Electronic Supplementary Information For:

Oxidation of olefins using molecular oxygen catalyzed by part-per-million level of recyclable copper catalyst under mild conditions

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1. Experimental methods

1.1 Materials and characterization methods

All solvents and chemicals were analytically pure agents purchased from commercial sources and were used without further purification unless otherwise indicated. The quantitative analysis of reactants and products was performed on a Shimadzu GC2014 gas chromatograph equipped with a WondaCAP-5 capillary column (5% Diphenyl 95% Dimethylpolysiloxane 30m×0.32mm×0.25μm) with a flame-ionization detector. A Shimadzu GCMS-QP2010 was used to identify substrates and their oxidation products resulting from catalysis. $^1$H NMR and $^{13}$C NMR spectra of ligands were recorded on a Bruker 400 MHz spectrometer. Ultraviolet-visible spectrum of different catalysts were recorded using a Shimadzu UV-3600 spectrophotometer (acetic acid as solvent). ESI Mass spectra of different catalysts were recorded using a Shimadzu LCMS-8030 ESI Mass Spectrometer.

1.2 General procedure for the synthesis of copper catalysts with an imidazole salt tag [Cu-Imace-R-H] $^\text{[X]}$ (X$^-$=F$^-$, Cl$^-$, Br$^-$, I$^-$, CF$_3$CO$_2$-, HSO$_4$-, NO$_3$-, PF$_6$-, or BF$_4$-; R=H or CH$_3$)

The catalysts were synthesized according our previous procedures (ref. 49). In a typical experiment, 12.6 g (0.01 mol) 1-imidazoleacetic acid (Imace-H) was reacted with 11.0 g (0.11 mol) hydrochloric acid (36%) in 60 ml water at 50 °C for 3 h. The reaction mixture was evaporated under reduced pressure at 80 °C, and a white powder was obtained. Water was used to recrystallize the powder, and pure [Imace-H-H][Cl] was obtained. Subsequently, 14.6 g (0.090 mol) [Imace-H-H][Cl] was reacted with 8.9 g (0.045 mol) Cu(OAc)$_2$•H$_2$O in 100 ml water at 100 °C. The generated acetic acid was removed using water vapor. New amount of water (50 ml) was continuously added into the reaction system until the reaction was completed. The reaction mixture was then evaporated under reduced pressure at 80 °C, and a light-green
powder was obtained. Water was used to recrystallize the powder to obtain pure \([\text{Cu-Imace-H-H-Cl}]\) (yield: 88.4%).

**Scheme S1** Generation method for preparing \([\text{Cu-Imace-R-H-X}]\) (X = F\(^-\), Cl\(^-\), Br\(^-\), I\(^-\), CO\(_2\)CF\(_3\)^-, SO\(_4\)H\(^-\), NO\(_3\)^-, PF\(_6\)^-, or BF\(_4\)^-; R=H or CH\(_3\))

### 1.3 Procedure for the synthesis of \([\text{Cu-Imace-H-CH}_3][\text{I}]\)

2.52g (0.02 mol) 1-imidazoleacetic acid (Imace-H) was reacted with 2.0 g (0.01 mol) Cu(OAc)\(_2\)•H\(_2\)O in 30 ml water at 100 °C. The generated acetic acid was removed using water vapor. New water was continuously added into the reaction system until the reaction was completed. The reaction mixture was then evaporated until the mixture left about 15mL under reduced pressure at 80 °C. The suspended mixture was cooled to room temperature. After filtration, the precipitate was washed repeatedly with water, and dried under vacuum at 60 °C. The pure Cu-Imace-H was obtained. Subsequently, 1.57g (0.005 mol) Cu-Imace-H was reacted with 1.7g (0.012 mol) CH\(_3\)I in 20 ml acetonitrile at 30 °C. The suspended mixture was stirred continuously for 24 h, then the reaction mixture was evaporated under reduced pressure at 50 °C, and a blue powder was obtained. Water was used to recrystallize the powder, and pure \([\text{Cu-Imace-H-CH}_3][\text{I}]\) was obtained. (Yield: 83.6%).
1.4 General procedure for cyclohexene epoxidation

The epoxidation reactions were carried out in tailored tubes equipped with a condensing unit (-30°C ethanol as a cooling medium for the condensing to prevent the volatilization of solvent). Typically, 50 mL acetonitrile, 0.2 mol substrate, 0.2mol isobutylaldehyde and 0.08%mol (relative to the molar equivalent of substrate) catalysts were mixed with stirring at 60 °C. Then, molecular oxygen (>99.0%) was bubbled through the solution and the reaction times were given in the tables or figures of the manuscript. o-dichlorobenzene was used as an internal standard for the determination of yield and selectivity. The filtered liquid samples were analyzed by GC and GC-MS.

1.5 General procedure for catalyst recycling

The epoxidation reactions were carried out in tailored tubes equipped with a condensing unit (-30°C ethanol as a cooling medium for the condensing to prevent the volatilization of solvent). 50 mL acetonitrile, 0.2 mol substrate, 0.2mol isobutylaldehyde and 0.08%mol (relative to the molar equivalent of substrate) catalysts were mixed with stirring at 60 °C. Then, molecular oxygen (>99.0%) was bubbled through the solution. The catalyst can be performed by simple filtration after the completion of the reactions, the recycled catalyst was washed by
diethyl ether, then dried at 60 °C overnight. The reactions were performed under the same conditions using the recovered catalyst.

2. **The influence of BHT for the oxidation**

Procedure for cyclohexene epoxidation in the presence of BHT (3,5-di-tert-butyl-p-hydroxytoluene): The epoxidation reactions were carried out in tailored tubes equipped with a condensing unit (-30°C ethanol as a cooling medium for the condensing to prevent the volatilization of solvent). 50 mL acetonitrile, 0.2 mol substrate, 0.2mol isobutyaldehyde and 0.08%mol (relative to the molar equivalent of substrate) catalysts were mixed with stirring at 60 °C. Then, molecular oxygen (>99.0%) was bubbled through the solution. After 2 hours, 0.1g BHT was added into the catalytic system.

![Fig. S1. The influence of BHT for the oxidation. Black line: normal reaction. Red line, 0.1g BHT was added after 2 hours.](image)

3. **The results of different reaction conditions**

3.1 **Reaction temperature**

3.1.1 **Solvent**
Fig. S2 Profile of the conversion rates of cyclohexene oxide for different amount of solvent (cyclohexene (0.2mol), solvent (CH₃CN, mL), isobutyraldehyde (0.2mol), the catalyst-to-substrate molar ratio is 800ppm, 60 °C, O₂ bubbling (1atm). Products formed in the epoxidation reactions with olefins were identified by GC and GC-MS.)

Fig. S3 The performance of loading different amount of solvent in the cyclohexene (cyclohexene (0.2mol), solvent (CH₃CN, mL), isobutyraldehyde (0.2mol), the catalyst-to-substrate molar ratio is 800ppm, 60 °C, O₂ bubbling (1atm), 10h. Products formed in the epoxidation reactions with olefins were identified by GC and GC-MS.)

3.2 The molar ratio of isobutyraldehyde-to- cyclohexene
The characterization results of the catalysts

[Imace-H-H][F]: ¹H-NMR (400MHz, D₂O) δ (ppm) 4.76 (2H, s, CH₂), 7.32 (H, m, N-CH), 8.58 (H, s, N-CH). ¹³C-NMR (100MHz, D₂O) δ (ppm) 51.34 (-CH₂-), 119.23 (N-CH), 122.87 (N-CH), 135.38 (N-CH-N), 172.01 (-COOH). [Cu-Imace-H-H][F]: UV-vis (Acetic acid) λ_max (nm) 247.38. Elemental analysis: C₁₀H₁₂F₂N₄O₄Cu·0.5H₂O, Calc. C 33.11, H 3.61, N 15.44; Found C 32.85, H 3.21, N 15.12. MS (ESI) m/z=157 ([Cu-Imace-H-H]²⁺).
[Imace-H-H][Cl]: $^1$H-NMR (400MHz, D$_2$O) $\delta$ (ppm) 4.99 (2H, s, CH$_2$), 7.31 (H, s, N-CH), 8.63 (H, s, N-CH). $^{13}$C-NMR (100MHz, D$_2$O) $\delta$ (ppm) 49.66 (-CH$_2$-), 119.43 (N-CH), 122.97 (N-CH), 135.81 (N-CH-N), 169.77(-COOH). [Cu-Imace-H-H][Cl]: UV-vis (Acetic acid) $\lambda_{\text{max}}$ (nm) 249.13. Elemental analysis: C$_{10}$H$_{12}$Cl$_2$N$_4$O$_4$Cu, Calc. C 31.06, H 3.13, N 14.49; Found C 30.04, H 2.90, N 15.07. MS (ESI) m/z=157 ([Cu-Imace-H-H]$^{2+}$).

[Imace-H-H][Br]: $^1$H-NMR (400MHz, D$_2$O) $\delta$ (ppm) 4.99 (2H, s, CH$_2$), 7.32 (H, d, N-CH), 8.64 (H, s, N-CH). $^{13}$C-NMR (100MHz, D$_2$O) $\delta$ (ppm) 49.85 (-CH$_2$-), 119.47 (N-CH), 123.04 (N-CH), 135.84 (N-CH-N), 169.63(-COOH). [Cu-Imace-H-H][Br]: UV-vis (Acetic acid) $\lambda_{\text{max}}$ (nm) 249.48. Elemental analysis: C$_{10}$H$_{12}$Br$_2$N$_4$O$_4$Cu, Calc. C 25.26, H 2.54, N 11.78; Found C 26.20, H 2.45, N 12.32. MS (ESI) m/z=157 ([Cu-Imace-H-H]$^{2+}$).

[Imace-H-H][I]: $^1$H-NMR (400MHz, D$_2$O) $\delta$ (ppm) 4.92 (2H, s, CH$_2$), 7.39 (H, s, N-CH), 8.67 (H, s, N-CH). $^{13}$C-NMR (100MHz, D$_2$O) $\delta$ (ppm) 50.79 (-CH$_2$-), 119.39 (N-CH), 123.01 (N-CH), 135.64 (N-CH-N), 171.11(-COOH). [Cu-Imace-H-H][I]: UV-vis (Acetic acid) $\lambda_{\text{max}}$ (nm) 248.77. Elemental analysis: C$_{10}$H$_{12}$I$_2$N$_4$O$_4$Cu, Calc. C 21.09, H 2.12, N 9.84; Found C 21.31, H 2.41, N 10.05. MS (ESI) m/z=157 ([Cu-Imace-H-H]$^{2+}$).

[Imace-H-H][NO$_3$]: $^1$H-NMR (400MHz, D$_2$O) $\delta$ (ppm) 4.98 (2H, s, CH$_2$), 7.32 (H, d, N-CH), 8.62 (H, s, N-CH). $^{13}$C-NMR (100MHz, D$_2$O) $\delta$ (ppm) 49.57 (-CH$_2$-), 119.42 (N-CH), 122.94 (N-CH), 135.88 (N-CH-N), 169.83(-COOH). [Cu-Imace-H-H][NO$_3$]: UV-vis (Acetic acid) $\lambda_{\text{max}}$ (nm) 250.34. Elemental analysis: C$_{10}$H$_{12}$N$_6$O$_{10}$Cu, Calc. C 27.31, H 2.75, N 19.11; Found C 27.99, H 3.02, N 19.30. MS (ESI) m/z=157 ([Cu-Imace-H-H]$^{2+}$).

[Imace-H-H][HSO$_4$]: $^1$H-NMR (400MHz, D$_2$O) $\delta$ (ppm) 4.86 (2H, s, CH$_2$), 7.24 (H, s, N-CH), 8.53 (H, s, N-CH). $^{13}$C-NMR (100MHz, D$_2$O) $\delta$ (ppm) 49.80 (-CH$_2$-), 119.40 (N-CH), 122.85 (N-CH), 135.77 (N-CH-N), 170.09(-COOH). [Cu-Imace-H-H][HSO$_4$]: UV-vis (Acetic acid) $\lambda_{\text{max}}$ (nm) 250.88. Elemental analysis: C$_{10}$H$_{14}$S$_2$N$_4$O$_{12}$Cu, Calc. C 23.56, H 2.77, N 10.99;

[Imace-H-H][CF₃COO]: ¹H-NMR (400MHz, D₂O) δ (ppm) 4.92 (2H, s, CH₂), 7.28 (H, d, N-CH), 8.58 (H, s, N-CH). ¹³C-NMR (100MHz, D₂O) δ (ppm) 49.61 (-CH₂⁻), 119.39 (N-CH), 122.90 (N-CH), 135.72 (N-CH-N), 169.82(-COOH). [Cu-Imace-H-H][CF₃COO]: UV-vis (Acetic acid) λmax (nm) 247.01. Elemental analysis: C₁₄H₁₂F₆N₄O₈Cu, Calc. C 31.04, H 2.23, N 10.34; Found C 32.07, H 2.43, N 10.04. MS (ESI) m/z=157 ([Cu-Imace-H-H]²⁺).

[Imace-H-H][BF₄]: ¹H-NMR (400MHz, D₂O) δ (ppm) 4.92 (2H, s, CH₂), 7.38 (H, s, N-CH), 8.65 (H, s, N-CH). ¹³C-NMR (100MHz, D₂O) δ (ppm) 50.85 (-CH₂⁻), 119.37 (N-CH), 122.96 (N-CH), 135.64 (N-CH-N), 170.89(-COOH). [Cu-Imace-H-H][BF₄]: UV-vis (Acetic acid) λmax (nm) 246.48. Elemental analysis: C₁₀H₁₂B₂F₈N₄O₄Cu, Calc. C 24.54, H 2.47, N 11.45; Found C 23.81, H 2.56, N 12.03. MS (ESI) m/z=157 ([Cu-Imace-H-H]²⁺).

[Imace-H-H][PF₆]: ¹H-NMR (400MHz, D₂O) δ (ppm) 5.02 (2H, s, CH₂), 7.39 (H, dt, N-CH), 8.68 (H, t, N-CH). ¹³C-NMR (100MHz, D₂O) δ (ppm) 49.83 (-CH₂⁻), 119.47 (N-CH), 122.97 (N-CH), 135.89 (N-CH-N), 170.27(-COOH). [Cu-Imace-H-H][PF₆]: UV-vis (Acetic acid) λmax (nm) 247.18. Elemental analysis: C₁₀H₁₂Cl₂N₄O₄Cu, Calc. C 24.54, H 2.47, N 11.45; Found C 25.08, H 2.66, N 11.62. MS (ESI) m/z=157 ([Cu-Imace-H-H]²⁺).

[Imace-CH₃-H][Cl]: ¹H-NMR (400MHz, D₂O) δ (ppm) 2.46 (H, s, -CH₃), 5.01 (2H, s, CH₂), 7.36 (H, s, N-CH). ¹³C-NMR (100MHz, D₂O) δ (ppm) 9.13 (-CH₃), 49.14 (-CH₂⁻), 122.36 (N-CH), 122.37 (N-CH), 146.86 (N-CH-N), 169.41 (-COOH). [Cu-Imace-CH₃-H][Cl]: UV-vis (Acetic acid) λmax (nm) 251.78. Elemental analysis: C₁₂H₁₆Cl₂N₄O₄Cu: Calc. C 34.75, H 3.89, N 13.51; Found C 35.01, H 3.30, N 14.04. MS (ESI) m/z=171 ([Cu-Imace-CH₃-H]²⁺).

5 The original NMR spectrum

$^1$HNMR

$^1$CNMR
$^1$HNMR

$[{\text{image-H-H}}][\text{Cl}]$

$^1$HNMR

$[{\text{image-H-H}}][\text{Cl}]$

$^1$CNMR

$[{\text{image-H-H}}][\text{Cl}]$
$^1$HNMR

[Imac-e-H-H][HSO$_4$]

$^{13}$CNMR

[Imac-e-H-H][HSO$_4$]
$^1$HNMR

[Imace-CH$_2$-H]

$^1$CNMR

[Imace-CH$_2$-H]
$^1$HNMR

$[\text{Imace-CH}_2\text{-H}][\text{Cl}]$

$^13$CNMR

$[\text{Imace-CH}_2\text{-H}][\text{Cl}]$
6 The GC conditions for each of the substrates tested

The quantitative analysis of reactants and products was performed on a Shimadzu GC2014 gas chromatograph equipped with a WondaCAP-5 capillary column (5% Diphenyl 95% Dimethylpolysiloxane 30m×0.32mm×0.25µm) with a flame-ionization detector. A Shimadzu GCMS-QP2010 was used to identify substrates and their oxidation products resulting from catalysis.

**GC Condition:**
- Injection Port SPL1
- Injection Mode: Split
- Carrier Gas: N2
- Flow Control: Pressure
- Pressure: 45.8 KPa
- Total Flow: 37.7 mL/min
- Column Flow: 1.33 mL/min
- Purge Flow: 3.0 mL/min
- Splitter Ratio: 25

**GC methods:**

**Method 1**
- Injection Port temperature: 280 °C
- FID Detector Temperature: 290 °C
- [Column Oven]
  - Initial Temperature: 50 °C
  - Equilibration Time: 2.0 min

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- Injection Port temperature: 280 °C
- FID Detector Temperature: 290 °C
- [Column Oven]
  - Initial Temperature: 50 °C
  - Equilibration Time: 2.0 min

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FID Detector Temperature: 300 °C

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7 The original GC-MS of products
行号#8 保留时间:4.360(扫描数#:773) 质量峰:314
原始模式:单个 4.360(773) 基峰:68.00(3558417)
背景模式:无 组1 - 事件1

命中#1 输入:1427 库号:NIST14.1ib
S1:98 分子式:C8H10O CAS:900-69-7 摩尔质量:96 保留指数:873
组分名称:2-Cyclohexen-1-one $$ Cyclohex-2-en-1-one $$ Cyclohexen-2-one $$ 1-Cyclohexen-3-one $$ 2-Cyclohexen

原始模式:单个 8.450(121) 基峰:70.05(6278336)
背景模式:无 组1 - 事件1

命中#1 输入:4655 库号:NIST14.1ib
S1:97 分子式:C12H20O2 CAS:1460-57-1 摩尔质量:216 保留指数:1096
组分名称:1,2-Cyclohexanediol, trans- $$ trans-1,2-Cyclohexanediol $$ trans-1,2-Dihydroxycyclohexane $$ 1,2-

行号#13 保留时间:4.750(扫描数#:751) 质量峰:397
原始模式:单个 4.750(751) 基峰:55.00(5724454)
背景模式:无 组1 - 事件1

命中#1 输入:0032 库号:NIST14.1ib
S1:96 分子式:C8H14O CAS:4925-71-7 摩尔质量:126 保留指数:970
组分名称:9-Oxabicyclo[6.1.0]nonane, cis- $$ 9-Oxabicyclo[6.1.0]nonane # $$