Supporting Information

Development of a Recyclable Fluorous Chiral Phase-Transfer Catalyst: Application to the Catalytic Asymmetric Synthesis of α -Amino Acids

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General. Infrared (IR) spectra were recorded on a Shimadzu FT-IR 8200A spectrometer. ^1H and ^{13}C NMR spectra were measured on a JEOL JNM-FX400 (400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR) spectrometer. High performance liquid chromatography (HPLC) was performed on Shimadzu 10A instruments using 4.6 mm $\times$ 25 cm Daicel Chiralcel OD and OD-H. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF₂₅₄, 0.25 mm) were used. The products were purified by preparative column chromatography on silica gel (E. Merck 9385). High-resolution mass spectra (HRMS) were performed on Applied Biosystems Mariner API-TOF workstation.

In experiments requiring dry solvents, tetrahydrofuran (THF) were purchased from Kanto Chemical Co. Inc. as “Dehydrated”. Toluene was dried over sodium metal. Dichloromethane (CH_2Cl_2) was stored over 4Å molecular sieves. Triethylamine (Et_3N) was stored over potassium hydroxide (KOH) pellets. Trifluoromethanesulfonic anhydride (Tf_2O) was kindly supplied by Central Glass Co., Ltd., and also *tert*-butyl glycinate hydrochloride was supplied by Watanabe Chemical Ind., Ltd. *tert*-Butyl glycinate benzophenone Schiff base (**2**) was prepared from *tert*-butyl glycinate hydrochloride and benzophenone imine according to the literature procedure.¹ Other simple chemicals were purchased and used as such.

Synthesis of a Fluorous Chiral Phase-Transfer Catalyst.

(R)-4,4',6,6'-Tetrabromo-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl (5). To a solution of (R)-4,4',6,6'-tetrabromo-1,1'-bi-2-naphthol (**4**)² (5.0 mmol) in THF (30 ml) was added sodium hydride (12 mmol) at 0 °C under argon atmosphere and the mixture was stirred for 15 min at this temperature. Then, chloromethyl methyl ether (12 mmol) was added and the mixture was allowed to warm to room temperature. After stirring for 2 h, the reaction mixture was quenched by water, and organic materials were extracted with CH₂Cl₂. The organic extracts were washed with brine, dried over Na₂SO₄ and concentrated. The residue was purified by recrystallization from CH₂Cl₂/Hexane to give **5** as a white solid (99% yield): $[\alpha]_D^{29} +54.5^\circ$ (*c* 0.50, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.43 (2H, d, *J* = 2.0 Hz, Ar-H), 7.94 (2H, s, Ar-H), 7.34 (2H, dd, *J* = 2.0, 9.2 Hz, Ar-H), 6.97 (2H, d, *J* = 9.2 Hz, Ar-H), 5.07 (2H, d, *J* = 6.8 Hz, OCH₂), 4.98 (2H, d, *J* = 6.8 Hz, OCH₂), 3.20 (6H, s, CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 152.4, 132.7, 130.7, 129.4, 127.2, 122.6, 121.8, 119.8, 119.6, 94.9, 56.1 ppm; IR (KBr) 2963, 2907, 2827, 1578, 1481, 1313, 1153, 1072, 1009, 970, 924 cm⁻¹. HRMS (ESI) Calcd for C₂₄H₁₈O₄NaBr₄: 708.7831 ([M + Na]⁺). Found: 708.7840 ([M + Na]⁺).

(R)-4,4',6,6'-Tetra[(1H,1H,2H,2H-heptafluorodecyl)(dimethyl)silyl]-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl (6). To a solution of **5** (1.0 mmol) in THF (25 ml) was added ^tBuLi (9.0 mmol) at -78 °C under argon atmosphere and the mixture was stirred for 15 min at this temperature. Then, (1H,1H,2H,2H-heptafluorodecyl)(dimethyl)chlorosilane (6.0 mmol) was added, and the mixture was warmed to room temperature. After stirring for 5 h, the resulting reaction mixture was quenched by water, and organic materials were extracted with CH₂Cl₂. The organic extracts were washed with brine, dried over Na₂SO₄. Evaporation of solvents and purification of the residue by column chromatography on silica gel (Et₂O/Hexane = 1/30 as eluent) afforded **6** as a colorless oil (78%

yield): $[\alpha]_D^{26} +9.8^\circ$ (c 0.89, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.21 (2H, s, Ar-H), 7.74 (2H, s, Ar-H), 7.30 (2H, d, $J = 8.4$ Hz, Ar-H), 7.18 (2H, d, $J = 8.4$ Hz, Ar-H), 5.07 (2H, d, $J = 6.8$ Hz, OCH_2), 4.95 (2H, d, $J = 6.8$ Hz, OCH_2), 3.10 (6H, s, CH_3), 1.95–2.23 (8H, m, CH_2CF_2), 1.26–1.32 (4H, m, SiCH_2), 0.97–1.02 (4H, m, SiCH_2), 0.61 (12H, s, SiCH_3), 0.37 (6H, s, SiCH_3), 0.36 (6H, s, SiCH_3) ppm; IR (neat) 2959, 2909, 1240, 1205, 1151, 1026, 839 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{72}\text{H}_{58}\text{O}_4\text{F}_{68}\text{NaSi}_4$: 2413.2219 ($[\text{M} + \text{Na}]^+$). Found: 2413.2201 ($[\text{M} + \text{Na}]^+$).

(*R*)-4,4',6,6'-Tetra[(1H,1H,2H,2H-heptafluorodecyl)(dimethyl)silyl]-1,1'-bi-2-naphthol (7). To a solution of **6** (0.50 mmol) in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ ($v/v = 1/1$) (50 ml) was added TsOH (1.0 mmol), and the reaction mixture was heated to 50 °C, stirred for 5 h, and then poured into water. After extraction with CH_2Cl_2 , the organic extracts were washed with brine and dried over Na_2SO_4 . Evaporation of solvents and purification of the residue by column chromatography on silica gel ($\text{Et}_2\text{O}/\text{Hexane} = 1/5$ as eluent) afforded **7** as a colorless viscous oil (92% yield): $[\alpha]_D^{26} -8.4^\circ$ (c 0.61, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.23 (2H, s, Ar-H), 7.58 (2H, s, Ar-H), 7.40 (2H, d, $J = 8.8$ Hz, Ar-H), 7.21 (2H, d, $J = 8.8$ Hz, Ar-H), 5.01 (2H, s, OH), 1.95–2.18 (8H, m, CH_2CF_2), 1.29–1.34 (4H, m, SiCH_2), 0.99–1.04 (4H, m, SiCH_2), 0.61 (12H, s, SiCH_3), 0.38 (12H, s, SiCH_3) ppm; IR (neat) 3531, 2959, 2909, 1240, 1204, 1148, 899, 841 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{68}\text{H}_{50}\text{O}_2\text{F}_{68}\text{NaSi}_4$: 2325.1694 ($[\text{M} + \text{Na}]^+$). Found: 2325.1689 ($[\text{M} + \text{Na}]^+$).

(*R*)-4,4',6,6'-Tetra[(1H,1H,2H,2H-heptafluorodecyl)(dimethyl)silyl]-2,2'-bis(trifluoromethanesulfonyl)-1,1'-binaphthyl (8). To a solution of **7** (0.40 mmol) and Et_3N (3.6 mmol) in CH_2Cl_2 (15 ml) was added Tf_2O (2.9 mmol) dropwise at 0 °C and the mixture was stirred for 2 h at this temperature. Then, the reaction mixture was poured into water. After extraction with CH_2Cl_2 ,

the organic extracts were washed with brine, dried over Na₂SO₄. Evaporation of solvents and purification of the residue by column chromatography on silica gel (Et₂O/Hexane = 1/50 as eluent) afforded **8** as a colorless viscous oil (64% yield): [α]_D²⁶ -26.5° (*c* 0.58, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.33 (2H, s, Ar-H), 7.72 (2H, s, Ar-H), 7.48 (2H, dd, *J* = 1.2, 8.4 Hz, Ar-H), 7.32 (2H, d, *J* = 8.4 Hz, Ar-H), 1.86-2.05 (8H, m, CH₂CF₂), 1.22-1.38 (4H, m, SiCH₂), 1.01-1.05 (4H, m, SiCH₂), 0.66 (6H, s, SiCH₃), 0.64 (6H, s, SiCH₃), 0.43 (6H, s, SiCH₃), 0.41 (6H, s, SiCH₃) ppm; IR (neat) 2961, 1427, 1244, 1205, 1146, 1114, 899, 860 cm⁻¹. HRMS (ESI) Calcd for C₇₀H₄₈O₆F₇₄NaSi₄S₂: 2589.0680 ([M + Na]⁺). Found: 2589.0691 ([M + Na]⁺).

(*R*)-4,4',6,6'-Tetra[(1H,1H,2H,2H-heptafluorodecyl)(dimethyl)silyl]-2,2'-

bis(methoxycarbonyl)-1,1'-binaphthyl (9). A mixture of **8** (0.25 mmol), Pd(OAc)₂ (0.12 mmol), DPPP (0.12mmol), ⁱPr₂NEt (2.0 mmol) in DMSO/MeOH (*v/v* = 1/1) (30 ml) was transferred into an autoclave. The autoclave was pressurized to 15 atm with a CO gas and the mixture was heated to 100 °C, and stirred for 120 h with the pressure keeping about 15 atm. After cooling of the autoclave to room temperature, the reaction mixture was poured into water and extracted with CH₂Cl₂. The organic extracts were washed with brine, and dried over Na₂SO₄. Evaporation of solvents and purification of the residue by column chromatography on silica gel (Et₂O/Hexane = 1/10 as eluent) afforded **9** as a colorless viscous oil (80% yield): [α]_D²⁸ -0.1° (*c* 0.36, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.35 (2H, s, Ar-H), 8.28 (2H, s, Ar-H), 7.32 (2H, d, *J* = 8.8 Hz, Ar-H), 7.07 (2H, d, *J* = 8.8 Hz, Ar-H), 3.49 (6H, s, COOCH₃), 1.92–2.10 (8H, m, CH₂CF₂), 1.29-1.34 (4H, m, SiCH₂), 0.98-1.03 (4H, m, SiCH₂), 0.64 (12H, s, SiCH₃), 0.37 (12H, s, SiCH₃) ppm; IR (neat) 2957, 2909, 1732, 1439, 1238, 1205, 1148, 1114, 899, 839 cm⁻¹. HRMS (ESI) Calcd for C₇₂H₅₅O₄F₆₈Si₄: 2387.2086 ([M + H]⁺). Found: 2387.2086 ([M + H]⁺).

(*R*)-4,4',6,6'-Tetra[(1H,1H,2H,2H-heptafluorodecyl)(dimethyl)silyl]-2,2'-

bis(hydroxymethyl)-1,1'-binaphthyl (10). To a solution of **9** (0.20 mmol) in THF (10 ml) was added LiAlH₄ (0.60 mmol) at 0 °C under argon atmosphere and the reaction mixture was stirred for 2 h at room temperature. The mixture was quenched by 1 *N*-HCl at 0 °C, and evaporated for the removal of THF. After extraction with CH₂Cl₂, the organic extracts were washed with brine and dried over Na₂SO₄. Evaporation of solvents and purification of the residue by column chromatography on silica gel (Et₂O/Hexane = 1/3 as eluent) afforded **10** as a colorless viscous oil (95% yield): [α]_D²⁹ −6.3° (*c* 0.75, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.27 (2H, s, Ar-H), 7.89 (2H, s, Ar-H), 7.33 (2H, dd, *J* = 0.8, 8.4 Hz, Ar-H), 7.07 (2H, d, *J* = 8.4 Hz, Ar-H), 4.44 (2H, d, *J* = 11.6 Hz, ArCH₂), 4.14 (2H, d, *J* = 11.6 Hz, ArCH₂), 3.08 (2H, s, OH), 1.94–2.17 (8H, m, CH₂CF₂), 1.26–1.34 (4H, m, SiCH₂), 1.00–1.04 (4H, m, SiCH₂), 0.62 (6H, s, SiCH₃), 0.61 (6H, s, SiCH₃), 0.37 (12H, s, SiCH₃) ppm; IR (neat) 3269, 2957, 1240, 1205, 1151, 897, 839, 814, 704 cm^{−1}. HRMS (ESI) Calcd for C₇₀H₅₄O₂F₆₈NaSi₄: 2353.2007 ([*M* + Na]⁺). Found: 2353.2020 ([*M* + Na]⁺).

(*R*)-4,4',6,6'-Tetra[(1H,1H,2H,2H-heptafluorodecyl)(dimethyl)silyl]-2,2'-

bis(bromomethyl)-1,1'-binaphthyl (11). To a solution of **10** (0.15 mmol) in THF (10 ml) were added PPh₃ (0.90 mmol) and CBr₄ (0.90 mmol) at 0 °C under argon atmosphere and the mixture was stirred for 3 h at room temperature. Then, the mixture was poured into water. After extraction with CH₂Cl₂, the organic extracts were washed with brine and dried over Na₂SO₄. Evaporation of solvents and purification of the residue by column chromatography on silica gel (Et₂O/Hexane = 1/50 as eluent) afforded **11** as a colorless viscous oil (95% yield): [α]_D²⁸ +24.8° (*c* 0.66, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.25 (2H, s, Ar-H), 7.89 (2H, s, Ar-H), 7.35 (2H, d, *J* = 8.4 Hz, Ar-H), 7.09 (2H, d, *J* = 8.4 Hz, Ar-H), 4.23 (4H, s, ArCH₂), 1.96–2.17 (8H, m, CH₂CF₂), 1.25–1.34 (4H, m, SiCH₂), 1.00–1.04 (4H, m, SiCH₂), 0.65 (6H, s, SiCH₃), 0.64 (6H, s, SiCH₃), 0.38 (12H, s, SiCH₃) ppm; IR (neat) 2959, 1242,

1205, 1148, 1134, 899, 839, 706 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{70}\text{H}_{52}\text{F}_{68}\text{NaSi}_4\text{Br}_2$: 2477.0319 ($[\text{M} + \text{Na}]^+$). Found: 2477.0302 ($[\text{M} + \text{Na}]^+$).

(*R,R*)-Fluorous Chiral Phase-Transfer Catalyst (1). A mixture of **11** (0.10 mmol) and 28% aqueous NH_3 (0.50 ml) in CH_3CN (5.0 ml) was heated under reflux for 12 h. Evaporation of solvents and purification of the residue by column chromatography on silica gel ($\text{CH}_2\text{Cl}_2/\text{MeOH} = 20/1$ as eluent) afforded **1** as a white viscous solid (90% yield): $[\alpha]_D^{26} +56.1^\circ$ (c 0.51, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.41 (4H, s, Ar-H), 8.06 (4H, s, Ar-H), 7.40 (4H, d, $J = 8.4$ Hz, Ar-H), 7.25 (4H, d, $J = 8.4$ Hz, Ar-H), 4.61 (4H, d, $J = 13.6$ Hz, ArCH_2), 4.26 (4H, d, $J = 13.6$ Hz, ArCH_2), 1.98-2.20 (16H, m, CH_2CF_2), 1.40-1.44 (8H, m, SiCH_2), 1.03-1.07 (8H, m, SiCH_2), 0.84 (12H, s, SiCH_3), 0.79 (12H, s, SiCH_3), 0.43 (12H, s, SiCH_3), 0.41 (12H, s, SiCH_3); IR (KBr) 2959, 1240, 1205, 1150, 1113, 899, 839, 820, 706 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{140}\text{H}_{104}\text{NF}_{136}\text{Si}_8$: 4606.4146 (M^+). Found: 4606.4138 (M^+).

General Procedure for Catalytic Enantioselective Alkylation of *tert*-Butyl Glycinate Benzophenone Schiff Base (2) under Phase Transfer Conditions (Benzylation). Benzyl bromide (0.36 mmol) was added at 0 °C under an argon atmosphere to a mixture of **2** (0.30 mmol) and catalyst **1** (0.0090 mmol) in toluene (3.0 mL). Then, 50% aqueous KOH (1.0 mL) was added dropwise and the resulting mixture was stirred vigorously for 96 h. The mixture was diluted with water (3.0 mL) and toluene (3.0 mL), and then catalyst **1** was extracted by adding FC-72 (3.0 mL $\times$ 3). After evaporation of fluorous solvent, the catalyst **1** was recovered almost quantitatively (>95%) and then used for the next cycle without further purification. The crude product **3** ($\text{R} = \text{CH}_2\text{Ph}$) was extracted from the remaining toluene/water mixture with Et_2O . The organic extracts were washed with brine and dried over Na_2SO_4 . Evaporation of solvents and purification of the residual oil by column chromatography on silica gel ($\text{Et}_2\text{O}/\text{Hexane} = 1/10$ as eluent) gave the benzylation product **3** ($\text{R} = \text{CH}_2\text{Ph}$) (94.8 mg, 0.246 mmol, 82% yield) as a colorless oil. The enantiomeric excess was determined to be 90% ee by chiral HPLC

analysis (DAICEL CHIRALCEL OD, hexane:isopropanol = 100:1, flow rate = 0.5 mL/min, retention time; 14.8 min (*R*) and 28.2 min (*S*)). The absolute configuration was determined by comparison of the HPLC retention time with the authentic sample independently synthesized by the reported procedure³: ¹H NMR (400 MHz, CDCl₃) δ 7.56-7.58 (2H, m, Ar-H), 7.26-7.38 (6H, m, Ar-H), 7.13-7.21 (3H, m, Ar-H), 7.04-7.06 (2H, m, Ar-H), 6.60 (2H, br d, *J* = 6.0 Hz, Ar-H), 4.10 (1H, dd, *J* = 4.4, 9.6 Hz, CHC=O), 3.23 (1H, dd, *J* = 4.4, 13.6 Hz, PhCH₂), 3.15 (1H, dd, *J* = 9.6, 13.6 Hz, PhCH₂), 1.44 (9H, s, C(CH₃)₃) ppm; IR (neat) 2978, 1732, 1624, 1576, 1495, 1447, 1367, 1286, 1150, 1082, 1030, 849, 756, 696 cm⁻¹.

***tert*-Butyl (*S*)-*N*-(Diphenylmethylene)-4-methylphenylalaninate {3 [R = CH₂-(4-CH₃-Ph)]}**³: ¹H NMR (400 MHz, CDCl₃) δ 7.56-7.58 (2H, m, Ar-H), 7.26-7.38 (6H, m, Ar-H), 6.98 (2H, d, *J* = 8.4 Hz, Ar-H), 6.93 (2H, d, *J* = 8.4 Hz, Ar-H), 6.63 (2H, br d, *J* = 6.0 Hz, Ar-H), 4.08 (1H, dd, *J* = 4.4, 9.2 Hz, CHC=O), 3.19 (1H, dd, *J* = 4.4, 13.6 Hz, ArCH₂), 3.10 (1H, dd, *J* = 9.2, 13.6 Hz, ArCH₂), 2.28 (3H, s, CH₃), 1.44 (9H, s, C(CH₃)₃) ppm; IR (neat) 2978, 2928, 1732, 1624, 1516, 1447, 1367, 1286, 1151, 910, 845, 779, 696 cm⁻¹.

***tert*-Butyl (*S*)-*N*-(Diphenylmethylene)-4-fluorophenylalaninate {3 [R = CH₂-(4-F-Ph)]}**³: ¹H NMR (400 MHz, CDCl₃) δ 7.56-7.58 (2H, m, Ar-H), 7.28-7.39 (6H, m, Ar-H), 6.99-7.03 (2H, m, Ar-H), 6.85-6.89 (2H, m, Ar-H), 6.67 (2H, br d, *J* = 7.2 Hz, Ar-H), 4.08 (1H, dd, *J* = 4.8, 8.8 Hz, CHC=O), 3.19 (1H, dd, *J* = 4.8, 13.6 Hz, ArCH₂), 3.12 (1H, dd, *J* = 8.8, 13.6 Hz, ArCH₂), 1.44 (9H, s, C(CH₃)₃) ppm; IR (KBr) 2978, 2928, 1728, 1626, 1508, 1447, 1369, 1285, 1221, 1148, 841, 781, 698 cm⁻¹.

***tert*-Butyl (*S*)-2-[(Diphenylmethylene)amino]pent-4-ynoate [3 (R = CH₂-C≡CH)]**³: ¹H NMR (400 MHz, CDCl₃) δ 7.64-7.67 (2H, m, Ar-H), 7.30-7.46 (6H, m, Ar-H), 7.25-7.28 (2H, m, Ar-

H), 4.18 (1H, dd, $J = 5.4, 7.8$ Hz, $\text{CHC}=\text{O}$), 2.79 (2H, m, $\text{CH}_2\text{C}\equiv\text{C}$), 1.95 (1H, t, $J = 2.4$ Hz, $\text{C}\equiv\text{CH}$), 1.45 (9H, s, $(\text{C}(\text{CH}_3)_3)$ ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 171.1, 169.3, 139.5, 136.1, 130.2, 128.8, 128.5, 128.2, 128.1, 127.8, 81.5, 81.2, 70.0, 64.8, 28.1, 23.4 ppm; IR (neat) 3296, 2978, 1732, 1624, 1578, 1447, 1369, 1286, 1153, 845, 781, 696, 638 cm^{-1} .

Catalytic Enantioselective Alkylation of *tert*-Butyl Glycinate Benzophenone Schiff Base (2) under Phase Transfer Conditions (Ethylation). Ethyl iodide (3.0 mmol) was added at -20 °C under an argon atmosphere to a mixture of **2** (0.30 mmol) and catalyst **1** (0.0090 mmol) in α,α,α -trifluorotoluene (3.0 mL). Then, $\text{CsOH}\cdot\text{H}_2\text{O}$ (3.0 mmol) was added and the resulting mixture was stirred vigorously for 10 h. Isolation of alkylated product **3** ($\text{R} = \text{CH}_2\text{CH}_3$)³ was performed in a manner similar to that described for benzylation: ^1H NMR (400 MHz, CDCl_3) δ 7.64-7.66 (2H, m, Ar-H), 7.30-7.50 (6H, m, Ar-H), 7.16-7.19 (2H, m, Ar-H), 3.85 (1H, dd, $J = 5.2, 7.6$ Hz, $\text{CHC}=\text{O}$), 1.86-1.95 (2H, m, CH_2CH_3), 1.44 (9H, s, $(\text{C}(\text{CH}_3)_3)$, 0.87 (3H, t, $J = 7.2$ Hz, CH_2CH_3) ppm; IR (neat) 2978, 1734, 1663, 1624, 1447, 1367, 1279, 1153, 696 cm^{-1} .

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