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Supporting Information

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Preparation and Selective Reactions of Mixed Bimetallic Aromatic and Heteroaromatic Boron-Magnesium Reagents

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General All reactions were carried out under an argon atmosphere in dried glassware. All starting materials were purchased from commercial sources and used without further purification. THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. Yields refer to isolated yields of compounds estimated to be > 95 % pure as determined by ^{1}H-NMR and capillary GC.

Preparation of the reagent *i*PrMgCl · LiCl:

Magnesium turnings (2.67 g, 110 mmol) were placed in an Ar-flushed flask and THF (50 mL) was added. A solution of *i*PrCl (7.85 g, 100 mmol) in THF (50 mL) was slowly added at room temperature. The reaction starts within a few minutes. After addition, the reaction mixture was stirred for 12 h at room temperature. The grey solution of *i*PrMgCl was cannulated to another flask, containing anhydrous LiCl (4.24 g, 100 mmol), which was stirred under vacuum for 3 h at 120 °C. A yield of ca. 95 - 98 % of *i*PrMgCl · LiCl is obtained and titrated prior to use by the method of Paquette.[1]

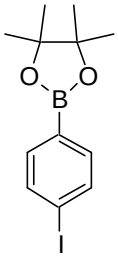
Typical procedure for the formation of boronic esters of type 4 from the corresponding diiodines (TP 1)

A dry and argon-flushed 100 mL round–bottom flask, equipped with a magnetic stirring bar and a septum, was charged with the corresponding diiodine (6.60 g, 20 mmol) and dry THF (40 mL) was added. The solution was cooled to -20 °C (in the case of **4a**, **4b**) or -78 °C (in the case of **4c**) and *i*PrMgCl·LiCl (25.0 mL, 20 mmol, 0.80 M in THF) was added dropwise over 15 min. The reaction mixture was stirred at the same temperature until completion of the I/Mg-exchange was detected by GC-analysis.[2] 2-Methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**10**) (3.16 g, 20 mmol) was added and the reaction mixture was allowed to warm to room temperature and kept stirring until full conversion to the corresponding boronic ester of type **4** was detected. The reaction mixture was quenched with a small amount of sat. aq. NH_4Cl solution, extracted four times with Et_2O (4 × 20 mL) and dried over Na_2SO_4. After filtration, the solvent was evaporated *in vacuo* and the product was purified by flash chromatography (short SiO_2-column) or recrystallization.

Typical procedure for the formation of functionalized aryl-boronicesters of type 6 *via* an I/Mg-exchange reaction (TP 2)

A dry and argon-flushed 25 mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with the corresponding boronic ester of type **4a-c** (396 mg, 1.2 mmol) and dry THF (2 mL) was added. The solution was cooled to -78 °C and *i*PrMgCl·LiCl (1.20 mL, 1.2 mmol, 1.00 M in THF) was added dropwise over a period of 15 min. The reaction mixture was stirred at the same temperature until completion of the I/Mg-exchange was detected by GC-analysis.[2] Depending on the electrophile CuCN·2LiCl (1.2 mL, 1.2 mmol, 1.0 M in THF) was added and the reaction mixture was kept stirring at -78 °C for 0.5 h. Then the corresponding electrophile was added (1.0 mmol) and the resulting mixture was allowed to warm to room temperature and kept stirring until full conversion to the corresponding functionalized boronic ester was detected by GC-analysis. The reaction mixture was quenched with a small amount of sat. aq. NH_4Cl solution, extracted four times with Et_2O (4 × 10 mL) and dried over Na_2SO_4. After filtration, the solvent was evaporated *in vacuo* and the product was purified by flash chromatography (short SiO_2-column) or recrystallization.

Synthesis of 2-(4-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4a):

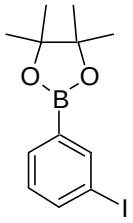


Prepared according to **TP 1** from 1,4-diiodobenzene (5,7 g, 17 mmol), *i*PrMgCl · LiCl (21.5 mL, 17 mmol, 0.79 M in THF) and 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **10** (2.7 g, 17 mmol). The I/Mg-exchange was complete at –20 °C after 1 h. Recrystallization from Et_2O yielded the boronic ester **4a** as a colourless solid (5.2 g, 91 %).

mp.: 93.9-98.4 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 7.74-7.73 (m, 1H), 7.72-7.70 (m, 1H), 7.53-7.52 (m, 1H), 7.50-7.49 (m, 1H), 1.34 (s, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 136.9, 136.3, 98.8, 84.0, 24.8. **MS** (70 eV, EI): m/z (%): 330 (92) [M^+], 315 (100), 244 (12), 230 (83), 117 (15), 104 (42), 94 (11), 85 (27), 77 (21), 57 (27), 41 (55). **IR** (KBr): ?/cm^{-1} = 3436 (s), 2976 (m), 1587 (s), 1388 (s), 1360 (vs), 1326 (m), 1143 (s), 1089 (s), 1007 (m), 858 (m), 820 (m), 650 (m). **HRMS** for **$C_{12}H_{16}BIO_2$** (330.0288): found 330.0259. **$C_{12}H_{16}BIO_2$**: calc.: C: 43.68; H: 4.89; I: 38.46; found: C: 43.90; H: 4.85; I: 37.69.

Spectral data match those reported in the literature.[3]

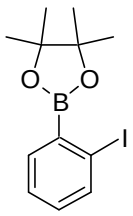
Synthesis of 2-(3-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4b):[4]



Prepared according to **TP 1** from 1,3-diiodobenzene (5.0 g, 15 mmol), *i*PrMgCl · LiCl (19.0 mL, 15 mmol, 0.79 M in THF) and 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **10** (2.4 g, 15 mmol). The I/Mg-exchange was complete at –20 °C after 1 h. Recrystallization from Et_2O yielded the boronic ester **4b** as a colourless solid (4.4 g, 88 %).

mp.: 71.1-71.9 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 8.19-8.18 (m, 1H), 7.79-7.75 (m, 2H), 7.09 (dd, ^3J(H,H) = 8 Hz, ^3J(H,H) = 8 Hz, 1H), 1.33 (s, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 143.2, 139.8, 133.5, 129.4, 94.4, 83.8, 24.7. **MS** (70 eV, EI): m/z (%): 330 (90) [M^+], 315 (59), 244 (100), 231 (50), 104 (15), 85 (12). **IR** (KBr): ?/cm^{-1} = 3436 (m), 2977 (s), 2932 (m), 1590 (m), 1550 (m), 1480 (m), 1403 (vs), 1351 (vs), 1324 (s), 1272 (m), 1142 (s), 1056 (m), 963 (m), 859 (s), 791 (s), 702 (s), 688 (s). **HRMS** for **$C_{12}H_{16}BIO_2$** (330.0288): found 330.0288.

Synthesis of 2-(2-iodophenyl)4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4c):

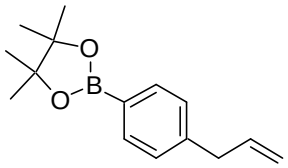


Prepared according to **TP 1** from 1,2-diiodobenzene (13.6 g, 41 mmol), *i*PrMgCl · LiCl (51.3 mL, 41 mmol, 0.80 M in THF) and 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **10** (6.5 g, 41 mmol). The I/Mg-exchange was complete at –78 °C after 3 h. Purification by flash chromatography (*n*-pentane : ether) yielded the boronic ester **4c** (11.6 g, 86 %) as a colourless oil.

^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): d = 7.83 (dd, ^3J(H,H) = 7 Hz, ^4J(H,H) = 1 Hz, 1H), 7.52 (dd, ^3J(H,H) = 7 Hz, ^4J(H,H) = 2 Hz, 1H), 7.31 (ddd, ^3J(H,H) = 7 Hz, ^3J(H,H) = 7 Hz, ^4J(H,H) = 1 Hz, 1H), 7.04 (ddd, ^3J(H,H) = 8 Hz, ^3J(H,H) = 8 Hz, ^4J(H,H) = 2 Hz, 1H), 1.38 (s, 12H). **^{13}C-NMR** (100 MHz, $CDCl_3$, 25 °C): d = 139.3, 136.1, 131.7, 126.8, 100.9, 84.4, 24.8. **MS** (70 eV, EI): m/z (%): 330 (100) [M^+], 315 (29), 230 (64), 203 (63), 161 (60), 117

(21), 103 (18), 85 (14). **IR** (film): ?/cm^{-1} = 3436 (w), 2978 (m), 2930 (w), 1586 (m), 1554 (w), 1472 (m), 1421 (m), 1381 (s), 1353 (vs), 1319 (s), 1264 (w), 1214 (w), 1144 (s), 1114 (m), 1097 (m), 1036 (m), 1011 (m), 962 (w), 857 (m), 755 (m), 726 (m). **HRMS** for **$C_{12}H_{16}BIO_2$** (330.0288): found 330.0292.

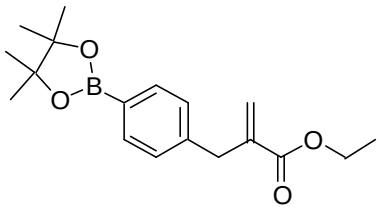
Synthesis of 2-(4-allylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6a):



Prepared according to **TP 2** from 2-(4-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **4a** (396 mg, 1.2 mmol), *i*PrMgCl · LiCl (1.20 mL, 1.2 mmol, 1.00 M in THF), CuCN · 2LiCl (1.2 mL, 1.2 mmol, 1.00 M in THF) and allyl bromide (121 mg, 1.0 mmol). The I/Mg-exchange was complete after 2 h. Purification by flash chromatography (*n*-pentane : ether) yielded the boronic ester **6a** (188 mg, 77 %) as a colourless oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.77-7.75 (m, 2H), 7.23-7.12 (m, 2H), 6.04-5.90 (m, 1 H), 5.12-5.06 (m, 2H), 3.41 (d, ^3J(H,H) = 7 Hz, 2H), 1.35 (s, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 143.4, 137.1, 135.0, 128.0, 115.9, 83.6, 40.4, 24.8. **MS** (70 eV, EI): m/z (%): 244 (37) [M$^+$], 229 (35), 203 (10), 158 (46), 145 (100), 116 (25), 85 (12). **IR** (film): ?/cm^{-1} = 2979 (m), 2927 (m), 1612 (m), 1399 (s), 1361 (vs), 1322 (m), 1272 (m), 1145 (s), 1090 (s), 1022 (w), 963 (w), 915 (w), 860 (m), 821 (w), 662 (m). **HRMS** for **$C_{15}H_{21}BO_2$** (244.1635): found 244.1655.

Synthesis of ethyl 2-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl]acrylate (6b):

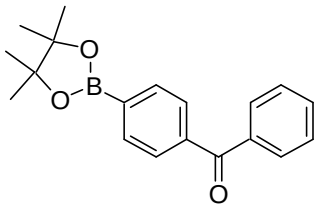


Prepared according to **TP 2** from 2-(4-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **4a** (396 mg, 1.2 mmol), *i*PrMgCl · LiCl (1.52 mL, 1.2 mmol, 0.79 M in THF), CuCN · 2LiCl (1.2 mL, 1.2 mmol, 1.0 M in THF) and ethyl 2-(brommethyl)acrylate (193 mg, 1.0 mmol). The I/Mg-exchange was complete after 2 h. Purification by flash chromatography (*n*-pentane : ether) yielded the boronic ester **6b** (211 mg, 67 %) as a yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.75-7.73 (m, 2H), 7.22-7.20 (m, 2H), 6.23 (s, 1H), 5.45 (m, 1H), 4.17 (q, ^3J(H,H) = 7 Hz, 2H), 3.64 (s, 2H), 1.34 (s, 12H), 1.26 (t, ^3J(H,H) = 7 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 166.8, 142.1, 140.1, 134.9, 128.5, 126.1, 83.7, 60.7, 38.2, 24.8, 14.1. **MS** (70 eV, EI): m/z (%): 316 (60) [M$^+$], 301 (30),

270 (67), 242 (41), 217 (38), 187 (48), 171 (47), 143 (100), 116 (32). **IR** (film): ?/cm^{-1} = 3429 (w), 2979 (m), 2932 (w), 1719 (s), 1612 (m), 1518 (w), 1399 (s), 1361 (vs), 1323 (m), 1273 (m), 1190 (m), 1145 (s), 1090 (s), 1023 (m), 963 (w), 860 (m), 820 (w), 667 (m). **HRMS** for **$C_{18}H_{25}BO_4$** (316.1846): found 316.1846.

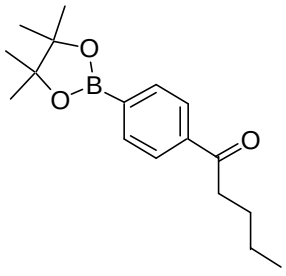
Synthesis of phenyl[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]methanone (6c):[5]



Prepared according to **TP 2** from 2-(4-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **4a** (380 mg, 1.2 mmol), *i*PrMgCl · LiCl (1.52 mL, 1.2 mmol, 0.79 M in THF), CuCN · 2LiCl (1.2 mL, 1.2 mmol, 1.0 M in THF) and benzoyl chloride (141 mg, 1.0 mmol). The I/Mg-exchange was complete after 2 h. Purification by flash chromatography (*n*-pentane : ether) yielded the boronic ester **6c** (223 mg, 72 %) as a colourless solid.

mp.: 114.8-117.9 °C. ^{1}**H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 7.94-7.91 (m, 2H), 7.81-7.44 (m, 7H), 1.37 (s, 12H). ^{13}**C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 196.9, 139.7, 136.9, 134.5, 130.0, 128.9, 128.2, 98.8, 84.2, 24.8. **MS** (70 eV, EI): m/z (%): 308 (54) [M^+], 293 (72), 265 (13), 231 (21), 222 (84), 209 (100), 105 (25), 77 (4). **IR** (KBr): ?/cm^{-1} = 3401 (w), 2978 (m), 2930 (w), 1659 (s), 1588 (m), 1507 (w), 1448 (w), 1398 (s), 1360 (vs), 1328 (s), 1313 (s), 1268 (s), 1214 (w), 1168 (w), 1143 (s), 1088 (s), 1007 (w), 927 (m), 857 (m), 703 (s). **HRMS** for **$C_{19}H_{21}BO_3$** (308.1584): found 308.1590.

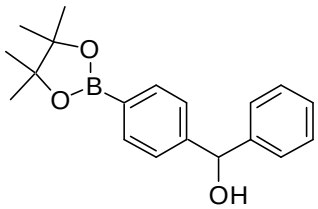
Synthesis of 1-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]pentan-1-one (6d):



Prepared according to **TP 2** from 2-(4-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **4a** (396 mg, 1.2 mmol), *i*PrMgCl · LiCl (1.20 mL, 1.2 mmol, 1.00 M in THF), CuCN · 2LiCl (1.2 mL, 1.2 mmol, 1.0 M in THF) and valeryl chloride (121 mg, 1.0 mmol). The I/Mg-exchange was complete after 2 h. Purification by flash chromatography (*n*-pentane : ether) yielded the boronic ester **6d** (209 mg, 73 %) as a yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.93-7.86 (m, 4H), 2.95 (t, ^3J(H,H) = 7 Hz, 2H), 1.70 (m, 2H), 1.45-1.30 (m, 14H), 0.93 (t, ^3J(H,H) = 7 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 200.8, 138.9, 134.8, 127.0, 84.1, 38.4, 26.4, 24.8, 22.4, 13.9. **MS** (70 eV, EI): m/z (%): 288 (0.5) [M^+], 246 (33), 231 (100), 205 (27), 189 (14), 160 (12), 131 (9), 103 (6), 83 (6), 41 (9). **IR** (film): ?/cm^{-1} = 3359 (w), 2978 (m), 2960 (m), 2933 (m), 2873 (w), 1688 (s), 1588 (w), 1508 (s), 1467 (w), 1398 (s), 1360 (vs), 1327 (s), 1272 (s), 1213 (m), 1167 (m), 1145 (s), 1089 (s), 1018 (w), 963 (m), 858 (m), 653 (m). **HRMS** for **$C_{17}H_{25}BO_3$** (288.1897): found 288.1895.

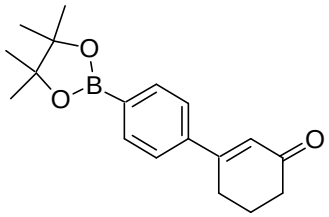
Synthesis of phenyl[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]methanol (6e):



Prepared according to **TP 2** from 2-(4-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **4a** (396 mg, 1.2 mmol), *i*PrMgCl · LiCl (1.20 mL, 1.2 mmol, 1.00 M in THF) and benzaldehyde (106 mg, 1.0 mmol). The I/Mg-exchange was complete after 2 h. Purification by flash chromatography (*n*-pentane : ether) yielded the boronic ester **6e** (257 mg, 83 %) as a yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.69-7.67 (m, 2H), 7.28-7.10 (m, 7H), 5.69 (s, 1H), 2.43 (s, 1H), 1.22 (s, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 146.8, 143.6, 134.9, 128.4, 127.5, 126.6, 125.7, 83.7, 76.0, 24.8. **MS** (70 eV, EI): m/z (%): 310 (13) [M^+], 293 (48), 231 (62), 209 (61), 183 (38), 166 (100), 118 (13), 105 (50), 101 (42), 84 (44), 79 (16). **IR** (film): ?/cm^{-1} = 3453 (m), 2979 (s), 1612 (s), 1399 (vs), 1361 (vs), 1321 (s), 1271 (s), 1168 (m), 1088 (s), 1020 (s), 963 (m), 859 (s), 700 (s), 667 (s). **HRMS** for **$C_{19}H_{23}BO_3$** (310.1740): found 310.1716.

Synthesis of 3-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]cyclohex-2-en-1-one (6f):

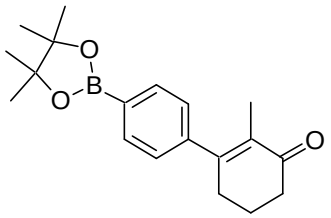


Prepared according to **TP 2** from 2-(4-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **4a** (390 mg, 1.2 mmol), *i*PrMgCl · LiCl (1.52 mL, 1.2 mmol, 0.79 M in THF), CuCN · 2LiCl (1.2 mL, 1.2 mmol, 1.0 M in THF) and 3-iodocyclohex-2-en-1-one (222 mg, 1.0 mmol). The

I/Mg-exchange was complete after 2 h. Purification by flash chromatography (*n*-pentane : ether) yielded the boronic ester **6f** (233 mg, 78 %) as a yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.85-7.82 (m, 2H), 7.53-7.50 (m, 2H), 6.44-6.43 (m, 1H), 2.80-2.75 (m, 2H), 2.51-2.46 (m, 2H), 2.21-2.11 (m, 2H), 1.35 (s, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 199.9, 159.8, 141.3, 135.1, 125.9, 125.3, 84.0, 37.2, 28.0, 24.8, 22.8. **MS** (70 eV, EI): m/z (%): 298 (100) [M^+], 283 (24), 270 (32), 213 (34), 199 (48), 188 (18), 170 (54), 154 (5), 142 (9), 128 (4), 115 (4), 83 (3). **IR** (film): ?/cm^{-1} = 3307 (w), 2977 (s), 2934 (m), 1940 (w), 1668 (s), 1607 (s), 1588 (s), 1548 (w), 1513 (w), 1455 (w), 1398 (s), 1359 (s), 1326 (s), 1262 (s), 1215 (w), 1144 (s), 1090 (s), 1019 (s), 962 (m), 858 (s), 820 (s), 804 (s), 743 (w), 655 (s). **HRMS** for **$C_{18}H_{23}BO_3$** (298.1740): found 298.1739.

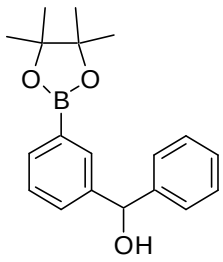
Synthesis of 2-methyl-3-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]cyclohex-2-en-1-one (6g):



Prepared according to **TP 2** from 2-(4-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **4a** (396 mg, 1.2 mmol), *i*PrMgCl · LiCl (1.52 mL, 1.2 mmol, 0.79 M in THF), CuCN · 2LiCl (1.2 mL, 1.2 mmol, 1.0 M in THF) and 2-methyl-3-iodocyclohex-2-en-1-one (236 mg, 1.0 mmol). The I/Mg-exchange was complete after 2 h. Purification by flash chromatography (*n*-pentane : ether) yielded the boronic ester **6g** (246 mg, 79 %) as a colourless solid.

mp.: 97.8-99.3 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 7.84-7.81 (m, 2H), 7.21-7.18 (m, 2H), 2.62-2.58 (m, 2H), 2.53-2.48 (m, 2H), 2.12-2.03 (m, 2H), 1.69-1.68 (m, 3H), 1.34 (s, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 199.8, 156.4, 144.1, 134.7, 131.8, 126.3, 83.8, 37.7, 32.7, 24.8, 22.8, 12.7. **MS** (70 eV, EI): m/z (%): 312 (12) [M^+], 297 (9), 213 (30), 185 (26), 168 (100), 153 (10), 141 (8), 128 (6), 84 (5). **IR** (KBr): ?/cm^{-1} = 3436 (m), 2980 (m), 2926 (m), 1667 (s), 1608 (m), 1397 (m), 1362 (vs), 1326 (m), 1263 (w), 1145 (m), 1090 (m), 1020 (w), 859 (w), 660 (m). **HRMS** for **$C_{19}H_{25}BO_3$** (312.1897): found 312.1840.

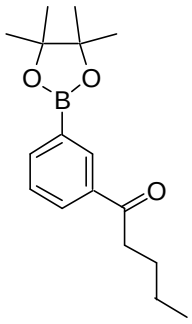
Synthesis of phenyl[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]methanol (6h):



Prepared according to **TP 2** from 2-(3-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **4b** (825 mg, 2.5 mmol), *i*PrMgCl · LiCl (2.94 mL, 2.5 mmol, 0.85 M in THF) and benzaldehyde (223 mg, 2.1 mmol). The I/Mg-exchange was complete after 1 h. Purification by flash chromatography (*n*-pentane : ether) yielded the boronic ester **6h** (464 mg, 71 %) as a yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.99 (m, 1H), 7.84-7.81 (m, 1H), 7.53-7.50 (m, 1 H), 7.44-7.26 (m, 6H), 5.83 (s, 1H), 3.35 (s, 1H), 1.40 (s, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 143.8, 143.1, 133.8, 132.7, 129.3, 128.1, 127.7, 127.1, 126.4, 83.6, 75.8, 24.6. **MS** (70 eV, EI): m/z (%): 309 (33) [M-H^+], 295 (34), 267 (11), 231 (100), 209 (74), 193 (27), 183 (31), 166 (65), 133 (12), 105 (27), 84 (13). **IR** (film): ?/cm^{-1} = 3436 (vs), 2979 (w), 2927 (w), 2855 (w), 1630 (m), 1493 (w), 1430 (w), 1359 (s), 1272 (w), 1144 (s), 1102 (m), 1080 (m), 1041 (m), 965 (w), 855 (w), 789 (w), 710 (m), 606 (w), 457 (s). **HRMS** for **$C_{19}H_{23}BO_3$** ([M-H^+] 309.1661): found [M-H^+] 309.1635.

Synthesis of 1-[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl]pentan-1-one (6i):

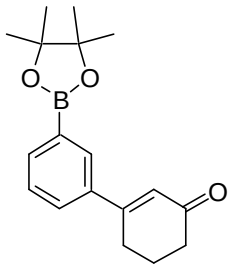


Prepared according to **TP 2** from 2-(3-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **4b** (825 mg, 2.5 mmol), *i*PrMgCl · LiCl (2.94 mL, 2.5 mmol, 0.85 M in THF), CuCN · 2LiCl (2.5 mL, 2.5 mmol, 1.0 M in THF) and valeryl chloride (254 mg, 2.1 mmol). The I/Mg-exchange was complete after 1 h. Purification by flash chromatography (*n*-pentane : ether) yielded the boronic ester **6i** (434 mg, 71 %) as a colourless solid.

mp.: 62.5-63.7 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 8.35 (m, 1H), 8.07-8.03 (m, 1H), 8.00-7.96 (m, 1 H), 7.49-7.43 (m, 1H), 3.00 (t, ^{3}J(H,H) = 8 Hz, 2H), 1.77-1.67 (m, 2H), 1.49-1.36 (m, 14H), 0.96 (t, ^{3}J(H,H) = 8 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 200.8,

139.1, 136.6, 134.3, 130.6, 128.0, 84.1, 38.4, 26.4, 24.9, 22.4, 14.0. **MS** (70 eV, EI): m/z (%): 289 (0.4) [M+H$^+$], 273 (3), 246 (29), 231 (100), 205 (9), 189 (9), 160 (6), 146 (6), 131 (7), 121 (4), 103 (5), 83 (12), 55 (3), 41 (5). **IR** (KBr): ?/cm^{-1} = 3401 (s), 2979 (s), 2958 (s), 2871 (w), 1694 (vs), 1600 (m), 1485 (w), 1420 (w), 1362 (vs), 1327 (s), 1268 (m), 1207 (s), 1151 (s), 1118 (m), 966 (m), 870 (m), 848 (m), 796 (m), 701 (s), 668 (w), 573 (w). **HRMS** for **$C_{17}H_{25}BO_3$** ([M+H$^+$] 289.1976): found [M+H$^+$] 289.1967.

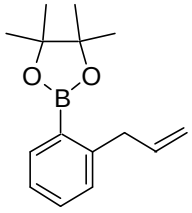
Synthesis of 3-[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl]cyclohex-2-en-1-one (6j):



Prepared according to **TP 2** from 2-(3-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **4b** (660 mg, 2.0 mmol), *i*PrMgCl · LiCl (2.35 mL, 2.0 mmol, 0.85 M in THF), CuCN · 2LiCl (2.0 mL, 2.0 mmol, 1.0 M in THF) and 3-iodocyclohex-2-en-1-one (377 mg, 1.7 mmol). The I/Mg-exchange was complete after 1 h. Purification by flash chromatography (*n*-pentane : ether) yielded the boronic ester **6j** (387 mg, 76 %) as a colourless solid.

mp.: 69.5-73.2 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 7.97 (m, 1H), 7.84-7.81 (m, 1H), 7.62-7.58 (m, 1 H), 7.42-7.37 (m, 1H), 6.44-6.43 (m, 1H), 2.81-2.76 (m, 2H), 2.49-2.44 (m, 2H), 2.18-2.09 (m, 2H), 1.34 (s, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 199.8, 160.0, 138.1, 136.2, 132.4, 128.7, 128.1, 125.4, 84.0, 37.2, 28.1, 24.8, 22.8. **MS** (70 eV, EI): m/z (%): 298 (81) [M$^+$], 283 (23), 270 (41), 241 (11), 213 (55), 199 (59), 188 (38), 170 (100), 154 (13), 142 (26), 128 (14), 115 (15), 83 (12), 41 (17). **IR** (KBr): ?/cm^{-1} = 3436 (m), 2980 (m), 1659 (vs), 1607 (s), 1485 (w), 1459 (w), 1409 (s), 1353 (vs), 1324 (vs), 1252 (m), 1142 (s), 1103 (m), 1078 (m), 964 (m), 850 (m), 706 (m), 681 (m). **HRMS** for **$C_{18}H_{23}BO_3$** (298.1740): found 298.1738.

Synthesis of 2-(2-allylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6k):

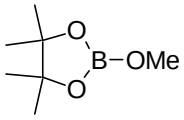


Prepared according to **TP 2** from 2-(2-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **4c** (543 mg, 1.7 mmol), *i*PrMgCl · LiCl (2.00 mL, 1.7 mmol, 0.85 M in THF) and allyl bromide (169 mg, 1.4 mmol). The I/Mg-exchange was complete after 12 h. Purification by

flash chromatography (*n*-pentane : ether) yielded the boronic ester **6k** (243 mg, 71 %) as a colourless oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.84-7.81 (m, 1H), 7.42-7.37 (m, 1H), 7.26-7.20 (m, 2H), 6.11-5.97 (m, 1H), 5.08-5.00 (m, 2H), 3.75-3.73 (m, 2H), 1.37 (s, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 146.7, 139.1, 136.0, 131.0, 129.1, 125.2, 114.7, 83.4, 39.8, 24.8. **MS** (70 eV, EI): m/z (%): 244 (11) [M^+], 229 (3), 186 (2), 171 (4), 159 (6), 144 (100), 126 (13), 116 (36), 91 (13), 57 (10), 43 (31). **IR** (film): ?/cm^{-1} = 3437 (w), 3070 (w), 2979 (s), 2930 (m), 1738 (w), 1637 (m), 1600 (s), 1488 (m), 1442 (s), 1382 (s), 1349 (vs), 1314 (s), 1260 (s), 1215 (w), 1146 (s), 1110 (s), 1090 (s), 1066 (s), 1040 (s), 963 (m), 907 (m), 862 (m), 799 (m), 762 (m), 749 (m), 664 (s). **HRMS** for **$C_{15}H_{21}BO_2$** (244.1635): found 244.1647.

Preparation of the reagent 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10): [6]

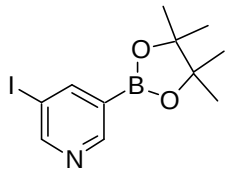


A 250 mL round-bottom flask, equipped with a magnetic stirring bar, was charged with $B(OMe)_3$ (36.9 g, 355 mmol) and anhydrous pinacol (42.0 g, 355 mmol). After stirring for 2 h at 68 °C, methanol was removed *in vacuo* at 25 °C/20 mbar. 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**10**) was distilled at 25 °C/ $4.3 \cdot 10^{-1}$ mbar (colourless liquid, 38.1 g, 241 mmol, 68 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 3.57 (s, 3H), 1.22 (s, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 82.6, 52.5, 24.5. **^{11}B-NMR** (87 MHz, $CDCl_3$, 25 °C): d = 20.9. **IR** (film): ?/cm^{-1} = 3413 (s), 2980 (vs), 1531 (vs), 1502 (vs), 1478 (vs), 1456 (vs), 1401 (vs), 1328 (vs), 1272 (s), 1218 (s), 1149 (vs), 1080 (s), 1033 (m), 1009 (m), 983 (s), 969 (vs), 895 (s), 851 (vs), 699 (m), 675 (vs), 576 (w). **$C_7H_{15}BO_3$:** calc.: C: 53.21; H: 9.57; found: C: 53.08; H: 9.88.

Spectral data match those reported in the literature.[6]

Synthesis of 3-iodo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (11):

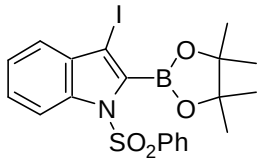


A dry and argon-flushed 100 mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with 3,5-diiodopyridine (**7**) (0.610 g, 1.8 mmol) and THF (30 mL). After cooling to -78 °C, *i*PrMgCl·LiCl (2.08 mL, 2.0 mmol, 0.96 M in THF) was added over 15 min. The reaction mixture was stirred at the same temperature for 2 h, then 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**10**) (0.284 g, 1.8 mmol) was added. The resulting mixture was allowed to warm to room temperature and kept stirring until full conversion was

detected. The reaction mixture was quenched with a small amount of sat. aq. NH_4Cl solution, extracted four times with Et_2O (4 × 15 mL), two times with CH_2Cl_2 (2 × 15 mL) and dried over Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Recrystallization from CH_2Cl_2 yielded the boronic ester **11** (377 mg, 76 %) as a colourless solid.

mp.: 70.9-73.2 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 8.87-8.86 (m, 1H), 8.84-8.83 (m, 1H), 8.37-8.36 (m, 1H), 1.33 (s, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 157.8, 153.5, 150.1, 93.7, 84.5, 24.8. **MS** (70 eV, EI): m/z (%): 331 (84) [M^+], 316 (100), 274 (28), 245 (24), 231 (44), 104 (10), 85 (11), 77 (11), 59 (18), 43 (23). **IR** (KBr): ?/cm^{-1} = 3437 (w), 2977 (w), 2921 (w), 2851 (w), 1574 (m), 1404 (s), 1354 (vs), 1273 (w), 1141 (s), 1106 (w), 1072 (w), 1016 (m), 962 (w), 858 (m), 712 (m). **HRMS** for **$C_{11}H_{15}BINO_2$** (331.0241): found 331.0245.

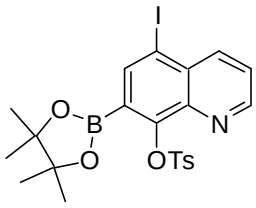
Synthesis of 3-iodo-1-(phenylsulfonyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (12):



A dry and argon-flushed 25 mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with 2,3-diiodo-1-(phenylsulfonyl)-1*H*-indole (**8**) (0.611 g, 1.2 mmol) and THF (8 mL). After cooling to -78 °C, *i*PrMgCl (1.48 mL, 1.3 mmol, 0.88 M in THF) was added. The reaction mixture was stirred at the same temperature for 2 h, then 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**10**) (0.158 g, 1.0 mmol) was added. The resulting mixture was allowed to warm to room temperature and kept stirring until full conversion was detected. The reaction mixture was quenched with a small amount of sat. aq. NH_4Cl solution, extracted four times with Et_2O (4 × 10 mL) and dried over Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Recrystallization from CH_2Cl_2 yielded the boronic ester **12** (387 mg, 76 %) as a colourless solid.

mp.: 114.8-116.9 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 7.99-7.96 (m, 2H), 7.84-7.81 (m, 1H), 7.43-7.32 (m, 3H), 7.27-7.17 (m, 4H), 1.44 (s, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 137.6, 135.7, 133.8, 133.3, 129.2, 127.4, 125.8, 123.9, 121.9, 113.4, 85.3, 76.1, 25.1. **MS** (70 eV, EI): m/z (%): 509 (97) [M^+], 393 (32), 368 (25), 310 (24), 266 (18), 242 (12), 183 (11), 141 (14), 125 (100), 77 (24). **IR** (KBr): ?/cm^{-1} = 3436 (m), 2975 (m), 2926 (m), 1538 (m), 1448 (s), 1364 (vs), 1342 (vs), 1266 (vs), 1231 (m), 1174 (vs), 1137 (vs), 1115 (m), 1090 (s), 1048 (s), 1019 (m), 962 (m), 934 (w), 844 (vs), 752 (vs), 742 (vs), 732 (vs), 707 (s), 683 (s), 666 (w), 593 (vs), 570 (vs), 558 (s), 548 (s). **HRMS** for **$C_{20}H_{21}BINO_4S$** (509.0329): found 509.0349.

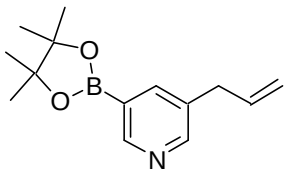
Synthesis of 5-iodo-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)quinolin-8-yl 4-methylbenzenesulfonate (13):



A dry and argon-flushed 250 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with 5,7-diiodoquinolin-8-yl 4-methylbenzene sulfonate (**9**) (6.42 g, 11.7 mmol) and THF (120 mL). After cooling to -78 °C, *i*PrMgCl (14.6 mL, 14.0 mmol, 0.96 M in THF) was added over 15 min. The reaction mixture was stirred at the same temperature for 2 h, then 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**10**) (1.85 g, 11.7 mmol) was added. The resulting mixture was allowed to warm to room temperature and kept stirring until full conversion was detected. The reaction mixture was quenched with a small amount of sat. aq. NH_4Cl solution, extracted four times with Et_2O (4 × 30 mL), two times with CH_2Cl_2 (2 × 20 mL) and dried over Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Recrystallization from CH_2Cl_2 yielded the boronic ester **13** (4.38 g, 81 %) as a colourless solid.

mp.: 135.2 °C (decomp.). **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 8.43-8.40 (m, 2H), 8.26-8.23 (m, 1H), 7.70-7.67 (m, 2H), 7.36-7.31 (m, 1H), 7.16-7.13 (m, 2H), 2.37 (s, 3H), 1.43 (s, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 150.5, 144.4, 141.9, 139.9, 133.6, 132.4, 129.5, 129.0, 128.9, 123.4, 96.1, 84.8, 24.9, 21.6. **MS** (70 eV, EI): m/z (%): 551 (0.2) [M^+], 537 (0.4), 536 (3), 493 (7), 487 (100), 297 (10), 170 (12), 139 (33), 91 (16). **IR** (KBr): ?/cm^{-1} = 3436 (s), 2980 (m), 2930 (w), 1594 (m), 1445 (s), 1399 (s), 1374 (vs), 1346 (vs), 1316 (s), 1270 (s), 1208 (s), 1190 (s), 1168 (vs), 1143 (vs), 1134 (vs), 1059 (vs), 966 (s), 851 (m), 817 (s), 780 (vs), 727 (s), 594 (w), 558 (s), 548 (s). **HRMS** for **$C_{22}H_{23}BINO_5S$** (551.0435): found 551.0439. **$C_{22}H_{23}BINO_5S$**: calc.: C: 47.94; H: 4.21; N: 2.54; S: 5.82 found: C: 47.85; H: 4.23; N: 2.53; S: 6.41.

Synthesis of 3-allyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (17a):

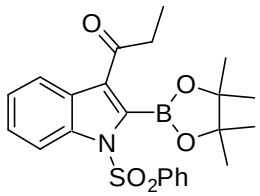


A dry and argon-flushed 25 mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with 3-iodo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (**11**) (0.397 g, 1.2 mmol) and THF (10 mL). After cooling to -78 °C, *i*PrMgCl·LiCl (1.46 mL, 1.4 mmol, 0.96 M in THF) was added over 15 min. The reaction mixture was stirred at the same temperature for 2 h, then CuCN·2LiCl (0.07 mL, 0.07 mmol, 1.0 M in THF) was added and the resulting mixture was stirred for an additional 30 min. After adding allyl bromide

(0.120 g, 1.0 mmol) the reaction mixture was allowed to warm to room temperature and kept stirring until full conversion was detected. The reaction mixture was quenched with a small amount of sat. aq. NH_4Cl solution, extracted four times with Et_2O (4 × 10 mL), three times with CH_2Cl_2 (3 × 8 mL) and dried over Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Recrystallization from CH_2Cl_2 yielded the boronic ester **17a** (203 mg, 83 %) as a colourless solid.

mp.: 91.8-93.6 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 8.78 (m, 1H), 8.49 (m, 1H), 7.87 (m, 1H), 5.99-5.86 (m, 1H), 5.09-5.04 (m, 2H), 3.37-3.35 (m, 2H), 1.33 (s, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 153.0, 151.9, 142.4, 136.1, 134.5, 116.7, 84.1, 37.2, 24.8. **MS** (70 eV, EI): m/z (%): 245 (49) [M^+], 230 (69), 188 (32), 160 (18), 146 (100), 117 (10), 91 (6), 85 (8), 59 (7), 41 (12). **IR** (KBr): ?/cm^{-1} = 3436 (vs), 2968 (s), 2926 (s), 1729 (w), 1640 (w), 1447 (m), 1371 (m), 1262 (s), 1157 (vs), 1081 (vs), 1039 (s), 967 (w), 913 (w), 854 (w), 803 (s), 746 (w), 721 (m). **HRMS** for **$C_{14}H_{20}BNO_2$** (245.1587): found 245.1591.

Synthesis of 1-[1-(phenylsulfonyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-3-yl]propan-1-one (17b):

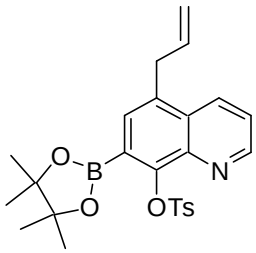


A dry and argon-flushed 100 mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with 3-iodo-1-(phenylsulfonyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**12**) (0.611 g, 1.2 mmol) and THF (25 mL). After cooling to -78 °C, *i*PrMgCl·LiCl (1.46 mL, 1.4 mmol, 0.96 M in THF) was added over 15 min. The reaction mixture was stirred at the same temperature for 1 h, then CuCN·2LiCl (1.2 mL, 1.2 mmol, 1.0 M in THF) was added and the resulting mixture was stirred for an additional 20 min. After adding propionyl chloride (0.093 g, 1.0 mmol) the reaction mixture was allowed to warm to room temperature and kept stirring until full conversion was detected. The reaction mixture was quenched with a small amount of sat. aq. NH_4Cl solution, extracted four times with Et_2O (4 × 10 mL), three times with CH_2Cl_2 (3 × 10 mL) and dried over Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Recrystallization from CH_2Cl_2 yielded the boronic ester **17b** (356 mg, 81 %) as a colourless solid.

mp.: 196.9-199.1 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 8.16-8.14 (m, 2H), 8.02-7.99 (m, 1H), 7.88-7.85 (m, 1H), 7.57-7.42 (m, 3H), 7.33-7.29 (m, 2H), 3.02 (q, ^3J(H,H) = 7 Hz, 2H), 1.58 (s, 12H), 1.25 (t, ^3J(H,H) = 7 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 197.4, 137.6, 136.9, 134.1, 129.3, 128.8, 127.7, 127.1, 124.9, 124.3, 121.1, 113.9, 85.3, 35.6, 25.5, 7.6. **MS** (70 eV, EI): m/z (%): 439 (11) [M^+], 424 (18), 381 (71), 352 (19), 323 (27), 310 (27), 259 (100), 240 (77), 200 (20), 198 (18), 170 (38), 141 (41), 125 (30), 83 (33),

77 (60), 43 (39). **IR** (KBr): ?/cm^{-1} = 3436 (s), 2977 (m), 2937 (w), 1668 (s), 1529 (s), 1476 (w), 1449 (m), 1373 (vs), 1341 (vs), 1281 (s), 1238 (w), 1212 (m), 1181 (vs), 1140 (vs), 1090 (s), 1023 (s), 982 (s), 950 (w), 846 (s), 763 (s), 746 (s), 724 (m), 688 (m), 616 (w), 596 (s), 576 (vs), 561 (s). **HRMS** for **$C_{23}H_{26}BNO_5S$** (439.1625): found 439.1618. **$C_{23}H_{26}BNO_5S$**: calc.: C: 62.88; H: 5.97; N: 3.19; S: 7.30; found: C: 62.93; H: 5.95; N: 3.15; S: 7.49.

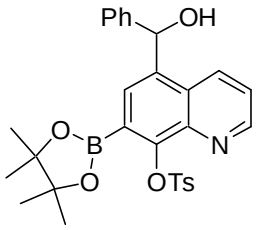
Synthesis of 5-allyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)quinolin-8-yl 4-methylbenzenesulfonate (17c):



A dry and argon-flushed 25 mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with 5-iodo-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)quinolin-8-yl 4-methylbenzene sulfonate (**13**) (0.661 g, 1.2 mmol) and THF (10 mL). After cooling to -78 °C, *i*PrMgCl·LiCl (1.46 mL, 1.4 mmol, 0.96 M in THF) was added over 15 min. The reaction mixture was stirred at the same temperature for 3 h, then CuCN·2LiCl (0.07 mL, 0.07 mmol, 1.0 M in THF) was added and the resulting mixture was stirred for an additional 30 min. After adding allyl bromide (0.120 g, 1.0 mmol) the reaction mixture was allowed to warm to room temperature and kept stirring until full conversion was detected. The reaction mixture was quenched with a small amount of sat. aq. NH_4Cl solution, extracted four times with Et_2O (4 × 10 mL), three times with CH_2Cl_2 (3 × 10 mL) and dried over Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Recrystallization from CH_2Cl_2 yielded the boronic ester **17c** (423 mg, 91 %) as a colourless solid.

mp.: 121.3-123.9 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 8.44-8.41 (m, 1H), 8.21-8.18 (m, 1H), 7.70-7.67 (m, 3H), 7.25-7.22 (m, 1H), 7.13-7.10 (m, 2H), 6.10-5.96 (m, 1H), 5.11-4.97 (m, 2H), 3.77-3.75 (m, 2H), 2.35 (s, 3H), 1.43 (s, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 149.9, 149.3, 144.1, 136.2, 135.2, 134.5, 133.9, 133.8, 132.0, 131.4, 128.9, 125.9, 121.8, 121.4, 116.7, 84.5, 36.5, 24.9, 21.5. **IR** (KBr): ?/cm^{-1} = 3436 (vs), 2977 (w), 2926 (w), 1630 (w), 1538 (w), 1448 (m), 1342 (vs), 1266 (vs), 1175 (vs), 1137 (vs), 1091 (s), 1049 (m), 844 (m), 733 (s), 707 (w), 684 (w), 593 (vs), 571 (s). **$C_{25}H_{28}BNO_5S$**: calc.: C: 64.52; H: 6.06; N: 3.01; S: 6.89; found: C: 64.33; H: 5.95; N: 2.96; S: 6.68.

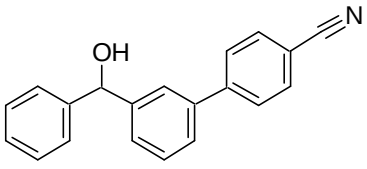
Synthesis of 5-[hydroxyl(phenyl)methyl]-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)quinolin-8-yl 4-methylbenzenesulfonate (17d):



A dry and argon-flushed 25 mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with 5-iodo-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)quinolin-8-yl 4-methylbenzenesulfonate (**13**) (0.661 g, 1.2 mmol) and THF (10 mL). After cooling to -78 °C, *i*PrMgCl·LiCl (1.46 mL, 1.4 mmol, 0.96 M in THF) was added over 15 min. The reaction mixture was stirred at the same temperature for 3 h, then benzaldehyde (0.106 g, 1.0 mmol) was added and the resulting mixture was allowed to warm to room temperature and kept stirring until full conversion was detected. The reaction mixture was quenched with a small amount of sat. aq. NH_4Cl solution, extracted four times with Et_2O (4 × 10 mL), three times with CH_2Cl_2 (3 × 10 mL) and dried over Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Recrystallization from CH_2Cl_2 yielded the boronic ester **17d** (414 mg, 78 %) as a colourless solid.

mp.: 87.1 °C (decomp.). **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 8.47-8.45 (m, 1H), 8.32-8.30 (m, 1H), 8.07 (s, 1H), 7.81-7.79 (m, 2H), 7.33-7.28 (m, 5H), 7.18-7.15 (m, 3H), 6.37 (s, 1H), 2.37 (s, 3H), 1.44 (s, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 148.9, 144.5, 142.4, 137.5, 133.5, 130.4, 129.1, 129.0, 128.6, 128.4, 127.8, 126.8, 121.5, 84.7, 74.3, 25.0, 21.6. **MS** (70 eV, EI): m/z (%): 516 (2) [M-CH_3^+], 467 (100), 450 (19), 360 (5), 301 (3), 260 (5), 216 (4), 139 (23), 105 (57), 91 (16). **IR** (KBr): ?/cm^{-1} = 3436 (vs), 2979 (w), 2927 (w), 1619 (w), 1599 (w), 1494 (w), 1451 (m), 1372 (vs), 1240 (w), 1192 (m), 1170 (vs), 1142 (vs), 1056 (s), 968 (w), 852 (m), 784 (m), 731 (m), 554 (m). **$C_{29}H_{30}BNO_6S$**: calc.: C: 65.54; H: 5.69; N: 2.64; found: C: 65.44; H: 5.45; N: 2.55.

Synthesis of 3'-[hydroxy(phenyl)methyl]biphenyl-4-carbonitrile (18):

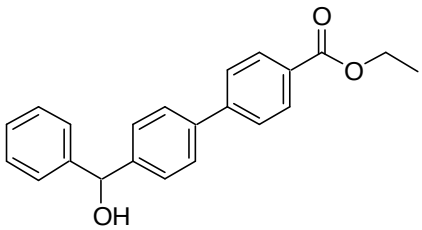


A 25 mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)diphenylmethanol (**6h**) (720 mg, 2.3 mmol), *p*-bromobenzonitrile (420 mg, 2.3 mmol), $PdCl_2$(dppf) (80 mg, 0.1 mmol, 5 mol%), K_2CO_3 (950 mg, 6.9 mmol), H_2O (0.5 mL), THF (6 mL), and DME (6 mL). The resulting mixture was kept stirring in the sealed tube at 60 °C for 9 h until full conversion was detected. The reaction mixture was quenched with sat. aq. NH_4Cl solution, extracted four times with Et_2O (4 × 10 mL) and dried over Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*.

Purification by flash chromatography (*n*-pentane : ether) yielded the alcohol **18** (610 mg, 92 %) as a colourless solid.

mp.: 108.2-110.3 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 7.61-7.54 (m, 5H), 7.41-7.16 (m, 8H), 5.81 (s, 1H), 2.33 (s, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 145.5, 144.7, 143.5, 139.3, 132.5, 129.2, 128.6, 127.8, 127.3, 126.8, 126.5, 126.3, 125.2, 118.9, 110.9, 76.0. **MS** (70 eV, EI): m/z (%): 285 (54) [M^+], 268 (9), 253 (2), 240 (3), 206 (77), 180 (27), 165 (3), 151 (13), 133 (9), 105 (100), 77 (21), 51 (3). **IR** (KBr): ?/cm^{-1} = 3400 (vs), 3058 (w), 2875 (w), 2224 (vs), 1605 (vs), 1482 (m), 1454 (m), 1398 (w), 1172 (m), 1058 (m), 1036 (m), 1026 (m), 838 (s), 793 (m), 774 (s), 758 (m), 710 (vs), 550 (w), 523 (w). **HRMS** for **$C_{20}H_{15}NO$** (285.1154): found 285.1166.

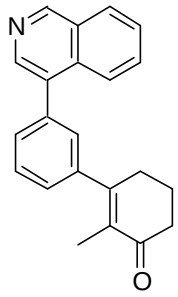
One-pot Synthesis of ethyl 4'-[hydroxy(phenyl)methyl]biphenyl-4-carboxylate (20):



A dry and argon-flushed 50 mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with 4,4,5,5-tetramethyl-2-(4-iodophenyl)-1,3,2-dioxaborolane (**4a**) (1.4 g, 4.3 mmol) and THF (5.7 mL). After cooling to -78 °C, *i*PrMgCl · LiCl (5.38 mL, 4.3 mmol, 0.80 M in THF) was added. The reaction mixture was stirred at the same temperature for 2 h, then benzaldehyde (456 mg, 4.3 mmol) was added. The resulting mixture was allowed to warm to room temperature and kept stirring for 1 h until full conversion was detected. Then H_2O (1.0 mL), DME (4 mL), $PdCl_2$(dppf) (220 mg, 0.3 mmol, 5 mol%), K_2CO_3 (1.78 g, 12.9 mmol) and ethyl 4-iodobenzoate (1.66 g, 6.0 mmol) was added. The resulting mixture was kept stirring in the sealed tube at 80 °C for 10 h until full conversion was detected. The reaction mixture was quenched with sat. aq. NH_4Cl solution, extracted three times with Et_2O (3 × 10 mL) and dried over Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. Purification by flash chromatography (*n*-pentane : ether) yielded the alcohol **20** (1.05 g, 73 %) as a colourless solid.

mp.: 111.5-114.5 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 8.12-8.07 (m, 2H), 7.65-7.58 (m, 4H), 7.50-7.29 (m, 7H), 5.91 (s, 1H), 4.40 (q, ^{3}J(H,H) = 7 Hz, 2H), 2.32 (s, 1H), 1.41 (t, ^{3}J(H,H) = 7 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 145.1, 143.8, 143.6, 139.3, 130.0, 129.3, 128.6, 127.7, 127.4, 127.1, 126.9, 126.5, 76.0, 61.0, 14.3. **MS** (70 eV, EI): m/z (%): 332 (72) [M^+], 287 (23), 253 (42), 226 (22), 181 (13), 152 (27), 105 (100), 77 (22). **IR** (KBr): ?/cm^{-1} = 3470 (w), 3062 (w), 3028 (w), 2982 (w), 2901 (w), 1689 (vs), 1607 (m), 1494 (w), 1452 (w), 1396 (m), 1371 (m), 1291 (vs), 1179 (m), 1116 (s), 1047 (m), 1022 (m), 1006 (m), 844 (w), 807 (w), 770 (s), 730 (m), 701 (s), 663 (w). **HRMS** for **$C_{22}H_{10}O_3$** (332.1412): found 332.1397.

One-pot Synthesis of 3-(3-isoquinolin-4-ylphenyl)-2-methylcyclohex-2-en-1-one (22):



A dry and argon-flushed 50 mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with 4,4,5,5-tetramethyl-2-(3-iodophenyl)-1,3,2-dioxaborolane (**4b**) (0.825 g, 2.5 mmol) and THF (4 mL). After cooling to -78 °C, *i*PrMgCl · LiCl (3.53 mL, 3.0 mmol, 0.85 M in THF) was added. The reaction mixture was stirred at the same temperature for 1 h, then CuCN·2LiCl (2.5 mL, 2.5 mmol, 1.0 M in THF) was added. The resulting mixture was kept stirring at -78 °C for 30 min, then 2-methyl-3-iodocyclohex-2-en-1-one (0.590 g, 2.5 mmol) was added and the resulting mixture was allowed to warm to room temperature. After full conversion was detected H_2O (1.0 mL), DME (4 mL), $PdCl_2$(dppf) (135 mg, 0.2 mmol, 5 mol%), K_2CO_3 (2.07 g, 15.0 mmol) and 4-bromoisoquinoline (0.780 g, 3.75 mmol) was added. The resulting mixture was kept stirring in the sealed tube at 80 °C for 15 h until full conversion was detected. The reaction was quenched with sat. aq. NH_4Cl solution, extracted four times with Et_2O (4 × 15 mL) and dried over Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. Purification by flash chromatography (*n*-pentane : ether) yielded **20** (413 mg, 52 %) as a colourless solid.

mp.: 126.7-130.1 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 9.31 (m, 1H), 8.52 (m, 1H), 8.11-8.07 (m, 1H), 7.94-7.91 (m, 1H), 7.77-7.66 (m, 2H), 7.60-7.55 (m, 1H), 7.50-7.47 (m, 1H), 7.36-7.32 (m, 2H), 2.73-2.68 (m, 2H), 2.56-2.52 (m, 2H), 2.17-2.08 (m, 2H), 1.82-1.81 (m, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 199.7, 155.7, 141.8, 136.9, 134.4, 132.3, 131.3, 129.5, 128.8, 128.7, 128.2, 127.6, 126.9, 124.6, 37.7, 33.0, 22.8, 13.0. **MS** (70 eV, EI): m/z (%): 313 (100) [M^+], 284 (13), 270 (5), 256 (27), 242 (17), 228 (4), 215 (5), 185 (12), 128 (7), 120 (6). **IR** (KBr): ?/cm^{-1} = 3042 (w), 2927 (m), 2867 (m), 1667 (vs), 1621 (m), 1568 (w), 1502 (w), 1453 (w), 1430 (w), 1387 (m), 1378 (m), 1354 (s), 1328 (m), 1296 (m), 1110 (s), 1042 (w), 898 (w), 869 (w), 797 (s), 755 (s), 732 (m), 711 (s). **HRMS** for **$C_{22}H_{19}NO$** (313.1467): found 313.1458.

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[2] An aliquot of the reaction mixture was hydrolysed with sat. aq. NH_4Cl solution and the organic compounds were extracted with Et_2O. The organic layer was subsequently subjected to GC-analysis.

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[6] (a) A. Finch, P. J. Gardner, E. J. Pearn, *Recl. Trav. Chim. Pays-Bas* **1964**, *83*, 1314; (b) R. W. Hoffmann, A. Endesfelder, H.-J. Zeiss, *Carbohydrate Res.* **1983**, *123*, 320.