Electronic Supplementary Information

Improved chemical recyclability of 2,5-furandicarboxylate polyesters enabled by acid-sensitive spirocyclic ketal units

Nitin G. Valsange,[1] Niklas Warlin,[1] Smita V. Mankar,[1] Nicola Rehnberg,[2] Baozhong Zhang,*[1] and Patric Jannasch*[1]

[1] *Centre for Analysis and Synthesis, Department of Chemistry, Lund University, P.O. Box 124, SE-22100 Lund, Sweden.*

[2] *Bona Sweden AB, Box 210 74, 200 21 Malmö, Sweden*

Corresponding authors

*E-mail: patric.jannasch@chem.lu.se (P.J.).

*E-mail: baozhong.zhang@chem.lu.se (B.Z.).

Contents

TABLES

Experimental section

Polyester synthesis

PBF homopolyester. Diethyl 2,5-furandicarboxylate (4.00 g, 18.8 mmol), 1,4-BD (1.87 g, 21.3 mmol), and DBTO (24 mg, 0.5 mol %) were added to a three-neck round bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and a vacuum distillation outlet. Subsequently, the reaction mixture was degassed by three successive vacuum-nitrogen cycles at room temperature. The reaction mixture was heated at 180 °C under nitrogen for 5 h (transesterification step), and at 200 °C under vacuum for 3 h (polycondensation step). Next, the highly viscous reaction mixture was dissolved in hexafluoroisopropanol (HFIP) (20 mL), and the product was precipitated in 500 mL cold methanol. The precipitate was washed with fresh methanol (2 × 100 mL) and dried under vacuum to obtain PBF as a white solid (3.48 g, 88.0% yield).

^{1}H NMR (400.13 MHz, $CDCl_3$:TFA (9:1), δ, ppm): 1.92-1.99 (m, 4H), 4.49 (bt, 4H), 7.33 (s, 2H).

^{13}C NMR (100.61 MHz, $CDCl_3$:TFA (9:1), δ, ppm): 25.37, 65.11, 118.56, 146.92, 158.06.

PHF homopolyester. Diethyl 2,5-furandicarboxylate (4.00 g, 18.8 mmol), 1,6-HD (2.34 g, 19.8 mmol), and DBTO (24 mg, 0.5 mol %) were added to a three-neck round bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and a vacuum distillation outlet. Subsequently, the reaction mixture was degassed by three successive vacuum-nitrogen cycles at room temperature. The reaction mixture was heated at 180 °C under nitrogen for 5 h (transesterification step) and at 200 °C under vacuum for 3 h (polycondensation step). Next, the highly viscous reaction mixture was dissolved in chloroform (20 mL), and the product was precipitated in 500 mL cold methanol. The precipitate was washed with fresh methanol (2 × 100 mL) and dried under vacuum to obtain PHF as a white solid (4.40 g, 98.0% yield).

^{1}H NMR (400.13 MHz, $CDCl_3$, δ, ppm): 1.41-1.53 (m, 4H), 1.66-1.85 (m, 4H), 4.33 (t, 4H), 7.18 (s, 2H).

^{13}C NMR (100.61 MHz, $CDCl_3$, δ, ppm): 25.58, 28.54, 65.48, 118.37, 146.93, 158.17.

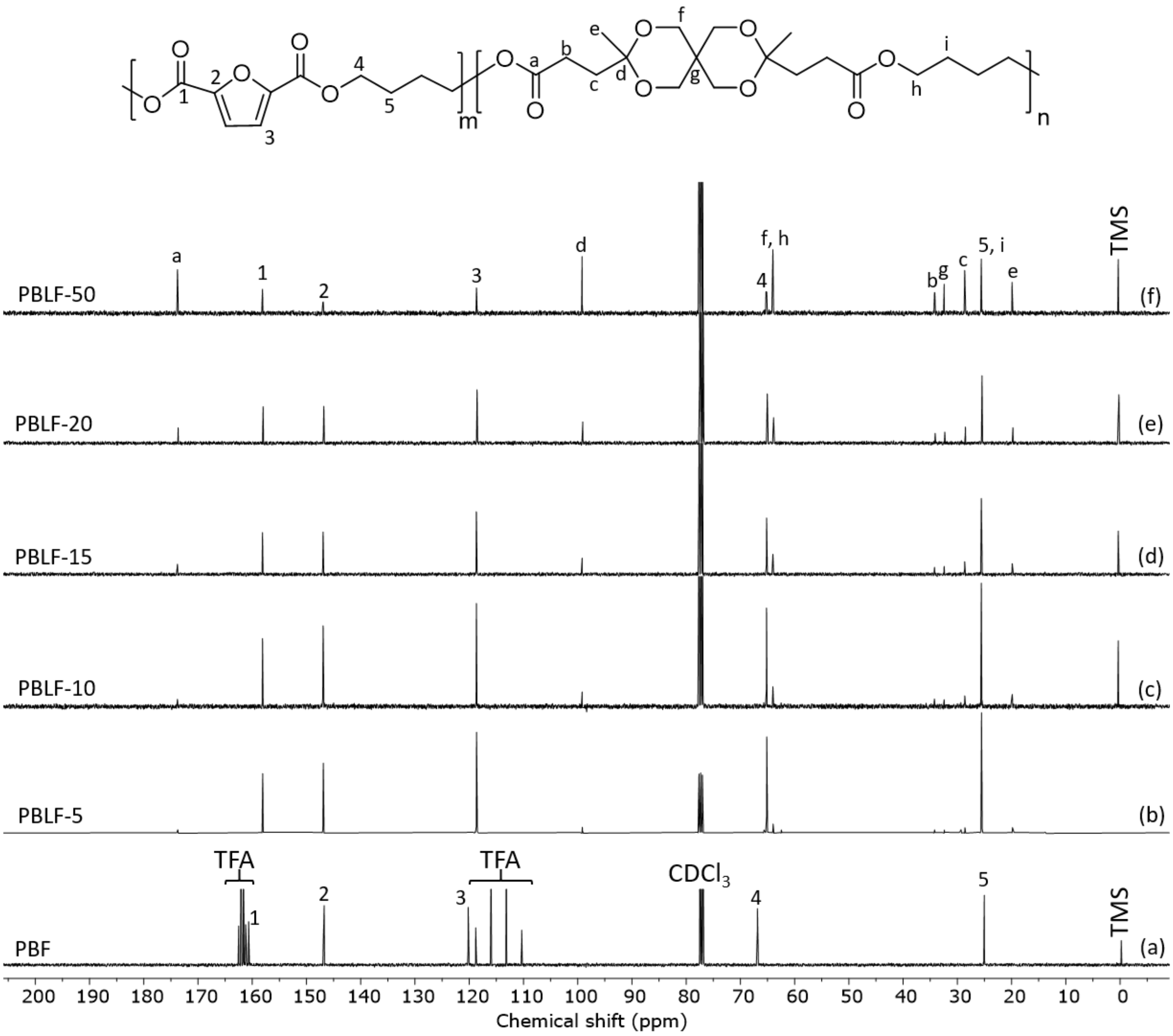


Figure S1. Stacked ^{13}C NMR spectra of samples in the PBLF series.

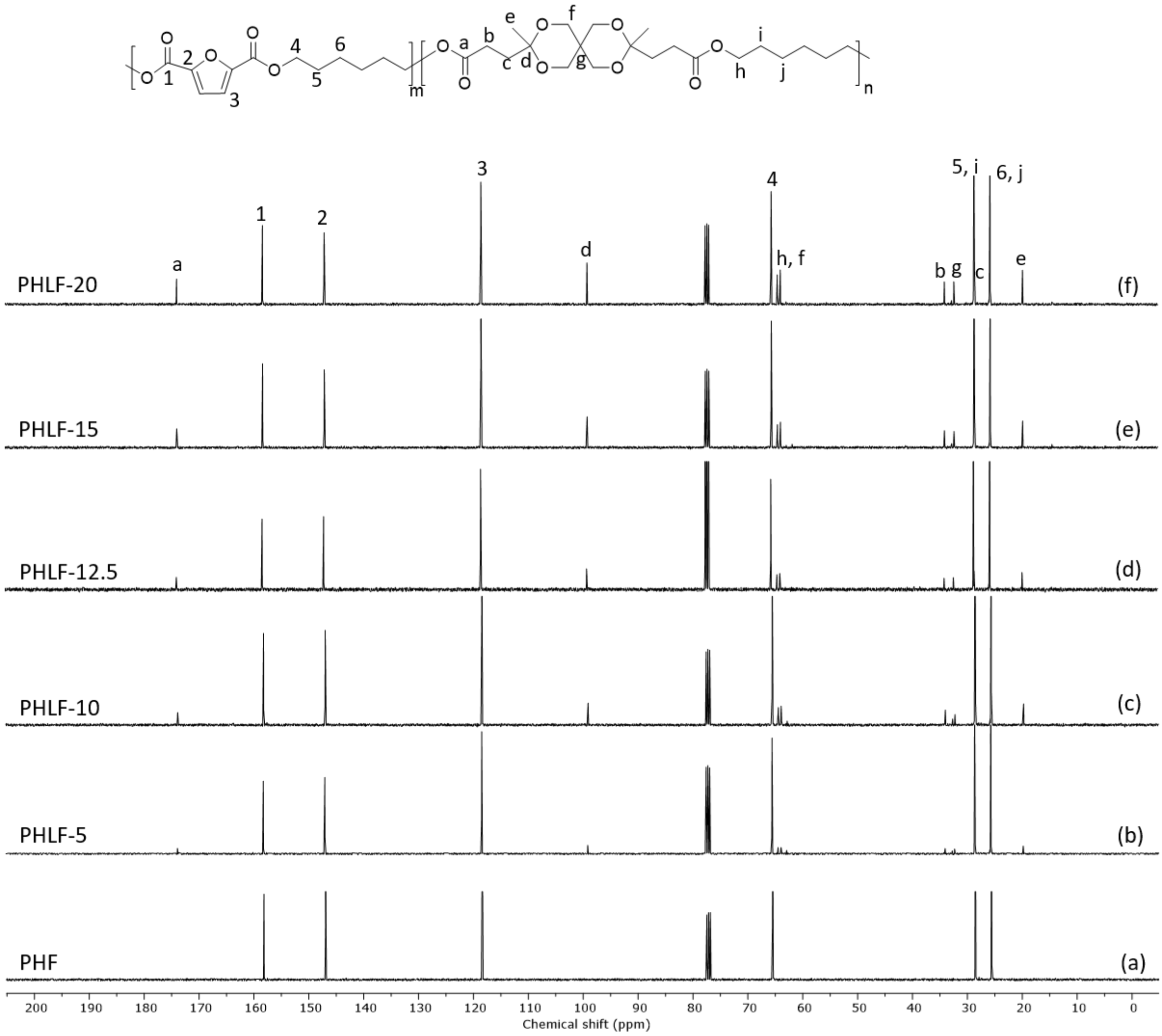


Figure S2. Stacked ^{13}C NMR spectra of samples in the PHLF series.

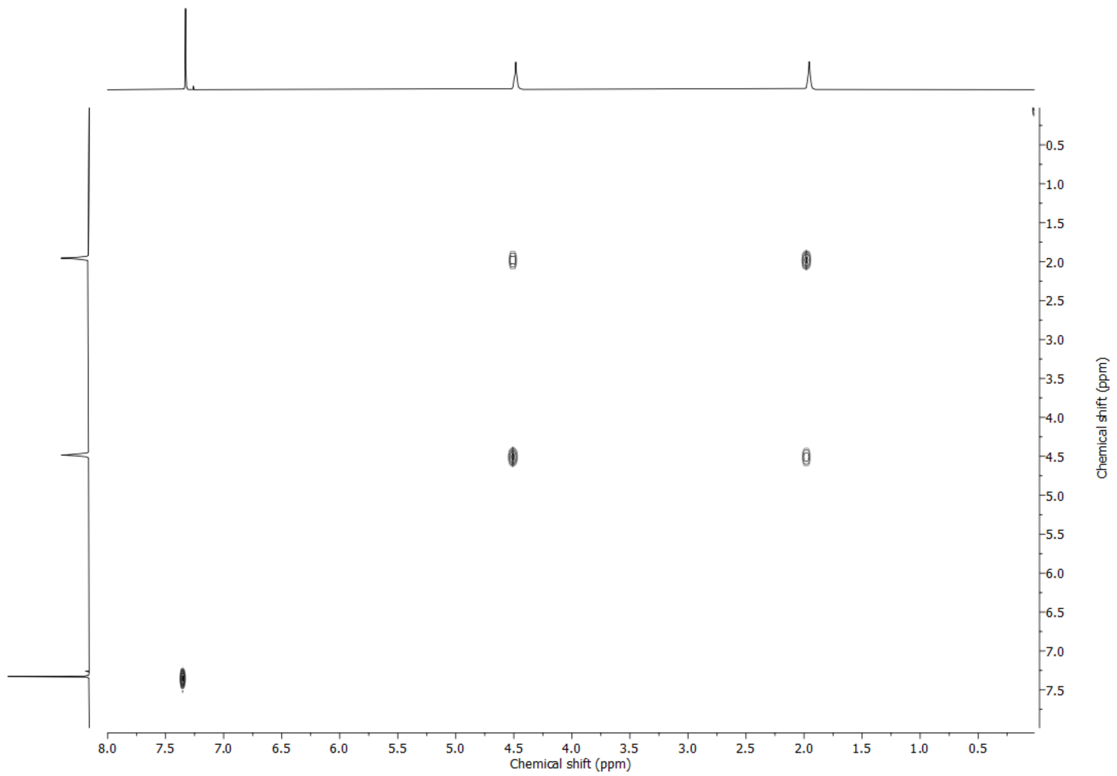


Figure S3. COSY spectrum of PBF.

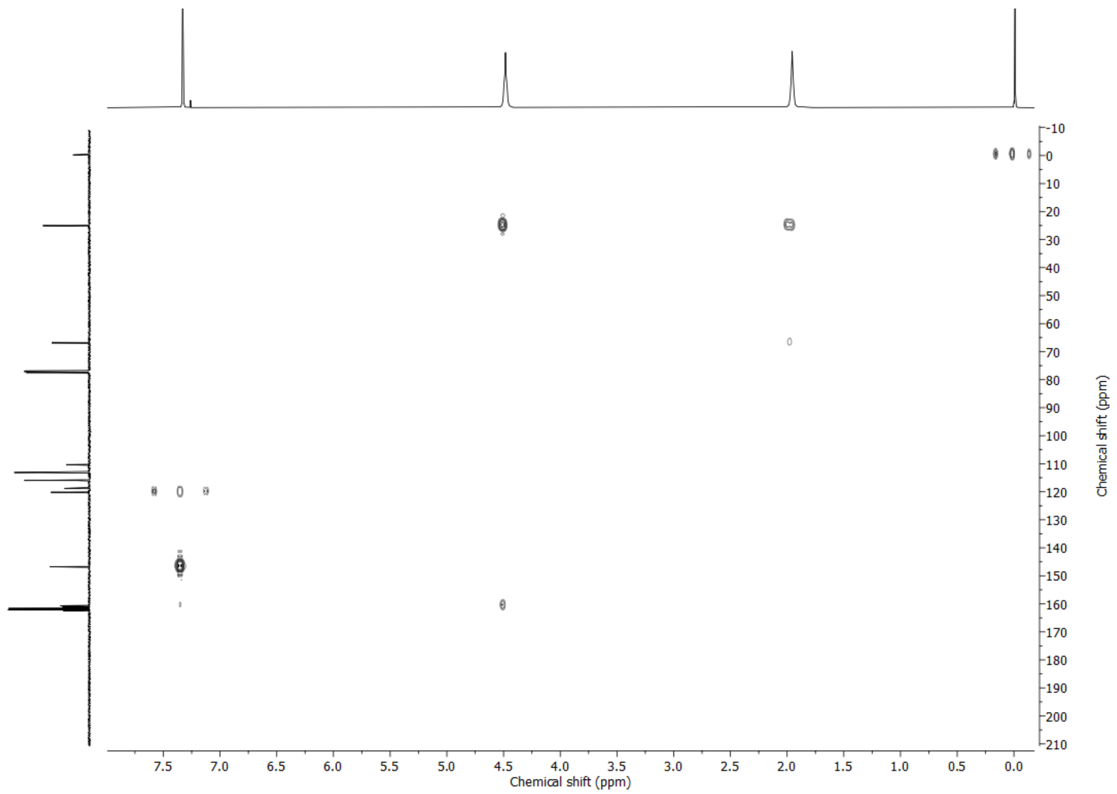


Figure S4. HMBC spectrum of PBF.

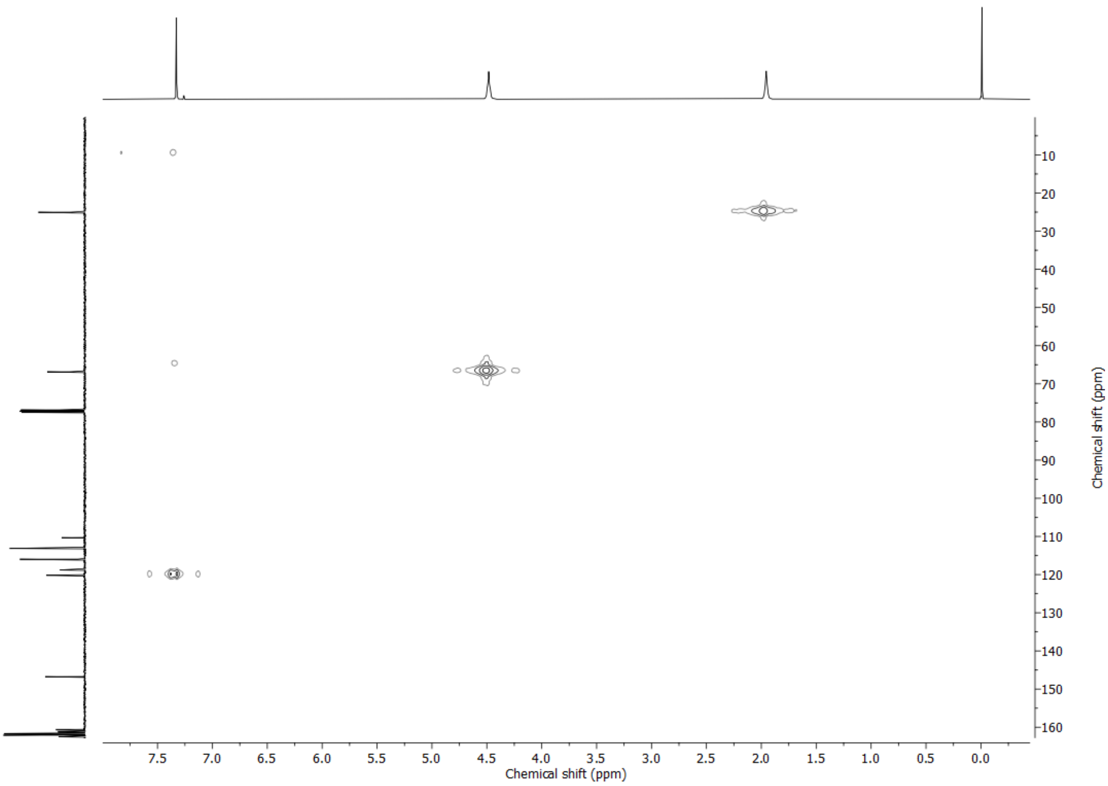


Figure S5. HMQC spectrum of PBF.

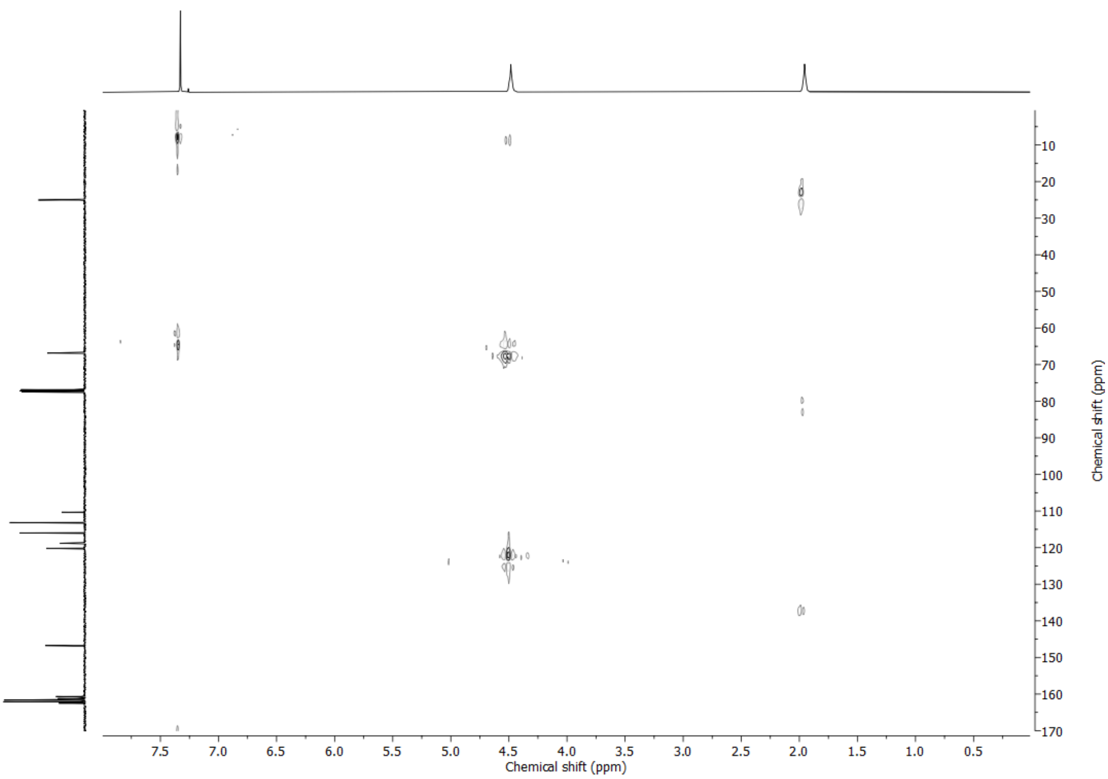


Figure S6. HSQC spectrum of PBF.

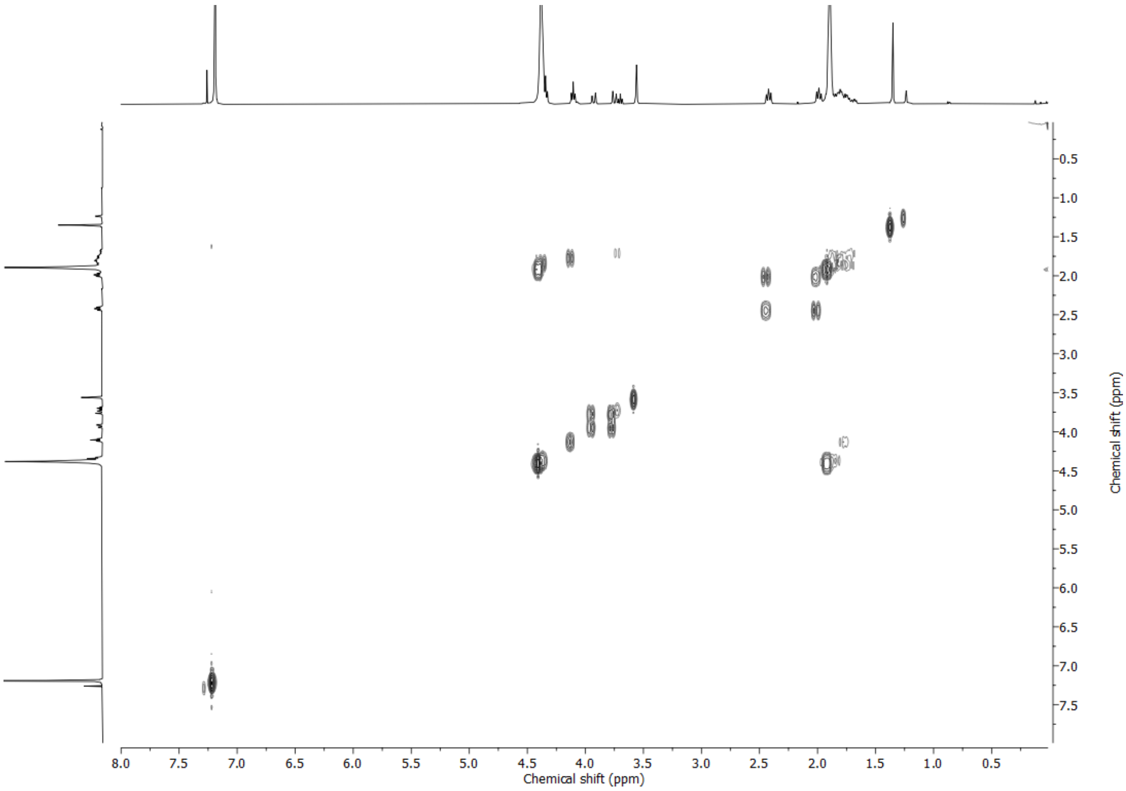


Figure S7. COSY spectrum of PBLF-10.

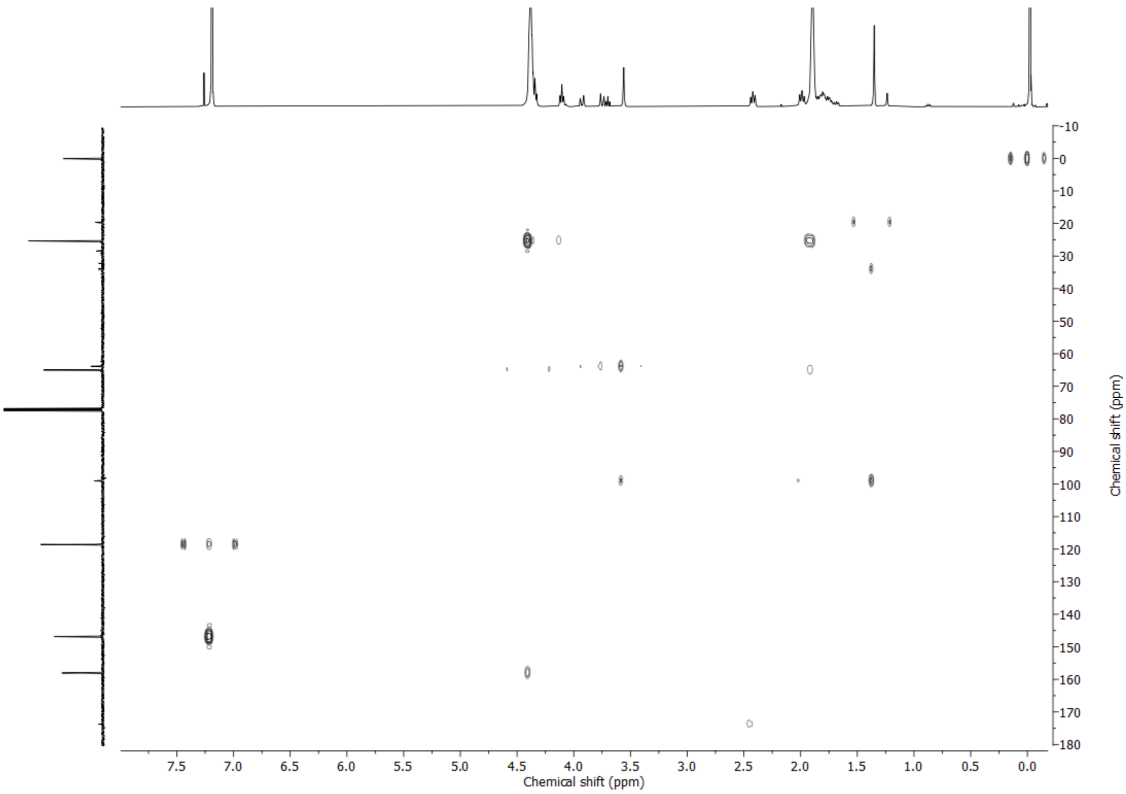


Figure S8. HMBC spectrum of PBLF-10.

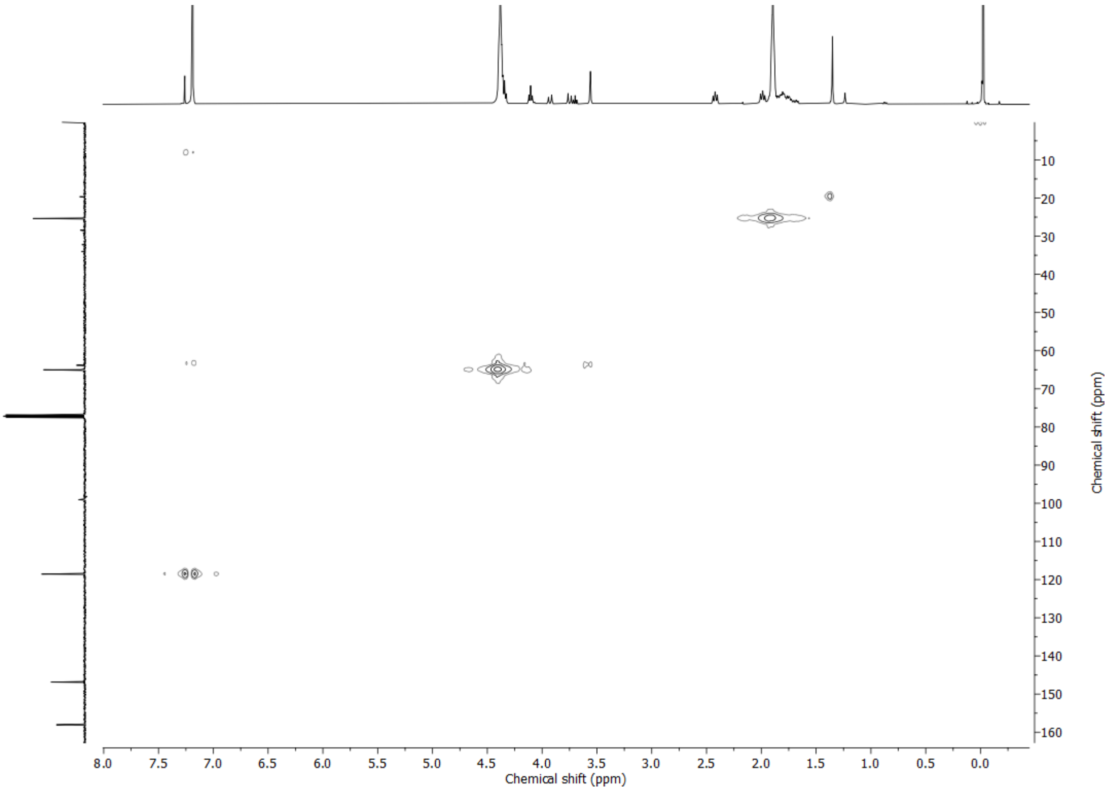


Figure S9. HMQC spectrum of PBLF-10.

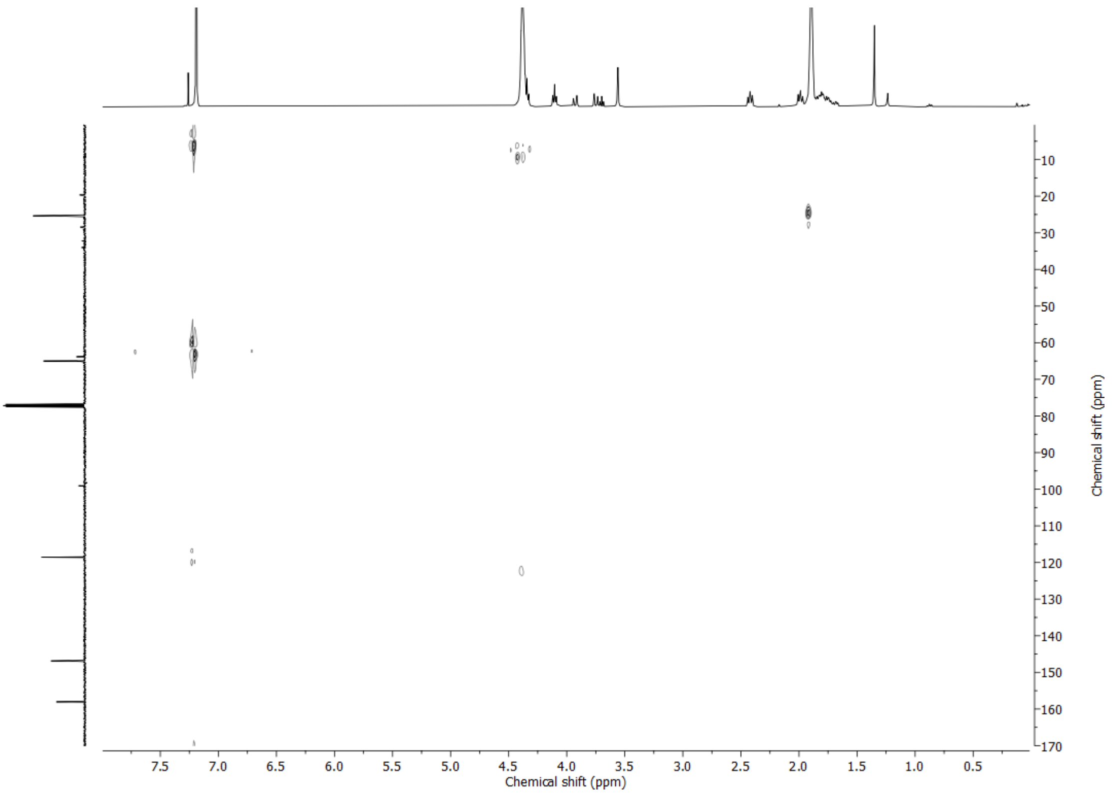


Figure S10. HSQC spectrum of PBLF-10.

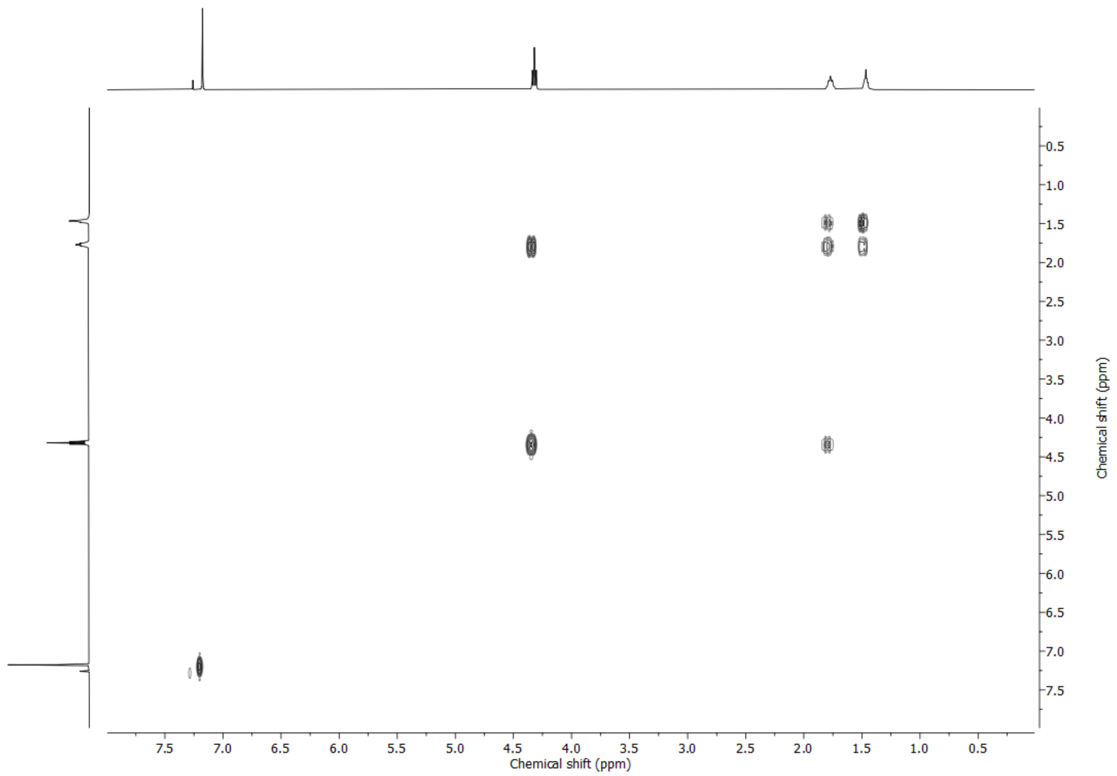


Figure S11. COSY spectrum of PHF.

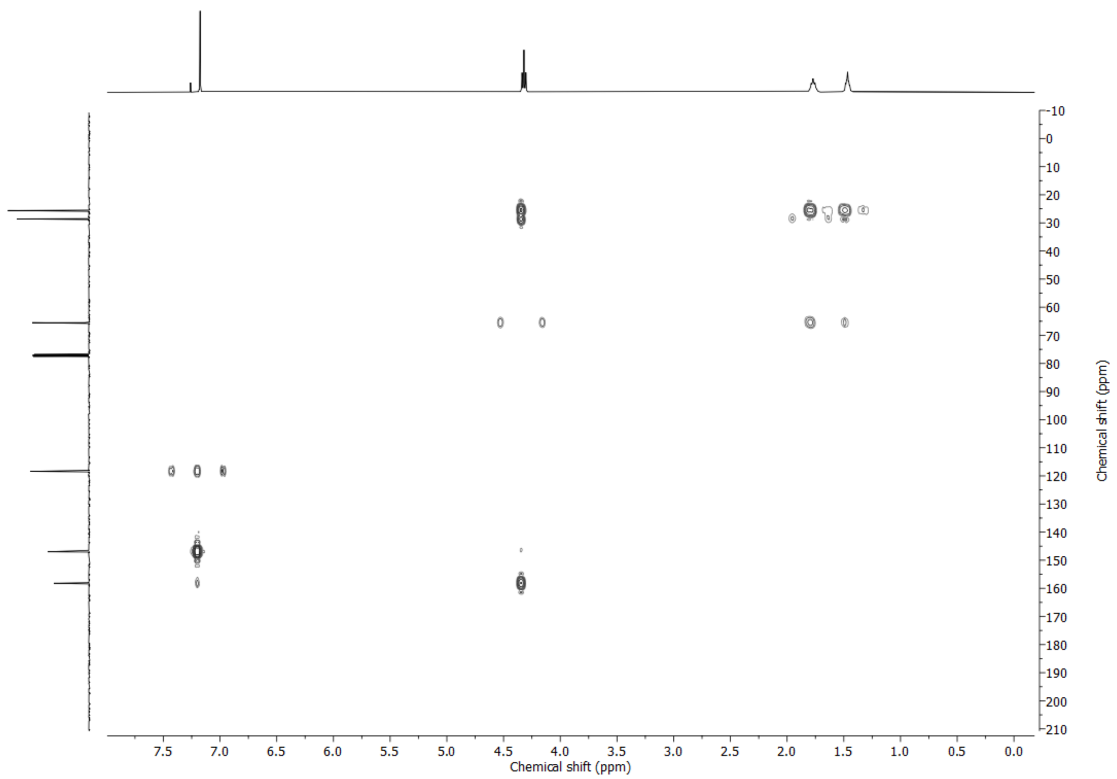


Figure S12. HMBC spectrum of PHF.

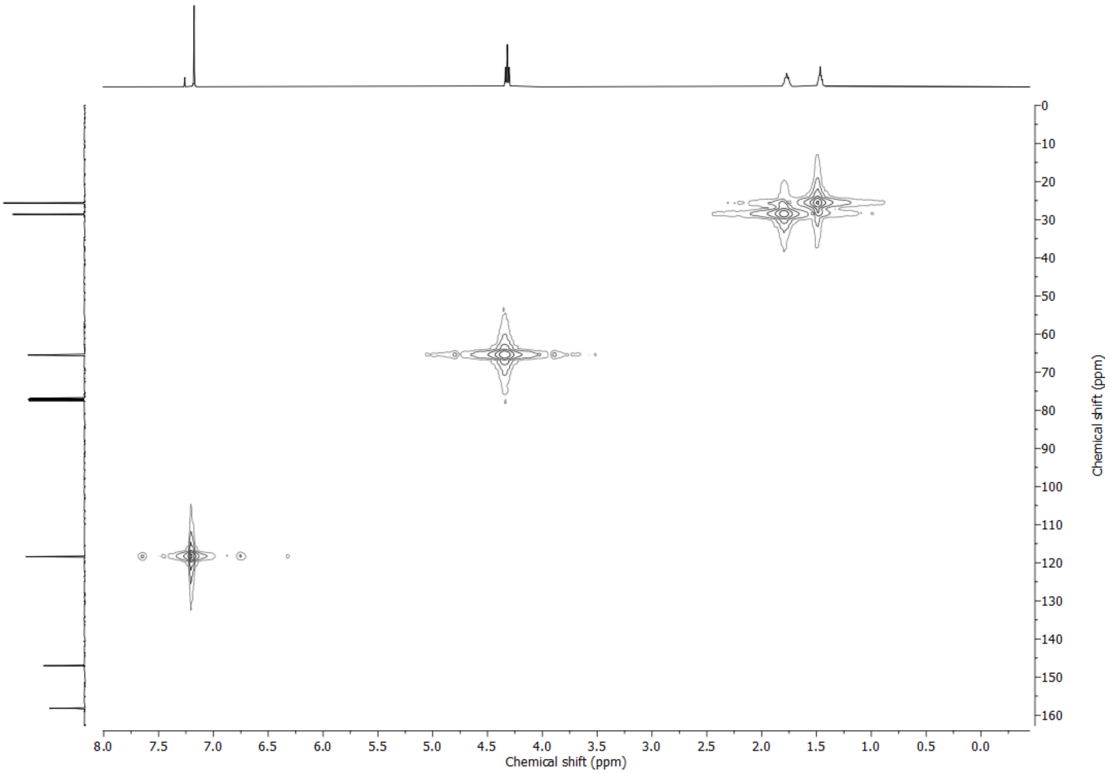


Figure S13. HMQC spectrum of PHF.

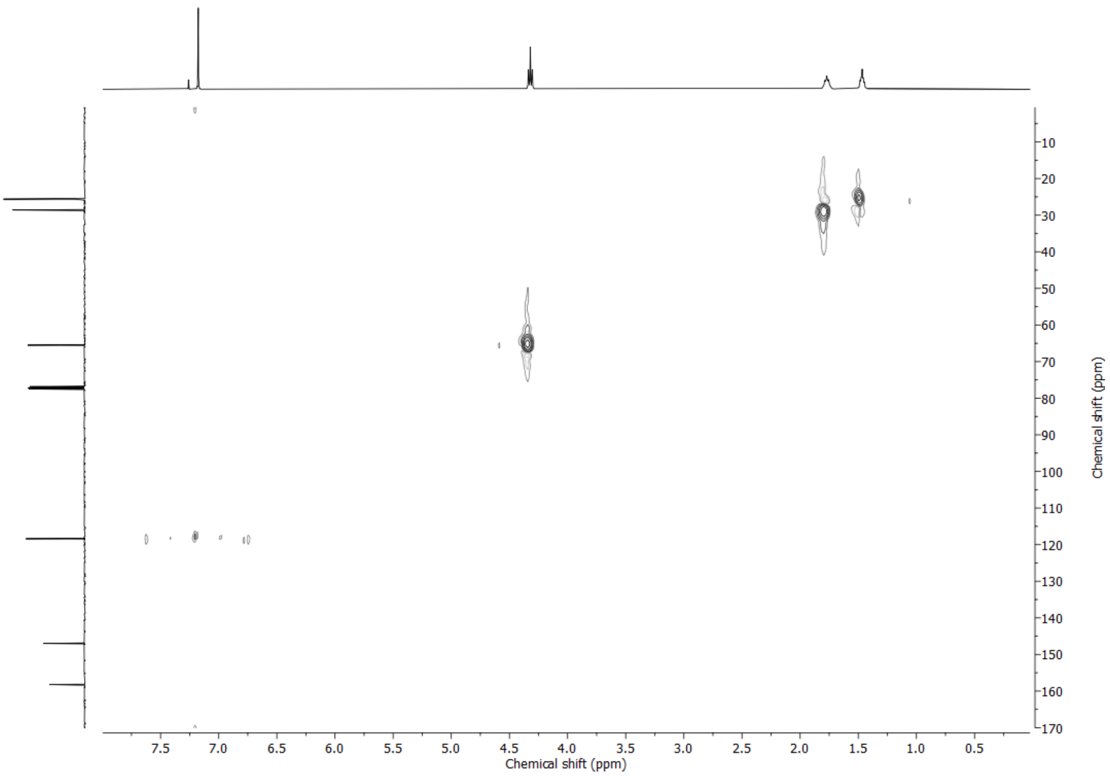


Figure S14. HSQC spectrum of PHF.

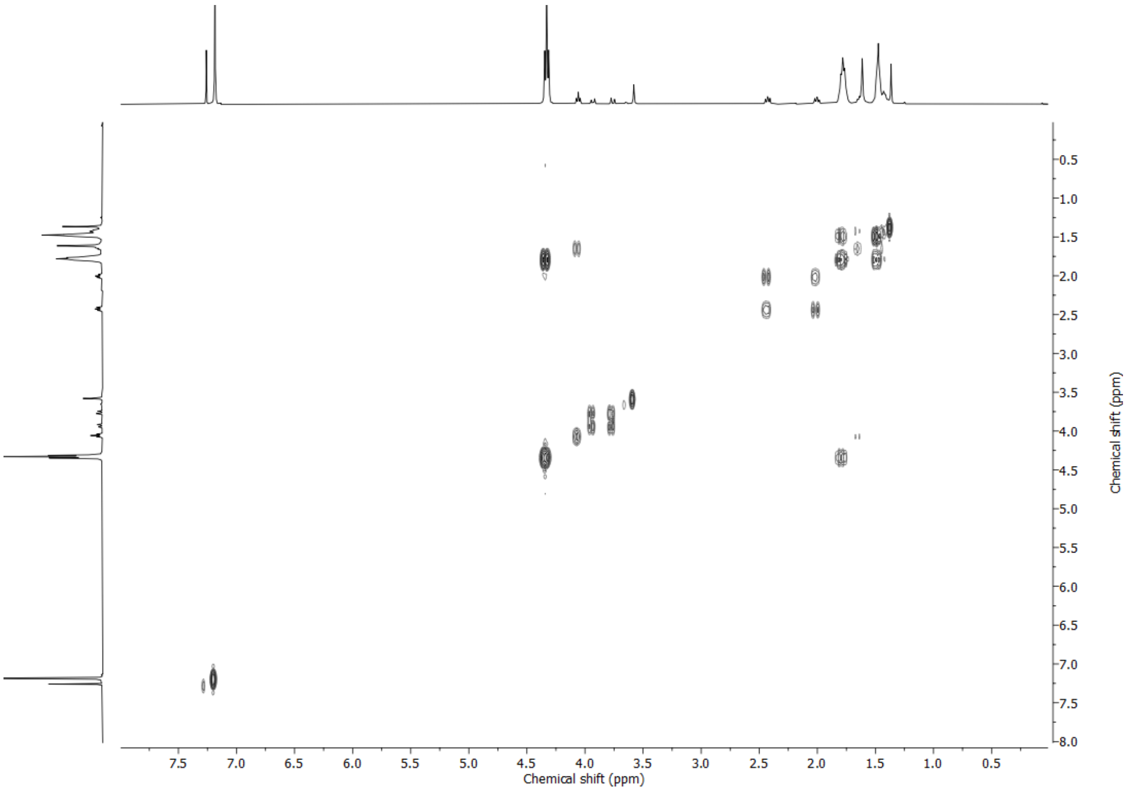


Figure S15. COSY spectrum of PHLF-10.

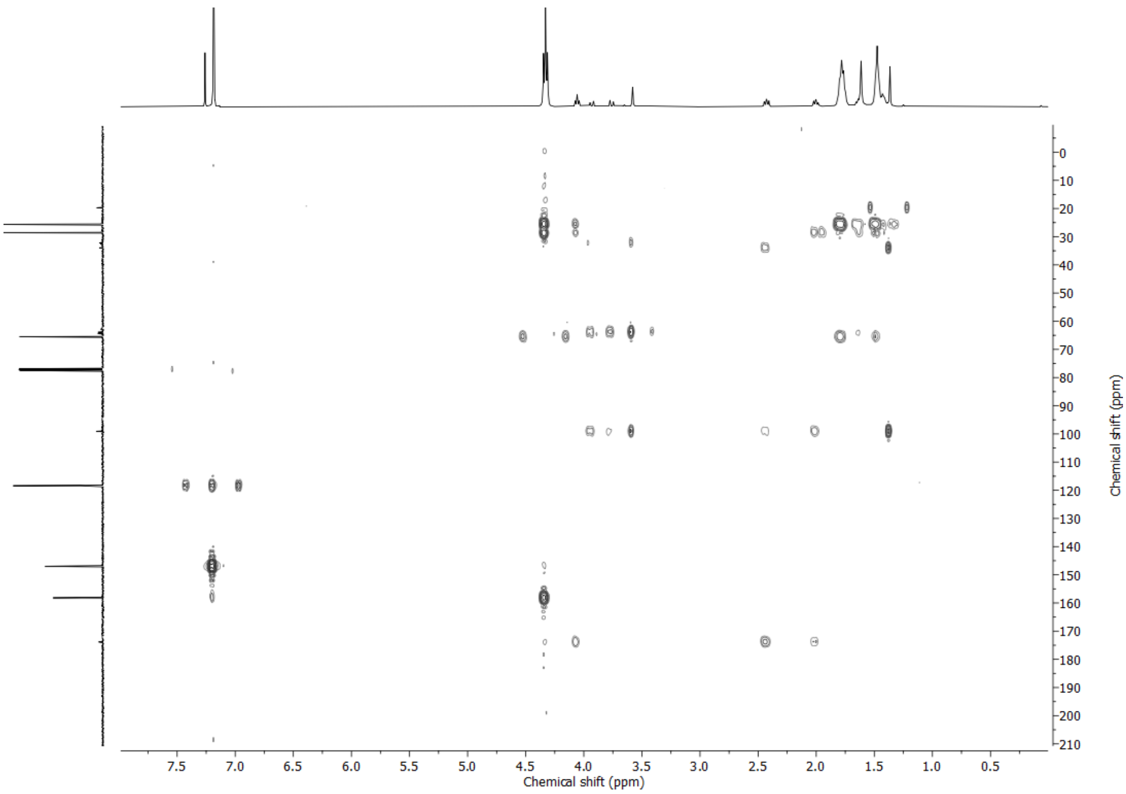


Figure S16. HMBC spectrum of PHLF-10.

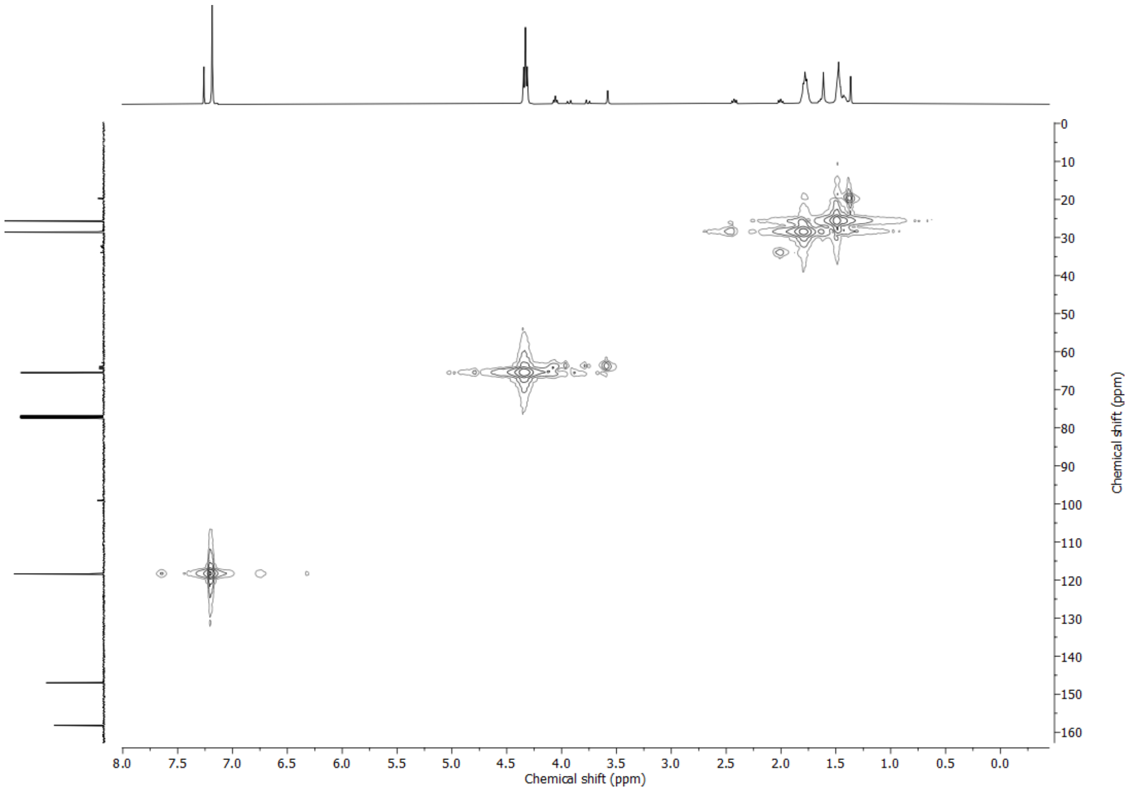


Figure S17. HMQC spectrum of PHLF-10.

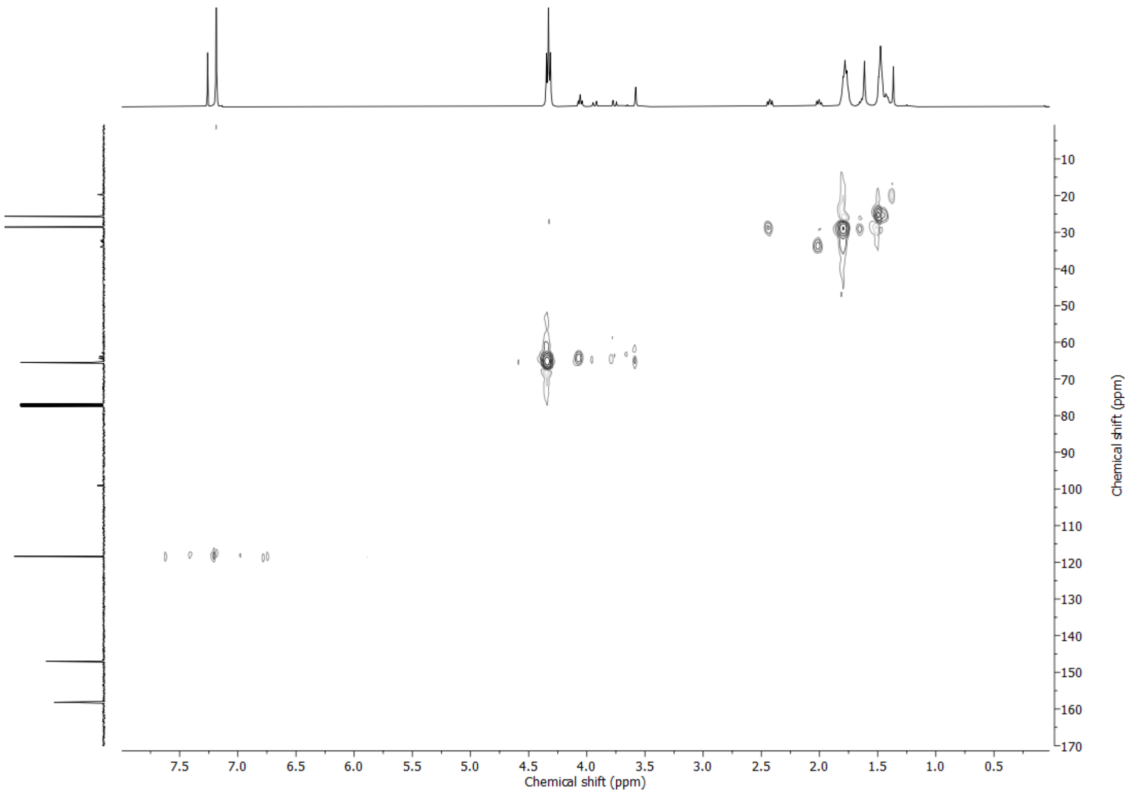


Figure S18. HSQC spectrum of PHLF-10.

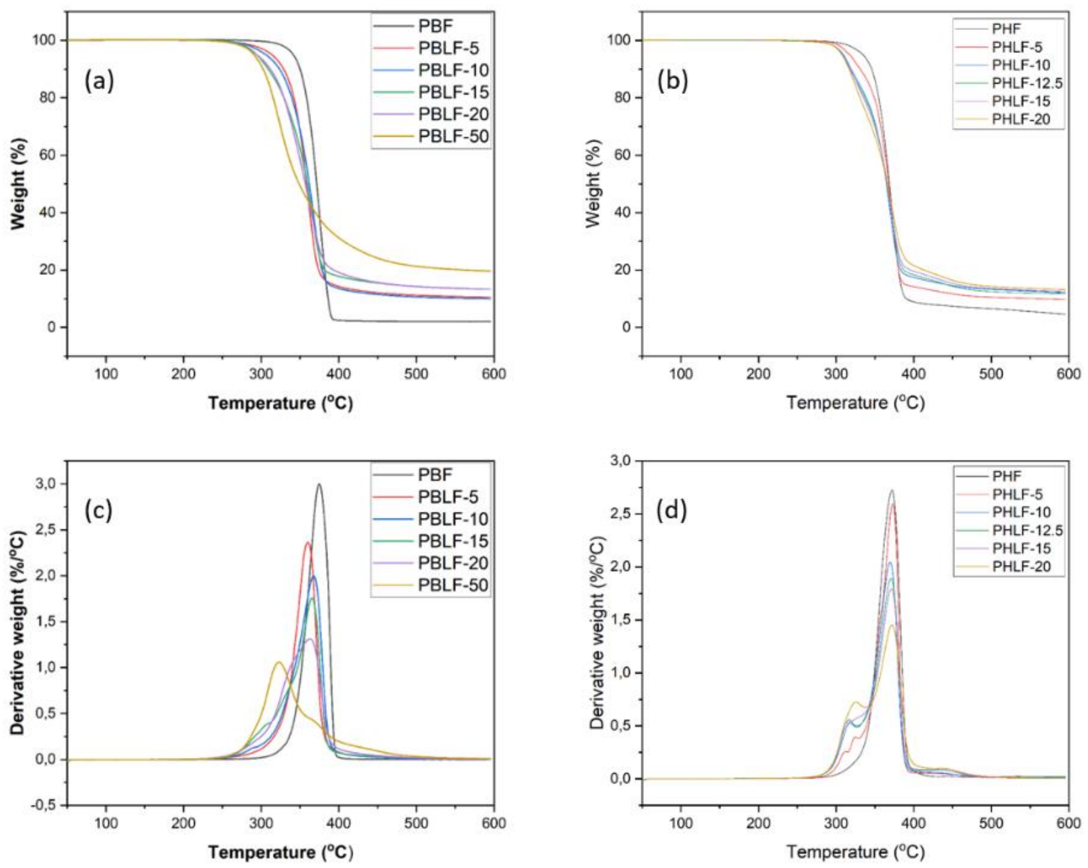


Figure S19. TGA thermograms and corresponding first derivative curves of the PBLF (a and c) and PHLF (b and d) series of copolyesters recorded under nitrogen atmosphere.

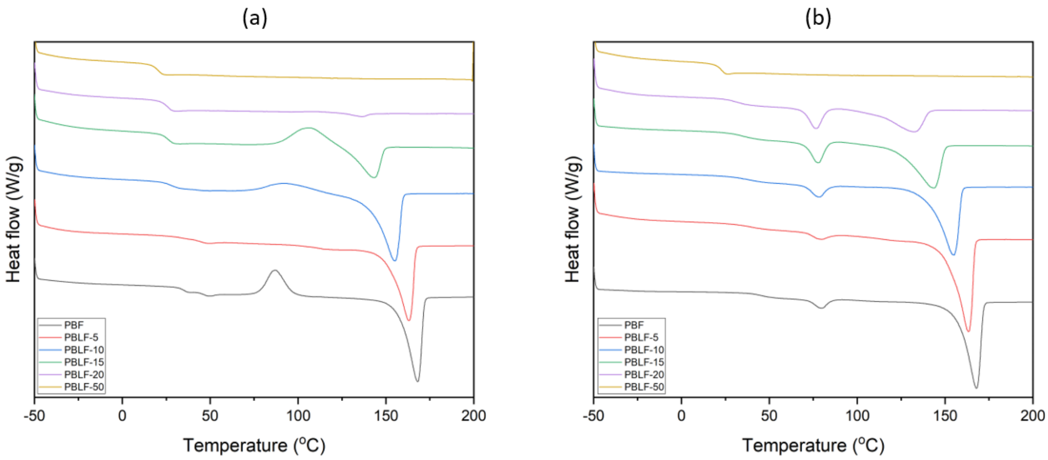


Figure S20. DSC heating traces of the polyesters in the PBLF series after storage at room temperature for 2 weeks (a) and at 50 °C during 40 h (b).

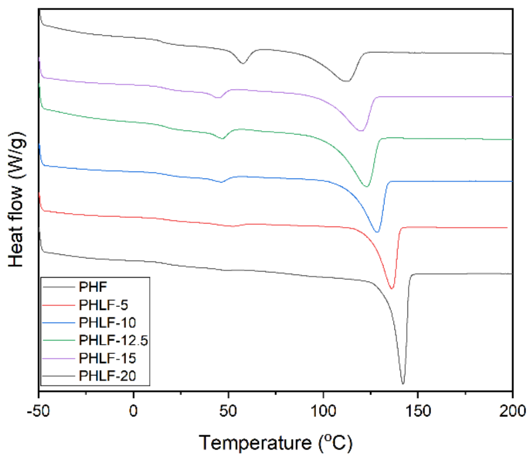


Figure S21. DSC heating traces of the polyesters in the PHLF series after storage at room temperature for 2 weeks.

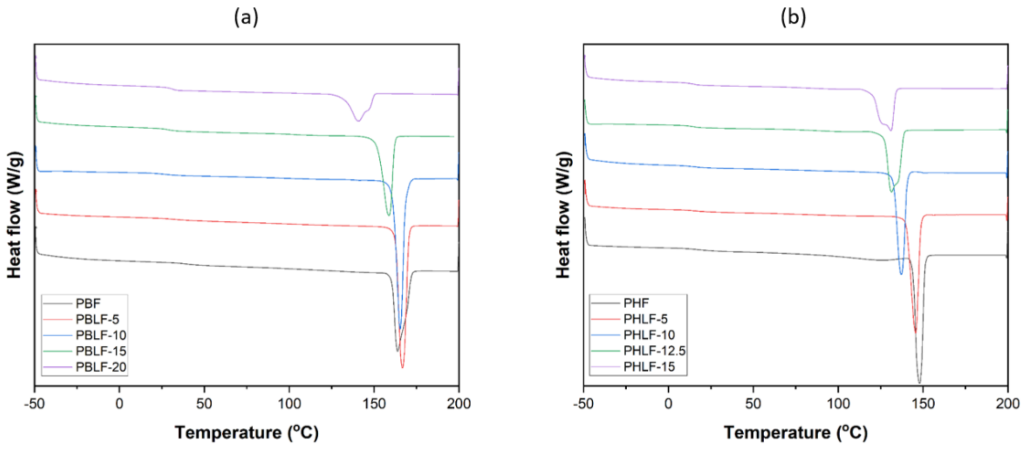
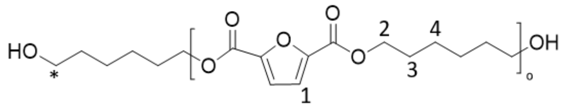


Figure S22. DSC heating traces of the polyesters in the PBLF (a) and PHLF (b) series of polyesters after annealing at approx. 10-15 °C below T_m for 4 h.

Table S1. DSC data of polymers annealed below T_m for 4 h

Polyester	T_m (°C)	Annealing temp. (°C)	T_g (°C)[a]	T_m (°C)[a]	ΔH_m (J/g)[a]
PBF	168	155	38	164	47
PBLF-5	165	150	31	167	56
PBLF-10	158	150	24	165	61
PBLF-15	150	135	28	159	42
PBLF-20	--	120	32	141	25
PHF	143	132	17	148	58
PHLF-5	136	130	18	145	68
PHLF-10	129	120	16	137	62
PHLF-12.5	125	115	15	131	51
PHLF-15	122	110	16	131	37

[a]Measured from the first heating DSC scan of the annealed samples



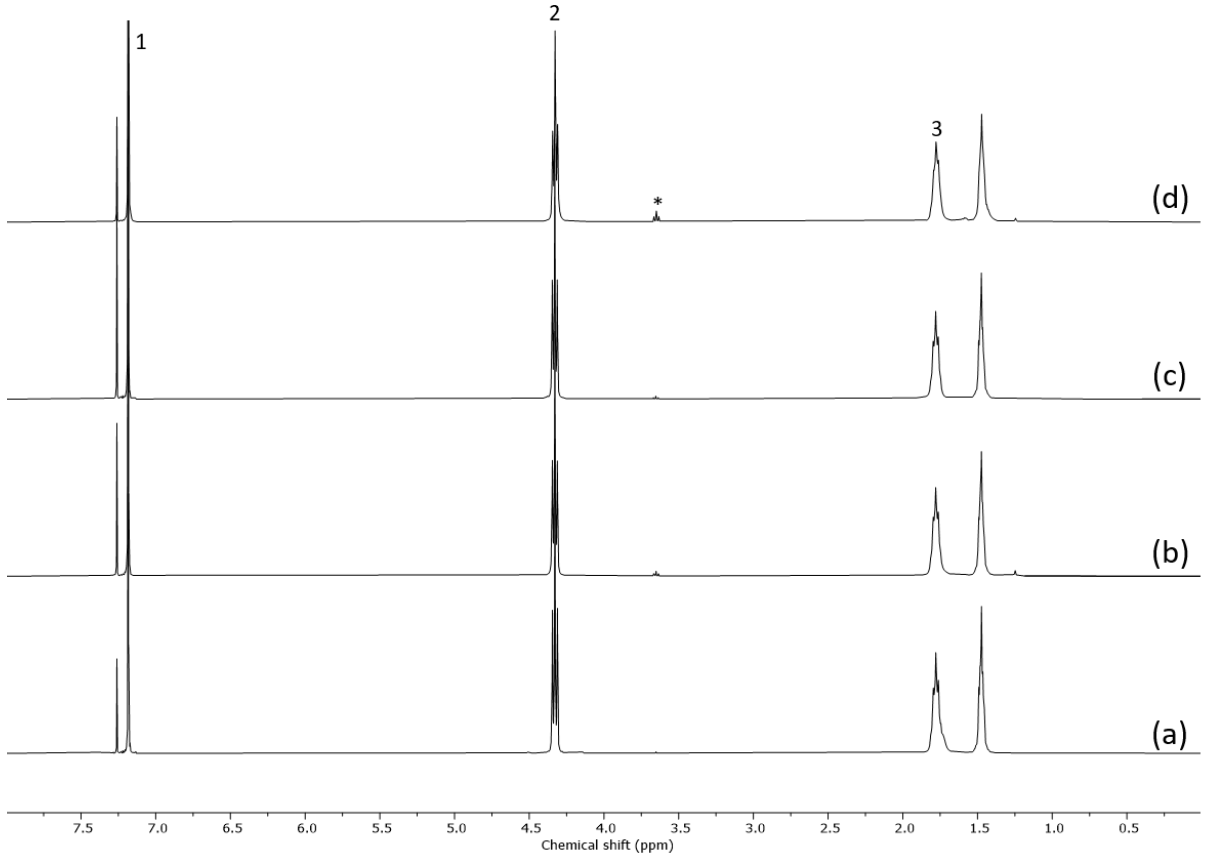


Figure S23. [1]H NMR spectra of PHF (a) and the remaining solid residues after acidic hydrolysis in 3 M (b), 6M (c) and 12 M (d) aqueous HCl at 60 °C.

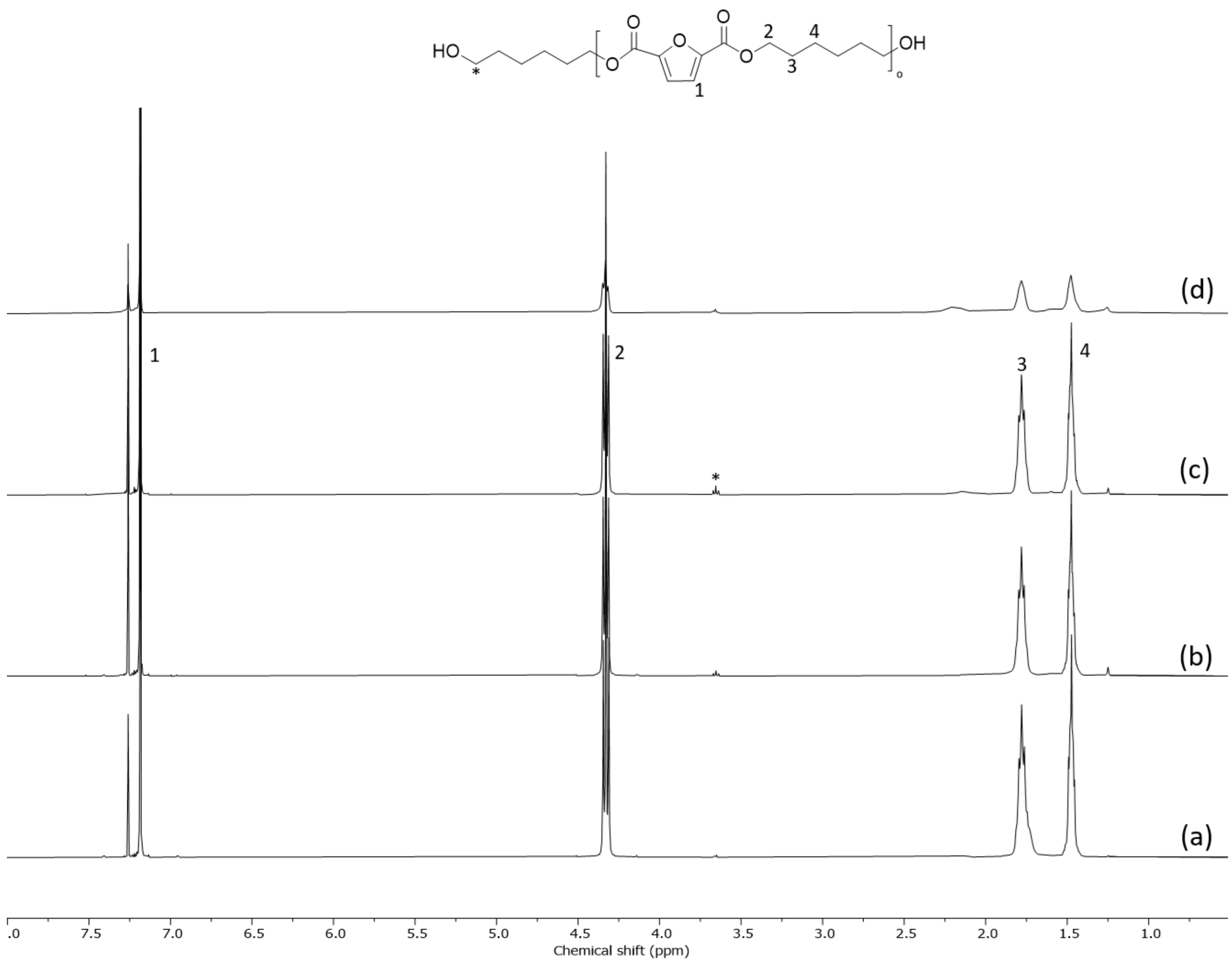


Figure S24. ^{1}H NMR spectra of PHF (a) and the remaining solid residues after acidic hydrolysis in 3 M (b), 6 M (c) and 12 M (d) aqueous HCl at 85 °C.

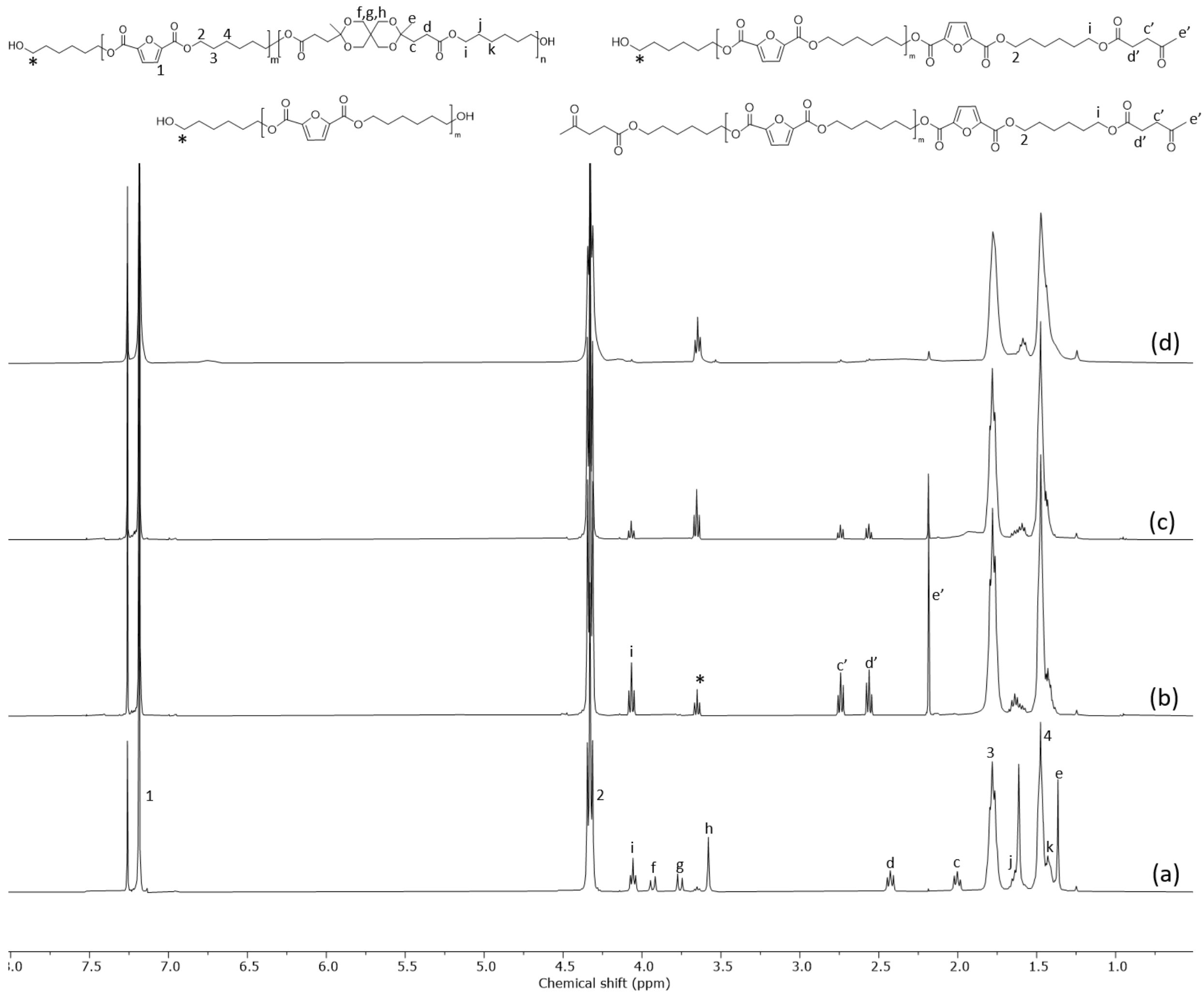


Figure S25. ^{1}H NMR spectra of PHLF-10 (a) and the remaining solid residues after acidic hydrolysis in 3 M (b), 6 M (c) and 12 M (d) aqueous HCl at 60 °C.

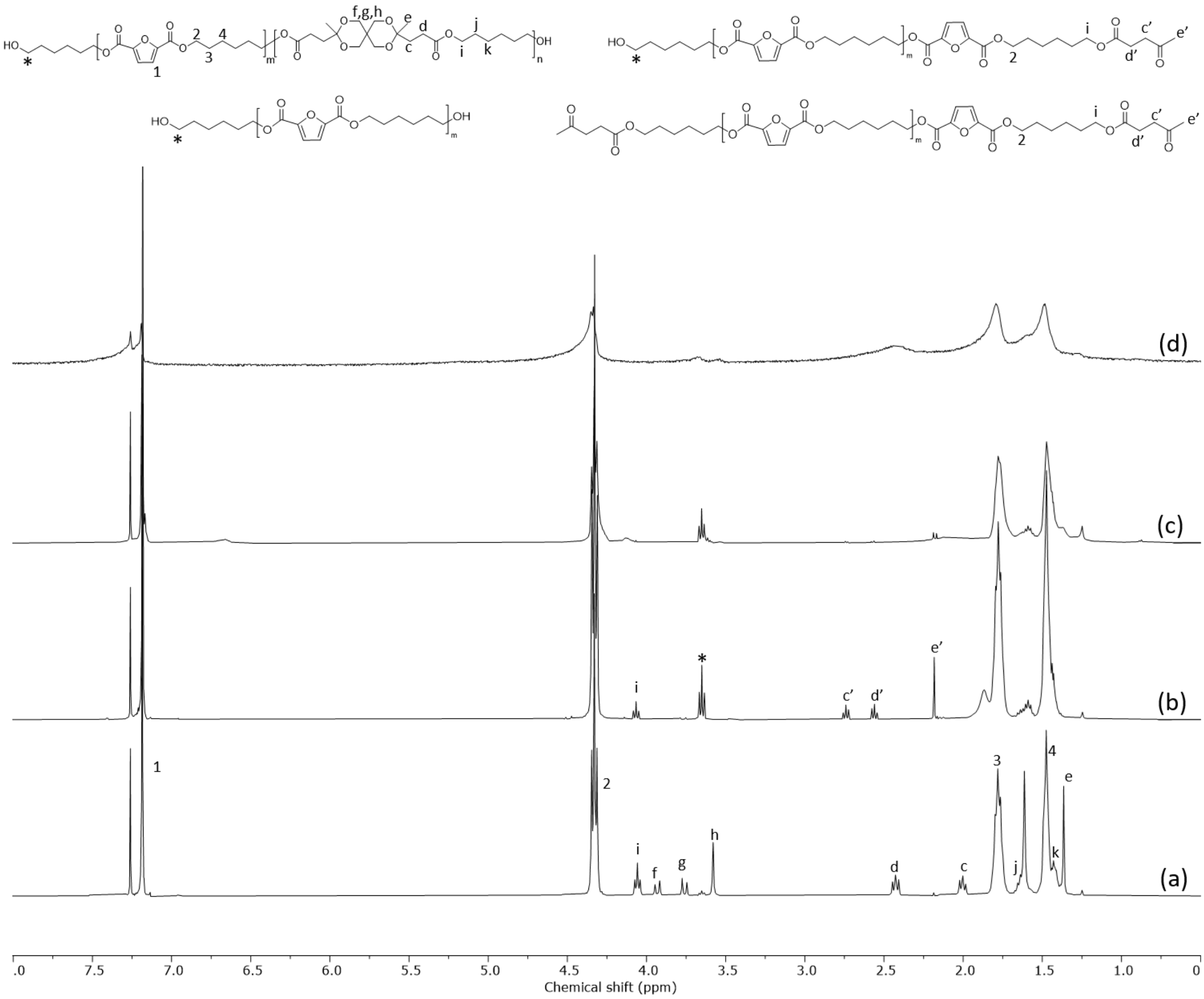


Figure S26. ^{1}H NMR spectra of PHLF-10 (a) and the remaining solid residues after acidic hydrolysis in 3 M (b), 6 M (c) and 12 M (d) aqueous HCl at 85 °C.

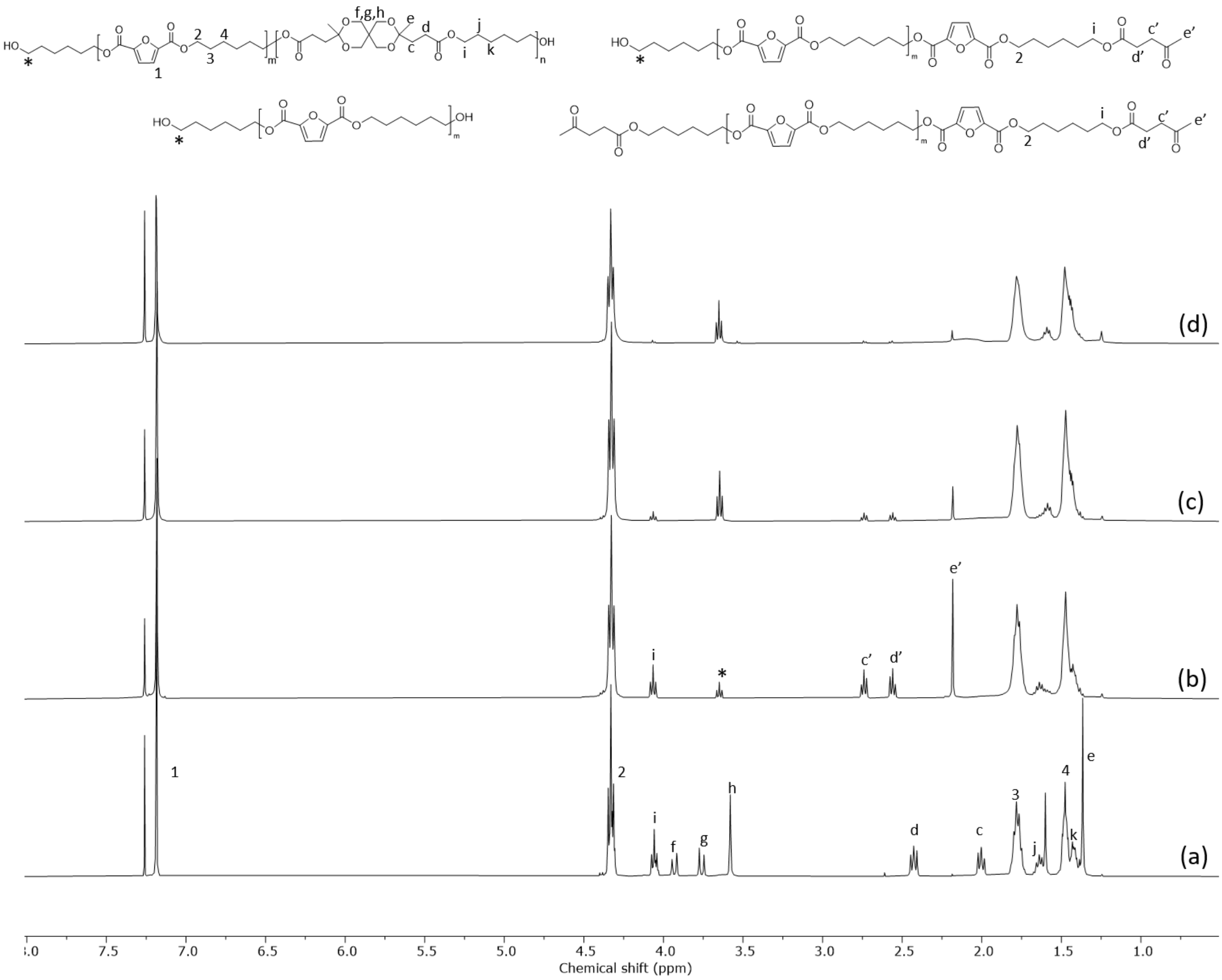


Figure S27. ^{1}H NMR spectra of PHLF-20 (a) and the remaining solid residues after acidic hydrolysis in 3 M (b), 6 M (c) and 12 M (d) aqueous HCl at 60 °C.

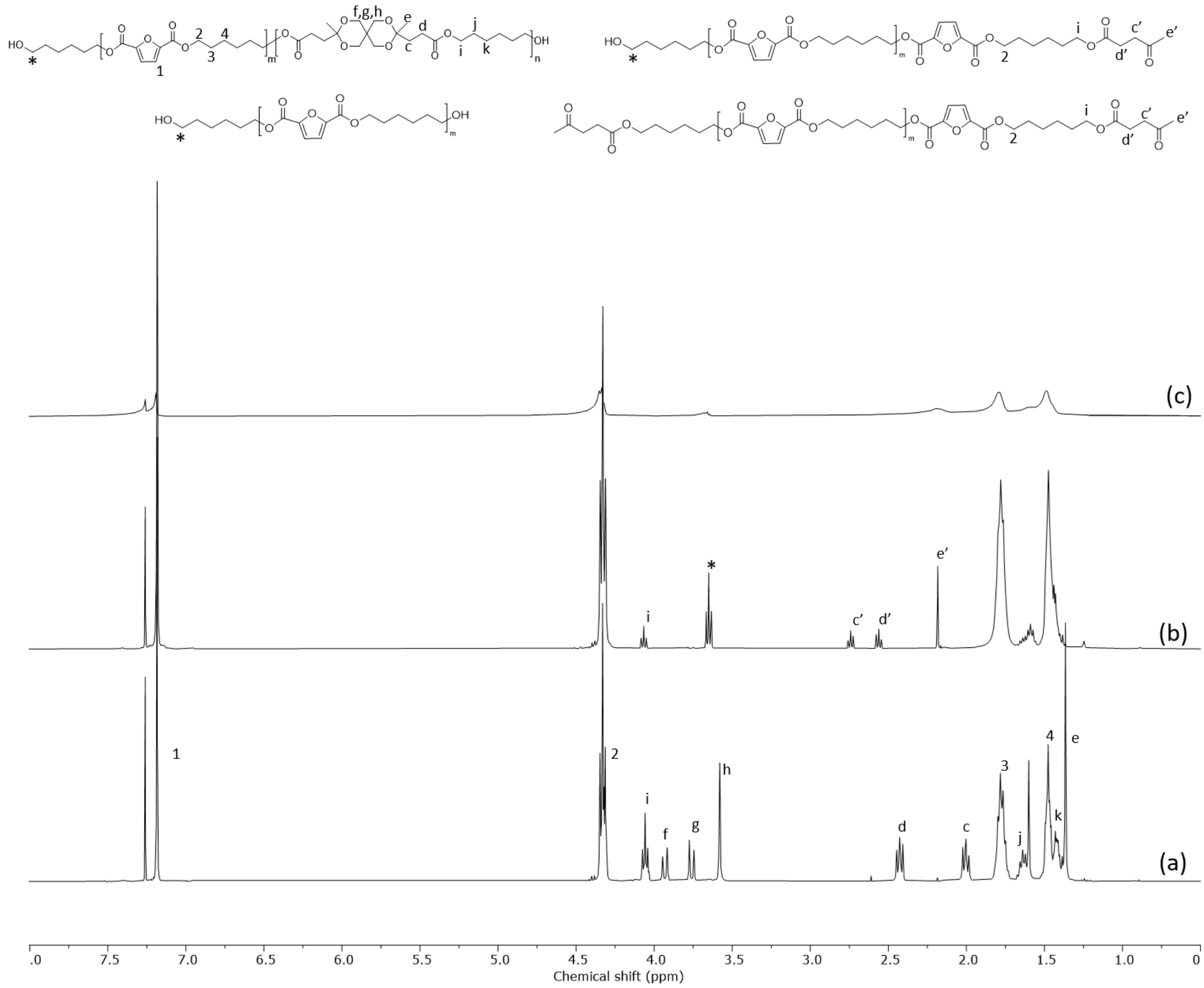


Figure S28. ^{1}H NMR spectra of PHLF-20 (a) and the remaining solid residues after acidic hydrolysis in 3 M (b) and 6 M (c) aqueous HCl at 85 °C.

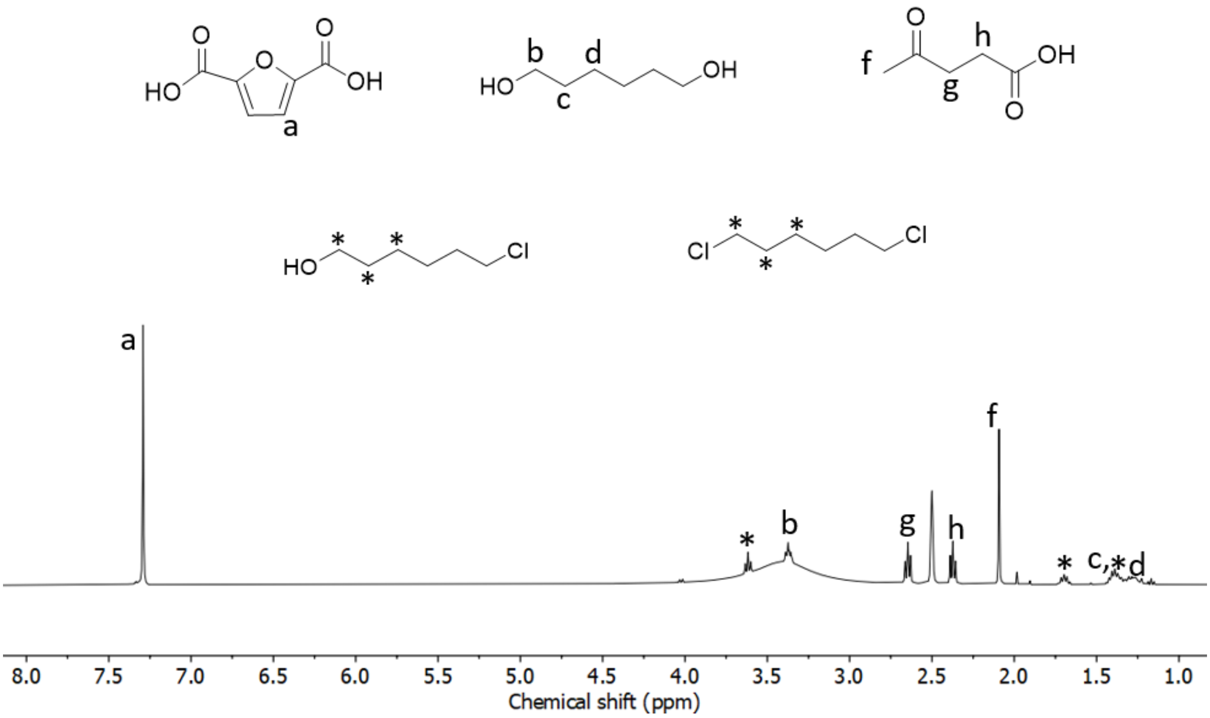


Figure S29. [1]H NMR spectrum recorded of the crude product extracted from the filtrate obtained after hydrolysis of PHLF-20 in 12 M aqueous HCl at 85 °C during 24 h. Signals originating from the original building block and monomers of PHLF-20, i.e., 2,5-furandicarboxylic acid, 1,6-hexanediol, and levulinic acid, are indicated. The signals of side products (1,6-dichlorohexane or 1-chlorohexanol) are denoted by asterisk (*).

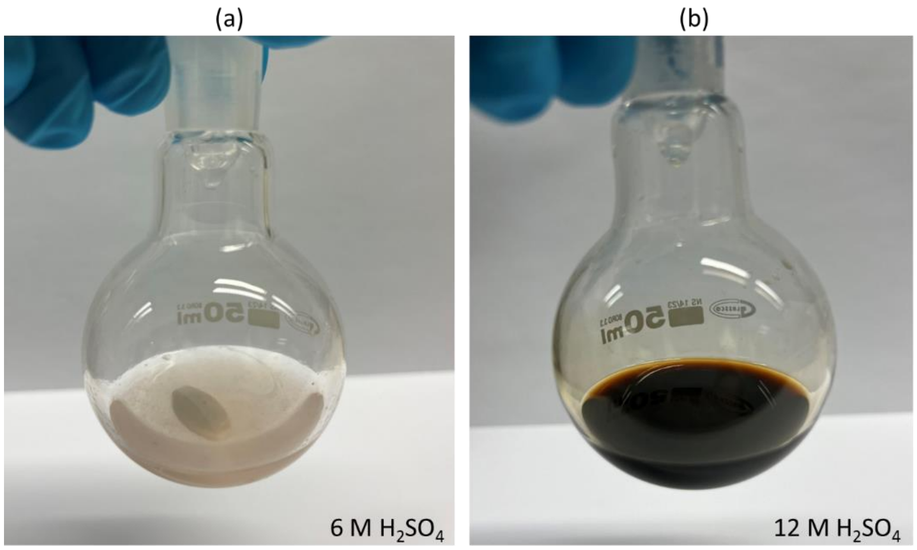


Figure S30. Photographs showing the reaction mixtures after the hydrolysis PHLF-20 in 6 M (a) and 12 M (b) aq. H_2SO_4 at 85 °C after 24 h.

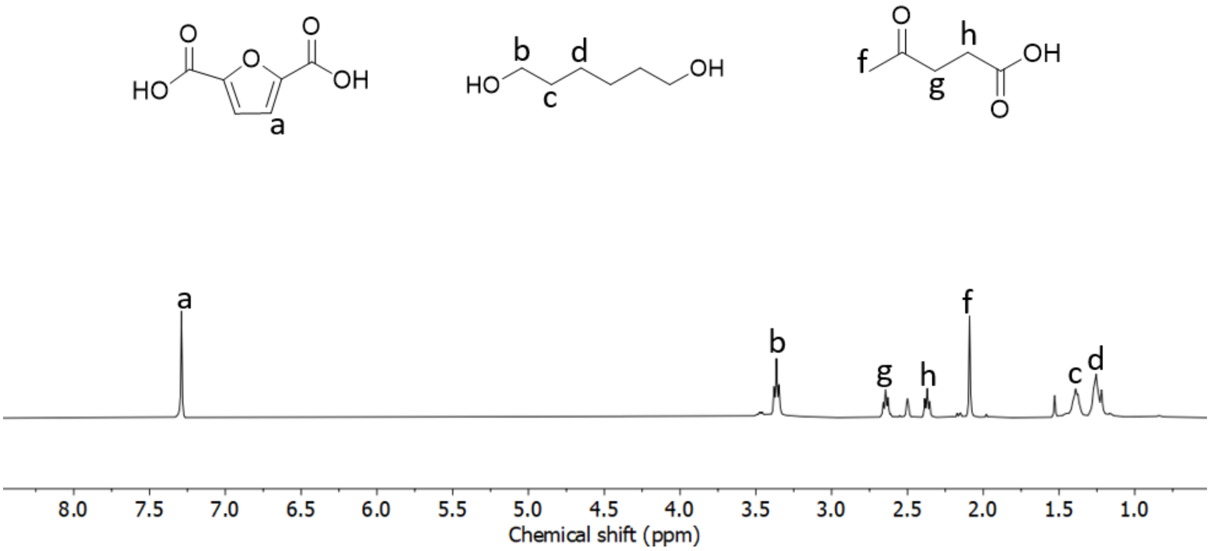


Figure S31. [1]H NMR spectrum recorded of the crude product extracted from the filtrate obtained after hydrolysis of PHLF-20 in 6 M aqueous H_2SO_4 at 85 °C after 24 h. Signals originating from the original building block and the monomers of PHLF-20 are indicated.

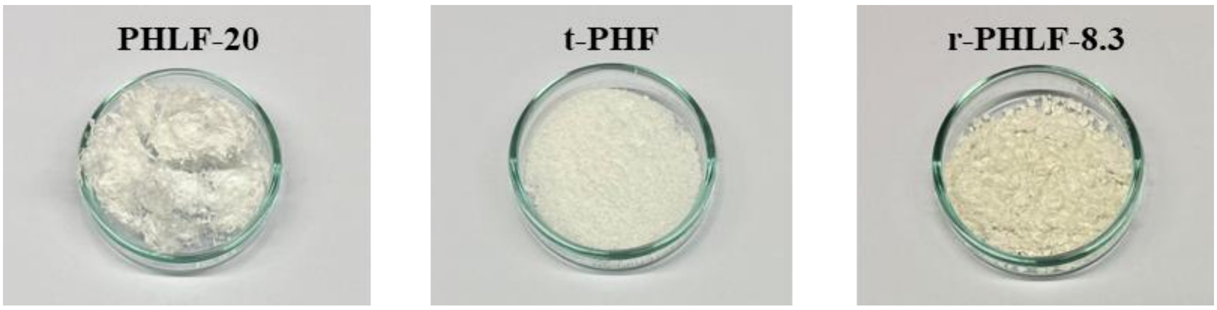


Figure S32. Photographic images of initial PHLF-20, t-PHF and r-PHLF-8.3 obtained after the repolymerization of t-PHF.