

## Electronic Supplementary Information

### Green and intrinsic safe pathway for the catalytic synthesis of diisocyanates containing the furan ring from 5-hydroxymethylfurfural

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## **Compound qualitative and catalyst characterization methods**

The NMR spectra were measured at 400 MHz using an AVANCE 400 NMR spectrometer manufactured by Bruker Biospin AG, Switzerland. The FTIR spectra were measured using a Nicolet NEXUS 470 FTIR spectrometer from the USA. The elemental compositions were measured using the Flash EA 1112 Automatic Elemental Analyzer from the USA, which has an accuracy of  $\leq 0.30\%$ . The liquid chromatography-mass spectra were measured using a Compact liquid chromatography-mass spectrometer manufactured by Bruker Scientific Instruments, and the mass accuracy of better than 1 ppm was ensured through automatic calibration. The melting points were determined using an Instrumental Material Light WRS-3A melting point meter with a heating rate of 1 °C/min. Each substance was tested three times and the average value was calculated. The pyrolysis of FDC and THFDC was conducted using a synchronous thermogravimetric analyzer model STA449-F3, coupled with a quadrupole mass spectrometer model QMS-403D. The furnace was gradually heated from room temperature to 900 °C at a ramp rate of 10 °C/min. The carrier gas, pure N<sub>2</sub> (99.999%), flowed at a rate at 30 mL/min. An electrically heated holding device was installed at the top of the thermogravimetric analyzer in the connection part between the exhaust gas outlet and the inlet capillary of the mass spectrometer to prevent gaseous products from condensing. The heating temperature was set to 220 °C. Qualitative analysis of compound structure was determined by Agilent 7890A GC-5975C MS.

The X-ray diffraction (XRD) patterns were collected using a Rigaku D/MAX-2500 X-ray diffractometer with Cu-K $\alpha$  radiation in the range of 5°-90° at a scanning rate of 6°/min for the physical analysis of the catalyst samples. The weaving properties of each catalyst were obtained using a fully automated Specific Surface and Porosity Analyzer Model ASAP2460, with nitrogen adsorption-desorption isotherms measured at -196 °C. Each sample was degassed under vacuum at 200 °C for 4 h before measurements. ICP-AES was determined using an Agilent725 instrument manufactured by Agilent, Inc. in the USA. Darkfield scanning transmission electron

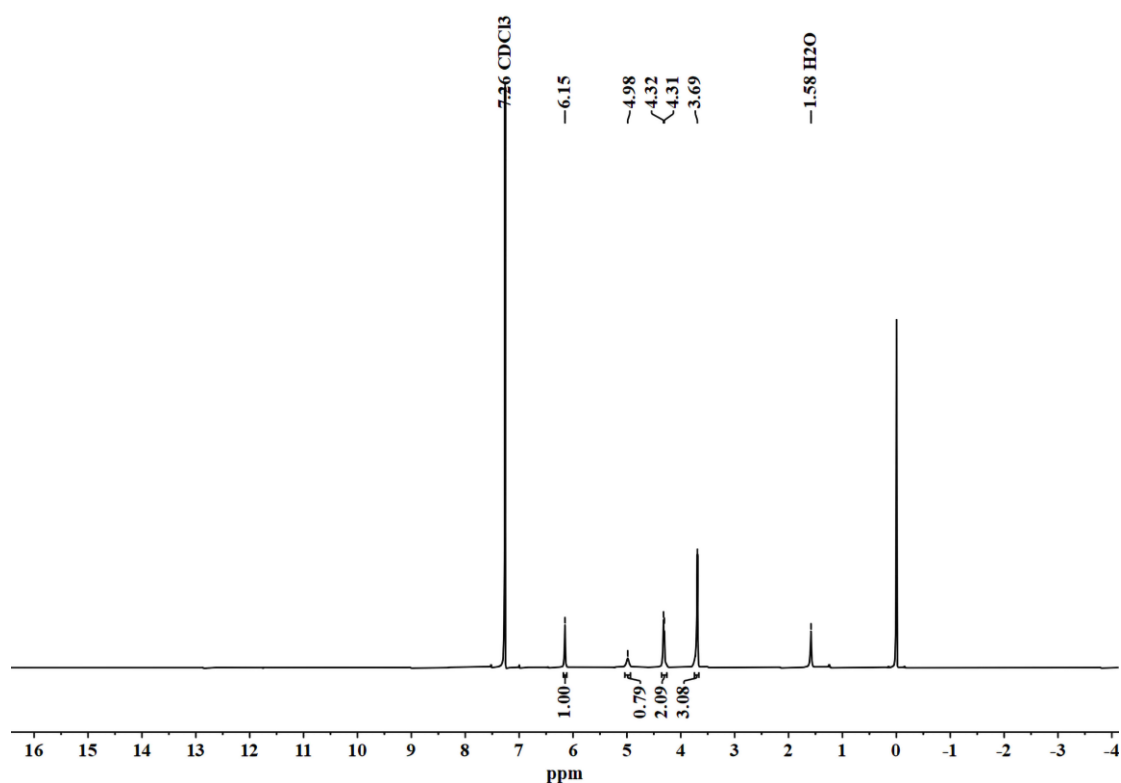
microscopy (HAADF-STEM) imaging and EDS elemental mapping were performed using a TalosF200S from FEI, USA. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250Xi spectrometer with Al K $\alpha$  X-ray radiation to analyze the surface chemical state of the catalyst. The C 1s signal of 284.8 eV from indeterminate carbon was used as a reference to correct for surface charge effects. The thermogravimetric analysis of the catalyst was performed using the TA Q50 thermal analyzer. The measurements were taken from room temperature to 900 °C at a rate of 2 °C/min in an air-dynamic atmosphere with a flow rate of 40 mL/min. Metal dispersion was measured using the AutoChemII 2920 instrument manufactured by Mac Instruments, USA. The samples were dried at 120 °C for 2 h and then pretreated in a He atmosphere at 200 °C for 1 h to remove adsorbed water. Subsequently, CO adsorption was determined at 35 °C. The acidity of the catalyst was analyzed using an AutoChem2920 temperature-programmed chemical adsorption instrument. The ramp-up procedure was conducted at a rate of 10 °C/min until reaching 300 °C, and it was maintained at this temperature for 1 h before being cooled down to 50 °C. After adsorbing NH<sub>3</sub> for 30 minutes, the catalyst was again ramped up to 800 °C at a rate of 10 °C/min.

### **Product qualitative analysis**

#### **(1) Methyl furan-2,5-dimethylene dicarbamate (FDC)**

The FDC compound is a white crystalline substance with no odor, soluble in organic solvents such as dimethyl sulfoxide, but it has limited solubility in water. It has a molecular weight of 242.0903 and melts between 143.3 °C and 143.9 °C. The NMR spectra of FDC are presented in Fig. S1 and Fig. S2: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 6.15 (s, 2H), 4.98 (s, 2H), 4.31-4.32 (d, J=4.0 Hz, 4H), 3.69 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 156.89, 151.50, 108.21, 52.46, 38.27. The HRMS spectrum of FDC (Fig. S3) exhibited m/z =243.0974 [M+H]<sup>+</sup>, which had a theoretical value of 243.0981; and m/z =265.0793 [M+Na]<sup>+</sup>, which had a theoretical value of 265.0800. FT-IR analysis (Fig. S4) revealed that the absorption peak at 3255 cm<sup>-1</sup> corresponds to the stretching

vibration of the N-H bond, while peaks at 2989  $\text{cm}^{-1}$  and 2956  $\text{cm}^{-1}$  represent methylene stretching vibrations. The peak at 1706  $\text{cm}^{-1}$  indicates characteristic absorption due to C=O functional group stretching vibration, whereas the peak at 1683  $\text{cm}^{-1}$  signifies sec-amine bending vibration. Additionally, peaks at 1203  $\text{cm}^{-1}$  and 1033  $\text{cm}^{-1}$  correspond to C-O-C stretching vibrations. The elemental analysis demonstrated that the calculated composition of FDC was as follows: C, 49.58%; H, 5.826%; N, 11.56%. The measured values showed that the actual composition of FDC was as follows: C, 49.22%; H, 5.765%; N, 12.23%.



**Fig. S1**  $^1\text{H}$  NMR of FDC.

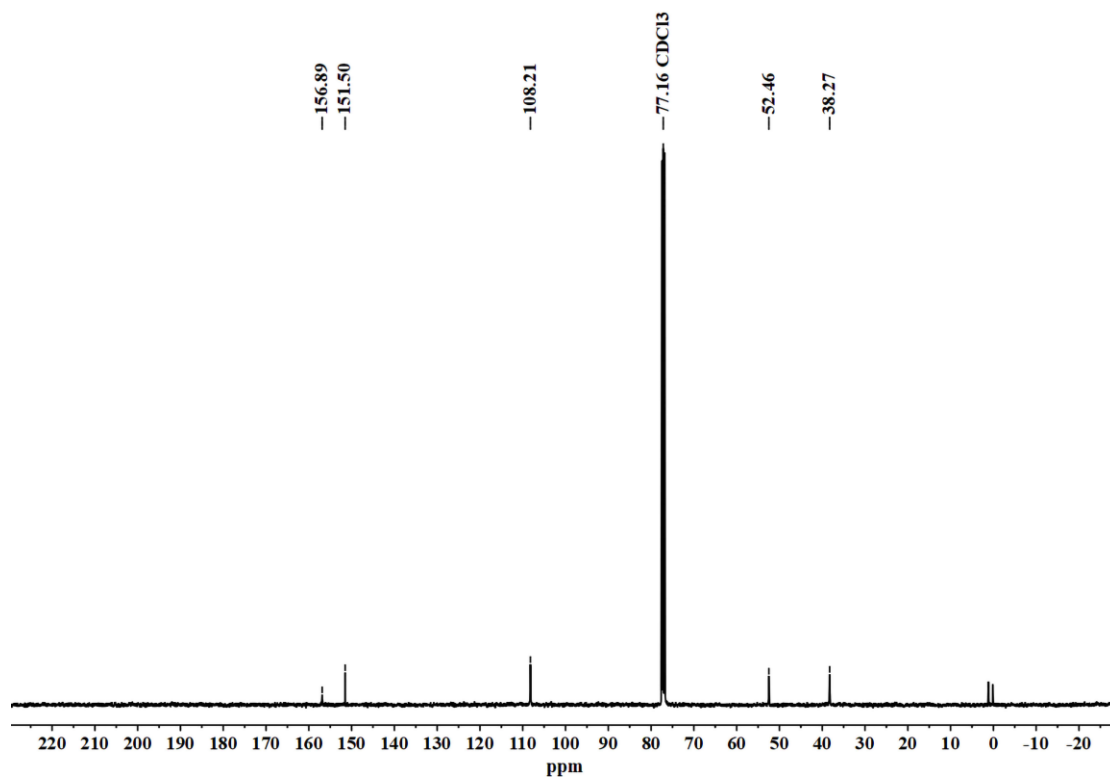


Fig. S2  $^{13}\text{C}$  NMR of FDC.

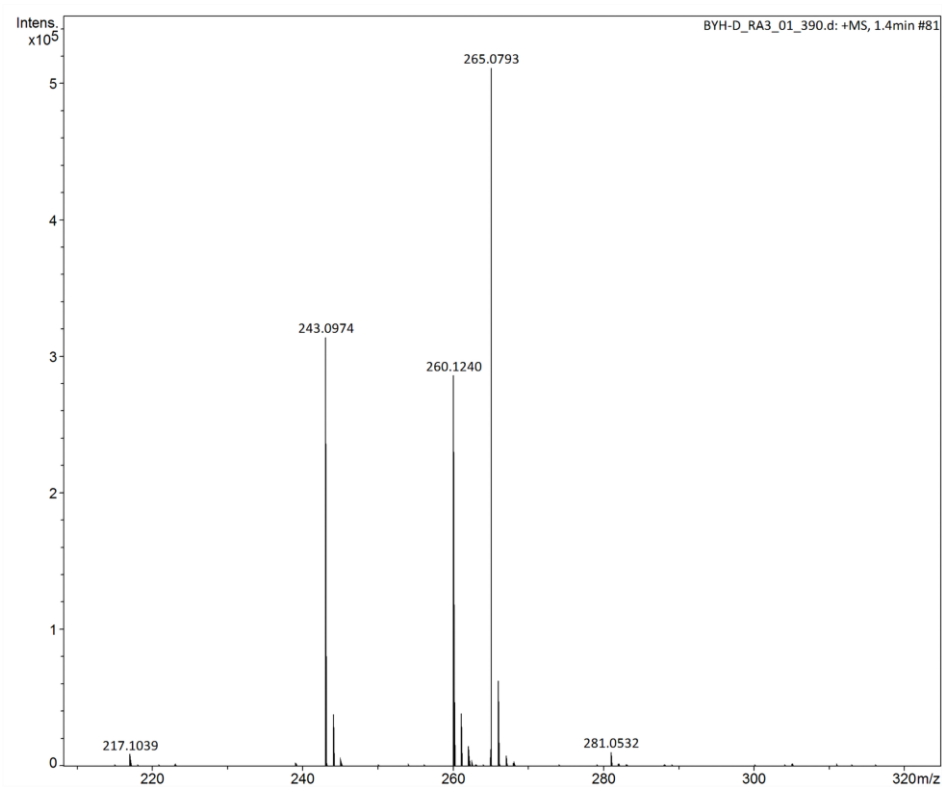


Fig. S3 HRMS of FDC.

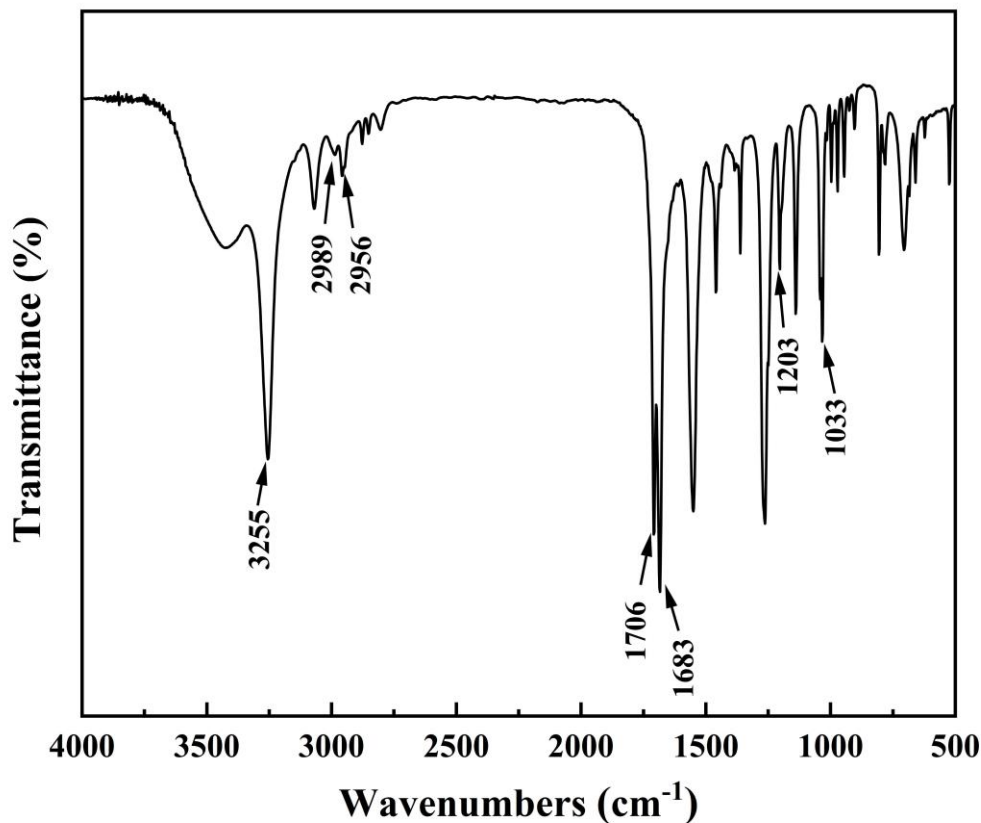


Fig. S4 FTIR of FDC.

(2) Methyl tetrahydrofuran-2,5-dimethylene dicarbamate (THFDC)

The THFDC compound is a white crystalline substance with no odor, soluble in organic solvents such as dimethyl sulfoxide and easily soluble in water. It has a molecular weight of 246.1216 and melts between 73.5 °C and 74.5 °C. The NMR spectra of THFDC are presented in Fig. S5 and Fig. S6: <sup>1</sup>H NMR (400 MHz, DMSO) δ: 7.13 (s, 2H), 3.85-3.79 (m, 2H), 3.52 (s, 6H), 3.04-3.00 (m, 4H), 1.89-1.79 (m, 2H), 1.56-1.49 (m, 2H); <sup>13</sup>C NMR (100 MHz, DMSO) δ: 156.96, 77.76, 51.30, 44.66, 27.82. The HRMS spectrum of THFDC (Fig. S7) exhibited m/z =247.1290 [M+H]<sup>+</sup>, which has a theoretical value of 247.1289; and m/z =269.1108 [M+Na]<sup>+</sup>, which has a theoretical value of 269.1107. The FTIR spectra of THFDC (Fig. S8) showed an absorption peak at 3338 cm<sup>-1</sup> corresponding to the stretching vibration of the N-H bond, another peak at 2873 cm<sup>-1</sup> for the anti-symmetric stretching vibration of saturated C-H, a characteristic absorption peak at 1697 cm<sup>-1</sup> indicating the stretching vibration of the

C=O functional group, a peak at 1543  $\text{cm}^{-1}$  representing the bending vibration of secondary amine, and peaks at 1078  $\text{cm}^{-1}$  and 916  $\text{cm}^{-1}$  denoting the anti-symmetric and symmetric stretching vibration of the C-O-C in tetrahydrofuran. The elemental analysis demonstrated that the calculated composition of THFDC was as follows: C, 48.77%; H, 7.372%; N, 11.38%. The measured values showed that the actual composition of THFDC was: C, 48.31%; H, 7.000%; N, 12.71%.

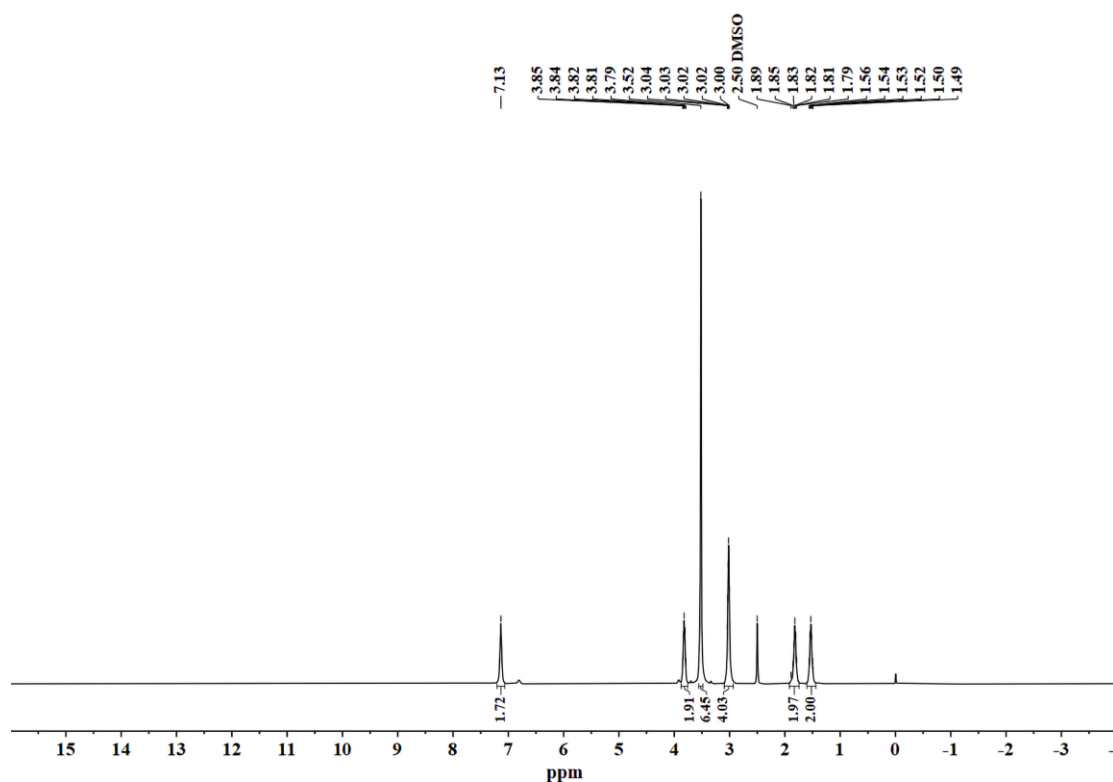


Fig. S5  $^1\text{H}$  NMR of THFDC.

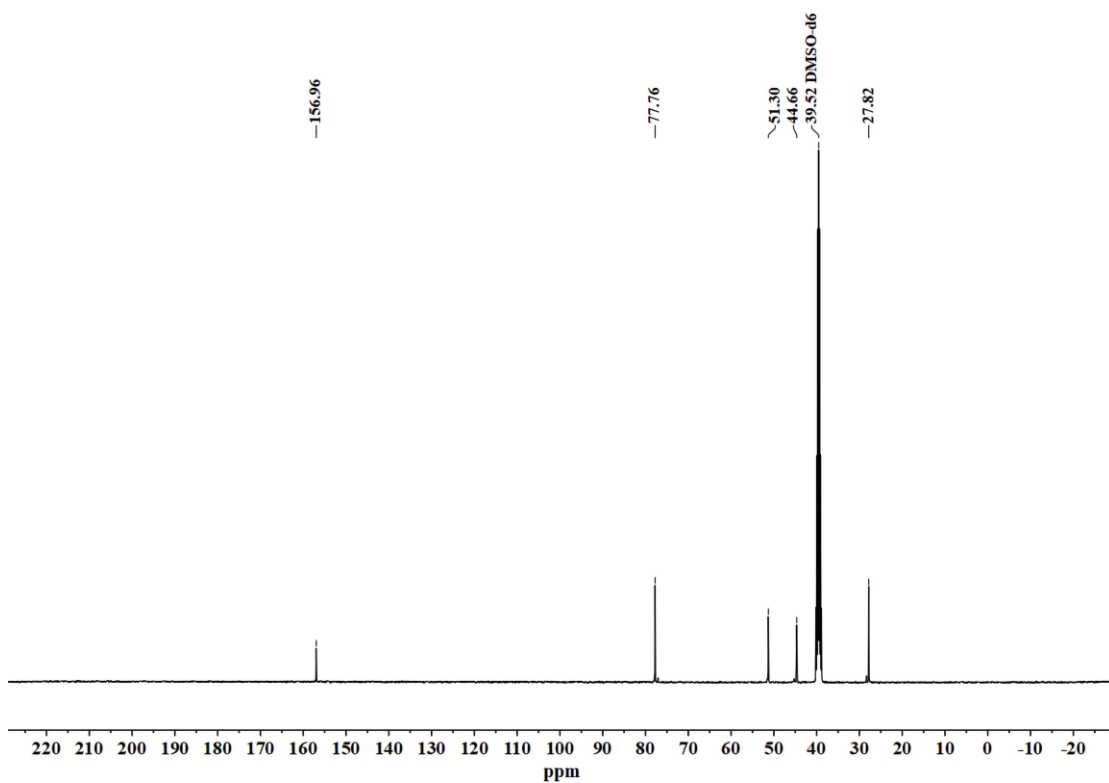


Fig. S6  $^{13}\text{C}$  NMR of THFDC.

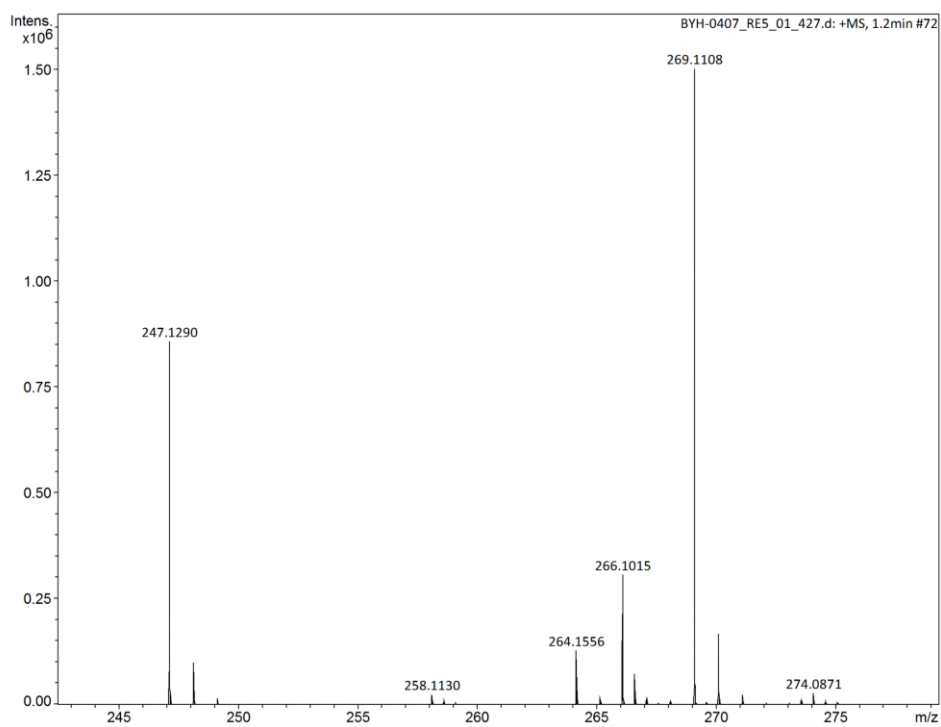


Fig. S7 HRMS of THFDC.



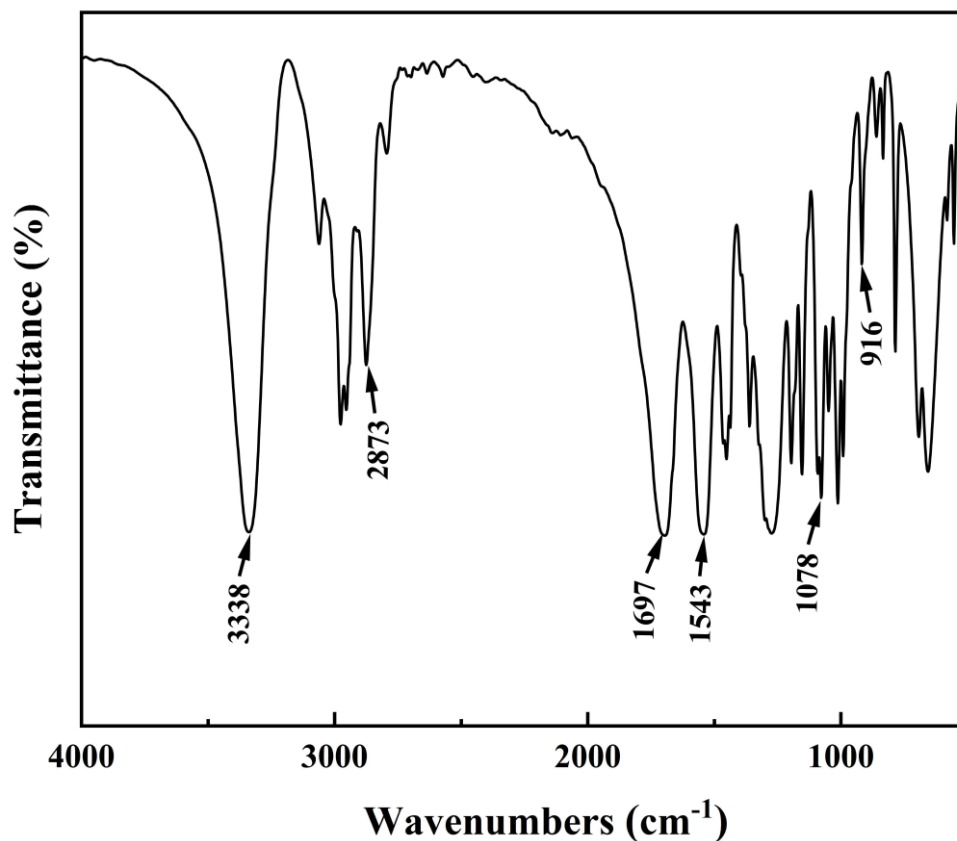


Fig. S8 FTIR of THFDC.

### (3) Furan-2,5-dimethylene-ethyl carbamate (FDU)

The synthesized FDU is a white crystalline substance with no odor, soluble in organic solvents such as dimethyl sulfoxide, but it has limited solubility in water. It has a molecular weight of 270.1216 and melts between 77.6 °C and 78.1 °C. The NMR spectra of FDU are presented in Fig. S9 and Fig. S10: <sup>1</sup>H NMR (400 MHz, DMSO) δ: 7.54 (t, J=6.3 Hz, 2H), 6.10 (s, 2H), 4.10 (d, J=5.9 Hz, 4H), 3.98 (q, J=7.3 Hz, 4H), 1.15 (t, 6H); <sup>13</sup>C NMR (100 MHz, DMSO) δ: 156.71, 152.07, 107.69, 60.33, 37.57, 14.91. The HRMS spectrum of FDU (Fig. S11) exhibited m/z =271.1288 [M+H]<sup>+</sup>, which has a theoretical value of 271.1294; and m/z =293.1103 [M+Na]<sup>+</sup>, which has a theoretical value of 293.1113. The FTIR spectra of FDU (Fig. S12) showed an absorption peak at 3320 cm<sup>-1</sup>, which was the stretching vibration of the N-H bond. The peaks at 2985 cm<sup>-1</sup> and 2931 cm<sup>-1</sup> represented methylene stretching vibration. There was a characteristic absorption peak at 1685 cm<sup>-1</sup> for the stretching vibration

of the C=O functional group. The peak at 1546  $\text{cm}^{-1}$  indicated secondary amine bending vibration, while the one at 1477  $\text{cm}^{-1}$  represented methylene bending vibration. There were C-O-C stretching vibration peaks observed at both 1261  $\text{cm}^{-1}$  and 1047  $\text{cm}^{-1}$ . The elemental analysis demonstrated that the calculated composition for FDU was as follows: C, 53.33%; H, 6.713%; N, 10.36%. The measured values showed that the actual composition of FDU was: C, 53.01%; H, 6.602%; N, 11.72%.

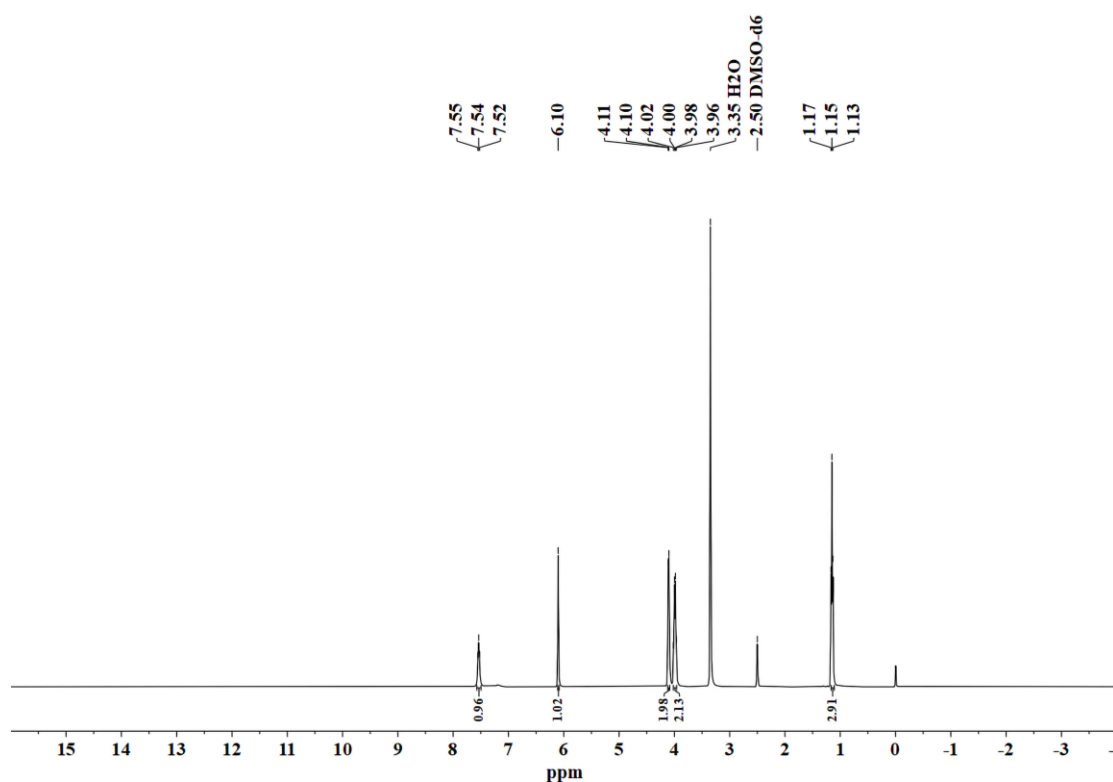


Fig. S9  $^1\text{H}$  NMR of FDU.

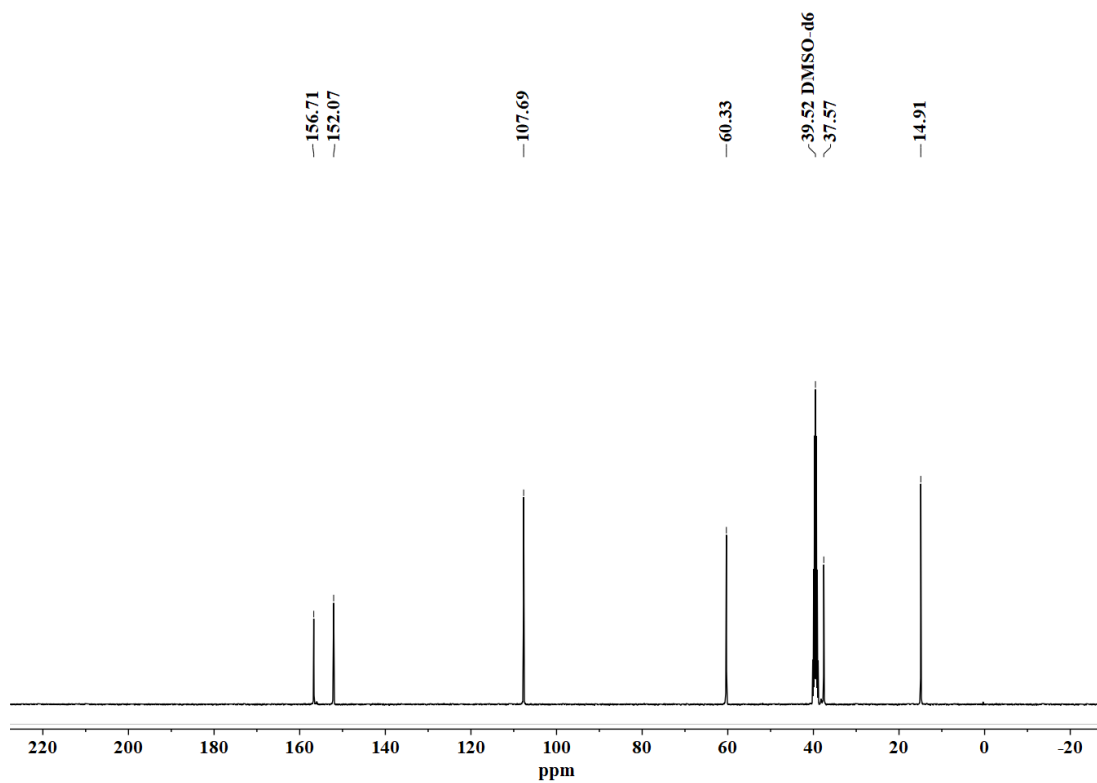


Fig. S10  $^{13}\text{C}$  NMR of FDU.

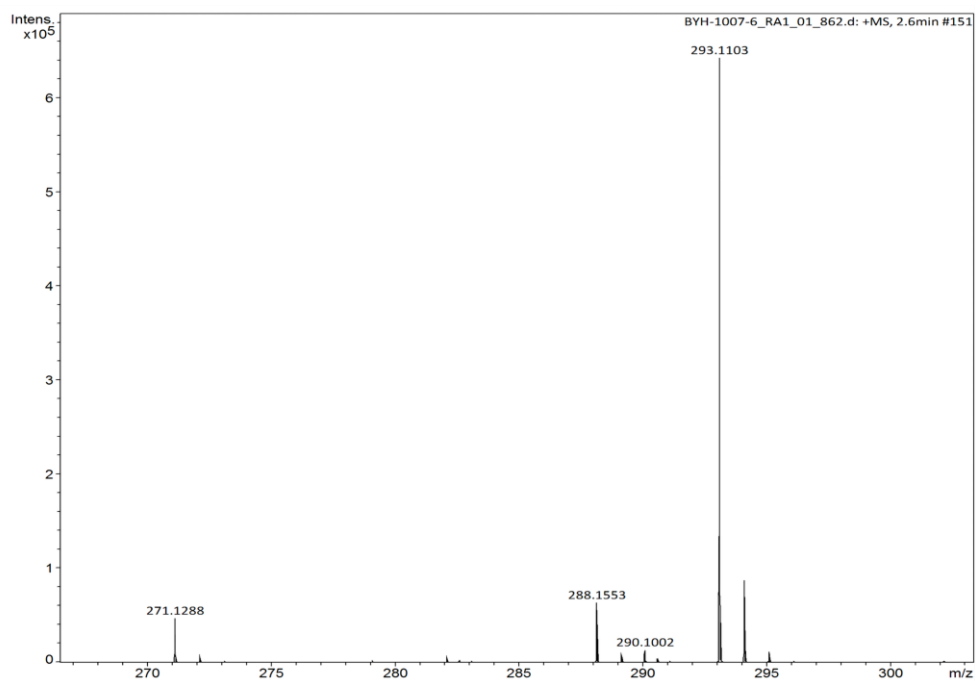


Fig. S11 HRMS of FDU.

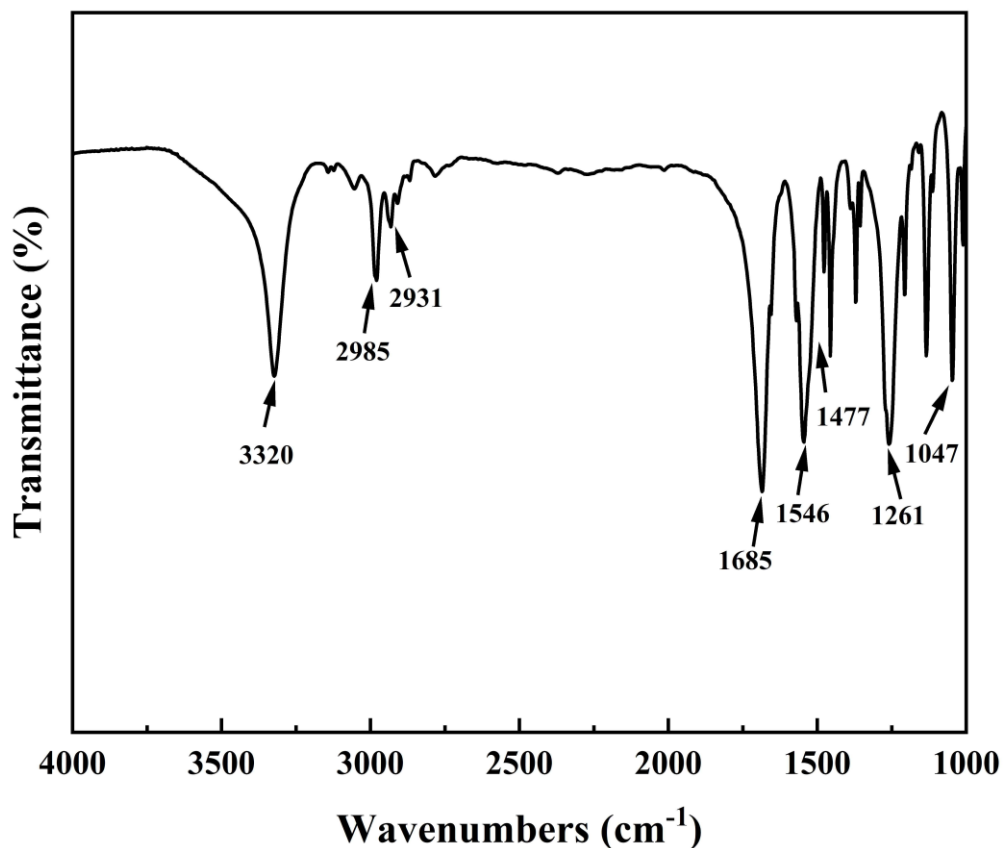
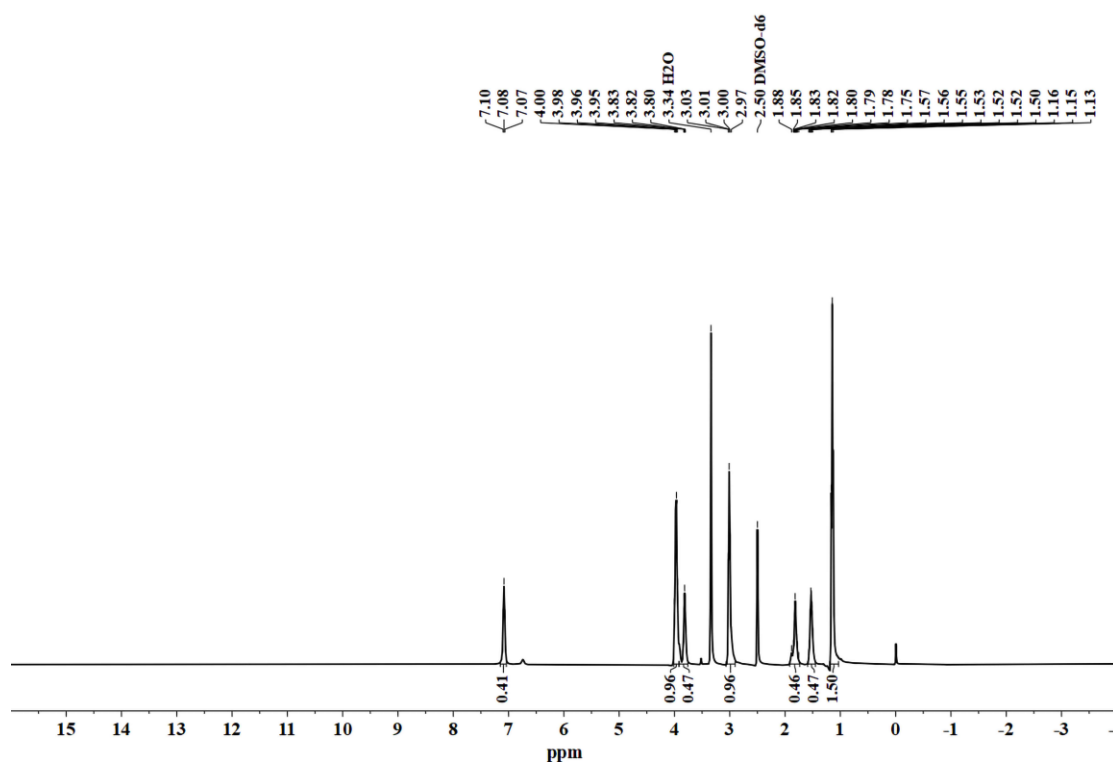


Fig. S12 FTIR of FDU.

#### (4) Tetrahydrofuran-2,5-dimethylene-ethyl carbamate (THFDU)

The THFDU compound is a white crystalline substance with no odor, soluble in organic solvents such as dimethyl sulfoxide and readily soluble in water. It has a molecular weight of 274.1529 and melts between 63.4 °C and 63.9 °C. The NMR spectra of THFDU are presented in Fig. S13 and Fig. S14: <sup>1</sup>H NMR (400 MHz, DMSO) δ: 7.08 (t, J=6.1 Hz, 2H), 3.97 (q, J=7.1 Hz, 4H), 3.82 (t, J= 5.6Hz, 2H), 3.01 (dd, J=6.0, 2.9 Hz, 4H), 1.88-1.75 (m, 2H), 1.57-1.50 (m, 2H), 1.15 (t, J=7.2 Hz, 6H); <sup>13</sup>C NMR (100 MHz, DMSO) δ: 156.54, 77.79, 59.63, 44.61, 27.85, 14.68. The HRMS spectrum of THFDU (Fig. S15) exhibited m/z =275.1603 [M+H]<sup>+</sup>, which has a theoretical value of 275.1607; and m/z =297.1404 [M+Na]<sup>+</sup>, which has a theoretical value of 297.1426. The FTIR spectra of THFDU (Fig. S16) showed an absorption peak at 3345 cm<sup>-1</sup> corresponding to the stretching vibration of the N-H bond, another peak at 2873 cm<sup>-1</sup> for the anti-symmetric stretching vibration of saturated C-H, a characteristic

absorption peak at  $1724\text{ cm}^{-1}$  indicating the stretching vibration of the C=O functional group, a bending vibration peak at  $1668\text{ cm}^{-1}$  representing secondary amine, and peaks at  $1089\text{ cm}^{-1}$  and  $1025\text{ cm}^{-1}$  for the anti-symmetric and symmetric stretching vibration of the C-O-C in tetrahydrofuran. The elemental analysis demonstrated that the calculated composition of THFDU was as follows: C, 52.54%; H, 8.081%; N, 10.21%. The measured values showed that the actual composition of THFDU was C, 52.06%; H, 7.858%; N, 11.39%.



**Fig. S13**  $^1\text{H}$  NMR of THFDU.

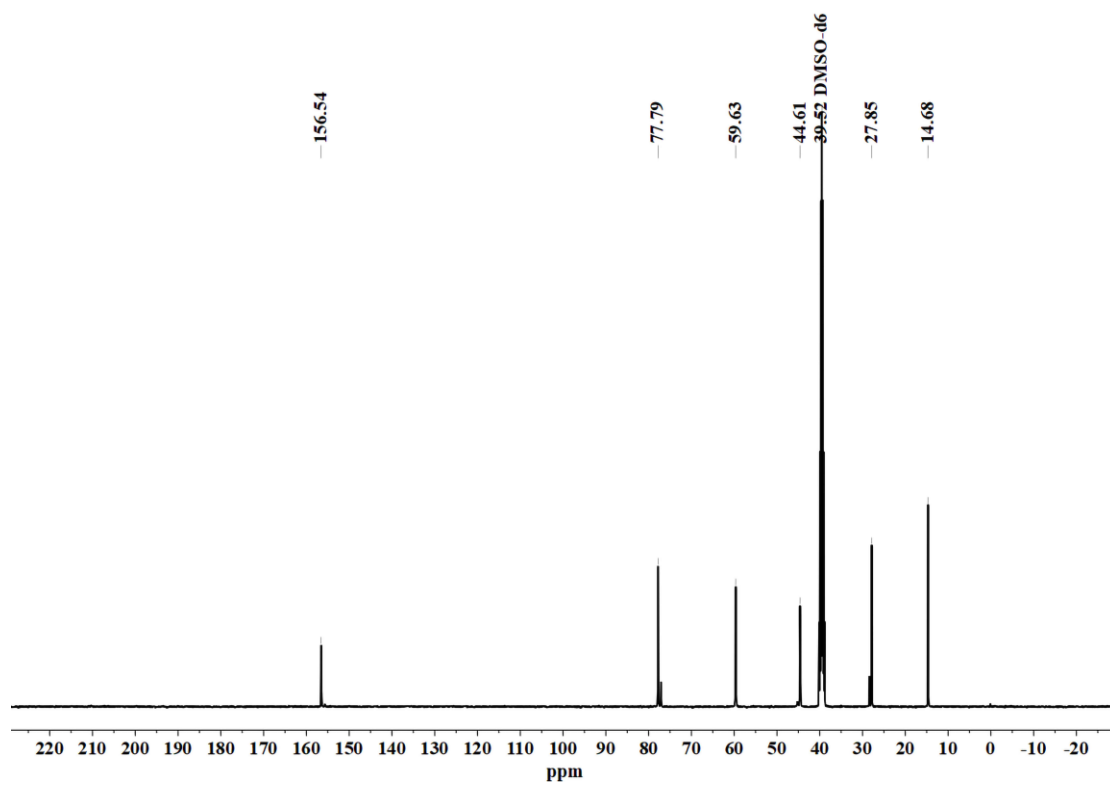


Fig. S14  $^{13}\text{C}$  NMR of THFDU.

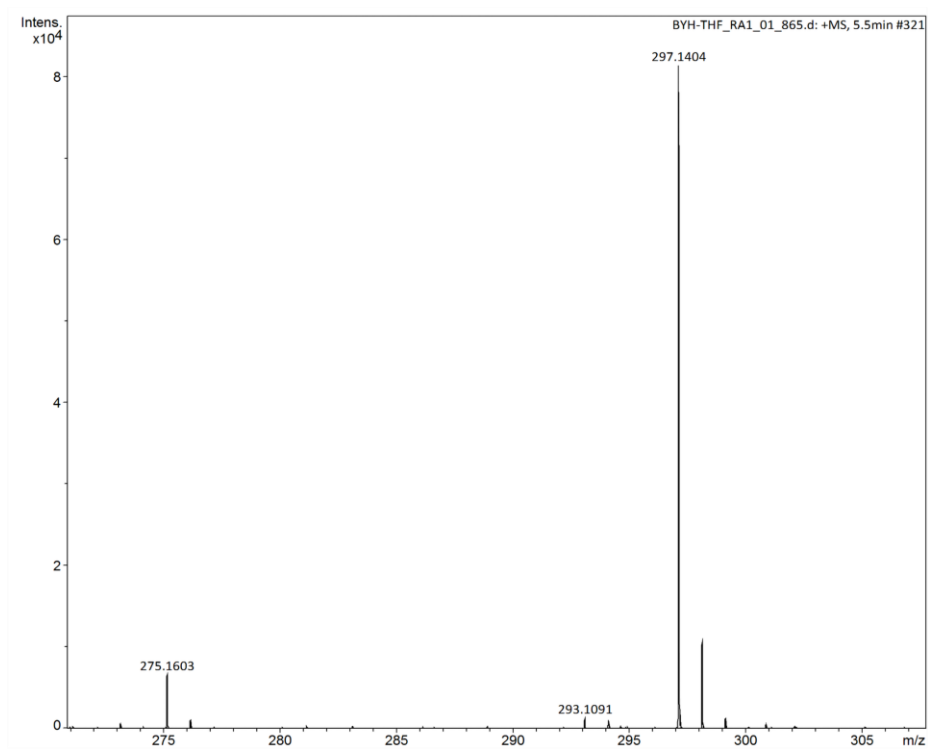


Fig. S15 HRMS of THFDU.

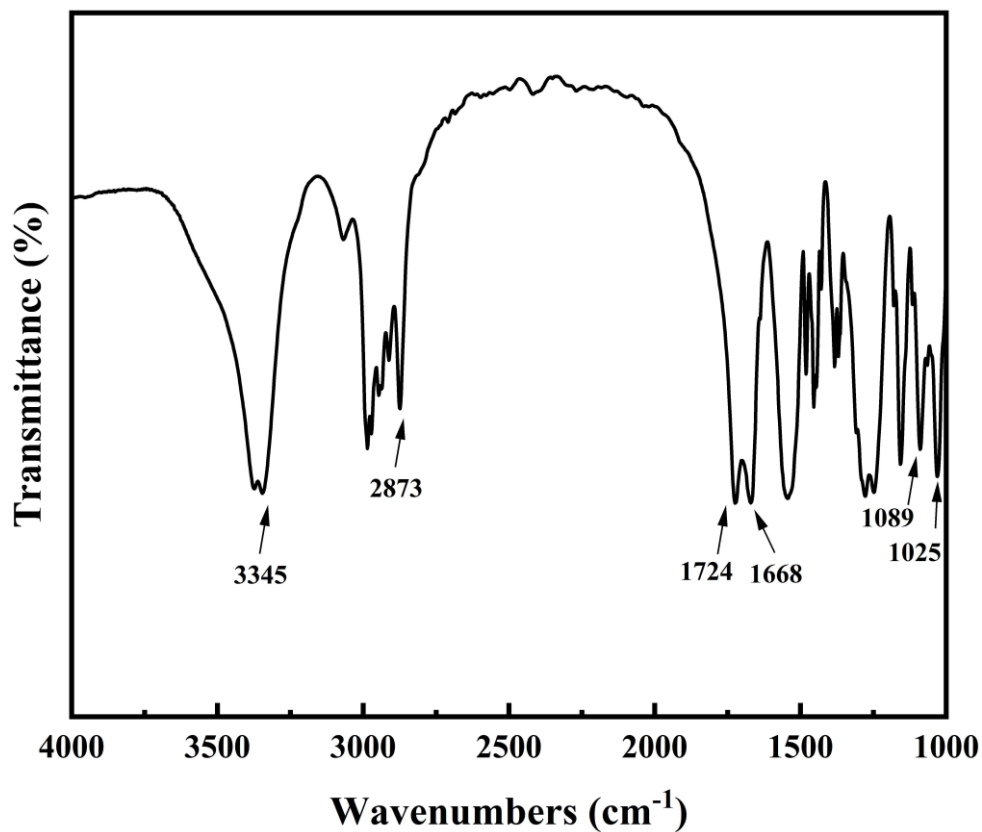
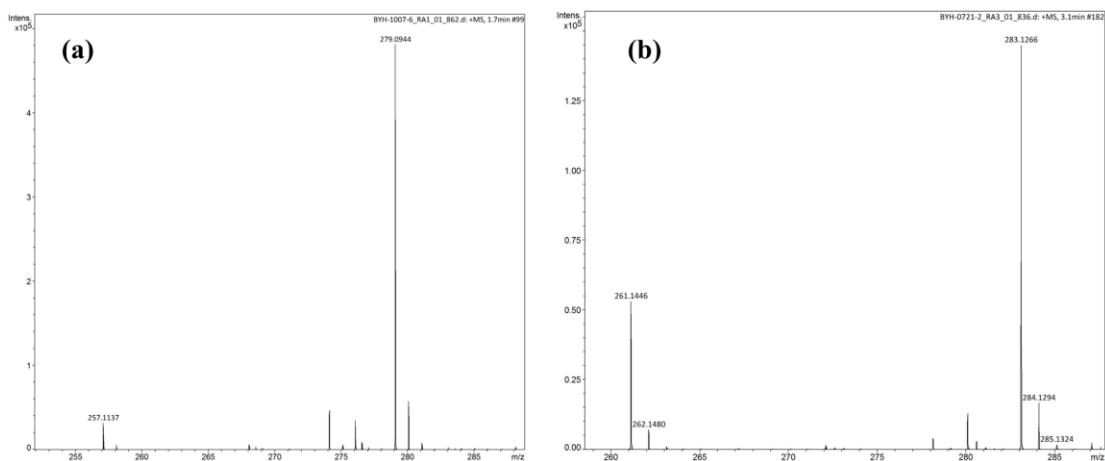


Fig. S16 FTIR of THFDU.

(5) Furan-2-methylenecarbamate methyl ester-5-methylenecarbamate ethyl ester (FMU) and tetrahydrofuran-2-methylenecarbamate methyl ester-5-methylenecarbamate ethyl ester (THFMU)

The HRMS spectrum of FMU (Fig. S17 (a)) exhibited  $m/z = 257.1137$   $[M+H]^+$ , which has a theoretical value of 257.1137; and  $m/z = 279.0944$   $[M+Na]^+$ , which has a theoretical value of 279.0957. The HRMS spectrum of THFMU (Fig. S17 (b)) exhibited  $m/z = 261.1446$   $[M+H]^+$ , which has a theoretical value of 261.1450; and  $m/z = 283.1266$   $[M+Na]^+$ , which has a theoretical value of 283.1270.



**Fig. S17** HRMS of the (a) FMU, (b) THFMU.



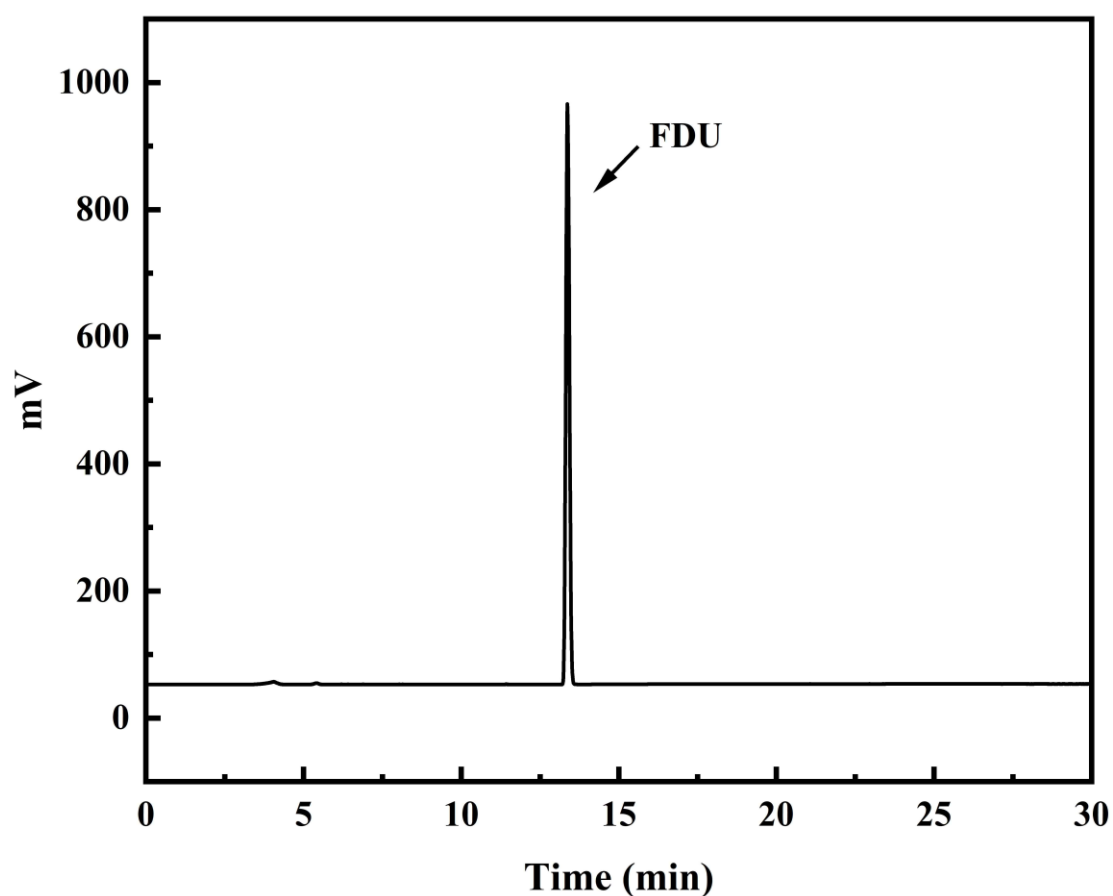
**Fig. S18** Physical diagram of the two-stage reaction of FDC and THFDC decomposition.

#### (6) Furan-2,5-dimethylene diisocyanate (FDI)

After the vacuum distillation experiment, the FDI obtained is a light yellow liquid with a pungent odor. The obtained FDI underwent ethanol derivatization, and the resulting liquid chromatogram is shown in Fig. S19. It can be seen that the



chromatogram only has one peak, and the position of the peak is consistent with that of the self-made FDU chromatographic peak. The  $^1\text{H}$  NMR spectra of FDI are presented in Fig. S20:  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ )  $\delta$ : 7.58-7.50 (m, 2H), 4.20 (dt,  $J = 11.8, 4.9$  Hz, 4H). The HRMS spectrum of FDI (Fig. S21) exhibited  $m/z = 201.0265$   $[\text{M}+\text{Na}]^+$ , which has a theoretical value of 201.0270. In the FTIR spectrum of FDI (Fig. S22), the peaks at  $2960\text{ cm}^{-1}$  and  $2930\text{ cm}^{-1}$  correspond to methylene stretching vibrations. The peak at  $2873\text{ cm}^{-1}$  represents the saturated C-H antisymmetric stretching vibration. The characteristic peak of -NCO is observed at  $2256\text{ cm}^{-1}$ . The absorption peak at  $1776\text{ cm}^{-1}$  indicates the presence of a C=N functional group, while the stretching vibration absorption peak of C=O functional group is observed at  $1720\text{ cm}^{-1}$ . The in-plane bending peak of the C-H functional group occurs at  $1461\text{ cm}^{-1}$ , and the peaks at  $1271\text{ cm}^{-1}$  and  $1112\text{ cm}^{-1}$  are associated with stretching vibrations of C-O-C. The GCMS spectrum of FDI is shown in Fig. S23.



**Fig. S19** Liquid chromatogram of FDU.

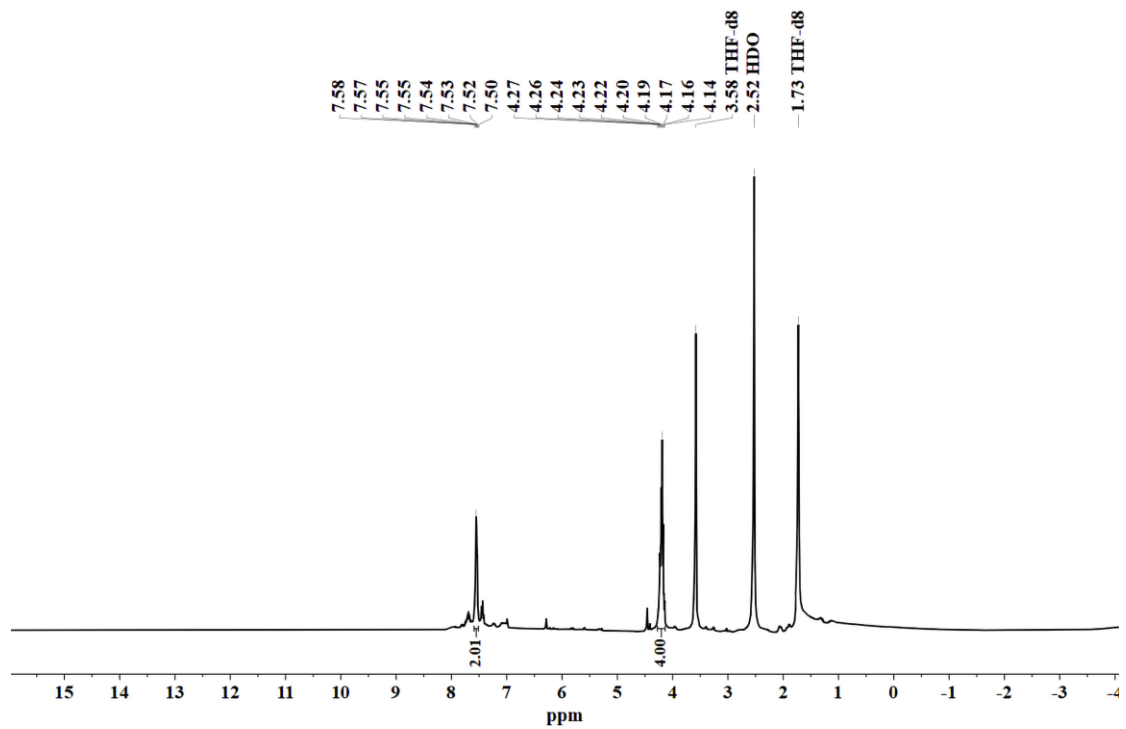


Fig. S20 <sup>1</sup>H NMR of FDI.

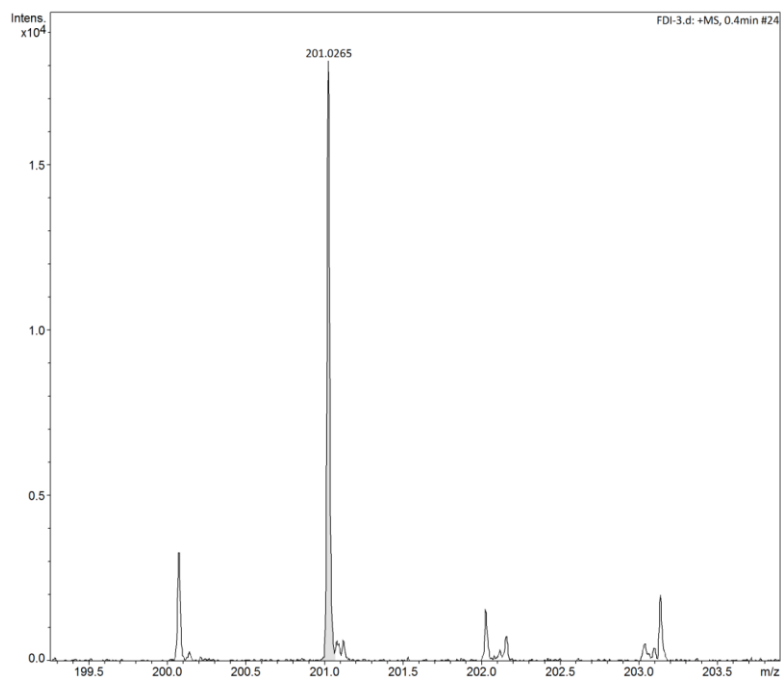


Fig. S21 HRMS of FDI.

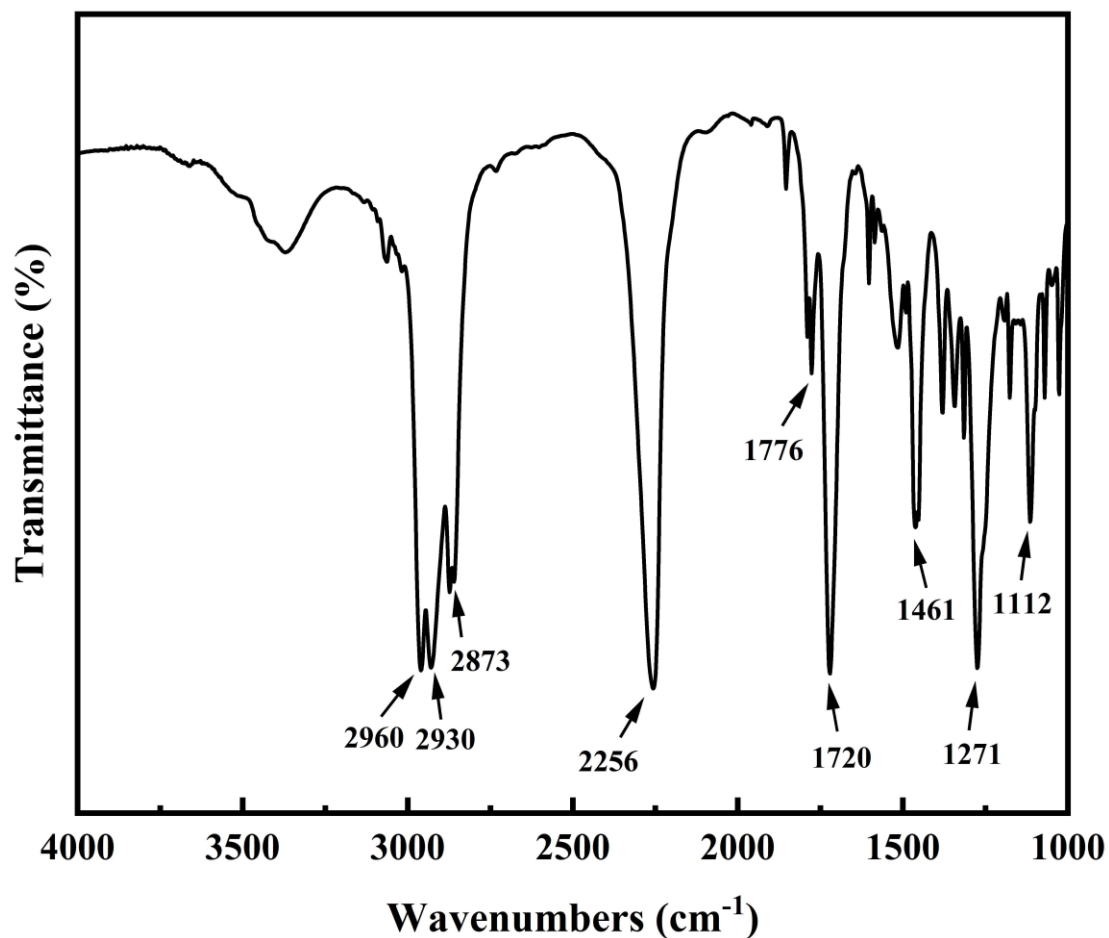


Fig. S22 FTIR of FDI.

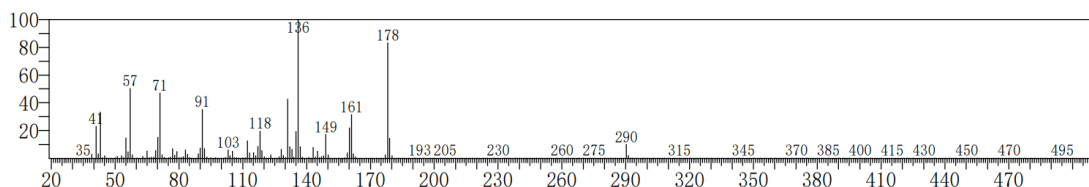
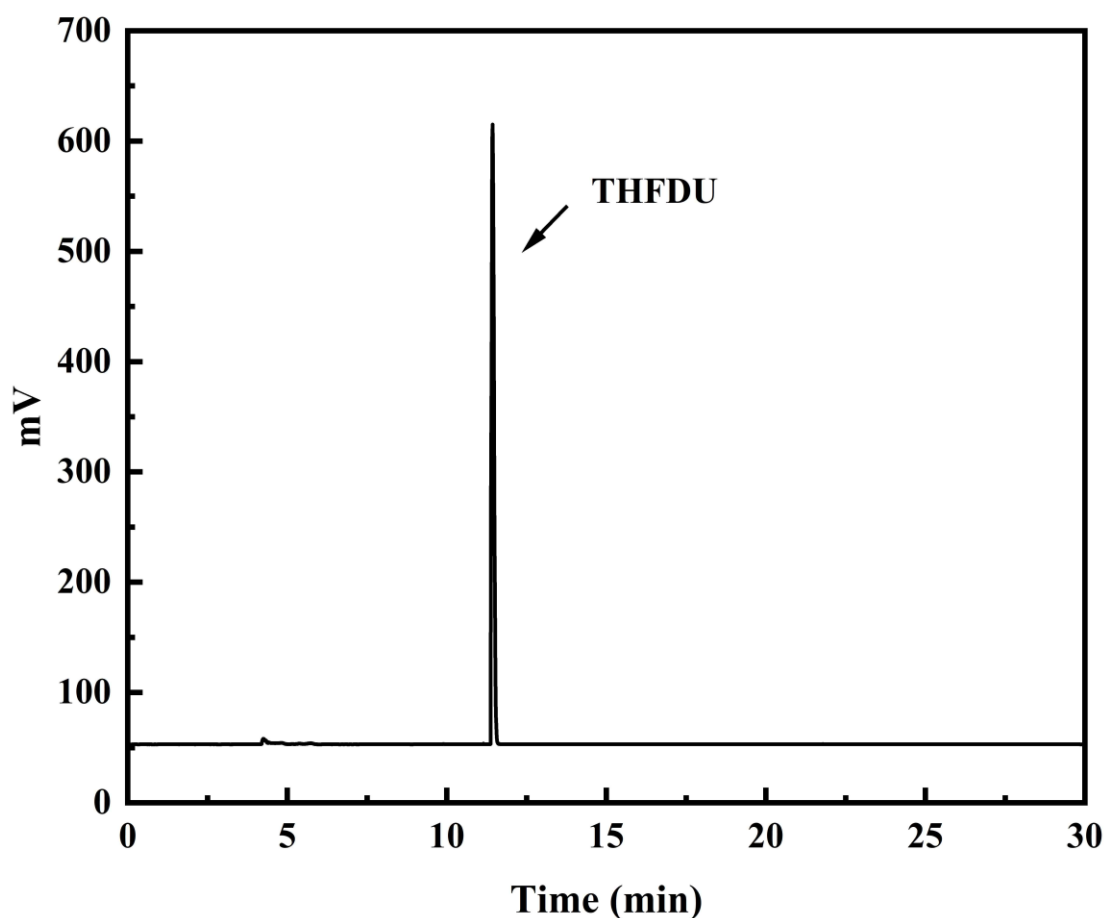


Fig. S23 GCMS of FDI.

### (7) Tetrahydrofuran-2,5-dimethylene diisocyanate (THFDI)

After vacuum distillation experiment, the obtained THFDI is a colorless transparent liquid with a pungent odor. The obtained THFDI underwent ethanol derivatization, and the resulting liquid chromatogram is shown in Fig. S24. It can be seen that the chromatogram only has one peak, and the position of the peak is consistent with that of the self-made THFDU chromatographic peak. The <sup>1</sup>H NMR spectra of THFDI are presented in Fig. S25: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.07 (dpt, J =

6.6, 4.6, 2.0 Hz, 2H), 3.46-3.40 (m, 2H), 3.26 (dd,  $J = 13.6, 5.4$  Hz, 2H), 2.08-1.96 (m, 2H), 1.79-1.68 (m, 2H). The HRMS spectrum of THFDI (Fig. S26) exhibited  $m/z = 205.0587$   $[M+Na]^+$ , which has a theoretical value of 205.0589. In the FTIR spectrum of THFDI (Fig. S27), the peaks at  $2960\text{ cm}^{-1}$  and  $2930\text{ cm}^{-1}$  correspond to methylene stretching vibrations; the peak at  $2873\text{ cm}^{-1}$  represents saturated C-H antisymmetric stretching vibration; the peak at  $2261\text{ cm}^{-1}$  is characteristic of -NCO; the absorption peak at  $1776\text{ cm}^{-1}$  indicates the presence of a C=N functional group; the stretching vibration absorption peak of C=O functional group occurs at  $1720\text{ cm}^{-1}$ ; the in-plane bending peak of C-H functional group is observed at  $1452\text{ cm}^{-1}$ ; and finally, the peaks at  $1030\text{ cm}^{-1}$  and  $903\text{ cm}^{-1}$  represent antisymmetric and symmetric stretching vibrations of tetrahydrofuran C-O-C. The GCMS spectrum of THFDI is shown in Fig. S28.



**Fig. S24** Liquid chromatogram of THFDU.

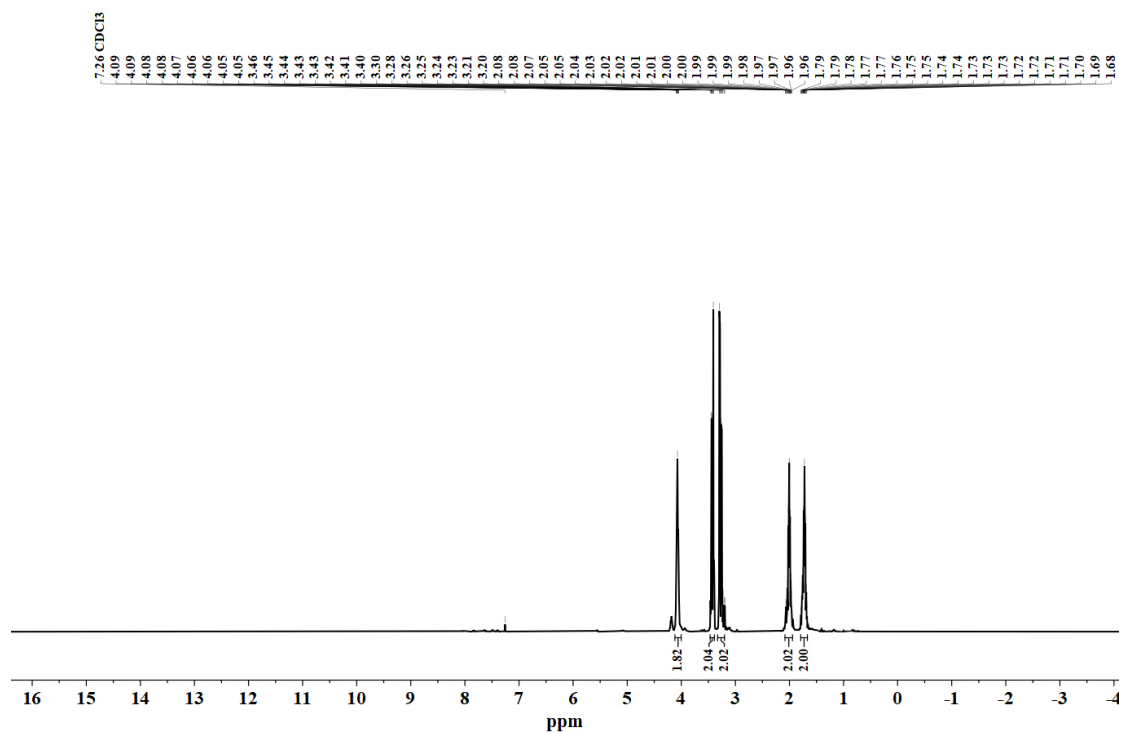


Fig. S25 <sup>1</sup>H NMR of THFDI.

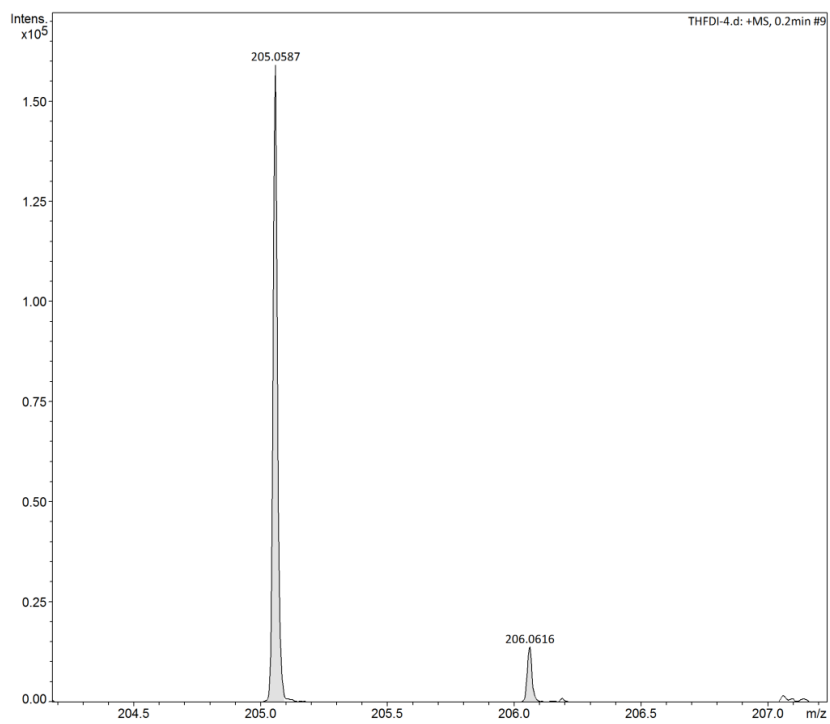


Fig. S26 HRMS of THFDI.

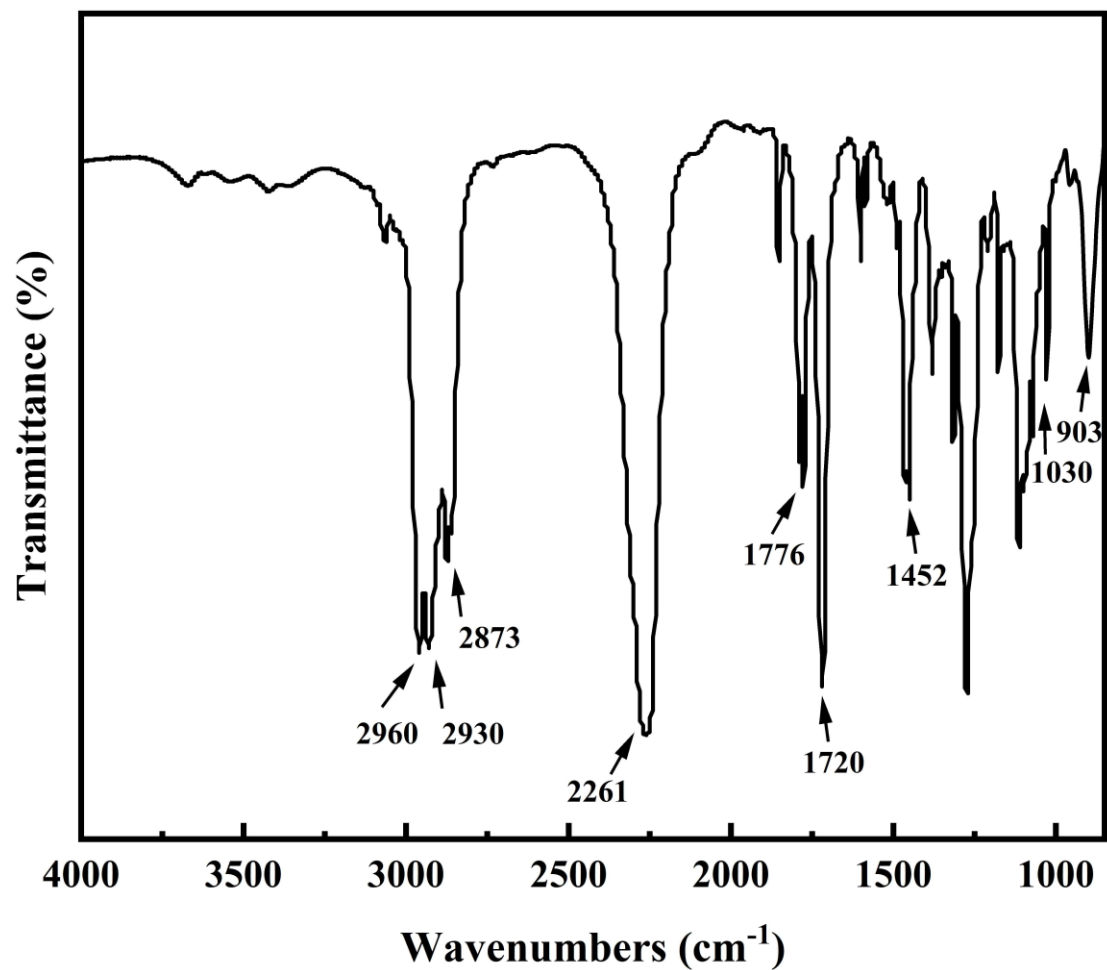


Fig. S27 FTIR of THFDI.

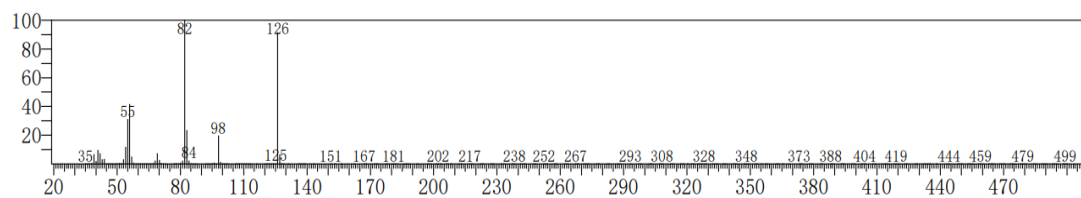
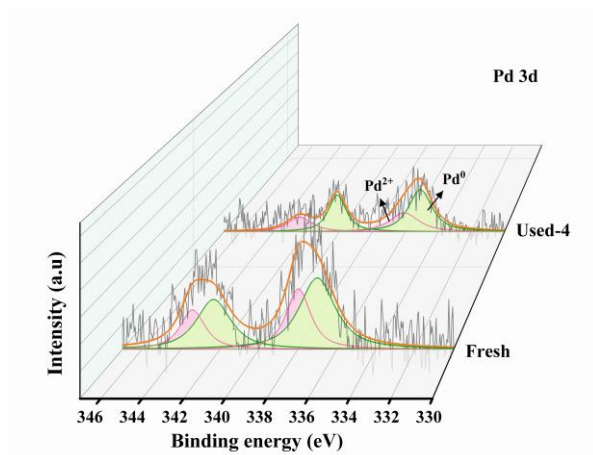
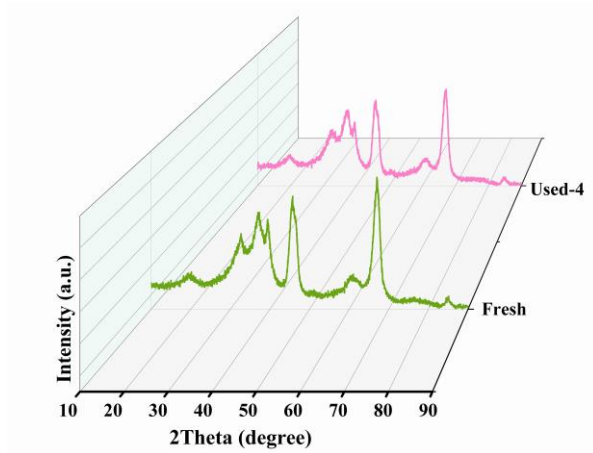


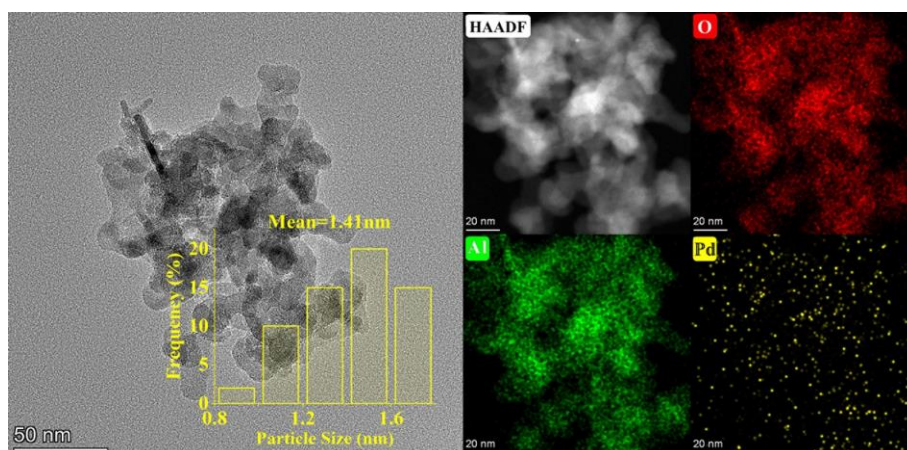
Fig. S28 GCMS of THFDI.



**Fig. S29** XPS spectra of the 0.5% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst before and after reaction.



**Fig. S30** XRD spectra of the 0.5% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst before and after reaction.



**Fig. S31** HAADF-STEM and EDS elemental mapping images of the 0.5% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst after reaction.