

Synthesis of Novel Ynone Trifluoroborates

Towards Functionalized Pyrazoles

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General Procedures

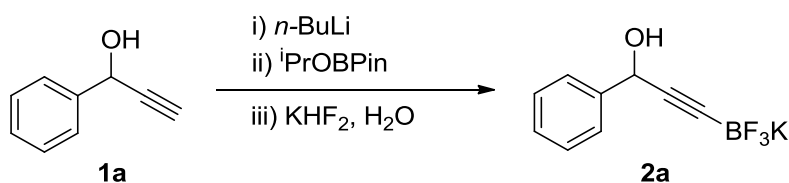
Infrared (IR) Spectra were recorded on a Perkin Elmer Paragon 100 FTIR spectrophotometer, ν_{\max} in cm^{-1} . Bands are characterised as broad (br), strong (s), medium (m), and weak (w). ^1H NMR spectra were recorded on a Bruker AC-250 (250 MHz) or AMX-400 (400 MHz) supported by an Aspect 3000 data 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 7.27 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. ^{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_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.

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). Ethynyl alcohols **1a**, **1e** and **1f** were purchased from Sigma Aldrich chemical co. and used as received. Ethynyl alcohols **1b**, **1c**, **1d** and **1g** were synthesised by reaction of ethynyl magnesium bromide with the corresponding commercially available aldehydes.¹ 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.

¹ Punner, F.; Hilt, G. *Chem. Comm.*, **2012**, 3617

General procedure 1: Synthesis of ethynyl alcohol trifluoroborates: The propargylic alcohol (1.0 mmol) was dissolved in 4 mL THF, then cooled to -78 °C under nitrogen. To this *n*-BuLi in hexanes (2.2 mmol) was added dropwise, and the resulting solution stirred at -78 °C for 1 h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.0 mmol) was added, and the mixture stirred for 1 h whilst the temperature was slowly raised from -78 °C to -20 °C. To this was added a saturated solution of potassium hydrogen difluoride (12 mmol) in water. The resulting slurry was stirred for 1 h as the temperature was raised from -20 °C to rt. The solvent was removed *in vacuo* and the resulting solid was dried under high vacuum for 2 h. Inorganic solids were removed via trituration with acetone, followed by filtration. Excess pinacol was removed via trituration with diethyl ether, affording the desired ethynyl alcohol trifluoroborate as a colourless crystalline solid.

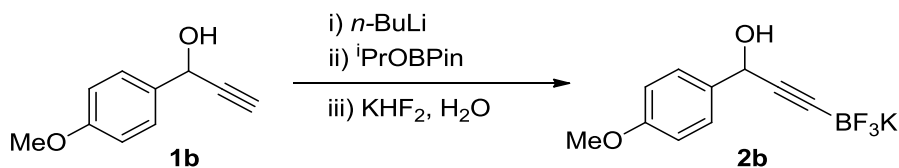
Synthesis of potassium trifluoro(3-hydroxy-3-phenylprop-1-yn-1-yl)borate **2a**



Using general procedure 1, with propargylic alcohol **1a** (0.50 g, 3.8 mmol), the product was isolated as a colourless solid, **2a**, 0.80 g, 92% yield, m.pt. = 232 – 235 °C.

¹H NMR (250 MHz, d⁶-DMSO): δ 5.15 (1H, d, *J* = 5.5 Hz, CHOH), 5.61 (1H, d, *J* = 5.5 Hz, CHOH), 7.21 – 7.34 (3H, m, Ar-*H*), 7.43 (2H, d, *J* = 6.5 Hz, Ar-*H*); ¹⁹F NMR (235.1 MHz, d₆-acetone): δ -134.9; ¹³C NMR (100.6 MHz, d⁶-DMSO): δ 63.6, 91.0, 127.0, 127.4, 128.3, 144.1; FTIR (neat, cm⁻¹) ν_{max}: 3414 (br), 2956 (w), 2916 (m), 1067 (m); HRMS calculated for C₉H₇¹¹BF₃KO (ES⁻) (-K): 199.0542. Found 199.0536.

Synthesis of potassium trifluoro(3-hydroxy-3-(4-methoxyphenyl)prop-1-yn-1-yl)borate **2b**

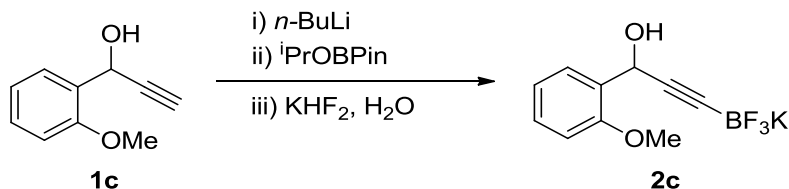


Using general procedure 1, with propargylic alcohol **1b** (0.32 g, 2.0 mmol), the product was isolated as a colourless solid, **2b**, 0.22 g, 42% yield, m.pt. = 283 – 284 °C.

¹H NMR (250 MHz, d₆-DMSO): δ 3.74 (3H, s, OCH₃), 5.28 (1H, d, *J* = 5.0 Hz, CHOH), 5.92 (1H, d, *J* = 5.0 Hz, CHOH), 6.98 (2H, d, *J* = 8.5 Hz, Ar-*H*) 7.36 (2H, d, *J* = 8.5 Hz, Ar-*H*); ¹³C NMR (100.6 MHz, d₆-DMSO)

δ 55.5, 63.1, 113.6, 101.2, 128.2, 136.4, 158.8; ^{19}F NMR (235.1 MHz, d_6 -acetone): δ -134.8; FTIR (neat, cm^{-1}) ν_{max} : 3435 (br), 1516 (m), 1214 (m); HRMS calculated for $\text{C}_{10}\text{H}_9^{11}\text{BF}_3\text{KO}_2$ (ES^-) (-K): 229.0648. Found 229.0637.

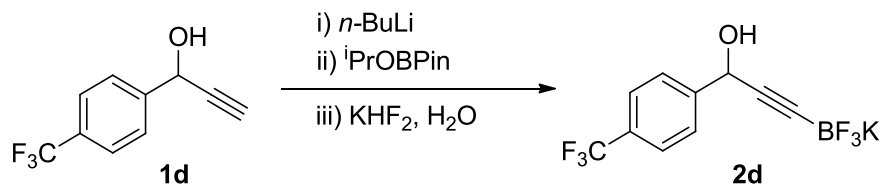
Synthesis of potassium trifluoro(3-hydroxy-3-(2-methoxyphenyl)prop-1-yn-1-yl)borate **2c**



Using general procedure 1, with propargylic alcohol **1c** (0.31 g, 1.9 mmol), the product was isolated as a colourless solid, **2c**, 0.32 g, 62% yield, m.pt. = 153 – 155 °C.

^1H NMR (250 MHz, d_6 -DMSO): δ 3.79 (1H, br s, CHOH), 3.84 (3H, s, OCH_3), 5.63 (1H, br s, CHOH), 6.89 – 6.95 (2H, m, Ar- H), 7.23 (1H, td, J = 8.0, 2.0 Hz, Ar- H), 7.73 (1H, dd, J = 8.0, 2.0 Hz, Ar- H); ^{13}C NMR (100.6 MHz, d_6 -DMSO): δ 55.9, 57.4, 91.0, 111.2, 120.6, 128.0, 128.7, 132.2, 156.0; ^{19}F NMR (235.1 MHz, d_6 -DMSO): δ -131.4; FTIR (neat, cm^{-1}) ν_{max} : 3529 (br), 2839 (w), 1491 (m), 1085 (s); HRMS calculated for $\text{C}_{10}\text{H}_9^{11}\text{BF}_3\text{KO}_2$ (ES^-) (-K): 227.0491. Found 227.0493.

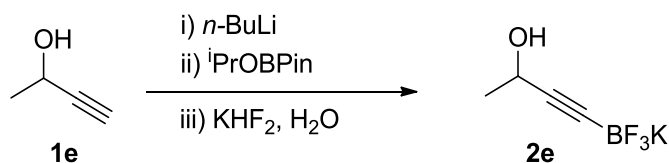
Synthesis of potassium trifluoro(3-hydroxy-3-(4-(trifluoromethyl)phenyl)prop-1-ynyl)borate **2d**



Using general procedure 1, with propargylic alcohol **1d** (0.50 g, 2.5 mmol), the product was isolated as a colourless solid, **2d**, 0.37 g, 48% yield, m.pt. = 238 °C (dec.).

^1H NMR (250 MHz, d_6 -DMSO): δ 5.27 (1H, d, J = 5.0 Hz, CHOH), 5.88 (1H, d, J = 5.0 Hz, CHOH), 7.66 (2H, d, J = 8.5 Hz, Ar- H), 7.70 (2H, d, J = 8.5 Hz, Ar- H); ^{13}C NMR (100.6 MHz, d_6 -DMSO) δ 63.0, 90.3, 124.9 (q, J = 272 Hz, CF_3), 125.4 (q, J = 3.8 Hz, CCCF_3), 127.6, 128.1 (q, J = 32 Hz, CCF_3), 148.8; ^{19}F NMR (235.1 MHz, d_6 -DMSO): δ -62.7, -134.9; FTIR (neat, cm^{-1}) ν_{max} : 3406 (br), 1330 (s), 1107 (s), 1004 (s), 939 (s); HRMS calculated for $\text{C}_{10}\text{H}_6^{11}\text{BF}_6\text{KO}$ (ES^-) (-K): 267.0416. Found 267.0429.

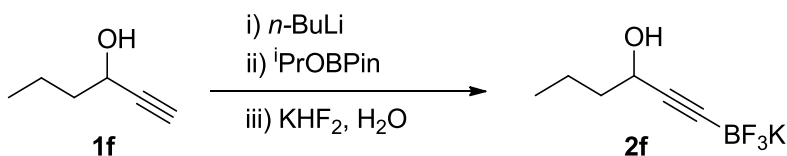
Synthesis of potassium trifluoro(3-hydroxybut-1-yn-1-yl)borate **2e**



Using general procedure 1, with propargylic alcohol **1e** (0.50 g, 7.1 mmol), the product was isolated as a colourless solid, **2e**, 0.60 g, 48% yield, m.pt. = 225 °C (dec.).

^1H NMR (400 MHz, $\text{d}_6\text{-DMSO}$): δ 1.18 (3H, d, J = 6.5 Hz, CH_3), 4.17 (1H, m, CHOH), 4.88 (1H, d, J = 5.0 Hz, CHOH); ^{13}C NMR (100.6 MHz, $\text{d}_6\text{-DMSO}$): δ 25.8, 57.2, 93.2; ^{19}F NMR (235.1 MHz, $\text{d}_6\text{-DMSO}$): δ -131.5; FTIR (neat, cm^{-1}) ν_{max} : 3419 (br), 2918 (w), 1636 (m), 1074 (m); HRMS calculated for $\text{C}_4\text{H}_5^{11}\text{BF}_3\text{KO}$ (ES^-) (-K): 137.0386. Found 137.0380.

Synthesis of potassium trifluoro(3-hydroxyhex-1-yn-1-yl)borate **2f**

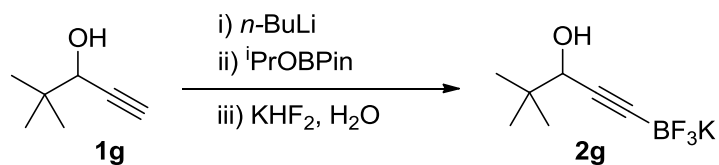


Using general procedure 1, with propargylic alcohol **1f** (0.50 g, 5.1 mmol), the product was isolated as a colourless solid, **2f**, 0.83 g, 80% yield, m.pt. = 245 °C (dec.).

^1H NMR (250 MHz, $\text{d}_6\text{-DMSO}$): δ 0.79 (3H, t, J = 7.0 Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.28 – 1.48 (4H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 4.01 (1H, d, J = 5.5 Hz, CHOH), 4.82 (1H, d, J = 5.5 Hz, CHOH); ^{13}C NMR (100.6 MHz, $\text{d}_6\text{-DMSO}$): δ 14.3, 18.7, 41.0, 61.1, 102.3; ^{19}F NMR (235.1 MHz, $\text{d}_6\text{-DMSO}$): δ -132.9. The compound gave satisfactory spectroscopic data.²

² Jouvin, K.; Couty, F.; Evano, G. *Org. Lett.* **2010**, 3272.

Synthesis of potassium trifluoro(3-hydroxy-4,4-dimethylpent-1-ynyl)borate **2g**



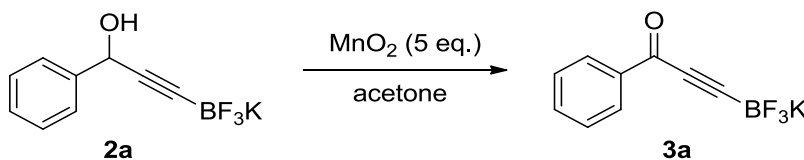
Using general procedure 1, with propargylic alcohol **1g** (0.62 g, 5.6 mmol), the product was isolated as a colourless solid, **2g**, 0.76 g, 63% yield, m.pt. = >250 °C.

¹H NMR (250 MHz, d⁶-acetone): δ 0.94 (9H, s, CH₃), 3.73 (1H, d, *J* = 5.5 Hz, CHOH), 3.84 (1H, br, CHOH); ¹⁹F NMR (235.1 MHz, d₆-acetone): δ -134.5; ¹³C NMR (100.6 MHz, d⁶-DMSO): δ 26.1, 35.8, 70.4, 90.2; FTIR (neat, cm⁻¹) ν_{max}: 3260 (br), 2960 (m), 2033 (w), 1091 (m), 952 (s); HRMS calculated for C₇H₁₁¹¹BF₃KO (ES⁻) (-K): 179.0855. Found 179.0853.

General procedure 2: Synthesis of ethynyl ketone trifluoroborates:

Ethynyl alcohol trifluoroborate (1.0 mmol) was added portionwise to a stirred solution of manganese dioxide (5 mmol) dispersed in 2.5 mL acetone under nitrogen. The reaction mixture was stirred for 2 h at room temperature. The resulting mixture was then filtered through celite, and the celite washed with acetone. Solvent was removed in vacuo to yield a colourless amorphous solid, which was washed with diethyl ether to yield desired ethynyl ketone trifluoroborate as a colourless crystalline solid.

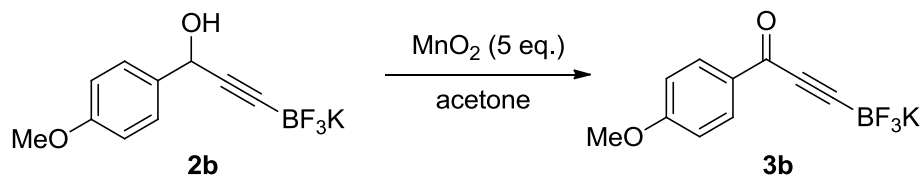
Synthesis of potassium trifluoro(3-oxo-3-phenylprop-1-yn-1-yl)borate **3a**



Using general procedure 2, with propargylic alcohol trifluoroborate **2a** (0.78 g, 3.3 mmol), the product was isolated as a colourless solid, **3a**, 0.60 g, 80% yield, m.pt. = 143 – 145 °C.

^1H NMR (400 MHz, d_6 -acetone): δ 7.53 (2H, t, J = 7.5 Hz, Ar- H), 7.64 (1H, tt, J = 7.5, 1.5 Hz, Ar- H), 8.18 (2H, dd, J = 7.5, 1.5 Hz, Ar- H); ^{13}C NMR (100.6 MHz, d_6 -acetone): δ 73.8, 128.4, 129.1, 133.2, 137.7, 178.4; ^{19}F NMR (235.1 MHz, d_6 -DMSO): δ -133.0; FTIR (neat, cm^{-1}) ν_{max} : 3464 (w), 2925 (w), 1629 (s), 1579 (m), 1027 (w); HRMS calculated for $\text{C}_9\text{H}_5^{11}\text{BF}_3\text{KO}$ (ES^-) (-K): 197.0386. Found 197.0379.

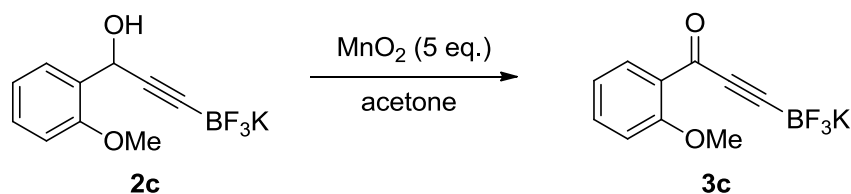
Synthesis of potassium trifluoro(3-(4-methoxyphenyl)-3-oxoprop-1-yn-1-yl)borate **3b**



Using general procedure 2, with propargylic alcohol trifluoroborate **2b** (100 mg, 0.4 mmol), the product was isolated as a colourless solid, **3b**, 82 mg, 78% yield, m.pt. = 133 – 135 °C.

^1H NMR (250 MHz, d_6 -DMSO): δ 3.73 (3H, s, OCH_3), 6.87 (2H, d, J = 8.0 Hz, Ar- H), 7.35 (2H, d, J = 8.0 Hz, Ar- H); ^{19}F NMR (235.1 MHz, d_6 -DMSO): δ -132.7; ^{13}C NMR (100.6 MHz, d_6 -DMSO): δ 56.1, 73.2, 114.5, 119.4, 130.6, 131.7, 164.2; FTIR (neat, cm^{-1}) ν_{max} : 2910 (w), 2102 (w), 1598 (s), 1261 (s), 1167 (m); HRMS calculated for $\text{C}_{10}\text{H}_7^{11}\text{BF}_3\text{KO}_2$ (ES^-) (-K): 227.0491. Found 227.0495.

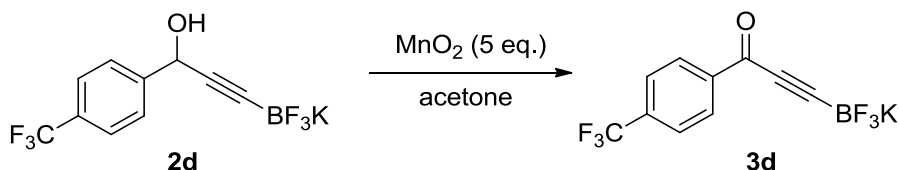
Synthesis of potassium trifluoro(3-(2-methoxyphenyl)-3-oxoprop-1-ynyl)borate **3c**



Using general procedure 2, with propargylic alcohol trifluoroborate **2c** (120 mg, 0.44 mmol), the product was isolated as a colourless solid, **3c**, 97 mg, 83% yield, m.pt. = 60 °C (dec.).

^1H NMR (250 MHz, d_6 -acetone): δ 3.87 (3H, s, OCH_3), 7.03 (1H, td, $J = 7.5, 0.5$ Hz, Ar- H), 7.11 (1H, dd, $J = 9.0, 0.5$ Hz, Ar- H), 7.52 (1H, ddd, $J = 9.0, 7.5, 1.5$ Hz, Ar- H), 8.04 (1H, dd, $J = 7.5, 1.5$ Hz, Ar- H); ^{13}C NMR (100.6 MHz, d_6 -DMSO): δ 56.2, 83.9, 113.3, 120.5, 127.7, 132.5, 134.7, 136.3, 159.1; ^{19}F NMR (235.1 MHz, d_6 -DMSO): δ -132.9; FTIR (neat, cm^{-1}) ν_{max} : 2094 (w), 1627 (s), 1486 (m), 1239 (s); HRMS calculated for $\text{C}_{10}\text{H}_7^{11}\text{BF}_3\text{KO}_2$ (ES^-) (-K): 227.0491. Found 227.0493.

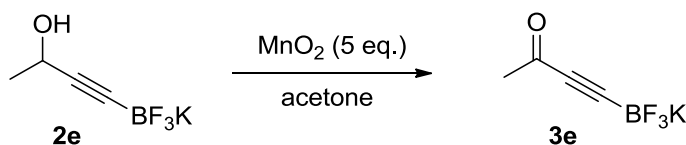
Synthesis of potassium trifluoro(3-oxo-3-(4-(trifluoromethyl)phenyl)prop-1-ynyl)borate **3d**



Using general procedure 2, with propargylic alcohol trifluoroborate **2d** (0.15 g, 0.5 mmol), the product was isolated as a colourless solid, **3d**, 0.14 g, 93% yield, m.pt. = 205 °C (dec.).

^1H NMR (250 MHz, d_6 -DMSO): δ 7.96 (2H, d, $J = 8.0$ Hz, Ar- H), 8.23 (2H, d, $J = 8.0$ Hz, Ar- H); ^{13}C NMR (100.6 MHz, d_6 -DMSO) δ 65.4, 124.2 (q, $J = 273$ Hz, CF_3), 126.4 (q, $J = 3.7$ Hz, CCCF_3), 130.1, 133.5 (q, $J = 32$ Hz, CCF_3), 140.1, 177.5; ^{19}F NMR (235.1 MHz, d_6 -DMSO): δ -61.5, -133.1; FTIR (neat, cm^{-1}) ν_{max} : 3602 (w), 2086 (w), 1633 (s), 984 (s); HRMS calculated for $\text{C}_{10}\text{H}_4^{11}\text{BF}_6\text{KO}$ (ES^-) (-K): 265.0259. Found 265.0255.

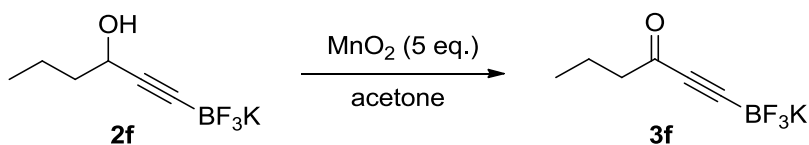
Synthesis of potassium trifluoro(3-oxobut-1-yn-1-yl)borate **3e**



Using general procedure 2, with propargylic alcohol trifluoroborate **2e** (0.10 g, 0.6 mmol), the product was isolated as a colourless solid, **3e**, 0.06 g, 60% yield, m.pt. = 142 – 144 °C.

^1H NMR (250 MHz, d_6 -DMSO): δ 2.19 (3H, s, CH_3); ^{13}C NMR (100.6 MHz, d_6 -DMSO): δ 33.2, 91.0, 185.7; ^{19}F NMR (235.1 MHz, d_6 -DMSO): δ -133.2; FTIR (neat, cm^{-1}) ν_{max} : 2969 (m), 1738 (s), 1365 (s), 1216 (s); HRMS calculated for $\text{C}_4\text{H}_3^{11}\text{BF}_3\text{KO}$ (ES^-) (-K): 135.0229. Found 135.0229.

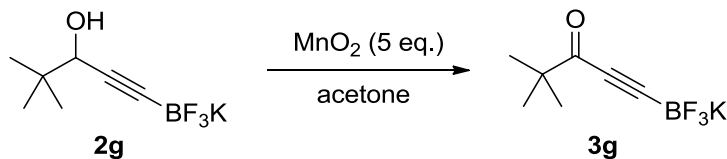
Synthesis of potassium trifluoro(3-oxohex-1-yn-1-yl)borate **3f**



Using general procedure 2, with propargylic alcohol trifluoroborate **2f** (0.20 g, 1.0 mmol), the product was isolated as a colourless solid, **3f**, 0.16 g, 81% yield, m.pt. = 109 – 110 °C.

^1H NMR (250 MHz, d_6 -DMSO): δ 0.85 (3H, t, $J = 7.5$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.55 (2H, sext, $J = 7.5$, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.41 (2H, t, $J = 7.5$, $\text{CH}_2\text{CH}_2\text{CH}_3$); ^{13}C NMR (100.6 MHz, d_6 -acetone): δ 13.0, 17.5, 47.1, 75.3, 175.4; ^{19}F NMR (235.1 MHz, d_6 -DMSO): δ -133.1; FTIR (neat, cm^{-1}) ν_{max} : 2962 (s), 1662 (s), 1153 (s); HRMS calculated for $\text{C}_6\text{H}_7^{11}\text{BF}_3\text{KO}$ (ES^-) (-K): 163.0542. Found 163.0536.

Synthesis of potassium trifluoro(4,4-dimethyl-3-oxopent-1-yn-1-yl)borate **3g**



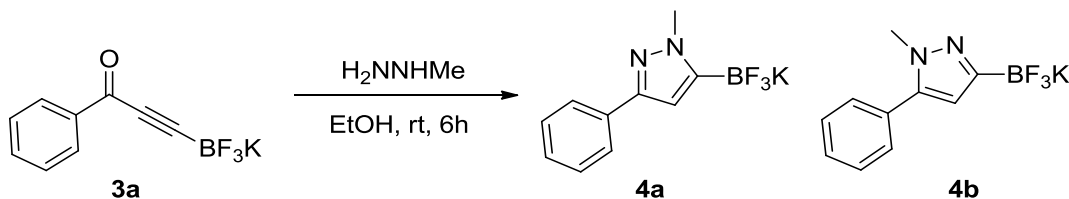
Using general procedure 2, with propargylic alcohol trifluoroborate **2g** (0.30 g, 1.4 mmol), the product was isolated as a colourless solid, **3g**, 0.27 g, 91% yield, m.pt. = 170 – 171 °C.

^1H NMR (250 MHz, d_6 -DMSO): δ 0.91 (9H, s, CH_3); ^{13}C NMR (100.6 MHz, d_6 -DMSO): δ 26.4, 44.2, 87.4, 157.0; ^{19}F NMR (235.1 MHz, d_6 -DMSO): δ -136.6; FTIR (neat, cm^{-1}) ν_{max} : 2924 (m), 1738 (s), 1365 (s), 1217 (m); HRMS calculated for $\text{C}_7\text{H}_9^{11}\text{BF}_3\text{KO}$ (ES^-) (-K): 177.0699. Found 177.0693.

General procedure 3: Synthesis of pyrazole trifluoroborates

To a solution of ynone trifluoroborate (1.0 mmol) in 2 mL ethanol was added hydrazine (1.2 mmol). The solution was stirred at r.t. under a nitrogen atmosphere, until judged complete by ^{19}F NMR spectroscopy.³ The solvent was removed in *vacuo* to yield crude material which was purified by recrystallization (acetone/diethyl ether) to afford the pyrazole product.

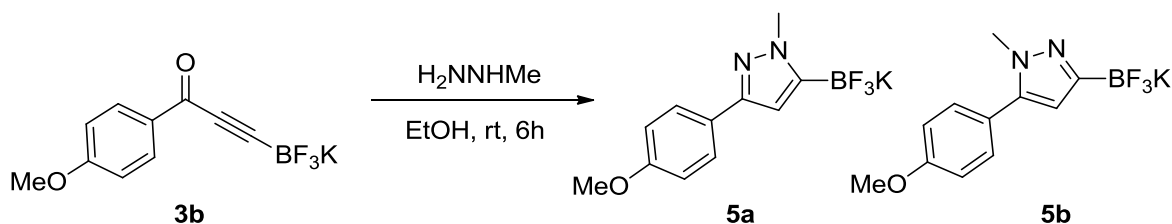
Synthesis of potassium trifluoro(1-methyl-3-phenyl-1H-pyrazol-5-yl)borate **4a** and potassium trifluoro(1-methyl-5-phenyl-1H-pyrazol-3-yl)borate **4b**



Using general procedure 3, with ynone **3a** (294 mg, 1.24 mmol), the product was isolated as an inseparable mixture of compounds **4a** and **4b** (16:1 ratio), as a colourless solid, 323 mg, 96% yield, m.pt. = 158 – 160 °C.

4a: ^1H NMR (250 MHz d_6 -DMSO): δ 3.79 (3H, s, NCH_3), 6.30 (1H, s, ArH), 7.18 (1H, tt, $J = 7.5, 1.0$, ArH), 7.30 (2H, t, $J = 7.5$ Hz, ArH), 7.70 (2H, m, ArH); ^{13}C NMR (100.6 MHz, d_6 -DMSO): δ 31.2, 105.9, 125.2, 126.6, 128.8, 135.5, 148.0; ^{19}F NMR (235.1 MHz, d_6 -acetone): δ -140.3; FTIR (neat, cm^{-1}) ν_{max} : 2928 (w), 1428 (w), 1195 (m), 1169 (m), 975 (s); HRMS calculated for $\text{C}_{10}\text{H}_9^{11}\text{BF}_3\text{KN}_2$ (ES^-) (-K): 225.0811. Found 225.0820.

Synthesis of potassium trifluoro(3-(4-methoxyphenyl)-1-methyl-1H-pyrazol-5-yl)borate **5a** and potassium trifluoro(5-(4-methoxyphenyl)-1-methyl-1H-pyrazol-3-yl)borate **5b**

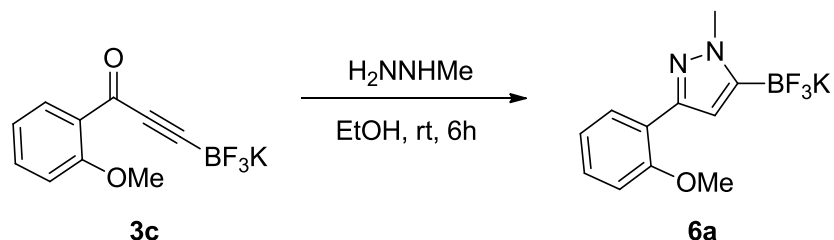


Using general procedure 3, with ynone **3b** (100 mg, 0.38 mmol), the product was isolated as an inseparable mixture of compounds **5a** and **5b** (7:1 ratio), as a colourless solid, 70 mg, 63% yield, m.pt. = 141 – 143 °C.

³ Formation of pyrazoles **8ab**, **9ab** and **11b** was found to be sluggish; therefore additional heating was required in order to ensure complete consumption of starting material.

5a: ^1H NMR (250 MHz, d_6 -acetone): δ 3.79 (3H, s, NCH_3), 3.85 (3H, s, OCH_3), 6.31 (1H, s, ArH), 6.87 (2H, d, $J = 9.0$ Hz, ArH), 7.70 (2H, d, $J = 9.0$ Hz, ArH); ^{13}C NMR (100.6 MHz, d_6 -DMSO): δ 38.5, 55.5, 105.3, 114.2, 126.4, 128.3, 147.9, 158.3; ^{19}F NMR (235.1 MHz, d_6 -acetone): δ -140.2; FTIR (neat, cm^{-1}) ν_{max} : 3418 (w), 2160 (m), 1619 (m), 1110 (s), 914 (s); HRMS calculated for $\text{C}_{11}\text{H}_{11}^{11}\text{BF}_3\text{KN}_2\text{O}$ (ES^-) (-K): 255.0917. Found 255.0912.

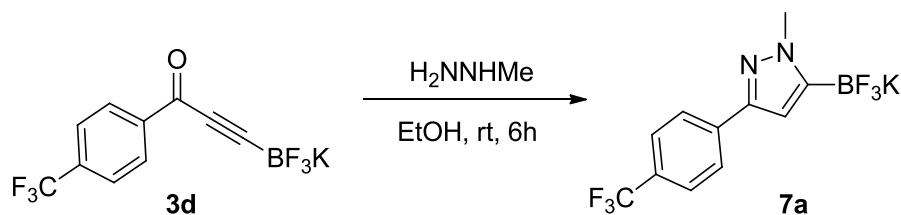
Synthesis of potassium trifluoro(3-(2-methoxyphenyl)-1-methyl-1H-pyrazol-5-yl)borate **6a**



Using general procedure 3, with ynone **3c** (35 mg, 0.13 mmol), the product was isolated as a single regioisomer **6a** (>98:2 ratio), as a colourless solid, 32 mg, 92% yield, m.pt. = 149 – 150 °C.

^1H NMR (400 MHz, d_6 -DMSO): δ 3.79 (3H, s, NCH_3), 3.83 (3H, s, OCH_3), 6.43 (1H, s, ArH), 6.92 (1H, t, $J = 7.5$ Hz, ArH), 7.02 (1H, d, $J = 8.0$ Hz, ArH), 7.17 – 7.22 (1H, m, ArH), 7.82 (1H, dd, $J = 7.5, 1.5$ Hz, ArH); ^{13}C NMR (100.6 MHz, d_6 -DMSO): δ 38.5, 55.8, 110.4, 112.2, 120.7, 124.1, 127.8, 128.2, 144.9, 156.7; ^{19}F NMR (235.1 MHz, d_6 -DMSO): δ -136.9; FTIR (neat, cm^{-1}) ν_{max} : 3412 (w), 2120 (m), 1645 (m), 1096 (s), 910 (s); HRMS calculated for $\text{C}_{11}\text{H}_{11}^{11}\text{BF}_3\text{KN}_2\text{O}$ (ES^-) (-K): 255.0917. Found 255.0919.

Synthesis of potassium trifluoro(1-methyl-3-(4-(trifluoromethyl)phenyl)-1H-pyrazol-5-yl)borate **7a**

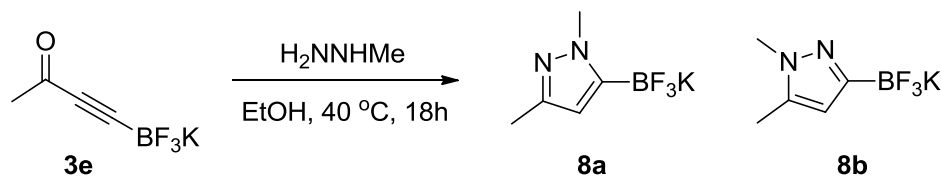


Using general procedure 3, with ynone **3d** (50 mg, 0.16 mmol), the product was isolated as a single regioisomer **7a** (>98:2 ratio), as a colourless solid, 52 mg, 98% yield, m.pt. = 133 – 135 °C.

^1H NMR (250 MHz, d_6 -DMSO): δ 3.84 (3H, s, NCH_3), 6.45 (1H, s, ArH), 7.67 (2H, d, $J = 8.5$ Hz, ArH), 7.93 (2H, d, $J = 8.5$ Hz, ArH); ^{13}C NMR (100.6 MHz, d_6 -DMSO): δ 38.7, 106.8, 125.0 (q, $J = 272$ Hz, CF_3), 125.6, 125.8 (q, $J = 3.7$ Hz, CCCF_3), 126.8 (q, $J = 32$ Hz, CCF_3), 139.3, 146.7. ^{19}F NMR (235.1 MHz, d_6 -

DMSO): δ -60.7, -137.3; FTIR (neat, cm^{-1}) ν_{max} : 2341 (w), 1625 (w), 1329 (s), 974 (s); HRMS calculated for $\text{C}_{11}\text{H}_8^{11}\text{BF}_6\text{KN}_2$ (ES^-) (-K): 293.0685. Found 293.0696.

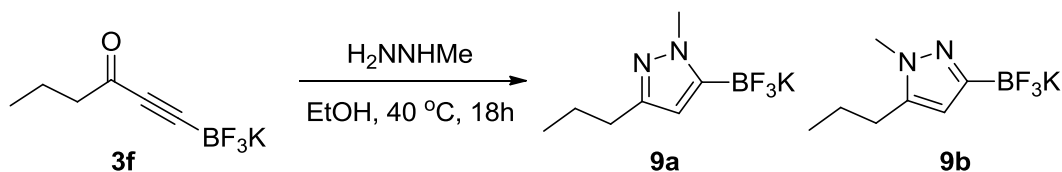
Synthesis of potassium (1,3-dimethyl-1H-pyrazol-5-yl)trifluoroborate **8a** and potassium (1,5-dimethyl-1H-pyrazol-3-yl)trifluoroborate **8b**



Using general procedure 3, with ynone **3e** (100 mg, 0.58 mmol), the product was isolated as an inseparable mixture of compounds **8a** and **8b** (6:1 ratio), as a colourless solid, 81 mg, 74% yield, m.pt. = 101 – 103 °C.

8a: ^1H NMR (250 MHz, d_6 -acetone): δ 2.25 (3H, s, ArCH_3), 3.92 (3H, s, NCH_3), 6.01 (1H, s, ArH); ^{13}C NMR (100.6 MHz, d_6 -acetone): δ 11.4, 36.9, 109.1, 144.5; ^{19}F NMR (235.1 MHz, d_6 -acetone): δ -141.7; FTIR (neat, cm^{-1}) ν_{max} : 3232 (w), 1432 (w), 1032 (s), 948 (s); HRMS calculated for $\text{C}_5\text{H}_7^{11}\text{BF}_3\text{KN}_2$ (ES^-) (-K): 163.0659. Found 163.0654.

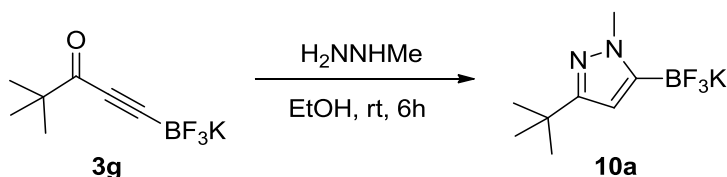
Synthesis of potassium trifluoro(1-methyl-3-propyl-1H-pyrazol-5-yl)borate **9a** and potassium trifluoro(1-methyl-5-propyl-1H-pyrazol-3-yl)borate **9b**



Using general procedure 3, with ynone **3f** (100 mg, 0.50 mmol), the product was isolated as an inseparable mixture of compounds **9a** and **9b** (8:1 ratio), as a yellow solid, 90 mg, 78% yield, m.pt. = 110 – 112 °C.

9a: ^1H NMR (250 MHz, d_6 -acetone): δ 0.91 (3H, t, $J = 7.5$ Hz, CH_2CH_3), 1.56 (2H, sext, $J = 7.5$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.43 (2H, t, $J = 7.5$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$), 3.73 (3H, s, NCH_3), 5.80 (1H, s, ArH); ^{13}C NMR (100.6 MHz, d_6 -acetone): δ 13.6, 23.2, 30.1, 37.2, 107.0, 149.5; ^{19}F NMR (235.1 MHz, d_6 -acetone): δ -141.7; FTIR (neat, cm^{-1}) ν_{max} : 2962 (w), 1427 (w), 1164 (m), 947 (s); HRMS calculated for $\text{C}_7\text{H}_{11}^{11}\text{BF}_3\text{KN}_2$ (ES^-) (-K): 191.0967. Found 191.0968.

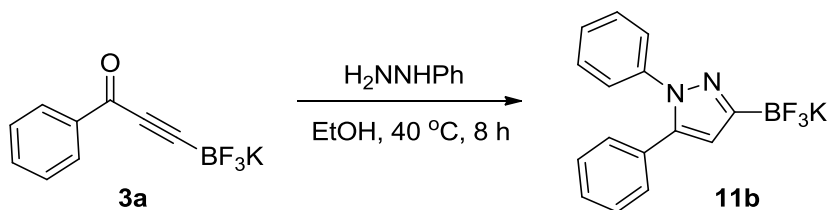
Synthesis of potassium (3-tert-butyl-1-methyl-1H-pyrazol-5-yl)trifluoroborate 10a



Using general procedure 3, with ynone **3g** (50 mg, 0.23 mmol), the product was isolated as a single regioisomer **10a** (>98:2 ratio), as a colourless solid, 55 mg, 92% yield, m.pt. = 118 – 120 °C.

¹H NMR (250 MHz, d₆-acetone): δ 1.25 (9H, s, CH₃), 3.79 (3H, s, NCH₃), 5.95 (1H, s, ArH); ¹³C NMR (100.6 MHz, d₆-acetone): δ 30.4, 31.3, 37.1, 104.8, 157.9; ¹⁹F NMR (235.1 MHz, d₆-acetone): δ -141.3; FTIR (neat, cm⁻¹) ν_{max}: 3485 (w), 1436 (m), 1139 (s); HRMS calculated for C₈H₁₃¹¹BF₃KN₂ (ES⁻) (-K): 205.1124. Found 205.1118.

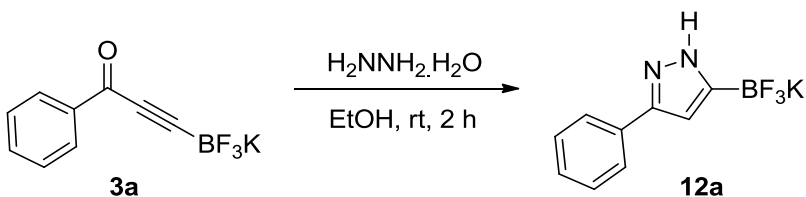
Synthesis of potassium (1,5-diphenyl-1H-pyrazol-3-yl)trifluoroborate 11b



Using general procedure 3, with ynone **3a** (50 mg, 0.21 mmol), the product was isolated as a single regioisomer **11b** (>98:2 ratio), as a pale yellow solid, 50 mg, 88% yield, m.pt. = 196 – 197 °C.

¹H NMR (250 MHz d₆-acetone): δ 6.46 (1H, s, ArH), 7.21 – 7.37 (10H, m, ArH); ¹³C NMR (100.6 MHz, d₆-DMSO): δ 112.7, 125.1, 126.6, 127.8, 128.6, 128.9, 129.1, 132.3, 141.1, 141.4; ¹⁹F NMR (235.1 MHz, d₆-acetone): δ -140.0; FTIR (neat, cm⁻¹) ν_{max}: 3042 (w), 1521 (m), 1081 (s), 957 (s); HRMS calculated for C₁₅H₁₁¹¹BF₃KN₂ (ES⁻) (-K): 287.0967. Found 287.0976.

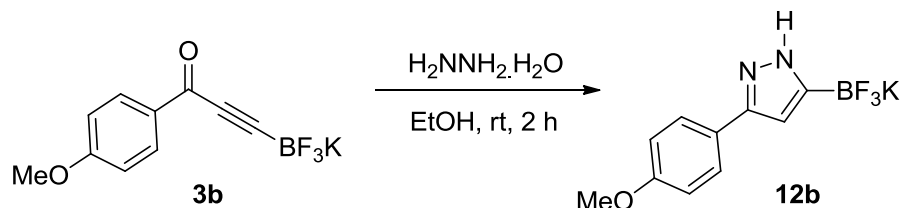
Synthesis of potassium trifluoro(3-phenyl-1H-pyrazol-5-yl)borate 12a



Using general procedure 3, with ynone **3a** (50 mg, 0.21 mmol), the product was isolated as a colourless solid **12a**, 40 mg, 76% yield, m.pt. = 180 °C (dec.).

^1H NMR (250 MHz d_6 -DMSO): δ 6.35 (1H, s, ArH), 7.21 (1H, tt, $J = 7.5, 1.0$ Hz, ArH), 7.35 (2H, t, $J = 7.5$ Hz, ArH), 7.75 (2H, dd, $J = 7.5, 1.0$ Hz, ArH), 12.19 (1H, br s, NH); ^{13}C NMR (100.6 MHz, d_6 -DMSO): δ 104.2, 125.4, 126.6, 128.8, 136.0, 149.1; ^{19}F NMR (235.1 MHz, d_6 -acetone): δ -148.3; FTIR (neat, cm^{-1}) ν_{max} : 3392 (w), 3061 (w), 1456 (w), 1157 (w), 964 (s); HRMS calculated for $\text{C}_9\text{H}_7^{11}\text{BF}_3\text{KN}_2$ (ES^-) (-K): 211.0654. Found 211.0652.

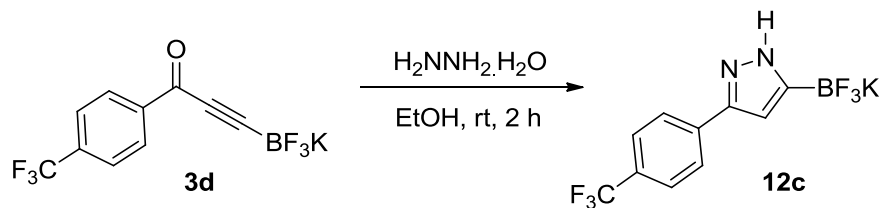
Synthesis of potassium trifluoro(3-(4-methoxyphenyl)-1H-pyrazol-5-yl)borate **12b**



Using general procedure 3, with ynone **3b** (100 mg, 0.38 mmol), the product was isolated as a colourless solid **12b**, 102 mg, 96% yield, m.pt. = 233 – 234 °C.

^1H NMR (250 MHz d_6 -DMSO): δ 3.75 (3H, s, CH_3), 6.19 (1H, s, ArH), 6.89 (2H, d, $J = 9.0$ Hz, ArH), 7.64 (2H, d, $J = 9.0$ Hz, ArH), 11.71 (1H, br s, NH); ^{13}C NMR (100.6 MHz, d_6 -DMSO): δ 55.5, 103.7, 114.2, 126.6, 128.8, 149.0, 158.3; ^{19}F NMR (235.1 MHz, d_6 -acetone): δ -136.4; FTIR (neat, cm^{-1}) ν_{max} : 3372 (w), 1424 (w), 1163 (w), 954 (s); HRMS calculated for $\text{C}_{10}\text{H}_9^{11}\text{BF}_3\text{KN}_2\text{O}$ (ES^-) (-K): 241.0760. Found 241.0758.

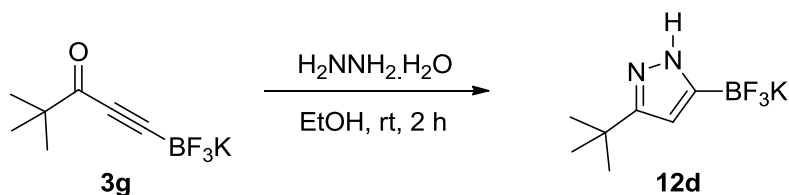
Synthesis of potassium trifluoro(3-(4-(trifluoromethyl)phenyl)-1H-pyrazol-5-yl)borate **12c**



Using general procedure 3, with ynone **3d** (35 mg, 0.12 mmol), the product was isolated as a colourless solid **12c**, 35 mg, 92% yield, m.pt. = 185 – 186 °C.

^1H NMR (250 MHz d_6 -DMSO): δ 6.40 (1H, s, ArH), 7.67 (2H, d, $J = 8.5$ Hz, ArH), 7.94 (2H, d, $J = 8.5$ Hz, ArH), 12.11 (1H, br s, NH); ^{13}C NMR (100.6 MHz, d_6 -DMSO): δ 105.0, 125.1 (q, $J = 271$ Hz, CF_3), 125.8 (x2, br), 126.8 (q, $J = 32$ Hz, CCF_3), 139.8, 147.7; ^{19}F NMR (235.1 MHz, d_6 -acetone): δ -60.6, -136.4; FTIR (neat, cm^{-1}) ν_{max} : 3403 (w), 1619 (m), 1326 (s), 1109 (s), 1061 (s), 911 (s); HRMS calculated for $\text{C}_{10}\text{H}_6^{11}\text{BF}_6\text{KN}_2$ (ES^-) (-K): 279.0528. Found 279.0524.

Synthesis of (3-tert-butyl-1H-pyrazol-5-yl)trifluoroborate 12d

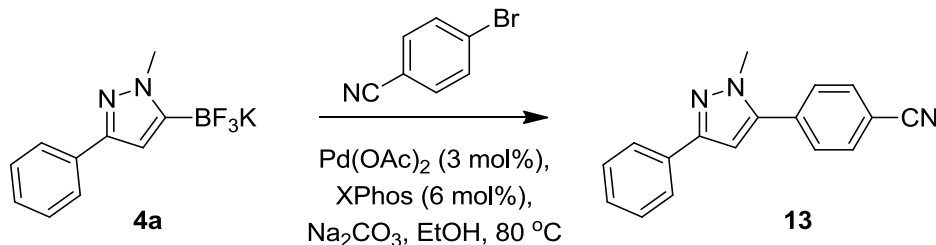


Using general procedure 3, with ynone **3g** (100 mg, 0.46 mmol), the product was isolated as a colourless solid **12d**, 51 mg, 48% yield, m.pt. = >250 °C (dec.).

^1H NMR (250 MHz d_6 -DMSO): δ 1.21 (9H, s, $\text{C}(\text{CH}_3)_3$), 5.84 (1H, s, ArH), 12.13 (1H, br s, NH); ^{13}C NMR (100.6 MHz, d_6 -DMSO): δ 31.0, 31.6, 104.1, 158.5; ^{19}F NMR (235.1 MHz, d_6 -acetone): δ -141.1; FTIR (neat, cm^{-1}) ν_{max} : 3283 (w), 2962 (m), 1208 (m), 978 (s); HRMS calculated for $\text{C}_7\text{H}_{11}^{11}\text{BF}_3\text{KN}_2$ (ES^-) (-K): 191.0967. Found 191.0964.

Functionalization of Pyrazole Trifluoroborates

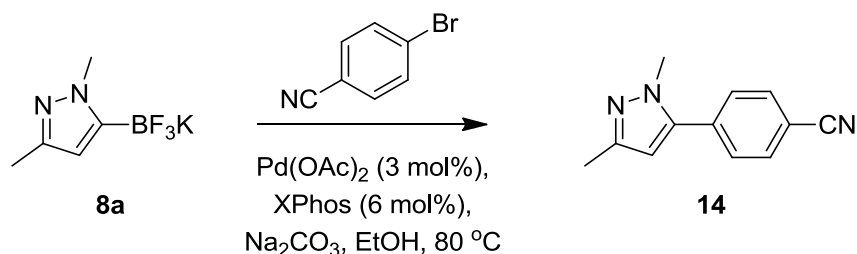
Synthesis of 4-(1-methyl-3-phenyl-1H-pyrazol-5-yl)benzonitrile **13**



To a solution of palladium(II) acetate (0.5 mg, 0.002 mmol), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (2 mg, 0.004 mmol) and sodium carbonate (15 mg, 0.14 mmol) in 0.4 mL ethanol were added 4-bromobenzonitrile (13 mg, 0.07 mmol) and pyrazole trifluoroborate **4a** (20 mg, 0.08 mmol) under a nitrogen atmosphere. The solution was heated to 80 °C and stirred for 12 h. The resulting mixture was then filtered through celite and washed with CH_2Cl_2 . Solvent was removed in vacuo to afford **13** as a pale yellow solid, 18 mg, 87% yield, m.pt. = 102 – 104 °C.

^1H NMR (400 MHz, CDCl_3): δ 3.98 (3H, s, CH_3), 6.70 (1H, s, Ar-*H*), 7.33 – 7.38 (1H, m, Ar-*H*), 7.42 – 7.46 (2H, m, Ar-*H*), 7.62 (2H, d, J = 8.5 Hz, Ar-*H*), 7.80 (2H, d, J = 8.5 Hz, Ar-*H*), 7.84 (2H, d, J = 8.5 Hz, Ar-*H*); ^{13}C NMR (100.6 MHz, CDCl_3): δ 37.9, 104.1, 112.3, 118.4, 125.6, 128.0, 128.7, 129.3, 132.9, 133.1, 135.1, 143.1, 159.0; ν_{max} : 3061 (w), 2930 (w), 2227 (s), 1610 (m), 1460 (m), 1273 (w), 1004 (w); HRMS calculated for $\text{C}_{17}\text{H}_{13}\text{N}_3$ (ES^+): 260.1188. Found 260.1177.

Synthesis of 4-(1,3-dimethyl-1H-pyrazol-5-yl)benzonitrile **14**

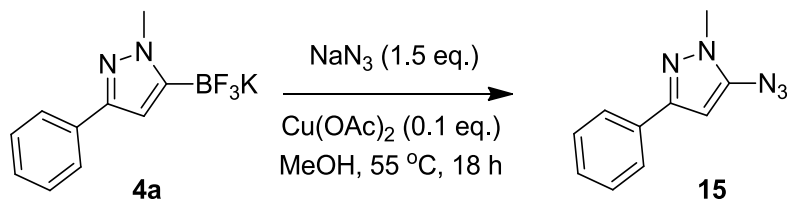


To a solution of palladium(II) acetate (0.9 mg, 0.004 mmol), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (3.9 mg, 0.008 mmol) and sodium carbonate (29 mg, 0.27 mmol) in 0.75 ml ethanol were added 4-bromobenzonitrile (25 mg, 0.14 mmol) and pyrazole trifluoroborate **8a** (30 mg, 0.15 mmol) under a nitrogen atmosphere. The solution was heated to 80 °C and stirred for 12 h. The resulting mixture was then

filtered through celite and washed with CH₂Cl₂. Solvent was removed in vacuo to afford **14** as a pale yellow solid, 15 mg, 48% yield, m.pt. = 71 – 72 °C.

¹H NMR (250 MHz, CDCl₃): δ 2.32 (3H, s, Ar-CH₃), 3.86 (3H, s, NCH₃), 6.18 (1H, s, Ar-H), 7.54 (2H, d, *J* = 8.5 Hz, Ar-H), 7.76 (2H, d, *J* = 8.5 Hz, Ar-H); ¹³C NMR (100.6 MHz, CDCl₃): δ 13.4, 37.4, 106.5, 112.0, 118.4, 129.0, 132.5, 135.3, 142.4, 148.1; FTIR (neat, cm⁻¹) ν_{max}: 3060 (w), 2978 (w), 2339 (w), 1267 (s); HRMS calculated for C₁₂H₁₁N₃ (ES⁺): 198.1031. Found 198.1030.

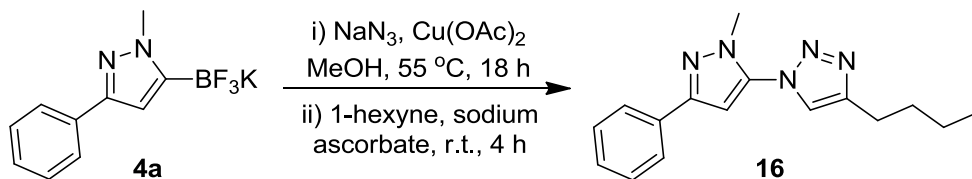
Synthesis of 5-azido-1-methyl-3-phenyl-1H-pyrazole **15**



To a solution of **4a** (100 mg, 0.38 mmol) dissolved in methanol (1.5 mL), was added NaN₃ (37 mg, 0.57 mmol) and Cu(OAc)₂ (7 mg, 0.038 mmol). The reaction was stirred at 55 °C for 18 h under air. Upon completion of reaction, the mixture was filtered through Celite. The product was purified by filtration through a small silica plug (eluting solvent 100% acetone), providing a brown oil **15**, 75 mg, 99% yield.

¹H NMR (250 MHz, CDCl₃): δ 3.71 (3H, s, NCH₃), 6.34 (1H, s, Ar-H), 7.33 – 7.45 (3H, m, Ar-H), 7.74 – 7.77 (2H, m, Ar-H); ¹³C NMR (100.6 MHz, CDCl₃): δ 35.0, 91.4, 125.3, 128.0, 128.7, 133.0, 138.9, 150.6; FTIR (neat, cm⁻¹) ν_{max}: 2136 (s), 1538 (s), 1266 (m), 750 (s); HRMS calculated for C₁₀H₉N₅ (ES⁺): 200.0936. Found 200.0932.

Synthesis of 4-*n*-butyl-1-(1-methyl-3-phenyl-1H-pyrazol-5-yl)-1H-1,2,3-triazole **16**

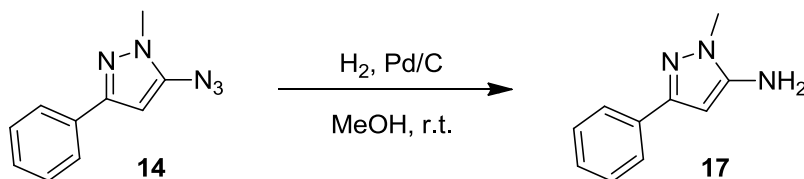


To a solution of **4a** (100 mg, 0.38 mmol) dissolved in methanol (2 mL), was added NaN₃ (37 mg, 0.57 mmol) and Cu(OAc)₂ (7 mg, 0.038 mmol). The reaction was stirred at 55 °C for 18 h under air. After cooling to room temperature, a mixture of sodium ascorbate (38 mg, 0.19 mmol) and 1-hexyne (0.065 mL, 0.57 mmol) in 1:1 CH₂Cl₂/H₂O (2 mL) was added to the reaction mixture. The reaction was stirred for a further 4 h at room temperature, then filtered through celite. Solvent was removed *in vacuo*, and the product was purified by

filtration through a small silica plug (eluting solvent 100% ethyl acetate) to provide a brown oil **16**, 105 mg, 98% yield.

^1H NMR (400 MHz, CDCl_3): δ 0.99 (3H, t, $J = 7.5$ Hz, CH_2CH_3), 1.46 (2H, sext, $J = 7.5$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.76 (2H, pent, $J = 7.5$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.84 (2H, t, $J = 7.5$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.94 (3H, s, NCH_3), 6.68 (1H, s, pyrazole- H), 7.36 (1H, tt, $J = 7.5, 1.0$ Hz, Ar- H), 7.44 – 7.46 (2H, m, Ar- H), 7.60 (1H, s, triazole- H), 7.79 – 7.82 (2H, m, Ar- H); ^{13}C NMR (100.6 MHz, CDCl_3): δ 13.8, 22.3, 25.2, 31.3, 37.2, 98.3, 122.6, 125.5, 128.3, 128.8, 132.5, 136.4, 148.8, 150.4; FTIR (neat, cm^{-1}) ν_{max} : 2935(w), 1461 (w), 1263 (m), 736 (s); HRMS calculated for $\text{C}_{16}\text{H}_{19}\text{N}_5$ (ES^+): 282.1719. Found 282.1707.

Synthesis of 1-methyl-3-phenyl-1H-pyrazol-5-amine **17**



To a solution of **14** (25 mg, 0.13 mmol) dissolved in methanol (2 mL), was added 10% palladium on charcoal (10 mg). The reaction was stirred under a hydrogen atmosphere, at r.t. for 6 h, then filtered through celite. Solvent was removed *in vacuo*, and the product was purified by filtration through a small silica plug (eluting solvent 100% ethyl acetate) to provide a brown oil **17**, 19 mg, 87% yield.

^1H NMR (400 MHz, CDCl_3): δ 3.57 (2H, br s, NH_2), 3.74 (3H, s, NCH_3), 5.89 (1H, s, Ar- H), 7.29 (1H, tt, $J = 7.0, 1.0$ Hz, Ar- H), 7.37 – 7.40 (2H, m, Ar- H), 7.73 – 7.75 (2H, m, Ar- H); ^{13}C NMR (100.6 MHz, CDCl_3): δ 34.4, 88.6, 125.3, 127.4, 128.5, 133.8, 145.5, 149.8. The compound gave satisfactory spectroscopic data.⁴

⁴ Bagley, M. C.; Davis, T.; Dix, M. C.; Widdowson, C. S.; Kipling, D. *Org. Biomol. Chem.*, **2006**, 4158.

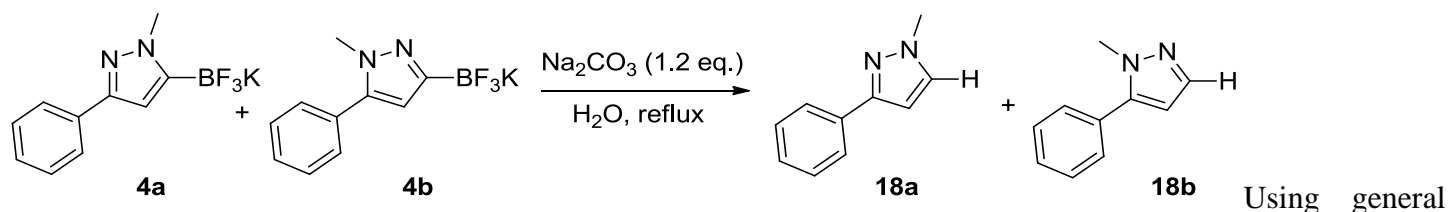
Regiochemical Assignment of Pyrazoles

In order to assign the regiochemistry of the pyrazoles formed, a selection of pyrazole trifluoroborate products were subjected to a base-mediated deborylation, affording a previously reported 1,3- or 1,5-substituted pyrazole as the major product in each case.

General procedure 4: Deborylation of Pyrazole Trifluoroborates

A mixture of pyrazole trifluoroborate (1 mmol) and sodium carbonate (1.2 mmol) in water (0.5 mL) was heated at reflux for 4 h. After cooling to room temperature, the mixture was extracted (25 mL CH₂Cl₂ and 25 mL water), the organic layer was dried (MgSO₄) then concentrated in *vacuo*, affording the desired pyrazole as an oil.

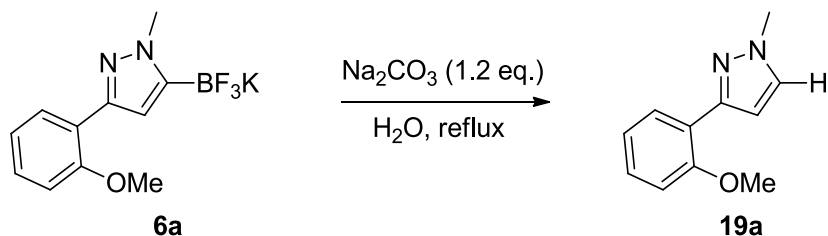
Deborylation of 4a and 4b



procedure 4, with pyrazoles **4a** and **4b** (20 mg, 0.08 mmol), the product was obtained as an inseparable mixture of compounds, **18a** and **18b** as a pale yellow oil, 10 mg, 84% yield.

18a: ¹H NMR (250 MHz, CDCl₃): δ 3.98 (3H, s, NCH₃), 6.56 (1H, d, *J* = 2.0 Hz, Ar-*H*), 7.30 – 7.45 (4H, m, Ar-*H*), 7.80 – 7.84 (2H, m, Ar-*H*); ¹³C NMR (100.6 MHz, CDCl₃): δ 39.1, 102.9, 125.6, 127.6, 128.6, 131.4, 133.5, 151.6. The compound gave satisfactory spectroscopic data.⁵

Deborylation of 6a

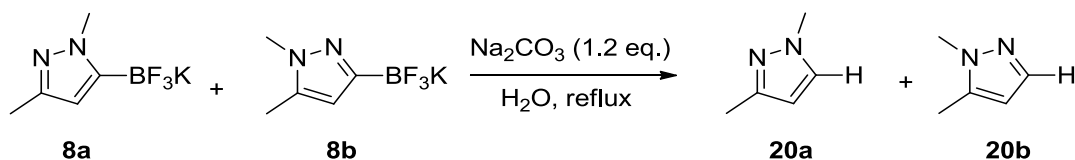


Using general procedure 4, with pyrazole **6a** (22 mg, 0.07 mmol), the product was isolated as a pale yellow oil, **19a**, 9 mg, 68% yield.

⁵ Pavlik, J. W.; Kebede, N. *J. Org. Chem.* **1997**, 62, 8325

^1H NMR (250 MHz, CDCl_3): δ 3.92 (3H, s, NCH_3), 3.98 (3H, s, OCH_3), 6.77 (1H, d, $J = 2.0$ Hz, pyrazole- H), 6.99 (1H, dd, $J = 8.5, 1.0$ Hz, Ar- H), 7.03 (1H, td, $J = 7.5, 1.0$ Hz, Ar- H), 7.31 (1H, ddd, $J = 8.5, 7.5, 2.0$ Hz, Ar- H), 7.40 (1H, d, $J = 2.0$ Hz, pyrazole- H), 7.91 (1H, dd, $J = 7.5, 2.0$ Hz, Ar- H); ^{13}C NMR (100.6 MHz, CDCl_3): δ 39.0, 55.5, 106.9, 111.2, 120.8, 122.5, 128.6, 128.7, 130.5, 148.4, 156.7. The product gave satisfactory spectroscopic data.⁶

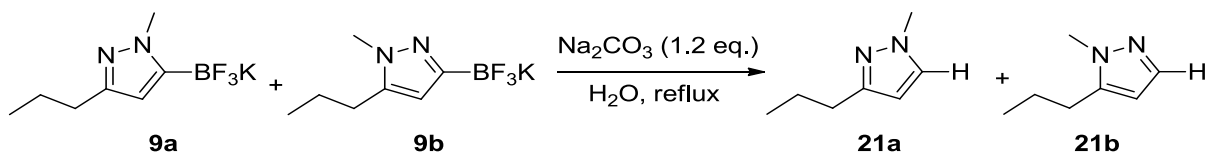
Deborylation of **8a** and **8b**



Using general procedure 4, with pyrazoles **8a** and **8b** (20 mg, 0.10 mmol), the volatile product was obtained as an inseparable mixture of compounds, **20a** and **20b**, as a yellow oil, 3 mg, 31% yield.

20a: ^1H NMR (250 MHz, CDCl_3): δ 2.29 (3H, s, CH_3), 3.85 (3H, s, NCH_3), 6.02 (1H, d, $J = 2.0$ Hz, Ar- H), 7.25 (1H, d, $J = 2.0$ Hz, Ar- H); ^{13}C NMR (100.6 MHz, CDCl_3): δ 40.2, 48.9, 107.3, 132.5, 156.1. The compound gave satisfactory spectroscopic data.⁷

Deborylation of **9a** and **9b**



Using general procedure 4, with pyrazoles **9a** and **9b** (20 mg, 0.09 mmol), the volatile product was obtained as an inseparable mixture of compounds, **21a** and **21b**, as a yellow oil, 2 mg, 18% yield.

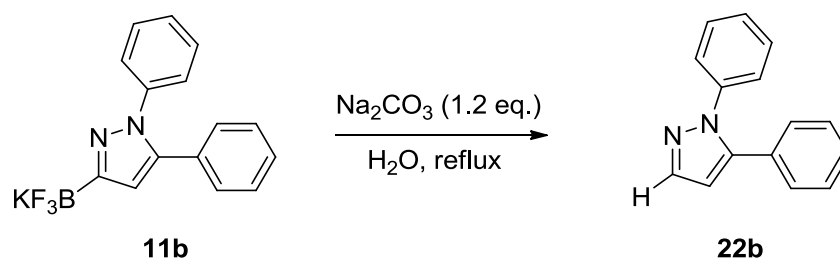
21a: ^1H NMR (250 MHz, CDCl_3): δ 0.98 (3H, t, $J = 7.5$ Hz, CH_3), 1.29 – 1.33 (2H, m, CH_2CH_3), 2.62 (2H, t, $J = 7.5$ Hz, CH_2CH_2), 3.88 (3H, s, NCH_3), 6.05 (1H, d, $J = 1.5$ Hz, Ar- H), 7.23 (1H, d, $J = 1.5$ Hz, Ar- H); ^{13}C

⁶ Catalan, J.; Fabero, F.; Claramunt, R. M.; Santa Maria, M. D.; de la Concepcion Foces-Foces, M.; Cano, F. H.; Martinez-Ripoll, M.; Elguero, J.; Sastre, R. *J. Am. Chem. Soc.* **1992**, *114*, 5039

⁷ Graham, S. R.; Brown, P. J.; Ford, J. G. *Org. Process Res. & Dev.* **2010**, *14*, 242

NMR (100.6 MHz, CDCl₃): δ 13.8, 22.4, 38.3, 45.9, 104.0, 130.5, 153.3. The compound gave satisfactory spectroscopic data.⁸

Deborylation of **11b**

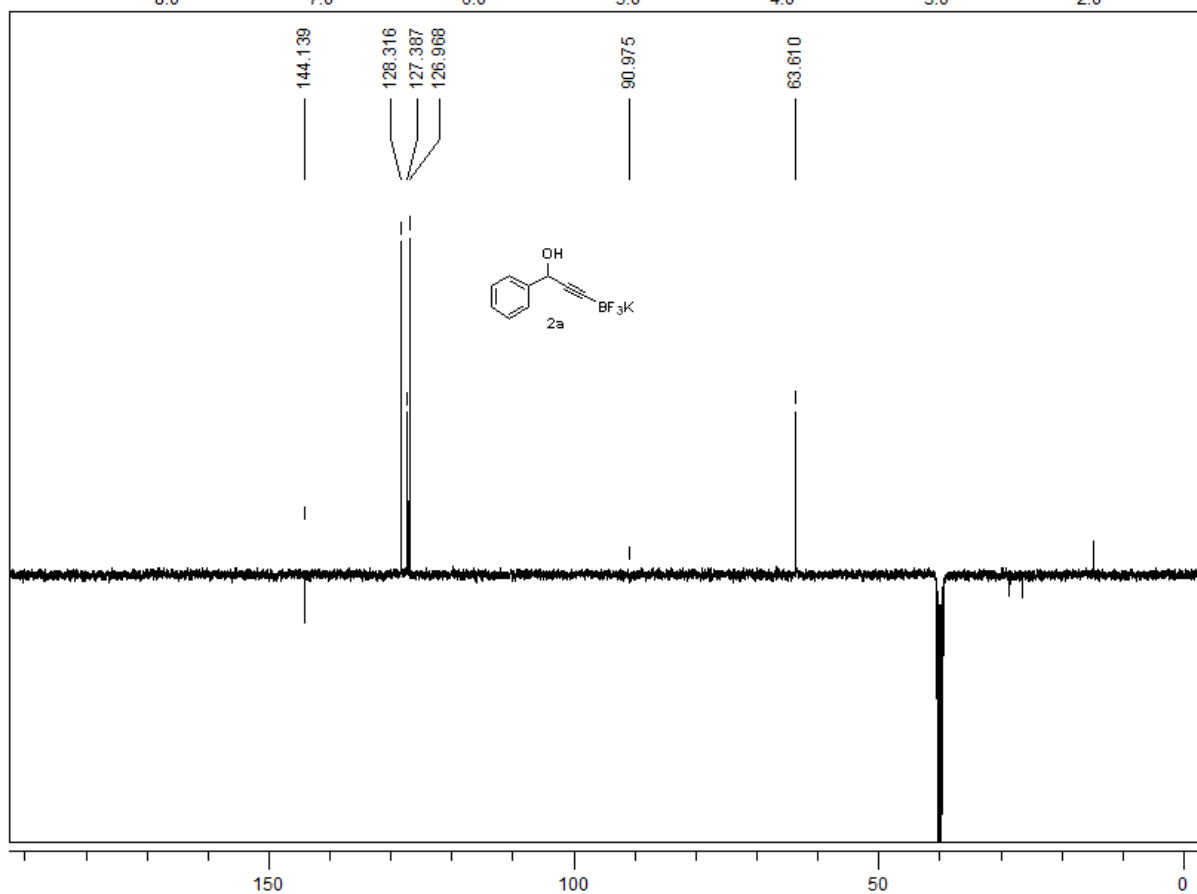
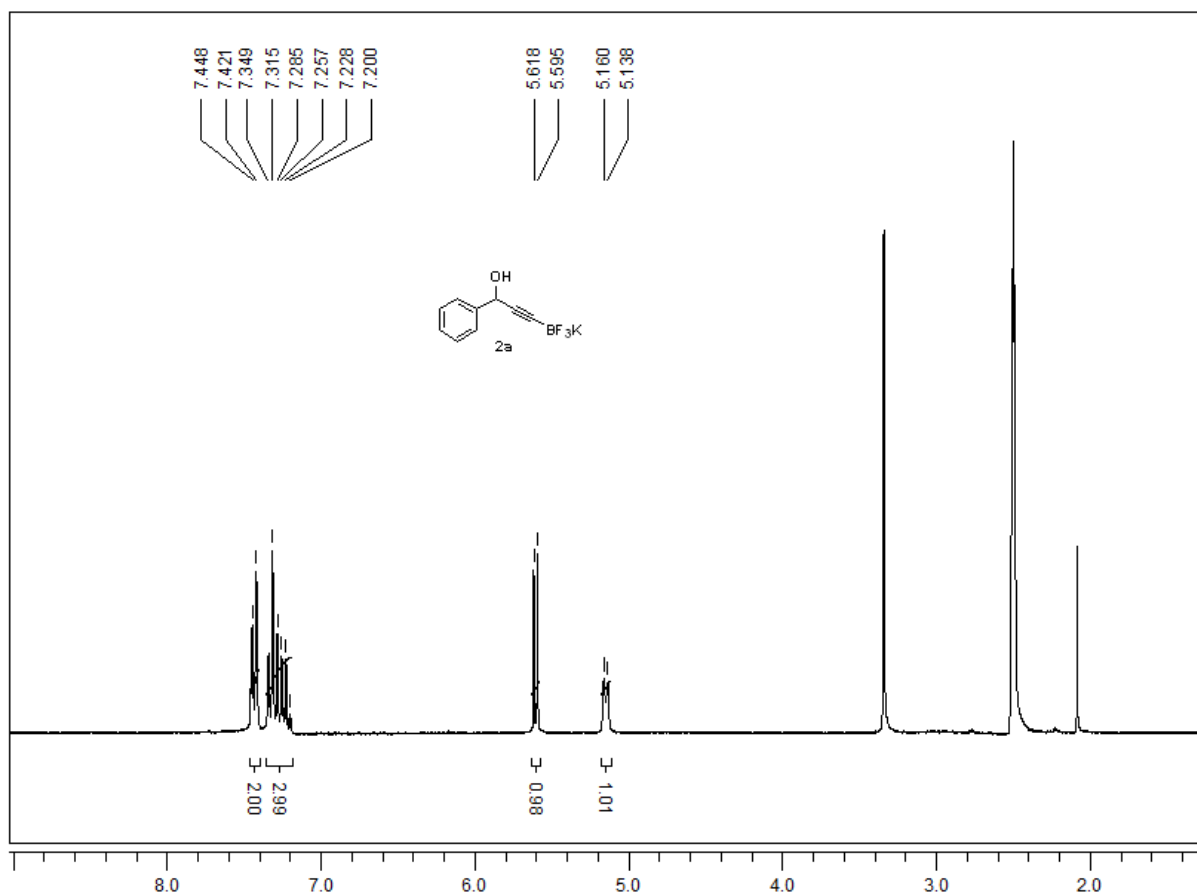


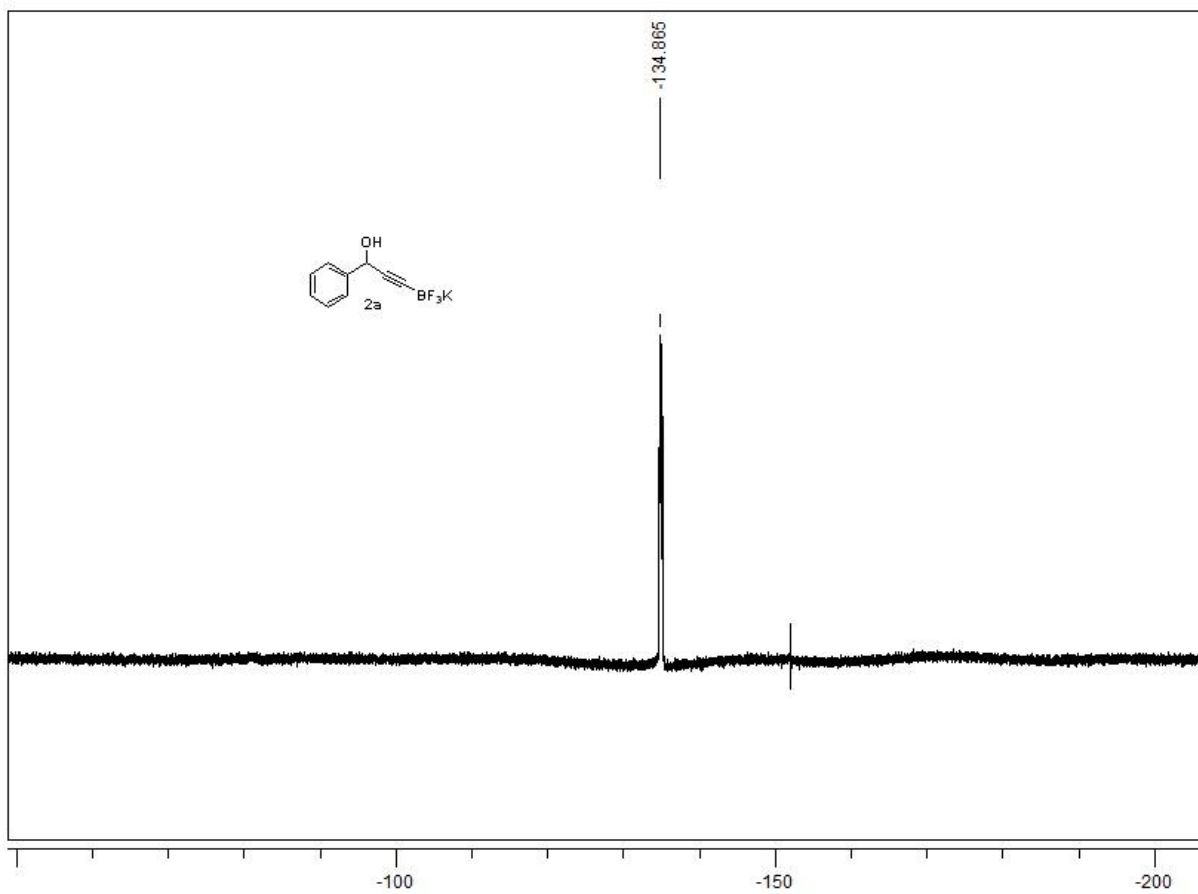
Using general procedure 4, with pyrazole **11b** (15 mg, 0.05 mmol), the product was isolated as a pale yellow oil, **22b**, 7 mg, 69% yield.

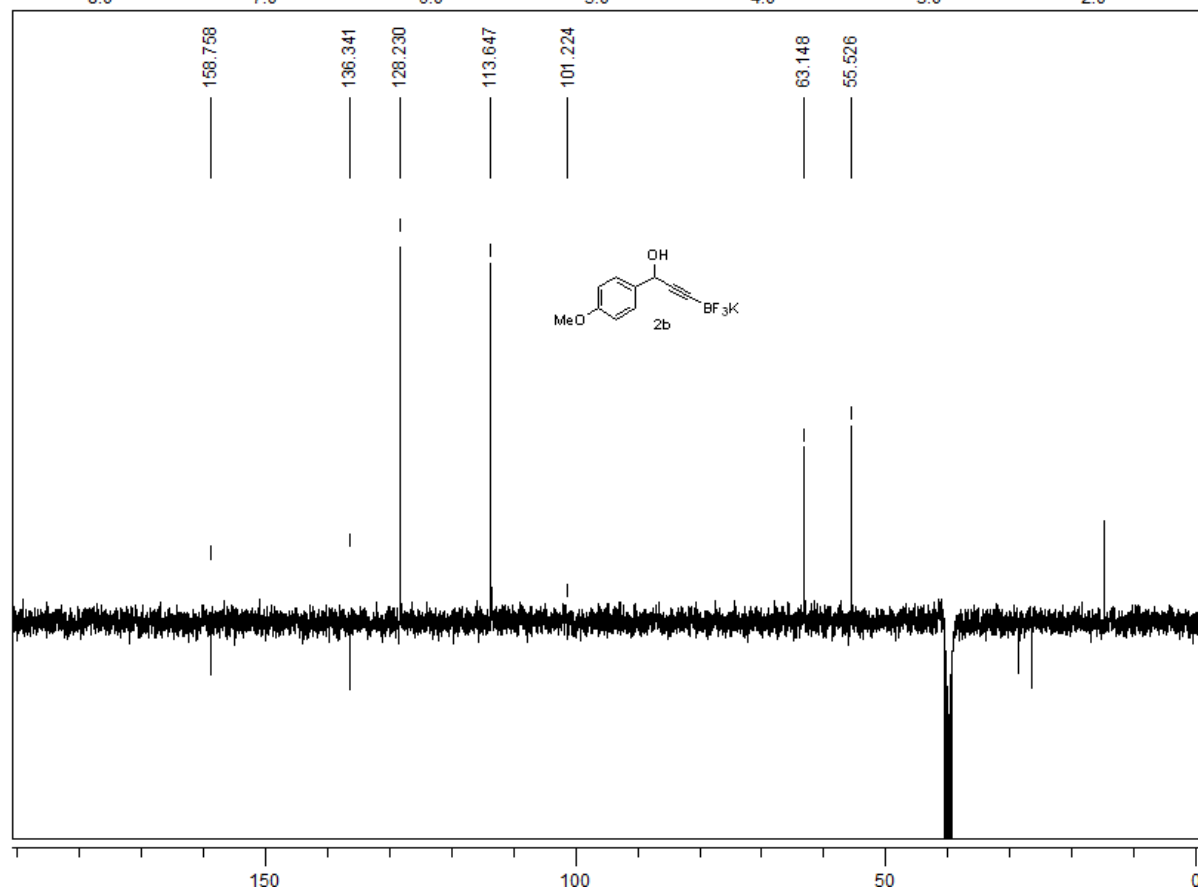
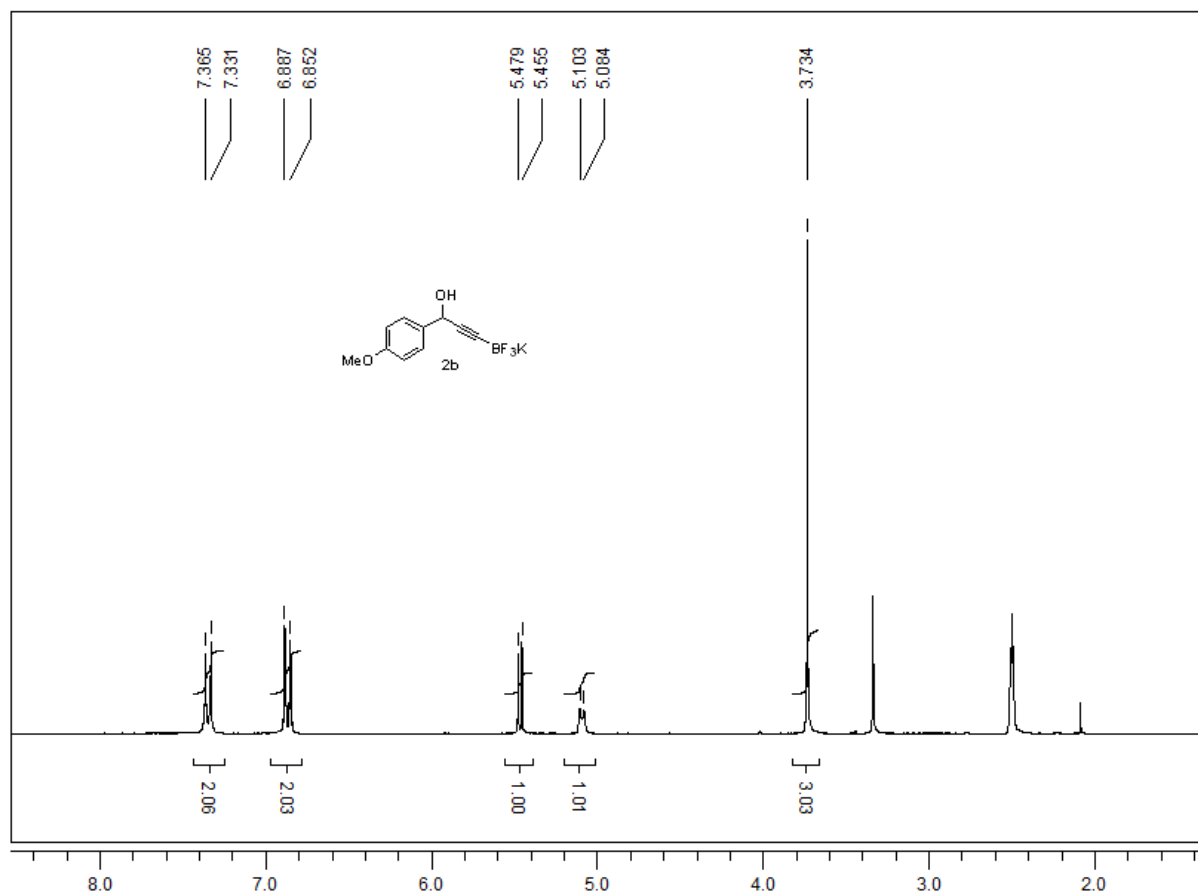
¹H NMR (250 MHz, CDCl₃): δ 6.54 (1H, d, J = 2.0 Hz, Ar-*H*), 7.22 – 7.41 (10H, m, Ar-*H*), 7.75 (1H, d, J = 2.0 Hz, Ar-*H*); ¹³C NMR (100.6 MHz, CDCl₃): δ 107.9, 125.2, 127.4, 128.2, 128.5, 128.8, 128.9, 130.6, 140.1, 140.3, 143.0. The compound gave satisfactory spectroscopic data.⁹

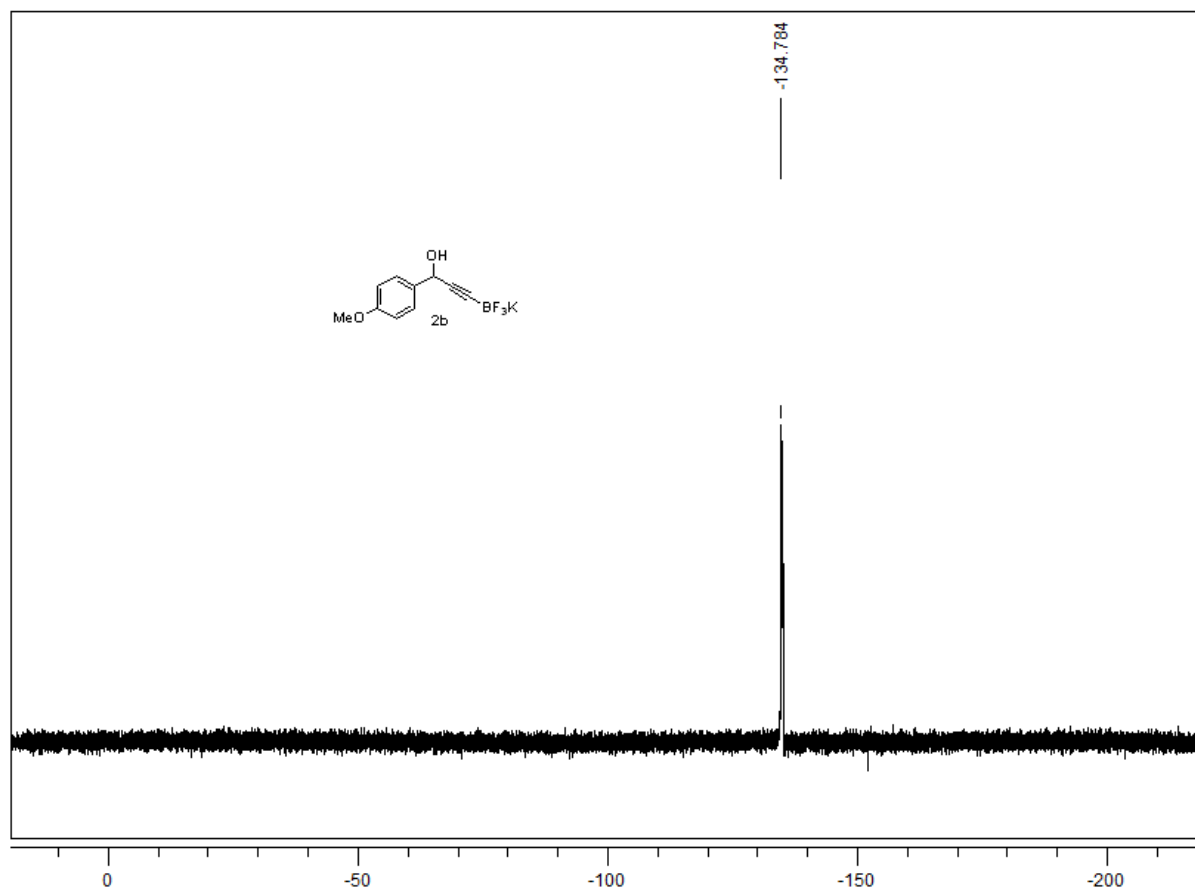
⁸ Bozhenkov, G. V.; Savosik, V. A.; Klyba, L. V.; Zhanchipova, E. R.; Mirskova, A. N.; Levkovskaya, G. G. *Russ. J. Org. Chem.*, **2008**, 1194

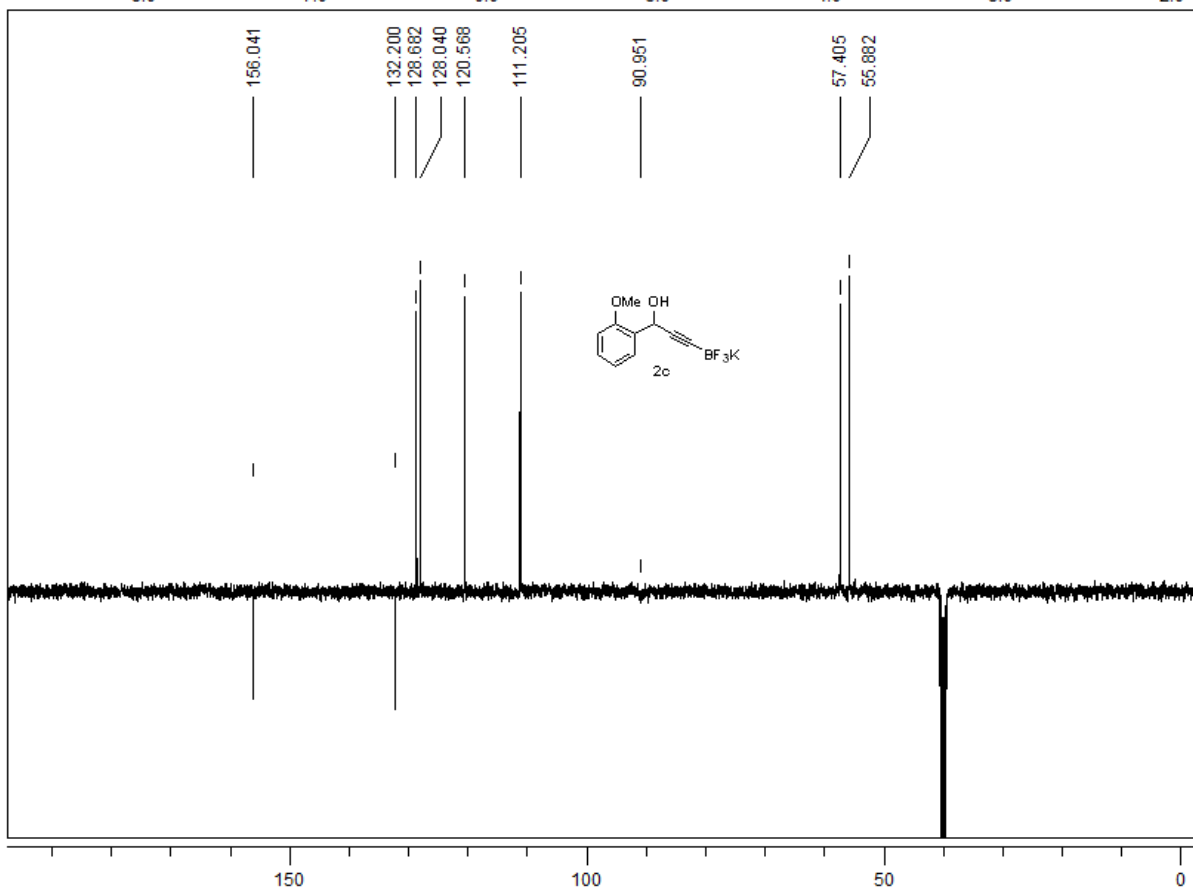
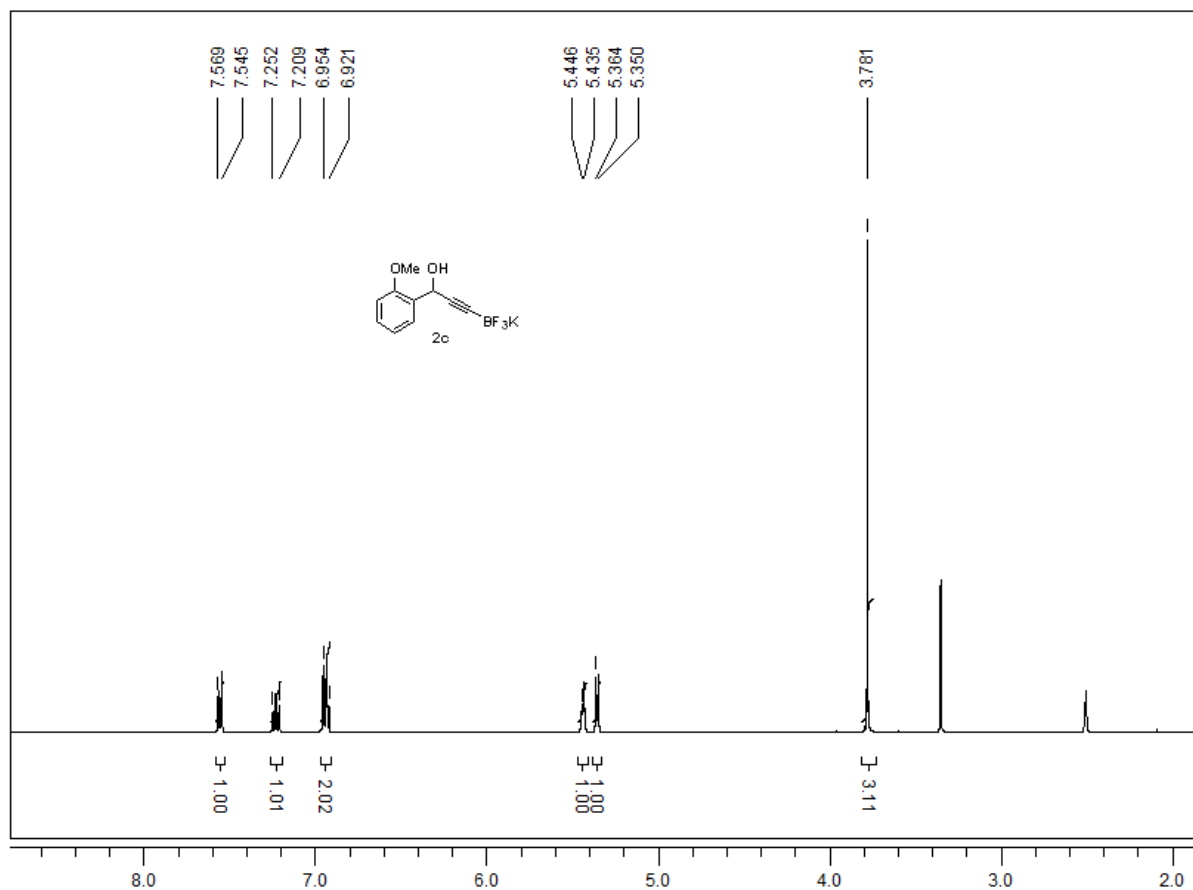
⁹ Bagley, M. C.; Lubinu, M. C.; Mason, C. *Synlett*, **2007**, 704

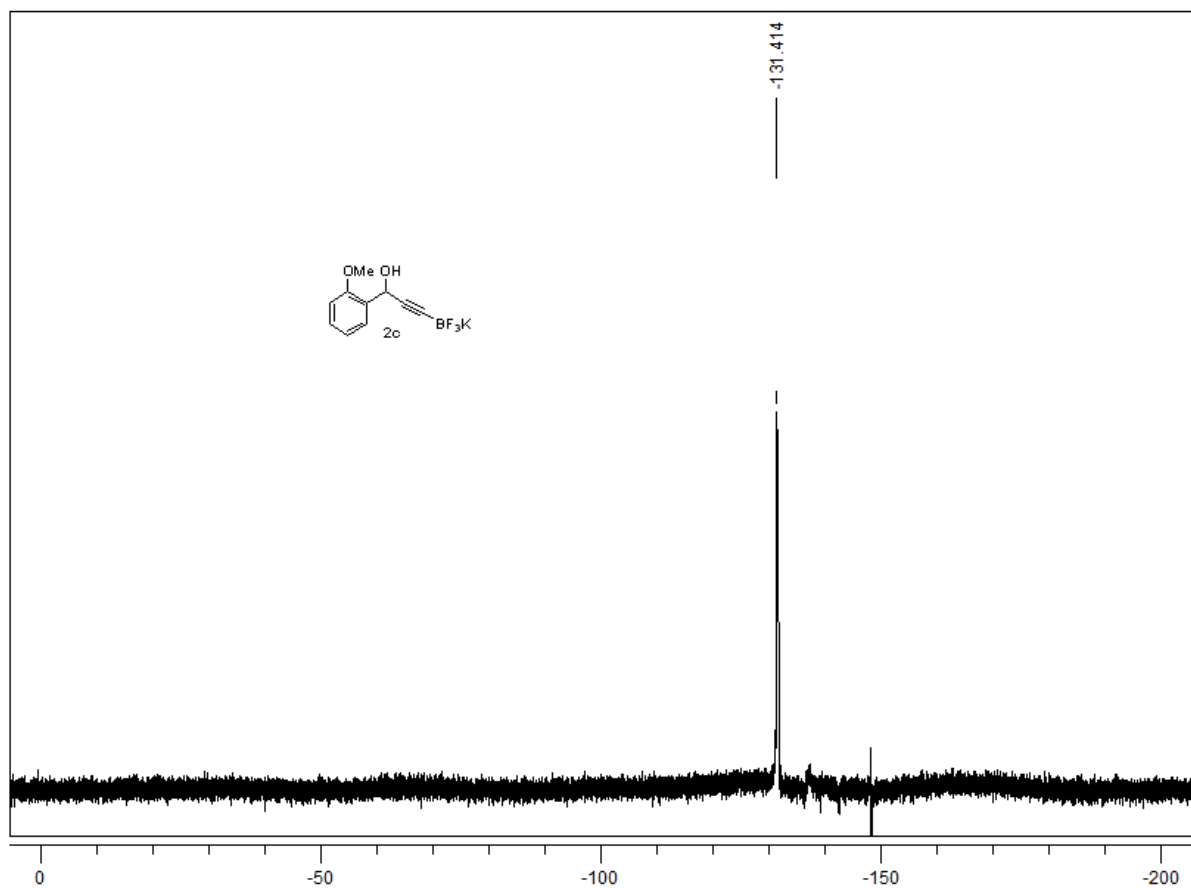


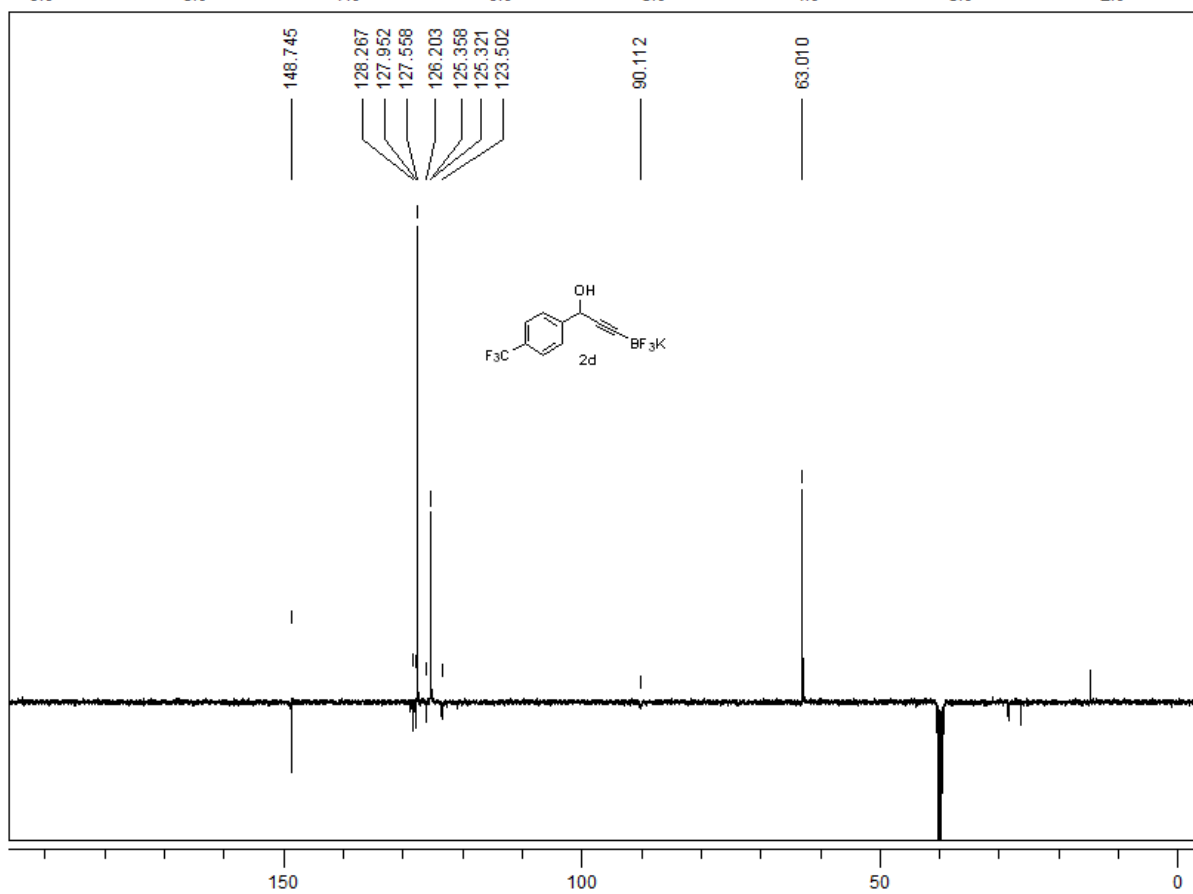
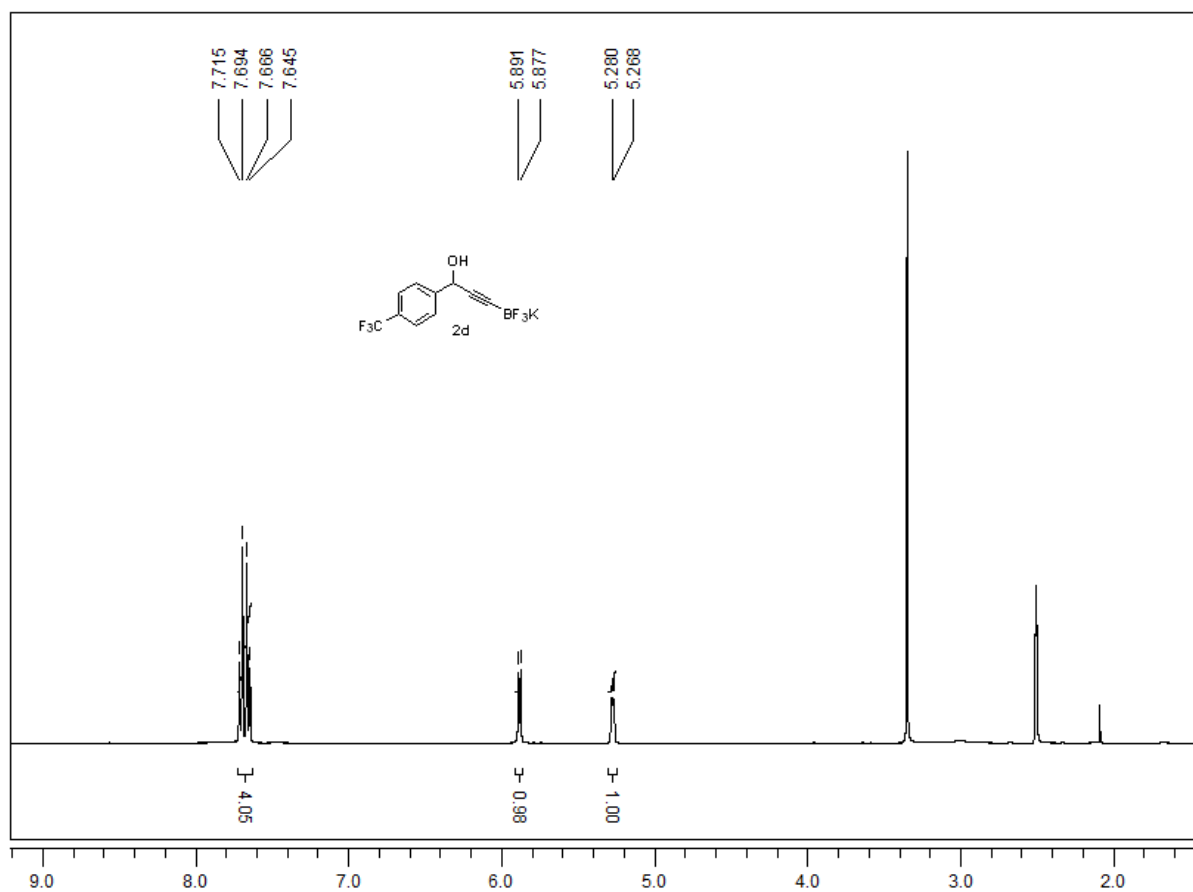


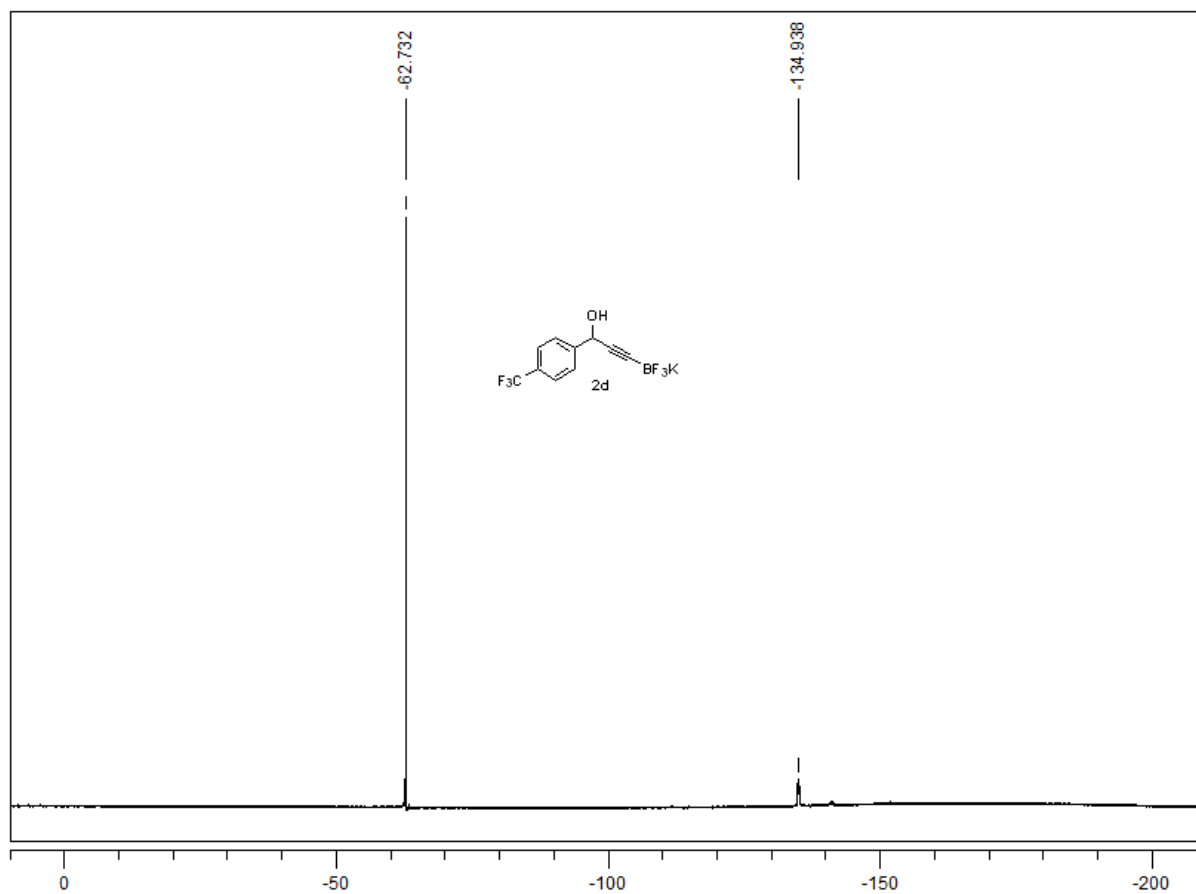


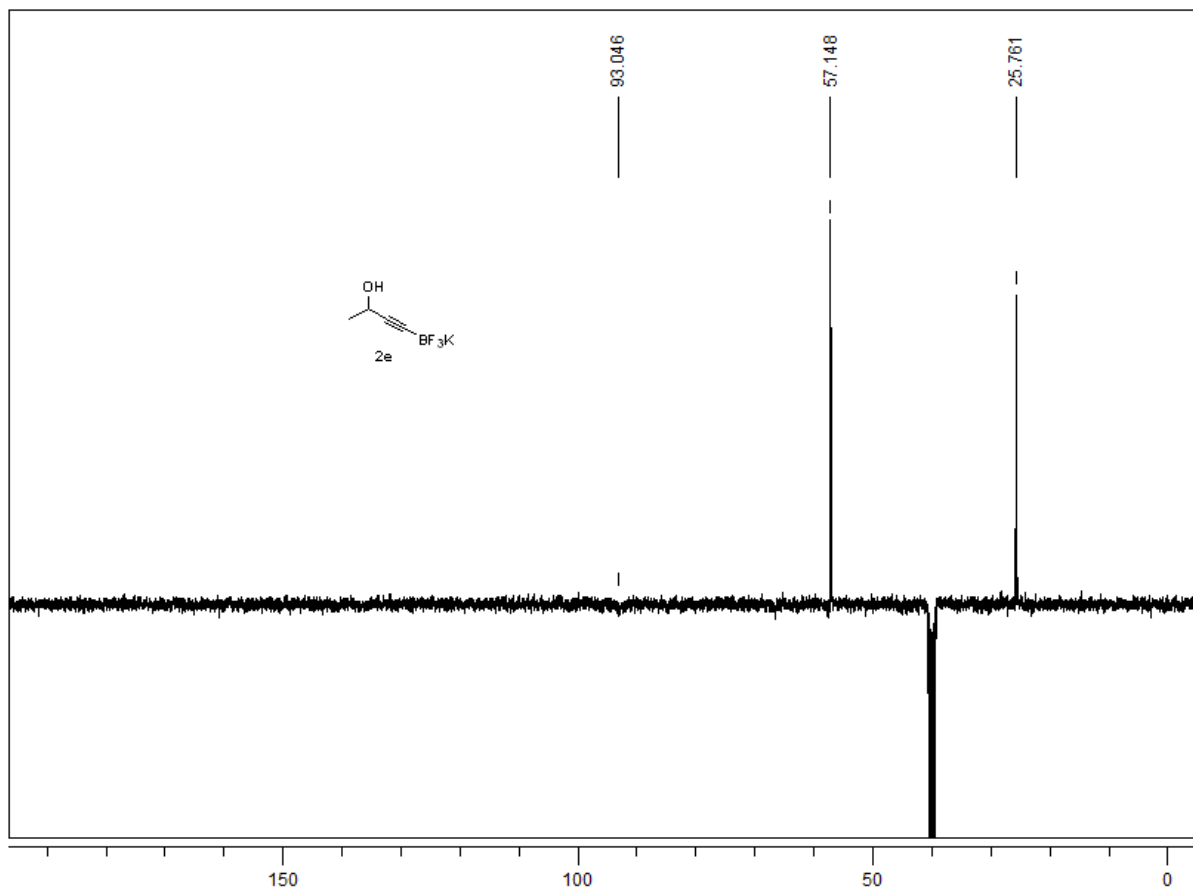
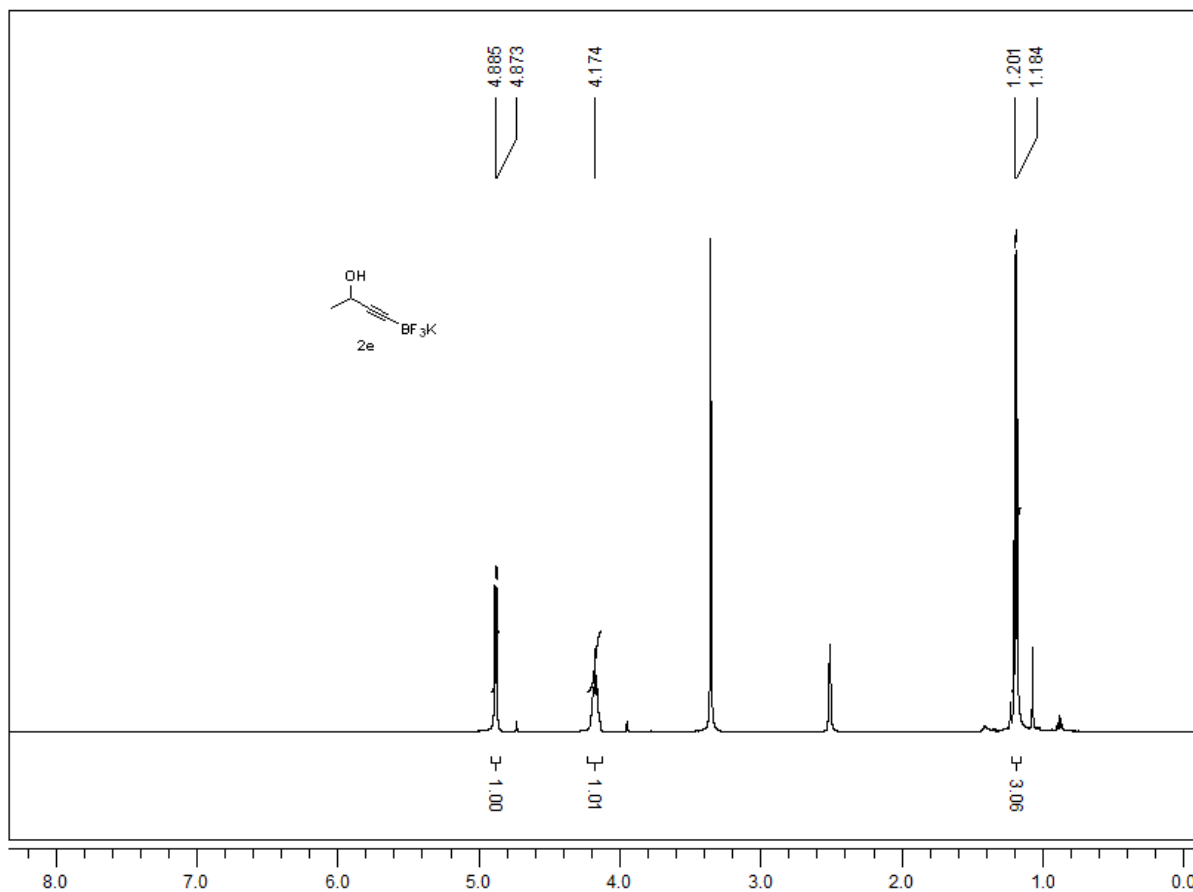












S30

