

SUPPLEMENTARY INFORMATION

Activated Lipidic Cyclic Carbonates for Non-Isocyanate Polyurethane Synthesis.

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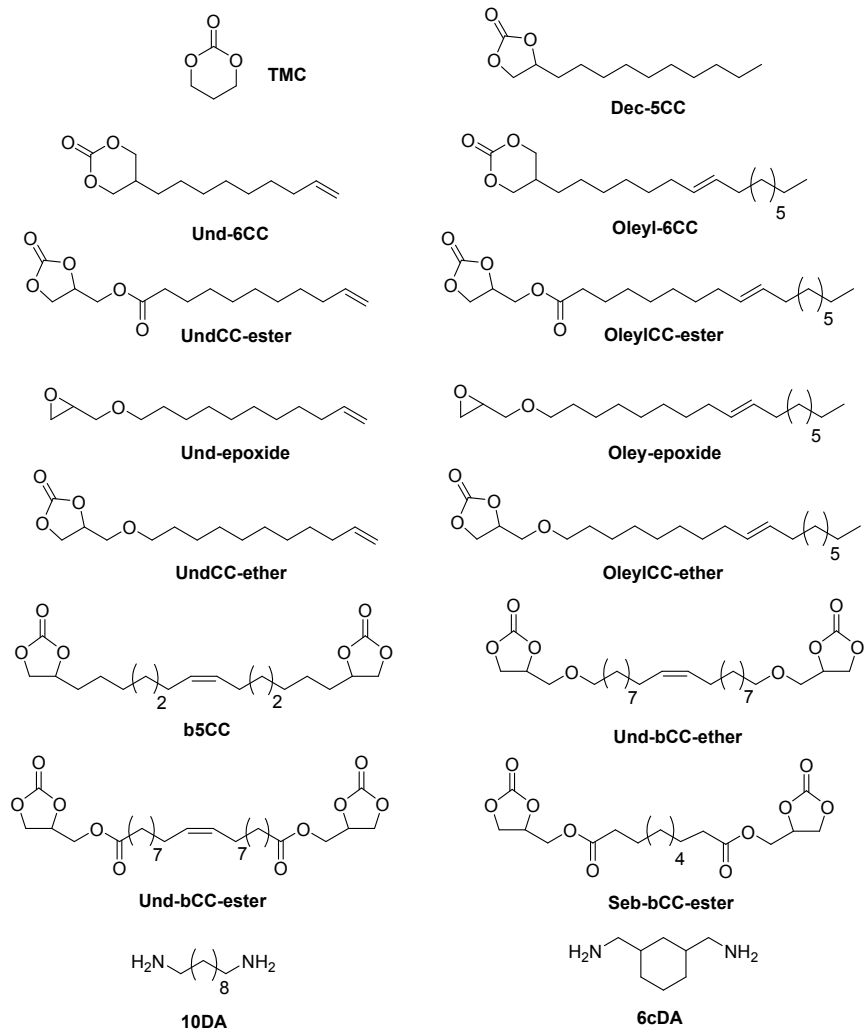
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2. Graphical data of kinetic measurements

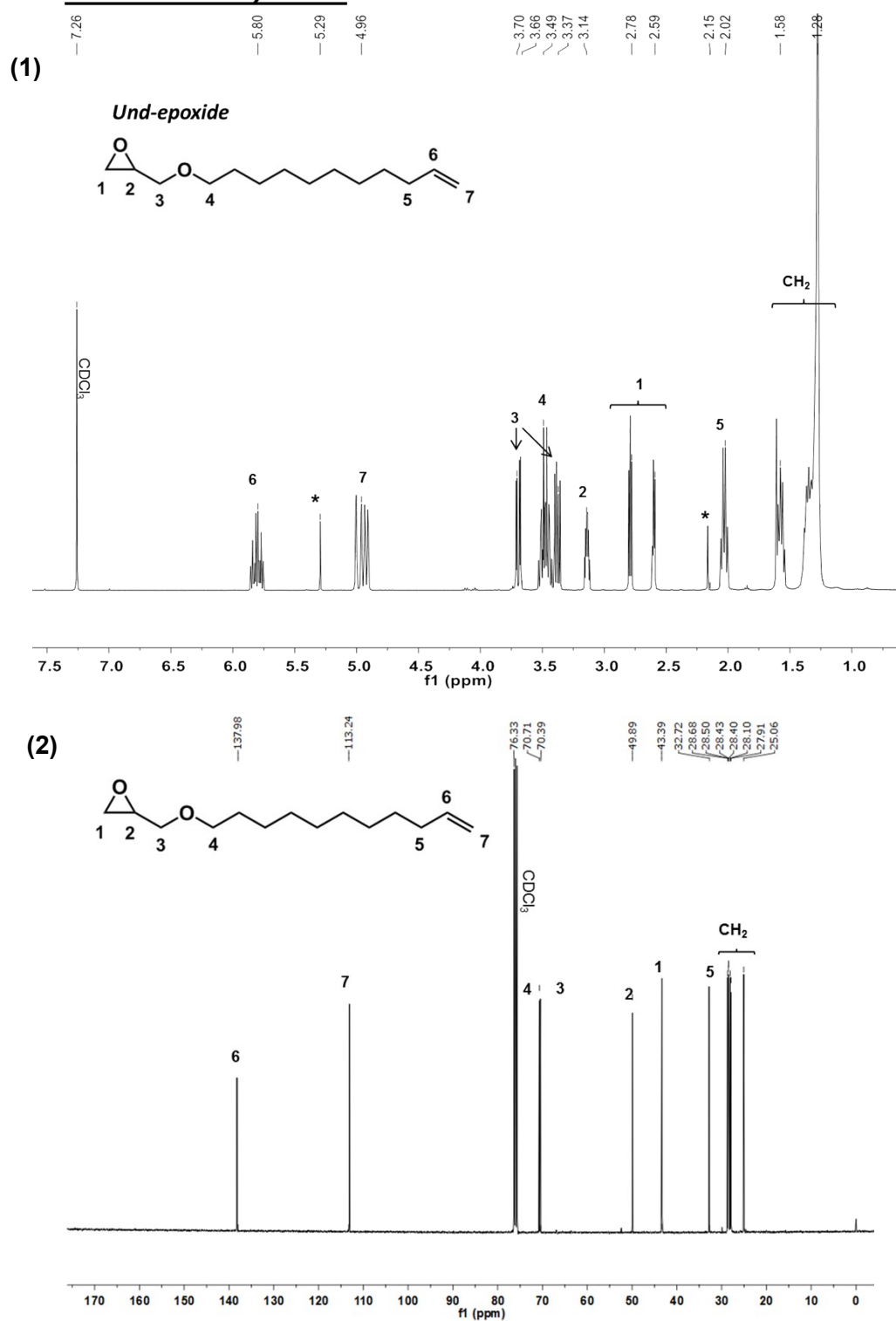
3. Graphical data of Poly(hydroxyurethane)s



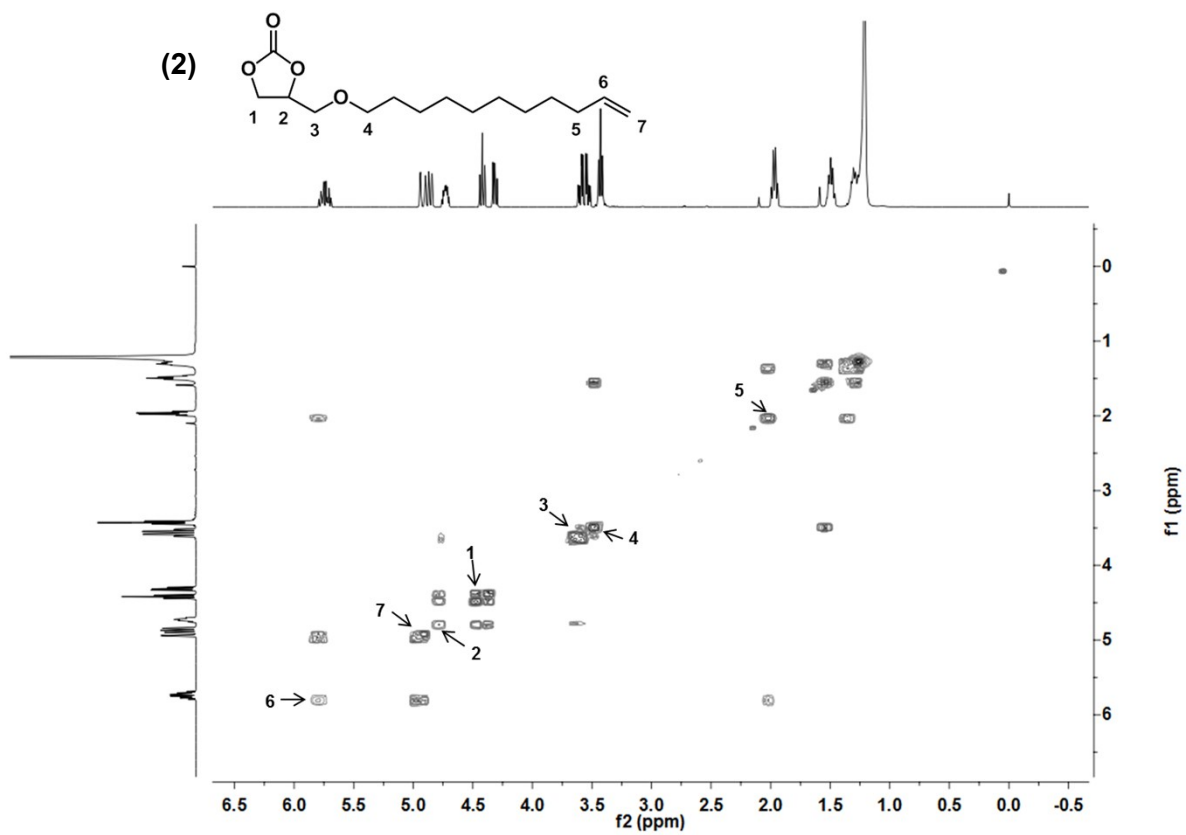
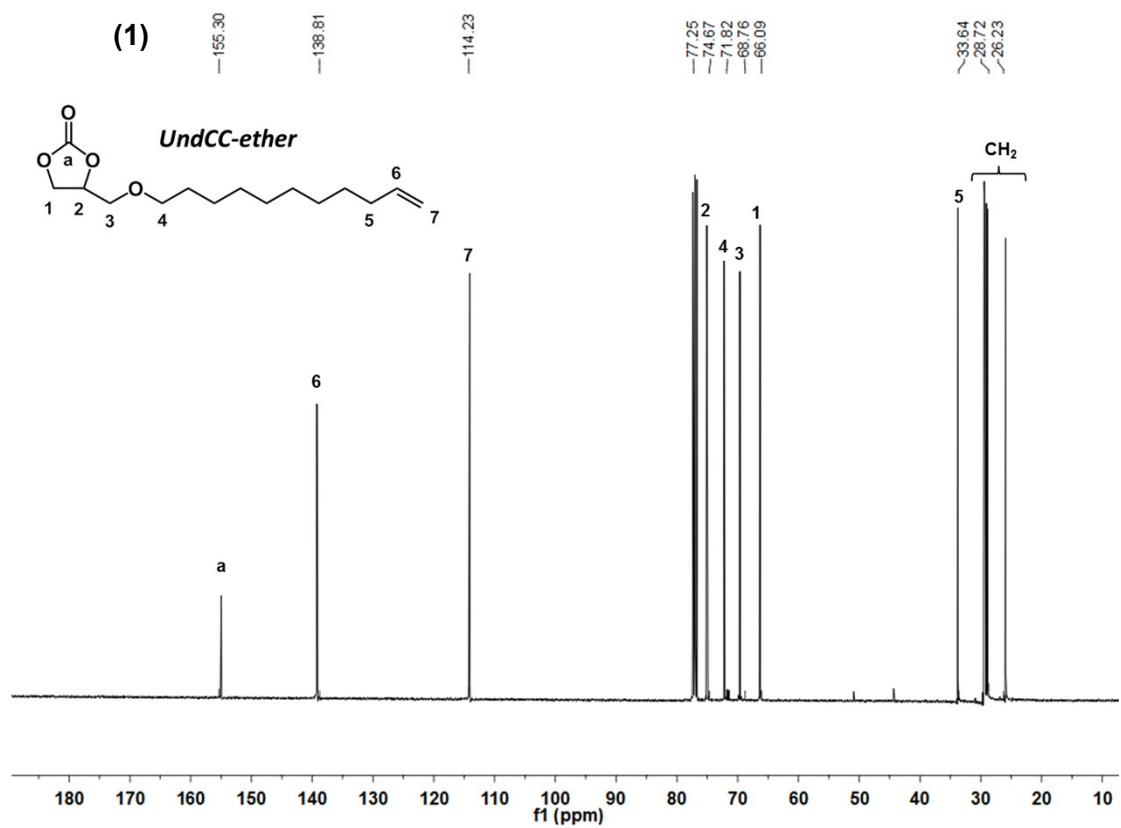
ESI Figure 1- Abbreviations and structures of epoxides, mono-cyclic carbonates, bis-cyclic carbonates and diamines.

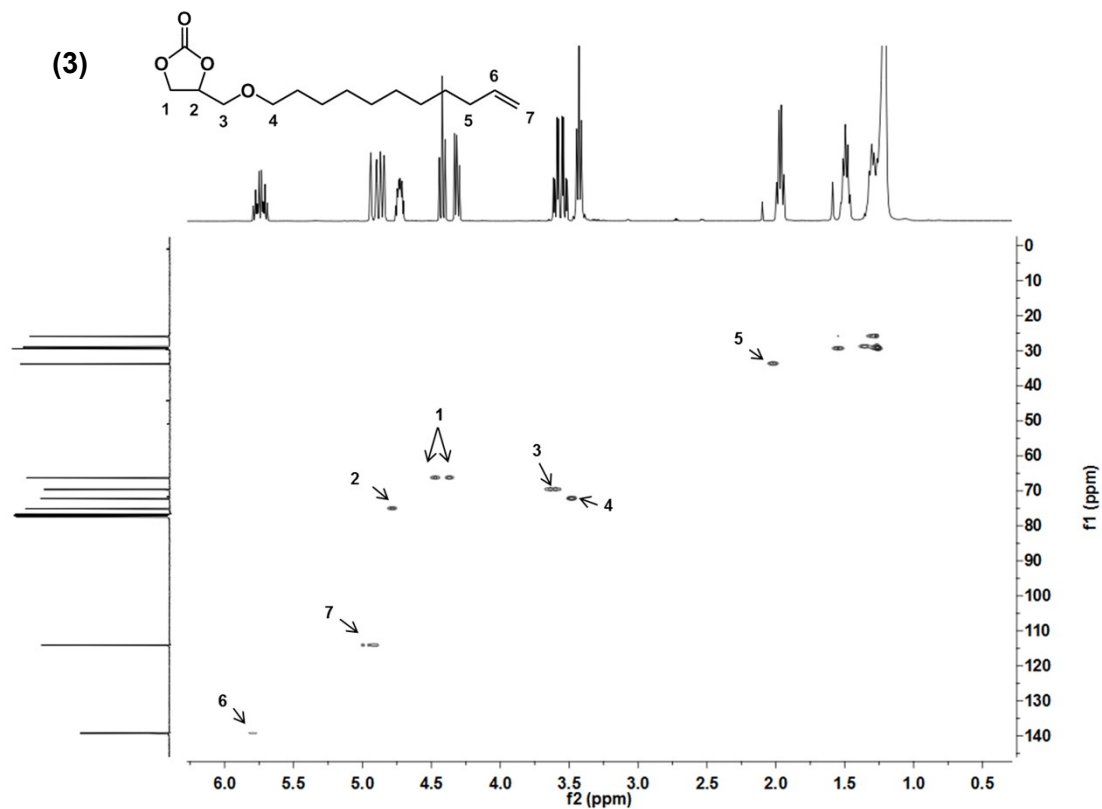
1. Graphical data of mono-cyclic carbonates and bis-cyclic carbonates

1.1. Und-bCC-ether synthesis

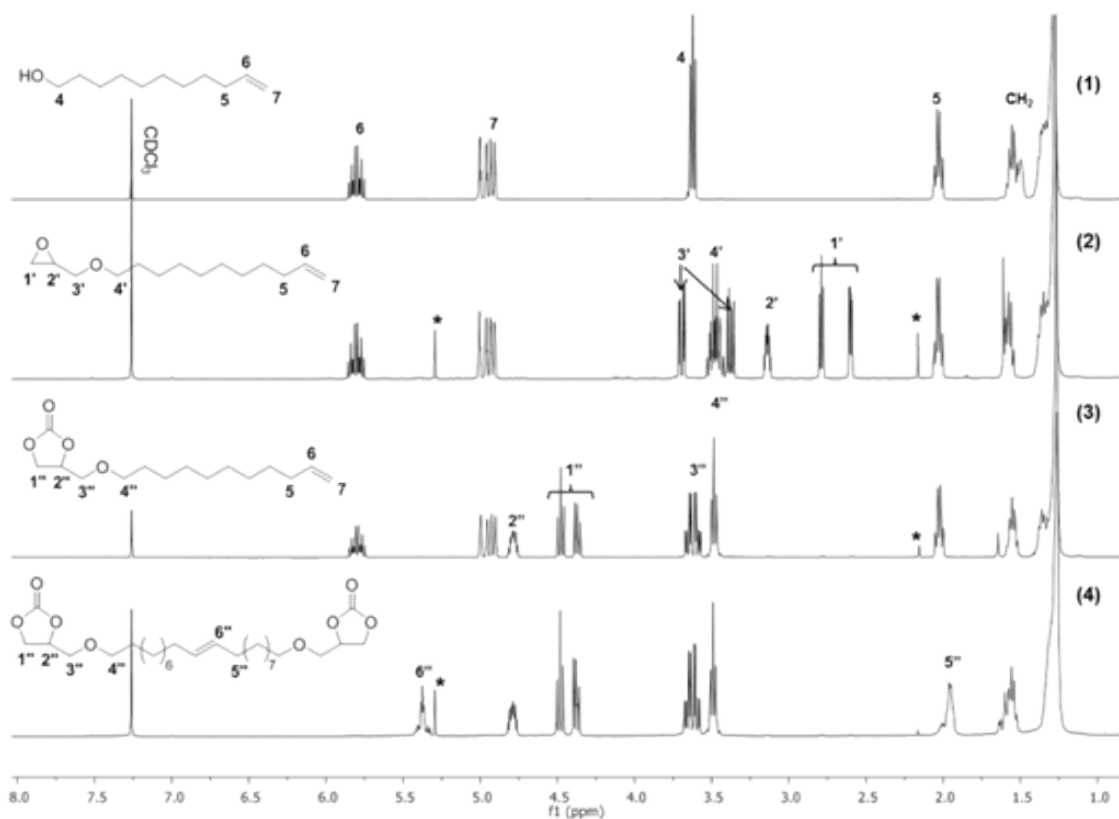


ESI Figure 2- Evidence of the formation of Und-epoxide: (1) ¹H NMR and (2) ¹³C NMR. (Analysis performed in CDCl₃.) (*: residual solvents)

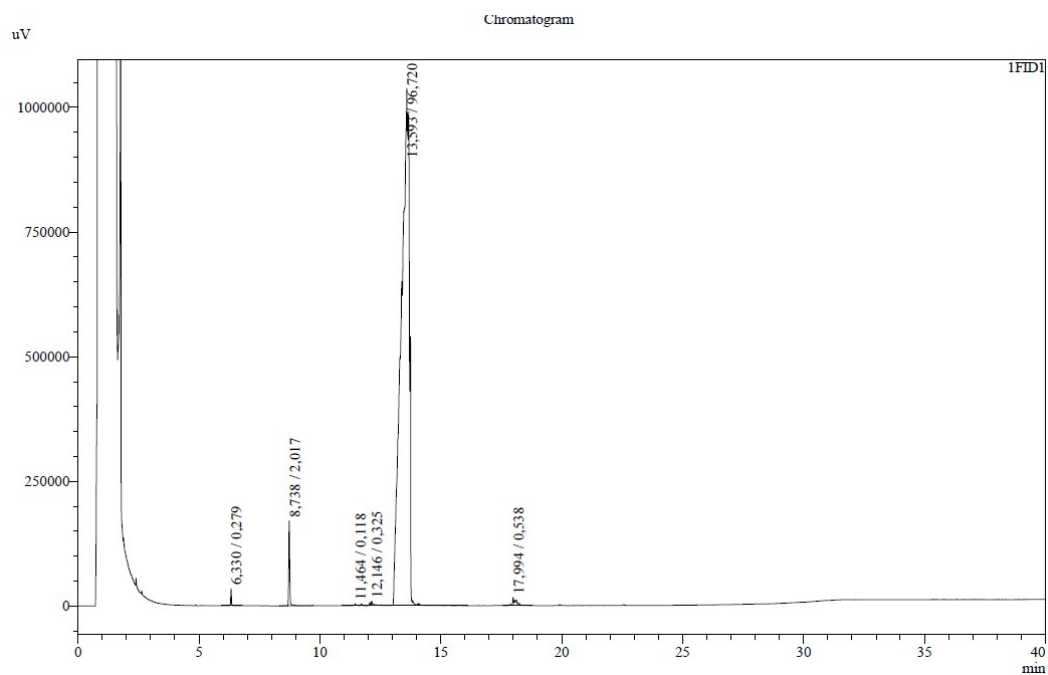




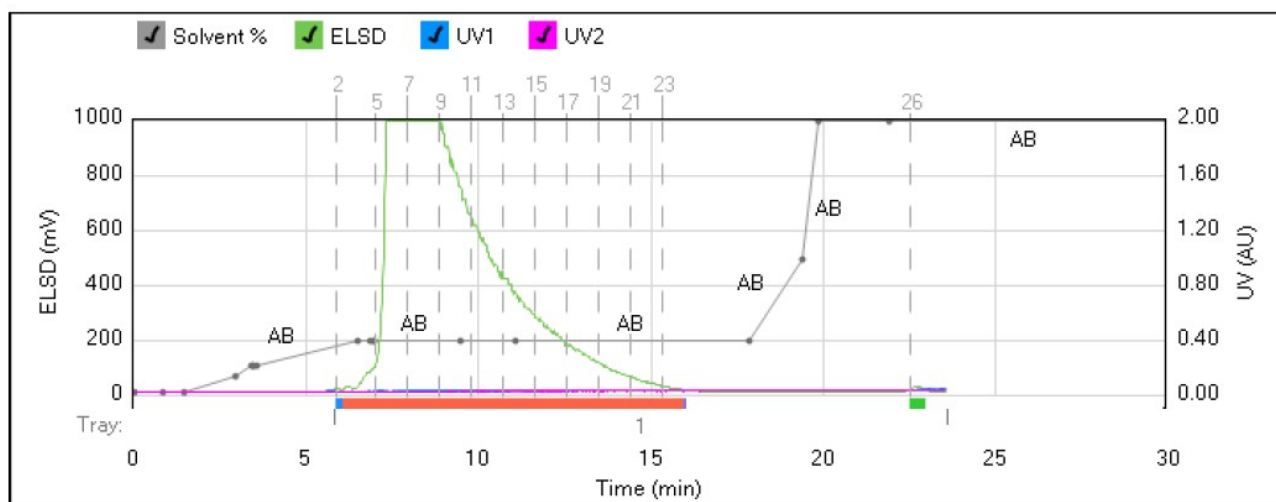
ESI Figure 3 - NMR analysis of purified UndCC-ether: (1) ^{13}C NMR, (2) ^1H - ^1H COSY NMR and (3) ^1H - ^{13}C HSQC-NMR. (Analysis performed in CDCl_3 .)



ESI Figure 4 - Stacked ^1H NMR spectra of (1) undecen-1-ol, (2) Und-epoxide, (3) UndCC-ether and (4) Und-bCC-ether (All analyses were performed in CDCl_3 .) (* : residual solvents)

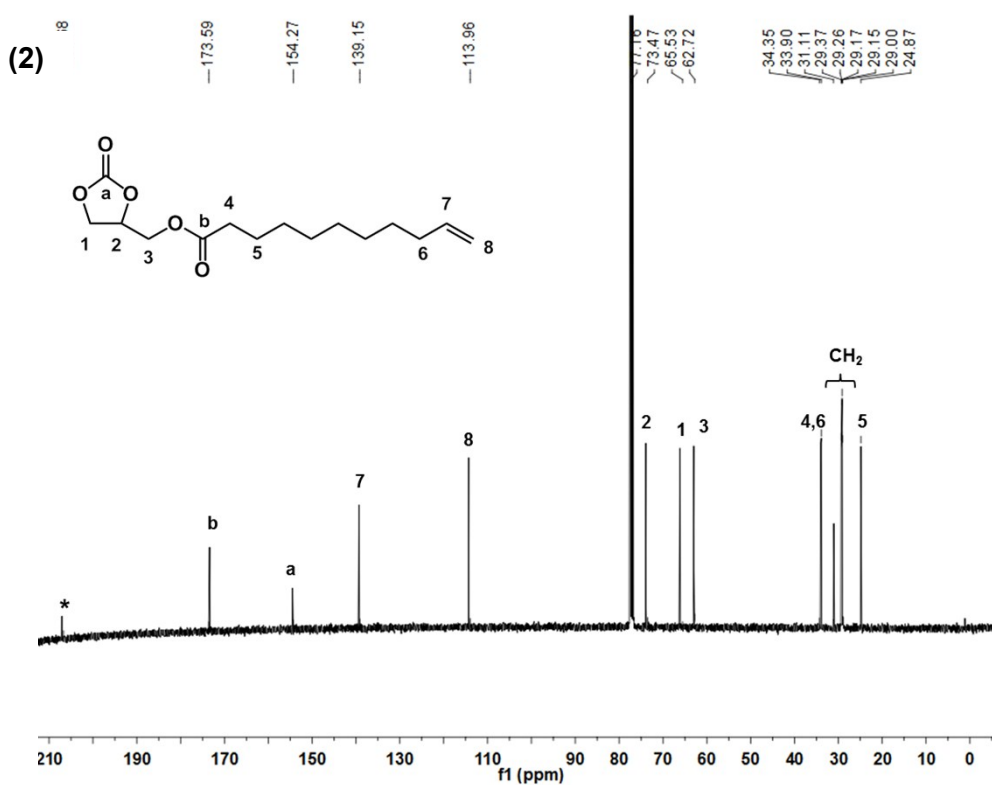
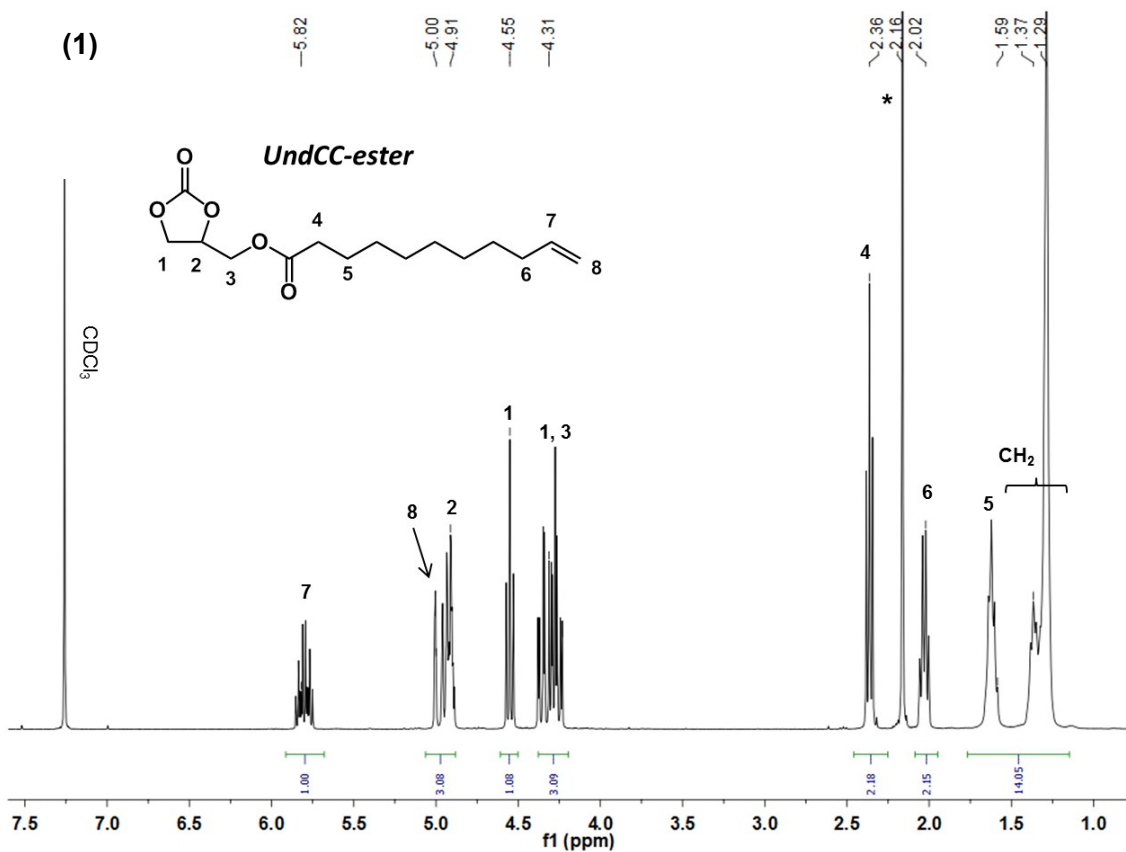


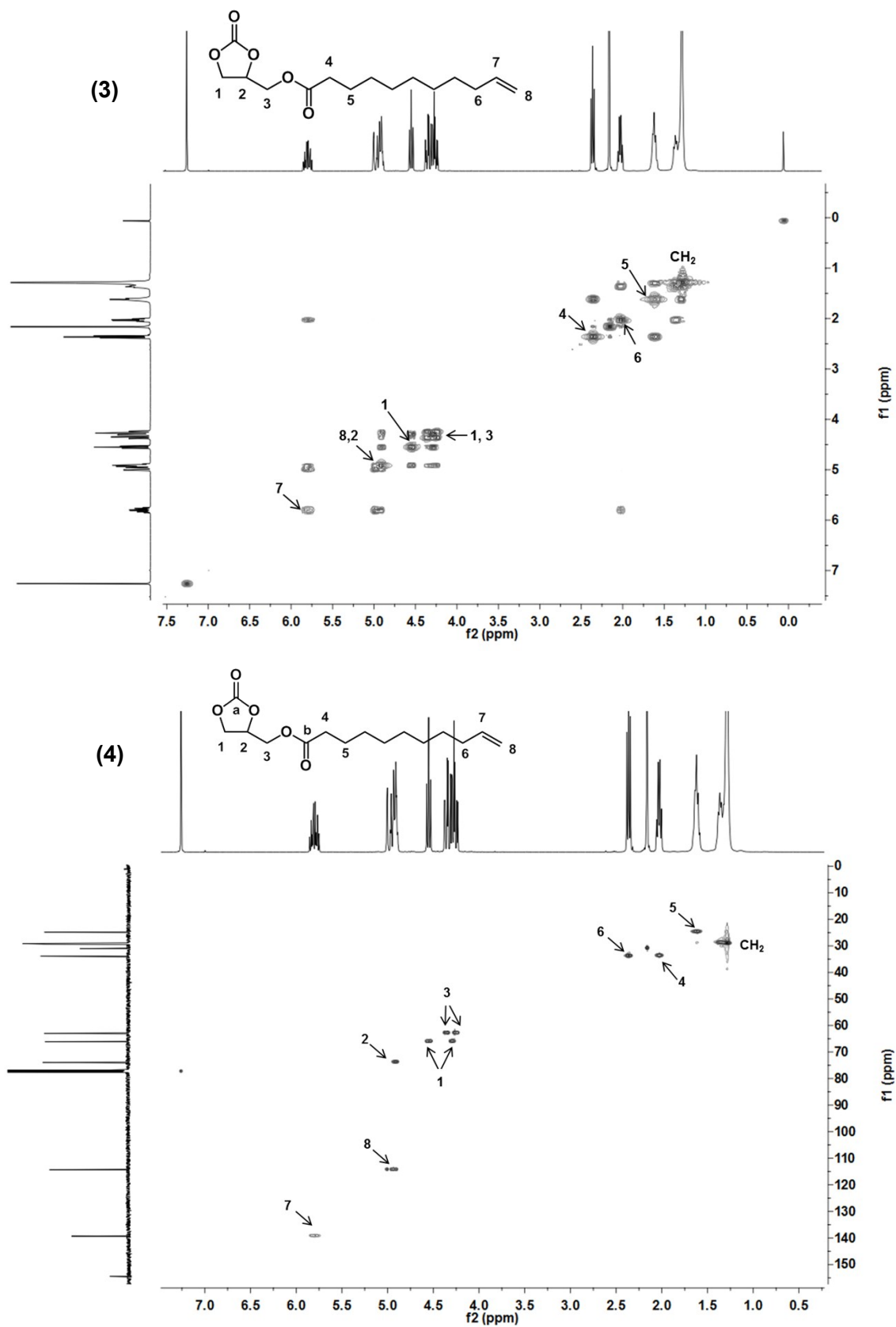
ESI Figure 5- Gas chromatography of UndCC-ether (96,7% purity).



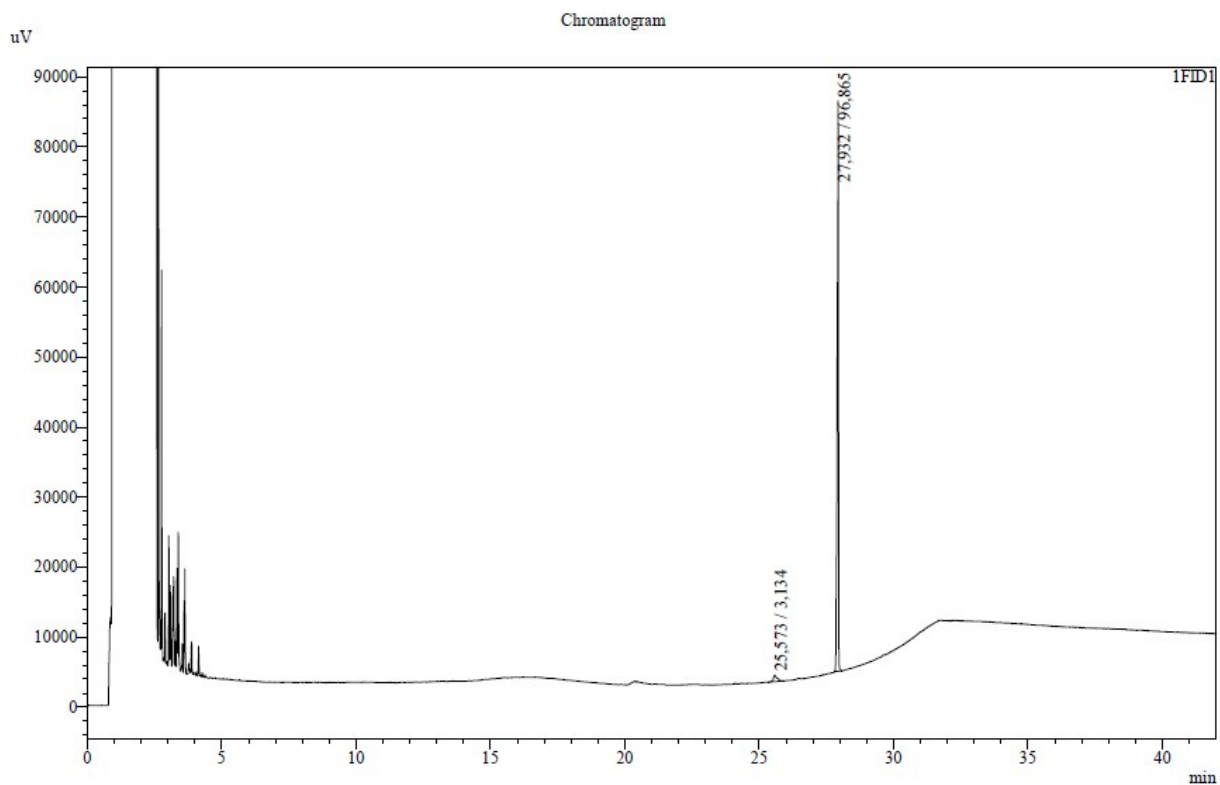
ESI Figure 6- Flash chromatogram of UndCC-ether.

1.2. Und-bCC-ester synthesis



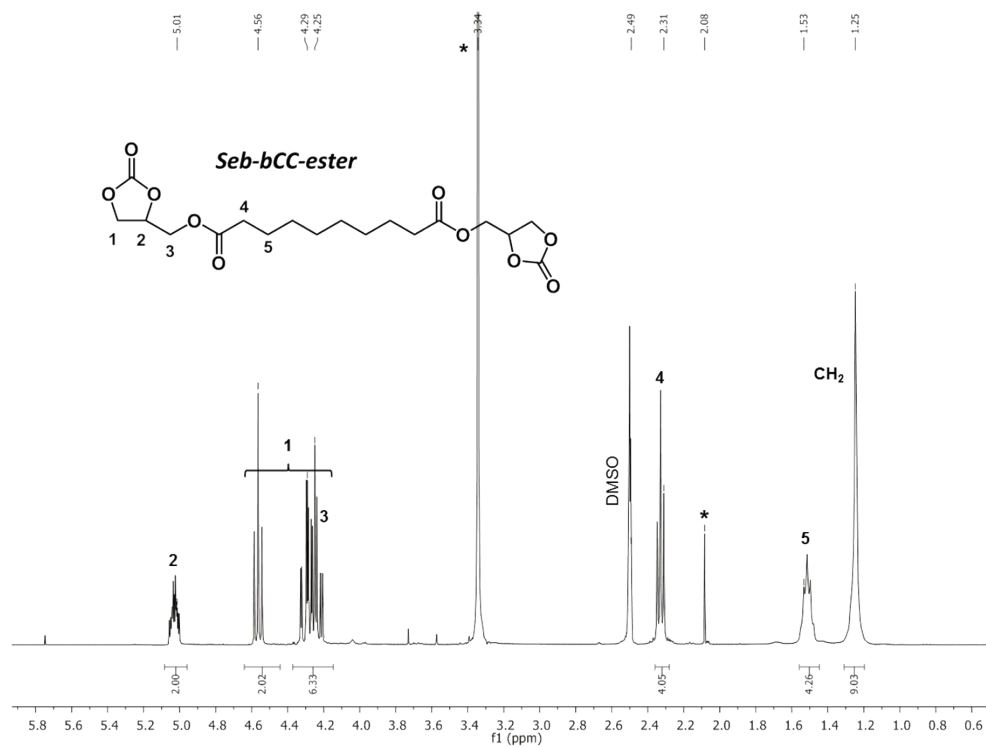


ESI Figure 7- NMR analysis of purified UndCC-ester (1) ^1H NMR, (2) ^{13}C NMR, (3) ^1H - ^1H COSY NMR and (4) ^1H - ^{13}C HSQC-NMR.
(Analysis performed in CDCl_3 .) (* : residual solvents)



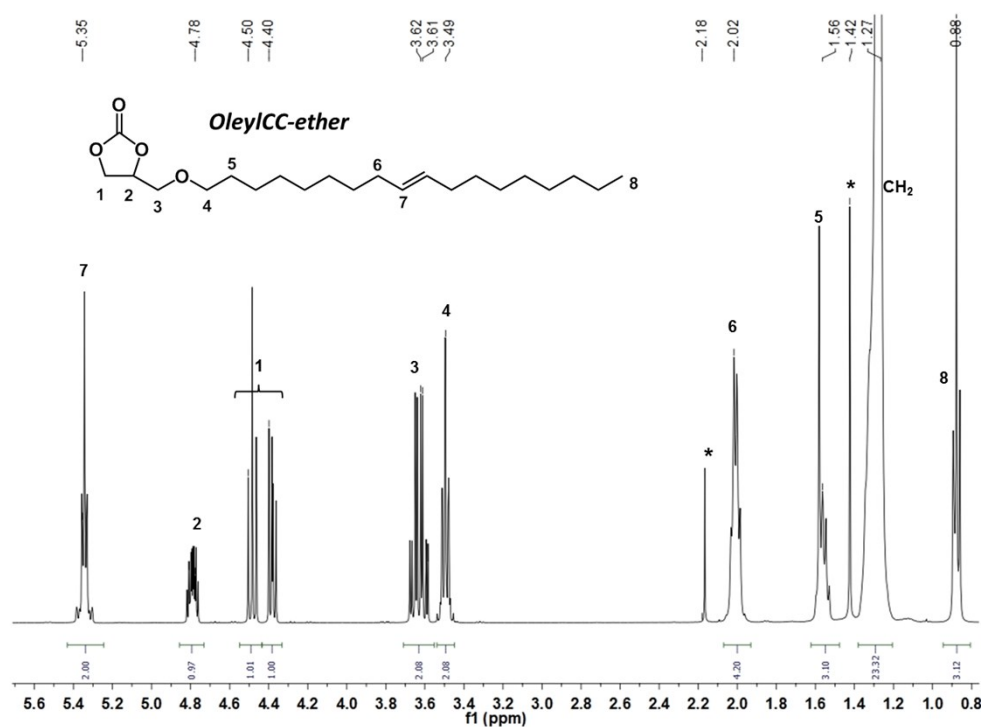
ESI Figure 8- Gas chromatography of UndCC-ester (96.8 % purity).

1.3. Seb-bCC-ester synthesis



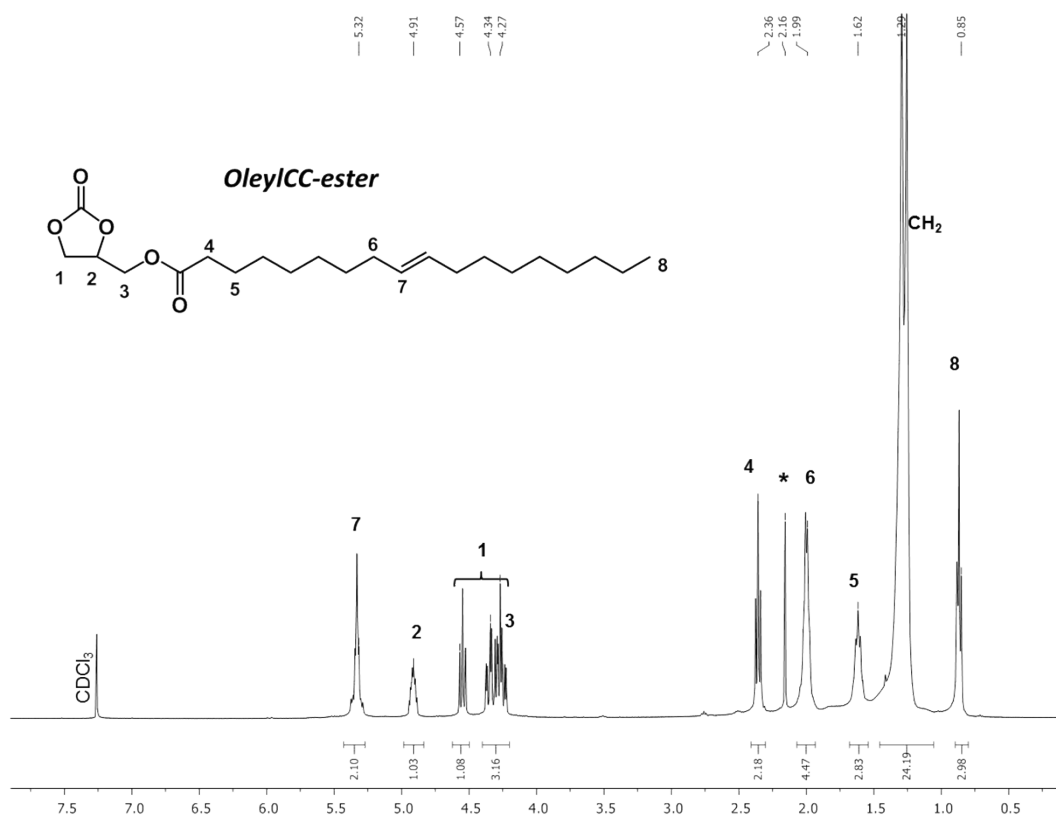
ESI Figure 9- ¹H NMR spectrum of Seb-bCC-ester (Analysis performed in DMSO-d₆.) (* : residual solvents)

1.4. OleylCC-ether synthesis



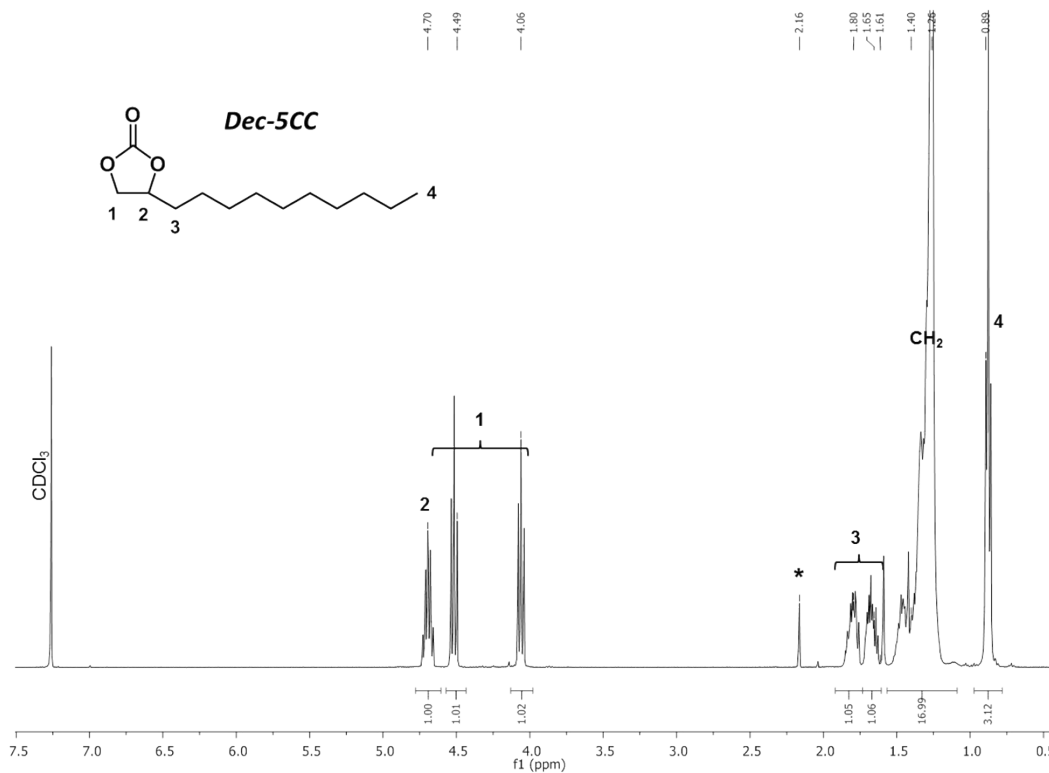
ESI Figure 10- ¹H NMR spectrum of OleylCC-ether (Analysis performed in CDCl₃.) (* : residual solvents)

1.5. OleylCC-ester synthesis



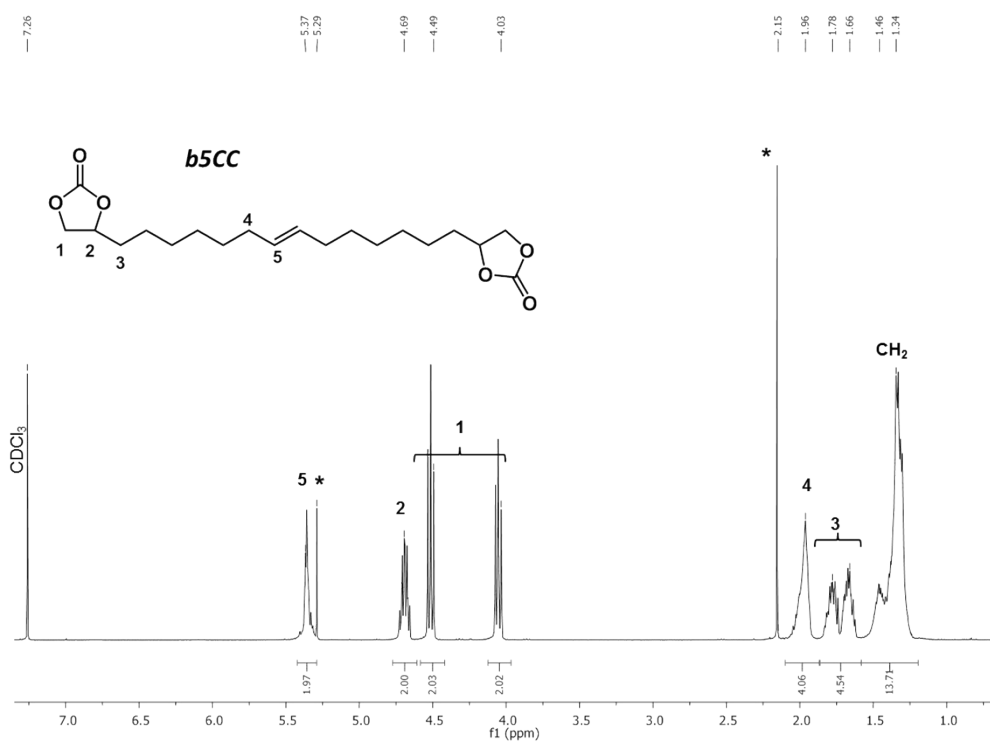
ESI Figure 11- ¹H NMR spectrum of OleylCC-ester (Analysis performed in CDCl₃.)

1.6. OleylCC-ester synthesis



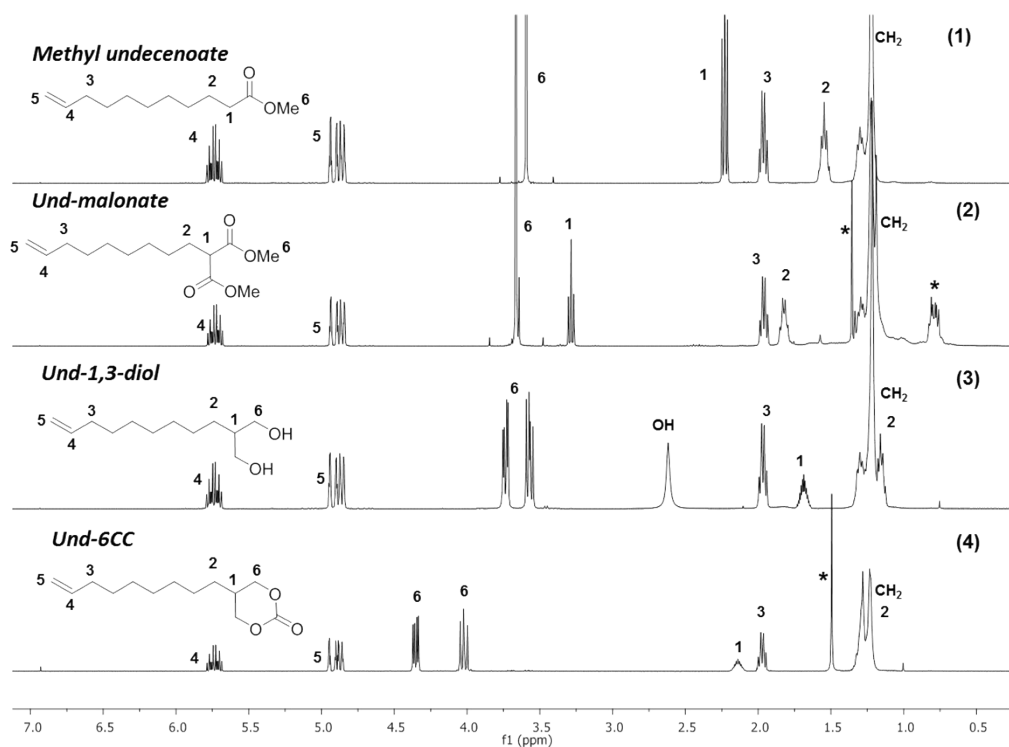
ESI Figure 12- ¹H NMR spectrum of Dec-5CC (Analysis performed in CDCl₃.) (* : residual solvents)

1.7. b5CC synthesis



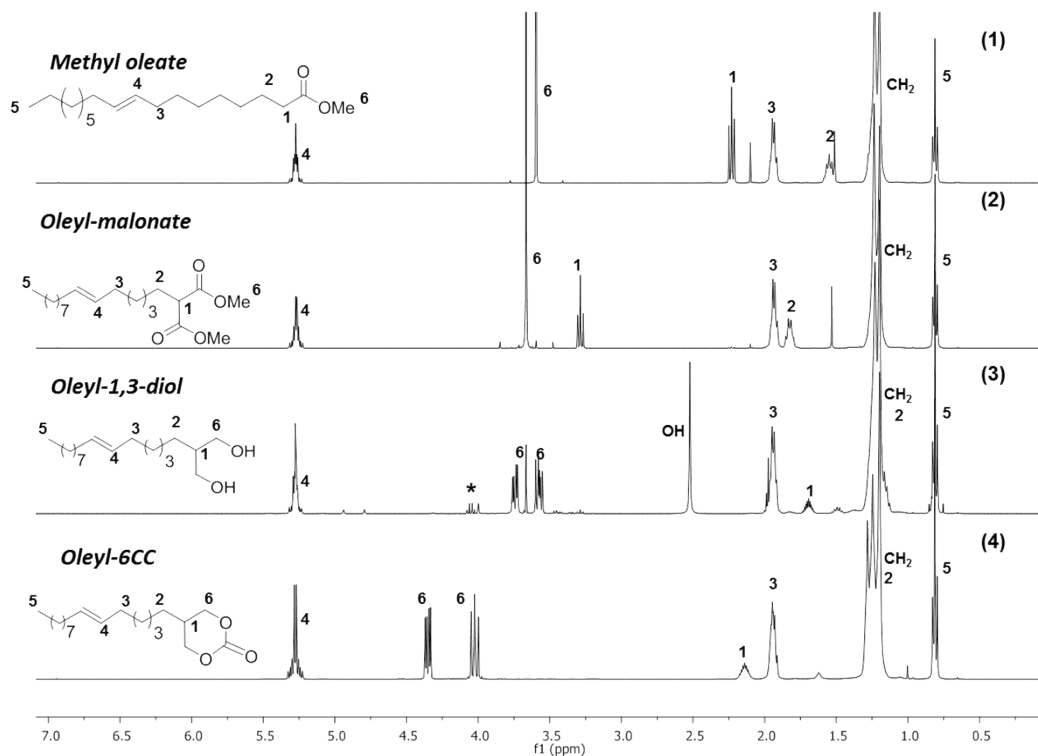
ESI Figure 13- ¹H NMR spectrum of b5CC (Analysis performed in CDCl₃.)(* : residual solvents)

1.8. Und-6CC synthesis



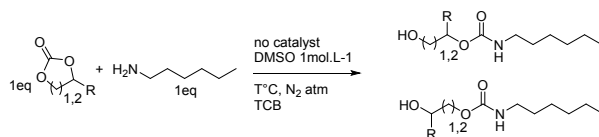
ESI Figure 14- Stacked ^1H NMR spectra of (1) methyl undecenoate, (2) Und-malonate, (3) Und-1,3-diol and (4) Und-6CC. (All analyses were performed in CDCl_3)(* : residual solvents)

1.9. Oleyl-6CC synthesis

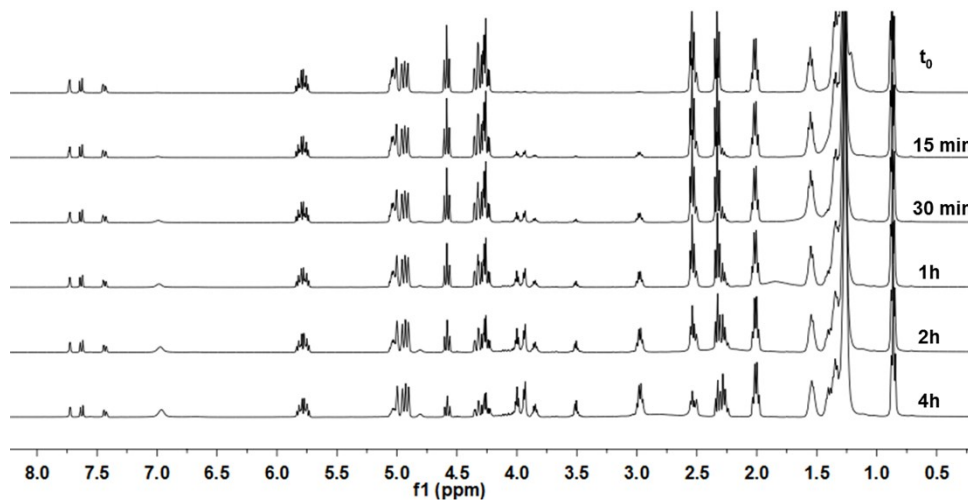


ESI Figure 15- Stacked ^1H NMR spectra of (1) methyl olate, (2) Oleyl-malonate, (3) Oleyl-1,3-diol and (4) Oleyl-6CC. (All analyses were performed in CDCl_3)(* : impurities).

2. Graphical data of kinetic measurements

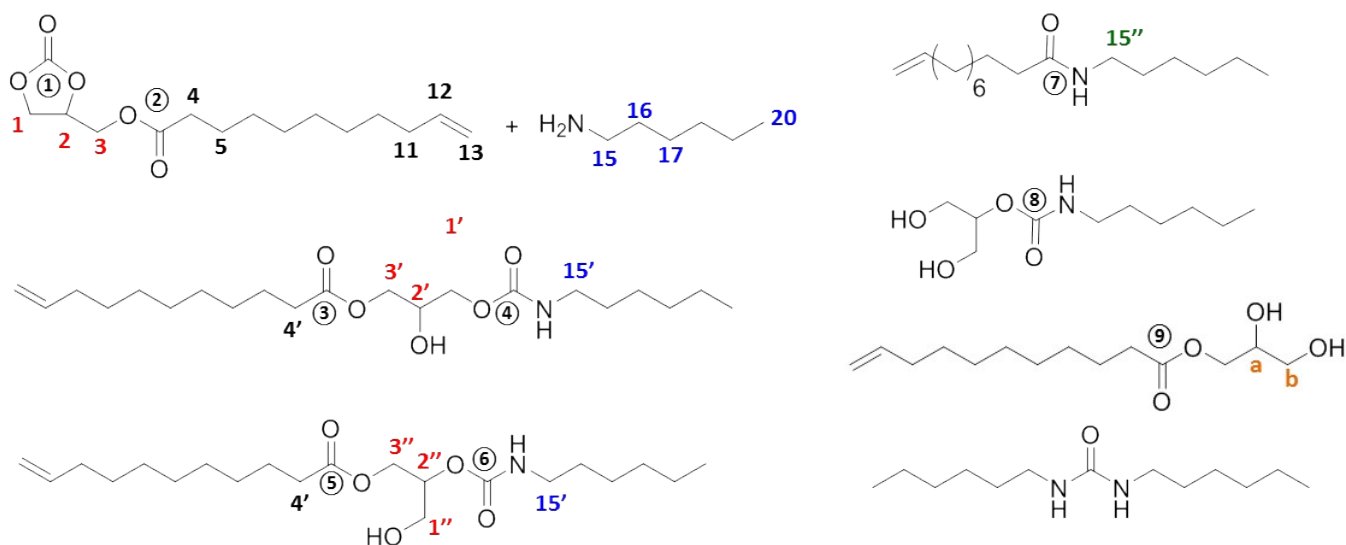


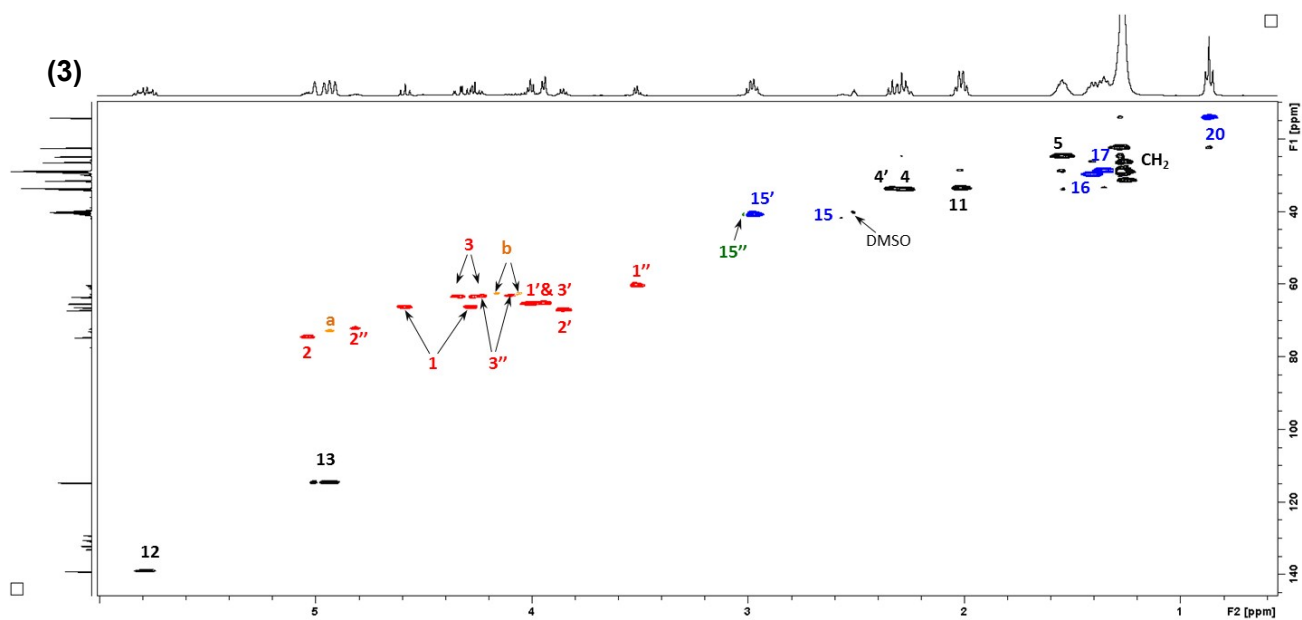
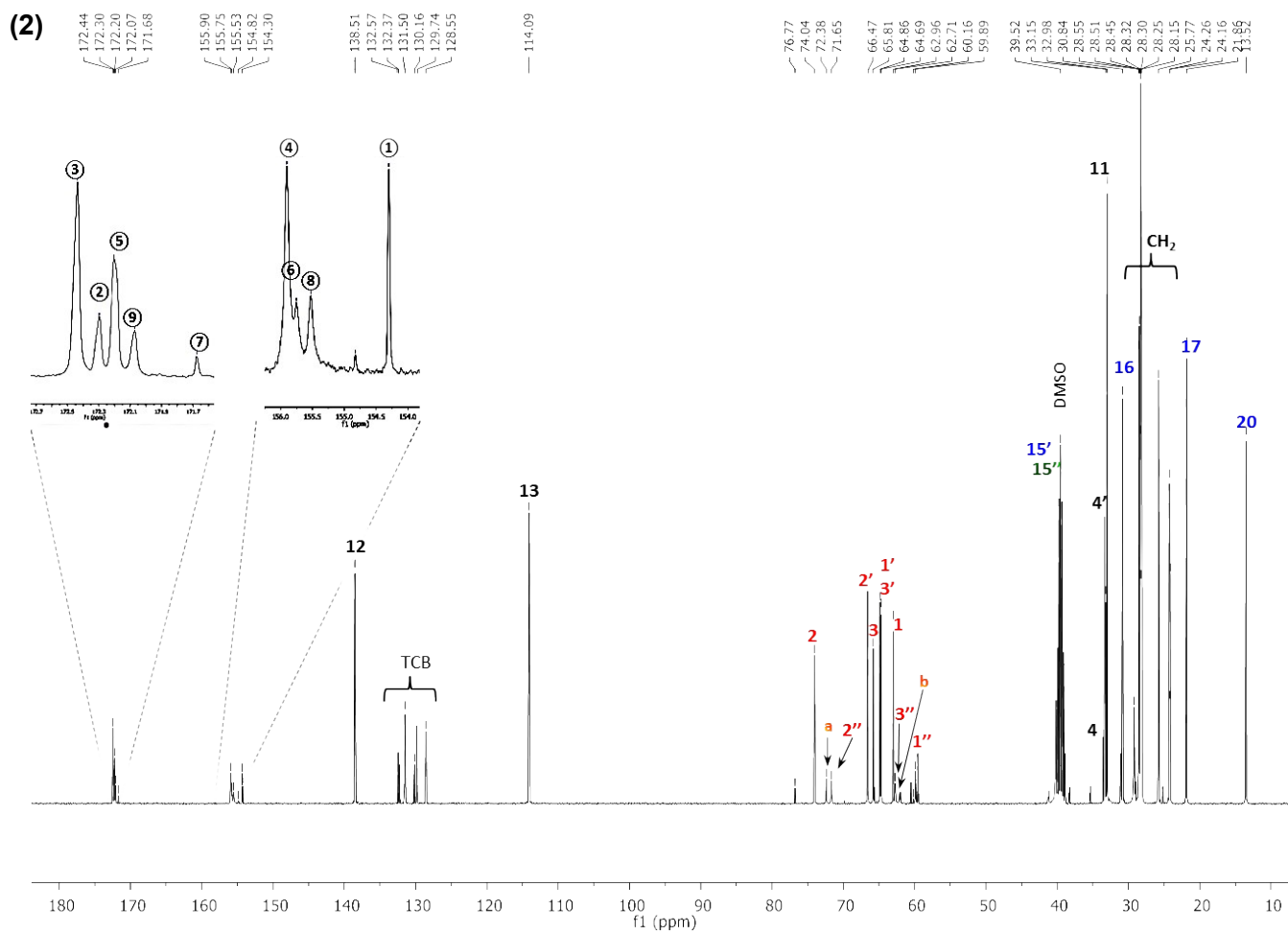
ESI Scheme 1- Model reaction of various cyclic carbonates with hexylamine in different conditions.



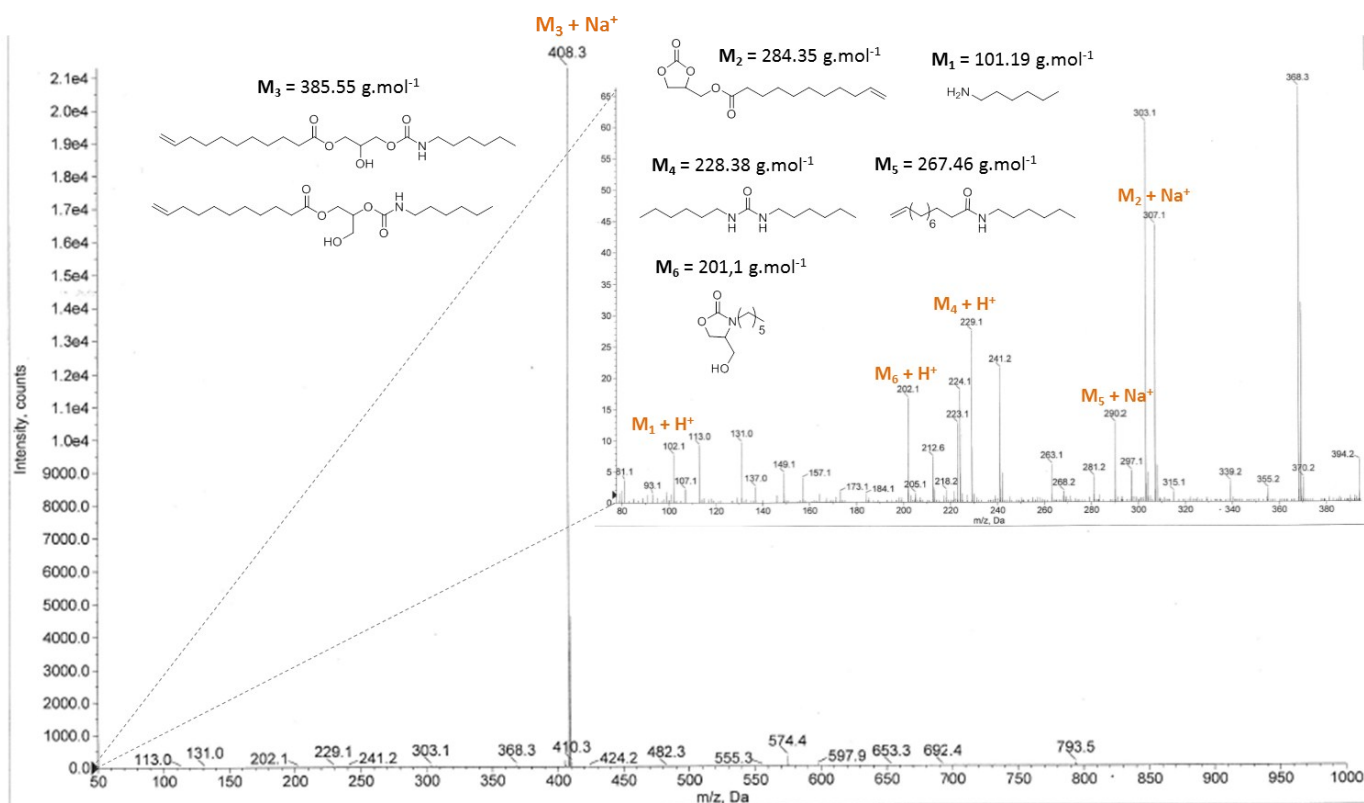
ESI Figure 16- Stacked ^1H NMR monitoring of the reaction between UndCC-ester and hexylamine with a ratio 1:1, at 50°C in DMSO-d_6 at 1 mol.L^{-1} .

(1)

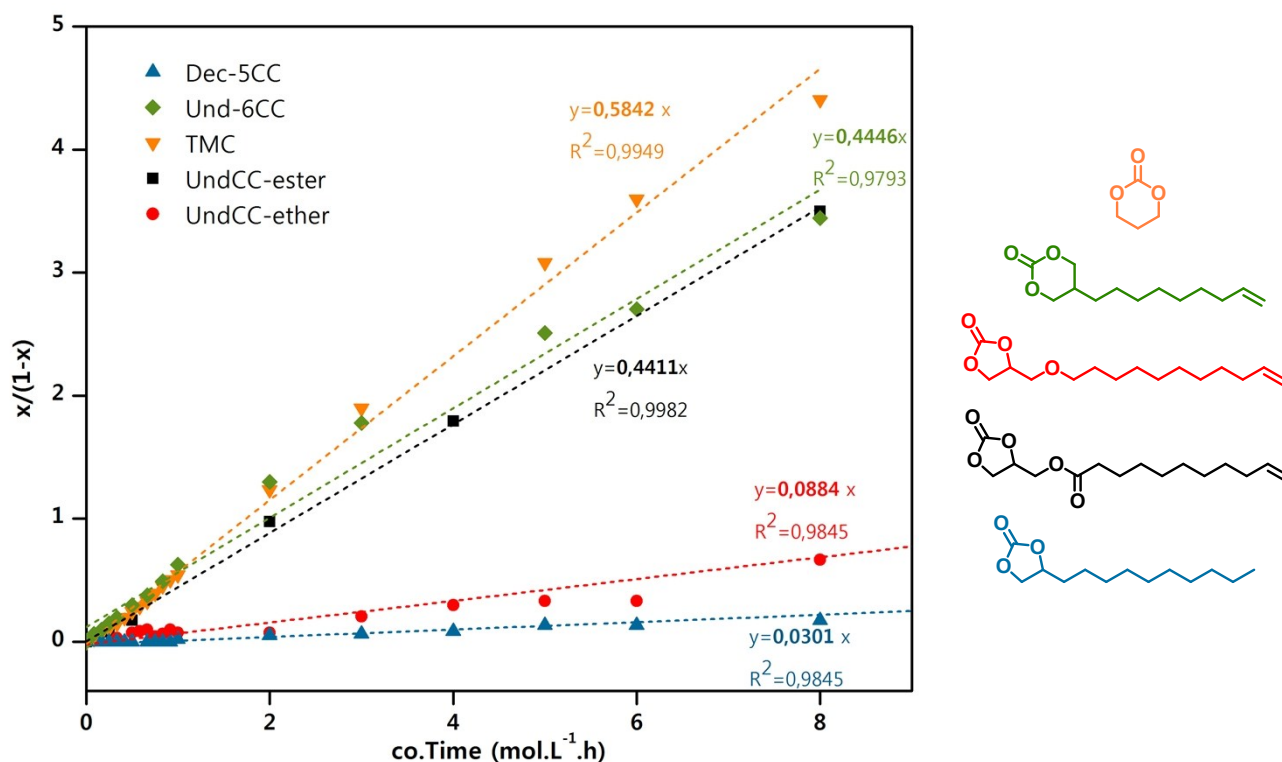




ESI Figure 17 – (1) Scheme of the different molecules identified by (2) ^{13}C and (3) ^1H - ^{13}C HSQC during the model reaction between UndCC-ester and hexylamine (ratio 1:1, in DMSO- d_6 at 50°C).



ESI Figure 18 – ESI analysis of the reaction between UndCC-ester and hexylamine at 50°C in bulk, with a ratio 1:1.



ESI Figure 19- 2nd order Kinetic law: Time-(x/(1-x)) relationships for the reactions of cyclic carbonates with hexylamine, at 50°C and in DMSO-d₆ (1 mol.L⁻¹).

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

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

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

$$\text{or } [CC] = C_0 - C_0x = C_0(1-x) \quad (E4)$$

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

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

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

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

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

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

$$k_{app} = A_{app} e^{\frac{-E_a}{RT}}$$

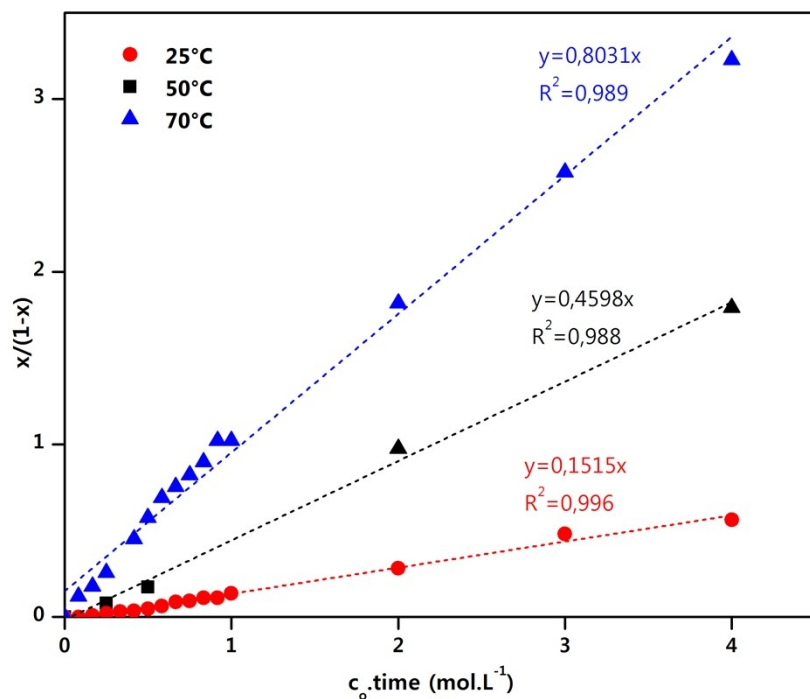
Note : The activation energy is not the only parameter to take into account in kinetic analysis. In the Arrhénius equation, A_{app} is the pre-exponential factor that indicates the rate of efficient collision. The bigger A_{app} , the more reactive the monomer is. A_{app} was calculated for 5CC and 6CC synthesized by Endo and coll.(reference 13) and for **UndCC-ester**.

A_{app} (6CC) = 13570 L.mol⁻¹.h⁻¹;

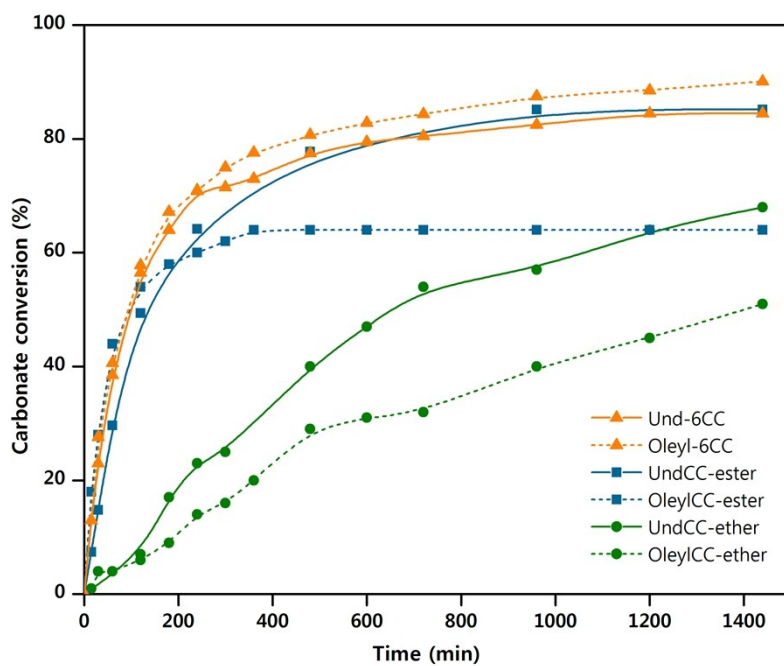
A_{app} (5CC) = 1.72 L.mol⁻¹.h⁻¹;

A_{app} (**UndCC-ester**) = 10282 L.mol⁻¹.h⁻¹.

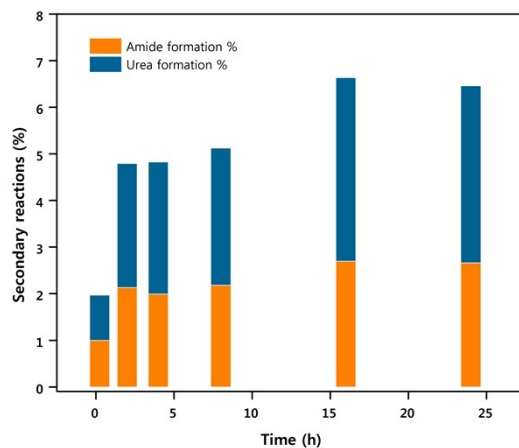
ESI Formula 3 – Arrhénius equation and calculation of A_{app} for 5CC, 6CC (Endo and coll.) and **UndCC-ester**.



ESI Figure 20 - Effect of the temperature on the kinetic of the reactions between UndCC-ester and hexylamine. (1 mol.L⁻¹ in DMSO-d₆, ratio 1:1)



ESI Figure 21 - Chain length effect on the kinetic of the reactions between reactive cyclic carbonates and hexylamine (1 mol.L⁻¹ in DMSO-d₆, ratio 1:1, 25°C)



ESI Figure 22 - Proportions of side reactions obtained during the reactions between UndCC-ester and hexylamine over 24h (1 mol.L⁻¹ in DMSO-d₆, 50°C, ratio 1:1).

3. Graphical data of Poly(hydroxyurethane)s

PHU-1[b5CC + 10DA] : ¹H NMR (DMSO-d₆, 25°C, 400 MHz) δ (ppm): (see ESI[†]). IR (cm⁻¹): 3600-3100, 2920, 2848, 1685, 1532.

PHU-2 [Und-bCC-ether + 10DA]: ¹H NMR (DMSO-d₆, 25°C, 400 MHz) δ (ppm): (see ESI[†]). IR (cm⁻¹): 3600-3100, 2928, 2853, 1663, 1505, 1093.

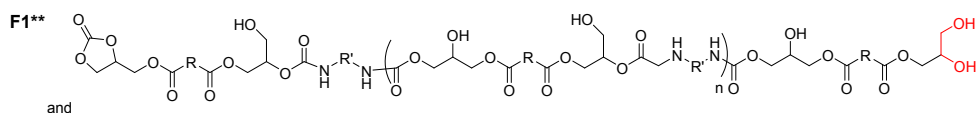
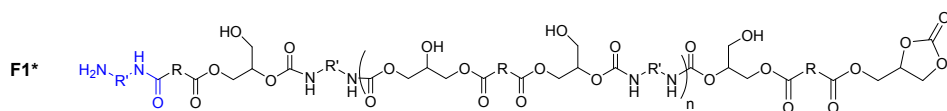
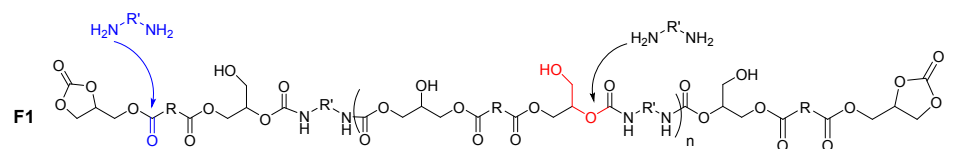
PHU-3 [Und-bCC-ester + 10DA]: ¹H NMR (DMSO-d₆, 25°C, 400 MHz) δ (ppm): (see ESI[†]). IR (cm⁻¹): 3600-3100, 2923, 2848, 1709, 1663, 1545.

PHU families	Description	Reaction	PHU 1 (M _{unit} = 712.49 g.mol ⁻¹)
F1	C-(C _{n-1} -A _n)-C	Polyaddition : urethane formation	n*(M _{unit})+M _C +M _{Na}
F2	C-(C _n -A _{n-1})-A	Polyaddition : urethane formation	n*(M _{unit})+M _A +M _{Na}
F3	A-(C _n -A _n)-C	Polyaddition : urethane formation	(n+1)*(M _{unit})+M _{Na}
F4	C-(C _{n-1} - U ^A -A _n)-C	1 Urea linkage within the chain	n*(M _{unit})+M _C +M _{urea} +M _{Na}
F5	C-(C _{n-1} - U ^A -U ^A -A _n)-C	2 Urea linkages within the chain	n*(M _{unit})+M _C + 2M _{urea} +M _{Na}
F1*	A _{amide} -(C _{n-1} -A _n)-C	Transamidification at the chain end or by cyclisation	n*(M _{unit})-M _{GC} +M _{amine} +M _{Na}
F3*	A-(C _n -A _n)-C _{GC}	Transamidification intra-chain	(n+1)*(M _{unit})+ M _{GC} +M _{Na}
F1**	C-(C _{n-1} -A _n)-C ^{OH}	Urea formation intra-chain resulting in the formation of hydroxyl groups at the chain-end	n*(M _{unit})+M _C -M _{C=O} +2M _H +M _{Na}
	C ^{OH} -(C _{n-1} -A _n)-C ^{OH}		n*(M _{unit})+M _C -2M _{C=O} +4M _H +M _{Na}
F3**	U ^A -(C _n -A _n)-C	Urea formation at the chain end	(n+1)*(M _{unit})+M _{urea} +M _{Na}

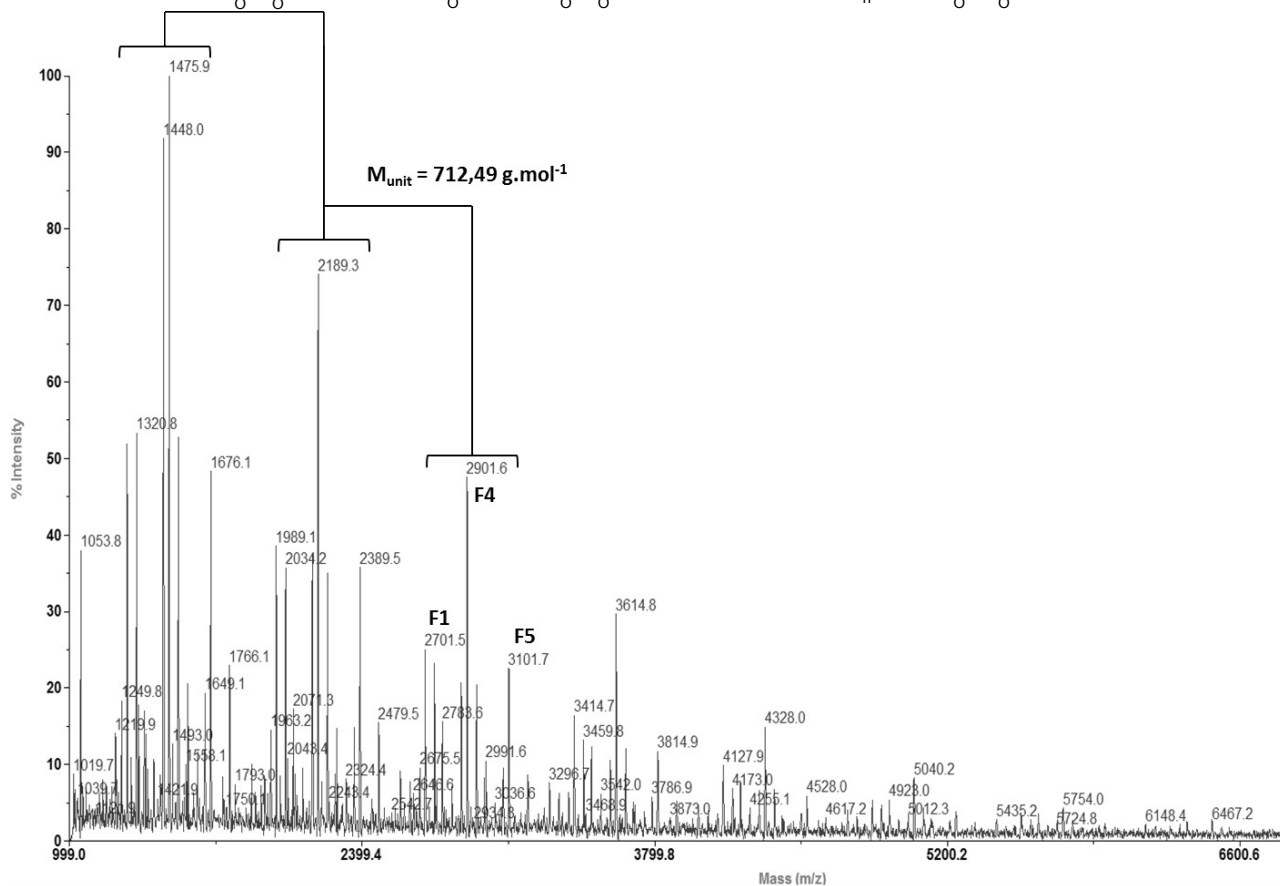
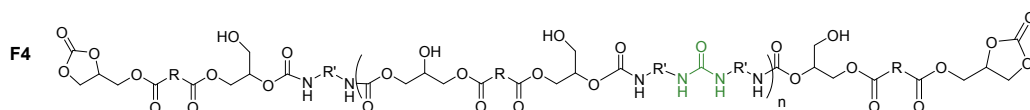
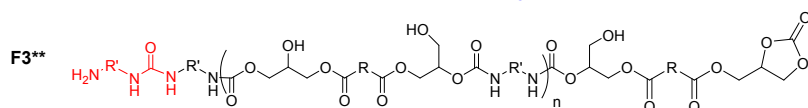
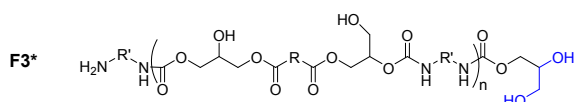
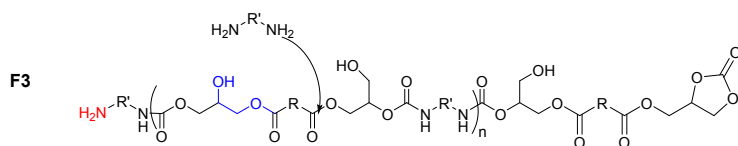
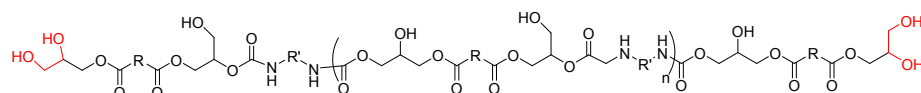
*amide formation

** urea formation

Abbreviations are as followed: C=Und-bCC-ester with M_C= 540.29 g.mol⁻¹; A=decane-1,10-diamine with M_A= 172.19 g.mol⁻¹; U^A=urea linkage on A with M_{urea}= M_A+M_{C=O}-2M_H= 198.19 g.mol⁻¹; GC=glycerol carbonate and equivalents in mass , with M_{GC}= 118.3 g.mol⁻¹; C^{OH} : chain end produced by urea formation : M_{COH}= M_C-M_{C=O}+2M_H=514.29 g.mol⁻¹



and



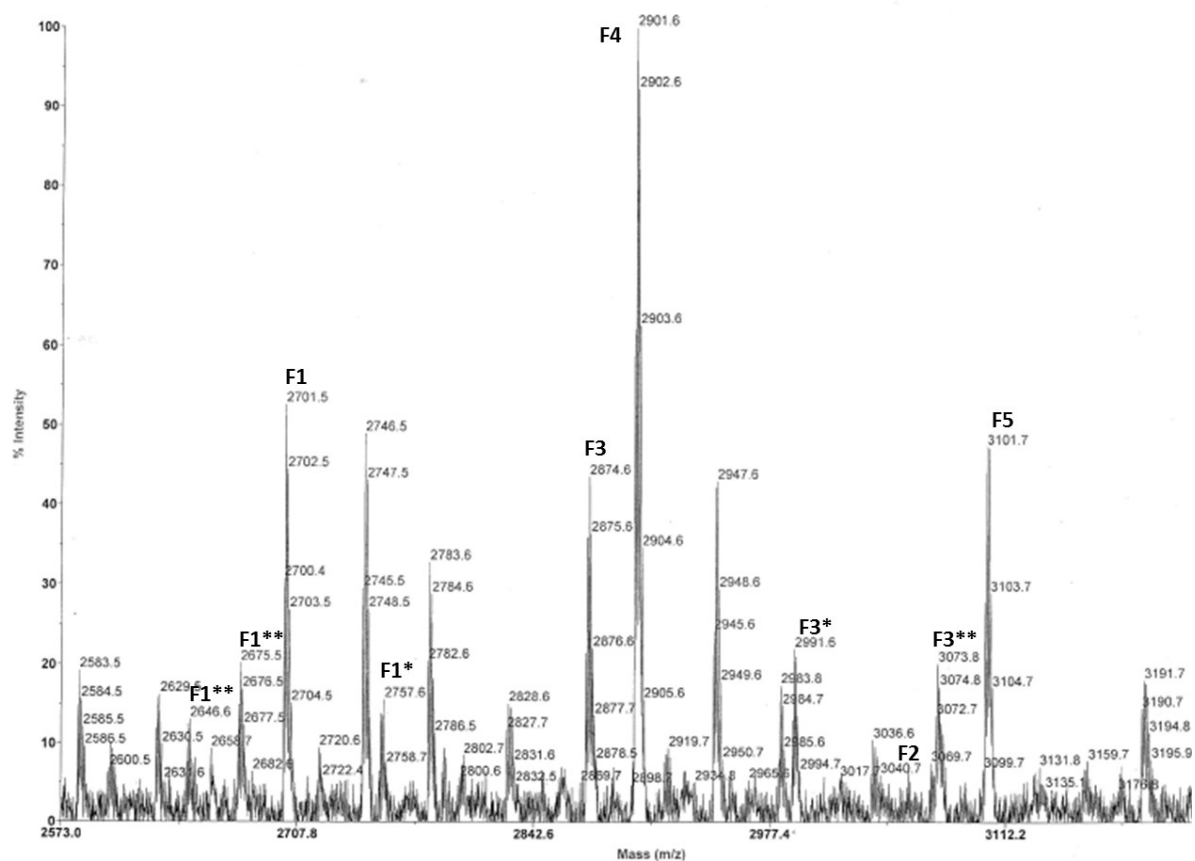


Figure 23 – Different PHU families in the sample PHU1 visible in MALDI-TOF MS

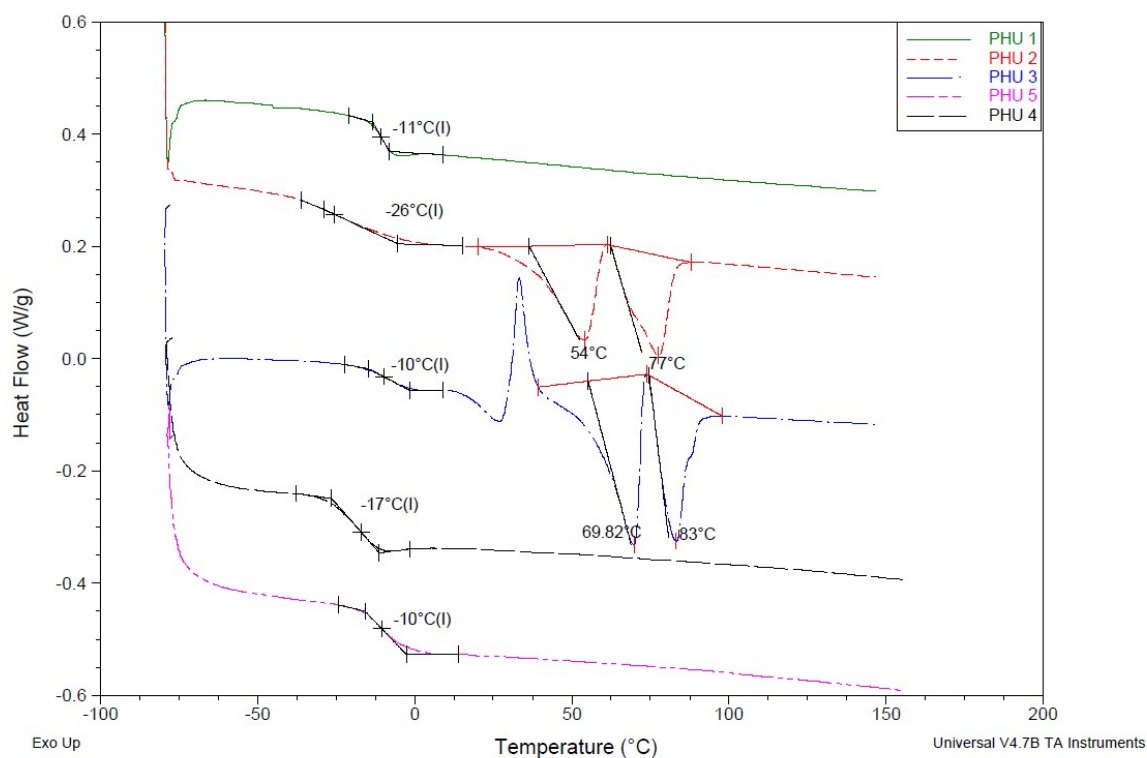


Figure 24 – DSC curves of the synthesized PHU (PHU 1-PHU 5).

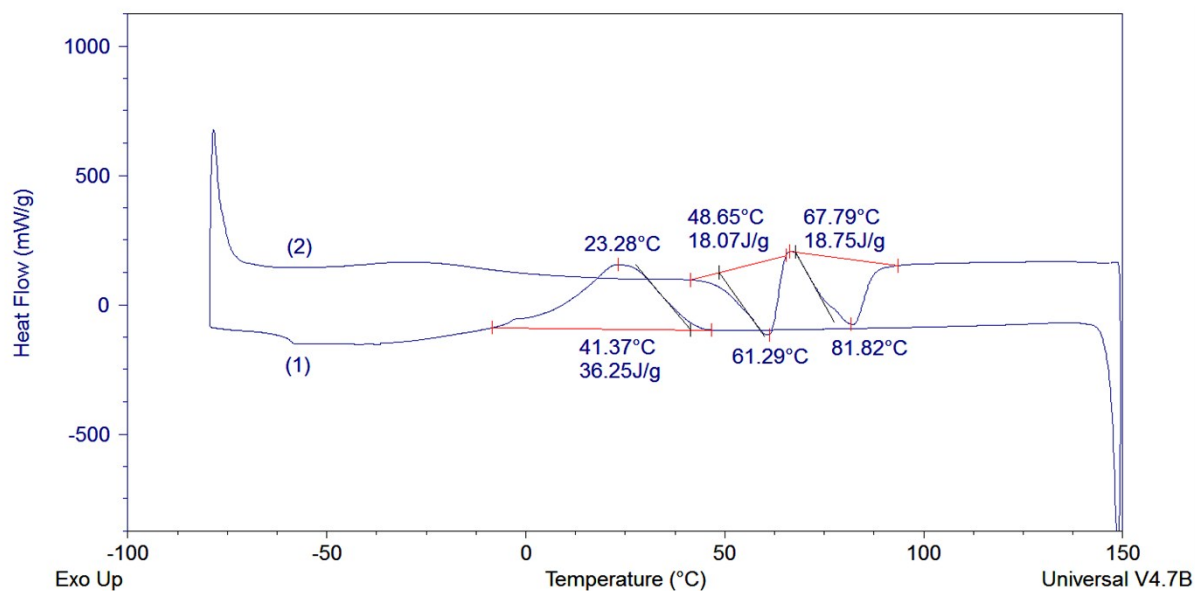


Figure 25 – DSC curves of the synthesized PHU 2 showing (1) the first cooling run and (2) the 2nd heating run.

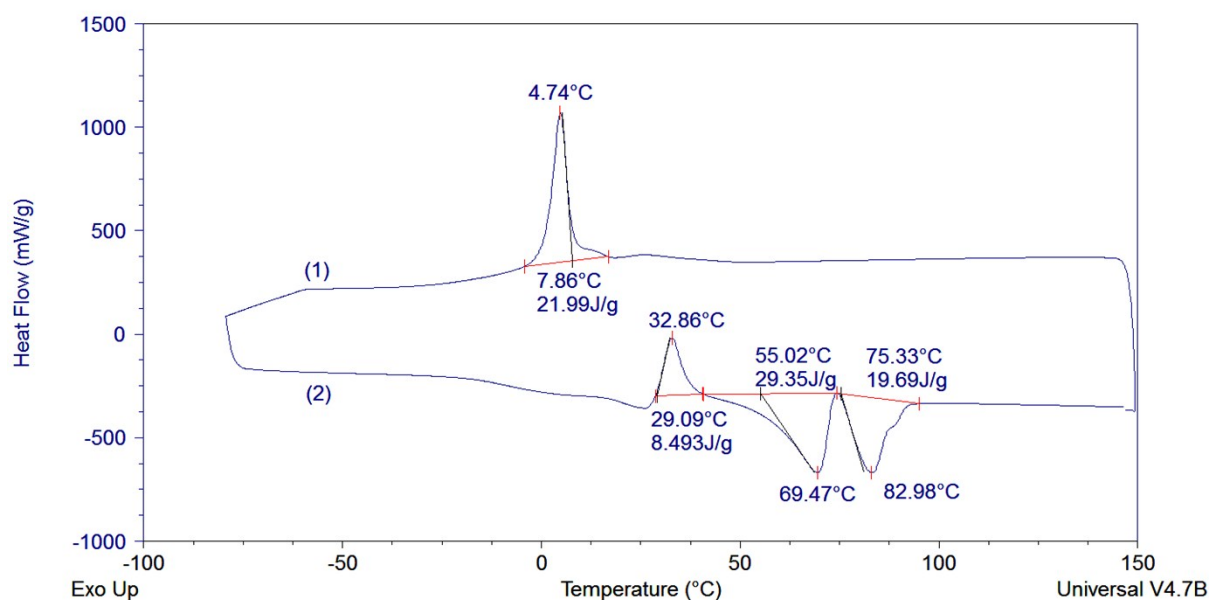


Figure 26 – DSC curves of the synthesized PHU 3 showing (1) the first cooling run and (2) the 2nd heating run.

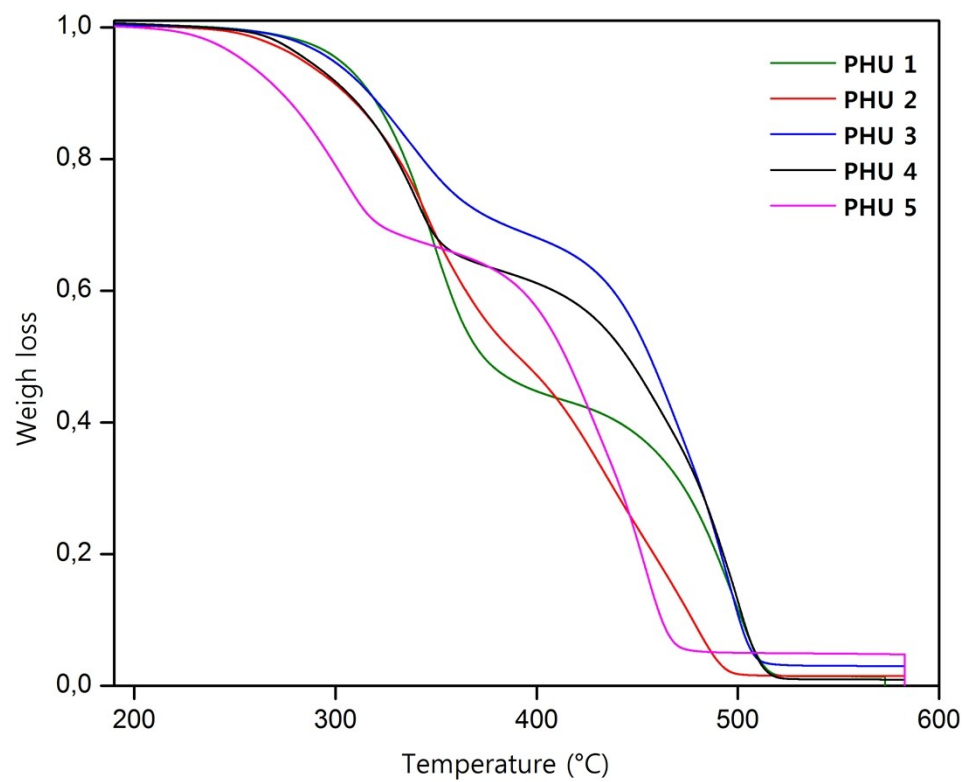


Figure 27 – TGA curves of the synthesized PHU (PHU 1-PHU 5) from 200°C (after DMF removal) to 600°C.