Supplementary Information (SI) for RSC Sustainability.

Supporting Information

Highly efficient mechanochemical depolymerisation of bio-based polyethylene furanoate and polybutylene furanoate

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General Information

Unless otherwise indicated, all commercially available starting materials and solvents were purchased and used as received without further purification. **$FuMe_2$** used for polymer synthesis was purchased from BLD pharm. Polyethylene furanoate (PEF) and polybutylene furanoate (PBF) were prepared using the procedure reported below. Sodium methoxide was freshly prepared by adding 0.5 g Na to 10 mL of MeOH solvent, followed by evaporation of the excess solvent in vacuum.

Melt polycondensations were carried out in a 2.4 L-stirring autoclave (Juchheim, Bernkastel Kues, Germany).

NMR spectra of PEF and PBF were recorded on an Avance III 500 NMR spectrometer (Bruker Biospin, USA) at 303 K in $CDCl_3$/TFA-*d* (v/v = 4:1) as the solvent. Chemical shifts are reported in ppm (δ) and were referenced to residual $CHCl_3$ (δ_H = 7.26 ppm).

SEC analysis was performed using a modular SEC consisting of an HPLC pump (1200 series, Agilent Technologies, USA), separation column PL MiniMIX-D (Agilent Technologies, USA), and differential refractometer (Knauer, Berlin, Germany). PFP/$CHCl_3$ (v/v = 1:2) was used as the eluent with a flow rate of 0.3 mL min^{-1} at a temperature of 45 °C. Narrowly dispersed polystyrene samples were employed as a standard for the calculation of the relative molar masses.

DSC analysis was carried out with a Q2000 (TA Instruments, New Castle, DE, USA) in a temperature range of −80 to 250 °C at a scan rate of 10 K min^{-1} using nitrogen as purge gas. The first heating, cooling and second heating runs were recorded. The examined sample amount was 5 mg.

TGA analysis was carried out with a Q5000 (TA Instruments, New Castle, DE, USA) with a heating rate of 10 K min^{-1} in the temperature range of 40–800 °C with nitrogen as purge gas and a sample quantity of 5 mg.

NMR spectra of depolymerisation products were recorded on AV300 and AV400 spectrometer (Bruker Biospin, USA) at 297 K in DMSO-d_6 as the solvent. Chemical shifts are reported in ppm (δ) and were referenced to residual DMSO-h_6 (δ_H = 2.50 ppm, δ_C = 39.5 ppm). 20 mg of the respective compound were dissolved in 0.4 mL of DMSO-d_6 and were used for ^1H and ^{13}C NMR analysis.

IR spectra were recorded on a Bruker Alpha FT-IR, ATR spectrometer.

ICP-OES analysis of PEF and a depolymerised sample was done using a Varian/Agilent 715-ES instrument.

Ball milling experiments were carried out with a *Retsch* MM400 (Retsch GmbH, Retsch-Allee 1-5, 42781 Haan, Deutschland) ball mill using 10 mL jar for small scale reaction and 25 mL stainless steel jar for high scale reaction. ZrO_2-Y (zirconia dioxide stabilized with Yttria) and stainless-steel milling jars (10 mL), ZrO_2-Y (10 mm) and stainless steel (10 mm, 15 mm) milling balls were used as milling equipment. Further details about the ball milling equipment used for the optimised reaction conditions are given below.

Small scale hydrolysis reaction	
Length of the Jar	49 mm
Diameter of the Jar	19 mm
Diameter of the ball	10 mm
Weight of one ball	4.0 g
Number of balls	1

Large scale hydrolysis reaction	
Length of the Jar	≈58 mm
Diameter of the Jar	26 mm
Diameter of the ball	15 mm
Weight of one ball	13.1 g
Number of balls	2

Small scale methanolysis reaction	
Length of the Jar	49 mm
Diameter of the Jar	19 mm
Diameter of the ball	15 mm
Weight of one ball	13.1 g
Number of balls	1

Large scale methanolysis reaction	
Length of the Jar	≈58 mm
Diameter of the Jar	26 mm
Diameter of the ball	15 mm
Weight of one ball	13.1 g
Number of balls	1

Synthesis and characterisation of polymers

General procedure: Dried monomers and catalysts were added to the pre-heated (150 °C) autoclave under nitrogen counterflow. After three cycles of evacuation and backfilling with inert gas, the polycondensations were facilitated following a specific temperature and atmosphere regimen (for details see the tables below). After the reaction was stopped, the autoclave was cooled, and the material was mechanically removed and granulated.

PEF

Feed: dimethyl-2,5-furandicarboxylate **FuMe$_2$** (442.0 g, 2.4 mol, 1.0 equiv.), 1,2-ethylene glycol **EG** (328.0 g, 5.3 mol, 2.2 equiv.), titanium tetraisopropoxide **TTIP** (0.87 g, 3.1 mmol, 400 ppm).

Table S1. Reaction conditions used for the synthesis of PEF.

Stage	Temperature [°C]	Time [min]	Atmosphere
1	25 to 150	10	Nitrogen flow
2	150	120	Nitrogen flow
3	150 to 170	10	Nitrogen flow
4	170	60	Nitrogen flow
5	170 to 190	10	Nitrogen flow
6	190	60	Nitrogen flow
7	190 to 230	20	Vacuum (approx. 0.1 mbar)
8	230	120	Vacuum (approx. 0.1 mbar)

Conditions adapted from the literature.[1]

Yield: 381 g

^{1}H NMR ($CDCl_3$/TFA-*d* 4:1, 500 MHz, 303 K): δ 3.99 (s, 3H, terminal OCH_3), 4.72 (s, 4H), 7.32 ppm (s, 2H).
SEC (pentafluorophenol/$CHCl_3$ 1:2, 318 K): M_n = 21,300 g/mol, M_w = 36,900 g/mol, $Đ$ = 1.82.

PBF

Feed: dimethyl-2,5-furandicarboxylate **$FuMe_2$** (442.0 g, 2.4 mol, 1.0 equiv.), 1,4-butanediol **BD** (433.0 g, 4.8 mol, 2.0 equiv.), Sb_2O_3 (8.75 g, 30.0 mmol, 1.0 wt-%).

Table S2. Reaction conditions used for the synthesis of PBF.

Stage	Temperature [°C]	Time [min]	Atmosphere
1	25 to 200	10	Nitrogen flow
2	200	20	Nitrogen flow
3	200 to 220	10	Nitrogen flow
4	220	35	Nitrogen flow
7	220	60	Vacuum (approx. 0.1 mbar)

Conditions adapted from the literature.[2]

Yield: 458 g

^{1}H NMR ($CDCl_3$/TFA-*d* 4:1, 500 MHz, 303 K): δ 1.95 (s, 4H), 4.00 (s, 3H, terminal OCH_3), 4.47 (s, 4H), 7.31 ppm (s, 2H).
SEC (pentafluorophenol/$CHCl_3$ 1:2, 318 K): M_n = 33,400 g/mol, M_w = 68,800 g/mol, $Đ$ = 2.06.

NMR data of PEF and PBF

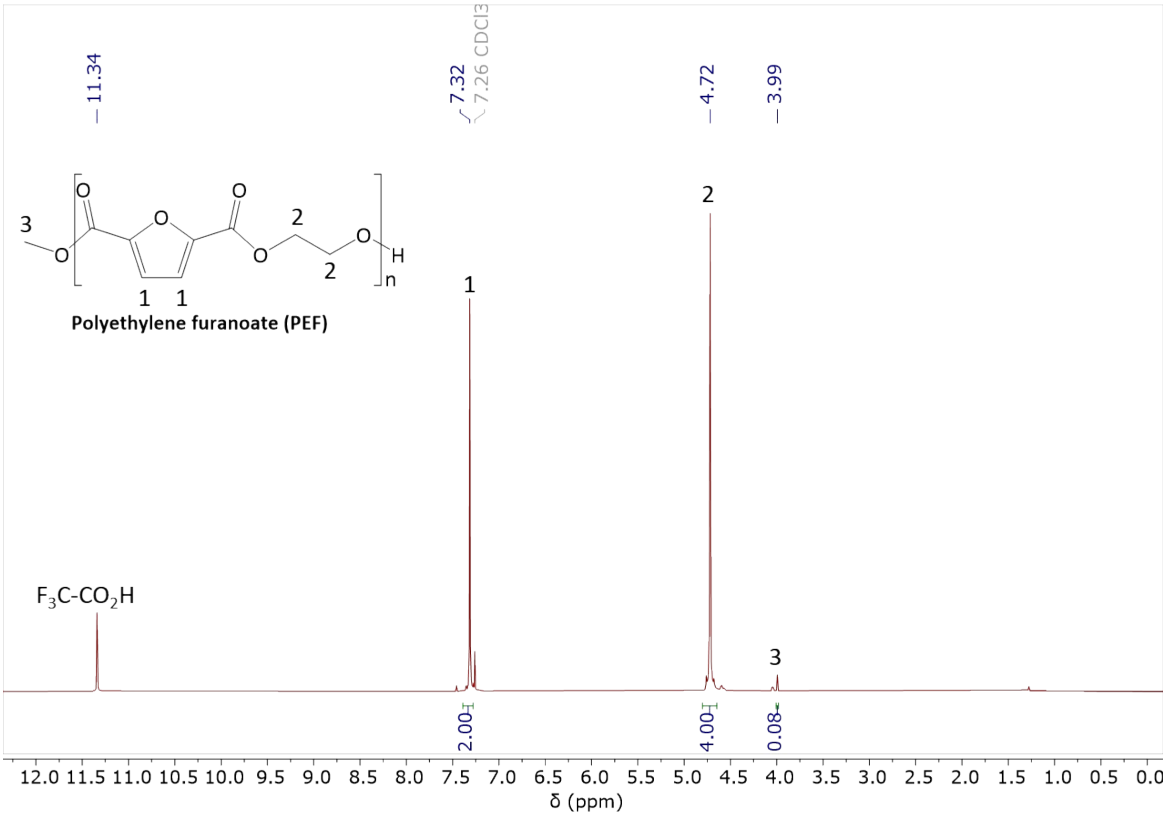


Figure S1. ^{1}H NMR spectrum of PEF in $CDCl_3$/TFA-*d* (v/v = 4:1).

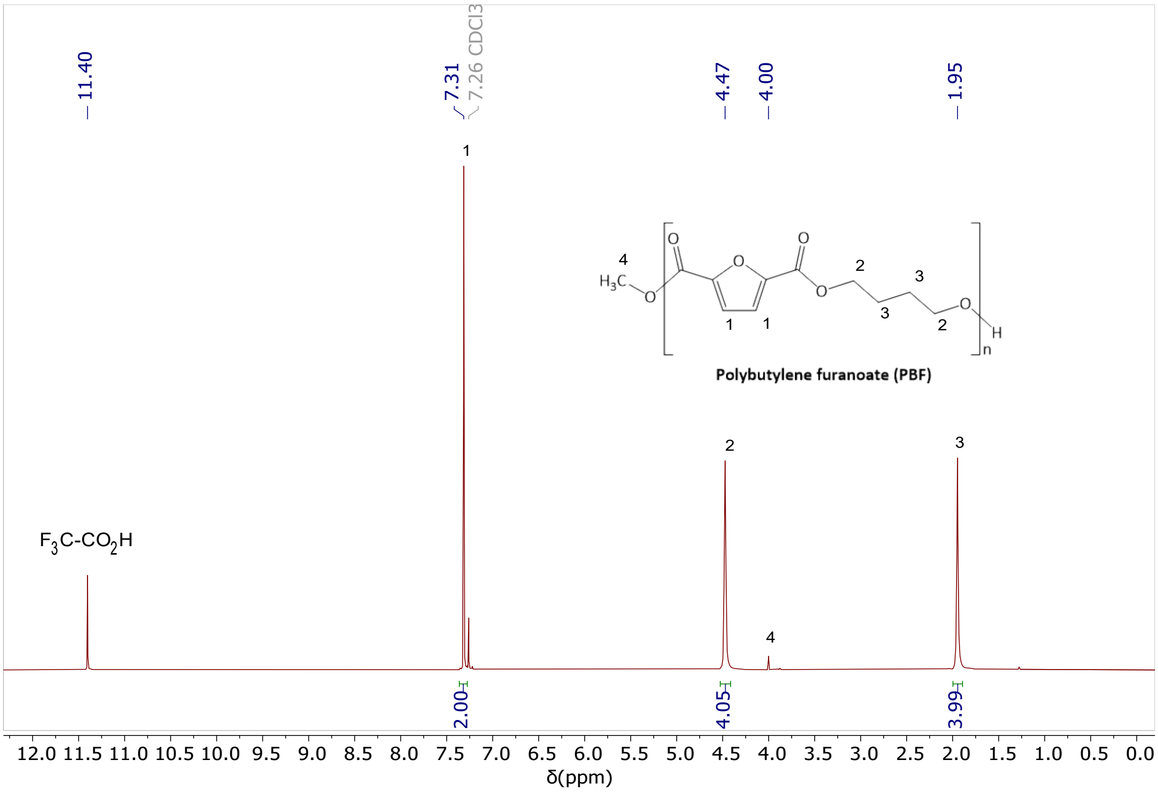


Figure S2. ^{1}H NMR spectrum of PBF in $CDCl_3$/TFA-*d* (v/v = 4:1).

SEC data of PEF and PBF

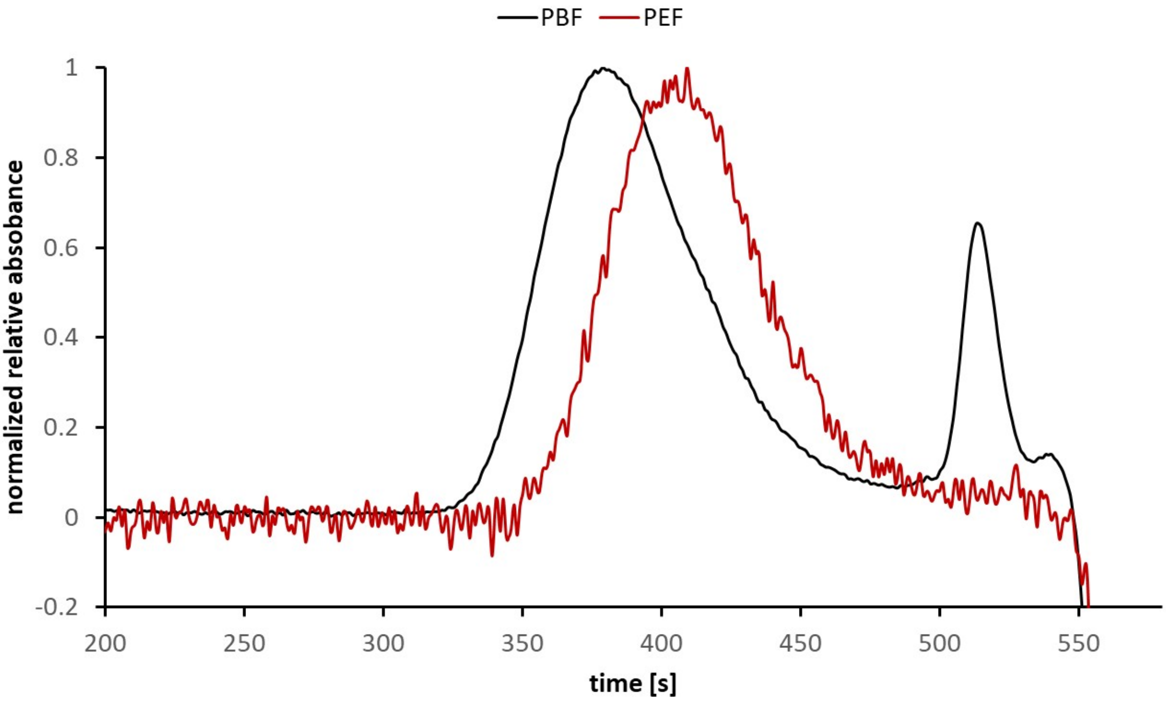


Figure S3. SEC traces of PEF and PBF measured in Pentafluorophenol/$CHCl_3$ (v/v = 1:2) at 318 K.

TGA data of PEF and PBF

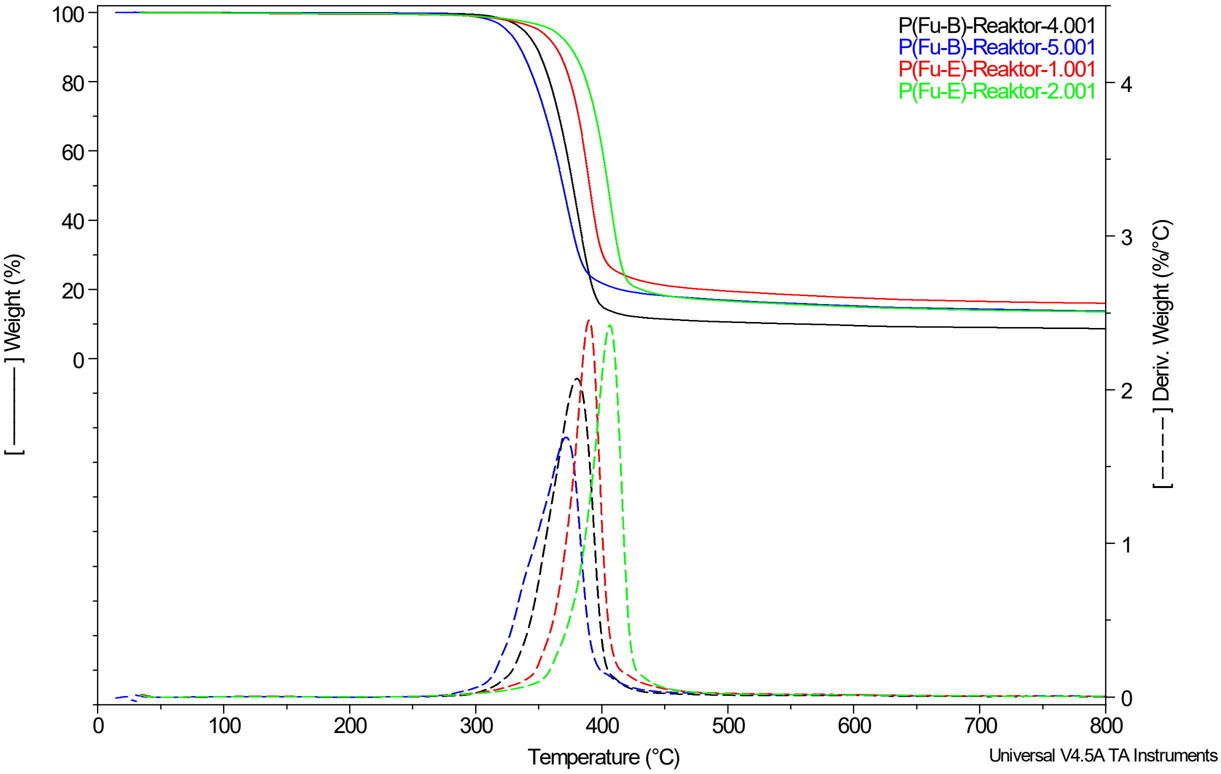


Figure S4. TGA data of PEF (denoted as "P(Fu-E)") and PBF (denoted as "P(Fu-B)").

DSC data of PEF and PBF

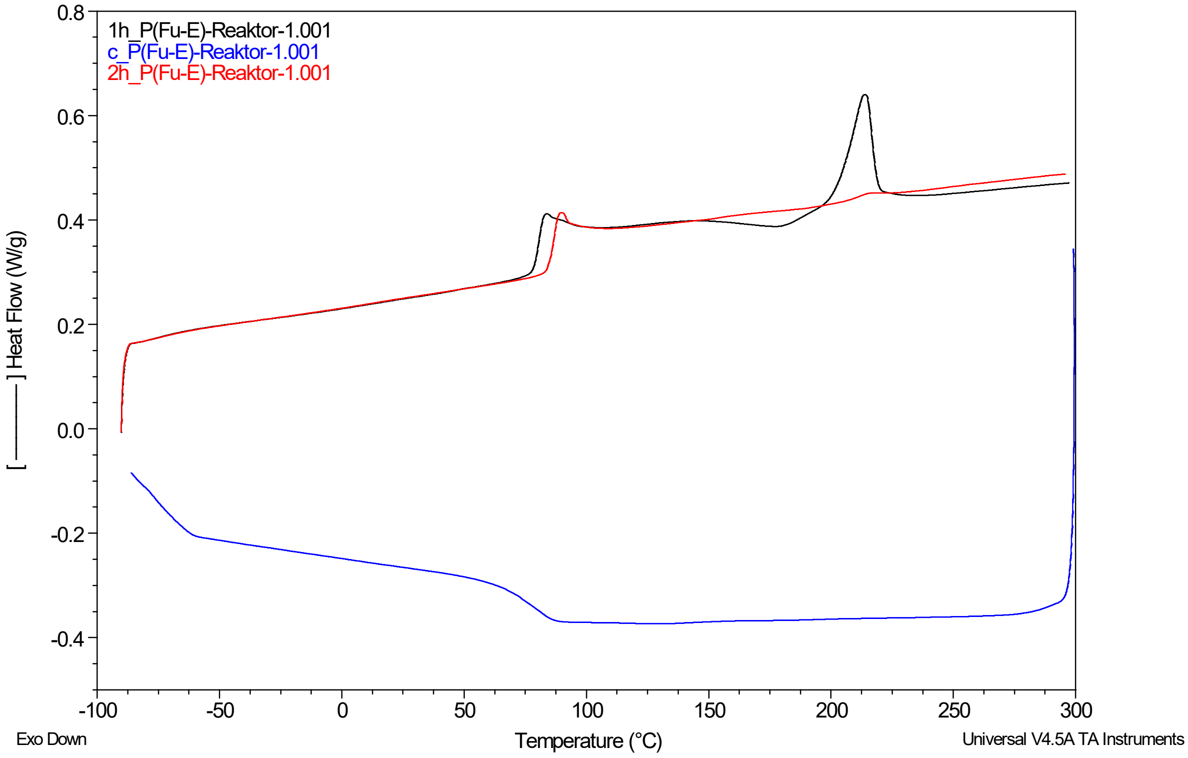


Figure S5. DSC data of PEF (denoted as “P(Fu-E)”).

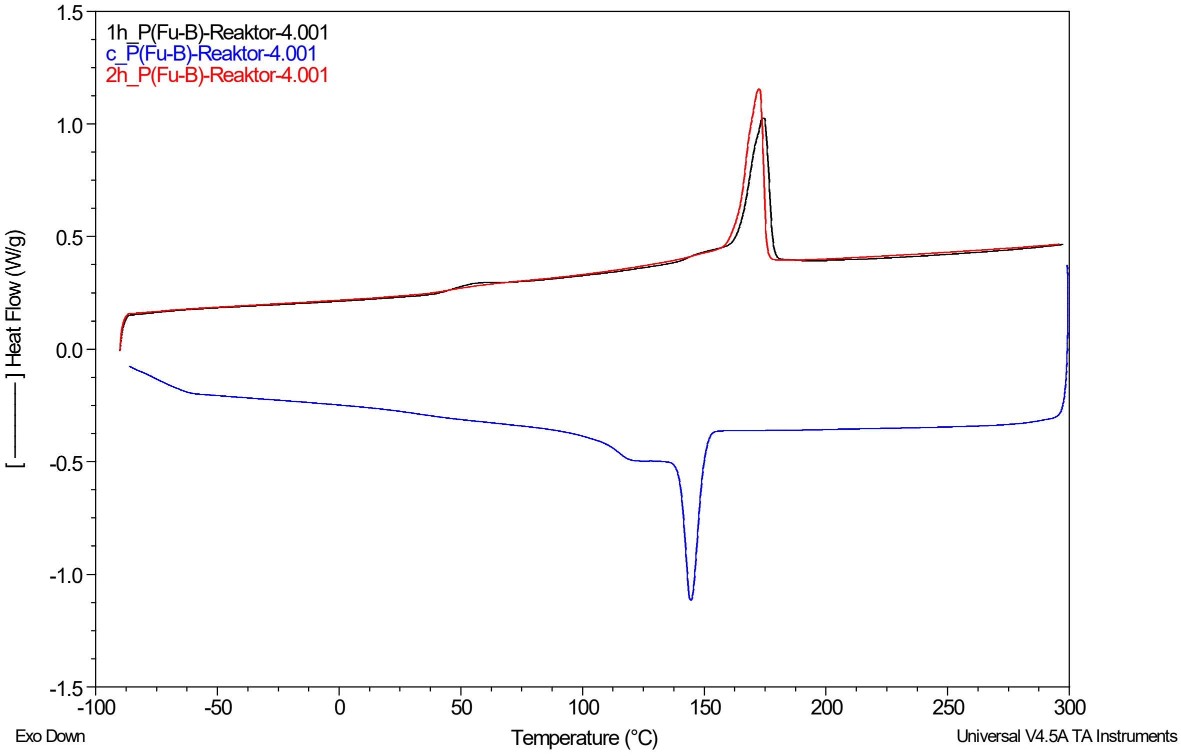
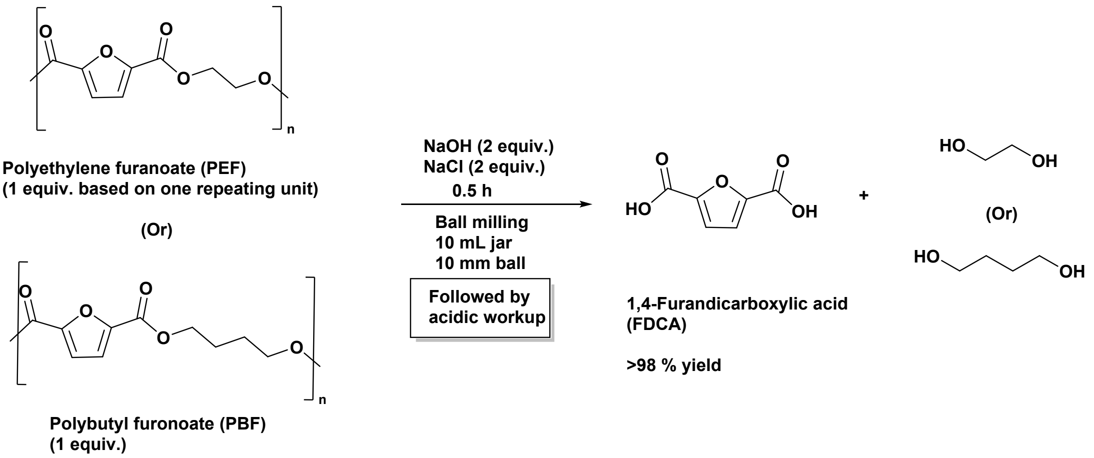


Figure S6. DSC data of PBF (denoted as “P(Fu-B)”).

General procedure for the mechanochemical hydrolysis of PEF and PBF



The hydrolysis was carried out in a Retsch MM400 mixer mill at the frequency of 30 Hz using a 10 mL stainless steel grinding jar and a ball of 10 mm diameter (m = 4 g). A mixture of PEF (0.25 g, 1.5 mmol of repeating units) or PBF (0.294 g, 1.5 mmol of repeating units), sodium hydroxide pellets (0.24 g, 3 mmol), and sodium chloride (0.175 g, 3 mmol) was ball milled in a 10 mL jar for 0.5 h. After the completion of the reaction, the crude mixture was suspended in 10 mL of distilled water and unreacted PEF was removed by filtration. The filtrate containing the disodium furanoate salt was acidified with 1 M hydrochloric acid solution in water to a pH ≈ 1–2, resulting in precipitation of 2,5-furandicarboxylic acid (FDCA), which was collected by filtration, washed with distilled water, and dried at 70 °C overnight. FDCA was obtained in more than 98% yield and was characterized by NMR analysis.

FDCA[3] from PEF:
^{1}H NMR (DMSO-d_6, 300 MHz, 298 K): δ 7.27 (s, 2H), 13.60 ppm (s, 2H).
^{13}C NMR (DMSO-d_6, 300 MHz, 298 K): δ 159, 147, 118 ppm.

FDCA from PBF:
^{1}H NMR (DMSO-d_6, 300 MHz, 298 K): δ 7.29 (s, 2H), 13.61 ppm (s, 2H).
^{13}C NMR (DMSO-d_6, 300 MHz, 298 K): δ 159, 147, 118 ppm.

NMR data of recovered diols using mentioned procedure (Figure S10)

Ethylene glycol from PEF,
^{1}H NMR (Acetone-d_8, 300 MHz, 298 K): δ 3.98 (s, 2H), 3.56 ppm (s, 4H).
^{13}C NMR (Acetone-d_8, 300 MHz, 298 K): δ 63 ppm.

Butane-1,4-diol from PBF,
^{1}H NMR (DMSO-d_6, 300 MHz, 298 K): δ 4.67 (2H), 3.39-3.35 (m, 4H), 1.43-1.39 ppm (m, 4H).
^{13}C NMR (DMSO-d_6, 300 MHz, 298 K): δ 61, 29 ppm.

Note: ICP analysis of crude material taken directly from the milling jar (i.e., before aqueous work-up) shows an Fe content of 0.0093 wt%, slightly increased compared to the value for PEF (0.00518 wt%). The Ti values decrease along this process (PEF: 0.0395 wt%, depolymerised sample: 0.0177 wt%, traces present from polymer synthesis, vide supra). No other traces of transition metals were found by ICP.

Optimisation of reaction conditions

Table S3. Optimisation of the mechanochemical hydrolysis of PEF into FDCA.

Entry	Reaction conditions[a]	PEF Conversion into product [%]	Yield FDCA [%]
1.	10 min	34	<10
2.	**0.5 h**	**>98**	**>98**
3.	1 h	>98	>98
4.	1.5 h	>98	>98
5.	NaOH (1 equiv.)	50	48
6.	NaOH (3 equiv.)	95	90
7.	Without NaOH	0	0
8.	KOH (2 equiv.)	>95	92
9.	Na_2CO_3 (2 equiv.) + H_2O (74 mL)	<10	<5
10.	Cs_2CO_3 (2 equiv.) + H_2O (74 mL)	<5	0
11.	MeOH (25 mL), LAG	96	94
12.	H_2O (25 mL), LAG	>97	96
13.	DMSO (25 mL), LAG	98	95
14.	Ethylene glycol (25 mL), LAG	>90	90
15.	10 Hz	0	0
16.	20 Hz	0	0
17.	25 Hz	<40	20
18.	26 Hz	57	38
19.	28 Hz	68	46
20.	15 mm SS ball, 25 Hz[b]	96	81
21.	10 mm ZrO_2 ball	91	86
22.	10 mL ZrO_2 jar	90	85
23.	10 mm ZrO_2 ball, 10 mL ZrO_2 jar	>90	84
24.	**Without NaCl**	**>92**	**91**

[a] **Reaction Conditions:** 0.25 g PEF, 2 equiv. NaOH, 2 equiv. NaCl, milling frequency 30 Hz, 10 mL jar and 10 mm ball (both stainless steel if not mentioned otherwise). Product conversion was quantified during filtration, isolated yields of FDCA was obtained after acidic workup using 1M HCl solution in water, 25 μL solvent was used as a LAG. NaCl has been used as an inert surface for all the experiments (unless it is mentioned, entry 24). 100% pure FDCA was obtained. [b]Unoptimised workup procedure.

Calculation of conversion and yield

The conversion *X* of PEF into product was calculated from the remaining amount of polymer $m_{\mathrm{PEF(t)}}$ divided by the amount of polymer used for the depolymerisation reaction $m_{\mathrm{PEF(0)}}$. The yield *Y* was calculated from the mmols of obtained pure FDCA divided by number of mmols of polymer repeating unit used.

$$X_{PEF} = \frac{m_{PEF(0)} - m_{PEF(t)}}{m_{PEF(0)}}$$

$$Y_{FDCA} = \frac{n_{FDCA}}{n_{repeating\ units}}$$

The values of the conversion are different from the yields as the final workup procedure (amount of water used during workup) was optimised with respect to optimised conditions where we obtained >98% conversion and yield, which has also been followed for all the experiments. In cases where the PEF conversion is lower, the formed product is more diluted (i.e., mixed with starting material and NaCl). As a result, during filtration the yield decreased because the product is slightly soluble in water.

Additional information

Similarly as for other ester hydrolysis reactions, the texture of the FDCA salts is strongly dependent on the alkaline anion. For example, Na carboxylates of long chain fatty acids are used as hard soaps whereas the corresponding K salts are more waxy/oily (‘soft soaps’, e.g., the K salt of palmitic acid). A change from NaOH to KOH thus produces sticky reaction mixtures that are more difficult to separate from the milling jar, thus leading to a slight decrease in yield.

We have furthermore reduced the amount of NaCl, using 1 equiv. of NaCl instead of 2 equiv., under otherwise standard, optimised conditions (vide supra). A sticky reaction mixture was obtained which leads to decrease in FDCA yield (Figure S7).

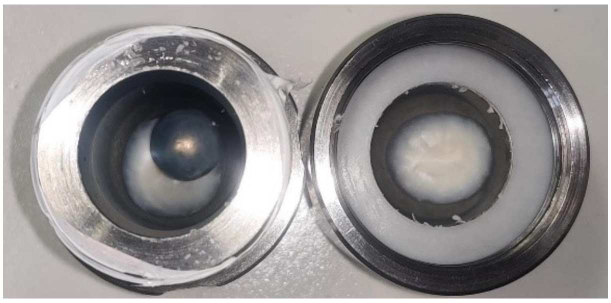


Figure S7. View of the milling jar after the mechanochemical hydrolysis reaction using 1 equiv. of NaCl as an additive under otherwise optimised reaction conditions (vide supra).

When performing the rection under optimised conditions using eight small balls of 5 mm diameter total weight of 4 g), we observed less efficient milling of the PEF granules due to a significant reduction in impact energy associated with reduced size and weight of one single ball (Figure S8). As a consequence, two equivalents of NaOH reacted only with a small amount of PEF. We have therefore not calculated the yield as this run was not done under the same conditions as before (i.e., with equimolar amount of the reactants PEF and NaOH). Assuming that a small amount of Na salt of FDCA has formed in this reaction, along with a large amount of residual NaOH, the moment this reaction mixture is dissolved it in water a large amount of unreacted PEF granules will be recovered and the minor amount of FDCA would not precipitate after acidification due to significant dilution of the work-up solution (much more HCl will be needed due to neutralise residual NaOH).

Figure S8. Views of the milling jar after the mechanochemical hydrolysis reaction using smaller balls, under otherwise optimised reaction conditions (vide supra).

FTIR-ATR spectra

The optimisation study for the PEF depolymerisation was monitored by FTIR-ATR analysis.

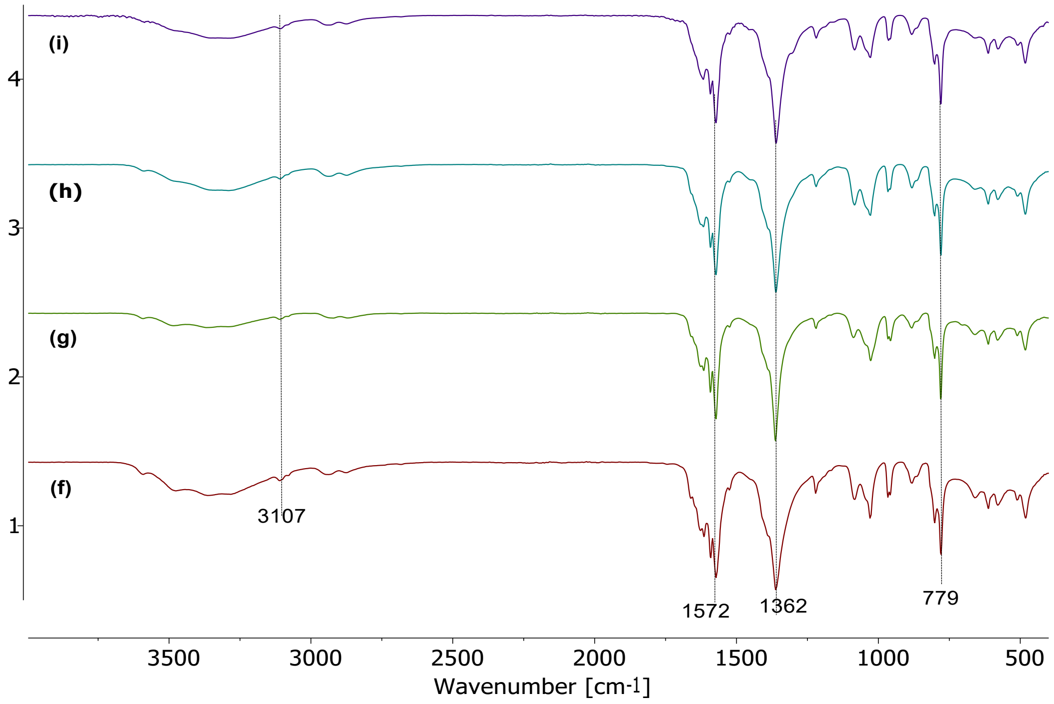


Figure S9. IR spectra of optimisation of PEF hydrolysis with LAG (25 μL), (f) H_2O, (g) DMSO, (h) ethylene glycol, (i) MeOH, using the same reaction conditions as in (d).

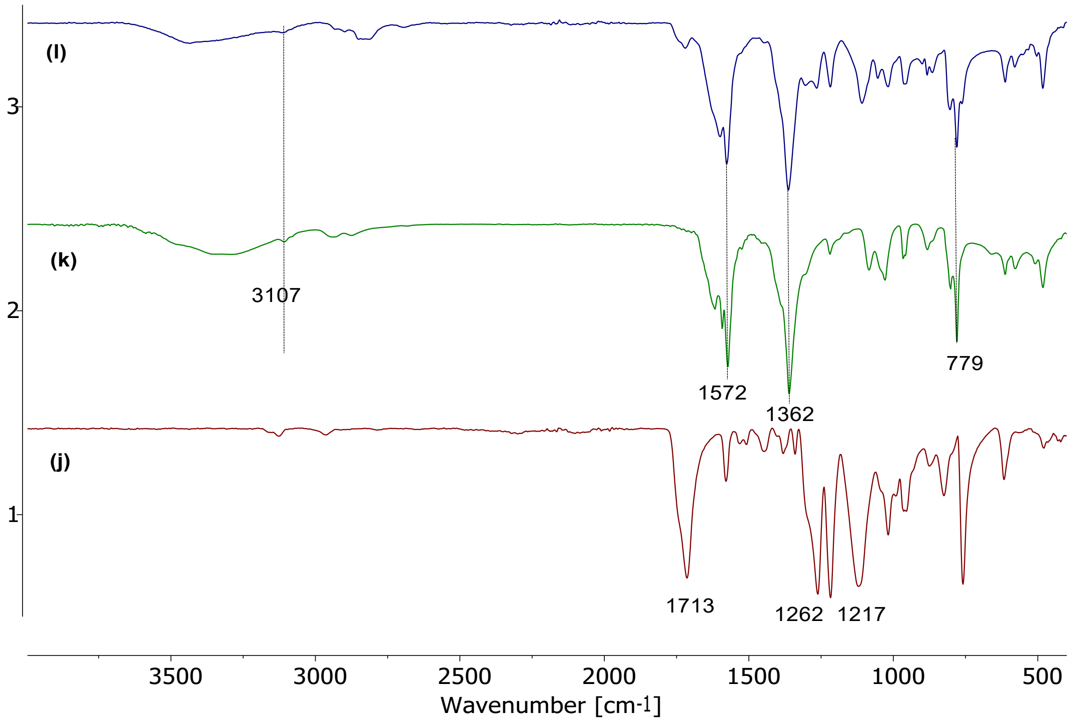


Figure S10. IR spectra of optimisation of PEF hydrolysis with 2 equiv. of NaOH on 0.25 g scale at 30 Hz frequency, (j) blank reaction without NaOH, (k) using 10 mL stainless steel jar, 10 mm stainless steel ball, (l) using 10 mL ZrO_2 jar, 10 mm ZrO_2 ball.

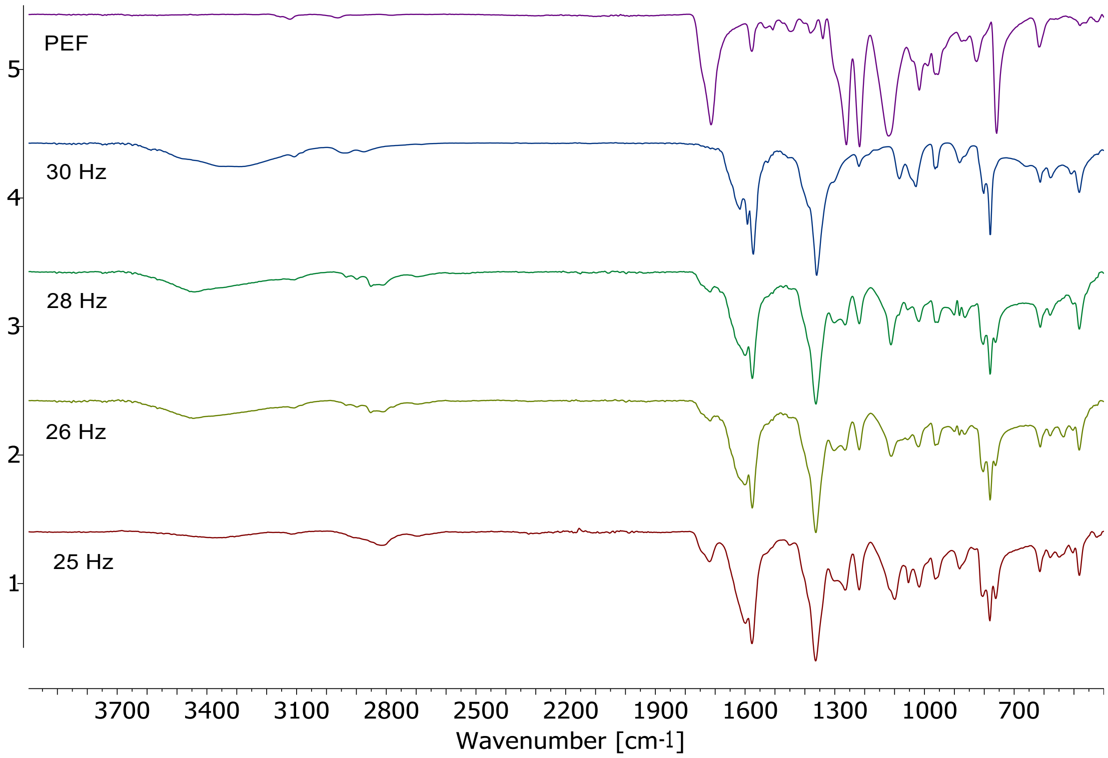


Figure S11. IR spectra of PEF hydrolysis at different frequencies, using the optimised conditions.

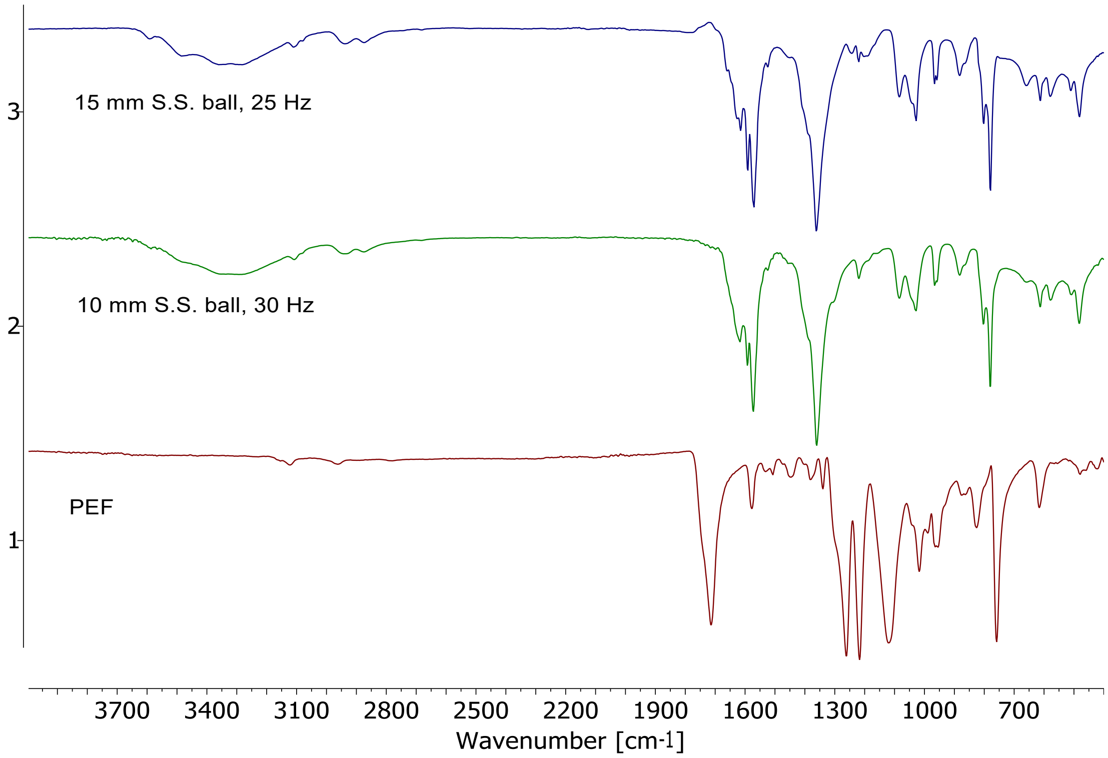


Figure S12. IR spectra of PEF hydrolysis at 25 Hz using 15 mm ball instead of 10 mm ball at 30 Hz, using the optimised conditions.

Scale up of mechanochemical hydrolysis of PEF and PBF

Mechanochemical PEF hydrolysis

2.5 g PEF (15 mmol based on one repeating unit, 1 equiv.), sodium hydroxide (1.32 g, 2.2 equiv.), and sodium chloride (3 g, 3.5 equiv.) were ball milled for 60 minutes at 30 Hz using a 25 mL stainless steel jar and two 15 mm stainless steel balls (Figure S13a). After completion of the reaction, the reaction mixture was suspended in 100 mL of water and filtered, the filtrate was collected (Figure S13b), which was further acidified (until pH<1) using 50 mL of 1M HCl solution in water and the FDCA precipitate was obtained (Figure S13c) which was collected by filtration (ethylene glycol remained in water, Figure S13d) and dried at 60 °C overnight (Figure S13e) (1.95 g, 12.5 mmol, 83% yield of FDCA).

Mechanochemical PBF hydrolysis,

1.94 g PBF (10 mmol based on one repeating unit, 1 equiv.), sodium hydroxide (0.88 g, 2.2 equiv.), and sodium chloride (2 g, 3.5 equiv.) were ball milled for 60 minutes at 30 Hz using a 25 mL stainless steel jar and two 15 mm stainless steel balls (Figure S13a). After completion of the reaction, the reaction mixture was suspended in 100 mL of water and filtered, the filtrate was collected (Figure S13b), which was further acidified using 40 mL of 1M HCl solution in water and the FDCA precipitate was obtained (Figure S13c) which was collected by filtration (butane-1,4-diol remained in water, Figure S13d) and dried at 60 °C overnight (Figure S13e) (1.4 g, 8.97 mmol, 90% yield of FDCA).

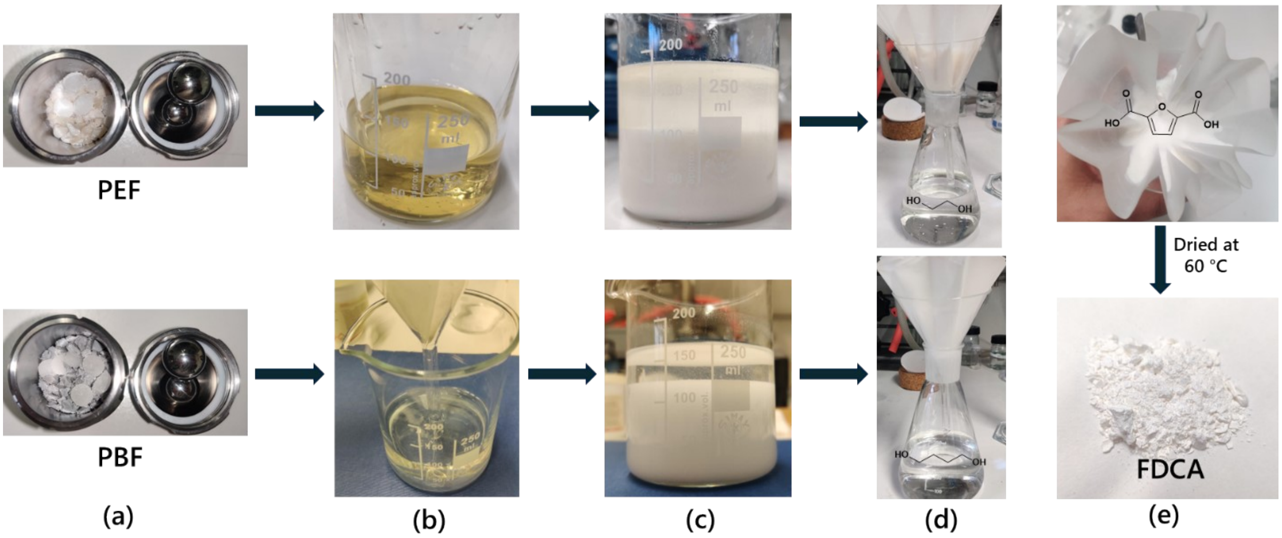


Figure S13. Large-scale reactions of mechanochemical hydrolysis of PEF and PBF, (a) Starting material, (b) Reaction mixture dissolved in water and subsequently filtered. (c) FDCA precipitation following acidification. (d) Filtration, resulting in FDCA collected on filter paper. (e) FDCA dried overnight at 60 °C.

Recovery of diols and sodium chloride

To recover diols as a byproduct of the hydrolysis reaction, the following procedure was used (Figure S14). In the PBF hydrolysis reaction, the filtrate remaining after FDCA precipitation (Figure S13d) was collected in a round-bottom flask. Water was evaporated using a rotary evaporator and dried under full vacuum. The obtained white solid mixture was then suspended in acetone and filtered. NaCl was collected on the filter paper, while the diol was dissolved in the dry acetone. The acetone was then evaporated using a rotary evaporator, resulting in a recovery of 90% butane-1,4-diol. The same procedure was followed for the recovery of ethylene glycol.

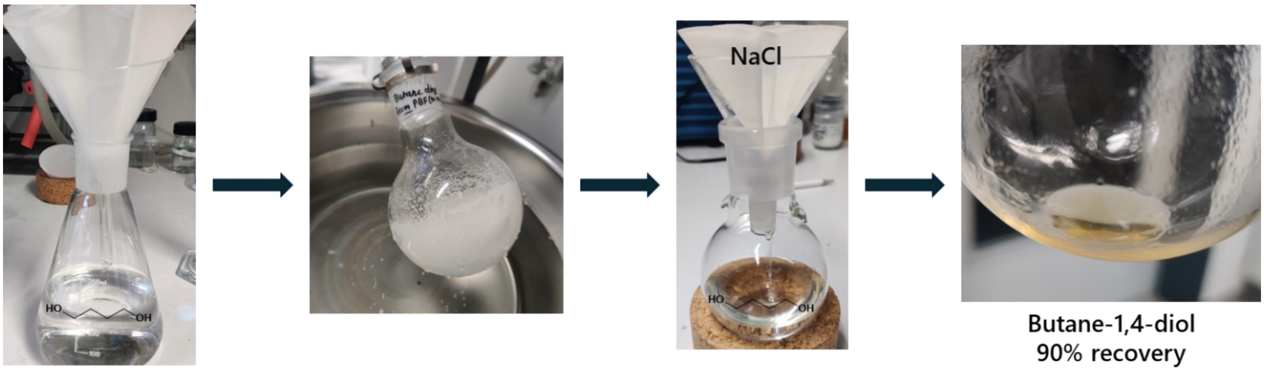
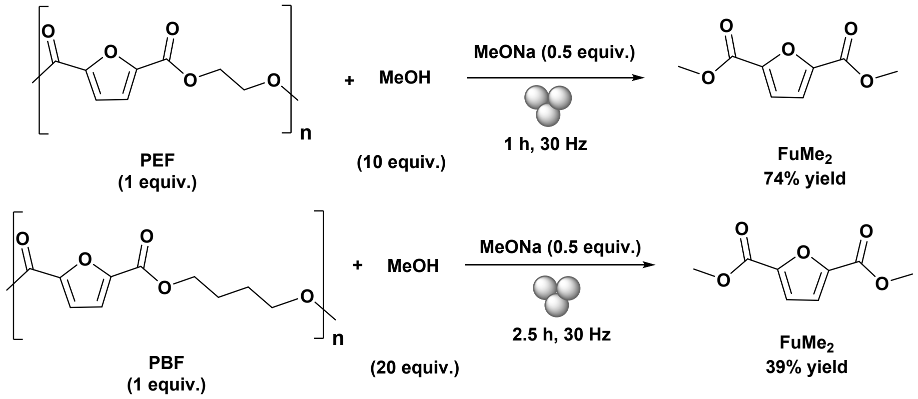


Figure S14. Demonstration of the recovery procedure of diol from mechanochemical PBF hydrolysis.

General procedure for the mechanochemical methanolysis of PEF and PBF



The methanolysis was carried out in a Retsch MM400 mixer mill at a frequency of 30 Hz using a 10 mL stainless steel grinding jar and a ball of 10 mm diameter (m = 13.1 g). A mixture of PEF (0.166 g, 1.0 mmol of repeating units) or PBF (0.194 g, 1.0 mmol of repeating units), NaOMe (0.027 g, 0.5 mmol), and MeOH (405 μL, 10 mmol for PEF and 810 mL, 20 mmol for PBF) was ball milled for 1 h and 2.5 h respectively. After completion of the reaction, the crude mixture was quenched with 2 mL of 1 M HCl solution and dissolved in ethanol: water (1:3) solution upon heating up to 80 °C. Unreacted polymer was removed by filtration. The filtrate containing dimethyl furan-1,2-dicarboxylate (**FuMe$_2$**) was recrystallised at 5 °C overnight and the product was collected by filtration, washed once with cold distilled water and dried at 40 °C overnight. **FuMe$_2$** was obtained in high purity and yields of 74% and 39% from PEF and PBF, respectively.

FuMe$_2$[4] *from PEF:*
^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 7.21 (s, 2H), 3.92 ppm (s, 6H).
^{13}C NMR ($CDCl_3$, 300 MHz, 298 K): δ 158, 147, 119, 53 ppm.

FuMe$_2$ *from PBF:*
^{1}H NMR (DMSO-d_6, 300 MHz, 298 K): δ 7.42 (s, 2H), 3.86 ppm (s, 6H).
^{13}C NMR (DMSO-d_6, 300 MHz, 298 K): δ 158, 146, 119, 52 ppm.

NMR data for optimisation of mechanochemical methanolysis of PEF

The reaction of PEF (0.166 g, 1 mmol, 1 equiv.) was performed with 2 equiv. MeONa instead of NaOH in 10 mL stainless steel jar using 10 mm stainless steel ball at 30 Hz for 1 hour. After completion of the reaction, the reaction mixture was quenched with 5 mL of 1M HCl solution and extracted using chloroform and water. In this case, PEF was converted into the product but some of the product was further hydrolysed into the monomethylated product due to highly basic conditions.

NMR analysis shows a mixture of both compounds A and B in 3:2 ratio with a total yield of 89%. Therefore, further methanolysis procedure was optimised by reducing the amount of MeONa and using a recrystallisation for work-up (vide supra).

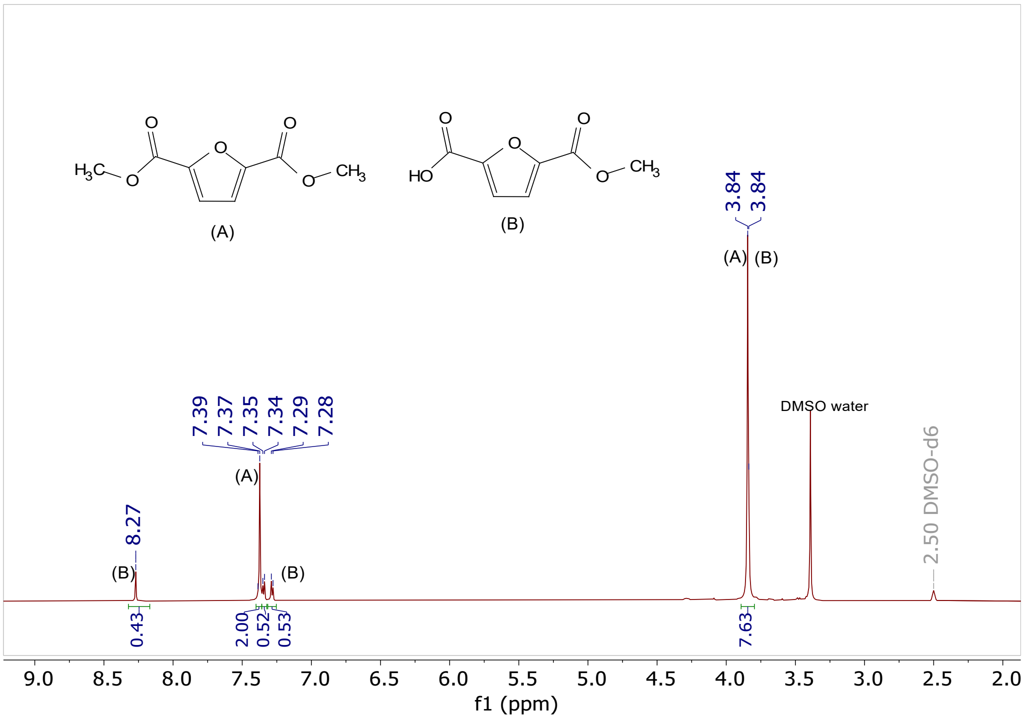


Figure S15. ^{1}H NMR spectrum of the reaction mixture of the reaction of PEF with 2 equiv. NaOMe.

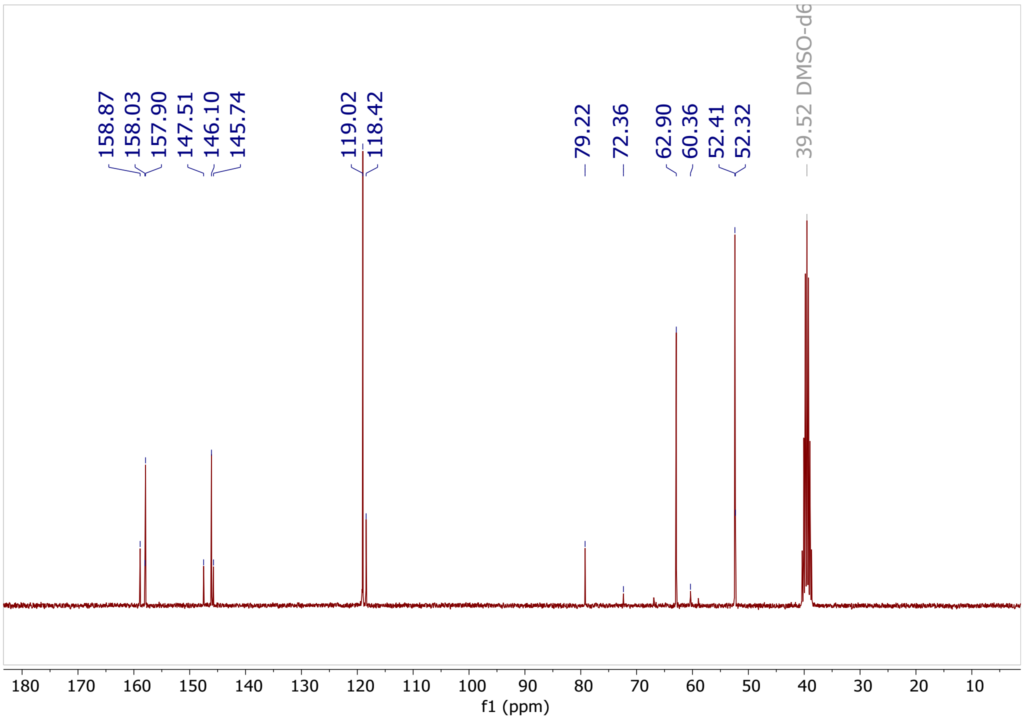


Figure S16. ^{13}C NMR spectrum of the reaction mixture of the reaction of PEF with 2 equiv. of NaOMe.

Scale up of mechanochemical methanolysis of PEF

The large scale methanolysis was carried out in a Retsch MM400 mixer mill at a frequency of 30 Hz using a 25 mL stainless steel grinding jar and a ball of 15 mm diameter (m = 13.1 g). A mixture (Figure S17a) of 1.66 g of PEF, 3 mL of methanol, and 108 mg NaOMe was ball milled at 30 Hz for 1 h. After completion of the reaction, a white coloured reaction mixture (Figure S17b) was obtained which was dissolved in 250 mL ethanol:H_2O (1:1) solution (Figure S17c) upon heating up to 80° C and recrystallised at 5 °C overnight (Figure S17d), resulting in the formation of colourless crystals of **FuMe$_2$**. These were filtered off and further purified by washing with cold distilled water followed by drying at 40 °C overnight (Figure S17e). **FuMe$_2$** was obtained with high purity and a good yield of 65% (1.2 g).

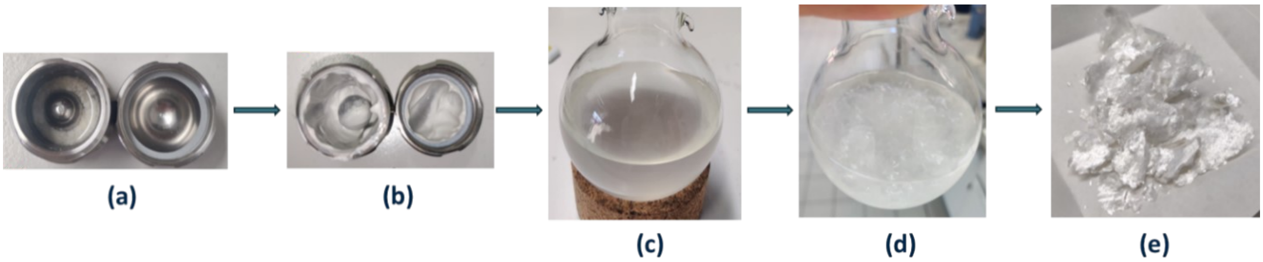


Figure S17. Demonstration of the reaction procedure of large-scale mechanochemical methanolysis of PEF.

NMR spectra of depolymerisation products

FDCA from PEF

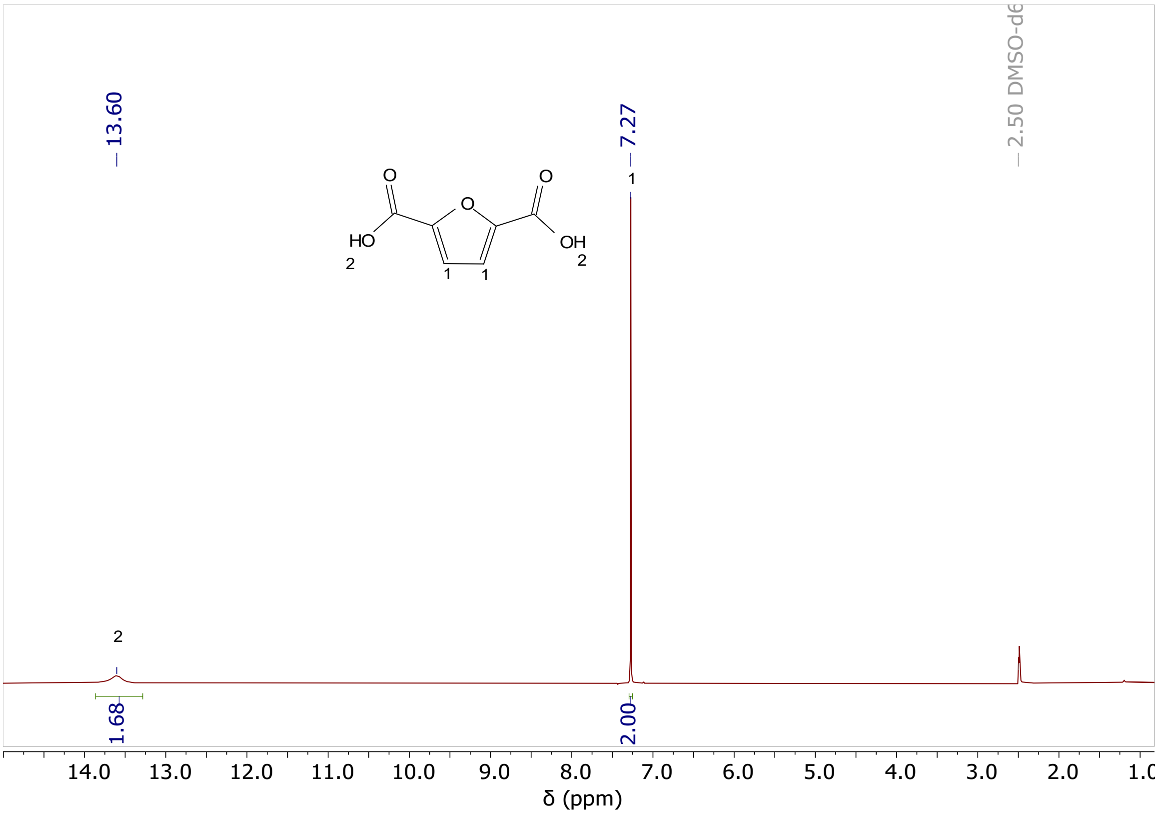


Figure S18. ^{1}H NMR spectrum of FDCA from PEF in DMSO-d_6.

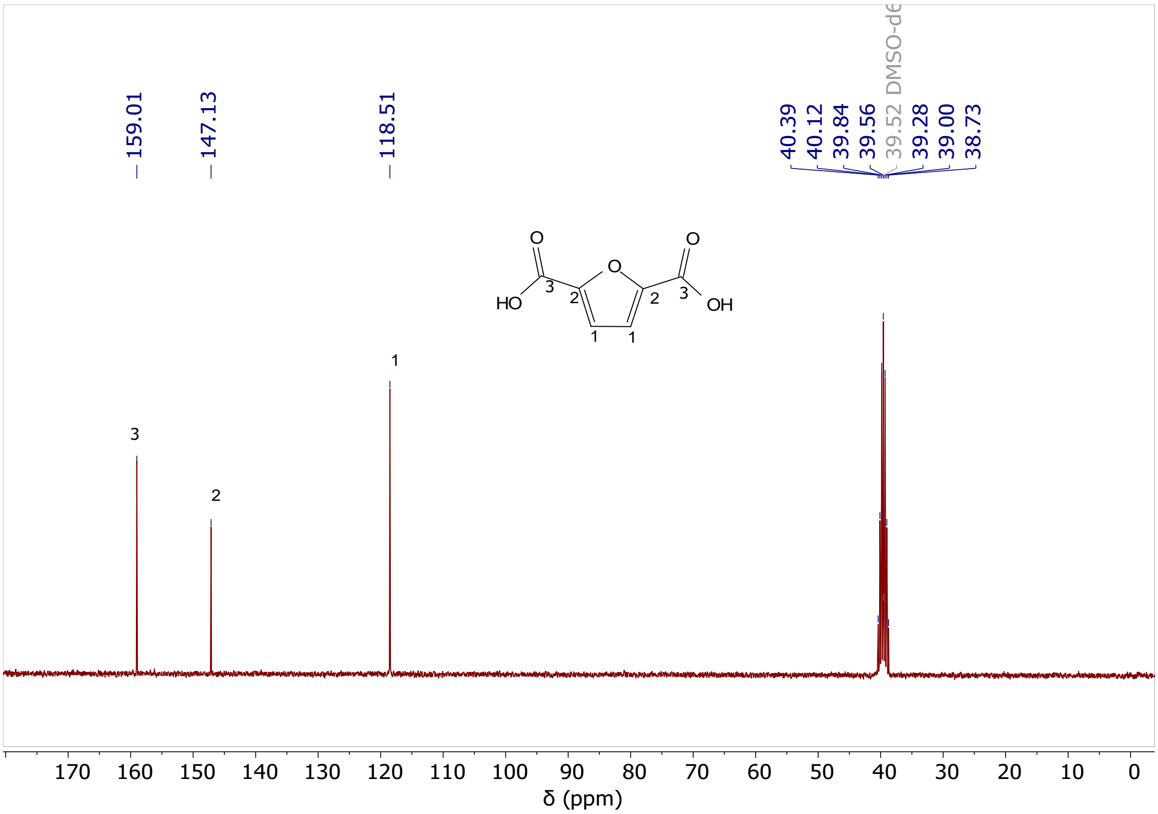


Figure S19. ^{13}C NMR spectrum FDCA from PEF in DMSO-d_6.

FDCA from PBF

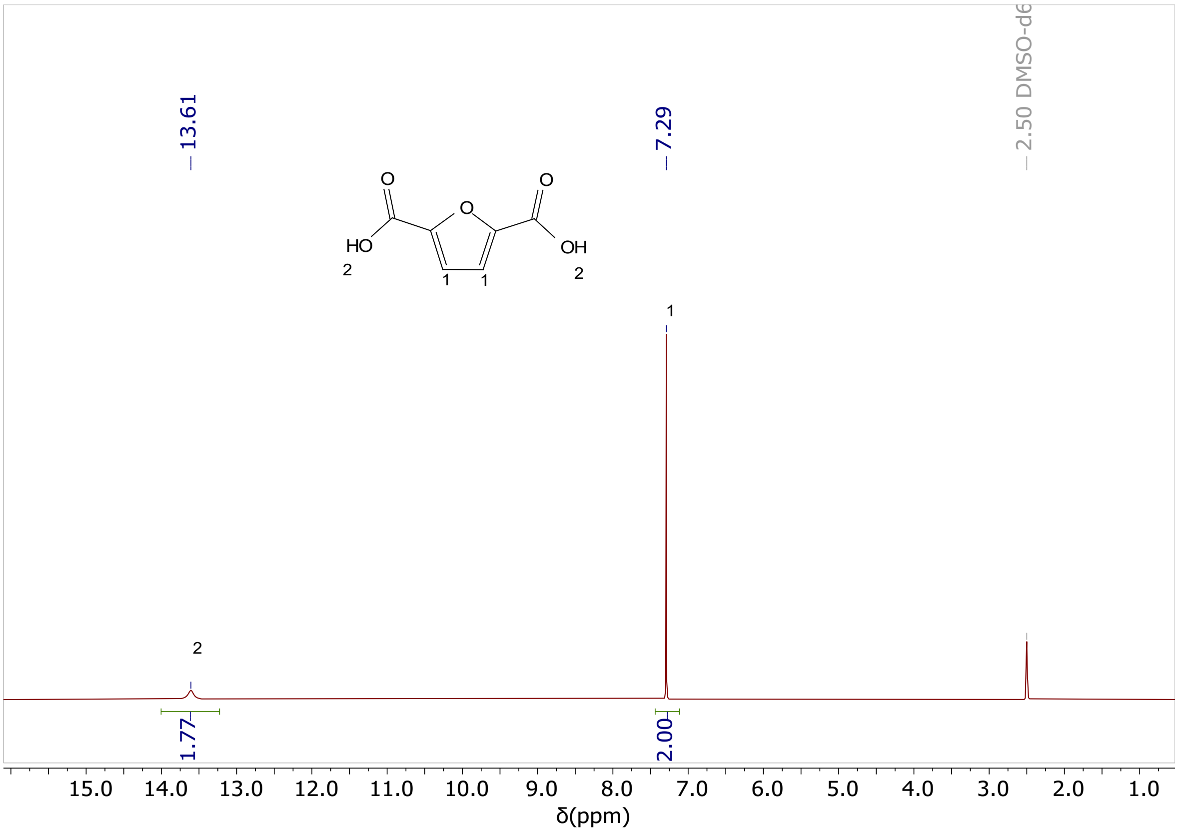


Figure S20. ^{1}H NMR spectrum of FDCA from PBF in DMSO-*d*$_6$.

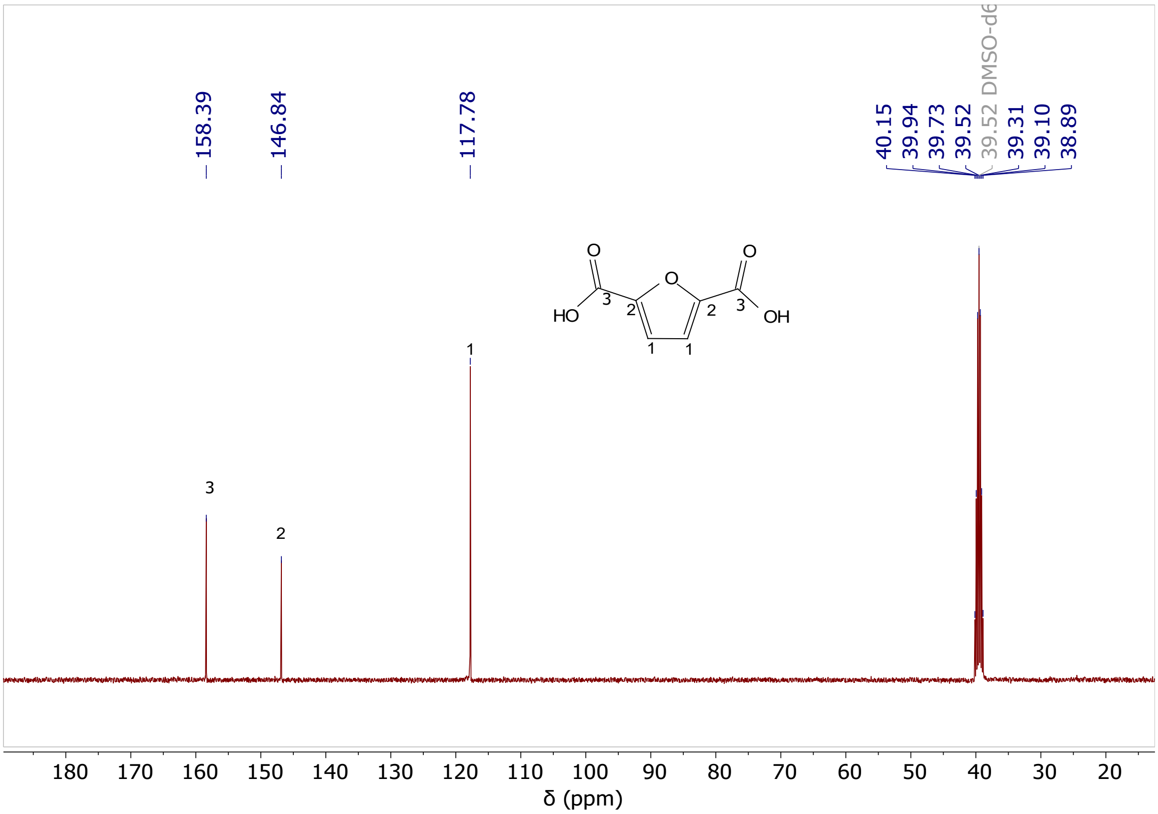


Figure S21. ^{13}C NMR spectrum of FDCA from PBF in DMSO-*d*$_6$.

Ethylene glycol from PEF

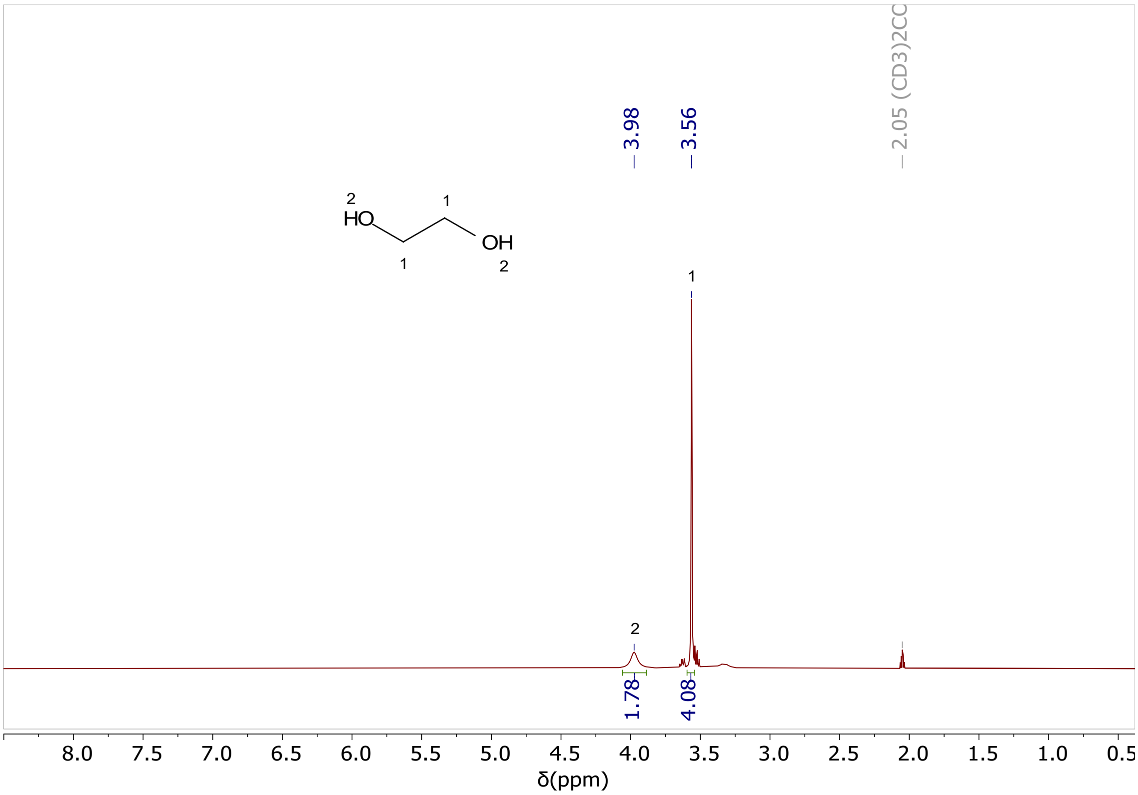


Figure S22. ^{1}H NMR spectrum of recovered ethylene glycol in acetone-d_6.

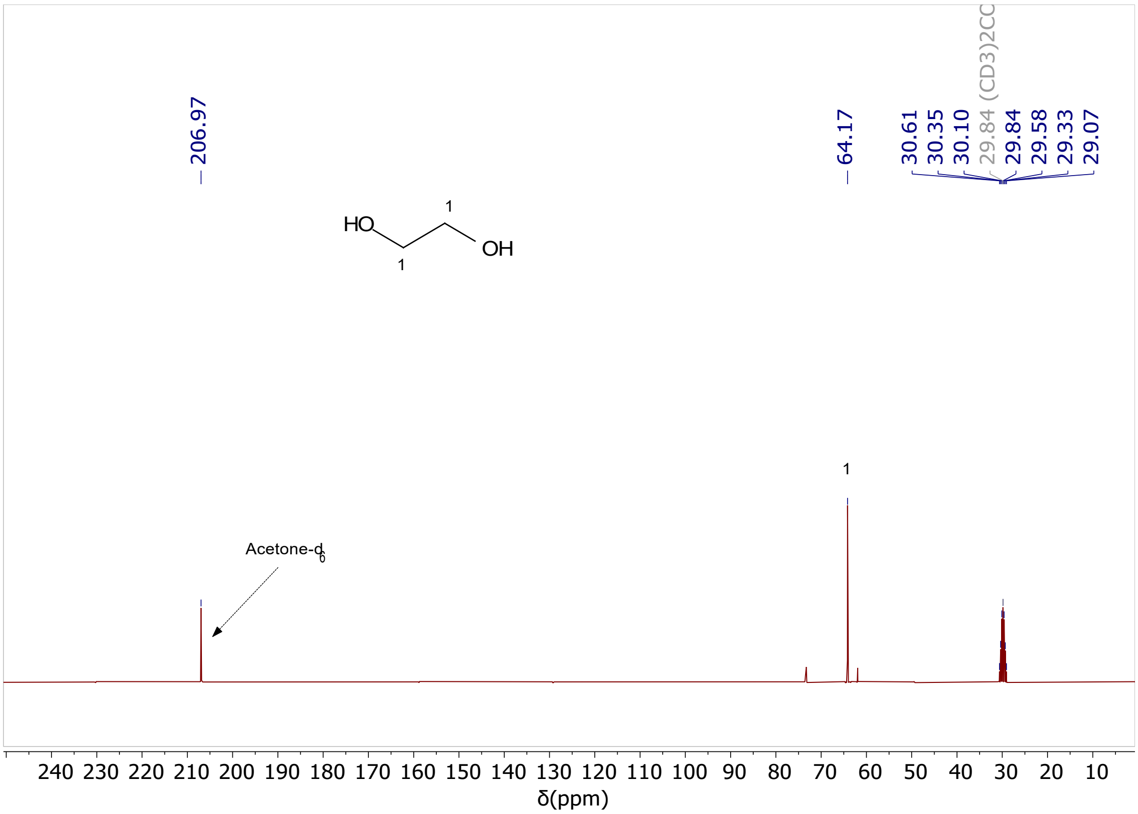


Figure S23. ^{13}C NMR spectrum of recovered ethylene glycol in acetone-d_6.

Butane-1,4-diol from PBF

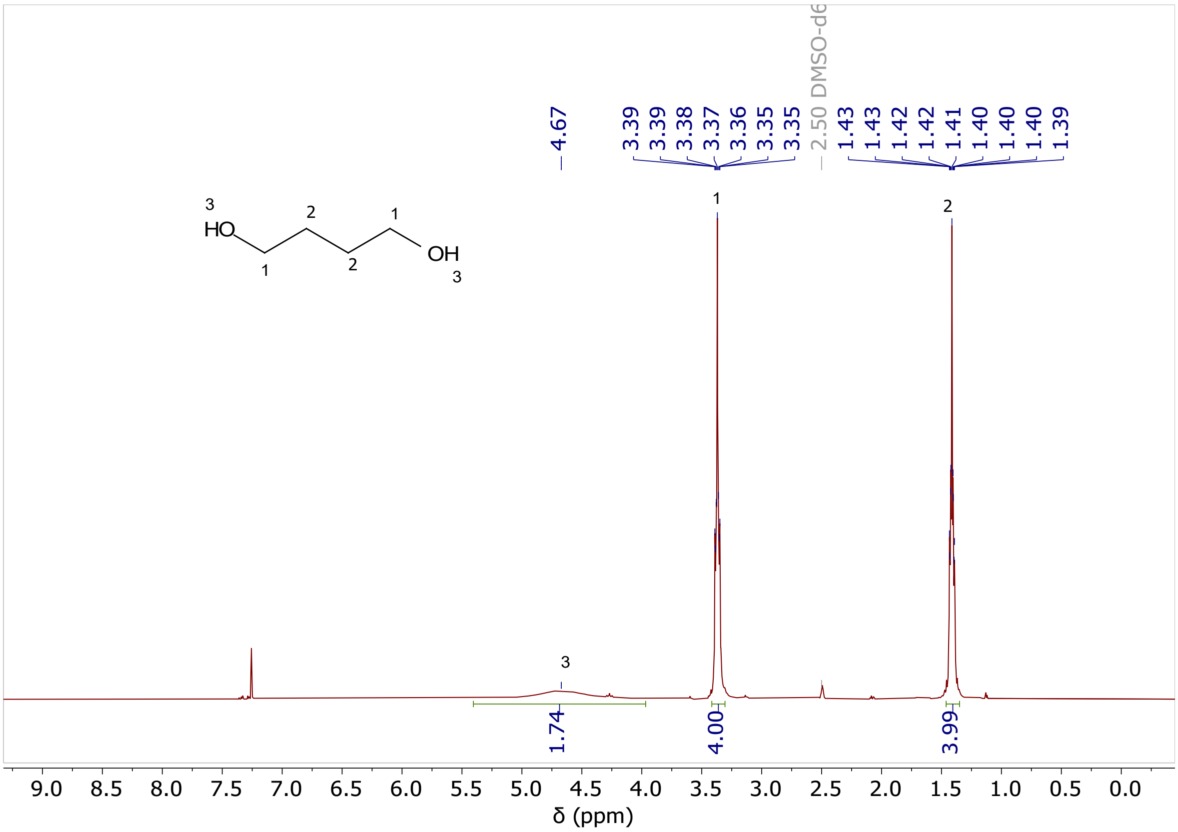


Figure S24. ^{1}H NMR spectrum of recovered butane-1,4-diol in DMSO-d_6.

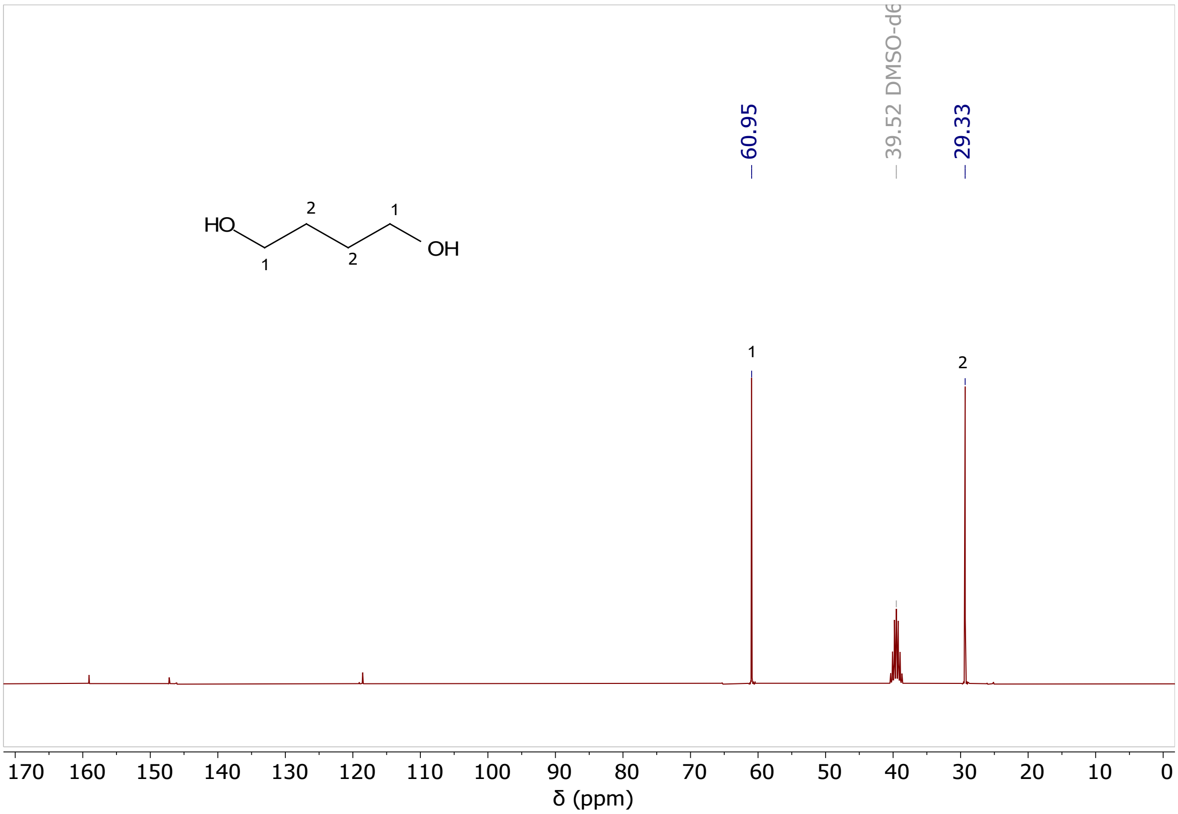


Figure S25. ^{13}C NMR spectrum of recovered butane-1,4-diol in DMSO-d_6.

FuMe$_2$* *from PEF

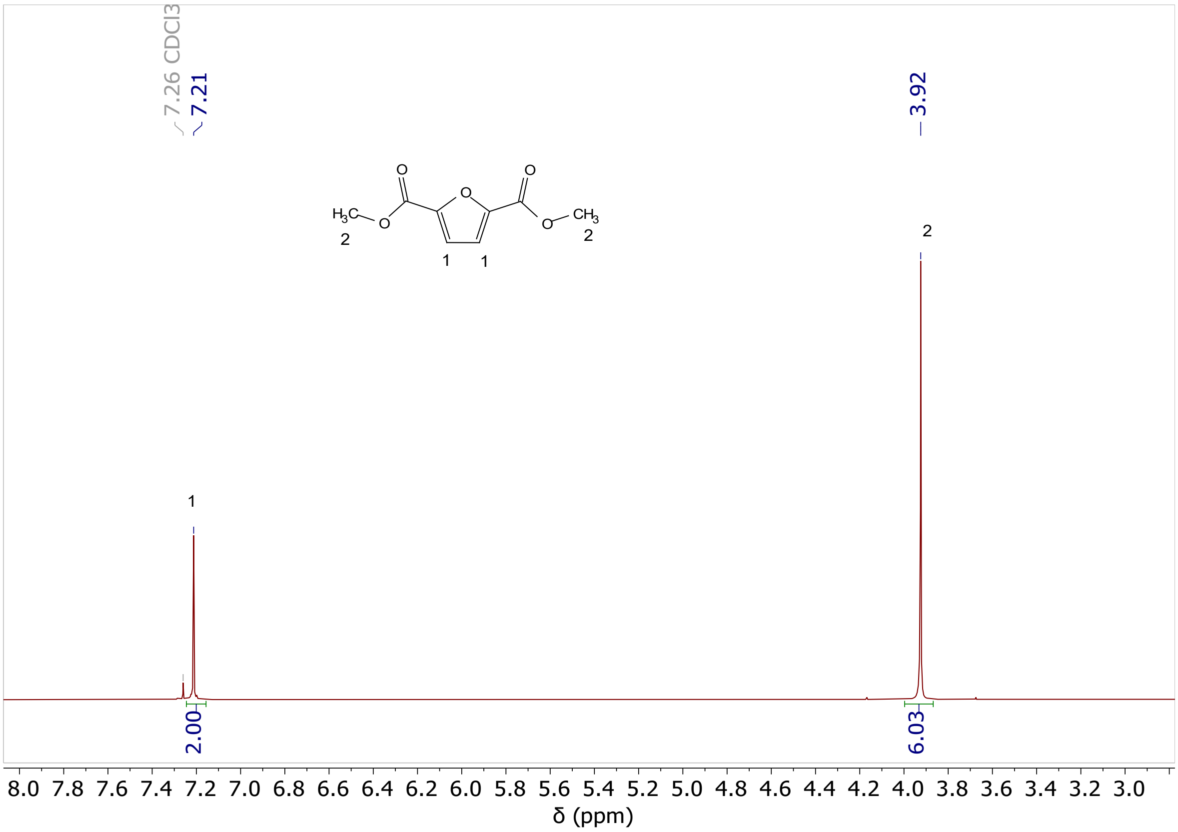


Figure S26. ^{1}H NMR spectrum of **FuMe$_2$** from PEF in CDCl$_3$.

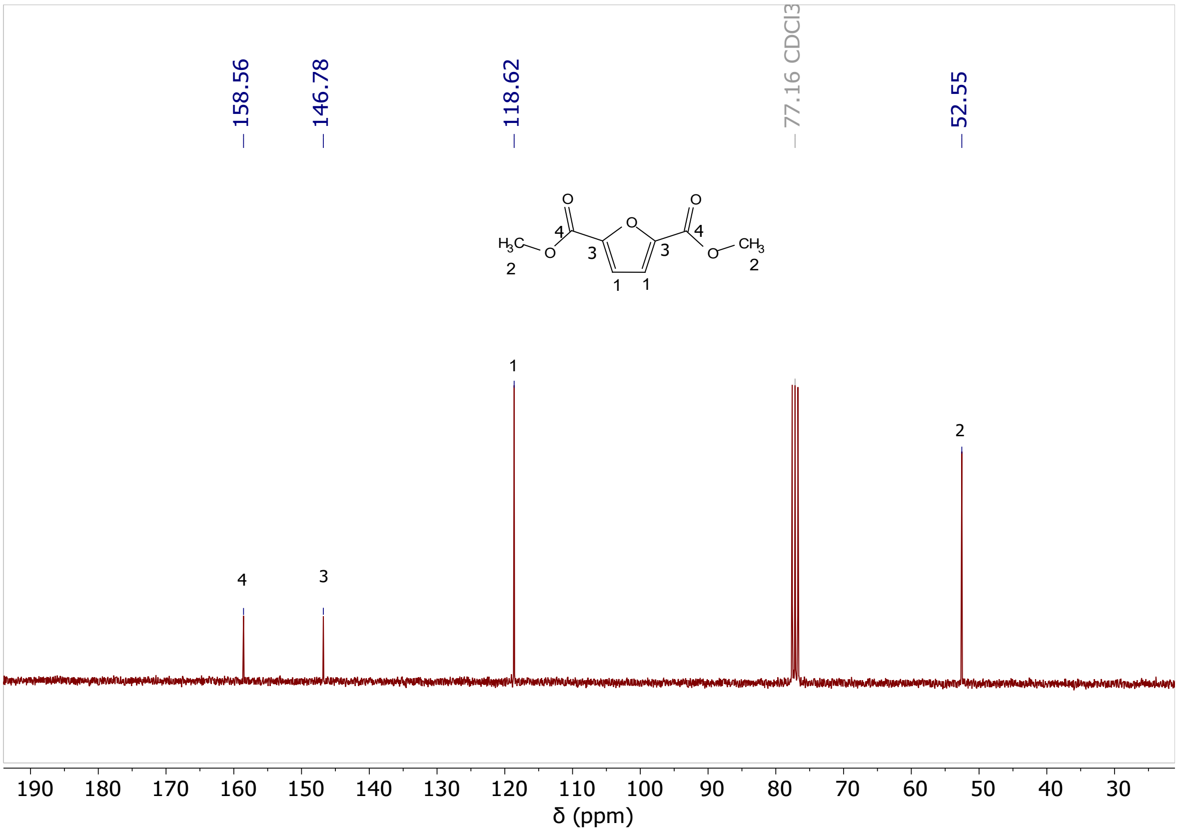


Figure S27. ^{13}C NMR spectrum of **FuMe$_2$** from PEF in CDCl$_3$.

***FuMe$_2$** from PBF*

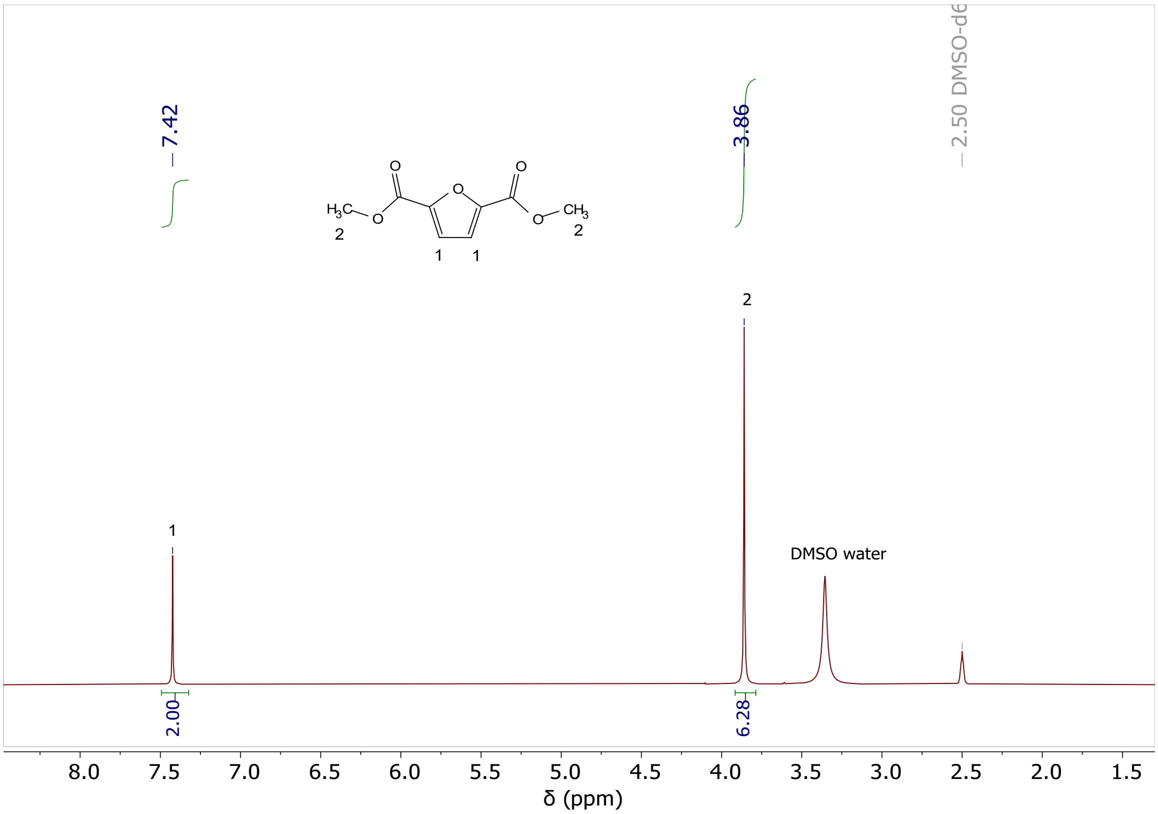


Figure S28. ^{1}H NMR spectrum of **FuMe$_2$** from PBF in DMSO-d_6.

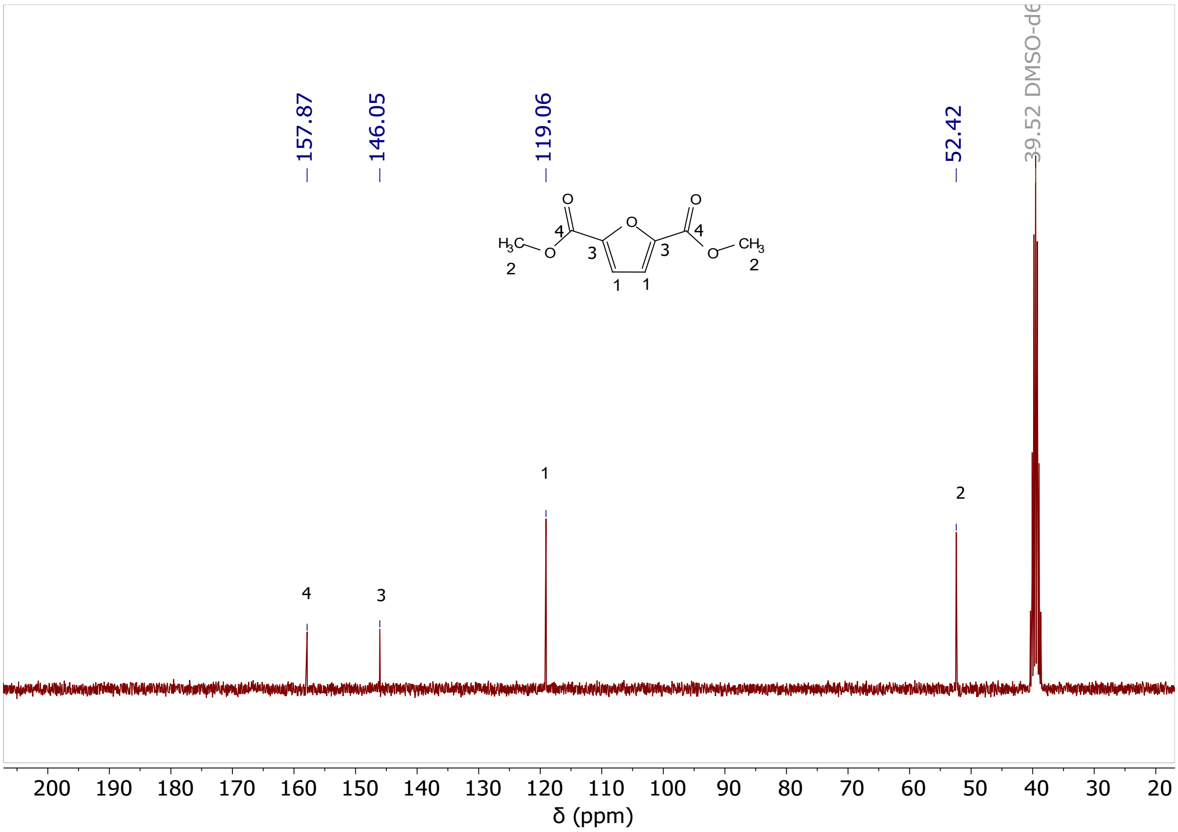


Figure S29. ^{13}C NMR spectrum of **FuMe$_2$** from PBF in DMSO-d_6.

Crystallographic details

General information. X-ray quality crystals were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at low temperature. Diffraction data were collected at 150(2) K on a Bruker Kappa APEX II Duo diffractometer using Mo-K_α radiation for **FuMe$_2$** or Cu-K_α radiation for **FuMe$_2$**_isomer. The structures were solved by iterative (SHELXT[5]) or direct methods (SHELXS-97[6]) and refined by full matrix least square techniques against F^2 (SHELXL-2014). Semi-empirical absorption corrections were applied (SADABS/Bruker[7]). The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in the theoretical positions and were refined by using the riding model. **FuMe$_2$_isomer** was refined as a two-component twin. The structure of **FuMe$_2$_isomer** has a poor quality because of an incomplete data set. However, the measurement provides additional structural evidence. DIAMOND (Crystal Impact GbR) was used for structure representations.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: int. code + (1223) 336-033; e-mail: deposit@ccdc.cam.ac.uk

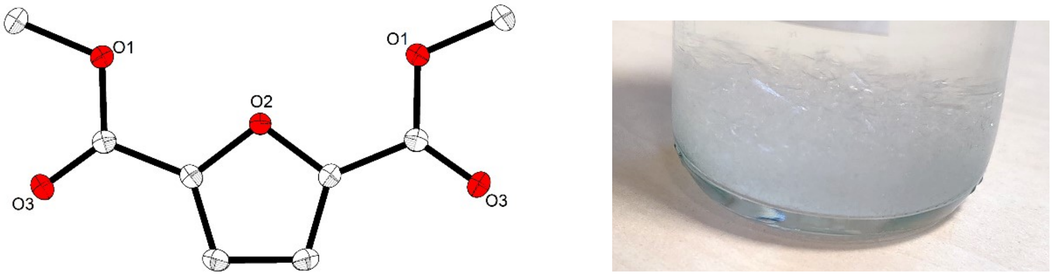


Figure S30. Left: Molecular structure of **FuMe$_2$**. Thermal ellipsoids correspond to 30% probability. Hydrogen atoms are removed for clarity. Right: Thin, needle-type crystals of **FuMe$_2$** after recrystallisation from ethanol/water (1:1).

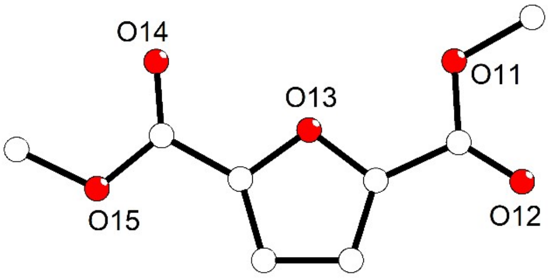


Figure S31. Molecular structure of **FuMe$_2$_isomer**, showing the connectivity and the presence of the second conformer (rotation of the ester group). Hydrogen atoms and further molecules present in the asymmetric unit are omitted for clarity.

Table S4. Crystallographic data.

Compound	**FuMe$_2$**	**FuMe$_2$_isomer** (structural confirmation)
Chem. Formula	$C_8H_8O_5$	$C_8H_8O_5$
Formula weight [g/mol]	184.14	184.14
Colour/description	colorless/plate	colorless/needle
Crystal system	monoclinic	triclinic
Space group	*C*m	$P\bar{1}$
a [Å]	6.1134(8)	10.7690(7)
b [Å]	20.587(3)	11.3447(7)
c [Å]	3.7976(5)	11.4890(8)
α [°]	90	79.281(4)
β [°]	122.799(7)	79.151(4)
γ [°]	90	62.178(4)
V [Å^3]	401.75(9)	1211.37(14)
Z	2	6
$\rho_{\text{calcd.}}$ [g/cm^3]	1.522	1.515
μ [mm^{-1}]	1.117	1.112
Measured reflections	2045	3941
Independent reflections	692	3941
Reflections with $I > 2\sigma(I)$	683	1148
R_{int}	0.0216	0.0938
$F(000)$	192	576
$R_1(R[F^2>2\sigma(F^2)])$	0.0294	0.0562
w$R_2(F^2)$	0.0761	0.1780
GooF	1.082	0.971
No. of Parameters	62	312
CCDC #	2448918	2448917

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