Supporting Information

A strategy of H-bond confinement catalysis for efficient degradation of polyethylene glycol into glycol diester over OH-functionalized ionic liquid

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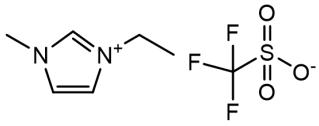
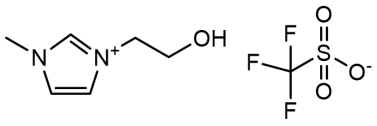
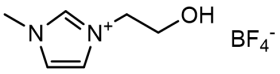


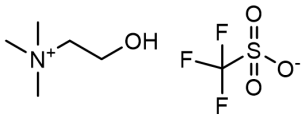
[EtMIm][OTf]



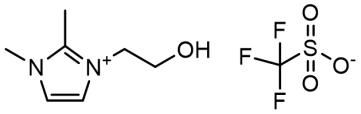
[HO-EtMIm][OTf]



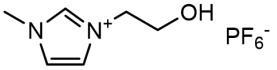
[HO-EtMIm][BF_4]



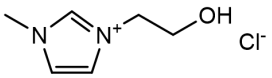
[HO-EtN_{111}][OTf]



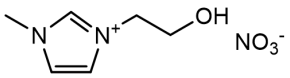
[HO-EtMMIm][OTf]



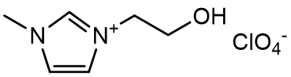
[HO-EtMIm][PF_6]



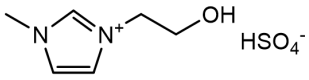
[HO-EtMIm][Cl]



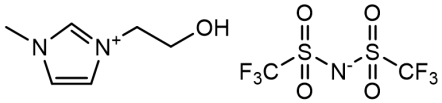
[HO-EtMIm][NO_3]



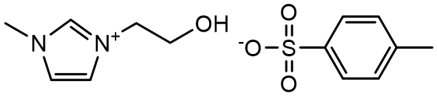
[HO-EtMIm][ClO_4]



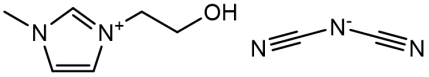
[HO-EtMIm][HSO_4]



[HO-EtMIm][NTf_2]



[HO-EtMIm][OTs]



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

Fig. S1 The chemical structures of ionic liquids used in this work

Table S1 Comparison of different catalysts for depolymerization of PEG.

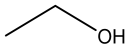
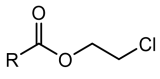
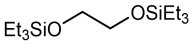
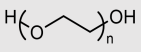
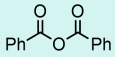
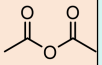
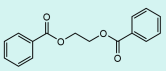
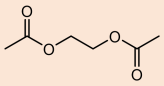
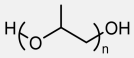
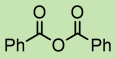
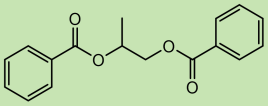
Entry	Substrate	Catalyst	Condition	Product	Yield (%)
1	PEG	Modified Cu slag CS-710	O_3, pH =9, 25℃	CO_2, HCOOH, CH_3COOH	97.4[7]
2	PEG, polyurethane	ethanolamine, zinc stearate	160-210℃	$R(NH\text{-}CO\text{-}O\text{-}R'\text{-}OH)_2$	15-25[8]
3	PEG (Mn~200)	CeO_2/Ni	160℃, 4.0MPa H_2		85[9]
4	PEG(Mn~300), 	$FeCl_2 \cdot nH_2O$	100℃, 24h		75-78[10]
5	PEG, Et_3SiH	$B(C_6F_5)_3$	RT, 3h		41[11]

Table S2 Comparative green chemistry metrics of [HO-EtMIm][OTf] *vs* traditional catalyst H_2SO_4.

Index	**value**	**Reference standard**	**Compared with traditional catalysts (H_2SO_4)**	**References**
E-factor	0.18	Sheldon Index	4.7 (a decrease of 97%)	[34]
Atomic economy	89%	Trost calculation method	68%	[34], [35]
Process mass Intensity (PMI)	4.3	ACS GCI Pharma Roundtable	18.9 (a decrease of 77%)	[34]
Carbon footprint	31 g CO_2-eq/mol	IPCC 2021 Methodology	127 g CO_2-eq/mol	[37]
Water ecological toxicity (EC50)	Class 1 (>100 mg/L)	OECD 202 (Algae)	Class 3	[36]
Energy intensity	2.4 kWh/mol	Life Cycle Inventory Analysis	8.7 kWh/mol	[37]

Table S3 Substrate Scope.

Substrate 1’	Average Mn	Anhydride		Product		Yield (%)	
PEG 	200			 2	 4	88	67
	400					79	63
	600					95	75
	800					90	70
	1000					85	65
	1500					83	71
	2000					91	68
	4000					83	63
PPG 	200			 3		66	
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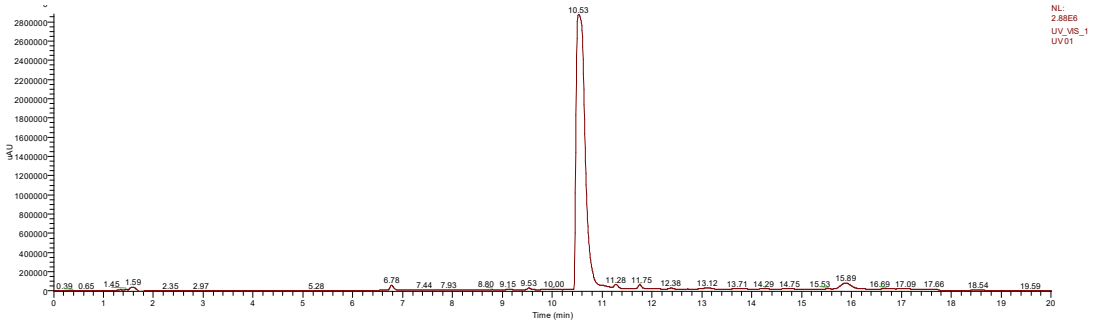

PEAK LIST

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RT: 0.00 - 20.01

Number of detected peaks: 6

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
1.61	1.45	1.73	336639.805	0.87	39757.163	1.26
6.78	6.66	6.89	379402.466	0.98	59307.300	1.88
10.53	10.40	10.89	36155426.084	92.92	2872951.252	91.06
11.28	11.13	11.40	450997.419	1.16	53533.585	1.70
11.75	11.66	11.87	395132.229	1.02	56798.632	1.80
15.89	15.65	16.14	1193789.650	3.07	72731.290	2.31

Fig. S2 The high performance liquid chromatography spectra of the product phase after reaction.

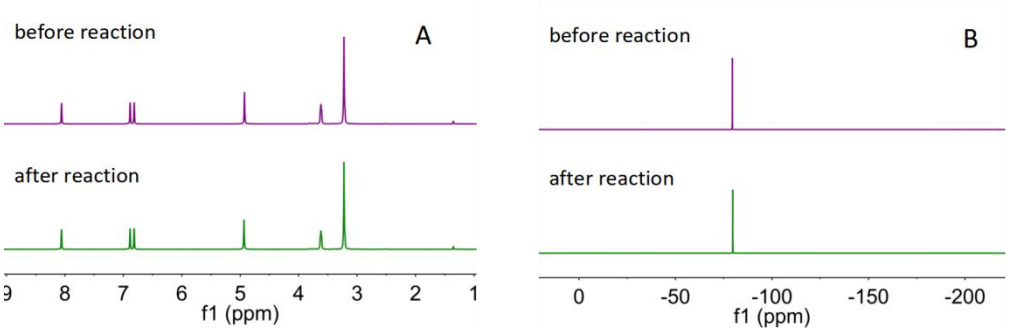

Fig. S3 (A, B) ^{1}H and ^{19}F NMR spectra of [HO-EtMIm][OTf] before and after reaction.

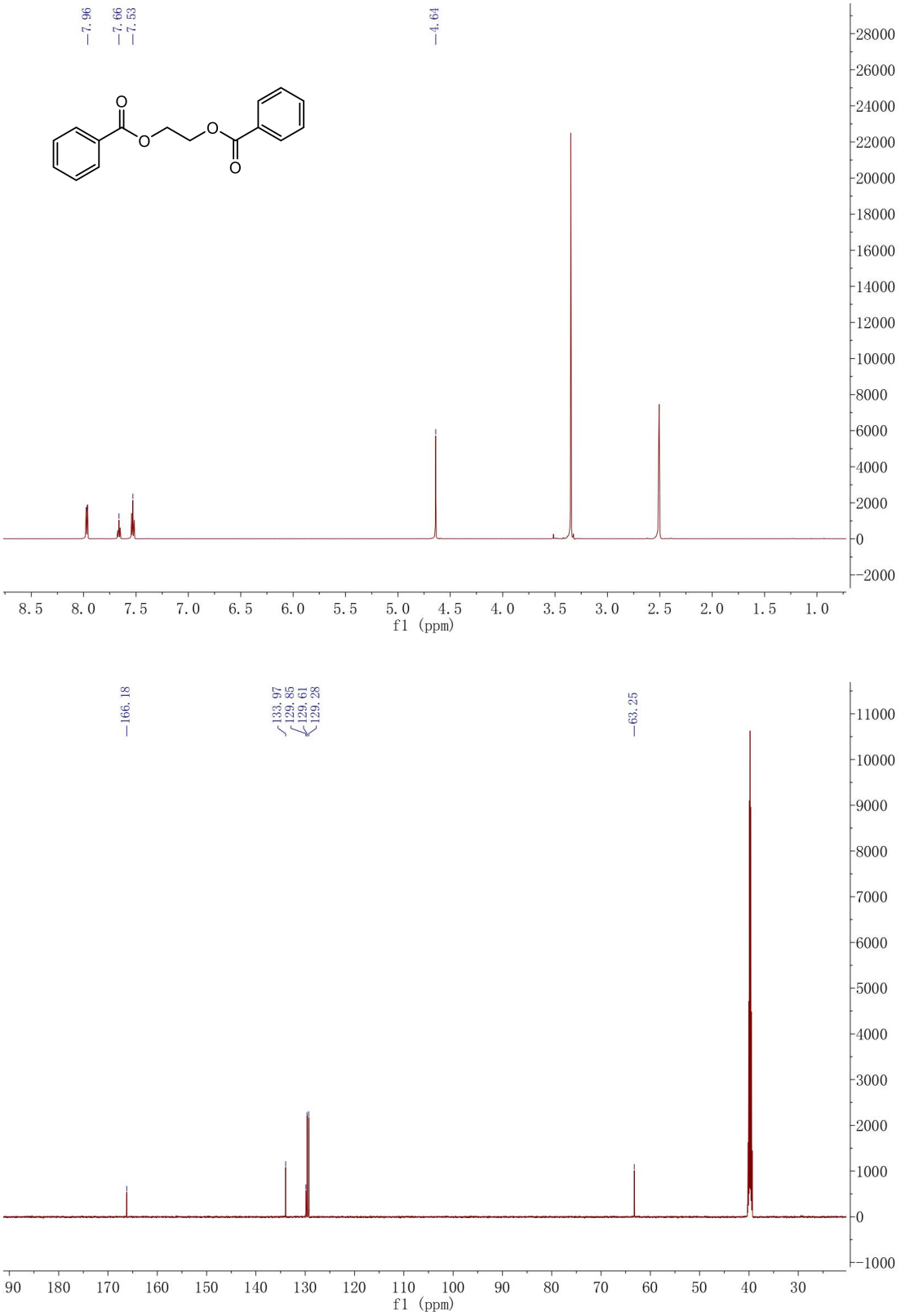

Fig. S4 (A, B) ^{1}H and ^{13}C NMR spectra of product 2.

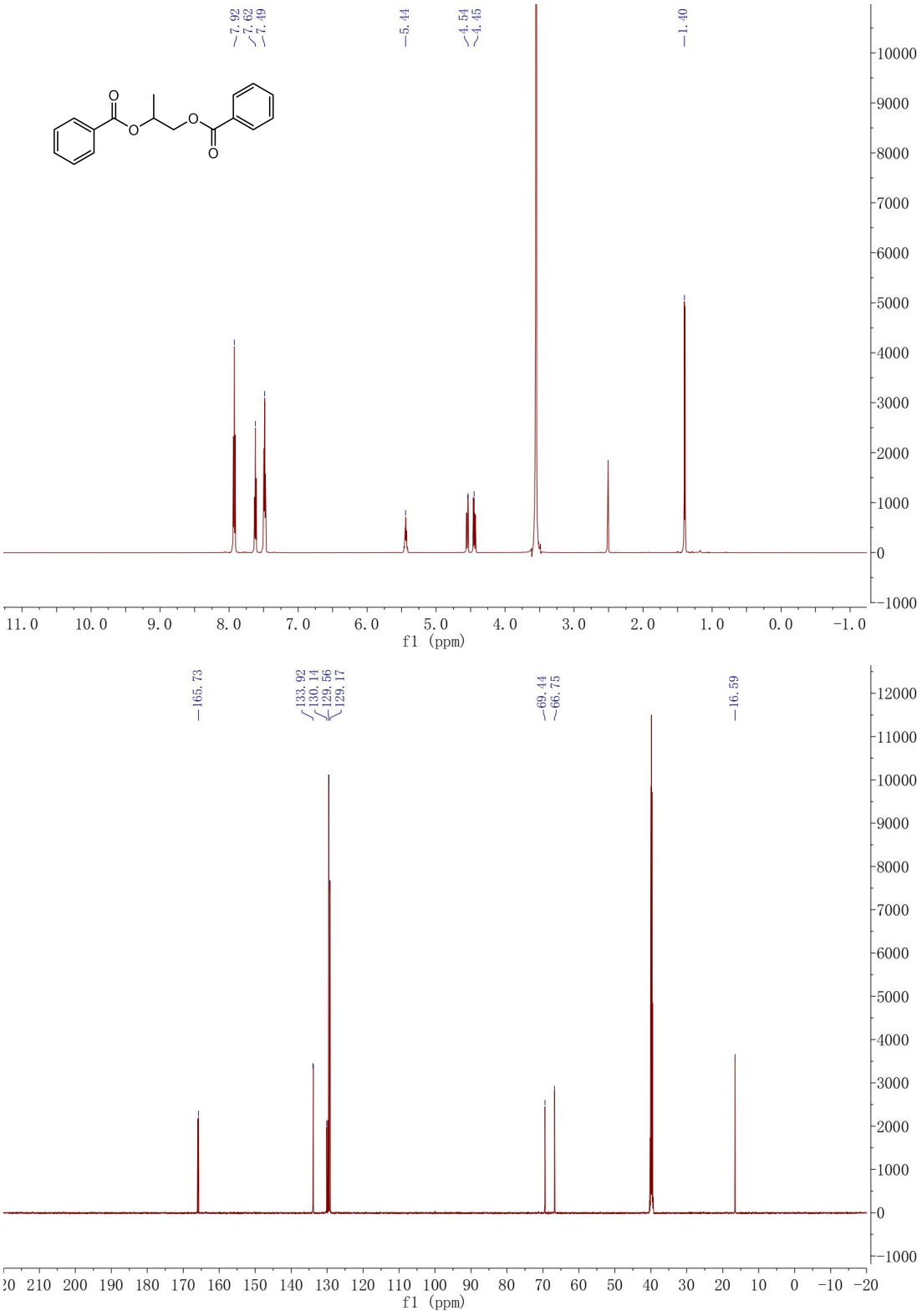

Fig. S5 (A, B) ^{1}H and ^{13}C NMR spectra of product 3.

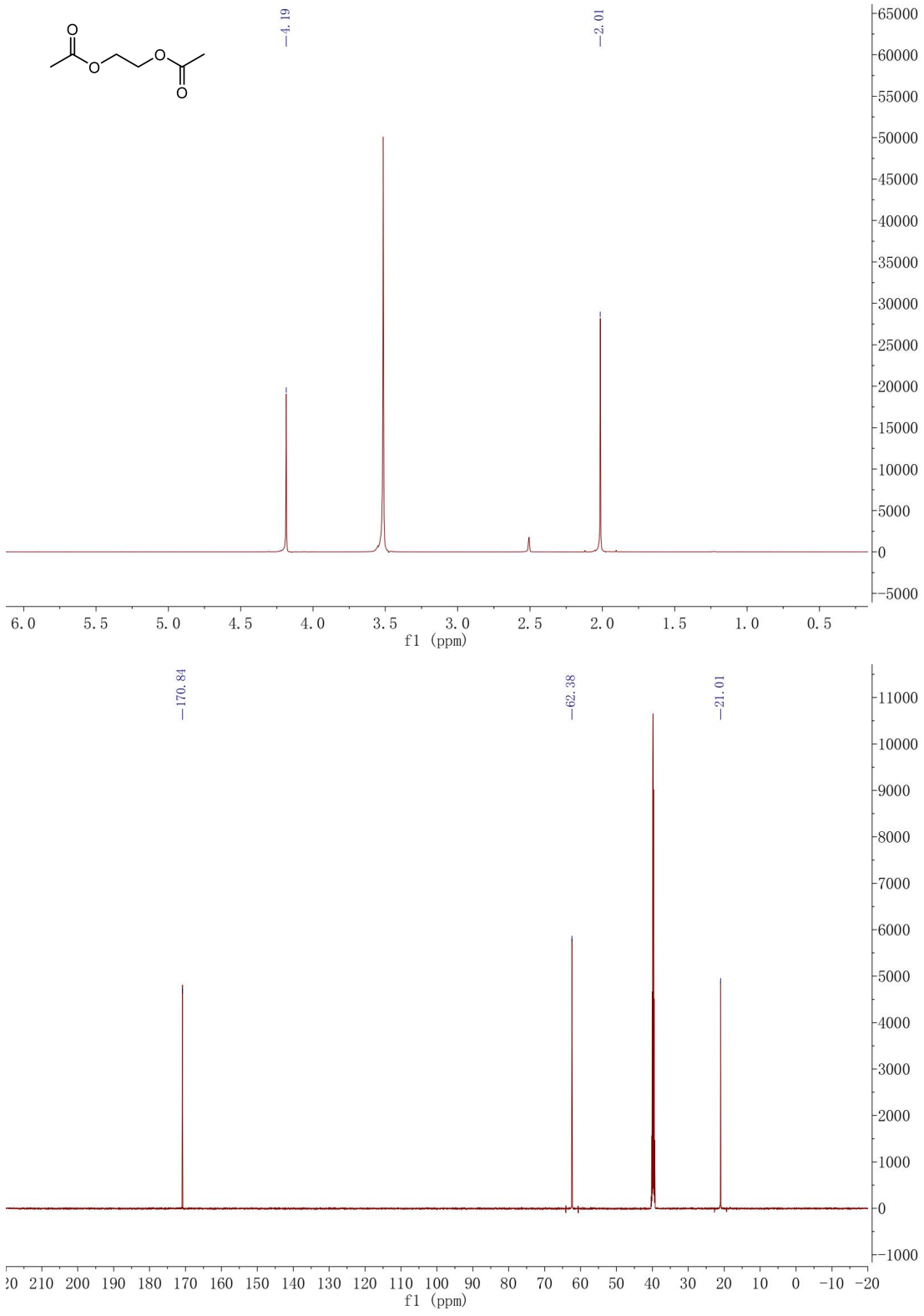

Fig. S6 (A, B) ^{1}H and ^{13}C NMR spectra of product 4.

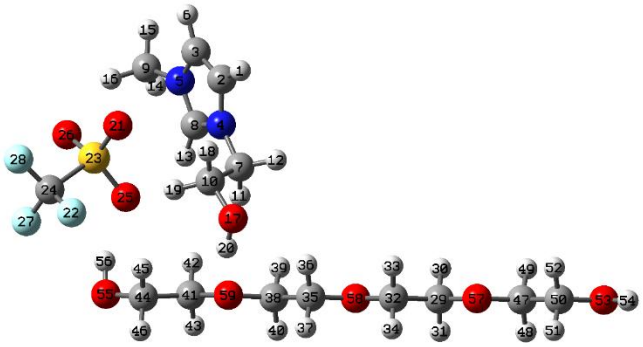

Fig. S7 The structure of tetraethylene glycol with [HO-EtMIm][OTf].

Table S4 The NPA charge values of each atom in tetraethylene glycol.

Atom type	Atom number	NPA charge	Atom type	Atom number	NPA charge
H	1	0.23053	H	30	0.15454
C	2	-0.01325	H	31	0.15734
C	3	-0.00769	C	32	-0.01995
N	4	-0.33272	H	33	0.15733
N	5	-0.33276	H	34	0.15809
H	6	0.22847	C	35	-0.03247
C	7	-0.19072	H	36	0.17173
C	8	0.28999	H	37	0.16159
C	9	-0.35878	C	38	-0.03811
C	10	-0.01688	H	39	0.14975
H	11	0.20421	H	40	0.16818
H	12	0.20384	C	41	-0.02079
H	13	0.2611	H	42	0.15521
H	14	0.20585	H	43	0.16359
H	15	0.20106	C	44	-0.01912
H	16	0.25959	H	45	0.15632
O	17	-0.75551	H	46	0.16657
H	18	0.1697	C	47	-0.02639
H	19	0.19203	H	48	0.15721
H	20	0.48182	H	49	0.15606
O	21	-0.97716	C	50	-0.01358
F	22	-0.35599	H	51	0.15185
S	23	2.20754	H	52	0.15097
C	24	0.88362	O	53	-0.7304
O	25	-1.03575	H	54	0.45153
O	26	-0.96064	O	55	-0.7445
F	27	-0.34436	H	56	0.4805
F	28	-0.3454	O	57	-0.58818
C	29	-0.01993	O	58	-0.5903
			O	59	-0.6164

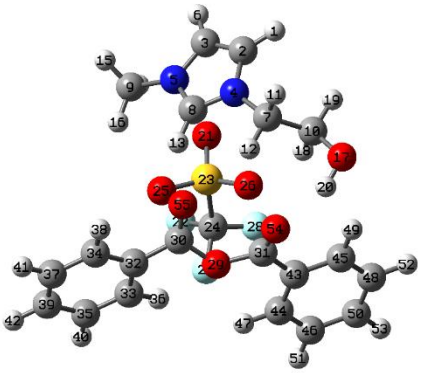

Fig. S8 The structure of benzoic anhydride with [HO-EtMIm][OTf].

Table S5 The NPA charge values of each atom in benzoic anhydride.

Atom type	Atom number	NPA charge	Atom type	Atom number	NPA charge
H	1	0.22741	F	28	-0.34766
C	2	-0.02791	O	29	-0.57587
C	3	-0.01163	C	30	0.86095
N	4	-0.33876	C	31	0.86864
N	5	-0.32929	C	32	-0.15237
H	6	0.22736	C	33	-0.14103
C	7	-0.20074	C	34	-0.15476
C	8	0.29351	C	35	-0.19805
C	9	-0.36246	H	36	0.22564
C	10	-0.02638	C	37	-0.20342
H	11	0.19628	H	38	0.21629
H	12	0.24503	C	39	-0.17191
H	13	0.27366	H	40	0.20546
H	14	0.23569	H	41	0.20384
H	15	0.19099	H	42	0.20238
H	16	0.24483	C	43	-0.15763
O	17	-0.74963	C	44	-0.14966
H	18	0.20335	C	45	-0.14279
H	19	0.15918	C	46	-0.19892
H	20	0.48212	H	47	0.21795
O	21	-0.9706	C	48	-0.19731
F	22	-0.35036	H	49	0.21887
S	23	2.21886	C	50	-0.16697
C	24	0.87951	H	51	0.20485
O	25	-0.9966	H	52	0.20586
O	26	-0.99421	H	53	0.20265
F	27	-0.36883	O	54	-0.6149
			O	55	-0.6105

Life Cycle Assessment (LCA) Report: Synthesis of Ethylene Glycol Dibenzoate Based on Recyclable Ionic Liquids

Product System: Ethylene glycol dibenzoate was synthesized by reacting tetraethylene glycol with benzoic anhydride under the catalysis of recyclable ionic liquid [HO-EtMIm][OTf].

1. Objectives and Scope Definition

1.1 Research Objectives

This life cycle assessment aims to evaluate the potential environmental impact of the chemical process of catalytic synthesis of ethylene glycol dibenzoate using recyclable [HO-EtMIm][OTf] at the laboratory scale. The core objective is: to quantify the fundamental improvement in overall environmental performance resulting from the recycling of ionic liquid; to identify the main environmental hotspots of the current process based on the actual yield (97%) and recovery rate (>95%); and to provide scientific basis for the further optimization of this green synthesis process.

1.2 Functional Unit

For fair comparison, the functional unit is defined as: "Producing 1 kg of 100% pure ethylene glycol dibenzoate product".

1.3 System Boundary

This assessment adopts the "from cradle to gate" approach. The system boundary includes:

Raw material production: synthesis of tetraethylene glycol, benzoic anhydride, and the initially introduced ionic liquid [HO-EtMIm][OTf].

Energy production: electricity consumption during the reaction process (heating, stirring) and the separation and purification process (extraction, vacuum drying).

Core reaction and separation processes: including reaction, extraction, vacuum drying, etc. unit operations.

Circulation system: incorporating the recovery and reuse of ionic liquid into the system boundary and allocating their environmental burden.

Waste treatment: handling waste solvents, unreacted raw materials, etc.

(Exclusion scope: production and scrapping of reactors and other laboratory equipment.)

1.4 Impact Assessment Method

The ReCiPe 2016 (H) method is adopted.

2. Life Cycle Inventory Analysis

This stage quantifies all the inputs and outputs required to produce 1 kg of the product. Key assumptions:

Cycle number of ionic liquid: calculated as 5 times (a conservative estimate).

Recycling rate: estimated to be >95% each time. Therefore, the environmental impact of the initial 1.2 mmol IL input needs to be distributed over multiple cycles.

Allocation method: a truncation-based recycling allocation method is adopted for [HO-EtMIm][OTf]. That is, the environmental impact of their initial production is allocated to the total amount of product produced throughout their entire lifespan.

(The background data were sourced from the Ecoinvent 3.8 database and the Chinese Life Cycle Database (CLCD), respectively.)

Table S6 List calculation (core part)

Input/Output	Amount per reaction	Total amount required to produce 1 kg of product (estimated)	Notes
Input	——		
Tetraethylene glycol	0.6 mmol	~0.10 kg	At a yield of 97%, the stoichiometric ratio is converted to 1 kg of product.
Benzoic anhydride	3.0 mmol	~0.91 kg	Benzoic anhydride is in excess. It is calculated based on the actual consumed phenylformic anhydride (corresponding to the yield) and the unreacted portion (becoming waste).
Ionic liquid [HO-EtMIm][OTf]	1.2 mmol	~0.015 kg	The initial burden of the IL environment is distributed over 5 reaction cycles.
Ethyl acetate (extracting solvent)	Assume 5 mL	~3.0 kg	Estimate.
Energy consumption for vacuum drying	Assume 0.02 kWh	~12 kWh	Estimate the energy consumption for the vacuum pump.
Energy consumption for reaction heating and stirring	~0.05 kWh	~30 kWh	Converted to produce 1 kg of product.
Output	——		
Product	2.328 mmol	1 kg	Target product.
By-products/Waste (Estimation)	-	~0.05 kg	Due to a selectivity of 93%, approximately 7% of the raw materials have been converted into non-target by-products.
Water produced during the reaction	0.582 mmol	~0.01 kg	Harmless.

Unreacted benzoic anhydride	0.672 mmol	~0.18 kg	The unreacted amount is calculated based on actual consumption.
Waste ethyl acetate	Assume 5 mL	~3.0 kg	Contains dissolved products and impurities, and requires solvent recovery or treatment as hazardous waste.
Loss of ionic liquid	< 0.06 mmol/time	~0.0007 kg	A 5% loss occurs in each cycle, which is very small when distributed over 1 kg of the product. (Estimation)

3. Life Cycle Impact Assessment

3.1 The following table summarizes the contribution rate (%) of each process to the main environmental impact categories.

(Note: The contribution rate is an approximate value based on list analysis and model estimation, and is used to reveal the main hotspots and trends. The specific values may vary due to factors such as the actual power grid structure, production processes, etc.)

Table S7 The contribution rate (%) of each process to the main environmental impact categories

Process/ Input	**Global Warming Potential (GWP) (kg CO_2 eq)**	**Acidification Potential (AP) (kg SO_2 eq)**	**Eutrophication Potential (EP) (kg PO_4^{3-} eq)**	**Photochemical Ozone Formation Potential (POCP) (kg C_2H_4 eq)**	**Non-renewable Resource Consumption (Fossil) (NRC) (MJ)**	**Water Resource Consumption (WRC) (m^3)**	**Human Toxicity (Carcinogenic) (HT-c) (CTUh)**	**Freshwater Ecotoxicity (FE) (kg 1,4-DCB eq)**
A. Raw material production	——							
benzoic anhydride (with excess portion)	25-35%	20-30%	20-30%	15-25%	30-40%	15-25%	20-30%	25-35%
tetraethylene glycol	5-10%	5-10%	5-10%	2-5%	8-12%	5-10%	5-10%	5-10%
Ionic liquid [HO-EtMIm]-[OTf]	10-20%	10-20%	10-20%	10-15%	15-25%	20-30%	25-35%	30-40%
B. Energy consumption	——							
Reaction heating and stirring	15-25%	25-35%	20-30%	10-20%	15-25%	30-40%	10-20%	10-20%
Separation (vacuum drying, etc.)	8-12%	10-15%	10-15%	5-10%	8-12%	8-12%	5-10%	5-10%

C. Separation and waste	———							
ethyl acetate (production and disposal)	15-25%	15-25%	20-30%	40-60%	20-30%	15-25%	30-40%	25-35%
Waste treatment (unreacted substances, etc.)	< 5%	< 5%	< 5%	< 5%	< 5%	< 5%	5-10%	5-10%

(Table Description--Classification and Unit Explanation:

Global Warming Potential (GWP): Measured in terms of carbon dioxide equivalent for greenhouse gas emissions.

Acidification Potential (AP): Measured in terms of sulfur dioxide equivalent for emissions causing acid rain.

Eutrophication Potential (EP): Measured in terms of phosphate equivalent for emissions causing water body eutrophication.

Photochemical Ozone Formation Potential (POFP): Measured in terms of ethylene equivalent for emissions causing photochemical smog precursors.

Non-renewable Resource Consumption (NRC): Measured in megajoules for the consumption of fossil fuels (such as coal, oil, and natural gas).

Water Resources Consumption (WRC): Measured in cubic meters for the amount of fresh water extracted.

Human Toxicity (HT-c): Measured in Comparative Toxic Unit for humans to assess the carcinogenic effects of chemicals on human health.

Freshwater Ecotoxicity (FE): Measured in 1,4-dichlorobenzene equivalent to assess the toxicity of chemicals to freshwater ecosystems.)

3.2 Key Findings

The core value of recycling: The repeated use of ionic liquid (5 times) has transformed the environmental profile of this process, turning it from a non-sustainable process due to the high environmental burden of IL into a green process with research value.

New environmental hotspots have shifted: After the issue of IL has been resolved, the lower atomic economy of the process (excessive amounts of benzoic anhydride), the energy consumption in the separation process, and the use of one-time solvents have become the main sources of environmental burdens.

The toxic impact is prominent: The production and disposal of ethyl acetate and ionic liquid are the main contributors to human toxicity and ecological toxicity.

Water footprint: The initial production of energy and the synthesis of ionic liquid are the main processes that consume water resources.

3.3 Comprehensive evaluation table of Green Chemistry Indicators

To further evaluate the process from the principles of Green Chemistry, the key indicators are summarized in Table S8 below.

Table S8 Comprehensive evaluation table of Green Chemistry Indicators

Indicator	Indicator value (based on the production of 1 kg product)	Key contributing factors
E-factor	3.23 (kg waste/kg product)	Solvent usage (~3.0 kg), unreacted substances, by-products
Process Mass Intensity (PMI)	4.23 (kg total input/kg product)	PMI = E-factor + 1
Atom Economy	~88.73%	The design of the actual reaction itself
Carbon Efficiency	~90.11% (actual value)	The selectivity resulting from the side reaction was 93%, causing the carbon loss.
Energy Intensity	42 kWh/kg product	Reaction heating and stirring (30 kWh), separation process such as vacuum drying (12 kWh)
Catalyst Recyclability (Cycles & Recovery Rate)	5times / >95%	Recovery and utilization of ionic liquid [HO-EtMIm][OTf]

Notes:

(1) E-factor = Total waste mass / Product mass = (0.18 kg unreacted benzoic anhydride + 0.05 kg by-products + 3.0 kg waste ethyl acetate) / 1 kg product = 3.23.

(This value could be reduced to 0.18 if solvent recovery is implemented.)

(2) PMI = Total input quality / Product quality = E-factor + 1 =4.23.

(3) Atom Utilization Rate = (Molecular weight of product / Total molecular weight of all reactants in stoichiometric ratio) × 100% = (4*270.28) / (194.23 + 4*226.23) × 100% × 97%× 93% ≈ 88.73%.

(stoichiometric ratio: 1 molecule of tetraethylene glycol + 4 molecules of benzoic anhydride = 4 molecules of ethylene glycol dibenzoate + 1 molecules of water; Actual atom utilization rate = Theoretical atom utilization rate × Yield × Selectivity.)

(4) Actual Carbon Efficiency = Carbon mass in the product / Total carbon consumed × 100% = (0.711kg/0.789kg)×100% ≈ 90.11%.

The mass of reactants consumed in the computational theory (calculated based on 100% yield and selectivity; theoretical yield: mass of reactants required for obtaining 1081.08 g product, based on the stoichiometric ratio): TEG theory mass = (194.22/1081.08)×1000g ≈ 0.180kg; BA theory mass = (904.88/1081.08)×1000g ≈ 0.837kg. (TEG: Tetraethylene glycol; BA: Benzoic anhydride)

The actual mass of reactants consumed (taking into account a 97% yield and a 93% selectivity): TEG actual consumption mass =0.180kg/(97%*93%) ≈ 0.200kg; BA actual consumption mass =0.837kg/(97%*93%) ≈ 0.928kg.

Calculate the carbon mass: The carbon mass in the product = 1kg×0.711 = 0.711kg; The total amount of carbon consumed = 0.099kg+0.690kg = 0.789kg (Carbon from TEG = 0.200kg×0.495 = 0.099kg, Carbon from BA = 0.928kg×0.743 ≈ 0.690kg).

These indicators align with the LCA findings that solvent use, reactants ratio and energy consumption are the key areas for improvement.

4. Explanation and Conclusion

4.1 Main Conclusion

After achieving efficient recovery and recycling of the ionic liquid [HO-EtMIm][OTf], the synthetic route of ethylene glycol dibenzoate demonstrates excellent potential for environmental sustainability.

The current environmental impact mainly stems from process engineering factors rather than the catalyst itself.

4.2 Suggestions for Improvement

Optimize the reaction ratio of reactants: Investigate the reduction of the excess proportion of benzoic anhydride to enhance atomic economy and reduce waste and raw material consumption at the source.

Realize solvent recycling: Develop a distillation system for recovering ethyl acetate. This will significantly reduce the potential impacts of this process on photochemical smog, toxicity, and global warming.

Process enhancement: Optimize reaction time and temperature, possibly shortening the 8-hour reaction period, thereby reducing energy consumption.

4.3 Limitations

The data on energy consumption and solvent usage are based on empirical estimates.

The assessment is based on laboratory scale.

The specific list data of ionic liquid and solvent production may vary depending on the supplier and production process.

4.4 Further outlook:

Recycling and reutilization is the foundation for achieving the greenification of this process. The future work focus should shift from the catalytic system to process optimization, including reducing reactant excess, achieving solvent recycling, and further exploring milder reaction conditions.