Electronic Supplementary Information

A recyclable catalyst for asymmetric transfer hydrogenation
with a formic acid-triethylamine mixture in ionic liquid

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General Experimental

Melting point was measured with a Yanaco MP micro-melting-point apparatus and uncorrected. IR spectra were taken with Shimadzu IR-435 spectrophotometer. NMR (1H, 13C and 19F) spectra were measured on Varian UNITY INOVA 400NB (1H: 400 MHz, 13C: 100 MHz, 19F: 376 MHz) and the chemical shifts were expressed in parts per million (ppm) downfield from tetramethylsilane as the internal standard (1H, 13C) or referenced to CF3CO2H (19F, external). Mass spectra were measured on JEOL JMS-SX 102A QQ (FAB+) spectrometer. Silica gel (Merck Art. 7737) was used for column chromatography.

Preparation of 9

NaH (60 % in oil, 400 mg, 10mmol) was to a stirred solution of 4-hydroxybenzensulfonic acid sodium salt dihydrate 8 (2.322 g, 10 mmol) in DMF (25 mL) at 0 °C under N2. After stirring for 1 h at the same temperature, 1-bromo-4-chlorobutane (1.152 mL, 10 mmol) was added and the whole was stirred for 84 h at 100 °C. After cooling, 2-propanol (120 mL) was added to the mixture, then insoluble precipitate was collected by filtration and dried \textit{in vacuo} to give a solid. The solid was dissolved in thionylchloride (29 mL) and DMF (4 mL) and the whole was stirred for 17 h at 90 °C. Ice water (10 mL) was added to the mixture at 0 °C, and products were extracted with CHCl3 (30 mL x 3). The organic layer was dried over anhydrous sodium sulfate, evaporated and chromatographed (AcOEt/n-hexane = 1/5) to give 9 as a pale yellow oil (1.529 g, 54%); νmax (CHCl3) cm\(^{-1}\) 2917, 1588, 1490, 1368, 1257, 1158, 573; δ H (CDCl3) 1.96-2.05 (4H, m), 3.63 (2H, t, J...
= 6.2 Hz), 4.12 (2H, t, J = 5.9 Hz), 7.03 (2H, d, J = 9.3 Hz), 7.97 (2H, d, J = 9.2 Hz); δC (CDCl3) 26.3, 29.0, 44.4, 67.9, 115.1, 129.5, 136.0, 164.2; m/z 305 (MNa+, 19%), 307 [(M+2)Na+, 13%], 309 [(M+4)Na+, 3%]; HRMS found 304.9779, C10H12Cl2O3SNa (MNa+) requires 304.9782.

Preparation of 10

A solution of 9 (189 mg, 0.67 mmol) in CH2Cl2 (1 mL) was added to a stirred solution of (1S,2S)-diphenylethylenediamine (142 mg, 0.67 mmol) and Et3N (0.185 mL, 1.33 mmol) in CH2Cl2 (2 mL) at 0 °C under N2. After stirring for 21 h at rt, a solution of Di-Boc (218 mg, 1 mmol) and Et3N (0.139 mL, 1 mmol) in CH2Cl2 (1 mL) was added to the mixture and the whole was stirred for 17 h at rt. The solvent was removed under reduced pressure, sat. NaHCO3 aq. (5 mL) was added to the residue, and products were extracted with AcOEt (20 mL x 3). The organic layer was dried over anhydrous sodium sulfate, evaporated, chromatographed (AcOEt/n-hexane = 1/2) and recrystallized from AcOEt to give 10 as a colorless powder (261 mg, 70%); mp 197 °C; [α]27D –21.0 (c 1.0 in CHCl3); νmax (CHCl3) cm⁻¹ 3410, 3350, 2950, 1686, 1593, 1491, 1152; δH (CDCl3) 1.47 (9H, s), 1.90-2.00 (4H, m), 3.61 (2H, t, J = 6.2 Hz), 3.95 (2H, t, J = 5.6 Hz), 4.56 (1H, dd, J = 7.0, 9.7 Hz), 4.78 (1H, t, J = 9.5 Hz), 5.25 (1H, d, J = 8.1 Hz), 6.08 (1H, br-s), 6.67 (2H, d, J = 9.0 Hz), 6.77-7.17 (10H, m), 7.46 (2H, d, J = 9.0 Hz); δC (CDCl3) 26.4, 28.3, 29.1, 44.5, 60.0, 63.9, 67.2, 80.6, 114.1, 127.2, 127.3, 127.4, 127.9, 128.0, 128.2, 128.5, 129.0, 133.1, 137.8, 138.1, 161.6; m/z 559 (MH+, 4%), 561 [(M+2)H+, 2%]; HRMS found 559.2039, C29H36ClN2O5S (M+H)+ requires 559.2033; Anal. Calcd for C29H35ClN2O5S: C, 62.30; H, 6.31; N, 5.01 found: C, 62.54; H, 6.49; N, 5.01.

Preparation of 11

A mixture of 10 (117 mg, 0.21 mmol) and 1-methylimidazole (0.076 mL, 0.95 mmol) was stirred for 8 h at 80 °C under N2. Excess of 1-methylimidazole was removed under reduced pressure, and the residue was washed with AcOEt and dried in vacuo to give 11 as a pale yellow viscous oil (128 mg, 95 %); [α]24D –33.1 (c 1.3 in MeOH); νmax (KBr) cm⁻¹ 3340, 3214, 3041, 2919, 1696, 1592, 1511, 1318, 1248, 1150; δH (CD3OD) 1.36 (9H, s), 1.73-1.80 (2H, m), 2.00-2.05 (2H, m), 3.87 (3H, s), 3.94 (2H, t, J = 6.2 Hz), 4.25 (2H, t, J = 7.3 Hz), 4.56 (1H, d, J = 8.4 Hz), 4.78 (1H, br-d, J = 8.6 Hz), 6.68 (2H, d, J = 8.8 Hz), 6.91-7.12 (10H, m), 7.37 (2H, d, J = 9.0 Hz), 7.52 (1H, d, J = 1.8 Hz), 7.61 (1H, d, J = 1.8 Hz), 8.94 (1H, s); δC (CD3OD) 26.7, 27.9, 28.7, 36.5, 50.4, 61.0, 64.0, 68.5, 80.5, 115.3, 123.5, 124.9, 128.1, 128.2, 128.3, 128.6, 129.0, 129.1, 129.8, 130.0, 134.0, 139.8, 140.9, 157.7, 162.9; HRMS found 605.2803, C33H35N4O5S (M)+ requires 605.2798.
Preparation of 12

TFA (0.15 mL) was added to 11 (124 mg, 0.19 mmol) at 0 °C under N₂. After stirring for 2 h at 0 °C, toluene (5 mL) was added to the mixture and the volatile was removed under reduced pressure to give 12 as a pale yellow viscous oil (135 mg, 97 %); [α]²⁴ D –41.6 (c 0.5 in MeOH); ν max (KBr) cm⁻¹ 3364, 3046, 2910, 1671, 1197, 1153; δ (CD₃OD) 1.73-1.80 (2H, m), 1.98-2.07 (2H, m), 3.90 (3H, s), 3.95 (2H, t, J = 6.0 Hz), 4.27 (2H, t, J = 7.3 Hz), 4.53 (1H, d, J = 10.8 Hz), 4.66 (1H, d, J = 10.8 Hz), 6.69 (2H, d, J = 8.8 Hz), 6.75-7.22 (10H, m), 7.47 (2H, d, J = 9.0 Hz), 7.54 (1H, d, J = 1.8 Hz), 7.63 (1H, d, J = 1.8 Hz), 8.97 (1H, s); δ (CD₃OD) 26.7, 27.9, 36.5, 50.4, 60.7, 63.0, 68.6, 115.4, 123.6, 125.0, 128.7, 128.8, 129.1, 129.2, 129.9, 130.1, 130.2, 130.3, 133.2, 134.8, 136.7, 137.9, 163.3; δ (CD₃OD) 1.80; HRMS found 505.2277, C₂₈H₃₃N₄O₃S (M⁺) requires 505.2273; Anal. Calcd for C₃₂H₃₄F₆N₄O₇S·2.5H₂O: C, 49.42; H, 5.05; N, 7.20 found: C, 49.45; H, 4.82; N, 6.85.

Typical recycling procedure

Acetophenone 6a (120 mg, 1.0 mmol) was added to a solution of the ionic ligand 12 (7.8 mg, 0.012 mmol) and [RuCl₂(benzene)]₂ (2.5 mg, 0.005 mmol) in [bmim][PF₆] 1 (1.0 mL) with stirring under N₂, followed by addition of the formic acid–triethylamine azeotropic mixture (bp 108 °C / 29 mmHg, 0.5 mL). The reaction mixture was stirred at rt for 24 h. Then, n-hexane (5 ml x 3) was added to the reaction mixture and the products were extracted by decantation of the upper layer, and the residual IL phase was dried in vacuo (rt / 2 mmHg) for 30 min. A small portion of n-hexane layers were analyzed by GLC* to determine the yield and ee. Acetophenone (120 mg, 1.0 mmol) and formic acid–triethylamine azeotropic mixture (0.5 mL) were added to the remained IL solution, and the second cycle of the reaction was started.

* GLC condition: Column; J&W CYCLODEXB (0.25 mm x 30 m)
Column Temp; 110 °C
Injection Temp; 200 °C
Carrier; He (1 mL / min)