Supporting Information

**Evidence of the Electronic Factor for the Highly Enantioselective
Catalytic Efficiency of *Cinchona*-derived Phase-Transfer Catalysts**

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General Methods.

Infrared (IR) spectra were recorded on a JASCO FT/IR-300E and Perkin-Elmer 1710 FT spectrometer. Nuclear magnetic resonance (^1H -NMR and ^{13}C -NMR) spectra were measured on JEOL JNM-LA 300 [300 MHz (^1H), 75 MHz (^{13}C)] spectrometer, JEOL JNM-GSX 400 [400 MHz (^1H), 100 MHz (^{13}C)] spectrometer, and Bruker AMX 500 [500 MHz (^1H), 125 MHz (^{13}C)] spectrometer, using CHCl_3 -*d* as solvents, and were reported in ppm relative to CHCl_3 (δ 7.26) for ^1H -NMR and relative to the central CDCl_3 (δ 77.23) resonance for ^{13}C -NMR. Coupling constants (*J*) in ^1H -NMR are in Hz. High performance liquid chromatography (HPLC) was performed on Hitachi L-7100 instruments using 4.6 mm $\times$ 250 mm Daicel Chiralpak OD columns. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. Low-resolution mass spectra (MS) were recorded on a VG Trio-2 GC-MS spectrometer, and high-resolution mass spectra (HRMS) were measured on a JEOL JMS-AX 505wA, JEOL JMS-HX/HX 110A spectrometer. Melting points were measured on a Buchi B-540 melting point apparatus and were not corrected. For thin-layer chromatography (TLC) analysis, Merck precoated TLC plate (silica gel 60 GF₂₅₄, 0.25 mm) were used. For flash column chromatography, E. Merck Kieselgel 60 (70~230 mesh) was used. All solvents and commercially available chemicals were used without additional purification.

Preparation of 2-picolyl chloride *N*-oxide

A mixture of 3-chloroperoxybenzoic acid (4.03 g, 18.0 mmol) with 2-picolyl chloride

hydrochloride (2.95 g, 18.0 mmol) in chloroform was stirred at room temperature for 4h. The reaction mixture was concentrated *in vacuo*. Purification of the residue by flash column chromatography afforded the 2-picolyl chloride *N*-oxide (1.68 g, 65% yield) as a white solid: mp 49 °C; IR 3396, 2960, 1615, 1490, 1441, 1282, 1225, 905, 856, 771, 677 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 8.22 (d, *J* = 7.1 Hz, 1 H), 7.55 (dd, *J* = 7.7, 1.9 Hz, 1 H), 7.29~7.19 (m, 2 H), 4.77 (s, 2 H) ppm; ¹³C NMR (300 MHz, CDCl₃) δ 147.4, 139.4, 125.9, 125.6, 125.2, 39.7 ppm; MS (EI): 143 [M]⁺.

Preparation of catalyst 10

***N*-(1-Oxy-pyridin-2-ylmethyl)hydrocinchonidinium bromide:** A mixture of (-)-hydrocinchonidine (3.0 g, 10.1 mmol) with 2-picolyl chloride *N*-oxide (1.6 g, 11.1 mmol) in a mixture of ethanol (7.5 mL), DMF (9 mL) and chloroform (3 mL) was stirred at 100 °C for 3 h. After cooling the reaction mixture to room temperature, the reaction mixture was diluted with methanol (50 mL) and then added to ether (400 mL) dropwise with stirring. The solid precipitated was filtered, washed with ether (600 mL). The crude solid was recrystallized from methanol-ether to afford 4.1 g (93% yield) of desired product as a light yellow solid: mp 158 °C; [α]_D²⁰ -154 (c 0.515, CH₃OH); IR(KBr) 3392, 2960, 1650, 1591, 1510, 1453, 1237, 1127, 1064, 892, 778 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ 8.93 (d, *J* = 4.4 Hz, 1 H), 8.45 (d, *J* = 5.7 Hz, 1 H), 8.28 (d, *J* = 8.62 Hz, 1 H), 8.13~8.05 (m, 2 H), 7.82~7.76 (m, 2 H), 7.70~7.65 (m, 1 H),

7.63~7.57 (m, 1 H), 7.53~7.48 (m, 1 H), 7.05 (d, $J = 4.8$ Hz, 1 H), 6.49 (d, $J = 4.2$ Hz, 1 H), 5.56 (d, $J = 12.5$ Hz, 1 H), 5.08 (d, $J = 12.3$ Hz, 1 H), 4.60~4.48 (m, 1 H), 4.03~3.96 (m, 2 H), 3.60~3.48 (m, 1 H), 3.45~3.38 (m, 1 H), 3.29~3.22 (m, 1 H), 2.07~2.05 (m, 1 H), 1.92~1.85 (m, 1 H), 1.75~1.67 (m, 2 H), 1.35~1.25 (m, 1 H), 1.22~1.11 (m, 2 H), 0.67 (t, $J = 7.3$ Hz, 3 H) ppm; ^{13}C NMR (100 MHz, DMSO- d_6) δ 150.1, 147.6, 145.5, 140.2, 139.4, 132.8, 129.8, 129.3, 128.3, 127.2, 125.3, 124.5, 123.8, 120.1, 68.2, 64.1, 62.9, 59.8, 56.4, 51.9, 35.5, 25.3, 23.2, 20.8, 11.3 ppm; MS (FAB): 404 $[\text{M}]^+$.

***N*-(1-Oxy-pyridin-2-ylmethyl)-*O*(9)-allylhydrocinchonidinium bromide (10):** To a suspension of *N*-(1-Oxy-pyridin-2-ylmethyl)hydrocinchonidinium bromide (2.0 g, 4.6 mmol) in dichloromethane (8 mL) was added allyl bromide (1.2 mL, 13.6 mmol) and 50% aqueous KOH (2.6 mL, 22.7 mmol). The resulting mixture was stirred vigorously at room temperature for 12 h, during which time all of solids dissolved. The mixture was diluted with water (5 mL) and was extracted with dichloromethane (3 x 20 mL). The combined organic extracts were dried over MgSO_4 , filtered and concentrated *in vacuo*. The crude solid was recrystallized from dichloromethane-hexane to yield 2.3 g (95% yield) of desired product **10** as a light yellow solid: mp 151 °C; $[\alpha]_D^{25} -140$ (c 0.555, CH_3OH); IR (KBr) 3402, 2960, 1620, 1446, 1237, 1130, 1072, 937, 891, 777 cm^{-1} ; ^1H -NMR (300 MHz, DMSO- d_6) δ 9.00 (d, $J = 4.4$ Hz, 1 H), 8.50 (d, $J = 6.4$ Hz, 1 H), 8.23 (d, $J = 8.0$ Hz, 1 H), 8.14~8.11 (m, 1 H), 8.03 (dd, $J = 7.8, 2.1$ Hz, 1 H), 7.88~7.83 (m, 1 H), 7.76~7.63 (m, 3 H), 7.58~7.53 (m, 1 H), 6.40 (s, 1H), 6.21~6.08 (m, 1 H), 5.55 (d, $J = 12.5$ Hz, 1 H), 5.43 (dd, $J = 17.2, 1.7$ Hz, 1 H), 4.94 (d, $J = 12.5$ Hz, 1 H), 4.30~4.24 (m, 2 H), 4.06~3.97 (m, 2 H), 3.52 (d, $J = 8.0$ Hz, 2 H), 3.30~3.28 (m, 1 H), 2.23~2.17 (m, 1 H), 2.12~1.90 (m, 2 H), 1.82~1.72 (m, 2 H), 1.48~1.38 (m, 1 H),

1.23~1.13 (m, 2 H), 0.70 (t, $J = 7.3$ Hz, 3 H) ppm; ^{13}C -NMR (75 MHz, $\text{DMSO}-d_6$) δ 150.2, 148.0, 141.1, 140.1, 139.1, 133.9, 132.7, 129.9, 129.6, 128.4, 127.3, 125.4, 125.1, 123.5, 119.6, 117.7, 72.8, 69.5, 67.7, 62.6, 56.8, 54.9, 52.0, 35.3, 25.2, 23.2, 20.6, 11.2 ppm; MS (FAB): 444 $[\text{M}]^+$; HRMS (ESI) calcd for $[\text{C}_{28}\text{H}_{34}\text{N}_3\text{O}_2]^+$: 481.2653, found: 481.2436.

Preparation of catalyst 11

***N*-(2'-Cyanobenzyl)hydrocinchonidininium bromide:** A mixture of (-)-hydrocinchonidine (3.0 g, 10.1 mmol) with 2-cyanobenzyl bromide (2.2 g, 11.1 mmol) in a mixture of ethanol (7.5 mL), DMF (9 mL) and chloroform (3 mL) was stirred at 100 °C for 4 h. After cooling the reaction mixture to room temperature, the reaction mixture was diluted with methanol (50 mL) and then added to ether (400 mL) dropwise with stirring. The solid precipitated was filtered, washed with ether (600 mL). The crude solid was recrystallized from methanol-ether to afford 4.7 g (92% yield) of desired product as a light pink solid: mp 165 °C; $[\alpha]_{\text{D}}^{20} -151$ (c 0.54, CH_3OH); IR 3400, 2959, 2227, 1649, 1511, 1459, 1129, 775, 615 cm^{-1} , ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 8.99 (d, $J = 4.2$ Hz, 1 H), 8.48 (d, $J = 8.4$ Hz, 1 H), 8.28 (d, $J = 7.9$ Hz, 1 H), 8.12~8.08 (m, 2 H), 7.98~7.93 (m, 1 H), 7.86~7.72 (m, 4 H), 6.86 (d, $J = 3.5$ Hz, 1 H), 6.61 (s, 1H), 5.43 (d, $J = 12.8$ Hz, 1 H), 5.31 (d, $J = 12.8$ Hz, 1 H), 4.60~4.45 (m, 1 H), 4.21~4.16 (m, 1 H), 4.08~3.98 (m, 1 H), 3.80~3.77 (m, 1 H), 3.42~3.34 (m, 1 H), 3.30~3.21 (m, 1 H),

2.16~2.09 (m, 2 H), 1.98~1.94 (m, 1 H), 1.78~1.75 (m, 2 H), 1.29~1.02 (m, 3 H), 0.69 (t, $J = 7.1$ Hz, 3 H) ppm; ^{13}C NMR (400 MHz, DMSO- d_6) δ 150.1, 147.5, 145.4, 135.7, 134.3, 133.7, 131.1, 130.9, 129.7, 129.5, 127.2, 124.4, 123.8, 120.2, 177.8, 115.7, 67.8, 64.6, 61.7, 60.6, 51.2, 35.4, 25.6, 24.9, 23.5, 20.7, 11.3 ppm; MS (FAB): 412 $[\text{M}]^+$,

***N*-(2'-Cyanobenzyl)-*O*(9)-allylhydrocinchonidinium bromide (11):** To a suspension of *N*-(2'-Cyanobenzyl)hydrocinchonidinium bromide (2.0 g, 4.06 mmol) in dichloromethane (8 mL) was added allyl bromide (1.0 mL, 12.18 mmol) and 50% aqueous KOH (2.0 mL, 20.2 mmol). The resulting mixture was stirred vigorously at room temperature for 4 h, during which time all of solids dissolved. The mixture was diluted with water (5 mL) and was extracted with dichloromethane (3 x 20 mL). The combined organic extracts were dried over MgSO_4 , filtered and concentrated *in vacuo*. The crude solid was recrystallized from dichloromethane-hexane to yield 2.0 g (94% yield) of desired product **11** as a light brown solid: mp 100 °C; $[\alpha]_D^{25} -147$ (c 0.675, CH_3OH); IR (KBr) 3435, 2961, 1635, 1516, 1493, 1460, 1311, 1164, 1074, 1022, 958, 777, 685, 428, 407 cm^{-1} ; ^1H -NMR (300 MHz, DMSO- d_6) δ 9.02 (d, $J = 4.6$ Hz, 1 H), 8.26 (d, $J = 8.4$ Hz, 1 H), 8.15~8.11 (m, 2 H), 8.02~7.93 (m, 2 H), 7.87~7.74 (m, 3 H), 7.70 (d, $J = 4.4$ Hz, 1 H), 6.48 (s, 1H), 6.18~6.06 (m, 1 H), 5.45~5.24 (m, 3 H), 5.00 (d, $J = 13.4$ Hz, 1 H), 4.33 (dd, $J = 12.2, 5.2$ Hz, 1 H), 4.28~4.15 (m, 1 H), 4.05~3.95 (m, 2 H), 3.46~3.39 (m, 2 H), 3.32~3.28 (m, 2 H), 2.30~2.20 (m, 1 H), 2.14~2.11 (m, 1 H), 1.83~1.70 (m, 2 H), 1.53~1.38 (m, 1 H), 1.24~1.14 (m, 2 H), 0.70 (t, $J = 7.2$ Hz, 3 H) ppm; ^{13}C NMR (400 MHz, DMSO- d_6) δ 150.2, 148.0, 140.9, 135.8, 134.3, 133.9, 133.7, 131.2, 130.7, 129.9, 129.6, 127.4, 125.1, 123.9, 119.7, 118.0, 117.8, 115.7, 69.4, 67.6, 61.5, 60.9, 51.3, 35.1, 25.4, 24.9, 23.5, 20.9, 11.2 ppm; MS (FAB): 452 $[\text{M}]^+$; HRMS

(ESI) calcd for $[\text{C}_{30}\text{H}_{34}\text{N}_3\text{O}]^+$: 452.2704, found: 452.2701.

Representative procedure for the enantioselective phase-transfer alkylation of *N*-(Diphenylmethylene)glycine *tert*-butyl ester **1 in the presence of **10** (benzylation):**

Benzyl bromide (0.1 mL, 0.85 mmol) was added to a mixture of *N*-(diphenylmethylene)glycine *tert*-butyl ester **1** (50 mg, 0.17 mmol) and the **8** (4.5 mg, 0.0085 mmol) in toluene/chloroform (7:3, 0.75 mL). The reaction mixture was then cooled to -20 °C, 50% aqueous KOH (0.25 mL) was added, and the reaction mixture was stirred at -20 °C until the starting material had been consumed (7 h). The suspension was diluted with ethyl ether (20 mL), washed with water (2 x 5 mL), dried over MgSO_4 , filtered, and concentrated *in vacuo*. Purification of the residue by flash column chromatography afforded the benzylated imine **2e** (61 mg, 93% yield) as a colorless oil. The enantiomeric excess of **2e** was determined by a chiral HPLC analysis [Chiralcel OD column, hexane:2-propanol = 500:2.5, flow rate = 1.0 mL/min, 23 °C, λ = 254 nm, retention times *R* (minor) 12.2 min, *S* (major) 22.5 min, 98% ee]. The absolute configuration was determined by comparison of the HPLC retention times and the $[\alpha]_D$ value with the reported data of an authentic sample.¹⁻³