Supporting Information

Rhodium-Catalyzed Asymmetric Phenylation of *N*-Phosphinoylarylimines with Triphenylborane.

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Experimental Section

General

All melting points are uncorrected. ^{1}H (500 MHz), ^{13}C (125 MHz), and ^{31}P NMR (202 MHz) were measured in $CDCl_3$ unless otherwise mentioned. Chemical shifts values were expressed in ppm relative to an internal reference of tetramethylsilane (0 ppm) for ^{1}H, $CDCl_3$ (77.0 ppm) for ^{13}C, and external 85% H_3PO_4 (0 ppm) for ^{31}P NMR. ^{13}C peak multiplicity assignments were made based on DEPT data. *J* values are presented in Hz. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; m, multiplet. IR spectroscopy of oil and solid samples were measured as neat liquid films and KBr pellets, respectively. The wave-numbers of maximum absorption peaks of IR spectroscopy were presented in cm^{-1}. *N*-(Diphenylphosphinoyl)imines **2a**, **2d**, **2f**, and **2h**;[1] **2b** and **2e**;[2] **2c**;[3] and **2g**[4] were prepared according to the reported procedures.[5]

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General Procedure for Catalytic Asymmetric Phenylation: Under argon atmosphere, a round-bottom flask was charged with Rh(acac)(C_2H_4)$_2$ (3.1 mg, 0.012 mmol), ligand **1** (6.5 mg, 0.013 mmol), imine **2** (0.20 mmol), triphenylborane (81 mg, 0.33 mmol), and 50% KF on celite (40 mg). To the flask were added *t*-BuOH (0.5 mL). The mixture was stirred and heated in a preheated oil bath at 100 °C. After the indicated period, the mixture was diluted with AcOEt, washed with brine, dried over Na_2SO_4, and then concentrated. The resulting residue was purified through silica gel column chromatography.

Specific rotation values and ^{1}H, ^{13}C, and ^{31}P NMR; IR; and MS spectra of the products **4b**, **4c**, **4e**, and **4f** were in agreement with those in our previous report.[6] The absolute configuration of the above products was determined on the basis of the specific rotation and that of the others was tentatively assigned by analogy.

Table 2, entry 2; (+)-*N*-[(3-methylphenyl)(phenyl)methyl]-*P*,*P*-diphenylphosphinamide (4d): Purification by column chromatography (hexane/AcOEt = 1/1) gave the product as a white solid (73 mg, 92%). mp: 149–150 °C. $[\alpha]_D^{25}$ +1.8 (*c* 1.02, $CHCl_3$). 96% ee (HPLC: Daicel Chiralcel OD-H, hexane/*i*-PrOH = 25/1, 1.0 mL/min, 254 nm, major 17.8 min and minor 16.4 min). ^{1}H NMR: 2.29 (3H, s), 3.59 (1H, dd, *J* = 6.7, 10.1), 5.42 (1H, dd, *J* = 10.1, 10.7), 7.01–7.09 (3H, m), 7.17–7.22 (1H, m), 7.23–7.32 (5H, m), 7.34-7.40 (4H, m), 7.41–7.49 (2H, m), 7.80–7.88 (4H, m). ^{13}C NMR: 21.4 (CH_3), 58.5 (CH), 124.6 (CH), 127.1 (CH), 127.6 (CH), 128.0 (CH), 128.4 (d, *J* = 15.4, CH), 128.5 (CH), 131.9 (d, *J* = 2.1, CH), 132.28 (d, *J* = 9.8, CH), 132.36 (d, *J* = 9.8, CH), 132.40 (d, *J* = 128, C), 132.5 (d, *J* = 128, C), 138.1 (C), 143.3 (d, *J* = 5.2, C), 143.5 (d, *J* = 5.2, C). ^{31}P NMR: 22.3. IR: 1188, 694. EIMS *m/z*: 397 (M^+). Anal. Calcd for $C_{26}H_{24}NOP$: C, 78.57; H, 6.09; N, 3.52. Found: C, 78.56; H, 6.13; N, 3.62.

Table 2, entry 5; (–)-*N*-[(2-chlorophenyl)(phenyl)methyl]-*P*,*P*-diphenylphosphinamide (4g): Purification by column chromatography (hexane/acetone = 4/1) gave the product as a pale yellow

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amorphous (70 mg, 84%). $[\alpha]_D^{25}$ –46.1 (*c* 1.01, $CHCl_3$). 93% ee (HPLC: Daicel Chiralcel OD-H, hexane/*i*-PrOH = 10/1, 1.0 mL/min, 254 nm, major 10.2 min and minor 9.4 min). ^{1}H NMR: 3.88 (1H, dd, *J* = 7.9, 9.9), 5.76 (1H, dd, *J* = 9.9, 10.8), 7.20–7.24 (2H, m), 7.25–7.35 (8H, m), 7.41–7.53 (5H, m), 7.74–7.82 (2H, m), 7.87–7.94 (2H, m). ^{13}C NMR: 56.4 (CH), 125.8 (CH), 127.0 (CH), 127.3 (CH), 127.4 (CH), 128.4 (d, *J* = 12.4, CH), 128.5 (d, *J* = 12.4, CH), 129.5 (CH), 130.0 (CH), 131.7 (d, *J* = 130, C), 131.9 (d, *J* = 3.1, CH), 132.0 (d, *J* = 3.1, CH), 132.1 (d, *J* = 10.3, CH), 132.4 (d, *J* = 10.3, CH), 132.8 (d, *J* = 128, C), 133.0 (C), 140.3 (d, *J* = 4.1, C), 142.0 (d, *J* = 4.1, C). ^{31}P NMR: 22.2. IR: 1188, 694. EIMS *m/z*: 417 (M^+). Anal. Calcd for $C_{25}H_{21}ClNOP$: C, 71.86; H, 5.07; N, 3.35. Found: C, 71.98; H, 5.18; N, 3.37.

Table 2, entry 7; (+)-*N*-[(2-naphthyl)(phenyl)methyl]-*P,P*-diphenylphosphinamide (4h): Purification by column chromatography (hexane/acetone = 4/1) gave the product as a pale yellow amorphous (81 mg, 94%). $[\alpha]_D^{25}$ +13.0 (*c* 1.00, $CHCl_3$). 90% ee (HPLC: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 4/1, 1.0 mL/min, 254 nm, major 11.6 min and minor 13.2 min). ^{1}H NMR: 3.69 (1H, dd, *J* = 6.4, 10.3), 5.63 (1H, dd, *J* = 10.3, 11.1), 7.25 (1H, m), 7.30–7.44 (10H, m), 7.45–7.49 (3H, m), 7.64 (1H, m), 7.75–7.88 (7H, m). ^{13}C NMR: 58.4 (CH), 125.9 (CH), 126.0 (CH), 126.19 (CH), 126.22 (CH), 127.3 (CH), 127.6 (CH), 127.7 (CH), 128.1 (CH), 128.43 (d, *J* = 12.4, CH), 128.46 (CH), 128.48 (d, *J* = 12.4, CH), 128.6 (CH), 131.9 (d, *J* = 3.1, CH), 132.0 (d, *J* = 3.1, CH), 132.3 (d, *J* = 130, C), 132.31 (d, *J* = 9.3, CH), 132.35 (d, *J* = 9.3, CH), 132.4 (d, *J* = 129, C), 132.7 (C), 133.2 (C), 140.7 (d, *J* = 5.1, C), 143.2 (d, *J* = 4.1, C). ^{31}P NMR: 22.4. IR: 1196, 694. EIMS *m/z*: 433 (M^+). Anal. Calcd for $C_{29}H_{24}NOP$: C, 80.35; H, 5.58; N, 3.23. Found: C, 80.22; H, 5.58; N, 3.25.

Table 2, entry 8; (+)-*N*-[(2-furyl)(phenyl)methyl]-*P,P*-diphenylphosphinamide (4i): Purification by column chromatography (hexane/acetone = 4/1) gave the product as a white solid (64 mg, 86%). mp: 134–135 °C. $[\alpha]_D^{25}$ +3.3 (*c* 1.02, $CHCl_3$). 91% ee (HPLC: Daicel Chiralpak

6 Hao, X.; Kuriyama, M.; Chen, Q.; Yamamoto, Y.; Yamada, K.; Tomioka, K. *Org. Lett.* **2009**, *11*, 4470–4473.

AD-H x 2, hexane/*i*-PrOH = 4/1, 0.5 mL/min, 254 nm, major 21.6 min and minor 20.3 min). ^{1}H NMR: 3.71 (1H, t, *J* = 8.6), 5.46 (1H, t, *J* = 10.4), 6.12 (1H, d, *J* = 3.1), 6.27 (1H, d, *J* = 3.1), 7.20–7.27 (1H, m), 7.28–7.33 (4H, m), 7.35 (1H, m), 7.36–7.44 (4H, m), 7.45–7.50 (2H, m), 7.81–7.89 (4H, m). ^{13}C NMR: 52.9 (CH), 107.6 (CH), 110.2 (CH), 127.2 (CH), 127.7 (CH), 128.4 (d, *J* = 12.4, CH), 128.5 (d, *J* = 12.4, CH), 128.6 (CH), 131.9 (d, *J* = 3.1, CH), 132.0 (d, *J* = 3.1, CH), 132.16 (d, *J* = 129, C), 132.17 (d, *J* = 10.3, CH), 132.36 (d, *J* = 9.3, CH), 132.40 (d, *J* = 128, C), 141.2 (d, *J* = 5.1, C), 142.3 (CH), 155.0 (d, *J* = 5.2, C). ^{31}P NMR: 22.2. IR: 1188, 732, 694. EIMS *m/z*: 373 (M^{+}). Anal. Calcd for $C_{23}H_{20}NO_2P$: C, 73.98; H, 5.40; N, 3.75. Found: C, 73.70; H, 5.57; N, 3.67.