

SUPPORTING INFORMATION

for

**The Hydrogenation/Transfer Hydrogenation Network:
Asymmetric Hydrogenation of Ketones with Chiral
 η^6 -Arene/*N*-Tosylethylenediamine–Ruthenium(II) Catalysts**

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(1) Procedure for silanization of glassware

The use of a silanized glass reaction vessel was necessary to secure the reproducibility. Although HMDS (hexamethyldisilazide) and TMSCl gave similar results, the HMDS treatment was more convenient. A 100-mL glass vessel was charged with 0.5 mL of HMDS, capped with a silicon rubber, and heated at 30 °C for 24 h. Then the vessel was washed with water and acetone, heated at 100 °C for 30 min, and dried under reduced pressure for 2 h. The vessel was stored under Ar gas.

(2) Procedure for the preparation of (*S,S*)-**8b**

A solution of TfOH (70 μ L, 0.79 mmol) in CH₂Cl₂ (10 mL) was added dropwise to a solution of (*S,S*)-**9** (570 mg, 0.95 mmol) in CH₂Cl₂ (55 mL) under an Ar atmosphere at room temperature over a period of 30 min. Then the solution was stirred for 30 min and evaporated to a volume of 15 mL. Cooling the solution to 0 °C gave an orange precipitate. The precipitate was filtered and dried under reduced pressure to give (*S,S*)-**8b** (380 mg, 65% yield).

¹H NMR (400 MHz, 21 mM in CD₂Cl₂) δ 1.30, 1.33 (each d, J = 7 Hz, 3H x 2, CH(CH₃)₂), 2.12 (s, 3H, CH₃), 2.27 (s, 3H, CH₃ of Ts), 2.76 (m, 1H, CH(CH₃)₂), 3.75 (m, 1H, CHNH₂), 4.21 (d, J = 8 Hz, 1H, CHNTs), 4.71 (m, 1H, NHH), 5.68 (m, 1H, NHH), 5.84 (d, J = 6 Hz, 1H, aromatic proton), 5.94 (m, 2H, aromatic proton), 6.11 (d, J = 6 Hz, 1H, aromatic proton), 6.63–7.25 (m, 14H, aromatic protons),

¹H NMR (400 MHz, 10 mM in THF-*d*₈) δ 1.37, 1.43 (each d, J = 7 Hz, 3H x 2, CH(CH₃)₂), 2.18 (s, 3H, CH₃), 2.29 (s, 3H, CH₃ of Ts), 2.98 (m, 1H, CH(CH₃)₂), 3.55 (m, 1H, CHNH₂), 3.85 (m, 1H, NHH), 3.94 (d, J = 11 Hz, 1H, CHNTs), 5.78 (d, J = 6 Hz, 1H, aromatic proton), 5.92–5.93 (m, 2H, aromatic protons), 6.15 (d, J = 6 Hz, 1H, aromatic proton), 6.5–7.1 (m, 14H, aromatic protons), 7.16 (m, 1H, NHH).

¹H NMR (400 MHz, 21 mM in CD₃OH) δ 1.40, 1.43 (each d, J = 7 Hz, 3H x 2, CH(CH₃)₂), 2.24 (s, 3H, CH₃), 2.37 (s, 3H, CH₃ of Ts), 3.02 (m, 1H, CH(CH₃)₂), 3.45 (m, 1H, NHH), 3.68 (m, 1H, CHNH₂), 4.02 (d, J = 11 Hz, 1H, CHNTs), 5.63 (d, J = 6

Hz, 1H, aromatic proton), 6.00–6.05 (m, 3H, aromatic protons), 6.60–7.19 (m, 14H, aromatic protons), 7.60 (m, 1H, NHH).

¹³C NMR (100.4 MHz, THF-*d*₈) δ 18.6, 21.1, 22.6, 22.8, 31.4, 70.3, 73.2, 82.4, 82.9, 84.2, 84.3, 97.0, 101.2, 127.0, 127.8, 128.1, 128.6, 128.7, 128.8, 129.2, 130.0, 139.7, 139.9, 140.3, 143.6.

Anal. calcd. for: C 51.26, H 4.70, N 3.74, found: C 51.09, H 4.47, N 3.74.

(3) Procedure for the asymmetric hydrogenation of 4-chromanone (**6a**) with (*S,S*)-**8a**

4-Chromanone (**6a**) (0.89 g, 6.0 mmol) and (*S,S*)-**8a** (1.3 mg, 2 μmol) were placed in a 100-mL glass autoclave. The atmosphere was replaced with Ar gas, and methanol (19.3 mL) was added to this mixture. Hydrogen was initially introduced into the autoclave at a pressure of 10 atm, before being reduced to 1 atm. This procedure was repeated three times. Then the autoclave was pressurized with H₂ gas (10 atm), and the solution was stirred vigorously at 60 °C for 15 h. The ¹H-NMR and HPLC analysis indicated that (*S*)-4-chromanol [(*S*)-**7a**] with 95% ee was obtained in 64% yield. Pure (*S*)-**7a** (0.52 g, 58% yield) was obtained by silica gel chromatography.

¹H NMR (400 MHz, CDCl₃) δ 1.99 (m, 1H, CHHCH(OH)), 2.08 (m, 1H, CHHCH(OH)), 2.31 (br, 1H, OH), 4.23 (m, 2H, CH₂O), 4.74 (m, 1H, CHOH), 6.8–6.9 (m, 2H, aromatic protons), 7.2–7.3 (m, 2H, aromatic protons).

The HPLC analytical conditions were used as follows: column, CHIRALCEL OJ-H (4.6 mm i.d. x 250 mm); eluent, hexane/2-propanol = 99/1; flow rate, 1.5 mL/min; temp, 35 °C; detection, UV (220 nm). The retention times were as follows: **6a**, 11.8 min, (*S*)-**7a**, 26.7 min, (*R*)-**7a**, 30.8 min.

[α]_D²⁵ –77 (*c* 0.5, C₂H₅OH), (lit. [α]_D²⁵ +80.4, *c* 0.5, C₂H₅OH, 100% ee (*R*), Zhang, X.; Takemoto, T.; Yoshizumi, T.; Kumobayashi, H.; Akutagawa, S.; Mashima, K.; Takaya, H. *J. Am. Chem. Soc.* **1993**, *115*, 3318–3319).

(4) Procedure for the asymmetric hydrogenation of 4-chromanone (**6a**) with (*S,S*)-**8b**

4-Chromanone (**6a**) (0.89 g, 6.0 mmol) and (*S,S*)-**8b** (1.5 mg, 2 μ mol) were placed in a 100-mL glass autoclave. The atmosphere was replaced with Ar gas, and methanol (5.3 ml) was added to this solution. Hydrogen was initially introduced into the autoclave at a pressure of 10 atm, before being reduced to 1 atm. This procedure was repeated three times. Then the autoclave was pressurized with H₂ gas (10 atm), and the solution was stirred vigorously at 60 °C for 15 h to give (*S*)-4-chromanol [(*S*)-**7a**] with 97% ee in 100% yield. The solvent was removed under reduced pressure and the Ru catalyst was removed by silica gel chromatography, giving (*S*)-**7a** (0.84 g, 93% yield).

(5) Analytical data of hydrogenation products

(*S*)- 6-Methyl-4-chromanol [(*S*)-**7b**]

¹H NMR (400 MHz, CDCl₃) δ 1.97–2.13 (m, 2H, CHHCH(OH)), 2.27 (s, 3H, CH₃), 4.21 (m, 2H, CH₂O), 4.72 (m, 1H, CHOH), 6.73 (d, *J* = 8.3 Hz, 1H, aromatic proton), 7.00 (d, *J* = 8.3 Hz, 1H, aromatic proton), 7.10 (s, 1H, aromatic proton).

The HPLC analytical conditions were as follows: column, CHIRALCEL OJ-H (4.6 mm i.d. x 250 mm); eluent, hexane/2-propanol = 99/1; flow rate, 1.5 mL/min; temp, 35 °C; detection, UV (220 nm). The retention times were: **6b**, 8.6 min, (*S*)-**7b**, 23.4 min, (*R*)-**7b**, 29.2 min.

$[\alpha]_{\text{D}}^{25}$ –38 (*c* 1.0, CHCl₃), (lit. $[\alpha]_{\text{D}}^{25}$ –22.9, *c* 1.46, CHCl₃, 59% ee (*S*), Ramadas, S.; Krupadanam, G. L. D. *Tetrahedron: Asymmetry* **1997**, 8, 3059–3066).

(*S*)- 6-Chloro-4-chromanol [(*S*)-**7c**]

¹H NMR (400 MHz, CDCl₃) δ 1.82 (br, 1H, OH), 2.00–2.16 (m, 2H, CHHCH(OH)), 4.26 (m, 2H, CH₂O), 4.77 (m, 1H, CHOH), 6.77 (d, *J* = 8.8 Hz, 1H, aromatic ring proton), 7.15 (d, *J* = 8.3 Hz, 1H, aromatic proton), 7.30 (s, 1H, aromatic proton).

The HPLC analytical conditions were as follows: column, CHIRALCEL OJ-H (4.6 mm i.d. x 250 mm); eluent, hexane/2-propanol = 99/1; flow rate, 1.5 mL/min; temp, 35 °C;

detection, UV (220 nm). The retention times were: **6c**, 9.9 min, (*R*)-**7c**, 33.7 min, (*S*)-**7c**, 36.9 min, $[\alpha]_{\text{D}}^{25} -24$ (*c* 1.0, CHCl₃), (lit. $[\alpha]_{\text{D}}^{25} -24$, *c* 1.0, CHCl₃, 80% ee (*S*), Ramadas, S.; Krupadanam, G. L. D. *Tetrahedron: Asymmetry* **1997**, 8,3059–3066).

(6) Procedure for the large-scale asymmetric hydrogenation of 4-chromanone (6a)

4-Chromanone (**6a**) (2.37 kg, 16 mol), (*S,S*)-**9** (9.6 g, 16 mmol), and TfOH (1.42 mL, 16 mmol) were added to methanol (8 L) placed in a 20-L SUS autoclave. Hydrogen was initially introduced into the autoclave at a pressure of 10 atm, before being reduced to 1 atm. This procedure was repeated three times. Then the autoclave was pressurized with H₂ gas (17 atm), and the solution was stirred vigorously at 60 °C for 15 h. The ¹H-NMR and HPLC analysis indicated that (*S*)-4-chromanol [(*S*)-**7a**] with 97% ee was produced in 99% yield.