Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for:

Synthesis of α,β-unsaturated esters of perfluoropolyalkylethers (PFPAEs) based on hexafluoropropylene oxide units for photopolymerization

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Outlines

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A. General Considerations

1. Materials and Methods

Maleic anhydride, methanol, ethanol, propan-2-ol, pentanol, benzyl alcohol, phenol, *tert*-butyl alcohol, *tert*-amyl alcohol, thionyl chloride, triethylamine, carbonyldiimidazole, Amberlyst-15 hydrogen form (strongly acidic, cation exchanger, dry), dicyclohexylcarbodiimide, dimethylamino pyridine, 2-hydroxy-2-methylpropiophenone and dichloromethane were purchased from Sigma Aldrich. Triethylamine and thionyl chloride were distilled before use. Triethylamine and trifluorotoluene were kept under activated molecular sieves (3A). The different alcohols were previously dried by using $MgSO_4$. 1,1,1,3,3-pentafluorobutane was purchased from Alfa Aesar. The 1250 g/mol oligo(HFPO) methylene alcohol was prepared from Krytox® acyl fluoride. The 1250 Krytox® acyl fluoride and the 2000 g/mol Krytox® methylene alcohol were kindly provided by E. I. du Pont de Nemours and Company.

2. Analytical Data

Gas Chromatography (GC) Mass Spectrometry (MS): An Agilent Technologies 6890N GC was coupled with an Agilent Technologies 7638B series injector and Agilent Technologies 5975B inert mass spectrometer (MSD) was employed with electron impact (EI) as the mode of ionization. The GC was equipped with a Zebron ZB-5ms column, 30 m x 0.18 mm internal diameter (ID), 0.18 µm film thickness (df). The detector and the injector temperatures were 200 °C and 280 °C, respectively. The temperature program started from 50 °C with a 2 min hold then the heating rate was 25 °C/min until reaching 250 °C and holding at 250 °C for 2 min. The total pressure 108 kPa, total flow was 25.9 mL/min, column flow 0.74 mL/min, purge flow 3mL/min, linear velocity 38.2 cm/s, and a split injection of 30:1. The sample was previously diluted in methoxyperfluorobutane (3M's Novec™ HFE-7100) in a GC vial.

Nuclear Magnetic Resonance (NMR) spectroscopy: The structure of the products was determined by NMR spectroscopy at room temperature (25 °C) except if specified. NMR spectra were recorded on a Bruker AVANCE III 400MHz spectrometer instruments using deuterated $CDCl_3$ and C_6D_6 capillaries as internal references for the oligo(HFPO) products. The experimental conditions were accomplished by using TopSpin 3.5 operating at 400.13 (^1H), 376.46 (^{19}F), 100.62 (^{13}C) MHz. The letters s, d, t, q, and sext stand for singlet, doublet, triplet, quartet, and sextet, respectively.

Matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI–TOF–MS): The homologue distributions of the products were determined with a Bruker AutoflexTM MALDI–TOF/TOF–MS spectrometer equipped with a 1 kHz smartbeam-II laser and reflector in positive ionization. For sample preparation, a 1 drop sample of oligo(HFPO) was added to a 1 mL solution of 50:50 1% LiCl in MeOH and 2% perfluorocinnamic acid dissolved in 50:50 MeOH:Methoxynonafluorobutane (3 M HFE-7100) or 50:50 MeOH:1,1,1,3,3-pentafluorobutane. A 1 µL solution was then pipetted on to a ground steel plate, dried, and irradiated for a minimum of 5000 shots.

Fourier-Transform (FT) – Real Time Infrared Spectroscopy (RTIR): Real-time infrared spectroscopy and photopolymerization kinetics were performed on a 6700 FTIR Nicolet apparatus by using OMNIC software. The UV light came from an OmniCure S2000 (Mercury lamp) equipment and the light output was controlled by OmniCure R2000 Radiometer. The real intensity provided to the sample was found to be 1 mW/cm^2 thanks to a radiometer from Solatell. The product was dropped by using a pipette and a polypropylene film (6µm) was used as air protector. The sample was irradiated during 600 s. 2-hydroxy-2-methylpropriophenone was added as photoinitiator (4% w/w). The following of the kinetics was made by following the disappearance of the band at 1622 cm^{-1} for the vinyl ether (and at 1645 cm^{-1} for the maleate). The calculated conversion rates were made based on the average of four repeats for the same experiment. The calculations were made by using the univariate method and confirmed by the peak deconvolution method.

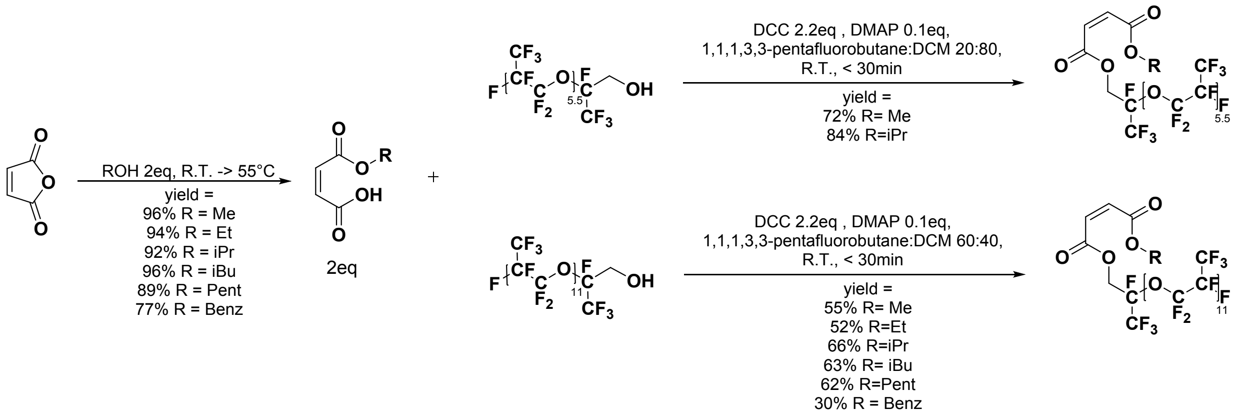
UV bench conveyor: Some photopolymerization experiments were also performed on an UV production curing unit, Fusion F300 UV (power output of 1200 W.cm^{-2}), and a LC6B Bench-top conveyor equipped with a microwave lamp. The sample was placed on a conveyor and passed repeatedly under the UV lamp at a speed of travel belt of 1 m.min^{-1}.

Thermogravimetric analyses (TGA): The degradation temperatures were determined with a NETZSCH TG209F1 at a heating rate of 20°C/min. Approximately 8 mg of the sample were placed in an alumina crucible and heated from room temperature to 600°C under inert atmosphere (40 mL/min).

Differential scanning calorimetry (DSC): The glass transition temperatures were determined with a NETZSCH DSC200F3 calorimeter. Constant calibration was performed using indium, n-octadecane and n-octane standards. 10-15 mg was placed in pierced aluminium pans and the thermal properties were recorded between -150 °C and 100 °C at 20 °C/min. The glass transition temperatures were measured at the second heating ramp and are the onset values. Nitrogen was used as the purge gas.

Contact angle measurements: The hydrophobicity was determined thanks to a contact angle system OCA20 from DataPhysics Instrument using the software SCA20 4.1. A CCD-camera was used to follow the droplets. The measurements were made in air at room temperature by the sessile drop technique with distilled water. Three repeats were made on three different samples previously irradiated. Their difference in the average value was no more than 3°.

3. General reaction scheme for the synthesis of maleates oligo(HFPO)



B. Experimental, IR, ^{1}H, ^{13}C-NMR and GC-MS Spectra of the monoalkyl maleates

In a general procedure, 10 mmol of maleic anhydride (981 mg) were dissolved in 20 mmol of the corresponding alcohol (2 eq). The mixture was stirred at room temperature or heated between 45 °C and 55 °C. The different reaction times and temperatures are reported in Table 1. The conversion of the reaction was followed by ^{1}H NMR by following the disappearance of the maleic anhydride. The solvent was then removed under high vacuum with increase of temperature if needed (until 60 °C). The final products were obtained in good yields from 77 % to 96 % (Table 1).

For the benzyl alcohol, a flash chromatography was performed (gradient from 20:80 EtOAc:Pentane to 100% EtOAc). Products were revealed under UV-light or with a $KMnO_4$ solution (Table 2).

Table 1: Different reaction conditions for the synthesis of monoalkyl maleates

Substituent	Reaction time	Temperature	Yield
Me-	5 h	R.T.	96 %
Et-	6 h	50 °C	94 %
iPr-	24 h (R.T => 45 °C)	45 °C	92 %
iBu-	5 h	45 °C	96 %
Pent-	6 h 30	50 °C	89 %
Benz-	7 h	55 °C	77 %

The six different starting maleates were characterized by NMR (^{1}H, ^{13}C, ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC), GC-MS and IR.

1. Monomethyl maleate **1a**

Colorless oil – Yield=96 %

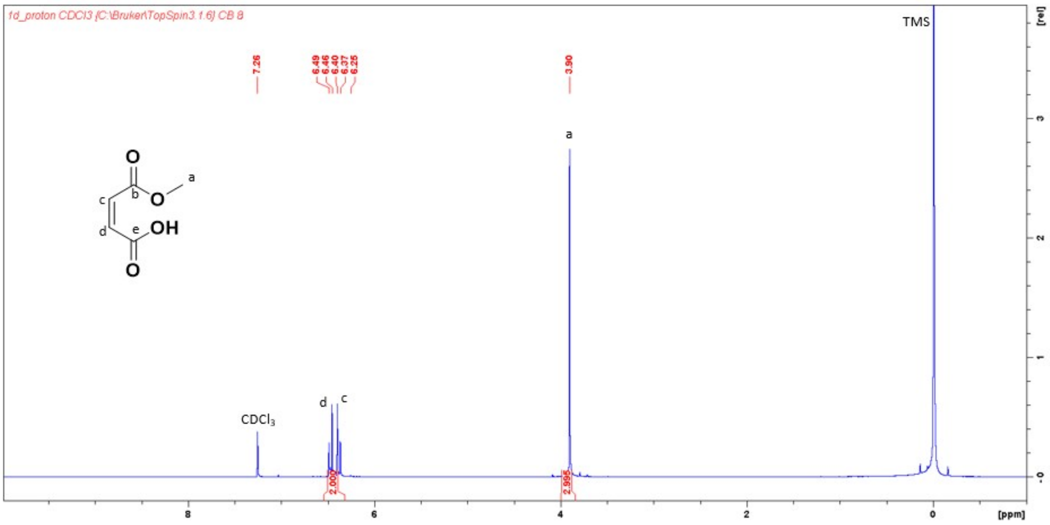


Figure 1: ^1H NMR spectrum of **1a**

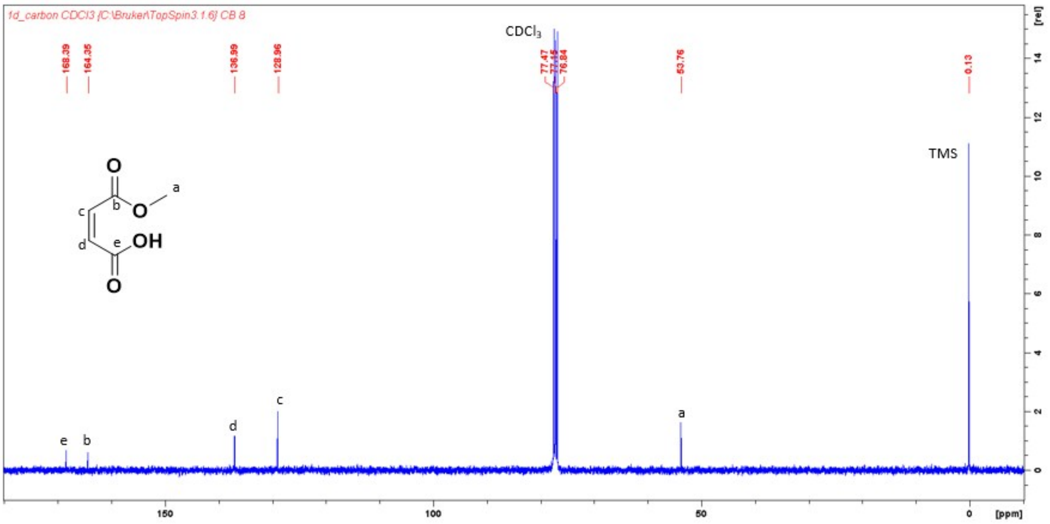


Figure 2: ^{13}C NMR spectrum of **1a**

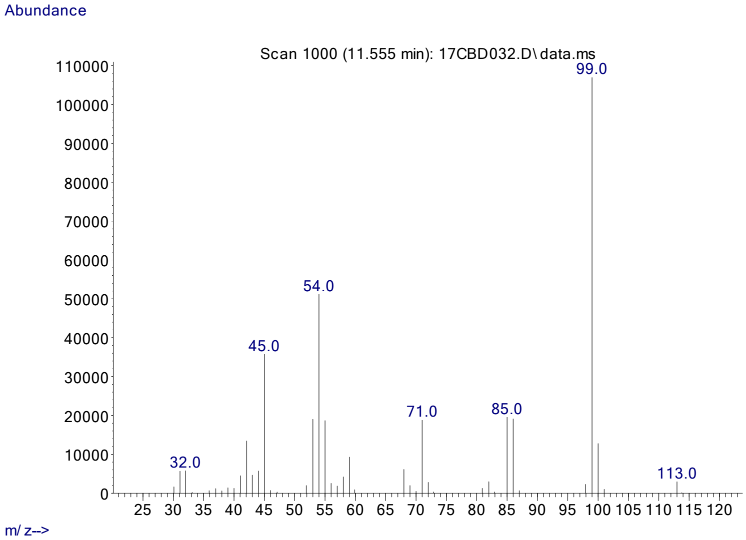


Figure 3: GC-MS spectrum of **1a**

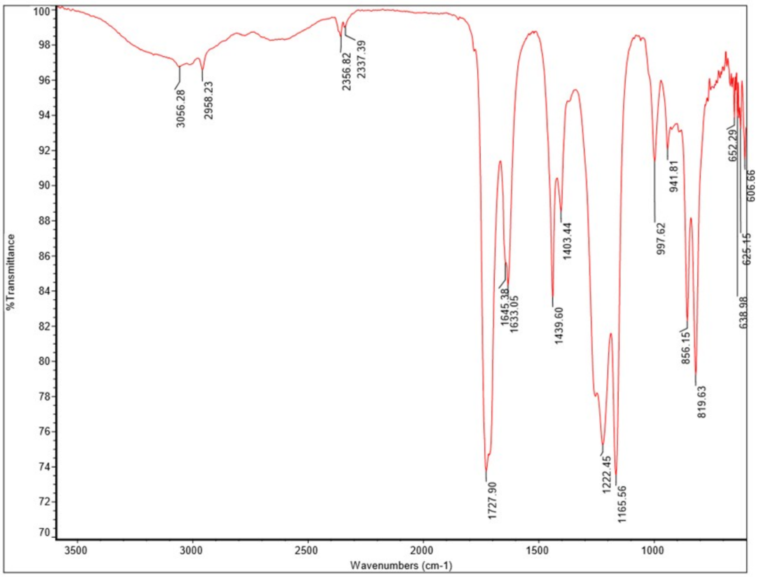


*Figure 4: IR spectrum of **1a***

2. Monoethyl maleate **1b**

Monoethyl maleate **1b** (50 °C, 6 h, yield=94 %, colorless oil): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ) : 1.35 (t, C$\mathbf{H_3}$$CH_2$OCO-, 3H , $^{3}J_{H\text{-}H}$=7.2 Hz), 4.30 (q, CH_3C$\mathbf{H_2}$OCO-, 2H , $^{3}J_{H\text{-}H}$=7.2 Hz), 6.40 (dd, -C**H**=C**H**COOH-, 2H, $^{3}J_{H\text{-}H}$= 12.9 Hz and 26.6 Hz), ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, δ): 13.8 (**C**H_3CH_2OCO-), 63.1 (CH_3**C**H_2OCO-), 129.8 (-**C**H=CHCOOH-), 137.7 (-**C**HCOOH), 165.2 (CH_3CH_2O**C**O-), 167.6 (-**C**OOH), GC-MS, 70 eV, *m/z*: 45 (27), 54 (29), 55 (18), 71 (12), 82 (15), 99 (100), 100 (19), FT-IR (ATR) ν_{max} (cm^{-1}): 821.2 – 857.8 – 1165.3 – 1234.8 – 1631.5 – 1724.5

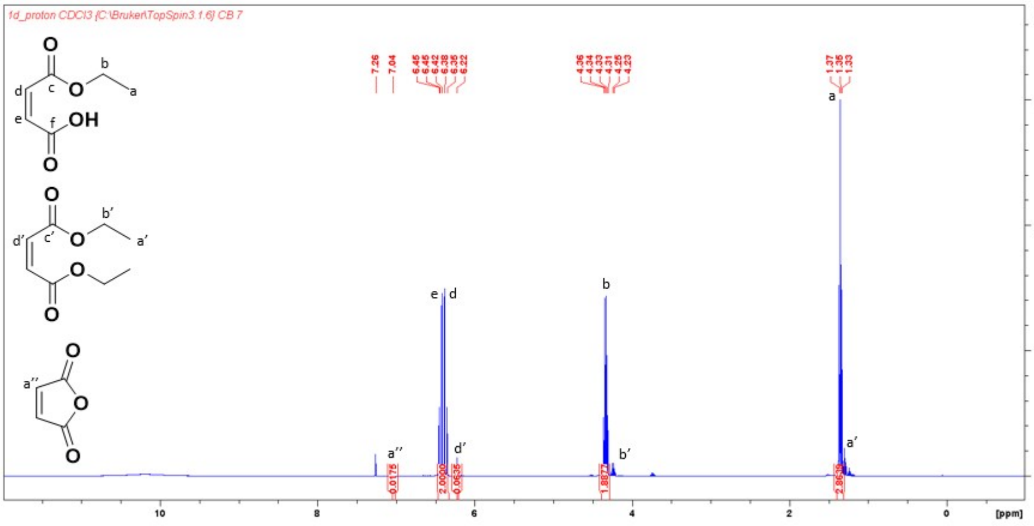


*Figure 5: ^{1}H NMR spectrum of **1b** (containing 3% of diester and >1% of maleic anhydride)*

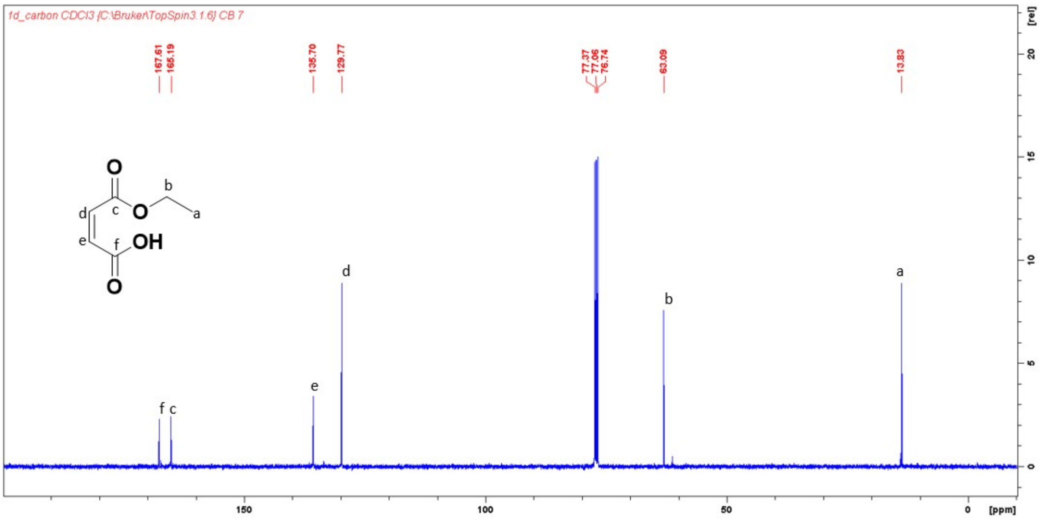


*Figure 6: ^{13}C NMR spectrum of **1b***

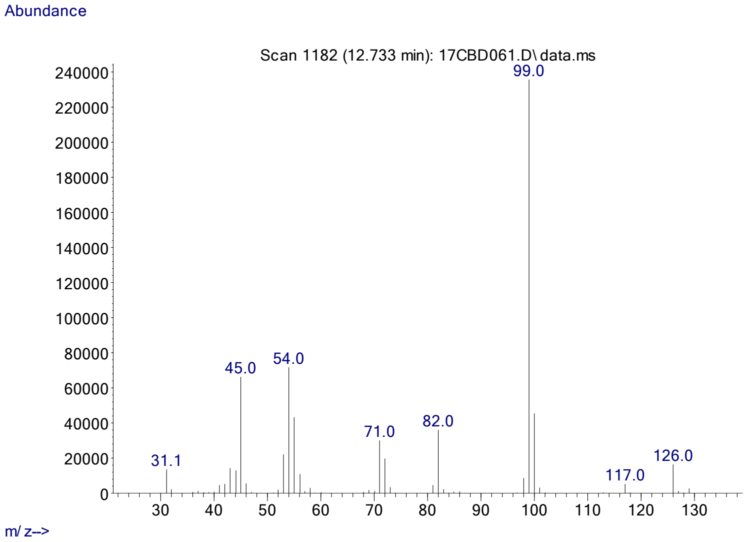


*Figure 7: GC-MS spectrum of **1b***

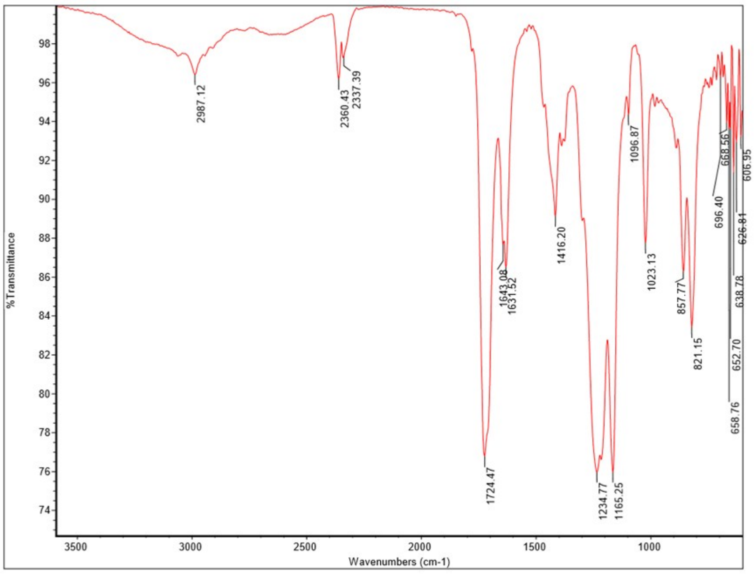


*Figure 8: IR spectrum of **1b***

3. Monoisopropyl maleate **1c**

Monoisopropyl maleate **1c** (45 °C, 24 h, yield=92 %, colorless oil): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 1.35 (d, $(C\mathbf{H_3})_2CHOCO$, 6H, $^3J_{H-H}$=6.3 Hz), 5.17 (spt, $(CH_3)_2C\mathbf{H}OCO$ -, 1H, $^3J_{H-H}$=6.3 Hz), 6.39 (dd, -C**H**=C**H**COOH-, 2H, $^3J_{H-H}$=12.9 Hz and 39.5 Hz), ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, δ): 21.6 ($(\mathbf{C}H_3)_2CH_2OCO$-), 72.0 ($(CH_3)_2\mathbf{C}HOCO$-), 129.7 (-**C**H=CHCOOH-), 137.5 (-**C**HCOOH), 164.1 ($(CH_3)_2CH_2O\mathbf{C}O$-), 167.8 (-**C**OOH), GC-MS, 70 eV, *m/z*: 42.1 (12), 45 (32), 53 (17), 54 (46), 55 (17), 71 (17), 85 (18), 86 (17), 99 (100), 100 (12), FT-IR (ATR) ν_{max} (cm^{-1}): 821.2 – 1103.5 – 1169.6 – 1223.9 – 1262.9 – 1632.1 – 1716.1

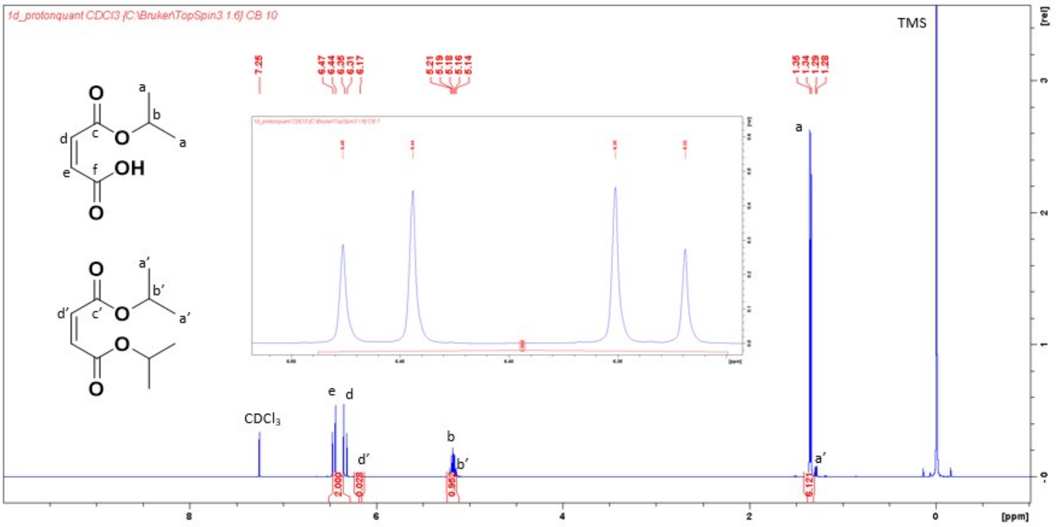


*Figure 9: ^{1}H NMR spectrum of **1c** (containing 1% of diester)*

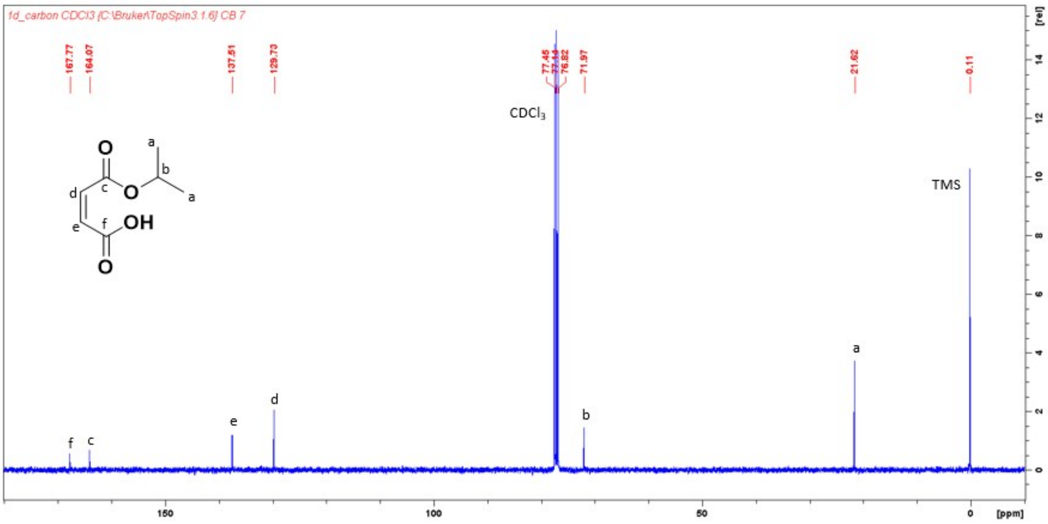


*Figure 10: ^{13}C NMR spectrum of **1c***

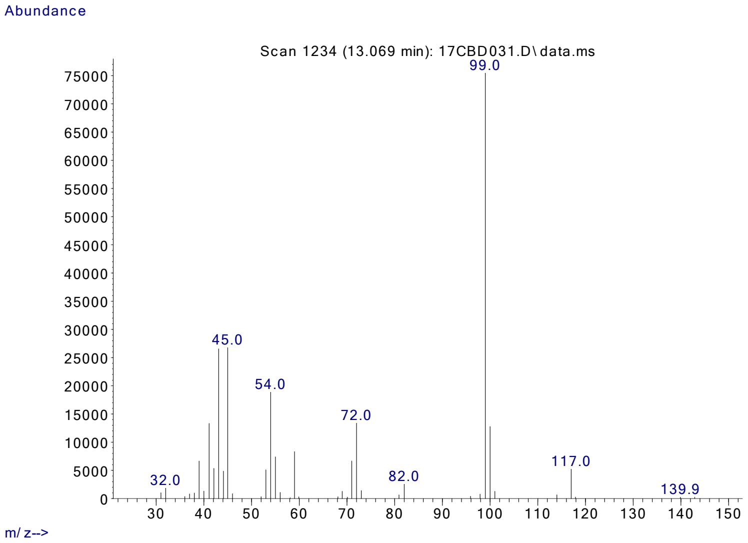


*Figure 11: GC-MS spectrum of **1c***

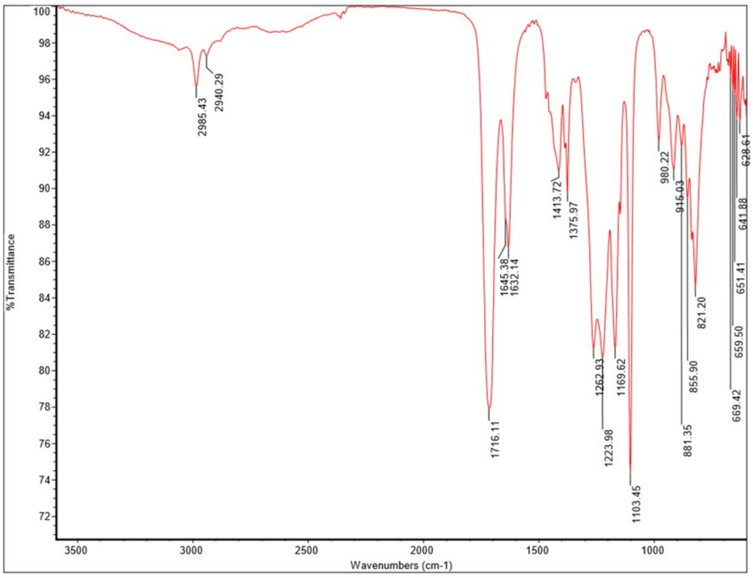


*Figure 12: IR spectrum of **1c***

4. Monoisobutyl maleate **1d**

Monoisobutyl maleate **1d** (45 °C, 5 h, yield=96 %, colorless oil): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 0.98 (d, $(C\mathbf{H_3})_2CHCH_2OCO$-, 6H, $^3J_{H\text{-}H}$=6.7 Hz), 2.03 (tspt, $(CH_3)_2C\mathbf{H}CH_2OCO$ -, 1H, $^3J_{H\text{-}H}$=6.7 Hz), 4.0 (d, $(CH_3)_2CHC\mathbf{H_2}OCO$ -, 2H, $^3J_{H\text{-}H}$=6.7 Hz), 6.44 (dd, -C**H**=C**H**COOH-, 2H, $^3J_{H\text{-}H}$=12.8 Hz and 27.5 Hz), ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, δ): 19.0 ($(\mathbf{C}H_3)_2CHCH_2OCO$-), 27.64 ($(CH_3)_2\mathbf{C}HCH_2OCO$-), 73.3 ($(CH_3)_2CH\mathbf{C}H_2OCO$-), 129.2 (-**C**H=CHCOOH-), 137.6 (-**C**HCOOH), 164.1 ($-CHCH_2O\mathbf{C}O$-), 168.3 (-**C**OOH), GC-MS, 70 eV, *m/z*: 39 (11), 41.1 (22), 45 (12), 54 (24), 56 (22), 57.1 (10), 99 (100), 100 (26), FT-IR (ATR) ν_{max} (cm^{-1}): 819.2 – 1166.2 – 1213.2 – 1634.0 – 1727.4

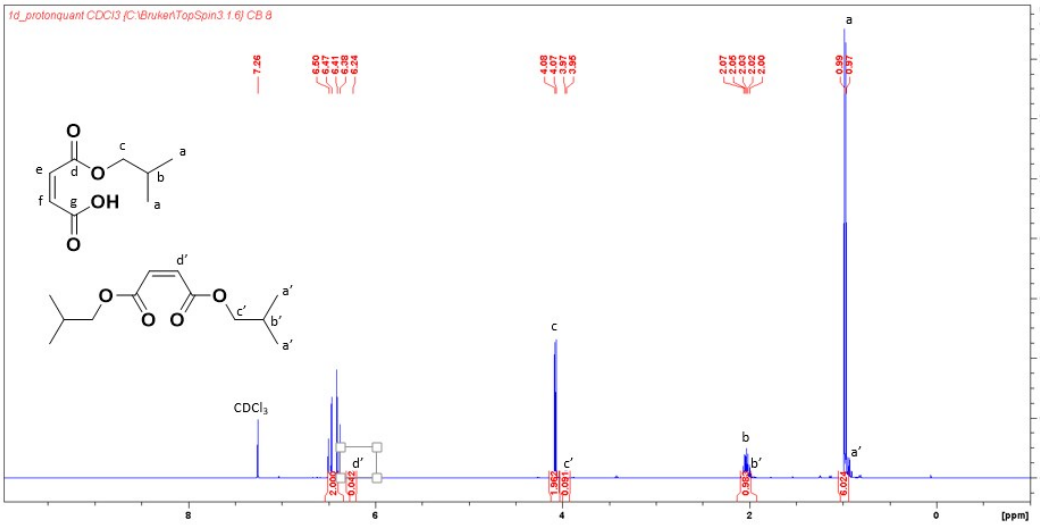


*Figure 13: ^{1}H NMR spectrum of **1d** (containing 2% of diester)*

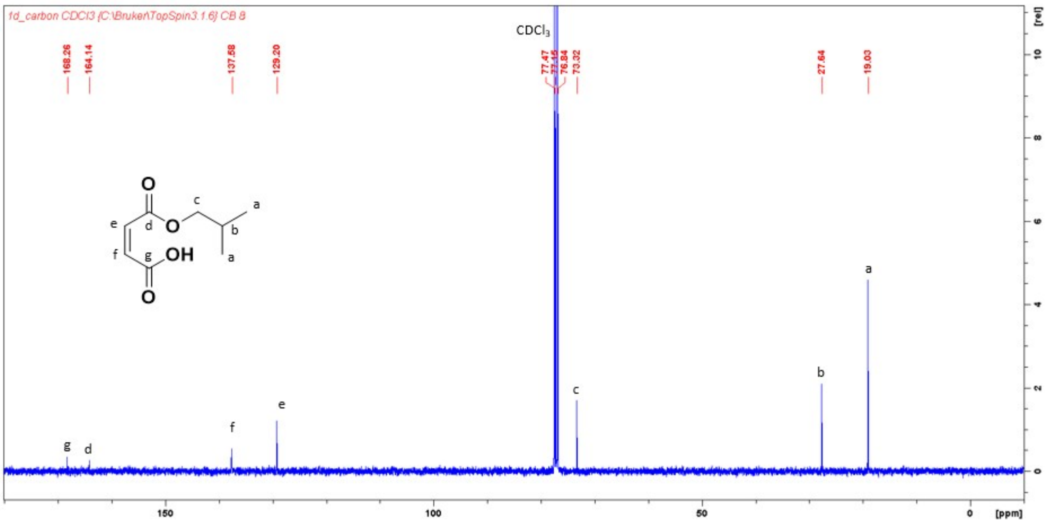


*Figure 14: ^{13}C NMR spectrum of **1d***

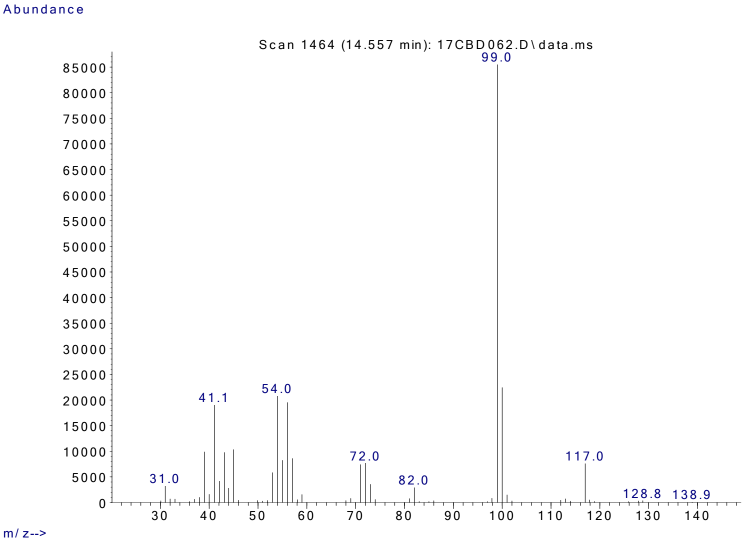


*Figure 15: GC-MS spectrum of **1c***

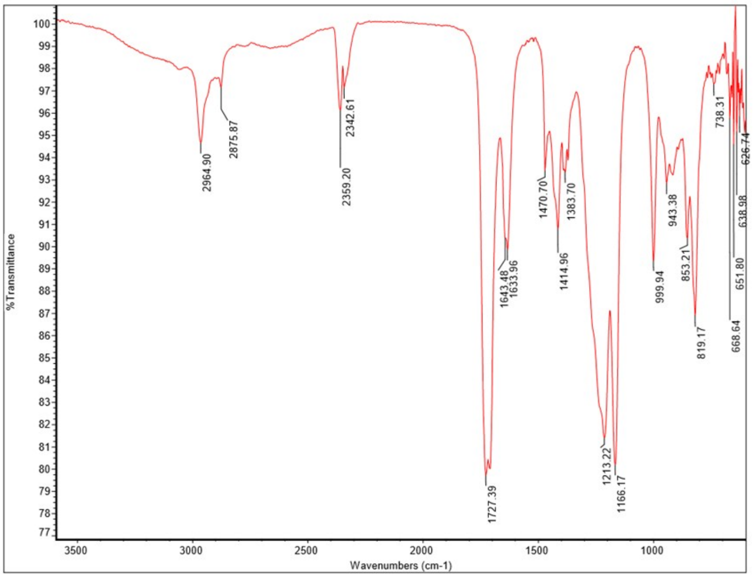


*Figure 16: IR spectrum of **1d***

5. Monopentyl maleate **1e**

Monopentyl maleate **1e** (50 °C, 6 h 30, yield=89 %, colorless oil): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 0.92 (t, $C\mathbf{H_3}(CH_2)_4OCO$-, 3H, $^3J_{H\text{-}H}$=6.9 Hz), 1.34-1.38 (m, $CH_3(C\mathbf{H_2})_2(CH_2)_2OCO$-, 4H), 1.69-1.76 (m, $CH_3(CH_2)_2C\mathbf{H_2}CH_2OCO$-, 2H), 4.28 (t, $CH_3(CH_2)_3C\mathbf{H_2}OCO$-, 2H, $^3J_{H\text{-}H}$=6.7 Hz), 6.42 (dd, -C**H**=C**H**COOH-, 2H, $^3J_{H\text{-}H}$=12.9 Hz and 40.6 Hz), ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, δ): 14.0 ($\mathbf{C}H_3(CH_2)_4OCO$-), 22.3 ($CH_3\mathbf{C}H_2(CH_2)_3OCO$-), 27.9 ($CH_3CH_2\mathbf{C}H_2(CH_2)_2OCO$-), 28.0 ($CH_3(CH_2)_2\mathbf{C}H_2CH_2OCO$-), 67.6 ($CH_3(CH_2)_3\mathbf{C}H_2OCO$-), 129.2 (-**C**H=CHCOOH-), 137.6 (-**C**HCOOH), 164.1 ($CH_3CH_2O\mathbf{C}O$-), 168.3 (-**C**OOH), GC-MS, 70 eV, *m/z*: 41.1 (17), 42.1 (14), 43.1 (14), 54 (19), 55.1 (21), 70.1 (16), 99 (100), 100 (17), 117 (13), FT-IR (ATR) ν_{max} (cm^{-1}): 821.0 – 1167.3 – 1208.7 – 1633.1 – 1729.1

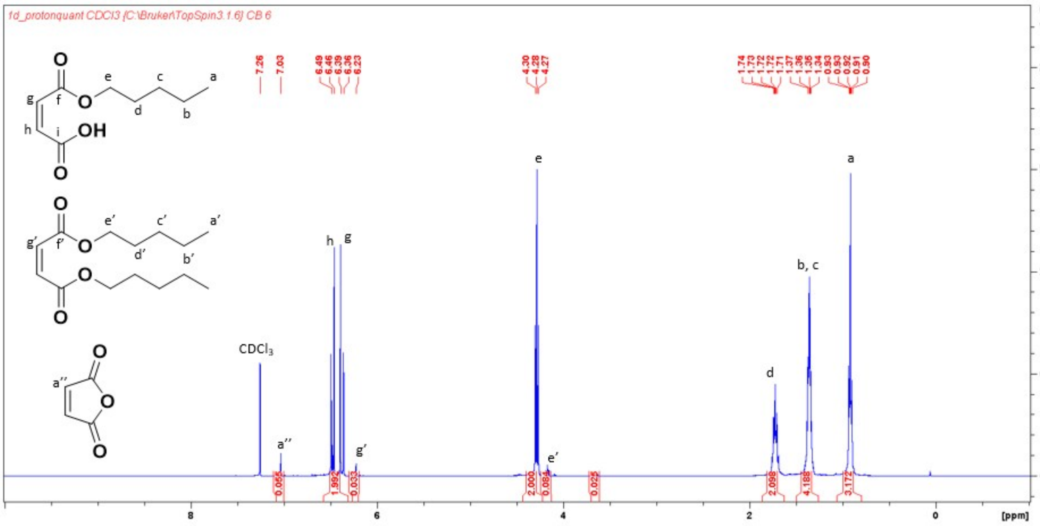


*Figure 17: ^{1}H NMR spectrum of **1e** (containing 1.5% of diester and 2.5% of maleic anhydride)*

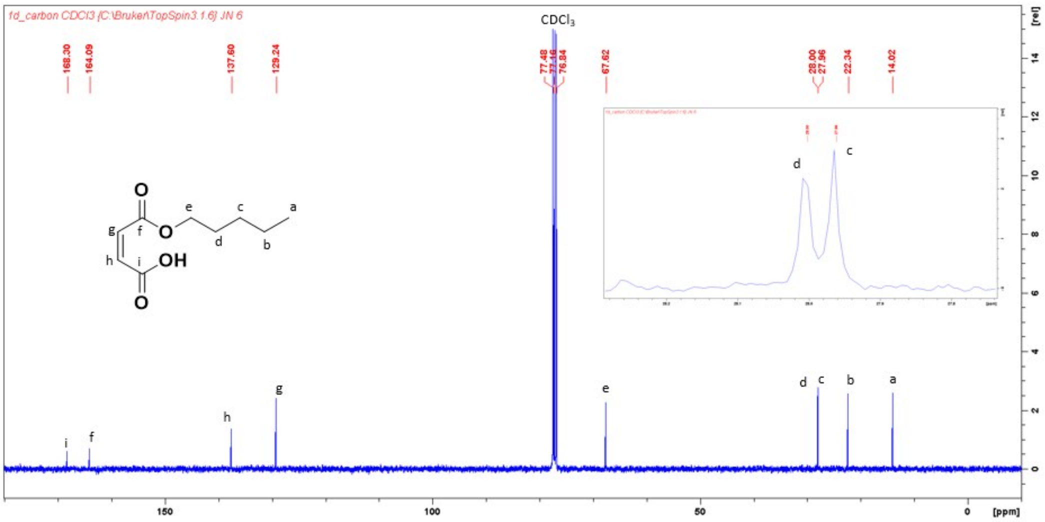


*Figure 18: ^{13}C NMR spectrum of **1e***

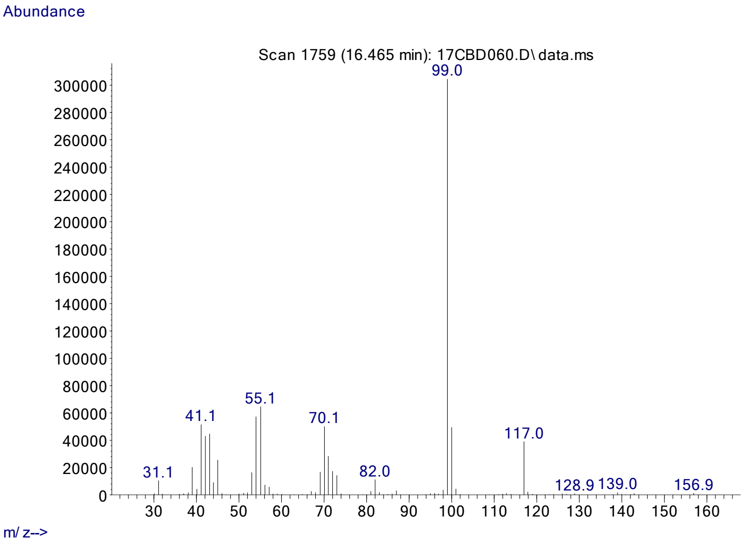


*Figure 19: GC-MS spectrum of **1e***

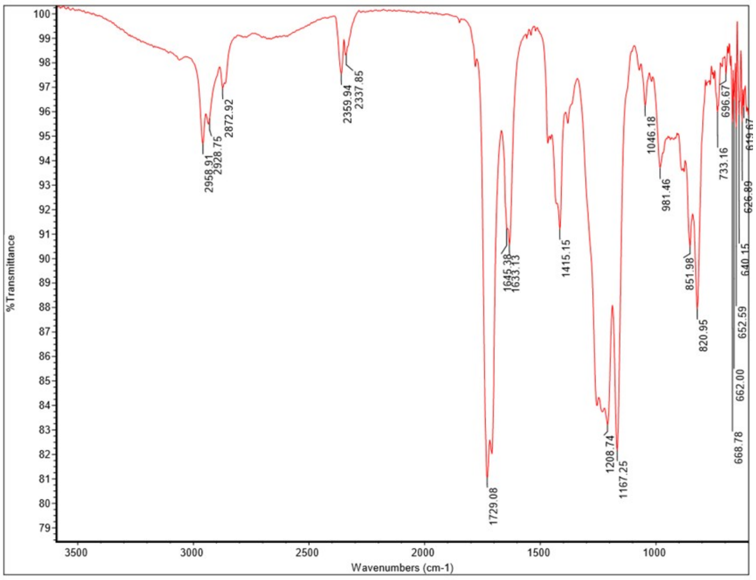


*Figure 20: IR spectrum of **1e***

6. Monobenzyl maleate **1f**

Monobenzyl maleate **1f** (55 °C, 7 h, yield=77 %, yellowish oil): (purified by flash chromatography from 20:80 EtOAc:Pentane to 100 % EtOAc) ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, δ): 5.29 (s, PhC**H$_2$**OCO -, 2H, $^3J_{H\text{-}H}$=6.3 Hz), 6.42 (dd, -C**H**=C**H**COOH-, 2H, $^3J_{H\text{-}H}$=12.7 Hz and 23.8 Hz), 7.39 (s, **Ph**CH$_2$OCO-, 5H), ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, δ): 68.7 (Ph**C**H$_2$OCO -), 128.8-129.1 & 134.0 (**Ph**CH$_2$OCO-), 129.3 (-**C**H=CHCOOH-), 136.2 (-**C**HCOOH), 164.8 (CH$_3$CH$_2$O**C**O-), 167.4 (-**C**OOH), FT-IR (ATR) ν_{max} (cm^{-1}): 697.6 – 1165.6 – 1212.8 – 1412.2 – 1634.5 – 1727.4

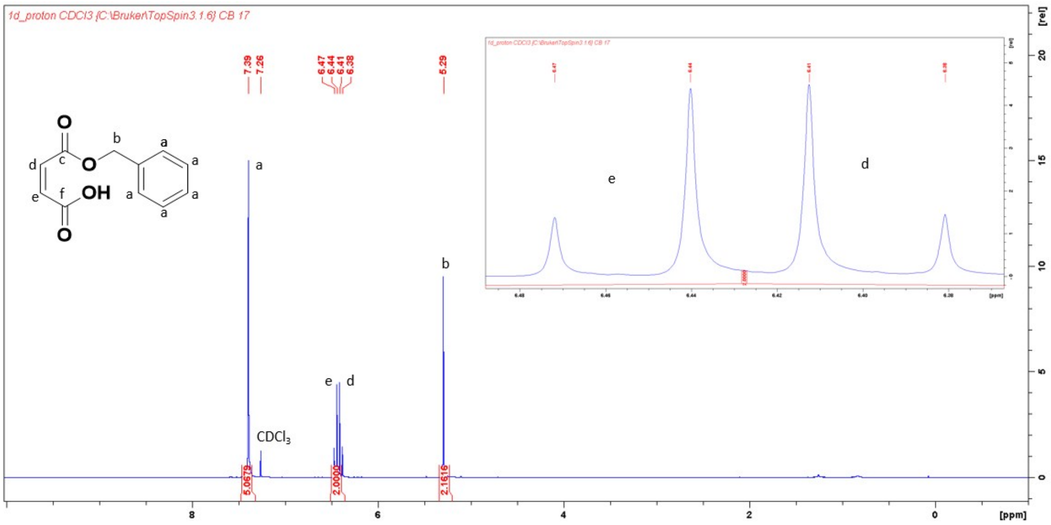


*Figure 21: ^{1}H NMR spectrum of **1f***

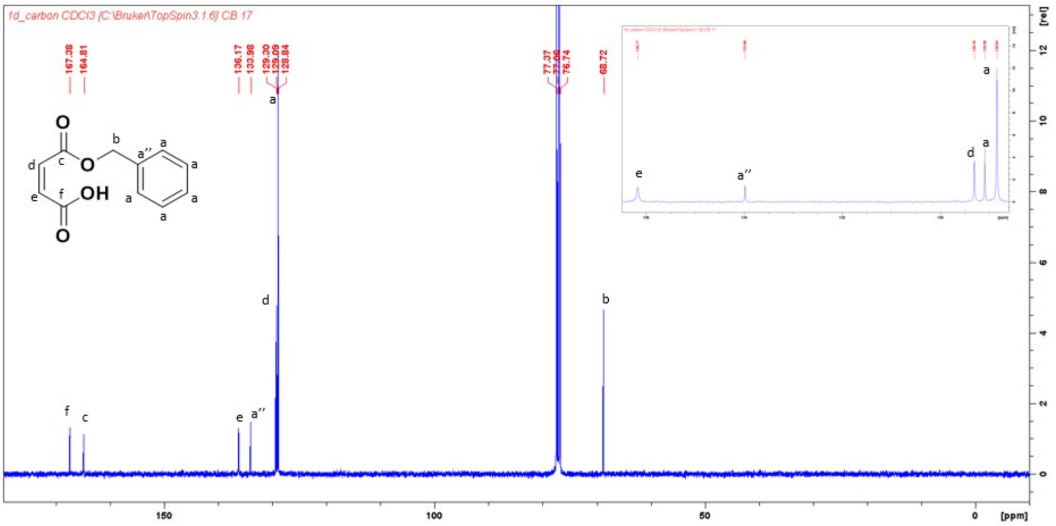


*Figure 22: ^{31}C NMR spectrum of **1f***

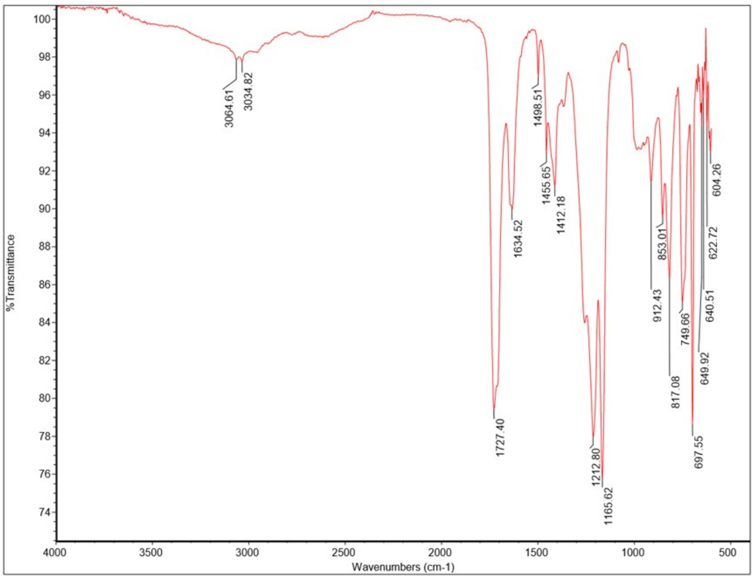


*Figure 23: IR spectrum of **1f***

No GC-MS of this product was obtained due to degradation of the product into maleic acid and benzyl alcohol under heat.

C. Experimental and NMR spectra of the different attempts for the synthesis of diesters

1. By direct esterification

i. By using sulfuric acid as catalyst

To a mixture of oligo(HFPO) alcohol Mw~1250 g/mol (2 g, 1 mmol) and monoethyl maleate (1.44 g, 10 eq), 1 drop (~0.2 mL) of concentrated acid was added. The reaction was allowed to stir at 80°C during 24h. A conversion of 12% was obtained.

ii. By using Amberlyst-15

To a mixture of oligo(HFPO) alcohol Mw~2000 g/mol (2 g, 1 mmol) and monoethyl maleate (288.3 mg, 2eq), Amberlyst-15 (40 mg, 1.5%wt) previously activated was added. The raction was allowed to stir at 120°C during 14h. No conversion was observed.

iii. Conclusion

The direct esterification of the monoethyl maleate with (oligo(HFPO) methylene alcohol) in acidic conditions was not successful. For example, no conversion was detected by heterogeneous catalysis by employing a strongly acidic cation exchange resin (Amberlyst-15) and only a conversion of the starting alcohol of 12% was evident after 24 h using sulfuric acid as catalyst.

2. By using thionyl chloride

i. Procedure

To a colorless solution of monoethyl maleate in DCM, 1.2 eq of freshly distilled triethylamine was added to get a clear yellow solution. Then distilled thionyl chloride (3 eq) in DCM (%v=1:10) was added dropwise at 0 °C. A sodium hydroxide trap was used to trap gaseous HCl. The mixture was then allowed to heat until reflux during 48 h.

^{1}H NMR rapidly showed the presence of isomerization (Figure 24). The trans-product was identified thanks to the coupling constant $^3J_{H-H}$=15.4 Hz and a chemical shift of 6.99 ppm for the doublet of doublet. The ^{1}H NMR spectrum after 48 h showed a perfect isomerization. After the cooling down of the reaction mixture, the mixture was filtrated to remove salts of triethylamine. An assay of distillation was performed. However, the product did not seem to be stable enough and was degraded under heat.

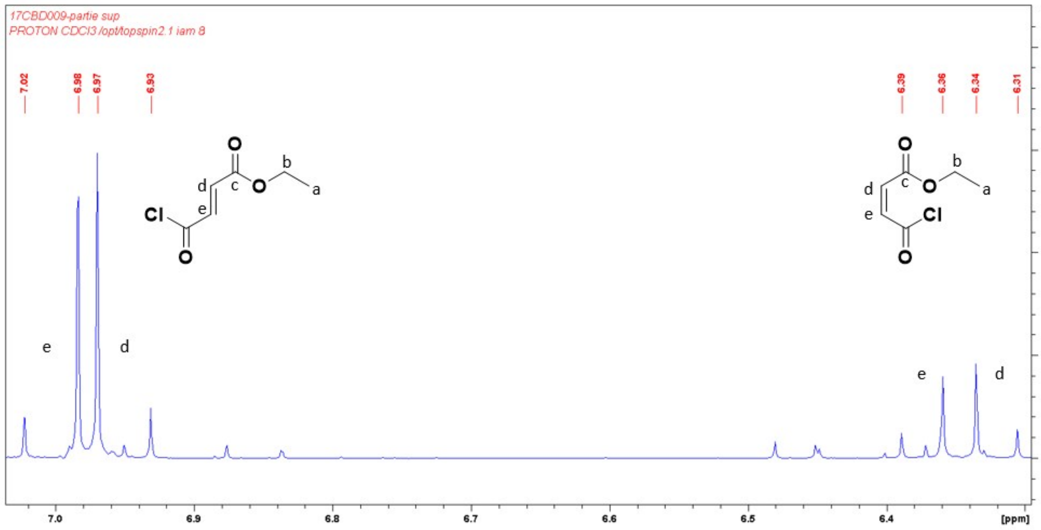


Figure 24: ^{1}H NMR spectrum of the reaction mixture showing the isomerization (zoom from 6.3 ppm to 7 ppm)

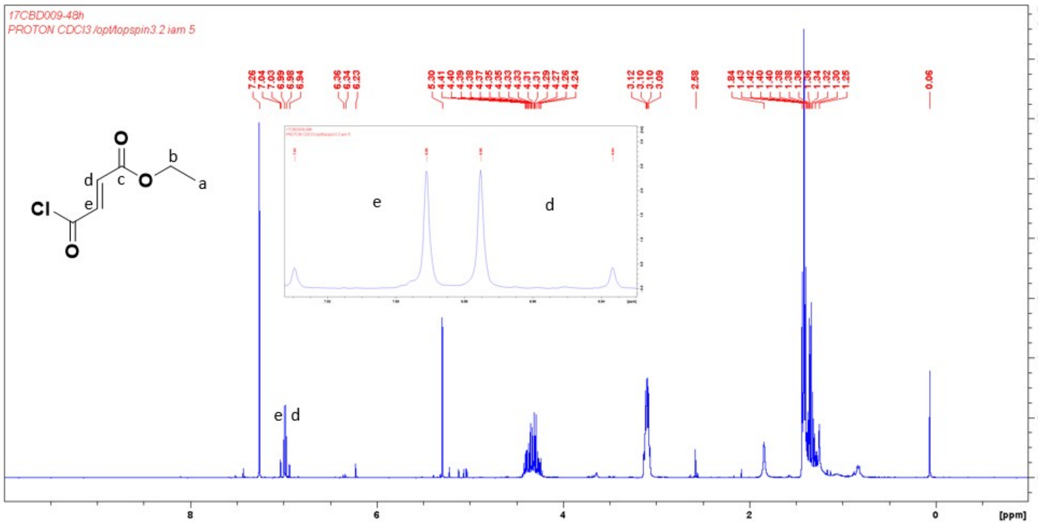
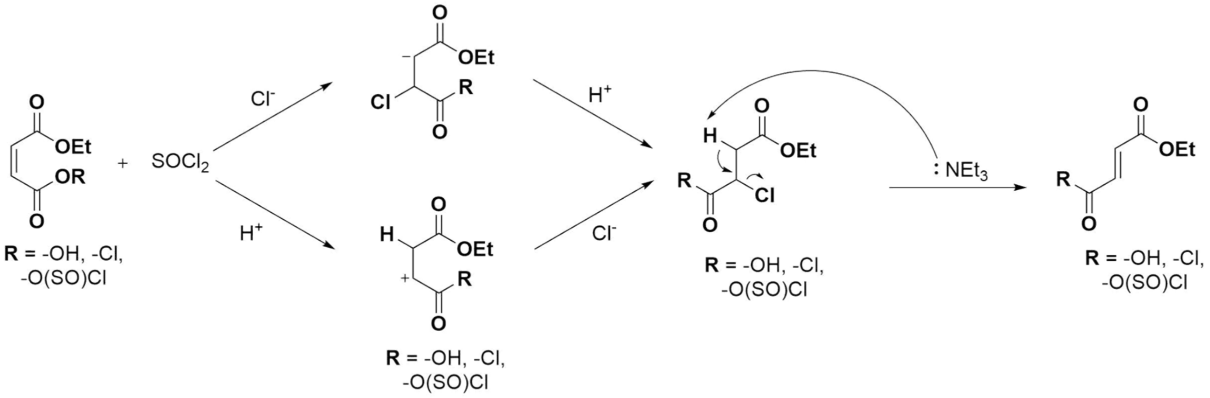


Figure 25: ^{1}H NMR spectrum of the trans acid chloride product (fumarate)

ii. Mechanistic explanation and conclusion

By using thionyl chloride as activating agent on the monoethyl maleate, the undesired *trans*-product was formed and confirmed by the coupling constant $^3J_{H\text{-}H}$ of the fumarate (15.4Hz). Moreover, several articles showed the formation of the fumarate instead of the initial maleate due to the use of different chlorinating agents: thionyl chloride[1,2] or oxalyl chloride.[3] ^{1}H NMR showed the presence of isomerization during the addition of $SOCl_2$. (See supporting information) The assumed mechanisms are either the addition of the chloride onto the double bond or the addition of the double bond onto the proton to permit the free rotation. The addition of the proton is the most likely assumed pathway as it represents the lowest energy of activation.

In any case, the β-halocarbonyl compound can undergo a E_{1cb} elimination reaction thanks to the triethylamine (Scheme 2).[4,5]



Scheme 1: Scheme of the isomerization of the maleate into the fumarate

3. By using carbonyldiimidazole (CDI)

i. Procedure

To a solution of monoethyl maleate in DCM ([C]=1 mol/L), 1.2 eq of CDI were added. A rapid carbon dioxide emission was observed. After 5 min of reaction, the activated acid was confirmed by TLC (R_f = 0.65 - cyclohexane:EtOAc 70:30) and the mixture became slightly pink. After 30 min, the mixture became dark red and the NMR confirmed the addition of the imidazole on the double bond with two dd at 3.45 ppm and 3.85 ppm and a triplet at 5.45 ppm.

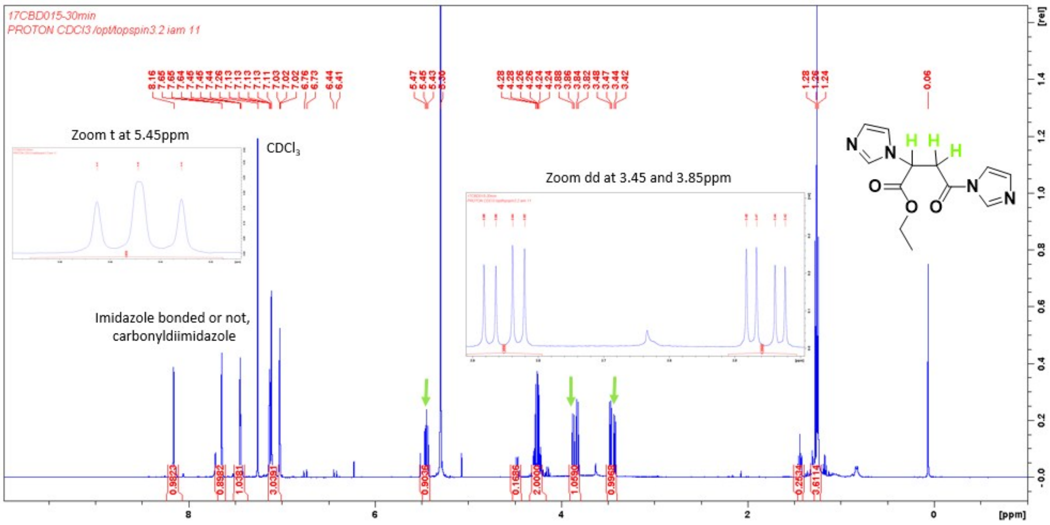
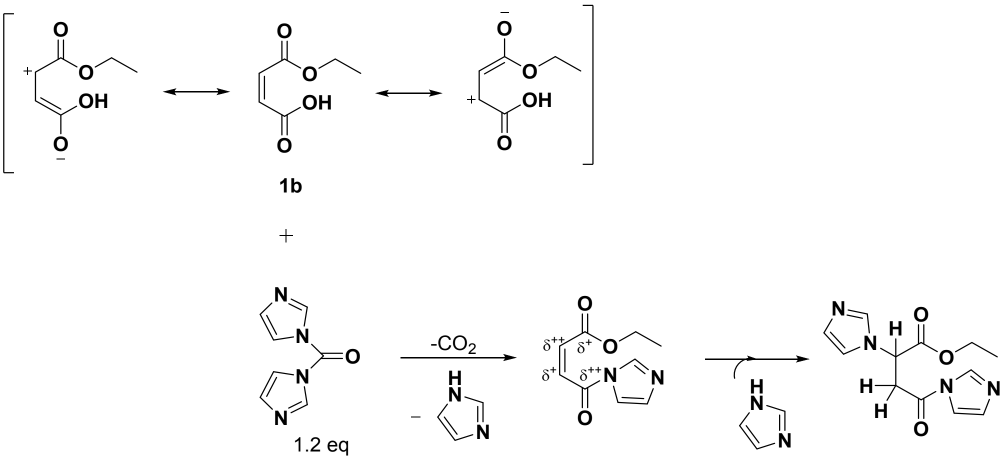


Figure 26: ^1H NMR spectrum highlighting the addition of imidazole on the double bond of the maleate

ii. Mechanistic explanation and conclusion

Carbonyldiimidazole has been already reported for esterification or amidation reactions.[6–8] It is a one-pot reaction constituted of two steps. Firstly, the acyl imidazole is formed and then by the addition of an alcohol or an amine, the ester or amide compound is obtained. However, the formation of imidazole during the first step caused imidazole to nucleophilically add onto the double bond of the maleate. Indeed, due to the high withdrawing effect of the two carbonyl groups, the addition of any nucleophilic compound is facilitated onto the double bond (Scheme 3) especially on the α-position of the ester. In absence of alcohol, this reaction, confirmed by ^{1}H NMR, was fast and completed in less than 30 min (See Supporting Information Figure 3). This addition was highlighted by the presence of two distinct doublets and one apparent triplet from the three hydrogens coming from the previous double bond.



Scheme 2: Scheme of the side-reaction from the imidazole

4. By using Steglich esterification (DCC/DMAP) on hydrogenated and partially fluorinated alcohols

To a solution of monoethyl maleate (432 mg) and DMAP (0.1 eq) in DCM, 1.1 eq of DCC in DCM were added dropwise at 0 °C under inert atmosphere. Then the corresponding alcohol was added dropwise (1.1 eq). After 5 min of reaction, the ice bath was removed. The reaction was monitored by TLC (100 % EtOAc) to follow the disappearance of the starting monoethyl maleate ($R_f = 0.73$). After 2 h, the reaction was stopped. The organic phase was washed with 0.5 N HCl and saturated $NaHCO_3$ solution. The organic phase was then dried with $MgSO_4$ and concentrated under vacuum.

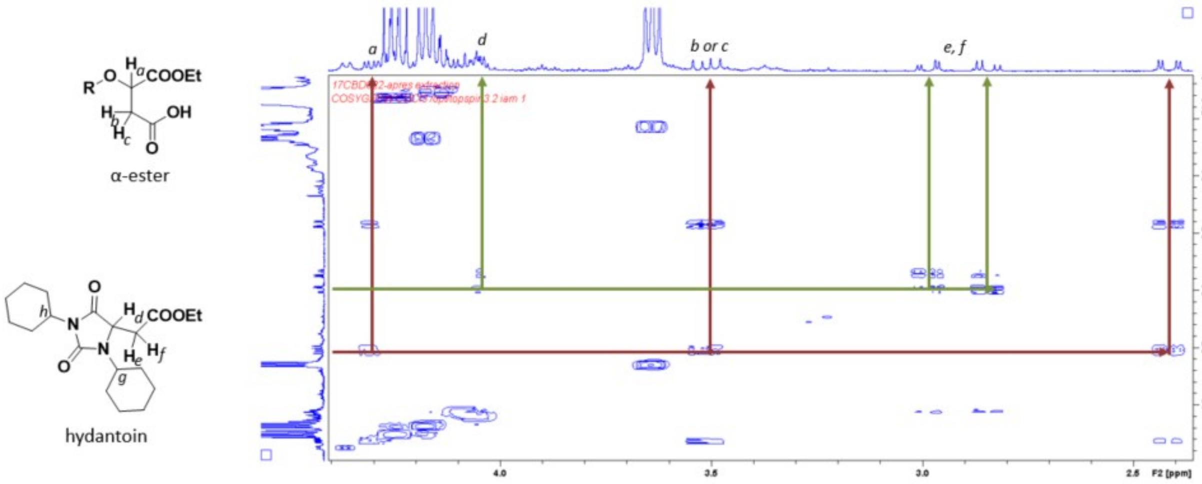


Figure 27: COSY NMR spectrum of ethyl octyl maleate (similar for any R)

In order to determine the percentage of each side-product, an internal reference was added (benzophenone). As an example for the reaction with octanol, $w_{\text{benzophenone PhCOPh}}$ = 9.9mg and w_{sample}=10.3mg. As M_{PhCOPh}=182.217g/mol, it provided n=0.0494mol for 1H so n=0.494mol for 10H. The calculation used is represented below.

$$\% \text{ desired product} = \frac{\int PhCOPh * H\ C = C\ cis}{\int C = C\ cis * HPhCOPH} * \frac{MPhCOPh}{mPhCOPh}$$

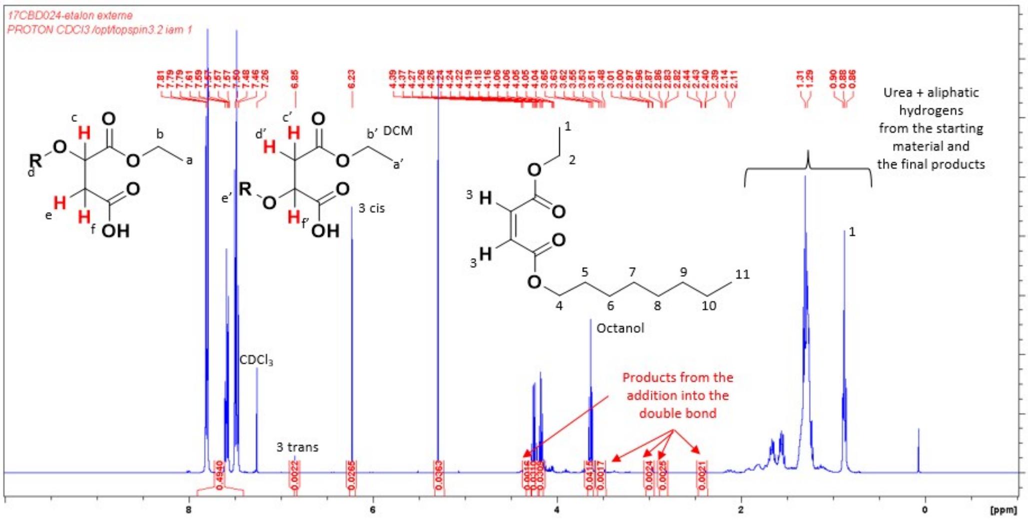


*Figure 28: ^{1}H NMR spectrum of the reaction between **1b** and octanol in presence of benzophenone*

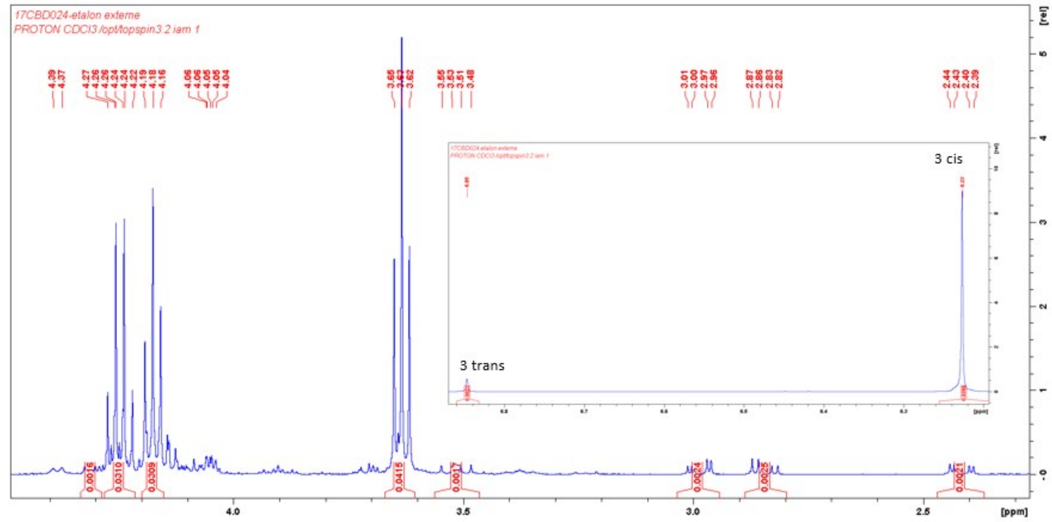


Figure 29: Zoom in the zone of the doublets of doublets

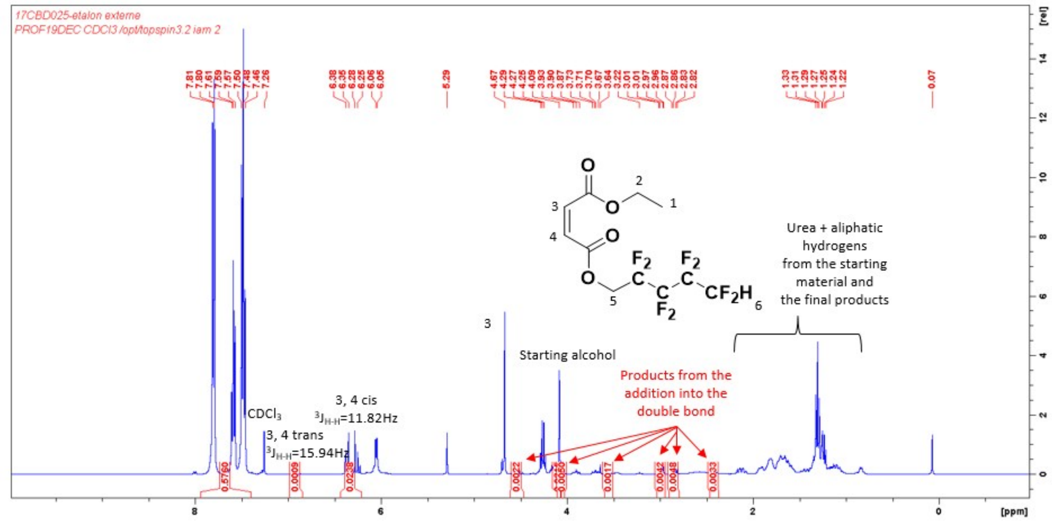


*Figure 30: ^1H-{^{19}F} NMR spectrum of the reaction between 1**b** and 2,2,3,3,4,4,5,5-octafluoropentanol in presence of benzophenone*

An experiment without addition of the alcohol was also carried out. Two products were confirmed: 1,3,5-hydantoin (Figure 31 - chemical shifts correlated with literature[9]) and the dicyclohexyl urea (Figure 32 for comparison with pure dicyclohexyl urea). Another product was observed. The signals are typical of the diester maleate: one triplet from the CH_3, one quadruplet from the -CH_2- and one singulet from the hydrogen of the double bonds (Figure 31). The only explanation would be the bonding of DCC onto the carboxylic acid and the product was stable enough in absence of nucleophile to be recovered.

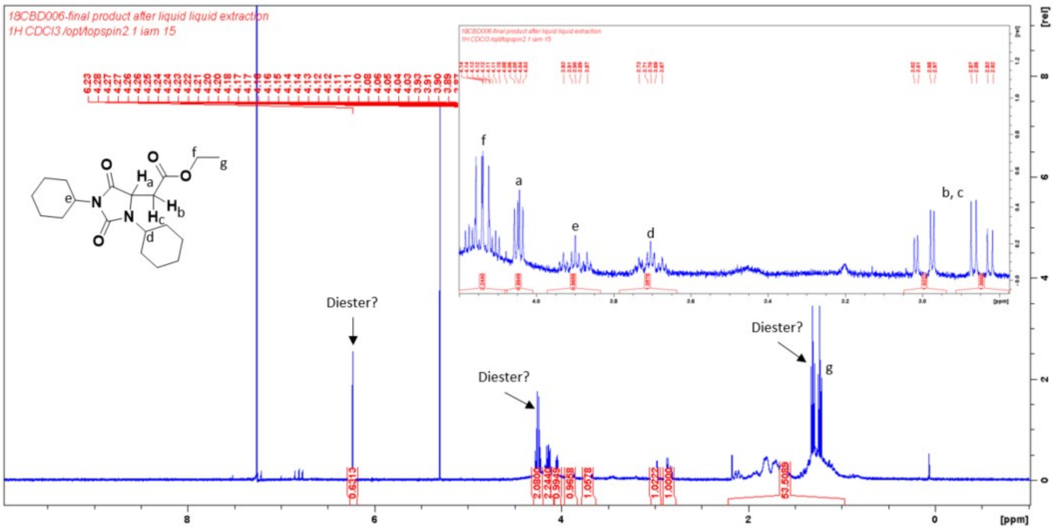


Figure 31 : ^{1}H NMR spectrum of the isolated hydantoin and another undetermined product (diester highly assumed)

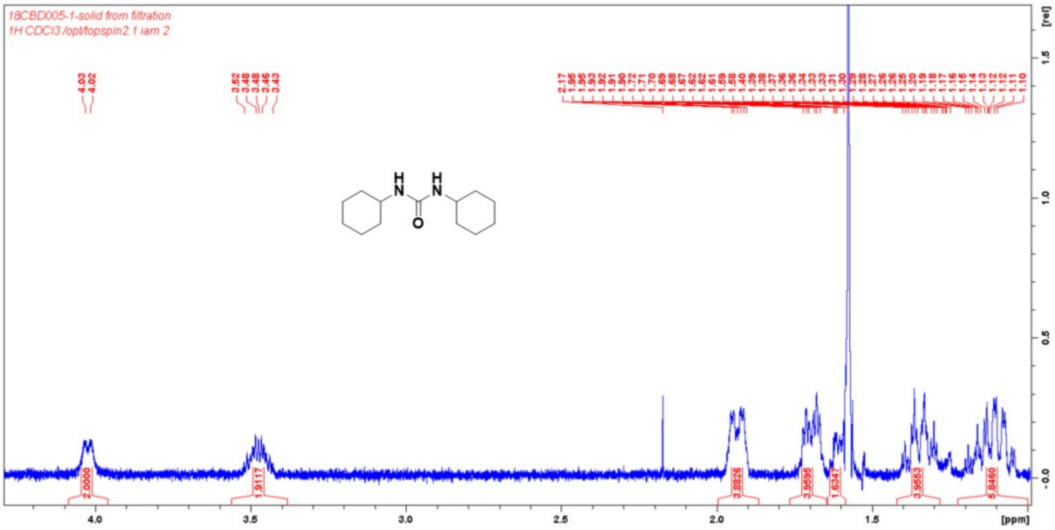


Figure 32: ^{1}H NMR spectrum of the dicyclohexyl urea

5. By using Steglich esterification (DCC/DMAP) on oligo(HFPO) Methylene Alcohol in DCM

To a solution of monoethyl maleate (144 mg, 1 eq), DMAP (12 mg, 0.1 eq) and Krytox® (2 g) in DCM (100 mL), 227 mg of DCC in 2.5 mL of DCM were added dropwise at 0°C. After 5 min of reaction, the ice bath was removed. After 2 h 30, 5 h, 7 h (Figure 31) and 21 h, a sampling was performed. DCM was removed under nitrogen flux and 1,1,1,3,3-pentafluorobutane was added to have enough product for NMR with C_6D_6 capillaries.

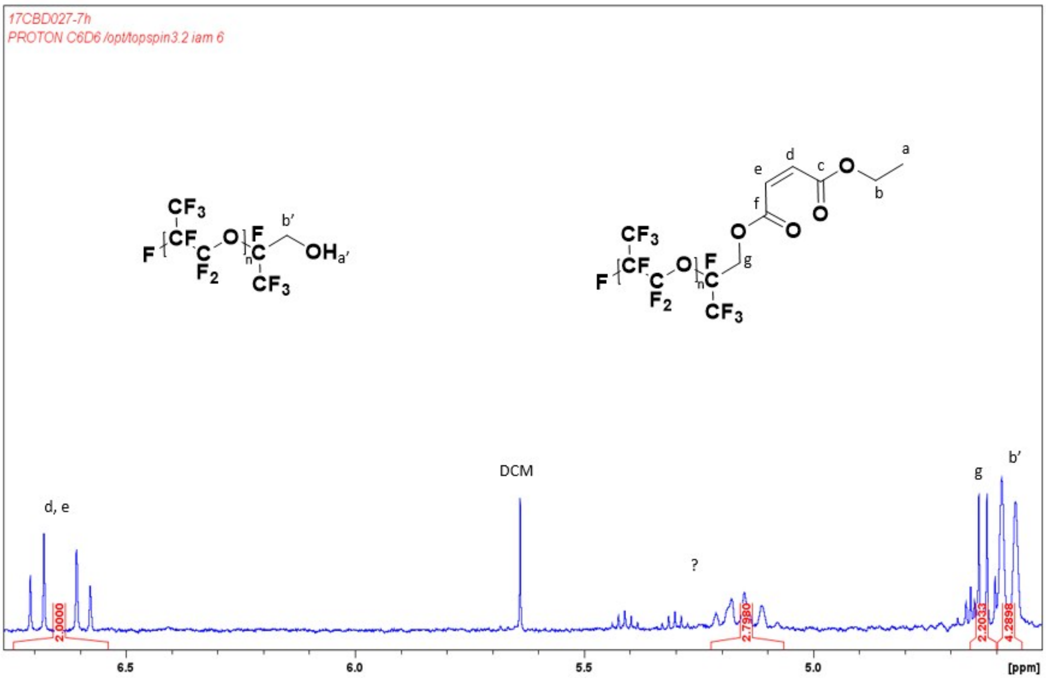


Figure 33: ^{1}H NMR spectrum of sampling after 7 h of reaction

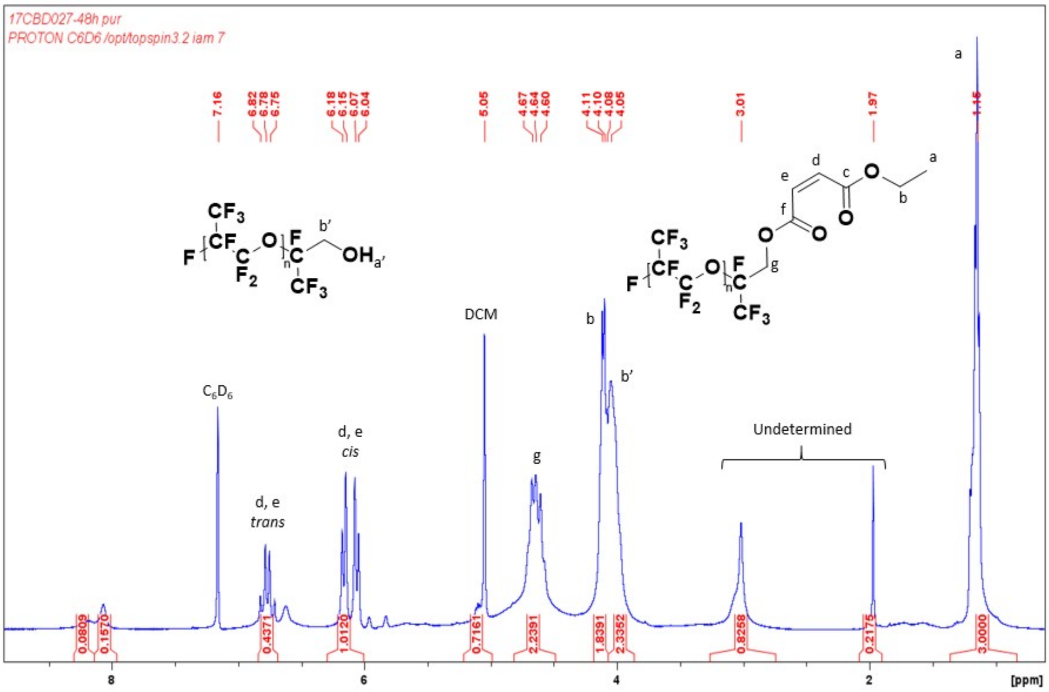


Figure 34: ^{1}H NMR spectrum of maleate oligo(HFPO) without purification

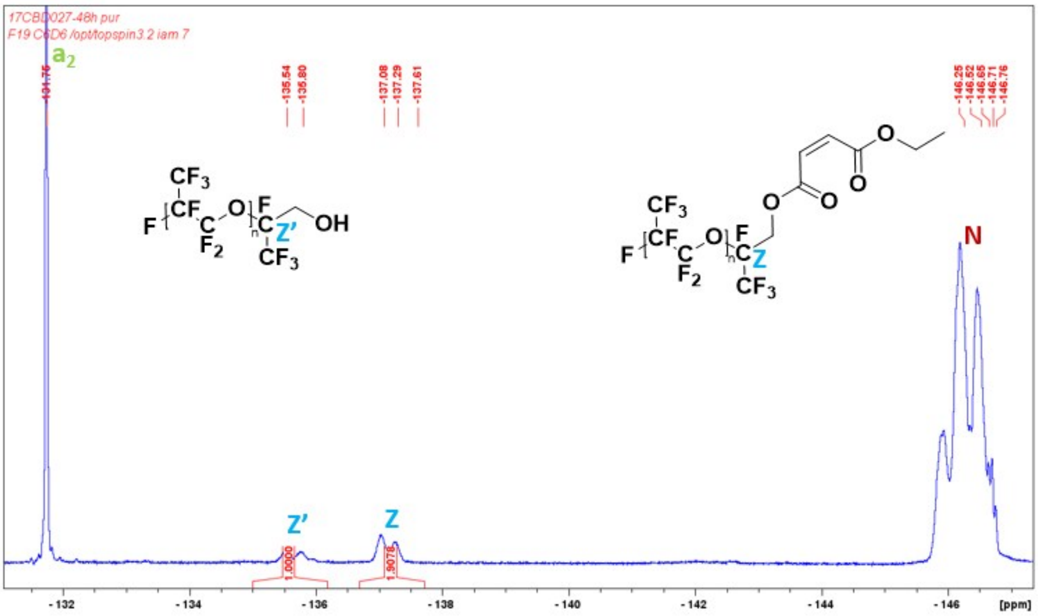


Figure 35: ^{19}F NMR spectrum of maleate oligo(HFPO) without purification

D. NMR of the starting oligo(HFPO) methylene alcohol (M_w~2000 g/mol)

The commercial product Krytox® M_w~2000 g/mol was firstly analyzed by NMR and the chemical shifts except for the $–CF(CF_3)CH_2OH$ are similar and can be kept for the NMR analysis of the final α,β-unsaturated esters. The attributions of the chemical shifts were made using the work made by Rinaldi and his team based on an oligomer of Krytox® (n = 2) with a different end group (-COOH).[10,11]

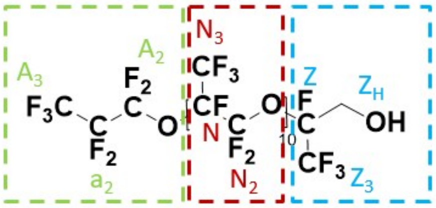


Figure 36: Structure of oligo(HFPO) methylene alcohol divided into three parts: A and Z as chain-end groups and N as repeat unit

Table 2: Summary of the different chemical shifts for ^1H, ^{19}F and ^{13}C

	^{1}H δ (ppm) (temperature dependent)	^{19}F δ (ppm)	^{13}C δ (ppm)
$-\mathbf{OH}$	2.88	-	-
$-\underline{\mathbf{CH_2}}OH$	3.96	-	60.37
$–\underline{\mathbf{CF}}(CF_3)CH_2OH$ (Z)	-	-137.66	108.48
$–CF(\underline{\mathbf{CF_3}})CH_2OH$ (Z_3)	-	-84.59	119.21
$-(OCF_2\underline{\mathbf{CF}}(CF_3))_n-$ (N)	-	-145.69	103.03
$-(O\underline{\mathbf{CF_2}}CF(CF_3))_n-$ (N_2)	-	From -80.8 to -82.86	116.12
$-(OCF_2CF(\underline{\mathbf{CF_3}}))_n-$ (N_3)	-	From -81.8 to -81.96	117.66
$\mathbf{-}\underline{\mathbf{CF_2}}CF_2CF_3$ (A_2)	-	From -82.7 to -83.45	115.65
$-CF_2\underline{\mathbf{CF_2}}CF_3$ (a_2)	-	-131.52	106.74
$-CF_2CF_2\underline{\mathbf{CF_3}}$ (A_3)	-	-83.77	117.21

The ^{1}H and ^{1}H-{^{19}F} NMR spectra were made at room temperature and at 50 °C to study the effect of temperature on the viscosity of Krytox®. In Figure 2, the higher temperature of 50 °C permitted to get a doublet with a good separation between the two signals. Another observation is the shift of the alcohol group from 3.68 ppm (R.T.) to 2.88 ppm (50 °C).

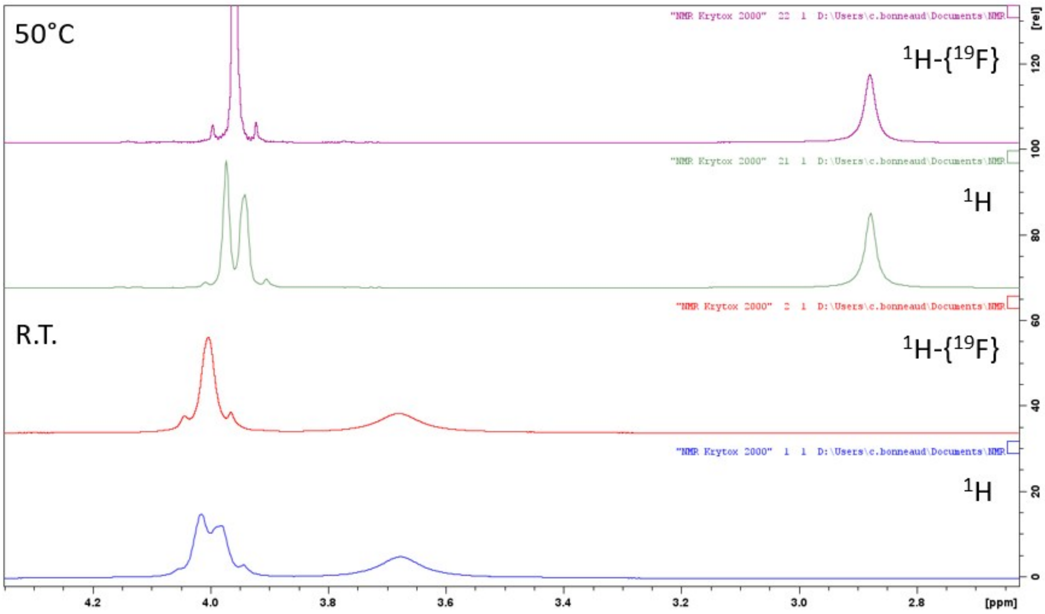


Figure 37: ^1H and 1H-{^{19}F} NMR at room temperature and at 50 °C

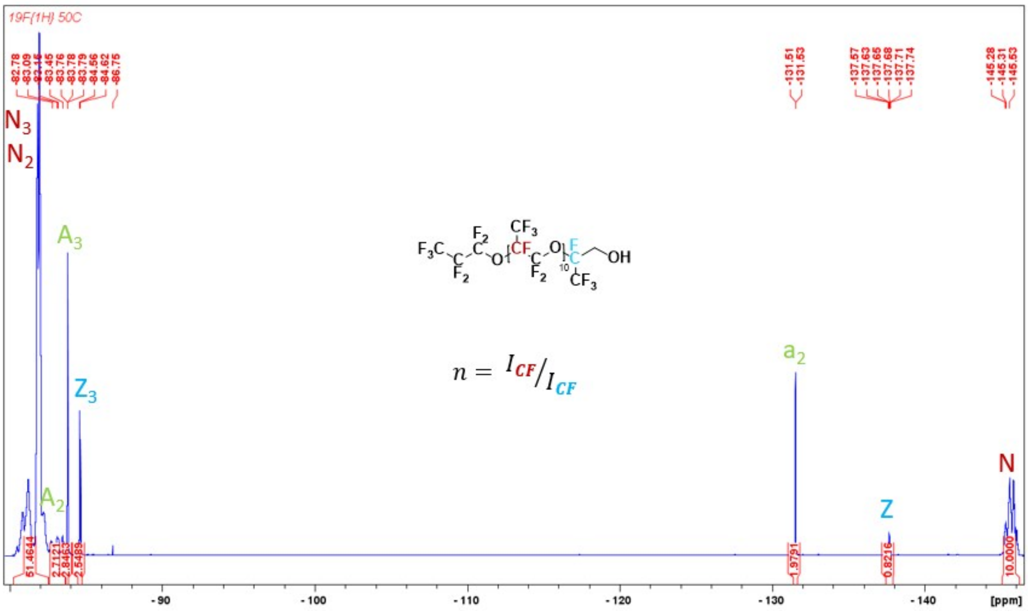


Figure 38: ^{19}F-{^1H} NMR spectrum with the corresponding assignments

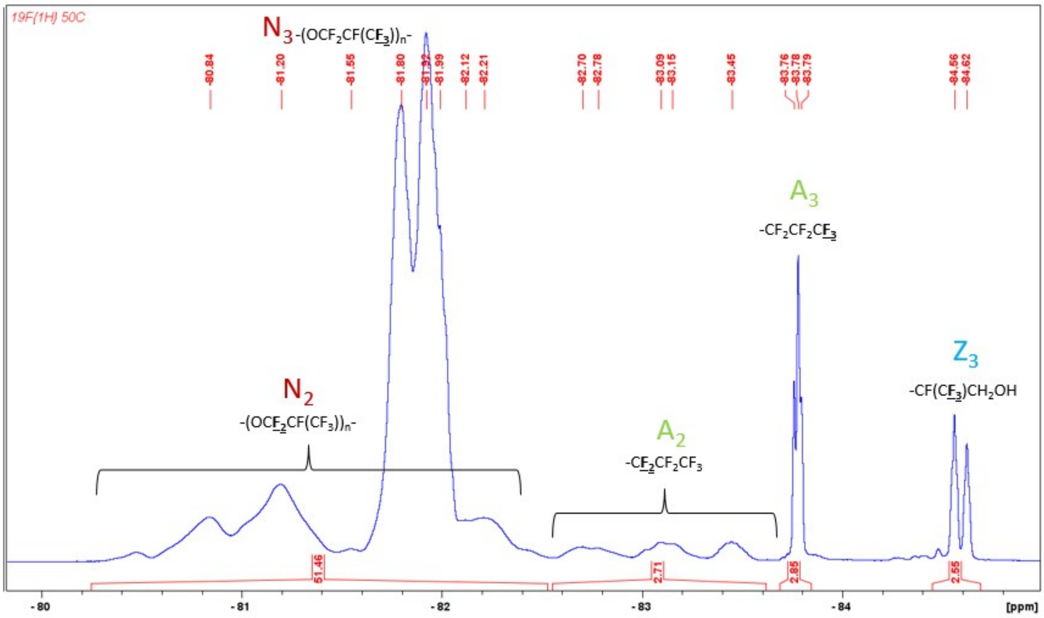


Figure 39: ^{19}F-{^{1}H} NMR spectrum with the corresponding assignments between -80 ppm and -85 ppm

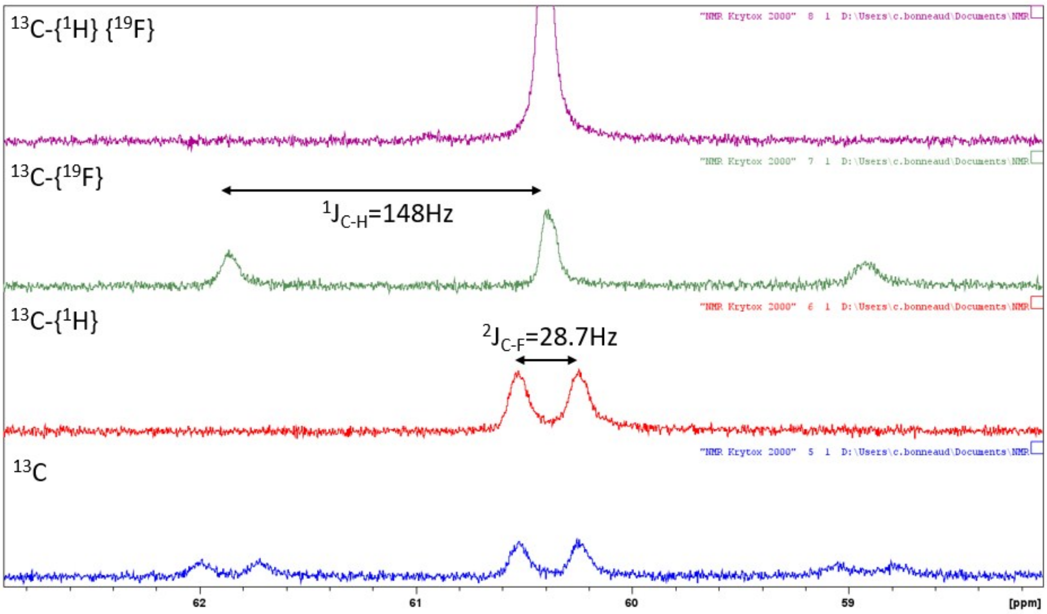


Figure 40: ^{13}C, ^{13}C-{^{1}H}, ^{13}C-{^{19}F} and ^{13}C-{^{1}H}{^{19}F} NMR spectra

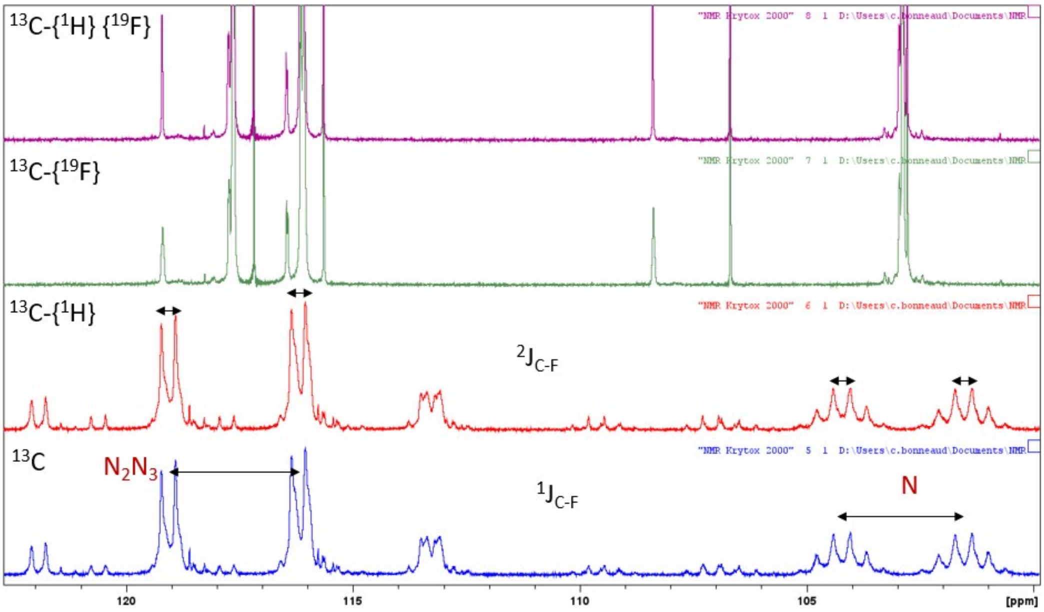


Figure 41: ^{13}C NMR spectra of Krytox 2000 with no change between ^{13}C and ^{13}C-{^{1}H}

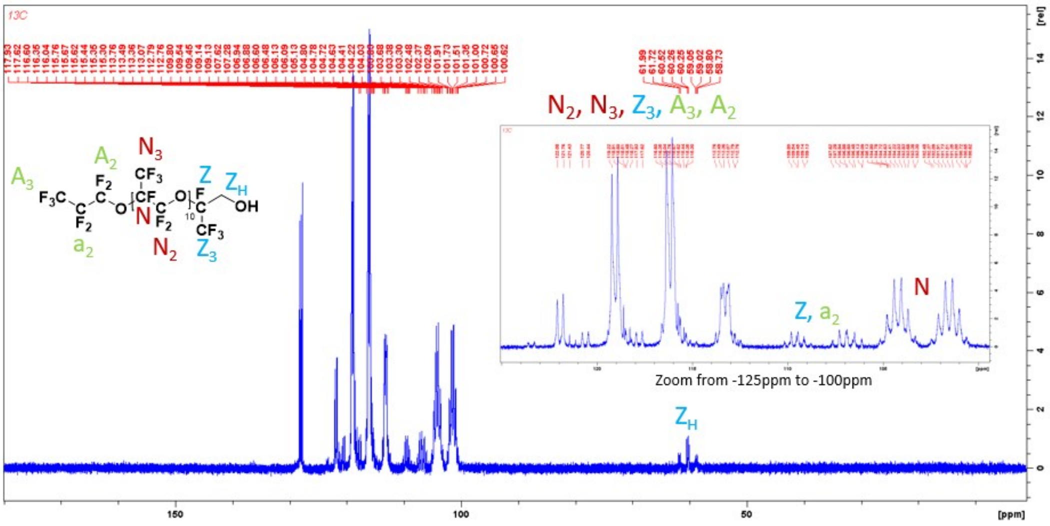


Figure 42: ^{13}C NMR spectrum

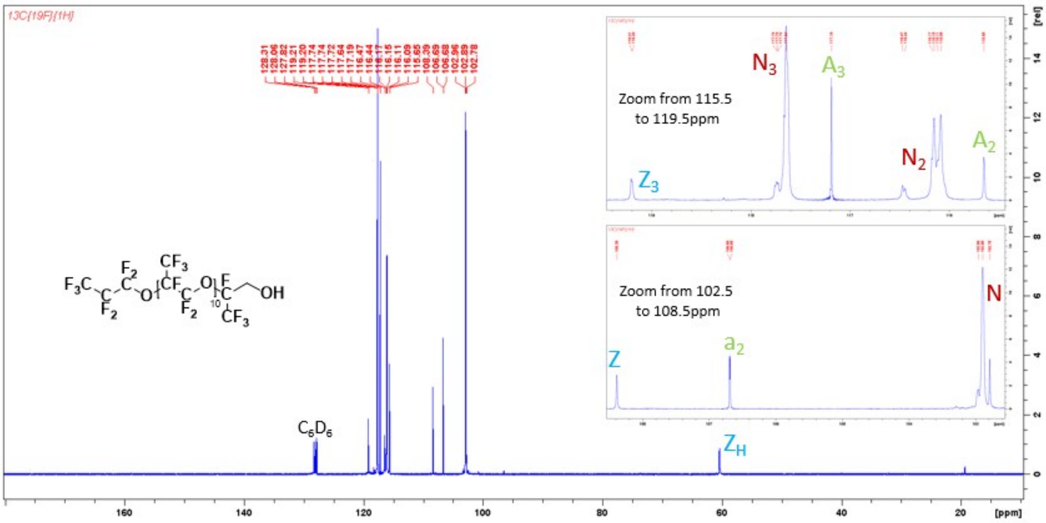
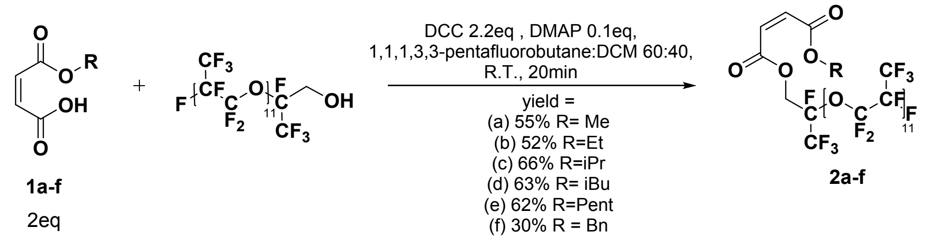


Figure 43: ^{13}C-{^{1}H}/{^{19}F} NMR spectrum

	$^{1}J_{C-H}$ (MHz)	$^{1}J_{C-F}$ (MHz)	$^{2}J_{C-F}$ (MHz)
Literature[10]	-	275	40
Our values	148	269	30

E. Experimental, IR, ^{1}H, ^{13}C-NMR and GC-MS Spectra of the different maleates oligo(HFPO) (M_w~2000 g/mol)

1. Experimental



1a-f
2eq

2a-f

To a solution of oligo(HFPO) alcohol (M_w=2000 g/mol, 2 g, 1 mmol), monoalkyl maleate (2 eq) and DMAP (0.1 eq) in 1,1,1,3,3-pentafluorobutane (15 mL), 2.2 eq of DCC in DCM (10 mL) were added dropwise at 0 °C during 30 min. After 5 min of reaction, the ice bath was removed. The conversion of the reaction was followed by ^{19}F NMR. After 20 min, the reaction was stopped. The reaction mixture was filtrated and concentrated under vacuum. A flash column chromatography (10:90 EtOAc:Pentane except 5:95 for the benzyl maleate oligo(HFPO)) by solid deposit was performed. The solvents were removed under vacuum to afford oil products.

2. Methyl maleate oligo(HFPO) **2a**

Clear colorless oil - Yield = 55 %

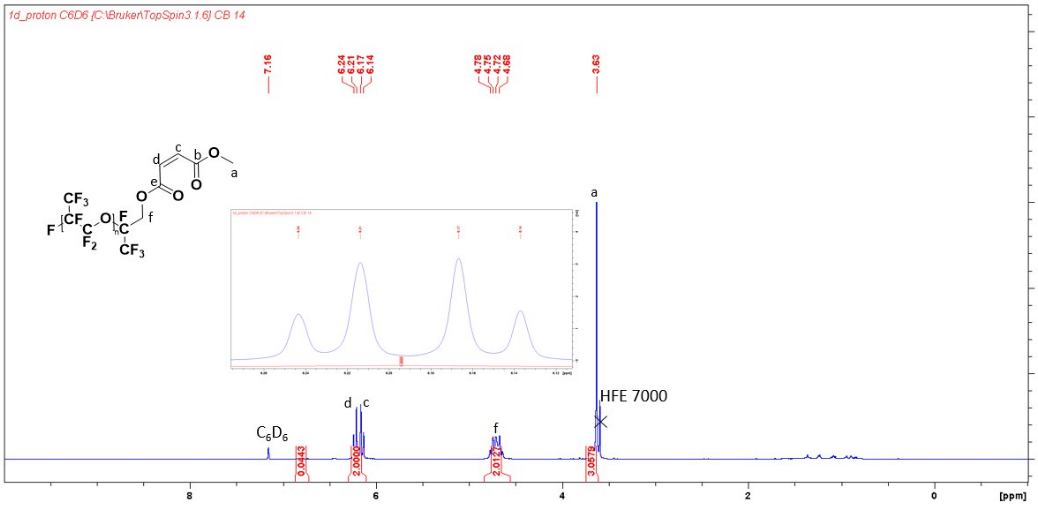


*Figure 44: ^{1}H NMR spectrum of **2a***

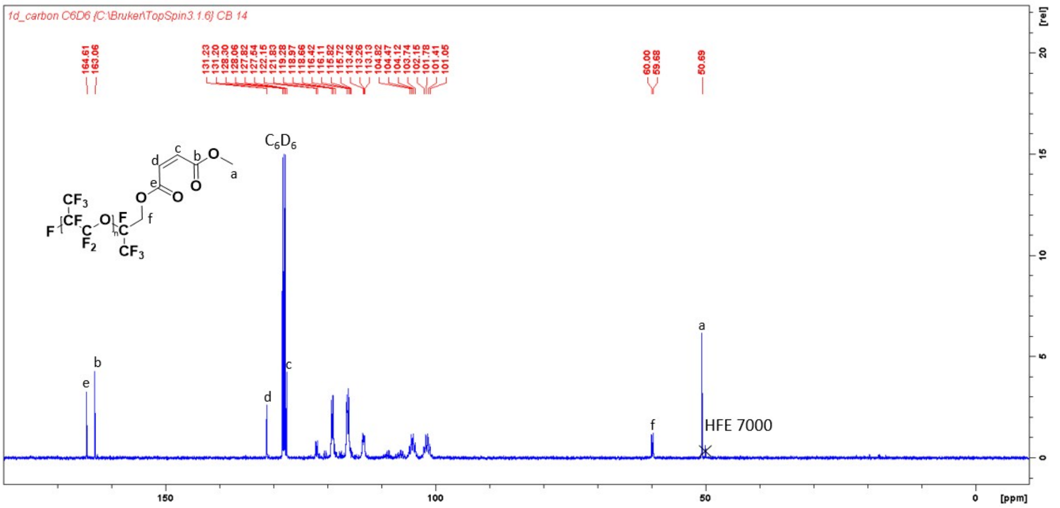


*Figure 45: ^{13}C NMR spectrum of **2a***

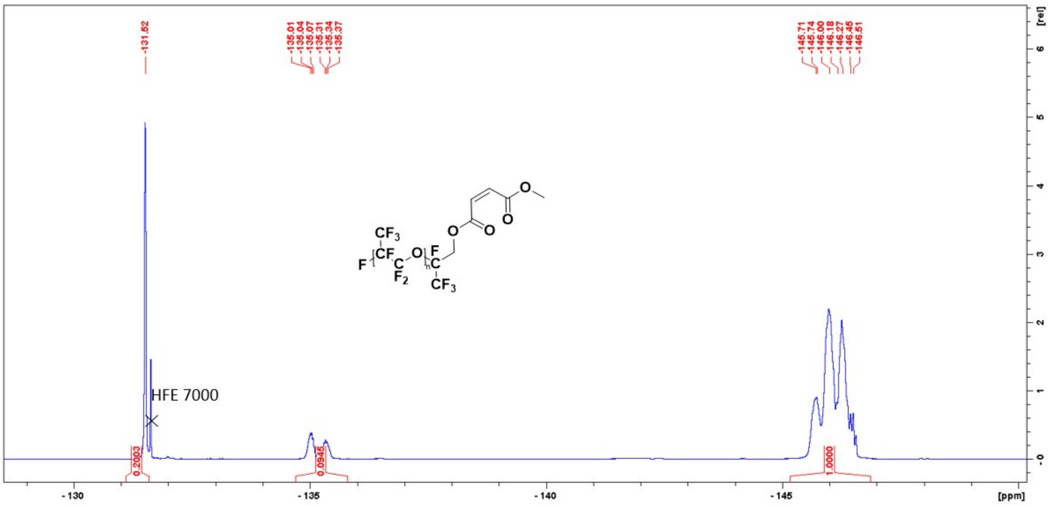


*Figure 46: ^{19}F NMR spectrum of **2a***

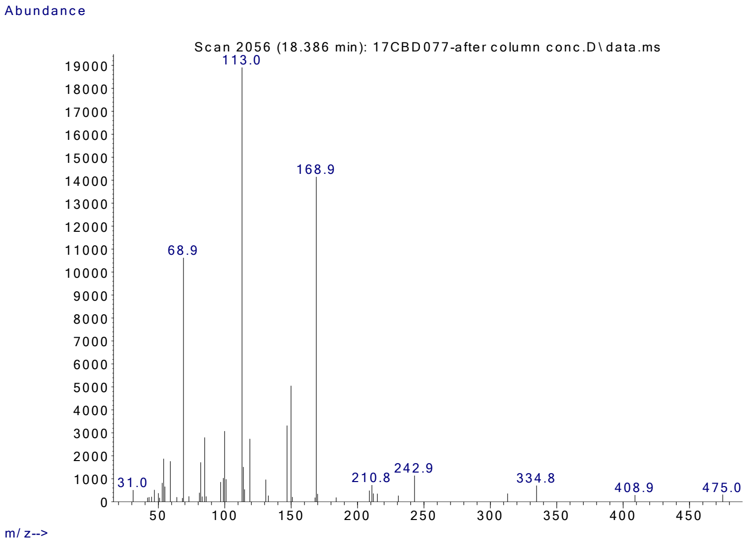


*Figure 47: GC-MS spectrum of **2a***

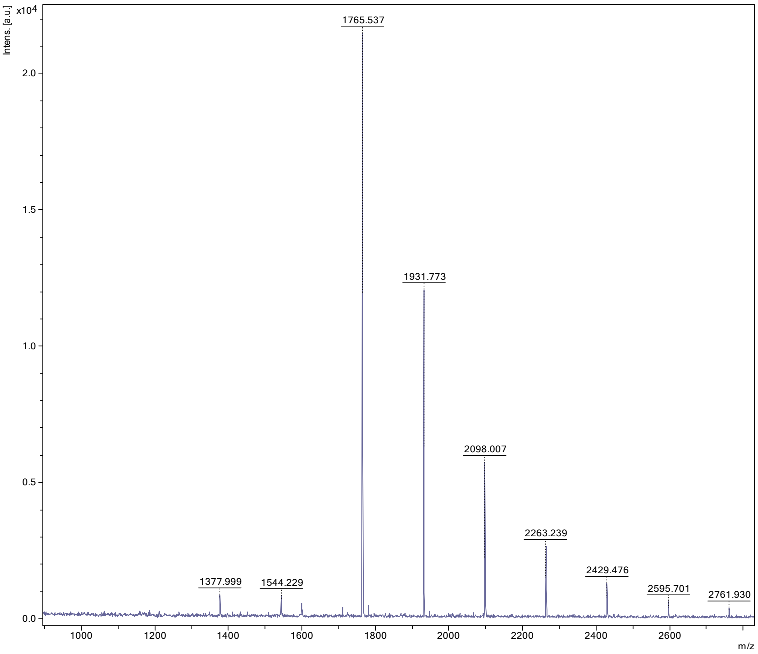


*Figure 48: MALDI-TOF spectrum of **2a***

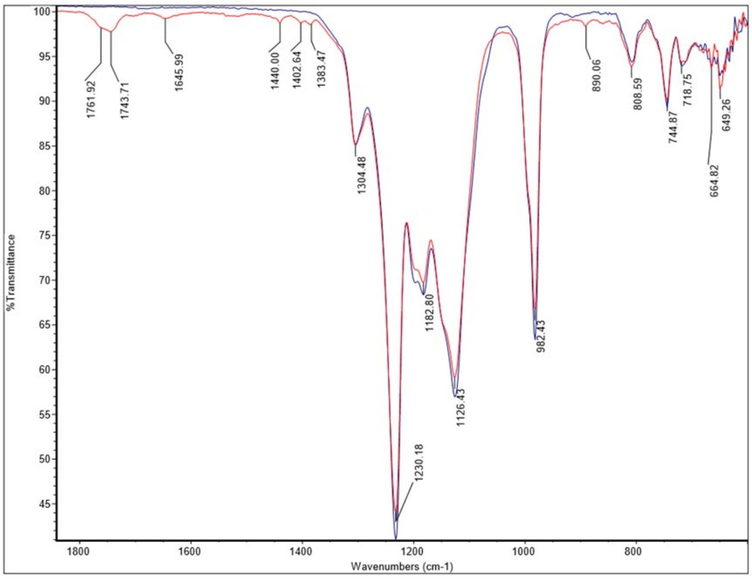


*Figure 49: IR spectra of **2a** (and oligo(HFPO) alcohol in blue)*

3. Ethyl maleate oligo(HFPO) **2b**

Ethyl maleate oligo(HFPO) **2b** (purified by flash chromatography 10:90 EtOAc:Pentane, yield=52 %, clear colorless oil): ^{1}H NMR (400 MHz, C_6D_6, 25 °C, δ): 0.87 (t, -$CH_2\mathbf{CH_3}$, 3H, $^3J_{H\text{-}H}$=7.1 Hz), 4.13 (q, -$\mathbf{CH_2}CH_3$,2H, $^3J_{H\text{-}H}$=7.1 Hz), 4.64-4.78 (m, HFPO-C$\mathbf{H_2}$O–, 2H), 6.20 (dd, -C**H**=C**H**- *cis*, 2H, $^3J_{H\text{-}H}$ = 11.8 Hz and 35.3 Hz), ^{13}C NMR (100 MHz, C_6D_6, 25 °C, δ): 12.5 ($\mathbf{C}H_3CH_2OCO$-), 59.8 (-COO$\mathbf{C}H_2R_f$), 60.6 ($CH_3\mathbf{C}H_2OCO$-), 127.2 (-**C**H=CHCOOCH$_2$-), 131.8 (-**C**HCOOCH$_2$R$_f$), 163.1 (-**C**OOCH$_2$-), 164.3 (R_fCH_2**C**OO-), ^{19}F NMR (376 MHz, C_6D_6, 25 °C, δ): -135.2 ($d_{R\text{-}S}$q, -**CF**(CF_3)CH_2R_h), GC-MS, 70 eV, *m/z*: 69 (34), 99.1 (55), 100 (16), 119.1 (13), 126.1 (19), 127.1 (25), 147 (25), 150 (29), 169 (100), MALDI-TOF, $[M+Li]^+$: 1779.6 – 1945.9 – 2112.1 – 2277.4 – 2443.6, FT-IR (ATR) ν_{max} (cm^{-1}): 982.5 – 1126.5 – 1230.2 – 1651.1 – 1738.2

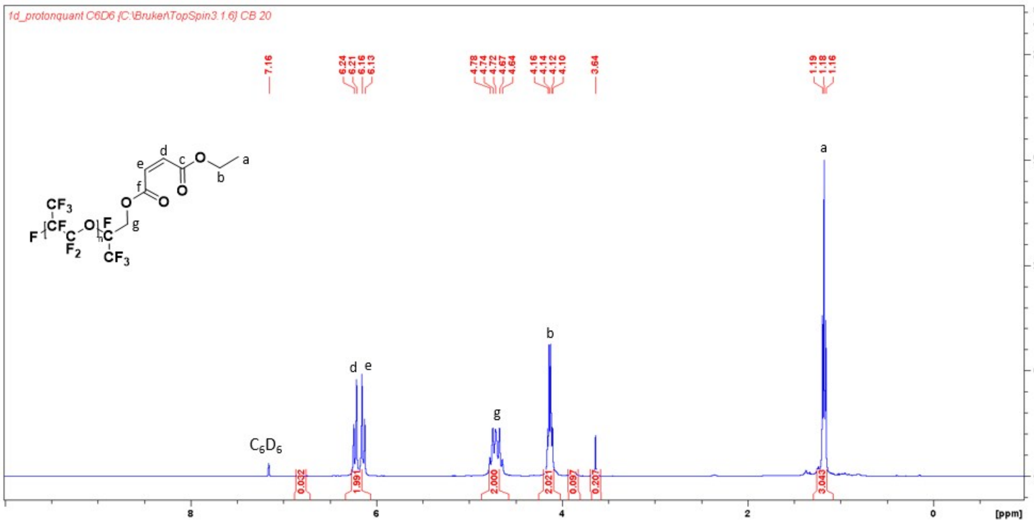


*Figure 50: ^{1}H NMR spectrum of **2b***

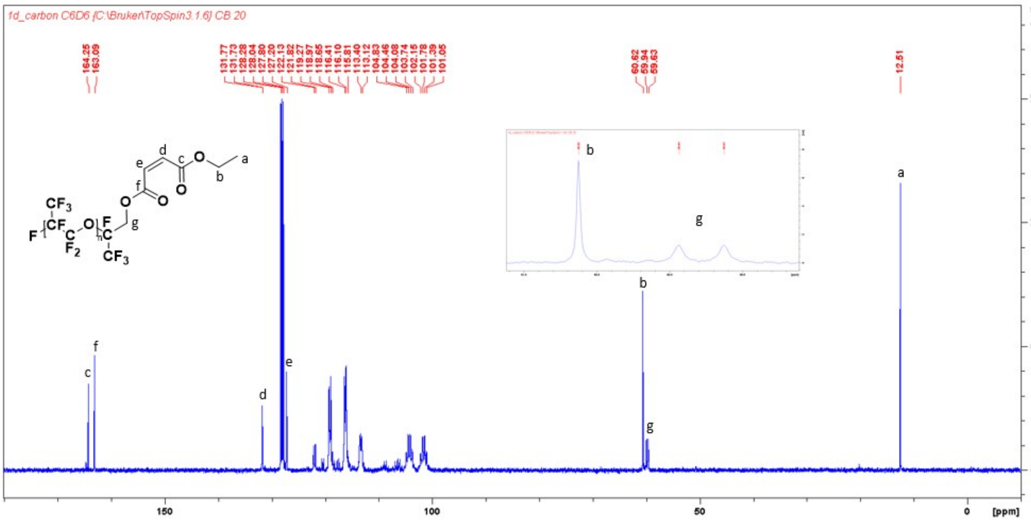


*Figure 51: ^{13}C NMR spectrum of **2b***

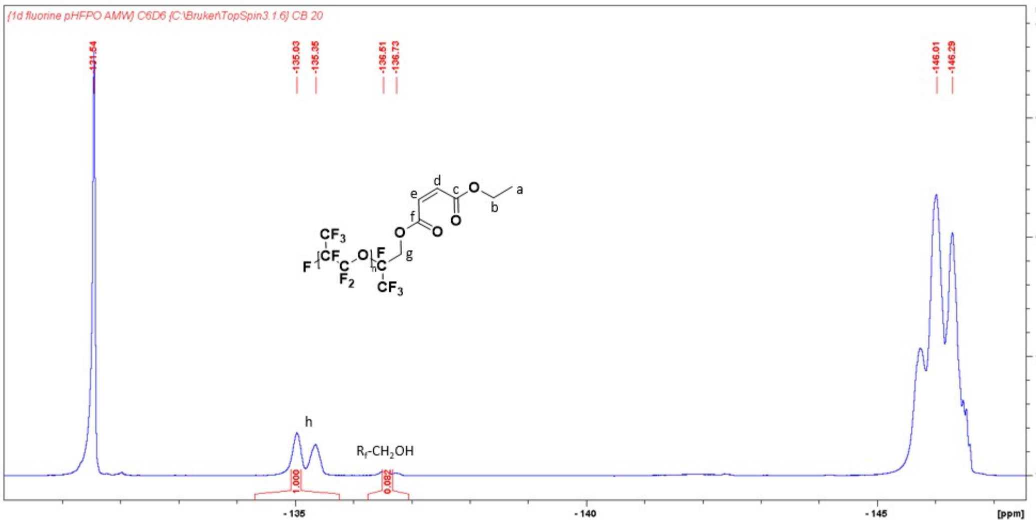


*Figure 52: ^{19}F NMR spectrum of **2b** (6% of alcohol)*

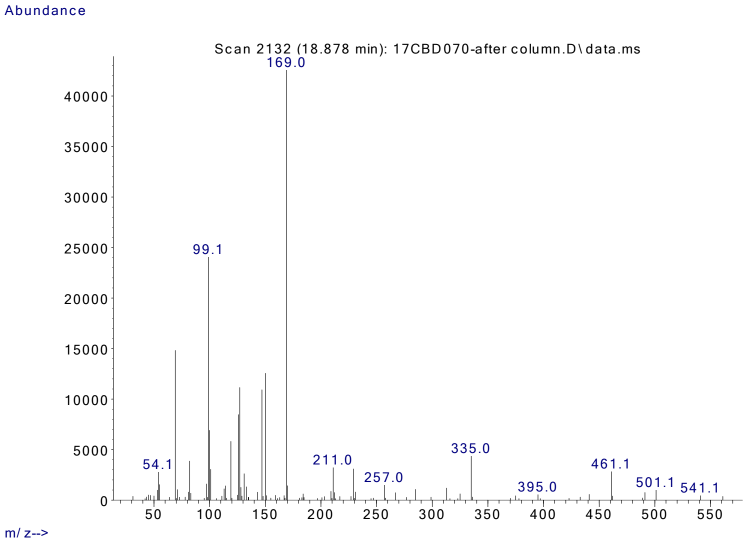


Figure 53: GC-MS spectrum of **2b**

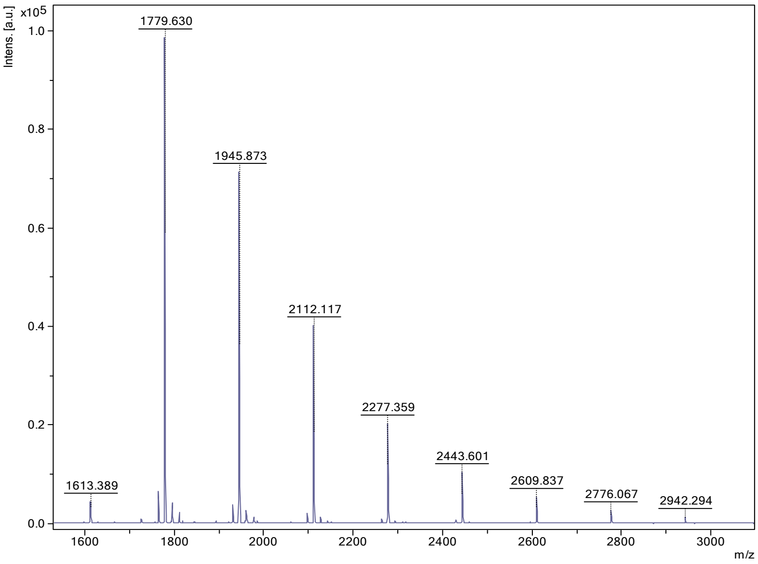


Figure 54: MALDI-TOF spectrum of **2b**

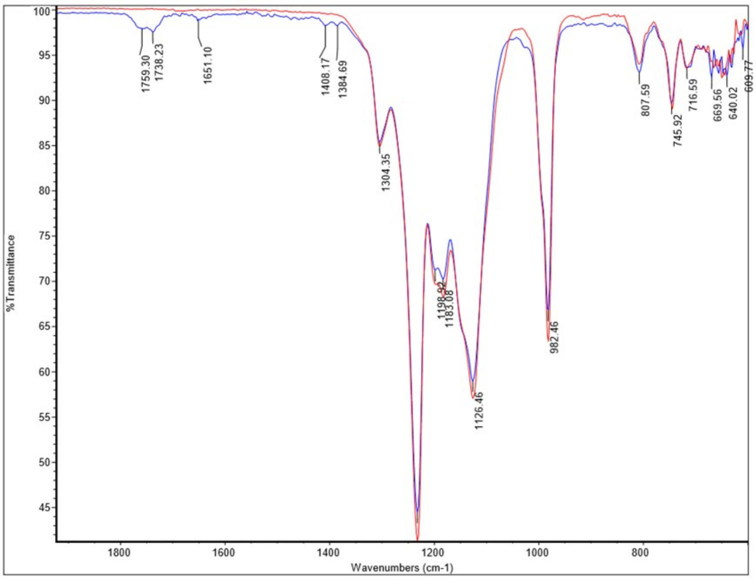


*Figure 55: IR spectrum of **2b** (and oligo(HFPO) alcohol in red)*

4. Isopropyl maleate oligo(HFPO) **2c**

Isopropyl maleate oligo(HFPO) **2c** (purified by flash chromatography 10:90 EtOAc:Pentane, yield=66 %, clear colorless oil): ^{1}H NMR (400 MHz, C_6D_6, 25 °C, δ): 1.18 (d, $-CH(C\mathbf{H_3})_{2,}$ 6H, $^3J_{H\text{-}H}$ = 6.3 Hz), 4.65-4.79 (m, HFPO-C**H₂**O–, 2H), 5.03 (spt, $-C\mathbf{H}(CH_3)_{2,}$ 1H, $^3J_{H\text{-}H}$ = 6.3 Hz), 6.17 (dd, -C**H**=C**H**- cis, 2H, $^3J_{H\text{-}H}$ = 11.7 Hz and 38.0 Hz), ^{13}C NMR (100 MHz, C_6D_6, 25 °C, δ): 20.3 ($-CH(\mathbf{C}H_3)_2$) – 59.7 ($-COO\mathbf{C}H_2R_f$), 68.4 ($-\mathbf{C}H(CH_3)_2$), 126.8 ($-\mathbf{C}H{=}CHCOOCH_2$-), 132.4 ($-\mathbf{C}HCOOCH_2R_f$), 163.0 (-**C**OOCH-), 163.6 ($R_fCH_2\mathbf{C}OO$-), ^{19}F NMR (376 MHz, C_6D_6, 25 °C, δ): -135.1 ($d_{R\text{-}S}$q, $-\mathbf{CF}(CF_3)CH_2R_h$), GC-MS, 70 eV, *m/z*: 43.1 (42), 69 (60), 82 (15), 99 (63), 100 (25), 100.9 (11), 119 (19), 141.1 (19), 147 (24), 150.1 (38), 169 (100), 229.1 (11), 312.9 (29), 335 (16), 461.1 (11), MALDI-TOF, $[M+Li]^+$: 1793.5 – 1959.7 – 2125.9 – 2291.2 – 2457.4, FT-IR (ATR) ν_{max} (cm^{-1}): 982.3 – 1126.5 – 1182.9 – 1230.2 – 1645.0 – 1731.0

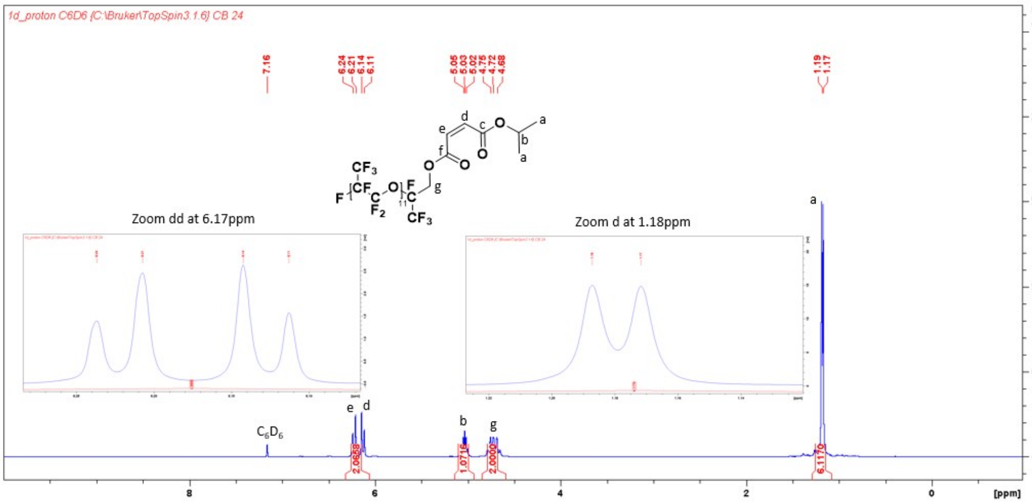


*Figure 56: ^{1}H NMR spectrum of **2c***

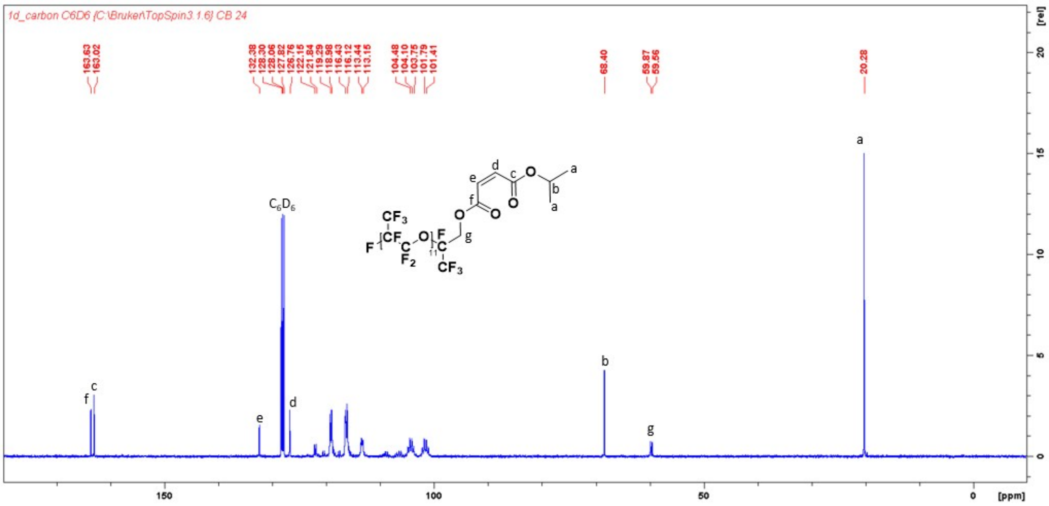


*Figure 57: ^{13}C NMR spectrum of **2c***

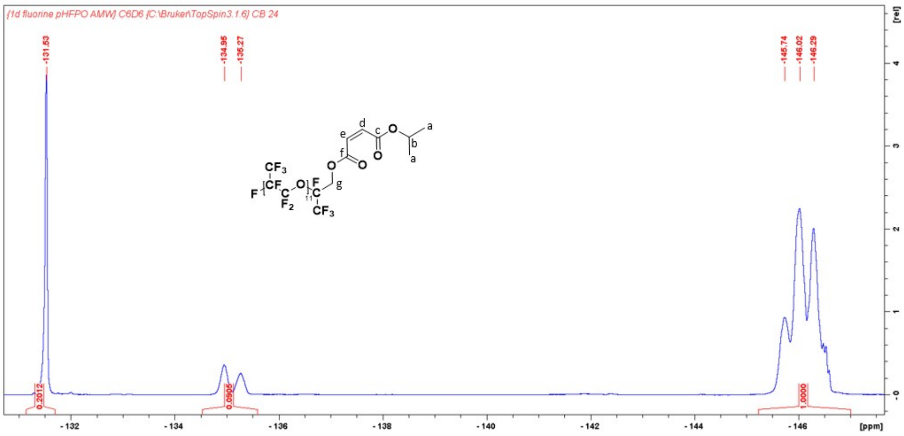


*Figure 58: ^{19}F NMR spectrum of **2c***

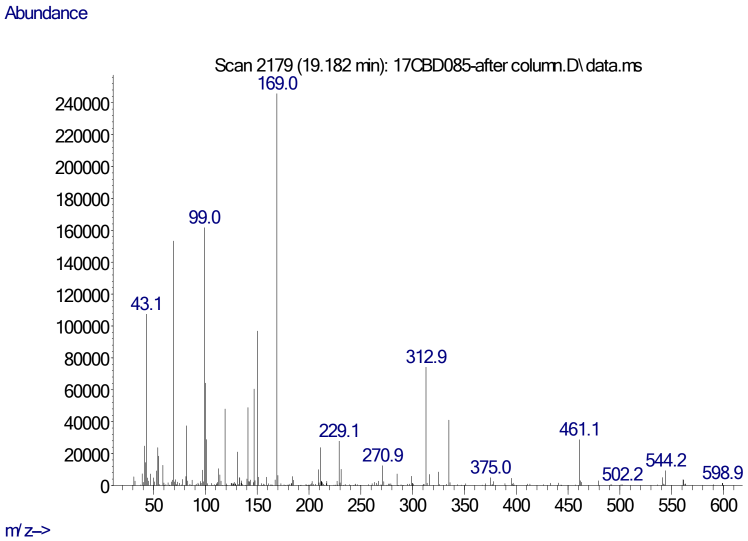


*Figure 59: GC-MS spectrum of **2c***

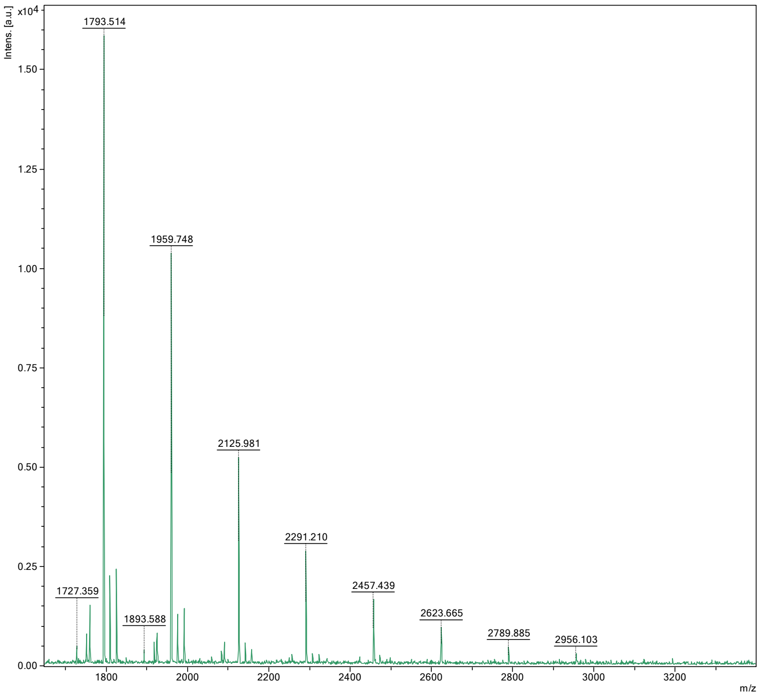


Figure 60: MALDI-TOF spectrum of ***2c***

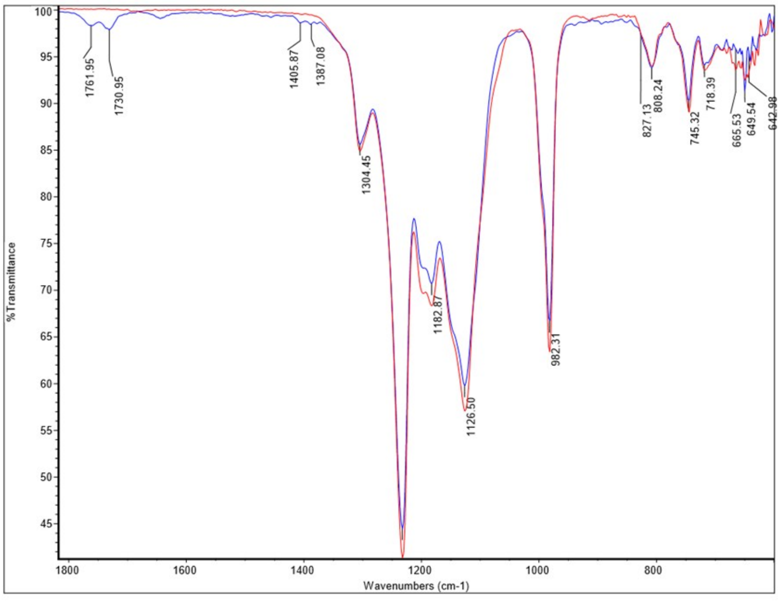


Figure 61: IR spectrum of ***2c*** *(and oligo(HFPO) alcohol in red)*

5. Isobutyl maleate oligo(HFPO) **2d**

Isobutyl maleate oligo(HFPO) **2d** (purified by flash chromatography 10:90 EtOAc:Pentane, yield=63 %, clear colorless oil): ^{1}H NMR (400 MHz, C_6D_6, 25 °C, δ): 0.87 (d, $-CH(C\mathbf{H_3})_2$, 6H, $^3J_{H\text{-}H}$=6.7 Hz), 1.90 (tspt, $-C\mathbf{H}(CH_3)_2$, 1H, $^3J_{H\text{-}H}$=6.7 Hz and $^3J_{H\text{-}H}$=6.6 Hz), 3.89 (d, $-C\mathbf{H_2}CH(CH_3)_2$, 2H, $^3J_{H\text{-}H}$=6.6 Hz), 4.65-4.78 (m, HFPO-C$\mathbf{H_2}$O–, 2H), 6.20 (dd, -C**H**=C**H**- *cis*, 2H, $^3J_{H\text{-}H}$ = 11.8 Hz and 41.3 Hz), ^{13}C NMR (100 MHz, C_6D_6, 25 °C, δ): 17.7 ($-CH(\mathbf{C}H_3)_2$) – 27.5 ($-\mathbf{C}H(CH_3)_2$) 59.8 ($-COO\mathbf{C}H_2R_f$) - 71.0 ($-\mathbf{C}H_2CH(CH_3)_2$) – 127.3 ($-\mathbf{C}H=CHCOOCH_2$-), 131.7 ($-\mathbf{C}HCOOCH_2R_f$), 163.1 ($-\mathbf{C}OOCH_2$-), 164.2 ($R_fCH_2\mathbf{C}OO$-), ^{19}F NMR (376 MHz, C_6D_6, 25 °C, δ): -135.1 ($d_{R\text{-}S}$q, $-\mathbf{CF}(CF_3)CH_2R_h$), GC-MS, 70 eV, *m/z*: 56.2 (14), 57.1 (71), 69.1

(34), 99.1 (55), 100 (16), 119.1 (13), 126.1 (19), 127.1 (25), 147 (25), 150 (29), 169 (100), MALDI-TOF, $[M+Li]^+$: 1807.6 – 1973.8 – 2140.0 – 2305.3 – 2471.5, FT-IR (ATR) ν_{max} (cm^{-1}): 982.4 – 1126.4 – 1183.0 – 1230.2 – 1644.5 – 1736.8

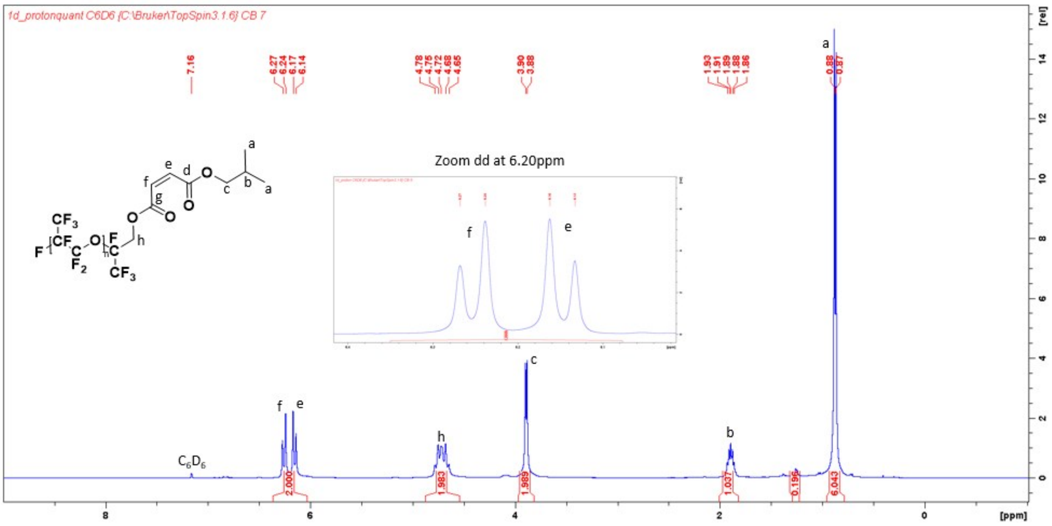


*Figure 62: ^1H NMR spectrum of **2d***

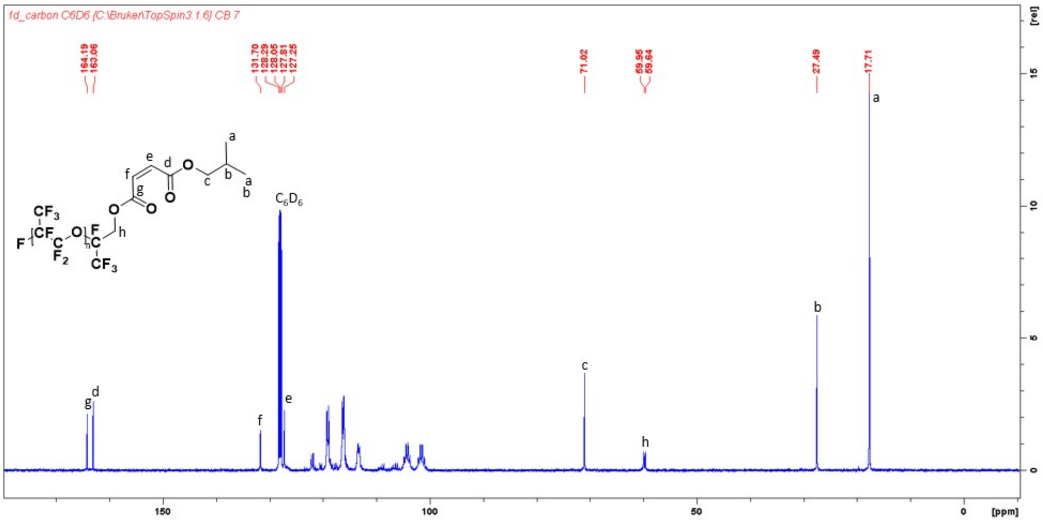


*Figure 63: ^{13}C NMR spectrum of **2d***

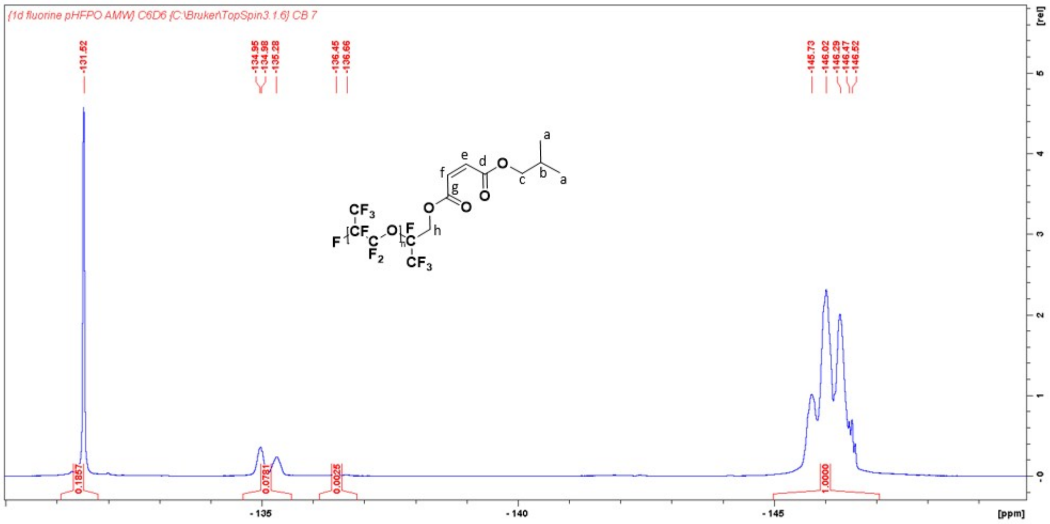


Figure 64: ^{19}F NMR spectrum of **2d** (3% of alcohol)

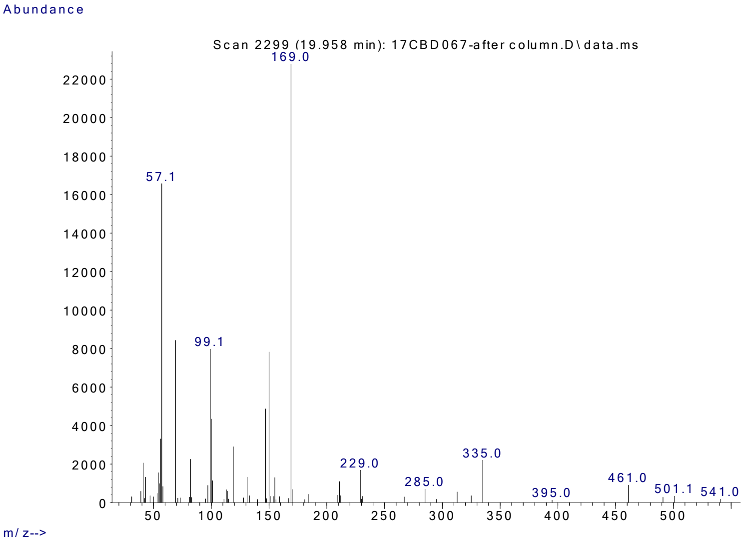


Figure 65: GC-MS spectrum of **2d**

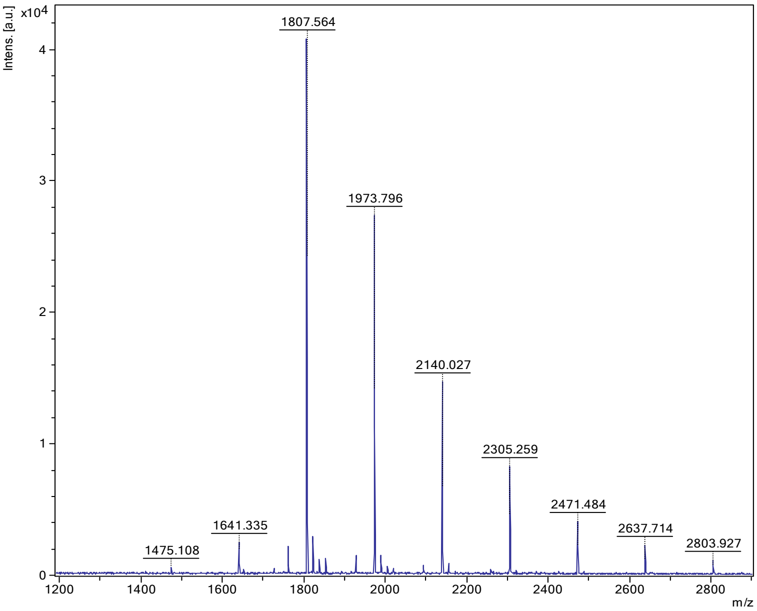


*Figure 66: MALDI-TOF spectrum of **2d***

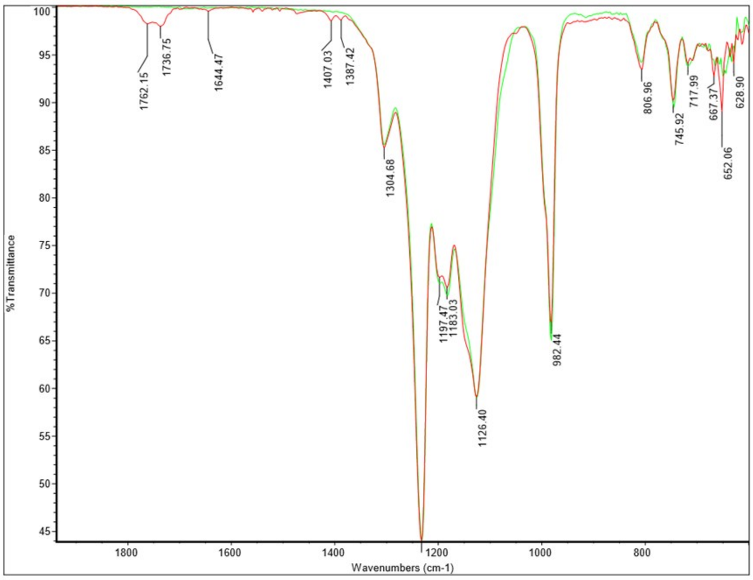


*Figure 67: IR spectrum of **2d** (and oligo(HFPO) alcohol in green)*

6. Pentyl maleate oligo(HFPO) **2e**

Pentyl maleate oligo(HFPO) **2e** (purified by flash chromatography 10:90 EtOAc:Pentane, yield=62 %, clear colorless oil): ^{1}H NMR (400 MHz, C_6D_6, 25 °C, δ): 0.87 (t, $-CH_2C\mathbf{H_3}$, 3H, $^3J_{H\text{-}H}$=6.4 Hz), 1.30 (br, $-C\mathbf{H_2}C\mathbf{H_2}CH_3)$, 4H), 1.61 (br, $-C\mathbf{H_2}CH_2CH_2CH_3)$, 2H), 4.11 (t, $-C\mathbf{H_2}(CH_2)_3CH_3$, 2H, $^3J_{H\text{-}H}$=6.4 Hz), 4.65-4.79 (m, HFPO-C$\mathbf{H_2}$O–, 2H), 6.20 (dd, -C**H**=C**H**- *cis*, 2H, $^3J_{H\text{-}H}$ = 11.8 Hz and 42.1 Hz), ^{13}C NMR (100 MHz, C_6D_6, 25 °C, δ): 12.5 ($\mathbf{C}H_3(CH_2)_4$OCO-), 21.9 ($CH_3\mathbf{C}H_2(CH_2)_3$OCO-), 27.9 ($CH_3CH_2\mathbf{C}H_2(CH_2)_2$OCO-), 28.0 ($CH_3(CH_2)_2\mathbf{C}H_2CH_2$OCO-), 59.8 (-COO$\mathbf{C}H_2R_f$), 65.0 ($CH_3(CH_2)_3\mathbf{C}H_2$OCO-), 127.1 (-**C**H=CHCOOCH$_2$-), 131.9 (-**C**HCOOCH$_2$R$_f$), 163.1 (-**C**OOCH$_2$-), 164.3 ($R_fCH_2\mathbf{C}$OO-), ^{19}F NMR (376 MHz, C_6D_6, 25 °C, δ): -135.1 ($d_{R\text{-}S}$q, -**CF**(CF_3)CH_2R_h) (% alcohol=6 %), GC-MS, 70 eV, *m/z*: 43.1 (15), 69.1 (37), 70.2 (14), 71.1 (52), 99.1 (32), 100 (16), 119 (12), 147 (21), 150 (29), 169 (100), MALDI-TOF, $[M+Li]^+$: 1821.6 – 1987.8 – 2154.0 – 2319.3 – 2485.5, FT-IR (ATR) ν_{max} (cm^{-1}): 982.4 – 1126.3 – 1230.2 – 1647.8 – 1736.8

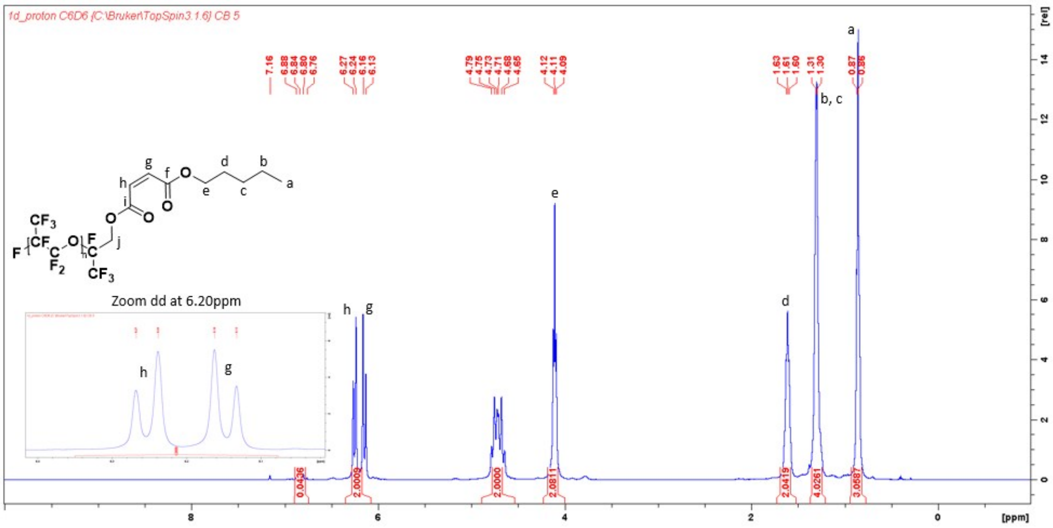


*Figure 68: ^{1}H NMR spectrum of **2e***

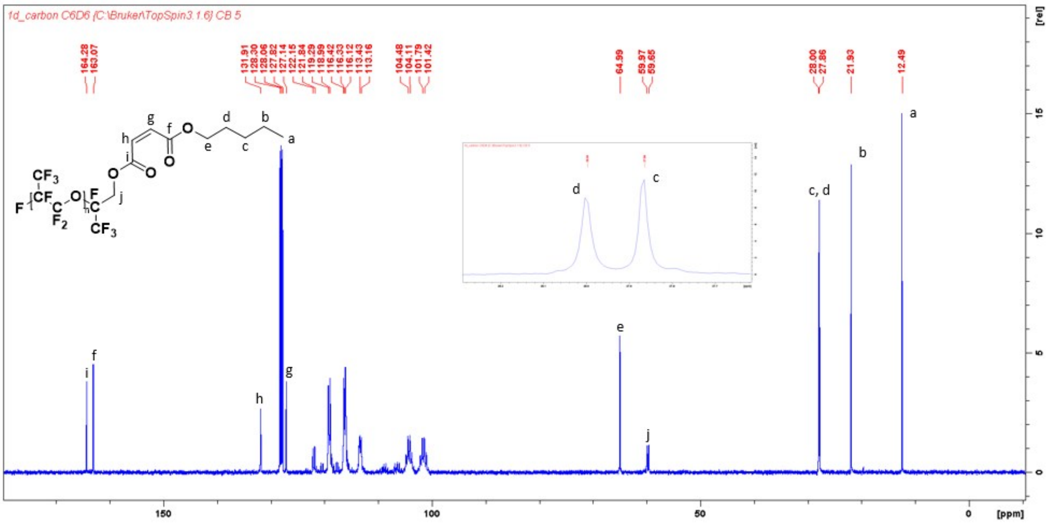


*Figure 69: ^{13}C NMR spectrum of **2e***

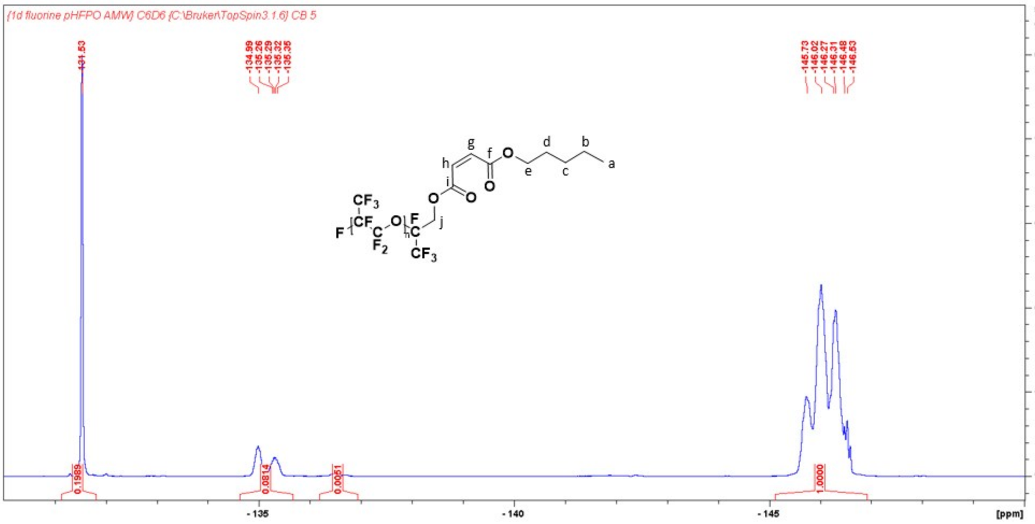


*Figure 70: ^{19}F NMR spectrum of **2e** (6% of alcohol))*

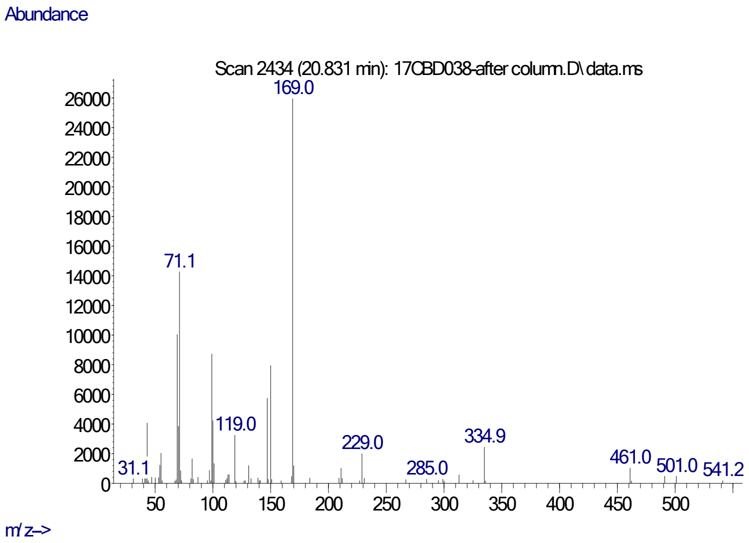


*Figure 71: GC-MS spectrum of **2e***

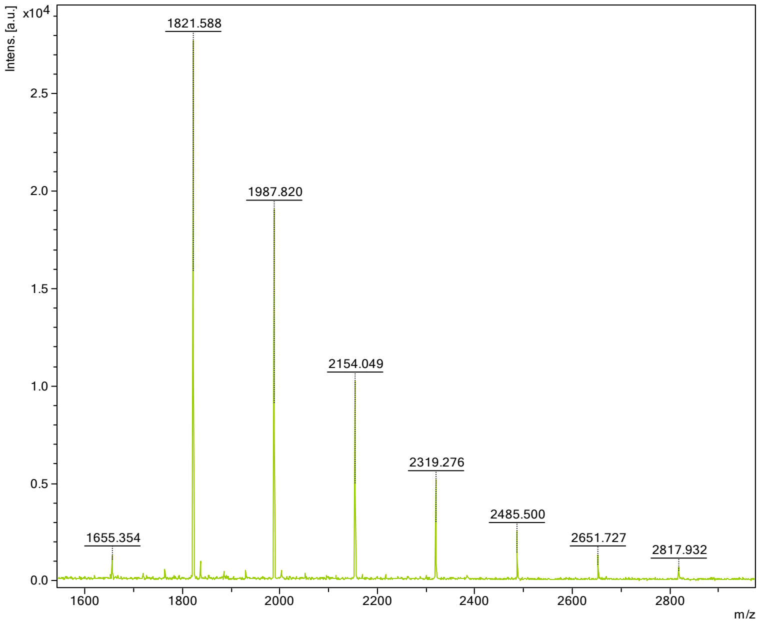


*Figure 72:MALDI-TOF spectrum of **2e***

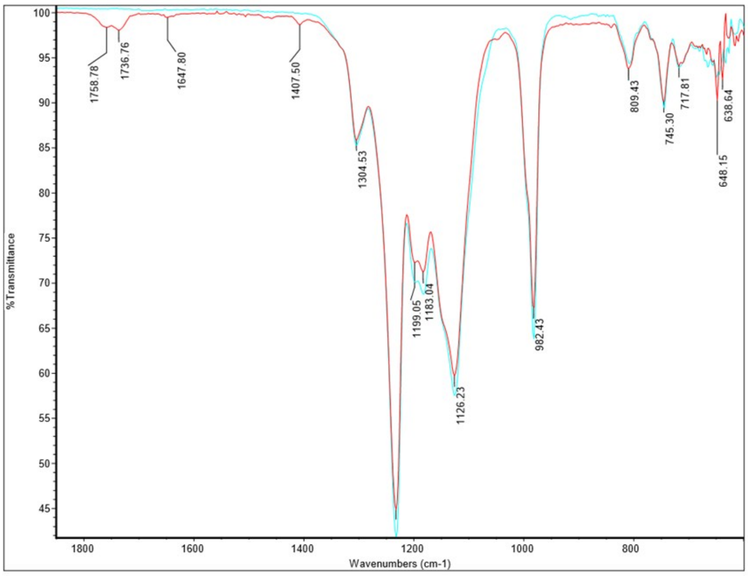


*Figure 73: IR spectrum of **2e** (and oligo(HFPO) alcohol in blue)*

7. Benzyl maleate oligo(HFPO) **2f**

Benzyl maleate oligo(HFPO) **2f** (purified by flash chromatography 5:95 EtOAc:Pentane, yield=30 %, blurry white highly viscous oil): ^{1}H NMR (400 MHz, C_6D_6, 25 °C, δ): 4.41-4.49 (m, HFPO-C$\mathbf{H_2}$O–, 2H), 4.94 (s, PhC$\mathbf{H_2}$OCO-, 2H), 5.98 (dd, -C**H**=C**H**- *cis*, 2H, $^{3}J_{H\text{-}H}$ = 11.9 Hz and 40.6 Hz), 7.07-7.11 (m, **Ph**CH$_2$OCO-), ^{13}C NMR (100 MHz, C_6D_6, 25°C, δ): 59.8 (-COO**C**H$_2$R$_f$), 66.7 (Ph**C**H$_2$OCO-), 127.2 (-**C**H=CHCOOCH$_2$-), 127.6 & 127.8 ($\mathbf{Ph_{a,b,c}}$CH$_2$OCO-), 131.2 (-**C**HCOOCH$_2$R$_f$), 135.3 ($\mathbf{Ph_{d}}$CH$_2$OCO-), 162.9 (R$_H$O**C**O-), 163.9 (R$_f$CH$_2$COO-), ^{19}F NMR (376 MHz, C_6D_6, 25 °C, δ): -135.1 (d$_{R\text{-}S}$q, -**CF**(CF$_3$)CH$_2$R$_h$), GC-MS, 70 eV, *m/z*: 32 (6), 65.1 (4), 69 (24), 77 (4), 78 (5), 79.1 (5), 81.8 (10), 90.2 (5), 91 (100), 92 (9), 98.8 (6), 99.9 (15), 105 (5), 107 (26), 114 (6), 118.9 (6), 146.8 (9), 150.1 (16), 169 (36), 335.1 (4), MALDI-TOF, [M+Li]$^+$: 1841.7 – 2007.9 – 2174.2 – 2339.4 – 2505.6, FT-IR (ATR) ν_{max} (cm^{-1}): 978.6, 1117.3, 1226.6, 1639.9, 1735.6

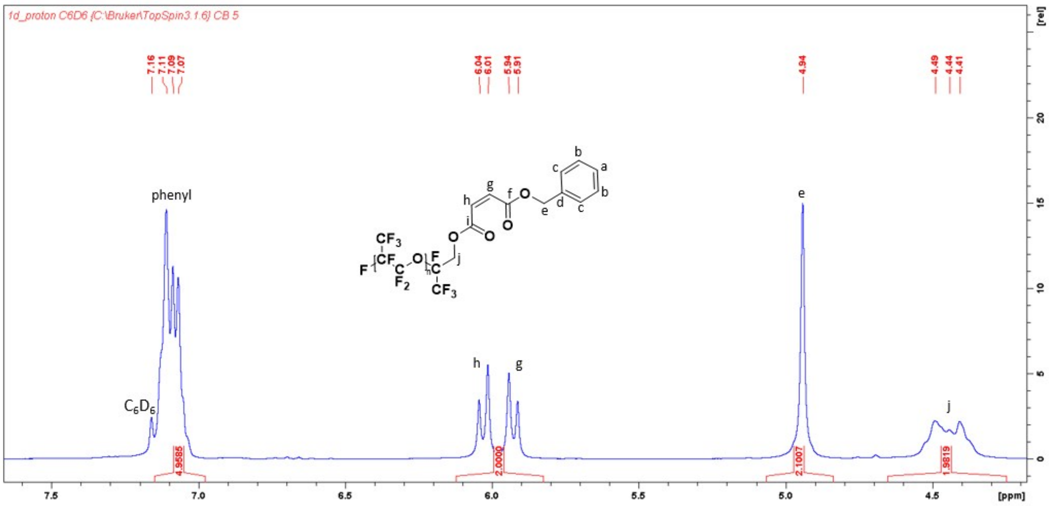


*Figure 74: ^{1}H NMR spectrum of **2f***

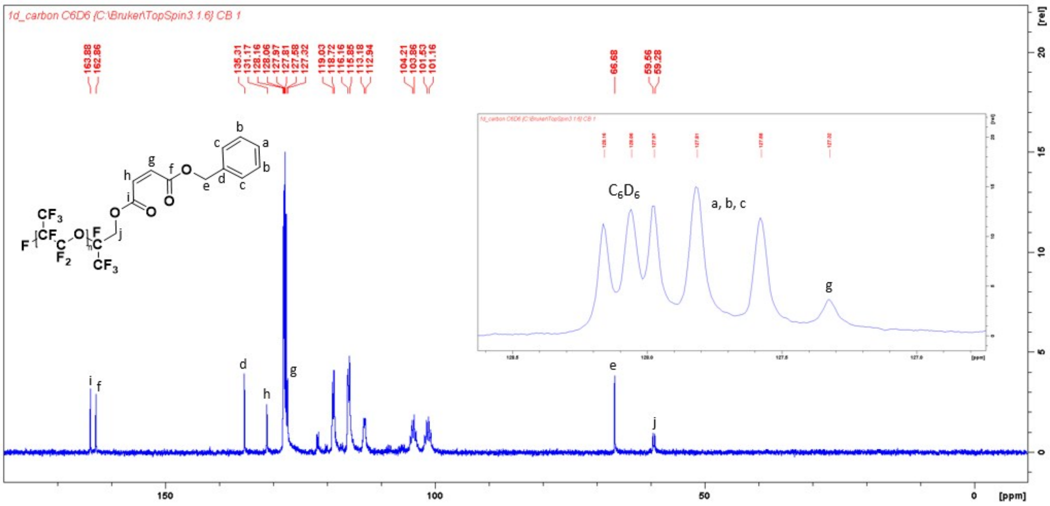


*Figure 75: ^{13}C NMR spectrum of **2f***

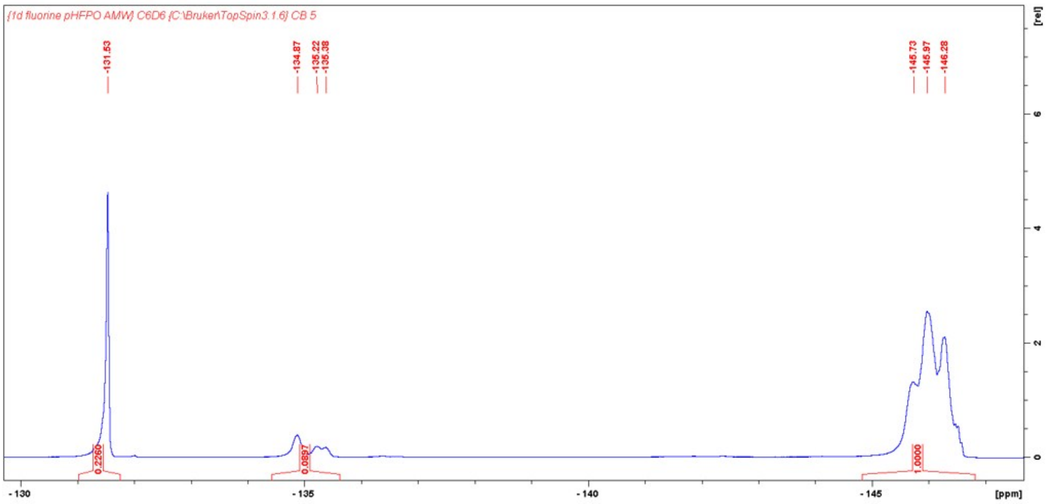


*Figure 76: ^{19}F NMR spectrum of **2f***

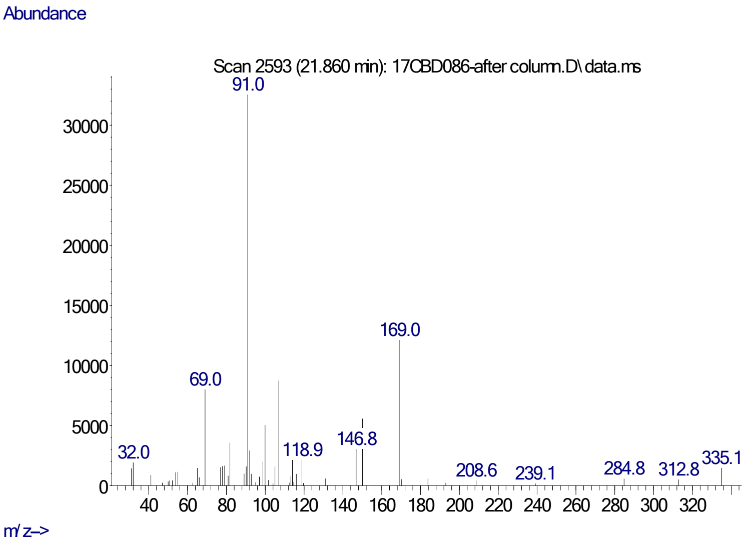


*Figure 77: GC-MS spectrum of **2f***

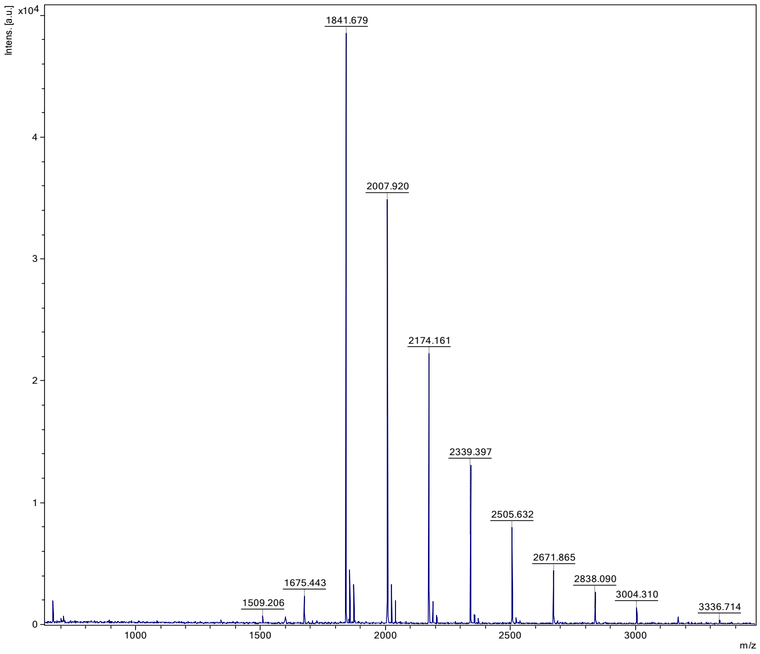


*Figure 78: MALDI-TOF spectrum of **2f***

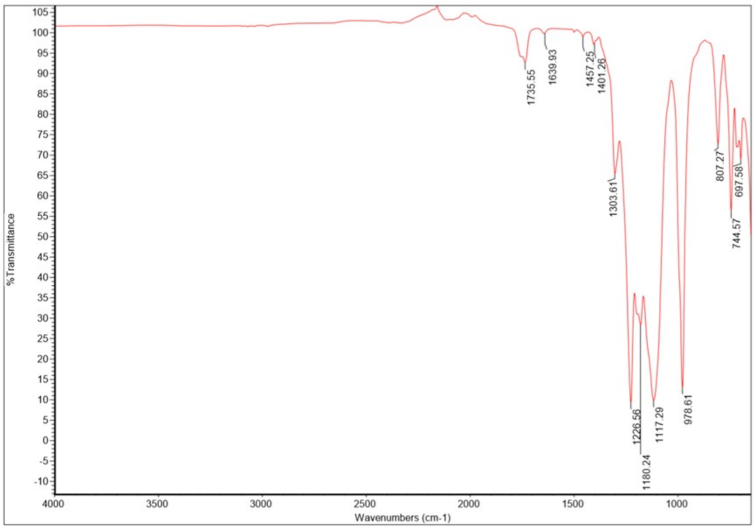
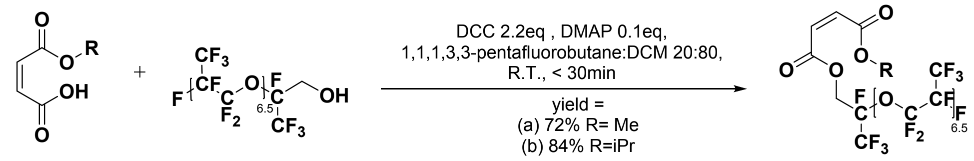


*Figure 79: IR spectrum of **2f***

F. Experimental, IR, ^{1}H, ^{13}C-NMR and GC-MS Spectra of the different maleates oligo(HFPO) (M_w~1250 g/mol)

1. Experimental



1a-f
2eq

3a-b

To a solution of oligo(HFPO) alcohol (M_w = 1250 g/mol, 938 mg, 0.75 mmol), monoalkyl maleate (2 eq) and DMAP (0.1 eq) in 1,1,1,3,3-pentafluorobutane (10 mL) and DCM (30 mL), 2.2 eq of DCC in DCM (10 mL) were added dropwise at 0 °C during 20 min. After 5 min of reaction, the ice bath was removed. The conversion of the reaction was followed by ^{19}F NMR. After 15 min, the reaction was stopped. The reaction mixture was filtrated and concentrated under vacuum. After filtration onto silica and then onto Celite®, the solvents were removed under vacuum to afford clear colorless oil products.

2. Methyl maleate oligo(HFPO) **3a**

Clear colorless oil - Yield = 55%

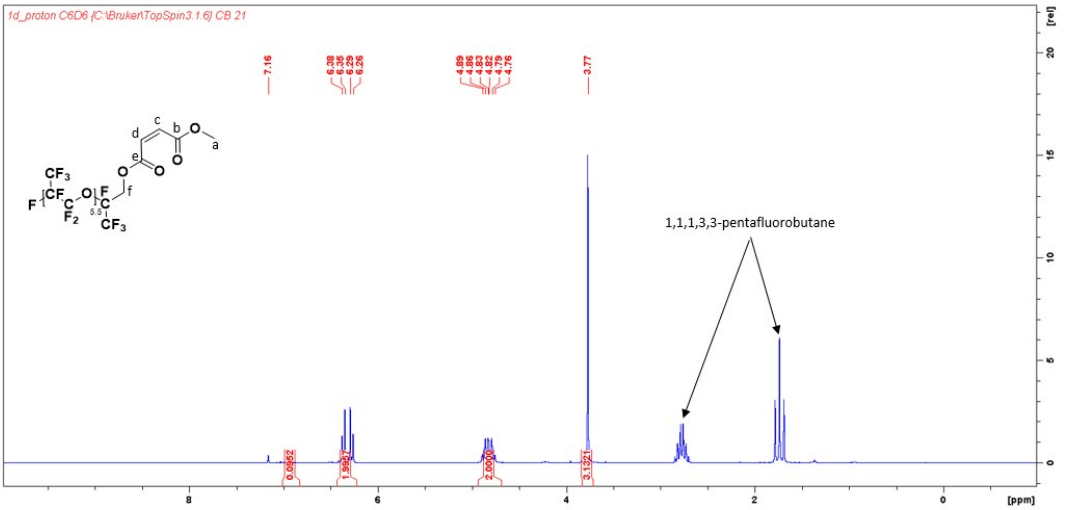


*Figure 80: ^{1}H NMR spectrum of **3a***

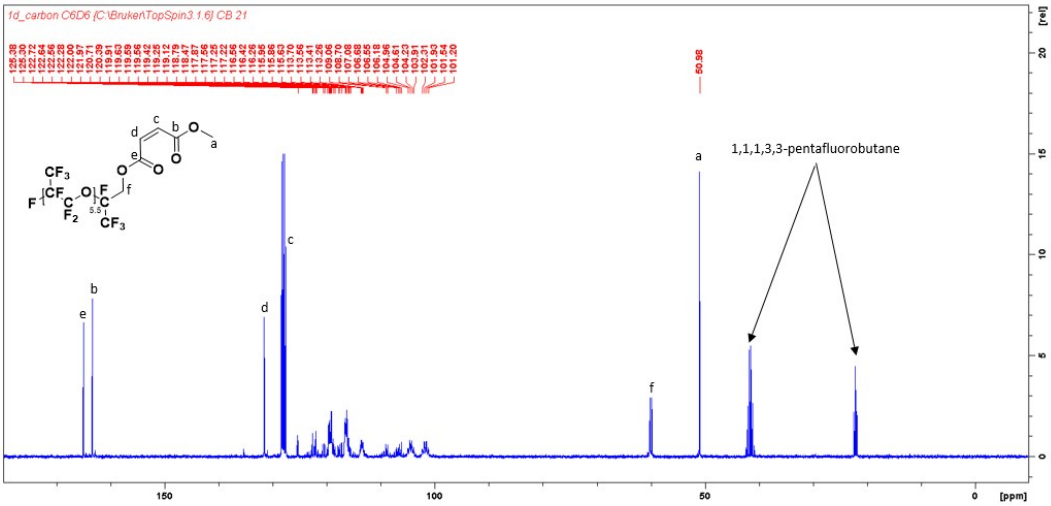


Figure 81: ^{13}C NMR spectrum of **3a**

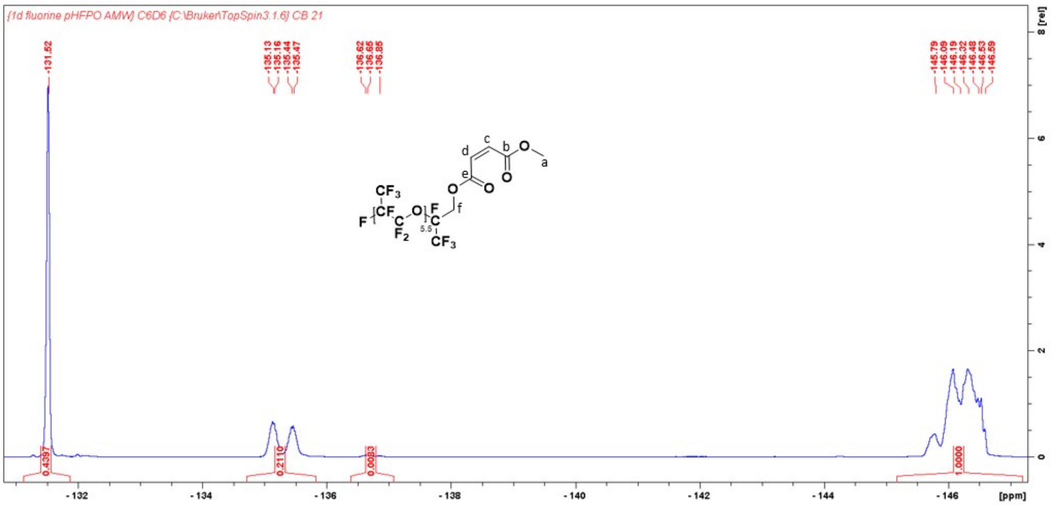


Figure 82: ^{19}F NMR spectrum of **3a** (4% of alcohol))

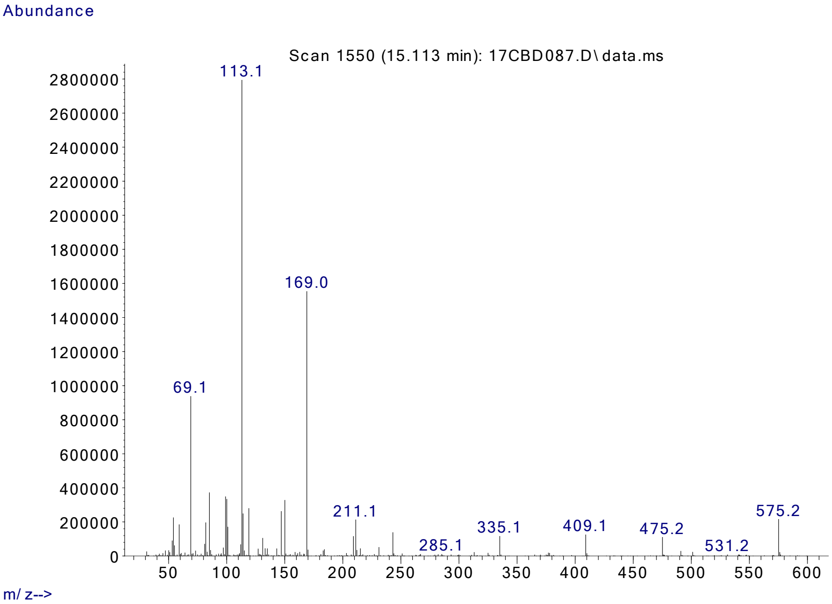


Figure 83: GC-MS spectrum of **3a**

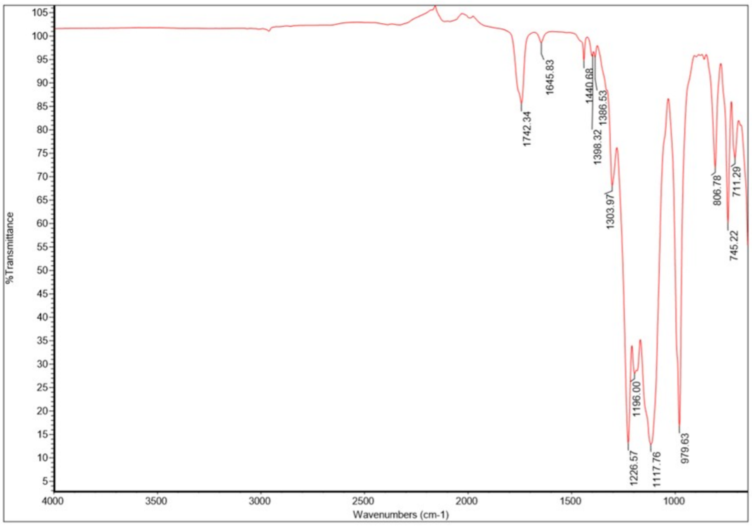


Figure 84: IR spectrum of ***3a***

3. Isopropyl maleate oligo(HFPO) **3b**

Isopropyl maleate oligo(HFPO) **3b** (yield=84 %, clear colorless oil): ^{1}H NMR (400 MHz, C_6D_6, 25 °C, δ): 1.26 (d, -CH(C$\mathbf{H_3}$)$_2$, 6H, $^{3}J_{H\text{-}H}$ = 6.2 Hz), 4.74-4.88 (m, HFPO-C$\mathbf{H_2}$O–, 2H), 5.11 (q, -C**H**(CH$_3$)$_2$, 1H, $^{3}J_{H\text{-}H}$ = 6.2 Hz), 6.28 (dd, -C**H**=C**H**- *cis*, 2H, $^{3}J_{H\text{-}H}$ = 11.9 Hz and 39.4 Hz), 6.88 (dd, -C**H**=C**H**- *cis*, 2H, $^{3}J_{H\text{-}H}$ = 15.9 Hz and 26.5 Hz) (%trans = 4.5 %), ^{13}C NMR (100 MHz, C_6D_6, 25 °C, δ): 20.3 (-CH(**C**H$_3$)$_2$), 59.7 (-COO**C**H$_2$R$_f$), 68.4 (-**C**H(CH$_3$)$_2$), 126.8 (-**C**H=CHCOOCH$_2$-), 132.4 (-**C**HCOOCH$_2$R$_f$), 163.0 (-**C**OOCH-), 163.6 (R$_f$CH$_2$**C**OO-), ^{19}F NMR (376 MHz, C_6D_6, 25 °C, δ): -135.1 (d$_{R\text{-}S}$q, -**CF**(CF$_3$)CH$_2$R$_h$), GC-MS, 70 eV, *m/z*: 41.1 (14), 42 (11), 43.1 (60), 54 (12), 69 (51), 82 (13), 99 (100), 100 (18), 119 (11), 147 (11), 150 (14), 169 (64), FT-IR (ATR) ν_{max} (cm^{-1}): 982.8 – 1128.1 – 1230.2 – 1644.0 – 1731.7

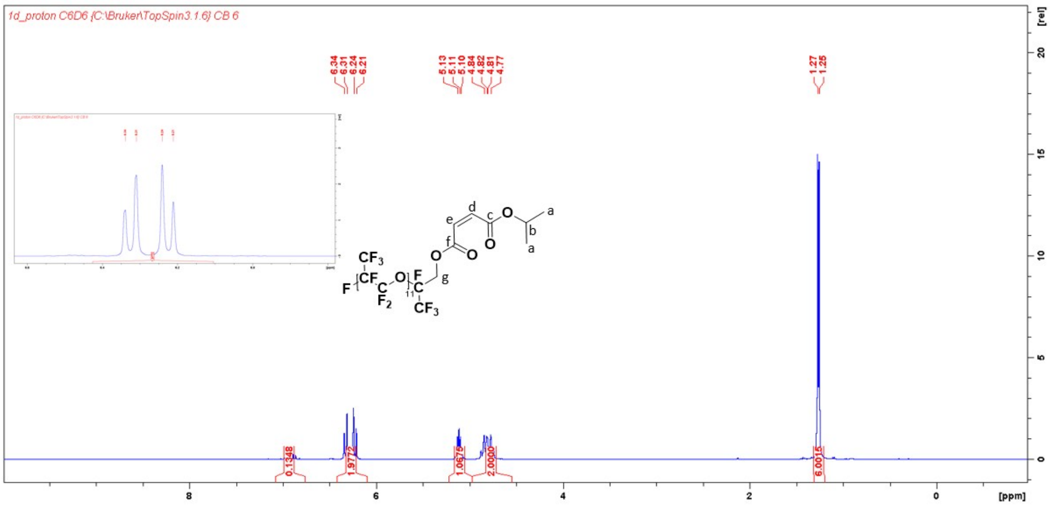


Figure 85: ^{1}H NMR spectrum of ***3b***

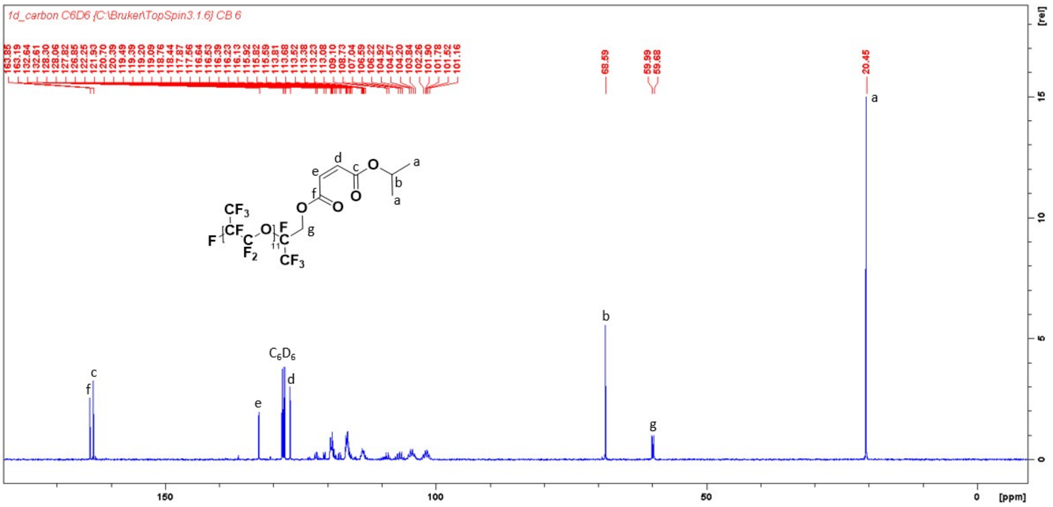


Figure 86: ^{13}C NMR spectrum of ***3b***

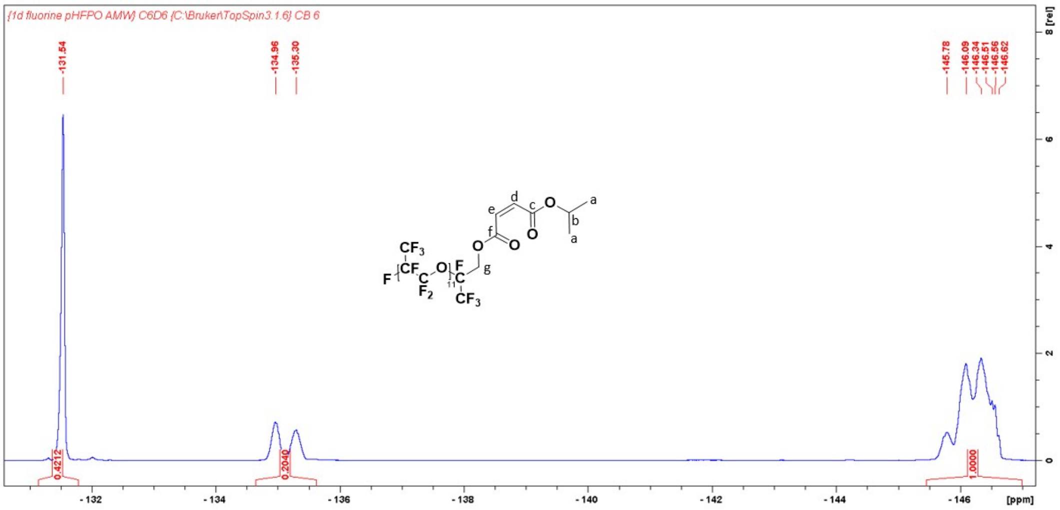


Figure 87: ^{19}F NMR spectrum of ***3b***

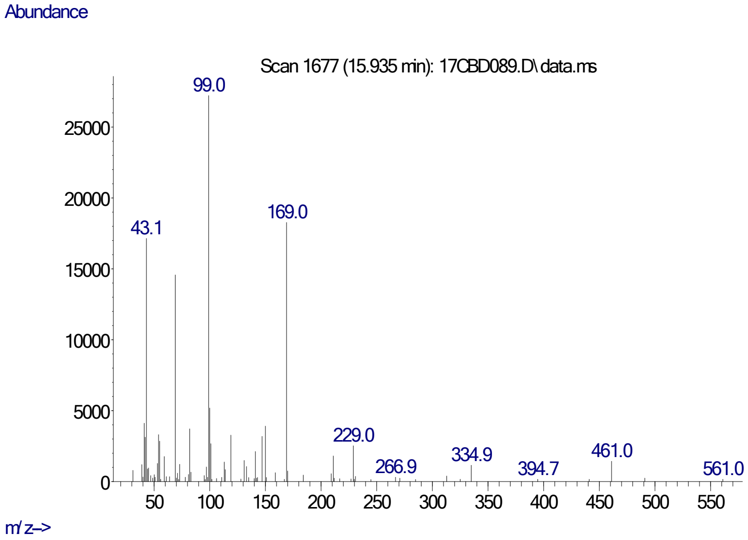


Figure 88: GC-MS spectrum of ***3b***

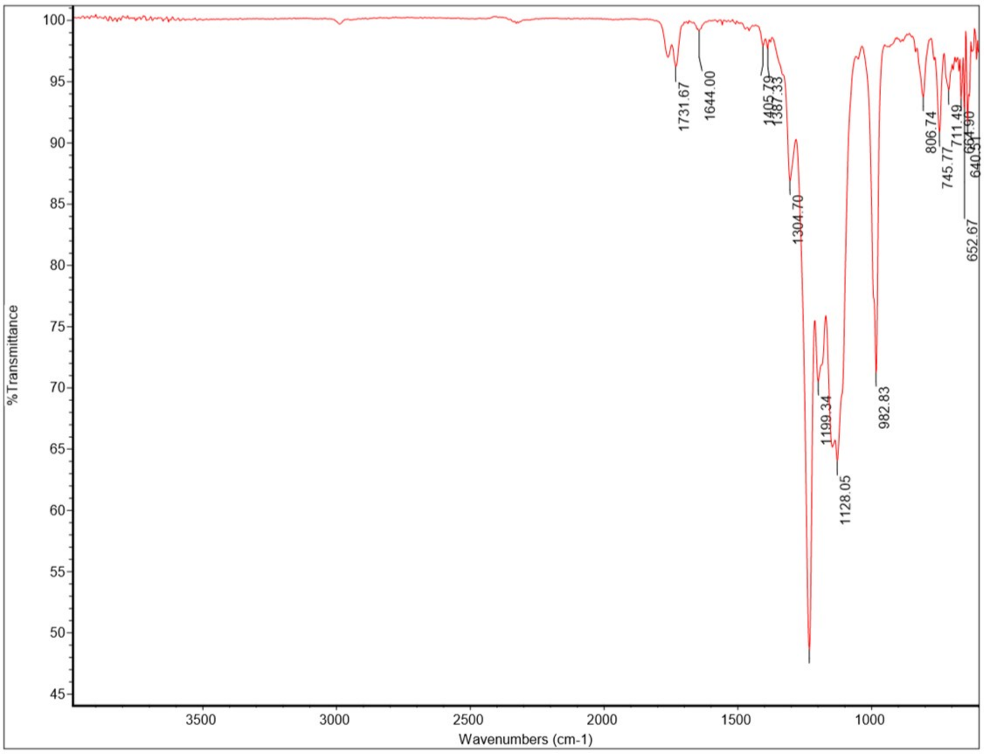
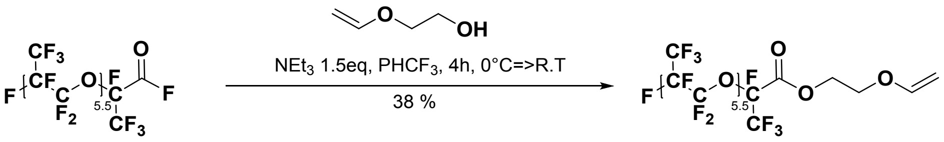


*Figure 89: IR spectrum of **3b***

G. Experimental, IR, ^{1}H, ^{13}C-NMR and GC-MS Spectra of the vinyl ether oligo(HFPO) (M_w~1250 g/mol)

1. Experimental **4**



4

To a solution of Krytox Acid Fluoride (2 g) in 5 mL of previously dried trifluorotoluene) with 363 µL of dry triethylamine (1.5 eq), 155 µL of ethylene glycol vinyl ether (1eq) in 5 mL of dry trifluorotoluene was added dropwise at 0°C. After 5 min, the ice bath was removed and the reaction mixture was left to stir at room temperature during 14h. The solvent and volatiles were removed under vacuum. The crude was then washed with water (5x) and acetone (3x). The solvent traces were then removed under vacuum.

2. Analyses

Clear colorless oil. Yield = 38 %

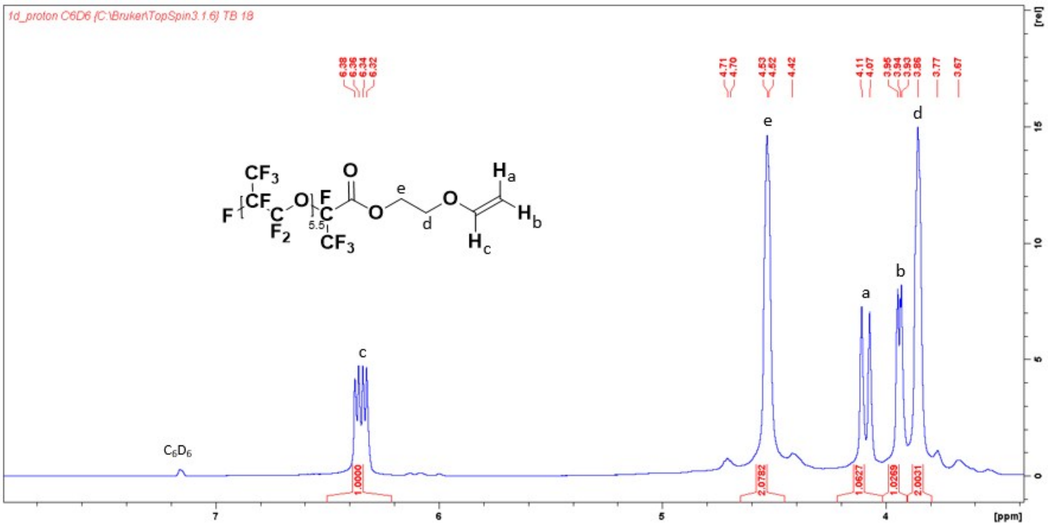


*Figure 90: ^{1}H NMR spectrum of vinyl ether oligo(HFPO) **4***

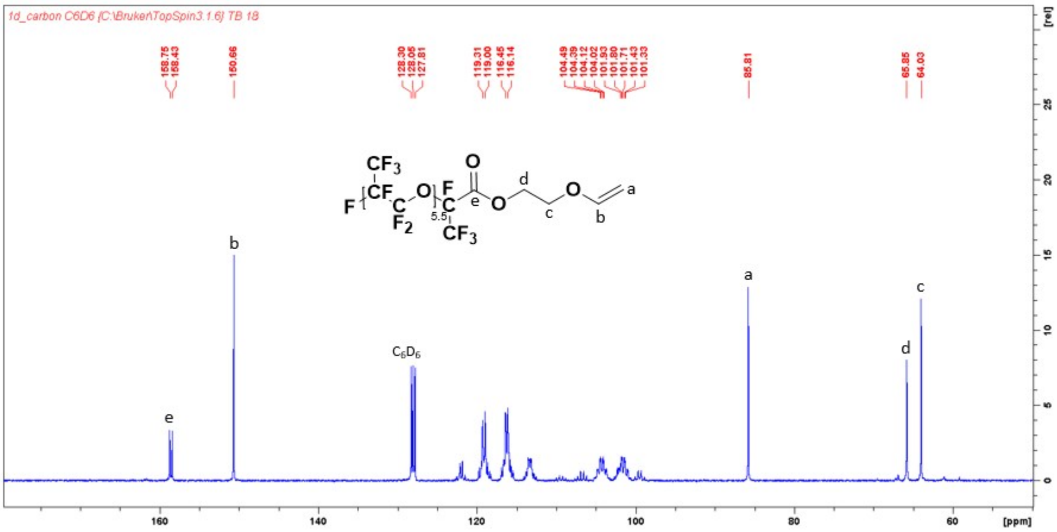


Figure 91: ^{13}C NMR spectrum of vinyl ether oligo(HFPO) ***4***

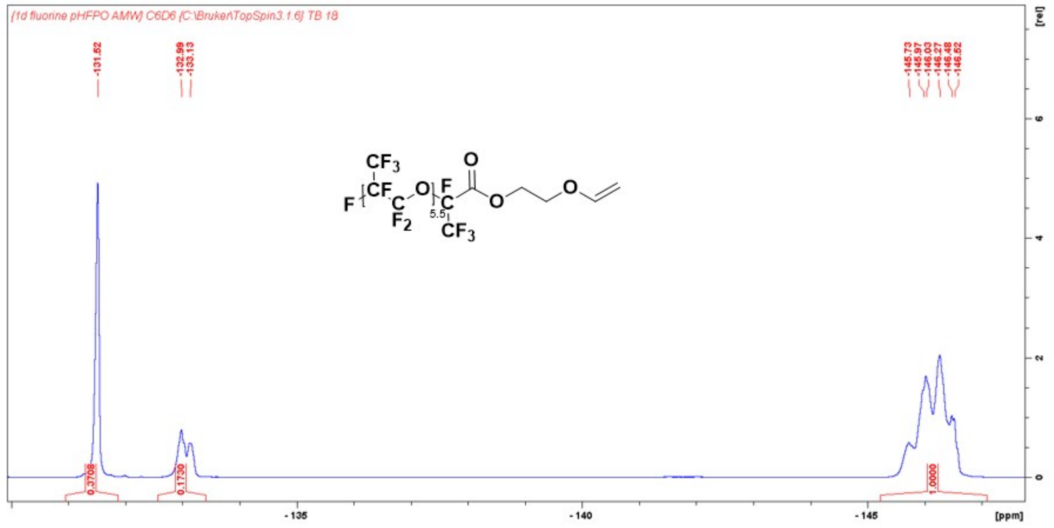


Figure 92: ^{19}F NMR spectrum of vinyl ether oligo(HFPO) ***4***

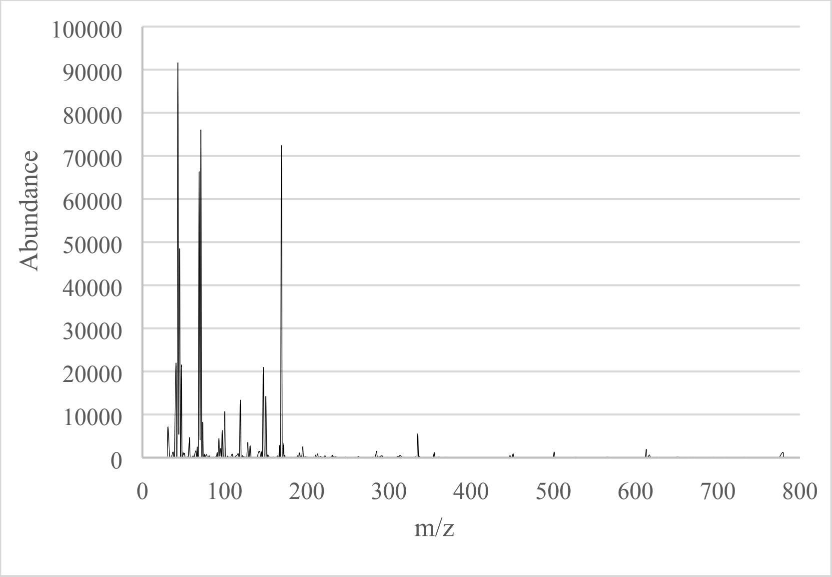


Figure 93: GC-MS spectrum of vinyl ether oligo(HFPO) ***4***

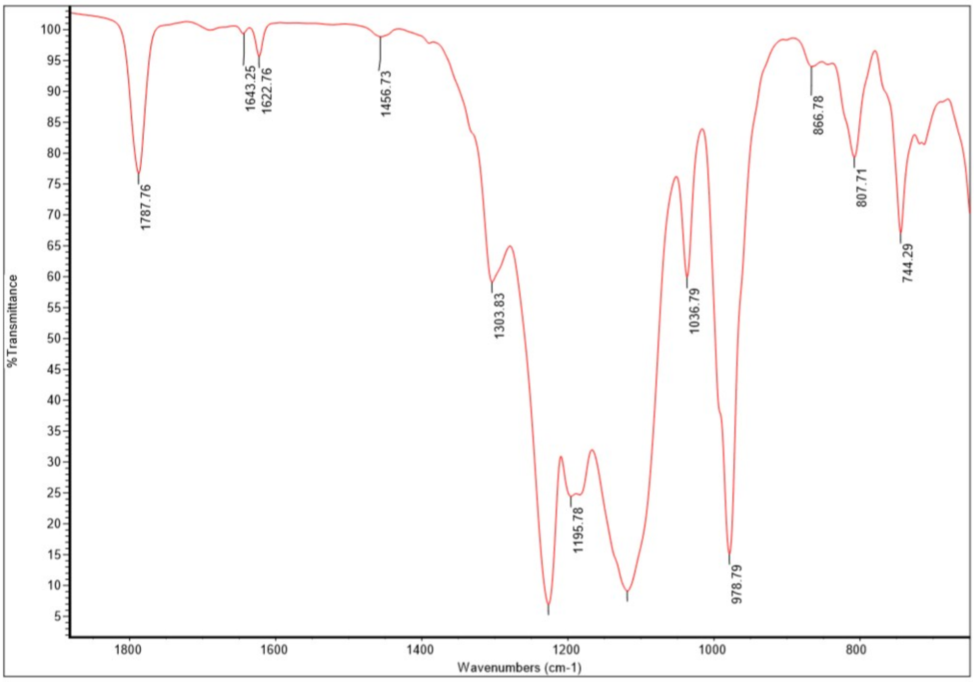


Figure 94: IR spectrum of vinyl ether oligo(HFPO) 4

G. Polymerization

1. Calculation of the area by the univariate method

The area of the peak of interest (i.e. at 1622 cm^{-1} for the vinyl ether) was calculated by using the initial height following this equation:

$$Conversion\,rate\ (\%) = \left(1 - \frac{A}{A_0}\right) * 100 \qquad (1)$$

The height was calibrated thanks to a peak of reference. In our case, the peak corresponding to the C-F band from the $-CF_3$ at 979 cm^{-1}.

2. Confirmation of the quantitative conversion by peak deconvolution

A quantitative conversion was confirmed by peak deconvolution as no peak at 1622 cm^{-1} could have been detected after 40s. The overlapped peaks from the vinyl ether, the maleate and the photoinitiator were separated.

3. Examples of series

Different spectra are provided to show the initial mixture before UV-light (Figure 95), the disappearance of the bands especially the vinyl ether (VE) band in absence of air (Figure 96) and in presence of air (Figure 97). The non-homopolymerization of vinyl ether is highlighted with no conversion after 500s (Figure 98). The partial homopolymerization was observed for the maleate (MA) (Figure 99) but as the vinyl ether showed a complete conversion for the copolymerization that means that the homopolymerization of the maleate was slower than the copolymerization. Besides, the photoinitiator (PI) presented bands almost overlapped with the maleate signals. These bands shifted under exposure of UV-light due to its decomposition (Figure 100). Then the use of the vinyl ether band was primordial to be sure to not take into account other signals.

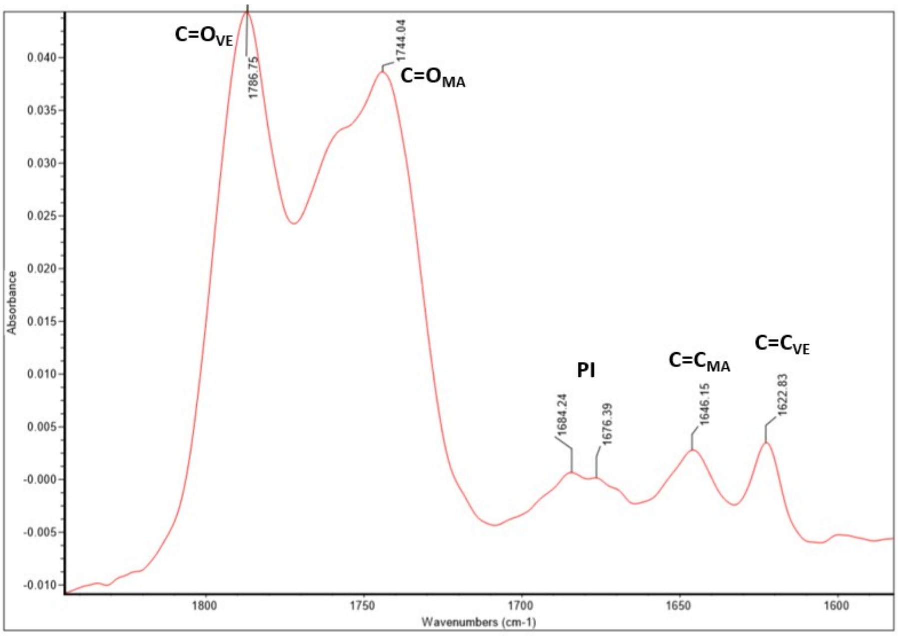


Figure 95: IR spectrum of the initial mixture before irradiation

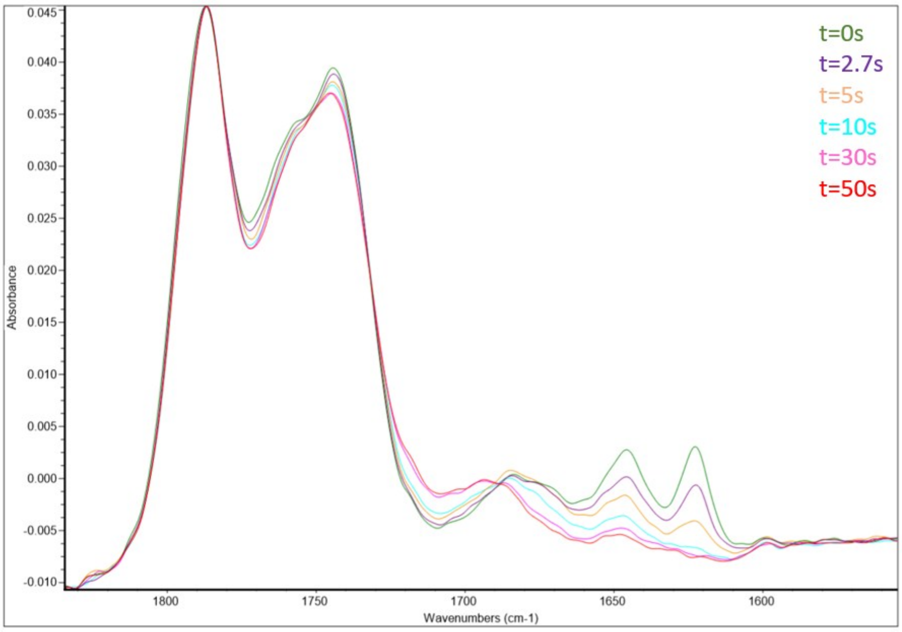


*Figure 96: IR spectra at different times under UV-light for the mixture **2a** : **4** with PP (polypropylene film)*

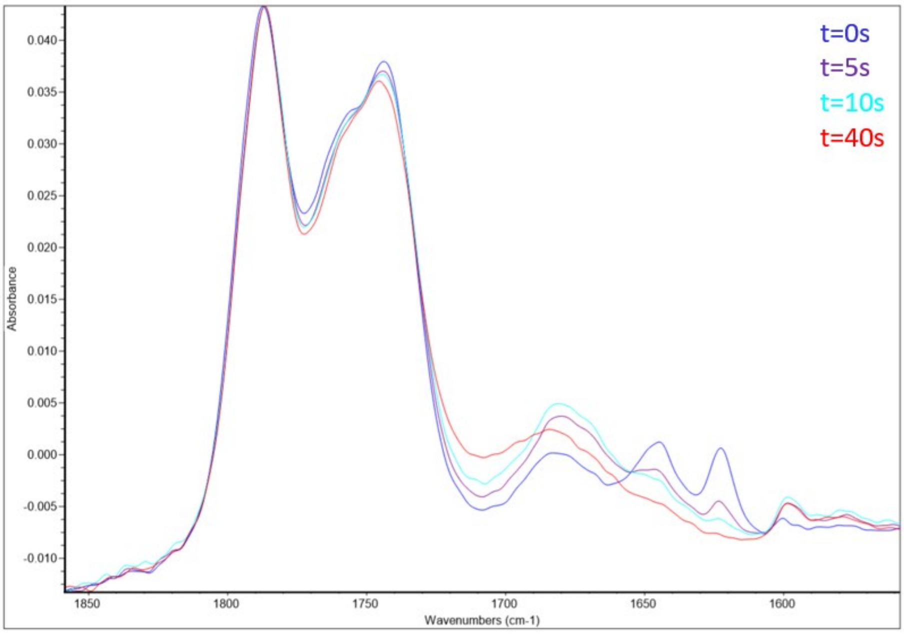


Figure 97: IR spectra at different times under UV-light for the mixture ***2a*** *:* ***4*** *without PP (polypropylene film – presence of air)*

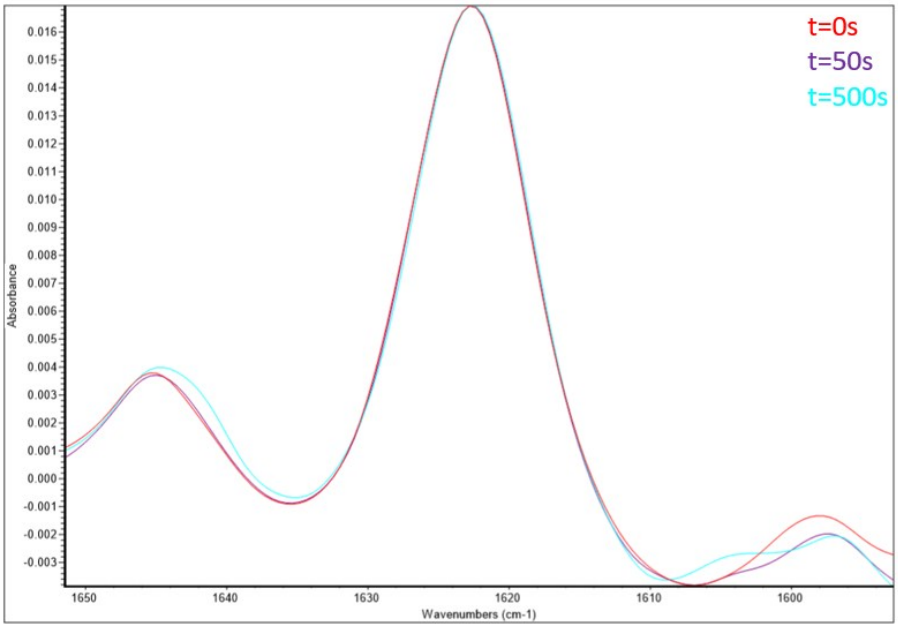


Figure 98: IR spectra at t=0, 50s and 500s in presence of photoinitiator at 1622cm^{-1} *for the vinyl ether* ***4***

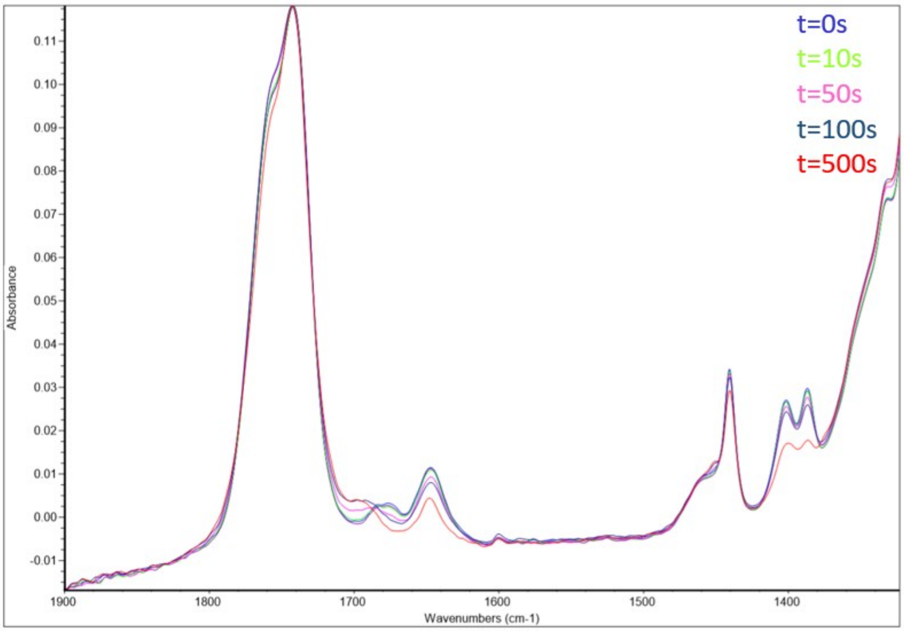


*Figure 99: IR spectra at t=0, 50s and 500s in presence of photoinitiator at 1645cm^{-1} for **2a***

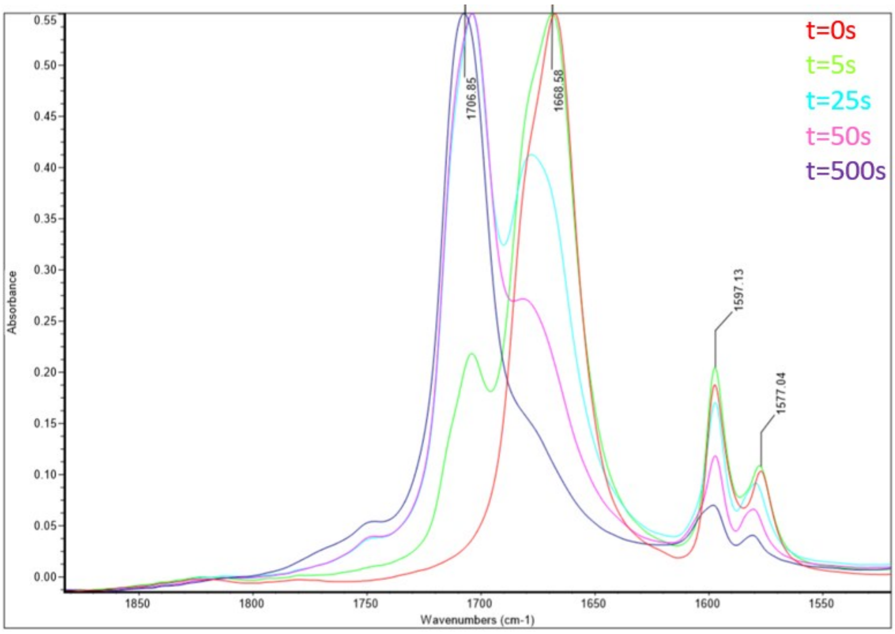


Figure 100: IR spectra at t=0, 5s, 25s, 50s and 500s for the photoinitiator

H. Thermal properties and contact angles

	$T_{d5\%}$ (°C)	T_g (°C)
Oligo(HFPO) alcohol M_w~1250g/mol	122	-75
Oligo(HFPO) alcohol M_w~2000g/mol	200	-68
2a	199	-69
2b	202	-69
2c	197	-67
2d	203	-69
2e	204	-71
2f	225	-66
3a	150	-76
3b	157	-73
4	161	-76
MA1:VE **3a:4**	174	-69
MA2:VE **2a:4**	200	-67

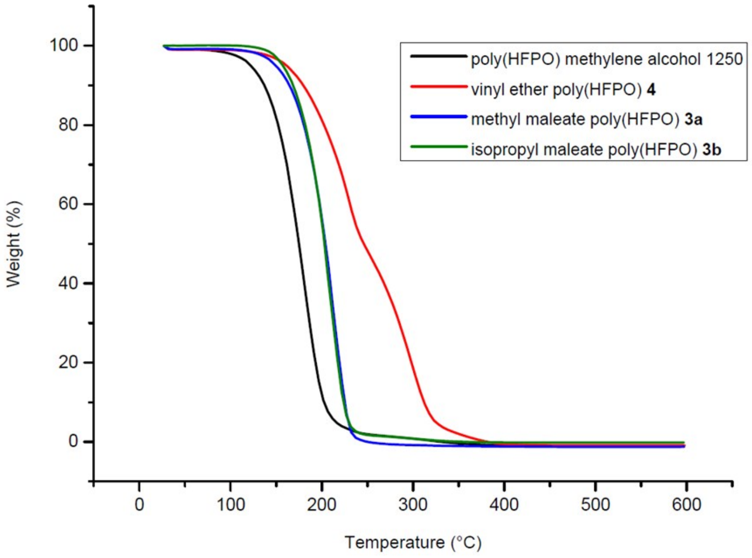


Figure 101: TGA curves of oligo(HFPO) products with M_w~1250 g/mol under nitrogen

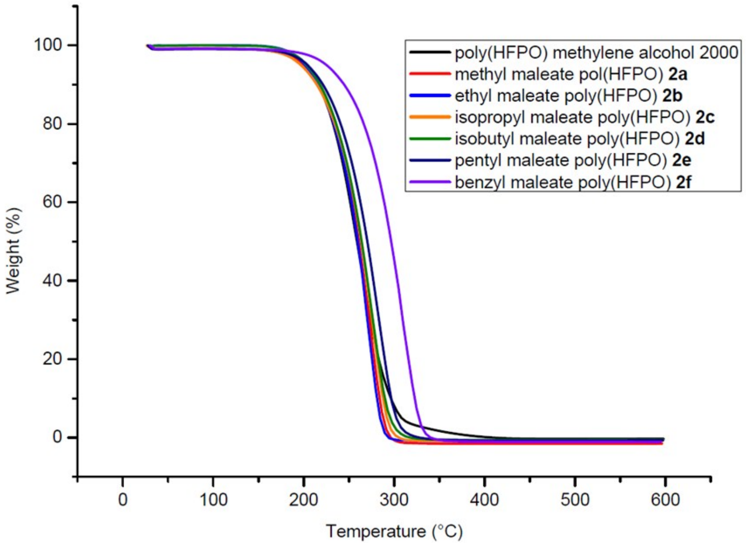


Figure 102: TGA curves of oligo(HFPO) products with Mw~2000 g/mol under nitrogen

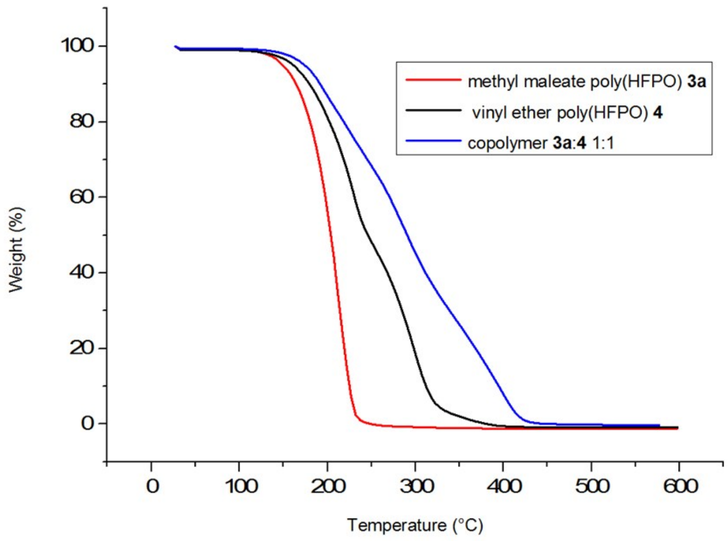


Figure 103: TGA curves of the monomers ***3a*** *and* ***4*** *and the copolymer under nitrogen*

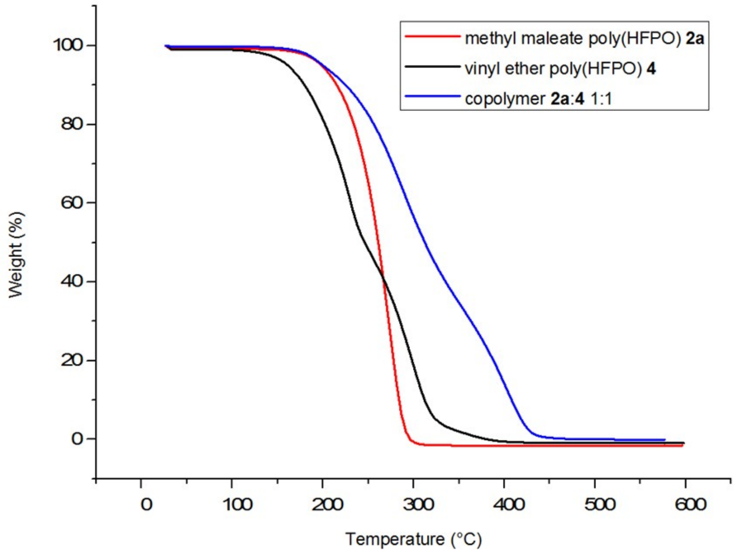


Figure 104: TGA curves of the monomers ***2a*** *and* ***4*** *and the copolymer under nitrogen*

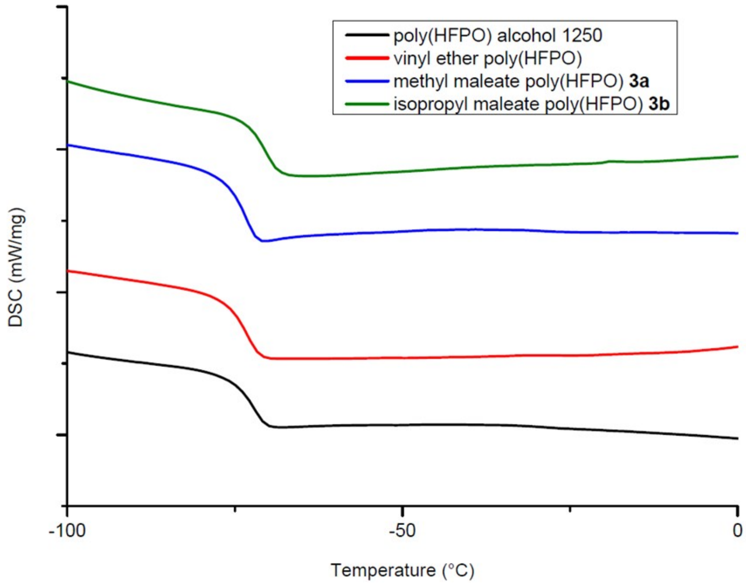


Figure 105: DSC curves of oligo(HFPO) products with Mw~1250 g/mol

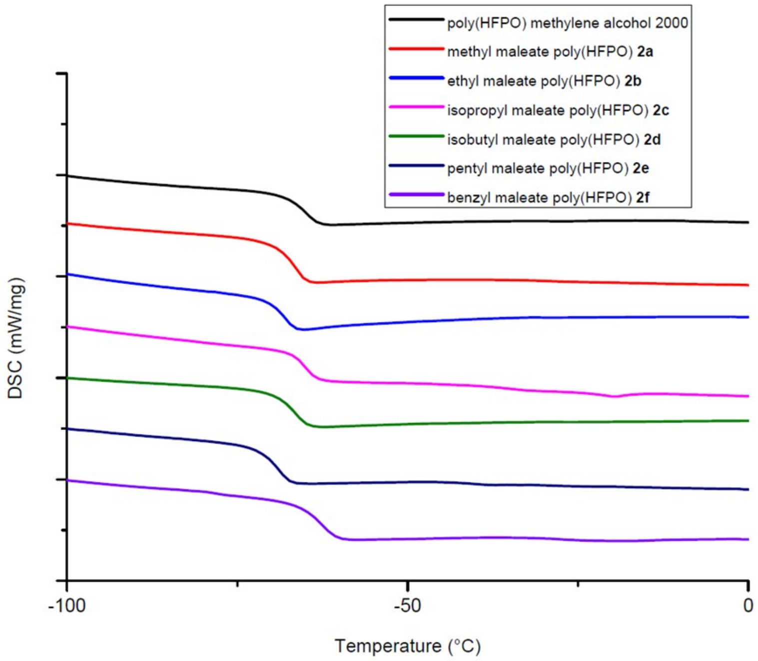


Figure 106: DSC curves of oligo(HFPO) products with Mw~2000 g/mol

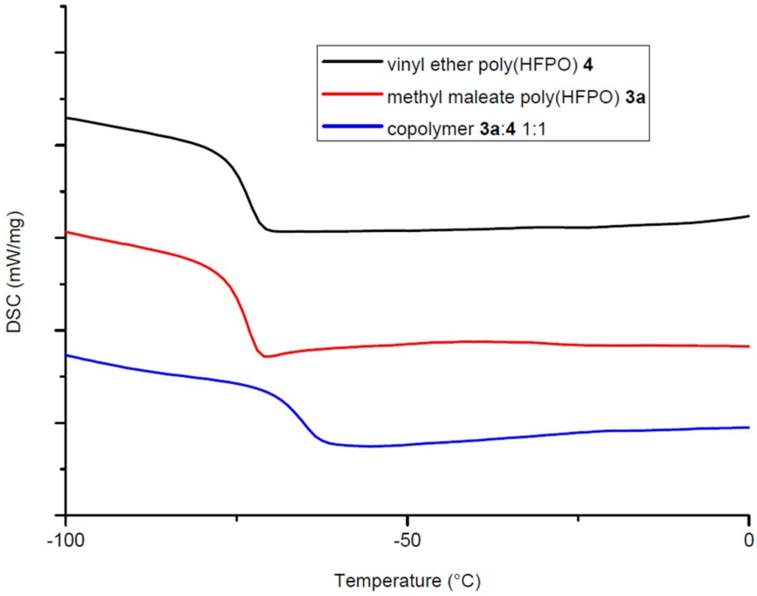


*Figure 107: DSC curves of the monomers **3a** and **4** and the copolymer*

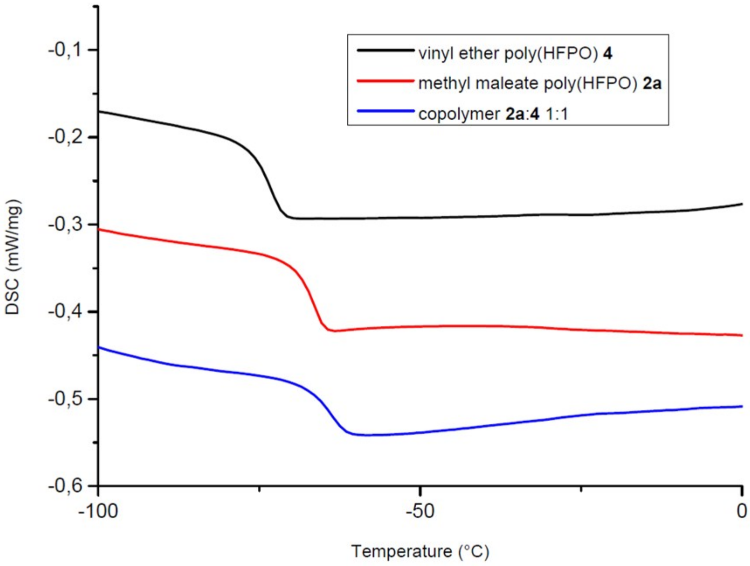


*Figure 108: DSC curves of the monomers **2a** and **4** and the copolymer under nitrogen*

The procedure we followed for the contact angle measurement was the following one:

5-6 drops of the corresponding mixture (i.e. for **3a**:**4** and **2a**:**4**) were dropped off on Teflon film and spin-coated during 60s at 3000rpm. Teflon films (4 repeats per mixture) were then taped on microscope glass slides and photopolymerized by using the UV bench. One repeat was used to control by IR the complete conversion of the sample and the three others were used for contact angle measurements (1 or 2 measures were made per repeat). Teflon films showed a contact angle of 105° for 6 measurements. Glass slides could not be used due to segregation during photopolymerization (formation of droplets of polymer).

Example:

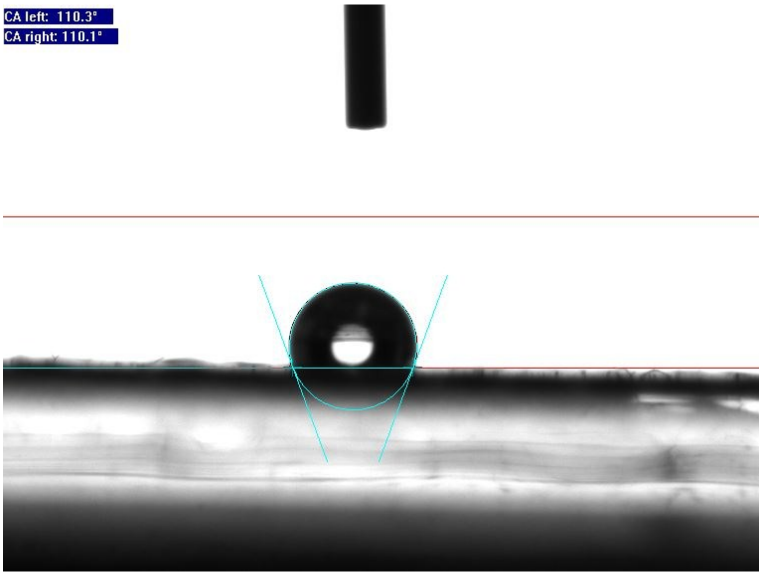


Figure 109: Contact angle of ***3a:4*** *after photopolymerization*

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