

## Supplementary information for

### Leveraging Molybdenum sulfur compounds as catalysts for synthesis of biobased poly(ethylene 2,5-furandicarboxylate) and recycling

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Figure S1. Coordination modes of phosphinoyldithioformate ligands to a metal center

Figure S2. ATR FTIR spectrum of **PEF\_1**

Figure S3. <sup>1</sup>H NMR spectrum of **PEF\_1** in CDCl<sub>3</sub> and TFA-*d*

Figure S4. <sup>13</sup>C NMR spectrum of **PEF\_1** in CDCl<sub>3</sub> and TFA-*d*

Figure S5. Tan δ traces of PEF samples measures at 1 and 10 Hz

Figure S6. DSC thermograms of PEF recorded during the a)1st heating and b) 2nd heating

Figure S7. TGA and DTG thermograms of PEF samples

Figure S8. Typical ATR-FTIR spectrum of the depolymerization product of **PEF\_1**

Figure S9. <sup>1</sup>H NMR spectrum of the depolymerization product of **PEF\_1** in TCE-*d*<sub>2</sub> and TFA-*d*

Figure S10. <sup>13</sup>C NMR spectrum of the depolymerization product of **PEF\_1** in TCE-*d*<sub>2</sub> and TFA-*d*

Figure S11-S13. The mass spectra of depolymerization product

Appendix S1. Polymer average molecular weight M<sub>n</sub> analysis

Figure S14. Examples of degree polymerization and polymer average molecular weight (M<sub>n</sub>) analysis

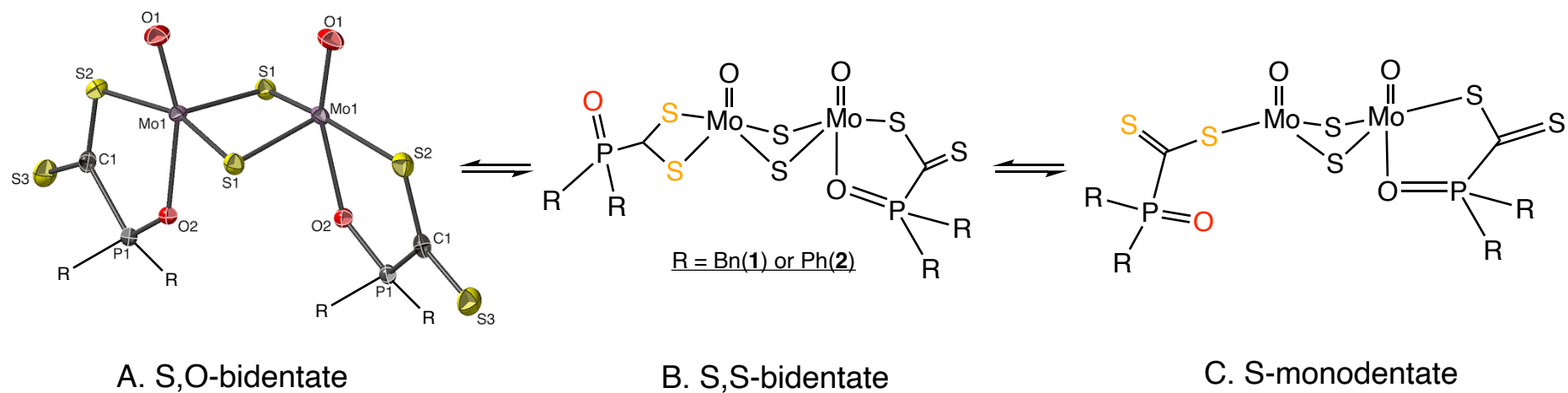


Figure S1. Coordination modes of phosphinoyldithioformate ligands to a metal center. Structure and labeling of **2** (A), DMF ligands are omitted for clarity

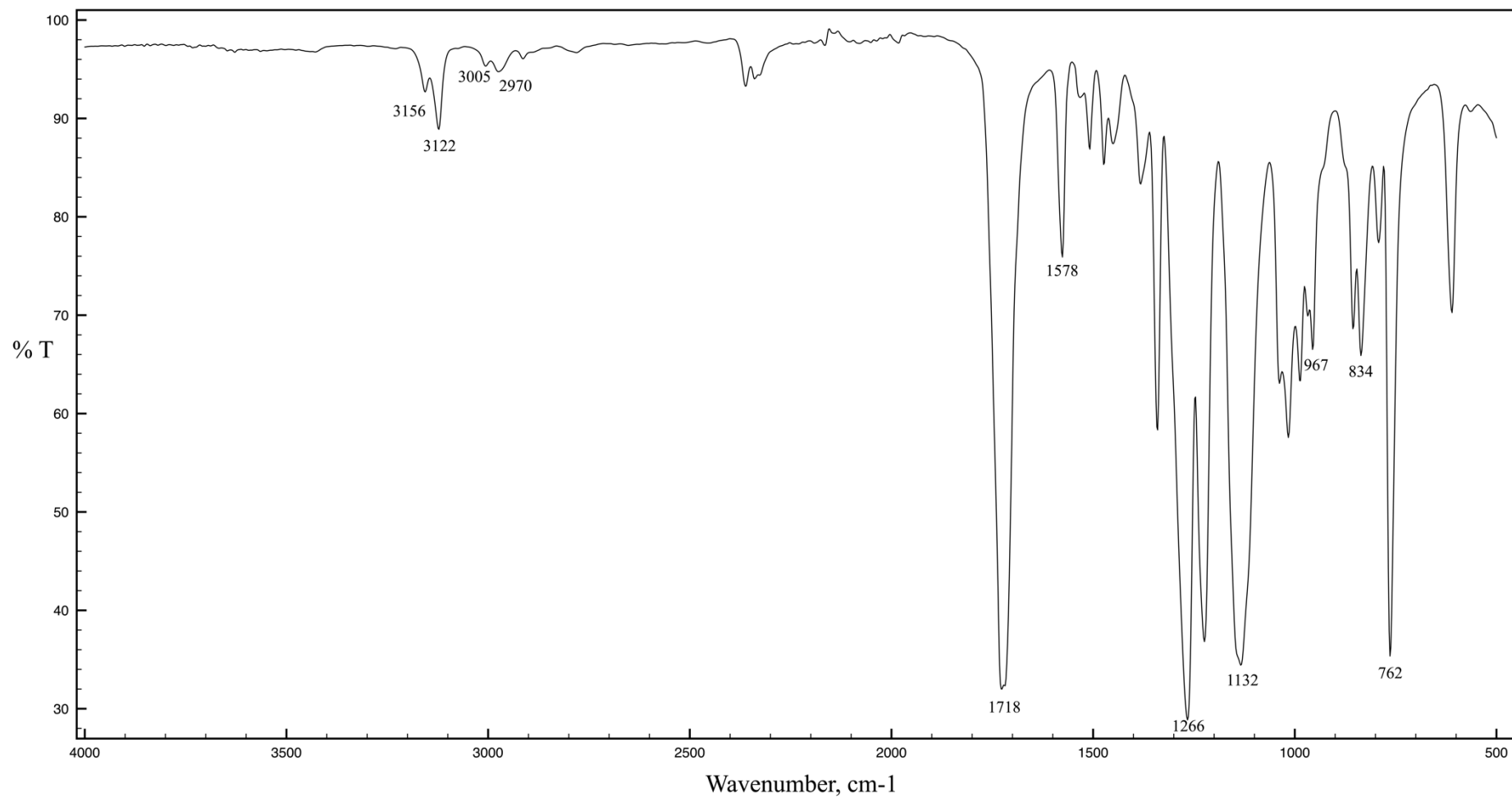


Figure S2. ATR FTIR spectrum of **PEF\_1**

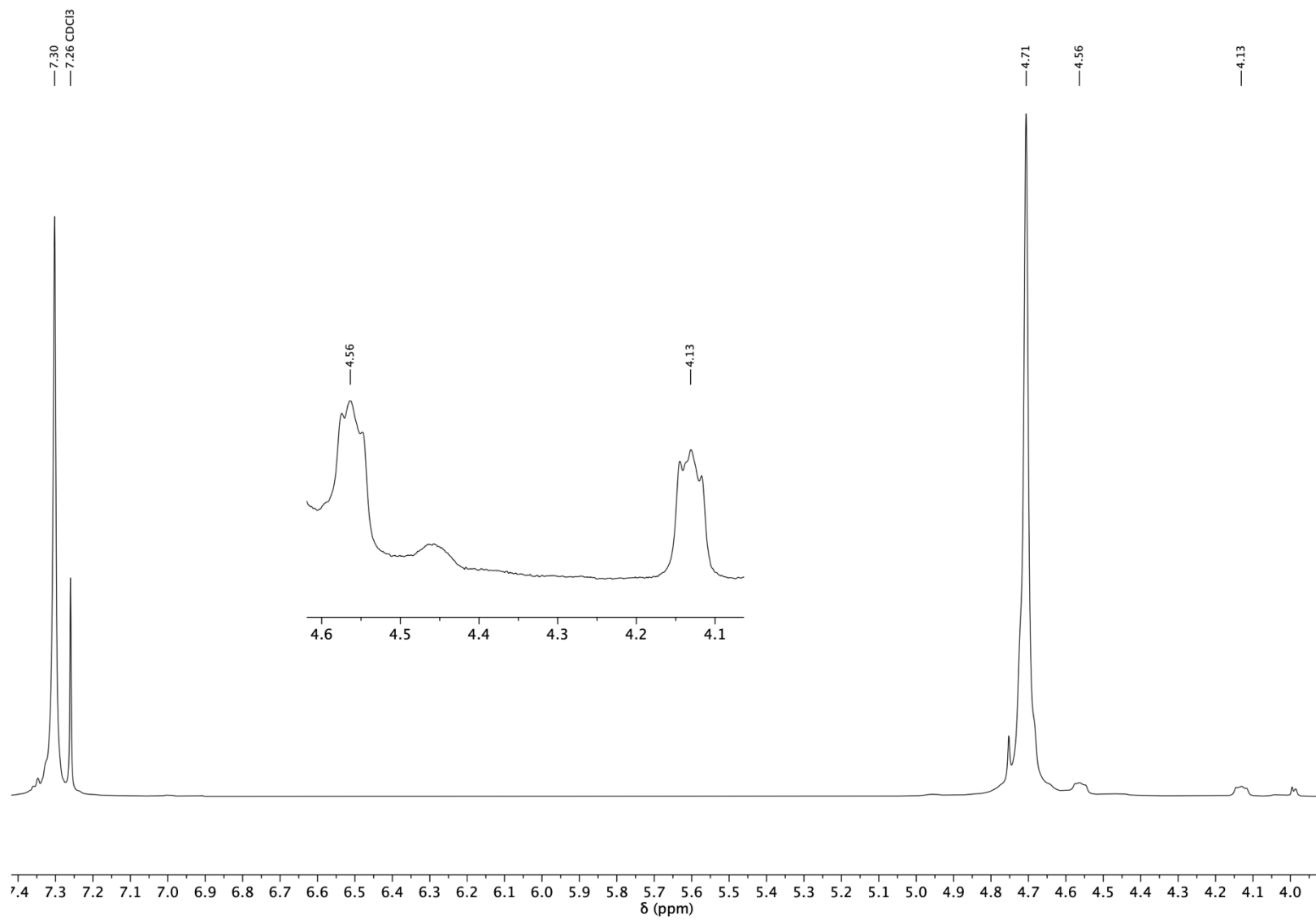


Figure S3.  $^1\text{H}$  NMR spectrum of **PEF\_1** in  $\text{CDCl}_3$  and  $\text{TFA-d}$

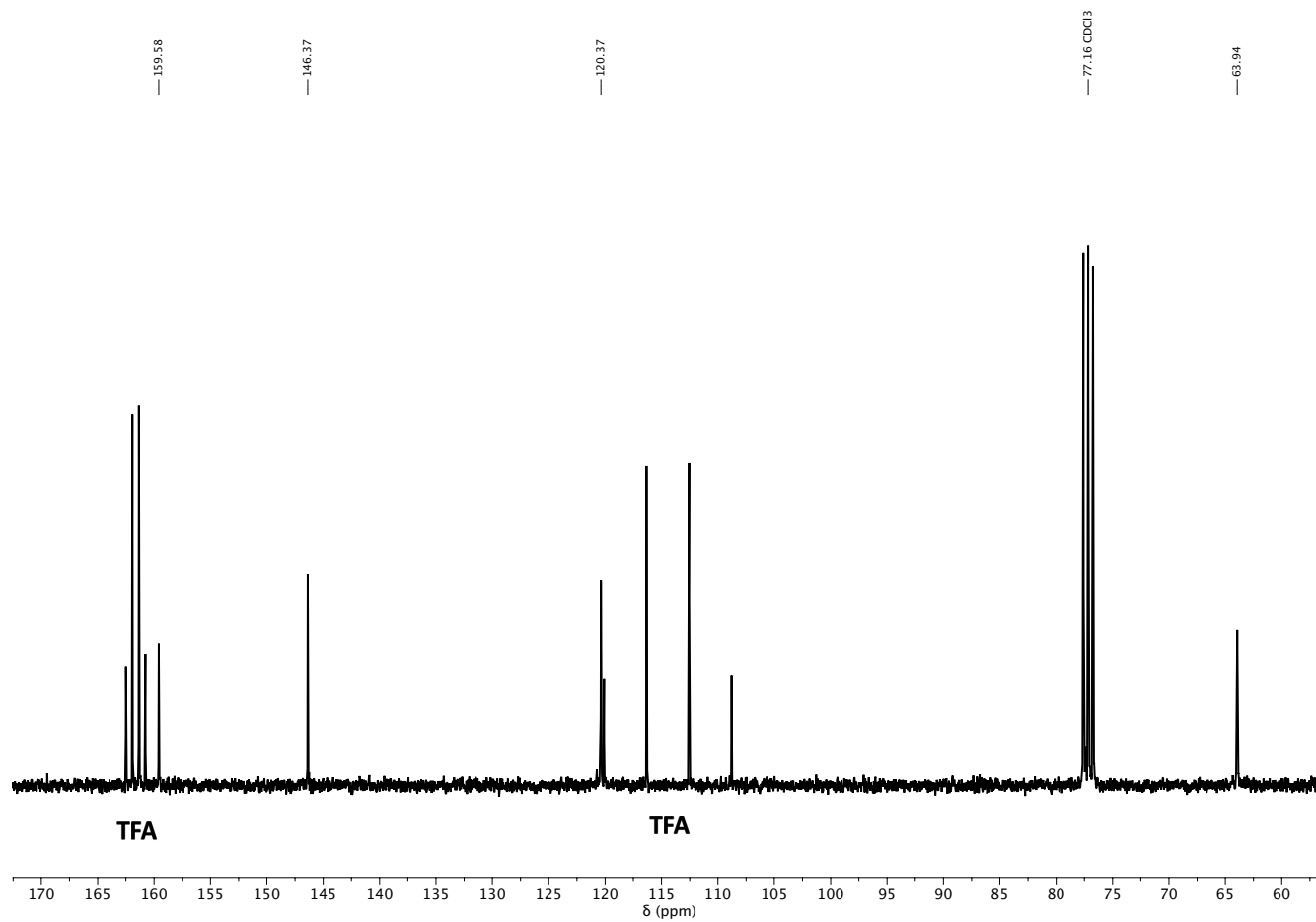


Figure S4.  $^{13}\text{C}$  NMR spectrum of **PEF\_1** in  $\text{CDCl}_3$  and  $\text{TFA-d}$

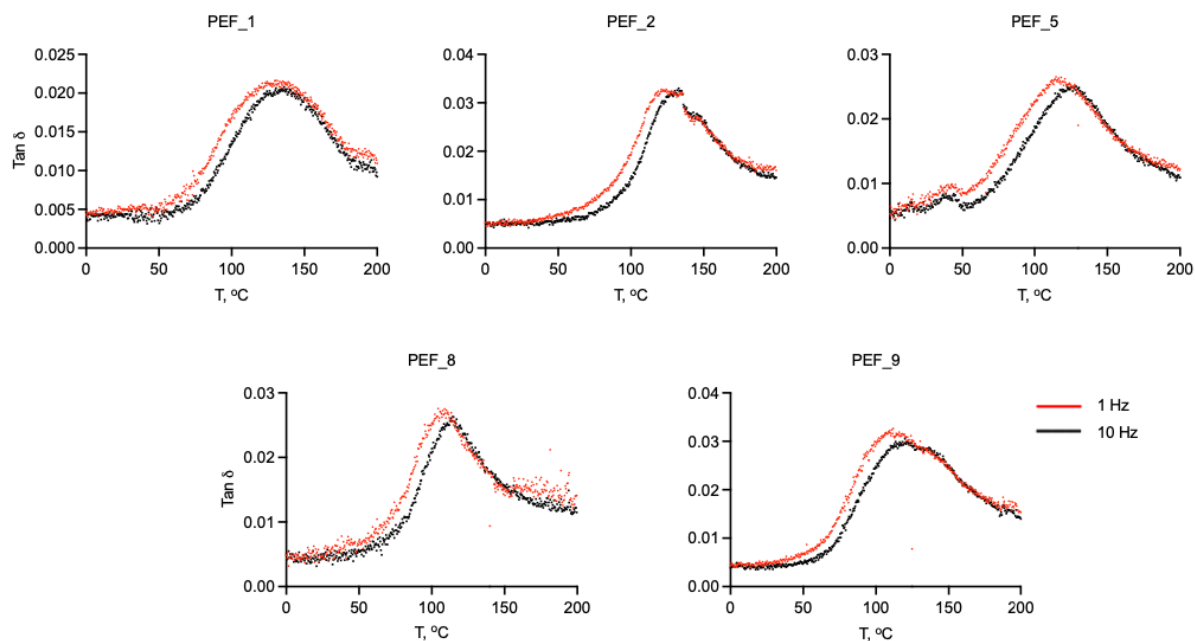


Figure S5. Tan  $\delta$  traces of PEF samples measures at 1 and 10 Hz

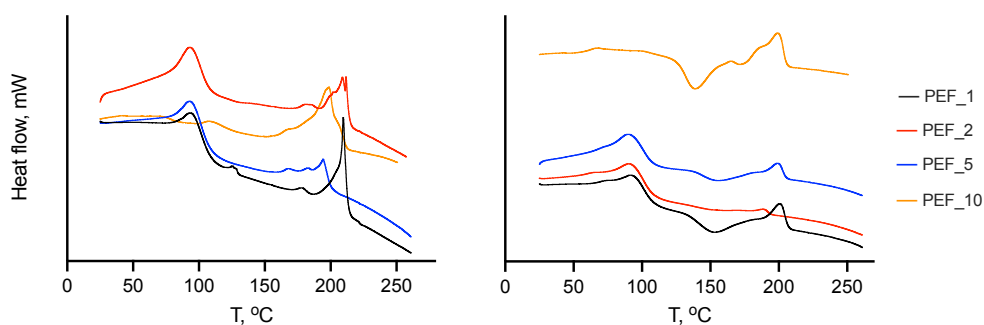


Figure S6. DSC thermograms of PEF recorded during the a) 1<sup>st</sup> heating and b) 2<sup>nd</sup> heating

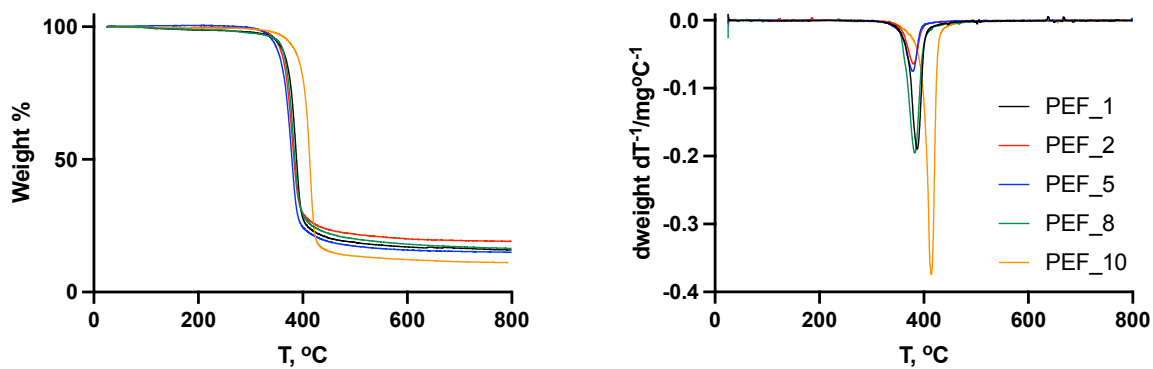


Figure S7. TGA and DTG thermograms of PEF samples

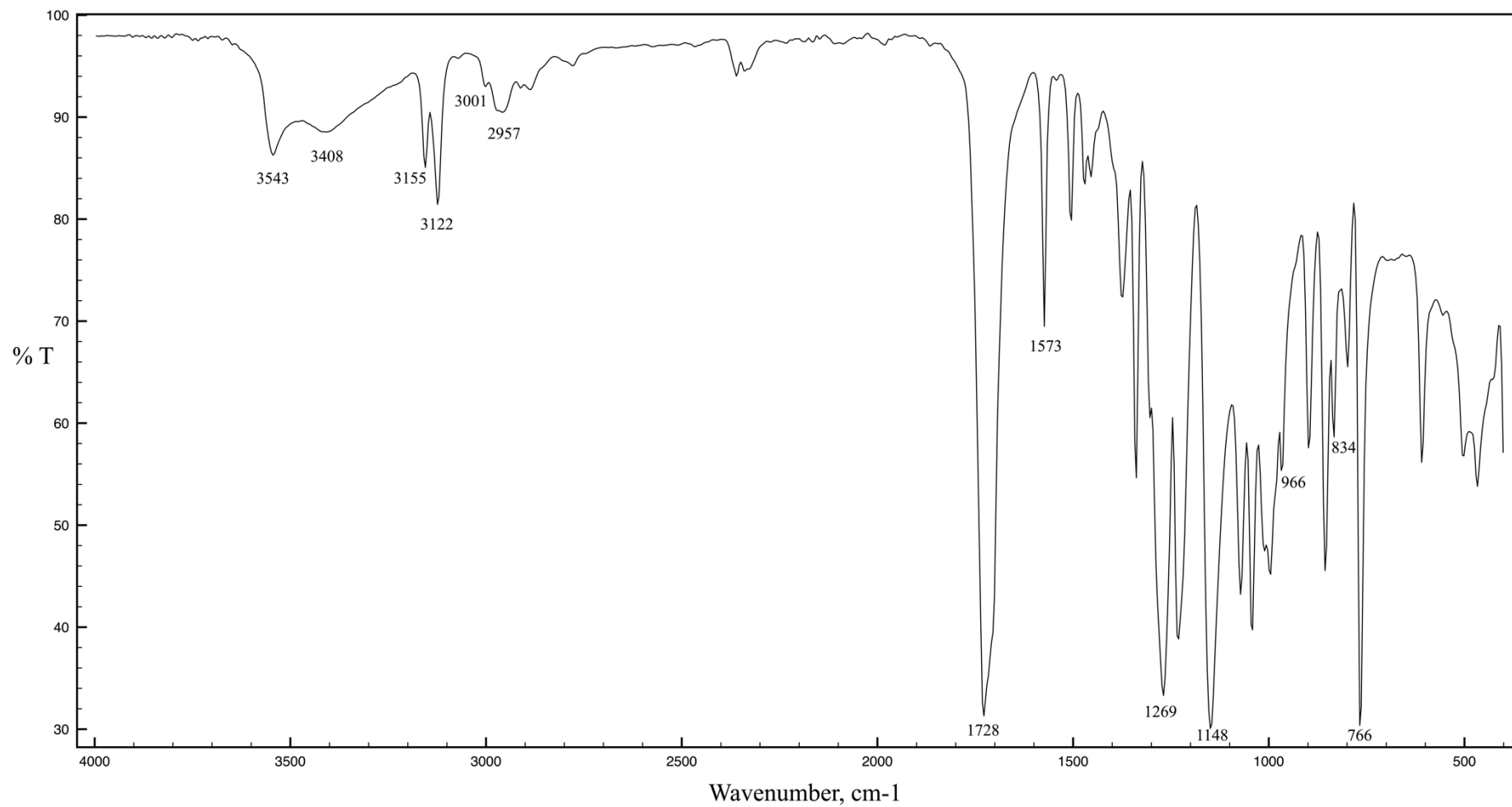


Figure S8. Typical ATR-FTIR spectrum of the depolymerization product of **PEF\_1**

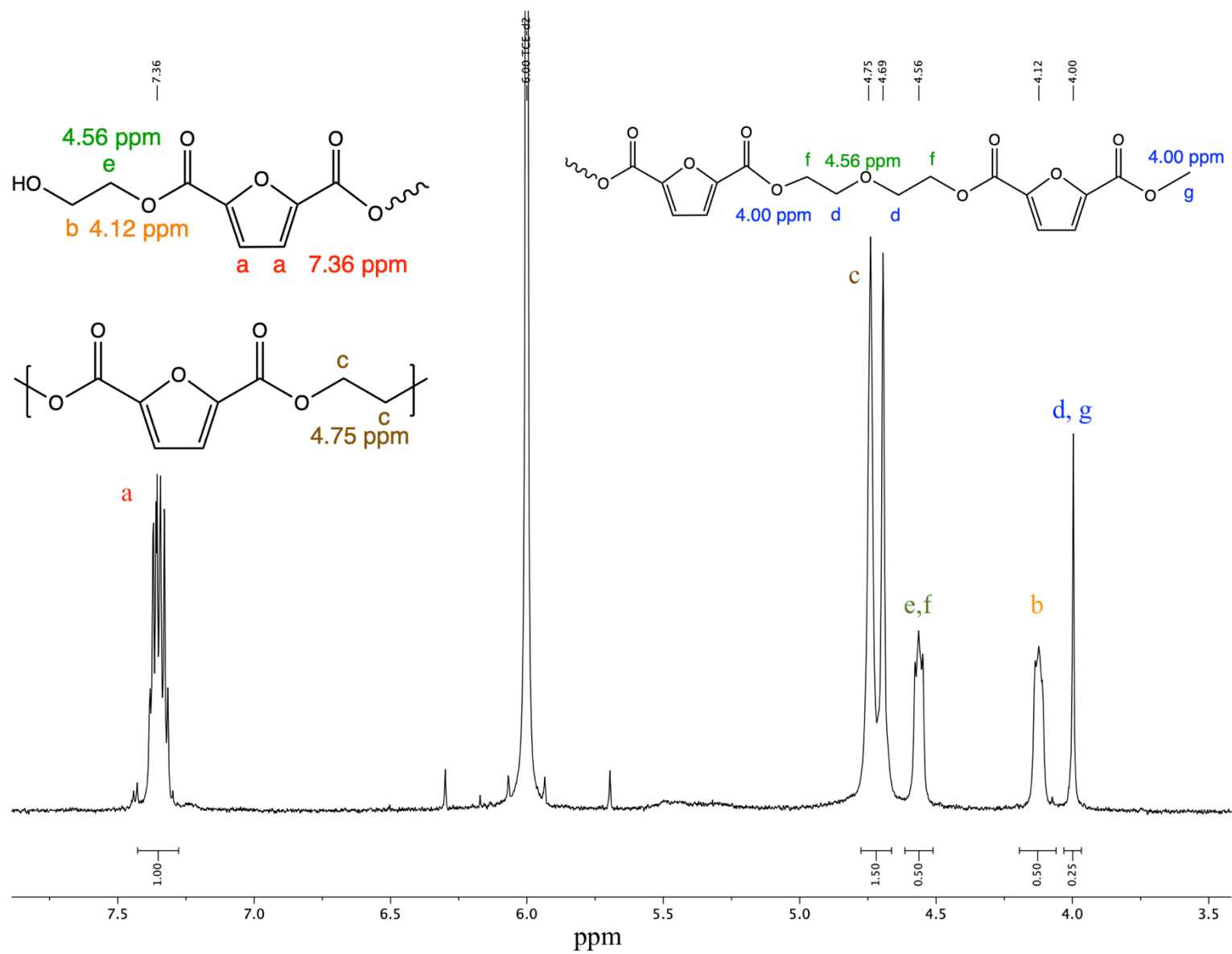


Figure S9.  $^1\text{H}$  NMR spectrum of the depolymerization product of **PEF\_1** in  $\text{TCE-}d_2$  and  $\text{TFA-}d$  and possible species



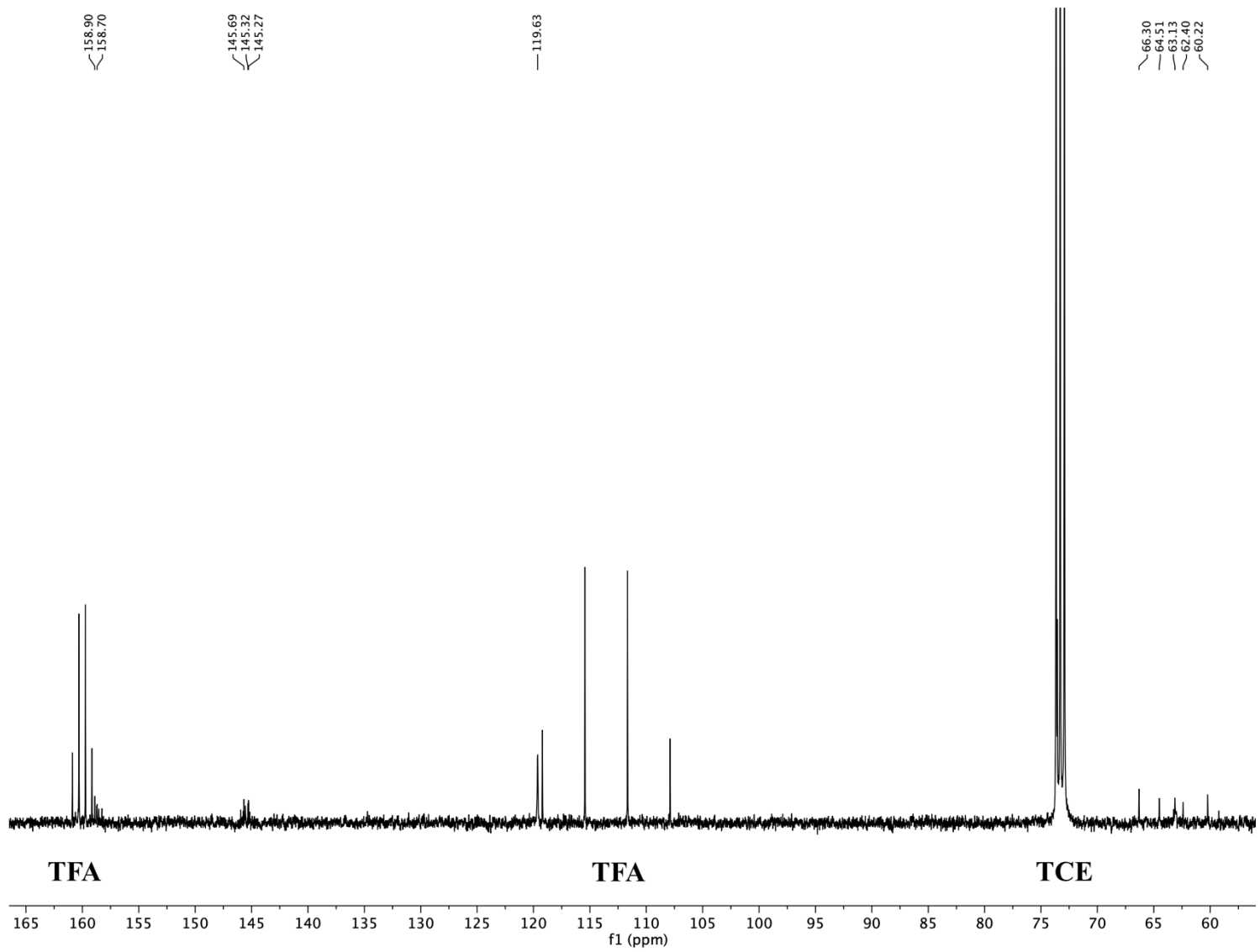
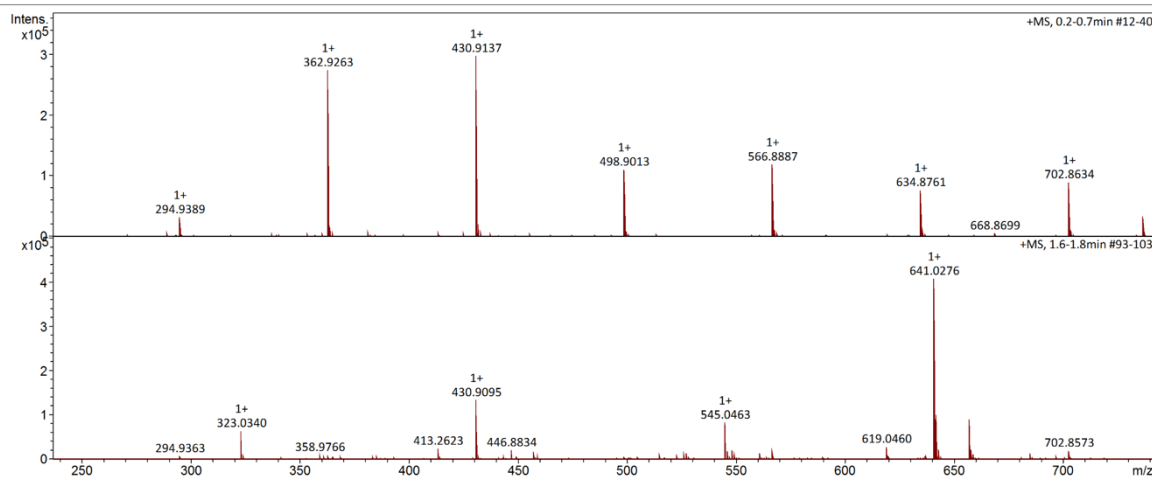


Figure S10. <sup>13</sup>C NMR spectrum of the depolymerization product of PEF\_1 in TCE-*d*<sub>2</sub> and TFA-*d*

## Display Report

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Method	Instrument	compact
Sample Name		8255754.20020
Comment		

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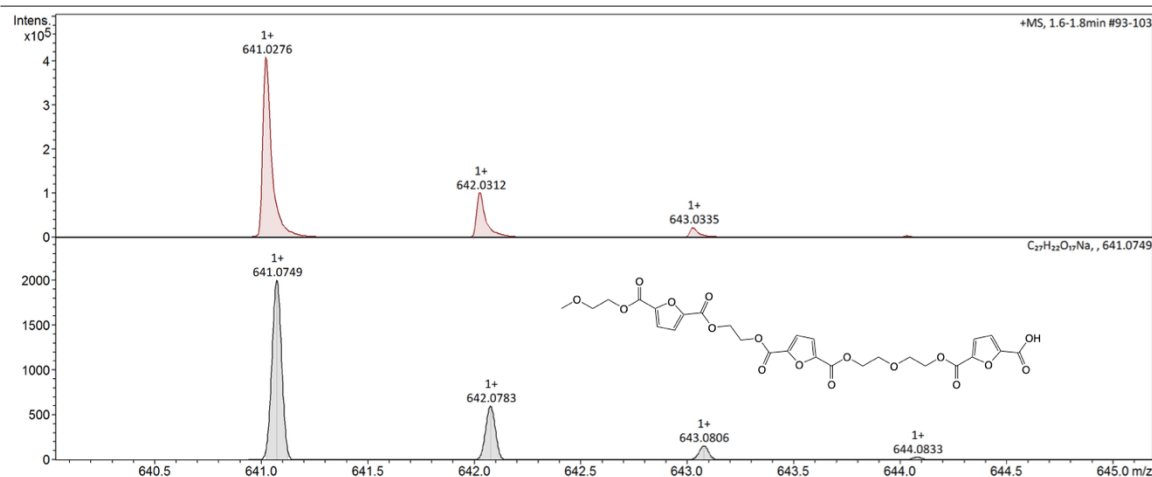
DMR\_4\_162\_1.d  
 Bruker Compass DataAnalysis 4.3 printed: 9/3/2024 3:05:22 PM by: BDAL@DE Page 1 of 1

Figure S11 The mass spectrum of depolymerization product (bottom) and baseline (top)

## Display Report

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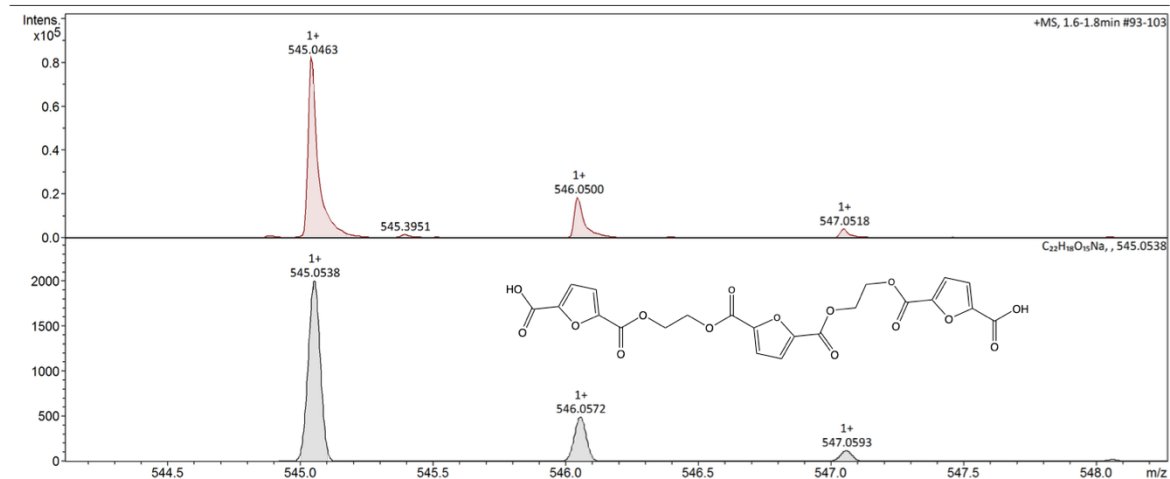


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Figure S12 The measured (top) and simulated (bottom) patterns of depolymerization product

## Display Report

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Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
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Bruker Compass DataAnalysis 4.3 printed: 9/3/2024 3:11:47 PM by: BDAL@DE Page 1 of 1

Figure S13 The measured (top) and simulated (bottom) patterns of depolymerization product

### Appendix S1. Degree polymerization and Polymer average molecular weight ( $M_n$ ) analysis

Number average molecular weight ( $M_n$ ) can be calculated by equation (1):

$$M_n = DP \times M_0 + M_e; \quad (1)$$

where DP is degree of polymerization or the number of repeating units;  $M_0$  is the molecular weight of one repeating unit (for PEF  $M_0=190$  g/mol) and  $M_e$  is the combined molecular weights of the end-groups ( $M_e(\text{OH group}) = 17$  g/mol and  $M_e(\text{CH}_2\text{CH}_2\text{OH group}) = 45$  g/mol).

Degree polymerization or number of repeating units can be found by equation (2):

$$DP = \frac{\text{integral of the repeating unit}}{\text{number of protons of the repeating unit}} / \frac{\text{integration of the end group}}{\text{number of protons of the end group}}; \quad (2)$$

For our polymer, the integral of the repeating units is 1.00, and the number of protons of the repeating unit is 2 (Figure S11); the integration of the end group is 0.06, and the number of protons of the end group is 4 (Figure S11). The polymer average molecular weight calculations are described in detail in reference 68.

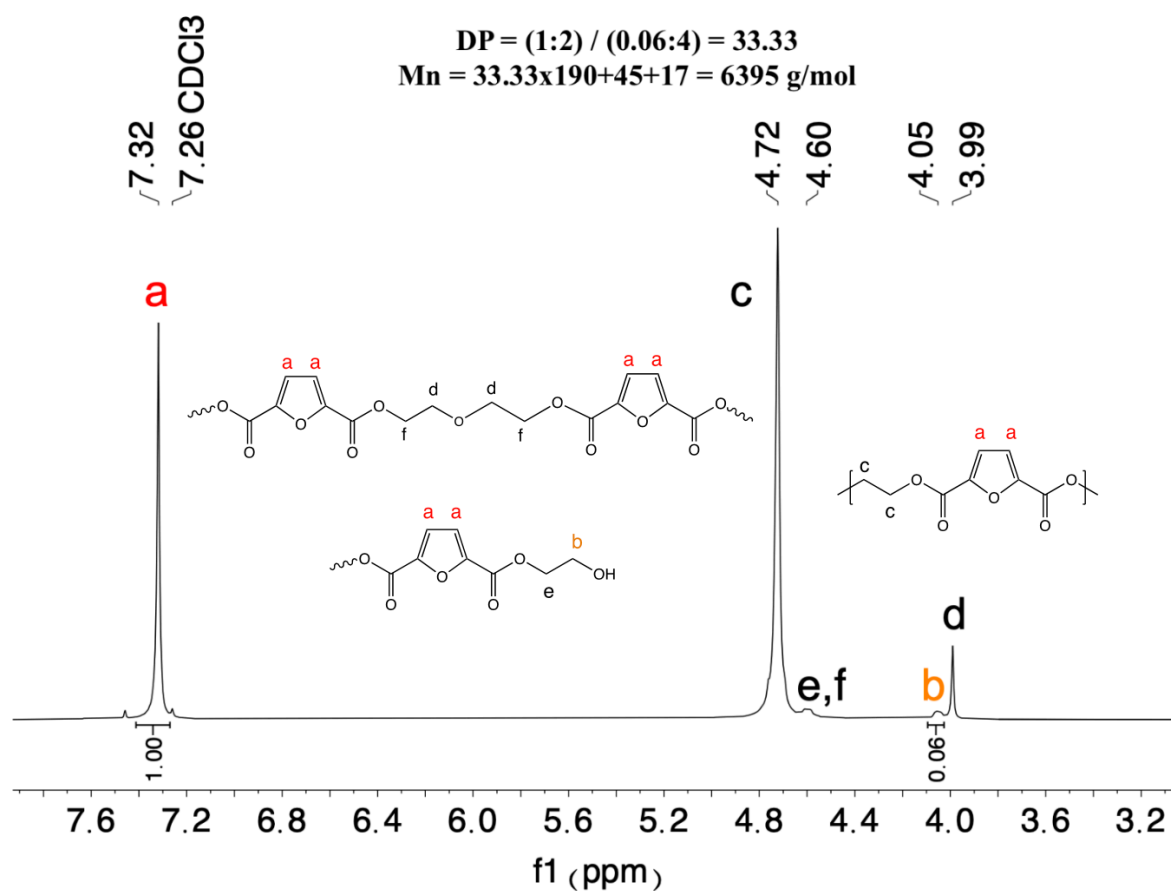


Figure S14. An example of polymer average molecular weight (Mn) analysis for **PEF<sub>2</sub>**. The integral of the repeating units is 1 for the depolymerization product, the number of protons of the repeating unit is 2, the integration of the end group is 0.5, and the number of protons of the end group is 4 (Figure S9). Number of repeating units of depolymerization product:

$$DP = \frac{1}{\frac{2}{0.5}} = 4$$