Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

Metal-free Photocatalytic Aerobic Oxidation of Biomass-based Furfural Derivatives to Prepare γ-butyrolactone

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I. General

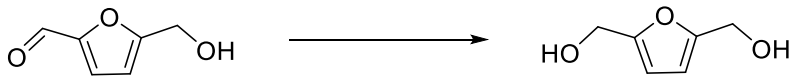
If not stated otherwise, the reaction was carried out in a 10 mL Schlenk tube and all commercially available compounds and chemicals were purchased from Alfa Aesar, sigma, Adamas-beta, Energy Chemical, TCI and aladdin. And used as received, unless otherwise noted specially. All glassware was either oven dried or flame-dried prior to use.

The Photo Reaction Setup (SCI-PCRS-3-455) was purchased from Anhui Kemi machinery technology Co., Ltd.

Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. UV-Vis spectrum was measured by UV-3600. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Multiplicities are described using the following abbreviations: chemical shift (ppm, scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiplet resonances, br = broad), coupling constant (Hz), and integration. Carbon chemical shifts are reported in ppm (δ) relative to TMS with the solvent resonance as the internal standard ($CDCl_3$, δ 77.16 ppm). NMR data were collected at 25 ℃. NMR spectra were processed using MestReNova.

II. Experimental Procedures

1. The synthesis of 2,5-dihydroxymethyltetrahydrofuran.



The 2,5-dihydroxymethyltetrahydrofuran was prepared from 5-hydroxymethylfurfural (5-HMF) by the hydrogenation experiments.[1] A 25 mL stainless steel autoclave (Purchased from Anhui Kemi machinery technology Co., Ltd.) with a stir bar was charged with 1.8 g of 5-HMF, Raney nickel catalyst (100 mg) and 10 mL of ethanol. The stainless steel autoclave was purged 3 times with nitrogen, and 2 times with hydrogen. And then the autoclave was pressurized to 5 MPa hydrogen and heated to 120 ° C for 3 hours. After cooling the stainless steel autoclave was vented and the solids were separated by filtration. The acetic acid solution was evaporated under vacuum to provide about 1.5 g of 2,5-dihydroxymethyltetrahydrofuran.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.10 (dq, J = 5.0, 2.9 Hz, 2H), 3.78 (dd, J = 11.8, 2.9 Hz, 2H), 3.52 (dd, J = 11.8, 5.3 Hz, 2H), 1.98-1.76 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 80.31, 64.95, 27.18.

2. The synthesis of tetrahydrofuran-2,5-dicarboxylic acid

The tetrahydrofuran-2,5-dicarboxylic acid was prepared from furan-2,5-dicarboxylic acid (FDCA) by the hydrogenation experiments. A 25 mL autoclave with a stir bar was charged with 2.0 g of furan-2,5-dicarboxylic acid (FDCA), 0.1 g of 10% Pd/C and 10 mL of acetic acid. The autoclave was purged 3 times with nitrogen, and 2 times with hydrogen. And then the autoclave was pressurized to 4 MPa hydrogen and heated to 150 ° C for 3 hours. After cooling the autoclave was vented and the solids were separated by filtration. The acetic acid solution was evaporated under vacuum to provide about 1.6 g of tetrahydrofuran-2,5-dicarboxylic acid.

^{1}H NMR (400 MHz, DMSO) δ 12.66 (s, 2H), 4.61-4.38 (m, 2H), 2.31-2.11 (m, 2H), 2.08-1.85 (m, 2H).

^{13}C NMR (101 MHz, DMSO) δ 174.10, 77.85, 29.11.

3. Photocatalytic reaction device

Typical reactions in this work were carried out in a 10 mL Schlenk tube under 370--465 nm LED light. To a 10 mL reaction tube with a stir bar was added the substrate (0.4 mmol) and then 10 mg catalyst was added to the reaction tube. Substrately, 1 mL MeCN was added as the solvent. The reaction mixture was stirred for 10 h at room temperature with a 390 nm light source at 1 atm O_2 pressure (O_2 Balloon). The conversion and yield were detected by GC with the diphenyl as the internal standard.

The Photo Reaction Setup (SCI-PCRS-3-455) was purchased from Anhui Kemi machinery technology Co., Ltd.

Figure S1. The Photo Reaction Setup

4. The UV/Vis absorption spectra of other semiconductor catalysts.

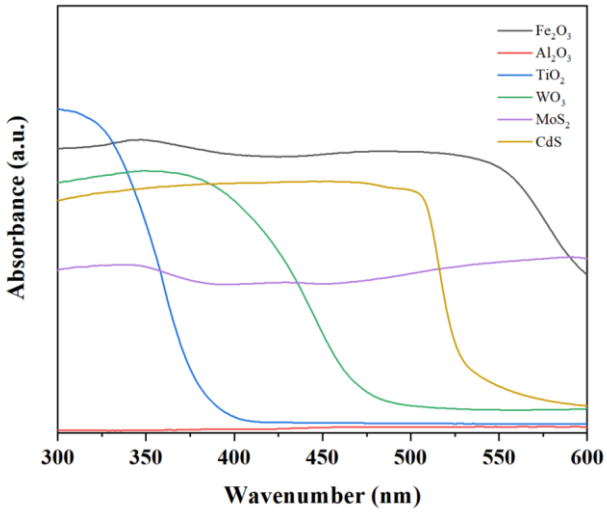


Figure S2. UV-Vis patterns of other catalysts.

5. The catalyst recycles

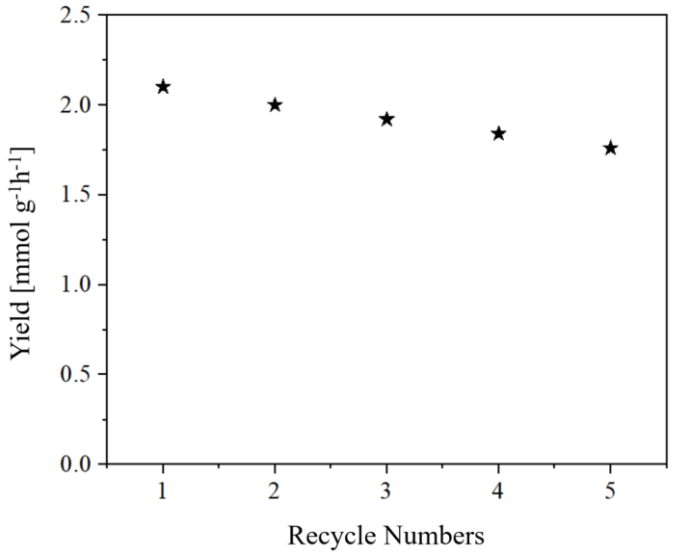


Figure S3. The recyclability of catalysts after five runs. Reaction conditions: 10 mL THFA, 100 mg catalyst, 390 nm LED, O_2 balloon, room temperature. Yields were determined by gas chromatography (GC) analysis using biphenyl as an internal standard.

6.

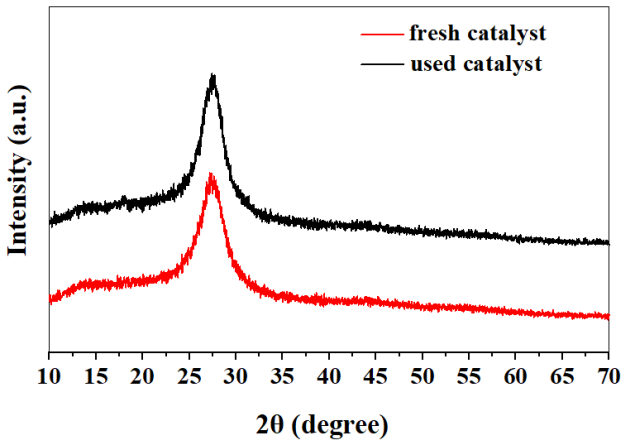


Figure S4. XRD spectra of the fresh and used catalyst.

7.

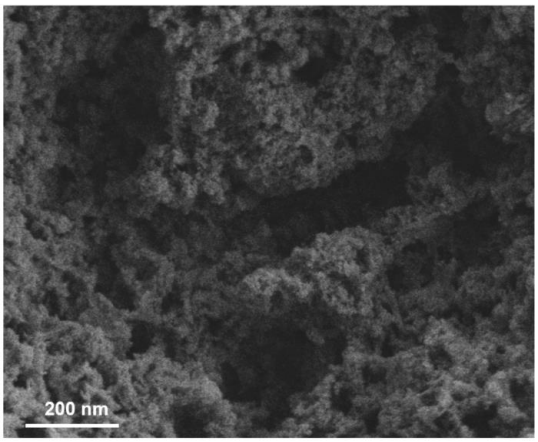


Figure S5. The SEM of the recycled catalyst.

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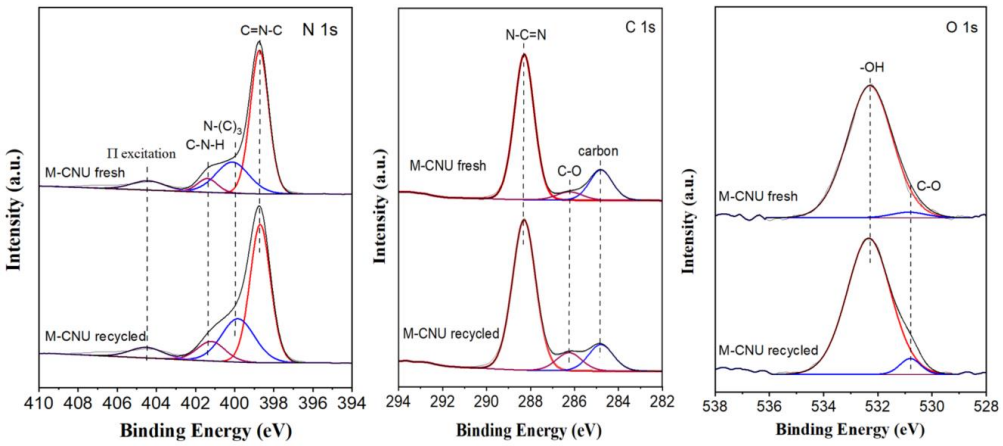


Figure S6. XPS spectra.

The ray photoelectron spectroscopy (XPS) was undertaken to accurately determine the specific bonding and structure of the catalysts before and after the reaction. In all samples, the typical C 1s and N 1s peaks were observed. The C 1s spectra showed C-C, N-C=N, and a trace amount of C-O bonding at 284.8, 288.3, and 286.2 eV, respectively. The weak peak of C-O bonding, probably due to calcination in air, increased after the reaction. It may be due to the adsorption of oxygen or reactants during the reaction. The N 1s spectra can be fitted to elucidate four separate signals, and provides a better idea of the bonding structure, since carbon spectra are susceptible to contamination. The N 1s core levels at 398.7, 400.1, and 401.3 eV correspond to sp2 C-N=C, sp3 N-$(C)_3$, and C-NH_x (amino functional groups), respectively. The weak peak at 404.4eV can be attributed to charging effects, or π excitations. The content of N element in each species did not change much before and after the reaction.

9.

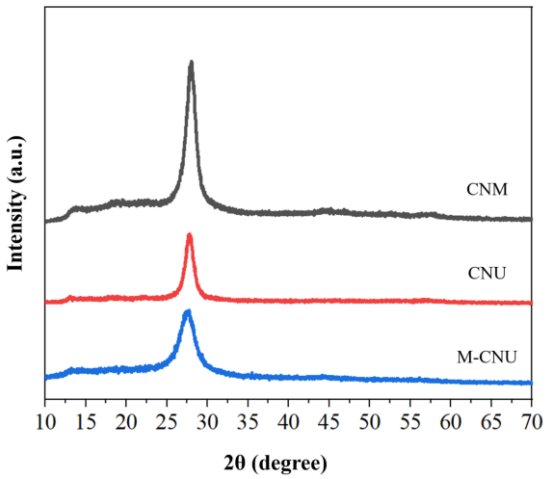
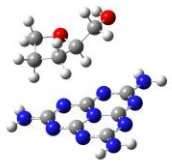


Figure S7. The XRD patterns of CNM, CNU and M-CNU

VI. The details for the density functional theory (DFT) calculations.

Gaussian 16 package[2] were used for all DFT calculations. The B3LYP functional[3-4] and 6-31G*[5] basis set were employed for the geometry optimization of the catalyst, reactants, intermediates, and products. The vibrational frequencies were then calculated at the same level used to obtain the zero-point energy (ZPE) corrections. For each transition state, only one imaginary frequency was found. Whereas, no imaginary frequencies were found for all the reactants, intermediates, and products. Afterward, the intrinsic reaction coordinate (IRC) analysis was conducted.

4) 3D images and Cartesian coordinates of the optimized geometries for all compounds



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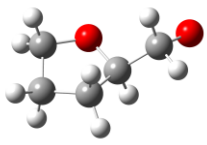

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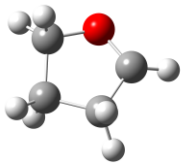

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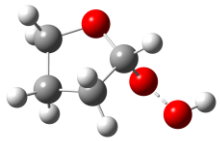

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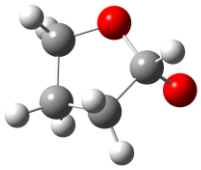

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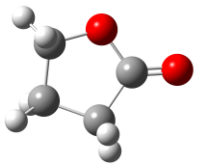

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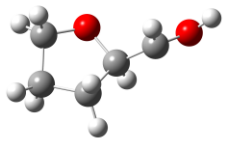

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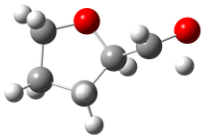

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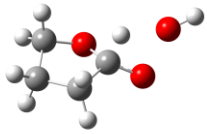

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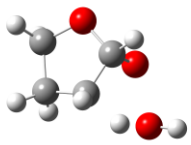

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C 0.92058300 1.28261800 -0.22471500

C -0.10810200 0.81029700 0.79041000

H 2.78330000 0.12972700 0.00668500

H 1.94159900 -0.21613400 -1.52625100

H 1.50294000 2.12342300 0.16615600

H 0.47231000 1.61207900 -1.16893100

H -0.07835700 1.19745100 1.80815100

H -1.48982300 0.92812500 0.25606800

H -0.40304000 -1.27951400 1.48986400

O -2.30409900 0.39475800 -0.36812900

H -3.03967200 0.06833800 0.18788400

O -0.93234500 -0.96807400 -0.50592400

Reference:

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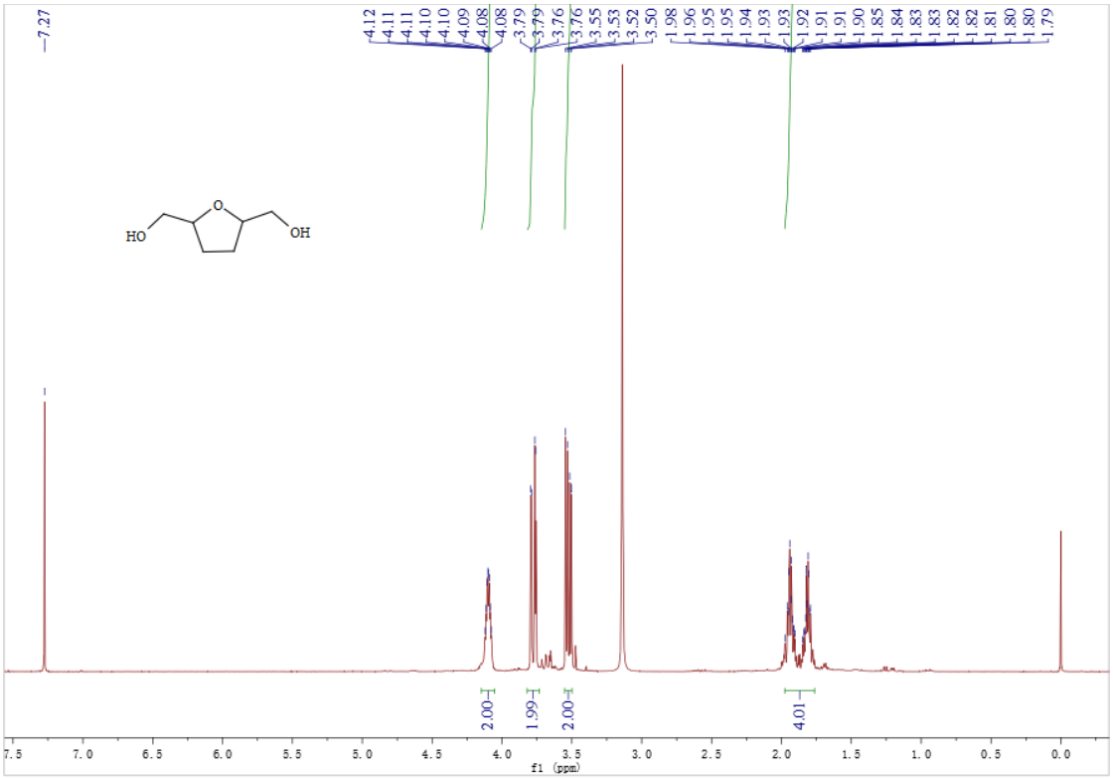
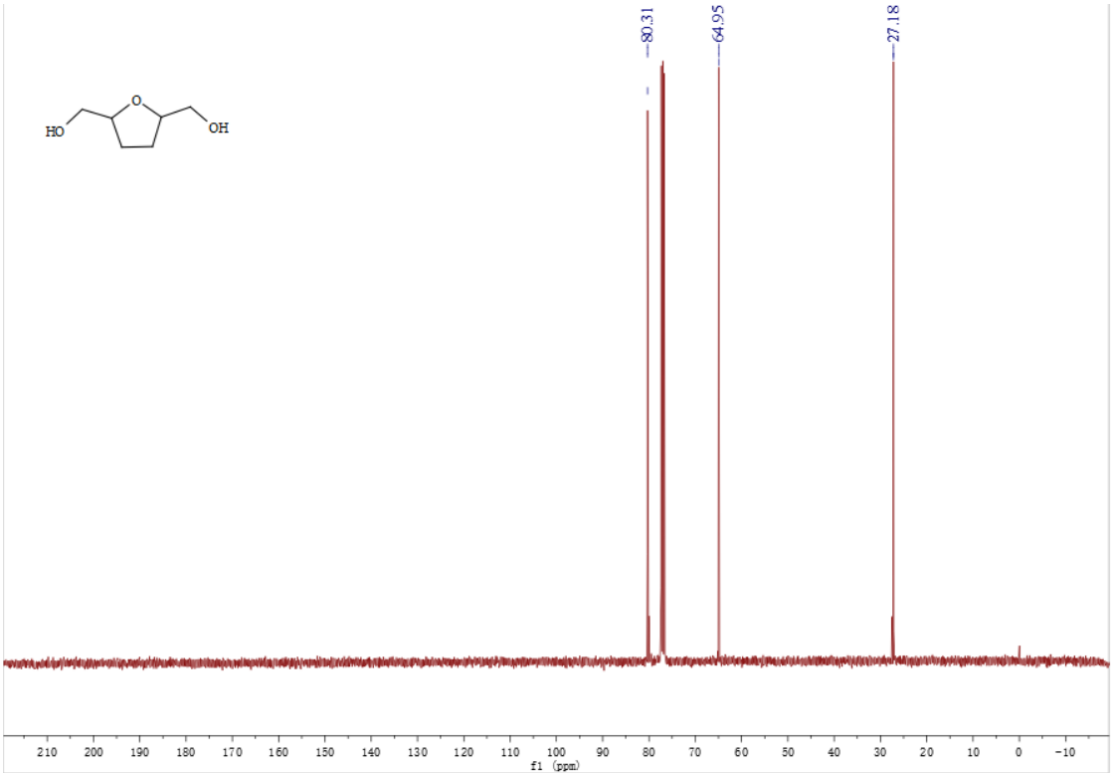
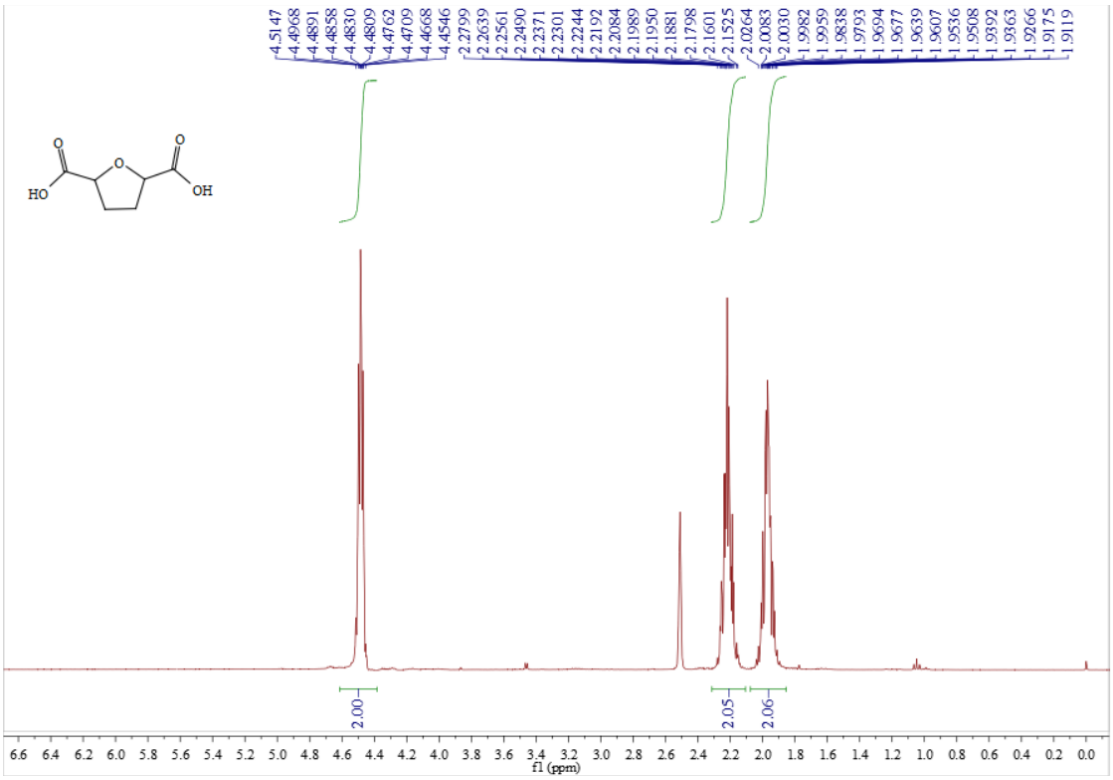
VII. NMR spectrum data



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4.4968
4.4891
4.4858
4.4830
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4.4762
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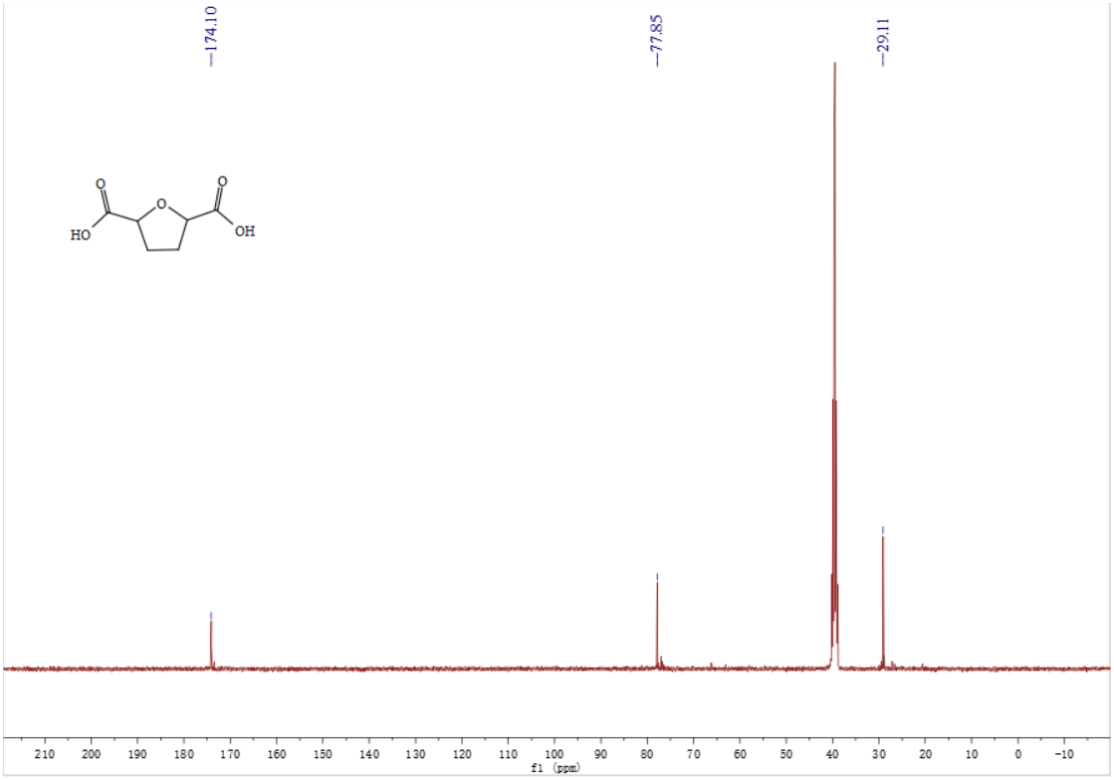
4.4668
4.4546
2.2799
2.2639
2.2561
2.2490
2.2371
2.2301
2.2244
2.2192
2.2084
2.1989
2.1950
2.1881
2.1798
2.1601
2.1525
2.0264
2.0083
2.0030
1.9982
1.9959
1.9838
1.9793
1.9694
1.9677
1.9639
1.9607
1.9536
1.9508
1.9392
1.9363
1.9266
1.9175
1.9119
HO
O
O
OH
2.00
2.05
2.06
f1 (ppm)


174.10
77.85
29.11
HO
O
O
OH
f1 (ppm)