Supplementary information for

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

Dmitrii Razinkov, [a] Beatriz Agostinho, [b] Sigridur G. Suman, [a,*] and Andreia F. Sousa [b,*]

[a] Science Institute, University of Iceland, Dunhagi 3, 107 Reykjavik, Iceland

[b] CICECO—Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

[c] Centre for Mechanical Engineering, Materials and Processes, Department of Chemical Engineering, University of Coimbra Rua Sílvio Lima – Polo II, 3030-790 Coimbra, Portugal

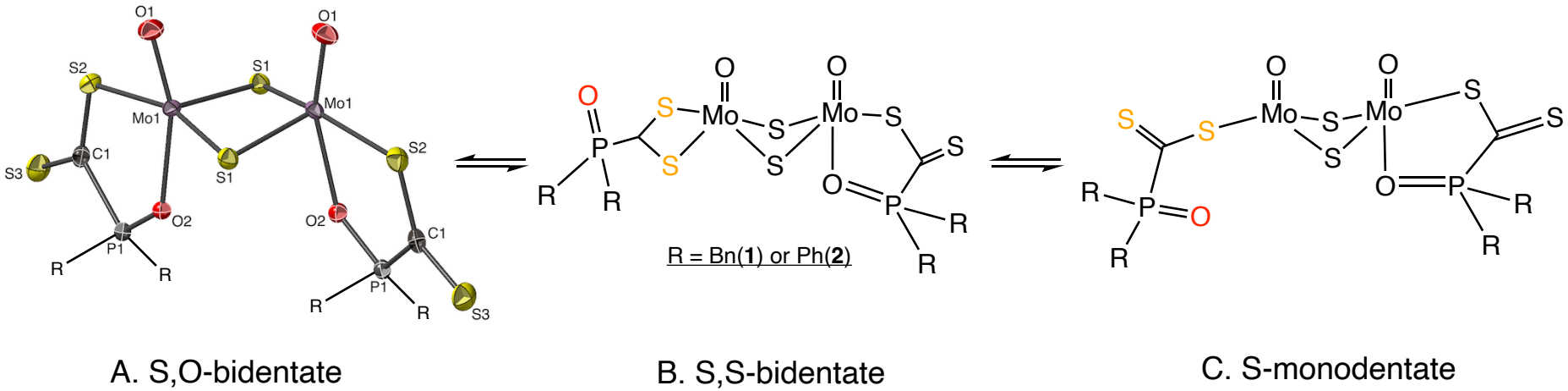

Figure S1. Coordination modes of phosphinoyldithioformate ligands to a metal center. Structure and labeling of **2** (A), DMF ligands are omitted for clarity

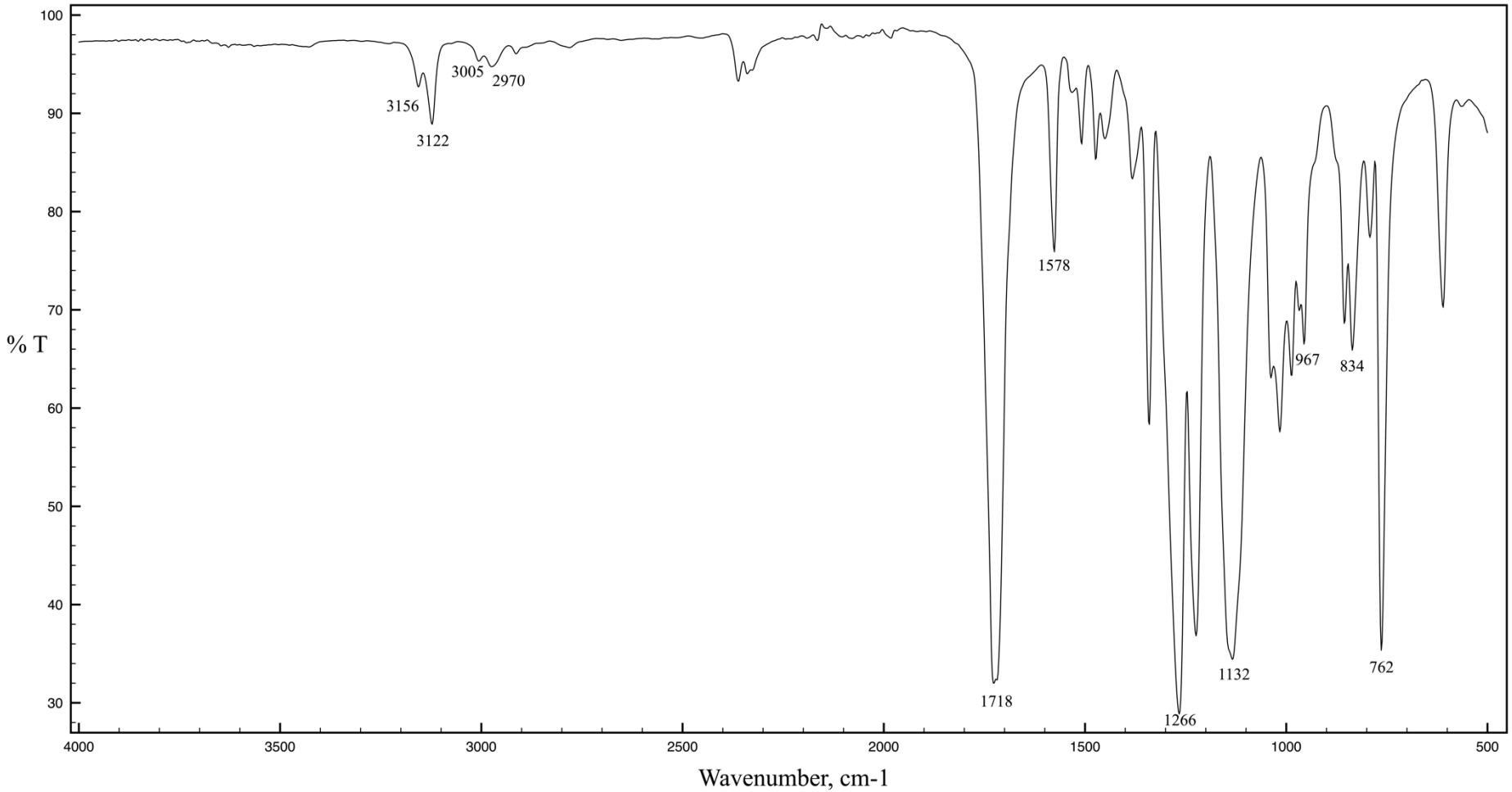

Figure S2. ATR FTIR spectrum of **PEF_1**

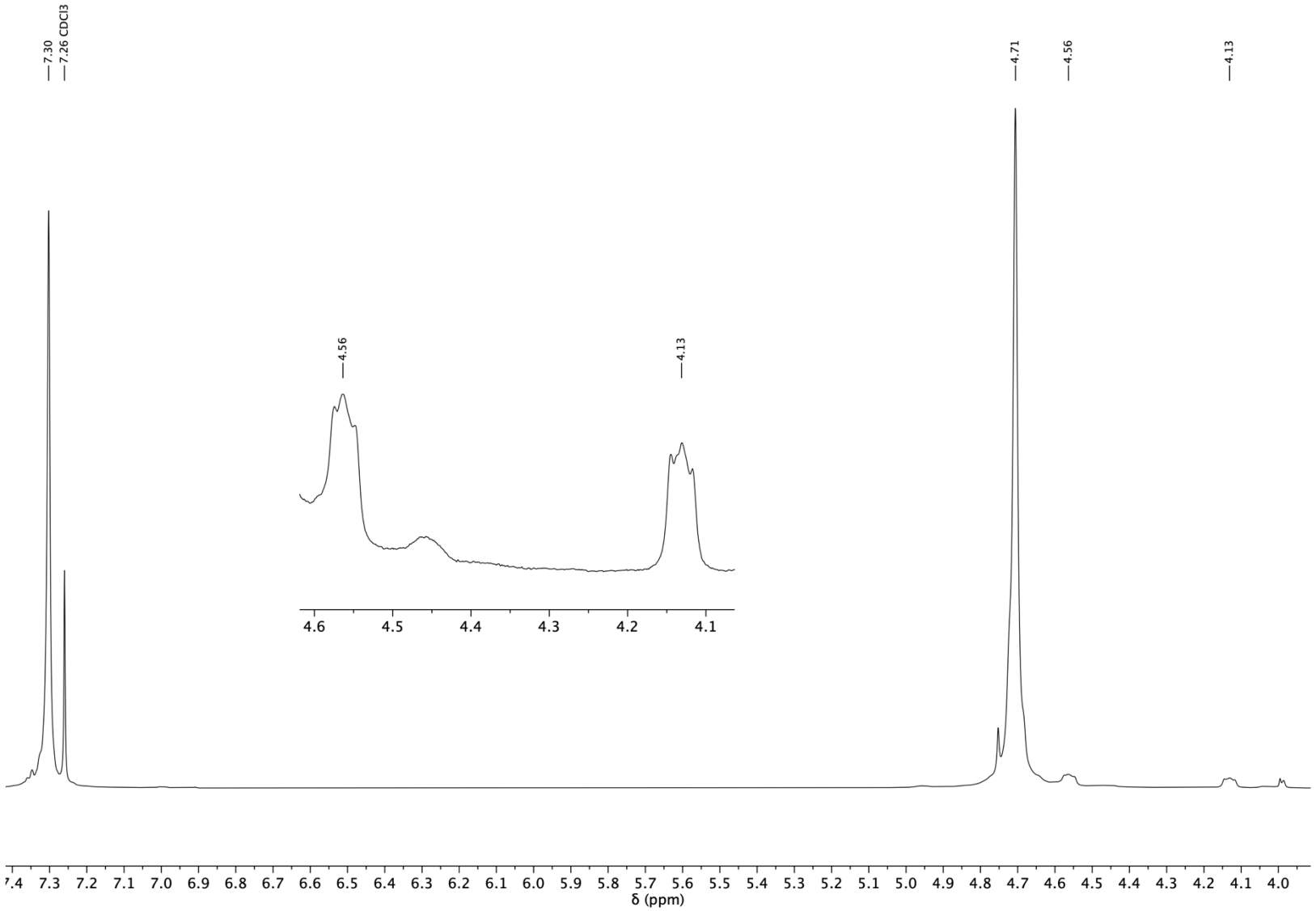

Figure S3. ^{1}H NMR spectrum of **PEF_1** in C*D*Cl$_3$ and TFA-*d*

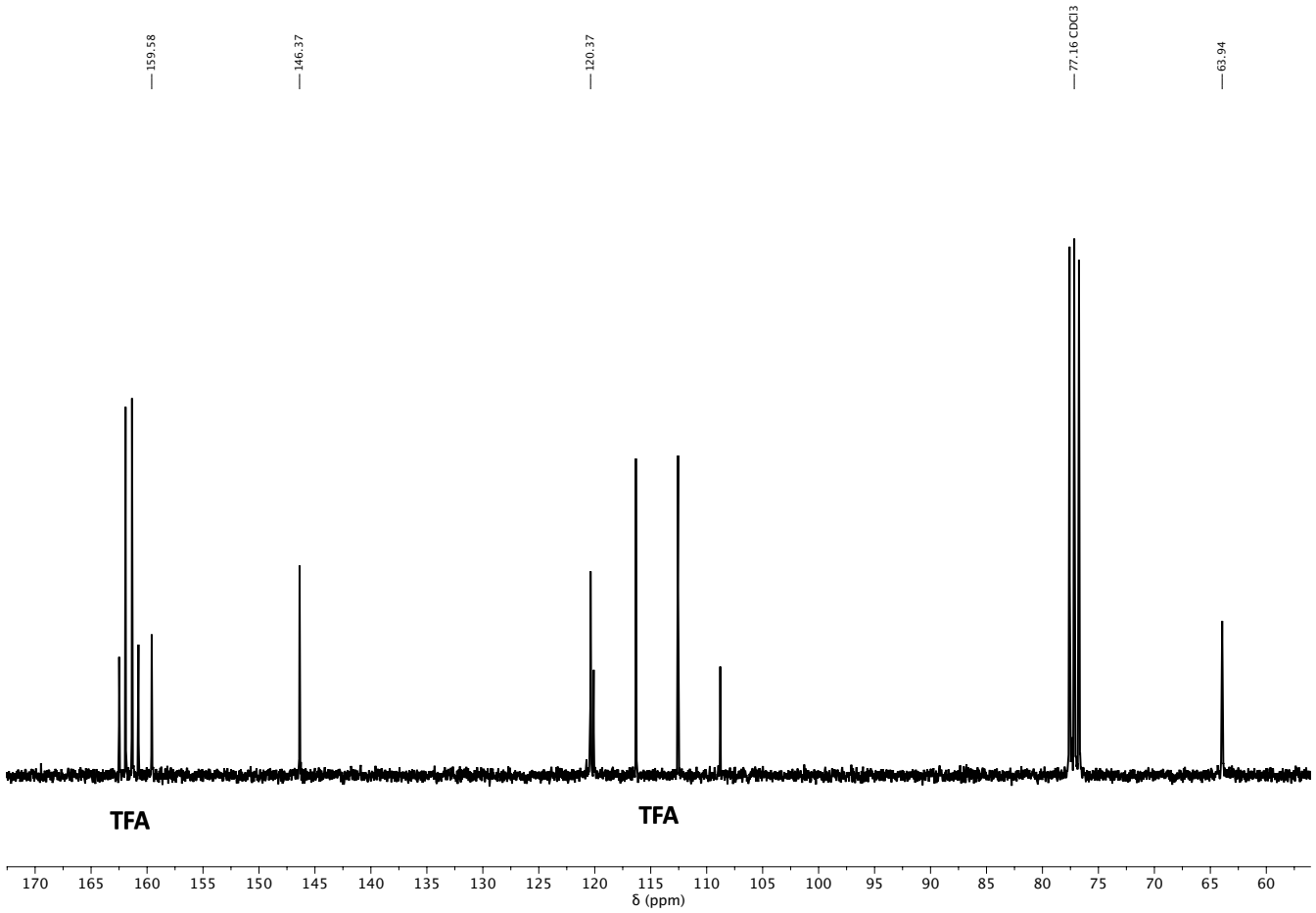

Figure S4. ^{13}C NMR spectrum of **PEF_1** in C*D*Cl_3 and TFA-*d*

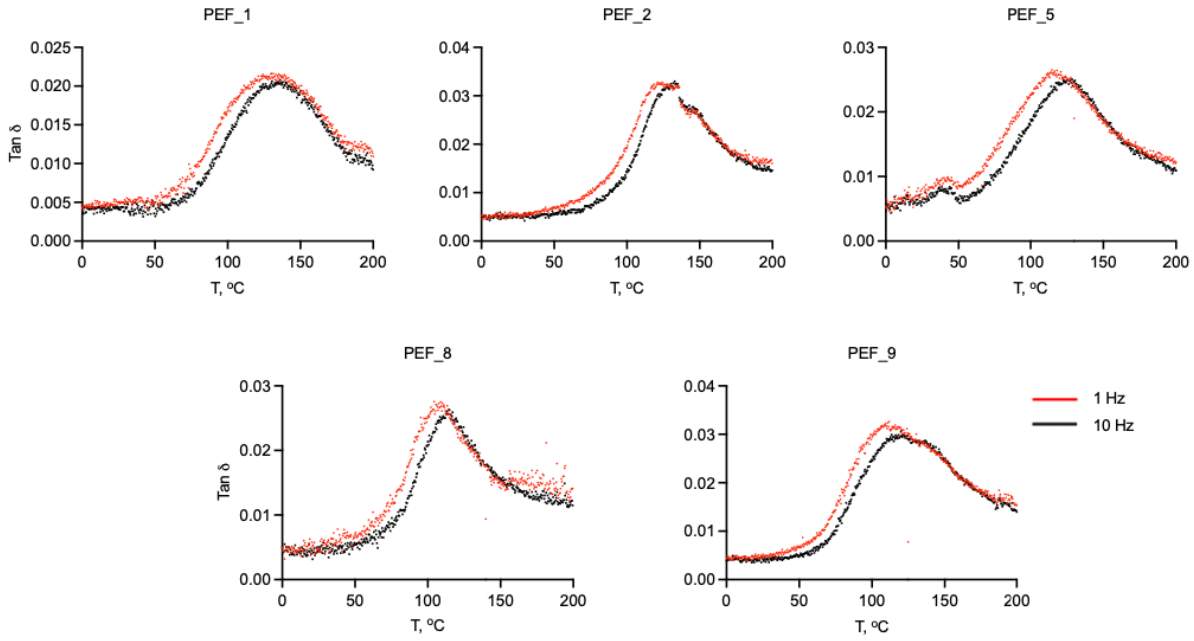

Figure S5. Tan δ traces of PEF samples measures at 1 and 10 Hz

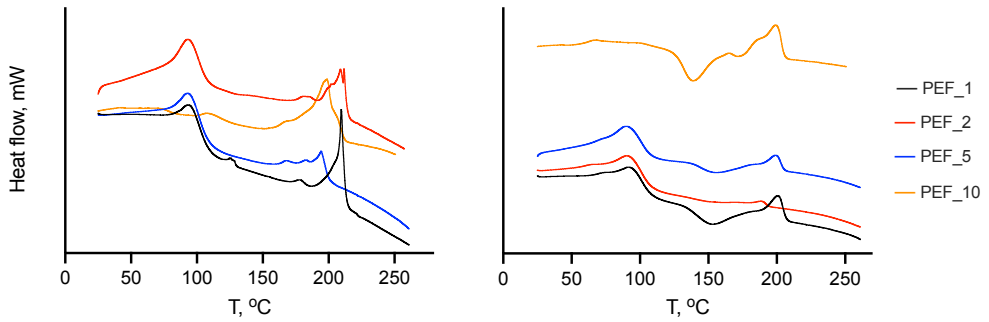

Figure S6. DSC thermograms of PEF recorded during the a)1st heating and b) 2nd heating

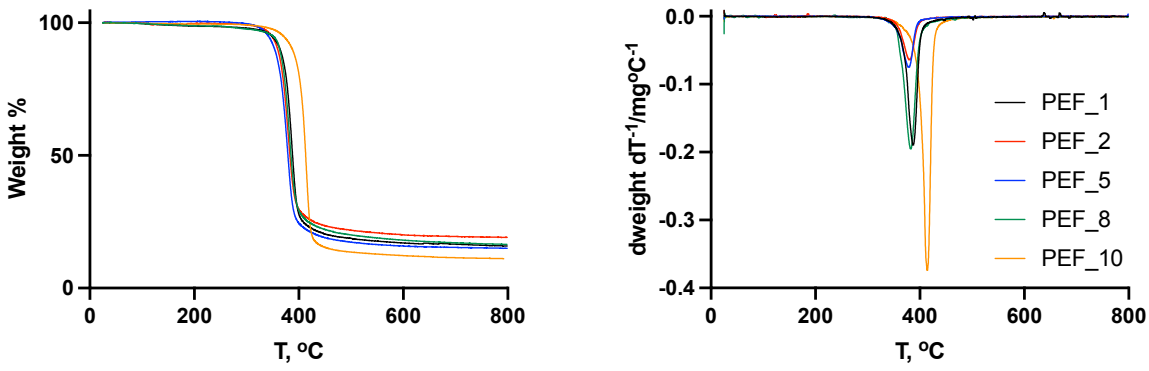

Figure S7. TGA and DTG thermograms of PEF samples

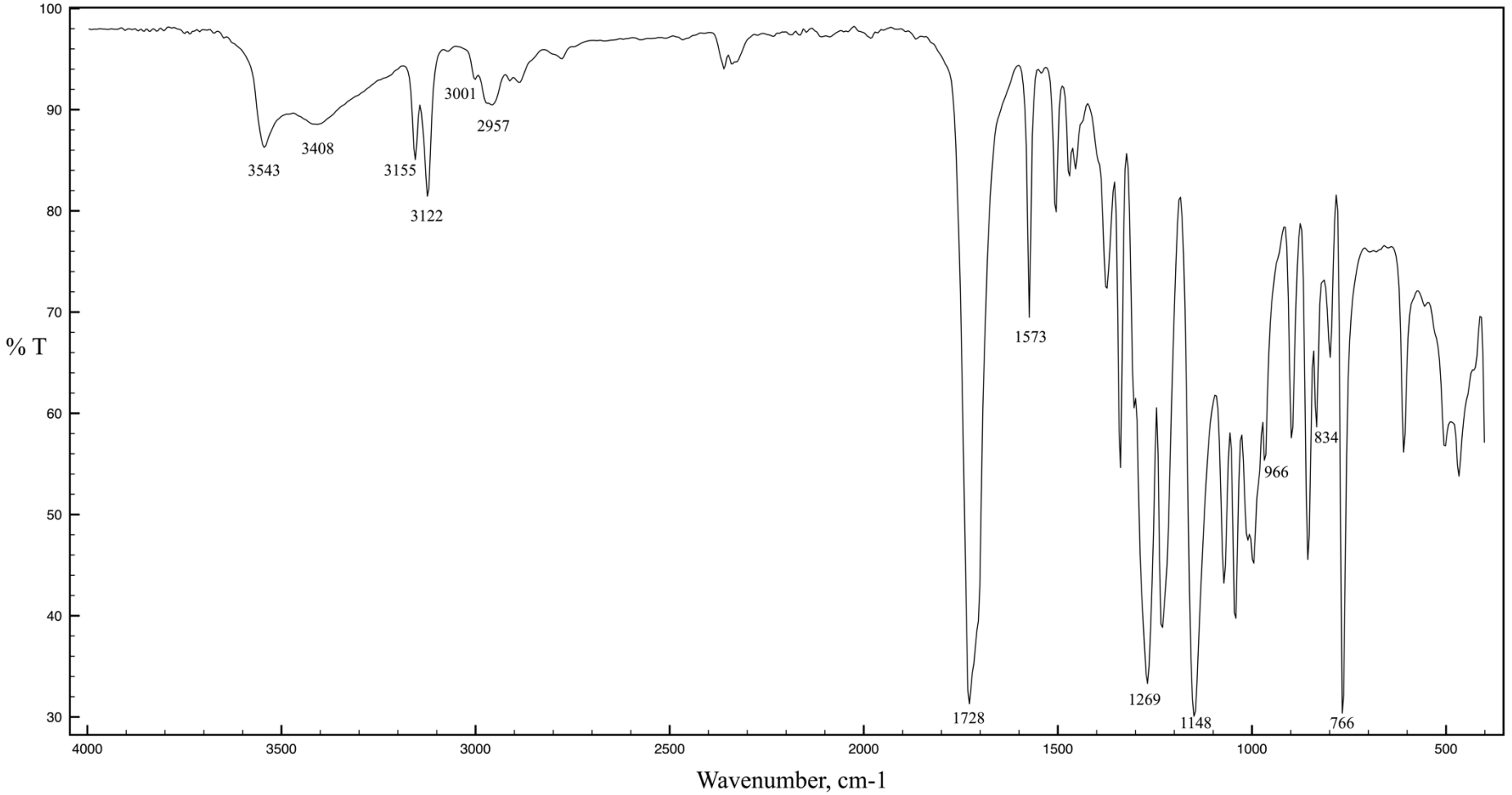

Figure S8. Typical ATR-FTIR spectrum of the depolymerization product of **PEF_1**

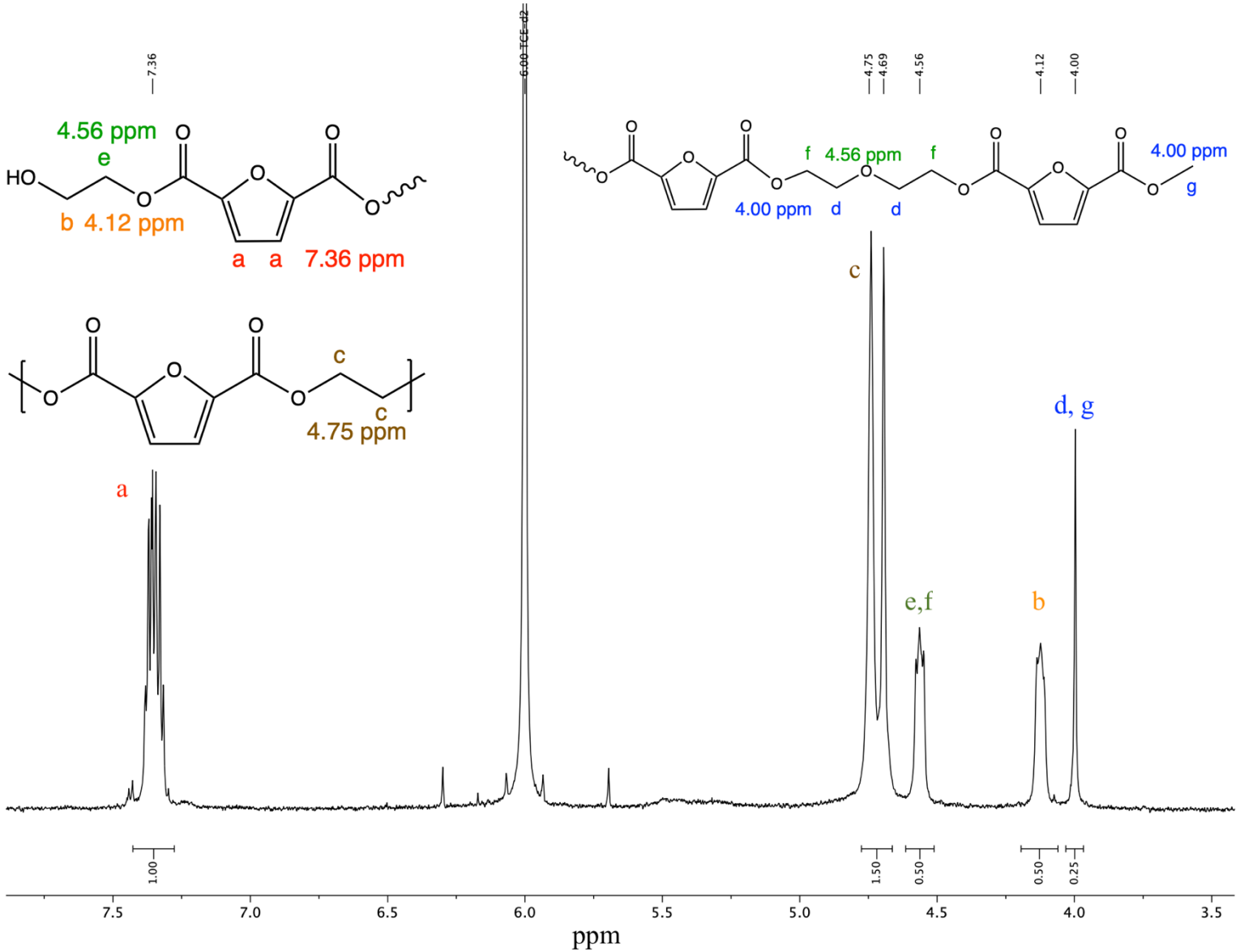

Figure S9. ^{1}H NMR spectrum of the depolymerization product of **PEF_1** in TCE-d_2 and TFA-*d* and possible species

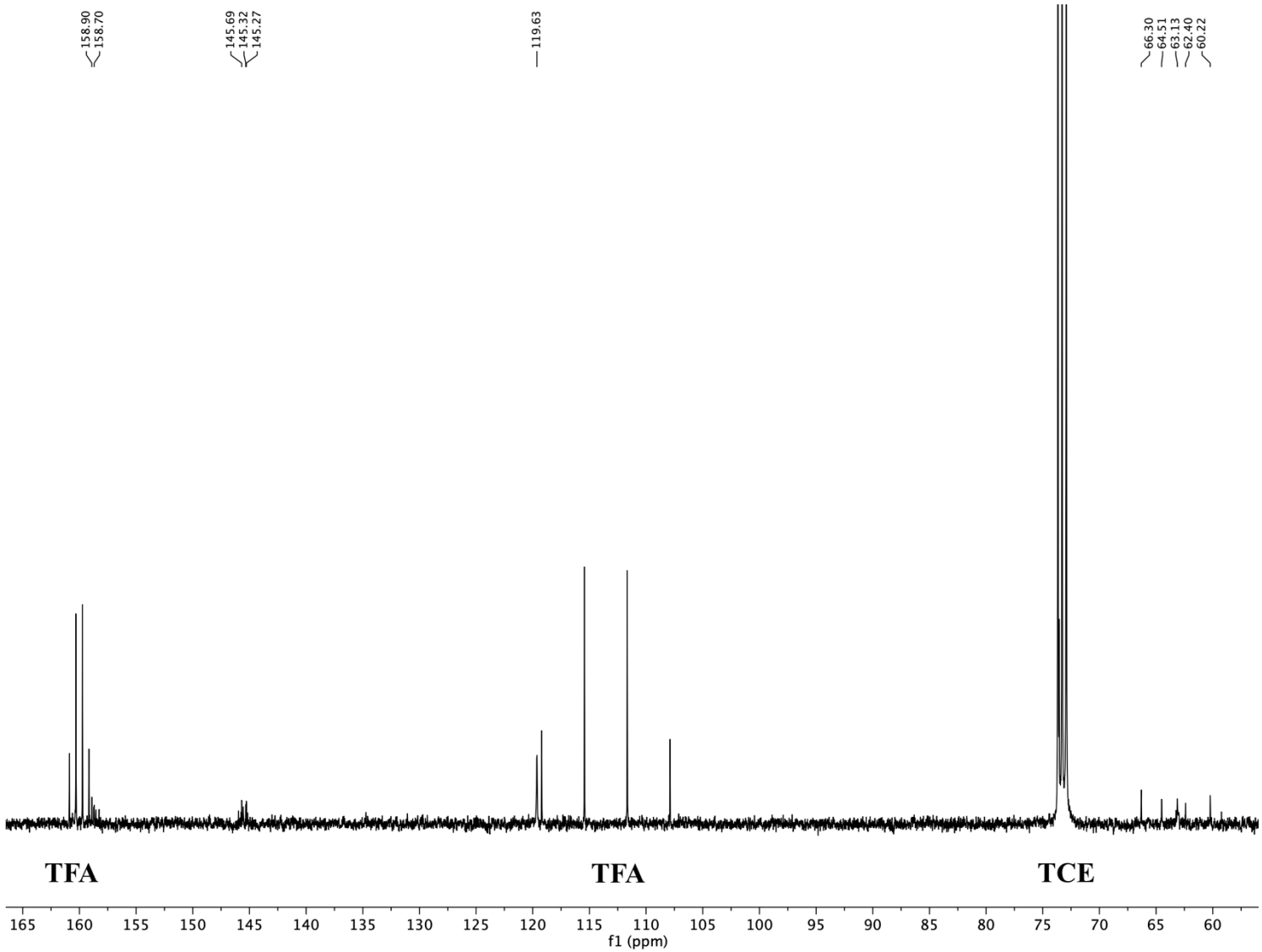

Figure S10. ^{13}C NMR spectrum of the depolymerization product of **PEF_1** in TCE-d_2 and TFA-*d*

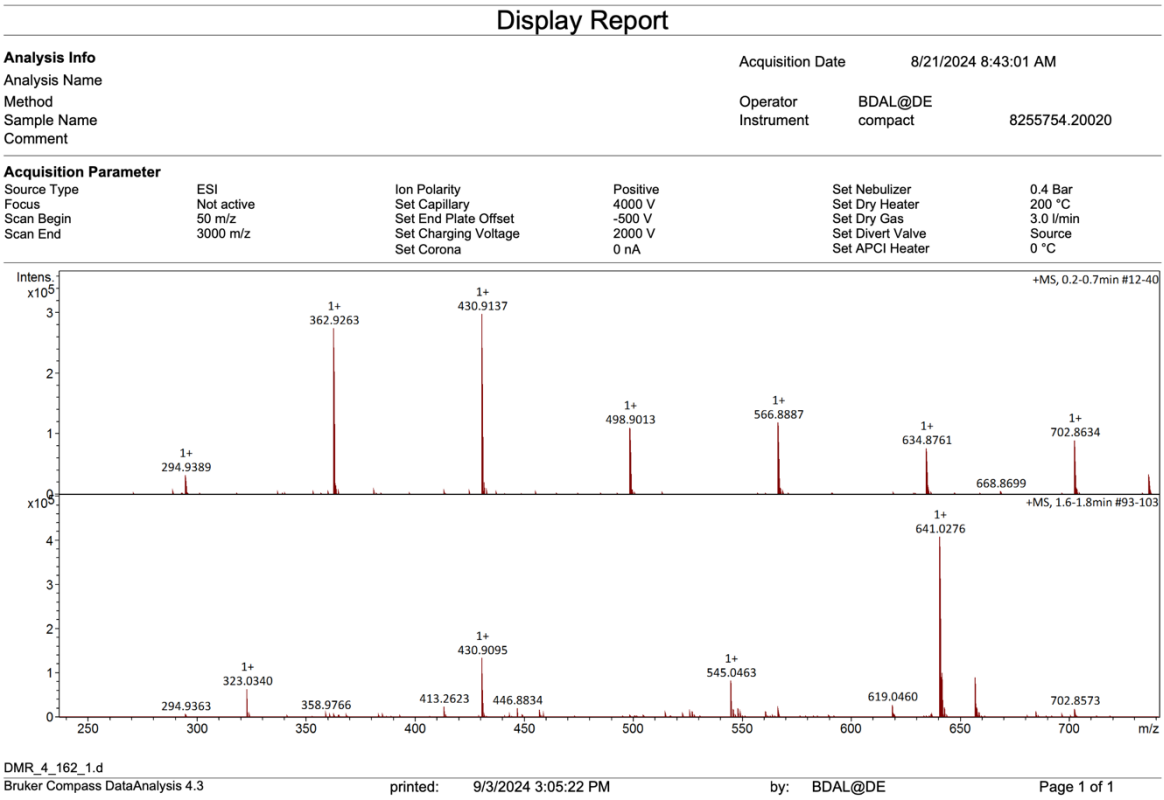

Figure S11 The mass spectrum of depolymerization product (bottom) and baseline (top)

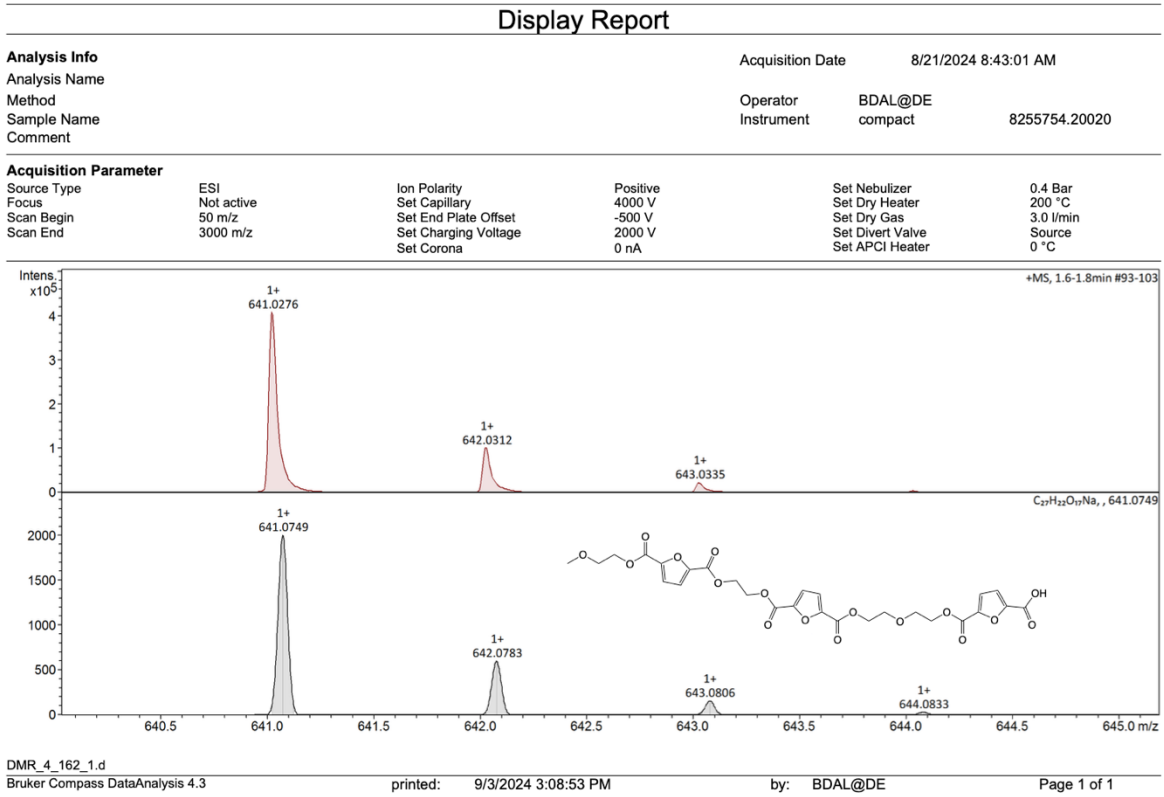

Figure S12 The measured (top) and simulated (bottom) patterns of depolymerization product

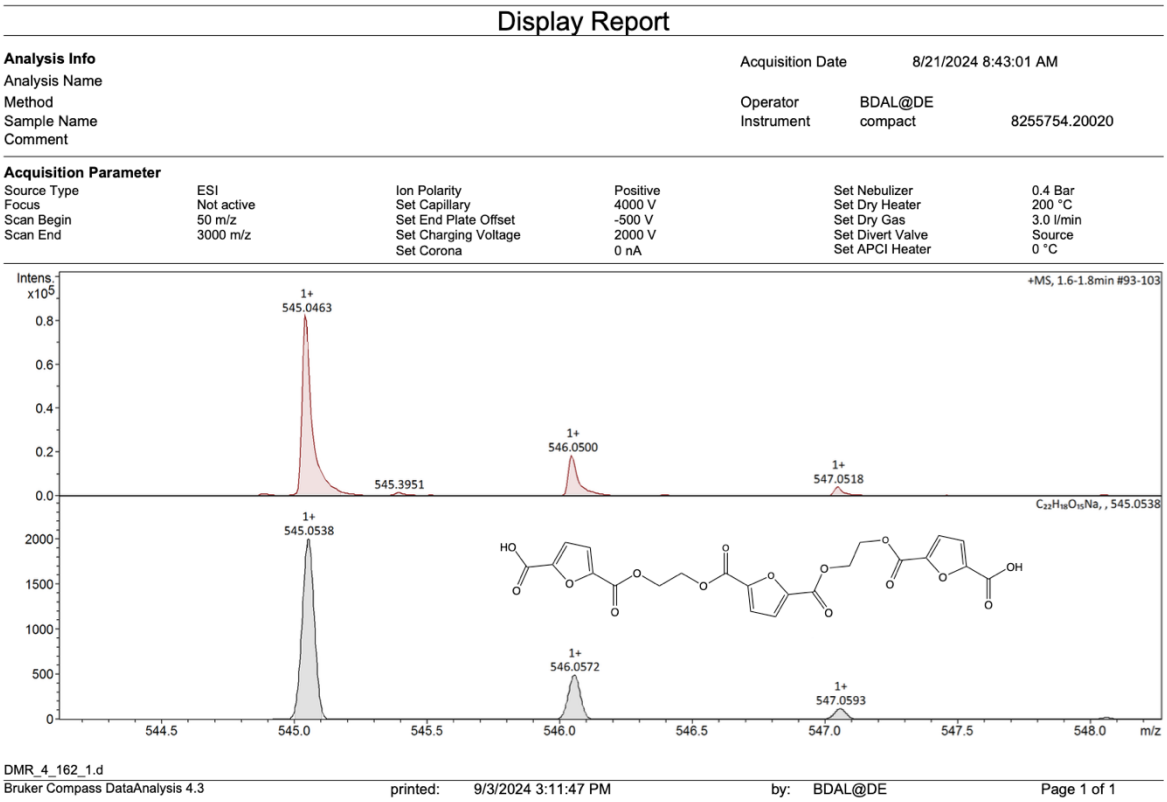

Figure S13 The measured (top) and simulated (bottom) patterns of depolymerization product

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

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

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

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(OH group) = 17 g/mol and M_e(CH_2CH_2OH group) = 45 g/mol).

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

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

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.

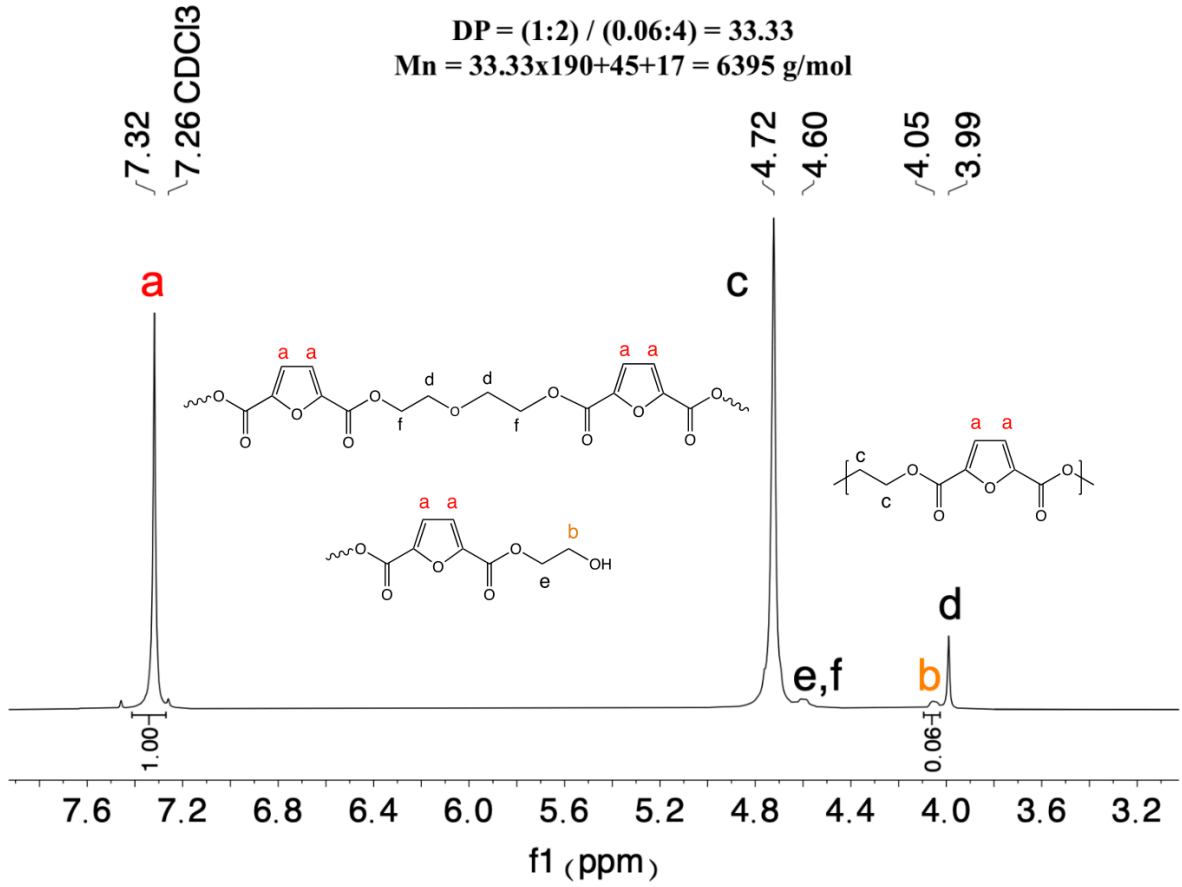

Figure S14. An example of polymer average molecular weight (Mn) analysis for **PEF_2**

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:

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