A cycloaddition route to novel triazole boronic esters

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1. General Information

All reactions were conducted in oven or flame-dried glassware under an inert atmosphere of dry nitrogen. Flash chromatography was performed on silica gel (BDH Silica Gel 60 43-60, or Fluorochem Davisil silica gel 43-60). The solvent system used was a gradient of petroleum ether or cyclohexane/ethyl acetate (90-10), increasing in polarity to ethyl acetate. 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. $^1$H/$^{13}$C NMR spectra were recorded on Bruker AC-250 or Av1-250 instruments or AMX-400 or AV1-400 instruments. $^1$H: Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CHCl$_3$: $\delta$7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, br=broad, m=multiplet), integration, coupling constants (J) in Hz, and assignment. $^{13}$C NMR spectra were with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl$_3$: $\delta$77.0 ppm). Infrared (FTIR) spectra were recorded on a Perkin Elmer Paragon 100 FTIR spectrophotometer, $\nu_{\text{max}}$ in cm$^{-1}$. Bands are characterized as broad (br), strong (s), medium (m) and weak (w). Samples were recorded as thin films using sodium chloride plates, as a DCM solution or as a KBr disc. Low resolution mass spectra were recorded on Micromass Autospec, operating in E.I., C.I. or FAB mode; or a Perkin-Elmer Turbomass Bench top 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 either FAB (FAB+), EI (EI+) or CI (CI+) mode. Melting points were performed on recrystallised solids and 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).
2. Synthesis of TMS-triazole boronic esters

![Image of compound 2]

A mixture of benzyl azide (500 mg, 3.80 mmol) and alkyne 1 (1.01 g, 4.50 mmol) in 1,2-dichlorobenzene (15 mL) was heated at 110 °C for 24 h under N₂. The crude product was purified by flash column chromatography on cyclohexane/ethyl acetate (4:1) to give triazole 2 (1.14 g, 84%) as a colourless solid. Mp 64-66 °C. ¹H NMR (250 MHz, CDCl₃) δ; 7.29-7.26 (5 H, m), 5.82 (2 H, s), 1.29 (12 H, s), 0.37 (9 H, s). ¹³C NMR (62.9 MHz, CDCl₃) δ; 156.6, 136.9, 128.4, 127.7 (x 2C), 84.7, 53.2, 24.8, -0.8. FTIR 2978 (m), 1503 (m), 1374 (s), 1348 (s), 1321 (s), 1142 (s), 1080 (s), 844 (s), 724 (m). HRMS (EI⁺) calculated for C₁₈H₂₈BN₃O₂Si: 357.2044. Found: 357.2059.

![Image of compound 3]

A mixture of 1-(azidomethyl)-4-tert-butylbenzene (76 mg, 0.40 mmol) and alkyne 1 (108 mg, 0.48 mmol) in 1,2-dichlorobenzene (1.6 mL) was heated at 110 °C for 24 h under N₂. The crude product was purified by flash column chromatography on cyclohexane/ethyl acetate (4:1) to give triazole 3 (114 mg, 69%) as a colourless solid. Mp 77-79 °C. ¹H NMR (400 MHz, CDCl₃) δ; 7.32 (2 H, d, J = 8.0 Hz), 7.24 (2 H, d, J = 8.0 Hz), 5.77 (2 H, s), 1.29 (12 H, s), 0.36 (9 H, s). ¹³C NMR (100.6 MHz, CDCl₃) δ; 156.3, 150.8, 133.8, 127.6, 125.3, 84.6, 52.9, 34.5, 31.3, 24.7, -0.8. FTIR 2962 (m), 1510 (s), 1374 (s), 1344

S3
A mixture of 1-(azidomethyl)-3-methylbenzene (147 mg, 1.0 mmol) and alkyne 1 (288 mg, 1.2 mmol) in 1,2-dichlorobenzene (4.0 mL) was heated at 110 °C for 24 h under N₂. The crude product was purified by flash column chromatography on cyclohexane/ethyl acetate (4:1) to give triazole 4 (271 mg, 73%) as a colourless oil. ¹H NMR (400 MHz, CDCl₃) δ; 7.20-7.15 (2 H, m), 7.09 (1 H, d, J = 8.0 Hz), 7.06 (1 H, d, J = 8.0 Hz), 5.76 (2 H, s), 2.30 (3 H, s), 1.29 (12 H, s), 0.36 (9 H, s). ¹³C NMR (100.6 MHz, CDCl₃) δ; 156.4, 138.0, 136.6, 128.6, 128.5, 128.2, 124.9, 84.5, 53.1, 24.7, 21.3, -0.9. FTIR 2978 (w), 1508 (m), 1474 (s), 1323 (s), 1141 (s), 1070 (s), 840 (s), 747 (m). HRMS (ESI+) calculated for C₁₉H₃₀BN₃O₂Si: 372.2273. Found: 372.2273.

A mixture of 1-(4-azidophenyl)ethanone (48 mg, 0.30 mmol) and alkyne 1 (81 mg, 0.36 mmol) in 1,2-dichlorobenzene (1.2 mL) was heated at 110 °C for 48 h under N₂. The crude product was purified by flash column chromatography on DCM/ethyl acetate (4:1) to give triazole 5 (75 mg, 65%) as a colourless solid. Mp: 91-93 °C. ¹H NMR (400 MHz, CDCl₃) δ; 8.08 (2 H, d, J = 8.0 Hz), 7.66 (2 H, d, J = 8.0 Hz), 2.68 (3 H, s), 1.27 (12 H, s), 0.43 (9 H, s). ¹³C NMR (100.6 MHz, CDCl₃) δ; 197.1, 164.7, 141.6, 137.2, 128.8,
A mixture of octyl azide (115 mg, 1.0 mmol) and alkyne 1 (288 mg, 1.2 mmol) in 1,2-dichlorobenzene (4 mL) was heated at 110 °C for 48 h under N₂. The crude product was purified by flash column chromatography on cyclohexane/ethyl acetate (4:1) to give triazole 6 (258 mg, 68%) as a colourless oil. ^1H NMR (400 MHz, CDCl₃) δ; 4.59 (2 H, t, \( J = 8.0 \) Hz), 1.86-1.81 (2 H, m), 1.36 (12 H, s), 1.31-1.23 (10 H, m), 0.88 (3 H, t, \( J = 8.0 \) Hz), 0.37 (9 H, s). ^13C NMR (100.6 MHz, CDCl₃) δ; 156.1, 84.5, 50.0, 31.8, 31.5, 29.1 (x 2C), 26.6, 24.9, 22.6, 14.1, -0.8. FTIR 2928 (m), 2852 (m), 1508 (s), 1458 (m), 1374 (m), 1319 (s), 1142 (m), 843 (s). HRMS (EI+) calculated for C₁₉H₂₉BN₃O₃Si: 380.2905. Found: 380.2907.

A mixture of ethyl azidoacetate (39 mg, 0.3 mmol) and alkyne 1 (81 mg, 0.36 mmol) in 1,2-dichlorobenzene (1.2 mL) was heated at 110 °C for 48 h under N₂. The crude product was purified by flash column chromatography on cyclohexane/ethyl acetate (2:1) to give triazole 7 (79 mg, 75%) as a colourless oil. ^1H NMR (400 MHz, CDCl₃) δ; 5.39 (2 H, s), 4.20 (2 H, q, \( J = 7.0 \) Hz), 1.31 (12 H, s), 1.26 (3 H, t, \( J = 7.0 \) Hz), 0.37 (9 H, s). ^13C
NMR (100.6 MHz, CDCl$_3$) $\delta$; 167.3, 156.4, 84.7, 61.7, 51.1, 24.7, 14.1, -0.9. FTIR 2987 (w), 1753 (s), 1464 (m), 1265 (s), 1212 (s), 1023 (m), 744 (m), 700 (s). HRMS (ESI+) calculated for C$_{15}$H$_{29}$BN$_3$O$_4$Si: 354.2015. Found: 354.2018.
3. Functional Group Transformations of TMS- Triazole Boronic Esters

A mixture of triazole boronic ester 2 (860 mg, 2.4 mmol), Pd$_2$dba$_3$ (100 mg, 5 mol%), tBu$_3$PH.BF$_4$ (80 mg, 12 mol%), K$_3$PO$_4$ (1020 mg, 4.8 mmol), iodobenzene (1.00 g, 4.8 mmol) in MeCN (20 mL) was heated at 50 °C under N$_2$ for 16 h, the reaction mixture was then filtered through celite and concentrated in vacuo. The crude product was purified by flash column chromatography on petroleum/ethyl acetate (10:1) to give triazole 8 (715 mg, 97%) as a clear colourless solid. Mp 40-42 °C. $^1$H NMR (250 MHz, CDCl$_3$) δ; 7.46-7.39 (3 H, m), 7.28-7.23 (3 H, m), 7.11-7.07 (2 H, m), 7.03-6.99 (2 H, m), 5.38 (2 H, s), 0.14 (9 H, s). $^{13}$C NMR (62.9 MHz, CDCl$_3$) δ; 146.2, 143.6, 135.7, 130.1, 129.4, 128.6, 128.5, 128.0, 127.6 (x 2C), 51.4, -0.9. FTIR 3072 (m), 2958 (s), 2895 (m), 1451 (s), 1412 (s), 1250 (s), 842 (s), 760 (s). HRMS (EI+) calculated for C$_{18}$H$_{21}$N$_3$Si: 307.1505. Found: 307.1510.

A mixture of triazole boronic ester 2 (43 mg, 0.12 mmol), Pd$_2$dba$_3$ (5 mg, 5 mol%), tBu$_3$PH.BF$_4$ (4 mg, 12 mol%), K$_3$PO$_4$ (51 mg, 0.24 mmol), 1-iodo-4-methoxybenzene (56 mg, 0.24 mmol) in MeCN (1 mL) was heated at 50 °C under N$_2$ for 16 h, the reaction mixture was then filtered through celite and concentrated in vacuo. The crude product
was purified by flash column chromatography on petroleum/ethyl acetate (10:1) to give triazole 9 (29 mg, 72 %) as a clear colourless solid. Mp 71-72 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$; 7.28-7.26 (3 H, m), 7.05-7.03 (2 H, m), 7.01 (2 H, d, $J = 8.0$ Hz), 6.92 (2 H, d, $J = 8.0$ Hz), 5.37 (2 H, s), 3.87 (3 H, s), 0.15 (9 H, s).$^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$; 160.4, 144.9, 143.4, 135.8, 131.3, 128.6, 128.0, 127.6, 120.4, 113.9, 55.3, 51.3, -0.8. FTIR 2965 (m), 1614 (s), 1481 (s), 1291 (s), 1250 (s), 1178 (s), 1034 (m), 843 (s). HRMS (EI+) calculated for C$_{19}$H$_{23}$N$_3$OSi : 337.1610. Found: 337.1613.

A mixture of triazole boronic ester 2 (71 mg, 0.2 mmol), Pd$_2$dba$_3$ (9 mg, 5 mol%), $^t$Bu$_3$PH.BF$_4$ (7 mg, 12 mol%), K$_3$PO$_4$ (85 mg, 0.4 mmol), 1-iodo-4-nitrobenzene (100 mg, 0.4 mmol) in MeCN (2 mL) was heated at 50 °C under N$_2$ for 16 h, the reaction mixture was then filtered through celite and concentrated in vacuo. The crude product was purified by flash column chromatography on petroleum/ethyl acetate (10:1) to give triazole 10 (46 mg, 66 %) as a clear colourless solid. Mp 100-102 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$; 8.23 (2 H, d, $J = 9.0$ Hz), 7.26-7.22 (5 H, m), 6.98-6.93 (2 H, m), 5.41 (2 H, s), 0.14 (9 H, s). $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$; 148.4, 145.9, 141.2, 135.7, 135.1, 131.1, 128.9, 128.4, 127.4, 123.6, 51.9, -0.8. FTIR 2928 (m), 1721 (m), 1524 (s), 1341 (s), 842 (s). HRMS (EI+) calculated for C$_{18}$H$_{20}$N$_4$O$_2$Si: 352.1356. Found: 352.1369.
A mixture of triazole boronic ester 2 (36 mg, 0.1 mmol) and copper(II) chloride (27 mg, 0.2 mmol) in MeCN (2 mL) was heated at 50 °C under N₂ for 16 h the reaction was then filtered through celite and concentrated in vacuo. The product was purified by flash column chromatography on petroleum/ethyl acetate (10:1) to give triazole 11 (20 mg, 75%) as a colourless oil. ¹H NMR (400 MHz, CDCl₃) δ; 7.39-7.30 (5 H, s), 5.53 (2 H, s), 0.36 (9 H, s). ¹³C NMR (100.6 MHz, CDCl₃) δ; 142.7, 134.2, 131.1, 128.9, 128.5, 127.9, 51.4, -1.6. FTIR 2958 (m), 1727 (w), 1467 (s), 1456 (s), 1250 (s), 840 (s), 721 (s). HRMS (ESI+) calculated for C₁₂H₁₇Cl₃N₃Si: 266.0875. Found: 266.0876.

A mixture of triazole boronic ester 2 (71 mg, 0.2 mmol) and copper(II) bromide (89 mg, 0.4 mmol) in MeCN (4 mL) was heated at 50 °C under N₂ for 16 h the reaction was then filtered through celite and concentrated in vacuo. The product was purified by flash column chromatography on petroleum/ethyl acetate (10:1) to give triazole 12 (51 mg, 82%) as a colourless oil. ¹H NMR (400 MHz, CDCl₃) δ; 7.37-7.29 (5 H, s), 5.57 (2 H, s), 0.38 (9 H, s). ¹³C NMR (100.6 MHz, CDCl₃) δ; 145.7, 134.3, 128.8, 128.4, 127.8, 117.1, 52.1, -1.5. FTIR 2957 (m), 1453 (s), 1250 (s), 1203 (s), 1026 (m), 837 (s), 720 (s). HRMS (ESI+) calculated for C₁₂H₁₇N₃SiBr: 310.0375. Found: 310.0372.
A mixture of triazole 8 (123 mg, 0.4 mmol) and NBS (356 mg, 2.0 mmol) in MeCN (10 mL) was heated at reflux under N₂ for 16 h. The reaction was then filtered through celite and concentrated *in vacuo*. The product was purified by flash column chromatography on petroleum ether/ethyl acetate (5:1) to give triazole 13 (125 mg, 99%) as a yellow solid. Mp 90-92 °C. ¹H NMR (250 MHz, CDCl₃) δ: 7.49-7.46 (3 H, m), 7.29-7.23 (5 H, m), 7.07-7.03 (2 H, m), 5.49 (2 H, s). ¹³C NMR (100.6 MHz, CDCl₃) δ: 136.2, 134.7, 130.1, 129.7, 129.0, 128.9, 128.5, 127.5, 125.4, 120.7, 53.1. FTIR 3068 (m) 3026 (m), 1496 (s), 1450 (s), 1265 (s), 988 (m), 767 (s), 694 (s). HRMS (EI+) calculated for C₁₅H₁₂N₃Br: 313.0215. Found: 313.0208.

A mixture of triazole 8 (200 mg, 0.65 mmol) and NIS (731 mg, 3.25 mmol) in MeCN (15 mL) was heated at reflux under N₂ for 4 days. The reaction was then filtered through celite and concentrated *in vacuo*. The product was purified by flash column chromatography on petroleum ether/ethyl acetate (5:1) to give triazole 14 (219 mg, 94%) as a yellow solid. Mp 68-70 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.53-7.45 (3 H, m), 7.30-7.26 (3 H, m), 7.23-7.20 (2 H, m), 7.05-7.03 (2 H, m), 5.51 (2 H, s). ¹³C NMR (100.6 MHz, CDCl₃) δ: 140.4, 134.8, 130.1, 129.9, 129.0, 128.8, 128.4, 127.5, 126.2, 90.4, 53.0. FTIR 3067 (m) 3037 (m), 1476 (s), 1450 (s), 1245 (s), 987 (s), 844 (s), 731 (s), 694 (s). HRMS (EI+) calculated for C₁₅H₁₂N₃I: 313.0215. Found: 313.0208.
A mixture of triazole 14 (54 mg, 0.15 mmol), Pd_{2}dba\textsubscript{3} (7 mg, 5 mol%), \textsuperscript{1}Bu\textsubscript{3}PH.BF\textsubscript{4} (5 mg, 12 mol%), K\textsubscript{3}PO\textsubscript{4} (64 mg, 0.30 mmol), 4-chlorobenzene boronic acid pinacol ester (64 mg, 0.30 mmol) in MeCN (2 mL) was heated at 50 °C under N\textsubscript{2} for 48 h, the reaction mixture was then filtered through celite and concentrated in vacuo. The crude product was purified by flash column chromatography on petroleum/ethyl acetate (10:1) to give triazole 15 (39 mg, 75 %) as a colourless oil. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ; 7.52-7.42 (5 H, m), 7.28-7.22 (5 H, m), 7.14 (2 H, dd, J = 7.0, 1.5 Hz), 7.04-7.02 (2 H, m), 5.42 (2 H, s). \textsuperscript{13}C NMR (100.6 MHz, CDCl\textsubscript{3}) δ; 143.6, 135.2, 134.0, 133.6, 131.6, 130.0, 129.9, 129.4, 129.3, 128.7 (x 2C), 128.2, 127.9, 127.5, 52.1. FTIR 2924 (m) 1455 (s), 1243 (s), 1026 (m), 983 (s), 794 (m), 763 (s). HRMS (ESI+) calculated for C\textsubscript{21}H\textsubscript{16}\textsuperscript{35}ClN\textsubscript{3}: 346.1106. Found: 346.1106.

A mixture of triazole 14 (54 mg, 0.15 mmol), Pd_{2}dba\textsubscript{3} (7 mg, 5 mol%), \textsuperscript{1}Bu\textsubscript{3}PH.BF\textsubscript{4} (5 mg, 12 mol%), K\textsubscript{3}PO\textsubscript{4} (64 mg, 0.30 mmol), 3-methoxylphenyl boronic acid pinacol ester (74 mg, 0.30 mmol) in MeCN (2 mL) was heated at 50 °C under N\textsubscript{2} for 48 h, the reaction mixture was then filtered through celite and concentrated in vacuo. The crude product
was purified by flash column chromatography on petroleum/ethyl acetate (10:1) to give triazole 16 (33 mg, 65 %) as a colourless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.51-7.41 (3 H, m), 7.27-7.25 (3 H, m), 7.19-7.13 (4 H, m), 7.11-7.08 (1 H, m), 7.04-7.02 (2 H, m), 6.81-6.78 (1 H, m), 5.42 (2 H, s), 3.68 (3 H, s). \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\): 175.8, 159.6, 144.4, 135.3, 134.0, 132.2, 130.2, 129.7, 129.5, 129.2, 128.7, 128.2, 127.5, 119.0, 114.3, 111.4, 55.1, 52.1. FTIR 1604 (m), 1584 (m), 1455 (m), 1290 (m), 1238 (s), 1042 (m), 854 (m), 701 (s). HRMS (ESI+) calculated for C\(_{22}\)H\(_{20}\)N\(_3\)O: 342.1601. Found: 342.1598.

![Structure of 16](image)

A mixture of triazole 14 (54 mg, 0.15 mmol), Pd\(_2\)dba\(_3\) (7 mg, 5 mol%), \(^1\)Bu\(_3\)PH.BF\(_4\) (5 mg, 12 mol%), K\(_3\)PO\(_4\) (64 mg, 0.30 mmol), 3-nitrophenyl boronic acid pinacol ester (75 mg, 0.30 mmol) in MeCN (2 mL) was heated at 50 °C under N\(_2\) for 16 h, the reaction mixture was then filtered through celite and concentrated in vacuo. The crude product was purified by flash column chromatography on petroleum/ethyl acetate (10:1) to give triazole 17 (37 mg, 70 %) as a colourless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.40 (1 H, app t, \(J = 2.0\) Hz), 8.08 (1 H, dd, \(J = 8.0, 2.0\) Hz), 7.92 (1 H, dd, \(J = 6.5, 1.5\) Hz), 7.57-7.53 (1 H, m), 7.50-7.42 (3 H, m), 7.29-7.26 (3 H, m), 7.18-7.15 (2 H, m), 7.05-7.03 (2 H, m), 5.44 (2 H, s, CH\(_2\)). \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\): 148.4, 142.4, 134.9 (x 2C), 132.7, 132.2, 130.3, 129.9, 129.6, 129.4, 128.8, 128.4, 127.6, 126.9, 122.3, 121.3, 52.2. FTIR 1616 (m), 1526 (s), 1344 (s), 1122 (m), 1112 (m), 851 (m), 693 (s). HRMS (EI+) calculated for C\(_{21}\)H\(_{17}\)N\(_4\)O\(_2\): 357.1346. Found: 357.1344.
A mixture of triazole 14 (54 mg, 0.15 mmol), Pd$_2$dba$_3$ (7 mg, 5 mol%), Bu$_3$PH.BF$_4$ (5 mg, 12 mol%), K$_3$PO$_4$ (64 mg, 0.30 mmol), 4-dimethylaminopnenyl boronic acid pinacol ester (74 mg, 0.30 mmol) in MeCN (2 mL) was heated at 50 °C under N$_2$ for 16 h, the reaction mixture was then filtered through celite and concentrated in vacuo. The crude product was purified by flash column chromatography on petroleum/ethyl acetate (10:1) to give triazole 18 (36 mg, 68 %) as a colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ; 7.47-7.39 (5 H, m, Ar), 7.28-7.25 (3 H, m), 7.92 (1 H, d, J = 7.0 Hz), 7.17 (2 H, d, J = 8.0 Hz), 7.05-7.03 (2 H, m), 6.63 (2 H, d, J = 8.0 Hz), 5.44 (2 H, s), 2.93 (6 H, s). $^{13}$C NMR (100.6 MHz, CDCl$_3$) δ; 149.9, 145.0, 135.6, 132.4, 130.3, 129.4, 129.0, 128.6, 128.4, 128.0, 127.6, 127.5, 119.0, 112.2, 52.0, 40.4. FTIR 2922 (m), 2851 (m), 1615 (s), 1518 (s), 1356 (m), 1198 (s), 944 (m), 823 (s). HRMS (ESI+) calculated for C$_{23}$H$_{23}$N$_4$: 355.1917. Found: 355.1914.
4. Other Triazole Boronic Ester and Derivatives

A mixture of benzyl azide (40 mg, 0.3 mmol) and alkyne 19 (82 mg, 0.36 mmol) in 1,2-dichlorobenzene (1.2 mL) was heated at 150 °C for 16 h under N₂. The crude product was purified by flash column chromatography on petroleum ether/ethyl acetate (2:1) to give triazole 22a (27 mg, 25%) as a colourless oil and triazole 22b (41 mg, 38%) as a colourless oil. **22a:** ¹H NMR (400 MHz, CDCl₃) δ; 7.95 (2 H, dd, J = 8.0, 1.5 Hz), 7.41-7.34 (3 H, m), 7.31-7.25 (3 H, m), 7.20 (2 H, dd, J = 8.0, 1.5 Hz), 5.85 (2 H, s), 1.21 (12 H, s). **13C NMR (100.6 MHz, CDCl₃) δ;** 156.0, 136.7, 131.5, 128.5 (x 2C), 128.2, 128.0, 127.9, 127.2, 84.7, 54.0, 24.6. FTIR 2978 (m), 1496 (s), 1456 (s), 1372 (s), 1332 (s), 1211 (m), 1142 (s), 853 (m), 698 (s). HRMS (ESI+) calculated for C₂₁H₂₅BN₂O₂: 362.2034. Found: 362.2035.

**22b:** ¹H NMR (400 MHz, CDCl₃) δ; 7.49-7.39 (3 H, m), 7.28-7.25 (5 H, m), 7.05-7.02 (2 H, m), 5.53 (2 H, s), 1.29 (12 H, s). **13C NMR (100.6 MHz, CDCl₃) δ;** 145.4, 135.6, 129.9, 129.3, 128.7, 128.2, 128.0, 127.2, 127.1, 83.9, 51.4, 24.7. FTIR 2977 (m), 2926 (m), 1496 (m), 1456 (s), 1372 (s), 1332 (s), 1211 (m), 1142 (s), 853 (m), 698 (s). HRMS (ESI+) calculated for C₂₁H₂₅BN₂O₂: 362.2034. Found: 362.2036.
A mixture of benzyl azide (40 mg, 0.30 mmol) and alkyne 20 (59 mg, 0.30 mmol) in 1,2-dichlorobenzene (1.2 mL) was heated at 150 °C for 24 h under N₂ to give an inseperable 40:60 mixture of 23a and 23b (98 mg, 99%) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ; 7.32-7.22 (5 H, m), 5.76 (0.8 H, s), 5.66 (1.2 H, s), 4.69 (0.8 H, s), 4.57 (1.2 H, s), 3.42 (1.2 H, s), 3.25 (1.8 H, s), 1.35 (7.2 H, s), 1.28 (4.8 H, s). ¹³C NMR (100.6 MHz, CDCl₃) δ; 153.5, 140.7, 136.2, 134.9, 128.7, 128.4, 128.1, 127.9, 127.6, 127.5, 84.6, 84.1, 65.1, 61.7, 58.1, 57.6, 53.6, 51.9, 24.7, 24.6. FTIR 2981 (m), 1561 (m), 1456 (s), 1372 (s), 1333 (s), 1140 (s), 1083 (s), 908 (s), 726 (m). HRMS (ESI+) calculated for C₁₇H₂₅BN₃O₃: 330.1984. Found: 330.1981.

A mixture of benzyl azide (40 mg, 0.30 mmol) and alkyne 21 (58 mg, 0.30 mmol) in 1,2-dichlorobenzene (1.2 mL) was heated at 150 °C for 24 h under N₂ to give an inseperable 40:60 mixture of 24a and 24b (96 mg, 98%) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ; 7.31-7.20 (3 H, m), 7.13-7.11 (2 H, m), 5.71 (0.8 H, s), 5.51 (1.2 H, s), 2.82 (0.8 H, t, J
= 7.0 Hz), 2.70 (1.2 H, t, J = 7.0 Hz), 1.68 (1.2 H, m), 1.54 (0.8 H, m), 1.32 (7.2 H, s), 1.23 (4.8 H, s), 0.91 (1.2 H, t, J = 7.0 Hz), 0.81 (1.8 H, t, J = 7.0 Hz). $^{13}$C NMR (100.6 MHz, CDCl$_3$) δ; 136.7, 135.3, 130.4, 128.7, 128.3, 128.0, 127.7, 127.5, 126.9, 84.2, 83.7, 53.5, 51.1, 27.8, 24.8, 24.7, 24.6, 23.4, 22.5, 21.5, 21.4. FTIR 1558 (m), 1454 (s), 1368 (s), 1342 (s), 1137 (s), 1085 (s), 912 (m), 730 (m). HRMS (ESI+) calculated for C$_{18}$H$_{26}$BN$_3$O$_2$: 328.2256. Found: 328.2254.
5. $^1$H and $^{13}$C NMR Spectra
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6. Regiochemistry Assignment
Supplementary Material (ESI) for Chemical Communications
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\(^1\)H NMR (400 MHz, CHLOROFORM-\(d\)) \(\delta\) ppm 8.12 (1 H, d, \(J=8.3\) Hz), 8.03 (1 H, s), 7.89 (1 H, d, \(J=8.8\) Hz), 2.66 (2 H, s), 0.39 (6 H, s)

Linear Notes: HMBC from SiMe's & 3a(127ppm) to 4(148.5ppm).
ROE(NOESY) between 3a and 7/11 supports regiochemistry depicted.