

Supporting Information for

CO₂ catalyzed recycling of polyester and polycarbonate plastics

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Experimental Section

Materials and instruments

All regular chemicals were purchased from Energy Chemical, Macklin, BidePharm, and Innochem. PLA resins R190 ($M_n = 98.1 \text{ kg mol}^{-1}$, $\bar{D} = 1.66$) and R290 ($M_n = 87.8 \text{ kg mol}^{-1}$, $\bar{D} = 1.46$) were produced from Zhejiang Hisun Biomaterials. PLA resin 4032D ($M_n = 111.0 \text{ kg mol}^{-1}$, $\bar{D} = 1.56$) was produced from NatureWorks. PET pellets were purchased from Macklin. BPA-PC pellets were purchased from Macklin ($M_n = 45.0 \text{ kg mol}^{-1}$, $\bar{D} = 1.60$). MeOH was purchased from Energy Chemical (with septum, extra dry with molecule sieves, water < 50 ppm). CO₂ (99.99% purity) was purchased from Changchun Jiuyang Gas Company. All reactions were conducted in 25 mL stainless-steel autoclaves. ¹H and ¹³C NMR spectra were recorded using a 300 MHz Bruker NMR spectrometer at 22 °C. ²H NMR spectra was recorded using a 400 MHz JEOL NMR spectrometer at 22 °C. Chirality of methyl lactate was determined by a Thermo Scientific gas chromatograph with chiral stationary phase.

General procedure of methanolysis of PLA, PET, and BPA-PC

In a glove box, PLA resin R190 (288 mg, 4 mmol ester units), MeOH (3.2 g, 100 mmol, 25 equiv. relative to ester units) were added to a 25 mL stainless-steel autoclave. Then, 1 MPa CO₂ was filled to the autoclave. The reaction mixture was heated at 140 °C. After a specified time, the autoclave was cooled to room temperature. A small aliquot was taken out for determination of conversion by ¹H NMR spectroscopy. The isolated yield of methyl lactate was 88% by distillation.

In a glove box, PET pellets (384 mg, 2 mmol ester units), MeOH (3.2 g, 100 mmol, 25 equiv. relative to ester units) were added to a 25 mL stainless-steel autoclave. Then, 1 MPa CO₂ was filled to the autoclave. The reaction mixture was heated at 200 °C. After 6 h, the tube was cooled to room temperature. A small aliquot was taken out for determination of the conversion by ¹H NMR spectroscopy. The isolated yield of dimethyl terephthalate was 83% by removing solvent *in vacuo*.

In a glove box, BPA-PC pellets (508 mg, 2 mmol carbonate units), MeOH (3.2 g, 100 mmol, 50 equiv. relative to carbonate units), were added to a 25 mL stainless-steel autoclave. Then, 1 MPa CO₂ was filled to the autoclave. The reaction mixture was heated at 140 °C. After a specified time, the tube was cooled to room temperature. a small aliquot was taken out for determination of the depolymerization rate by ¹H NMR spectroscopy. The isolated yield of bisphenol A was 82% by removing solvent *in vacuo*.

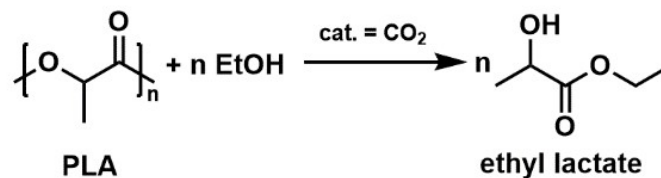
Procedure for pre-treatment with THF

In an autoclave, a specific amount of polymer material (288 mg PLA, or 384 mg PET, or 508 mg BPA-PC) and 3 mL of THF were added. The autoclave was then sealed and heated to 65 °C for 1 hour. After heating, the autoclave was cooled to room temperature and opened. Next, 3 mL of MeOH and 1 MPa CO₂ was filled to the autoclave for the standard methanolysis process.

Computational method:

All density functional theory calculations were performed with the Gaussian 16 software package. [Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; et al., Gaussian 16. Rev. A.03; Gaussian Inc: Wallingford, CT, 2016.] After functional test based on the molecular geometry information check, the geometry optimizations in this work were carried out with the ω B97XD functional [J.-D. Chai and M. Head-Gordon, Phys. Chem. Chem. Phys., 2008, 10, 6615–6620.]. The basis set of def2-TZVP including diffuse and polarization functions was used for all atoms [Weigend, F.; Ahlrichs, R.; Peterson, K. A.; Dunning, T. H.; Pitzer, R. M.; Bergner, A. Physical Chemistry Chemical Physics 2005, 7, 3297]. All structures were subsequently analyzed by harmonic vibrational frequencies at the same level as geometry optimizations to characterize each stationary point and to obtain the thermodynamic corrections to Gibbs free energy. The structures of the transition state (TS) with one imaginary frequency were confirmed by the intrinsic reaction coordinate (IRC) [Cancès, E.; Mennucci, B.; Tomasi, J. A New Integral Equation Formalism for the Polarizable Continuum Model: Theoretical Background and Applications to Isotropic and Anisotropic Dielectrics. A. J. Chem. Phys. 1997, 107, 3032– 3041]. The implicit solvation model based on electron density (SMD) was used in all computations to reflect the solvation effect of the molecules in the MeOH environment. [Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. J. Phys. Chem. B 2009, 113, 6378–6396.] The Gibbs free energy in solution is reported here, which includes the free-energy corrections calculated in the gas phase. The cartesian coordinates for all geometries and the three-dimensional geometry visualization were conducted using the GaussView software [R. Dennington, T. Keith and J. Millam, GaussView 6 Software, 2009.]. The weak interaction analysis and local electron attachment energy (LEAE) was performed with Multiwfn software [Lu, T.; Chen, F. Multiwfn: A multifunctional wavefunction analyzer. J. Comput. Chem. 2012, 33, 580–592.].

Table S1. Ethanolysis of PLA catalyzed by CO₂.



entry	time (h)	conversion (%)
1	6	16
2	15	77
3	24	89

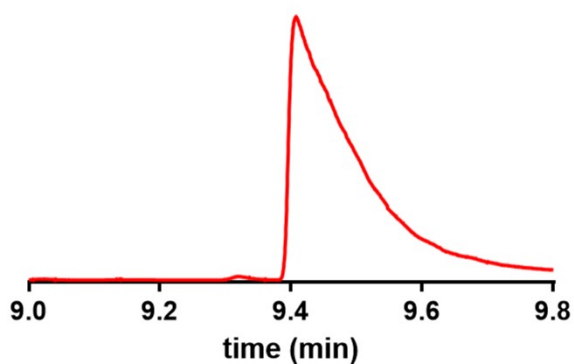
Reaction condition: PLA (R190, 4 mmol ester units, 288 mg), EtOH (100 mmol, 4.6 g, 25 equiv. relative to ester units), CO₂ (1 MPa), *T* = 140 °C. Conversions were determined by ¹H NMR spectroscopy.

Table S2. Screening of CO₂ pressure for methanolysis of PLA.

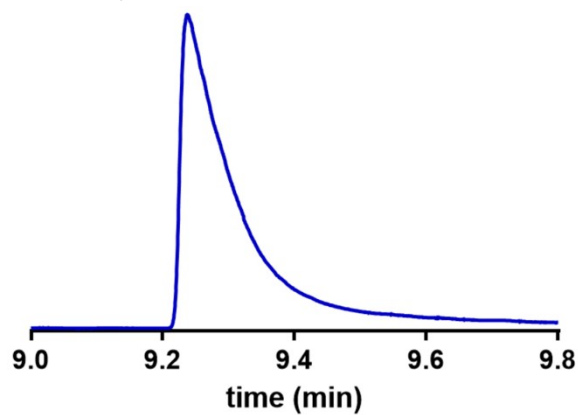
CO ₂ pressure (MPa)	time (h)	conversion (%)
0.2	6	27
1	2	6
	4	27
	6	89
2	2	42
	4	83
	6	99

Reaction condition: PLA (R190, 4 mmol ester units, 288 mg), MeOH (100 mmol, 3.2 g, 25 equiv. relative to ester units), $T = 140$ °C. Conversions were determined by ¹H NMR spectroscopy.

(a) methyl L-lactate standard ($t = 9.43$ min):



(b) methyl D-lactate standard ($t = 9.24$ min):



(c) methyl L-lactate depolymerized from PLLA ($t = 9.44$ min):

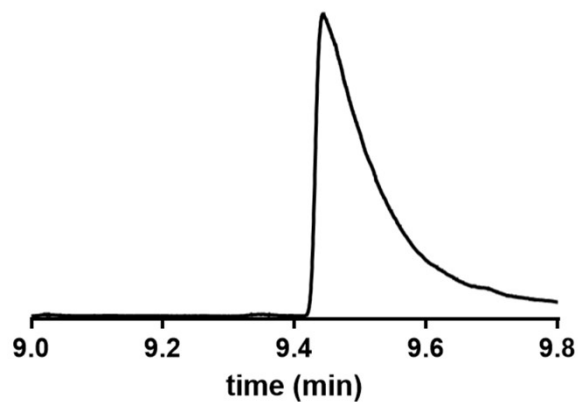


Figure S1. Determination of chirality of the depolymerization methyl lactate by gas chromatograph with chiral stationary phase.

Table S3. Calculation of green metrics for methanolysis of PLA.

metric	formula	value
atom economy (AE)	$\frac{\text{formula weight of product}}{\text{formula weight of all reactants}}$	100%
environmental factor (e-factor)	$\frac{\text{total mass of waste}}{\text{total mass of product(s)}}$	7.38
process mass intensity (PMI)	$\frac{\text{total mass used in the process}}{\text{total mass of product(s)}}$	8.38

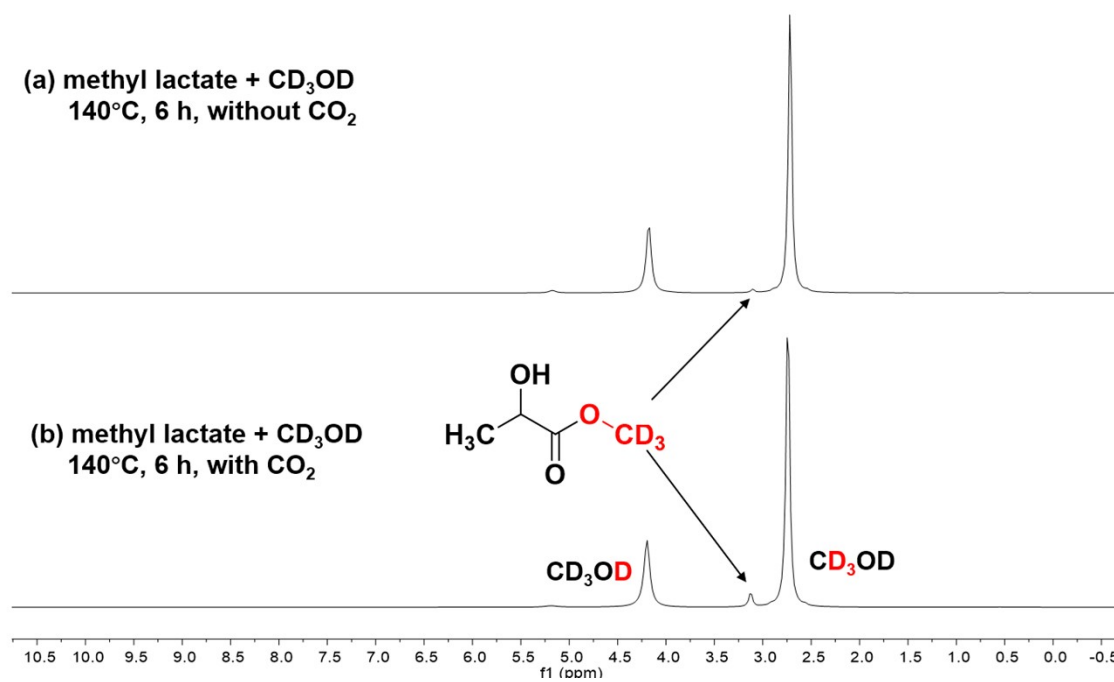
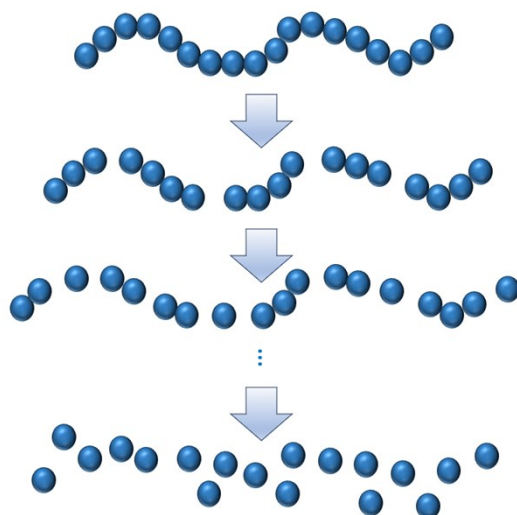
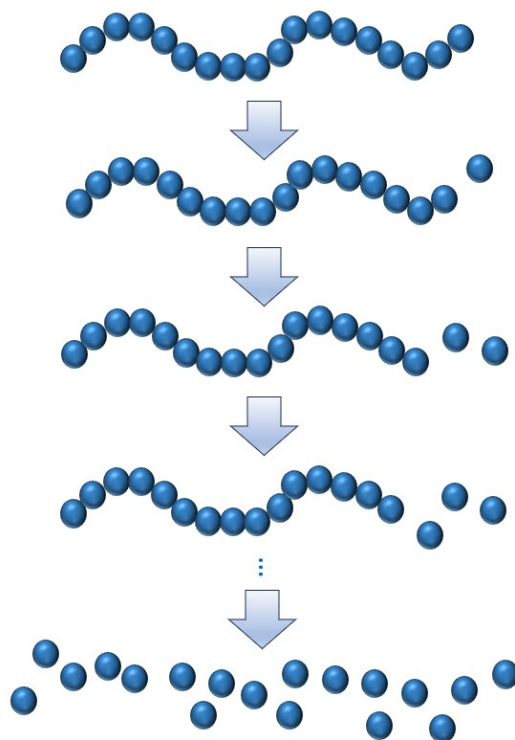


Figure S2. ²H NMR spectroscopy (61.4 MHz, in CD₃OD) for the transesterification between methyl lactate and CD₃OD.

(a) random chain scission



(b) chain unzipping



Scheme S1. The comparison of different depolymerization mode.

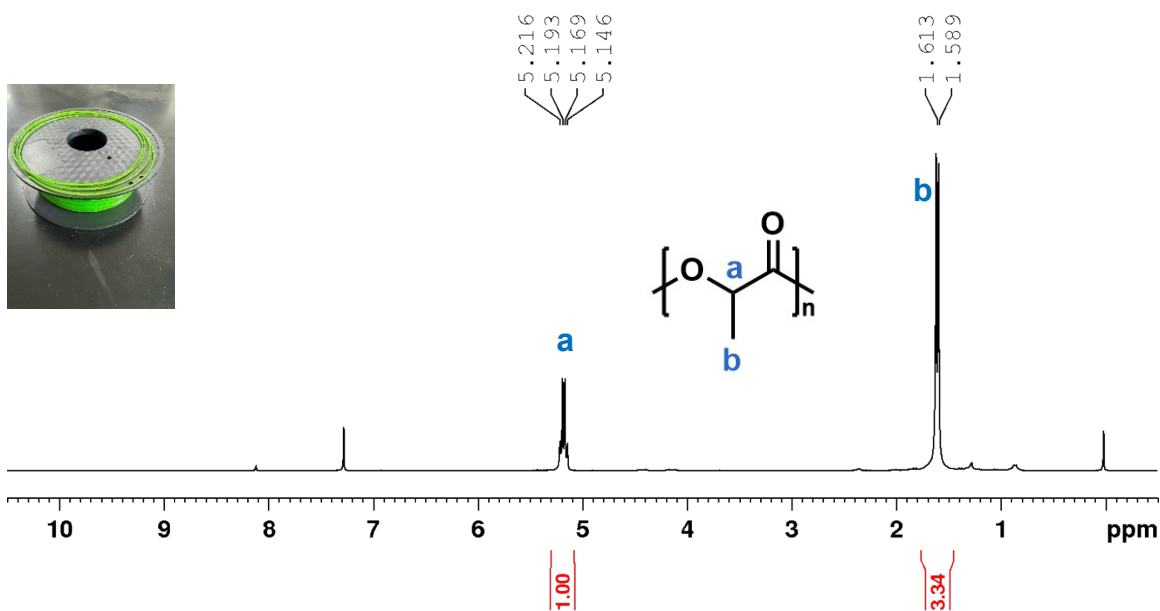


Figure S3. ^1H NMR spectroscopy (300 MHz, CDCl_3) of PLA based 3D printing material.

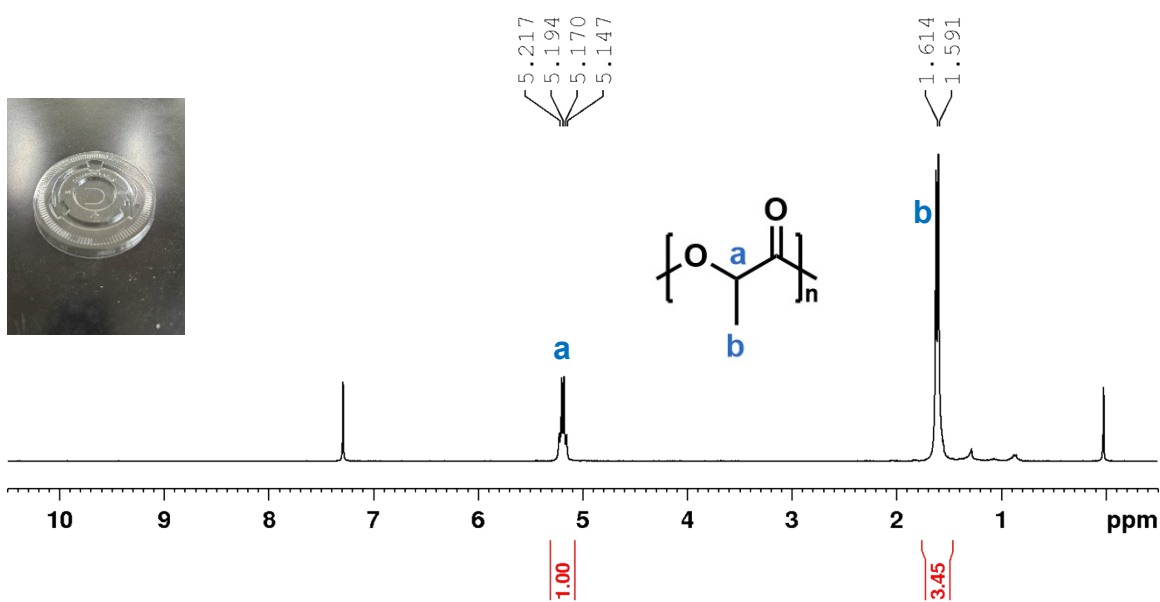


Figure S4. ^1H NMR spectroscopy (300 MHz, CDCl_3) of PLA based cup lid.

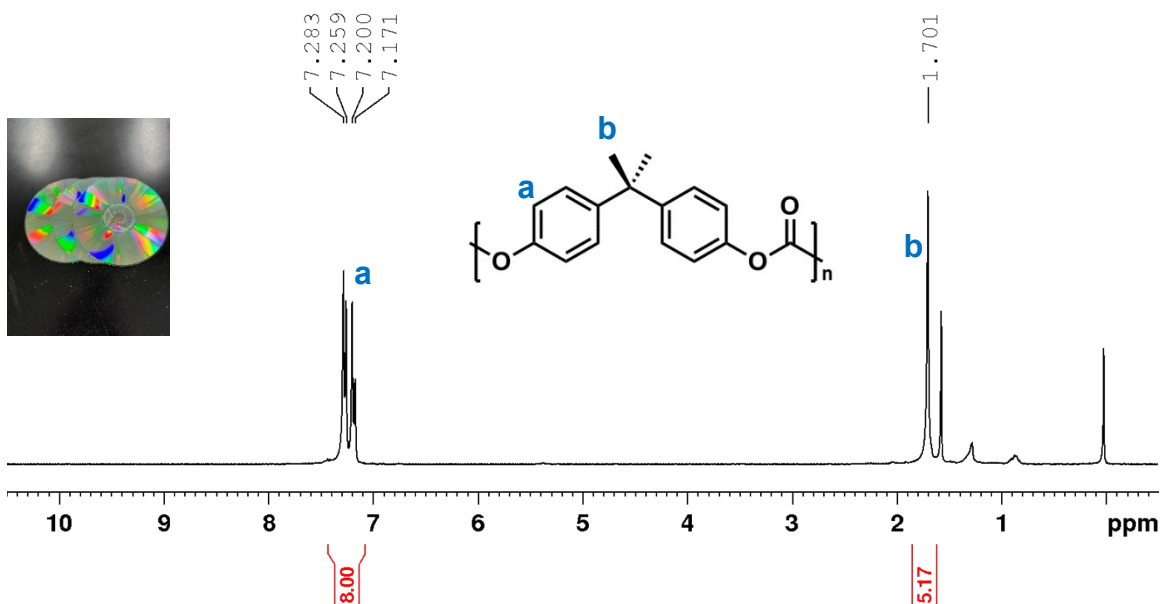


Figure S5. ¹H NMR spectroscopy (300 MHz, CDCl₃) of BPA-PC based digital disc.

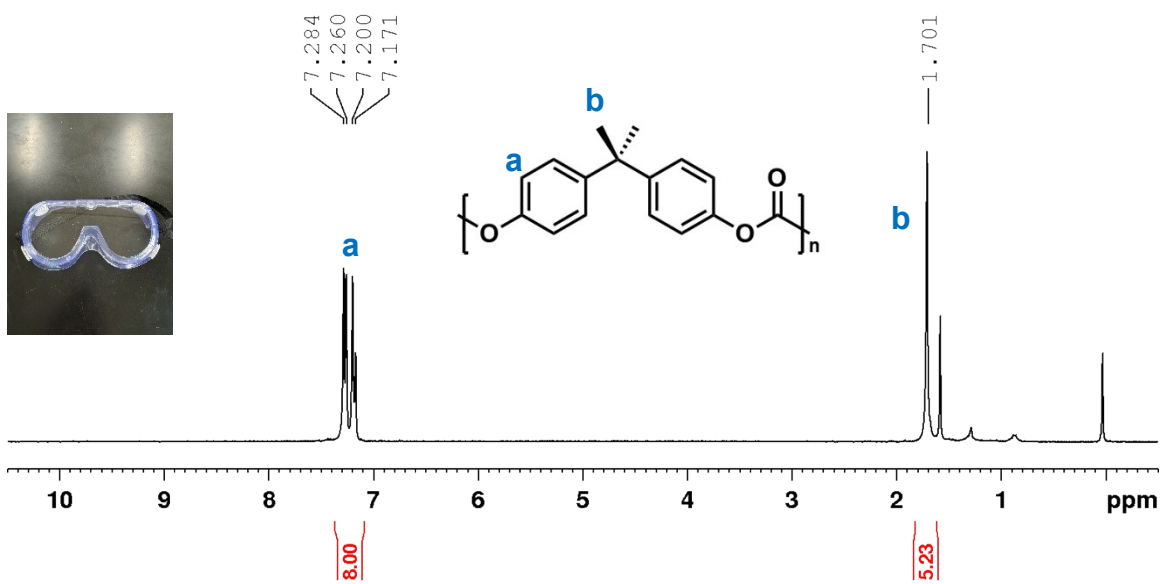


Figure S6. ¹H NMR spectroscopy (300 MHz, CDCl₃) of BPA-PC based goggles.

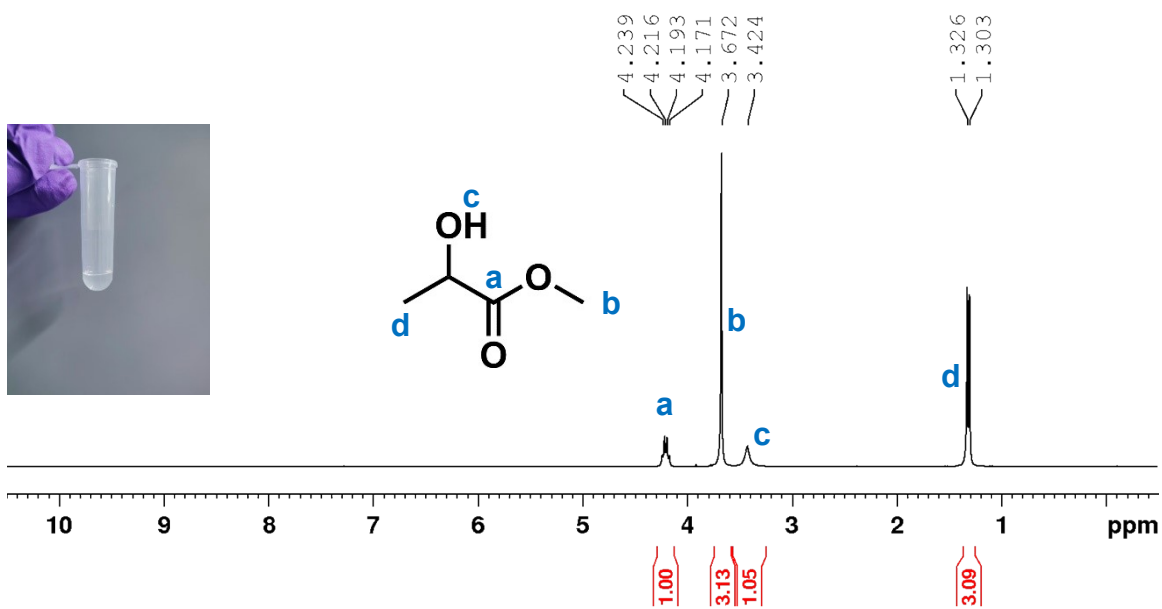


Figure S7. ¹H NMR spectroscopy (300 MHz, CDCl₃) of purified methyl lactate.

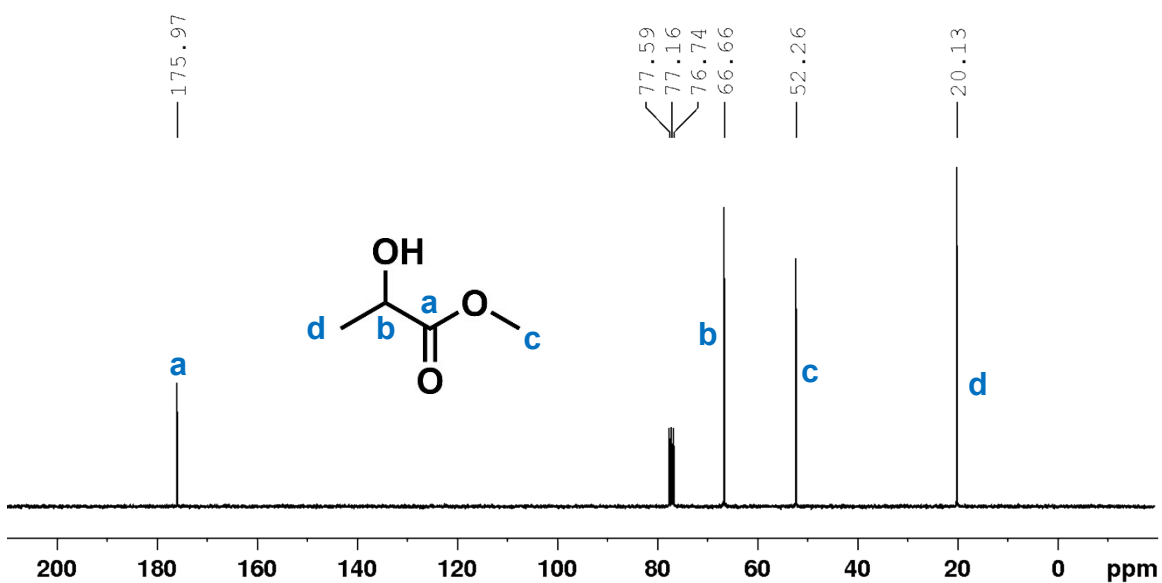


Figure S8. ¹³C NMR spectroscopy (75 MHz, CDCl₃) of purified methyl lactate.

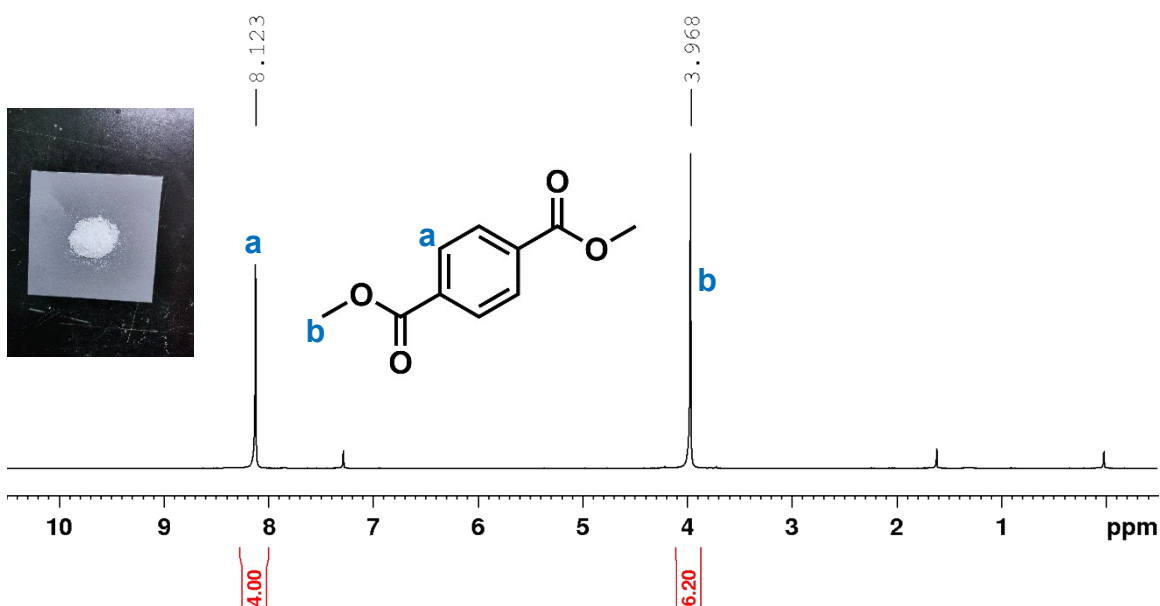


Figure S9. ^1H NMR spectroscopy (300 MHz, CDCl_3) of purified dimethyl terephthalate.

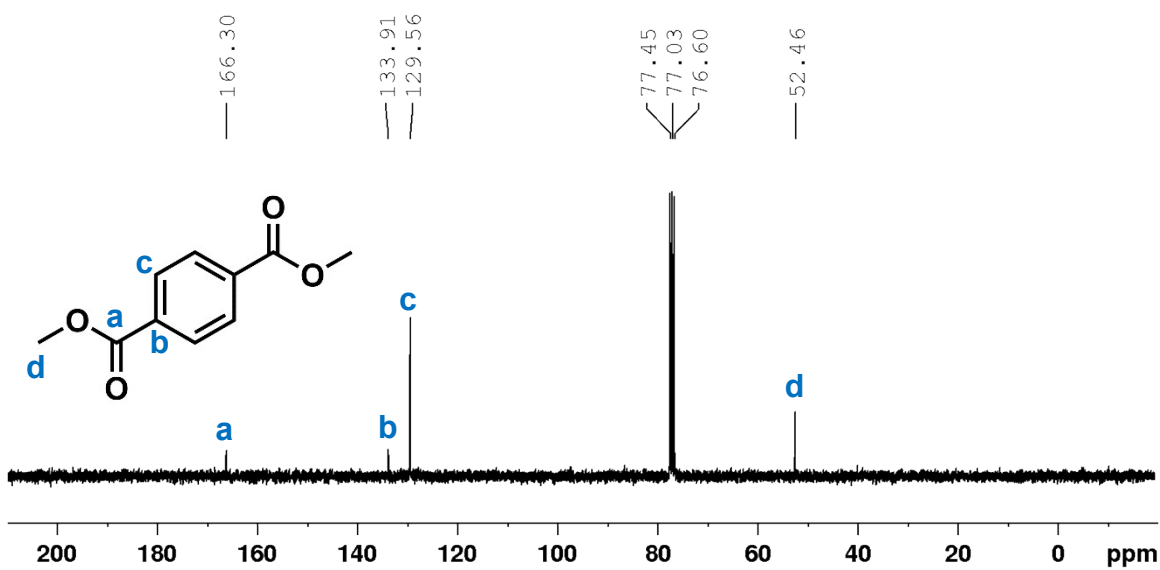


Figure S10. ^{13}C NMR spectroscopy (75 MHz, CDCl_3) of purified dimethyl terephthalate.

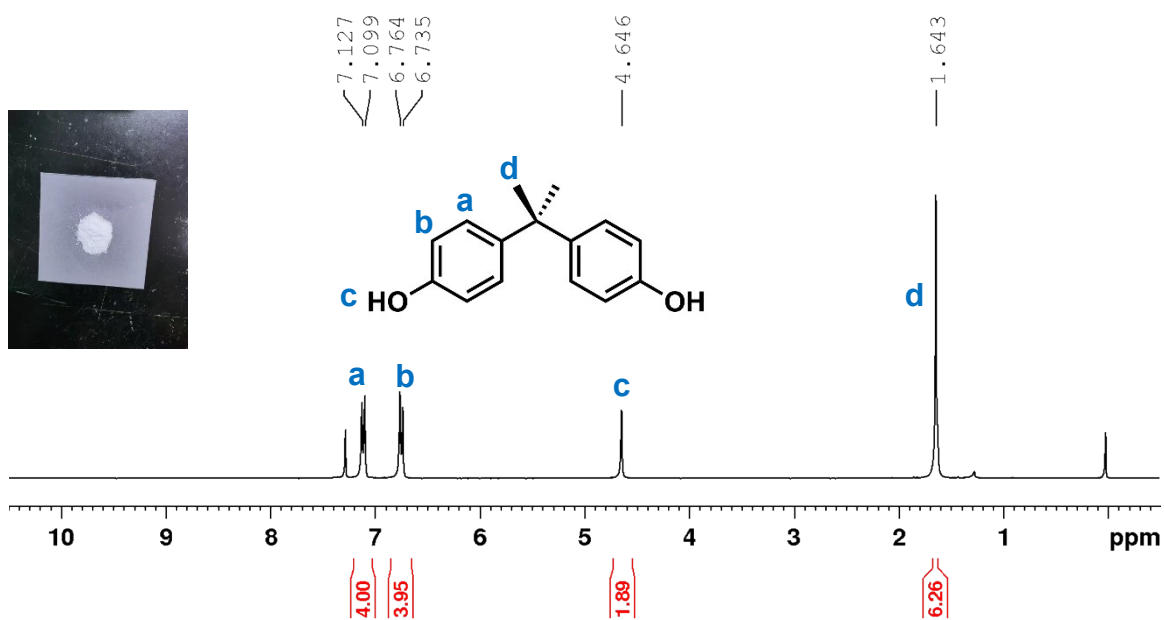


Figure S11. ^1H NMR spectroscopy (300 MHz, CDCl_3) of purified bisphenol A.

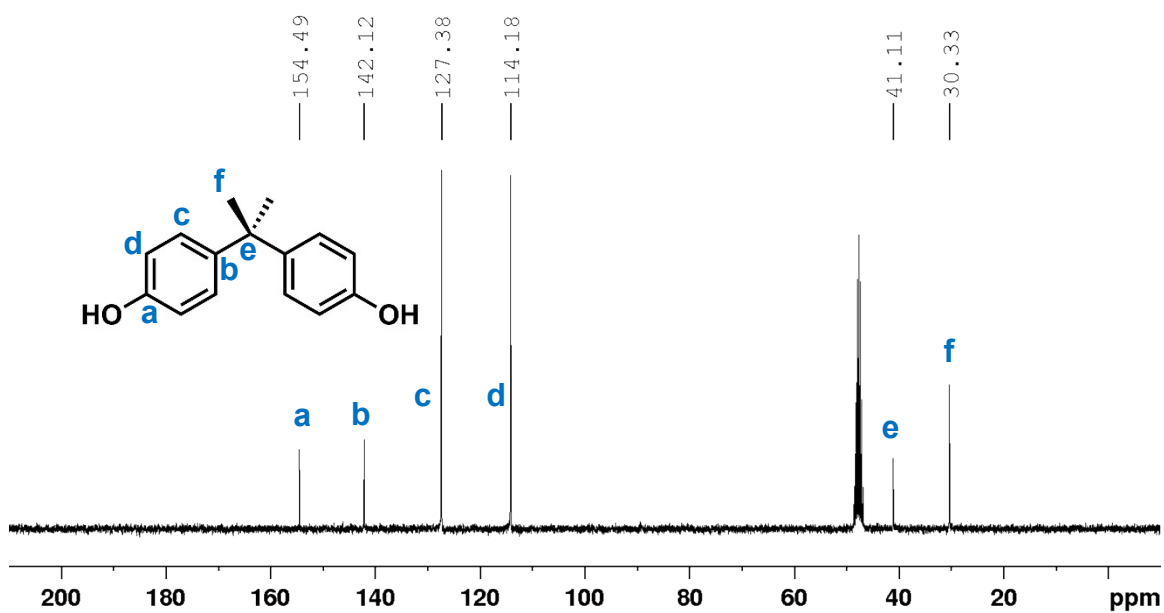


Figure S12. ^{13}C NMR spectroscopy (75 MHz, CD_3OD) of purified bisphenol A.