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Supplementary Information

Hydrogen-Bonding-Catalyzed the Degradation of Polyethylene Glycol to 1,4-Dioxane over OH-functionalized Ionic Liquid

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1. Experimental Procedures

1.1 Materials

Polyethylene glycol (PEG, average Mn: 200, 400, 600, 800 and1000) was obtained from Tianjin Damao Chemical Reagent Co., Ltd. 1,4-Dioxane (99.7% with molecular sieves, stabilized with BHT), n-dodecane (>99.0%), tetraethylene glycol (99%), methyl sulfoxide-d_6 (DMSO-d_6, 99.8 atom% of D) and chloroform-d (CDCl$_3$, 99.8 atom% of D) were purchased from Macklin's Reagent Co., Ltd. Diethyl ether (>99.5%) was obtained from Sinopharm Chemical Reagent Co., Ltd. All chemical regents were used as received.

Ionic liquids were obtained from the Center for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, and freeze-dried before use, their chemical structures are provided in Fig. S1.

1.2 Instrumentation

NMR spectra were recorded on Bruker Avance III 400 HD or 500 WB spectrometer equipped with 5 mm pulsed-field-gradient (PFG) probes. Chemical shifts are given in ppm relative to tetramethylsilane (TMS). To eliminate the effect of solvent, wilmad coaxial insert NMR tubes were used for ^{1}H NMR, ^{19}F NMR and ^{17}O NMR at 333.15 K. DMSO-d_6 was added in the inner tube, and the sample was added in the outer tube. The product was quantitatively analyzed by using gas chromatography GC (GC9720, Fuli instrument) with a FID detector and a nonpolar capillary column (DB-5, 30 m × 0.25 mm × 0.25 μm). The GC-MS analysis was performed using gas chromatography-mass spectrometry (GC-MS, SHIMADZU-QP2010) with a packed column DB-5 MS.

All density functional theory (DFT) calculations were performed with the Gaussian 09 package.[1] Geometry optimizations were carried out at the M062X-D3[2]/def2-TZVP[3] level at 393.15 K. The frequency calculations were carried out at the M062X-D3/def2-TZVP level using the optimized structures to confirm that the reactant and product have no imaginary frequencies and that the transition states (TSs) have only one imaginary frequency. The intrinsic reaction coordinate calculations were used to verify these TSs. Solvation corrections[4, 5] were calculated by a self-consistent reaction field using the SMD-GIL model.

1.3 Detailed experimental procedure for polyethylene glycol degradation

All reactions were performed in a sealed tube (15 mL of inner volume) equipped with a magnetic stirrer. Typically, 40 mg of PEG (average Mn: 400) and 0.4 mmol of [HO-EtMIm][OTf] were sequentially added into the reactor and sealed under nitrogen atmosphere. Then the reactor was moved to an oil bath with the desired temperature (e.g., 130 °C) for 12 h. After reaction, the reactor was cooled down in ice water. For GC analysis, 2 ml of diethyl ether and 0.017 g of n-dodecane (the internal standard) were added to the reaction mixture. After vigorous stirring and centrifugation, the upper layer liquid (product phase) and the IL phase were collected, respectively. The products were qualitatively and quantitatively analyzed by GC-MS and GC, respectively. The standard curve of the product is shown in Fig. S3. And the yield of product was calculated according to the following equation:

$$\text{Yield of product} = \text{Moles of the product obtained} / \text{Theoretic moles of the product} \times 100\%$$

1.4 Recycling tests

The reusability of [HO-EtMIm][OTf] was tested as follows:

After reaction, the reaction mixture was centrifuged and the IL phase was collected through simple phase separation. Subsequently, the collected [HO-EtMIm][OTf] was distilled under vacuum to remove the generated H_2O. Then, the [HO-EtMIm][OTf] was directly reused for the next run.
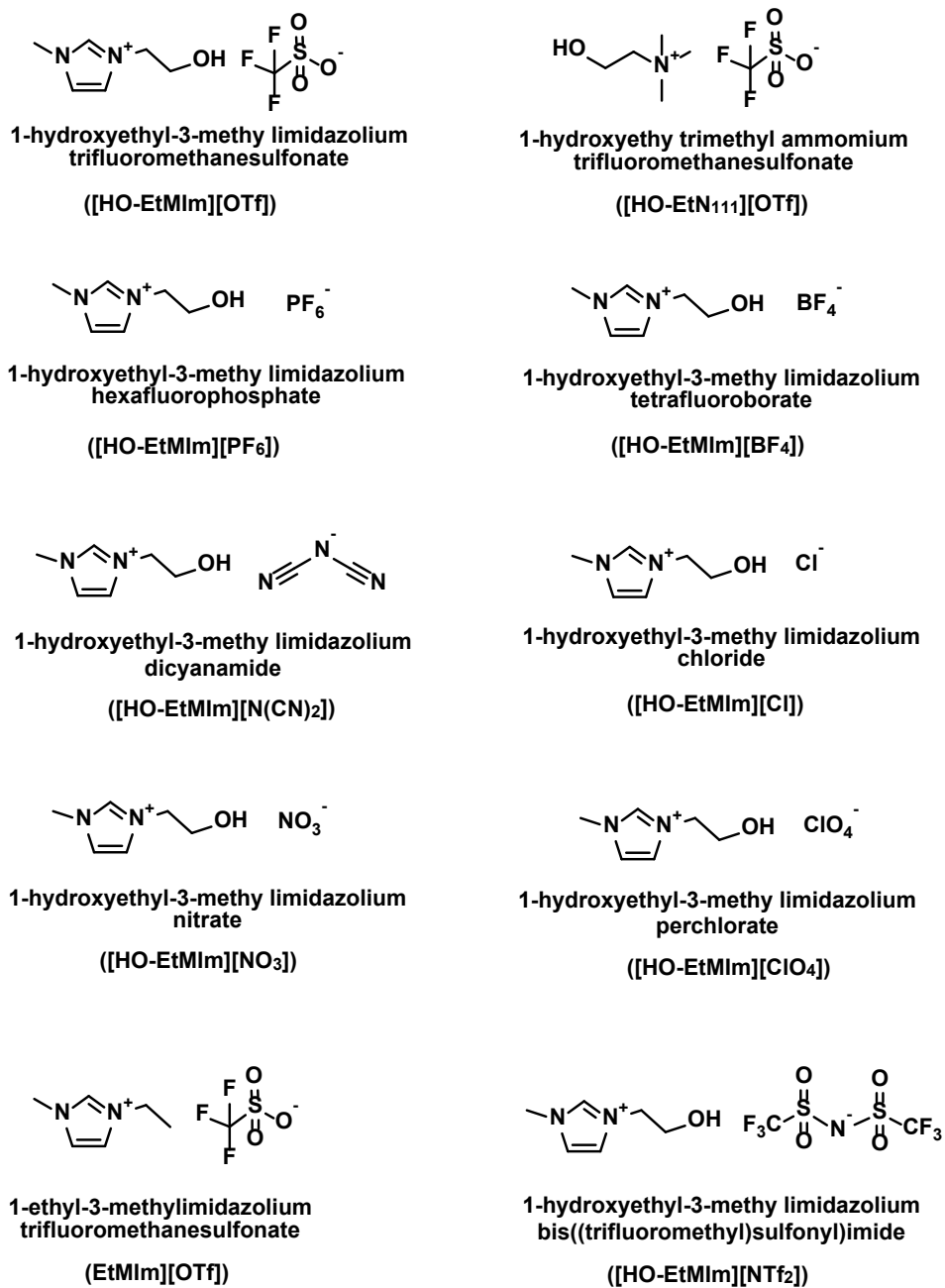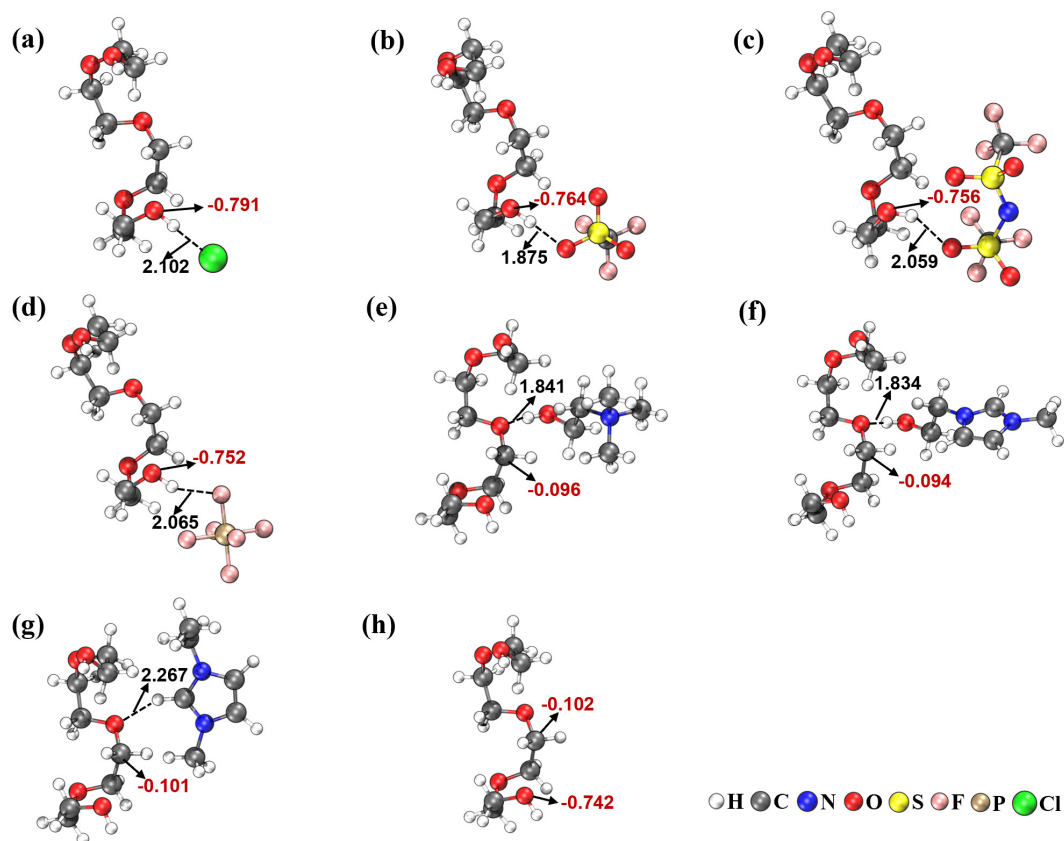
2. Additional data

1-hydroxyethyl-3-methy limidazolium trifluoromethanesulfonate

([HO-EtMIm][OTf])

1-hydroxyethy trimethyl ammomium trifluoromethanesulfonate

([HO-EtN$_{111}$][OTf])

1-hydroxyethyl-3-methy limidazolium hexafluorophosphate

([HO-EtMIm][PF$_6$])

1-hydroxyethyl-3-methy limidazolium tetrafluoroborate

([HO-EtMIm][BF$_4$])

1-hydroxyethyl-3-methy limidazolium dicyanamide

([HO-EtMIm][N(CN)$_2$])

1-hydroxyethyl-3-methy limidazolium chloride

([HO-EtMIm][Cl])

1-hydroxyethyl-3-methy limidazolium nitrate

([HO-EtMIm][NO$_3$])

1-hydroxyethyl-3-methy limidazolium perchlorate

([HO-EtMIm][ClO$_4$])

1-ethyl-3-methylimidazolium trifluoromethanesulfonate

(EtMIm][OTf])

1-hydroxyethyl-3-methy limidazolium bis((trifluoromethyl)sulfonyl)imide

([HO-EtMIm][NTf$_2$])

Fig. S1 The ILs used in this work.

Fig. S2 Possible structures of **M** interacted with (a) Cl⁻, (b) [OTf]⁻, (c) [NTf₂]⁻, (d) [PF₆]⁻, (e) [HO-EtMIm]⁺, (f) [HO-EtN₁₁₁]⁺, (g) [EtMIm]⁺ and (h) pure **M** optimized at M062X-D3/def2-TZVP level, on which the natural bond orbital (NBO) charges and hydrogen bond distances [red word: NBO charges, black word: atom distance (Å)] are marked.

Peak 1

Peak 2

+EI 扫描 (rt: 2.226 min) HO-130.D
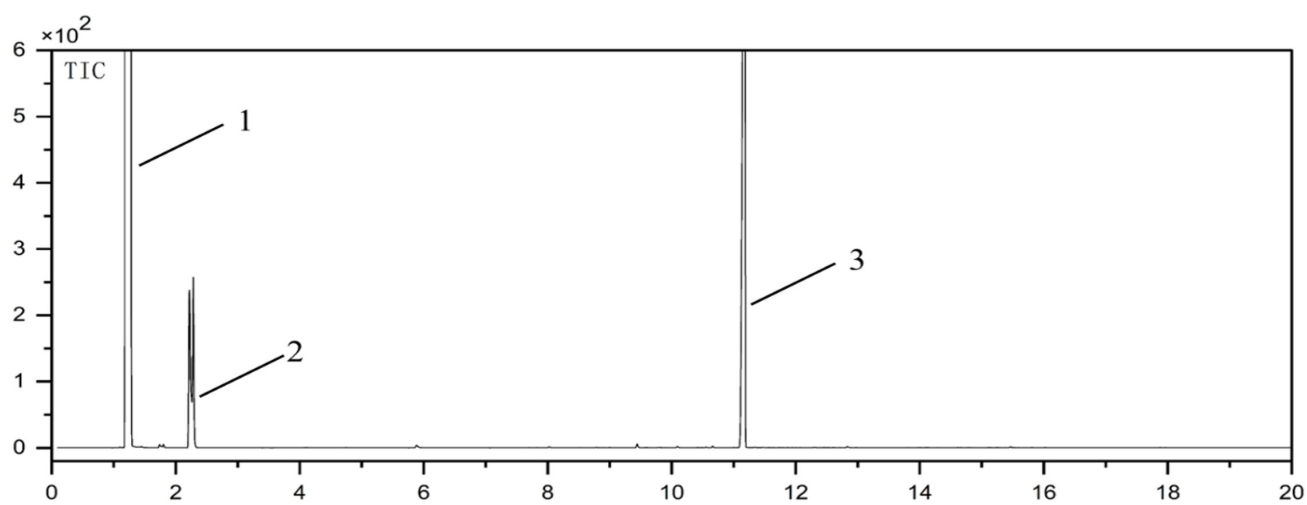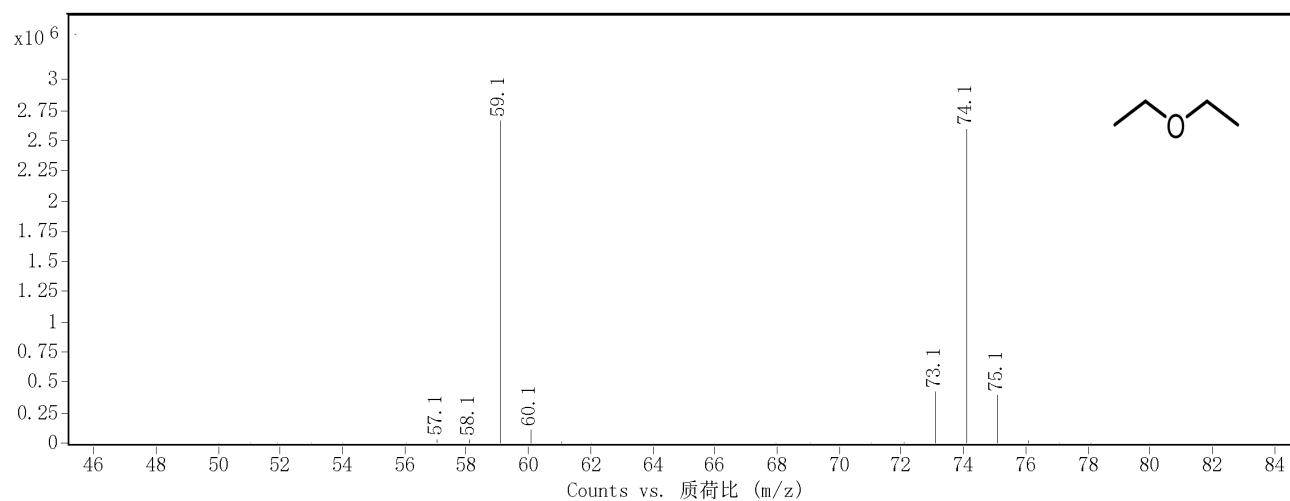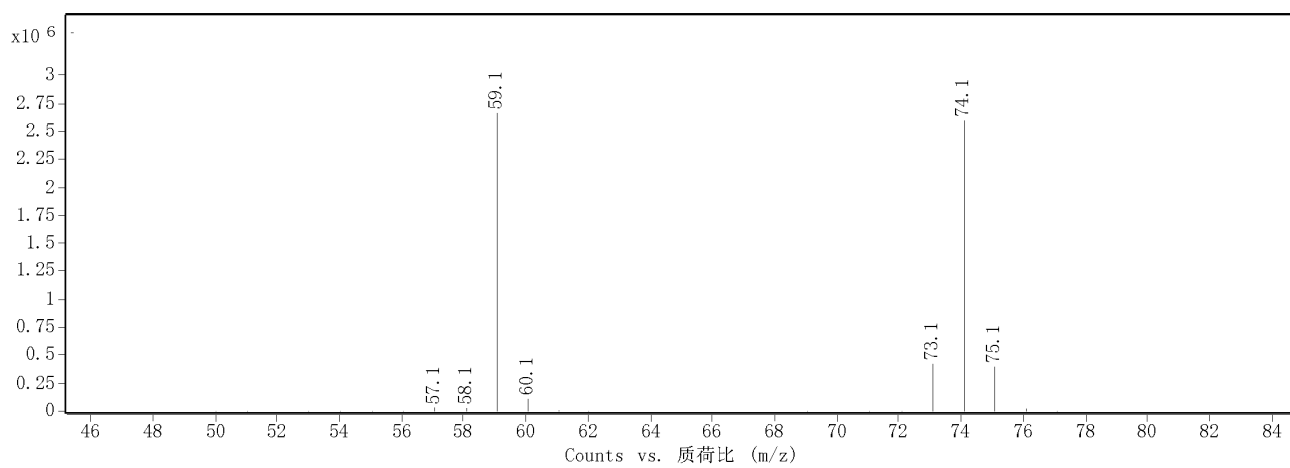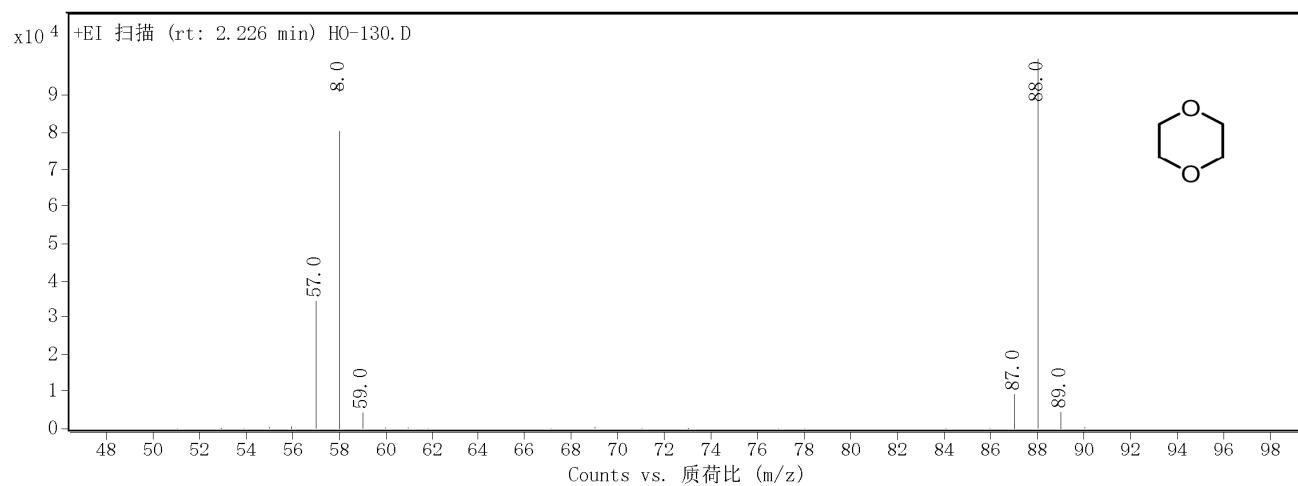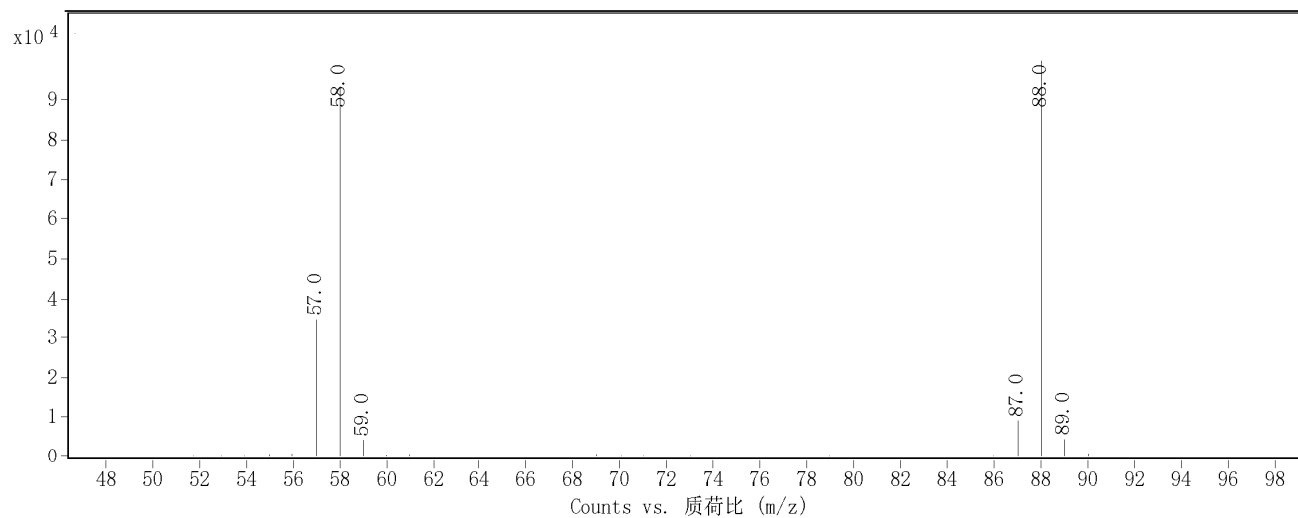
Peak 3
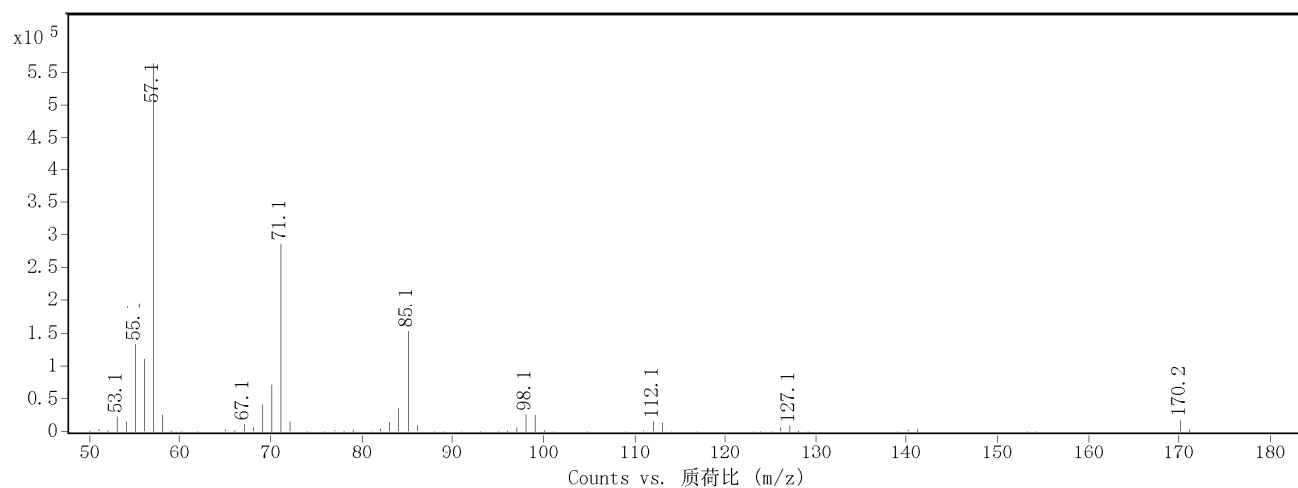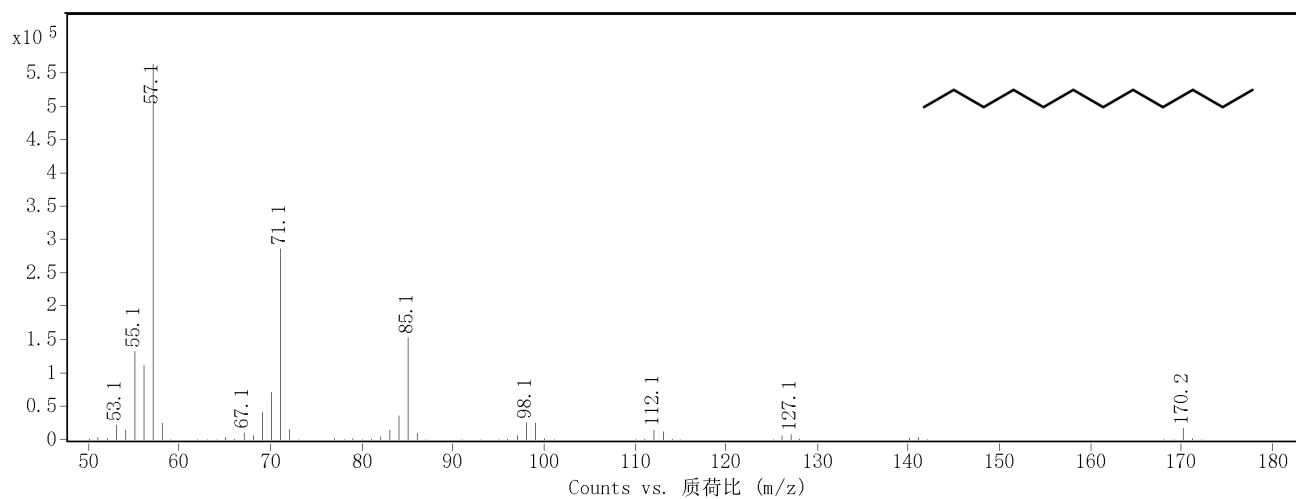
Fig. S3 GC-MS spectra of the product phase after reaction. Reaction conditions: PEG (average Mn: 400, 40 mg), [HO-EtMIm][OTf] (0.4 mmol), 130 °C, 12 h. (Note: Diethyl ether and n-dodecane were the solvent and internal standard, respectively.)
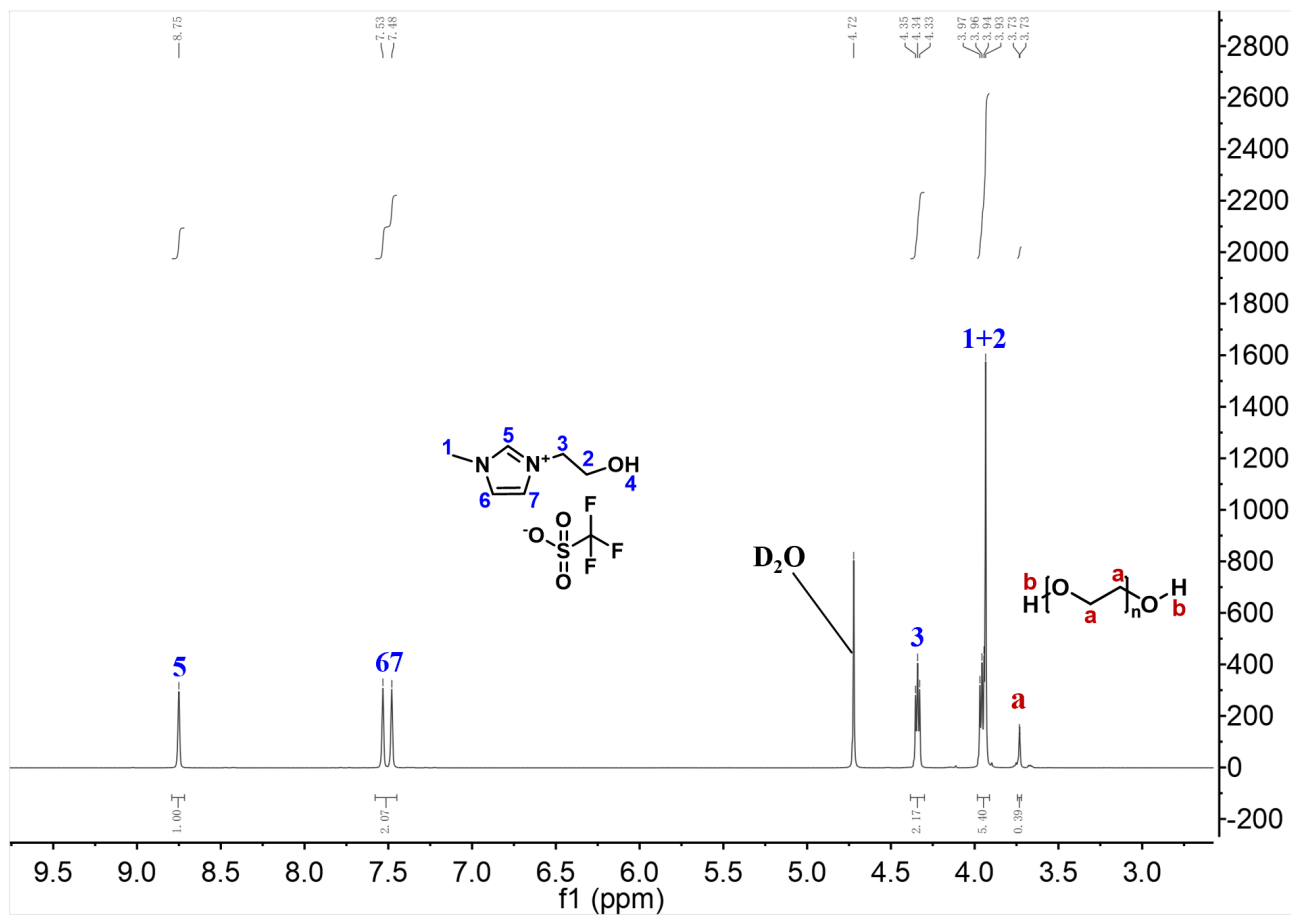
Fig. S4 ^{1}H NMR spectrum of the IL phase after reaction. Reaction conditions: PEG (average Mn: 400, 40 mg), [HO-EtMIm][OTf] (0.4 mmol), 130 °C, 12 h.

Note: From ^{1}H NMR spectrum of the IL phase, it was clear that only [HO-EtMIm][OTf] and very little amount of unreacted PEG were detected, and no 1,4-dioxane were present in the IL phase (Fig. S4). This means that there was no 1,4-dioxane residue in the IL, and IL is stable for the reaction.

The standard curve of the product

$y = 0.1725x - 0.0085$
$R^2 = 0.999$
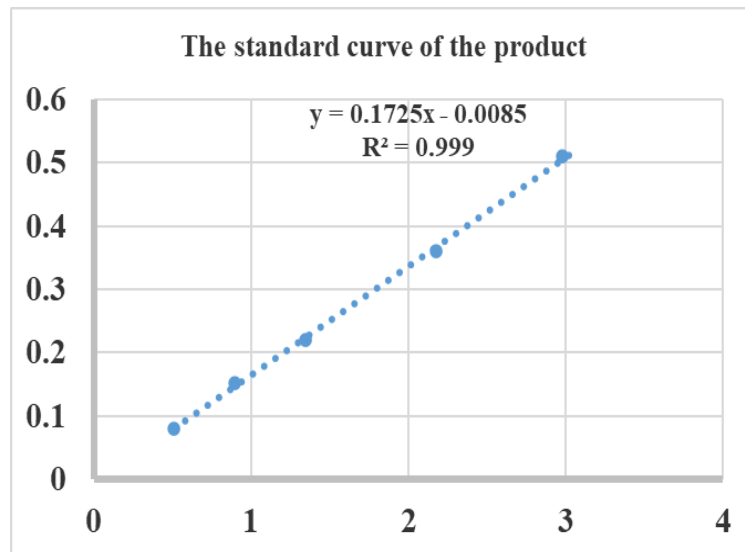
Fig. S5 The standard curve of the product.
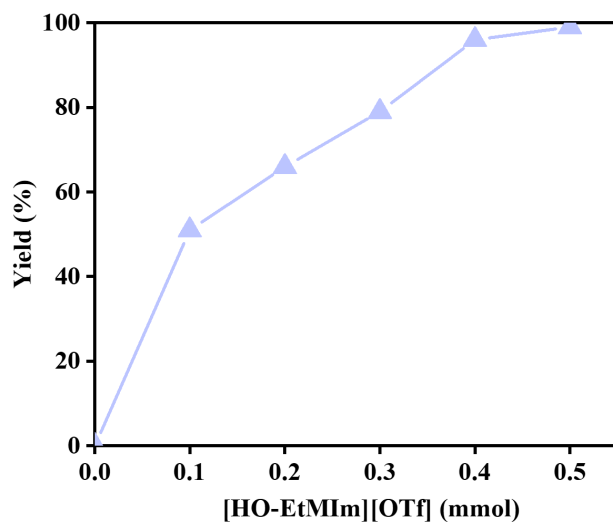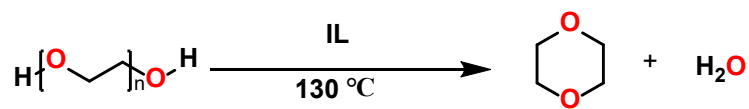
Fig. S6 Effect of the catalyst loadings. Reaction conditions: PEG (average Mn: 400, 40 mg), 12 h, 130 ℃. The product yields were determined by GC analysis with n-dodecane as an internal standard.

Note: As shown in Fig. S6, the yield of 1,4-dioxane increased with addition of [HO-EtMIm][OTf] and achieved 99% with 0.5 mmol of [HO-EtMIm][OTf].
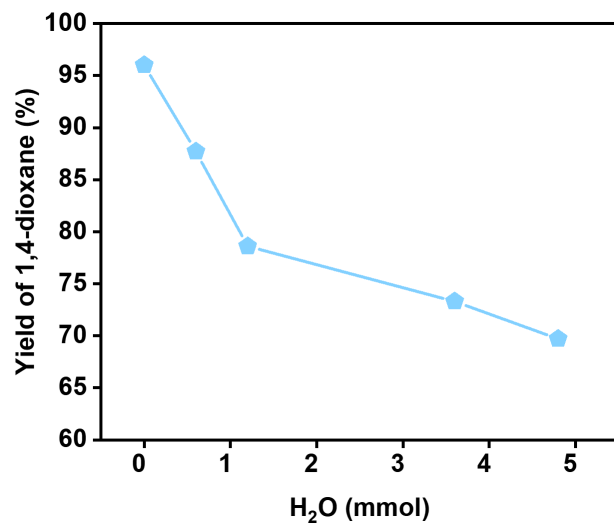
Fig. S7 Effect of water amounts on the degradation of PEG. Reaction conditions: PEG (average Mn: 400, 40 mg), [HO-EtMIm][OTf] (0.4 mmol), 130 °C, 12 h.

Before reaction
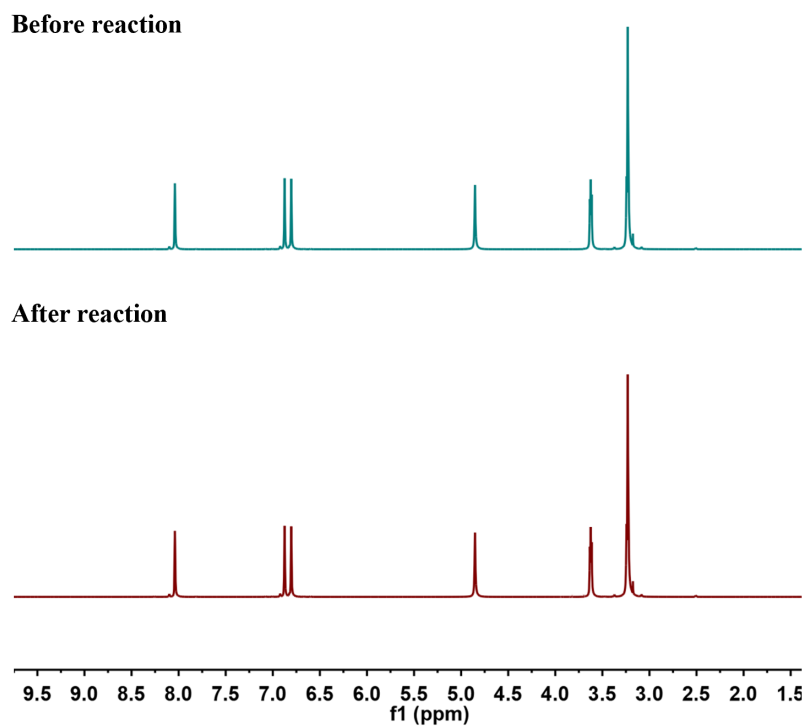
After reaction

Fig. S8 ^{1}H NMR spectra of [HO-EtMIm][OTf] before and after reaction.

Before reaction

After reaction

-40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120
f1 (ppm)
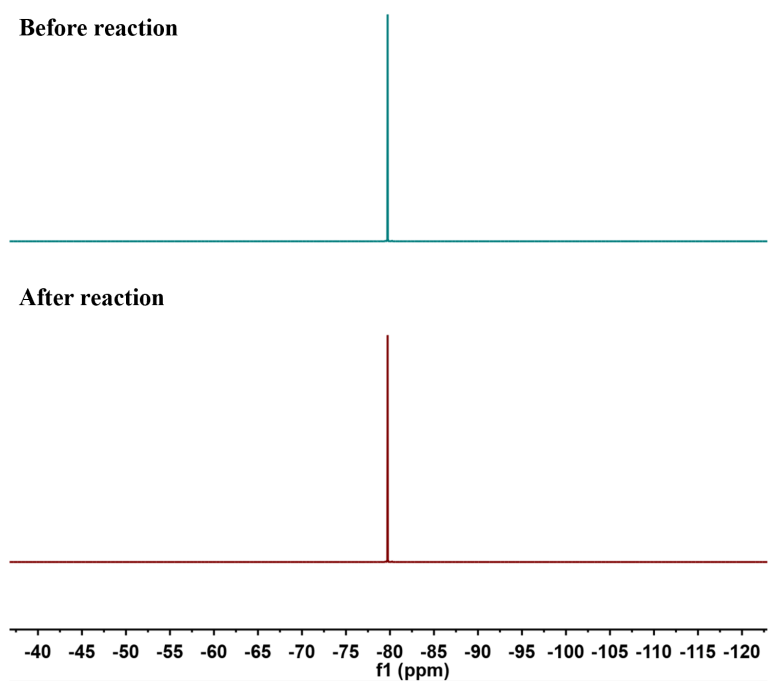
Fig. S9 ^{19}F NMR spectra of [HO-EtMIm][OTf] before and after reaction.
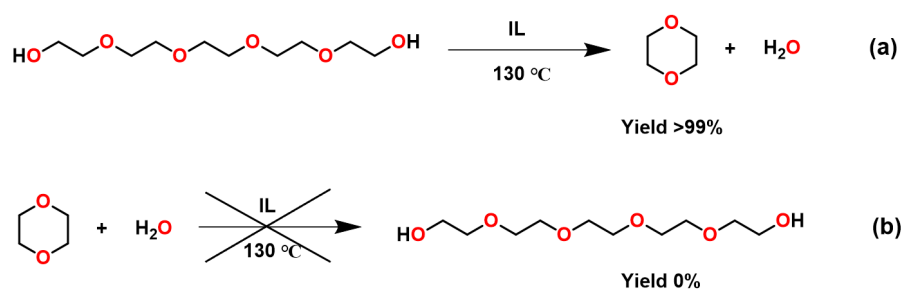
Fig. S10 Control experiment. Reaction conditions: [HOEtMIm][OTf] (0.4 mmol), 130 °C, 12 h for (a) tetraethylene glycol (**M**, 0.3 mmol), and (b) 1,4-dioxane (0.3 mmol), H_2O (0.15 mmol).

Note: As displayed in Fig. S10, the yield of 1,4-dioxane achieved >99% in the reaction **a**, while no **M** was detected in the reaction of 1,4-dioxane and H_2O, indicating that the degradation of PEG to 1,4-dioxane is irreversibly.
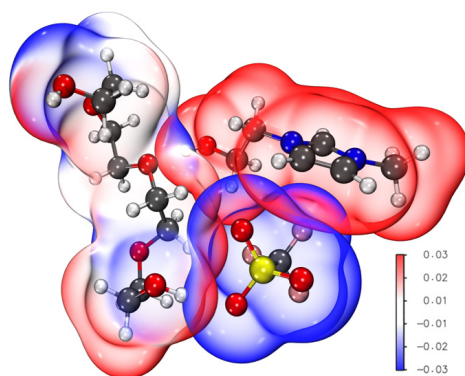
Fig. S11 Electrostatic potential (ESP) distribution of [HO-EtMIm][OTf] with **M**.

Note: As shown in Fig. S11, the electrostatic potential (ESP) distribution of **M** with [HO-EtMIm][OTf] was performed. Obviously, at the areas where the hydrogen bonds (HBs) formed, the positive surface potentials (red areas) of -OH in **M** and [HO-EtMIm]$^+$ overlap with the negative surface potentials (blue areas) of O in [OTf]$^-$ and ether O in **M**, respectively; indicating the electrostatic attraction of HBs formed between [HO-EtMIm][OTf] and **M**.[6-8]
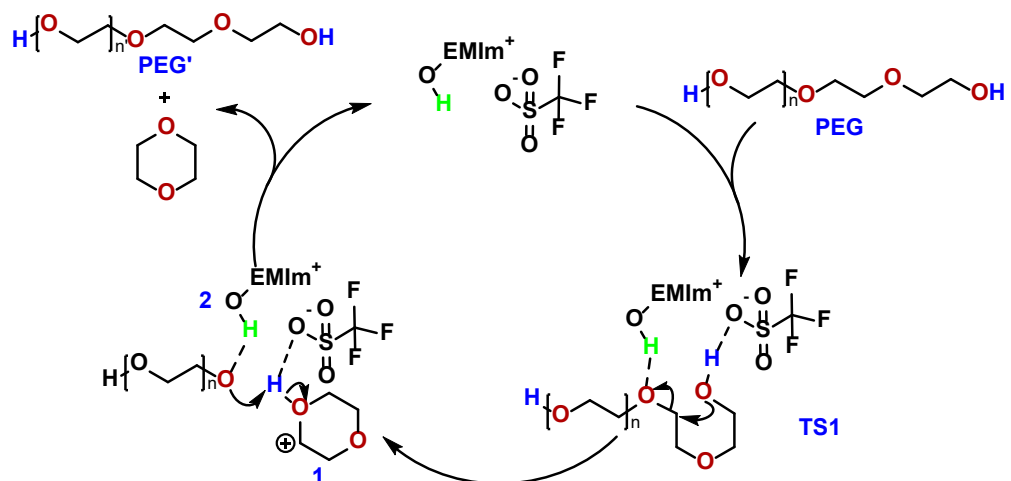
Fig. S12 Proposed reaction pathway.

Table S1 Comparison of various catalysts for the degradation of PEG[9-15].
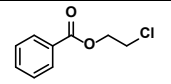
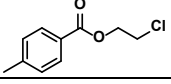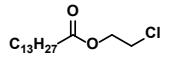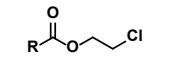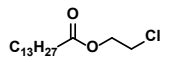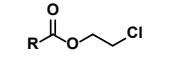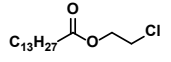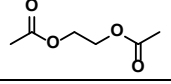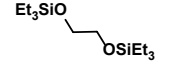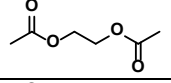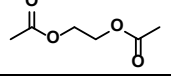| Catalyst	Substrate 1	Substrate 2	Reaction conditions	Product	Yield/%	Ref.
ammonium polyphosphate	PEG $Mn \approx 1000$ & 1500	/	200-400 °C	1,4-dioxane	/	[9]
$FeCl_2 \cdot 4H_2O$	PEG $Mn \approx 100000$	[benzoyl chloride]; [p-toluoyl chloride]	100 °C, 24 h	[2-chloroethyl benzoate]; [2-chloroethyl p-toluate]	89; 91	[10]
$FeCl_2 \cdot 4H_2O$	PEG $Mn \approx 300$	[$C_{13}H_{27}COCl$]	100 °C, 24 h	[$C_{13}H_{27}CO$-O-chloroethyl ester]	78	[10]
$FeCl_2 \cdot 4H_2O$	PEG $Mn \approx 300$ / PEG $Mn \approx 1000$	[$RCOCl$]; [$C_{13}H_{27}COCl$]	100 °C, 24 h	[RCO-O-chloroethyl ester]; [$C_{13}H_{27}CO$-O-chloroethyl ester]	75-78; 69	[11]
$ZnCl_2$	PEG $Mn \approx 300$ / PEG $Mn \approx 1000$	[$RCOCl$]; [$C_{13}H_{27}COCl$]	130 °C, 24 h	[RCO-O-chloroethyl ester]; [$C_{13}H_{27}CO$-O-chloroethyl ester]	91-94; 91	[12]
$Zn(OTf)_2$	PEG $Mn \approx 300$	Ac_2O	150 °C, 24 h	[ethylene glycol diacetate]	19	[12]
$B(C_6F_5)_3$	PEG	Et_3SiH	RT, 3h	[Et_3SiO-CH$_2$CH$_2$-$OSiEt_3$]; C_2H_6	41; 58	[13]
H-mont	PEG $Mn \approx 350$ / PEG $Mn \approx 8000$	[Ph-CO-O-CO-Ph, benzoic anhydride]	100 °C, 12 h; 100 °C, 24 h	Glycol dibenzoate	99; 86	[14]
H-mont	PEG $Mn \approx 350$	Ac_2O/AcOH	160 °C, 48 h	[ethylene glycol diacetate]	92	[14]
H^+-mont	PEG $Mn \approx 400$	AcOH	160 °C, 24 h	[ethylene glycol diacetate]	85	[15]

Table S2 The Kamlet-Taft parameters (α, β) of four typical ionic liquids[16].

IL	Yield of 1,4-dioxane	α	β	α-β
[HO-EtMIm][OTf]	96%	0.797066005	0.875947287	-0.078881281
[HO-EtN$_{111}$][OTf]	19%	1.121082285	0.411879099	0.709203186
[HO-EtMIm][Cl]	0%	0.797066005	0.84000972	-0.042943715
[HO-EtMIm][ClO$_4$]	0%	0.805913554	0.798476096	0.007437458

Note: To investigate the correlation between the catalytic activity of the ionic liquids and their Kamlet-Taft parameters (α, β), the Kamlet-Taft parameters (α, β) of four typical ionic liquids featuring good hydrogen bond donor and acceptor (including [HO-EtMIm][OTf], [HO-EtMIm][Cl], [HO-EtMIm][ClO$_4$] and [HO-EtN$_{111}$][OTf]) were evaluated (Table S2). The results indicated that there is no correlation between the catalytic activity of the ionic liquids and their Kamlet-Taft parameters (α, β).

NMR spectra:
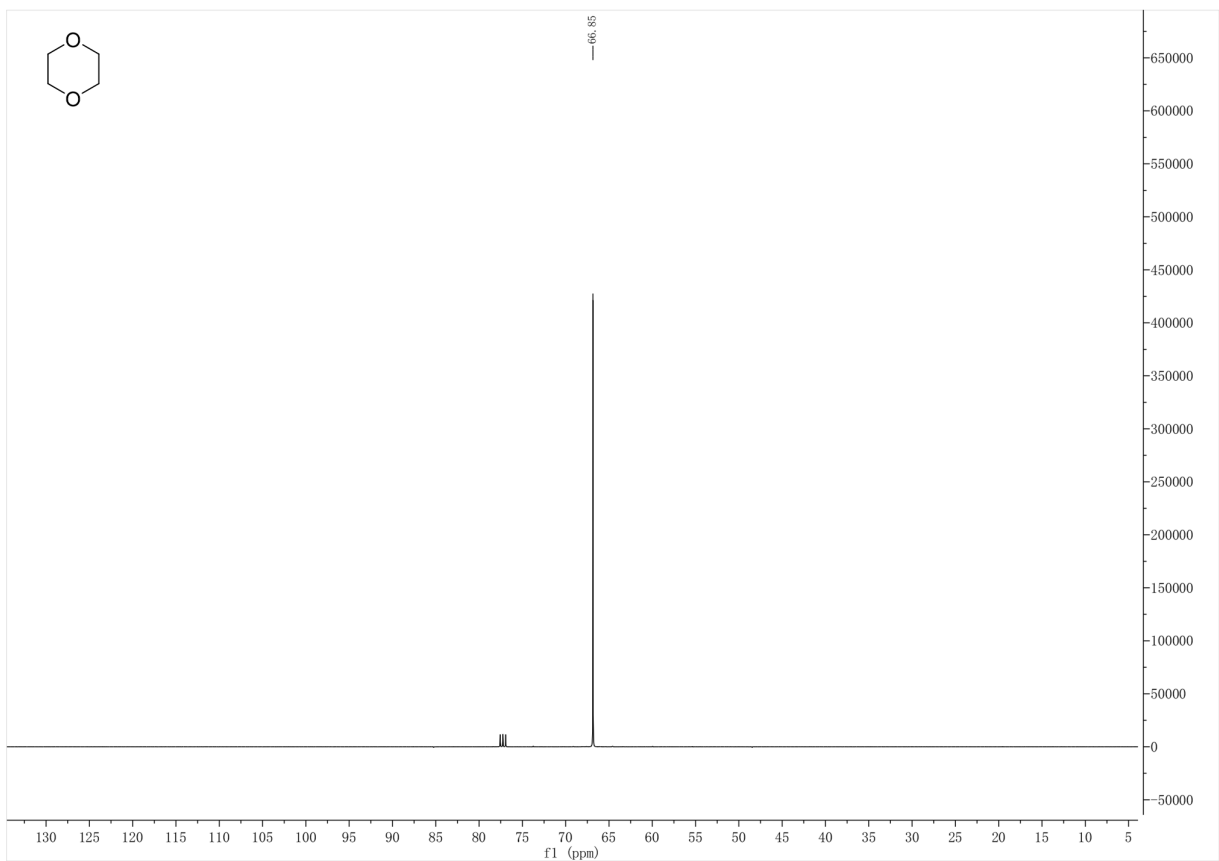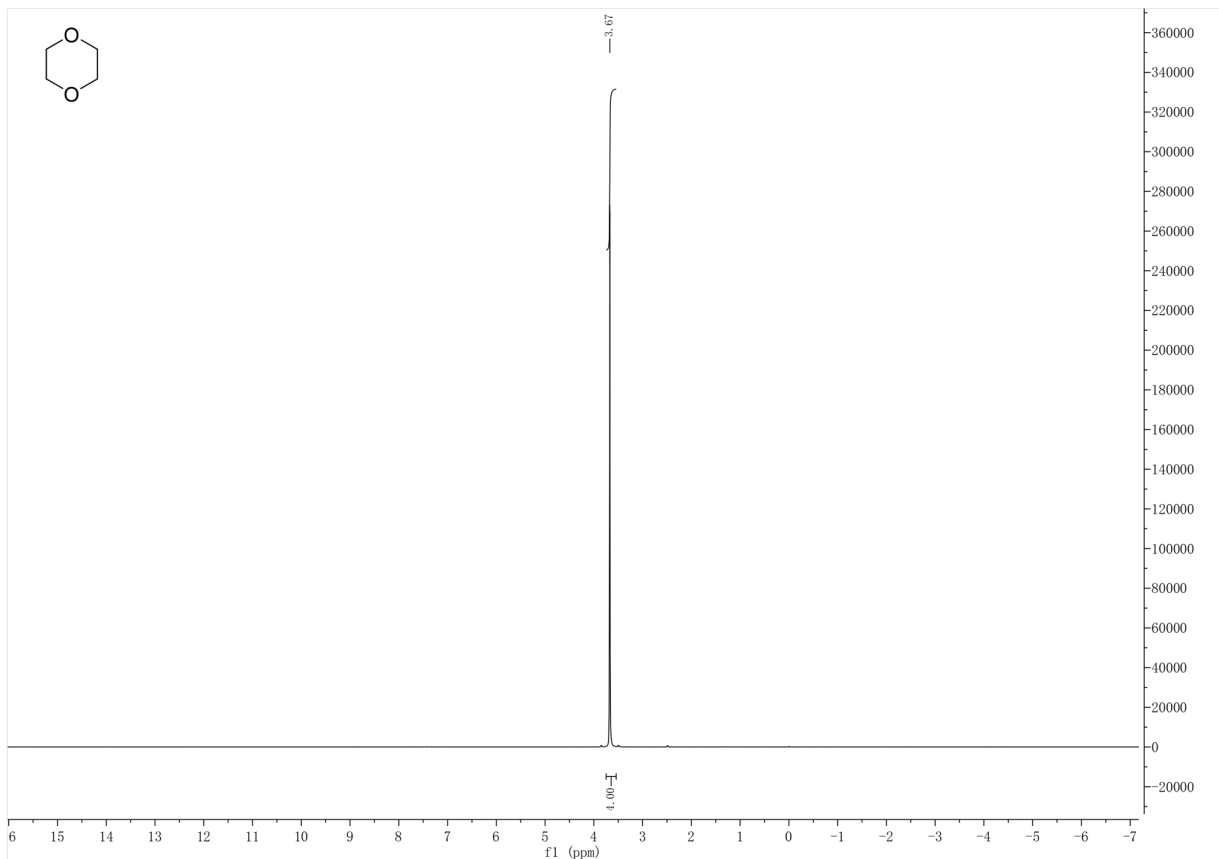
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