SUPPORTING INFORMATION

Efficient dynamic kinetic resolution of racemic secondary alcohols by a chemoenzymatic system using bifunctional iridium complexes with C-N chelate amido ligands

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**General information.** Toluene was purchased from Kanto Chemical and was used after drying over sodium benzophenone ketyl and the following distillation under argon. Synthesis of the C-N chelate Ir complexes, Cp*Ir[κ²(N,C)-{NHC(CH₃)₂-2-C₆H₄}] (3a) and Cp*Ir[κ²(N,C)-{NHC(C₆H₅)₂-2-C₆H₄}] (3b), was presented in our previous paper.¹ Other reagents were used as delivered. The ¹H, and ¹³C NMR spectra were acquired on JEOL JNM-LA300 and JNM-ECX400 spectrometers. NMR chemical shifts were referenced to SiMe₄ by using residual proton impurities in the deuterated solvent. Analytical gas chromatography was performed with a Shimadzu GC-17A gas chromatograph equipped with a DB-1 capillary column (0.25 mm × 30 m) purchased from Agilent Technologies. Recycling preparative HPLC was performed on a Japan Analytical Industry LC-918 system connected to RI and UV detectors. According to the reported methods, analytical chiral HPLC was performed on a Chiralcel OD column (4.6 mm × 25 cm), a Chiralcel OJ-H column (4.6 mm × 25 cm) and a Chiralcel AD-H column (4.6 mm × 25 cm) with hexane/2-propanol as the eluent where baseline separation was obtained.

**General Procedure for Racemization of (R)-1-Phenylethanol Promoted by Amido Complexes.**

The Ir complex (10 µmol) was dissolved in toluene (2.0 mL) and (R)-1-phenylethanol (1.0 mmol) was added under an argon atmosphere. The solution was stirred at 30 ºC and monitored over a period by taking aliquots (10 µL) that were filtered over a short pad of Florizil (eluent: toluene), and analyzed by HPLC equipped with a Chiralcel OD column.
Screening Experiments of Dynamic Kinetic Resolution of 1-Phenylethanol.

A 20-mL Schlenk flask was charged with catalyst (50 μmol), CALB (7.0 mg), and toluene (5.0 mL) under Ar atmosphere. (R)-1-phenylethanol (1 mmol) and acyl donor (1.0 mmol) were added and the mixture was stirred at 30 °C for 6 h. After durene (11.2 mg, 0.08 mmol; an internal standard) was added, the reaction mixture was filtered through a PTFE filter (0.45 μm). Product yield was determined by GC analysis and optical yield was determined by HPLC equipped with a Chiralcel OJ-H column.

General Procedure for Dynamic Kinetic Resolution of Secondary Alcohols Catalyzed by 1a.

A 20-mL Schlenk flask was charged with 1a (10 μmol), CALB (7 mg), and toluene (1 mL) under Ar atmosphere. Secondary alcohol (1 mmol) and phenyl acetate (1.05 mmol) were added. After the reaction was carried out at 30 °C for 12 h, the product was purified by flash column chromatography on silica gel (ethyl acetate) and further chromatographed with a recycling preparative HPLC apparatus with JAIGEL-1H and JAIGEL-2H columns (polystyrene gels) using chloroform as an eluent. Optical yield was determined by HPLC equipped with a Chiralcel OJ-H column or a Chiralcel AD-H column.
Characterization Data for the Isolated products.

(R)-1-Phenylethyl acetate (2a)

Isolated yield: 92% yield. $^1$H NMR (399.8 MHz, CDCl$_3$, rt, δ/ppm): 1.54 (d, 3H, $^3$J$_{HH}$ = 6.7 Hz; C$_6$H$_5$CHCH$_3$), 2.08 (s, 3H; CH$_3$COO), 5.89 (q, 1H, $^3$J$_{HH}$ = 6.7 Hz; C$_6$H$_5$CHCH$_3$), 7.28-7.36 (m, 5H; C$_6$H$_5$CHCH$_3$). $^{13}$C{$^1$H} NMR (100.5 MHz, CDCl$_3$, rt, δ/ppm): 21.3, 22.1, 72.2, 126.0, 127.8, 128.4, 141.6, 170.2. The ee determined by chiral HPLC analysis was 99%: column, Chiralcel OJ-H; eluent, 0.8:99.2 2-propanol-hexane; temp, 30 °C; flow rate, 0.5 mL/min; detection, 254-nm light; t$_R$ of R isomer, 21.3 min; t$_R$ of S isomer, 27.6 min.

(R)-1-(4-Chlorophenyl)ethyl acetate (2b)

Isolated yield: 89% yield. $^1$H NMR (399.8 MHz, CDCl$_3$, rt, δ/ppm): 1.51 (d, 3H, $^3$J$_{HH}$ = 6.7 Hz; C$_6$H$_4$ClCHCH$_3$), 2.07 (s, 3H; CH$_3$COO), 5.84 (q, 1H, $^3$J$_{HH}$ = 6.7 Hz; C$_6$H$_4$ClCHCH$_3$), 7.27-7.33 (m, 4H; C$_6$H$_4$ClCHCH$_3$). $^{13}$C{$^1$H} NMR (100.5 MHz, CDCl$_3$, rt, δ/ppm): 21.2, 22.1, 71.5, 127.4, 128.6, 133.5, 140.1, 170.1. The ee determined by chiral HPLC analysis was 99%: column, Chiralcel OJ-H; eluent, 1:99
2-propanol-hexane; temp, 30 °C; flow rate, 0.5 mL/min; detection, 254-nm light; t_R of R isomer, 15.1 min; t_R of S isomer, 18.8 min.

(R)-1-(4-Methoxyphenyl)ethyl acetate (2c)

Isolated yield: 72% yield. ^1^H NMR (399.8 MHz, CDCl₃, rt, δ/ppm): 1.53 (d, 3H, JHH = 6.7 Hz; C₆H₄OCH₃CH₂), 2.05 (s, 3H; CH₃COO), 3.80 (s, 3H; C₆H₄OCH₃CH₂), 5.85 (q, 1H, JHH = 6.7 Hz; C₆H₄OCH₃CH₂), 6.86-7.32 (m, 4H; C₆H₄OCH₃CH₂). ^1^C{^1^H} NMR (100.5 MHz, CDCl₃, rt, δ/ppm): 21.3, 21.8, 55.2, 71.9, 113.8, 127.5, 133.7, 159.2, 170.3. The ee determined by chiral HPLC analysis was 99%: column, Chiralcel OJ-H; eluent, 1:99 2-propanol-hexane; temp, 30 °C; flow rate, 0.5 mL/min; detection, 254-nm light; t_R of R isomer, 36.4 min; t_R of S isomer, 44.4 min.

(R)-2,3-Dihydro-1H-inden-1-yl acetate (2d)

Isolated yield: 93% yield. ^1^H NMR (399.8 MHz, CDCl₃, rt, δ/ppm): 2.07 (s, 3H; CH₃COO), 2.08-3.16 (m, 4H; C₄H₇CH(CH₂)₂), 6.19-6.22 (m, 1H; C₆H₄CH(CH₃)₂), 7.21-7.43 (m, 4H; C₆H₄CH(CH₃)₂). ^1^C{^1^H} NMR (100.5 MHz, CDCl₃, rt, δ/ppm): 21.3, 30.1, 32.2, 78.3, 124.7, 125.5, 126.6, 128.9, 141.0, 144.4, 171.0. The ee determined by chiral HPLC analysis was 99%: column, Chiralcel OJ-H; eluent, 1:99
2-propanol-hexane; temp, 30 °C; flow rate, 0.5 mL/min; detection, 254-nm light; t<sub>r</sub> of S isomer, 12.8 min; t<sub>r</sub> of R isomer, 17.0 min.

*(R)-1,2,3,4-Tetrahydronaphthalen-1-yl acetate (2e)*<sup>2</sup>

![Chemical structure](image)

Isolated yield: 81% yield. <sup>1</sup>H NMR (399.8 MHz, CDCl<sub>3</sub>, rt, δ/ppm): 1.82-2.90 (m, 6H; C<sub>6</sub>H<sub>4</sub>CH(CH<sub>2</sub>)<sub>3</sub>), 2.09 (s, 3H; CH<sub>3</sub>COO), 6.00-6.02 (m, 1H; C<sub>6</sub>H<sub>4</sub>CH(CH<sub>2</sub>)<sub>3</sub>), 7.12-7.29 (m, 4H; C<sub>6</sub>H<sub>4</sub>CH(CH<sub>2</sub>)<sub>3</sub>). <sup>13</sup>C<sup>{1}H</sup> NMR (100.5 MHz, CDCl<sub>3</sub>, rt, d/ppm): 18.7, 21.4, 28.9, 29.0, 69.9, 126.0, 128.0, 129.0, 129.4, 134.5, 137.9, 170.7. The ee determined by chiral HPLC analysis was 99%: column, Chiralcel OJ-H; eluent, 1:99 2-propanol-hexane; temp, 30 °C; flow rate, 0.5 mL/min; detection, 254-nm light; t<sub>r</sub> of S isomer, 12.3 min; t<sub>r</sub> of R isomer, 14.6 min.

*(R)-1-(2-Naphthyl)ethyl acetate (2f)*<sup>2</sup>

![Chemical structure](image)

Isolated yield: 81% yield. <sup>1</sup>H NMR (399.8 MHz, CDCl<sub>3</sub>, rt, δ/ppm): 1.63 (d, 3H, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz; C<sub>10</sub>H<sub>7</sub>CHCH<sub>3</sub>), 2.11 (s, 3H; CH<sub>3</sub>COO), 6.06 (q, 1H, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz; C<sub>10</sub>H<sub>7</sub>CHCH<sub>3</sub>), 7.47-7.86 (m, 7H; C<sub>10</sub>H<sub>7</sub>CHCH<sub>3</sub>). <sup>13</sup>C<sup>{1}H</sup> NMR (100.5 MHz, CDCl<sub>3</sub>, rt, d/ppm): 21.3, 22.1, 72.4, 124.0, 124.9, 126.0, 126.1, 127.6, 127.9, 128.3, 132.9, 133.1, 138.9, 170.3. The ee determined by chiral HPLC analysis was 99%: column, Chiralcel
OJ-H; eluent, 1:99 2-propanol-hexane; temp, 30 °C; flow rate, 0.5 mL/min; detection, 254-nm light; $t_R$ of $R$ isomer, 37.8 min; $t_R$ of $S$ isomer, 48.3 min.

\[(R)-1-(1-Naphthyl)ethyl acetate (2g)\]

Isolated yield: 92% yield. $^1$H NMR (399.8 MHz, CDCl$_3$, rt, $\delta$/ppm): 1.71 (d, 3H, $^3J_{HH} = 6.7$ Hz; C$_{10}$H$_7$CHC$_3$), 2.13 (s, 3H; C$_3$H$_3$COO), 6.66 (q, 1H, $^3J_{HH} = 6.7$ Hz; C$_{10}$H$_7$CHC$_3$), 7.46-8.10 (m, 7H; C$_{10}$H$_7$CH). $^{13}$C{${^1}$H} NMR (100.5 MHz, CDCl$_3$, rt, d/ppm): 21.3, 21.6, 69.4, 123.08, 123.12, 125.3, 125.6, 126.2, 128.4, 128.8, 130.2, 133.7, 137.3, 170.3. The ee determined by chiral HPLC analysis was 99%: column, Chiralcel AD-H; eluent, 1:99 2-propanol-hexane; temp, 30 °C; flow rate, 0.5 mL/min; detection, 254-nm light; $t_R$ of $R$ isomer, 15.2 min; $t_R$ of $S$ isomer, 16.3 min.

\[(R)-1-(2-Pyridyl)ethyl acetate (2h)\]

Isolated yield: 92% yield. $^1$H NMR (399.8 MHz, CDCl$_3$, rt, $\delta$/ppm): 1.58 (d, 3H, $^3J_{HH} = 6.7$ Hz; C$_5$H$_4$NCH$_3$CHC$_3$), 2.11 (s, 3H; CH$_3$COO), 5.90 (q, 1H, $^3J_{HH} = 6.7$ Hz; C$_5$H$_4$NCHCH$_3$), 7.17-8.58 (m, 4H; C$_5$H$_4$NCHCH$_3$). $^{13}$C{${^1}$H} NMR (100.5 MHz, CDCl$_3$, rt, d/ppm): 20.6, 21.2, 72.9, 120.4, 122.6, 136.7, 149.2, 160.2, 170.2. The ee determined by chiral HPLC analysis was 99%: column, Chiralcel OJ-H; eluent, 0.7:99.3
2-propanol-hexane; temp, 30 °C; flow rate, 0.5 mL/min; detection, 254-nm light; t_R of R isomer, 24.2 min; t_R of S isomer, 26.3 min.

References