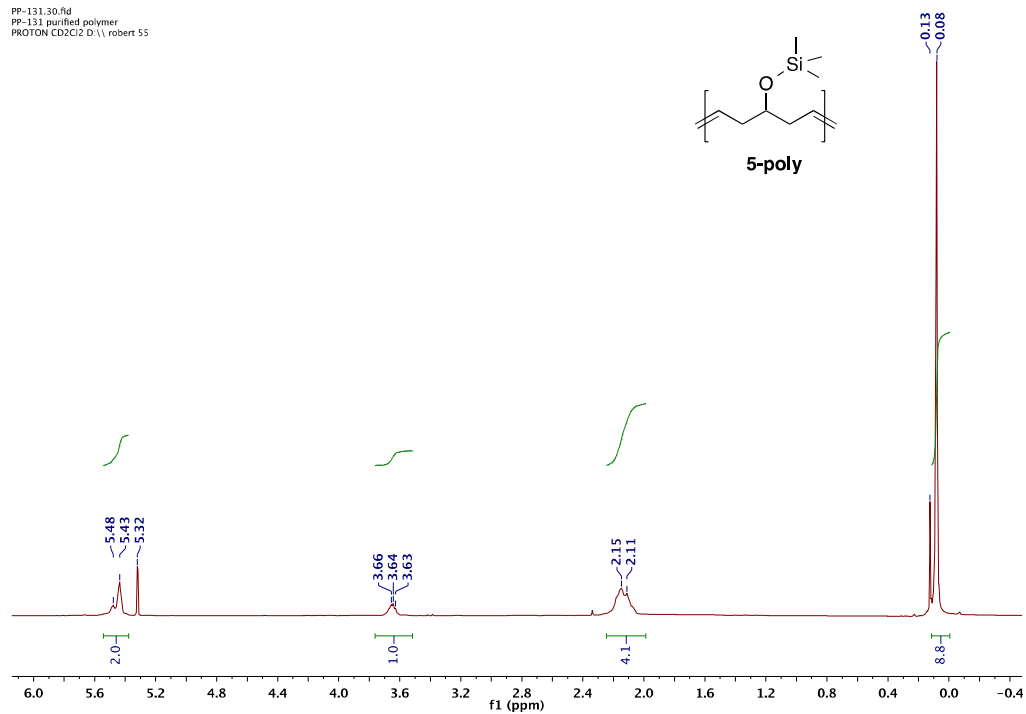


Figure S8. ¹H NMR spectra of 5-poly (CD₂Cl₂)

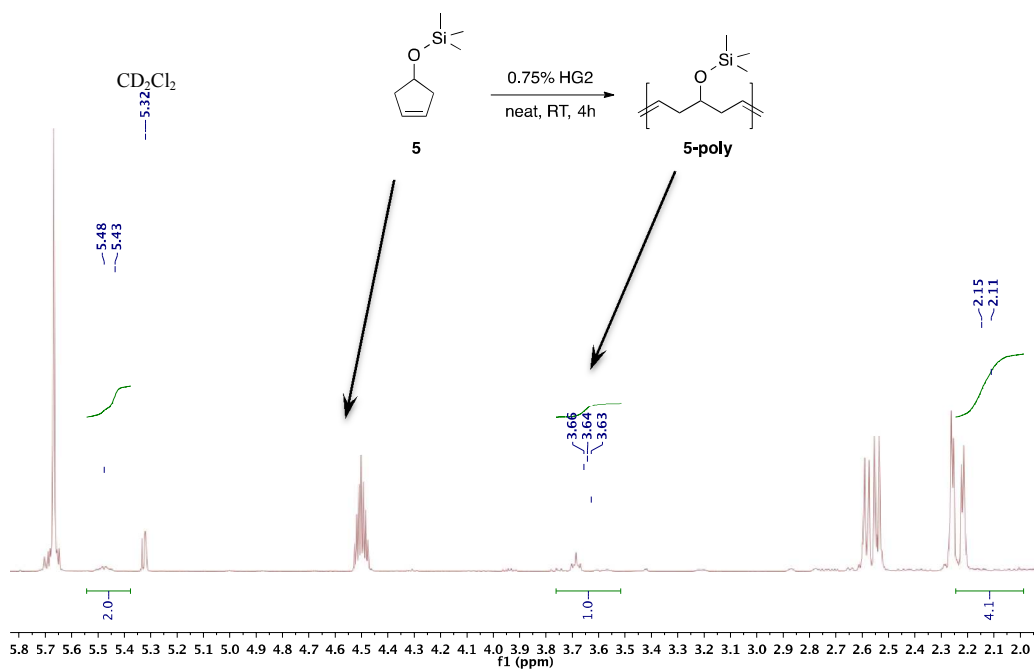


Figure S9. Overlapping of ^1H NMR spectra of **5 (black) and **5-poly** (green) (CD_2Cl_2)**

PP-131.51.fid
PP-131 purified polymer
C13CPD CD2Cl2 D:\robert 55

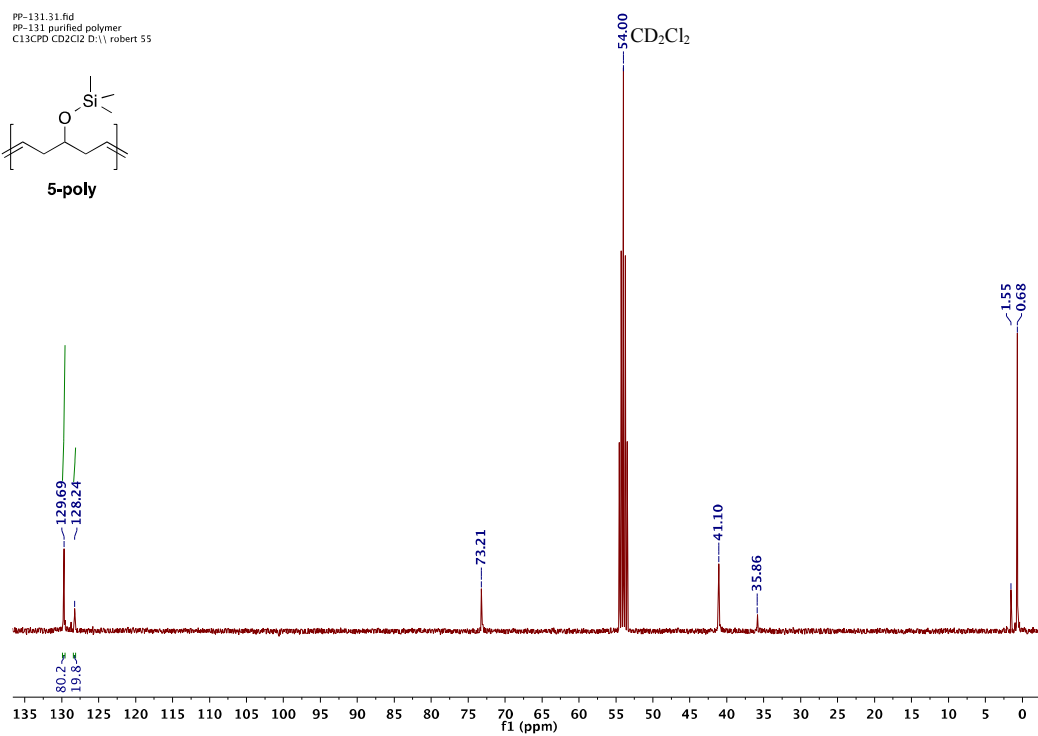
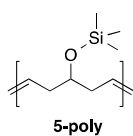


Figure S10. ¹³C NMR spectra of 5-poly (CD₂Cl₂)

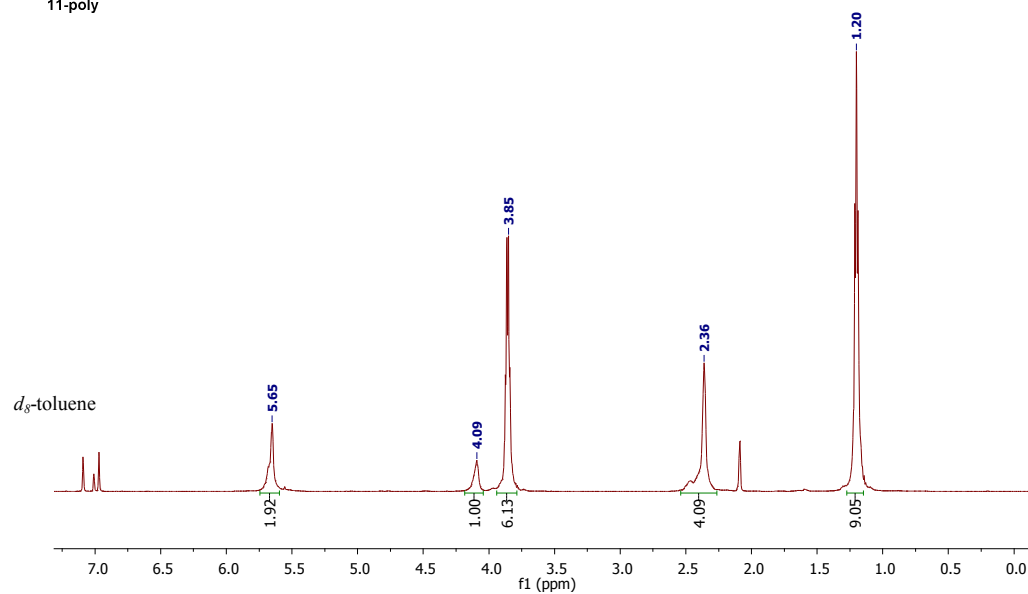
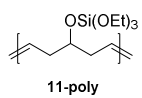


Figure S11. ^1H NMR spectrum of 11-poly (toluene- d_8)

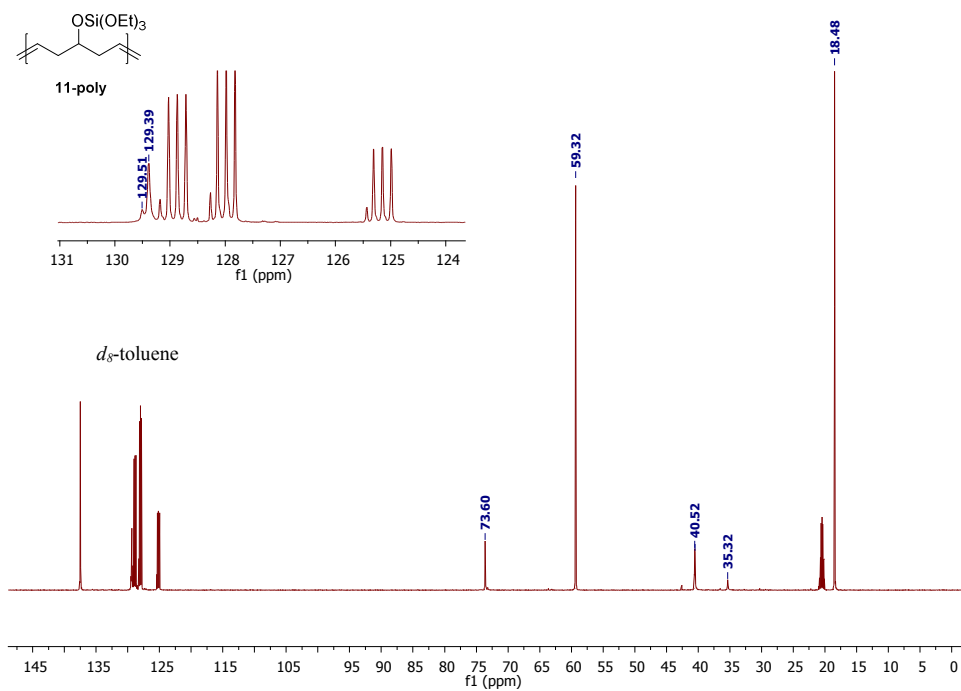


Figure S12. ¹³C NMR spectrum of 11-poly (toluene-*d*₈)

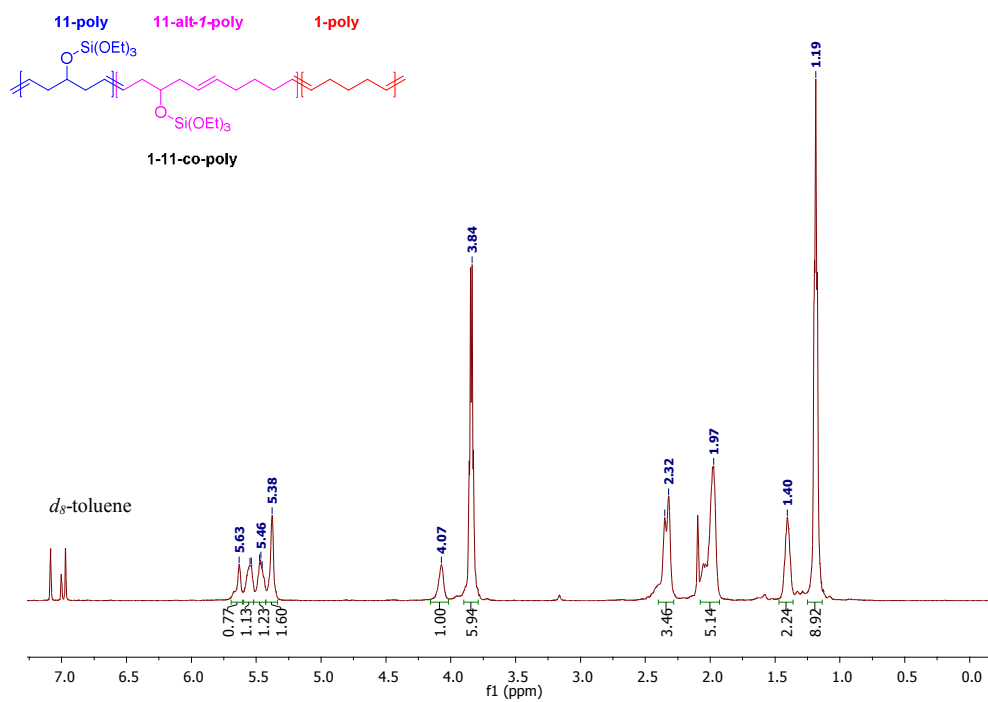
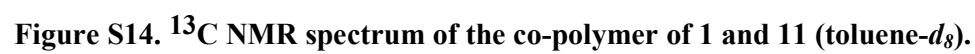


Figure S13. ¹H NMR spectrum of the co-polymer of 1 and 11 (toluene-*d*₈).



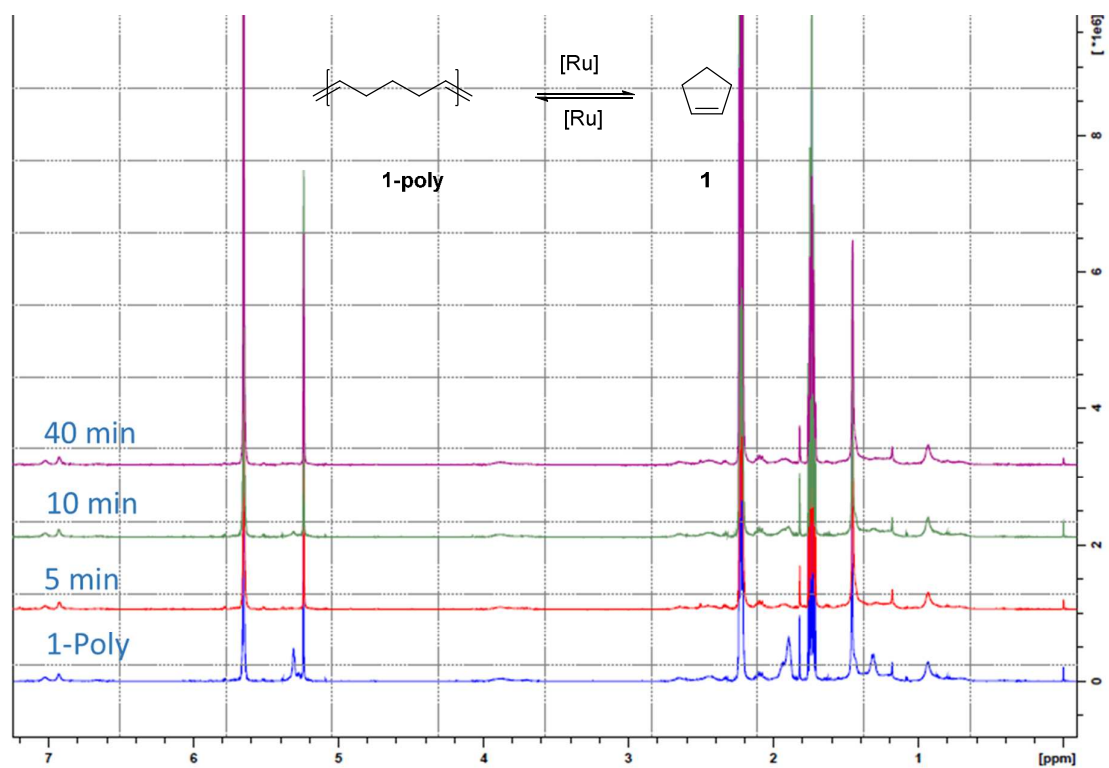


Figure S15. ^1H -NMR spectrum of the recording depolymerisation of 1-Poly

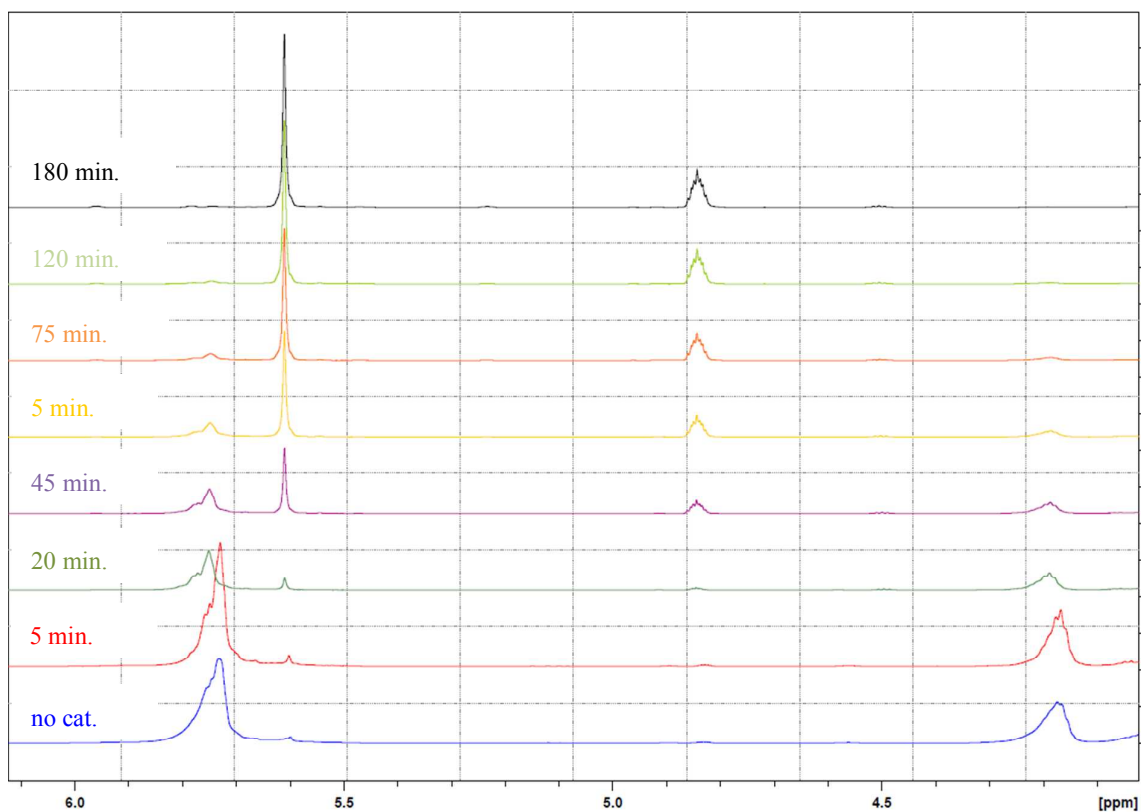
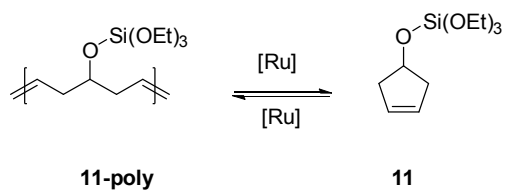


Figure S16. ^1H NMR spectra of the depolymerization of 11-poly (toluene- d_8)

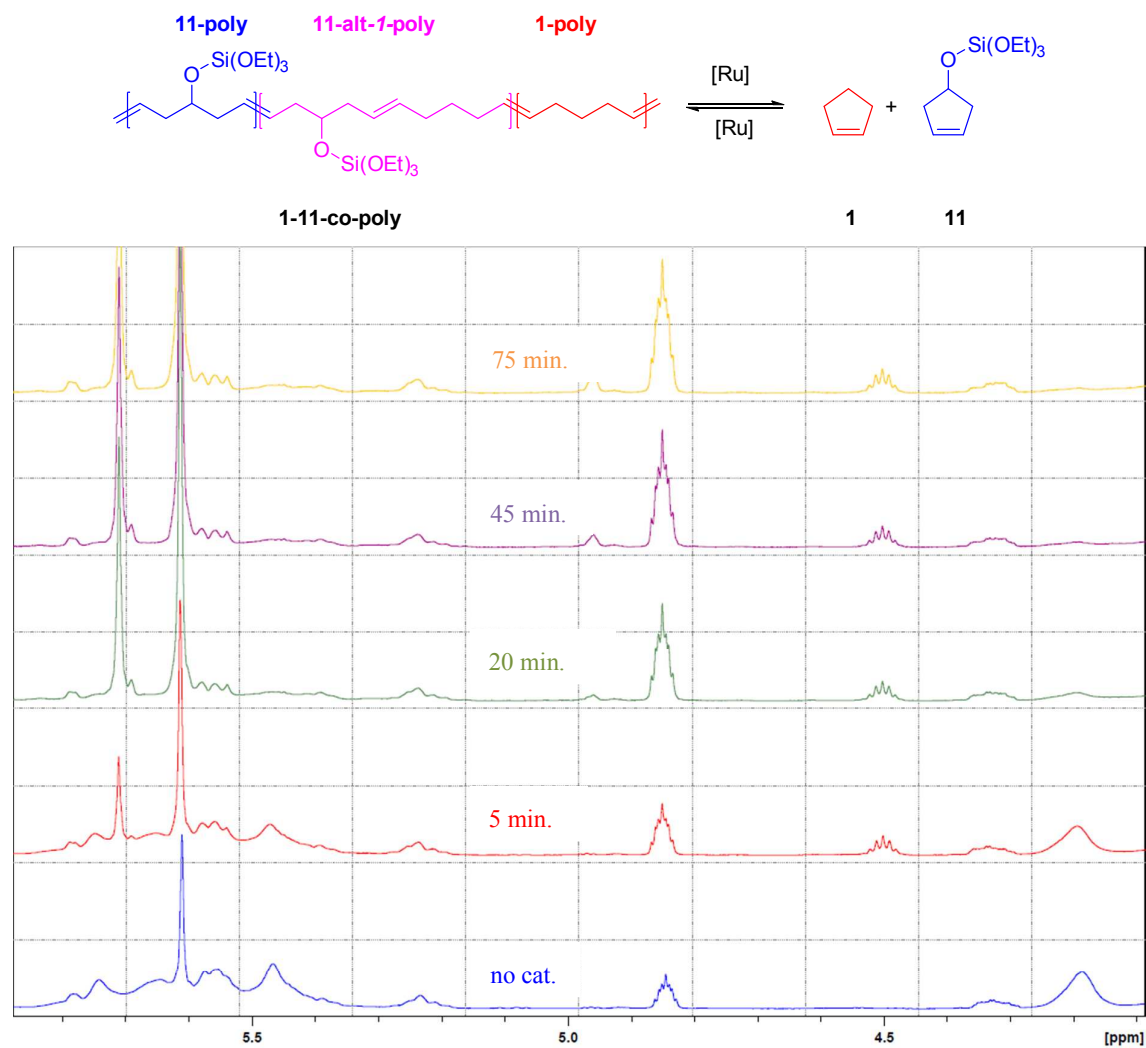


Figure S17. ¹H NMR spectra of the depolymerization of 1-11-copoly (toluene-*d*₈)