

SUPPORTING INFORMATION

Title: Efficient Heterogeneous Asymmetric Transfer Hydrogenation Catalyzed by Recyclable Silica-Supported Ruthenium Complexes

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1. General:

^1H NMR and ^{13}C NMR spectra were recorded on Varian Mercury-plus 300 BB with TMS as internal standard. The inductively coupled plasma atomic emission spectrometry (ICP-AES) was performed on Perkin-Elmer ICP/6500 inductively coupled plasma spectrometer. Optical rotation values were measured on Perkin-Elmer 341 polarimeter. Enantiomeric excess values were determined by GC with a CP-Chirasil-DEX CB column (25 m \times 0.32 mm) on Varian CP-3800 or by HPLC with Chiralcel OD column on Agilent 1100 Series.

2. Determination of the leaching of Ru from the catalyst Ru-5 in the recycling reductions of acetophenone.

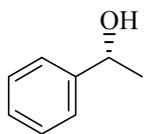
The predried recovered catalyst Ru-5 (50.0 mg) with the powder mixture of KOH (1.0 g) and KNO_3 (0.2 g) was heated to 650 $^\circ\text{C}$ for 5-10 min, then cooled, dissolved in hot water and added 12 M HCl (4 mL) to acidify the solution, then the solution was diluted to 50.0 mL and the amount of metal Ru was determined by ICP-AES.

The leached Ru in organic solutions after the reaction was dissolved in 0.3 M HCl (10 mL) and determined by ICP-AES.

Ru/SiO₂ (weight): before use: 0.54%, after 5 uses: 0.35%.

Amount of leached Ru in organic solutions: after the 1st run: 0.011 mg, after the 2nd run: 0.015 mg, after the 3rd run: 0.017 mg, after the 4th run: 0.024 mg, after the 5th run: 0.034 mg.

3. Analytical data for obtained chiral aromatic alcohols:



$\text{C}_8\text{H}_{10}\text{O}$, FW = 122.16

$[\alpha]_{\text{D}}^{28} +52$ (*c* 1.1, CHCl_3); ^1H NMR (300 MHz, CDCl_3 , 97% *ee*) δ 1.45 (d, *J* = 6.6 Hz, 3H), 2.29

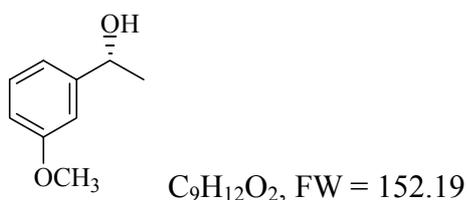
(s, 1H, OH), 4.80-4.86 (m, 1H), 7.23-7.35 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 25.0, 70.2, 125.3, 127.3, 128.4, 145.8; GC analysis: CP-Chirasil-DEX CB column (25 m \times 0.32 mm), column temperature = 126 $^\circ\text{C}$, (isothermal), injector temperature = 250 $^\circ\text{C}$, detector temperature (FID) = 300, carrier gas: N_2 , inlet pressure = 7 psi; t_R = 8.1 min, t_S = 8.8 min.



$[\alpha]_D^{28}$ +38 (*c* 1.2, CHCl_3 , 93% *ee*); ^1H NMR (300 MHz, CDCl_3) δ 1.53 (d, J = 6.6 Hz, 3H), 2.20 (s, 1H, OH), 4.96-5.03 (m, 1H), 7.43-7.47 (m, 2H), 7.75-7.80 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 25.0, 70.4, 123.8, 125.7, 126.1, 127.6, 127.9, 128.2, 132.8, 133.3, 143.2; GC analysis: CP-Chirasil-DEX CB column (25 m \times 0.32 mm), column temperature = 127 $^\circ\text{C}$, (isothermal), injector temperature = 250 $^\circ\text{C}$, detector temperature (FID) = 300, carrier gas : N_2 , inlet pressure = 7 psi; t_R = 9.7 min, t_S = 10.5 min.

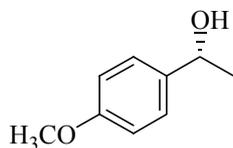


$[\alpha]_D^{28}$ +48 (*c* 1.7, CHCl_3 , 93% *ee*); ^1H NMR (300 MHz, CDCl_3) δ 1.42 (d, J = 6.3 Hz, 3H), 2.81 (s, 1H, OH), 5.14-5.20 (m, 1H), 7.08 (t, J = 7.5 Hz, 1H), 7.30 (t, J = 7.2 Hz, 1H), 7.45-7.54 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 23.5, 69.0, 121.5, 126.6, 127.7, 128.6, 132.5, 144.6; GC analysis: CP-Chirasil-DEX CB column (25 m \times 0.32 mm), column temperature = 170 $^\circ\text{C}$, (isothermal), injector temperature = 250 $^\circ\text{C}$, detector temperature (FID) = 300, carrier gas: N_2 , inlet pressure = 7 psi; t_R = 6.5 min, t_S = 7.3 min.



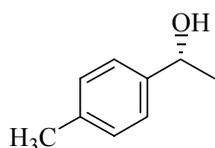
$[\alpha]_D^{28}$ +39 (*c* 1.0, CHCl_3 , 96% *ee*); ^1H NMR (300 MHz, CDCl_3) δ 1.48 (d, J = 6.3 Hz, 3H), 2.02 (s, 1H, OH), 3.81 (s, 3H), 4.82-4.88 (m, 1H), 6.79-6.82 (m, 1H), 6.92-6.95 (m, 2H), 7.25 (t, J = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 25.1, 55.2, 70.3, 110.9, 112.9, 117.7, 129.5, 147.6, 159.8;

GC analysis: CP-Chirasil-DEX CB column (25 m × 0.32 mm), column temperature = 146 °C, (isothermal), injector temperature = 250 °C, detector temperature (FID) = 300, carrier gas: N₂, inlet pressure = 7 psi; t_R = 11.0 min, t_S = 11.7 min.



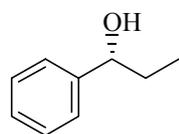
C₉H₁₂O₂, FW = 152.19

$[\alpha]_D^{20}$ +52 (*c* 1.6, CHCl₃, 96% *ee*); ¹H NMR (300 MHz, CDCl₃) δ 1.45 (d, *J* = 6.6 Hz, 3H), 2.07 (s, 1H, OH), 3.79 (s, 3H), 4.79-4.85 (m, 1H), 6.87 (d, *J* = 9.0 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 25.0, 55.2, 69.8, 113.7, 126.6, 138.0, 158.9; GC analysis: CP-Chirasil-DEX CB column (25 m × 0.32 mm), column temperature = 128 °C, (isothermal), injector temperature = 250 °C, detector temperature (FID) = 300, carrier gas: N₂, inlet pressure = 7 psi; t_R = 22.3 min, t_S = 25.2 min.



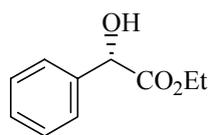
C₉H₁₂O, FW = 136.19

$[\alpha]_D^{20}$ +55 (*c* 1.5, CHCl₃, 95% *ee*); ¹H NMR (300 MHz, CDCl₃) δ 1.48 (d, *J* = 6.6 Hz, 3H), 2.03 (s, 1H, OH), 2.36 (s, 3H), 4.82-4.89 (m, 1H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 21.0, 25.0, 70.1, 125.3, 129.1, 137.1, 142.8; GC analysis: CP-Chirasil-DEX CB column (25 m × 0.32 mm), column temperature = 137 °C, (isothermal), injector temperature = 250 °C, detector temperature (FID) = 300, carrier gas: N₂, inlet pressure = 7 psi; t_R = 7.9 min, t_S = 8.6 min.



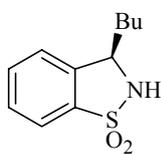
C₉H₁₂O, FW = 136.19

$[\alpha]_D^{20}$ +47 (*c* 0.8, CHCl₃, 94% *ee*); ¹H NMR (300 MHz, CDCl₃) δ 0.90 (t, *J* = 7.5 Hz, 3H), 1.70-1.83 (m, 2H), 2.03 (s, 1H, OH), 4.56 (t, *J* = 6.6 Hz, 1H), 7.24-7.37 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 10.1, 31.8, 75.9, 125.9, 127.4, 128.3, 144.6; GC analysis: CP-Chirasil-DEX CB column (25 m × 0.32 mm), column temperature = 129 °C, (isothermal), injector temperature = 250 °C, detector temperature (FID) = 300, carrier gas: N₂, inlet pressure = 7 psi; t_R = 11.9 min, t_S = 12.5 min.



$C_{10}H_{12}O_3$, FW = 180.20

$[\alpha]_D^{28} +91$ (c 1.2, $CHCl_3$, 71% ee); 1H NMR (300 MHz, $CDCl_3$) δ 1.19-1.26 (m, 3H), 3.61 (s, br, 1H), 4.13-4.28 (m, 2H), 5.15 (s, 1H), 7.31-7.44 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 62.1, 72.8, 126.5, 128.3, 128.5, 138.4, 173.6; GC analysis: CP-Chirasil-DEX CB column (25 m \times 0.32 mm), column temperature = 110 $^\circ C$, (isothermal), injector temperature = 250 $^\circ C$, detector temperature (FID) = 300 $^\circ C$, carrier gas: N_2 , inlet pressure = 7 psi; t_R = 51.1 min, t_S = 52.9 min.



$C_{11}H_{15}NO_2S$, FW = 225.31

Mp: 68-71 $^\circ C$; $[\alpha]_D^{28} +47$ (c 1.6, $CHCl_3$, 92% ee); 1H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, J = 6.9 Hz, 3H), 1.29-1.50 (m, 4H), 1.68-1.81 (m, 1H), 1.91-2.01 (m, 1H), 4.65-4.71 (m, 1H), 5.26 (d, J = 4.5 Hz, 1H), 7.37 (d, J = 7.8 Hz, 1H), 7.49 (t, J = 7.2 Hz, 1H), 7.60 (t, J = 7.2 Hz, 1H), 7.73 (d, J = 7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7, 22.2, 27.7, 35.3, 57.8, 121.1, 124.1, 129.0, 132.9, 135.4, 140.6; HPLC analysis: Chiralcel OD column, 2-propanol:hexane = 20:80 (1.0 mL/min), t_S = 9.3 min, t_R = 16.6 min.