SUPPLEMENTARY MATERIAL

Efficient Nickel-mediated Intramolecular Amination of Aryl Chlorides

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General Considerations. All reactions were carried out using standard Schlenk techniques under an atmosphere of nitrogen. Gas chromatographic analyses were performed on a capillary gas chromatograph fitted with an "Optima 5" column (22 m x 0.25 mm, ID x 0.25 μm). All quantifications of reaction constituents were achieved by gas chromatography using a known quantity of decane as reference standard. Melting points were taken on a Tottoli apparatus and were uncorrected. The ^{1}H spectra were recorded at 400.13 or 200.13 MHz using $CDCl_3$ as solvent. The ^{13}C NMR spectra were recorded at 100 MHz using $CDCl_3$ as solvent. IR spectra were recorded using NaCl cells or mixtures of compounds/KBr. Compounds previously described were characterized by ^{1}H and ^{13}C NMR and their purity was confirmed by GC analysis. All new compounds were fully characterized by ^{1}H and ^{13}C NMR, IR and elemental analysis. Mass spectra were obtained on a GC/MS Shimadzu QP-5050 (EI, 70 eV).

THF and dioxane were distilled under nitrogen from sodium benzophenone ketyl. *Tert*-butanol was distilled from sodium before use. Sodium hydride (65% in mineral oil) was purchased from Fluka and used after two washings with THF under nitrogen. Nickel(II) acetylacetonate was purchased from Acros and used as received. Nickel(II) acetate, $Ni(OAc)_4$. 4 H_2O, was dried at 110°C under vacuum (30 mm Hg) before use. 1,1'-Bis(diphenylphosphino)ferrocene (dppf) was purchased from Strem and used as received. 2,2'-Bipyridine was purchased from Fluka and recristallised from hexane before use. All imidazolium salts were synthetized according to literature procedures.[1] Dihydroimidazolium chloride SIPr.HCl is commercially available from Strem Chemical Co.

General Procedure for the Intramolecular Aryl Aminations using the Ni/bpy Catalyst.

A 50 mL Schlenk tube was loaded with degreased NaH (11.5 mmol), $Ni(OAc)_2$ (0.5 mmol), 2,2'-bipyridine (1.5 mmol) and 8 mL of THF and the mixture was heated to reflux. A solution of *t*-BuOH (1 mmol) in 2 mL of THF was then added dropwise and the mixture was further stirred for

[1] (a) Arduengo, A.J., III. U.S. Patent 5 077 414, 1991. (b) Arduengo, A.J., III; Krakczyk, R.; Schmutzler, R. *Tetrahedron* **1999**, *55*, 14523-14534.

one hour. A solution of the amino aryl chloride (10 mmol) and styrene (0.5 mmol) in 5 mL THF was then added and the reaction was monitored by GC. After complete consumption of the starting material, the mixture was cooled to room temperature and adsorbed onto silica gel. The crude reaction mixture was purified by silica gel chromatography.

General Procedure for the Intramolecular Aryl Aminations using the Ni/SIPr Catalyst.

A 50 mL Schlenk tube was loaded with degreased NaH (15.4 mmol), $Ni(acac)_2$ (0.2 mmol), SIPr.HCl (0.2 mmol) and 8 mL of dioxane and the mixture was heated to reflux. A solution of *t*-BuOH (15 mmol) in 2 mL dioxane was then added dropwise and the mixture was further stirred for half an hour. A solution of the amino aryl chloride (10 mmol) in 5 mL dioxane was then added and the reaction was monitored by GC. After complete consumption of the starting material, the mixture was cooled to room temperature and adsorbed onto silica gel. The crude reaction mixture was purified by silica gel chromatography.

Indoline[2] (Table 2, entry 1)

The title compound was isolated as a colorless oil (98 % using the Ni/SIPr catalyst).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, J = 7.2 Hz, 1H), 7.08 (dd, J = 7.2, 7.2 Hz, 1H), 6.77 (dd, J = 7.2, 7.2 Hz, 1H), 6.70 (d, J = 7.2 Hz, 1H), 3.88 (NH), 3.53 (t, J = 7.8 Hz, 2H), 3.01 (t, J = 7.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$,) δ 151.34, 129.29, 127.12, 124.54, 118.66, 109.45, 47.29, 29.76.

FT-IR (NaCl): 3380, 3042, 2945, 2845, 1604, 1486, 1320, 1245, 1021, 746 cm^{-1}.

MS: m/z 119.

1-Butylindoline[3] (Table 2, entries 2 and 3)

The title compound was isolated as a colorless oil (82% using the Ni/bpy catalyst, 87% using the Ni/SIPr catalyst).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06-6.96 (m, 2H), 6.59 (dd, J = 7.6, 7.6 Hz, 1H), 6.43 (d, J = 7.6 Hz, 1H), 3.26 (t, J = 8.4 Hz, 2H), 2.99 (t, J = 6.8 Hz, 2H), 2.88 (t, J = 8.4 Hz, 2H), 1.63-1.48 (m, 2H), 1.46-1.26 (m, 2H), 0.94 (t, J = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$,) δ 152.55, 129.78, 127.10, 124.15, 117.19, 106.77, 52.89, 48.89, 29.37, 28.44, 20.31, 13.85.

FT-IR (NaCl): cm^{-1}.

MS: m/z 175.

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[2] O'Brien, S. ; Smith, D.C.C. *J. Chem. Soc*. **1960**, 4609-4612.

[3] Beller, M. ; Breindl, C. ; Riermeier, T.H. ; Tillack, A. *J. Org. Chem.* **2001**, *66*, 1403-1412.

1-Benzylindoline[4] (Table 2, entries 4 and 5)

The title compound was isolated as a colorless oil (84% using the Ni/bpy catalyst, 95% using the Ni/SIPr catalyst).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.22 (m, 5H), 7.11-7.02 (m, 2H), 6.66 (dd, J = 7.6, 7.6 Hz, 1H), 6.50 (d, J = 7.6 Hz, 1H), 4.23 (s, 2H), 3.29 (t, J = 8.4 Hz, 2H), 2.95 (t, J = 8.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$,) δ 152.33, 138.28, 129.69, 128.34, 127.82, 127.19, 126.86, 124.26, 117.54, 106.87, 53.41, 53.32, 28.32.

FT-IR (NaCl): 3025, 2906, 2820, 1605, 1491, 1419, 1370, 1100, 742 cm^{-1}.

MS: m/z 209.

1,2,3,4-Tetrahydroquinoline[5] (Table 2, entry 6)

The title compound was isolated as a colorless oil (96 % using the Ni/SIPr catalyst).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97-6.88 (m, 2H), 6.57 (dd, J = 7.6, 7.6 Hz, 1H), 6.42 (d, J = 7.6 Hz, 1H), 3.27-3.20 (m, 2H), 2.76-2.69 (m, 2H), 1.95-1.85 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$,) δ 144.64, 129.32, 126.54, 121.18, 116.70, 114.00, 41.80, 26.84, 22.03.

FT-IR (NaCl): 3405, 3017, 2946, 2928, 2890, 2840, 1607, 1584, 1505, 1472, 1436, 1312, 1096, 746 cm^{-1}.

MS: m/z 133.

1-Ethyl-1,2,3,4-tetrahydroquinoline[6] (Table 2, entries 7 and 8)

The title compound was isolated as a colorless oil (83% using the Ni/bpy catalyst, 82% using the Ni/SIPr catalyst).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (dd, J = 7.6, 7.6 Hz, 1H), 6.90 (d, J = 7.6 Hz, 1H), 6.56 (d, J = 7.6 Hz, 1H), 6.52 (dd, J = 7.6, 7.6 Hz, 1H), 3.29 (q, J = 7.2 Hz, 2H), 3.20 (t, J = 6.2 Hz, 2H), 2.71 (t, J = 6.2 Hz, 2H), 1.95-1.88 (m, 2H), 1.10 (t, J = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$,) δ 144.86, 129.01, 126.93, 122.26, 115.26, 110.40, 48.27, 45.17, 28.09, 22.22, 10.69.

FT-IR (NaCl): 3321, 3037, 2925, 2902, 2837, 1614, 1483, 1432, 1245, 743 cm^{-1}.

MS: m/z 161.

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[4] Guram, A.S. ; Rennels, R.A. ; Buchwald, S.L. *Angew. Chem*. **1995**, *34*, 1348-1350.
[5] Pitts, M.R. ; Harrison, J.R. ; Moody, C.J. *J. Chem. Soc. Perkin Trans 1*, **2001**, 955-977.
[6] Micovic, M. *J. Org. Chem.* **1953**, *18*, 1190-1196.

1-Benzyl-1,2,3,4-tetrahydroquinoline[7] (Table 2, entries 9 and 10)

The title compound was isolated as a colorless oil. (95% using the Ni/bpy catalyst, 93 % using the Ni/SIPr catalyst).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.15 (m, 5H), 6.97-6.90 (m, 2H), 6.53 (brdd, 1H), 6.48 (brd, 1H), 4.42 (s, 2H), 3.35-3.27 (m, 2H), 2.82-2.73 (m, 2H), 2.01-1.93 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$,) δ 145.49, 138.84, 128.89, 128.46, 127.09, 126.64, 126.48, 122.08, 115.78, 110.88, 55.07, 49.76, 28.15, 22.31.

FT-IR (NaCl): 2907, 2831, 1649, 1580, 1487, 1421, 1371, 1107, 1035, 951, 732 cm^{-1}.

MS: *m / z* 223.

2,3,4,5-Tetrahydro -1*H*-1-benzazepine[8] (Table 2, entry 11)

The title compound was isolated as a colorless oil (81% using the Ni/SIPr catalyst).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, J = 7.6 Hz, 1H), 6.99 (dd, J = 7.6, 7.6 Hz, 1H), 6.79 (dd, J = 7.6, 7.6 Hz, 1H), 6.66 (d, J = 7.6 Hz, 1H), 3.59 (NH), 3.00-2.93 (brt, 2H), 2.78-2.71 (brt, 2H), 1.79-1.71 (m, 2H), 1.64-1.55 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$,) δ 150.21, 133.43, 130.51, 126.33, 120.55, 119.13, 48.61, 35.87, 31.78, 26.73.

FT-IR (NaCl): 3395, 3051, 2963, 2917, 2870, 1609, 1584, 1486, 1444, 1375, 1258, 747 cm^{-1}.

MS: *m / z* 147.

1-Ethyl-2,3,4,5-tetrahydro -1*H*-1-benzazepine[9] (Table 2, entries 12 and 13)

The title compound was isolated as a colorless oil (70% using the Ni/bpy catalyst, 73% using the Ni/SIPr catalyst).

^{1}H NMR (200 MHz, $CDCl_3$) δ 7.18-7.04 (m, 2H), 6.95-6.78 (m, 2H), 3.15 (q, J = 6.80 Hz, 2H), 2.95-2.88 (brt, 2H), 2.83-2.71 (brt, 2H), 2.83-2.71 (brt, 2H), 1.88-1.52 (m, 4H), 1.18 (t, J = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$,) δ 149.52, 134.12, 130.41, 127.12, 123.05, 117.02, 49.27, 47.51, 35.01, 29.99, 26.02, 11.05.

FT-IR (NaCl): 3025, 2916, 2847, 1603, 1497, 1453, 1319, 1141, 771, 700 cm^{-1}.

MS: *m / z* 175.

1-Benzyl-2,3,4,5-tetrahydro –1*H*-1-benzazepine[4] (Table 2, entries 14 and 15)

The title compound was isolated as a colorless oil (72% using the Ni/bpy catalyst, 78% using the Ni/SIPr catalyst).

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[7] Wolfe, J.P. ; Rennels, R.A. ; Buchwald, S.L. *Tetrahedron* **1996**, *52*, 7525-7546.
[8] Grunewald, G.L. ; Dahanukar, V.H. ; Ching, P. ; Criscione, K.R. *J. Med. Chem*. **1996**, *39*, 3539-3546.
[9] Michel, S. ; Le Gall, E. ; Hurvois, J.P. ; Moinet, C. ; Tallec, A. ; Uriac, P. ; Toupet, L. *Liebigs Ann*., *Recueil* **1997**, *1*, 259-267.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.2 Hz, 2H), 7.32 (dd, J = 7.2, 7.2 Hz, 2H), 7.23 (dd, J = 7.2, 7.2 Hz, 1H), 7.17-7.10 (m, 2H), 6.97 (d, J = 8.4 Hz, 1H), 6.87 (dd, J = 7.2, 7.2 Hz, 1H), 4.30 (s, 2H), 2.92-2.82 (m, 4H), 1.63-1.57 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$,) δ 153.15, 140.35, 136.59, 130.10, 128.81, 128.75, 127.37, 127.14, 121.67, 118.07, 59.13, 53.85, 35.52, 30.52, 26.29.

FT-IR (NaCl): 2893, 2821, 1652, 1582, 1493, 1427, 1365, 1101, 1031, 940, 747, 667 cm^{-1}.

MS: m / z 223.

4-Benzyl-3,4-dihydro-2*H*-1,4-benzoxazine[10] (Table 3, entries 1 and 2).

The title compound was isolated as a yellow oil (51 % using the Ni/bpy catalyst; 47 % using the Ni/SIPr catalyst).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-6.80 (m, 4H), 4.42 (s, 2H), 4.26 (t, J = 4.40 Hz, 2H), 3.35 (t, J = 4.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$,) δ 143.93, 138.04, 130.34, 128.75, 127.10, 127.06, 121.59, 117.75, 116.32, 112.52, 64.56, 54.96, 47.32.

FT-IR (NaCl): 3062, 2959, 2924, 2865, 1603, 1501, 1450, 1342, 1307, 1242, 1164, 1050, 907, 807, 743, 701 cm^{-1}.

MS: m / z 225.

4-(2,3-Dimethoxyphenetyl)-3,4-dihydro-2*H*-1,4-benzoxazine (Table 3, entries 3 and 4).

The title compound was isolated as a yellow oil (46 % using the Ni/bpy catalyst; 41 % using the Ni/SIPr catalyst).

^{1}H NMR (200 MHz, $CDCl_3$) δ 7.25 (brt, 2H), 6.84-6.66 (m, 5H), 4.16 (t, J = 4.60 Hz, 2H), 3.86 (s, 6H), 3.49 (t, J = 7.40 Hz, 2H), 3.25 (t, J = 4.6 Hz, 2H), 2.83 (t, J = 7.40 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$,) δ 156.03, 147.48, 143.85, 134.66, 132.14, 121.59, 120.60, 117.08, 116.30, 112.02, 111.63, 111.31, 64.27, 55.82, 55.79, 52.85, 47.33, 31.95.

FT-IR (NaCl): 3060, 2931, 2875, 2843, 1603, 1581, 1509, 1454, 1258, 1234, 1153, 1035 cm^{-1}.

MS: m / z 299.

Anal. Calcd. for $C_{18}H_{21}NO_3$: C, 72.22, H, 7.07, N, 4.68. Found: C, 72.3, H, 7.3, N, 4.0.

5-Butyl-2,3,4,5-tetrahydro-1,5-benzoxazepine (Table 3, entries 5 and 6).

The title compound was isolated as a yellow oil (50 % using the Ni/bpy catalyst).

^{1}H NMR (200 MHz, $CDCl_3$) δ 6.96-6.71 (m, 4H), 4.14 (t, J = 6.20 Hz, 2H), 3.28 (t, J = 4.80 Hz, 2H), 3.17 (t, J = 7.40 Hz, 2H), 2.27-1.90 (m, 2H), 1.70-1.52 (m, 2H), 1.47-1.27 (m, 2H), 0.94 (t, J = 7.20 Hz, 3H).

[10] Butler, R.C.M. ; Chapleo, C.B. ; Myers, P.L. ; Welbourn, A.P. *J. Heterocycl. Chem.* **1985**, *22*, 177-181.

^{13}C NMR (100 MHz, $CDCl_3$,) δ 151.65, 143.85, 123.69, 121.76, 120.54, 118.67, 70.75, 53.42, 50.58, 30.31, 29.94, 20.82, 14.42.

FT-IR (NaCl): 2955, 2934, 2867, 1597, 1495, 1461, 1252, 1162, 1060, 929, 744 cm^{-1}.

MS: *m / z* 205.

Anal. Calcd. for $C_{13}H_{19}NO$: C, 76.06, H, 9.33, N, 6.82. Found: C, 76.0, H, 9.5, N, 6.5.

5-Benzyl-2,3,4,5-tetrahydro-1,5-benzoxazepine (Table 3, entries 7 and 8).

The title compound was isolated as a white solid. Mp = 68°C. (47% using the Ni/bpy catalyst).

^{1}H NMR (200 MHz, $CDCl_3$) δ.7.41-7.25 (m, 5H), 6.98-6.73 (m, 4H), 4.40 (s, 2H), 4.18 (t, *J* = 5.6 Hz, 2H), 3.25 (t, *J* = 5.6 Hz, 2H), 2.02-1.87 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$,) δ 151.50, 144.26, 139.63, 128.94, 128.18, 127.49, 123.91, 121.82, 121.11, 118.84, 70.94, 57.76, 50.04, 29.86.

FT-IR (NaCl): 2961, 2934, 2867, 1615, 1597, 1495, 1461, 1439, 1252, 1162, 1060, 825, 744 cm^{-1}.

MS: *m / z* 205.

Anal. Calcd. for $C_{16}H_{17}NO$: C, 80.30, H, 7.16, N, 5.85. Found: C, 80.2, H, 7.3, N, 5.7.

5-(2,2-Diethoxyethyl)-2,3,4,5-tetrahydro-1,5-benzoxazepine (Table 3, entries 9 and 10).

The title compound was isolated as a thick yellow oil (53 % using the Ni/bpy catalyst).

^{1}H NMR (200 MHz, $CDCl_3$) δ 7.37-7.15 (m, 2H), 6.95-6.85 (m, 2H), 4.61 (t, *J* = 5.6 Hz, 1H), 4.10 (t, *J* = 5.8 Hz, 2H), 3.70 (q, *J* = 7.2 Hz, 4H), 2.87 (t, *J* = 6.8 Hz, 2H), 2.76 (d, J = 5.6 Hz, 2H), 2.10-1.90 (m, 2H), 1.20 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$,) δ 154.80, 130.52, 129.72, 127.97, 121.60, 120.92, 113.82, 102.44, 67.69, 62.75, 52.61, 47.08, 29.93, 15.74.

FT-IR (NaCl): 2969, 2869, 1590, 1486, 1462, 1369, 1292, 1248, 1125, 1061, 750 cm^{-1}.

MS: *m / z* 265.

Anal. Calcd. for $C_{15}H_{23}NO$: C, 67.90, H, 8.74, N, 5.28. Found: C, 68.0, H, 9.0, N, 5.1.

Benzo[e]indolizidine[7]

The title compound was isolated as a pale yellow oil (85% using the Ni/bpy catalyst, 81% using the Ni/SIPr catalyst).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (dd, *J* = 7.8, 7.9 Hz, 1H), 6.98 (d, *J* = 7.3 Hz, 1H), 6.54 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.39 (d, *J* = 7.6 Hz, 1H), 3.45-3.14 (m, 3H), 2.90-2.68 (m, 2H), 2.16-1.83 (m, 4H), 1.55-1.35 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$,) δ 144.72, 128.34, 127.11, 121.13, 114.67, 109.82, 57.92, 46.81, 33.12, 28.10, 27.33, 23.95.

FT-IR (NaCl): 2935, 2837, 1604, 1502, 1460, 1355, 1326, 741 cm^{-1}.

MS: *m / z* 173.

2,3-Dimethoxy-5,6-dihydroindolo[2,1-a]isoquinoline[11]

After treatment with HCO_2NH_4 over Pd/C, the title compound was isolated as a yellow oil (87% using the Ni/bpy catalyst, 79% using the Ni/SIPr catalyst).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.6 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H), 7.22 (s, 1H), 7.17 (ddd, J = 7.2, 7.2, 1.2 Hz, 1H), 7.08 (ddd, J = 7.2, 7.2, 1.2 Hz, 1H), 6.74 (s, 2H), 4.21 (t, J = 6.4 Hz, 2H), 3.95 (s, 3H), 3.90 (s, 3H), 3.10 (t, J = 6.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$,) δ.148.69, 136.55, 135.78, 128.87, 124.89, 121.54, 121.23, 120.34, 119.71, 111.18, 108.71, 107.28, 95.04, 56.04, 55.97, 40.17, 28.68.

FT-IR (NaCl): 3075, 3010, 2956, 2861, 1596, 1552, 1503, 1463, 1263, 1241, 1155, 1017 cm^{-1}.

MS: m / z 284.

[11] (a) Orito, K.; Miyazawa, M.; Kanbayashi, R.; Tokuda, M.; Sugimone, H. *J. Org. Chem.* **1999**, *64*, 6583-6596. (b) Orito, K.; Harada, R.; Uchiito, S.; Tokuda, M. *Org. Lett*. **2000**, *2*, 1799-1801.