Supporting Information for

Hydrogen-Bonding Makes A Difference in the Rhodium-Catalyzed Enantioselective Hydrogenation Using Monodentate Phosphoramidites.

Yan Liu,[†] Christian A. Sandoval,[†] Yoshiki Yamaguchi,[‡] Xue Zhang,[†]
Zheng Wang,[†] Koichi Kato,[‡] and Kuiling Ding^{*,†}

[†]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry (SIOC), Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, P. R. China, and*

[‡]*Graduate School of Pharmaceutical Sciences, Nagoya City University, Mizuho, Nagoya 467-8603, Japan*

General Methods

NMR spectra were recorded in deuteriochloroform on Varian Mercury 300 (¹H 300 MHz; ¹³C 75 MHz) or Bruker DMX 500 spectrometers in CDCl₃, CD₂Cl₂, CD₃OD/CD₂Cl₂ and CD₃OD/CD₃Cl. Chemical shifts were expressed in ppm with TMS as an internal standard ($\delta = 0$ ppm) for ¹H NMR. Coupling constants, *J*, are listed in hertz. ³¹P NMR spectra were referenced with an external H₃PO₄ sample. The IR spectra were measured on Rio-Rad FTS-185 spectrometer in KBr pellets. EI mass (70 ev). ESI mass spectra were obtained on Mariner LC-TOF spectrometer. HRMS were determined on a IonSpect 4.7 TESLA FTMS. Elemental analyses were performed with an Elemental VARIO EL apparatus. Optical rotations were measured on a Perkin-Elmer 341 automatic polarimeter. HPLC analyses were carried out on a JASCO 1580 liquid chromatograph with a JASCO CD-1595 detector and AS-1555 autosampler. GC analyses were measured on Agilent 6890N network system. Dichloromethane, 1,2-dichloroethane and chloroform were freshly distilled from calcium hydride, THF and toluene were freshly distilled from sodium benzophenone ketyl. All manipulations involving air- and moisture-sensitive organometallic compounds were carried out using standard Schlenk technique under argon atmosphere.

Ligand Synthesis

Dimethyl-2,2'-dimethoxybenzil

The following procedure was adapted from Bette V.; Mortreux, A.; Ferioli, F.; Martelli, G.; Savoia, D.; Carpentier, J-F. *Euro. J. Org. Chem.* **2004**, 3040.

A 1-L round-bottomed flask equipped magnetic stirring bar and a reflux condenser was charged with 300 mL of methanol, 27.2 g (0.2 mol) of 2-methoxybenzaldehyde and 10.8 g (0.4 mol) of Al-powder. With stirring, 67 g (1.2 mol) of KOH is added in portions, then stirred for a further 0.5 h. After cooling to room temperature, the volume is reduced to 50 mL and 300 mL of water added. The mixture was extracted with CH₂Cl₂ (300 mL × 3). The combined organic phase was washed with brine and dried over MgSO₄. After removal of the solvent, the residue was transferred to a 500-mL round-bottomed flask, and 250 mL of DMSO and 40 mL of HBr (40%) added. The mixture was heated to 120 °C. After the mixture was stirred for 3 h, Na₂CO₃ was added until a pH = 7 was reached. The mixture was poured into 1 L of vigorously stirred water. The mixture was left overnight to cool to room temperature, the solid collected by filtration, washed 4 times with water, and dried under reduced pressure to afford **10** as a brown solid. This product was further purified by recrystallization from hexane/EtOAc. (17.9 g, 65% yield). M.p: 130-132 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.08 (dd, *J* = 1.8, 7.8 Hz, 2 H), 7.54-7.59 (m, 2 H), 7.09-7.15 (m, 2 H), 6.95 (d, *J* = 8.1 Hz, 2 H), 3.59 (s, 6 H) ppm. ¹³C NMR (75.4 MHz, CDCl₃): δ = 55.75, 112.36, 121.22, 123.21, 130.27, 135.53, 160.24, 192.42.

Compound 11

A 0.5-L round-bottomed flask equipped magnetic stirring bar and a reflux condenser was charged with 150 mL of glacial acetic acid, 17.9 g of compound **10**, 38 g of ammonium acetate and 8.5 mL of cyclohexanone. The mixture was stirred and refluxed for 2 h. While hot, the mixture was poured into 1 L of vigorously stirred water. The mixture was left overnight to cooled to room temperature, the solid was collected by filtration, washed twice with water,

dried under reduced pressure to afford **11** as the yellowish-green solid, which was further purified by recrystallization from H₂O/MeOH. (21.5 g, yield: 93.5%), M.p: 110 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.49 (dd, *J* = 1.5, 7.2 Hz, 2 H), 7.27-7.29 (m, 2 H), 7.00 (t, *J* = 7.2 Hz, 2 H), 6.71 (d, *J* = 8.4 Hz, 2 H), 3.16 (s, 6 H), 1.76-1.79 (m, 1 H), 1.84-1.86 (m, 2 H), 1.96-1.98 (m, 2 H) ppm. ¹³C NMR (75.4 MHz, CDCl₃): δ = 23.98, 25.53, 34.43, 54.34, 104.19, 110.36, 120.39, 124.15, 129.97, 130.09, 156.99, 164.80. Anal. Calcd. for C₂₆H₃₆N₂O₆ : C, 75.83; H, 6.94; N, 8.04% ; Found: C, 75.76; H, 6.86; N, 8.07%

(±)-1,2-Di-(2-methoxyphenyl)-1,2-ethylenediamine((±)-12).

A 1-L four-necked round-bottomed flask equipped with a mechanical stirrer, thermometer and dry ice condenser was charged with 28 g (0.073 mol) of **11**. The flask was flushed with argon, and 150 mL of dry THF was added. The mixture was cooled to -78 °C and treated with a stream of gaseous ammonia until the volume of liquid increased by 150 mL. 2.8 g (0.46 mol) of lithium was slowly introduced by cutting the wire with scissors in a gentle stream of argon. The rate of lithium addition is such that the temperature did not rise above -65 °C. The mixture was stirred for 30 min and 15 mL of ethanol was added. The mixture was stirred for an additional 20 min and 12.4 g of ammonium chloride was added. The cooling bath was removed, the mixture was allowed to warm to 0 °C, and then 150 mL of water was carefully introduced, and the phases separated. The mixture was extracted with ether (200 mL × 3). The combined organic phase was washed with brine and dried over MgSO₄. The volume was reduced to 70 mL, the solution cooled to 0 °C and then treated with 100 mL of 2N aqueous hydrochloric acid. The mixture was vigorously stirred for 1 h, then 200 mL of water was added and the biphasic mixture separated. The organic phase was washed with water (30 mL × 3) and the combined aqueous phase were washed with 100 mL of dichloromethane. The aqueous solution was treated with 100 mL of 2N aqueous sodium hydroxide and the mixture was extracted 4 times with 100 mL of dichloromethane. The combined organic phase was washed with brine and dried over MgSO₄. Solvent was removed to give **12** as a pale yellow solid (19 g, yield: 94%), M.p: 85 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.21-7.24 (m, 2 H), 7.10-7.20 (m, 2 H), 6.76-6.85 (m, 4 H), 4.47 (s, 2 H), 3.80 (s, 6 H), 1.83 (s, 4 H) ppm.

The resolution of (±)-12

A 250-mL round-bottomed flask was charged with 13.5 g (0.05 mol) of (*d,l*)-**12** and 60 mL ethanol. The mixture was heated to 70 °C, and a homogeneous solution of L-(+)-tartaric acid (7.5 g, 0.05 mol) in 60 mL ethanol was added. The tartrate salts precipitate immediately, and the mixture was cooled to ambient temperature. The solid were collected by filtration, washing twice with ethanol, and dried under reduced pressure. The tartrate salts were recrystallized twice using ethanol/water to give 5g of colorless crystals. The salt was transferred to a 250-mL, round-bottomed flask and suspended in 75 mL water. After the mixture was cooled to 0-5 °C, under vigorously stirring, 6 mL of 50% aqueous NaOH was added dropwise followed by 50 mL dichloromethane, and stirring is continued for 1 h. The aqueous phase was extracted with CH₂Cl₂ (50 mL × 3). The combined organic phase was washed with brine and dried over MgSO₄. Removal of the volatile material under reduced pressure gave (*S,S*)-**12** as a white solid (2.6 g, yield: 40%), [α]_D²⁰ = -54.9.

The filtrates from all crystallizations are combined and the solvent is evaporated under vacuum. The residual is transferred to a A 250-mL, round-bottomed flask, and suspended in 75 mL of water, After the mixture was cooled to 0-5 °C, under vigorously stirring, 6 mL of 50% aqueous NaOH was added dropwise followed by 50 mL dichloromethane, and stirring is continued for 1 h. The aqueous phase was extracted with CH₂Cl₂ (50 mL × 3). The combined organic phase was washed with brine and dried over MgSO₄. Removal of the volatile material under reduced pressure gave enriched (*R,R*)-**12** as pale-yellow solid. This material was treated in the same manner as described for the opposite enantiomer to give 3 g of white solid, yield: 45 %, [α]_D²⁰ = +53.7° (c = 0.5, CHCl₃).

General procedure for the synthesis of 2a-e

The key starting materials **13a-c** were prepared from (*R,R*)-**12** by following a literature

procedure.^[1] Compound **13** (0.8 mmol) was dissolved in dry toluene (2 mL) at 80°C under nitrogen, and then a solution of PCl₃ (1.6 mmol) in toluene (2 mL) was added. The mixture was heated to reflux for 2.5 h, and the solvent and the excessive PCl₃ were removed under the reduced pressure. The amine R'NH₂ (2.0 mmol) in dry toluene was introduced to the reaction system at 0°C. The mixture was stirred at room temperature for 8 h. After removal of the solvent, the residue was purified by column chromatography on silica (eluent: ethyl acetate/hexane = 1:10-1:5) to give corresponding phosphoramidites **2** in good yields.

(*R, R*)-**2a** (R = Et, R' = PhCH₂), 70 % yield. M.p = 138°C; [α]_D²⁰ = +5° (c = 0.2 in CHCl₃); ¹H NMR (300 MHz, CDCl₃) : δ = 7.17-7.40 (m, 12 H), 6.98-7.01 (m, 1 H), 4.61 (d, *J* = 3.6 Hz, 1 H), 4.57 (d, *J* = 3.6 Hz, 1 H), 4.21-4.28 (m, 2 H), 3.80 -3.92 (m, 1 H), 3.58-3.70 (m, 1 H), 3.26 (dd, *J* = 14.1, 7.2 Hz, 1 H), 2.83-2.95 (m, 1 H), 2.66-2.78 (m, 1 H), 1.02 (t, *J* = 7.2 Hz, 3 H), 0.88 (t, *J* = 7.2 Hz, 3 H); ³¹P NMR (121 MHz , CDCl₃): δ = 131.82 ppm; FT-IR (KBr): ν = 3247, 1686, 1482, 1269, 1203, 769cm⁻¹; EI-MS (70 ev) (*m/z*): 461 (*M*⁺, 51), 354 (46), 256 (30), 91 (100); HRMS calcd. for C₂₆H₂₈N₃O₃P : 461.1941. Found : 461.1953.

(*R, R*)-**2b** (R = PhCH₂, R' = PhCH₂), 85 % yield. M.p = 134°C; [α]_D²⁰ = -411° (c = 0.1 in CHCl₃); ¹H NMR (300 MHz, CDCl₃) : δ = 6.88-7.35 (m, 23 H), 5.29 (d, *J* = 15.6 Hz, 1 H), 5.05 (d, *J* = 15.0 Hz, 1 H), 4.43 (d, *J* = 4.2 Hz, 1 H), 4.38 (d, *J* = 3.9 Hz, 1 H), 4.03 - 4.08 (m, 2 H), 3.81 (d, *J* = 15.6 Hz, 1 H), 3.63 (d, *J* = 15.3 Hz, 1 H), 3.13 (dd, *J* = 13.8, 7.5 Hz, 1 H); ³¹P NMR (121 MHz , CDCl₃): δ = 131.96 ppm; FT-IR (KBr): ν = 3206, 1675, 1482, 1454, 1225, 771cm⁻¹; EI-MS (70 ev) (*m/z*): 585 (*M*⁺, 3), 494 (21), 405 (18), 387(16), 91 (100); HRMS calcd. for C₃₆H₃₂N₃O₃P : 585.2254. Found: 585.2251.

(*R, R*)-**2c** (R = 3,5-(Me)₂PhCH₂, R' = PhCH₂), 91 % yield. M.p = 65°C, [α]_D²⁰ = -200° (c = 1.2 in CHCl₃); ¹H NMR (300 MHz, CDCl₃) : δ = 7.07-7.33 (m, 13 H), 6.82-6.85 (m, 1 H), 6.57-6.70 (m, 5 H), 5.22 (d, *J* = 15.0 Hz, 1 H), 4.99 (d, *J* = 15.9 Hz, 1 H), 4.36 (d, *J* = 3.6 Hz, 1 H), 4.32 (d, *J* = 3.6 Hz, 1 H), 3.93-3.99 (m, 2 H), 3.66 (d, *J* = 15.3 Hz, 1 H), 3.50 (d, *J* = 15.3 Hz, 1 H), 3.05-3.08 (m, 1 H), 2.08 (s, 12 H) ppm; ³¹P NMR (121 MHz , CDCl₃): δ = 131.9 ppm; FT-IR (KBr): ν = 2963, 2917, 1686, 1481, 1453, 1262, 800 cm⁻¹; ESI-MS (*m/z*): [*M*⁺+1], 642.3, HRMS(ESI) calcd. for C₄₀H₄₁N₃O₃P⁺: 642.2880. Found: 642.2894.

(*S, S, R*)-**2d** (R = PhCH₂, R' = (*R*)- α -Ph(CH₃)CH), 89 % yield. M.p = 74°C; [α]_D²⁰ = +261° (c = 0.12 in CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ = 6.99-7.35 (m, 22 H), 6.48 (d, *J* = 8.1 Hz, 1 H), 5.30 (d, *J* = 15.3 Hz, 1 H), 5.00 (d, *J* = 15.3 Hz, 1 H), 4.33-4.39 (m, 3 H), 3.81 (d, *J* = 15.0 Hz, 1 H), 3.59 (d, *J* = 15.0 Hz, 1 H), 3.17-3.18 (m, 1 H), 1.52 (d, *J* = 6.6 Hz, 3 H) ppm; ³¹P NMR (121 MHz, CDCl₃): δ = 132.8 ppm; FT-IR (KBr): ν = 3258, 2924, 1687, 1482, 1452, 1225, 1206, 700 cm⁻¹; EI-MS (70 ev) (*m/z*): 599 (*M*⁺, 19), 508 (33), 405(40), 387 (12), 105 (51), 91(100); HRMS calcd. for C₃₇H₃₄N₃O₃P: 599.2411. Found: 599.2419

(*S, S, S*)-**2e** (R = PhCH₂, R' = (*S*)- α -Ph(CH₃)CH), 77 % yield. M.p = 35°C; [α]_D²⁰ = +356° (c

= 0.59 in CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ = 7.13-7.33 (m, 18 H), 6.92-7.02 (m, 5 H), 5.31 (d, *J* = 15.0 Hz, 1 H), 5.01 (d, *J* = 15.3 Hz, 1 H), 4.48-4.56 (m, 1 H), 4.43 (d, *J* = 3.6 Hz, 1 H), 4.35 (d, *J* = 3.6 Hz, 1 H), 3.82 (d, *J* = 15.3 Hz, 1 H), 3.63 (d, *J* = 15.3 Hz, 1 H), 3.16 (d, *J* = 7.8 Hz, 1 H), 1.54 (d, *J* = 6.6 Hz, 3 H); ³¹P NMR (121 MHz, CDCl₃) δ = 133.8 ppm; FT-IR (KBr): ν = 3255, 2924, 1687, 1482, 1452, 1226, 1206, 770, 700 cm⁻¹; EI-MS (70 ev) (*m/z*): 599 (*M*⁺, 9), 508 (31), 405(20), 387 (29), 105 (41), 91(100); HRMS calcd. for C₃₇H₃₄N₃O₃P: 599.2411. Found: 599.2392

General procedure for Substrate Synthesis

Synthesis of 4a-g

Compounds **4a-g** were prepared by following a literature procedure.^[2]

(Z)-4a, 76% yield. Oil, ¹H NMR (300 MHz, CDCl₃) δ 7.57-7.60 (m, 2 H), 7.37-7.40 (m, 3 H), 7.32 (s, 1 H), 3.85(s, 3 H), 2.34(s, 3 H) ppm.

(Z)-4b, 84% yield. Oil, ¹H NMR (300 MHz, CDCl₃) δ 6.40 (d, *J* = 9.9 Hz, 1 H), 3.77 (s, 3 H), 2.59-2.67 (m, 1 H), 2.24 (s, 3 H), 1.04 (d, *J* = 6.9 Hz, 6 H) ppm.

(Z)-4c, 86% yield. Oil, ¹H NMR (300 MHz, CDCl₃) δ 6.57 (t, *J* = 7.5 Hz, 1 H), 3.78 (s, 3 H), 2.26 (s, 3 H), 2.09-2.16 (m, 2 H), 1.43-1.51 (m, 2 H), 0.94 (t, *J* = 7.5 Hz, 3 H) ppm.

(Z)-4d, 71% yield. Oil, ¹H NMR (300 MHz, CDCl₃) δ 7.56-7.61 (m, 2 H), 7.28 (s, 1 H), 7.05-7.11 (m, 2 H), 3.85(s, 3 H), 2.34(s, 3 H) ppm; ¹³C NMR (75.4 MHz, CDCl₃): δ = 20.21, 24.67, 43.34, 52.26, 115.46, 115.75, 125.77, 127.90, 127.95, 131.76, 131.88, 136.26, 136.29, 161.28, 162.59, 164.62, 168.17; ESI-MS (*m/z*): [*M*⁺+1], 239.2, HRMS (ESI) calcd. for C₁₂H₁₁O₄FN⁺: 261.0533. Found: 261.0535.

(Z)-4e, 69% yield. Oil, ¹H NMR (300 MHz, CDCl₃) δ 7.59 (s, 1 H), 7.42-7.45 (m, 1 H), 7.32-7.34 (m, 2 H), 7.24 (s, 1 H), 3.86 (s, 3 H), 2.34 (s, 3 H) ppm; ¹³C NMR (75.4 MHz, CDCl₃): δ = 20.53, 52.66, 125.73, 128.10, 129.63, 129.87, 129.90, 133.56, 134.53, 137.74, 162.59, 168.28; ESI-MS (*m/z*): [*M*⁺+1], 255.2; Anal. calcd. for C₁₂H₁₁ClO₄: C, 56.59; H, 4.35. Found: C, 56.95; H, 4.27.

(Z)-4f, 65% yield. Oil, ^1H NMR (300 MHz, CDCl_3) δ 7.61-7.65 (m, 3 H), 7.18-7.35 (m, 2 H), 3.88 (s, 3 H), 2.26 (s, 3 H) ppm; ^{13}C NMR (75.4 MHz, CDCl_3): δ = 20.18, 52.49, 124.67, 125.78, 127.18, 129.99, 130.51, 131.63, 132.80, 137.84, 162.59, 168.28; ESI-MS (m/z): $[\text{M}^++1]$, 299.2, HRMS (ESI) calcd. for $\text{C}_{12}\text{H}_{11}\text{O}_4\text{BrNa}^+$: 320.9733. Found: 320.9729.

(Z)-4g, 85% yield. Oil, ^1H NMR (300 MHz, CDCl_3) δ 8.03 (s, 1 H), 7.81-7.86 (m, 3 H), 7.73-7.74 (m, 1 H), 7.49-7.54 (m, 3 H), 3.88 (s, 3 H), 2.38 (s, 3 H) ppm; ^{13}C NMR (75.4 MHz, CDCl_3): δ = 20.72, 52.67, 126.25, 126.61, 127.36, 127.64, 128.43, 128.56, 129.51, 130.94, 133.05, 133.63, 136.92, 163.09, 168.61; ESI-MS (m/z): $[\text{M}^++1]$, 271.2; Anal. calcd. for $\text{C}_{16}\text{H}_{14}\text{O}_4$: C, 71.10; H, 5.22. Found: C, 71.41; H, 5.14.

General procedure for the synthesis of 5a-g

Compounds **5a-f** were prepared by following a literature procedure.^[3]

(E)-5a, 46% yield. Oil, ^1H NMR (300 MHz, CDCl_3) δ 7.90 (s, 1 H), 7.33-7.41 (m, 5 H), 3.82 (s, 3 H), 3.73 (s, 3 H), 3.54 (s, 2 H) ppm.

(E)-5b, 51% yield. Oil, ^1H NMR (300 MHz, CDCl_3) δ 7.86 (s, 1 H), 7.32-7.37 (m, 2 H), 7.06-7.12 (m, 2 H), 3.83 (s, 3 H), 3.74 (s, 3 H), 3.52 (s, 2 H) ppm; ^{13}C NMR (75.4 MHz, CDCl_3): δ = 33.33, 52.23, 52.31, 115.61, 115.90, 125.70, 130.88, 130.99, 141.02, 167.63, 171.51; ESI-MS (m/z): $[\text{M}^++\text{Na}]$, 275.1, HRMS (ESI) calcd. for $\text{C}_{13}\text{H}_{13}\text{O}_4\text{FNa}^+$: 275.0690. Found: 275.0682.

(E)-5c, 38% yield. Oil, ^1H NMR (300 MHz, CDCl_3) δ 7.83 (s, 1 H), 7.20-7.35 (m, 4 H), 3.84 (s, 3 H), 3.74 (s, 3 H), 3.51 (s, 2 H) ppm.

(E)-5d, 41% yield. M.p: 126°C ; ^1H NMR (300 MHz, CDCl_3) δ 8.06 (s, 1 H), 7.83-7.87 (m, 4 H), 7.42-7.53 (m, 3 H), 3.86 (s, 3 H), 3.76 (s, 3 H), 3.62 (s, 2 H) ppm.

(E)-5e, 39% yield. Oil, ^1H NMR (300 MHz, CDCl_3) δ 7.88 (s, 1 H), 7.62 (d, J = 7.8 Hz, 1 H), 7.26-7.33 (m, 3 H), 3.85 (s, 3 H), 3.72 (s, 3 H), 3.39 (s, 2 H) ppm; ^{13}C NMR (75.4 MHz, CDCl_3): δ = 33.49, 52.16, 52.36, 123.87, 127.31, 127.39, 129.89, 130.18, 132.77, 135.34, 141.34, 167.15, 171.35; ESI-MS (m/z): $[\text{M}^++\text{Na}]$, 335.0, HRMS (ESI) calcd. for $\text{C}_{13}\text{H}_{13}\text{BrO}_4\text{Na}^+$: 334.9889. Found: 334.9893. Anal. calcd. for $\text{C}_{13}\text{H}_{13}\text{BrO}_4$: C, 49.86; H, 4.18. Found: C, 49.90; H, 4.20.

(E)-5f, 58% yield. Oil, ^1H NMR (300 MHz, CDCl_3) δ 7.87 (s, 1 H), 7.30 (t, J = 8.7 Hz, 1 H), 6.88-6.93 (m, 3 H), 3.83 (s, 3 H), 3.80 (s, 3 H), 3.73 (s, 3 H), 3.55 (s, 2 H) ppm.

General procedure for catalytic asymmetric hydrogenation

$[\text{Rh}(\text{cod})_2]\text{BF}_4$ (2.0 mg, 0.005 mmol), ligand (0.011 mmol) were dissolved in CH_2Cl_2 (1 mL) under nitrogen and the solution was stirred at room temperature for 10 min. The substrate (0.5 mmol) in CH_2Cl_2 (1.5 mL) was added to the above catalyst solution. The mixture was then transferred to a stainless steel autoclave under nitrogen atmosphere, and then sealed. After purging with hydrogen for 3 times, final H_2 pressure was adjusted to the value shown in Table 1. After stirring at room temperature for 10 h, H_2 was released. After removal of the solvent under the reduced pressure, the residue of the product was passed through a pad of Celite and submitted to ^1H NMR analysis to assess the conversion of the starting materials. The enantiomeric excess of the product was determined by chiral HPLC or GC.

Crystal structural data of **(S,S,R)-2d**

$\text{C}_{37}\text{H}_{34}\text{N}_3\text{O}_3\text{P}$, M_r = 599.64, orthorhombic, $P2_12_12_1$, a = 11.8569(7) Å, b = 19.6421(12) Å, c = 27.9528(18) Å; V = 6510.1(7) Å³; $2.92 < 2\theta < 54.00$ degree; ρ_{calc} = 1.224 g cm⁻³, Z = 8, R_{int} = 0.124. Goodness of fit indicator = 0.739, Final $R1$ = 0.0529, $wR2$ = 0.0872 on F^2 for observed data, P_{max} , P_{min} = 1.000, 0.685 Å⁻³; Absolute structure parameter was 0.04(10). CCDC-605891 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk)

95°C, t_R = 32.7 min (minor), 34.0 min (major).

(-)-6d: >99% conv., 99.4% ee, $[\alpha]_D^{20} = -5.2^\circ$ ($c = 1.0$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.09-7.14 (m, 2 H), 6.89-6.95 (m, 2 H), 5.10-5.14 (m, 1 H), 3.66 (s, 3 H), 3.00-3.07 (m, 2 H), 2.02 (s, 3 H) ppm; ^{13}C NMR (75.4 MHz, CDCl_3): δ = 20.57, 36.51, 52.37, 72.80, 115.20, 115.48, 130.73, 130.84, 169.96, 170.27; ESI-MS (m/z): $[\text{M}^+ + 1]$, 241.2; Anal. calcd. for $\text{C}_{12}\text{H}_{11}\text{FO}_4$: C, 60.00; H, 5.45. Found: C, 60.33; H, 5.88.

The enantiomeric excess was determined by HPLC on Chiralcel OJ column, hexane : isopropanol = 97 : 3; flow rate = 0.7 mL/min; UV detection at $\lambda = 230$ nm; $t = 22.1$ min (minor), 25.4 min (major), respectively.

(-)-6e: >99% conv., 96.6% ee, $[\alpha]_D^{20} = -5.8^\circ$ ($c = 1.0$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.22-7.27 (m, 3 H), 7.09-7.12 (m, 1 H), 5.18-5.23 (m, 1 H), 3.74 (s, 3 H), 3.02-3.19 (m, 2 H), 2.10 (s, 3 H) ppm; ^{13}C NMR (75.4 MHz, CDCl_3): δ = 20.54, 36.88, 52.41, 72.49, 127.29, 127.41, 129.44, 129.71, 134.18, 137.83, 169.81, 170.23; ESI-MS (m/z): $[\text{M}^+ + 1]$, 257.2, HRMS(ESI) calcd. for $\text{C}_{12}\text{H}_{14}\text{O}_4\text{Cl}^+$: 257.0575. Found: 257.0574. The enantiomeric excess was determined by HPLC on Chiralcel OJ column, hexane : isopropanol = 97 : 3; flow rate = 0.7 mL/min; UV detection at $\lambda = 230$ nm; $t = 21.4$ min (minor), 25.6 min (major), respectively.

(-)-6f: >99% conv., 96.6% ee, $[\alpha]_D^{20} = -9.8^\circ$ ($c = 1.0$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.56 (d, $J = 8.1$ Hz, 1 H), 7.24-7.26 (m, 2 H), 7.12-7.16 (m, 1 H), 5.29-5.33 (m, 1 H), 3.75 (s, 3 H), 3.15-3.43 (m, 2 H), 2.07 (s, 3 H) ppm; ^{13}C NMR (75.4 MHz, CDCl_3): δ = 20.53, 37.43, 52.42, 71.41, 124.76, 127.34, 128.82, 131.57, 132.97, 135.31, 170.08, 170.21; ESI-MS (m/z): $[\text{M}^+ + 1]$, 301.2, HRMS(ESI) calcd. for $\text{C}_{12}\text{H}_{13}\text{O}_4\text{BrNa}^+$: 322.9889. Found: 322.9891. The enantiomeric excess was determined by HPLC on Chiralcel OJ column, hexane : isopropanol = 97 : 3; flow rate = 0.7 mL/min; UV detection at $\lambda = 230$ nm; $t = 22.0$ min (minor), 26.1 min (major), respectively.

(+)-6g: >99% conv., 98.0% ee, $[\alpha]_D^{20} = +9.7^\circ$ ($c = 1.0$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.78-7.84 (m, 3 H), 7.68 (s, 1 H), 7.46-7.48 (m, 2 H), 7.36 (d, $J = 8.4$ Hz, 1 H), 5.29-5.34 (m, 1 H), 3.73 (s, 3 H), 3.21-3.38 (m, 2 H), 2.08 (s, 3 H) ppm; ^{13}C NMR (75.4 MHz, CDCl_3): δ = 20.56, 37.51, 52.32, 72.94, 125.74, 126.17, 127.31, 127.59, 127.63, 127.99, 128.12, 132.45, 133.40, 170.16, 170.30; ESI-MS (m/z): $[\text{M}^+ + 23]$, 295.2, HRMS(ESI) calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_4\text{Na}^+$: 295.0941. Found: 295.0949. The enantiomeric excess was determined by HPLC on Chiralcel OD column, hexane : isopropanol = 95 : 5; flow rate = 1.0 mL/min; UV detection at $\lambda = 230$ nm; $t = 9.3$ min (major), 10.3 min (minor), respectively.

(R)-7a: >99% conv., 97.5% ee, $[\alpha]_D^{20} = +46.0^\circ$ ($c = 0.3$ in CHCl_3), [Lit. $[\alpha]_D^{20} = +26.4^\circ$ ($c = 1.00$ in EtOAc) for (*R*)-enantiomer]^[7]; ^1H NMR (300 MHz, CDCl_3) δ 7.14-7.32 (m, 5 H), 3.67 (s, 3 H), 3.64 (s, 3 H), 3.02-3.13 (m, 2 H), 2.64-2.79 (m, 2 H), 2.37-2.44 (m, 1 H) ppm.

The enantiomeric excess was determined by HPLC on Chiralcel OD column, hexane : isopropanol = 95 : 5; flow rate = 1.0 mL/min; UV detection at $\lambda = 230$ nm; $t_R = 9.4$ min (major), 10.8 min (minor), respectively.

(+)-7b: >99% conv., 99.0% ee, $[\alpha]_D^{20} = +20.8^\circ$ ($c = 1.4$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.08-7.14 (m, 2 H), 6.95-7.02 (m, 2 H), 3.66 (s, 3 H), 3.65 (s, 3 H), 2.97-3.13 (m, 2 H), 2.64-2.79 (m, 2 H), 2.37-2.44 (m, 1 H) ppm; ^{13}C NMR (75.4 MHz, CDCl_3): $\delta = 34.88, 36.86, 41.83, 51.83, 51.95, 115.22, 115.51, 130.38, 130.48, 172.17, 174.55$; ESI-MS (m/z): $[\text{M}^+ + \text{Na}]$, 277.1, HRMS(ESI) calcd. for $\text{C}_{13}\text{H}_{15}\text{O}_4\text{FNa}^+$: 277.08466. Found: 277.0846. The enantiomeric excess was determined by HPLC on Chiralcel OD column, hexane : isopropanol = 95 : 5; flow rate = 1.0 mL/min; UV detection at $\lambda = 230$ nm; $t = 8.1$ min (major), 13.1 min (minor), respectively.

(R)-7c^[8]: >99% conv., 96.7% ee, $[\alpha]_D^{20} = +20.6^\circ$ ($c = 4.0$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.16-7.23 (m, 3 H), 7.03-7.06 (m, 1 H), 3.68 (s, 3 H), 3.66 (s, 3 H), 2.99-3.14 (m, 2 H), 2.64-2.79 (m, 2 H), 2.37-2.45 (m, 1 H) ppm. The enantiomeric excess was determined by HPLC on Chiralcel OD column, hexane : isopropanol = 97 : 3; flow rate = 1.0 mL/min; UV detection at $\lambda = 230$ nm; $t_R = 13.6$ min (major), 18.1 min (minor), respectively.

(R)-7d^[8]: >99% conv., 96.1% ee, $[\alpha]_D^{20} = +36.9^\circ$ ($c = 5.0$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.77-7.82 (m, 3 H), 7.60 (s, 1 H), 7.44-7.47 (m, 2 H), 7.30 (d, $J = 8.1$ Hz, 1 H), 3.67 (s, 3 H), 3.62 (s, 3 H), 3.19-3.25 (m, 2 H), 2.90-2.96 (m, 1 H), 2.68-2.76 (m, 1 H), 2.40-2.48 (m, 1 H) ppm. The enantiomeric excess was determined by HPLC on Chiralcel OD column, hexane : isopropanol = 95 : 5; flow rate = 1.0 mL/min; UV detection at $\lambda = 230$ nm; $t_R = 10.3$ min (major), 13.7 min (minor), respectively.

(+)-7e: >99% conv., 96.1% ee, $[\alpha]_D^{20} = +16.8^\circ$ ($c = 1.0$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.55 (d, $J = 7.8$ Hz, 1 H), 7.07-7.24 (m, 3 H), 3.66 (s, 3 H), 3.65 (s, 3 H), 3.14-3.29 (m, 2 H), 2.89-2.96 (m, 1 H), 2.70-2.79 (m, 1 H), 2.43-2.50 (m, 1 H) ppm; ^{13}C NMR (75.4 MHz, CDCl_3): $\delta = 35.04, 37.78, 41.24, 51.78, 51.97, 124.70, 127.44, 128.49, 131.22, 133.05, 137.63, 172.08, 174.53$; ESI-MS (m/z): $[\text{M}^+ + \text{Na}]$, 337.0, HRMS(ESI) calcd. for $\text{C}_{13}\text{H}_{15}\text{O}_4\text{BrNa}^+$: 337.0046. Found: 337.0057. The enantiomeric excess was determined by HPLC on Chiralcel OD column, hexane : isopropanol = 95 : 5; flow rate = 1.0 mL/min; UV detection at $\lambda = 230$ nm; $t = 10.6$ min (major), 14.5 min (minor), respectively.

(R)-7f^[8]: >99% conv., 99.1% ee, $[\alpha]_D^{20} = +20.9^\circ$ ($c = 0.9$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.21 (t, $J = 7.8$ Hz, 1 H), 6.70-6.79 (m, 3 H), 3.79 (s, 3 H), 3.69 (s, 3 H), 3.64 (s, 3 H), 3.01-3.16 (m, 2 H), 2.63-2.76 (m, 2 H), 2.39-2.46 (m, 1 H) ppm. The enantiomeric excess was determined by HPLC on Chiralcel OD column, hexane : isopropanol = 95 : 5; flow rate = 1.0 mL/min; UV detection at $\lambda = 230$ nm; $t_R = 16.5$ min (major), 19.4 min (minor), respectively.

Catalyst Optimization

Table S1. Rh(I) catalyzed enantioselective hydrogenation of (Z)-methyl α -(acetoxy)acrylates(**2**).^a

^a Conditions: [Rh(cod)BF₄] = 2 mM; [**2**] = 4 mM (Rh/**2** = 1/2); [**4a**] = 0.2 M; S/C = 100; *T* = 25 °C; *t* = 10 h. Conversion was determined by ¹H NMR. ^b Determined by chiral HPLC or GC. ^c Absolute configurations determined by [α]_D.

Table S2. Optimization of the hydrogenation of β -aryl-itaconate derivatives.^a

Entry	solvent	L	conv.(%)	ee (%) ^b
1	CH_2Cl_2	3c	100	76.1
2	$\text{CH}_2\text{Cl}_2/\text{i-PrOH}$	3c	N.R	
3	i-PrOH	3c	N.R	
4	CHCl_3	3c	N.R	
5	DCE	3c	100	67.7
6	Toluene	3c	N.R	
7	benzene	3c	N.R	
8	CH_2Cl_2	3b	100	74.8
9	CH_2Cl_2	2b	100	98.1
10	CH_2Cl_2	2c	100	97.7
11	CH_2Cl_2	2d	100	87.7
12	CH_2Cl_2	2e	100	87.1

^a Conditions: $[\text{Rh}(\text{cod})\text{BF}_4] = 2 \text{ mM}$; $[\mathbf{2}] = 4 \text{ mM}$ ($\text{Rh}/\mathbf{2} = 1/2$); $[\mathbf{4a}] = 0.2 \text{ M}$; $\text{S/C} = 100$; $T = 25^\circ\text{C}$; $t = 10 \text{ h}$. Conversion was determined by ^1H NMR. ^b Determined by chiral HPLC or GC.

Calculated Structure for Rh/**2b**-complex

The calculations were performed on the simplified structural mimic of the catalyst precursor Rh/**2b** by using the Gaussian 03 program.^[9] Geometry optimization was done using DFT at the B3LYP level^{[10], [11]} with ECP LANL2DZ as the basis set for rhodium^[12] and 6-31G(d) for all other atoms (C, H, N, P and O). The single-crystal X-ray structure of **1**/Rh was taken as the starting geometry, where one of the amino methyl groups in each ligand was replaced by H. Although in principle there could be two different starting structures as a result of potential types of H-bond interactions (N–H···N or N–H···O) present between the two ligands in Rh/**2b**, geometrical optimizations using either one as the starting point always converged to the same structure, as shown in Figure S2. The H···O distance of 2.4 Å and N–H···O bond angle of 150° suggested a N–H···O hydrogen bonding is present between the two ligands in the C₂-symmetric model complex.

Table S2. Cartesian coordinates of the structure

Rh	-0.759472	-0.774746	0.029035	H	-2.535158	4.899044	-3.175412
P	1.552049	-0.750703	-0.013826	H	-4.394417	4.602659	-1.882159
P	-0.781266	1.536799	-0.015825	H	5.065587	-2.317853	3.078759
O	2.269969	-0.274622	1.409861	H	4.758748	-4.230599	1.868610
O	2.145365	-2.262881	-0.248081	C	-1.971724	2.846591	-3.189101
O	-0.373801	2.208648	-1.482640	C	-1.050641	1.919666	-2.682335
O	-2.295460	2.109698	0.253656	C	-2.560125	2.548013	-4.427677
N	2.313390	0.280680	-1.075069	C	-0.708763	0.760499	-3.381233
N	0.273473	2.357796	0.975645	C	-2.246846	1.386103	-5.131646
C	-0.908097	-2.875993	-0.888907	H	-3.271143	3.254765	-4.848383
C	-0.876327	-3.071663	0.478022	C	-1.313408	0.489319	-4.608712
C	-2.821427	-0.928225	1.031501				
C	-3.068792	-0.952468	-0.327177	H	0.035974	0.087686	-2.968047
C	4.244213	-2.164113	2.371538	H	-2.715542	1.190916	-6.091468
C	4.072648	-3.460588	1.502872	H	-1.041995	-0.407035	-5.158945
C	3.703930	0.757735	-0.977649	C	-2.682130	3.358537	0.779142
C	-2.338273	4.108371	-2.444297	C	-2.487262	3.612647	2.136182
C	-3.597444	3.945642	-1.520809	C	-3.344922	4.260230	-0.065225
C	0.717929	3.752416	0.807878	C	-2.928585	4.821641	2.674802
H	0.042731	-2.957171	-1.410814	H	-1.993263	2.871791	2.755102
H	0.100805	-3.257611	0.915971	C	-3.780089	5.463457	0.508032
H	-2.902493	0.040145	1.520111	C	-3.572119	5.751564	1.857115
H	-3.290998	0.003482	-0.794023	H	-2.777011	5.027670	3.730142
H	4.541018	-1.329376	1.731231	H	-4.302452	6.180024	-0.120694
H	3.061708	-3.855997	1.645442	H	-3.924142	6.691940	2.270233
H	4.000375	1.162565	-1.948789	C	2.040043	-0.910234	2.644372
H	4.369712	-0.073385	-0.744356	C	0.901126	-0.563900	3.373705
H	3.820924	1.531836	-0.210948	C	3.004015	-1.793295	3.149722
H	-1.486299	4.445203	-1.848013	C	0.688616	-1.125927	4.632599
H	-3.977348	2.922725	-1.610235	H	0.198134	0.151401	2.958763
H	1.153951	4.093004	1.750614	C	2.764224	-2.339179	4.420129
H	-0.135009	4.393061	0.583070	C	1.623339	-2.021265	5.155702
H	1.459210	3.854920	0.007414	H	-0.191867	-0.850693	5.206070
H	1.677405	0.937176	-1.517060	H	3.500699	-3.019859	4.840031
H	0.958700	1.751892	1.416260	H	1.473941	-2.456311	6.139292

C	3.381417	-2.645470	-0.805810	C	-2.071597	-3.372293	1.367085
C	3.580636	-2.497926	-2.177903	C	-3.377926	-2.186375	-1.158664
C	4.327421	-3.258092	0.027906	C	-2.125899	-2.842559	-1.784494
C	4.777480	-2.936411	-2.745217	H	-3.735188	-2.356529	2.344213
H	2.807205	-2.042237	-2.786277	H	-2.152056	-1.795362	2.846498
C	5.517086	-3.691848	-0.574004	H	-1.736369	-4.010855	2.190949
C	5.750296	-3.530266	-1.939943	H	-2.806755	-3.960006	0.810445
H	4.940810	-2.821490	-3.812589	H	-2.365531	-3.866405	-2.110857
H	6.267189	-4.175971	0.046156	H	-1.856245	-2.293191	-2.693226
H	6.681614	-3.879852	-2.375063	H	-4.053649	-1.895149	-1.969513
C	-2.729437	-2.110027	1.970181	H	-3.929153	-2.910798	-0.552800

Catalyst NMR

Figure S2. ^1H in CDCl_3 (a), ^1H - ^{15}N HSQC (b), and ^1H - ^{13}C HMQC (c) NMR spectra of $[\text{Rh}(^{15}\text{N}\text{-}\mathbf{2b})_2(\text{cod})]\text{BF}_4$ complex in CD_2Cl_2 . (d) Comparison of $\mathbf{2b}$ and $[\text{Rh}(^{15}\text{N}\text{-}\mathbf{2b})_2(\text{cod})]\text{BF}_4$ showing the downfield shift for NHa-protons (red arrows) in CD_2Cl_2 .

(c)

(d)

Figure S3. ^1H (a), ^1H - ^{15}N HSQC (b), and ^1H - ^{13}C HMQC (c) NMR spectra of $[\text{Rh}(^{15}\text{N}\text{-}\mathbf{3b})_2(\text{cod})]\text{BF}_4$ complex. (d) Comparison of $\mathbf{23}$ and $[\text{Rh}(^{15}\text{N}\text{-}\mathbf{23})_2(\text{cod})]\text{BF}_4$ showing the downfield shift for NHa-protons (red arrows).

d

References

- (1) Liu, Y.; Ding, K. L. *J. Am. Chem. Soc.* **2005**, *127*, 10488.
- (2) Schmidt, U.; Langner, J. L.; Kirschbaum, B.; Braun, C. *Synthesis* **1994**, 1138.
- (3) Miguel del Corral, J.; Gordaliza, M.; Castro, M.; Salinero, M.; Dorado, J.; Feliciano, A. *Synthesis* **2000**, 154.
- (4) Burkard, U.; Effenberger, F. *Chem. Ber.* **1986**, *119*, 1594.
- (5) Bartlett, E.; Kuna, T.; Levene, L. *J. Biol. Chem.* **1937**, *118*, 515.
- (6) Burk, M. J.; Kalberg, C. S.; Pizzano, A. *J. Am. Chem. Soc.* **1998**, *120*, 4345.
- (7) Caro, Y.; Masaguer, C.; Ravina, E. *Tetrahedron: Asymmetry* **2003**, *141*, 381.
- (8) Tang, W.; Liu, D.; Zhang, X. *Org. Lett.* **2003**, *5*, 205.
- (9) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. Gaussian 03, Revision C.02; Gaussian, Inc.: Wallingford, CT, **2004**.
- (10) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
- (11) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. A* **1988**, *37*, 785.
- (12) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

Asymmetric Hydrogenation Results

Chiral HPLC or GC charts of products 5 and 7

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	32.719	BB	0.2332	865.82178	44.25956	50.01937
2	34.056	BB	0.2382	865.15131	43.28893	49.98063

Totals : 1730.97308 87.54848

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	32.693	BP	0.2381	10.09076	5.07243e-1	0.68498
2	34.037	BP	0.2385	1463.06226	72.79648	99.31502

Totals : 1473.15302 73.30372

(GC, 95°C, N₂ flow: 1.1 mL/min)

=====
Area Percent Report
=====

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	23.081	BV	0.1742	1198.54504	83.15367	50.00293
2	23.663	VB	0.1722	1198.40442	85.16383	49.99707

Totals : 2396.94946 168.31750

=====
Area Percent Report
=====

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	23.029	BB	0.1637	22.25898	1.60613	0.63945
2	23.708	BB	0.1773	3458.71118	231.50320	99.36055

Totals : 3480.97016 233.10934

Results obtained with enhanced integrator!

HPLC-OJ column (hexane : i-PrOH = 95 : 5, 1.0 mL/min)

File name : ly-13-84035.CH2

Info :

Vial # = 1 Rack # = 1
Injection Date : 5-Dec-2005 21:07:26
Curr. Date : 5-Dec-2005 22:15:46
User : LY
Group : DATA
Control Method : LY-H

#	Name	RT	Area[μV.Sec]	%Area
1		16.100	12345.281	0.099
2		19.775	12471910.277	99.901

Total Area of Peak = 12484255.558 [μV.Sec]

File name : ly-13-84-r036.CH2

Info :

Vial # = 1 Rack # = 1
Injection Date : 5-Dec-2005 21:43:26
Curr. Date : 5-Dec-2005 22:15:46
User : LY
Group : DATA
Control Method : LY-H

#	Name	RT	Area[μV.Sec]	%Area
1		16.158	9686602.000	51.537
2		19.725	9108939.963	48.463

Total Area of Peak = 18795541.963 [μV.Sec]

HPLC-OJ column (hexane : i-PrOH = 95 : 5, 1.0 mL/min)

File name : ly-13-93-r042.CH2

Info :

Vial # = 1 Rack # = 1
 Injection Date : 15-Dec-2005 11:39:34
 Curr. Date : 15-Dec-2005 12:49:54
 User : LY
 Group : DATA
 Control Method : LY-13-93

#	Name	RT	Area[μV.Sec]	%Area
1		22.058	5530704.755	51.121
2		25.425	5288200.929	48.879

Total Area of Peak = 10818905.684 [μV.Sec]

File name : ly-13-99043.CH2

Info :

Vial # = 1 Rack # = 1
 Injection Date : 15-Dec-2005 12:14:56
 Curr. Date : 15-Dec-2005 12:49:54
 User : LY
 Group : DATA
 Control Method : LY-13-93

#	Name	RT	Area[μV.Sec]	%Area
1		22.367	21849.903	0.293
2		25.067	7447962.930	99.707

Total Area of Peak = 7469812.833 [μV.Sec]

HPLC-OJ column (hexane : i-PrOH = 95 : 5, 1.0 mL/min)

File name : ly-14-enoester-m-cl044.CH2

Info :

Vial # = 1 Rack # = 1
 Injection Date : 15-Dec-2005 12:55:16
 Curr. Date : 15-Dec-2005 14:11:20
 User : LY
 Group : DATA
 Control Method : LY-13-93

#	Name	RT	Area[μV.Sec]	%Area
1		21.350	18432232.486	49.256
2		25.567	18988827.927	50.744

Total Area of Peak = 37421060.412 [μV.Sec]

File name : ly-14-9045.CH2

Info :

Vial # = 1 Rack # = 1
 Injection Date : 15-Dec-2005 13:35:20
 Curr. Date : 15-Dec-2005 14:11:20
 User : LY
 Group : DATA
 Control Method : LY-13-93

#	Name	RT	Area[μV.Sec]	%Area
1		21.700	829005.535	1.680
2		25.283	48530251.868	98.320

Total Area of Peak = 49359257.403 [μV.Sec]

HPLC-OJ column (hexane : i-PrOH = 95 : 5, 1.0 mL/min)

File name : ly-14-br-raci052.CH2

Info :

Vial # = 1 Rack # = 1
 Injection Date : 16-Dec-2005 12:38:42
 Curr. Date : 16-Dec-2005 13:49:26
 User : LY
 Group : DATA
 Control Method : LY-13-93

#	Name	RT	Area[μV.Sec]	%Area
1		21.992	18359477.192	49.227
2		26.125	18936051.017	50.773

Total Area of Peak = 37295528.209 [μV.Sec]

File name : ly-14-11053.CH2

Info :

Vial # = 1 Rack # = 1
 Injection Date : 16-Dec-2005 13:16:44
 Curr. Date : 16-Dec-2005 13:49:26
 User : LY
 Group : DATA
 Control Method : LY-13-93

#	Name	RT	Area[μV.Sec]	%Area
1		22.125	1650914.500	1.670
2		25.142	97225991.866	98.330

Total Area of Peak = 98876906.366 [μV.Sec]

HPLC-OD column (hexane : i-PrOH = 95 : 5, 1.0 mL/min)

File name : ly-14-12060.CH2

Info :

Vial # = 1 Rack # = 1
 Injection Date : 19-Dec-2005 11:03:42
 Curr. Date : 12-May-2006 21:13:10
 User : LY
 Group : DATA
 Control Method : LY-H

#	Name	RT	Area[$\mu V \cdot Sec$]	%Area
1		9.283	2334638.750	99.020
2		10.325	23095.750	0.980

Total Area of Peak = 2357734.500 [$\mu V \cdot Sec$]

File name : ly-14-8-r058.CH2

Info :

Vial # = 1 Rack # = 1
 Injection Date : 19-Dec-2005 10:27:46
 Curr. Date : 12-May-2006 21:13:10
 User : LY
 Group : DATA
 Control Method : LY-H

#	Name	RT	Area[$\mu V \cdot Sec$]	%Area
1		9.325	14499567.128	48.819
2		10.383	15200925.933	51.181

Total Area of Peak = 29700493.061 [$\mu V \cdot Sec$]

HPLC-OD column (hexane : i-PrOH = 95 : 5, 1.0 mL/min)

File name : ly-13-37005.CH2

Info :

Vial # = 1 Rack # = 1
 Injection Date : 2-Nov-2005 22:01:40
 Curr. Date : 12-May-2006 21:15:46
 User : LY
 Group : DATA
 Control Method : LY-H

#	Name	RT	Area[$\mu V \cdot Sec$]	%Area
1		9.058	4935246.048	99.071
2		10.450	46282.000	0.929

Total Area of Peak = 4981528.048 [$\mu V \cdot Sec$]

File name : ly-13-24-raci003.CH2

Info :

Vial # = 1 Rack # = 1
 Injection Date : 31-Oct-2005 8:46:12
 Curr. Date : 12-May-2006 21:15:46
 User : LY
 Group : DATA
 Control Method : LY-H

#	Name	RT	Area[$\mu V \cdot Sec$]	%Area
1		9.417	3306534.818	49.214
2		10.783	3412112.750	50.786

Total Area of Peak = 6718647.568 [$\mu V \cdot Sec$]

HPLC-OD column (hexane : i-PrOH = 95 : 5, 1.0mL/min)

File name : ly-13-k-f-r020.CH2

Info :

Vial # = 1 Rack # = 1
 Injection Date : 22-Nov-2005 10:23:38
 Curr. Date : 12-May-2006 21:19:20
 User : LY
 Group : DATA
 Control Method : LY-H

#	Name	RT	Area[µV.Sec]	%Area
1		8.133	1096730.547	48.828
2		13.158	1149371.000	51.172

Total Area of Peak = 2246101.547 [µV.Sec]

File name : ly-13-62021.CH2

Info :

Vial # = 1 Rack # = 1
 Injection Date : 22-Nov-2005 10:41:30
 Curr. Date : 12-May-2006 21:19:20
 User : LY
 Group : DATA
 Control Method : LY-H

#	Name	RT	Area[µV.Sec]	%Area
1		8.100	3308521.088	100.000

Total Area of Peak = 3308521.088 [µV.Sec]

HPLC-OD column (hexane : i-PrOH = 97 : 3, 1.0 mL/min)

File name : ly-13-y-cl-r009.CH2

Info :

Vial # = 1 Rack # = 1
 Injection Date : 17-Nov-2005 21:34:28
 Curr. Date : 17-Nov-2005 22:23:48
 User : LY
 Group : DATA
 Control Method : LY-YKS

#	Name	RT	Area[μV.Sec]	%Area
1		13.642	3505829.364	49.199
2		18.058	3620003.110	50.801

Total Area of Peak = 7125832.473 [μV.Sec]

File name : ly-13-63010.CH2

Info :

Vial # = 1 Rack # = 1
 Injection Date : 17-Nov-2005 21:57:22
 Curr. Date : 17-Nov-2005 22:23:48
 User : LY
 Group : DATA
 Control Method : LY-YKS

#	Name	RT	Area[μV.Sec]	%Area
1		13.483	4955630.032	97.877
2		18.008	107512.000	2.123

Total Area of Peak = 5063142.032 [μV.Sec]

HPLC-OD column (hexane : i-PrOH = 95 : 5, 1.0 mL/min)

File name : ly-13-68011.CH2

Info :

Vial # = 1 Rack # = 1
 Injection Date : 18-Nov-2005 21:54:06
 Curr. Date : 18-Nov-2005 22:16:58
 User : LY
 Group : DATA
 Control Method : LY-H

#	Name	RT	Area[μV.Sec]	%Area
1		10.925	11648844.339	98.559
2		15.125	170295.000	1.441

Total Area of Peak = 11819139.339 [μV.Sec]

File name : ly-13-y-br-r007.CH2

Info :

Vial # = 1 Rack # = 1
 Injection Date : 16-Nov-2005 15:54:00
 Curr. Date : 18-Nov-2005 22:16:58
 User : LY
 Group : DATA
 Control Method : LY-H

#	Name	RT	Area[μV.Sec]	%Area
1		10.567	2835736.750	52.806
2		14.475	2534402.615	47.194

Total Area of Peak = 5370139.365 [μV.Sec]

HPLC-OD column (hexane : i-PrOH = 95 : 5, 1.0 mL/min)

File name : ly-13-k-69-r018.CH2

Info :

Vial # = 1 Rack # = 1
 Injection Date : 22-Nov-2005 9:38:54
 Curr. Date : 22-Nov-2005 10:02:26
 User : LY
 Group : DATA
 Control Method : LY-H

#	Name	RT	Area[µV.Sec]	%Area
1		15.958	22834880.500	50.084
2		18.717	22758675.611	49.916

Total Area of Peak = 45593556.111 [µV.Sec]

File name : ly-13-k-69016.CH2

Info :

Vial # = 1 Rack # = 1
 Injection Date : 22-Nov-2005 8:51:58
 Curr. Date : 22-Nov-2005 10:02:26
 User : LY
 Group : DATA
 Control Method : LY-H

#	Name	RT	Area[µV.Sec]	%Area
1		16.508	15824571.964	99.559
2		19.433	70110.000	0.441

Total Area of Peak = 15894681.964 [µV.Sec]

HPLC-OD column (hexane : i-PrOH = 95 : 5, 1.0 mL/min)

File name : ly-13-y-nap-r005.CH2

Info :

Vial # = 1 Rack # = 1
 Injection Date : 16-Nov-2005 15:12:30
 Curr. Date : 17-Nov-2005 19:17:10
 User : LY
 Group : DATA
 Control Method : LY-H

#	Name	RT	Area[$\mu V \cdot Sec$]	%Area
1		10.292	14759752.844	47.215
2		13.700	16500905.500	52.785

Total Area of Peak = 31260658.344 [$\mu V \cdot Sec$]

File name : ly-13-67007.CH2

Info :

Vial # = 1 Rack # = 1
 Injection Date : 17-Nov-2005 16:42:28
 Curr. Date : 17-Nov-2005 19:17:10
 User : LY
 Group : DATA
 Control Method : LY-H

#	Name	RT	Area[$\mu V \cdot Sec$]	%Area
1		10.475	12815736.500	98.043
2		13.958	255833.500	1.957

Total Area of Peak = 13071570.000 [$\mu V \cdot Sec$]

(GC, 95°C, N₂ flow: 1.1 mL/min)

racemic

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	13.962	BB	0.1629	662.02618	53.66928	50.18151
2	14.758	PB	0.1880	657.23706	45.63980	49.81849

Totals : 1319.26324 99.30907

Results obtained with enhanced integrator!

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	12.842	BP	0.1838	915.02991	74.24416	97.25143
2	13.750	BP	0.1975	25.86100	2.13299	2.74857

Totals : 940.89091 76.37715

Results obtained with enhanced integrator!