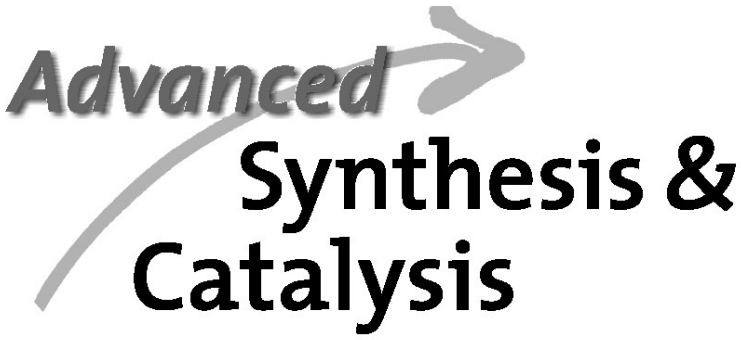

Supporting Information

Aryl-Alkenyl-Dihalides as Substrates for Palladium Catalysed Tandem C-N Bond Formation: Efficient Synthesis of 1-Substituted Indoles

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C-N Bond Formation/ Heterocycles / Homogeneous catalysis / Indoles/ Palladium / Tandem Reactions

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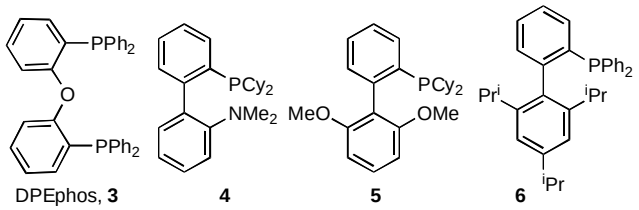
Supporting Information

General Considerations

Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1600 FT IR spectrophotometer, using NaCl discs. ^{1}H NMR spectra were obtained on a Bruker Avance 300 spectrometer operating at 300 MHz, using the residual solvent as an internal standard. *J* values are given in Hz. ^{13}C NMR spectra were obtained on a Bruker Avance 300 spectrometer operating at 75 MHz, using the residual solvent as an internal standard. Mass spectrometry measurements were performed at the EPSRC National Spectrometry Service Centre, University of Wales Swansea. All accurate mass measurements are reported for the lighter isotopes. Elemental analyses were performed at the microanalysis service, University of Bath, using an Exeter Analytical Inc. CE-440 elemental analyser. All dry solvents were obtained by passing through anhydrous alumina columns[i] using an Innovative Technology Inc. PS-400-7 solvent purification system. Dioxane was distilled over calcium hydride and stored over 4Å molecular sieves. Petroleum ether refers to that fraction obtained between 40-60^{o}C. All glassware was dried in an oven and allowed to cool under nitrogen prior to use. All commercial reagents were used as obtained. The

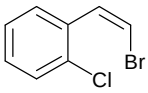
phosphine ligands **4**, **5** and **6** were purchased from Aldirch chemical company and DPEphos **3** was purchased from Strem chemicals. Flash chromatography was conducted under medium pressure, using matrix 60 silica.

Ligands used in this investrigation:



DPEphos, **3** **4** **5** **6**

General procedure A for the Wittig reactions using potassium *tert*-butoxide, exemplified by: (*Z*)-1-(2-Bromovinyl)-2-chlorobenzene, 2b

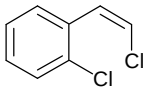


Potassium *tert*-butoxide (1.92 g, 17.11 mmol) was added portion-wise to a stirred solution of (bromomethyl)triphenylphosphonium bromide (7.43 g, 17.11 mmol) in anhydrous tetrahydrofuran (25 mL) at -78 °C under nitrogen. The resulting mixture was stirred for 1.5 hours to give a bright yellow suspension, which was then treated dropwise with 2-chlorobenzaldehyde (1.60 mL, 14.21 mmol). The resulting reaction mixture was allowed to slowly warm to 0 °C and stirred for 16 hours. The reaction mixture was quenched with petroleum ether (10 mL) and cast into petroleum ether (150 mL). The white suspension was filtered through a celite pad, washing with petroleum ether (100 mL). The filtrate was partially reduced in *vacuo*. The suspension was filtered through a second celite pad, washing with petroleum ether (150 mL). The filtrate was reduced in *vacuo*. The product was separated by flash chromatography (elutant: Petroleum ether) to yield the *vinyl bromide* (1.89 g, 61%, *Z:E* 6:1), as a pale amber oil: $?_{max}$ (liquid film)/cm^{-1} 3073, 3019, 2924, 1617, 1565, 1467, 1434, 1321, 1277, 1219, 1126, 1051, 1035, 946, 935, 831, 761, 726, 682, 658; d_H ($CDCl_3$, (*Z*)-isomer) 6.59 (1H, d, *J* = 8.1, C=CHBr), 7.23-7.30 (3H, m, ArH and CH(Ar)=C), 7.37-7.43 (1H, m, ArH), 7.79-7.86 (1H, m, ArH); d_H ($CDCl_3$, (*E*)-isomer) 6.79 (1H, d, *J* = 14.0, C=CHBr), 7.19-7.32 (2H, m, ArH), 7.33-7.43 (2H, m, ArH), 7.46 (1H, d, *J* = 14.0, CH(Ar)=C); d_C ($CDCl_3$) 109.2, 109.4,

126.2, 126.9, 127.0, 129.3, 129.4, 129.4, 129.9, 129.9, 130.3, 132.4, 133.3, 133.5, 133.7, 134.1.

Data in accordance with that reported in the reported literature.[ii]

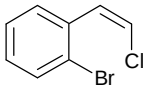
(*Z*)-1-chloro-2-(2-chlorovinyl)-benzene, 2d



Prepared following general procedure A using (chloromethyl)triphenylphosphonium chloride (4.44 g, 12.80 mmol) and 2-chlorobenzaldehyde (1.50 g, 10.67 mmol). The product was separated by flash chromatography (elutant: Petroleum ether) to yield the *vinyl chloride* (1.62 g, 88%, *Z:E* 3:1), as a pale amber oil: $?_{max}$ (liquid film)/cm^{-1} 3073, 2926, 1608, 1566, 1469, 1437, 1340, 1282, 1240, 1127, 1051, 1037, 946, 932, 872, 846, 823, 763, 749, 701, 648; d_H ($CDCl_3$, (*Z*)-isomer) 6.42 (1H, d, *J* = 8.1, C=CHCl), 6.91 (1H, d, *J* = 8.1, CH(Ar)=C), 7.17-7.32 (2H, m, ArH), 7.38-7.43 (1H, m, ArH), 7.86-7.90 (1H, m, ArH); d_H ($CDCl_3$, (*E*)-isomer) 6.66 (1H, d, *J* = 13.6, C=CHCl), 7.17-7.32 (3H, m, ArH and CH(Ar)=C), 7.34-7.43 (2H, m, ArH); d_C ($CDCl_3$) 120.0, 121.2, 126.3, 126.4, 126.8, 127.0, 129.2, 129.3, 129.4, 129.9, 129.9, 130.5, 132.1, 132.6, 133.1, 133.6; *m/z* LRMS (EI^+) 171.9 ($^{35}Cl^{35}Cl$-M^+, 100%), 137.0 (50), 102.1 (30), 75.0 (20), 49.1 (40); *m/z* LRMS (EI^+) 171.9 ($^{35}Cl^{35}Cl$-M^+, 100%), 137.0 (50), 102.1 (30), 75.0 (20), 49.1 ($CH_2{}^{35}Cl^+$, 40); HRMS (EI^+) 171.9836 (M^+. $C_8H_6Cl_2$ requires: 171.9841).

Data in accordance with that reported in the literature.[iii]

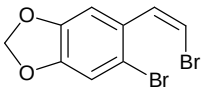
(*Z*)-1-Bromo-2-(2-chlorovinyl)benzene, 2c



Prepared following general procedure A using (chloromethyl)triphenylphosphonium chloride (2.25 g, 6.49×10^{-3} mol) and 2-bromobenzaldehyde (1.00 g, 5.4×10^{-3} mol). The product was separated by flash chromatography (elutant: Petroleum ether) to yield the *vinyl chloride* (1.04 g, 89%, *Z:E* 4:1), as a pale amber oil: $?_{max}$ (liquid film)/cm^{-1} 3071, 2925, 1606, 1588, 1562, 1464, 1431, 1338, 1279, 1238, 1182, 1117, 1045, 1025, 946, 930, 871, 846, 820, 762, 742, 699, 663, 646; d_H ($CDCl_3$, (*Z*)-isomer) 6.41 (1H, d, *J* = 8.1, C=CHCl), 6.86 (1H, dd, *J* = 8.1 and 0.4, CH(Ar)=C), 7.11-7.21 (1H, m, ArH), 7.29-7.42

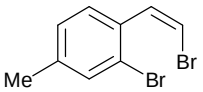
(1H, m, ArH), 7.61 (1H, dd, *J* = 8.0 and 1.2, ArH), 7.83 (1H, dd, *J* = 7.8 and 1.6, ArH); d_H ($CDCl_3$, (*E*)-isomer) 6.62 (1H, d, *J* = 13.6, C=CHCl), 7.11-7.21 (1H, m, CH(Ar)=C), 7.24-7.28 (2H, m, ArH), 7.29-7.42 (2H, ArH), 7.57 (1H, dd, *J* = 8.0 and 1.3, ArH); d_C ($CDCl_3$) 119.9, 121.2, 123.0, 123.9, 126.9, 127.0, 127.6, 128.9, 129.5, 130.7, 132.4, 132.6, 133.1, 133.9, 134.9; *m/z* LRMS (EI^+) 217.9 ($^{35}Cl^{81}Br$-M^+, 100%), 180.9 (40), 137.0 (28), 102.0 (68), 74.0 (30), 49.1 (70); HRMS (EI^+) 215.9339 (M+. C_8H_6BrCl requires: 215.9336).

(*Z*)-5-Bromo-6-(2-bromovinyl)benzo(1,3)dioxole



Prepared following general procedure A using (bromomethyl)triphenylphosphonium bromide (5.78 g, 0.013 mol) and 6-bromopiperonal (2.43 g, 0.011 mol). The product was separated by flash chromatography (elutant: 1% Diethyl ether – petroleum ether) to yield the *vinyl bromide* (2.30 g, 71%, *Z:E* 4:1), as a tan coloured solid: mp 68-71 °C; $?_{max}$ (nujol mull)/cm^{-1} 2924, 2854, 1612, 1504, 1465, 1412, 1377, 1304, 1244, 1104, 1040, 930, 863, 838, 736; d_H ($CDCl_3$, (*Z*)-isomer) 6.01 (2H, s, OCH_2O), 6.48 (1H, d, *J* = 8.0, C=CHBr), 7.05 (1H, s, ArH), 7.12 (1H, dd, *J* = 8.0 and 0.4, CH(Ar)=C), 7.34 (1H, s, ArH); d_H ($CDCl_3$, (*E*)-isomer) 5.98 (2H, s, OCH_2O), 6.61 (1H, d, *J* = 13.9, C=CHBr), 6.85 (1H, s, ArH), 6.99 (1H, s, ArH), 7.35 (1H, d, *J* = 13.9, CH(Ar)=C); d_C ($CDCl_3$) 101.9, 102.0, 107.4, 108.2, 109.8, 112.6, 112.8, 114.1, 115.1, 128.1, 129.1, 131.9, 135.9, 136.4, 146.8, 147.7, 148.2, 148.4; *m/z* LRMS (EI^+) 305.9 ($^{79}Br^{81}Br$-M^+, 40%), 146.0 (50), 87.1 (100); HRMS (EI^+) 303.8729 (M^+. $C_9H_6Br_2O_2$ requires: 303.8729).

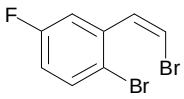
(*Z*)-2-Bromo-1-(2-bromovinyl)-4-methylbenzene



Prepared following general procedure A using (bromomethyl)triphenylphosphonium bromide (2.63 g, 6.03×10^{-3} mol) and 2-bromo-4-methylbenzaldehyde (1.00 g, 5.03×10^{-3} mol). The product was separated by flash chromatography (elutant: Petroleum ether) to yield the *vinyl bromide* (970 mg, 70%, *Z:E* 9:1), as a pale yellow oil: $?_{max}$ (liquid

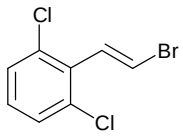
film)/cm^{-1} 3074, 3029, 2921, 2856, 1600, 1556, 1481, 1447, 1391, 1319, 1220, 1040, 934, 871, 829, 790, 729, 674; d_H ($CDCl_3$, (*Z*)-isomer) 2.34 (3H, s, Me), 6.54 (1H, d, *J* = 8.0, C=CHBr), 7.09-7.15 (H, m, ArH), 7.15 (1H, d, *J* = 8.0, CH(Ar)=C), 7.42-7.45 (1H, m, ArH), 7.69 (1H, d, *J* = 7.9, ArH); d_H ($CDCl_3$, (*E*)-isomer) 2.31 (3H, s, Me), 6.71 (1H, d, *J* = 13.9, C=CHBr), 7.05-7.10 (1H, m, ArH), 7.28 (1H, br d, *J* = 8.0, ArH), 7.38-7.50 (2H, m, ArH and CH(Ar)=C); d_C ($CDCl_3$) 20.8, 20.9, 108.2, 108.6, 122.5, 123.5, 126.7, 127.7, 128.5, 130.1, 132.0, 132.1, 133.0, 133.5, 139.8, 140.0; *m/z* LRMS (EI$^+$) 275.9 ($^{79}Br^{81}Br$-M$^+$, 20%), 195.0 (20), 114.9 (100), 89.1 (40); HRMS (EI$^+$) 273.8985 (M$^+$. $C_9H_8Br_2$ requires: 273.8987).

(*Z*)-1-Bromo-2-(2-bromovinyl)-4-fluorobenzene



Prepared following general general procedure A using (bromomethyl)triphenyl-phosphonium bromide (3.64 g, 8.35×10^{-3} mol) and 2-bromo-5-fluorobenzaldehyde (1.41 g, 7.00×10^{-3} mol). The product was separated by flash chromatography (elutant: 1% Petroleum ether) to yield the *vinyl bromide* (1.34 g, 69%, *Z:E* 9:1), as a pale amber oil: ?$_{max}$ (liquid film)/cm^{-1} 3299, 3076, 3023, 2925, 1618, 1599, 1576, 1459, 1411, 1320, 1273, 1222, 1198, 1146, 1104, 1033, 959, 936, 878, 813, 780, 730, 693, 674; d_H ($CDCl_3$, (*Z*)-isomer) 6.64 (1H, d, *J* = 8.1, C=CHBr), 6.86-6.99 (1H, m, ArH), 7.16 (1H, d, *J* = 8.1, CH(Ar)=C), 7.50-7.59 (2H, m, ArH); d_H ($CDCl_3$, (*E*)-isomer) 6.80 (1H, d, *J* = 13.9, C=CHBr), 6.86-6.99 (1H, m, ArH), 7.11 (1H, dd, *J* = 9.4 and 3.0, ArH), 7.39 (1H, dd, *J* = 13.9 and 1.2, CH(Ar)=C), 7.50-7.59 (1H, m, ArH); d_C ($CDCl_3$) 103.4, (d, $^4J_{CF}$ = 4.3), 105.8 (d, $^2J_{CF}$ = 23.6), 110.6 (d, $^2J_{CF}$ = 26.7), 111.2 (d, $^3J_{CF}$ = 9.3), 124.3, 126.6, 129.4, 129.5, 129.7, 132.4, 139.6, 158.1 (d, $^1J_{CF}$ = 235.1); *m/z* LRMS (EI$^+$) 279.9 ($^{79}Br^{81}Br$-M$^+$, 13%), 206.0 (48), 198.8 (35), 178.0 (53), 120.1 (100), 83.9 (50); HRMS (EI$^+$) 277.8735 (M$^+$. $C_8H_5Br_2F$ requires: 277.8737).

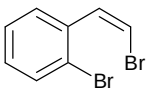
(*E*)-2-(2-Bromovinyl)-1,3-dichlorobenzene



Prepared following general general procedure A using (bromomethyl)triphenyl-phosphonium bromide (2.99 g, 6.86×10^{-3} mol) and 2,6-dichlorobenzaldehyde (1.00 g, 5.713×10^{-3} mol). The product was separated by flash chromatography (elutant: Petroleum ether) to yield the *vinyl bromide* (965 mg, 67%, *Z:E* 1:20), as a pale amber oil: $?_{max}$ (liquid film)/cm^{-1} 3298, 3085, 2924, 2824, 2854, 2644, 1613, 1579, 1556, 1427, 1217, 1174, 1148, 1091, 935, 854, 775, 746, 697; d_H ($CDCl_3$) 6.97 (1H, d, *J* = 14.2, C=CHBr), 7.14 (1H, ddd, *J* = 8.7, 7.5 and 0.5, ArH), 7.18 (1H, dd, *J* = 14.2 and 0.3, CH(Ar)=C), 7.32 (2H, app d, *J* = 8.2, ArH); d_C ($CDCl_3$) 114.7, 128.6, 128.9, 130.6, 132.7, 134.1; *m/z* LRMS (EI^+) 251.9 (^{35}Cl-$^{35}Cl^{81}Br$-M^+, 30%), 170.9 (63), 134.9 (55), 121.1 (65), 99.1 (100), 83.9 (65), 74.1 (93); HRMS (EI^+) 249.8947 (M^+. $C_8H_5BrCl_2$ requires: 249.8946).

^1H and ^{13}C in accordance with the reported literature.[2]

General procedure B for the Wittig reactions using sodium hydride, exemplified by: (*Z*)-1-Bromo-2-(2-bromovinyl)benzene, 2a

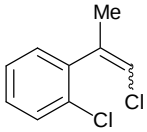


(Bromomethyl)triphenylphosphonium bromide (2.83 g, 6.49×10^{-3} mol) was added portion-wise to a stirred suspension of sodium hydride (60% dispersion in mineral oil, 0.260 g, 6.49×10^{-3} mol) in anhydrous tetrahydrofuran (25 mL) under nitrogen at 0 °C. The reaction was allowed to stir at 0 °C for 90 minutes, before 2-bromobenzaldehyde (1.00 g, 5.405×10^{-3} mol) was added slowly to the resultant pale orange suspension. The reaction was allowed to warm to room temperature and stirred for 3 hours under nitrogen. The reaction mixture was quenched with petroleum ether (10 mL) and cast into petroleum ether (150 mL). The white suspension was filtered through a celite pad, washing with petroleum ether (100 mL). The filtrate was partially reduced in *vacuo*. The suspension was filtered through a second celite pad, washing with petroleum ether (150 mL). The filtrate was reduced in *vacuo*. The product was separated by flash

chromatography (elutant: Petroleum ether) to yield the *vinyl bromide* (1.26 g, 90%, *Z:E* 9:2) as a pale amber oil: $?_{max}$ (liquid film)/cm^{-1} 3294, 3070, 3014, 2923, 2853, 1617, 1588, 1562, 1463, 1438, 1428, 1318, 1044, 1024, 981, 759, 715; d_H ($CDCl_3$, (*Z*)-isomer) 6.59 (1H, d, *J* = 8.1, C=CHBr), 7.17-7.23 (2H, m, ArH and CH(Ar)=C), 7.31-7.37 (1H, m, ArH), 7.61 (1H, dd, *J* = 8.1 and 1.2, ArH), 7.76-7.80 (1H, m, ArH); d_H ($CDCl_3$, (*E*)-isomer) 6.77 (1H, d, *J* = 13.9, C=CHBr), 7.12-7.24 (1H, m, ArH), 7.27-7.31 (1H, m, ArH), 7.37-7.42 (1H, m, arH), 7.44 (1H, d, *J* = 13.9, CH(Ar)=C), 7.54-7.58 (2H, m, ArH); d_C ($CDCl_3$) 109.2, 109.3, 122.7, 123.7, 126.9, 127.1, 127.6, 129.6, 130.5, 132.3, 132.6, 134.6, 135.1, 136.0, 136.2.

Data in accordance with that reported in the reported literature.[2]

1-Chloro-2-(2-chloro-1-methylvinyl)benzene



Prepared following general procedure B using (chloromethyl)triphenylphosphonium chloride (2.695 g, 7.76×10^{-3} mol) and 2'-chloroacetophenone (1.00 g, 0.84 mL, 6.17×10^{-3} mol). The product was separated by flash chromatography (elutant: 1% Diethyl ether – petroleum ether) to yield the product across three fractions. (*E*)-isomer (294 mg, 25% yield) a mixture of isomers (*E:Z*: 1:1.7, 407 mg, 35% yield) and (*Z*)-isomer (170 mg, 15% yield).

(*E*)-isomer:

Pale amber oil: $?_{max}$ (liquid film)/cm^{-1} 3072, 2920, 2853, 1634, 1592, 1566, 1471, 1428, 1375, 1315, 1260, 1233, 1128, 1087, 1042, 988, 811, 751, 723, 683; d_H ($CDCl_3$) 2.18 (3H, d, *J* = 1.5, Me), 6.12 (1H, q, *J* = 1.5, C=CHCl), 7.17-7.32 (3H, m, ArH), 7.38-7.45 (1H, m, ArH); d_C ($CDCl_3$) 18.2, 118.1, 126.8, 129.0, 129.8, 130.1, 132.6, 138.1, 140.0.

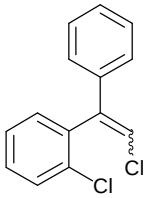
Data in accordance with the reported literature.[iv]

(*Z*)-isomer:

Pale amber oil: $?_{max}$ (liquid film)/cm^{-1} 3068, 2972, 2915, 1634, 1568, 1473, 1430, 1374, 1327, 1258, 1206, 1126, 1092, 1042, 1014, 944, 833, 801, 760, 748, 728, 670; d_H ($CDCl_3$) 2.05 (3H, d, *J* = 1.6, Me), 6.16 (1H, q, *J* = 1.6, C=CHCl), 7.10-7.17 (1H, m, ArH), 7.20-7.31 (2H, m, ArH), 7.37-7.45 (1H, m, ArH); d_C ($CDCl_3$) 22.3, 115.2, 126.9, 128.9, 129.6, 129.6, 132.0, 137.6, 138.3.

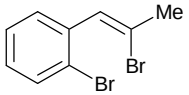
Data in accordance with the reported literature.[4]

1-Chloro-2-(2-chloro-1-phenylvinyl)benzene



Prepared following general procedure B using 2-chlorobenzophenone (1.34, 6.17×10^{-3} mol) and (chloromethyl)triphenylphosphonium bromide (2.695 g, 7.76×10^{-3} mol), heating at reflux for 2 days. The product was separated by flash chromatography (elutant: Hexane) to yield the *vinyl chloride* (254 mg, 17%, 7:2), as a pale amber oil: $?_{max}$ (liquid film)/cm^{-1} 3065, 3024, 2927, 2856, 1599, 1566, 1495, 1468, 1443, 1336, 1259, 1235, 1158, 1127, 1056, 1034, 949, 937, 816, 756, 728, 695, 624; d_H ($CDCl_3$, Major) 6.39 (1H, s, C=CHCl), 7.13-7.42 (9H, m, ArH); d_H ($CDCl_3$, Minor) 6.77 (1H, s, C=CHCl), 7.13-7.42 (8H, m, ArH), 7.44-750 (1H, m, ArH); d_C ($CDCl_3$) 118.3, 118.4, 126.4, 126.7, 126.9, 127.9, 128.0, 128.2, 128.6, 129.3, 129.4, 129.8, 130.0, 130.1, 131.3, 131.7, 133.5, 133.7, 136.5, 136.6, 137.8, 139.3, 141.0, 141.6; *m/z* LRMS (EI^+) 248.0 (^{35}Cl-^{35}Cl-M^+, 55%), 213.0 (25), 178.0 (100), 151.0 (12), 121.1 (65), 74.0 (12); HRMS (EI^+) 248.0149 (M^+. $C_{14}H_{10}Cl_2$ requires: 248.0154).

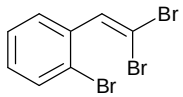
1-Bromo-2-(2-bromoprop-1-enyl)benzene



LiHMDS (20% w/v in tetrahydrofuran, 0.94 mL, 1.12×10^{-3} mol) was added slowly to a stirred suspension of (1-bromoethyl)triphenylphosphonium bromide[v] (0.55 g, 1.12×10^{-3} mol) in anhydrous tetrahydrofuran (5.0 mL) under nitrogen at 0 ^oC. After stirring for 30 minutes, 2-bromobenzaldehyde was added slowly and the reaction stirred at 0 ^oC for 1

hour and at room temperature for 3 hours. The reaction mixture was diluted with petroleum ether (40 mL) and filtered through a celite pad, washing with petroleum ether (50 mL). The filtrate was partially reduced *in vacuo* and filtered through a second celite pad, washing with petroleum ether (60 mL). The filtrate was reduced *in vacuo*. The product was purified *via* flash chromatography (elutant: Hexane) to yield the *vinyl bromide* (0.185 g, 60%, 10:9 mixture of isomers) as a pale amber oil oil: n_{max} (liquid film)/cm^{-1} 3055, 2954, 2917, 1634, 1588, 1561, 1465, 1431, 1377, 1264, 1074, 1047, 1024, 967, 945, 870, 840, 822, 751, 732, 670, 565; d_H ($CDCl_3$) 2.35 (3H, d, J = 1.3, major isomer, Me), 2.52 (3H, d, J = 1.4, minor isomer, Me), 6.73-6.77 (1H, m, minor isomer, CH(Ar)=C), 6.93-6.97 (1H, m, major isomer, CH(Ar)=C), 7.11-7.18 (2H, m, ArH), 7.21-7.25 (1H, m, ArH), 7.27-7.34 (2H, m, ArH), 7.55-7.64 (3H, m, ArH); d_C ($CDCl_3$) 24.8, 30.0, 123.5, 123.6, 124.7, 124.9, 126.8, 127.2, 127.9, 128.9, 129.0, 130.3, 131.1, 131.8, 132.3, 132.7, 136.7, 136.9; *m/z* LRMS (EI$^+$) 207.1 (M^+, 95%), 121.0 (30), 103.1 (30), 77.1 ($[C_6H_5]^+$, 100), 51.1 (40); HRMS (ES$^+$) 208.1120 ($[M+H]^+$. $C_{15}H_{14}N$ requires: 208.1121).

1-Bromo-2-(2,2-dibromovinyl)benzene

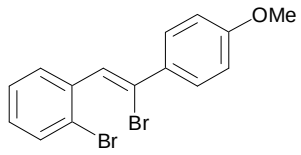


A solution of carbon tetrabromide (7.163 g, 0.022 mol) in anhydrous dichloromethane (40 ml) was added dropwise to a stirred solution of triphenylphosphine (11.331 g, 0.043 mol) in anhydrous dichloromethane (60 ml) at 0 °C with under nitrogen. The reaction mixture was stirred for 30 minutes to give a pale orange solution, which was then treated dropwise with 2-bromobenzaldehyde (2.42 g, 0.0131 mol). The reaction mixture was stirred for 2 hours, slowly allowing to warm to room temperature and stirred for an additional hour. The reaction mixture was cast into petroleum ether (200 mL) and filtered through a celite pad, washing with petroleum ether (150 mL). The filtrate was partially reduced in *vacuo* and filtered through a second celite pad, washing with petroleum ether (200 mL). The filtrate was reduced in *vacuo*. The crude product was purified *via* flash column chromatography (elutant: Petroleum ether) to yield the *vinyl bromide* (4.314 g, 97%), as a pale amber oil: ?$_{max}$ (liquid film)/cm^{-1} 3066, 3019, 2923, 2853, 1606, 1586,

1561, 1463, 1436, 1428, 1317, 1277, 1256, 1161, 1118, 1046, 1025, 946, 881, 854, 830, 790, 747, 710, 662; d_H ($CDCl_3$) 7.18-7.24 (1H, m, ArH), 7.30-7.37 (1H, m, ArH), 7.51 (1H, br s, CH(Ar)=C), 7.57-7.62 (2H, m, ArH); d_C ($CDCl_3$) 92.9, 123.1, 127.2, 129.9, 130.4, 132.7, 136.1, 136.7.

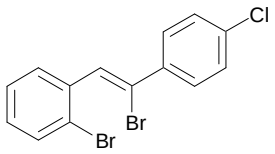
^1H and ^{13}C in accordance with the reported literature.[vi]

(*Z*)-1-Bromo-2-(2-bromophenyl)-1-(4-methoxyphenyl)ethene[vii]



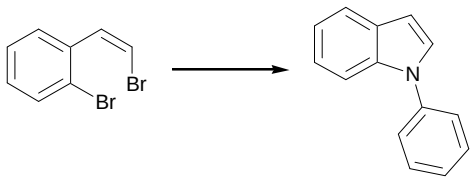
p-Methoxyphenylboronic acid (87 mg, 5.71×10^{-4} mol) was added to a flask charged with $Pd_2(dba)_3$ (12 mg, 1.30×10^{-5} mol) and tri(2-furyl)phosphine (18 mg, 7.79×10^{-5} mol) under nitrogen. The flask was flushed with nitrogen and the reagents suspended in degassed DME (2.60 mL). To this, a degassed 1M solution of sodium carbonate (1.04 mL) and 1-bromo-2-(2,2-dibromovinyl)benzene (177 mg, 5.192×10^{-4} mol) were added and the reaction heated at 70 ^oC for 4 hours. After cooling, the reaction mixture was partitioned with water (25 mL) and the product extracted with diethyl ether (3×25 mL). The combined organic extracts were washed with brine (25 mL), dried over $MgSO_4$, filtered and reduced in *vacuo*. The crude product was purified *via* flash column chromatography (elutant: 0.5 to 1% Diethyl ether – petroleum ether) to yield the *vinyl bromide* (131 mg, 69%), as colourless prisms: mp 75-77.5 ^oC (hexane); $?_{max}$ (nujol mull)/cm^{-1} 2923, 2854, 1624, 1602, 1574, 1560, 1509, 1464, 1436, 1377, 1299, 1285, 1253, 1174, 1114, 1025, 944, 909, 838, 813, 778, 744, 667, 589, 546; d_H ($CDCl_3$) 3.86 (3H, s, OMe), 6.89-6.96 (2H, m, ArH), 7.15-7.22 (2H, m, ArH and CH(Ar)=C), 7.32-7.40 (1H, m, ArH), 7.59-7.68 (3H, m, ArH), 7.74-7.79 (1H, m, ArH); d_C ($CDCl_3$) 55.4, 113.7, 124.2, 126.7, 126.8, 127.9, 129.1, 129.3, 131.0, 132.4, 132.6, 137.3, 160.3; Anal. Calc. for $C_{15}H_{12}Br_2O$: C, 48.95; H, 3.29. Found: C, 49.0; H, 3.29%.

(*Z*)-1-Bromo-2-(2-bromophenyl)-1-(4-chlorophenyl)ethene[vii]



4-Chlorophenylboronic acid (223 mg, 1.43×10^{-3} mol) was added to a flask charged with $Pd_2(dba)_3$ (29.7 mg, 3.25×10^{-5} mol) and tri(2-furyl)phosphine (45.2 mg, 1.95×10^{-4} mol) under nitrogen. The flask was flushed with nitrogen and the reagents suspended in degassed DME (6.50 mL). To this, a degassed 1M solution of sodium carbonate (2.60 mL) and 1-bromo-2-(2,2-dibromovinyl)benzene (442 mg, 1.298×10^{-3} mol) were added and the reaction heated at 70 ^{o}C for 4 hours. After cooling, the reaction mixture was partitioned with water (50 mL) and the product extracted with diethyl ether (3×60 mL). The combined organic extracts were washed with brine (50 mL), dried over $MgSO_4$, filtered and reduced in *vacuo*. The crude product was purified *via* flash column chromatography (elutant: Hexane) to yield the *vinyl bromide* (251 mg, 51%), as fine white needles: mp 78-79.5 ^{o}C (hexane); $?_{max}$ (nujol mull)/cm^{-1} 2923, 2853, 1615, 1586, 1564, 1490, 1461, 1437, 1397, 1377, 1302, 1230, 1188, 1096, 1023, 1013, 944, 905, 831, 810, 746, 719, 704, 663, 590; d_H ($CDCl_3$) 7.21 (1H, dddd, J = 8.0, 7.5, 1.7 and 05, ArH), 7.25 (1H, d, J = 0.5, CH(Ar)=C), 7.34-7.41 (3H, m, ArH), 7.60-7.67 (3H, m, ArH), 7.73-7.78 (1H, m, ArH); d_C ($CDCl_3$) 124.1, 125.5, 127.0, 128.6, 129.2, 129.5, 129.9, 130.9, 132.5, 135.1, 136.8, 138.6; Anal. Calc. for $C_{14}H_9Br_2Cl$: C, 45.14; H, 2.44. Found: C, 45.3; H, 2.44%.

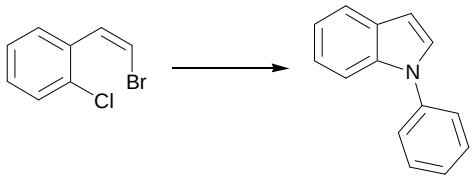
Tandem palladium catalysed C-N bond formation to form the indole nucleus. General procedure C, exemplified by: 1-Phenylindole from 1-bromo-2-(2-bromovinyl)benzene (Table 2, entry 1)



Sodium *tert*-butoxide (125 mg, 1.30×10^{-3} mol) was added to an oven dried flask charged with $Pd_2(dba)_3$ (12 mg, 1.30×10^{-5} mol) and ligand **5** (16 mg, 3.97×10^{-5} mol) under nitrogen. The flask was flushed with nitrogen and the reagents suspended in anhydrous

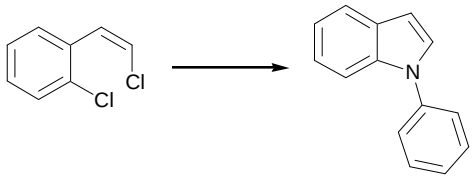
toluene (1.04 mL). To this, 1-bromo-2-(2-bromovinyl)benzene (136 mg, 5.192×10^{-4} mol) and aniline (58 mg, 57 μL, 6.230×10^{-4} mol) were added and the reaction heated at 80 ^{o}C for 5 hours under nitrogen. After cooling, the reaction mixture was diluted with diethyl ether (5 mL) and filtered through a celite pad, washing with diethyl ether (30 mL). The filtrate was reduced in *vacuo*. The product was separated *via* flash chromatography (elutant: 0.5% Diethyl ether – hexane) to yield the *indole* (88 mg, 85%) as a pale amber oil: n_{max} (liquid film)/cm^{-1} 3055, 2924, 2854, 1597, 1515, 1497, 1456, 1331, 1233, 1213, 1135, 1014, 953, 774, 740, 695; d_H ($CDCl_3$) 6.71 (1H, dd, *J* = 3.3 and 0.8, ArH), 7.16-7.28 (2H, m, ArH), 7.34-7.42 (1H, m, ArH), 7.37 (1H, d, *J* = 3.3, ArH), 7.52-7.55 (4H, m, ArH), 7.57-7.62 (1H, m, ArH), 7.67-7.74 (1H, m, ArH); d_C ($CDCl_3$) 103.5, 110.5, 120.3, 121.1, 122.3, 124.4, 126.4, 127.9, 129.3, 129.6, 135.8, 139.8; *m/z* LRMS (EI^+) 193.1 (M^+, 100%), 165.0 (35), 89.1 (20).
Data in accordance with that reported in the reported literature.[viii]

1-Phenylindole from 1-(2-bromovinyl)-2-chlorobenzene



Prepared following general procedure C, using 1-(2-bromovinyl)-2-chlorobenzene (113 mg, 5.19×10^{-4} mol) and ligand **4** (15 mg, 3.970×10^{-5} mol) as the supporting ligand. The product was purified *via* flash chromatography (elutant: 0.5% Diethyl ether – hexane) to yield the *indole* (76 mg, 76%) as a pale amber oil.

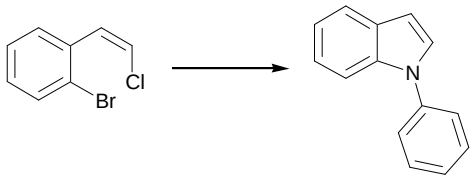
1-Phenylindole from 1-chloro-2-(2-chlorovinyl)benzene



Prepared following general procedure C, using 1-(2-chlorovinyl)-2-chlorobenzene (90 mg, 5.19×10^{-4} mol) and ligand **4** (15 mg, 3.97×10^{-5} mol) as the supporting ligand. The

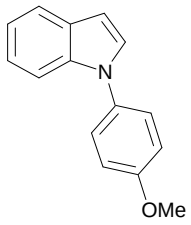
product was purified *via* flash chromatography (elutant: 0.5% Diethyl ether – hexane) to yield the *indole* (76 mg, 76%) as a pale amber oil.

1-Phenylindole from 1-bromo-2-(2-chlorovinyl)benzene



Prepared following general procedure C, using 1-bromo-2-(2-chlorovinyl)benzene (113 mg, 5.19×10^{-4} mol) and ligand **4** (15 mg, 3.97×10^{-5} mol) as the supporting ligand. The product was purified *via* flash chromatography (elutant: 0.5% Diethyl ether – hexane) to yield the *indole* (80 mg, 80%) as a pale amber oil.

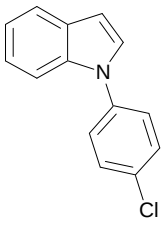
1-(4-Methoxyphenyl)indole (Table 2, entry 2)



Prepared following general procedure C, using *p*-anisidine (77 mg, 6.23×10^{-4} mol), heating for 6 hours. The product was purified *via* flash chromatography (elutant: 1% Diethyl ether – hexane) to yield the *indole* (90 mg, 75%) as fine white needles: mp 59.5-61 ^{o}C (EtOH. Lit:[ix] 59.5-60.5 ^{o}C); n_{max} (nujol mull)/cm^{-1} 2923, 2854, 1518, 1461, 1377, 1300, 1250, 1214, 1170, 1135, 1040, 833, 738, 722; d_H ($CDCl_3$) 3.88 (3H, s, OMe), 6.66 (1H, dd, J = 3.2 and 0.8, ArH), 7.01-7.07 (2H, m, ArH), 7.13-7.24 (2H, m, ArH), 7.29 (1H, d, J = 3.2, ArH), 7.38-7.44 (2H, m, ArH), 7.44-7.49 (1H, m, ArH), 7.67-7.71 (1H, m, ArH); d_C ($CDCl_3$) 55.6, 102.8, 110.3, 114.7, 120.0, 121.0, 122.1, 126.0, 128.3, 128.9, 132.8, 136.3, 158.2; ; *m/z* LRMS (EI$^+$) 223.1 (M^+, 100%), 208.0 ([M-Me]$^+$, 92), 180.1 (40), 152.1 (45), 121.1 (30), 89.0 (15), 63.1 (20).

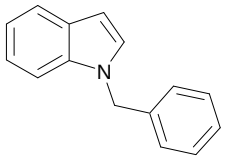
^{1}H and ^{13}C in accordance with the reported literature.[9]

1-(4-Chlorophenyl)indole (Table 2, entry 3)



Prepared following general procedure C, using 4-chloroaniline (80 mg, 6.23×10^{-4} mol), heating for 5 hours. The product was purified *via* flash chromatography (elutant: 0.5% Diethyl ether – hexane) to yield the *indole* (90 mg, 77%) as a colourless oil: n_{max} (liquid film)/cm^{-1} 3054, 2926, 2854, 1596, 1517, 1496, 1456, 1334, 1312, 1235, 1212, 1135, 1091, 1013, 953, 832, 762, 742, 719; d_H ($CDCl_3$) 6.70 (1H, dd, J = 3.3 and 0.8), 7.16-7.28 (2H, m), 7.30 (1H, d, J = 3.3), 7.42-7.55 (5H, m), 7.68-7.72 (1H, m); d_C ($CDCl_3$) 104.0, 110.2, 120.6, 121.2, 122.6, 125.5, 127.7, 129.3, 129.7, 131.9, 135.7, 138.3; *m/z* LRMS (EI^+) 227.0 (^{35}Cl-M^+, 100%), 191.1 ($[M\text{-}HCl]^+$, 15), 164.9 (25), 89.0 (50), 75.1 (25), 63.1 (20); HRMS (ES^+) 228.0576 ($[^{35}Cl\text{-}M+H]^+$. $C_{14}H_{11}ClN$ requires: 228.0575).

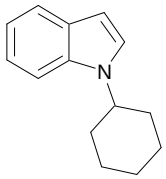
1-Benzylindole (Table 2, entry 4)



Prepared following general procedure C, using 1-bromo-2-(2-bromovinyl)benzene (200 mg, 7.64×10^{-4} mol), benzylamine (98 mg, 100 μL, 9.16×10^{-4} mol) and DPEphos **3** (25 mg, 4.58×10^{-5} mol) as the supporting ligand, heating at 100 ^oC for 20 hours. The product was separated by flash chromatography (elutant: 0.5% Diethyl ether – hexane) to yield the *indole* (110 mg, 70%), as tan coloured plates: mp 43.5-45 ^oC (EtOH. Lit:[x] 43 ^oC); ?$_{max}$ (neat)/cm^{-1} 3086, 3056, 3029, 2923, 2857, 1604, 1586, 1512, 1485, 1463, 1463, 1454, 1439, 1398, 1356, 1334, 1317, 1256, 1197, 1182, 1077, 1046, 1029, 1012, 883, 740, 720, 695, 623; d_H ($CDCl_3$) 5.32 (2H, s, CH_2Ph), 6.55 (1H, dd, J = 3.2 and 0.9, ArH), 7.07-7.20 (5H, m, ArH), 7.24-7.33 (4H, m, ArH), 7.63-7.67 (1H, m, ArH); d_C ($CDCl_3$) 50.1, 101.7, 110.0, 119.5, 120.9, 121.7, 126.8, 127.6, 128.2, 128.7, 128.7 136.3, 137.5; *m/z* LRMS (EI^+) 207.0 (M^+, 70%), 91.0 ($[C_7H_7]^+$, 100), 65.0 (65).

Data in accordance with that reported in the reported literature.[xi]

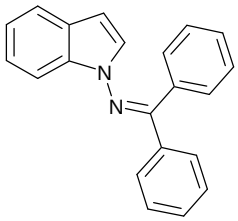
1-Cyclohexylindole (Table 2, entry 5)



Prepared following general procedure C, using 1-bromo-2-(2-bromovinyl)benzene (200 mg, 7.64×10^{-4} mol), cyclohexylamine (91 mg, 105 μL, 9.16×10^{-4} mol) and DPEphos **3** (25 mg, 4.58×10^{-5} mol) as the supporting ligand, heating at 100 ^{o}C for 20 hours. The product was separated by flash chromatography (elutant: 0.5% Diethyl ether – Hexane) to yield the *indole* (95 mg, 63%) as an amber oil: $?_{max}$ (liquid film)/cm^{-1} 3051, 2930, 2854, 1611, 1509, 1476, 1461, 1374, 1312, 1265, 1213, 1091, 1014, 893, 737, 712; d_H ($CDCl_3$) 1.22-1.41 (1H, m), 1.43-1.61 (2H, m), 1.64-1.87 (3H, m), 1.90-2.02 (2H, m), 2.10-2.22 (2H, m), 4.24 (1H, tt, *J* = 11.8 and 3.8), 6.53 (1H, dd, *J* = 3.2 and 0.7, ArH), (1H, ddd, *J* = 7.8, 7.0 and 1.1, ArH), 7.17-7.26 (2H, m, ArH), 7.37-7.43 (1H, m, ArH), (1H, ddd, *J* = 7.8, 1.2 and 0.8, ArH); d_C ($CDCl_3$) 25.7, 26.0, 33.5, 55.1, 100.9, 109.4, 119.2, 120.9, 121.0, 124.0, 128.4, 135.5.

Data in accordance with that reported in the literature.[xii]

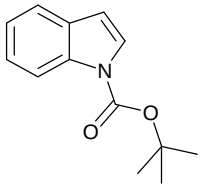
Benzhydrylideneindol-1-yl amine (Table 2, entry 6)



Prepared following general procedure C, using benzophenone hydrazone (122 mg, 6.24×10^{-4} mol), heating for 6 hours. The product was purified *via* flash chromatography (elutant: 0.5% Diethyl ether – hexane) to yield the *indole* (95 mg, 62%) as an amorphous canary yellow solid: mp 77-78.5 ^{o}C (EtOH); n_{max} (nujol mull)/cm^{-1} 3158, 3057, 3030, 2923, 2854, 1686, 1615, 1598, 1560, 1541, 1510, 1492, 1452, 1444, 1377, 1313, 1283,

1205, 1178, 1160, 1142, 1120, 1088, 1074, 1030, 1010, 967, 928, 880, 773, 760, 742, 724, 699, 666, 655; d_H ($CDCl_3$) 6.27 (1H, dd, *J* = 3.6 and 0.8), 6.44 (1H, d, *J* = 3.6), 7.16 (1H, ddd, *J* = 7.8, 7.1 and 1.1), 7.26-7.36 (3H, m), 7.38-7.55 (7H, m), 7.73-7.78 (2H, m), (1H, ddd, *J* = 8.2, 1.8 and 0.8); d_C ($CDCl_3$) 102.4, 111.1, 120.5, 120.9, 122.6, 123.5, 125.9, 128.3, 128.4, 128.9, 129.3, 129.6, 130.1, 135.6, 137.5, 138.4, 157.2; *m/z* LRMS (EI^+) 296.2 (M^+, 40%), 180.0 ($[Ph_2C=N]^+$, 100), 77.0 ($[C_6H_5]^+$, 48); HRMS (ES^+) 297.1391 ($[M+H]^+$. $C_{21}H_{17}N_2$ requires: 297.1386).

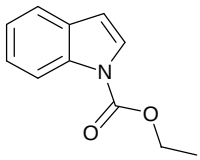
Indole-1-carboxylic acid *tert*-butyl ester (Table 2, entry 7)



Prepared following general procedure C, using 1-bromo-2-(2-bromovinyl)benzene (68 mg, 2.60×10^{-4} mol), *tert*-butylcarbamate (36 mg, 3.12×10^{-4} mol), cesium carbonate (211 mg, 6.49×10^{-4} mol) as the base, $Pd_2(dba)_3$ (5.9 mg, 6.49×10^{-6} mol) and ligand **6** (9.3 mg, 1.95×10^{-5} mol) as the supporting ligand, heating at 110 ^oC in anhydrous dioxane (0.52 mL) for 10 hours. The product was purified *via* flash chromatography (elutant: 0.5% Diethyl ether – hexane) to yield the *indole* (38 mg, 68%) as a pale amber oil: n_{max} (liquid film)/cm^{-1} 3054, 2979, 2973, 2855, 1733, 1584, 1534, 1474, 1453, 1380, 1348, 1299, 1252, 1212, 1159, 1119, 1098, 1024, 884, 855, 768, 746, 724; d_H ($CDCl_3$) 1.69 (9H, s, $CO_2{}^tBu$), 6.58 (1H, dd, *J* = 3.7 and 0.7, ArH), 7.20-7.27 (1H, m, ArH), 7.28-7.38 (1H, m, ArH), 7.55-7.59 (1H, m, ArH), 7.61 (1H, d, *J* = 3.7, ArH), 8.16 (1H, d, *J* = 8.2, ArH); d_C ($CDCl_3$) 28.2, 83.6, 107.2, 115.1, 120.9, 122.6, 124.2, 125.9, 130.5, 135.1, 149.8; *m/z* LRMS (EI^+) 217.1 (M^+, 13%), 161.0 ($[M+H-{}^tBu]^+$, 20), 117.1 ($[M+H-CO_2{}^tBu]^+$, 62), 89.0 (15), 57.1 (100); HRMS (ES^+) 218.1173 ($[M+H]^+$. $C_{12}H_{16}NO_2$ requires: 218.1176).

Data in accordance with that reported in the literature.[xiii]

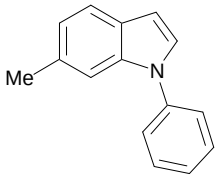
Indole-1-carboxylic acid ethyl ester (Table 2, entry 8)



Prepared following general procedure C, using urethane (56 mg, 6.23×10^{-4} mol), cesium carbonate (423 mg, 1.30×10^{-3}) as the base and ligand **6** (18.6 mg, 3.97×10^{-5} mol) as the supporting ligand, heating at 110 ^{o}C in anhydrous dioxane (1.04 mL) for 24 hours. The product was purified *via* flash chromatography (elutant: 0.5% Diethyl ether – hexane) to yield the *indole* (52 mg, 54%) as a pale amber oil: n_{max} (liquid film)/cm^{-1} 3153, 3120, 3054, 2982, 2935, 1736, 1607, 1584, 1534, 1474, 1454, 1402, 1380, 1368, 1344, 1327, 1245, 1212, 1177, 1120, 1081, 1046, 885, 764, 746, 723, 594; d_H ($CDCl_3$) 1.48 (3H, t, *J* = 7.1, CH_3), 4.50 (2H, q, *J* = 7.1, OCH_2), 6.60 (1H, dd, *J* = 3.7 and 0.7, ArH), 7.22-7.28 (1H, m, ArH), 7.31-7.37 (1H, m, ArH), 7.55-7.60 (1H, m, ArH), 7.63 (1H, d, *J* = 3.7, ArH), 8.20 (1H, br d, *J* = 8.2, ArH); d_C ($CDCl_3$) 14.4, 63.1, 107.9, 115.1, 120.9, 122.9, 124.4, 125.5, 130.5, 135.2, 151.1.

Data in accordance with that reported in the literature.[xiv]

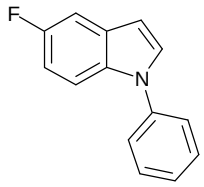
6-Methyl-1-phenylindole (Table 3, entry 1)



Prepared following general procedure C, using 2-bromo-1-(2-bromovinyl)-4-methylbenzene (143 mg, 5.19×10^{-4} mol)), heating for 5 hours. The product was purified *via* flash chromatography (elutant: 0.5% Diethyl ether – hexane) to yield the *indole* (79 mg, 73%) as a colourless oil: n_{max} (liquid film)/cm^{-1} 3104, 3063, 3032, 2919, 2857, 1598, 1499, 1456, 1342, 1325, 1296, 1237, 1214, 1194, 1131, 1105, 1074, 1026, 925, 859, 803, 765, 748, 716, 967, 686, 599; d_H ($CDCl_3$) 2.48 (3H, s, Me), 6.65 (1H, dd, *J* = 3.3 and 0.8, ArH), 7.03 (1H, ddd, *J* = 8.1, 1.4 and 0.4, ArH), 7.29 (1H, d, *J* = 3.3, ArH), 7.34-7.42 (2H, m, ArH), 7.50-7.61 (5H, m, ArH); d_C ($CDCl_3$) 21.9, 103.3, 110.4, 120.7, 122.1, 124.4, 126.3, 127.0, 127.4, 129.6, 132.2, 136.2, 139.9; *m/z* LRMS (EI^+) 207.1 (M^+, 95%),

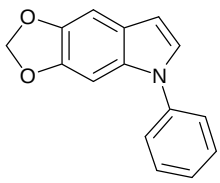
121.0 (30), 103.1 (30), 77.1 ($[C_6H_5]^+$, 100), 51.1 (40); HRMS (ES^+) 208.1120 ($[M+H]^+$. $C_{15}H_{14}N$ requires: 208.1121).

5-Fluoro-1-phenylindole (Table 3, entry 2)



Prepared following general procedure C, using 1-bromo-2-(2-bromovinyl)-4-fluorobenzene (145 mg, 5.19×10^{-4} mol)), heating for 11 hours. The product was purified *via* flash chromatography (elutant: 0.5% Diethyl ether – hexane) to yield the *indole* (65 mg, 59%) as a pale amber oil: n_{max} (liquid film)/cm^{-1} 3068, 2925, 1622, 1598, 1500, 1473, 1458, 1446, 1377, 1338, 1290, 1269, 1250, 1213, 1141, 1104, 1074, 1028, 960, 849, 799, 751, 718, 697; d_H ($CDCl_3$) 6.63 (1H, dd, J = 3.2 and 0.8, ArH), 6.96 (1H, td, J = 9.1 and 2.6, ArH), 7.32 (1H, dd, J = 9.4 and 2.5, ArH), 7.37 (1H, d, J = 3.2, ArH), 7.33-7.40 (1H, m, ArH), 7.43-7.56 (5H, m, ArH); d_C ($CDCl_3$) 103.4 (d, $^4J_{CF}$ = 4.7), 105.8 (d, $^2J_{CF}$ = 23.3), 110.6 (d, $^2J_{CF}$ = 26.1), 111.2 (d, $^3J_{CF}$ = 9.6), 124.3, 126.7, 129.4, 129.6, 129.7, 132.5, 139.6, 158.1 (d, $^1J_{CF}$ = 235.1); *m/z* LRMS (EI^+) 211.1 (M^+, 100%), 183.0 (47), 107.0 (22), 77.1 ($[C_6H_5]^+$, 18), 51.1 (16); HRMS (ES^+) 212.0869 ($[M+H]^+$. $C_{14}H_{11}FN$ requires: 212.0870).

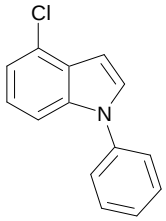
1-Phenyl[1,3]dioxolo[4,5-*f*]indole (Table 3, entry 3)



Prepared following general procedure C, using 5-bromo-6-(2-bromovinyl)-benzo(1,3)dioxole (159 mg, 5.19×10^{-4} mol), heating for 9 hours. The product was purified *via* flash chromatography (elutant: 1% Diethyl ether – hexane) to yield the *indole* (83 mg, 67%) as white needles: mp 69-72 ^oC (EtOH); n_{max} (nujol mull)/cm^{-1} 3103, 2923, 2854, 2774, 1602, 1515, 1502, 1467, 1398, 1378, 1354, 1333, 1277, 1238, 1206, 1172,

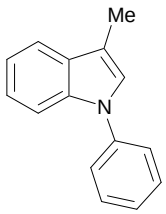
1159, 1137, 1042, 950, 834, 778, 761, 748, 718, 697; d_H ($CDCl_3$) 5.94 (2H, s, O-CH_2-O, ArH), 6.55 (1H, dd, *J* = 3.2 and 0.8, ArH), 7.02 (1H, app. t, *J* = 0.7, ArH), 7.05 (1H, d, *J* = 0.5, ArH), 7.21 (1H, d, *J* = 3.2, ArH), 7.31-7.38 (1H, m, ArH), 7.44-7.55 (4H, m, ArH); d_C ($CDCl_3$) 91.6, 99.4, 100.7, 103.6, 123.1, 124.2, 126.4, 126.6, 129.6, 130.9, 139.8, 143.3, 145.2; *m/z* LRMS (EI^+) 237.1 (M^+, 85%), 178.0 (55), 152.1 (25), 104.1 (25), 77.1 ($[C_6H_5]^+$, 100), 63.1 (27), 51.2 (80); HRMS (ES^+) 238.0860 ($[M+H]^+$. $C_{15}H_{12}NO_2$ requires: 238.0863).

4-Chloro-1-phenylindole (Table 3, entry 4)



Prepared following general procedure C, using 2-(2-bromovinyl)-1,3-dichlorobenzene (0.131 g, 5.19×10^{-4} mol) and ligand **4** (15 mg, 3.89×10^{-5} mol) as the supporting ligand, heating for 4 hours at 100 ^oC. The product was purified *via* flash chromatography (elutant: 0.5% Diethyl ether – hexane) to yield the *indole* (94 mg, 80%) as a pale amber oil: n_{max} (liquid film)/cm^{-1} 3110, 3054, 2954, 2867, 1597, 1565, 1514, 1498, 1477, 1456, 1434, 1352, 1329, 1310, 1292, 1272, 1183, 1156, 1132, 1072, 1052, 1027, 970, 898, 835, 778, 745, 695, 545; d_H ($CDCl_3$) 6.80 (1H, dd, *J* = 3.3 and 0.8, ArH), 7.11-7.20 (2H, m, ArH), 7.36-7.58 (6H, m, ArH), 7.38 (1H, d, *J* = 3.3, ArH); d_C ($CDCl_3$) 102.0, 109.2, 120.0, 122.9, 124.5, 126.2, 126.9, 128.0, 128.5, 129.7, 136.6, 139.4; *m/z* LRMS (EI^+) 227.1 (^{35}Cl-M^+, 100%), 191.2 ($[M-HCl]^+$, 20), 165.1 (30), 113.9 (20), 95.6 (40), 89.1 (52), 77.1 ($[C_6H_5]^+$, 48), 51.1 (70); HRMS (ES^+) 228.0575 ($[M+H]^+$. $C_{14}H_{11}ClN$ requires: 228.0575).

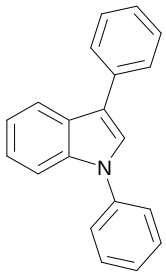
3-Methyl-1-phenylindole (Table 3, entry 5)



Prepared following general procedure C, using 1-chloro-2-(2-chloro-1-methylvinyl)-benzene (97 mg, 5.19×10^{-4} mol), heating at 100 ^{o}C for 25 hours. The product was purified *via* flash chromatography (elutant: 0.5% Diethyl ether – hexane) to yield the *indole* (84 mg, 78%) as a pale amber oil: n_{max} (liquid film)/cm^{-1} 3054, 2916, 2884, 1260, 1600, 1564, 1500, 1387, 1372, 1362, 1318, 1298, 1280, 1229, 1174, 1157, 1134, 1073, 1016, 994, 927, 907, 775, 738, 695, 658, 588, 558; d_H ($CDCl_3$) 2.41 (3H, d, J = 1.1, Me), 7.14-7.27 (3H, m, ArH), 7.29-7.37 (1H, m, ArH), 7.47-7.55 (4H, m, ArH), 7.56-7.60 (1H, m, ArH), 7.62-7.66 (1H, m, ArH); d_C ($CDCl_3$) 9.6, 110.3, 112.8, 119.1, 119.7, 122.3, 123.9, 125.4, 125.9, 129.5, 129.7, 135.9, 139.9; *m/z* LRMS (EI^+) 206.1 (M^+, 100%), 128.0 (30), 102.1 (28), 77.1 ($[C_6H_5]^+$, 70), 51.1 (52); HRMS (ES^+) 208.1122 ($[M+H]^+$. $C_{15}H_{14}N$ requires: 208.1121).

^{1}H and ^{13}C in accordance with the reported literature.[11]

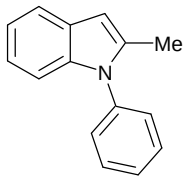
1,3-diphenylindole (Table 3, entry 6)



Prepared following general procedure C, using 1-chloro-2-(2-chloro-1-methylvinyl)-benzene (97 mg, 5.19×10^{-4} mol), heating at 100 ^{o}C for 25 hours. The product was purified *via* flash chromatography (elutant: 0.5% Diethyl ether – hexane) to yield the *indole* (131 mg, 94%) as pale cream needles: mp 107-108.5 ^{o}C (EtOH. Lit:[xi] 103-104 ^{o}C); n_{max} (nujol mull)/cm^{-1} 2924, 2854, 1600, 1555, 1504, 1457, 1380, 1323, 1302, 1259, 1229, 1177, 1164, 1140, 1078, 1026, 973, 910, 812, 771, 753, 740, 700, 609; d_H ($CDCl_3$) 7.20-7.43 (4H, m, ArH), 7.43-7.58 (7H, m, ArH), 7.58-7.63 (1H, m, ArH), 7.69-7.74 (2H,

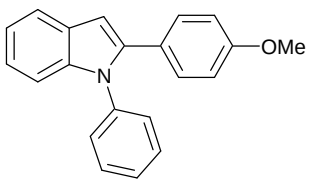
m, ArH), 7.96-8.03 (1H, m, ArH); d_C ($CDCl_3$) 110.8, 119.1, 120.1, 120.8, 122.8, 124.4, 125.5, 126.2, 126.6, 127.1, 127.6, 128.8, 129.7, 135.1, 136.6, 139.5; *m/z* LRMS (EI^+) 269.2 (M^+, 100%), 165.0 (70), 77.0 ($[C_6H_5]^+$, 50), 51.1 (33); Anal. Calc. for $C_{20}H_{15}N$: C, 89.19; H, 5.61; N, 5.20. Found: C, 89.40; H, 5.62; N, 5.06%.
^1H and ^{13}C in accordance with the reported literature.[11]

2-Methyl-1-phenylindole (Table 3, entry 7)



Prepared following general procedure C, using 1-bromo-2-(2-bromopropenyl)-benzene (143 mg, 5.19×10^{-4} mol), heating at 80 ^oC for 4 hours. The product was purified *via* flash chromatography (elutant: 0.5% Diethyl ether – hexane) to yield the *indole* (85 mg, 79%) as a pale amber oil: n_{max} (liquid film)/cm^{-1} 3056, 2981, 2919, 1596, 1556, 1498, 1457, 1387, 1360, 1323, 1236, 1206, 1173, 1152, 1074, 1032, 1018, 926, 847, 761, 746, 698, 654, 628, 604, 564; d_H ($CDCl_3$) 2.32 (3H, d, J = 0.9, Me), 6.39-6.44 (1H, m, ArH), 7.05-7.16 (3H, m, ArH), 7.33-7.40 (2H, m, ArH), 7.41-7.49 (1H, m, ArH), 7.50-7.61 (3H, m, ArH); d_C ($CDCl_3$) 13.4, 101.3, 110.0, 119.5, 120.0, 121.0, 127.7, 128.0, 128.2, 129.4, 137.0, 138.0, 138.2; *m/z* LRMS (EI^+) 207.1 (M^+, 100%), 164.9 (15), 127.9 (10), 102.0 (10), 77.0 ($[C_6H_5]^+$, 25), 49.0 (42); HRMS (ES^+) 208.1120 ($[M+H]^+$. $C_{15}H_{14}N$ requires: 208.1121); Anal. Calc. for $C_{15}H_{13}N$: C, 86.92; H, 6.32; N, 6.76. Found: C, 86.7; H, 6.40; N, 6.98%.

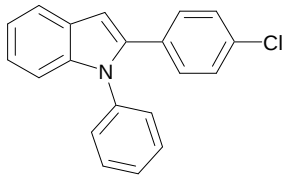
2-(4-Methoxyphenyl)-1-phenylindole (Table 3, entry 8)



Prepared following general procedure C, using 1-bromo-2-(2-bromophenyl)-1-(4-methoxyphenyl)ethene (120 mg, 3.26×10^{-4} mol), heating at 100 ^oC for 5 hours. The

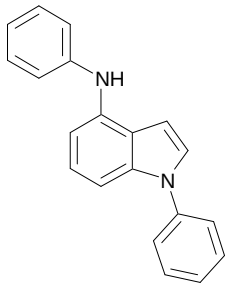
product was purified *via* flash chromatography (elutant: 1% Diethyl ether – hexane) to yield the *indole* (79 mg, 81%) as colourless needles: mp 119-121 ^{o}C (EtOH); n_{max} (nujol mull)/cm^{-1} 2923, 2854, 1610, 1598, 1578, 1546, 1502, 1456, 1378, 1284, 1246, 1178, 1154, 1111, 1026, 834, 788, 766, 740, 702, 596; d_H ($CDCl_3$) 3.79 (3H, s, OMe), 6.74 (1H, br, s, ArH), 6.76-6.83 (2H, m, ArH), 7.13-7.23 (4H, m, ArH), 7.23-7.31 (3H, m, ArH), 7.32-7.47 (3H, m, ArH), 7.64-7.71 (1H, m, ArH); d_C ($CDCl_3$) 55.2, 102.7, 110.5, 113.6, 120.2, 120.6, 122.0, 125.0, 127.1, 128.1, 128.3, 129.2, 130.1, 138.6, 138.8, 140.6, 158.9; *m/z* LRMS (EI$^+$) 299.1 (M$^+$, 100%), 284.1 ([M-Me]$^+$, 50), 254.1 (50), 127.2 (20), 77.1 ([C_6H_5]$^+$, 42), 51.1 (67); HRMS (ES$^+$) 300.1383 ([M+H]$^+$. $C_{21}H_{18}NO$ requires: 300.1383).

2-(4-Chlorophenyl)-1-phenylindole (Table 3, entry 9)



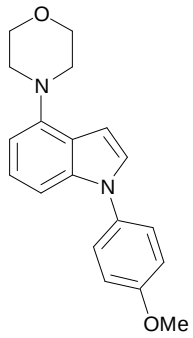
Prepared following general procedure C, using 1-bromo-2-(2-bromophenyl)-1-(4-chlorophenyl)ethene (122 mg, 3.26×10^{-4} mol), heating at 100 ^{o}C for 4 hours. The product was purified *via* flash chromatography (elutant: 0.5% Diethyl ether – hexane) to yield the *indole* (51 mg, 51%) as colourless needles: mp 174-176 ^{o}C (DCM – hexane); n_{max} (nujol mull)/cm^{-1} 2924, 2854, 1595, 1533, 1498, 1488, 1456, 1409, 1377, 1353, 1318, 1299, 1256, 1211, 1178, 1148, 1092, 1016, 833, 787, 760, 739, 697; d_H ($CDCl_3$) 6.81 (1H, d, J = 0.8, ArH), 7.16-7.32 (9H, m, ArH), 7.34-7.48 (3H, m, ArH), 7.66-7.73 (1H, m, ArH); d_C ($CDCl_3$) 104.0, 110.6, 120.6, 120.8, 122.6, 127.4, 128.0, 128.1, 128.4, 129.4, 130.0, 131.0, 133.3, 138.2, 139.1, 139.4; *m/z* LRMS (EI$^+$) 303.1 (^{35}Cl-M$^+$, 100%), 267.2 ([M-HCl]$^+$, 22), 165.1 (30), 133.7 (45), 77.0 ([C_6H_5]$^+$, 18), 51.1 (28); HRMS (ES$^+$) 304.0885 ([M+H]$^+$. $C_{20}H_{15}ClN$ requires: 304.0888); Anal. Calc. for $C_{20}H_{14}ClN$: C, 79.07; H, 4.65; N, 4.61. Found: C, 79.3; H, 4.63; N, 4.73%.

1-Phenyl-4-(Phenylamino)indole (Scheme 3, entry 1)



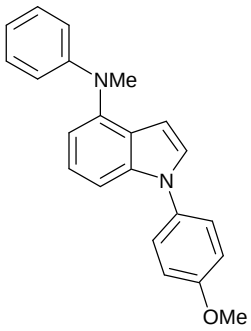
Prepared following general procedure C, using 2-(2-bromovinyl)-1,3-dichlorobenzene (0.131 g, 5.19×10^{-4} mol), aniline (0.106 mL, 1.142×10^{-3} mol), sodium *tert*-butoxide (175 mg, 1.81×10^{-3} mol) and Davephos (15 mg, 3.89×10^{-5} mol) as the supporting ligand, heating at 100 ^{o}C for 6 hours. The product was purified *via* flash chromatography (elutant: 1 - 2% Diethyl ether – hexane) to yield the *indole* (96 mg, 65%) as a pale tan coloured plates: mp 131.5-133 ^{o}C (EtOH); n_{max} (nujol mull)/cm^{-1} 3402, 3051, 2923, 2854, 1592, 1575, 1515, 1497, 1485, 1456, 1412, 1378, 1355, 1318, 1281, 12121, 1166, 1152, 1076, 1032, 936, 767, 758, 731, 694, 647; d_H ($CDCl_3$) 5.95 (1H, br s, NH), 6.62 (1H, dd, J = 3.3 and 0.6, ArH), 6.94 (1H, tt, J = 7.3 and 1.1, ArH), 7.02 (1H, dd, J = 7.4 and 0.8, ArH), 7.10-7.18 (3H, m, ArH), 7.21 (1H, br d, J = 8.3, ArH), 7.26-7.33 (3H, m, ArH), 7.34-7.42 (1H, m, ArH), 7.53 (4H, br d, J = 4.3, ArH); d_C ($CDCl_3$) 100.5, 104.6, 108.0, 118.0, 120.8, 121.4, 123.2, 124.5, 126.6, 126.8, 129.2, 129.6, 135.8, 137.1, 139.8, 143.5; *m/z* LRMS (EI$^+$) 284.2 (M$^+$, 100%), 206.1 (12), 180.0 (18); HRMS (ES$^+$) 285.1385 ([M+H]$^+$. $C_{20}H_{17}N_2$ requires: 285.1386); Anal. Calc. for $C_{20}H_{16}N_2$: C, 84.48; H, 5.97; N, 9.85. Found: C, 84.40; H, 5.66; N, 9.55%.

One-pot sequential cyclisation – amination coupling. General procedure D, exemplified by: 1-(4-Methoxyphenyl)-4-morpholin-4-yl indole (Scheme 3, entry 2)



Sodium *tert*-butoxide (175 mg, 1.817×10^{-3} mol) and *p*-anisidine (67 mg, 5.45×10^{-4} mol) were added to an oven dried flask charged with $Pd_2(dba)_3$ (12 mg, 1.30×10^{-5} mol) and ligand **4**(15 mg, 3.89×10^{-5} mol) under nitrogen. The flask was flushed with nitrogen and the reagents suspended in anhydrous toluene (1.04 mL). To this, 2-(2-bromovinyl)-1,3-dichlorobenzene (0.131 g, 5.19×10^{-4} mol) was added and the reaction heated at 100 ^{o}C for 30 minutes. After this time, morpholine (0.054 mL, 6.230×10^{-4} mol) was added and heating continued for 16 hours. After cooling, the reaction mixture was diluted with diethyl ether (5 mL) and filtered through a celite pad, washing with diethyl ether (30 mL). The filtrate was reduced in *vacuo*. The product was purified *via* flash chromatography (elutant: 20% Diethyl ether – hexane) to yield the *indole* (88 mg, 55%) as pale tan needles: mp 122-124.5 ^{o}C (EtOH); n_{max} (nujol mull)/cm^{-1} 2923, 2851, 1600, 1574, 1519, 1488, 1457, 1436, 1391, 1374, 1334, 1299, 1252, 1175, 1150, 1116, 1022, 1010, 944, 888, 873, 746, 721, 646, 614; d_H ($CDCl_3$) 3.24-3.32 (4H, m, CH_2N), 3.88 (3H, s, OMe), 3.94-4.02 (4H, m, CH_2O), 6.62-6.70 (1H, br m, ArH), 6.65 (1H, d, J = 3.3, ArH), 7.00-7.06 (2H, m, ArH), 7.10-7.18 (2H, m, ArH), 7.23 (1H, d, J = 3.3, ArH), 7.36-7.42 (2H, m, ArH); d_C ($CDCl_3$) 52.0, 55.6, 67.3, 101.2, 105.5, 107.0, 114.7, 122.2, 122.8, 126.2, 127.0, 132.8, 137.6, 145.7, 158.3; *m/z* LRMS (EI$^+$) 308.2 (M^+, 100%), 250.1 (75), 208.1 (25), 178.1 (20), 152.1 (15), 116.1 (15), 89.1 (20), 77.1 ($[C_6H_5]^+$, 12); Anal. Calc. for $C_{19}H_{20}N_2O_2$: C, 74.00; H, 6.54; N, 9.08. Found: C, 73.90; H, 6.63; N, 8.85%.

[1-(4-Methoxyphenyl)indol-4-yl]methylphenylamine (Scheme 3, entry 3)



Prepared following general procedure D, using 2-(2-bromovinyl)-1,3-dichlorobenzene (0.131 g, 5.19×10^{-4} mol), *p*-anisidine (67 mg, 5.45×10^{-4} mol) and *N*-methylaniline (0.067 mL, 6.230×10^{-4} mol), heating at 100 ^{o}C for 16 hours. The product was purified

via flash chromatography (elutant: 1 - 2% Diethyl ether – hexane) to yield the *indole* (98 mg, 57%) as fine white needles: mp 101.5-104.5 ^{o}C (EtOH); n_{max} (nujol mull)/cm^{-1} 3054, 2923, 2854, 1598, 1572, 1519, 1496, 1488, 1462, 1386, 1377, 1339, 1296, 1253, 1181, 1107, 1078, 1034, 934. 832, 753, 698; d_H ($CDCl_3$) 3.47 (3H, s, NMe), 3.89 (3H, s, OMe), 6.28 (1H, dd, *J* = 3.3 and 0.8, ArH), 6.77-6.90 (3H, m, ArH), 6.99 (1H, dd, *J* = 7.4 and 1.0, ArH), 7.00-7.07 (2H, m, ArH), 7.16 (1H, d, *J* = 3.3, ArH), 7.16-7.26 (3H, m, ArH), 7.28 (1H, app. dt, *J* = 8.2 and 0.9, ArH), 7.38-7.45 (2H, m, ArH); d_C ($CDCl_3$) 40.3, 55.6, 101.8, 107.3, 114.7, 115.9, 116.1, 118.3, 122.9, 125.3, 126.1, 127.6, 128.8, 132.8, 137.9, 141.4, 149.5, 158.3; *m/z* LRMS (EI$^+$) 328.2 (M$^+$, 100%), 205.2 (18), 178.1 (20), 77.1 ([C_6H_5]$^+$, 70), 51.1 (42); HRMS (ES$^+$) 329.1648 ([M+H]$^+$. $C_{22}H_{21}N_2O$ requires: 329.1648); Anal. Calc. for $C_{22}H_{20}N_2O$: C, 80.46; H, 6.14; N, 8.53. Found: C, 80.40; H, 6.15; N, 8.35%.

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