Supporting Information

for

Mono- and di-cyclocarbonate telechelic polyolefins synthesized from Ring-Opening Metathesis Polymerization using glycerol carbonate derivatives as chain-transfer agents

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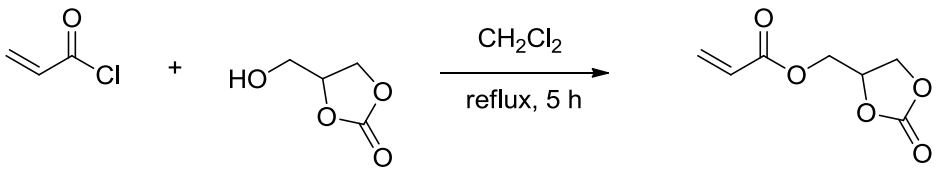
Experimental Details

General Considerations. All manipulations of sensitive materials were carried out under an argon atmosphere using Schlenk or glove box techniques. Glycerol carbonate was purchased from ABCR chemicals and used as received. Grubbs second-generation catalyst (G2), 4-vinyl-1,3-dioxolan-2-one, maleic acid, fumaryl chloride and acryloyl chloride were purchased from Aldrich and used as received. Cyclooctene (COE) was purchased from Aldrich, distilled over CaH_2 and degassed prior to use. Tetrahydrofuran (THF) was refluxed over Na/benzophenone, distilled and degassed thoroughly prior to use. All other solvents were used as received.

NMR spectra were recorded on a AM-500 or AM-400 Bruker spectrometers at 298 K in $CDCl_3$. A relaxation delay of 3 s was used during the acquisition to yield quantitative ^1H NMR spectra. The chemical shifts were referenced to tetramethylsilane (TMS) using the residual protio-solvent (^1H) or the carbon (^{13}C) resonance of the deuterated solvent. Molecular weights (M_n and M_w) and molar mass distribution (M_w/M_n) of polymers were determined by size-exclusion chromatography (SEC) using a Polymer Laboratories PL-GPC 50 instrument equipped with a PLgel 5Å MIXED-C column and a refractive index detector. The column was eluted with THF at 30 °C at 1 mL·min^{-1} and was calibrated using 11 monodisperse PS standards (range of 580 to 380,000 g·mol^{-1}); reported M_n values are uncorrected. FTIR spectra of the polymers were acquired on a Shimadzu IRAffinity-1 equipped with an ATR. ESI-HRMS spectra of the polymers were recorded at the Centre de Recherche de Mesures Physiques de l'Ouest (CRMPO, University Rennes 1) on a MicrOTOF-Q2 II apparatus, in the positive mode, with a 4 kV acceleration, using CH_3OH/CH_2Cl_2 (95/5) solutions.

Synthesis of (2-oxo-1,3-dioxolan-4-yl)methyl acrylate (2)[†]



[†] For the initial synthesis of **2**, see: J. C. Brosse, D. Couvret, S. Chevalier and J.-P. Senet, *Makromol. Chem.-Rapid Comm.* 1990, **11**, 123-128; J. C. Brosse, D. Couvret, S. Chevalier and J.-P. Senet, *Macromol. Chem. Phys.* 1990, **191**, 1311-1319; K. Moussa, C. Decker, J. Brosse, S. Chevalier and D. Couvert (Société Nationale des Poudres et Explosifs), *US Pat.* 5047261 (Sept. 10, 1991).

To a solution of glycerol carbonate (7.00 g, 59.0 mmol) in dry dichloromethane (15 mL) was added dropwise acryloyl chloride (4.8 mL, 5.7 g, 63.0 mmol) at room temperature. The resulting clear solution was slowly warmed at 45 °C and refluxed for additional 5 h. After this time period, the solution was cooled at room temperature and the solvent was distilled off. The crude oily product was purified by distillation under vacuum. A clear colorless liquid was obtained (9.2 g, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 4.3-4.6 (m, 4H, C*H*$_2$-CH-C*H*$_2$OCOO), 4.9 (1H, m, CH_2-C*H*-CH_2OCOO), 5.9 (1H, d, J_{HH} = 10.7 Hz, C*H*$_2$=CH), 6.1 (1H, m, CH_2=C*H*), 6.4 (1H, d, J_{HH} = 17.2 Hz, C*H*$_2$=CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 298 K): δ 63.2, 66.2 (*C*H_2-5CC), 74.0 (*C*H-5CC), 127.2 (CH_2=*C*H-), 132.5 (*C*H_2=CH-), 154.8 (O=*C*OO), 165.5 (O=*C*O).

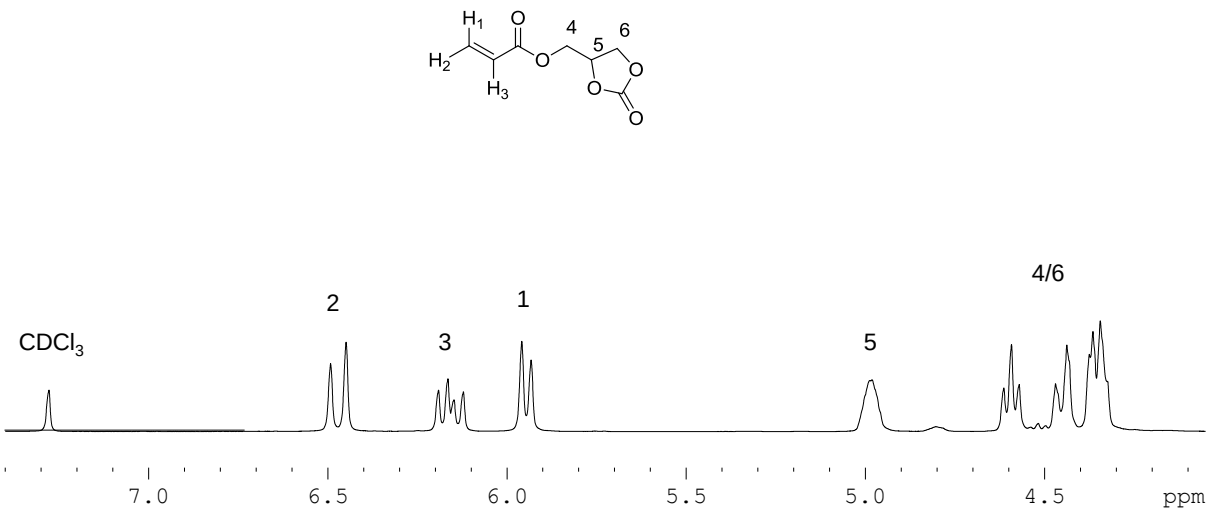


Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of (2-oxo-1,3-dioxolan-4-yl)methyl acrylate (**2**).

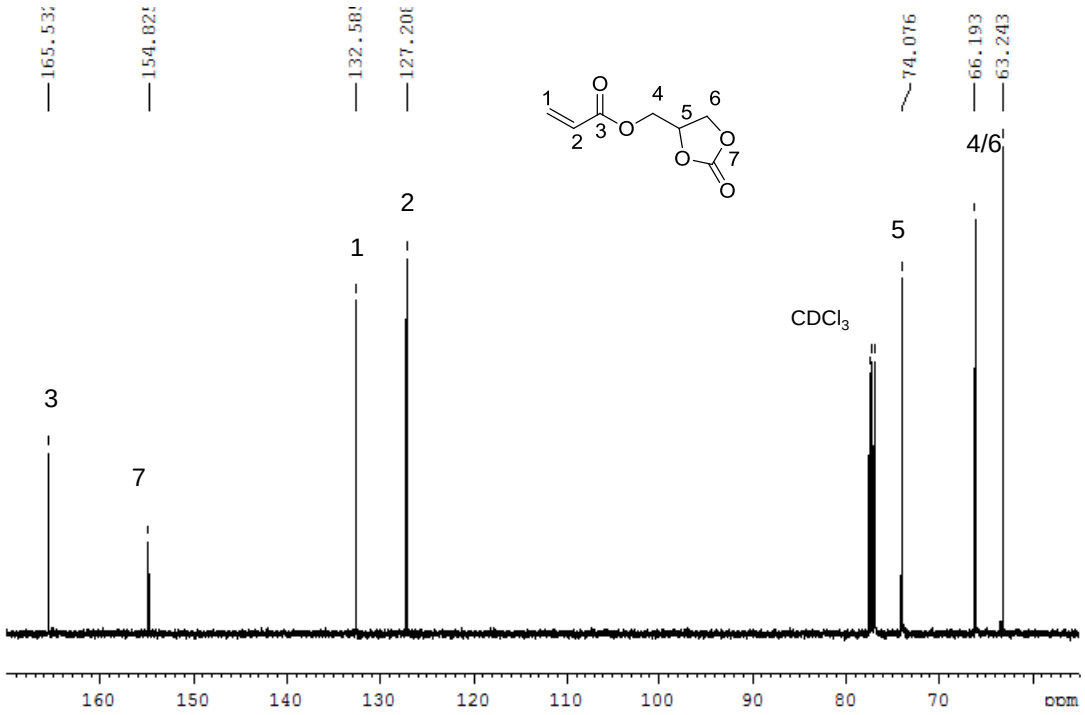
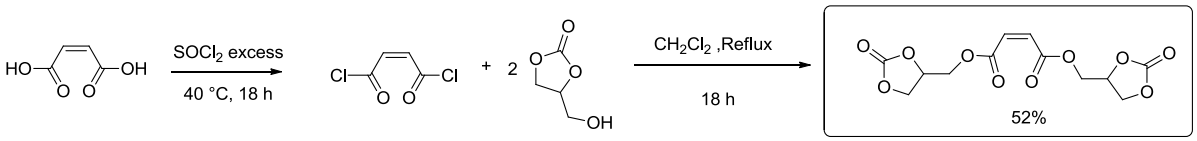


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 125 MHz, 298 K) of (2-oxo-1,3-dioxolan-4-yl)methyl acrylate (**2**).

Synthesis of bis((2-oxo-1,3-dioxolan-4-yl)methyl)maleate (3)



In a three necked 100 mL-flask equipped with a condenser and magnetic bar, was charged sequentially with maleic acid (2.00 g, 17.0 mmol) and thionyl chloride (7.5 mL, 103 mmol). The resulting suspension was warmed at 40 °C and stirred overnight. A trap for the neutralization of the gasses formed during the reaction was placed on the top of the condenser. After the reaction time period, the clear solution was cooled at room temperature and the excess of thionyl chloride was eliminated under vacuum and an aliquot of the final liquid was analyzed by gas chromatography and NMR. ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.42 (2H, s, -C*H*=C*H*-). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz, 298 K): δ 139.5 (-*C*H=*C*H-), 165.2 (O=*C*O). To a solution of maleoyl chloride (2.13 g, 14.0 mmol) in dry dichloromethane (15 mL) was added glycerol carbonate (3.1 g, 26 mmol) at room temperature. The resulting clear solution was slowly warmed at 45 °C and refluxed overnight. After this time period, the solution was cooled at room temperature and the solvent was distilled off. The product was purified by crystallization from hot chloroform. A white powder was obtained (2.30 g, 52%).

EI-MS: *m/z* = 339 $[M+Na]^+$. ^1H NMR ($CDCl_3$, 500 MHz, 298 K): δ 3.63-3.90 (m, 4H, C*H*$_2$-CH-C*H*$_2$OCOO), 4.35-4.50 (m, 4H, C*H*$_2$-CH-C*H*$_2$OCOO), 4.77 (m, 2H, CH_2-C*H*-CH_2OCOO), 7.03 (s, 2H, -C*H*=C*H*-). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 298 K): δ 61.6, 66.0 (*C*H$_2$-5CC), 76.9 (*C*H-5CC), 136.6 (-*C*H=*C*H), 155.7 (O=*C*OO), 164.5 (O=*C*O).

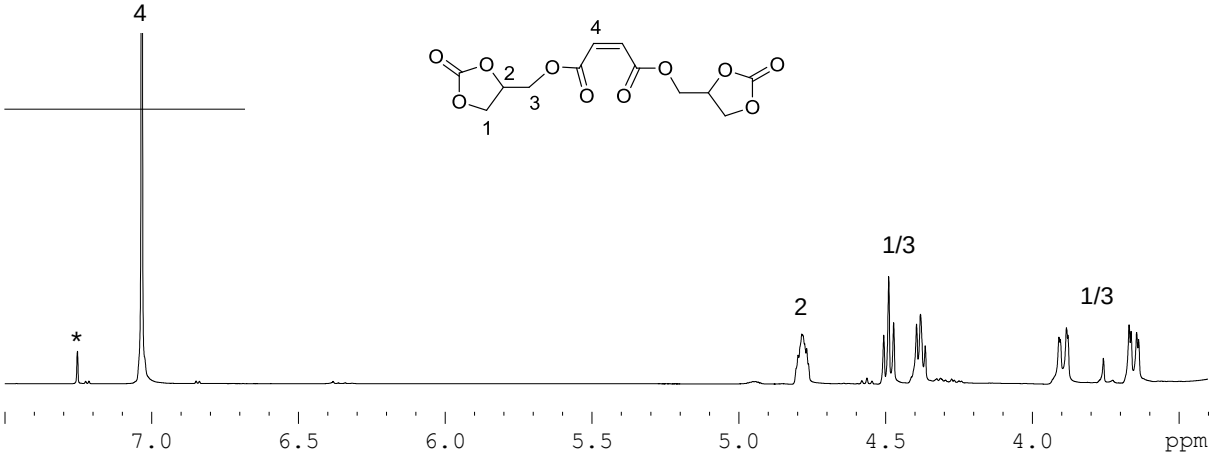
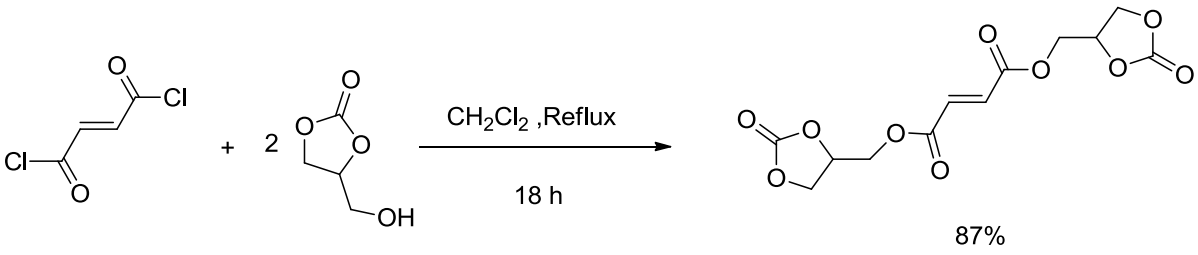


Figure S4. ^1H NMR spectrum ($CDCl_3$, 500 MHz, 298 K) of bis((2-oxo-1,3-dioxolan-4-yl)methyl) maleate (**3**).

Synthesis of bis((2-oxo-1,3-dioxolan-4-yl)methyl) fumarate (4)



To a solution of glycerol carbonate (10.9 g, 92 mmol) in dry dichloromethane (20 mL) was added dropwise fumaryl chloride (5.2 mL, 7.40 g, 48 mmol) at room temperature. The resulting clear solution was slowly warmed at 45 °C and refluxed overnight. After this time period, the solution was cooled at room temperature and the solvent was distilled off. The product was purified by extracting the unreacted reagents with $CHCl_3$ (4 × 10 mL). A white powder was obtained (12.6 g, 87%). EI-MS: *m/z* = 339 $[M+Na]^+$. ^1H NMR (DMSO, 400 MHz, 298 K): δ 4.35-4.64 (m, 8H, C*H*$_2$-CH-C*H*$_2$OCOO), 5.10 (m, 2H, CH_2-C*H*-CH_2OCOO), 6.79 (2H, s, -C*H*=C*H*-). $^{13}C\{^1H\}$ NMR (DMSO, 125 MHz, 298 K): δ 64.8, 66.4 (*C*H$_2$-5CC), 74.5 (*C*H-5CC), 133.5 (-*C*H=*C*H-), 155.1 (O=*C*OO), 164.2 (O=*C*O).

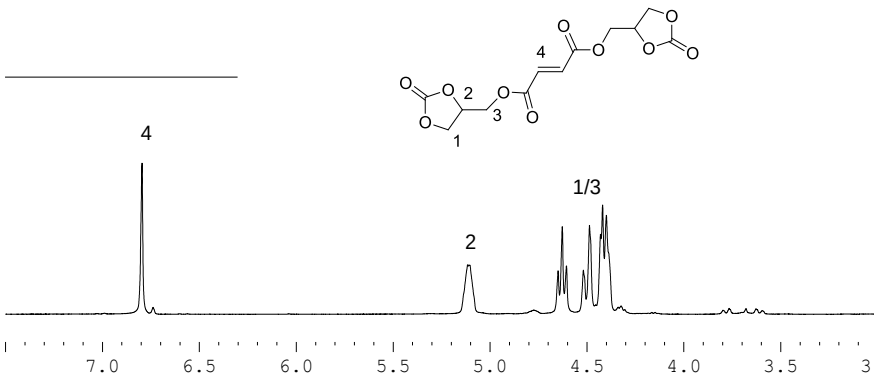
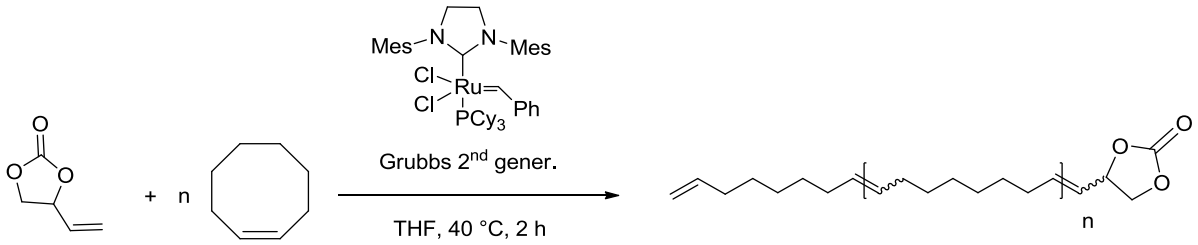


Figure S3. ^{1}H NMR spectrum (DMSO, 400 MHz, 298 K) of bis((2-oxo-1,3-dioxolan-4-yl)methyl) fumarate (**4**).

Attempted self-metathesis of compounds 1 and 2.

The self-metathesis of 4-vinyl-1,3-dioxolan-2-one (**1**) and (2-oxo-1,3-dioxolan-4-yl)methyl acrylate (**2**) was attempted using 3 to 8 mol% of Grubbs 1st or 2nd-generation catalyst, as 1.0 M solutions either in dichloromethane at 45 °C overnight or in toluene at 110 °C overnight, in opened vessels under an argon atmosphere. The reactions were monitored by ^{1}H NMR spectroscopy. In all cases, only the starting reagents were observed in the final reaction mixtures.

Table S1. [1]Ring-Opening polymerization of cyclooctene (COE) promoted by Grubbs 2nd-generation catalyst in presence of 4-vinyl-1,3-dioxolan-2-one (**1**) as chain-transfer agent



Entry[a]	[**1**]/[Ru]	[COE]/[**1**]	Conv. (%)	$M_{n_{theo}}$ [b] (g/mol)	$M_{n_{SEC}}$ [c] (g/mol)	$M_{n_{NMR}}$ [d] (g/mol)	$Đ_M$ [c]
1	5	400	100	44 000	56 800	46 600	1.62
2	10	200	100	22 000	16 800	14 600	1.48
3	20	100	100	11 000	8 900	6 800	1.43
4	30	66	100	7 300	6 700	5 400	1.41
5	50	40	100	4 400	3 500	3 200	1.45
6[b]	20	50	100	5 500	6 500	5 700	1.43

[a] conditions: Catalyst = 5.0 µmol, COE = 2 000 equiv., THF = 7 mL, T = 40 °C; 2 h; [b] COE = 1 000 equiv, THF = 4 mL. [b] Calculated assuming quantitative monomer conversion and one vinyl/one cyclocarbonate terminal group per polymer chain; [c] Determined by Size-Exclusion Chromatography in THF at 30 °C vs. PS standards; [d] Calculated by ^{1}H NMR from the integral value ratio of the signals of chain-end group(s) and repeating units.

Example of ROMP of COE in the presence of 1

In a typical polymerization procedure, a 100 mL-flask, equipped with a magnetic bar, was charged sequentially with THF (5 mL), *cis*-cyclooctene (1.4 mL) and the proper amount of chain-transfer agent (4-vinyl-1,3-dioxolan-2-one, **1**). The resulting solution was thermostated at 40 °C and the polymerization was started by injection of the pre-catalyst solution, prepared by dissolving Grubbs second-generation catalyst (5.0 mg, 5.3 µmol) in THF (3 mL). After 2 h, the mixture was poured into cold acidified methanol. When present, the polymers were recovered by filtration and dried at 25 °C in vacuum. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): repeat unit *trans*: 1.30, 1.97, 5.39; *cis*: 1.30, 2.03, 5.34; chain-end cyclocarbonate: 4.12, 4.56 (t, 2H, -CH=CH-CH-C*H*$_2$OCOO), 5.09 (m, 1H, -CH=CH-C*H*-CH_2OCOO), 5.53 (dt, 1H, J_{trans} = 15.0 Hz, -CH=C*H*-CH-CH_2OCOO), 5.97 (m, J_{trans} = 14.8 Hz, J = 7.0 Hz, 1H, -

C*H*=CH-C*H*-CH_2OCOO), chain-end vinyl: 2.14 (m, 2H, -CH_2-CH=CH_2), 4.98 (dt, *J* = 17.7 and 10.7 Hz, 2H, -CH_2-CH=CH_2), 5.83 (m, 1H, -CH_2-C*H*=CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 298 K): repeat unit 130.34 (*trans*), 129.88 (*cis*), 32.63, 29.77, 29.69, 29.24, 29.20, 29.07, 27.26 chain-end cyclic carbonate: 69.51 (-CH=CH-CH-*C*H_2OCOO), 78.24 (-CH=CH-*C*H-CH_2OCOO), 123.89 (-CH=*C*H-CH-CH_2OCOO), 140.02 (-*C*H=CH-CH-CH_2OCOO), 155.10 (O=*C*O), chain-end vinyl: 34.20 (-*C*H_2-CH=CH_2), 114.40 (-CH_2-CH=*C*H_2), 139.6 (-CH_2-*C*H=CH_2).

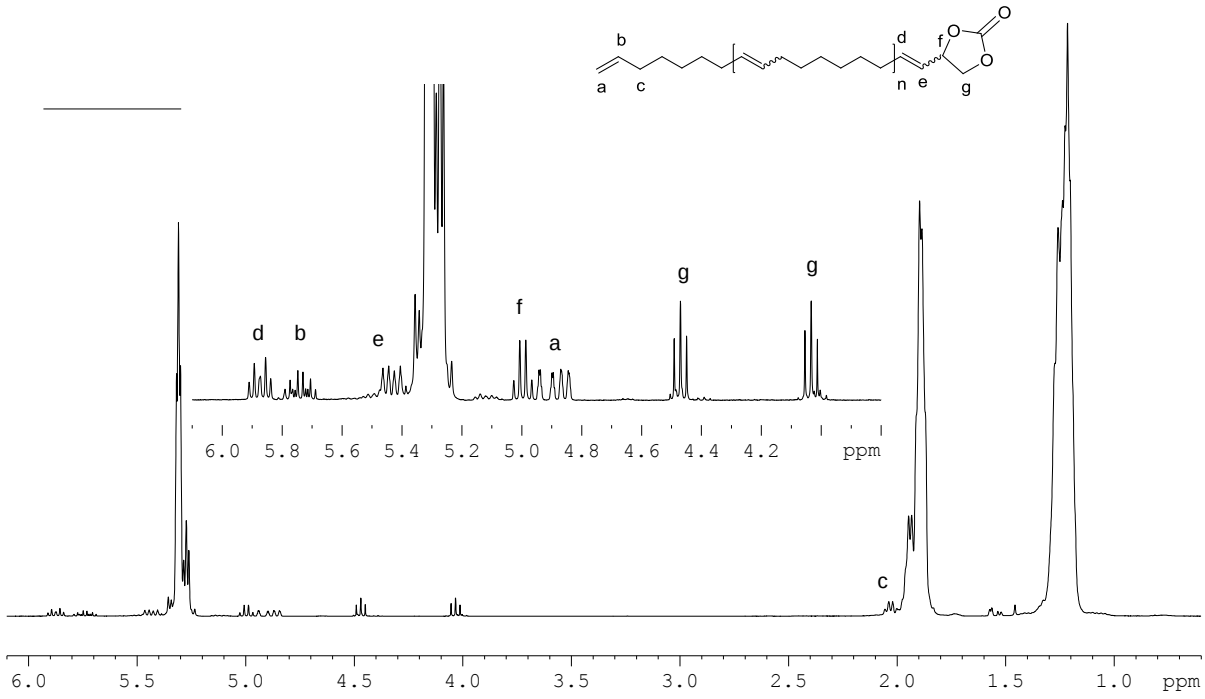


Figure S5. ^1H NMR spectrum ($CDCl_3$, 500 MHz, 298 K) of a polycyclooctene (PCOE) mono-end-functionalized with cyclocarbonate (Table S1, entry 4).

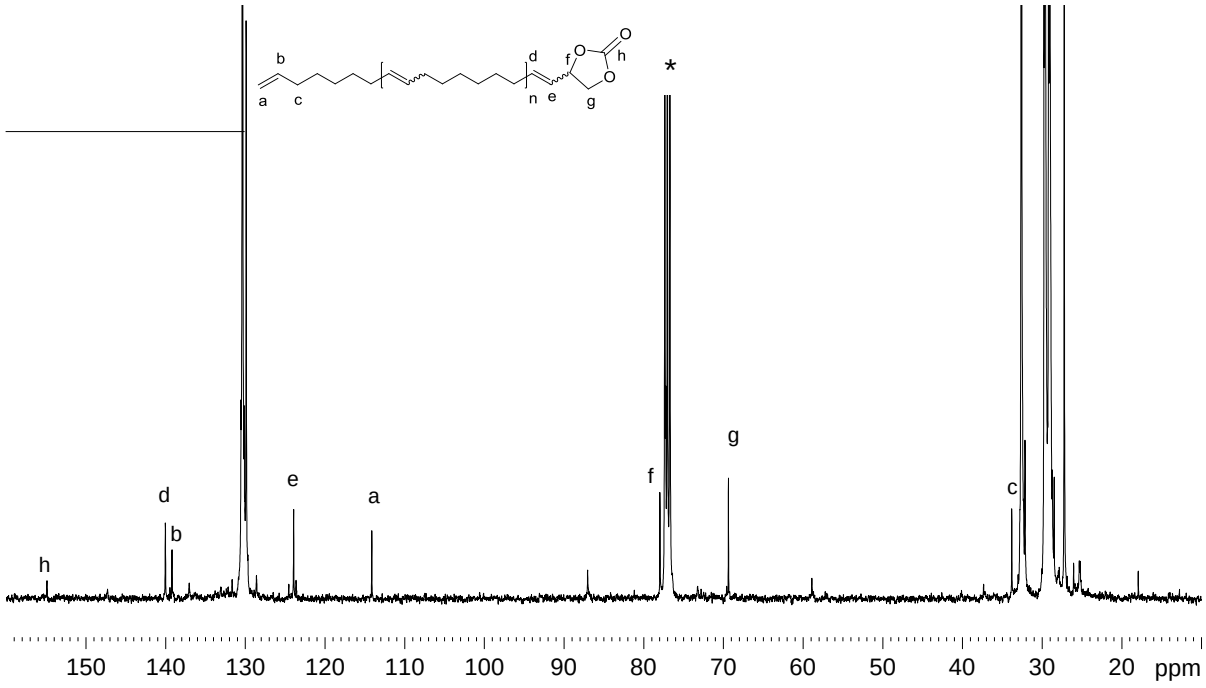


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 125 MHz, 298 K) of an α-vinyl, ω-cyclocarbonate polycyclooctene (Table S1, entry 4) (* stands for residual resonances of $CDCl_3$).

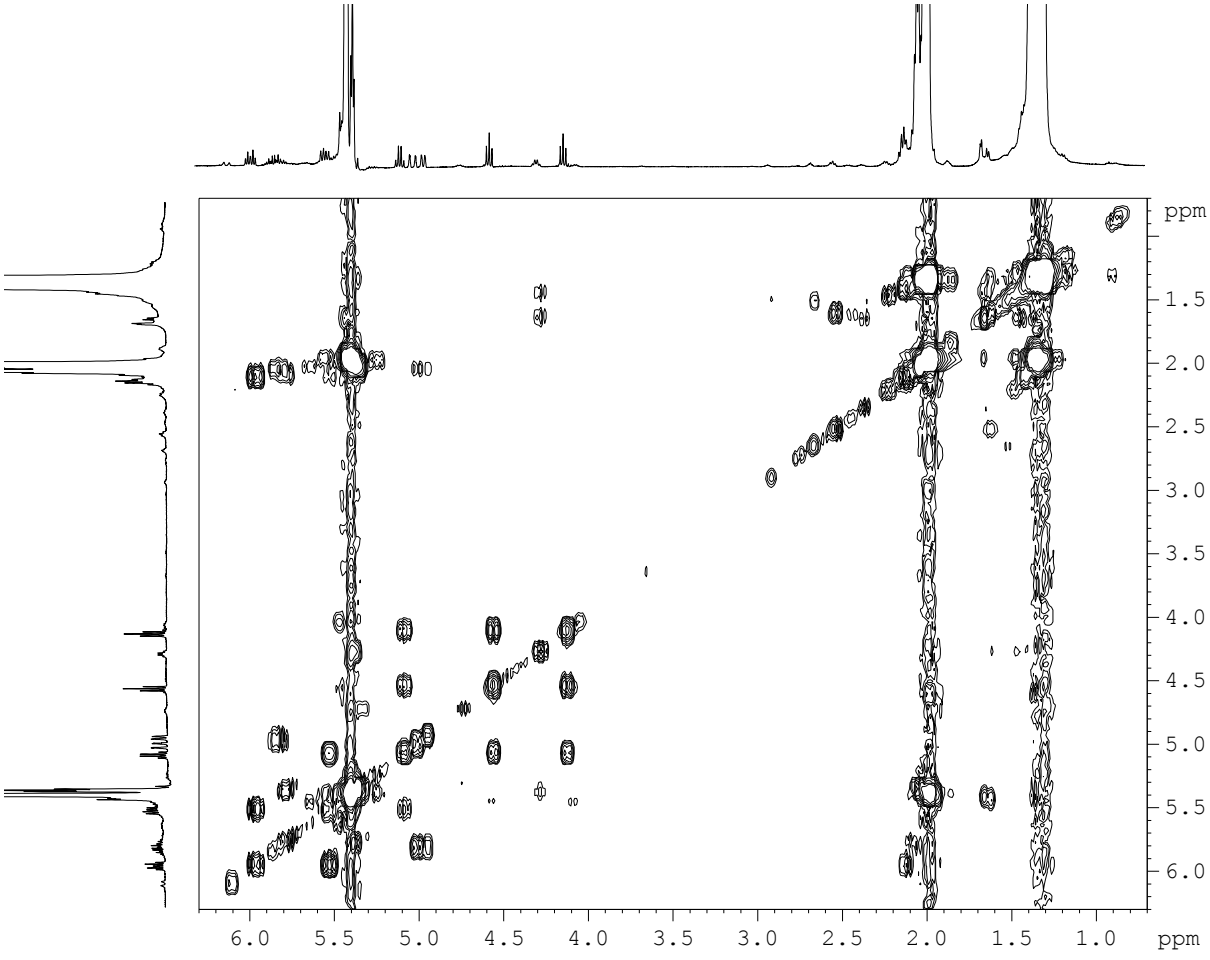


Figure S7. ^{1}H-^{1}H COSY NMR spectrum ($CDCl_3$, 500 MHz, 298 K) of an α-vinyl, ω-cyclocarbonate polycyclooctene (Table S1, entry 4).

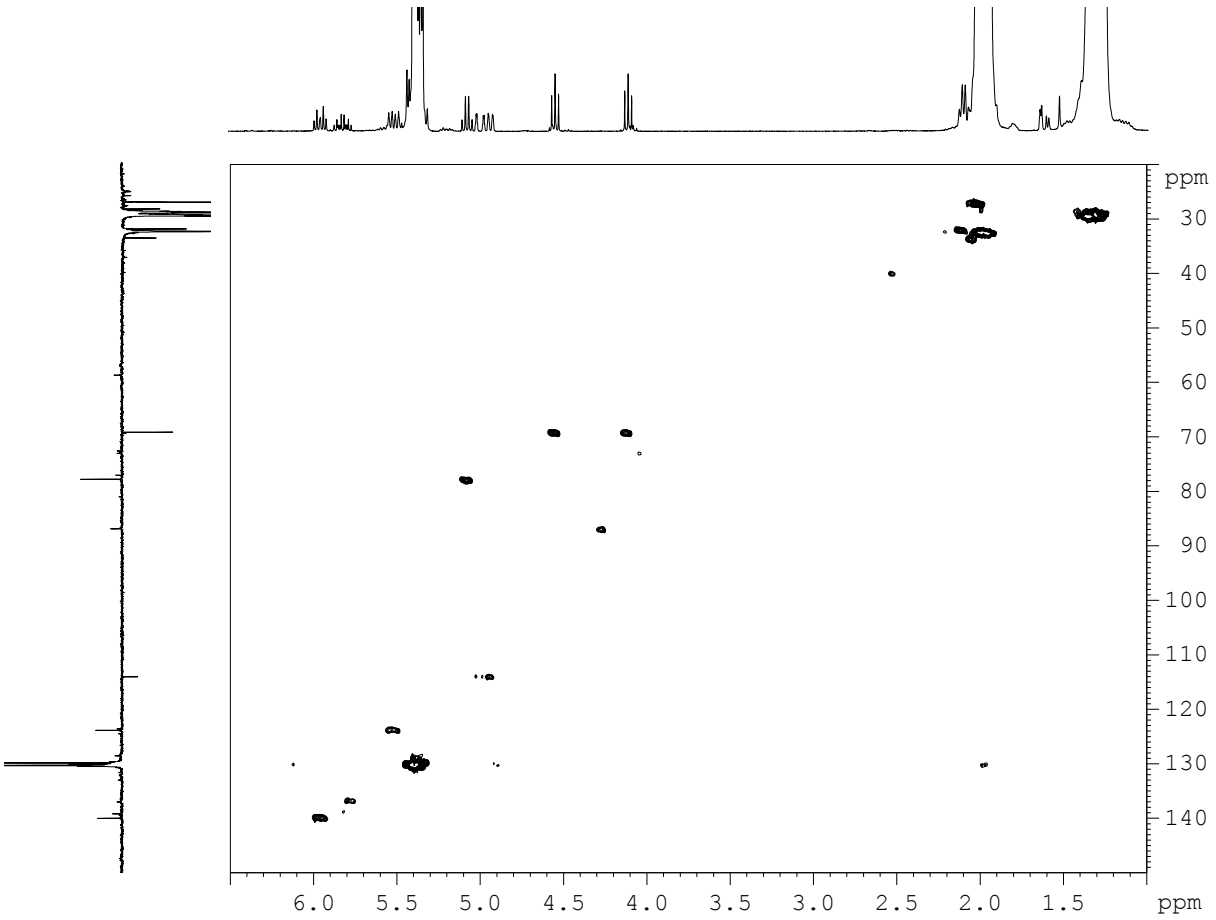


Figure S8. ^{1}H-^{13}C(DEPT) HMQC NMR spectrum ($CDCl_3$, 500 MHz, 298 K) of an α-vinyl,ω-cyclocarbonate polycyclooctene (Table S1, entry 4).

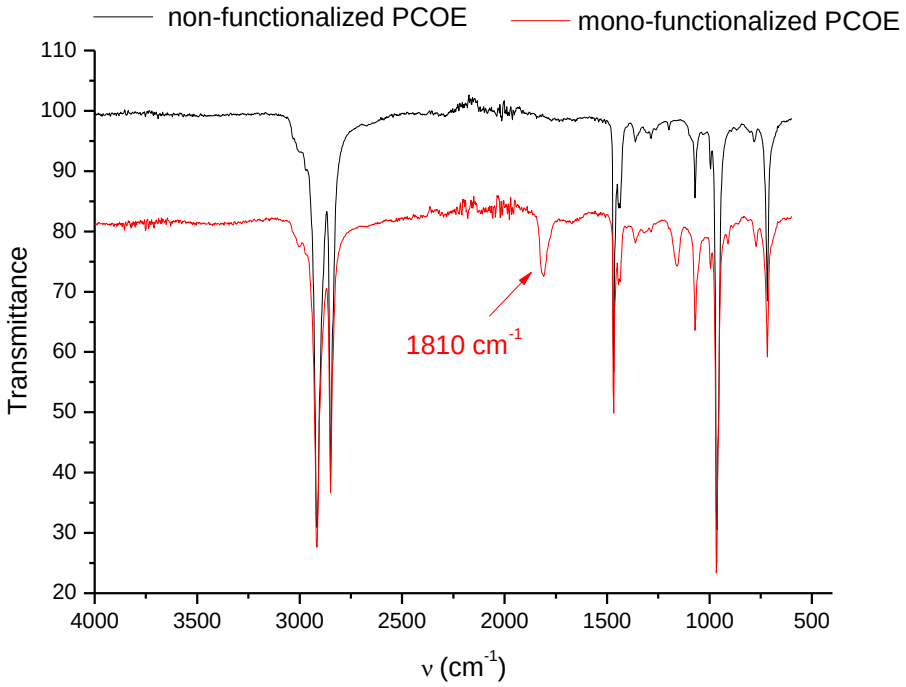


Figure S9. FT-IR spectra (ATR) of a non-end-functionalized polycyclooctene (black trace) and of an α-vinyl,ω-cyclocarbonate polycyclooctene (red trace) (Table S1, entry 4).

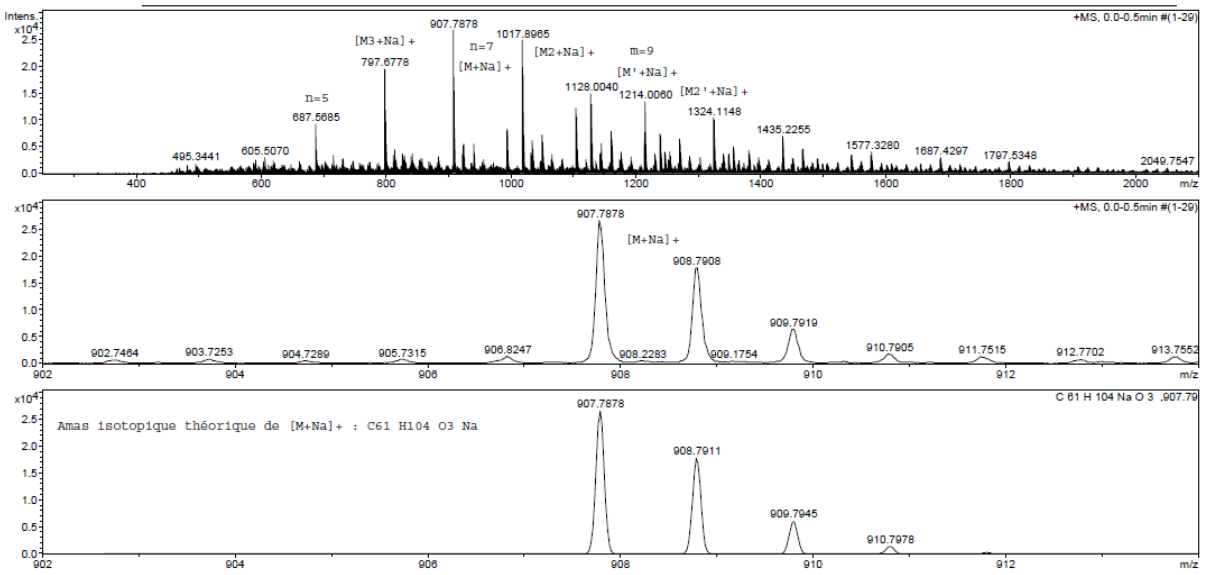
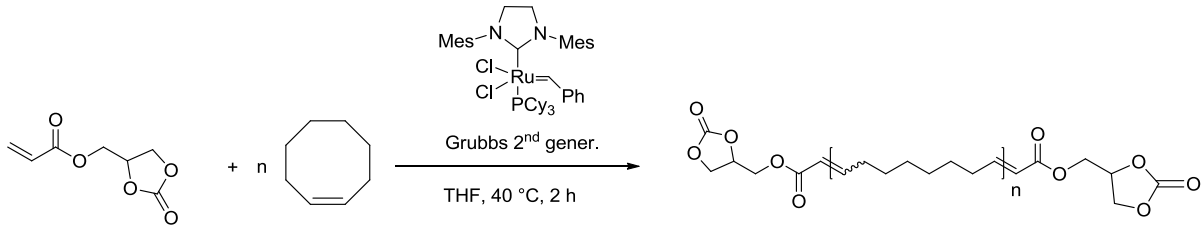


Figure S10. ESI-HRMS spectrum of an α-vinyl,ω-cyclocarbonate polycyclooctene (Table S1, entry 4) (top: full spectrum; medium: detail of the isotopic distribution of the central peak; bottom: calculated isotopic distribution for this peak (n = 8)).

Table S2. Ring-Opening polymerization of cyclooctene promoted by Grubbs 2nd-generation catalyst in presence of acryloyl-glycerol carbonate (**2**) as chain-transfer agent



Entry[a]	[**2**]/[Ru]	[COE]/[**2**]	Conv. (%)	$M_{n_{theo}}$[b] (g/mol)	$M_{n_{SEC}}$[c] (g/mol)	$M_{n_{NMR}}$[d] (g/mol)	$Đ_M$[c]
1	30	66	100	7 300	47 800	30 500	1.60
2	50	40	100	4 400	12 200	7 400	1.69
3	80	80	100	2 750	7 900	5 800	1.48
4[b]	50	3	100	300	2 200	900	1.51

[a] conditions: Catalyst = 5.0 µmol, COE = 2000 equiv., THF = 7 mL, T = 40 °C; 2 h; [b] COE = 150 equiv. THF = 2 mL. [b] Calculated assuming quantitative monomer conversion and one vinyl/one cyclocarbonate terminal group per polymer chain; [c] Determined by Size-Exclusion Chromatography in THF at 30 °C vs. PS standards; [d] Calculated by ^{1}H NMR from the integral value ratio of the signals of chain-end group(s) and repeating units.

Example of ROMP of COE in the presence of 2

In a typical polymerization procedure, a 100 mL-flask, equipped with a magnetic bar, was charged sequentially with THF (5 mL), cyclooctene (1.4 mL) and the proper amount of chain-transfer agent (acryloyl glycerol carbonate, **2**). The resulting solution was thermostated at 40 °C and the polymerization was started by injection of the pre-catalyst solution, prepared by dissolving Grubbs second-generation catalyst (G2) (5.0 mg, 5.3 µmol) in THF (3 mL). After 2 h, the mixture was poured into cold acidified methanol. When present, the polymers were recovered by filtration and dried at 25 °C in vacuum. ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): repeat unit *trans*: 1.30, 1.97, 5.39; *cis*: 1.30, 2.03, 5.34; chain-end group: 2.25 (m, 2H, -C*H*$_2$-CH=CH-COO), 4.30, 4.63 (m, 4H, -C*H*$_2$-CH-C*H*$_2$OCOO), 4.96 (m, 1H, -CH$_2$-C*H*-CH$_2$OCOO), 5.87 (d, J_{trans} = 15.2 Hz, 1H, -CH=C*H*-COO), 7.07 (m, 1H, -C*H*=CH-COO, J_{trans} =15.0 Hz, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): repeat unit: 130.34 (*trans*), 129.88 (*cis*), 32.63, 29.77, 29.69, 29.24, 29.20, 29.07, 27.26; chain-end groups: 62.80, 66.0 -*C*H$_2$-CH-*C*H$_2$OCOO), 73.87 (-CH$_2$-*C*H-CH$_2$OCOO), 119.50 (-CH=*C*H-COO-), 152.04 (-*C*H=CH-COO), 154.6 (O=*C*OO), 165.9 (OC=O).

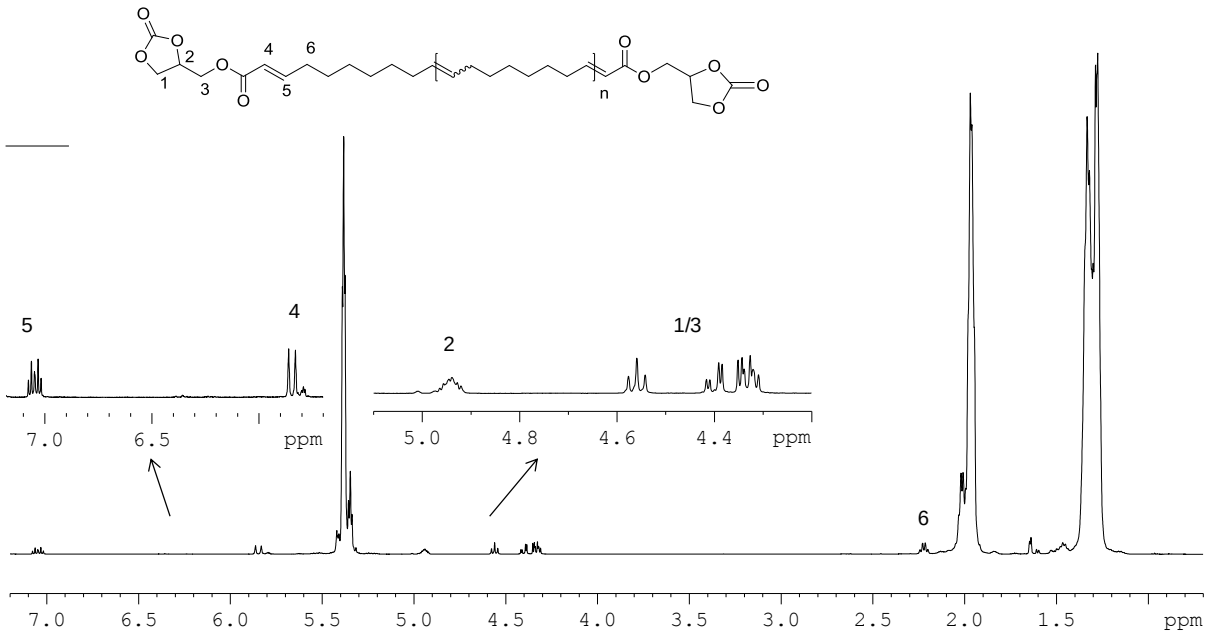


Figure S11. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz, 298 K) of an α,ω-dicyclocarbonate polycyclooctene (Table S2, entry 2).

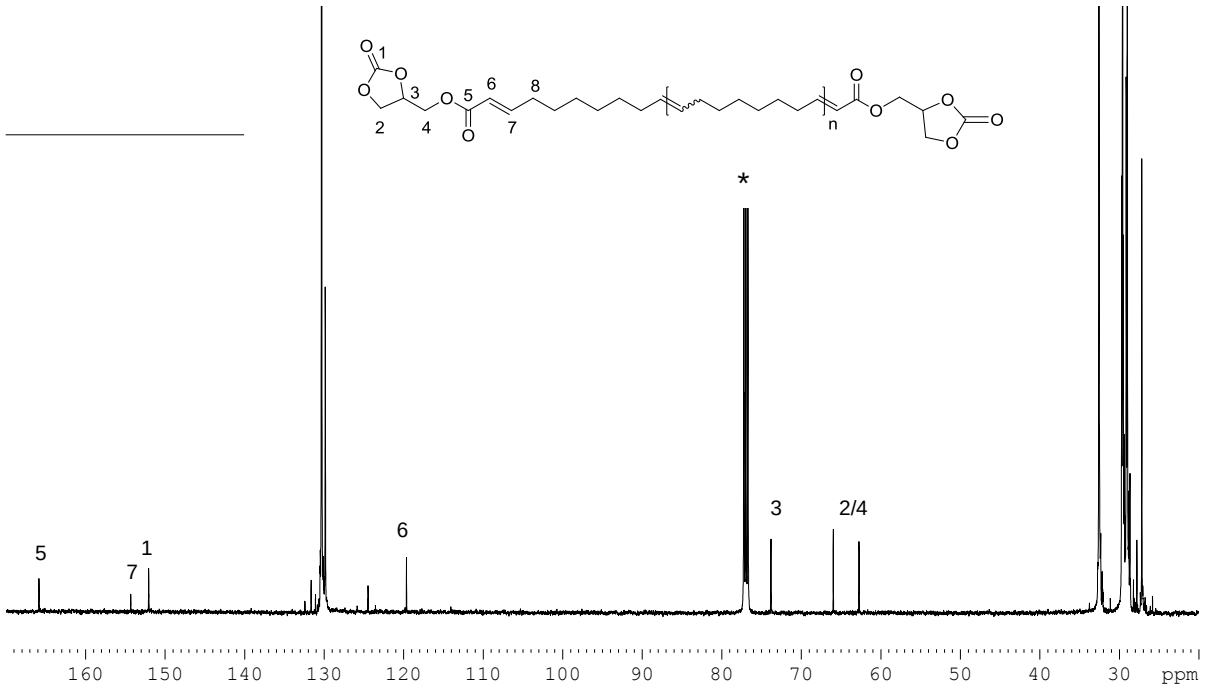


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 125 MHz, 298 K) of an α,ω-dicyclocarbonate polycyclooctene (Table S2, entry 2) (* stands for residual resonance for $CDCl_3$).

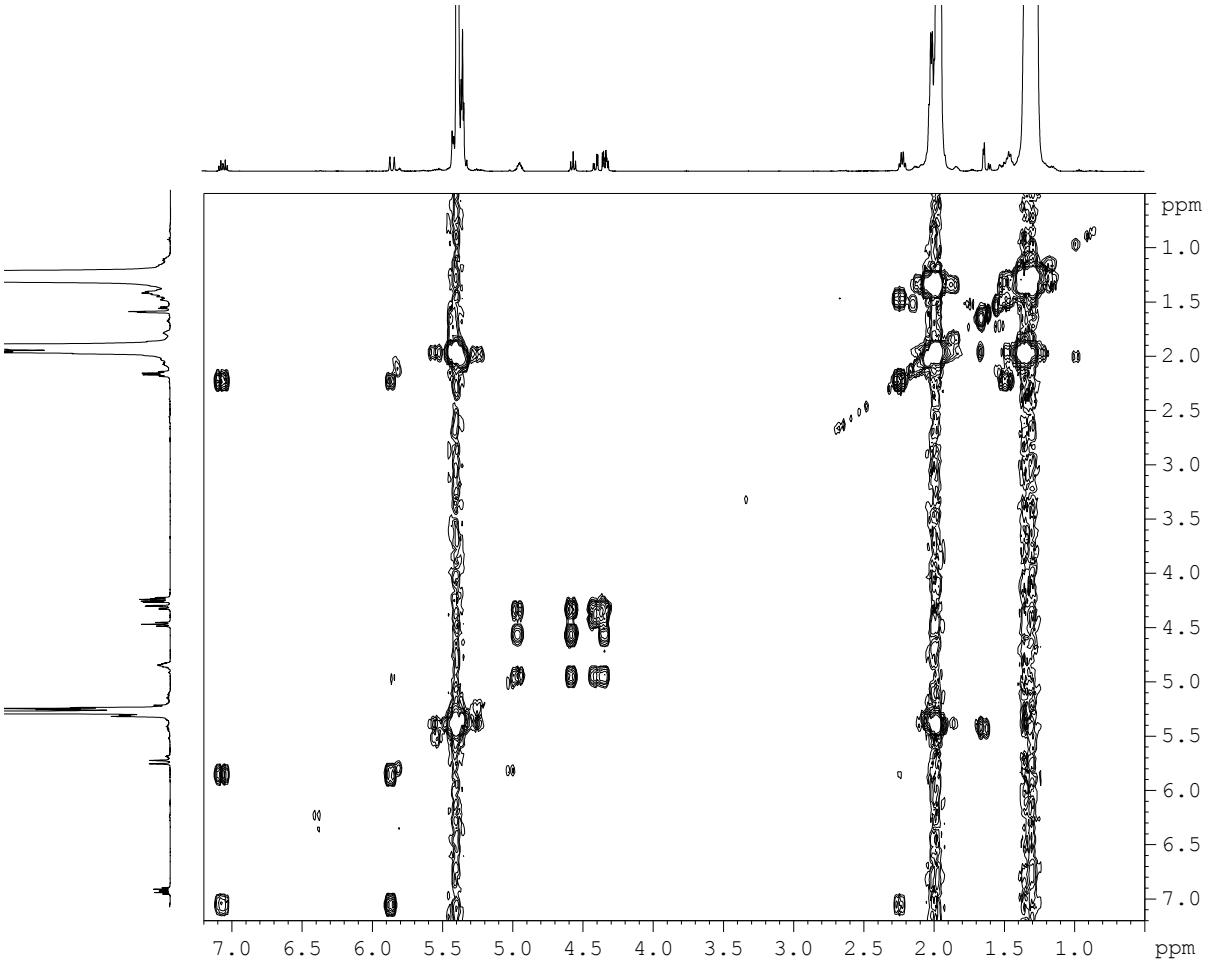


Figure S13. ^{1}H-^{1}H COSY NMR spectrum ($CDCl_3$, 500 MHz, 298 K) of an α,ω-dicyclocarbonate polycyclooctene (Table S2, entry 2).

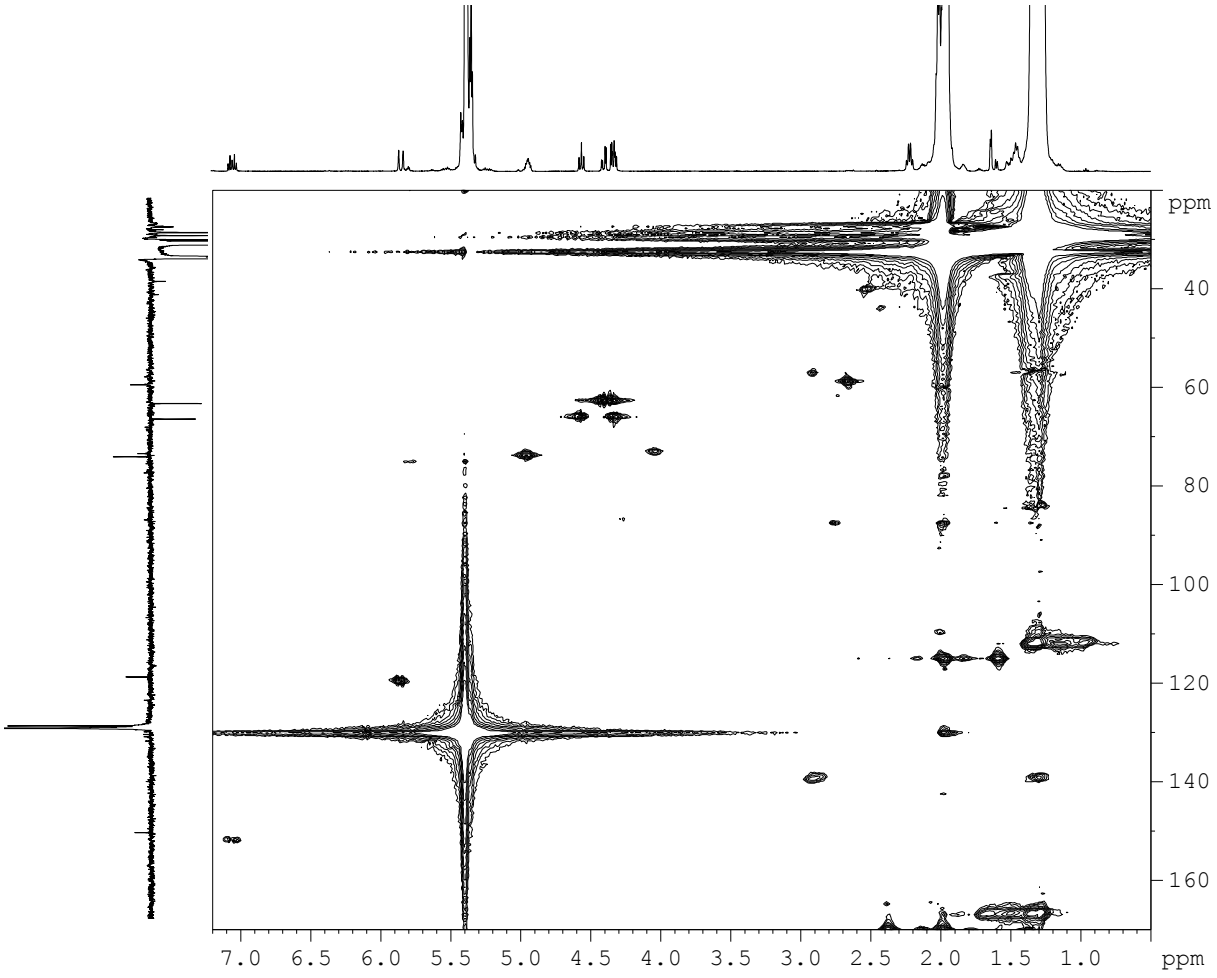


Figure S14. ^{1}H-^{13}C(DEPT) HMQC NMR spectrum ($CDCl_3$, 500 MHz, 298 K) of an α,ω-dicyclocarbonate polycyclooctene (Table S2, entry 2).

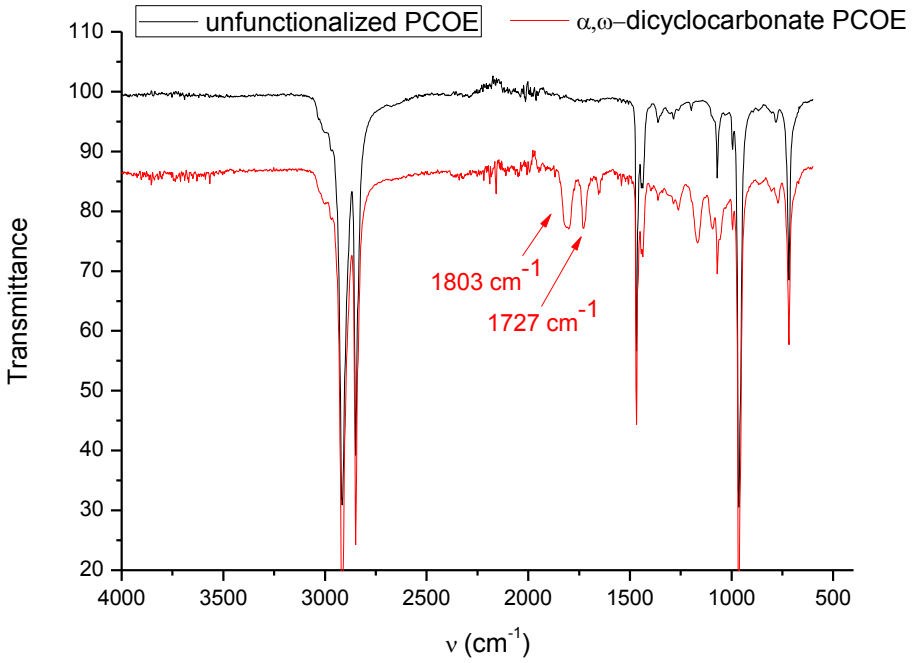
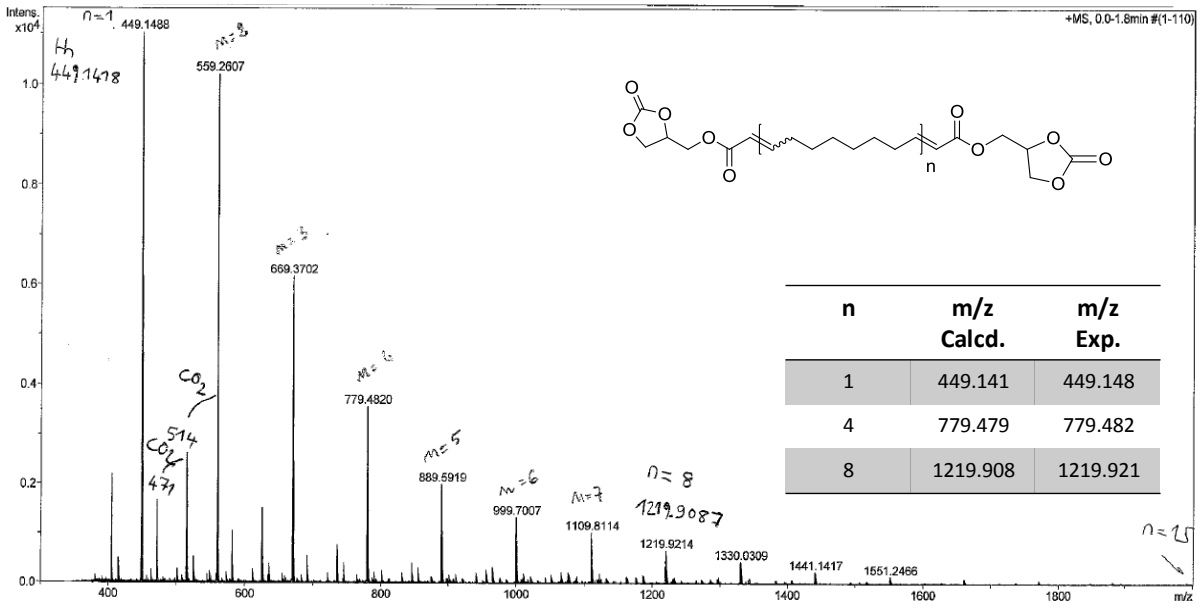


Figure S15. FT-IR spectra (ATR) of a non-end-functionalized polycyclooctene (black trace) and of an α,ω-dicyclocarbonate polycyclooctene (red trace) (Table S2, entry 2).



n	m/z Calcd.	m/z Exp.
1	449.141	449.148
4	779.479	779.482
8	1219.908	1219.921

Figure S16. ESI-HR-mass spectrum of an α,ω-dicyclocarbonate polycyclooctene (Table S2, entry 4).

Table S3. Ring-opening polymerization of cyclooctene promoted by Grubbs 2nd-generation catalyst in the presence of maleoyl di(glycerol carbonate) (**3**) or fumaryl di(glycerol carbonate) (**4**) as potential chain-transfer agent.

Entry[a]	CTA	[CTA]/[Ru]	[COE]/[CTA]	Conv. (%)	$M_{n\ theor}$[b] (g/mol)	$M_{n_{GPC}}$[c] (g/mol)	$M_{n_{NMR}}$[d] (g/mol)	$Đ_M$[c]
1	**4**	10	200	100	22 000	110 290	*nd*	2.10
2	**3**	10	200	100	22 000	99 540	*nd*	1.95
3	**3**	20	100	100	11 000	60 580	*nd*	1.82
4	**3**	30	66	100	7 300	25 200	40 320	1.60
5	**3**	20	100	100	11 000	68 600	*nd*	1.72
6[e]	**3**	20	100	100	11 000	38 200	62 300	1.63

[a] conditions: Catalyst = 5.0 μmol, COE = 2000 equiv, THF = 7 mL, T = 40 °C; 2 h; [b] Calculated assuming quantitative monomer conversion and one vinyl/one cyclocarbonate terminal group per polymer chain; [c] Determined by Size-Exclusion Chromatography in THF at 30 °C vs. PS standards; [d] Calculated by ^{1}H NMR from the integral value ratio of the signals of chain-end group(s) and repeating units. [e] T = 60 °C.

Example of ROMP of COE in the presence of 3 or 4

In a typical polymerization procedure, a 100 mL-flask, equipped with a magnetic bar, was charged sequentially with THF (5 mL), cyclooctene (1.4 mL) and the proper amount of potential chain-transfer agent (**3** or **4**). The resulting solution was thermostated at 40 °C and the polymerization was started by injection of the pre-catalyst solution, prepared by dissolving Grubbs second-generation catalyst (G2) (5.0 mg, 5.3 μmol) in THF (3 mL). After 2 hours, the mixture was poured into cold acidified methanol. When present, the polymers were recovered by filtration and dried at 25 °C in vacuum.

Hydrogenation of mono-end-functionalized and telechelic cyclocarbonate-PCOE

In a typical procedure, a 50 mL-steel reactor, equipped with a magnetic bar, was charged sequentially with 0.500 g of polymer, toluene (20 mL), and Pd/C (10 mol-%). The reactor was charged with 40 bar of hydrogen at room temperature and was then thermostated at 100 °C overnight. After this time-period, the mixture was cooled at room temperature, the reactor was evacuated, and the suspension was poured into methanol. The polymers were recovered by filtration and dried at 25 °C in vacuum. The polymers were separated from the insoluble Pd/C

by extraction with boiling toluene. The clear solution was poured again into methanol and the clean powder was recovered by filtration a dried at 40 °C in vacuum.

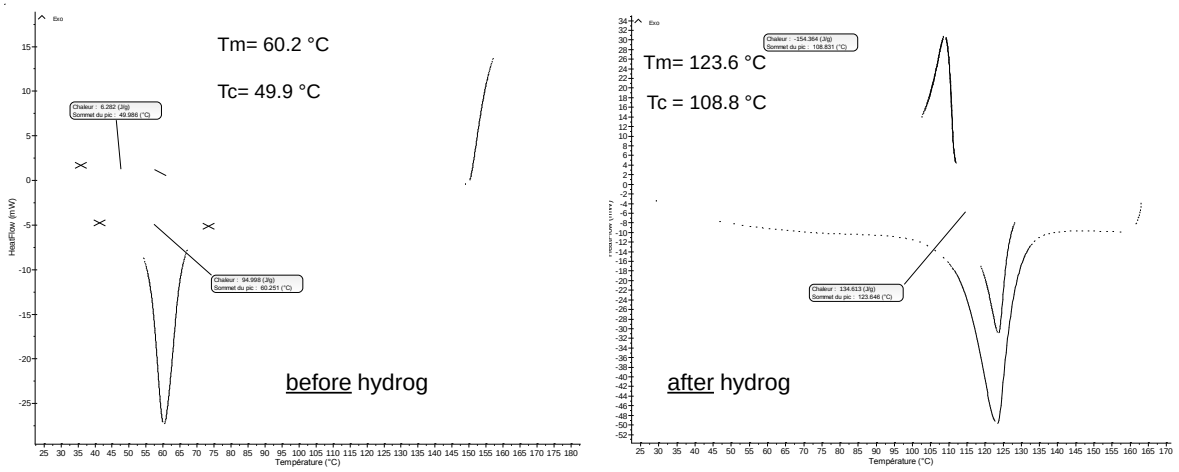


Figure S17. DSC traces of an α-vinyl,ω-cyclocarbonate-polycyclooctene before (left) and after (right) hydrogenation (Table S1, entry 4).

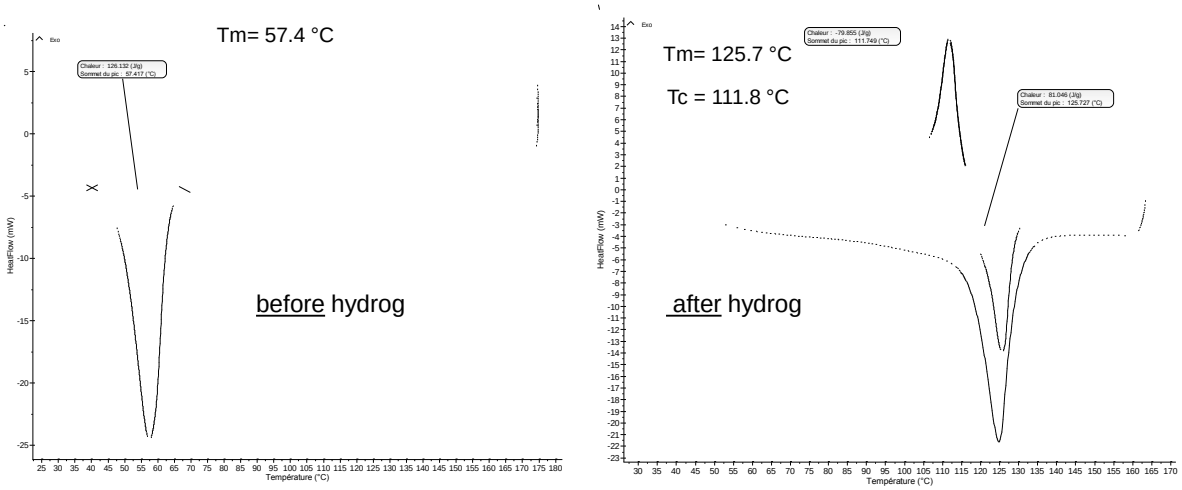


Figure S18. DSC traces of an α,ω-dicyclocarbonate-polycyclooctene before (left) and after (right) the hydrogenation (Table S2, entry 2).

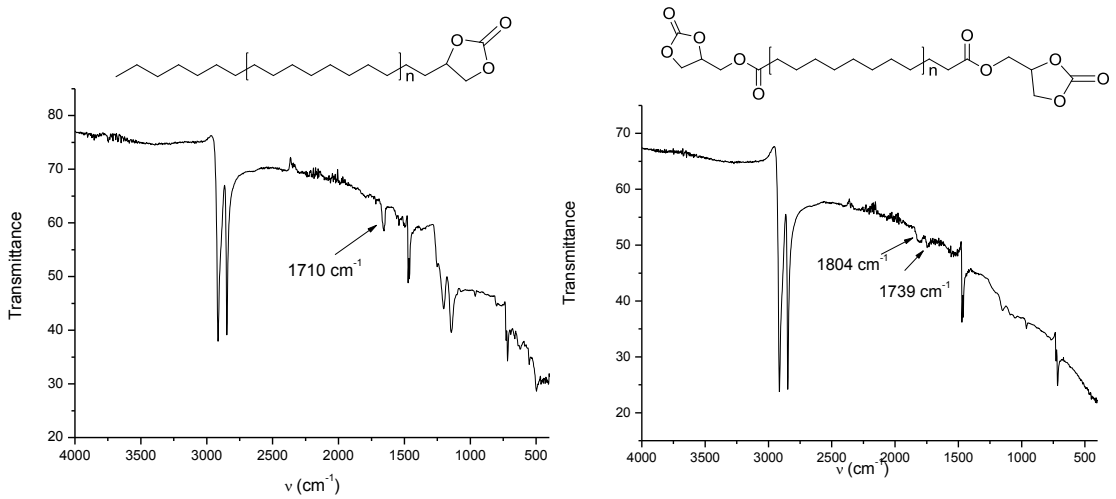


Figure S19. FT-IR spectra (ATR) of α-vinyl,ω-cyclocarbonate- and α,ω-dicyclocarbonate-polyethylenes obtained by hydrogenation of the respective polycyclooctene samples (Table S1, entry 4 and Table S2, entry 2).

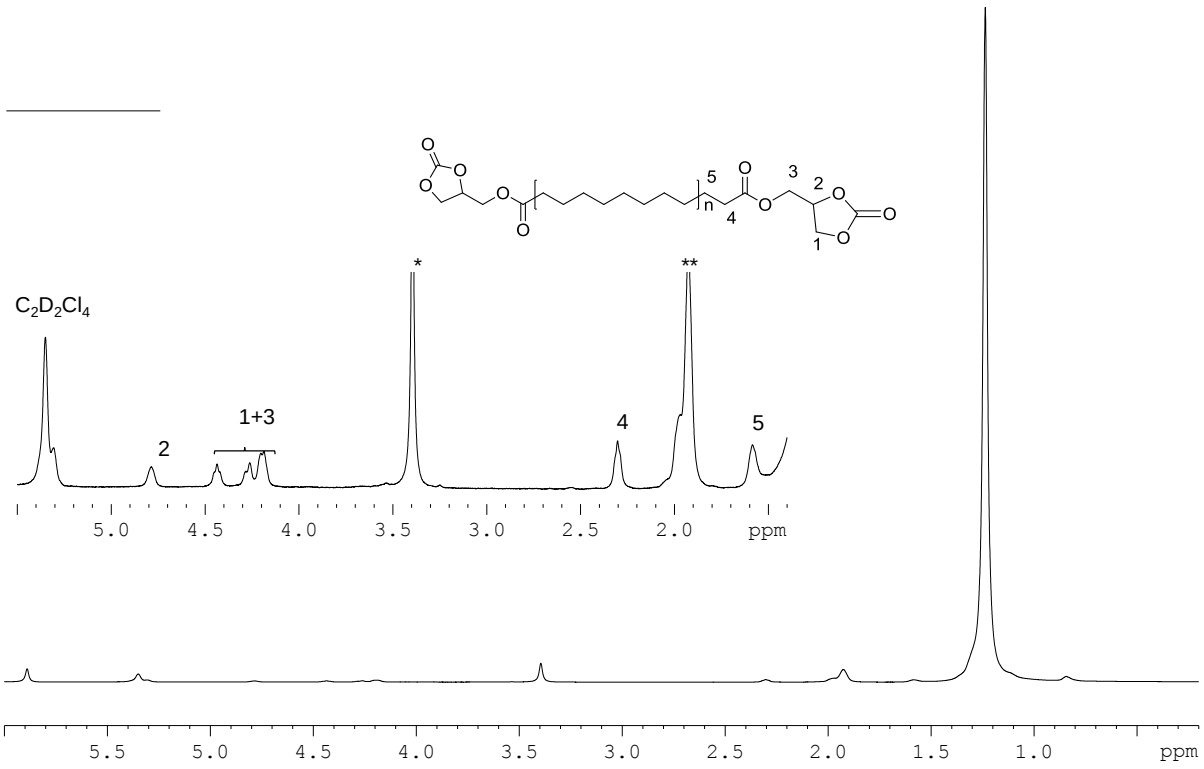


Figure S20. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 500 MHz, 373 K) of an α,ω-di(cyclocarbonate)-polyethylene obtained by hydrogenation of the corresponding α,ω-di(cyclocarbonate)-polycyclooctene (Table S2, entry 2)