Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

for

Angew. Chem. Int. Ed. **200**460060

A New Palladium-Catalyzed Synthesis of N-Aryl Pyrrolidines from γ–(*N*-Arylamino)alkenes. Evidence for Chemoselective Alkene Insertion into the Pd–N Bonds of Intermediate Palladium(Aryl)(Amido) Complexes.[**]

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Experimental Section

General: All reactions were carried out under an argon or nitrogen atmosphere in oven or flame dried glassware. Tris(dibenzylideneacetone)dipalladium (0) and all phosphine ligands were purchased from Strem Chemical Co. and used without further purification. All aryl bromides were obtained from commercial sources (Aldrich Chemical CO or Acros Chemical CO) and were used as obtained. Toluene and THF were purified using a GlassContour solvent purification system. Product regiochemistry was assigned on the basis of ^{1}H NMR 2-D COSY experiments; stereochemistry was assigned on the basis of ^{1}H NMR nOe experiments. Ratios of regioisomers and/or diastereomers were determined by either ^{1}H NMR or capillary GC analysis of crude reaction mixtures. Yields refer to isolated yields of compounds estimated to be ≥95% pure as determined by ^{1}H NMR, and either capillary GC (known compounds) or combustion analysis (new compounds). The yields reported in the supporting information describe the result of a single experiment, whereas the yields reported in Table 1 are average yields of two or more experiments. Thus, the yields reported in the supporting information may differ from those shown in Table 1.

Synthesis of γ-(N-Arylamino)alkenes

Pent-4-enylphenylamine (**1a**).[i] An oven-dried round-bottom flask was charged with 1,1'-carbonyldiimidazole (4.8 g, 29.4 mmol) and then purged with argon. THF (30 mL) and 4-pentenoic acid (3 mL, 2.9 g, 29.4 mmol) were added via syringe. The mixture was stirred at room temperature for 1 h. Aniline (2.7 mL, 2.74 g, 29.4 mmol) was added via syringe and the mixture was then stirred at room temperature for 2 h. The reaction mixture was diluted with ethyl acetate (100 mL) and H_2O (50 mL). The layers were separated and the aqueous layer was extracted with ethyl acetate (2 x 50 mL). The combined organic extracts were washed

with saturated aqueous $NaHCO_3$ (50 mL), dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo* to afford 4.83 g (93%) of pent-4-enoic acid phenylamide[ii] as a tan solid, m.p. 89-91 °C. A flame-dried round-bottom flask was charged with pent-4-enoic acid phenylamide and then purged with argon. THF (30 mL) was added via syringe and the resulting solution was cooled to 0 °C. A solution of $LiAlH_4$ in ether (80 mL, 80 mmol, 1.0 M) was added dropwise via syringe. The reaction mixture was then warmed to room temperature and stirred 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 (200 mL) and quenched slowly with H_2O (6 mL). Aqueous 10 M NaOH was added slowly until all insoluble material had precipitated. The organic supernatant was decanted to a clean Erlenmeyer flask and the precipitate was washed with ether (100 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 4.25 g (96 %) of the title compound as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19–7.15 (m, 2 H), 6.69 (t, *J* = 7.5 Hz, 1 H), 6.60 (d, *J* = 7.5 Hz, 2 H), 5.89–5.80 (m, 1 H), 5.09–4.98 (m, 2 H), 3.62 (br s, 1 H), 3.14 (t, *J* = 7.0 Hz, 2 H), 2.21–2.15 (m, 2 H), 1.76-1.59 (m, 2 H).

(4-Methoxyphenyl)pent-4-enylamine (**1b**). An oven-dried flask was purged with argon and charged with *p*-anisidine (3.7 g, 30.0 mmol). THF (30 mL) was added and the resulting solution was cooled to 0 °C. A solution of MeMgBr in THF (9.5 mL, 28.5 mmol, 3.0 M) was added dropwise and the resulting mixture was warmed to rt and stirred for 6 h. The mixture was cooled to 0 °C, ethyl pent-4-eneoate (3.2 g, 25 mmol) was added dropwise and the resulting solution was warmed to rt and stirred for 12 h. A solution of saturated aqueous ammonium chloride (30 mL) was slowly added, the mixture was stirred at rt for 5 min, and transferred to a separatory funnel. The mixture was extracted with ethyl acetate (3 x 60 mL) and the combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel to afford 2.92 g (61%) of pent-4-enoic acid-(4-methoxyphenyl)amide as a tan solid. The amide product was dissolved in ether (45 mL) and THF (10 mL) under argon in a round-bottom flask. The solution was cooled to 0 °C and a solution of $LiAlH_4$ in ether (31 mL, 31 mmol, 1.0 M) was added dropwise. The resulting solution was warmed to rt and stirred for 14 h, then was cooled to 0 °C. Water (1.5 mL) was added dropwise then 10 M NaOH (4 mL) and additional water (6 mL) were added. The resulting slurry was stirred at rt for 5 min until all

solids were deposited on the sides of the flask. The solution was decanted, dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo* to afford 2.54 g (94%) of the title compound as a pale yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.79 (d, J = 8.5 Hz, 2 H), 6.58 (d, J = 8.5 Hz, 2 H), 5.89–5.80 (m, 1 H), 5.09–4.98 (m, 2 H), 3.75 (s, 3 H), 3.36 (br s, 1 H), 3.09 (t, J = 7.0 Hz, 2 H), 2.20–2.14 (m, 2 H), 1.74–1.67 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9, 142.7, 138.1, 115.0, 114.8, 114.0, 55.8, 44.4, 31.3, 28.7; IR (neat) 3389, 1511 cm^{-1}. Anal calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.16; H, 8.91; N, 7.41.

4-Pent-4-enylaminobenzonitrile (**1c**). A flame-dried Schlenk flask charged with $Pd_2(dba)_3$ (46 mg, 0.05 mmol), 2-(di-*tert*-butylphosphino)biphenyl (30 mg, 0.1 mmol), NaO*t*Bu (577 mg, 6.0 mmol), and 4-bromobenzonitrile (910 mg, 5.0 mmol). The tube was purged with argon and a solution of pent-4-enylamine[iii] (1.1 mL, 10.0 mmol) and toluene (20 mL) was added. The mixture was heated to 60 °C with stirring until the starting material had been consumed as judged by GC analysis (4 h). The reaction mixture was cooled to room temperature, quenched with H_2O (20 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 640 mg (69 %) of the title compound as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.8 Hz, 2 H), 6.54 (d, J = 8.8 Hz, 2H), 5.88–5.76 (m, 1 H), 5.10–5.00 (m, 2 H), 4.17 (br s, 1H), 3.21–3.14 (m, 2 H), 2.22–2.14 (m, 2 H), 1.78–1.70 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.3, 137.5, 133.7, 120.5, 115.5, 112.0, 98.3, 42.5, 31.0, 28.1; IR (neat) 3365, 2213, 1604, 1524 cm^{-1}. Anal calcd for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.35; H, 7.43; N, 14.80.

***N*-(1-methylpent-4-enyl)-*p*-anisidine** (**1d**).[iv] An oven-dried flask was purged with argon and charged with allylacetone (3.5 mL, 30.0 mmol), *p*-anisidine (3.7 g, 30.0 mmol), acetic acid (60 μL, 1.0 mmol), and benzene (30 mL). The flask was equipped with a Dean-Stark trap and was heated to reflux with azeotropic removal of water for 10 h. The reaction mixture was cooled to rt and concentrated *in vacuo*. The crude imine product was dissolved in THF (30 mL) and cooled to 0 °C. A solution of $LiAlH_4$ in THF (30 mL, 30.0 mmol, 1.0 M), was added slowly dropwise, and the resulting mixture was warmed to rt and stirred for 3 h. The reaction mixture was then cooled to 0 °C and water (2 mL) was added dropwise followed by 10 M NaOH (4 mL) and additional water (6 mL). The resulting slurry was stirred at rt for 5 min until all solids were deposited on the sides of the flask. The solution was decanted, dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was

purified by flash chromatography on silica gel using 5% ethyl acetate:hexanes as the eluant to afforded 3.81 g (62 %) of the title compound as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.77 (d, *J* = 9.0 Hz, 2 H), 6.55 (d, *J* = 9.0 Hz, 2 H), 5.87–5.79 (m, 1 H), 5.05–4.96 (m, 2 H), 3.75 (s, 3 H), 3.40 (q, *J* = 6.5 Hz, 1 H), 3.12 (s, br, 1 H), 2.19–2.14 (m, 2 H), 1.70–1.62 (m, 1 H), 1.54–1.46 (m, 1 H), 1.16 (d, *J* = 6.5 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.8, 141.8, 138.4, 114.9, 114.7, 114.6, 55.7, 48.9, 36.2, 30.4, 20.7.

***N*-(1-Phenylpent-4-enyl)-*p*-anisidine** (**1e**). This compound was prepared on a 14.6 mmol scale using a procedure analogous to that employed for the synthesis of **1d** except allylacetophenone[v] was used in place of allylacetone. This two-step procedure afforded 2.42 g (62 %) of the title compound as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.29 (m, 4 H), 7.24–7.20 (m, 1 H), 6.68 (d, *J* = 9.0 Hz, 2 H), 6.47 (d, *J* = 9.0 Hz, 2 H), 5.86–5.79 (m, 1 H), 5.05–4.98 (m, 2 H), 4.27 (t, *J* = 6.5 Hz, 1 H), 3.83 (s, br, 1 H), 3.69 (s, 3 H), 2.19–2.09 (m, 2 H), 1.94–1.82 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.8, 144.1, 141.6, 137.9, 128.5, 126.9, 126.4, 115.2, 114.7, 114.5, 58.5, 55.7, 37.8, 30.5; IR (film) 3393, 1513 cm^{-1}. Anal calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92; N, 5.24. Found: C, 80.83; H, 7.89; N, 5.22.

***N*-(2-Phenylpent-4-enyl)-*p*-anisidine** (**1f**). To a suspension of pyridinium chlorochromate (2.59 g, 12.0 mmol) in CH_2Cl_2 (20 mL) was added 2-phenyl-4-penten-1-ol[vi] (1.6 g, 10.0 mmol). The mixture was stirred at rt for 6 h then diluted with ether (60 mL), filtered through a pad of silica gel, and concentrated *in vacuo*. The resulting crude aldehyde product was dissolved in benzene (20 mL) and *p*-anisidine (1.23 g, 10.0 mmol) was added. The flask was equipped with a Dean-Stark trap and was heated to reflux with azeotropic removal of water for 10 h. The reaction mixture was cooled to rt and concentrated *in vacuo*. The crude imine product was dissolved in THF (10 mL) and cooled to 0 °C. A solution of $LiAlH_4$ in THF (10 mL, 10.0 mmol, 1.0 M), was added slowly dropwise, and the resulting mixture was warmed to rt and stirred for 3 h. The reaction mixture was then cooled to 0 °C and water (1 mL) was added dropwise followed by 10 M NaOH (2 mL) and additional water (3 mL). The resulting slurry was stirred at rt for 5 min until all solids were deposited on the sides of the flask. The solution was decanted, dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel using 5% ethyl acetate:hexanes as the eluant to afforded 456 mg (17 %) of the title compound as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.0 Hz, 2 H), 7.29–7.27 (m, 1 H), 7.24 (d, *J* = 7.0 Hz, 2 H), 6.79 (d, *J* = 9.0 Hz, 2 H), 6.55 (d, *J* = 9.0 Hz, 2 H), 5.80–5.72 (m, 1 H), 5.09–5.00 (m, 2 H), 3.77 (s, 3 H), 3.47 (dd, *J* = 5.0, 12.0 Hz, 1 H), 3.31 (s, br, 1 H), 3.21 (dd, *J* = 9.0, 12.0 Hz, 1 H),

3.04–2.98 (m, 1 H), 2.56–2.44 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 142.7, 142.2, 136.3, 128.6, 127.8, 126.7, 116.5, 114.8, 114.4, 55.7, 49.9, 44.9, 38.7; IR (film) 3399 cm^{-1}. Anal calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92; N, 5.24. Found: C, 81.18; H, 8.04; N, 5.24.

***N*-(3-Phenylpent-4-enyl)-*p*-anisidine** (**1g**). This compound was prepared on a 14.6 mmol scale using a procedure analogous to that employed for the synthesis of **1b** except 3-phenylpent-4-enoic acid ethyl ester[vii] was used in place of ethyl pent-4-eneoate. This two-step procedure afforded 915 mg (31 %) of the title compound as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.32 (m, 2 H), 7.25–7.22 (m, 3 H), 6.78 (d, *J* = 8.5 Hz, 2 H), 6.53 (d, *J* = 9.0 Hz, 2 H), 6.04–5.97 (m, 1 H), 5.12–5.07 (m, 2 H), 3.75 (s, 3 H), 3.43 (q, *J* = 7.5 Hz, 1 H), 3.32 (s, br, 1 H), 3.13–3.05 (m, 2 H), 2.09–1.98 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.0, 143.7, 142.5, 141.7, 128.6, 127.5, 126.4, 114.8, 114.4, 114.1, 55.8, 47.6, 43.1, 35.0; IR (film) 3394 cm^{-1}. Anal calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92; N, 5.24. Found: C, 80.83; H, 8.03; N, 5.13.

***N*-(2-Cyclopent-2-enylethyl)-*p*-anisidine** (**4**). This compound was prepared on a 10 mmol scale using a procedure analogous to that employed for the synthesis of **1** except *p*-anisidine was used in place of aniline and cyclopent-2-eneyl acetic acid was used in place of 4-pentenoic acid. This two-step procedure afforded 800 mg (36 %) of the title compound as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (d, *J* = 9.2 Hz, 2 H), 6.60 (d, *J* = 9.2 Hz, 2 H), 5.79–5.76 (m, 1 H), 5.72–5.70 (m, 1 H), 3.76 (s, 3 H), 3.35 (s, br, 1 H), 3.14–3.10 (m, 2 H), 2.84–2.76 (m, 1 H), 2.44–2.26 (m, 2 H), 2.16–2.06 (m, 1 H), 1.78–1.69 (m, 1 H), 1.66–1.56 (m, 1 H), 1.52–1.43 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9, 142.7, 134.5, 130.7, 114.8, 114.0, 55.8, 43.6, 43.3, 35.8, 31.9, 29.8; IR (film) 3392 cm^{-1}. Anal calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.45; H, 8.48; N, 6.35.

General procedure for the palladium-catalyzed synthesis of pyrrolidines. An oven or flame-dried Schlenk tube was cooled under a stream of argon or nitrogen and charged with $Pd_2(dba)_3$ (1 mol % complex, 2 mol % Pd), dppb (2 mol %), NaO*t*Bu (1.1–1.3 equiv), and the aryl bromide (1.1–1.3 equiv). The tube was purged with argon or nitrogen and a solution of the amine substrate (1.0 equiv), undecane (internal standard, 1.0 equiv), and toluene (4 mL/mmol aryl bromide) were added. The mixture was heated to 60–110 °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 NH_4Cl (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.

2-Naphthalen-2-ylmethyl-1-phenylpyrrolidine (**2a**). Reaction of 81 mg (0.5 mmol) of **1a** with 2-bromonaphthalene (114 mg, 0.55 mmol) and NaO*t*Bu (58 mg, 0.6 mmol) following the general procedure afforded 142 mg (95 %) of the title compound as a pale yellow oil. This compound was obtained as a ca. 25:1 mixture of inseparable regioisomers as judged by ^{1}H NMR analysis. The structure of the minor isomer was assigned on the basis of ^{1}H NMR analysis of the mixture of regioisomers and was confirmed by GC/MS analysis. Major isomer (**2a**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.81 (m, 3 H), 7.70 (s, 1 H), 7.53–7.45 (m, 2 H), 7.42 (dd, *J* = 1.6, 8.4 Hz, 1 H), 7.37–7.31 (m, 2 H), 6.82–6.73 (m, 3 H), 4.15–4.08 (m, 1 H), 3.50–3.43 (m, 1 H), 3.29–3.19 (m, 2 H), 2.76 (dd, *J* = 9.6, 13.6 Hz, 1 H), 1.99–1.84 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 137.0, 133.5, 132.1, 129.3, 127.9, 127.6, 127.4, 126.0, 125.3, 115.5, 111.8, 59.6, 48.3, 38.6, 29.4, 23.0 (two sets of aromatic signals are incidentally equivalent); IR (film) 1596, 1503 cm^{-1}. Anal calcd for $C_{21}H_{21}N$: C, 87.76; H, 7.36; N, 4.87. Found: C, 87.83; H, 7.39; N, 4.93. Minor isomer (**3a**): Partial ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.39 (d, *J* = 6.0, 3H, -CH_3); MS (EI) 287, 272, 133 (287 calcd for $C_{21}H_{21}N$).

2-(4-[1,3]Dioxolane-2-ylbenzyl)-1-phenylpyrrolidine (**2b**). Reaction of 81 mg (0.5 mmol) of **1a** with 2-(4-bromophenyl)-[1,3]dioxolane[viii] (126 mg, 0.55 mmol) and NaO*t*Bu (58 mg, 0.6 mmol) following the general procedure afforded 115 mg (74 %) of the title compound as a pale yellow oil. This compound was obtained as a ca. 16:1 mixture of inseparable regioisomers as judged by ^{1}H NMR analysis; data are for the major isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2 H), 7.30–7.23 (m, 4 H), 6.73–6.67 (m, 3 H), 5.80 (s, 1 H), 4.17–4.12 (m, 2 H), 4.09–4.00 (m, 2 H), 3.99–3.92 (m, 1 H), 3.44–3.38 (m, 1 H), 3.21–3.13 (m, 1 H), 3.07 (dd, *J* = 3.2, 13.6 Hz, 1 H), 2.58 (dd, *J* = 9.6, 13.6 Hz, 1H), 1.95-1.80 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 140.6, 135.7, 129.3, 126.5, 115.4, 111.7, 103.6, 65.3, 65.2, 59.6, 48.3, 38.2, 29.3, 22.9 (two aromatic signals are incidentally equivalent); IR (film) 1596,1503 cm^{-1}. Anal calcd for $C_{20}H_{23}NO_2$: C, 77.64; H, 7.49; N, 4.53. Found: C, 77.79; H, 7.67; N, 4.45.

Dimethyl-[4-(1-phenylpyrrolidin-2-ylmethyl)phenyl]amine (**2c**). Reaction of 81 mg (0.5 mmol) of **1a** with 4-bromo-*N*,*N*-dimethylaniline (110 mg, 0.55 mmol) and NaO*t*Bu (58 mg, 0.6 mmol) following the general procedure afforded 115 mg (82%) of the title compound as a pale yellow oil. This compound was obtained as a ca. 35:2:1 mixture of inseparable regioisomers as judged by ^{1}H NMR analysis; data are for the major isomer. ^{1}H NMR (500

MHz, $CDCl_3$) δ 7.34–7.30 (m, 2 H), 7.18–7.14 (d, *J* = 8.5 Hz, 2 H), 6.78–6.70 (m, 5 H), 3.98–3.93 (m, 1 H), 3.48–3.44 (m, 1 H), 3.24–3.18 (m, 1 H), 3.02 (dd, *J* = 2.5, 13.5 Hz, 1 H), 2.97 (s, 6 H), 2.50 (dd, *J* = 9.5, 13.5 Hz, 1 H), 2.00–1.84 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.2, 147.0, 129.9, 129.3, 127.5, 115.2, 112.8, 111.7, 60.0, 48.3, 40.8, 37.5, 29.4, 23.0; IR (film) 1504 cm^{-1}. Anal calcd for $C_{19}H_{24}N_2$: C, 81.38; H, 8.63; N, 9.99. Found: C, 81.19; H, 8.62; N, 10.04.

Phenyl-[4-(1-phenylpyrrolidin-2-ylmethyl)phenyl]methanone (**2d**). Reaction of 81 mg (0.5 mmol) of **1a** with 4-bromobenzophenone (144 mg, 0.55 mmol) and NaO*t*Bu (58 mg, 0.6 mmol) following the general procedure afforded 83 mg (49%) of the title compound as a pale yellow oil. This compound was obtained as a ca. 35:2:1 mixture of inseparable regioisomers as judged by ^{1}H NMR analysis; data are for the major isomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83–7.77 (m, 4 H), 7.60 (tt, *J* = 1.5, 7.5 Hz, 1 H), 7.52–7.48 (m, 2 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.32–7.28 (m, 2 H), 6.75–6.70 (m, 3 H), 4.08–4.03 (m, 1 H), 3.47–3.43 (m, 1 H), 3.25–3.18 (m, 1 H), 3.14 (dd, *J* = 3.0, 8.5 Hz, 1 H), 2.71 (dd, *J* = 9.5, 14.0 Hz, 1 H), 2.00–1.86 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.4, 146.8, 144.6, 137.7, 135.6, 132.3, 130.3, 130.0, 129.3, 129.3, 128.2, 115.7, 111.8, 59.4, 48.3, 38.7, 29.6, 23.0; IR (film) 1654, 1503 cm^{-1}. MS (ESI) 342.1852 (342.1858 calcd for $C_{24}H_{23}NO$, M + H^+).

1-(4-Methoxyphenyl)-2-naphthalen-2-ylmethylpyrrolidine (**2e**). Reaction of 96 mg (0.5 mmol) of **1b** with 2-bromonaphthalene (114 mg, 0.55 mmol) and NaO*t*Bu (58 mg, 0.6 mmol) following the general procedure afforded 110 mg (69%) of the title compound as a pale yellow oil. This compound was obtained as a ca. 14:1 mixture of inseparable regioisomers as judged by ^{1}H NMR analysis; data are for the major isomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89–7.82 (m, 3 H), 7.71 (s, 1 H), 7.54–7.47 (m, 2 H), 7.44 (dd, *J* = 1.8, 8.0 Hz, 1 H), 6.99 (d, *J* = 9.0 Hz, 2 H), 6.77 (d, *J* = 9.0 Hz, 2 H), 4.09–4.04 (m, 1 H), 3.84 (s, 3 H), 3.49–3.44 (m, 1 H), 3.25 (dd, *J* = 3.0, 8.5 Hz, 1 H), 3.19 (d, *J* = 8.0 Hz, 1 H), 2.77 (dd, *J* = 4.5, 14.0 Hz, 1 H), 1.98-1.86 (m, 4 H); ^{13}C NMR (125 MHz) δ 150.7, 142.0, 137.2, 133.5, 132.0, 127.9, 127.8, 127.6, 127.6, 127.4, 125.9, 125.3, 115.2, 112.7, 60.1, 55.9, 48.9, 38.9, 29.6, 23.2; IR (film) 1512 cm^{-1}. Anal calcd for $C_{22}H_{23}NO$: C, 83.24; H, 7.30; N, 4.41. Found: C, 83.41; H, 7.36; N, 4.46.

1-(4-Methoxyphenyl)-2-(2-methylbenzyl)pyrrolidine (**2f**). Reaction of 96 mg (0.5 mmol) of **1b** with 2-bromotoluene (66 μL, 94 mg, 0.55 mmol) and NaO*t*Bu (58 mg, 0.6 mmol) following the general procedure afforded 112 mg (79%) of the title compound as a pale yellow oil. This compound was obtained as a ca. 35/1 mixture of inseparable regioisomers as judged by ^{1}H NMR analysis; data are for the major isomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26–7.14 (m, 4 H),

6.91 (d, *J* = 9.5 Hz, 2 H), 6.67 (d, *J* = 9.0 Hz, 2 H), 4.09–4.03 (m, 1 H), 3.81 (s, 3 H), 3.49 (dt, *J* = 3.0, 7.5 Hz, 1 H), 3.24-3.16 (m, 1 H), 3.12 (dd, *J* = 4.0, 14.5 Hz, 1 H), 2.61 (dd, *J* = 4.5, 9.0 Hz, 1 H), 2.41 (s, 3H), 2.10–1.96 (m, 2 H), 1.90–1.83 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.7, 142.1, 137.9, 136.4, 130.3, 129.7, 126.1, 125.9, 115.1, 112.6, 59.1, 55.9, 48.8, 35.4, 29.5, 23.3, 20.1; IR (film) 1510 cm^{-1}. Anal calcd for $C_{19}H_{23}NO$: C, 81.10; H, 8.24; N, 4.98. Found: C, 81.23; H, 8.29; N, 5.05.

4-[2-(4-*tert*-Butylbenzyl)pyrrolidin-1-yl]benzonitrile (**2g**). Reaction of 94 mg (0.5 mmol) of **1c** with 1-bromo-4-*tert*-butylbenzene (95 _L, 117 mg, 0.55 mmol) and NaO*t*Bu (58 mg, 0.6 mmol) following the general procedure afforded 128 mg (81%) of the title compound as a pale yellow oil. This compound was obtained as a ca. 100:1 mixture of inseparable regioisomers as judged by ^{1}H NMR analysis; data are for the major isomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 11.5 Hz, 2 H), 7.35 (d, *J* = 10.5 Hz, 2 H), 7.14 (d, *J* = 10.0 Hz, 2 H), 6.62 (d, *J* = 11.0 Hz, 2 H), 4.08–4.00 (m, 1 H), 3.49–3.42 (m, 1 H), 3.28–3.20 (m, 1 H), 2.97 (dd, *J* = 4.0, 17.5 Hz, 1 H), 2.56 (dd, *J* = 7.0, 17.5 Hz, 1 H), 2.05–1.87 (m, 4 H), 1.34 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.4, 149.2, 135.3, 133.5, 128.8, 125.4, 120.8, 111.7, 96.7, 59.7, 48.1, 37.4, 34.4, 31.3, 29.4, 22.7; IR (film) 2212, 1520 cm^{-1}. Anal calcd for $C_{22}H_{26}N_2$: C, 82.97; H, 8.23; N, 8.80. Found: C, 82.99; H, 8.12; N, 8.82.

4-[2-(4-Benzoylbenzylpyrrolidin-1-yl]benzonitrile (**2h**). Reaction of 94 mg (0.5 mmol) of **1c** with 4-bromobenzophenone (144 mg, 0.55 mmol) and NaO*t*Bu (58 mg, 0.6 mmol) following the general procedure afforded 160 mg (87%) of the title compound as a pale yellow solid, m.p. 54-58 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.75 (m, 4 H), 7.63–7.57 (m, 1 H), 7.52–7.47 (m, 4 H), 7.31 (d, *J* = 8.0, 2 H), 6.63 (d, *J* = 8.8 Hz, 2 H), 4.14–4.07 (m, 1 H), 3.48–3.42 (m, 1 H), 3.29–3.22 (m, 1 H), 3.07 (dd, *J* = 3.2, 13.6 Hz, 1H), 2.74 (dd, *J* = 9.2, 13.6 Hz, 1H), 2.05–1.87 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 149.1, 143.4, 137.5, 135.8, 133.5, 132.3, 130.3, 129.8, 129.1, 128.2, 120.6, 111.8, 97.0, 59.2, 48.1, 38.0, 29.4, 22.6; IR (film) 2210, 1653, 1601, 1518. MS (ESI) 389.1627 (389.1630 calcd for $C_{25}H_{22}N_2O$, M + Na^+).

(±)-(2*S*,5*S*)-2-(4-*t*-Butylbenzyl)-1-(4-methoxyphenyl)-5-methylpyrrolidine (**2i**). Reaction of 103 mg (0.5 mmol) of **1d** with 1-bromo-4-*t*-butylbenzene (104 μL, 0.6 mmol) and NaO*t*Bu (58 mg, 0.6 mmol) following the general procedure using dppe as ligand and a reaction temperature of 100 °C provided a ca. 12:1 mixture of regioisomers as judged by GC analysis which were separated by flash chromatography on silica gel to afford 109 mg (64%) of the title compound as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.5 Hz, 2

H), 7.18 (d, *J* = 8.0 Hz, 2 H), 6.87 (d, *J* = 9.5 Hz, 2 H), 6.68 (d, *J* = 9.0 Hz, 2 H), 3.80–3.77 (m, 1 H), 3.78 (s, 3 H), 3.69 (q, *J* = 7.0 Hz, 1 H), 3.14 (dd, *J* = 3.5, 14 Hz, 1 H), 2.55 (dd, *J* = 9.5, 13.5 Hz, 1 H), 2.05–1.98 (m, 1 H), 1.87–1.80 (m, 2 H), 1.68–1.61 (m, 1 H), 1.32 (s, 9 H), 1.22 (d, *J* = 6.5 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.0, 148.9, 142.4, 136.5, 129.0, 125.2, 114.9, 113.4, 63.2, 56.9, 56.0, 41.0, 34.4, 32.2, 31.4, 29.3, 21.8; IR (film) 1503 cm^{-1}. Anal calcd for $C_{23}H_{31}NO$: C, 81.85; H, 9.26; N, 4.15. Found: C, 81.68; H, 9.40; N, 4.14.

(±)-(2*S*,5*R*)-2-(4-Methoxybenzyl)-1-(4-methoxyphenyl)-5-phenylpyrrolidine (**2j**). Reaction of 135 mg (0.5 mmol) of **1e** with 4-bromoanisole (69 μL, 0.55 mmol) and NaO*t*Bu (58 mg, 0.6 mmol) following the general procedure using dppe as ligand and a reaction temperature of 100 °C afforded 133 mg (72 %) of the title compound as a pale yellow oil. This compound was obtained as a ca. 8:1 mixture of inseparable regioisomers as judged by ^{1}H NMR analysis; data are for the major isomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.30 (m, 4 H), 7.26–7.21 (m, 3 H) 6.89 (d, *J* = 8.4 Hz, 2 H), 7.79 (d, *J* = 9.2 Hz, 2 H), 6.57 (d, *J* = 9.2 Hz, 2 H), 4.60 (t, *J* = 6.8 Hz, 1 H), 4.00–3.92 (m, 1 H), 3.82 (s, 3 H), 3.73 (s, 3 H), 3.39 (dd, *J* = 3.2, 13.6 Hz, 1 H), 2.67 (dd, *J* = 10.0, 13.6 Hz, 1 H), 2.38–2.32 (m, 1 H), 1.99–1.80 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.1, 151.2, 145.2, 142.2, 131.5, 130.1, 128.6, 126.6, 125.6, 114.7, 113.9, 113.8, 66.6, 63.6, 55.7, 55.2, 40.3, 35.1, 29.2; IR (film) 1509 cm^{-1}. MS(ESI) 374.2114 (374.2120 calcd for $C_{25}H_{28}NO_2$, M + H^+).

(±)-(2*S*,4*R*)-1-(4-Methoxyphenyl)-2-(4-methylbenzyl)-4-phenylpyrrolidine (**2k**). Reaction of 134 mg (0.5 mmol) of **1f** with 4-bromotoluene (74 μL, 0.6 mmol) and NaO*t*Bu (58 mg, 0.6 mmol) following the general procedure using dppe as ligand and a reaction temperature of 100 °C afforded 158 mg (88 %) of the title compound as a pale yellow oil. This compound was obtained as a ca. 2:1 mixture of inseparable diastereomers which contained ca. 5% of a regioisomer as judged by ^{1}H NMR analysis. Major Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.10 (m, 9 H), 6.96 (d, *J* = 7.2 Hz, 2 H), 6.72 (d, *J* = 7.6 Hz, 2 H), 4.11–4.05 (m, 1 H), 3.88–3.82 (m, 1 H), 3.83 (s, 3 H), 3.54–3.49 (m, 1 H), 3.22 (t, *J* = 7.2 Hz, 1 H), 3.15 (dd, *J* = 2.4, 10.8 Hz, 1 H), 2.74 (dd, *J* = 7.6, 10.8 Hz, 1 H), 2.39 (s, 3 H), 2.30–2.23 (m, 1 H), 2.14–2.10 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.9, 142.1, 141.9, 136.2, 135.8, 129.2, 129.1, 128.5, 127.2, 126.6, 115.2, 112.4, 61.1, 56.2, 56.0, 41.7, 39.1, 37.2, 21.04; Minor Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.10 (m, 9 H), 6.96 (d, *J* = 7.2 Hz, 2 H), 6.77 (d, *J* = 7.2 Hz, 2 H), 4.11–4.05 (m, 1 H), 3.84 (s, 3 H), 3.74–3.70 (m, 1 H), 3.59 (t, *J* = 7.6 Hz, 1 H), 3.38–3.27 (m, 2 H), 2.61–2.56 (m, 1 H), 2.50–2.44 (m, 1 H), 2.37 (s, 3 H), 2.10–2.00 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.2, 142.2, 142.1, 135.9, 135.6, 129.2, 129.0, 128.4, 127.3, 126.5, 115.0, 114.2, 60.2, 57.8, 55.9,

42.8, 39.8, 38.9, 21.03_; IR (film) 1511 cm^{-1}. Anal calcd for $C_{25}H_{27}NO$: C, 83.99; H, 7.61; N, 3.92. Found: C, 83.89; H, 7.63; N, 3.97.

(±)-(2*S*,3*S*)-2-(3-Methoxybenzyl)-1-(4-methoxyphenyl)-3-phenylpyrrolidine (**2l**). Reaction of 135 mg (0.5 mmol) of **1g** with 3-bromoanisole (81 μL, 0.65 mmol) and NaO*t*Bu (63 mg, 0.65 mmol) following the general procedure using dppe as ligand and a reaction temperature of 100 °C afforded 118 mg (63 %) of the title compound as a pale yellow oil. This compound was obtained as a ca. 10:1 mixture of inseparable regioisomers and also contained ca 8% of 1-(*p*-methoxyphenyl)-2-(*m*-methoxybenzyl)-3-phenylpyrrole as judged by ^{1}H NMR analysis. The mixture was separated by preparative HPLC for analysis. Major product (**2l**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22–7.16 (m, 3 H), 7.15–7.12 (m, 1 H), 6.97 (d, *J* = 9.0 Hz, 2 H), 6.92 (d, *J* = 11.5 Hz, 2 H), 6.81 (d, *J* = 9.5 Hz, 1 H), 6.77–6.74 (m, 2 H), 6.68 (d, *J* = 11.5 Hz, 2 H), 4.12–4.07 (m, 1 H), 3.80 (s, 3 H), 3.77 (s, 3 H), 3.42–3.28 (m, 3 H), 3.04 (dd, *J* = 3.5, 17.5 Hz, 1 H), 2.77 (dd, *J* = 11.0, 17.0 Hz, 1 H), 2.35–2.26 (m, 1 H), 1.96–1.88 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 150.8, 145.3, 141.0, 140.5, 129.3, 128.5, 126.9, 126.1, 121.9, 115.3, 115.2, 112.8, 111.4, 65.9, 55.9, 55.1, 47.6, 47.4, 38.2, 31.3; IR (film) 1583 cm^{-1}. MS(ESI) 374.2112 (374.2120 calcd for $C_{25}H_{28}NO_2$, M + H^+).

Regioisomer:**(±)-(2*S*,3*R*)-1-(4-Methoxyphenyl)-3-(3-methoxyphenyl)-2-methyl-3-phenylpyrrolidine** (**3l**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.28 (m, 2 H), 7.24–7.20 (m, 3 H), 7.04 (m, 1 H), 6.90 (d, *J* = 9.0 Hz, 2 H), 6.65–6.62 (m, 1 H), 6.58 (d, *J* = 8.5 Hz, 2 H), 6.53-6.50 (m, 1 H), 6.50–6.48 (m, 1 H), 4.49 (q, *J* = 6.5 Hz, 1 H), 3.78 (s, 3 H), 3.47 (s, 3 H), 3.43–3.37 (m, 1 H), 3.04–2.95 (m, 1 H), 2.91–2.84 (m, 1 H), 2.24–2.18 (m, 1 H), 0.87 (d, *J* = 6.0 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 150.6, 149.7, 144.9, 141.1, 128.9, 128.4, 128.2, 126.3, 120.1, 115.4, 113.0, 111.5, 111.5, 60.2, 58.0, 56.0, 54.8, 45.0, 33.9, 17.7; MS (ESI) *m*/*z* 396.1938 (396.1939 calcd for $C_{25}H_{27}NO_2$, M + Na^+).

Minor product: **1-(*p*-Methoxyphenyl)-2-(*m*-methoxybenzyl)-3-phenylpyrrole.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.43 (m, 2 H), 7.32 (m, 2 H), 7.22–7.17 (m, 1 H), 7.08 (m, 1 H), 7.05 (d, *J* = 8.5 Hz, 2 H), 6.82–6.78 (m, 3 H), 6.66 (dd, *J* = 3.0, 8.0 Hz, 1 H), 6.51 (d, *J* = 8.0 Hz, 1 H), 6.47 (d, *J* = 3.0 Hz, 1 H), 6.46–6.44 (m, 1 H), 4.02 (s, 2 H), 3.80 (s, 3 H), 3.67 (s, 3 H); MS (ESI) *m*/*z* 392.1623 (392.1626 calcd for $C_{25}H_{23}NO_2$, M + Na^+).

Reaction of 4-Bromobiphenyl with *N*-(2-Cyclopent-2-enylethyl)-*p*-anisidine (eq 2). Reaction of 109 mg (0.5 mmol) of *N*-(2-cyclopent-2-enylethyl)-*p*-anisidine with 4-bromobiphenyl (148 mg, 0.65 mmol) and NaO*t*Bu (63 mg, 0.65 mmol) following the general procedure using P(*o*-tol)$_3$ (6.1 mg, 0.02 mmol) as ligand and a reaction temperature of 110 °C afforded a **6:7:2:1** mixture of **5**, **6**, **7**, and **8**. Purification of this material by flash

chromatography led to isolation of **5** (35 mg, 19%), **6** (60 mg, 32 %), and **7** (23 mg, 12 %). Compound **8** was isolated (for the purposes of characterization) in a separate experiment conducted following the general procedure using dppe as ligand which afforded a 2:1:2:4 ratio of **5**:**6**:**7**:**8**.

Biphenyl-4-yl-(2-cyclopent-2-eneylethyl)-4-methoxyphenylamine (5). White solid, m.p. 91–92 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.6 Hz, 2 H), 7.40–7.34 (m, 3 H), 7.24–7.20 (m, 1 H), 7.10 (d, *J* = 8.4 Hz, 2 H), 6.90 (d, *J* = 8.8 Hz, 2 H), 6.75 (d, *J* = 8.4 Hz, 2 H), 5.76–5.62 (m, 2 H), 3.81 (s, 3 H), 3.68 (t, *J* = 8.4 Hz, 2 H), 2.76–2.63 (m, 1 H), 2.40–2.20 (m, 2 H), 2.10–2.00 (m, 1 H), 1.85–1.73 (m, 1 H), 1.70–1.60 (m, 1 H), 1.48–1.38 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.7, 148.4, 141.1, 140.4, 134.3, 130.8, 130.2, 128.6, 127.9, 127.6, 126.3, 126.1, 115.1, 114.9, 55.5, 51.1, 43.3, 33.5, 32.0, 29.8; IR (film) 1505 cm^{-1}. MS(ESI) *m*/*z* 370.2160 (370.2171 calcd for $C_{26}H_{28}NO_2$, m + H$^+$).

(±)-(3a*R*,6*S*,6a*S*)-6-Biphenyl-4-yl-1-(4-methoxyphenyl)octahydrocyclopenta[*b*]pyrrole (6). White solid, m.p. 94–95 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48–7.45 (m, 2 H), 7.36 (t, *J* = 11.2 Hz, 2 H), 7.30–7.21 (m, 5 H), 6.51 (d, *J* = 12.4 Hz, 2 H), 6.24 (d, *J* = 12.0 Hz, 2 H), 4.11 (t, *J* = 10.4 Hz, 1 H), 3.60 (s, 3 H), 3.60–3.54 (m, 1 H), 3.21–3.18 (m, 2 H), 2.98–2.88 (m, 1 H), 2.20–2.10 (m, 1 H), 2.06–1.92 (m, 2 H), 1.90–1.75 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.6, 143.1, 141.2, 141.0, 138.5, 129.8, 128.5, 126.9, 126.7, 126.0, 113.9, 113.5, 68.1, 55.7, 51.2, 51.0, 44.0, 33.6, 31.1, 30.1; IR (film) 1508 cm^{-1}. MS(ESI) *m*/*z* 370.2169 (370.2171 calcd for $C_{26}H_{28}NO_2$, m + H$^+$).

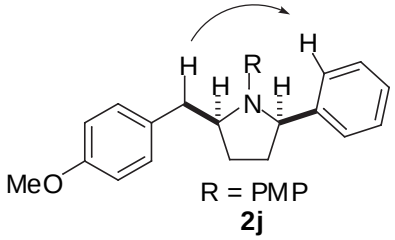
(±)-(3a*R*,5*R*,6*R*)-5-Biphenyl-4-yl-1-(4-methoxyphenyl)octahydrocyclopenta[*b*]pyrrole (7). White solid, m.p. 104–105 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 9.0 Hz, 2 H), 7.49 (d, *J* = 10.5 Hz, 2 H), 7.42 (t, *J* = 9.5 Hz, 2 H), 7.34–77.27 (m, 3 H), 6.84 (d, *J* = 11.0 Hz, 2 H), 6.62 (d, *J* = 11.5 Hz, 2 H), 4.20 (q, *J* = 10.5 Hz, 1 H), 3.76 (s, 3 H), 3.45–3.32 (m, 2 H), 3.23–3.14 (m, 1 H), 2.96–2.88 (m, 1 H), 2.67–2.60 (m, 1 H), 2.36–2.30 (m, 1 H), 2.18–2.08 (m, 1 H), 1.90–1.82 (m, 1 H), 1.61–1.47 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.0, 143.1, 142.2, 141.0, 139.1, 128.7, 127.3, 127.00, 126.98, 114.9, 113.8, 64.2, 55.9, 47.8, 45.9, 43.5, 40.8, 39.9, 30.5; IR (film) 1508 cm^{-1}. Anal calcd for $C_{26}H_{27}NO_2$: C, 84.51; H, 7.37; N, 3.79. Found: C, 84.25; H, 7.37; N, 3.69.

(±)-(3a*R*,6a*S*)-1-(4-Methoxyphenyl)-1,2,3,3a,4,6a-hexayhdrocyclopenta[*b*]pyrrole (8). Colorless oil, this material contained ca. 5% **6** as judged by ^{1}H NMR analysis. ^{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), 2.96–1.99 (m, 1 H), 2.64–2.58 (m, 1 H), 2.24–2.18 (m, 2 H), 1.74–1.67 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.1, 143.1, 131.4, 130.7, 115.0, 113.3, 70.9, 55.9, 48.1, 39.9, 38.0, 32.6; IR (film) 1510 cm^{-1}; MS (EI) *m*/*z* 215.1309 (215.1310 calcd for $C_{14}H_{17}NO$).

Assignment of Stereochemistry

2,5-Disubstituted Pyrrolidines **2i** and **2j**

The *cis* stereochemistry of the 2,5-disubstituted pyrrolidine product 2-(4-methoxybenzyl)-1-(4-methoxyphenyl)-5-phenylpyrrolidine (**2j**) was assigned on the basis of nOe signals between the *ortho* protons of the C5 phenyl group and one of the benzylic hydrogens on C1'as shown below.



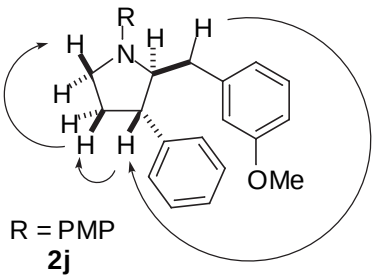
The *cis* stereochemistry of the 2,5-disubstituted pyrrolidine product **2i** was assigned based on analogy to the above example.

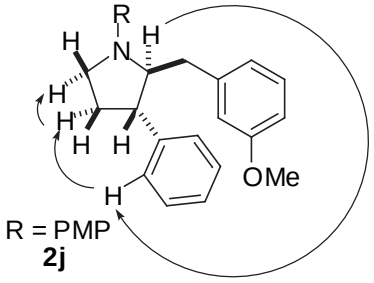
2,4-Disubstituted Pyrrolidine **2k**

The 2,4-disubstituted pyrrolidine **2k** was obtained as a 2:1 mixture of inseparable diastereomers. The major diastereomer has been assigned as *cis*-1-(4-Methoxyphenyl)-2-(4-methylbenzyl)-4-phenylpyrrolidine based on comparison of the relative ^{1}H NMR and ^{13}C NMR chemical shifts of this mixture of diastereomers to the related *cis* and *trans* isomers of the known, structurally similar 2-(3-methoxybenzyl)-4-phenyltetrahydrofuran.[ix]

2,3-Disubstituted Pyrrolidine **2l**

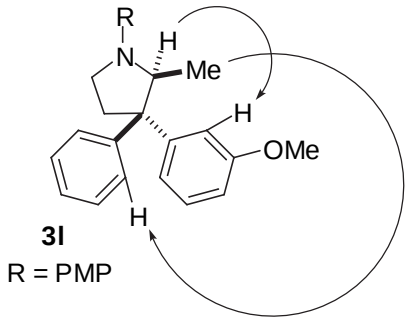
The *trans* stereochemistry of the 2,3-disubstituted pyrrolidine product 2-(3-methoxybenzyl)-1-(4-methoxyphenyl)-3-phenylpyrrolidine (**2l**) was assigned on the basis of nOe signals as shown below.





2-Methylpyrrolidine Regioisomers **3a–3l**

The stereochemistry of regioisomer **3l** was assigned on the basis of nOe signals as shown below. The nOe experiments were performed on a pure sample of **3l** that was isolated by preparative HPLC.

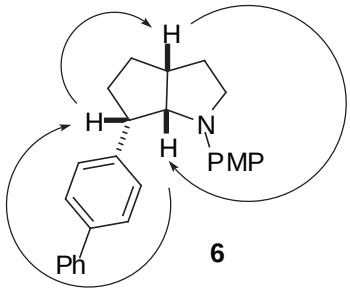


3l
R = PMP

The stereochemistry of other regioisomeric products **3a–3k** were assigned on the basis of analogy to **3l**.

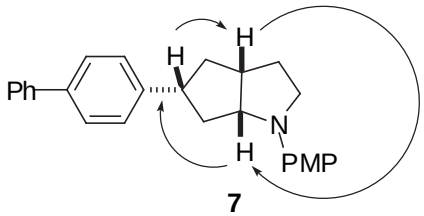
Pyrrolizidine regioisomers **6** and **7**

The stereochemistry of 6-biphenyl-4-yl-1-(4-methoxyphenyl)octahydrocyclopenta[*b*]pyrrole **(6)** was assigned on the basis of nOe signals as shown below.



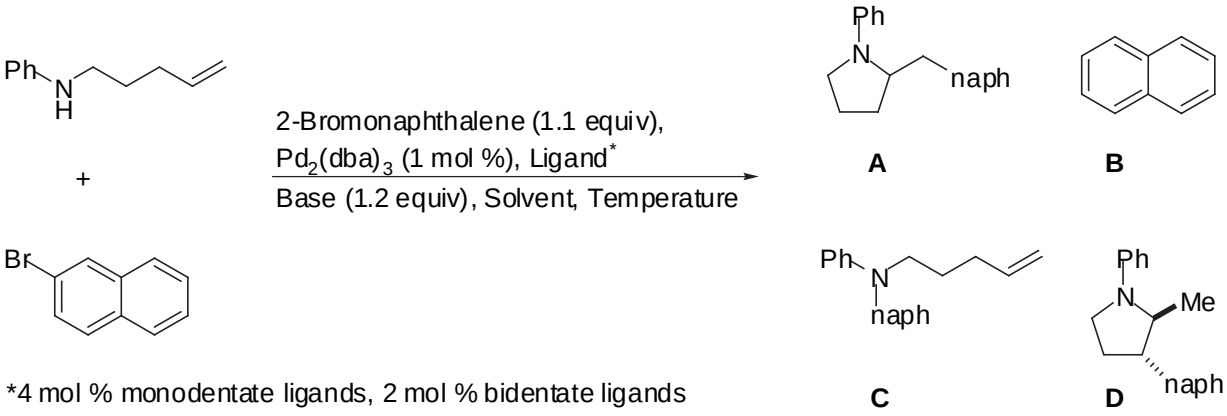
6

The stereochemistry of 5-biphenyl-4-yl-1-(4-methoxyphenyl)octahydrocyclopenta[*b*]pyrrole (**7**). was assigned on the basis of nOe signals as shown below.



7

Optimization of Reaction Conditions



*4 mol % monodentate ligands, 2 mol % bidentate ligands

Ligand	Base	Solvent	Temp.	A:B (GC)	A:C (GC)	A:D (GC)	GC Yield	Isolated Yield
P(*o*-tol)$_3$	KO*t*-Bu	Toluene	110 °C	2:1	>20:1	>15:1	73%	
Dppe	KO*t*-Bu	Toluene	110 °C	8:1	>20:1	15:1	100%	
Dppb	KO*t*-Bu	Toluene	110 °C	5:1	>20:1	14:1	94%	
Dppf	KO*t*-Bu	Toluene	110 °C	8:1	>20:1	17:1	81%	
2-(Dicyclohexyl-phosphino)-biphenyl	KO*t*-Bu	Toluene	110 °C	8:1	8:1	>20:1	80%	
Rac-BINAP	KO*t*-Bu	Toluene	110 °C	6:1	6:1	>10:1	65%	
DPEphos	KO*t*-Bu	Toluene	110 °C	10:1	>20:1	21:1	85%	
2-(Di-*t*-butyl-phosphino)-biphenyl	KO*t*-Bu	Toluene	110 °C	>20:1	1:20	N/A	<5%	
2-Dicyclohexyl-phosphino-2'-(*N*,*N*-dimethyl-amino)-biphenyl	KO*t*-Bu	Toluene	110 °C	15:1	3:2	>15:1	70%	
Dppp	KO*t*-Bu	Toluene	110 °C	5:1	>20:1	>20:1	60%	
DPEphos	NaO*t*-Bu	Toluene	110 °C	16:1	3:1	>15:1	64%	

2-(Diphenyl-phosphino)-2'-(*N*,*N*-dimethyl-amino) biphenyl	KO*t*-Bu	Toluene	110 °C	15:1	3:2	>15:1	55%	
DPEphos	K_2CO_3	Toluene	110 °C	No Rxn				
DPEphos	$K_3PO_4 \cdot H_2O$	Toluene	110 °C	No Rxn				
P(*o*-tol)$_3$	NaO*t*-Bu	Toluene	110 °C	3:1	>20:1	>20:1	76%	
Dppe	NaO*t*-Bu	Toluene	110 °C	14:1	>20:1	14:1	100%	
Dppf	NaO*t*-Bu	Toluene	110 °C	13:1	10:1	>20:1	72%	
Dppe	NaO*t*-Bu	Toluene	60 °C	19:1	>20:1	18:1	N/A	
Dppb	NaO*t*-Bu	Toluene	60 °C	26:1	194:1	25:1	100%	95%
P(*o*-tol)$_3$	NaO*t*-Bu	Toluene	60 °C	3:1	322:1	51:1	76%	60%
P(*o*-tol)$_3$	LiO*t*-Bu	Toluene	60 °C	Very Low Conversion				
P(*o*-tol)$_3$	NaO*t*-Bu	THF	60 °C	3:1	110:1	51:1	82%	
P(*o*-tol)$_3$	LiO*t*-Bu	THF	60 °C	2:1	179:1	>50:1	44%	
Dppm	NaO*t*-Bu	Toluene	60 °C	No Rxn				
Bis(diphenyl-phosphino) benzene	NaO*t*-Bu	Toluene	60 °C	2:1	1:7	N/A	N/A	

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