

Supporting Information

Hypercrosslinked ionic polymers with high ionic content for efficient conversion of carbon dioxide into cyclic carbonates

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Supplementary tables

Table S1. The effect of mass ratio of allyl chloride/ HCP on specific surface area and chloromethyl content of HCP-CH₂-Cl-X^a.

^a mass of ratio allyl chloride/ HCP	1.0	2.0	3.0	4.0	5.0	6.0	9.0
Chlorine content ^b (mmol g ⁻¹)	0.2	1.2	2.0	2.5	3.1	2.5	2.3
S _{BET} ^c (m ² g ⁻¹)	910	836	750	650	530	427	333

^a Reaction conditions: mass of ratio H₂SO₄/ HCP = 1.5, 50 °C, 24 h.

^b Chlorine content calculated by Mohr method.

^c BET surface area.

Table S2. The effect of mass ratio of H₂SO₄/ HCP on specific surface area and chloromethyl content of HCP-CH₂-Cl-X^a.

^a mass of ratio H ₂ SO ₄ / HCP	0.5	1.0	1.5	2.0	2.5
Chlorine content ^b (mmol g ⁻¹)	2.0	2.7	3.1	2.1	1.7
S _{BET} ^c (m ² g ⁻¹)	783	641	530	515	431

^a Reaction conditions: mass of ratio allyl chloride/ HCP = 5, 50 °C, 24 h.

^b Chlorine content calculated by Mohr method.

^c BET surface area.

Table S3. The effect of reaction time on specific surface area and chloromethyl content of HCP-CH₂-Cl-X^a.

Reaction time (h)	8	16	24	32	40
Chlorine content ^b (mmol g ⁻¹)	1.5	2.6	3.1	2.9	3.0
S _{BET} ^c (m ² g ⁻¹)	755	623	530	380	250

^a Reaction conditions: mass of ratio allyl chloride/ HCP = 5, mass of ratio H₂SO₄/ HCP=1.5, 50 °C.

^b Chlorine content calculated by Mohr method.

^c BET surface area.

Table S4. The effect of reaction temperature on specific surface area and chloromethyl content of HCP-CH₂-Cl-X^a.

Temperature (°C)	30	40	50	60	70
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Chlorine content^b (mmol g⁻¹)	2.7	2.9	3.1	2.8	2.7
S_{BET}^c (m²g⁻¹)	711	635	530	343	320

^a Reaction conditions: mass of ratio allyl chloride/ HCP = 5, mass of ratio H₂SO₄/ HCP=1.5, 24 h.

^b Chlorine content calculated by Mohr method.

^c BET surface area.

Table S5. The synthesis conditions of HCP-CH₂-Cl-X.

Sample	mass ratio of allyl chloride to HCP	mass ratio of H₂SO₄ to HCP	reaction time (h)	reaction temperature (°C)
HCP-CH ₂ -Cl-1	5	1.5	24	50
HCP-CH ₂ -Cl-2	5	0.5	24	50
HCP-CH ₂ -Cl-3	5	2.5	24	50
HCP-CH ₂ -Cl-4	5	1.5	8	50
HCP-CH ₂ -Cl-5	5	1.5	40	50
HCP-CH ₂ -Cl-6	5	1.5	24	30
HCP-CH ₂ -Cl-7	5	1.5	24	70

Table S6. Textual properties of [HCP-CH₂-Im][Cl]-X.

Sample	S_{BET}^a (m²g⁻¹)	V_p^b (cm³g⁻¹)	D_{total}^c (nm)	IL content^d (mmol g⁻¹)
[HCP-CH ₂ -Im][Cl]-1	385	0.332	3.445	2.10
[HCP-CH ₂ -Im][Cl]-2	510	0.661	5.182	0.99
[HCP-CH ₂ -Im][Cl]-3	386	0.573	5.928	0.48
[HCP-CH ₂ -Im][Cl]-4	503	0.721	5.730	0.85
[HCP-CH ₂ -Im][Cl]-5	183	0.450	9.825	1.65
[HCP-CH ₂ -Im][Cl]-6	406	0.652	6.408	1.81
[HCP-CH ₂ -Im][Cl]-7	295	0.414	5.601	1.26

^a BET surface area.

^b Total pore volume.

^c Average pore size for total pores.

^d IL content calculated by elemental analysis.

Table S7. Activity of porous ionic polymers in the cycloaddition of CO₂ with styrene oxide.

Catalyst	t (h)	Tem. (K)	CO₂ (MPa)	Co-catalyst	Yield (%)	Ref.
HPILs-Cl-2	9	343	0.1	TBAB	88	1
POM3-IM	12	393	1	None	89	2
PDmBr	12	393	0.1	None	91	3
CPBr-2	7	363	2.5	None	79	4
ZnBr ₂ @Bpy-PHP-4	72	373	0.1	None	99	5
Zn/POF2	9	363	0.25	TBAB	87	6
SYSU-Zn@IL2	24	353	1	None	80	7
PIL-4	48	373	1	None	52	8
COP-222	24	373	0.1	None	99	9
HP-[BZPhIm]Cl-DCX-1	24	393	0.1	None	91	10
PEAMC1	12	393	0.1	None	94	11
ImIP@TT-COF	48	393	1	None	99	12

IP-2	18	373	0.1	None	36	13
HNM	36	373	0.1	None	79	14
NUP-3	24	363	0.1	KI	88	15
CCTF-350	48	393	0.4	None	79	16
Catalyst 5b	3	423	4	None	53	17
[HCP-CH ₂ -Im][Cl]-1	20	373	0.1	None	93	This work
[HCP-CH ₂ -Im][Cl]-1	8	393	0.1	None	94	This work
[HCP-CH ₂ -Im][Cl]-1	5	403	0.1	None	93	This work
[HCP-CH ₂ -Im][Cl]-1	5	413	0.1	None	99	This work

Supplementary Figures

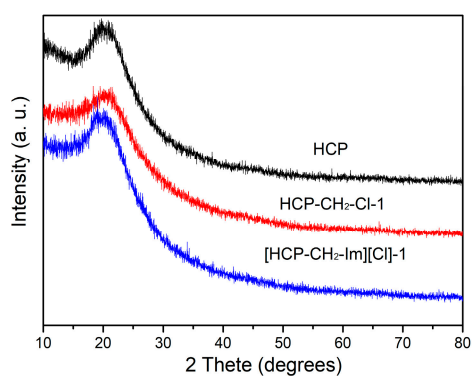


Fig. S1. XRD patterns of polymers.

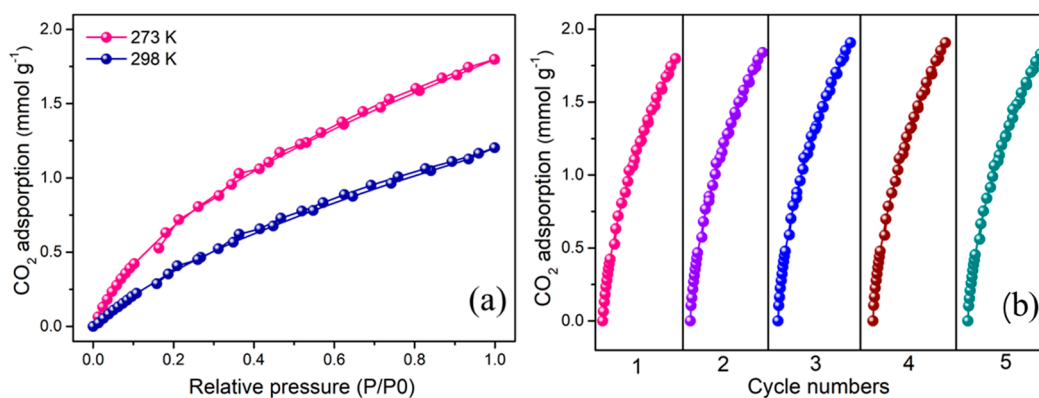


Fig. S2 (a) CO₂ adsorption isotherms of [HCP-CH₂-Im][Cl] (1) at 273 K and 298 K, (b) recycling performance of [HCP-CH₂-Im][Cl] (1) at 273 K

¹H NMR spectra of cyclic carbonates

Calculate the yield by using dibromomethane as a standard sample and significant peak is about 4.9 ppm.

Fig. S3 ^1H NMR spectra (in CDCl_3) of the reaction mixture using $[\text{HCP-CH}_2\text{-Im}][\text{Cl}]\text{-1}$ as a catalyst for the cycloaddition reaction of Propylene oxide (^1H NMR spectrum was obtained from the crude sample). ^1H NMR (500 MHz, CDCl_3) δ : 4.84 (m, 1H), 4.45 (t, $J = 8.6$ Hz, 1H), 4.54 (t, $J = 8.0$ Hz, 1H), 4.01 (t, $J = 7.4$ Hz, 1H), 1.46 (d, $J = 6.2$ Hz, 3H).

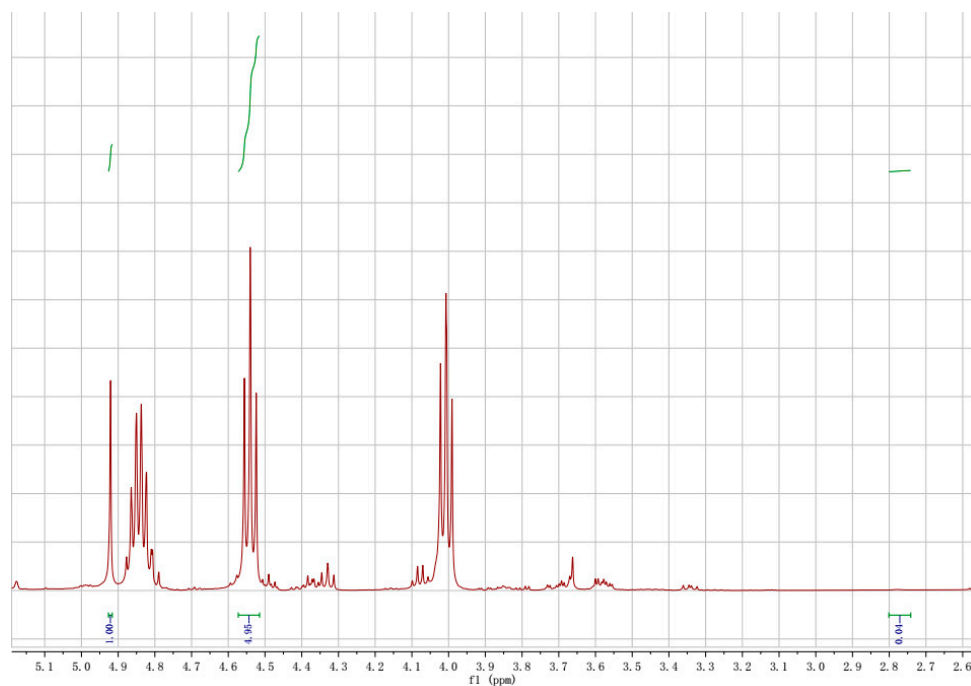


Fig. S4 ^1H NMR spectra (in CDCl_3) of the reaction mixture using $[\text{HCP-CH}_2\text{-Im}][\text{Cl}]\text{-1}$ as a catalyst for the cycloaddition reaction of Epichlorohydrin (^1H NMR spectrum was obtained from the crude sample). ^1H NMR

(500 MHz, CDCl₃) δ : 5.00 (m, 1H), 4.49 (t, J = 8.6 Hz, 1H), 4.39 (dd, J = 2.9, 5.9 Hz, 1H), 3.81 (dd, J = 4.1, 12.4 Hz, 1H), 3.61 (dd, J = 4.9, 12.2 Hz, 1H).

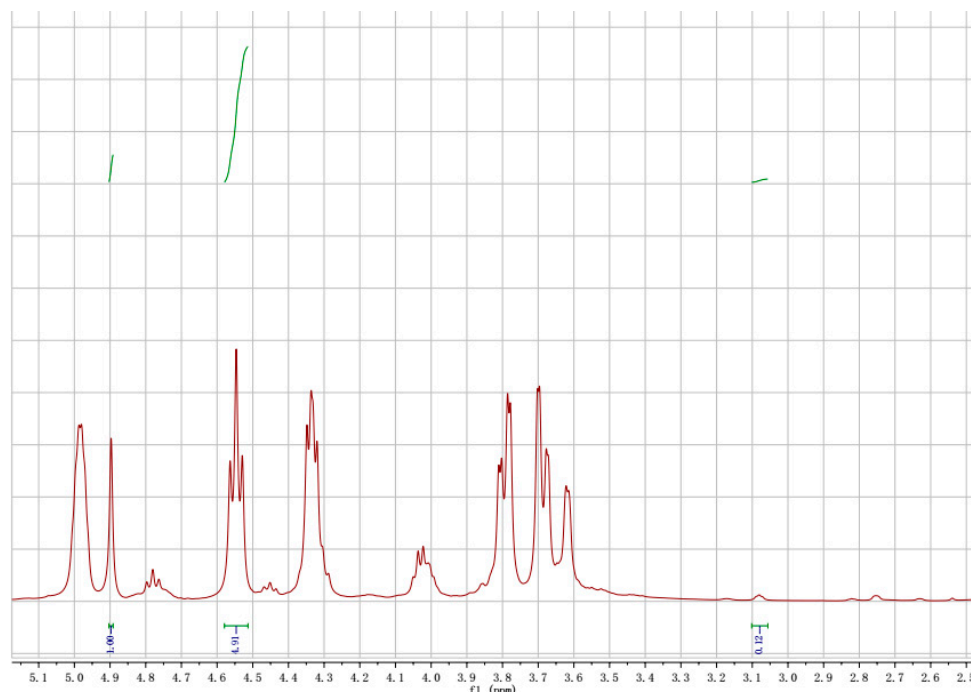


Fig. S5 ¹H NMR spectra (in CDCl₃) of the reaction mixture using [HCP-CH₂-Im][Cl]-1 as a catalyst for the cycloaddition reaction of Epibromohydrin (¹H NMR spectrum was obtained from the crude sample). ¹H NMR

(500 MHz, CDCl₃) δ : 4.96 (m, 1H), 4.58 (t, J = 8.6 Hz, 1H), 4.32 (dd, J = 3.0, 5.8 Hz, 1H), 3.62 (dd, J = 5.6, 11.3 Hz, 1H), 3.56 (dd, J = 3.7, 11.4 Hz, 1H).

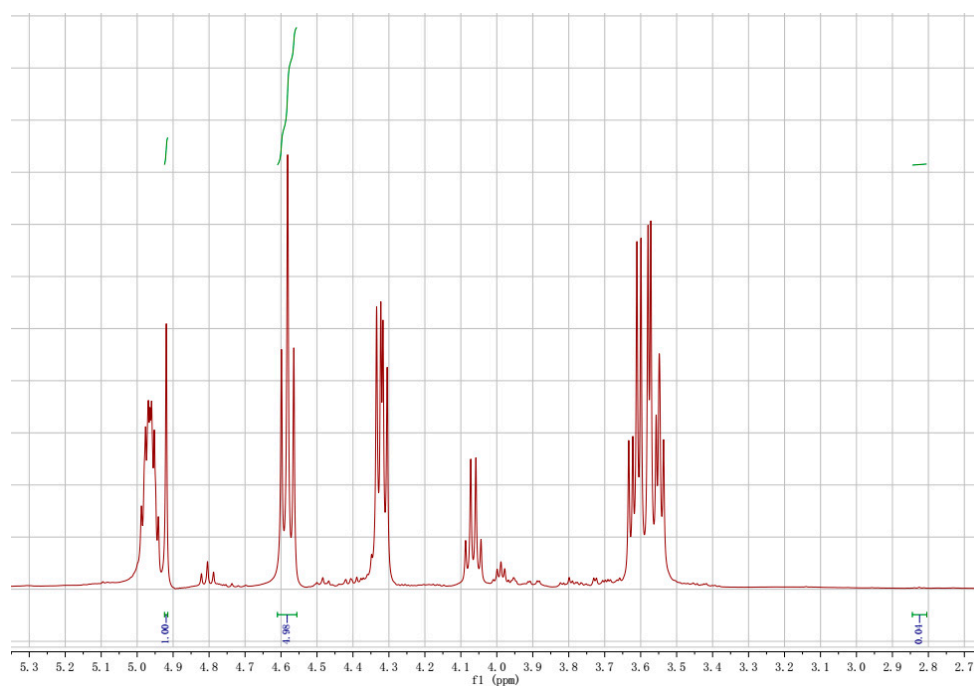


Fig. S6 ¹H NMR spectra (in CDCl₃) of the reaction mixture using [HCP-CH₂-Im][Cl]-1 as a catalyst for the cycloaddition reaction of Styrene oxide (¹H NMR spectrum was obtained from the crude sample). ¹H NMR

(500 MHz, CDCl₃) δ : 7.41-7.34 (m, Ar-H, 5H), 5.65 (t, J = 8.1 Hz, 1H), 4.77 (t, J = 8.4 Hz, 1H), 4.29 (t, J = 8.3 Hz, 1H).

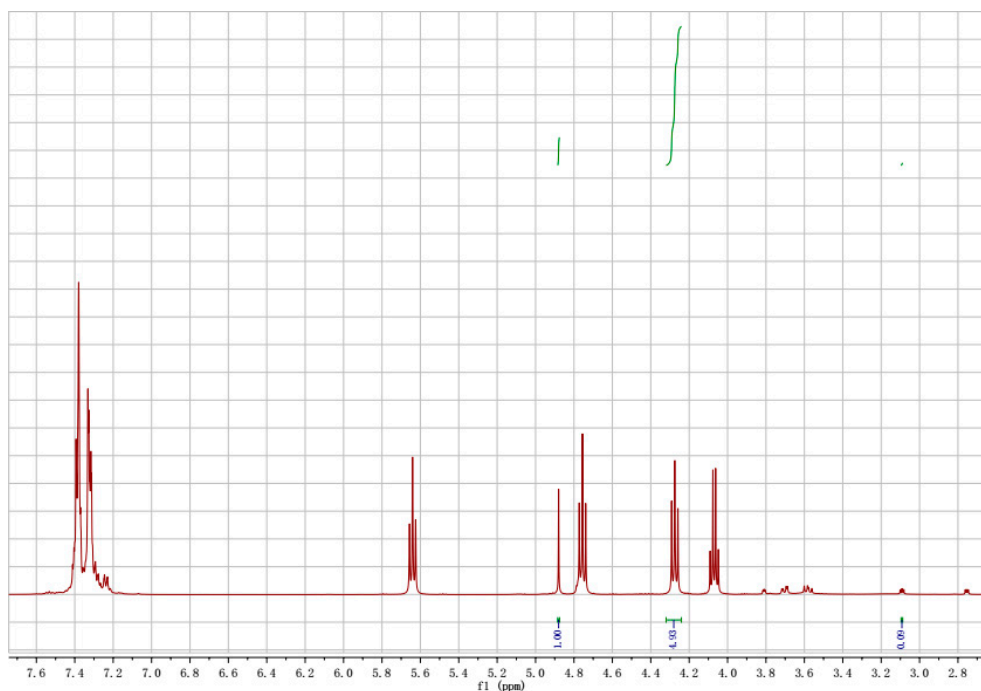


Fig. S7 ¹H NMR spectra (in CDCl₃) of the reaction mixture using [HCP-CH₂-Im][Cl]-1 as a catalyst for the cycloaddition reaction of Allyl glycidyl ether (¹H NMR spectrum was obtained from the crude sample). ¹H

NMR (500 MHz, CDCl₃) δ : 5.93 (m, 1H), 5.24 (dd, J = 1.2, 17.3 Hz, 1H), 5.17 (d, J = 10.4 Hz, 1H), 4.81 (m, 1H), 4.47 (t, J = 8.4 Hz, 1H), 4.34 (dd, J = 2.1, 6.0 Hz, 1H), 4.01 (m, 1H), 3.66 (dd, J = 3.2, 11.2 Hz, 1H), 3.56 (dd, J = 3.6, 11.1 Hz, 2H).

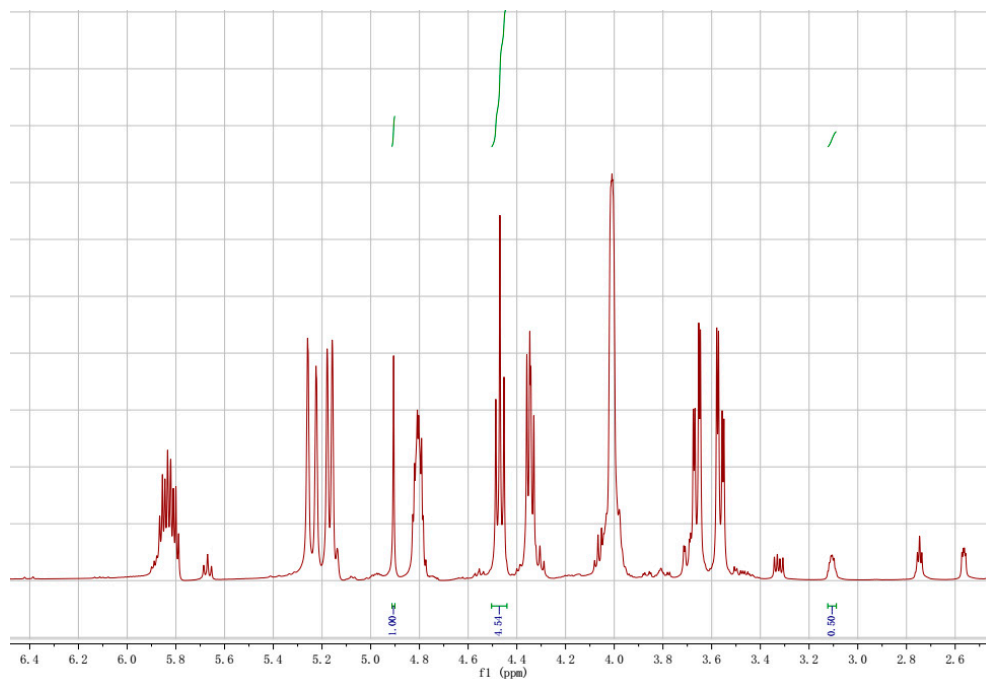


Fig. S8 ¹H NMR spectra (in CDCl₃) of the reaction mixture using [HCP-CH₂-Im][Cl]-1 as a catalyst for the cycloaddition reaction of Butyl glycidyl ether (¹H NMR spectrum was obtained from the crude sample). ¹H

NMR (500 MHz, CDCl_3) δ : 4.77 (m, 1H), 4.44 (t, $J = 8.3$, 1H), 4.31 (dd, $J = 2.3$, 6.0 Hz, 1H), 4.04 (dd, $J = 7.1$, 14.3 Hz, 1H), 3.61 (dd, $J = 3.4$, 11.4 Hz, 1H), 3.52 (dd, $J = 3.7$, 11.2 Hz, 1H), 3.44 (dd, $J = 1.4$, 6.5 Hz, 2H), 1.48 (m, 2H), 1.30 (m, 2H), 1.19 (m, 3H).

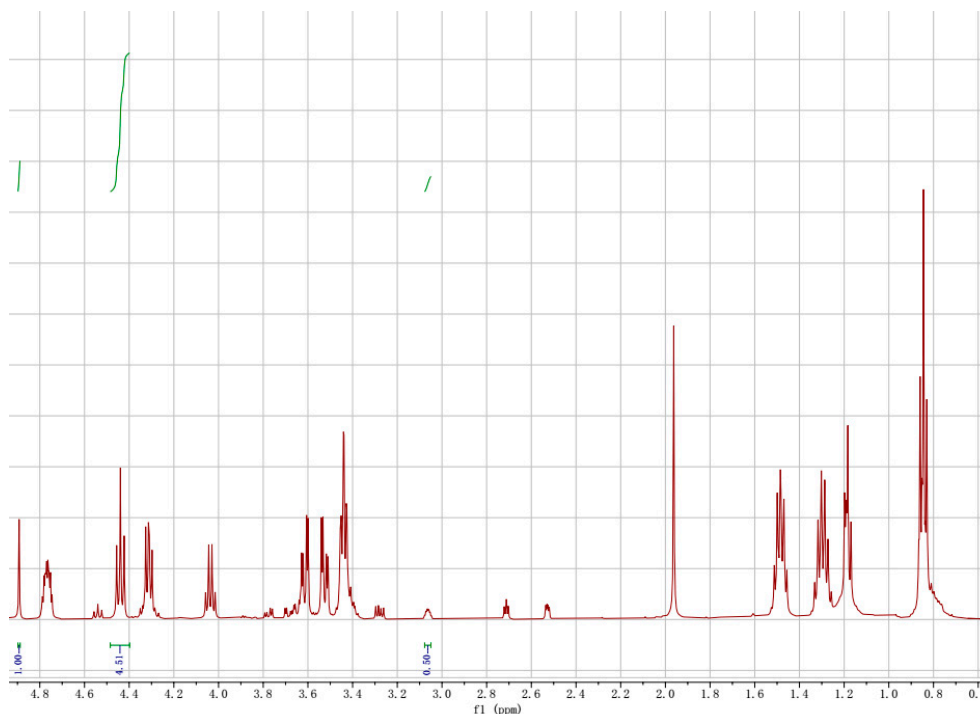


Fig. S9 ^1H NMR spectra (in CDCl_3) of the reaction mixture using $[\text{HCP-CH}_2\text{-Im}][\text{Cl}]\text{-1}$ as a catalyst for the cycloaddition reaction of Glycidyl phenyl ether (^1H NMR spectrum was obtained from the recrystallization).

^1H NMR (500 MHz, CDCl_3) δ : 7.33 (t, $J = 8.0$ Hz, 2H), 7.04 (t, $J = 7.1$ Hz, 1H), 6.94 (d, $J = 8.1$ Hz, 2H), 5.05 (m, 1H), 4.64 (t, $J = 8.5$ Hz, 1H), 4.56 (td, $J = 2.6, 5.9$ Hz, 1H), 4.26 (dd, $J = 4.2, 10.5$ Hz, 1H), 4.17 (dd, $J = 3.6, 10.6$ Hz, 1H).

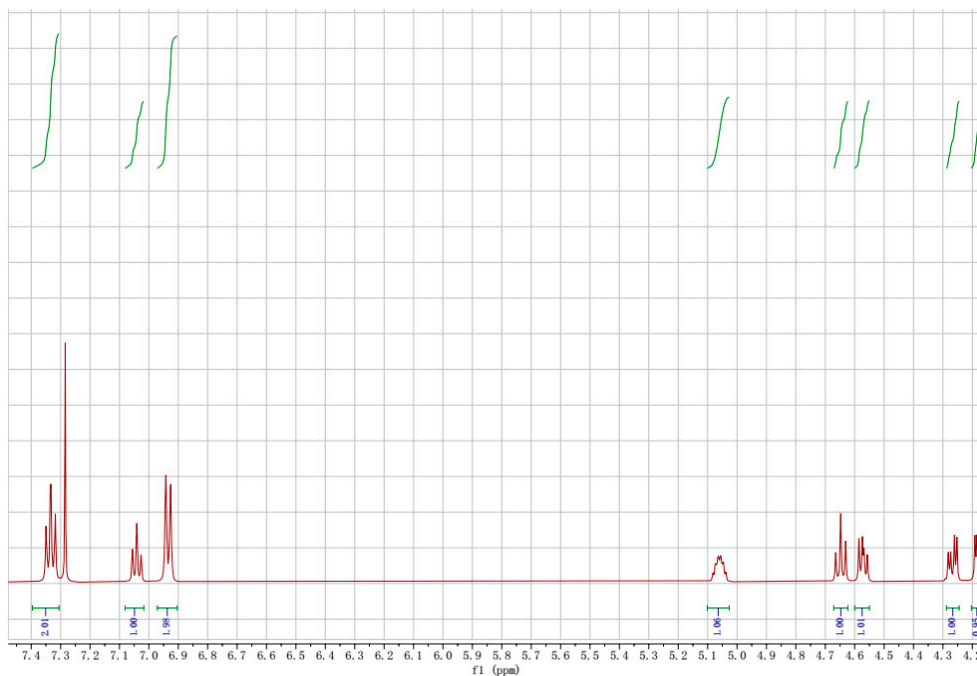
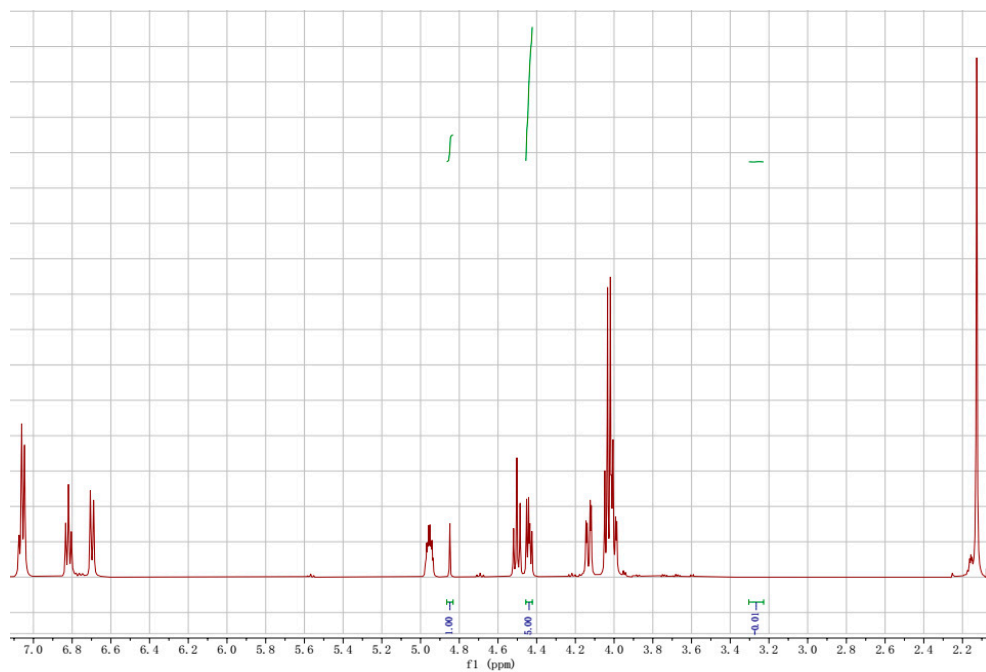


Fig. S10 ^1H NMR spectra (in CDCl_3) of the reaction mixture using $[\text{HCP-CH}_2\text{-Im}][\text{Cl}]\text{-1}$ as a catalyst for the cycloaddition reaction of O-Tolyl glycidyl ether (^1H NMR spectrum was obtained from the crude sample). ^1H

NMR (500 MHz, CDCl₃) δ : 7.06 (t, J = 7.4 Hz, 2H), 6.82 (t, J = 7.2 Hz, 1H), 6.70 (d, J = 8.4 Hz, 1H), 4.95 (m, 1H), 4.50 (t, J = 8.5 Hz, 1H), 4.44 (td, J = 3.1, 6.7 Hz, 1H), 4.13 (dd, J = 2.9, 10.8 Hz, 1H), 3.99 (dd, J = 3.2, 10.7 Hz, 1H), 2.13 (s, 3H).



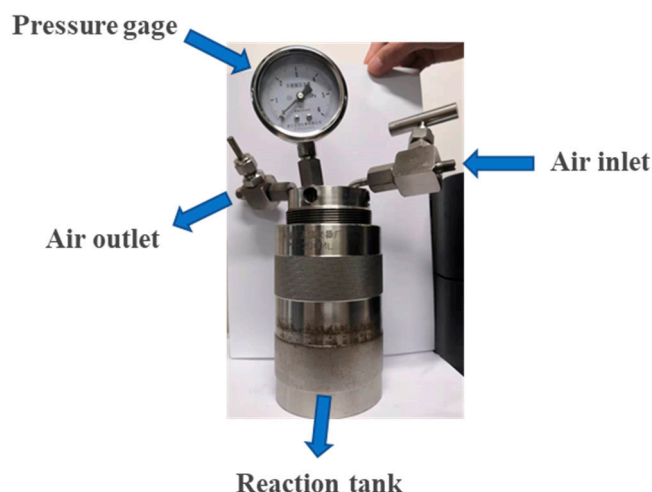


Fig. S11 The schematic of high-pressure stainless steel autoclave.

Reference

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