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Supporting Information

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A Sydnone Cycloaddition Strategy to Pyrazole Boronic Esters

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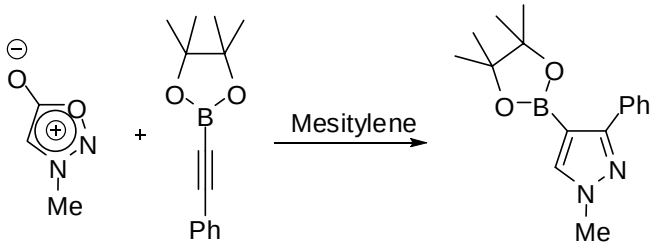
General Procedures.

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). Alternatively, flash chromatography performed with an added cake of impregnated silica (10% silver nitrate)can be employed to avoid co-elution of compounds **2a**,**2b** or **2c** with the desired pyrazole product. Thin layer chromatography (TLC) was performed on aluminium backed plates pre-coated with silica (0.2 mm, Merck DC-alufolien Kieselgel 60 F_{254}) and 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 ($CHCl_3$:δ7.27 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 ($CDCl_3$: δ77.0 ppm). Infrared (FTIR) spectra were recorded on a Perkin Elmer Paragon 100 FTIR spectrophotometer, n_{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. 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 either FAB (FAB^+), EI (EI^+) or CI (CI^+) mode. Elemental microanalysis performed using a Perkin-Elmer 2400 CHNS / O Series II Elemental Analyser. 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).

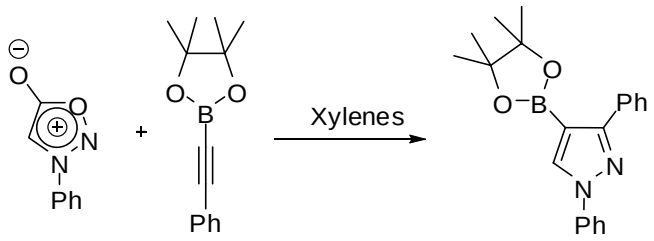
Synthesis of 1-methyl-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrazole



2a

To N-methylsydnone (1 mmol, 100 mg) and **2a** (2 mmol, 456 mg) was added mesitylene (4 mL). Reaction mixture was stirred at reflux for 72 hours before the volatiles were removed in vacuo. Reaction was purified by flash chromatography on silica gel. Title compound was isolated as a yellow oil (151 mg 53%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.82-7.91 (m, 2H, Ar-H), 7.64 (s, 1H, pyrazole-H), 7.17 (m, 3H, Ar-H), 3.83 (s, 3H, CH_3), 1.23 (s, 12H, pinacol-CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 157.0, 139.8, 134.2, 128.2, 127.9, 127.6, 83.3, 38.7, 24.9; FTIR: 3057 (w), 2977 (m),2929 (w), 1531 (s), 1448 (m), 1371 (m), 1333 (s) 1302 (m), 1216 (w), 1178 (m), 1118 (s), 989 (m), 959 (w) cm^{-1}; HRMS (ES): m/z $[MH]^+$ calcd. for $C_{16}H_{22}BN_2O_2$ 285.1774. found: 285.1767.

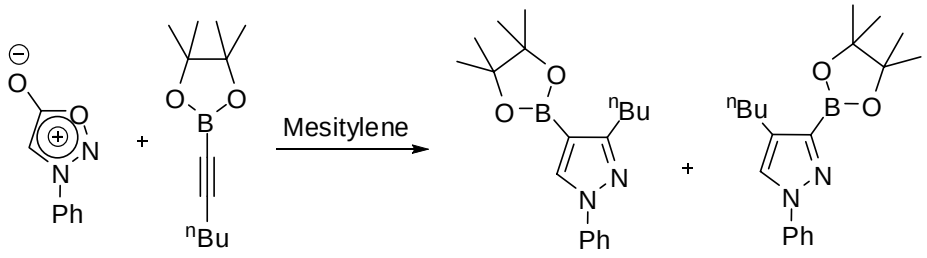
Synthesis of 1,3-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrazole（3a）



1a **2a** **3a**

To **1a** (0.5 mmol, 81 mg) and **2a** (1 mmol, 228 mg) was added xylenes (0.5 mL). Reaction mixture was stirred at reflux for 8 hours before rapidly cooling in an ice bath. Reaction was purified by flash chromatography on silica gel (gradient; starting with 100% petroleum ether, ending with 30% ethyl acetate in petroleum ether). Product **3a** was isolated as a colourless solid (100 mg, 58%). Further purification could be carried out by trituration with diethyl ether. ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.30 (s, 1H, pyrazole-H), 8.02-8.10 (m, 2H, Ar-H), 7.75-7.83 (m, 2H, Ar-H), 7.25-7.50 (m, 6H, Ar-H), 1.34 (s, 12H, pinacol CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 157.9, 139.8, 136.3, 133.9, 129.4, 128.4, 128.0, 126.6, 119.3 (2C), 83.6, 24.8; FTIR (CH_2Cl_2): 2978 (m), 1600 (m), 1532 (s), 1446 (m), 1356 (m), 1307 (m), 1217 (m), 1146 (m), 1126 (m), 1062 (m), 993 (m), 958 (m) cm^{-1}; HRMS (EI): m/z $[M]^+$ calcd for $C_{21}H_{23}BN_2O_2$: 346.1853, found: 346.1866. M.p. 158-160 ˚C.

Synthesis of 3-butyl-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrazole (4a) and 4-butyl-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrazole (4b).

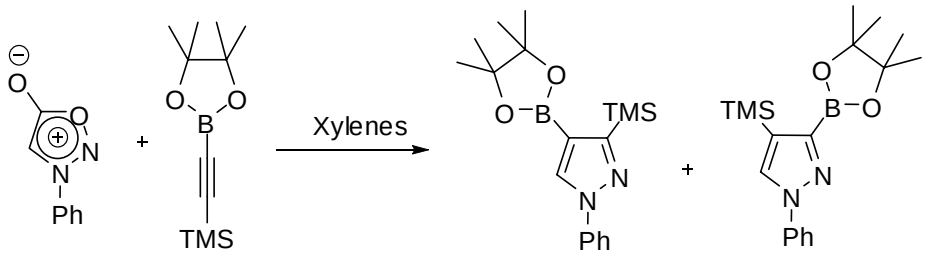


1a **2b** **4a** **4b**

To **1a** (0.5 mmol, 81 mg) and **2b** (1 mmol, 208 mg) was added mesitylene (0.5 mL). Reaction mixture was stirred at reflux for 16 hours before rapidly cooling in an ice bath. Reaction was purified by flash chromatography on silica gel (gradient; starting with 100% petroleum ether, ending with 25% ethyl acetate in petroleum ether). Product **4a** was isolated as a brown oil (75 mg, 46%), and product **4b** as a brown oil (30 mg, 18%). **(4a)** ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.05 (s, 1H, pyrazole-H), 7.55-7.62 (m, 2H, Ar-H), 7.32 (t, 2H, J = 8.0 Hz, Ar-H), 7.10-7.20 (m, 1H, Ar-H), 2.73-2.83 (m, 2H, CH_2), 1.55-1.69 (m, 2H, CH_2), 1.25-1.42 (m, 2H, CH_2), 1.24 (s, 12H, pinacol CH_3), 0.87 (t, 3H, J = 7.5 Hz, CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 161.5, 139.9, 134.6, 129.3, 126.1, 119.2, 83.1, 32.6, 28.2, 24.8, 22.6, 13.9; FTIR (CH_2Cl_2):2958 (m), 2931 (m), 2872 (w), 1601 (m), 1551 (s), 1465 (m), 1382 (m), 1307 (s), 1146 (s), 1077 (s), 958 (m).cm^{-1}; HRMS (ES): m/z $[MH]^+$ calcd for $C_{19}H_{28}BN_2O_2$: 327.2244, found: 327.2260. **(4b)** ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.63-7.70 (m, 3H, pyrazole-H + Ar-H), 7.28-7.37 (m, 2H, Ar-H), 7.13-7.21 (m,

1H, Ar-H), 2.64 (t, 2H, J = 7.5 Hz, CH_2), 1.44-1.58 (m, 2H, CH_2), 1.22-138 (m, 14H, pinacol CH_3 + CH_2), 0.86 (t, 3H, J = 7.0 Hz, CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 140.2, 132.6, 129.1, 126.3, 125.4, 119.8, 83.7, 33.7, 24.9, 24.1, 22.4, 13.9; FTIR (CH_2Cl_2): 2956 (m), 2930 (m), 2860 (w), 1601 (m), 1485 (s), 1372 (m), 1297 (m), 1145 (s), 1100 (m), 1082 (m), 962 (m) cm^{-1}; HRMS (ES): m/z $[MH]^+$ calcd for $C_{19}H_{28}BN_2O_2$: 327.2244, found: 327.2260.

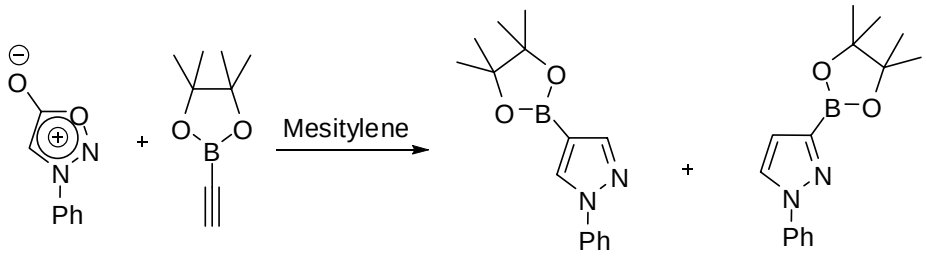
Synthesis of 1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trimethylsilyl)-1H-pyrazole (5a) and 1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trimethylsilyl)-1H-pyrazole (5b).



1a **2c** **5a** **5b**

To **1a** (0.5 mmol, 81 mg) and **2c** (1 mmol, 224 mg) was added xylenes (0.5 mL). Reaction mixture was stirred at reflux for 8 hours before rapidly cooling in an ice bath. Reaction was purified by flash chromatography on silica gel (gradient; starting with 100% petroleum ether, ending with 25% ethyl acetate in petroleum ether). Product **5a** was isolated as a colourless solid (85 mg, 50%), and product **5b** as a colourless solid (43 mg, 25%). **(5a)** ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.29 (s, 1H, pyrazole-H), 7.70-7.76 (m, 2H, Ar-H), 7.37-7.46 (m, 2H, Ar-H), 7.21-7.29 (m, 1H, Ar-H), 1.33 (s, 12H, pinacol CH_3), 0.38 (s, 9H, TMS); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 161.2, 140.0, 135.0, 129.3, 126.3, 119.5, 83.3, 24.9, -0.9; FTIR (CH_2Cl_2): 2978 (m), 1601 (m), 1528 (s), 1507 (m), 1427 (m), 1372 (m), 1305 (s), 1264 (s), 1145 (s), 1051 (s), 960 (m), 845 (s) cm^{-1}; HRMS (EI): m/z $[M]^+$ calcd for $C_{18}H_{27}BN_2O_2Si$: 342.1935, found: 342.1918. M.p. 103-105 ˚C. **(5b)** ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.82 (s, 1H, pyrazole-H), 7.72-7.78 (m, 2H, Ar-H), 7.36-7.45 (m, 2H, Ar-H), 7.22-7.30 (m, 1H, Ar-H), 1.37 (s, 12H, pinacol CH_3), 0.31 (s, 9H, TMS); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 139.9, 132.9, 129.1, 126.6, 125.2, 120.4, 84.0, 24.9, -0.2; FTIR (CH_2Cl_2): 2974 (m), 1599 (m), 1510 (m), 1460 (s), 1381 (m), 1342 (m), 1305 (m), 1243 (s), 1142 (s),1054 (s), 964 (m), 840 (s) cm^{-1}; HRMS (ES): m/z $[MH]^+$ calcd for $C_{18}H_{28}BN_2O_2Si$: 343.2013, found: 343.2023. M.p. 206-208 ˚C.

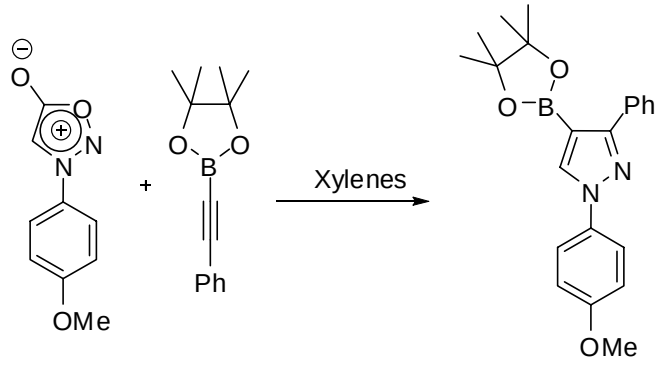
Synthesis of 1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrazole (6a) and 1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrazole (6b).



1a **2d** **6a** **6b**

To **1a** (0.5 mmol, 81 mg) and **2d** (1 mmol, 152 mg) was added mesitylene (0.5 mL). Reaction mixture was stirred at reflux for 16 hours before rapidly cooling in an ice bath. Reaction was purified by flash chromatography on silica gel (gradient; starting with 100% petroleum ether, ending with 25% ethyl acetate in petroleum ether). Product **6a** was isolated as a brown oil (10 mg, 7%), and product **6b** as a brown oil (63 mg, 47%) both **6a/b** appeared to partially protodeboronate during flash chromatography as evidenced by their ^{1}H NMR spectra. **(6a)** ^{1}H NMR (250 MHz, $CDCl_3$): δ. 8.17 (d, J = 0.5 Hz, 1H, pyrazole-H), 7.91 (d, J = 0.5 Hz, 1H, pyrazole-H), 7.6-7.66 (m, 2H, Ar-H), 7.34-7.42 (m, 2H, Ar-H), 7.21-7.26 (m, 1H, Ar-H), 1.28 (s, 12H, pinacol-CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 146.8, 139.9, 133.6, 129.4, 126.7, 119.4, 83.5, 24.8; FTIR (CH_2Cl_2): 2923 (m), 2852 (w), 1598 (w), 1559 (s), 1507 (m), 1402 (m), 1370 (m), 1306 (m), 1267 (m), 1134 (s), 986 (m), 954 (m) cm^{-1}; HRMS (ES): m/z $[MH]^+$ calcd for $C_{15}H_{20}BN_2O_2$: 271.1618, found: 271.1620. **(6b)** ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.84 (d, J = 2.5 Hz, 1H, pyrazole-H), 7.63-7.69 (m, 2H, Ar-H), 7.27-7.35 (m, 2H, Ar-H), 7.13-7.20 (m, 1H, Ar-H), 6.77 (d, J = 2.5 Hz, 1H, pyrazole-H), 1.28, (s, 12H, pinacol-CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 140.1, 129.2, 127.3, 126.8, 120.1, 115.1, 84.1, 24.9; FTIR (CH_2Cl_2): 2979 (m), 2932 (w), 1756 (w), 1600 (m), 1502 (s), 1460 (s), 1352 (s), 1292 (s), 1166 (m), 1140 (s), 1048 (m), 980 (m), 947 (m) cm^{-1}; HRMS (ES): m/z $[MH]^+$ calcd for $C_{15}H_{20}BN_2O_2$: 271.1618, found: 271.1616.

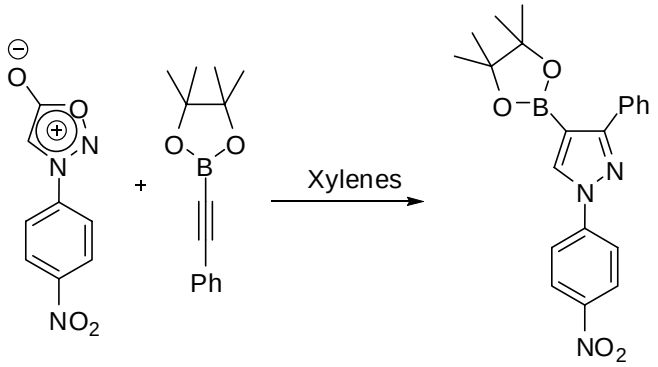
Synthesis of 1-(4-methoxyphenyl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrazole (7a).



1b **2a** **7a**

To **1b** (0.5 mmol, 96 mg) and **2a** (1 mmol, 228 mg) was added xylenes (0.5 mL). Reaction mixture was stirred at reflux for 24 hours before rapidly cooling in an ice bath. Reaction was purified by flash chromatography on silica gel (gradient; starting with 100% petroleum ether, ending with 20% ethyl acetate in petroleum ether). Product **7a** was isolated as a colourless solid (105 mg, 56%). Further purification could be carried out by trituration with diethyl ether. **(7a)** ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.13 (s, 1H, pyrazole-H), 7.95- 8.01 (m, 2H, Ar-H), 7.57-7.64 (m, 2H, Ar-H), 7.26-7.37 (m, 3H, Ar-H), 6.86-6.93 (m, 2H, Ar-H), 3.77 (s, 3H, OCH_3), 1.27 (s, 12H, pinacol-CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 158.3, 157.6, 136.3, 134.0, 133.6, 128.4, 128.0 (2C), 120.9, 114.5, 83.5, 55.6, 24.8; FTIR (CH_2Cl_2): 2977 (w), 1521 (s), 1450 (m), 1354 (m), 1330 (m), 1302 (m), 1255 (m), 1210 (m), 1146 (m), 1124 (m), 1062 (m), 1034 (m), 993 (m), 961 (m), 830 (m) cm^{-1}; HRMS (ES): m/z $[MH]^+$ calcd for $C_{22}H_{26}BN_2O_3$: 377.2036, found: 377.2050. M.p. 114-116 ˚C.

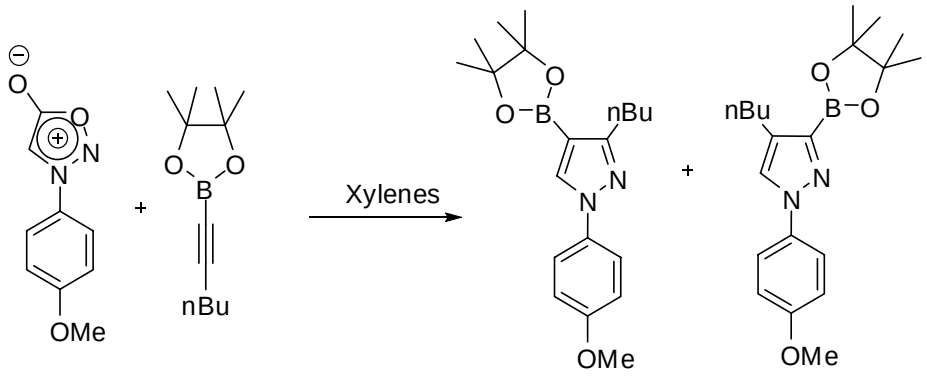
Synthesis of 1-(4-nitrophenyl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrazole (8a).



1c **2a** **8a**

To **1c** (1.16 mmol, 240 mg) and **2a** (1 mmol, 529 mg) was added xylenes (0.5 mL). Reaction mixture was stirred at reflux for 4 hours before rapidly cooling in an ice bath. Reaction was purified by flash chromatography on silica gel (gradient; starting with 100% petroleum ether, ending with 20% ethyl acetate in petroleum ether). Product **8a** was isolated as a colourless solid (345 mg, 76%). Further purification could be carried out by trituration with acetone. ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.33 (s, 1H, pyrazole-H), 8.22-8.27 (m, 2H, Ar-H), 7.97-8.01 (m, 2H, Ar-H), 7.86-7.91 (m, 2H, Ar-H), 7.31-7.40 (m, 3H, Ar-H), 1.28 (s, 12H, pinacol-CH_3) ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 159.1, 145.5, 144.0, 136.6, 133.2, 128.8, 128.5, 128.1, 125.3, 118.6, 83.9, 24.8; FTIR (CH_2Cl_2): 2979 (m), 1598 (s), 1524 (s), 1445 (m), 1338 (s), 1273 (m), 1216 (m), 1146 (m), 1126 (m), 1112(m), 1055 (m), 994 (m), 956 (m), 853 (m) cm^{-1}; HRMS (ES): m/z $[MH]^+$ calcd for $C_{21}H_{23}BN_3O_4$: 392.1782, found: 392.1788. M.p. 166-168 ˚C.

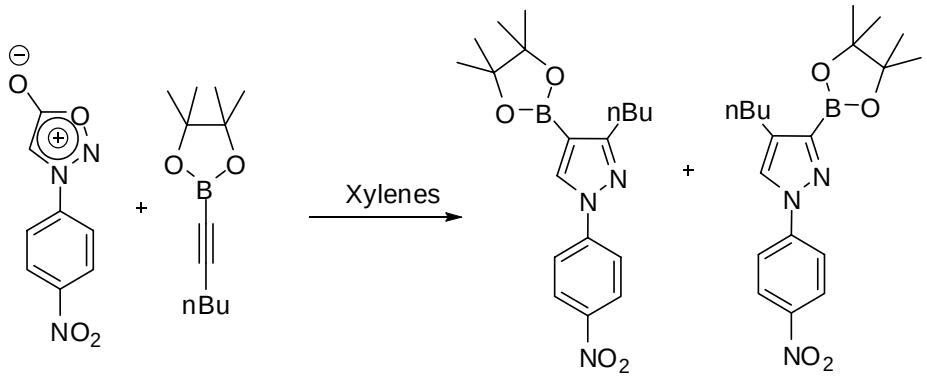
Synthesis of 3-butyl-1-(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrazole (9a) and 4-butyl-1-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrazole (9b)



1b **2b** **9a** **9b**

To **1b** (0.5 mmol, 96 mg) and **2b** (1 mmol, 209 mg) was added ortho-dichlorobenzene (0.5 mL). Reaction mixture was stirred at reflux for 24 hours before rapidly cooling in an ice bath. Reaction was purified by flash chromatography on silica gel (gradient; starting with 100% petroleum ether, ending with 20% ethyl acetate in petroleum ether). Product **9a** and product **9b** were isolated as an inseparable mixture (5:1, **9a:b**) as an orange oil that contained a small amount of protodeboronated material as evidenced by the ^{1}H NMR spectrum (98 mg, 55%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.03 (s, 0.8H, pyrazole-H), 7.52-7.60 (m, 2.2H, Ar-H and pyrazole-H) 6.90-6.96 (m, 2H, Ar-H), 3.80 (s, 3H, OCH_3), 2.82-2.88 (m, 1.67H, CH_2), 2.68-2.74 (m, 0.33H, CH_2), 1.25-1.75 (m, 16H, CH_2, CH_2 and pinacol-CH_3) 0.90-1.00 (pair of t, J = 7 Hz, 3H, CH_3); ^{13}C NMR (major isomer only)(62.9 MHz, $CDCl_3$): δ 161.2, 158.0, 134.6, 133.8, 120.8, 114.4, 83.1, 55.5, 32.8, 28.2, 24.8, 22.6, 14.0; FTIR (CH_2Cl_2): 2958 (m), 2932 (m), 2871 (w), 1548 (s), 1520 (s), 1467 (m), 1381 (m), 1306 (s), 1252 (s), 1146 (s), 1077 (s), 1048 (m), 960 (m), 859 (m) cm^{-1}; HRMS (ES): m/z $[MH]^+$ calcd for $C_{20}H_{30}BN_2O_3$:357.2349, found: 357.2334.

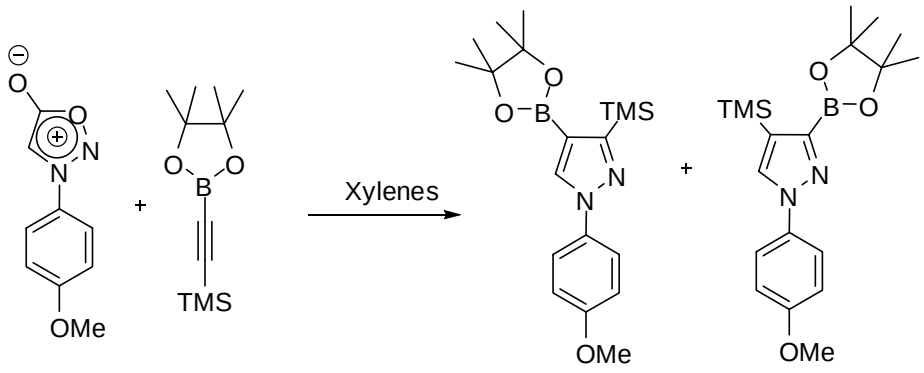
Synthesis of 3-butyl-1-(4- nitrophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrazole (10a) and 4-butyl-1-(4- nitrophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrazole (10b)



1c **2b** **10a** **10b**

To **1c** (0.5 mmol, 104 mg) and **2b** (1 mmol, 209 mg) was added xylenes (0.5 mL). Reaction mixture was stirred at reflux for 8 hours before rapidly cooling in an ice bath. Reaction was purified by flash chromatography on silica gel (gradient; starting with 100% petroleum ether, ending with 20% ethyl acetate in petroleum ether). Product **10a** and product **10b** was isolated as an inseparable mixture (5:1, **10a:b**) as an orange oil that contained a small amount of protodeboronated material as evidenced by the ^{1}H NMR spectrum (115 mg, 62%). ^{1}H NMR (250 MHz, $CDCl_3$) (major isomer **10a**): δ 8.17-8.23 (m, 2H, Ar-H), 8.15 (s, 1H, pyrazole-H), 7.71-7.79 (m, 2H, Ar-H), 2.73-2.80 (m, 2H, CH_2), 1.55-1.67 (m, 2H, CH_2), 1.22-1.40 (m, 14H, CH_2 and pinacol-CH_3), 0.87 (t, J = 7.5, 3H, CH_3); ^{13}C NMR (major isomer **10a**)(62.9 MHz, $CDCl_3$): δ 162.9, 145.1, 144.1, 135.0, 125.3, 118.3, 83.5, 32.2, 28.1, 24.8, 22.5, 13.9; FTIR (CH_2Cl_2): 2958 (m), 2931 (m), 2861 (w), 1599 (m), 1556 (s), 1522 (s), 1469 (m), 1338 (s), 1310 (m), 1145 (m), 1077 (m), 951 (m). cm^{-1}; HRMS (ES): m/z $[MH]^+$ calcd for $C_{19}H_{27}BN_3O_4$: 372.2095, found: 372.2113.

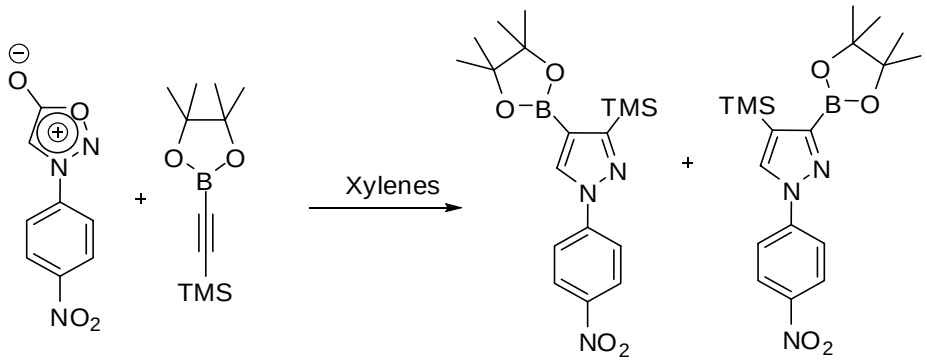
Synthesis of 1-(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trimethylsilyl)-1H-pyrazole (11a) and 1-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trimethylsilyl)-1H-pyrazole (11b)



1b **2c** **11a** **11b**

To **1b** (0.5 mmol, 96 mg) and **2c** (1 mmol, 224 mg) was added xylenes (0.5 mL). Reaction mixture was stirred at reflux for 22 hours before rapidly cooling in an ice bath. Reaction was purified by flash chromatography on silica gel (gradient; starting with 100% petroleum ether, ending with 20% ethyl acetate in petroleum ether). Product **11a** was isolated as a colourless solid (72 mg, 40%) and product **11b** was isolated as a colourless solid (38 mg, 21%) compound **11b** appeared to be unstable towards flash chromatography as evidenced by its ^{1}H NMR spectrum. **(11a)** ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.06 (s, 1H, pyrazole-H), 7.45-7.52 (m, 2H, Ar-H), 6.76-6.82 (m, 2H, Ar-H), 3.67 (s, 3H, OCH_3), 1.19 (s, 12H, pinacol CH_3), 0.24 (s, 9H, CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 160.8, 158.2, 135.0, 133.8, 121.1, 114.4, 83.3, 55.5, 24.9, -0.9; FTIR (CH_2Cl_2): 2977 (m), 1618 (w), 1520 (s), 1422 (m), 1372 (m), 1318 (m), 1249 (s), 1169 (m), 1145 (m), 1051 (m), 962 (m), 845 (s) cm^{-1}; HRMS (ES): m/z $[MH]^+$ calcd for $C_{19}H_{30}BN_2O_3Si$: 373.2119, found: 373.2126. **(11b)** ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.67 (s, 1H, pyrazole-H), 7.50-7.56 (m, 2H, Ar-H), 6.86-6.92 (m, 2H, Ar-H), 3.77 (s, 3H, OCH_3), 1.30 (s, 12H, pinacol-CH_3), 0.26 (s, 9H, CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 159.6, 134.6, 132.6, 125.6, 123.1, 114.9, 84.8, 55.9, 25.2, 0.0; FTIR (CH_2Cl_2): 2928 (m), 1610 (w), 1513 (s), 1461 (m), 1373 (m), 1304 (m), 1253 (S), 1170 (m), 1140 (s), 1050 (m), 961 (m). cm^{-1}; HRMS (ES): m/z $[MH]^+$ calcd for $C_{19}H_{30}BN_2O_3Si$: 373.2119, found: 373.2126.

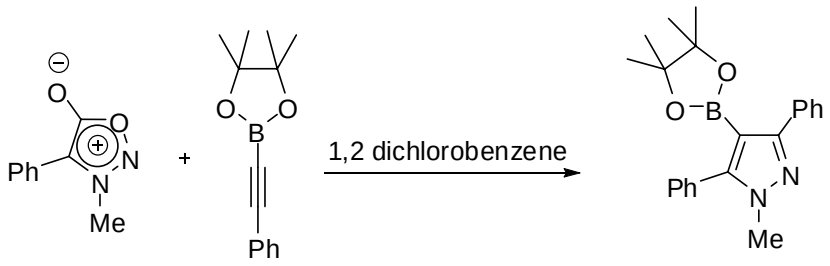
Synthesis of 1-(4- nitrophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trimethylsilyl)-1H-pyrazole (12a) and 1-(4- nitrophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trimethylsilyl)-1H-pyrazole (12b)



1c **2c** **12a** **12b**

To **1c** (0.5 mmol, 104 mg) and **2c** (1 mmol, 224 mg) was added xylenes (0.5 mL). Reaction mixture was stirred at reflux for 4 hours before rapidly cooling in an ice bath. Reaction was purified by flash chromatography on silica gel (gradient; starting with 100% petroleum ether, ending with 20% ethyl acetate in petroleum ether). Product **12a** and product **12b** were isolated as an inseparable mixture (3:2, **12a:b**) which was a colourless solid (161 mg, 83%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.32 (s, 0.6H, pyrazole-H), 8.20-8.26 (m, 2H, Ar-H), 7.92 (s, 0.4H, pyrazole-H), 7.82-7.88 (m, 2H, Ar-H), 1.31 (s, 4.6H, pinacol-CH_3), 1.27 (s, 7.4, pinacol-CH_3), 0.32 (s, 5.5H, TMS), 0.25 (s, 3.5, TMS); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 164.3 (2C), 146.8, 146.5, 145.3, 145.2, 136.3, 133.9, 126.4, 126.3, 120.8, 120.0, 85.5, 84.8, 26.0 (2C), 0.7, 0.0; FTIR (CH_2Cl_2): 2979 (m), 2900 (w), 2361 (w), 1599 (s), 1529 (s), 1457 (m), 1382 (m), 1342 (s), 1263 (m), 1144 (s), 1112 (m), 1048 (s), 956 (m) cm^{-1}; HRMS (ES): m/z $[MH]^+$ calcd for $C_{18}H_{27}BN_3O_4Si$: 388.1864, found: 388.1861.

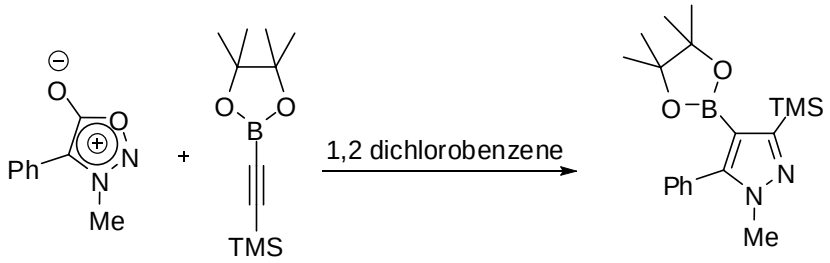
Synthesis of 1-methyl-3,5-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrazole (15).



13 **2a** **15**

To **13** (1 mmol, 176 mg) and **2a** (2 mmol, 456 mg) was added 1,2 dichlorobenzene (1 mL). Reaction mixture was stirred at reflux for 48 hours before rapidly cooling in an ice bath. Reaction was purified by flash chromatography on silica gel (gradient; starting with 100% petroleum ether, ending with 15% ethyl acetate in petroleum ether). Product **15** was isolated as an orange solid (270 mg, 75%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.81-7.86 (m, 2H, Ar-H), 7.42 (s, 5H, Ar-H), 7.30-7.39 (m, 3H, Ar-H), 3.80 (s, 3H, CH_3), 1.14 (s, 12H, pinacol-CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 150.7, 149.2, 143.6, 134.4, 131.1, 130.1, 128.6, 128.2, 128.0, 127.6, 83.3, 37.0, 24.5; FTIR (CH_2Cl_2): 2978 (m), 1605 (w), 1535 (m), 1493 (s), 1444 (m), 1412 (m), 1372 (m), 1344 (m), 1304 (s), 1210, 1138 (s), 1017 (m), 993 (w), 859 (m) cm^{-1}; HRMS (ES): m/z $[MH]^+$ calcd for $C_{22}H_{26}BN_2O_2$: 361.2087, found: 361.2103. M.p. 133-136 ˚C.

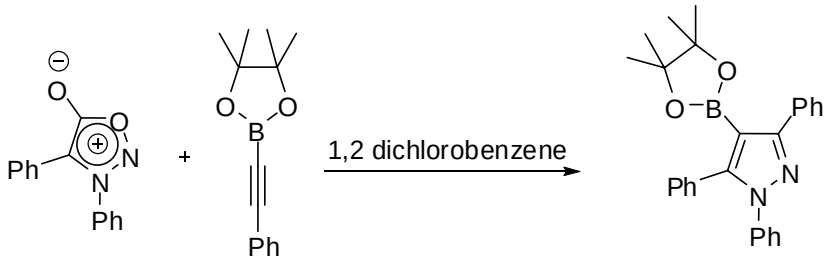
Synthesis of 1-methyl-5-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trimethylsilyl)-1H-pyrazole (16).



13 **2c** **16**

To **13** (0.5 mmol, 88 mg) and **2c** (1 mmol, 224 mg) was added 1,2 dichlorobenzene (1 mL). Reaction mixture was stirred at reflux for 48 hours before rapidly cooling in an ice bath. Reaction was purified by flash chromatography on silica gel (gradient; starting with 100% petroleum ether, ending with 25% ethyl acetate in petroleum ether). Product **16** was isolated as an orange solid (122 mg, 68%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.20-7.30 (m, 5H, Ar-H), 3.65 (s,3H, CH_3), 1.04 (s, 12H, pinacol-CH_3), 0.24 (s, 9H, TMS); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 158.5, 150.9, 131.4, 130.2, 128.2, 127.6, 82.7, 36.9, 24.7, -0.5; FTIR (CH_2Cl_2): 2978 (m), 1534 (m), 1488 (s), 1410 (m), 1308 (m), 1244 (m), 1203 (w), 1145 (m), 1047 (m), 843 (s) cm^{-1}; HRMS (ES): m/z $[MH]^+$ calcd for $C_{19}H_{30}BN_2O_2Si$: 357.2170, found: 357.2157. M.p. 110-112 ˚C.

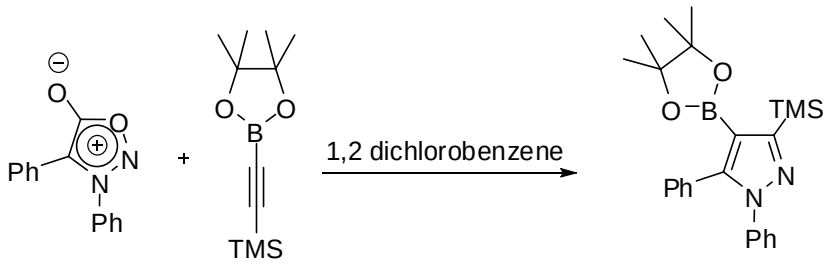
Synthesis of 1,3,5-triphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrazole (17).



14 **2a** **17**

To **14** (0.5 mmol, 119 mg) and **2a** (1 mmol, 228 mg) was added 1,2 dichlorobenzene (1 mL). Reaction mixture was stirred at reflux for 48 hours before rapidly cooling in an ice bath. Reaction was purified by flash chromatography on silica gel (gradient; starting with 100% petroleum ether, ending with 10% ethyl acetate in petroleum ether). Product **17** was isolated as an orange solid (125 mg, 59%).^{1}H NMR (250 MHz, $CDCl_3$): δ 7.88-7.95 (m, 2H, Ar-H), 7.22-7.45 (m, 13H, Ar-H), 1.19 (s, 12H, pinacol-CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 156.9, 149.6, 139.8, 134.2, 130.4 (2C), 128.7, 128.3, 128.0, 127.9 (2C), 127.2, 125.4, 83.6, 24.6; FTIR (CH_2Cl_2): 2978 (w), 1537 (w), 1498 (s), 1442 (m), 1420 (m), 1372 (w), 1345 (m), 1312 (m), 1140 (s), 1087 (w), 974 (w), 857 (w) cm^{-1}; HRMS (ES): m/z $[MH]^+$ calcd for $C_{27}H_{28}BN_2O_2$: 423.2244, found: 423.2240. M.p. 150-153 ˚C.

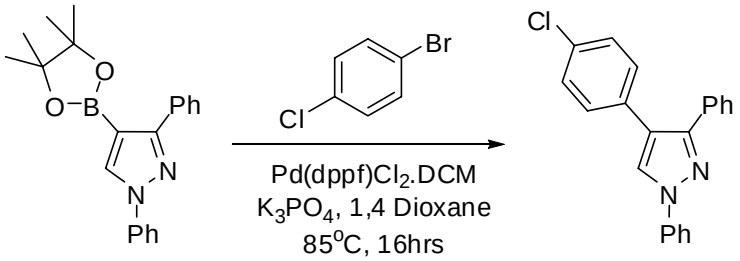
Synthesis of 1,5-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trimethylsilyl)-1H-pyrazole (18).



14 **2c** **18**

To **14** (0.5 mmol, 119 mg) and **2c** (1 mmol, 224 mg) was added 1,2 dichlorobenzene (1 mL). Reaction mixture was stirred at reflux for 48 hours before rapidly cooling in an ice bath. Reaction was purified by flash chromatography on silica gel (gradient; starting with 100% petroleum ether, ending with 10% ethyl acetate in petroleum ether). Product **18** was isolated as an orange solid (153 mg, 73%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.00-7.10 (m, 10H, Ar-H), 1.03 (s, 12H, pinacol CH_3), 0.25 (s, 9H, TMS); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 159.7, 149.9, 140.1, 131.4, 130.6, 128.6, 128.0, 127.5, 126.9, 125.3, 83.1, 24.9, -0.5; FTIR (CH_2Cl_2): 2978 (m), 2361 (w), 1598 (m), 1534 (m), 1499 (s), 1415 (s), 1309 (s), 1264 (m), 1244(m), 1143 (s), 1046 (s), 1028 (m), 974 (w), 845 (s) cm^{-1}; HRMS (ES): m/z $[MH]^+$ calcd for $C_{24}H_{32}BN_2O_2Si$: 419.2326, found: 419.2342. M.p. 153-155 ˚C.

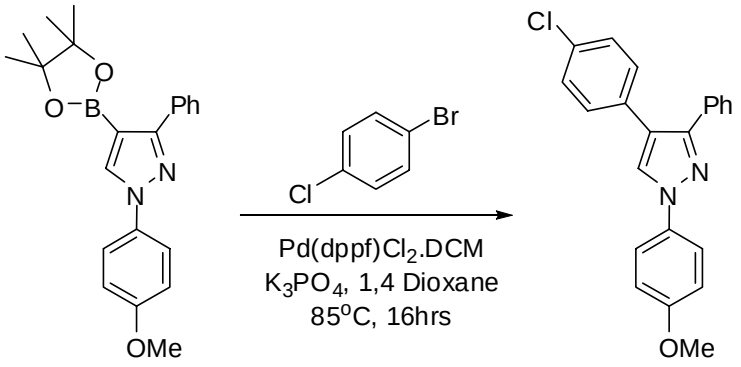
Synthesis of 4-(4-chlorophenyl)-1,3-diphenyl-1H-pyrazole (19)



3a **19**

To **3a** (120 mg, 0.35 mmol) was added $Pd(dppf)Cl_2$ (26 mg, 0.035), 1-bromo-4-chlorobenzene (135 mg, 0.71 mmol), K_3PO_4 (223 mg, 1.05 mmol) and 1,4 dioxane (2.2 mL). The reaction was stirred at 85°C for 16 hrs before quenching with H_2O and extracting with DCM. The organics were washed with saturated brine, dried with $MgSO_4$ and concentrated in vacuo before purification by flash chromatography (starting with 100% petroleum ether, ending with 10% ethyl acetate in petroleum ether) product **19** was isolated as a colourless solid (102 mg, 88%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.03 (s, 1H, pyrazole-H), 7.80-7.84 (m, 2H, Ar-H), 7.59-7.63 (m, 2H, Ar-H), 7.49-7.53 (m, 2H, Ar-H), 7.30-7.40 (m, 8H, Ar-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 150.5, 139.9, 132.9, 131.4, 129.9, 129.5, 128.8, 128.5 (2C), 128.1, 126.6, 124.7, 121.8, 119.0 (2C); FTIR (CH_2Cl_2): 1599 (s), 1551 (s), 1503 (s), 1487 (m), 1447 (m), 1411 (m), 1348 (w), 1217 (m), 1094 (m), 1059 (m), 1015 (w), 971 (m), 958 (m), 836 (m) cm^{-1}; HRMS (ES): m/z $[MH]^+$ calcd for $C_{21}H_{16}N_2{}^{35}Cl$: 331.1002, found: 331.0986. M.p. 120-122 ˚C.

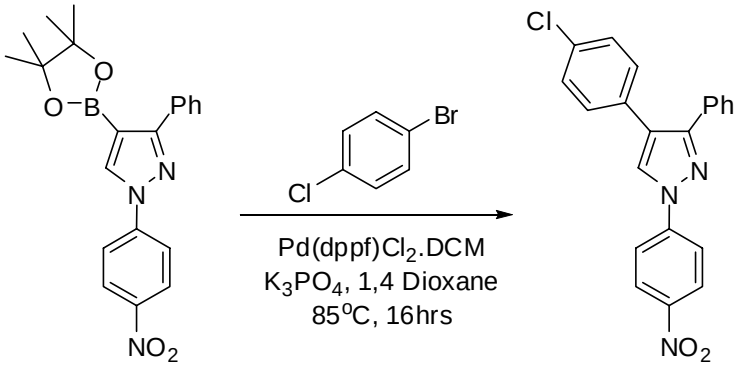
Synthesis of 4-(4-chlorophenyl)-1-(4-methoxyphenyl)-3-phenyl-1H-pyrazole (20).



7a **20**

To **7a** (34 mg, 0.09 mmol) was added $Pd(dppf)Cl_2$ (7 mg, 0.9 μmol), 1-bromo-4-chlorobenzene (36 mg, 0.19 mmol), K_3PO_4 (57 mg, 0.27 mmol) and 1,4 dioxane (0.6 mL). The reaction was stirred at 85°C for 16 hrs before quenching with H_2O and extracting with DCM. The organics were washed with saturated brine, dried with $MgSO_4$ and concentrated in vacuo before purification by flash chromatography (starting with 100% petroleum ether, ending with 10% ethyl acetate in petroleum ether) product **20** was isolated as a colourless solid (27 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 1H, pyrazole-H), 7.58-7.63 (m, 2H, Ar-H), 7.46-7.51 (m, 2H, Ar-H), 7.16-7.29 (m, 7H, Ar-H), 6.89-6.95 (m, 2H, Ar-H), 3.78 (s, 3H, OCH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): 158.4, 150.0, 133.6, 133.0, 132.7, 131.5, 129.9, 128.7, 128.4 (2C), 128.0, 126.7, 121.3, 120.7, 114.6, 55.6; δ; FTIR (CH_2Cl_2): 2934 (w), 1549 (m), 1518 (s), 1488 (w), 1443 (w), 1347(w), 1245 (m), 1214(w), 1093(m), 1060 (m), 1015 (w), 972 (m), 960 (m), 832(m). cm^{-1}; HRMS (ES): m/z $[MH]^+$ calcd for $C_{22}H_{18}{}^{35}ClN_2O$: 361.1108, found: 361.1110. M.p. 135-137 °C.

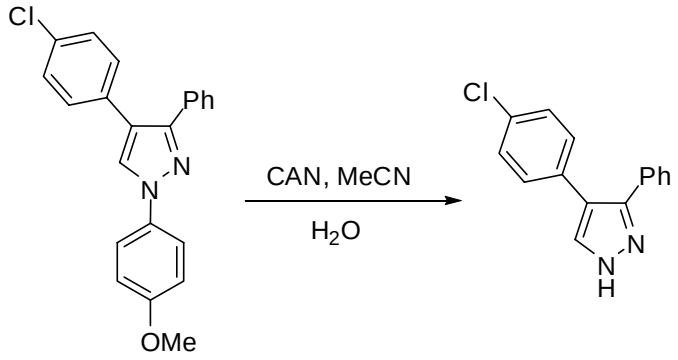
Synthesis of 4-(4-chlorophenyl)-1-(4-nitrophenyl)-3-phenyl-1H-pyrazole (21).



8a **21**

To **8a** (215 mg, 0.55 mmol) was added $Pd(dppf)Cl_2$ (40 mg, 0.055), 1-bromo-4-chlorobenzene (213 mg, 1.11 mmol), K_3PO_4 (350 mg, 1.65 mmol) and 1,4 dioxane (3.7 mL). The reaction was stirred at 85°C for 16 hrs before quenching with H_2O and extracting with DCM. The organics were washed with saturated brine, dried with $MgSO_4$ and concentrated in vacuo before purification by flash chromatography (starting with 100% petroleum ether, ending with 10% ethyl acetate in petroleum ether) product **21** was isolated as a yellow solid (156 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35-8.39 (m, 2H, Ar-H), 8.13 (s, 1H, pyrazole-H), 7.96- 8.00 (m, 2H, Ar-H), 7.56-7.61 (m, 2H, Ar-H), 7.33-7.42 (m, 5H, Ar-H), 7.27-7.30 (m, 2H, Ar-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 152.3, 145.4, 144.0, 133.5, 132.0, 130.5, 130.0, 128.9, 128.7, 128.6, 128.4, 126.6, 125.4, 123.6, 118.2; FTIR (CH_2Cl_2): 1646 (w), 1596 (m), 1551 (s), 1519 (m), 1494 (w), 1434 (w), 1406 (w), 1340 (s), 1223 (w), 1094 (w), 1052 (w), 1015 (w), 970 (m), 952 (m), 852 (m). HRMS (EI): m/z $[M]^+$ calcd for $C_{21}H_{14}{}^{35}ClN_3O_2$: 375.0775, found: 375.0780. M.p. 150-152 °C.

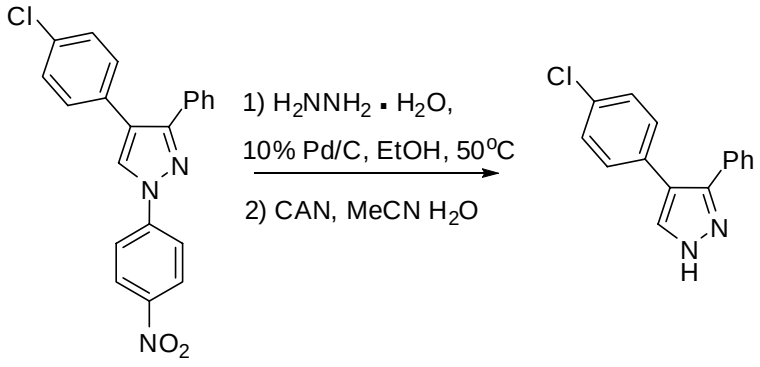
Synthesis of 4-(4-chlorophenyl)-3-phenyl-1H-pyrazole (22).



20 **22**

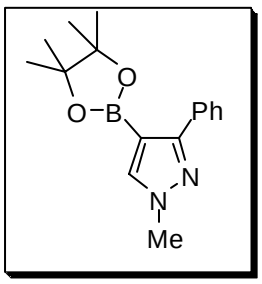
To a stirring solution of **20** (90 mg, 0.25 mmol) in MeCN (9 mL) at 5 ^{O}C was added a solution of CAN (684 mg, 1.2 mmol) in H_2O (6 mL). Reaction mixture went green to yellow to orange during addition of CAN. After 1.5 hours stirring at 5 ^{O}C reaction was neutralised to pH 7 with saturated $NaHCO_3$ solution and extracted with DCM. The organics were dried with $MgSO_4$ and concentrated in vacuo before purification by flash chromatography (starting with 100% petroleum ether, ending with 70% ethyl acetate in petroleum ether) product **22** was isolated as a brown oil (40 mg, 63%). Characterisation data identical to product derived from **21** (*vide infra*).

Synthesis of 4-(4-chlorophenyl)-3-phenyl-1H-pyrazole (22).



21 **22**

To a stirring solution of **21** (104 mg, 0.3 mmol) in EtOH (7 mL) was added 10% Pd on charcoal (15 mg, ~0.015 mmol), followed by hydrazine monohydrate (64 μL, 1.3 mmol). Reaction mixture was stirred at 50 °C for 3 hours before filtering through celite and evaporating to dryness in vacuo. To the resultant colourless solid stirring in MeCN (11 mL) at 5 °C, was added; dropwise, a solution of CAN (822 mg, 1.5 mmol) in H_2O (9 mL). Reaction mixture went purple on addition of CAN solution. After 3 hours stirring at 5 °C (reaction mixture now brown) reaction was neutralised to pH 7 with saturated $NaHCO_3$ solution and extracted with DCM. The organics were dried with $MgSO_4$ and concentrated in vacuo before purification by flash chromatography (starting with 100% petroleum ether, ending with 70% ethyl acetate in petroleum ether) product **22** was isolated as a brown oil (37 mg, 48%).^{1}H NMR (250 MHz, $CDCl_3$): δ 8.65 (br, 1H, N-H), 7.50-7.70 (br, 1H, pyrazole-H), 7.10-7.40 (m, 9H, Ar-H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 132.5, 131.4, 130.8, 129.6, 128.8, 128.7, 128.5, 128.4, 128.1, 126.7, 125.8; FTIR (CH_2Cl_2): 3161 (br), 2918 (br), 1668 (w), 1603 (w), 1551 (w), 1520 (m), 1487 (m), 1446 (m), 1400 (w), 1345 (m), 1266 (m), 1179 (m), 1094 (s), 1072 (m), 1016 (m), 969 (m), 952 (m), 908 (s), 832 (s);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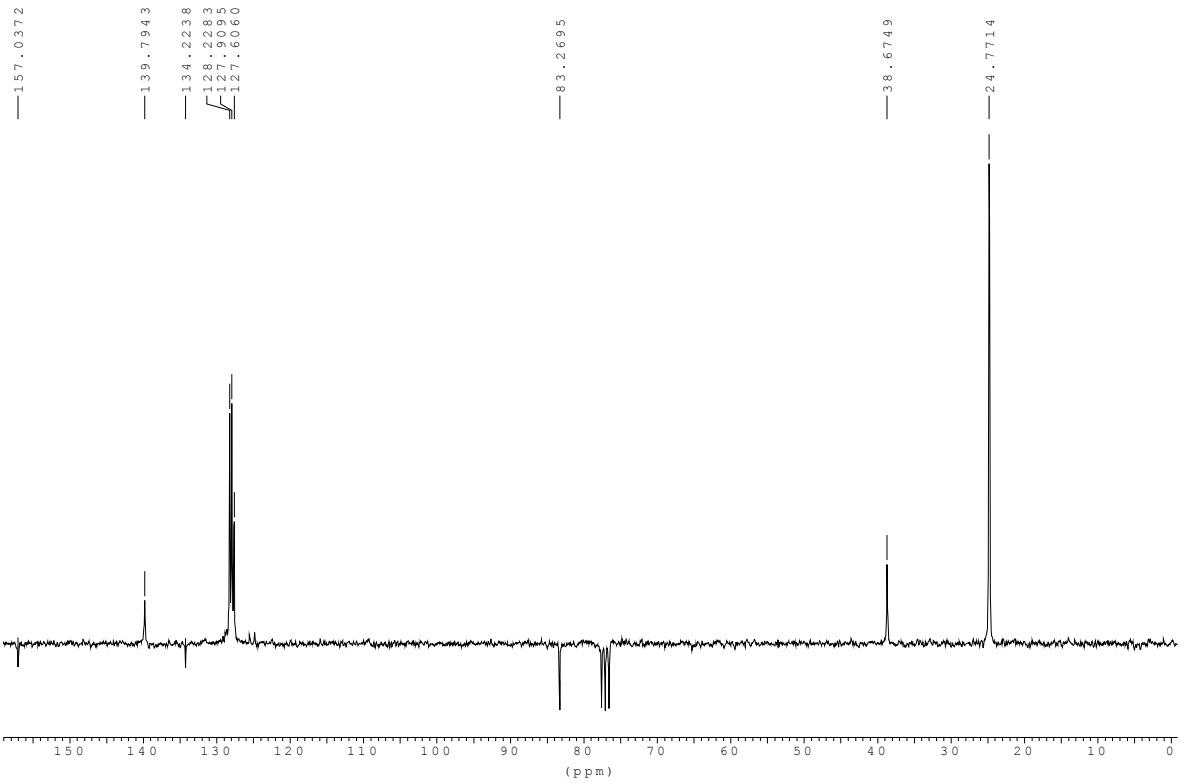
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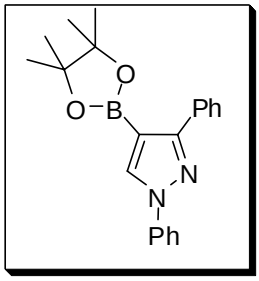
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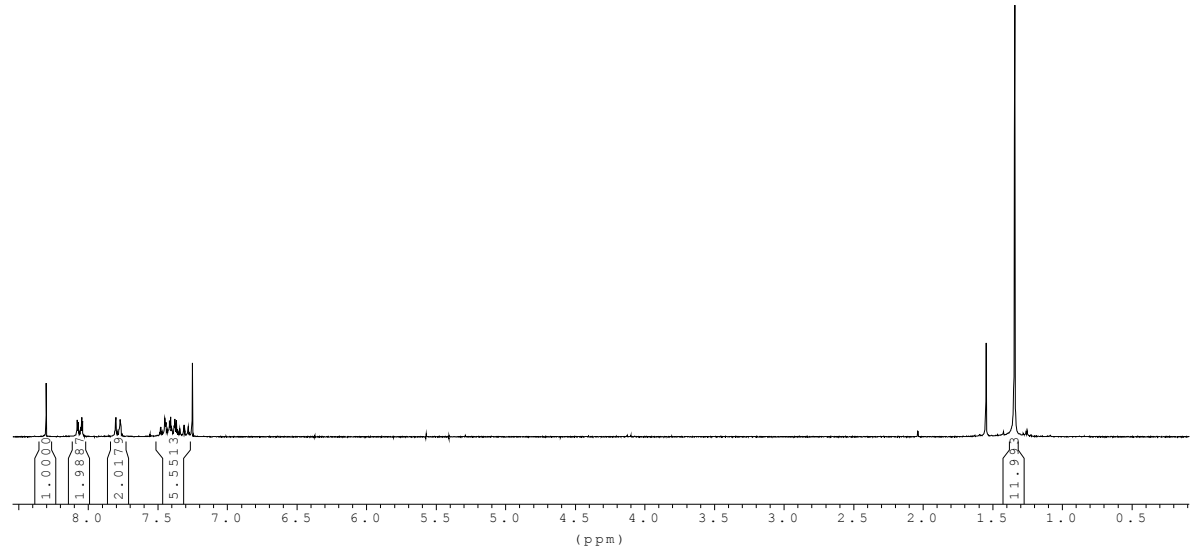
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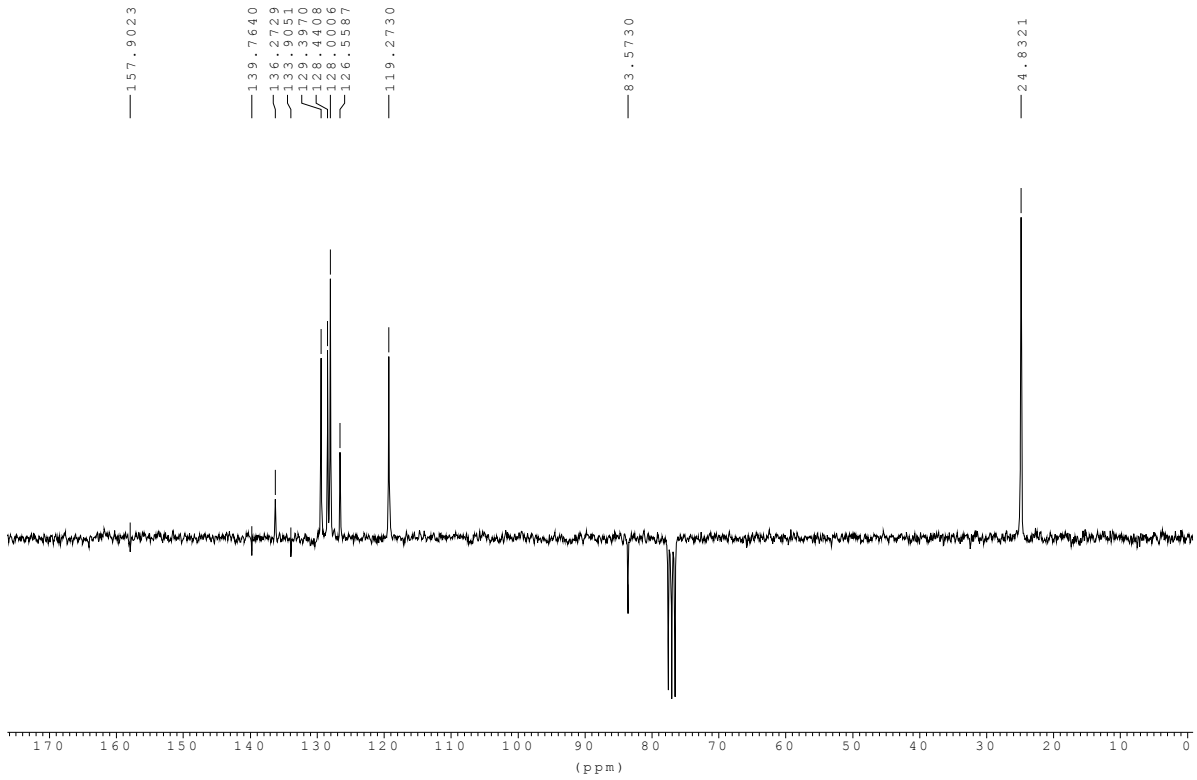
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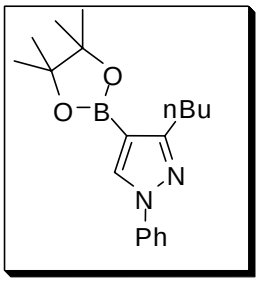
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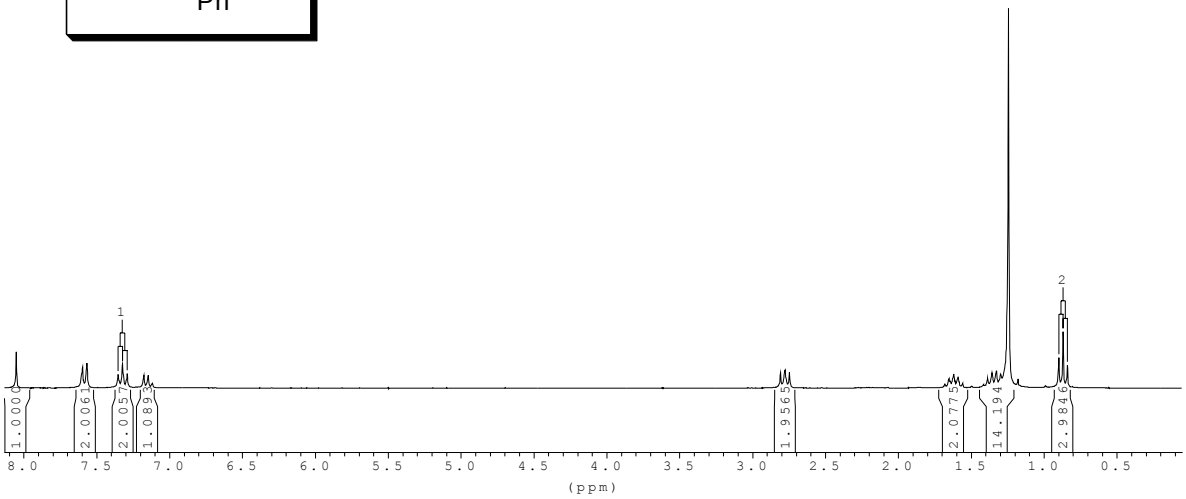
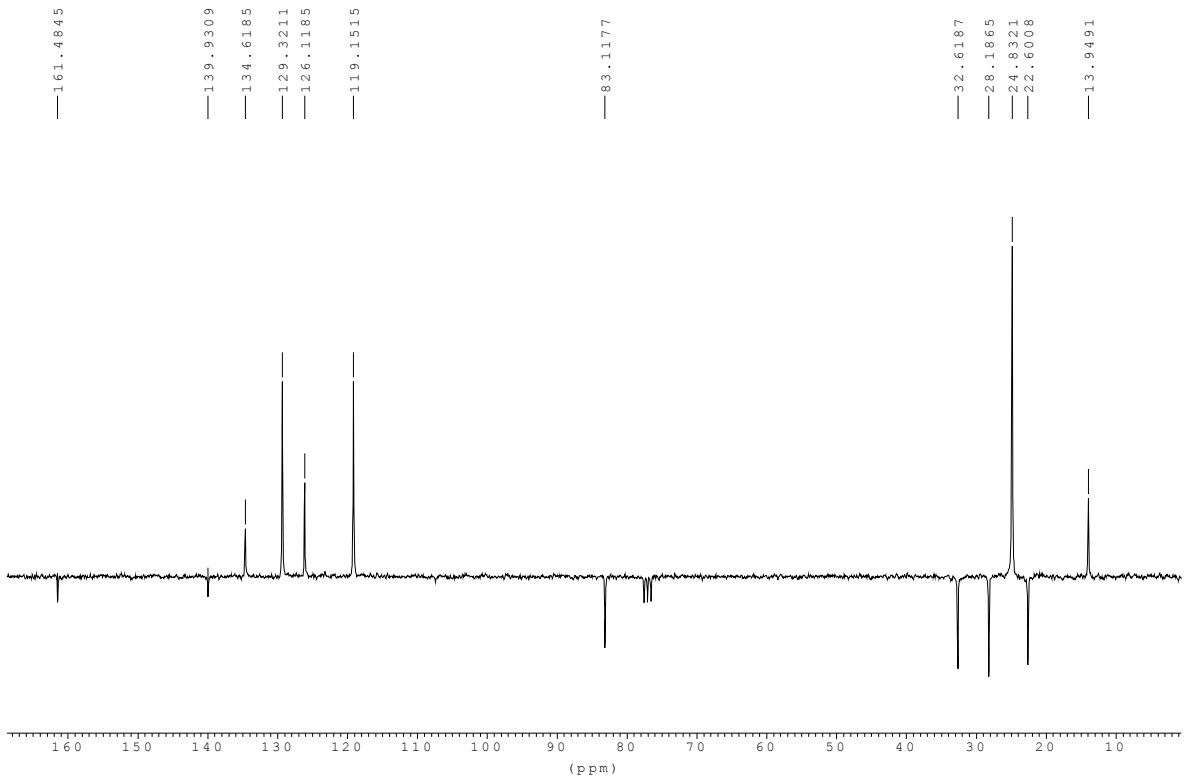
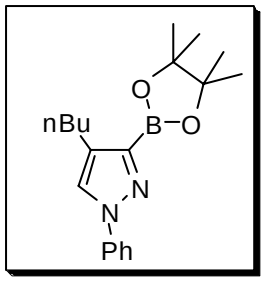
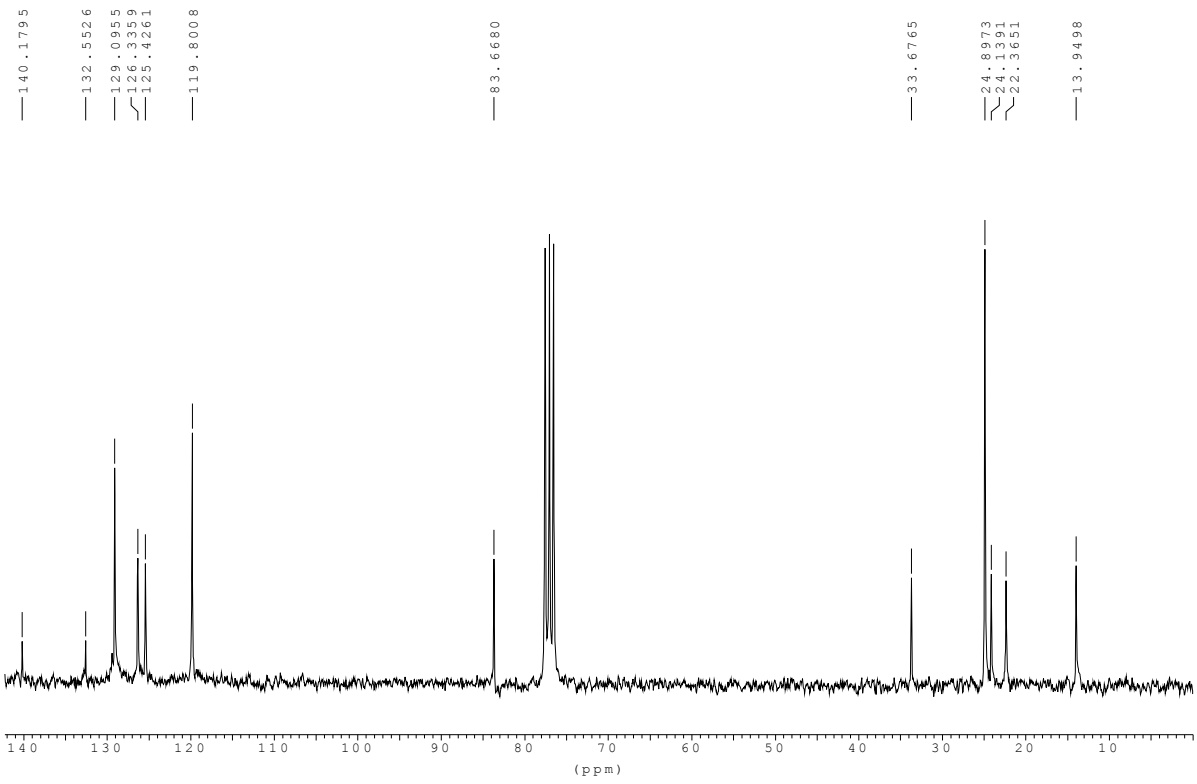
N
Ph

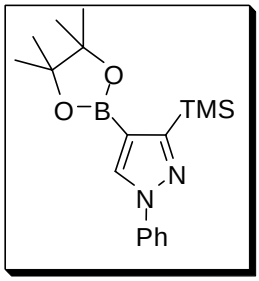

1
2
1.000
2.006
2.005
1.089
1.956
2.077
14.194
2.984
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

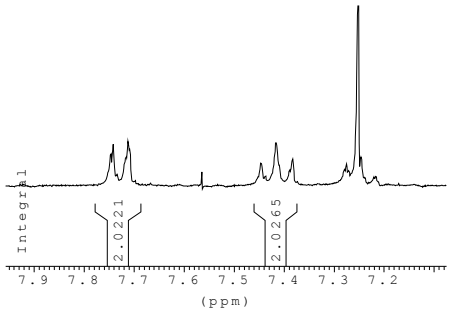

161.4845
139.9309
134.6185
129.3211
126.1185
119.1515
83.1177
32.6187
28.1865
24.8321
22.6008
13.9491
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)


O
nBu
B–O
N
N
Ph

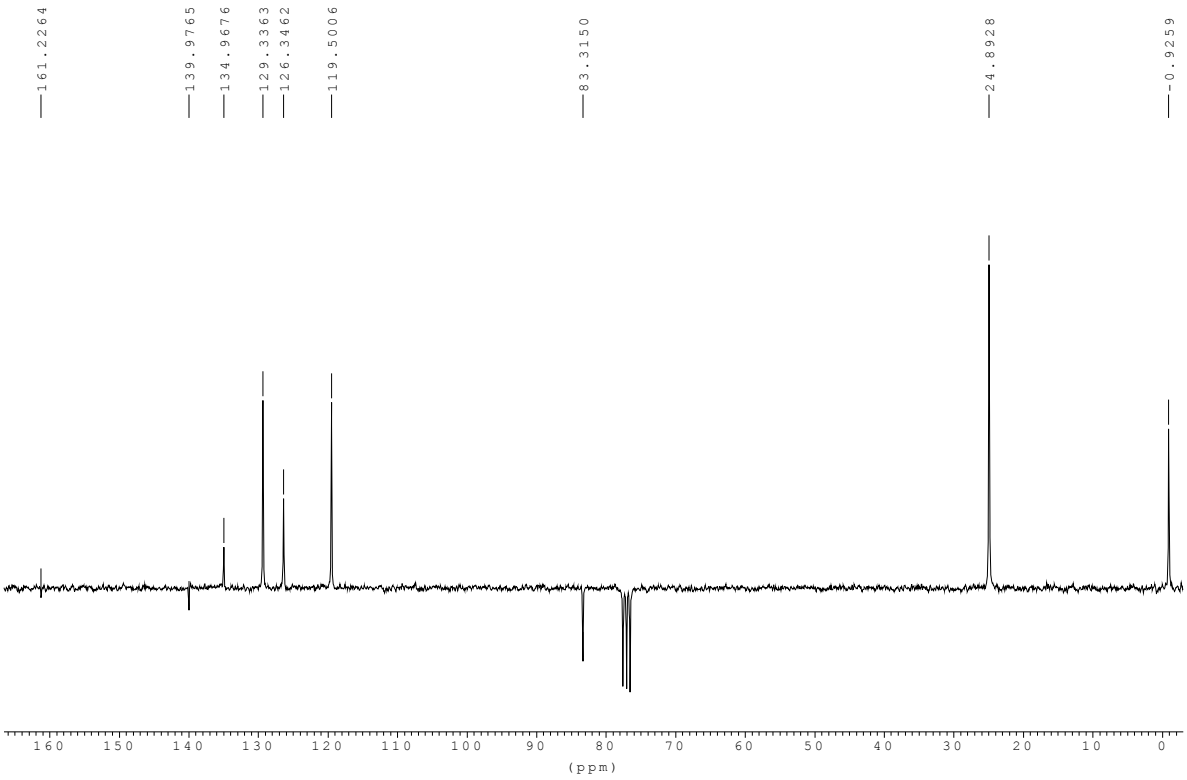
Integral
2.9376
2.3072
1.5053
2.0000
2.1099
14.3944
3.0679
1
2
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

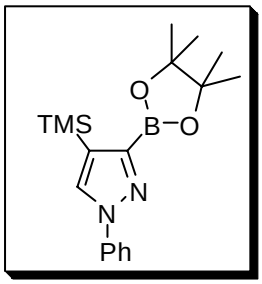

140.1795
132.5526
129.0955
126.3359
125.4261
119.8008
83.6680
33.6765
24.8973
24.1391
22.3651
13.9498
140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

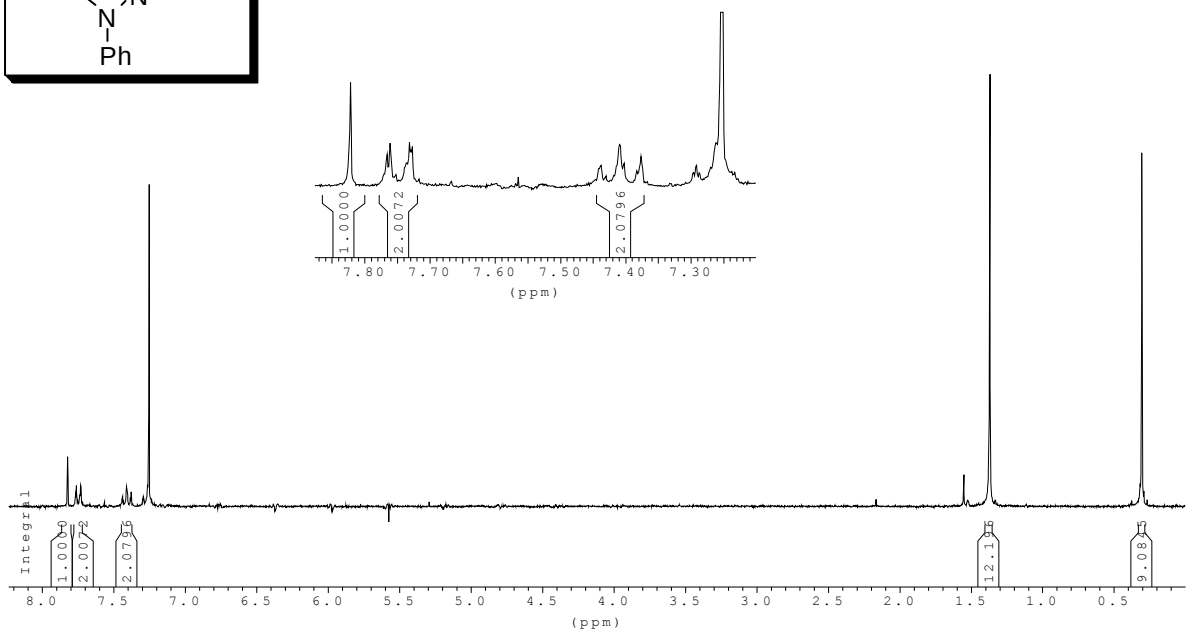

O
O⁻B
TMS
N
N
Ph

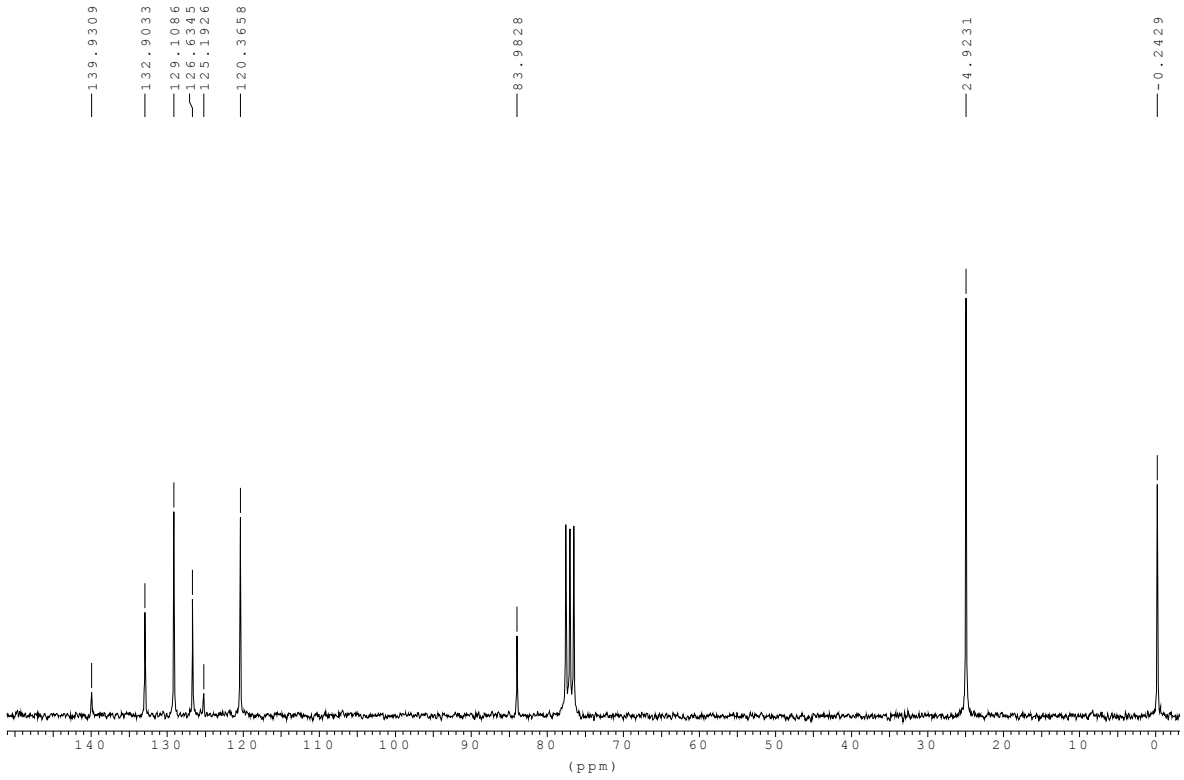

Integral
2.0221
2.0265
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
(ppm)

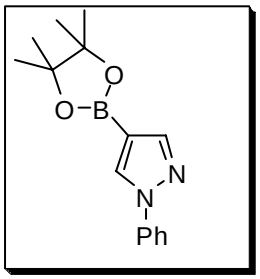
Integral
1.0000
2.0221
2.0265
11.9728
9.1540
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)


161.2264
139.9765
134.9676
129.3363
126.3462
119.5006
83.3150
24.8928
0.9259
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

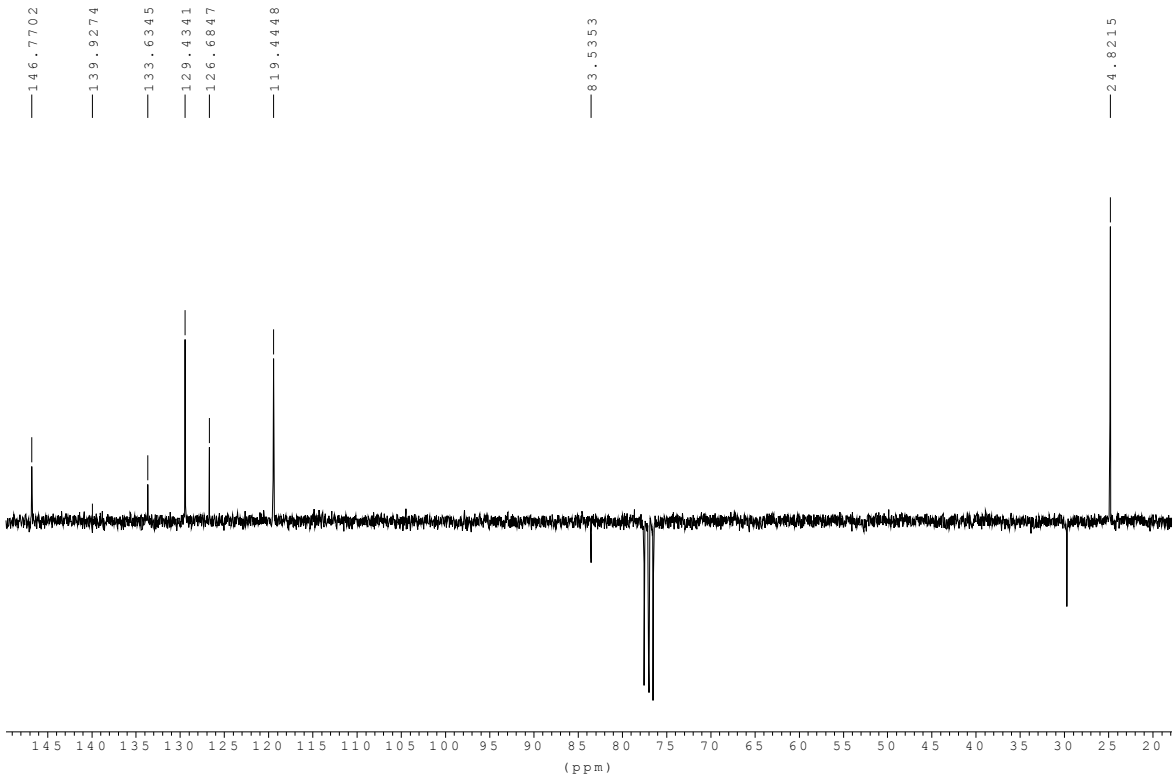

TMS
O
B
O
N
N
Ph

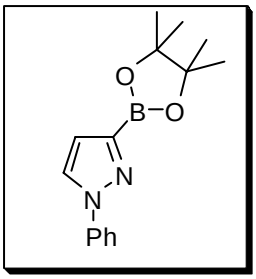

1.0000
2.0072
2.0796
7.80 7.70 7.60 7.50 7.40 7.30
(ppm)
Integral
1.0000
2.0072
2.0755
12.1165
9.0847
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)


139.9309
132.9033
129.1086
126.6345
125.1926
120.3658
83.9828
24.9231
0.2429
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

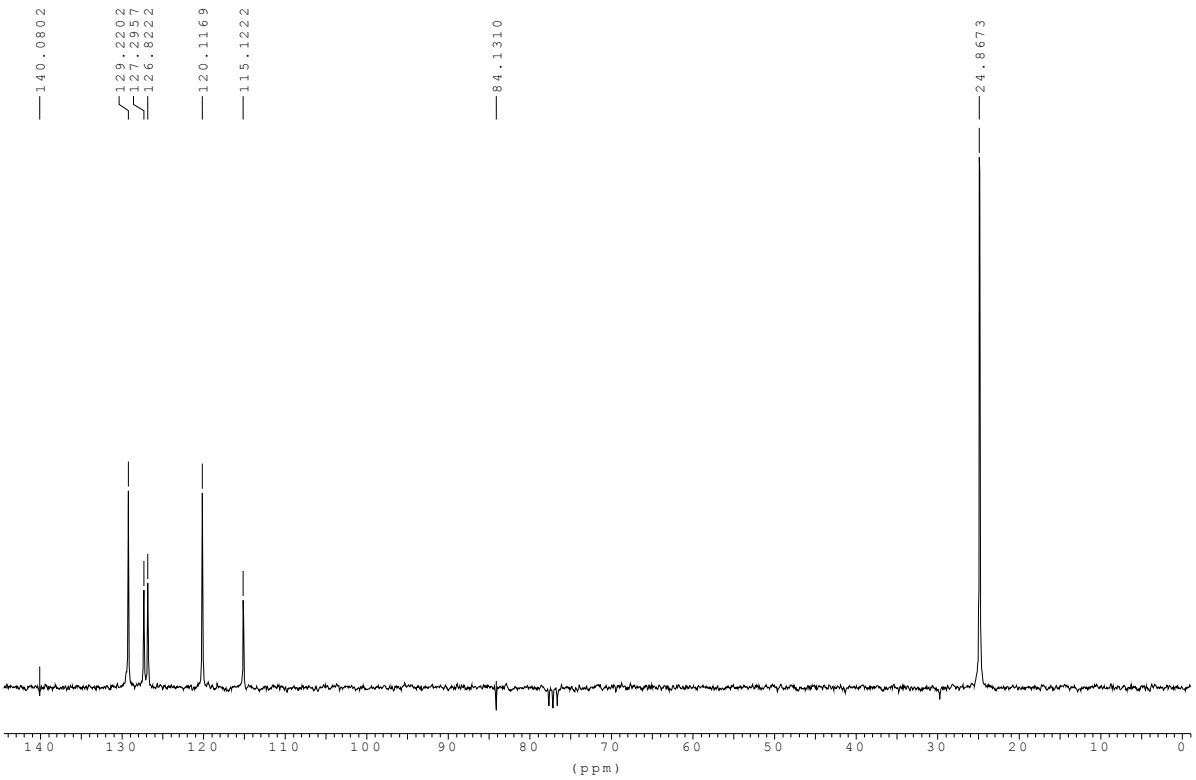

O
O
B
N
N
Ph

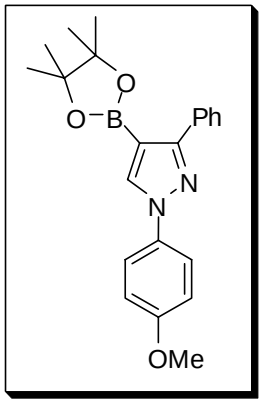
1.00
1.00
2.13
2.36
1.07
12.6
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

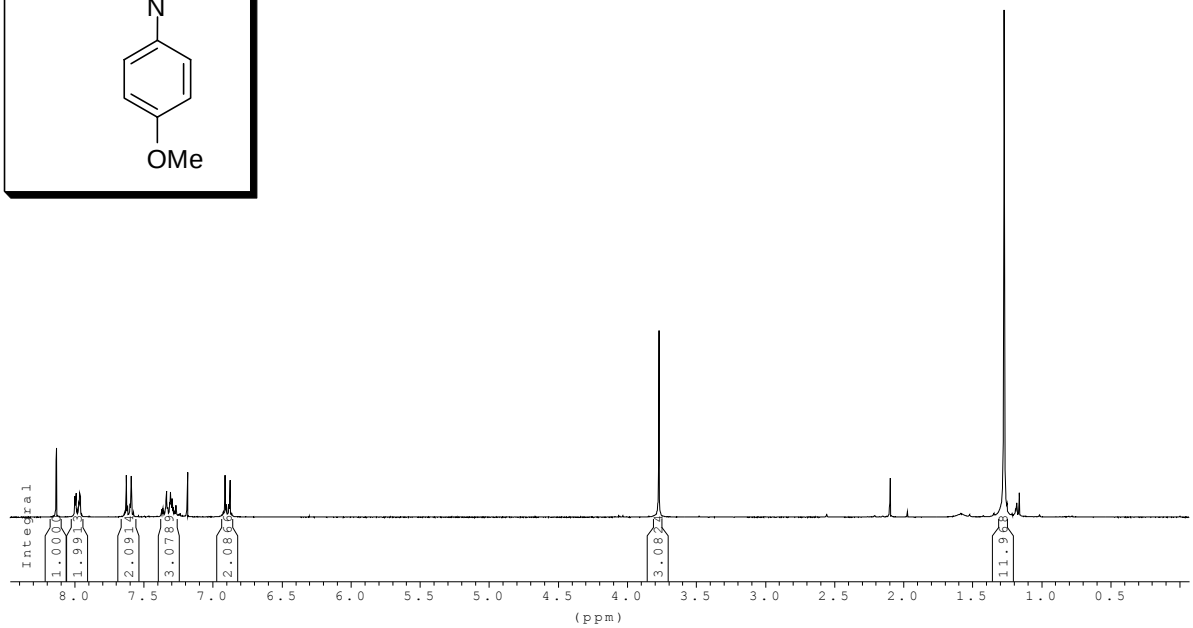

146.7702
139.9274
133.6345
129.4341
126.6847
119.4448
83.5353
24.8215
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
(ppm)

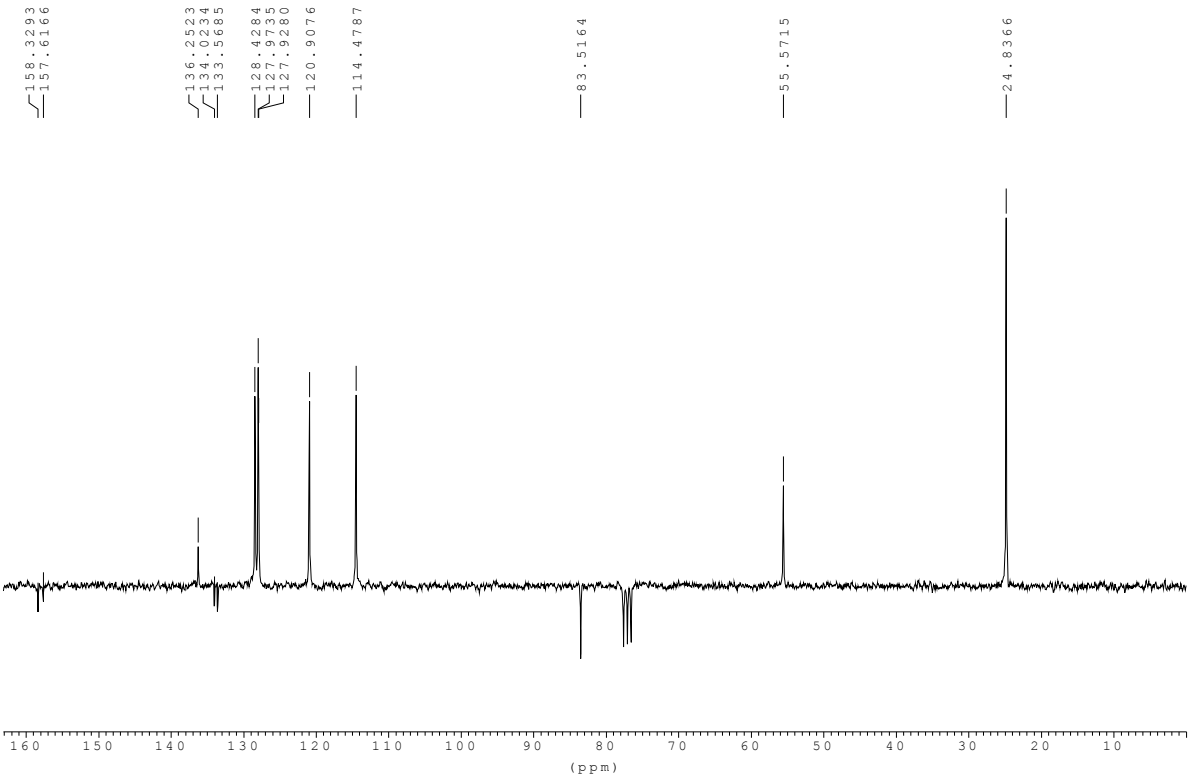

O
B
O
N
N
Ph

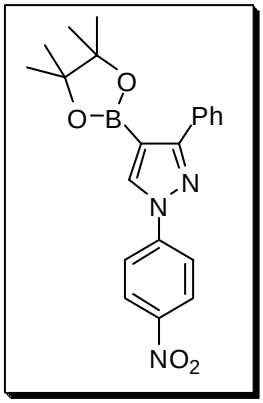
1.00
2.02
2.12
1.09
0.97
12.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)


140.0802
129.2202
127.2957
126.8222
120.1169
115.1222
84.1310
24.8673
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

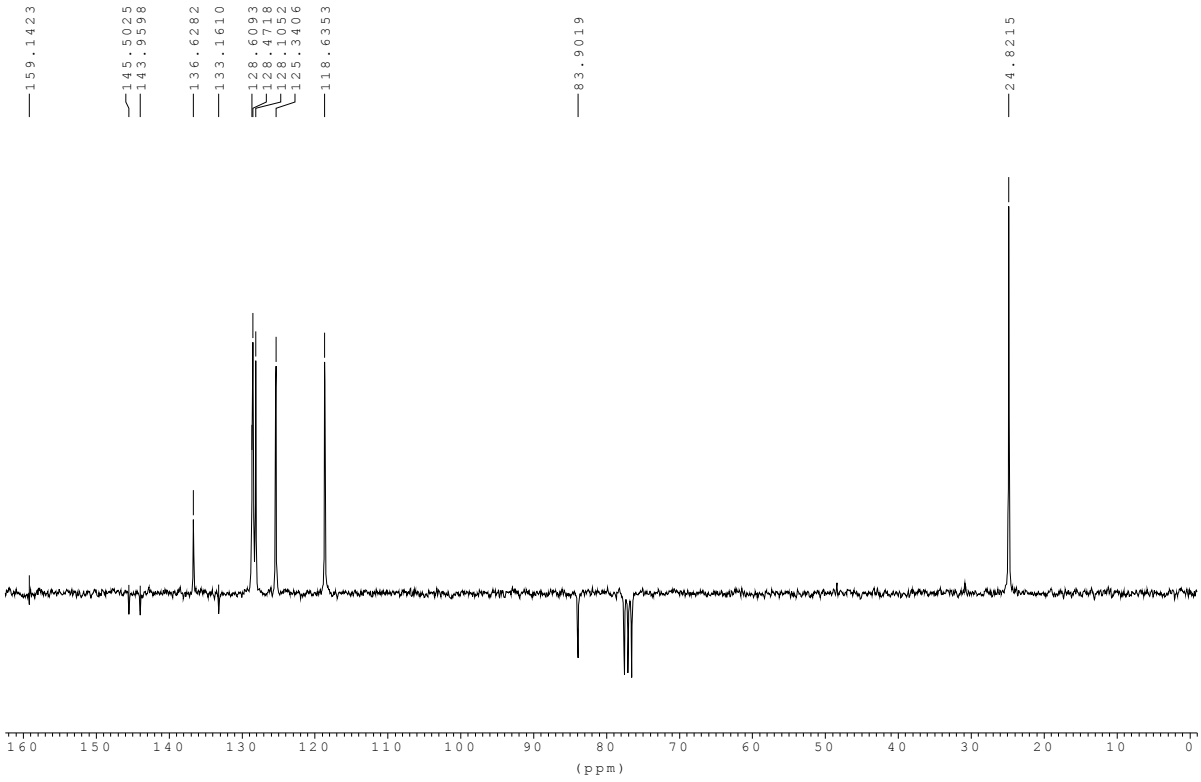

O
O
B
Ph
N
N
OMe

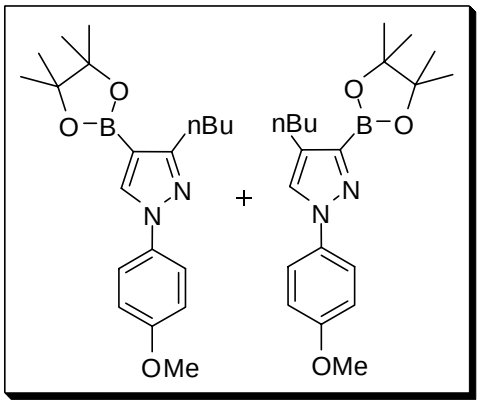

Integral
1.00
1.99
2.09
3.08
2.08
3.08
11.97
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)


158.3293
157.6166
136.2523
134.0234
133.5685
128.4284
127.9735
127.9280
120.9076
114.4787
83.5164
55.5715
24.8366
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

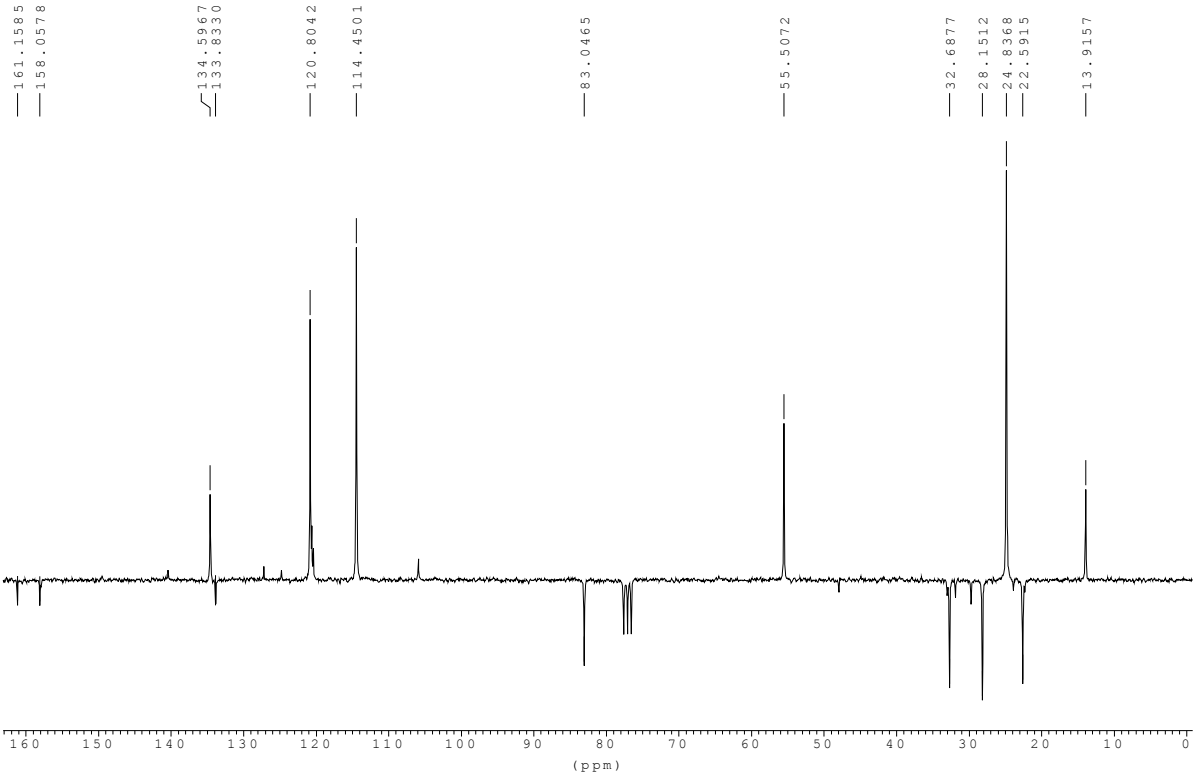

O
O
B
Ph
N
N
NO2

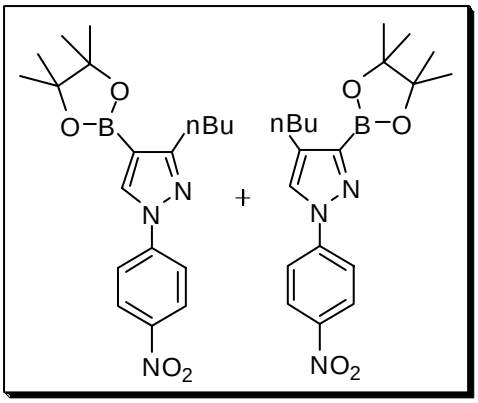
Integral
1.00
2.02
2.02
2.05
3.10
11.9
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)


159.1423
145.5025
143.9598
136.6282
133.1610
128.6093
128.4718
128.1052
125.3406
118.6353
83.9019
24.8215
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

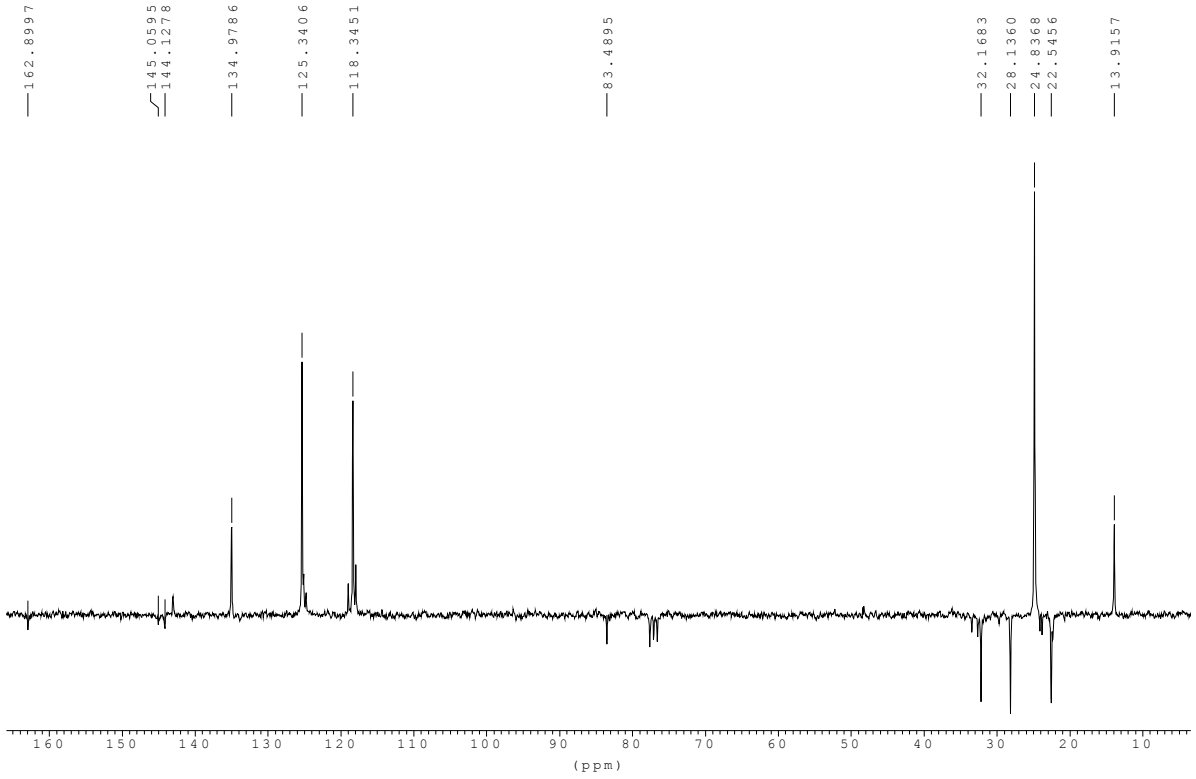

O
O−B
nBu
N
N
OMe
+
nBu
B−O
O
N
N
OMe

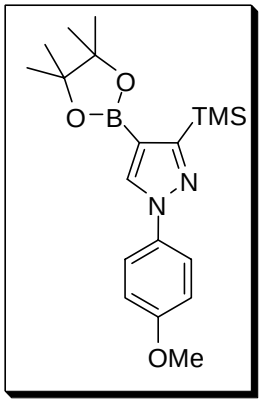
1.000
2.879
2.627
3.943
2.008
0.391
19.304
4.090
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

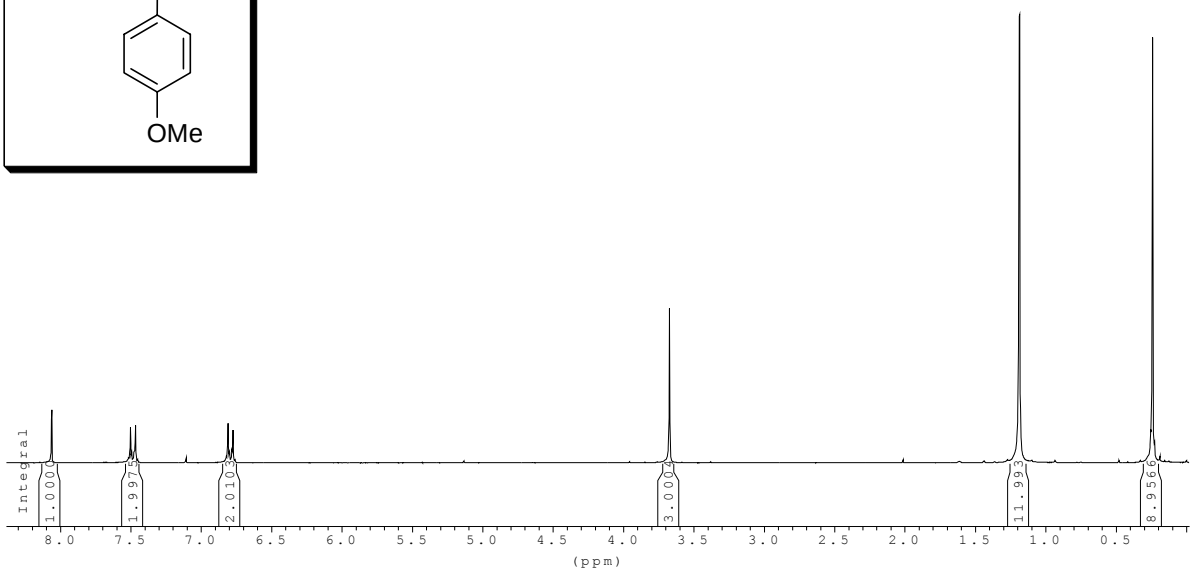

161.1585
158.0578
134.5967
133.8330
120.8042
114.4501
83.0465
55.5072
32.6877
28.1512
24.8368
22.5915
13.9157
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

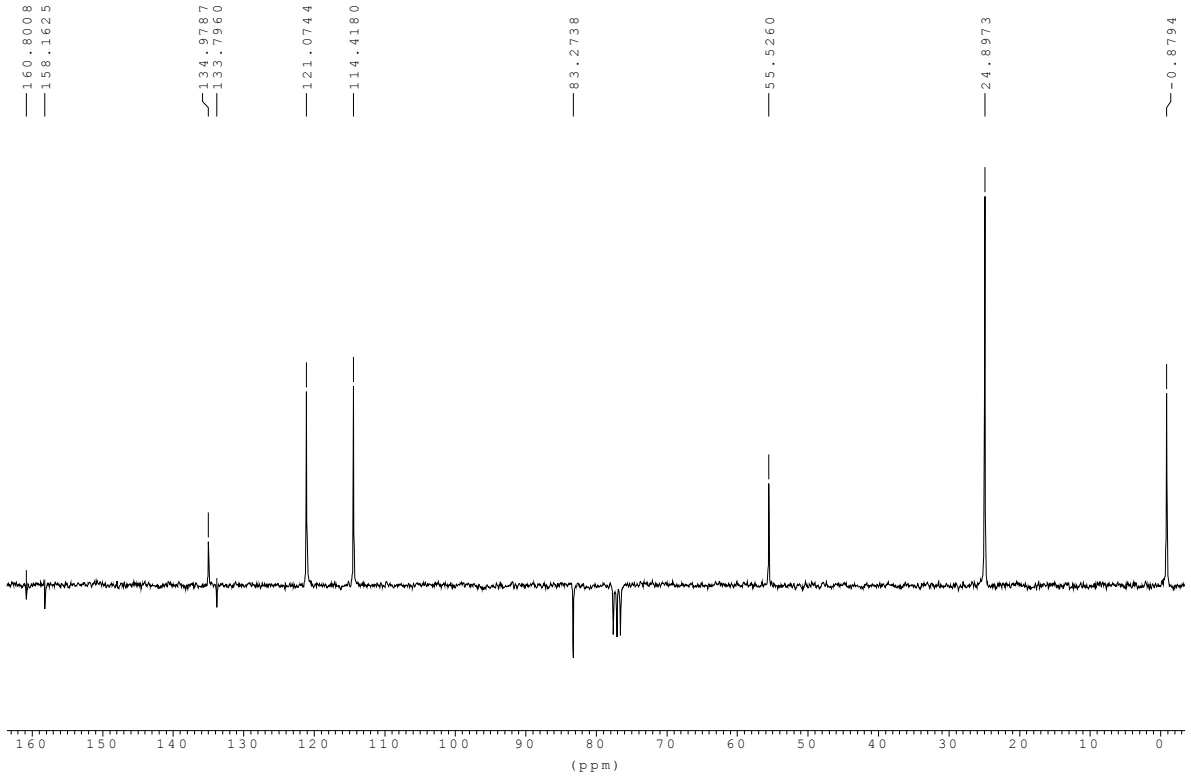

O
O–B
nBu
N
N
+
nBu
B–O
O
N
N
NO2
NO2

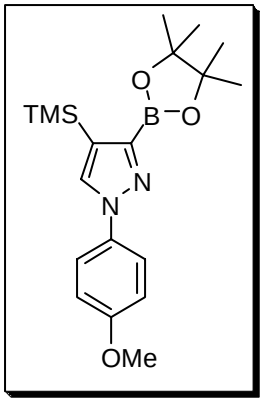
2.6915
1.0000
2.8121
2.0000
0.3768
3.0968
17.4780
4.4297
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)


162.8997
145.0595
144.1278
134.9786
125.3406
118.3451
83.4895
32.1683
28.1360
24.8368
22.5456
13.9157
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

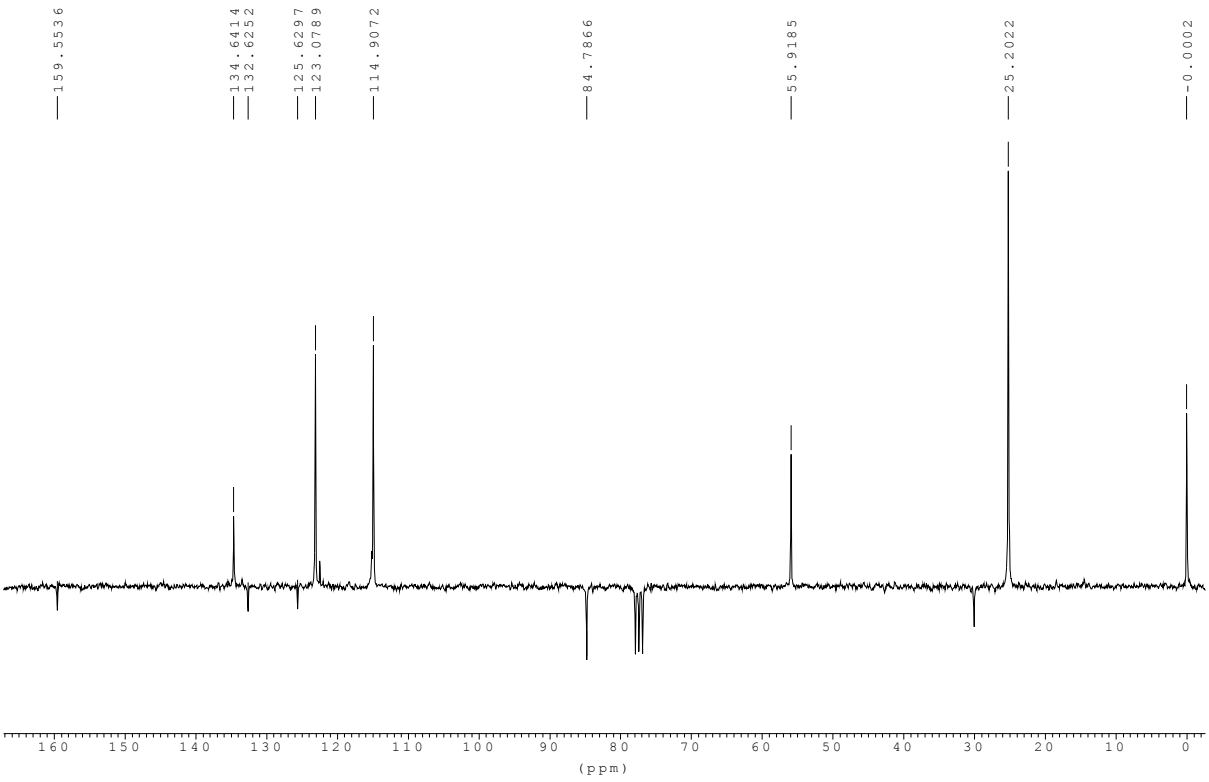

O
O
B
TMS
N
N
OMe

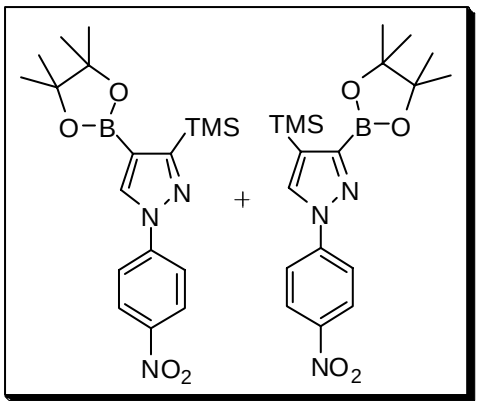

Integral
1.0000
1.9975
2.0103
3.0000
11.9933
8.9566
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)


160.8008
158.1625
134.9787
133.7960
121.0744
114.4180
83.2738
55.5260
24.8973
-0.8794
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

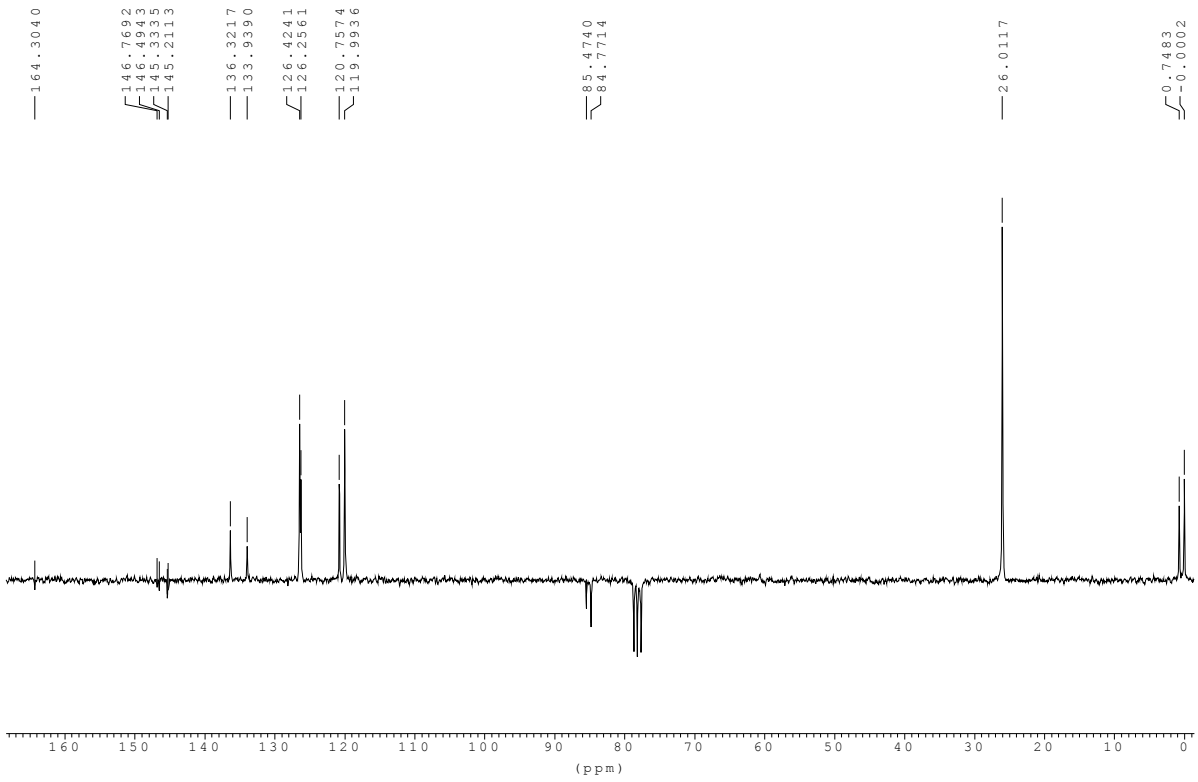

TMS
O
B
O
N
N
OMe

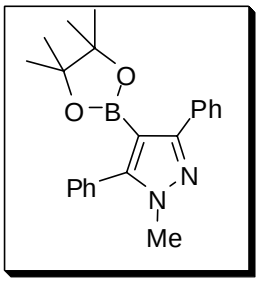
Integral
1.00
2.02
2.05
3.04
12.32
8.83
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)


159.5536
134.6414
132.6252
125.6297
123.0789
114.9072
84.7866
55.9185
25.2022
0.0002
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

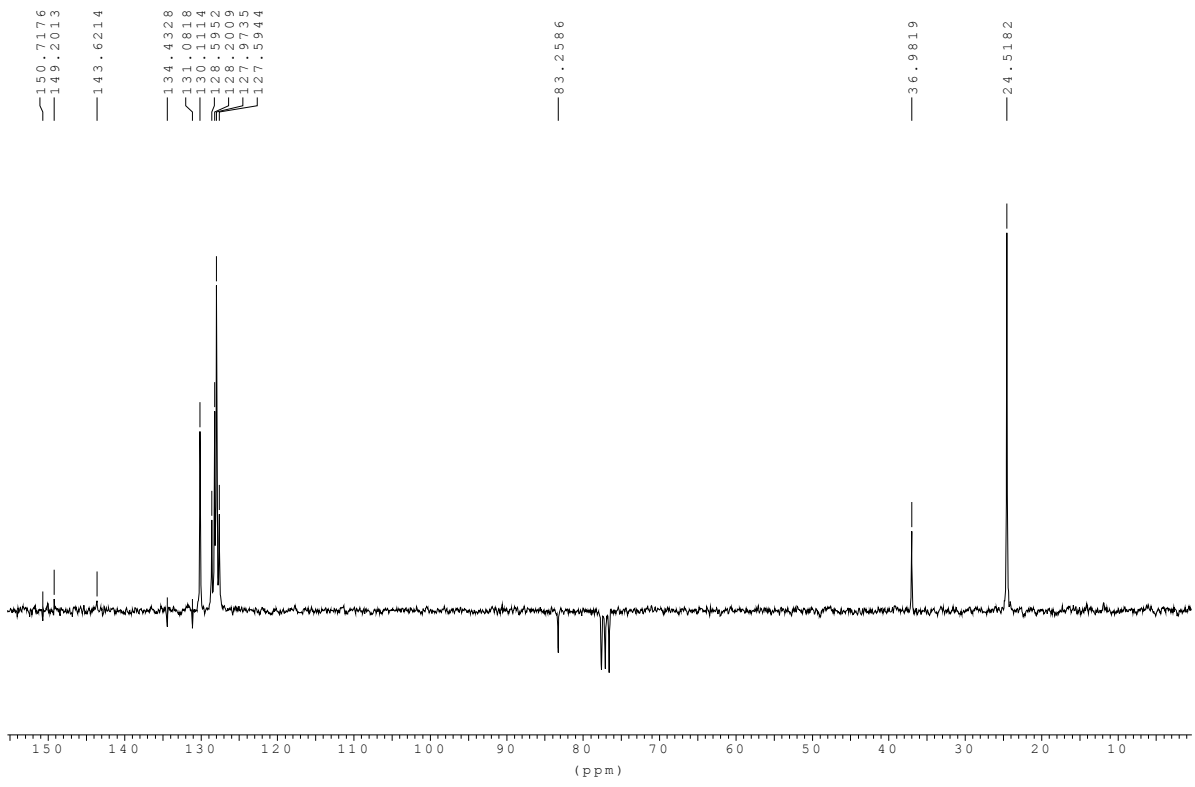

O
O
B
TMS
N
N
NO2
+
TMS
O
B
O
N
N
NO2

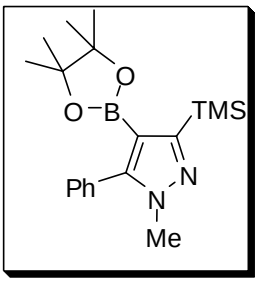
1.0000
3.5494
4.4556
7.4602
12.0000
9.0558
5.8107
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)


164.3040
146.7692
146.4943
145.3335
145.2213
136.3217
133.9390
126.4241
126.2561
120.7574
119.9936
85.4740
84.7714
26.0117
0.7483
-0.0002
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

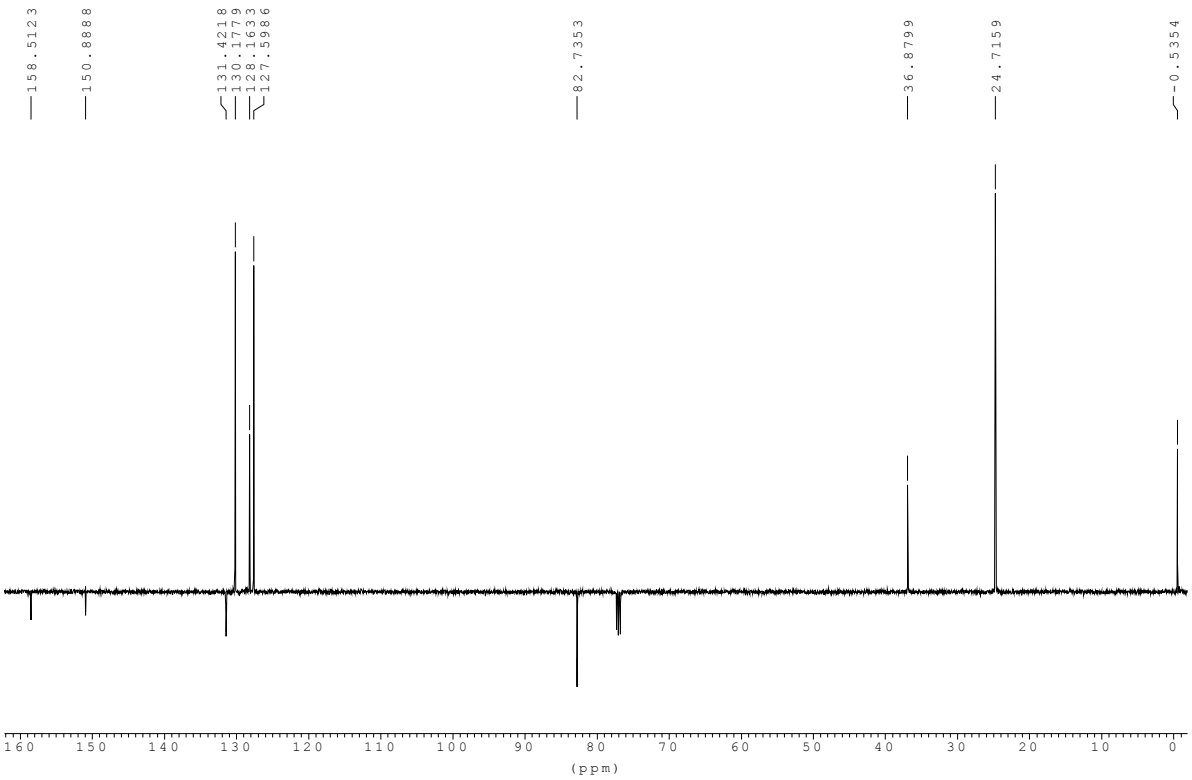

O
O
B
Ph
Ph
N
N
Me

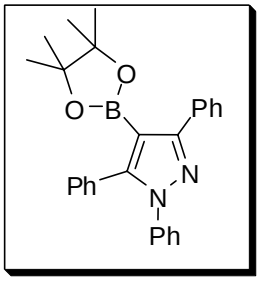
Integral
2.00
5.04
3.00
3.00
12.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)


150.7176
149.2013
143.6214
134.4328
131.0818
130.1114
128.5952
128.2009
127.9735
127.5944
83.2586
36.9819
24.5182
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

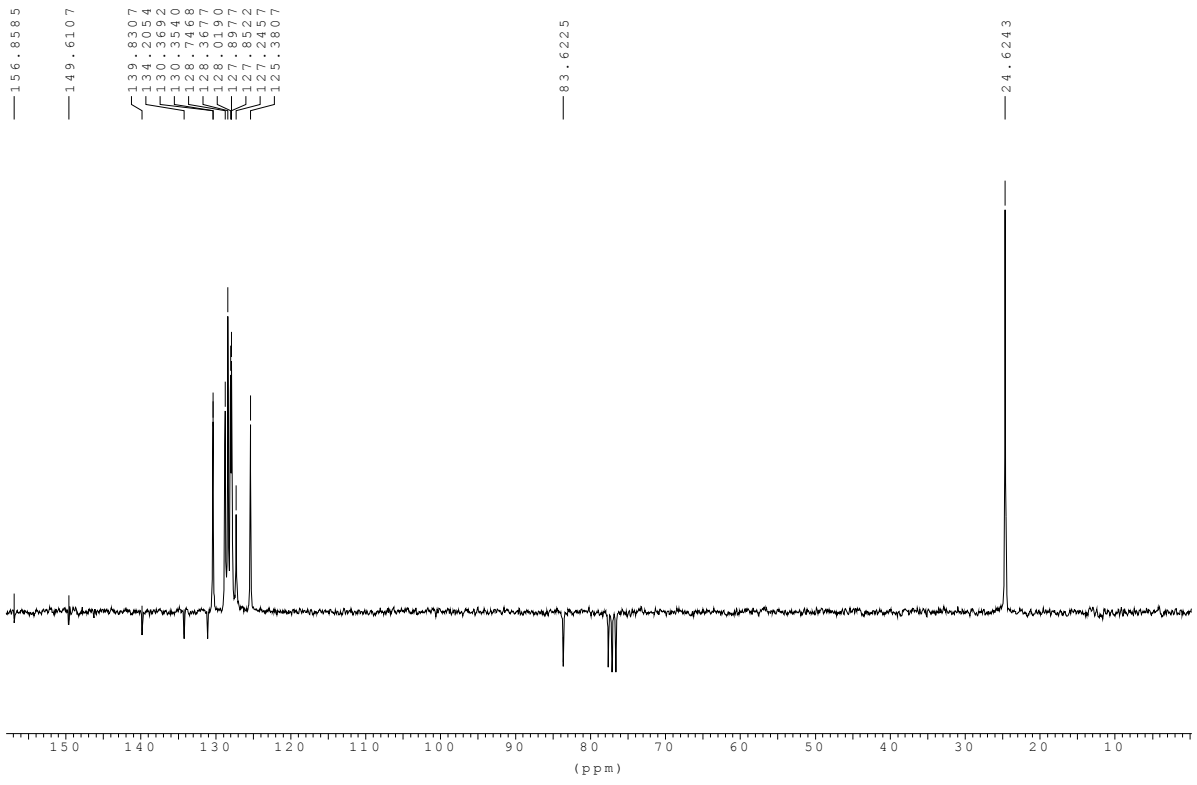

O
O
B
TMS
Ph
N
N
Me

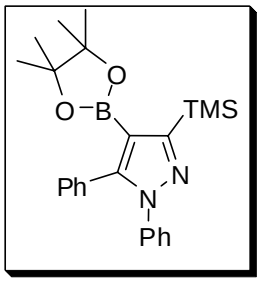
4.9948
3.0000
11.967
8.9870
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)


158.5123
150.8888
131.4218
130.1779
128.1633
127.5986
82.7353
36.8799
24.7159
0.5354
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

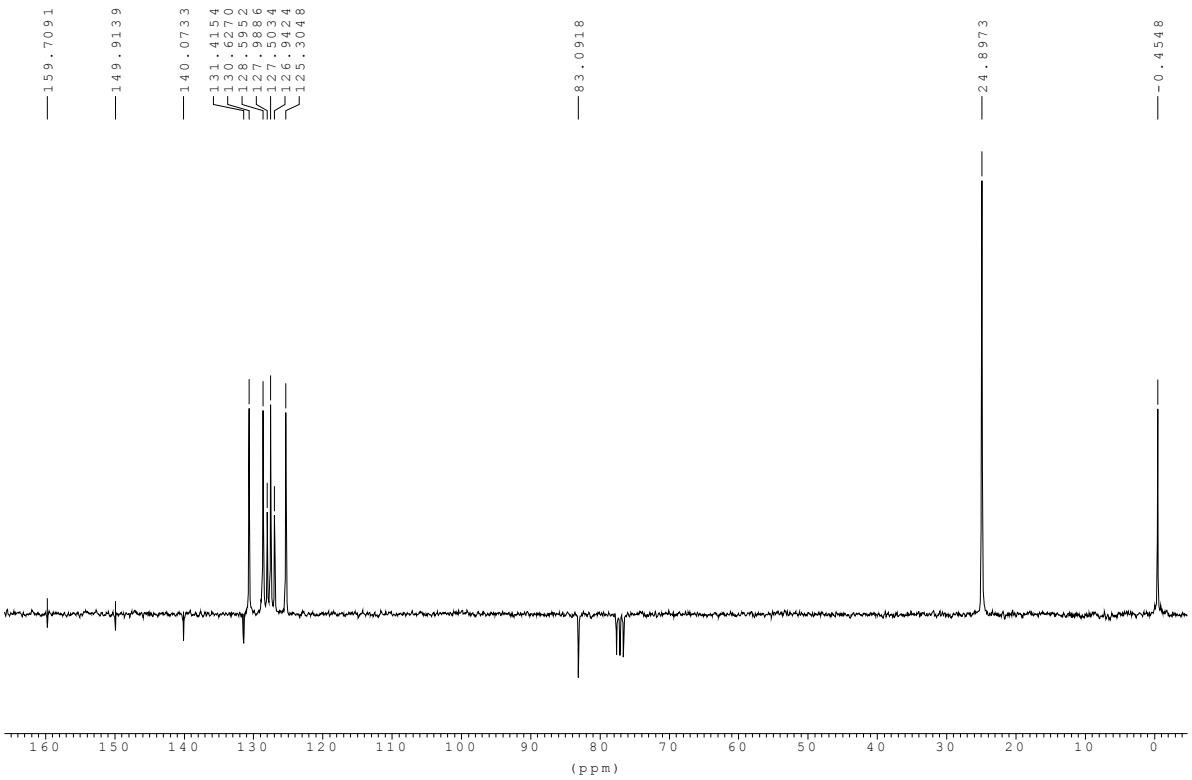

O
O
B
Ph
Ph
N
N
Ph

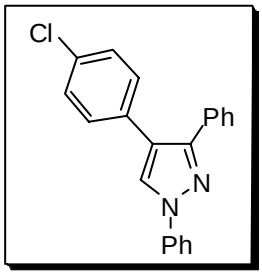
Integral
2.000
13.179
11.705
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

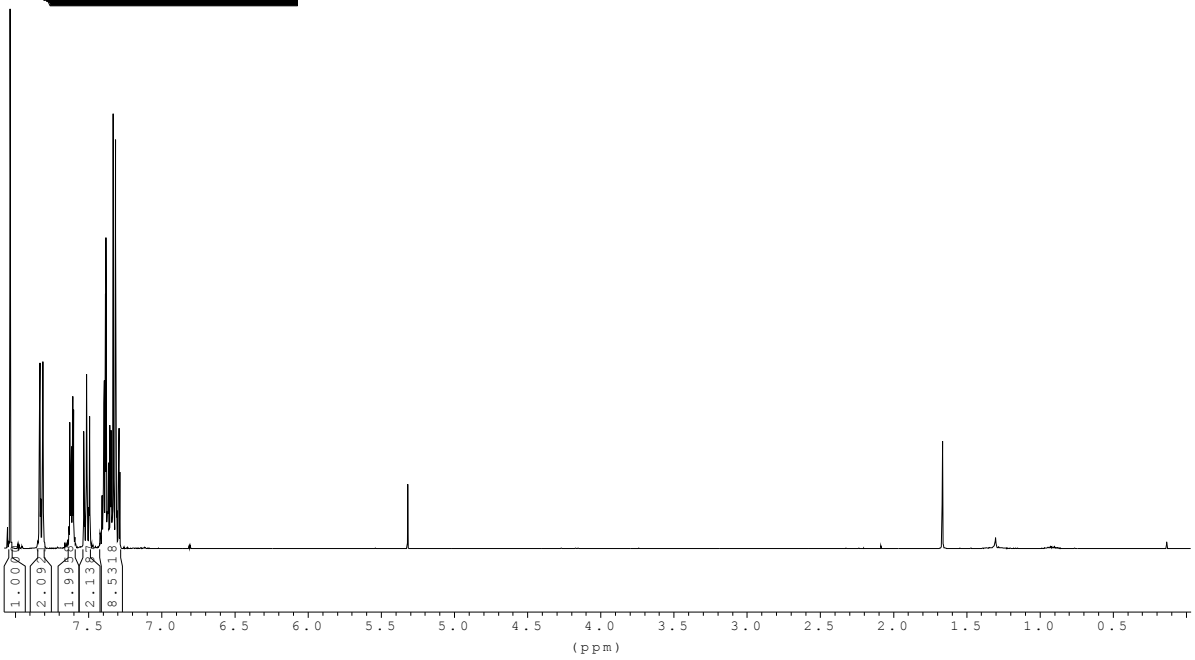

156.8585
149.6107
139.8307
134.2054
130.3692
130.3540
128.7468
128.3677
128.0190
127.8977
127.8522
127.2457
125.3807
83.6225
24.6243
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

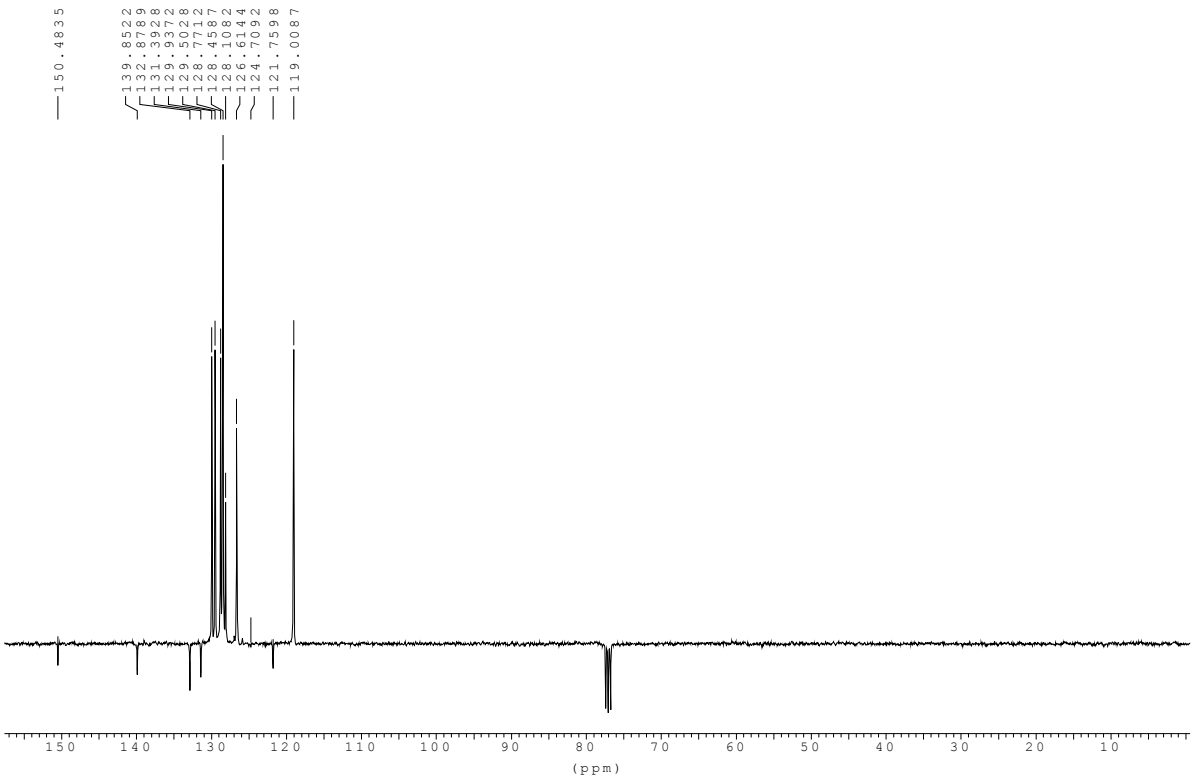

O
O
B
TMS
Ph
N
N
Ph

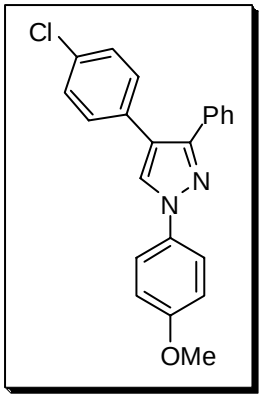
Integral
10.072
12.000
8.8630
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)


159.7091
149.9139
140.0733
131.4154
130.6270
128.5952
127.9886
127.5034
126.9424
125.3048
83.0918
24.8973
0.4548
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

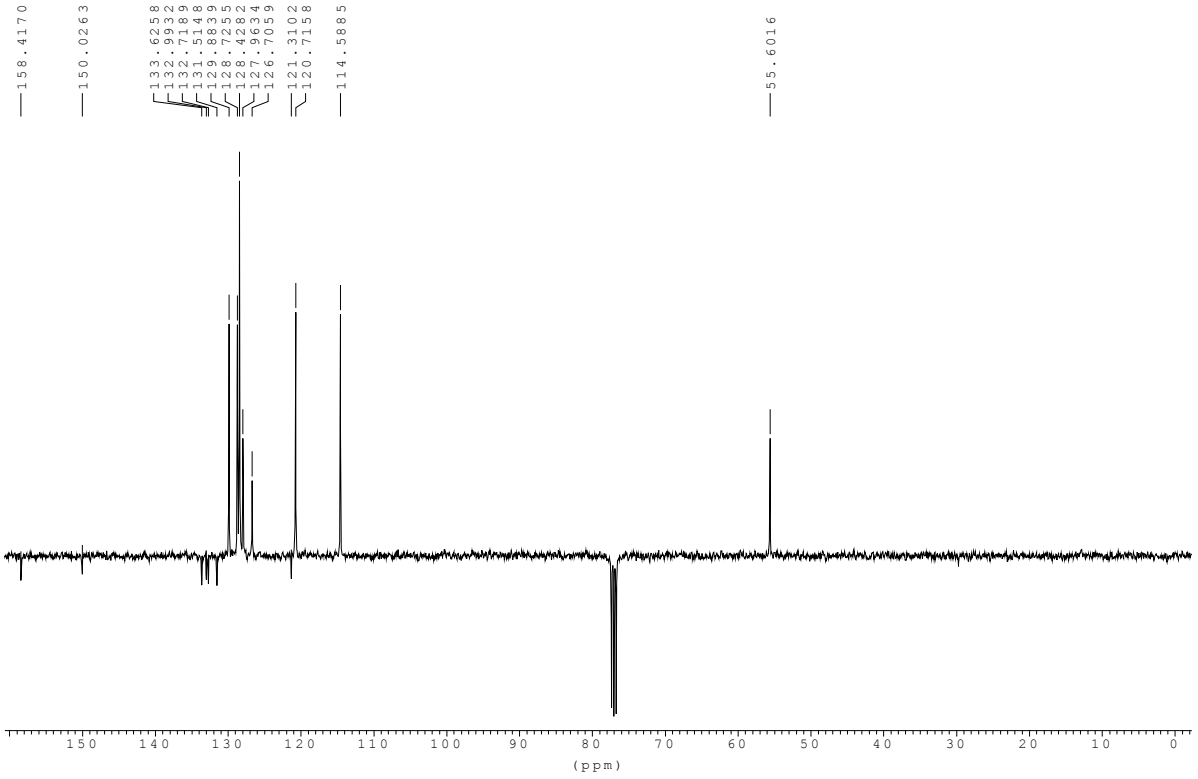

Cl
Ph
N
N
Ph

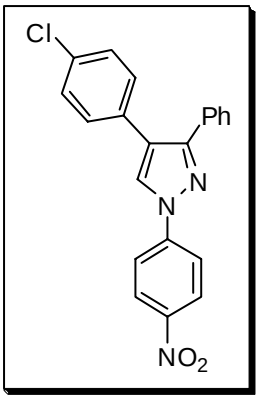

1.00
2.09
1.93
2.13
8.53
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

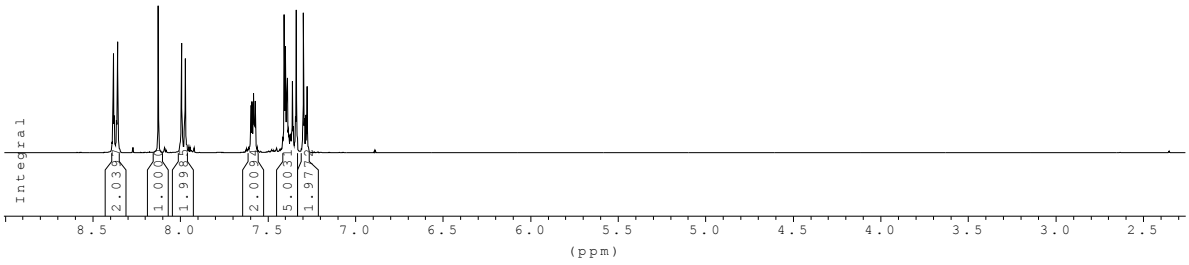

150.4835
139.8522
132.8789
131.3928
129.9372
129.5028
128.7712
128.4587
128.1082
126.6144
124.7092
121.7598
119.0087
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

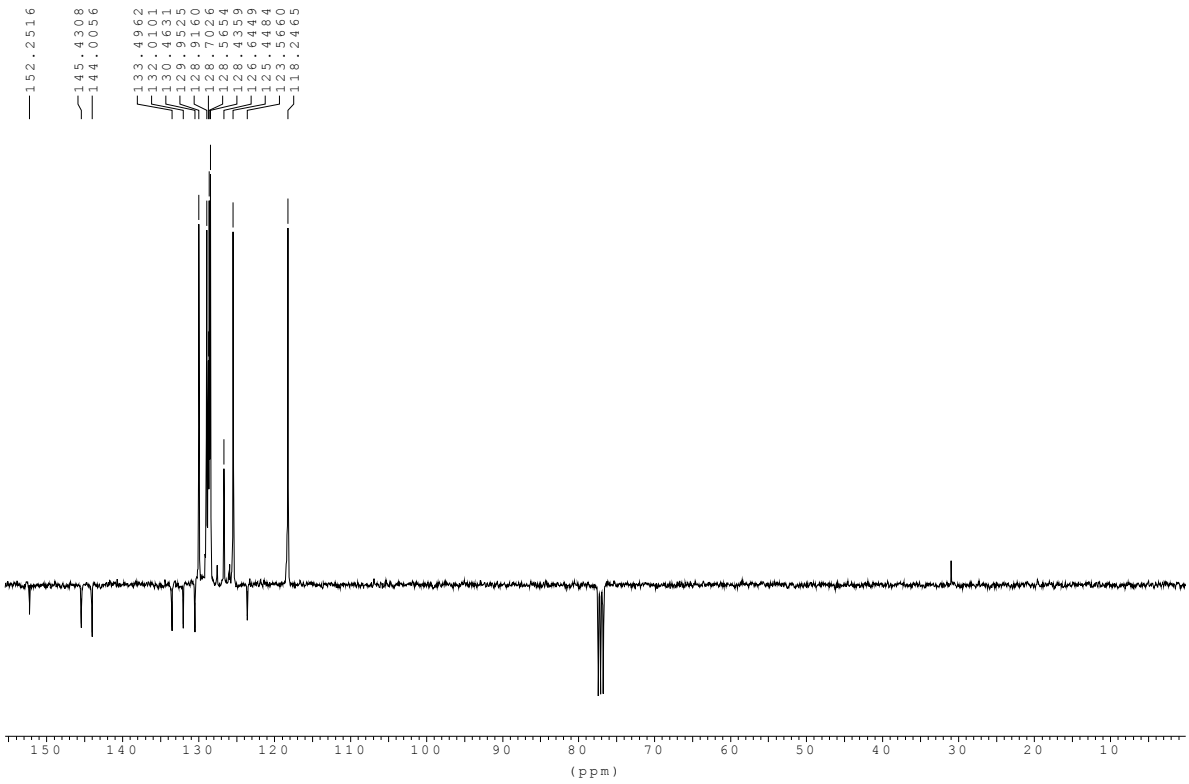

Cl
Ph
N
N
OMe

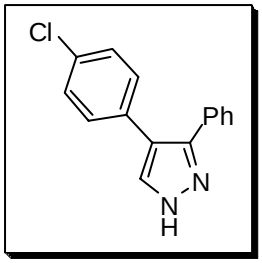
Integral
1.00
2.02
1.98
7.5401
2.06
3.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)


158.4170
150.0263
133.6258
132.9932
132.7189
131.5148
129.8839
128.7255
128.4282
127.9634
126.7059
121.3102
120.7158
114.5885
55.6016
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

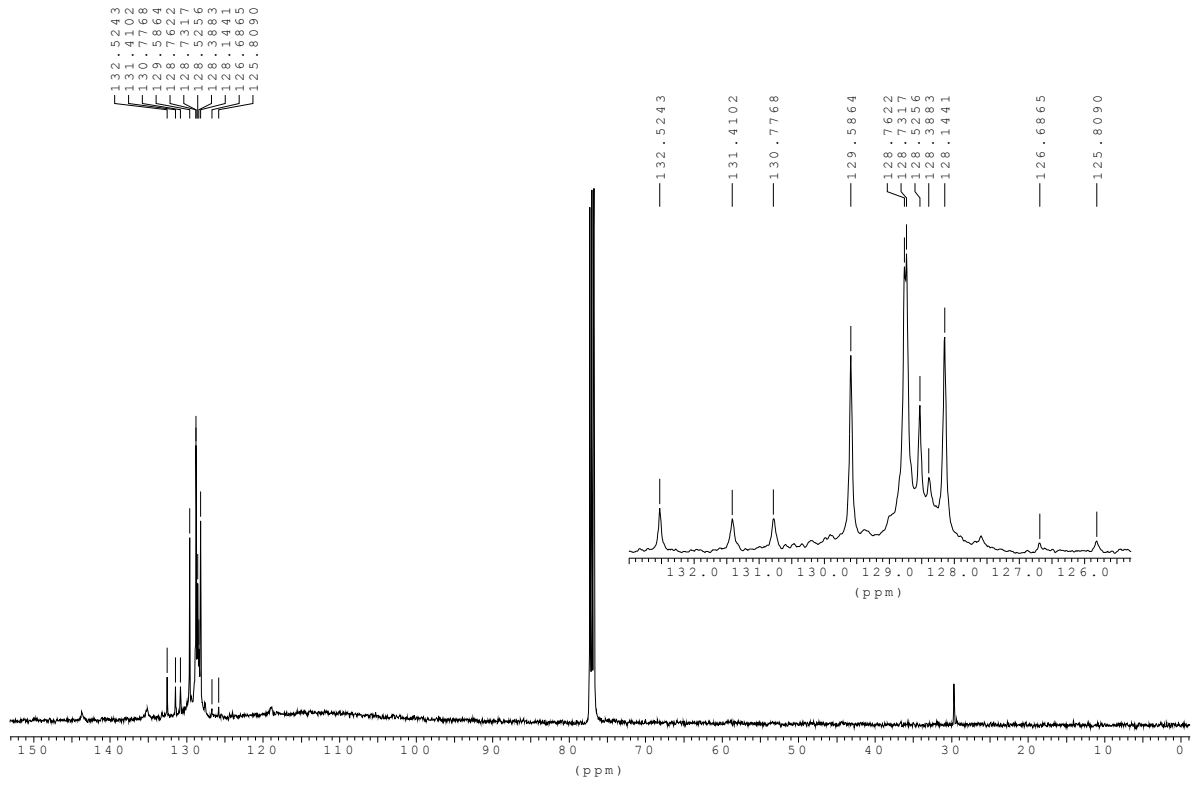

Cl
Ph
N
N
NO_2


Integral
2.03
1.00
1.99
2.00
5.00
1.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
(ppm)


152.2516
145.4308
144.0056
133.4962
132.0101
130.4631
129.9525
129.9160
128.7026
128.5654
128.4359
126.6449
125.4484
123.5660
118.2465
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)


Cl
Ph
N
N
H

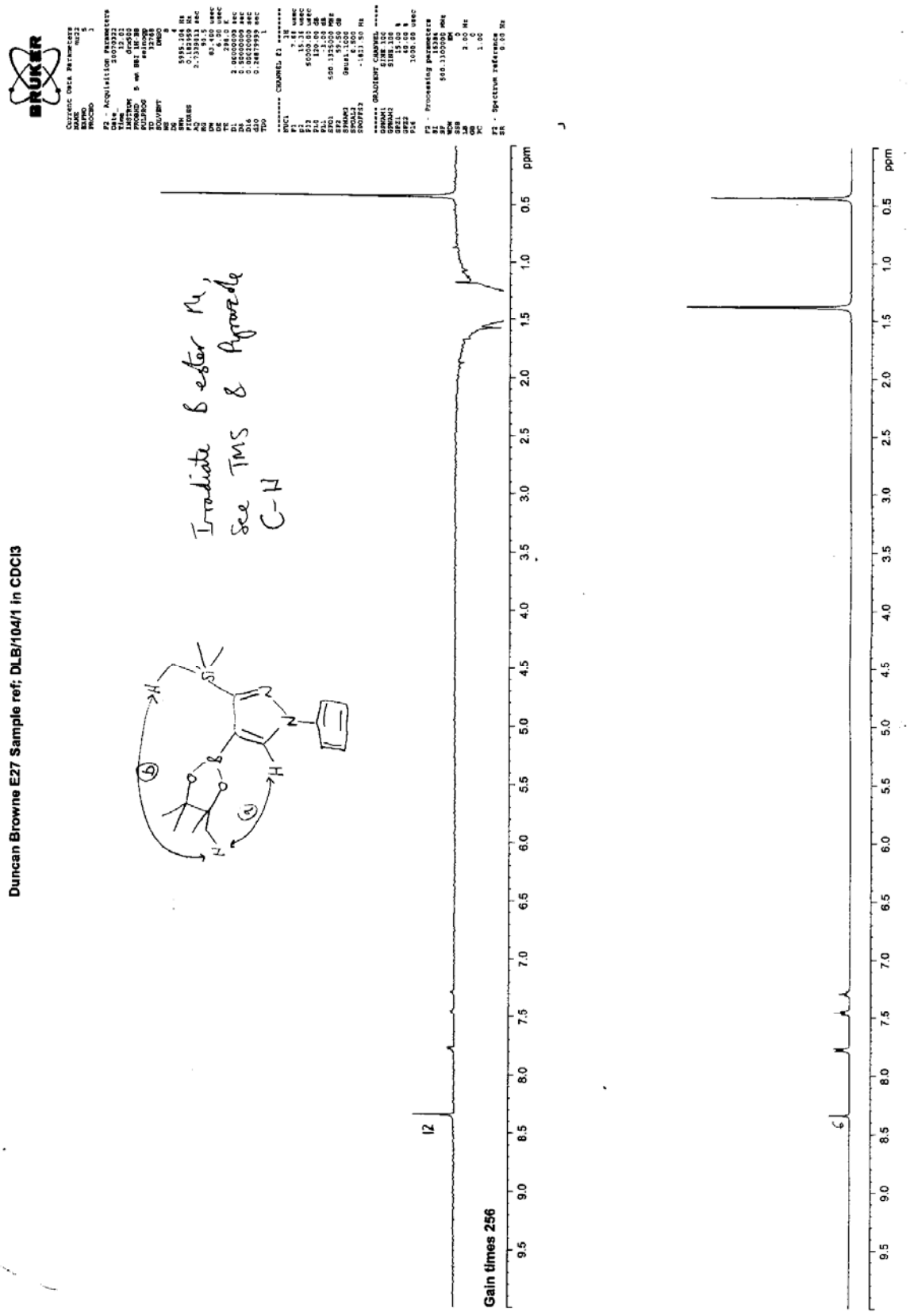
Integral
0.9892
1.0000
9.0512
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
(ppm)


132.5243
131.4102
130.7768
129.5864
128.7622
128.7317
128.5256
128.3883
128.1441
126.6865
125.8090
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)
132.0 131.0 130.0 129.0 128.0 127.0 126.0
(ppm)

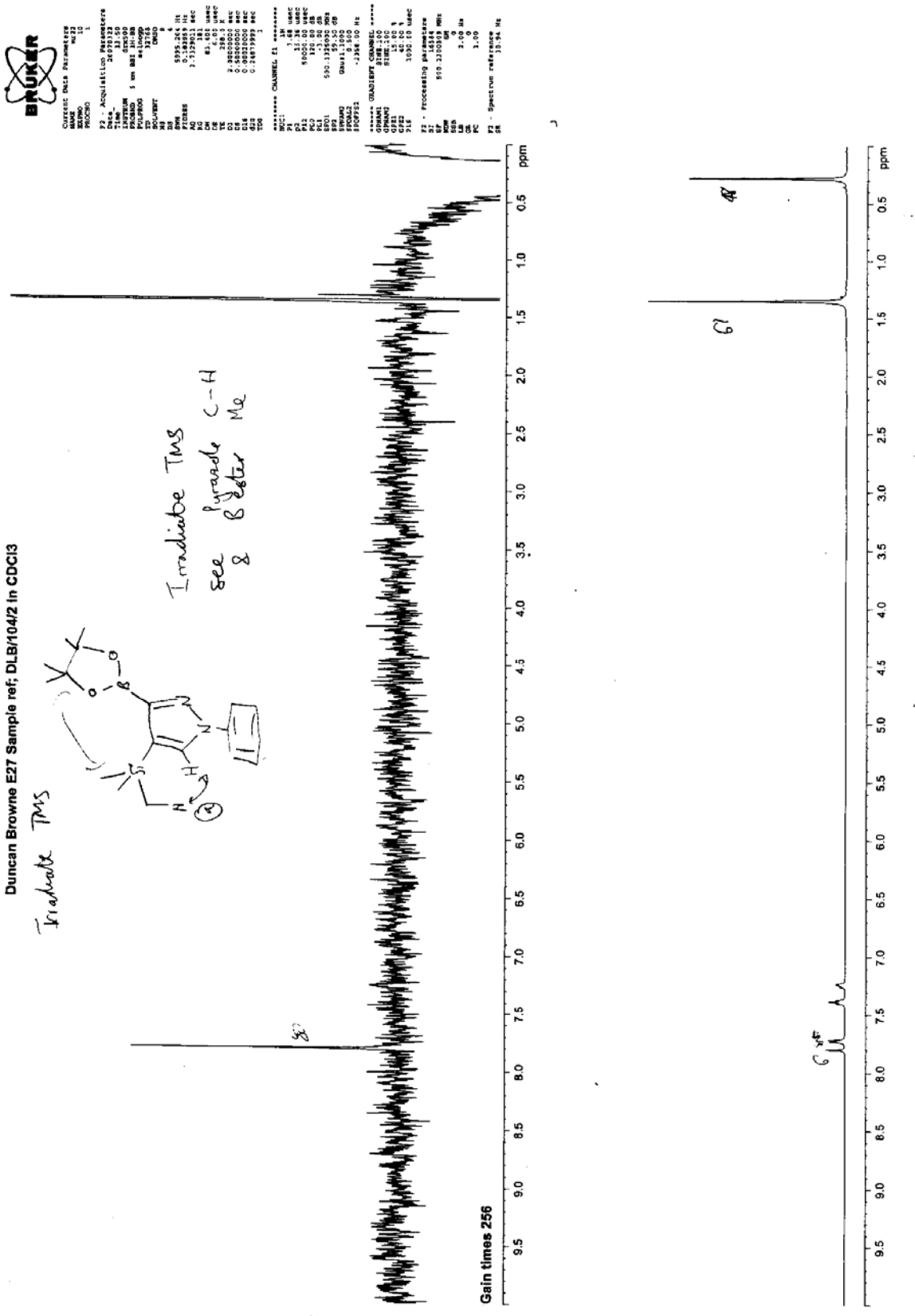
On the Assignment of Regiochemistry

Compound **3a** was assigned by X-ray crystallography (**CCDC 656450**). Regiochemistry of compounds **5a** and **5b** was assigned by nOe studies. All other trisubstituted pyrazoles were assigned by their diagnostic C-5 proton shift.
Regiochemistry for tetrasubstituted pyrazoles **15** and **16** were assigned by nOe. Compounds **17** and **18** were assumed to form with identical regiochemistry.

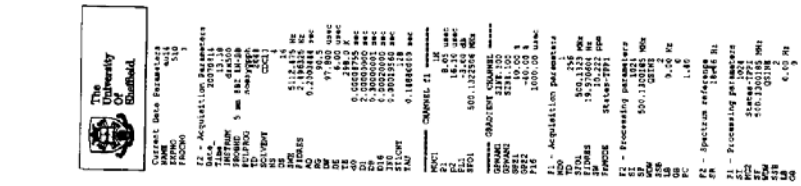
Regiochemical assignment of 5a by nOe

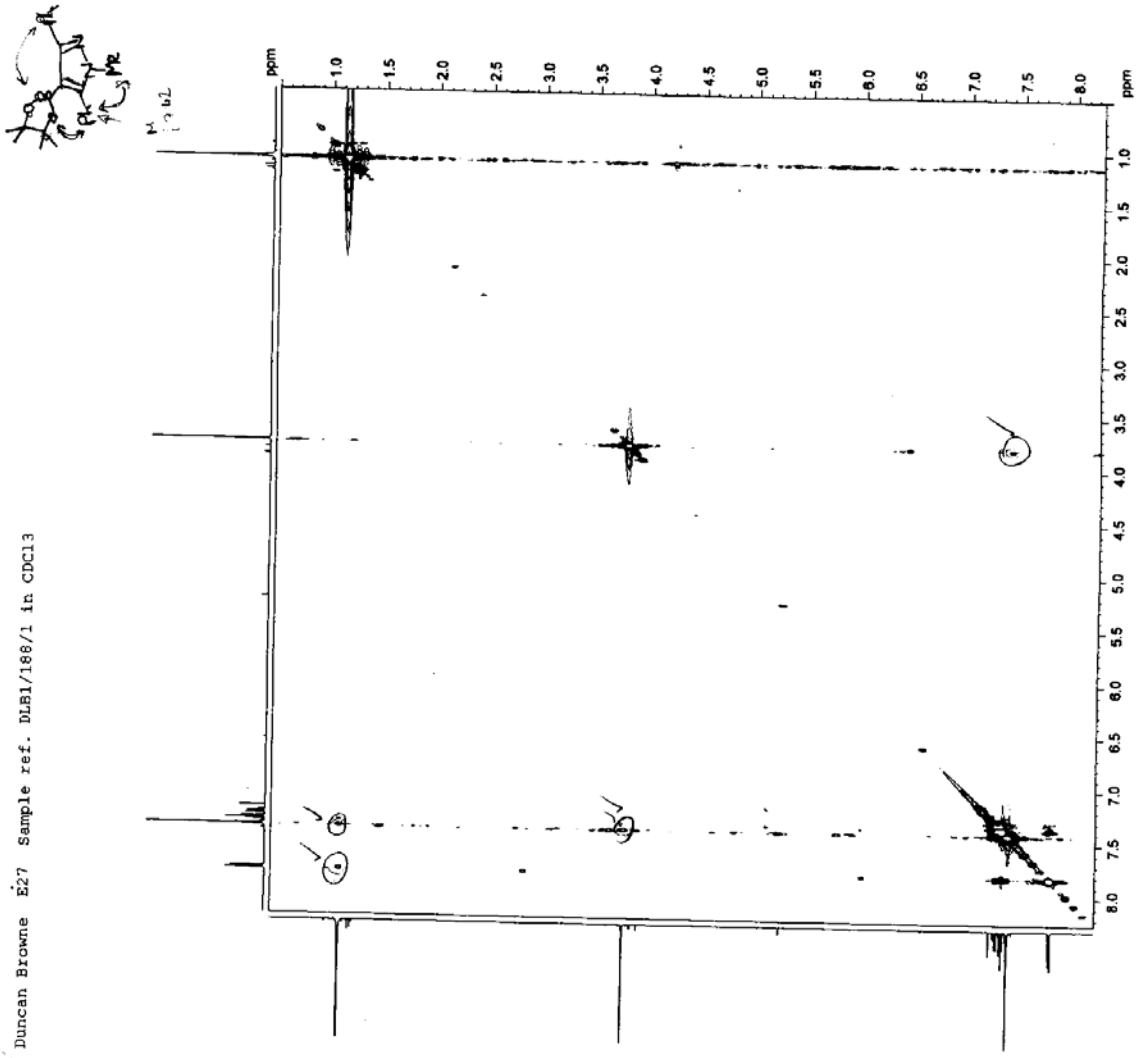


Regiochemical assignment of 5b by nOe



Regiochemical assignment of 15 by nOe





Regiochemical assignment of 16 by nOe