SUPPORTING INFORMATION

for

Highly Enantioselective Hydrogenation of Aryl Vinyl Ketones to the Allylic Alcohols Catalyzed by Tol-binap/dmapen– Ruthenium(II) Complex

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(A) General Remarks

NMR spectra were obtained on a JEOL JNM-EX270, JNM-A400, and JNM-ECX400 spectrometer. Carbon multiplicity was assigned by DEPT experiment. IR spectra were recorded on JASCO FT/IR-4100 spectrophotometer. Optical rotations were taken on JASCO DIP-360 polarimeter. Silica gel column chromatography was performed with Kanto Chemical Co., Inc. Silica Gel 60N (63-210 µm) or Fuji Silicia Co., Ltd. FL60D. Preparative thin layer chromatography was carried out with Wako Gel B-5F (Wako Pure Chemical Industries, Ltd.). Solvents and reagents were used
after appropriate purification, if necessary.\textsuperscript{[1]} Mass spectrometry and elemental analyses were carried out at Center for Instrumental Analysis, Hokkaido University.

(B) Preparation of Starting Materials

Ruthenium complex \((S,R)-3\) was prepared according to the method previously reported.\textsuperscript{[2]} Chalcones \(1a\) and \(1j\) are commercially available. Other chalcone derivatives are synthesized according to the known methods.\textsuperscript{[3]}

(C) General Procedure for Asymmetric Hydrogenation

A small-scale reaction (approx. 1 mmol of substrate) was conducted in a 100-mL glass autoclave. An example is given by hydrogenation of chalcone \((1a)\).

Ruthenium complex \((S,R)-3\) (1.1 mg, 1.1 \(\mu\)mol) and chalcone \((1a)\) (225.2 mg, 1.1 mmol) were placed in a 100-mL glass autoclave equipped with a Teflon-coated magnetic stirring bar, a pressure gauge, and a gas inlet tube attached to a hydrogen source. Air present in the autoclave was replaced by argon. A solution of \(t\)-C\(_4\)H\(_9\)OK (10 mmol dm\(^{-3}\) in 2-propanol, 0.50 mL, 5.0 \(\mu\)mol) in 2-propanol (2.5 mL) which had been degassed by four freeze–thaw cycles was added to the precooled (ice-bath) autoclave under a stream of argon. Air present in the gas inlet tube was removed by flushing with a stream of hydrogen. Hydrogen was initially introduced into the autoclave at a pressure of 4 atm, before being reduced to 1 atm by carefully releasing the stop valve. After this procedure was repeated ten times, the vessel was pressurized to 8 atm. The reaction mixture was vigorously stirred at 0 °C. After stirring for 5 h and carefully venting the hydrogen gas, the solvent was removed under reduced pressure. The residue was purified by silica-gel column chromatography giving \((S)-(E)-1,3\)-diphenyl-2-propen-1-ol \([S]-2a\) (colorless oil, 225.2 mg, 99% yield, 97% ee), accompanied by 1,3-diphenyl-1-propanone \((4a)\) (2.5 mg, 1% yield). The enantiomeric excess of \(2a\) and the absolute configuration of the major isomer were determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol=90:10; flow, 1.0 mL min\(^{-1}\); column temp, 40 °C; detection, UV 254 nm; \(t_R\) of \((S)-2a\), 12.8 min
(98.5%); \( t_R \) of (R)-2a, 15.8 min (1.5%), lit.\[^{[4]}\] \( t_R = 13.41 \) min for (S), \( t_R = 17.40 \) min for (R). \(^1\)H NMR (270 MHz, CDCl\(_3\)) \( \delta \) 2.01 (br s, 1H, OH), 5.40 (br m, 1H, CHO\(_2\)), 6.39 (dd, 1H, \( J = 15.9, 6.5 \) Hz, CH(OH)CH=CH), 6.70 (d, 1H, \( J = 15.9 \) Hz, CH(OH)CH=CH), 7.21–7.45 (m, 10H, aromatics).

(D) Reaction Conditions of Asymmetric Hydrogenation and Analytical Data of Products

Hydrogenation of (E)-1-(4-Methylphenyl)-3-phenyl-2-propen-1-one (1b). Conditions: (S,R)-3 (1.0 mg, 1.0 \( \mu \)mol), 1b (218.5 mg, 0.983 mmol), \( t-C_4H_9\)OK (10 mmol dm\(^{-3}\) in 2-propanol, 0.50 mL, 5.0 \( \mu \)mol), 2-propanol (2.5 mL), 8 atm H\(_2\), 0 °C, 4 h, giving (S)-(E)-1-(4-methylphenyl)-3-phenyl-2-propen-1-ol \([(S)-2b]\)\(^{[5]}\) (223.8 mg, 100% yield, 98% ee). The enantiomeric excess of 2b was determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol=90:10; flow, 1.0 mL min\(^{-1}\); column temp, 40 °C; detection, UV 254 nm; \( t_R \) of (S)-2b, 11.0 min (1.0%); \( t_R \) of (R)-2b, 14.8 min (99%). \([\alpha]_D^{23} = -37.0^o (c 1.02, CHCl_3)\), lit.\(^{[5]}\) \([\alpha]_D^{23} = -35.3^o (c 1.03, CHCl_3)\) for (S)-2b of 97% ee. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 1.96 (d, 1H, \( J = 3.6 \) Hz, OH), 2.36 (s, 3H, CH\(_3\)), 5.37 (br t, 1H, CHO\(_2\)), 6.39 (dd, 1H, \( J = 15.9, 6.4 \) Hz, CH(OH)CH=CH), 6.69 (d, 1H, \( J = 15.9 \) Hz, CH(OH)CH=CH), 7.18–7.40 (m, 9H, aromatic). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 21.1 (CH\(_3\)), 74.9 (CH), 126.3 (CH), 126.6 (CH), 127.7 (CH), 128.5 (CH), 129.3 (CH), 130.3 (CH), 131.6 (CH), 136.5 (C), 137.6 (C), 139.8 (C).

Hydrogenation of (E)-1-(2-Fluorophenyl)-3-phenyl-2-propen-1-one (1c). Conditions: (S,R)-3 (1.1 mg, 1.1 \( \mu \)mol), 1c (242.7 mg, 1.07 mmol), \( t-C_4H_9\)OK (10 mmol dm\(^{-3}\) in 2-propanol, 0.50 mL, 5.0 \( \mu \)mol), PPh\(_3\) (1.0 mmol dm\(^{-3}\) in 2-propanol, 1.1 mL, 1.1 \( \mu \)mol), 2-propanol (1.4 mL), 8 atm H\(_2\), 0 °C, 15.5 h, giving (S)-(E)-1-(2-fluorophenyl)-3-phenyl-2-propen-1-ol \([(S)-2c]\) (232.0 mg, 95% yield, 97% ee). The enantiomeric excess of 2c was determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol=90:10; flow, 1.0 mL min\(^{-1}\); column temp, 40 °C;
detection, UV 254 nm; \( t_R \) of (S)-2c, 10.6 min (98.5%); \( t_R \) of (S)-2c, 12.2 min (1.5%). 

\[ \alpha_d^{25} \approx -30.9^\circ \text{ (c 1.17, CHCl}_3) \]. IR (KBr, neat) 3323, 3027, 1615, 1585, 1489, 1455, 1227, 965, 824, 758, 693 cm\(^{-1}\). 

\(^1\)H NMR (270 MHz, CDCl\(_3\)) \( \delta \) 2.11 (d, 1H, \( J = 4.4 \) Hz, O\( H \)), 5.70 (br t, 1H, C\( \text{H} \)OH), 6.41 (dd, 1H, \( J = 15.8, 6.3 \) Hz, CH(OH)CH=CH), 6.71 (d, 1H, \( J = 15.8 \) Hz, CH(OH)CH=CH), 7.02–7.09 (m, 1H, aromatic), 7.14–7.41 (m, 7H, aromatic), 7.53 (apparent dt, 1H, aromatic). 

\(^{13}\)C NMR (67.8 MHz, CDCl\(_3\)) \( \delta \) 69.9 (d, CH, \( J_{C-F} = 3.4 \) Hz), 115.5 (d, CH, \( J_{C-F} = 21.2 \) Hz), 124.4 (d, CH, \( J_{C-F} = 3.9 \) Hz), 126.6 (CH), 127.6 (d, CH, \( J_{C-F} = 4.4 \) Hz), 127.8 (CH), 128.5 (CH), 129.2 (d, CH, \( J_{C-F} = 8.4 \) Hz), 129.8 (d, C, \( J_{C-F} = 13.4 \) Hz), 130.1 (CH), 130.7 (CH), 136.4 (C), 159.9 (d, C, \( J_{C-F} = 246 \) Hz). HRMS (EI\(^+\)), \textit{m/z} (\( M^+ \)) calcld 228.0950, obsd 228.0943. The procedure used to determine the absolute configuration is described in Part G.

**Hydrogenation of (E)-1-(4-Fluorophenyl)-3-phenyl-2-propen-1-one (1d).**

Conditions: (S,R)-3 (1.0 mg, 1.0 \( \mu \)mol), 1d (222.9 mg, 0.985 mmol), \( t-C_4H_9\)OK (10 mmol dm\(^{-3}\) in 2-propanol, 0.50 mL, 5.0 \( \mu \)mol), 2-propanol (2.5 mL), 8 atm H\(_2\), 0 \(^\circ\)C, 3 h, giving (S)-1-(4-fluorophenyl)-3-phenyl-2-propen-1-ol [(S)-1d] (215.0 mg, 96% yield, 96% ee). The enantiomeric excess of 2d was determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol=90:10; flow, 1.0 mL min\(^{-1}\); column temp, 40 \(^\circ\)C; detection, UV 254 nm; \( t_R \) of (S)-2d, 11.7 min (2%); \( t_R \) of (R)-2d, 16.4 min (98%). \[ \alpha_d^{25} \approx -21.9^\circ \text{ (c 1.16, CHCl}_3) \]. \(^1\)H NMR (270 MHz, CDCl\(_3\)) \( \delta \) 2.00 (d, 1H, \( J = 3.8 \) Hz, \( OH \)), 5.39 (br t, 1H, CHOH), 6.35 (dd, 1H, \( J = 16.2, 6.2 \) Hz, CH(OH)CH=CH), 6.68 (d, 1H, \( J = 16.2 \) Hz, CH(OH)CH=CH), 7.06 (distorted t, 2H, adjacent to F), 7.21-7.43 (m, 7H, aromatic). \(^{13}\)C NMR (67.7 MHz, CDCl\(_3\)) \( \delta \) 74.2 (CH), 115.2 (d, CH, \( J_{C-F} = 21.2 \) Hz), 126.5 (CH), 127.8 (CH), 128.0 (d, CH, \( J_{C-F} = 8.4 \) Hz), 128.5 (CH), 130.6 (CH), 131.2 (CH), 136.3 (C), 138.4 (d, C, \( J_{C-F} = 2.8 \) Hz), 162.2 (d, C, \( J_{C-F} = 246 \) Hz). Only racemic 2d is known in the literature.\(^6\) The procedure used to determine the absolute configuration is described in Part G.
Hydrogenation of (E)-3-Phenyl-1-(4-trifluoromethylphenyl)-2-propen-1-one (1e). Conditions: (S,R)-3 (1.0 mg, 1.0 µmol), 1e (272.2 mg, 0.985 mmol), t-C₄H₈OK (10 mmol dm⁻³ in 2-propanol, 0.50 mL, 5.0 µmol), 2-propanol (1.5 mL), DMF (1 mL), 8 atm H₂, 0 °C, 2 h, giving (S)-(E)-1-(4-trifluoromethylphenyl)-3-phenyl-2-propen-1-ol [(S)-2e][7] (258.7 mg, 94% yield, 92% ee). The enantiomeric excess of 2e and the absolute configuration of the major isomer were determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol=90:10; flow, 1.0 mL min⁻¹; column temp, 40 °C; detection, UV 254 nm; tₑ of (S)-2e, 11.5 min (96%); tₑ of (R)-2e, 17.3 min (4%). Lit.[7] eluent, hexane:2-propanol=80:20; flow, 0.6 mL min⁻¹ tₑ = 20.3 min for (S), tₑ = 33.0 min for (R). [α]D²⁴ = -4.5° (c 1.05, CHCl₃). ¹H NMR (270 MHz, CDCl₃) δ 2.10 (d, 1H, J = 3.5 Hz, OH), 5.46 (br t, 1H, CH(OH)), 6.33 (dd, 1H, J = 15.7, 6.8 Hz, CH(OH)CH=CH), 6.71 (d, 1H, J = 15.7 Hz, CH(OH)CH=CH), 7.28–7.41 (m, 5H, aromatic), 7.56 (distorted d, 2H, aromatic), 7.63 (distorted d, 2H, aromatic). ¹³C NMR (67.7 MHz, CDCl₃) δ 74.6 (CH), 125.5 (q, CH, J₁-C₂-F = 3.9 Hz), 126.5 (CH), 128.1 (q, C, J₁-C₂-F = 272 Hz), 128.1 (CH), 128.6 (CH), 129.9 (q, C, J₁-C₂-F = 32.3 Hz), 130.7 (CH), 131.6 (CH), 136.1 (C), 146.6 (C).

Hydrogenation of (E)-1-(4-Methoxyphenyl)-3-phenyl-2-propen-1-one (1f). Conditions: (S,R)-3 (1.0 mg, 1.0 µmol), 1f (235.5 mg, 0.988 mmol), t-C₄H₈OK (10 mmol dm⁻³ in 2-propanol, 0.50 mL, 5.0 µmol), 2-propanol (1.5 mL), DMF (2 mL), 8 atm H₂, 0 °C, 3 h, giving (S)-(E)-1-(4-methoxyphenyl)-3-phenyl-2-propen-1-ol [(S)-2f] (228.8 mg, 96% yield, 95% ee). The enantiomeric excess of 2f was determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol=90:10; flow, 1.0 mL min⁻¹; column temp, 40 °C; detection, UV 254 nm; tₑ of (S)-2f, 15.3 min (97.5%); tₑ of (R)-2f, 20.7 min (25.5%). [α]D²⁴ = -31.1° (c 1.01, CHCl₃). IR (KBr, neat) 3335, 3025, 2835, 1610, 1510, 1246, 1176, 1033, 965, 828, 693 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 2.00 (d, 1H, J = 3.9 Hz, OH), 3.82 (s, 3H, CH₃), 5.36 (br t, 1H, CH(OH)), 6.39 (dd, 1H, J = 15.9, 6.4 Hz, CH(OH)CH=CH), 6.68 (d, 1H, J = 15.9 Hz, CH(OH)CH=CH), 6.91 (d, 2H, J = 8.6 Hz, adjacent to OCH₃), 7.2–7.41 (m, 7H, aromatic). ¹³C NMR (100 MHz, CDCl₃) δ 55.3 (CH₃), 74.7 (CH), 114.0 (CH), 126.5
(CH), 127.7 (CH, maybe overlapping), 128.5 (CH), 130.1 (CH), 131.6 (CH), 134.9 (C), 136.5 (C), 159.2 (C). HRMS(ESI\(^+\)), \(m/z\) (M+Na\(^+\)) calcd 263.1048, obsd 263.1038. Only racemic 2f is known in the literature.\(^8\) The procedure used to determine the absolute configuration is described in Part G.

**Hydrogenation of \((E)-1-(2-Naphthyl)-3-phenyl-2-propen-1-one (1g)\).** Conditions: (S,R)-3 (1.0 mg, 1.0 \(\mu\)mol), 1g (258.0 mg, 1.00 mmol), \(t\)-C\(_4\)H\(_9\)OK (10 mmol dm\(^{-3}\) in 2-propanol, 0.50 mL, 5.0 \(\mu\)mol), 2-propanol (1.5 mL), DMF (1 mL), 8 atm H\(_2\), 0 °C, 5 h, giving (S)-(E)-1-(2-naphthyl)-3-phenyl-2-propen-1-ol [(S)-2g]\(^7\] (250.6 mg, 96% yield, 95% ee). The enantiomeric excess of 2g and the absolute configuration of the major isomer were determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol=90:10; flow, 1.0 mL min\(^{-1}\); column temp, 40 °C; detection, UV 254 nm; \(t\)_R of (S)-2g, 17.8 min (97.5%); \(t\)_R of (R)-2g, 14.8 min (2.5%), lit.\(^7\) column, CHIRALCEL OD-H; eluent, hexane:2-propanol=80:20; flow, 0.6 mL min\(^{-1}\); \(t\)_R of (S)-2g, 28.5 min; \(t\)_R of (R)-2g, 43.1 min. Mp. 89.0–90.0 °C (hexane–Et\(_2\)O), lit.\(^7\) 77–78 °C. \([\alpha]_D^{24}\) \(=–35.8^\circ\) (c 1.24, CHCl\(_3\)), lit.\(^7\) \([\alpha]_D^{22}\) \(=–25.2^\circ\) (c 0.33, CH\(_2\)Cl\(_2\)) for (S)-2g of 91% ee. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.13 (d, 1H, \(J = 3.5\) Hz, \(CH(OH)\)), 6.75 (m, 4H, aromatic), 6.59 (d, 1H, J = 15.9 Hz, CH(OH)CH\(=\)CH), 7.22–7.56 (m, 8H, aromatic), 7.83–7.90 (m, 4H, aromatic). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 75.1 (CH), 124.9 (CH), 125.9 (CH), 126.2 (CH), 126.6 (CH), 127.6 (CH), 127.8 (CH), 128.0 (CH), 128.4 (CH), 128.5 (CH), 130.7 (CH), 131.3 (CH), 132.9 (C), 133.3 (C), 136.4 (C), 140.0 (C).

**Hydrogenation of \((E)-1-(2-Furyl)-3-phenyl-2-propen-1-one (1h)\).** Conditions: (S,R)-3 (1.0 mg, 1.0 \(\mu\)mol), 1h (195.3 mg, 0.985 mmol), \(t\)-C\(_4\)H\(_9\)OK (10 mmol dm\(^{-3}\) in 2-propanol, 0.50 mL, 5.0 \(\mu\)mol), PPh\(_3\) (1.0 mmol dm\(^{-3}\) in 2-propanol, 1.0 mL, 1.0 \(\mu\)mol), 2-propanol (0.5 mL), DMF (1 mL), 8 atm H\(_2\), 0 °C, 8 h, giving (S)-(E)-1-(2-furyl)-3-phenyl-2-propen-1-ol [(S)-2h] (192.7 mg, 98% yield, 92% ee). The enantiomeric excess of 2h was determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol=90:10; flow, 1.0 mL min\(^{-1}\); column temp, 40 °C; \(t\)_R of (S)-2h, 11.1 min (96%); \(t\)_R of (R)-2h, 14.9 min (4%). \([\alpha]_D^{25}\) \(=–16.3^\circ\) (c 0.249, benzene), lit.\(^9\)
[α]D<sup>28</sup> –4.4° (c 1.6, CHCl<sub>3</sub>) for 2h of 45% ee (absolute configuration was not shown).

IR (KBr-disk) 3383, 3027, 1497, 1146, 1010, 766, 743, 693 cm<sup>–1</sup>. <sup>1</sup>H NMR<sup>9b</sup> (400 MHz, CDCl<sub>3</sub>) δ 2.16 (d, 1H, J = 5.0 Hz, O<sub>H</sub>), 5.41 (br t, 1H, C<sub>H</sub>OH), 6.30–6.31 (m, 1H, furan), 6.35–6.50 (m, 1H, furan), 6.47 (dd, 1H, J = 16.3, 6.8 Hz, CH(OH)CH=CH), 6.74 (d, 1H, J = 16.3 Hz, CH(OH)CH=CH), 7.23–7.35 (m, 3H, aromatic), 7.40–7.43 (m, 3H, aromatic and furan). <sup>1</sup>3C NMR (100 MHz, CDCl<sub>3</sub>) δ 68.5 (CH), 106.8 (CH), 110.3 (CH), 126.7 (CH), 127.9 (CH), 128.0 (CH), 128.6 (CH), 131.9 (CH), 136.3 (C), 142.5 (CH), 155.0 (C). HRMS(EI<sup>+</sup>), m/z (M<sup>+</sup>) calcd 200.0837, obsd 200.0827. The procedure used to determine the absolute configuration is described in Part G.

Hydrogenation of (E)-3-(4-Methylphenyl)-1-phenyl-2-propen-1-one (1i).

Conditions: (S,R)-3 (1.1 mg, 1.1 µmol), 1i (107.2 mg, 0.482 mmol), t-C<sub>4</sub>H<sub>9</sub>OK (10 mmol dm<sup>–3</sup> in 2-propanol, 0.50 mL, 5.0 µmol), 2-propanol (2.5 mL), 8 atm H<sub>2</sub>, 0 °C, 13 h, giving (S)-(E)-3-(4-methylphenyl)-1-phenyl-2-propen-1-ol [(S)-2i] (100.2 mg, 93% yield, 97% ee). The enantiomeric excess of 2i was determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol=90:10; flow, 1.0 mL min<sup>–1</sup>; column temp, 40 °C; t<sub>R</sub> of (R)-2i, 10.4 min (1.5%); t<sub>R</sub> of (S)-2i, 12.7 min (98.5%). [α]<sub>D</sub><sup>24</sup> –36.4° (c 0.740, CHCl<sub>3</sub>). IR (KBr-neat) 3343, 3027, 2919, 1513, 1493, 1451, 1016, 967, 822, 760, 699 cm<sup>–1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.05 (d, 1H, J = 3.6 Hz, O<sub>H</sub>), 2.33 (s, 3H, CH<sub>3</sub>), 5.37 (dd, 1H, J = 6.8, 3.6 Hz, C<sub>H</sub>OH), 6.33 (dd, 1H, J = 15.9, 6.8 Hz, CH(OH)CH=CH), 6.65 (d, 1H, J = 15.9 Hz, CH(OH)CH=CH), 7.11 (d, 2H, J = 8.1 Hz, aromatic), 7.27–7.44 (m, 7H, aromatic and furan). <sup>1</sup>3C NMR (100 MHz, CDCl<sub>3</sub>) δ 21.2 (CH<sub>3</sub>), 75.2 (CH), 126.3 (CH), 126.5 (CH), 127.7 (CH), 128.6 (CH), 129.2 (CH), 130.4 (CH), 130.5 (CH), 133.6 (C), 137.7 (C), 142.8 (C). HRMS(EI<sup>+</sup>), m/z (M<sup>+</sup>) calcd 224.1201, obsd 224.1200. Only racemic 2i is known in the literature.<sup>10</sup> The procedure used to determine the absolute configuration is described in Part G.

Hydrogenation of (E)-3-(4-Chlorophenyl)-1-phenyl-2-propen-1-one (1j).

Conditions: (S,R)-3 (1.0 mg, 1.0 µmol), 1j (245.7 mg, 1.01 mmol), t-C<sub>4</sub>H<sub>9</sub>OK (10 mmol dm<sup>–3</sup> in 2-propanol, 0.50 mL, 5.0 µmol), 2-propanol (2.5 mL), 8 atm H<sub>2</sub>, 0 °C, 5 h,
giving (S)-(E)-3-(4-chlorophenyl)-1-phenyl-2-propen-1-ol [(S)-2j] (247.8 mg, 99% yield, 97% ee). The enantiomeric excess of 2j was determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol=90:10; flow, 1.0 mL min⁻¹; column temp, 40 °C; tᵣ of (R)-2j, 18.8 min (1.5%); tᵣ of (S)-2j, 23.0 min (98.5%). [α]D²³ −44.5° (c 1.11, CHCl₃). IR (KBr-neat) 3336, 3030, 1593, 1491, 1452, 1405, 1090, 1012, 967, 823, 761, 698 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 2.02 (d, 1H, J = 3.6 Hz, OCH), 5.39 (br t, 1H, CH(OH)), 6.36 (dd, 1H, J = 15.9, 6.4 Hz, CH(OH)CH=CH₂), 6.65 (d, 1H, J = 15.9 Hz, CH(OH)CH=CH₂), 7.27–7.44 (m, 9H, aromatic). ¹³C NMR (100 MHz, CDCl₃) δ 74.9 (CH), 126.3 (CH), 127.7 (CH), 127.9 (CH), 128.6 (CH), 128.7 (CH), 129.1 (CH), 132.1 (CH), 133.3 (C), 135.0 (C), 142.5 (C). HRMS (EI⁺), m/z (M⁺) calcd 244.0655, obsd 244.0644. Only racemic 2j is known in the literature.¹¹ The procedure used to determine the absolute configuration is described in Part G.

**Hydrogenation of (E)-1,3-Diphenyl-2-buten-1-one (1k).** Conditions: (S,R)-3 (0.9 mg, 0.9 µmol), 1k (103.9 mg, 0.467 mmol), t-C₄H₉OK (10 mmol dm⁻³ in 2-propanol, 0.50 mL, 5.0 µmol), 2-propanol (2.5 mL), 50 atm H₂, 0 °C, 43 h, giving (S)-(E)-1,3-diphenyl-2-buten-1-ol [(S)-2k] (102.1 mg, 97% yield, 89% ee). The enantiomeric excess of 2j was determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol=90:10; flow, 1.0 mL min⁻¹; column temp, 40 °C; tᵣ of (S)-2j, 8.5 min (94.5%); tᵣ of (R)-2j, 12.1 min (5.5%). [α]D²⁴ −24.8° (c 0.460, CHCl₃). ¹H NMR (270 MHz, CDCl₃) δ 1.91 (d, 1H, J = 3.9 Hz, OH), 2.21 (d, 1H, J = 1.4 Hz, CH₂), 5.66 (br dd, 1H, CH(OH)), 6.01 (br dt, 1H, CH(OH)CH), 7.27–7.47 (m, 10H, aromatic). ¹³C NMR (67.8 MHz, CDCl₃) δ 16.4 (CH₂), 71.0 (CH), 125.9 (CH), 126.0 (CH), 127.3 (CH), 127.5 (CH), 128.2 (CH), 128.5 (CH), 130.1 (CH), 137.1 (C), 142.7 (C), 143.6 (C). Only racemic 2j is known in the literature.¹² The procedure used to determine the absolute configuration is described in Part G.

**Hydrogenation of (E)-4,4-Dimethyl-1-phenyl-2-penten-1-one (1l).** Conditions: (S,R)-3 (0.9 mg, 0.9 µmol), 1l (170.0 mg, 0.90 mmol), t-C₄H₉OK (10 mmol dm⁻³ in 2-propanol, 0.50 mL, 5.0 µmol), 2-propanol (2.5 mL), 8 atm H₂, 0 °C, 8 h, giving (S)-(E)-
4,4-Dimethyl-1-phenyl-2-penten-1-ol [(S)-2l][13] (147.2 mg, 86% yield, 97% ee), accompanied with recovered 1l (21.2 mg, 13%). The enantiomeric excess of 2l and the absolute configuration of the major isomer were determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol=99:1; flow, 1.0 mL min⁻¹; column temp, 40 °C; detection, UV 254 nm; tₖ of (R)-2l, 13.4 min (98.5%); tₖ of (S)-2l, 18.2 min (1.5%). [α]ᵣ₂₄ +44.5° (c 1.13, CHCl₃), lit.[13] [α]ᵣ₂₄ –46.4° (c 0.13, CH₂Cl₂) for (R)-2l of 96% ee. IR (KBr-neat) 3358, 2957, 1659, 1452, 1362, 972, 698 cm⁻¹. 

1H NMR (270 MHz, CDCl₃) δ 1.02 (s, 9H, C(CH₃)₃), 1.87 (br s, 1H, OHH), 5.15–5.17 (br d, 1H, CH(OH)OH), 5.57 (dd, 1H, J = 15.7, 7.0 Hz, CH(OH)CH=CH), 5.80 (dd, 1H, J = 15.7, 1.0 Hz, CH(OH)CH=CH), 7.27–7.39 (m, 5H, aromatic). 13C NMR (67.7 MHz, CDCl₃) δ 29.4 (CH₃), 32.9 (C), 75.3 (CH), 126.1 (CH), 127.1 (CH), 127.4 (CH), 128.4 (CH), 143.4 (C), 143.5 (CH).

(E) Asymmetric Hydrogenation of Chalcone (1a) (S/C = 10 000)

Ruthenium complex (S,R)-3 (1.1 mg, 1.1 μmol) and chalcone (1a) (2.26 g, 10.8 mmol) were placed in a 50-mL SUS autoclave equipped with a glass inner vessel, a Teflon-coated magnetic stirring bar, a pressure gauge, and a gas inlet tube attached to a hydrogen source. Air present in the autoclave was replaced by argon. A solution of t-C₄H₉OK (10 mmol dm⁻³) in 2-propanol (5.0 mL, 50 μmol) which had been degassed by five freeze–thaw cycles was added to the precooled (ice-bath) autoclave under a stream of argon. Air present in the gas inlet tube was removed by flushing with a stream of hydrogen. Hydrogen was initially introduced into the autoclave at a pressure of 30 atm, before being reduced to 1 atm by carefully releasing the stop valve. After this procedure was repeated seven times, the vessel was pressurized to 40 atm. The reaction mixture was vigorously stirred at 0 °C. After stirring for 3 h and carefully venting the hydrogen gas, the solvent was removed under reduced pressure. The residue was purified by silica-gel column chromatography giving (S)-(E)-1,3-diphenyl-2-propen-1-ol [(S)-2a] (colorless oil, 2.24 g, 99% yield, 97% ee).
(F) **Isomerization of (S)-2a under the Hydrogenation Conditions**

Ruthenium complex (S,R)-3 (1.4 mg, 1.4 µmol) was placed in a 100-mL glass autoclave equipped with a Teflon-coated magnetic stirring bar, a pressure gauge, and a gas inlet tube attached to a hydrogen source. Air present in the autoclave was replaced by argon. A solution of (S)-1,3-diphenyl-2-propan-1-ol [(S)-2a] (76.5 mg, 0.364 mmol) and t-C₄H₉OK (10 mmol dm⁻³ in 2-propanol, 0.50 mL, 5.0 µmol) in 2-propanol (2.5 mL) which had been degassed by four freeze–thaw cycles was added to the autoclave under a stream of argon. Air present in the gas inlet tube was removed by flushing with a stream of hydrogen. Hydrogen was initially introduced into the autoclave at a pressure of 4 atm, before being reduced to 1 atm by carefully releasing the stop valve. After this procedure was repeated ten times, the vessel was pressurized to 8 atm. The reaction mixture was vigorously stirred at 30 °C. After stirring for 1 h and carefully venting the hydrogen gas, the solvent was removed under reduced pressure to afford a mixture of 2a, 4a, and 5a (10 : 1 : 1 by ¹HNMR).

(G) **Determination of the Absolute Configuration of Products**

G-1: The absolute configurations of (S)-2d, (S)-2k were estimated by ¹H-NMR analysis after converting the corresponding hydrogenated products to the (R)- and (S)-2-methoxy-2-phenyl-2-(trifluoromethyl)acetic acid (MTPA) esters according to the literature.[¹⁴] Data is shown in the scheme below (R = 2-methoxy-2-phenyl-2-(trifluoromethyl)acetyl).

\[ \Delta \delta = \delta_S - \delta_R \]

\[ \begin{align*}
\text{OR} & \quad \text{corresponds to} \\
\text{F} & \quad \text{OH} \\
\end{align*} \]

\[ (S)-2d \]
Determination of the absolute configuration of 2k

$$\Delta \delta = \delta_S - \delta_R$$

\[ \begin{align*}
\text{positive} & \quad -0.051 \\
\text{corresponds to} & \\
\text{(S)-2k} & \\
\end{align*} \]

G-2: The absolute configurations of (S)-2c, (S)-2f, (S)-2i, (S)-2j were determined by comparison of the sign of $\alpha_D$ with the literature after converting to the corresponding mandelic acid derivatives as follows:

A solution of (S)-2j (51.0 mg, 0.208 mmol), imidazole (36.5 mg, 0.536 mmol), and \( t \)-butyldimethylchlorosilane (44.6 mg, 0.296 mmol) in DMF (0.5 mL) was stirred for 2 h at 20 °C. After usual work-up, TBS ether of (S)-2j was obtained (64.4 mg, 86%). Ozone was bubbled through a solution of this silyl ether in dichloromethane (7 mL) at –78 °C until the solution became slightly blue. After excess ozone was expelled by Ar bubbling, PPh\(_3\) (115.0 mg, 0.438 mmol) was added, and the solution was allowed to warm to room temperature. The mixture was evaporated to dryness. Chromatographic purification gave (R)-2-(\( t \)-butyldimethylchlorosiloxy)phenylacetaldehyde (17.8 mg, 40%), $\alpha_D^{26} = –49.1^\circ$ (c 0.775, ethanol), lit.\(^{[15]}\) $\alpha_D^{22} = –39.5^\circ$ (c 0.612, ethanol). This is consistent with the (S)-configuration of starting 2j.

2c: Converted to 2-fluoromandelic acid by a NaClO\(_2\) oxidation\(^{[16]}\) of the corresponding aldehyde. Obsd. $\alpha_D^{25} = –102^\circ$ (c 0.17, acetone), lit.\(^{[17]}\) $\alpha_D^{578} = –145^\circ$ (c 1, acetone) for (R)-2-fluoromandelic acid.

2f: Converted to 4-methoxymandelic acid by a NaClO\(_2\) oxidation\(^{[15]}\) of the corresponding aldehyde. Obsd. $\alpha_D^{28} = –94.4^\circ$ (c 0.095, H\(_2\)O), lit.\(^{[18]}\) $\alpha_D^{25} = –141^\circ$ (c 0.3, H\(_2\)O) for (R)-4-methoxymandelic acid.

2i: Converted to (R)-2-(\( t \)-butyldimethylchlorosiloxy)phenylacetaldehyde.\(^{[15]}\) Obsd. $\alpha_D^{24} = –46.3^\circ$ (c 0.805, ethanol), lit.\(^{[15]}\) $\alpha_D^{22} = –39.5^\circ$ (c 0.612, ethanol).
G-3: The absolute configuration of (S)-2h was determined by comparison of HPLC with an authentic sample which was prepared by titanium mediated epoxidation with kinetic resolution\(^{[19]}\). Column, CHIRALCEL OD-H; eluent, hexane:2-propanol=90:10; flow, 1.0 mL min\(^{-1}\); column temp, 40 °C; \(t_R\) of major 2h, 11.07 min (96%); \(t_R\) of minor 2h, 14.91 min (4%). HPLC of (R)-rich 2h obtained according to the literature\(^{[19]}\) under the same conditions: \(t_R\) of minor 2h, 11.07 min; \(t_R\) of major 2h, 14.95 min. This means the absolute configuration of our sample is (S).
(S)-2h (our sample)

authentic 2h ((R)-rich)

authentic 2h (racemic)
(H) References


[11] Though racemic 2j appeared in the literatures, physical properties were not given.


