SUPPLEMENTARY INFORMATION FOR

Polymers from sugars and unsaturated fatty acids: ADMET polymerisation of monomers derived from D-xylose, D-mannose and castor oil

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1 NMR AND MS SPECTRA OF MONOMERS AND POLYMERS

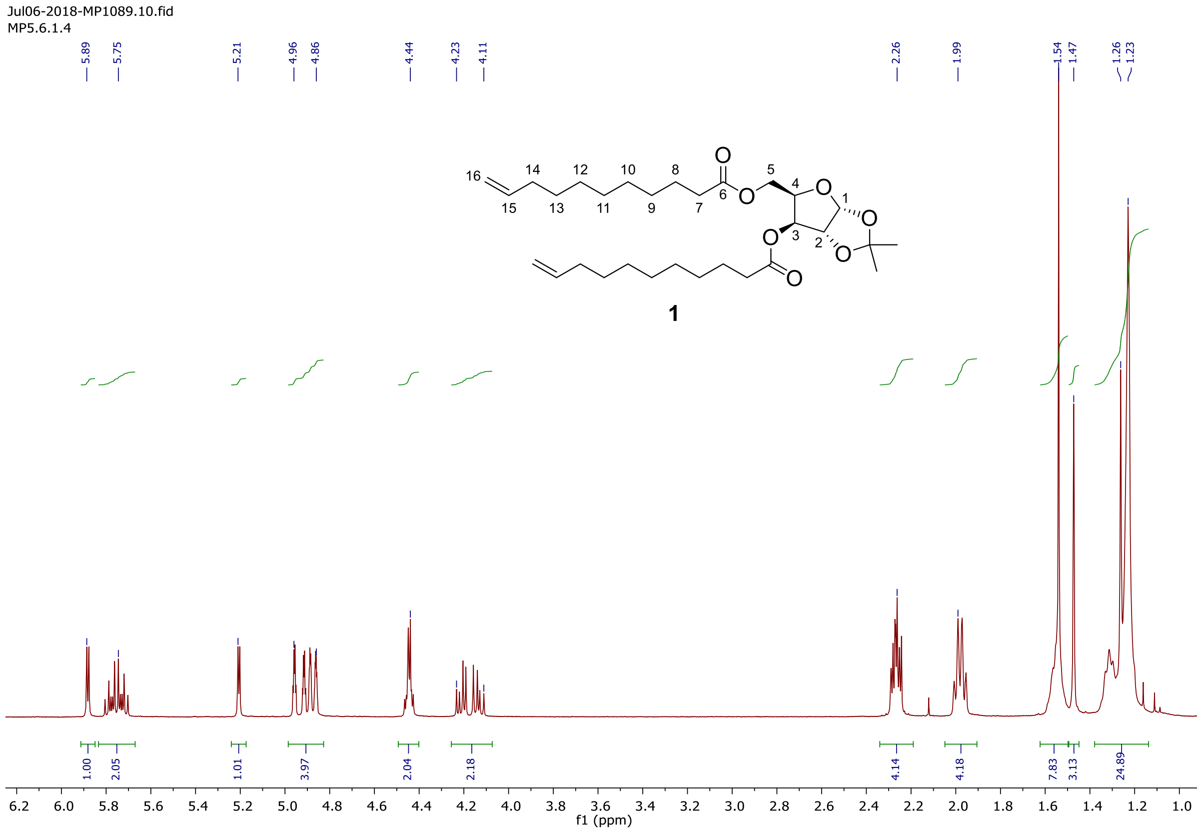

Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of monomer **1**

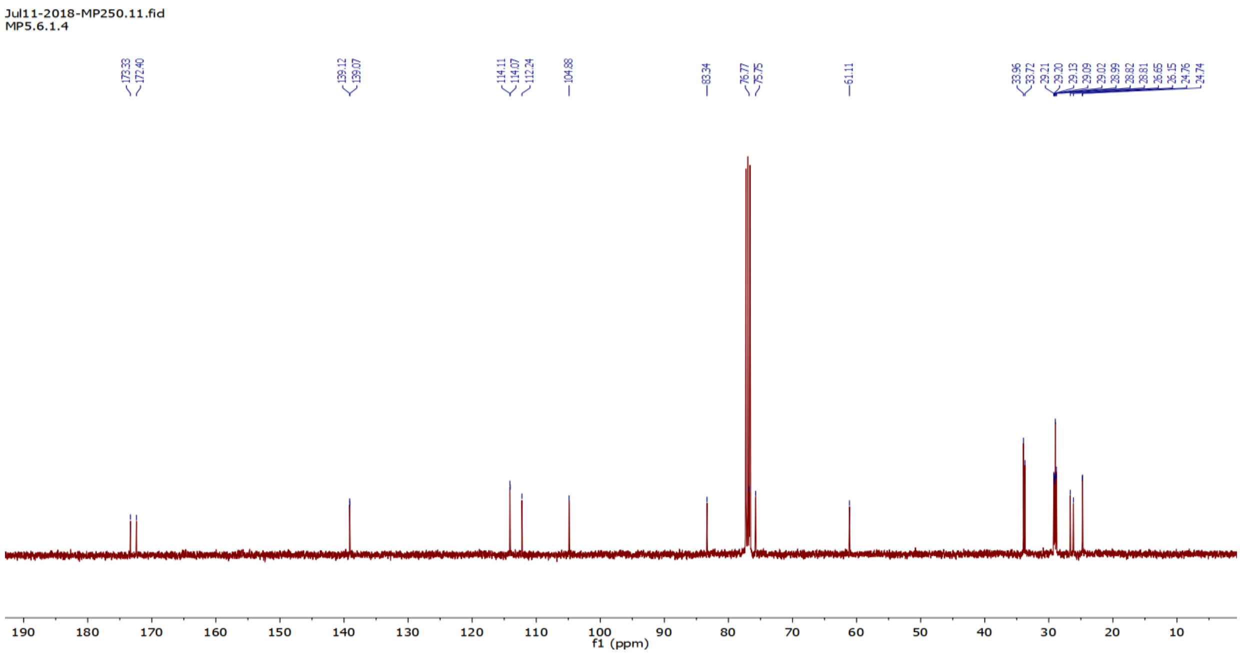

Figure S2. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of monomer **1**

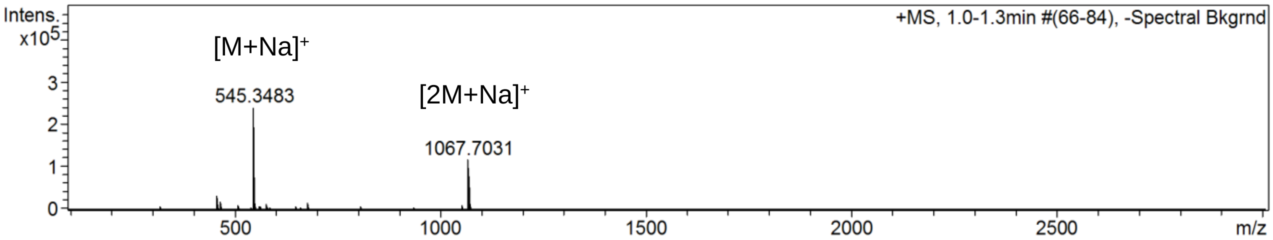

Figure S3. +MS spectrum of monomer **1**

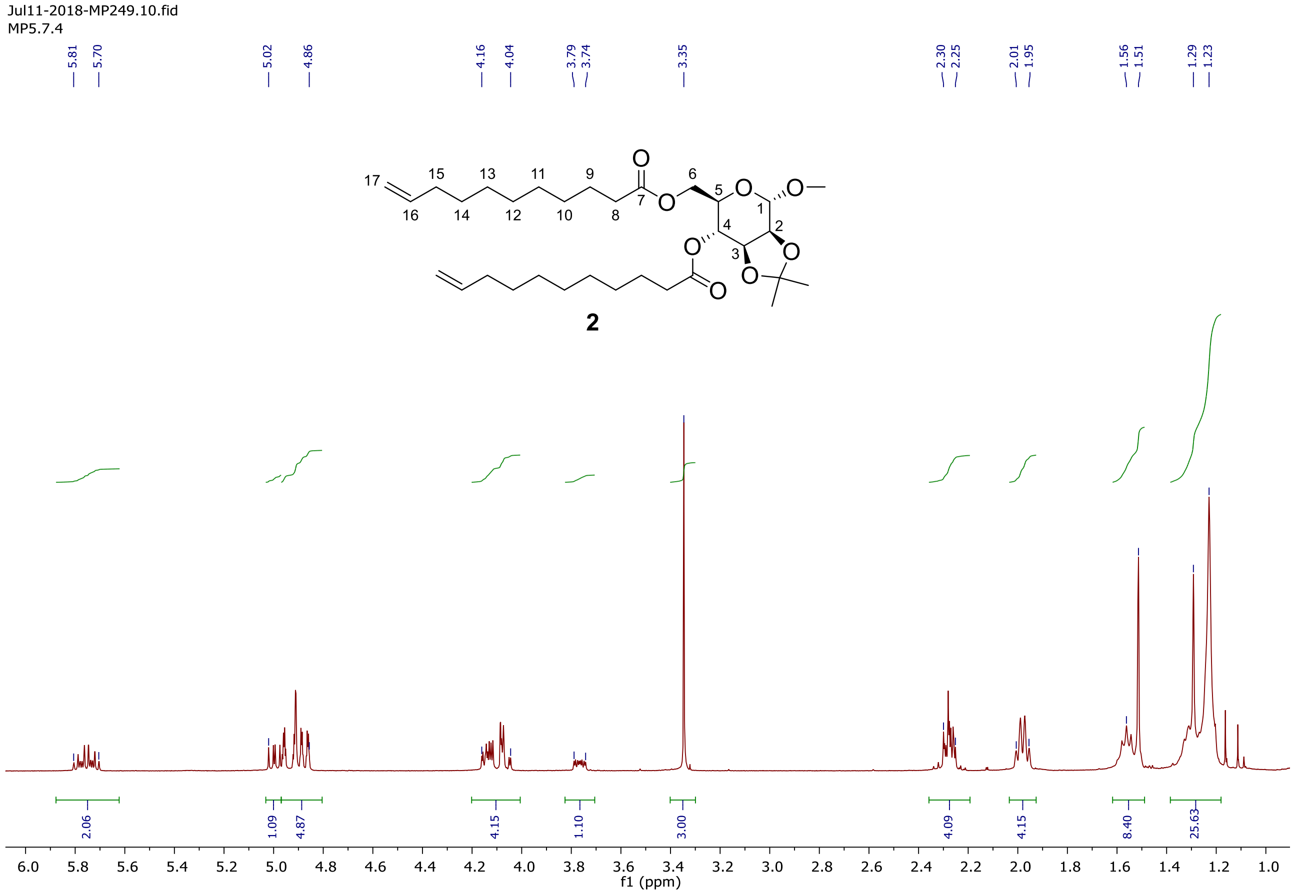

Figure S4. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of monomer **2**

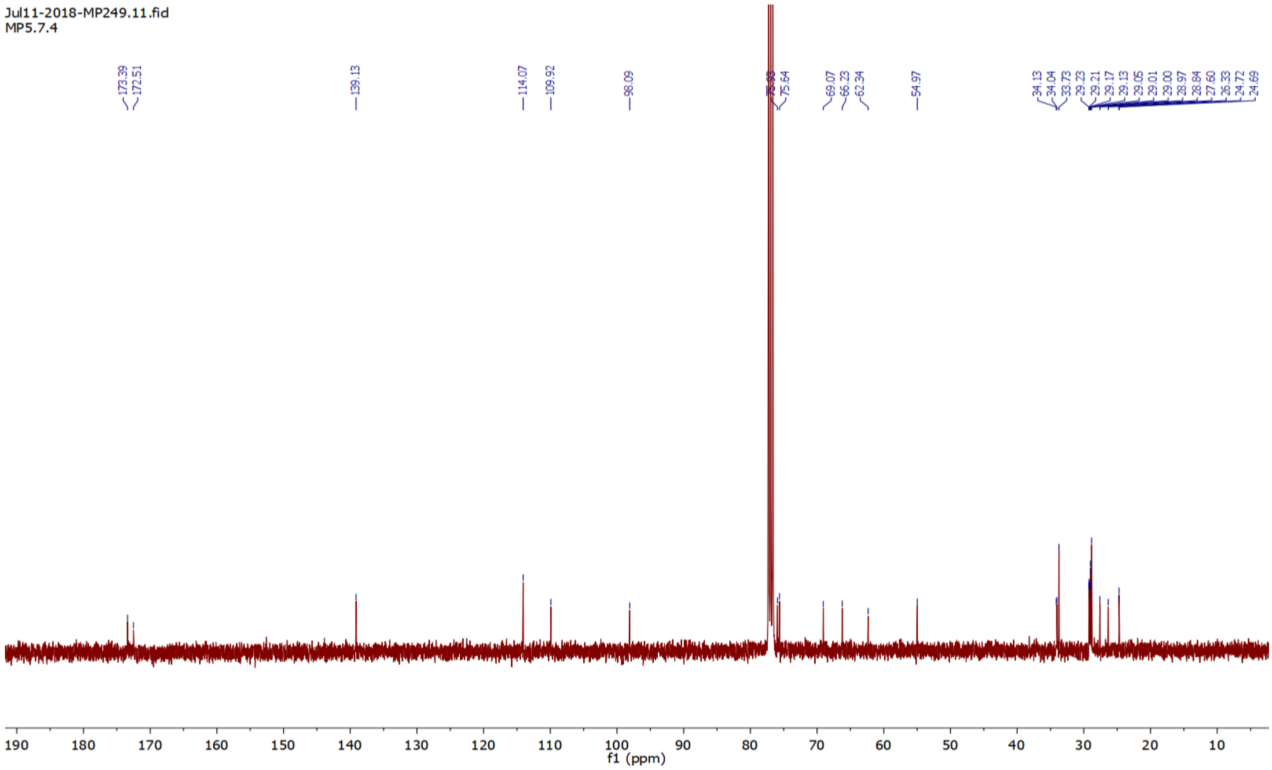

Figure S5. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of monomer **2**

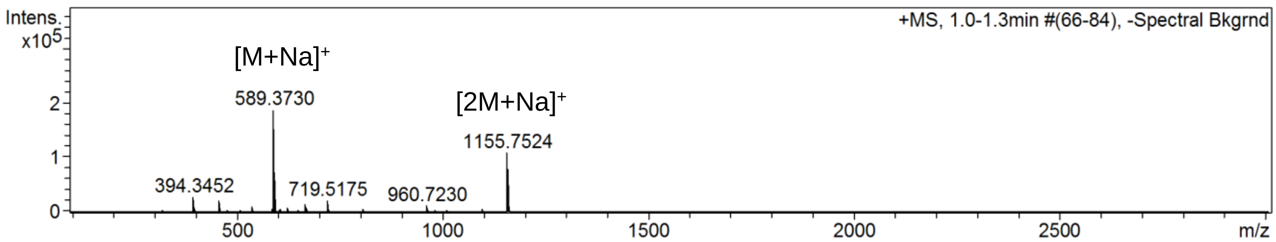

Figure S6. +MS spectrum of monomer **2**

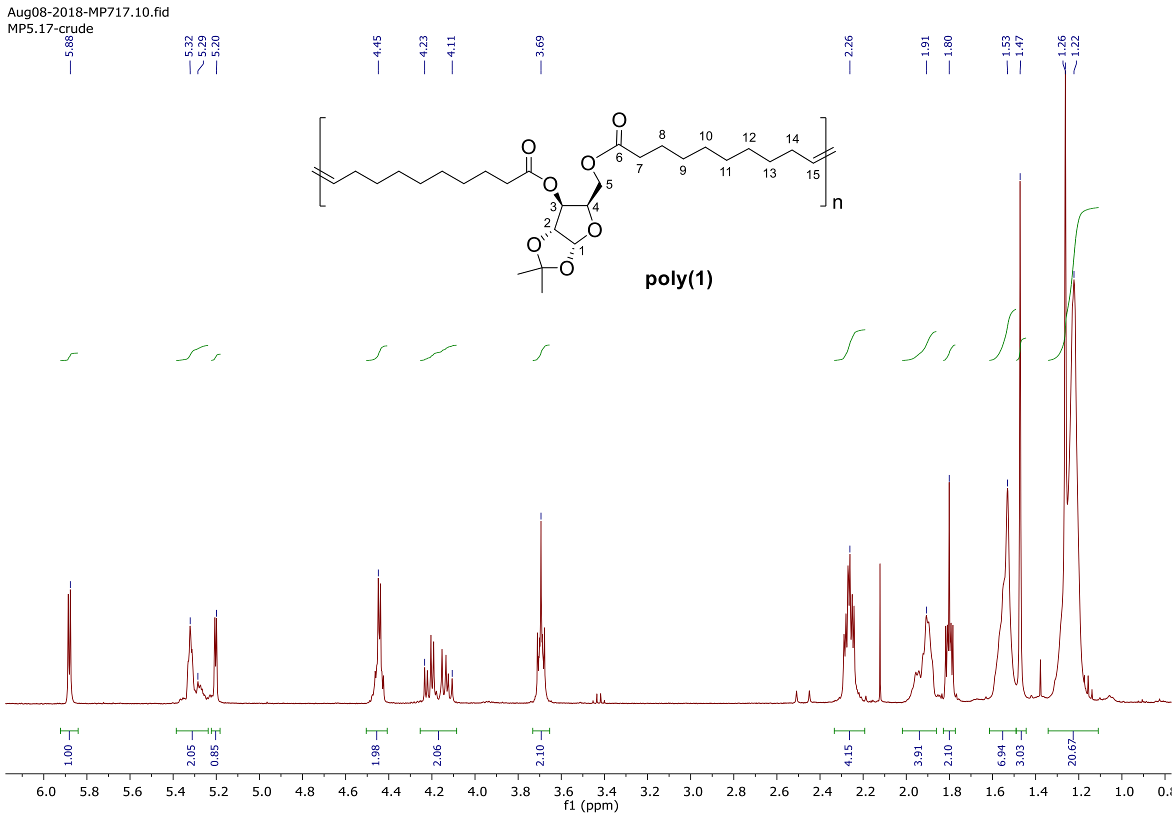

Figure S7. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of polymer **poly(1)**

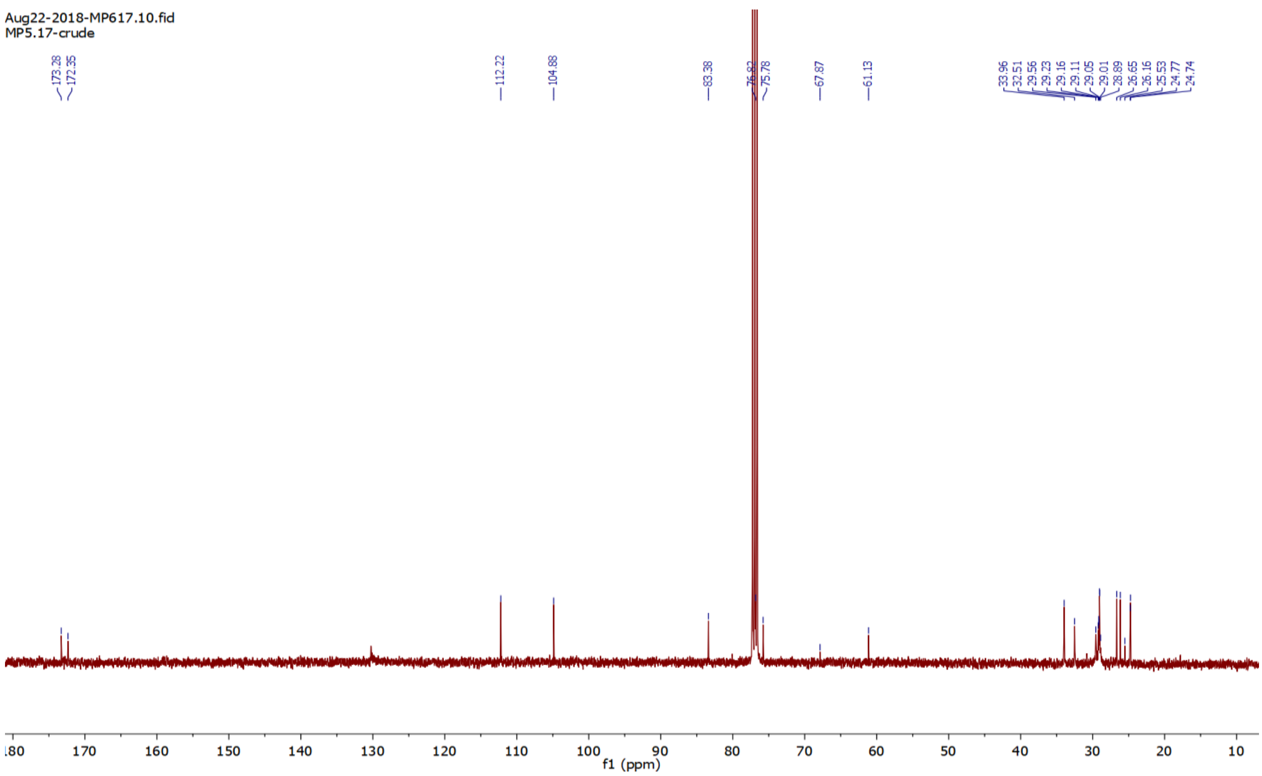

Figure S8. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of polymer **poly(1)**

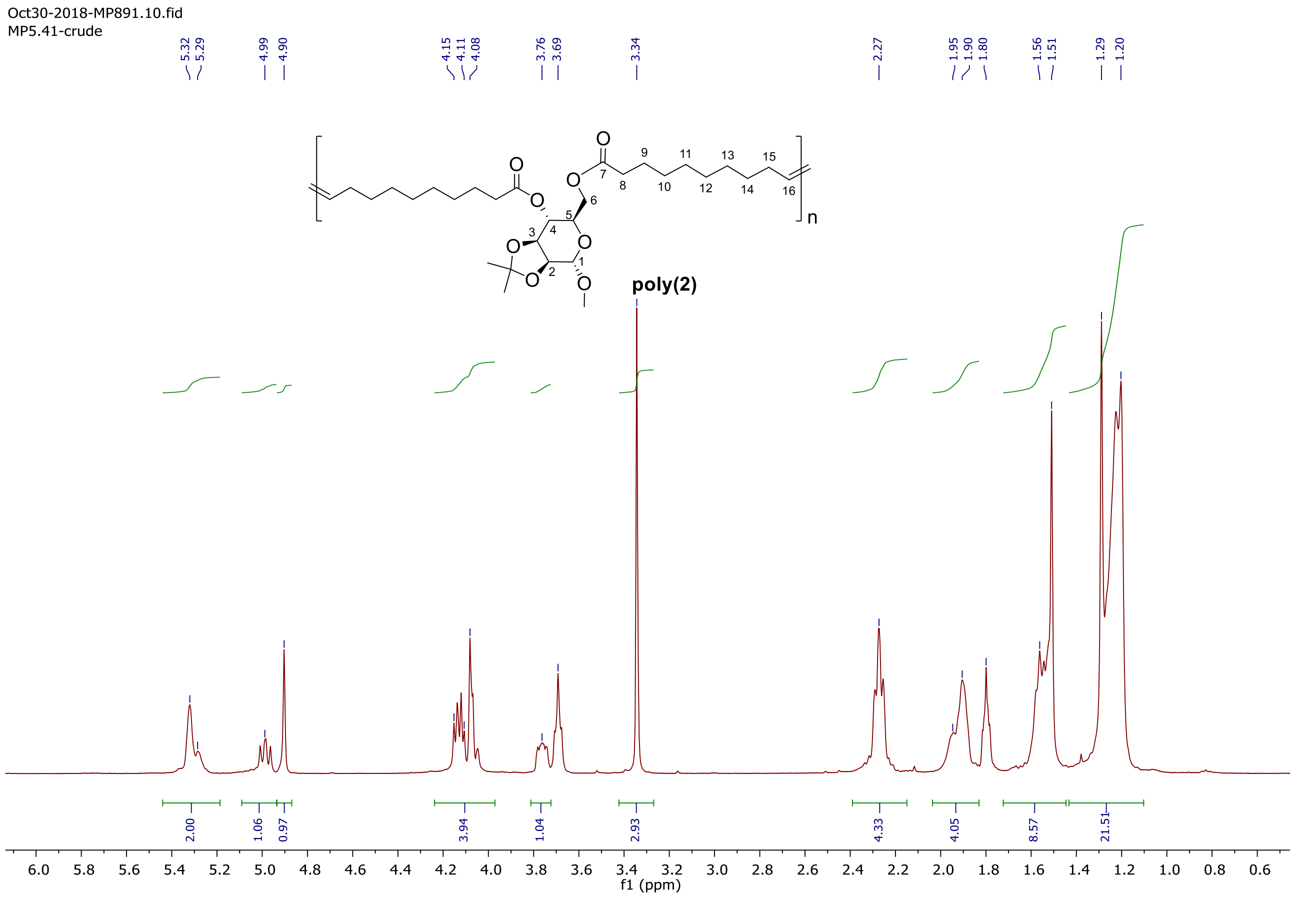

Figure S9. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of polymer **poly(2)**

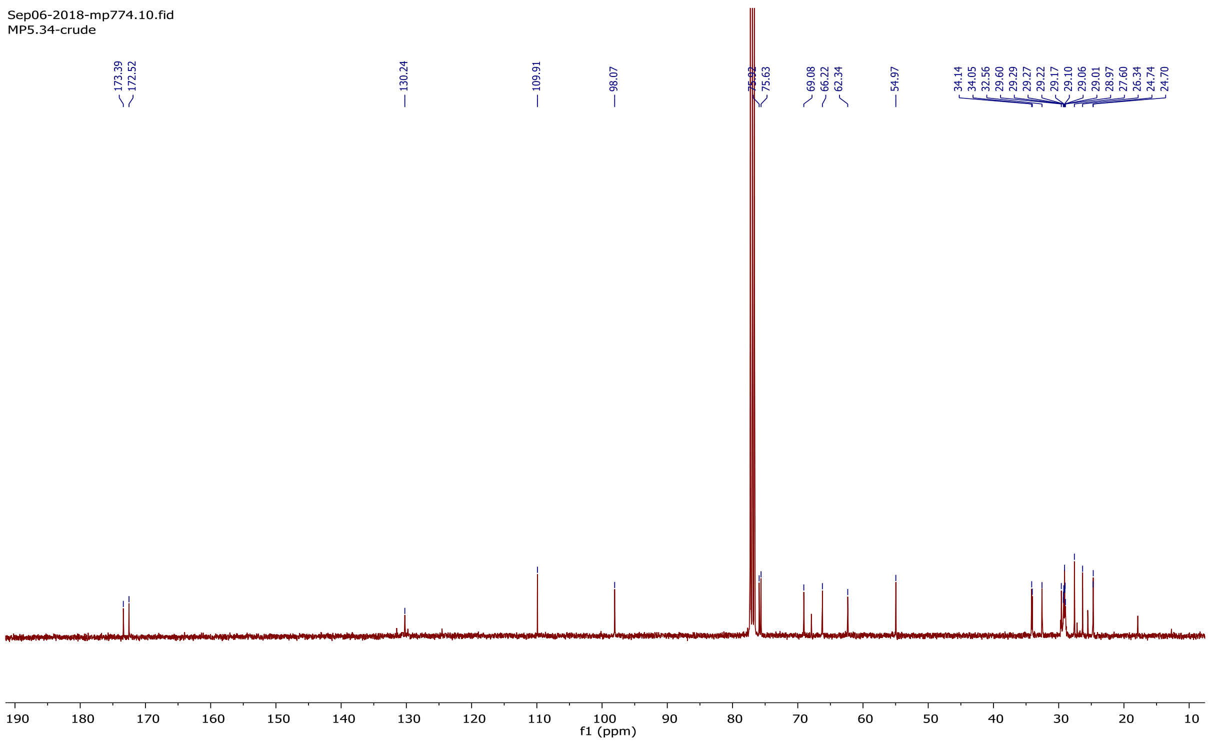

Figure S10. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of polymer **poly(2)**

2 SEC TRACES

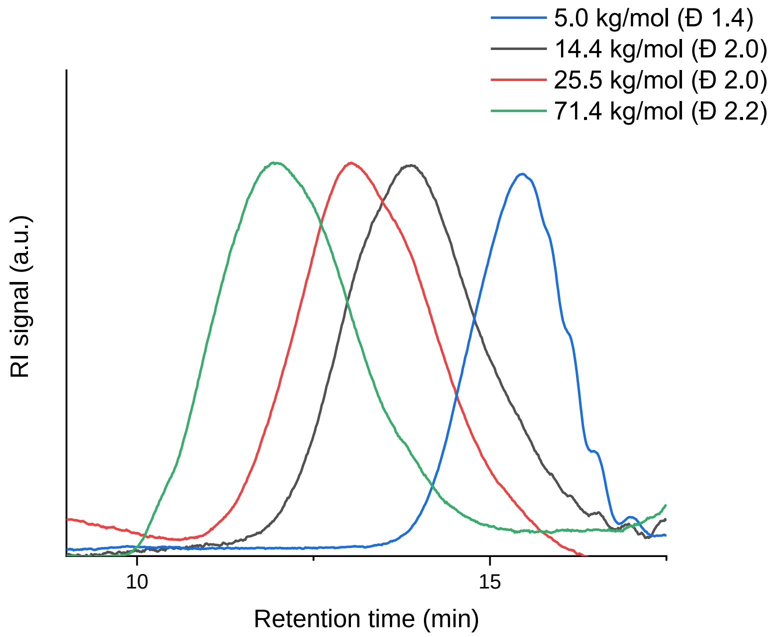

Figure S11. SEC traces (RI detector) of selected xylose-based polymers **poly(1)**

3 THERMOGRAVIMETRIC ANALYSIS

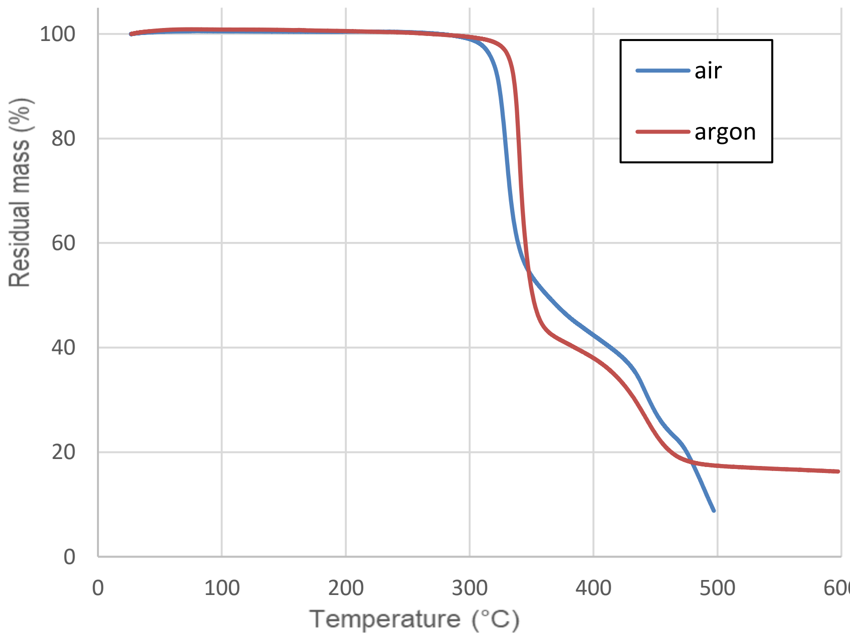

Figure S12. Thermogravimetric analysis of **poly(1)-71** carried out under flow of argon (red line; $T_{d5\%}$ = 332 °C) and air (blue line; $T_{d5\%}$ = 318 °C)

4 POST-POLYMERISATION KETAL DEPROTECTION

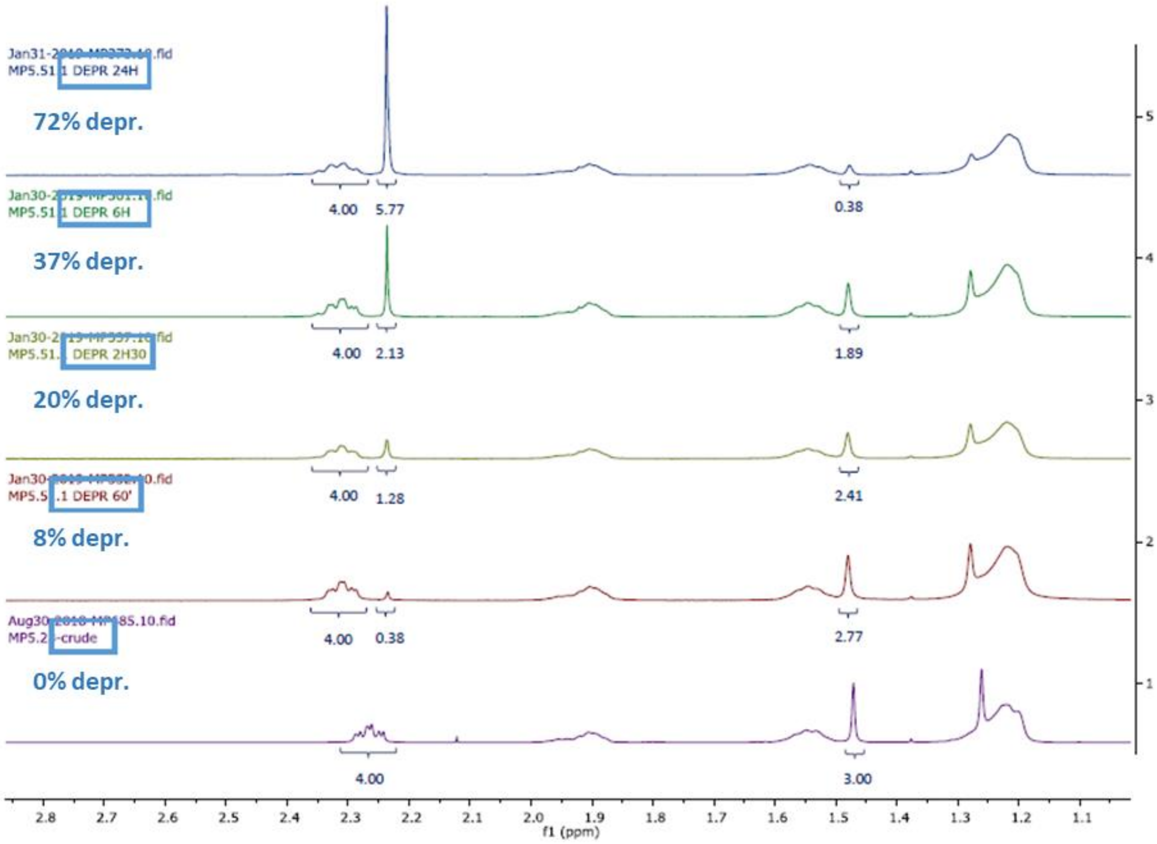

Figure S13. [1]H NMR monitoring of ketal deprotection on **poly(1)** *vs* time (0, 1, 2.5, 6, 24 hours), including relative integration of isopropylidene methyl groups (s, 3H, 1.48 ppm), acetone formed by ketal deprotection (s, 3H, 2.24 ppm) compared with a methylene group on the 10-undecenoic acid chain (m, 4H, 2.31 ppm)

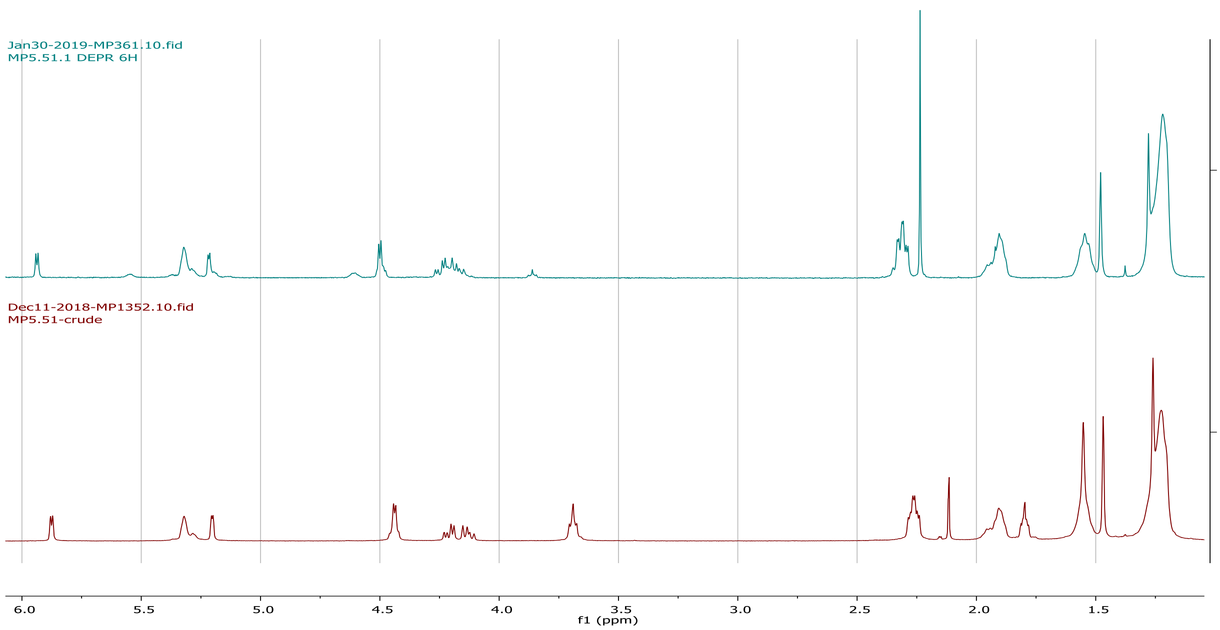

Figure S14. [1]H NMR spectrum of **poly(1)** (bottom) and **poly(1)-depr6h** (37% ketal groups deprotected; top)

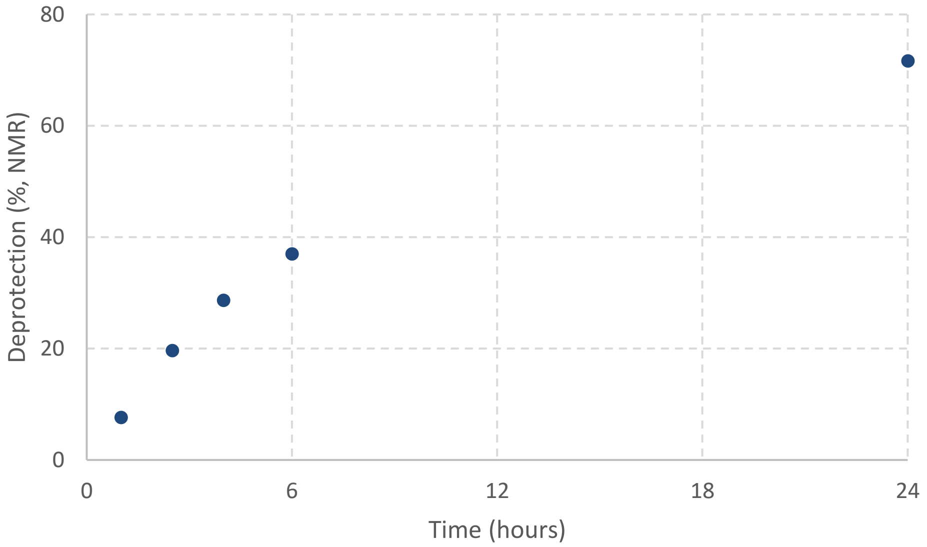

Figure S15. Deprotection of ketal groups on **poly(1)**: monitoring of percent of ketal deprotection (calculated by relative integration of ^{1}H NMR signals) over time

5 POST-POLYMERISATION HYDROXYL FUNCTIONALISATION

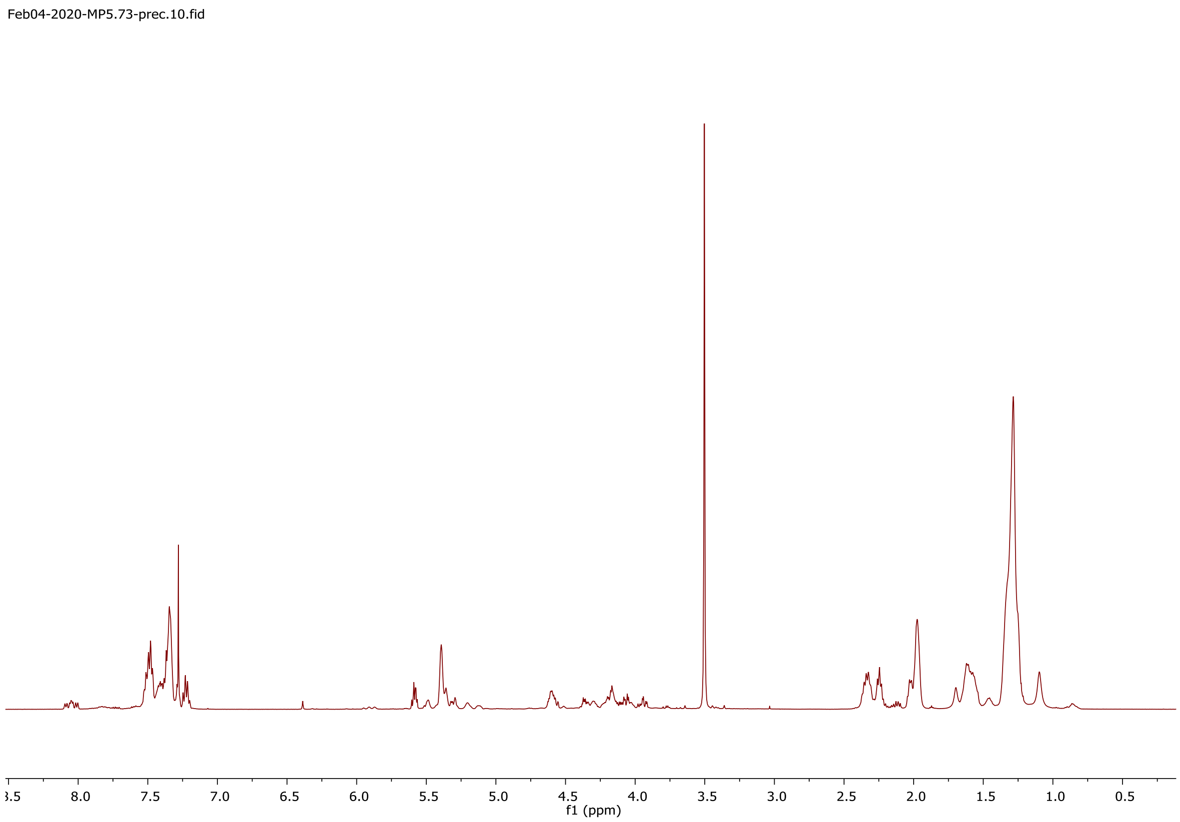

Figure S16. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **poly(1)-depr3h** functionalised with chlorodiphenylphosphine

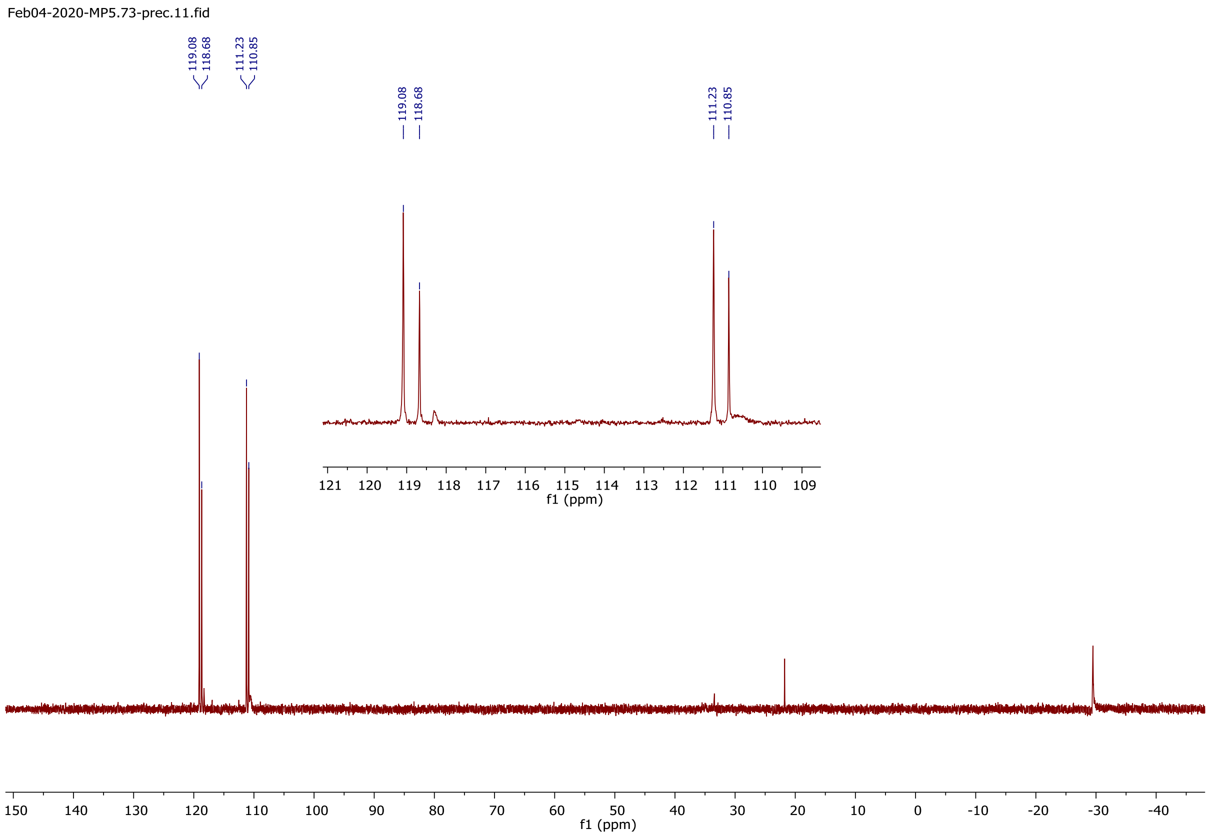

Figure S17. ^{31}P {^{1}H} NMR spectrum ($CDCl_3$, 162 MHz) of **poly(1)-depr3h** functionalised with chlorodiphenylphosphine (residual signals: 21.8 ppm probably phosphine oxide impurity, -29.5 ppm other unidentified impurity)

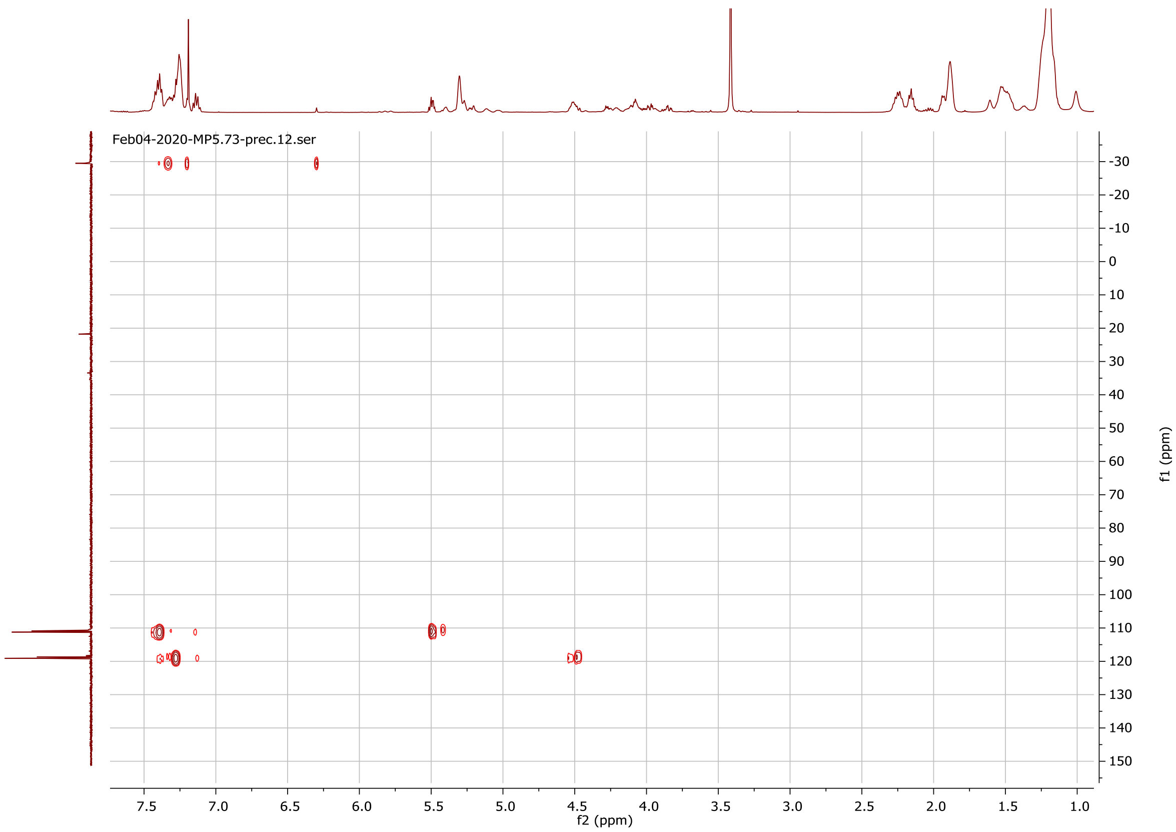

Figure S18. ^{1}H-^{31}P {^{1}H} HMBC NMR spectrum ($CDCl_3$) of **poly(1)-depr3h** functionalised with chlorodiphenylphosphine

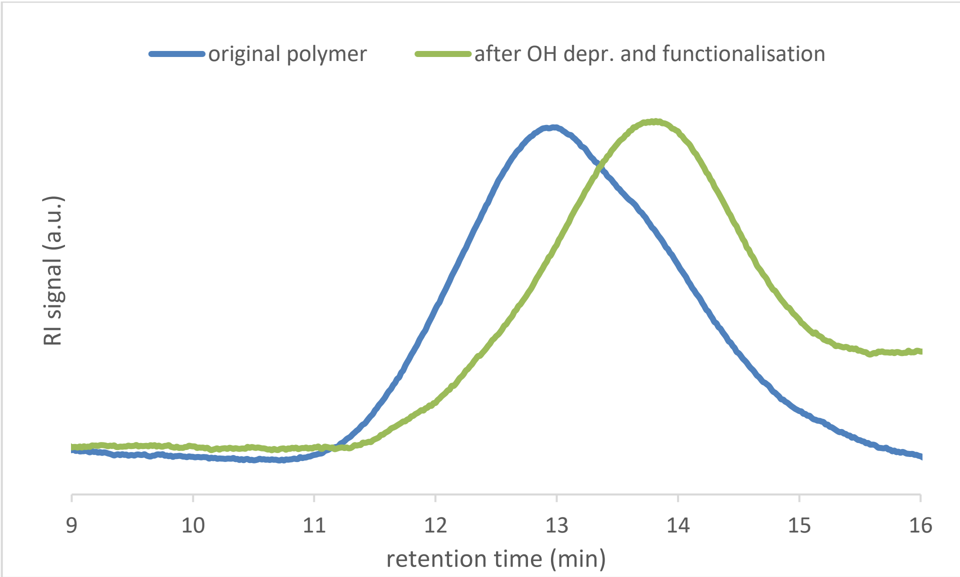

Figure S19. SEC traces (RI detector) for **poly(1)-depr3h** after chlorodiphosphine functionalisation (25.4 kg mol^{-1}, green trace) and its unmodified **poly(1)** precursor (31.0 kg mol^{-1}, blue trace)

6 HYDROLYTIC STABILITY ASSESSMENT

Table S1. SEC data for **poly(1)** and **poly(2)** before and after hydrolytic testing (60 days, room temperature)[a]

polymer	*hydrolytic solution*	M_n *(kg mol^{-1})*	*Đ*
poly(1) [b]	none (original polymer)	71.6	2.3
poly(1) [b]	H_2O	76.1	2.3
poly(1) [b]	HCl 1M	75.1	2.3
poly(1) [b]	NaOH 1M	73.2	2.4
poly(2) [c]	none (original polymer)	60.8	3.5
poly(2) [c]	H_2O	68.1	2.5
poly(2) [c]	HCl 1M	64.2	2.6
poly(2) [c]	NaOH 1M	62.4	2.6

[a] For conditions, see Experimental section. [b] Polymer from Table 1, entry 13. [c] Polymer from Table 2, entry 4.

7 CHARACTERISATION OF POLYMER FILMS

Table S2. Data for partially deprotected polymers **poly(1)–depr2h** and **poly(1)–depr2h** used for the production of polymer films

partially deprotected polymer				precursor polymer		
name	SEC M_n	SEC Đ	ketal depr.	name	SEC M_n	SEC Đ
	kg mol⁻¹		*%*		*kg mol⁻¹*	
poly(1)–depr2h	35.5	1.5	20	**poly(1)**	31.0	1.9
poly(2)–depr2h	30.0	1.6	n.d.	**poly(2)**	41.1	2.6

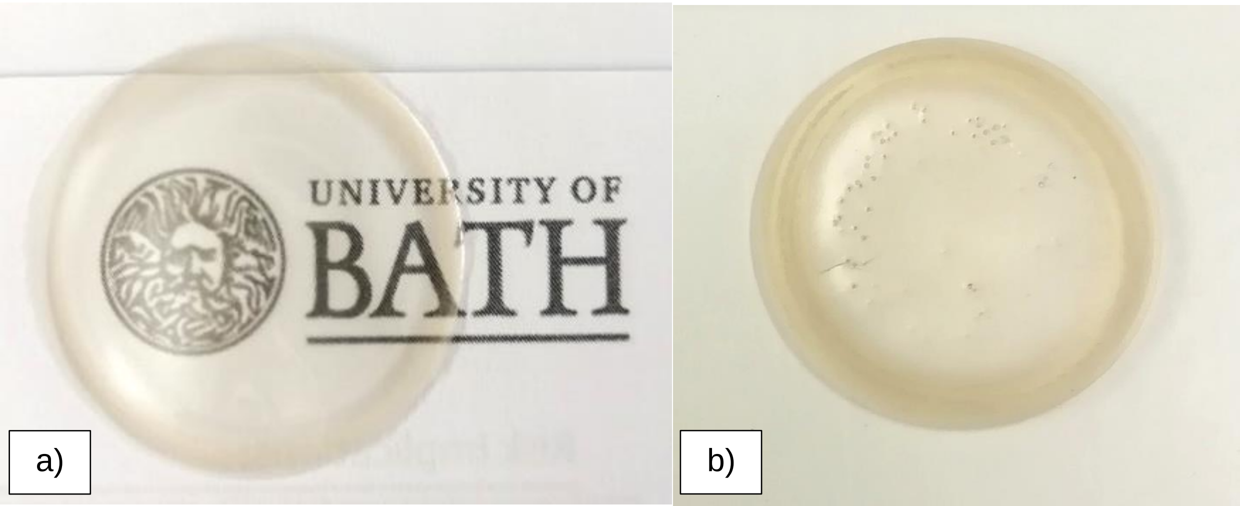

Figure S20. Films obtained from solution casting of (a) **poly(1)–depr2h** (a) and **poly(2)–depr2h** (b)

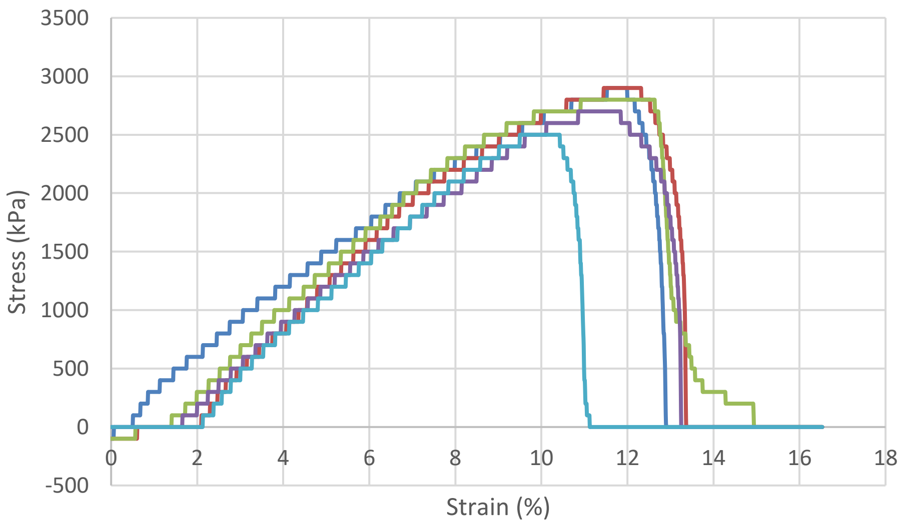

Figure S21. Stress vs strain curve of **poly(1)–depr2h** film (5 repeated measurements)

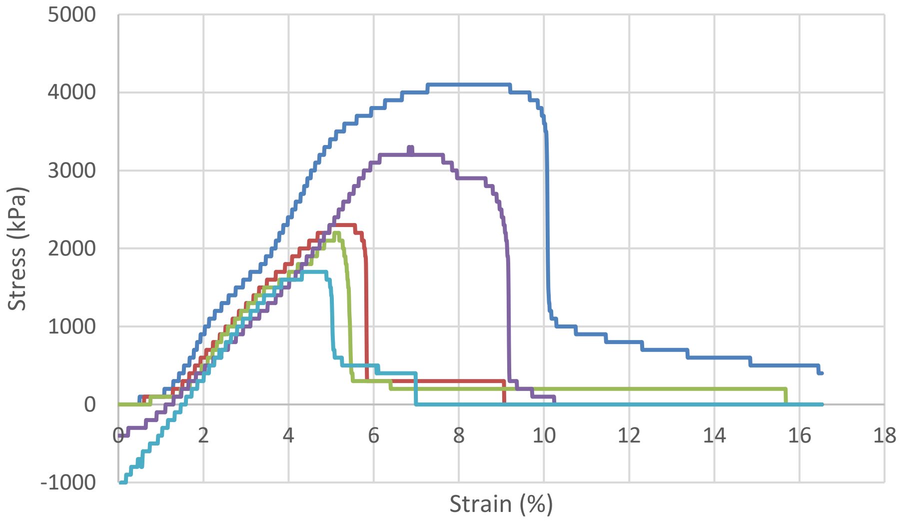

Figure S22. Stress vs strain curve of **poly(2)–depr2h** film (5 repeated measurements)

Table S3. Tensile properties of polymer films obtained from **poly(1)–depr2h** and **poly(2)–depr2h**.[a]

Polymer film	*Young modulus (MPa)*	*Elongation at break (%)*	*Ultimate tensile strength (MPa)*
poly(1)–depr2h	31.3 ± 1.4	11.8 ± .04	2.7 ± 0.1
poly(2)–depr2h	64.3 ± 5.1	6.5 ± 0.8	2.7 ± 0.4

[a] All parameters expressed as average value of 5 repeated measurements ± standard error (see Experimental section)

Table S4. Water contact angle (time zero) for films obtained from **poly(1)–depr2h** and **poly(2)–depr2h**.[a]

Polymer film	*water contact angle (°)*	
	surface side	PTFE side
poly(1)–depr2h	69.6 ± 1.1	81.1 ± 1.3
poly(2)–depr2h	85.6 ± 0.8	85.2 ± 0.5

[a] Expressed as average value of left and right angles for 15 repeated measurements ± standard error (see Experimental section)

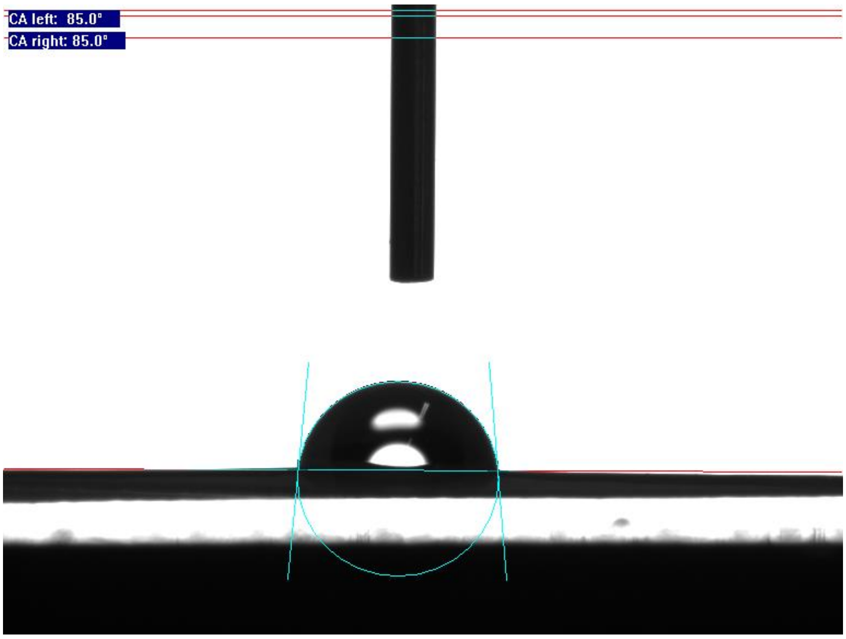

Figure S23. Example of water contact angle measurement (time zero) for film **poly(1)–depr2h**

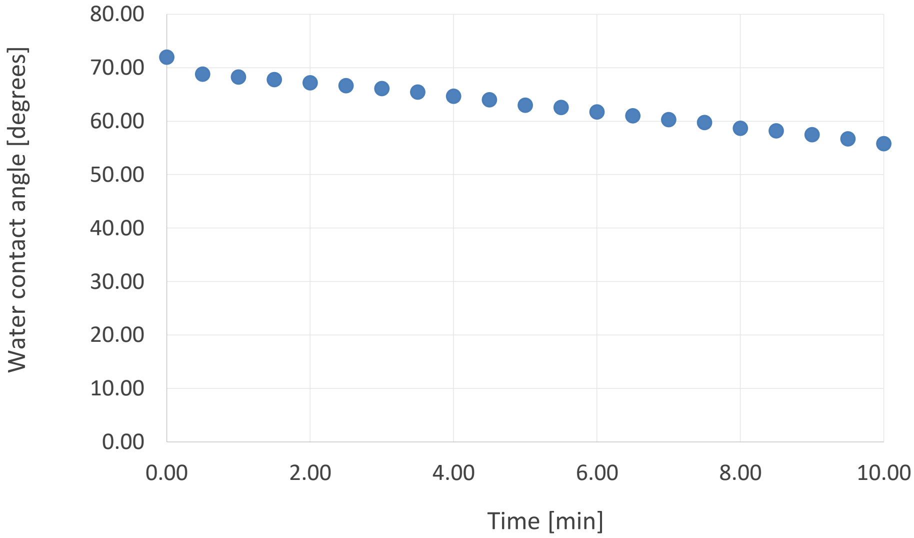

Figure S24. Water contact angle behaviour over time for film **poly(1)–depr2h** (contact angle expressed as average of left and right angles)