# Thioglycerol route to bio-based bis-cyclic carbonates: Poly(hydroxyurethane) preparation and post-functionalization

Océane Lamarzelle [a,b], Geoffrey Hibert [a,b], Sébastien Lecommandoux [a,b] , Etienne Grau [a,b*] and Henri Cramail [a,b*]

## Experimental and Supporting Information

### Materials and Methods

#### Materials

Sodium hydroxide (NaOH, pellet), sodium hydride (NaH, 60% in oil), potassium carbonate ($K_2CO_3$, 98%), tetrabutylammonium bromide (TBABr, 99%), hexylamine (99%), dimethyl carbonate (DMC, 99%), 1,2,4-trichlorobenzene (TCB, 99%), 1,5,7-triazabicyclodec-5-ene (TBD, 98%), 2,2-bis(hydroxymethyl)propionic acid (DMPA, 98%), ammonium chloride (99.5 %), sodium sulfate ($Na_2SO_3$, magnesium sulfate ($MgSO_4$), sodium carbonate ($NaHCO_3$), 1-thioglycerol (>99%), 1-decene (94%), *meta*-chloroperbenzoic acid (mCPBA, 77%), O-(Benzotriazol-1-yl)-N,N,N′,N′-tetramethyluronium tetrafluoroborate (TBTU) (97%), N,N-Diisopropylethylamine (DIPEA) (99%), and *Candida Antarctica* Lipase B (CALB, polymer-bound) were obtained from **Sigma-Aldrich**. 1-bromo-10-undecene (96%), was purchased from **Alfa Aesar**. Pyridine (>99%), 10-undecen-1-ol (>98%), methyl 10-undecenoate (>96.0%), 1,10-decanediamine (10DA, >98%), 1,3-dioxane-2-one (trimethylene carbonate, TMC, >98%) and 1,10-diaminodecane (10DA, >97%) were supplied by **TCI, Europe**. *Priamine*® 1075 was kindly supplied by CRODA. Oleyl alcohol (99.9%), oleyl methanesulfonate (>99%) and methyl oleate (99%) were purchased from **Nu-Check-Prep**. Anhydrous trehalose (99%) was purchased from Fisher

#### Methods

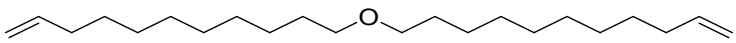
$^1$H and $^{13}$C-NMR spectra were recorded on Bruker Avance 400 spectrometer (400.20 MHz or 400.33 MHz and 100.63 MHz for $^1$H and $^{13}$C, respectively) by using CDCl3 as a solvent at room temperature, except otherwise mentioned. Two-dimensional analyses comprising $^1$H-$^1$H COSY

(COrrelation SpectroscopY) and $^{1}H$-$^{13}C$ HSQC (Heteronuclear Single Quantum Spectroscopy) were also performed. Infrared spectra (FTIR-ATR) were obtained on a Bruker-Tensor 27 spectrometer, equipped with a diamond crystal, using the attenuated total reflection mode. The spectra were acquired using 16 scans at a resolution of 4 wavenumbers. The High-Performance Liquid Chromatography (HPLC) was performed at the ITERG using a Shimadzu instrument fitted with an Agilent PLgel 5µm MIXED-D column (300 mm, 7.5 mm diameter) and compounds were detected by a RID detector at 40°C. The samples were diluted in THF at 10 $mg.L^{-1}$ and filtered before injection in the column. The analyses were performed with THF as eluent at 40°C. Size exclusion chromatography (SEC) analyses of PHUs were performed in DMF (25°C) on a PL-GPC 50 plus Integrated GPC from Polymer laboratories-Varian with a series of three columns from Polymer Laboratories (PLgel: PLgel 5µm Guard (guard column 7.5 mm ID x 5.0 cm L); PLgel 5µm MIXED-D (7.5 mm ID x 30.0 cm L) and PLgel 5µm MIXED-D (7.5 mm ID x 30.0 cm L)). SEC were also performed in THF (25°C) on a PL GPC50 and with four TSK columns: HXL-L (guard column), G4000HXL (particles of 5 mm, pore size of 200A, and exclusion limit of 400000 g/mol), G3000HXL (particles of 5 mm, pore size of 75A, and exclusion limit of 60000 g/mol), G2000HXL (particles of 5 mm, pore size of 20 A, and exclusion limit of 10000 g/mol) at an elution rate of 1 mL/min. In both cases, the elution times of the filtered samples were monitored using UV and RI detectors and SEC were calibrated using polystyrene standards. Differential scanning calorimetry (DSC) thermograms were measured using a DSC Q100 apparatus from TA instruments. For each sample, two cycles from -50 to 160 °C at 10 °C.min-1 (additional isotherm of 15 min at 160°C at the end of the first cycle to remove the residual DMF) were performed and then the glass transition and melting temperatures were calculated from the second heating run. Thermogravimetric analyses (TGA) were performed on TGA-Q50 system from TA instruments at a heating rate of 10 $°C.min^{-1}$ under nitrogen atmosphere from room temperature to 600°C, with an isotherm at 160°C for 15 min to remove the residual DMF. DFT calculations were done using GAUSSIAN0932 with the B3PLYP hybrid functional and a high quality 6-311++G(d) basis set.

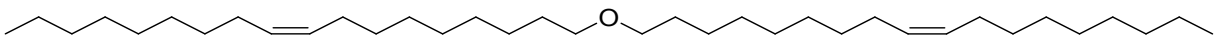
## Experimental

***Und(ether)-diene*** **synthesis:** Into a round bottom flask, 2 eq. of sodium hydride (0.55 g, 22.8 mmol) were stirred with 70 mL of DMSO under inert atmosphere. 1 eq. of 10-undecen-1-ol (1.94

g, 11.4 mmol) was slowly added. The reaction mixture was then stirred at room temperature for 10 min. To this, 1-bromo-10-undecene (2.66 g, 11.4 mmol) was added drop-wise. After 16h, DMSO was removed under reduced pressure and excess sodium hydride was deactivated by aqueous solution of ammonium chloride. DCM (50 mL) was added and the organic layer was washed with saturated $NaHCO_3$ 3 times and with water. The organic layer was dried over anhydrous magnesium sulphate, filtered and reconcentrated. Conversion: 100%. The crude product was purified by flash column chromatography using a mixture of cyclohexane-ethyl acetate (100:0 to 80:20) as eluent and obtained as a white powder. Yield: 36%. Purity by GC: 100%. $^1$H NMR ($CDCl_3$, 25°C, 400 MHz), δ (ppm): 5.73 (m, 2H), 4.96 (m, 4H), 3.36 (t, 4H), 1.94 (q, 4H), 1.49 (m, 4H), 1.20-1.27 (m, 24H).

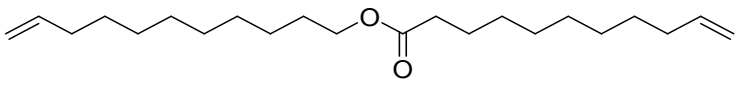


***Oleyl(ether)-diene*** **synthesis:** Into a round bottom flask, 2 eq. of sodium hydride (0.89 g, 37.2 mmol) were stirred with 70 mL of DMSO under inert atmosphere. 1 eq. of oleyl alcohol (5 g, 18.6 mmol) was slowly added. The reaction mixture was then stirred at room temperature for 10 min. To this, oleyl methanesulfonate (6.45 g, 18.6 mmol) was added drop-wise. After 16h, DMSO was removed under reduced pressure and excess sodium hydride was deactivated by aqueous solution of ammonium chloride. DCM (50 mL) was added and the organic layer was washed with saturated $NaHCO_3$ 3 times and with water. The organic layer was dried over anhydrous magnesium sulphate, filtered and reconcentrated. Conversion: 100%. The crude product was purified by flash column chromatography using a mixture of cyclohexane-ethyl acetate (100:0 to 70:30) as eluent and obtained as viscous transparent oil. Yield: 37%. Purity by GC: 100%. $^1$H NMR ($CDCl_3$, 25°C, 400 MHz), δ (ppm): 5.33 (m, 4H), 3.39 (t, 4H), 1.99 (m, 8H), 1.54 (m, 4H), 1.30 (m, 44H), 0.86 (t, 6H).



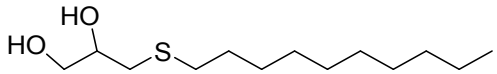
***Und(ester)-diene*** **synthesis*:*** 1 eq. of methyl 10-undecenoate (17.47 g, 88 mmol), 1 eq. of 10-undecen-1-ol (15 g, 88 mmol) and 0.05 eq. of TBD were stirred under nitrogen flow 4h at 120°C, 2h at 160°C then 1h under vacuum at 160°C. Conversion: 90%. The product was purified using flash column chromatography (eluent: cyclohexane-ethyl acetate, 80:20) and obtained as a white

powder. Yield: 83%. Purity by GC: 100%. $^1$H NMR ($CDCl_3$, 25°C, 400 MHz), δ (ppm): 5.81 (m, 2H), 4.97 (m, 4H), 4.07 (t, 2H), 2.28 (t, 2H), 2.03 (q, 4H), 1.64 (m, 4H), 1.38-1.29 (m, 24H).

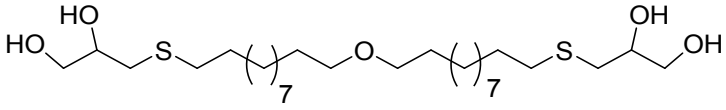


ꕥ **General procedure for thiol-ene coupling**: Dimerized bis-unsaturated fatty acids were reacted with thioglycerol in DCM using DMPA as photoinitiator. The reaction was carried out in a UV reactor (365 nm) for 1h, or 48h in the case of the ***Oleyl(ether)-tetraol*** synthesis.

***Dec-diol*** **synthesis*:***1-decene (1 eq., 2 g, 14.3 mmol), thioglycerol (1 eq., 1.54 g, 14.3 mmol) were reacted in 2 mL of DCM for 1h in a UV reactor, with 0.5 w.% of DMPA (10 mg) as photoinitiator. Conversion: 100%. The solvent was evaporated under reduced pressure and the product was obtained as a transparent oil after purification by flash chromatography (eluent: DCM:methanol from 100:0 to 95:5). Yield: 78%. $^1$H NMR (DMSO-d6, 25°C, 400 MHz), δ (ppm): 3.78 (m, 1H), 3.73 and 3.56 (q, 2H), 2.77 and 2.61 (dd, 2H), 2.53 (t, 2H), 1.58 (m, 2H), 1.26 (m, 14H), 0.85 (t, 3H).

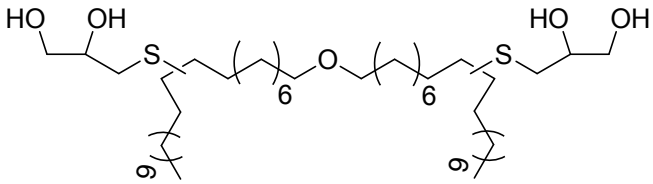


***Und(ether)-tetraol*** **synthesis**: ***Und(ether)-diene*** (1 eq., 2 g, 6.2 mmol), thioglycerol (2 eq., 1.34 g, 12.4 mmol) were reacted in 2 mL of DCM for 1h in a UV reactor, with 0.5 w.% of DMPA (10 mg) as photoinitiator. Conversion: 100%. The heterogeneous mixture obtained was filtered and the resulting white powder was abundantly washed with petroleum ether. Yield: 99%. $^1$H NMR (DMSO, 25°C, 400 MHz), δ (ppm): 4.58 (m, 4H), 3.57 (m, 2H), 3.35 (t, 4H), 3.33 (t, 4H), 2.62 and 2.43 (dd, 4H), 2.53 (t, 4H), 1.52-1.27 (m, 34H).

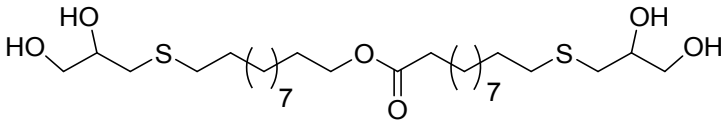


***Oleyl(ether)-tetraol*** **synthesis**: ***Oleyl(ether)-diene*** (1 eq., 2.5 g, 4.82 mmol), thioglycerol (2 eq., 1.04 g, 9.6 mmol) were reacted in 2 mL of DCM for 48h in a UV reactor, with 1.5 w.% of DMPA (38 mg) as photoinitiator. Conversion: 90%. The solvent was evaporated and the crude product was purified by flash column chromatography (eluent: DCM:methanol from 100:0 to

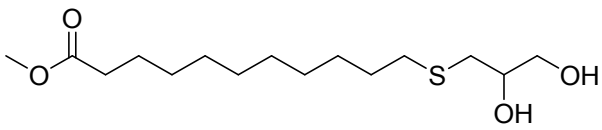
90:10) to obtain a transparent viscous liquid. Yield: 30%. $^1$H NMR (DMSO-d6, 25°C, 400 MHz), δ (ppm): 4.68 (d, 2H), 4.51 (t, 2H), 3.51 (m, 2H), 3.35 (t, 4H), 3.33 (t, 4H), 2.59 (m, 2H), 2.54 and 2.37 (dd, 4H), 1.45-1.25 (m, 60H), 0.88 (t, 6H).




***Und(ester)-tetraol* synthesis***: **Und(ester)-diene*** (1 eq., 3 g, 8.9 mmol), thioglycerol (2 eq., 1.93 g, 17.8 mmol) were reacted in 2 mL of DCM 1h in a UV reactor, with 0.5 w.% of DMPA (15 mg) as photoinitiator. Conversion: 100%. The heterogeneous mixture obtained was filtered and the resulting white powder was abundantly washed with petroleum ether. Yield: 99%. $^1$H NMR ($CDCl_3$, 25°C, 400 MHz), δ (ppm): 4.07 (t, 2H), 3.78 (m, 2H), 3.75 and 3.35 (q, 4H), 2.73 and 2.69 (dd, 4H), 2.62 (t, 4H), 2.30 (m, 6H), 1.60-1.27 (m, 34H).

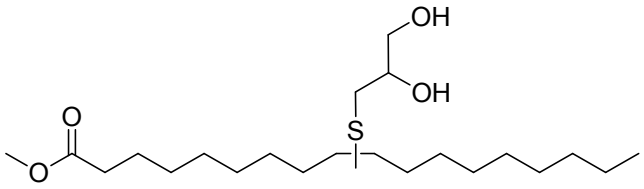



***Methyl-Und-diol:*** Methyl 10-undecenoate (10 g, 50 mmol.) and 1-thioglycerol (2 eq., 10 g, 100 mmol) were stirred during 2 h under irradiation using UV light ($\lambda$=365 nm). Then the reaction was quenched by turning off the UV light. Purification over silica gel flash chromatography was performed using DCM/MeOH 98/2 eluent. Yield: 80%. $^1$H NMR ($CDCl_3$, 400 MHz), δ (ppm): 3.74 (m, 2H), 3.64 (s, 3H), 3.53 (m, 1H), 2.65 (m, 2H), 2.51 (m, 2H), 2.28 (t, 2H), 1.59-1.25 (m, 16H).



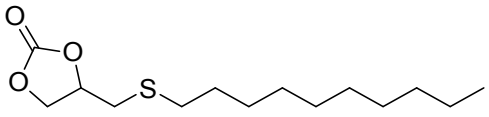

***Methyl-Oleyl-diol:*** Methyl oleate (10 g, 33 mmol.) and 1-thioglycerol (10 eq., 36 g, 337 mmol) were stirred under irradiation using UV light ($\lambda$=365 nm) until total conversion of the internal double bond. Then the reaction was quenched by turning off the UV light. Purification over silica

gel flash chromatography was performed using DCM/MeOH 98/2 eluent. Yield: 76 %. $^1$H NMR ($CDCl_3$, 400 MHz), δ (ppm): 3.72 (m, 2H), 3.63 (s, 3H), 3.53 (m, 1H), 2.63 (m, 3H), 2.27 (t, 2H), 1.58-1.24 (m, 26H), 0.85 (t, 3H).



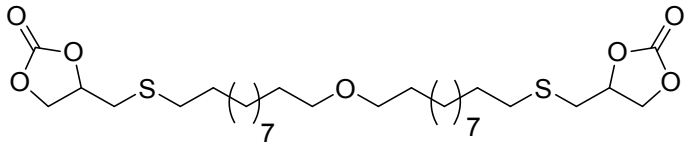

ꕥ **General procedure for carbonation**: Fatty acids tetraols were dried under vacuum and were subsequently reacted under nitrogen atmosphere with an excess of anhydrous dimethylcarbonate (DMC, 15 eq.), using 3 mol.% of $K_2CO_3$ per diol as transesterification catalyst. The reaction was carried out for 4h at 70°C under reflux.

***Dec-CC-S* synthesis*: Dec-diol*** (1 eq., 1 g, 7 mmol), DMC (15 eq., 8.5 mL, 105 mmol), $K_2CO_3$ (0.03 eq., 29 mg, 0.21 mmol). Conversion: 100%. DCM was added to the crude mixture and washed with brine three times. The organic phase was dried with magnesium sulfate and reconcentrated using a rotary evaporator. The product was obtained as a transparent viscous liquid after purification by flash column chromatography (eluent: DCM:methanol from 100:0 to 95:5). Yield: 30%. Purity: 90.1% (HPLC). $^1$H NMR ($CDCl_3$, 25°C, 400 MHz), δ (ppm): 4.84 (m, 1H), 4.55 and 4.31 (t, 2H), 2.94 and 2.77 (dd, 2H), 2.59 (t, 2H), 1.58 (m, 2H), 1.37-1.26 (m, 14H), 0.86 (t, 3H). $^{13}$C NMR ($CDCl_3$, 25°C, 100 MHz), δ (ppm): 154.5 (O-C=O-O), 75.6 ($CH_2$-$\underline{C}$H-$CH_2$), 68.7 (O-$\underline{C}H_2$-CH), 34.7 ($CH_2$-CH-$\underline{C}H_2$-S), 33.2 (S-$\underline{C}H_2$-$CH_2$), 32-23 ($CH_2$), 14.4 ($CH_3$).

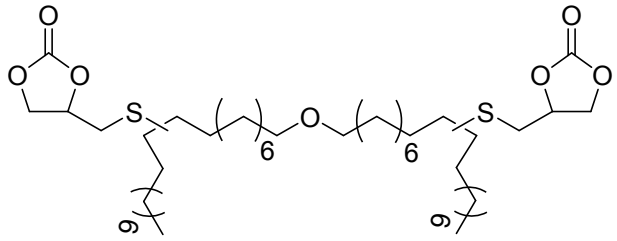



***Und(ether)-bCC* synthesis**: ***Und(ether)-tetraol*** (1 eq., 1 g, 1.86 mmol), DMC (15 eq., 2.34 mL, 28 mmol), $K_2CO_3$ (0.06 eq., 15 mg, 0.11 mmol). Conversion: 100%. DCM was added to the crude mixture and washed with brine three times. The organic phase was dried with magnesium sulfate and reconcentrated using a rotary evaporator. The product was obtained as a white powder. Yield: 88%. Purity: 95.4% (HPLC). $^1$H NMR (DMSO-d6, 25°C, 400 MHz), δ (ppm): 4.82 (m, 2H), 4.57 and 4.27 (t, 4H), 3.37 (t, 4H), 2.91 and 2.75 (dd, 4H), 2.57 (t, 4H), 1.56-1.27

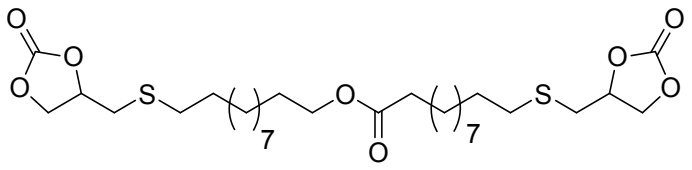
(m, 34H). $^{13}$C NMR (DMSO, 25°C, 100 MHz), δ (ppm): 154.6 (O-C=O-O), 75.6 ($CH_2$-$\underline{C}$H-$CH_2$),71.2 ($\underline{C}H_2$-O-$CH_2$), 68.8 (O-$\underline{C}H_2$-CH), 34.9 (CH-$\underline{C}H_2$-S), 33.2 (S-$\underline{C}H_2$-$CH_2$), 30-26.1 ($CH_2$). $T_m$=93°C.



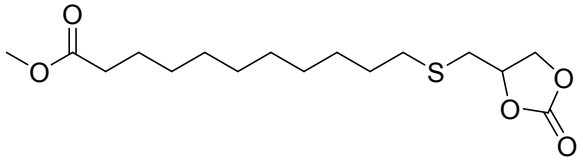
***Oleyl(ether)-bCC* synthesis**: ***Oleyl(ether)-tetraol*** (1 eq., 0.75 g, 1 mmol), DMC (15 eq., 1.26 mL, 15 mmol), $K_2CO_3$ (0.06 eq., 8.3 mg, 0.11 mmol). Conversion: 97%. DCM was added to the crude mixture and washed with brine three times. The organic phase was dried with magnesium sulfate and reconcentrated using a rotary evaporator. The product was obtained as a viscous transparent liquid. Yield: 71%. Purity: 98.5% (HPLC). $^1$H NMR ($CDCl_3$, 25°C, 400 MHz), δ (ppm): 4.78 (m, 2H), 4.53 and 4.28 (t, 4H), 3.38 (t, 4H), 2.90 and 2.72 (dd, 4H), 2.12 (m, 2H), 1.60-1.26 (m, 60H), 0.87 (t, 6H). $^{13}$C NMR ($CDCl_3$, 25°C, 100 MHz), δ (ppm): 154.9 (O-C=O-O), 75.7 ($CH_2$-$\underline{C}$H-$CH_2$-S), 71.4 ($\underline{C}H_2$-O-$CH_2$), 68.5 (O-$\underline{C}H_2$-CH), 47.3 (S-$\underline{C}$H-$CH_2$), 32.9 ($\underline{C}$H-$CH_2$-S-CH), 35-22.8 ($CH_2$), 14.1 ($CH_3$).$T_m$=nd, $T_g$=-59°C.



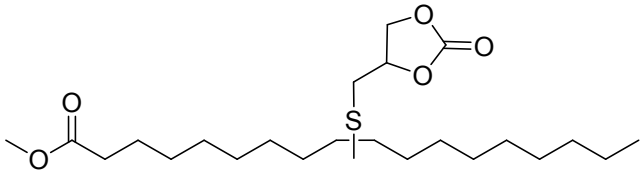
***Und(ester)-bCC* synthesis*: Und(ester)-tetraol*** (1 eq., 0.75 g, 1.36 mmol), DMC (15 eq., 1.71 mL, 20.4 mmol), $K_2CO_3$ (0.06 eq., 11 mg, 0.08 mmol). Conversion: 99%. DCM was added to the crude mixture and washed with brine three times. The organic phase was dried with magnesium sulfate and reconcentrated using a rotary evaporator. The product was obtained as a white powder. Yield: 90%. Purity: 88.9% (HPLC). $^1$H NMR ($CDCl_3$, 25°C, 400 MHz), δ (ppm): 4.83 (m, 2H), 4.75 and 4.29 (t, 4H), 4.04 (t, 2H), 2.94 and 2.79 (dd, 4H), 2.60 (t, 4H), 2.29 (t, 2H), 1.58-1.28 (m, 34H). $^{13}$C NMR ($CDCl_3$, 25°C, 100 MHz), δ (ppm): 174.2 ($CH_2$-$\underline{C}$=O-O-), 154.8 (O-C=O-O), 75.7 ($CH_2$-$\underline{C}$H-$CH_2$), 68.6 (O-$\underline{C}H_2$-CH), 64.5 (O=C-O-$\underline{C}H_2$), 34.9 (CH-$\underline{C}H_2$-S), 34.7 ($\underline{C}H_2$-C=O-O-$CH_2$), 33.3 (S-$\underline{C}H_2$-$CH_2$), 29.9-28.9 ($CH_2$). $T_m$=89°C.



***Ester-Und-CC:*** In a flame-dried round bottom flask equipped with a reflux condenser, (3 mol.%, 68 mg, 0.5 mmol) potassium carbonate ($K_2CO_3$) was added to a solution of ***Methyl-Und-diol*** (5 g, 16.3 mmol) dissolved in dimethyl carbonate (DMC) (25 eq., 34 mL, 0.4 mol). The reaction mixture was stirred during 6 h under reflux. At the end of the reaction, the DMC was evaporated with a rotary evaporator. Purification over silica gel flash chromatography was performed using DCM/MeOH 98/2 eluent. $^1$H NMR ($CDCl_3$, 400 MHz), δ (ppm): 4.83 (m, 1H), 4.57 (m, 1H), 4.28 (m, 1H), 3.66 (s, 3H), 2.91 (m, 2H), 2.59 (t, 2H), 2.30 (t, 2H), 1.56-1.27 (m, 16H).

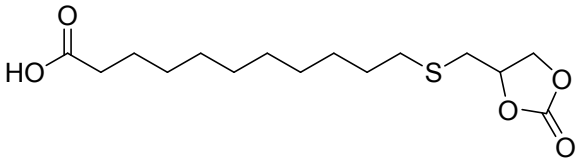


***Ester-Oleyl-CC:*** In a flame-dried round bottom flask equipped with a reflux condenser, potassium carbonate ($K_2CO_3$ 3 mol.%, 48 mg, 0.3 mmol.) was added to a solution of ***Methyl-Oleyl-diol*** (5 g, 11.6 mmol.) dissolved in dimethyl carbonate (DMC 25 eq., 24 mL, 0.3 mol.). The reaction mixture was stirred during 6 h under reflux. At the end of the reaction, the DMC was evaporated with a rotary evaporator. Purification over silica gel flash chromatography was performed using DCM/MeOH 98/2 eluent. $^1$H NMR (DMSO-d6, 400 MHz), δ (ppm): 4.92 (m, 1H), 4.57 (m, 1H), 4.19 (m, 1H), 3.57 (s, 3H), 2.88 (m, 2H), 2.69 (t, 2H), 2.28 (t, 2H), 1.51-1.25 (m, 16H), 0.86 (t, 3H).

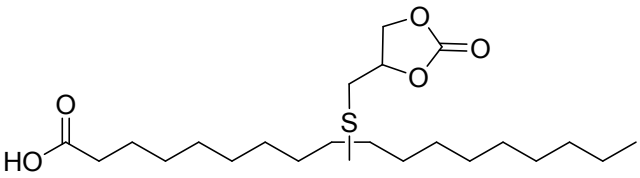


ꕥ **General procedure for ester hydrolysis:** Carbonated fatty acids methyl esters were hydrolyzed with lipase B from *Candida Antarctica* in water/acetone mixture (1:1) for 48 h at 60°C.

***Acid-Und-CC:*** In a round bottom flask, ***Ester-Und-CC*** (5 g, 15 mmol.) was dissolved in a solution water/acetone (2:5) (2 mL/10 mL). Then, lipase B from *Candida Antartica* (1g, 20 wt.%) was added to the reaction medium. The reaction mixture was stirred during 48 h at 60°C. At the end of the reaction, the solvent was evaporated with a rotary evaporator. Purification over silica gel flash chromatography was performed using DCM/MeOH 98/2. $^1$H NMR ($CDCl_3$, 400 MHz), δ (ppm): 4.83 (m, 1H), 4.57 (m, 1H), 4.28 (m, 1H), 2.91 (m, 2H), 2.59 (t, 2H), 2.30 (t, 2H), 1.56-1.27 (m, 16H).



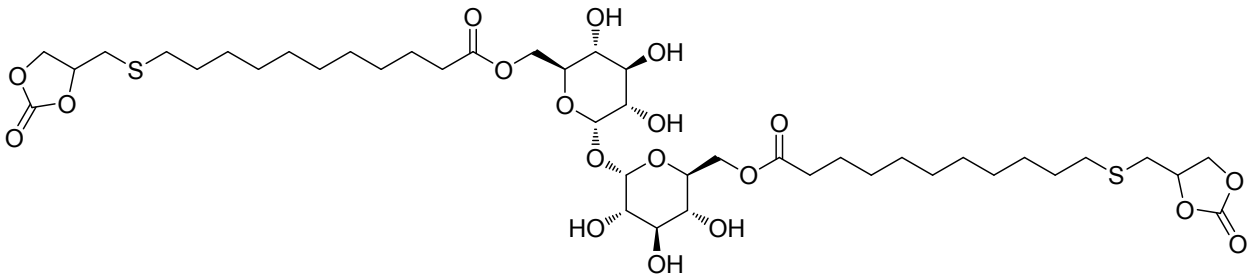

***Acid-Oleyl-CC:*** In a round bottom flask, ***Ester-Oleyl-CC*** (5 g, 11 mmol.) was dissolved in a solution water/acetone (2:5) (4 mL/10 mL). Then, lipase B from *Candida Antartica* (1g, 20 wt.%) was added to the reaction medium. The reaction mixture was stirred during 48 h at 60°C. At the end of the reaction, the solvent was evaporated with a rotary evaporator. Purification over silica gel flash chromatography was performed using DCM/MeOH 98/2. $^1$H NMR (DMSO-d6, 400 MHz), δ (ppm): 4.92 (m, 1H), 4.57 (m, 1H), 4.19 (m, 1H), 2.88 (m, 2H), 2.69 (t, 2H), 2.28 (t, 2H), 1.51-1.25 (m, 16H), 0.86 (t, 3H).




ꕥ **General procedure for trehalose diester synthesis:** In an oven-dried round bottomed flask equipped with a magnetic stir bar, fatty acid (2.1 equiv), TBTU (2.1 equiv) and DIPEA (4 equiv) were dissolved in dry pyridine. The resulting mixture was stirred at room temperature for 30 min under a nitrogen atmosphere. A solution of trehalose (1 eq) in dry pyridine was then slowly injected into the reaction mixture and stirred at room temperature for 72 h.

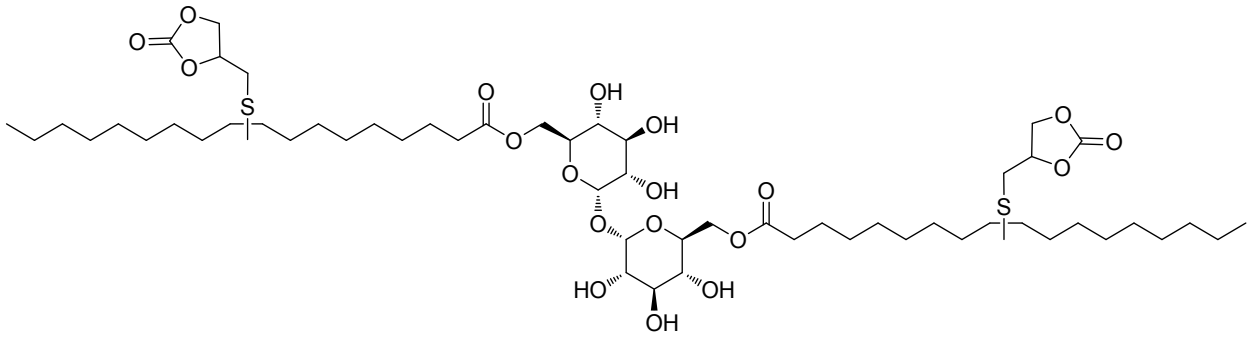
***Trehal-Und-bCC:*** In a flame-dried round bottom flask equipped, ***Acid-Und-CC*** (2.1 eq., 3.9 g, 12 mmol.), TBTU (2.1 eq., 3.9 g, 12 mmol.) and DIPEA (2 eq., 1.9 mL, 11 mmol) were dissolved in dry pyridine (20 mL). The resulting mixture was stirred at room temperature for 30 min under

a nitrogen atmosphere. Then the reaction mixture was slowly injected into a solution of trehalose (1 eq, 5.8 mmol) in dry pyridine (20 mL) and stirring was continued at room temperature for 72 h. Pyridine was removed under vacuum and the resulting residue centrifuged in water to remove the by-products of the reaction. The precipitate was dried and purified by flash chromatography using an elution gradient of 5-25% methanol in EtOAc-DCM (1:1) to give diester of trehalose as a gummy solid. Purity: 81.1% (HPLC). $^{1}$H NMR (DMSO-$d_6$, 400MHz), δ (ppm): 5.06 (d, 2H), 4.96 (m, 1H), 4.90 (d, 2H), 4.81 (d, 2H), 4.77 (d, 2H), 4.58 (m, 2H), 4.21 (d, 2H), 4.20 (m, 2H), 4.04 (m, 2H), 3.88 (m, 2H), 3.54 (m, 2H), 3.25 (m, 2H), 3.11 (m, 2H), 2.90 (m, 2H), 2.54 (t, 2H), 2.27 (t, 2H), 1.51-1.24 (m, 16H). $^{13}$C NMR (DMSO-$d_6$, 100 MHz) δ (ppm): 172.80 (-$CH_2$-$\underline{C}$OO-$CH_3$), 93.48 (-$\underline{C}$H-, H1), 75.92 (-$\underline{C}$H-O-), 72.72 (-$\underline{C}$H-, H3), 71.44 (-$\underline{C}$H-, H2), 70.08 (-$\underline{C}$H-, H4), 69.72 (-$\underline{C}$H-, H5), 68.50 (-$\underline{C}H_2$-O-), 63.06 (-$\underline{C}$H-, H6), 33.79 (-S-$\underline{C}H_2$-CH-), 33.55 (-$\underline{C}H_2$-COO-$CH_3$), 31.85 (-$CH_2$-$\underline{C}H_2$-S-$CH_2$-), 29.17 - 24.48 (aliphatic -$C\underline{H}_2$-).$T_m$=120°C.



***Trehal-Oleyl-CC:*** In a flame-dried round bottom flask equipped, ***Acid-Oleyl-CC*** (2.1 eq., 2.5 g, 6.1 mmol.), TBTU (2.1 eq., 1.9 g, 6.1 mmol) and DIPEA (2 eq., 0.9 mL, 5.8 mmol) were dissolved in dry pyridine (15 mL). The resulting mixture was stirred at room temperature for 30 min under a nitrogen atmosphere. Then the reaction mixture was slowly injected into a solution of trehalose (1 eq., 5.8 mmol) in dry pyridine (15 mL) and stirring was continued at room temperature for 72 h. Pyridine was removed under vacuum and the resulting residue centrifuged in water to remove the by-products of the reaction. The precipitate was dried and purified by flash chromatography using an elution gradient of 5-25% methanol in EtOAc-DCM (1:1) to give diester of trehalose as a gummy solid. Purity: 98.5% (HPLC). $^{1}$H NMR (DMSO-$d_6$, 400MHz), δ (ppm): 5.04 (d, 2H), 4.92 (m, 1H), 4.89 (d, 2H), 4.82 (d, 2H), 4.76 (d, 2H), 4.57 (m, 2H), 4.24 (d, 2H), 4.19 (m, 2H), 4.03 (m, 2H), 3.88 (m, 2H), 3.54 (m, 2H), 3.25 (m, 2H), 3.12 (m, 2H), 2.88 (m, 2H), 2.69 (t, 2H), 2.28 (t, 2H), 1.51-1.25 (m, 16H), 0.86 (t, 3H). $^{13}$C NMR (DMSO-$d_6$, 100 MHz), δ (ppm): 172.57 (-$CH_2$-$\underline{C}$OO-$CH_3$), 93.70 (-$\underline{C}$H-, H1), 76.43 (-$\underline{C}$H-O-), 72.32 (-$\underline{C}$H-, H3),

(-CH-, H2), 69.97 (-CH-, H4), 69.32 (-CH-, H5), 68.23 (-$CH_2$-O-), 63.06 (-CH-, H6), 45.16 (-$CH_2$-$CH_2$-S-$CH_2$-), 33.33 (-$CH_2$-COO-$CH_3$), 32.46 (-S-$CH_2$-CH-), 30.73 - 22.34 (aliphatic -$CH_2$-), 13.94 (-$CH_3$). $T_m$=109°C.



ꕥ **General procedure for kinetic experiments:** The kinetic experiments were performed in NMR tube at 1 mol.$L^{-1}$ in DMSO-d6, at 50°C and with a ratio 1:1 between cyclic carbonate and hexylamine. All reagents were dried on molecular sieves or distilled before the reaction. Hexylamine was dried under $CaH_2$ and distilled of after drying. The cyclic carbonate was directly dried overnight in a NMR tube caped with a septum, under vacuum. 0.5 mL of dried DMSO-d6 and 12.5 µL of TCB were added *via* the septum and the mixture was homogenized. The hexylamine (66 µL, 0.5 mmol, 1 eq.) was then added just before putting the tube in the NMR apparatus. The reaction was monitored with $^1$H NMR spectroscopy with the disappearance of the cyclic carbonate protons for 24h.

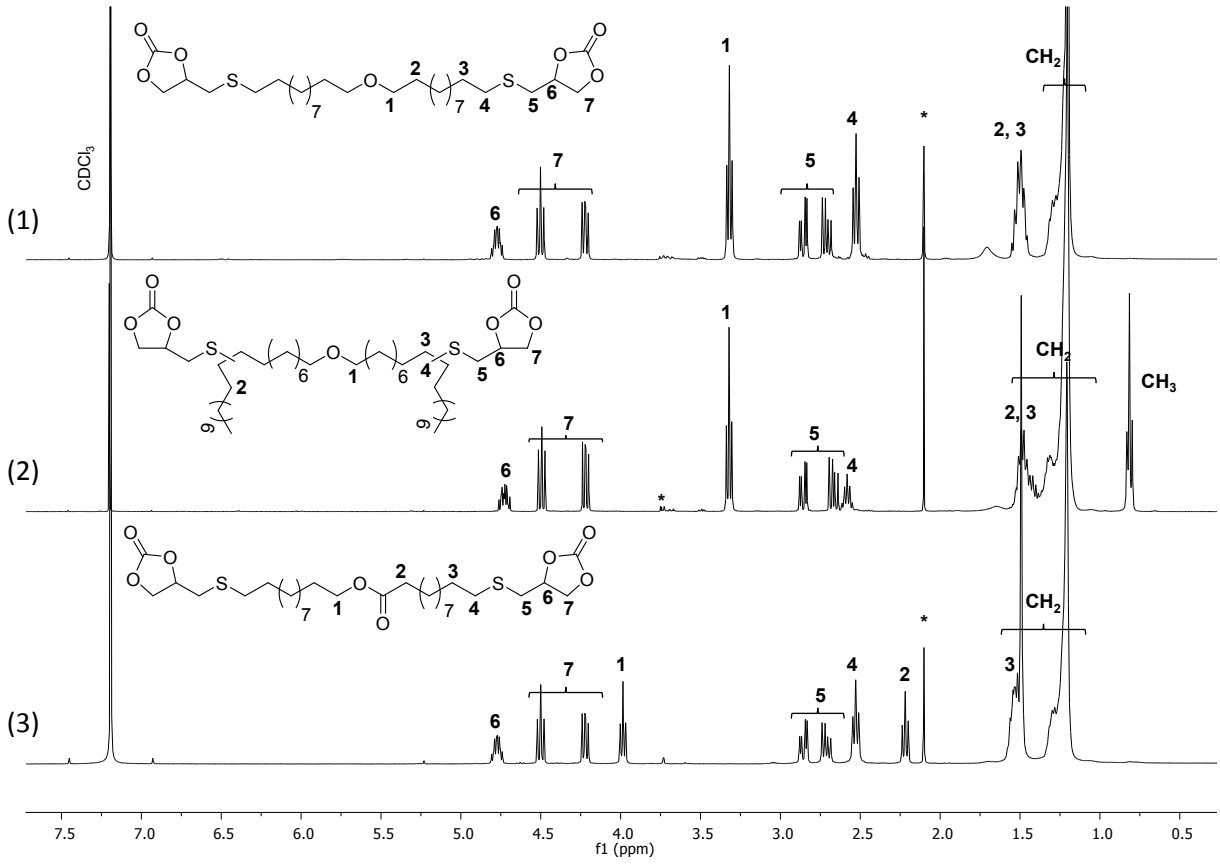
ꕥ **General procedure for polymerizations:** PHUs were prepared from ***Und(ether)-bCC, Und(ester)-bCC***, ***Oleyl(ether)-bCC, Trehal-Und-bCC*** and ***Trehal-Oleyl-bCC*** with 1,10-diaminodecane (10DA), isophorone diamine (IPDA) and *Priamine* as comonomers with a molar ratio 1:1. PHU syntheses were performed in DMF (1 mol.$L^{-1}$) at 70°C into a schlenk tube under magnetic stirring and nitrogen atmosphere for 7 days. No catalysts were added for the polymerization reactions. Conversions were determined by $^1$H NMR spectroscopy after 24h and 7 days of polymerization.

ꕥ **General procedure for sulfonation:** 1 eq. of sulphur-activated cyclic carbonate was reacted with 3 eq. of m-chloroperbenzoic acid (mCPBA) per sulphur atom in DCM (1 g /20 mL) during

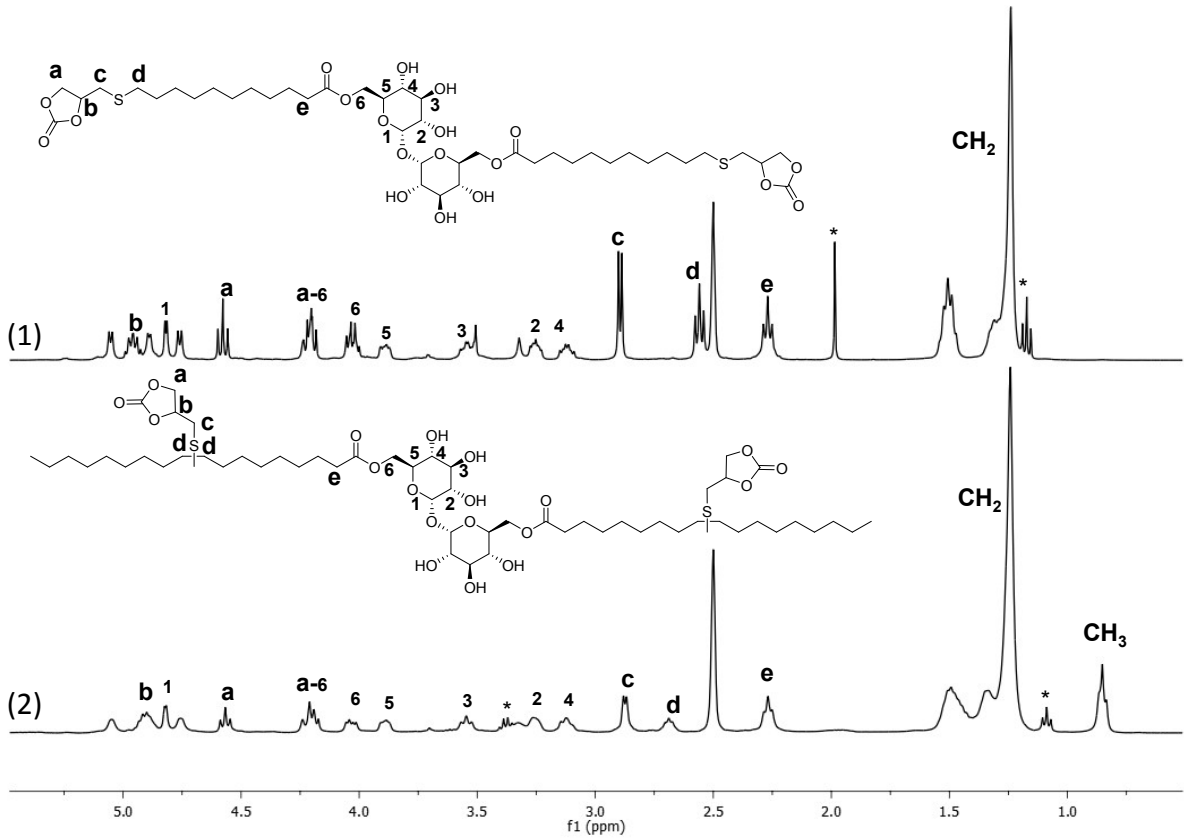
24h at room temperature. The reaction mixture was then cooled up at 0°C to ensure the precipitation in DCM of the acidic form of mCPBA that was subsequently filtrated. The resulting organic phase was washed 4 times with $Na_2SO_3$ saturated solution, three times with $NaHCO_3$ saturated solution and rinsed with deionized water in order to remove residual mCPBA. The organic phase was dried over magnesium sulphate and reconcentrated using rotary evaporator. No further purification was required. This procedure was applied to PHU post-functionalization. In the case of glycolipid-based PHU, the sulfonation was conducted in DMF and the purification was realized by dialysis in water in order to precipitate the polysulfone and to remove DMF, mcpba and its corresponding acidic form.

**PHU 5-sulfone:** IR ($cm^{-1}$): 3328, 2919, 2850, 1725, 1687, 1534, 1387, 1281, 1247, 1117, 1127, 1048, 1009.






**ESI Figure 1 - Stacked $^1$H NMR spectra of (1) Und(ether)-bCC (2) Und(ester)-bCC and (3) Oleyl(ether)-bCC in $CDCl_3$ (* impurities or solvent traces).**




**ESI Figure 2 - Stacked $^{1}$H NMR spectra of (1) Trehal-Und-bCC and (2)Trehal-Oleyl-bCC in DMSO-$d_6$ (*) Impurities.**

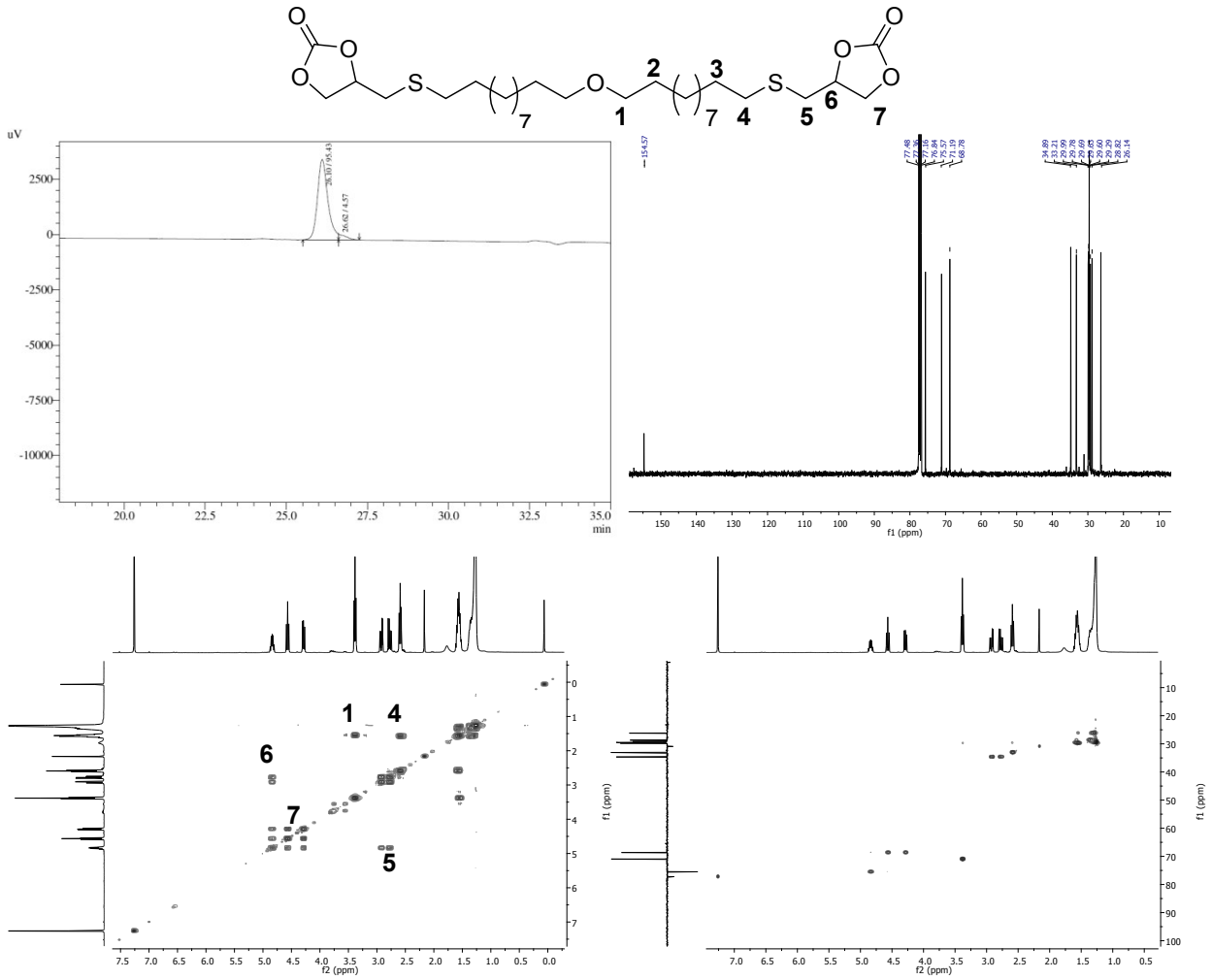



**Figure ESI 3 - Characterization of Und(ether)-bCC (1) HPLC (95.4% purity), (2) $^{13}C$ NMR, (3) $^{1}H$-$^{1}H$ COSY NMR and (4) $^{1}H$-$^{13}C$ HSQC-NMR (Analysis performed in $CDCl_3$).**

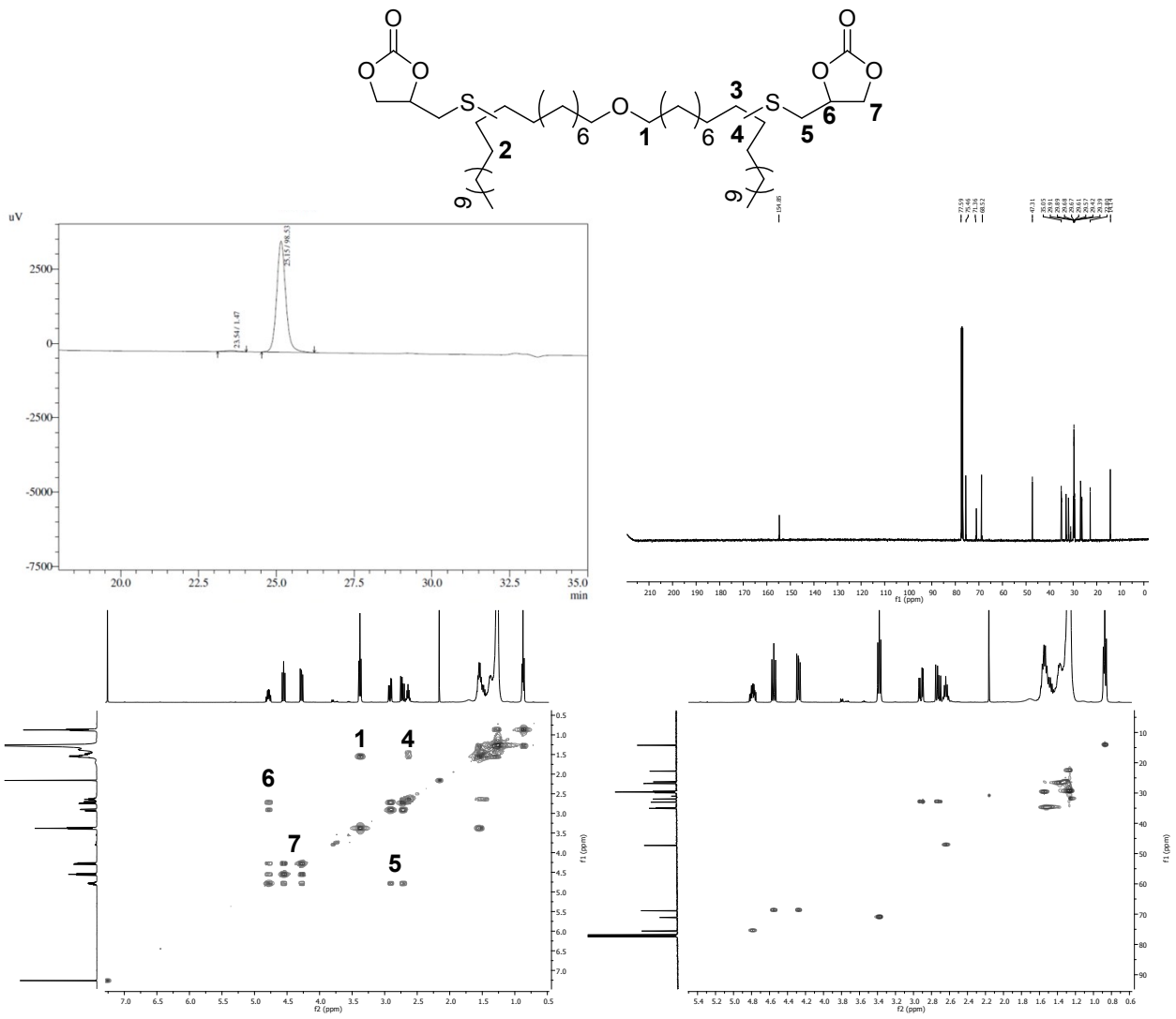



**Figure ESI 4 - Characterization of Oleyl(ether)-bCC (1) HPLC (98.5% purity), (2) $^{13}C$ NMR, (3) $^{1}H$-$^{1}H$ COSY NMR and (4) $^{1}H$-$^{13}C$ HSQC-NMR (Analysis performed in $CDCl_3$).**

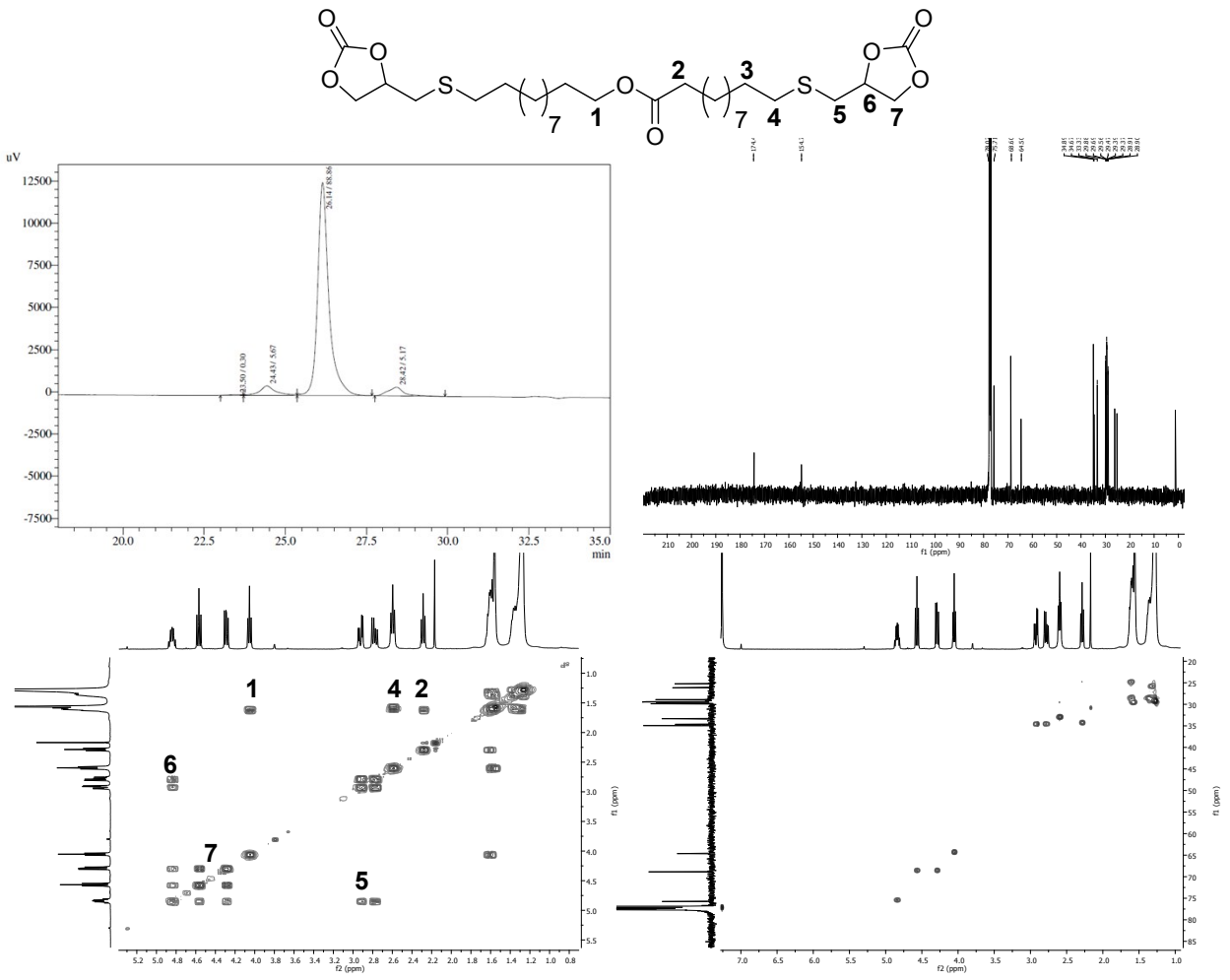



**Figure ESI 5 - Characterization of Und(ester)-bCC (1) HPLC (88.9% purity), (2) $^{13}C$ NMR, (3) $^{1}H$-$^{1}H$ COSY NMR and (4) $^{1}H$-$^{13}C$ HSQC-NMR (Analysis performed in $CDCl_3$).**

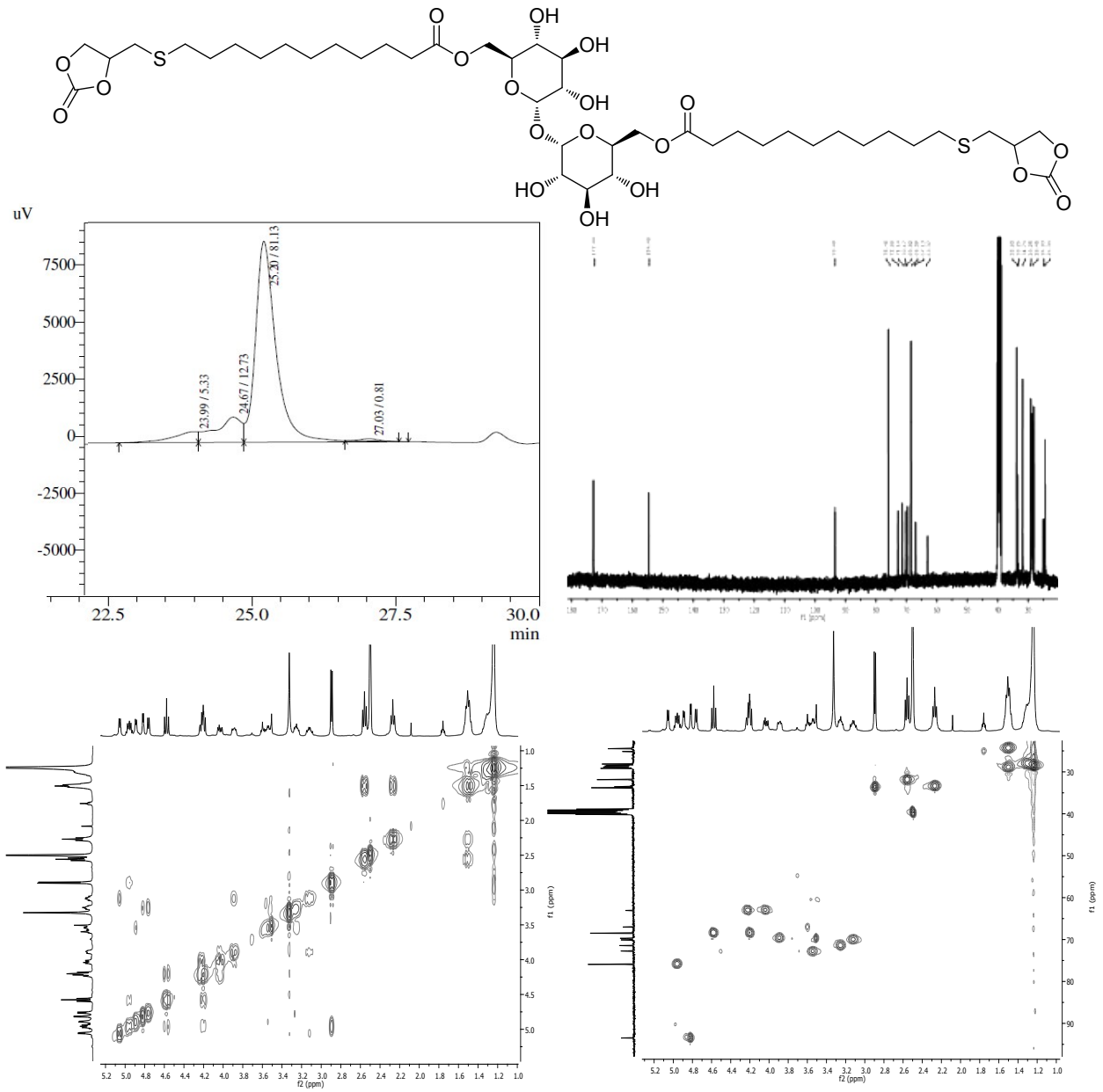



**Figure ESI 6 - Characterization of Trehal-Und-bCC: (1) HPLC (81.1% purity), (2) $^{13}C$ NMR, (3) $^{1}H$-$^{1}H$ COSY NMR and (4) $^{1}H$-$^{13}C$ HSQC-NMR (Analysis performed in $CDCl_3$).**

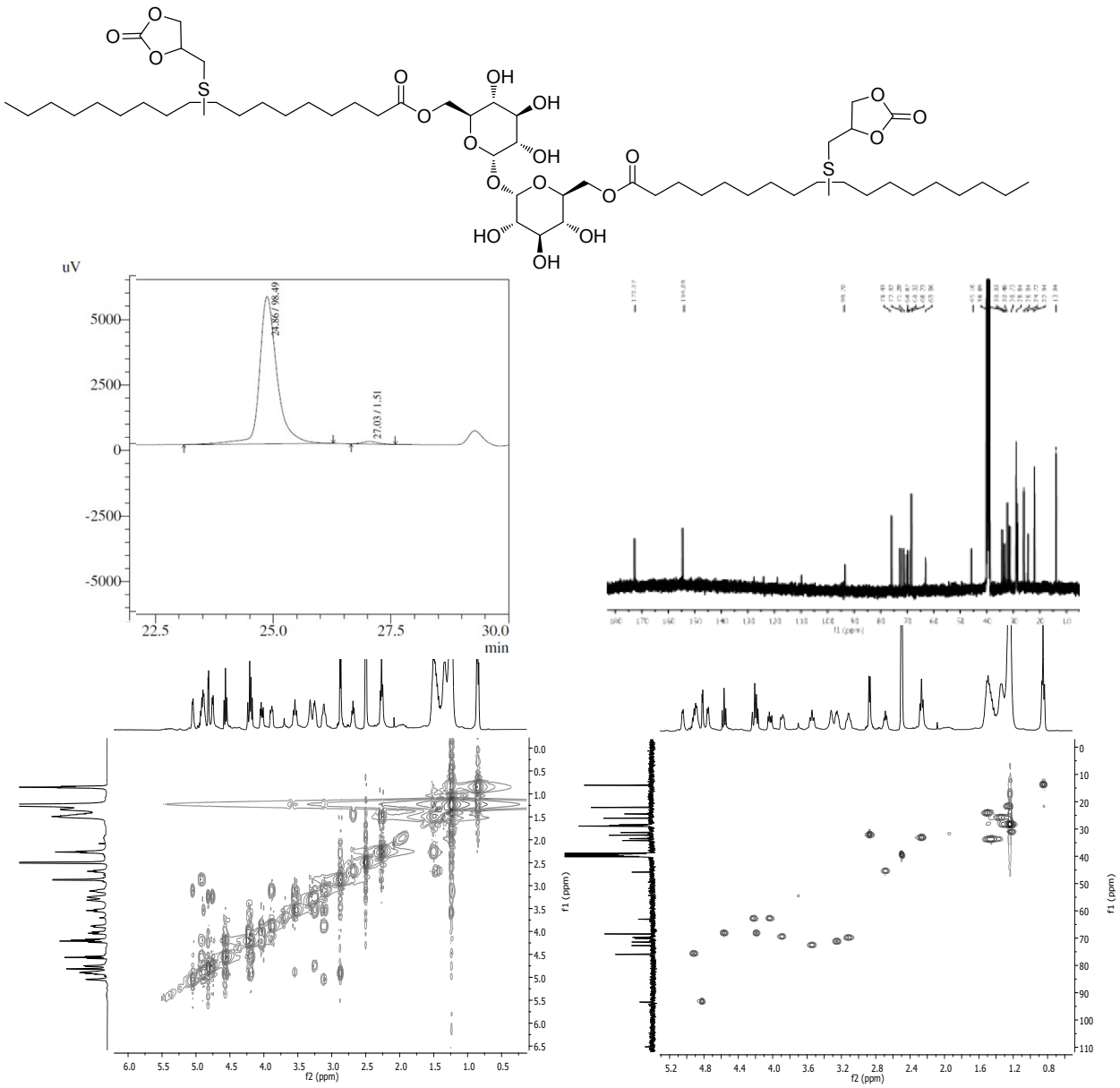
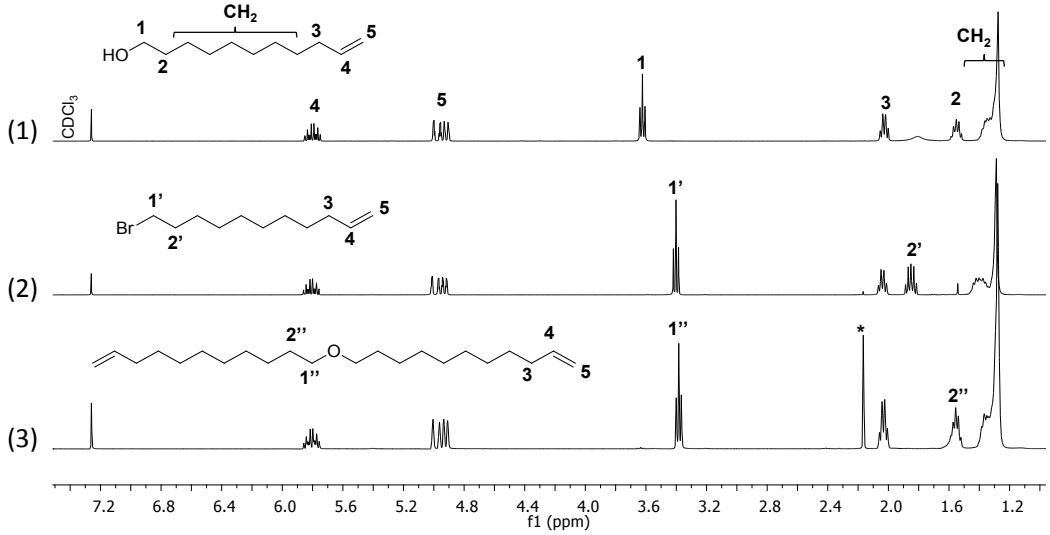
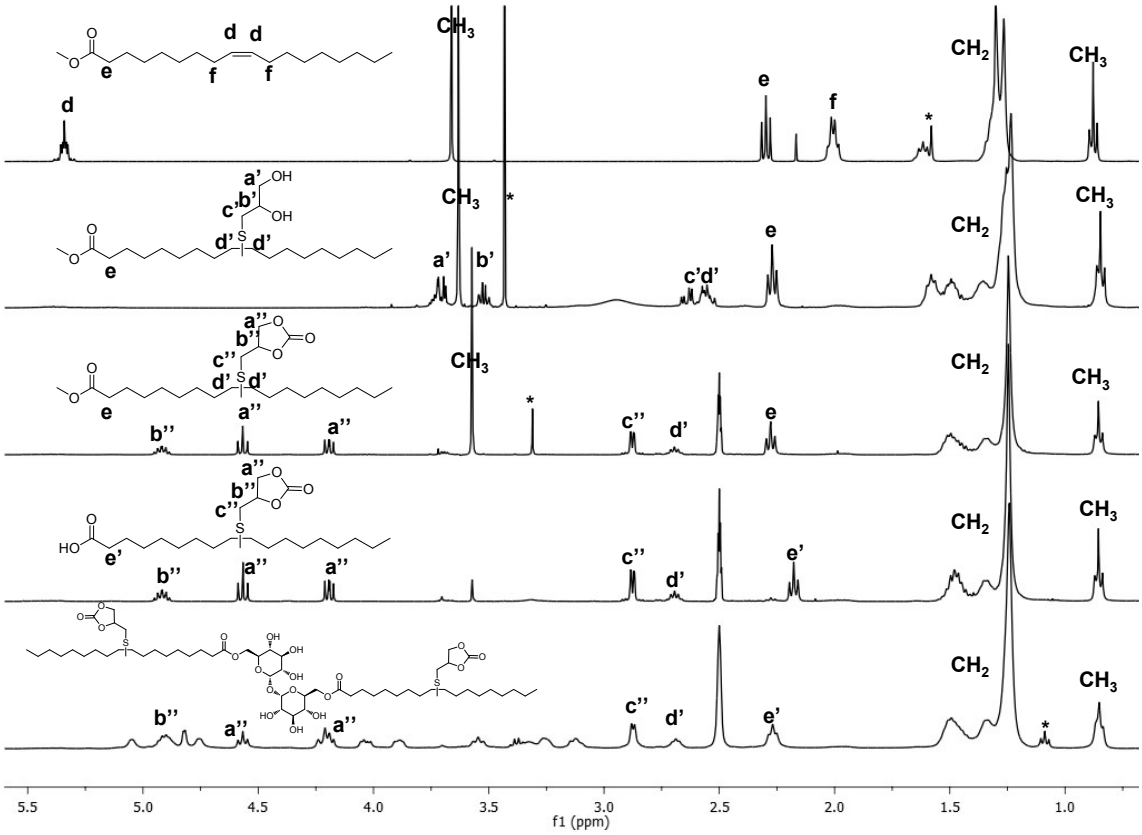



**Figure ESI 7 - Characterization of Trehal-Oleyl-bCC: (1) HPLC (98.5% purity), (2) $^{13}C$ NMR, (3) $^{1}H$-$^{1}H$ COSY NMR and (4) $^{1}H$-$^{13}C$ HSQC-NMR (Analysis performed in $CDCl_3$).**




**ESI Figure 8 - Stacked $^{1}$H NMR spectra of (1) 10-undecen-1-ol, (2) 1-bromo-10-undecene and (3) Und(ether)-diene in $CDCl_3$ (*) Impurities.**




**ESI Figure 9- Stacked $^{1}$H NMR spectra of intermediates of Trehal-Oleyl-bCC (*) Impurities.**

$$-\frac{d[CC]}{dt} = k_{app}[CC][A] = k_{app}[CC]^2 \quad \text{(E1)}$$

$$-\frac{d[CC]}{[CC]^2} = k_{app}dt \quad \text{(E2)}$$

$$\frac{1}{[CC]} - \frac{1}{C_0} = k_{app}\Delta t \quad \text{(E3)}$$

or $[CC] = C_0 - C_0x = C_0(1-x)$ (E4)

$$\frac{x}{1-x} = k_{app}C_0\Delta t \quad \text{(E5)}$$

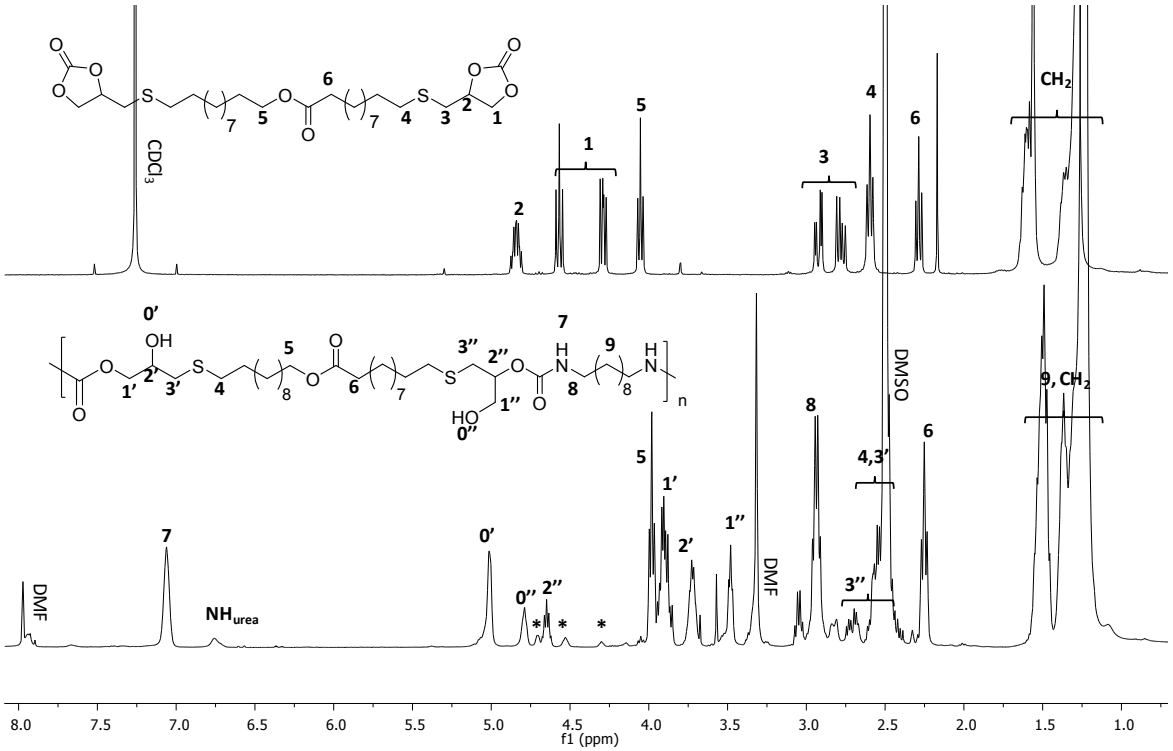
**ESI Formula 1 - 2nd order Kinetic law formula: Time-(x/(1-x))**

$$\%\ Urea = \frac{\int H_{urea}}{\int H_{urea} + \int H_{amide} + \int H_{urethane}} \quad (E)$$

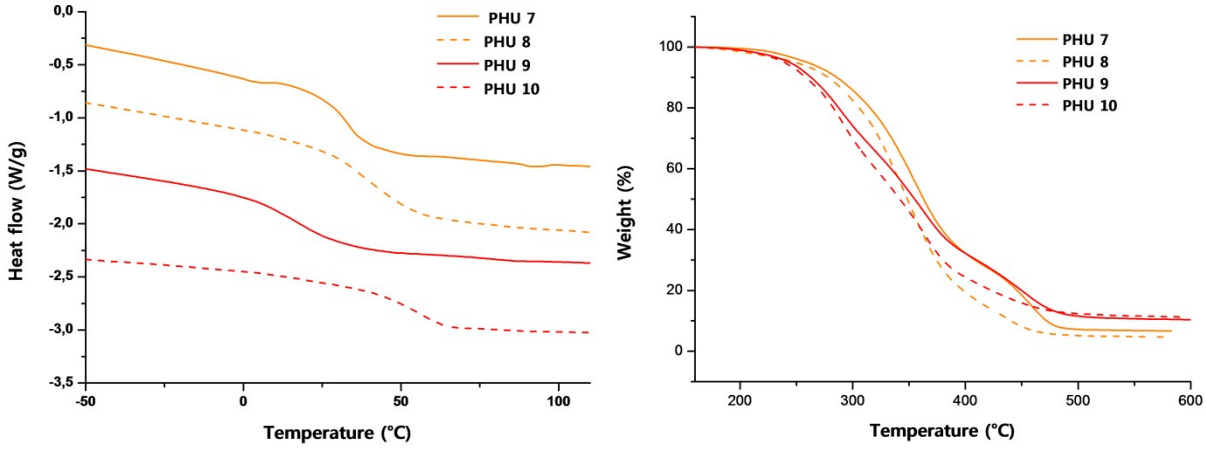
$$\%\ Amide = \frac{\int H_{amide}}{\int H_{urea} + \int H_{amide} + \int H_{urethane}} \quad (E')$$

$$\%\ Urethane = \frac{\int H_{urethane}}{\int H_{urea} + \int H_{amide} + \int H_{urethane}} \quad (E'')$$

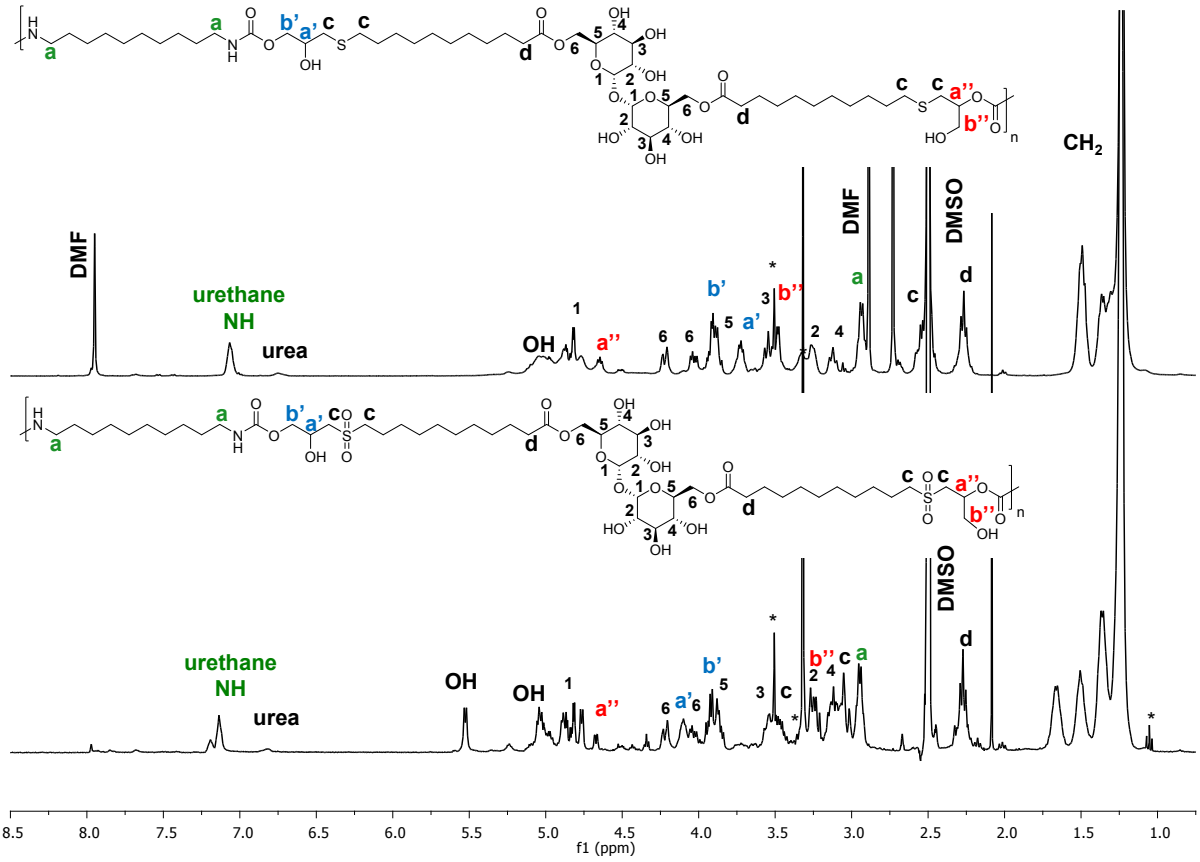
**ESI Formula 2 - Formula used for the calculation of % of urea, amide and urethane formed during kinetic measurements and polymerization, using $^1$H NMR integrations of labile protons ( $H_{urea}$, $H_{amide}$ and $H_{urethane}$) in DMSO-d6 .**




**ESI Figure 10 - Stacked $^{1}$H NMR spectra of (1) Und(ester)-bCC in $CDCl_3$ and (2) PHU 5 in DMSO-d6. (*chain ends).**




**ESI Figure 11 – DSC second heating cycles (10°C/min) PHU 7 to PHU 10 and corresponding TGA traces from 160 to 600 °C (after an isothermal procedure of 15 min at 160°C to remove the residual DMF).**




**ESI Figure 12 - Stacked $^{1}$H NMR spectra of (1) PHU 7 and (2) PHU 7-sulfone in DMSO-d6. (*chain ends).**