**Electronic Supplementary Information**

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

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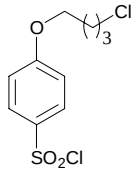
**General Experimental**

Melting point was measured with a Yanaco MP micro-melting-point apparatus and uncorrected. IR spectra were taken with Shimadzu IR-435 spectrophotometer. NMR ($^{1}$H, $^{13}$C and $^{19}$F) spectra were measured on Varian UNITY INOVA 400NB ($^{1}$H: 400 MHz, $^{13}$C: 100 MHz, $^{19}$F: 376 MHz) and the chemical shifts were expressed in parts per million (ppm) downfield from tetramethylsilane as the internal standard ($^{1}$H, $^{13}$C) or referenced to $CF_3CO_2H$ ($^{19}$F, external). Mass spectra were measured on JEOL JMS-SX 102A QQ (FAB+) spectrometer. Silica gel (Merck Art. 7737) was used for column chromatography.

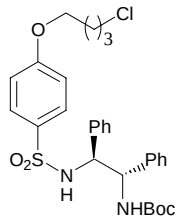
**Preparation of 9**




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 $N_2$. 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 *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 $CHCl_3$ (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%); $\nu_{max}$ ($CHCl_3$) cm$^{-1}$ 2917, 1588, 1490, 1368, 1257, 1158, 573; $\delta_H$ ($CDCl_3$) 1.96-2.05 (4H, m), 3.63 (2H, t, *J*

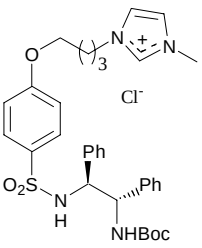
= 6.2 Hz), 4.12 (2H, t, *J* = 5.9 Hz), 7.03 (2H, d, *J* = 9.3 Hz), 7.97 (2H, d, *J* = 9.2 Hz); $\delta_C$ ($CDCl_3$) 26.3, 29.0, 44.4, 67.9, 115.1, 129.5, 136.0, 164.2; *m/z* 305 ($MNa^+$, 19%), 307 [$(M+2)Na^+$, 13%], 309 [$(M+4)Na^+$, 3%]; HRMS found 304.9779, $C_{10}H_{12}Cl_2O_3SNa$ ($MNa^+$) requires 304.9782.

**Preparation of 10**



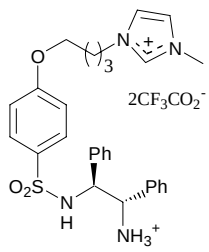

A solution of **9** (189 mg, 0.67 mmol) in $CH_2Cl_2$ (1 mL) was added to a stirred solution of (1*S*,2*S*)-diphenylethylenediamine (142 mg, 0.67 mmol) and $Et_3N$ (0.185 mL, 1.33 mmol) in $CH_2Cl_2$ (2 mL) at 0 °C under $N_2$. After stirring for 21 h at rt, a solution of Di-Boc (218 mg, 1 mmol) and $Et_3N$ (0.139 mL, 1 mmol) in $CH_2Cl_2$ (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. $NaHCO_3$ 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; $[\alpha]^{27}_D$ –21.0 (*c* 1.0 in $CHCl_3$); $\nu_{max}$ ($CHCl_3$) $cm^{-1}$ 3410, 3350, 2950, 1686, 1593, 1491, 1152; $\delta_H$ ($CDCl_3$) 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): $\delta_C$ ($CDCl_3$) 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, $C_{29}H_{36}ClN_2O_5S$ $(M+H)^+$ requires 559.2033; *Anal.* Calcd for $C_{29}H_{35}ClN_2O_5S$: C, 62.30; H, 6.31; N, 5.01 found: C, 62.54; H, 6.49; N, 5.01.

**Preparation of 11**



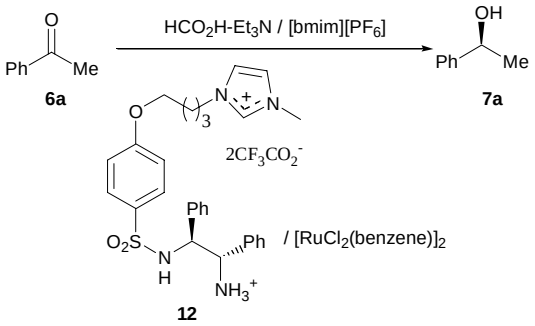

A mixture of **10** (117 mg, 0.21 mmol) and 1-methylimidazole (0.076 mL, 0.95 mmol) was stirred for 8 h at 80 °C under $N_2$. Excess of 1-methylimidazole was removed under reduced pressure, and the residue was washed with AcOEt and dried *in vacuo* to give **11** as a pale yellow viscous oil (128 mg, 95 %); $[\alpha]^{24}_D$ –33.1 (*c* 1.3 in MeOH); $\nu_{max}$ (KBr) $cm^{-1}$ 3340, 3214, 3041, 2919, 1696, 1592, 1511, 1318, 1248, 1150; $\delta_H$ ($CD_3OD$) 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) ; $\delta_C$ ($CD_3OD$) 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, $C_{33}H_{41}N_4O_5S$ $(M)^+$ requires 605.2798.

**Preparation of 12**



TFA (0.15 mL) was added to **11** (124 mg, 0.19 mmol) at 0 °C under $N_2$. 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 %); $[\alpha]^{24}_{D}$ –41.6 (*c* 0.5 in MeOH); $\nu_{max}$ (KBr) $cm^{-1}$ 3364, 3046, 2910, 1671, 1197, 1153; $\delta_H$ ($CD_3OD$) 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); $\delta_C$ ($CD_3OD$) 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, 130.2, 130.3, 133.2, 134.8, 136.7, 137.9, 163.3; $\delta_F$ ($CD_3OD$) 1.80; HRMS found 505.2277, $C_{28}H_{33}N_4O_3S$ $(M)^+$ requires 505.2273; *Anal*. Calcd for $C_{32}H_{34}F_6N_4O_7S{\cdot}2.5H_2O$: 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 $[RuCl_2(benzene)]_2$ (2.5 mg, 0.005 mmol) in [bmim][$PF_6$] **1** (1.0 mL) with stirring under $N_2$, 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)