Supporting Information

Cation-Anion Confined Hydrogen-Bonding Catalysis Strategy for Ring-Closing C-O/O-H Metathesis of Alkoxy Alcohols under Metal-Free Conditions

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1. Experimental Procedures

1.1 Materials

n-hexane (95%) were purchased from J&K Scientific Ltd. 1,4-Butanediol monomethyl ether (>98%) and 4-butoxy-1-butanol were purchased from TCI Shanghai Co., Ltd. Diethylene glycol monoethyl ether (99%, stabilized with BHT), chloroform-d (CDCl₃, 99.8 atom% of D), deuterium oxide (D₂O, 99.9 atom% of D) and methyl sulfoxide-d6 (DMSO-d₆, 99.8 atom% of D) were purchased from Innochem. 5-Benzylosy-1-pentanol was obtained from Alfa. (2-(Methoxyphenyl)phenyl)methanol (95%+) and 6benzyloxy-1-hexanol were purchased from Shanghai Bide Pharmatech Ltd. 2-(2methoxymethylphenyl)ethanol was obtained from Shanghai Kean Chemical Technology Co., Ltd. Di(propylene glycol) propyl ether, mixture of isomers (98.5%) was purchased from Macklin. 4-Benzyloxy-1,3-butanediol (97%) was purchased from Aladdin. All reagents were used as received without further purification.

The ionic liquids (ILs) were provided by Centre of Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences (CAS), and their chemical structures are shown 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 ¹H NMR, ¹⁹F NMR, ¹⁷O NMR and ¹³C NMR at 333.15 K. DMSO-d₆ was added in the inner tube, and the sample was added in the outer tube. The GC-MS analysis was performed using gas chromatography-mass spectrometry (GC-MS, SHIMADZU-QP2010) with a packed column DB-5 MS. High-resolution electrospray ionization mass spectrometry (HR-ESI-MS) were performed on Bruker FT-ICR-MS (Solarix 9.4T). The ionization method and mode of detection employed was indicated for the corresponding experiment and all masses are reported in atomic units per elementary charge (m/z) with an intensity normalized to the most intense peak. The contents of the residual metal in the ionic liquids were determined by inductively coupled plasma-mass spectrometry (ICP-MS). All density functional theory (DFT) calculations were performed with the Gaussian 09 package.¹ Geometry optimizations were carried out at the M062X-D3²/def2-TZVP³ 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 General procedures for ring-closing C-O/O-H metathesis of Alkoxy Alcohols

All reactions were conducted in a sealed tube (15 mL of inner volume) equipped with a magnetic stirrer. In a typical experiment, [HO-EtMIm][OTf] (0.2 mmol) and 1,4-butanediol monomethyl ether (2 mmol) were sequentially added into the reactor and sealed under nitrogen atmosphere. Subsequently, the reactor was moved to an oil-bath of desired temperature (e.g., 120 °C) and stirred for 12 h. After reaction, the reactor was cooled down in ice-water. For NMR analysis, 1,3,5-trioxane (0.0450 g) as an internal standard and CHCl₃ (1.5 ml) were added into the reaction mixture. After being stirred vigorously and followed by centrifugation, the lower layer liquid (products) and the IL phase were collected, respectively. The qualitative analysis of the products was conducted using a GC-MS (Agilent 5975C-7890A) and by comparing with authentic samples. The yields of corresponding ethers were quantitatively analyzed by ¹H NMR using 1,3,5-trioxane as an internal standard. The yields of the reactions were calculated on the basis of the following equations:

Moles of the product obtained = Moles of the internal standard \times Peak area of the corresponding product obtained \times 6 / (Peak area of the internal standard \times The H number of corresponding product obtained)

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

To obtain the pure target product, the upper layer liquid of the mixture after reaction was collected by phase separation, and distilled under vacuum to remove MeOH.

1.4 Recycling of the catalyst

The reusability of the IL [HO-EtMIm][OTf] was tested using the benchmark reaction of **1a** ring-closing metathesis. After the reaction, the reaction mixture in the reactor was transferred into a centrifuge tube. After centrifugation, the IL phase was collected by phase separation and distilled under vacuum to remove the generated methanol. Then, [HO-EtMIm][OTf] was reused directly for the next run.

2. Additional data

О	IL (10 mol%)	C + MeOH
1a		1b
Entry	T (°C)	Yield of
		1b
1	140	94%
2	130	92%
3	120	91%
4	110	75%
5	100	47%
6	90	29%
7	80	17%
8	70	10%
9	60	0

 Table S1 Effect of temperature on the ring-closing metathesis of 1a.

Reaction conditions: **1a** (2 mmol), [HO-EtMIm][OTf] (10 mol%), 12 h. The products yields were determined by ¹H NMR analysis with 1,3,5-trioxane as an internal standard.

Note: As shown in Table S1, the reaction could take place even at 70 °C, and the yield of **1b** increased with temperature achieving 94% at 140 °C within 12 h.

[∧]N⁺ → ^{OH} F ↓ S → O⁻

1-hydroxyethyl-3-methyl imidazolium trifluoromethanesulfonate ([HO-EtMIm][OTf])

00 , ∽^{OH}F₃C^S, N^S, CF₃

1-hydroxyethyl-3-methyl imidazolium bis(trifluoro-methylsulfonate)imine ([HO-EtMIm][NTf₂])

[⊗]N⁺-∕_OH CI-

1-hydroxyethyl-3-methyl imidazolium chloride ([HO-EtMIm][CI])

[∞],N⁺ → ^{OH} cio₄-

1-hydroxyethyl-3-methyl limidazolium perchlorate ([HO-EtMIm][ClO₄])

Fig. S1 The ILs used in this work.

N⁺ → OH F ↓ S ∪ /

1-hydroxyethyl-2, 3-dimethyl imidazolium trifluoromethanesulfonate ([HO-EtMMIm][OTf])

,OH BF4

1-hydroxyethyl-3-methyl imidazolium tetrafluoroborate ([HO-EtMIm][BF₄])

° ∾_{N⁺}∽∽^{0H} ·0−s

1-butylsulfonate-3-methyl imidazolium tosylate ([HO-EtMIm][OTs])

NO₃

1-hydroxyethyl-3-methyl limidazolium nitrate ([HO-EtMIm][NO₃])

1-hydroxyethyl trimethyl ammonium trifluoromethanesulfonate ([HO-EtN₁₁₁][OTf])

N+.

1-hydroxyethyl-3-methyl imidazolium hexafluorophosphate ([HO-EtMIm][PF₆])

1-hydroxyethyl-3-methyl limidazolium dicyanamide ([HO-EtMIm][N(CN)₂])

^N^N⁺~ F↓S _/ 0.

1-hydroxyethyl-3-methyl limidazolium trifluoromethanesulfonate ([EMIm][OTf])



Fig. S2 Possible interaction structures of **1a** with (a) $[HO-EtMIm]^+$, (b) $[HO-EtN_{111}]^+$, (c) $[EtMIm]^+$, (d) $[OTf]^-$, (e) Cl⁻, (f) $[PF_6]^-$, and (g) **1a** optimized at M062X-D3/def2-TZVP level, on which the hydrogen bond distances and natural bond orbital (NBO) charges [black word: atom distance (Å), red word: NBO charges] are marked.





Fig. S3 GC-MS spectra of the ring-closing metathesis reactions of 1,4-butanediol monomethyl ether (1a). Reaction conditions: **1a** (2 mmol), [HO-EtMIm][OTf] (10 mol%), 120 °C, 12h.

Note: During the reaction, a small amount of dimethyl ether (DME) (Peak 1) and 1,4-dimethoxybutan (Peak 5) were obtained through the intermolecular dehydration etherification of methanol (the another proudct) and **1a** with methanol, respectively.



Fig. S4 Control experiment. Reaction conditions: **1b** (2 mmol), MeOH (2 mmol), 10 mol% of [HO-EtMIm][OTf], 120 °C, 12 h.



Fig. S5 ¹H NMR spectra of [HO-EtMIm][OTf] before and after reaction (after five cycles) recorded at 333.15K.



Fig. S6 ¹⁹F NMR spectra of [HO-EtMIm][OTf] before and after reaction (after five cycles) recorded at 333.15K.

Note: After five cycles, pure [HO-EtMIm][OTf] was collected via simple phase separation and drying under vacuum to remove unreacted alkoxy alcohols and generated MeOH. As shown in Figs. S5 and S6, the ¹H and ¹⁹F NMR of the [HO-EtMIm][OTf] before and after reaction remain unchanged, also supporting the good stability of the [HO-EtMIm][OTf].



Fig. S7 GC-MS spectra of the ring-closing metathesis reactions of 4-butoxy-1-butanol (**1a'**). Reaction conditions: **1a'** (2 mmol), [HO-EtMIm][OTf] (10 mol%), 120 °C, 36 h.













Fig. S8 GC-MS spectra of the ring-closing metathesis reactions of 5-benzyloxy-1-pentanol (**2a**). Reaction conditions: **2a** (2 mmol), [HO-EtMIm][OTf] (10 mol%), 120 °C, 48h.

Note: After the reaction, a small amount of benzyl ether (Peak 4) was obtained through the intermolecular dehydration etherification of benzyl alcohol (another product).





Fig. S9 GC-MS spectra of the ring-closing metathesis reactions of 2-(2-methoxymethylphenyl)ethanol (4a). Reaction conditions: **4a** (2 mmol), [HO-EtMIm][OTf] (50 mol%), 120 °C, 48 h.

Note: After the reaction, a small amount of DME (Peak 1) was obtained through the intermolecular dehydration etherification of methanol (the another proudct).





Fig. S10 GC-MS spectra of the ring-closing metathesis reactions of diethylene glycol monoethyl Ether (6a). Reaction conditions: 6a (2 mmol), [HO-EtMIm][OTf] (10 mol%), 120 °C, 48 h.

Note: After the reaction, a small amount of ether (Peak 1) was obtained through the intermolecular dehydration etherification of ethanol (the another proudct).



Fig. S11 The interaction figurations of **1a** with [HO-EtN₁₁₁][OTf] (a) and [HO-EtMMIm][OTf] (b) optimized at M062X-D3/def2-TZVP level [black word: atom distance (Å), red word: NBO charges].



Fig. S12 ¹⁹F NMR spectra of [HO-EtMIm][OTf] and the mixture of **1a** with [HO-EtMIm][OTf] recorded at 333.2 K.

Note: As shown in Fig. S12, the chemical shift assigned to the F atoms of $[OTf]^-$ shifted upfield as **1a** mixed with [HO-EtMIm][OTf], which may due to the electron transfer from the O atom of $[OTf]^-$ to the hydroxyl H atom when the hydroxyl H atom of **1a** forms H-bond with O atom of $[OTf]^-$ resulting in the electron transfer from the F atoms to the C atom of $[OTf]^-$. These results indicated that the F atoms play a key role in promoting the forming of H-bond between hydroxyl H atom of **1a** and O atom of $[OTf]^-$.



Fig. S13 In-situ ¹H NMR spectra recorded in **1a** transformation process catalyzed by [HO-EMIm][OTf] at 393.2 K.

Note: The time-dependent in-situ ¹H NMR spectra of the reaction systems were recorded in **1a** transformation process over [HO-EtMIm][OTf] at 120 °C. The ¹H NMR spectra were recorded every 60 s from 0 to 2 h, and 17 representative in-situ ¹H NMR spectra were selected to analyze the intermediates during the reaction process. As the reaction proceeded, it is obvious that the amounts of **1a** (the peaks at $\delta = 2.00$ and 3.99 ppm) declined with increases in the amounts of **1b** (the peaks at $\delta = 2.21$ and 4.06 ppm) and MeOH (the peak at $\delta = 3.75$ ppm). As shown in Fig. S13, the peak of hydroxyl H atoms of [HO-EMIm][OTf] and **1a** became broader at the beginning, which may be assigned to the hydroxyl H atoms of **TS1** formed from **1a** interacting with [HO-EMIm][OTf].



Fig. S14 Proposed reaction pathway.

NMR Data and Spectra

Tetrahydrofuran (1b)

¹H NMR (400 MHz, CDCl₃): δ/ppm= 4.08 – 3.41 (m, 4H), 2.46 – 1.46 (m, 4H).
¹³C NMR (101 MHz, CDCl₃): δ/ppm= 67.66, 25.41.
HR-MS(ESI+) calc. for C₄H₈ONa [M+Na]⁺ 95.04674, found 95.04674.

Phthalan (3b)



¹H NMR (400 MHz, CDCl₃): δ/ppm= 7.17 – 6.96 (m, 1H), 4.92 (d, 1H).
¹³C NMR (101 MHz, CDCl₃): δ/ppm= 139.32, 127.05, 120.82, 73.18.
HR-MS(ESI+) calc. for C₈H₈ONa [M+Na]⁺ 143.04674, found 143.04672.

Isochroman (4b)



¹**H NMR** (400 MHz, CDCl₃): δ/ppm= 7.02-6.96 (m, 2H), 6.92 – 6.86 (m, 1H), 6.74 – 6.71 (m, 1H), 4.55 (s, 2H), 3.74 – 3.65 (m, 2H), 2.63 – 2.46 (m, 2H).

¹³C NMR (101 MHz, CDCl₃): δ/ppm= 135.28, 133.40, 128.96, 126.37, 125.99, 124.50, 67.81, 65.21, 28.38.

HR-MS(ESI+) calc. for C₉H₁₀ONa [M+Na]⁺ 157.06239, found 157.06237.

1,4-Dioxane (6b)

0___0 6b

¹H NMR (400 MHz, CDCl₃): δ/ppm= 3.67 (s, 4H).

¹³C NMR (101 MHz, CDCl₃): δ/ppm= 66.85.

HR-MS(ESI+) calc. for C₄H₈O₂Na [M+Na]⁺ 111.04165, found 111.041766.









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