Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

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Supplementary Notes 1: Supplementary methods

Solvents and reagents were obtained from commercial sources and used as received unless stated otherwise. NMR spectra were recorded by using a Jeol JNM-ECA 400II, Bruker Advance 600 and 700 MHz spectrometer. ^{1}H and $^{13}C\{^{1}H\}$ chemical shifts are referenced to the residual proton resonance of the deuterated solvents. ^{19}F chemical shifts are referenced to $CFCl_3$ at 0 ppm.

Cat5 (C5) was obtained from abcr and used as received. Cat1-4 (C1-C4) were synthesised according to literature.[1-3] PO and ^{F}PO were dried over calcium hydride at room temperature for 3 days followed by vacuum transfer and three freeze pump thaw degassing cycles and stored inside an argon filled glovebox prior to use. DCM was dried by using an MBraun Solvent Purification System MB-SPS 800 filled with Al_2O_3 followed by drying over 4Å molecular sieves. PA was purified according to literature.[4] ^{F}PA was sublimed under dynamic vacuum at 100 °C and recrystallised twice under argon in dry DCM before being dried in vacuum and transferred to an argon filled glovebox prior to use. All other reagents were used as received if not stated otherwise.

High-resolution mass spectra were obtained using a Waters UPLC-Synapt G2-S HDMS. Infrared spectra were measured using a Thermo-Nicolet Nexus 670 FTIR spectrometer with DuraSampl IR accessory in total reflection at room temperature. DSC was measured on a Netzsch 204 F1 “Phoenix”. Films were prepared by hot-pressing 100 mg of polymer between two aluminium plates covered with Teflon sheets heated with two LLG hotplates (held in place by a 5 kg weight put on top) at 80 °C for 5 minutes.

The molecular mass and polydispersity of the polymers were determined by a Waters 1515 gel permeation chromatography (GPC) instrument equipped with two linear PLgel columns (Mixed-C) following a guard column and a differential refractive index detector using tetrahydrofuran as the eluent at a flow rate of 1.0 mL/min at 30 °C and a series of narrow polystyrene standards for the calibration of the columns. Each polymer sample was dissolved in HPLC-grade THF (6 mg/mL) and filtered through a 0.20 μm porous filter frit prior to analysis.

Supplementary Notes 2: Polymerisation and degradation procedures

General polymerisation protocol:

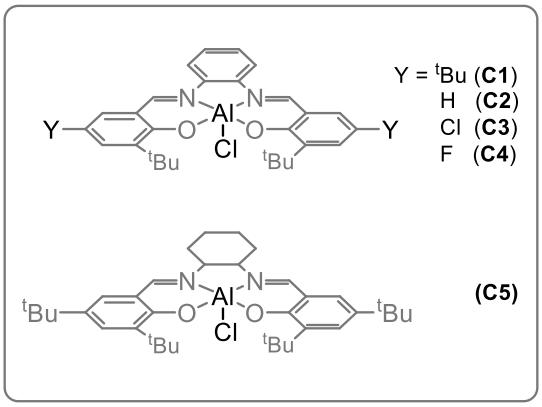
The catalyst, cocatalyst and monomers were added to a oven dried vial equipped with an oven dried stirrer bar and sealed with a melamine cap containing a Teflon inlay inside an argon filled glovebox. The vial was brought outside the glovebox and placed in a pre-heated aluminium block at the specified temperature for the specified time. At the specified end point of the reaction, the polymerisation mixture was cooled down to room temperature and an aliquot was removed and analysed by ^{1}H and ^{19}F NMR for the determination of the conversion. The mixture was solubilized with ca. 5 ml of DCM and then added to 50 mL of MeOH causing the precipitation of the polymer which was isolated by centrifugation and dried in a vacuum oven set to 50 °C for 2 h. Aliquots during the reaction for kinetic data measurements were cooled to RT before taking a sample under a stream of argon, resealing and returning it into the aluminium heating block.

Degradation protocols:

Hydrolysis: 200 mg pressed film of the polymer material was added to a 5 wt.% NaOH in 6:4 EtOH:H_2O solution and left stirring at 40 °C. When the film has been fully decomposed the solution was further analysed.

Methanolysis: 200 mg pressed film of the polymer material was added to a 5 wt.% NaOMe in methanol solution and stirred at 110 °C overnight. The product was diluted with DCM and separated from the solid by centrifugation. The DCM was removed under reduced pressure and the resulting liquid purified by distillation at 80 °C under dynamic vacuum. The solid material was used as is for further analysis.

Supplementary Notes 3: Polymerisation Data

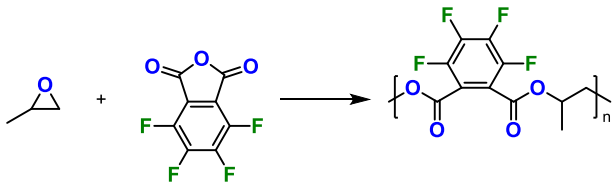


Supplementary Figure 1 – Catalysts 1-5 (C1-C5) used in polymerisations

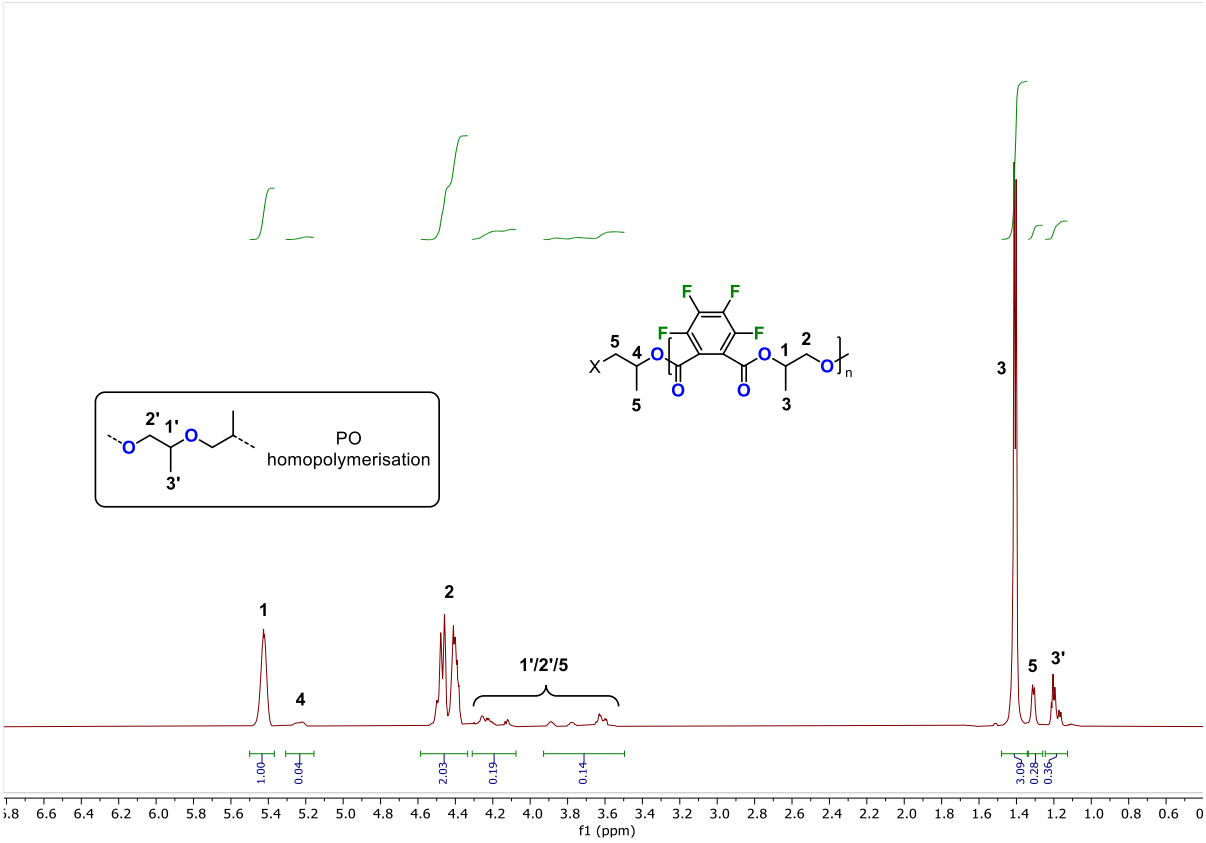
Entry[a]	Monomer Combination	Catalyst	Time (h)	% Conversion[b]	TOF (h^{-1})[c]	M_n (Đ)[d]
1	PO/^{F}PA	C1	1.5	85	311	11.50 (1.11)
2	PO/^{F}PA	C2	1.75	83	260	16.96 (1.30)
3	PO/^{F}PA	C3	1.75	85	267	15.83 (1.25)
4	PO/^{F}PA	C4	1.5	83	304	14.29 (1.27)
5	PO/^{F}PA	C5	1.75	85	267	13.46 (1.31)
6	PO/PA	C1	8	83	57	12.91 (1.31)
7	PO/PA	C2	2.5	95	209	17.75 (1.44)
8	PO/PA	C3	4	86	118	22.96 (1.48)
9	PO/PA	C4	2.5	84	185	21.55 (1.38)
10	PO/PA	C5	9	78	48	7.0 (1.32)
11	^{F}PO/^{F}PA	C2	24	82	19	16.46 (1.28)

Table S 1 - [a]ROCOP conditions: 1 Cat.:1 PPNCl: 500 epoxide: 550 anhydride at 80 °C [b]% Conversion calculated by comparing anhydride monomer and polymer signals in ^{1}H and ^{19}F NMR [c]TOF measured by TON/time where TON is number of moles of monomer consumed per mole of catalyst [d]determined by gel permeation chromatography (GPC) in THF using narrow dispersity polystyrene standards to calibrate; Đ = M_w/M_n

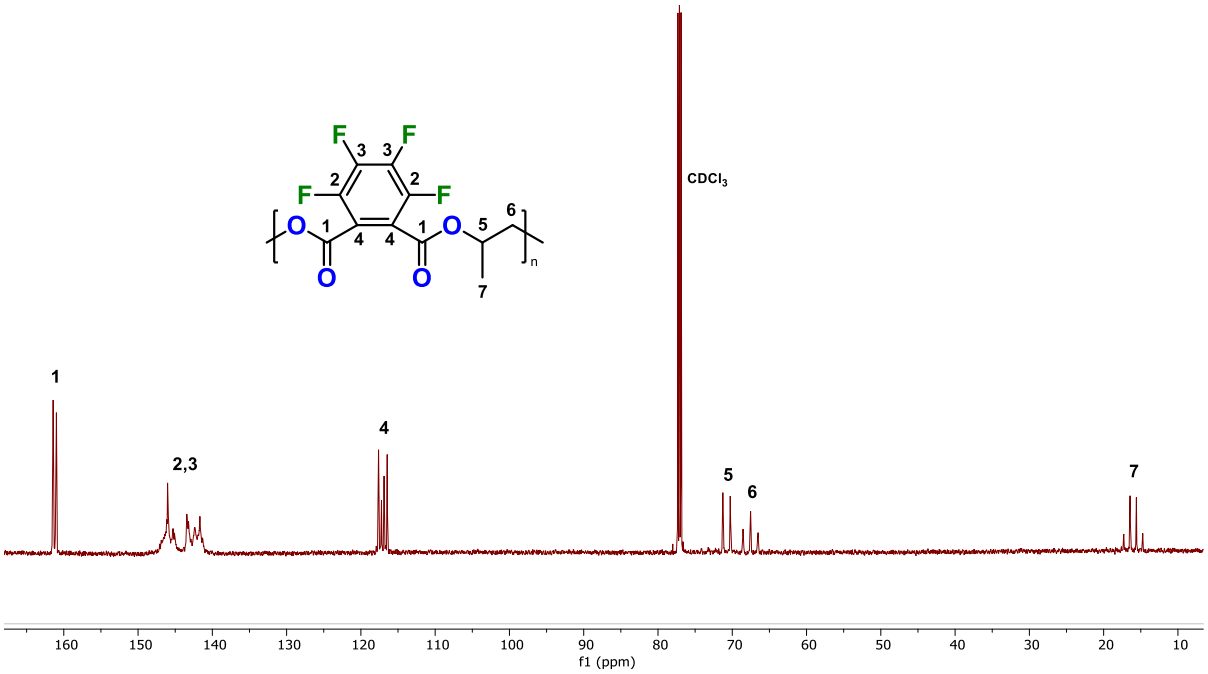
Supplementary Notes 4: PO/^{F}PA Copolymerisation



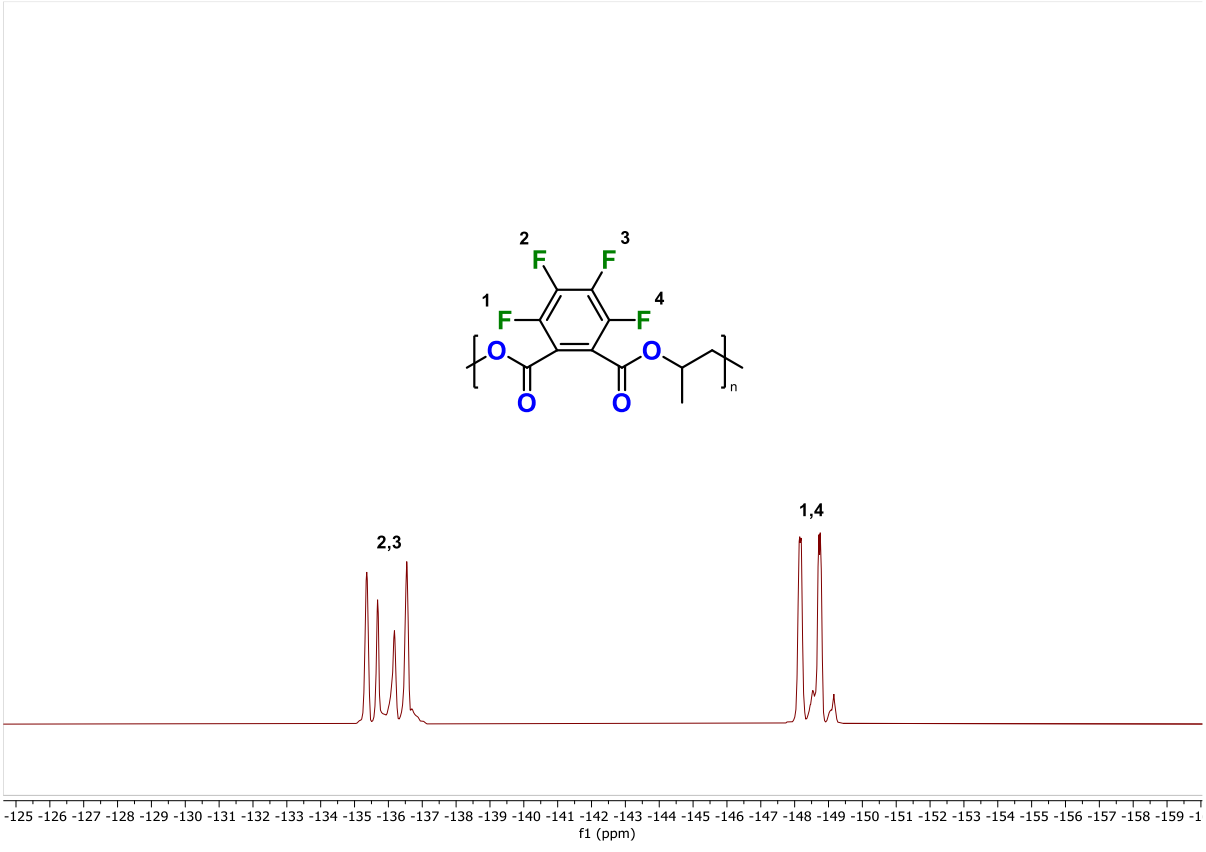
Supplementary Figure 2 - Copolymerisation of PO/^{F}PA



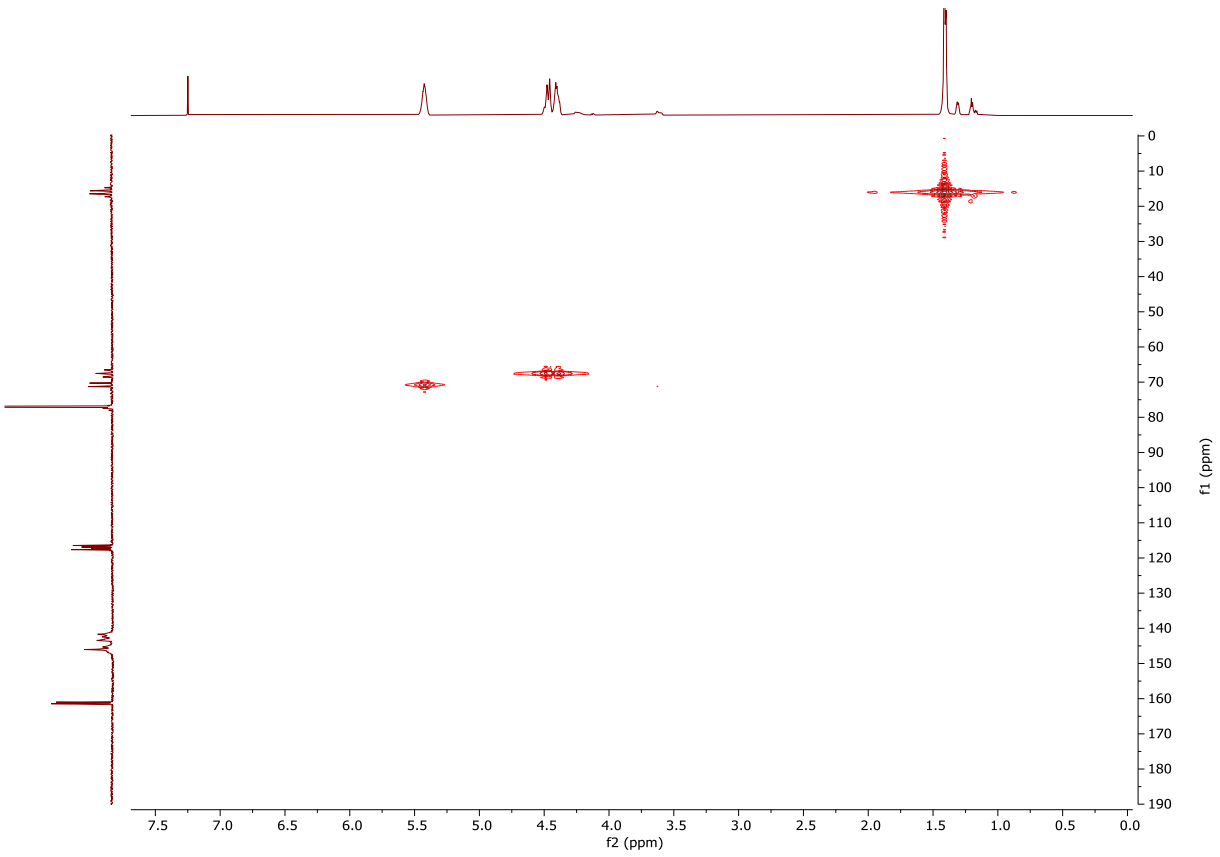
Supplementary Figure 3 – ^{1}H NMR (400 MHz, $CDCl_3$) of PO/^{F}PA copolymer corresponding to Table S1 entry 2
X = Cl, OH



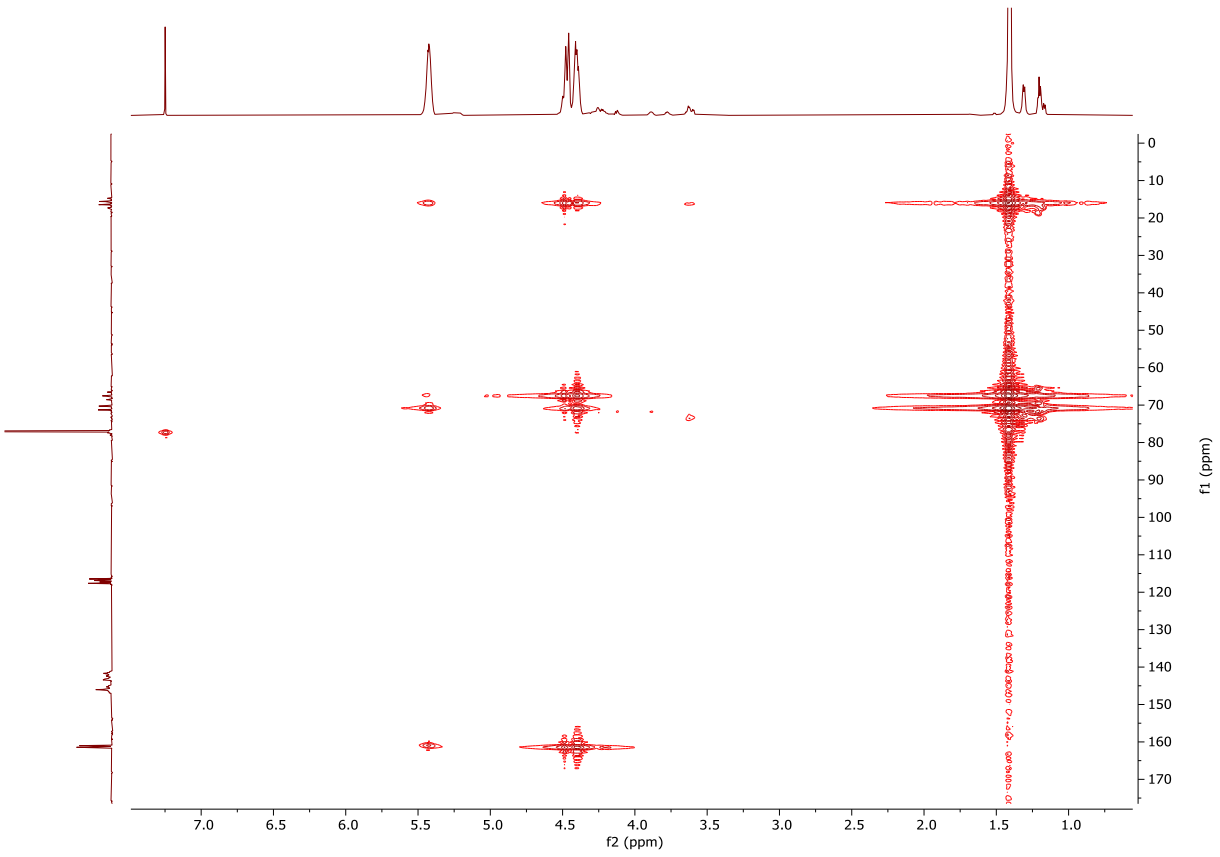
Supplementary Figure 4 - ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of PO/^{F}PA copolymer corresponding to Table S1 entry 2



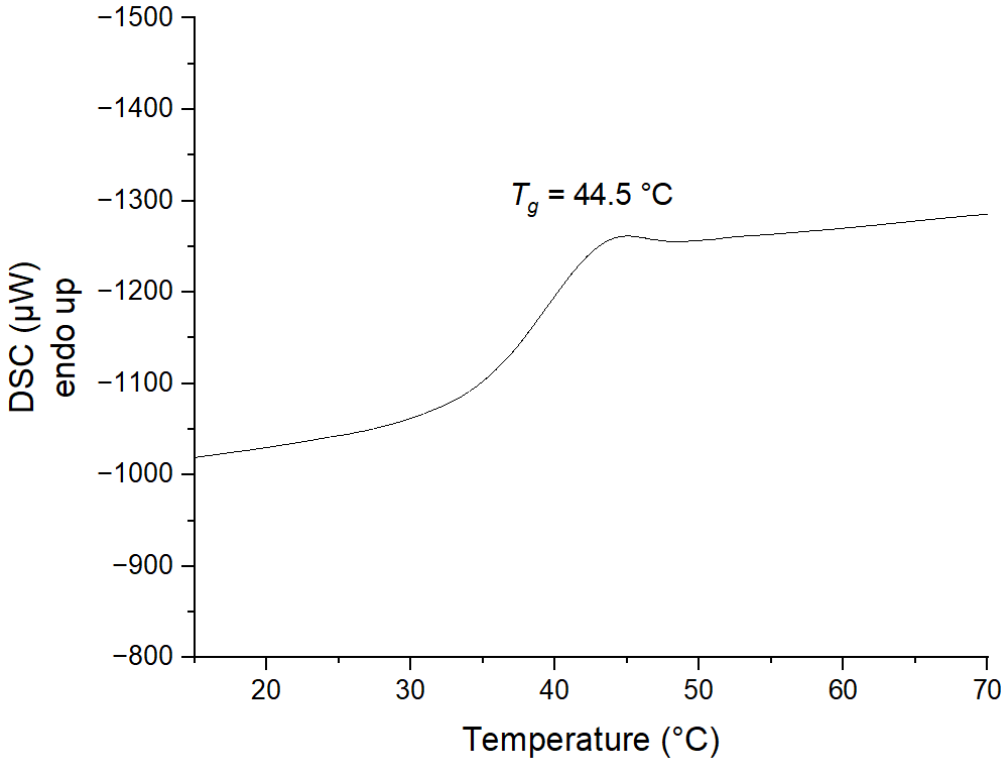
Supplementary Figure 5 – ^{19}F NMR spectrum (376 MHz, $CDCl_3$) of PO/^{F}PA copolymer corresponding to Table S1 entry 2



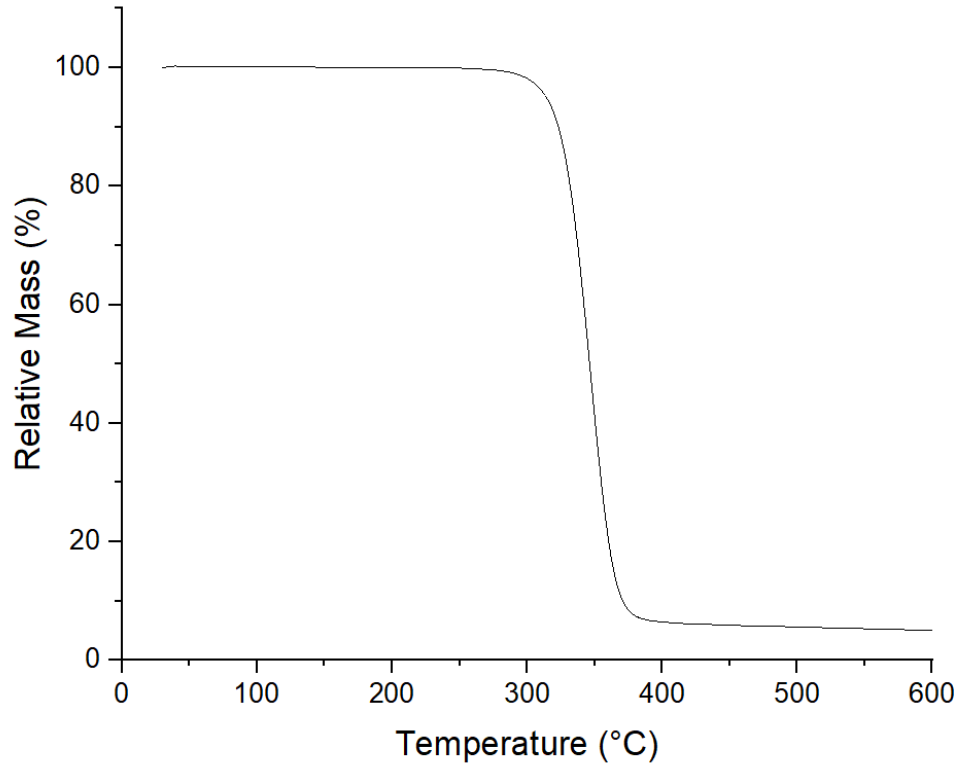
Supplementary Figure 6 - ^{1}H-^{13}C HSQC NMR spectrum ($CDCl_3$) spectrum of the PO/^{F}PA copolymer corresponding to Table S1 entry 2



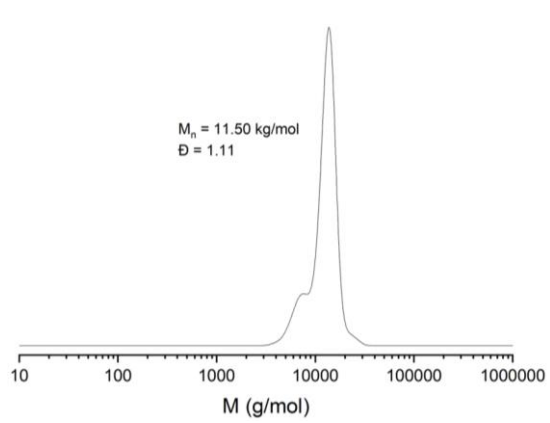
Supplementary Figure 7 - ^{1}H-^{13}C HMBC NMR spectrum ($CDCl_3$) spectrum of the PO/^{F}PA copolymer corresponding to Table S1 entry 2



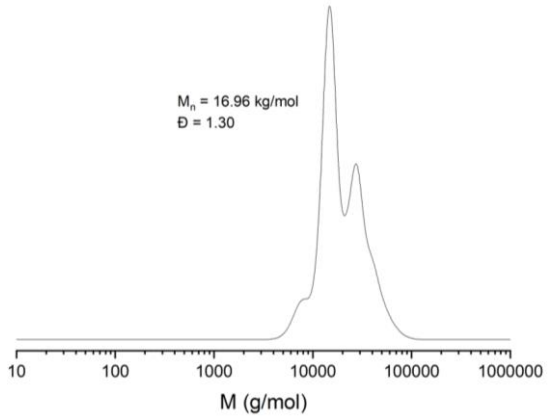
Supplementary Figure 8 – DSC data from the second heating cycle corresponding to PO/^{F}PA copolymer corresponding to Table S1 entry 2



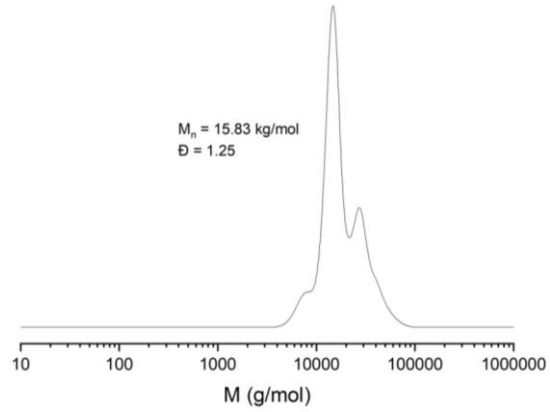
Supplementary Figure 9 - TGA data of copolymer corresponding to PO/^{F}PA copolymer corresponding to Table S1 entry 2. $T_{d,5\%}$ = 314.5 ºC.



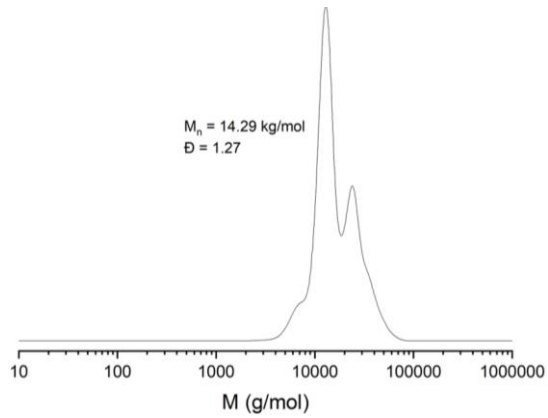
C1



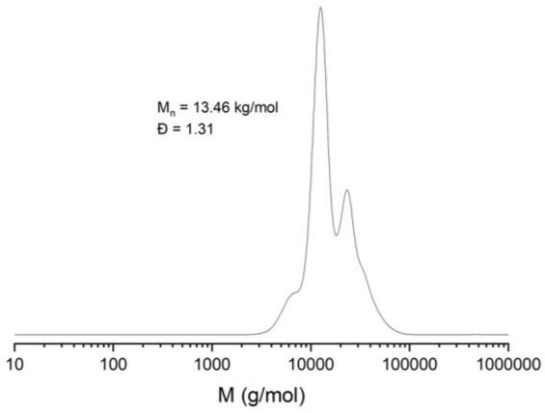
C2



C3



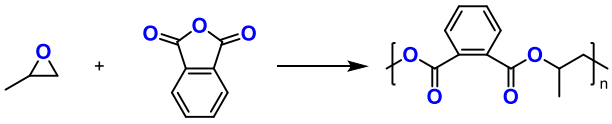
C4



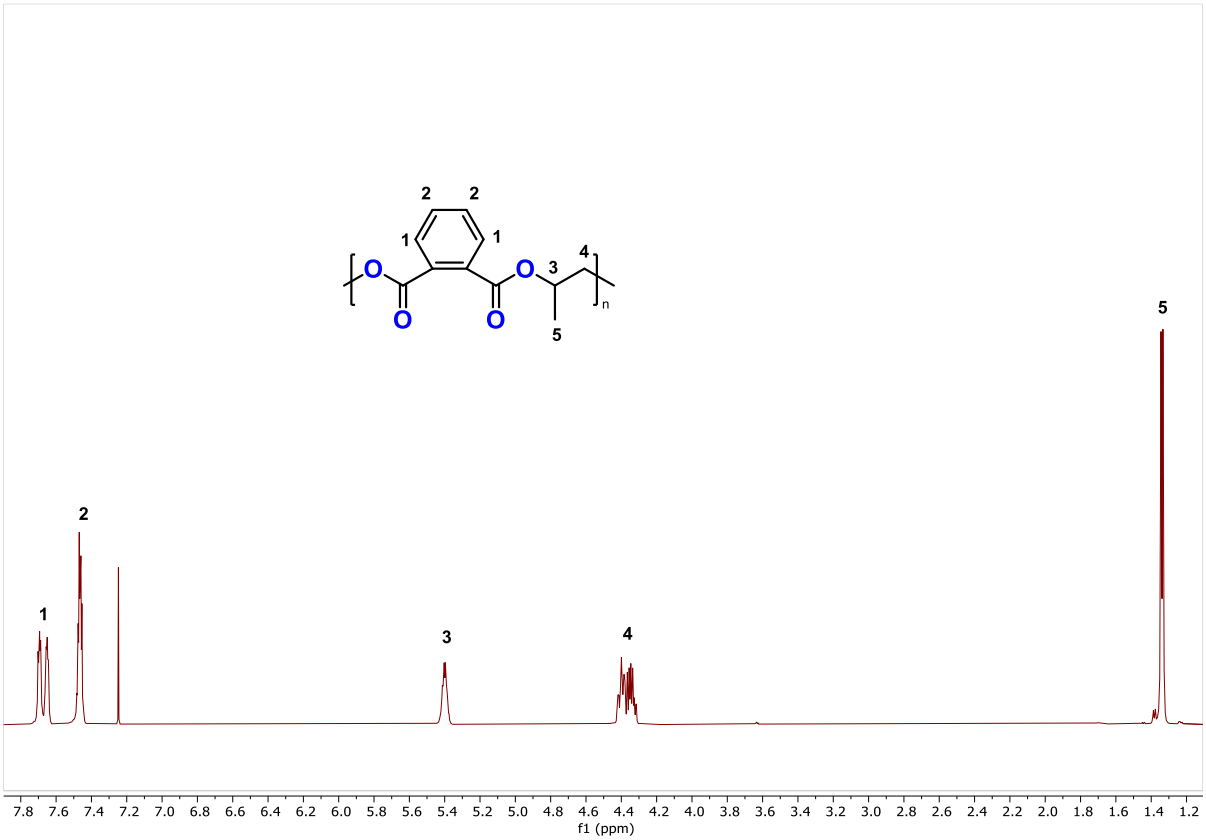
C5

Supplementary Figure 10 - GPC traces of PO/^{F}PA copolymer corresponding to Table S1 entries 1-5 with Cat1-5

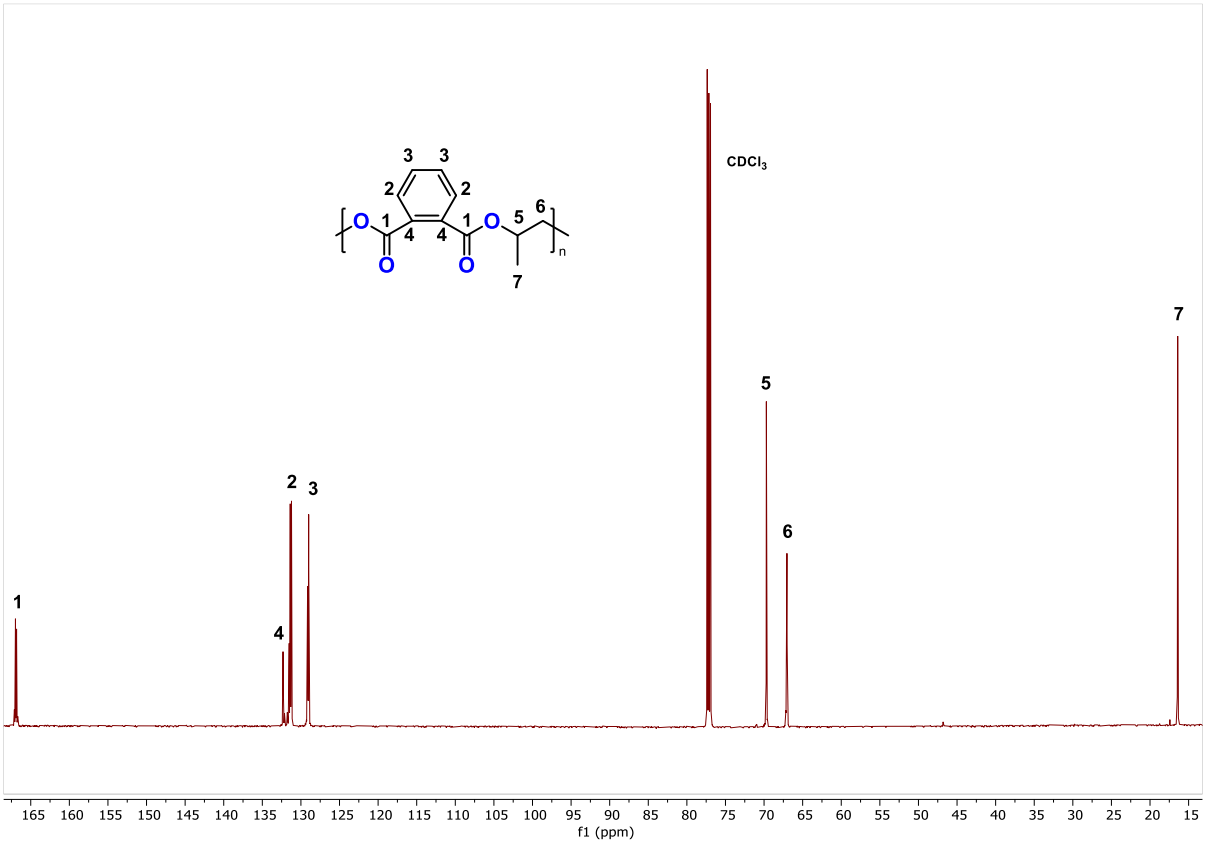
Supplementary Notes 5: PO/PA Copolymerisation



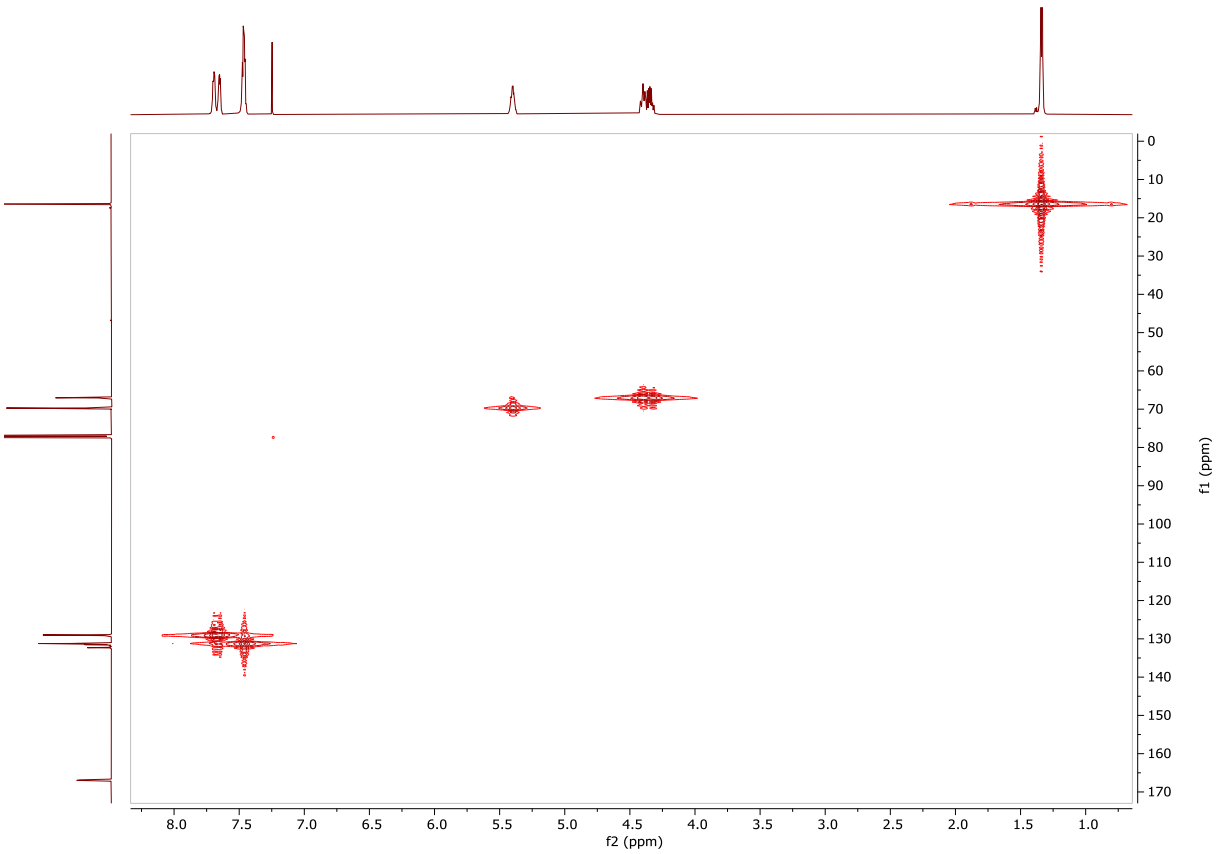
Supplementary Figure 11 – Copolymerisation of PO/PA



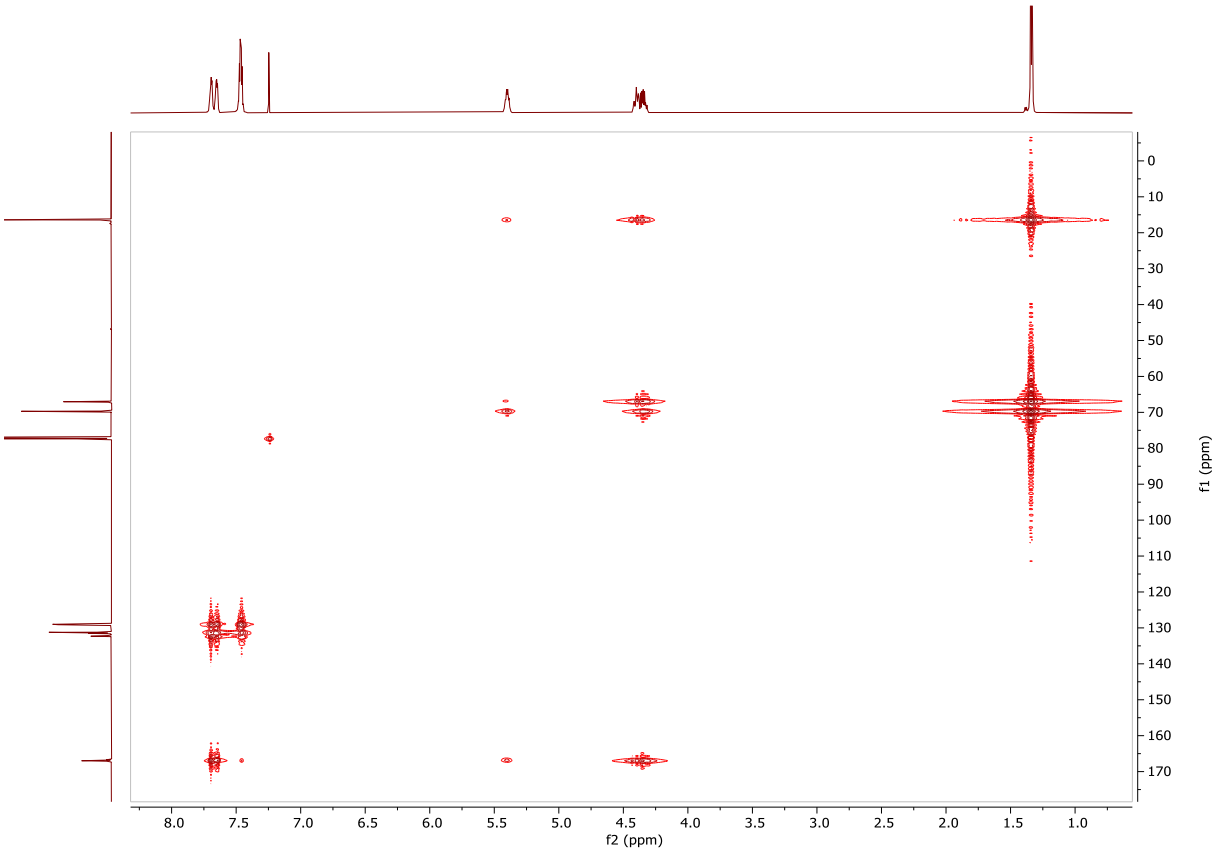
Supplementary Figure 12 - ^{1}H NMR (400 MHz, $CDCl_3$) of PO/PA copolymer corresponding to Table S1 entry 7



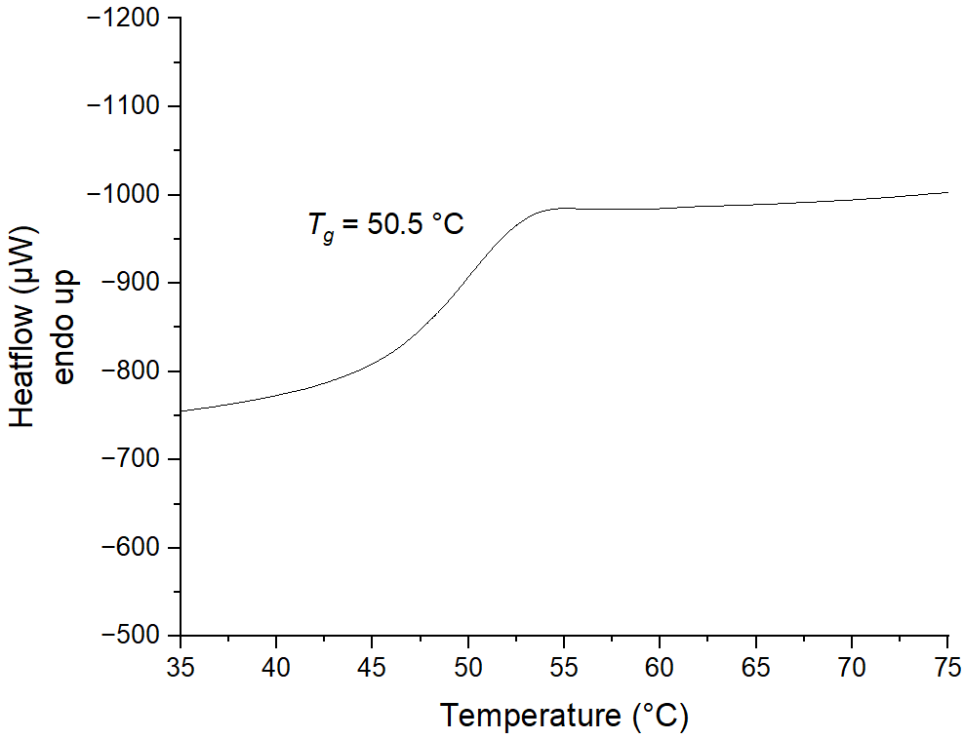
Supplementary Figure 13 - ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of PO/PA copolymer corresponding to Table S1 entry 7



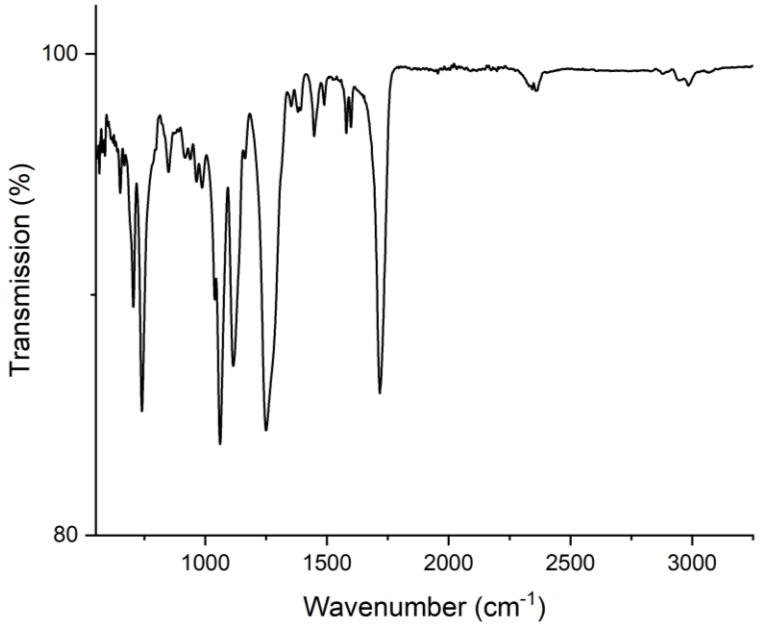
Supplementary Figure 14 - ^{1}H-^{13}C HSQC NMR spectrum ($CDCl_3$) spectrum of the PO/PA copolymer corresponding to Table S1 entry 7



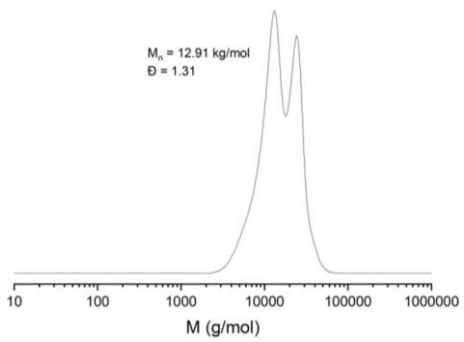
Supplementary Figure 15 - ^{1}H-^{13}C HMBC NMR spectrum ($CDCl_3$) spectrum of the PO/PA copolymer corresponding to Table S1 entry 7



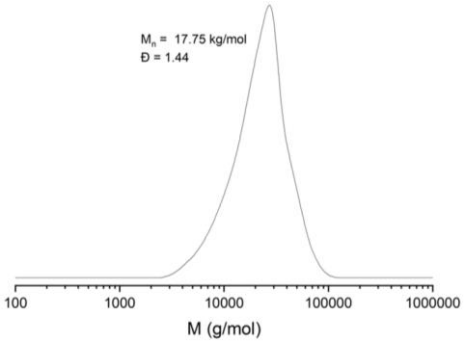
Supplementary Figure 16 - DSC data from the second heating cycle corresponding to PO/PA copolymer corresponding to Table S1 entry 7



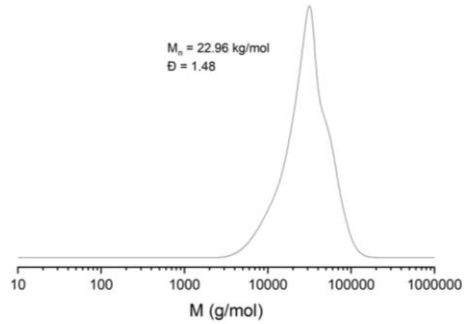
Supplementary Figure 17 – IR spectra of PO/PA copolymer corresponding to Table S1 entry 7



C1



C2



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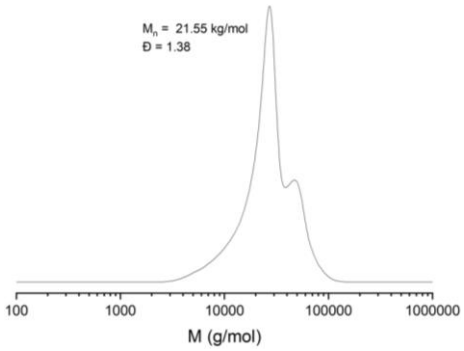

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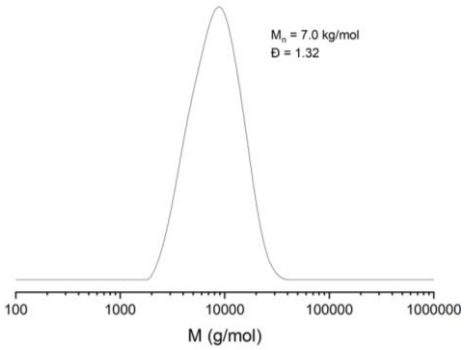
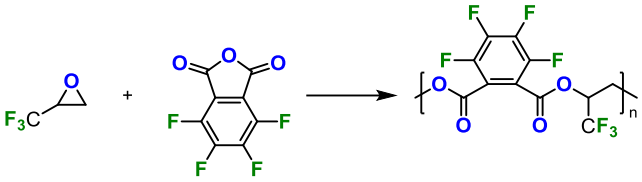


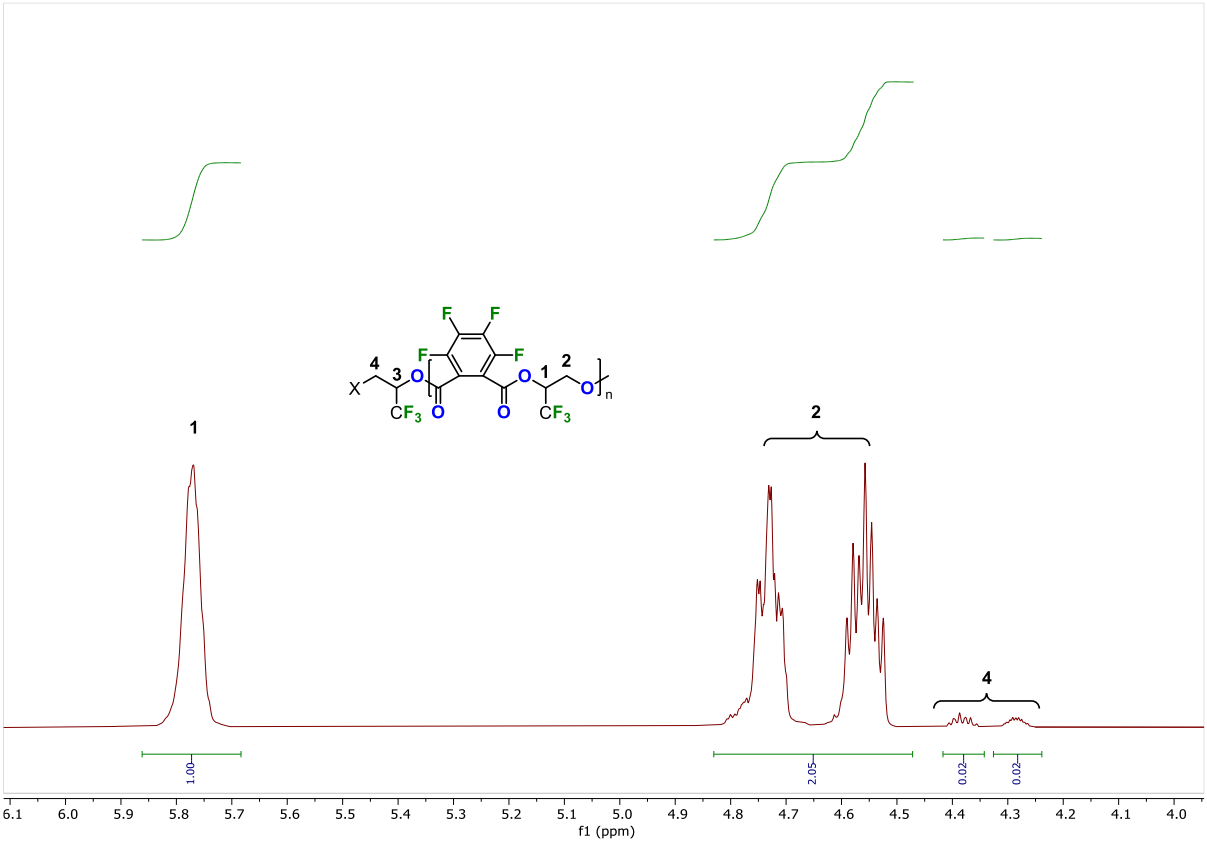
C5

Supplementary Figure 18 - GPC traces of PO/PA copolymer corresponding to Table S1 entries 6-10 Cat1-5

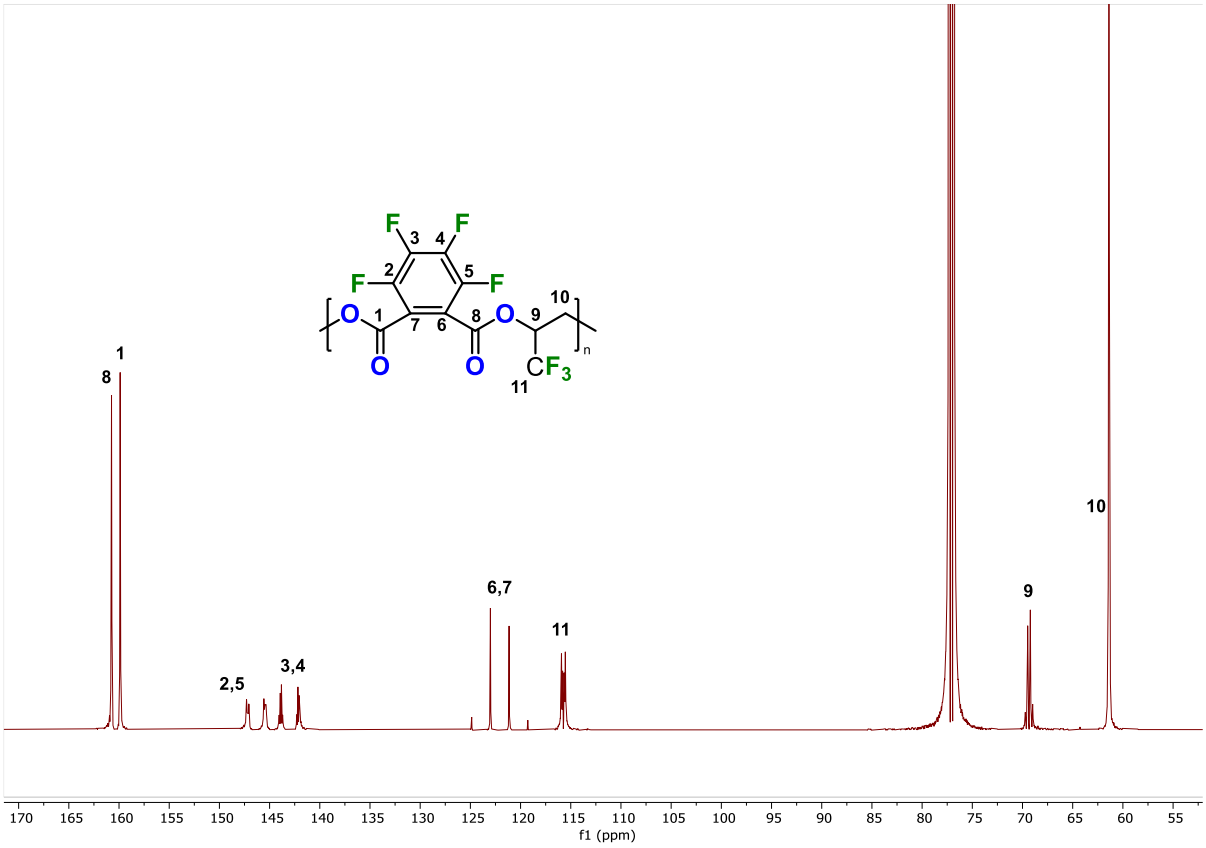
Supplementary Notes 6: ^{F}PO/^{F}PA Copolymerisation



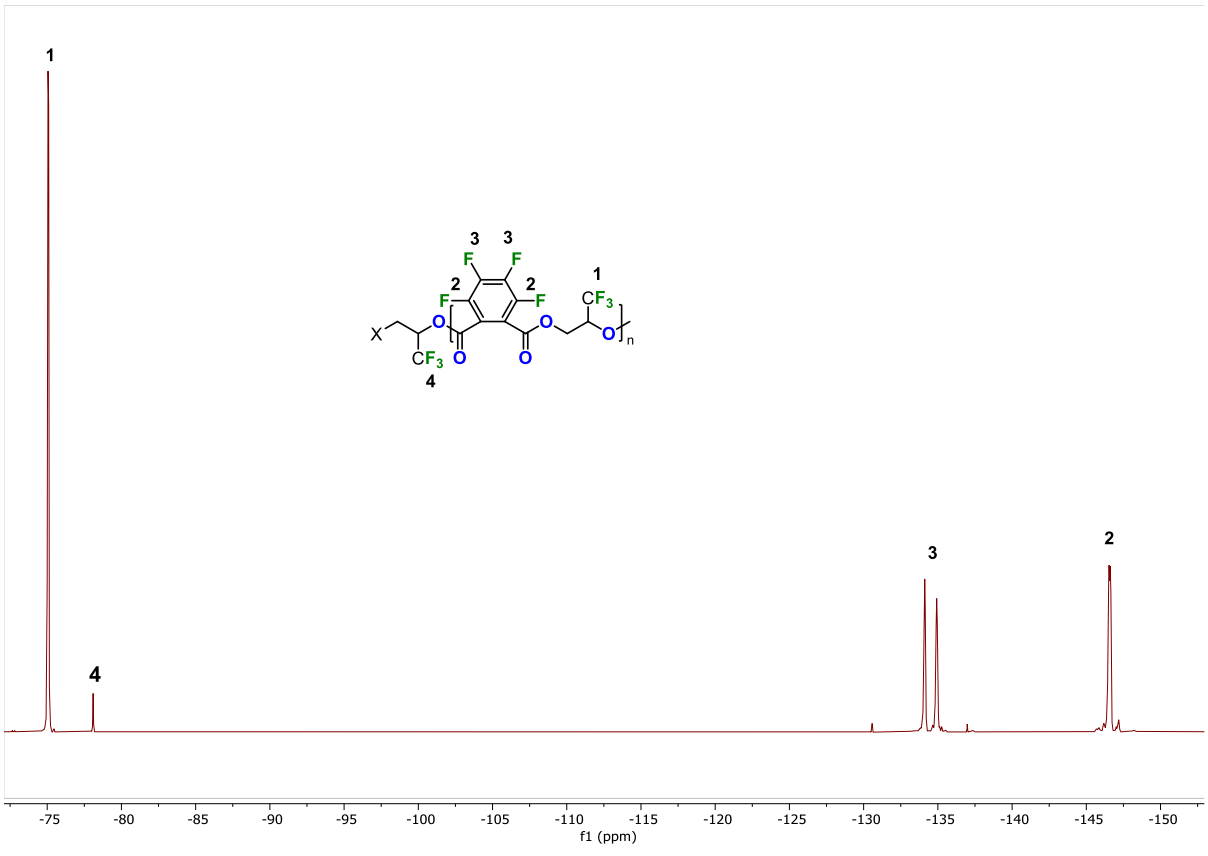
Supplementary Figure 19 – Copolymerisation of ^{F}PO/^{F}PA



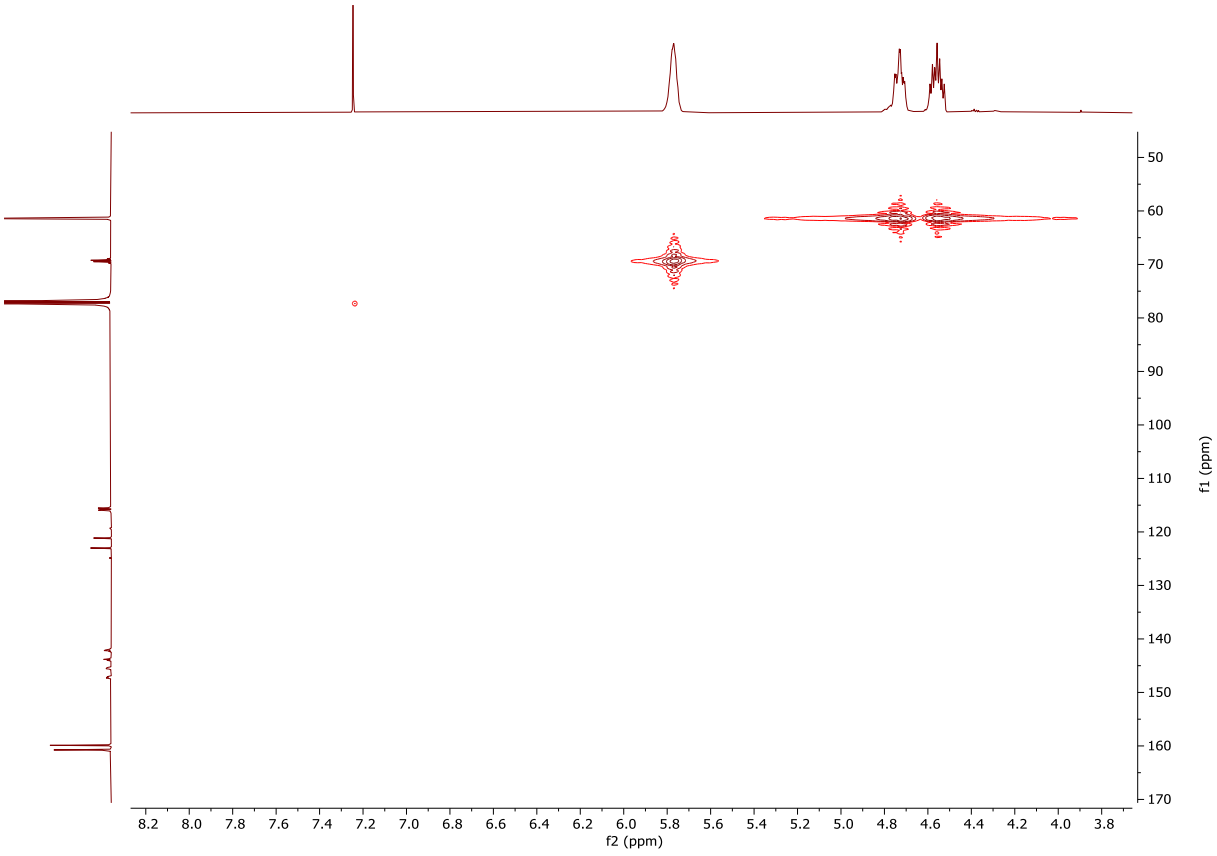
Supplementary Figure 20 - ^{1}H NMR (400 MHz, $CDCl_3$) of ^{F}PO/^{F}PA copolymer corresponding to Table S1 entry 11 X = Cl, OH



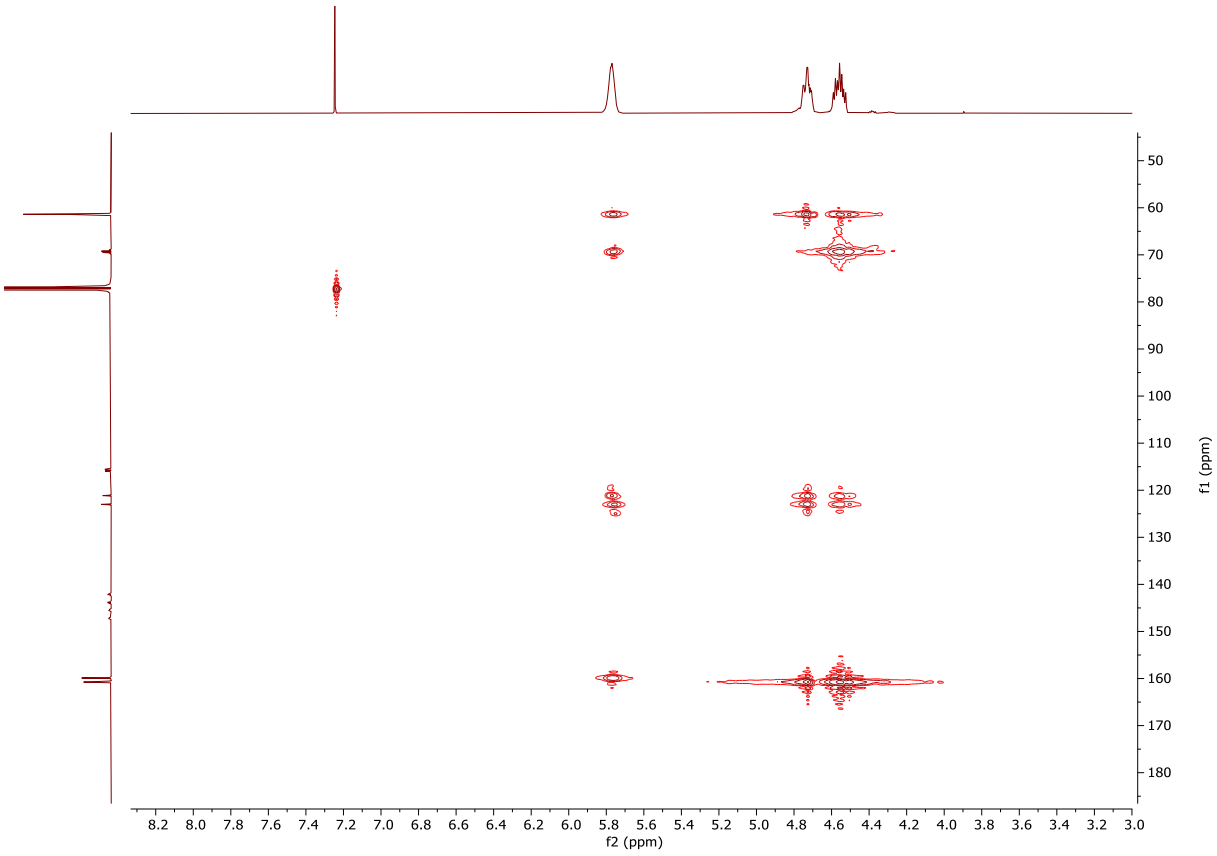
Supplementary Figure 21 - ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of ^{F}PO/^{F}PA copolymer corresponding to Table S1 entry 11



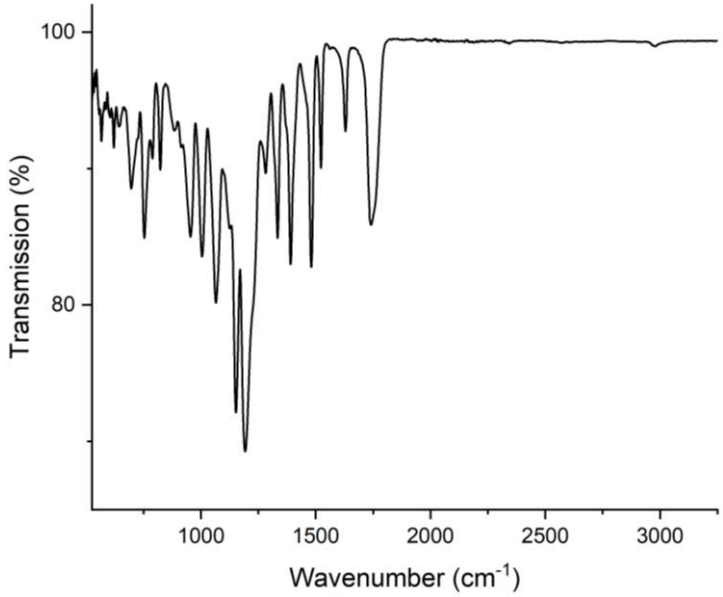
Supplementary Figure 22 - ^{19}F NMR spectrum (376 MHz, $CDCl_3$) of ^{F}PO/^{F}PA copolymer corresponding to Table S1 entry 11 X = Cl, OH



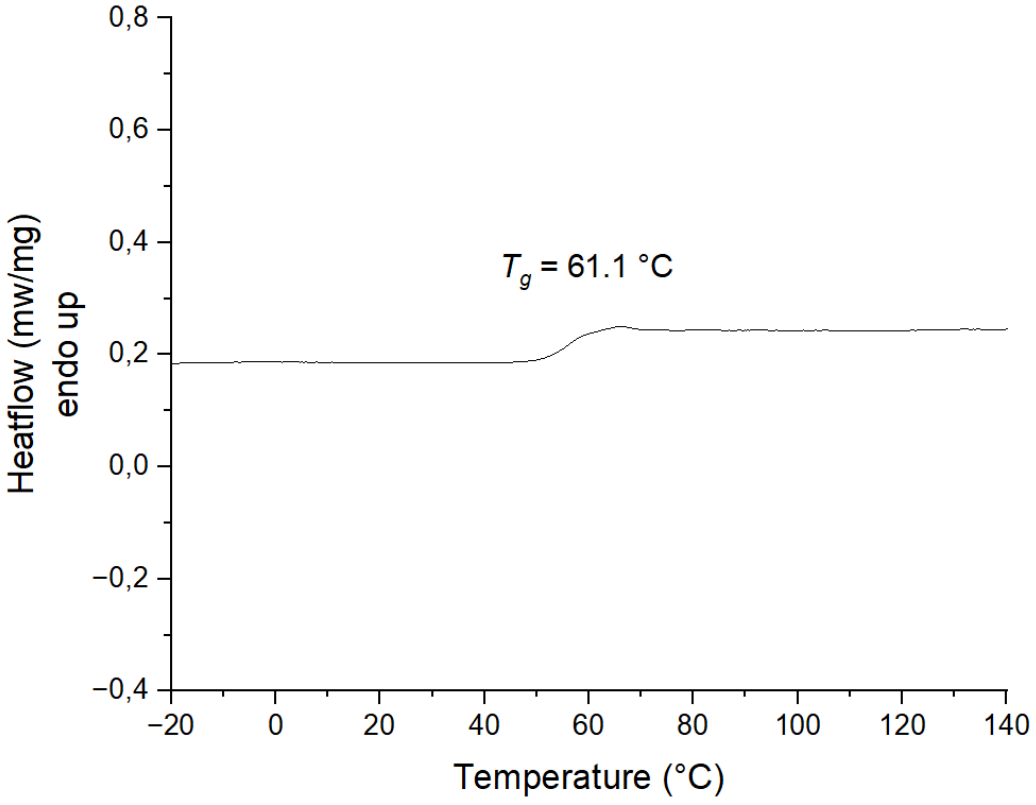
Supplementary Figure 23 - ^{1}H-^{13}C HSQC NMR spectrum ($CDCl_3$) spectrum of the ^{F}PO/^{F}PA copolymer corresponding to Table S1 entry 11



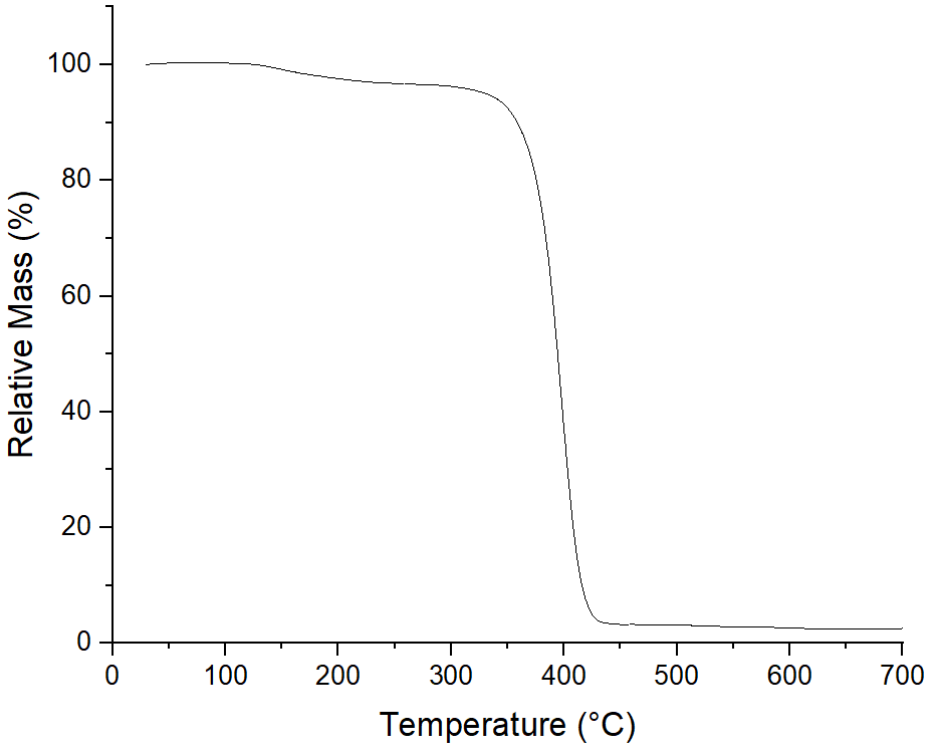
Supplementary Figure 24 - ^{1}H-^{13}C HMBC NMR spectrum ($CDCl_3$) spectrum of the ^{F}PO/^{F}PA copolymer corresponding to Table S1 entry 11



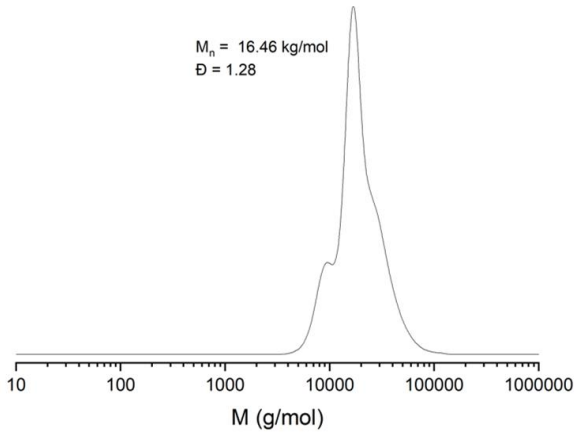
Supplementary Figure 25 – IR spectrum of ^{F}PO/^{F}PA copolymer corresponding to Table S1 entry 11



Supplementary Figure 26 - DSC data from the second heating cycle corresponding to ^{F}PO/^{F}PA copolymer corresponding to Table S1 entry 11



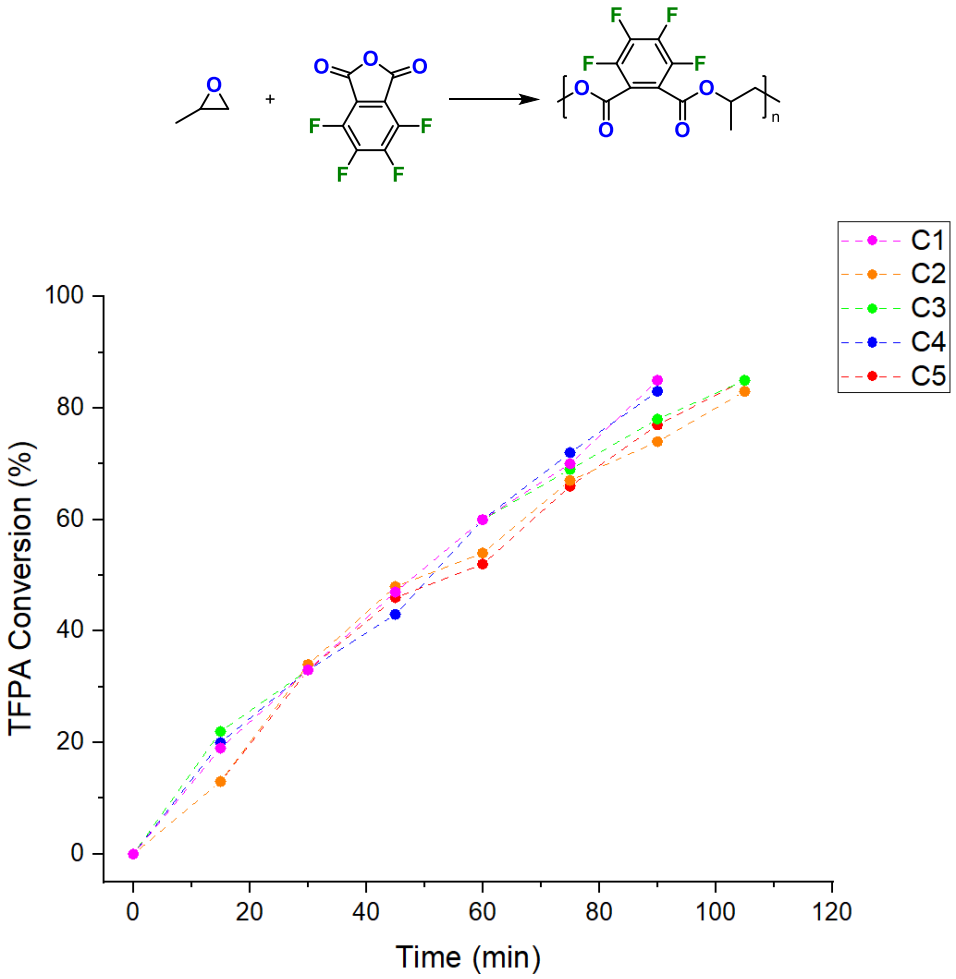
Supplementary Figure 27 - TGA data of copolymer corresponding to ^{F}PO/^{F}PA copolymer corresponding to Table S1 entry 11. $T_{d,5\%}$ = 350 ºC.



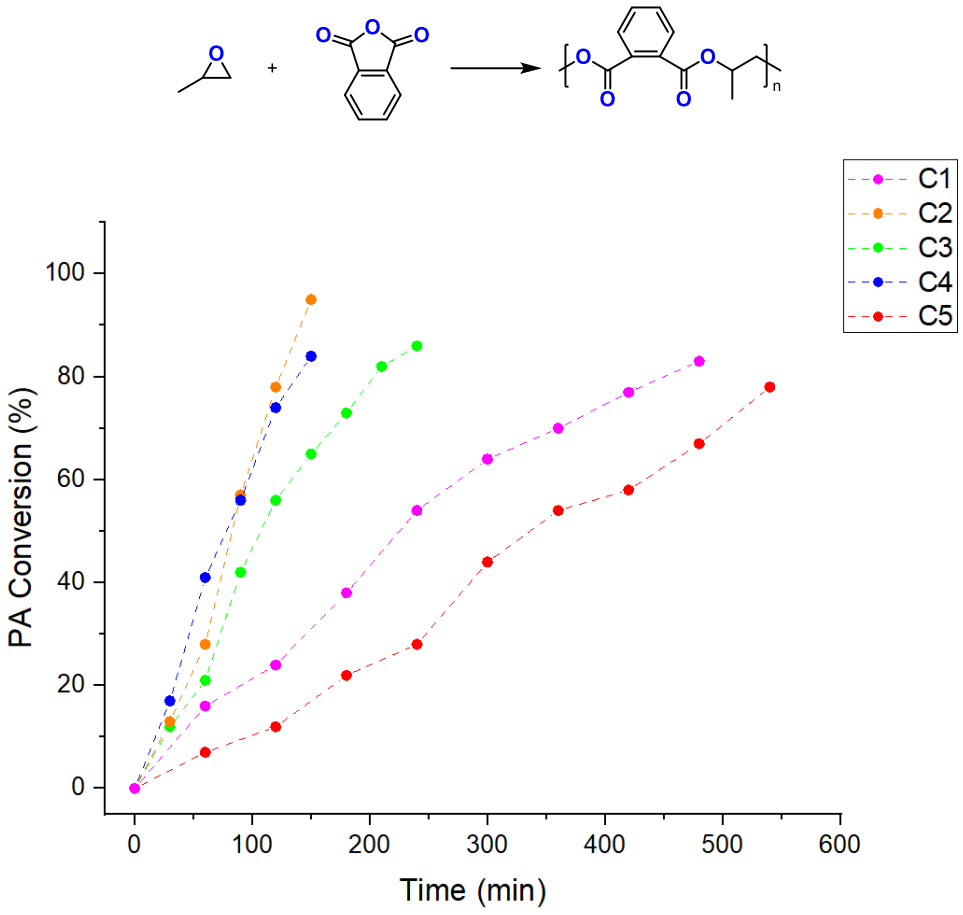
C3

Supplementary Figure 28 - GPC trace of ^{F}PO/^{F}PA copolymer corresponding to Table S1 entry 11 with Cat3

Supplementary Notes 7: Kinetic Data

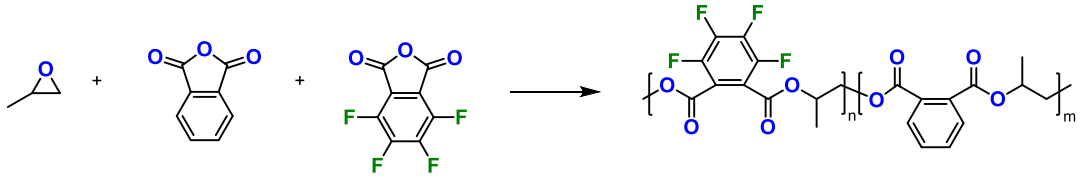


Supplementary Figure 29 – Kinetic data for Cat1-5 for the PO/^{F}PA copolymerisation

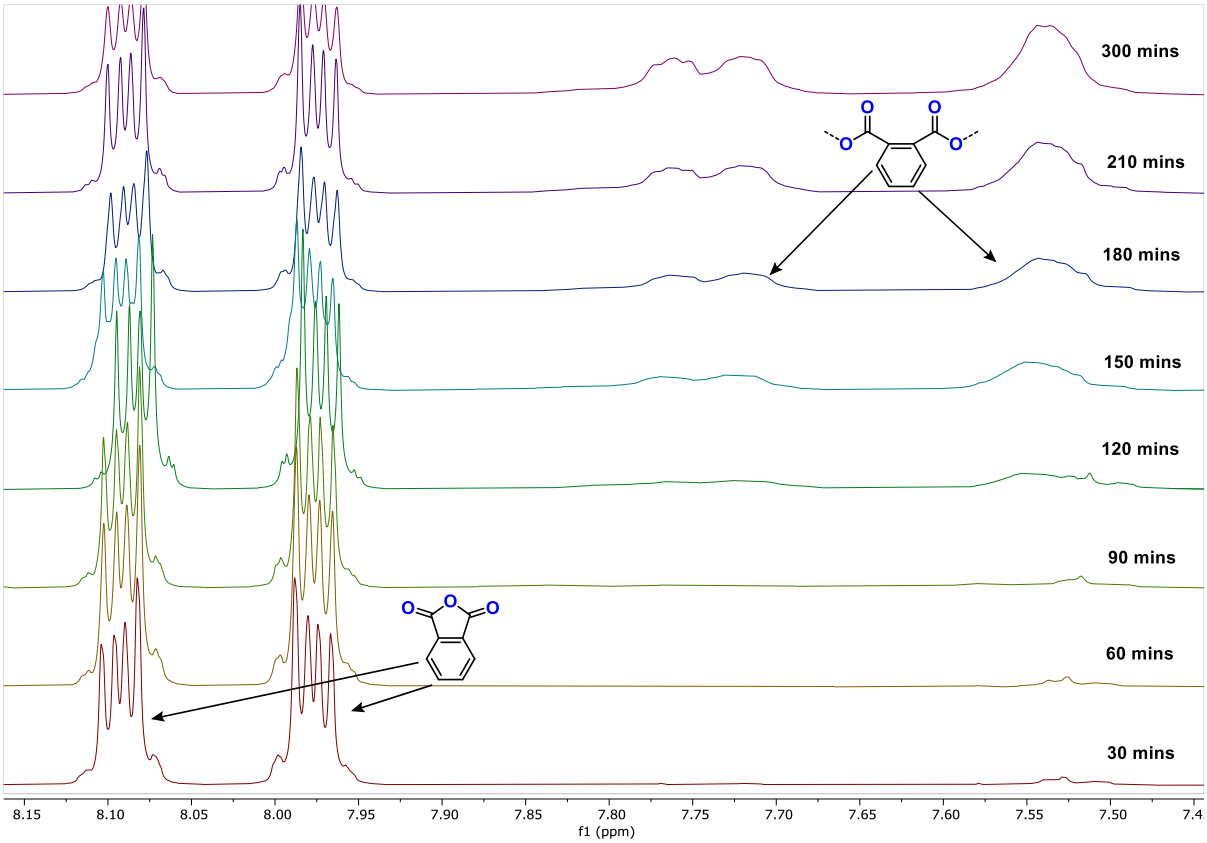


Supplementary Figure 30 - Kinetic data for Cat1-5 for the PO/PA copolymerisation

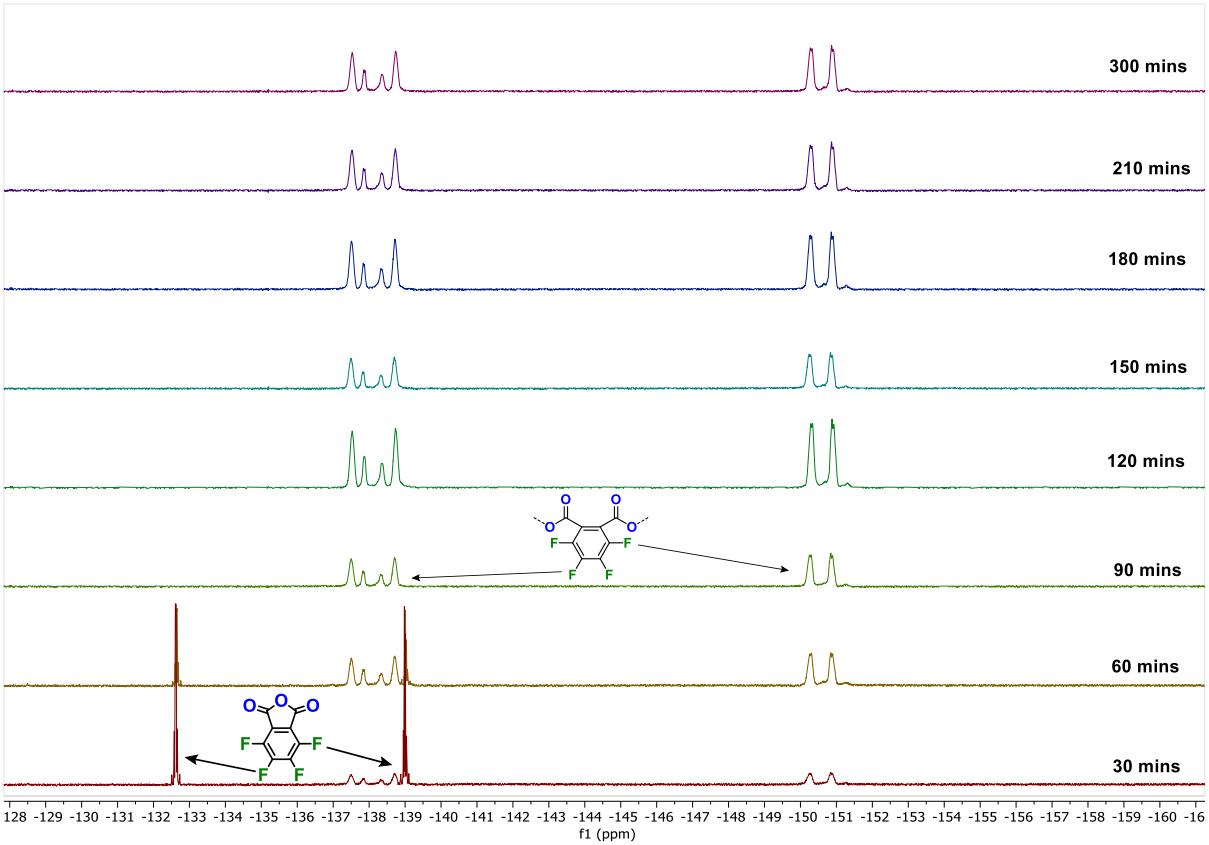
Supplementary Notes 8: Ter- and Tetra-polymerisations



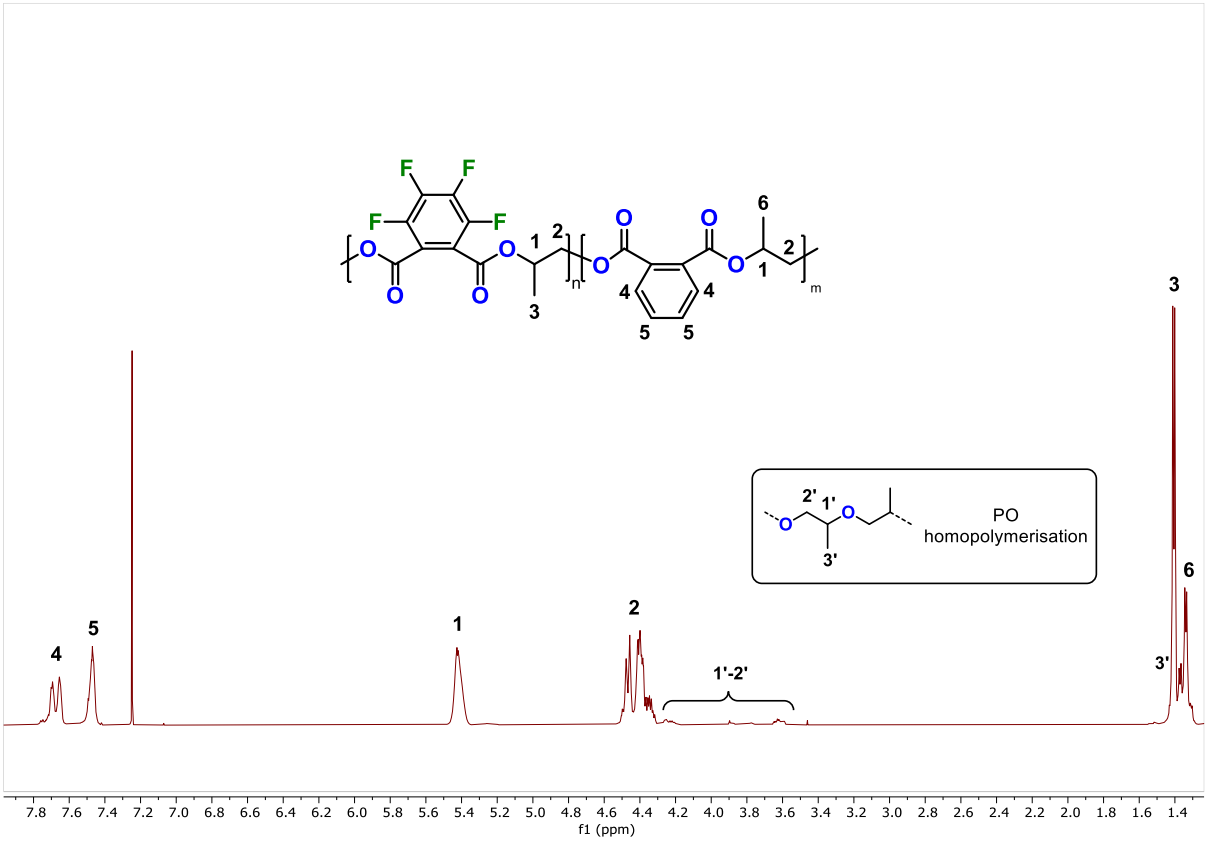
Supplementary Figure 31 – Terpolymerisation of PO/PA/^{F}PA with 1 C3: 1 PPNCl: 500 PO: 250 PA: 250 ^{F}PA at 80 °C



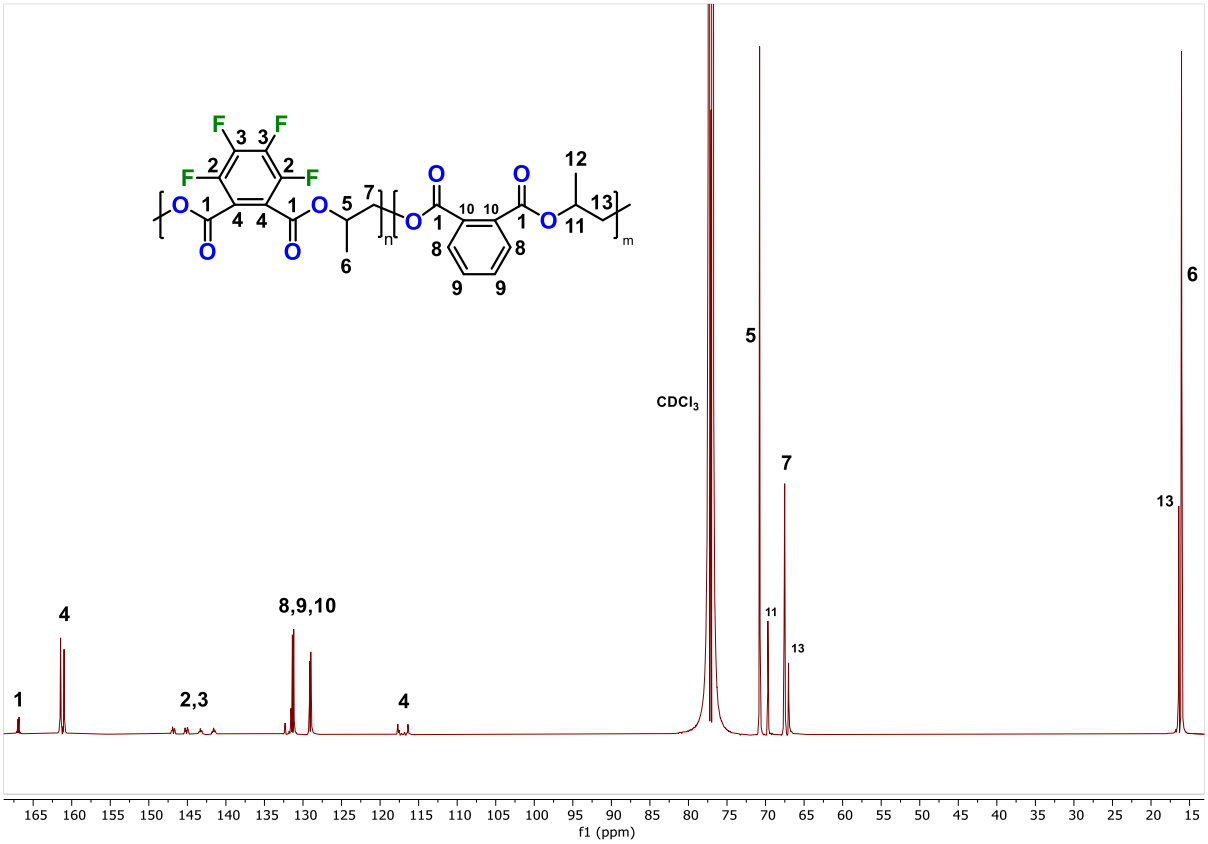
Supplementary Figure 32 - ^{1}H NMR (400 MHz, $CDCl_3$) of aliquots of PO/PA/^{F}PA terpolymerisation removed at regular times intervals of 30 minutes



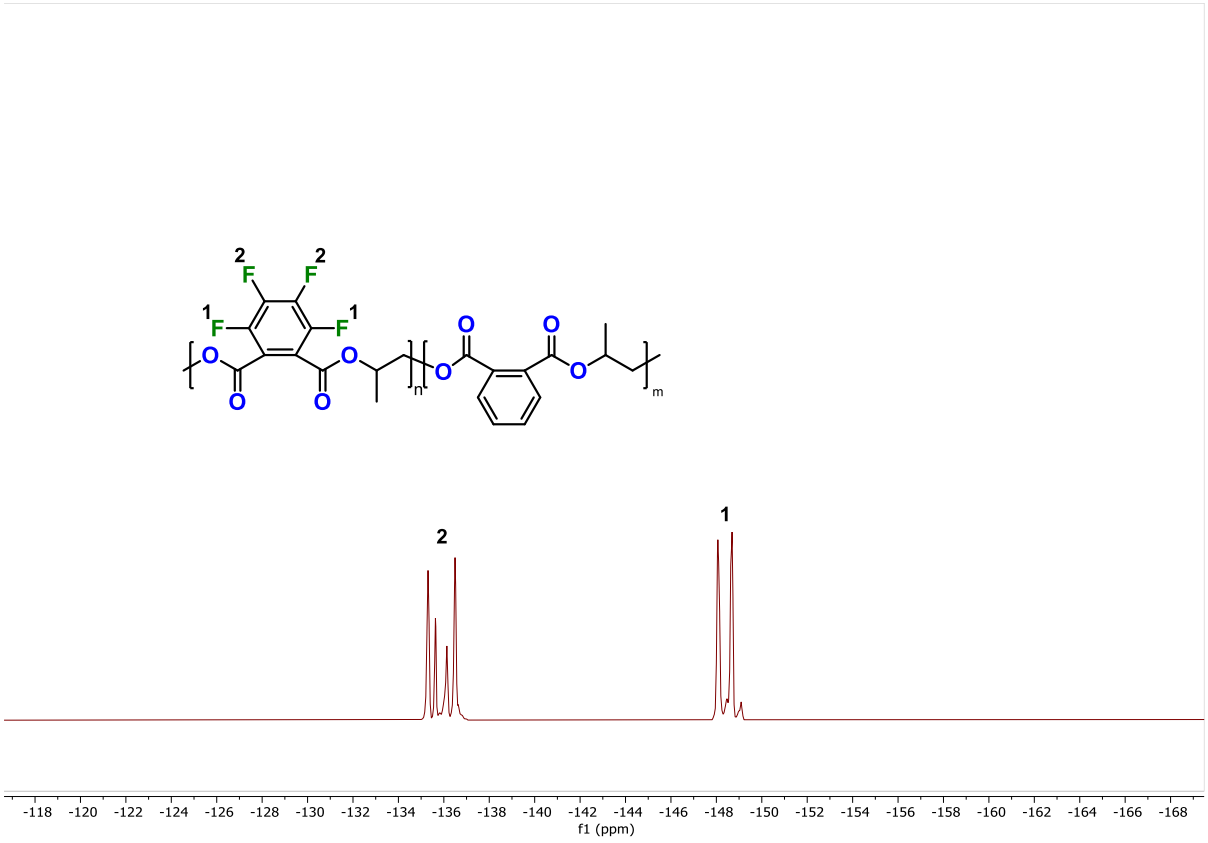
Supplementary Figure 33 - ^{19}F NMR spectrum (376 MHz, $CDCl_3$) of aliquots of PO/PA/^{F}PA terpolymerisation removed at regular times intervals of 30 minutes



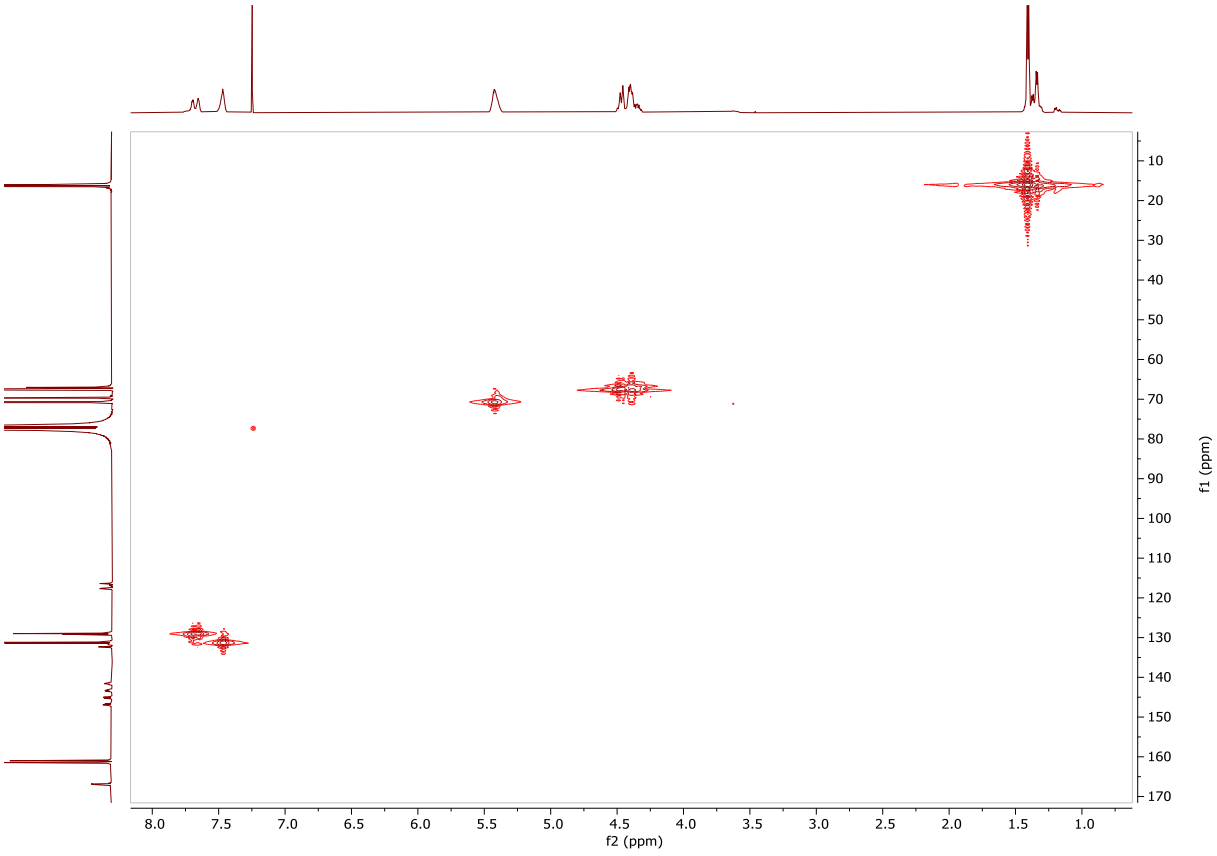
Supplementary Figure 34 - ^{1}H NMR (400 MHz, $CDCl_3$) of PO/PA/^{F}PA terpolymer



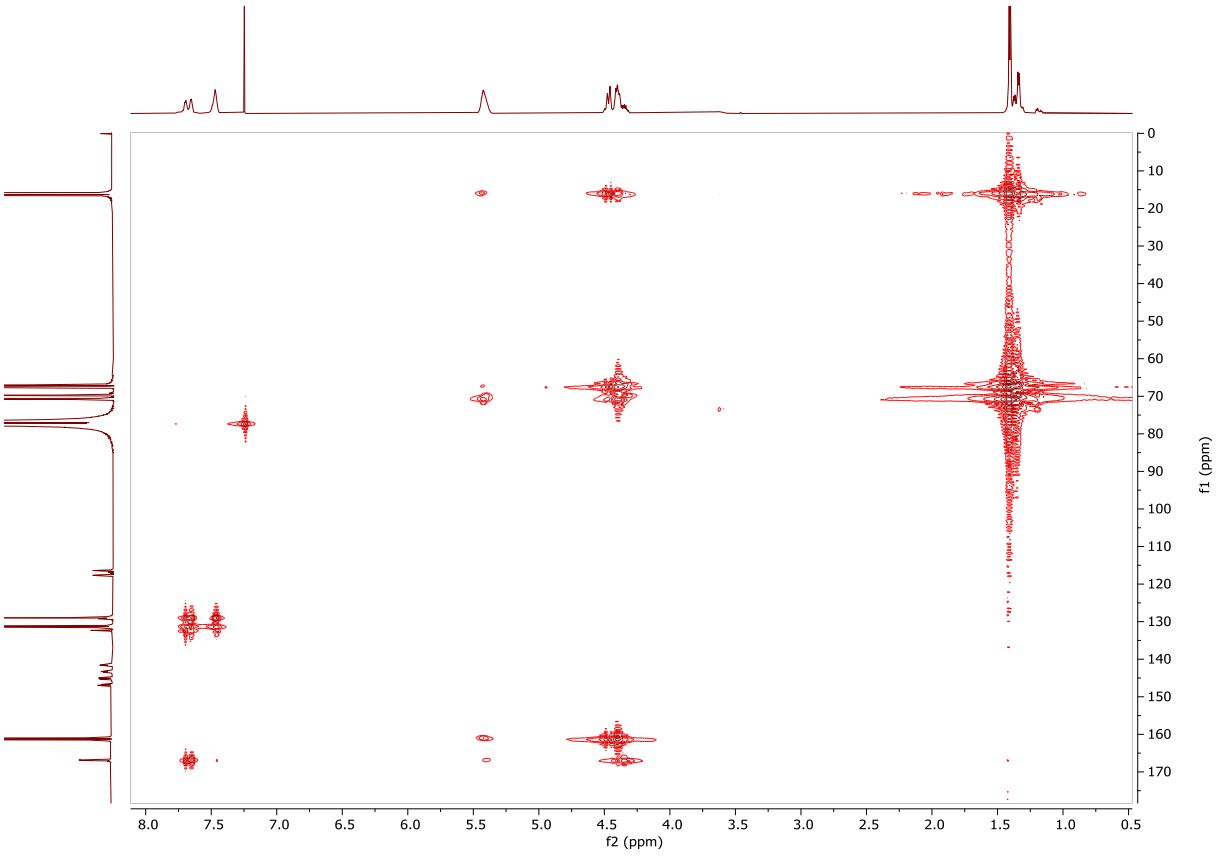
Supplementary Figure 35 - ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of PO/PA/^{F}PA terpolymer



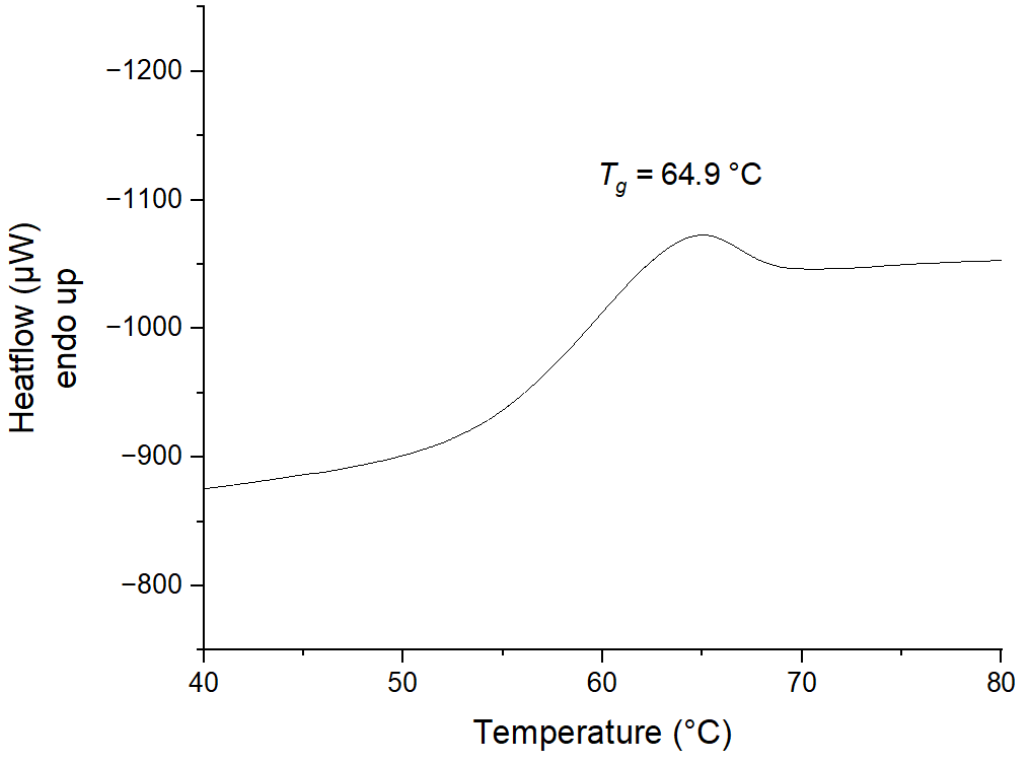
Supplementary Figure 36 - ^{19}F NMR spectrum (376 MHz, $CDCl_3$) of PO/PA/^{F}PA terpolymer



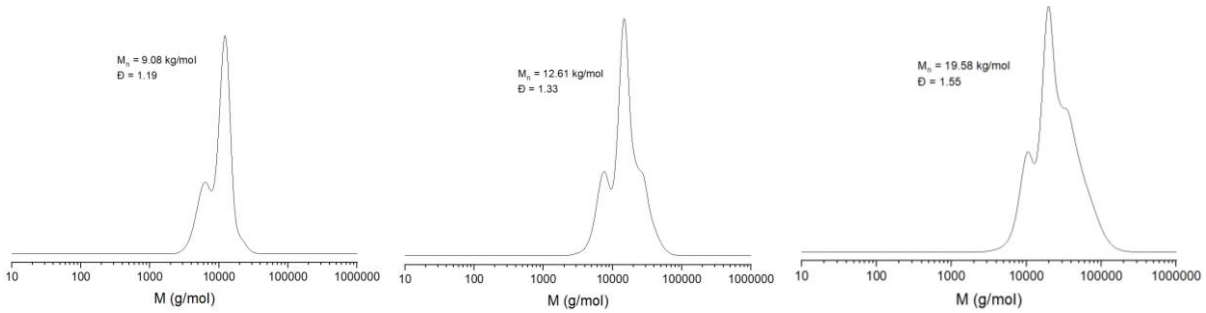
Supplementary Figure 37 - ^{1}H-^{13}C HSQC NMR spectrum ($CDCl_3$) spectrum of the PO/PA/^{F}PA terpolymer



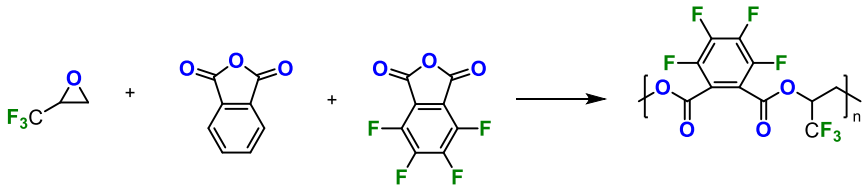
Supplementary Figure 38 - ^{1}H-^{13}C HMBC NMR spectrum ($CDCl_3$) spectrum of the PO/PA/^{F}PA copolymer



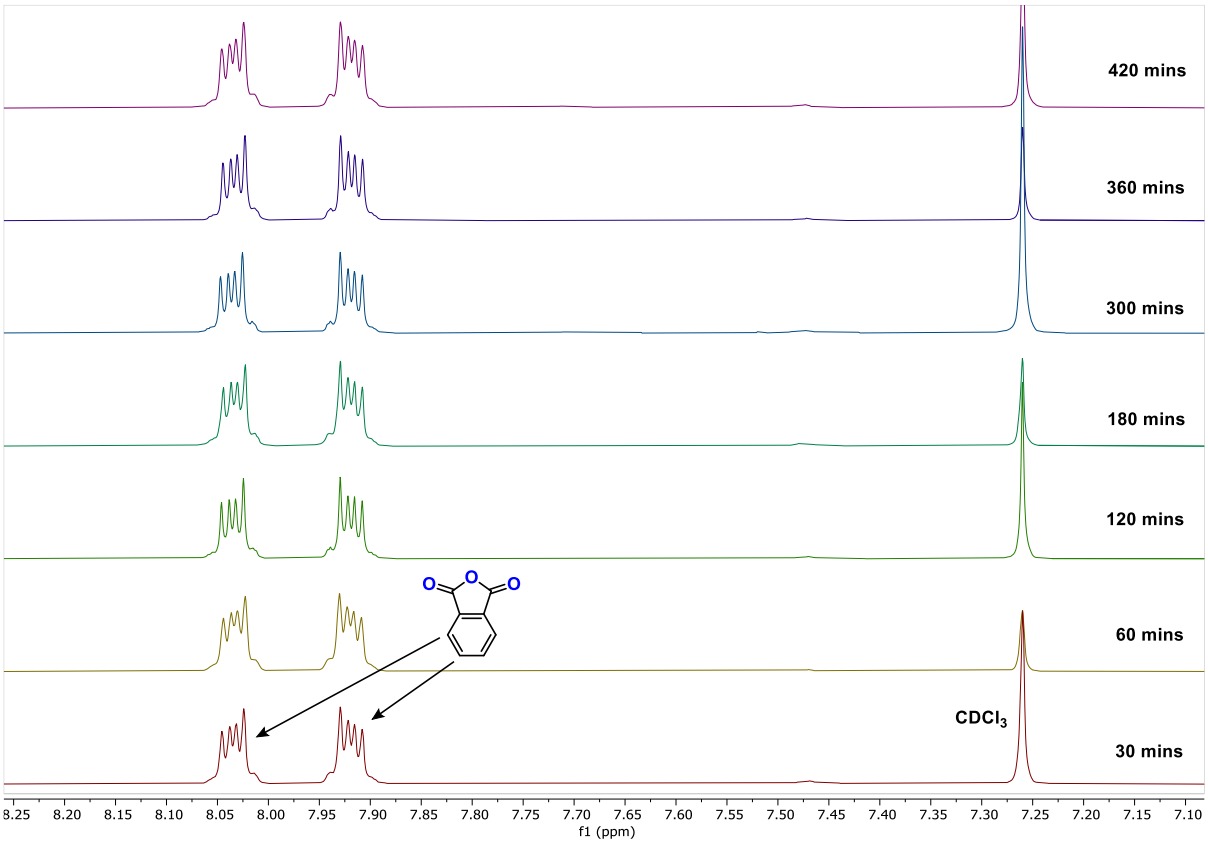
Supplementary Figure 39 - DSC data of the second heating cycle corresponding to PO/PA/^{F}PA terpolymer



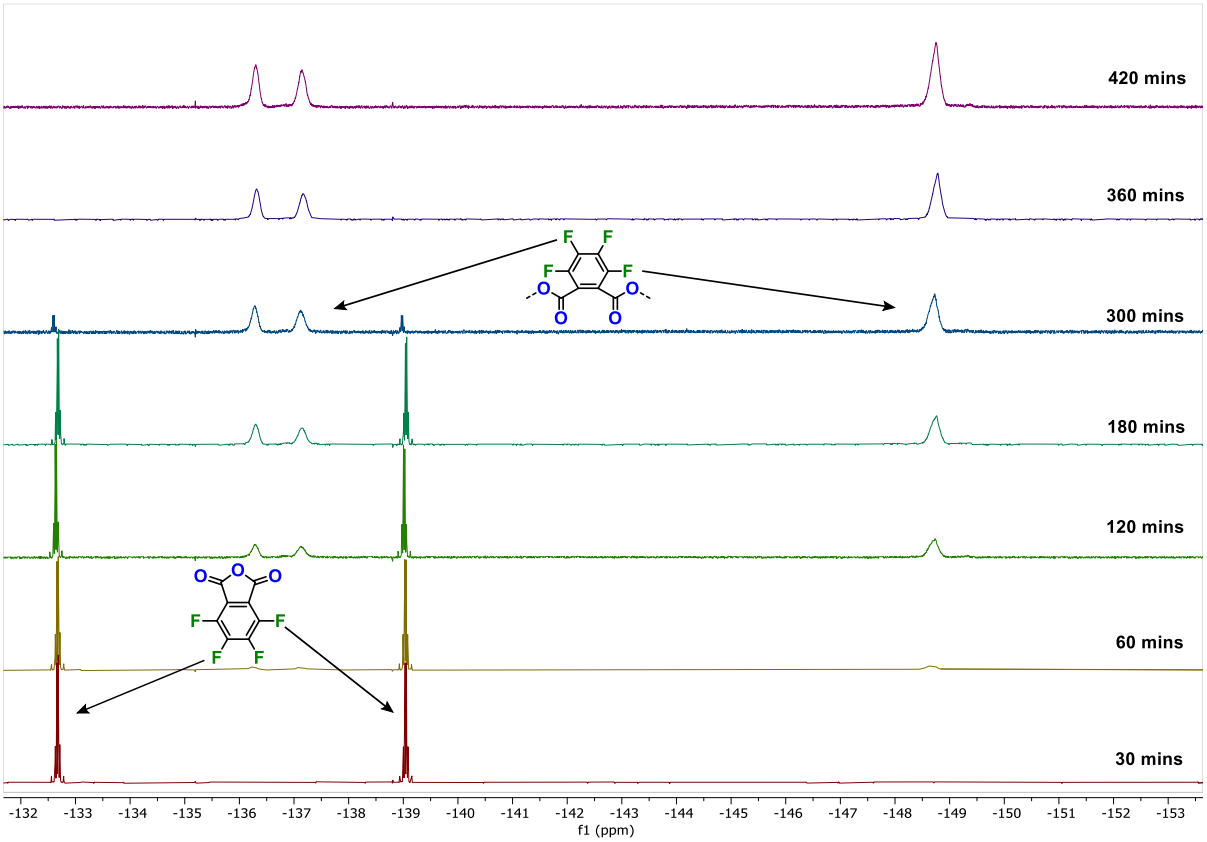
Supplementary Figure 40 – GPC trace after 1hour (left), 2 hours (middle) and 3 hours (right) of PO/PA/^{F}PA terpolymerisation



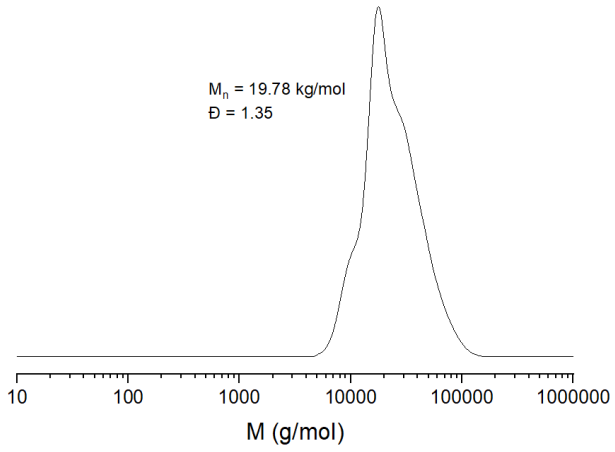
Supplementary Figure 41 – Terpolymerisation of ^{F}PO/PA/^{F}PA with 1 C3: 1 PPNCl: 500 ^{F}PO: 250 PA: 250 ^{F}PA at 80 °C



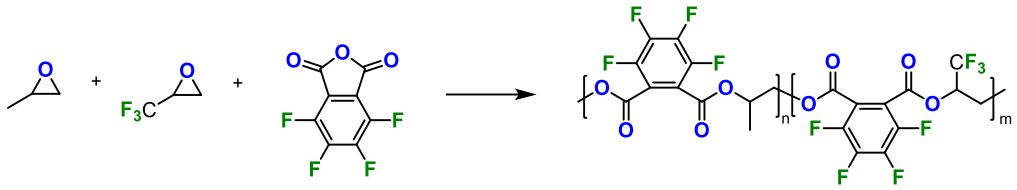
Supplementary Figure 42 - ^{1}H NMR (400 MHz, $CDCl_3$) of aliquots of ^{F}PO/PA/^{F}PA terpolymerisation removed at regular times intervals of 60 minutes



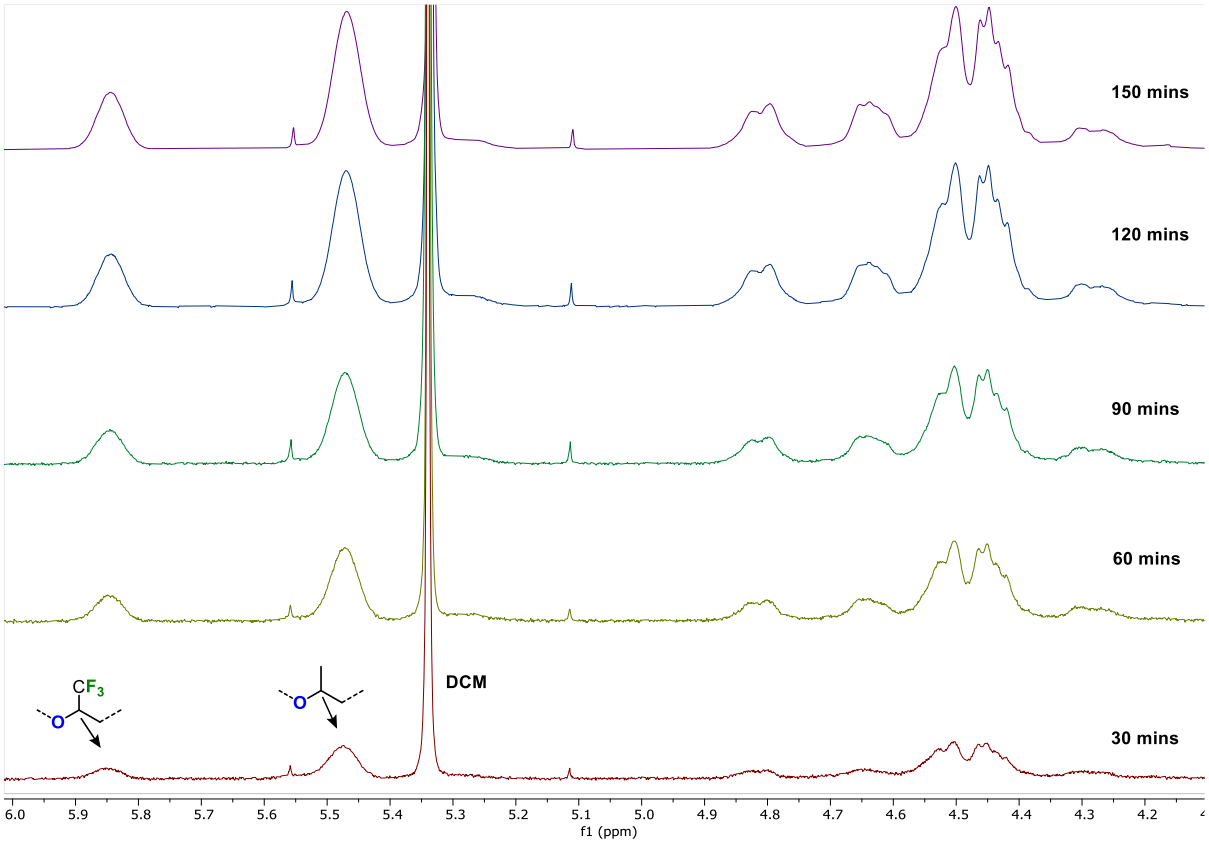
Supplementary Figure 43 - ^{19}F NMR spectrum (376 MHz, $CDCl_3$) of aliquots of ^{F}PO/PA/^{F}PA terpolymerisation removed at regular times intervals of 60 minutes



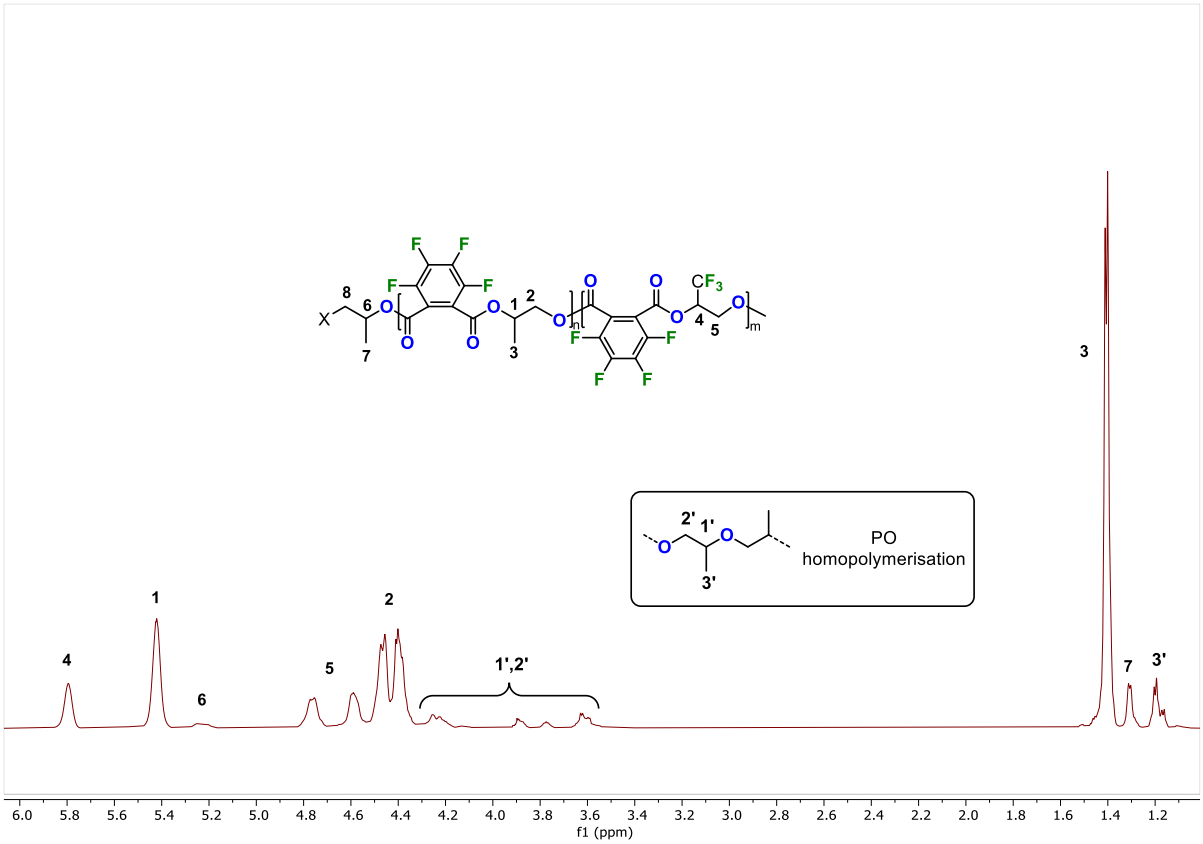
Supplementary Figure 44 – GPC trace of ^{F}PO/PA/^{F}PA terpolymer



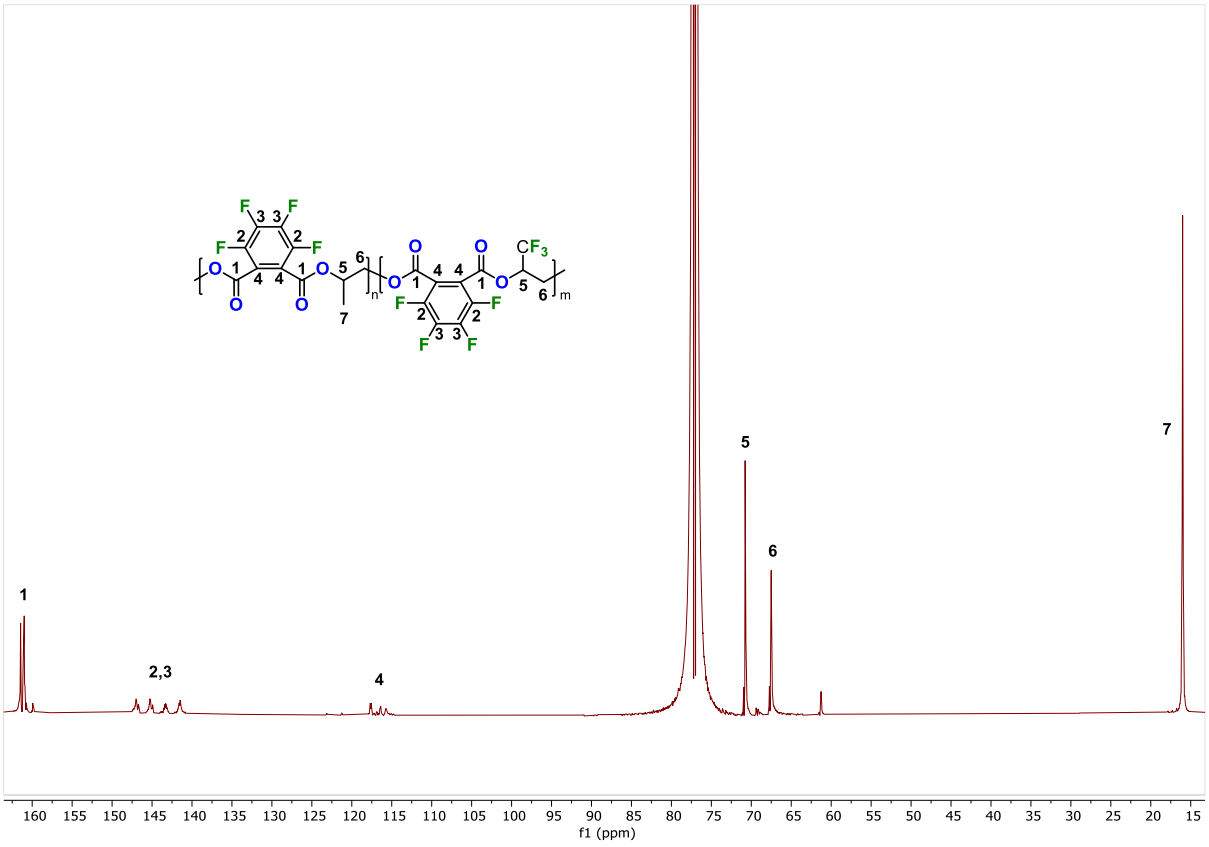
Supplementary Figure 45 – Terpolymerisation of PO/^{F}PO/^{F}PA with 1 C3: 1 PPNCl: 250 ^{F}PO: 250 ^{F}PO: 500 ^{F}PA at 80 °C



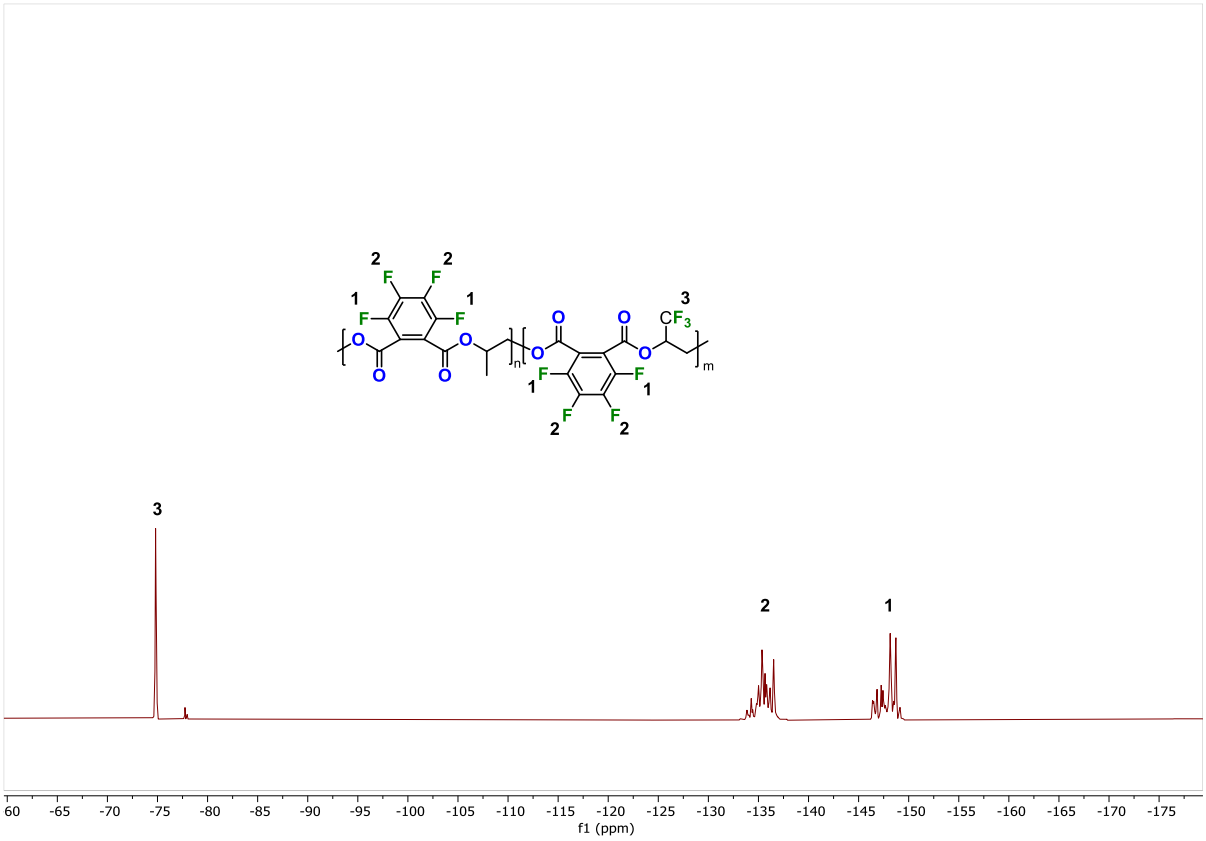
Supplementary Figure 46 - ^{1}H NMR (400 MHz, $CDCl_3$) of aliquots of ^{F}PO/PO/^{F}PA terpolymerisation removed at regular times intervals of 30 minutes



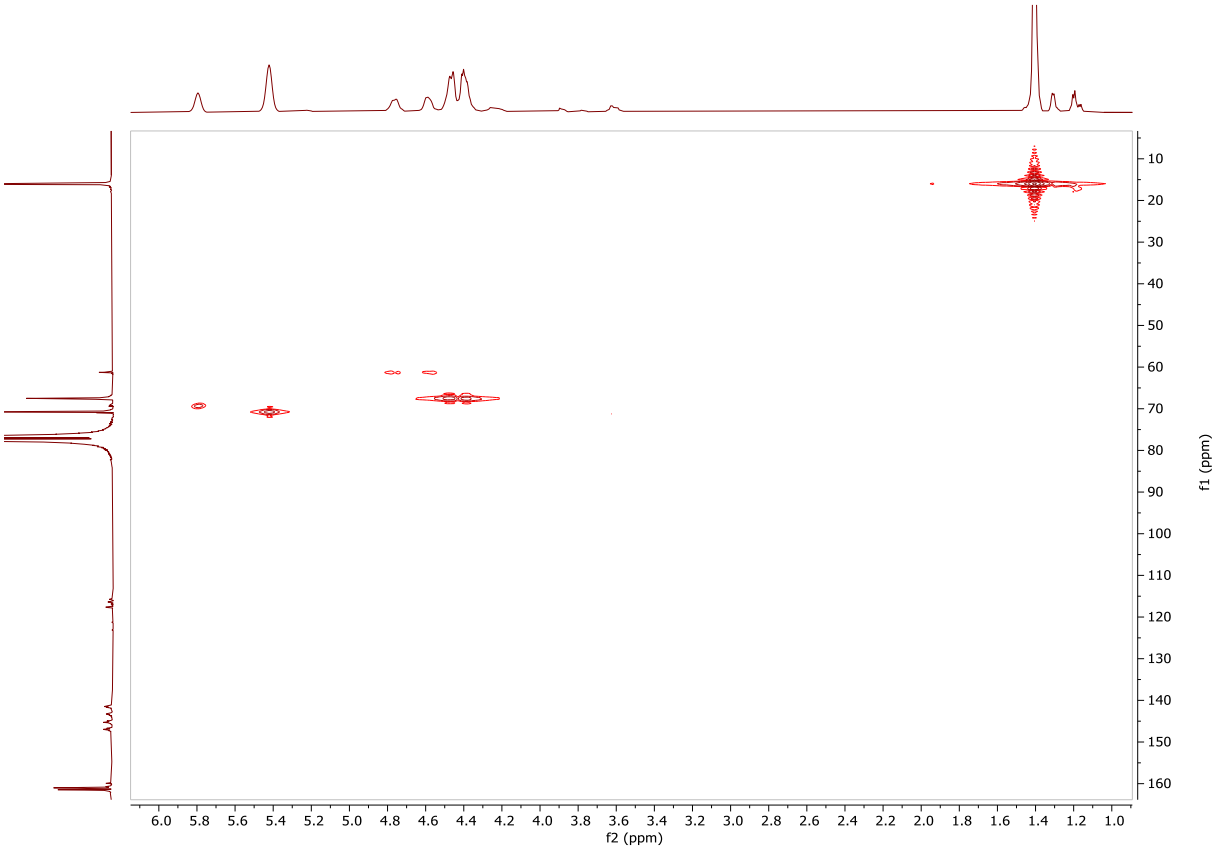
Supplementary Figure 47 - ^{1}H NMR (400 MHz, $CDCl_3$) of PO/^{F}PO/^{F}PA terpolymer, X = Cl, OH



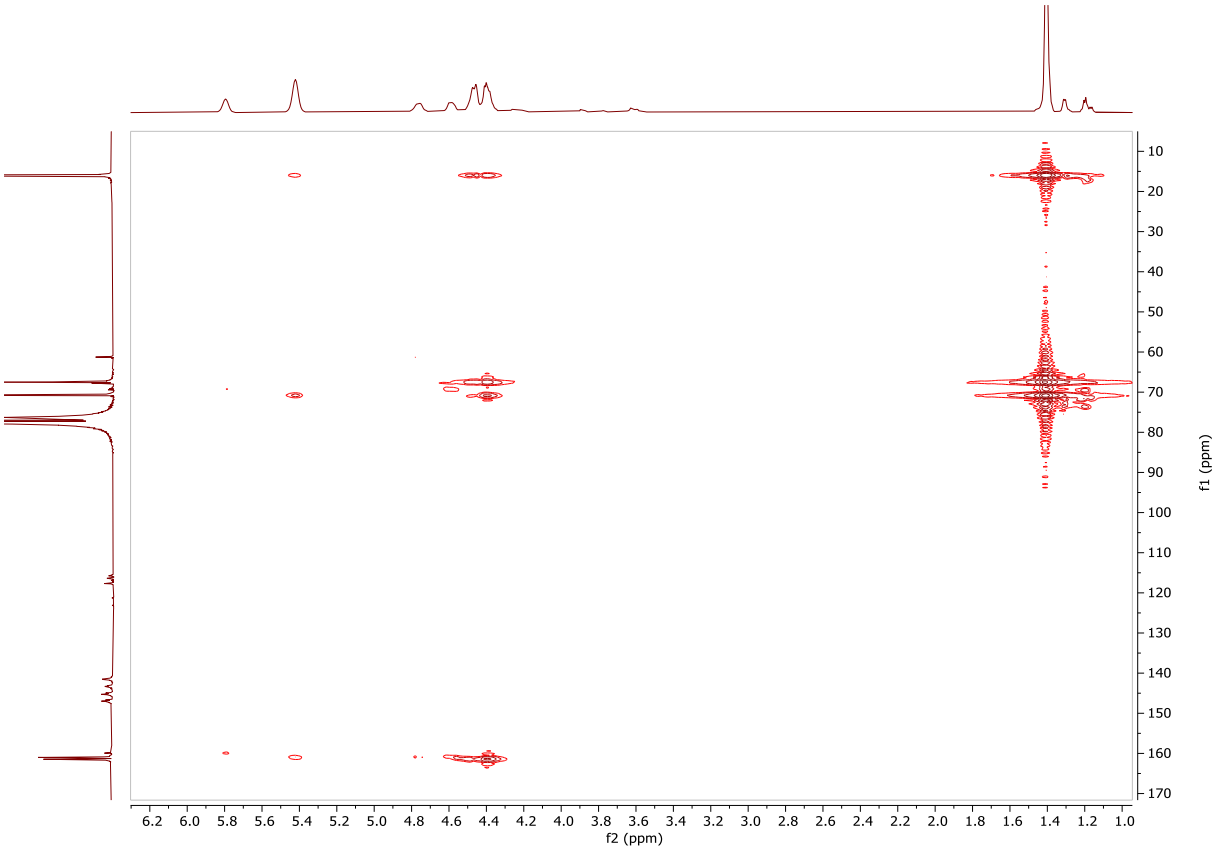
Supplementary Figure 48 - ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of PO/^{F}PO/^{F}PA terpolymer



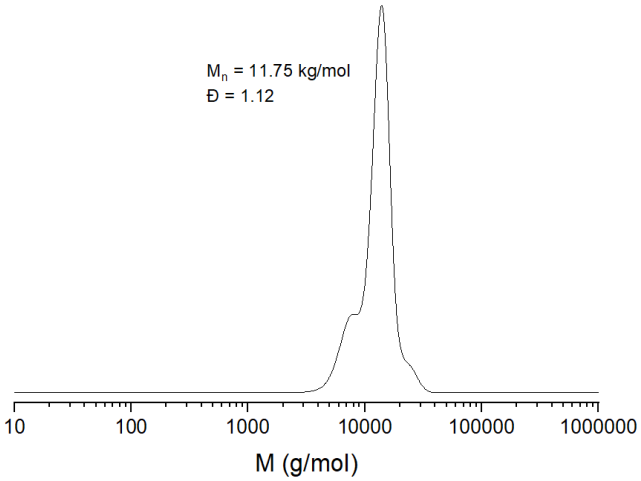
Supplementary Figure 49 - ^{19}F NMR spectrum (376 MHz, $CDCl_3$) of PO/^{F}PO/^{F}PA terpolymer



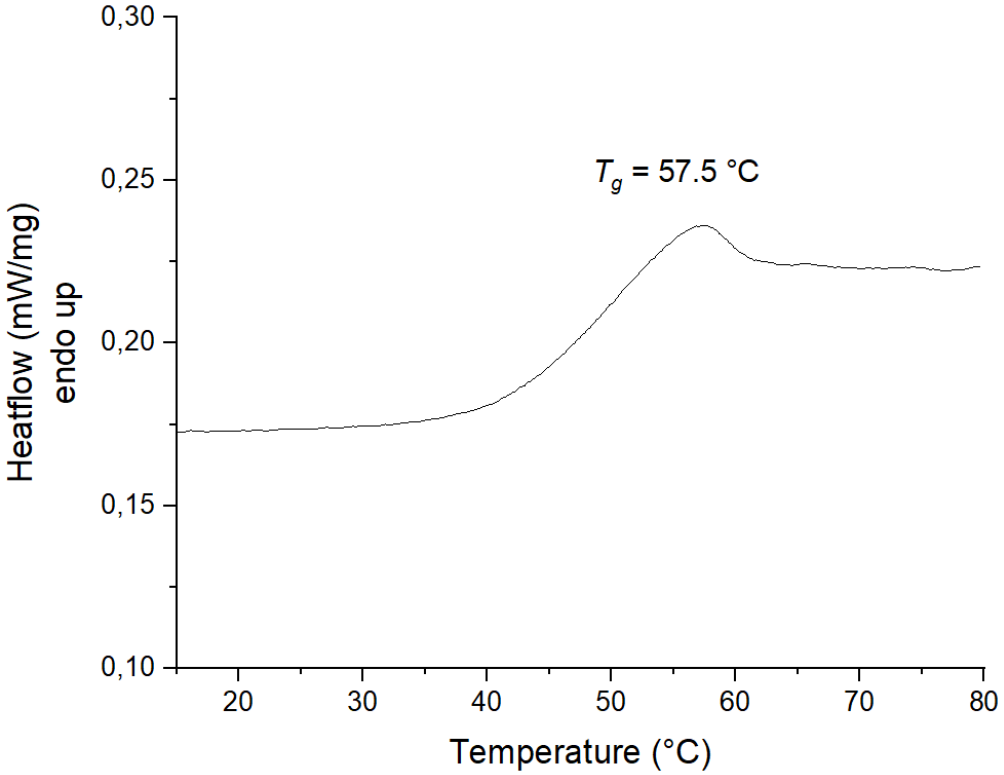
Supplementary Figure 50 - ^{1}H-^{13}C HSQC NMR spectrum ($CDCl_3$) spectrum of the PO/^{F}PO/^{F}PA terpolymer



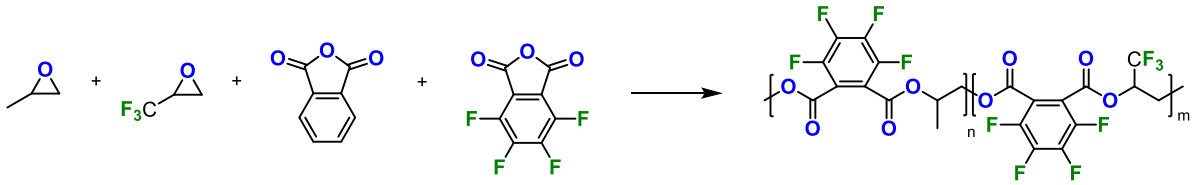
Supplementary Figure 51 - ^{1}H-^{13}C HMBC NMR spectrum ($CDCl_3$) spectrum of the PO/^{F}PO/^{F}PA copolymer



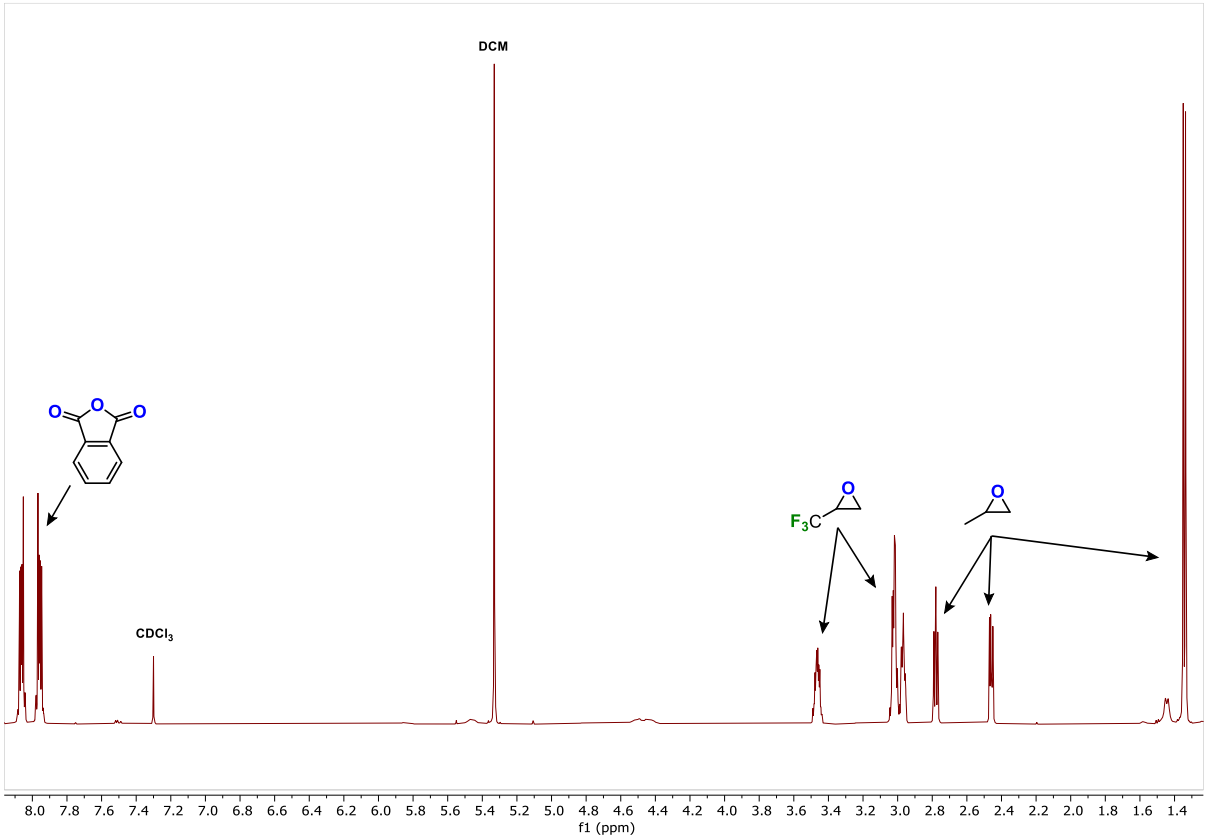
Supplementary Figure 52 – GPC trace for PO/^{F}PO/^{F}PA terpolymer



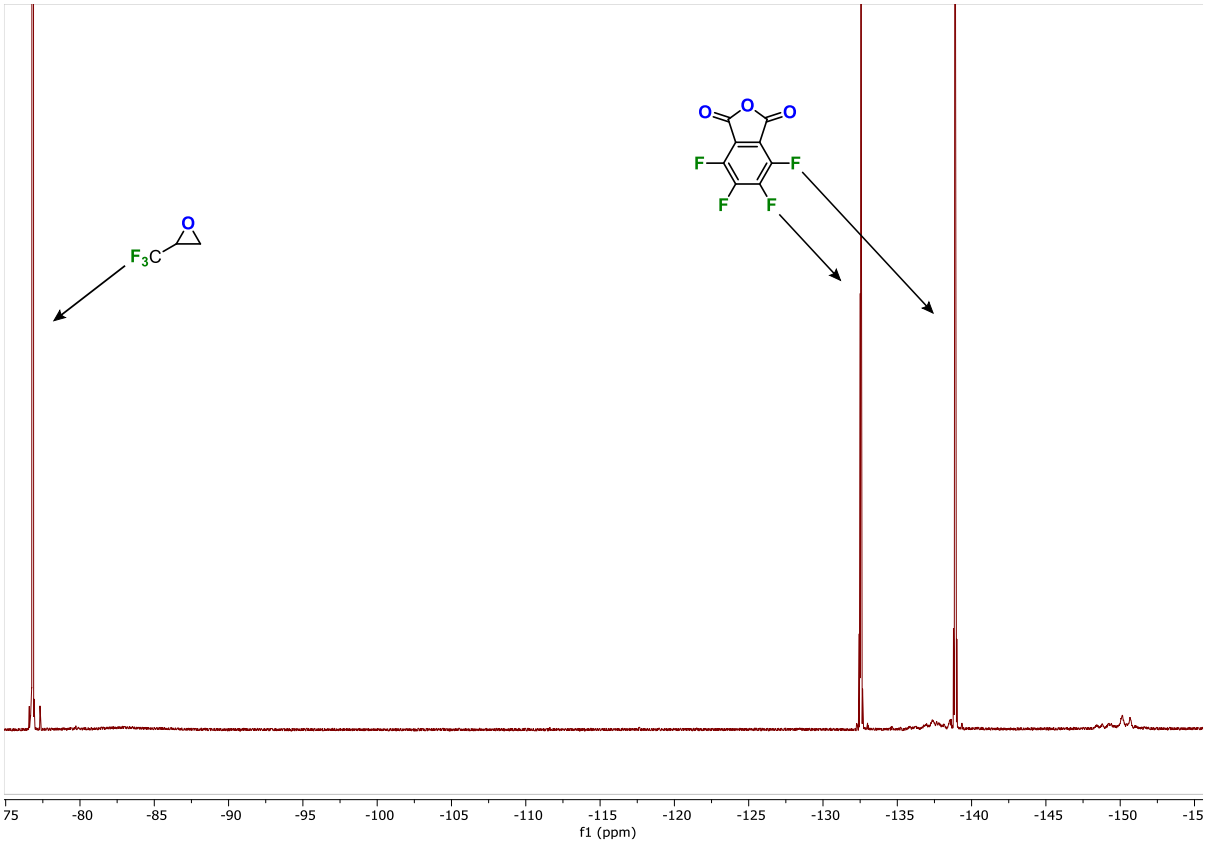
Supplementary Figure 53 - DSC data of the second heating cycle corresponding to PO/^{F}PO/^{F}PA terpolymer



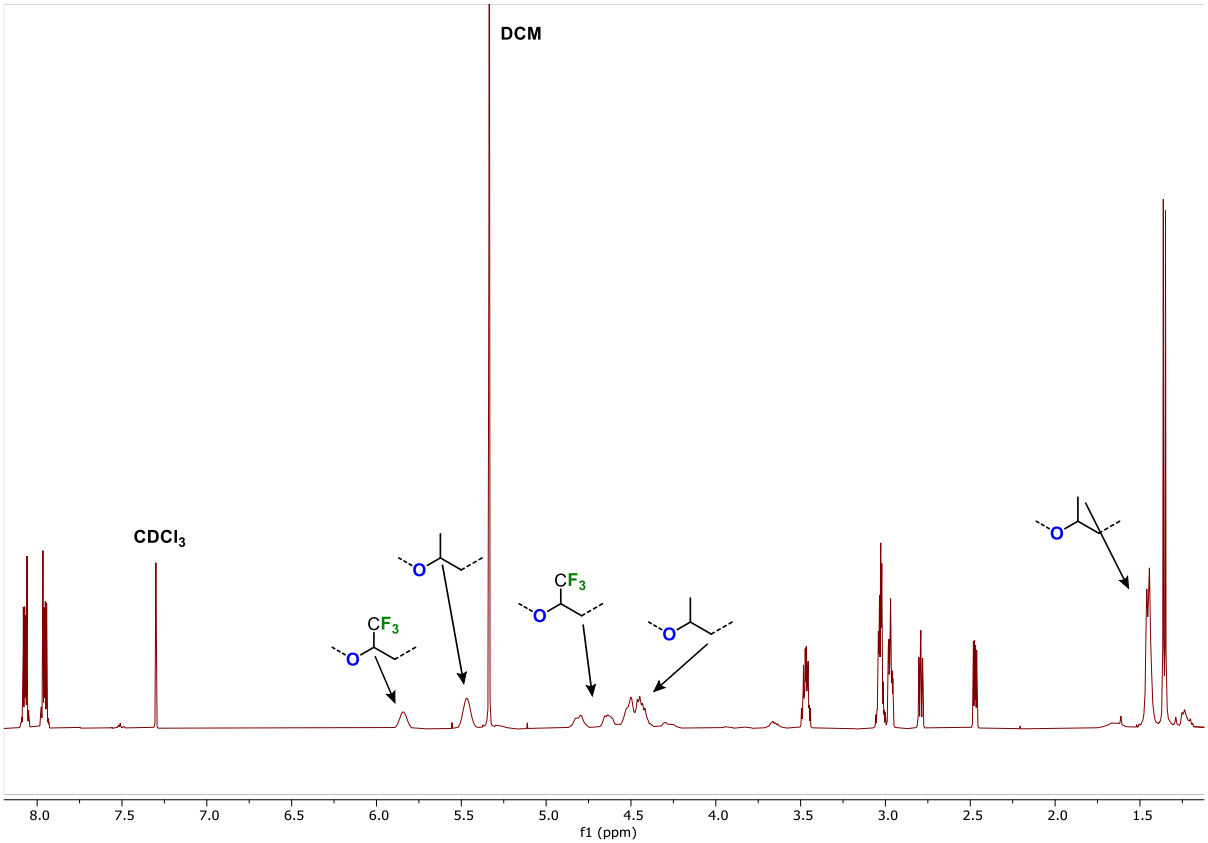
Supplementary Figure 54 – Tetrapolymerisation of PO/^{F}PO/PA/^{F}PA with 1 C3: 1 PPNCl: 250 ^{F}PO: 250 ^{F}PO: 250 PA: 250 ^{F}PA at 80 °C



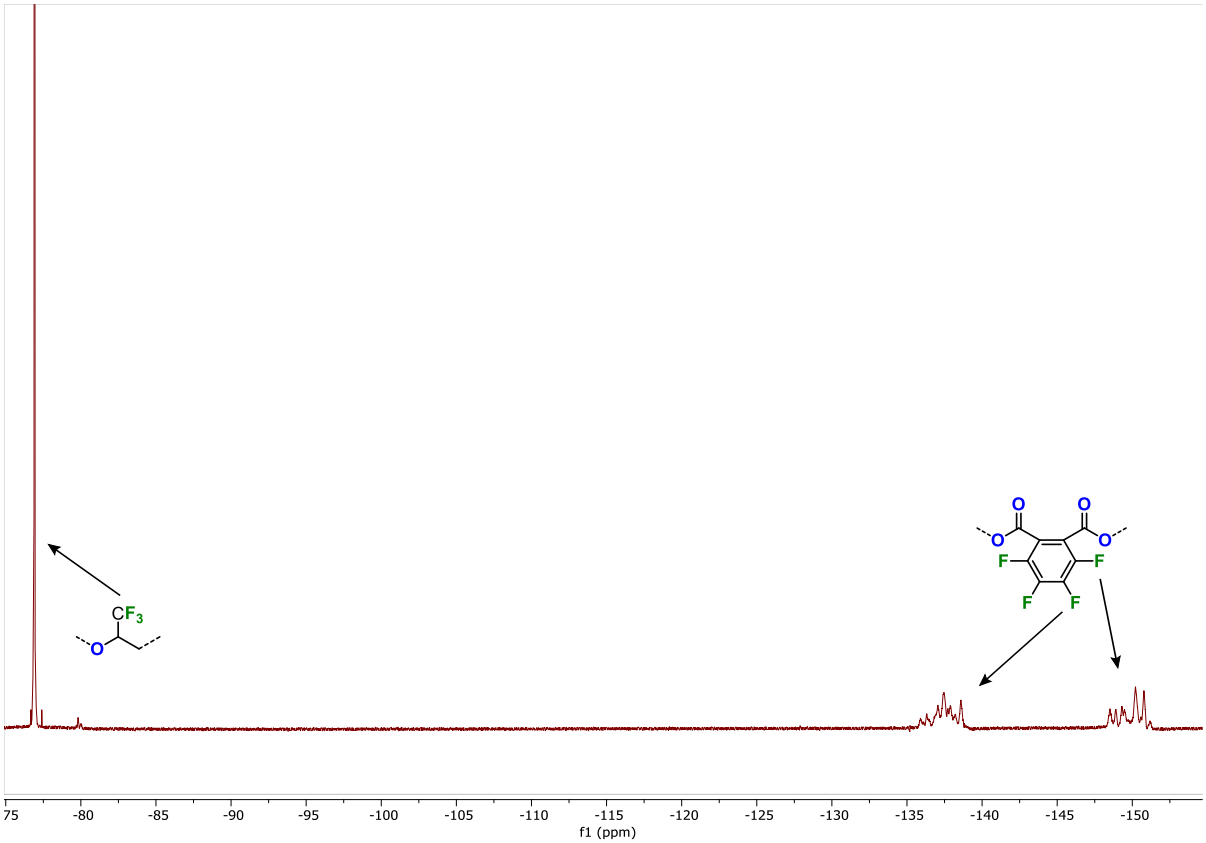
Supplementary Figure 55 - ^{1}H NMR (400 MHz, $CDCl_3$) of tetra-polymerisation after 30 minutes reaction time



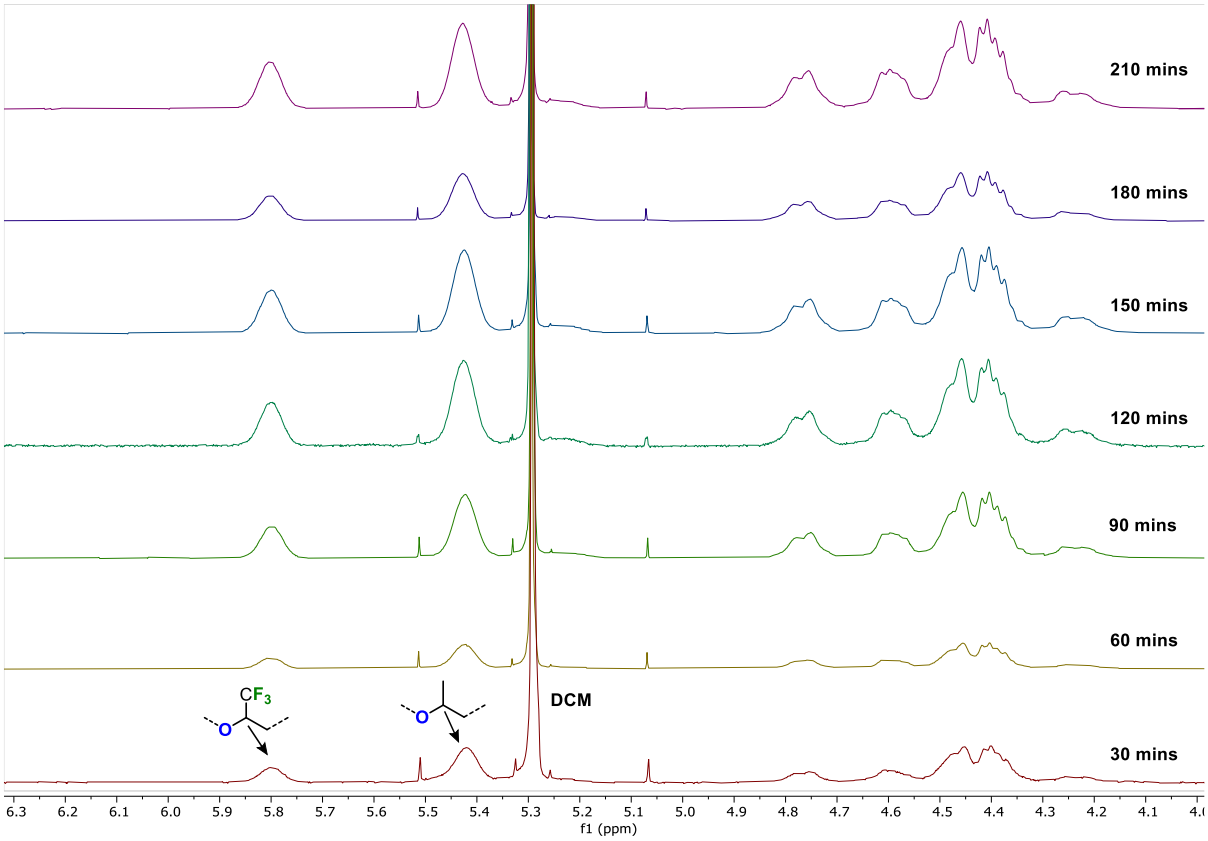
Supplementary Figure 56 - ^{19}F NMR (376 MHz, $CDCl_3$) of tetra-polymerisation after 30 minutes reaction time



Supplementary Figure 57 - ^{1}H NMR (400 MHz, $CDCl_3$) of tetra-polymerisation after 210 minutes reaction time

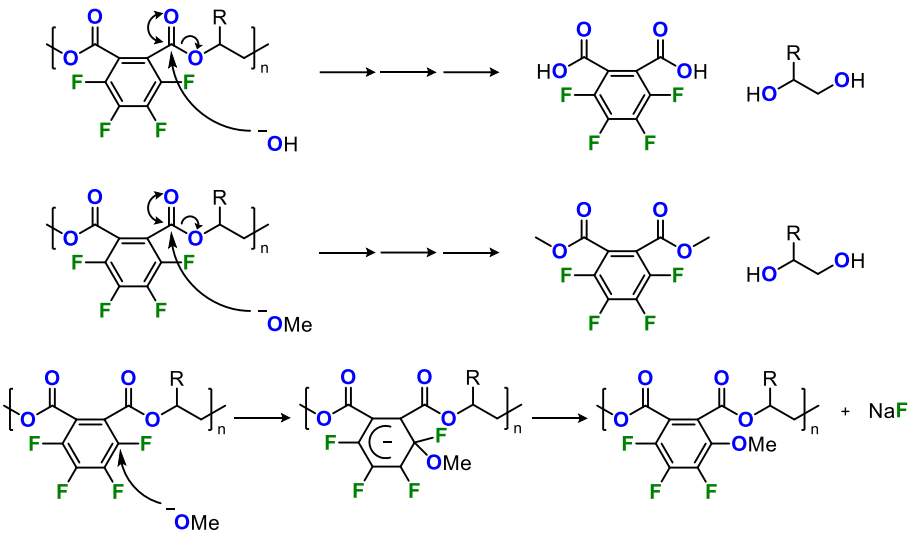


Supplementary Figure 58 - ^{19}F NMR (376 MHz, $CDCl_3$) of tetra-polymerisation after 210 minutes reaction time

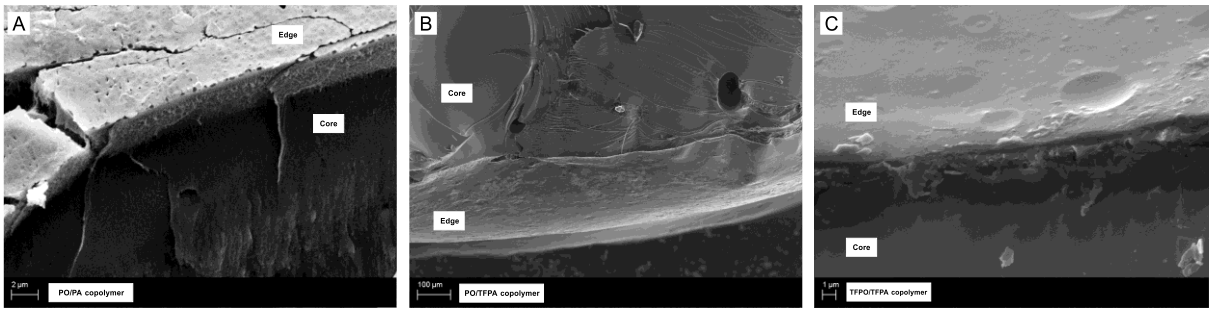


Supplementary Figure 59 - ^{1}H NMR (400 MHz, $CDCl_3$) of aliquots of PO/^{F}PO/PA/^{F}PA tetrapolymerisation removed at regular times intervals of 30 minutes

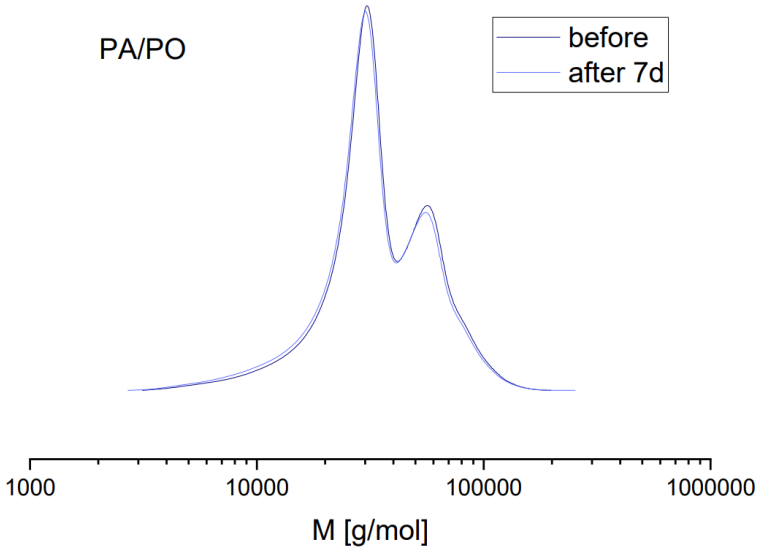
Supplementary Notes 9: Degradation studies



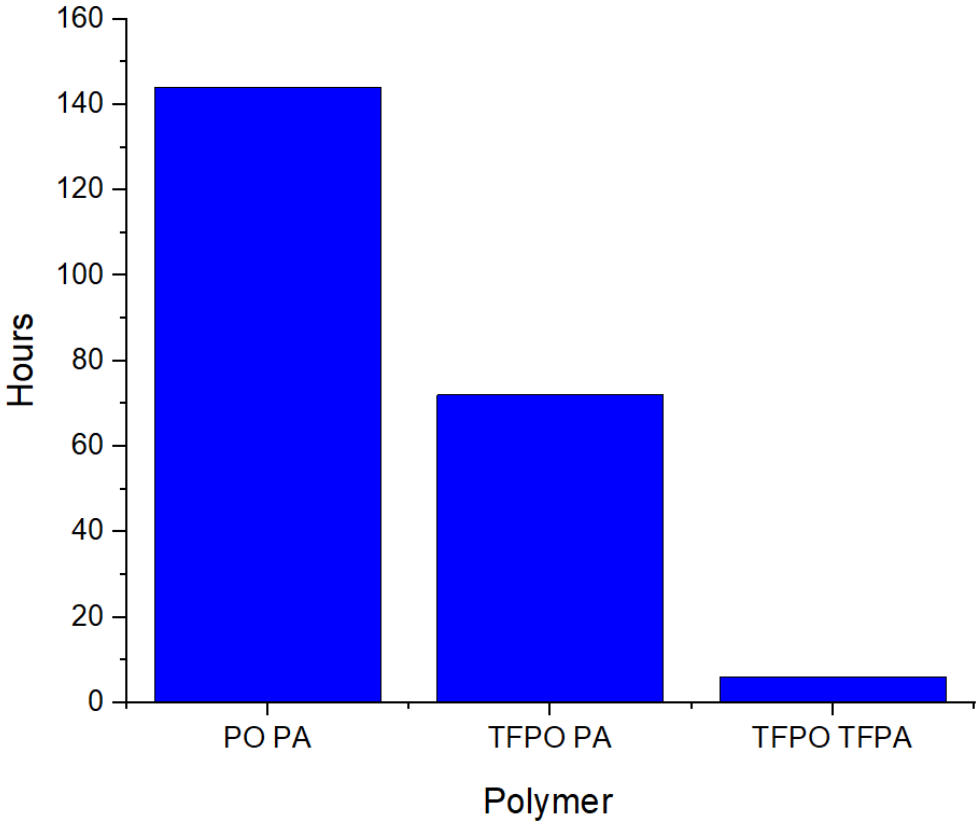
Supplementary Figure 60 - Possible degradation pathways using NaOH and NaOMe



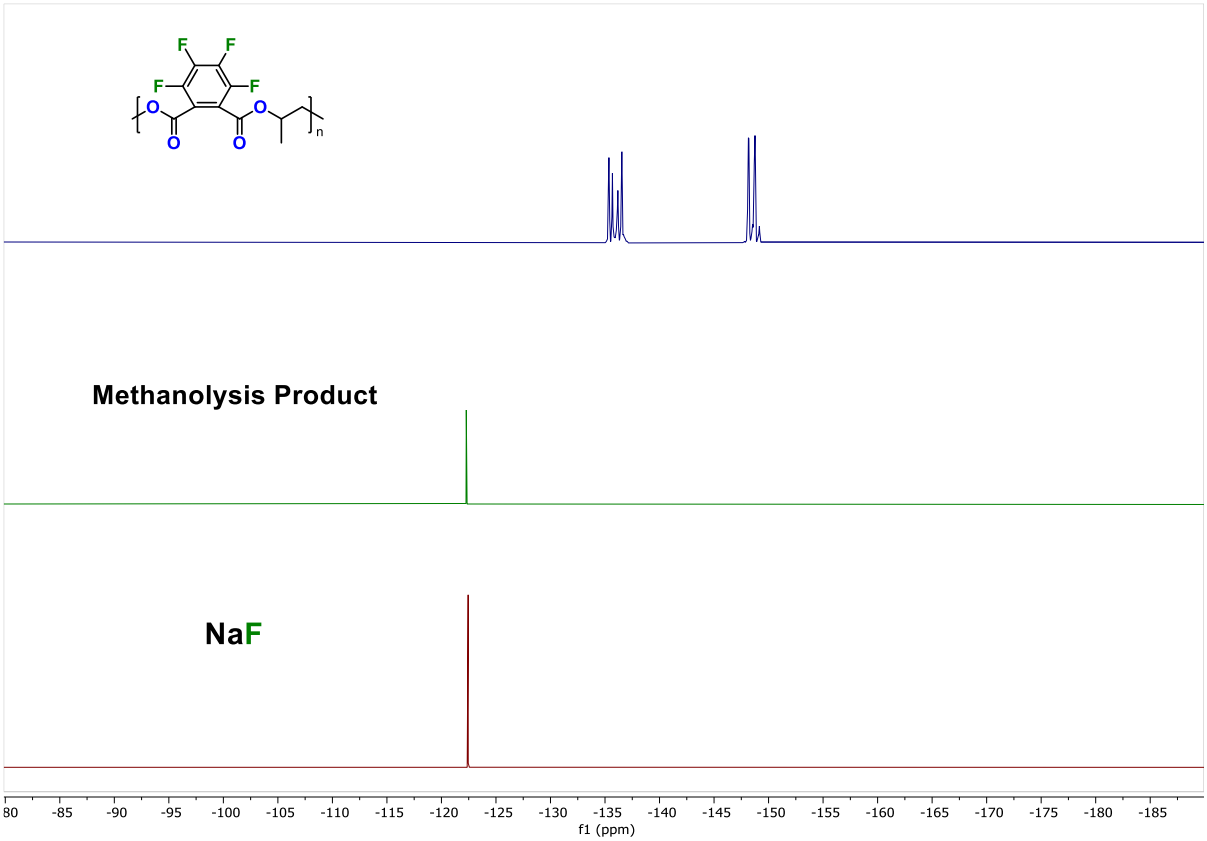
Supplementary Figure 61 - SEM images of cross-section of polymer films after degradation in 5 wt.% NaOH 6:4 EtOH:H_2O hydrolysis solution at 40 °C.



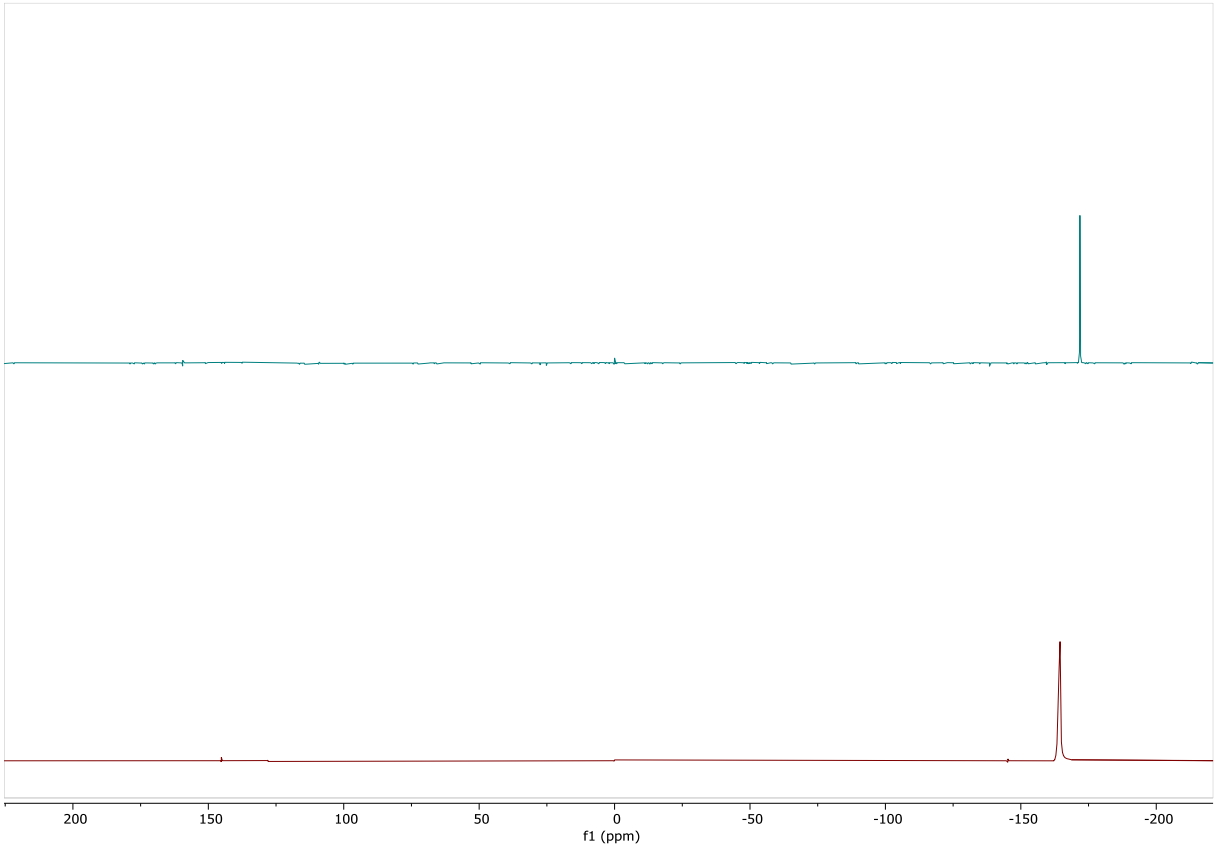
Supplementary Figure 62 – GPC trace showing film of PO/PA copolymer before degradation and after 7 days in basic 5 wt.% NaOH 6:4 EtOH:H_2O hydrolysis solution



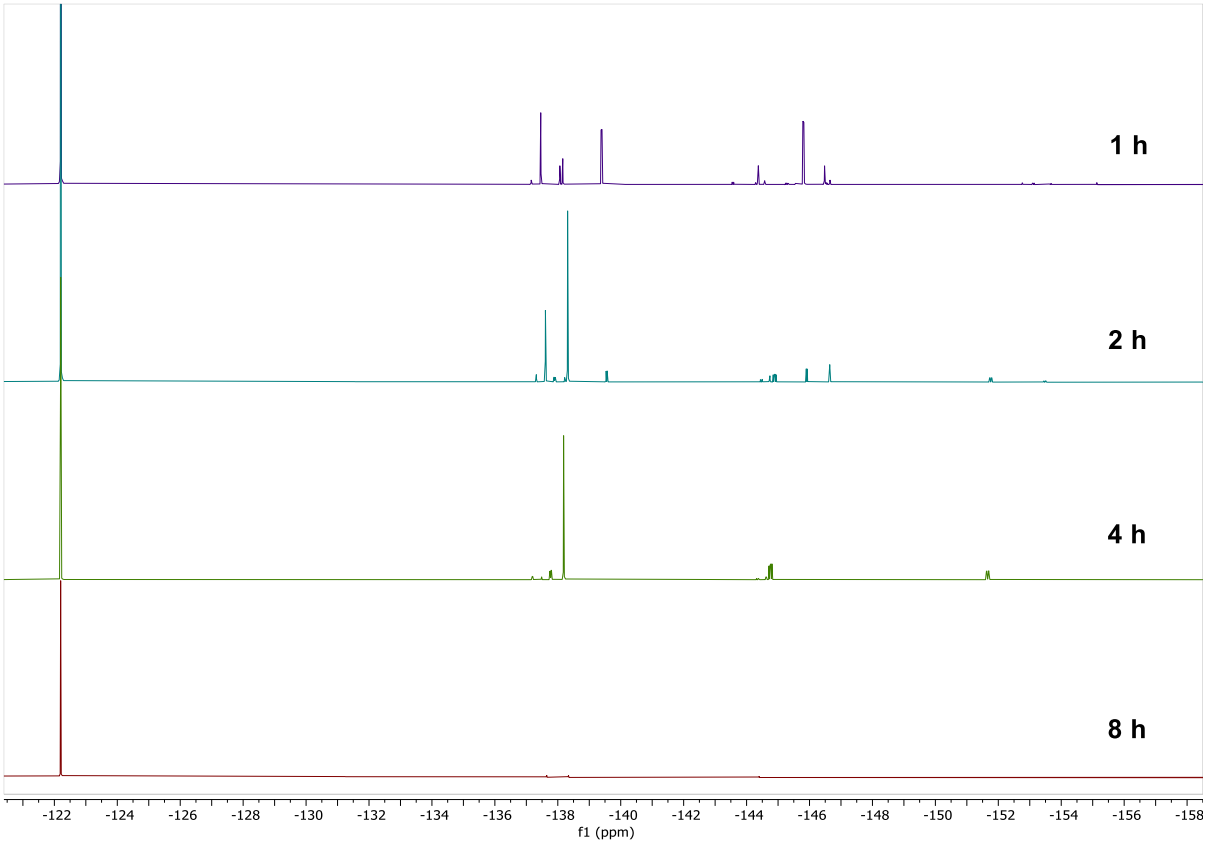
Supplementary Figure 63 – Bar chart comparing the different polymers' hydrolysis degradation times in the 6:4 EtOH:H_2O 5 wt.% NaOH solution



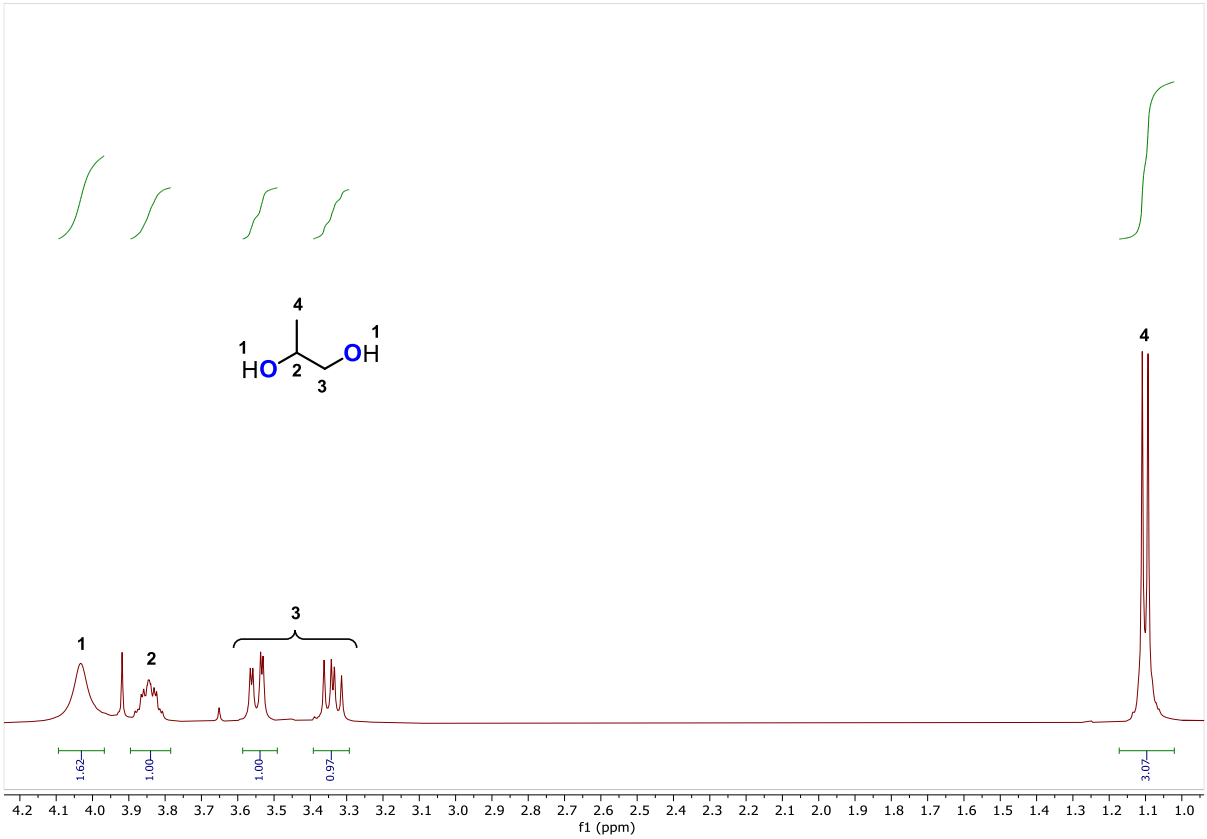
Supplementary Figure 64 – ^{19}F NMR (376 Hz) of PO/TFPA copolymer in $CDCl_3$ (top), crude product after methanolysis in D_2O (middle) and NaF in D_2O



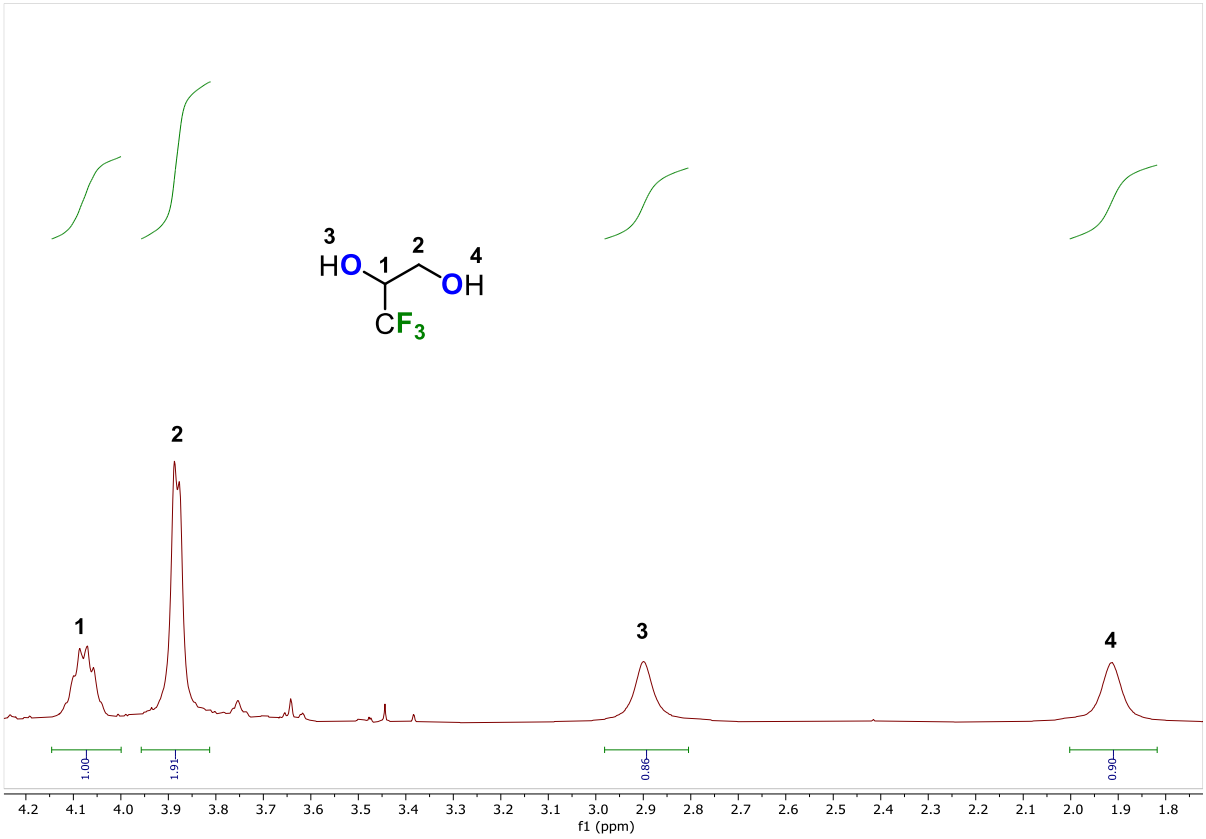
Supplementary Figure 65 - ^{19}F-NMR (376 Hz, Pyridine-d5) of; HF-Py from reaction of methanolysis product with H_2SO_4 (top) and Olah's reagent as a reference (bottom)



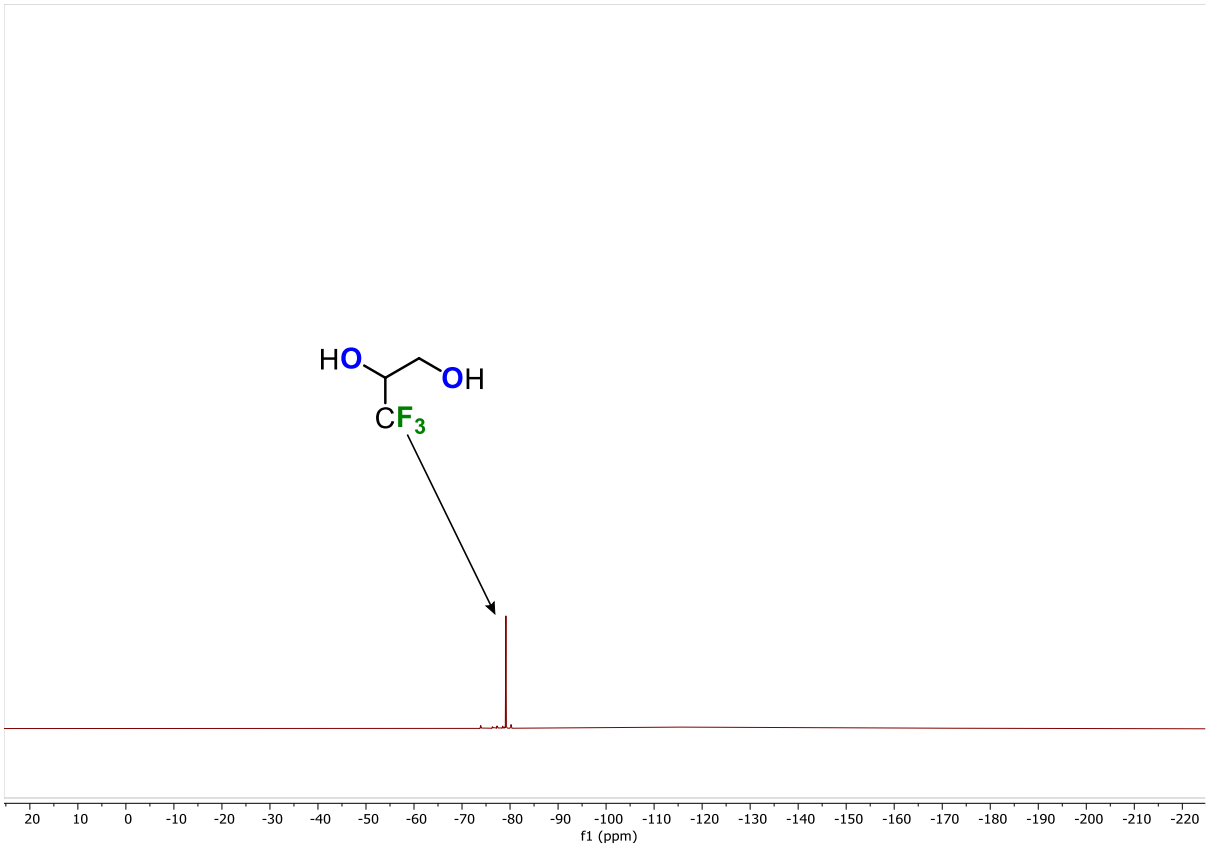
Supplementary Figure 66 - ^{19}F-NMR (376 Hz, $CDCl_3$) of the crude methanolysis product of the PO/^{F}PA copolymer over time showing disappearance of aromatic fluorine atoms



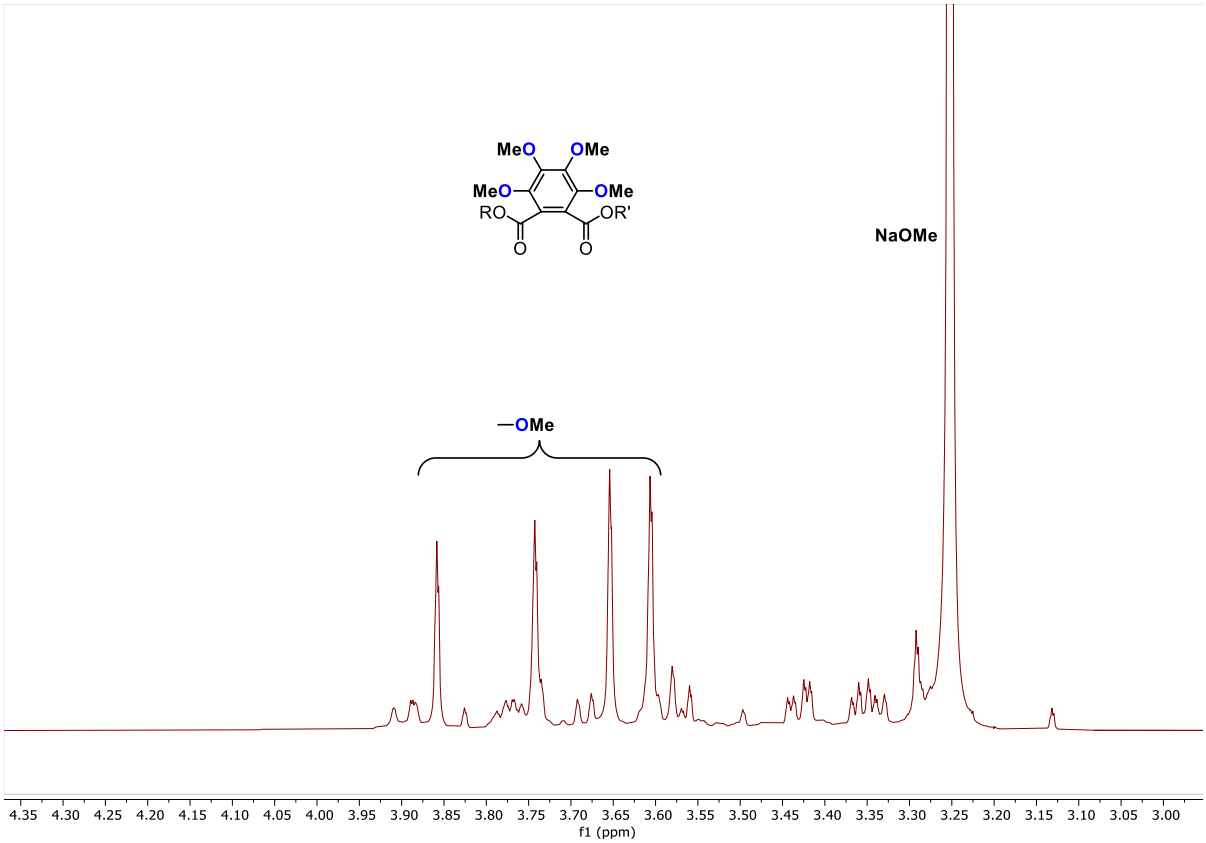
Supplementary Figure 67 – ^{1}H-NMR (400 Hz, $CDCl_3$) of the distillation product from the crude methanolysis of the PO/^{F}PA copolymer



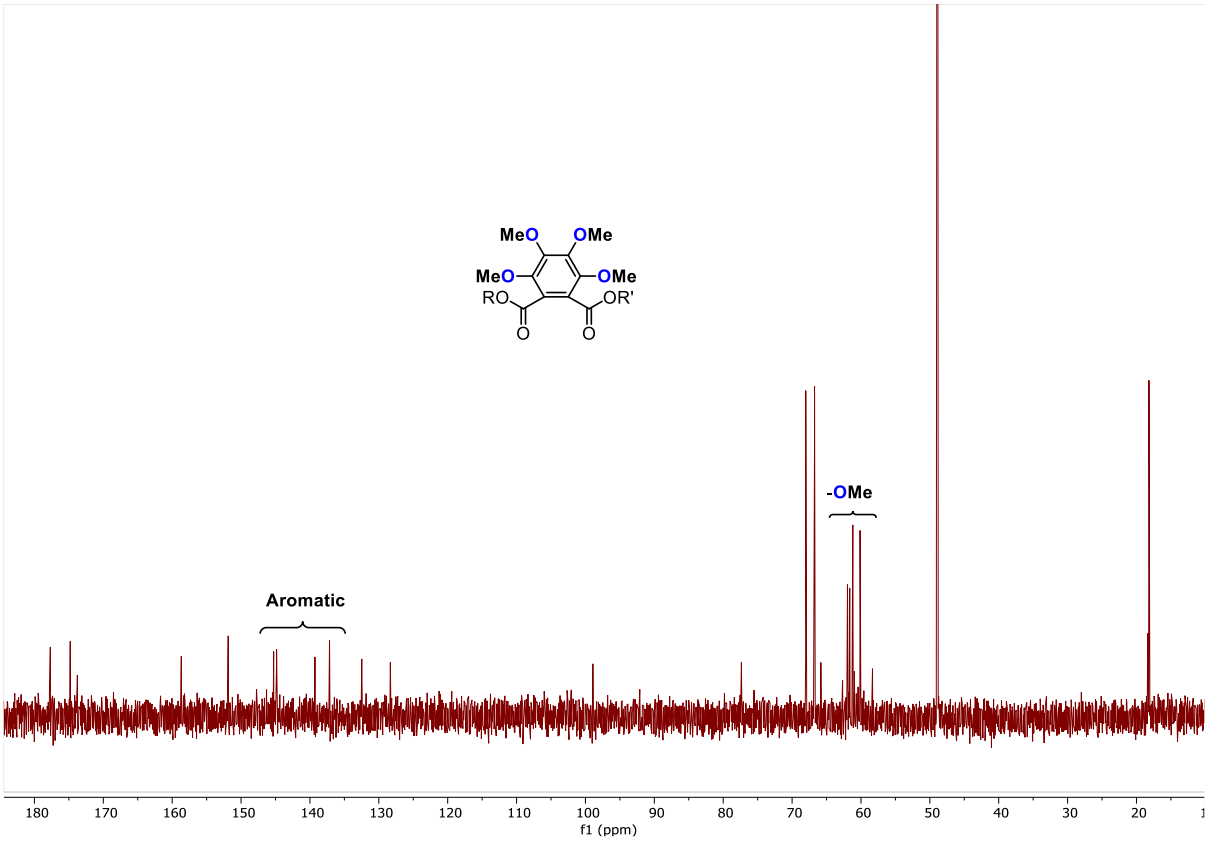
Supplementary Figure 68 - ^{1}H-NMR (400 Hz, $CDCl_3$) of the distillation product from the crude methanolysis of the ^{F}PO/^{F}PA copolymer



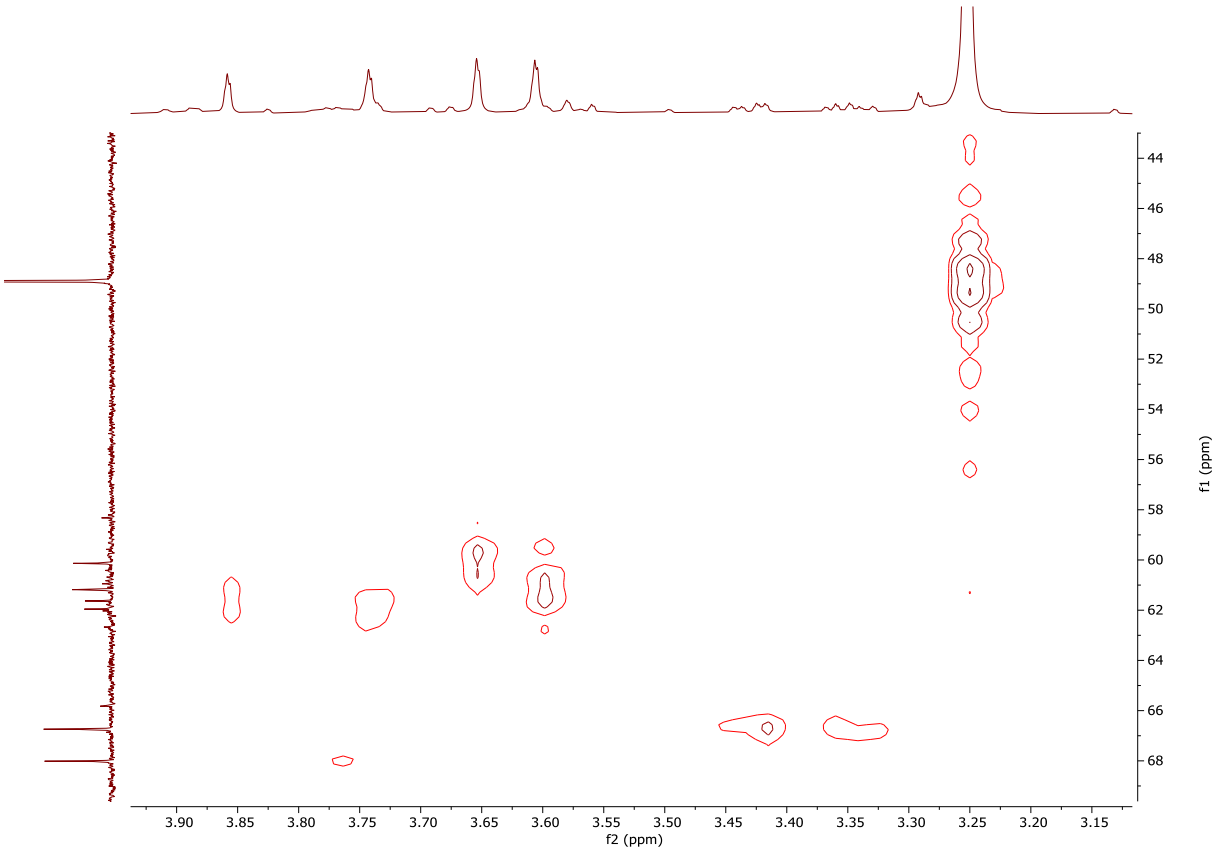
Supplementary Figure 69 – ^{19}F-NMR (376 Hz, $CDCl_3$) of the distillation product from the crude methanolysis of the ^{F}PO/^{F}PA copolymer



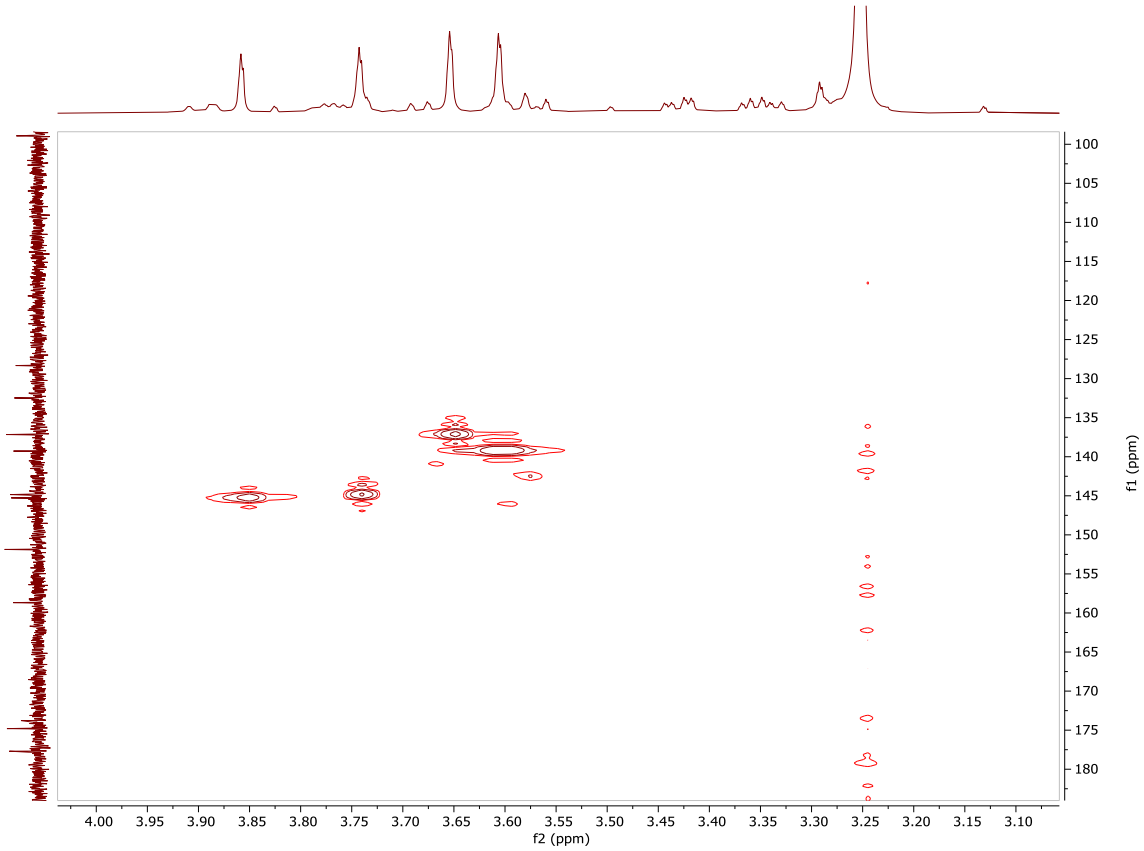
Supplementary Figure 70 - ^{1}H-NMR (400 Hz, $CDCl_3$) of the precipitate from the crude methanolysis of the PO/^{F}PA copolymer. R, R' = H, Na, Me



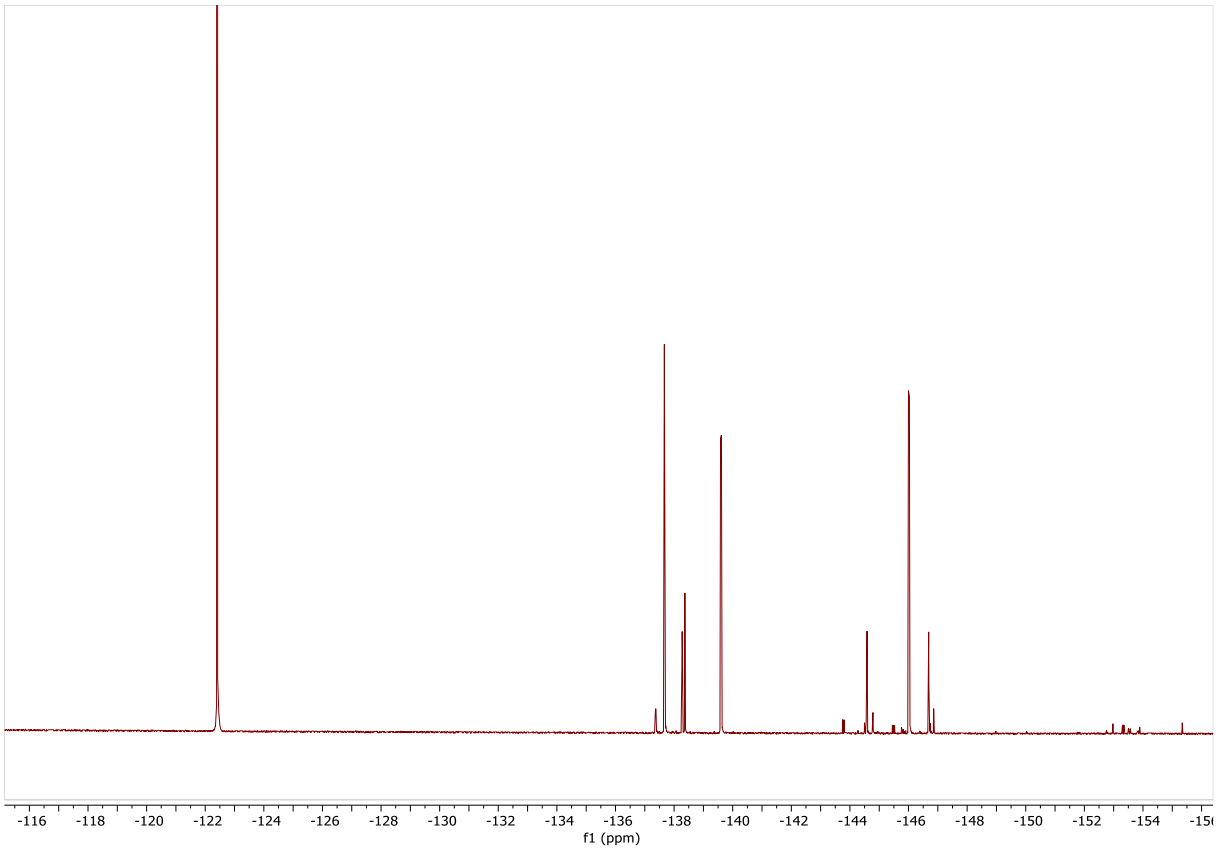
Supplementary Figure 71 - ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of the precipitate from the crude methanolysis of the PO/^{F}PA copolymer. R, R' = H, Na, Me



Supplementary Figure 72 - ^{1}H-^{13}C HSQC NMR spectrum ($CDCl_3$) spectrum of the crude methanolysis product



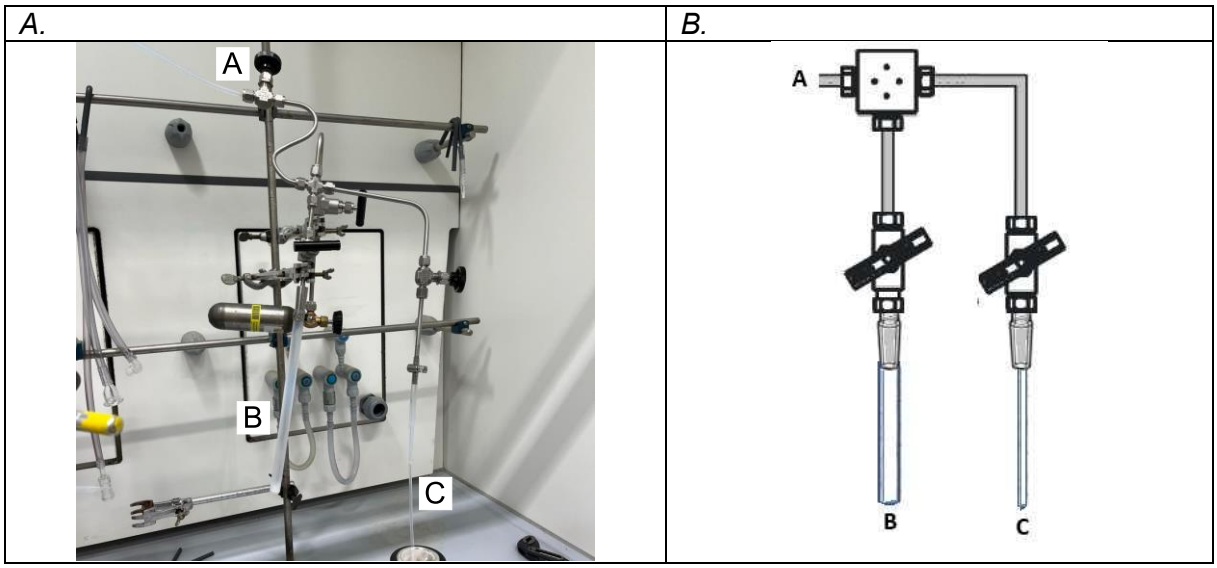
Supplementary Figure 73 - ^{1}H-^{13}C HMBC NMR spectrum ($CDCl_3$) spectrum of the crude methanolysis product



Supplementary Figure 74 - ^{19}F-NMR (376 Hz, $CDCl_3$) of methanolysis solution with PO/^{F}PA copolymer after 1 hour of heating at 110 °C showing de-symmetrisation of the aromatic fluorine backbone.

HF experiments were performed under rigorous conditions using classical Schlenk techniques in a custom made stainless-steel line equipped with Swagelock and FITOK valves connected to a normal Schlenk line set up (see supplementary figure **71**). The reaction was performed in a Perfluoroalkoxy alkane (PFA) tube (8 mm diameter). Analysis of the Olah's reagent (^{19}F NMR) was achieved via a sealed PFA tube (1 mm diameter) inserted into a normal glass NMR tube.

! : Extreme caution is required for the generation & handling of HF as well as the generation of Olah's reagent (strongly exothermic)



Supplementary Figure 75 - A. Picture of the equipment B. Diagram of set-up; (A) Toward vacuum, (C) 8 mm PFA reaction tube, (D) 1 mm PFA NMR tube.

Generation of hydrogen fluoride (HF) and Olah's reagent (HF-Py)

Under argon, sulfuric acid (H_2SO_4, 1.4 ml) was added to a (8 mm diameter) PFA tube. The tube was frozen (using liquid nitrogen) and the polymer degradation product (200 mg) was added in one portion under argon flux. Freeze-Pump-Thaw (FTP) degassing of the reaction medium was done. (Note: during the warming process, the reaction between sulfuric acid and the polymer degradation product occurs rapidly, forming a bubbling yellow solution). The reaction was gently heated to 100 °C until no further bubbling was observed. (Note: solution went from light yellow to dark brown).

Volatile HF (bp: 19.5 °C) from the crude reaction mixture was then vacuum transferred to a 1 mm PFA tube containing 0.3 mL of degassed pyridine-d5, which was cooled down to –30 °C to ensure a controlled formation of the Olah's reagent. The tube was frozen, evacuated and sealed. ^{19}F NMR (see supplementary figure **62**) shows the formation of the Olah's reagent.

Supplementary Notes 10: AFM Results

All atomic force microscopy (AFM) measurements were performed with a MFP3D (Oxford Instruments, UK). For tapping mode images, a PPP-NCHR (NANOSENSORS, Switzerland) probe was used with a drive frequency of 321 kHz and a tip radius of <10 nm. For force measurements a probe with a tip radius of 300 nm and a spring constant of 46 N/m was used.

Film thickness of individual samples was assessed by topography measurements of a film-substrate step. Surface roughness was calculated by the standard deviation of the mean surface height of a 12 µm x 12 µm surface area.

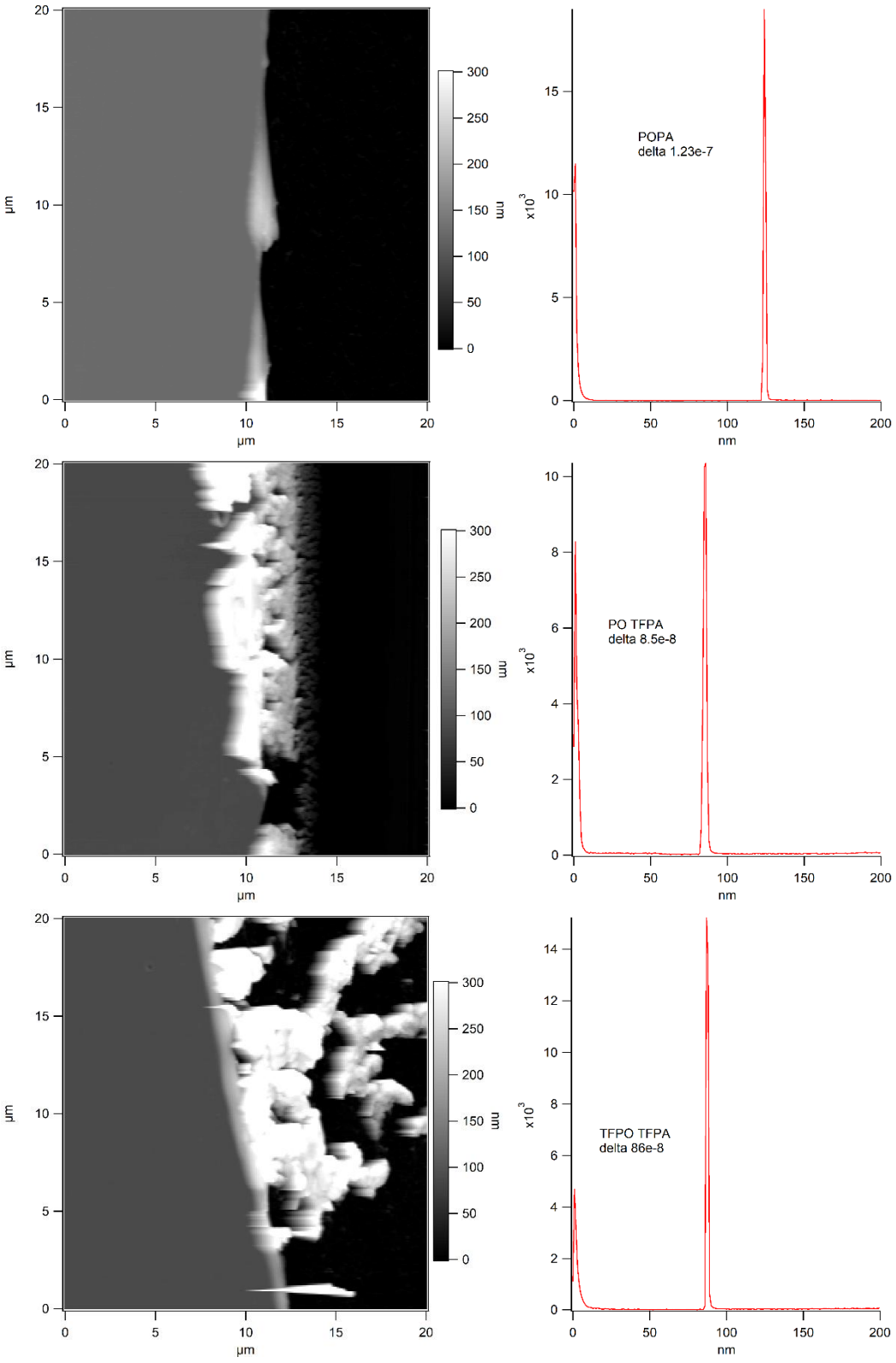
Stiffness and adhesion/attraction force for each sample was estimated from averaged force distance curves (FDC, 12 x 12 points on a 12 µm x 12 µm surface area). FDCs were recorded with a frequency of 1 Hz and a maximum applied force of F_{max} = 4.6 µN. Glass substrates were measured in the same manner for reference.

For friction measurements lateral bending of trace and retrace of the AFM cantilever was recorded during contact mode scans (setpoint 14 nN, 128x128 points on a 1 µm x 1 µm area, scan rate 1 Hz, scan direction 270°). Since torsional modulus of the cantilever is not known we present the l-b signal of the AFM photodiode in mV, which is proportional to the cantilever bending.

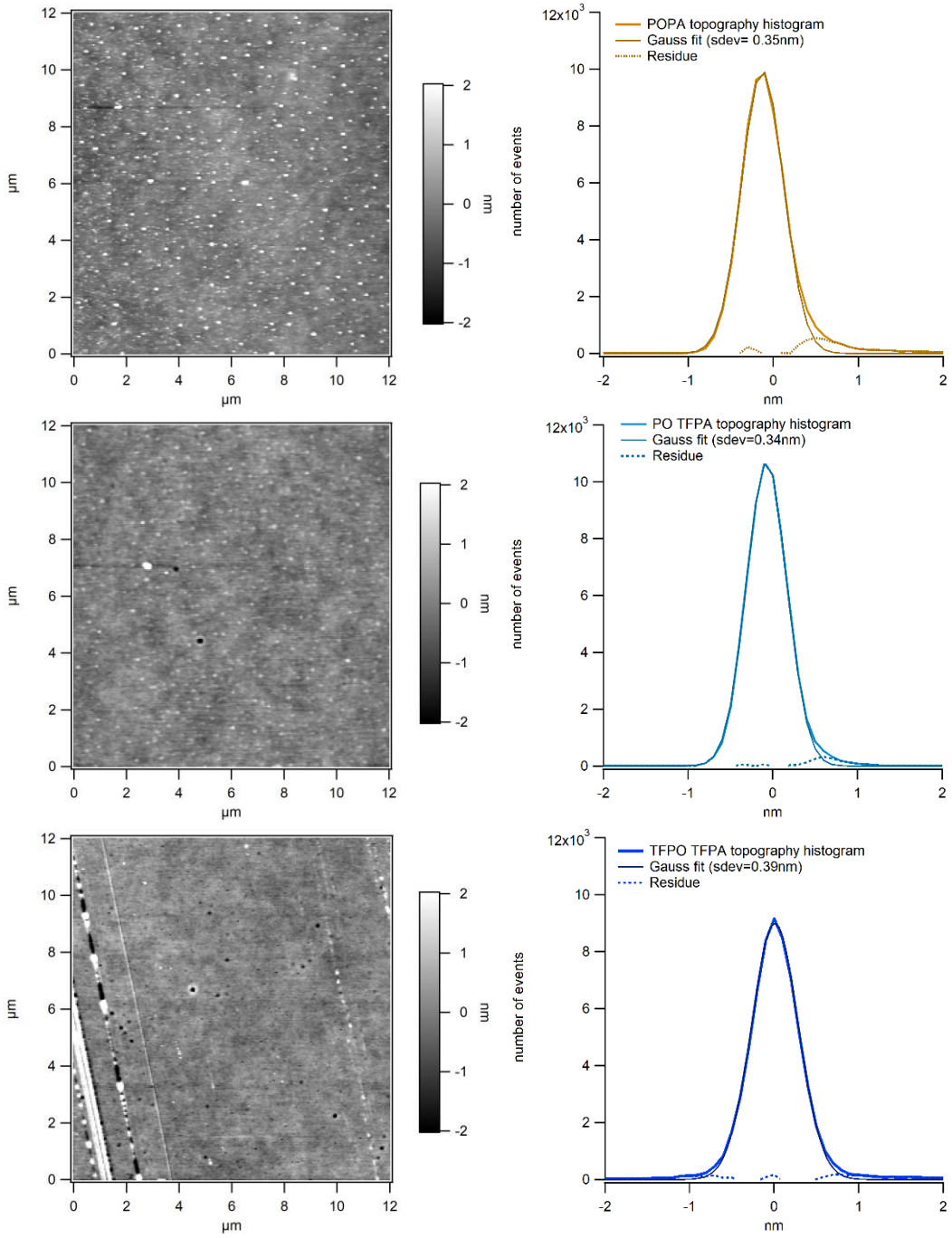
Results:

Sample	thickness t [nm]	roughness r [nm]	attractive force F_{attr}[nN]	Adhesion force F_{adh}[nN]	Plastic deformation D_{pla}[nm]	reduced Modulus E^*[GPa]	lateral deflection δ_{lat}[mV]
PO/PA	123	±0.35*	50	139	5.72	7.4	33.3
PO/^{F}PA	85	±0.34*	41	128	6.95	6.2	33.5
^{F}PO/^{F}PA	86	±0.39	38	111	7.07	5.9	40.3
Reference glass	-	-	62	76	1.33	70	8.0

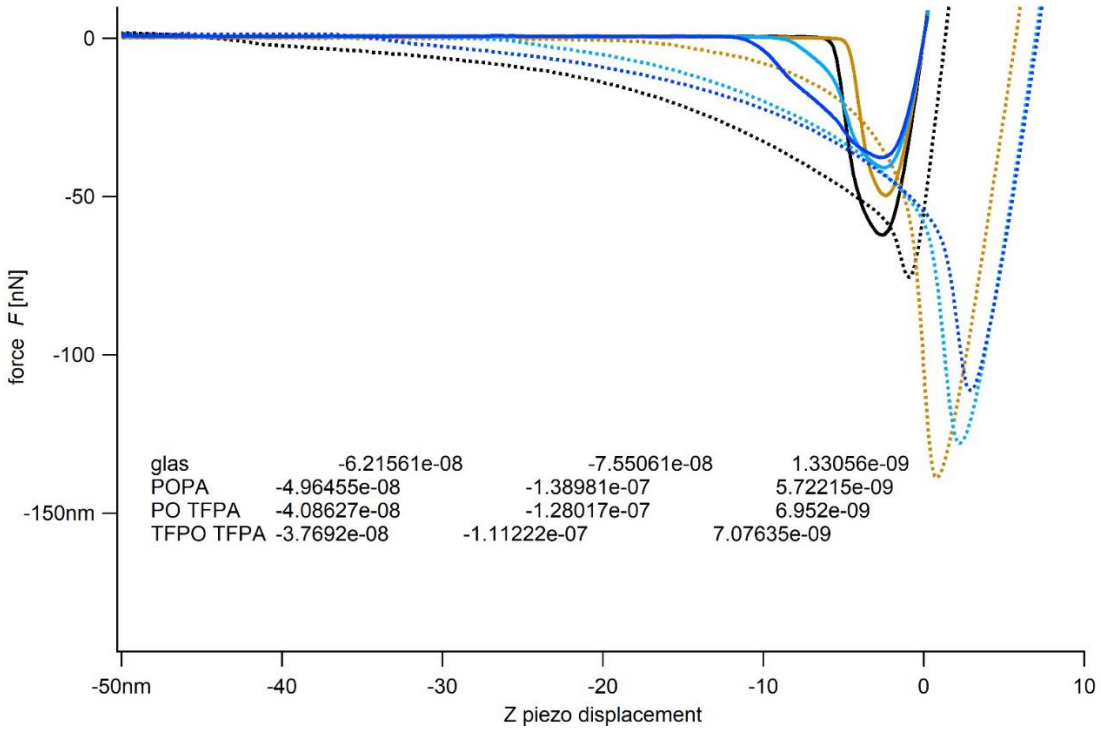
Table S 2 - Comparison of AFM results for thin films of PO/PA, PO/^{F}PA and ^{F}PO/^{F}PA



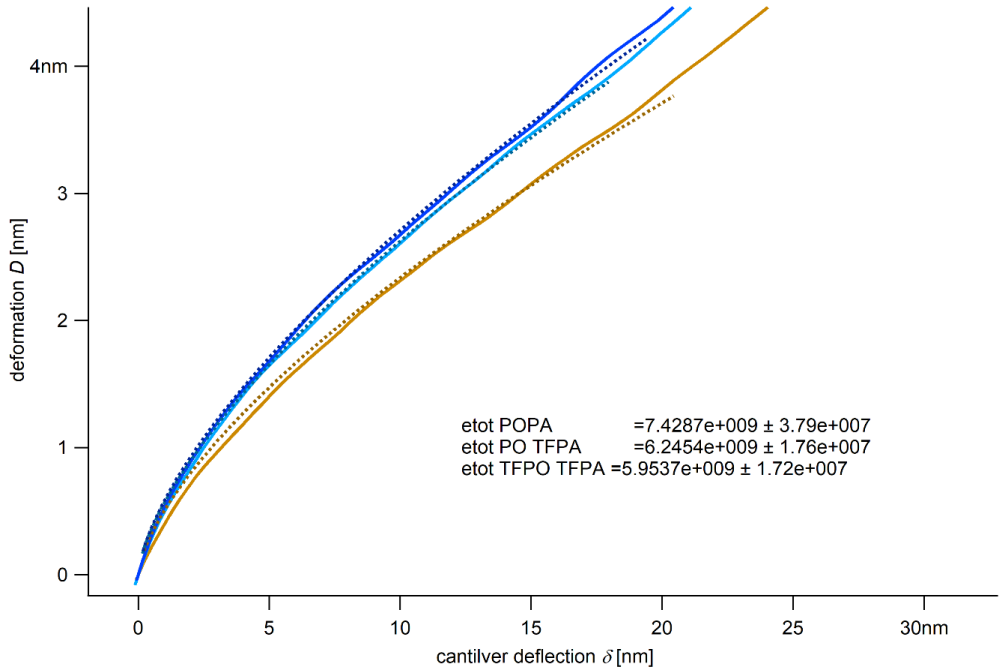
Supplementary Figure 76 - left AFM tapping mode topography of film/substrate step (20 µm x 20 µm, 256 x 256 points); right topography histogram peak delta equals film thickness.



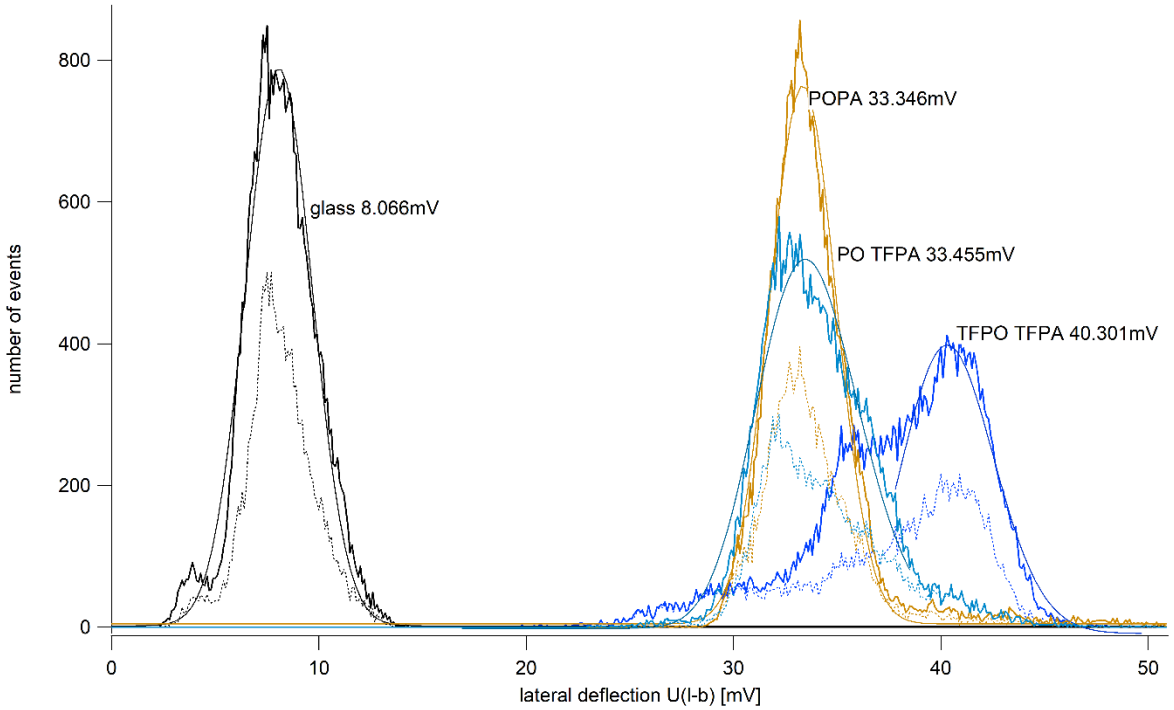
Supplementary Figure 77 - left AFM tapping mode topography of film (12 µm x 12 µm, 256 x 256 points); right topography histogram peak with gaussian fit, standard deviation equals roughness. PO/PA and PO/TFPA show small features droplet like features on the films surface. Those features are evident in the histogram as the part which cannot covered by the gaussian fit (see residue). Stripes in the Film of TFPO/TFPA are scratches from handling and do not influence the main peak shown on the right side.



Supplementary Figure 78 – 12 x 12 AFM Force distance curves were averaged for each sample. The attractive regime of approach curve (solid lines) and retract (dotted lines) is shown. Please note that attractive forces are measured by deflection of the cantilever towards the sample, which is defined negative. For the maximum forces F_{attr} (approach) and F_{adh}(retract) we take the absolute value. The plastic deformation is the difference of Z displacement between approach and retract curve.



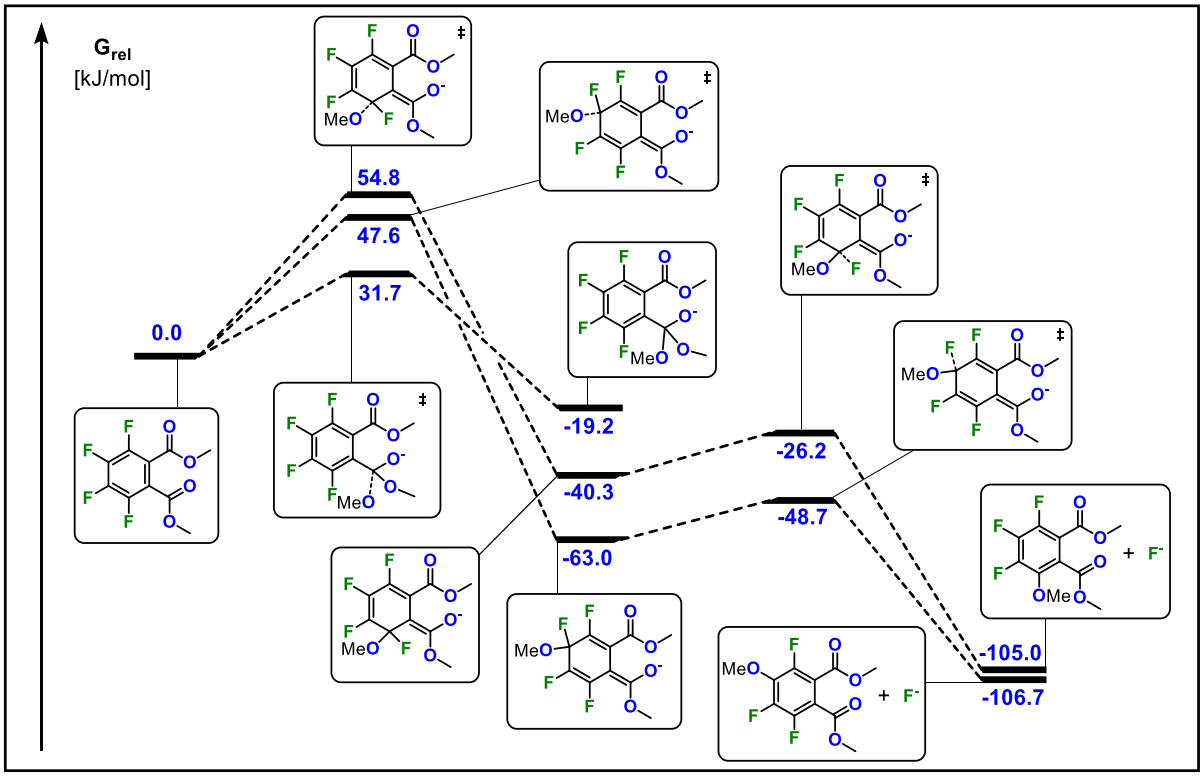
Supplementary Figure 79 – 12 x 12 AFM Force distance curves were averaged for each sample. The contact regime of the approach curves (solid lines) are shown. Maximum considered deformation is between 5 and 4 nm. This way we assure that the influence of the substrate on the measured mechanical properties is negligible. The reduced Modulus was estimated by a fit with the Hertz Theory (Tip radius 300 nm, kc 46 N/m).



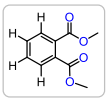
Supplementary Figure 80 - Histogram of the lateral deflection. Since the lateral sensitivity and torsional force is unknown, we take the U(L-B) signal in mV, which is proportional to the lateral force. Depending on the scan direction (trace and retrace) the cantilever bends in positive (trace) or negative (retrace) direction. For evaluation we took the absolute value and added the histograms of trace and retrace lateral deflection (thick solid lines). The main peak is fitted by a gaussian fit (thin solid line) and x_0 is taken as value for the friction. For comparison histogram of trace is also shown (dotted lines).

Supplementary Notes 11: Computational Details

In this computational study, we have conducted a conformational space exploration by CREST/2.11[5] utilizing xTB/2.11[6] with GFN2 parametrization[7] and methanol as solvent included with the ALPB solvation model.[8] The ensemble was refined through CENSO/1.2[9] interfacing TURBOMOLE/7.6.[10] The r2scan-3c composite method[11] and thermal corrections at the xTB level[12] delivered a reasonable compromise between speed and accuracy. These have been combined with COSMO as implicit solvation model using the dielectric constant of methanol (ε = 32.7).[13] The lowest energy conformer was further processed using ORCA/5.0.3.[14] The structure optimization with wB97X-D4/def2-TZVP[15,16] lead to minimum geometric structures confirmed by normal mode analysis. The electronic structure optimization further included RI approximation and the CPCM solvation model with methanol as solvent. Transition states were obtained after scanning the reaction coordinate, by nuged elastic band calculations and follow-up transition state optimization leading to one confirmed imaginary mode. The employed range-separated functional is recommended for transition state optimizations of organic molecules.[17] Thermal corrections at the wB97X-D4/def2-TZVP level were calculated using 1 atm and 383 K applying the rigid rotator harmonic oscillator approximation (RRHO) as implemented in Orca. Furthermore, a factor of RTln(24.5) = 10.2 kJ/mol was added to the Gibbs free energy values for correcting the assumed ideal gas concentration in the entropy term, as recommended in the Orca documentation.[18]



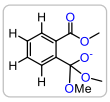
Supplementary Figure 81 - Energy profile of the computational modelling approach. Gibbs free energy values are calculated at the wB97x-D4/def2-TZVP level of theory. The double cross indicates transition states, while other Lewis structures represent confirmed minima of the reaction path



No. of atoms: 24

G=-1806264.51, E_el=-1806625.47, (kJ/mol), wB97X-D4/def2-TZVP, Descr.: Subst=H, Educt

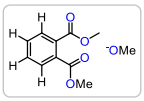
C	-0.12495254712379	3.26250684086367	0.01083046110134
C	0.82501681093716	2.27561821101845	0.22534549329557
C	0.48214848536384	0.93555720765102	0.10948167383068
C	-0.83112859227167	0.58217638788049	-0.20514818631036
C	-1.77569549789078	1.57406453466822	-0.42775103157821
C	-1.42437859070502	2.91147271853001	-0.32054421398489
H	1.84764523491937	2.53972975229033	0.46641222720698
C	1.56955351346308	-0.07469566370616	0.28187828723551
O	1.50501055977442	-1.03975093817037	-0.62932891319869
C	2.47699358895559	-2.08964143829631	-0.51354177183302
C	-1.28892914632386	-0.84005789243395	-0.27165231613589
O	-1.94443259040652	-1.29358402359929	-1.17791532136060
H	-2.79369347443124	1.29286349173609	-0.66961100315065
H	-2.17014814942655	3.67831814401970	-0.49121795167091
H	0.15354818773399	4.30581072604093	0.09549631396068
O	2.43130509601225	0.00186123623781	1.12396021068283
O	-0.93163908764904	-1.52939673298788	0.80632886084822
C	-1.27875885719095	-2.92229913677477	0.81299580132800
H	2.25798129370528	-2.78163003376580	-1.32142276411811
H	3.48164647073200	-1.68260124207075	-0.61862082368766
H	2.37707263780585	-2.58409384807441	0.45241894565472
H	-2.35847395033654	-3.04134274641669	0.73658946503377
H	-0.79025633122483	-3.42897964531361	-0.01932084065079
H	-0.91656604642207	-3.30944742542675	1.76081985130144



No. of atoms: 29

G=-2108721.26, E_el=-2109168.94, (kJ/mol), wB97X-D4/def2-TZVP, Descr.: Subst=H, MeO- at Carbonyl, TS

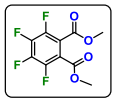
C	-0.65401716583640	-1.24262195144564	-0.19990120678589
C	-0.47433333146291	-2.59174004901163	-0.47483134948664
C	0.76707448365181	-3.18425875865168	-0.29723914260508
C	1.83066335736549	-2.42151013238925	0.15962472006452
C	1.65394360897912	-1.07242539234980	0.42730424483735
C	0.41583709791976	-0.46489164771192	0.24365952598249
C	0.20318775857703	0.98752268193519	0.54148074821063
O	1.26281832843820	1.52869983796256	1.17281971713712
C	1.18500287431901	2.92953703935366	1.40164656114587
C	-2.02478940422885	-0.67926409270146	-0.42841420496158
O	-2.79118165954642	-0.78388968312510	0.65363402758545
C	-4.12285443809345	-0.26867570796489	0.53307035590243
O	-0.90272527494051	1.50287784093772	0.55417841234605
O	0.85818992454781	1.55233446539431	-1.49208590140252
C	2.20753236777005	1.48368785296975	-1.69695555936924
O	-2.42347202012603	-0.28068497996918	-1.49666849737331
H	2.48328868549028	-0.47776579441608	0.78485953520244
H	-1.31409753106304	-3.18302001394117	-0.82349534682110
H	0.89888166040128	-4.23848014808292	-0.50966283581170
H	2.80302438648405	-2.87649509430753	0.30768504382265
H	0.35357516649407	3.17484997294183	2.06342776625242
H	2.12632121250412	3.21374751071890	1.86686143391021
H	1.06168930885017	3.44680961854792	0.44867687699144
H	-4.58788166196553	-0.42145957942207	1.50290910895862
H	-4.09068951349869	0.79337416413963	0.29005010337295
H	-4.66951021033161	-0.80600404737004	-0.24113604669214
H	2.51466021725840	1.80076917428759	-2.71514440218242
H	2.80049122884752	2.11947107400196	-1.00142831136304
H	2.62937054319530	0.45950583966933	-1.57492537686796



No. of atoms: 29

G=-2108757.26, E_el=-2109214.56, (kJ/mol), wB97X-D4/def2-TZVP, Descr.: Subst=H, MeO- at Carbonyl, Product

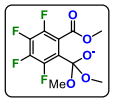
C	1.08922985839438	-2.92369673529068	-0.09887106034905
C	2.20360617643482	-2.09311726073908	-0.05741458359624
C	2.03830789565614	-0.71934767865126	-0.03917341723099
C	0.77187967777106	-0.13792203945341	-0.05922813805194
C	-0.33384176575210	-0.97686666573268	-0.09976393972067
C	-0.17486510221497	-2.36337034060118	-0.12188882131582
C	0.62040504059893	1.40617103053561	-0.04669408664526
O	1.44825448939146	1.91441605303428	-1.13723195321388
C	-1.74533434304416	-0.47331728284737	-0.15792285330349
O	-2.28371785221704	-0.34741711237993	1.05572649888713
C	-3.63698933976876	0.11431732663432	1.09760839549607
O	1.43321233711913	1.89857834781916	1.06111984846118
C	0.86119490651878	1.65001476253910	2.32135737376179
O	-0.59457747496716	1.82748912094514	-0.05300293122958
O	-2.38396382873969	-0.36676828840061	-1.18040114746068
H	2.90537866664150	-0.07022685306554	-0.00956726662550
H	-1.05222761873162	-3.00109157541889	-0.15520658309165
H	1.20657539106952	-4.00088023278029	-0.11398796189619
H	3.19984702085361	-2.52041102020477	-0.03998312282078
H	0.76653793835651	0.57425565325373	2.52233332121010
H	1.52425010763251	2.08425165970499	3.07044828058907
H	-0.12922140636333	2.10628024260476	2.41065934173178
H	-3.90468472259174	0.15281635493714	2.15005271474492
H	-3.70578412430767	1.10697811590028	0.65164857483291
H	-4.29318132141683	-0.57198736845315	0.56334264013233
C	0.89238538294904	1.68126912285385	-2.40795957643455
H	1.56221920567358	2.12900309248618	-3.14293199874014
H	0.80514274231482	0.60807972100055	-2.62551146569579
H	-0.09900711776071	2.13412195786979	-2.50232848952510



No. of atoms: 24

G=-2848734.53, E_el=-2848990.57, (kJ/mol), wB97X-D4/def2-TZVP, Descr.: Subst=F, MeO- at Carbonyl

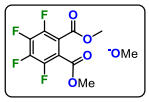
C	1.17553541113794	1.28420310215791	-0.28418625554248
C	-0.04760596151319	0.65870010035530	-0.15690632731196
C	-0.09243378103218	-0.70701574911756	0.13758052274477
C	1.08863900304353	-1.40444691437871	0.29323279687860
C	2.31439902346978	-0.77094733205214	0.15903583294460
C	2.35803867761273	0.57844403532504	-0.12396587560245
C	-1.30217068094386	1.46559577131274	-0.32113606260047
O	-1.53407451612640	2.15389943638759	-1.27982302836378
F	1.09039893994126	-2.71185716699607	0.54376627693033
F	3.43952703791373	-1.45842274253975	0.29599226622503
F	3.52505549528593	1.19623191855259	-0.23803003391617
F	1.25803486478484	2.58961752901404	-0.53372541337427
O	-2.10167291789746	1.31930541681757	0.72427596648499
C	-3.38654428298298	1.95999455567286	0.63465072313788
C	-1.39689781543877	-1.43561658429435	0.26945851120678
H	-3.89638775013716	1.72159599889090	1.56299509902351
H	-3.26046382966979	3.03620353971627	0.52951482568455
H	-3.93422886763822	1.56257980343067	-0.21958302829034
O	-2.18871279683299	-1.18184331321319	-0.76138050703202
O	-1.67259337326010	-2.15587250861054	1.19249891027216
C	-3.51433326794619	-1.73669607167770	-0.69715282885951
H	-4.00921239578643	-1.40965352187126	-1.60642965096969
H	-3.46236255944891	-2.82333861564945	-0.65510694564751
H	-4.02928217453506	-1.35195961383276	0.18271435947747



No. of atoms: 29

G=-3151201.49, E_el=-3151542.57, (kJ/mol), wB97X-D4/def2-TZVP, Descr.: Subst=F, MeO- at Carbonyl, Prereactive Complex instead of TS

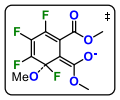
C	-0.00957101837592	-0.03439514645482	-0.07997817815819
C	1.38974474997551	-0.03461372845301	-0.04864355801729
C	2.08352401426721	1.15388531216156	-0.03687862594822
C	1.42742490617062	2.37278119182482	-0.04017475121624
C	0.05078484160874	2.38479157980533	-0.04861708592247
C	-0.65773501416224	1.19215679113372	-0.06710276370938
C	2.21930591329275	-1.29238600958309	0.02326602488244
O	2.61301208330686	-1.75258882925874	1.06412233551593
F	3.42119198368706	1.15448019618673	-0.01786667367765
F	2.10919113828823	3.51154192165745	-0.03103401399427
F	-0.59948239179801	3.54496270702275	-0.04738052488680
F	-1.98414834333027	1.30777461163981	-0.07235218406040
C	-0.71329768494939	-1.35540571786108	-0.13998411775815
O	-0.54100652155691	-0.91202079903302	-2.91870363241559
C	-0.57566968974383	0.41592259571064	-3.21477122216717
O	-2.03084251047787	-1.26138340951871	-0.15839676494910
C	-2.73963587804281	-2.50081785990884	-0.27509718856307
O	-0.11555586206931	-2.40526879987261	-0.08865865719600
O	2.53695300376105	-1.74277948049540	-1.17657939723576
C	3.31813628870360	-2.94760254198049	-1.21207454872507
H	-2.46155968979518	-2.99764236143035	-1.20432053218174
H	-2.51644639633959	-3.14778516715321	0.57234847691340
H	-3.79276331207540	-2.23515269014110	-0.28465894317819
H	3.46897820697323	-3.16637455528913	-2.26485282020089
H	4.27294713870783	-2.79256711924764	-0.71160696875280
H	2.77154253241709	-3.75538625347836	-0.72635113298535
H	-0.72798121704558	0.64615927640676	-4.29556092692164
H	0.35308830594112	0.97530562851054	-2.94027358022796
H	-1.39309631739151	0.98118217889544	-2.70398334733611



No. of atoms: 29

G=-3151252.37, E_el=-3151606.65, (kJ/mol), wB97X-D4/def2-TZVP, Descr.: Subst=F, MeO- at Carbonyl, Product

C	2.26025277531944	-0.72157820694914	0.04290381187819
C	2.21312846580520	0.65821696531468	0.03402271459826
C	0.99070056955434	1.30753591370718	0.04871628127486
C	-0.21097811489268	0.61692486643206	0.07625346188545
C	-0.14816972566484	-0.77344273047178	0.08906517916131
C	1.07260403581843	-1.42318626316393	0.06990393308341
F	3.35065633248110	1.35488925331427	0.01244291544789
F	1.03597366380038	2.64583575059208	0.03633964303610
C	-1.60546911190816	1.33352095891099	0.10046175811039
O	-1.61585508353255	2.27065747840444	-1.00352355277652
C	-1.36850173646690	-1.65534982456486	0.16431989730446
O	-1.78793051832991	-2.01339508088564	-1.04472357008315
C	-2.94050702836304	-2.86284346558840	-1.07991164871472
F	1.12639515409223	-2.76449646056708	0.07550923301399
F	3.43386560049298	-1.35399364063517	0.02600368063553
O	-1.56801971982594	2.28105534099980	1.19486573286680
C	-1.67807276932973	1.67715657958914	2.46232036916757
O	-2.58331682627098	0.50435917975455	0.12561597718668
O	-1.78142800631379	-2.12856987689180	1.19490667411128
H	-1.70488178836805	2.47988262577365	3.19919597481353
H	-2.59038981140924	1.08071135614684	2.54525547772872
H	-0.81811441867755	1.03015192858789	2.68214754477242
H	-3.13904504982356	-3.04875072079336	-2.13169835344032
H	-2.74159281262115	-3.79838199036238	-0.55838827163730
H	-3.78717466690162	-2.35581677894681	-0.61645517049401
C	-1.77416636429697	1.65528874082859	-2.26005134760400
H	-0.91720210058226	1.01638394145718	-2.51255223102399
H	-2.68246056707732	1.04798981872246	-2.29797697409130
H	-1.84304407110779	2.45139625738455	-3.00145963401149



No. of atoms: 29

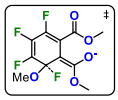
G=-3151178.43, E_el=-3151520.12, (kJ/mol), wB97X-D4/def2-TZVP, Descr.: Subst=F, MeO- at Meta, TS 1

C	2.20881976876761	1.54546628019033	0.46510317536921
C	1.43863270578921	2.66442203470288	0.38834338249036
C	0.04533244004926	2.54545589432366	0.40714396451061
C	-0.54717376437518	1.32111909929106	0.51276988695402
C	0.23827282767978	0.14943823136861	0.59999184803711
C	1.62948803380248	0.26232198939569	0.49391054726334
F	2.00010055599405	3.86965422420385	0.29023492111630
F	-0.68664096357092	3.67255047474146	0.31900832940251
C	-2.05085262882582	1.30195604249483	0.54774015346293
O	-2.70165574756402	1.61934697446215	1.51081415195876
C	-0.45857191182108	-1.14218596158408	0.76773390355813
O	0.31946025661182	-2.21008659503639	0.63095715538299
C	-0.32176683058121	-3.48066218119952	0.79595667450788
O	2.03298307800260	-0.19365817555878	-1.55113644578665
F	3.54117690144401	1.64619933035572	0.45301464197637
O	-2.55920879376650	0.98890677799239	-0.63529738607588
C	-3.99073349779515	0.91200866392283	-0.70253298901910
O	-1.64628425455701	-1.22756392548368	1.00805504132525
F	2.43926305611678	-0.71137991971324	0.92510382879412
H	-4.22245858478949	0.64222833053161	-1.72863034945092
H	-4.35131026762572	0.14826034324965	-0.01384681397893
H	-4.43211874116178	1.87529484728066	-0.45057216299077
H	-1.09323202340459	-3.61689497682728	0.03875505130675
H	0.46360760914465	-4.22099682305579	0.67281456212183
H	-0.76552612395469	-3.55563579844320	1.78800497516350
C	3.11087015897374	-1.00734532214448	-1.81663959457466
H	4.07886130349542	-0.59218040273052	-1.46749469632949
H	3.03522091768539	-2.01052224827174	-1.34930483960861
H	3.24544452023634	-1.19551720845867	-2.90000091688696

No. of atoms: 29

G=-3151273.46, E_el=-3151624.10, (kJ/mol), wB97X-D4/def2-TZVP, Descr.: Subst=F, MeO- at Meta, Intermediate

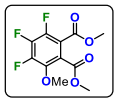
C	2.02374911288196	0.85174768479351	0.13795705045003
C	1.27301093176231	1.96153282274698	0.07023551455206
C	-0.14222094100449	1.87575517692851	0.06575344045235
C	-0.74021582858601	0.66315906962815	0.10820873149082
C	0.00641381752571	-0.54490359244170	0.17225666882436
C	1.48366513922513	-0.52165423020824	0.25065925131117
F	1.84463638805618	3.17115475866660	-0.01092917796383
F	-0.85082511059755	3.03579753813262	-0.00419641457186
C	-2.24308049963564	0.67628437770898	0.08896082109812
O	-2.93077300341432	0.81816021058914	1.06986444856740
C	-0.72866360117377	-1.78450536480076	0.21959635445656
O	0.03297133294378	-2.88814442234281	0.35074211074900
C	-0.66465842869637	-4.12986875004508	0.41467554014468
O	2.18648678114802	-1.40444688505041	-0.59811742176591
F	3.37155685568275	0.95364798113592	0.12425306308343
O	-2.71415897048632	0.63295746427610	-1.15272806653005
C	-4.14053978996540	0.63146473303939	-1.28758709665008
O	-1.95091710357604	-1.87867190291347	0.15904200906677
F	1.95054888875339	-1.02920240326152	1.53498735790258
H	-4.33519055722235	0.57887352152570	-2.35514175523203
H	-4.56171924905250	-0.23717266102158	-0.78145730463593
H	-4.56301667209275	1.54373823084749	-0.86783854979916
H	-1.24209746697169	-4.29961863998019	-0.49441264945055
H	0.10297867048490	-4.89307554281798	0.51841036715857
H	-1.33343259970904	-4.15572771304199	1.27541923433609
C	1.90670398603529	-1.24242631755128	-1.97483928285984
H	0.86417425971681	-1.48291440663701	-2.20331880792638
H	2.11473086228989	-0.22060697836909	-2.31099642852849
H	2.56110719297813	-1.93181081263594	-2.50564830452988



No. of atoms: 29

G=-3151259.44, E_el=-3151609.41, (kJ/mol), wB97X-D4/def2-TZVP, Descr.: Subst=F, MeO- at Meta, TS 2

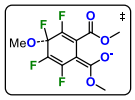
C	2.08028142066295	1.56158150146513	-0.38662677470203
C	1.28846862410345	2.63856644640913	-0.19370009450746
C	-0.06728014495758	2.47057343360918	0.14470446476476
C	-0.59014738825695	1.22002048533425	0.22762557675912
C	0.21520795729399	0.07383027633831	0.01846147532017
C	1.63450729516933	0.20070510200233	-0.16505898714750
F	1.77300860368544	3.87681976053086	-0.35324068806008
F	-0.81079580999248	3.57874396477879	0.38634376758480
C	-2.03422593877180	1.11671282437445	0.62882876005268
O	-2.40094405684696	0.87321423845608	1.75192300986370
C	-0.45054644880759	-1.22682585247142	0.06585775157376
O	0.35093598385586	-2.26747534058968	0.31495901433427
C	-0.27558510841075	-3.55101383795777	0.35057644968742
O	2.20232655433631	-0.75185532057989	-0.97290967531775
F	3.35787881442143	1.75319089502854	-0.77581339373363
O	-2.85058816231214	1.41457625497233	-0.37365976591469
C	-4.25344310940214	1.35303687735010	-0.08114066736629
O	-1.65480879178310	-1.37402176534568	-0.07439764334641
F	2.38768576183932	-0.14815687752418	1.33869575875145
H	-4.75817873441726	1.62697744834648	-1.00311383226219
H	-4.52655543184887	0.34104884882809	0.21726410384705
H	-4.50485200957266	2.05333193842063	0.71442810888038
H	-0.75777130960871	-3.77012500781412	-0.60211488501262
H	0.52394248376542	-4.26254998854653	0.54040996652447
H	-1.01590711310593	-3.59662677765470	1.14911451324130
C	3.53353352431676	-1.20364105767098	-0.74570055623967
H	4.22898758902397	-0.38127285046506	-0.58865143339511
H	3.56388291583936	-1.87160365582461	0.11440328277706
H	3.81098202978131	-1.74776196380003	-1.64746760695697



No. of atoms: 28

G=-2888764.93, E_el=-2889120.28, (kJ/mol), wB97X-D4/def2-TZVP, Descr.: Subst=F, MeO- at Meta, Product

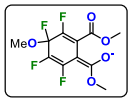
C	-1.56417096133846	0.45270360491258	0.32882403180941
C	-2.22984116981878	-0.75883696048190	0.48809590094162
C	-1.54248899814717	-1.95334655460983	0.45620616363449
C	-0.16790666566332	-1.94900454019152	0.28707072485437
C	0.52483779442329	-0.76162426176533	0.13344412657141
C	-0.18970185511967	0.43929539016653	0.14036290241569
F	-3.54380727929746	-0.77528085774942	0.69328718421298
F	-2.19554258416483	-3.10179357640874	0.59676881543504
F	0.45161624415820	-3.12770083058940	0.25008409517420
C	2.01410663597479	-0.79231289273586	-0.02387662420796
O	2.41986003097836	0.05355567199714	-0.96056762163935
C	3.84115285228686	0.19207125447322	-1.12502237016799
C	0.50012864472799	1.76281228745301	-0.02688259127746
O	0.27790622666826	2.52235870890606	-0.93389127817316
O	-2.24321449774165	1.61946668831722	0.44723805689658
C	-3.01685108210373	1.98600957048477	-0.70484830088112
O	2.74319716923568	-1.49529929490994	0.62715387385485
O	1.36267684051144	1.98506218782359	0.95345275502551
C	2.13377090027848	3.19468248759579	0.85768169119930
H	4.27650057854376	-0.75959207127666	-1.42505522366844
H	3.97242491603170	0.93588394572474	-1.90525060081003
H	4.28920679949433	0.53198905677969	-0.19187371569675
H	2.73056532801968	3.18021570440686	-0.05426425943347
H	1.47383968086674	4.06071567654863	0.85599601135442
H	2.77331731438843	3.20244855784965	1.73496343988857
H	-3.53870132606215	2.90222113790634	-0.44055790968955
H	-2.35359629009098	2.16356791737443	-1.55324087558366
H	-3.74166958423982	1.20669423429836	-0.94714536483951



No. of atoms: 29

G=-3151185.58, E_el=-3151524.57, (kJ/mol), wB97X-D4/def2-TZVP, Descr.: Subst=F, MeO- at Para, TS 1

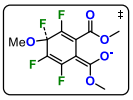
C	0.45140687402246	-0.85307919388961	0.48869539941288
C	0.03967987548212	0.48715257022322	0.61699188816571
C	-1.28540329960677	0.79942046223204	0.74105010271877
C	-2.29008489310522	-0.16845787273754	0.69167650671834
C	-1.88060193086963	-1.49280848572254	0.64650799355711
C	-0.55062241040283	-1.82405175861019	0.50906494233633
C	1.00913482077641	1.63642517560003	0.69610805203458
O	1.46978441438828	2.04240187517595	1.73246696119867
F	-1.66683144266693	2.08355242305815	0.87166927538404
O	-2.93372271429336	0.09538007163165	-1.38243415464546
C	-4.26849985930420	0.33300587000181	-1.60861606603605
F	-3.51404700888576	0.12451069048519	1.12542543407857
F	-2.81154167149258	-2.45588810518046	0.66051714121984
F	-0.28034001471933	-3.12792584929616	0.39931035321578
C	1.89657381208284	-1.13606997037435	0.33635453216039
O	2.20306058516874	-2.42692634148494	0.32770855333784
C	3.59469240323649	-2.74084518848695	0.17748139793666
O	2.72962191050018	-0.26145529417106	0.23009863372732
O	1.20741998904817	2.19268683176057	-0.48819041928400
C	2.13042721716421	3.29217868831042	-0.51929455892253
H	3.65059894211062	-3.82543785959960	0.19010216262517
H	3.97038566561466	-2.35005975278973	-0.76726221222179
H	4.16627799637499	-2.31912171979520	1.00322170772388
H	1.77564726438947	4.10022889373422	0.11886298253904
H	3.11183240949485	2.95858659855523	-0.18322903142244
H	2.16949971257400	3.61236597581402	-1.55619159709132
H	-4.62412913375009	1.30994766429701	-1.21889923778400
H	-4.52915079709754	0.33782600409763	-2.68662130616062
H	-4.94106871623424	-0.42354240283884	-1.15257543652271



No. of atoms: 29

G=-3151296.18, E_el=-3151647.13, (kJ/mol), wB97X-D4/def2-TZVP, Descr.: Subst=F, MeO- at Para, Intermediate

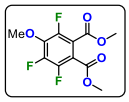
C	0.73916132028540	-0.63333286312322	0.02562623612196
C	0.24992294858783	0.68868591193896	0.25650681281236
C	-1.06424660659613	0.95752025526027	0.37028196839250
C	-2.16078435402271	-0.02234270412006	0.33493082219196
C	-1.59911685811030	-1.33588171274186	0.01348219373680
C	-0.28005896956987	-1.61102679983894	-0.10276028355043
C	1.17885724278678	1.86220618997018	0.39325016843606
O	1.53517804596673	2.31950508062594	1.45064984822979
F	-1.47955564918095	2.24669548793945	0.55004371564145
O	-3.26439047014713	0.35363190716406	-0.44887162166657
C	-2.98062092051821	0.49523072778781	-1.83214500251742
F	-2.80115960197123	-0.06519434357506	1.63018500507771
F	-2.51076423094596	-2.33208975634895	-0.15939227891625
F	0.03172028896720	-2.89073405228272	-0.37393142804619
C	2.15819411462285	-0.86631406642076	-0.03504794035388
O	2.51391149888797	-2.14921926335656	-0.23965748247567
C	3.91578159359735	-2.40896808368914	-0.29662410235587
O	3.00806266053239	0.00795380691927	0.08754520981190
O	1.48173189443321	2.38741051195222	-0.78793372372505
C	2.38669628363467	3.49863728110533	-0.76683949471265
H	4.00955356828699	-3.48266110495270	-0.44018315419690
H	4.37527034558821	-1.87901357646734	-1.13123322257112
H	4.40317749463496	-2.11102115230905	0.63165135557445
H	1.94677054936199	4.33478555101597	-0.22441281515595
H	3.32461978443714	3.20515691647399	-0.29579855104091
H	2.55047235294358	3.76448157187716	-1.80723357791486
H	-2.64183601752574	-0.44910927345287	-2.26813190987097
H	-3.91231781588365	0.79901571803557	-2.30494157750033
H	-2.21964936748340	1.26199925361304	-2.00676072935590



No. of atoms: 29

G=-3151281.91, E_el=-3151631.51, (kJ/mol), wB97X-D4/def2-TZVP, Descr.: Subst=F, MeO- at Para, TS 2

C	0.46310408830547	-0.93210064983749	0.21681792348576
C	-0.09327110835361	0.37252000402999	0.20329533532667
C	-1.41595385117711	0.58330036963909	-0.00103014315730
C	-2.40545287051731	-0.45840858429086	-0.11636468833550
C	-1.78703083364043	-1.74247298360213	-0.22375516089080
C	-0.45915090745159	-1.96653091424104	-0.01863670358239
C	0.75154714747693	1.60060180989361	0.40265850880473
O	0.83216463143799	2.19959414070312	1.44562097968254
F	-1.87625728534849	1.86380432529069	-0.02933855819795
O	-3.51224202351618	-0.33832879477017	-0.88784112527738
C	-4.34479107344234	0.81634926000001	-0.76708264732476
F	-3.15513834853468	-0.43853731126088	1.44374915501688
F	-2.59977983090373	-2.79887384183021	-0.46272580995640
F	-0.06696526610559	-3.24818884453725	-0.07203048921364
C	1.88561580440351	-1.10255717294631	0.47107986802011
O	2.31973243199574	-2.36516554081217	0.38170699966475
C	3.70864155794069	-2.57237491977201	0.64954670511694
O	2.64112745843050	-0.18510315129239	0.74531316682962
O	1.32259626636724	1.98831828008466	-0.73031492161930
C	2.17776331953230	3.13616630366583	-0.64358246440459
H	3.87489247384225	-3.63816892405093	0.51729907551763
H	4.32373309908425	-2.00402271911978	-0.04739711894802
H	3.94978617029966	-2.27706413068401	1.67067639463839
H	1.61198960716366	4.00609189031804	-0.31242649696757
H	2.99286487318932	2.93894538785120	0.05255870615058
H	2.56347484117063	3.29179610701207	-1.64697515377858
H	-3.91891877230281	1.66131395168701	-1.30762931471888
H	-5.29711335710958	0.53847748334127	-1.21430358726991
H	-4.48696824223671	1.07061916953104	0.28111156538836



No. of atoms: 28

G=-2888766.71, E_el=-2889122.64, (kJ/mol), wB97X-D4/def2-TZVP, Descr.: Subst=F, MeO- at Para, Product

C	0.27601404028786	0.57749403722623	0.00581118023398
C	-0.94682053107348	1.18601128654598	-0.12952951169893
C	-2.15385549711343	0.47989994810410	-0.22046706997051
C	-2.05674779009496	-0.90459178231230	-0.17939122602343
C	-0.82821440203683	-1.53273885105821	-0.02662194047661
C	0.34908114910137	-0.81946963681763	0.06681216799170
F	-1.02245000734243	2.52333768817321	-0.14463314602929
O	-3.26465888373304	1.20361210304432	-0.36604590894695
C	-4.53512912986716	0.66601132743305	0.03257893337139
F	-3.13847722752031	-1.67828595275280	-0.31081942944159
F	-0.82921425004342	-2.86552091705457	-0.02688295673511
C	1.64904223004516	-1.53973267651431	0.21028760098995
O	1.80826967267597	-2.52502944457580	0.88491264766930
C	1.49840114010278	1.42945576635795	0.20461410928644
O	1.77519408646430	2.15100976461305	-0.86559745014904
C	2.92361141655753	3.01219965814570	-0.77204495461177
O	2.60398605131709	-0.95744464933992	-0.50365059505291
C	3.92500330797910	-1.50695439945265	-0.37221710397658
O	2.12306785187350	1.44699853546512	1.23464442299446
H	3.93275063625873	-2.54265785528743	-0.70838524371119
H	4.55885160665531	-0.89369141378645	-1.00554396514250
H	4.24802042813122	-1.45028568182858	0.66655425339615
H	2.77394561989913	3.74629753608759	0.01822391987311
H	3.81440183992884	2.41959236946739	-0.56803236035621
H	3.00004188899635	3.49953961192624	-1.73915601716674
H	-4.90591941106226	-0.03969836956720	-0.70826930901959
H	-4.45486461810239	0.18716408666764	1.00872641805647
H	-5.19906175478453	1.52394122229026	0.09469144584599

No. of atoms: 1

G=-262573.23, E_el=-262533.65, (kJ/mol), wB97X-D4/def2-TZVP, Descr.: Fluoride

F 0.0 0.0 0.0

No. of atoms:

G=-302498.66, E_el=-302527.32, (kJ/mol), wB97X-D4/def2-TZVP, Descr.: MeO-

O	-0.00004794400420	-0.00000003309313	-0.05197589554601
C	-0.00002636374914	0.00000001219420	1.30934443715517
H	1.01572077750437	-0.00000003952749	1.77759434719960
H	-0.50782270869185	-0.87976454556687	1.77751715464877
H	-0.50782276865917	0.87976460959328	1.77751693464246

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