Supporting Information
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Ionophilic imidazolium-tagged cinchona ligand on LDH-immobilized osmium: recyclable and recoverable catalytic system for asymmetric dihydroxylation reaction of olefins

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SUPPORTING INFORMATION

Methods and Materials

$^1$H NMR was recorded in CDCl$_3$ on a 400 MHz Bruker Avance instrument using TMS as the internal standard reference. IR spectra were recorded on a Perkin Elmer Spectrum 400, FT-IR spectrometer. HPLC was done on a Waters HPLC system with PDA detector. Quinine, 1,4-dichloropthalazine and olefins were purchased from Sigma Aldrich, USA. The experiments were done in triplicate and the reported yields are within an error of ±2%

Synthesis of 1, 4-Bis (9-O-quininyl)phthalazine ((QN)$_2$-PHAL) (3)

To a 250 mL three-neck round-bottom flask equipped with a Dean-Stark condenser was added quinine (2, 6.36 g, 19.62 mmol), 1, 4-dichloropthalazine (1, 2.03 g, 10.22 mmol), K$_2$CO$_3$ (4.15 g, 30.05 mmol) and 100 mL of anhydrous toluene. After refluxing for 2 h under nitrogen atmosphere, KOH pellets (1.68 g, 30.05 mmol) were added and then the reaction was continued for 14 h. The reaction was followed by TLC. The light orange solution was cooled to room temperature, mixed with water, and then extracted with EtOAc. The organic layer was washed with water and brine, dried over MgSO$_4$, and evaporated to dryness. Recrystallization from Et$_2$O gave a white powder (3, 5.78 g) in 71 % yield.

m.p = 159-160°C; $^1$H NMR (CDCl$_3$, 400MHz) δ: 1.48-1.51 (m, 2H, quinuclidine-H), 1.82-1.90 (m, 12H, quinuclidine-H), 2.25 (bs, 2H, quinuclidine-H), 2.60-2.62 (m, 2H, quinuclidine-H), 2.98-3.04 (m, 2H, quinuclidine-H), 3.47-3.49 (m, 2H, quinuclidine-H), 3.90 (s, 6H, -OCH$_3$), 4.92-5.00 (m, 4H, -CH$_2$=CH-), 5.77-5.81 (m, 2H, -CH$_2$=CH-), 7.34 (d, 1H, $J = 2.6$ Hz, -CH-O-), 7.36 (d, 1H, $J = 2.6$ Hz, -CH-O-), 7.42 (d, 2H, $J = 4.5$ Hz, 2 x Quinolyl-H), 7.52 (d, 2H, $J = 4.5$ Hz, 2 x Quinolyl-H), 7.57 (d, 2H, $J = 2.6$ Hz, 2 x quinolyl-H), 7.92-7.98 (m, 4H, phthalazine-H), 8.29-8.31 (m, 2H, 2 x quinolyl-H), 8.65 (d, 2H, $J = 4.5$ Hz, 2 x quinolyl-H); $^{13}$C NMR (CDCl$_3$, 400MHz) δ: 23.8, 27.7, 27.7, 27.9, 39.9, 42.8, 55.9,
56.8, 60.3, 76.3, 102.9, 114.5, 118.6, 122.0, 122.6, 123.2, 127.4, 131.7, 132.7, 137.6, 142.2, 147.4, 155.6, 158.1.

Synthesis of (QN)₂PHAL-[C₄mim]Br (5)

(QN)₂PHAL (3, 5.00 g, 6.50 mmol) was heated with 1-pentyl-3-methyl imidazolium bromide (4, 7.54 g, 32.5 mmol) in dry DCM under reflux for 72h. This was followed by removal of the solvent under vacuum to give the crude product which was purified by flash chromatography (CHCl₃/Methanol 20:1) to yield light yellow sticky solid (5, 3.9 g) in 55% yield.

¹H NMR (CDCl₃, 400MHz) δ: 1.36-1.44 (m, 2H, -N-CH₂-CH₂-CH₂-CH₂-CH₂-imidazolium), 1.48-1.53 (m, 2H, quinuclidine-H), 1.74-1.88 (m, 10H, quinuclidine-H), 1.91-1.99 (m, 4H, -N⁺-CH₂-CH₂-CH₂-CH₂-CH₂-imidazolium), 2.04-2.13 (m, 4H, -N⁺-CH₂-CH₂-CH₂-CH₂-CH₂-imidazolium), 2.13-2.17 (m, 2H, quinuclidine-H), 2.68-2.78 (m, 2H, quinuclidine-H), 2.80-2.91 (m, 2H, quinuclidine-H), 3.15-3.18 (m, 2H, quinuclidine-H), 3.38-3.48 (m, 2H, quinuclidine-H), 3.54 (t, 2H, J = 6.4 Hz, -N⁺-CH₂-CH₂-CH₂-CH₂-CH₂-imidazolium), 3.93 (s, 6H, -OCH₃), 4.01 (s, 3H, -N-CH₃), 4.35 (t, 2H, J = 7.4 Hz, -CH₂-CH₂-imidazolium), 5.02-5.17 (m, 4H, -CH₂=CH-), 5.52-5.56 (m, 2H, CH₂=CH-H), 7.28 (d, 1H, J = 2.7 Hz, -CH-O-), 7.30 (d, 1H, J = 2.7 Hz, -CH-O-), 7.31 (s, 1H, Imidazolium-H), 7.32-7.39 (m, 2H, pthalazine-H), 7.45 (d, 2H, J = 1.8 Hz, imidazolium-H), 7.50-7.52 (m, 2H, 2 x quinolyl-H), 7.81-7.83 (m, 2H, pthalazine-H), 7.91-7.93 (m, 2H, 2 x quinolyl-H), 8.08 (d, 2H, J = 8.5 Hz, 2 x quinolyl-H), 8.31-8.35 (m, 2H, quinolyl-H), 8.72 (d, 1H, J = 4.8 Hz, quinolyl-H), 8.78 (d, 1H, J = 4.6 Hz, quinolyl-H); ¹³C NMR (CDCl₃, 400MHz) δ: 157.3, 145.8, 143.5, 142.7, 142.4, 136.2, 136.0, 130.1, 124.4, 122.3, 121.7, 121.3, 118.0, 116.4, 99.1, 65.5, 65.0, 63.4, 59.1, 56.3, 55.4, 53.7, 52.6, 43.1, 36.6, 36.0, 35.6, 29.9, 28.6, 28.2, 25.9, 25.2, 24.2, 23.7, 23.2, 21.2, 17.1.

MS (ES⁺): m/z (%) = 945.1 (20) [M + H]⁺, 325.5 (100) [M – C₃₈H₄₅N₆O₂]⁺.

Synthesis of LDH-(Mg-Al-Cl)

MgCl₂.6H₂O (10.16 g, 0.05 mmol) and AlCl₃.6H₂O (4.02 g, 0.016 mmol) was dissolved in deionized water (50 mL). To this aqueous solution, NaOH solution (2M, 30 mL) was slowly added at 25°C at pH 10 under a nitrogen flow. The pH of reaction mixture was maintained at this value by the continuous addition of 2M NaOH and was stirred overnight under a nitrogen flow at 70°C. The solid product was isolated by filtration, washed thoroughly with deionized water, dried overnight at 80°C. All the synthetic steps were carried out using deionized water.
IR (KBr)/ν_max cm⁻¹: 3465.0, 3145.6, 1640.3, 960.2.

XRD : d_003 ~ 7.8Å.

Synthesis of LDH-OsO₄

LDH-(Mg-Al-Cl) (0.75 g) was suspended in 75 mL of aqueous potassium osmate solution (0.344 g, 0.935 mmol) and stirred at 25 °C for 12 h under nitrogen atmosphere. The solid catalyst was filtered, washed thoroughly with 250 mL of water, and vacuum-dried to obtain 0.954 g of LDH-OsO₄ (0.932 mmol of Os per g).

IR (KBr)/ν_max cm⁻¹: 3479.7, 1646.4, 1368.8, 672.3.

XRD : d_003 ~ 7.8Å.

HPLC DATA

Fig 1: HPLC of entry 1 (diol)
Fig 2: HPLC of entry 2 (diol)

Fig 3: HPLC of entry 3 (diol)
Fig 4: HPLC of entry 4 (diol)
**Peak Results**

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Fig 5: HPLC of entry 5 (diol)

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**Peak Results**

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Fig 6: HPLC of entry 6 (diol)