Supplementary Information (1)

Arylboronic Acids and Arylpinacolboronate Esters in Suzuki Coupling Reactions Involving Indoles. Partner Role Swapping and Heterocycle Protection

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Contents

Experimental	S4-S40
6-Bromoindole 1b	S4
1-Boc-5-bromoindole 1d	S5
1-Boc-6-bromoindole 1e	S5

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1-Tos-5-bromoindole 1f	S6
1-Tos-6-bromoindole 1g	S7
Pinacol indol-5-ylboronate 1m	S7
Pinacol 4-methoxyphenylboronate 2i	S8
Preparations of 5-(4-Methylphenyl)indole 3a	S8
Preparations of 5-(2-Methylphenyl)indole 3c	S10
Preparations of 5-(2-Methoxyphenyl)indole 3d	S12
Preparations of 6-(4-Methoxyphenyl)indole 3e	S13
Preparations of 6-(2-Methoxyphenyl)indole 3f	S15
Preparations of 7-(4-Methoxyphenyl)indole 3g	S16
Preparations of 7-(2-Methoxyphenyl)indole 3h	S18
Preparations of 1- <i>tert</i> -Butoxycarbonyl-5-(4-methoxyphenyl)indole 3j	S19
Preparations of 1- <i>tert</i> -Butoxycarbonyl-5-(2-methylphenyl)indole 3k	S23
Preparations of 1- <i>tert</i> -Butoxycarbonyl-5-(2-methoxyphenyl)indole 3l	S24
Preparations of 1- <i>tert</i> -Butoxycarbonyl-6-(4-methoxyphenyl)indole 3m	S27
Preparations of 1- <i>tert</i> -Butoxycarbonyl-6-(2-methoxyphenyl)indole 3n	S30
Preparations of 1-(<i>p</i> -Toluenesulfonyl)-5-(4-methylphenyl)indole 3o	S32
Preparations of 1-(<i>p</i> -Toluenesulfonyl)-5-(2-methylphenyl)indole 3q	S33
Preparations of 1-(<i>p</i> -Toluenesulfonyl)-5-(2-methoxyphenyl)indole 3r	S33
Preparations of 1-(<i>p</i> -Toluenesulfonyl)-6-(4-methoxyphenyl)indole 3s	S36
Preparations of 1-(<i>p</i> -Toluenesulfonyl)-6-(2-methoxyphenyl)indole 3t	S38
References for Experimental	S40

¹ H and ¹³ C Spectra	S41-S101
6-Bromoindole 1b	S42
1-Boc-5-bromoindole 1d	S44
1-Boc-6-bromoindole 1e	S46
1-Tos-5-bromoindole 1f	S48
1-Tos-6-bromoindole 1g	S50
Pinacol indol-5-ylboronate 1m	S52
Pinacol indol-6-ylboronate 1n	S54
Pinacol 1-Boc-indol-5-ylboronate 1m	S56
Pinacol 4-methoxyphenylboronate 2i	S58
5-(4-Methylphenyl)indole 3a	S61
5-(4-Methoxyphenyl)indole 3b	S63
5-(2-Methylphenyl)indole 3c	S65
5-(2-Methoxyphenyl)indole 3d	S67
6-(4-Methoxyphenyl)indole 3e	S69
6-(2-Methoxyphenyl)indole 3f	S71
7-(4-Methoxyphenyl)indole 3g	S73
7-(2-Methoxyphenyl)indole 3h	S75
1- <i>tert</i> -Butoxycarbonyl-5-(4-methylphenyl)indole 3i	S77
1- <i>tert</i> -Butoxycarbonyl-5-(4-methoxyphenyl)indole 3j	S79
1- <i>tert</i> -Butoxycarbonyl-5-(2-methylphenyl)indole 3k	S82
1- <i>tert</i> -Butoxycarbonyl-5-(2-methoxyphenyl)indole 3l	S84

1- <i>tert</i> -Butoxycarbonyl-6-(4-methoxyphenyl)indole 3m	S86
1- <i>tert</i> -Butoxycarbonyl-6-(2-methoxyphenyl)indole 3n	S88
1-(<i>p</i> -Toluenesulfonyl)-5-(4-methylphenyl)indole 3o	S90
1-(<i>p</i> -Toluenesulfonyl)-5-(4-methoxyphenyl)indole 3p	S92
1-(<i>p</i> -Toluenesulfonyl)-5-(2-methylphenyl)indole 3q	S94
1-(<i>p</i> -Toluenesulfonyl)-5-(2-methoxyphenyl)indole 3r	S96
1-(<i>p</i> -Toluenesulfonyl)-6-(4-methoxyphenyl)indole 3s	S98
1-(<i>p</i> -Toluenesulfonyl)-6-(2-methoxyphenyl)indole 3t	S100

Experimental

6-Bromoindole **1b**

A solution of 4-bromo-2-nitrotoluene (1.0 g, 4.6 mmol), dimethyl formamide dimethyl acetal (0.79 mL, 5.6 mmol) and pyrrolidine (0.46 mL, 5.6 mmol) in DMF (10 mL) was heated at 110 °C for 2 h. After cooling to 0 °C, 4M NH₄OAc (20 mL), DMF (40 mL) and 15% TiCl₃ in 10% HCl (23 mL, 22 mmol) were added. After stirring for 15 min the resulting grey suspension was brought to pH 9 by adding 4M NaOH. Extraction with Et₂O, followed by drying and solvent removal gave the crude product. Column chromatography [silica, hexanes-EtOAc (9:1)] gave a white solid (0.82 g, 90%), m.p. 91-92 °C (lit.¹ 92-93 °C); δ_H (200 MHz, CDCl₃) 6.52 (m, 1H), 7.15-7.20 (m, 1H), 7.23-7.24 (m, 1H), 7.47 (s, 1H), 7.52-7.53 (m, 1H), 8.11 (bs, 1H); δ_C (50 MHz, CDCl₃) 102.8 (CH),

113.9 (CH), 115.4 (C), 121.9 (CH), 123.1 (CH), 124.9 (CH); m/z 197 (M^+ , 94%), 195 (M^+ , 100%); HRMS (EI) calcd for C_8H_6BrN : 194.968360; found: 194.969085.

1-Boc-5-bromoindole **1d**

DMAP (0.071 g, 0.58 mmol) was added to a solution of 5-bromoindole (1.0 g, 5.1 mmol) and Boc_2O (1.36 g, 6.23 mmol) in anhydrous MeCN (5.1 mL) and the mixture stirred at r.t. for 1h. DEAEA (0.215 mL, 1.53 mmol) was added and, after stirring for 10 min, the mixture was diluted with 1M $KHSO_4$ and extracted with Et_2O . The combined extracts were washed with 1M $KHSO_4$, 1M $NaHCO_3$ and brine. Drying and solvent removal gave the crude product. Column chromatography [silica, hexanes-EtOAc (95:5)] gave a white solid (1.30 g, 86%), m.p. 90-91 °C; δ_H (200 MHz, $CDCl_3$) 1.66 (s, 9H), 6.50 (d, J 3.7, 1H), 7.39 (dd, J_1 9, J_2 2.2, 1H), 7.58 (d, J 3.6, 1H), 7.68 (d, J 1.8, 1H), 8.02 (d, J 8.8, 1H); δ_C (50 MHz, $CDCl_3$) 28.2 (CH_3), 84.1 (C), 106.4 (CH), 115.9 (C), 116.5 (CH), 123.4 (CH), 126.9 (CH), 132.1 (C); m/z 297 [$(M)^+$, 5%], 295 [$(M)^+$, 5%], 57 (100%); HRMS (EI) calcd for $C_{13}H_{14}BrNO_2$: 295.020790; found: 295.020270.

1-Boc-6-bromoindole **1e**

DMAP (0.012 g, 0.1 mmol) was added to a solution of 6-bromoindole (0.2 g, 1.03 mmol) and Boc_2O (0.278 g, 1.24 mmol) in anhydrous MeCN (1 mL) and the mixture stirred at r.t. for 1h. DEAEA (0.042 mL, 0.3 mmol) was added and, after stirring for 10 min, the mixture was diluted with 1M $KHSO_4$ and extracted with Et_2O . The combined

extracts were washed with 1M KHSO₄, NaHCO₃ 1M and brine. Drying and solvent removal gave the crude product. Column chromatography [silica, EtOAc in hexanes (0-5%)] gave a white solid (0.287 g, 95%); m.p. 102-103 °C; δ_{H} (200 MHz, CDCl₃) 1.67 (s, 9H), 6.52 (d, *J* 3.8, 1H), 7.31-7.43 (m, 2H), 7.55 (d, *J* 3.6, 1H), 8.36 (s, 1H); δ_{C} (50 MHz, CDCl₃) 28.1 (CH₃), 84.2 (C), 107.0 (CH), 117.8 (C), 118.3 (CH), 121.9 (CH), 125.8 (CH), 126.2 (CH); *m/z* 298 [(M+1)⁺, 70%], 296 [(M+1)⁺, 75%], 240 (100%); HRMS (EI) calcd for C₁₃H₁₄BrNO₂: 295.020790; found: 295.020726.

1-Tos-5-bromoindole **1f**

ⁿBuLi (11.6 mL 7.65 mmol) was added to a solution of 5-bromoindole (1.5 g, 7.65 mmol) in anhydrous THF (1.25 mL) at -78 °C. The mixture was allowed to warm to 0 °C and stirred for 45 min. After re-cooling to -78 °C, TosCl (1.6 g, 8.4 mmol) was added dropwise over 1 min. Stirring was then continued for 12 h at r.t. The mixture was diluted with 5% aq. NaHCO₃ and extracted with CH₂Cl₂. The combined extracts were washed with H₂O and brine. Drying followed by solvent removal gave a light-brown solid, which was crystallized from Et₂O-CH₂Cl₂ (6:1), giving a white solid (2.22 g, 76%); m.p. 136-137 °C (lit.² 133-134 °C); δ_{H} (200 MHz, CDCl₃) 2.34 (s, 3H), 6.58 (d, *J* 3.6, 1H), 7.20-7.25 (m, 2H), 7.39 (dd, *J*₁ 8.8, *J*₂ 1.8, 1H), 7.55 (d, *J* 2.2, 1H), 7.65 (d, *J* 2.2, 1H), 7.73 (m, 2H), 7.85 (d, *J* 8.8, 1H); δ_{C} (50 MHz, CDCl₃) 21.6 (CH₃), 108.2 (CH), 114.9 (CH), 116.7 (C), 124.0 (CH), 126.7 (CH), 127.4 (CH), 127.5 (CH), 129.9 (CH), 132.4 (C), 133.4 (C), 134.9 (C), 145.2 (C) *m/z* 368 [(M+18)⁺, 100%], 366 [(M+18)⁺, 91%]; HRMS (EI) calcd for C₁₅H₁₂BrSNO₂: 350.975166; found: 350.976296.

1-Tos-6-bromoindole **1g**

ⁿBuLi (2.5 mL, 2.6 mmol) was added to a solution of 6-bromoindole (0.51 g, 2.6 mmol) in anhydrous THF (2.5 mL) at -78 °C. The mixture was allowed to warm to 0 °C and stirred for 45 min. After re-cooling to -78 °C, TosCl (0.54 g, 2.8 mmol) was added dropwise over 1 min. Stirring was then continued for 12 h at r.t. The mixture was diluted with 5% aq. NaHCO₃ and extracted with CH₂Cl₂. The combined extracts were washed with H₂O and brine. Drying followed by solvent removal gave a light-brown solid, which was crystallized from Et₂O-CH₂Cl₂ (6:1), giving a white solid (0.66 g, 72%), m.p. 132-134 °C; δ_H (200 MHz, CDCl₃) 2.35 (s, 3H), 6.61 (dd, *J*₁ 3.6, *J*₂ 0.8, 1H), 7.24 (d, *J* 8.4, 2H), 7.34 (m, 2H), 7.52 (d, *J* 3.8, 1H), 7.75 (d, *J* 8.4, 2H), 8.17 (m, 1H); δ_C (50 MHz, CDCl₃) 21.6 (CH₃), 108.7 (CH), 116.5 (CH), 118.1 (C), 122.4 (CH), 126.6 (CH), 126.7 (CH), 129.4 (C), 130.0 (CH), 134.9 (C), 135.3 (C), 145.2 (C); *m/z* 352 [(M+1)⁺, 96%], 350 [(M+1)⁺, 100%]; HRMS (EI) calcd for C₁₅H₁₂BrSNO₂: 350.975166; found: 350.975691.

Pinacol indol-5-ylboronate **1m**

KOAc (0.29 g, 3.0 mmol), bis(pinacolato)diboron (0.28 g, 1.1 mmol), 5-bromoindole (0.20 g, 1.0 mmol) and PdCl₂(dppf) (0.02 g, 0.03 mmol) in 1,4-dioxane (6 mL) were heated at 100 °C under argon for 48 h. After cooling the solvent was removed and the crude product was purified by chromatography [silica, hexanes-EtOAc, (9:1)]

giving a pale yellow oil (0.21 g, 86%); δ_{H} (200 MHz, CDCl_3) 1.36 (s, 12H), 6.56 (m, 1H), 7.17 (t, J 2.8, 1H), 7.37 (d, J 8.4, 1H), 7.64 (dd, J_1 8.4, J_2 1.2, 1H), 8.20 (m, 2H); δ_{C} (50 MHz, CDCl_3) 24.9 (CH_3), 83.4 (C), 103.0 (CH), 110.4 (CH), 124.1 (CH), 128.0 (CH), 128.6 (CH), 138.0 (C); m/z (%) 244[$(M+1)$, 100]; HRMS (CI) calcd for $\text{C}_{14}\text{H}_{18}\text{BNO}_2$: 243.143059; found: 243.141349.

Pinacol 4-methoxyphenylboronate **2i**

KOAc (0.23 g, 2.29 mmol), bis(pinacolato)diboron (0.22 g, 1.1 mmol), 4-bromoanisole (0.097 mL, 0.76 mmol) and $\text{PdCl}_2(\text{dppf})$ (0.04 g, 0.05 mmol) in 1,4-dioxane (4 mL) were heated at 80 °C under argon for 24 h. After cooling the solvent was removed leaving the crude boronate as a pale brown oil. The crude product was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving a clear oil³ (0.11 g, 62%); δ_{H} (200 MHz, CDCl_3) 1.33 (s, 12H), 3.83 (s, 3H), 6.90 (d, J 8.8, 2H), 7.75 (d, J 8.4, 2H); δ_{C} (50 MHz, CDCl_3) 24.9 (CH_3), 55.0 (CH_3), 83.5 (C), 113.2 (CH), 136.4 (CH), 162.0 (C); m/z (%) 235[$(M+1)$, 100]; HRMS (CI) calcd for $\text{C}_{13}\text{H}_{20}\text{BNO}_3$: 235.150550; found: 235.150327.

Preparations of 5-(4-Methylphenyl)indole **3a**

From 5-bromoindole 1a and 4-methylphenylboronic acid 2a: Aqueous Na_2CO_3 (4 mL of a 1M solution, 4 mmol) and $\text{Pd}(\text{Ph}_3\text{P})_4$ (0.10 g, 0.08 mmol) in 1:1 toluene-EtOH (10 mL) were added to a solution of 5-bromoindole (0.32 g, 1.70 mmol) and 4-

methylphenylboronic acid (0.45 g, 3.40 mmol) in 1:1 toluene-EtOH (4 mL) and the resulting mixture heated at reflux under argon for 1 h. Pd(Ph₃P)₄ (0.10 g, 0.08 mmol) in 1:1 toluene-EtOH (4 mL) was added and heating at reflux under argon continued for a further 4 h. After cooling, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a clear pale yellow oil (0.33 g, 97%).

From indol-5-ylboronic acid 1h and 4-bromotoluene 2e: KH (0.10 g, 2.60 mmol) was suspended in THF (4 mL) under argon at 0 °C. 5-Bromoindole (0.50 g, 2.6 mmol) was added and the mixture stirred for 15 min. The resulting solution was cooled to –78 °C and ^tBuLi (3.4 mL of a 1.5 M solution in pentane, 5.1 mmol) was added over 1 min. The cooling bath was removed and the mixture stirred for 10 min. After re-cooling to –78 °C, B(OMe)₃ (0.60 mL, 5.10 mmol) was added and the mixture was allowed to warm to r.t. and stirred for 3h. H₂O (15 mL) was added and the mixture was extracted with EtOAc (3x15 mL). The aqueous phase was acidified to pH 1 with 10% HCl and extracted with EtOAc (3x25 mL). The combined organic extracts were dried and the solvent removed furnishing the crude indolylboronic acid as a light-brown oil.

The crude boronic acid (0.41 g, 2.60 mmol) in 1:1 toluene-EtOH (4 mL) was added to 4-bromotoluene (0.082 mL, 0.68 mmol), 1M aqueous Na₂CO₃ (1.8 mL of a 1M solution, 1.8 mmol) and Pd(Ph₃P)₄ (0.037 g, 0.03 mmol) in 1:1 toluene-EtOH (1.5 mL) and the mixture was heated at reflux under argon for 1h. Pd(Ph₃P)₄ (0.037 g, 0.03 mmol) in 1:1 toluene-EtOH (1.5 mL) was added and heating at reflux under argon continued for a further 4 h. After cooling, the solvent was removed and the resulting crude was purified

by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a pale oil (0.20 g, 65%); δ_{H} (200 MHz, CDCl_3) 2.40 (s, 3H), 6.56 (m, 1H), 7.24 (m, 3H), 7.43 (d, J 1.4, 2H), 7.55 (d, J 8, 1H), 7.84 (s, 2H), 8.20 (bs, 1H); δ_{C} (50 MHz, CDCl_3) 21.1 (CH_3), 102.9 (CH), 115.0 (CH), 118.9 (CH), 121.8 (CH), 124.7 (CH), 127.2 (CH), 129.3 (CH), 133.0 (C), 134.9 (C), 136.1 (C), 140.1 (C); m/z (%) 208[($M+1$), 100]; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{13}\text{N}$: 207.104800; found: 207.104538.

Preparations of 5-(2-Methylphenyl)indole **3c**

From 5-bromoindole 1a and 2-methylphenylboronic acid 2c: Aqueous Na_2CO_3 (4 mL of a 1M solution, 4 mmol) and $\text{Pd}(\text{Ph}_3\text{P})_4$ (0.10 g, 0.08 mmol) in 1:1 toluene-EtOH (10 mL) were added to a solution of 5-bromoindole (0.33 g, 1.70 mmol) and 4-methylphenylboronic acid (0.45 g, 3.40 mmol) in 1:1 toluene-EtOH (4 mL) and the resulting mixture was heated at reflux under argon for 1 h. $\text{Pd}(\text{Ph}_3\text{P})_4$ (0.10 g, 0.08 mmol) in 1:1 toluene-EtOH (4 mL) was added and heating at reflux under argon continued for a further 4 h. After cooling, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a pale yellow oil (0.35 g, 99%).

From indol-5-ylboronic acid 1h and 2-bromotoluene 2g: KH (0.10 g, 2.60 mmol) was suspended in THF (4 mL) under argon at 0 °C. 5-Bromoindole (0.50 g, 2.6 mmol) was added and the mixture stirred for 15 min. The resulting solution was cooled to -78 °C and $t\text{-BuLi}$ (3.4 mL of a 1.5 M solution in pentane, 5.1 mmol) was added over 1 min. The

cooling bath was removed and the mixture stirred for 10 min. After re-cooling to $-78\text{ }^{\circ}\text{C}$, B(OMe)_3 (0.60 mL, 5.10 mmol) was added and the mixture was allowed to warm to r.t. and stirred for 3h. H_2O was added and the mixture was extracted with EtOAc. The aqueous phase was acidified to pH 1 with 10% HCl and extracted with EtOAc (3x25 mL). The combined organic extracts were dried and the solvent removed furnishing the crude indolylboronic acid as a light-brown oil.

The crude boronic acid (0.41 g, 2.60 mmol) in 1:1 toluene-EtOH (4 mL) was added to 2-bromotoluene (0.082 mL, 0.68 mmol), 1M aqueous Na_2CO_3 (1.8 mL of a 1M solution, 1.8 mmol) and $\text{Pd(Ph}_3\text{P)}_4$ (0.037 g, 0.03 mmol) in 1:1 toluene-EtOH (1.5 mL) and the mixture was heated at reflux under argon for 1h. $\text{Pd(Ph}_3\text{P)}_4$ (0.037 g, 0.03 mmol) in 1:1 toluene-EtOH (1.5 mL) was added and heating at reflux under argon was continued for a further 4 h. After cooling, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a pale oil (0.18 g, 60%); δ_{H} (200 MHz, CDCl_3) 2.31 (s, 3H), 6.58 (m, 1H), 7.28 (m, 7H), 7.58 (m, 1H), 8.10 (bs, 1H); δ_{C} (50 MHz, CDCl_3) 20.8 (CH_3), 102.8 (CH), 110.4 (CH), 121.1 (CH), 123.7 (CH), 124.6 (CH), 125.6 (CH), 126.6 (CH), 127.7 (CH), 130.1 (CH), 130.3 (CH), 133.7 (C), 134.7 (C), 135.7 (C), 143.0 (C); m/z (%) 225[($M+\text{NH}_4$) $^+$, 5], 208[($M+1$), 100]; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{13}\text{N}$: 207.104800; found: 207.105524.

Preparations of 5-(2-Methoxyphenyl)indole **3d**

*From 5-bromoindole **1a** and 2-methoxyphenylboronic acid **2d**:* Aqueous Na₂CO₃ (1.3 mL of a 1M solution, 1.3 mmol) and Pd(Ph₃P)₄ (0.03 g, 0.026 mmol) in 1:1 toluene-EtOH (4 mL) was added to a solution of 5-bromoindole (0.103 g, 0.53 mmol) and 2-methoxyphenylboronic acid (0.165 g, 1.03 mmol) in 1:1 toluene-EtOH (4 mL) and the resulting mixture was heated at reflux under argon for 1 h. Pd(Ph₃P)₄ (0.03 g, 0.026 mmol) in 1:1 toluene-EtOH (4 mL) was added and heating at reflux under argon continued for a further 4 h. After cooling, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid (0.105 g, 91%).

*From indol-5-ylboronic acid **1h** and 2-bromoanisole **2h**:* KH (0.03 g, 0.77 mmol) was suspended in THF (1.5 mL) under argon at 0 °C. 5-Bromoindole (0.15 g, 0.77 mmol) was added and the mixture stirred for 15 min. The resulting solution was cooled to –78 °C and *t*-BuLi (0.9 mL of a 1.7 M solution in pentane, 1.53 mmol) was added over 1 min. The cooling bath was removed and the mixture stirred for 10 min. After re-cooling to –78 °C, B(OMe)₃ (0.18 mL, 1.53 mmol) was added and the mixture was allowed to warm to r.t. and stirred for 3h. H₂O was added and the mixture was extracted with EtOAc. The aqueous phase was acidified to pH 1 with 10% HCl and extracted with EtOAc. The combined organic extracts were dried and the solvent removed furnishing the crude indolylboronic acid as a light-brown oil.

The crude boronic acid (0.12 g, 0.77 mmol) in 1:1 toluene-EtOH (2 mL) was added to 2-bromoanisole (0.025 mL, 0.19 mmol), 1M aqueous Na₂CO₃ (0.50 mL, 0.50 mmol) and Pd(Ph₃P)₄ (0.0011 g, 0.009 mmol) in 1:1 toluene-EtOH (1.4 mL) and the mixture was heated at reflux under argon for 1h. Pd(Ph₃P)₄ (0.0011 g, 0.009 mmol) in 1:1 toluene-EtOH (1.4 mL) was added and heating at reflux under argon was continued for a further 4 h. After cooling, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid (0.04 g, 94%), m.p. 95-97 °C (lit.⁴ 98-100 °C); δ_H (200 MHz, CDCl₃) 3.81 (s, 3H), 6.57 (m, 1H), 6.97-7.07 (m, 2H), 7.14-7.39 (m, 5H), 7.77 (m, 1H), 8.06 (bs, 1H); δ_C (50 MHz, CDCl₃) 55.6 (CH₃), 102.8 (CH), 110.4 (CH), 111.2 (CH), 120.7 (CH), 121.5 (CH), 124.1 (CH), 124.4 (CH), 127.8 (CH), 130.2 (C), 131.3 (CH), 132.0 (C), 134.9 (C), 156.5 (C); *m/z* (%) 241[(*M*+NH₄)⁺, 100], 224[(*M*+1), 43]; HRMS (EI) calcd for C₁₅H₁₃NO: 223.099714; found: 223.100481.

Preparations of 6-(4-Methoxyphenyl)indole **3e**

From 6-bromoindole 1b and 4-methoxyphenylboronic acid 2b: Aqueous Na₂CO₃ (1.3 mL of a 1M solution, 1.3 mmol) and Pd(Ph₃P)₄ (0.03 g, 0.026 mmol) in 1:1 toluene-EtOH (4 mL) was added to a solution of 6-bromoindole (0.100 g, 0.51 mmol) and 4-methoxyphenylboronic acid (0.163 g, 1.02 mmol) in 1:1 toluene-EtOH (4 mL) and the resulting mixture was heated at reflux under argon for 1 h. Pd(Ph₃P)₄ (0.03 g, 0.026 mmol) in 1:1 toluene-EtOH (4 mL) was added and heating at reflux under argon continued for a further 4 h. After cooling, the solvent was removed and the resulting

crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid (0.087 g, 76%).

From indol-6-ylboronic acid 1i and 4-bromoanisole 2f: KH (0.17 g, 4.3 mmol) was suspended in THF (8 mL) under argon at 0 °C. 6-Bromoindole (0.84 g, 0.43 mmol) was added and the mixture stirred for 15 min. The resulting solution was cooled to –78 °C and *t*BuLi (5.7 mL of a 1.5 M solution in pentane, 8.6 mmol) was added over 1 min. The cooling bath was removed and the mixture stirred for 10 min. After re-cooling to –78 °C, B(OMe)₃ (1.0 mL, 8.6 mmol) was added and the mixture was allowed to warm to r.t. and stirred for 3h. H₂O was added and the mixture was extracted with EtOAc. The aqueous phase was acidified to pH 1 with 10% HCl and extracted with EtOAc. The combined organic extracts were dried and the solvent removed furnishing the crude indolylboronic acid as a light-brown oil.

The crude boronic acid (0.23 g, 1.20 mmol) in 1:1 toluene-EtOH (8 mL) was added to 4-bromoanisole (0.038 mL, 0.31 mmol), 1M aqueous Na₂CO₃ (0.8 mL, 0.80 mmol) and Pd(Ph₃P)₄ (0.017 g, 0.01 mmol) in 1:1 toluene-EtOH (2 mL) and the mixture was heated at reflux under argon for 1h. Pd(Ph₃P)₄ (0.017 g, 0.01 mmol) in 1:1 toluene-EtOH (2 mL) was added and heating at reflux under argon continued for a further 4 h. After cooling, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid (0.05 g, 75%), m.p. 125-130 °C (lit.⁵ 181-183 °C); δ_{H} (200 MHz, CDCl₃) 3.85 (s, 3H), 6.55 (m, 1H), 6.78 (s, 1H), 6.97 (d, *J* 8.8, 2H), 7.19 (m, 1H), 7.41 (m, 1H), 7.58 (m, 2H), 7.69 (d, *J* 8.8, 1H), 8.13 (bs, 1H); δ_{C} (50 MHz, CDCl₃) 55.4 (CH₃), 102.4 (CH), 109.0 (CH), 114.1

(CH), 119.5 (CH), 120.7 (CH), 124.5 (CH), 128.2 (CH), 135.1 (C), 158.5 (C); m/z (%) 241[($M+NH_4$)⁺, 5], 224[($M+1$), 100]; HRMS (EI) calcd for C₁₅H₁₃NO: 223.099714; found: 223.099961.

Preparations of 6-(2-Methoxyphenyl)indole **3f**

*From 6-bromoindole **1b** and 2-methoxyphenylboronic acid **2d**:* Aqueous Na₂CO₃ (1 mL of a 1M solution, 1.0 mmol) and Pd(Ph₃P)₄ (0.02 g, 0.02 mmol) in 1:1 toluene-EtOH (4 mL) was added to a solution of 6-bromoindole (0.09 g, 0.41 mmol) and 2-methoxyphenylboronic acid (0.12 g, 0.80 mmol) in 1:1 toluene-EtOH (6 mL) and the resulting mixture was heated at reflux under argon for 1 h. Pd(Ph₃P)₄ (0.02 g, 0.02 mmol) in 1:1 toluene-EtOH (4 mL) was added and heating at reflux under argon continued for a further 4 h. After cooling, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a clear oil (0.105 g, 80%).

*From indol-6-ylboronic acid **1i** and 2-bromoanisole **2h**:* KH (0.17 g, 4.31 mmol) was suspended in THF (1.5 mL) under argon at 0 °C. 6-Bromoindole (0.84 g, 4.3 mmol) was added and the mixture stirred for 15 min. The resulting solution was cooled to –78 °C and ^tBuLi (5.7 mL of a 1.5 M solution in pentane, 8.6 mmol) was added over 1 min. The cooling bath was removed and the mixture stirred for 10 min. After re-cooling to –78 °C, B(OMe)₃ (1 mL, 8.6 mmol) was added and the mixture was allowed to warm to r.t. and stirred for 3h. H₂O (10 mL) was added and the mixture was extracted with EtOAc (2x15

mL). The aqueous phase was acidified to pH 1 with 10% HCl and extracted with EtOAc. The combined organic extracts were dried and the solvent removed furnishing the crude indolylboronic acid as a light-brown oil.

The crude boronic acid (0.14 g, 0.86 mmol) in 1:1 toluene-EtOH (4 mL) was added to 2-bromoanisole (0.027 mL, 0.22 mmol), 1M aqueous Na₂CO₃ (0.54 mL, 0.54 mmol) and Pd(Ph₃P)₄ (0.012 g, 0.01 mmol) in 1:1 toluene-EtOH (1.5 mL) and the mixture was heated at reflux for 1h. Pd(Ph₃P)₄ (0.012 g, 0.01 mmol) in 1:1 toluene-EtOH (1.5 mL) was added and heating at reflux under argon continued for a further 4 h. After cooling, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as an oil (0.03 g, 65%); δ_{H} (200 MHz, CDCl₃) 3.79 (s, 3H), 6.53 (m, 1H), 7.01 (m, 2H), 7.14 (m, 1H), 7.33 (m, 3H), 7.51 (s 1H), 7.65 (d *J* 8, 1H), 8.07 (bs, 1H); δ_{C} (50 MHz, CDCl₃) 55.6 (CH₃), 102.4 (CH), 111.2 (CH), 111.9 (CH), 119.9 (CH), 120.7 (CH), 121.9 (CH), 124.5 (CH), 126.8 (C), 127.0 (CH), 131.2 (CH), 131.6 (C), 132.3 (C), 135.7 (C), 156.4 (C); *m/z* (%) 223[(*M*)⁺, 100], 208 [(*M*- Me)⁺, 44]; HRMS (EI) calcd for C₁₅H₁₃NO: 223.099714; found: 223.099192.

Preparations of 7-(4-Methoxyphenyl)indole **3g**

From 7-bromoindole 1c and 4-methoxyphenylboronic acid 2b: Aqueous Na₂CO₃ (1.3 mL of a 1M solution, 1.30 mmol) and Pd(Ph₃P)₄ (0.03 g, 0.03 mmol) in 1:1 toluene-EtOH (4 mL) was added to a solution of 7-bromoindole (0.10 g, 0.51 mmol) and 4-methoxyphenylboronic acid (0.165 g, 1.03 mmol) in 1:1 toluene-EtOH (6 mL) and the

resulting mixture was heated at reflux under argon for 1 h. $\text{Pd}(\text{Ph}_3\text{P})_4$ (0.03 g, 0.03 mmol) in 1:1 toluene-EtOH (4 mL) was added and heating at reflux under argon continued for a further 4 h. After cooling, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid (0.075 g, 67%).

From indol-7-ylboronic acid 1j and 4-bromoanisole 2f: KH (0.06 g, 1.56 mmol) was suspended in THF (1.5 mL) under argon at 0 °C. 7-Bromoindole (0.30 g, 1.53 mmol) was added and the mixture stirred for 15 min. The resulting solution was cooled to -78 °C and *t*-BuLi (2 mL of a 1.5 M solution in pentane, 3.0 mmol) was added over 1 min. The cooling bath was removed and the mixture stirred for 10 min. After re-cooling to -78 °C, $\text{B}(\text{OMe})_3$ (0.36 mL, 3.1 mmol) was added and the mixture was allowed to warm to r.t. and stirred for 3h. H_2O was added and the mixture was extracted with EtOAc. The aqueous phase was acidified to pH 1 with 10% HCl and extracted with EtOAc. The combined organic extracts were dried and the solvent removed furnishing the crude indolylboronic acid as a light-brown oil.

The crude boronic acid (0.25 g, 1.53 mmol) in 1:1 toluene-EtOH (25 mL) was added to 4-bromoanisole (0.05 mL, 0.40 mmol), 1M aqueous Na_2CO_3 (1.0 mL, 1.0 mmol) and $\text{Pd}(\text{Ph}_3\text{P})_4$ (0.022 g, 0.018 mmol) in 1:1 toluene-EtOH (1.4 mL) and the mixture was heated at reflux under argon for 1h. $\text{Pd}(\text{Ph}_3\text{P})_4$ (0.025 g, 0.018 mmol) in 1:1 toluene-EtOH (1.4 mL) was added and heating at reflux under argon continued for a further 4 h. After cooling, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid

(0.044 g, 52%), m.p. 103-108 °C; δ_{H} (200 MHz, CDCl_3) 3.87 (s, 3H), 6.61 (dd, J_1 3.4 J_2 1.8, 1H), 7.04 (m, 2H), 7.20 (m, 3H), 7.58 (m, 3H), 8.37 (bs, 1H); δ_{C} (50 MHz, CDCl_3) 55.4 (CH_3), 103.0 (CH), 114.5 (CH), 119.5 (CH), 120.2 (CH), 121.6 (CH), 124.2 (CH), 125.3 (CH), 128.1 (C), 129.2 (CH), 131.6 (C), 158.9 (C); m/z (%) 224 [$(M+H)^+$, 100]; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{13}\text{NO}$: 223.099714; found: 223.099175

Preparations of 7-(2-Methoxyphenyl)indole **3h**

From 7-bromoindole 1c and 2-methoxyphenylboronic acid 2d: Aqueous Na_2CO_3 (1.3 mL of a 1M solution, 1.30 mmol) and $\text{Pd}(\text{Ph}_3\text{P})_4$ (0.03 g, 0.03 mmol) in 1:1 toluene-EtOH (4 mL) was added to a solution of 7-bromoindole (0.10 g, 0.51 mmol) and 2-methoxyphenylboronic acid (0.165 g, 1.03 mmol) in 1:1 toluene-EtOH (6 mL) and the resulting mixture was heated at reflux under argon for 1 h. $\text{Pd}(\text{Ph}_3\text{P})_4$ (0.03 g, 0.03 mmol) in 1:1 toluene-EtOH (4 mL) was added and heating at reflux under argon continued for a further 4 h. After cooling, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid (0.075 g, 66%).

From indol-7-ylboronic acid 1j and 2-bromoanisole 2h: KH (0.168 g, 4.32 mmol) was suspended in THF (1.5 mL) under argon at 0 °C. 7-Bromoindole (0.852 g, 4.35 mmol) was added and the mixture stirred for 15 min. The resulting solution was cooled to -78 °C and *t*-BuLi (5.2 mL of a 1.65 M solution in pentane, 8.6 mmol) was added over 1 min. The cooling bath was removed and the mixture stirred for 10 min. After re-cooling to -78

°C, B(OMe)₃ (1.0 mL, 8.6 mmol) was added and the mixture was allowed to warm to r.t. and stirred for 3h. H₂O was added and the mixture was extracted with EtOAc. The aqueous phase was acidified to pH 1 with 10% HCl and extracted with EtOAc. The combined organic extracts were dried and the solvent removed furnishing the crude indolylboronic acid as a light-brown oil.

The crude boronic acid (0.70 g, 4.35 mmol) in 1:1 toluene-EtOH (25 mL) was added to 2-bromoanisole (0.20 mL, 1.08 mmol), 1M aqueous Na₂CO₃ (2.8 mL, 2.80 mmol) and Pd(Ph₃P)₄ (0.055 g, 0.048 mmol) in 1:1 toluene-EtOH (1.4 mL) and the mixture was heated at reflux under argon for 1h. Pd(Ph₃P)₄ (0.055 g, 0.048 mmol) in 1:1 toluene-EtOH (1.4 mL) was added and heating at reflux under argon was continued for a further 4 h. After cooling, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a clear oil (0.31 g, 87%); δ_H (200 MHz, CDCl₃) 3.79 (s, 3H), 6.59 (dd, *J*₁ 3.4 *J*₂ 2.2, 1H), 7.04-7.23 (m, 5H), 7.38 (dd, *J*₁ 7.6 *J*₂ 1.8, 1H), 7.45 (m, 1H), 7.65 (m, 1H), 8.23 (bs, 1H); δ_C (50 MHz, CDCl₃) 55.9 (CH₃), 102.5 (CH), 111.6 (CH), 119.8 (CH), 120.0 (CH), 121.3 (CH), 122.4 (C), 123.2 (CH), 124.1 (CH), 127.8 (C), 128.0 (C), 129.0 (CH), 131.8 (CH), 156.5 (C); *m/z* (%) 224[(*M*+H)⁺, 100]; HRMS (EI) calcd for C₁₅H₁₃NO: 223.099714; found: 223.099987.

Preparations of 1-*tert*-Butoxycarbonyl-5-(4-methoxyphenyl)indole **3j**

From 1-Boc-5-bromoindole 1d and 4-methoxyphenylboronic acid 2b: Aqueous Na₂CO₃ (2.7 mL of a 1M solution, 2.7 mmol) and Pd(Ph₃P)₄ (0.06 g, 0.06 mmol) in 1:1 toluene-

EtOH (10 mL) were added to a solution of 1-Boc-5-bromoindole (0.32 g, 1.10 mmol) and 4-methoxyphenylboronic acid (0.33 g, 2.20 mmol) in 1:1 toluene-EtOH (4 mL) and the resulting mixture was heated at reflux under argon for 1 h. Pd(Ph₃P)₄ (0.06 g, 0.06 mmol) in 1:1 toluene-EtOH (4 mL) was added and heating at reflux under argon continued for a further 4 h. After cooling, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid (0.29 g, 70%).

*From 1-Boc-indol-5-ylboronic acid **1k** and 4-bromoanisole **2f***: KH (0.07 g, 1.72 mmol) was suspended in THF (4 mL) under argon at 0 °C. 1-Boc-5-bromoindole (0.51 g, 1.72 mmol) was added and the mixture stirred for 15 min. The resulting solution was cooled to -78 °C and *t*-BuLi (2.3 mL of a 1.5 M solution in pentane, 3.5 mmol) was added over 1 min. The cooling bath was removed and the mixture stirred for 10 min. After re-cooling to -78 °C, B(OMe)₃ (0.40 mL, 3.40 mmol) was added and the mixture was allowed to warm to r.t. and stirred for 3h. H₂O was added and the mixture was extracted with EtOAc. The aqueous phase was acidified to pH 1 with 10% HCl and extracted with EtOAc. The combined organic extracts were dried and the solvent removed furnishing the crude indolylboronic acid as a light-brown oil.

The crude boronic acid (0.44 g, 1.70 mmol) in 1:1 toluene-EtOH (4 mL) was added to 4-bromoanisole (0.09 g, 0.47 mmol), 1M aqueous Na₂CO₃ (1.2 mL of a 1M solution, 1.2 mmol) and Pd(Ph₃P)₄ (0.025 g, 0.02 mmol) in 1:1 toluene-EtOH (1.5 mL) and the mixture was heated at reflux under argon for 1h. Pd(Ph₃P)₄ (0.025 g, 0.02 mmol) in 1:1 toluene-EtOH (1.5 mL) was added and heating at reflux under argon continued for

a further 5 h. After cooling, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid (0.08 g, 50%).

From 1-Boc-5-bromoindole 1d and pinacol 4-methoxyphenylboronate 2i: KOAc (0.23 g, 2.29 mmol), bis(pinacolato)diboron (0.22 g, 1.1 mmol), 4-bromoanisole (0.097 mL, 0.76 mmol) and PdCl₂(dppf) (0.04 g, 0.05 mmol) in 1,4-dioxane (4 mL) were heated at 80 °C under argon for 14 h. After cooling the solvent was removed leaving the crude boronate as a pale brown oil.

This boronate (0.071 g, 0.31 mmol), potassium phosphate (0.28 g, 1.26 mmol), PdCl₂(dppf) (0.008 g, 0.008 mmol) and 1-Boc-5-bromoindole (0.134 g, 0.38 mmol) in 1,4-dioxane (2 mL) were heated at 100 °C under argon for 1h. PdCl₂(dppf) (0.004 g, 0.004 mmol) and boronate (0.036 g, 0.15 mmol) were added and heating at 100 °C under argon continued for a further 1h. The addition of catalyst and boronate were repeated twice more at hourly intervals and the mixture was kept at 100 °C under argon for a further 24h. After cooling and filtration, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid (0.027 g, 22%).

From pinacol 1-Boc-indol-5-ylboronate 1o and 4-bromoanisole 2f: KOAc (0.23 g, 2.29 mmol), bis(pinacolato)diboron (0.22 g, 1.1 mmol), 1-Boc-5-bromoindole (0.23 g, 0.76 mmol) and PdCl₂(dppf) (0.04 g, 0.05 mmol) in 1,4-dioxane (4 mL) were heated at 100 °C

under argon 48 h. After cooling the solvent was removed leaving the crude boronate as a pale brown oil.

This boronate (0.12 g, 0.31 mmol), potassium phosphate (0.28 g, 1.26 mmol), PdCl₂(dppf) (0.008 g, 0.008 mmol) and 4-bromoanisole (0.05 mL, 0.38 mmol) in 1, 4-dioxane (2 mL) were heated at 100 °C under argon for 1h. PdCl₂(dppf) (0.004 g, 0.004 mmol) and boronate (0.06 g, 0.15 mmol) were added and the mixture heated at 100 °C under argon for a further 1h. The addition of catalyst and boronate were repeated twice more at hourly intervals and the mixture was kept at 100 °C under argon for a further 70h. After cooling and filtration, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid (0.045 g, 36%), m.p. 78-80 °C; δ_{H} (200 MHz, CDCl₃) 1.68 (s, 9H), 3.85 (s, 3H), 6.59 (d, *J* 3.6, 1H), 6.98 (d, *J* 8.8, 2H), 7.55 (m, 4H), 7.71 (d, *J* 1.4, 1H), 8.16 (d, *J* 8.8, 1H); δ_{C} (50 MHz, CDCl₃) 28.2 (CH₃), 55.4 (CH₃), 83.7 (C), 107.4 (CH), 114.1 (CH), 115.2 (CH), 118.8 (CH), 123.4 (CH), 126.3 (CH), 128.2 (CH), 131.0 (C), 134.2 (C), 135.6 (C), 149.7 (C), 158.7 (C); *m/z* (%) 324[(*M*+1), 82], 224(100); HRMS (EI) calcd for C₂₀H₂₁NO₃: 323.152144; found 323.150634.

In addition, pinacol 1-Boc-indol-5-ylboronate **1o** (0.09 g, 48%) was also isolated. It had m.p. 125-128 °C; δ_{H} (200 MHz, CDCl₃) 1.36 (s, 12H), 1.67 (s, 9H), 6.57 (d, *J* 3.6, 1H), 7.57 (d, *J* 3.6, 1H), 7.76 (dd, *J*₁ 8.4, *J*₂ 1, 1H), 8.06 (s, 1H), 8.14 (d, *J* 8.4, 1H); δ_{C} (50 MHz, CDCl₃) 24.9 (CH₃), 28.2 (CH₃), 83.6 (C), 107.5 (CH), 114.1 (CH), 114.4 (CH), 125.8 (CH), 128.2 (CH), 130.1 (C), 130.5 (CH), 137.2 (C); *m/z* (%) 344[(*M*+1), 100]; HRMS (EI) calcd for C₁₉H₂₆BNO₃: 343.195489; found: 343.196165.

Preparations of 1-*tert*-Butoxycarbonyl-5-(2-methylphenyl)indole **3k**

From 1-Boc-5-bromoindole 1d and 2-methylphenylboronic acid 2c: Aqueous Na₂CO₃ (2.7 mL of a 1M solution, 2.7 mmol) and Pd(Ph₃P)₄ (0.06 g, 0.06 mmol) in 1:1 toluene-EtOH (10 mL) were added to a solution of 1-Boc-5-bromoindole (0.33 g, 1.10 mmol) and 2-methylphenylboronic acid (0.33 g, 2.20 mmol) in 1:1 toluene-EtOH (4 mL) and the resulting mixture was heated at reflux under argon for 1 h. Pd(Ph₃P)₄ (0.06 g, 0.06 mmol) in 1:1 toluene-EtOH (4 mL) was added and heating at reflux under argon continued for a further 4 h. After cooling, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid (0.34 g, 99%).

From 1-Boc-indol-5-ylboronic acid 1k and 2-bromotoluene 2g: KH (0.08 g, 2.0 mmol) was suspended in THF (4 mL) under argon at 0 °C. 1-Boc-5-bromoindole (0.60 g, 2.0 mmol) was added and the mixture stirred for 15 min. The resulting solution was cooled to –78 °C and *t*BuLi (2.5 mL of a 1.5 M solution in pentane, 3.8 mmol) was added over 1 min. The cooling bath was removed and the mixture stirred for 10 min. After re-cooling to –78 °C, B(OMe)₃ (0.46 mL, 4.0 mmol) was added and the mixture was allowed to warm to r.t. and stirred for 3h. H₂O was added and the mixture was extracted with EtOAc. The aqueous phase was acidified to pH 1 with 10% HCl and extracted with EtOAc. The combined organic extracts were dried and the solvent removed furnishing the crude indolylboronic acid as a light-brown oil.

The crude boronic acid (0.53 g, 2.0 mmol) in 1:1 toluene-EtOH (4 mL) was added to 2-bromotoluene (0.073 mL, 0.61 mmol), 1M aqueous Na₂CO₃ (1.7 mL of a 1M solution, 1.7 mmol) and Pd(Ph₃P)₄ (0.035 g, 0.03 mmol) in 1:1 toluene-EtOH (1.5 mL) and the mixture was heated at reflux under argon for 1h. Pd(Ph₃P)₄ (0.035 g, 0.03 mmol) in 1:1 toluene-EtOH (1.5 mL) was added and heating at reflux under argon continued for a further 4 h. After cooling, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid (0.09 g, 18%), m.p. 31-32 °C; δ_{H} (200 MHz, CDCl₃) 1.68 (s, 9H), 2.28 (s, 3H), 6.59 (d, *J* 3.6, 1H), 7.27 (m, 5H), 7.51 (d, *J* 1.4, 1H), 7.63 (d, *J* 3.5, 1H), 8.16 (d, *J* 8.8, 1H); δ_{C} (50 MHz, CDCl₃) 20.6 (CH₃), 28.2 (CH₃), 84.2 (C), 107.3 (CH), 114.5 (CH), 121.3 (CH), 125.6 (CH), 126.3 (CH), 127.0 (CH), 127.1 (CH), 128.0 (C), 129.7 (CH), 130.1 (CH), 130.5 (C), 130.1 (C), 136.1 (C), 142.1 (C); *m/z* (%) 308[(*M*+1), 100], 208 (100); HRMS (EI) calcd for C₂₀H₂₁NO₂: 307.157229; found 307.157936.

Preparations of 1-*tert*-Butoxycarbonyl-5-(2-methoxyphenyl)indole **3I**

From 1-Boc-5-bromoindole 1d and 2-methoxyphenylboronic acid 2d: Aqueous Na₂CO₃ (2.9 mL of a 1M solution, 2.73 mmol) and Pd(Ph₃P)₄ (0.06 g, 0.05 mmol) in 1:1 toluene-EtOH (10 mL) were added to a solution of 1-Boc-5-bromoindole (0.33 g, 1.10 mmol) and 2-methoxyphenylboronic acid (0.33 g, 2.20 mmol) in 1:1 toluene-EtOH (4 mL) and the resulting mixture was heated at reflux under argon for 1 h. Pd(Ph₃P)₄ (0.06 g, 0.05 mmol) in 1:1 toluene-EtOH (4 mL) was added and heating at reflux under argon continued for a further 4 h. After cooling, the solvent was removed and the resulting crude was purified

by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a clear oil (0.34 g, 94%).

*From 1-Boc-indol-5-ylboronic acid **1k** and 2-bromoanisole **2h**:* KH (0.07 g, 1.72 mmol) was suspended in THF (4 mL) under argon at 0 °C. 1-Boc-5-bromoindole (0.51 g, 1.72 mmol) was added and the mixture stirred for 15 min. The resulting solution was cooled to -78 °C and *t*-BuLi (2.3 mL of a 1.5 M solution in pentane, 3.5 mmol) was added over 1 min. The cooling bath was removed and the mixture stirred for 10 min. After re-cooling to -78 °C, B(OMe)₃ (0.40 mL, 3.40 mmol) was added and the mixture was allowed to warm to r.t. and stirred for 3h. H₂O was added and the mixture was extracted with EtOAc. The aqueous phase was acidified to pH 1 with 10% HCl and extracted with EtOAc. The combined organic extracts were dried and the solvent removed furnishing the crude indolylboronic acid as a light-brown oil.

The crude boronic acid (0.44 g, 1.70 mmol) in 1:1 toluene-EtOH (4 mL) was added to 2-bromoanisole (0.06 mL, 0.47 mmol), 1M aqueous Na₂CO₃ (1.2 mL of a 1M solution, 1.2 mmol) and Pd(Ph₃P)₄ (0.025 g, 0.02 mmol) in 1:1 toluene-EtOH (1.5 mL) and the mixture was heated at reflux under argon for 1h. Pd(Ph₃P)₄ (0.025 g, 0.02 mmol) in 1:1 toluene-EtOH (1.5 mL) was added and heating at reflux under argon continued for a further 5 h. After cooling, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a clear oil (0.05 g, 8%).

From 1-Boc-5-bromoindole **1d** and pinacol 2-methoxyphenylboronate **2j**: KOAc (0.23 g, 2.29 mmol), bis(pinacolato)diboron (0.22 g, 1.1 mmol), 2-bromoanisole (0.094 mL, 0.76 mmol) and PdCl₂(dppf) (0.04 g, 0.05 mmol) in 1,4-dioxane (4 mL) were heated at 80 °C under argon for 14 h. After cooling the solvent was removed leaving the crude boronate as a pale brown oil.

This boronate (0.071 g, 0.31 mmol), potassium phosphate (0.28 g, 1.26 mmol), PdCl₂(dppf) (0.008 g, 0.008 mmol) and 1-Boc-5-bromoindole (0.134 g, 0.38 mmol) in 1,4-dioxane (2 mL) were heated at 100 °C under argon for 1h. PdCl₂(dppf) (0.004 g, 0.004 mmol) and boronate (0.036 g, 0.15 mmol) were added and the mixture heated at 100 °C under argon for a further 1h. The addition of catalyst and boronate were repeated twice more at hourly intervals and the mixture was kept at 100 °C under argon for a further 24h. After cooling and filtration, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid (0.010 g, 8%).

From pinacol 1-Boc-indol-5-ylboronate **1o** and 2-bromoanisole **2h**: KOAc (0.23 g, 2.29 mmol), bis(pinacolato)diboron (0.22 g, 1.1 mmol), 1-Boc-5-bromoindole (0.23 g, 0.76 mmol) and PdCl₂(dppf) (0.04 g, 0.05 mmol) in 1,4-dioxane (4 mL) were heated at 100 °C under argon for 48 h. After cooling the solvent was removed leaving the crude boronate as a pale brown oil.

This boronate (0.12 g, 0.31 mmol), potassium phosphate (0.28 g, 1.26 mmol), PdCl₂(dppf) (0.008 g, 0.008 mmol) and 2-bromoanisole (0.05 mL, 0.38 mmol) in 1,4-dioxane (2 mL) were heated at 100 °C under argon for 1h. PdCl₂(dppf) (0.004 g, 0.004

mmol) and boronate (0.06 g, 0.15 mmol) were added and the mixture heated at 100 °C under argon for a further 1h. The addition of catalyst and boronate were repeated twice more at hourly intervals and the mixture was kept at 100 °C under argon for a further 70h. After cooling and filtration, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a clear oil (0.02, 16%); δ_{H} (200 MHz, CDCl_3) 1.72 (s, 9H), 3.84 (s, 3H), 6.64 (d, J 3.8, 1H), 7.06 (m, 2H), 7.37 (m, 2H), 7.54 (dd, J_1 8.4 J_2 1.4, 1H), 7.66 (d, J 3.8, 1H), 7.75 (d, J 1, 1H), 8.20 (d, J 8.8, 1H); δ_{C} (50 MHz, CDCl_3) 28.2 (CH_3), 55.5 (CH_3), 83.5 (C), 107.5 (CH), 111.5 (CH), 114.5 (CH), 120.7 (CH), 121.7 (CH), 126.0 (CH), 128.2 (CH), 130.4 (C), 131.0 (CH), 133.0 (C), 134.1 (C), 149.7 (C), 156.4 (C); m/z (%) 341[($M+\text{NH}_4$)⁺, 100]; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{21}\text{NO}_3$: 323.152144; found 323.151819.

In addition, pinacol indol-5-ylboronate **1m** and pinacol 1-Boc-indol-5-ylboronate **1o** were also isolated.

Preparations of 1-*tert*-Butoxycarbonyl-6-(4-methoxyphenyl)indole **3m**

From 1-Boc-6-bromoindole 1e and 4-methoxyphenylboronic acid 2b: Aqueous Na_2CO_3 (1.6 mL of a 1M solution, 1.6 mmol) and $\text{Pd}(\text{Ph}_3\text{P})_4$ (0.04 g, 0.03 mmol) in 1:1 toluene-EtOH (10 mL) were added to a solution of 1-Boc-6-bromoindole (0.19 g, 0.64 mmol) and 4-methoxyphenylboronic acid (0.19 g, 1.28 mmol) in 1:1 toluene-EtOH (4 mL) and the resulting mixture was heated at reflux under argon for 1 h. $\text{Pd}(\text{Ph}_3\text{P})_4$ (0.04 g, 0.03 mmol) in 1:1 toluene-EtOH (4 mL) was added and heating at reflux under argon continued for a further 4 h. After cooling, the solvent was removed and the resulting crude was purified

by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a clear oil (0.14 g, 67%).

*From 1-Boc-6-bromoindole **1e** and pinacol 4-methoxyphenylboronate **2i**:* KOAc (0.23 g, 2.29 mmol), bis(pinacolato)diboron (0.22 g, 1.1 mmol), 4-bromoanisole (0.097 mL, 0.76 mmol) and PdCl₂(dppf) (0.04 g, 0.05 mmol) in 1,4-dioxane (4 mL) were heated at 80 °C under argon for 14 h. After cooling the solvent was removed leaving the crude boronate as a pale brown oil.

This boronate (0.071 g, 0.31 mmol), potassium phosphate (0.28 g, 1.26 mmol), PdCl₂(dppf) (0.008 g, 0.008 mmol) and 1-Boc-6-bromoindole (0.11 g, 0.38 mmol) in 1,4-dioxane (2 mL) were heated at 100 °C under argon for 1h. PdCl₂(dppf) (0.004 g, 0.004 mmol) and boronate (0.036 g, 0.15 mmol) were added and the mixture heated at 100 °C under argon for a further 1h. The addition of catalyst and boronate were repeated twice more at hourly intervals and the mixture was then kept at 100 °C under argon for a further 48h. After cooling and filtration, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid (0.024 g, 19%).

*From pinacol 1-Boc-6-indolylboronate **1p** and 4-bromoanisole **2f**:* KOAc (0.23 g, 2.29 mmol), bis(pinacolato)diboron (0.22 g, 1.1 mmol), 1-Boc-5-bromoindole (0.23 g, 0.76 mmol) and PdCl₂(dppf) (0.04 g, 0.05 mmol) in 1,4-dioxane (4 mL) were heated at 100 °C under argon for 48 h. After cooling the solvent was removed leaving the crude boronate as a pale brown oil.

This boronate (0.12 g, 0.31 mmol), potassium phosphate (0.28 g, 1.26 mmol), PdCl₂(dppf) (0.008 g, 0.008 mmol) and 4-bromoanisole (0.05 g, 0.38 mmol) in 1, 4-dioxane (2 mL) were heated at 100 °C under argon for 1h. PdCl₂(dppf) (0.004 g, 0.004 mmol) and boronate (0.06 g, 0.15 mmol) were added and the mixture heated at 100 °C under argon for a further 1h. The addition of catalyst and boronate were repeated twice more at hourly intervals and the mixture was then kept at 100 °C under argon for a further 70h. After cooling and filtration, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a clear oil (0.048, 39%); δ_{H} (200 MHz, CDCl₃) 1.70 (s, 9H), 3.86 (s, 3H), 6.59 (d, *J* 3.8, 1H), 7.00 (d, *J* 8.8 2H), 7.46 (dd, *J*₁ 8.4, *J*₂ 1.8, 1H), 7.61 (m, 4H), 8.42 (s, 1H); δ_{C} (50 MHz, CDCl₃) 28.2 (CH₃), 55.3 (CH₃), 83.6 (C), 107.1 (CH), 113.4 (CH), 114.1 (CH), 120.9 (CH), 121.8 (CH), 126.1 (CH), 128.3 (CH), 129.2 (C), 134.4 (C), 135.8 (C), 137.2 (C), 158.8 (C); *m/z* (%) 324[(*M*+H)⁺, 100]; HRMS (EI) calcd for C₂₀H₂₁NO₃: 323.152144; found 323.152380.

In addition, pinacol indol-6-ylboronate **1n** was also isolated as a white solid (0.02 g, 11%), m.p. 167-172 °C; δ_{H} (200 MHz, CDCl₃) 1.37 (s, 12H), 6.55 (m, 1H), 7.25 (m, 1H), 7.56 (d, *J* 8, 1H), 7.66 (d, *J* 8, 1H), 7.91 (s, 1H), 8.24 (bs, 1H); δ_{C} (50 MHz, CDCl₃) 24.9 (CH₃), 83.5 (C), 102.7 (CH), 118.0 (CH), 120.0 (CH), 125.5 (CH), 130.3 (C), 135.4 (C); *m/z* (%) 244[(*M*+1), 100]; HRMS (EI) calcd for C₁₄H₁₈BNO₂: 243.143059; found: 243.143871.

Preparations of 1-*tert*-Butoxycarbonyl-6-(2-methoxyphenyl)indole **3n**

From 1-Boc-6-bromoindole 1e and 2-methoxyphenylboronic acid 2d: Aqueous Na₂CO₃ (1.3 mL of a 1M solution, 1.3 mmol) and Pd(Ph₃P)₄ (0.03 g, 0.02 mmol) in 1:1 toluene-EtOH (10 mL) were added to a solution of 1-Boc-6-bromoindole (0.16 g, 0.53 mmol) and 2-methoxyphenylboronic acid (0.16 g, 1.06 mmol) in 1:1 toluene-EtOH (4 mL) and the resulting mixture was heated at reflux under argon for 1 h. Pd(Ph₃P)₄ (0.03 g, 0.02 mmol) in 1:1 toluene-EtOH (4 mL) was added and the reaction heated at reflux under argon for a further 4 h. After cooling, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a clear oil (0.09 g, 84%).

From 1-Boc-6-bromoindole 1e and pinacol 2-methoxyphenylboronate 2j: KOAc (0.23 g, 2.29 mmol), bis(pinacolato)diboron (0.22 g, 1.1 mmol), 2-bromoanisole (0.094 mL, 0.76 mmol) and PdCl₂(dppf) (0.04 g, 0.05 mmol) in 1,4-dioxane (4 mL) were heated at 100 °C under argon for 48 h. After cooling the solvent was removed leaving the crude boronate as a pale brown oil.

This boronate (0.071 g, 0.31 mmol), potassium phosphate (0.28 g, 1.26 mmol), PdCl₂(dppf) (0.008 g, 0.008 mmol) and 1-Boc-6-bromoindole (0.114 g, 0.38 mmol) in 1,4-dioxane (2 mL) were heated at 100 °C under argon for 1h. PdCl₂(dppf) (0.004 g, 0.004 mmol) and boronate (0.036 g, 0.15 mmol) were added and the mixture heated at 100 °C under argon for a further 1h. The addition of catalyst and boronate were repeated twice more at hourly intervals and the mixture was then kept at 100 °C under argon for a further

70h. After cooling and filtration, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid (0.42 g, 34%).

*From pinacol 1-Boc-6-indolylboronate **1p** and 2-bromoanisole **2h**:* KOAc (0.23 g, 2.29 mmol), bis(pinacolato)diboron (0.22 g, 1.1 mmol), 1-Boc-5-bromoindole (0.267 g, 0.76 mmol) and PdCl₂(dppf) (0.04 g, 0.05 mmol) in 1,4-dioxane (4 mL) were heated at 100 °C under argon for 48 h. After cooling the solvent was removed leaving the crude boronate as a pale brown oil.

This boronate (0.12 g, 0.31 mmol), potassium phosphate (0.28 g, 1.26 mmol), PdCl₂(dppf) (0.008 g, 0.008 mmol) and 2-bromoanisole (0.05 g, 0.38 mmol) in 1, 4-dioxane (2 mL) were heated at 100 °C under argon for 1h. PdCl₂(dppf) (0.004 g, 0.004 mmol) and boronate (0.06 g, 0.15 mmol) were added and the mixture heated at 100 °C under argon for a further 1h. The addition of catalyst and boronate were repeated twice more at hourly intervals and the mixture was then kept at 100 °C under argon for a further 70h. After cooling and filtration, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a clear oil (0.037, 30%); δ_{H} (200 MHz, CDCl₃) 1.69 (s, 9H), 3.85 (s, 3H), 6.62 (d, *J* 3.4, 1H), 7.05 (m, 2H), 7.40 (m, 3H), 7.62 (m, 2H), 8.39 (s, 1H); δ_{C} (50 MHz, CDCl₃) 28.2 (CH₃), 55.6 (CH₃), 83.5 (CH), 107.1 (CH), 111.1 (CH), 116.2 (CH), 120.1 (CH), 120.7 (CH), 124.5 (CH), 126.1 (CH), 128.2 (CH), 128.5 (C), 129.4 (C), 131.2 (CH), 131.3 (C), 135.7 (C), 156.4 (C); *m/z* (%) 344[(*M*+NH₄)⁺, 34], 324[(*M*+H)⁺, 100]; HRMS (EI) calcd for C₂₀H₂₁NO₃; 323.152144; found 323.151976.

In addition, pinacol indol-6-ylboronate **1n** and pinacol Boc-indol-6-ylboronate **1p** were also isolated.

Preparations of 1-(*p*-Toluenesulfonyl)-5-(4-methylphenyl)indole **3o**

From 1-Tos-5-bromoindole 1f and 4-methylphenylboronic acid 2a: Aqueous Na₂CO₃ (1.5 mL of a 1M solution, 1.5 mmol) and Pd(Ph₃P)₄ (0.06 g, 0.06 mmol) in 1:1 toluene-EtOH (10 mL) were added to a solution of 1-Tos-5-bromoindole (0.36 g, 1.0 mmol) and 4-methylphenylboronic acid (0.28 g, 2.10 mmol) in 1:1 toluene-EtOH (4 mL) and the resulting mixture was heated at reflux under argon for 1 h. Pd(Ph₃P)₄ (0.06 g, 0.06 mmol) in 1:1 toluene-EtOH (4 mL) was added and heating at reflux under argon continued for a further 4 h. After cooling, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid (0.26 g, 70%), m.p. 144-145 °C; δ_H (200 MHz, CDCl₃) 2.34 (s, 3H), 2.39 (s, 3H), 6.68 (dd, *J*₁ 3.7, *J*₂ 0.7, 1H), 7.23 (m, 4H), 7.48 (d, *J* 8, 2H), 7.55 (d, *J* 1.8, 1H), 7.57 (d, *J* 3.7, 1H), 7.70 (d, *J* 1.1, 1H), 7.79 (d, *J* 8, 2H), 8.04 (d, *J* 8.8, 1H); δ_C (50 MHz, CDCl₃) 21.1 (CH₃), 22.2 (CH₃), 109.2 (CH), 113.6 (CH), 119.5 (CH), 124.0 (CH), 126.8 (CH), 127.1 (CH), 129.4 (CH), 129.8 (CH), 131.2 (C), 134.2 (C), 135.6 (C), 136.1 (C), 138.1 (C), 145.2 (C); *m/z* (%) 379[(*M*+NH₄)⁺, 66], 362[(*M*+1), 100]; HRMS (EI) calcd for C₂₂H₁₉NO₂S: 361.113651; found 361.112506.

Preparations of 1-(*p*-Toluenesulfonyl)-5-(2-methylphenyl)indole **3q**

From 1-Tos-5-bromoindole 1f and 2-methylphenylboronic acid 2c: Aqueous Na₂CO₃ (1.5 mL of a 1M solution, 1.5 mmol) and Pd(Ph₃P)₄ (0.06 g, 0.06 mmol) in 1:1 toluene-EtOH (10 mL) were added to a solution of 1-Tos-5-bromoindole (0.35 g, 1.0 mmol) and 2-methylphenylboronic acid (0.28 g, 2.10 mmol) in 1:1 toluene-EtOH (4 mL) and the resulting mixture was heated at reflux under argon for 1 h. Pd(Ph₃P)₄ (0.06 g, 0.06 mmol) in 1:1 toluene-EtOH (4 mL) was added and the reaction heated at reflux under argon for a further 4 h. After cooling, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a clear oil (0.27 g, 74%); δ_{H} (200 MHz, CDCl₃) 2.25 (s, 3H), 2.36 (s, 3H), 6.62 (d, *J* 1.8, 1H), 7.27 (m, 7H), 7.4 (s, 1H), 7.63 (d, *J* 1.8, 1H), 7.82 (d, *J* 8, 2H), 8.11 (d, *J* 8.3, 1H); δ_{C} (50 MHz, CDCl₃) 20.6 (CH₃), 21.6 (CH₃), 109.0 (CH), 112.9 (CH), 121.7 (CH), 125.6 (CH), 126.0 (CH), 126.6 (CH), 126.8 (CH), 127.1 (CH), 129.9 (CH), 130.0 (CH), 130.2 (C), 134.0 (C), 135.1 (C), 137.1 (C), 142.2 (C), 145.4 (C); *m/z* (%) 379[(*M*+NH₄)⁺, 74], 362[(*M*+1), 100]; HRMS (EI) calcd for C₂₂H₁₉NO₂S: 361.113651; found 361.114314.

Preparations of 1-(*p*-Toluenesulfonyl)-5-(2-methoxyphenyl)indole **3r**

From 1-Tos-5-bromoindole 1f and 2-methoxyphenylboronic acid 2d: Aqueous Na₂CO₃ (2.2 mL of a 1M solution, 2.20 mmol) and Pd(Ph₃P)₄ (0.05 g, 0.04 mmol) in 1:1 toluene-EtOH (10 mL) were added to a solution of 1-Tos-5-bromoindole (0.31 g, 0.90 mmol) and 2-methoxyphenylboronic acid (0.20 g, 1.30 mmol) in 1:1 toluene-EtOH (4 mL) and the

resulting mixture was heated at reflux under argon for 1 h. Pd(Ph₃P)₄ (0.05 g, 0.04 mmol) in 1:1 toluene-EtOH (4 mL) was added and the reaction heated at reflux under argon for a further 4 h. After cooling, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid (0.32 g, 97%).

From 1-Tos-5-bromoindole 1f and pinacol 2-methoxyphenylboronate 2j: KOAc (0.23 g, 2.29 mmol), bis(pinacolato)diboron (0.22 g, 1.1 mmol), 4-bromoanisole (0.097 mL, 0.76 mmol) and PdCl₂(dppf) (0.04 g, 0.05 mmol) in 1,4-dioxane (4 mL) were heated at reflux under argon for 24 h. After cooling the solvent was removed leaving the crude boronate as a pale brown oil.

This boronate (0.071 g, 0.31 mmol), potassium phosphate (0.28 g, 1.26 mmol), PdCl₂(dppf) (0.008 g, 0.008 mmol) and 1-Tos-5-bromoindole (0.134 g, 0.38 mmol) in 1,4-dioxane (2 mL) were heated at 100 °C under argon for 1h. PdCl₂(dppf) (0.004 g, 0.004 mmol) and boronate (0.036 g, 0.15 mmol) were added and the mixture heated at 100 °C under argon for a further 1h. The addition of catalyst and boronate were repeated twice more at hourly intervals and the mixture was then kept at 100 °C under argon for a further 48h. After cooling and filtration, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid (0.07 g, 45%).

From pinacol 1-Tos-5-indolylboronate 1q and 2-bromoanisole 2h: KOAc (0.23 g, 2.29 mmol), bis(pinacolato)diboron (0.22 g, 1.1 mmol), 1-Tos-5-bromoindole (0.267 g, 0.76

mmol) and PdCl₂(dppf) (0.04 g, 0.05 mmol) in 1,4-dioxane (4 mL) were heated at 100 °C under argon for 48 h. After cooling the solvent was removed leaving the crude boronate as a pale brown oil.

This boronate (0.12 g, 0.31 mmol), potassium phosphate (0.28 g, 1.26 mmol), PdCl₂(dppf) (0.008 g, 0.008 mmol) and 2-bromoanisole (0.05 mL, 0.38 mmol) in 1, 4-dioxane (2 mL) were heated at 100 °C under argon for 1h. PdCl₂(dppf) (0.004 g, 0.004 mmol) and boronate (0.06 g, 0.15 mmol) were added and the mixture heated at 100 °C under argon for a further 1h. The addition of catalyst and boronate were repeated twice more at hourly intervals and the mixture was then kept at 100 °C under argon for a further 70h. After cooling and filtration, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid (0.10 g, 24%), m.p. 149-151 °C; δ_{H} (200 MHz, CDCl₃) 2.33 (s, 3H), 3.79 (s, 3H), 6.66 (dd, J_1 3.6, J_2 0.8, 1H), 7.00 (m, 2H), 7.26 (m, 4H), 7.48 (dd, J_1 8.4, J_2 1.4, 1H), 7.57 (d, J 3.6, 1H), 7.67 (m, 1H), 7.80 (d, J 8.4, 1H), 8.00 (d, J 8.8, 1H); δ_{C} (50 MHz, CDCl₃) 21.6 (CH₃), 55.5 (CH₃), 109.1 (CH), 111.1 (CH), 112.9 (CH), 120.8 (CH), 122.1 (CH), 126.4 (CH), 126.8 (CH), 128.4 (CH), 129.8 (CH), 130.5 (C), 130.6 (C), 131.1 (CH), 133.6 (C), 133.7 (C), 135.3 (C), 144 .8 (C), 156 .3 (C); m/z (%) 378[(M +1)⁺, 100]; HRMS (EI) calcd for C₂₂H₁₉NO₃S: 377.108565; found 377.109200.

Preparations of 1-(*p*-Toluenesulfonyl)-6-(4-methoxyphenyl)indole **3s**

From 1-Tos-6-bromoindole 1g and 4-methoxyphenylboronic acid 2b: Aqueous Na₂CO₃ (0.9 mL of a 1M solution, 0.9 mmol) and Pd(Ph₃P)₄ (0.02 g, 0.02 mmol) in 1:1 toluene-EtOH (10 mL) were added to a solution of 1-Tos-6-bromoindole (0.13 g, 0.40 mmol) and 4-methoxyphenylboronic acid (0.12 g, 0.80 mmol) in 1:1 toluene-EtOH (4 mL) and the resulting mixture was heated at reflux under argon for 1 h. Pd(Ph₃P)₄ (0.02 g, 0.02 mmol) in 1:1 toluene-EtOH (4 mL) was added and heating at reflux under argon continued for a further 4 h. After cooling, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid (0.12 g, 80%).

From 1-Tos-6-bromoindole 1g and pinacol 4-methoxyphenylboronate 2i: KOAc (0.23 g, 2.29 mmol), bis(pinacolato)diboron (0.22 g, 1.1 mmol), 4-bromoanisole (0.097 mL, 0.76 mmol) and PdCl₂(dppf) (0.04 g, 0.05 mmol) in 1,4-dioxane (4 mL) were heated at reflux under argon for 48 h. After cooling the solvent was removed leaving the crude boronate as a pale brown oil.

This boronate (0.071 g, 0.31 mmol), potassium phosphate (0.28 g, 1.26 mmol), PdCl₂(dppf) (0.008 g, 0.008 mmol) and 1-Tos-6-bromoindole (0.134 g, 0.38 mmol) in 1,4-dioxane (2 mL) were heated at 100 °C under argon for 1h. PdCl₂(dppf) (0.004 g, 0.004 mmol) and boronate (0.036 g, 0.15 mmol) were added and the mixture heated at 100 °C for a further 1h. The addition of catalyst and boronate were repeated twice more at hourly intervals and the mixture was then kept at 100 °C under argon for a further 70h. After

cooling and filtration, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid (0.08 g, 55%).

From pinacol 1-Tos-6-indolylboronate 1r and 4-bromoanisole 2f: KOAc (0.23 g, 2.29 mmol), bis(pinacolato)diboron (0.22 g, 1.1 mmol), 1-Tos-5-bromoindole (0.27 g, 0.76 mmol) and PdCl₂(dppf) (0.04 g, 0.05 mmol) in 1,4-dioxane (4 mL) were heated at 100 °C under argon for 48 h. After cooling the solvent was removed leaving the crude boronate as a pale brown oil.

This boronate (0.12 g, 0.31 mmol), potassium phosphate (0.28 g, 1.26 mmol), PdCl₂(dppf) (0.008 g, 0.008 mmol) and 4-bromoanisole (0.05 g, 0.38 mmol) in 1, 4-dioxane (2 mL) were heated at 100 °C under argon for 1h. PdCl₂(dppf) (0.004 g, 0.004 mmol) and boronate (0.06 g, 0.15 mmol) were added and the mixture heated at 100 °C for a further 1h. The addition of catalyst and boronate were repeated twice more at hourly intervals and the mixture was then kept at 100 °C under argon for a further 70h. After cooling and filtration, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid (0.09 g, 62%), m.p. 125-126 °C; δ_{H} (200 MHz, CDCl₃) 2.29 (s, 3H), 3.85 (s, 3H), 6.64 (d, *J* 3.6, 1H), 7.00 (d, *J* 8.8 2H), 7.18 (d, *J* 7.6, 2H), 7.41 (dd, *J*₁ 8.4 *J*₂ 1.6, 1H), 7.55 (m, 4H), 7.76 (d, *J* 8.4, 2H), 8.17 (s, 1H); δ_{C} (50 MHz, CDCl₃) 21.6 (CH₃), 55.4 (CH₃), 108.9 (CH), 111.4 (CH), 114.2 (CH), 121.4 (CH), 122.6 (CH), 126.5 (CH), 126.7 (CH), 128.4 (CH), 129.4 (C), 129.9 (CH), 133.8 (C), 135.2 (C), 135.4 (C), 137.7 (C), 144.9 (C), 159.0 (C);

m/z (%) 378[($M+H$)⁺, 100]; HRMS (EI) calcd for C₂₂H₁₉NO₃S: 377.108565; found 377.108239.

Preparations of 1-(*p*-Toluenesulfonyl)-6-(2-methoxyphenyl)indole **3t**

From 1-Tos-6-bromoindole 1g and 2-methoxyphenylboronic acid 2d: Aqueous Na₂CO₃ (0.9 mL of a 1M solution, 0.90 mmol) and Pd(Ph₃P)₄ (0.02 g, 0.02 mmol) in 1:1 toluene-EtOH (10 mL) were added to a solution of 1-Tos-6-bromoindole (0.13 g, 0.40 mmol) and 2-methoxyphenylboronic acid (0.12 g, 0.80 mmol) in 1:1 toluene-EtOH (4 mL) and the resulting mixture was heated at reflux under argon for 1 h. Pd(Ph₃P)₄ (0.02 g, 0.02 mmol) in 1:1 toluene-EtOH (4 mL) was added and heating at reflux under argon continued for a further 4 h. After cooling, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid (0.13 g, 89%).

From 1-Tos-6-bromoindole 1g and pinacol 2-methoxyphenylboronate 2j: KOAc (0.23 g, 2.29 mmol), bis(pinacolato)diboron (0.22 g, 1.1 mmol), 2-bromoanisole (0.097 mL, 0.76 mmol) and PdCl₂(dppf) (0.04 g, 0.05 mmol) in 1,4-dioxane (4 mL) were heated at reflux under argon for 14 h. After cooling the solvent was removed leaving the crude boronate as a pale brown oil.

This boronate (0.071 g, 0.31 mmol), potassium phosphate (0.28 g, 1.26 mmol), PdCl₂(dppf) (0.008 g, 0.008 mmol) and 1-Tos-6-bromoindole (0.134 g, 0.38 mmol) in 1,4-dioxane (2 mL) were heated at 100 °C under argon for 1h. PdCl₂(dppf) (0.004 g, 0.004

mmol) and boronate (0.036 g, 0.15 mmol) were added and the mixture heated at 100 °C under argon for a further 1h. The addition of catalyst and boronate were repeated twice more at hourly intervals and the mixture was then kept at 100 °C under argon for a further 24h. After cooling and filtration, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid (0.06 g, 40%).

*From pinacol 1-Tos-6-indolylboronate **1r** and 2-bromoanisole **2h**:* KOAc (0.23 g, 2.29 mmol), bis(pinacolato)diboron (0.22 g, 1.1 mmol), 1-Tos-6-bromoindole (0.267 g, 0.76 mmol) and PdCl₂(dppf) (0.04 g, 0.05 mmol) in 1,4-dioxane (4 mL) were heated at 100 °C under argon for 48 h. After cooling the solvent was removed leaving the crude boronate as a pale brown oil.

This boronate (0.12 g, 0.31 mmol), potassium phosphate (0.28 g, 1.26 mmol), PdCl₂(dppf) (0.008 g, 0.008 mmol) and 2-bromoanisole (0.05 mL, 0.38 mmol) in 1, 4-dioxane (2 mL) were heated at 100 °C under argon for 1h. PdCl₂(dppf) (0.004 g, 0.004 mmol) and boronate (0.06 g, 0.15 mmol) were added and the mixture heated at 100 °C under argon for a further 1h. The addition of catalyst and boronate were repeated twice more at hourly intervals and the mixture was then kept at 100 °C under argon for a further 70h. After cooling and filtration, the solvent was removed and the resulting crude was purified by chromatography [silica, hexanes-EtOAc, (9:1)] giving the product as a white solid (0.06 g, 42%), m.p. 149-151 °C; δ_{H} (200 MHz, CDCl₃) 2.31 (s, 3H), 3.82 (s, 3H), 6.64 (d, *J* 3.8, 1H), 6.99 (d, *J* 8, 1H), 7.06 (d, *J* 7.4, 1H), 7.14 (d, *J* 8, 2H), 7.38 (m, 3H), 7.55 (m, 2H), 7.78 (d, *J* 8.6, 2H), 8.21 (s, 1H); δ_{C} (50 MHz, CDCl₃) 21.5 (CH₃), 55.5

(CH₃), 108.8 (CH), 111.2 (CH), 114.5 (CH), 120.5 (CH), 120.8 (CH), 125.1 (CH), 126.4 (CH), 126.8 (CH), 128.5 (CH), 129.5 (C), 129.7 (CH), 130.6 (C), 131.1 (CH), 134.7 (C), 134.9 (C), 135.2 (C), 144.7 (C), 156.3 (C); *m/z* (%) 378[(*M*+H)⁺, 100]; HRMS (EI) calcd for C₂₂H₁₉NO₃S: 377.108565; found 377.108908.

References for Experimental

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