Supporting Information

Conversion of CO₂ into cyclic carbonates using an ionic porous

organic cage

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Table of Contents

- 1. Materials and methods
- 2. Synthetic procedures and characterization data
 - 2.1 Synthesis of OFT-RCC36+6Br-
 - 2.2 Synthesis of $OFT-RCC3^{6+}6NTf_2^{-}$
 - 2.3 Synthesis of OFT-RCC3⁶⁺6OTf⁻
 - 2.4 Synthesis of Model molecule (OFT-RMM²⁺2Br⁻)
- 3. Catalytic conversion of CO_2 and epoxide into cyclic carbonates
- 4. References

1. Materials and methods

All reagents were commercially available, used as supplied without further purification. ¹H and ¹³C{¹H} Nuclear Magnetic Resonance (NMR) spectra were collected on a Bruker Avance spectrometer (operating at 600 MHz for ¹H NMR and 151 MHz for ¹³C{¹H} NMR). Mass spectra were measured with an Agilent G6545 Q-TOF ESI MS instrument or MALDI-TOF-MS instrument.

2. Synthetic procedures and characterization data

2.1 Synthesis of OFT-RCC3⁶⁺6Br⁻

OFT-RCC3⁶⁺6Br⁻ was synthesized according to literature procedure.¹ **FT-RCC3** (120 mg, 0.099 mmol) was immersed in 1,2-dimethoxyethane (10 mL). *N*-Bromacetamide (106 mg, 0.77 mmol, 7.8 eq.) was added in two portions (0.385 mmol each) with an interval of 15 min. After addition of the second portion, the reaction mixture was stirred for 3 hours. The product precipitated and was isolated by filtration. After washing by Et₂O, **OFT-RCC3⁶⁺6Br**⁻ was purified and obtained. Yield: 140 mg, 84 %. ¹H NMR (600 MHz, CDCl₃, 298 K) δ (ppm): 8.27 (s, 6H, -N=CH), 7.52 (s, 12H, -ArH), 4.86 (d, 12H, -ArCH₂), 4.67 (d, 12H, -ArCH₂), 3.95 (d, 12H, CH on cyclohexane), 2.25 (d, 12H, CH₂ on cyclohexane), 1.98 (d, 12H, CH₂ on cyclohexane), 1.78 (s, 12H, CH₂ on cyclohexane), 1.46 (m, 12H, CH₂ on cyclohexane), 1.78 (s, 12H, CDCl₃, 298 K) δ (ppm): 162.08, 135.47,127.94, 69.16, 49.47, 27.14, 23.83.





Figure S2 ¹³C{¹H} NMR spectrum (151 MHz, CDCl₃, 298 K) of OFT-RCC3⁶⁺6Br⁻.



Figure S3 ESI-MS spectrum of OFT-RCC36+6Br⁻

2.2 Synthesis of OFT-RCC3⁶⁺6NTf₂⁻

Anion exchange: OFT-RCC3⁶⁺6Br⁻ (84 mg, 0.05 mmol) was dissolved in CH₃OH (10 ml) and stirred vigorously with 7.8 equiv. of AgNTf₂ (152 mg, 0.39 mmol) for 4 h. The filtrate was collected by filtration with the yellow precipitate separated from the solution, and the solvent was then removed under vacuum. OFT-RCC3⁶⁺6NTf₂⁻ was obtained after washing by dichloromethane. Yield: 115.5 mg, 80%. ¹H NMR (600 MHz, DMSO-*d*₆, 298 K) δ (ppm): 7.89 (s, 6H, -NCHN-), 7.28 (s, 12H, -ArH), 4.75 (d, 12H, -ArCH₂), 4.64 (d, 12H, -ArCH₂), 3.61- 3.60 (m, 12H, CH on cyclohexane), 2.46 (d, 12H, CH₂ on cyclohexane), 1.58 (d, 12H, CH₂ on cyclohexane), 1.40 (s, 12H, CH₂ on cyclohexane). ¹³C {¹H} NMR (151MHz, DMSO-*d*₆, 298 K) δ (ppm): 160.35 (N-C-N), 136.22 (ArC), 128.12 (ArC), 122.66, 120.52, 118.39, 116.26 (NTf₂-C), 68.69 (N-CH on cyclohexane), 48.86 (ArCH₂N), 27.03 (CH₂ on cyclohexane), 23.28 (CH₂ on cyclohexane). MS (ESI-HRMS): m/z [M-2NTf₂]²⁺ calcd for [C₈₀H₁₀₂F₂₄N₁₆O₁₆S₈]²⁺: 1163.7589, found: 1163.7590; [M-5NTf₂]⁵⁺ calcd for [C₈₀H₁₀₂F₆N₁₃O₄S₂]⁵⁺: 442.1721, found: 442.2414.

-7.88 -7.28 -7.28 4.76 4.63 4.63 3.61 4.63 3.61 (1.58 (1.58) (1.1.99 (1.1.98) (1.1.99) (1.1.20) (1.1.2









Figure S6 ESI-MS spectrum of OFT-RCC3⁶⁺6NTf₂⁻

2.3 Synthesis of OFT-RCC36+6OTf-

Anion exchange: OFT-RCC3⁶⁺6Br⁻ (84 mg, 0.05 mmol) was dissolved in CH₃OH (10 ml) and stirred vigorously with 7.8 equiv. of AgOTf (100 mg, 0.39 mmol) for 4 h. The filtrate was collected by filtration with the yellow precipitate separated from the solution, and the solvent was then removed under vacuum. OFT-RCC3⁶⁺6OTf⁻ was obtained after washing by dichloromethane. Yield: 83 mg, 79%. ¹H NMR (600 MHz, CDCl₃, 298 K) δ (ppm): 7.68 (s, 6H, -N=CH), 7.19 (s, 12H, -ArH), 4.71 (d, 12H, -ArCH₂), 4.51 (d, 12H, -ArCH₂), 3.80 (d, 12H, CH on cyclohexane), 2.30 (d, 12H, CH₂ on cyclohexane), 2.00 (d, 12H, CH₂ on cyclohexane), 1.75 (m, 12H, CH₂ on cyclohexane) 1.47 (s, 12H, CH₂ on cyclohexane). ¹³C {¹H} NMR (151MHz, DMSO-*d*₆, 298 K) δ (ppm): 160.81 (N-C-N), 135.35 (ArC), 128.25 (ArC), 121.71, 119.58 (OTf-C), 68.12 (N-CH on cyclohexane), 49.15 (ArCH₂N), 26.90 (CH₂ on cyclohexane), 23.45 (CH₂ on cyclohexane). MS (ESI-MS): m/z [M-OTf]⁺ calcd for: 1951.5947, found: 1951.5913; [M-2OTf]²⁺ calcd for: 901.3210 found: 901.3222; [M-3OTf]³⁺ calcd for: 551.2287; [M-4OTf]⁴⁺ calcd for: 376.1842, found: 376.1843.



Figure S7 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of OFT-RCC3⁶⁺6OTf⁻.



Figure S8 ${}^{13}C{}^{1}H$ NMR spectrum (151 MHz, DMSO- d_6 , 298 K) of OFT-RCC3⁶⁺6OTf⁻



Figure S9 ESI-MS spectrum of OFT-RCC36+6OTf-

2.4 Synthesis of Model molecule (OFT-RMM²⁺2Br⁻)

RMM: Here, (1R,2R)-*N*,*N*'-dibenzyl-1,2-diaminocyclohexane is called **RMM** for convenience, and **RMM** was synthesized according to literature procedure.²(*R*,*R*)-1,2-Diaminocyclohexane (2.283 g, 20.0 mmol) was dissolved in ethanol (40.0 mL). Benzaldehyde (4.062 mL, 40.0 mmol) was added dropwise to this solution at rt and stirred 24 h. The solution was cooled to 0 °C and diluted with 20.0 mL of ethanol. Sodium borohydride (1.513 g, 40.0 mmol) was added in portions to the reaction and stirred for another 24 h at rt. The solvent under vacuum was evaporated and the reaction was then quenched by the addition of water (100 mL) followed by the extraction with DCM (3×100 mL). The separated organics were dried over anhydrous sodium sulfate, filtered and the solvent evaporated to give the diamine **RMM** as a colorless oil. (5.87 g, 99 %). ¹H NMR (600 MHz, CDCl₃, 298 K) δ (ppm): 7.28-7.18 (m, 10H, ArH), 3.85 (d, 2H, PhCH₂N), 3.61 (d, 2H, PhCH₂N), 2.24-2.22 (m, 2H, CH on cyclohexane), 2.18 (m, 2H, NH), 2.12-2.10 (m, 2H, CH₂ on cyclohexane), 1.02-1.00 (m, 2H, CH₂ on cyclohexane), 1.02-1.00 (m, 2H, CH₂ on cyclohexane).



Figure S10 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of RMM.

FT-RMM: Paraformaldehyde (120 mg, 2 eq.) dissolved in CH₃OH (20 mL) was stirred at 70 °C. To this clear solution was added **RMM** (300 mg, 1.02 mmol) dissolved in CH₃OH (20 mL). The reaction was stirred for a further 2 h at 70 °C. The reaction was cooled to room temperature and the solvent was then removed under vacuum to give the product **FT-RMM**. Yield: 234 mg, 75%.¹H NMR (600 MHz, CDCl₃, 298 K) δ (ppm): 7.29 - 7.23 (m, 8H, ArH), 7.19-7.22 (m, 2H, ArH), 3.93 (d, 2H, PhCH₂N), 3.47 (s, 2H, NCH₂N), 3.32 (d, 2H, PhCH₂N), 2.33-2.27 (m, 2H, CH on cyclohexane), 1.89 (d, 2H, CH₂ on cyclohexane), 1.76 (d, 2H, CH₂ on cyclohexane), 1.24 (d, 4H, CH₂ on cyclohexane). ¹³C{¹H} NMR (151MHz, CDCl₃, 298 K) δ (ppm): 139.67, 128.65, 128.36, 126.95 (Ar-C), 77.46 (N-C-N), 69.43, 58.10, 29.78, 24.54 (C on cyclohexane).MS (ESI-MS): m/z [M+H]⁺ calcd for: 307.2174, found: 307.2171.

7.28 7.26 7.25 7.25 7.25 7.25 7.19

3.94 3.92 3.347 3.347 3.347 3.347 3.31 2.30 2.30 2.330 2.3312 2.331 2.3312 2.331





Figure S11 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of FT-RMM.



Figure S12 ${}^{13}C{}^{1}H$ NMR spectrum (151 MHz, CDCl₃, 298 K) of FT-RMM.



Figure S13 QTOF ESI-MS spectrum of FT-RMM

OFT-RMM²⁺**2Br⁻: FT-RMM** (160 mg, 0.53 mmol) was immersed in 1,2dimethoxyethane (10 mL). *N*-Bromacetamide (190 mg, 1.4 mmol, 2.6 eq.) was added in two portions (0.7 mmol each) with an interval of 15 min. After addition of the second portion, the reaction mixture was stirred for 3 hours. The solvent was then removed under vacuum and **OFT-RMM**²⁺**2Br**⁻ was purified by washing with Et₂O. Yield: 180 mg, 88%. ¹H NMR (600 MHz, CDCl₃, 298 K) δ (ppm): 9.41 (s, 1H, NCHN), 7.42 -7.40 (m, 10H, ArH), 4.93 (d, 2H, PhCH₂N), 4.83 (d, 2H, PhCH₂N), 3.47 (d, 2H, CH on cyclohexane), 2.08 (d, 2H, CH₂ on cyclohexane), 1.83 (d, 2H, CH₂ on cyclohexane), 1.45-1.42 (m, 2H, CH₂ on cyclohexane), 1.22 (m, 2H, CH₂ on cyclohexane). ¹³C{¹H} NMR (151MHz, CDCl₃, 298 K) δ (ppm): 160.33 (N-C-N) 132.53, 129.39, 129.08, 128.53 (Ar-C), 66.11, 51.55, 27.53, 22.71 (C on cyclohexane). MS (ESI-MS): m/z [M-Br]⁻ calcd for: 305.2013, found: 305.2014.



Figure S15 ¹³C{¹H} NMR spectrum (151 MHz, CDCl₃, 298 K) of OFT-RMM²⁺2Br⁻.



Figure S16 QTOF ESI-MS spectrum of OFT-RMM²⁺2Br⁻

3. Catalytic conversion of CO₂ and epoxide into cyclic carbonates

General experimental procedure: Each batch of **OFT-RCC3⁶⁺6Br**⁻ was activated under vacuum at 85 °C for 12 h before use. **OFT-RCC3⁶⁺6Br**⁻ (0.027 mmol, 45 mg) and 90 mmol of epoxides were added into a reaction kettle (25 mL), followed by DBU (0.03 mol%) in some cases. After the reaction kettle was evacuated, 0.5 MPa CO₂ was introduced into the reaction mixture under stirring. The reaction mixture was stirred at 100 °C for 24 h. The reaction mixture was cooled and all the product yields were analyzed by ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard.



Figure S17 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with epichlorohydrin as substrate without catalyst. Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S18 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with epichlorohydrin as substrate catalyzed by **OFT-RCC3⁶⁺6Br**⁻ (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S19 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with epibromohydrin as substrate catalyzed by **OFT-RCC3⁶⁺6Br⁻** (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S20 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with glycidol as substrate catalyzed by **OFT-RCC3⁶⁺6Br**⁻ (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S21 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with 3,4-epoxy-1-butene as substrate catalyzed by **OFT-RCC3⁶⁺6Br⁻** (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S22 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with 1,2-epoxybutane as substrate catalyzed by **OFT-RCC3⁶⁺6Br**⁻ (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S23 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with glycidyl methacrylate as substrate catalyzed by **OFT-RCC3⁶⁺6Br⁻** (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S24 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with allyl glycidyl ether as substrate catalyzed by **OFT-RCC3⁶⁺6Br⁻** (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S25 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with glycidyl propargyl ether as substrate catalyzed by **OFT-RCC3⁶⁺6Br**⁻ (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S26 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with t-butyl glycidyl ether as substrate catalyzed by **OFT-RCC3⁶⁺6Br⁻** (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S27 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with 1,2-epoxyhexane as substrate catalyzed by **OFT-RCC3⁶⁺6Br**⁻ (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S28 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with styrene oxide as substrate catalyzed by **OFT-RCC3⁶⁺6Br⁻** (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S29 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with phenyl glycidyl ether as substrate catalyzed by **OFT-RCC3⁶⁺6Br⁻** (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S30 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with (S)-(+)-glycidyl Phthalimide as substrate catalyzed by **OFT-RCC3⁶⁺6Br⁻** (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S31 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with 2-decyloxirane as substrate catalyzed by **OFT-RCC3⁶⁺6Br**⁻ (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S32 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with epichlorohydrin as substrate catalyzed by **OFT-RCC3⁶⁺6Br**⁻ (0.03 mol%) and DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S33 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with epibromohydrin as substrate catalyzed by **OFT-RCC3⁶⁺6Br**⁻ (0.03 mol%) and DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S34 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with glycidol as substrate catalyzed by **OFT-RCC3⁶⁺6Br**⁻ (0.03 mol%) and DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S35 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with 3,4-epoxy-1-butene as substrate catalyzed by **OFT-RCC3⁶⁺6Br⁻** (0.03 mol%) and DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S36 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with 1,2-epoxybutane as substrate catalyzed by **OFT-RCC3⁶⁺6Br⁻** (0.03 mol%) and DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S37 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with glycidyl methacrylate as substrate catalyzed by **OFT-RCC3⁶⁺6Br**⁻ (0.03 mol%) and DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S38 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with allyl glycidyl ether as substrate catalyzed by **OFT-RCC3⁶⁺6Br**⁻ (0.03 mol%) and DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S39 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with glycidyl propargyl ether as substrate catalyzed by **OFT-RCC3⁶⁺6Br**⁻ (0.03 mol%) and DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S40 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with t-butyl glycidyl ether as substrate catalyzed by **OFT-RCC3⁶⁺6Br**⁻ (0.03 mol%) and DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S41 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with 1,2-epoxyhexane as substrate catalyzed by **OFT-RCC3⁶⁺6Br**⁻ (0.03 mol%) and DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S42 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with styrene oxide as substrate catalyzed by **OFT-RCC3⁶⁺6Br**⁻(0.03 mol%) and DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S43 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with phenyl glycidyl ether as substrate catalyzed by **OFT-RCC3⁶⁺6Br**⁻ (0.03 mol%) and DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S44 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with (S)-(+)-glycidyl Phthalimide as substrate catalyzed by **OFT-RCC3⁶⁺6Br**⁻ (0.03 mol%) and DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S45 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with cyclohexene oxide as substrate catalyzed by **OFT-RCC3⁶⁺6Br**⁻ (0.03 mol%) and DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S46 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with 2-decyloxirane as substrate catalyzed by **OFT-RCC3⁶⁺6Br⁻** (0.03 mol%) and DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S47 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with epichlorohydrin as substrate catalyzed by DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S48 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with epibromohydrin as substrate catalyzed by DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S49 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with glycidol as substrate catalyzed by DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S50 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with 3,4-epoxy-1-butene as substrate catalyzed by DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S51 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with 1,2-epoxybutane as substrate catalyzed by DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S52 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with glycidyl methacrylate as substrate catalyzed by DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S53 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with allyl glycidyl ether as substrate catalyzed by DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S54 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with glycidyl propargyl ether as substrate catalyzed by DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S55 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with t-butyl glycidyl ether as substrate catalyzed by DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S56 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with 1,2-epoxyhexane as substrate catalyzed by DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S57 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with styrene oxide as substrate catalyzed by DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S58 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with phenyl glycidyl ether as substrate catalyzed by DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.



Figure S59 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of the reaction mixture with (S)-(+)-glycidyl Phthalimide as substrate catalyzed by DBU (0.03 mol%). Reaction condition: epoxides 90 mmol, solvent free, temperature 100 °C, reaction pressure 0.5 MPa, time 24 h.

Catalysts	Yield (%)	TON	Ref.
OFT-RCC3 ⁶⁺ 6Br ⁻	86	2867	This work
$ \begin{array}{c} & \overset{Bu}{}_{N} \\ & \overset{Bu}{}_{N} \\ & \overset{Bu}{}_{N} \\ & \overset{Bu}{}_{Bu} \end{array} $	99	132	3
(OH) ₆ (OH) ₆ (OH) ₁₄ $(OH)_{14}$ $(OH)_{14}$	86	259	4
$\bigcup_{\substack{N\\ \oplus}}^{OH} Br Bu Br Bu IL-2$	90	900	5
$\begin{array}{c} HO \xrightarrow{/} N \\ BU \xrightarrow{N} Br \end{array} \begin{array}{c} Br \end{array} Br $	97	97	6
$ \begin{array}{c} \stackrel{\textcircled{\oplus}}{}_{N} \stackrel{\overset{}{}}{}_{N} \stackrel{\overset{\overset{}{}}}{}_{R} = n \text{-hexyl} \\ \hline C_1 C_6 \text{Im} HCO_3 \end{array} $	82	41	7
$Bu \xrightarrow{N} N \xrightarrow{R} R = i - Bu$ $\downarrow \odot OH 12$	99	50	8
	98	123	9
[HEBim][Asp]			
$HN \xrightarrow{N}_{\oplus} N \xrightarrow{H}_{O} N \xrightarrow{H}_{O} N \xrightarrow{H}_{O} UDIL-1-I$	99	83	10

Table S1 Comparison of catalytic TON and yield using epichlorohydrin as substrateamong imidazolium-based catalysts and OFT-RCC3⁶⁺6Br⁻

(APbim][Glu] = 0	98	327	11
HO VIMEtOH][Br]-72	100	76	12
HN N HCPImBr	84	168	13
Br 1 Br 1	87	48	14
$ \begin{array}{c} F_{3}C \\ \hline \\ \hline \\ \\ \hline \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $	99	495	15
$ \begin{array}{c} $	99	99	16
$ \underbrace{ \sum_{\substack{N \\ \oplus}} Cl^{\ominus} }_{\mathbb{T}} 1c $	91	362	17

Entry	Substrate	Product	Catalyst	Yield ^b (%)	Conv. (%)	TON°	TOF (h ⁻¹) ^d
1		Ö	Cage	86	86	2867	119
		o o	Cage+DBU	100	100	3333	139
		Cl	DBU	70	71	2333	97
	_	o O Br	Cage	90	90	3000	125
2	Br		Cage+DBU	100	100	3333	139
	~		DBU	88	91	2933	122
		о он	Cage	60	99	2000	83
3	ОН		Cage+DBU	76	99	2533	105
	`		DBU	50	99	1666	69
	0		Cage	30	30	1000	42
4			Cage+DBU	84	84	2800	117
	·		DBU	20	20	666	28
	0	O II	Cage	31	31	1033	43
5		0,00	Cage+DBU	66	68	2200	92
	•		DBU	7	15	233	10
			Cage	61	61	2033	85
6			Cage+DBU	93	93	3100	129
			DBU	0	0	0	0
			Cage	47	48	1567	65
7			Cage+DBU	90	93	3000	125
			DBU	10	10	333	14
			Cage	34	34	1133	47
8			Cage+DBU	52	52	1733	72
			DBU	0	0	0	0
	Q	γ°	Cage	30	30	1000	42
9	γ_{0}		Cage+DBU	83	83	2767	115
			DBU	0	0	0	0
10 <			Cage	40	41	1333	56
	\sim		Cage+DBU	66	66	2200	92
	~ ~		DBU	0	0	0	0
11			Cage	45	45	1500	63
			Cage+DBU	74	76	2467	103
			DBU	5	5	167	7
12			Cage	50	50	1667	69
			Cage+DBU	85	85	2833	118
			DBU	23	24	767	32

 Table S2 Cycloaddition Reaction of CO2 with various Epoxides^a.

13	$\left \begin{array}{c} \begin{array}{c} \begin{array}{c} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \end{array} \right\rangle \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} $		Cage	61	61	2033	85
		Cage+DBU	80	80	2667	111	
		Ő	DBU	0	0	0	0
14	\sim	Cage	6	11	200	8	
			Cage+DBU	9	10	300	13
			DBU	0	0	0	0
15		\land 0	Cage	4	4	133	6
			Cage+DBU	6	10	200	8
			DBU	0	0	0	0

^aReaction conditions: 90 mmol epichlorohydrin, solvent free, **OFT-RCC3⁶⁺6Br**⁻ (0.03 mol%) and/or DBU (0.03 mol%). ^b1,1,2,2-Tetrachloroethane was used as an internal standard and crude yields were checked by ¹H NMR. ^cTON (turnover number) = mole of the product/mole of the catalyst. ^dTOF = turnover frequency.



Figure S60 Proposed mechanism for the formation of cyclic carbonates from epoxides and CO_2 catalyzed by OFT-RCC3⁶⁺6Br⁻. The rest of the structure has been omitted for clarity.

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