Electronic Supplementary Material (ESI) for ChemComm.
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Supporting Information for

Hydrogen Bonding-Catalysed Alcoholysis of Propylene Oxide at Room Temperature

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Experimental section

Materials

Propylene oxide (99.5%), 1,2-butylene oxide (99%), epichlorohydrin (97%), epibromohydrin (97%), cyclohexene oxide (97%), styrene oxide (97.5%), methanol (99.9%), 1-propanol (99.7%), 2-propanol (99.7%), 1-butanol (99.5%), benzyl alcohol (99%), imidazole (99%), 2-methyl imidazole (98%), mesitylene (99%) and d_6-DMSO (99.8%) were purchased from J&K Scientific Ltd. 1-ethyl-3-methyl imidazolium chloride ([EtMIm][Cl], 99%), 1-hydroxyethyl-3-methyl imidazolium chloride ([HO-EtMIm][Cl], 99%), 1-hydroxyethyl-3-methyl imidazolium acetate ([HO-EtMIm][OAc], 98%), 1-hydroxyethyl-3-methyl imidazolium tetrafluoroborate ([HO-EtMIm][BF_4], 99%), 1-hydroxyethyl-3-methyl imidazolium bis ((trifle-oromethyl)sulfonyl)imde ([HO-EtMIm][NTf_2], 99%) and 1-hydroxyethyl-3-methyl imidazolium hexafluorophosphate ([HO-EtMIm][PF_6], 99%) were provided by Centre of Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences (CAS). All the chemicals were used as received.

Instrumentation

Liquid ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance III 400 HD NMR spectrometer. ^{17}O NMR spectra were recorded on AVANCE III 500WB NMR spectrometer. IR spectra were record on Bruker Tensor-27 FTIR spectrometer using ATR method. The product selectivity was determined by gas chromatography (Agilent 7890B) with a FID detector and a column DB-5(0.25 μm×30 m).

General procedure for the synthesis of ionic liquid catalysts

In a typical experiment, imidazole (3.40 g, 50 mmol) was added to a solution of NaOH (2.00 g,50 mmol) in MeOH (30 mL) and the mixture was stirred for 2 h at room temperature. Subsequently, the solution of [HO-EtMIm][Cl] (8.13 g, 50 mmol) in MeOH (20 mL) was added into the above solution, and stirred for 12 h. Then, 50 ml of diethyl ether was added, and large amounts of white precipitate formed. Anhydrous Na_2SO_4(3.56 g, 25 mmol) was added, and the mixture was stand for 12 h in refrigerator. Finally, the white precipitate was removed by centrifugation, and the yellow solution was evaporated under vacumm, and the as-synthesized [HO-EtMIm][Im] was obtained.

General procedure for the synthesis of glycol ethers

The reactions were conducted in a 5 ml sample bottle equipped with a magnetic stirrer. In a typical experiment, [HO-EtMIm][Im](0.5 mmol), methanol (20 mmol), and PO (10 mmol) were sequentially added into a sample bottle, then the bottle was sealed. Subsequently, the bottle was placed into an air-bath of 30 ^{o}C and stirred at 300 r.p.m for 8 h. Finally, the reaction mixture was cooled in ice water. Quantitative analysis was performed by using ^{1}H NMR spectroscopy and GC with mesitylene as an internal standard.

DFT Calculation

All calculations were performed with the Gaussian 09 package.[1] Geometry optimizations and NBO charge distribution calculations were carried out at the M06-2X[2]/def2-TZVP[3] level at 0 K.

Results and discussion

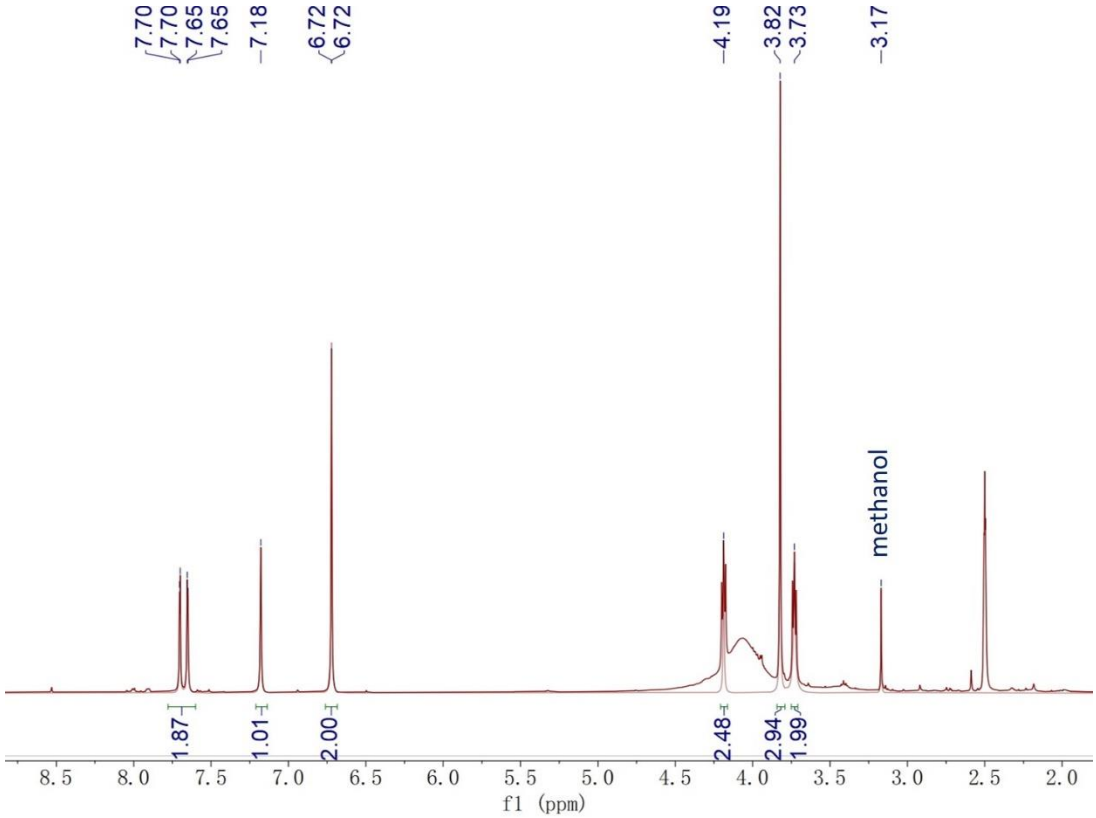


Figure S1 ^{1}H NMR spectrum of the as-synthesized [HO-EtMIm][Im].

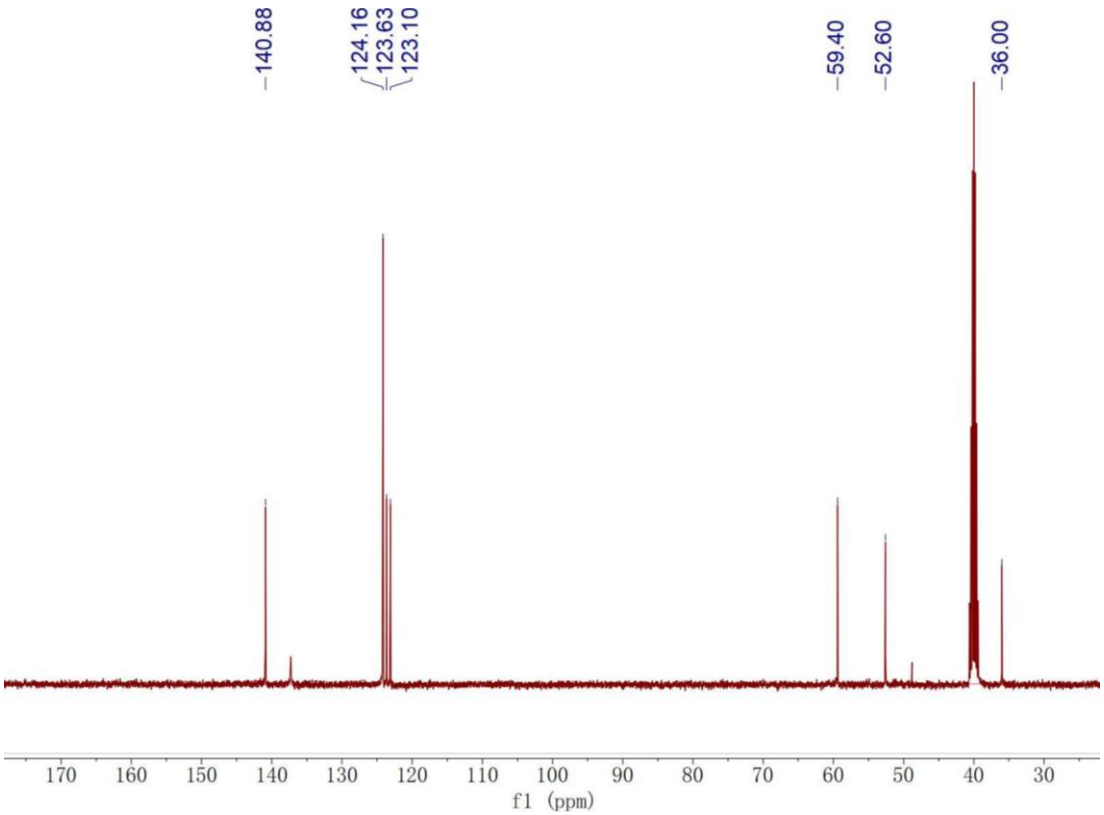


Figure S2 ^{13}C NMR spectrum of the as-synthesized [HO-EtMIm][Im].

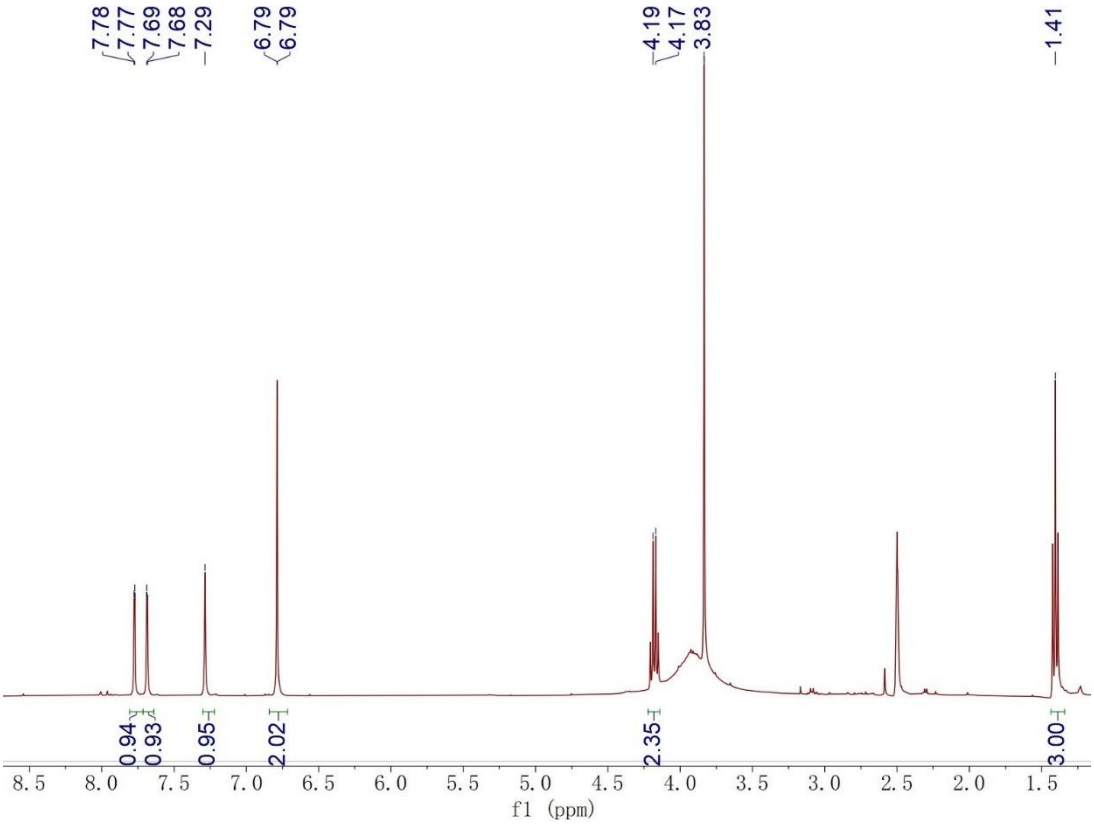


Figure S3 ^{1}H NMR spectrum of the as-synthesized [EtMIm][Im].

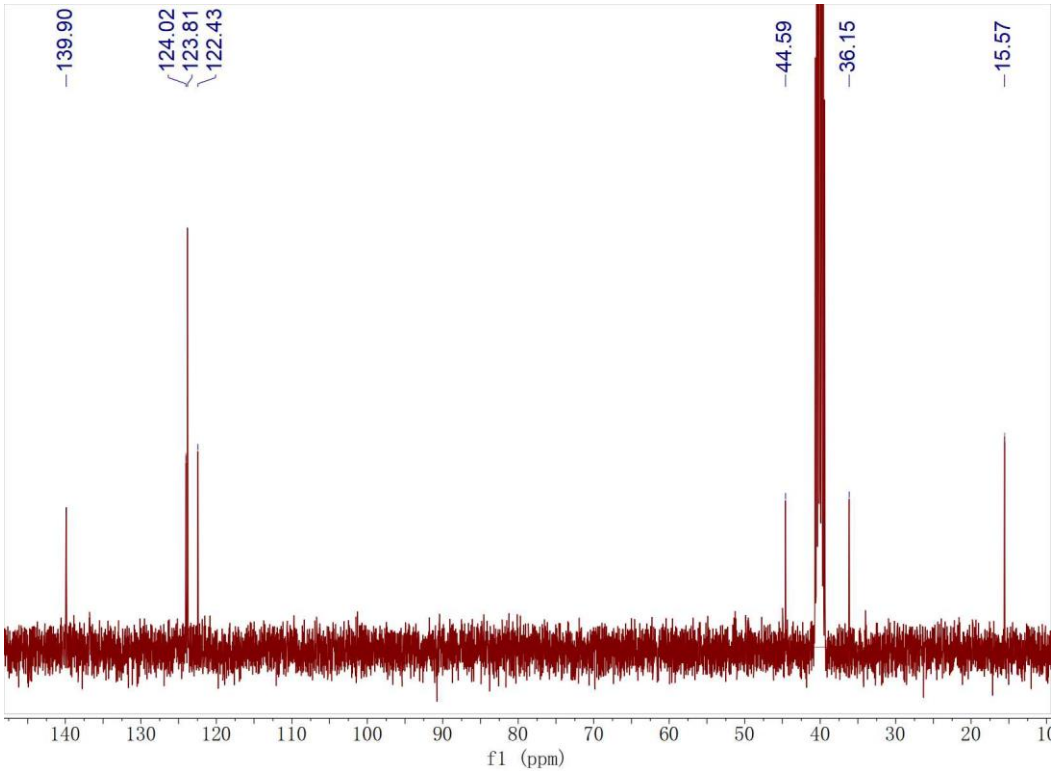


Figure S4 ^{13}C NMR spectrum of the as-synthesized [EtMIm][Im].

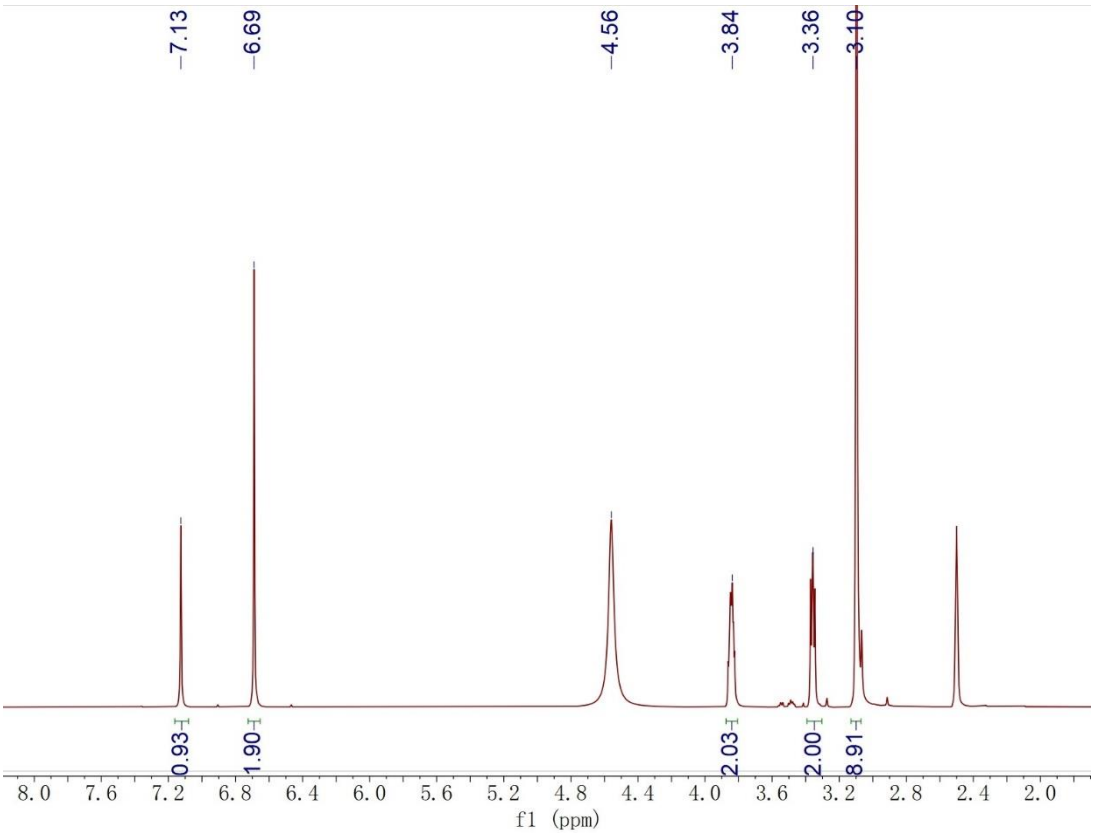


Figure S5 ^{1}H NMR spectrum of the as-synthesized [Ch][Im].

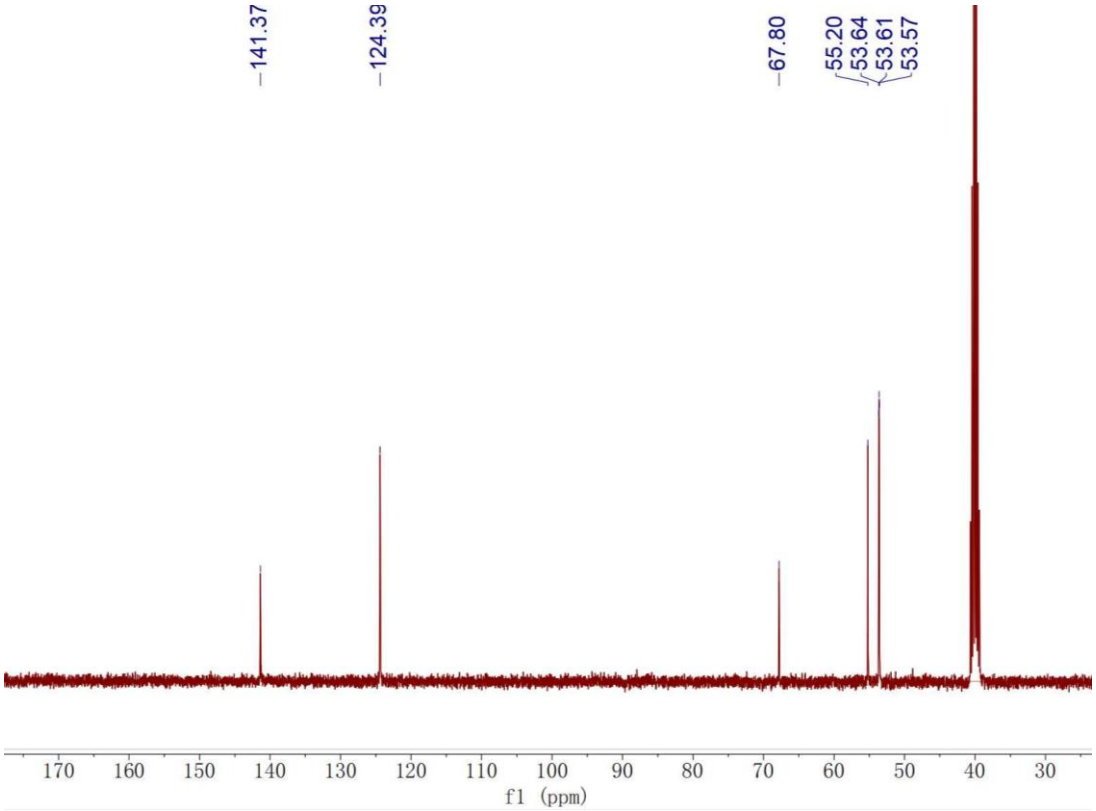


Figure S6 ^{13}C NMR spectrum of the as-synthesized [Ch][Im].

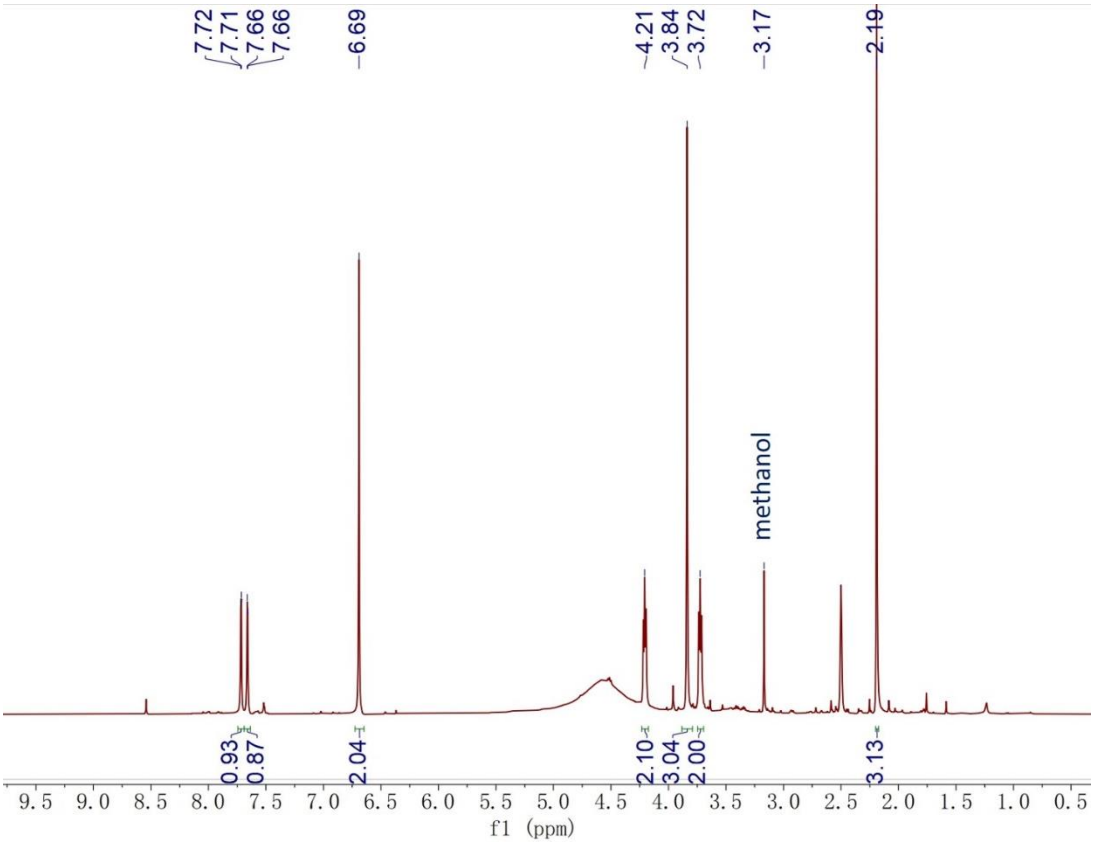


Figure S7 ^{1}H NMR spectrum of the as-synthesized [HO-EtMIm][2-MIm].

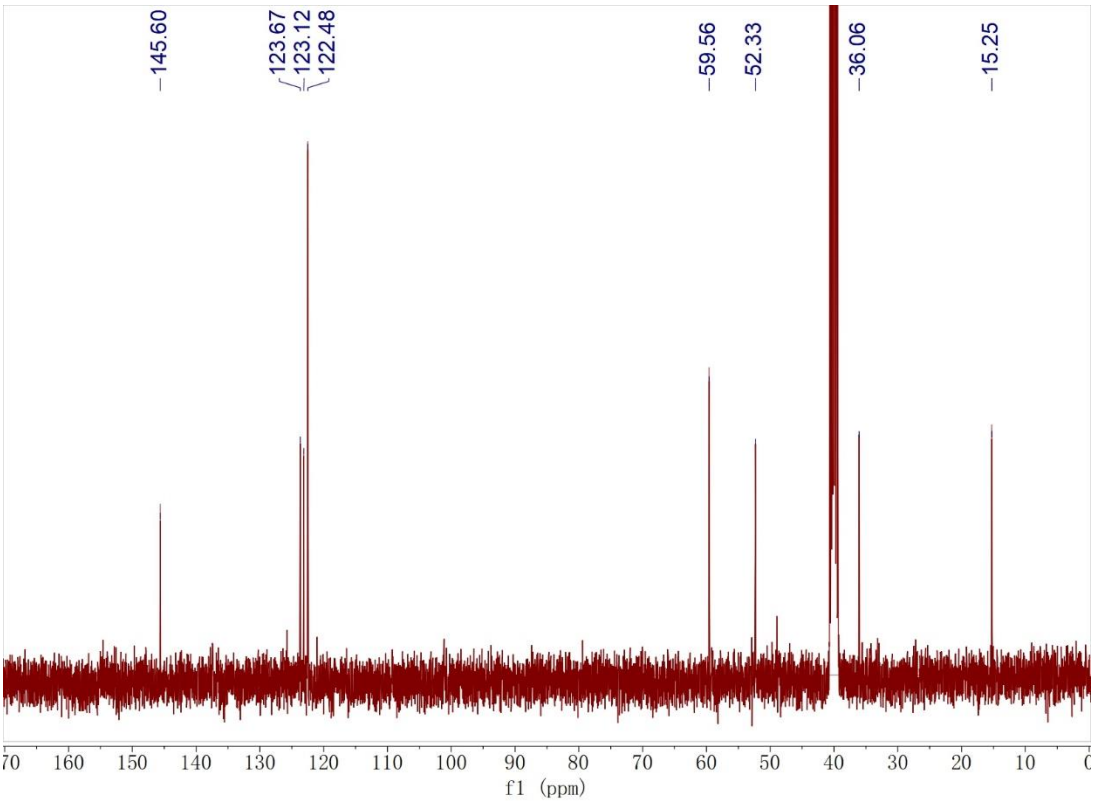
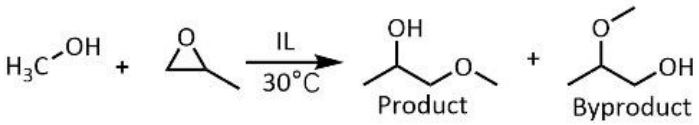


Figure S8 ^{13}C NMR spectrum of the as-synthesized [HO-EtMIm][2-MIm].

Table S1 Effect of methanol/PO molar ratios on the alcoholysis reaction[a]



Entry	Methanol/PO molar ratio	Yield[b]	Selectivity[b]
1	1:1	53%	>99%
2[c]	1:1	77%	>99%
3	2:1	55%	>99%
4[c]	2:1	87%	>99%
5	3:1	45%	>99%
6	5:1	44%	>99%

[a] Reaction conditions: [HO-EtMIm][Im] (0.5 mmol), PO (10mmol), 30°C, 8h. [b]The yield and selectivity of 1-methoxyl-2-propanol were determined by ^{1}H NMR spectroscopy and GC with mesitylene as the internal standard, respectively. [c]24h.

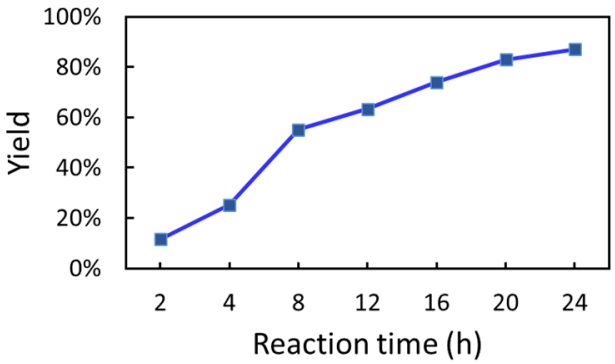


Figure S9 The dependence of 1-methoxyl-2-propanol yields on reaction time. Reaction conditions: [HO-EtMIm][Im] (0.5 mmol), methanol (20mmol), PO (10mmol), 30 °C.

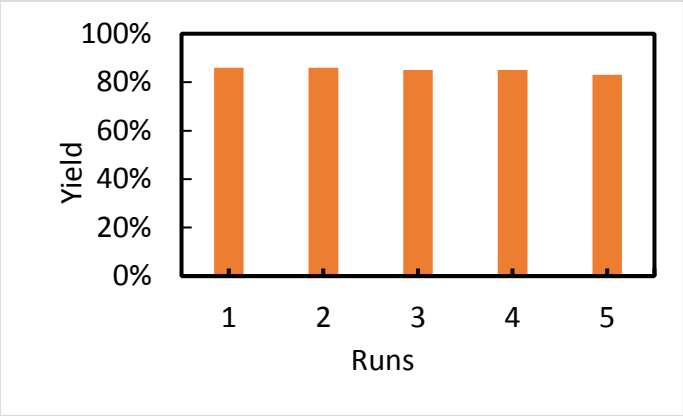


Figure S10 Stability test of [HO-EtMIm][Im]. Reaction conditions: [HO-EtMIm][Im] (0.5 mmol), methanol (20mmol), PO (10mmol), at 30 °C, 24h.

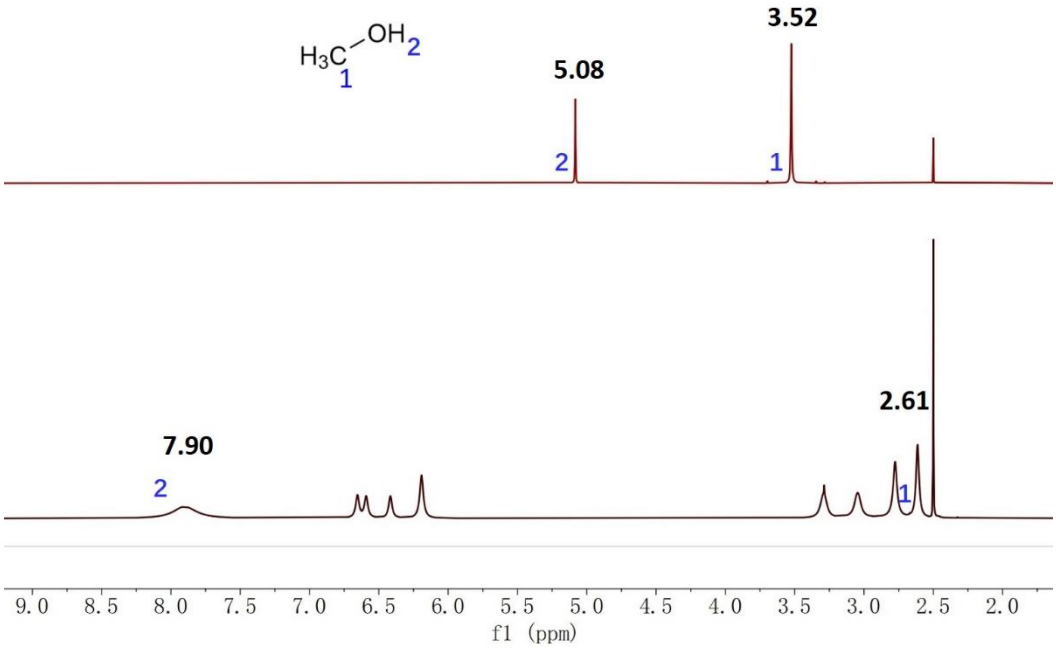


Figure S11 ^{1}H NMR spectra of methanol (a) and methanol-IL mixture of 1:1 (b).

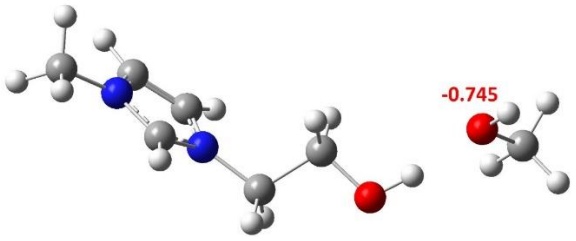


Figure S12 Possible interaction structure of methanol with cation and NBO charge distribution.

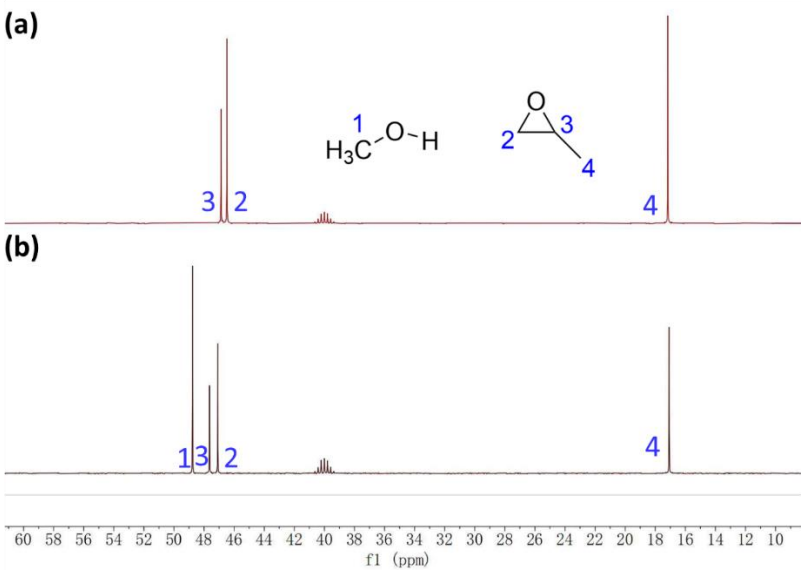


Figure S13 ^{13}C NMR spectra of PO (a) and methanol-PO mixture (1.5:1) (b).

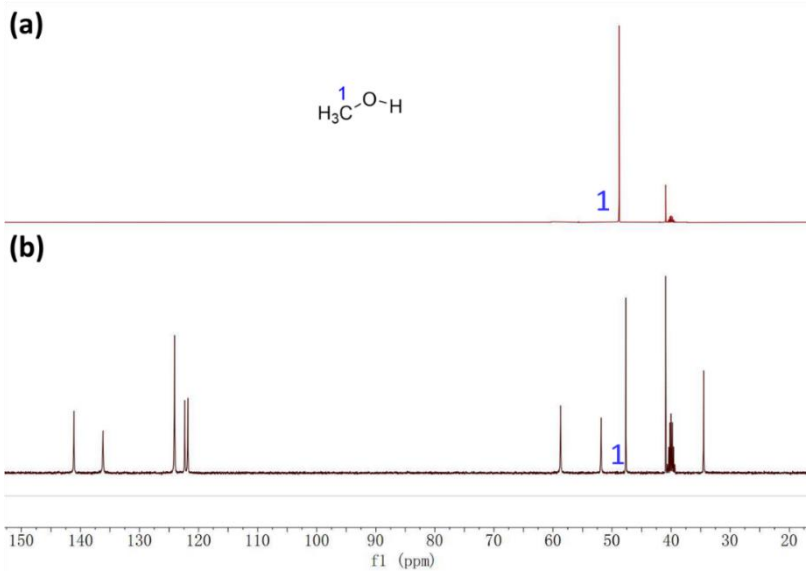


Figure S14 ^{13}C NMR spectra of methanol (a) and methanol-IL mixture (1:1) (b).

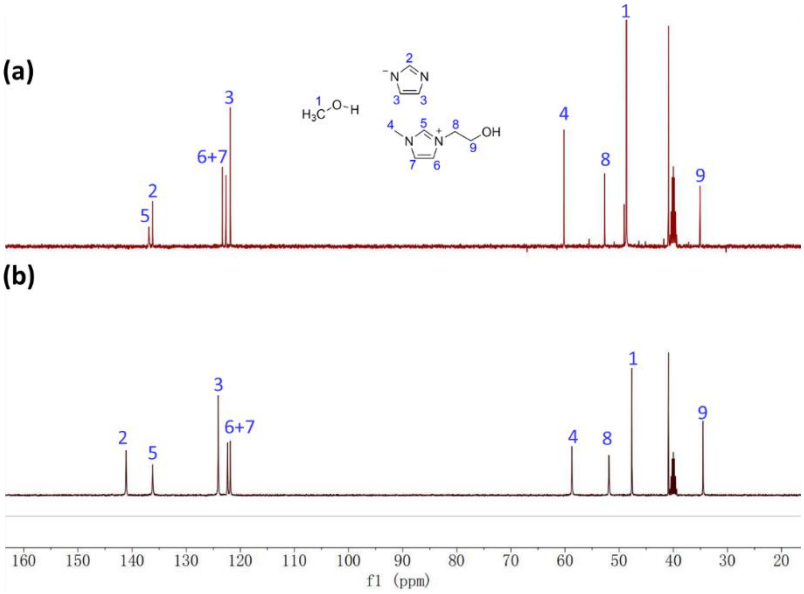


Figure S15 ^{13}C NMR spectra of 1:1 mixture of methanol-IL (a) and methanol-IL mixture (30:1) (b)

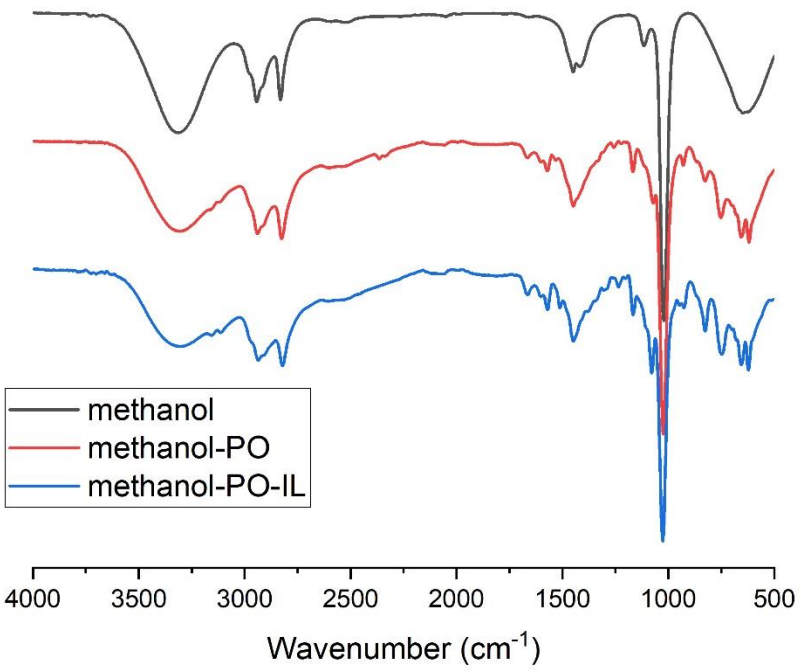


Figure S16 IR spectra of methanol, methanol-PO mixture (2:1), and methanol-PO-IL mixture (2:1:0.2)

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