Supporting Information

for

The Development of Efficient Protocols for the Palladium-Catalyzed Cyclization Reactions of Secondary Amides and Carbamates

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Complete spectral data for all products (6 pages).

General Considerations. All reactions were run in oven-dried glassware under an atmosphere of argon using the representative experimental procedure described in the text. Toluene was distilled from sodium under argon. Granular anhydrous potassium carbonate was grinded into a fine powder with a mortar and pestle. DPEphos, Xantphos, and (±)-MOP were prepared according to the literature procedures.[1] All other reagents were commercially available and used without further manipulation. Preparative flash chromatography was performed using ICN Flash Silica Gel, 230–430 mesh. Yields refer to the average of two or more isolated yields of 95% or higher purity as determined by GC, ^{1}H NMR, ^{13}C NMR, and elemental analysis for new compounds. NMR spectra were obtained in $CDCl_3$ on a Varian XL-300 MHz or a Varian Unity 300 MHz spectrometer. IR spectra were recorded on an ASi ReactIR 1000 (where solids were measured neat on a DiComp probe). Gas chromatography analyses were performed on a Hewlett-Packard 6890 Gas Chromatograph with an FID and a 25 meter capillary column with a dimethylpolysiloxane stationary phase. Melting points were determined using a Haake Buchler Melting Point Apparatus and are uncorrected.

***N*-Benzyl-2-indolinone** (**5a**): The general procedure using (±)-MOP as ligand and K_2CO_3 as base afforded the title compound as a yellow oil, which based on GC and GC/MS analysis and comparison to the known ^{1}H and ^{13}C NMR spectra[2] was estimated to be ≥95% pure after purification by flash column chromatography (30% EtOAc–hexanes): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.4–6.9 (m, 8H), 6.71 (d, 1H, *J* = 7.8 Hz), 4.90 (s, 2H), 3.62 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.1, 144.3, 135.8, 128.7, 127.8, 127.6, 127.3, 124.4, 124.3, 122.3, 109.0, 43.7, 35.7; FTIR (neat) 1708 cm^{-1}; GC/MS *m*/*z* (relative intensity) 223 (20), 132 (10), 91 (100), 65 (12).

***N*-Benzyl-1,2,3,4-tetrahydroisoquinoline-2-one** (**5b**): The general procedure using (±)-MOP as ligand and K_2CO_3 as base afforded the title compound as a colorless oil, which based on GC and GC/MS analysis and comparison to the known ^1H and ^{13}C NMR spectra[2] was estimated to be ≥95% pure after purification by flash column chromatography (37% EtOAc–hexanes): ^1H NMR (300 MHz, $CDCl_3$) δ 7.3–6.8 (m, 9H), 5.17 (s, 2H), 2.95 (m, 2H), 2.78 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 139.8, 136.9, 128.7, 127.8, 127.4, 127.0, 126.3, 122.9, 115.5, 46.1, 31.9, 25.5; FTIR (neat) 1674 cm^{-1}; GC/MS *m*/*z* (relative intensity) 237 (27), 131 (10), 118 (10), 91 (100).

1-Benzyl-1,3,4,5-tetrahydro-2*H*-1-benzazepin-2-one (**5c**): The general procedure using (±)-MOP as ligand and Cs_2CO_3 as base was employed with the exception that the reaction was run at 0.06 M in substrate, using 5.0 mol % $Pd(OAc)_2$ and 7.5 mol % ligand. The title product was obtained as a yellow oil, which based on GC and GC/MS analysis and comparison to the known ^1H NMR spectrum[3] was estimated to be ≥95% pure after purification by flash column chromatography (33% EtOAc–hexanes): ^1H NMR (300 MHz, $CDCl_3$) δ 7.4–7.1 (m, 9H), 5.02 (s, 2H), 2.53 (t, 2H, *J* = 6.4 Hz), 2.33 (t, 2H, *J* = 6.4 Hz), 2.15 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.4, 142.6, 138.1, 136.0, 129.5, 128.6, 128.2, 127.6, 127.4, 126.5, 122.9, 51.4, 33.3, 30.1, 29.1; FTIR (neat) 1663 cm^{-1}; GC/MS *m/z* (relative intensity) 251 (50), 196 (23), 132 (57), 91 (100), 65 (21).

***N*-Acetylindoline** (**6a**): The general procedure using DPEphos as ligand and Cs_2CO_3 as base afforded the title compound as a yellow oil after purification by flash column chromatography (70% EtOAc–hexanes): ^1H NMR (300 MHz, $CDCl_3$) δ (mixture of rotamers) 8.18 (d, 1H, *J* = 8.1 Hz), 7.25–7.00 (m, 2H), 6.99 (t, 1H, *J* = 6.9 Hz), 4.13 (t, 2H, *J* = 8.2 Hz), 4.04 (t, 2H, *J* = 8.8 Hz), 3.19 (t, 2H, *J* = 8.5 Hz), 3.04 (t, 2H, *J* = 8.5 Hz), 2.42 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (75 MHz,

$CDCl_3$) δ 168.5, 142.7, 131.0, 127.2, 124.3, 123.3, 116.6, 48.5, 27.7, 24.0; FTIR (neat) 1650 cm^{-1}; Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51, H, 6.88. Found: C, 74.75; H, 6.80.

***N*-Acetyl-1,2,3,4-tetrahydroquinoline** (**6b**): The general procedure using (±)-MOP as ligand and Cs_2CO_3 as base afforded the title compound as a yellow oil, which based on GC and GC/MS analysis and comparison to the known ^1H and ^{13}C NMR spectra[2] was estimated to be ≥95% pure after purification by flash column chromatography (65% EtOAc–hexanes): ^1H NMR (300 MHz, $CDCl_3$) δ 7.26–7.10 (m, 4H), 3.80 (t, 3H, *J* = 6.5 Hz), 2.72 (t, 3H, *J* = 6.7 Hz), 2.23 (s, 3H), 1.94 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1, 128.4, 126.1, 125.2, 124.6, 41.5, 26.9, 24.1, 23.2; FTIR (neat) 1655 cm^{-1}; GC/MS *m/z* (relative intensity) 175 (40), 133 (95), 132 (100), 118 (15), 77 (14).

1-Acetyl-2,3,4,5-tetrahydro-benzo<*b*>azepine (**6c**): The general procedure using Xantphos as ligand and Cs_2CO_3 as base afforded the title compound as a yellow oil with identical spectral characteristics as reported previously[4] after purification by flash column chromatography (60% EtOAc–hexanes): mp 74–75 °C (lit.[5] 80 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 7.30–7.10 (m, 4H), 4.68 (m, 2H), 2.70 (m, 4H), 1.83 (s, 3H), 1.81 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.5, 143.6, 140.5, 130.0, 127.8, 127.5, 127.2, 47.0, 34.4, 29.0, 26.5, 22.6; FTIR (neat) 1660 cm^{-1}; Anal. Calcd for $C_{12}H_{15}NO$: C, 76.16; H, 7.99. Found: C, 75.92; H, 7.99.

1-(Carbobenzyloxy)indoline (**7a**): The general procedure using DPEphos as ligand and Cs_2CO_3 as base afforded the title compound as a yellow oil after purification by flash column chromatography (18% EtOAc–hexanes): ^1H NMR (300 MHz, $CDCl_3$) δ 7.88 (m, 1H), 7.50–6.90 (m, 8H), 5.26 (s, 2H), 4.06 (t, 2H, *J* = 8.6 Hz), 3.12 (t, 2H, *J* = 8.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8, 142.4, 136.3, 130.7, 128.5, 128.1, 127.9, 127.4, 124.6, 122.5, 114.7, 66.7, 47.3, 27.4;

FTIR (neat) 1708 cm^{-1}; Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97. Found: C, 75.90; H, 5.97.

1-(Carbobenzyloxy)-1,2,3,4-tetrahydroquinoline (**7b**): The general procedure using (±)-BINAP as ligand and Cs_2CO_3 as base afforded the title compound as a yellow oil after purification by flash column chromatography (14% EtOAc–hexanes): ^1H NMR (300 MHz, $CDCl_3$) δ 7.61 (m, 1H), 7.35–6.91 (m, 8H), 5.15 (s, 2H), 3.70 (t, 2H, *J* = 4.9 Hz), 2.67 (t, 2H, *J* = 6.5 Hz), 1.84 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.6, 138.0, 136.3, 129.9, 128.5, 128.4, 128.0, 127.9, 125.9, 123.8, 123.6, 67.4, 44.8, 27.2, 23.3; FTIR (neat) 1700 cm^{-1}; Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41. Found: C, 76.15; H, 6.40.

1-(Carbobenzyloxy)-2,3,4,5-tetrahydro-benzo<*b*>-azepine (**7c**): The general procedure using (±)-MOP as ligand and Cs_2CO_3 as base afforded the title compound as a yellow oil after purification by flash column chromatography (13% EtOAc–hexanes): ^1H NMR (300 MHz, $CDCl_3$) δ (mixture of rotamers) 7.50–6.90 (m, 9H), 5.20 (m, 2H), 5.02 (m, 2H), 4.39 (m, 2H), 2.70 (m, 2H), 1.77 (m, 2H), 1.50 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (mixture of rotamers) 154.6, 142.1, 139.8, 136.9, 130.0, 129.8, 128.5, 128.3, 128.05, 127.97, 127.7, 127.6, 127.2, 127.1, 127.0, 126.9, 126.6, 67.2, 66.8, 49.1, 49.0, 34.6, 30.2, 29.5, 26.3, 26.2; FTIR (neat) 1704 cm^{-1}; Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81. Found: C, 77.08; H, 6.86.

1-(*tert*-Butoxycarbonyl)indoline (**8a**): The general procedure using DPEphos as ligand and Cs_2CO_3 as base afforded the title compound as a yellow oil, which based on GC analysis and comparison to the known ^1H NMR spectrum[6] was estimated to be ≥95% pure after purification by flash column chromatography (9% EtOAc–hexanes): ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 (m, 1H), 7.14 (m, 2H), 6.92 (t, 2H, *J* = 7.6 Hz), 3.94 (t, 2H, *J* = 8.7 Hz), 3.09 (t, 2H, *J* = 8.7 Hz), 1.57 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.6, 127.2, 124.6, 122.0,

114.6, 80.5, 47.5, 28.4, 15.4; FTIR (neat) 1706 cm^{-1}; GC/MS *m/z* (relative intensity) 219 (8), 163 (62), 119 (40), 118 (54), 91 (9), 57 (100).

1-(*tert*-Butoxycarbonyl)-1,2,3,4-tetrahydroquinoline (**8b**): The general procedure using (±)-BINAP as ligand and Cs_2CO_3 as base afforded the title compound as a yellow oil after purification by flash column chromatography (9% EtOAc–hexanes): ^1H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, 1H, *J* = 8.2 Hz), 7.40–6.90 (m, 3H), 3.71 (t, 2H, *J* = 6.0 Hz), 2.77 (t, 2H, *J* = 6.6 Hz), 1.92 (pn, 2H, *J* = 6.2 Hz), 1.52 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.9, 138.6, 129.9, 128.5, 125.7, 124.1, 123.2, 80.7, 44.6, 28.4, 27.5, 23.6; FTIR (neat) 1704 cm^{-1}; Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21. Found: C, 72.15; H, 8.33.

1-(*tert*-Butoxycarbonyl)-2,3,4,5-tetrahydro-benzo<*b*>-azepine (**8c**):[7] The general procedure using (±)-MOP as ligand and Cs_2CO_3 as base afforded the title compound as a yellow oil after purification by flash column chromatography (9% EtOAc–hexanes): ^1H NMR (300 MHz, $CDCl_3$) δ (mixture of rotamers) 7.20–7.00 (m, 4H), 4.37 (m, 2H), 2.72 (m, 2H), 1.80 (m, 2H), 1.51 (m, 2H), 1.34 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (mixture of rotamers) 154.3, 139.7, 130.2, 129.7, 128.5, 128.4, 127.1, 127.0, 126.6, 126.5, 80.1, 79.8, 49.4, 48.4, 34.9, 30.3, 29.7, 28.6, 28.5, 26.5; FTIR (neat) 1698 cm^{-1}; Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56. Found: C, 72.90; H, 8.62.

References

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