# Synthesis of Polycyclic Nitrogen Heterocycles via Alkene Aminopalladation/Carbopalladation Cascade Reactions

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**Supporting Information**

**Experimental procedures and characterization data for new compounds in Tables 1–2, and eq 1–2 (102 pages).**

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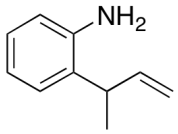
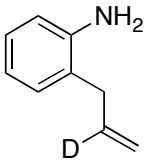
**General:** All reactions were carried out under an argon or nitrogen atmosphere in oven- or flame-dried glassware. All catalysts, reagents, and aryl bromides were obtained from commercial sources and were used without further purification. 2-Allylaniline and 4-methoxy-2-allylaniline were prepared according to published procedures.[1] Toluene, THF, ether, and dichloromethane were dried and purified using a GlassContour solvent purification system. Structural and stereochemical assignments were made on the basis of 2-D COSY, HSQC, and NOESY experiments. Ratios of diastereomers were determined by $^1$H NMR and/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, GC, and/or combustion analysis. The yields reported in the supporting information describe the result of a single experiment, whereas the yields reported in Tables 1–2 and eq 1–2 are average yields of two or more experiments. Thus, the yields reported in the supporting information may differ from those shown in Tables 1–2 and eq 1–2.

**Synthesis of Substrates**

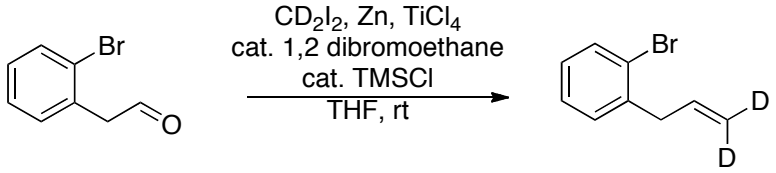



**2-(But-3-en-2-yl)aniline (S1).** A flame dried glass pressure tube equipped with a magnetic stirbar and a rubber septum was cooled under a stream of nitrogen and charged with a solution of *N*-(but-2-enyl)aniline[2] (1.37 g, 9.30 mmol) in xylenes (7.5 mL). The solution was cooled to 0 °C and $BF_3$•$OEt_2$ (1.62 mL, 13.9 mmol) was added slowly. The reaction mixture was warmed to rt and stirred for 15 min, then the tube was sealed with a Teflon screwcap stopper and placed in a 180 °C oil bath for 4 h. The mixture was then cooled to rt, the stopper was removed, and a solution of 1 M NaOH (10 mL) was added. The mixture was transferred to a separatory funnel, the layers were separated, and the aqueous layer was extracted with ethyl acetate (3 x 20 mL). The organic layers were combined, washed with brine (1 x 20 mL), dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography to afford 0.619 g (45%) of the title compound. $^1$H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, *J* = 7.6 Hz, 1 H), 7.03 (t, *J* = 7.6 Hz, 1 H), 6.76 (t, *J* = 7.6 Hz, 1 H), 6.65 (d, *J* = 7.6 Hz, 1 H), 5.96–5.88(m, 1 H), 5.08–5.03 (m, 2 H), 3.66 (s, br, 2 H), 3.45 (p, *J* = 6.8 Hz, 1 H), 1.37 (d, *J* = 6.8 Hz, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 144.3, 142.1, 128.8, 127.1, 127.0, 118.9, 116.2, 113.8, 38.2, 18.7; IR (film) 3448, 3366, 1621 $cm^{-1}$. MS (EI) 147.1050 (147.1048 calcd for $C_{10}H_{13}N$).



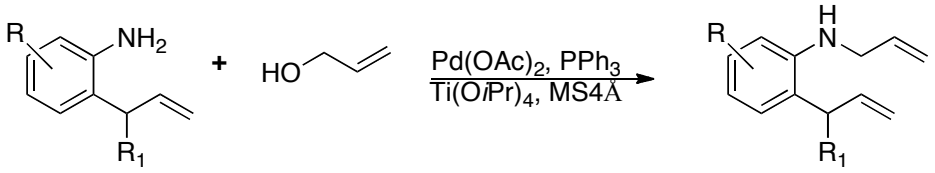

**2-(2-Deuterioallyl)aniline (S2).** The procedure described above for the aza-Claisen rearrangement of *N*-(but-2-enyl)aniline to **S1** was employed for the reaction of *N*-(2-deuterioallyl)aniline[3] (541 mg, 4.0 mmol) with $BF_3$•$OEt_2$ (0.69 mL, 6.0 mmol) in 4 mL of xylenes. This procedure afforded 331 mg (62%) of the title compound as a yellow oil with 91% D incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.07–7.02 (m, 2 H), 6.73 (t, *J* = 11.2 Hz, 1 H), 6.66 (d, *J* = 7.6 Hz, 1 H), 5.11–5.08 (m, 2 H), 3.64 (s, br, 2 H), 3.29 (s, 2 H); $^{13}$C NMR (100

MHz, $CDCl_3$) δ 144.7, 135.6 (t, $J$ = 23.8 Hz), 130.1, 127.5, 123.9, 118.8, 115.9, 115.8, 36.3; IR (film) 3449, 3370, 1621 $cm^{-1}$. MS (EI) 134.0957 (134.0954 calcd for $C_9H_{10}DN$).

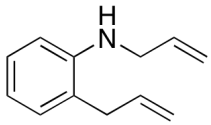



**1-Bromo-2-(3,3-dideuterioallyl)benzene (S3).** Zinc activation procedure:[4] A flame dried round bottom flask equipped with a magnetic stirbar was charged with Zn[5] (1.79 g, 27.5 mmol) and suspended in 30 ml of THF. Neat 1,2-dibromoethane (0.08 mL, 0.96 mmol) was added and the reaction mixture was heated to 60 °C for 2 min. The resulting mixture was cooled to room temperature, neat TMSCl (0.10 mL, 0.82 mmol) was added, and the stirring was continued for 15 min at rt.

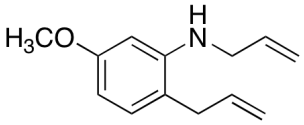
Carbonyl methylenation procedure:[6] Neat $CD_2I_2$ (4.1 g, 15.3 mmol) was added to the suspension of activated zinc, and the solution turned grey. The mixture was stirred at rt for 30 min, then $TiCl_4$ (0.42 mL, 3.82 mmol) was added to afford a brown reaction mixture. This mixture was stirred at rt for 30 min, then 2-(2-bromophenyl)acetaldehyde (761 mg, 3.82 mmol) was added. The mixture was stirred at rt for 20 min, at which time TLC analysis indicated the aldehyde had been completely consumed. Aqueous 3 M HCl (30 mL) was added and the mixture was transferred to a separatory funnel. The solution was extracted with ethyl acetate (3 x 30 mL), then the combined organic layers were washed with saturated aqueous $NaHCO_3$ (1 x 30 mL), and brine (1 x 30 mL). The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo* to afford a red oil. The crude product was purified by flash chromatography to afford 368 mg (48%) of the title compound as a yellow oil. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.51 (d, $J$ = 7.6 Hz, 1 H), 7.24–7.18 (m, 2 H), 7.06–7.02 (m, 1 H), 5.96–5.91 (m, 1 H), 3.48 (d, $J$ = 6.8 Hz, 2 H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 139.4, 135.2, 132.7, 130.3, 127.7, 127.4, 124.5, 115.9 (p, $J$ = 23.7 Hz), 40.0; IR (film) 3008, 1566, 1468, 1025 $cm^{-1}$. MS (EI) 198.0015 (198.0013 calcd for $C_9H_7D_2Br$).



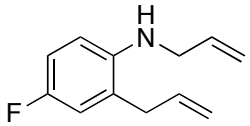

**General Procedure 1: Pd-catalyzed synthesis of *N*-allylanilines.**[2] A flame-dried Schlenk tube equipped with a magnetic stirbar was cooled under a stream of nitrogen and charged with MS4Å (200 mg/mmol substrate), $Pd(OAc)_2$ (1 mol %), $PPh_3$ (4 mol %), $Ti(OiPr)_4$ (25 mol %), the appropriate aniline derivative (1 equiv), allyl alcohol (1.2 equiv), and benzene (0.2 M). The resulting mixture was heated to 60 °C for 2–3.5 h until the starting material was consumed as judged by TLC analysis. The mixture was cooled to room temperature and quenched with 1 M NaOH (10–15 mL). The reaction mixture was transferred to a separatory funnel and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was then purified by flash chromatography.



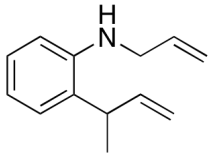

***N*,2-Diallylaniline (1).**[7] General procedure 1 was employed for the alkylation of 2-allylaniline[1] (2.04 g, 15.3 mmol) with allyl alcohol (1.07 g, 18.4 mmol), $Pd(OAc)_2$ (34.3 mg, 0.15 mmol), $PPh_3$ (161 mg, 0.61 mmol), $Ti(OiPr)_4$ (1.16 mL, 3.82 mmol), and MS4Å (3.06 g) in 76 mL of benzene. This procedure afforded 2.17 g (82%) of the title compound as a light yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, $J$ = 8.0 Hz, 1 H), 7.07 (d, $J$ = 7.6 Hz, 1 H), 6.72 (t, $J$ = 7.6 Hz, 1 H), 6.65 (d, $J$ = 8.4 Hz, 1 H), 6.04–5.92 (m, 2 H), 5.28 (d, $J$ = 10.8 Hz, 1 H), 5.20–5.10 (m, 3 H), 3.88 (s, br, 1 H), 3.81 (d, $J$ = 7.2 Hz, 2 H), 3.32 (d, $J$ = 6.0 Hz, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 146.1, 136.0, 135.4, 129.8, 127.6, 123.6, 117.3, 116.3, 116.0, 110.8, 46.3, 36.5; IR (film) 3433, 1509 cm$^{-1}$. MS (ESI) 174.1285 (174.1283 calcd for $C_{12}H_{15}N$, M + H$^+$).



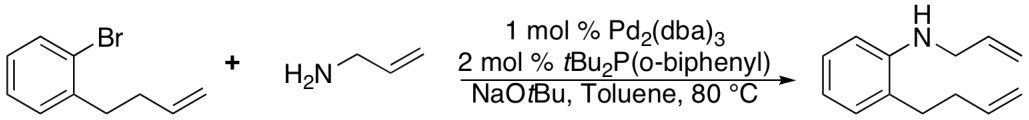
***N*,2-Diallyl-5-methoxyaniline (16).** General procedure 1 was employed for the alkylation of 2-allyl-5-methoxyaniline[1] (700 mg, 4.3 mmol) with allyl alcohol (299 mg, 5.1 mmol), $Pd(OAc)_2$ (9.6 mg, 0.043 mmol), $PPh_3$ (45.1 mg, 0.17 mmol), $Ti(O\textit{i}Pr)_4$ (0.33 mL, 1.07 mmol), and MS4Å (860 mg) in 22 mL of benzene. This procedure afforded 705 mg (81%) of the title compound as a clear oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 6.95 (d, *J* = 8.0 Hz, 1 H), 6.25 (d, *J* = 8.4 Hz, 1 H), 6.22 (s, 1 H), 6.00–5.88 (m, 2 H), 5.27 (dd, *J* = 2.4, 14.8 Hz, 1 H), 5.17 (dd, *J* = 1.6, 8.0 Hz, 1 H), 5.12–5.07 (m, 2 H), 3.89 (s, br, 1 H), 3.78–3.75 (m, 5 H), 2.25 (d, *J* = 6.4 Hz, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 159.7, 147.2, 136.5, 135.2, 130.3, 116.4, 116.1, 115.9, 101.1, 98.0, 55.1, 46.3, 35.9; IR (film) 3435, 3054, 1519 $cm^{-1}$. MS (EI) 203.1317 (203.1310 calcd for $C_{13}H_{17}NO$).



***N*,2-Diallyl-4-fluoroaniline (17).** General procedure 1 was used for the alkylation of 2-allyl-4-fluoroaniline[8] (960 mg, 6.3 mmol) with allyl alcohol (442 mg, 7.6 mmol), $Pd(OAc)_2$ (14.1 mg, 0.063 mmol), $PPh_3$ (66.1 mg, 0.25 mmol), $Ti(O\textit{i}Pr)_4$ (0.48 mL, 1.58 mmol), and MS4Å (1.26 g) in 30 mL of benzene. This procedure afforded 774 mg (64%) of the title compound as a clear oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 6.83–6.76 (m, 2 H), 6.51 (dd, *J* = 4.4, 8.8 Hz, 1 H), 5.97–5.84 (m, 2 H), 5.22 (d, *J* = 15.6 Hz, 1 H), 5.15–5.04 (m, 3 H), 3.72 (s, 2 H), 3.62 (s, br, 1 H), 3.23 (d, *J* = 4.8 Hz, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.6 (d, *J* = 234.8 Hz), 142.2, 135.3, 135.1, 125.4 (d, *J* = 6.9 Hz), 116.8, 116.4 (d, *J* = 22.2 Hz), 116.1, 113.3 (d, *J* = 21.8 Hz), 111.5 (d, *J* = 7.7 Hz), 46.8, 36.2; IR (film) 3428, 3080, 1511 $cm^{-1}$. MS (EI) 191.1113 (191.1110 calcd for $C_{12}H_{14}FN$).

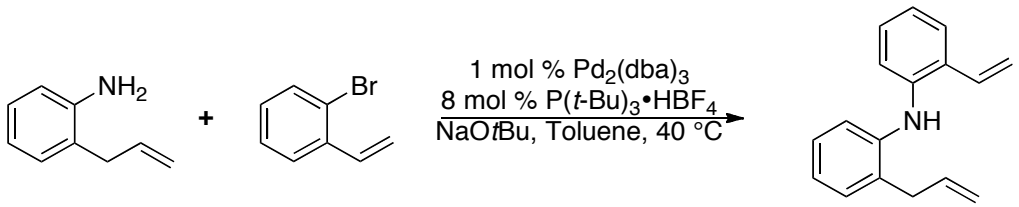


***N*-Allyl-2-(but-3-en-2-yl)aniline (18).** General procedure 1 was used for the alkylation of **S1** (430 mg, 2.9 mmol) with allyl alcohol (203 mg, 3.5 mmol), $Pd(OAc)_2$ (6.5 mg, 0.029 mmol), $PPh_3$ (30.4 mg, 0.12 mmol), $Ti(O\textit{i}Pr)_4$ (0.22 mL, 0.72 mmol), and MS4Å (580 mg) in 15 mL of benzene. This procedure afforded 469 mg (86%) of the title compound as a clear oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.14–7.09 (m, 2 H), 6.73 (t, *J* = 7.6 Hz, 1 H), 6.62 (d, *J* = 8.0 Hz, 1 H), 6.00–5.87 (m, 2 H), 5.25 (d, *J* = 17.2 Hz, 1 H), 5.16–5.04 (m, 3 H), 3.93 (s, br, 1 H), 3.76 (s, 2 H), 3.45 (p, *J* = 6.8 Hz, 1 H), 1.39 (d, *J* = 6.8 Hz, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 144.5, 142.3, 135.4, 128.4, 127.2, 126.7, 117.4, 116.0, 113.9, 111.2, 46.4, 37.9, 18.8; IR (film) 3430, 1508 cm$^{-1}$. MS (EI) 187.1370 (187.1361 calcd for $C_{13}H_{17}N$).

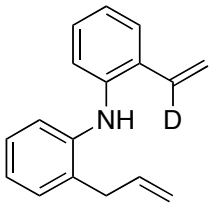



***N*-Allyl-2-(but-3-enyl)aniline (19).**[9] A flame-dried Schlenk tube equipped with a magnetic stirbar was cooled under a stream of nitrogen and charged with $Pd_2(dba)_3$ (42.2 mg, 0.046 mmol), 2-(di-*tert*-butylphosphino)biphenyl (27.5 mg, 0.092 mmol), and sodium *tert*-butoxide (620 mg, 6.45 mmol). The tube was purged with nitrogen, then toluene (9 mL), 1-bromo-2-(but-3-enyl)benzene[10] (973 mg, 4.61 mmol), and allylamine (263 mg, 4.61 mmol) were added. The resulting mixture was heated to 80 °C for 14 h, at which time the starting material had been completely consumed as judged by TLC analysis. The mixture was cooled to room temperature, quenched with saturated aqueous ammonium chloride (5 mL), and transferred to a separatory funnel. The mixture was extracted with EtOAc (3 x 20 mL), and the combined organic layers were washed with brine (20 mL), dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography to afford 667 mg (84%) of the title compound as an orange oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, *J* = 8.0 Hz, 1 H), 7.09 (d, *J* = 7.6 Hz, 1 H), 6.74 (t, *J* = 7.6 Hz, 1 H), 6.67 (d, *J* = 8.4 Hz, 1 H), 6.07–5.90 (m, 2 H), 5.33 (d, *J* = 15.6 Hz, 1 H), 5.22 (d, *J* = 8.8 Hz, 1 H), 5.13 (d, *J* = 17.1 Hz, 1 H), 5.05 (d, *J* = 10.0 Hz, 1 H), 3.84 (s, 2 H), 3.76 (s, 1 H), 2.62 (t, *J* = 7.6 Hz, 2 H), 2.45–2.40 (m, 2 H); $^{13}$C NMR (100

MHz, $CDCl_3$) δ 145.4, 138.1, 135.5, 128.9, 127.1, 125.5, 117.2, 116.1, 115.0, 110.6, 46.5, 32.6, 30.6; IR (film) 3437, 3054, 1509 $cm^{-1}$. MS (EI) 187.1364 (187.1361 calcd for $C_{13}H_{17}N$).

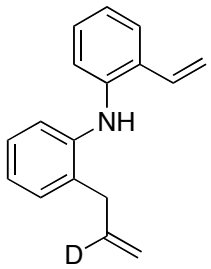



**2-Allyl-*N*-(2-vinylphenyl)aniline (30).** A flame-dried Schlenk tube equipped with a magnetic stirbar was cooled under a stream of nitrogen and charged with 2-allylaniline (1.50 g, 11.2 mmol), 2-bromostyrene (2.06 g, 11.2 mmol), sodium *tert*-butoxide (1.62 g, 16.9 mmol), $Pd_2(dba)_3$ (103 mg, 0.11 mmol), $P(tBu)_3{\cdot}HBF_4$ (261 mg, 0.90 mmol) and toluene (15 mL). The resulting mixture was heated to 40 °C for 14 h, at which time the starting material had been completely consumed as judged by TLC analysis. The mixture was cooled to room temperature, quenched with saturated aqueous ammonium chloride (5 mL), and transferred to a separatory funnel. The mixture was extracted with EtOAc (3 x 20 mL), and the combined organic layers were washed with brine (20 mL), dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography to afford 1.72 g (89%) of the title compound as light yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, $J$ = 7.6 Hz, 1 H), 7.22–7.15 (m, 3 H), 7.11–7.08 (m, 2 H), 7.01–6.93 (m, 2 H), 6.84 (dd, $J$ = 11.2, 17.2 Hz, 1 H), 6.08–5.98 (m, 1 H), 5.71 (d, $J$ = 16.0 Hz, 2 H), 5.32 (d, $J$ = 11.2 Hz, 1 H), 5.21 (d, $J$ = 7.2 Hz, 1 H), 5.15 (d, $J$ = 17.2 Hz, 1 H), 3.43 (d, $J$ = 6.0 Hz, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 142.3, 140.8, 136.4, 132.8, 130.6, 129.0, 128.5, 128.3, 127.4, 127.2, 121.6, 121.3, 119.1, 118.2, 116.5, 116.2, 36.9; IR (film) 3422, 2961, 1459 $cm^{-1}$. MS (EI) 235.1352 (235.1361 calcd for $C_{17}H_{17}N$).

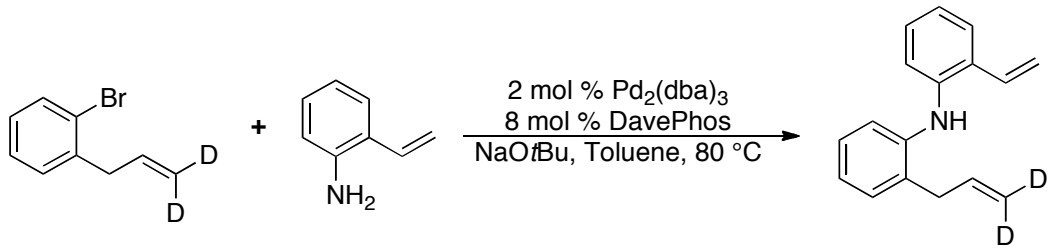



**2-Allyl-*N*-[2-(1-deuteriovinyl)phenyl]aniline (33a)**. The procedure described above for the synthesis of **30** was employed for the coupling of α-D-*o*-bromostyrene[11] (512 mg, 2.77 mmol) with 2-allylaniline (383 mg, 2.87 mmol), sodium *tert*-butoxide (413 mg, 4.31 mmol), $Pd_2(dba)_3$

(26.3 mg, 0.029 mmol), P(*t*Bu)$_3$·HBF$_4$ (66.6 mg, 0.23 mmol) and toluene (5 mL). The crude product was purified by flash chromatography to afford 494 mg (77%) of the title compound as a clear oil with 96% D incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.6 Hz, 1 H), 7.19–7.12 (m, 3 H), 7.06 (t, *J* = 9.2 Hz, 2 H), 6.96 (t, *J* = 7.6 Hz, 1 H), 6.92 (t, *J* = 7.2 Hz, 1 H), 5.99 (ddt, *J* = 5.9, 10.4, 16.4 Hz, 1 H), 5.66 (d, *J* = 3.4 Hz, 1 H), 5.64 (s, br, 1 H), 5.28 (s, 1 H), 5.18 (d, *J* = 9.9 Hz, 1 H), 5.12 (d, *J* = 17.2 Hz, 1 H), 3.40 (d, *J* = 5.9 Hz, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 142.3, 140.7, 136.4, 132.4 (t, *J* = 23.4 Hz), 130.6, 128.9, 128.6, 128.3, 127.4, 127.1, 121.7, 121.3, 119.1, 118.2, 116.5, 116.0, 36.9; IR (film) 3412, 3075, 1454 cm$^{-1}$. MS (EI) 236.1422 (236.1424 calcd for $C_{17}H_{16}DN$).

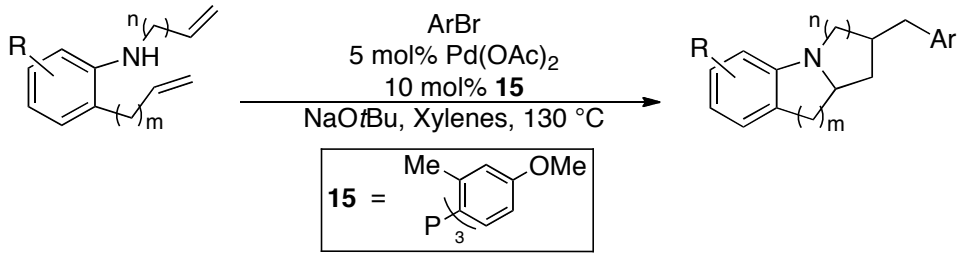



**2-(2-Deuterioallyl)-*N*-(2-vinylphenyl)aniline (33b).** The procedure described above for the synthesis of **30** was employed for the coupling of 2-bromostyrene (423 mg, 2.29 mmol) with **S2** (309 mg, 2.29 mmol), sodium *tert*-butoxide (330 mg, 3.43 mmol), $Pd_2(dba)_3$ (20.9 mg, 0.023 mmol), P(*t*Bu)$_3$·HBF$_4$ (53.1 mg, 0.18 mmol) and toluene (4 mL). The crude product was purified by flash chromatography to afford 400 mg (74%) of the title compound as a clear oil with 91% D incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.6 Hz, 1 H), 7.19–7.11 (m, 3 H), 7.06 (t, *J* = 7.2 Hz, 2 H), 6.97–6.89 (m, 2 H), 6.80 (dd, *J* = 11.2, 17.6 Hz, 1 H), 5.66 (dd, *J* = 1.6, 17.2 Hz, 1 H), 5.62 (s, 1 H), 5.28 (dd, *J* = 1.2, 10.8 Hz, 1 H), 5.16 (d, *J* = 1.6 Hz, 1 H), 5.10 (d, *J* = 1.6 Hz, 1 H), 3.39 (s, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 142.3, 140.7, 136.1 (t, *J* = 23.7 Hz), 132.8, 130.5, 129.0, 128.5, 128.3, 127.4, 127.2, 121.6, 121.3, 119.1, 118.3, 116.3, 116.2, 36.7; IR (film) 3411, 3073, 1455 cm$^{-1}$. MS (ESI) 237.1494 (237.1502 calcd for $C_{17}H_{16}DN$, M + H$^+$).

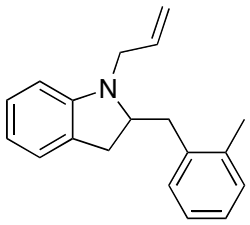



**2-(3,3-Dideuterioallyl)-*N*-(2-vinylphenyl)aniline (33c).** A flame-dried Schlenk tube equipped with a magnetic stirbar was cooled under a stream of nitrogen and charged with 2-vinylaniline (221 mg, 1.85 mmol), **S3** (368 mg, 1.85 mmol), sodium *tert*-butoxide (249 mg, 2.59 mmol), $Pd_2(dba)_3$ (33.8 mg, 0.037 mmol), DavePhos (58.2 mg, 0.15 mmol) and 5 mL toluene (5 mL). The resulting mixture was heated to 80 °C for 1 h, at which time the starting material had been completely consumed as judged by TLC analysis. The mixture was cooled to room temperature, quenched with saturated aqueous ammonium chloride (3 mL), and transferred to a separatory funnel. The mixture was extracted with EtOAc (3 x 10 mL) and dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography to afford 256 mg (58%) of the title compound (98% D incorporation) as a light yellow oil. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, $J$ = 7.5 Hz, 1 H), 7.19–7.11 (m, 3 H), 7.06 (t, $J$ = 8.5 Hz, 2 H), 6.95 (t, $J$ = 7.5 Hz, 1 H), 6.91 (t, $J$ = 7.6 Hz, 1 H), 6.79 (dd, $J$ = 10.5, 17.5 Hz, 1 H), 5.97 (s, br, 1 H), 5.66 (dd, $J$ = 1.5, 17.5 Hz, 1 H), 5.63 (s, br, 1 H), 5.27 (dd, $J$ = 1.5, 11.0 Hz, 1 H), 3.39 (d, $J$ = 5.9 Hz, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 142.3, 140.7, 136.2, 132.7, 130.5, 129.0, 128.5, 128.3, 127.3, 127.1, 121.6, 121.3, 119.0, 118.2, 116.2, 36.8 (one carbon signal is absent due to incidental equivalence); IR (film) 3412, 2924, 1456 cm$^{-1}$. MS (EI) 237.1488 (237.1487 calcd for $C_{17}H_{15}D_2N$).

**Synthesis and Characterization of Heterocyclic Products**

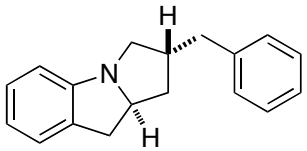



**General Procedure 2: Synthesis of polycyclic nitrogen heterocycles via Pd-catalyzed cascade cyclization.** A flame-dried Schlenk tube equipped with a magnetic stir bar was cooled under a stream of nitrogen and charged with $Pd(OAc)_2$ (5 mol %), tri(*p*-methoxy-*o*-tolyl)phosphine (**15**)[12] (10 mol %), and sodium *tert*-butoxide (1.5 equiv). The tube was purged with nitrogen, then a solution of amine substrate (1 equiv) and aryl halide (1.5 equiv) in xylenes (0.4 M substrate concentration) was added via syringe. The resulting mixture was heated to 125 °C until the starting material had been consumed as judged by GC analysis (ca. 14 h). The mixture was cooled to room temperature, saturated aqueous ammonium chloride (3 mL) was added, and the resulting mixture was transferred to a separatory funnel. The mixture was extracted with ethyl acetate (3 x 5 mL), the organic layers were combined, washed with brine (5 mL), dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was then purified by flash chromatography.

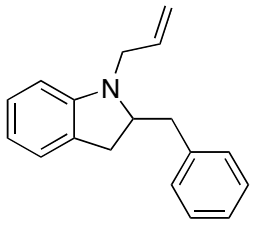


**1-Allyl-2-(2-methylbenzyl)indoline (4, R = allyl).** General procedure 2 was used for the reaction of **1** (40 mg, 0.23 mmol) with 2-bromotoluene (58 mg, 0.34 mmol), sodium *tert*-butoxide (33.2 mg, 0.34 mmol), $Pd(OAc)_2$ (2.6 mg, 0.011 mmol), and ligand **15** (9.1 mg, 0.023 mmol) in xylenes (1 mL). The crude product was formed as a ca. 3:1 mixture of monocyclized to dicyclized products as judged by $^1$H NMR analysis. Purification by flash chromatography afforded 44 mg (72%) of the monocyclized adduct as a yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.13–7.04 (m, 4 H), 6.96 (t, $J$ = 7.6 Hz, 1 H), 6.91 (d, $J$ = 7.2 Hz, 1 H), 6.55 (t, $J$ = 7.2 Hz, 1 H), 6.39 (d, $J$ = 7.6 Hz, 1 H), 5.85–5.78 (m, 1 H), 5.20 (dd, $J$ = 1.6, 16.0 Hz, 1 H), 5.11 (dd, $J$ =

1.6, 8.8 Hz, 1 H), 3.85 (dd, *J* = 4.4, 16.4 Hz, 1 H), 3.83–3.76 (m, 1 H), 3.60 (dd, *J* = 7.2, 16.4 Hz, 1 H), 3.14 (dd, *J* = 4.4, 13.2, 1 H), 2.84 (dd, *J* = 8.4, 15.6 Hz, 1 H), 2.66 (dd, *J* = 8.8, 16.0 Hz, 1 H), 2.61 (dd, *J* = 9.2, 13.2 Hz, 1 H), 2.25 (s, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 151.9, 136.9, 136.2, 134.2, 130.3, 130.0, 128.6, 127.3, 126.4, 125.9, 124.2, 117.6, 117.1, 107.2, 64.0, 49.7, 37.5, 34.9, 19.7; IR (film) 3022, 2926, 1698, 1606, 1461, 1238, 1155, 919, 743 cm$^{-1}$. MS (ESI) 264.1756 (264.1752 calcd for $C_{19}H_{21}N$, M + $H^+$).

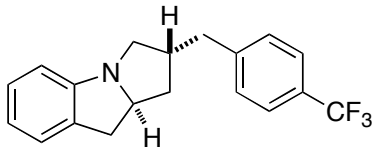



**(2*R*,9a*S*)-2-Benzyl-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]indole (12).** General procedure 2 was used for the reaction of **1** (70 mg, 0.40 mmol) with bromobenzene (95 mg, 0.60 mmol), sodium *tert*-butoxide (57.6 mg, 0.60 mmol), $Pd(OAc)_2$ (4.5 mg, 0.020 mmol), and ligand **15** (15.8 mg, 0.040 mmol) in xylenes (1 mL). The crude product was formed as a 4:1 mixture of diastereomers with 5:1 selectivity for dicyclization:monocyclization as judged by $^1$H NMR analysis. Purification by flash chromatography afforded 51 mg (51%) of the title compound as a yellow oil with 14:1 dr. Data are for the major isomer. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.29–7.26 (m, 2 H), 7.20–7.15 (m, 3 H), 7.09–7.04 (m, 2 H), 6.73 (t, *J* = 7.2 Hz, 1 H), 6.57 (d, *J* = 7.6 Hz, 1 H), 4.17–4.10 (m, 1 H), 3.38 (dd, *J* = 6.8, 11.2 Hz, 1 H), 3.20 (dd, *J* = 9.2, 16.0 Hz, 1 H), 3.06 (dd, *J* = 6.4, 11.2 Hz, 1 H), 2.86 (dd, *J* = 3.2, 16.0 Hz, 1 H), 2.70 (d, *J* = 7.6 Hz, 2 H), 2.42–2.36 (m, 1 H), 1.74 (ddd, *J* = 5.2, 7.6, 12.8 Hz, 1 H), 1.55 (dt, *J* = 7.9, 16.0 Hz, 1 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 154.2, 140.9, 130.3, 128.8, 128.4, 127.5, 125.9, 124.7, 119.5, 111.3, 63.5, 58.3, 40.2, 40.1, 37.7, 35.2; IR (film) 3023, 1602, 1479 cm$^{-1}$. MS (EI) 249.1513 (249.1518 calcd for $C_{18}H_{19}N$).




**1-Allyl-2-benzylindoline (13).** For purposes of characterization, monocyclized product **13** was isolated from the reaction of **1** (100 mg, 0.58 mmol) with bromobenzene (182 mg, 1.15 mmol),

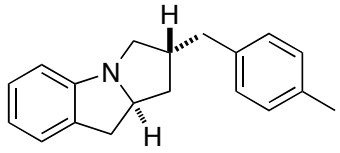
sodium *tert*-butoxide (83.6 mg, 0.87 mmol), $Pd(OAc)_2$ (6.5 mg, 0.029 mmol), in xylenes (2 mL) according to general procedure 2 except nixantphos (15.9 mg, 0.029 mmol) was used in place of ligand **15**. This procedure afforded the title compound (31 mg, 22 %) as a colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.2 Hz, 2 H), 7.22–7.19 (m, 3 H), 7.04 (t, *J* = 7.6 Hz, 1 H), 6.98 (d, *J* = 7.2 Hz, 1 H), 6.62 (t, *J* = 7.2 Hz, 1 H), 6.46 (d, *J* = 7.6 Hz, 1 H), 5.93–5.83 (m, 1 H), 5.29 (dd, *J* = 1.6, 17.2 Hz, 1 H), 5.20 (dd, *J* = 1.6, 10.4 Hz, 1 H), 3.94–3.82 (m, 2 H), 3.69 (dd, *J* = 7.6, 16.4 Hz, 1 H), 3.18 (dd, *J* = 4.0, 13.2 Hz, 1 H), 2.91 (dd, *J* = 8.4, 15.6 Hz, 1 H), 2.75–2.66 (m, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 152.0, 138.7, 134.2, 129.2, 128.6, 128.4, 127.3, 126.2, 124.2, 117.5, 117.0, 107.1, 65.5, 49.7, 40.2, 34.8; IR (film) 3026, 2921, 1606, 1483, 1238 $cm^{-1}$. MS (ESI) 250.1599 (250.1596 calcd for $C_{18}H_{19}N$, $M + H^+$).



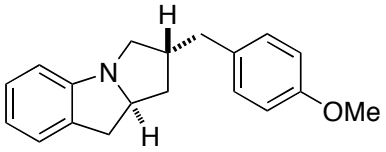

**(2*R*,9a*S*)-2-[4-(Trifluoromethyl)benzyl]-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]indole (20).** General procedure 2 was used for the reaction of **1** (50 mg, 0.29 mmol) with 4-bromobenzotrifluoride (97 mg, 0.43 mmol), sodium *tert*-butoxide (41.7 mg, 0.43 mmol), $Pd(OAc)_2$ (3.2 mg, 0.015 mmol), and ligand **15** (11.4 mg, 0.029 mmol) in xylenes (1 mL). The crude product was formed as a 5:1 mixture of diastereomers with 10:1 selectivity for dicyclization:monocyclization as judged by $^1$H NMR analysis. Purification by flash chromatography afforded 45 mg (46%) of the title compound as a red oil with >20:1 dr. In addition, a small amount of the minor (cis) diastereomer (4 mg, 4 %) was also isolated.

**Major (trans) diastereomer:** $^1$H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2 H), 7.26 (d, *J* = 8.0 Hz, 2 H), 7.08 (t, *J* = 7.6 Hz, 1 H), 7.02 (d, *J* = 7.2 Hz, 1 H), 6.75 (t, *J* = 7.6 Hz, 1 H), 6.57 (d, *J* = 7.6 Hz, 1 H), 4.17–4.10 (m, 1 H), 3.39 (dd, *J* = 6.8, 11.2 Hz, 1 H), 3.21 (dd, *J* = 9.6, 16.0 Hz, 1 H), 3.05 (dd, *J* = 6.4, 11.6 Hz, 1 H), 2.87 (dd, *J* = 3.2, 16.4 Hz, 1 H), 2.76 (d, *J* = 8.0 Hz, 2 H), 2.45–2.40 (m, 1 H), 1.76–1.70 (m, 1 H), 1.61–1.54 (m, 1 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 154.0, 145.0, 130.2, 129.0, 127.6, 126.9 (q, *J* = 268 Hz), 125.3 (q, *J* = 3.7 Hz), 124.8, 119.7, 111.3, 63.5, 58.2, 39.9, 39.8, 37.6, 35.2 (one carbon signal is absent due to incidental equivalence); IR (film) 3054, 1421 $cm^{-1}$. MS (EI) 317.1378 (317.1391 calcd for $C_{19}H_{18}F_3N$).

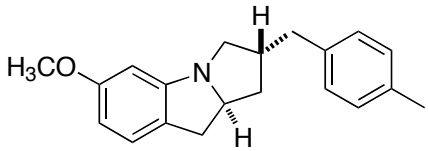
**Minor (cis) diastereomer:** $^1$H NMR (400 MHz, $C_6D_6$) δ 7.32 (d, *J* = 7.9 Hz, 2 H), 7.15 (t, *J* = 7.9 Hz, 1 H), 7.04 (d, *J* = 7.2 Hz, 1 H), 6.83 (t, *J* = 8.0 Hz, 1 H), 6.65 (d, *J* = 7.9 Hz, 2 H), 6.55 (d, *J* = 7.9 Hz, 1 H), 3.71–3.64 (m, 1 H), 3.33 (dd, *J* = 7.6, 9.9 Hz, 1 H), 2.90 (dd, *J* = 9.6, 15.9 Hz, 1 H), 2.63 (dd, *J* = 2.8, 15.9 Hz, 1 H), 2.51 (dd, *J* = 8.4, 9.9 Hz, 1 H), 2.18–2.14 (m, 1 H), 2.10–1.98 (m, 2 H), 1.29 (dt, *J* = 5.6, 11.2 Hz, 1 H), 0.67 (m, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 154.9, 144.9, 129.5, 129.1, 128.8, 127.7, 127.5 (q, *J* = 168.6 Hz), 125.3 (q, *J* = 3.5 Hz), 124.9, 119.4, 110.9, 65.4, 58.4, 42.5, 40.1, 38.3, 33.6; IR (film) 3059, 1482 cm$^{-1}$. MS (ESI) 318.1459 (318.1470 calcd for $C_{19}H_{18}F_3N$, M + H$^+$).




**(2*R*,9a*S*)-2-(4-Methylbenzyl)-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]indole (21).** General procedure 2 was used for the reaction of **1** (80 mg, 0.46 mmol) with 4-bromotoluene (118 mg, 0.69 mmol), sodium *tert*-butoxide (66.3 mg, 0.69 mmol), $Pd(OAc)_2$ (5.2 mg, 0.023 mmol), and ligand **15** (18.2 mg, 0.046 mmol) in xylenes (1 mL). The crude product was formed as a 10:1 mixture of diastereomers with 3:1 selectivity for dicyclization:monocyclization as judged by $^1$H NMR analysis. Purification by flash chromatography afforded 80 mg (66%) of the title compound as an orange oil with 10:1 dr. Data are for the major isomer. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.08–7.02 (m, 6 H), 6.72 (t, *J* = 6.8 Hz, 1 H), 6.55 (d, *J* = 8.0 Hz, 1 H), 4.15–4.08 (m, 1 H), 3.36 (dd, *J* = 7.2, 11.6 Hz, 1 H), 3.18 (dd, *J* = 9.6, 16 Hz, 1 H), 3.05 (dd, *J* = 6.4, 11.2 Hz, 1 H), 2.84 (dd, *J* = 2.8, 16 Hz, 1 H), 2.65 (d, *J* = 8.0 Hz, 2 H), 3.39–2.33 (m, 1 H), 2.30 (s, 3 H), 1.72 (ddd, *J* = 5.2, 7.2, 12.4 Hz, 1 H), 1.54 (dt, *J* = 8.4, 16.4 Hz, 1 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 154.2, 137.8, 135.4, 130.3, 129.0, 128.6, 127.5, 124.7, 119.5, 111.3, 63.5, 58.3, 40.2, 39.7, 37.6, 35.1, 21.0; IR (film) 3053, 1479 cm$^{-1}$. MS (EI) 263.1674 (263.1674 calcd for $C_{19}H_{21}N$).

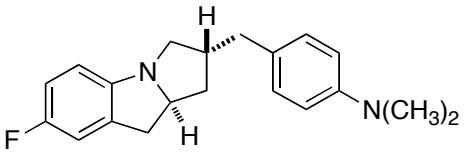



**(2*R*,9a*S*)-2-(4-Methoxybenzyl)-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]indole (22).** General procedure 2 was used for the reaction of **1** (50 mg, 0.29 mmol) with 4-bromoanisole (81 mg, 0.43 mmol), sodium *tert*-butoxide (41.6 mg, 0.43 mmol), $Pd(OAc)_2$ (3.3 mg, 0.014 mmol), and ligand **15** (11.4 mg, 0.029 mmol) in xylenes (1 mL). The crude product was formed as a 5:1 mixture of diastereomers with 5:1 selectivity for dicyclization:monocyclization as judged by $^1$H NMR analysis. Purification by flash chromatography afforded 45 mg (56%) of the title compound as a red oil with 13:1 dr. Data are for the major isomer. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.07–7.03 (m, 4 H), 6.81 (d, *J* = 8.4 Hz, 2 H), 6.72 (t, *J* = 7.6 Hz, 1 H), 6.55 (d, *J* = 7.6 Hz, 1 H), 4.14–4.07 (m, 1 H), 3.77 (s, 3 H), 3.36 (dd, *J* = 7.2, 11.6 Hz, 1 H), 3.18 (dd, *J* = 9.2, 16.0 Hz, 1 H), 3.04 (dd, *J* = 6.0, 11.2 Hz, 1 H), 2.85 (dd, *J* = 2.4, 16.0 Hz, 1 H), 2.63 (d, *J* = 7.6 Hz, 2 H), 2.37–2.32 (m, 1 H), 1.72 (ddd, *J* = 5.2, 7.2, 12.4 Hz, 1 H), 1.54 (dt, *J* = 8.0, 12.8 Hz, 1 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.9, 154.2, 132.9, 130.3, 129.7, 127.5, 124.7, 119.5, 113.8, 111.2, 63.5, 58.3, 55.2, 40.4, 39.2, 37.6, 35.1; IR (film) 3054, 1512 cm$^{-1}$. MS (EI) 279.1621 (279.1623 calcd for $C_{19}H_{21}NO$).

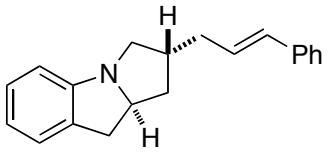



**(2*R*,9a*S*)-6-Methoxy-2-(4-methylbenzyl)-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]indole (23).** General procedure 2 was used for the reaction of **16** (70 mg, 0.34 mmol) with 4-bromotoluene (88 mg, 0.52 mmol), sodium *tert*-butoxide (49.6 mg, 0.52 mmol), $Pd(OAc)_2$ (3.8 mg, 0.017 mmol), and ligand **15** (13.6 mg, 0.034 mmol) in xylenes (1 mL). The crude product was formed as a 5:1 mixture of diastereomers with 2:1 selectivity for dicyclization:monocyclization as judged by $^1$H NMR analysis. Purification by flash chromatography afforded 58 mg (57%) of the title compound as a yellow oil with 10:1 dr. Data are for the major isomer. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.09–7.03 (m, 4 H), 6.91 (d, *J* = 7.6 Hz, 1 H), 6.29–6.27 (m, 1 H), 6.14 (d, *J* = 2.4 Hz, 1 H), 4.16–4.09 (m, 1 H), 3.74 (s, 3 H), 3.35 (dd, *J* = 6.8, 11.2 Hz, 1 H), 3.13 (dd, *J* = 8.8, 15.6 Hz, 1 H), 3.03 (dd, *J* = 6.0, 11.6 Hz, 1 H), 2.78 (dd, *J* = 2.4, 15.6 Hz, 1 H), 2.65 (d, *J* = 8.0 Hz, 2

H), 2.41–2.35 (m, 1 H), 2.31 (s, 3 H), 1.72 (ddd, *J* = 4.8, 7.2, 12.4 Hz, 1 H), 1.53 (dt, *J* = 8.4, 16.4 Hz, 1 H) ; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 160.1, 155.6, 137.8, 135.4, 129.1, 128.7, 124.8, 122.5, 104.3, 98.0, 64.3, 58.0, 55.3, 40.3, 39.8, 37.6, 34.3, 20.9; IR (film) 2918, 1616, 1293, 1207 cm$^{-1}$. MS (EI) 293.1776 (293.1780 calcd for $C_{20}H_{23}NO$).

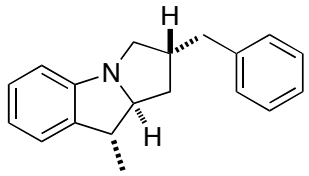



**(2*R*,9a*S*)-4-(7-Fluoro-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)methyl-*N*,*N*-dimethylaniline (24).** General procedure 2 was used for the reaction of **17** (80 mg, 0.42 mmol) with 4-bromo-*N*,*N*-dimethylaniline (125 mg, 0.63 mmol), sodium *tert*-butoxide (60.3 mg, 0.63 mmol), $Pd(OAc)_2$ (4.7 mg, 0.021 mmol), and ligand **15** (16.5 mg, 0.042 mmol) in xylenes (1 mL). The crude product was formed as a 3:1 mixture of diastereomers with 2:1 selectivity for dicyclization:monocyclization as judged by $^1$H NMR analysis. Purification by flash chromatography afforded 85 mg (65%) of the title compound as a red oil with 7:1 dr. Data are for the major isomer. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 8.4 Hz, 2 H), 6.74 (d, *J* = 8.8 Hz, 2 H), 6.66 (d, *J* = 6.4 Hz, 2 H), 6.45–6.42 (m, 1 H), 4.16–4.09 (m, 1 H), 3.26 (dd, *J* = 6.8, 11.2 Hz, 1 H), 3.18 (dd, *J* = 9.2, 16.4 Hz, 1 H), 3.03 (dd, *J* = 6.4, 11.6 Hz, 1 H), 2.89 (s, 6 H), 2.82 (dd, *J* = 3.2, 16.4 Hz, 1 H), 2.58 (d, *J* = 6.8 Hz, 2 H), 2.36–2.29 (m, 1 H), 1.74 (ddd, *J* = 5.2, 7.2, 12.4 Hz, 1 H), 1.54 (dt, *J* = 7.9, 12.8 Hz, 1 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.5 (d, *J* = 236 Hz), 150.4, 149.1, 131.9 (d, *J* = 8.0 Hz), 129.3, 128.8, 113.5 (d, *J* = 23 Hz), 112.8, 111.9 (d, *J* = 24 Hz), 111.5 (d, *J* = 8.4 Hz), 64.2, 58.9, 40.7, 40.5, 38.9, 37.7, 35.4; IR (film) 3401, 2926, 1521, 1483 cm$^{-1}$. MS (ESI) 311.1928 (311.1924 calcd for $C_{20}H_{23}FN_2$, M + H$^+$).



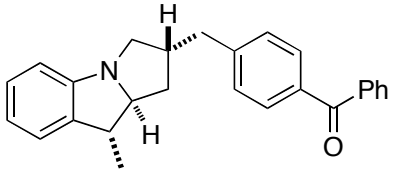

**(2*R*,9a*S*)-2-Cinnamyl-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]indole (25).** General procedure 2 was used for the reaction of **1** (80 mg, 0.46 mmol) with β-bromostyrene (169 mg, 0.92 mmol), sodium *tert*-butoxide (66.6 mg, 0.69 mmol), $Pd(OAc)_2$ (5.2 mg, 0.023 mmol), and ligand **15** (18.2 mg, 0.046 mmol) in xylenes (1 mL). The crude product was formed as a 3:1 mixture of

diastereomers with 3:1 selectivity for dicyclization:monocyclization as judged by $^1$H NMR analysis. Purification by flash chromatography afforded 56 mg (44%) of the title compound as a red oil with 3:1 dr. Data are for the mixture. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.36–7.28 (m, 4 H), 7.23–7.19 (m, 1 H), 7.12–7.07 (m, 2 H), 6.76 (t, *J* = 7.2 Hz, 1 H), 6.61 (d, *J* = 7.6 Hz, 0.75 H), 6.57 (d, *J* = 7.6 Hz, 0.25 H), 6.43 (d, *J* = 15.6 Hz, 0.75 H), 6.36 (d, *J* = 15.6 Hz, 0.25 H), 6.21–6.13 (m, 1 H), 4.13–4.06 (m, 0.75 H), 4.06–4.00 (m, 0.25 H), 3.67 (dd, *J* = 8.0, 10.4 Hz, 0.25 H), 3.47 (dd, *J* = 6.8, 11.2 Hz, 0.75 H), 3.21 (dd, *J* = 9.2, 16.4 Hz, 0.75 H), 3.15 (d, *J* = 9.6 Hz, 0.25 H), 3.08 (dd, *J* = 5.6, 11.2 Hz, 0.75 H), 2.95 (dd, *J* = 2.8, 16.4 Hz, 0.25 H), 2.89 (dd, *J* = 2.8, 16 Hz, 0.75 H), 2.78 (t, *J* = 10.4 Hz, 0.25 H), 2.50–2.42 (m, 0.25 H), 2.34–2.21 (m, 2.75 H), 2.02 (dt, *J* = 5.6, 11.2 Hz, 0.25 H), 1.76 (ddd, *J* = 4.4, 7.2, 12.4 Hz, 0.75 H), 1.61 (dt, *J* = 8.0, 12.4 Hz, 0.75 H), 1.18–1.10 (m, 0.25 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.1, 154.2, 137.5, 131.2, 130.9, 130.2, 129.6, 128.9, 128.8, 128.6, 128.5, 127.7, 127.6, 127.1, 126.0, 124.9, 124.8, 119.5, 119.2, 111.2, 110.9, 65.6, 63.6, 58.3, 58.2, 41.0, 38.4, 38.2, 37.6, 37.5, 35.0, 33.7; IR (film) 2925, 1602 cm$^{-1}$. MS (ESI) 276.1744 (276.1752 calcd for $C_{20}H_{21}N$, M + $H^+$).

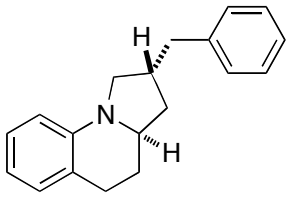



**(2*R*,9*R*,9a*S*)-2-Benzyl-9-methyl-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]indole (26).** General procedure 2 was used for the reaction of **18** (80 mg, 0.42 mmol) with bromobenzene (100 mg, 0.64 mmol), sodium *tert*-butoxide (61.6 mg, 0.64 mmol), $Pd(OAc)_2$ (4.8 mg, 0.021 mmol), and ligand **15** (16.9 mg, 0.043 mmol) in xylenes (1 mL). The crude product was formed as a 7:1 mixture of diastereomers with 7:1 selectivity for dicyclization:monocyclization as judged by $^1$H NMR analysis. Purification by flash chromatography afforded 76 mg (68%) of the title compound as an orange oil with >20:1 dr. Data are for the major isomer. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.33–7.29 (m, 2 H), 7.26–7.19 (m, 3 H), 7.12 (t, *J* = 7.2 Hz, 1 H), 7.07 (d, *J* = 7.6 Hz, 1 H), 6.80 (t, *J* = 7.2 Hz, 1 H), 6.61 (d, *J* = 8.0 Hz, 1 H), 3.78–3.73 (m, 1 H), 3.38 (dd, *J* = 7.2, 11.2 Hz, 1 H), 3.21–3.15 (m, 1 H), 3.09 (dd, *J* = 6.4, 11.2 Hz, 1 H), 2.74 (d, *J* = 7.6 Hz, 2 H), 2.46–2.40 (m, 1 H), 1.82 (ddd, *J* = 6.0, 7.6, 12.8 Hz, 1 H), 1.62 (dt, *J* = 7.6, 12.8 Hz, 1 H), 1.35 (d, *J* = 7.2 Hz, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.6, 140.9, 136.3, 128.7, 128.3, 127.8, 126.0,

123.8, 119.7, 111.7, 72.2, 58.2, 42.8, 40.2, 40.0, 37.3, 21.5; IR (film) 3054, 1421 $cm^{-1}$. MS (EI) 263.1672 (263.1674 calcd for $C_{19}H_{21}N$).

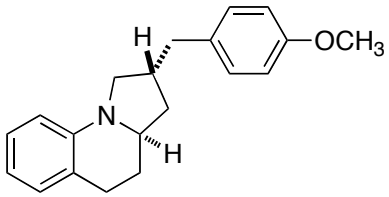



**(2*R*,9*R*,9a*S*)-4-{(9-Methyl-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]indol-2-ylmethyl)phenyl}phenylmethanone (27).** General procedure 2 was used for the reaction of **18** (70 mg, 0.37 mmol) with 4-bromobenzophenone (146 mg, 0.56 mmol), sodium *tert*-butoxide (53.9 mg, 0.56 mmol), $Pd(OAc)_2$ (4.2 mg, 0.019 mmol), and ligand **15** (14.7 mg, 0.037 mmol) in xylenes (1 mL). The crude product was formed as a 10:1 mixture of diastereomers with 7:1 selectivity for dicyclization:monocyclization as judged by $^1$H NMR analysis. Purification by flash chromatography afforded 94 mg (69%) of the title compound as a bright yellow oil with >20:1 dr. Data are for the major isomer. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 6.8 Hz, 2 H), 7.74 (d, *J* = 4.8 Hz, 2 H), 7.58 (t, *J* = 7.6 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 7.09 (t, *J* = 7.6 Hz, 1 H), 7.04 (d, *J* = 7.6 Hz, 1 H), 6.78 (t, *J* = 7.2 Hz, 1 H), 6.59 (d, *J* = 7.6 Hz, 1 H), 3.76–3.71 (m, 1 H), 3.38 (dd, *J* = 7.2, 11.6 Hz, 1 H), 3.19–3.13 (m, 1 H), 3.06 (dd, *J* = 6.8, 11.6 Hz, 1 H), 2.79 (d, *J* = 8.0 Hz, 2 H), 2.47–2.39 (m, 1 H), 1.80 (ddd, *J* = 6.4, 7.6, 13.2 Hz, 1 H), 1.62 (dt, *J* = 7.6, 12.8 Hz, 1 H), 1.32 (d, *J* = 7.2 Hz, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 196.3, 153.4, 146.0, 137.8, 136.2, 135.5, 132.2, 130.4, 129.9, 128.7, 128.2, 127.8, 123.9, 119.9, 111.7, 72.2, 58.2, 42.8, 40.0, 39.9, 37.3, 21.5; IR (film) 3078, 1604, 1455 $cm^{-1}$. MS (ESI) 368.2004 (368.2014 calcd for $C_{26}H_{25}NO$, M + $H^+$)



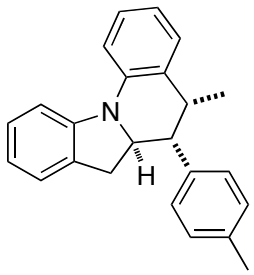

**(2*R*,3a*R*)-2-Benzyl-1,2,3,3a,4,5-hexahydropyrrolo[1,2-*a*]quinoline (28).** General procedure 2 was used for the reaction of **19** (100 mg, 0.53 mmol) with bromobenzene (126 mg, 0.80 mmol), sodium *tert*-butoxide (76.9 mg, 0.80 mmol), $Pd(OAc)_2$ (5.9 mg, 0.027 mmol), and ligand **15** (21.1 mg, 0.053 mmol) in xylenes (2 mL). The crude product was formed as a 3:1 mixture of

diastereomers with 5:1 selectivity for dicyclization:monocyclization as judged by $^1$H NMR analysis. Purification by flash chromatography afforded 104 mg (73%) of the title compound as a clear oil with 3:1 dr. Data are for the mixture. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.33–7.28 (m, 2 H), 7.24–7.16 (m, 3 H), 7.04 (t, *J* = 8.0 Hz, 1 H), 6.99–6.95 (m, 1 H), 6.57–6.53 (m, 1 H), 6.37 (d, *J* = 7.6 Hz, 0.75 H), 6.33 (d, *J* = 8.0 Hz, 0.25 H), 3.66–3.56 (m, 0.75 H), 3.52–3.45 (m, 0.25 H), 3.42–3.34 (m, 1 H), 3.09 (dd, *J* = 2.8, 9.6 Hz, 0.75 H), 2.94–2.88 (m, 0.75 H), 2.86–2.80 (m, 0.75 H), 2.78–2.77 (m, 0.75 H), 2.74–2.72 (m, 2 H), 2.71–2.60 (m, 1 H), 2.14 (dt, *J* = 5.2, 11.2 Hz, 0.25 H), 2.10–2.04 (m, 1 H), 1.95 (ddd, *J* = 2.0, 6.0, 12.4 Hz, 0.75 H), 1.65 (ddd, *J* = 7.2, 9.6, 12.0 Hz, 0.75 H), 1.47–1.36 (m, 1 H), 1.27 (q, *J* = 11.6 Hz, 0.25 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 144.8, 140.8, 140.7, 129.3, 128.9, 128.6, 128.5, 128.4, 127.2, 127.1, 126.1, 126.0, 121.4, 121.1, 115.0, 114.7, 110.4, 109.6, 59.1, 58.4, 56.0, 52.8, 52.7, 40.6, 40.4, 39.9, 39.6, 38.2, 37.9, 28.2, 28.1, 27.4; IR (film) 2929, 1602, 1504, 1326, 742 cm$^{-1}$. MS (ESI) 264.1756 (264.1752 calcd for $C_{19}H_{21}N$, M + $H^+$).

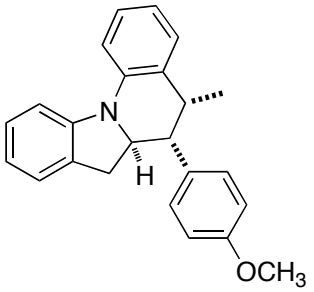



**(2*R*,3a*R*)-2-(4-Methoxybenzyl)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-*a*]quinoline (29).** General procedure 2 was used for the reaction of **19** (80 mg, 0.43 mmol) with 4-bromoanisole (119 mg, 0.64 mmol), sodium *tert*-butoxide (61.5 mg, 0.64 mmol), $Pd(OAc)_2$ (4.8 mg, 0.021 mmol), and ligand **15** (16.8 mg, 0.043 mmol) in xylenes (1 mL). The crude product was formed as a 3:1 mixture of diastereomers with 5:1 selectivity for dicyclization:monocyclization as judged by $^1$H NMR analysis. Purification by flash chromatography afforded 60 mg (48%) of the title compound as a bright yellow oil with 3:1 dr. Data are for the mixture. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.14–7.09 (m, 2 H), 7.04 (t, *J* = 7.6 Hz, 1 H), 6.99–6.95 (m, 1 H), 6.85 (d, *J* = 7.6 Hz, 2 H), 6.57–6.51 (m, 1 H), 6.37 (d, *J* = 8.0 Hz, 0.75 H), 6.33 (d, *J* = 8.0 Hz, 0.25 H), 3.80 (s, 3 H), 3.65–3.57 (m, 0.75 H), 3.53–3.46 (m, 0.25 H), 3.41–3.33 (m, 1 H), 3.08 (dd, *J* = 2.4, 9.6 Hz, 0.75 H), 2.93–2.85 (m, 1.25 H), 2.79–2.72 (m, 1.5 H), 2.69–2.66 (m, 1.5 H), 2.64–2.54 (m, 1 H), 2.16–2.04 (m, 1.25 H), 1.93 (ddd, *J* = 1.6, 6.0, 12.4 Hz, 0.75 H), 1.64 (ddd, *J* = 7.2, 9.9, 12.4 Hz, 0.75 H), 1.46–1.36 (m, 1 H), 1.25 (q, *J* = 11.6 Hz, 0.25 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ

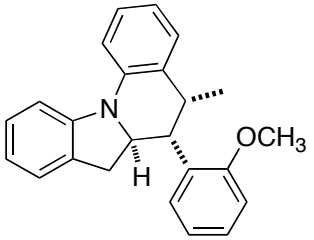
157.9, 144.8, 144.5, 132.9, 132.8, 129.9, 129.5, 128.5, 128.4, 127.2, 127.1, 121.4, 121.0, 115.0, 114.7, 113.8, 110.4, 109.6, 58.4, 55.9, 55.2, 52.7, 52.6, 39.9, 39.8, 39.7, 39.5, 38.3, 37.8, 28.2, 28.1, 27.4; IR (film) 2932, 2835, 1602, 1510, 1245 $cm^{-1}$. MS (ESI) 294.1860 (294.1858 calcd for $C_{20}H_{23}NO$, M + $H^+$).




**(5*R*,6*R*,6a*R*)-5-Methyl-6-(*p*-tolyl)-5,6,6a,7-tetrahydroindolo[1,2-*a*]quinoline (31a).** General procedure 2 was used for the reaction of **30** (75 mg, 0.32 mmol) with 4-bromotoluene (82 mg, 0.48 mmol), sodium *tert*-butoxide (45.9 mg, 0.49 mmol), $Pd(OAc)_2$ (3.6 mg, 0.016 mmol), and ligand **15** (12.3 mg, 0.032 mmol) in xylenes (1 mL). The crude product was formed as a 9:1 mixture of diastereomers with 20:1 selectivity for dicyclization:monocyclization as judged by $^1H$ NMR analysis. Purification by flash chromatography followed by recrystallization from ethyl acetate/hexanes afforded 60 mg (57%) of the title compound as a white solid, mp 169 °C, with >20:1 dr. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.4 Hz, 1 H), 7.31 (d, *J* = 8.0 Hz, 1 H), 7.24–7.06 (m, 8 H), 6.90 (t, *J* = 7.2 Hz, 1 H), 6.78 (t, *J* = 7.2 Hz, 1 H), 4.64 (dt, *J* = 7.2, 11.6 Hz, 1 H), 3.23–3.17 (m, 2 H), 3.08–3.02 (p, *J* = 7.2 Hz, 1 H), 2.77 (dd, *J* = 6.8, 15.6 Hz, 1 H), 2.37 (s, 3 H), 1.11 (d, *J* = 7.2 Hz, 3 H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 146.7, 139.6, 137.3, 136.1, 131.5, 130.2, 129.5, 129.1, 128.7, 127.0, 126.6, 125.0, 119.8, 119.5, 116.6, 109.6, 58.4, 46.3, 38.9, 33.9, 21.0, 18.8; IR (film) 3053, 1593 $cm^{-1}$. MS (EI) 325.1832 (325.1830 calcd for $C_{24}H_{23}N$)

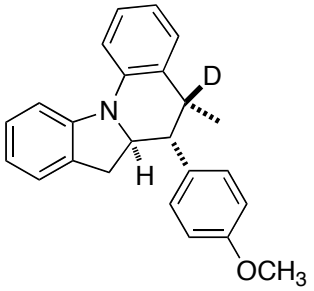



**(5*R*,6*R*,6a*R*)-6-(4-Methoxyphenyl)-5-methyl-5,6,6a,7-tetrahydroindolo[1,2-*a*]quinoline (31b).** General procedure 2 was used for the reaction of **30** (100 mg, 0.43 mmol) with 4-bromoanisole (119 mg, 0.64 mmol), sodium *tert*-butoxide (61.3 mg, 0.64 mmol), $Pd(OAc)_2$ (4.8 mg, 0.021 mmol), and ligand **15** (16.8 mg, 0.042 mmol) in xylenes (1 mL). The crude product was formed as a 10:1 mixture of diastereomers with 20:1 selectivity for dicyclization:monocyclization as judged by $^1$H NMR analysis. Purification by flash chromatography followed by recrystallization from ethyl acetate/hexanes afforded 77 mg (54%) of the title compound as a white solid, mp 163 °C, with >20:1 dr. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.6 Hz, 1 H), 7.30 (d, *J* = 7.6 Hz, 1 H), 7.22 (t, *J* = 7.6 Hz, 1 H), 7.17 (d, *J* = 7.6 Hz, 1 H), 7.13–7.07 (m, 4 H), 6.93–6.88 (m, 3 H), 6.77 (t, *J* = 7.2 Hz, 1 H), 4.61 (dt, *J* = 7.6, 11.2 Hz, 1 H), 3.82 (s, 3 H), 3.22–3.16 (m, 2 H), 3.03 (p, *J* = 6.8 Hz, 1 H), 2.77 (dd, *J* = 7.2, 15.6 Hz, 1 H), 1.06 (d, *J* = 7.2 Hz, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.2, 146.7, 139.6, 132.5, 131.5, 130.2, 129.7, 129.6, 127.0, 126.6, 125.0, 119.9, 119.5, 116.6, 113.9, 109.6, 58.6, 55.2, 45.9, 39.0, 33.9, 18.8; IR (film) 3054, 1513 cm$^{-1}$. MS (EI) 341.1785 (341.1780 calcd for $C_{24}H_{23}NO$).

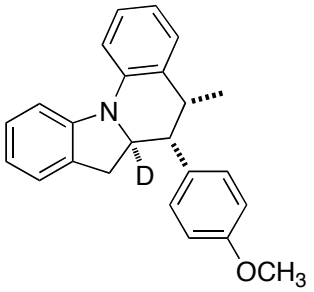



**(5*R*,6*R*,6a*R*)-6-(2-Methoxyphenyl)-5-methyl-5,6,6a,7-tetrahydroindolo[1,2-*a*]quinoline (31c).** General procedure 2 was used for the reaction of **30** (100 mg, 0.43 mmol) with 2-bromoanisole (119 mg, 0.64 mmol), sodium *tert*-butoxide (61.3 mg, 0.64 mmol), $Pd(OAc)_2$ (4.8 mg, 0.021 mmol), and ligand **15** (16.8 mg, 0.042 mmol) in xylenes (1 mL). The crude product was formed as a 5:1 mixture of diastereomers with 6:1 selectivity for dicyclization:monocyclization as judged by $^1$H NMR analysis. Purification by flash

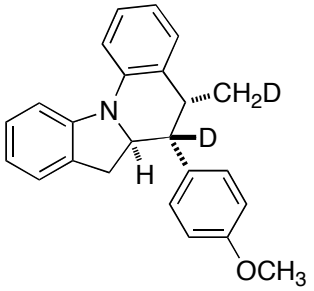
chromatography followed by recrystallization from ethyl acetate/hexanes afforded 39 mg (27%) of the title compound as a white solid, mp 174–175°C, with >20:1 dr. $^1$H NMR (400 MHz, $C_6D_6$) δ 7.58 (d, *J* = 7.9 Hz, 1 H), 7.35 (d, *J* = 7.9 Hz, 1 H), 7.17–7.13 (m, 1 H), 7.11–7.03 (m, 3 H), 6.90–6.83 (m, 3 H), 6.78–6.73 (m, 2 H), 6.54 (d, *J* = 8.4 Hz, 1 H), 4.44 (s, br, 1 H), 3.79 (s, br, 1 H), 3.29 (s, br, 1 H), 3.11 (s, 3 H), 2.98 (dd, *J* = 8.8, 15.6 Hz, 1 H), 2.64 (dd, *J* = 6.4, 15.9 Hz, 1 H), 0.98 (d, *J* = 7.2 Hz, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.8, 146.8, 139.6, 132.2, 130.1, 129.8, 128.8, 128.5, 127.3, 126.9, 126.3, 124.9, 120.0, 119.9, 119.2, 117.3, 110.5, 108.9, 57.9, 55.2, 39.7, 35.7, 33.7, 19.5; IR (film) 3059, 1594 cm$^{-1}$. MS (EI) 341.1793 (341.1780 calcd for $C_{24}H_{23}NO$).




**(5*S*,6*R*,6a*R*)-5-Deuterio-6-(4-methoxyphenyl)-5-methyl-5,6,6a,7-tetrahydroindolo[1,2-*a*]quinoline (34a).** General procedure 2 was used for the reaction of **33a** (80 mg, 0.33 mmol) with 4-bromoanisole (93 mg, 0.50 mmol), sodium *tert*-butoxide (48.8 mg, 0.51 mmol), $Pd(OAc)_2$ (3.8 mg, 0.017 mmol), and ligand **15** (13.5 mg, 0.033 mmol) in xylenes (1 mL). The crude product was formed as a 9:1 mixture of diastereomers with 13:1 selectivity for dicyclization:monocyclization as judged by $^1$H NMR analysis. Purification by flash chromatography followed by recrystallization from ethyl acetate/hexanes afforded 55 mg (47%) of the title compound as a white solid, mp 168–169°C, with >20:1 dr. $^1$H NMR (400 MHz, $C_6D_6$) δ 7.59 (d, *J* = 8.4 Hz, 1 H), 7.37 (d, *J* = 8.0 Hz, 1 H), 7.17 (t, *J* = 8.8 Hz, 1 H), 7.09 (t, *J* = 8.0 Hz, 1 H), 7.04 (d, *J* = 7.6 Hz, 1 H), 6.96 (d, *J* = 7.2 Hz, 1 H), 6.91 (t, *J* = 7.6 Hz, 1 H), 6.81 (t, *J* = 7.2 Hz, 1 H), 6.76 (d, *J* = 8.4 Hz, 2 H), 6.67 (d, *J* = 8.8 Hz, 2 H), 4.32–4.25 (m, 1 H), 3.36 (s, 3 H), 2.91–2.85 (m, 2 H), 2.56 (dd, *J* = 7.2, 16.0 Hz, 1 H), 0.94 (s, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.2, 146.7, 139.6, 132.5, 131.5, 130.2, 129.7, 129.5, 127.0, 126.6, 125.0, 119.9, 119.5, 116.5, 113.9, 109.6, 58.6, 55.2, 45.9, 38.5 (t, *J* = 19.2 Hz), 33.9, 18.6; IR (film) 2960, 1590 cm$^{-1}$. MS (EI) 342.1842 (342.1842 calcd for $C_{24}H_{22}DNO$).




**(5*R*,6*R*,6a*S*)-6a-Deuterio-6-(4-methoxyphenyl)-5-methyl-5,6,6a,7-tetrahydroindolo[1,2-*a*]quinoline (34b).** General procedure 2 was used for the reaction of **33b** (80 mg, 0.33 mmol) with 4-bromoanisole (93 mg, 0.50 mmol), sodium *tert*-butoxide (48.8 mg, 0.51 mmol), $Pd(OAc)_2$ (3.8 mg, 0.017 mmol), and ligand **15** (13.5 mg, 0.033 mmol) in xylenes (1 mL). The crude product was formed as a 9:1 mixture of diastereomers with 18:1 selectivity for dicyclization:monocyclization as judged by $^1$H NMR analysis. Purification by flash chromatography followed by recrystallization from ethyl acetate/hexanes afforded 62 mg (53%) of the title compound as a white solid, mp 168–169°C, with >13:1 dr. $^1$H NMR (400 MHz, $C_6D_6$) δ 7.59 (d, *J* = 7.9 Hz, 1 H), 7.37 (d, *J* = 8.0 Hz, 1 H), 7.17 (t, *J* = 8.4 Hz, 1 H), 7.09 (t, *J* = 7.6 Hz, 1 H), 7.04 (d, *J* = 7.6 Hz, 1 H), 6.96 (d, *J* = 7.2 Hz, 1 H), 6.91 (t, *J* = 7.6 Hz, 1 H), 6.81 (t, *J* = 7.6 Hz, 1 H), 6.76 (d, *J* = 8.4 Hz, 2 H), 6.67 (d, *J* = 8.4 Hz, 2 H), 3.35 (s, 3 H), 2.91–2.86 (m, 2 H), 2.83–2.78 (m, 1 H), 2.56 (d, *J* = 15.6 Hz, 1 H), 0.95 (d, *J* = 7.2 Hz, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.2, 146.7, 139.6, 132.5, 131.5, 130.2, 129.7, 129.5, 127.0, 126.6, 125.0, 119.9, 119.5, 116.6, 113.9, 109.6, 58.2 (t, *J* = 21.1 Hz), 55.2, 45.8, 38.9, 33.8, 18.7; IR (film) 2960, 1590 cm$^{-1}$. MS (EI) 342.1839 (342.1842 calcd for $C_{24}H_{22}DNO$).

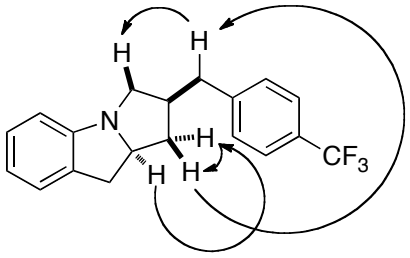



**(5*R*,6*S*,6a*R*)-6-Deuterio-5-(deuteriomethyl)-6-(4-methoxyphenyl)-5,6,6a,7-tetrahydroindolo[1,2-a]quinoline (34c).** General procedure 2 was used for the reaction of **33c** (80 mg, 0.34 mmol) with 4-bromoanisole (93 mg, 0.50 mmol), sodium *tert*-butoxide (48.6 mg, 0.51 mmol), $Pd(OAc)_2$ (3.8 mg, 0.017 mmol), and ligand **15** (13.3 mg, 0.034 mmol) in xylenes

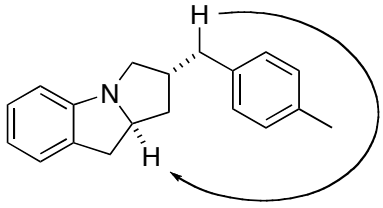
(1 mL). The crude product was formed as a 8:1 mixture of diastereomers with 12:1 selectivity for dicyclization:monocyclization as judged by $^1$H NMR analysis. Purification by flash chromatography followed by recrystallization from ethyl acetate/hexanes afforded 57 mg (49%) of the title compound as a white solid, mp 168–169°C, with >20:1 dr. $^1$H NMR (400 MHz, $C_6D_6$) δ 7.58 (d, *J* = 7.6 Hz, 1 H), 7.36 (d, *J* = 7.9 Hz, 1 H), 7.16 (t, *J* = 6.8 Hz, 1 H), 7.06 (t, *J* = 7.9 Hz, 1 H), 7.03 (d, *J* = 7.9 Hz, 1 H), 6.95 (d, *J* = 7.2 Hz, 1 H), 6.90 (t, *J* = 8.4 Hz, 1 H), 6.80 (t, *J* = 7.2 Hz, 1 H), 6.76–6.73 (m, 2 H), 6.67–6.65 (m, 2 H), 4.27 (t, *J* = 6.8 Hz, 1 H), 3.34 (s, 3 H), 2.86 (dd, *J* = 8.8, 15.6 Hz, 1 H), 2.77 (t, *J* = 7.2 Hz, 1 H), 2.55 (dd, *J* = 6.8, 16 Hz, 1 H), 0.92 (d, *J* = 7.2 Hz, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.3, 146.7, 139.6, 132.4, 131.5, 130.2, 129.7, 129.6, 127.0, 126.6, 125.0, 119.9, 119.5, 116.6, 113.8, 109.6, 58.5, 55.2, 45.66 (t, *J* = 19.6 Hz), 38.8, 33.9, 18.5 (t, *J* = 19.6 Hz); IR (film) 2931, 1592, 1491 cm$^{-1}$. MS (ESI) 344.1974 (344.1983 calcd for $C_{24}H_{21}D_2NO$, M + H$^+$).

**Assignment of Stereochemistry**

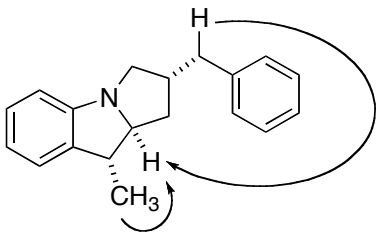
The relative stereochemistry of compound **20-minor diastereomer** was assigned on the basis of observed $^1$H NMR nOe experiments. Significant nOe relationships are shown below.



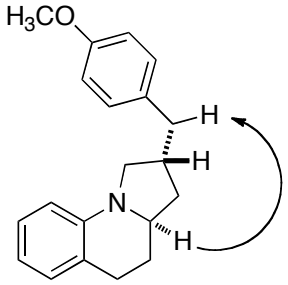

The relative stereochemistry of compound **21** was assigned on the basis of observed $^1$H NMR nOe experiments. Significant nOe relationships are shown below.



The relative stereochemistry of compound **26** was assigned on the basis of observed $^1$H NMR nOe experiments. Significant nOe relationships are shown below.

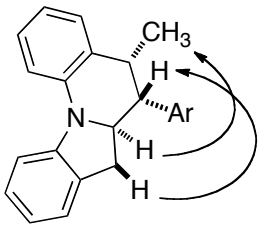



The relative stereochemistry of compound **29** was assigned on the basis of observed $^1$H NMR nOe experiments. Significant nOe relationships are shown below.



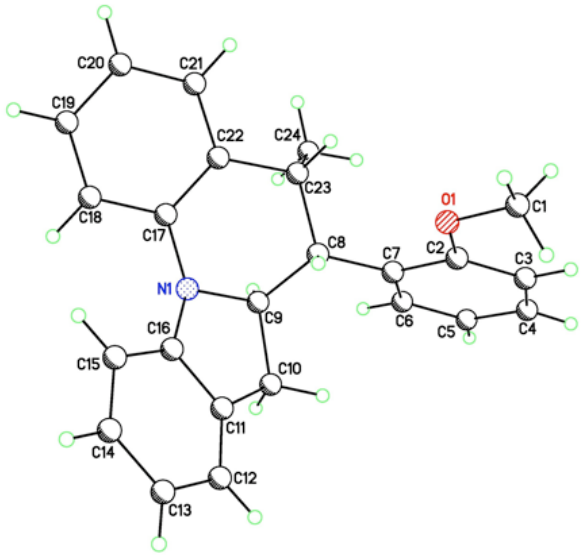

The relative stereochemistry of compound **31c** was assigned on the basis of observed $^1$H NMR nOe experiments, with significant nOe relationships shown below. Further evidence of the relative stereochemistry was accomplished by single-crystal x-ray analysis of compound **31c**, which was recrystallized from EtOAc/hexanes.

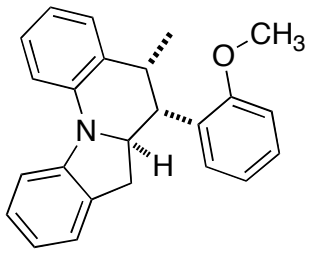
**nOe Relationships:**




Ar = *o*-MeOPh

**Single-Crystal X-Ray Structure of 31c:**

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