Enantioselective Hydrogenation of Acyclic Aromatic *N*-Aryl Imines Catalyzed by an Iridium Complex of (*S,S*)-1,2-Bis(*tert*-butylmethylphosphino)ethane

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Supporting Information

General. All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or glovebox techniques under prepurified argon. NMR spectra were recorded on a JEOL JNM LA-500 spectrometer (500 MHz for ^1H and 125 MHz for ^{13}C) and LA-400 spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C , and 160 MHz for ^{31}P). Chemical shifts are reported in δ ppm referenced to an internal SiMe_4 standard for ^1H NMR and chloroform-*d* (δ 77.00) for ^{13}C NMR. ^{31}P NMR chemical shifts are externally referenced to 85% H_3PO_4 . High performance liquid chromatography (HPLC) was performed at 254 nm UV detector.

Materials. Anhydrous dichloromethane was distilled from CaH_2 under nitrogen and stored in a glass flask with a Teflon stopcock under nitrogen. Toluene was distilled from sodium benzophenone-ketyl under nitrogen and stored in a glass flask with a Teflon stopcock under nitrogen. $[\text{IrCl}(\text{cod})]_2$ ¹ and $\text{Na}[\text{BARF}]$ ² were prepared according to the reported procedures. All starting materials for the preparation of imines were purchased and used without further purification.

Preparation of $[\text{Ir}((S,S)\text{-}t\text{-Bu-BisP}^*)(\text{cod})][\text{BARF}]$: $\text{Na}[\text{BARF}]$ (268 mg, 0.310 mmol) and excess COD (2.2 mL, 1.94 g, 17.9 mmol) were added to a solution of $[\text{IrCl}(\text{cod})]_2$ (86.8 mg, 0.130 mmol) in dry CH_2Cl_2 (5 mL) under a nitrogen atmosphere. After stirring for 20 min, a solution of freshly prepared (*S,S*)-*t*-Bu-BisP³ (72.6 mg, 0.310 mmol) in CH_2Cl_2 (3 mL) was added to the mixture, and stirring was continued for 20 min. The reaction mixture was washed with degassed H_2O three times and the organic layer was dried over MgSO_4 . The solvent was evaporated, and the residual solid was purified by column chromatography on alumina gel with CH_2Cl_2 under a nitrogen atmosphere to afford the desired complex (187 mg, 52% yield) as a brown powder. ^1H NMR (CDCl_3) δ 1.13 (d, J = 14.6 Hz, 18H), 1.35 (d, J = 8.0 Hz, 6H), 1.44-1.55 (m, 2H), 1.63-1.82 (m, 4H), 1.94-2.01 (m, 2H), 2.09-2.20 (m, 2H), 2.39-2.45 (m, 2H), 4.83 (br s, 1H), 5.18 (br s, 1H), 7.55 (s, 4H), 7.73 (s, 8H); ^{31}P NMR (CDCl_3) δ 50.7; HRMS (FAB) calcd for $\text{C}_{20}\text{H}_{40}\text{P}_2\text{Ir} [\text{M}^+]$ 535.2235, found 535.2233.

General Procedure for the Preparation of Imines

Imines were prepared by modification of a known method⁴ and their characterization of data were identical to those published in the literatures. A representative procedure is described for the preparation of *N*-(1-phenylethylidene)aniline. To a solution of acetophenone (6.00 mL, 52.7 mmol) and aniline (5.50 mL, 60.4 mmol) in dry toluene (25 mL) was added 4 Å molecular sieves (25 g) that had been activated in a microwave oven. After being heated to reflux overnight, the reaction mixture was filtered through Celite. The Celite was washed with toluene. Evaporation of the solvent *in vacuo* and distillation of the residue afforded *N*-(1-phenylethylidene)aniline (7.64 g, 74%) as a pale yellow solid. Spectral data were in accordance with

those previously reported.⁴ ¹H NMR (CDCl₃) δ 2.19 (s, 3H), 6.78 (d, *J* = 7.3 Hz, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.40-7.44 (m, 3H), 7.95 (dd, *J* = 7.7, 2.2 Hz, 2H).

***N*-(1-(4-Methoxyphenyl)ethylidene)aniline:** Prepared according to the general procedure. Yield: 67%; pale yellow solid. Spectral data were in accordance with those previously reported.⁵ ¹H NMR (CDCl₃) δ 2.16 (s, 3H), 3.80 (s, 3H), 6.75-6.78 (s, 2H), 6.90-6.95 (m, 2H), 7.04 (tt, *J* = 6.5, 1.2 Hz, 1H), 7.31 (dd, *J* = 8.2, 7.5 Hz, 2H), 7.90-7.96 (m, 2H).

***N*-(1-(4-Fluorophenyl)ethylidene)aniline:** Prepared according to the general procedure. Yield: 47%; pale yellow solid. Spectral data were in accordance with those previously reported.⁵ ¹H NMR (CDCl₃) δ 2.22 (s, 3H), 6.77-6.80 (m, 2H), 7.07-7.15 (m, 3H), 7.33-7.38 (m, 2H), 7.96-8.00 (m, 2H).

***N*-(1-Phenylethylidene)-4-methoxyaniline:** Prepared according to the general procedure. Yield: 49%; pale yellow solid. Spectral data were in accordance with those previously reported.⁶ ¹H NMR (CDCl₃) δ 2.25 (s, 3H), 3.81 (s, 3H), 6.76 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 7.41-7.48 (m, 3H), 7.93-7.98 (m, 2H).

***N*-(1-Phenylethylidene)-4-fluoroaniline:** Prepared according to the general procedure. Yield: 74%; pale yellow solid. Mp 86-87 °C; IR (KBr) 1630 (C=N), 1495, 1205, 770, 695; ¹H NMR (CDCl₃) δ 2.22 (s, 3H), 6.73-6.76 (m, 2H), 7.02-7.06 (m, 2H), 7.41-7.47 (m, 3H), 7.94-7.97 (m, 2H); ¹³C NMR (CDCl₃) δ 17.29, 115.58 (d, *J* = 22 Hz), 120.68 (d, *J* = 8.2 Hz), 127.11, 128.35, 130.54, 139.31, 147.60 (d, *J* = 2.4 Hz), 159.30 (d, *J* = 241 Hz), 166.25; MS (FAB) 214 ([M⁺+H] 100%), 213 ([M⁺] 89%), 136 ([M⁺-C₆H₅] 22%); HRMS (FAB) calcd for C₁₄H₁₂FN [M⁺] 213.0954, found 213.0942.

***N*-(1-Phenylethylidene)-4-chloroaniline:** Prepared according to the general procedure. Yield: 47%; pale yellow solid. Mp 73-74 °C; IR (KBr) 1635 (C=N), 1480, 1285, 1210, 1090, 845; ¹H NMR (CDCl₃) δ 2.22 (s, 3H), 6.71-6.75 (m, 2H), 7.32-7.41 (m, 2H), 7.42-7.49 (m, 3H), 7.94-7.98 (m, 2H); ¹³C NMR (CDCl₃) δ 17.39, 120.76, 127.13, 128.38, 128.45, 128.99, 130.66, 139.09, 150.10, 166.21; MS (FAB) 230 ([M⁺+H] 100%), 229 ([M⁺] 83%), 152 ([M⁺-C₆H₅] 19%); HRMS (FAB) calcd for C₁₄H₁₂ClN [M⁺] 229.0658, found 229.0663.

***N*-(1-Phenylethylidene)-(4-(trifluoromethyl)phenyl)aniline:** Prepared by a known method.⁸ Yield: 67%; pale yellow solid. Mp 80-81 °C; IR (KBr) 1630 (C=N), 1450, 1340, 1100, 1070, 860, 765, 695; ¹H NMR (CDCl₃) δ 2.22 (s, 3H), 6.86 (d,

$J = 8.3$ Hz, 2H), 7.45-7.48 (m, 3H), 7.59 (d, $J = 8.2$ Hz, 2H), 7.96-7.98 (m, 2H); ^{13}C NMR (CDCl_3) δ 17.53, 119.38, 125.29 (q, $J = 32.0$ Hz), 125.32 (q, $J = 271$ Hz), 126.24 (q, $J = 4.1$ Hz), 127.23, 128.44, 130.88, 138.81, 154.83, 166.15; MS (FAB) 332 ($[\text{M}^+ + \text{H}]$ 100%), 331 ($[\text{M}^+]$ 82%), 254 ($[\text{M}^+ - \text{C}_6\text{H}_5]$ 30%); MS (FAB) HRMS (FAB) calcd for $\text{C}_{15}\text{H}_{12}\text{F}_3\text{N}$ [M^+] 263.0922, found 263.0912.

***N*-(1-Phenylethylidene)-(3,5-bistrifluoromethyl)aniline:** Prepared by a known method.⁸ Yield: 45%; pale yellow oil. IR (neat) 1640 (C=N), 1445, 1380, 1280, 1175, 1125, 990, 885, 845, 765, 680; ^1H NMR (CDCl_3) δ 2.27 (s, 3H), 7.25 (d, $J = 8.0$ Hz, 2H), 7.45-7.54 (m, 3H), 7.60 (s, 1H), 7.97-8.00 (m, 2H); ^{13}C NMR (CDCl_3) δ 17.68, 116.78 (sept, $J = 4.1$ Hz), 119.68 (q, $J = 3.3$ Hz), 123.30 (q, $J = 270$ Hz), 127.32, 128.54, 131.31, 132.37 (q, $J = 34$ Hz), 138.30, 152.86; HRMS (FAB) calcd for $\text{C}_{16}\text{H}_{11}\text{F}_6\text{N}$ [M^+] 331.0796, found 331.0771.

***N*-(1-(4-Methoxyphenyl)ethylidene)-4-methoxyaniline:** Prepared according to the general procedure. Yield: 32%; pale yellow solid. Spectral data were in accordance with those previously reported.⁷ ^1H NMR (CDCl_3) δ 2.22 (s, 3H), 3.82 (s, 3H), 3.87 (s, 3H), 6.73 (d, $J = 8.7$ Hz, 2H), 6.90 (d, $J = 8.7$ Hz, 2H), 6.95 (d, $J = 9.2$ Hz, 2H), 7.93 (d, $J = 8.9$ Hz, 2H).

Asymmetric Hydrogenation

A Typical Procedure for Ir-Catalyzed Asymmetric Hydrogenation of Imines:

In a glove box $[\text{Ir}((S,S)\text{-}t\text{-Bu-BisP}^*)(\text{cod})][\text{BARF}]$ (3.5 mg, 2.5 μmol) and *N*-(1-phenylethylidene)aniline (98.0 mg, 0.500 mmol) were placed in a 20 mL Schlenk flask. Freshly distilled dichloromethane (6 mL) was added and the resulting solution was placed under partial vacuum. Subsequently, hydrogen gas was introduced to the vessel. After stirring for 1.5 h, the solvent was removed on a rotary evaporator and the residue was purified by column chromatography on silica gel using AcOEt/hexane (1:4) as the eluent. The enantiomeric excess of the product was determined by HPLC analysis using a chiral column (Chiralcel OD-H).

(*R*)-*N*-(1-Phenylethyl)aniline⁴: 86% ee, $[\alpha]_D^{20} = -4.3$ ($c = 1.00$ in CHCl_3). Enantiomeric excess was determined by HPLC analysis (Chiralcel OD-H, 0.5 mL/min, *n*-hexane/2-propanol (98:2)). $t_R = 17.9$ min (*S*) minor, 21.6 min (*R*) major. ^1H NMR (CDCl_3) δ 1.50 (d, $J = 7.1$ Hz, 3H), 3.97 (br s, 1H), 4.47 (q, $J = 6.7$ Hz, 1H), 6.50 (d, $J = 7.9$ Hz, 2H), 6.63 (t, $J = 7.4$ Hz, 1H), 7.08 (dd, $J = 8.6, 7.3$ Hz, 2H), 7.21 (t, $J = 7.4$ Hz, 1H), 7.31 (t, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 7.3$ Hz, 2H). The

absolute configuration was determined by comparison with the reported analytical date.⁴

(+)-*N*-(1-(4-Methoxyphenyl)ethyl)aniline⁵: 69% ee, $[\alpha]_D^{20} = +7.1$ ($c = 0.98$ in CHCl_3). Enantiomeric excess was determined by HPLC analysis (Chiralcel OD-H, 1.0 mL/min, *n*-hexane/2-propanol (199:1)). $t_R = 25.5$ min (–) minor, 27.9 min (+) major. ^1H NMR (CDCl_3) δ 1.49 (d, $J = 6.7$ Hz, 3H), 3.78 (s, 3H), 3.99 (br s, 1H), 4.44 (q, $J = 6.8$ Hz, 1H), 6.51 (d, $J = 7.7$ Hz, 2H), 6.64 (t, $J = 7.5$ Hz,

1H), 6.85 (d, $J = 8.7$ Hz, 2H), 7.09 (t, $J = 7.5$ Hz, 2H), 7.28 (d, $J = 8.4$ Hz, 2H).

(-)-*N*-(1-(4-Fluorophenyl)ethyl)aniline⁵: 84% ee, $[\alpha]_D^{20} = -20.3$ ($c = 1.00$ in CHCl_3). Enantiomeric excess was determined by HPLC analysis (Chiralcel OD-H, 0.5 mL/min, *n*-hexane/2-propanol (98:2)). $t_R = 22.9$ min (+) minor, 27.5 min (–) major. ^1H NMR (CDCl_3) δ 1.47 (d, $J = 6.8$ Hz, 3H), 3.78 (br s, 1H), 4.44 (q, $J = 6.8$ Hz, 1H), 6.47 (d, $J = 7.5$ Hz, 2H), 6.65 (t, $J = 7.2$ Hz, 1H), 6.98 (t, $J = 8.7$ Hz, 2H), 7.08 (dd, $J = 7.5, 1.9$ Hz, 2H), 7.30 (dd, $J = 8.5, 5.6$ Hz, 2H).

(*R*)-*N*-(1-Phenylethyl)-4-methoxyaniline⁹: 86% ee, $[\alpha]_D^{20} = +1.1$ ($c = 1.00$ in CHCl_3). Enantiomeric excess was determined by HPLC analysis (Chiralcel OD-H, 0.5 mL/min, *n*-hexane/2-propanol (98:2)). $t_R = 22.0$ min (*R*) major, 25.2 min (*S*) minor. ^1H NMR (CDCl_3) δ 1.49 (d, $J = 6.8$ Hz, 3H), 3.46 (br s, 1H), 3.68 (s, 3H), 4.40 (q, $J = 6.5$ Hz, 1H), 6.46 (d, $J = 9.2$ Hz, 2H), 6.68 (d, $J = 8.9$ Hz, 2H), 7.21 (t, $J = 7.2$ Hz, 1H), 7.31 (t, $J = 7.7$ Hz, 2H), 7.35 (d, $J = 7.2$ Hz,

2H). The absolute configuration was determined by comparison with the reported analytical data.⁹

(-)-*N*-(1-Phenylethyl)-4-fluoroaniline¹⁰: 84% ee, $[\alpha]_D^{20} = -16.8$ ($c = 1.00$ in CHCl_3). Enantiomeric excess was determined by HPLC analysis (Chiralcel OD-H, 0.5 mL/min, *n*-hexane/2-propanol (98:2)). $t_R = 16.5$ min (–) major, 19.5 min (+) minor. ^1H NMR (CDCl_3) δ 1.49 (d, $J = 6.8$ Hz, 3H), 3.92 (br s, 1H), 4.40 (q, $J = 6.5$ Hz, 1H), 6.40–6.43 (m, 2H), 6.75–6.80 (m, 2H), 7.20–7.23 (m, 1H), 7.24–7.35 (m, 4H).

(+)-*N*-(1-Phenylethyl)-4-chloroaniline¹⁰: 83% ee, $[\alpha]_D^{20} = +6.6$ ($c = 1.00$ in CHCl_3). Enantiomeric excess was determined by HPLC analysis (Chiralcel OD-H, 0.5 mL/min, *n*-hexane/2-propanol (98:2)). $t_R = 20.5$ min (+) major, 27.7 min (–) minor. ^1H NMR (CDCl_3) δ 1.48 (d, $J = 6.8$ Hz, 3H), 3.87 (br s, 1H), 4.41 (q, $J = 6.8$ Hz, 1H), 6.40 (d, $J = 8.9$ Hz, 2H), 7.00 (d, $J = 8.9$ Hz, 2H), 7.18–7.26 (m, 1H), 7.28–7.53 (m, 4H).

(-)-*N*-(1-Phenylethyl)-(4-trifluoromethyl)aniline¹¹: 99% ee, $[\alpha]_D^{20} = -0.76$ ($c = 0.99$ in CHCl_3). Enantiomeric excess was determined by HPLC analysis (Chiralcel OD-H, 0.5 mL/min, *n*-hexane/2-propanol (98:2)). $t_R = 17.9$ min (+) minor, 21.4 min (–) major. ^1H NMR (CDCl_3) δ 1.53 (d, $J = 6.8$ Hz, 3H), 4.36 (br s, 1H), 4.49–4.54 (m, 1H), 6.44–6.51 (m, 2H), 7.12–7.40 (m, 7H).

(-)-*N*-(1-Phenylethyl)-(3,5-bis(trifluoromethyl)phenyl)aniline¹⁰: 90% ee, $[\alpha]_D^{20} = -2.2$ ($c = 0.99$ in CHCl_3). Enantiomeric excess was determined by HPLC analysis (Chiralcel OD-H, 0.5 mL/min, *n*-hexane/2-propanol (98:2)). $t_R = 16.6$ min (+) minor, 23.7 min (–) major. ^1H NMR (CDCl_3) δ 1.57 (d, $J = 6.5$ Hz, 3H),

4.49 (br s, 1H), 4.52 (q, $J = 6.5$ Hz, 1H), 6.85 (s, 2H), 7.09 (s, 1H), 7.25-7.29 (m, 1H), 7.33-7.36 (m, 4H).

(+)-*N*-(1-(4-Methoxyphenyl)ethyl)-4-methoxyaniline⁹: 83% ee, $[\alpha]_D^{20} = +12.9$ ($c = 1.00$ in CHCl_3). Enantiomeric excess was determined by HPLC analysis (Chiralcel OD-H, 0.5 mL/min, *n*-hexane/2-propanol (98:2)). $t_R = 29.1$ min (+) major, 33.9 min (–) minor. ^1H NMR (CDCl_3) δ 1.46 (d, $J = 6.7$ Hz, 3H), 3.50 (br s, 1H), 3.67 (s, 3H), 3.77 (s, 3H), 4.36 (q, $J = 6.7$ Hz, 1H), 6.47 (d, $J = 8.9$ Hz, 2H), 6.69 (d, $J = 8.9$ Hz, 2H), 6.85 (d, $J = 8.7$ Hz, 2H), 7.27 (d, $J = 8.7$ Hz, 2H).

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