Supplementary Information

A fluorinated dendritic TsDPEN-Ru(II) catalyst for asymmetric transfer hydrogenation of prochiral ketones in aqueous media

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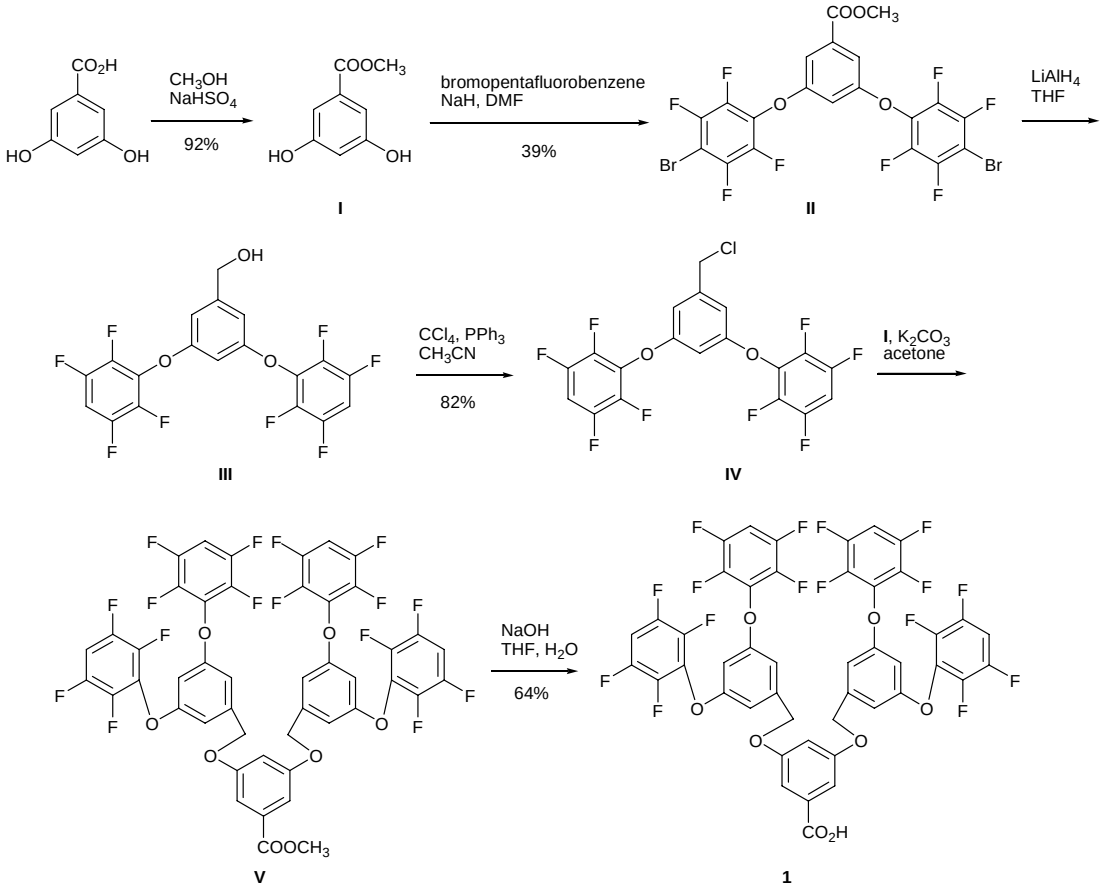
General Experimental Procedures

The ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were acquired in $CDCl_3$ as solvent on a Bruker DMX 500 or a JEOL ECA-400 spectrometer. The chemical shifts (δ) are expressed in ppm (parts per million) relative to TMS (CF_3COOH, for ^{19}F NMR). Spin-spin coupling constants (J) were measured directly from the spectra and were given in Hz. Exact mass spectra (HR-MS) were recorded on IonSpec 4.7 Tesla FTMS. IR spectra were obtained on an Avatar 360 FT-IR spectrometer. Optical rotations were measured on an Autopol IV automatic polarimeter. Enantiomeric excesses were determined on chiral HPLC. The reactions were monitored by thin layer chromatography coated with silica gel.

All solvents were purified and dried by standard procedures and kept over a suitable drying agent prior to use. Unless otherwise noted, all reagents were purchased from commercial sources and were used without further purification. The *p*-hydroxyphenylsulfonamido modified chiral ligand (*S,S*)-**2** was synthesized according to our previously reported method.[1] $[RuCl_2(p\text{-cymene})]_2$ was purchased from Lancaster and used as received. The ketone substrates were obtained from Lancaster or previously synthesized and purified by washing with *aq*. NaOH solution (0.1 M) and distillation or recrystallization prior to use.

Catalyst Preparation



Synthesis of **II**: A solution of 3,5-dihydroxybenzoic acid (15.41 g, 0.10 mol) and sodium bisulfate monohydrate (0.55 g, 4 mmol) in methanol (60 mL) was refluxed for 20 h, then cooled and evaporated. Recrystallization from water afforded white crystals **I** (15.47 g, 92 mmol, 92%). To a stirred and cooled (0 ºC) solution of NaH (4.80 g, 60%, 120 mmol) in DMF (20 mL) was added a solution of **I** (6.72 g, 40 mmol) in DMF (20 mL). The resulting mixture was stirred at 70 ºC for 1 h. After cooling to 0 ºC, bromopentafluorobenzene (19.76 g, 80 mmol) was added slowly. The reaction mixture was stirred at 65 ºC under nitrogen for 96 h. The slurry was cooled to 0 ºC, and treated with 50 mL 3M HCl over 1 h. Ether (50 mL) was added and the biphasic mixture was settled, the aqueous layer discarded. The organic extracts were washed with saturated brine (60 mL) and then dried (Na_2SO_4). The solvent was removed to give a crude solid, which was purified by silica gel column chromatography (eluent: 10% v/v ethyl acetate/hexane) to afford the product **II** as a white solid (9.61 g, 15.45 mmol, 39%).

*Characterization of **II***: mp 99.2-100.3 ºC. IR (cm^{-1}) 3447, 2924, 2843, 2550, 1734, 1600, 1491, 1436, 1384, 1308, 1233, 1141, 1077, 979, 834, 753; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.29 (2H, d, J = 2.3 Hz, Ar*H*), 7.00 (1H, t, J = 2.3 Hz, Ar*H*), 3.89 (3H, s, COOCH_3); ^{13}C NMR (125.8 MHz, $CDCl_3$, δ): 165.1 (*C*OOCH$_3$), 157.9 (2 Ar-*C*), 145.5 (dd, $^{1}J_{FC}$ = 250.3 Hz, $^{2}J_{FC}$ = 13.0 Hz, 4 Ar-*C*-F), 141.7 (dd, $^{1}J_{FC}$ = 257.3 Hz, $^{2}J_{FC}$ = 13.8 Hz, 4 Ar-*C*-F), 133.5, 132.2, 111.5, 109.1 (6 Ar-*C*), 96.7 (t, $^{2}J_{FC}$ = 22.8 Hz, 2 Ar-*C*-Br), 52.7 (*C*H$_3$O); ^{19}F NMR (470.5 MHz, $CDCl_3$, δ): –130.7 (4F, d, $^{3}J_{FF}$ = 14.6 Hz), –150.8 (4F, d, $^{3}J_{FF}$ = 14.6 Hz).

Synthesis of **1**: A solution of **II** (6.22 g, 10 mmol) in THF (30 mL) was added slowly to a solution of $LiAlH_4$ (1.52 g, 40 mmol) in THF (15 mL). The reaction mixture was refluxed for 24 h, cooled to 0 ºC, then water (50 mL) was added dropwise over 1 h. Ether (70 mL) was added, and the phases were separated. The organic extracts were washed with saturated brine (60 mL) and then dried (Na_2SO_4). The solvent was evaporated to give **III** as a solid. The crude product **III** was dissolved in acetonitrile (30 mL), and the solution was then used directly in the next step.

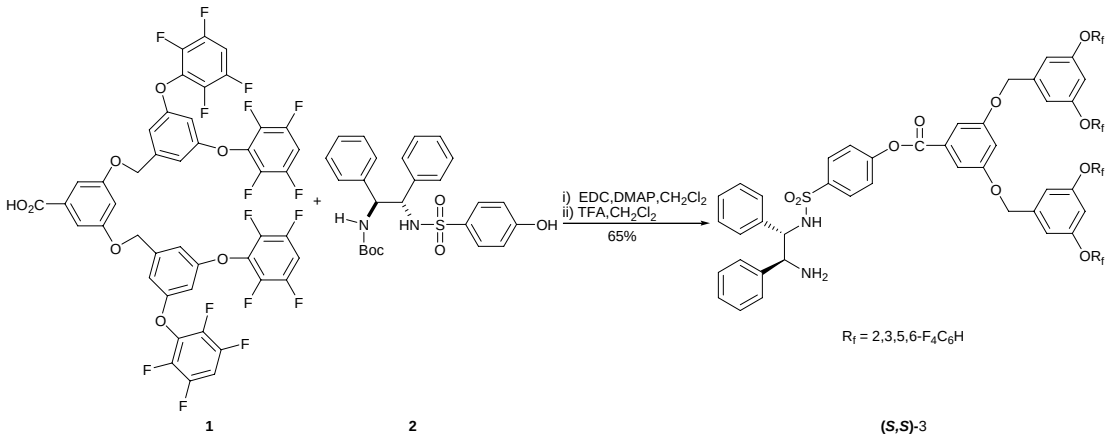
In a separate vessel, a mixture of triphenylphosphine (3.93 g, 15 mol) and CCl_4 (10 mL) in acetonitrile (30 mL) was stirred at room temperature for 0.5 h. The acetonitrile solution of **III** prepared above was then added slowly to the mixture and stirred at room temperature under nitrogen for 10 h. Water (30 mL) was added, and the organic extracts were washed with saturated brine (60 mL) and then dried (Na_2SO_4). The solvent was removed to give a crude solid which was purified by silica gel column chromatography (5% v/v ethyl acetate/hexane) to afford the product **IV** as a white solid (3.73 g, 8.22 mmol, 82% over two steps).

I (0.84 g, 5 mmol), **IV** (4.54 g, 10 mmol), TBAI (tetrabutylammonium iodide) (0.74 g, 2 mmol) and K_2CO_3 (2.76 g, 20 mmol) were dissolved in 50 mL of acetone, and the resultant solution was refluxed for 10 h. The solvent was removed under reduced pressure, then ethyl acetate (60 mL) and water (60 mL) were added. The organic extracts were washed with saturated brine (50 mL) and dried (Na_2SO_4). The solvent was removed to give the crude solid **V**.

The crude product **V** was dissolved in 30 mL of THF. To this, a solution of NaOH

(1.20 g, 30 mmol) in water (30 mL) was added. The reaction mixture was refluxed for 2 h, and then allowed to cool 0 ºC. The mixture was quenched with 3N HCl (20 mL) then extracted with ethyl acetate (50 mL). The organic layer was washed with saturated brine (60 mL), dried over Na_2SO_4. The solvent was removed to give the crude product **1**. Purification by silica gel column chromatography (eluent: 50 → 90% v/v ethyl acetate/hexane) afforded pure **1** as a white solid (3.15 g, 3.18 mmol, 64% over two steps).

*Characterization of **1***: mp 186.9-188.8 ºC. IR (cm^{-1}) 3405, 3088, 2925, 2638, 2228, 2115, 1696, 1599, 1521, 1450, 1379, 1298, 1234, 1139, 1071, 945, 842, 762, 748, 716, 666; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.31-7.28 (2H, m, Ar*H*), 7.09-6.91 (4H, m, Ar*H*), 6.89-6.52 (7H, m, Ar*H*), 5.04, 5.01 (4H, s, s, ArCH_2O); ^{13}C NMR (125.8 MHz, $CDCl_3$, δ): 170.9 (*C*OOH), 159.3, 158.4 (6 Ar-*C*), 147.6-145.4 (m, 8 Ar-*C*-F), 141.4 (dd, $^1J_{FC}$ = 252.1 Hz, $^2J_{FC}$ = 12.7 Hz, 8 Ar-*C*-F), 140.2, 133.5, 131.3, 109.3, 108.3, 103.9 (16 Ar-*C*), 102.8 (t, $^2J_{FC}$ = 22.8 Hz, 4 Ar-*C*-H), 69.3 (2 Ar*C*H_2O); ^{19}F NMR (470.5 MHz, $CDCl_3$, δ): −136.9∼−137.1 (8F, m), −152.4∼−152.6 (8F, m).



1 **2** **(*S*,*S*)-3**

*Synthesis of **3***: To a stirred and cooled (0 ºC) solution of the *p*-hydroxyphenylsulfonamido modified chiral ligand (*S,S*)-**2** (0.94 g, 2 mmol), EDC-HCl (0.46 g, 2.4 mmol) and 4-dimethylaminopyridine (30 mg, 0.24 mmol) in CH_2Cl_2 (20 mL) was slowly added a solution of **1** (1.98 g, 2 mmol) in CH_2Cl_2 (30 mL) over 0.5 h. After stirring at 0 ºC for 10 h, the solvent was removed and ethyl acetate (50 mL) was added. The solution was washed with saturated 1N HCl (70 mL), brine (60 mL) and then dried over Na_2SO_4. The solvent was removed and the crude solid residue was dissolved in CH_2Cl_2 (20 mL). The mixture was cooled to 0 ºC, and a solution of trifluoroacetic acid (6

mL) in CH_2Cl_2 (10 mL) was added. After the solution was stirred at 0 ºC for 0.5 h, an aqueous saturated $NaHCO_3$ solution (45 mL) was added slowly. The organic phase was separated, washed with saturated brine (50 mL) and dried over Na_2SO_4. The solvent was removed to give the crude product **3**, which was purified by silica gel column chromatography (eluent: 50 → 100% v/v ethyl acetate/hexane) to afford the pure **3** as a white solid (1.72 g, 1.32 mmol, 65% over two steps).

*Characterization of **3***: mp 156.5-158.1 ºC. IR (cm^{-1}) 3432, 3073, 2925, 2351, 1742, 1598, 1521, 1486, 1450, 1384, 1301, 1140, 1070, 945, 846, 753, 692, 564; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.48-7.44 (1H, m, Ar*H*), 7.45-7.41 (1H, m, Ar*H*), 7.40-7.33 (2H, m, Ar*H*), 7.25-7.14 (10H, m, Ar*H*), 7.09-6.94 (5H, m, Ar*H*), 6.86-6.82 (2H, m, Ar*H*), 6.71-6.79 (4H, m, Ar*H*), 6.69-6.61 (1H, m, Ar*H*), 6.60-6.54 (1H, m, Ar*H*), 6.17 (1H, br s, N*H*SO_2Ar), 5.06, 5.04 (4H, s, s, 2 ArCH_2O), 4.45 (1H, d, J = 4.6 Hz, C*H* $NHSO_2$), 4.18 (1H, d, J = 4.6 Hz, C*H* NH_2), 1.49 (2H, br s, NH_2); ^{13}C NMR (125.8 MHz, $CDCl_3$, δ): 163.6 (*C*OOAr), 159.5, 158.4, 153.4 (7 Ar-*C*), 147.6-145.4 (m, 8 Ar-*C*-F), 141.4 (dd, $^1J_{FC}$ = 252.7 Hz, $^2J_{FC}$ = 15.7 Hz, 8 Ar-*C*-F),141.4, 140.1, 139.1, 137.9, 133.6, 131.1, 128.6, 128.5, 128.4, 127.6, 127.7, 127.0, 126.5, 121.7, 112.2, 109.9, 109.4, 109.3, 108.2, 105.8, 104.7, 103.8 (33 Ar-*C*), 102.5 (t, $^2J_{FC}$ = 22.8 Hz, 4 Ar-*C*-H), 69.4 (2 Ar*C*H_2O), 63.3, 60.5 (2 *C*H); ^{19}F NMR (470.5 MHz, $CDCl_3$, δ): −136.8~−136.9 (8F, m), −152.4~−152.6 (8F, m); HRMS (MALDI-MS) *m/z* $[M + Na]^+$ calc for $[C_{65}H_{36}F_{16}N_2O_{10}S + Na]$:1363.1733; found: 1363.1725±0.004.

General Procedure for Transfer Hydrogenation

Preparation of the pre-catalyst Ru-FTsDPEN: $[RuCl_2(p\text{-cymene})]_2$ (3.0 mg, 0.005 mmol), ligand (*S,S*)-**3** (14.35 mg, 0.011 mmol) and Et_3N (2.0 mg, 0.02 mmol) were sequentially dissolved in 1 mL of CH_2Cl_2. After the solution was stirred at 35 ºC for 10 h, hexane (20 mL) was added and the product began to precipitate from solution. The solids were washed with degassed water (10 mL) and hexane (10 mL) and then dried under vacuum to provide Ru-(*S,S*)-**3** as a yellow solid. This was directly used as the pre-catalyst in the following asymmetric transfer hydrogenation reactions.

Reduction of ketones using catalyst Ru-FTsDPEN in azeotrope[2] *(formic acid:triethylamine mole ratio 5:2)*: Ru-(*S,S*)-**3** (0.01 mmol) and ketone (1.0 mmol) were added in the azeotrope (formic acid : triethylamine *mole ratio* 5:2, 1 mL), and the mixture was stirred at 40 ºC under nitrogen for a certain period of time. After the reaction was completed (monitored by TLC), ethyl acetate (20 mL) was added. The organic phase was separated, washed with saturated $NaHCO_3$ (20 mL), saturated brine (20 mL), and then dried over anhyd Na_2SO_4. The product was purified by flash chromatography on silica gel to afford pure alcohol product.

Reduction of ketones using catalyst Ru-FTsDPEN in azeotrope[3] *(formic acid:triethylamine mole ratio 1.2:1) and water*: The catalyst Ru-(*S,S*)-**3** (0.01 mmol), ketone (1.0 mmol) and azeotrope (*formic acid:triethylamine mole ratio* 1.2:1, 1 mL) were added in degassed water (1 mL), and the mixture was stirred at 40 ºC under nitrogen for a certain period of time. After the reaction was completed (monitored by TLC), the reaction mixture was extracted with ethyl acetate (20 mL). The organic phase was dried over anhyd Na_2SO_4 and concentrated under reduced pressure. The product was purified by flash chromatography on silica gel to afford pure alcohol product.

Reduction of ketones using catalyst Ru-FTsDPEN in water:[4] The catalyst Ru-(*S,S*)-**3** (0.01 mmol), CH_2Cl_2 (0.5 mL) and ketone (1.0 mmol) were added to 5 M liquor of HCO_2Na (6 mL), and the mixture was stirred at 40 ºC under nitrogen for a certain period of time. After the reaction was completed (monitored by TLC), the reaction mixture was extracted with ethyl acetate (20 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The product was purified by flash chromatography on silica gel to afford pure alcohol product.

Reduction of ketones using catalyst Ru-FTsDPEN in water with addition of TBAI:[5] To 5 M liquor of HCO_2Na (6 mL) were sequentially added the catalyst Ru-(*S,S*)-**3** (0.01 mmol), ketone (1.0 mmol), CH_2Cl_2 (0.5 mL) and TBAI (tetrabutylammonium iodide, 185 mg, 0.5 mmol). The resultant mixture was stirred at 40 ºC under nitrogen for a certain period of time. After the reaction was completed (monitored by TLC), the reaction mixture was extracted with ethyl acetate (20 mL). The organic phase was dried over anhyd Na_2SO_4 and concentrated under reduced pressure. The product was purified by

flash chromatography on silica gel to afford pure alcohol product.

Characterization of products:

(*S*)-1-Phenylethanol (Table 1, entry 4): CHIRAIPAK OB-H 0.46 cm × 25 cm, 90% hexanes, 10% IPA, 0.7 mL/min, UV 214 nm, 25 °C, t_r = 8.5 min (*S*), 11.8 min (*R*). $[\alpha]_D^{16}$ –47.6° (*c* 1.16 in CH_2Cl_2) 97%ee (*S*) (lit.[1] $[\alpha]_D^{23}$ –50.0° (*c* 1.00 in CH_2Cl_2) 96%ee (*S*)). ^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.36-7.34 (m, 4H), 7.30-7.25 (m, 1H), 4.83 (q, *J* = 6.4 Hz, 1H), 1.51 (d, *J* = 6.4 Hz, 3H).

(*S*)-1-(4-Chlorophenyl)ethanol (Table 2, entry 1): CHIRAIPAK OB-H 0.46 cm × 25 cm, 90% hexanes, 10% IPA, 0.7 mL/min, UV 214 nm, 25 °C, t_r = 7.5 min (*S*), 8.4 min (*R*). $[\alpha]_D^{16}$ –46.7° (*c* 0.64 in ether) 94%ee (*S*) (lit.[1] $[\alpha]_D^{23}$ –46.3° (*c* 2.05 in ether) 95%ee (*S*)). ^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.36-7.27 (m, 4H), 4.89 (q, *J* = 6.4 Hz, 1H), 1.88 (br, 1H), 1.47 (d, *J* = 6.4 Hz, 3H).

(*S*)-1-*p*-Tolyl-ethanol (Table 2, entry 2): CHIRAIPAK OB-H 0.46 cm × 25 cm, 90% hexanes, 10% IPA, 0.7 mL/min, UV 214 nm, 25 °C, t_r = 8.9 min (*S*), 10.8 min (*R*). $[\alpha]_D^{16}$ –50.4° (*c* 0.77 in $CHCl_3$) 97%ee (*S*) (lit.[6] $[\alpha]_D^{25}$ –45.3 (*c* 1.26 in $CHCl_3$) 72%ee (*S*)). ^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.27 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 4.87 (q, *J* = 6.4 Hz, 1H), 2.35 (s, 3H), 1.80 (br, 1H), 1.49 (d, *J* = 6.4 Hz, 3H).

(*S*)-1-*o*-Tolyl-ethanol (Table 2, entry 3): CHIRAIPAK OB-H 0.46 cm × 25 cm, 90% hexanes, 10% IPA, 0.7 mL/min, UV 214 nm, 25 °C, t_r = 7.1 min (*S*), 10.0 min (*R*). $[\alpha]_D^{16}$ –70.1° (*c* 0.75 in $CHCl_3$) 66%ee (*S*) (lit.[6] $[\alpha]_D^{25}$ –71.9 (*c* 1.06 in $CHCl_3$) 99%ee (*S*)). ^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.51 (d, *J* = 7.3 Hz, 1H), 7.19-7.08 (m, 3H), 5.14 (q, *J* = 6.4 Hz, 1H), 2.35 (s, 3H), 1.47 (d, *J* = 6.4 Hz, 3H).

(*S*)-1-*m*-Tolyl-ethanol (Table 2, entry 4): CHIRAIPAK OB-H 0.46 cm × 25 cm, 90% hexanes, 10% IPA, 0.7 mL/min, UV 214 nm, 25 °C, t_r = 7.9 min (*S*), 10.6 min (*R*). $[\alpha]_D^{16}$ –47.3 (*c* 0.84 in $CHCl_3$) 90%ee (*S*) (lit.[7] $[\alpha]_D^{25}$ +28.6° (neat) 82.6%ee (*R*)). ^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.26-7.05 (m, 4H), 4.87 (q, *J* = 6.4 Hz, 1H), 2.36 (s, 3H), 1.80 (br, 1H), 1.48 (d, *J* = 6.4 Hz, 3H).

(*S*)-3-Hydroxy-3-phenylpropionic acid ethyl ester (Table 2, entry 5): CHIRAIPAK OD-H 0.46 cm × 25 cm, 80% hexanes, 20% IPA, 0.7 mL/min, UV 214 nm, 25 °C, t_r = 8.3 min (*S*), 10.3 min (*R*). $[\alpha]_D^{16}$ –47.8° (*c* 1.293 in $CHCl_3$) 92%ee (*S*) (lit.[8]

$[\alpha]_D^{25}$ –33.1° (*c* 1.0 in $CHCl_3$) 98.7%ee (*S*)). ^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.39-7.26 (m, 5H), 5.14-5.10 (m, 1H), 4.17 (q, *J* = 7.3 Hz, 2H), 2.85-2.65 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H).

(*S*)-1-(1'-Naphthyl)ethanol (Table 2, entry 6): CHIRAIPAK OD-H 0.46 cm × 25 cm, 80% hexanes, 20% IPA, 0.7 mL/min, UV 214 nm, 25 °C, t_r = 9.4 min (*S*), 13.4 min (*R*). $[\alpha]_D^{16}$ –69.2° (*c* 0.70 in ether) 55%ee (*S*) (lit.[1] $[\alpha]_D^{23}$ –67.4° (*c* 0.95 in ether) 83%ee (*S*)). ^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 8.12 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 6.9 Hz, 1H), 7.56-7.46 (m, 3H), 5.65 (q, *J* = 6.4 Hz, 1H), 1.66 (d, *J* = 6.4 Hz, 3H).

(*S*)-2-Thienylethanol (Table 2, entry 7): CHIRAIPAK OB-H 0.46 cm × 25 cm, 90% hexanes, 10% IPA, 0.7 mL/min, UV 214 nm, 25 °C, t_r = 11.2 min (*S*), 13.3 min (*R*). $[\alpha]_D^{16}$ –39.9° (*c* 0.46 in $CHCl_3$) 78%ee (*R*) (lit.[9] $[\alpha]_D^{22}$ +25.6° (*c* 0.50 in $CHCl_3$) 97%ee (*R*)). ^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.24-7.20 (m, 1H), 7.01-6.95 (m, 2H), 5.12 (q, *J* = 6.4 Hz, 1H), 2.06 (br, 1H), 1.59 (d, *J* = 6.4 Hz, 3H).

Recovery and reuse of the catalyst Ru-FTsDPEN in the transfer hydrogenation in water:

$[RuCl_2(p\text{-cymene})]_2$ (3.0 mg, 0.005 mmol), ligand (*S,S*)-**3** (14.35 mg, 0.011 mmol) and Et_3N (2.0 mg, 0.020 mmol) were dissolved in CH_2Cl_2 (0.5 mL). After the solution was stirred at 35 ºC for 10 h, the mixture of ketone (1.0 mmol) and TBAI (tetrabutylammonium iodide, 185 mg, 0.5 mmol) in 5 M liquor of HCO_2Na (6 mL) was added. The reaction mixture was stirred at 40 ºC under nitrogen for a certain period of time. After the reaction was completed (monitored by TLC), hexane (20 mL) was added to the reaction mixture, whereby the catalyst as well as TBAI began to precipitate from the solution. The upper organic phase was carefully removed by using an even-pinpoint syringe, washed with saturated brine (20 mL) and then dried (Na_2SO_4). The solvent was evaporated, the product was purified by flash chromatography on silica gel to afford pure alcohol product.

For the next run to be conducted, 1 equiv. HCO_2H (0.1 mL, 10 M) was added to adjust the pH. A new reduction was started by feeding another portion of ketone (1.0

mmol) in 0.5 mL of CH_2Cl_2. The solution was allowed to react and the same workup procedure was used as above. Subsequent runs were performed in the same manner as the second.

Table . Recovery and reuse of the catalyst Ru-FTsDPEN in the transfer hydrogenation of acetophenone in water

run[a]	t(h)	%conv[b]	%ee[b]
1	4	>99	93
2	4	>99	95
3	4	>99	95
4	4	99	95
5	4	98	95
6	4	99	95
7	4	99	94
8	4	95	94
9	4	98	93
10	5	>99	93
11	5	98	92
12	5	93	93
13	8	>99	94
14	8	>99	94
16	8	97	93
17	12	98	92
18	12	98	93
19	12	95	92
20	12	92	92
21	18	96	91
22	18	98	92
23	18	>99	93
24	18	93	91
25	20	85	89
26	24	93	88
27	24	59	87
28	48	75	82
29	48	38	61
30[c]	48	90	22

[a] The reactions were carried out at 40 °C; [b] Determined by chiral HPLC. The configuration of alcohol was S; [c] The 30th run was performed at 60 °C.

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