Electronic Supplementary Material (ESI) for ChemComm.

# Catalytic epoxidation by perrhenate through the formation of organic-phase supramolecular ion pairs

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## Supporting Information

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# 1. Synthesis and characterization of the [HL$^n$][ReO$_4$] SIPs

## 1.1. General remarks

All preparations were carried out in the air. Perrhenic acid 99.99% (trace metal basis), 76.5% solution in water and cis-cyclooctene (95%) were purchased from Acros Organics and used without further purification. Hydrogen peroxide solution 50 wt. % in $H_2O$ was purchased from Sigma Aldrich. 2-(4,6-di-tert-butylpyridin-2-yl)-N,N'-dihexylmalonamide (L$^1$), N-[(Di-n-hexylamino)methyl]benzamide (L$^2$) and N-[(Di-n-hexylamino)methyl]-3,5,5-trimethylhexanamide (L$^3$) were synthesized according to literature procedures.[S1,S2]

Microanalyses of the obtained products were carried out in the Mikroanalytisches Labor of the Technische Universität München in Garching.

$^1$H- and $^{13}$C{$^1$H} NMR spectra were recorded in $CDCl_3$ and toluene-d$_8$ with a 400-MHz Bruker Avance DPX-400 spectrometer ($^1$H: 400 MHz; $^{13}$C{$^1$H} 101 MHz). DOSY NMR spectra were recorded using a Bruker Avance 500 spectrometer in $C_6D_6$ and $CD_3CN$.

IR spectra were recorded on a Varian IR FT670 using a diamond crystal ATR cell.

Catalytic runs were monitored by GC on a Hewlett-Packard HP 5890 Series II chromatograph equipped with a FID, a Supelco column Alphadex 120 and a Hewlett-Packard integration unit 3396 Series II.

TGA-MS experiments were carried out on a Netzsch STA 409 PC instrument with argon as carrier gas and a temperature step rate of 10 °C per minute in the range of 25-1000 °C.

The melting point of [HL$^1$][ReO$_4$] was determined on a MPM-H2 melting point meter.

ESI FT-ICR MS experiments were recorded on a Bruker 12 T SolariX FT-ICR MS in positive-ion mode with the source temperature set to 50 °C.

### 1.2. General synthesis of [HL$^n$][ReO$_4$] (n = 1, 2, 3)

To a stirred solution of 500 mg (1.0 mmol, 1.0 equiv.) L$^1$ in 1 mL toluene, 0.15 mL (1.0 mmol, 1.0 equiv.) of perrhenic acid (76.5% solution in $H_2O$) was added and stirred for 16 h at room temperature. (**[HL$^2$][ReO$_4$]**: 319 mg (1.0 mmol, 1.0 equiv.) L$^2$ and 0.15 mL (1.0 mmol, 1.0 equiv.) of perrhenic acid (76.5% solution in $H_2O$); **[HL$^3$][ReO$_4$]**: 355 mg (1.0 mmol, 1.0 equiv.) L$^3$ and 0.15 mL (1.0 mmol, 1.0 equiv.) of perrhenic acid (76.5 % solution in $H_2O$). Afterwards the organic phase was separated, washed with $H_2O$, dried over $Na_2SO_4$ and evaporated to dryness under vacuum. The resulting residue was washed three times with *n*-hexane to yield the analytically pure, toluene-soluble perrhenate salts [HL$^n$][ReO$_4$] (n = 1, 2, 3).

**[HL$^1$][ReO$_4$]**: colorless solid; Yield: 90 %; $^1$H NMR ($CDCl_3$): δ(ppm) = 14.67 (s, 1H, py-N*H*), 7.97 – 7.82 (m, 3H, 2NH, arom.-*H*), 7.64 (s, 1H, arom.-*H*), 5.32 (s, 1H, C*H*CO), 3.31 (dq, $^3$J(H,H)=13.5,7.1 Hz, 2H, NC*H$_2$*), 3.18 (dq, $^3$J(H,H)=13.5, 7.1 Hz, 2H, NC*H$_2$*), 1.58 (s, 9H, tBu), 1.56 (m, 4HNC*H$_2$*C*H$_2$*), 1.42 (s, 9H, tBu), 1.38–1.22 (m, 12H, $CH_3$C*H$_2$*C*H$_2$*C*H$_2$*), 0.92–0.82 (m, 6H, C*H$_3$*$CH_2$). $^{13}$C{$^1$H} NMR ($CDCl_3$): δ(ppm) = 172.89, 164.55, 162.03, 147.29, 122.82, 118.97, 53.53, 40.97, 37.20, 36.83, 31.50, 30.39, 29.33, 28.99, 26.60, 22.68, 14.17; m.p. 148 °C; IR (ATR, neat): $\tilde{\nu}$ = 914 cm$^{-1}$ (Re=O asymmetric), 900 cm$^{-1}$ (Re=O asymmetric), 887 cm$^{-1}$ (Re=O asymmetric); m.p. decomp. 210 °C; elemental analysis (%): calcd. C 47.31, H 7.09, N 5.91, Re 26.19; found C 47.43, H 7.18, N 5.94, Re 26.40.

**[HL$^2$][ReO$_4$]**: colorless oil; Yield: 60 %; $^1$H NMR (toluene-*d$_8$*) δ(ppm) = 9.02 (t, $^3$J(H,H) = 6.8 Hz, 1H, N*H*), 8.26 (d, $^3$J(H,H) = 7.0 Hz, 2H, arom.-*H*), 7.30 – 7.23 (m, 2H, arom.-*H*), 7.22 – 7.16 (m, 1H, arom.-*H*), 4.70 (d, $^3$J(H,H) = 6.8 Hz, 2H, $NHCH_2N^+H$), 2.58 (t, $^3$J(H,H) = 8.0 Hz, 4H, NC*H$_2$*$CH_2$), 1.65 (m, 4H, $NCH_2$C*H$_2$*), 1.47–1.10 (m, 12H, $CH_2$C*H$_2$*C*H$_2$*C*H$_2$*$CH_3$), 0.91 (m, 6H, $CH_2$C*H$_3$*); $^{13}$C{$^1$H} NMR (toluene-*d$_8$*): δ(ppm) = 168.89, 132.62, 131.55, 128.95, 128.06, 58.09, 48.46, 31.41, 26.29, 23.74, 22.47, 13.88; m.p. decomp. 172 °C; IR (ATR, neat): $\tilde{\nu}$ = 924 cm$^{-1}$ (Re=O asymmetric), 905 cm$^{-1}$ (Re=O asymmetric), 882 cm$^{-1}$ (Re=O asymmetric); elemental analysis (%): calcd. C 42.16, H 6.19, N 4.92, Re 32.68; found C 40.61, H 6.25, N 4.66, Re 34.23.

**[HL$^3$][ReO$_4$]**: colorless oil; Yield: 89 %; $^1$H NMR (toluene-*d$_8$*): δ(ppm) = 8.36 (t, $^3$J(H,H) = 7.0 Hz, 1H, N*H*$CH_2N^+H$), 7.93 (s, multiple signal $NHCH_2N^+$*H*), 6.60 (s, multiple signal $NHCH_2N^+$*H*), 5.99 (s, multiple signal $NHCH_2N^+$*H*), 4.51 (d, $^3$J(H,H) = 7.0 Hz, 2H

NHC$H_2$N$^+$H), 2.67–2.63 (m, 4H, NC$H_2$CH$_2$), 2.55–1.96 (m, 2H, NHCOC$H_2$CH), 1.94–1.78 (m, 1H, NHCOCH$_2$C*H*), 1.80–1.46 (m, 4H, N(CH$_2$C$H_2$)$_2$), 1.46–0.78 (m, 34H, aliphatic protons); $^{13}$C{$^1$H} NMR (toluene-$d_8$): δ(ppm) = 174.21, 57.08, 50.96, 50.43, 48.31, 45.37, 39.20, 31.30, 29.90, 27.10, 26.23, 23.97, 22.38, 13.80; m.p. decomp. 192 °C; IR (ATR, neat): $\tilde{\nu}$ = 923 cm$^{-1}$ (Re=O asymmetric), 905 cm$^{-1}$ (Re=O asymmetric), 879 cm$^{-1}$ (Re=O asymmetric); elemental analysis (%): calcd. C 43.62, H 7.82, N 4.62, Re 30.74; found C 43.56, H 7.88, N 4.65, Re 30.68.

## 2. Spectroscopic data

### 2.1. IR spectrum of [HL$^1$][ReO$_4$]

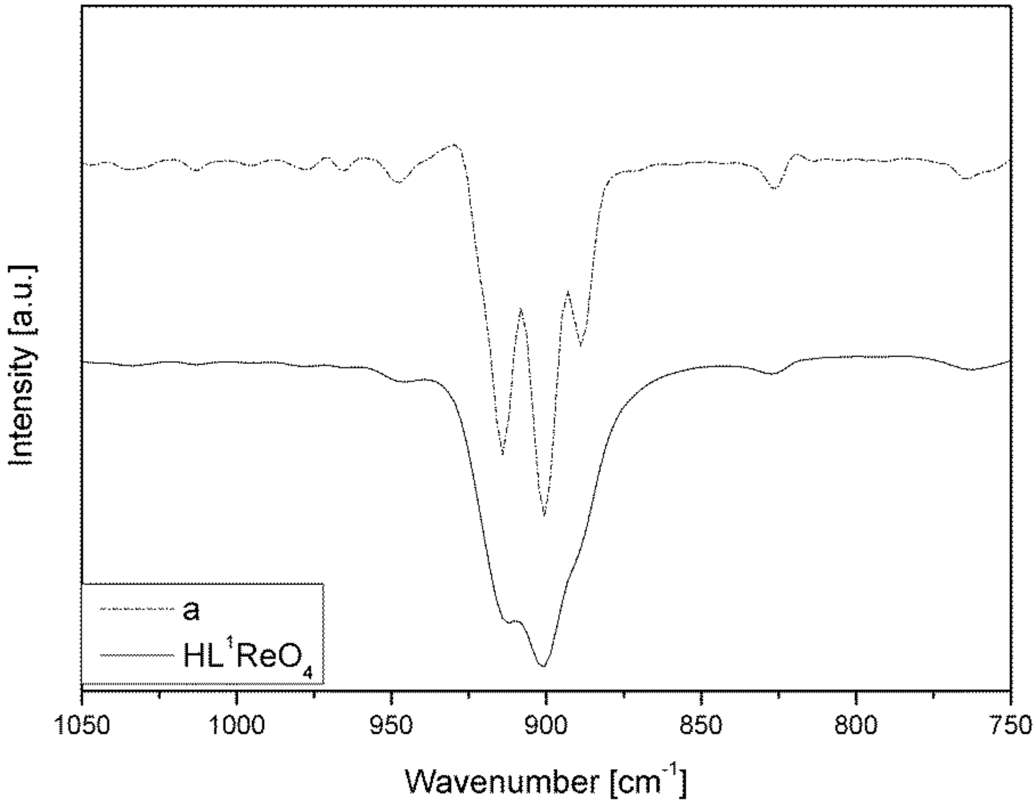

**Figure S1.** (-) FTIR spectrum of [HL$^1$][ReO$_4$] between 1050 and 750 cm$^{-1}$; (a) deconvoluted spectrum.

## 2.2. NMR experiments

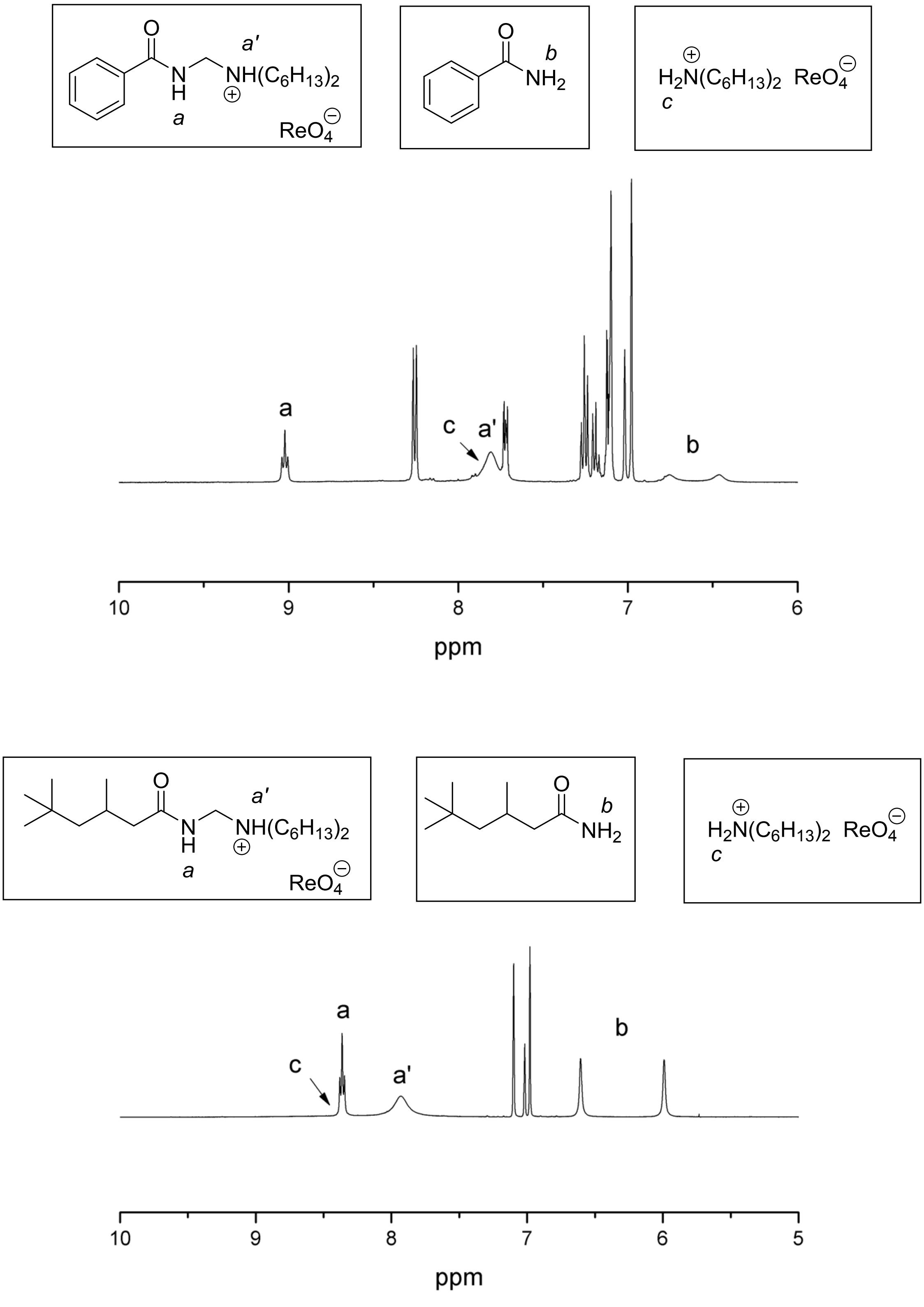

**Figure S2.** $^1$H-NMR spectra of partially decomposed [HL$^2$][ReO$_4$] (top) and [HL$^3$][ReO$_4$] (bottom) in toluene-d$_8$.

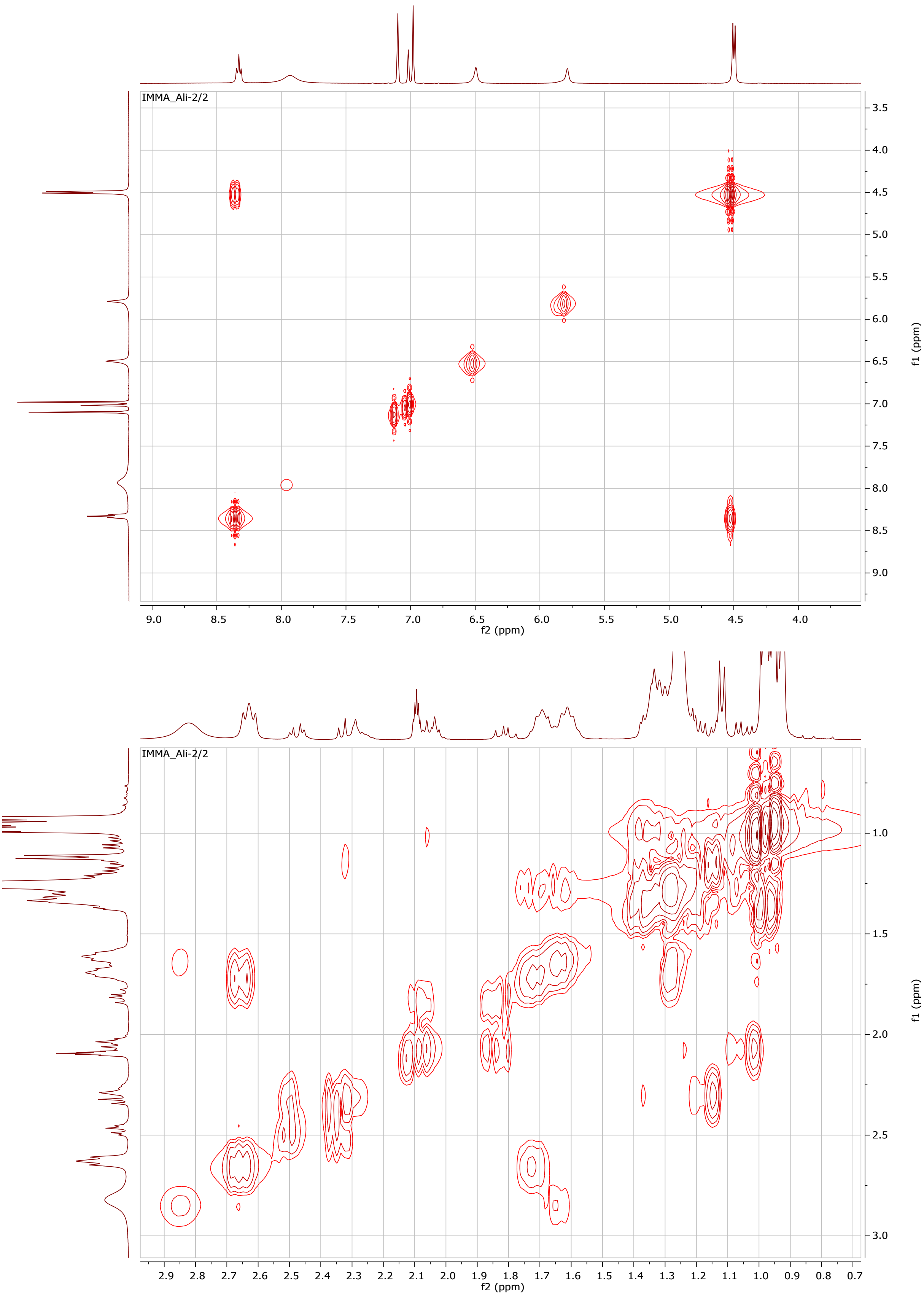

**Figure S3.** COSY NMR spectra of $[HL^3][ReO_4]$ in toluene-$d_8$.

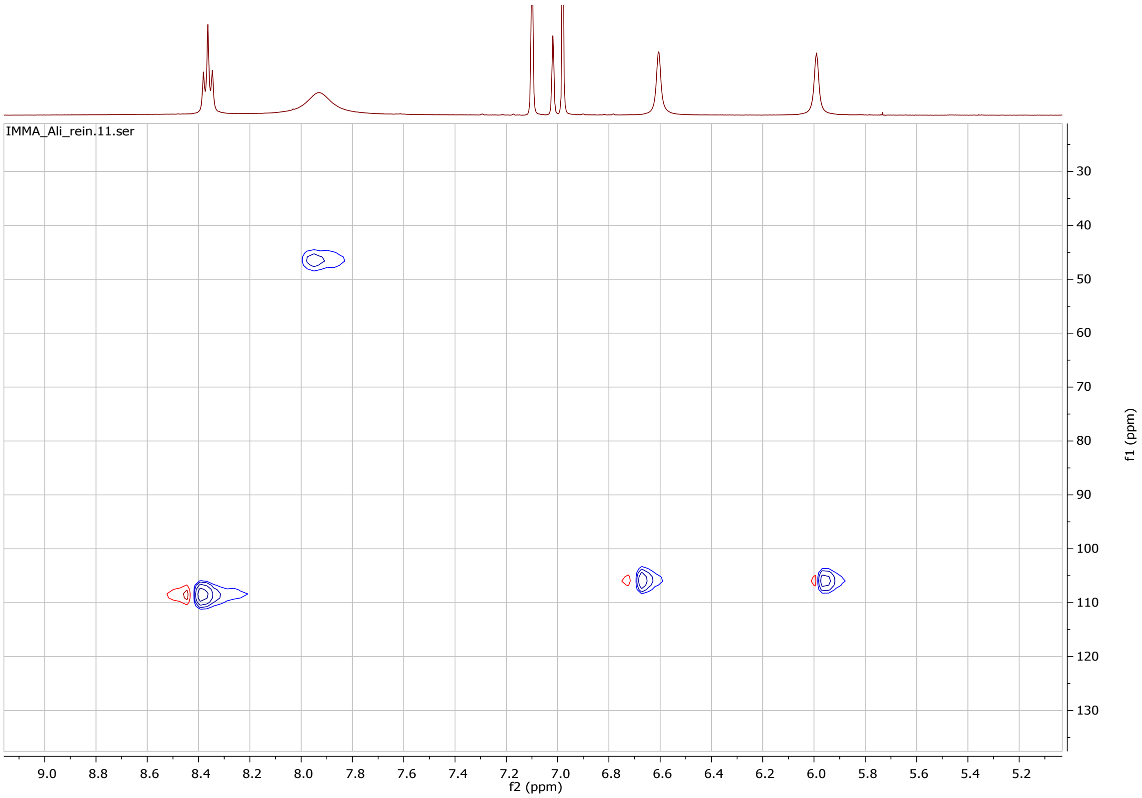

**Figure S4.** $^1$H-/$^{15}$N-HSQC NMR spectrum of [HL$^3$][ReO$_4$] in toluene-d$_8$ in the range of 9.0 ppm to 5.2 ppm.

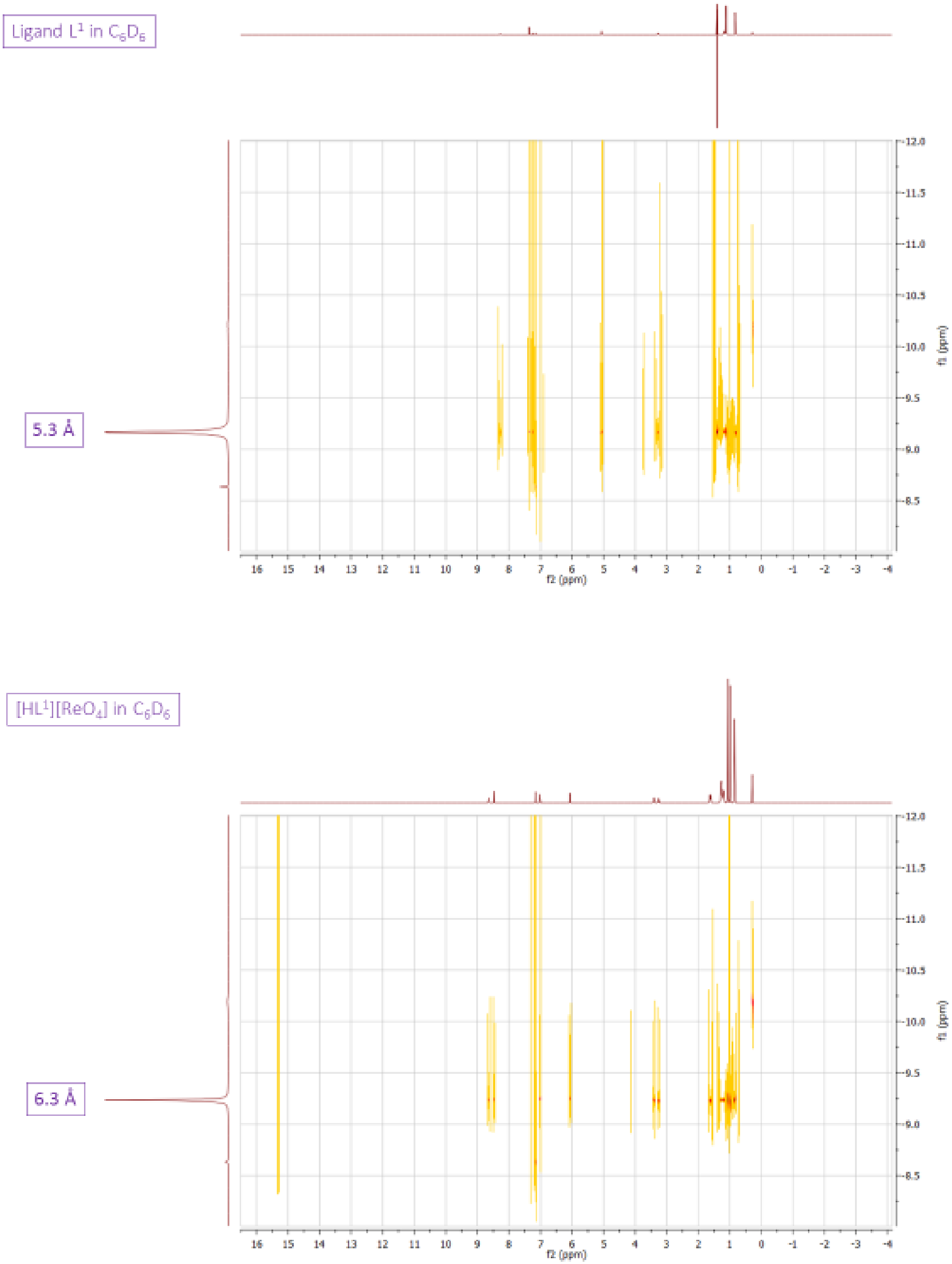

**Figure S5.** DOSY NMR spectra of $L^1$ (top) and $[HL^1][ReO_4]$ (bottom) in $C_6D_6$.

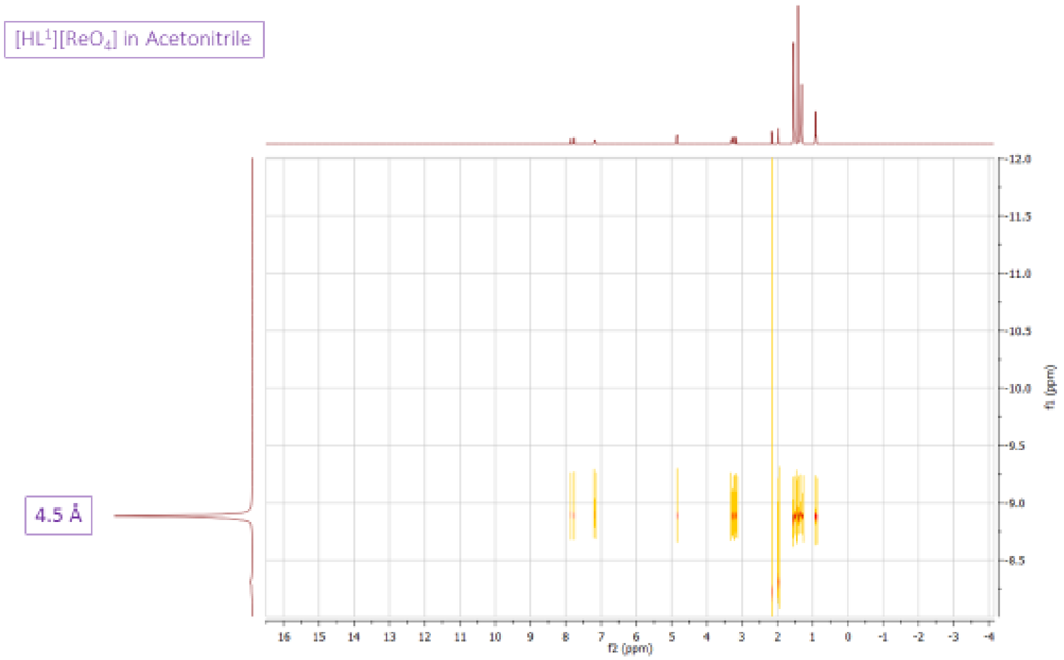

**Figure S6.** DOSY NMR spectrum of $[HL^1][ReO_4]$ in $CD_3CN$.

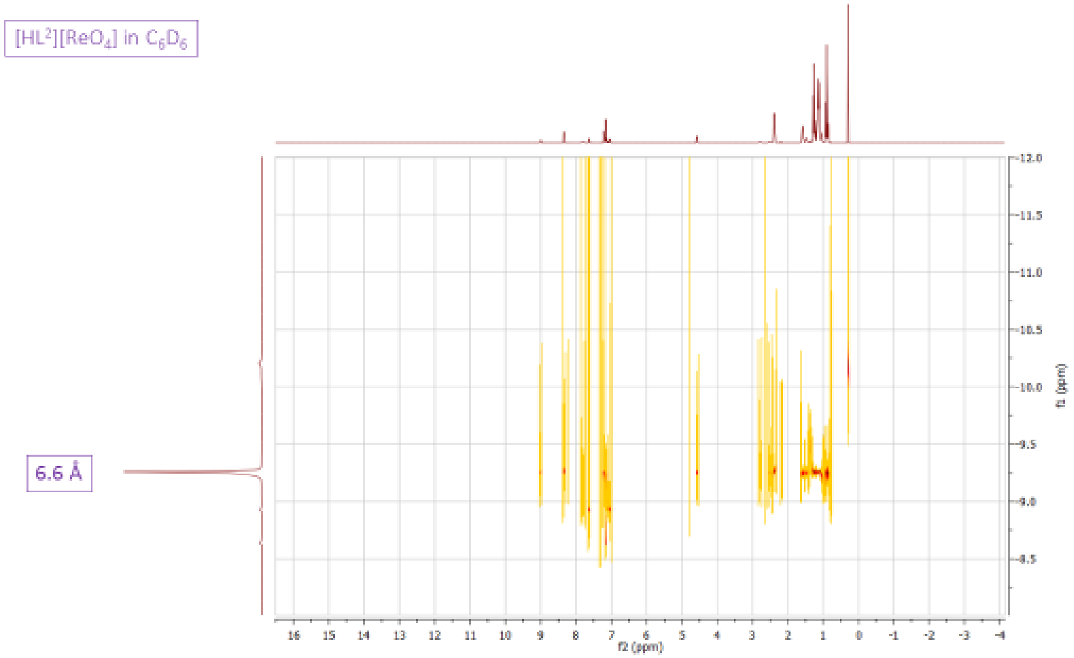

**Figure S7.** DOSY NMR spectrum of $[HL^2][ReO_4]$ in $C_6D_6$.

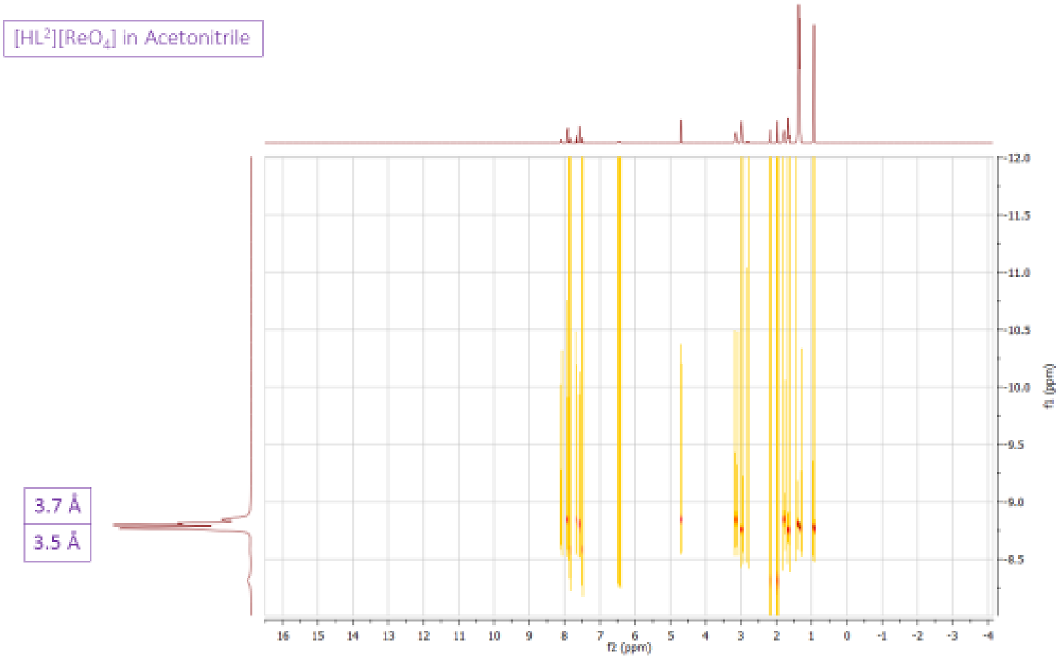

**Figure S8.** DOSY NMR spectrum of $[HL^2][ReO_4]$ in $CD_3CN$.

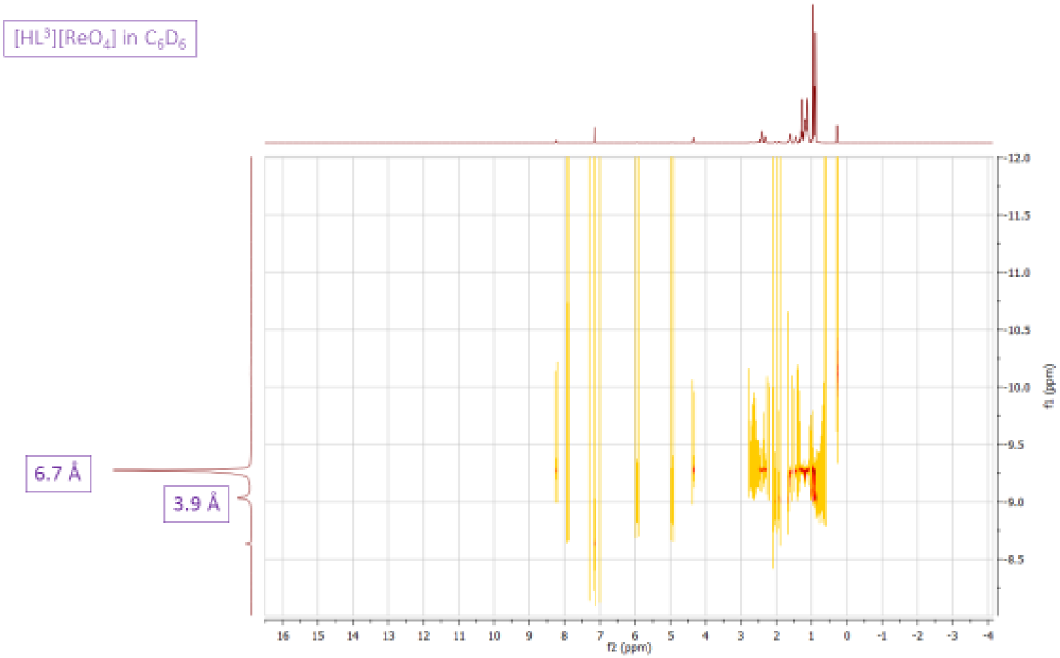

**Figure S9.** DOSY NMR spectrum of $[HL^3][ReO_4]$ in $C_6D_6$.

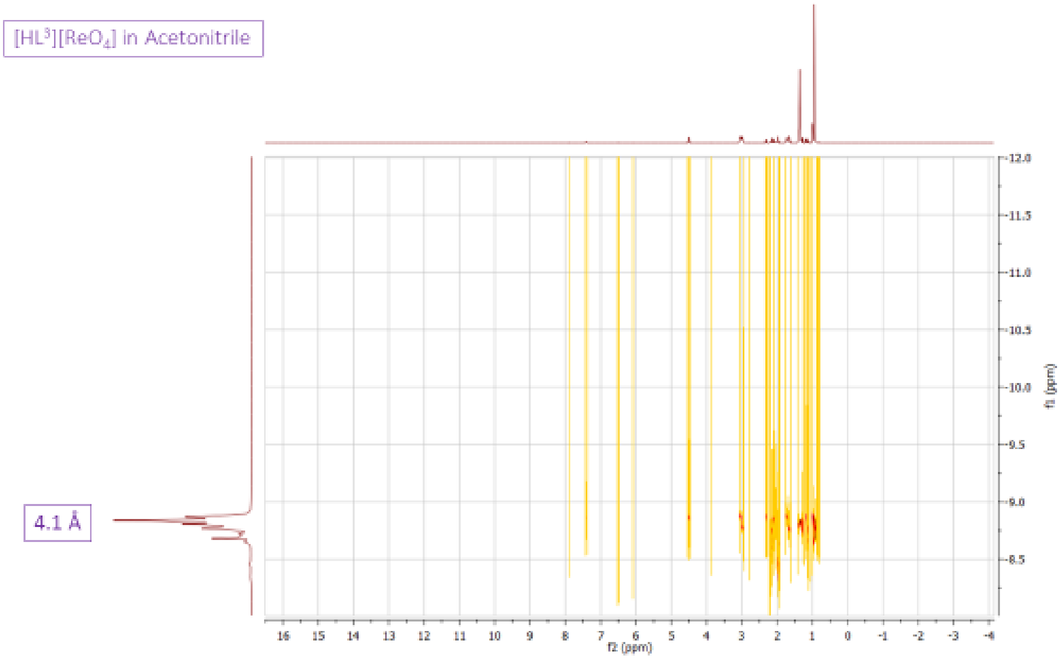

**Figure S10.** DOSY NMR spectrum of [HL$^3$][ReO$_4$] in CD$_3$CN.

## 2.3. Spectroscopic study of $[HL^1][ReO_4]$ in catalysis

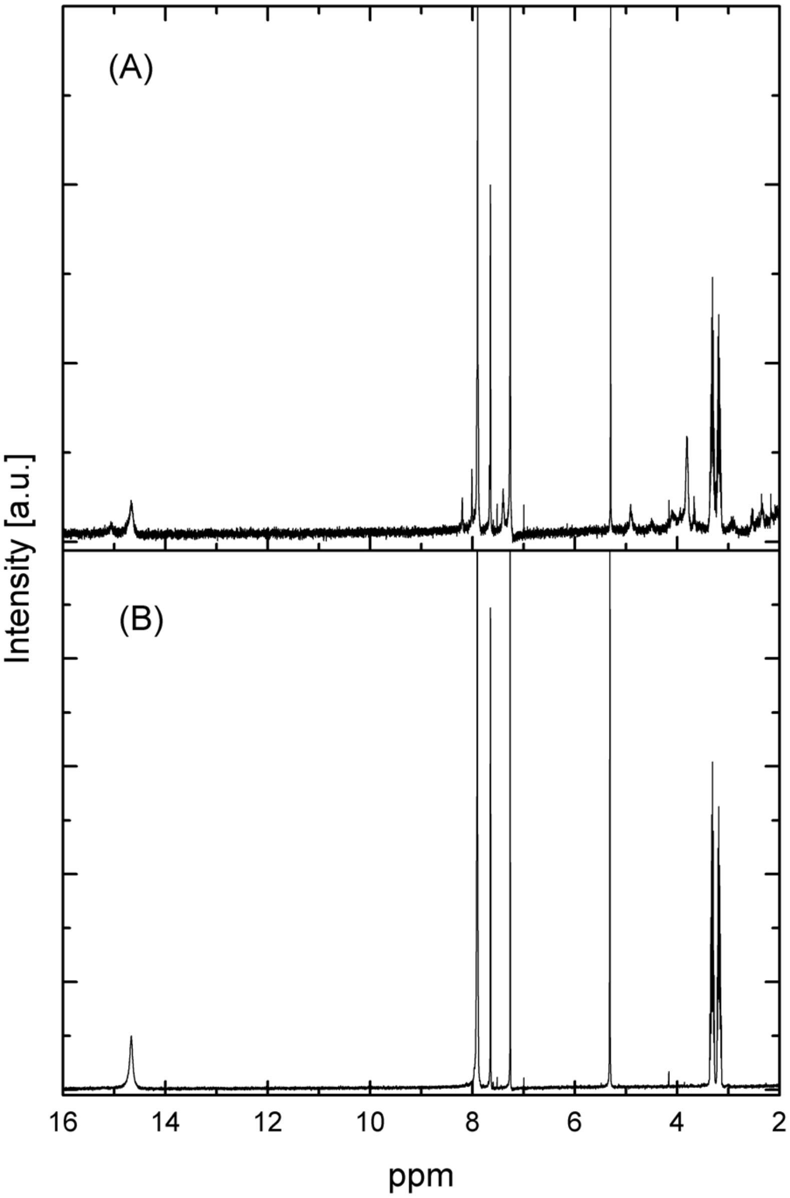

**Figure S11.** $^1H$ NMR spectra of (A) $[HL^1][ReO_4]$ after 6 catalytic cycles and (B) $[HL^1][ReO_4]$ between 16 and 2 ppm in $CDCl_3$.

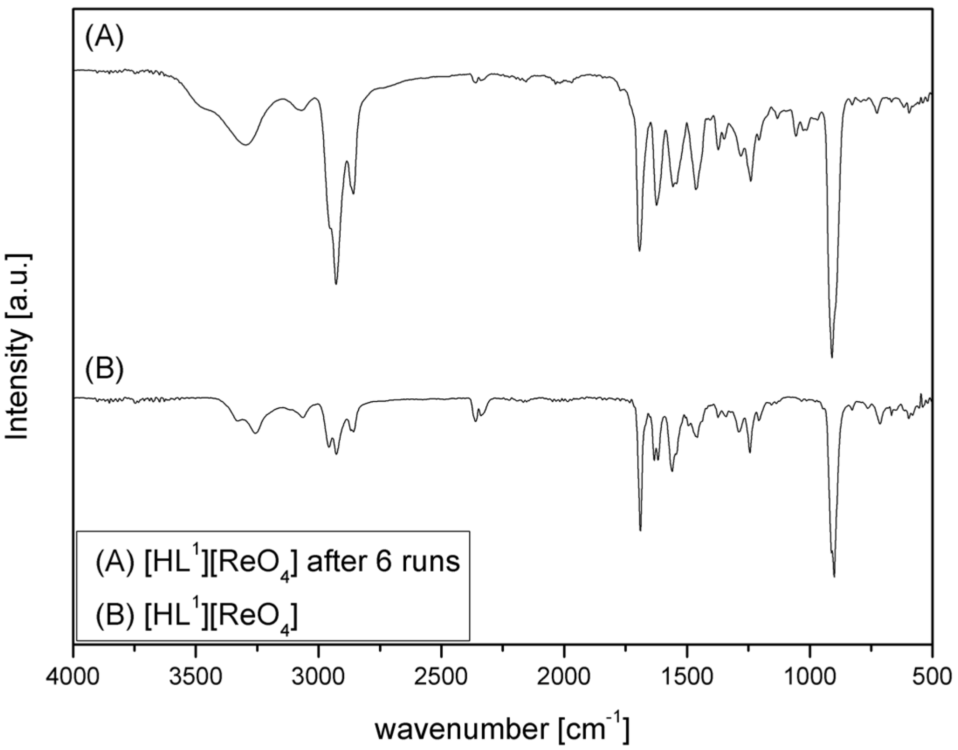

**Figure S12.** FTIR spectrum of (A) [HL$^1$][ReO$_4$] after 6 catalytic cycles and (B) [HL$^1$][ReO$_4$] before catalysis, in the range between 4000 and 500 cm$^{-1}$.

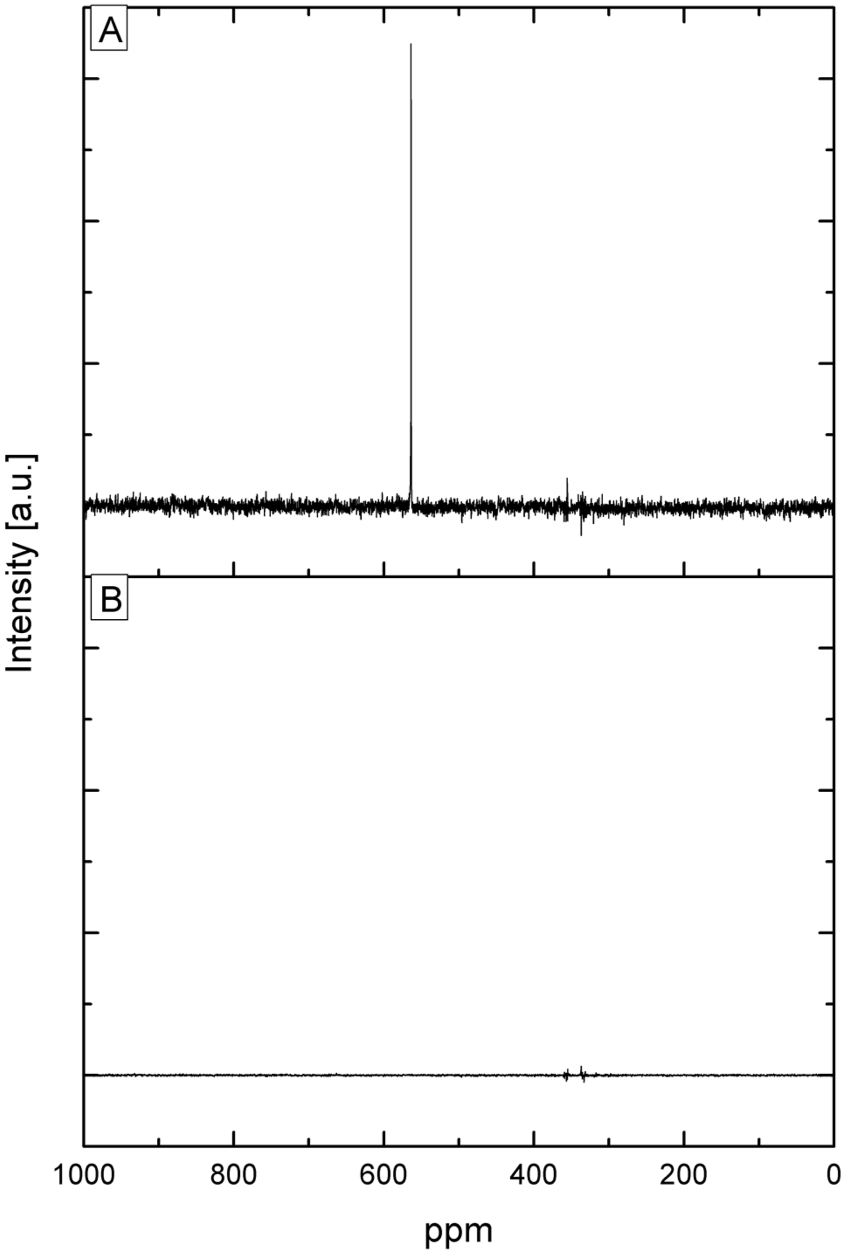

**Figure S13.** $^{17}O$ NMR spectra of (A) $^{17}O$ labeled [HL$^1$][ReO$_4$]; (B) cyclooctene oxide in n-hexane after synthesis with $^{17}O$ labeled [HL$^1$][ReO$_4$] as catalyst.

### 2.4. ESI-MS data

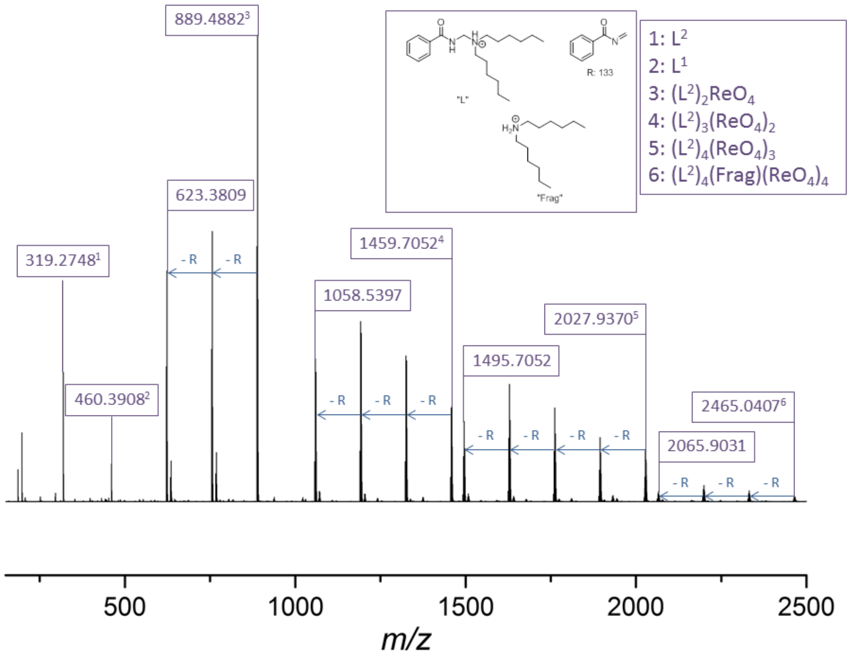

**Figure S14.** ESI-MS data for $[HL^2][ReO_4]$ in $CH_3CN$.

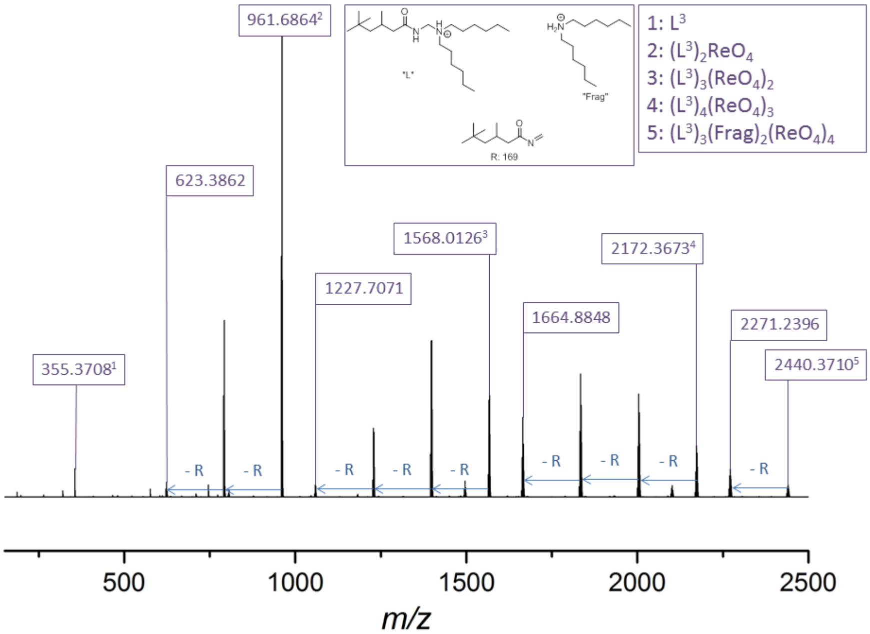

**Figure S15.** ESI-MS data for $[HL^3][ReO_4]$ in $CH_3CN$.

## 2.5. TG-MS data

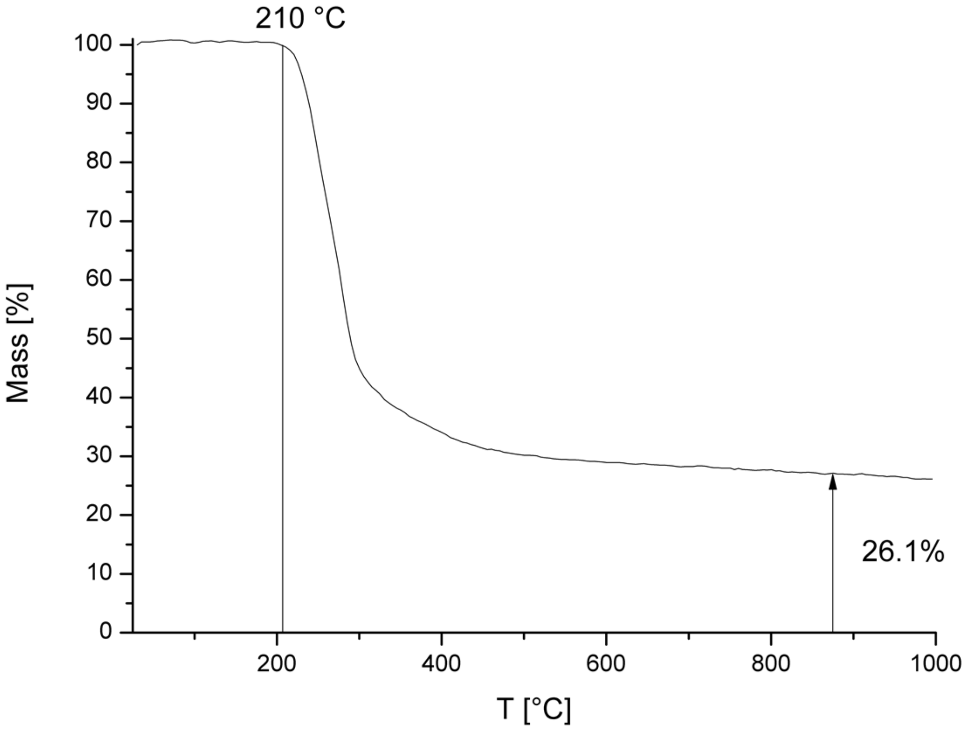

**Figure S16.** TG-MS data of [$HL^1$][$ReO_4$] between 25 °C and 1000 °C.

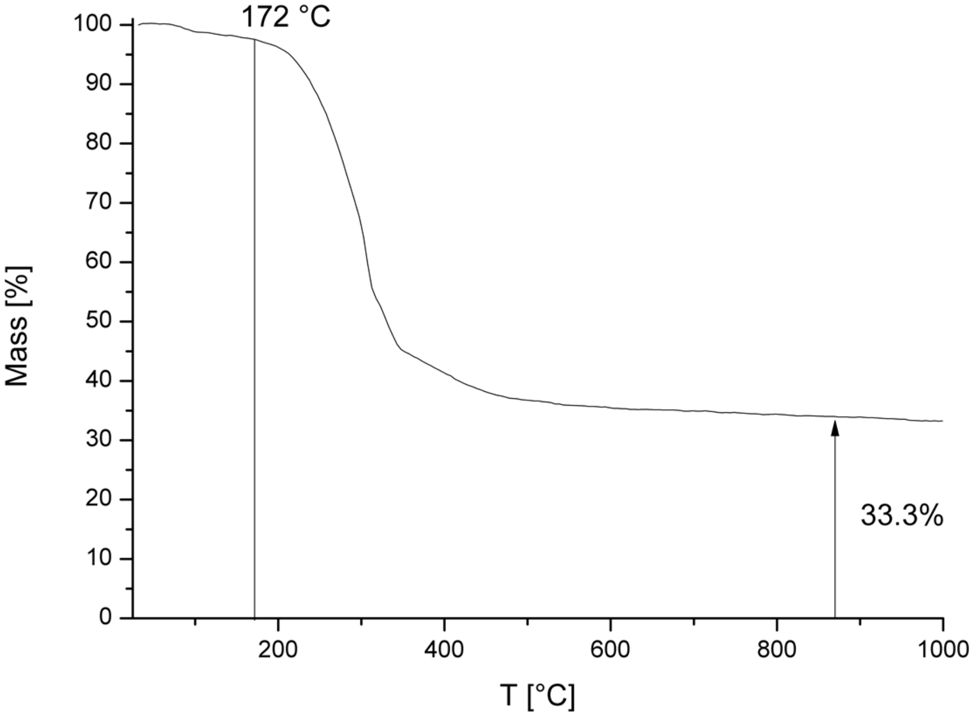

**Figure S17.** TG-MS data of [$HL^2$][$ReO_4$] between 25 °C and 1000 °C.

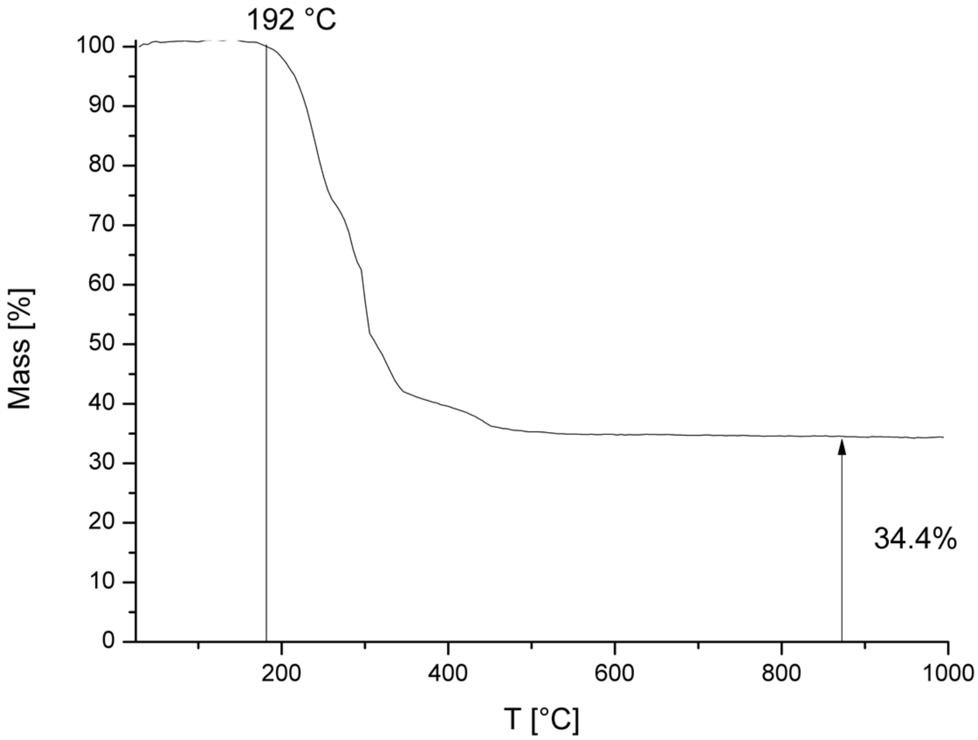

**Figure S18.** TG-MS data of [HL$^3$][ReO$_4$] between 25 °C and 1000 °C.

# 3. Catalysis experiments

## 3.1. Experimental

In a Radleys reaction tube with magnetic stir bar 0.5 mmol [HL$^n$][ReO$_4$] (n = 1, 2, 3) was weighed in and placed in a Radleys Carousel reaction station. After addition of first 10.0 mmol cyclooctene followed by 25.0 mmol aqueous $H_2O_2$ (50 wt.-% in $H_2O$) the round bottom flask was plugged and the two-phase mixture was heated to the desired temperature. For determining the yield and selectivity of the catalytic reaction samples were taken from the organic phase and analyzed by GC.

## 3.2. Influence of the reaction temperature on the catalytic activity

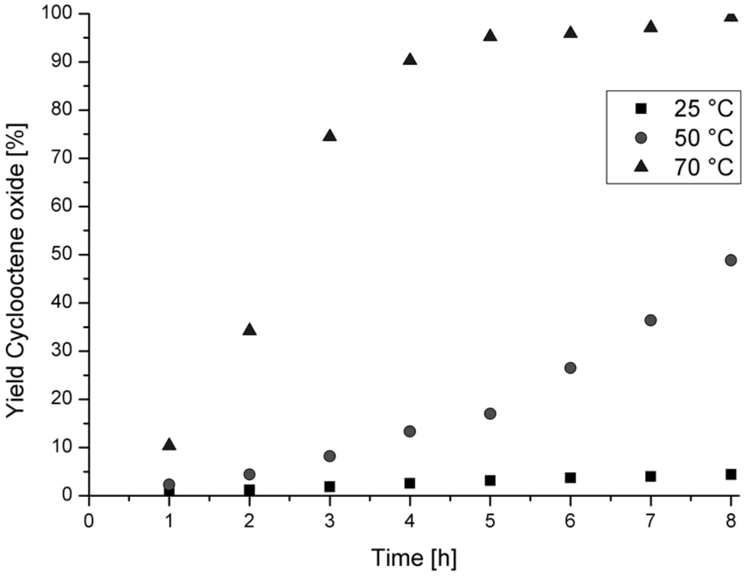

**Figure S19.** Influence of the reaction temperature on the epoxidation of cyclooctene using [HL$^1$][ReO$_4$] as catalyst; Reaction conditions: 5:100:250 cat: substrate: oxidant ratio, neat.

### 3.3. Influence of the catalyst:substrate ratio

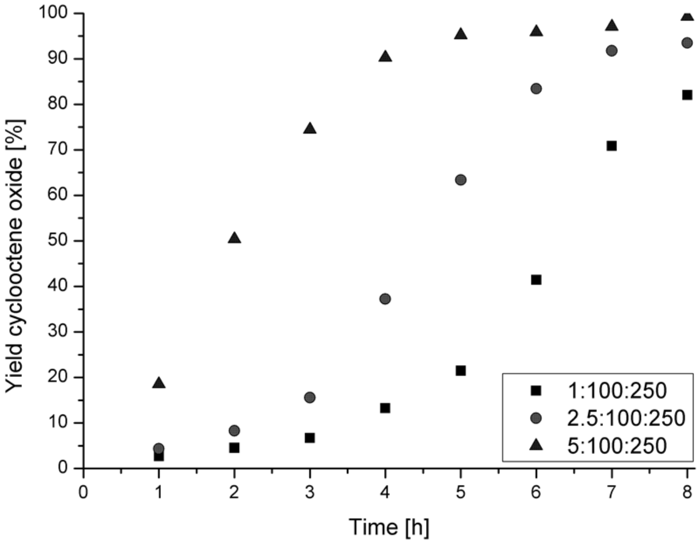

**Figure S20.** Influence of the catalyst:substrate ratio on the epoxidation of cyclooctene using [HL$^1$][ReO$_4$] as catalyst; Reaction conditions: substrate:oxidant 100:250, 70 °C.

### 3.4. Influence of the substrate:oxidant ratio

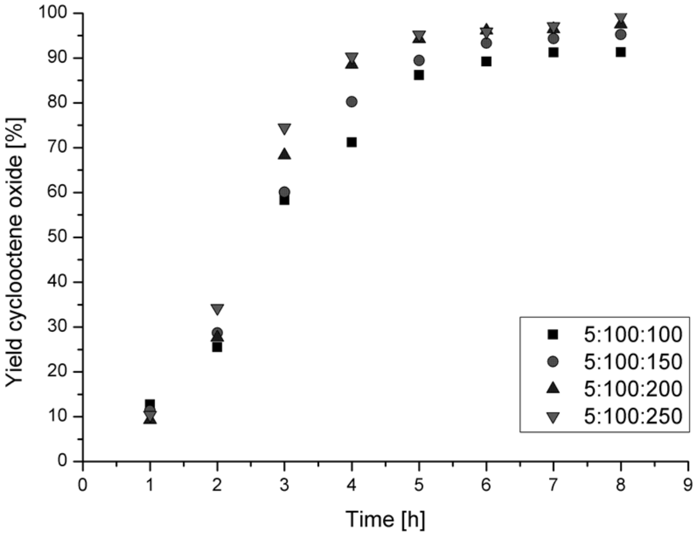

**Figure S21.** Influence of substrate:oxidant ratio. Reaction conditions: 5 mol % [HL$^1$][ReO$_4$], 70 °C.

## 3.5. Solvent influence

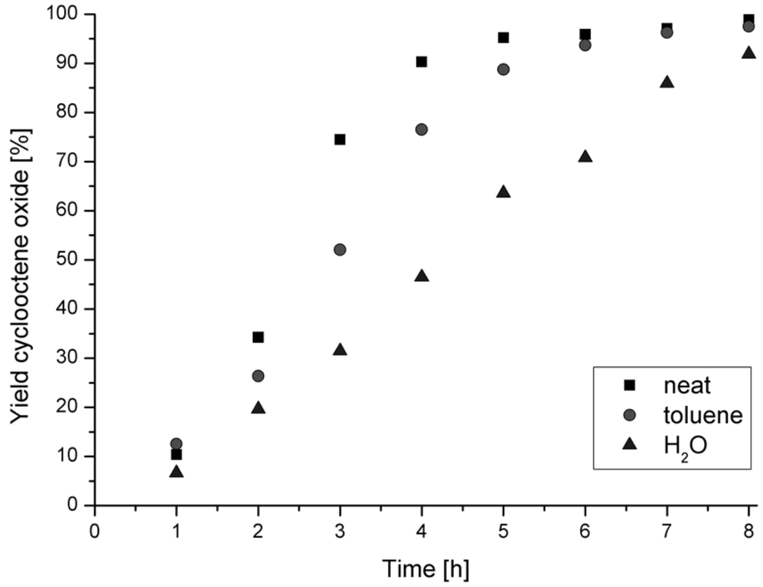

**Figure S22.** Influence of the solvent on the catalytic activity; Reaction conditions: 5 mol% [HL$^1$][ReO$_4$], 5:100:250 cat: substrate: oxidant ratio, 70 °C.

## 3.6. Recycling studies

For recycling studies, after 4 h at 70 °C, the SIP catalyst and cyclooctene oxide were separated from the excess peroxide with and water by extraction into toluene. Thereupon, cyclooctene oxide was distilled from the organic phase and the next catalytic run started by adding additional olefin (10.0 mmol) and oxidant (25 mmol).

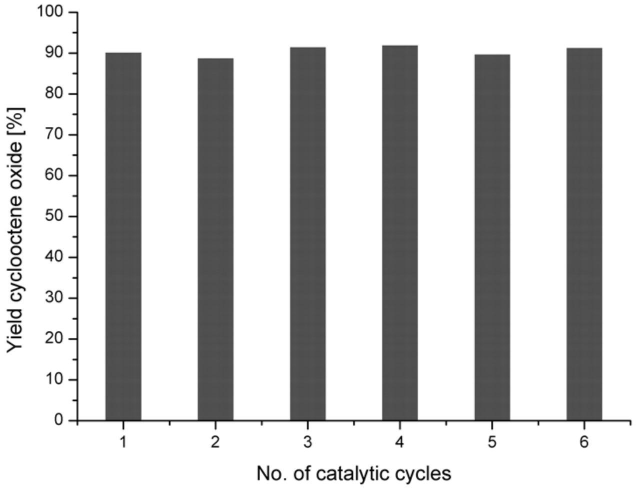

**Figure S23.** Illustration of the reusability of SIP epoxidation catalysts. Reaction conditions: 5 mol % [HL$^1$][ReO$_4$], aqueous $H_2O_2$ as oxidant, cat:substrate:oxidant ratio 5:100:250, 70 °C, 4 h.

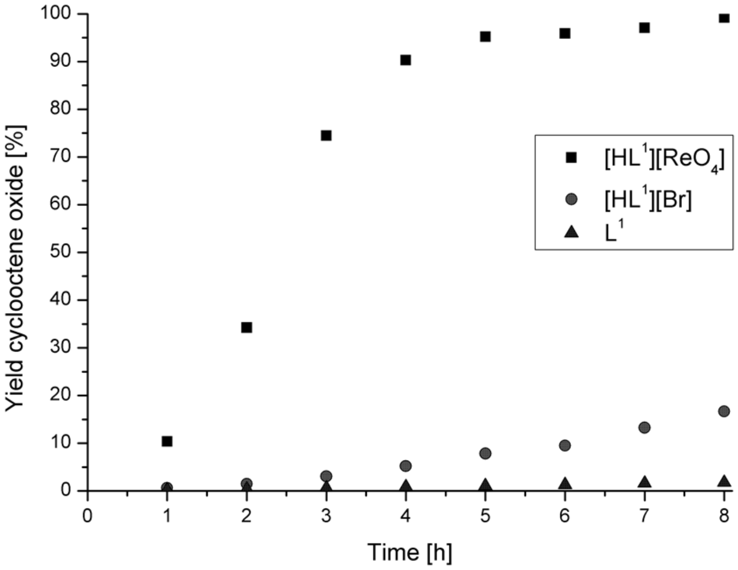

**Figure S24.** Comparison of the catalytic activity of [HL$^1$][ReO$_4$], [HL$^1$][Br] and L$^1$; Reaction conditions: aqueous $H_2O_2$ as oxidant, cat:substrate:oxidant ratio 5:100:250, 70 °C, 4 h.

# 4. X-ray single crystal diffraction data

## 4.1. Measurement and refinement details

Data were collected on a Bruker APEX II X-ray single crystal diffractometer equipped with a $\kappa$-CCD detector, a Bruker AXS FR591 rotating anode with $MoK_\alpha$ radiation ($\lambda$ = 0.71073 Å), and a Montel mirror by using the APEX 2 software package.[S3] The measurements were carried out on a single crystal coated with perfluorinated ether that was fixed on the top of a glass fiber, transferred to the diffractometer, and frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT.[S4] Absorption corrections, including odd and even-ordered spherical harmonics were performed using SADABS.[S4] Space group assignments were based upon systematic absences, *E* statistics, and successful refinement of the structure. The structure was solved by direct methods with the aid of successive difference Fourier maps,[S3] and refined against all data using SHELXL-97[S5] in conjunction with SHELXLE.[S6] Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were placed in ideal positions using the SHELXL riding model. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2-F_c^2)^2$ with SHELXL-97[S5] weighting scheme. Neutral atom-scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.[S8] Images of the crystal structures were generated by PLATON.[S7] Crystallographic data for the structure of compound $[HL^1][ReO_4]$ have been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 1030881). Copies of the data can be obtained free of charge from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax (+44)1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

## 4.2. Crystallographic data of compound [HL$^1$][ReO$_4$]

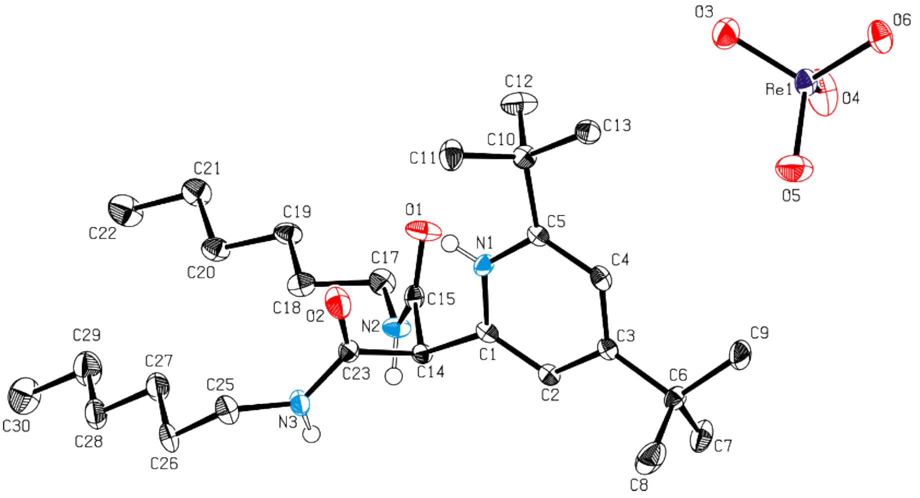

**Figure S25**. Solid-state structure of [HL$^1$][ReO$_4$] (displacement ellipsoids are drawn at 50 % probability).[S5] For clarity, hydrogen atoms are omitted except for those at N1, N2 and N3. Selected bond lengths (Å) and angles (°): Re1–O3 1.701(2), Re1–O4 1.715(2), Re1–O5 1.715(2), Re1–O6 1.738(2), O3-Re1–O4 108.25(11), O3–Re1–O5 108.34(10), O4–Re1–O5 109.58(11), O3–Re–O6 110.61(10), O4–Re–O6 110.21(10), O5–Re1–O6 109.81(10), N1···O1 2.717, N1···O2 2.710.

***Table S1.*** Sample and crystal data for compound [HL$^1$][ReO$_4$].

| | | |
|---|---|---|
| Chemical formula | $C_{28}H_{50}N_3O_6Re$ | |
| Formula weight | 710.91 | |
| Temperature | 123(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal size | 0.060 x 0.260 x 0.310 mm | |
| Crystal habit | colorless prism | |
| Crystal system | monoclinic | |
| Space group | P 1 21/c 1 | |
| Unit cell dimensions | a = 11.2427(2) Å | α = 90° |
| | b = 25.9864(4) Å | β = 90.415(2)° |
| | c = 11.3945(2) Å | γ = 90° |
| Volume | 3191.75(9) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.497 g/cm$^3$ | |
| Absorption coefficient | 3.848 mm$^{-1}$ | |
| F(000) | 1448 | |

***Table S2.*** Data collection and structure refinement for compound [HL$^1$][ReO$_4$].

| | | |
|---|---|---|
| Diffractometer | Bruker Kappa APEX II CCD | |
| Radiation source | Fine-focus tube, Mo | |
| Theta range for data collection | 2.02 to 25.39° | |
| Index ranges | -13<=h<=13, -31<=k<=31, -13<=l<=13 | |
| Reflections collected | 74426 | |
| Independent reflections | 5865 [$R_{int}$ = 0.0454] | |
| Coverage of independent reflections | 99.8% | |
| Absorption correction | multi-scan | |
| Max. and min. transmission | 0.7908 and 0.3788 | |
| Structure solution technique | direct methods | |
| Structure solution program | SHELXS-97 (Sheldrick, 2008) | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Refinement program | SHELXL-97 (Sheldrick, 2008) and SHELXLE (Huebschle, 2011) | |
| Function minimized | $\Sigma$ w($F_o^2$ - $F_c^2$)$^2$ | |
| Data / restraints / parameters | 5865 / 0 / 351 | |
| Goodness-of-fit on $F^2$ | 1.034 | |
| $\Delta/\sigma_{max}$ | 0.003 | |
| Final R indices | 4973 data; I>2σ(I) | $R_1$ = 0.0218, $wR_2$ = 0.0383 |
| | all data | $R_1$ = 0.0324, $wR_2$ = 0.0409 |
| Weighting scheme | w=1/[$\sigma^2(F_o^2)+(0.0128P)^2+3.2365P$]<br>where P=($F_o^2+2F_c^2$)/3 | |
| Largest diff. peak and hole | 0.674 and -0.436 eÅ$^{-3}$ | |
| R.M.S. deviation from mean | 0.076 eÅ$^{-3}$ | |

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