

Supporting Information

A "one-step" approach to the highly efficient synthesis of lactide through the confinement catalysis of covalent organic frameworks

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Materials and methods

Materials

Unless otherwise specified, all other reagents were purchased commercially and used as received. Organic solvents were purchased from Adamas. Ortho-hydroxybenzaldehyde, para-hydroxybenzaldehyde, para-phenylenediamine, 2-aminoterephthalic acid, and 1,3,5-benzenetricarboxaldehyde were purchased from Energy Chemical. 1,3,5-triformylphloroglucinol (TFP), 2,5-diamino-1,4-benzenedicarboxylic acid (DABDA), and 3,3'-dicarboxy-4,4'-diaminobiphenyl were purchased from Zhengzhou Alpha Chemical Co. LTD. Industrial-grade L-lactic acid was purchased from Ji Nan Chao Yi Xing Chemical Co., Ltd.. Nitrogen stored in the high-pressure gas cylinder was ordered from Dehai Gas, Qingdao.

Methods

All reactions were carried out under nitrogen conditions unless otherwise noted. Column chromatography was carried out on silica gel (200-300 mesh). TLC analysis was performed on precoated silica gel plates (0.2 mm thick).

¹H and ¹³C NMR spectra were performed on 400 MHz spectrometers (Bruker AVANCE NEO 400 Ascend) in the indicated solvents at room temperature. High-resolution solid-state NMR spectra were recorded on Agilent NMR Spectrometer (600-54-ASC) using a standard CP pulse sequence probe with 4 mm (outside diameter) zirconia rotors.

Attenuated total reflectance (ATR) FT-IR spectra were recorded on a Bruker Tensor 27 Spectrometer.

TGA from 40-800 °C was carried out on an American TA-Q20 in nitrogen atmosphere using a 10 °C/min ramp without equilibration delay.

MALDI-TOF mass spectrometry analysis was performed on a Bruker Microflex-LRF mass spectrometer in positive ion.

Scanning electron microscope (SEM) images were collected using scanning electron microscope (JEOL, JSM-7500F) at an accelerating voltage of 5.0 kV.

Transmission electron microscope (TEM) was performed on a JEM-2100 electron microscope with an accelerating voltage of 200 kV.

Powder X-ray diffraction (PXRD) patterns were obtained on a PANalytical Empyrean X-ray diffractometer with Cu K α line focused radiation at 40 kV and 40 mA from $2\theta = 1.0^\circ$ up to 40° with 0.02° increment by Bragg-Brentano. The powdered sample was added to the glass and compacted for measurement.

N₂ adsorption isotherms were measured up to 1 bar at 77 K using a Micrometrics ASAP 2460 surface area analyzer. Prior to measurements, samples (ca. 50 mg) were degassed for over 12 h at 120 °C. UHP grade N₂ and He were used throughout the adsorption experiments. Oil-free vacuum pumps and oil-free pressure regulators were used for measurements to prevent contamination of the samples during the degassing process and isotherm measurement.

High-Performance Liquid Chromatography (HPLC): The quantitative determination of synthesized lactide was conducted by HPLC (alliance e2695). The HPLC was equipped with C18 column and UV detector at 210 nm. Acetonitrile (HPLC grade, with the addition of 2 mL of 85% H₃PO₄ per L) and water (with the addition of 2 mL of 85% H₃PO₄ per L) were used as mobile phases. The LC column and oven temperature were maintained at 40 °C. The mobile phase flow rate was maintained at 0.7 mL/min. The elution program (water/acetonitrile, V/V) was as follows: (98/2) from 0 to 2 min; linear ramp to (0/100) from 2 to 30 min; (0/100) from 30 to 60 min; (98/2) from 30 to 60 min.¹

Synthetic procedures

REF-COF was synthesized according to the literature.²

REF-OH-COF was synthesized according to the literature.³

REF-OH-COOH-COF was synthesized according to the literature.⁴

REF-1 was synthesized according to the literature.⁵

REF-2 was synthesized according to the literature.⁶

OH-COOH-COF: **TFP** (20 mg, 0.09 mmol) and **DABDA** (28 mg, 0.14 mmol) were added to a Pyrex tube containing a mixture of 1,4-dioxane/mesitylene (5/6 (v/v)) mixed solvent (2 mL) and 6 M acetic acid (0.2 mL). The tube was then sealed and heated at 120 °C for 3 days. The resultant precipitate was collected by filtration and washed with tetrahydrofuran and deionized water. The reddish powders of **OH-COOH-COF** were obtained after drying under a vacuum at 120 °C overnight with a yield of 96% (41 mg).

REF-AM-OH-COOH-COF: **TFP** (20 mg, 0.09 mmol) and **DABDA** (28 mg, 0.14 mmol) were added to a Pyrex tube containing H₂O (2 mL) and 6 M acetic acid (0.2 mL). The tube was stirred at 120 °C for 2 days. The resultant precipitate was collected by filtration and washed with tetrahydrofuran and deionized water. The reddish powders of **REF-AM-OH-COOH-COF** were obtained after drying under a vacuum at 120 °C overnight.

Catalytic procedure and analysis for the lactide

500 mg catalyst and 1 g of 80 wt% L-lactic acid were added to 50 mL toluene in the distillation equipment with a condenser and a water separator (**Supplementary Fig. S8**). The mixtures were heated up to 140 °C for 3.5 hours. The water separator allows removing the resulting water from the reaction, thus enabling the reaction to proceed continuously. After 3.5 hours, the reaction was cooled to room temperature. After concentration under reduced pressure, the crude lactide was obtained and sent for ¹H NMR.

Structural simulation

Structural modeling of **OH-COOH-COF** was performed in the Materials Studio 7.0 software package. The space groups were obtained from the Reticular Chemistry Structure Resource. P1 was chosen for AA. The theoretical models were then optimized by the Forcite module.

Pawley refinements of the PXRD patterns were done in the Reflex module using data from 1 to 40°. The integrated intensities were extracted using Pseudo-Voigt profile. The

unit cell parameters a , b , c , FWHM parameters U , V , W , profile parameters NA , NB , and zero-point were refined. The background was refined with 20th-order polynomial.

Table S1. Unit cell parameters and fractional atomic coordinates of **OH-COOH-COF** based on AA topology after unit cell correction and Pawley refinement.

Space group	P1		
Calculated unit cell	a = 22.785 Å, b = 22.785 Å, c = 3.345 Å and $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$		
Atom	X	Y	Z
C	1.75285	-0.93629	0.01705
C	1.80052	-0.9627	0.04334
C	1.87146	-0.9142	0.15642
C	1.85332	-0.81555	-0.00711
C	1.77882	-0.8621	0.02564
O	1.69186	-0.97537	0.02004
O	1.8752	-0.75663	-0.10494
O	1.90409	-0.93463	0.33824
C	1.73393	-0.8399	0.05328
N	1.75263	-0.77117	0.14899
C	1.7074	-0.74465	0.09824
C	1.73304	-0.67502	0.01886
C	1.68743	-0.65112	-0.02902
C	1.61714	-0.6937	0.01926
C	1.59162	-0.76315	0.1062
C	1.63715	-0.78725	0.14635
N	1.57188	-0.66746	-0.0406
C	1.58987	-0.59876	0.04982
C	1.51833	-0.81232	0.16432
C	1.80685	-0.62626	-0.02936
C	1.4466	-0.52804	0.14098
C	1.42074	-0.60192	0.10465
C	1.4701	-0.62602	0.14242
C	1.54397	-0.5781	0.09413
C	1.56829	-0.50432	0.10915
C	1.51965	-0.4789	0.08494
O	1.40824	-0.50746	0.23277
O	1.62859	-0.46456	0.15729
O	1.44975	-0.68505	0.23054
C	1.53969	-0.41287	0.02382
N	1.60633	-0.36464	-0.1184
C	1.63517	-0.2921	-0.10701
C	1.70656	-0.24781	-0.09803
C	1.73182	-0.17771	-0.12891

C	1.689	-0.14993	-0.13229
C	1.61807	-0.19395	-0.12259
C	1.59246	-0.26408	-0.12346
N	1.71707	-0.0779	-0.17507
C	1.78191	-0.02847	-0.01545
C	1.56888	-0.16916	-0.10815
C	1.75668	-0.27187	-0.05814
C	1.35444	-0.64775	0.05021
C	0.96861	-0.79857	-0.00515
N	1.01976	-0.81809	0.01748
C	1.09158	-0.77058	-0.01675
C	1.13808	-0.79276	-0.11442
C	1.2075	-0.74509	-0.13073
C	1.23277	-0.67645	-0.0391
C	1.18662	-0.65401	0.05565
C	1.11709	-0.70152	0.06961
N	1.30454	-0.62964	-0.06143
C	1.20824	-0.58215	0.14953
C	1.11666	-0.86476	-0.20806
C	1.90131	-0.84125	0.05383
O	1.83554	-0.5585	0.08624
O	1.49418	-0.88148	0.11234
O	1.84377	-0.64478	-0.17587
O	1.47913	-0.79332	0.26493
O	1.1612	-0.56001	0.12752
O	1.15634	-0.89315	-0.09947
O	1.26619	-0.54243	0.25185
O	1.06414	-0.90023	-0.38804
O	1.50181	-0.21177	-0.22601
O	1.82094	-0.23093	0.1074
O	1.58583	-0.11264	0.01722
O	1.74322	-0.32766	-0.17688
H	1.68083	-0.87653	0.01909
H	1.79854	-0.74066	0.2936
H	1.70711	-0.59944	-0.12554
H	1.61734	-0.83932	0.23543
H	1.5265	-0.69809	-0.18993
H	1.64294	-0.56104	0.06554
H	1.50262	-0.39703	0.0591
H	1.6297	-0.38359	-0.30217
H	1.78556	-0.14462	-0.16862
H	1.53834	-0.29678	-0.14176
H	1.69132	-0.06173	-0.36157

H	1.81851	-0.04402	0.05129
H	1.33863	-0.70092	0.07463
H	0.98457	-0.74727	-0.09663
H	1.0049	-0.86885	0.04364
H	1.24203	-0.76131	-0.23482
H	1.08296	-0.68448	0.16784
H	1.32031	-0.58322	-0.20029
H	1.8037	-0.54826	0.24288
H	1.44367	-0.91012	0.16273
H	1.18146	-0.51042	0.20059
H	1.19588	-0.86318	0.08028
H	1.47298	-0.18956	-0.19985
H	1.82684	-0.18915	0.24944

Pore size simulation

The pore limiting diameter (PLD) and pore size distribution (PSD) were computed using a nitrogen probe with a radius of 1.86 Å in Zeo++ software package.

Supplementary Figures

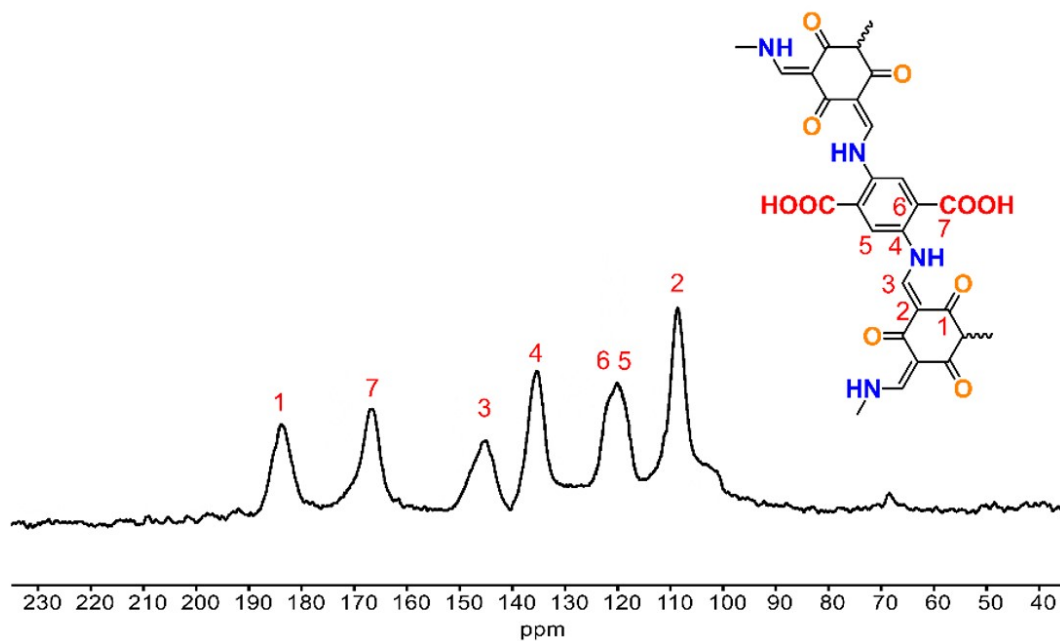


Figure S1. ^{13}C CP/MAS solid-state NMR spectrum of **OH-COOH-COF**.

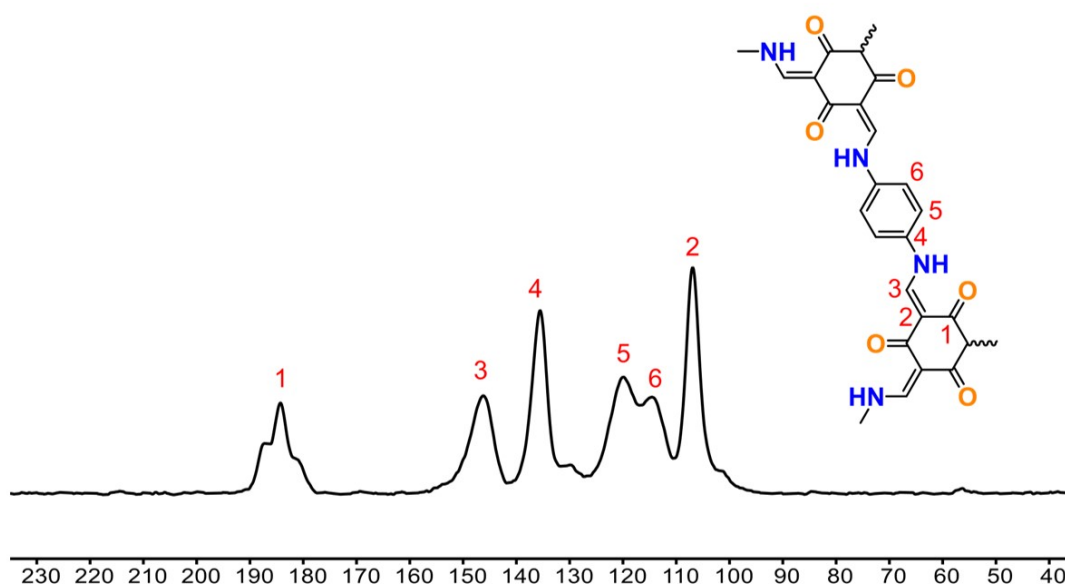


Figure S2. ^{13}C CP/MAS solid-state NMR spectrum of **REF-OH-COF**.

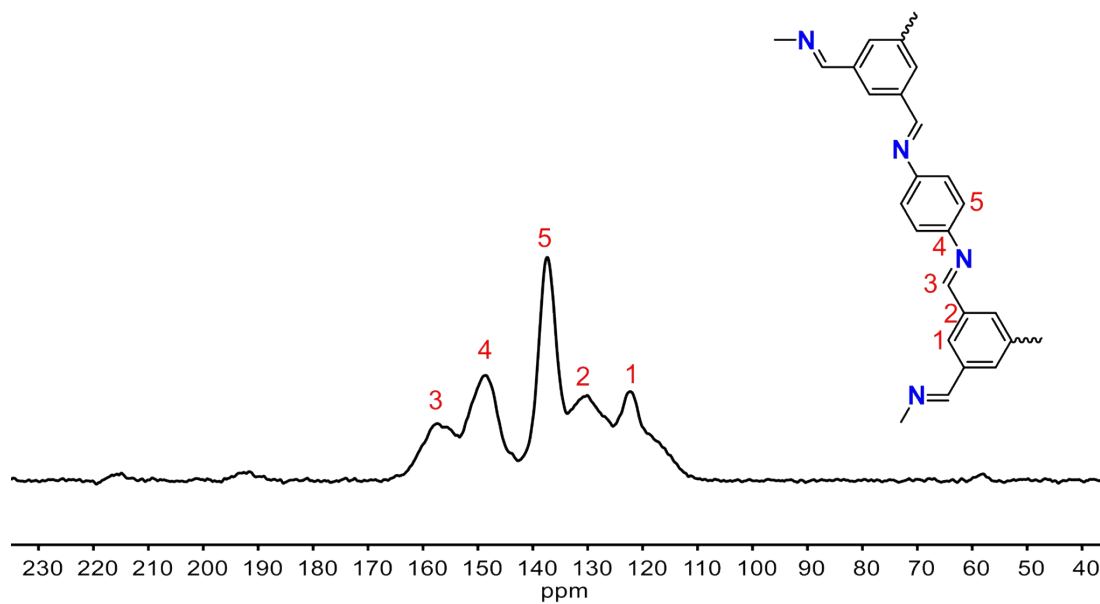


Figure S3. ^{13}C CP/MAS solid-state NMR spectrum of **REF-COF**.

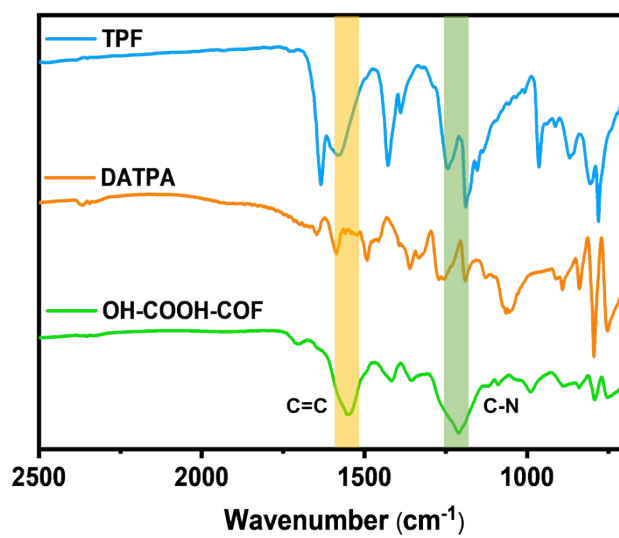


Figure S4. FT-IR spectra of **OH-COOH-COF** and corresponding monomers.

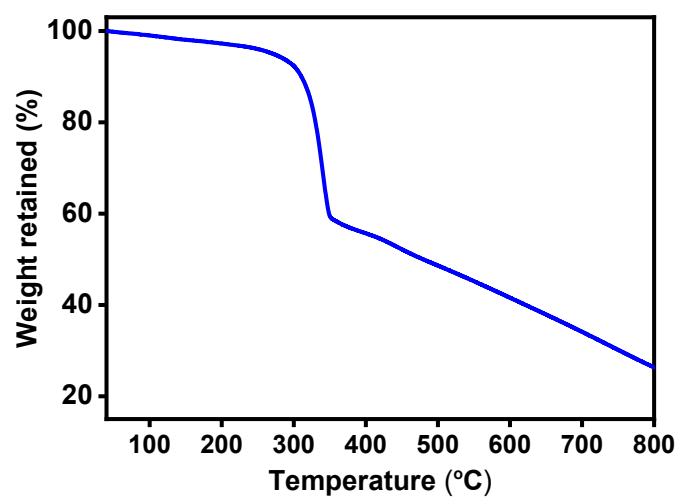


Figure S5. Thermal gravimetric analysis (TGA) profiles of **OH-COOH-COF**.

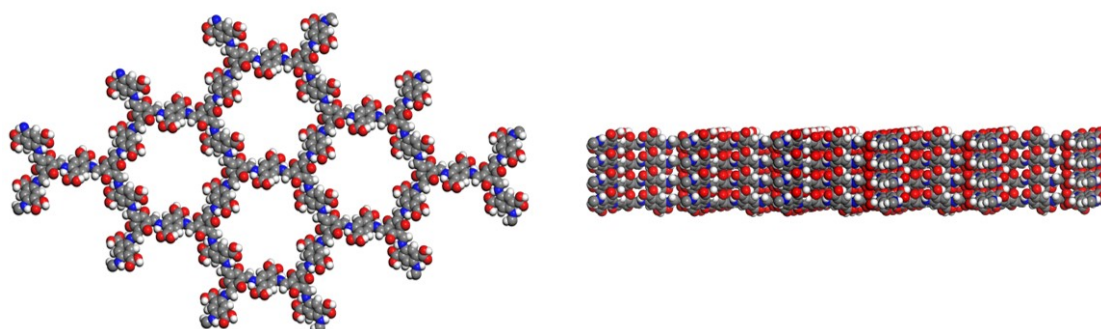


Figure S6. Top and side view of the simulated structure of AA stacking.

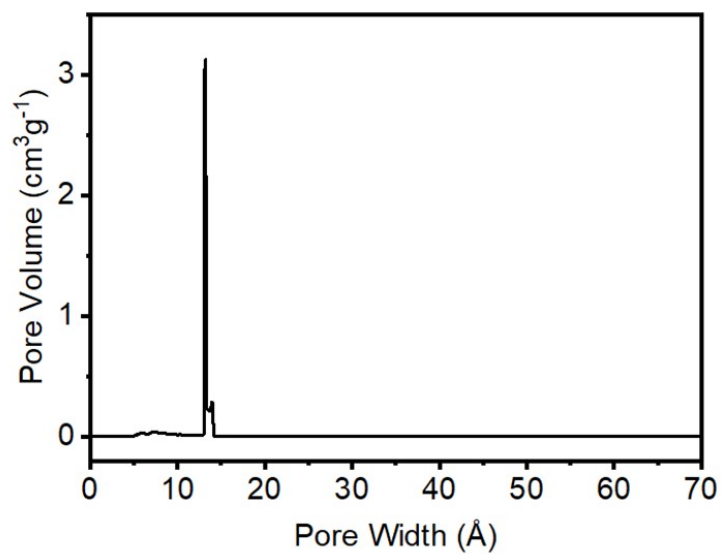


Figure S7. The simulated pore size distribution of **OH-COOH-COF** in Zeo++ software package.

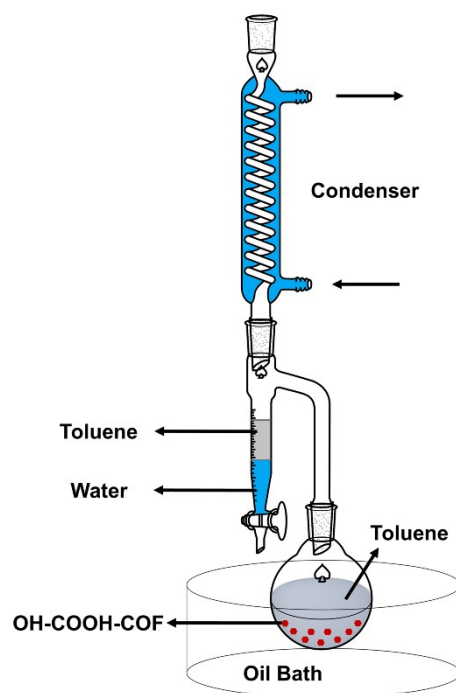


Figure S8. The distillation equipment for the condensation reaction.

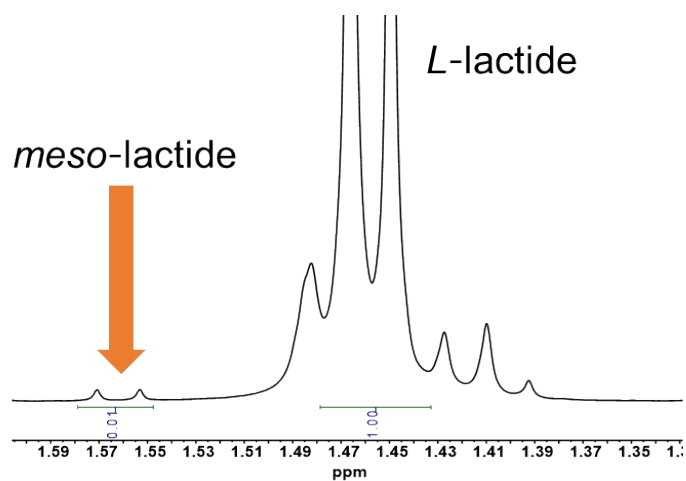


Figure S9 $^1\text{H-NMR}$ of the raw reaction products of L-lactide in $d_6\text{-DMSO}$ at room temperature.

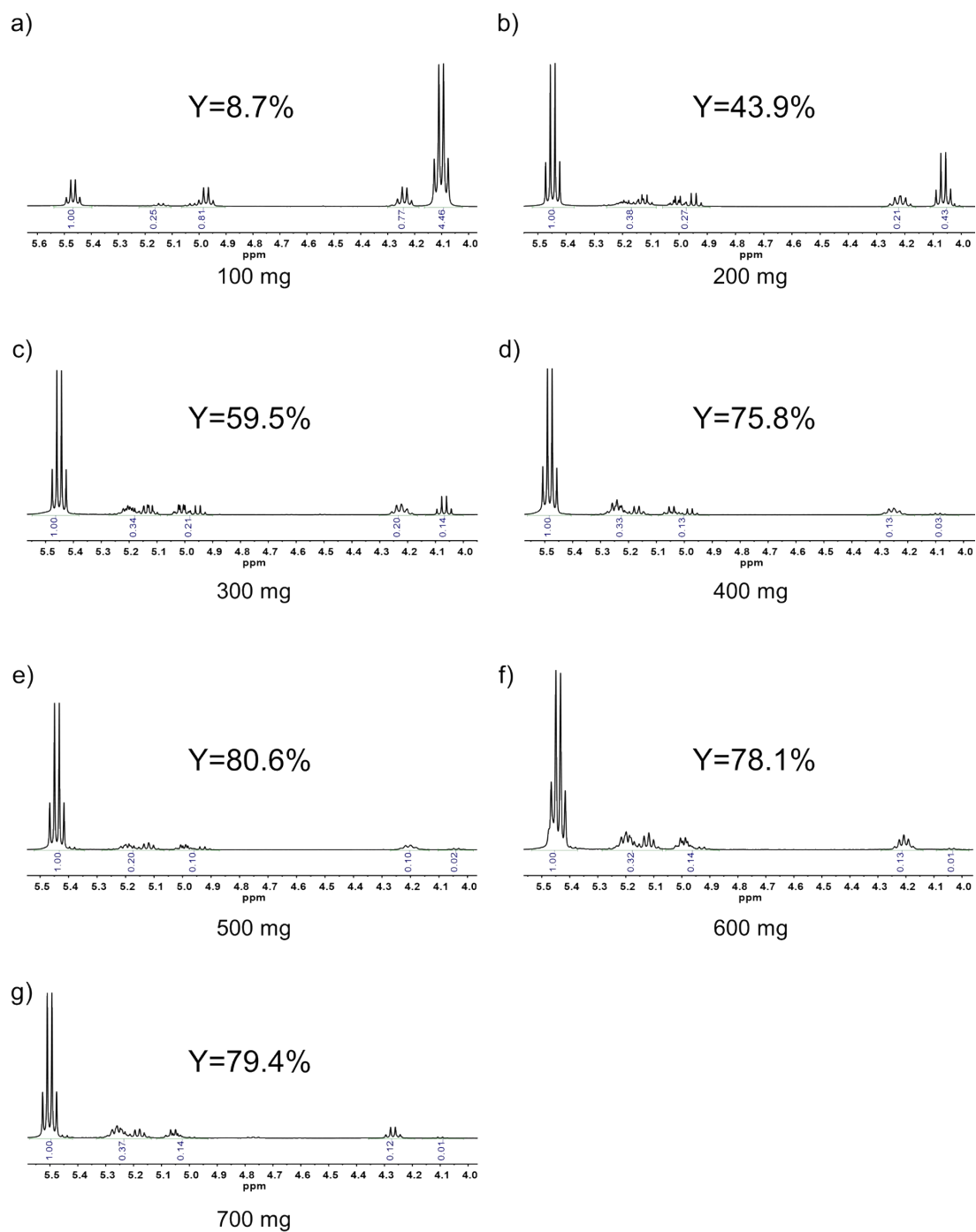


Figure S10. $^1\text{H-NMR}$ of the products with different amounts of catalyst **OH-COOH-COF** in $\text{DMSO-}d_6$. Reaction conditions: 1 g of 80 wt% L-lactic acid, 50 mL toluene, 140 $^\circ\text{C}$, 3.5 h, the catalyst.

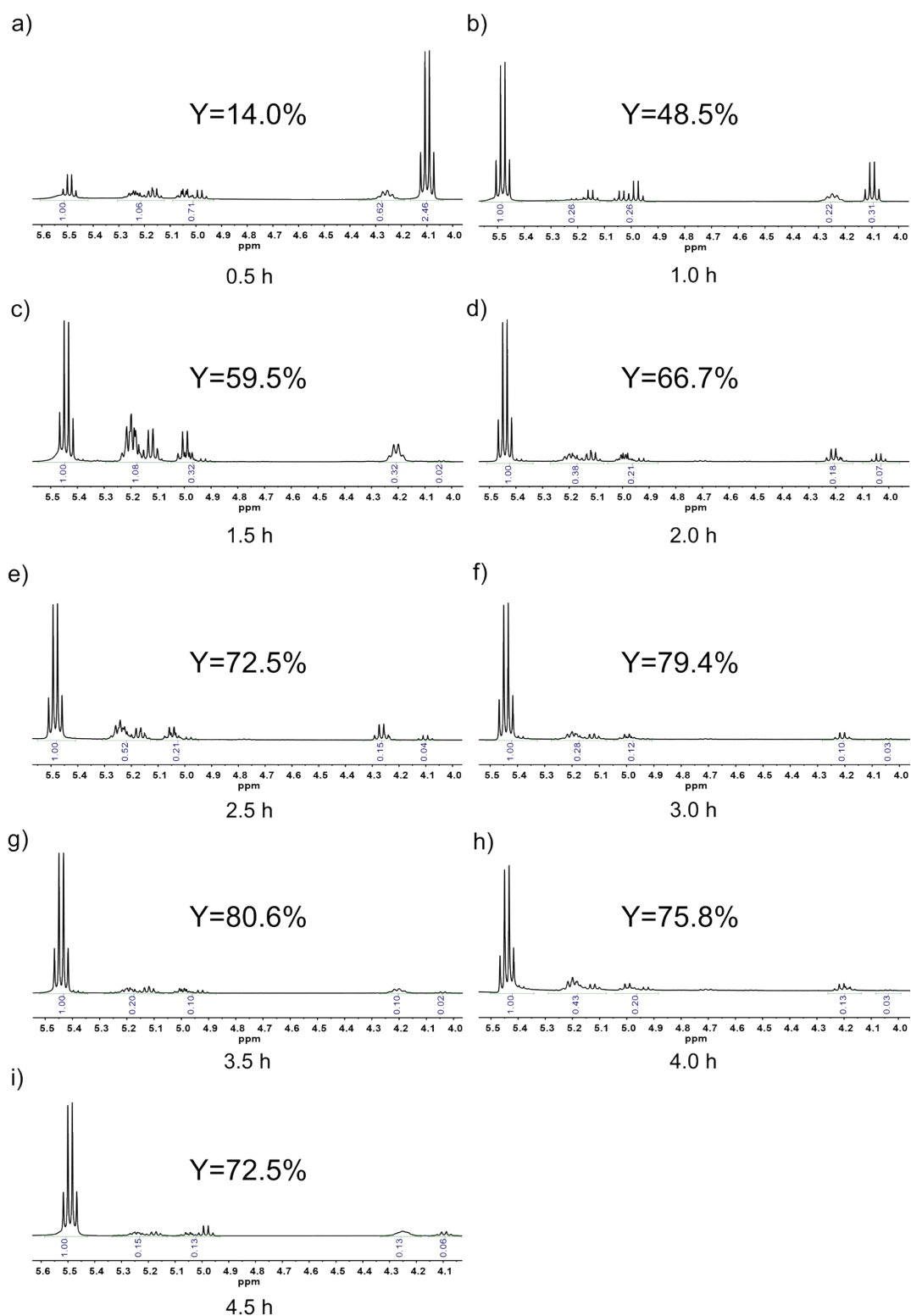


Figure S11. $^1\text{H-NMR}$ of the products at different reaction times in $\text{DMSO-}d_6$. Reaction conditions: 1 g of 80 wt% L-lactic acid, 500 mg **OH-COOH-COF**, 50 mL toluene, 140 $^\circ\text{C}$.

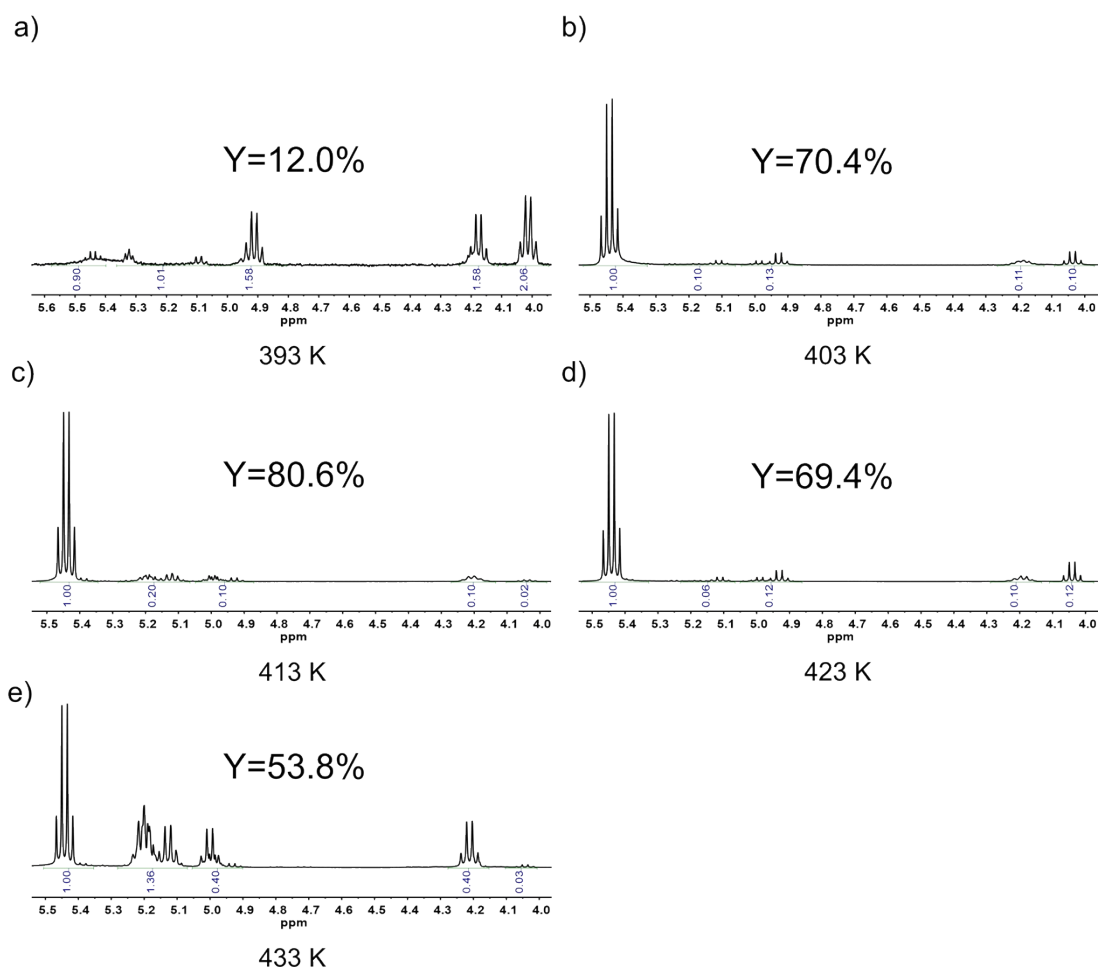


Figure S12. $^1\text{H-NMR}$ of the products obtained from different temperatures during the reaction in $\text{DMSO-}d_6$. Reaction conditions: 1 g of 80 wt% L-lactic acid, 500 mg **OH-COOH-COF**, 50 mL toluene, 3.5 h.

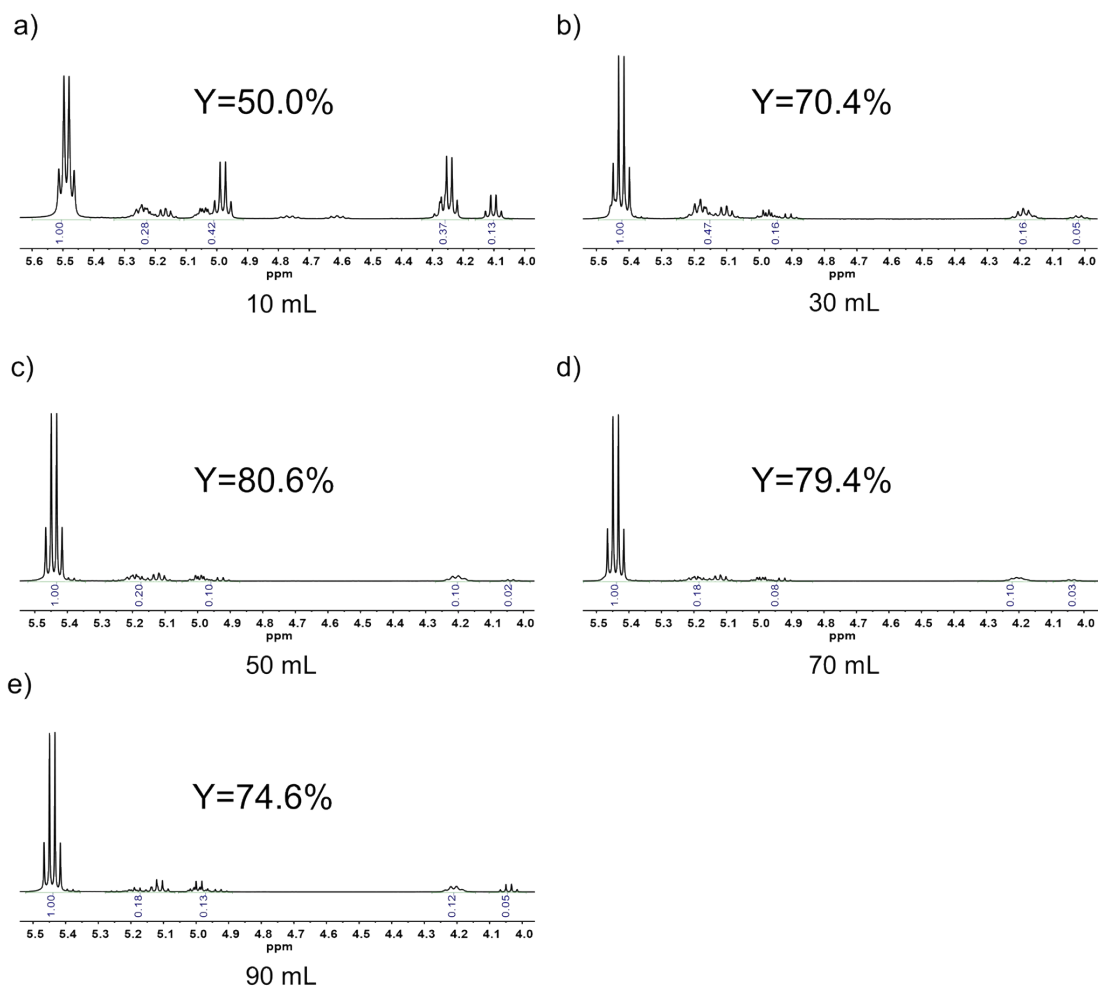


Figure S13. $^1\text{H-NMR}$ of the products with different volumes of toluene in $\text{DMSO-}d_6$. Reaction conditions: 1 g of 80 wt% L-lactic acid, 500 mg **OH-COOH-COF**, 140 °C, 3.5 h.

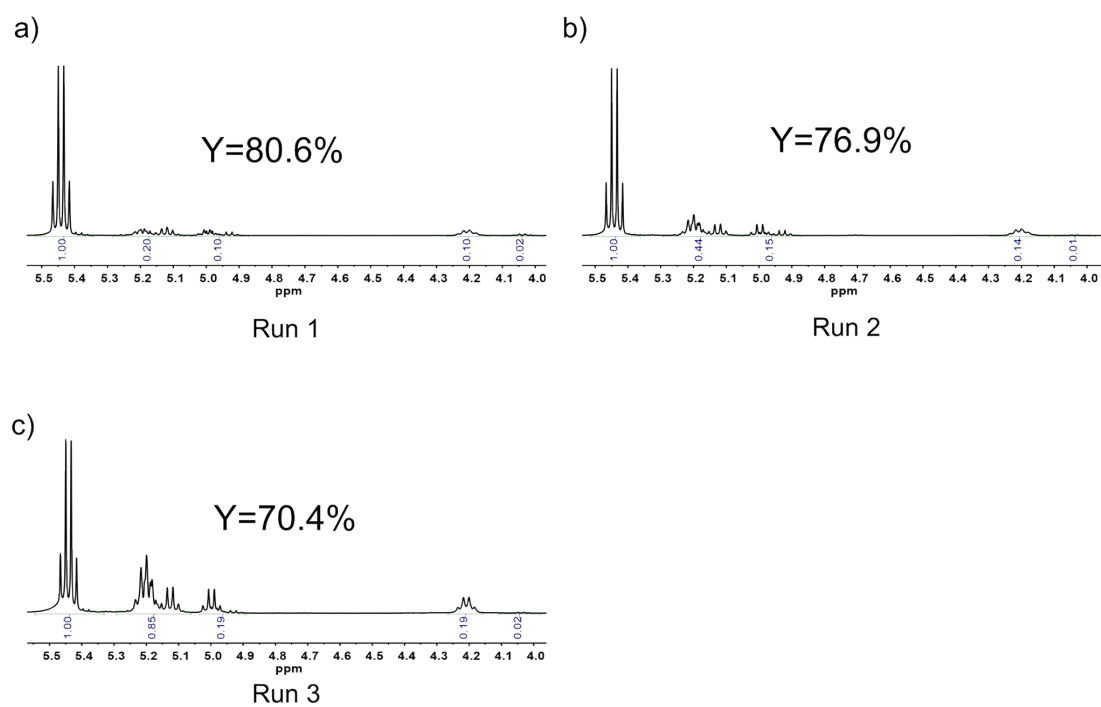


Figure S14. $^1\text{H-NMR}$ of the products with run 3 times in $\text{DMSO-}d_6$. Reaction conditions: 1 g of 80 wt% L-lactic acid, 500 mg **OH-COOH-COF**, 50 mL toluene, 140 $^\circ\text{C}$, 3.5 h.

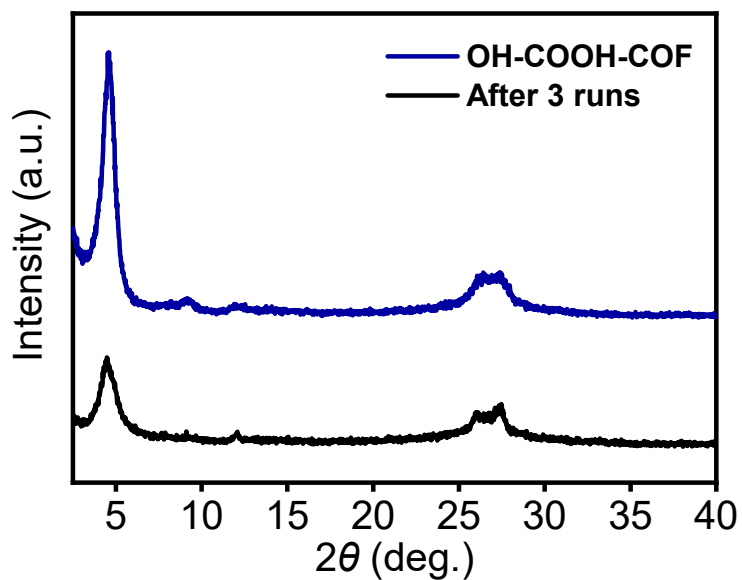


Figure S15. PXRD patterns of **OH-COOH-COF** after recycling test.

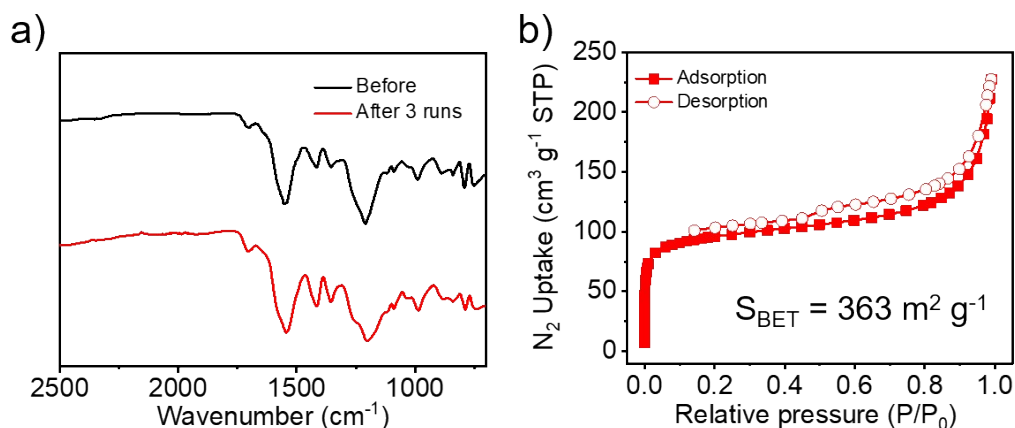


Figure S16. (a) FT-IR spectra and (b) nitrogen adsorption-desorption isotherms (77 K) of **OH-COOH-COF** after 3 runs.

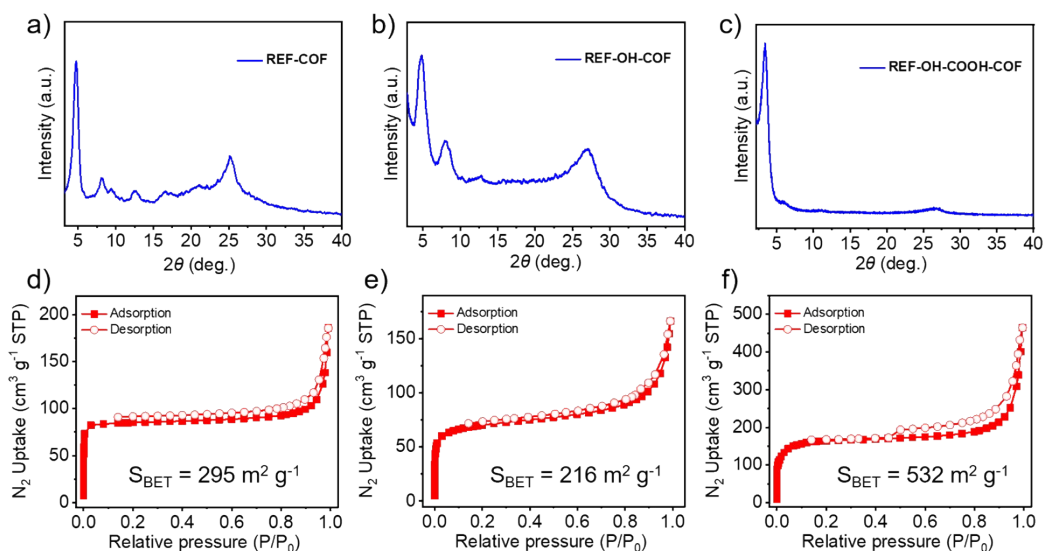


Figure S17. (a, b, c) PXRD patterns and (d, e, f) nitrogen adsorption-desorption isotherms (77 K) of **REF-COF**, **REF-OH-COF**, and **REF-OH-COOH-COF**.

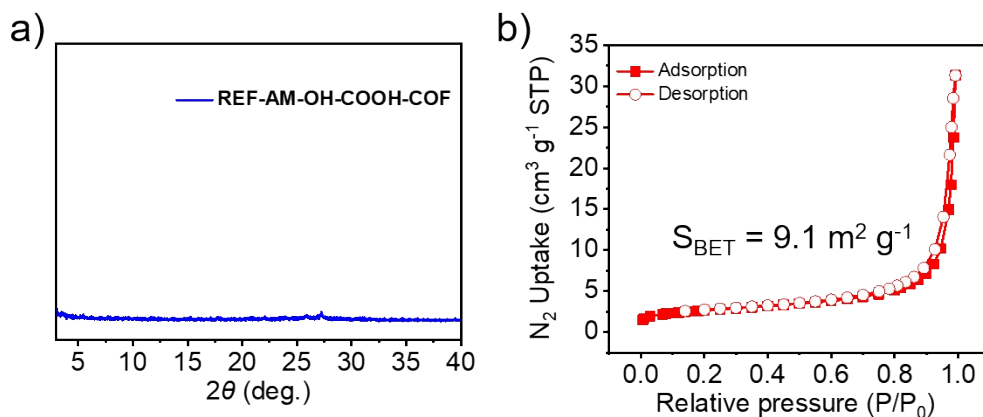


Figure S18. (a) PXRD patterns and (b) nitrogen adsorption-desorption isotherms (77 K) of **REF-AM-OH-COOH-COF**.

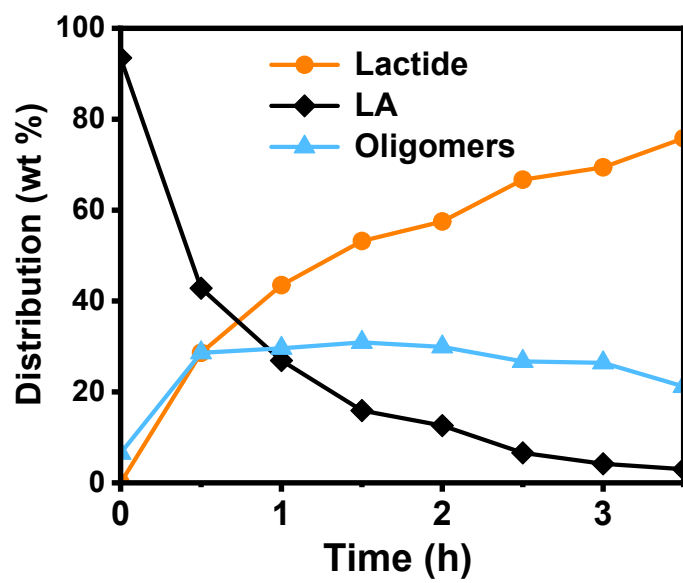


Figure S19. Kinetic study catalytic reaction of OH-COOH-COF.

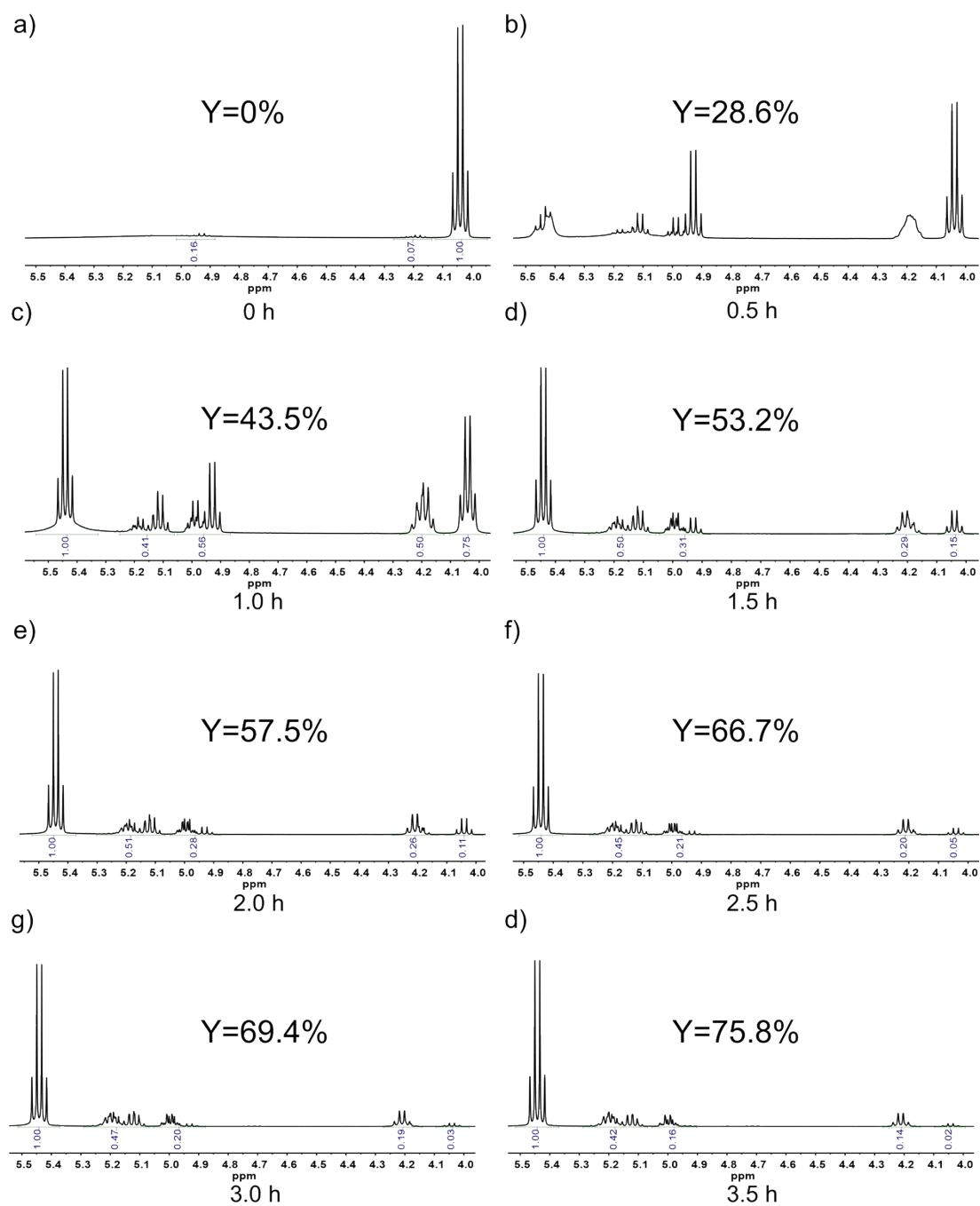


Figure S20. Typical ^1H -NMR analysis of the reaction products with **OH-COOH-COF** kinetics in $\text{DMSO-}d_6$. Reaction conditions: 1 g of 80 wt% L-lactic acid, 500 mg **OH-COOH-COF**, 50 mL toluene, 140 °C.

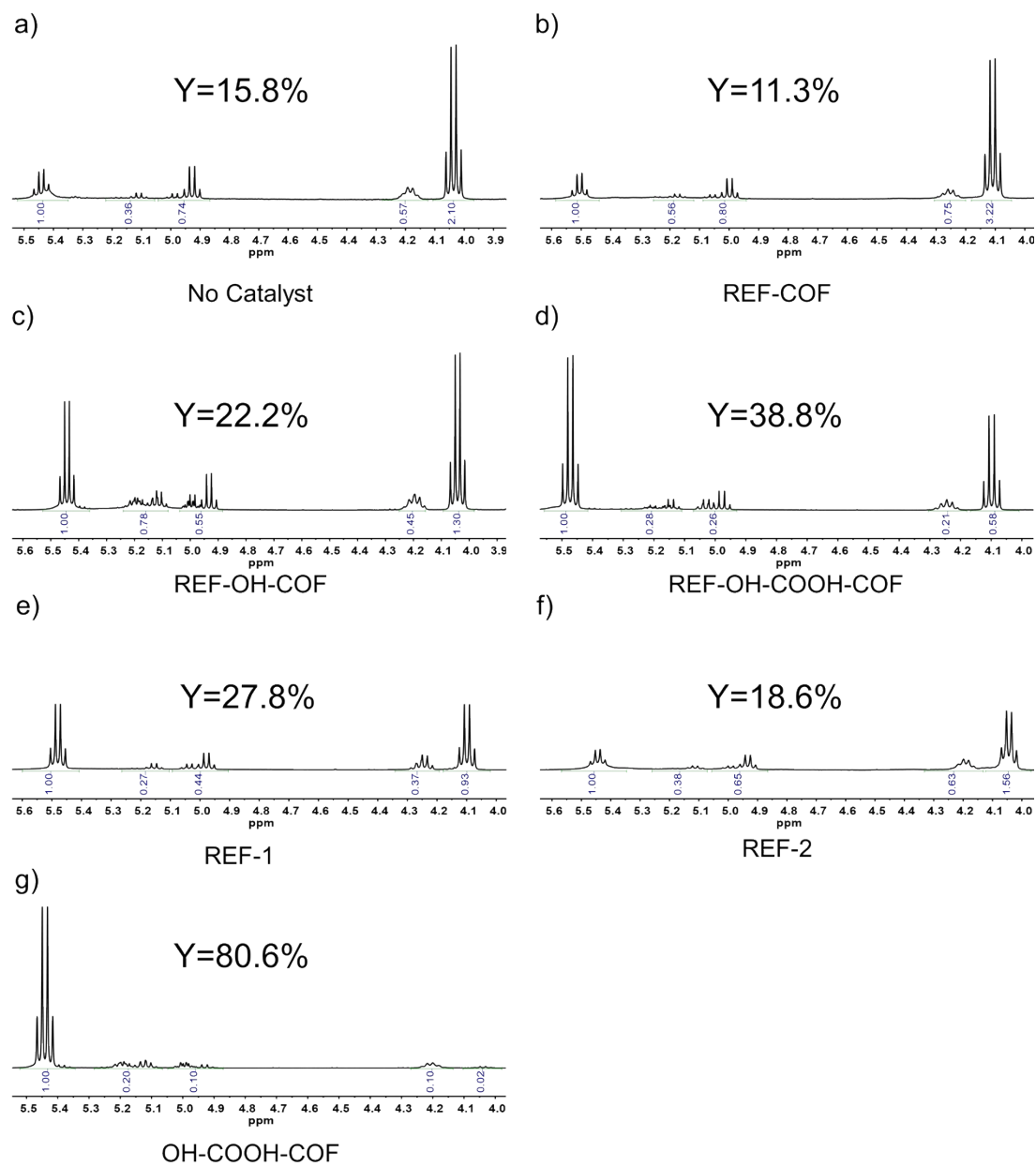


Figure S21. Typical $^1\text{H-NMR}$ analysis of the reaction products using 500mg of different catalysts in $\text{DMSO-}d_6$. Reaction conditions: 1 g of 80 wt% L-lactic acid, 50 mL toluene, 140 $^\circ\text{C}$, 3.5 h.

References

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