Supplementary Material

An Alkynylboronate Cycloaddition Strategy to
Functionalised Benzyne Precursors.

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General Procedures

Infrared (IR) Spectra were recorded on a Perkin Elmer Paragon 100 FTIR spectrophotometer, ν\textsubscript{max} in cm\textsuperscript{-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). \textsuperscript{1}H 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\textsubscript{3}: δ7.27ppm). 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. \textsuperscript{13}C 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\textsubscript{3}: δ77.0ppm). 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\textsuperscript{+}) or a MicroMass Prospec operating in FAB (FAB\textsuperscript{+}), EI (EI\textsuperscript{+}) or CI (CI\textsuperscript{+}) mode.
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, Armarego, and Perrin (Pergamon Press, 1966). Starting alkynylboronates and pyranones were prepared according to established procedures. Coumaric acid and methyl coumalate were purchased from Aldrich chemical co. and used as received. 3-Bromo-methyl coumalate was prepared as previously reported. 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-alufolien Kieselgel 60 F254) which were developed using standard visualizing agents: Ultraviolet light or potassium permanganate.

General Procedure 1: The cycloaddition of halo-pyranones with trimethylsilylalkynyl boronic ester

A mixture of the pyranone (0.2 mmol) and trimethylsilylalkynylboronate (0.4 mmol) in mesitylene (0.2 mL) was heated at 155 °C and stirred for 16 h under N2. The product was purified by flash column chromatography (starting with petroleum ether, ending with 10% ethyl acetate in petroleum ether).

Synthesis of (4-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)trimethylsilane 10a and (5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)trimethylsilane 10b

Using General Procedure 1, with pyranone 1 (25 mg, 0.19 mmol), the product was isolated as an inseparable mixture of compounds 10a and 10b (4:3 ratio), as a clear oil, 41 mg, 70% yield.

\[ {^1}H \text{ NMR (250 MHz, CDCl}_3\text{)}: 10a: \delta 0.35 (9H, s, Si-CH}_3\text{), } 1.38 (12H, s, CH}_3\text{), } 7.38 (1H, dd, J = 2.0, 8.0 Hz, Ar-H), 7.55 (1H, d, J = 8.0 Hz, Ar-H), 7.89 (1H, d, J = 2.0 Hz, Ar-H); 10b: \delta 0.37 (9H, s, Si-CH}_3\text{), } 1.38 (12H, s, CH}_3\text{), } 7.34 (1H, dd, J = 2.0, 8.0 Hz, Ar-H), 7.57 (1H, d, J = 2.0 Hz, Ar-H), 7.87 (1H, d, J = 8.0 Hz, Ar-H). \]

\[ {^{13}}C \text{ NMR (62.9 MHz, CDCl}_3\text{)}: 10a/b: \delta 0.0, 0.1, 24.6 (x2), 83.6, 86.9, 127.4, 129.2, 130.7, 132.3, 133.8, 135.0, 135.4, 135.5, 136.3, 137.3. \]

FTIR (CH\(_2\)Cl\(_2\), thin film): 2980 (s), 1570 (m), 1388 (s), 1340 (s), 1145 (s), 845 (s) cm\(^{-1}\). HRMS calculated for C\(_{15}\)H\(_{24}\)B\(_3\)ClO\(_2\)Si (EI\(^+\)): 310.1327. Found: 310.1335.

Synthesis of (4-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)trimethylsilane 10a and (5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)trimethylsilane 10b

Using General Procedure 1, with pyranone 2 (25 mg, 0.19 mmol), the product was isolated as an inseparable mixture of compounds 10a and 10b (3:5 ratio), as a clear oil, 40 mg, 70% yield. The mixture provided the same spectroscopic data as for the compounds above.
Synthesis of (4-bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)trimethylsilane 11a and (5-bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)trimethylsilane 11b

Using General Procedure 1, with pyranone 3 (50 mg, 0.29 mmol), the product was isolated as an inseparable mixture of compounds 11a and 11b (3:2 ratio), as a clear oil, 82 mg, 80% yield.

$^1$H NMR (400 MHz, CDCl$_3$): 11 a or b: δ 0.36 (9H, s, Si-CH$_3$), 1.38 (12H, s, CH$_3$), 7.50 (1H, m, Ar-H), 7.54 (1H, m, Ar-H), 8.06 (1H, d, J = 2.0 Hz, Ar-H); 11 a or b: δ 0.38 (9H, s, Si-CH$_3$), 1.38 (12H, s, CH$_3$), 7.48 (1H, m, Ar-H), 7.74 (1H, d, J = 2.0 Hz, Ar-H), 7.80 (1H, d, J = 8.0 Hz, Ar-H). $^{13}$C NMR (62.9 MHz, CDCl$_3$): 11a/b: δ 0.5 (x2), 25.0 (x2), 84.0, 84.2, 123.4, 125.9, 130.8, 132.6, 136.0, 137.0, 137.9, 138.7, 145.6, 150.3. FTIR (CH$_2$Cl$_2$, thin film): 2980 (s), 2977 (w), 1454 (w) cm$^{-1}$. HRMS calculated for C$_{15}$H$_{24}$B$_7$O$_2$Si (EI$^+$): 355.1504. Found: 355.1507.

Synthesis of 2-(2,4-dichloro-6-trimethylsilanyl-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 12a and 2-(3,5-dichloro-2-trimethylsilanyl-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 12b

Using General Procedure 1, with pyranone 4 (25 mg, 0.15 mmol), the product was isolated as an inseparable mixture of compounds 12a and 12b (1:1 ratio), as a clear oil, 37 mg, 71% yield.
$^1$H NMR (250 MHz, CDCl$_3$): **12a/b**: $\delta$ 0.36 (9H, s, Si-CH$_3$), 0.43 (9H, s, Si-CH$_3$), 1.39 (12H, s, CH$_3$), 1.45 (12H, s, CH$_3$), 7.34 – 7.44 (4H, m, Ar-H). $^{13}$C NMR (62.9 MHz, CDCl$_3$): **12a/b**: $\delta$ 0.0, 1.7, 25.3, 25.8, 84.6, 84.9, 113.2, 115.6, 119.1, 128.7, 130.3, 131.9 (x2), 135.0, 135.3, 138.7. FTIR (CH$_2$Cl$_2$, thin film): 2981 (s), 1562 (m), 1318 (s), 1142 (s), 1050 (m), 846 (s) cm$^{-1}$. HRMS calculated for C$_{15}$H$_{23}$B$_3$Cl$_2$O$_2$Si (EI$^+$): 344.0937. Found: 344.0932.

**General Procedure 2: The cycloaddition of nitrile-pyranones with trimethylsilyl alkynyl boronic ester**

A mixture of the pyranone (0.2 mmol) and trimethylsilyl alkynyl boronate (0.4 mmol) in o-dichlorobenzene (0.2 mL) was heated at 175 °C and stirred for 18 h under N$_2$. The product was purified by flash column chromatography (starting with petroleum ether, ending with 10% ethyl acetate in petroleum ether).

**Synthesis of 3-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-4-trimethylsilanyl-benzonitrile 15a and 4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-3-trimethylsilanyl-benzonitrile 15b**

Using General Procedure 2, with pyranone 7 (25 mg, 0.21 mmol), the product was isolated as an inseparable mixture of compounds **15a** and **15b** (1:1 ratio), as a clear oil, 62 mg, 99% yield.

$^1$H NMR (250 MHz, CDCl$_3$): **15a/b**: $\delta$ 0.37 (18H, s, Si-CH$_3$), 1.38 (24H, s, CH$_3$), 7.60 – 7.73 (3H, m, Ar-H), 7.85 (1H, d, $J = 1.0$ Hz, Ar-H), 7.98 (1H, d, $J = 7.5$ Hz, Ar-H), 8.17 (1H, d, $J = 1.0$ Hz, Ar-H). $^{13}$C NMR (62.9 MHz, CDCl$_3$): **15a/b**: $\delta$ 0.0, 0.1, 24.7 (x2), 84.3 (x2), 111.6, 113.1, 118.8, 119.1, 130.6, 132.1, 134.3, 135.8, 137.0, 138.7, 148.4, 153.4. FTIR (CH$_2$Cl$_2$, thin film): 2980 (s), 2229 (s), 1342 (s), 1143 (s), 1053 (m), 843 (s) cm$^{-1}$. HRMS calculated for C$_{16}$H$_{24}$BNO$_2$Si (EI$^+$): 302.1748. Found: 302.1735.
Synthesis of 15a and 15b was also performed on gram scale: Using General Procedure 2, with pyranone 7 (0.50 g, 4.13 mmol), the product was isolated as an inseparable mixture of compounds 15a and 15b (1:1 ratio), as a clear oil, 1.28 g, quant.

Synthesis of 3-bromo-5-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-4-trimethylsilanyl-benzonitrile 16a and 3-bromo-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-5-trimethylsilanyl-benzonitrile 16b

Using General Procedure 2, with pyranone 8 (25 mg, 0.13 mmol), the product was isolated as an inseparable mixture of compounds 16a and 16b (1:1 ratio), as a clear oil, 46 mg, 96% yield.

$^1$H NMR (250 MHz, CDCl$_3$): 16a/b: δ 0.38 (9H, s, Si-CH$_3$), 0.48 (9H, s, Si-CH$_3$), 1.39 (12H, s, CH$_3$), 1.48 (12H, s, CH$_3$), 7.71 (1H, d, $J$ = 1.5 Hz, Ar-H$_1$), 7.75 (1H, d, $J$ = 1.5 Hz, Ar-H$_1$), 7.77 (1H, d, $J$ = 1.5 Hz, Ar-H$_1$), 7.81 (1H, d, $J$ = 1.5 Hz, Ar-H$_1$). $^{13}$C NMR (62.9 MHz, CDCl$_3$): 16a/b: δ 0.0, 1.9, 25.5, 26.1, 85.1, 85.6, 113.5, 113.8, 117.6, 117.9, 127.9, 131.3, 131.5, 134.8, 135.2, 135.3, 136.5, 149.0. FTIR (CH$_2$Cl$_2$, thin film): 2981 (s), 2232 (m), 1332 (s), 1140 (m), 1048 (m), 847 (s) cm$^{-1}$. HRMS calculated for C$_{16}$H$_{23}$B$_7$BrNO$_2$Si (EI$^+$): 379.0774. Found: 379.0777.

General Procedure 3: The oxidation of aromatic boronic esters

To a mixture of the aromatic boronic ester (0.2 mmol) dissolved in ethanol (8 mL), was added Na$_2$CO$_3$ (0.2 mmol). To this mixture 30% w/v H$_2$O$_2$ (2 mL) was added dropwise. The reaction was stirred at r.t.. Upon completion of reaction, 20 mL H$_2$O was added, and the product extracted from DCM (3 x 20 mL). The organic layers were combined and dried over MgSO$_4$, then concentrated in vacuo. The product was purified by flash column chromatography (eluting solvent 10 % ethyl acetate in petroleum ether).
Synthesis of 5-chloro-2-trimethylsilanyl-phenol and 4-chloro-2-trimethylsilanyl-phenol

Using General Procedure 3, with 10a,b (63 mg, 0.20 mmol), the product was isolated as an inseparable mixture of compounds (5:3 ratio) as a clear oil, 30 mg, 75 % yield.

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\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 0.32 (3.4H, s, Si-CH}_3\text{)}, 0.33 (5.6H, s, Si-CH}_3\text{)}, 4.87 (0.6H, br s, O-H), 4.98 (0.4H, br s, O-H), 6.63 (0.6H, d, J = 8.5 Hz, Ar-H), 6.72 (0.4H, d, J = 2.0 Hz, Ar-H), 6.94 (0.4H, dd, J = 2.0, 8.0 Hz, Ar-H), 7.19 (0.6H, dd, J = 2.5, 8.5 Hz, Ar-H), 7.28 – 7.30 (1H, m, Ar-H). 13C NMR (100.6 MHz, CDCl}_3\text{): -0.7, -0.6, 115.2, 116.3, 121.2, 124.4, 126.1, 128.5, 130.6, 135.2, 136.3, 136.6, 159.1, 161.3. FTIR (CH2Cl2, thin film): 3425 (br, s), 2956 (m), 1589 (m), 1479 (m), 1381 (s), 840 (s) cm\(^{-1}\). HRMS calculated for C9H14ClOSi (M+): 200.0424. Found: 200.0428.

Synthesis of 5-bromo-2-trimethylsilanyl-phenol and 4-bromo-2-trimethylsilanyl-phenol

Using General Procedure 3, with 11a,b (130 mg, 0.37 mmol), the product was isolated as an inseparable mixture of compounds (3:2 ratio) as a clear oil, 67 mg, 75 % yield.

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\text{H NMR (250 MHz, CDCl}_3\text{): } \delta 0.33 (5.4H, s, Si-CH}_3\text{)}, 0.34 (3.6H, s, Si-CH}_3\text{)}, 5.01 (0.6H, br s, O-H), 5.13 (0.4H, br s, O-H), 6.59 (0.4H, d, J = 8.5 Hz, Ar-H), 6.88 (0.6H, d, J = 1.5 Hz, Ar-H), 7.10 (0.6H, dd, J = 1.5, 8.0 Hz, Ar-H), 7.24 (0.6H, d, J = 8.0 Hz, Ar-H), 7.34 (0.4H, dd, J = 2.0, 8.5 Hz, Ar-H), 7.45 (0.4H, d, J = 2.0 Hz, Ar-H). 13C NMR (100.6 MHz, CDCl}_3\text{): -0.7, -0.6, 113.8, 116.9, 118.1, 124.1, 124.4, 125.0, 129.3, 133.6, 136.9, 138.1, 160.0, 161.4. FTIR (CH2Cl2, thin film): 3347 (br, s), 2956 (m), 2232 (s), 1588 (s), 1401 (s), 842 (s) cm\(^{-1}\). HRMS calculated for C9H13BrOSi (El+): 243.9919. Found: 243.9925.
Synthesis of 3,5-dichloro-2-trimethylsilanyl-phenol and 2,4-dichloro-6-trimethylsilanyl-phenol

Using General Procedure 3, with 12a,b (123 mg, 0.36 mmol), the product was isolated as an inseparable mixture of compounds (1:1 ratio) as a clear oil, 56 mg, 95 % yield.

\(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta 0.33 \text{ (9H, s, Si-C}_3\text{H}_3\)), 0.46 (9H, s, Si-C\(_3\)H\(_3\)), 4.70 – 6.23 (2H, br, OH), 6.65 (1H, d, J = 2.0 Hz, Ar-H\(_A\)), 6.96 (1H, d, J = 2.0 Hz, Ar-H\(_B\)), 7.20 (1H, d, J = 2.5 Hz, Ar-H\(_C\)), 7.34 (1H, d, J = 2.5 Hz, Ar-H\(_D\)). \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)): -1.3, 1.7, 114.2, 119.9, 121.9, 122.4, 125.4, 129.0, 129.1, 133.4, 136.0, 142.1, 153.9, 161.8. FTIR (CH\(_2\)Cl\(_2\), thin film): 3415 (br, s), 2959 (s), 1698 (s), 1577 (s), 1378 (s), 847 (s) cm\(^{-1}\). HRMS calculated for C\(_9\)H\(_{12}\)Cl\(_2\)OSi (EI\(^+\)): 234.0034. Found: 234.0024.

Synthesis of 3-hydroxy-4-trimethylsilanyl-benzoic acid methyl ester and 4-hydroxy-3-trimethylsilanyl-benzoic acid methyl ester

Using General Procedure 3, with 13a,b (385 mg, 1.15 mmol), the product was isolated as an inseparable mixture of compounds (3:2 ratio) as a clear oil, 180 mg, 70 % yield.

\(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta 0.35 \text{ (9H, s, Si-C}_3\text{H}_3\)), 3.92 (1.2H, s, C\(_3\)H\(_3\)), 3.94 (1.8H, s, C\(_3\)H\(_3\)), 5.60 (0.6H, br s, OH), 5.77 (0.4H, br s, OH), 6.74 (0.4H, d, J = 8.5 Hz, Ar-H\(_A\)), 7.45 (1.2H, m, Ar-H\(_B\)), 7.59 (0.6H, dd, J = 1.5, 7.5 Hz, Ar-H\(_C\)), 7.96 (0.4H, dd, J = 2.0, 8.5 Hz, Ar-H\(_D\)), 8.09 (0.4H, d, J = 2.0 Hz, Ar-H\(_D\)). \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)): \(\delta\) -1.1, -1.2, 51.9, 52.3, 114.3, 114.9, 121.3, 122.3, 125.7, 132.1 (x2), 132.9, 135.4, 137.6, 160.6, 164.5, 167.3, 167.4. FTIR (CH\(_2\)Cl\(_2\), thin film): 3375 (br, s), 2957 (m), 1687 (s), 1593 (m), 1395 (s), 1266 (s), 837 (s) cm\(^{-1}\). HRMS calculated for C\(_{11}\)H\(_{16}\)O\(_3\)Si (MH\(^+\)): 225.0947. Found: 225.0948.
Synthesis of 3-bromo-5-hydroxy-4-trimethylsilyl-benzoic acid methyl ester and 3-bromo-4-hydroxy-5-trimethylsilyl-benzoic acid methyl ester

Using General Procedure 3, with 14a,b (201 mg, 0.49 mmol), the product was isolated as an inseparable mixture of compounds (3:2 ratio) as a colourless solid, 119 mg, 81 % yield, m.pt. = 97 – 99 °C.

$^1$H NMR (250 MHz, CDCl$_3$): δ 0.35 (5.4H, s, Si-C$_3$H$_3$), 0.50 (3.6H, s, Si-C$_3$H$_3$), 3.91 (1.2H, s, C$_3$H$_3$), 3.92 (1.8H, s, CH$_3$), 6.22 (0.6H, br s, OH), 6.85 (0.4H, br s, OH), 7.45 (0.4H, d, J = 1.5 Hz, Ar-H), 7.74 (0.4H, d, J = 1.5 Hz, Ar-H). 8.00 (0.6H, d, J = 2.0 Hz, Ar-H), 8.19 (0.6H, d, J = 2.0 Hz, Ar-H). $^{13}$C NMR (100.6 MHz, CDCl$_3$): δ -0.9, -0.3, 52.6, 52.8, 110.7, 123.2, 124.1, 127.4, 127.5, 131.8, 133.2, 133.8, 135.2, 136.4, 136.8, 140.7, 166.3, 166.6. FTIR (CH$_2$Cl$_2$, thin film): 3315 (br, s), 2951 (m), 1703 (s), 1687 (s), 1258 (s), 843 (s) cm$^{-1}$. HRMS calculated for C$_{11}$H$_{15}$BrO$_3$Si (MH$^+$): 303.0052. Found: 303.0057.

Synthesis of 3-hydroxy-4-trimethylsilyl-benzonitrile 36a and 4-hydroxy-3-trimethylsilyl-benzonitrile 36b

Using General Procedure 3, with 15a,b (49 mg, 0.16 mmol), the product was isolated as an inseparable mixture of compounds (1:1 ratio) as a colourless solid, 11 mg, 71 % yield, m.pt. = 82 – 84 °C.

$^1$H NMR (250 MHz, CDCl$_3$): δ 0.34 (18H, s, Si-CH$_3$), 5.34 (1H, br s, OH), 5.75 (1H, br s, OH), 7.00 (1H, d, J = 1.0 Hz, Ar-H), 7.24 (1H, dd, J = 1.0, 7.5 Hz, Ar-H), 7.46 (1H, d, J = 7.5 Hz, Ar-H), 7.48 (1H, dd, J = 2.0, 8.0 Hz, Ar-H), 7.74 (1H, d, J = 2.0 Hz, Ar-H), 7.80 (1H, d, J = 8.0 Hz, Ar-H). $^{13}$C NMR (100.6 MHz, CDCl$_3$): δ -1.3 (x2), 103.6, 113.3, 115.1, 116.9, 118.8, 119.7, 123.9, 127.9, 133.3, 134.9, 136.1, 139.9, 160.6, 164.1. FTIR (CH$_2$Cl$_2$, thin film): 3347 (br, s), 2951 (m), 2232 (s), 1588 (s), 1401 (s), 843 (s) cm$^{-1}$. HRMS calculated for C$_{10}$H$_{13}$NO$_2$Si (MH$^+$): 192.0845. Found: 192.0846.
Synthesis of 3-bromo-5-hydroxy-4-trimethylsilanyl-benzonitrile and 3-bromo-4-hydroxy-5-trimethylsilanyl-benzonitrile

Using General Procedure 3, with 16a,b (43 mg, 0.14 mmol), the product was isolated as an inseparable mixture of compounds (3:2 ratio) as a clear oil, 26 mg, 84 % yield.

\[\text{H NMR (250 MHz, CDCl}_3\text{): }\delta 0.34 (5.4H, s, Si-CH}_3\text{), 0.50 (3.6H, s, Si-CH}_3\text{), 6.21 (0.4H, br s, OH), 6.24 (0.6H, br s, OH), 6.96 (0.6H, d, J = 1.5 Hz, Ar-H), 7.40 (0.6H, d, J = 1.5 Hz, Ar-H), 7.59 (0.4H, d, J = 2.0 Hz, Ar-H), 7.80 (0.4H, d, J = 2.0 Hz, Ar-H).}\]

\[\text{C NMR (100.6 MHz, CDCl}_3\text{): -1.1, 2.3, 105.7, 110.9, 114.8, 117.2, 117.6, 118.5, 128.9, 129.4, 131.6, 133.4, 136.9, 139.2, 160.1, 162.2.}\]

\[\text{FTIR (CH}_2\text{Cl}_2\text{, thin film): 3354 (br s), 2925 (s), 2232 (m), 1580 (m), 1249 (s), 844 (s) cm}^{-1}.\]

HRMS calculated for C\text{10}H\text{11}\text{79BrNOSi (M} -\text{)}: 267.9793. Found: 267.9793.

General Procedure 4: The sulfonylation of o-trimethylsilyl phenols

A solution of the phenol (1.0 mmol) and \text{Pr}_2\text{NEt (2.0 mmol), in DCM (1 mL) was cooled to 0 °C and stirred for 10 mins. To this mixture Tf}_2\text{O (1.5 mmol) was added dropwise. The reaction was stirred at 0 °C for a further 10 mins, then left stirring overnight at r.t.. To the reaction was added Et}_2\text{O (approx. 20 mL), then this mixture washed successively with sat. aq. NH}_4\text{Cl, sat. aq. NaHCO}_3\text{ and sat. aq. NaCl. The organic layers were then combined, dried with MgSO}_4\text{ and concentrated in vacuo. If necessary, products were purified by flash column chromatography (eluting solvent 10 % ethyl acetate in petroleum ether).}\]

Synthesis of trifluoromethanesulfonic acid 5-chloro-2-trimethylsilanyl-phenyl ester 17a and trifluoromethanesulfonic acid 4-chloro-2-trimethylsilanyl-phenyl ester 17b

\[\text{Cl-OTf + Cl-SiMe}_3\]
Using General Procedure 4 with the appropriate phenol (30 mg, 0.10 mmol), the product was isolated as an inseparable mixture of compounds 17a and 17b (5:3 ratio) as a brown oil, 48 mg, 94 % yield.

$^1$H NMR (250 MHz, CDCl$_3$): 17a/b: $\delta$ 0.37 (3.4H, s, CH$_3$), 0.39 (5.6H, s, CH$_3$), 7.24 – 7.52 (3H, m, Ar-H). $^{13}$C NMR (100.6 MHz, CDCl$_3$): 17a/b: $\delta$ -1.0, -0.9, 118.4 (x2) (q, J = 320 Hz, CF$_3$), 120.2, 121.0, 127.9, 131.0, 131.1, 133.5, 135.3, 135.9, 136.6, 136.9, 153.1, 154.7.

FTIR (CH$_2$Cl$_2$, thin film): 2928 (m), 1587 (s), 1424 (s), 1214 (s), 1140 (s), 845 (s) cm$^{-1}$. HRMS calculated for C$_{10}$H$_{12}$ClF$_3$O$_3$Si (AP$^+$): 332.9992. Found: 332.9995.

Synthesis of trifluoromethanesulfonic acid 5-bromo-2-trimethylsilanyl-phenyl ester 18a and trifluoromethanesulfonic acid 4-bromo-2-trimethylsilanyl-phenyl ester 18b

Using General Procedure 4 with the appropriate phenol (67 mg, 0.27 mmol), the product was isolated as an inseparable mixture of compounds 18a and 18b (3:2 ratio) as a brown oil, 114 mg, 100 % yield.

$^1$H NMR (250 MHz, CDCl$_3$): 18a/b: $\delta$ 0.38 (5.4H, s, CH$_3$), 0.40 (3.6H, s, CH$_3$), 7.24 (0.4H, d, J = 9.0 Hz, Ar-H), 7.43 (0.6H, m, Ar-H), 7.51 (1.2H, m, Ar-H), 7.57 (0.4H, dd, J = 2.5, 9.0 Hz, Ar-H), 7.63 (0.4H, d, J = 2.5 Hz, Ar-H). $^{13}$C NMR (100.6 MHz, CDCl$_3$): 18a/b: $\delta$ -0.6, -0.5, 118.8 (x2) (q, J = 320 Hz, CF$_3$), 121.8, 122.1, 123.4, 124.6, 131.2, 132.0, 134.4, 136.2, 137.6, 139.2, 154.1, 155.1. FTIR (CH$_2$Cl$_2$, thin film): 2960 (m), 1581 (s), 1424 (s), 1215 (s), 1141 (s), 845 (s) cm$^{-1}$. HRMS calculated for C$_{10}$H$_{12}$BrF$_3$O$_3$Si (EI$^+$): 375.9412. Found: 375.9412.
Synthesis of trifluoromethanesulfonic acid 3,5-dichloro-2-trimethylsilanyl-phenyl ester 19a and trifluoromethanesulfonic acid 2,4-dichloro-6-trimethylsilanyl-phenyl ester 19b

Using General Procedure 4 with the appropriate phenol (21 mg, 0.09 mmol), the product was isolated as an inseparable mixture of compounds 19a and 19b (1:1 ratio) as a brown oil, 18 mg, 53 % yield.

$^1$H NMR (250 MHz, CDCl$_3$): 19 a or b: $\delta$ 0.50 (9H, s, $\text{CH}_3$), 7.29 (1H, d, $J = 2.0$ Hz, Ar-H), 7.41 (1H, d, $J = 2.0$ Hz, Ar-H). 19 a or b: $\delta$ 0.43 (9H, s, $\text{CH}_3$), 7.40 (1H, d, $J = 2.5$ Hz, Ar-H), 7.52 (1H, d, $J = 2.5$ Hz, Ar-H). $^{13}$C NMR (100.6 MHz, CDCl$_3$): 19a/b: $\delta$ 0.2, 1.7, 118.9 (q, $J = 321$ Hz, CF$_3$), 119.0 (q, $J = 321$ Hz, CF$_3$), 120.0, 128.9, 130.2, 130.9, 132.4, 134.8, 134.9, 136.8, 139.8, 143.3, 147.0, 154.6. FTIR (CH$_2$Cl$_2$, thin film): 2927 (s), 1732 (w), 1607 (m), 1416 (s), 1211 (s), 820 (s) cm$^{-1}$. HRMS calculated for C$_{10}$H$_{11}$Cl$_2$F$_3$O$_3$Si (EI$^+$): 365.9527. Found: 365.9541.

Synthesis of 3-trifluoromethanesulfonyloxy-4-trimethylsilanyl-benzoic acid methyl ester 20a and 4-trifluoromethanesulfonyloxy-3-trimethylsilanyl-benzoic acid methyl ester 20b

Using General Procedure 4 with the appropriate phenol (120 mg, 0.54 mmol), the product was isolated as an inseparable mixture of compounds 20a and 20b (3:2 ratio) as a clear oil, 187 mg, 98 % yield.

$^1$H NMR (250 MHz, CDCl$_3$): 20a/b: $\delta$ 0.41 (9H, s, $\text{CH}_3$), 3.95 (1.2H, s, $\text{CH}_3$), 3.96 (1.8H, s, $\text{CH}_3$) 7.44 (0.4H, d, $J = 9.0$ Hz, Ar-H), 7.64 (0.6H, d, $J = 7.5$ Hz, Ar-H), 7.97 (0.6H, m, Ar-H), 8.01 (0.6H, dd, $J = 1.5$, 7.5 Hz, Ar-H), 8.12 (0.4H, dd, $J = 2.0$, 9.0 Hz, Ar-H), 8.22 (0.4H, d, $J = 2.0$ Hz, Ar-H). $^{13}$C NMR (100.6 MHz, CDCl$_3$): 20a/b: $\delta$ -0.6 (x2), 52.9, 53.1, 118.9 (x2) (q, $J$
Synthesis of 3-bromo-5-trifluoromethanesulfonyloxy-4-trimethylsilanyl-benzoic acid methyl ester 21a and 3-bromo-4-trifluoromethanesulfonyloxy-5-trimethylsilanyl-benzoic acid methyl ester 21b

Using General Procedure 4 with the appropriate phenol (121 mg, 0.40 mmol), the product was isolated as an inseparable mixture of compounds 21a and 21b (3:2 ratio) as a clear oil, 132 mg, 76 % yield.

$^1$H NMR (250 MHz, CDCl$_3$): 21a/b: $\delta$ 0.46 (5.4H, s, CH$_3$), 0.55 (3.6H, s, CH$_3$), 3.95 – 3.99 (3H, br, CH$_3$), 7.90 (0.4H, d, $J = 1.5$ Hz, Ar-$H$), 8.18 (0.6H, d, $J = 2.0$ Hz, Ar-$H$), 8.23 (0.4H, d, $J = 1.5$ Hz, Ar-$H$), 8.34 (0.6H, d, $J = 2.0$ Hz, Ar-$H$). $^{13}$C NMR (100.6 MHz, CDCl$_3$): 21a/b: $\delta$ 0.0, 1.5, 52.7, 52.9, 116.8, 118.5 (q, $J = 321$ Hz, CF$_3$), 118.6 (q, $J = 321$ Hz, CF$_3$), 120.3, 130.8, 131.4, 133.4, 134.0, 136.8, 136.9, 138.3, 139.8, 151.8, 154.2, 164.1, 164.7. FTIR (CH$_2$Cl$_2$, thin film): 2960 (m), 1732 (s), 1428 (s), 1214 (s), 844 (s) cm$^{-1}$. HRMS calculated for C$_{12}$H$_{15}$F$_3$O$_5$Si (AP$^+$): 434.9545. Found: 434.9541.

Synthesis of trifluoromethanesulfonic acid 5-cyano-2-trimethylsilanyl-phenyl ester 22a and trifluoromethanesulfonic acid 4-cyano-2-trimethylsilanyl-phenyl ester 22b

$^1$H NMR (250 MHz, CDCl$_3$): 21a/b: $\delta$ 0.46 (5.4H, s, CH$_3$), 0.55 (3.6H, s, CH$_3$), 3.95 – 3.99 (3H, br, CH$_3$), 7.90 (0.4H, d, $J = 1.5$ Hz, Ar-$H$), 8.18 (0.6H, d, $J = 2.0$ Hz, Ar-$H$), 8.23 (0.4H, d, $J = 1.5$ Hz, Ar-$H$), 8.34 (0.6H, d, $J = 2.0$ Hz, Ar-$H$). $^{13}$C NMR (100.6 MHz, CDCl$_3$): 21a/b: $\delta$ 0.0, 1.5, 52.7, 52.9, 116.8, 118.5 (q, $J = 321$ Hz, CF$_3$), 118.6 (q, $J = 321$ Hz, CF$_3$), 120.3, 130.8, 131.4, 133.4, 134.0, 136.8, 136.9, 138.3, 139.8, 151.8, 154.2, 164.1, 164.7. FTIR (CH$_2$Cl$_2$, thin film): 2960 (m), 1732 (s), 1428 (s), 1214 (s), 844 (s) cm$^{-1}$. HRMS calculated for C$_{12}$H$_{15}$F$_3$O$_5$Si (AP$^+$): 434.9545. Found: 434.9541.
Using General Procedure 4 with the appropriate phenol (200 mg, 1.05 mmol), the product was isolated as an inseparable mixture of compounds 22a and 22b (1:1 ratio) as a brown oil, 375 mg, 100 % yield.

$^1$H NMR (250 MHz, CDCl$_3$): 22a/b: δ 0.41 (18H, s, CH$_3$), 7.50 (1H, d, $J = 8.5$ Hz, Ar-H), 7.85 (3H, m, Ar-H), 7.77 (1H, dd, $J = 2.0$, 8.5 Hz, Ar-H), 7.84 (1H, d, $J = 2.0$ Hz, Ar-H). $^{13}$C NMR (100.6 MHz, CDCl$_3$): 22a/b: δ -0.72, -0.68, 114.8 (x2) (q, $J = 478$ Hz, CF$_3$), 115.3, 117.5, 118.1, 120.4, 120.6, 123.1, 131.1, 135.4, 135.5, 137.6, 140.3, 140.7, 154.7, 157.5. FTIR (CH$_2$Cl$_2$, thin film): 2924 (s), 2236 (s), 1426 (s), 1216 (s), 846 (s) cm$^{-1}$. HRMS calculated for C$_{11}$H$_{12}$F$_3$NO$_3$SSi (AP$^+$): 324.0338. Found: 324.0329.

Synthesis of trifluoromethanesulfonic acid 3-bromo-5-cyano-2-trimethylsilanyl-phenyl ester 23a and trifluoromethanesulfonic acid 2-bromo-4-cyano-6-trimethylsilanyl-phenyl ester 23b

![Diagram of 23a and 23b](image)

Using General Procedure 4 with the appropriate phenol (248 mg, 0.92 mmol), the product was isolated as an inseparable mixture of compounds 23a and 23b (1:1 ratio) as a clear oil, 220 mg, 60 % yield.

$^1$H NMR (250 MHz, CDCl$_3$): 23a/b: δ 0.44 (9H, s, CH$_3$), 0.55 (9H, s, CH$_3$), 7.58 (1H, d, $J = 1.5$ Hz, Ar-H), 7.80 (1H, d, $J = 1.5$ Hz, Ar-H), 7.87 (1H, d, $J = 2.0$ Hz, Ar-H), 7.98 (1H, d, $J = 2.0$ Hz, Ar-H). $^{13}$C NMR (100.6 MHz, CDCl$_3$): 23a/b: δ 0.3, 1.8, 115.8, 116.0, 116.2 (q, $J = 403$ Hz, CF$_3$), 116.7, 118.9 (q, $J = 321$ Hz, CF$_3$), 123.0, 132.5, 136.3, 139.1, 139.8, 139.1, 139.8, 140.6, 141.7, 152.0, 154.2. FTIR (CH$_2$Cl$_2$, thin film): 2926 (m), 2237 (s), 1524 (m), 1414 (s), 1136 (s), 844 (s) cm$^{-1}$. HRMS calculated for C$_{11}$H$_{11}$BrF$_3$NO$_3$SSi (AP$^+$): 401.9443. Found: 401.9429.
General Procedure 5: The cycloaddition of benzyne precursors with benzyl azide

To a mixture of benzyne precursor (0.12 mmol) and benzyl azide (0.10 mmol), dissolved in MeCN (0.12 mL), was added CsF (0.2 mmol). The reaction was then left to stir at r.t. for 18 hrs. The mixture was poured onto sat. aq. NaHCO₃, and then extracted with DCM (3 x 10 mL). The organic layers were combined, dried over MgSO₄, and concentrated in vacuo. The crude product was purified via flash column chromatography (eluting solvent 10 % ethyl acetate in petroleum ether).

Synthesis of 1-benzyl-5-bromo-1H-benzotriazole 24a and 1-benzyl-6-bromo-1H-benzotriazole 24b

Using General Procedure 5, with benzyne precursor 18a,b (50 mg, 0.08 mmol), the product was isolated as an inseparable mixture of compounds 24a and 24b (2:1 ratio), as a brown solid, 23 mg, 70 % yield, m.pt. = 83 – 85 °C.

\(^1\)H NMR (250 MHz, CDCl₃): δ 5.84 (0.7H, s, CH₂), 5.86 (1.3H, s, CH₂), 7.25 (0.7H, dd, \(J = 0.5, 9.0\) Hz, Ar-H), 7.27 – 7.42 (5H, m, Ar-H), 7.47 (0.3H, dd, \(J = 1.5, 9.0\) Hz, Ar-H), 7.51 (0.7H, dd, \(J = 1.5, 9.0\) Hz, Ar-H), 7.57 (0.3H, dd, \(J = 0.5, 1.5\) Hz, Ar-H), 7.96 (0.3H, dd, \(J = 0.5, 9.0\) Hz, Ar-H), 8.25 (0.7H, dd, \(J = 0.5, 1.5\) Hz, Ar-H).\(^{13}\)C NMR (100.6 MHz, CDCl₃): 24a/b: δ 52.8, 53.0, 111.5, 113.0, 117.7, 121.7, 122.2, 123.1, 126.4, 128.0, 128.2, 129.1, 129.5, 129.6, 131.2, 132.2, 134.3, 134.7, 141.2, 145.6, 148.0, 151.2. FTIR (CH₂Cl₂, thin film): 2923 (m), 1605 (m), 1474 (m), 1203 (s), 734 (s) cm⁻¹. HRMS calculated for \(\text{C}_{13}\text{H}_{10}^7\text{BrN}_3\) (ES⁺): 288.0136. Found: 288.0132.
Synthesis of 1-benzyl-1H-benzotriazole-5-carboxylic acid methyl ester 25a and 3-benzyl-3H-benzotriazole-5-carboxylic acid methyl ester 25b

Using General Procedure 5, with benzyne precursor 20a,b (50 mg, 0.14 mmol), the product was isolated as an inseparable mixture of compounds 25a and 25b (1:1 ratio), as a brown solid, 21 mg, 67 % yield, m.pt.= 75 – 78 °C.

1H NMR (400 MHz, CDCl₃): 25a/b: δ 3.97 (3H, s, CH₃), 3.99 (3H, s, CH₃), 5.90 (2H, s, CH₂), 5.92 (2H, s, CH₂), 7.30 – 7.43 (11H, m, Ar-H), 8.05 (1H, dd, J = 1.5, 8.5 Hz, Ar-H), 8.10 – 8.15 (2H, m, Ar-H), 8.19 (1H, dd, J = 1.0, 1.5 Hz, Ar-H), 8.82 (1H, dd, J = 1.0, 1.5 Hz, Ar-H).

13C NMR (100.6 MHz, CDCl₃): 25a/b: δ 52.9 (x3), 53.0, 110.0, 112.7, 120.4, 123.4, 125.1, 126.8, 128.0 (x2), 128.7, 129.1, 129.6, 129.7, 133.0, 134.7, 134.8, 135.5, 146.5, 148.7, 149.1, 157.0, 166.9 (x2). FTIR (CH₂Cl₂, thin film): 2953 (m), 1722 (s), 1436 (s), 1288 (s), 733 (s) cm⁻¹. HRMS calculated for C₁₅H₁₃N₃O₂ (M⁺): 268.1086. Found: 268.1086.

Synthesis of 1-benzyl-1H-benzotriazole-5-carbonitrile 26a and 3-benzyl-3H-benzotriazole-5-carbonitrile 26b

Using General Procedure 5, with benzyne precursor 22a,b (25 mg, 0.08 mmol), the product was isolated as an inseparable mixture of compounds 26a and 26b (2:1 ratio), as a brown solid, 10 mg, 65 % yield, m.pt.= 72 – 74 °C.

1H NMR (250 MHz, CDCl₃): δ 5.91 (1.3H, s, CH₂), 5.92 (0.7H, s, CH₂), 7.29 – 7.43 (5H, m, Ar-H), 7.47 (0.7H, dd, J = 0.5, 8.5 Hz), 7.57 (0.3H, dd, J = 1.5, 8.5 Hz, Ar-H), 7.63 (0.7H, dd, J = 1.5, 8.5 Hz, Ar-H), 7.74 (0.3H, s, Ar-H), 8.19 (0.3H, dd, J = 0.5, 8.5 Hz, Ar-H), 8.47 (0.7H, s, Ar-H). 13C NMR (100.6 MHz, CDCl₃): δ 52.8, 53.0, 107.9 (x2), 111.3 (x2), 115.7 (x2), 115.7 (x2),
118.5, 119.1, 121.6 (x2), 126.3, 126.4, 127.7, 129.0, 129.3, 129.7, 133.8, 134.4, 135.8, 138.0, 141.4, 145.5. FTIR (CH₂Cl₂, thin film): 2924 (m), 2232 (m), 1569 (m), 1432 (m), 1205 (m), 720 (m) cm⁻¹. HRMS calculated for C₁₄H₁₀N₄ (MH⁺): 235.0984. Found: 235.0975.

**General Procedure 6: The cycloaddition of benzyne precursors with furans**

To a mixture of benzyne precursor (0.10 mmol) and furan (0.50 mmol), dissolved in MeCN (3 mL), was added CsF (0.30 mmol). The reaction was then left to stir at r.t. for 18 hrs. The mixture was then poured onto sat. aq. NaHCO₃, and then extracted from DCM (3 x 10 mL). The organic layers were combined, dried over MgSO₄, and concentrated in vacuo. The crude product was purified via flash column chromatography (eluting solvent 10 % ethyl acetate in petroleum ether).

**Synthesis of 11-Oxa-tricyclo[6.2.1.0²,⁷]undeca-2,4,6,9-tetraene-4-carboxylic acid methyl ester 27**

![Structure of compound 27](image)

Using General Procedure 6, with benzyne precursor **20a,b** (25 mg, 0.07 mmol), the product 27 was isolated as a colourless solid, 10 mg, 68 % yield. The compound gave satisfactory spectroscopic data in comparison with the literature.⁴

¹H NMR (250 MHz, CDCl₃): δ 3.91 (3H, s, CH₃), 5.77 (2H, m, CH), 7.05 (2H, m, CH), 7.32 (1H, d, J = 7.5 Hz, Ar-H), 7.78 (1H, d, J = 7.5 Hz, Ar-H), 7.89 (1H, s, Ar-H). ¹³C NMR (100.6 MHz, CDCl₃): 52.5, 82.6 (x2), 120.4, 121.1, 127.7, 128.5, 142.8, 143.8, 150.0, 154.8, 167.4.

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⁴ Kitamura, T.; Wasai, K.; Todaka, M.; Fujiwara, Y. *Synlett*. 1999, 6, 731
Synthesis of 11-Oxa-tricyclo[6.2.1.0²⁷]undeca-2,4,6,9-tetraene-4-carbonitrile 28

Using General Procedure 6, with benzyne precursor 22a,b (50 mg, 0.16 mmol), the product 28 was isolated as a colourless solid, 17 mg, 66 % yield. The compound gave satisfactory spectroscopic data in comparison with the literature.

\[ ^1H\text{ NMR (250 MHz, CDCl}_3\rrbracket: \delta 5.79 (2H, m, CH), 7.06 (2H, m, CH), 7.36 (2H, m, Ar-H), 7.48 (1H, s, Ar-H). \]

\[ ^{13}C\text{ NMR (100.6 MHz, CDCl}_3\rrbracket: \delta 82.3, 82.6, 119.6, 121.1, 123.2, 131.4, 135.4, 140.9, 143.0, 143.5, 155.8. \]

Synthesis of 1-tert-Butyl-11-oxa-tricyclo[6.2.1.0²⁷]undeca-2,4,6,9-tetraene-4-carboxylic acid methyl ester 29a and 8-tert-Butyl-11-oxa-tricyclo[6.2.1.0²⁷]undeca-2,4,6,9-tetraene-4-carboxylic acid methyl ester 29b

Using General Procedure 6, with benzyne precursor 20a,b (30 mg, 0.08 mmol), the product was isolated as an inseparable mixture of compounds 29a and 29b (1:1 ratio), 14 mg, 63 % yield.

\[ ^1H\text{ NMR (250 MHz, CDCl}_3\rrbracket: 29a/b: \delta 1.29 (9H, s, CH}_3, 1.33 (9H, s, CH}_3, 3.90 (3H, s, CH}_3) 3.91 (3H, s, CH}_3, 5.69 (1H, m, CH), 5.70 (1H, m, CH), 6.93 – 7.08 (4H, m, CH), 7.26 (1H, d, J = 7.5 Hz, Ar-H), 7.45 (1H, d, J = 7.5 Hz, Ar-H), 7.74 (2H, m, Ar-H), 7.82 (1H, d, J = 1.0 Hz, Ar-H), 8.00 (1H, m, Ar-H). \]

\[ ^{13}C\text{ NMR (100.6 MHz, CDCl}_3\rrbracket: 29a/b: \delta 27.0 (x2), 32.9 (x2), 52.5 (x2), 81.6, 81.7, 100.1 (x2), 120.0, 120.6, 121.7, 122.4, 127.0, 127.1, 127.9, 128.0, 142.7, \]

143.6, 144.2, 145.2, 150.2, 153.1, 155.3, 158.0, 167.4, 167.5. FTIR (CH₂Cl₂, thin film): 2958 (m), 1720 (s), 1435 (s), 1258 (s), 769 (s) cm⁻¹. HRMS calculated for C₁₅H₁₈O₃ (ES⁺): 259.1334. Found: 259.1337.

**Synthesis of 3-benzyl-7-bromo-3H-benzotriazole-5-carbonitrile 30a and 1-benzyl-7-bromo-1H-benzotriazole-5-carbonitrile 30b**

To a mixture of benzyne precursor 23a/b (50 mg, 0.12 mmol) and benzyl azide (80 mg, 0.60 mmol), dissolved in MeCN (0.6 mL), was added CsF (91 mg, 0.60 mmol). The reaction was then left to stir at r.t. for 18 hrs. The mixture was then poured onto sat. aq. NaHCO₃, and then extracted from DCM (3 x 10 mL). The organic layers were combined, dried over MgSO₄, and concentrated in vacuo. The crude product was purified via flash column chromatography (eluting solvent 10 % ethyl acetate in petroleum ether). The product was isolated as an inseparable mixture of compounds 30a and 30b (5:1 ratio), as a brown oil, 11 mg, 29 % yield.

¹H NMR (250 MHz, CDCl₃): 30a/b: δ 5.92 (1.7H, s, CH₂), 6.23 (0.3H, s, CH₂), 7.08 – 7.46 (5H, m, Ar-H), 7.67 (0.8H, d, J = 1.0 Hz, Ar-H), 7.78 (1H, d, J = 0.8 Hz, Ar-H), 7.87 (0.2H, d, J = 1.0 Hz, Ar-H). ¹³C NMR (100.6 MHz, CDCl₃): δ 52.9, 53.6, 112.0, 112.7, 114.5, 114.8 (x2), 115.2, 117.1, 117.3, 117.9, 123.4, 123.9, 125.3, 126.8, 127.1, 127.7, 128.6, 129.0, 129.1, 129.4, 129.5, 133.1, 133.3. FTIR (CH₂Cl₂, thin film): 2924 (m), 2232 (m), 1569 (m), 1432 (m), 1205 (m), 720 (m) cm⁻¹. HRMS calculated for C₁₄H₇⁷BrN₄ (ES⁺): 313.0078. Found: 313.0089.