Supporting Information

CO_2-based polycarbonates from biobased cyclic terpenes with end-of-life usage potential

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General procedures and materials

All solvents and chemicals were purchased from commercial suppliers (*Sigma-Aldrich, Alfa Aesar, Acros, TCI*) and used without prior purification, unless explicitly specified otherwise. Deuterated solvents were purchased from *Deutero GmbH*. All terpenoids were purchased from *Sigma-Aldrich* and *TCI*. To ensure fully dry monomers for the polymerization, all monomers were stirred over calcium hydride (CaH_2) for 24 h and the pure monomers were isolated by cryo-transfer (partially by applying heat). Carbon dioxide was acquired from *Westfalen AG* with a purity of 99.999% and stored over molecular sieve for two days prior use. Bis(triphenylphosphine)iminium chloride ([PPN]Cl) was received from *abcr GmbH*. To improve purity, a saturated dichloromethane [PPN]Cl solution was prepared and precipitated in diethyl ether (procedure was repeated three times). Subsequently, the solid was dried with a dichloromethane/benzene mixture via freeze-pump-thaw cycles, repeating this process three times under vacuum, and then dried for five days at 70 °C under vacuum. The catalyst (*R, R*)-(salcy)-Co(III)Cl (Co(Salen)Cl) was synthesized following literature procedures*,* dried using a dichloromethane/benzene mixture via freeze-pump-thaw cycles (repeated three times under vacuum), and then dried for five days at 50 °C under vacuum.[1] 1,4-Benezendimethanol (BDM) was recrystallized three times from hot toluene. Triethylborane (1M in THF) (TEB) was utilized without additional purification steps. All steel reactor components and glass/Teflon inlets were dried in an oven at 140 °C for one day prior use. The monomer mixtures were prepared in glass tubes and transferred into steel reactors within an *MBRAUN* glovebox under an argon atmosphere, followed by pressurizing the reactors with carbon dioxide prior polymerization.

1. Methods

Size exclusion chromatography with THF and PS standards (SEC (THF, PS))

SEC characterization was performed with an *Agilent 1100 series SEC system* with an SDV column set from *PSS* (SDV 103, SDV 105, SDV 106) with UV (254 nm) and RI detectors. Tetrahydrofuran (THF) was used as an eluent (flow rate 1 mL min^{-1}). The measurements were carried out at 30 °C with an RI and UV (254 nm) detector. Polystyrene (PS) standards were provided by *PSS* for calibration. All measurements were normalized to an internal toluene standard and the data recording and processing was realized with the software *PSS WinGPC UniChrom*.

SEC with universal calibration and viscosity measurement

The universal calibration is based on the determination of polystyrene calibration standards in combination with intrinsic viscosity measurements, relying on a PSS SDV 5 µm 10^3Å / 10^5Å / 10^6Å column set. The measurements were detected by a SECurity 1260 RI detector and SECurity viscometer DVD 1260 detector. Tetrahydrofuran (THF) was used as eluent (flow rate 1 mL min^{-1}) under 23 °C. The analysis was conducted by *PSS*.

Differential scanning calorimetry (DSC)

DSC measurements were carried out on a *DSC 250 device, TA Instruments*, applying indium and *n*-octane as calibration standard. The polymer samples were pre-dried under vacuum for one day, sealed in an aluminum pan and measured against an empty pan as reference under a nitrogen atmosphere. The samples were cooled from 40 °C to -90 °C and then heated to 100 °C, followed by an additional cooling and heating cycle in the temperature range of -90 °C and 100 °C. Heating and cooling cycles were set to a rate of 20 °C min^{-1}. All glass transition temperature (T_g) values were evaluated from the second heating cycle. The samples were analyzed with the software *TA Instruments Trios*.

Thermal gravimetric analysis (TGA)

TGA measurements were realized with a *Mettler-Toledo TGA/DSC 3+*. The polymer samples were pre-dried under vacuum for one day and then heated during measurement from 25 to 600 °C with a heating rate of 10 °C min^{-1} under nitrogen flow with 30 mL min^{-1}. The samples were analyzed with the software *STARe-Software*. $T_{5\%}$ is defined as the temperature at which 5% of the sample weight had decomposed during measurement.

Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR spectra were recorded at 23 °C on a *Bruker Avance III HD 300* spectrometer for all polymers and on a *Bruker Avance II HD 400* spectrometer for the glycidyl ether monomers, referenced internally to residual signals of chloroform-d_1 for ^{1}H and ^{13}C spectra. Diffusion-Ordered Spectroscopy (DOSY) and 2D NMR were recorded on a *Bruker Avance III HD 400* spectrometer operated at 400 MHz. Spectra were analyzed using *MestReNova software 14.2.0*. NMR spectroscopy data is reported as follows: chemical shift, signal multiplicity and integration. Spectra annotation uses lowercase letters for proton signals and capital letters for carbon signals.

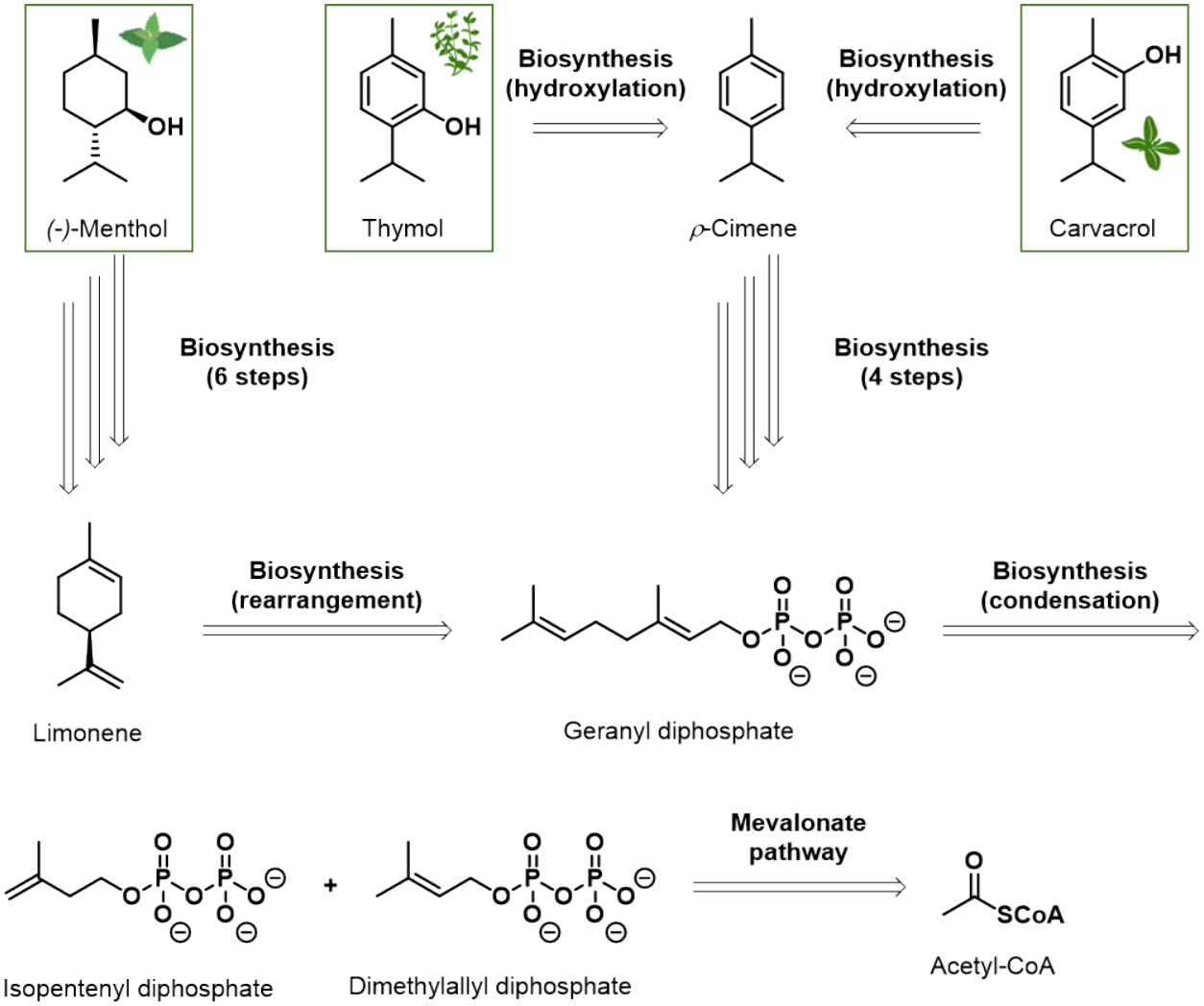
Matrix-assisted Laser Desorption Ionization Time-of-Flight (MALDI-ToF) Mass Spectrometry

MALDI-ToF was carried out on a *Bruker autoflex maX MALDI-ToF-MS/MS* with multi target plate in linear mode. Spotting method for polycarbonates: solutions of polymer (10 mg mL^{-1} in THF), KTFA (10 mg mL^{-1} in MeOH), and dithranol (10 mg mL^{-1} in THF) were mixed in 1:1:4 ratio and spotted onto the MALDI-ToF sample holder plate. The samples were dried overnight.

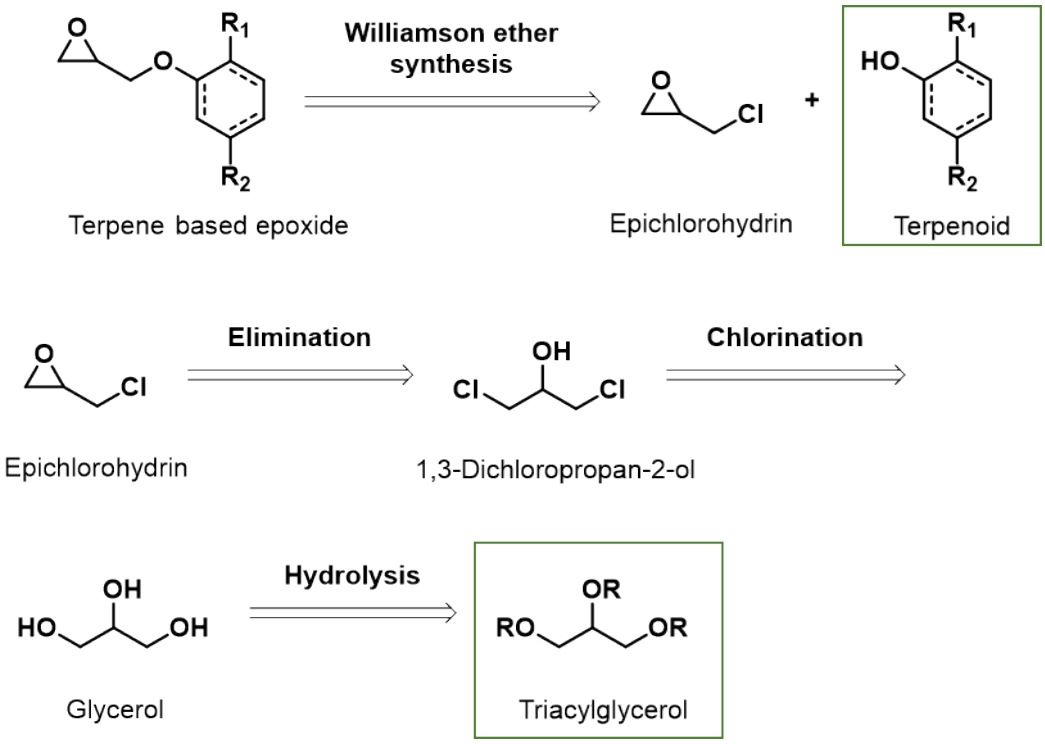
Tensile testing

Stress-strain experiments were realized with an *EZ Test EZ-LX* instrument by *Shimadzu*, Japan. Polymer films were prepared by solvent casting from chloroform (1.0 g in 10 mL $CHCl_3$). The films were then sintered for 6 hours at 100 °C and afterwards stored for 2 days under vacuum. The "dog-bones" (DIN 53 504 S3A) were cut out from the films. A force transducer (50 N capacity) *SM-50N-168* was used with a speed of 0.1 mm min^{-1}. All measurements were recorded using the software *TRAPEZIUMX*.

1. Biological terpene formation and synthesis of studied monomers



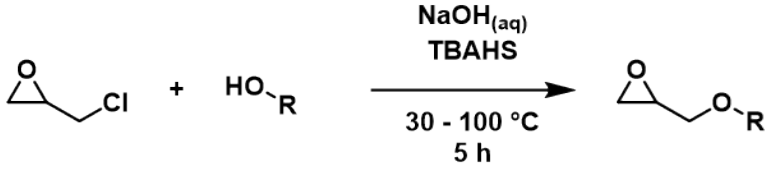
Scheme S1: Bio-sourced formation of presented terpenoids from acetyl-CoA.[2]



Scheme S2: Derivation of bio-sourced epichlorohydrin.[3]

2. Experimental procedures

General procedure for phenyl group monomer synthesis

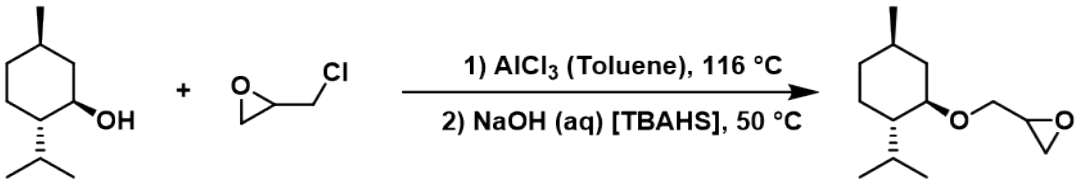


The bio-based phenyl glycidyl ether synthesis was used as guideline and was slightly changed accordingly to achieve the presented phenyl group containing terpenyl glycidyl ethers.[4] In the following, the synthesis of thymyl glycidyl ether is described exemplary.

A three-necked flask, equipped with a mechanical stirrer, dropping funnel, and reflux condenser, was loaded with thymol (30 mL, 29.3 g, 0.20 mol, 1 equiv.), epichlorohydrin (91.7 mL, 108.3 g, 1.17 mol, 6 equiv.) and tetrabutylammonium hydrogen sulfate (TBAHS, 3.31 g, 0.010 mol, 0.05 equiv.) and stirred at 100 °C for one hour. After cooling the reaction mixture to room temperature, a mixture of NaOH (22.2 g, 0.55 mol, 2.85 equiv.), water (110 mL) and TBAHS (3.31 g, 0.010 mol, 0.05 equiv.) was added dropwise during 15 minutes under vigorous stirring at 30 °C. The reaction was stirred for additional 90 minutes. The crude product was extracted with

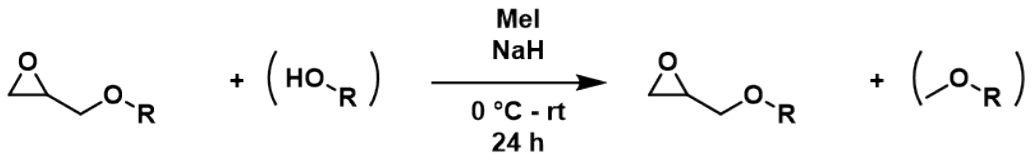
ethyl acetate (3 x 100 ml). The combined organic phases were washed with brine until neutrality, dried over $NaSO_4$, filtered and concentrated by using rotary evaporation. All high boiling substances were segregated by a bulb-to-bulb distillation under high vacuum (8 – $12 \cdot 10^{-3}$ mbar) at 140 °C. All low boiling substances like unreacted alcohol and diglycidyl ether were separated by a high vacuum distillation with Vigreux column (8 – $12 \cdot 10^{-3}$ mbar) at 150 °C during 6 hours. The final product ThyGE was collected from the residue of the distillation. The purified ThyGE was isolated as a colorless liquid in yields of 89%. Afterwards, the procedure for masking protic impurities was applied.

Synthesis of menthyl glycidyl ether



The synthesis described in a patent was carried out as follows.[5] A three-necked flask, equipped with a mechanical stirrer, dropping funnel, reflux condenser, was loaded with menthol (30 g, 0.19 mol, 1 equiv.), toluene (71 mL) and anhydrous aluminum chloride (2.05 g, 0.02 mol, 0.08 equiv.) under inert conditions. The reaction was heated to 116 °C and epichlorohydrin (18 mL, 21.32 g, 0.23 mol, 1.2 equiv.) mixed with toluene (40 mL) was added dropwise over two hours. After stirring for one more hour, the reaction was cooled down to 50 °C and NaOH (15.36 g, 0.38 mol, 2 equiv.) mixed with water (25 mL) and TBAHS (2.61g, 0.008 mol, 0.04 equiv.) was added. The reaction was stirred for another two hours at 75 °C. The reaction was quenched with water (70 mL) and the crude product was extracted with toluene (3 x 70 mL). The combined organic phases were washed with brine until neutrality, dried over $NaSO_4$, filtered and concentrated by using rotary evaporation. All high boiling substances were segregated by a bulb-to-bulb distillation under high vacuum (8 – $12 \cdot 10^{-3}$ mbar) at 120 °C. All low boiling substances like unreacted alcohol and diglycidyl ether were separated by a high vacuum distillation with Vigreux column (8 – $12 \cdot 10^{-3}$ mbar) at 150 °C during 6 hours. The final product MeGE was collected from the residue of the distillation. The purified MeGE was isolated as a colorless liquid in yields of 74%. Afterwards the procedure for masking protic impurities was applied.

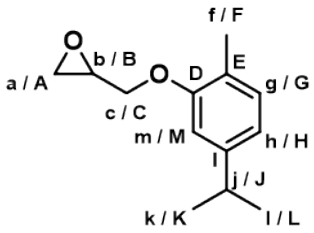
General procedure for masking protic impurities in the epoxide monomer



All epoxides were pretreated prior storage with sodium hydride (NaH) and methyl iodide (MeI) to deactivate any protic impurities according to literature.[6]

A Schlenk flask was charged with NaH (0.22 equiv.), cooled to 0 °C and TGE (1.00 equiv.) was added. After 2 h, MeI (0.10 equiv.) was added into the flask and the reaction mixture was slowly warmed up to r.t.. After 24 h, the mixture was centrifuged at -10 °C and 4500 rpm for 15 minutes. The residue was washed with *n*-hexane and again centrifuged. Low boiling substances were removed by vacuum and the epoxide was isolated in quantitative yields by bulb-to-bulb distillation.

Carvacryl glycidyl ether (CarGE)



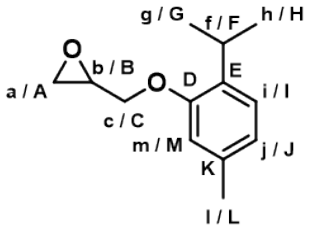
Yield: 84%

Purification by bulb-to-bulb distillation: $p = 9 \cdot 10^{-3}$ mbar, $T_{\text{bulb-to-bulb, CarGE}}$ = ~140 °C

^{1}H NMR (400 MHz, chloroform-d_1): δ (ppm) = 7.10 (dd, J = 7.6, 0.9 Hz, 1H, H_g), 6.80 (dd, J = 7.6, 1.7 Hz, 1H, H_h), 6.73 (s, 1H, H_m), 4.40 – 3.93 (m, 2H, H_c), 3.41 (m, 1H, H_b), 3.09 – 2.70 (m, 3H, H_a, H_j), 2.26 (s, 3H, H_f), 1.28 (d, J = 6.9 Hz, 6H, H_k, H_l).

^{13}C NMR (101 MHz, chloroform-d_1): δ (ppm) = 156.66 (C_E), 148.05 (C_I), 130.69 (C_H), 124.44 (C_D), 118.81 (C_G), 109.93 (C_M), 68.87 (C_C), 50.50 (C_B), 44.83 (C_A), 34.21 (C_J), 24.23 ($C_{K/L}$), 15.92 (C_F).

Thymyl glycidyl ether (ThyGE)



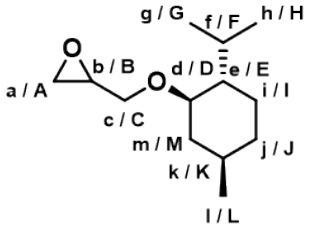
Yield: 89%

Purification by bulb-to-bulb distillation: $p = 7 \cdot 10^{-3}$ mbar, $T_{\text{bulb-to-bulb, ThyGE}} = \sim 140$ °C

^{1}H NMR (400 MHz, chloroform-d_1): δ (ppm) = 7.12 (d, J = 7.7 Hz, 1H, H_i), 6.82 – 6.72 (m, 1H, H_j), 6.65 (s, 1H, H_m), 4.34 – 3.82 (m, 2H, H_c), 3.39 (m, 1H, H_b), 3.32 (h, J = 6.9 Hz, 1H, H_f), 3.07 – 2.70 (m, 2H, H_a), 2.33 (s, 3H, H_l), 1.23 (d, J = 6.9 Hz, 6H, H_g, H_h).

^{13}C NMR (101 MHz, chloroform-d_1): δ (ppm) = 155.76 (C_D), 136.46 (C_K), 134.44 (C_E), 126.16 (C_I), 121.87 (C_J), 112.69 (C_M), 68.83 (C_C), 50.50 (C_B), 44.77 (C_A), 26.72 (C_F), 22.88 ($C_{G/H}$), 21.43 (C_L).

Menthyl glycidyl ether (MeGE)



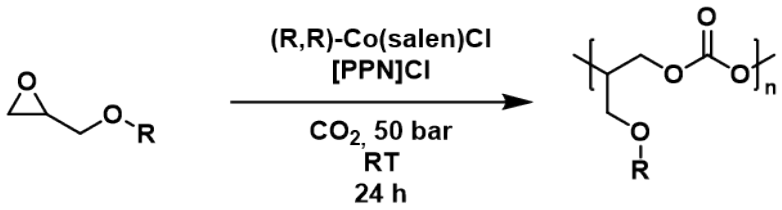
Yield: 74%

Purification by bulb-to-bulb distillation: $p = 8 \cdot 10^{-3}$ mbar, $T_{\text{bulb-to-bulb, MeGE}} = \sim 120$ °C

^{1}H NMR (400 MHz, chloroform-d_1): δ (ppm) = 3.78 (dd, J = 11.3, 3.4 Hz, 0.5H, H_c), 3.63 – 3.49 (m, 1H, H_c), 3.35 (dd, J = 11.3, 5.7 Hz, 0.5H, H_c), 3.20 – 3.01 (m, 2H, H_b, H_d), 2.83 – 2.50 (m, 2H, H_a), 2.21 (dpd, J = 12.0, 7.0, 2.7 Hz, 1H, H_f), 2.07 (m, 1H, H_m), 1.70 – 1.54 (m, 2H, $H_{i/j}$), 1.34 (ttd, J = 15.1, 6.6, 3.2 Hz, 1H, H_k), 1.28 – 1.18 (m, 1H, H_e), 1.03 – 0.83 (m, 8H, H_j, H_m, H_h, H_l), 0.83 – 0.74 (m, 4H, H_i, H_g).

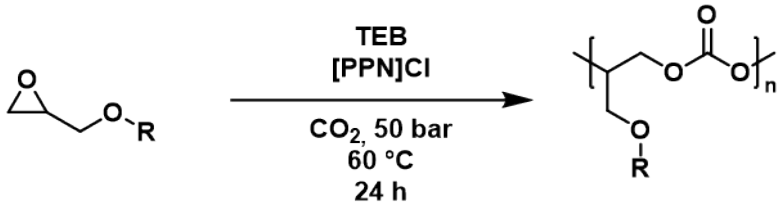
^{13}C NMR (101 MHz, chloroform-d_1): δ (ppm) = 80.21 (C_B), 79.21 (C_B), 69.80 (C_C), 69.27 (C_C), 51.42 (C_D), 51.25 (C_D), 48.35 (C_E), 44.90 (C_A), 44.60 (C_A), 40.66 (C_M), 40.30 (C_M), 34.62 (C_J), 31.64 (C_K), 25.77 (C_F), 23.49 (C_I), 22.44 (C_L), 21.06 (C_H), 16.39 (C_G).

General procedure for copolymerization of epoxide and CO_2 with cobalt based catalyst



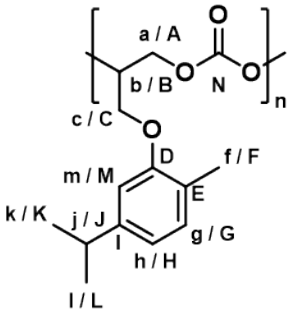
The general polymerization procedure for copolymerization of epoxides and CO_2 with Co(Salen)Cl is detailed in the following for one experiment. ThyGE (1.0 mL, 1.0 g, 4.85 mmol, 1 equiv.), Co(Salen)Cl (5.20 mg, 0.01 mmol, 0.002 equiv.) and [PPN]Cl (5.60 mg, 0.01 mmol, 0.002 equiv.) were placed in a steel autoclave, equipped with a stir bar, in an inert argon atmosphere. The reaction mixture was stirred at a carbon dioxide pressure of 50 bar at r.t. for 24 hours. The crude product was dissolved in dichloromethane and the catalyst was deactivated with 0.5 mL of a 5 vol% HCl solution in methanol. The product was precipitated using ice-cold methanol as a non-solvent. The precipitated product was collected *via* centrifugation at 4500 rpm at -10 °C for 20 minutes. The precipitation procedure was repeated twice. The obtained colorless solid was dried under reduced pressure ($8 \cdot 10^{-3}$ mbar) for 48 hours.

General procedure for copolymerization of epoxide and CO_2 with borane based catalyst



The general polymerization procedure for copolymerization of epoxides and CO_2 with triethylborane (TEB) is detailed in the following for one experiment. ThyGE (1.0 mL, 1.0 g, 4.85 mmol, 1 equiv.), TEB (0.12 mL 1M THF solution, 0.12 mmol, 0.024 equiv.) and [PPN]Cl (5.60 mg, 0.01 mmol, 0.002 equiv.) were placed in a steel autoclave, equipped with a stir bar, in an inert argon atmosphere. The reaction mixture was stirred at a carbon dioxide pressure of 50 bar at 50 °C for 24 hours. The crude product was dissolved in dichloromethane and the catalyst was deactivated with 0.5 mL of a 5 vol% HCl solution in methanol. The product was precipitated using ice-cold methanol as a non-solvent. The precipitated product was collected via centrifugation at 4500 rpm at -10 °C for 20 minutes. The precipitation procedure was repeated twice. The obtained colorless solid was dried under reduced pressure ($8 \cdot 10^{-3}$ mbar) for 48 hours.

Poly(carvacryl glycidyl ether carbonate) (PCarGEC)

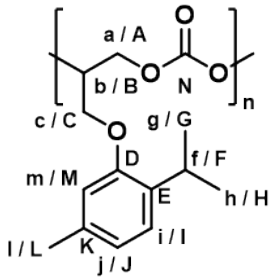


Yield: 54 – 86%

^{1}H NMR (300 MHz, chloroform-d_1): δ (ppm) = 7.02 (dd, J = 7.6, 4.0 Hz, 1H, H_g), 6.74 (dd, J = 8.0, 3.2 Hz, 1H, H_h), 6.65 (s, 1H, H_m), 5.42 – 5.12 (m, 1H, H_b), 4.70 – 4.33 (m, 2H, H_a), 4.24 – 4.08 (m, 2H, H_c), 2.83 (h, J = 6.9 Hz, 1H, H_j), 2.13 (s, 3H, H_f), 1.22 (d, J = 7.0, 2.0 Hz, 6H, H_k, H_l).

^{13}C NMR (101 MHz, chloroform-d_1): δ (ppm) = 156.07 (C_E), 154.64 (C_N), 148.10 (C_I), 130.73 (C_G), 124.26 (C_D), 119.01 (C_H), 109.48 (C_M), 73.93 (C_B), 66.06 ($C_{A/C}$), 65.52 ($C_{A/C}$), 34.19 (C_J), 24.22 ($C_{K/L}$), 15.82 (C_F).

Poly(thymyl glycidyl ether carbonate) (PThyGEC)

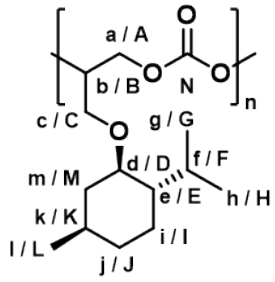


Yield: 69 – 91%

^{1}H NMR (300 MHz, chloroform-d_1): δ (ppm) = 7.02 (dd, J = 7.7, 3.1 Hz, 1H, H_i), 6.74 (dd, J = 8.1, 3.8 Hz, 1H, H_j), 6.65 – 6.46 (m, 1H, H_m), 5.25 (m, 1H, H_b), 4.44 (m, 2H, H_a), 4.25 – 4.00 (m, 2H, H_d), 3.20 (m, 1H, H_f), 2.27 (s, 3H, H_l), 1.15 (d, J = 6.6 Hz, 6H, H_g, H_h).

^{13}C NMR (101 MHz, chloroform-d_1): δ (ppm) = 155.10 (C_D), 154.28 (C_N), 136.53 (C_K), 134.16 (C_E), 126.16 (C_I), 122.09 (C_J), 112.23 (C_M), 74.00 (C_B), 66.07 ($C_{A/C}$), 65.66 ($C_{A/C}$), 26.71 (C_F), 22.76 ($C_{G/H}$), 21.38 (C_L).

Poly(menthyl glycidyl ether carbonate) (PMeGEC)

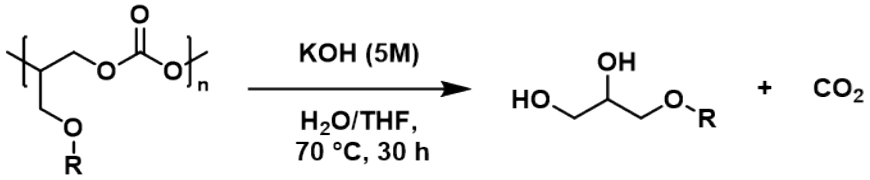


Yield: 49 – 88%

^{1}H NMR (300 MHz, chloroform-d_1): δ (ppm) = 4.96 (m, 1H, H_b), 4.50 – 4.12 (m, 2H, H_a), 3.96 – 3.72 (m, 1H, H_c), 3.47 (m, 1H, H_c), 3.04 (td, J = 10.7, 4.5 Hz, 1H, H_d), 2.13 (m, 1H, H_f), 2.08 – 1.95 (m, 1H, H_m), 1.61 (m, 2H, H_i, H_j), 1.39 – 1.26 (m, 1H, H_k), 1.21 (m, 1H, H_e), 1.04 – 0.64 (m, 12H, H_i, H_j, H_m, H_h, H_l, H_g).

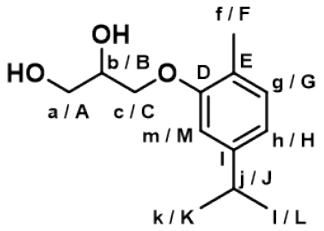
^{13}C NMR (101 MHz, chloroform-d_1): δ (ppm) = 154.35 (C_N), 81.35 (C_D), 74.87 (C_B), 66.30 (C_A), 65.90 (C_C), 50.47 (C_E), 41.61 (C_M), 34.61 (C_J), 31.56 (C_K), 25.75 (C_F), 23.41 (C_I), 22.43(C_L), 21.01 (C_H), 16.30 (C_G).

General procedure for polycarbonate degradation



The general degradation procedure is detailed in the following for one experiment. PThyGEC (200 mg) was dissolved in THF (10 mL). The solution was added to an aqueous KOH solution (45 mL) and stirred for 30 h at 70 °C. The reaction was stopped and the aqueous phase was extracted with dichloromethane (2 x 20 mL). The combined organic phases were washed with brine until neutrality, dried over $NaSO_4$, filtered and concentrated by using rotary evaporation. The resulting liquid or solid was colorless.

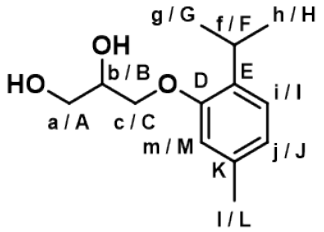
3-(Carvacryl)oxy)propane-1,2-diol (CarPD)



^{1}H NMR (300 MHz, chloroform-d_1): δ (ppm) = 7.07 (dd, J = 7.6, 0.9 Hz, 1H, H_g), 6.78 (dd, J = 7.6, 1.7 Hz, 1H, H_h), 6.71 (s, 1H, H_m), 4.14 (qd, J = 5.5, 3.7 Hz, 1H, H_b), 4.06 (d, J = 5.3 Hz, 2H, H_c), 3.93 – 3.70 (m, 2H, H_a), 2.87 (p, J = 6.9 Hz, 1H, H_j), 2.71 (m, 2H, H_n), 2.20 (s, 3H, H_f), 1.24 (d, J = 6.9 Hz, 6H, H_k, H_l).

^{13}C NMR (101 MHz, chloroform-d_1): δ (ppm) = 156.45 (C_E), 148.27 (C_I), 130.72 (C_G), 124.01 (C_D), 118.91 (C_H), 109.74 (C_M), 70.72 (C_B), 69.29 (C_C), 64.01 (C_A), 34.22 (C_J), 24.22 ($C_{K/L}$), 15.96 (C_F).

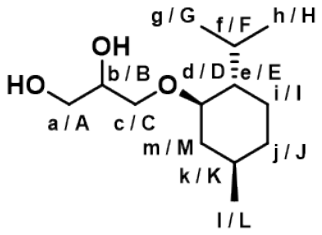
3-(Thymyl)oxy)propane-1,2-diol (ThyPD)



^{1}H NMR (300 MHz, chloroform-d_1): δ (ppm) = 7.11 (d, J = 7.7 Hz, 1H, H_i), 6.85 – 6.71 (m, 1H, H_j), 6.68 (s, 1H, H_m), 4.15 (qd, J = 5.4, 3.6 Hz, 1H, H_b), 4.04 (d, J = 5.3 Hz, 2H, H_c), 3.95 – 3.70 (m, 2H, H_a), 3.24 (h, J = 6.9 Hz, 1H, H_f), 2.66 (m, 2H, H_n), 2.32 (s, 3H, H_l), 1.21 (d, J = 6.9 Hz, 6H, H_g, H_h)

^{13}C NMR (101 MHz, chloroform-d_1): δ (ppm) = 155.42 (C_D), 136.64 (C_K), 134.04 (C_E), 126.10 (C_I), 121.96 (C_J), 112.59 (C_M), 70.79 (C_B), 69.28 (C_C), 64.03 (C_A), 26.68 (C_F), 22.93 ($C_{G/H}$), 21.40 (C_L).

3-(Menthyl)oxy)propane-1,2-diol (MePD)



^{1}H NMR (300 MHz, chloroform-d_1): δ (ppm) = 3.83 (ddd, J = 6.5, 3.2, 1.4 Hz, 1H, H_b), 3.74 – 3.57 (m, 3H, H_a, H_c), 3.46 – 3.31 (m, 1H, H_c), 3.07 (tdd, J = 10.6, 4.2, 3.0 Hz, 1H, H_d), 2.63 (s, 2H, H_n), 2.22 – 2.04 (m, 2H, H_f, H_m), 1.71 – 1.54 (m, 2H, H_i, H_j), 1.40 – 1.26 (m, 1H, H_k), 1.26 – 1.15 (m, 1H, H_e), 1.05 – 0.72 (m, 12H, H_i, H_j, H_m, H_h, H_l, H_g).

^{13}C NMR (101 MHz, chloroform-d_1): δ (ppm) = 80.10 (C_D), 70.95 (C_C), 70.23 (C_B), 64.46 (C_A), 48.32 (C_E), 40.35 (C_M), 34.58 (C_J), 31.60 (C_K), 25.93 (C_F), 23.38 (C_I), 22.41 (C_L), 21.07 (C_H), 16.29 (C_G).

3. NMR spectra of terpene based epoxides and polycarbonates

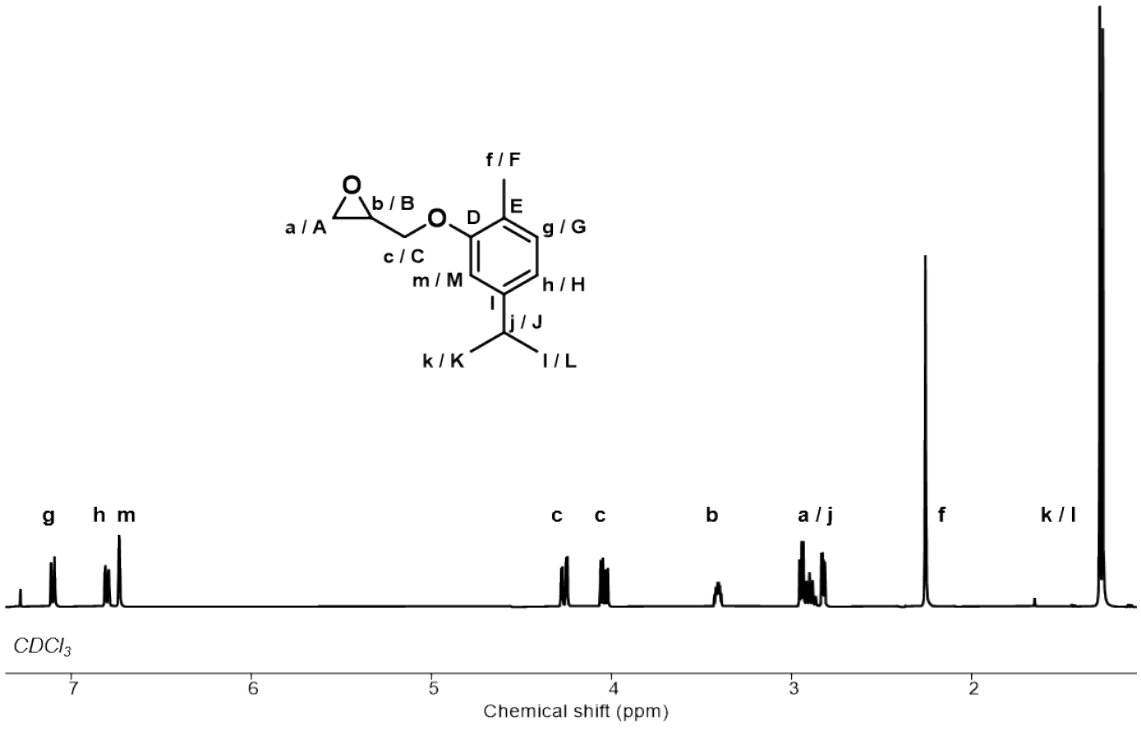


Figure S1: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of CarGE.

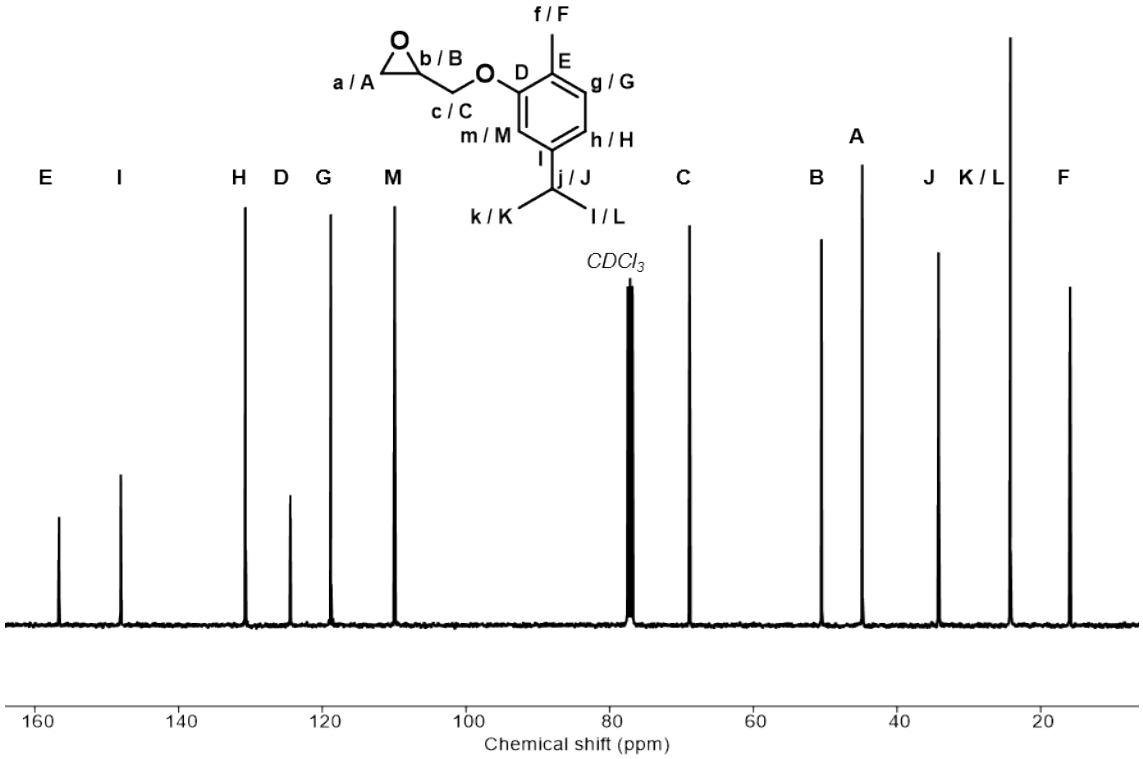


Figure S2: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of CarGE.

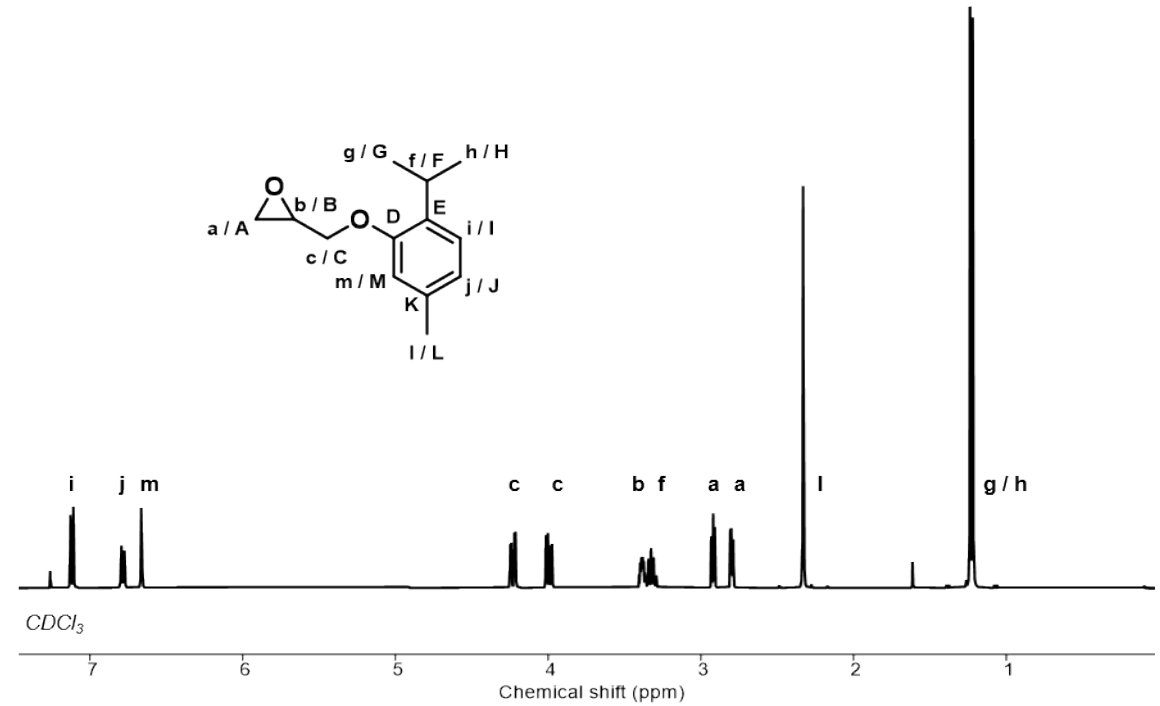


Figure S3: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of ThyGE.

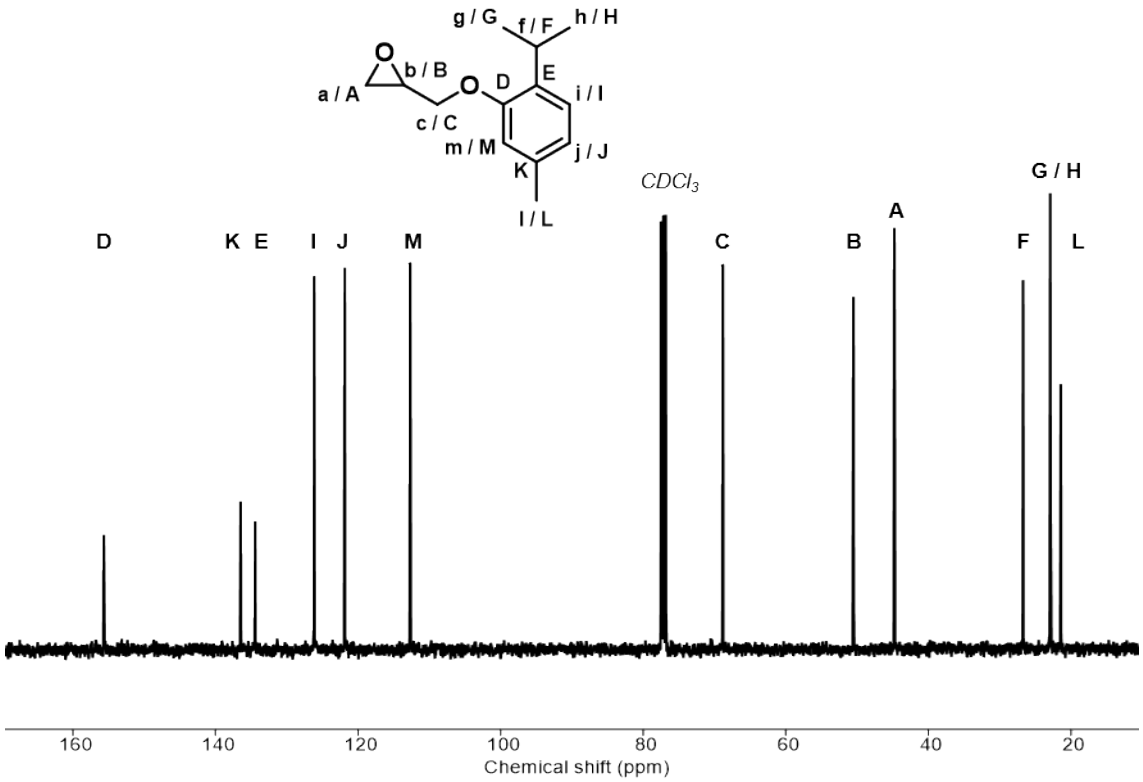


Figure S4: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of ThyGE.

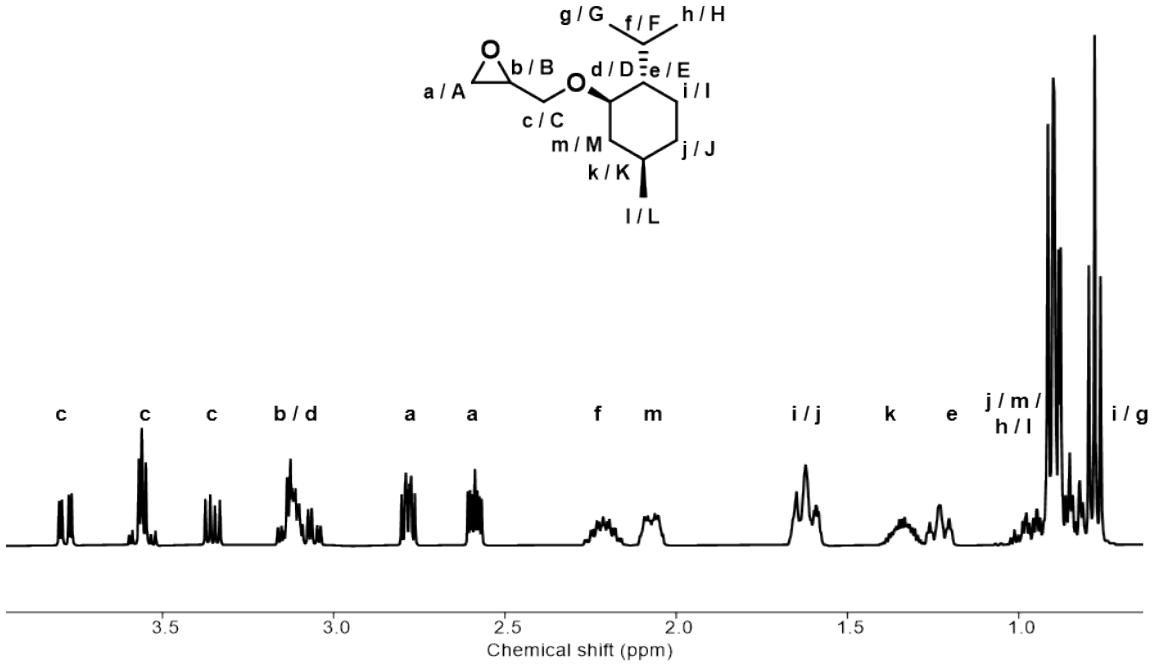


Figure S5: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of MeGE.

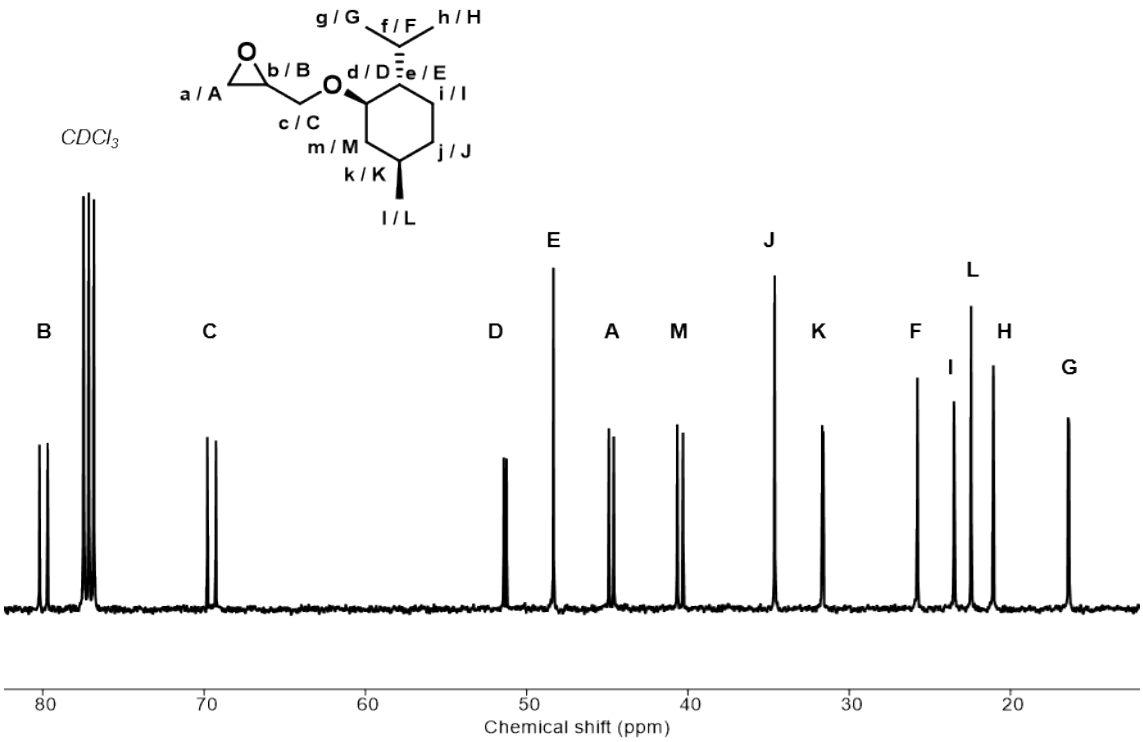


Figure S6: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of MeGE.

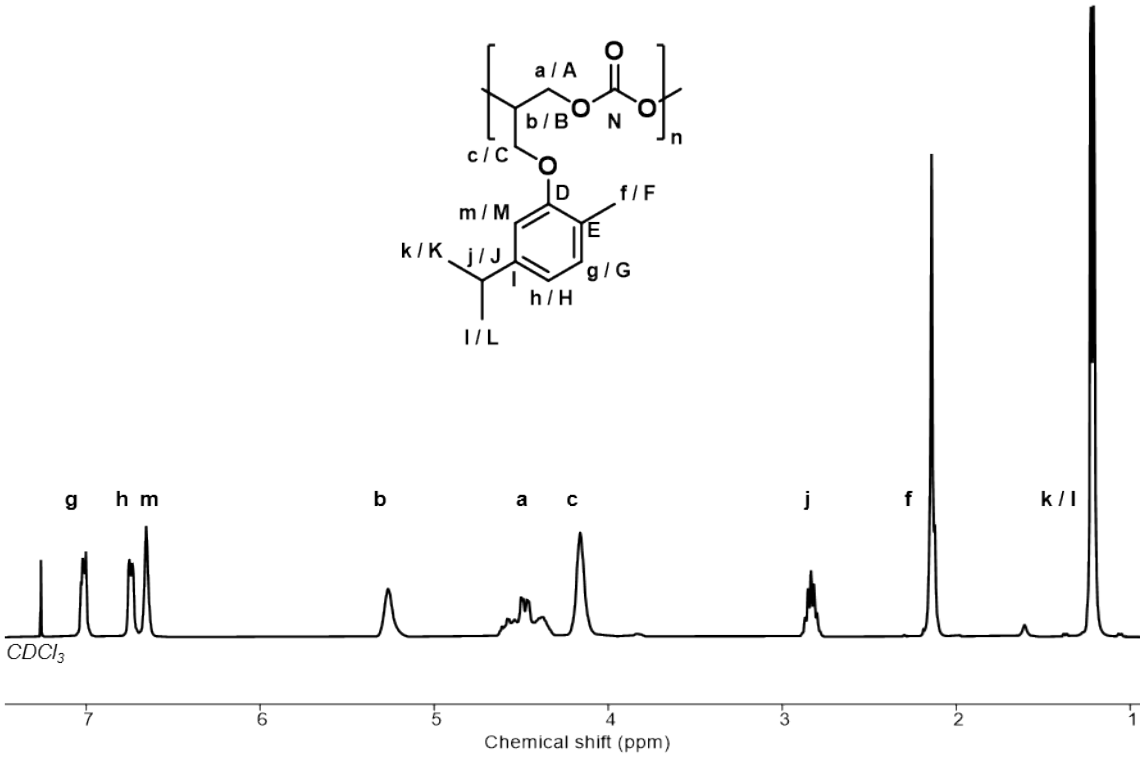


Figure S7: ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of PCarGEC.

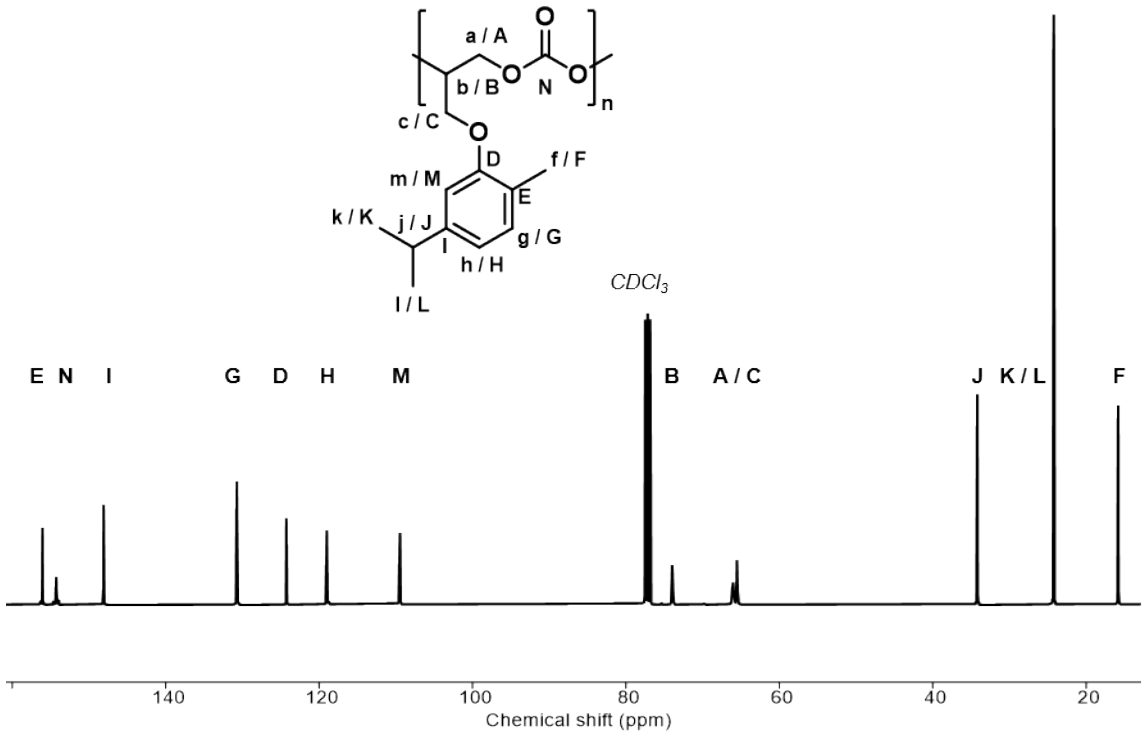


Figure S8: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of PCarGEC.

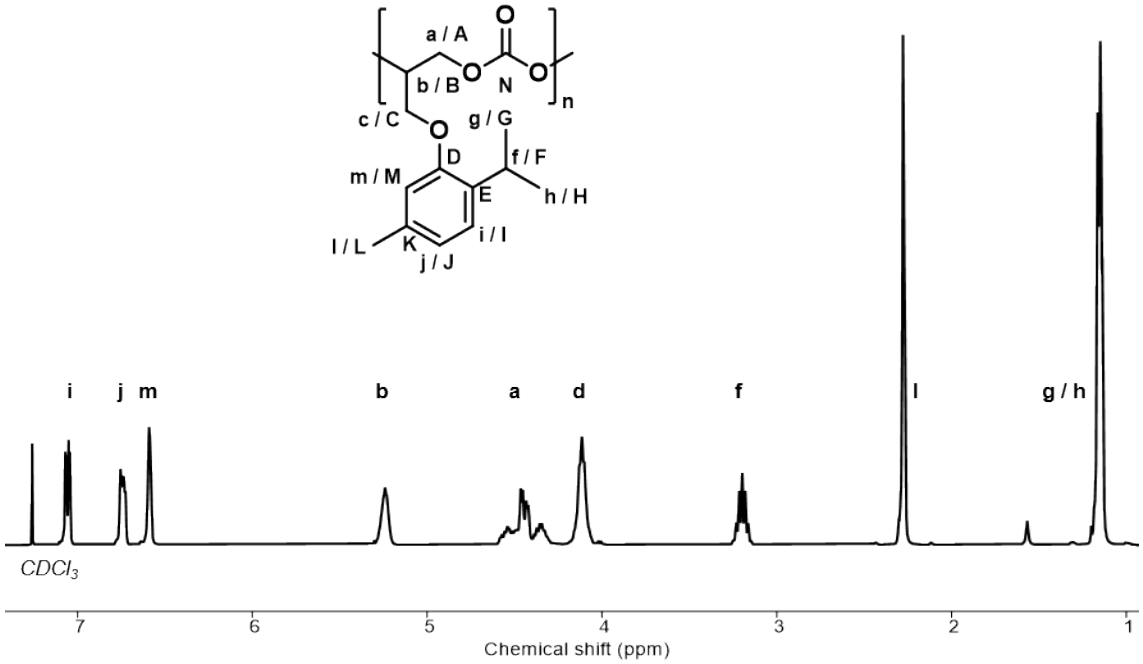


Figure S9: ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of PThyGEC.

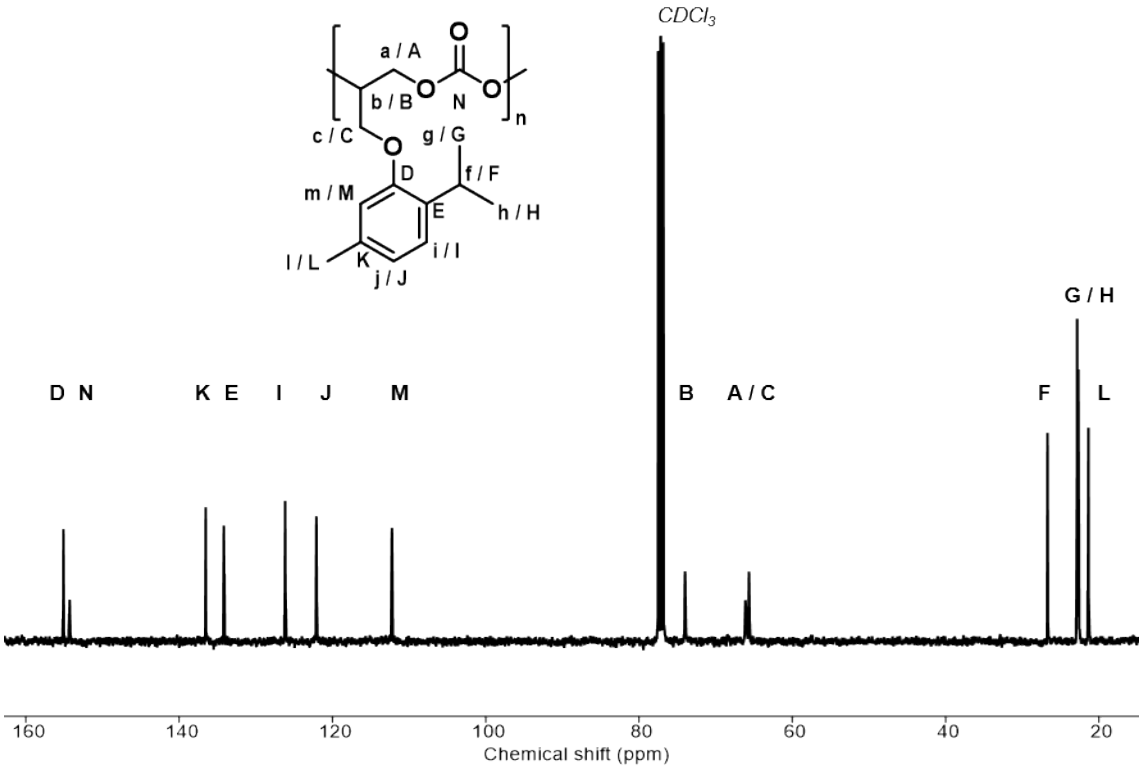


Figure S10: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of PThyGEC.

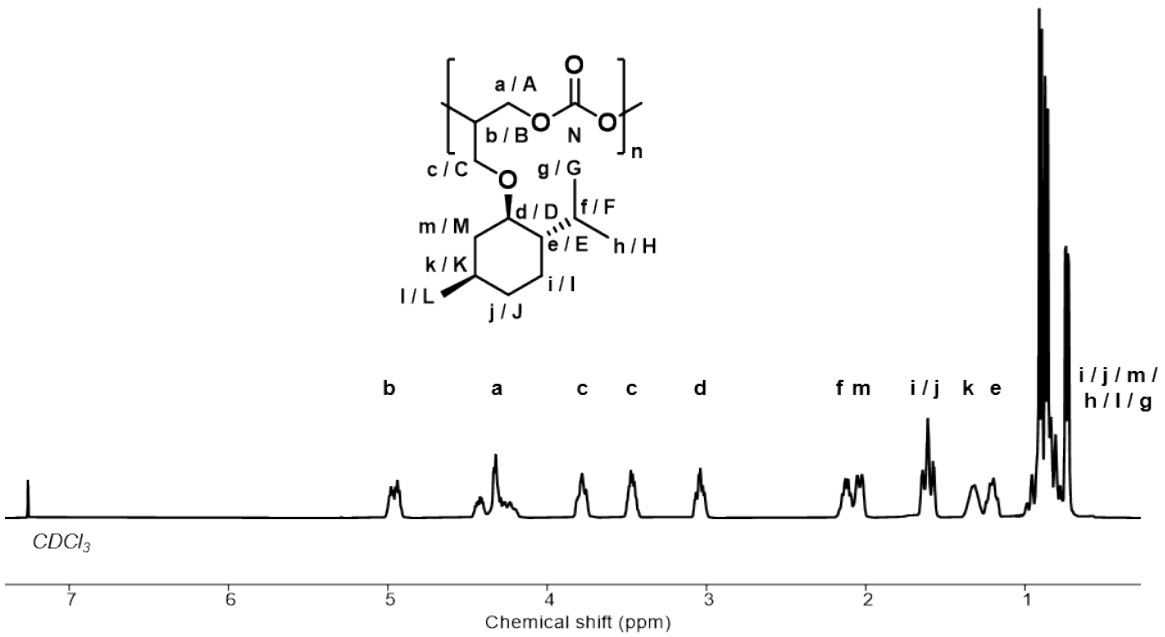


Figure S11: ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of PMeGEC.

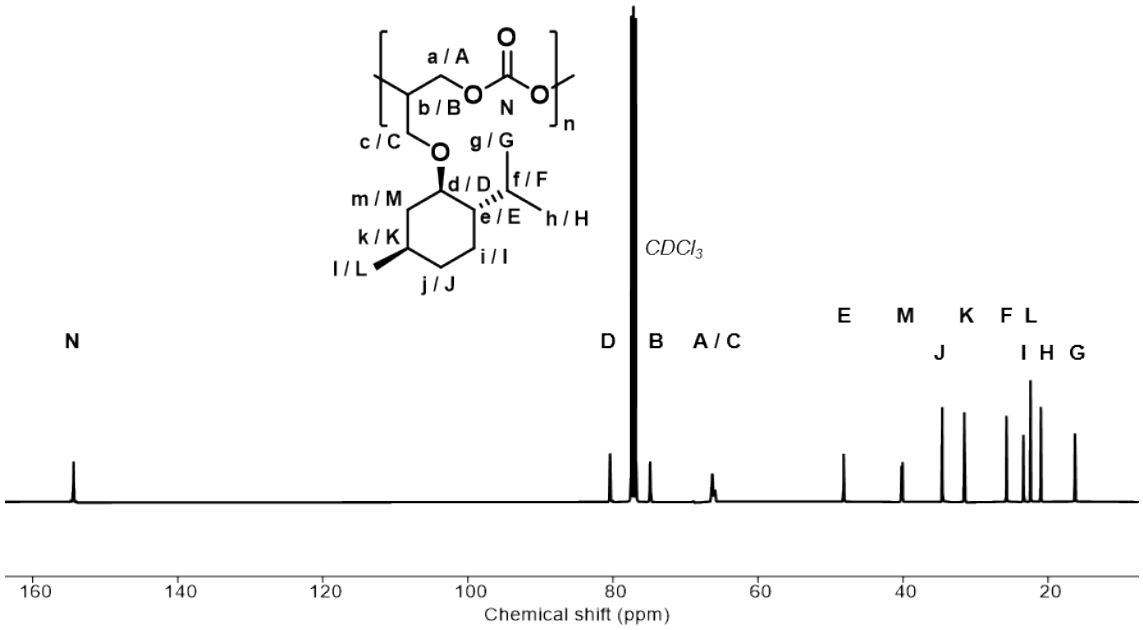


Figure S12: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of PMeGEC.

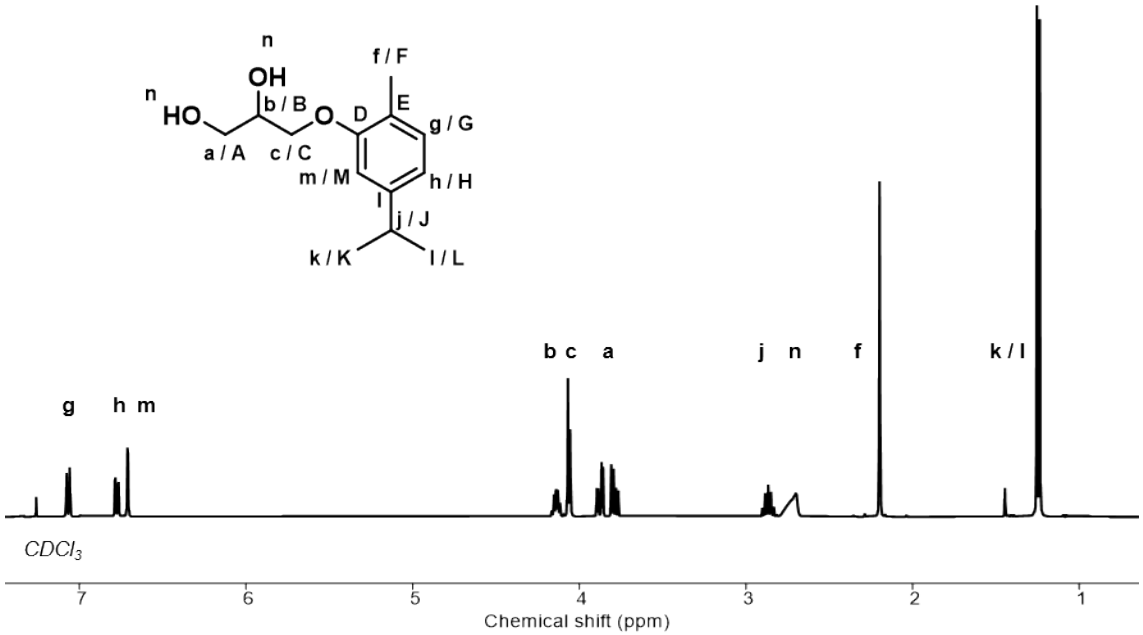


Figure S13: ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of CarPD.

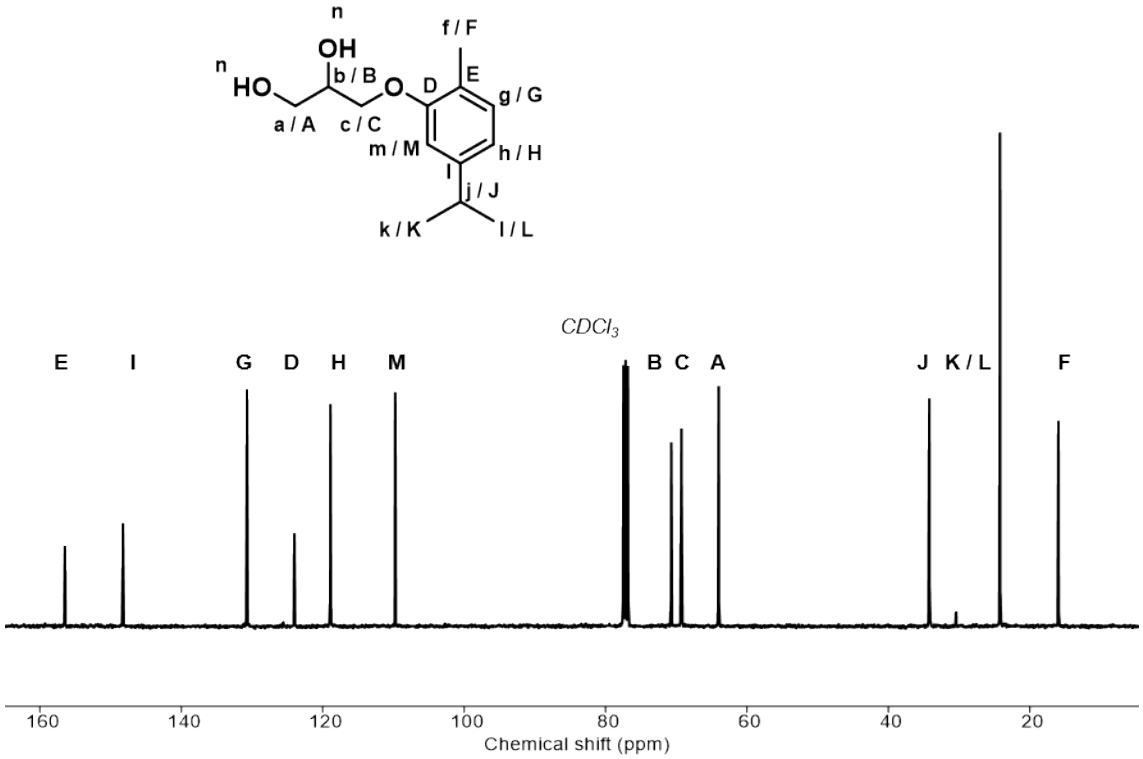


Figure S14: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of CarPD.

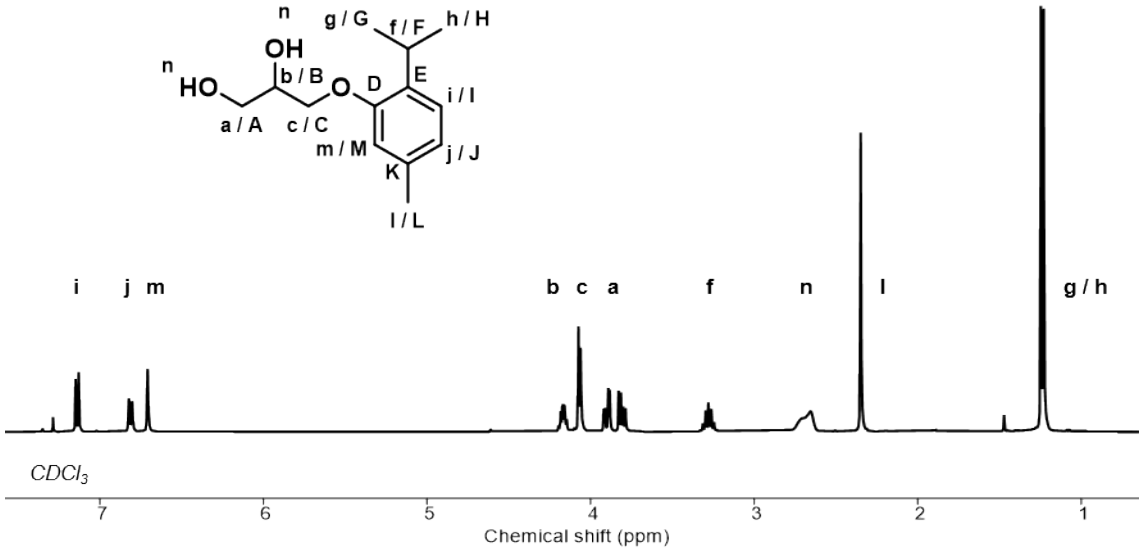


Figure S15: ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of ThyPD.

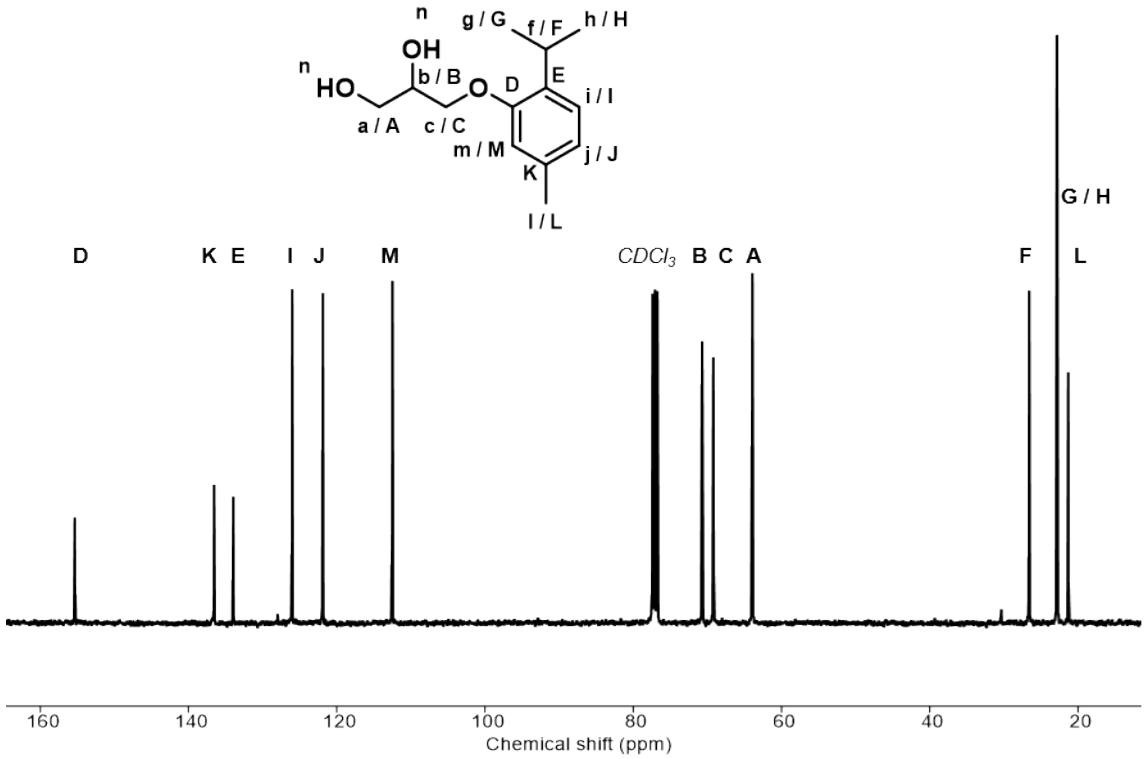


Figure S16: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of ThyPD.

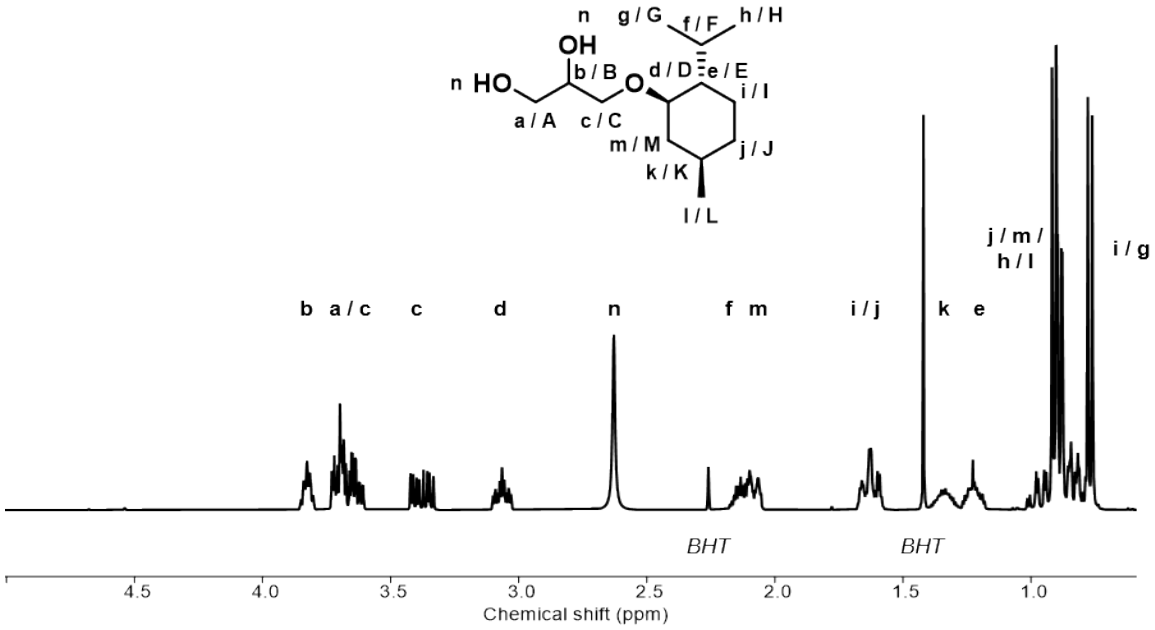


Figure S17: ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of MePD.

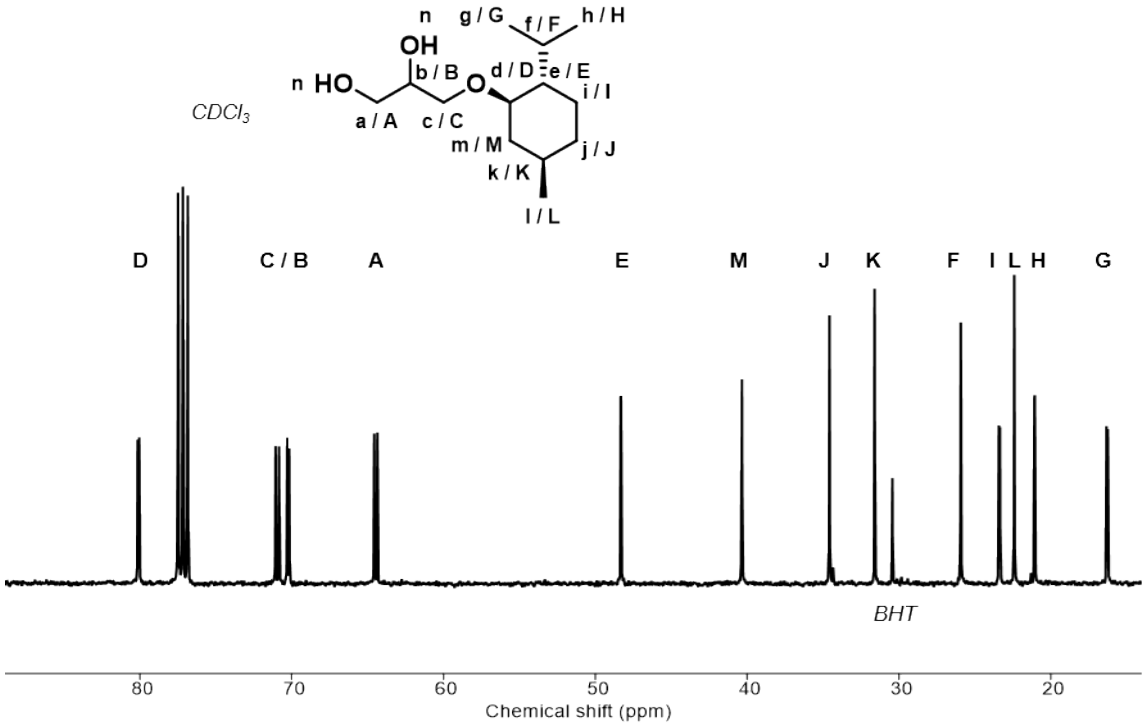


Figure S18: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of MePD.

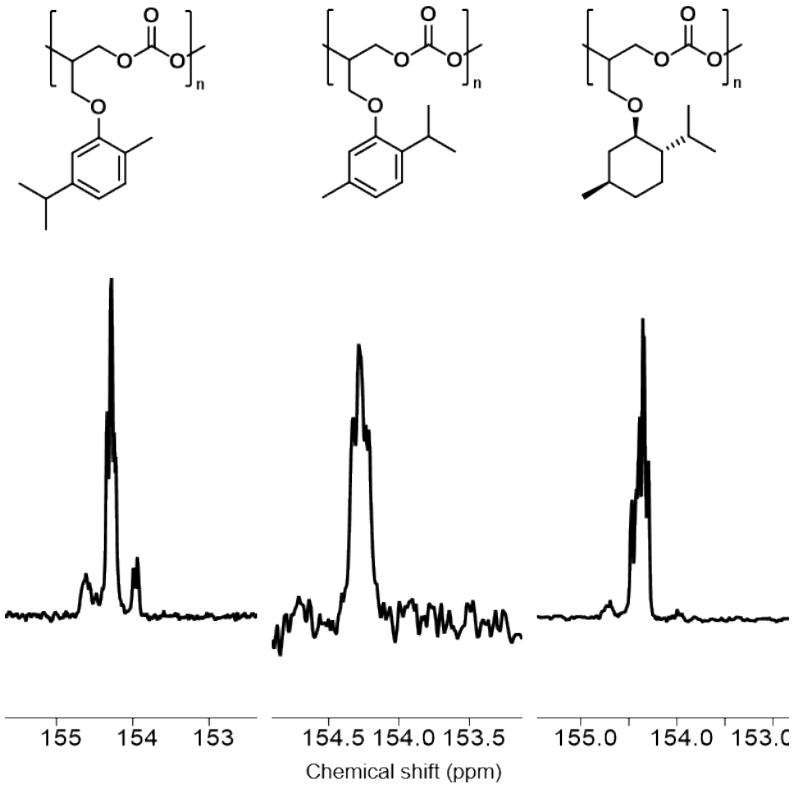


Figure S19: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of PCarGEC, PThyGEC and PMeGEC for the carbonate carbon atom for the evaluation of head-to-tail polymerization efficiency.

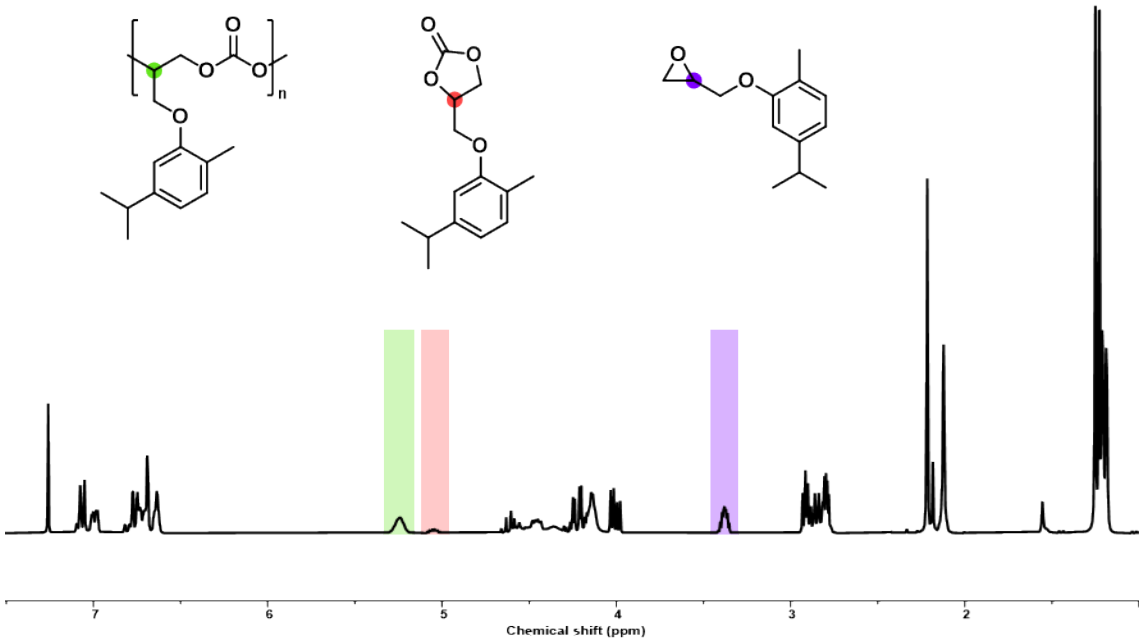


Figure S20: Exemplary determination of conversion and polymer selectivity via ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of the crude reaction mixture.

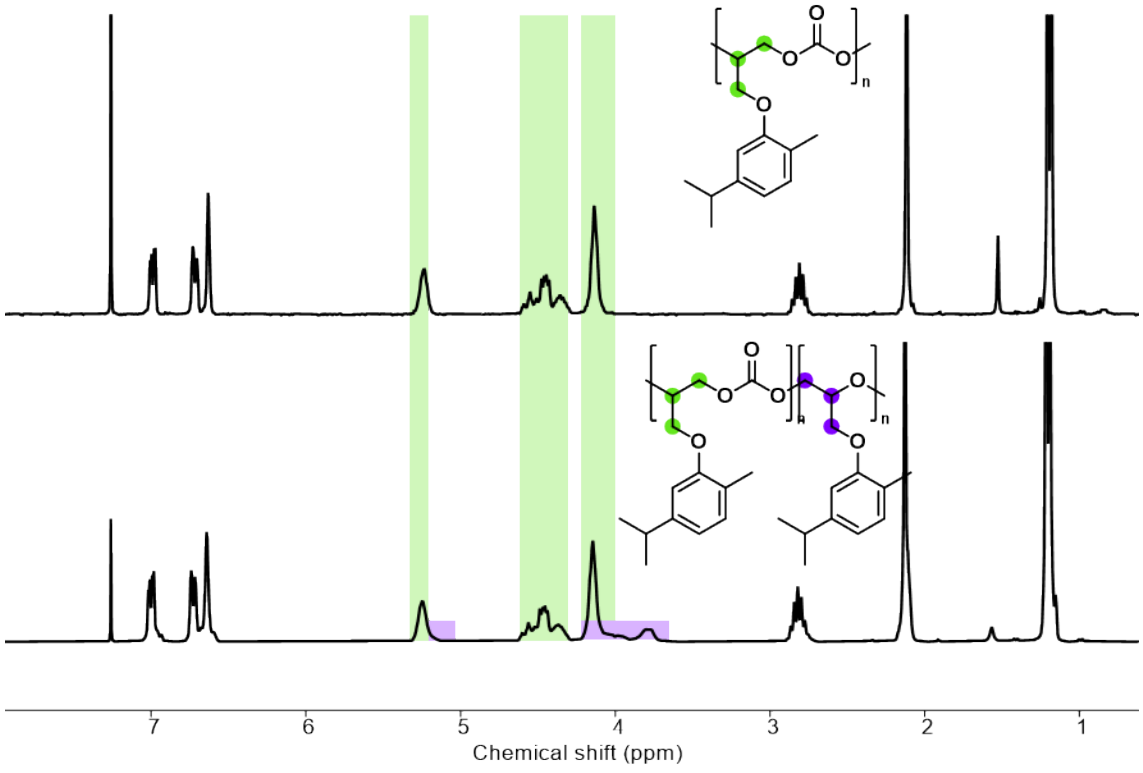


Figure S21: Exemplary determination of polyether content in final polycarbonate via ^{1}H NMR spectrum (400 MHz, $CDCl_3$).

4. MALDI-ToF of terpene-based polycarbonates

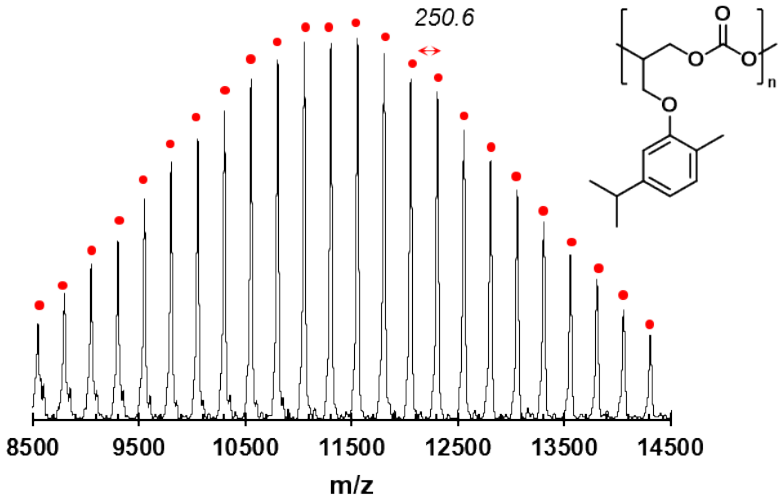


Figure S22: MALDI-ToF spectrum of PCarGEC. $M_{n,\ calc.}$ (repeat unit) = 250.6 g mol^{-1}, $M_{n,\ theo.}$ (repeat unit) = 250.3 g mol^{-1}.

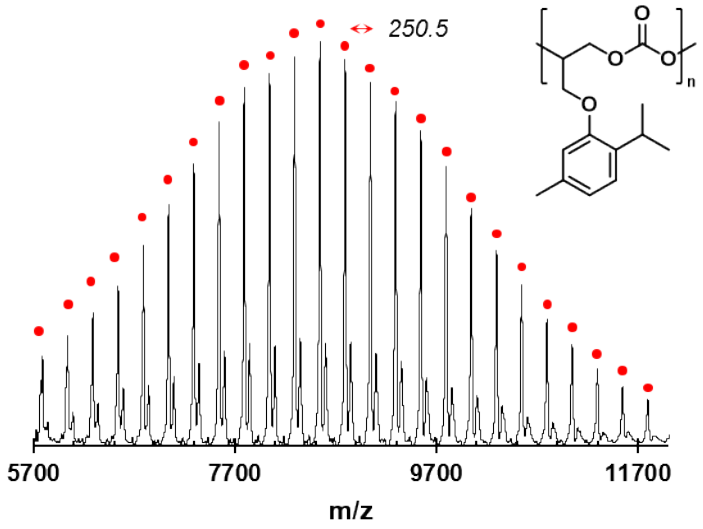


Figure S23: MALDI-ToF spectrum of PThyGEC. $M_{n,\ calc.}$ (repeat unit) = 250.5 g mol^{-1}, $M_{n,\ theo.}$ (repeat unit) = 250.3 g mol^{-1}.

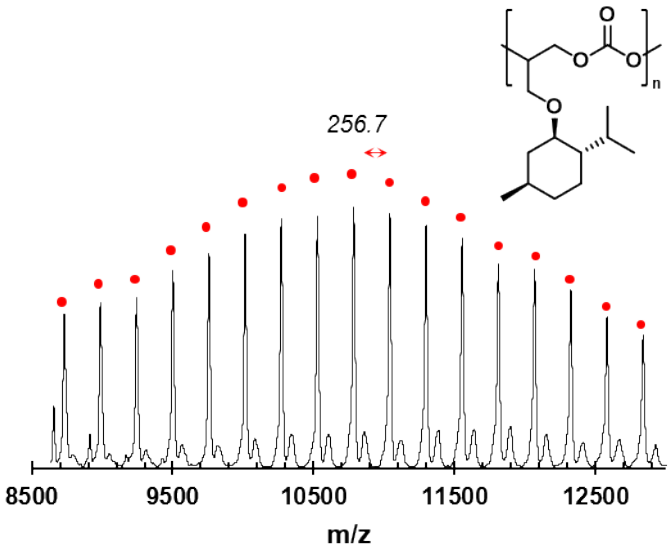


Figure S24: MALDI-ToF spectrum of PMeGEC. $M_{n,\ calc.}$ (repeat unit) = 256.7 g mol^{-1}, $M_{n,\ theo.}$ (repeat unit) = 256.3 g mol^{-1}.

5. Additional polymerization experiments and SEC results

Table S1: Polymerization of ThyGE with different catalysts and ratios.

Entry	Monomer	Catalyst	$[m]_0:[i]_0:[cat]_0$[a]	Conv.[b] (%)	Select.[c] (%)	PC[d] (%)	M_n[e] ($Đ$) (kg mol^{-1})	T_g (°C)
1	ThyGE[f]	Co(Salen)Cl	1000:7:2	99	96	>99	21.5 (1.12)	56
2	ThyGE[g]	Co(Salen)Cl	1000:2:2	100	91	>99	34.4 (1.16)	56
3	ThyGE	TEB	1000:3:36	100	63	82	13.2 (1.17)	48

Reaction conditions: Co(Salen)Cl or TEB as a catalyst and [PPN]Cl as an initiator, monomer (1 mL), 50 bar CO_2, r.t. (reaction with TEB at 60 °C), 24 hours. [a]$[m]_0$ = monomer equivalents, $[i]_0$ = initiator equivalents, $[cat]_0$ = catalyst equivalents. [b]Determined via ^{1}H NMR spectrum from the non-purified reaction mixture after opening the reactor; conv. = epoxide conversion determined via comparison of the relative integrals in the ^{1}H NMR spectrum of PC, CC, PE, and monomer. [c]Determined via ^{1}H NMR spectrum from the non-purified reaction mixture after opening the reactor; select. = polymer selectivity determined via comparison of the relative integrals in the ^{1}H NMR spectrum for PC against CC. [d]Determined via comparison of the relative integrals in the ^{1}H NMR spectrum for PC against PE. [e]Determined via THF-SEC with polystyrene standard and RI detector. [f]BDM was added as CTA. The concentration sum of [PPN]Cl and BDM is indicated as$[i]_0$. [PPN]Cl and Co(Salen)Cl have the same ratio. [g]0.3 mL toluene was added to the reaction mixture.

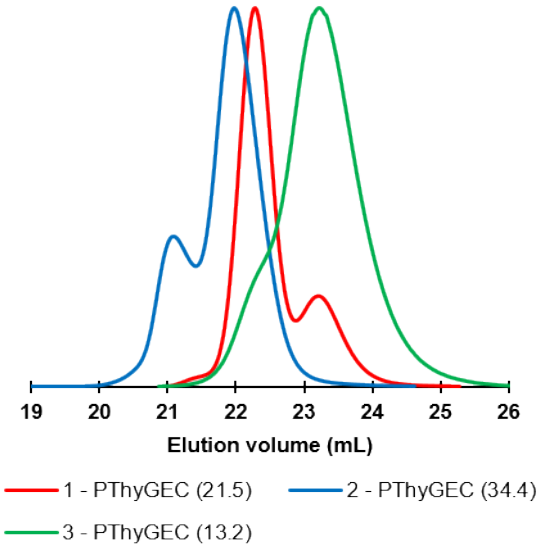


Figure S25: SEC traces (THF, PS, RI detector) of ThyGE based polycarbonates in Table S1. Entry and M_n of the respective polymer is shown in the legend.

Table S2: Polymerization of MeGE with different catalysts and ratios.

Entry	Monomer	Catalyst	$[m]_0:[i]_0:[cat]_0$[a]	Conv.[b] (%)	Select.[c] (%)	PC[d] (%)	M_n[e] ($Đ$) (kg mol^{-1})	T_g (°C)
1	MeGE	Co(Salen)Cl[f]	1000:7:2	99	97	99	16.7 (1.15)	40
2	MeGE	Co(Salen)Cl[g]	1000:2:2	100	98	99	25.2 (1.11)	41
3	MeGE	TEB	1000:1:12	66	0	0	10.0 (1.10)	0
4	MeGE	TEB	1000:3:36	100	89	30	15.1 (1.21)	8
5	MeGE	TEB	1000:2:24	100	68	57	13.6 (1.19)	19

Reaction conditions: Co(Salen)Cl or TEB as a catalyst and [PPN]Cl as an initiator, monomer (1 mL), 50 bar CO_2, r.t. (reaction with TEB at 60 °C), 24 hours. [a]$[m]_0$ = monomer equivalents, $[i]_0$ = initiator equivalents, $[cat]_0$ = catalyst equivalents. [b]Determined via ^{1}H NMR from the non-purified reaction mixture after opening the reactor; conv. = epoxide conversion determined via comparison of the relative integrals in the ^{1}H NMR spectrum of PC, CC, PE, and monomer. [c]Determined via ^{1}H NMR from the non-purified reaction mixture after opening the reactor; select. = polymer selectivity determined via comparison of the relative integrals in the ^{1}H NMR spectrum for PC against CC. [d]Determined via comparison of the relative integrals in the ^{1}H NMR spectrum for PC against PE. [e]Determined via THF-SEC with polystyrene standard and RI detector. [f]BDM was added as CTA. The concentration sum of [PPN]Cl and BDM is indicated as$[i]_0$. [PPN]Cl and Co(Salen)Cl have the same ratio. [g]0.3 mL toluene was added to the reaction mixture.

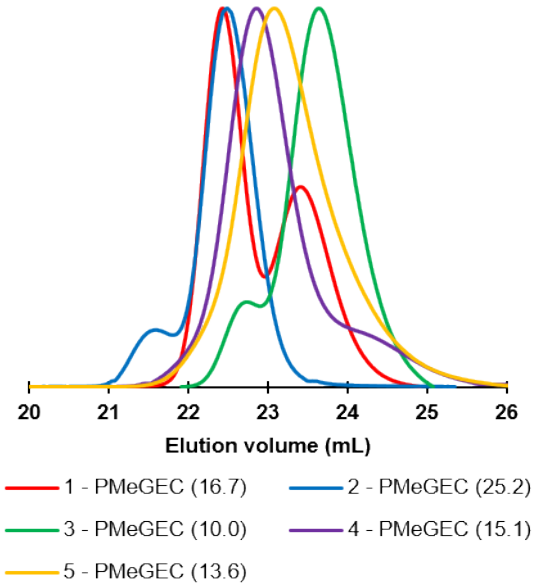


Figure S26: SEC traces (THF, PS, RI detector)) of MeGE based polycarbonates in Table S2. Entry and M_n of the respective polymer is shown in the legend.

Table S3: Polymerization of CarGE, ThyGE, MeGE for 6 hours.

Entry	Monomer	Reaction time (h)	$[m]_0:[i]_0:[cat]_0$[a]	Conv.[b] (%)	Select.[c] (%)	PC[d] (%)	M_n[e] ($Đ$) (kg mol^{-1})	T_g (°C)
1	CarGE	6	1000:2:2	70	94	>99	31.2 (1.12)	50
2	ThyGE	6	1000:2:2	81	95	>99	43.1 (1.11)	56
3	MeGE	6	1000:2:2	89	98	>99	23.0 (1.10)	40

Reaction conditions: Co(Salen)Cl as a catalyst and [PPN]Cl as an initiator, monomer (1 mL), 50 bar CO_2, r.t. [a]$[m]_0$ = monomer equivalents, $[i]_0$ = initiator equivalents, $[cat]_0$ = catalyst equivalents. [b]Determined via ^{1}H NMR from the non-purified reaction mixture after opening the reactor; conv. = epoxide conversion determined via comparison of the relative integrals in the ^{1}H NMR spectrum of PC, CC, PE, and monomer. [c]Determined via ^{1}H NMR from the non-purified reaction mixture after opening the reactor; select. = polymer selectivity determined via comparison of the relative integrals in the ^{1}H NMR spectrum for PC against CC. [d]Determined via comparison of the relative integrals in the ^{1}H NMR spectrum for PC against PE. [e]Determined via THF-SEC with polystyrene standard and RI detector.

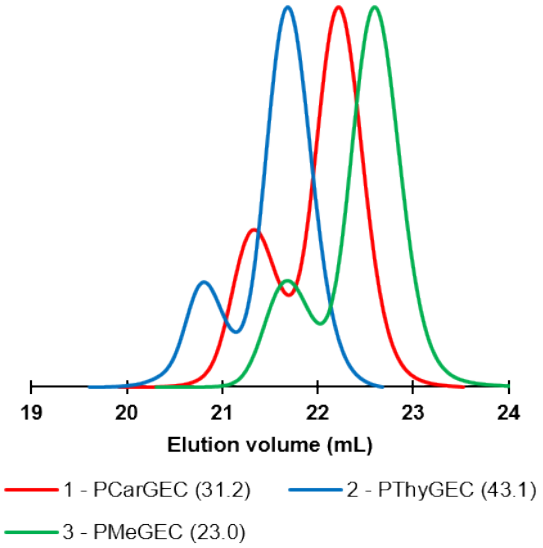


Figure S27: SEC traces (THF, PS, RI detector) of MeGE, ThyGE and CarGE based polycarbonates with 6 hours reaction time in Table S3. Entry and M_n of the respective polymer is shown in the legend.

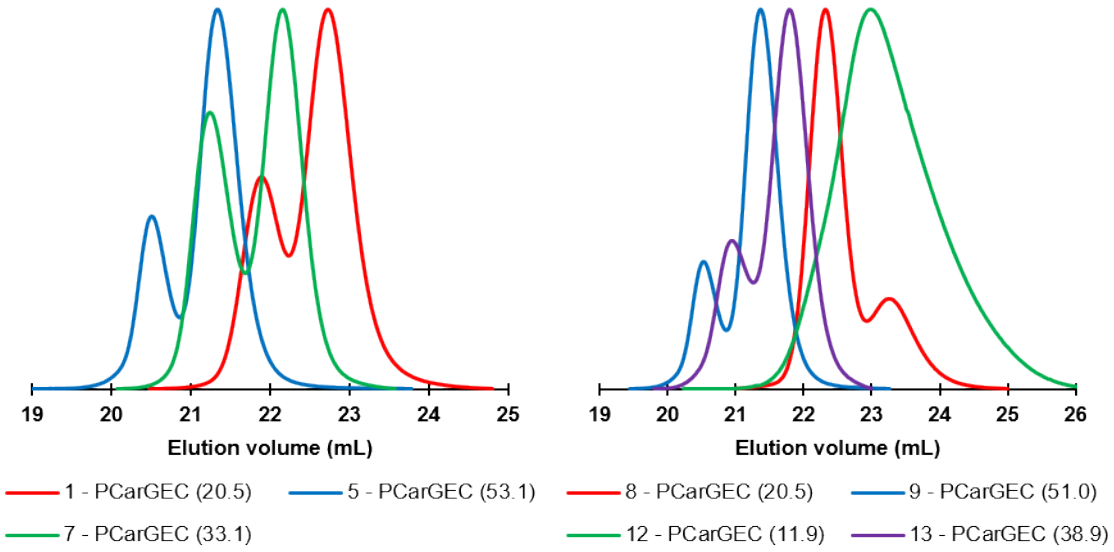


Figure S28: SEC traces (THF, PS, RI detector) of CarGE based polycarbonates in Table 1. Entry and M_n of the respective polymer is shown in the legend.

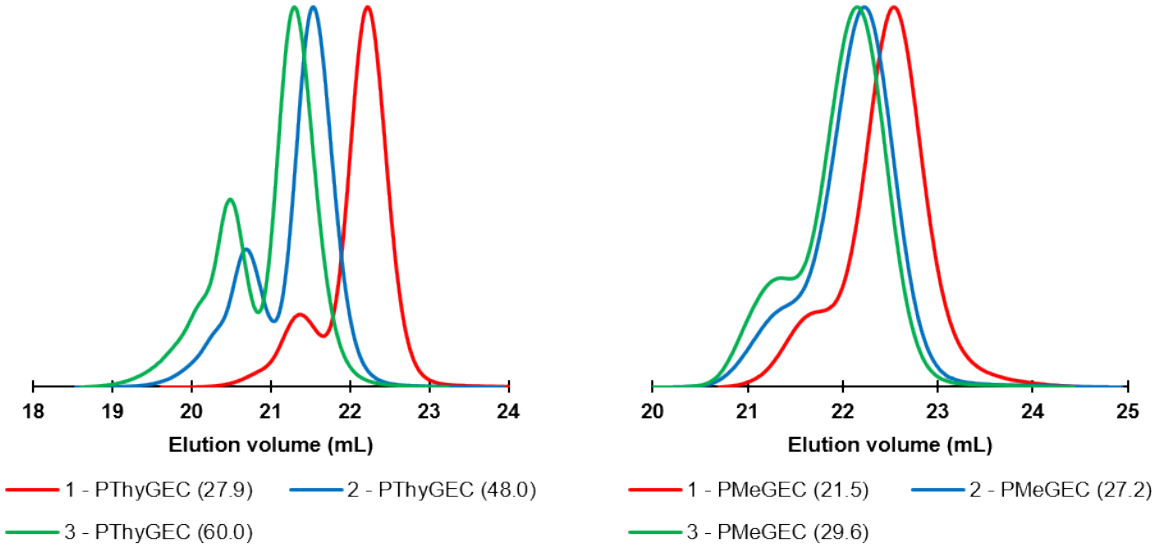


Figure S29: SEC traces (THF, PS, RI detector) of CarGE based polycarbonates in Table 2. Entry and M_n of the respective polymer is shown in the legend.

6. M_n determination by universal calibration with intrinsic viscosity measurements

Table S4: Comparison of THF (PS) SEC with universal calibration/intrinsic viscosity SEC of different PCs.

Entry	Polymer	M_n[a] (Đ) (kg mol^{-1})	M_n[b] (Đ) (kg mol^{-1})	Deviation (%)
1	PCarGEC	20.5 (1.13)	24.9 (1.15)	18
2	PCarGEC	43.8 (1.10)	49.8 (1.14)	12
3	PCarGEC	59.5 (1.15)	68.4 (1.16)	13
4	PThyGEC	27.9 (1.10)	32.4 (1.16)	14
5	PThyGEC	48.0 (1.18)	55.6 (1.27)	14
6	PThyGEC	60.0 (1.24)	69.3 (1.35)	13
7	PMeGEC	16.7 (1.14)	20.2 (1.17)	17
8	PMeGEC	23.0 (1.10)	28.1 (1.13)	18
9	PMeGEC	29.6 (1.12)	35.2 (1.14)	16

[a]Determined via SEC (THF, PS) and RI detector. [b]Determined via SEC with universal calibration in combination with intrinsic viscosity measurement.

7. Thermal characterization of PCs dependent on polyether content

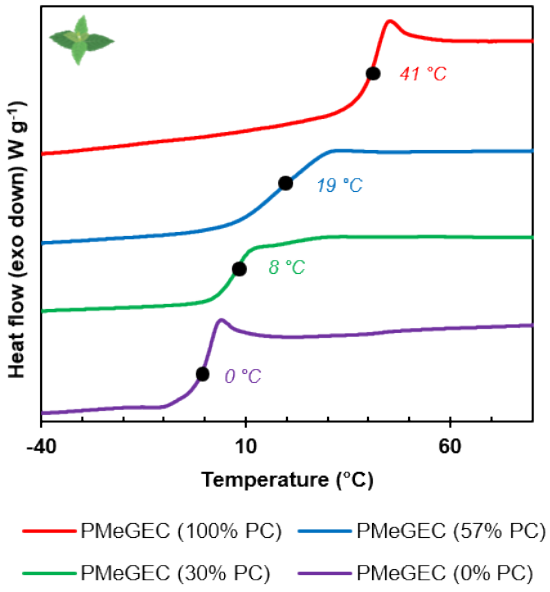


Figure S30: Visualized DSC measurements of PMeGEC with different percentages of polycarbonate linkages shown in Table S2, measured with a heat rate of 20 K min^{-1}.

8. Degradation of polycarbonates

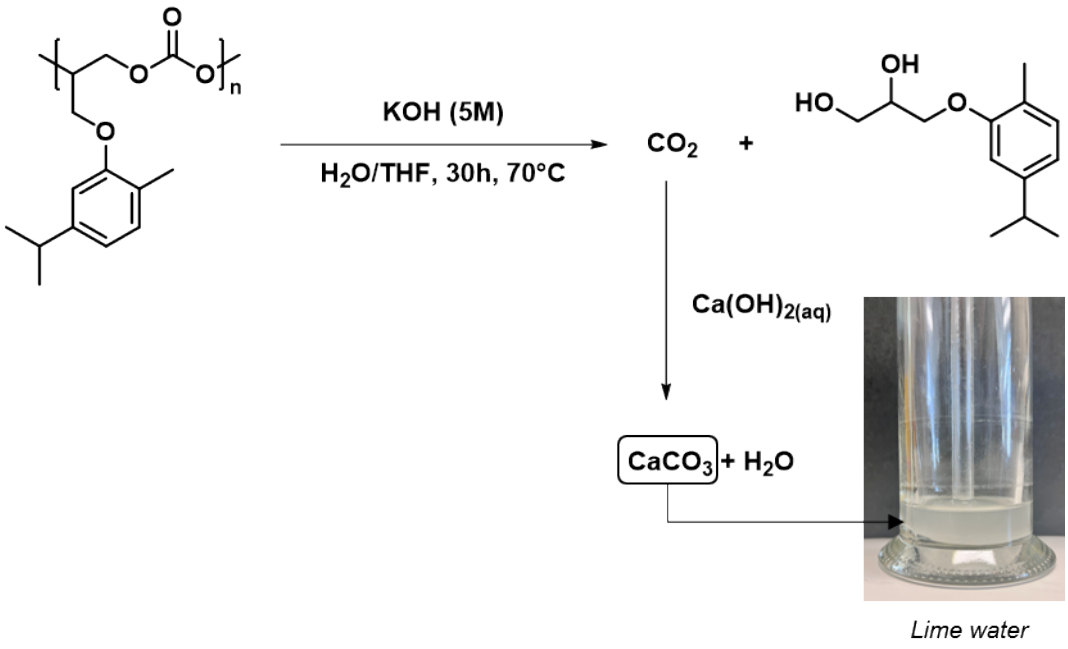


Figure S31: Degradation of PCarGEC under basic conditions to diol with CO_2 detection reaction via lime water.

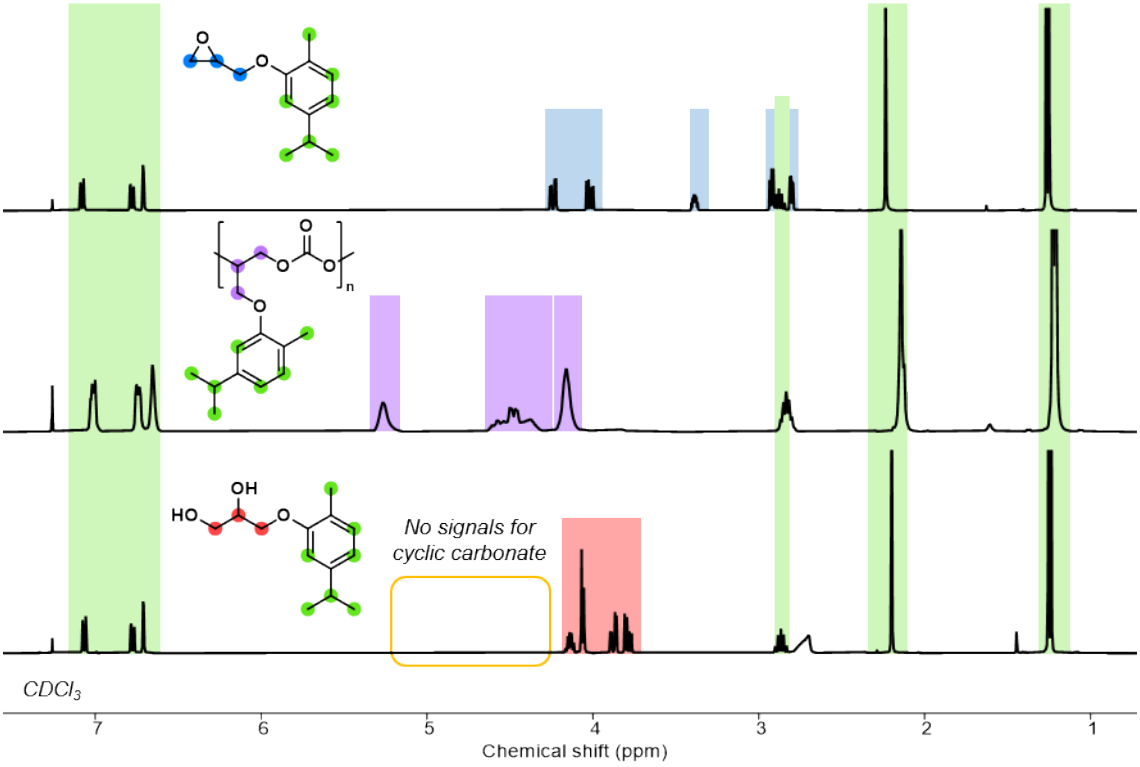


Figure S32: ^1H NMR comparison of CarGE, PCarGEC and CarPD in $CDCl_3$.

9. Tensile testing

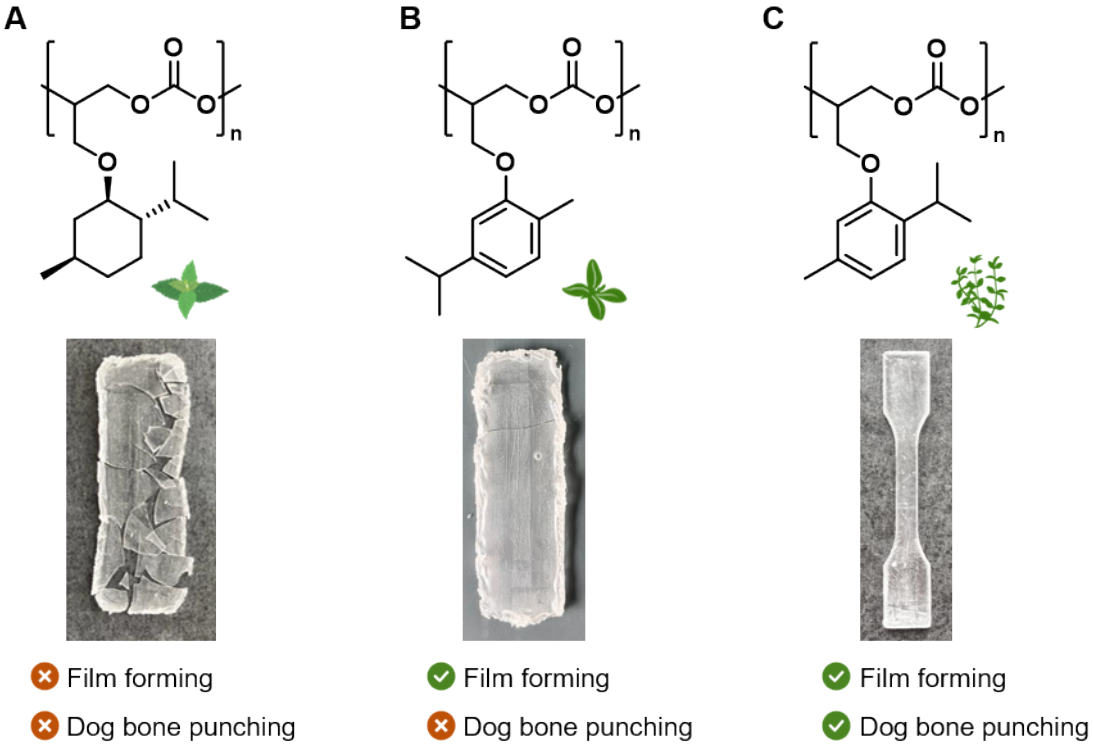


Figure S33: Processability of PMeGEC, PCarGEC, PThyGEC.

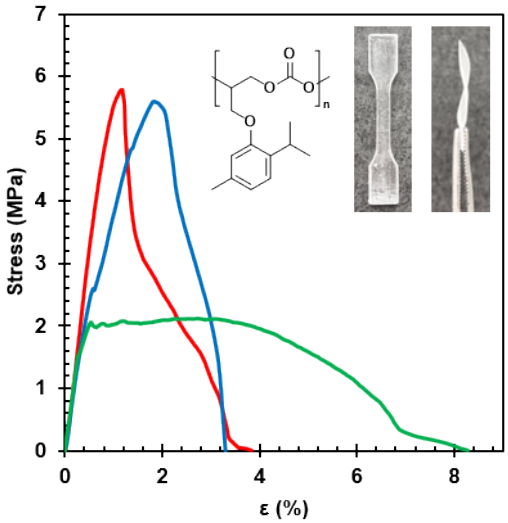


Figure S34: Stress-strain testing of PThyGEC.

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