

Supporting Information (SI)

Transition-Metal Free [3 + 2] Cycloaddition of Nitroolefins and Diazoacetonitrile: A Facile Access to Multi-substituted Cyanopyrazoles

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1. General Information

^1H , ^{19}F and ^{13}C NMR were recorded at 400 MHz (^1H NMR), 376 MHz (^{19}F NMR) and 100 MHz (^{13}C NMR), respectively. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($\text{d}_4\text{-MeOH}$: $\delta_{\text{H}} = 4.87, 3.31$ ppm, $\delta_{\text{C}} = 49.15$ ppm; CDCl_3 : $\delta_{\text{H}} = 7.26$ ppm, $\delta_{\text{C}} = 77.20$ ppm; $\text{d}_6\text{-DMSO}$: $\delta_{\text{H}} = 2.50$ ppm, $\delta_{\text{C}} = 39.52$ ppm; THF: $\delta_{\text{H}} = 1.73$ and 3.58 ppm, $\delta_{\text{C}} = 25.37$ and 65.57 ppm;). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and dd (doublet of doublets). Coupling constants were reported in Hertz (Hz). High resolution mass spectrometry (HRMS) spectra were obtained on a microTOF-QII or Waters Micromass GCT Premier Instrument. IR spectra were recorded on an AVATAR 360 FT-IR spectrometer. Melting points were measured on a WRS-1A digital melting point apparatus and are uncorrected.

Materials: Tetrahydrofuran (THF) and toluene were distilled from sodium/benzophenone; CH_2Cl_2 (DCM), CHCl_3 , and *N, N*-dimethylformamide (DMF) was distilled from CaH_2 ; CH_3CN was distilled from P_2O_5 . All commercially available reagents were used without further purification. Analytical thin layer chromatography was performed on 0.20 mm silica gel plates. Silica gel (200–300 mesh) was used for flash chromatography.

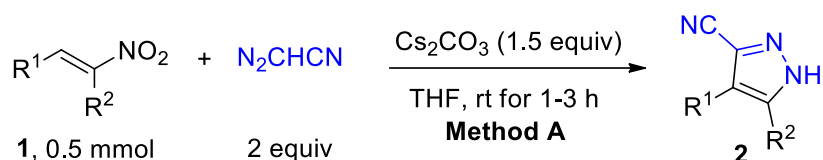
CAUTION: *diazoacetonitrile (N_2CHCN) is potentially explosive! Although no accident occurred during the course of this study, stringent safety precautions are necessary for all reactions of N_2CHCN .*

2. Experimental Section

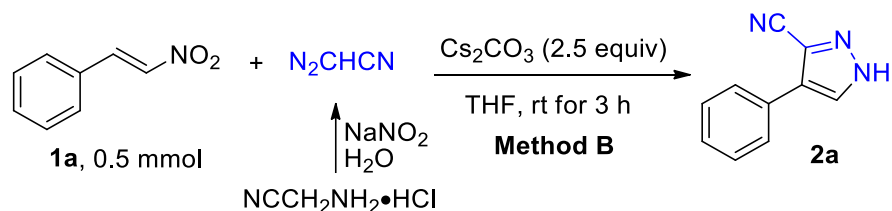
2.1 General procedure for the preparation of N₂CHCN

2-Aminoacetonitrile hydrochloride (4.63 g, 50 mmol) was dissolved in water (10 mL) in a 50 mL round-bottomed flask immersed in an ice-water bath, and then CH₂Cl₂ (20 mL) was added. The mixture was stirred vigorously, and NaNO₂ (3.45 g, 50 mmol) was added over 5 min. After stirring for another 15 min, the mixture was extracted with CH₂Cl₂ (50 mL), and the organic layer was washed with saturated aqueous NaHCO₃ solution and dried over Na₂SO₄. Removing the solvent at 0 °C under vacuum gave the desired N₂CHCN as a yellow liquid.

2.2 General procedure for one-pot transformation of nitroolefins with N₂CHCN

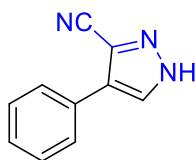


Method A: An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with nitroolefin **1** (0.5 mmol, 1.0 equiv), and Cs₂CO₃ (244.4 mg, 0.75 mmol, 1.5 equiv). Then THF (5 mL) and N₂CHCN (67.0 mg, 1.0 mmol, 2.0 equiv) were added. The resulting mixture was stirred at room temperature for a specific time until nitroolefins **1** disappeared. Then the insoluble solid was filtered, rinsed with ethyl acetate, and the filtrate was concentrated in reduced pressure. The residue was further purified by a silica gel column chromatography (PE/EA = 6/1) to yield the corresponding 3-cyanopyrazoles **2**.

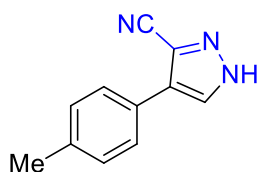


Method B: A 25 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-aminoacetonitrile hydrochloride (2.0 mmol) and water (0.2 mL). This solution was cooled to 0 °C before dropwise addition of an aqueous solution of NaNO₂ (2.1 mmol in 0.3 mL of water). After completion of addition, the reaction mixture was allowed to warm to room temperature and stirred

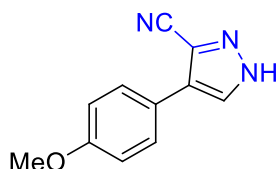
for 1 h. Then THF (5 mL), nitroolefins **1** (0.5 mmol) and Cs₂CO₃ (1.25 mmol) were added successively, and the mixture was stirred at room temperature for an additional 3 h. The insoluble solid was filtered, rinsed with ethyl acetate, and the filtrate was concentrated in reduced pressure. The residue was further purified by a silica gel column chromatography (PE/EA = 6/1) to yield the corresponding 3-cyanopyrazoles **2**.



4-Phenyl-1H-pyrazole-3-carbonitrile (2a): Method A: 71.0 mg, 84% yield; Method B: 64.5 mg, 76%; white solid; m.p.: 146 – 147 °C; **IR** (KBr) ν 3261, 3049, 2926, 2245, 1706, 1447, 1158, 812, 758, 695 cm⁻¹; **¹H NMR** (400 MHz, MeOD) δ 8.05 (s, 1H), 7.66 – 7.57 (m, 2H), 7.42 – 7.35 (m, 2H), 7.34 – 7.26 (m, 1H), 4.87 (s, 1H). **¹³C NMR** (100 MHz, MeOD) δ 131.28, 130.16, 129.11, 128.84, 128.04, 127.79, 123.10, 115.94. **HRMS** (ESI): m/z calculated for C₁₀H₈N₃⁺ [M + H]⁺: 170.0713, found: 170.0711.

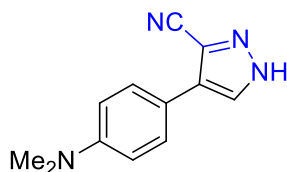


4-(p-Tolyl)-1H-pyrazole-3-carbonitrile (2b): Method A: 80.5 mg, 88% yield; Method B: 60.5 mg, 66%; white solid; m.p.: 143.5 – 144.5 °C; **IR** (KBr) ν 3150, 2994, 2232, 1704, 1490, 1338, 800 cm⁻¹; **¹H NMR** (400 MHz, MeOD) δ 7.97 (s, 1H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 4.87 (s, 1H), 2.29 (s, 3H). **¹³C NMR** (100 MHz, MeOD) δ 139.08, 130.71, 128.48, 128.25, 128.06, 127.59, 122.88, 116.05, 21.33. **HRMS** (ESI): m/z calculated for C₁₁H₁₀N₃⁺ [M + H]⁺: 184.0869, found: 184.0870.

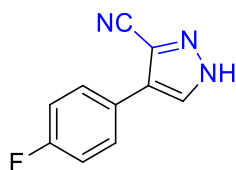


4-(4-Methoxyphenyl)-1H-pyrazole-3-carbonitrile (2c): Method A: 81.4 mg, 82% yield; white solid; m.p.: 134 – 135 °C; **IR** (KBr) ν 3264, 2925, 2853, 2241, 1715, 1506, 1252, 1027, 807 cm⁻¹; **¹H NMR** (400 MHz, DMSO) δ 14.04 (s, 1H), 8.33 (s, 1H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.03 (d, *J* = 8.7

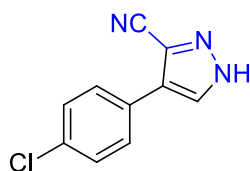
Hz, 2H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 158.99, 127.68, 125.78, 122.18, 120.53, 118.89, 115.42, 114.55, 55.20. HRMS (ESI): m/z calculated for $\text{C}_{11}\text{H}_{10}\text{N}_3\text{O}^+$ $[\text{M} + \text{H}]^+$: 200.0819, found: 200.0820.



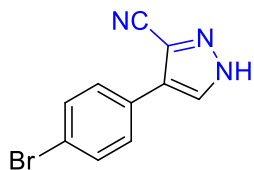
4-(4-(Dimethylamino)phenyl)-1H-pyrazole-3-carbonitrile (2d): Method A: 68.0 mg, 64% yield; yellow solid; m.p.: 171 – 172 °C; IR (KBr) ν 3231, 2912, 2240, 1715, 1607, 1510, 1352, 781 cm^{-1} ; ^1H NMR (400 MHz, DMSO) δ 13.95 (s, 1H), 8.25 (s, 1H), 7.51 (d, $J = 8.8$ Hz, 2H), 6.78 (d, $J = 8.8$ Hz, 2H), 2.91 (s, 6H). ^{13}C NMR (100 MHz, DMSO) δ 149.88, 127.09, 127.00, 126.50, 120.09, 117.34, 115.78, 112.59, 39.99. HRMS (ESI): m/z calculated for $\text{C}_{12}\text{H}_{13}\text{N}_4^+$ $[\text{M} + \text{H}]^+$: 213.1135, found: 213.1139.



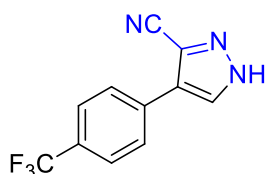
4-(4-Fluorophenyl)-1H-pyrazole-3-carbonitrile (2e): Method A: 82.5 mg, 88% yield; white solid; m.p.: 168 – 169 °C; IR (KBr) ν 3527, 2925, 2240, 1707, 1476, 805 cm^{-1} ; ^1H NMR (400 MHz, MeOD) δ 8.05 (s, 1H), 7.66 – 7.59 (m, 2H), 7.17 – 7.09 (m, 2H), 4.87 (s, 1H). ^{19}F NMR (376 MHz, MeOD) δ -115.80 (m). ^{13}C NMR (100 MHz, MeOD) δ 163.92 (d, $J = 244.9$ Hz), 129.79 (d, $J = 8.2$ Hz), 128.86, 127.65 (d, $J = 3.2$ Hz), 127.05, 123.09, 116.97 (d, $J = 21.8$ Hz), 115.81. HRMS (ESI): m/z calculated for $\text{C}_{10}\text{H}_7\text{FN}_3^+$ $[\text{M} + \text{H}]^+$: 188.0619, found: 188.0618.



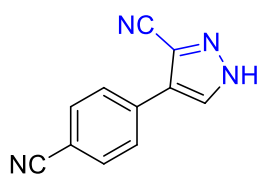
4-(4-Chlorophenyl)-1H-pyrazole-3-carbonitrile (2f): Method A: 95.5 mg, 94% yield; white solid; m.p.: 157 – 158 °C; IR (KBr) ν 3150, 2903, 2235, 1708, 1481, 1342, 1096, 813 cm^{-1} ; ^1H NMR (400 MHz, MeOD) δ 8.07 (s, 1H), 7.63 – 7.52 (m, 2H), 7.43 – 7.28 (m, 2H), 4.87 (s, 1H). ^{13}C NMR (100 MHz, MeOD) δ 134.85, 130.24, 129.97, 129.14, 129.01, 126.68, 123.03, 115.74. HRMS (ESI): m/z calculated for $\text{C}_{10}\text{H}_7\text{N}_3\text{Cl}^+$ $[\text{M} + \text{H}]^+$: 204.0323, found: 204.0326.



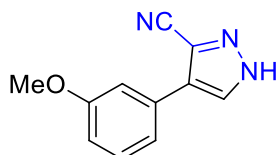
4-(4-Bromophenyl)-1H-pyrazole-3-carbonitrile (2g): Method A: 119.0 mg, 96% yield; Method B: 115.5 mg, 93% yield; white solid; m.p.: 165 – 166 °C; **IR** (KBr) ν 3116, 2919, 2236, 1706, 1471, 1002, 809 cm^{-1} ; **^1H NMR** (400 MHz, MeOD) δ 8.08 (s, 1H), 7.55 – 7.47 (s, 4H), 4.88 (s, 1H). **^{13}C NMR** (100 MHz, MeOD) δ 133.24, 130.37, 129.37, 129.00, 126.70, 122.99, 122.84, 115.71. **HRMS** (ESI): m/z calculated for $\text{C}_{10}\text{H}_7\text{BrN}_3^+$ $[\text{M} + \text{H}]^+$: 247.9818, found: 247.9812.



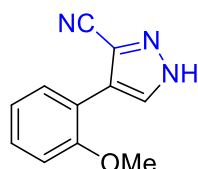
4-(4-(Trifluoromethyl)phenyl)-1H-pyrazole-3-carbonitrile (2h): Method A: 103.0 mg, 87% yield; Method B: 73.5 mg, 62% yield; white solid; m.p.: 138 – 139 °C; **IR** (KBr) ν 3275, 2941, 2244, 1706, 1327, 1122, 831 cm^{-1} ; **^1H NMR** (400 MHz, DMSO) δ 14.28 (s, 1H), 8.59 (s, 1H), 7.86 (dd, $J = 23.4, 8.3$ Hz, 4H). **^{19}F NMR** (376 MHz, DMSO) δ -61.12 (s). **^{13}C NMR** (100 MHz, DMSO) δ 133.97, 129.48, 128.11 (q, $J = 31.8$ Hz), 126.93, 126.12 (q, $J = 3.8$ Hz), 124.20 (q, $J = 270.3$ Hz), 124.19, 121.12, 114.95. **HRMS** (ESI): m/z calculated for $\text{C}_{11}\text{H}_7\text{F}_3\text{N}_3^+$ $[\text{M} + \text{H}]^+$: 238.0587, found: 238.0587.



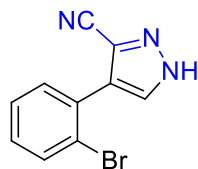
4-(4-Cyanophenyl)-1H-pyrazole-3-carbonitrile (2i): Method A: 80.5 mg, 83% yield; white solid; m.p.: 272 – 273 °C; **IR** (KBr) ν 3124, 2374, 2312, 1719, 1518 cm^{-1} ; **^1H NMR** (400 MHz, DMSO) δ 14.26 (s, 1H), 8.56 (s, 1H), 7.85 (dd, $J = 22.5, 8.0$ Hz, 4H). **^{13}C NMR** (100 MHz, DMSO) δ 134.49, 133.03, 129.61, 126.70, 123.84, 121.09, 118.67, 114.88, 110.19. **HRMS** (ESI): m/z calculated for $\text{C}_{11}\text{H}_6\text{N}_4\text{Na}^+$ $[\text{M} + \text{Na}]^+$: 217.0485, found: 217.0480.



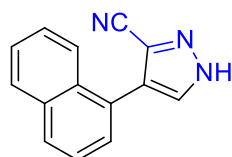
4-(3-Methoxyphenyl)-1H-pyrazole-3-carbonitrile (2j): Method A: 87.5 mg, 88% yield; white solid; m.p.: 145 – 146 °C; **IR** (KBr) ν 3144, 2931, 2240, 1715, 1592, 1470, 1250, 782 cm^{-1} ; **^1H NMR** (400 MHz, DMSO) δ 14.13 (s, 1H), 8.45 (s, 1H), 7.37 (t, $J = 7.9$ Hz, 1H), 7.29 – 7.23 (m, 2H), 6.97 – 6.84 (m, 1H), 3.79 (s, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 159.77, 131.11, 130.26, 128.61, 125.66, 120.90, 118.55, 115.34, 113.26, 112.04, 55.14. **HRMS** (ESI): m/z calculated for $\text{C}_{11}\text{H}_{10}\text{N}_3\text{O}^+$ $[\text{M} + \text{H}]^+$: 200.0819, found: 200.0817.



4-(2-Methoxyphenyl)-1H-pyrazole-3-carbonitrile (2k): Method A: 83.7 mg, 84% yield; white solid; Method B: 81.5mg, 82% yield; white solid; m.p.: 148 – 149 °C; **IR** (KBr) ν 3177, 2950, 2240, 1707, 1473, 1250, 1019, 751 cm^{-1} ; **^1H NMR** (400 MHz, DMSO) δ 14.04 (s, 1H), 8.22 (s, 1H), 7.57 – 7.46 (m, 1H), 7.40 – 7.30 (m, 1H), 7.11 (d, $J = 8.3$ Hz, 1H), 7.03 (t, $J = 7.5$ Hz, 1H), 3.83 (s, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 155.96, 129.90, 129.53, 129.25, 122.88, 121.83, 120.70, 118.50, 115.24, 111.64, 55.26. **HRMS** (ESI): m/z calculated for $\text{C}_{11}\text{H}_{10}\text{N}_3\text{O}^+$ $[\text{M} + \text{H}]^+$: 200.0819, found: 200.0817.

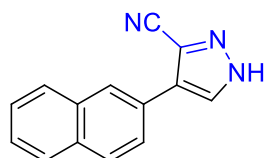


4-(2-Bromophenyl)-1H-pyrazole-3-carbonitrile (2l): Method A: 108.0 mg, 87% yield; white solid; m.p.: 172 – 173 °C; **IR** (KBr) ν 3144, 2242, 1713, 1501, 1464, 1404, 753 cm^{-1} ; **^1H NMR** (400 MHz, DMSO) δ 14.20 (s, 1H), 8.27 (s, 1H), 7.76 (d, $J = 8.0$ Hz, 1H), 7.47 (d, $J = 4.3$ Hz, 2H), 7.38 – 7.31 (m, 1H). **^{13}C NMR** (100 MHz, DMSO) δ 133.13, 131.84, 130.77, 130.33, 130.20, 128.05, 124.84, 123.47, 122.94, 114.41. **HRMS** (ESI): m/z calculated for $\text{C}_{10}\text{H}_7\text{BrN}_3^+$ $[\text{M} + \text{H}]^+$: 247.9818, found: 247.9816.

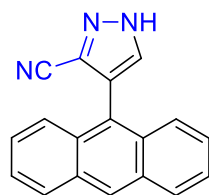


4-(Naphthalen-1-yl)-1H-pyrazole-3-carbonitrile (2m): Method A: 100.0 mg, 91% yield; white

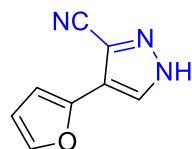
solid; m.p.: 175 – 176 °C; **IR** (KBr) ν 3153, 2939, 2232, 1710, 1510, 774 cm^{-1} ; **^1H NMR** (400 MHz, DMSO) δ 14.33 (s, 1H), 8.40 (s, 1H), 8.02 – 7.97 (m, 2H), 7.89 (d, $J = 7.7$ Hz, 1H), 7.64 – 7.54 (m, 4H). **^{13}C NMR** (100 MHz, DMSO) δ 133.44, 131.08, 130.56, 128.70, 128.49, 127.93, 127.37, 126.85, 126.31, 125.56, 124.89, 124.16, 123.90, 114.72. **HRMS** (ESI): m/z calculated for $\text{C}_{14}\text{H}_9\text{N}_3^+$ $[\text{M} + \text{H}]^+$: 220.0869, found: 220.0873.



4-(Naphthalen-2-yl)-1H-pyrazole-3-carbonitrile (2n): Method A: 95.7 mg, 87% yield; white solid; m.p.: 190.5 – 191.5 °C; **IR** (KBr) ν 3265, 2952, 2240, 1711, 1512, 1266, 793, 741 cm^{-1} ; **^1H NMR** (400 MHz, DMSO) δ 14.24 (s, 1H), 8.54 (s, 1H), 8.21 (s, 1H), 8.06 – 7.75 (m, 4H), 7.51 – 7.47 (m, 2H). **^{13}C NMR** (100 MHz, DMSO) δ 133.16, 132.32, 128.79, 127.91, 127.70, 127.41, 126.78, 126.40, 125.81, 124.81, 124.79, 121.18, 115.48. **HRMS** (ESI): m/z calculated for $\text{C}_{14}\text{H}_9\text{N}_3^+$ $[\text{M} + \text{H}]^+$: 220.0869, found: 220.0872.

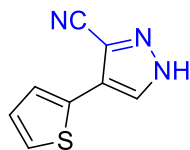


4-(Anthracen-9-yl)-1H-pyrazole-3-carbonitrile (2o): Method A: 121.5 mg, 90% yield; yellow solid; m.p.: 191 – 192 °C; **IR** (KBr) ν 3277, 3046, 2927, 2241, 1711, 1512, 1271, 875, 733 cm^{-1} ; **^1H NMR** (400 MHz, DMSO) δ 14.52 (s, 1H), 8.75 (s, 1H), 8.43 (s, 1H), 8.17 (d, $J = 8.1$ Hz, 2H), 7.70 (d, $J = 8.3$ Hz, 2H), 7.59 – 7.48 (m, 4H). **^{13}C NMR** (100 MHz, DMSO) δ 131.92, 130.86, 130.62, 128.67, 128.07, 126.66, 125.56, 125.40, 123.55, 121.54, 114.37. **HRMS** (ESI): m/z calculated for $\text{C}_{18}\text{H}_{12}\text{N}_3^+$ $[\text{M} + \text{H}]^+$: 270.1026, found: 270.1026.

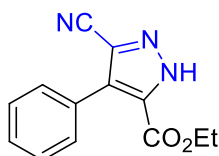


4-(Furan-2-yl)-1H-pyrazole-3-carbonitrile (2p): Method A: 71.5 mg, 90% yield; white solid; m.p.: 191 – 192 °C; **IR** (KBr) ν 3280, 3159, 2927, 2242, 1627, 1536, 1474, 1348, 1150, 1007, 800, 735 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3) δ 12.11 (s, 1H), 7.98 (s, 1H), 7.46 (d, $J = 1.3$ Hz, 1H), 6.81 (d, $J = 3.3$ Hz, 1H), 6.50 (dd, $J = 3.3, 1.8$ Hz, 1H). **^{13}C NMR** (100 MHz, CDCl_3) δ 144.24, 142.48,

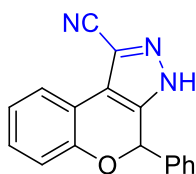
126.34, 120.95, 119.22, 113.76, 111.82, 107.42. **HRMS** (ESI): m/z calculated for $C_8H_5N_3NaO^+ [M + Na]^+$: 182.0325, found: 182.0327.



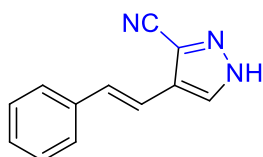
4-(Thiophen-2-yl)-1H-pyrazole-3-carbonitrile (2q): Method A: 80.5 mg, 92% yield; white solid; m.p.: 162 – 163 °C; **IR** (KBr) ν 3257, 2241, 1712, 792, 686 cm^{-1} ; **1H NMR** (400 MHz, DMSO) δ 14.17 (s, 1H), 8.41 (s, 1H), 7.56 (dd, $J = 5.0, 0.6$ Hz, 1H), 7.40 (d, $J = 2.8$ Hz, 1H), 7.15 (dd, $J = 5.0, 3.6$ Hz, 1H). **^{13}C NMR** (100 MHz, DMSO) δ 131.05, 128.20, 128.10, 125.83, 124.95, 120.58, 120.04, 114.74. **HRMS** (ESI): m/z calculated for $C_8H_6N_3S^+ [M + H]^+$: 176.0277, found: 176.0276.



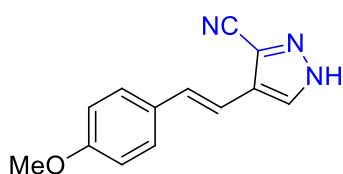
Ethyl 3-cyano-4-phenyl-1H-pyrazole-5-carboxylate (2r): Method A: 105.0 mg, 87% yield; white solid; m.p.: 122 – 123 °C; **IR** (KBr) ν 3240, 2922, 2246, 1721, 1298, 1206, 1023, 767, 700 cm^{-1} ; **1H NMR** (400 MHz, DMSO) δ 15.17 (s, 1H), 7.58 – 7.40 (m, 5H), 4.24 (q, $J = 7.1$ Hz, 2H), 1.17 (t, $J = 7.1$ Hz, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 158.06, 131.24, 129.72, 129.50, 129.07, 128.70, 128.36, 128.25, 128.15, 61.37, 13.70. **HRMS** (ESI): m/z calculated for $C_{13}H_{12}N_3O_2^+ [M + H]^+$: 242.0924, found: 242.0922.



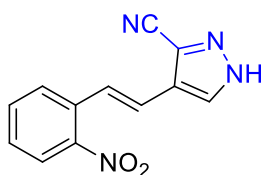
4-Phenyl-3,4-dihydrochromeno[3,4-c]pyrazole-1-carbonitrile (2s): Method A: 116.0 mg, 85% yield; white solid; m.p.: 143 – 144 °C; **IR** (KBr) ν 3258, 3056, 2916, 2239, 1706, 1462, 1269, 750, 694 cm^{-1} ; **1H NMR** (400 MHz, DMSO) δ 14.34 (s, 1H), 7.68 (dd, $J = 7.5, 1.2$ Hz, 1H), 7.46 – 7.32 (m, 5H), 7.26 – 7.18 (m, 1H), 7.12 – 06 (m, 1H), 7.01 (d, $J = 8.0$ Hz, 1H), 6.72 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.59, 137.95, 129.42, 129.12, 128.83, 127.28, 122.45, 122.20, 117.36, 116.04, 74.02. **HRMS** (ESI): m/z calculated for $C_{17}H_{12}N_3O^+ [M + H]^+$: 274.0975, found: 274.0976.



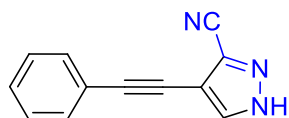
(E)-4-Styryl-1H-pyrazole-3-carbonitrile (2t): Method A: 70.0 mg, 72% yield; white solid; m.p.: 130 – 131 °C; **IR** (KBr) ν 3158, 2936, 2240, 1710, 957, 754, 696 cm^{-1} ; **^1H NMR** (400 MHz, DMSO) δ 14.05 (s, 1H), 8.29 (s, 1H), 7.52 (d, $J = 7.5$ Hz, 2H), 7.36 (t, $J = 7.4$ Hz, 2H), 7.31 – 7.22 (m, 1H), 7.12 (dd, $J = 53.1, 16.5$ Hz, 2H). **^{13}C NMR** (100 MHz, DMSO) δ 136.47, 130.00, 128.84, 128.41, 127.97, 126.31, 123.91, 121.58, 116.00, 114.78. **HRMS** (ESI): m/z calculated for $\text{C}_{12}\text{H}_{10}\text{N}_3^+$ [$\text{M} + \text{H}$] $^+$: 196.0869, found: 196.0865.



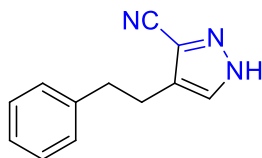
(E)-4-(4-Methoxystyryl)-1H-pyrazole-3-carbonitrile (2u): Method A: 75.5 mg, 67% yield; white solid; m.p.: 157 – 158 °C; **IR** (KBr) ν 3249, 3115, 2952, 2240, 1711, 1506, 1245, 806 cm^{-1} ; **^1H NMR** (400 MHz, DMSO) δ 13.99 (s, 1H), 8.24 (s, 1H), 7.47 (d, $J = 8.6$ Hz, 2H), 7.12 (d, $J = 16.5$ Hz, 1H), 6.96 – 6.85 (m, 3H), 3.75 (s, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 159.23, 129.73, 129.08, 127.91, 127.66, 124.27, 121.32, 114.91, 114.28, 113.61. **HRMS** (ESI): m/z calculated for $\text{C}_{13}\text{H}_{12}\text{N}_3\text{O}^+$ [$\text{M} + \text{H}$] $^+$: 226.0975, found: 226.0980.



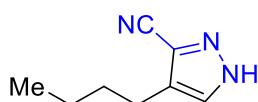
(E)-4-(2-Nitrostyryl)-1H-pyrazole-3-carbonitrile (2v): Method A: 96.0 mg, 80% yield; white solid; m.p.: 190 – 191 °C; **IR** (KBr) ν 3279, 3953, 2928, 2238, 1719, 1518, 958 cm^{-1} ; **^1H NMR** (400 MHz, DMSO) δ 14.13 (s, 1H), 8.38 (s, 1H), 8.02 – 7.89 (m, 2H), 7.73 (t, $J = 7.4$ Hz, 1H), 7.57 – 7.45 (m, 2H), 7.15 (d, $J = 16.3$ Hz, 1H). **^{13}C NMR** (100 MHz, DMSO) δ 147.71, 133.59, 131.18, 129.53, 128.86, 127.93, 124.54, 123.84, 123.09, 121.71, 121.22, 114.45. **HRMS** (ESI): m/z calculated for $\text{C}_{12}\text{H}_9\text{N}_4\text{O}_2^+$ [$\text{M} + \text{H}$] $^+$: 241.0720, found: 241.0725.



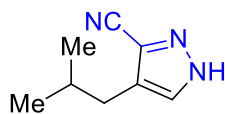
4-(Phenylethynyl)-1H-pyrazole-3-carbonitrile (2w): Method A: 70.5 mg, 73% yield; Method B: 53.0 mg, 55%; white solid; m.p.: 133 – 134 °C; **IR** (KBr) ν 3260, 2250, 1705, 1476, 751 cm^{-1} ; **¹H NMR** (400 MHz, DMSO) δ 14.33 (s, 1H), 8.43 (s, 1H), 7.56 – 7.50 (m, 2H), 7.47 – 7.37 (m, 3H). **¹³C NMR** (100 MHz, DMSO) δ 133.49, 131.35, 129.19, 128.86, 126.11, 121.67, 113.44, 107.19, 93.50, 77.67. **HRMS** (ESI): m/z calculated for $\text{C}_{12}\text{H}_8\text{N}_3^+$ [M + H]⁺: 194.0713, found: 194.0714.



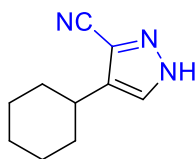
4-Phenethyl-1H-pyrazole-3-carbonitrile (2x): Method A: 81.0 mg, 82% yield; white solid; m.p.: 65 – 66 °C; **IR** (KBr) ν 3274, 2931, 2241, 1707, 1452, 1350, 748, 705 cm^{-1} ; **¹H NMR** (400 MHz, CDCl_3) δ 12.39 (s, 1H), 7.40 (s, 1H), 7.32 – 7.24 (m, 2H), 7.23 – 7.13 (m, 3H), 2.97 – 2.88 (m, 4H). **¹³C NMR** (100 MHz, CDCl_3) δ 140.34, 128.61, 128.52, 126.52, 126.46, 124.50, 113.72, 36.28, 25.36. **HRMS** (ESI): m/z calculated for $\text{C}_{12}\text{H}_{12}\text{N}_3^+$ [M + H]⁺: 198.1026, found: 198.1029.



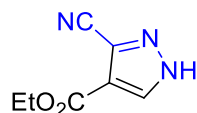
4-Butyl-1H-pyrazole-3-carbonitrile (2y): Method A: 44.7 mg; 60% yield; yellow oil; **IR** (KBr) ν 3273, 2946, 2242, 1707, 1463, 1351, 1137 cm^{-1} ; **¹H NMR** (400 MHz, CDCl_3) δ 12.59 (s, 1H), 7.56 (s, 1H), 2.70 – 2.54 (m, 2H), 1.60 (dt, $J = 15.3, 7.6$ Hz, 2H), 1.37 (dq, $J = 14.6, 7.3$ Hz, 2H), 0.93 (t, $J = 7.3$ Hz, 3H). **¹³C NMR** (100 MHz, CDCl_3) δ 128.35, 127.82, 124.50, 113.95, 32.36, 23.28, 22.26, 13.83. **HRMS** (ESI): m/z calculated for $\text{C}_8\text{H}_{12}\text{N}_3^+$ [M + H]⁺: 150.1026, found: 150.1026.



4-Isobutyl-1H-pyrazole-3-carbonitrile (2z): Method A: 55.0 mg, 74% yield; yellow oil; **IR** (KBr) ν 3187, 2959, 2241, 1705, 1465, 1142 cm^{-1} ; **¹H NMR** (400 MHz, CDCl_3) δ 12.74 (s, 1H), 7.56 (s, 1H), 2.49 (d, $J = 7.0$ Hz, 2H), 1.97 – 1.79 (m, 1H), 0.92 (d, $J = 6.6$ Hz, 6H). **¹³C NMR** (100 MHz, CDCl_3) δ 128.93, 126.36, 124.99, 114.02, 32.63, 29.52, 22.16. **HRMS** (ESI): m/z calculated for $\text{C}_8\text{H}_{12}\text{N}_3^+$ [M + H]⁺: 150.1026, found: 150.1024.

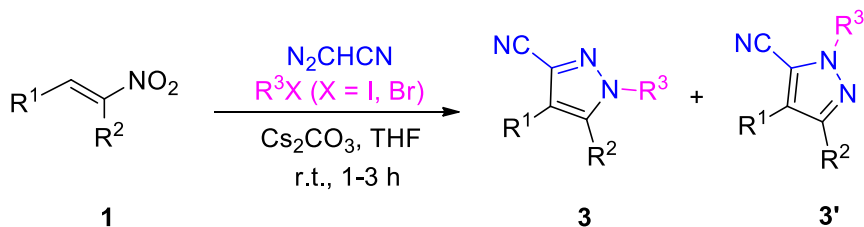


4-Cyclohexyl-1H-pyrazole-3-carbonitrile (2a'): Method A: 75.5 mg, 86% yield; white solid; m.p.: 91 – 92 °C; IR (KBr) ν 3271, 2928, 2856, 2240, 1706, 1450, 1348 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 12.72 (s, 1H), 7.53 (s, 1H), 2.73 – 2.55 (m, 1H), 2.02 – 1.93 (m, 2H), 1.86 – 1.68 (m, 3H), 1.45 – 1.29 (m, 4H), 1.27 – 1.21 (m, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 133.53, 126.94, 123.05, 114.24, 33.89, 33.82, 26.33, 25.80. HRMS (ESI): m/z calculated for $\text{C}_{10}\text{H}_{14}\text{N}_3^+$ $[\text{M} + \text{H}]^+$: 176.1182, found: 176.1185.

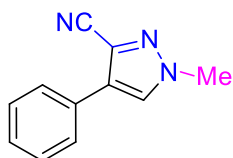


Ethyl 3-cyano-1H-pyrazole-4-carboxylate (2b'): Method A: 45.5 mg, 55% yield; white solid; m.p.: 140 – 141 °C; IR (KBr) ν 3254, 3152, 2982, 2247, 1708, 1090, 762 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, DMSO) δ 14.46 (s, 1H), 8.61 (s, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 1.28 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, DMSO) δ 160.43, 134.13, 124.78, 116.99, 113.22, 60.70, 14.04. HRMS (ESI): m/z calculated for $\text{C}_7\text{H}_7\text{N}_3\text{O}_2\text{Na}^+$ $[\text{M} + \text{Na}]^+$: 188.0430, found: 188.0428.

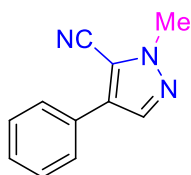
2.3 General procedure for three component reaction of nitroolefins **1**, N_2CHCN and alkyl halides.



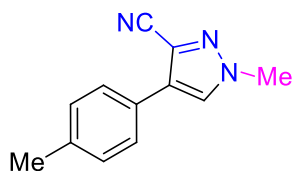
An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with nitroolefin **1** (1.0 mmol, 1.0 equiv), and Cs_2CO_3 (814.6 mg, 2.5 mmol, 2.5 equiv). Then THF (10 mL), N_2CHCN (134.1 mg, 2.0 mmol, 2.0 equiv) and alkyl halide (1.5 mmol, 1.5 equiv) were added successively. The resulting mixture was stirred at room temperature for a specific time until nitroolefins **1** disappeared. Then the insoluble solid was filtered, rinsed with ethyl acetate, and the filtrate was concentrated in reduced pressure. The residue was further purified by a silica gel column chromatography (PE/EA = 8/1 to PE/EA = 4/1) to yield the corresponding 3-cyanopyrazoles **3** and 5-cyanopyrazole **3'**.



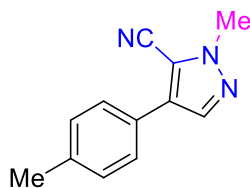
1-Methyl-4-phenyl-1H-pyrazole-3-carbonitrile (3a): 133.5 mg, 73% yield; colorless oil; **IR** (KBr) ν 3129, 2951, 2850, 2236, 1610, 1443, 1163, 1010, 760 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3) δ 7.62 (s, 1H), 7.59 (d, $J = 7.4$ Hz, 2H), 7.42 (t, $J = 7.5$ Hz, 2H), 7.34 (t, $J = 7.3$ Hz, 1H), 3.98 (s, 3H). **^{13}C NMR** (100 MHz, CDCl_3) δ 129.55, 129.24, 128.79, 128.28, 126.76, 121.99, 114.52, 40.25. **HRMS** (ESI): m/z calculated for $\text{C}_{11}\text{H}_{10}\text{N}_3^+$ $[\text{M} + \text{H}]^+$: 184.0869, found: 184.0865.



1-Methyl-4-phenyl-1H-pyrazole-5-carbonitrile (3a'): 33.0 mg, 18% yield; white solid; m.p.: 61.5 – 62.5 $^\circ\text{C}$; **IR** (KBr) ν 3054, 2853, 2229, 1555, 1449, 1391, 764, 694 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3) δ 7.69 (s, 1H), 7.56 (d, $J = 7.4$ Hz, 2H), 7.35 (t, $J = 7.5$ Hz, 2H), 7.28 (t, $J = 7.3$ Hz, 1H), 3.93 (s, 3H). **^{13}C NMR** (100 MHz, CDCl_3) δ 136.65, 129.25, 129.02, 128.84, 128.07, 126.04, 111.49, 111.18, 38.15. **HRMS** (ESI): m/z calculated for $\text{C}_{11}\text{H}_{10}\text{N}_3^+$ $[\text{M} + \text{H}]^+$: 184.0869, found: 184.0871.

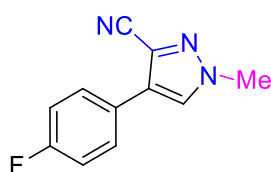


1-Methyl-4-(p-tolyl)-1H-pyrazole-3-carbonitrile (3b): 118.0 mg, 60% yield; white solid; m.p.: 128 – 129 $^\circ\text{C}$; **IR** (KBr) ν 3096, 3019, 2952, 2866, 2237, 1563, 1441, 1163, 1012, 809 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3) δ 7.59 (s, 1H), 7.47 (d, $J = 8.1$ Hz, 2H), 7.21 (d, $J = 7.9$ Hz, 2H), 3.94 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (100 MHz, CDCl_3) δ 138.04, 129.75, 128.58, 128.10, 126.52, 126.45, 121.49, 114.65, 40.06, 21.19. **HRMS** (ESI): m/z calculated for $\text{C}_{12}\text{H}_{12}\text{N}_3^+$ $[\text{M} + \text{H}]^+$: 198.1026, found: 198.1025.

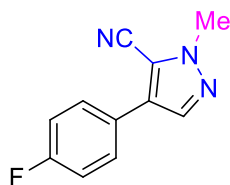


1-Methyl-4-(p-tolyl)-1H-pyrazole-5-carbonitrile (3b'): 37.5 mg, 19% yield; white solid; m.p.: 68

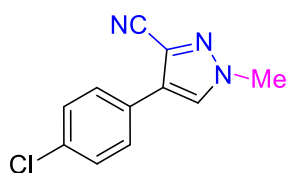
– 69 °C; **IR** (KBr) ν 3030, 2922, 2918, 2226, 1558, 1504, 1451, 964, 815, 516, 476 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3) δ 7.62 (s, 1H), 7.40 (d, $J = 8.1$ Hz, 2H), 7.11 (d, $J = 7.9$ Hz, 2H), 3.92 (s, 3H), 2.25 (s, 3H). **^{13}C NMR** (101 MHz, CDCl_3) δ 138.45, 136.95, 129.93, 129.86, 126.46, 126.35, 111.65, 111.61, 77.52, 77.20, 76.88, 38.50, 21.26. **HRMS** (ESI): m/z calculated for $\text{C}_{12}\text{H}_{12}\text{N}_3^+$ [$\text{M} + \text{H}$] $^+$: 198.1026, found: 198.1028.



4-(4-Fluorophenyl)-1-methyl-1H-pyrazole-3-carbonitrile (3c): 129.0 mg, 64% yield; white solid; m.p.: 143 – 144 °C; **IR** (KBr) ν 3126, 2961, 2847, 2235, 1614, 1556, 1400, 1228, 819 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3) δ 7.60 (s, 1H), 7.56 – 7.47 (m, 2H), 7.11 – 7.02 (m, 2H), 3.96 (s, 3H). **^{19}F NMR** (376 MHz, CDCl_3) δ -113.22 – -113.33 (m). **^{13}C NMR** (100 MHz, CDCl_3) δ 162.53 (q, $J = 246.5$ Hz), 128.78, 128.47 (q, $J = 8.2$ Hz), 127.19, 125.66 (q, $J = 3.3$ Hz), 121.66, 116.12 (q, $J = 21.6$ Hz), 114.41, 40.17. **HRMS** (ESI): m/z calculated for $\text{C}_{11}\text{H}_9\text{FN}_3^+$ [$\text{M} + \text{H}$] $^+$: 202.0775, found: 202.0777.

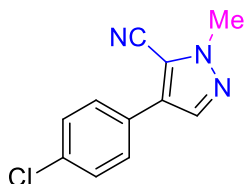


4-(4-Fluorophenyl)-1-methyl-1H-pyrazole-5-carbonitrile (3c'): 36.0 mg, 18% yield; white solid; m.p. 62 – 63°C; **IR** (KBr) ν 3119, 3066, 2948, 2856, 2229, 1558, 1503, 1233, 834, 756, 522 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3) δ 7.70 (s, 1H), 7.56 (dd, $J = 7.8, 5.5$ Hz, 2H), 7.09 (t, $J = 8.5$ Hz, 2H), 4.04 (s, 3H). **^{19}F NMR** (376 MHz, CDCl_3) δ -112.44 – -112.74 (m). **^{13}C NMR** (100 MHz, CDCl_3) δ 162.69 (d, $J = 248.6$ Hz), 136.97, 128.92, 128.30 (d, $J = 8.2$ Hz), 125.55 (d, $J = 3.4$ Hz), 116.25 (d, $J = 21.8$ Hz), 111.87, 111.35, 38.61. **HRMS** (ESI): m/z calculated for $\text{C}_{11}\text{H}_9\text{FN}_3^+$ [$\text{M} + \text{H}$] $^+$: 202.0775, found: 202.0773.

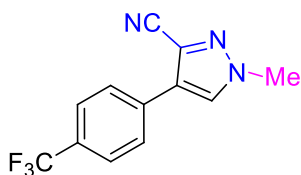


4-(4-Chlorophenyl)-1-methyl-1H-pyrazole-3-carbonitrile (3d): 135.0 mg, 62% yield; white

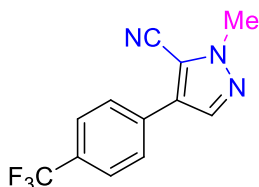
solid; m.p.: 100 – 101 °C; **IR** (KBr) ν 3127, 2948, 2237, 1552, 1487, 1163, 1095, 1006, 820 cm^{-1} ;
 ^1H NMR (400 MHz, CDCl_3) δ 7.65 (s, 1H), 7.53 – 7.47 (m, 2H), 7.39 – 7.32 (m, 2H), 3.99 (s, 3H).
 ^{13}C NMR (100 MHz, CDCl_3) δ 133.98, 129.29, 128.90, 127.94, 127.85, 126.88, 121.61, 114.34,
40.24. **HRMS** (ESI): m/z calculated for $\text{C}_{11}\text{H}_9\text{N}_3\text{Cl}^+$ $[\text{M} + \text{H}]^+$: 218.0480, found: 218.0483.



4-(4-Chlorophenyl)-1-methyl-1H-pyrazole-5-carbonitrile (3d'): 37.0 mg, 17% yield; white solid;
m.p. 56 – 57°C; **IR** (KBr) ν 3116, 3054, 2920, 2851, 2230, 1550, 1487, 1094, 965, 828, 730, 479
 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3) δ 7.75 (s, 1H), 7.59 – 7.52 (m, 2H), 7.43 – 7.37 (m, 2H), 4.08 (s,
3H). **^{13}C NMR** (100 MHz, CDCl_3) δ 137.18, 134.55, 129.56, 128.85, 127.96, 127.86, 112.14,
111.35, 38.80. **HRMS** (ESI): m/z calculated for $\text{C}_{11}\text{H}_9\text{N}_3\text{Cl}^+$ $[\text{M} + \text{H}]^+$: 218.0480, found: 218.0485.

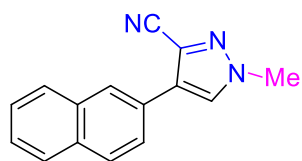


1-Methyl-4-(4-(trifluoromethyl)phenyl)-1H-pyrazole-3-carbonitrile (3e): 183.5 mg, 73% yield;
white solid; m.p.: 109 – 110°C; **IR** (KBr) ν 3133, 2237, 1321, 1107, 828 cm^{-1} ; **^1H NMR** (400 MHz,
 CDCl_3) δ 7.73 – 7.63 (m, 5H), 4.02 (s, 3H). **^{19}F NMR** (376 MHz, CDCl_3) δ -62.72 (s). **^{13}C NMR**
(100 MHz, CDCl_3) δ 133.13, 130.17 (q, $J = 32.5$ Hz), 129.33, 126.96, 126.71, 126.25 (q, $J = 3.8$
Hz), 124.08 (q, $J = 270.4$ Hz), 122.21, 114.17, 40.40. **HRMS** (ESI): m/z calculated for $\text{C}_{12}\text{H}_9\text{F}_3\text{N}_3^+$
 $[\text{M} + \text{H}]^+$: 252.0743, found: 252.0743.

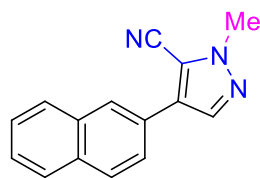


1-Methyl-4-(4-(trifluoromethyl)phenyl)-1H-pyrazole-5-carbonitrile (3e'): 50.0 mg, 20% yield;
white solid; m.p.: 98 – 99°C; **IR** (KBr) ν 3118, 3054, 2230, 1620, 1330, 1161, 1111, 1071, 841, 597,
478 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3) δ 7.81 (s, 1H), 7.69 (dd, $J = 25.4, 8.2$ Hz, 4H), 4.08 (s, 3H).
 ^{19}F NMR (376 MHz, CDCl_3) δ -62.77 (s). **^{13}C NMR** (100 MHz, CDCl_3) δ 137.15, 132.87, 129.92
(q, $J = 32.5$ Hz), 127.96, 126.50, 126.06 (q, $J = 3.8$ Hz), 123.91 (q, $J = 270.4$ Hz), 112.36, 110.96,

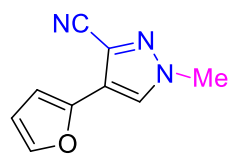
38.55. **HRMS** (ESI): m/z calculated for $C_{12}H_9F_3N_3^+$ $[M + H]^+$: 252.0743, found: 252.0745.



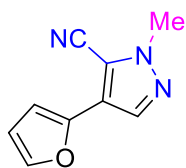
1-Methyl-4-(naphthalen-2-yl)-1H-pyrazole-3-carbonitrile (3f): 147.0 mg, 63% yield; white solid; m.p.: 112 – 123 °C; **IR** (KBr) ν 3129, 3056, 2949, 2235, 1609, 1403, 1161, 814, 751 cm^{-1} ; **1H NMR** (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.84 – 7.67 (m, 3H), 7.58 – 7.40 (m, 4H), 3.80 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 133.36, 132.70, 129.00, 128.85, 128.07, 127.86, 127.69, 126.71, 126.68, 126.45, 125.25, 124.47, 121.63, 114.72, 40.10. **HRMS** (ESI): m/z calculated for $C_{15}H_{12}N_3^+$ $[M + H]^+$: 234.1026, found: 234.1025.



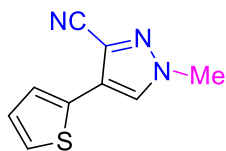
1-Methyl-4-(naphthalen-2-yl)-1H-pyrazole-5-carbonitrile (3f'): 46.5 mg, 20% yield; white solid; m.p.: 108 – 109°C; **IR** (KBr) ν 3055, 2941, 2851, 2378, 2229, 1603, 1439, 1393, 853, 817, 751, 474 cm^{-1} ; **1H NMR** (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.74 – 7.66 (m, 4H), 7.60 – 7.54 (m, 1H), 7.44 – 7.34 (m, 2H), 3.84 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.92, 133.15, 132.68, 129.26, 128.68, 127.94, 127.49, 126.45, 126.37, 126.31, 124.98, 123.80, 111.61, 111.39, 38.19. **HRMS** (ESI): m/z calculated for $C_{15}H_{12}N_3^+$ $[M + H]^+$: 234.1026, found: 234.1028.



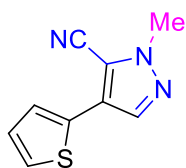
4-(Furan-2-yl)-1-methyl-1H-pyrazole-3-carbonitrile (3g): 123.0 mg, 71% yield; white solid; m.p.: 69 – 70°C; **IR** (KBr) ν 3129, 2926, 2855, 2239, 1535, 1156, 1010, 807, 743 cm^{-1} ; **1H NMR** (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.40 (s, 1H), 6.73 (d, $J = 3.3$ Hz, 1H), 6.44 (dd, $J = 3.0, 1.7$ Hz, 1H), 3.95 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.50, 142.03, 127.49, 120.23, 119.60, 113.86, 111.64, 106.79, 40.23. **HRMS** (ESI): m/z calculated for $C_9H_8N_3O^+$ $[M + H]^+$: 174.0662, found: 174.0665.



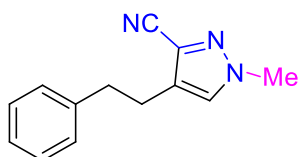
4-(Furan-2-yl)-1-methyl-1H-pyrazole-5-carbonitrile (3g'): 36.5 mg, 21% yield; white solid; m.p.: 65 – 66°C; **IR** (KBr) ν 3120, 2947, 2230, 1631, 1464, 1399, 1343, 989, 891, 756, 593 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3) δ 7.63 (s, 1H), 7.35 (d, $J = 1.1$ Hz, 1H), 6.58 (d, $J = 3.3$ Hz, 1H), 6.36 (dd, $J = 3.2, 1.8$ Hz, 1H), 3.92 (s, 3H). **^{13}C NMR** (100 MHz, CDCl_3) δ 144.42, 142.40, 135.47, 121.17, 111.62, 110.70, 110.39, 107.22, 38.44. **HRMS** (ESI): m/z calculated for $\text{C}_9\text{H}_8\text{N}_3\text{O}^+$ $[\text{M} + \text{H}]^+$: 174.0662, found: 174.0663.



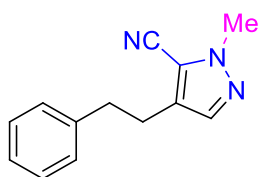
1-Methyl-4-(thiophen-2-yl)-1H-pyrazole-3-carbonitrile (3h): 126.5 mg, 67% yield; white solid; m.p.: 48 – 49 °C; **IR** (KBr) ν 3117, 2944, 2237, 1720, 1453, 1405, 1350, 1156, 815, 709 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3) δ 7.58 (s, 1H), 7.32 (dd, $J = 3.6, 1.0$ Hz, 1H), 7.24 (dd, $J = 5.1, 1.0$ Hz, 1H), 7.02 (dd, $J = 5.1, 3.6$ Hz, 1H), 3.88 (s, 3H). **^{13}C NMR** (100 MHz, CDCl_3) δ 130.47, 128.32, 127.59, 124.73, 124.44, 121.47, 120.45, 113.96, 39.70. **HRMS** (ESI): m/z calculated for $\text{C}_9\text{H}_8\text{N}_3\text{S}^+$ $[\text{M} + \text{H}]^+$: 190.0433, found: 190.0434.



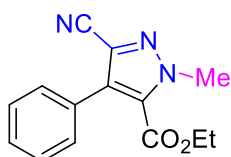
1-Methyl-4-(thiophen-2-yl)-1H-pyrazole-5-carbonitrile (3h'): 36.0 mg, 19% yield; white solid; m.p.: 73 – 74 °C; **IR** (KBr) ν 3106, 2942, 2856, 2227, 1436, 1392, 952, 837, 707, 468 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3) δ 7.55 (s, 1H), 7.24 (dd, $J = 3.6, 0.9$ Hz, 1H), 7.17 (dd, $J = 5.1, 0.9$ Hz, 1H), 6.94 (dd, $J = 5.1, 3.7$ Hz, 1H), 3.89 (s, 3H). **^{13}C NMR** (100 MHz, CDCl_3) δ 136.58, 130.85, 127.91, 125.43, 124.96, 123.97, 111.21, 110.92, 38.47. **HRMS** (ESI): m/z calculated for $\text{C}_9\text{H}_8\text{N}_3\text{S}^+$ $[\text{M} + \text{H}]^+$: 190.0433, found: 190.0437.



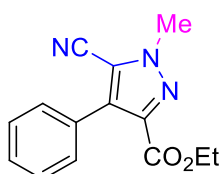
1-Methyl-4-phenethyl-1H-pyrazole-3-carbonitrile (3i): 113.5 mg, 54% yield; colorless oil; **IR** (KBr) ν 3130, 3027, 2935, 2860, 2234, 1614, 1450, 1400, 747, 699 cm^{-1} ; **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.29 – 7.24 (m, 2H), 7.21 – 7.13 (m, 3H), 7.08 (s, 1H), 3.83 (s, 3H), 2.91 – 2.82 (m, 4H). **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 140.46, 129.71, 128.45, 128.41, 127.22, 126.28, 123.97, 113.85, 39.82, 36.21, 25.35. **HRMS** (ESI): m/z calculated for $\text{C}_{13}\text{H}_{14}\text{N}_3^+$ $[\text{M} + \text{H}]^+$: 212.1182, found: 212.1182.



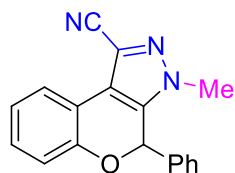
1-Methyl-4-phenethyl-1H-pyrazole-5-carbonitrile (3i'): 27.5 mg, 13% yield; colorless liquid; **IR** (KBr) ν 3062, 3028, 2938, 2861, 2230, 1726, 1600, 1493, 1449, 1396, 1314, 1006, 850, 745, 701, 493 cm^{-1} ; **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.26 – 7.20 (m, 3H), 7.18 – 7.10 (m, 3H), 3.85 (s, 3H), 2.90 – 2.80 (m, 4H). **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 140.16, 138.35, 129.34, 128.27, 128.21, 126.11, 113.73, 110.41, 38.04, 35.96, 25.49. **HRMS** (ESI): m/z calculated for $\text{C}_{13}\text{H}_{14}\text{N}_3^+$ $[\text{M} + \text{H}]^+$: 212.1182, found: 212.1183.



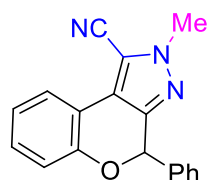
Ethyl 3-cyano-1-methyl-4-phenyl-1H-pyrazole-5-carboxylate (3j): 79.1 mg, 31% yield; light yellow solid; m.p.: 101 – 102 $^{\circ}\text{C}$; **IR** (KBr) ν 3060, 2986, 2944, 2235, 1727, 1461, 1292, 1028, 699, 646 cm^{-1} ; **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.50 – 7.47 (m, 2H), 7.46 – 7.42 (m, 3H), 4.34 (q, $J = 7.1$ Hz, 2H), 4.17 (s, 3H), 1.28 (t, $J = 7.1$ Hz, 3H). **$^{13}\text{C NMR}$** (101 MHz, CDCl_3) δ 160.97, 140.11, 133.22, 129.69, 129.23, 128.50, 128.31, 116.50, 110.13, 61.68, 39.56, 14.23. **HRMS** (ESI): m/z calculated for $\text{C}_{14}\text{H}_{14}\text{N}_3\text{O}_2^+$ $[\text{M} + \text{H}]^+$: 256.1081, found: 256.1083.



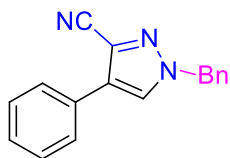
Ethyl 5-cyano-1-methyl-4-phenyl-1H-pyrazole-3-carboxylate (3j'): 122.5 mg, 48% yield; yellow solid; m.p.: 40 – 41 °C; **IR** (KBr) ν 3062, 2986, 2907, 2333, 2241, 1724, 1443, 1294, 1213, 1112, 761, 702, 490 cm^{-1} ; **¹H NMR** (400 MHz, CDCl_3) δ 7.43 – 7.37 (m, 5H), 4.23 (s, 3H), 4.23 – 4.18 (q, $J = 7.1$ Hz, 2H), 1.10 (t, $J = 7.1$ Hz, 3H). **¹³C NMR** (101 MHz, CDCl_3) δ 159.05, 132.06, 130.70, 129.74, 129.09, 128.80, 128.22, 123.88, 113.10, 61.85, 41.50, 13.66. **HRMS** (ESI): m/z calculated for $\text{C}_{14}\text{H}_{14}\text{N}_3\text{O}_2^+$ $[\text{M} + \text{H}]^+$: 256.1081, found: 256.1086.



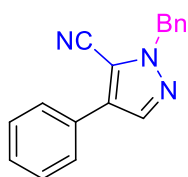
3-Methyl-4-phenyl-3,4-dihydrochromeno[3,4-c]pyrazole-1-carbonitrile (3k): 137.9 mg, 48% yield; yellow solid; m.p.: 112 – 113 °C; **IR** (KBr) ν 3062, 3039, 2946, 2359, 2237, 1659, 1446, 1301, 1210, 1018, 978, 757, 700, 459 cm^{-1} ; **¹H NMR** (400 MHz, CDCl_3) δ 7.80 (dd, $J = 7.6, 1.5$ Hz, 1H), 7.36 – 7.32 (m, 3H), 7.25 (dt, $J = 7.6, 3.9$ Hz, 2H), 7.12 (td, $J = 8.1, 1.6$ Hz, 1H), 6.99 (td, $J = 7.5, 1.1$ Hz, 1H), 6.85 (dd, $J = 8.1, 0.9$ Hz, 1H), 6.38 (s, 1H), 3.52 (s, 3H). **¹³C NMR** (100 MHz, CDCl_3) δ 149.95, 136.64, 136.43, 129.93, 129.37, 129.30, 127.64, 122.65, 122.43, 117.92, 117.77, 117.30, 115.92, 114.15, 74.54, 37.90. **HRMS** (ESI): m/z calculated for $\text{C}_{18}\text{H}_{14}\text{N}_3\text{O}^+$ $[\text{M} + \text{H}]^+$: 288.1131, found: 288.1134.



2-Methyl-4-phenyl-2,4-dihydrochromeno[3,4-c]pyrazole-1-carbonitrile (3k'): 89.1 mg, 31% yield; yellow solid; m.p.: 124 – 125 °C; **IR** (KBr) ν 3062, 3038, 2941, 2864, 2229, 1612, 1446, 1208, 1035, 975, 751, 699, 459 cm^{-1} ; **¹H NMR** (400 MHz, CDCl_3) δ 7.71 (d, $J = 7.5$ Hz, 1H), 7.43 – 7.41 (m, 2H), 7.39 – 7.33 (m, 3H), 7.25 – 7.21 (m, 1H), 7.04 (t, $J = 7.7$ Hz, 2H), 6.37 (s, 1H), 4.02 (s, 3H). **¹³C NMR** (100 MHz, CDCl_3) δ 152.27, 146.84, 138.54, 130.29, 128.98, 128.84, 127.29, 123.72, 122.62, 119.58, 118.01, 115.70, 111.13, 109.24, 75.87, 38.64. **HRMS** (ESI): m/z calculated for $\text{C}_{18}\text{H}_{14}\text{N}_3\text{O}^+$ $[\text{M} + \text{H}]^+$: 288.1131, found: 288.1139.

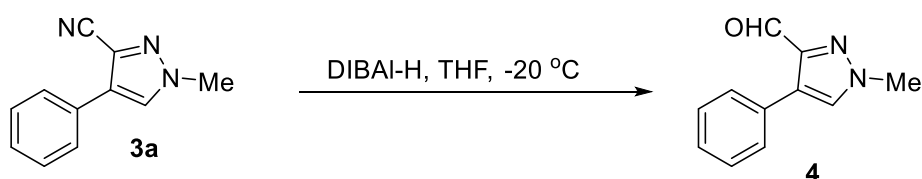


1-Benzyl-4-phenyl-1H-pyrazole-3-carbonitrile (3l): 173.5 mg, 67% yield; white solid; m.p.: 56 – 57 °C; **IR** (KBr) ν 3126, 3039, 2947, 2236, 1607, 1426, 1346, 1155, 1011, 749, 696 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3) δ 7.59 (s, 1H), 7.53 (d, $J = 7.3$ Hz, 2H), 7.35 – 7.21 (m, 8H), 5.25 (s, 2H). **^{13}C NMR** (100 MHz, CDCl_3) δ 134.53, 129.25, 128.95, 128.94, 128.65, 128.02, 128.00, 127.97, 127.92, 126.44, 121.68, 114.58, 57.09. **HRMS** (ESI): m/z calculated for $\text{C}_{17}\text{H}_{14}\text{N}_3^+$ [$\text{M} + \text{H}$] $^+$: 260.1182, found: 260.1180.

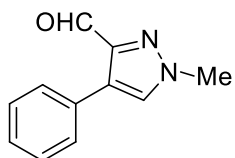


1-Benzyl-4-phenyl-1H-pyrazole-5-carbonitrile (3l'): 26.0 mg, 10% yield; white solid; m.p.: 67 – 68 °C; **IR** (KBr) ν 3037, 2945, 2357, 2228, 1604, 1552, 1362, 765, 734, 469 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3) δ 7.76 (s, 1H), 7.65 – 7.53 (m, 2H), 7.37 – 7.23 (m, 8H), 5.39 (s, 2H). **^{13}C NMR** (100 MHz, CDCl_3) δ 137.44, 134.84, 130.10, 129.15, 129.07, 128.90, 128.56, 128.42, 128.00, 126.40, 111.53, 111.09, 55.58. **HRMS** (ESI): m/z calculated for $\text{C}_{17}\text{H}_{14}\text{N}_3^+$ [$\text{M} + \text{H}$] $^+$: 260.1182, found: 260.1184.

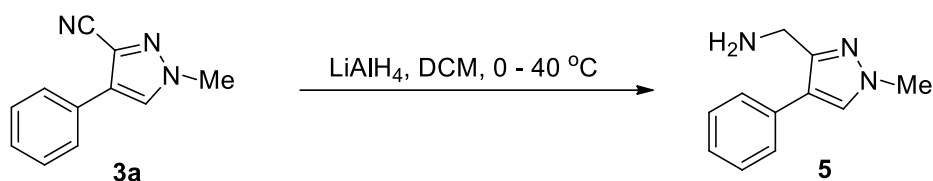
2.4 General procedure for transformation of 4a.



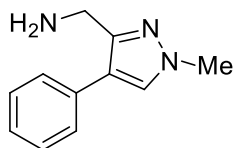
To a well-stirred solution of **4a** (0.5 mmol) in dry THF (5 mL) at -78 °C was added DIBAL-H (1.0 mL, 1.0 M in toluene) dropwise under argon atmosphere. The reaction was allowed to warm to -20 °C and stirred at the same temperature for 2 h until the starting material disappeared. Then the reaction was quenched with 5% HCl, and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over MgSO_4 , and concentrated under vacuo. The residue was further purified by a silica gel column chromatography (PE/EA = 5/1) to yield the desired product.



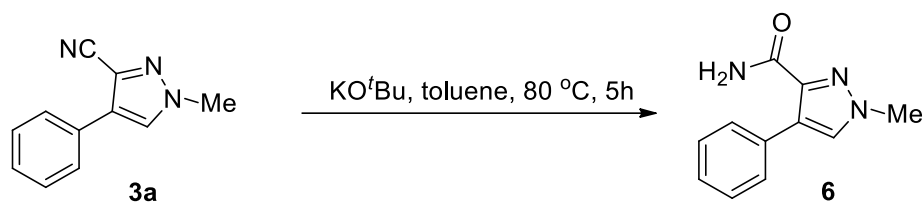
1-Methyl-4-phenyl-1H-pyrazole-3-carbaldehyde (4): 56.0 mg, 60% yield; white solid; m.p.: 83 – 84 °C; **IR** (KBr) ν 3083, 2945, 2825, 2767, 1693, 1452, 1331, 1172, 842, 781, 698 cm^{-1} ; **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 10.00 (s, 1H), 7.54 – 7.48 (m, 2H), 7.44 (s, 1H), 7.36 – 7.29 (m, 2H), 7.28 – 7.22 (m, 1H), 3.85 (s, 3H). **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 185.96, 146.03, 130.90, 130.42, 128.39, 128.10, 127.34, 125.41, 39.37. **HRMS** (ESI): m/z calculated for $\text{C}_{11}\text{H}_{11}\text{N}_2\text{O}^+$ $[\text{M} + \text{H}]^+$: 187.0866, found: 187.0869.



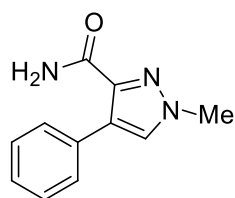
A 25 mL two-necked, round-bottomed flask fitted with a condenser was charged with lithium aluminum hydride, and the flask was thoroughly purged with a steady stream of Ar. After 5 min, DCM (6 mL) was added. The mixture was cooled to 0 °C with an ice bath before dropwise addition of a solution of **3a** (0.5 mmol, 91.5 mg) in DCM (1 mL) via a syringe over 10 min. After vigorous H_2 gas evolution ceased, the resulting mixture was allowed to reflux at 40 °C for 3h. Then the solution was cooled to room temperature, diluted with 6 mL DCM, and quenched by water. The precipitate was filtered through celite, and the filtrate was concentrated to give product **5**.



(1-Methyl-4-phenyl-1H-pyrazol-3-yl)methanamine (5): 81.5 mg, 87% yield; light yellow oil; **IR** (KBr) ν 3422, 3055, 2929, 1603, 1560, 1447, 1162, 1014, 763, 699 cm^{-1} ; **$^1\text{H NMR}$** (600 MHz, CDCl_3) δ 7.37 – 7.33 (m, 5H), 7.22 (t, $J = 6.7$ Hz, 1H), 3.95 (s, 2H), 3.84 (s, 3H), 1.56 (s, 2H). **$^{13}\text{C NMR}$** (151 MHz, CDCl_3) δ 150.65, 133.06, 129.11, 128.70, 127.57, 126.36, 120.39, 38.85, 38.75. **HRMS** (ESI): m/z calculated for $\text{C}_{11}\text{H}_{11}\text{N}_2^+$ $[\text{M} - \text{NH}_3 + \text{H}]^+$: 171.0919, found: 171.0917.



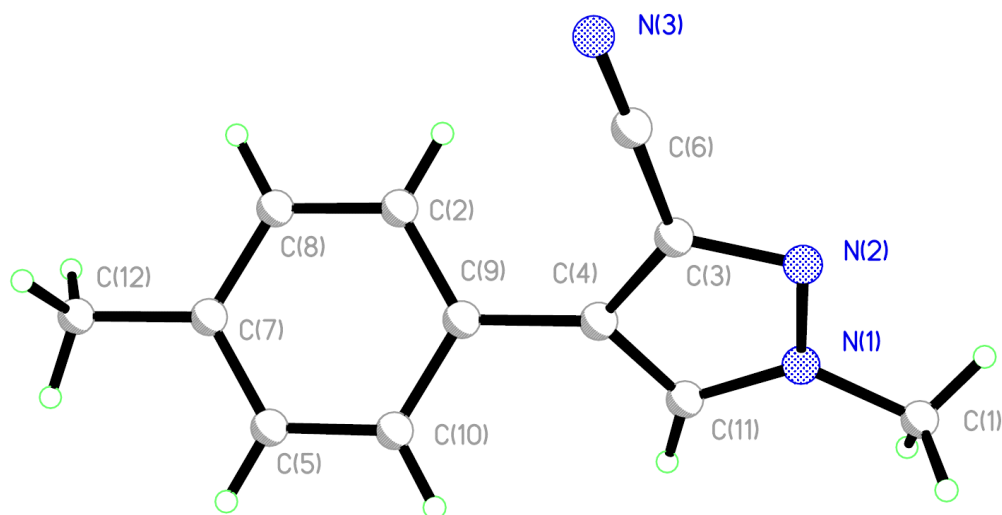
A flame-dried flask equipped with a magnetic stir bar was charged with **3a** (0.25 mmol, 45.8 mg), KO^tBu (0.75 mmol, 3 equiv, 84.2 mg) and dry toluene (3 mL). The reaction mixture was stirred at 80 °C for 5 h under nitrogen atmosphere, and progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was treated with water. The insoluble solid amide was filtered, washed with water, and dried under vacuum to provide the corresponding amide **6**.



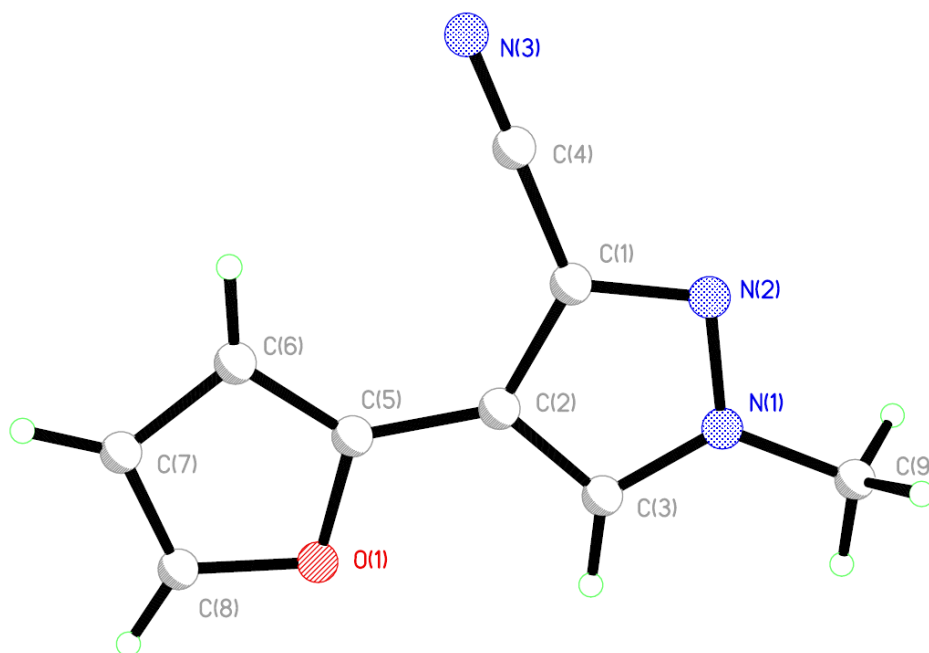
1-Methyl-4-phenyl-1H-pyrazole-3-carboxamide (6): 49.8 mg, 99% yield; light yellow solid; m.p.: 202 – 203 °C; **IR** (KBr) ν 3462, 3344, 3293, 2922, 2854, 1693, 1469, 1348, 1024, 842, 762, 696 cm^{-1} ; **¹H NMR** (400 MHz, DMSO) δ 7.97 (s, 1H), 7.55 (d, $J = 7.3$ Hz, 2H), 7.49 (s, 1H), 7.33 (t, $J = 7.5$ Hz, 2H), 7.24 (t, $J = 7.2$ Hz, 2H), 3.89 (s, 3H). **¹³C NMR** (101 MHz, DMSO) δ 164.34, 142.14, 132.26, 131.78, 128.54, 127.90, 126.45, 122.53, 38.91. **HRMS** (ESI): m/z calculated for $\text{C}_{11}\text{H}_{11}\text{N}_3\text{NaO}^+$ $[\text{M} + \text{Na}]^+$: 224.0794, found: 224.0797.

3. X-Ray Crystallographic data

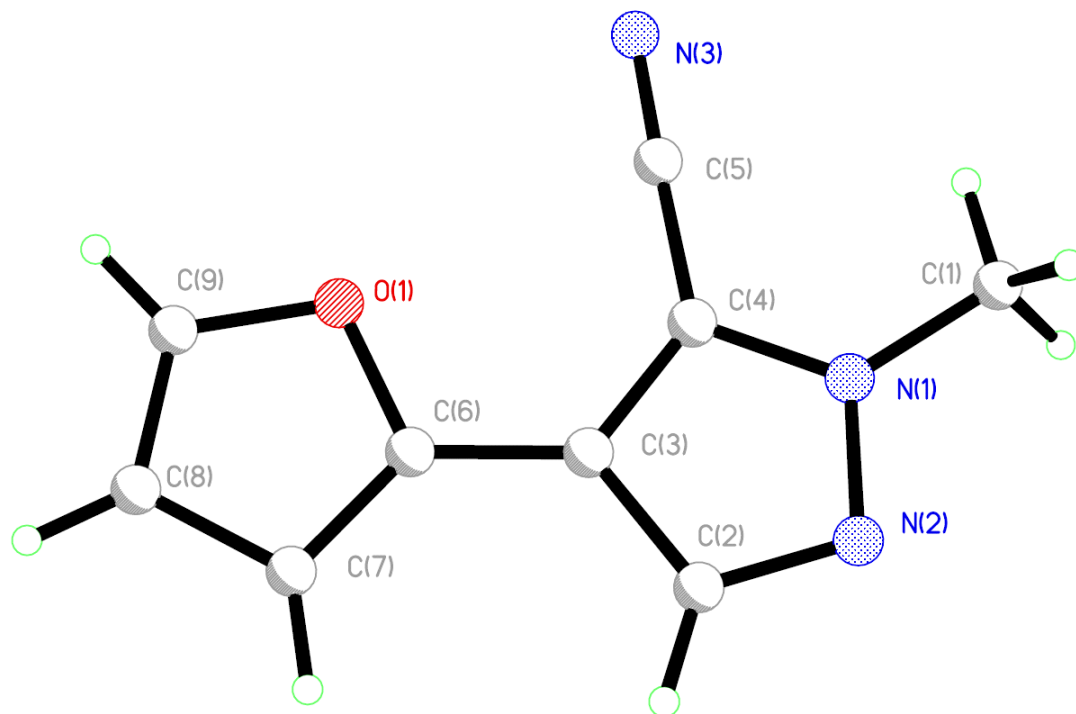
The X-ray crystallographic structure for **3b** (ORTEP representation with 50% probability thermal ellipsoids) has been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 1523275. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.



The X-ray crystallographic structure for **3g** (ORTEP representation with 50% probability thermal ellipsoids) has been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 1813397. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

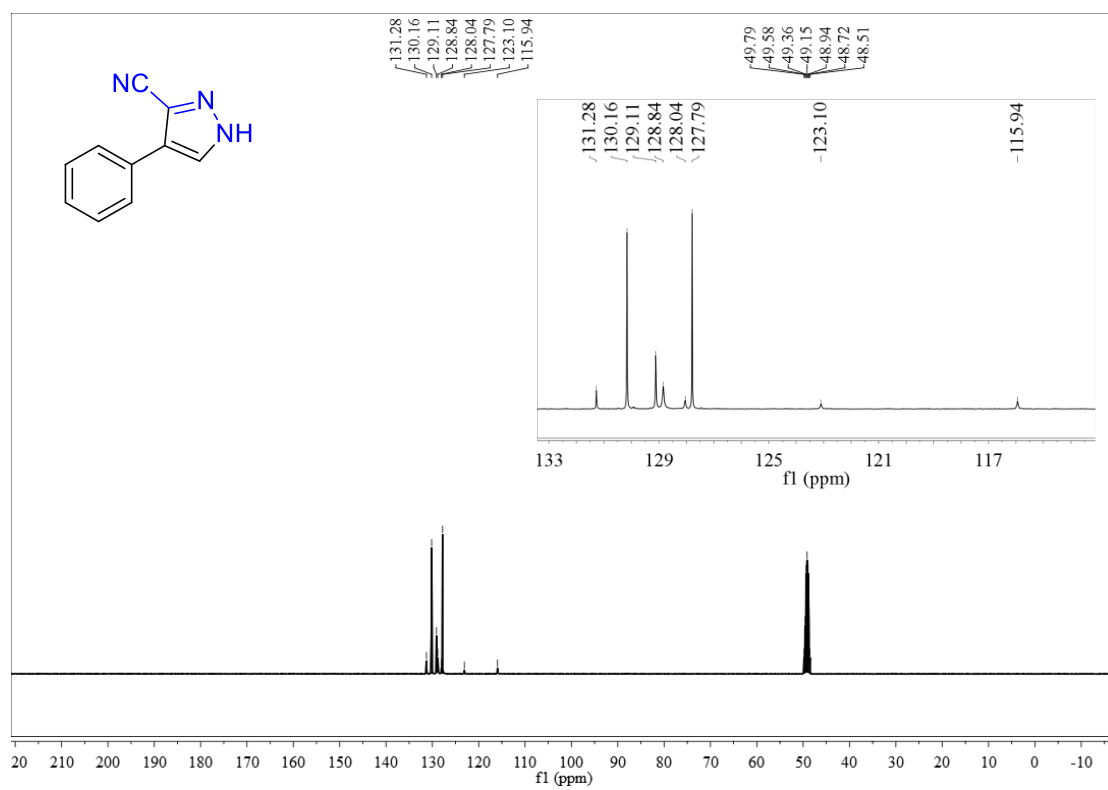
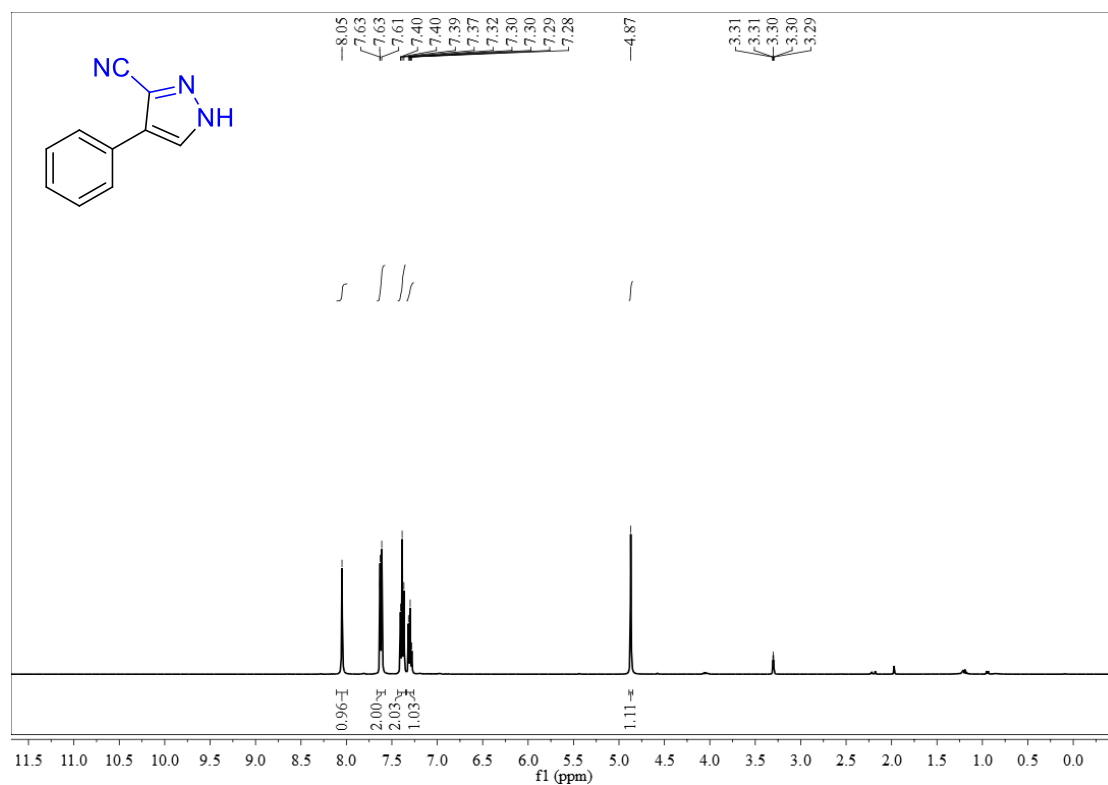


The X-ray crystallographic structure for **3g'** (ORTEP representation with 50% probability thermal ellipsoids) has been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 1813396. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

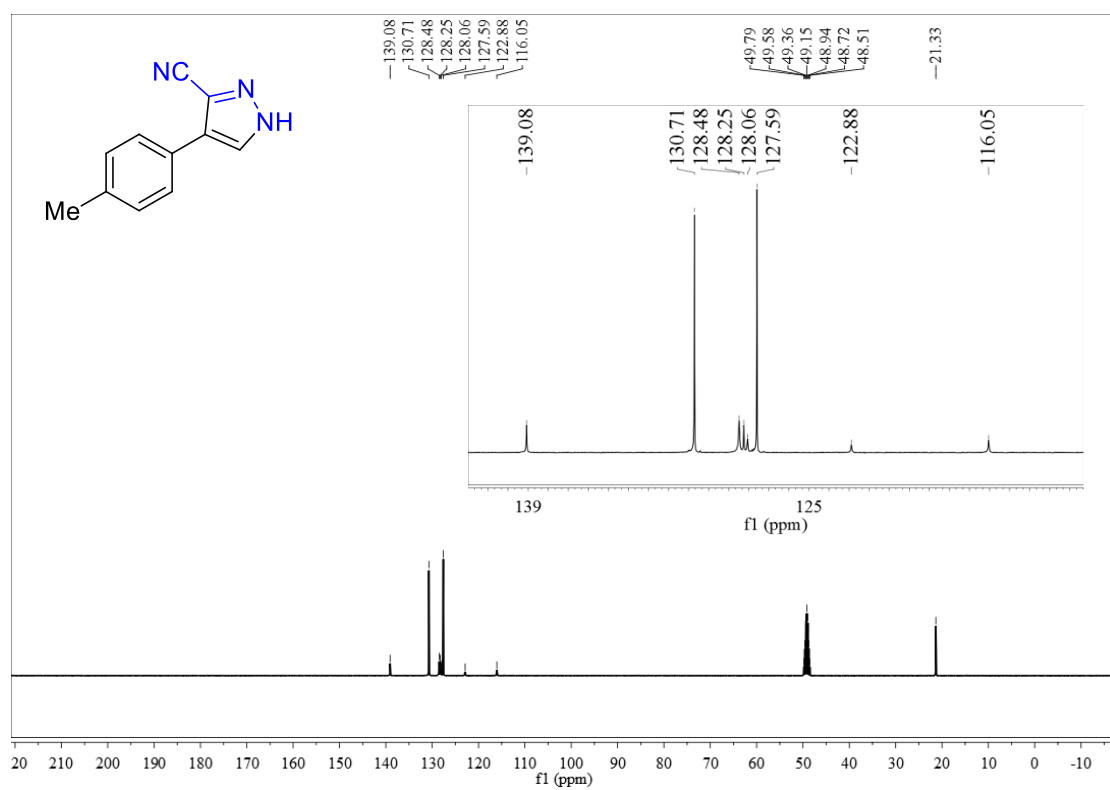
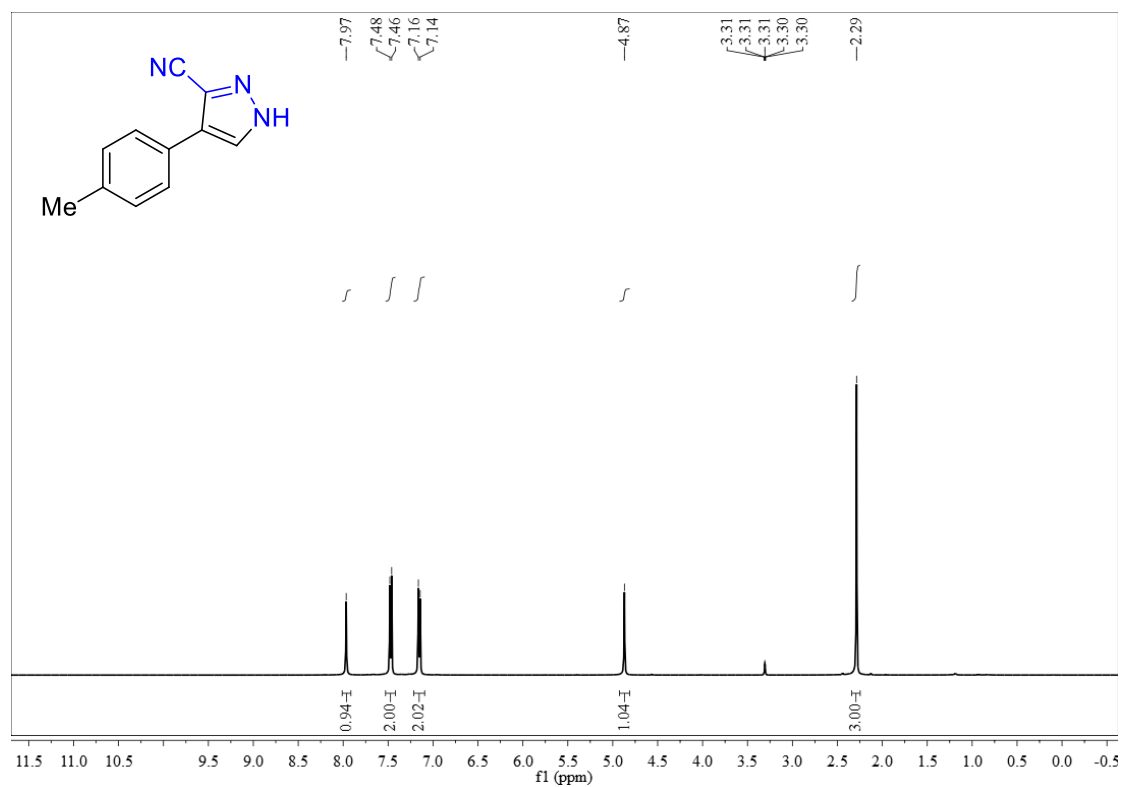


4. NMR Spectra

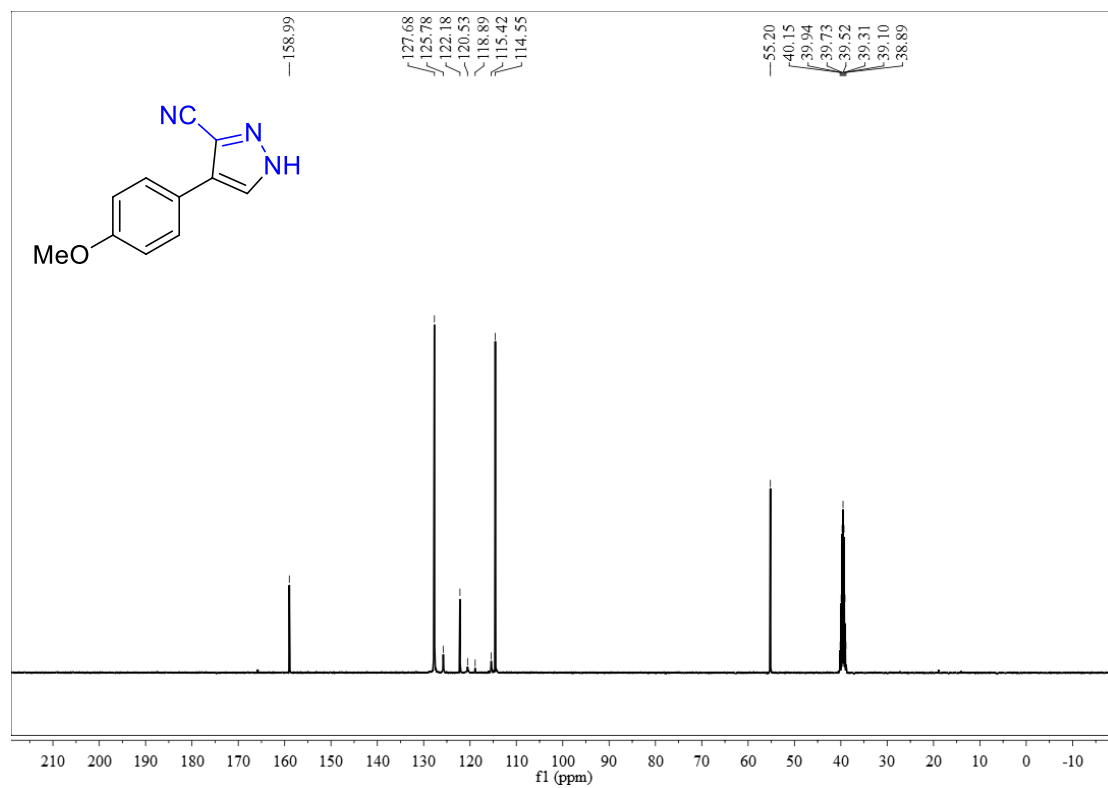
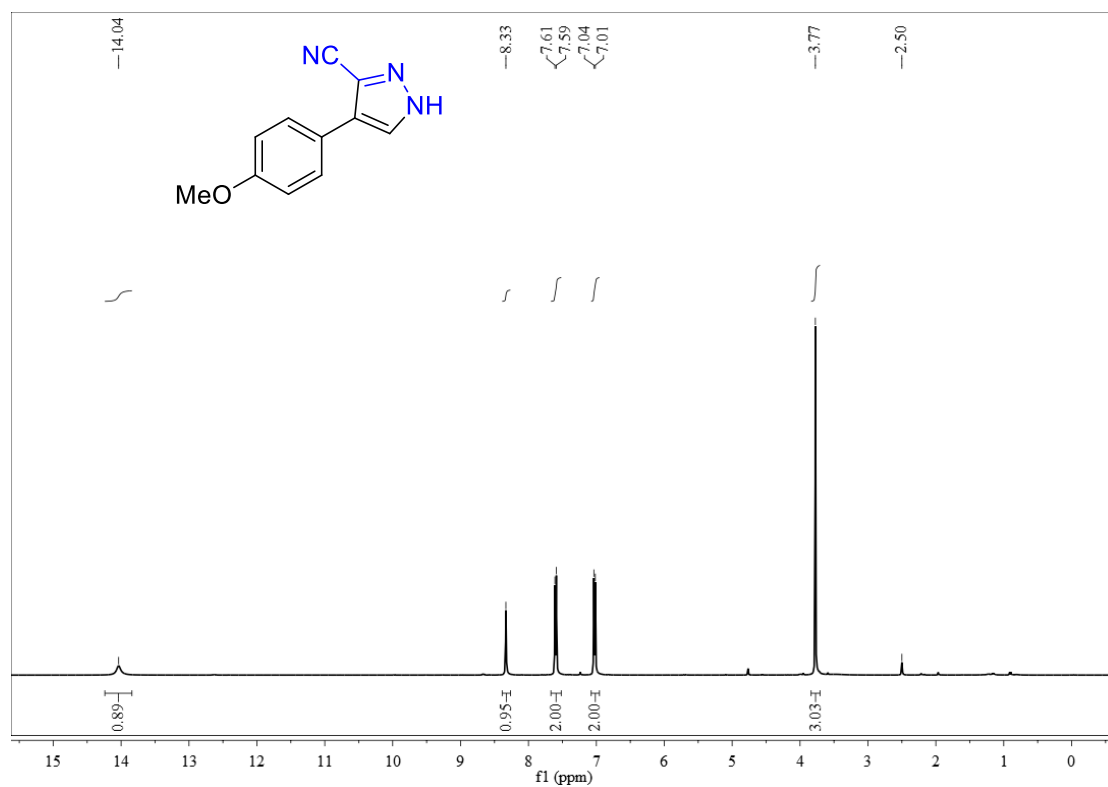
4-Phenyl-1H-pyrazole-3-carbonitrile (2a)



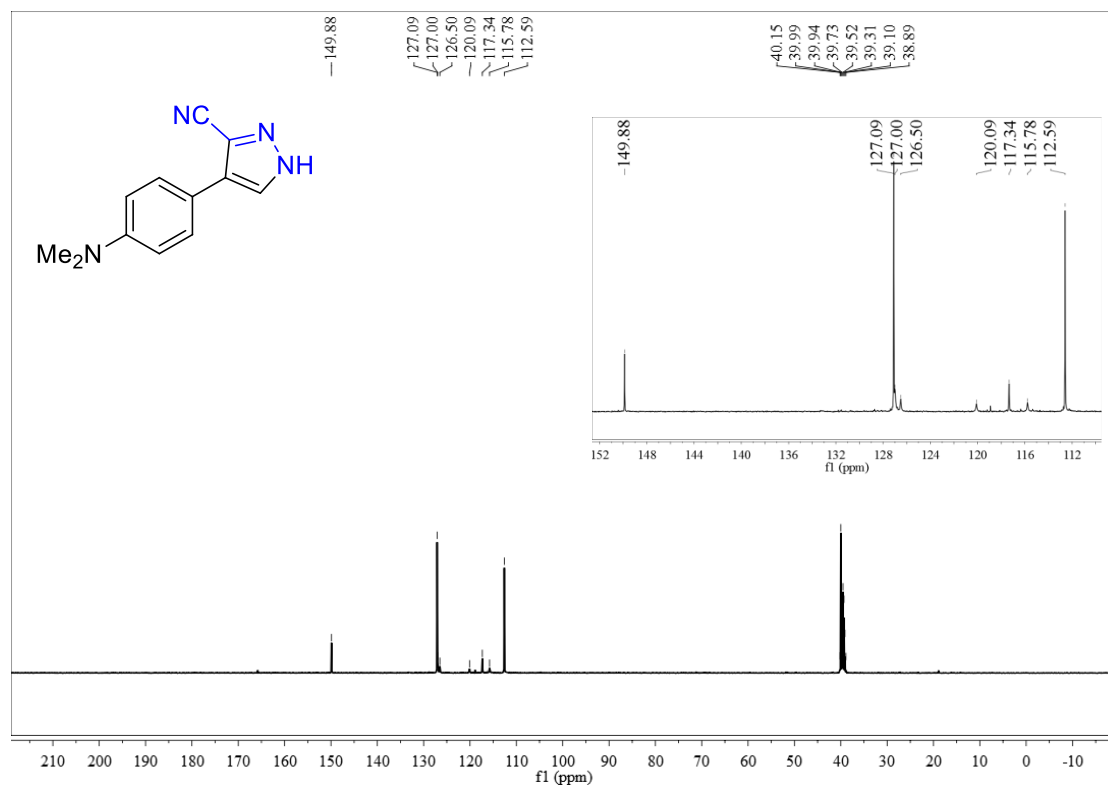
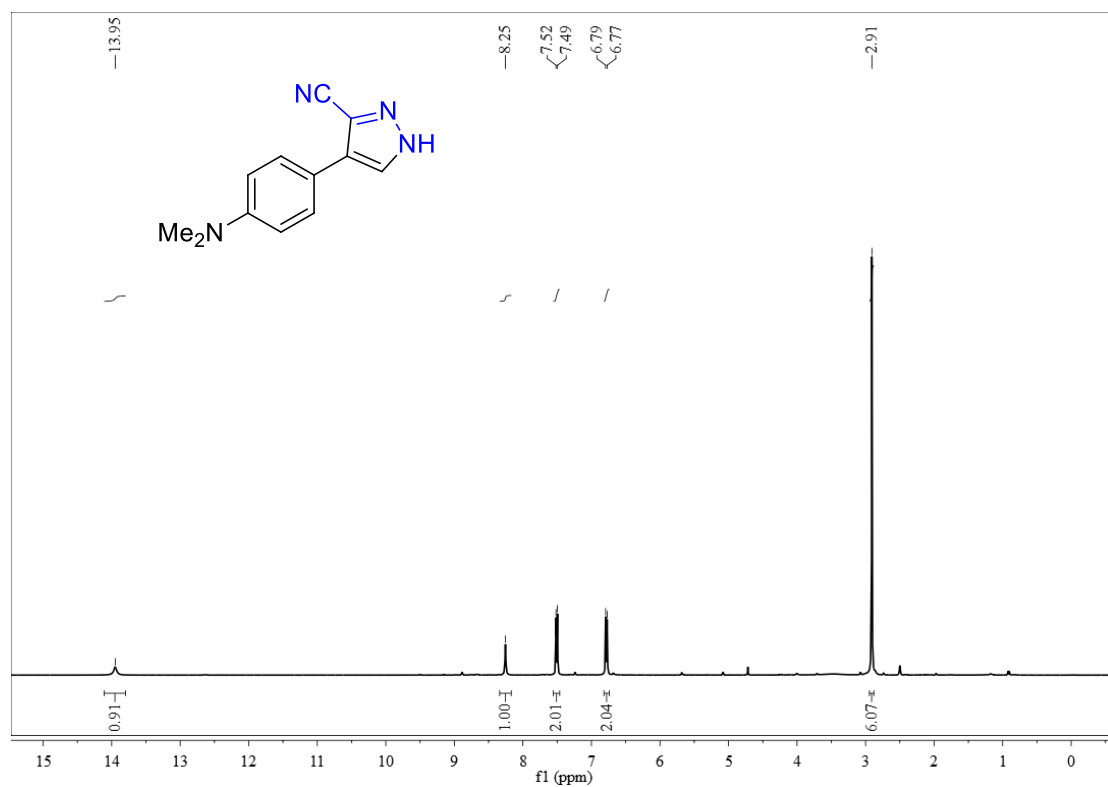
4-(*p*-Tolyl)-1*H*-pyrazole-3-carbonitrile (2b)



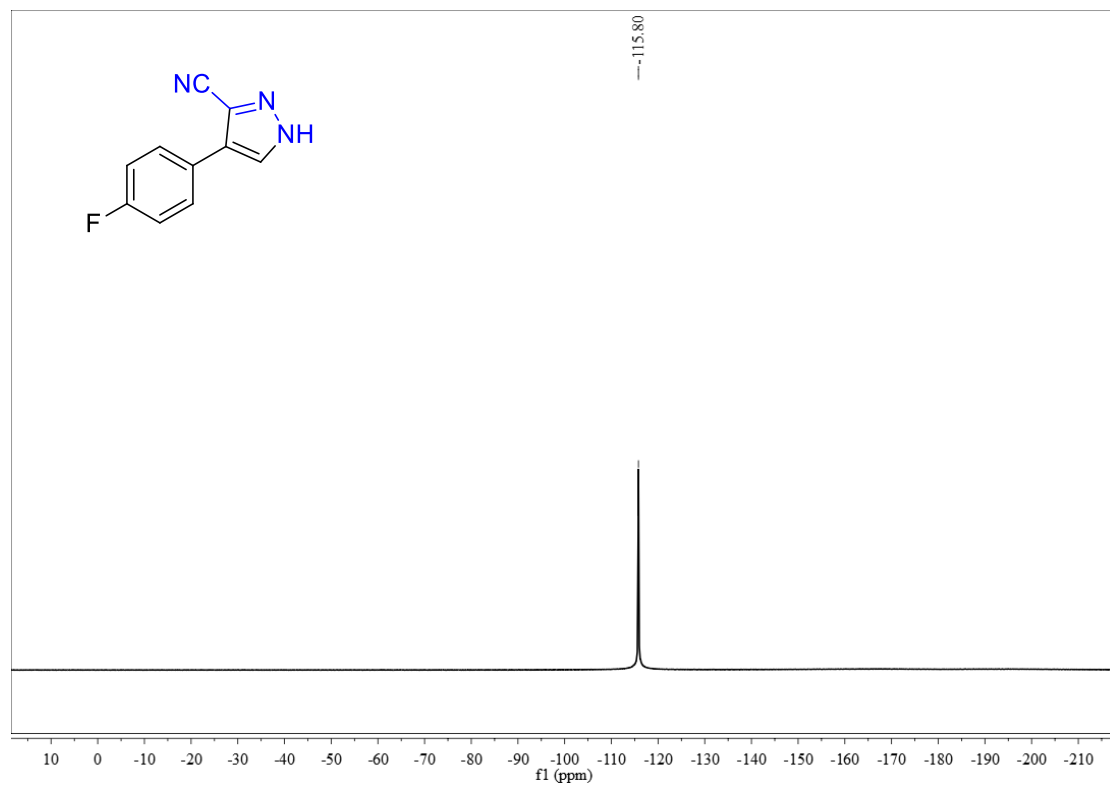
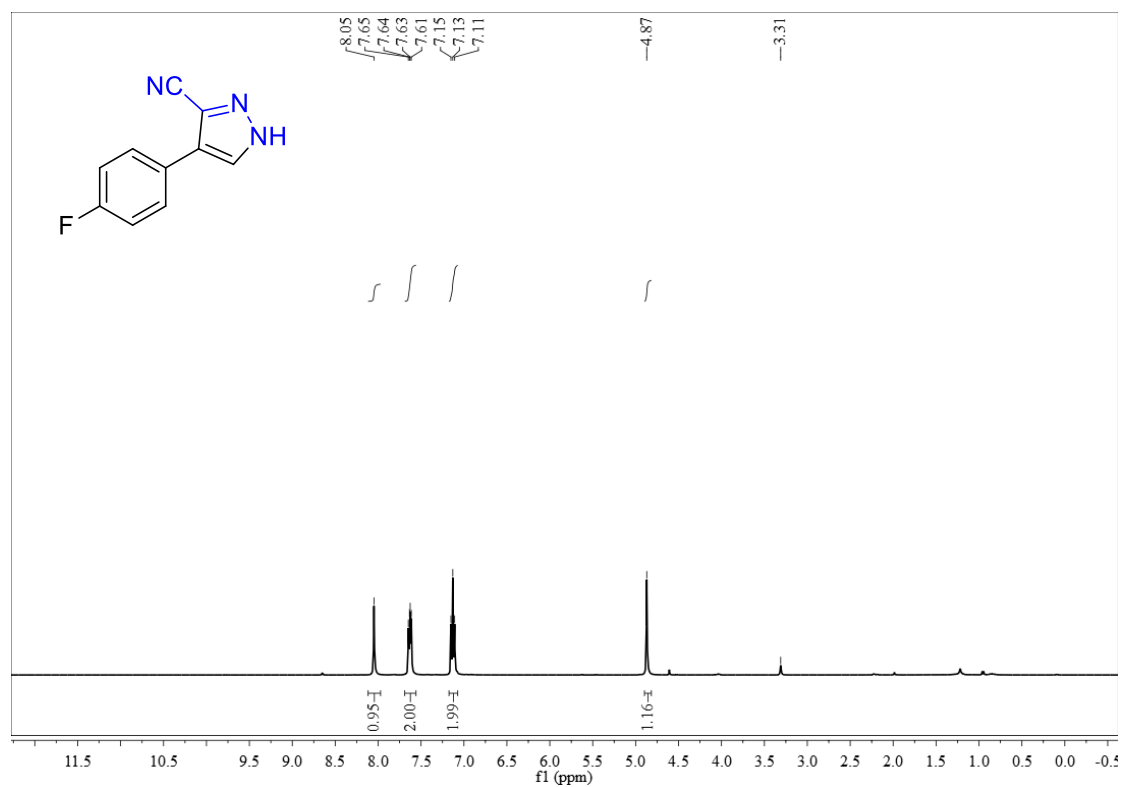
4-(4-Methoxyphenyl)-1H-pyrazole-3-carbonitrile (2c)

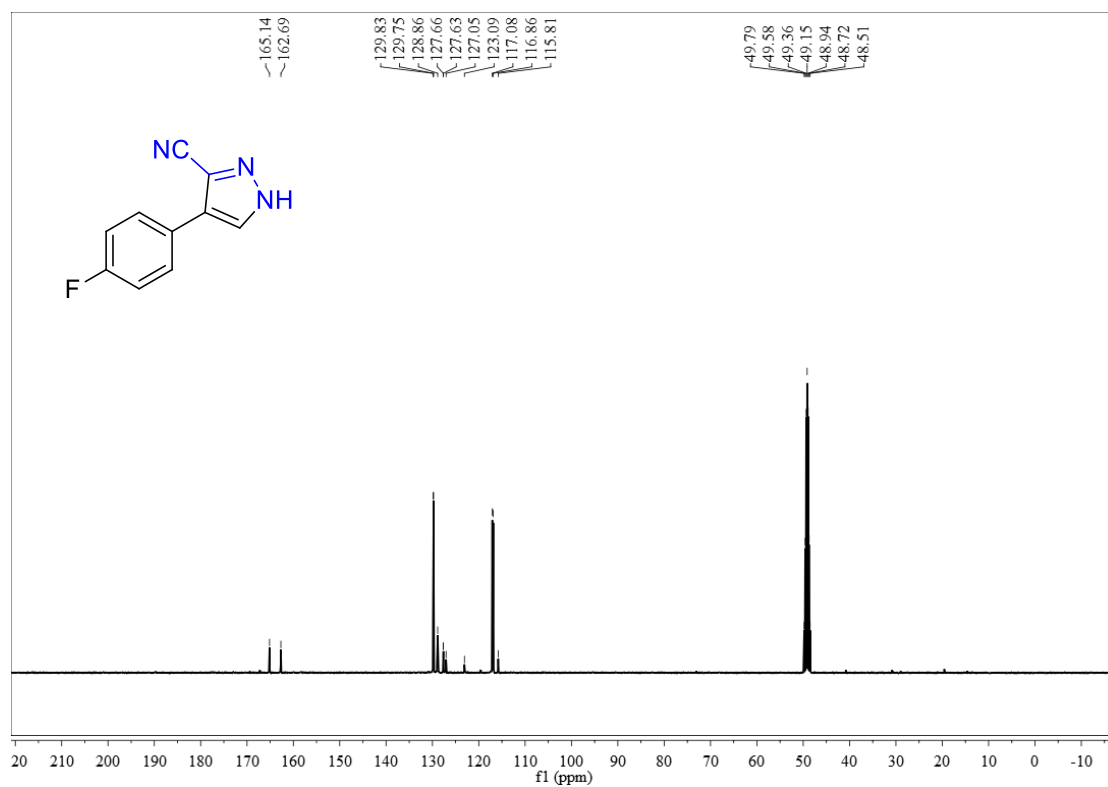


4-(4-(Dimethylamino)phenyl)-1H-pyrazole-3-carbonitrile (2d)

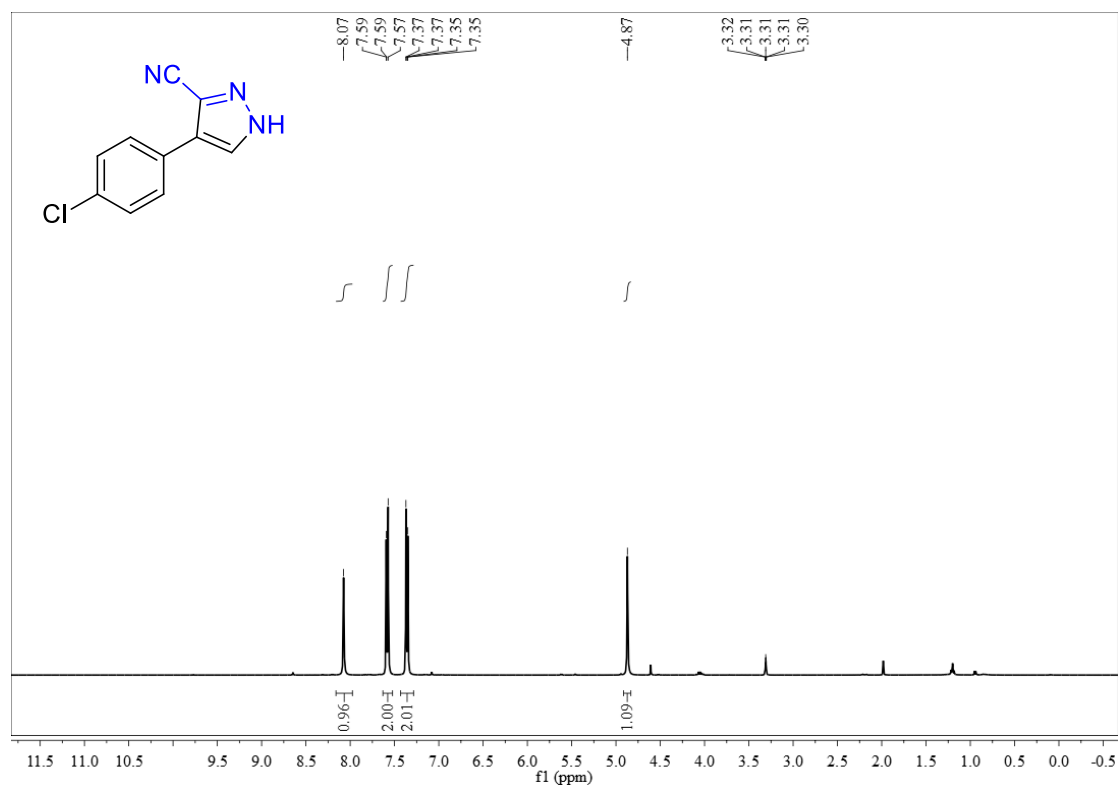


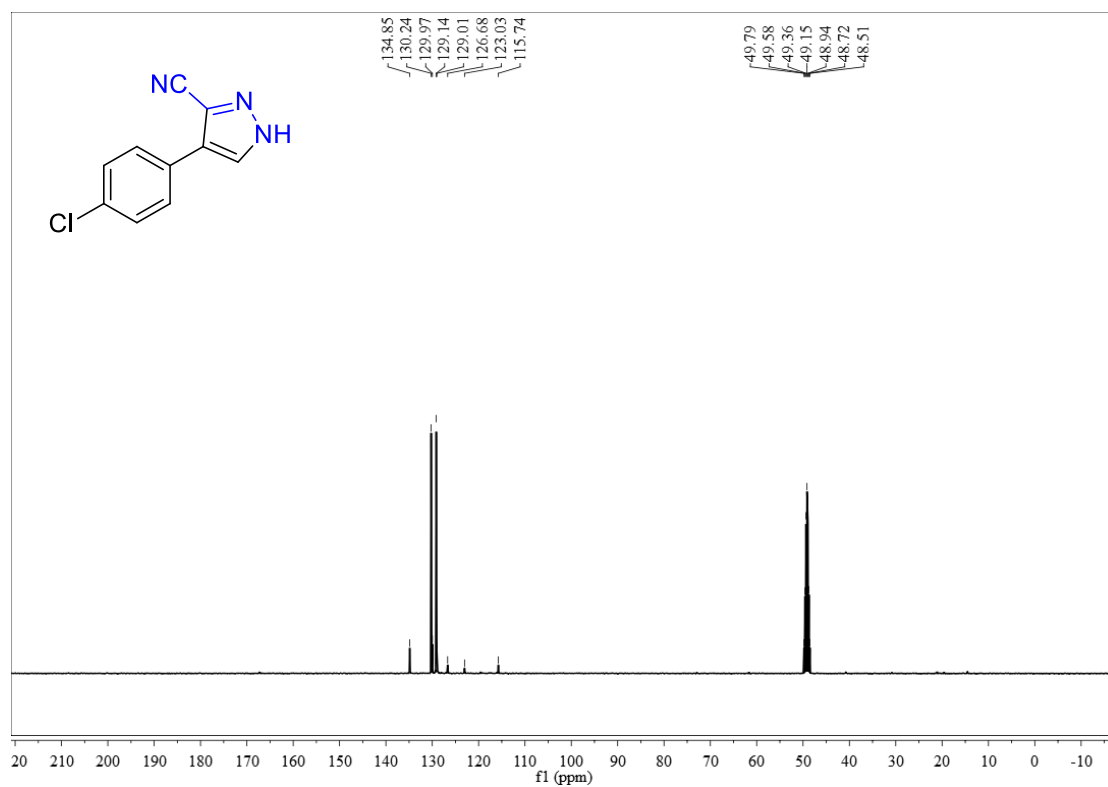
4-(4-Fluorophenyl)-1H-pyrazole-3-carbonitrile (2e)



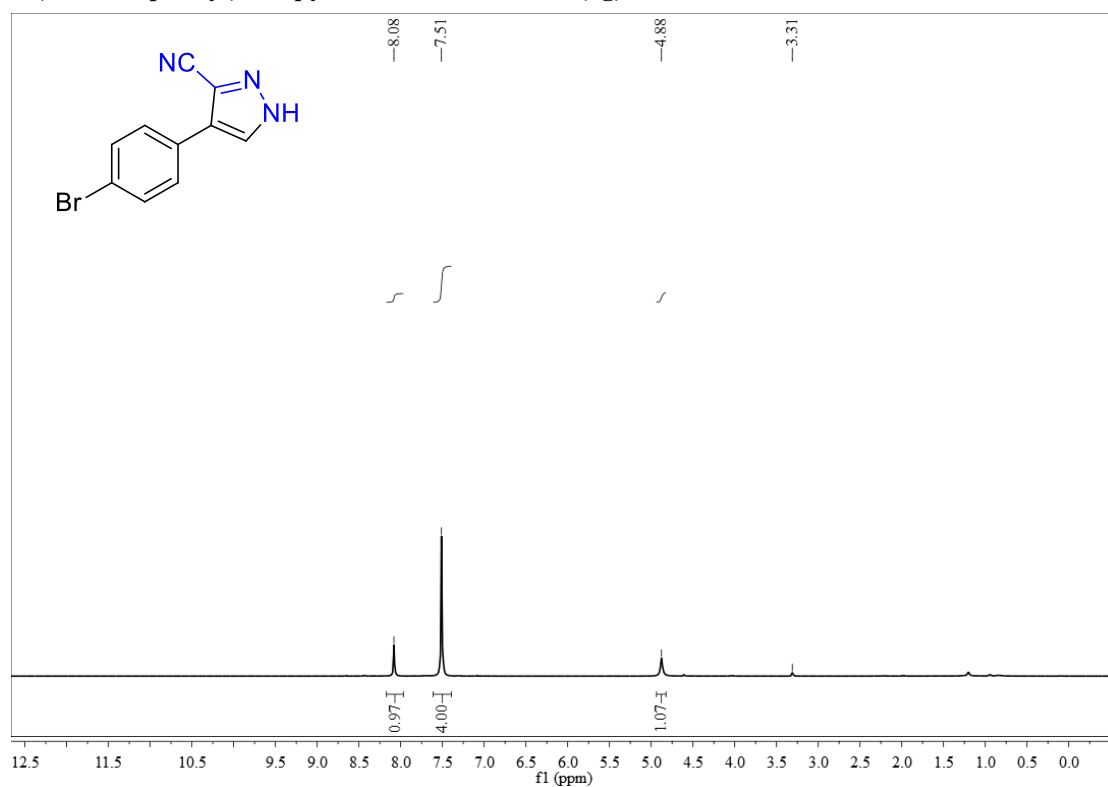


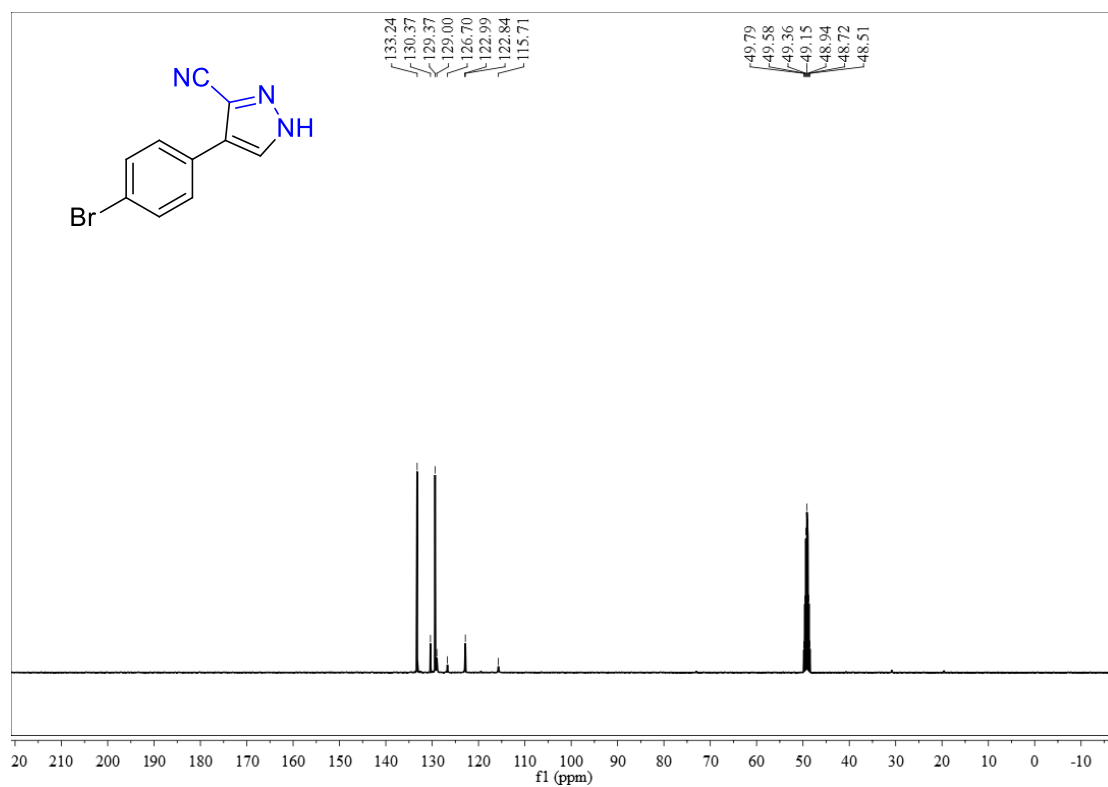
4-(4-Chlorophenyl)-1H-pyrazole-3-carbonitrile (2f)



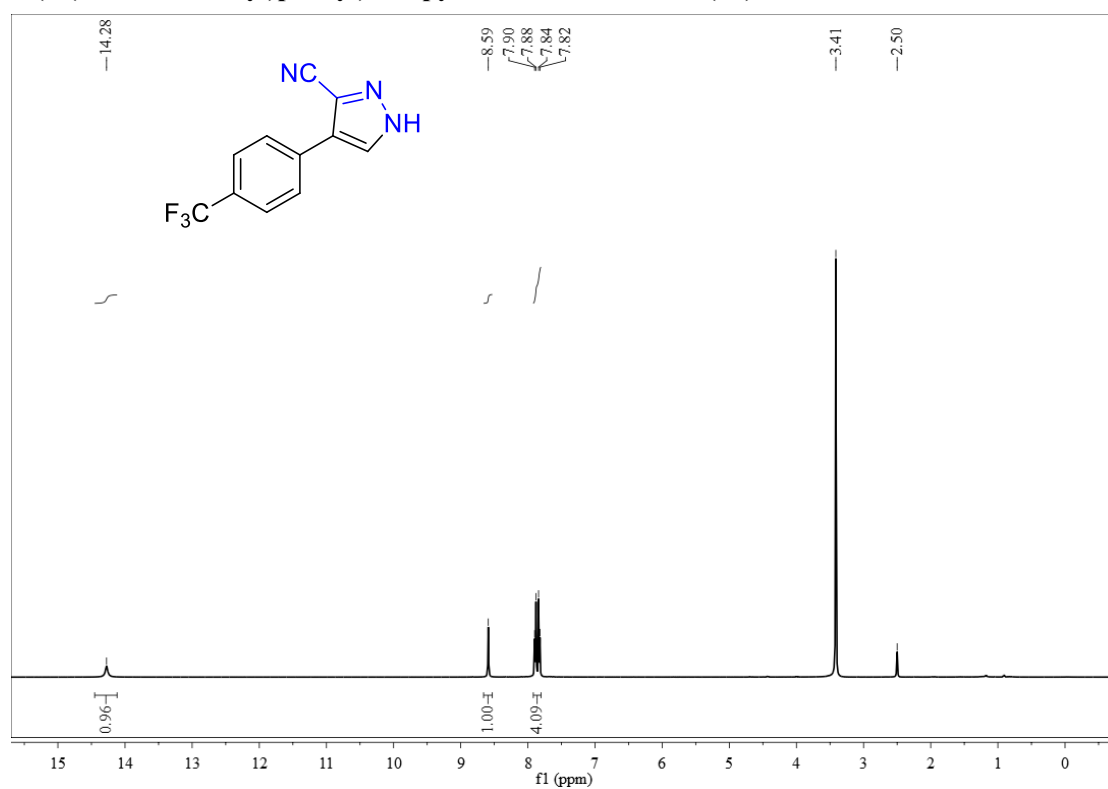


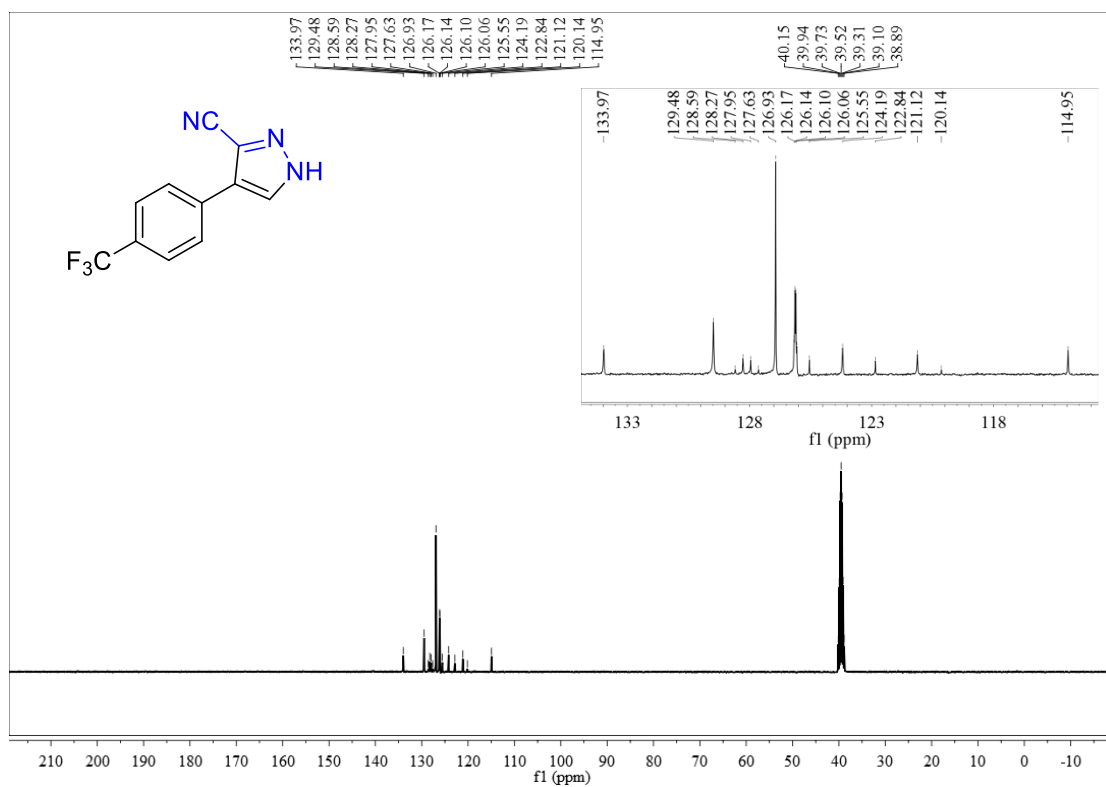
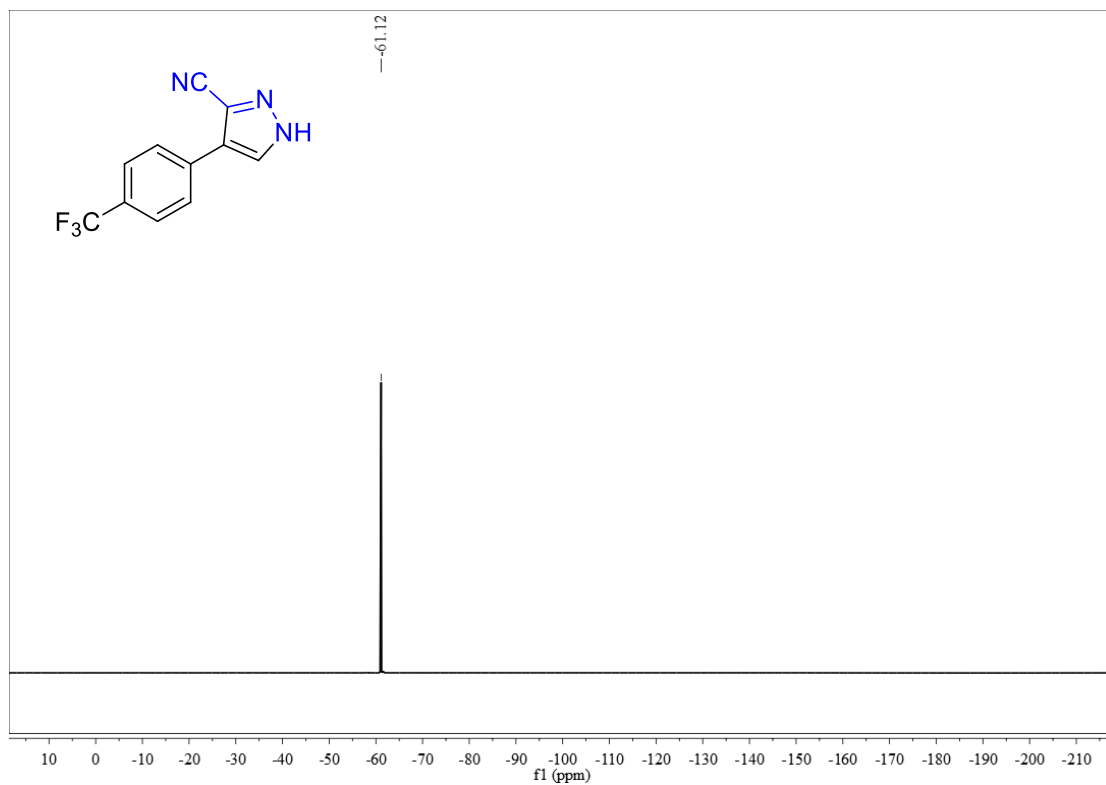
4-(4-Bromophenyl)-1H-pyrazole-3-carbonitrile (2g)



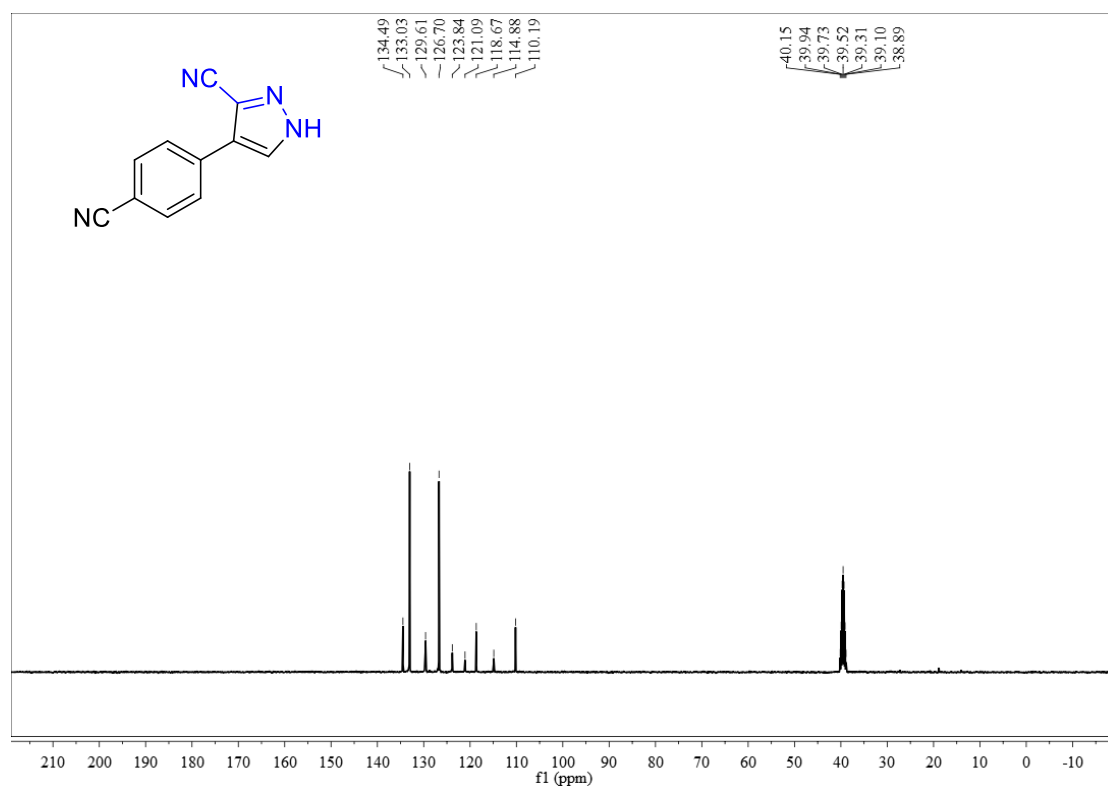
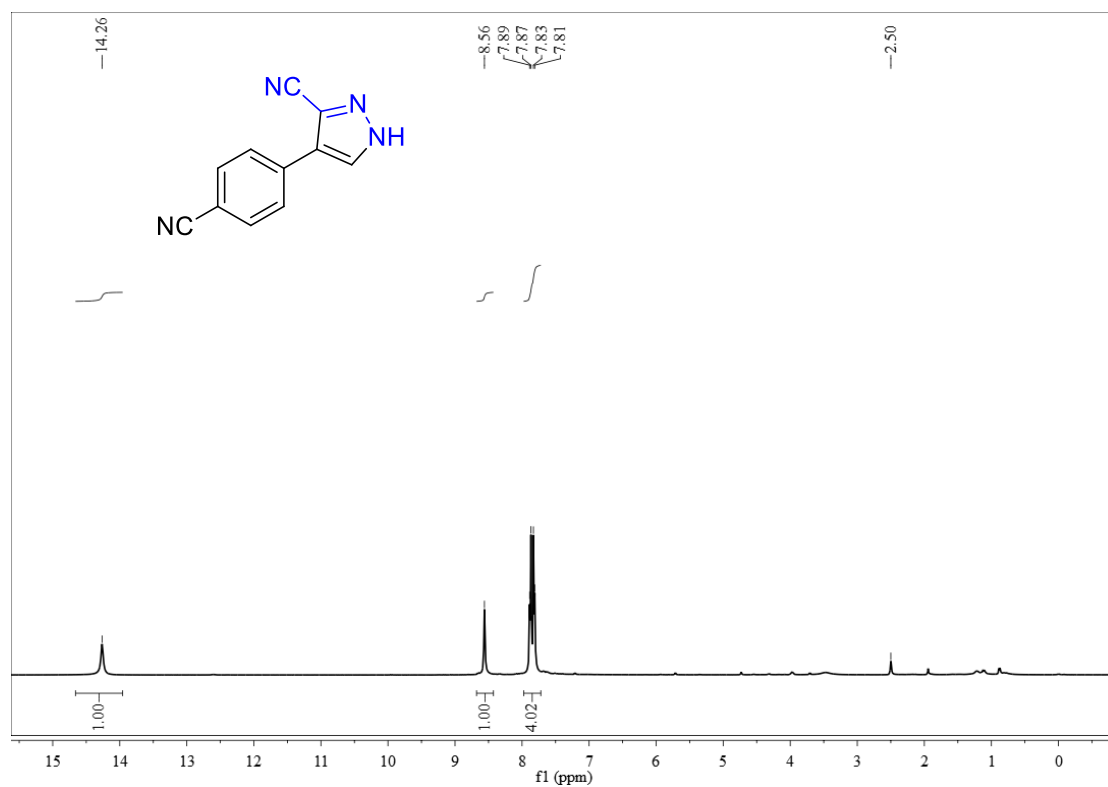


4-(4-(Trifluoromethyl)phenyl)-1H-pyrazole-3-carbonitrile (2h)

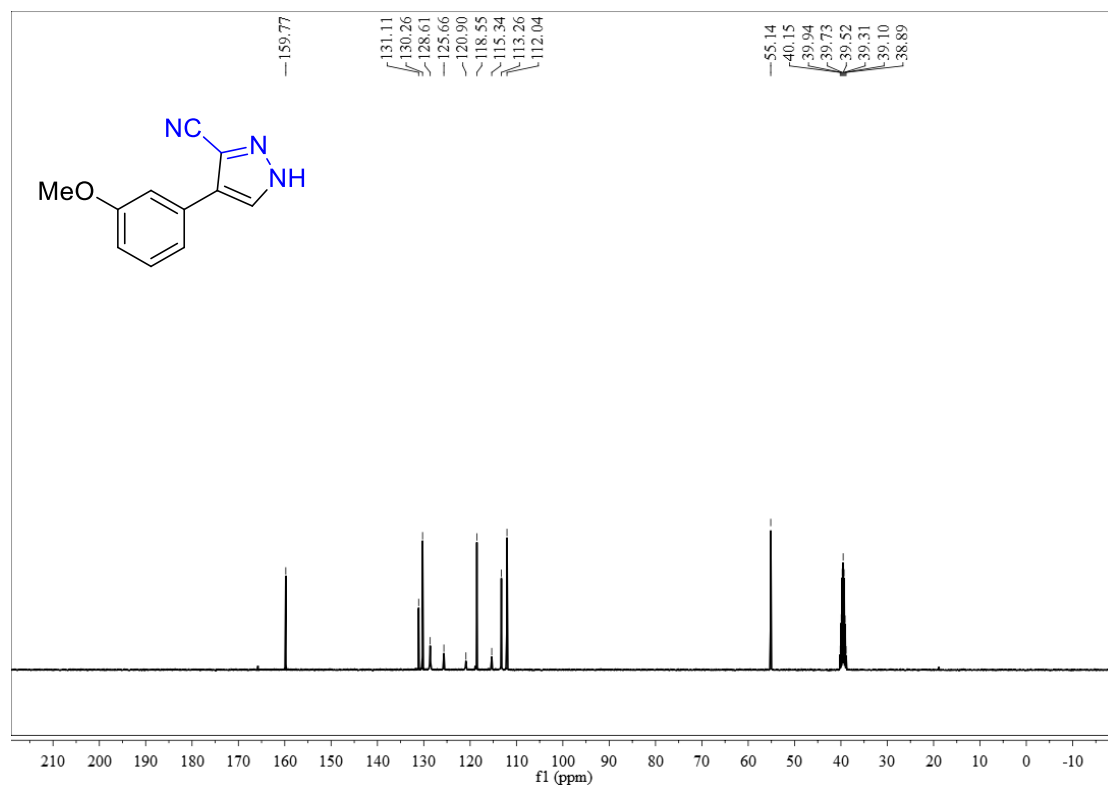
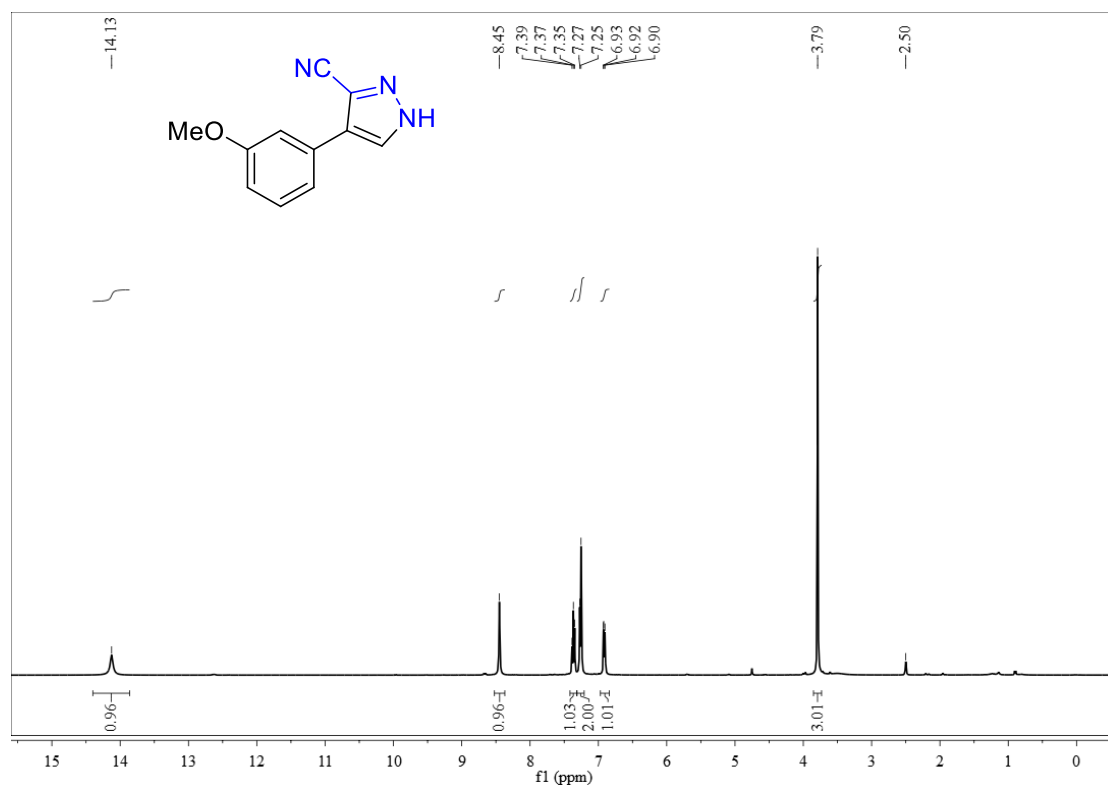




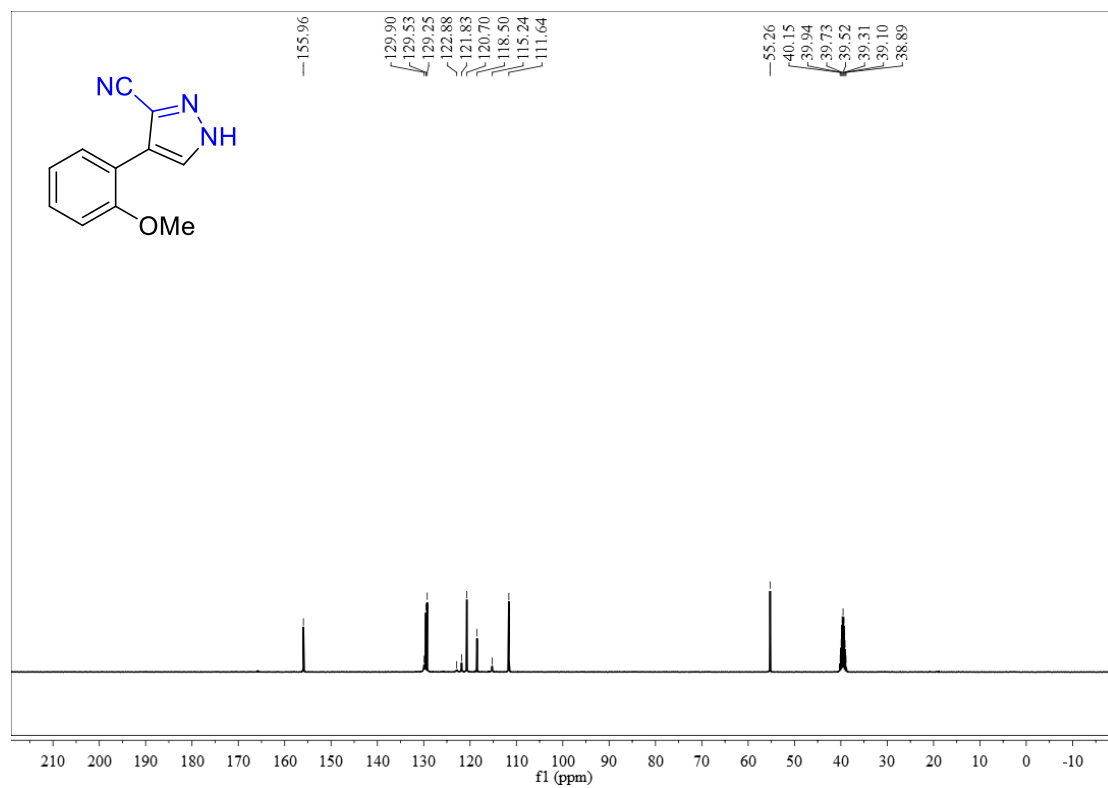
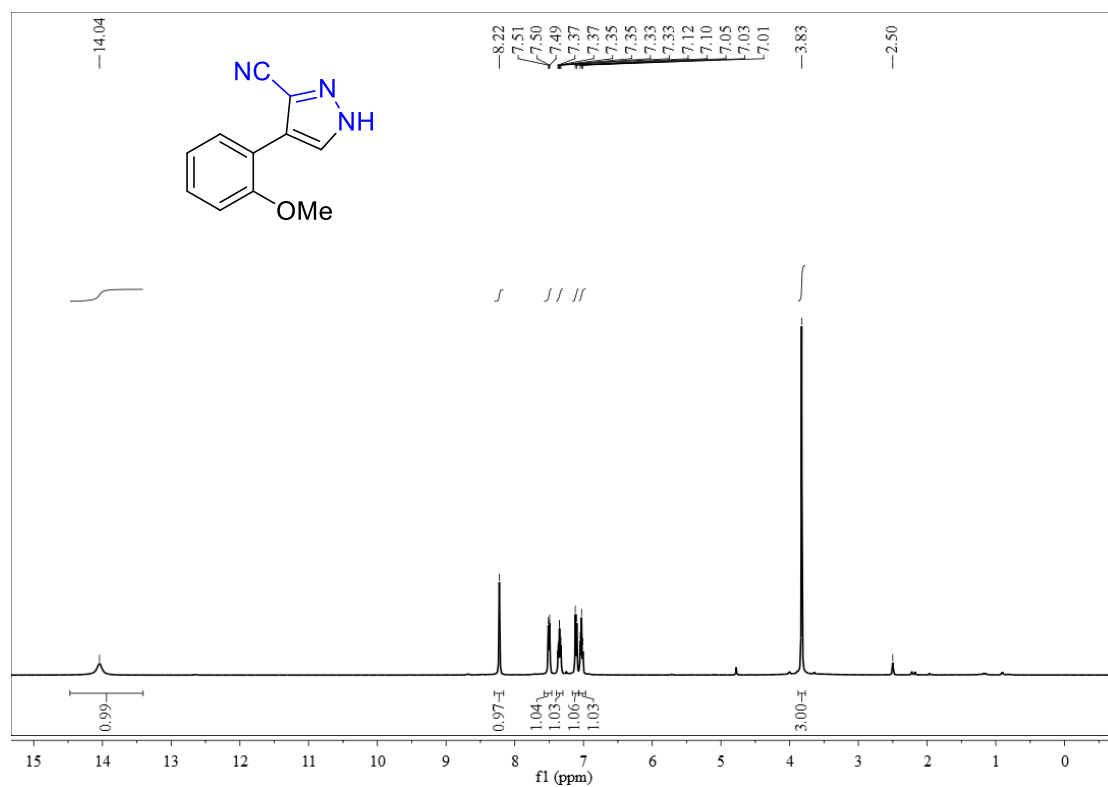
4-(4-Cyanophenyl)-1H-pyrazole-3-carbonitrile (2i)



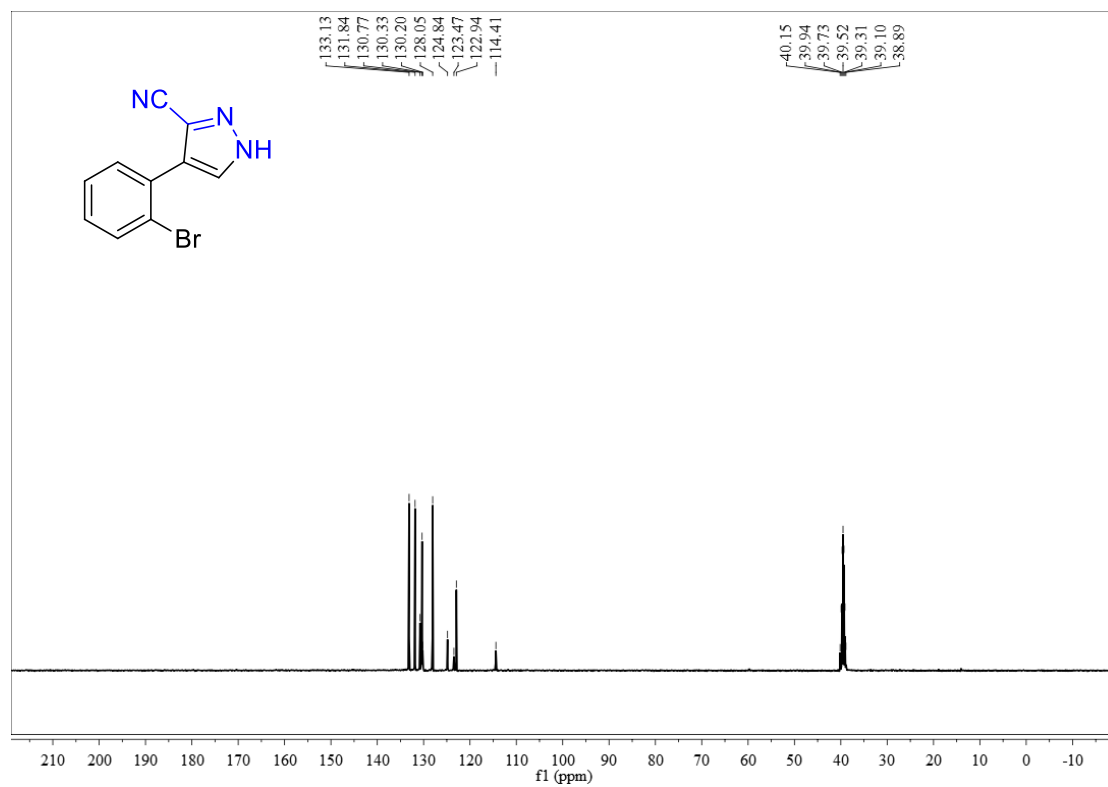
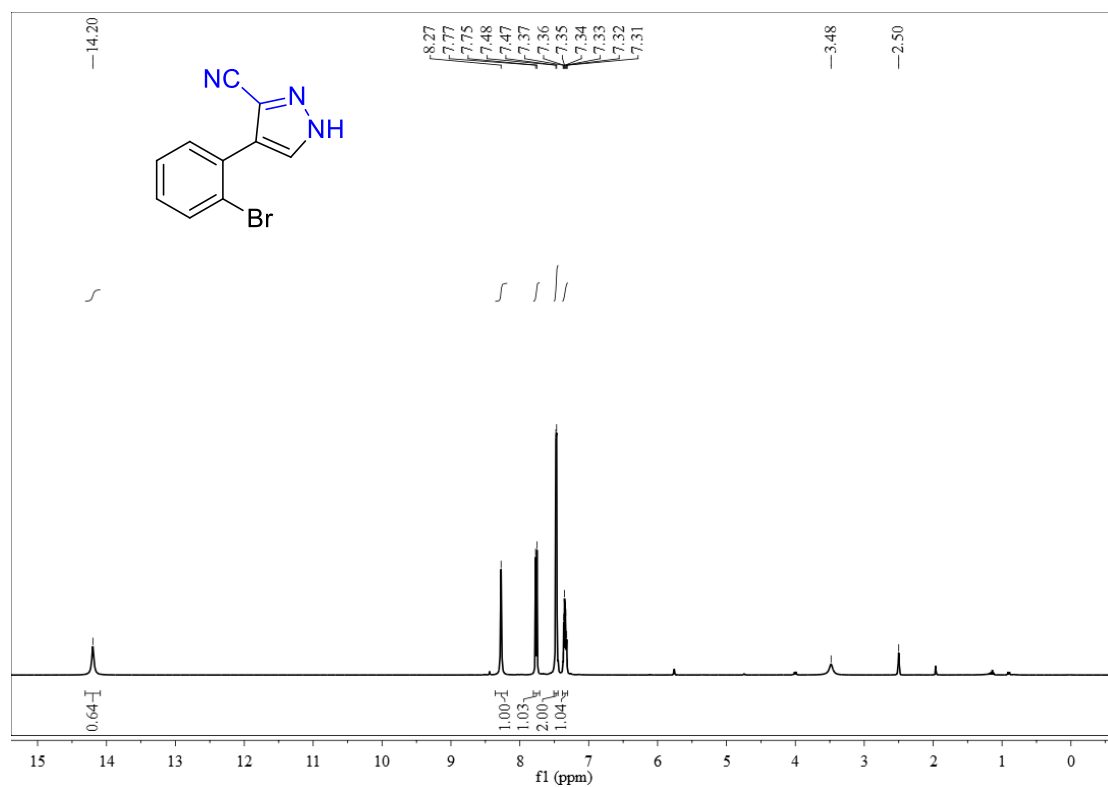
4-(3-Methoxyphenyl)-1H-pyrazole-3-carbonitrile (2j)



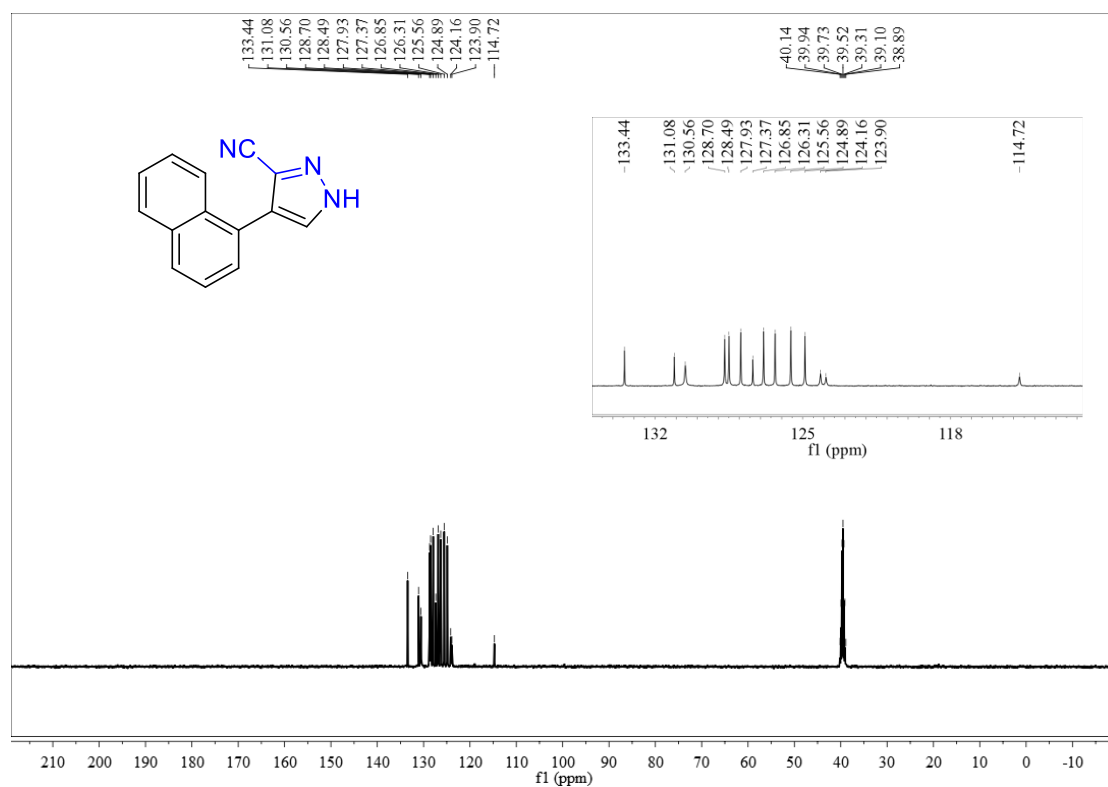
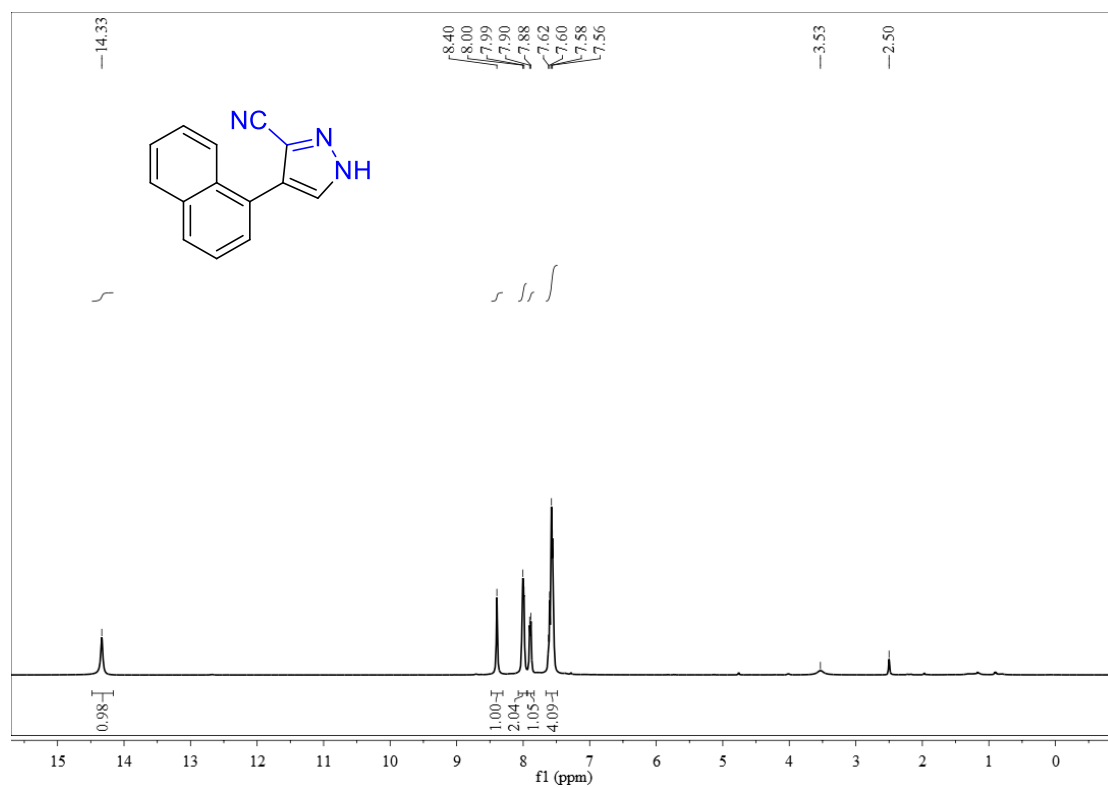
4-(2-Methoxyphenyl)-1H-pyrazole-3-carbonitrile (2k)



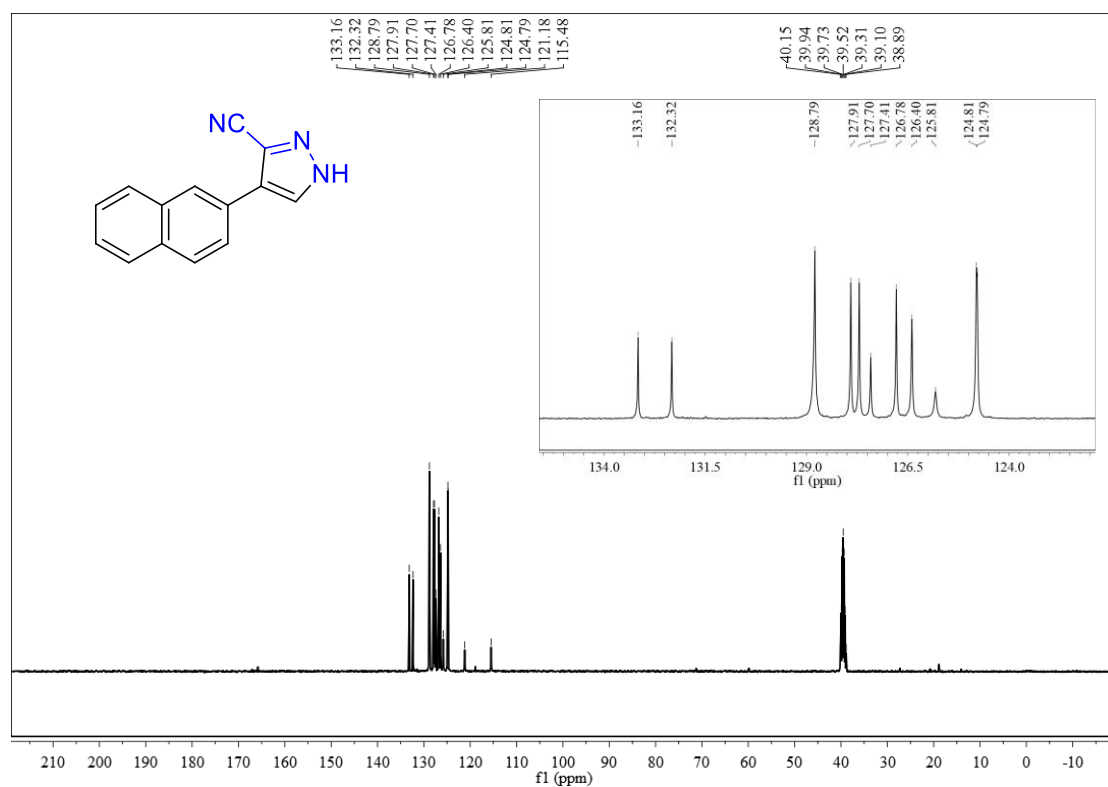
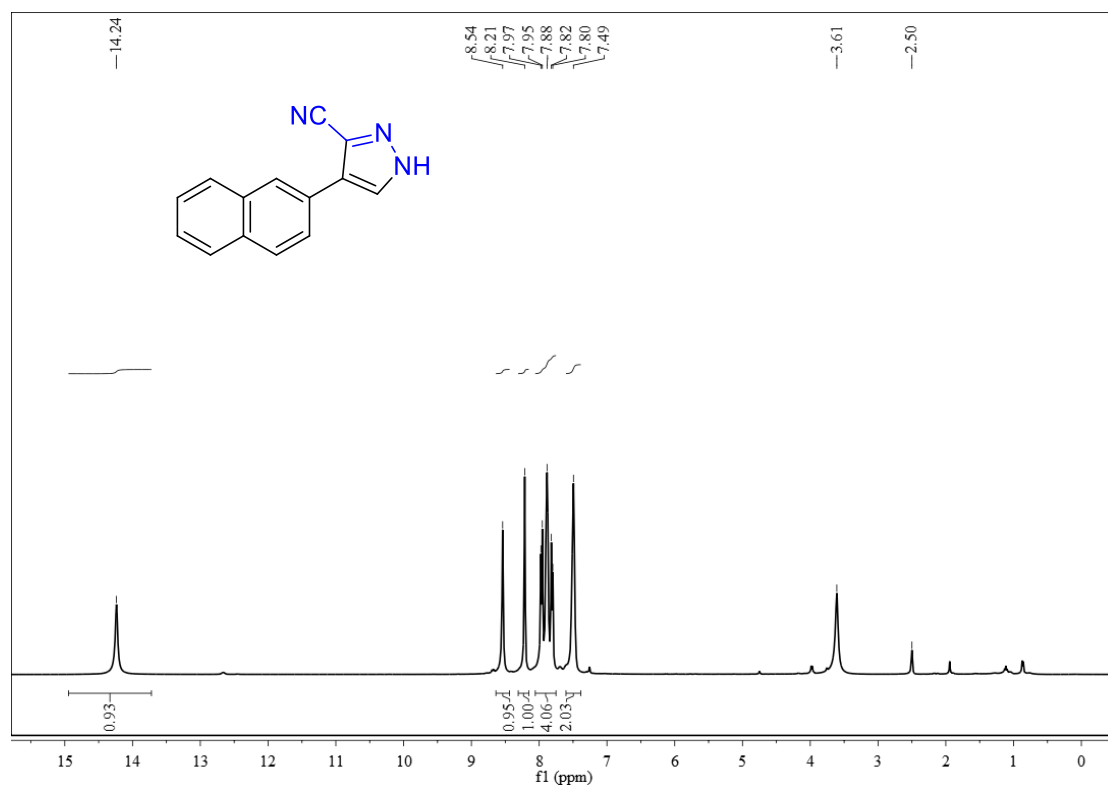
4-(2-Bromophenyl)-1H-pyrazole-3-carbonitrile (2l)



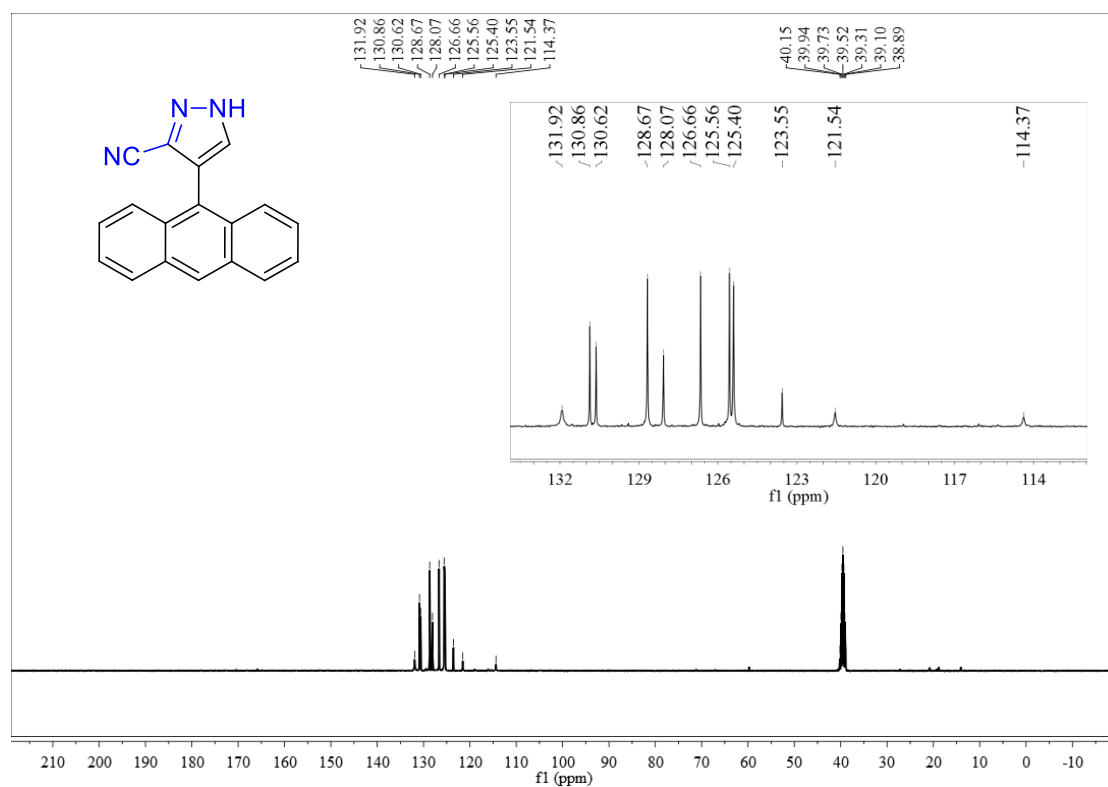
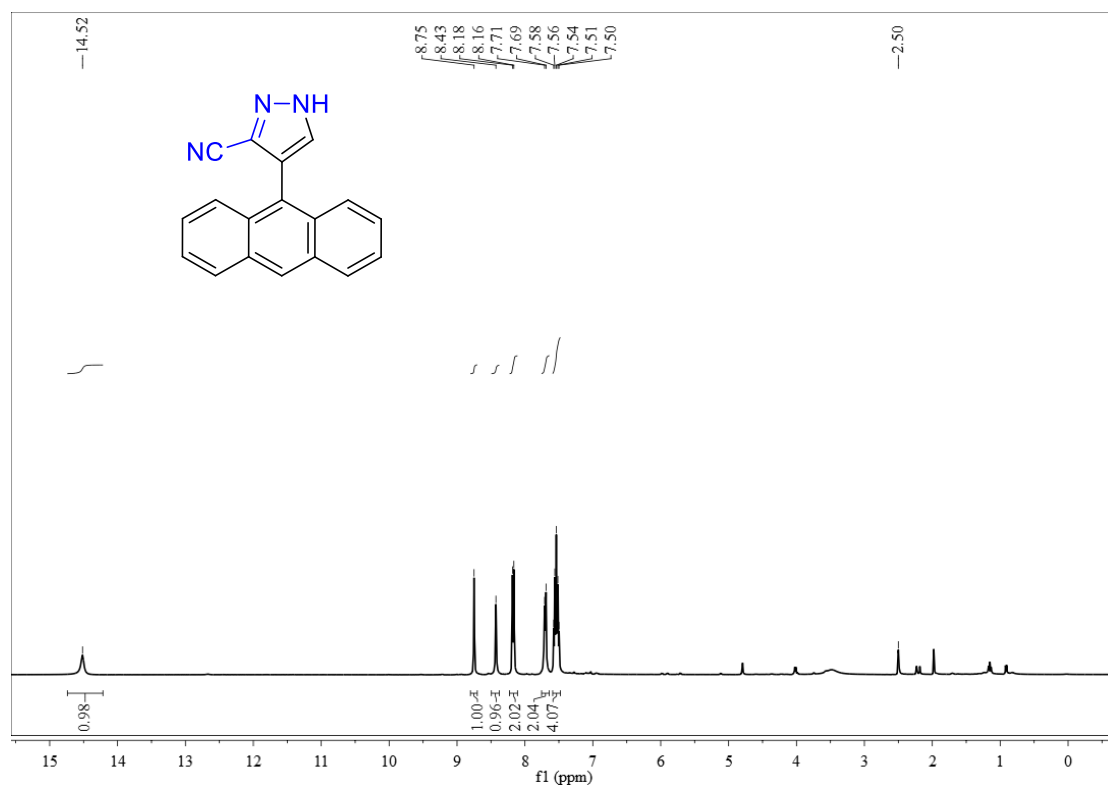
4-(Naphthalen-1-yl)-1H-pyrazole-3-carbonitrile (2m)



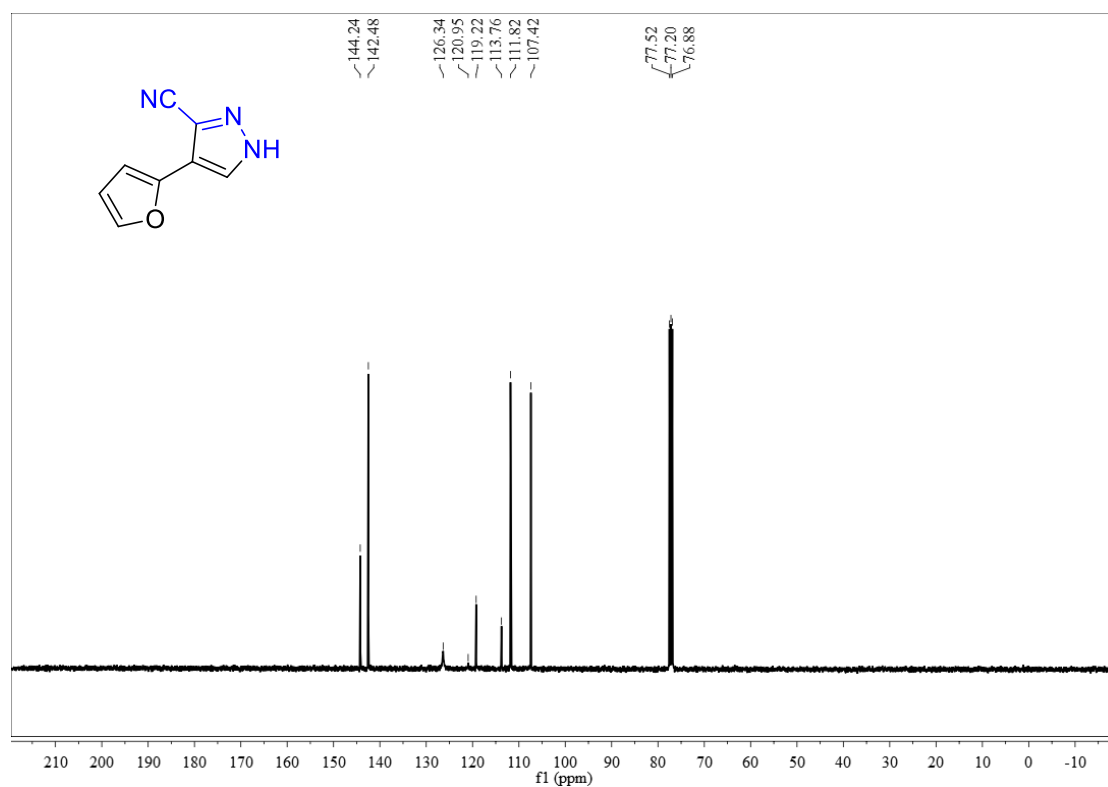
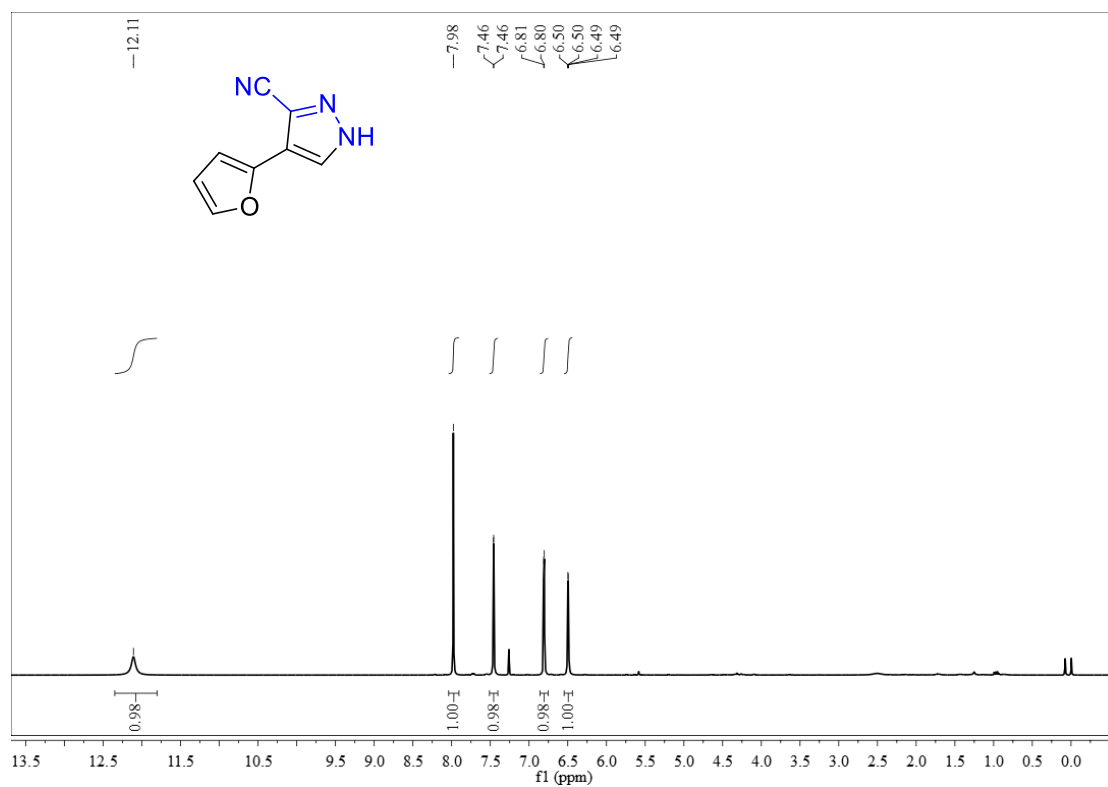
4-(Naphthalen-2-yl)-1H-pyrazole-3-carbonitrile (2n)



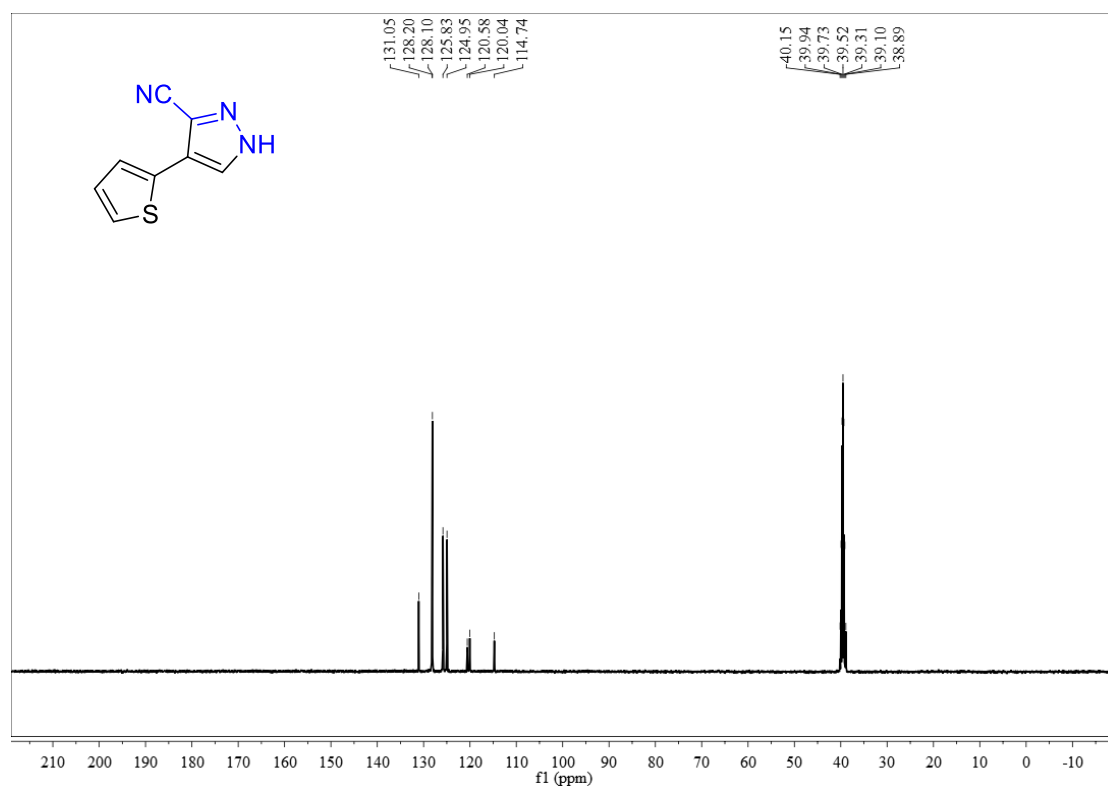
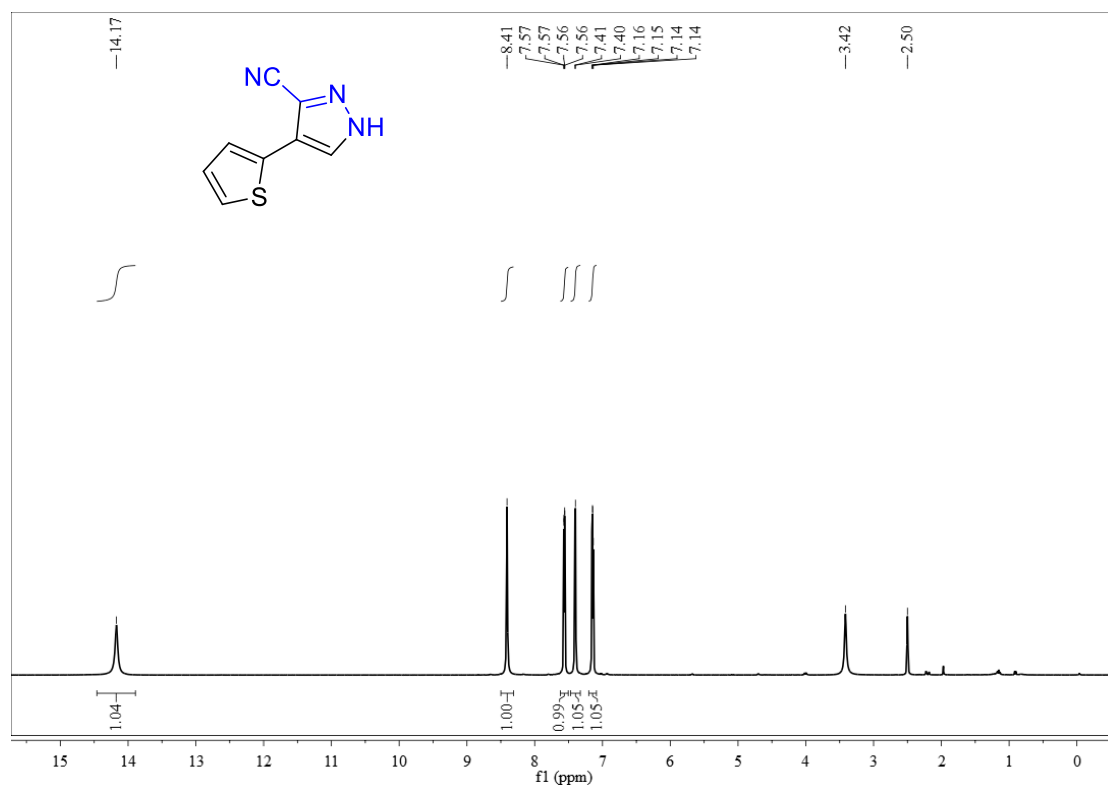
4-(Anthracen-9-yl)-1H-pyrazole-3-carbonitrile (2o)



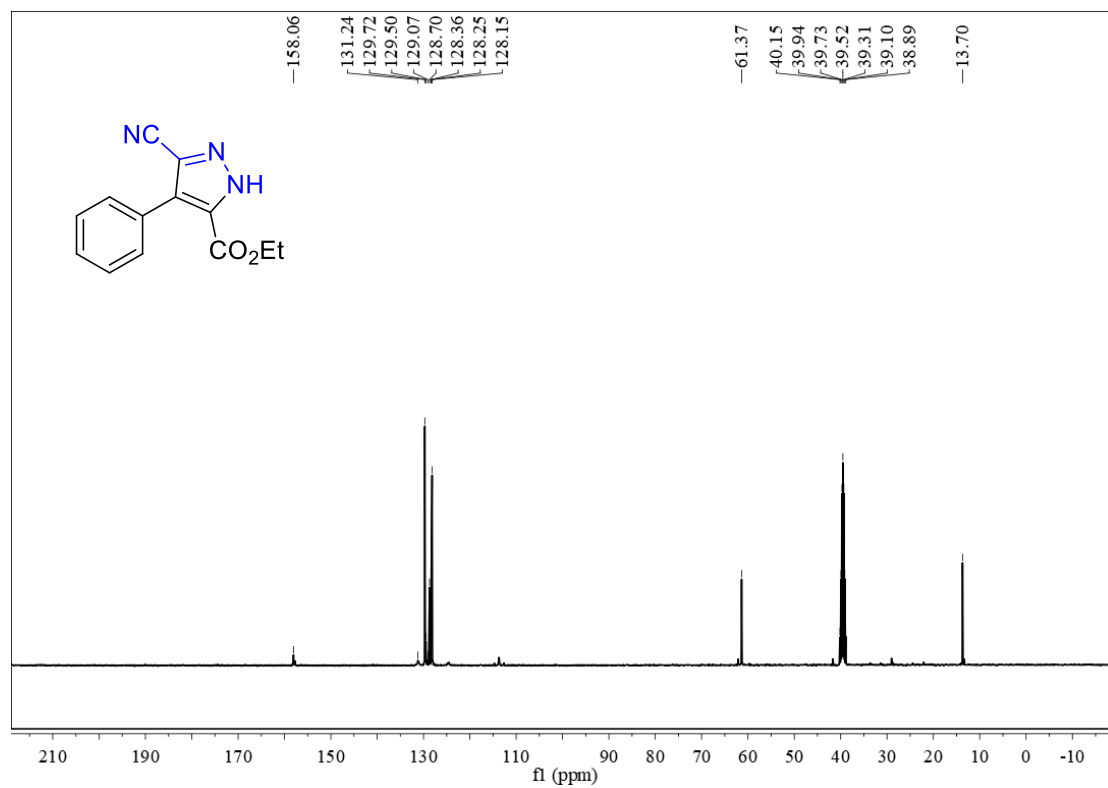
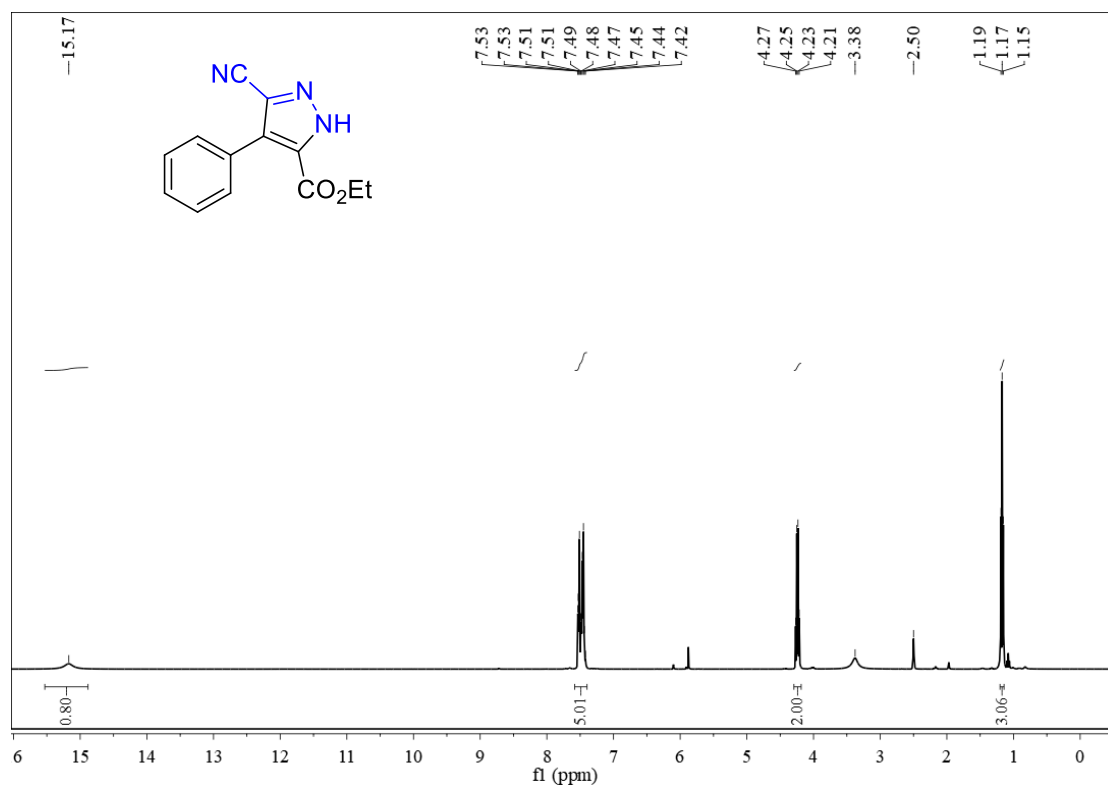
4-(Furan-2-yl)-1H-pyrazole-3-carbonitrile (2p)



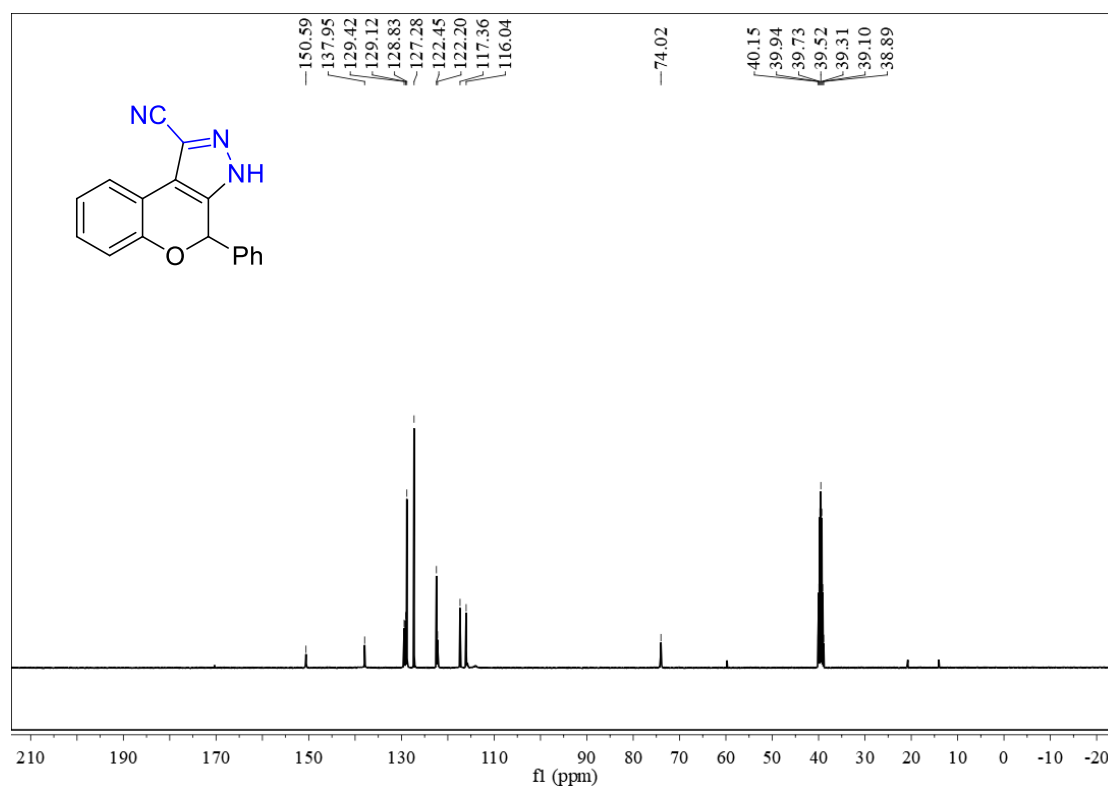
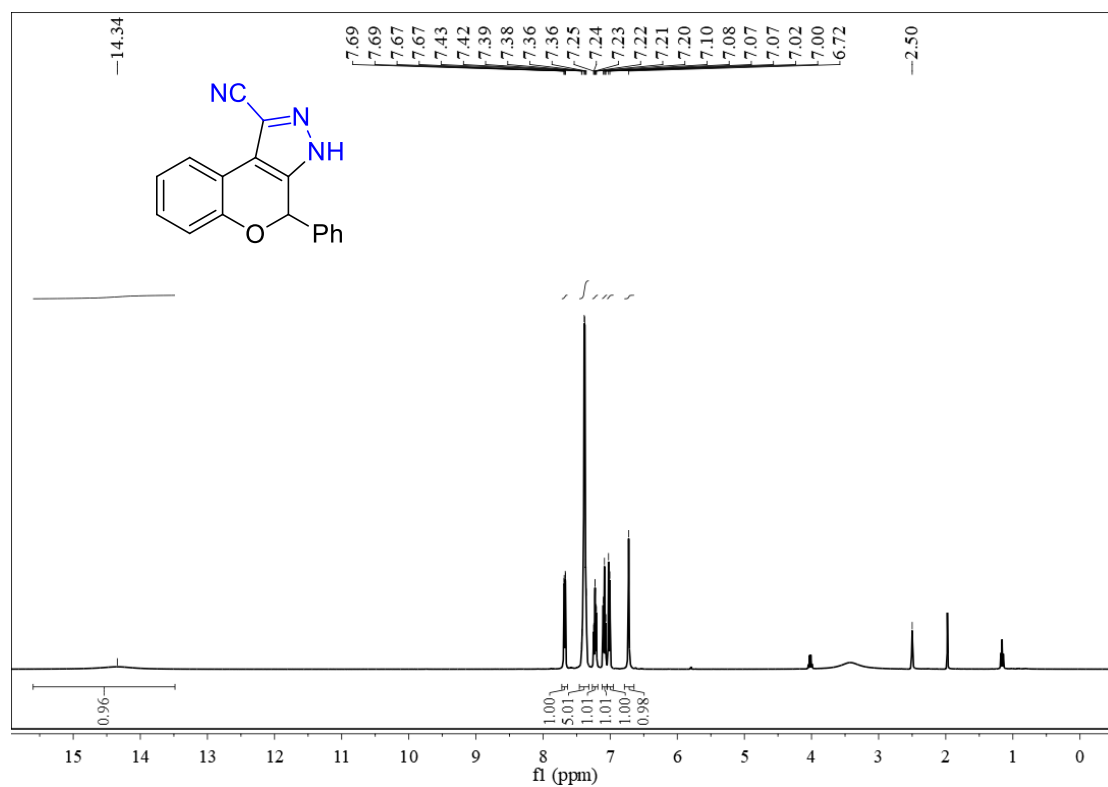
4-(Thiophen-2-yl)-1H-pyrazole-3-carbonitrile (2q)



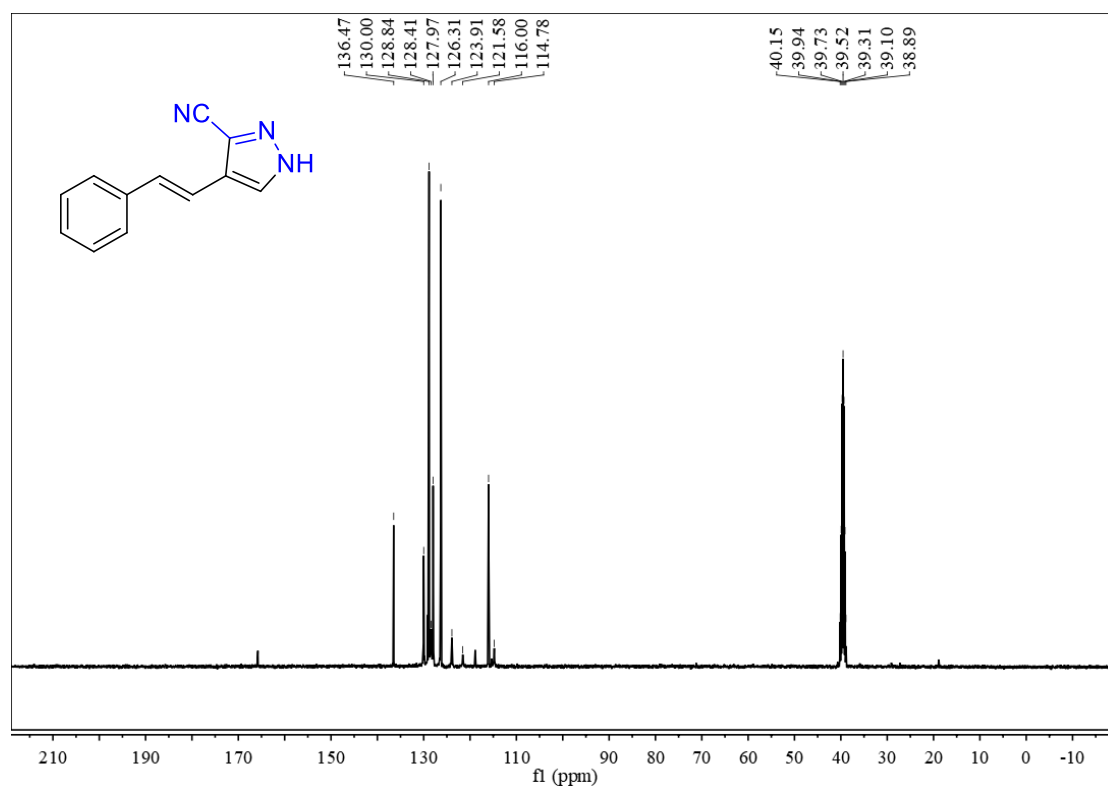
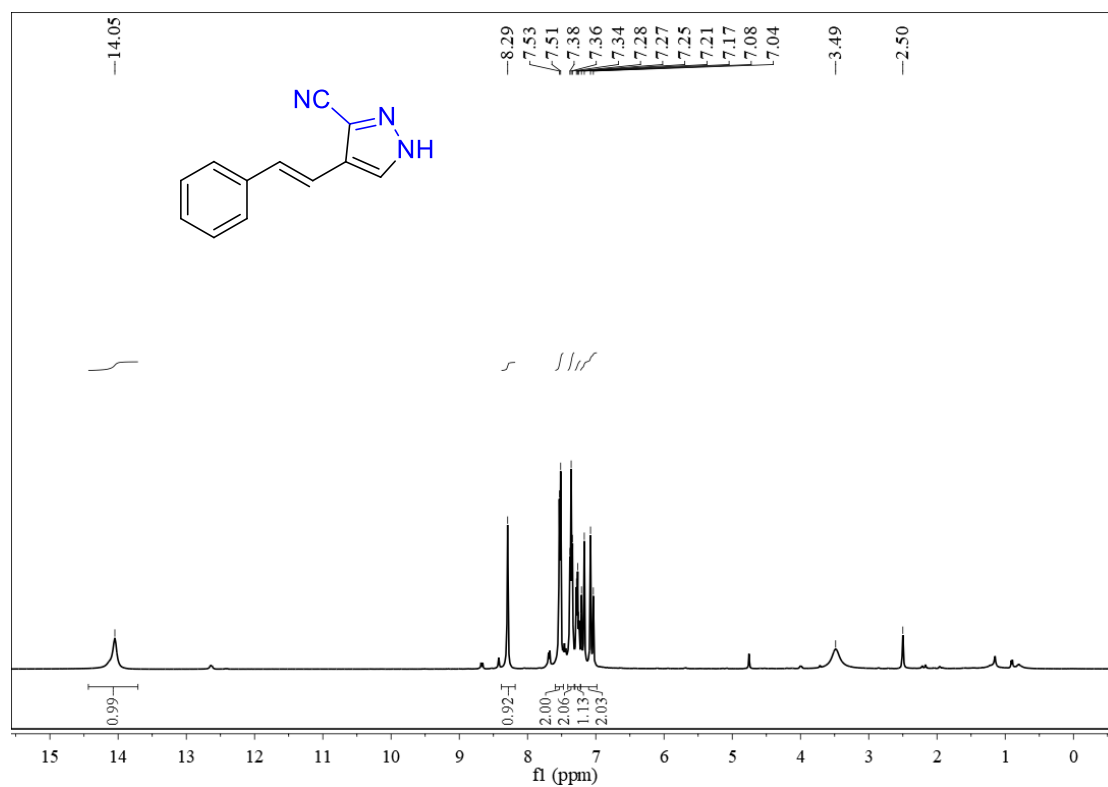
Ethyl 3-cyano-4-phenyl-1H-pyrazole-5-carboxylate (2r)



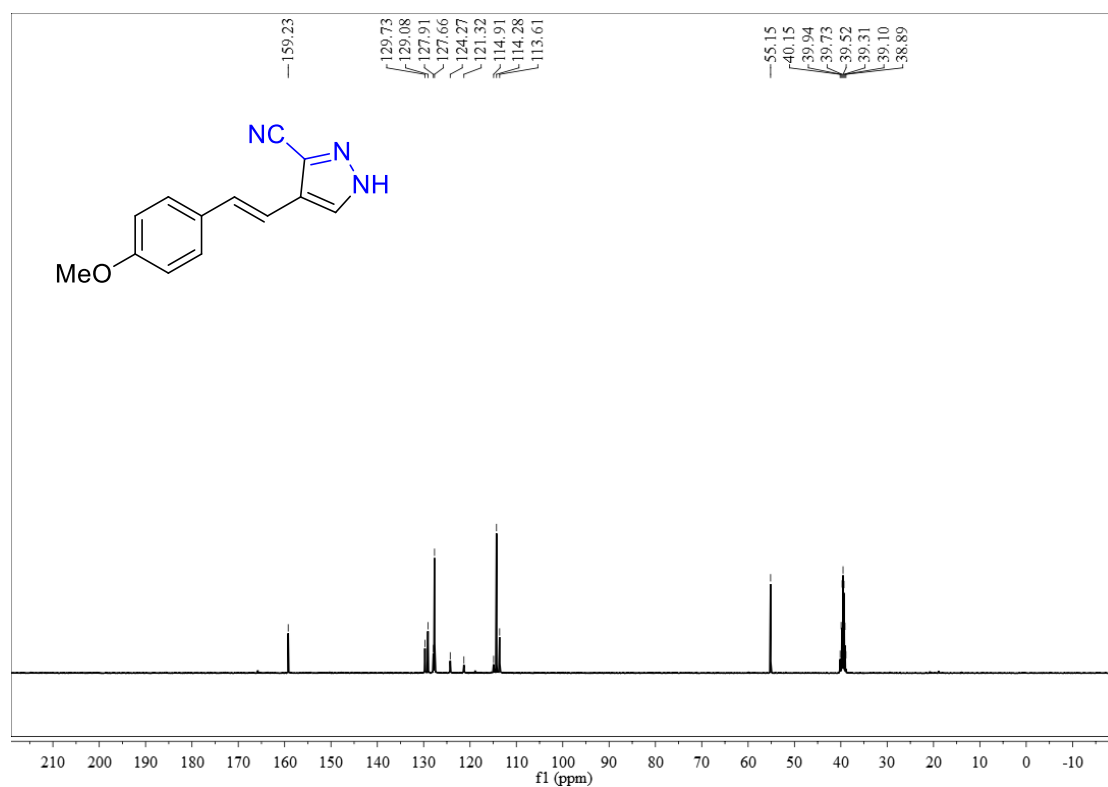
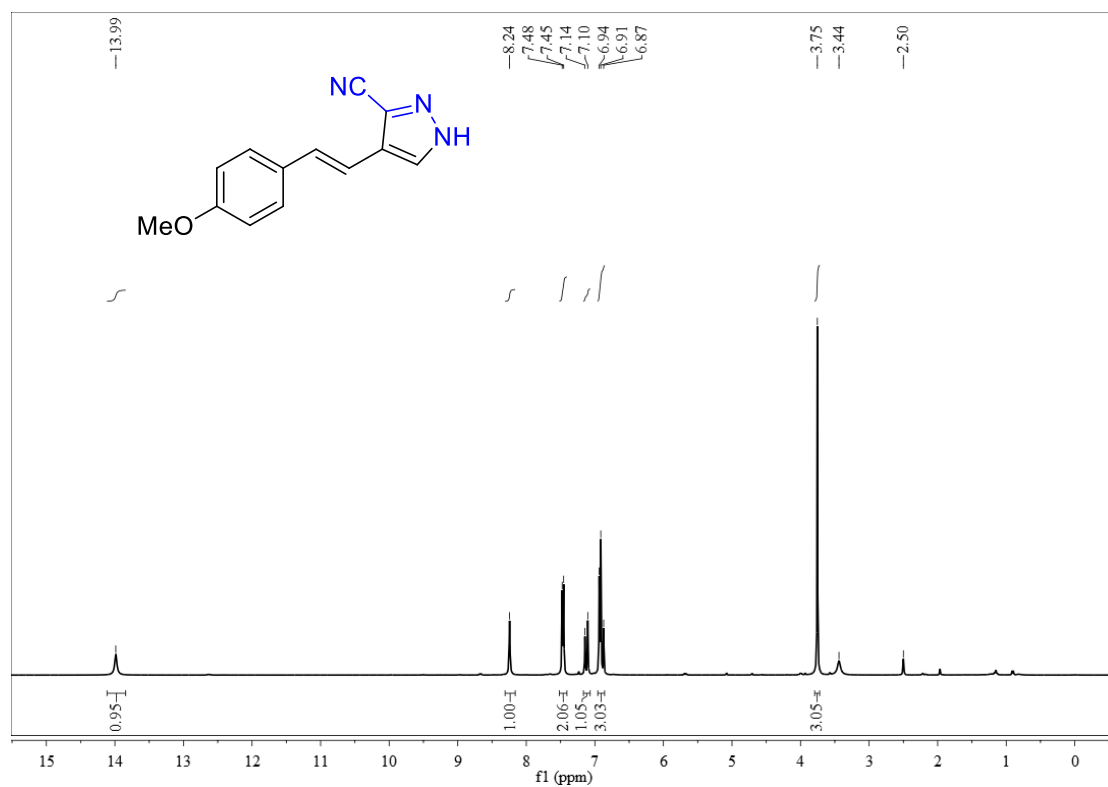
4-Phenyl-3,4-dihydrochromeno[3,4-c]pyrazole-1-carbonitrile (2s)



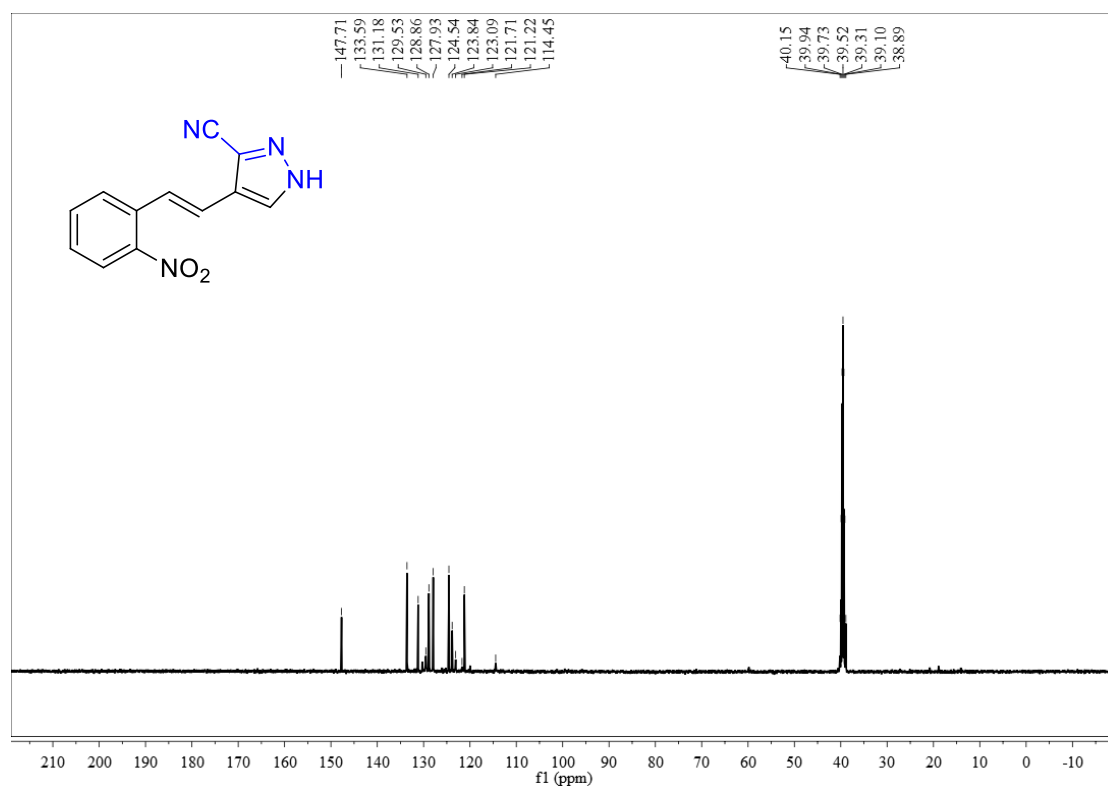
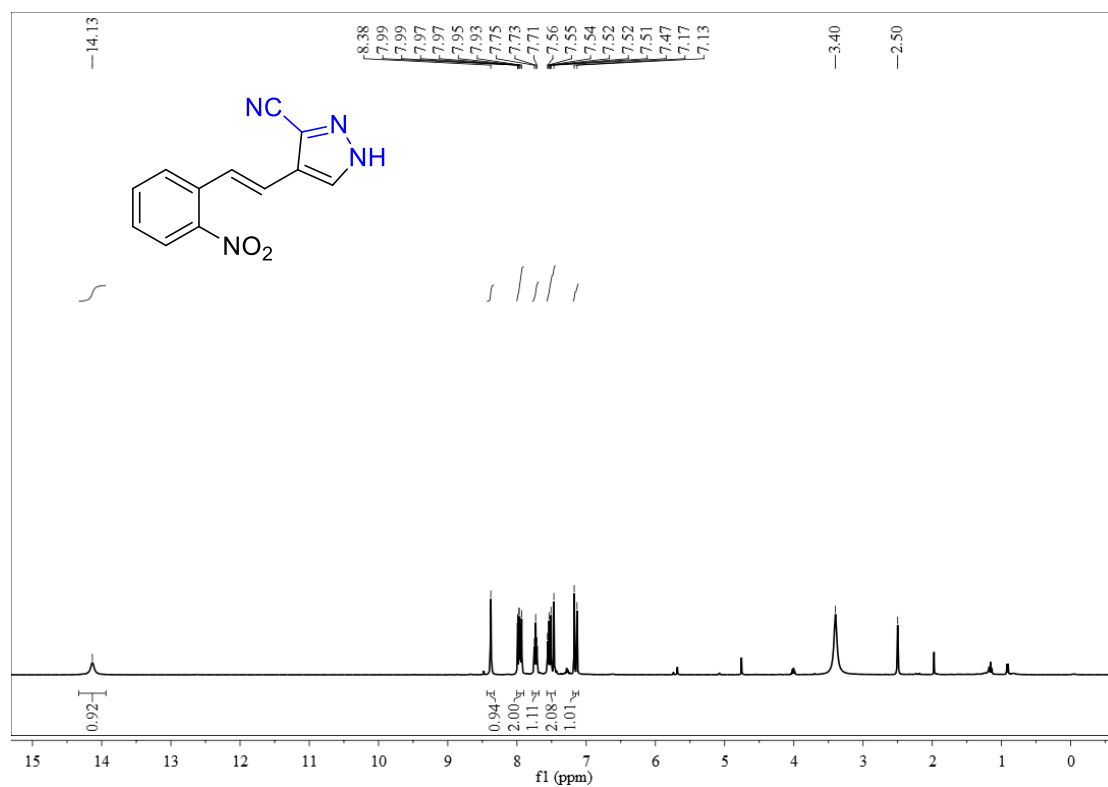
(E)-4-Styryl-1H-pyrazole-3-carbonitrile (2t)



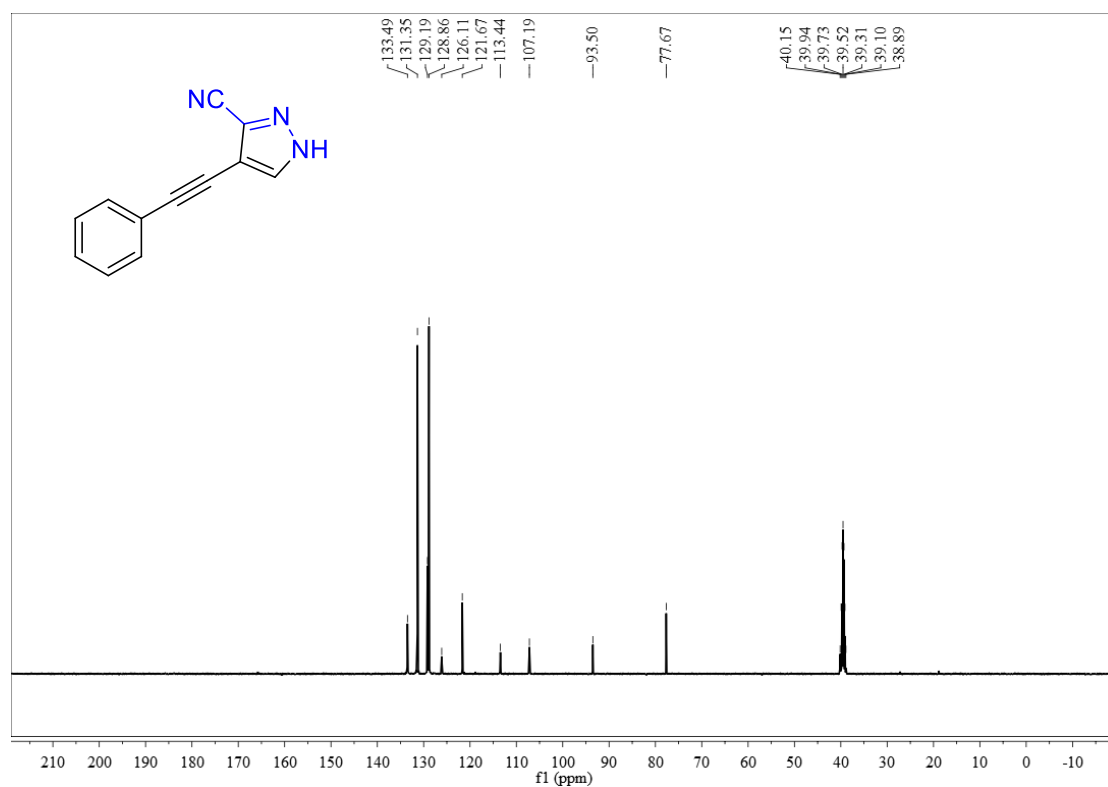
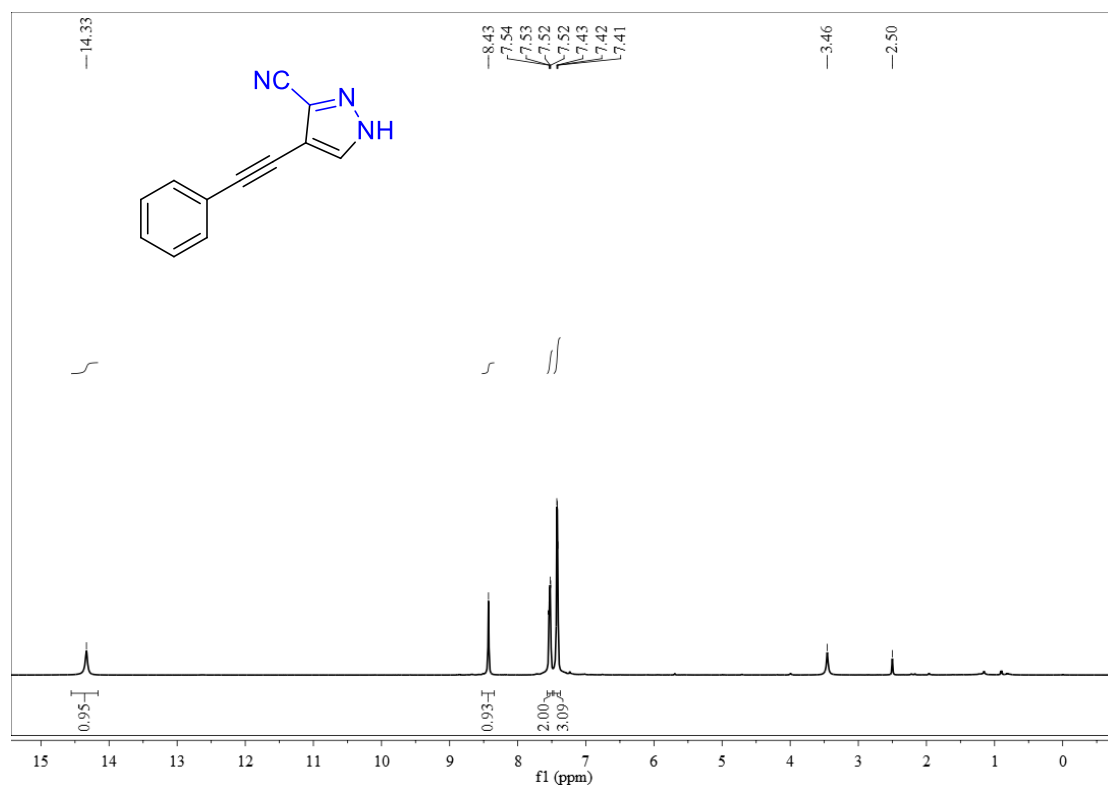
(E)-4-(4-Methoxystyryl)-1H-pyrazole-3-carbonitrile (2u)



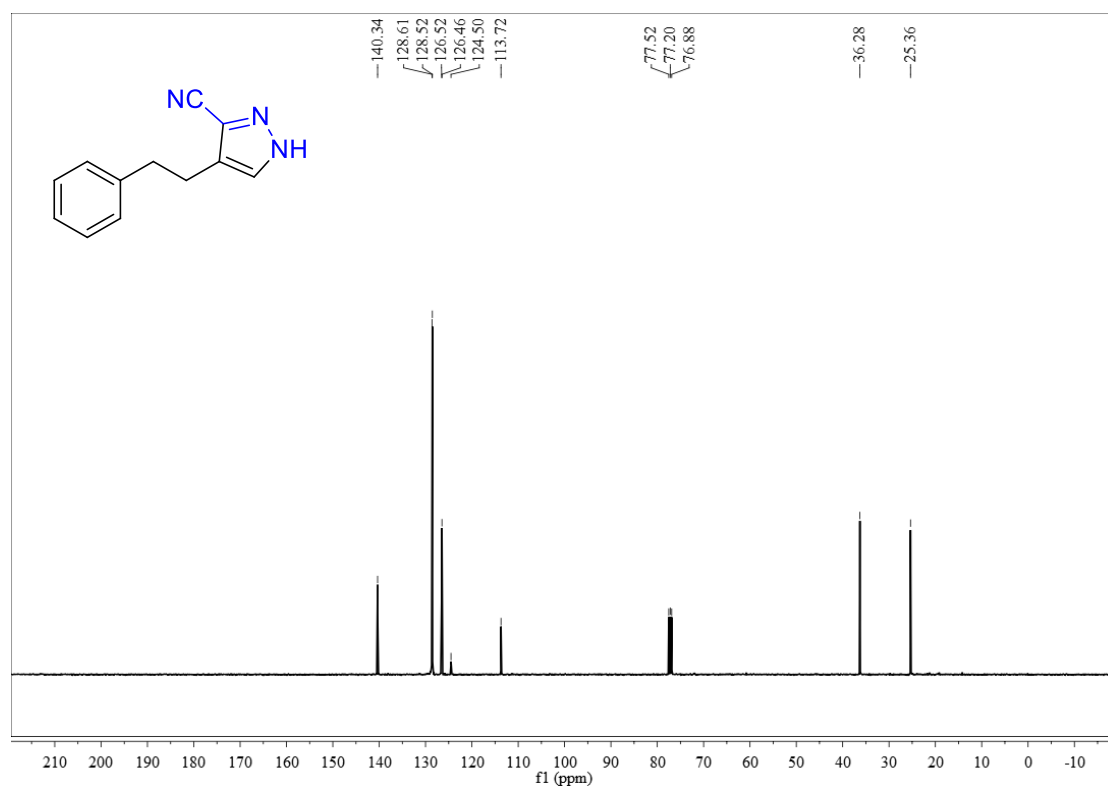
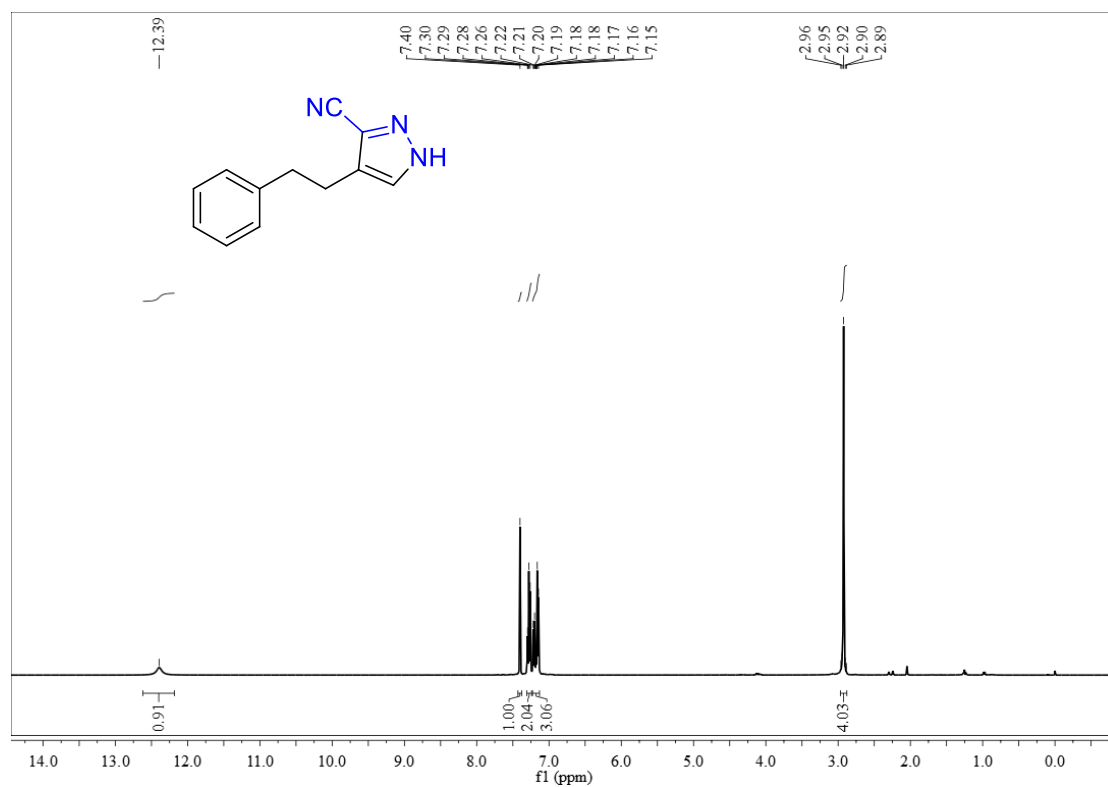
(E)-4-(2-Nitrophenyl)-1H-pyrazole-3-carbonitrile (2v)



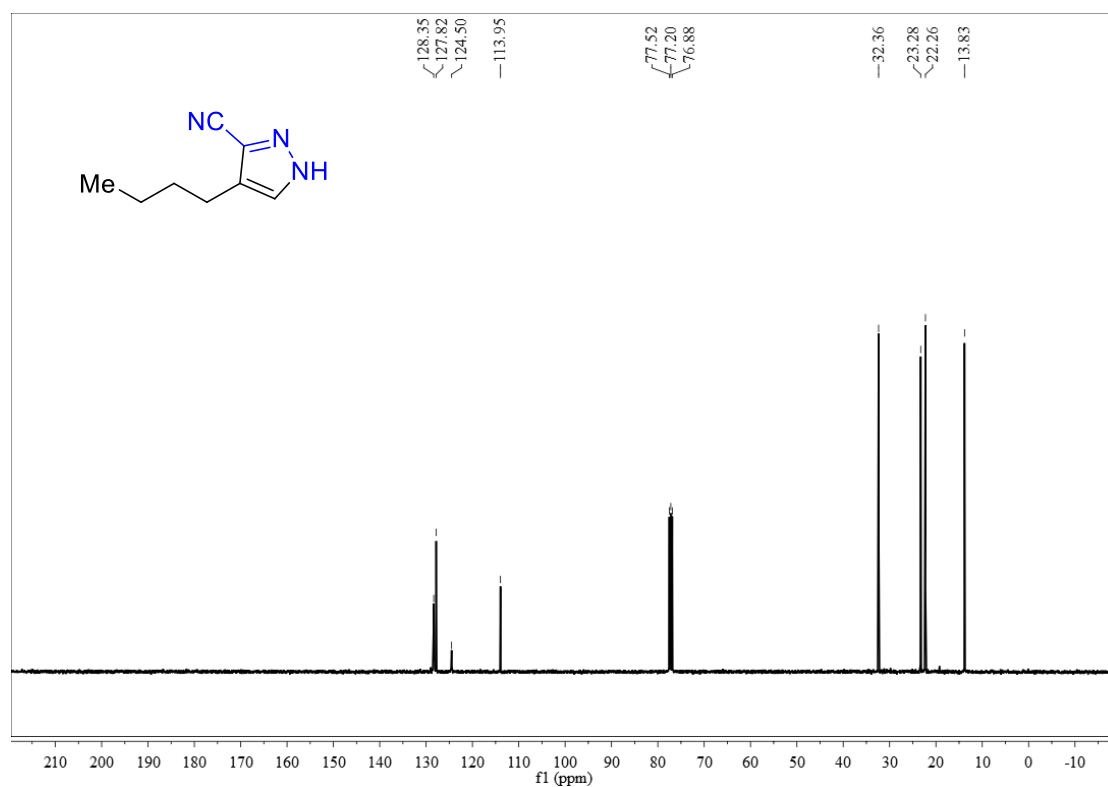
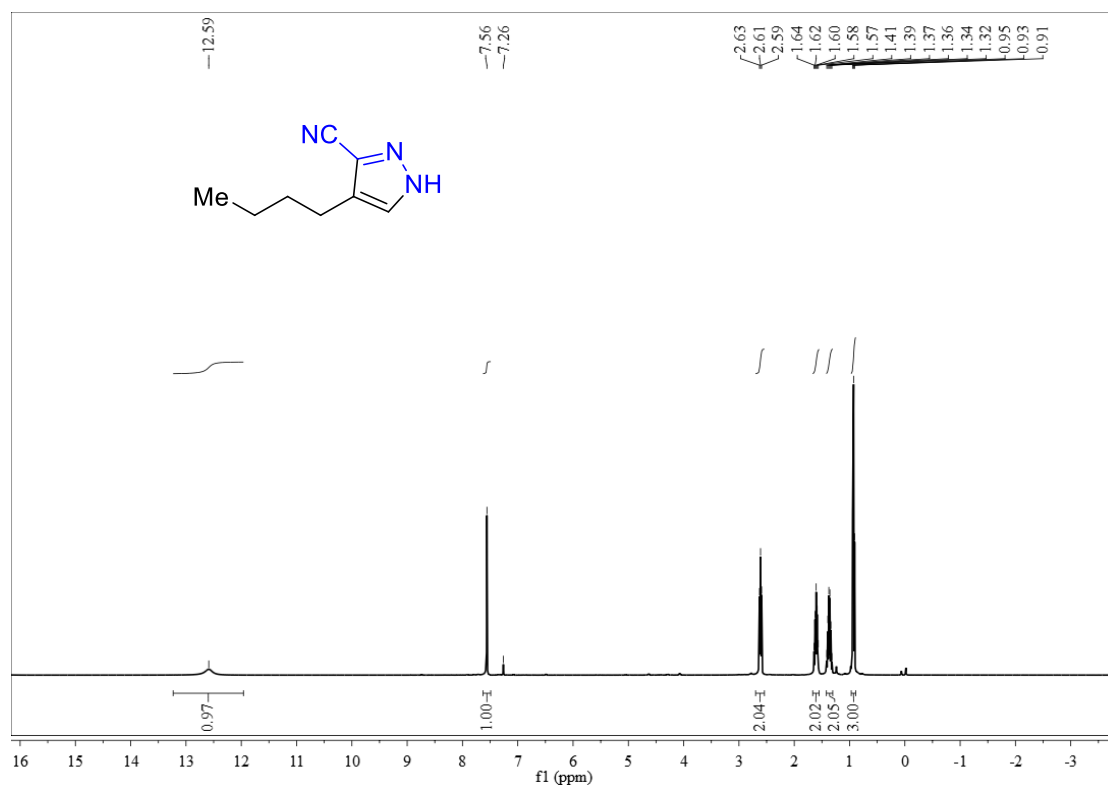
4-(Phenylethynyl)-1H-pyrazole-3-carbonitrile (2w)



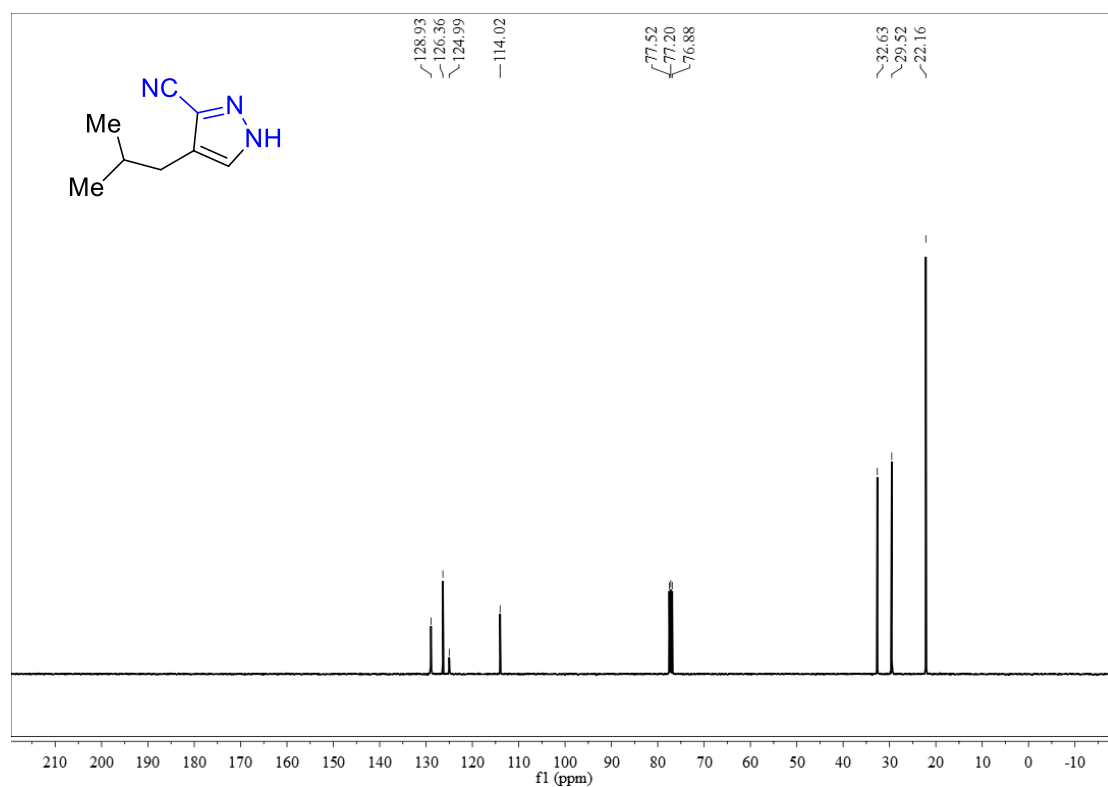
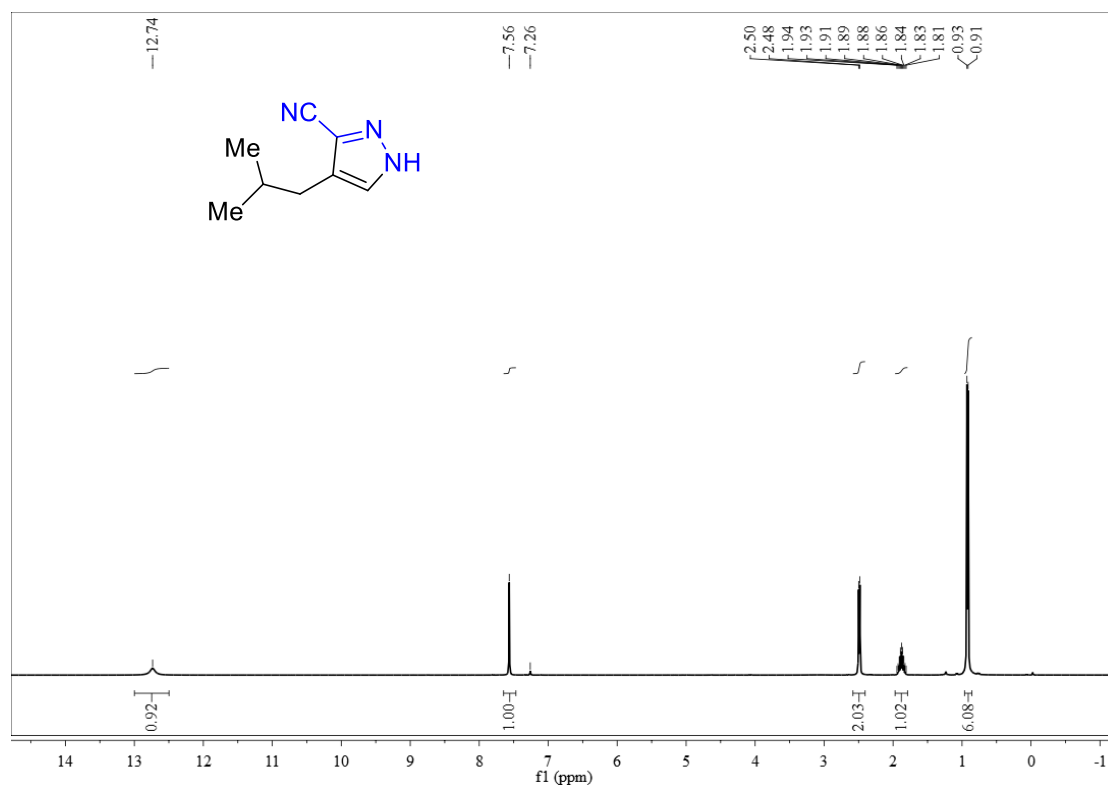
4-Phenethyl-1H-pyrazole-3-carbonitrile (2x)



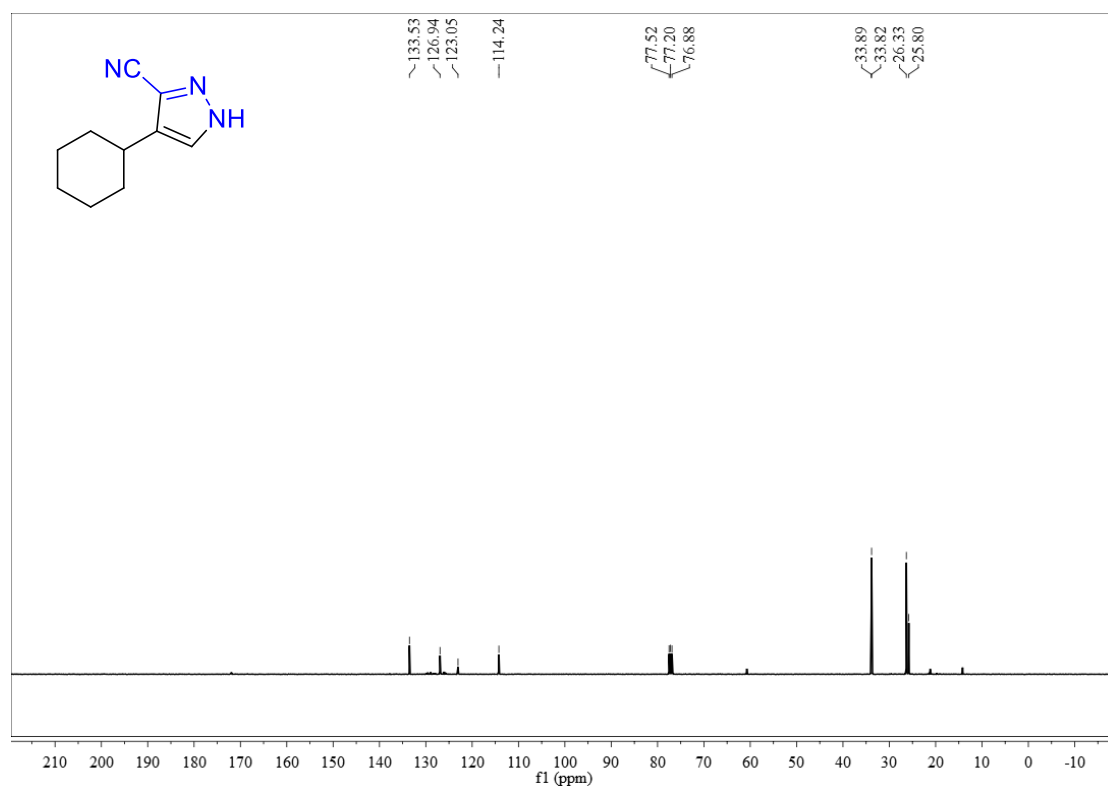
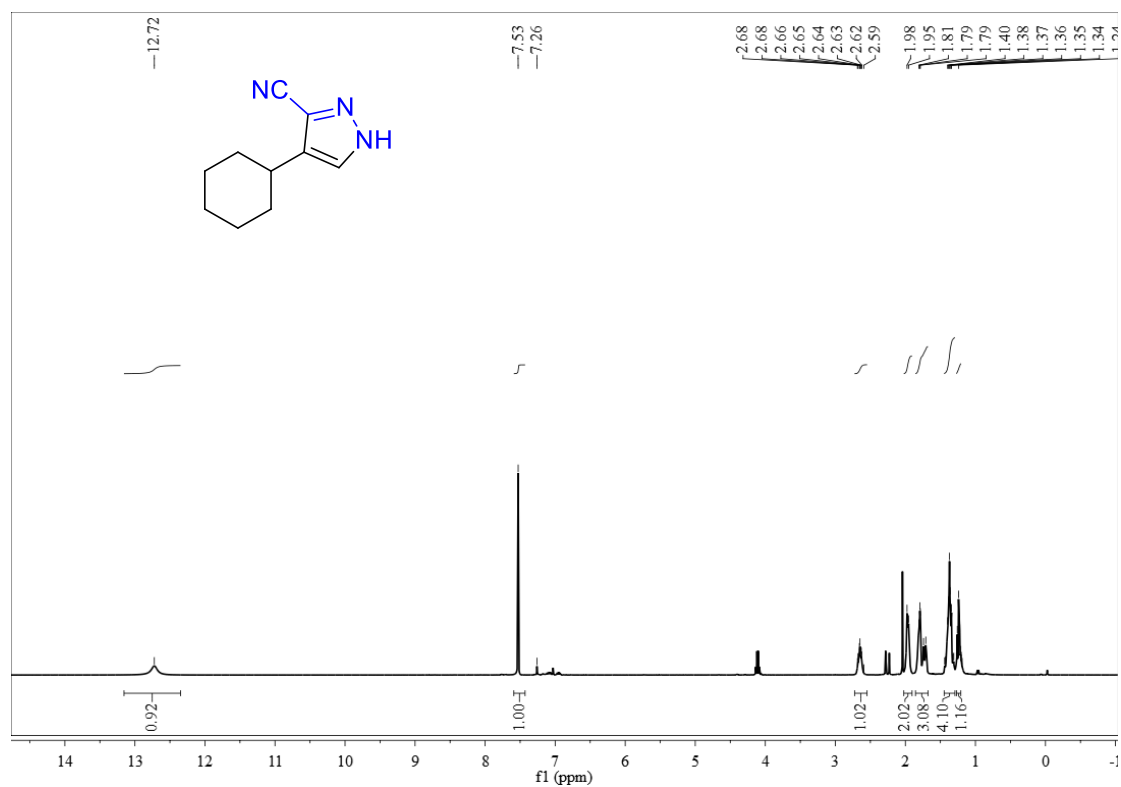
4-Butyl-1H-pyrazole-3-carbonitrile (2y)



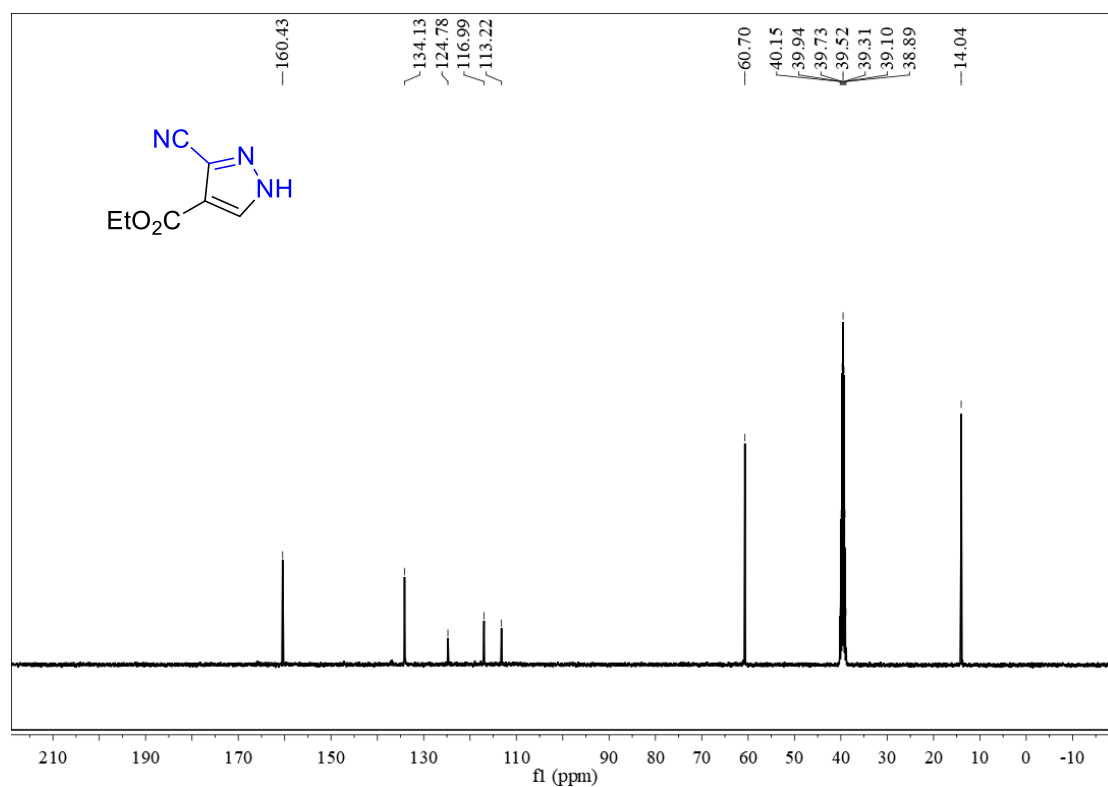
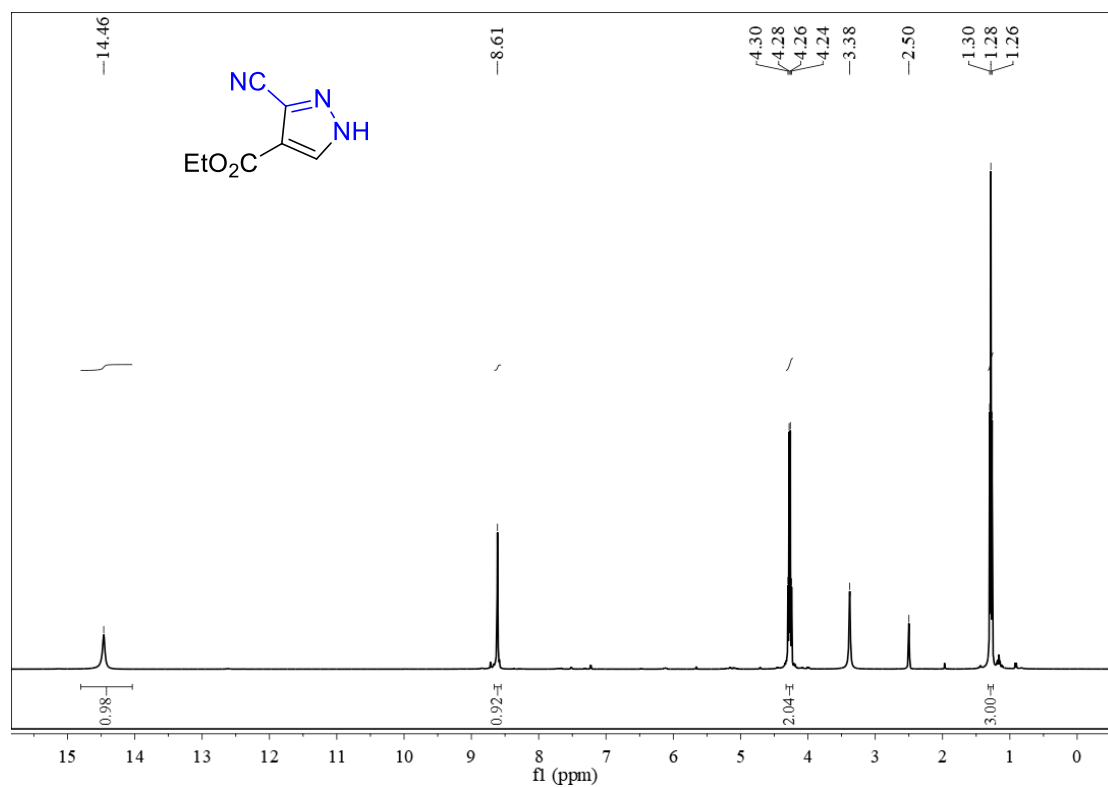
4-Isobutyl-1H-pyrazole-3-carbonitrile (2z)



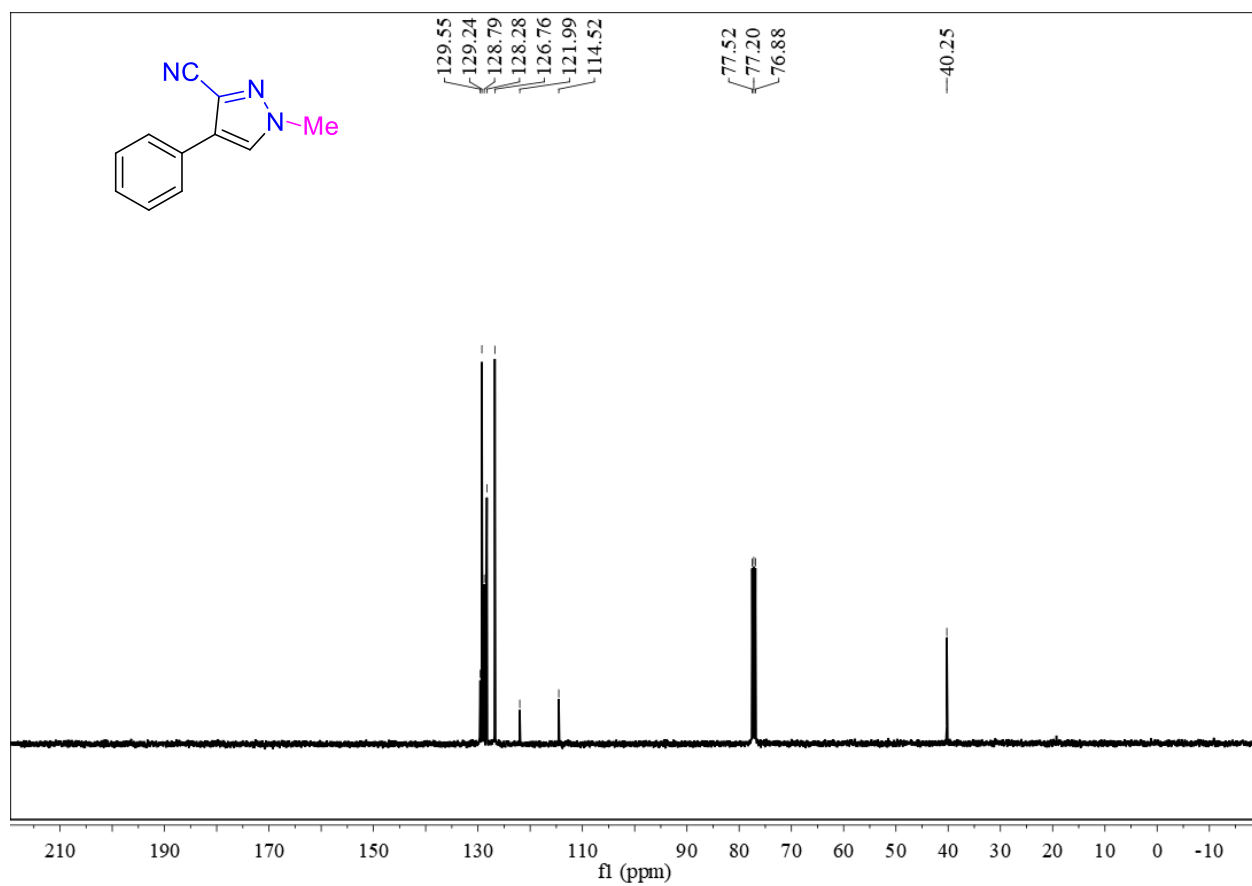
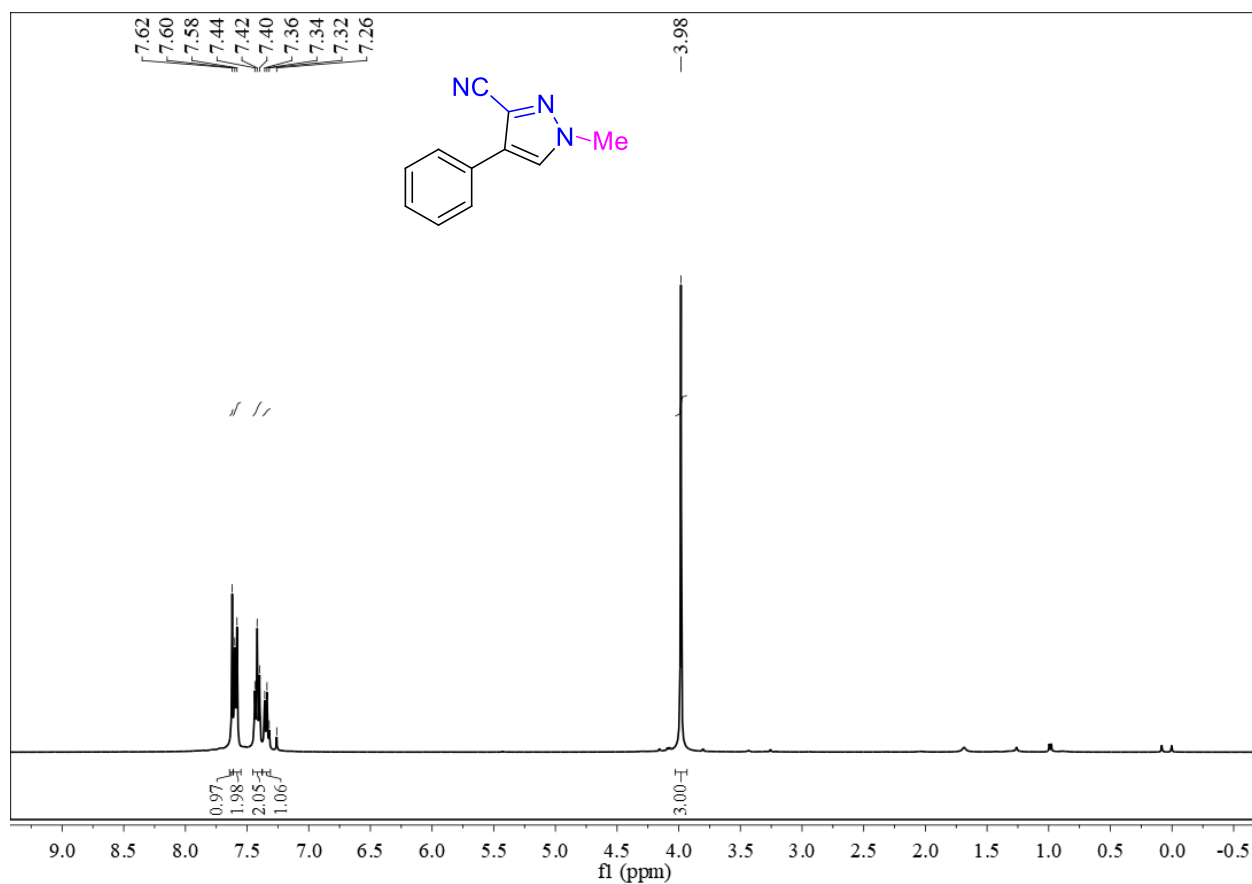
4-Cyclohexyl-1H-pyrazole-3-carbonitrile (2a')



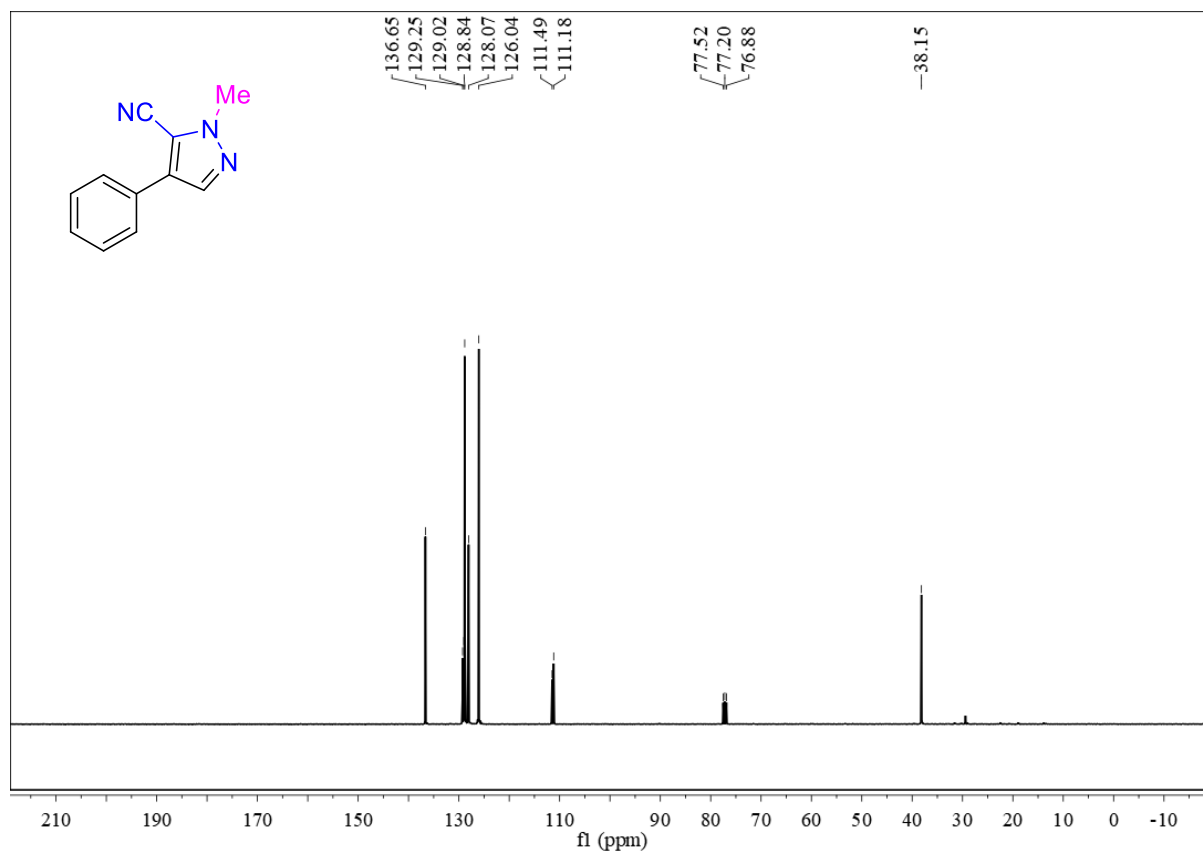
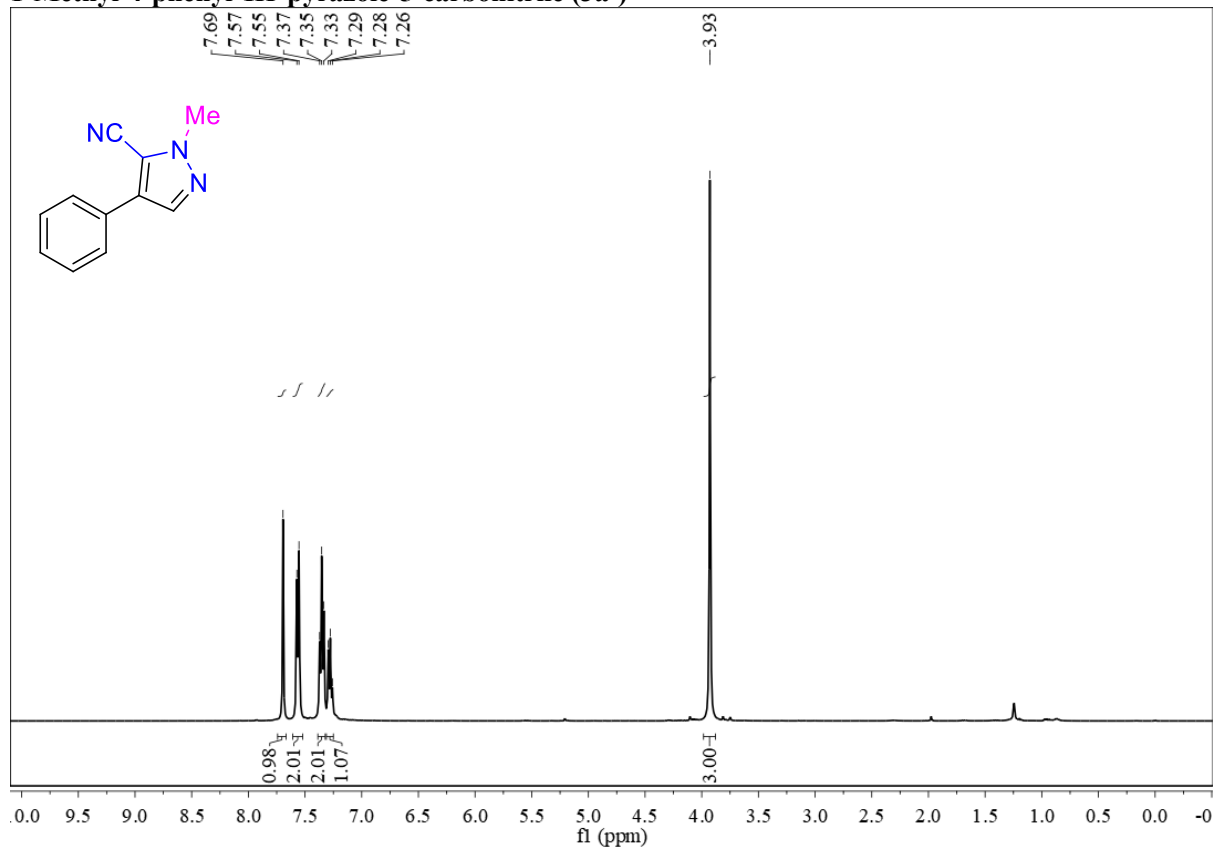
Ethyl 3-cyano-1H-pyrazole-4-carboxylate (2b')



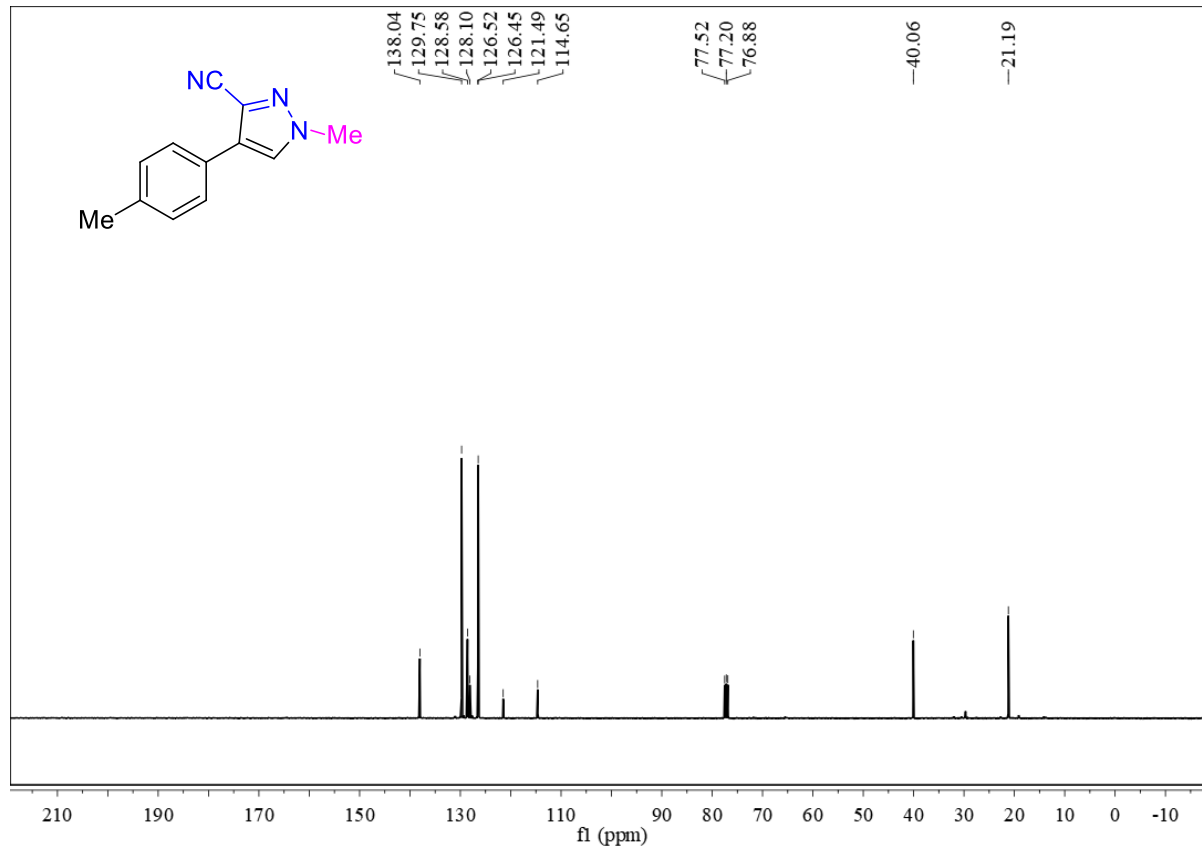
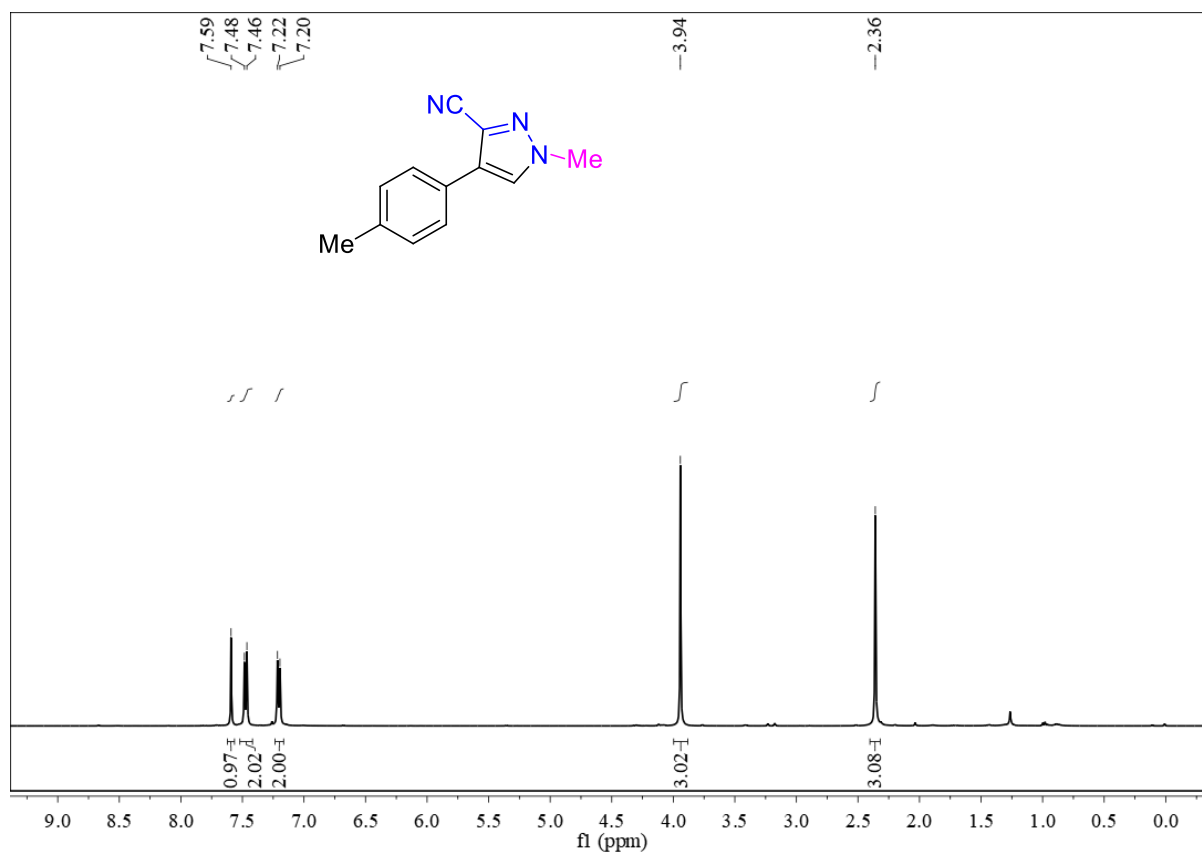
1-Methyl-4-phenyl-1H-pyrazole-3-carbonitrile (3a)



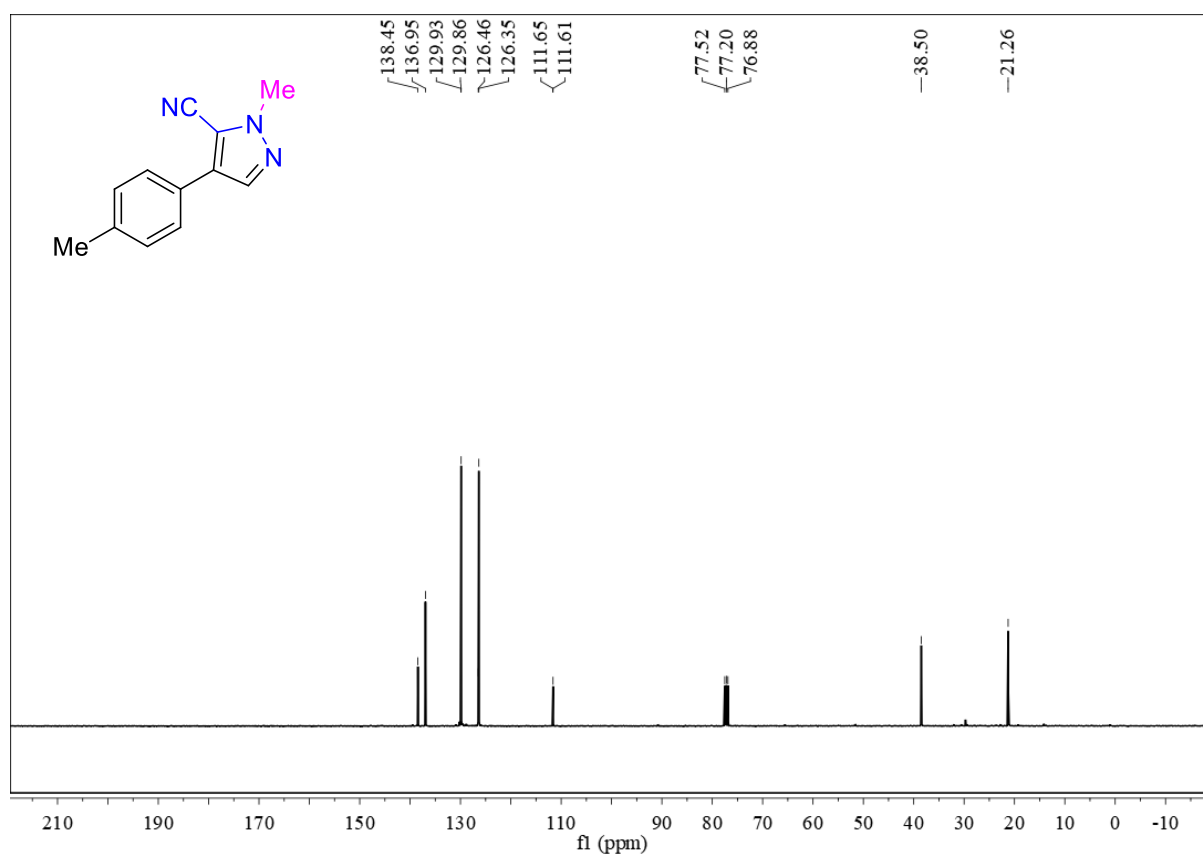
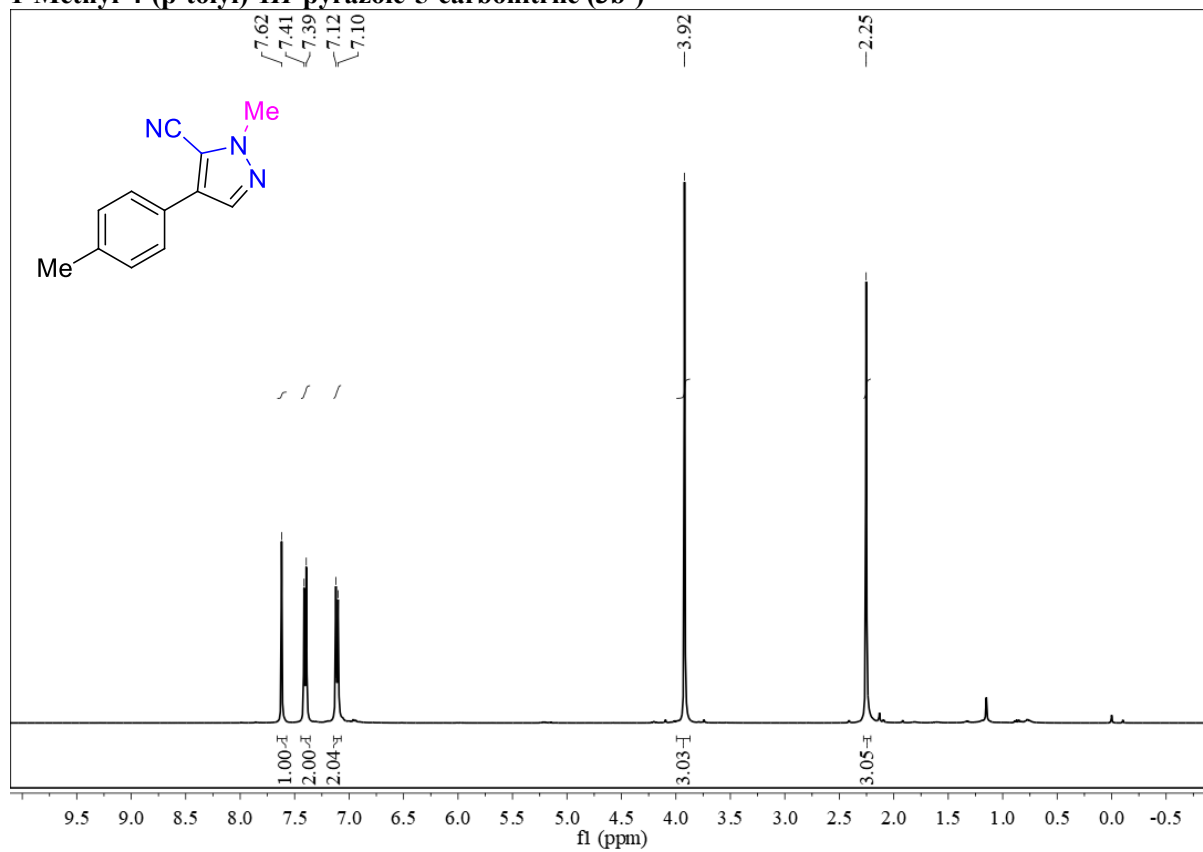
1-Methyl-4-phenyl-1H-pyrazole-5-carbonitrile (3a')



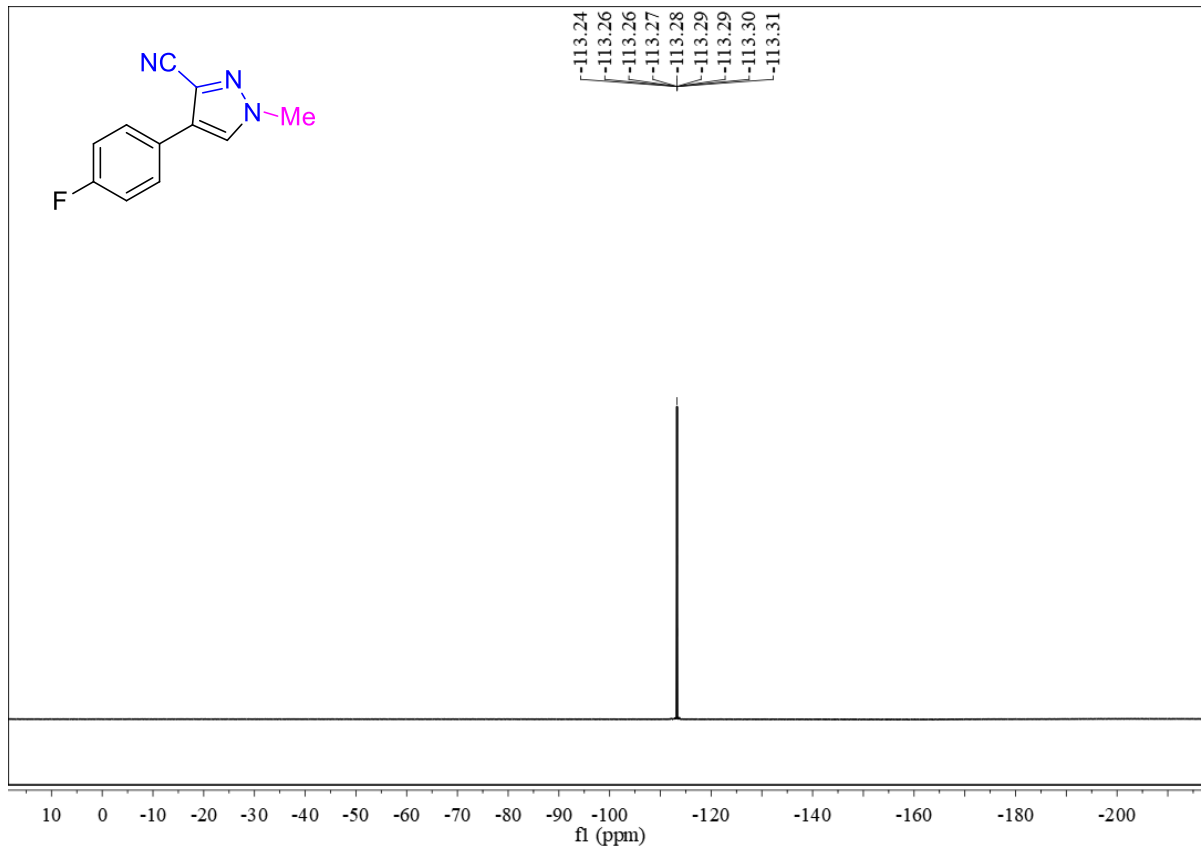
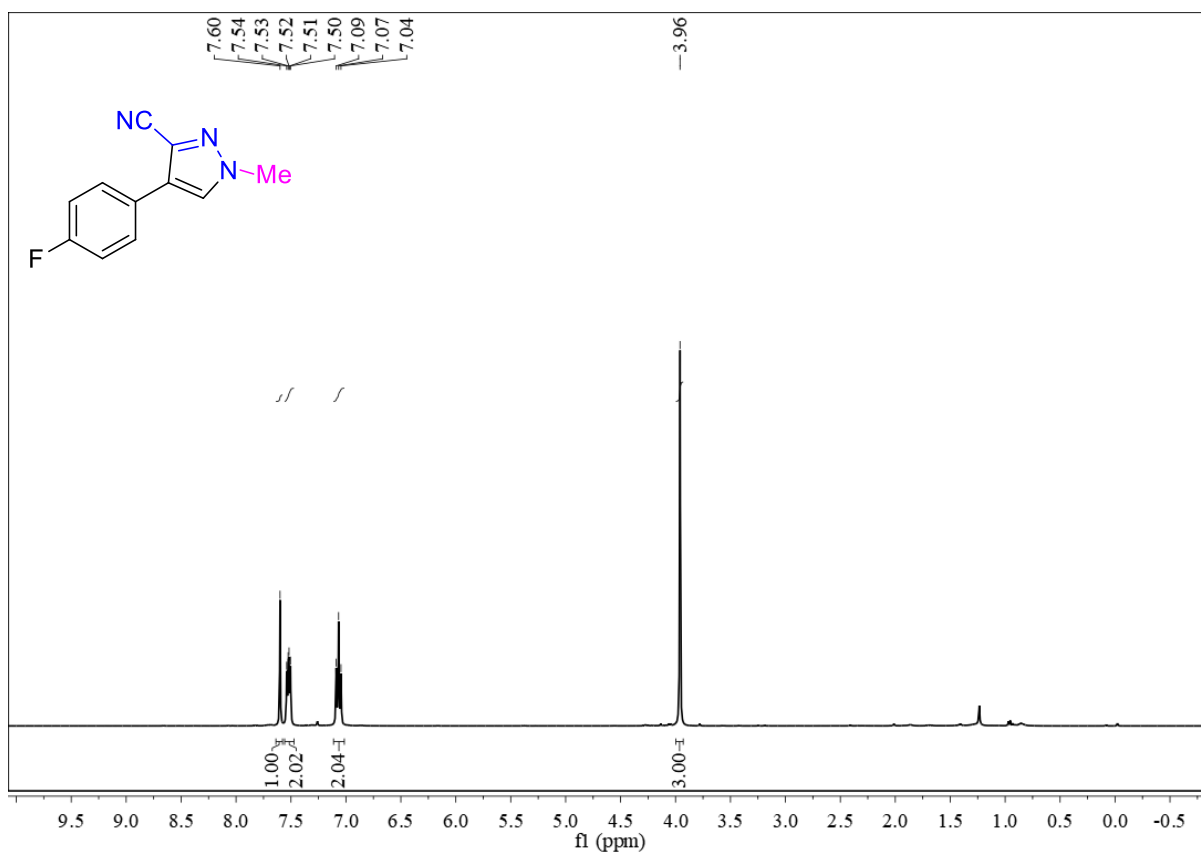
1-Methyl-4-(p-tolyl)-1H-pyrazole-3-carbonitrile (3b)

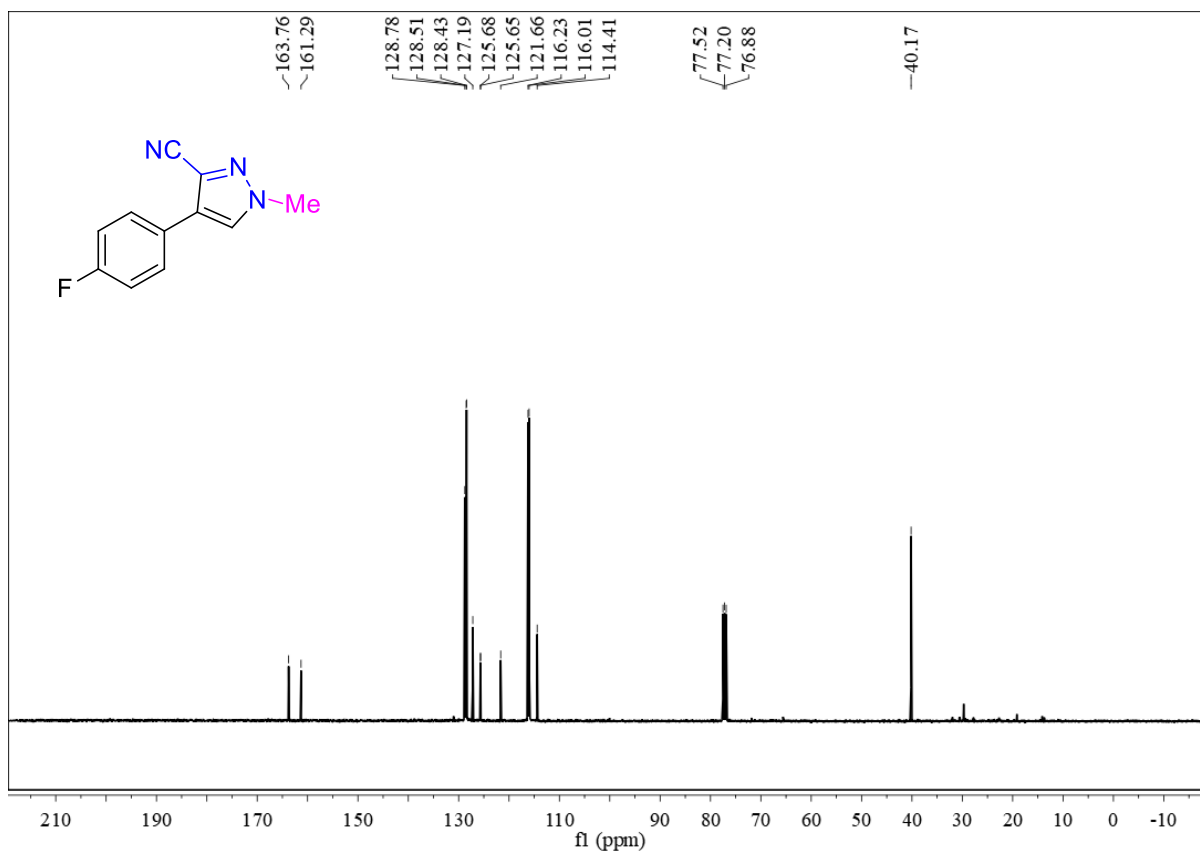


1-Methyl-4-(p-tolyl)-1H-pyrazole-5-carbonitrile (3b')

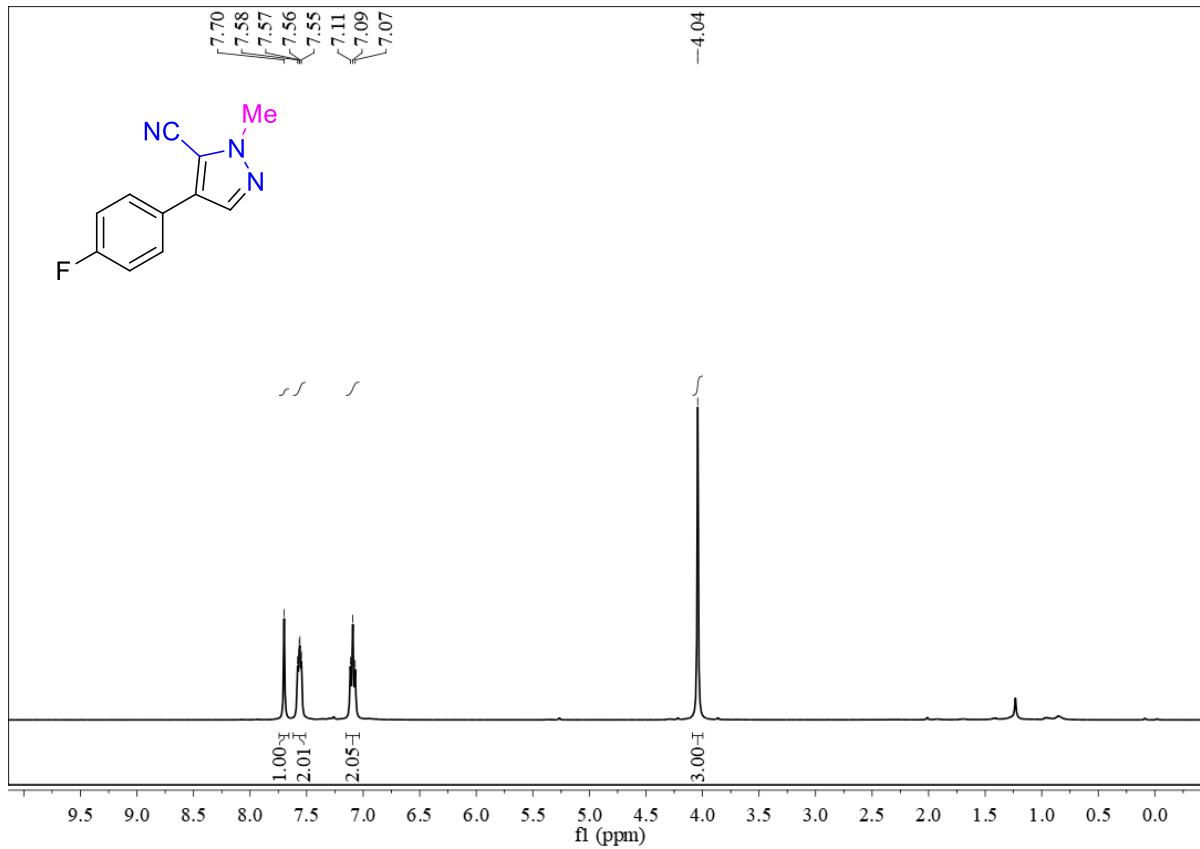


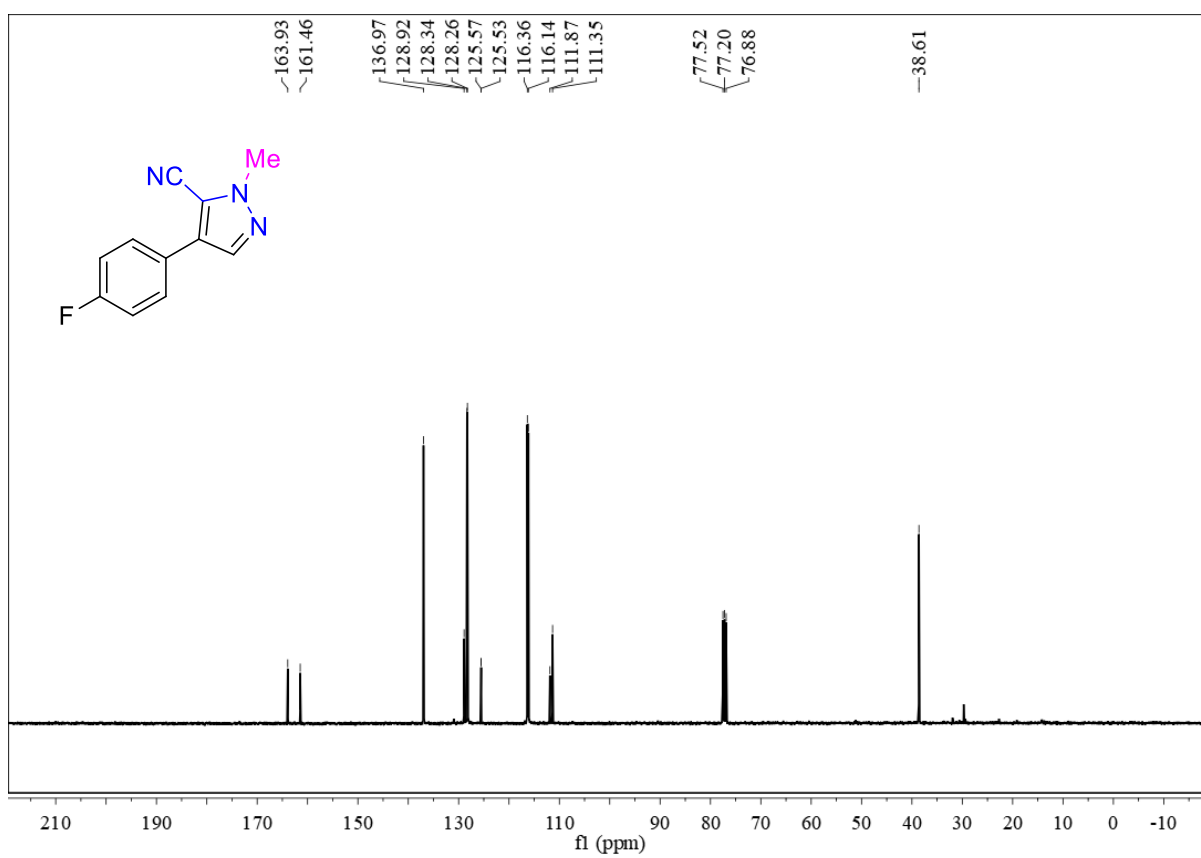
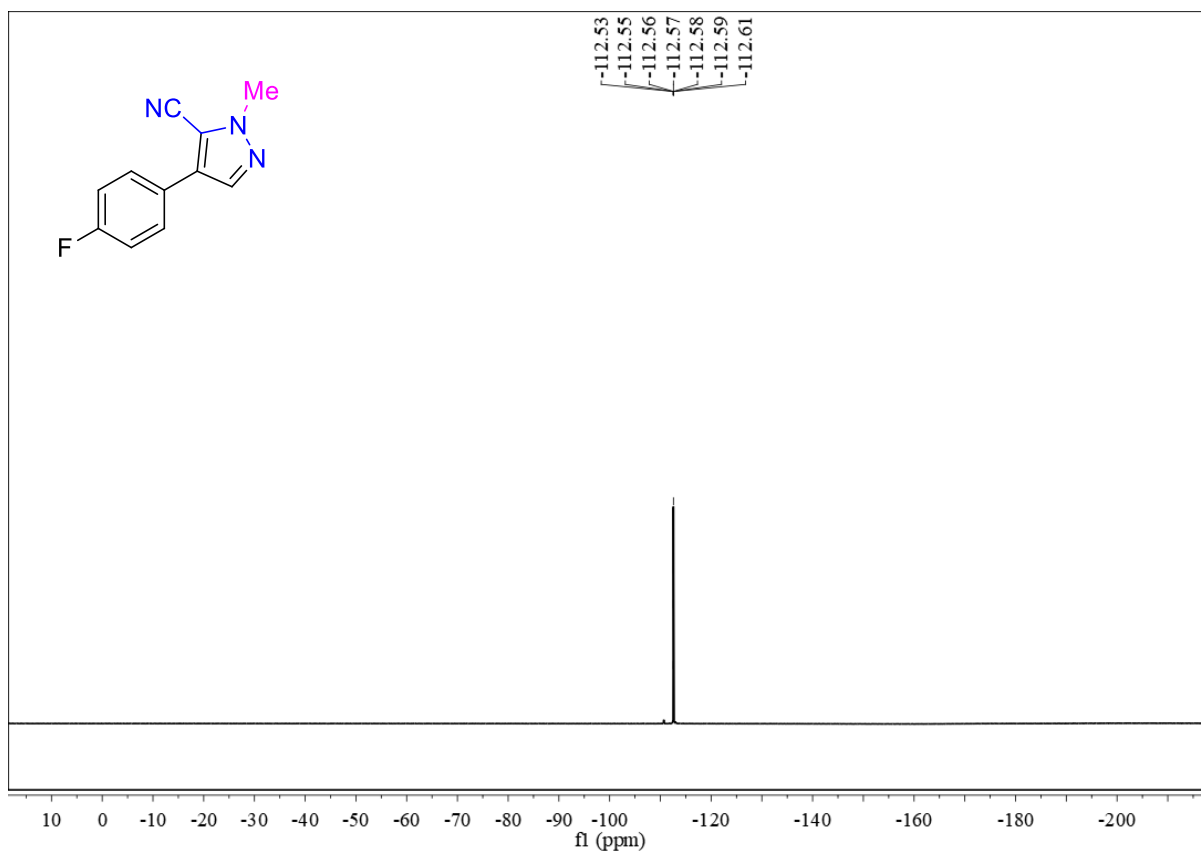
4-(4-Fluorophenyl)-1-methyl-1H-pyrazole-3-carbonitrile (3c)



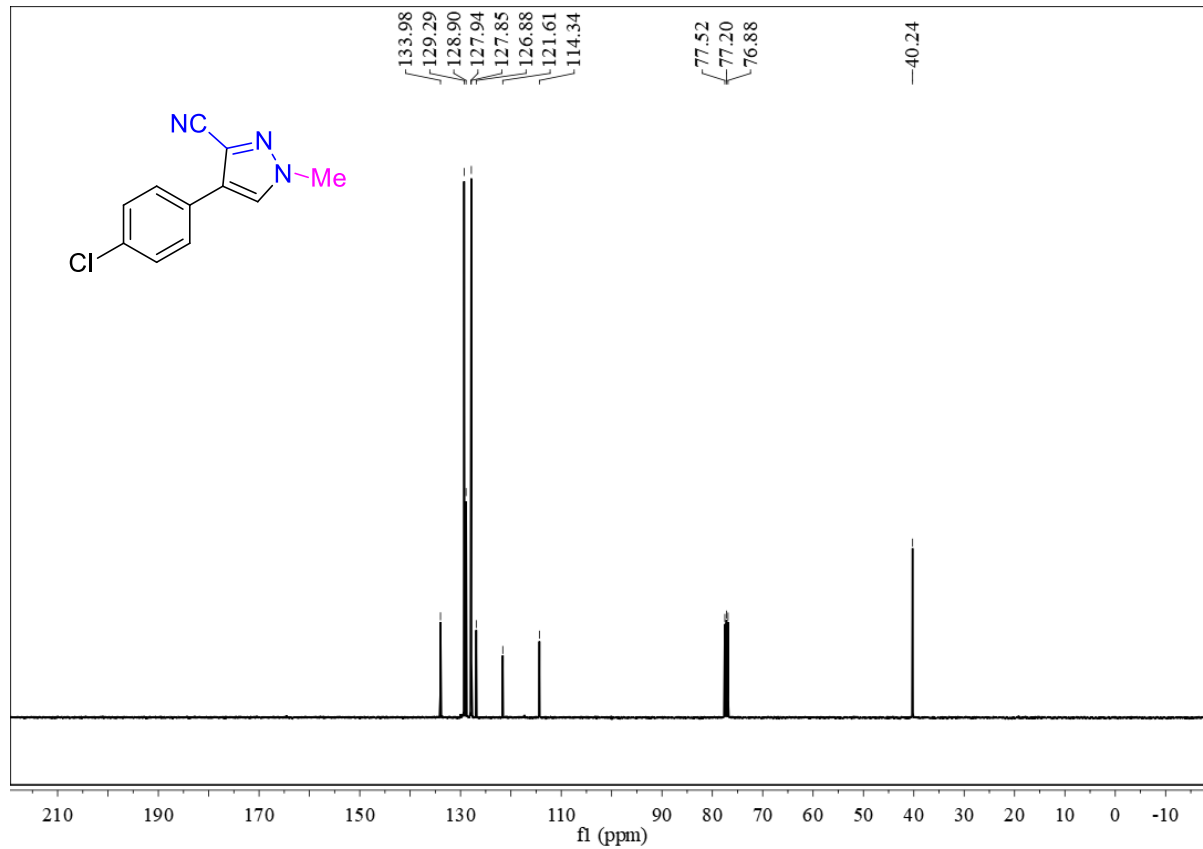
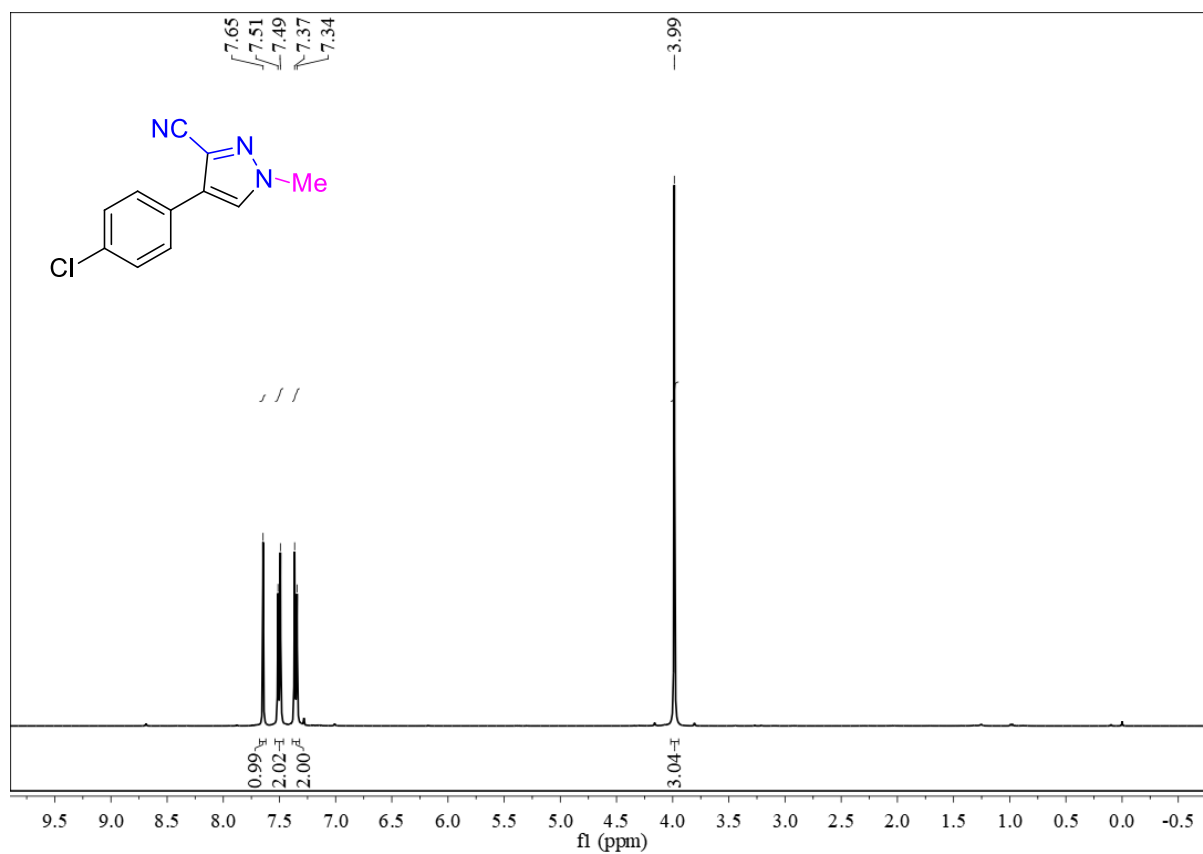


4-(4-Fluorophenyl)-1-methyl-1H-pyrazole-5-carbonitrile (3c')

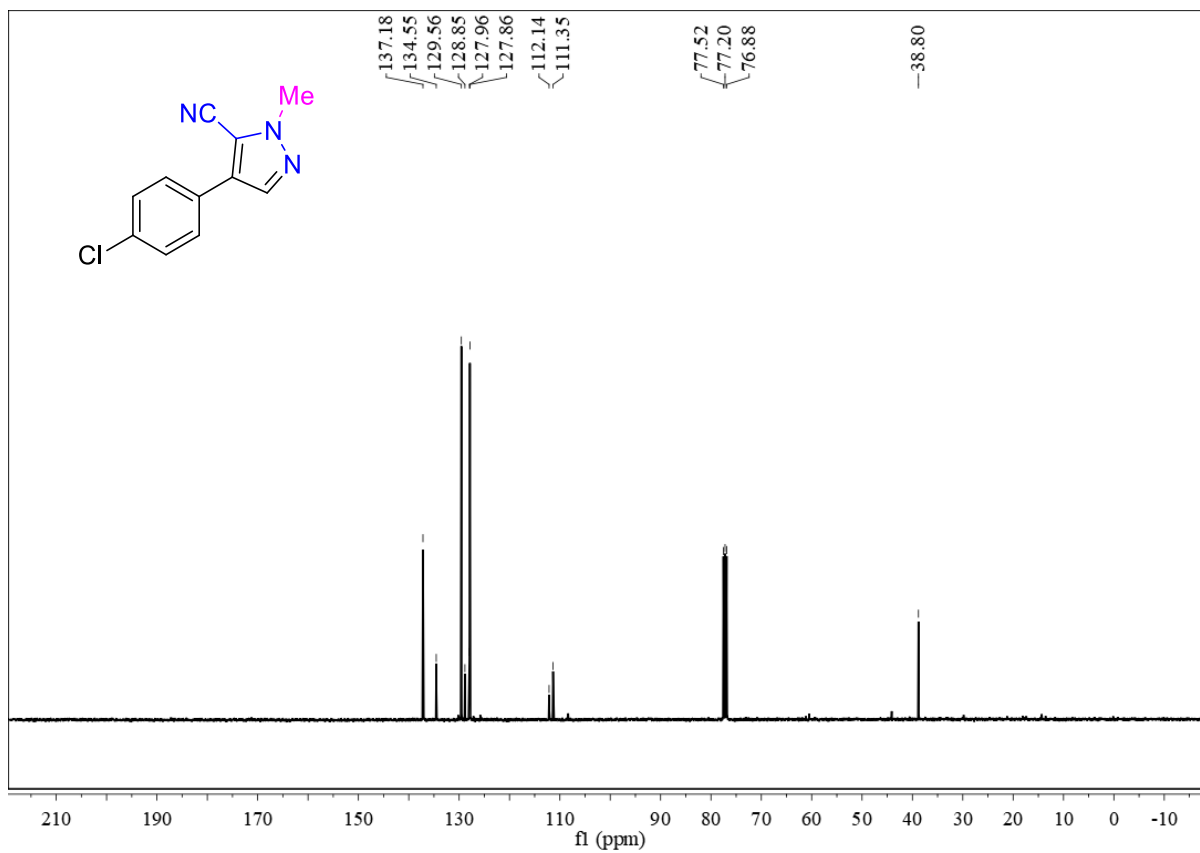
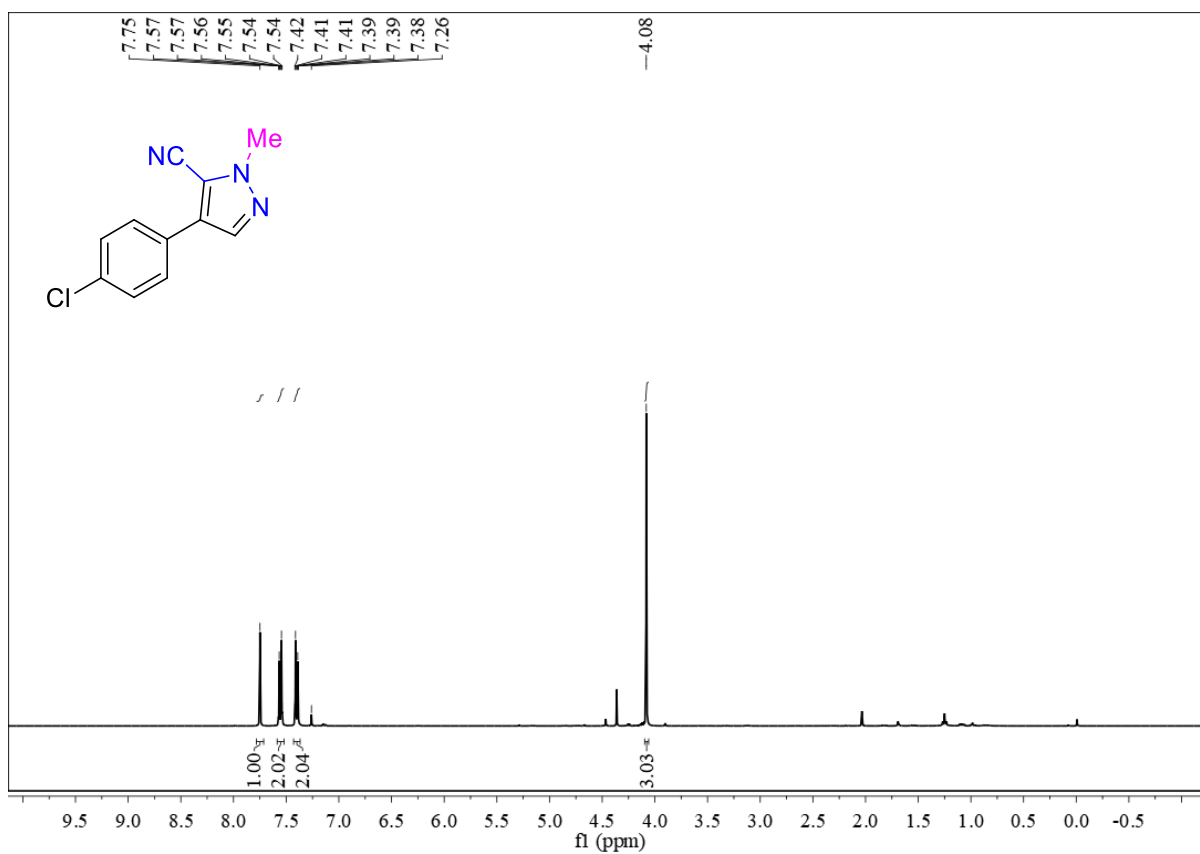




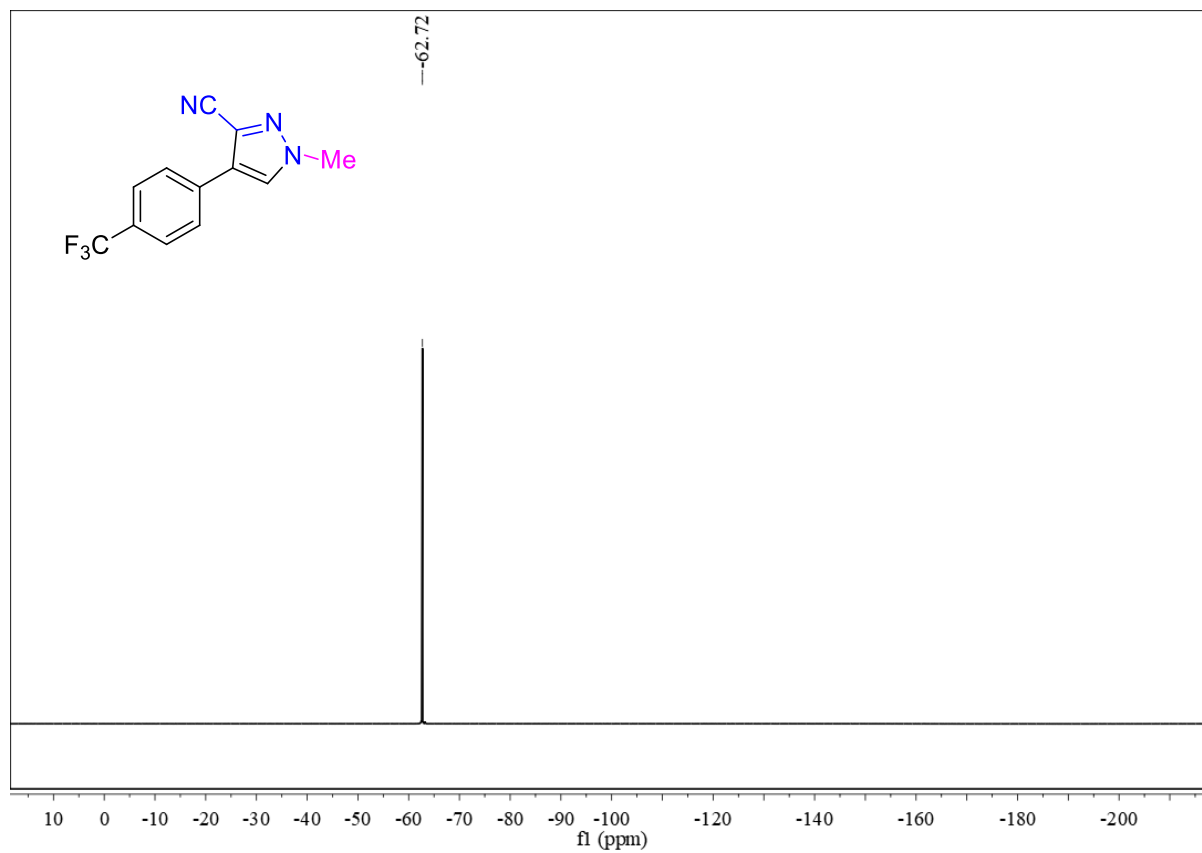
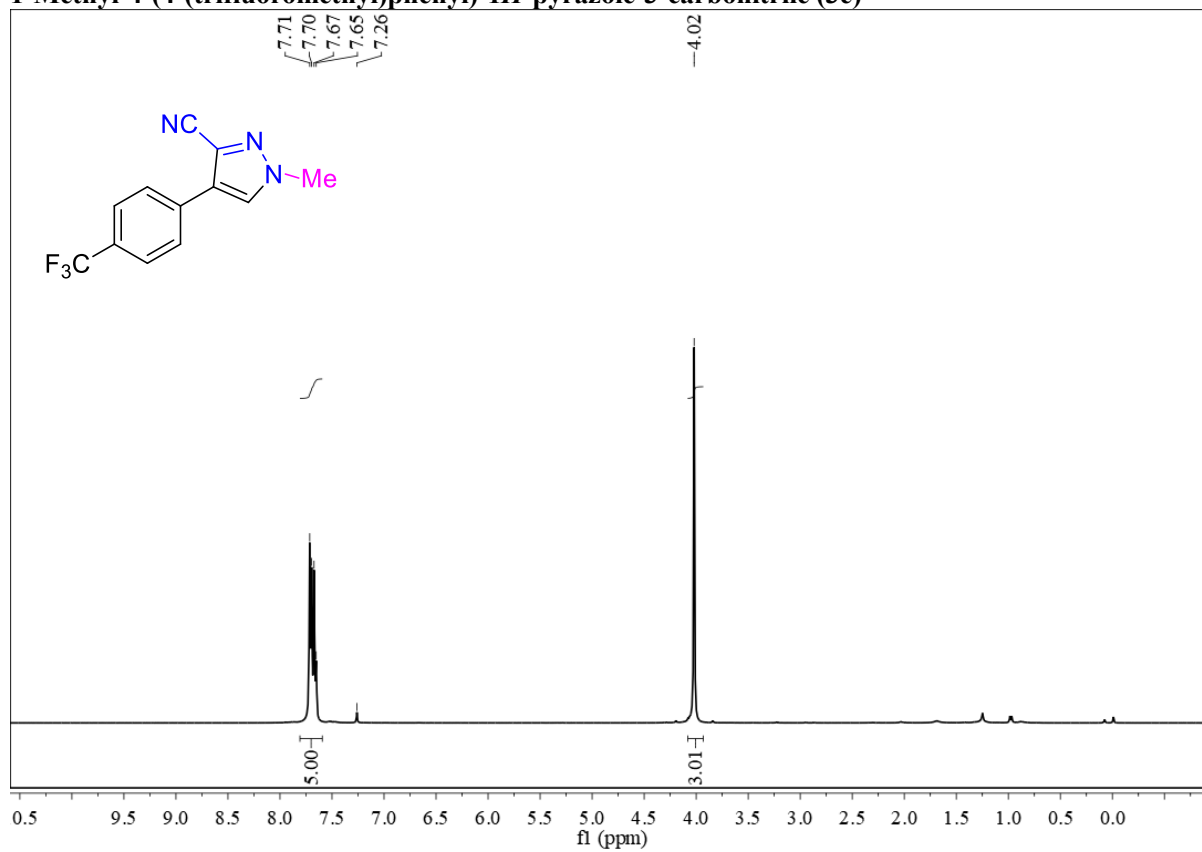
4-(4-Chlorophenyl)-1-methyl-1H-pyrazole-3-carbonitrile (3d)

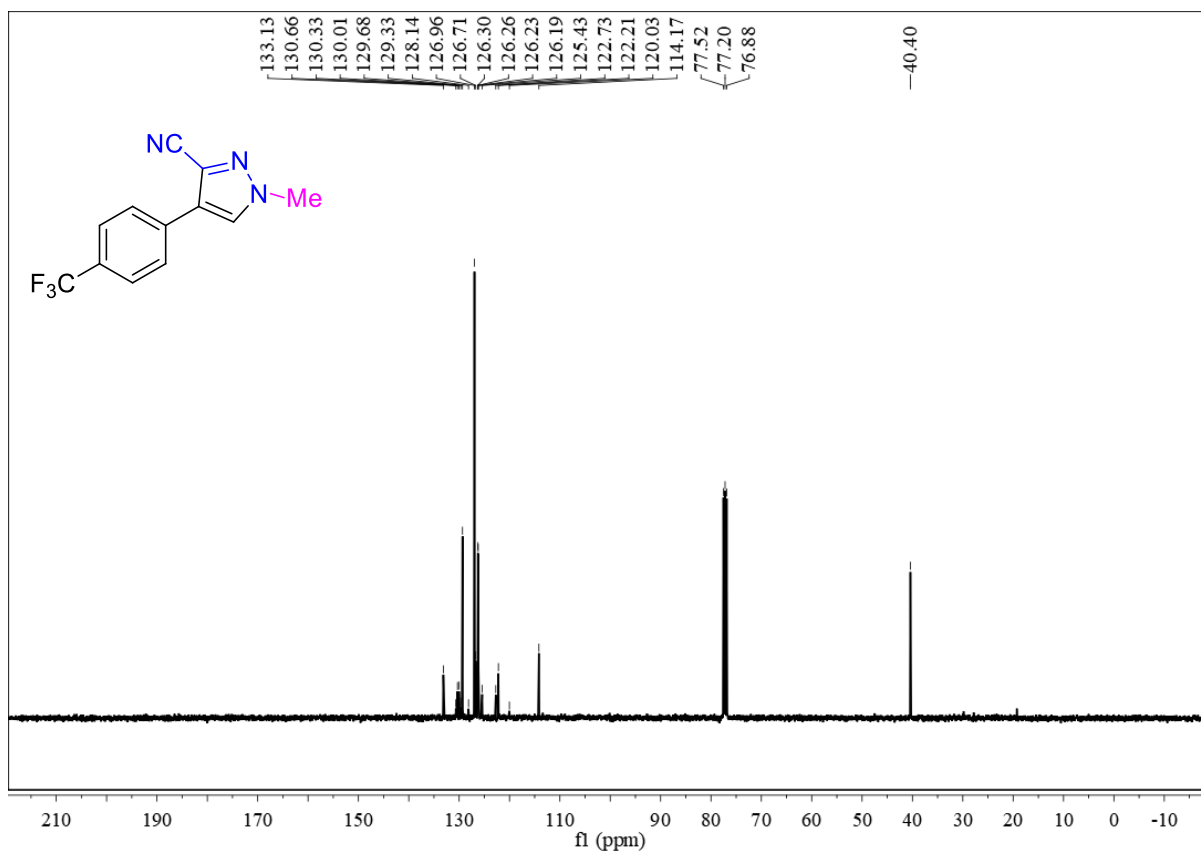


4-(4-Chlorophenyl)-1-methyl-1H-pyrazole-5-carbonitrile (3d³)

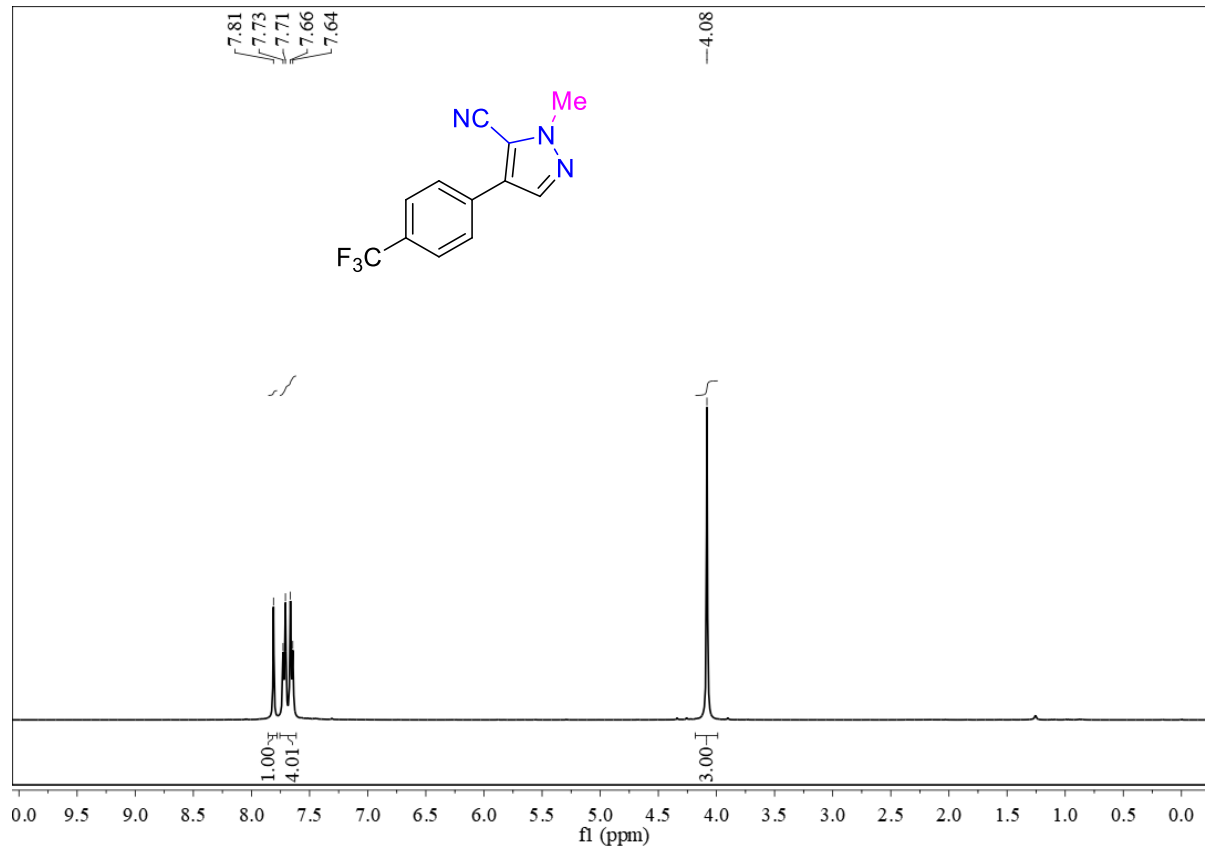


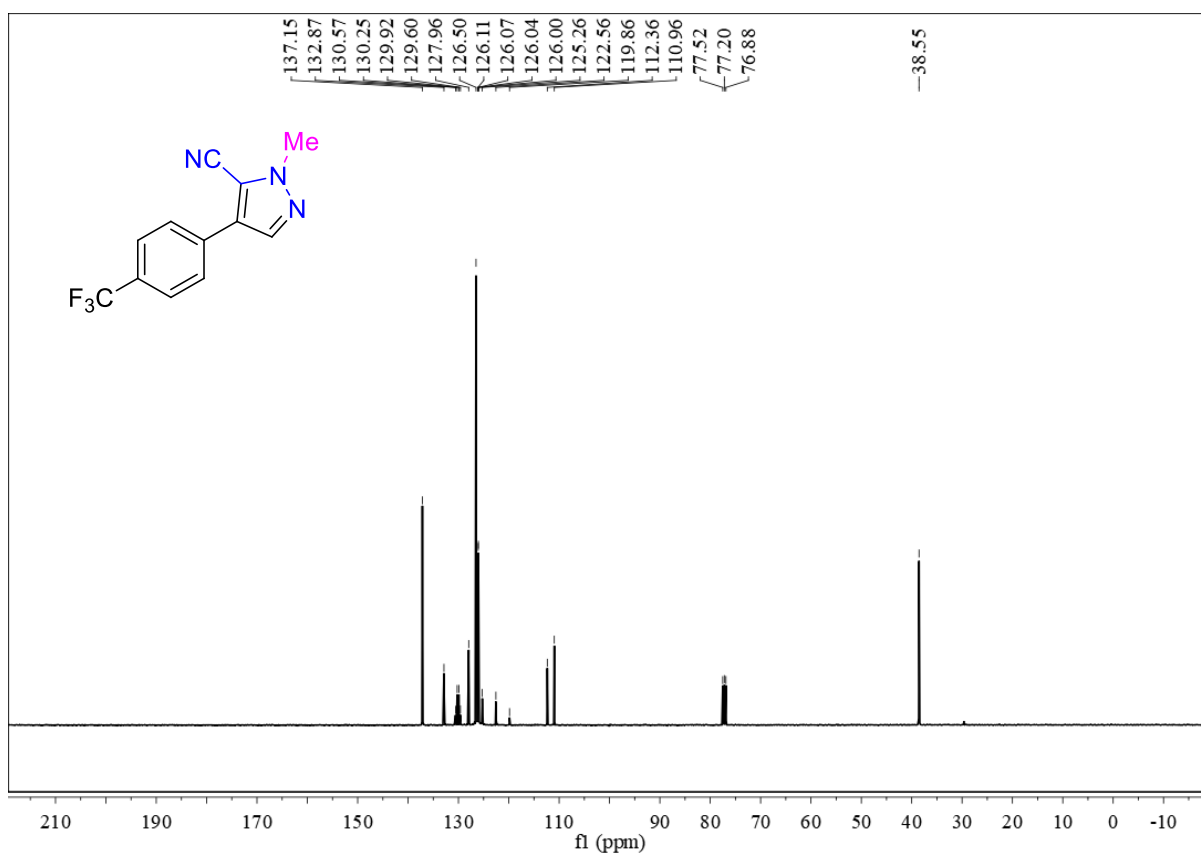
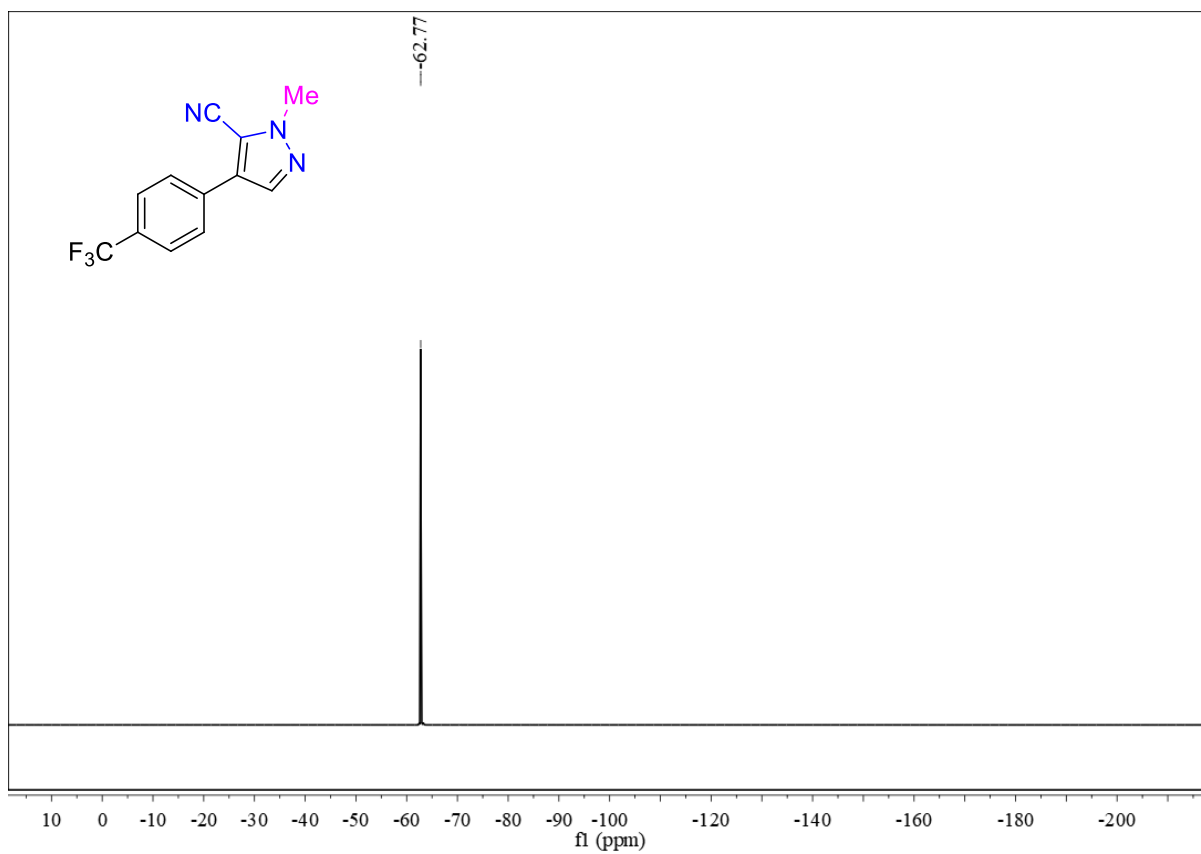
1-Methyl-4-(4-(trifluoromethyl)phenyl)-1H-pyrazole-3-carbonitrile (3e)



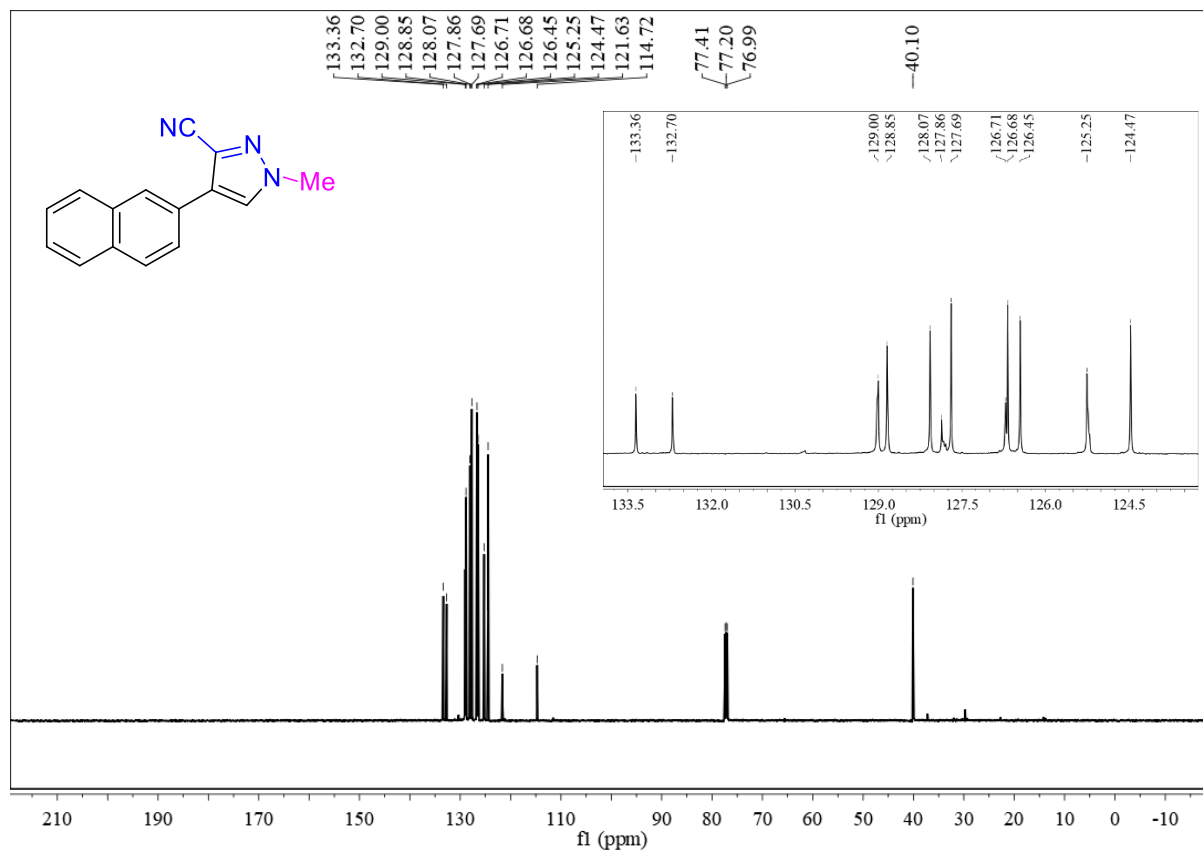
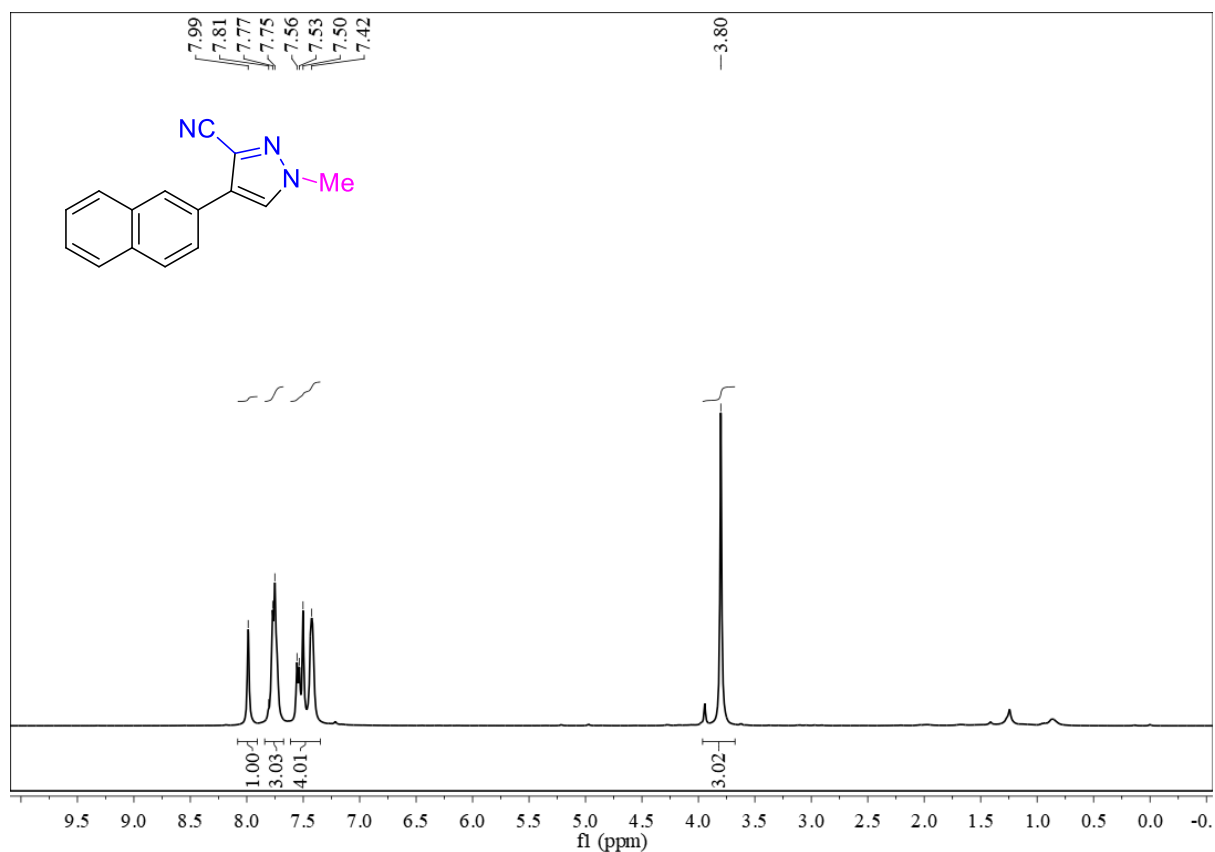


1-Methyl-4-(4-(trifluoromethyl)phenyl)-1H-pyrazole-5-carbonitrile (3e')

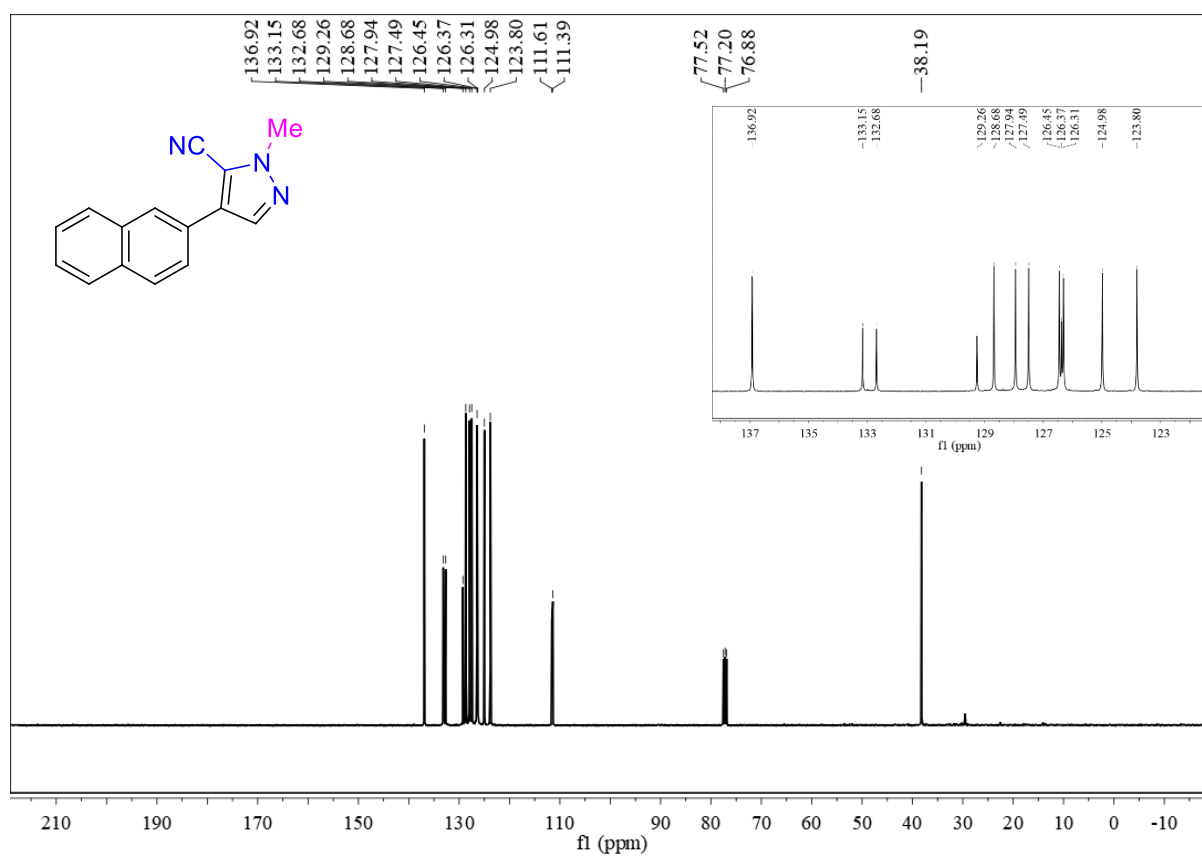
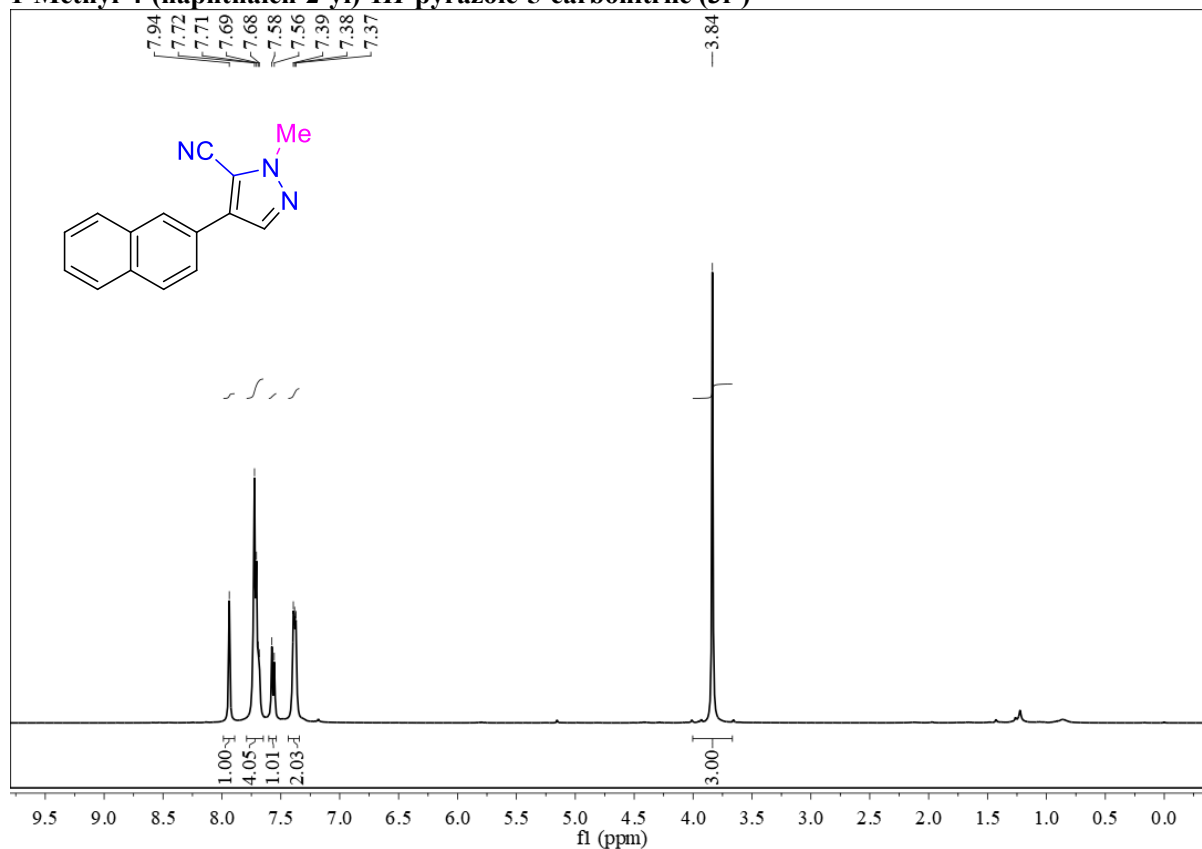




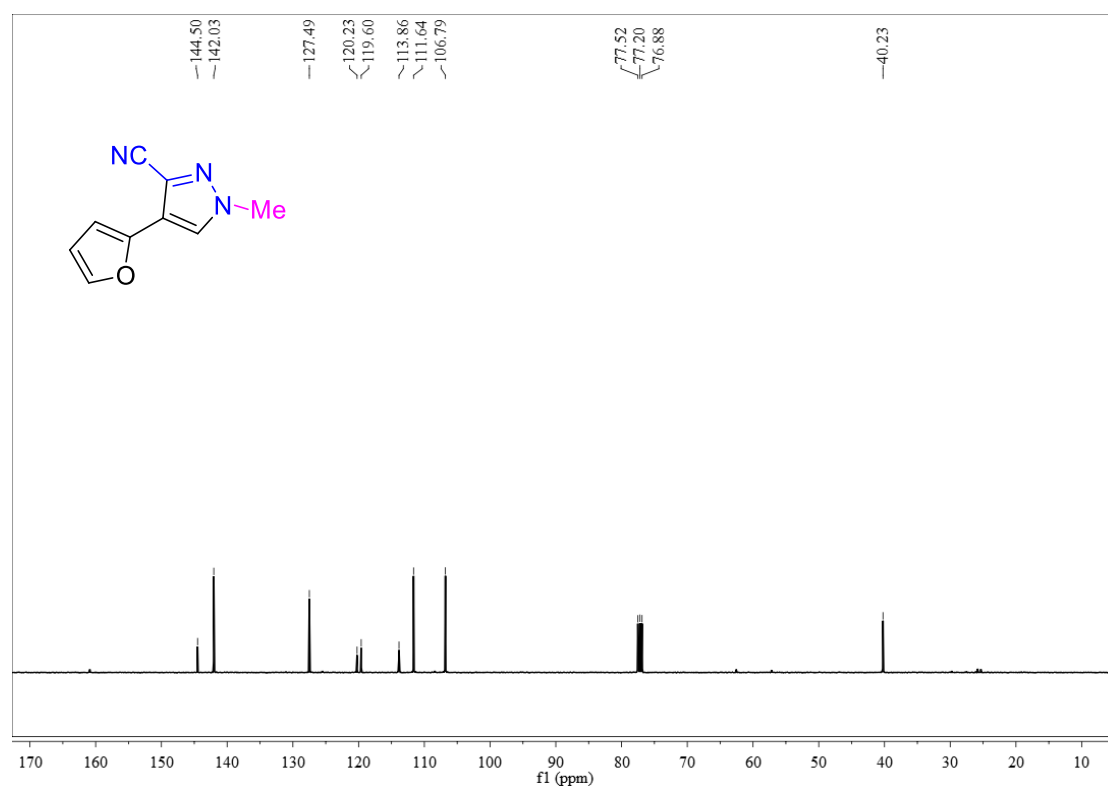
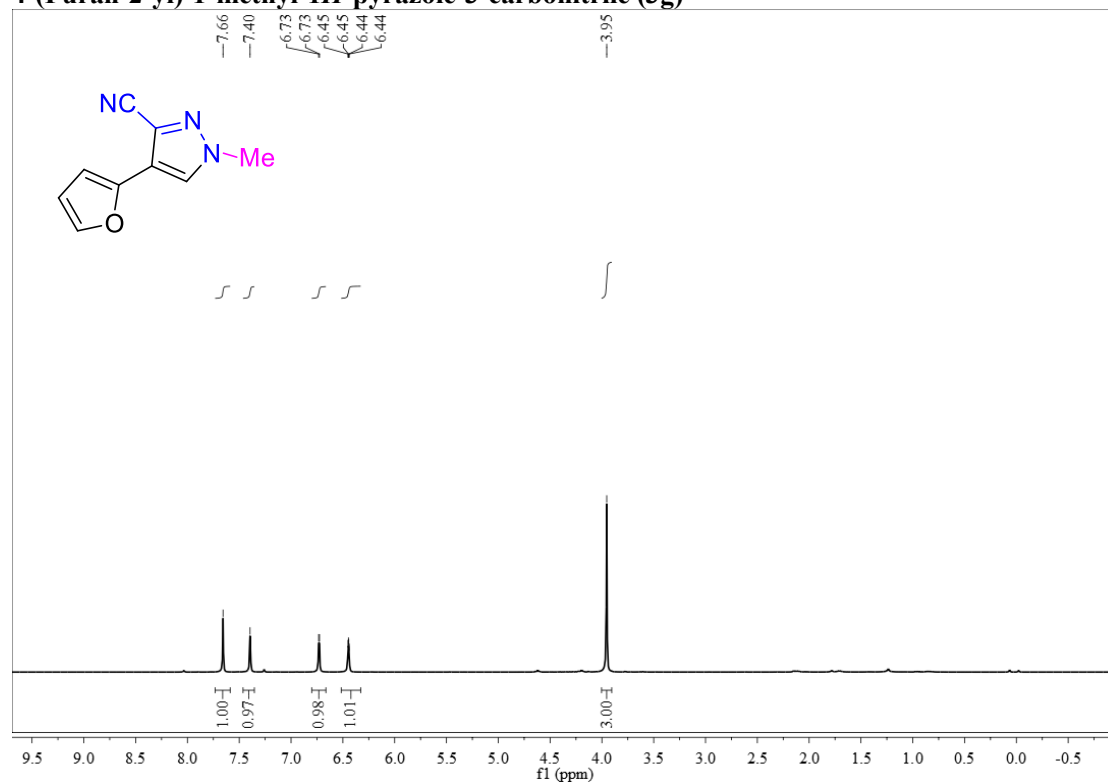
1-Methyl-4-(naphthalen-2-yl)-1H-pyrazole-3-carbonitrile (3f)



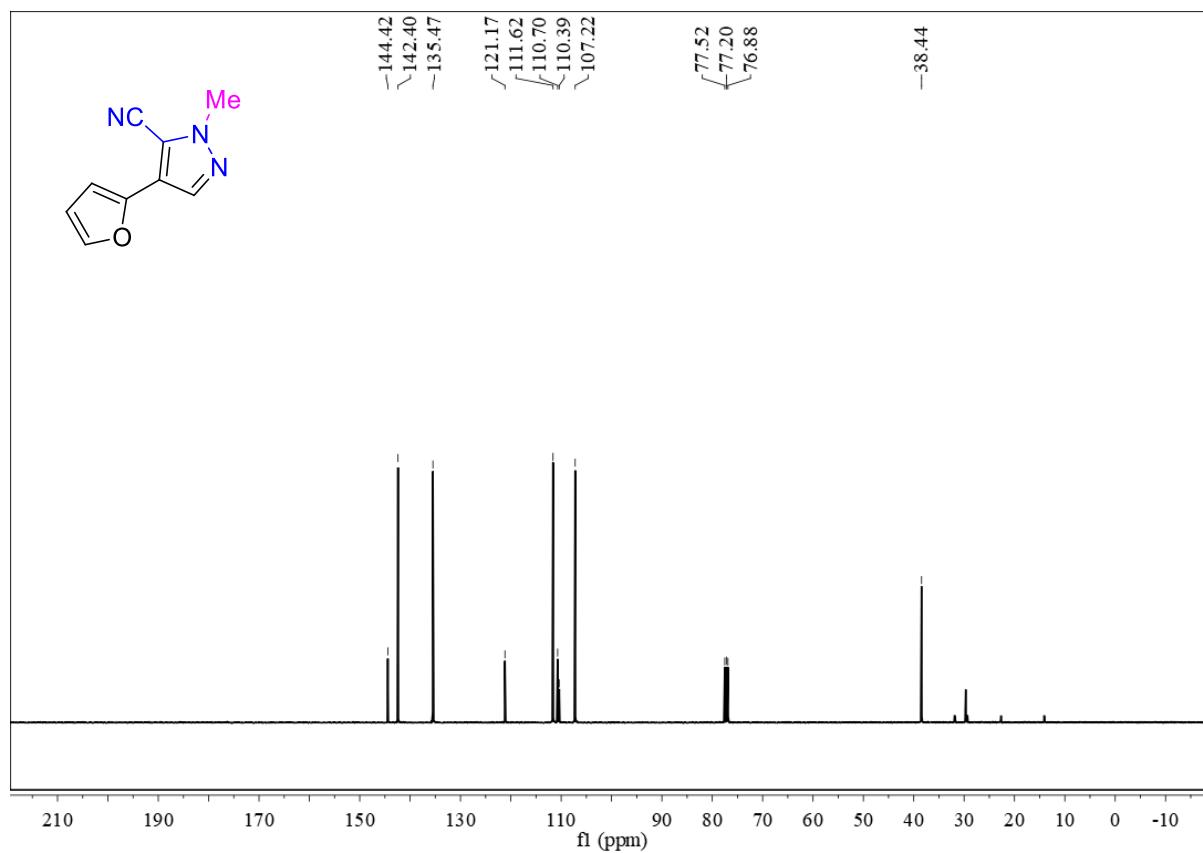
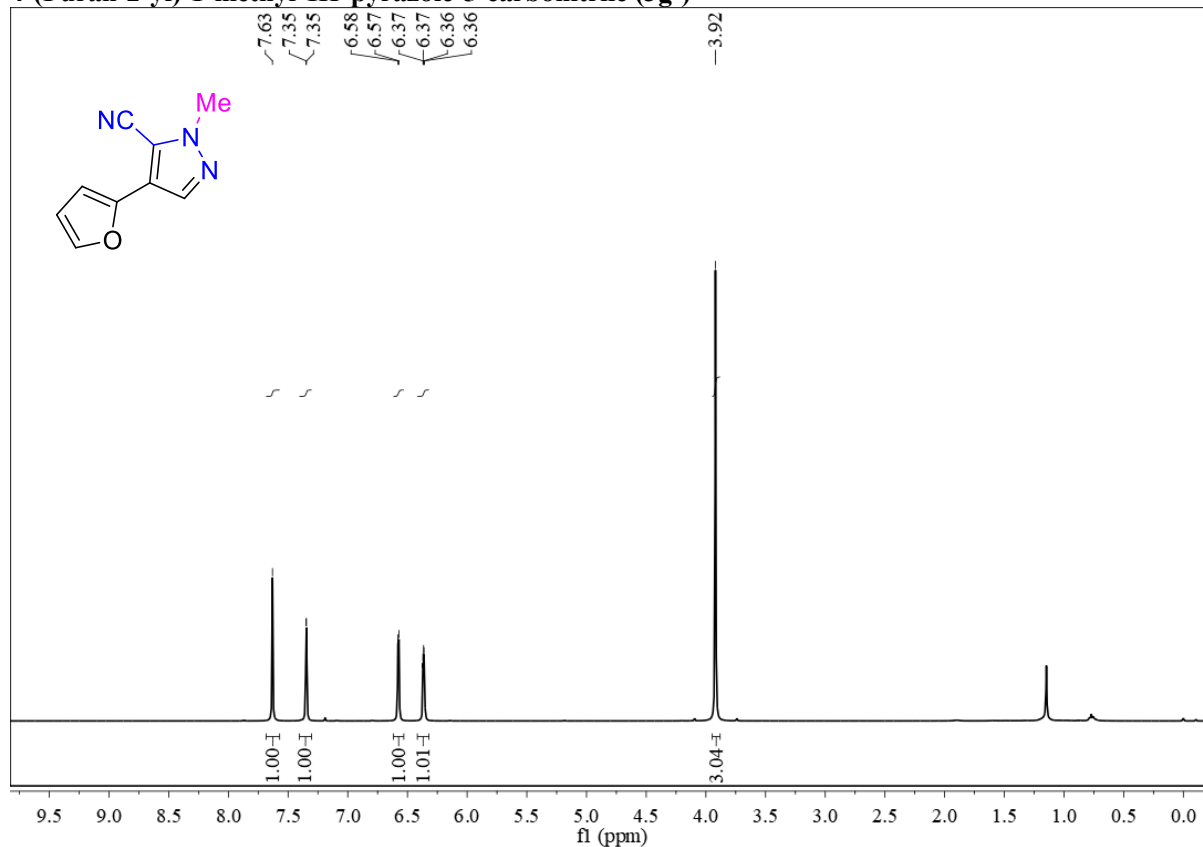
1-Methyl-4-(naphthalen-2-yl)-1H-pyrazole-5-carbonitrile (3f')



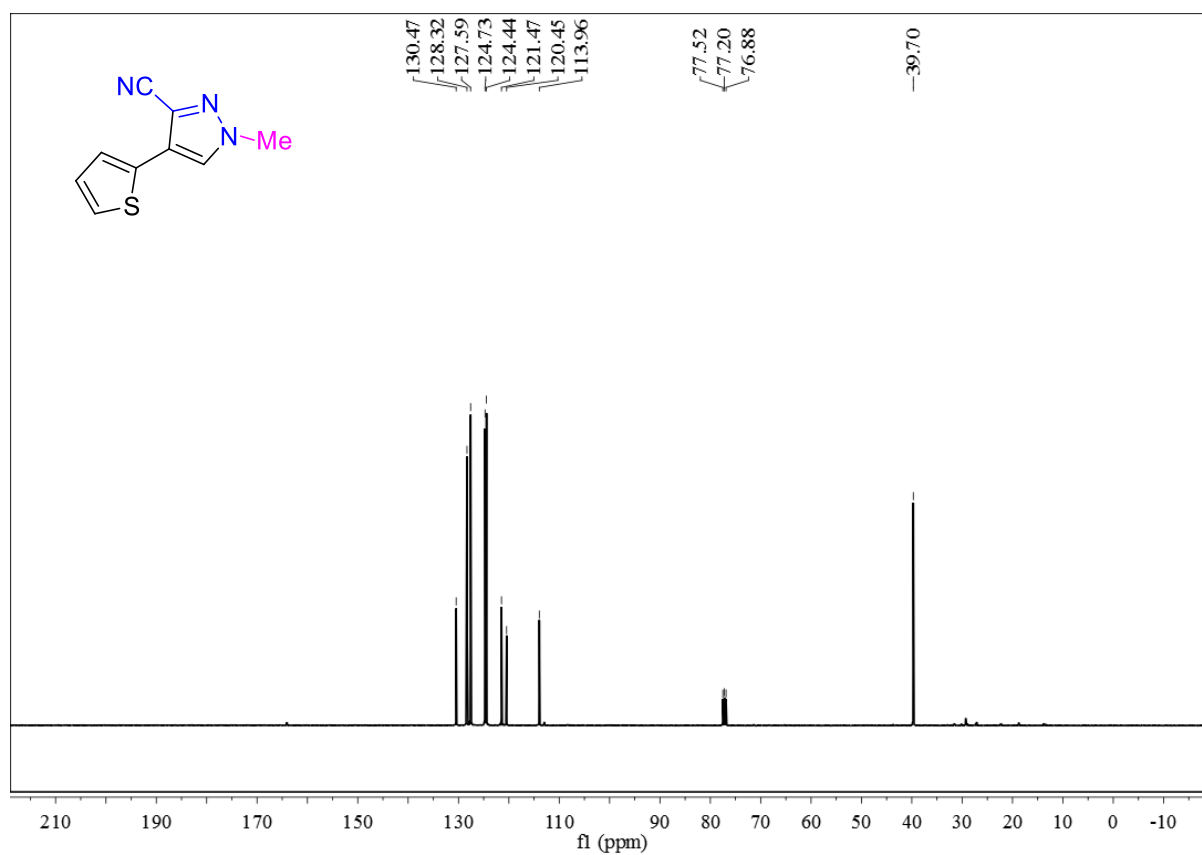
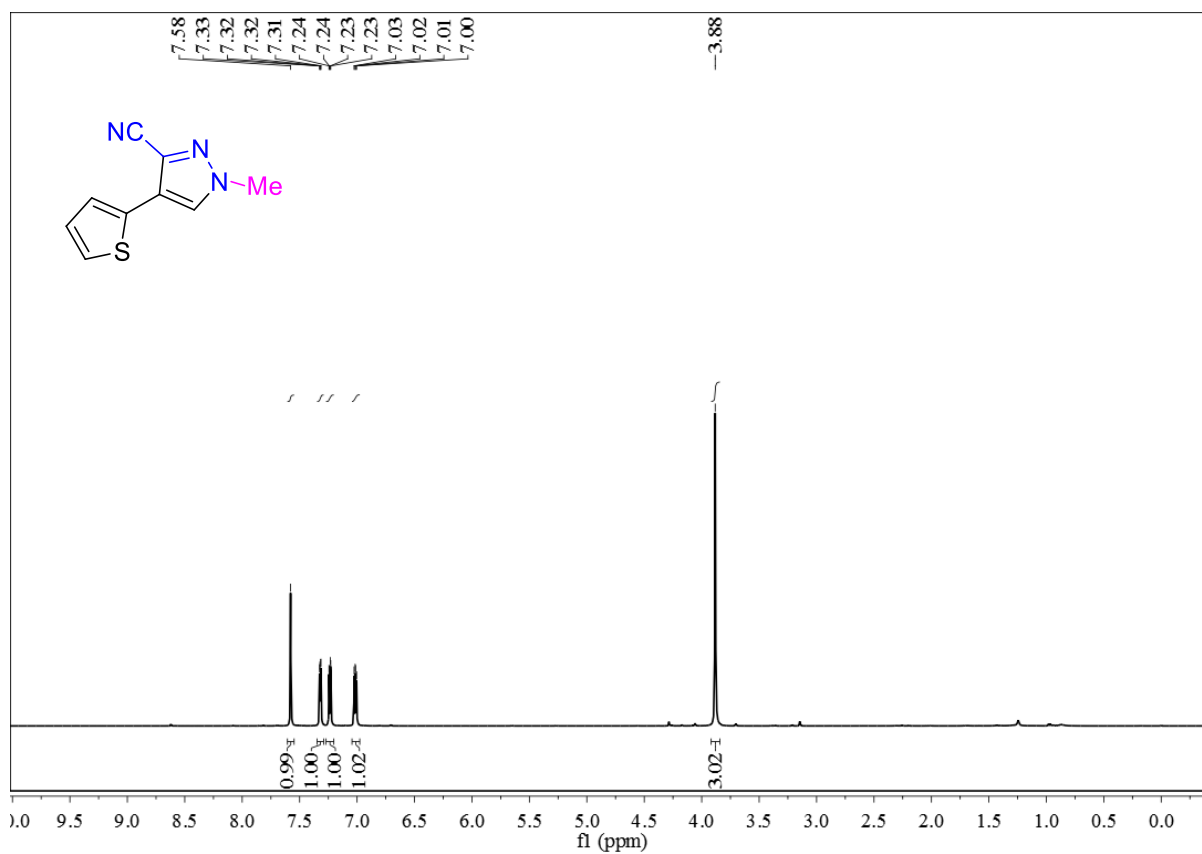
4-(Furan-2-yl)-1-methyl-1H-pyrazole-3-carbonitrile (3g)



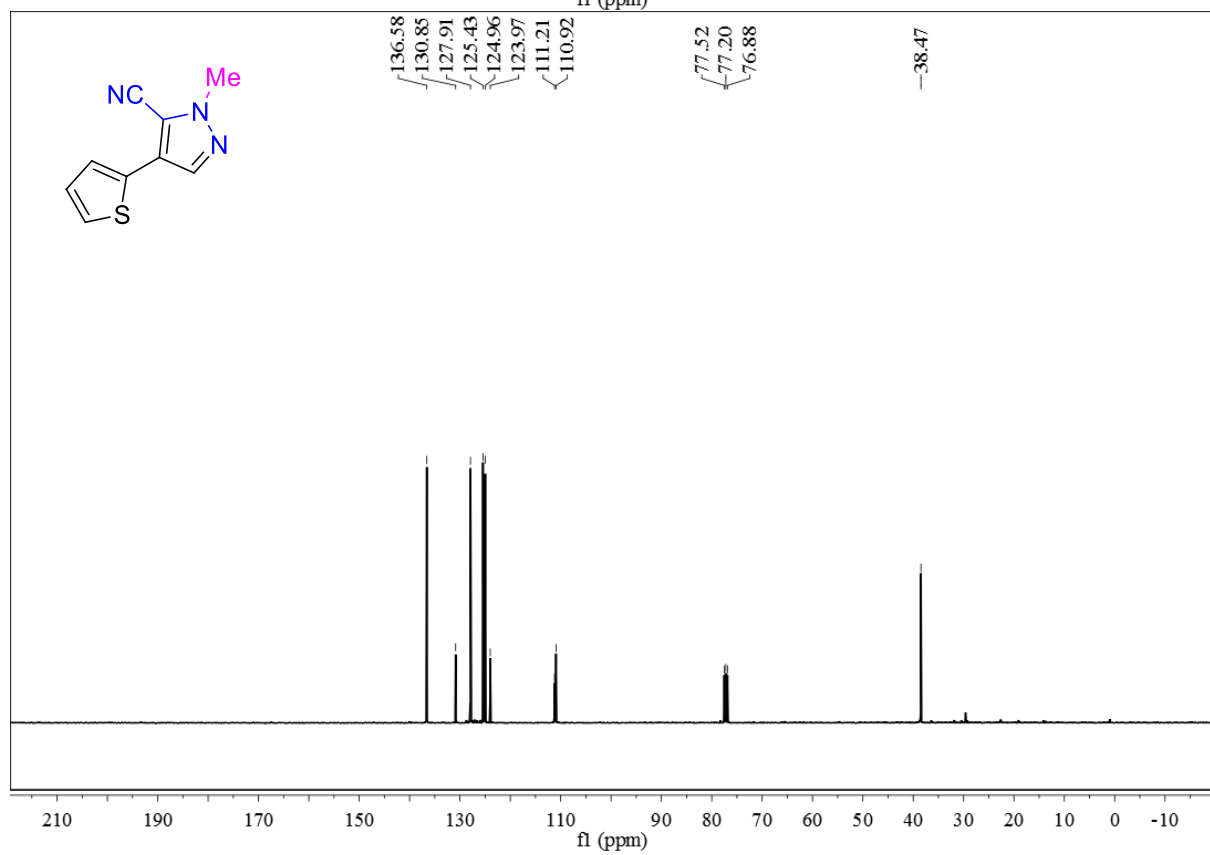
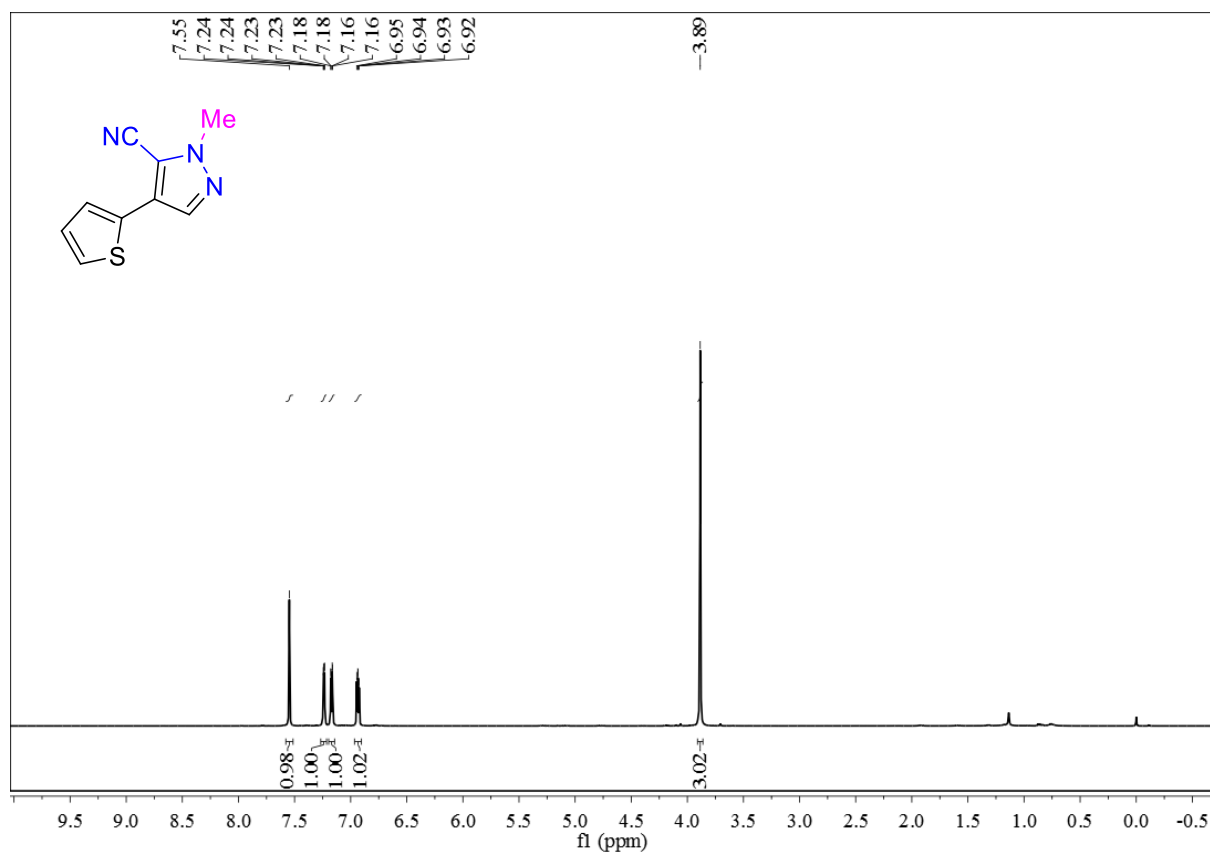
4-(Furan-2-yl)-1-methyl-1H-pyrazole-5-carbonitrile (3g')



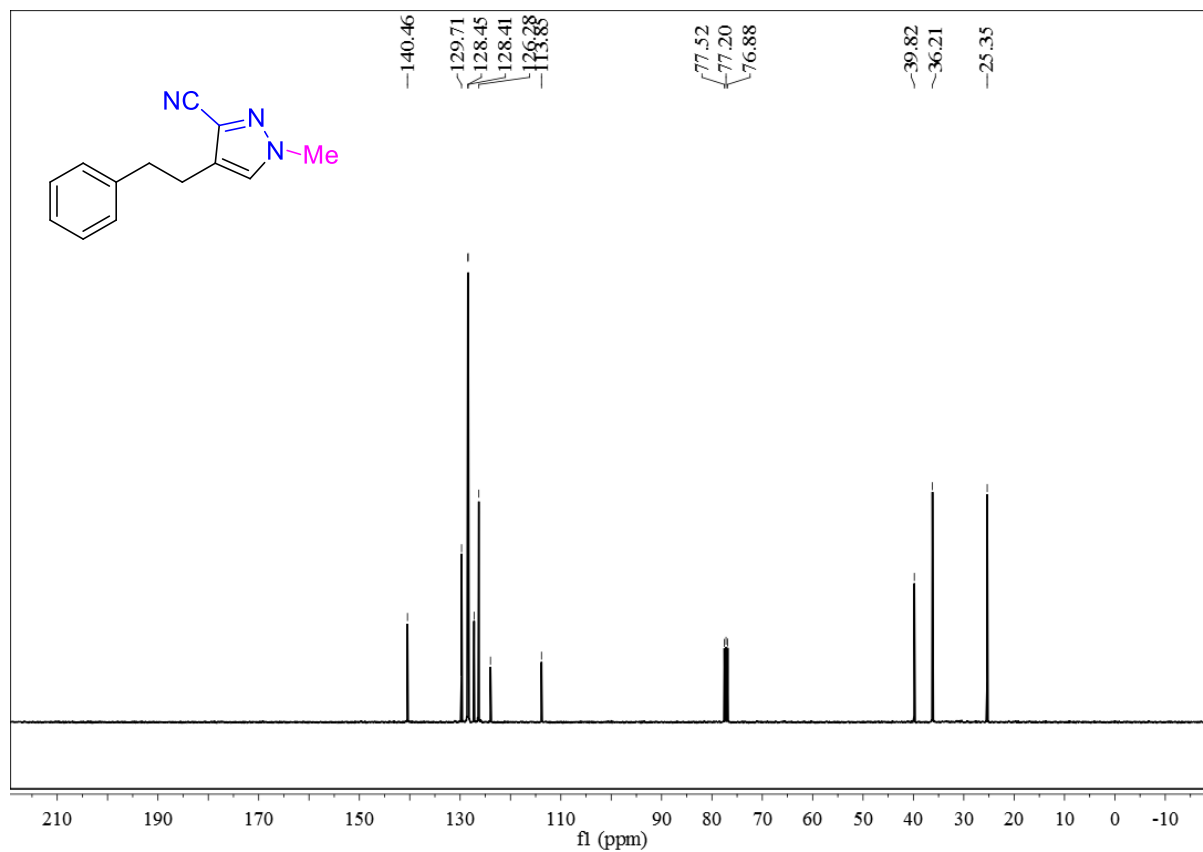
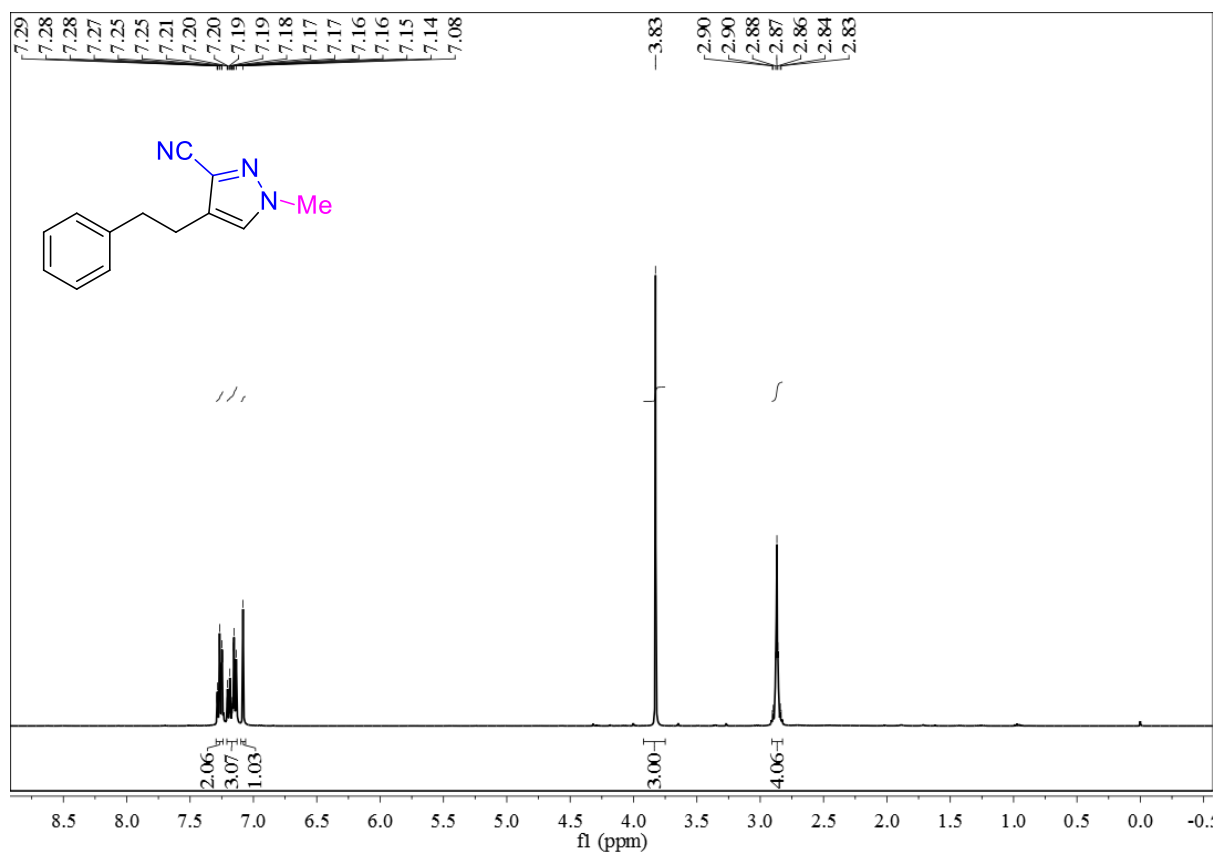
1-Methyl-4-(thiophen-2-yl)-1H-pyrazole-3-carbonitrile (3h)



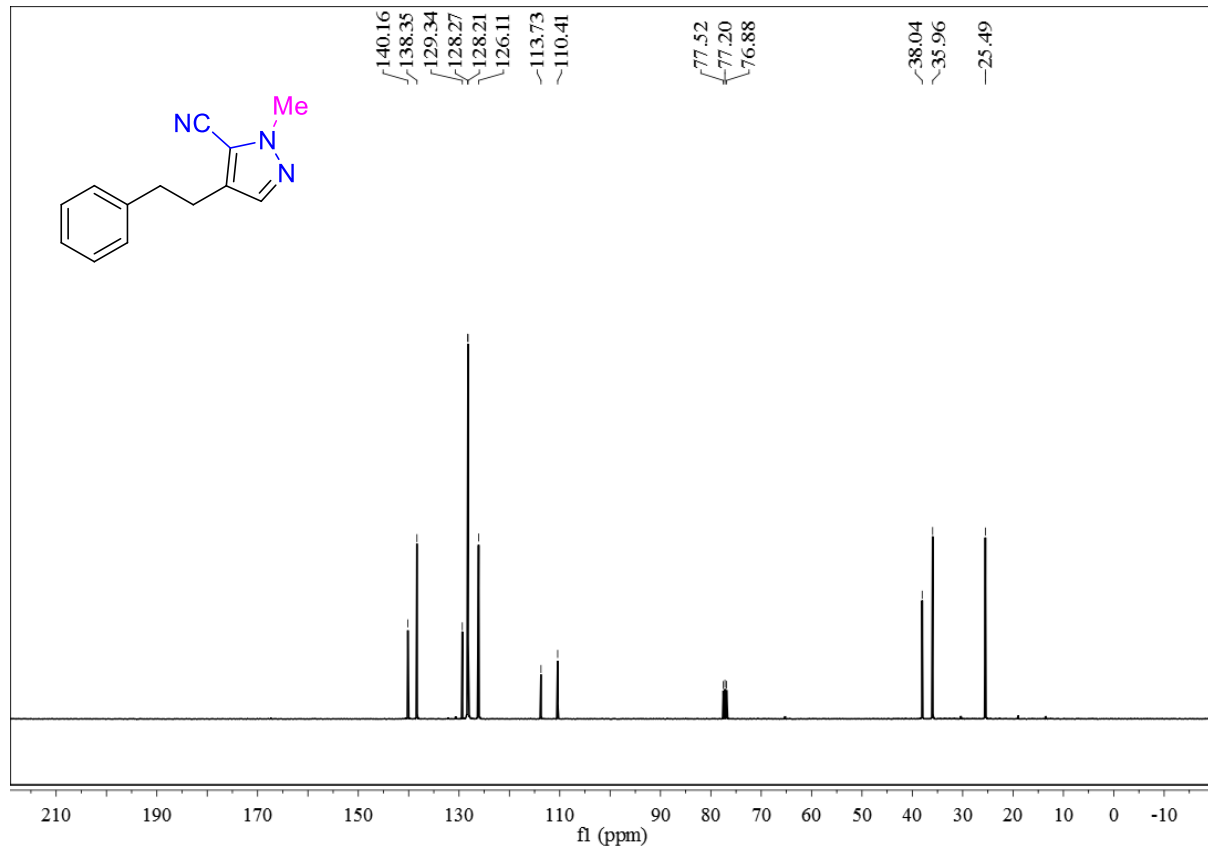
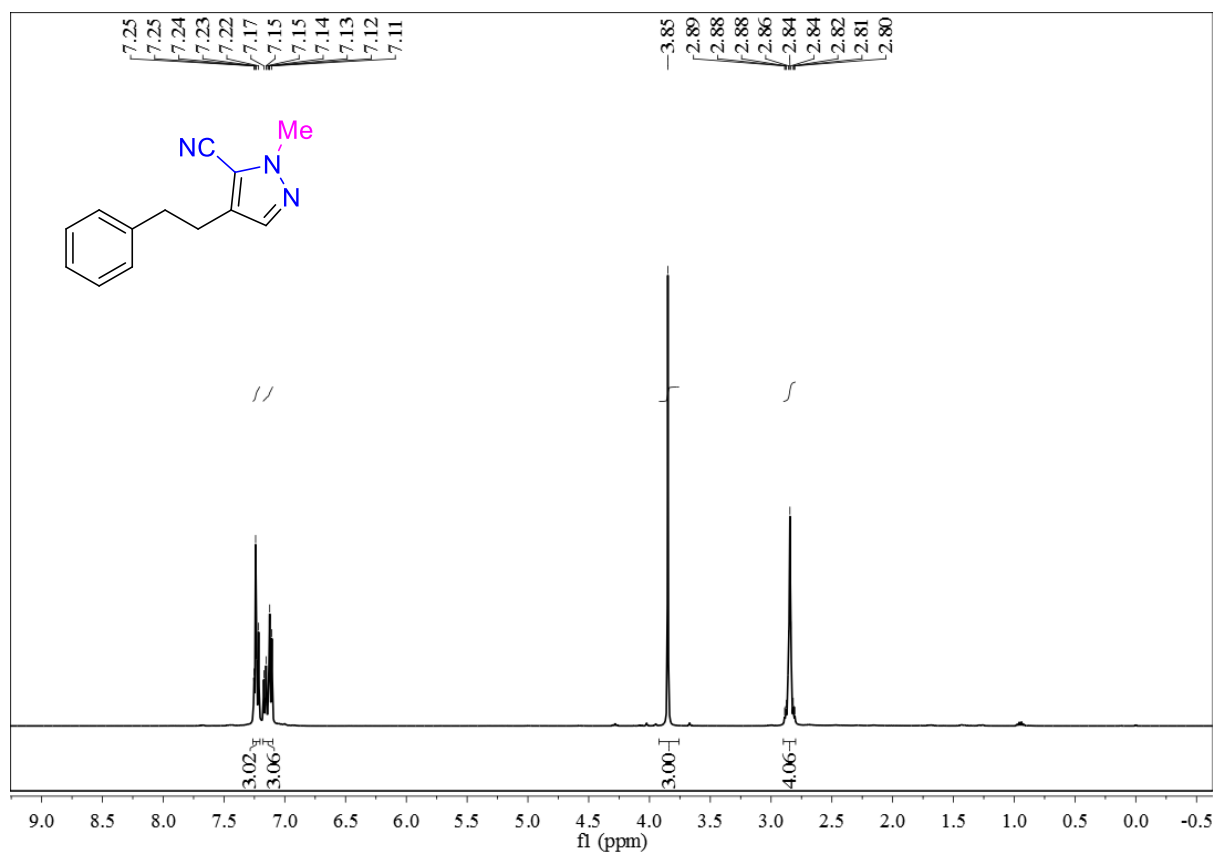
1-Methyl-4-(thiophen-2-yl)-1H-pyrazole-5-carbonitrile (3h')



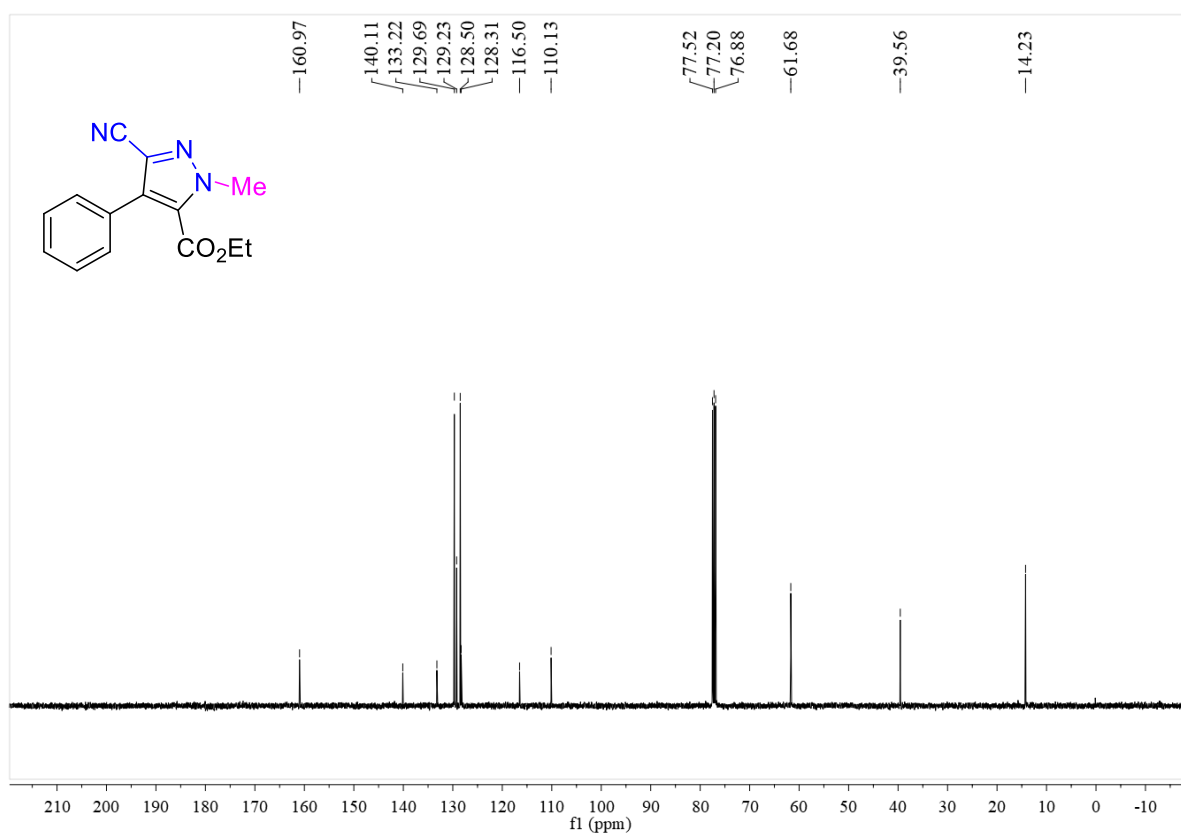
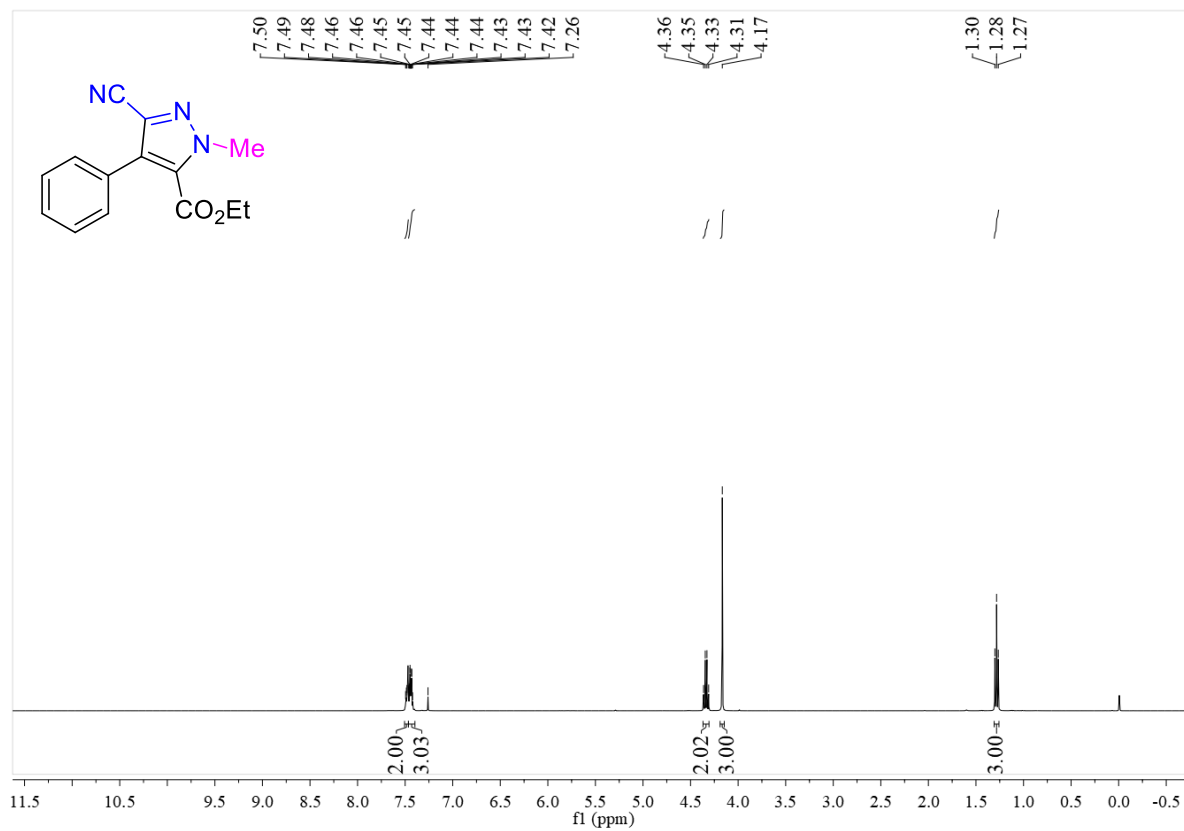
1-Methyl-4-phenethyl-1H-pyrazole-3-carbonitrile (3i)



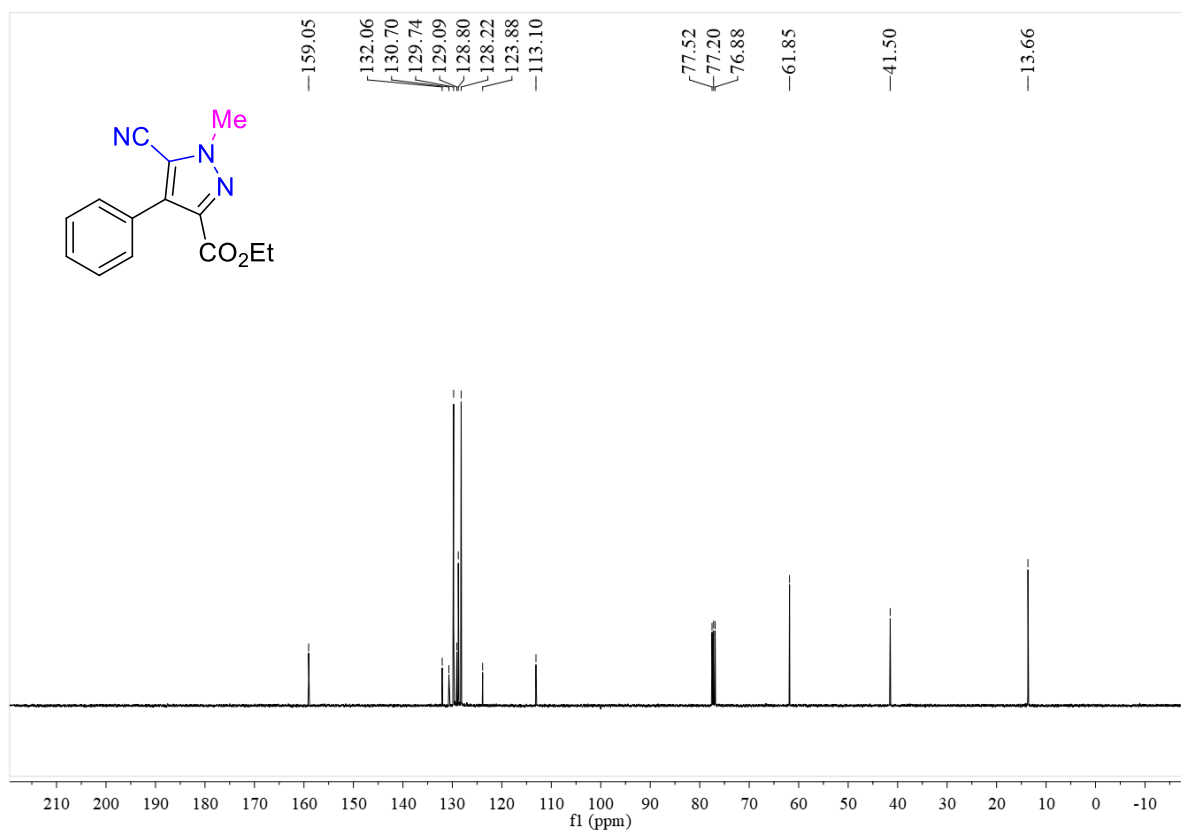
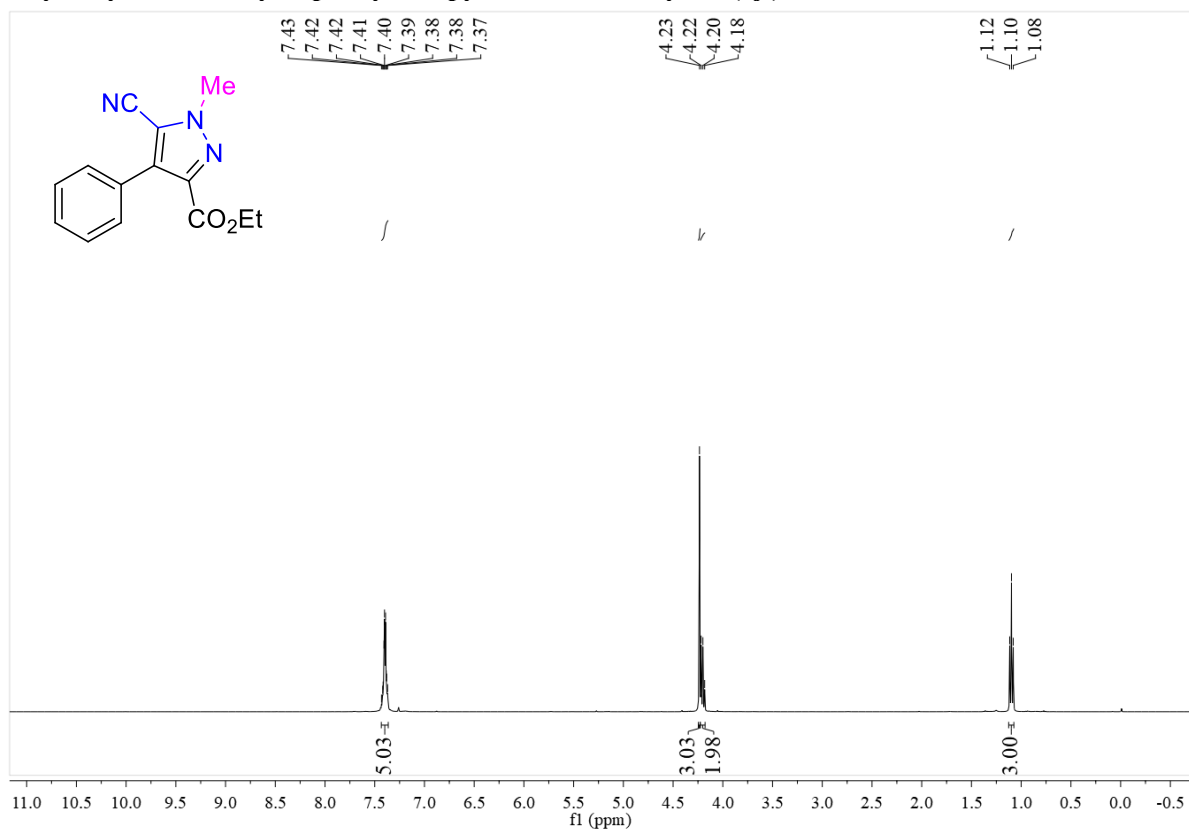
1-Methyl-4-phenethyl-1H-pyrazole-5-carbonitrile (3i')



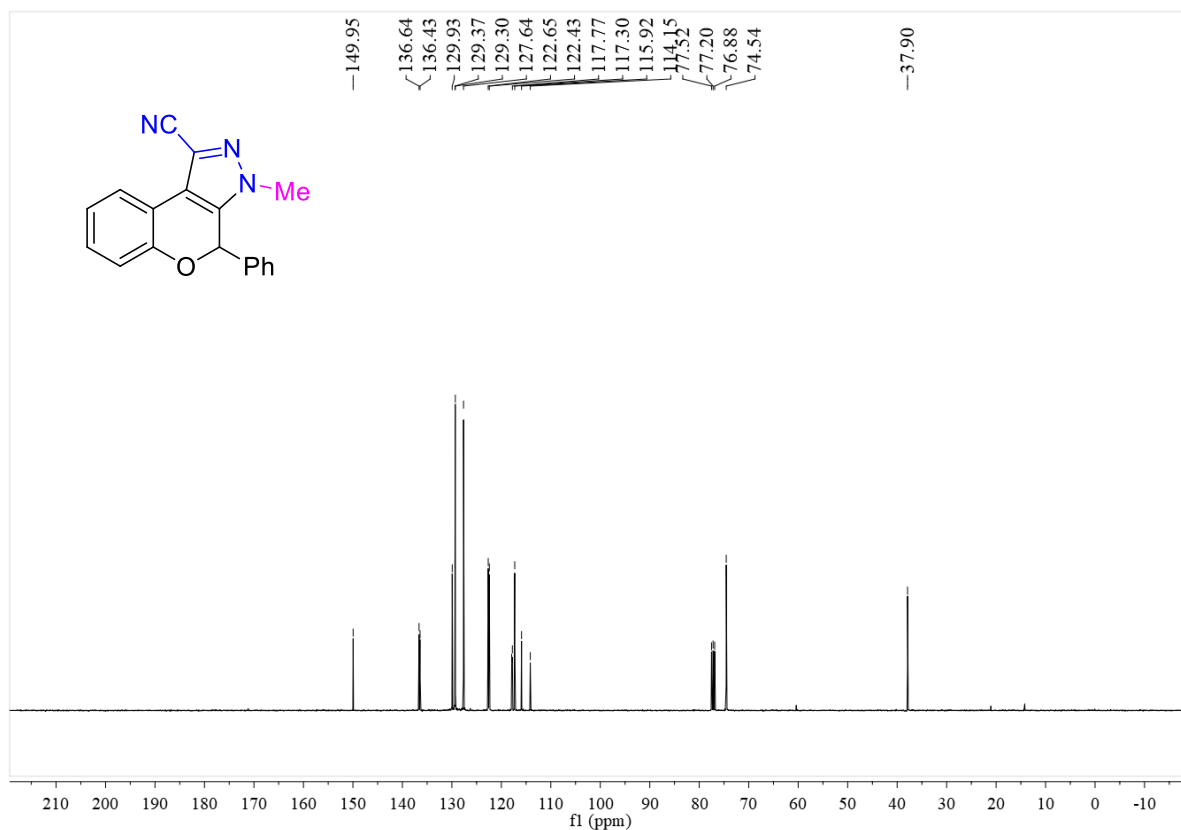
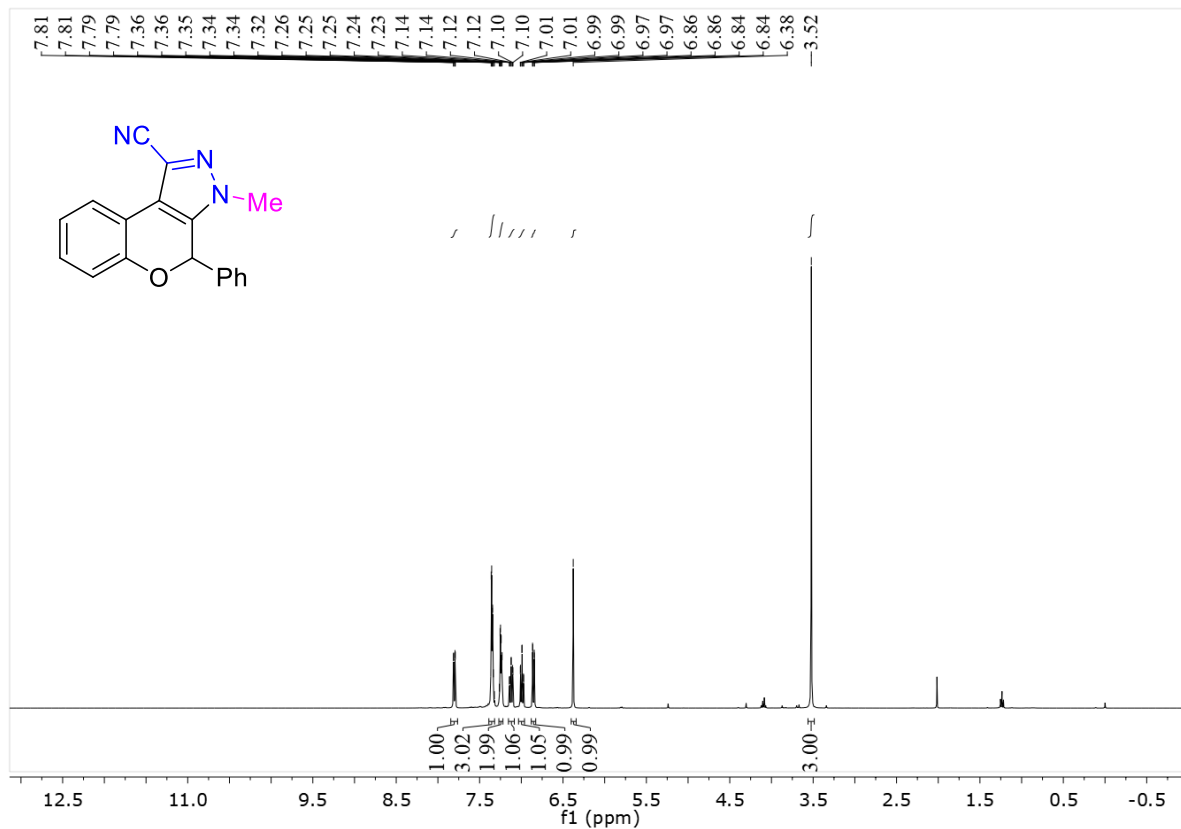
Ethyl 3-cyano-1-methyl-4-phenyl-1H-pyrazole-5-carboxylate (3j)



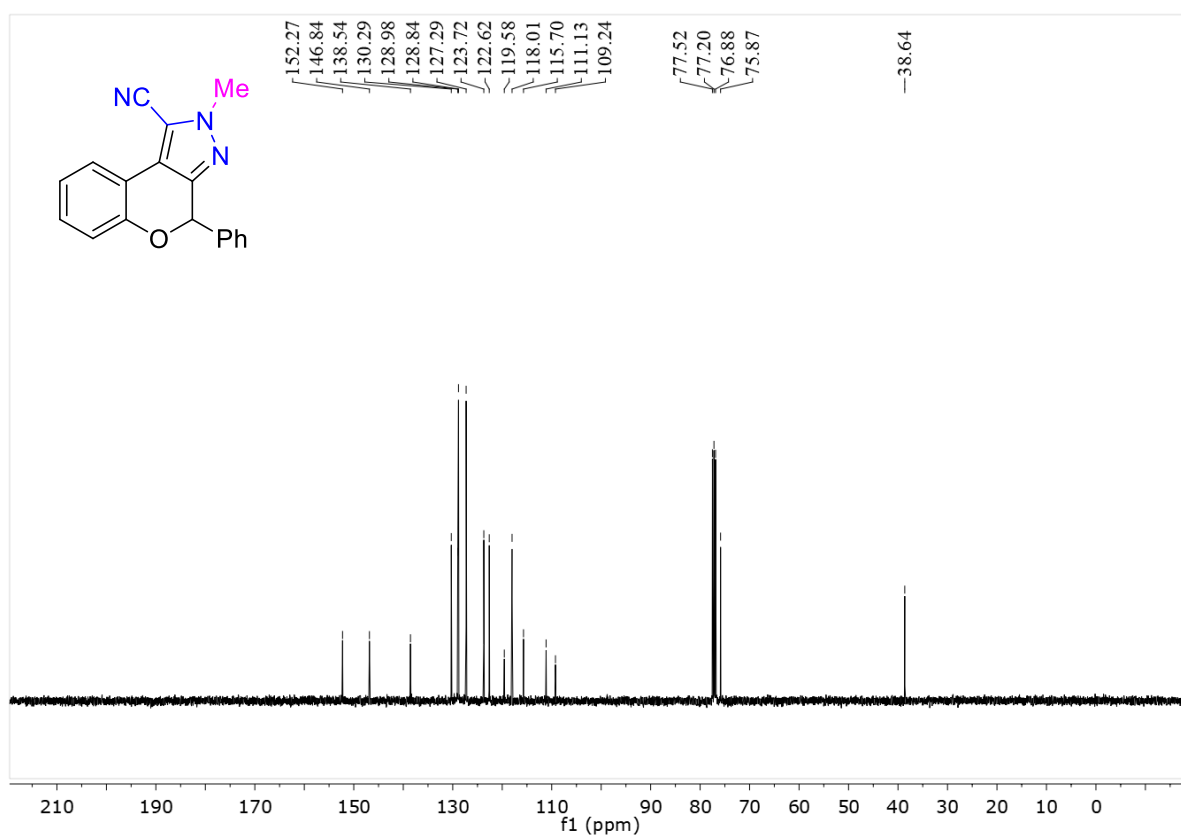
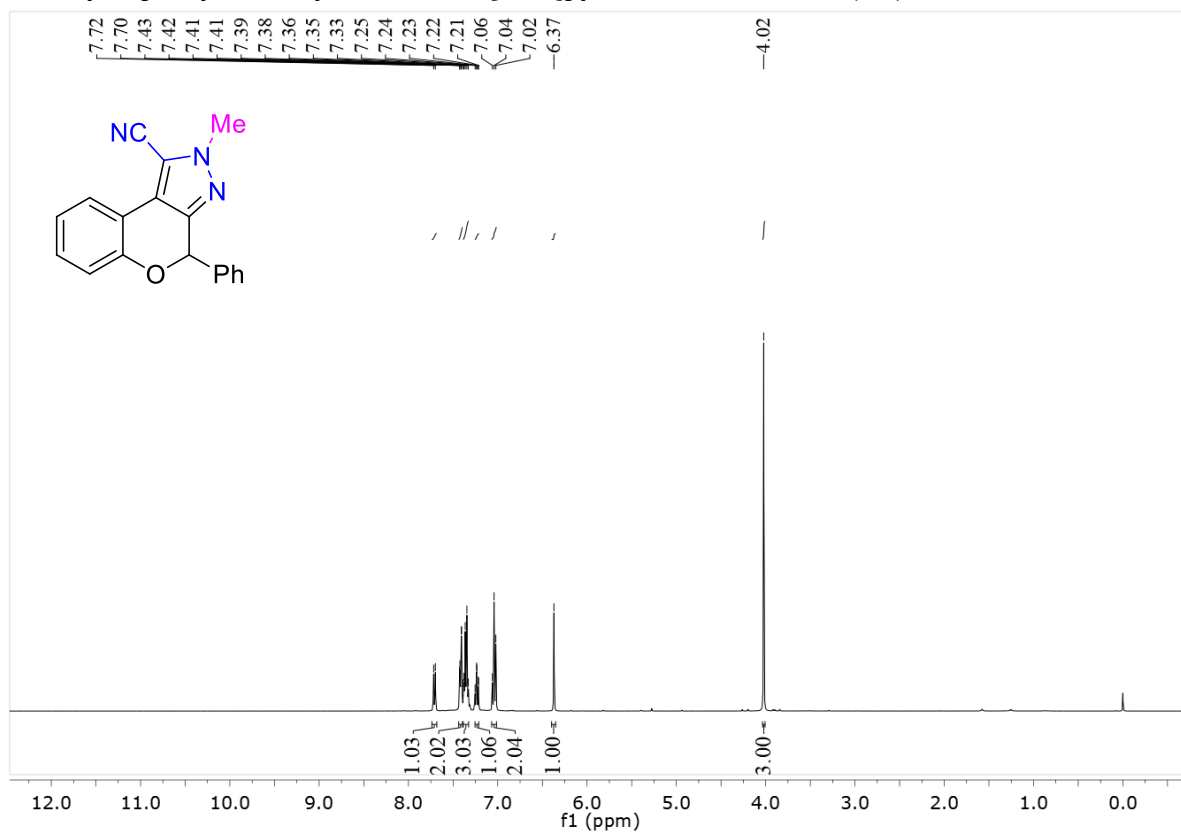
Ethyl 5-cyano-1-methyl-4-phenyl-1H-pyrazole-3-carboxylate (3j')



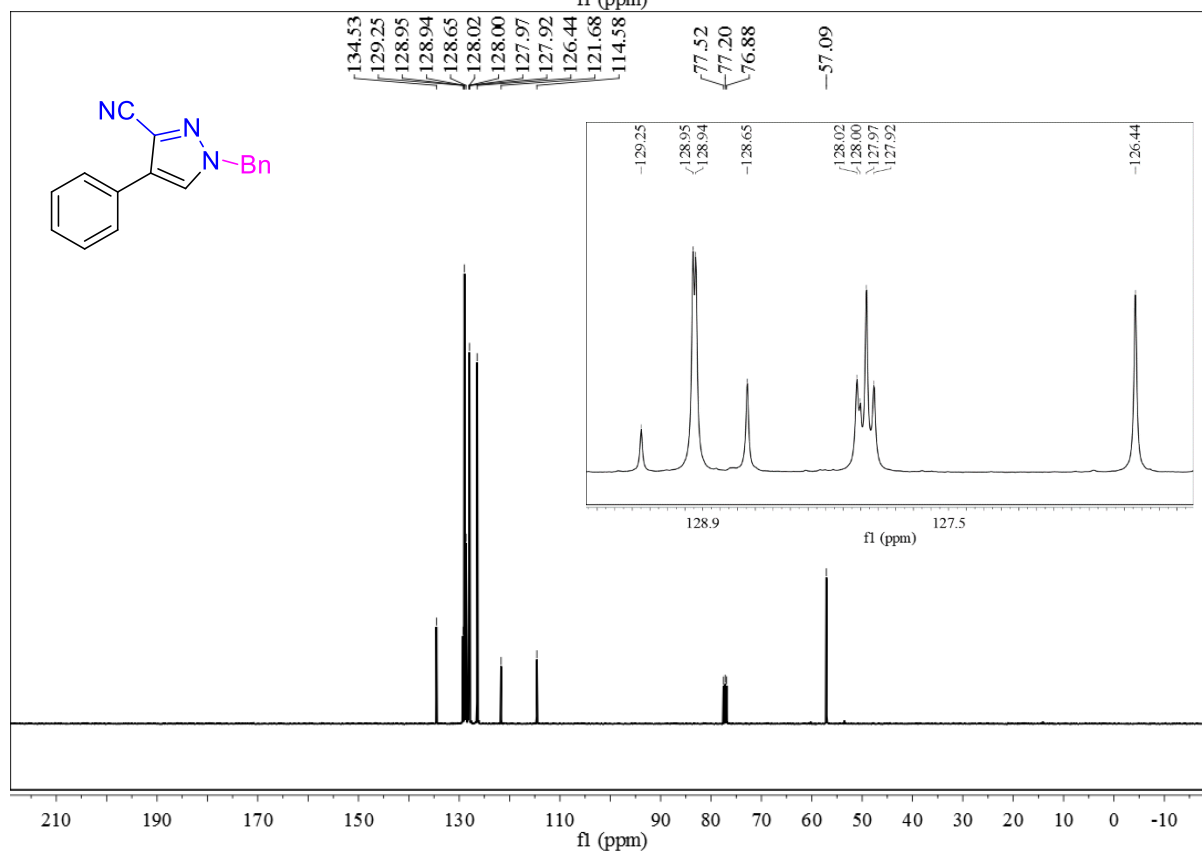
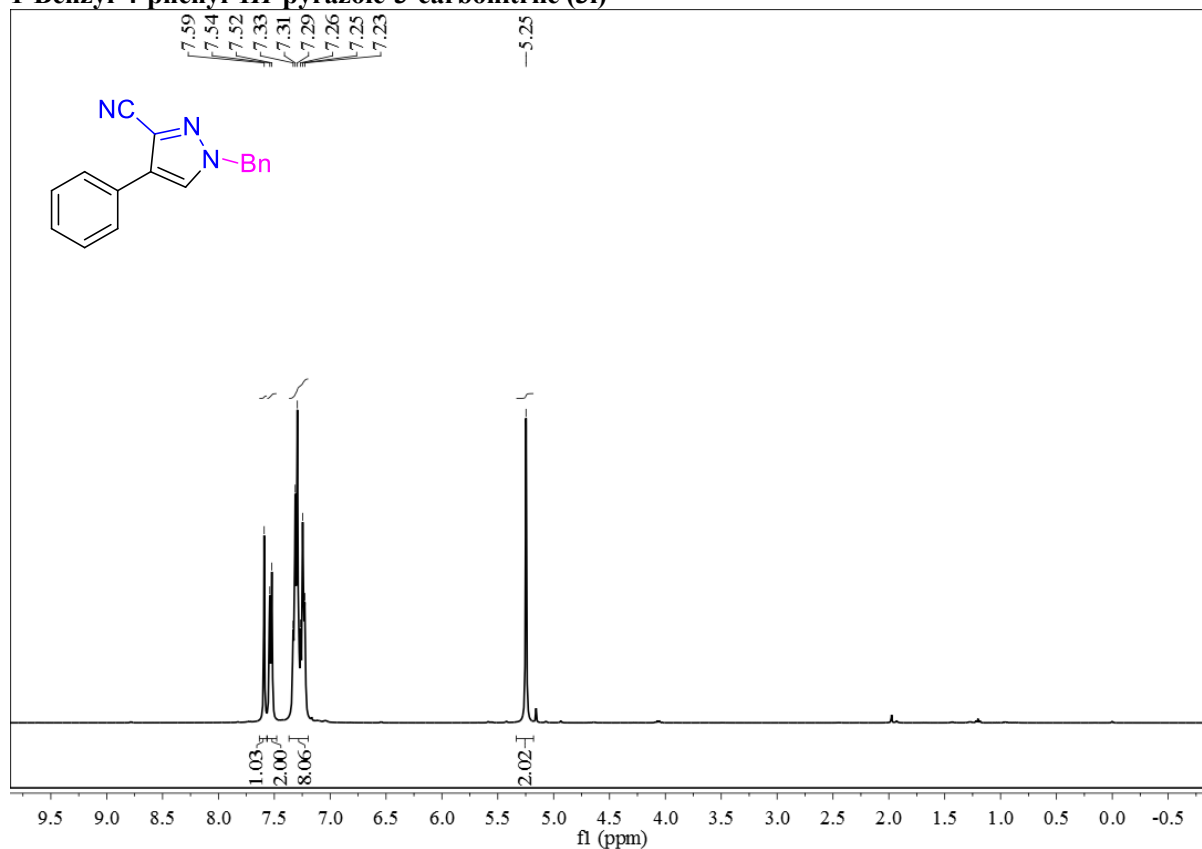
3-Methyl-4-phenyl-3,4-dihydrochromeno[3,4-c]pyrazole-1-carbonitrile (3k)



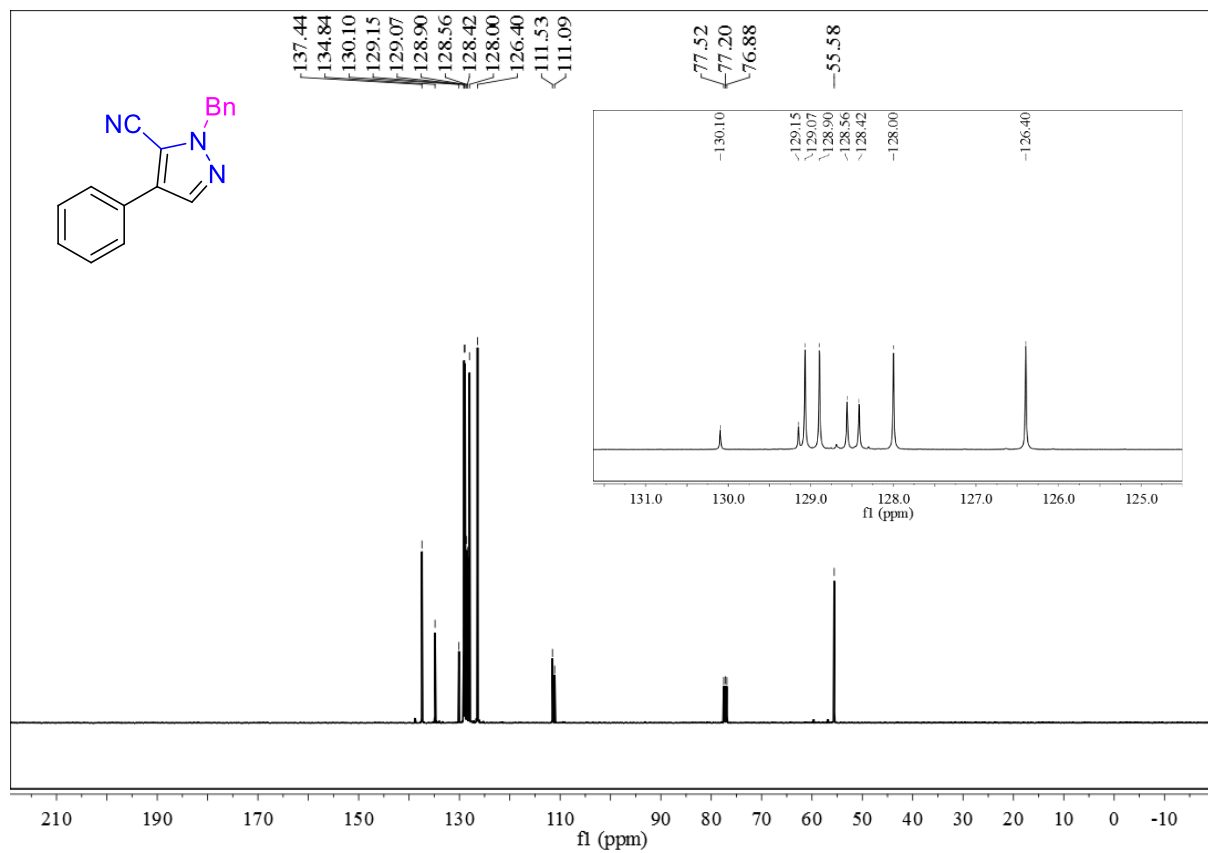
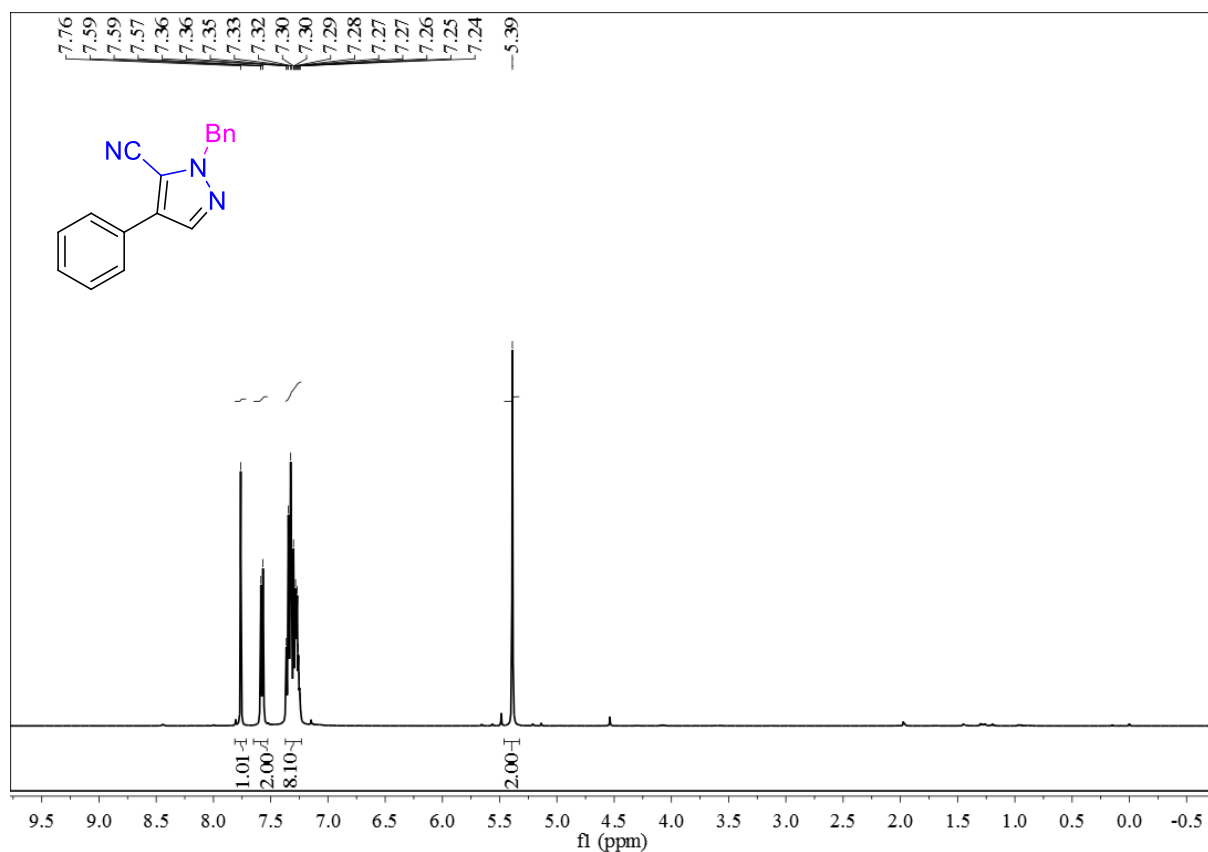
2-Methyl-4-phenyl-2,4-dihydrochromeno[3,4-c]pyrazole-1-carbonitrile (3k')



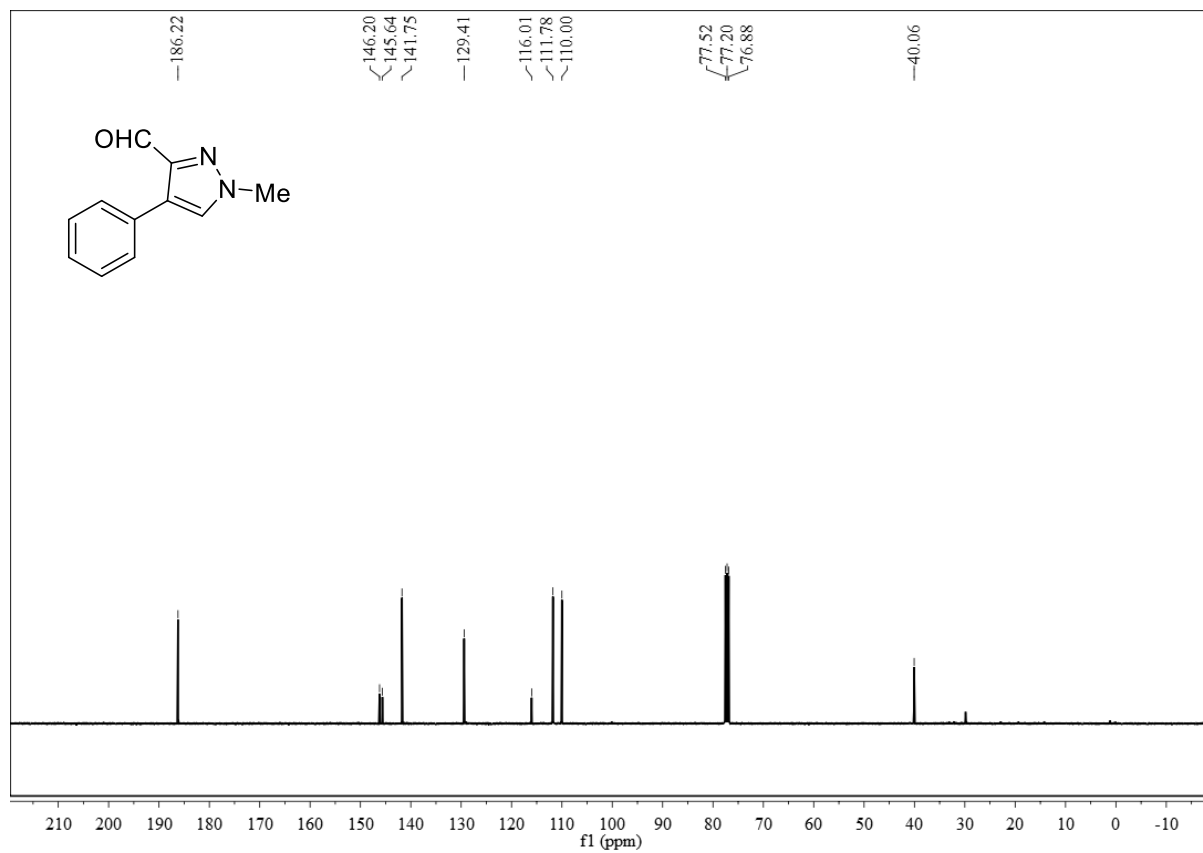
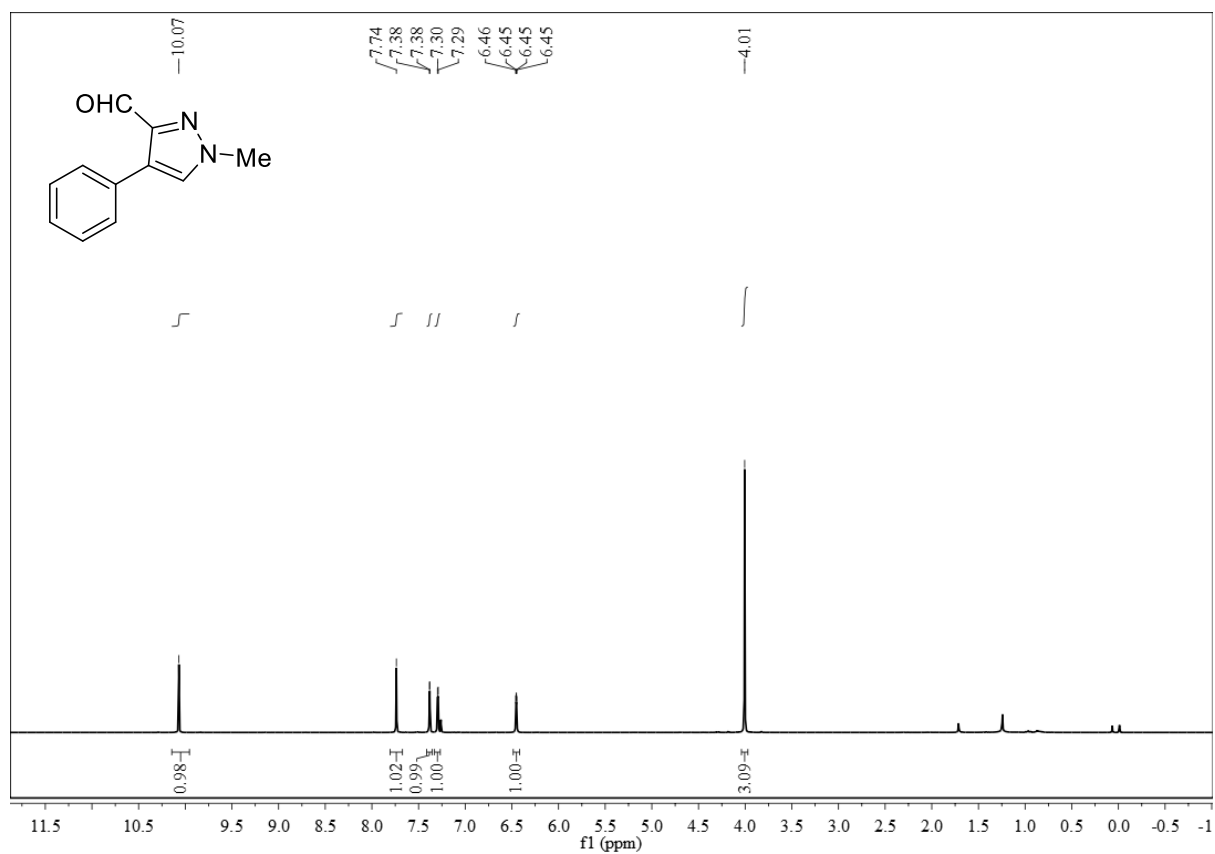
1-Benzyl-4-phenyl-1H-pyrazole-3-carbonitrile (3l)



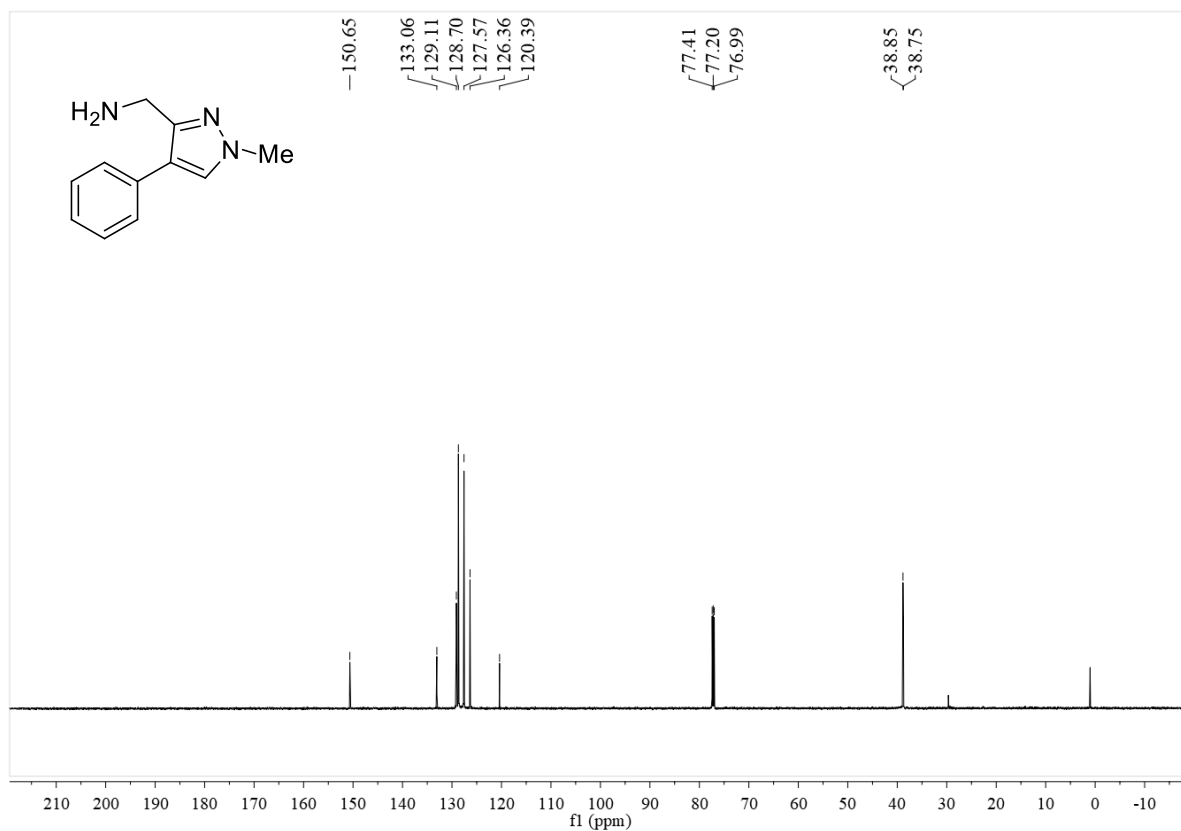
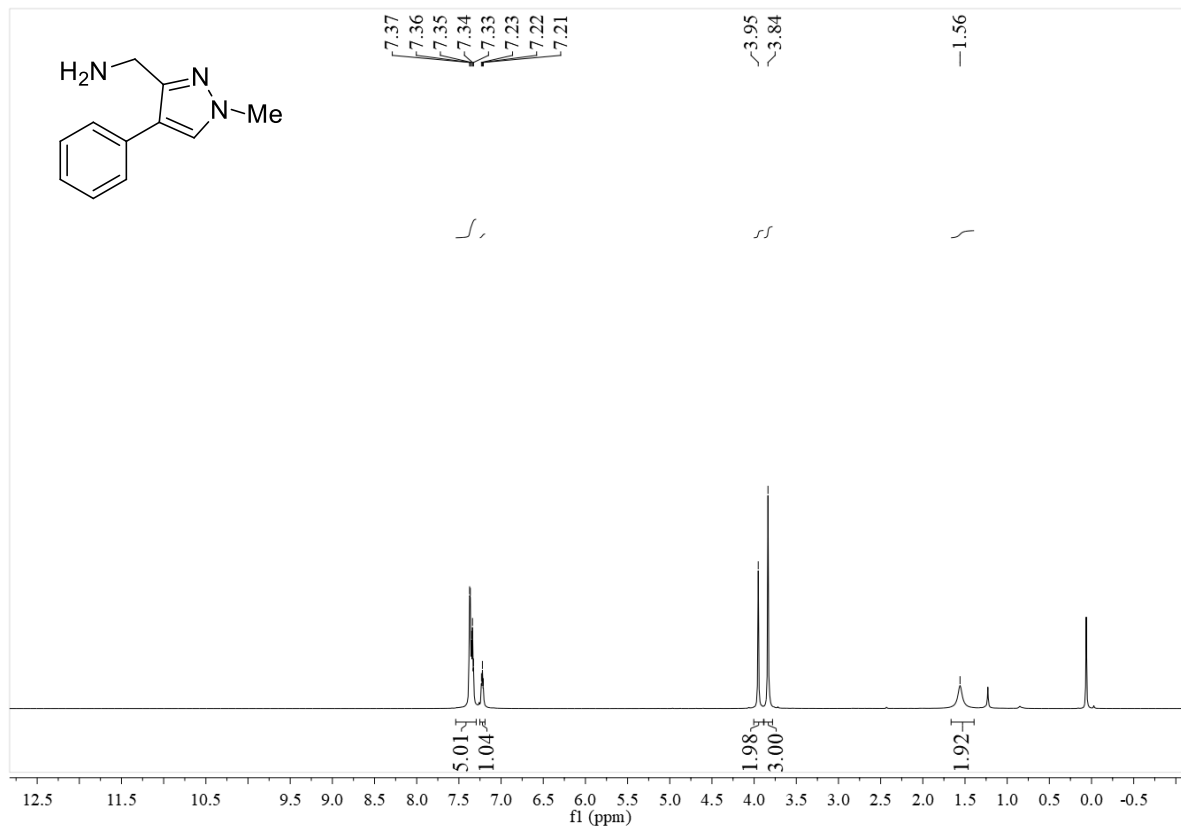
1-Benzyl-4-phenyl-1H-pyrazole-5-carbonitrile (3l')



1-Methyl-4-phenyl-1H-pyrazole-3-carbaldehyde (4)



(1-Methyl-4-phenyl-1H-pyrazol-3-yl)methanamine (5)



1-Methyl-4-phenyl-1H-pyrazole-3-carboxamide(6)

