Selective Synthesis of 5- or 6-Aryl Octahydrocyclopenta[*b*]pyrroles from a Common Precursor Through Control of Competing Pathways in a Pd-Catalyzed Reaction

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Supporting Information

Experimental procedures and characterization data for new compounds in equations 3–4 and Tables 4–5, complete descriptions of stereochemical assignments, and descriptions of optimization studies (21 pages).

General All reactions were carried out under an argon atmosphere in flame-dried glassware. Tris(dibenzylidineacetone)dipalladium(0) and all phosphine ligands except those noted below were purchased from Strem Chemical Co. and used without further purification. All aryl bromides except for 4-bromobenzoic acid *tert*-butyl ester were obtained from commercial sources (Aldrich Chemical Co. or Acros Chemical Co.) and were used as obtained. 4-Bromobenzoic acid *tert*-butyl ester[1], (2-cyclopent-2-enylethyl)-(4-methoxyphenyl)amine (**1a**)[2], 1,2-bis[bis(*p*-trifluoromethylphenyl)phosphino]ethane[3], 1,2-bis(di-*p*-methoxyphenylphosphino)ethane[3], tris(*o*-trifluoromethylphenyl)phosphine[4], tris(*m*-trifluoromethylphenyl)phosphine[4], tris(*p*-trifluoromethylphenyl)phosphine[4], and tri(*p*-methoxyphenyl)phosphine[5] were prepared according to literature procedures. Toluene was purified using a GlassContour solvent purification system.

Yields refer to isolated yields of compounds estimated to be ≥95% pure as determined by ^{1}H NMR and/or combustion analysis. The yields reported in the supporting information describe the result of a single experiment, whereas the yields reported in equations 1 and 2 and Tables 1 and 2 are average yields of two or more experiments. Thus, the yields reported in the supporting information may differ from those shown in equations 1 and 2 and Tables 1 and 2.

Synthesis of *N*-(2-Cyclopent-2-enylethyl)arylamines (1a–e)

***N*-(2-Cyclopent-2-enylethyl)-4-chloroaniline (1b)**. A flame-dried round-bottom flask was charged with 1,1'-carbonyl diimidazole (2.7 g, 16.6 mmol), purged with argon, and then THF (20 mL) and 2-cyclopenten-1-acetic acid (2 mL, 2.09 g, 16.6 mmol) were added via syringe. The mixture was stirred at room temperature for 1.5 h and then 4-chloroaniline (2.1 g, 16.6 mmol) was added via syringe and the resulting mixture was stirred at room temperature for 3.5 h. The reaction mixture was diluted with ethyl acetate (75 mL) and H_2O (50 mL), the layers were separated, and the aqueous layer was extracted with ethyl acetate (2 x 100 mL). The combined organic extracts were washed with aqueous 1 M HCl (50 mL) and then saturated aqueous $NaHCO_3$ (50 mL), dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo* to afford 3.75 g (96 %) of *N*-(4-chlorophenyl)-2-(cyclopent-2-enyl)acetamide as a white solid, m.p. 130–132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.8 Hz, 2 H), 7.28 (d, J = 8.8 Hz, 2 H), 7.13 (s, 1 H), 5.84-5.80 (m, 1 H), 5.75–5.71 (m, 1 H), 3.26–3.16 (m, 1 H), 2.46–2.30 (m, 3 H), 2.24–2.14 (m, 1 H), 1.58–1.48 (m, 2 H).

A flame-dried round-bottom flask was charged with *N*-(4-chlorophenyl)-2-(cyclopent-2-enyl)acetamide, purged with argon, and then THF (16 mL) was added via syringe. The resulting solution was cooled to 0 °C and a solution of $LiAlH_4$ in ether (48 mL, 48 mmol, 1.0 M) was

added dropwise via syringe. The reaction mixture was then warmed to room temperature for 21 h at which time the starting material had been consumed as judged by TLC analysis. The reaction mixture was cooled to 0 °C, diluted with ether (300 mL), and quenched slowly with aqueous 10 M NaOH until all insoluble material had precipitated. The organic supernatant was decanted to a clean Erlenmeyer flask and the precipitate was washed with ether (200 mL). The combined organic extracts were diluted further with hexane (200 mL), dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was then purified by flash chromatography on silica gel to afford 2.83 g (91 %) of the title compound as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, J = 9.0 Hz, 2 H), 6.54 (d, J = 9.0 Hz, 2 H), 5.83–5.80 (m, 1 H), 5.75-5.72 (m, 1 H), 3.64 (s, 1 H), 3.18–3.09 (m, 2 H), 2.84–2.76 (m, 1 H), 2.47–2.31 (m, 2 H), 2.18–2.10 (m, 1 H), 1.79–1.70 (m, 1 H), 1.66–1.58 (m, 1 H), 1.56–1.45 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.9, 134.2, 130.8, 128.9, 121.4, 113.6, 43.2, 42.6, 35.5, 31.9, 29.7; IR (film) 3416, 1601, 1503 cm^{-1}. Anal calcd for $C_{13}H_{16}ClN$: C, 70.42; H, 7.27; N, 6.32. Found: C, 70.58; H, 7.30; N, 6.44.

***N*-(2-Cyclopent-2-enylethyl)amine**. A flame-dried round-bottomed flask was charged with 2-cyclopenten-1-acetic acid (20 mL, 21.0 g, 166 mmol) and thionyl chloride (48 mL, 79 g, 664 mmol) and was stirred at room temperature for 2 h. The excess thionyl chloride was removed by distillation to afford a crude acid chloride product, which was added dropwise via syringe to 28 % aqueous ammonium hydroxide (600 mL) with stirring. The resulting mixture was stirred at room temperature for 48 h then was extracted with ethyl acetate (3 x 250 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo* to afford 14.7 g (71 %) of 2-(cyclopent-2-enyl)acetamide as a tan solid, m.p. 119–122 °C. ^{1}H NMR

(400 MHz, $CDCl_3$) δ 5.81–5.77 (m, 1 H), 5.73–5.68 (m, 1 H), 5.37 (s, 2 H), 3.16–3.07 (m, 1 H), 2.40–2.10 (m, 5 H), 1.53–1.43 (m, 1 H).

A flame-dried round-bottom flask was charged with 2-(cyclopent-2-enyl)acetamide, purged with argon, and then ether (120 mL) was added via syringe. The resulting suspension was cooled to 0 °C and a solution of $LiAlH_4$ in ether (352 mL, 352 mmol, 1.0 M) was added via syringe. The reaction mixture was then warmed to room temperature for 18 h at which time the starting material had been consumed as judged by TLC analysis. The reaction mixture was cooled to 0 °C, diluted with ether (1300 mL), and quenched slowly with aqueous 10 M NaOH until all insoluble material had precipitated. The organic supernatant was decanted to a clean Erlenmeyer flask and the precipitate was washed with ether (200 mL). The combined organic extracts were diluted further with pentane (500 mL), dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was then distilled from calcium hydride to afford 9.24 g (71 %) of the title compound as a colorless liquid, b.p. 120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73–5.69 (m, 1 H), 5.68–5.63 (m, 1 H), 2.75–2.64 (m, 3 H), 2.39–2.20 (m, 2 H), 2.08–1.98 (m, 1 H), 1.61–1.50 (m, 1 H), 1.47–1.35 (m, 2 H), 1.10 (s, br, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.8, 130.4, 43.1, 40.9, 40.2, 31.9, 29.8; IR (film) 3339, 1570, 1488 cm^{-1}.

4-(2-Cyclopent-2-enylethylamino)benzonitrile (1c). A flame-dried Schlenk flask was charged with $Pd_2(dba)_3$ (110 mg, 0.12 mmol, 1 mol %), 2-(di-*tert*-butylphosphino)biphenyl (**10**) (72 mg, 0.24 mmol, 2 mol %), NaO*t*-Bu (2.81 g, 28.8 mmol), and 4-bromobenzonitrile (2.2 g, 12.0 mmol). The flask was purged with argon, and toluene (50 mL) was added followed by *N*-(2-cyclopent-2-enylethyl)amine (2.0 g, 18.0 mmol) via syringe. The resulting mixture was heated to 100 °C with stirring until the starting material had been consumed as judged by GC analysis (1.5 h). The reaction mixture was cooled to room temperature, quenched with saturated aqueous

ammonium chloride (50 mL) and diluted with ethyl acetate (100 mL). The layers were separated and the aqueous layer was extracted with ethyl acetate (2 x 100 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was then purified by flash chromatography on silica gel to afford 1.79 g (72 %) of the title compound as a yellow solid, m.p. 44–45 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.8 Hz, 2 H), 6.53 (d, J = 8.8 Hz, 2 H), 5.76–5.72 (m, 1 H), 5.68–5.64 (m, 1 H), 4.49 (br s, 1 H), 3.22–3.08 (m, 2 H), 2.79–2.70 (m, 1 H), 2.41–2.22 (m, 2 H), 2.13–2.02 (m, 1 H), 1.77–1.67 (m, 1 H), 1.65–1.54 (m, 1 H), 1.48–1.38 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 133.7, 133.3, 130.9, 120.4, 111.8, 97.6, 42.9, 41.5, 34.9, 31.7, 29.5; IR (film) 3370, 2212, 1608, 1526 cm^{-1}. Anal calcd for $C_{14}H_{16}N_2$: C, 79.21; H, 7.60; N, 13.20. Found: C, 79.15; H, 7.60; N, 13.03.

4-(2-Cyclopent-2-enylethylamino)benzoic acid *tert*-butyl ester (1d). A flame-dried Schlenk flask was charged with $Pd_2(dba)_3$ (110 mg, 0.12 mmol, 1 mol %), 2-(di-*tert*-butylphosphino)biphenyl (**10**) (72 mg, 0.24 mmol 2 mol %), and NaO*t*-Bu (2.81 g, 28.8 mmol). The flask was purged with argon, and toluene (50 mL) was added followed by *N*-(2-cyclopent-2-enylethyl)amine (2.0 g, 18.0 mmol) and 4-bromobenzoic acid *tert*-butyl ester (3.1 g, 12.0 mmol) via syringe. The resulting mixture was heated to 100 °C with stirring until the starting material had been consumed as judged by GC analysis (3 h). The reaction mixture was cooled to room temperature, quenched with saturated aqueous ammonium chloride (50 mL) and diluted with ethyl acetate (100 mL). The layers were separated and the aqueous layer was extracted with ethyl acetate (2 x 100 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was then purified by flash chromatography on silica gel to afford 2.5 g (74 %) of the title compound as a pale yellow solid, m.p. 82–86 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 9.0 Hz, 2 H), 6.53 (d, J = 9.0 Hz, 2

H), 5.79–5.75 (m, 1 H), 5.71–5.67 (m, 1 H), 4.06–4.00 (m, 1 H), 3.24–3.16 (m, 2 H), 2.81–2.74 (m, 1 H), 2.42–2.26 (m, 2 H), 2.14–2.06 (m, 1 H), 1.78–1.71 (m, 1 H), 1.66–1.58 (m, 1 H), 1.56 (s, 9 H), 1.50–1.42 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 151.7, 134.1, 131.3, 131.0, 119.9, 111.1, 79.7, 43.1, 41.9, 35.4, 31.9, 29.7, 28.3; IR (film) 3378, 1682, 1605 cm^{-1}. Anal calcd for $C_{18}H_{25}NO_2$: C, 75.22; H, 8.77; N, 4.87. Found: C, 75.09; H, 8.68; N, 4.97.

***N*-(2-Cyclopent-2-enylethyl)aniline (1e)**. A flame-dried round-bottom flask was charged with 1,1'-carbonyl diimidazole (2.7 g, 16.6 mmol), purged with argon, and then THF (20 mL) and 2-cyclopenten-1-acetic acid (2 mL, 2.09 g, 16.6 mmol) were added via syringe. The mixture was stirred at room temperature for 1 h and then aniline (1.5 mL, 1.5 g, 16.6 mmol) was added via syringe and the resulting mixture was stirred at room temperature for 22 h. The reaction mixture was diluted with ethyl acetate (75 mL) and H_2O (50 mL), the layers were separated, and the aqueous layer was extracted with ethyl acetate (2 x 100 mL). The combined organic extracts were washed with aqueous 1 M HCl (50 mL) and then saturated aqueous $NaHCO_3$ (50 mL), dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo* to afford 3.3 g (100 %) of *N*-phenyl-2-(cyclopent-2-enyl)acetamide[6] as a tan solid, m.p. 78–80 °C (lit. 85–86 °C).[6]

A flame-dried round-bottom flask was charged with *N*-phenyl-2-(cyclopent-2-enyl)acetamide, purged with argon, and then THF (15 mL) was added via syringe. The resulting solution was cooled to 0 °C and a solution of $LiAlH_4$ in ether (50 mL, 50 mmol, 1.0 M) was added dropwise via syringe. The reaction mixture was then warmed to room temperature with stirring for 15 h at which time the starting material had been consumed as judged by TLC analysis. The reaction mixture was cooled to 0 °C, diluted with ether (300 mL), and quenched slowly with aqueous 10 M NaOH until all insoluble material had precipitated. The organic supernatant was decanted into a clean Erlenmeyer flask and the precipitate was washed with

ether (200 mL). The combined organic extracts were diluted further with hexane (200 mL), dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was then purified by flash chromatography on silica gel to afford 2.83 g (91 %) of the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.18 (m, 2 H), 6.76–6.71 (m, 1 H), 6.67–6.62 (m, 2 H), 5.83–5.79 (m, 1 H), 5.77–5.73 (m, 1 H), 3.63 (s, br, 1 H), 3.25–3.14 (m, 2 H), 2.88–2.77 (m, 1 H), 2.48–2.29 (m, 2 H), 2.19–2.08 (m, 1 H), 1,83–1.73 (m, 1 H), 1.70–1.60 (m, 1 H), 1.56–1.46 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 134.4, 130.8, 129.2, 117.1, 112.6, 43.3, 42.5, 35.7, 31.9, 29.8; IR (film) 3410, 1603, 1506 cm^{-1}. Anal calcd for $C_{13}H_{17}N$: C, 83.37; H, 9.15; N, 7.48. Found: C, 83.46; H, 9.17; N, 7.58.

Synthesis of 1,6-diaryloctahydrocyclopenta[*b*]pyrroles (3a–g)

General procedure. A flame-dried Schlenk tube was cooled under a stream of argon and charged with $Pd_2(dba)_3$ (1 mol % complex, 2 mol % Pd), 2-(diphenylphosphino)-2'-(N,N-dimethylaminobiphenyl) (**11**) (2 mol %), and NaO*t*-Bu (1.2 equiv). The tube was purged with argon and toluene (4 mL/mmol amine substrate), the amine substrate (1.0 equiv), and the aryl bromide (1.4 equiv) were added via syringe. The mixture was heated to 110 °C with stirring until the starting material had been consumed as judged by GC or ^{1}H NMR analysis. The reaction mixture was cooled to room temperature, quenched with saturated aqueous ammonium chloride (2 mL), and diluted with ethyl acetate (10 mL). The layers were separated and the aqueous layer was extracted with ethyl acetate (2 x 10 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was then purified by flash chromatography on silica gel.

(±)-(3a*R*,6*S*,6a*S*)-1-(4-Methoxyphenyl)-6-*p*-tolyloctahydrocyclopenta[*b*]pyrrole (3a). Reaction of 54 mg (0.25 mmol) of **1a** with 4-bromotoluene (43 μL, 60 mg, 0.35 mmol), and NaO*t*-Bu (29 mg, 0.3 mmol) following the general procedure using dppp as ligand afforded a 25:65:10 mixture of **2**:**3**:**4** as the sole detectable products as judged by ^{1}H NMR analysis. This mixture was separated by flash chromatography on silica gel to afford 35 mg (45 %) of the title compound as a white solid, m.p. 90–92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, J = 8.0 Hz, 2 H), 6.88 (d, J = 8.0 Hz, 2 H), 6.56 (d, J = 9.2 Hz, 2 H), 6.25 (d, J = 9.2 Hz, 2 H), 4.09–4.03 (m, 1 H), 3.66 (s, 3 H), 3.59–3.52 (m, 1 H), 3.14-3.06 (m, 2 H), 2.96–2.86 (m, 1 H), 2.19 (s, 3 H), 2.19–2.09 (m, 1 H), 2.04–1.70 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 143.3, 138.7, 135.0, 129.2, 128.1, 113.9, 113.4, 68.1, 55.8, 51.0, 50.9, 44.0, 33.8, 30.9, 29.9, 20.9; IR (film) 1511 cm^{-1}. Anal calcd for $C_{21}H_{25}NO$: C, 82.04; H, 8.20; N, 4.56. Found: C, 81.97; H, 8.15; N, 4.51.

Use of **11** as ligand for the above transformation afforded a 48:48:2:2 mixture of **2**:**3**:**4**:**5** as judged by ^{1}H NMR analysis of the crude reaction mixture. The desired product was not isolated from this mixture, as superior results were obtained with dppp as ligand (as described above).

(±)-(3a*R*,6*S*,6a*S*)-1-(4-Chlorophenyl)-6-*p*-tolyloctahydrocyclopenta[*b*]pyrrole (3b). Reaction of 55 mg (0.25 mmol) of **1b** with 4-bromotoluene (43 μL, 60 mg, 0.35 mmol), and NaO*t*-Bu (29 mg, 0.3 mmol) following the general procedure using dppp as ligand afforded a 20:70:10 mixture of **2**:**3**:**4** as the sole detectable products as judged by ^{1}H NMR analysis. This mixture was separated by flash chromatography on silica gel to afford 51 mg (65 %) of the title compound as a white solid, m.p. 107–108 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 (d, J = 8.0 Hz, 2 H), 6.88–6.82 (m, 4 H), 6.18 (d, J = 9.0 Hz, 2 H), 4.13–4.08 (m, 1 H), 3.54–3.48 (m, 1 H), 3.17–3.09 (m, 2 H), 2.96–2.88 (m, 1 H), 2.18 (s, 3 H), 2.17–2.12 (m, 1 H), 2.04–1.98 (m, 1 H),

1.96–1.71 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.9, 138.3, 135.3, 129.1, 128.2, 127.8, 120.1, 113.5, 67.6, 50.8, 50.3, 44.0, 33.8, 30.7, 29.9, 20.9; IR (film) 1598, 1497 cm^{-1}. Anal calcd for $C_{20}H_{22}ClN$: C, 77.03; H, 7.11; N, 4.49. Found: C, 77.12; H, 7.08; N, 4.62.

Use of **11** as ligand for the above transformation afforded a 30:65:2:3 mixture of **2**:**3**:**4**:**5** as judged by ^{1}H NMR analysis of the crude reaction mixture. The desired product was not isolated from this mixture, as superior results were obtained with dppp as ligand (as described above).

(±)-(3a*R*,6*S*,6a*S*)-4-(6-*p*-Tolyloctahydrocyclopenta[*b*]pyrrol-1-yl)benzonitrile (3c). Reaction of 53 mg (0.25 mmol) of **1c** with 4-bromotoluene (43 μL, 60 mg, 0.35 mmol), and NaO*t*-Bu (29 mg, 0.3 mmol) following the general procedure afforded a 10:80:10 mixture of **2**:**3**:**4** as the sole detectable products as judged by ^{1}H NMR analysis. This mixture was separated by flash chromatography on silica gel to afford 53 mg (70 %) of the title compound as a white solid, m.p. 158–160 °C. This material contained ca. 7 % of (±)-(3a*R*,6a*S*)-4-(1,2,3,3a,4,6a-hexahydrocyclopenta[*b*]pyrrol-1-yl)benzonitrile (**4c**) as an inseparable impurity; data are for the major product. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, J = 9.0 Hz, 2 H), 6.93 (d, J = 8.0 Hz, 2 H), 6.84 (d, J = 8.0 Hz, 2 H), 6.21 (d, J = 9.0 Hz, 2 H), 4.31–4.26 (m, 1 H), 3.56–3.51 (m, 1 H), 3.33–3.24 (m, 1 H), 3.23–3.17 (m, 1 H), 3.02–2.94 (m, 1 H), 2.25–2.16 (m, 1 H), 2.17 (s, 3 H), 2.08–2.02 (m, 1 H), 1.98–1.81 (m, 3 H), 1.80–1.74 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.1, 137.6, 135.8, 132.4, 129.0, 128.3, 121.0, 112.3, 96.4, 67.0, 50.8, 49.8, 43.7, 33.5, 30.5, 30.1, 20.7; IR (film) 2209, 1604, 1518 cm^{-1}. Anal calcd for $C_{21}H_{22}N_2$: C, 83.40; H, 7.33; N, 9.26. Found: C, 83.19; H, 7.30; N, 9.29.

(±)-(3a*R*,6*S*,6a*S*)-4-(6-Naphthalen-2-yloctahydrocyclopenta[*b*]pyrrol-1-yl)benzonitrile (3d). Reaction of 53 mg (0.25 mmol) of **1c** with 2-bromonaphthalene (72 mg, 0.35 mmol), and NaO*t*-Bu (29 mg, 0.3 mmol) following the general procedure afforded **3d** as the sole detectable

product as judged by ^{1}H NMR analysis. Flash chromatography on silica gel afforded 56 mg (66 %) of the title compound as a tan solid, m.p. 162–165 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68-7.64 (m, 2 H), 7.55 (s, 1 H), 7.51 (d, *J* = 8.5 Hz, 1 H), 7.41-7.35 (m, 2 H), 7.16 (dd, *J* = 2.0, 8.5 Hz, 1 H), 7.01 (d, *J* = 8.5 Hz, 2 H), 6.23 (d, *J* = 8.5 Hz, 2 H), 4.41–4.36 (m, 1 H), 3.60–3.54 (m, 1 H), 3.46–3.39 (m, 1 H), 3.34–3.27 (m, 1 H), 3.07–2.99 (m, 1 H), 2.28–2.20 (m, 1 H), 2.16–2.04 (m, 2 H), 2.01–1.89 (m, 2 H), 1.88–1.82 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.0, 138.4, 133.0, 132.3, 132.0, 127.8, 127.4, 127.2, 127.2, 126.9, 125.6, 125.3, 120.7, 112.2, 96.6, 67.2, 51.1, 49.8, 43.8, 33.4, 30.6, 30.2; IR (film) 2204, 1601, 1516 cm^{-1}. Anal calcd for $C_{24}H_{22}N_2$: C, 85.17; H, 6.55; N, 8.28. Found: C, 84.96; H, 6.41; N, 7.95.

(±)-(3a*R*,6*S*,6a*S*)-4-(6-*p*-Tolyloctahydrocyclopenta[*b*]pyrrol-1-yl)benzoic acid *tert*-butyl ester (3e). Reaction of 72 mg (0.25 mmol) of **1d** with 4-bromotoluene (43 μL, 60 mg, 0.35 mmol), and NaO*t*-Bu (29 mg, 0.3 mmol) following the general procedure afforded **3e** as the sole detectable product as judged by ^{1}H NMR analysis. Flash chromatography on silica gel afforded 70 mg (74 %) of the title compound as a white solid, m.p. 100–105 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.5 Hz, 2 H), 6.97 (d, *J* = 8.0 Hz, 2 H), 6.86 (d, *J* = 7.5 H, 2 H), 6.25 (d, *J* = 9.0 Hz, 2 H), 4.30–4.25 (m, 1 H), 3.56–3.51 (m, 1 H), 3.32–3.19 (m, 2 H), 2.99–2.91 (m, 1 H), 2.22–2.14 (m, 1 H), 2.16 (s, 3 H), 2.09–2.03 (m, 1 H), 2.00–1.92 (m, 1 H), 1.92–1.80 (m, 2 H), 1.80–1.74 (m, 1 H), 1.53 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 150.8, 138.0, 135.4, 130.2, 129.0, 128.3, 118.2, 111.4, 79.4, 67.4, 50.4, 49.9, 43.8, 33.8, 30.5, 29.8, 28.3, 20.9; IR (film) 1697, 1605, 1518 cm^{-1}. Anal calcd for $C_{25}H_{31}NO_2$: C, 79.54; H, 8.28; N, 3.71. Found: C, 79.57; H, 8.33; N, 3.72.

(±)-(3a*R*,6*S*,6a*S*)-4-[6-(4-Methoxyphenyl)octahydrocyclopenta[*b*]pyrrol-1-yl]benzoic acid *tert*-butyl ester (3f). Reaction of 72 mg (0.25 mmol) of **1d** with 4-bromoanisole (44 μL, 65

mg, 0.35 mmol), and NaO*t*-Bu (29 mg, 0.3 mmol) following the general procedure afforded a 90:10 mixture of **3**:**4** as the sole detectable products as judged by ^{1}H NMR analysis. This mixture was separated by flash chromatography on silica gel to afford 59 mg (60 %) of the title compound as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 9.2 Hz, 2 H), 6.99 (d, *J* = 8.4 Hz, 2 H), 6.60 (d, *J* = 8.8 Hz, 2 H), 6.24 (d, *J* = 8.8 Hz, 2 H), 4.29–4.23 (m, 1 H), 3.66 (s, 3 H), 3.56–3.50 (m, 1 H), 3.32–3.18 (m, 2 H), 3.00–2.88 (m, 1 H), 2.22–2.13 (m, 1 H), 2.09–2.01 (m, 1 H), 1.99–1.73 (m, 4 H), 1.54 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 157.8, 150.8, 133.2, 130.2, 129.9, 118.3, 113.1, 111.4, 79.4, 67.3, 55.1, 49.9, 43.7, 33.7, 30.6, 29.8, 28.3 (two aliphatic resonances are incidentally equivalent); IR (film) 1695, 1605, 1514 cm^{-1}. Anal calcd for $C_{25}H_{31}NO_3$: C, 76.30; H, 7.94; N, 3.56. Found: C, 76.40; H, 7.84; N, 3.57.

(±)-(3a*R*,6*S*,6a*S*)-4-[6-(4-Carbo-*tert*-butoxyphenyl)octahydrocyclopenta[*b*]pyrrol-1-yl]benzoic acid *tert*-butyl ester (3g). Reaction of 72 mg (0.25 mmol) of **1d** with 4-bromobenzoic acid *tert*-butyl ester (90 mg, 0.35 mmol), and NaO*t*-Bu (29 mg, 0.3 mmol) following afforded a 30:60:10 mixture of **2**:**3**:**4** as the sole products as judged by ^{1}H NMR analysis. This mixture was separated by flash chromatography on silica gel to afford 62 mg (53 %) of the title compound as a white solid, m.p. 198–200 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.5 Hz, 2 H), 7.58 (d, *J* = 8.5 Hz, 2 H), 7.14 (d, *J* = 8.5 Hz, 2 H), 6.24 (d, *J* = 9.0 Hz, 2 H), 4.31–4.26 (m, 1 H), 3.59–3.54 (m, 1 H), 3.34–3.24 (m, 2 H), 3.01–2.92 (m, 1 H), 2.24–2.16 (m, 1 H), 2.12–2.04 (m, 1 H), 2.00–1.76 (m, 4 H), 1.53 (s, 9 H), 1.52 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 165.8, 150.6, 146.4, 130.3, 129.6, 128.9, 128.7, 118.7, 111.5, 80.6, 79.6, 67.6, 50.7, 50.0, 4.0, 34.1, 30.3, 29.7, 28.3, 28.1; IR (film) 1700, 1605 cm^{-1}. Anal calcd for $C_{29}H_{37}NO_4$: C, 75.13; H, 8.04; N, 3.02. Found: C, 75.09; H, 7.95; N, 3.03.

Synthesis of 1,5-diaryloctahydrocyclopenta[*b*]pyrroles (5a–g)

General procedure. A flame-dried Schlenk tube was cooled under a stream of argon and charged with $Pd_2(dba)_3$ (1 mol % complex, 2 mol % Pd), di-*t*-butylmethylphosphonium tetrafluoroborate (4 mol %), and NaO*t*-Bu (1.2 equiv). The tube was purged with argon and toluene (4 mL/mmol amine substrate), the amine substrate (1.0 equiv), and the aryl bromide (1.4 equiv) were added via syringe. The mixture was heated to 110 °C with stirring until the starting material had been consumed as judged by GC or ^{1}H NMR analysis. The reaction mixture was cooled to room temperature, quenched with saturated aqueous ammonium chloride (2 mL), and diluted with ethyl acetate (10 mL). The layers were separated and the aqueous layer was extracted with ethyl acetate (2 x 10 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was then purified by flash chromatography on silica gel.

(±)-(3a*R*,5*R*,6a*R*)-1-(4-Methoxyphenyl)-5-*p*-tolyloctahydrocyclopenta[*b*]pyrrole (5a). Reaction of 54 mg (0.25 mmol) of **1a** with 4-bromotoluene (43 μL, 60 mg, 0.35 mmol), and NaO*t*-Bu (29 mg, 0.3 mmol) following the general procedure afforded **5a** as the sole detectable product as judged by ^{1}H NMR analysis. Flash chromatography on silica gel afforded 60 mg (78 %) of the title compound as a pale yellow solid, m.p. 87–89 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14–7.07 (m, 4 H), 6.85 (d, J = 9.2 Hz, 2 H), 6.63 (d, J = 9.2 Hz, 2 H), 4.21–4.14 (m, 1 H), 3.77 (s, 3 H), 3.45–3.31 (m, 2 H), 3.17–3.05 (m, 1 H), 2.95–2.85 (m, 1 H), 2.63–2.55 (m, 1 H), 2.31 (s, 3 H), 2.33–2.25 (m, 1 H), 2.18–2.07 (m, 1 H), 1.89–1.81 (m, 1 H), 1.57–1.41 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 142.2, 140.8, 135.5, 128.9, 126.7, 114.8, 113.8, 64.2, 55.9, 47.8, 45.9, 43.4, 40.8, 40.0, 30.5, 20.9; IR (film) 1513 cm^{-1}. Anal calcd for $C_{21}H_{25}NO$: C, 82.04; H, 8.20; N, 4.56. Found: C, 81.88; H, 8.22; N, 4.55.

(±)-(3a*R*,5*R*,6a*R*)-1,5-Bis(4-methoxyphenyl)octahydrocyclopenta[*b*]pyrrole (5b). Reaction of 54 mg (0.25 mmol) of **1a** with 4-bromoanisole (44 μL, 65 mg, 0.35 mmol), and NaO*t*-Bu (29 mg, 0.3 mmol) following the general procedure afforded **5b** as the sole detectable product as judged by ^{1}H NMR analysis. Flash chromatography on silica gel afforded 62 mg (77 %) of the title compound as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, J = 8.4 Hz, 2 H), 6.87–6.80 (m, 4 H), 6.62 (d, J = 8.8 Hz, 2 H), 4.21–4.14 (m, 1 H), 3.78 (s, 3 H), 3.77 (s, 3 H), 3.44–3.31 (m, 2 H), 3.15–3.04 (m, 1 H), 2.94–2.84 (m, 1 H), 2.62–2.54 (m, 1 H), 2.32–2.23 (m, 1 H), 2.17–2.07 (m, 1 H), 1.88–1.80 (m, 1 H), 1.54–1.39 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 150.9, 142.2, 136.0, 127.7, 114.8, 113.8, 113.6, 64.2, 55.9, 55.2, 47.8, 45.4, 43.3, 40.9, 40.1, 30.5; IR (film) 1512 cm^{-1}. Anal calcd for $C_{21}H_{25}NO_2$: C, 77.98; H, 7.79; N, 4.33. Found: C, 78.05; H, 7.87; N, 4.36.

(±)-(3a*R*,5*R*,6a*R*)-4-[1-(4-Chlorophenyl)octahydrocyclopenta[*b*]pyrrol-5-yl]benzoic acid *tert*-butyl ester (5c). Reaction of 55 mg (0.25 mmol) of **1b** with 4-bromobenzoic acid *tert*-butyl ester (90 mg, 0.35 mmol), and NaO*t*-Bu (29 mg, 0.3 mmol) following the general procedure afforded a 15:85 mixture of **3**:**5** as the sole detectable products as judged by ^{1}H NMR analysis. This mixture was separated by flash chromatography on silica gel to afford 70 mg (71 %) of the title compound as a white solid, m.p. 136–138 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 8.5 Hz, 2 H), 7.23 (d, J = 8.5 Hz, 2 H), 7.15 (d, J = 9.0 Hz, 2 H), 6.53 (d, J = 9.0 Hz, 2 H), 4.22–4.16 (m, 1 H), 3.45–3.36 (m, 2 H), 3.24–3.15 (m, 1 H), 2.97–2.88 (m, 1 H), 2.68–2.61 (m, 1 H), 2.33–2.26 (m, 1 H), 2.16–2.08 (m, 1 H), 1.91–1.84 (m, 1 H), 1.58 (s, 9 H), 1.59–1.52 (m, 1 H), 1.51–1.42 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 148.5, 145.5, 130.0, 129.5, 128.8, 126.7, 120.6, 113.7, 80.7, 63.6, 47.3, 46.2, 43.6, 40.5, 39.3, 30.0, 28.2; IR (film) 1709, 1600,

1499 cm^{-1}. Anal calcd for $C_{24}H_{28}ClNO_2$: C, 72.44; H, 7.09; N, 3.52. Found: C, 72.59; H, 7.17; N, 3.58.

(±)-(3a*R*,5*R*,6a*R*)-4-(5-*o*-Tolyloctahydrocyclopenta[*b*]pyrrol-1-yl)benzoic acid *tert*-butyl ester (5d). Reaction of 72 mg (0.25 mmol) of **1d** with 2-bromotoluene (42 μL, 60 mg, 0.35 mmol), and NaO*t*-Bu (29 mg, 0.3 mmol) following the general procedure afforded a 10:90 mixture of **3**:**5** as the sole detectable products as judged by ^{1}H NMR analysis. This mixture was separated by flash chromatography on silica gel to afford 66 mg (70 %) of the title compound as a white solid, m.p. 46–48 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 9.0 Hz, 2 H), 7.22–7.18 (m, 1 H), 7.16–7.07 (m, 3 H), 6.57 (d, *J* = 9.0 Hz, 2 H), 4.31–4.25 (m, 1 H), 3.56–3.51 (m, 2 H), 3.39–3.30 (m, 1 H), 2.99–2.90 (m, 1 H), 2.70–2.63 (m, 1 H), 2.38 (s, 3 H), 2.26–2.20 (m, 1 H), 2.18–2.09 (m, 1 H), 1.96–1.90 (m, 1 H), 1.63–1.43 (m, 2 H), 1.58 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 149.8, 141.2, 135.7, 131.0, 130.2, 126.1, 126.0, 125.0, 118.5, 111.5, 79.6, 63.3, 46.9, 43.6, 42.2, 40.1, 38.2, 29.6, 28.3, 19.7; IR (film) 1695, 1605, 1521 cm^{-1}. Anal calcd for $C_{25}H_{31}NO_2$: C, 79.54; H, 8.28; N, 3.71. Found: C, 79.44; H, 8.20; N, 3.73.

(±)-(3a*R*,5*R*,6a*R*)-4-(5-Pyridin-3-yloctahydrocyclopenta[*b*]pyrrol-1-yl)benzonitrile (5e). Reaction of 53 mg (0.25 mmol) of **1c** with 3-bromopyridine (34 μL, 55 mg, 0.35 mmol), and NaO*t*-Bu (29 mg, 0.3 mmol) following the general procedure afforded a 5:10:10:75 mixture of **2**:**3**:**4**:**5** as judged by ^{1}H NMR analysis. This mixture was separated by flash chromatography on silica gel to afford 50 mg (69 %) of the title compound as a yellow oil. This material contained ca. 7 % of (±)-(3a*R*,6*S*,6a*S*)-4-(6-pyridin-3-yloctahydrocyclopenta[*b*]pyrrol-1-yl)benzonitrile (**3**) as an inseparable impurity; data are for the major product. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46–8.44 (m, 1 H), 8.42 (dd, *J* = 1.2, 4.8 Hz, 1 H), 7.50-7.45 (m, 1 H), 7.42 (d, *J* = 8.8 Hz, 2 H), 7.18 (dd, *J* = 4.8, 8.0 Hz, 1 H), 6.54 (d, *J* = 8.8 Hz, 2 H), 4.29–4.21 (m, 1 H), 3.53–3.45 (m, 2 H),

3.24–3.14 (m, 1 H), 3.00–2.94 (m, 1 H), 2.78–2.68 (m, 1 H), 2.36–2.27 (m, 1 H), 2.19–2.08 (m, 1 H), 1.96–1.89 (m, 1 H), 1.60–1.50 (m, 1 H), 1.49–1.39 (m, 1 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 149.2, 148.8, 147.8, 138.4, 133.9, 133.3, 123.2, 120.6, 112.3, 97.3, 63.3, 46.9, 43.7, 43.5, 40.6, 38.6, 29.4; IR (film) 2210, 1605, 1520 cm^{-1}. Anal calcd for $C_{19}H_{19}N_3$: C, 78.86; H, 6.62; N, 14.52. Found: C, 78.28; H, 6.61; N, 14.37.

(±)-(3a*R*,5*R*,6a*R*)-Phenyl[4-(1-phenyloctahydrocyclopenta[*b*]pyrrol-5-yl)phenyl]methanone (5f). Reaction of 47 mg (0.25 mmol) of **1e** with 4-bromobenzophenone (91 mg, 0.35 mmol), and NaO*t*-Bu (29 mg, 0.3 mmol) following the general procedure afforded a 10:90 mixture of **3**:**5** as the sole detectable products as judged by ^{1}H NMR analysis. This mixture was separated by flash chromatography on silica gel to afford 80 mg (87 %) of the title compound as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.2 Hz, 2 H), 7.73 (d, J = 8.4 Hz, 2 H), 7.61–7.56 (m, 1 H), 7.51–7.45 (m, 2 H), 7.33 (d, J = 8.0 Hz, 2 H), 7.28–7.22 (m, 2 H), 6.73–6.64 (m, 3 H), 4.30–4.23 (m, 1 H), 3.53–3.42 (m, 2 H), 3.31–3.20 (m, 1 H), 3.01–2.90 (m, 1 H), 2.77–2.69 (m, 1 H), 2.39–2.31 (m, 1 H), 2.20–2.09 (m, 1 H), 1.94–1.86 (m, 1 H), 1.68–1.52 (m, 2 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 196.2, 149.0, 147.0, 137.9, 135.5, 132.1, 130.2, 129.8, 129.0, 128.1, 126.8, 115.9, 112.7, 63.6, 47.1, 46.2, 43.6, 40.8, 39.3, 30.1; IR (film) 1655, 1598, 1504 cm^{-1}. Anal calcd for $C_{26}H_{25}NO$: C, 84.98; H, 6.86; N, 3.81. Found: C, 84.63; H, 6.95; N, 3.81.

(±)-(3a*R*,5*R*,6a*R*)-4-(1-Phenyloctahydrocyclopenta[*b*]pyrrol-5-yl)benzonitrile (5g). Reaction of 47 mg (0.25 mmol) of **1e** with 4-bromobenzonitrile (64 mg, 0.35 mmol), and NaO*t*-Bu (29 mg, 0.3 mmol) following the general procedure afforded **5g** as the sole detectable product as judged by ^{1}H NMR analysis. Flash chromatography on silica gel afforded 56 mg (78 %) of the title compound as a white solid, m.p. 80–82 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 8.5

Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.27–7.22 (m, 2 H), 6.73–6.69 (m, 1 H), 6.65 (d, *J* = 8.0 Hz, 2 H), 4.29–4.23 (m, 1 H), 3.48-3.44 (m, 2 H), 3.27–3.18 (m, 1 H), 3.00–2.91 (m, 1 H), 2.74–2.66 (m, 1 H), 2.35–2.28 (m, 1 H), 2.18–2.10 (m, 1 H), 1.92–1.86 (m, 1 H), 1.59–1.47 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.5, 146.8, 132.1, 129.1, 127.7, 119.0, 115.9, 112.7, 109.8, 63.4, 47.0, 46.2, 43.6, 40.6, 39.1, 29.9; IR (film) 2226, 1598, 1505 cm^{-1}. Anal calcd for $C_{20}H_{20}N_2$: C, 83.30; H, 6.99; N, 9.71. Found: C, 83.25; H, 7.10; N, 9.82.

Oxidative Cyclization of (2-Cyclopent-2-enylethyl)-(4-methoxyphenyl)amine (1a)

(±)-(3a*R*,6a*S*)-1-(4-Methoxyphenyl)-1,2,3,3a,4,6a-hexahydrocyclopenta[*b*]pyrrole (4).[2] A flame-dried Schlenk tube was cooled under a stream of argon and charged with $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol, 1 mol %), ligand (0.01 mmol, 4 mol %), and NaO*t*-Bu (29 mg, 0.3 mmol). The tube was purged with argon and toluene (1 mL), **1a** (54 mg, 0.25 mmol), and 4-bromotoluene (43 μL, 60 mg, 0.35 mmol) were added via syringe. The mixture was heated to 110 °C with stirring until the starting material had been consumed as judged by GC analysis. The reaction mixture was cooled to room temperature, quenched with saturated aqueous ammonium chloride (2 mL), and diluted with ethyl acetate (10 mL). The layers were separated and the aqueous layer was extracted with ethyl acetate (2 x 10 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was then purified by flash chromatography on silica gel to afford the title compound as a colorless oil. The yields obtained with four different ligands are shown below in Table S1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86 (d, *J* = 9.5 Hz, 2 H), 6.65 (d, *J* = 9.0 Hz, 2 H), 5.94–5.92 (m, 1 H), 5.81–5.79 (m, 1 H), 4.58–4.55 (m, 1 H), 3.77 (s, 3 H), 3.34–3.29 (m, 1 H), 3.14–3.08 (m, 1 H), 2.99–2.86 (m, 1 H), 2.64–2.58 (m, 1 H), 2.24–2.18 (m, 2 H), 1.74–1.67 (m, 1 H).

Table S1: Synthesis of 4

Ligand	Isolated Yield
$P(2\text{-furyl})_3$	53%
$PMePh_2$	44%
PMe_2Ph	54%
PMe_3	61%

***N*-Arylation of *N*-(2-cyclopent-2-enylethyl)-*p*-anisidine (1a)**

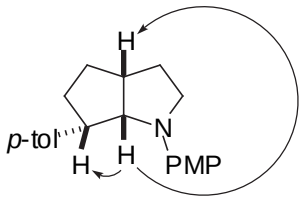
***N*-(2-Cyclopent-2-enylethyl)-*N*-(4-methylphenyl)-*p*-anisidine (2)**. A flame-dried Schlenk tube was cooled under a stream of argon and charged with $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol, 1 mol %), 2-(di-*tert*-butylphosphino)biphenyl (**10**) (1.8 mg, 0.005 mmol, 2 mol %), and NaO*t*-Bu (29 mg, 0.3 mmol). The tube was purged with argon and toluene (1 mL), **1a** (54 mg, 0.25 mmol), and 4-bromotoluene (37 μL, 51 mg, 0.3 mmol) were added via syringe. The resulting mixture was heated to 60 °C with stirring until the starting material had been consumed as judged by GC analysis. The reaction mixture was cooled to room temperature, quenched with saturated aqueous ammonium chloride (2 mL), and diluted with ethyl acetate (10 mL). The layers were separated and the aqueous layer was extracted with ethyl acetate (2 x 10 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was then purified by flash chromatography on silica gel to afford 71 mg (92 %) of the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05–7.00 (m, 4 H), 6.88 (d, J = 8.6 Hz, 2 H), 6.73 (d, J = 8.6 Hz, 2 H), 5.77–5.73 (m, 1 H), 5.71–5.67 (m, 1 H), 3.82 (s, 3 H), 3.70–3.62 (m, 2 H), 2.77–2.66 (m, 1 H), 2.42–2.24 (m, 2 H), 2.28 (s, 3 H), 2.13–2.04 (m, 1 H), 1.84–1.74 (m, 1 H), 1.69–1.59 (m, 1 H), 1.50–1.40 (m, 1 H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 155.6, 146.6, 141.4, 134.5, 130.6, 129.5, 127.9, 125.6, 117.2, 114.7, 55.5, 51.1, 43.3, 33.5, 31.9, 29.8, 20.4; IR (film) 1616, 1508 cm^{-1}. Anal calcd for $C_{21}H_{25}NO$: C, 82.04; H, 8.20; N, 4.56. Found: C, 81.97; H, 8.15; N, 4.46.

Assignment of Stereochemistry

1,6-Diaryloctahydrocyclopenta[*b*]pyrroles (3a–g)

The stereochemistry of (±)-(3a*R*,6*S*,6a*S*)-1-(4-Methoxyphenyl)-6-*p*-tolyloctahydrocyclopenta[*b*]pyrrole (**3a**) was assigned on the basis of nOe signals as shown below.

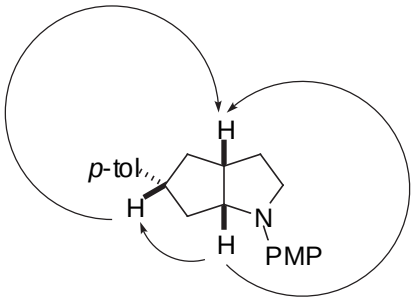


3a

The stereochemistry of the 1,6-diaryloctahydrocyclopenta[*b*]pyrrole products **3b–g** was assigned based on analogy to the above example.

1,5-Diaryloctahydrocyclopenta[*b*]pyrroles (5a–g)

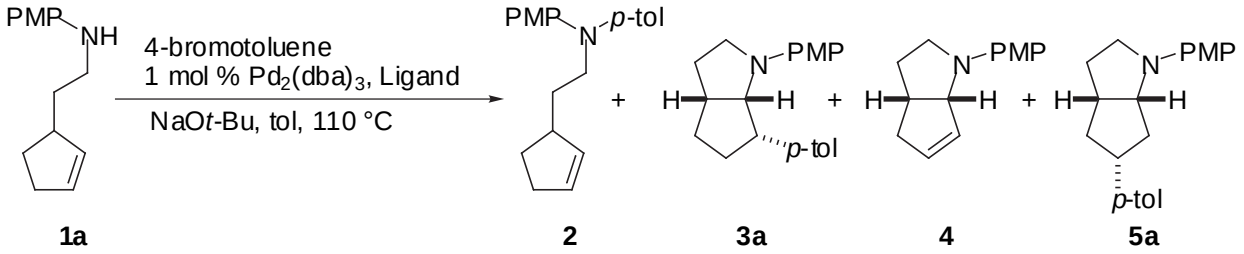
The stereochemistry of (±)-(3a*R*,5*R*,6a*R*)-1-(4-Methoxyphenyl)-5-*p*-tolyloctahydrocyclopenta[*b*]pyrrole (**5a**) was assigned on the basis of nOe signals as shown below.



5a

The stereochemistry of the 1,5-diaryloctahydrocyclopenta[*b*]pyrrole products **5b–g** was assigned based on analogy to the above example.

Ligand Effects[a]



1a **2** **3a** **4** **5a**

Entry	Ligand	2	3a	4	5a
1	Pd[P(*t*-Bu)$_3$]$_2$	**100**	0	0	0
2[b]	P(*t*-Bu)$_3$•HBF$_4$	**98**	2	0	0
3	*t*-Bu$_2$P(*o*-biphenyl) (**10**)	**94**	6	0	0
4	Dpp-benzene	**87**	3	7	4
5	Pd[P(*t*-Bu)$_2$Cy]$_2$	**81**	5	0	14
6	2-(Dicyclohexylphosphino)-2'-(*N,N*-dimethylamino)biphenyl	**76**	24	0	0
7	2-(Diphenylphosphino)-2'-(*N,N*-dimethylamino)biphenyl (**11**)	**56**	40	2	2
8	Xantphos	**54**	46	0	0
9	Cy$_2$P(*o*-biphenyl)	**52**	39	1	8
10	dppp	31	**58**	8	3
11	dppf	27	**42**	12	19
12	P(*o*-tol)$_3$	18	**42**	9	31
13[b,c]	PMe$_3$•HBF$_4$	0	0	**98**	2
14[b,c]	PEt$_3$•HBF$_4$	0	0	**92**	8

15[b]	PMe_2Ph	0	0	**92**	8
16	$PMePh_2$	0	0	**86**	14
17	P(2-furyl)$_3$	0	8	**82**	10
18	dppe-*p*-OMe	3	4	**69**	24
19[d]	dppe	5	7	**63**	25
20	P[C_6H_4(*p*-OMe)]$_3$	0	5	**59**	36
21[d]	Dppb	4	10	**56**	30
22	PPh_3	3	9	**55**	33
23	Dppm	12	11	**51**	26
24	(±)–BINAP	32	9	**37**	22
25	Dpe-phos	19	27	**37**	17
26	dppe-*p*-CF_3	20	25	**28**	27
27	MeP(*t*-Bu)$_2$•HBF_4	0	0	0	**100**
28	Pd[MeP(*t*-Bu)$_2$]$_2$	0	0	0	**100**
29	Pd[PCy_3]$_2$	1	2	1	**96**
30	PCy_3	2	2	6	**90**
31	Pd[P(*t*-Bu)Cy_2]$_2$	6	6	0	**88**
32	Dppf-*i*-Pr	13	12	0	**75**
33	dcpe	11	4	19	**66**
34	P[C_6H_4(*p*-CF_3)]$_3$	3	28	26	**43**
35	P[C_6H_4(*m*-CF_3)]$_3$	4	31	32	**33**
36	P[C_6H_4(*o*-CF_3)]$_3$	Very Low Conversion			
37	P(C_6F_5)$_3$	Very Low Conversion			
38	Tris(2,4,6-trimethoxyphenyl) phosphine	Very Low Conversion			

39	Trimesitylphosphine	Complex Mixture

(*a*) Conditions: 1.0 equiv **1a**, 2.0 equiv 4-bromotoluene, 1.2 equiv NaO*t*Bu, 1 mol % $Pd_2(dba)_3$, 2 mol % ligand (bis phosphines) or 4 mol% ligand (mono phosphines), toluene (0.25 M), 110 °C. The product ratios refer to GC ratios of products **2**–**5** that have been corrected for GC response factor. All reactions proceed to completion unless otherwise noted. (*b*) The reaction was conducted with 1.4 equiv 4-bromotoluene. (*c*) The reaction proceeded only to c.a. 80 % conversion. (*d*) Approximately 3% of an imine side product derived from substrate oxidation was detected by GC and GC/MS analysis of the crude reaction mixture.

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