Supplementary Material

An alkynylboronic ester cycloaddition route to functionalised aromatic boronic esters

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General Procedures

Infrared (IR) Spectra were recorded on a Perkin Elmer Paragon 100 FTIR spectrophotometer, ν max in cm -1. Samples were recorded as thin films using sodium chloride plates, as a DCM solution. Bands are characterised as broad (br), strong (s), medium (m), and weak (w). 1H NMR spectra were recorded on a Bruker AC-250 (250 MHz) or AMX-400 (400 MHz) supported by an Aspect 3000 data system, unless otherwise stated. Chemical shifts are reported in ppm from tetramethylsilane with the residual protic solvent resonance as the internal standard (CHCl 3: δ 77.27 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s=singlet, d=doublet, q=quartet, pent=pentet, sext=sextet, br=broad, m=multiplet, app=apparent), coupling constants (Hz), and assignment. 13C NMR spectra were recorded on a Bruker AC-250 (62.9 MHz) or AMX-400 (100.6 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal reference (CDCl 3: δ 77.0 ppm). Low resolution mass spectra were recorded on Micromass Autospec, operating in E.I., C.I. or FAB mode; or a Perkin-Elmer Turbomass Benchtop GC-MS operating in either E.I. or C.I mode. High-resolution mass spectra (HRMS) recorded for accurate mass analysis, were performed on either a MicroMass LCT operating in Electrospray mode (TOF ES +) or a MicroMass Prospec operating in FAB (FAB +), EI (EI +) or CI (CI +) mode. Elemental microanalysis was performed using a Perkin-Elmer 2400 CHNS / O Series II Elemental Analyser. Melting points performed on recrystallised solids, were recorded on a Gallenkamp melting point apparatus and are uncorrected. All solvents and reagents were purified using standard laboratory techniques according to methods published in “Purification of Laboratory Chemicals” by Perrin, Armarago, and Perrin (Pergamon Press, 1966). Starting alkynylboronates 1 and pyranones 2 were prepared according to established procedures. Methyl coumalate was purchased from Aldrich chemical co. and used as received. Flash chromatography was performed on silica gel (BDH Silica Gel 60 43-60). Thin layer chromatography (TLC) was performed on aluminium backed plates pre-coated with

silica (0.2 mm, Merck DC-alufoil Kieselgel 60 F_{254}) which were developed using standard visualizing agents: Ultraviolet light or potassium permanganate. X-Ray data for compounds 13 and 15 have been deposited with the CCDC, supplementary entry numbers: 608269 and 608270 respectively.

1.1. [4+2] Cycloaddition

Cycloaddition of 1 with 2a

A mixture of 1 (0.1 g, 1.04 mmol) and 2a (0.466 g, 2.08 mmol) was heated at 170 °C and stirred for 15 h under N\textsubscript{2}. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give compound 3 as crystalline colourless solid, wt. 0.247 g, 86% yield.

\textbf{Mp} 84-86 °C \textbf{\textsuperscript{1}H NMR} (250 MHz, CDCl\textsubscript{3}): δ0.33 (9H, s, SiMe\textsubscript{3}), 1.34 (12H, s, 4 x CH\textsubscript{3}), 7.36 (2H, m, Ar-H) 7.61 (1H, m, Ar-H), 7.90 (1H, m, Ar-H); \textbf{\textsuperscript{13}C NMR} (62.9 MHz, CDCl\textsubscript{3}) δ 1.1, 25.0, 83.8, 127.8, 129.7, 134.3, 136.1, 146.0; \textbf{FTIR}: ν\textsubscript{max}/CHCl\textsubscript{3}, 2981 (s) cm\textsuperscript{-1}; \textbf{HRMS (EI\textsuperscript{+})} calcd for C\textsubscript{15}H\textsubscript{25}BO\textsubscript{2}Si: 276.1717. Found: 276.1715.

Cycloaddition of 4 with 2a

A mixture of 4 (0.1 g, 0.649 mmol) and 2a (0.291 g, 1.298 mmol) was heated at 170 °C and stirred for 15 h under N\textsubscript{2}. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give 6a and 6b (3:1 ratio) as colourless
Cycloaddition of 5 with 2a

A mixture of 5 (0.2 g, 1.298 mmol) and 2a (0.582 g, 2.595 mmol) was heated at 170 °C and stirred for 15 h under N₂. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give the separated title compounds 6a and 6b (1:1 ratio) as colourless oils, wt. 0.384 g, 83% yield.

Cycloaddition of 4 with 2b

A mixture of 4 (0.1 g, 0.649 mmol) and 2a (0.296 g, 1.298 mmol) was heated at 170 °C and stirred for 15 h under N₂. The product was purified by flash column chromatography (eluting...
solvent petroleum ether/ethyl acetate 25:1 ratio) to give 7a and 7b (1:1 ratio) as a clear oil, 0.092g, 42%.

7a $^1$H NMR: δ1.23 (12H, s, 4 x CH₃), 3.95 (3H, s, CO₂C₃H₃), 7.35-7.48 (6H, m, Ar-H), 8.12 (1H, dd, J=8.0, 2.0 Hz, Ar-H), 8.38 (1H, dd, J=2.0, 0.5 Hz, Ar-H); $^{13}$C NMR (62.9 MHz, CDCl₃) δ24.6, 52.1, 84.0, 127.0, 127.5, 127.9, 128.9, 129.0, 130.0, 135.6, 142.1, 151.9, 167.0.

7b $^1$H NMR: δ1.21 (12H, s, 4 x CH₃), 3.92 (3H, s, CO₂C₃H₃), 7.35-7.48 (5H, m, Ar-H), 7.56 (1H, d, J=8.0 Hz, Ar-H), 7.98 (1H, dd, J=8.0, 1.5 Hz, Ar-H), 8.04 (1H, dd, J= 1.0, 0.5 Hz, Ar-H); $^{13}$C NMR (62.9 MHz, CDCl₃) δ24.7, 52.2, 84.1, 127.0, 127.2, 127.5, 128.0, 129.0, 129.1, 135.7, 142.0, 147.9, 167.0.

FTIR: $\nu_{max}$/CHCl₃, 2991 (w), 2979 (w), 2940 (w), 1723 (s), 1600 (w) cm⁻¹; HRMS (EI⁺) calcd. for C₂₀H₂₃O₄B: 338.1689 Found: 338.1687.

**Cycloaddition of 5 with 2b**

A mixture of 5 (0.1 g, 0.649 mmol) and 2b (0.296 g, 1.298 mmol) was heated at 170 °C and stirred for 15 h under N₂. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give compounds 7a and 7b (1:14 ratio) as a clear oil, 0.127g, 57% yield. The regiochemistry was determined by 2-D NMR experiment (nOesy) of the major regioisomer 7b.

**Cycloaddition of 4 with 2c**

A mixture of 4 (0.1 g, 0.649 mmol) and 2c (0.270 g, 1.298 mmol) was heated at 170 °C and stirred for 15 h under N₂. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give compounds 8a and 8b (10:1 ratio) as
a clear oil, wt. 0.050 g, 24% yield. The regiochemistry was determined by 2-D NMR experiment (nOesy) of the major regioisomer 8a.

8a 1H NMR: δ 0.85 (3H, t, J=7.5 Hz, CH2C3H), 1.28 (12H, s, 4 x C3H), 1.22-1.37 (2H, m, CH2C3H), 1.38-1.56 (2H, m, CH2CH2C3H), 2.85 (2H, app t, J=8.0 Hz, C=CH2), 3.88 (3H, s, CO2C3H), 7.16 (1H, d, J=8.0 Hz, Ar-H), 7.92 (1H, dd, J=8.0, 2.0 Hz, Ar-H), 8.34 (1H, d, J=2.0 Hz, Ar-H); 13C NMR (62.9 MHz, CDCl3) δ 13.9, 22.7, 24.8, 35.3, 35.6, 51.9, 83.7, 126.8, 129.3, 131.8, 137.2, 155.5, 167.3.

8b 1H NMR: δ 0.85 (3H, t, J=7.5 Hz, CH2C3H), 1.28 (12H, s, 4 x C3H), 1.22-1.37 (2H, m, CH2C3H), 1.38-1.56 (2H, m, CH2CH2C3H), 2.85 (2H, app t, J=8.0 Hz, C=CH2), 3.89 (3H, s, CO2C3H), 7.79 (2H, s, Ar-H), 7.81 (1H, s, Ar-H); 13C NMR (62.9 MHz, CDCl3) δ 13.9, 22.7, 24.8, 35.2, 35.4, 52.0, 83.8, 125.6, 129.9, 131.8, 135.8, 150.2, 167.3.

FTIR: νmax/CHCl3,2977 (m), 2956 (m), 2931 (m), 2870 (m), 1723 (s) cm⁻¹ HRMS (EI⁺) calcd. for C18H27O4B: 318.2002 Found: 318.2012

Cycloaddition of 5 with 2c

A mixture of 5 (0.1 g, 0.649 mmol) and 2c (0.270 g, 1.298 mmol) was heated at 170 °C and stirred for 15 h under N2. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give compounds 8a and 8b (1:3 ratio) as a clear oil, wt. 0.127 g, 59% yield. The regiochemistry was determined by 2-D NMR experiment (nOesy) of the major regioisomer 8b.

Cycloaddition of 5 with 2d
A mixture of 5 (0.1 g, 0.649 mmol), 2d (0.09 g, 0.649 mmol) and diphenylether (1 mL) were heated at 170 °C with stirring, for 15 hours under a nitrogen atmosphere. The product was purified by flash column chromatography (eluting solvent 100: 1 petroleum ether: EtOAc) to give colourless crystalline solid of regioisomers in 5: 1 ratio (Major regioisomer was 9a) wt. 0.130 g, 77% yield.

9a: ¹H NMR (250 MHz, CDCl₃): δ 1.28 (12H, s, CH₃), 3.84 (3H, s, CH₃OCO), 7.79 (2H, d, J=8.5 Hz, ArH), 7.96 (2H, d, J=8.5 Hz, ArH). ¹³C NMR (62.9 MHz, CDCl₃): δ 24.8, 52.1, 84.1, 127.8, 135.8, 134.6, 167.1

9b: ¹H NMR δ 1.28 (12H, s, CH₃), 3.84 (3H, s, CH₃OCO), 7.38 (1H, t, J=8.0 Hz, ArH), 7.90 (1H, m, ArH), 8.05 (1H, dt, J=8.0, 1.0 Hz, ArH), 8.39 (1H, br, ArH). ¹³C NMR (62.9 MHz, CDCl₃): δ 24.8, 52.0, 84.1, 128.6 (x 2), 132.3 (x 2), 139.1, 167.1.

FTIR: ν max/CHCl₃, cm⁻¹ 2979 (w), 1727 (s), 1606 (w), 1510 (w), 1399 (m), 1361 (s). HRMS (EI⁺) Calcd for C₂₉H₂₄O₄ 431.9927 Found: 431.9909.

Cycloaddition of 10 with 2a

A mixture of 10 (0.100 g, 0.394 mmol) and 2a (0.176 g, 0.788 mmol) and mesitylene (1 mL) was heated at 155 °C and stirred for 15 h under N₂. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give compounds 12a and 12b (1:1 ratio) as a brown oil, wt. 0.111 g, 65% yield.

12a/b mixture: ¹H NMR δ 0.29 (9H, s, CH₃), 0.37 (9H, s, CH₃), 1.29 (12H, s, CH₃), 1.37 (12H, s, CH₃), 7.47 (1H, d, J=2.0 Hz, ArH), 7.51 (1H, d, J=2.0 Hz, ArH), 7.59 (1H, d, J=2.0 Hz, ArH), 7.64 (1H, d, J=2.0 Hz, ArH). ¹³C NMR (62.9 MHz, CDCl₃): δ 0.5, 1.8, 24.7, 25.3, 84.5, 85.5, 112.5(x2), 134.3(x2), 134.8(x2), 135.0(x2), 136.3(x2).

FTIR: ν max/CHCl₃, cm⁻¹ 2980 (s), 1315 (s), 846 (s). HRMS (EI⁺) Calcd for C₁₉H₂₃Br₂O₂Si 431.9927 Found: 431.9909.

Cycloaddition of 10 with 2b

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Br   Br
O       O
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\     \  |O      O|
Br   Br
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A mixture of 10 (0.200 g, 0.788 mmol) and 2b (0.269 g, 1.182 mmol) and mesitylene (1 mL) was heated at 155 °C and stirred for 15 h under N₂. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give compound 13 as brown solid, 0.214 g, 62% yield. The regiochemistry was determined by X-ray crystallography.

**Mp** 54-56 °C. ¹H NMR δ 1.06 (12H, s, CH₃), 7.28 (2H, m, ArH), 7.36 (3H, m, ArH), 7.72 (1H, d, J=2.0 Hz, ArH), 7.85 (1H, d, J=2.0 Hz, ArH). ¹³C NMR (62.9 MHz, CDCl₃): δ 24.4, 84.2, 113.3, 114.0, 115.0, 117.5, 122.0, 127.6, 129.5, 135.4, 136.3. FTIR: νmax/CHCl₃, cm⁻¹ 2979 (w), 2979 (s), 1458 (w), 1145 (w). HRMS (El⁺) Calcd for C₁₈H₁₉BBr₂O₂: 381.0490 Found: 381.0486.

Cycloaddition of 10 with 2c

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Br   Br
O       O
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|     |   |B\     \  |
\     \  |O      O|
Br   Br
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A mixture of 10 (0.100 g, 0.394 mmol) and 2c (0.123 g, 0.591 mmol) and mesitylene (1 mL) was heated at 155 °C and stirred for 15 h under N₂. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give compounds 14a and 14b as a brown oil, wt. 0.077 g, 47% yield. The regiochemistry was determined by NMR experiment (nOe) of the major regioisomer 14a.

14a: ¹H NMR δ 0.87 (3H, t, CH₂CH₃), 1.26 (12H, s, CH₃), 1.27-1.36 (4H, m, CH₂CH₂CH₃), 2.92 (2H, t, J=8.0 Hz, C=CH₂), 7.66 (1H, d, J=1.0 Hz, ArH), 7.73 (1H, d, J=1.0 Hz, ArH). ¹³C NMR (62.9 MHz, CDCl₃): δ 13.9, 22.9, 24.8, 34.4, 35.4, 81.5, 125.6, 130.4, 134.9, 137.3, 137.7.
**Supplementary Material (ESI) for Chemical Communications**

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**FTIR**: $\nu_{\text{max/CHCl}_3}$, cm$^{-1}$ 2958 (s). **HRMS** (EI$^+$) Calcd for C$_{16}$H$_{23}$BBr$_2$O$_2$ 416.0158 Found: 416.0162.

**Cycloaddition of 11 with 2b**

A mixture of 11 (0.1 g, 0.429 mmol) and 2b (0.391 g, 1.716 mmol) was heated at 170 °C and stirred for 15 h under vacuum 10 mmHg. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give compound 89 as brown solid, 0.099 g, 56% yield. The regiochemistry was determined by X-ray crystallography.

**Mp** 109-111 °C. **$^1$H NMR** $\delta$1.01 (12H, s, CH$_3$), 3.85 (3H, s, CH$_3$OCO), 7.30 (2H, m, ArH), 7.71 (3H, m, ArH), 8.17 (1H, d, J= 2.0 Hz, ArH), 8.28 (1H, d, J= 2.0 Hz ArH). **$^{13}$C NMR** (62.9 MHz, CDCl$_3$): $\delta$24.9, 52.6, 82.1, 122.9, 128.5, 128.8, 129.5, 130.9, 131.6, 134.7, 140.6, 147.4, 166.1. **FTIR**: $\nu_{\text{max/CHCl}_3}$, cm$^{-1}$ 2978 (w), 1727 (s). **HRMS** (EI$^+$) Calcd for C$_{20}$H$_{22}$BBrO$_4$ 417.0873 Found: 417.0886.

**Suzuki reaction of 13 with p-iodotoluene**

A round bottom flask was charged with 13 (0.260 g, 0.594 mmol), PdCl$_2$(dpff)DCM (0.043 g, 0.059 mmol), K$_3$PO$_4$ (0.378 g, 1.780 mmol), dioxane (1 ml) and iodo toluene (0.259 g, 1.187 mmol). The flask was fitted with a reflux condenser and heated at 85 °C under N$_2$. After stirring for 48 h the reaction was cooled to room temperature and quenched by the addition of distilled water (10 ml), the product was extracted into dichloromethane (3 x 10 ml), dried (MgSO$_4$), filtered and conc. in vacuo. The product was purified by flash column
chromatography (eluting solvent petroleum ether/ethyl acetate 15:1 ratio) to give compound 16 as clear oil, wt. 0.133 g, 56% yield.

$^1$H NMR $\delta$2.24 (3H, s, CH$_3$), 6.86-6.95 (4H, m, ArH), 7.24-7.20 (2H, m, ArH), 7.49-7.50 (3H, m, ArH), 7.49 (1H, d, $J$=2.0 Hz, ArH), 7.81 (1H, d, $J$=2.0, Hz, ArH). $^{13}$C NMR (62.9 MHz, CDCl$_3$): $\delta$21.3, 113.1, 113.9, 114.2, 115.1, 126.5, 127.3, 127.7, 128.5, 129.3, 130.1, 130.4, 133.8, 134.3, 135.0. FTIR: $\nu$$_{\text{max}}$/CHCl$_3$, cm$^{-1}$ 2923 (w). HRMS (EI$^+$) Calcd for C$_{19}$H$_{14}$Br$_2$ 399.9462 Found: 399.9462.

**Suzuki reaction of 13 with p-iodotoluene**

A round bottom flask was charged with 14 (0.088 g, 0.211 mmol), PdCl$_2$(dpff)DCM (0.015 g, 0.021 mmol), K$_3$PO$_4$ (.134 g, 0.633 mmol), dioxane (1 ml) and iodotoluene (0.092 g, 0.422 mmol). The flask was fitted with a reflux condenser and heated at 85 °C under N$_2$. After stirring for 48 h the reaction was cooled to room temperature and quenched by the addition of distilled water (10 ml), the product was extracted into dichloromethane (3 x 10 ml), dried (MgSO$_4$), filtered and conc. in vacuo. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 15:1 ratio) to give compound 17 as colourless oil, wt. 0.076 g, 70% yield.

$^1$H NMR $\delta$2.18 (3H, s, CH$_3$), 3.85 (3H, s, CH$_3$OCO), 6.82-6.90 (4H, m, ArH), 6.98-7.02 (2H, m, ArH), 7.18 (3H, m, ArH), 7.94 (1H, d, $J$=1.5 Hz, ArH), 8.25 (1H, d, $J$=1.5 Hz, ArH). $^{13}$C NMR (62.9 MHz, CDCl$_3$): $\delta$21.1, 52.4, 124.7, 127.4, 127.7, 128.5, 129.4, 130.2, 130.4, 132.5, 133.4, 136.7, 137.2, 139.5, 143.7, 145.5, 165.7. FTIR: $\nu$$_{\text{max}}$/CHCl$_3$, cm$^{-1}$ 2360 (w) 1725 (s), 1240 (s). HRMS (EI$^+$) Calcd for C$_{21}$H$_{17}$BrO$_2$ 380.0412 Found: 380.0413.
Supplementary Material (ESI) for Chemical Communications
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2SHarry10 100
Scan Cl+ 2.46e5
100%

P. Delaney PD157.1521
2SHarry10 400 (7.359)
Scan Cl+ 3.77e4

P. Delaney PD157.1521
2SHarry10 405 (7.450)
Scan Cl+ 1.11e4
M$^{18}$ = mass ion + NH$_3$