Supporting Information

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- Experimental procedures and spectroscopic data
- $^1$H NMR and $^{13}$C NMR spectra for compounds 4 and 8a-m

Experimental procedures and spectroscopic data

General Considerations: All reactions were carried out under nitrogen atmosphere in a RR98030 12 place Carousel Reaction Station™ from Radleys Discovery Technologies, equipped with gas-tight threaded caps with a valve, cooling reflux head system, and digital temperature controller. Dioxane was continuously refluxed and freshly distilled from sodium/benzophenone under nitrogen. NMR spectra were recorded at 400 or 300 MHz for $^1$H and 100.6 or 75.45 MHz for $^{13}$C, with tetramethylsilane as internal standard for $^1$H and the residual solvent signals as standard for $^{13}$C. Chemical shifts are given in ppm. Mass spectra were obtained by EI (70eV). Pd$_2$(dba)$_3$ was purchased from Strem Chemical co. and used without further purification. All phosphine ligands used are commercially available from Strem or Aldrich and were used without further purification. Commercial NaO'Bu and Cs$_2$CO$_3$ were used after lyophilization. Non-commercial imines 1a, 1b, 1c, 1d, 1j and 1k were prepared according to literature procedures. Imines 1e-i were prepared by refluxing in a Dean-Stark apparatus a mixture of the corresponding ketones and primary amines in toluene, in the presence of a catalytic amount of p-TsOH.
Palladium catalyzed a-arylation of ketimine 1 with aryl bromide 2.

Synthesis of \(N-(2,2\text{-bis}(3\text{-methoxyphenyl})-1\text{-phenylvinyl})\text{benzenamine 4:}\)

A reaction tube under nitrogen atmosphere was charged with XPhos (19.6 mg, 0.04 mmol, 4 mol %), tris(dibenzylideneacetone)dipalladium (0) (18.3 mg, 0.02 mmol, 2 mol %), sodium tert-butoxide (268 mg, 2.8 mmol, 2.8 eq.) and dioxane (3 mL). After 1 min 3-bromoanisole (374 mg, 2 mmol) was added under nitrogen and heated to 110º C. After 5 min the imine 1 (1 mmol) was added under nitrogen with stirring for 14 h. The mixture was allowed to cool to room temperature, taken up in hexanes (15 mL), and filtered through Celite. The solvents were evaporated under reduced pressure. Purification by flash chromatography (SiO\(_2\), Hex/EtOAc, 9:1) afforded 310 mg (76%) of 4.

\[\text{H-NMR (CDCl}_3, 300 \text{ MHz): } \delta = 7.41-7.38 (m, 2H), 7.26-7.15 (m, 4H), 7.10-7.01 (m, 4H), 6.92-6.74 (m, 4H), 6.68-6.60 (m, 2H), 6.57-6.54 (m, 2H), 5.83 (s, 1H), 3.63 (s, 3H), 3.57 (s, 3H).\]

\[\text{C-NMR (CDCl}_3, 75 \text{ MHz): } 159.6, 158.8, 144.4, 143.4, 143.2, 137.8, 137.0, 130.6, 129.4, 128.7, 128.4, 128.0, 127.5, 126.2, 124.2, 122.3, 119.6, 117.4, 116.8, 114.8, 112.9, 111.9, 54.9 \text{ ppm.}\]

General Procedure for the synthesis of indoles 8a-1 by palladium catalyzed reaction of imines 1a-k with o-dihaloarenes 5a-d – Method A:

A reaction tube under nitrogen atmosphere was charged with XPhos (19.6 mg, 0.04 mmol, 4 mol %), tris(dibenzylideneacetone)dipalladium (0) (18.3 mg, 0.02 mmol, 2 mol %), sodium tert-butoxide (268 mg, 2.8 mmol, 2.8 eq.) and dioxane (3 mL). After 1 min the dihalide 5 (1 mmol) was added under nitrogen and heated to 110º C. After 5 min the imine 1 (1 mmol) was added under nitrogen with stirring until completely disappear of dihalide 5 determined by GC. The mixture was allowed to cool to room temperature, taken up in hexanes (15 mL), and filtered through Celite. The solvents were evaporated under reduced pressure. Purification by flash chromatography (SiO\(_2\), Hex/EtOAc, 20:1) afforded indoles 8a-1.

Using this procedure were prepared:

\[1,2\text{-Diphenyl indole 8a:}\]

From \(N-(1\text{-phenylethylidene})\text{benzenamine 1a} \text{ (195 mg, 1 mmol)}\) and \(1,2\text{-dibromobenzene} \text{ (146 \muL, 1 mmol), following the general procedure and after 14h of reaction 239 mg (86 \%)}\) of 8a were obtained. \[\text{H-NMR (CDCl}_3, 400 \text{ MHz): } 7.67-\]
7.65 (m, 1H), 7.38-7.25 (m, 2H), 7.31-7.13 (m, 11H), 6.78 (s, 1H) ppm. 
$^{13}$C NMR (CDCl$_3$, 100.6 MHz) 140.6, 138.9, 138.4, 132.5, 129.2, 128.8, 128.2, 128.1, 128.0, 127.2, 127.1, 122.3, 120.6, 120.4, 110.5, 103.6 ppm. EI HRMS calcd for C$_{26}$H$_{15}$N, 269.1204; found, 269.1203. Spectroscopic data in agreement with those reported in the literature.

1-benzyl-2-phenylindole 8b:

From phenyl-$N$-(1-phenylethylidene)methanamine 1b (209 mg, 1 mmol) and 1,2-dibromobenzene (146 µL, 1 mmol), following the general procedure and after 20h of reaction 158 mg (56 %) of 8b were obtained. $^1$H NMR (CDCl$_3$, 400 MHz) 7.76-7.74 (m, 2H), 7.55-7.50 (m, 3H), 7.44-7.42 (m, 4H), 7.35-7.21 (m, 5H), 6.73 (s, 1H), 5.43 (s, 2H) ppm. $^{13}$C NMR (CDCl$_3$, 100.6 MHz) 141.8, 138.2, 138.0, 132.7, 129.2, 128.8, 128.6, 128.4, 128.0, 127.2, 126.0, 121.9, 120.6, 120.2, 110.6, 102.4, 47.7 ppm. EI HRMS calcd for C$_{21}$H$_{17}$N, 283.1361; found, 283.1361. Spectroscopic data in agreement with those reported in the literature.

1-(2-chlorophenyl)-2-phenylindole 8c:

From 2-chloro-$N$-(1-phenylethylidene)benzenamine 1c (229 mg, 1 mmol) and 1,2-dibromobenzene (146 µL, 1 mmol), following the general procedure and after 14h of reaction 233 mg (77 %) of 8c were obtained. $^1$H NMR (CDCl$_3$, 400 MHz) 7.65-7.62 (m, 1H), 7.47-7.44 (m, 1H), 6.25-6.11 (m, 10H), 6.94-6.91 (m, 1H), 6.77 (s, 1H) ppm. $^{13}$C NMR (CDCl$_3$, 100.6 MHz) 141.3, 138.8, 136.4, 133.6, 132.3, 131.1, 130.5, 129.4, 128.3, 128.2, 127.6, 127.4, 122.3, 120.7, 120.5, 110.7, 103.3 ppm. EI HRMS calcd for C$_{20}$H$_{14}$ClN, 303.0815; found, 303.0813.

1-(4-methoxyphenyl)-2-phenylindole 8d:

From 4-methoxy-$N$-(1-phenylethylidene)benzenamine 1d (225 mg, 1 mmol) and 1,2-dibromobenzene (146 µL, 1 mmol), following the general procedure and after 24h of reaction 239 mg (80 %) of 8d were obtained. $^1$H NMR (CDCl$_3$, 400 MHz) 7.76-7.74 (m, 1H), 7.37-7.23 (m, 10H), 7.00-6.97 (d, 2H, 8.8 Hz), 6.86 (s, 1H), 3.89 (s, 3H) ppm. $^{13}$C NMR (CDCl$_3$, 100.6 MHz) 158.6, 140.9, 139.4, 132.6, 131.3, 129.2, 128.9, 128.2, 128.1, 127.3, 122.2, 120.6, 120.5, 114.5, 110.7, 103.2, 55.5 ppm. EI HRMS calcd for C$_{22}$H$_{16}$NO, 299.1310; found, 299.1304. Spectroscopic data in agreement with those reported in the literature.
2-(4-methoxyphenyl)-3-methyl-1-phenylindole 8e:

From N-(1-(4-methoxyphenyl)propylidene)benzenamine 1e (239 mg, 1 mmol) and 1,2-dibromobenzene (146 µL, 1 mmol), following the general procedure and after 14h of reaction 206 mg (66 %) of 8e were obtained. ¹H NMR (CDCl₃, 400 MHz) 7.70-7.68 (m, 1H), 7.40-7.33 (m, 3H), 7.31-7.27 (m, 1H), 7.24-7.20 (m, 4H), 7.18-7.15 (d, 2H, 8.5 Hz), 6.86-6.84 (d, 2H, 8.5 Hz), 3.82 (s, 3H), 2.44 (s, 3H) ppm. ¹³C NMR (CDCl₃, 100.6 MHz) 158.6, 138.7, 137.4, 136.7, 131.7, 129.0, 127.9, 126.5, 124.4, 122.2, 120.0, 118.7, 113.5, 110.2, 110.1, 55.2, 9.6 ppm. EI HRMS calcd for C₂₂H₁₉NO, 313.1467; found, 313.1466.

4-phenyl-1,2,3,4-tetrahydrocyclopenta[b]indole 8f:

From N-cyclopentylidenebenzenamine 1f (159 mg, 1 mmol) and 1,2-dibromobenzene (146 µL, 1 mmol), following the general procedure and after 14h of reaction 200 mg (86 %) of 8f were obtained. ¹H NMR (CDCl₃, 400 MHz) 7.57-7.50 (m, 5H), 7.41-7.37 (m, 1H), 7.21-7.18 (m, 3H), 3.01-2.95 (m, 4H), 2.65-2.58 (m, 2H) ppm. ¹³C NMR (CDCl₃, 100.6 MHz) 145.7, 141.0, 139.0, 129.5, 126.2, 125.1, 124.8, 120.9, 120.4, 120.1, 118.7, 110.8, 28.4, 26.3, 24.6 ppm. Spectroscopic data in agreement with those reported in the literature.⁵,⁶

9-phenyl-6,7,8,9-tetrahydro-5H-carbazole 8g:

From N-cyclohexylidenebenzenamine 1g (173 mg, 1 mmol) and 1,2-Dibromobenzene (146 µL, 1 mmol), following the general procedure and after 14h of reaction 163 mg (66 %) of 8g were obtained. ¹H NMR (CDCl₃, 400 MHz) 7.59-7.53 (m, 3H), 7.45-7.41 (m, 3H), 7.29-7.27 (m, 1H), 7.18-7.13 (m, 2H), 2.86 (m, 2H), 2.66 (m, 2H), 1.95 (m, 4H) ppm. ¹³C NMR (CDCl₃, 100.6 MHz) 138.0, 137.1, 135.8, 129.3, 127.2, 127.0, 124.2, 121.3, 119.6, 117.7, 110.9, 109.8, 23.4, 23.3, 23.2, 21.1 ppm. EI HRMS calcd for C₁₈H₁₇N, 247.1355; found, 247.1352. Spectroscopic data in agreement with those reported in the literature.⁵,⁶

5-phenyl-5,6,7,8,9,10-hexahydrocyclohepta[b]indole 8h:

From N-cycloheptylidenebenzenamine 1h (187 mg, 1 mmol) and 1,2-dibromobenzene (146 µL, 1 mmol), following the general procedure and after 14h of reaction 208 mg (80 %) of 8h were obtained. ¹H NMR (CDCl₃, 400 MHz) 7.63-7.56
(m, 3H), 7.50-7.46 (m, 1H), 7.39-7.37 (m, 2H), 7.22-7.14 (m, 3H), 2.99 (m, 2H), 2.79 (m, 2H), 1.99 (m, 2H), 1.90 (m, 2H), 1.78 (m, 2H) ppm.

\(^{13}\)C NMR (CDCl\(_3\), 100.6 MHz) 139.5, 138.2, 136.6, 129.3, 128.4, 128.2, 127.4, 120.9, 119.6, 117.6, 115.0, 110.1, 32.0, 28.4, 27.4, 27.2, 24.6 ppm. EI HRMS calcd for C\(_{19}\)H\(_{19}\)N, 261.1512; found, 261.1507. Spectroscopic data in agreement with those reported in the literature.\(^5^,\)\(^6\)

**2-pentyl-1-phenylindole 8i**

From \(N\)-(heptan-2-ylidene)benzamine \(1i\) (189 mg, 1 mmol) and 1,2-dibromobenzene (146 \(\mu\)L, 1 mmol), following the general procedure and after 14h of reaction 208 mg (73\% ) of a 5:1 mixture of \(8i\) and 3-butyl-2-methyl-1-phenylindole \(8i'\) were obtained. \(8i\): \(^{1}H\) NMR (CDCl\(_3\), 300 MHz) 7.69-7.15 (m, 9H), 6.52 (s, 1H), 2.70 (t, 2H, 7.7Hz) 1.67 (m, 2H), 1.36 (m, 4H), 0.93 (t, 3H, 7Hz) ppm. \(^{13}\)C NMR (CDCl\(_3\), 75.45 MHz) 144.0, 140.3, 140.1, 131.4, 130.3, 130.1, 129.8, 123.0, 121.9, 121.6, 112.0, 102.1, 33.4, 30.3, 29.1, 24.4, 16.0 ppm. GC/LRMS (EI) \(8i\): 263(33) M\(^+\), 206(100)(M-57)\(^+\). \(8i'\): 263(30) M\(^+\), 220(100)(M-43)\(^+\). EI HRMS calcd for C\(_{19}\)H\(_{21}\)N, 263.1668; found, 263.1664.

**2-methyl-1-phenylindole 8j**:

From \(N\)-(propan-2-ylidene)benzamine \(1j\) (133 mg, 1 mmol) and 1,2-dibromobenzene (146 \(\mu\)L, 1 mmol), following the general procedure and after 14h of reaction 147 mg (71\% ) of \(8j\) were obtained. \(^{1}H\) NMR (CDCl\(_3\), 300 MHz) 7.64-7.62 (m, 1H), 7.53-7.51 (m, 1H), 7.43-7.41 (m, 2H), 7.19-7.16 (m, 3H), 6.48 (s, 1H), 2.37 (s, 3H) ppm. \(^{13}\)C NMR (CDCl\(_3\), 75.45 MHz) 137.8, 137.6, 136.6, 129.0, 127.8, 127.6, 127.3, 120.6, 119.6, 119.2, 109.6, 100.9, 13.0 ppm. Spectroscopic data in agreement with those reported in the literature.\(^7\)

**1-tert-butyl-2-phenylindole 8k**:

From 2-methyl-\(N\)-(1-phenylethylidene)propan-2-amine \(1k\) (175 mg, 1 mmol) and 1,2-dibromobenzene (146 \(\mu\)L, 1 mmol), following the general procedure and after 14h of reaction 179 mg (72\% ) of \(8k\) were obtained. \(^{1}H\) NMR (CDCl\(_3\), 400 MHz) 7.80-7.78 (d, 1H, 8.4 Hz), 7.65-7.63 (d, 1H, 8.2 Hz), 7.49-7.40 (m, 5H), 7.27-7.14 (m, 2H), 6.37 (s, 1H), 1.66 (s, 9H) ppm. \(^{13}\)C NMR (CDCl\(_3\), 100.6 MHz) 141.83, 138.20, 137.29, 130.20, 129.06, 127.56, 127.43, 120.67, 120.53, 119.37, 115.06, 106.19, 58.93, 32.09 ppm. EI HRMS calcd for C\(_{18}\)H\(_{21}\)N, 249.1512; found, 249.1509.
6-(benzyloxy)-2-(4-methoxyphenyl)-3-methyl-1-phenylindole 8l.

From N-(1-(4-methoxyphenyl)propylidene benzenamine 1e (239 mg, 1 mmol) and 1-((4-bromo-3-chlorophenoxy)methyl)benzene 5d (297 mg, 1 mmol), following the general procedure and after 14h of reaction 293 mg (70 %) of 8l were obtained. ¹H NMR (CDCl₃, 400 MHz) 7.56-7.54 (m, 1H), 7.47-7.45 (m, 2H), 7.41-7.33 (m, 5H), 7.30-7.26 (m, 1H), 7.17-7.12 (m, 4H), 6.99-6.96 (m, 1H), 6.93-6.92 (m, 1H), 6.84-6.82 (m, 2H), 5.08 (s, 2H), 3.80 (s,3H), 2.40 (s, 3H) ppm. ¹³C NMR (CDCl₃, 75.45 MHz) 158.5, 155.9, 138.7, 138.1, 137.5, 135.9, 131.6, 129.1, 128.5, 127.8, 127.6, 126.5, 124.6, 123.8, 119.3, 113.5, 110.2, 110.0, 95.8, 70.7, 55.2, 9.7 ppm. EI HRMS calcd for C₂₉H₂₅NO₂, 419.1879; found, 419.1878.
General Procedure for the Pd-catalyzed three-components synthesis of indoles from primary amines, bromoalkenes and dihalobenzenes – Method B:

A reaction tube under nitrogen atmosphere was charged with XPhos (19.6 mg, 0.04 mmol, 4 mol %), tris(dibenzylideneacetone)dipalladium (0) (18.3 mg, 0.02 mmol, 2 mol %), sodium tert-butoxide (403 mg, 4.2 mmol, 4.2 eq.) and dioxane (4 mL). After 1 min the bromoalkene (1 mmol) and the amine (1 mmol) were added under nitrogen and heated to 110ºC. After 5 min the dihalide (1 mmol) was added under nitrogen with stirring until completely disappear of starting materials determined by GC. The mixture was allowed to cool to room temperature, taken up in hexanes (15 mL), and filtered through Celite. The solvents were evaporated under reduced pressure. Purification by flash chromatography (SiO₂, Hex/EtOAc, 20:1) afforded indoles 8a, 8b, 8j and 8m.

Using this procedure were prepared:

1,2-Diphenylindole 8a:

From aniline (93 mg, 1 mmol), a-Bromostyrene (183 mg, 1 mmol) and 1,2-dibromobenzene 5a (146 µL, 1 mmol), following the general procedure and after 20h of reaction 204 mg (76 %) of 8a were obtained.

1-benzyl-2-phenyl indole 8b:

From N-benzylamine (107 mg, 1 mmol), a-Bromostyrene (183 mg, 1 mmol) and 1,2-dibromobenzene 5a (146 µL, 1 mmol), following the general procedure and after 20h of reaction 184 mg (65 %) of 8b were obtained.

2-methyl-1-phenylindole 8j:

From aniline (93 mg, 1 mmol), 2-bromopropene (121 mg, 1 mmol) and 1,2-dibromobenzene 5a (146 µL, 1 mmol), following the general procedure and after 20h of reaction 141 mg (68 %) of 8j were obtained.

6-(benzyloxy)-1,2-diphenylindole 8m:

From aniline (93 mg, 1 mmol), a-Bromostyrene (183 mg, 1 mmol) and 1-((4-bromo-3-chlorophenoxy)methyl)benzene 5d (297 mg, 1 mmol), following the general procedure and after 20h of reaction 214 mg (57 %) of 8m were obtained. "H NMR (CDCl₃, 400 MHz) 7.61-7.59 (d, 1H, 8.5 Hz), 7.48-7.35
(m, 8H), 7.29–7.25 (m, 7H), 6.98–6.96 (m, 1H), 6.91 (s, 1H), 6.78 (s, 1H), 5.08 (s, 2H) ppm. $^{13}$C NMR (CDCl$_3$, 75.45 MHz) 155.7, 139.9, 139.6, 138.5, 137.2, 132.6, 129.2, 128.5, 128.4, 128.0, 127.8, 127.8, 127.6, 127.1, 126.9, 122.7, 121.0, 110.9, 103.5, 95.9, 70.6 ppm. EI HRMS calcd for C$_{27}$H$_{21}$NO, 375.1617; found, 375.1611.

References

3 B. S. Lane, D. Sames, Org. Lett. 2004, 6, 2897.