

Molecular Iodine-Catalyzed Multicomponent Synthesis of α -Cyanopyrrolines with Ambient Air as the Oxidant under Neat Conditions

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1. General Information

All reactions were carried out in anhydrous solvent and commercially available reagents were used as received unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on precoated aluminium-backed silica gel 60 F₂₅₄ plates (EMD Millipore, 200 μ m thickness). TLC plates were visualized with ultraviolet light and treatment with KMnO₄ or vanillin stains followed by heating. Flash column chromatography was performed using Tsingtao silica gel (200-300). ¹H and ¹³C NMR spectra were recorded on a Bruker Avance DRX - 400 spectrometers; chemical shifts (δ) are given in ppm and calibrated using the signal of residual undeuterated solvent as internal reference (CDCl₃: δ_{H} = 7.26 ppm and δ_{C} = 77.16 ppm; DMSO-*d*₆: δ_{H} = 2.54 ppm and δ_{C} = 39.60 ppm). Data for ¹H NMR and ¹³C NMR are reported as follows: chemical shift (δ , ppm), multiplicity, integration, and coupling constant (Hz).

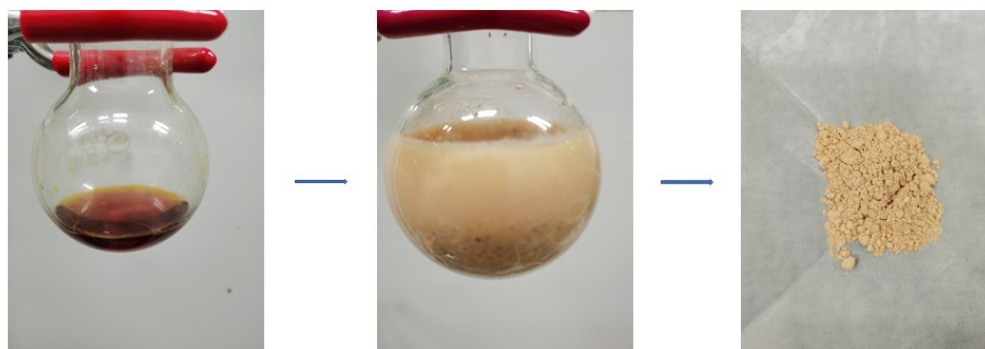
2. Experimental Section

General experimental procedures for compounds 4

In a vial was placed alkene (0.5 mmol), TMSCN (0.5 mmol), *N,N*-disubstituted formamide (0.5 mmol) and molecular iodine (0.05 mmol), then the contents were reacted under 80 °C for 4 h. Upon completion, the reaction mixture was quenched by addition of 10 mL of water. The aqueous layer was extracted three times with EtOAc (10 mL \times 3), and the combine organic layers were washed with saturated sodium sulfite solution and dried over anhydrous sodium sulfate, evaporated to dryness, and purified by column chromatography to afford the desired products.

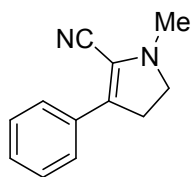
Large-scale synthesis of 4o

In a flask (50 mL) equipped with a stir bar, 4-nitrostyrene (20 mmol, 2.98 g), TMSCN (20 mmol, 1.98 g), *N,N*-disubstituted formamide (20 mmol, 1.54 g) and molecular iodine (2 mmol, 0.51 g) were added, then the contents were reacted under 80 °C for 4 h. After completion, saturated sodium sulfite solution (25 mL) was added dropwise into the mixture. The precipitates were formed and collected by filtration and wash with ethyl acetate to give the product **4o** (3.8 g, 83% yield).



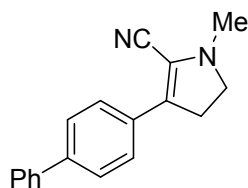
3. Characterization data of products

*1-methyl-3-phenyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4a)*¹



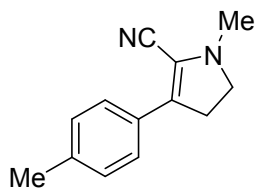
¹H NMR (400 MHz, CDCl₃): δ 7.50 (d, *J* = 8.4 Hz, 2 H), 7.27 (t, *J* = 7.6 Hz, 2 H), 7.17 (t, *J* = 7.6 Hz, 1 H), 3.14 (t, *J* = 9.6 Hz, 2 H), 2.86 (t, *J* = 9.6 Hz, 2 H), 2.68 (s, 3 H); ¹³C NMR (101 MHz, CDCl₃): δ 133.05, 130.76, 128.76, 127.86, 125.58, 120.14, 114.66, 54.86, 39.09, 32.46.

3-([1,1'-biphenyl]-4-yl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4b)



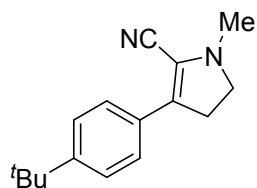
¹H NMR (400 MHz, CDCl₃): δ 7.69 – 7.67 (m, 2 H), 7.63 – 7.60 (m, 4 H), 7.46 (t, *J* = 7.2 Hz, 2 H), 7.36 (t, *J* = 7.2 Hz, 1 H), 3.26 (t, *J* = 10.0 Hz, 2 H), 2.99 (t, *J* = 9.6 Hz, 2 H), 2.79 (s, 3 H); ¹³C NMR (101 MHz, CDCl₃): δ 174.94, 141.02, 140.05, 139.10, 128.80, 128.39, 127.55, 127.26, 127.15, 125.96, 108.27, 47.80, 30.20, 27.97; HRMS (ESI) *m/z* calcd. for C₁₈H₁₇N₂ [M+H]⁺: 261.1386, found: 261.1390.

*1-methyl-3-(*p*-tolyl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4c)*



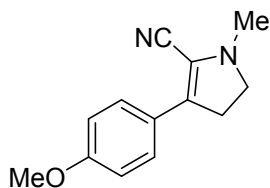
¹H NMR (400 MHz, CDCl₃): δ 7.49 (d, *J* = 8.4 Hz, 2 H), 7.17 (d, *J* = 8.0 Hz, 2 H), 3.21 (t, *J* = 10.0 Hz, 2 H), 2.93 (t, *J* = 9.2 Hz, 2 H), 2.75 (s, 3 H), 2.35 (s, 3 H); ¹³C NMR (101 MHz, CDCl₃): δ 138.01, 131.35, 129.50, 126.58, 125.59, 119.42, 114.89, 54.97, 39.31, 32.58, 21.39; HRMS (ESI) *m/z* calcd. for C₁₃H₁₅N₂ [M+H]⁺: 199.1230, found: 199.1235.

*3-(4-(*tert*-butyl)phenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4d)*



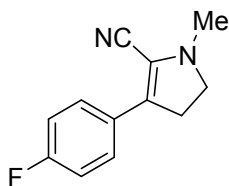
¹H NMR (400 MHz, CDCl₃): δ 7.55 (d, *J* = 8.4 Hz, 2 H), 7.22 (d, *J* = 8.4 Hz, 2 H), 3.21 (t, *J* = 9.2 Hz, 2 H), 2.94 (t, *J* = 9.6 Hz, 2 H), 2.76 (s, 3 H), 1.36 – 1.32 (m, 9 H); ¹³C NMR (101 MHz, CDCl₃): δ 151.17, 131.15, 127.59, 125.69, 125.39, 119.47, 114.86, 54.93, 39.24, 34.77, 32.48, 31.30; HRMS (ESI) *m/z* calcd. for C₁₆H₂₁N₂ [M+H]⁺: 241.1699, found: 241.1704.

3-(4-methoxyphenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4e)



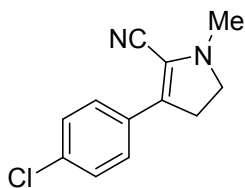
^1H NMR (400 MHz, CDCl_3): δ 7.54 (d, $J = 8.8$ Hz, 2 H), 7.44 (d, $J = 8.4$ Hz, 2 H), 3.82 (s, 3 H), 3.19 (t, $J = 9.6$ Hz, 2 H), 2.91 (t, $J = 9.2$ Hz, 2 H), 2.73 (s, 3 H); ^{13}C NMR (101 MHz, CDCl_3): δ 159.32, 131.33, 126.95, 125.57, 118.33, 114.99, 114.13, 55.31, 54.85, 39.35, 32.57; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 215.1179, found: 215.1184.

3-(4-fluorophenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4f)



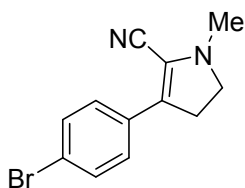
^1H NMR (400 MHz, CDCl_3): δ 7.57 – 7.54 (m, 2 H), 7.05 (t, $J = 8.8$ Hz, 2 H), 3.22 (t, $J = 8.8$ Hz, 2 H), 2.92 (q, $J = 9.6$ Hz, 2 H), 2.75 (s, 3 H); ^{13}C NMR (101 MHz, CDCl_3): δ 163.45 (d, $J = 249.3$ Hz), 129.80, 129.33 (d, $J = 3.5$ Hz), 127.38 (d, $J = 8.1$ Hz), 119.95, 115.92 (d, $J = 21.8$ Hz), 114.62, 54.84, 39.15, 32.66; HRMS (ESI) m/z calcd. for $\text{C}_{12}\text{H}_{12}\text{FN}_2$ $[\text{M}+\text{H}]^+$: 203.0979, found: 203.0981.

3-(4-chlorophenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4g)



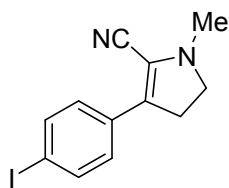
^1H NMR (400 MHz, CDCl_3): δ 7.52 – 7.48 (m, 2 H), 7.33 – 7.28 (m, 2 H), 3.24 (t, $J = 10.0$ Hz, 2 H), 2.92 (t, $J = 9.6$ Hz, 2 H), 2.76 (s, 3 H); ^{13}C NMR (101 MHz, CDCl_3): δ 133.32, 131.57, 129.08, 128.94, 126.70, 120.57, 114.43, 54.72, 38.92, 32.35; HRMS (ESI) m/z calcd. for $\text{C}_{12}\text{H}_{12}\text{ClN}_2$ $[\text{M}+\text{H}]^+$: 218.0684, found: 218.0690.

3-(4-bromophenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4h)



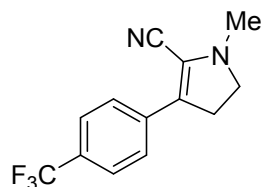
^1H NMR (400 MHz, CDCl_3): δ 7.48 – 7.42 (m, 4 H), 7.24 (t, $J = 9.6$ Hz, 2 H), 2.92 (t, $J = 9.6$ Hz, 2 H), 2.76 (s, 3 H); ^{13}C NMR (101 MHz, CDCl_3): δ 131.93, 131.33, 129.18, 126.98, 121.49, 120.71, 114.42, 54.74, 38.91, 32.31; HRMS (ESI) m/z calcd. for $\text{C}_{12}\text{H}_{12}\text{BrN}_2$ $[\text{M}+\text{H}]^+$: 263.0178, found: 263.0182.

3-(4-iodophenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4i)



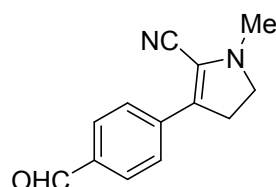
¹H NMR (400 MHz, CDCl₃): δ 7.66 (d, *J* = 8.4 Hz, 2 H), 7.30 (d, *J* = 8.4 Hz, 2 H), 3.24 (t, *J* = 10.0 Hz, 2 H), 2.90 (t, *J* = 9.6 Hz, 2 H), 2.76 (s, 3 H); ¹³C NMR (101 MHz, CDCl₃): δ 137.82, 132.54, 128.98, 127.07, 120.75, 114.36, 92.84, 54.67, 38.83, 32.14; HRMS (ESI) *m/z* calcd. for C₁₂H₁₂N₂ [M+H]⁺: 311.0040, found: 311.0046.

1-methyl-3-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4j)



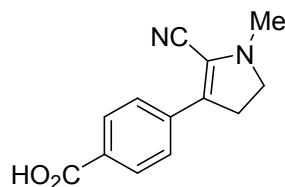
¹H NMR (400 MHz, CDCl₃): δ 7.65 (d, *J* = 8.4 Hz, 2 H), 7.58 (d, *J* = 8.4 Hz, 2 H), 3.29 (t, *J* = 9.6 Hz, 2 H), 4.07 (t, *J* = 9.6 Hz, 2 H), 2.80 (s, 3 H); ¹³C NMR (101 MHz, CDCl₃): δ 136.61, 129.27, 128.94, 127.72 (d, *J* = 3.8 Hz), 125.45, 122.86, 122.02, 114.11, 54.57, 38.57, 32.15; HRMS (ESI) *m/z* calcd. for C₁₃H₁₂F₃N₂ [M+H]⁺: 253.0947, found: 253.0950.

3-(4-formylphenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4k)



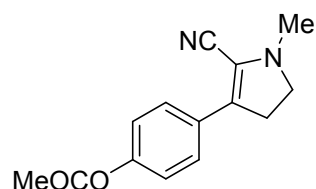
¹H NMR (400 MHz, CDCl₃): δ 9.96 (s, 1 H), 7.84 (d, *J* = 8.4 Hz, 2 H), 7.70 (d, *J* = 8.4 Hz, 2 H), 3.33 (t, *J* = 10.0 Hz, 2 H), 3.00 (t, *J* = 9.6 Hz, 2 H), 2.83 (s, 3 H); ¹³C NMR (101 MHz, CDCl₃): δ 191.40, 139.10, 134.86, 130.21, 127.39, 125.50, 122.68, 114.04, 54.41, 38.31, 31.97; HRMS (ESI) *m/z* calcd. for C₁₃H₁₃N₂O [M+H]⁺: 213.1022, found: 213.1026.

4-(2-cyano-1-methyl-4,5-dihydro-1H-pyrrol-3-yl)benzoic acid (4l)



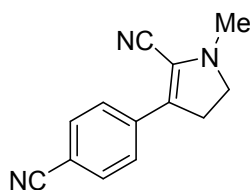
¹H NMR (400 MHz, DMSO-*d*₆): δ 12.96 (s, 1 H), 7.97 (d, *J* = 8.4 Hz, 2 H), 7.66 (d, *J* = 8.4 Hz, 2 H), 3.31 (t, *J* = 10.0 Hz, 2 H), 3.01 (t, *J* = 9.6 Hz, 2 H), 2.76 (s, 3 H); ¹³C NMR (101 MHz, DMSO-*d*₆): δ 166.87, 136.93, 129.77, 129.18, 128.35, 124.92, 121.08, 114.16, 53.96, 37.98, 31.52; HRMS (ESI) *m/z* calcd. for C₁₆H₁₉N₂O₂ [M+H]⁺: 229.0972, found: 229.0976.

4-(2-cyano-1-methyl-4,5-dihydro-1H-pyrrol-3-yl)phenyl acetate (4m)



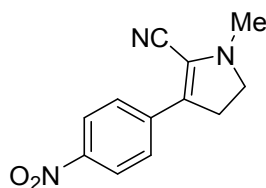
¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, *J* = 8.8 Hz, 2 H), 7.08 (d, *J* = 8.8 Hz, 2 H), 3.22 (t, *J* = 7.3 Hz, 2 H), 2.92 (t, *J* = 9.2 Hz, 2 H), 2.75 (s, 3 H), 2.29 (s, 3 H); ¹³C NMR (101 MHz, CDCl₃): δ 169.37, 150.05, 130.77, 129.72, 126.59, 121.93, 120.17, 114.55, 54.78, 39.02, 32.50, 21.18; HRMS (ESI) *m/z* calcd. for C₁₄H₁₅N₂O₂ [M+H]⁺: 243.1128, found: 243.1134.

3-(4-cyanophenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4n)



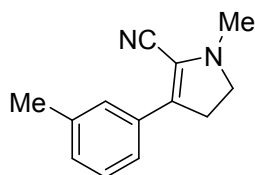
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.64 – 7.59 (m, 4 H), 3.33 (t, $J = 9.6$ Hz, 2 H), 2.96 (t, $J = 9.6$ Hz, 2 H), 2.83 (s, 3 H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 168.87, 137.61, 132.53, 128.97, 125.49, 122.89, 113.84, 110.22, 54.37, 38.27, 31.84; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{12}\text{N}_3$ $[\text{M}+\text{H}]^+$: 210.1026, found: 210.1030.

1-methyl-3-(4-nitrophenyl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4o)



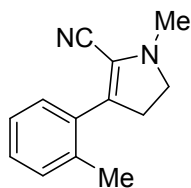
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.14 (d, $J = 9.2$ Hz, 2 H), 7.63 (d, $J = 9.2$ Hz, 2 H), 3.36 (t, $J = 10.0$ Hz, 2 H), 2.98 (t, $J = 10.0$ Hz, 2 H), 2.84 (s, 3 H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 145.78, 139.61, 125.49, 125.19, 124.09, 123.39, 113.68, 54.11, 37.92, 31.72; HRMS (ESI) m/z calcd. for $\text{C}_{12}\text{H}_{12}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+$: 230.0924, found: 230.0928.

1-methyl-3-(*m*-tolyl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4p)



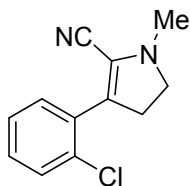
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.41 (t, $J = 8.0$ Hz, 1 H), 7.38 (s, 1 H), 7.25 (t, $J = 7.6$ Hz, 1 H), 7.09 (d, $J = 7.6$ Hz, 1 H), 3.22 (t, $J = 9.2$ Hz, 2 H), 2.94 (t, $J = 9.2$ Hz, 2 H), 2.76 (s, 3 H) 2.36 (s, 3 H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 138.36, 133.00, 131.11, 128.76, 126.26, 122.81, 120.01, 114.73, 108.40, 54.92, 39.19, 32.56, 21.57; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{15}\text{N}_2$ $[\text{M}+\text{H}]^+$: 199.1230, found: 199.1235.

1-methyl-3-(*o*-tolyl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4q)



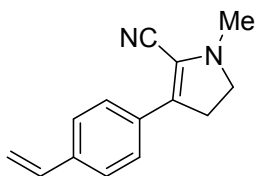
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.28 – 7.19 (m, 4 H), 3.26 (t, $J = 9.6$ Hz, 2 H), 2.90 (t, $J = 9.6$ Hz, 2 H), 2.76 (s, 3 H) 2.38 (s, 3 H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 136.18, 134.11, 133.24, 130.80, 128.92, 128.39, 126.08, 123.68, 113.61, 55.94, 39.57, 35.38, 20.44; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{15}\text{N}_2$ $[\text{M}+\text{H}]^+$: 199.1230, found: 199.1236.

3-(2-chlorophenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4r)



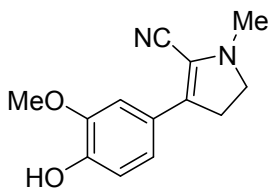
^1H NMR (400 MHz, CDCl_3): δ 7.43 – 7.41 (m, 1 H), 7.40 – 7.38 (m, 1 H), 7.31 – 7.28 (m, 1 H), 7.27 – 7.25 (m, 1 H), 3.29 (t, J = 10.0 Hz, 2 H), 3.04 (t, J = 8.8 Hz, 2 H), 2.78 (s, 3 H); ^{13}C NMR (101 MHz, CDCl_3): δ 133.10, 132.69, 131.21, 130.59, 130.28, 129.51, 127.09, 124.56, 113.24, 55.91, 39.14, 34.31; HRMS (ESI) m/z calcd. for $\text{C}_{12}\text{H}_{12}\text{ClN}_2$ $[\text{M}+\text{H}]^+$: 219.0684, found: 219.0688.

1-methyl-3-(4-vinylphenyl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4s)



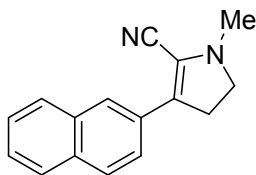
^1H NMR (400 MHz, CDCl_3): δ 7.55 (d, J = 8.4 Hz, 2 H), 7.39 (d, J = 8.4 Hz, 2 H), 6.73 – 6.66 (m, 1 H), 5.76 (d, J = 17.6 Hz, 1 H), 5.26 (d, J = 10.8 Hz, 1 H), 3.23 (t, J = 9.6 Hz, 2 H), 2.92 (t, J = 9.6 Hz, 2 H), 2.77 (s, 3 H); ^{13}C NMR (101 MHz, CDCl_3): δ 137.05, 136.36, 132.43, 130.40, 126.58, 125.68, 120.00, 114.76, 114.30, 54.82, 39.08, 32.36; HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{15}\text{N}_2$ $[\text{M}+\text{H}]^+$: 211.1230, found: 211.1234.

3-(4-hydroxy-3-methoxyphenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4t)



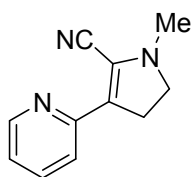
^1H NMR (400 MHz, CDCl_3): δ 7.35 (d, J = 2.0 Hz, 1 H), 6.96 – 6.93 (m, 1 H), 6.89 (d, J = 8.4 Hz, 1 H), 5.76 (s, 1 H), 3.92 (s, 3 H), 3.19 (t, J = 9.6 Hz, 2 H), 2.92 (t, J = 9.2 Hz, 2 H), 2.74 (s, 3 H); ^{13}C NMR (101 MHz, CDCl_3): δ 146.69, 145.92, 131.92, 125.47, 119.61, 118.43, 115.30, 114.58, 107.93, 56.13, 55.01, 39.51, 32.72; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 231.1128, found: 231.1132.

1-methyl-3-(naphthalen-2-yl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4u)



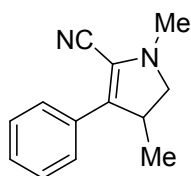
^1H NMR (400 MHz, CDCl_3): δ 7.94 – 7.92 (m, 1 H), 7.82 – 7.80 (m, 4 H), 7.50 – 7.44 (m, 2 H), 3.27 (t, J = 10.4 Hz, 2 H), 3.06 (q, J = 9.2 Hz, 2 H), 2.80 (s, 3 H); ^{13}C NMR (101 MHz, CDCl_3): δ 174.99, 137.44, 133.56, 132.58, 128.60, 127.83, 127.67, 126.74, 126.15, 126.06, 125.77, 108.54, 48.24, 47.86, 30.24, 28.04; HRMS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{15}\text{N}_2$ $[\text{M}+\text{H}]^+$: 235.1230, found: 235.1235.

1-methyl-3-(pyridin-2-yl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4v)



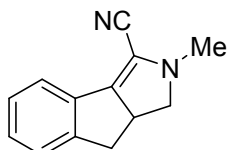
^1H NMR (400 MHz, CDCl_3): δ 8.57 (d, $J = 4.4$ Hz, 1 H), 7.65 – 7.61 (m, 1 H), 7.54 (t, $J = 8.0$ Hz, 1 H), 7.11 – 7.08 (m, 1 H), 3.30 (t, $J = 10.0$ Hz, 2 H), 3.04 (t, $J = 9.6$ Hz, 2 H), 2.81 (s, 3 H); ^{13}C NMR (101 MHz, CDCl_3): δ 151.89, 149.53, 136.30, 129.53, 123.04, 121.66, 119.89, 114.04, 54.86, 38.37, 31.16; HRMS (ESI) m/z calcd. for $\text{C}_{11}\text{H}_{12}\text{N}_3$ $[\text{M}+\text{H}]^+$: 186.1026, found: 186.1030.

1,4-dimethyl-3-phenyl-1H-pyrrole-2-carbonitrile (4w)



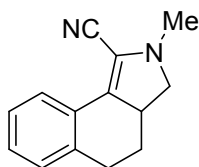
^1H NMR (400 MHz, CDCl_3): δ 7.48 – 7.46 (m, 2 H), 7.29 (t, $J = 8.0$ Hz, 2 H), 7.19 (t, $J = 7.6$ Hz, 1 H), 3.40 – 3.31 (m, 1 H), 3.20 (t, $J = 9.6$ Hz, 1 H), 2.92 – 2.86 (m, 1 H), 2.67 (s, 3 H), 1.09 (d, $J = 6.8$ Hz, 3 H); ^{13}C NMR (101 MHz, CDCl_3): δ 136.16, 132.35, 128.88, 127.83, 126.31, 119.88, 114.66, 62.73, 38.92, 29.84, 18.14; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{15}\text{N}_2$ $[\text{M}+\text{H}]^+$: 199.1230, found: 199.1234.

2-methyl-1,2,8,8a-tetrahydroindeno[1,2-c]pyrrole-3-carbonitrile (4x)



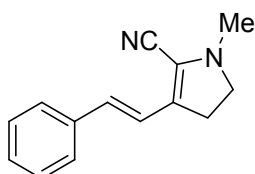
^1H NMR (400 MHz, CDCl_3): δ 7.57 (t, $J = 3.2$ Hz, 1 H), 7.22 (d, $J = 7.2$ Hz, 3 H), 3.97 (t, $J = 8.4$ Hz, 1 H), 3.67 (t, $J = 9.2$ Hz, 1 H), 7.34 – 7.21 (m, 2 H), 3.09 – 3.06 (m, 1 H), 2.77 (s, 3 H); ^{13}C NMR (101 MHz, CDCl_3): δ 173.88, 141.94, 139.50, 127.86, 127.27, 125.14, 124.80, 113.20, 55.76, 53.61, 38.90, 34.62, 29.76; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{13}\text{N}_2$ $[\text{M}+\text{H}]^+$: 197.1073, found: 197.1076.

2-methyl-3,3a,4,5-tetrahydro-2H-benzo[e]isoindole-1-carbonitrile (4y)



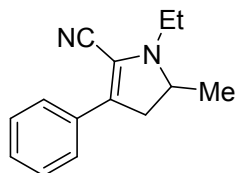
^1H NMR (400 MHz, CDCl_3): δ 8.08 (d, $J = 7.2$ Hz, 1 H), 7.21 – 7.14 (m, 3 H), 3.65 (t, $J = 8.8$ Hz, 1 H), 3.23 – 3.13 (m, 1 H), 2.90 – 2.88 (m, 1 H), 2.73 (s, 3 H), 2.51 (q, $J = 8.8$ Hz, 1 H), 2.16 – 2.10 (m, 1 H), 1.71 – 1.60 (m, 2 H); ^{13}C NMR (101 MHz, CDCl_3): δ 136.62, 132.14, 129.44, 128.64, 128.03, 126.75, 124.24, 116.81, 114.97, 61.78, 43.42, 39.15, 29.99, 27.86; HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{15}\text{N}_2$ $[\text{M}+\text{H}]^+$: 211.1230, found: 211.1234.

(E)-1-methyl-3-styryl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4z)



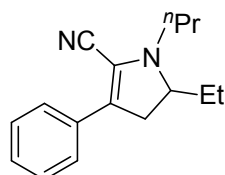
¹H NMR (400 MHz, CDCl₃): δ 7.43 (d, *J* = 7.6 Hz, 2 H), 7.33 (t, *J* = 7.2 Hz, 2 H), 7.23 (t, *J* = 7.2 Hz, 1 H), 7.06 (d, *J* = 16.0 Hz, 1 H), 6.39 (d, *J* = 15.6 Hz, 1 H), 3.26 (t, *J* = 9.6 Hz, 2 H), 2.82 (t, *J* = 9.2 Hz, 2 H), 2.75 (s, 3 H); ¹³C NMR (101 MHz, CDCl₃): δ 137.17, 132.13, 129.29, 128.87, 127.82, 126.53, 123.37, 120.72, 113.21, 55.00, 38.60, 29.85; HRMS (ESI) *m/z* calcd. for C₁₄H₁₅N₂ [M+H]⁺: 211.1230, found: 211.1236.

1-ethyl-5-methyl-3-phenyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4aa)



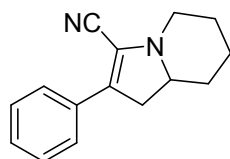
¹H NMR (400 MHz, CDCl₃): δ 7.57 (d, *J* = 7.6 Hz, 2 H), 7.35 (t, *J* = 7.6 Hz, 2 H), 7.23 (t, *J* = 7.6 Hz, 1 H), 3.65 – 3.55 (m, 1 H), 3.31 – 3.22 (m, 1 H), 3.19 – 3.09 (m, 2 H), 2.62 – 2.55 (m, 1 H), 1.31 (d, *J* = 6.0 Hz, 3 H), 1.16 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (101 MHz, CDCl₃): δ 133.34, 128.74, 128.27, 127.49, 125.39, 118.32, 114.99, 57.17, 42.53, 40.53, 19.68, 12.15; HRMS (ESI) *m/z* calcd. for C₁₄H₁₇N₂ [M+H]⁺: 213.1386, found: 213.1390.

5-ethyl-3-phenyl-1-propyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4ab)



¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, *J* = 7.6 Hz, 2 H), 7.34 (t, *J* = 7.6 Hz, 2 H), 7.23 (t, *J* = 7.6 Hz, 1 H), 3.48 – 3.40 (m, 1 H), 3.11 – 3.05 (m, 2 H), 2.66 – 2.59 (m, 1 H), 1.85 – 1.75 (m, 1 H), 1.70 – 1.49 (m, 4 H), 0.96 (t, *J* = 7.2 Hz, 6 H); ¹³C NMR (101 MHz, CDCl₃): δ 133.45, 128.72, 127.33, 127.22, 125.32, 118.98, 115.08, 63.80, 50.89, 37.70, 26.83, 21.03, 11.59, 9.65; HRMS (ESI) *m/z* calcd. for C₁₆H₂₁N₂ [M+H]⁺: 241.1699, found: 241.1704.

2-phenyl-1,5,6,7,8,8a-hexahydroindolizine-3-carbonitrile (4ac)



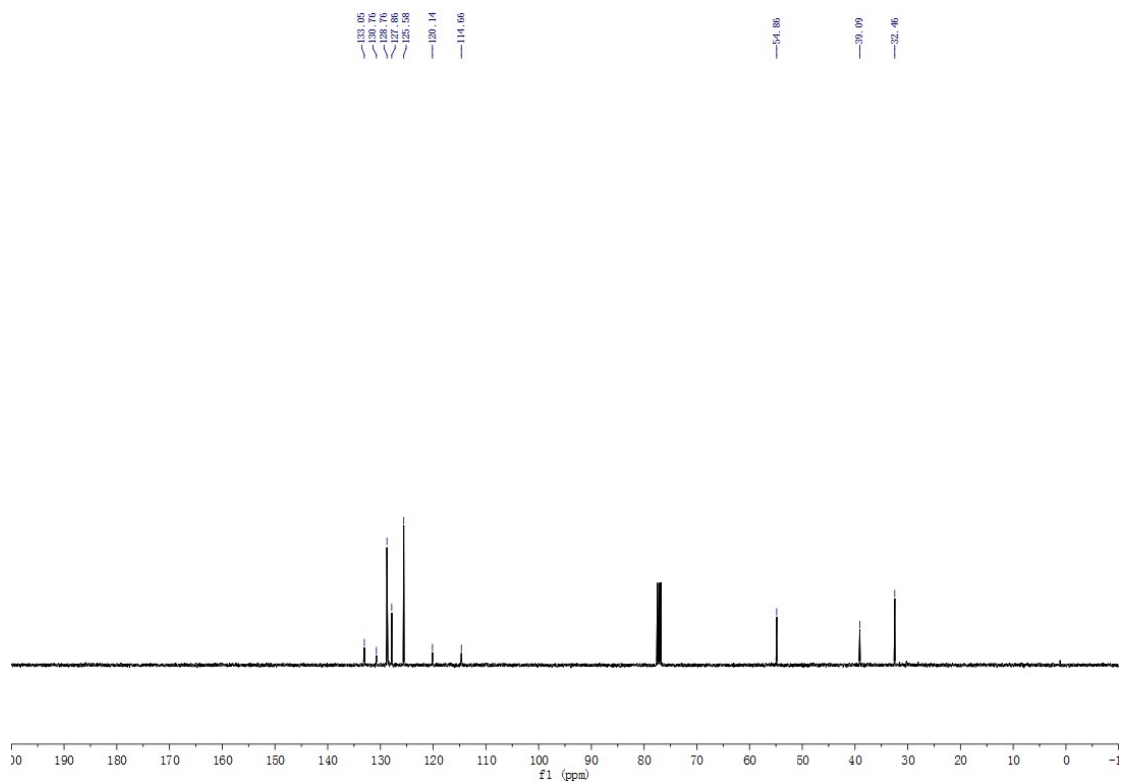
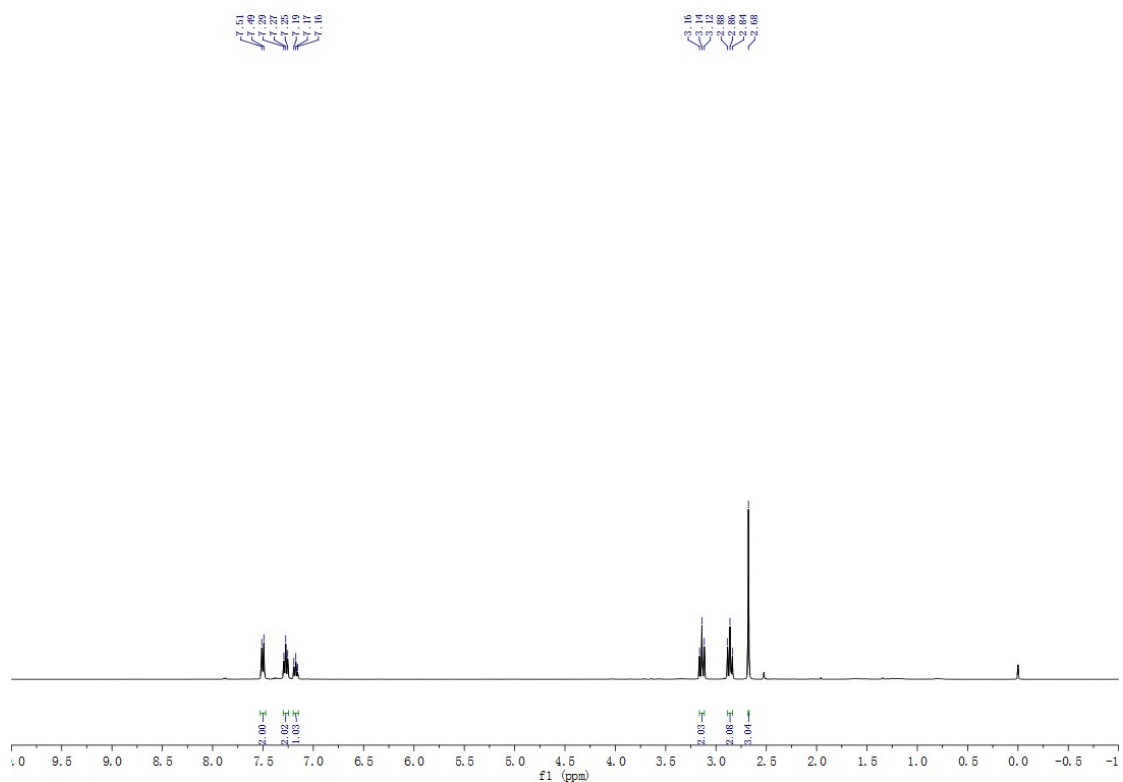
¹H NMR (400 MHz, CDCl₃): δ 7.57 (d, *J* = 7.2 Hz, 2 H), 7.35 (t, *J* = 7.6 Hz, 2 H), 7.23 (t, *J* = 7.6 Hz, 1 H), 3.69 – 3.65 (m, 1 H), 3.25 – 3.17 (m, 1 H), 2.98 – 2.92 (m, 1 H), 2.76 – 2.70 (m, 1 H), 2.60 – 2.53 (m, 1 H), 1.87 (d, *J* = 12.8 Hz, 1 H), 1.76 – 1.68 (m, 2 H), 1.62 – 1.51 (m, 2 H), 1.46 – 1.35 (m, 1 H); ¹³C NMR (101 MHz, CDCl₃): δ 133.63, 128.74, 128.36, 127.39, 125.27, 118.20, 114.39, 63.81, 47.57, 38.44, 29.68, 25.25, 24.13; HRMS (ESI) *m/z* calcd. for C₁₅H₁₇N₂ [M+H]⁺: 225.1386, found: 225.1388.

4. References

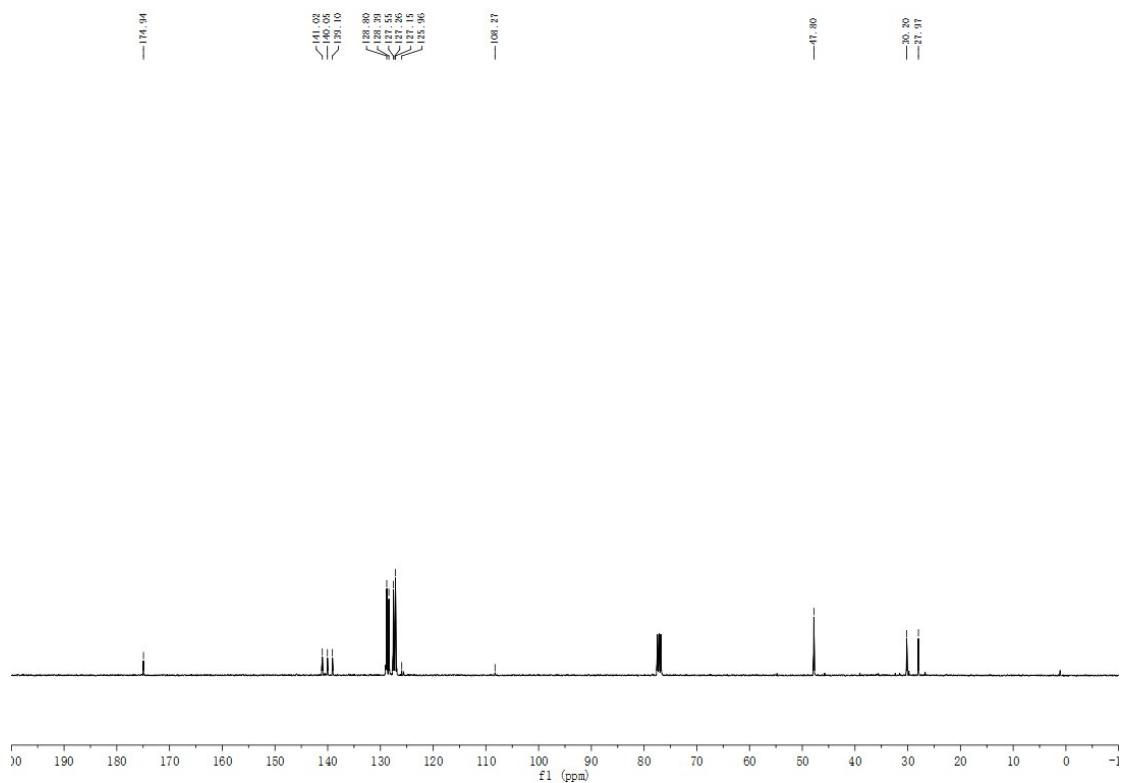
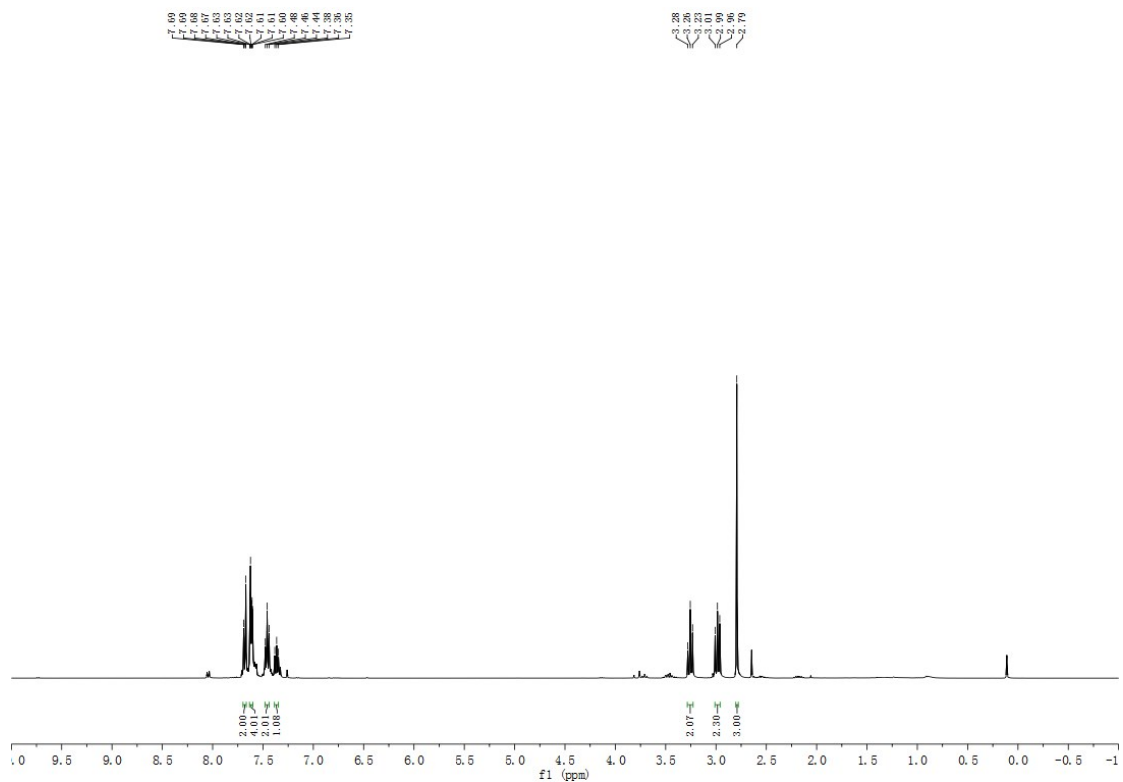
1. X.-Q. Mou.; Z.-L. Xu.; L. Xu.; S.-H. Wang.; B.-H. Zhang.; D. Zhang.; J. Wang.; W.-T. Liu.; W. Bao., *Org. Lett.* **2016**, *18* (16), 4032-4035.

5. ^1H and ^{13}C NMR spectra of products

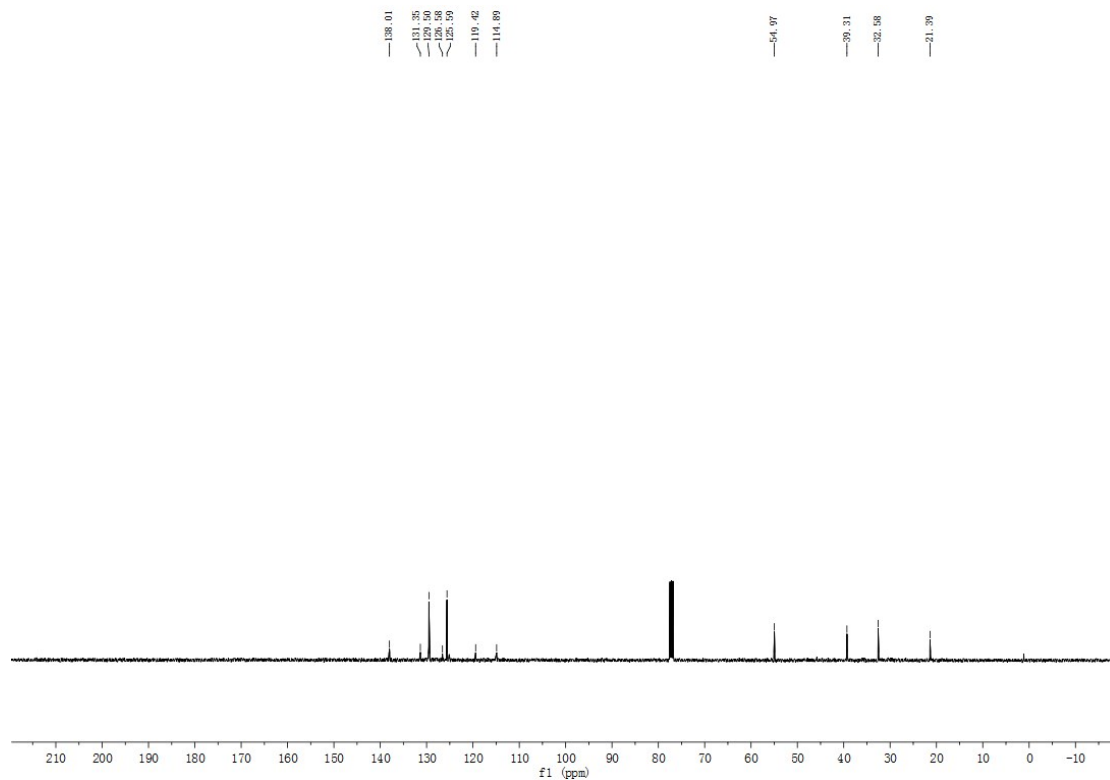
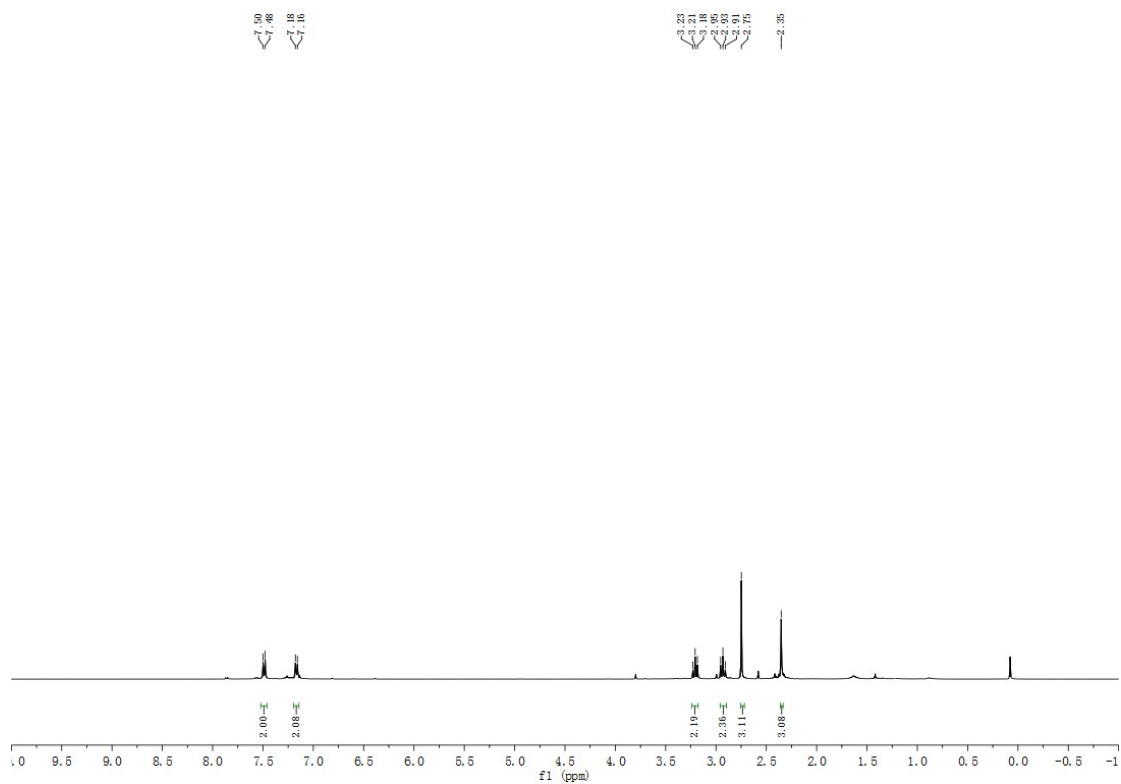
1-methyl-3-phenyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4a)



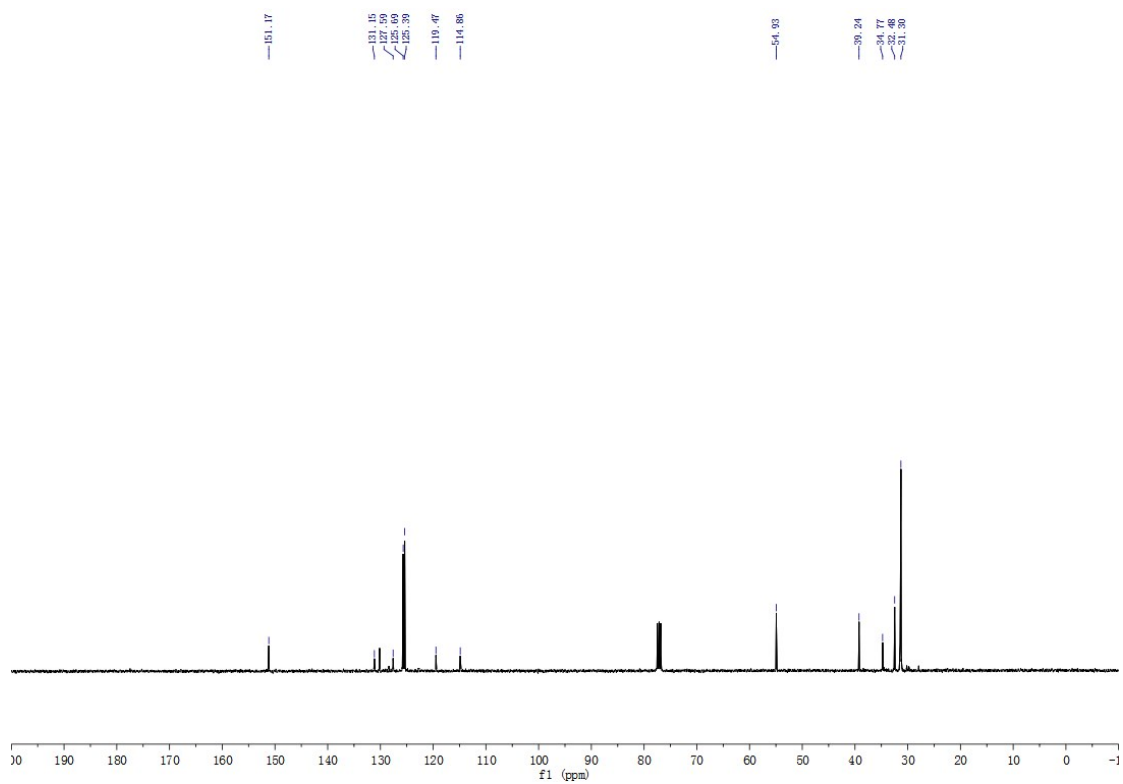
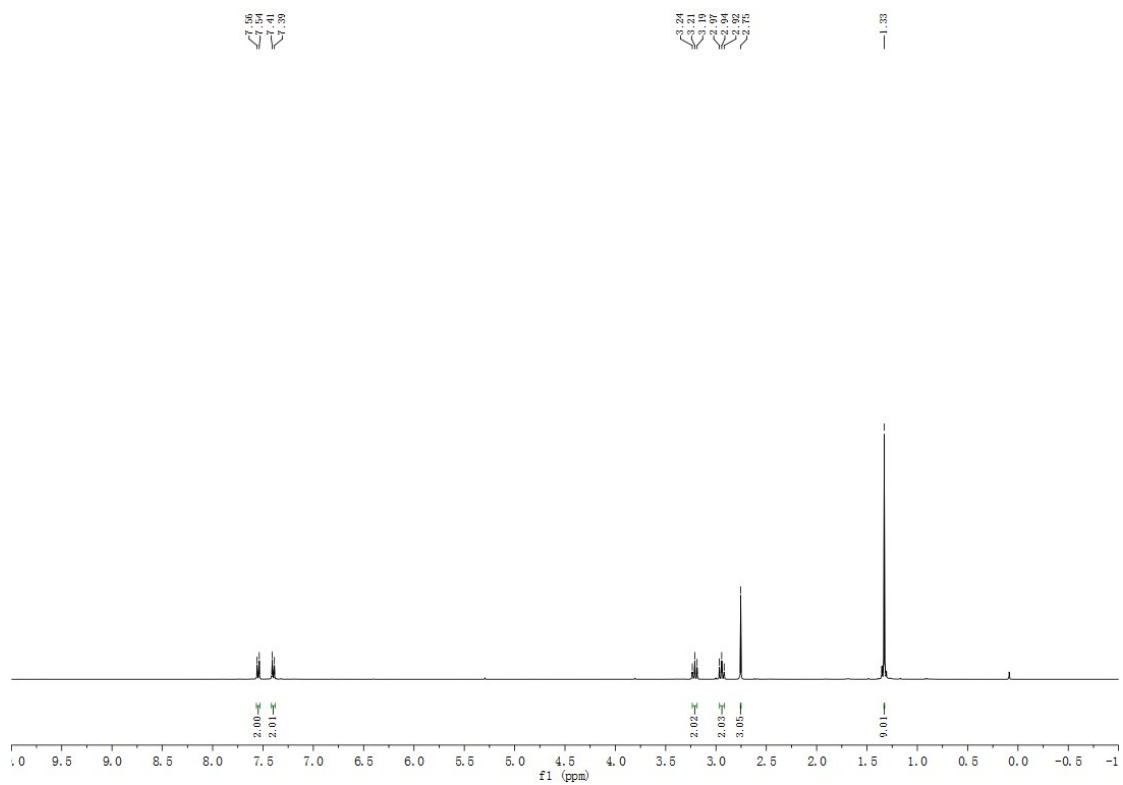
3-([1,1'-biphenyl]-4-yl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4b)



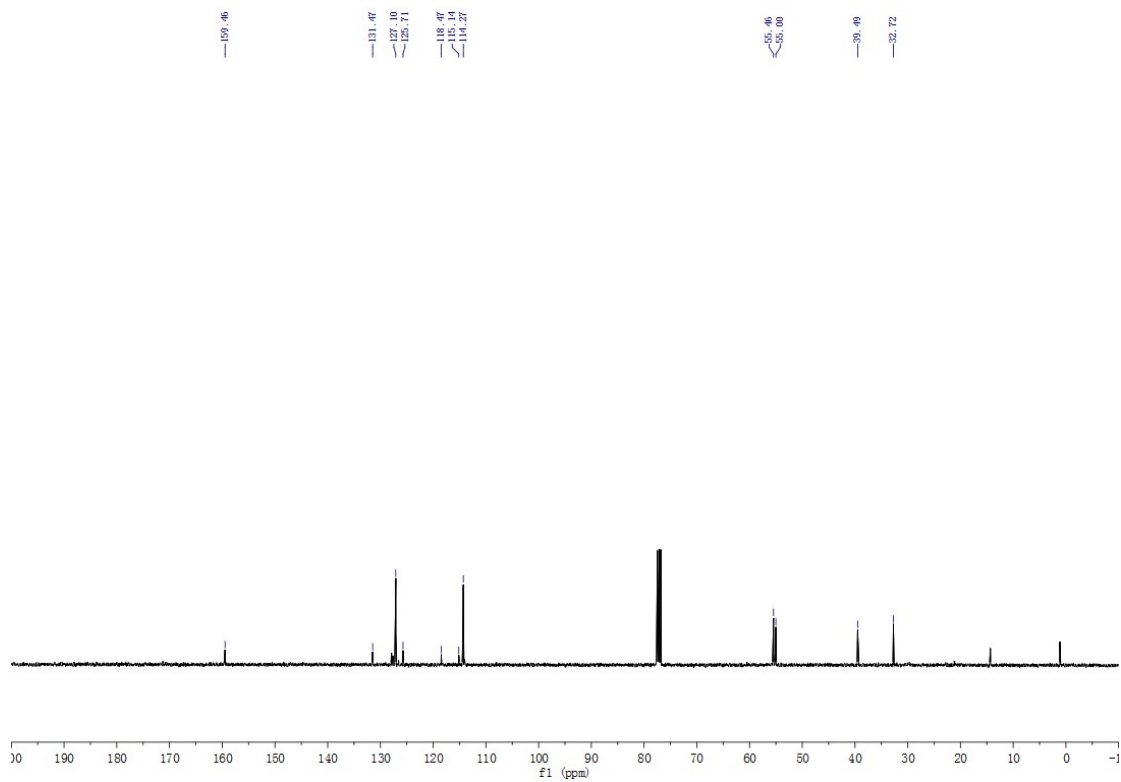
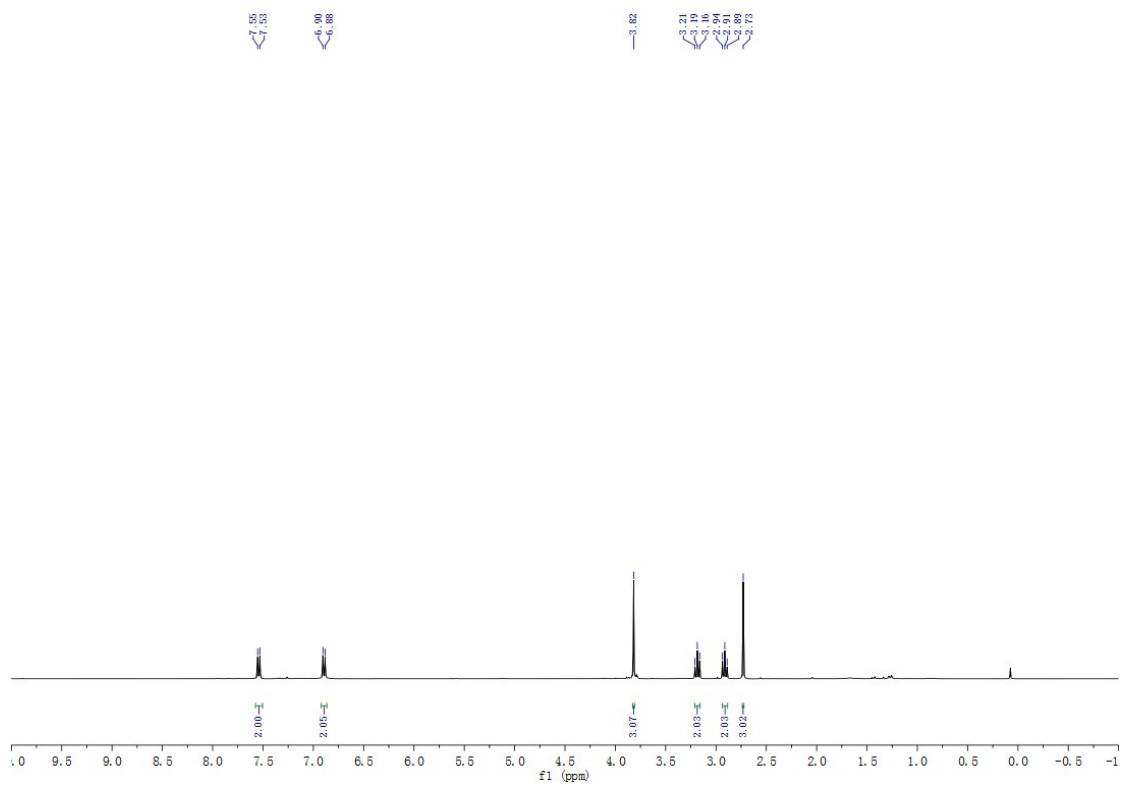
1-methyl-3-(p-tolyl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4c)



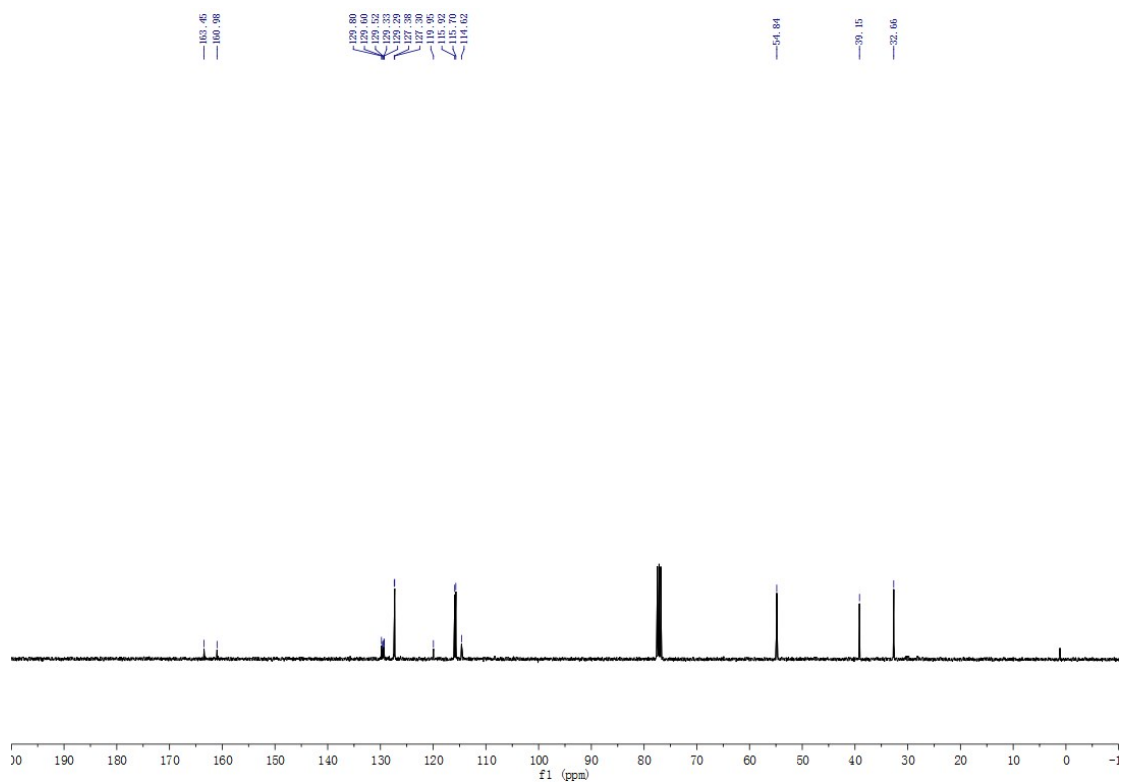
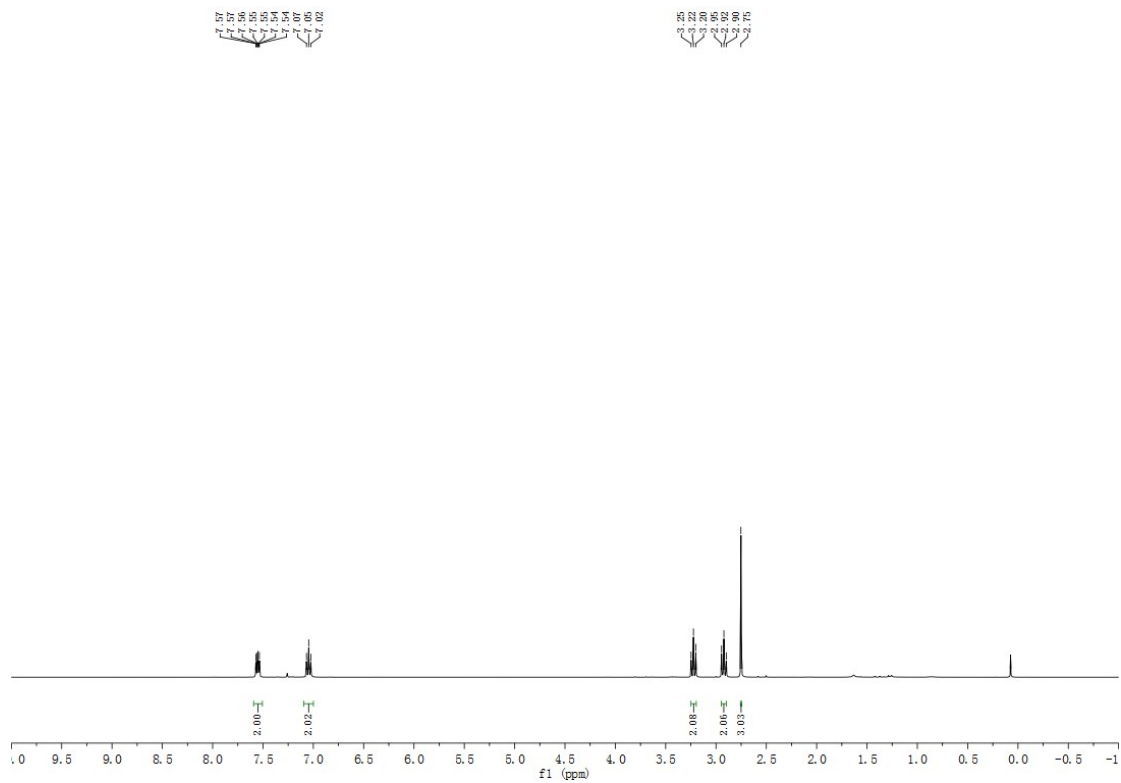
3-(4-(tert-butyl)phenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4d)



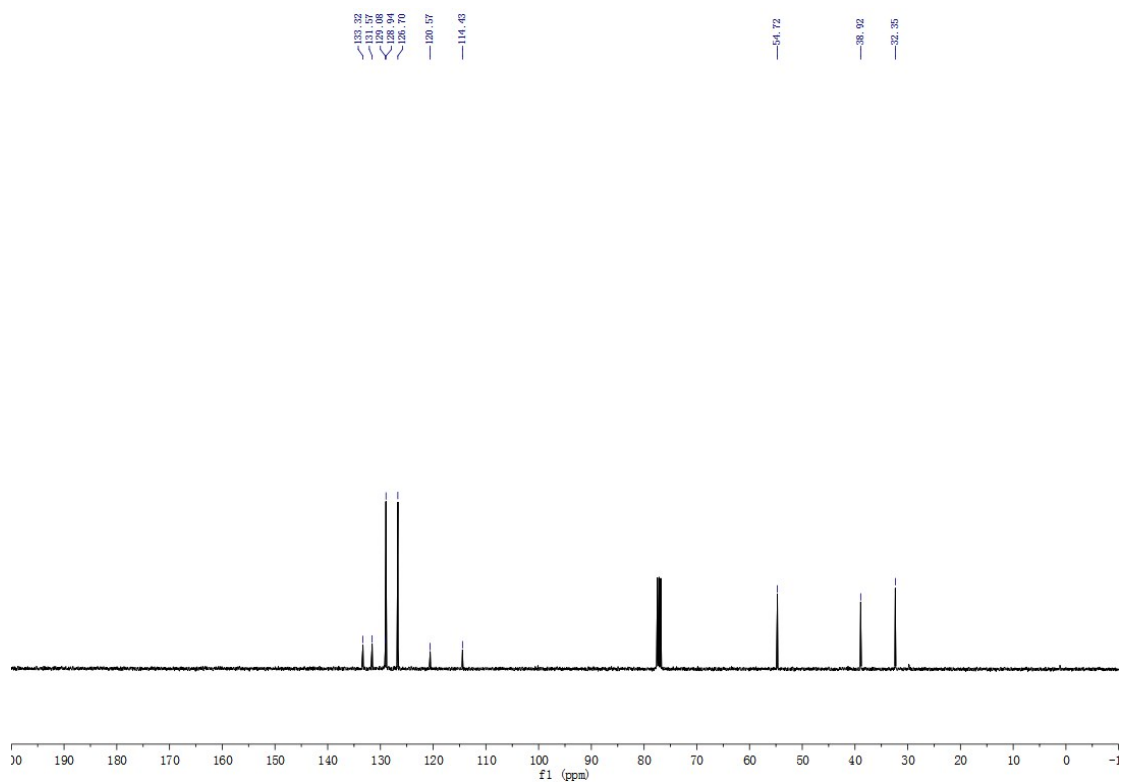
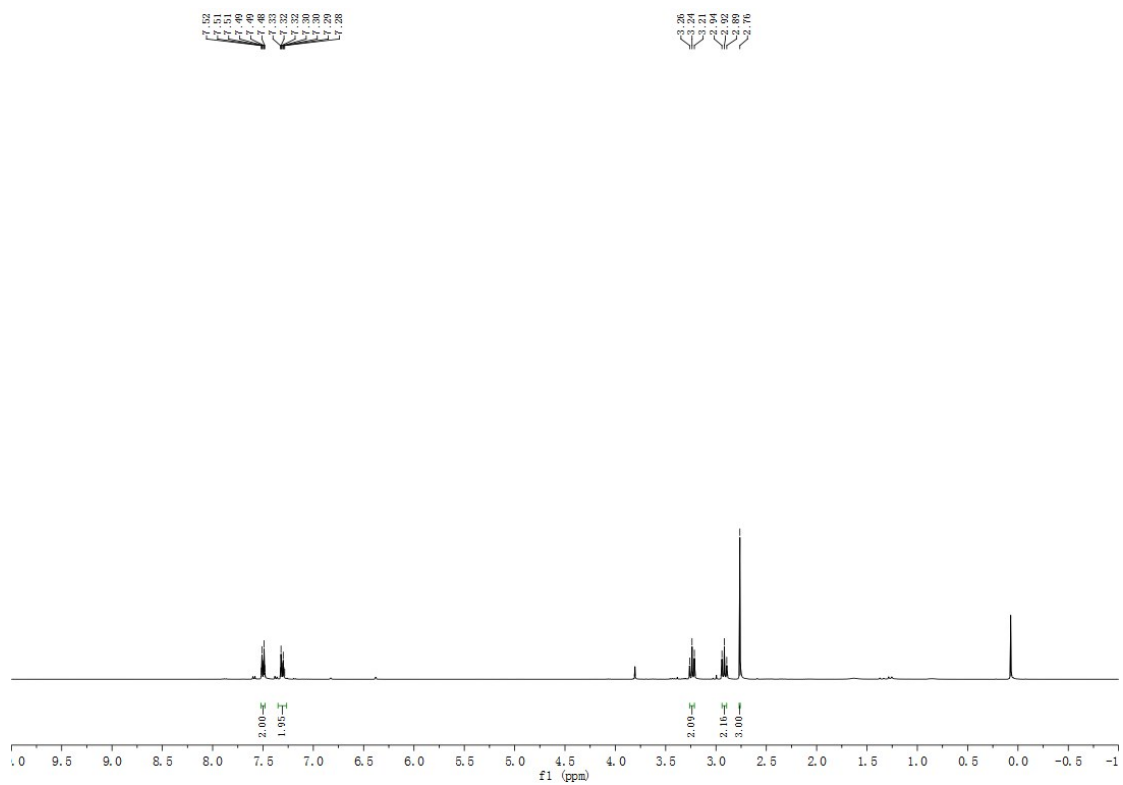
3-(4-methoxyphenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4e)



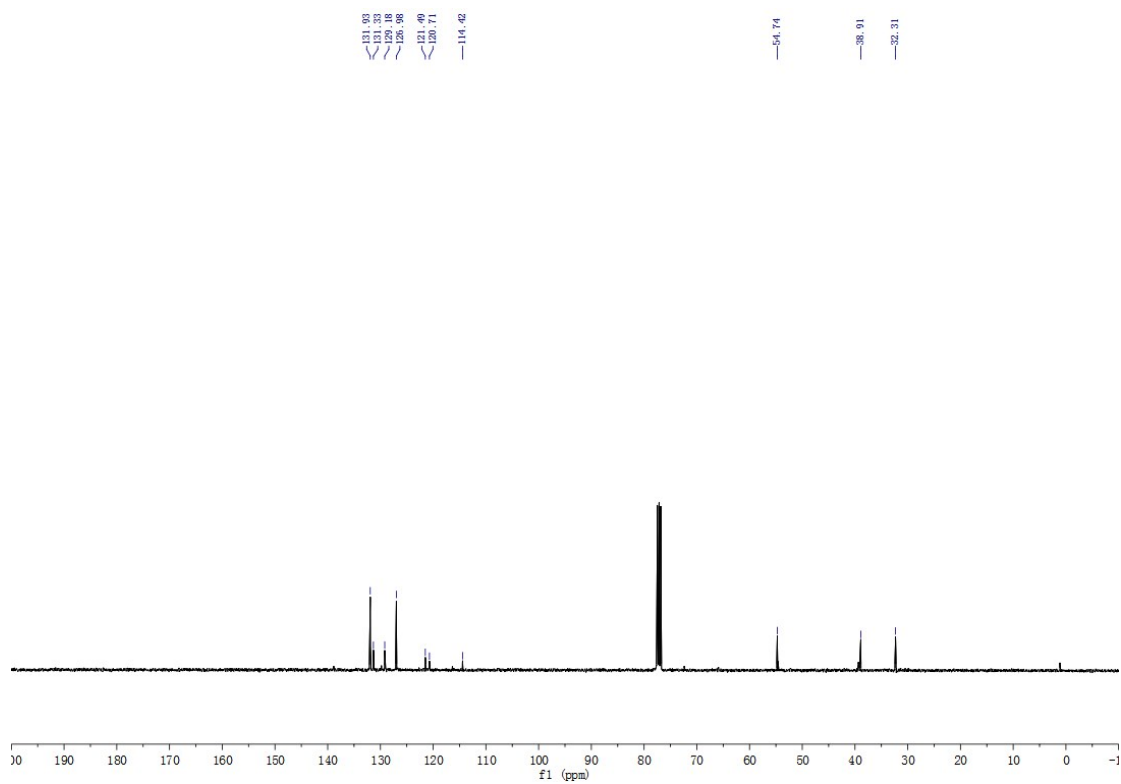
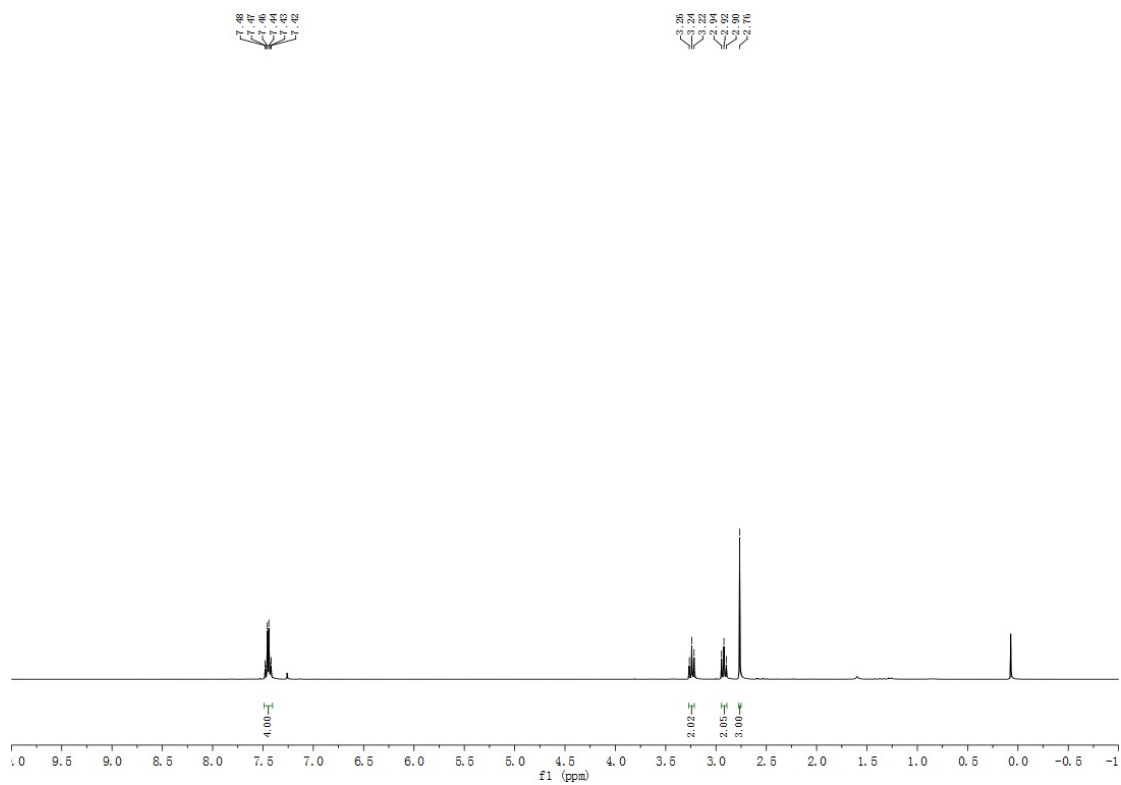
3-(4-fluorophenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4f)



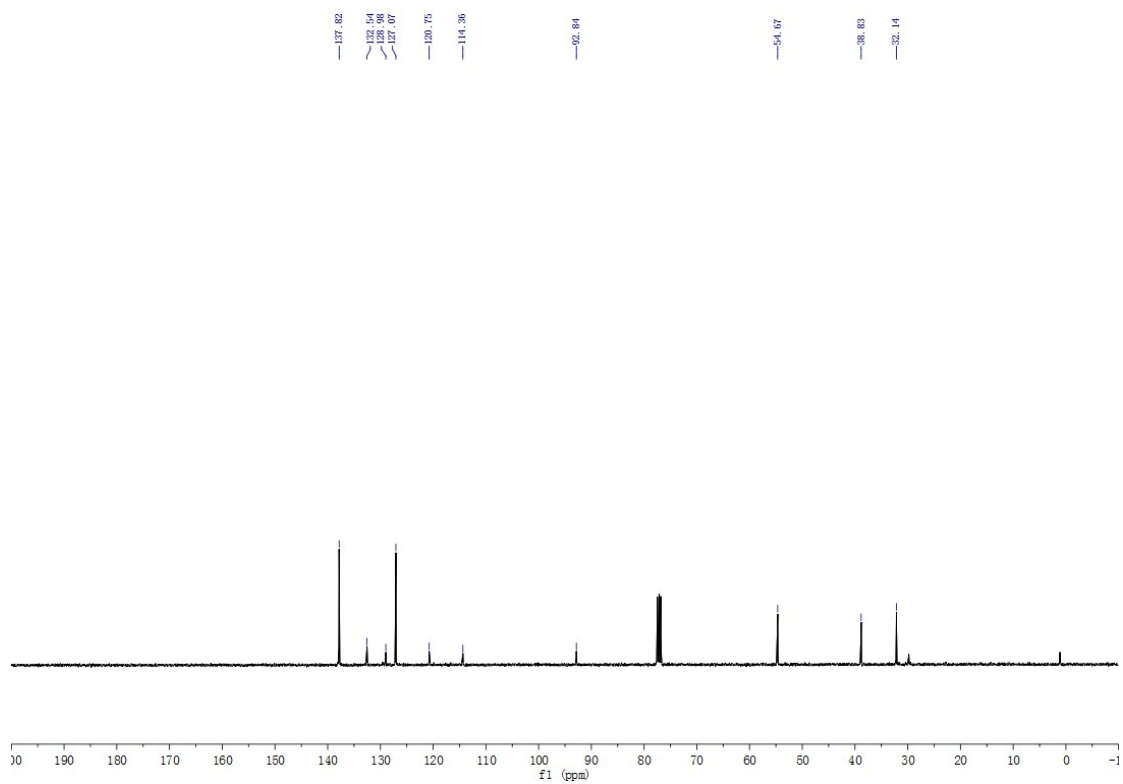
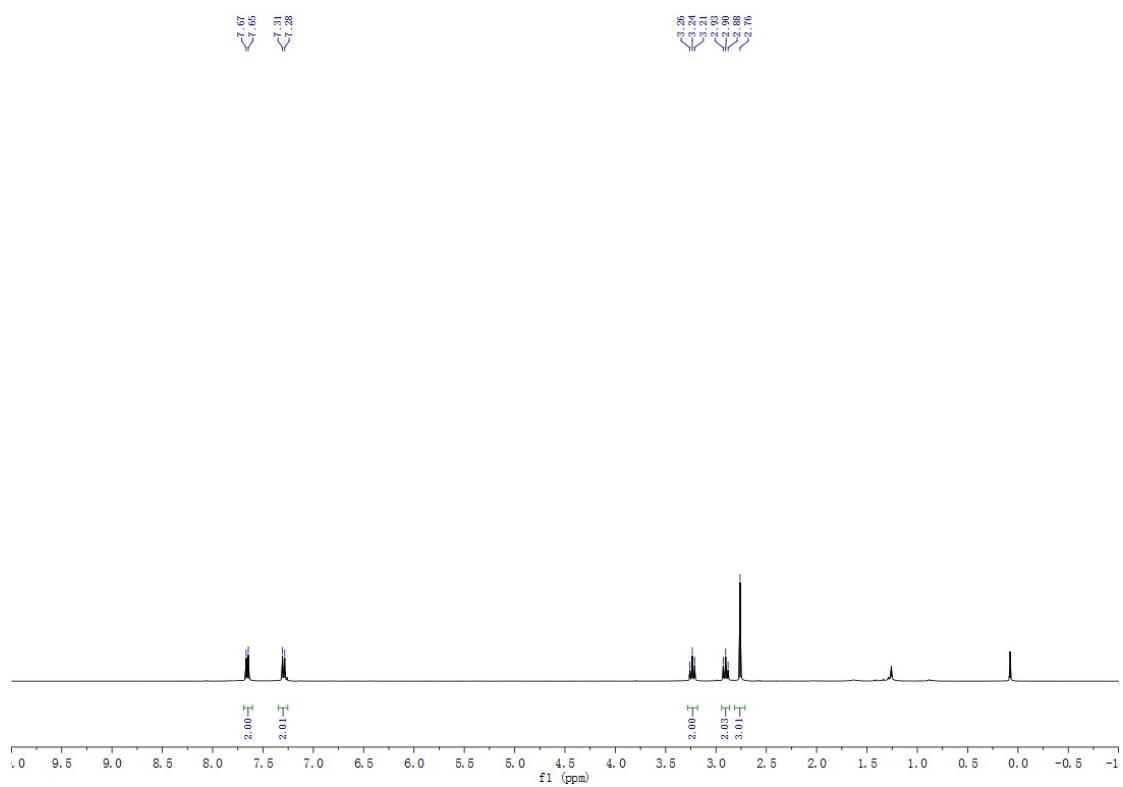
3-(4-chlorophenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4g)



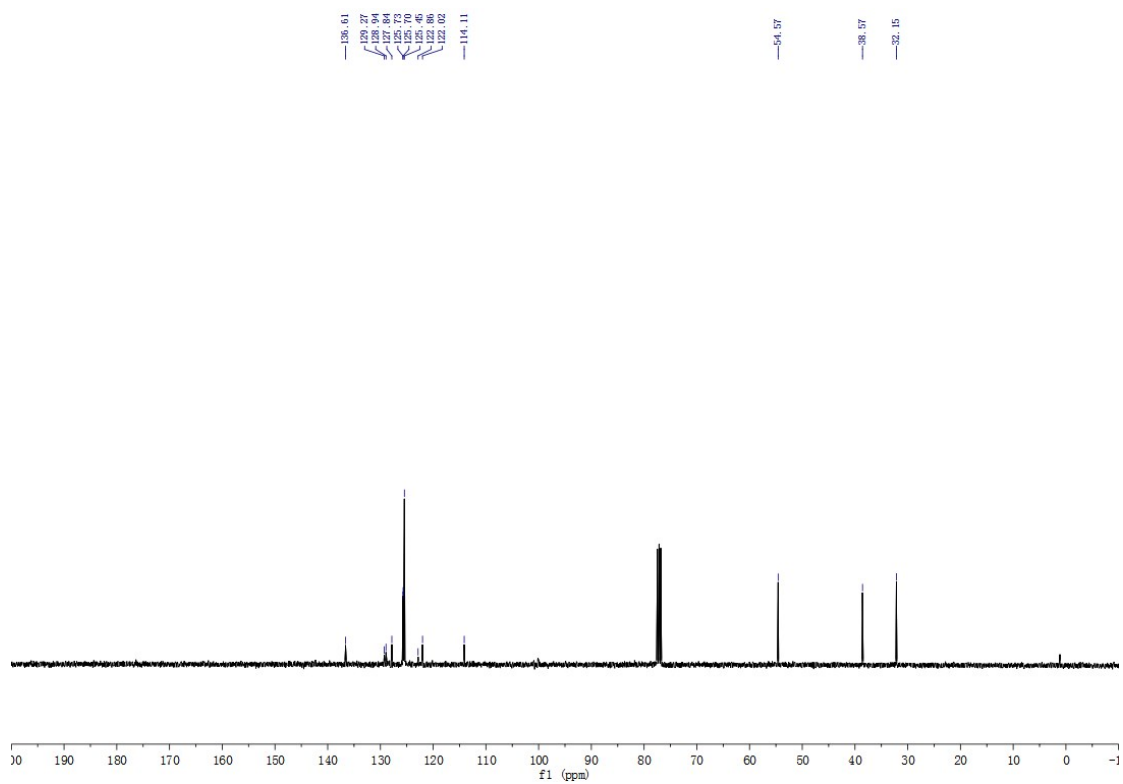
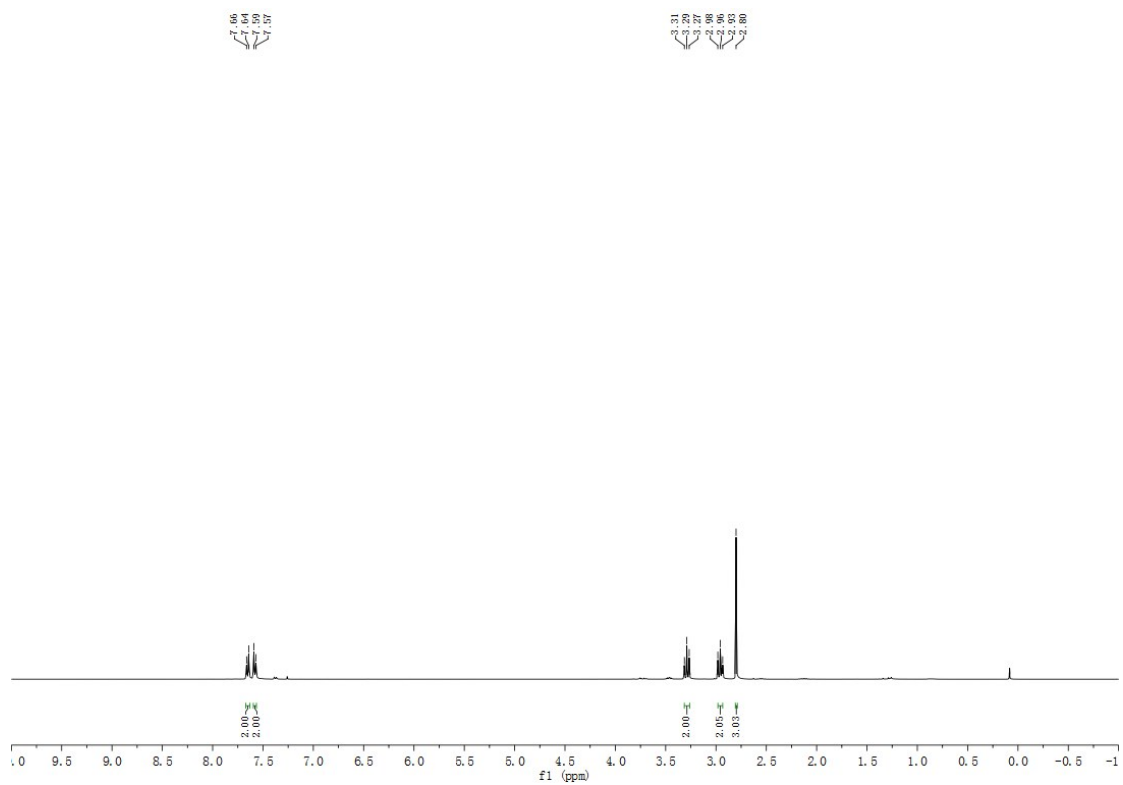
3-(4-bromophenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4h)



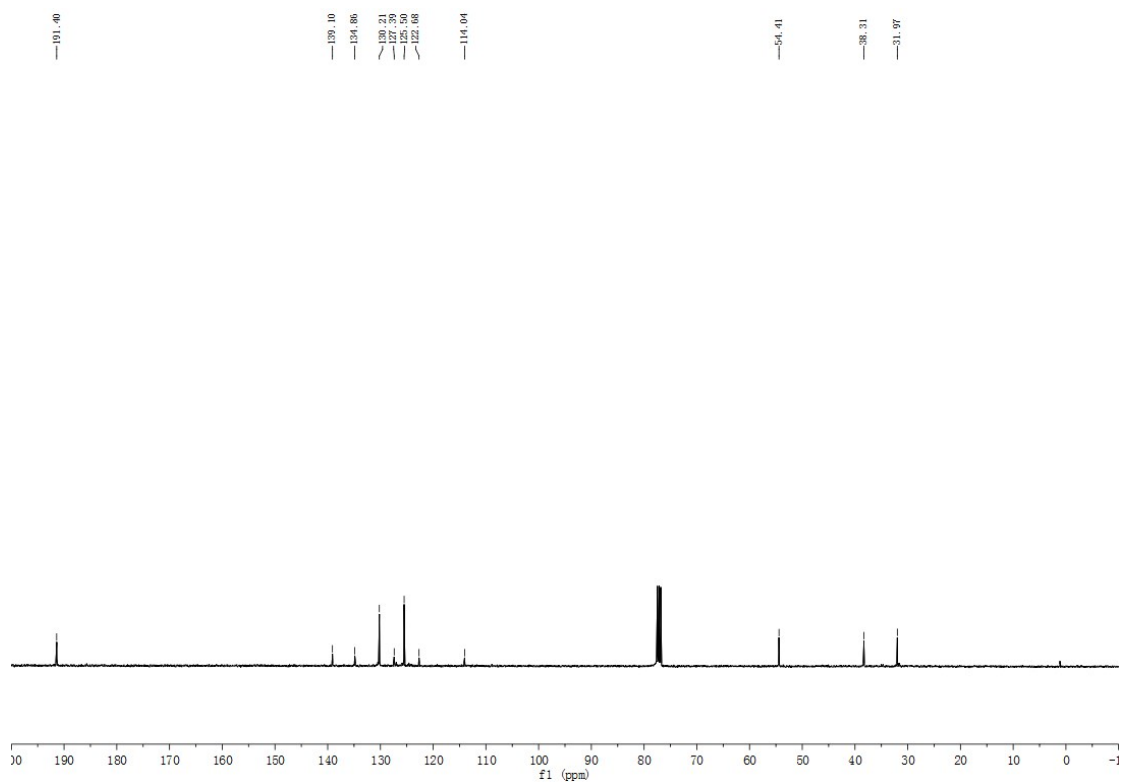
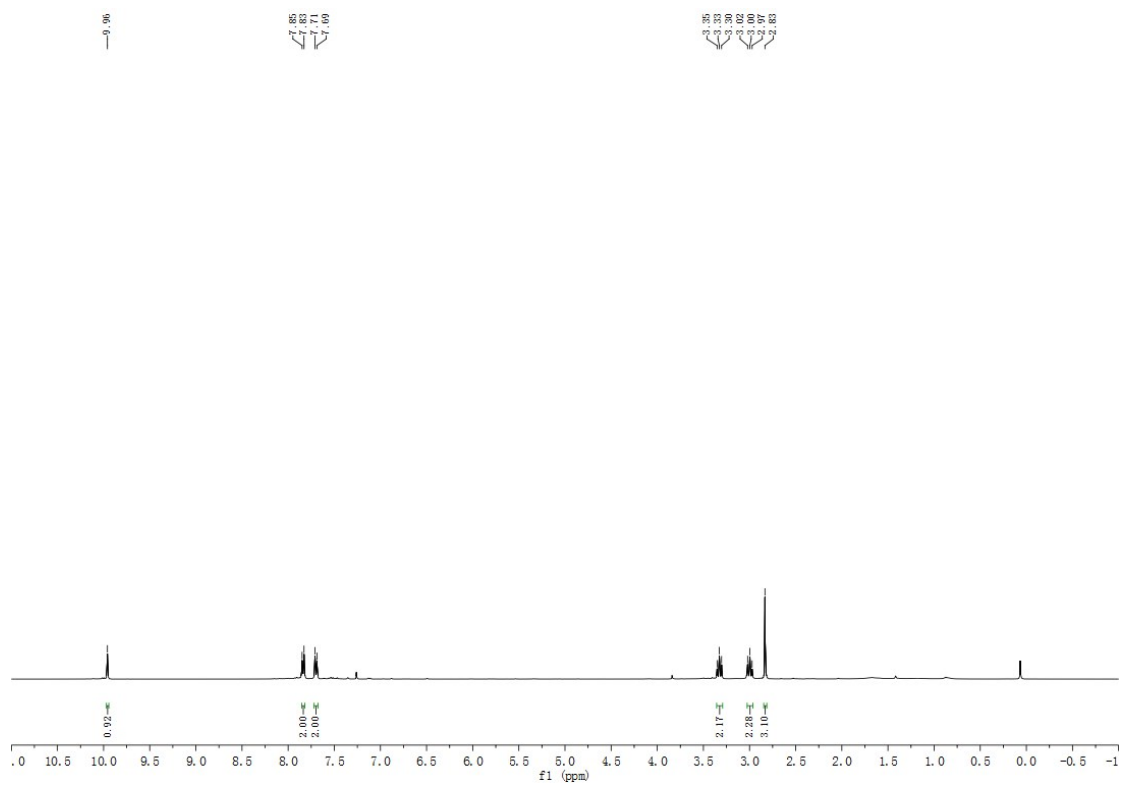
3-(4-iodophenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4i)



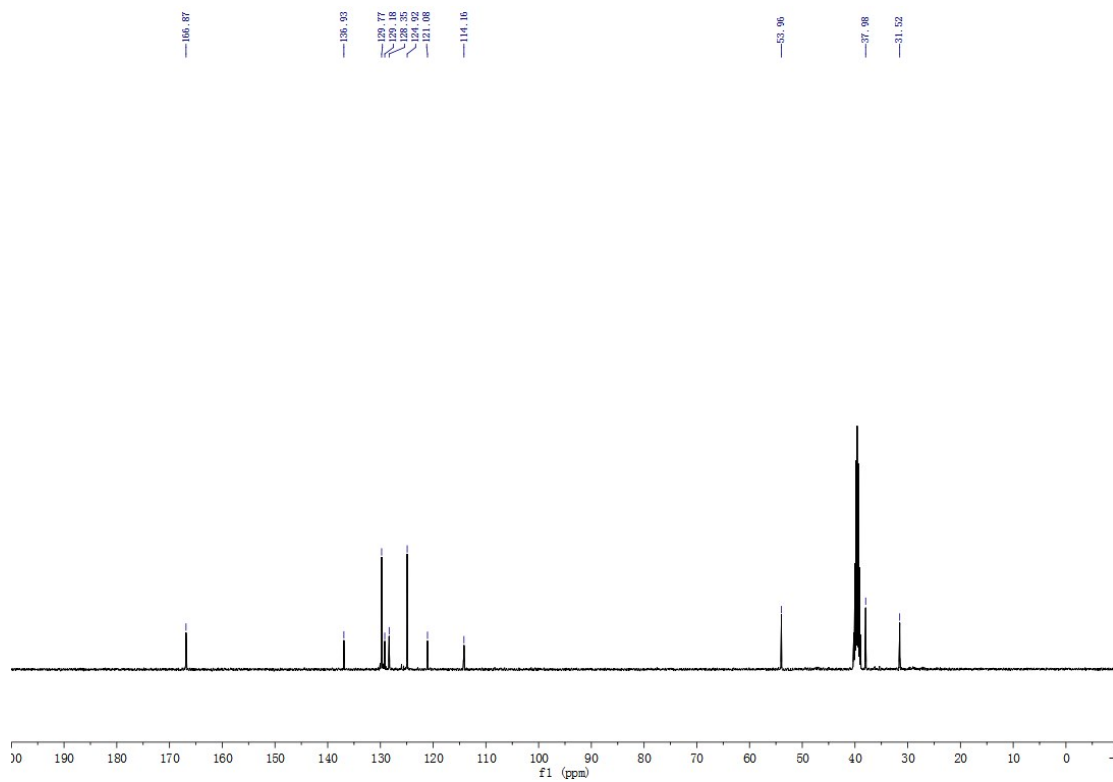
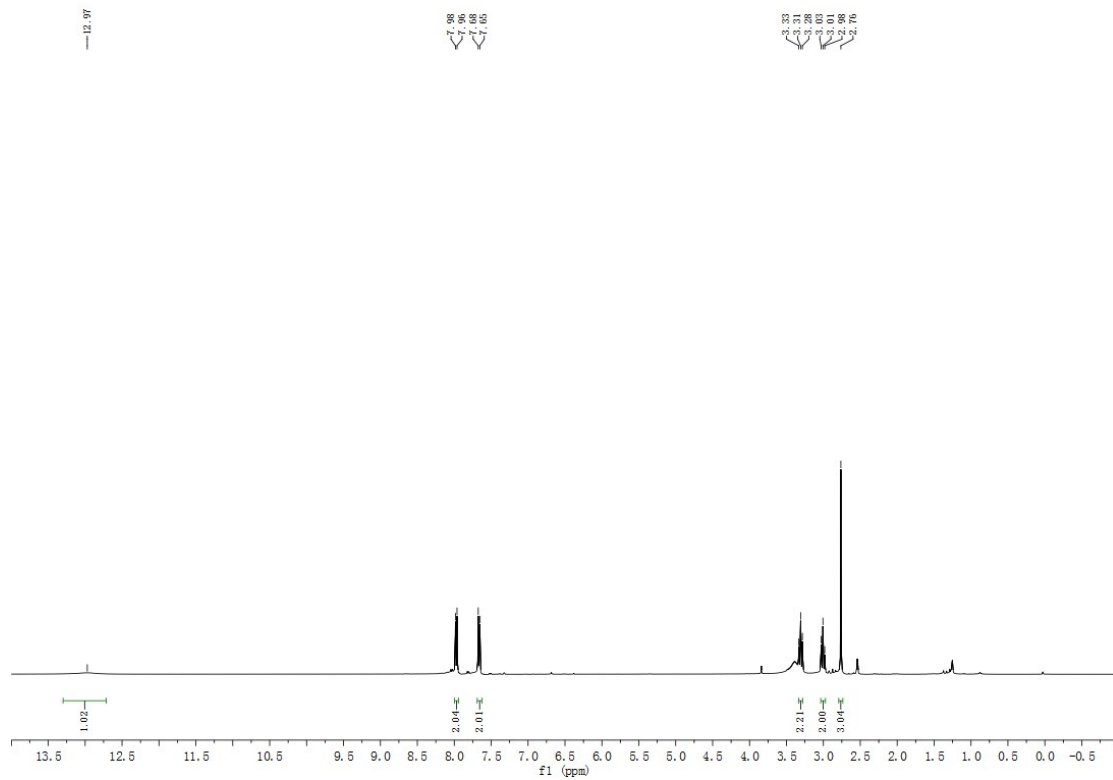
1-methyl-3-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4j)



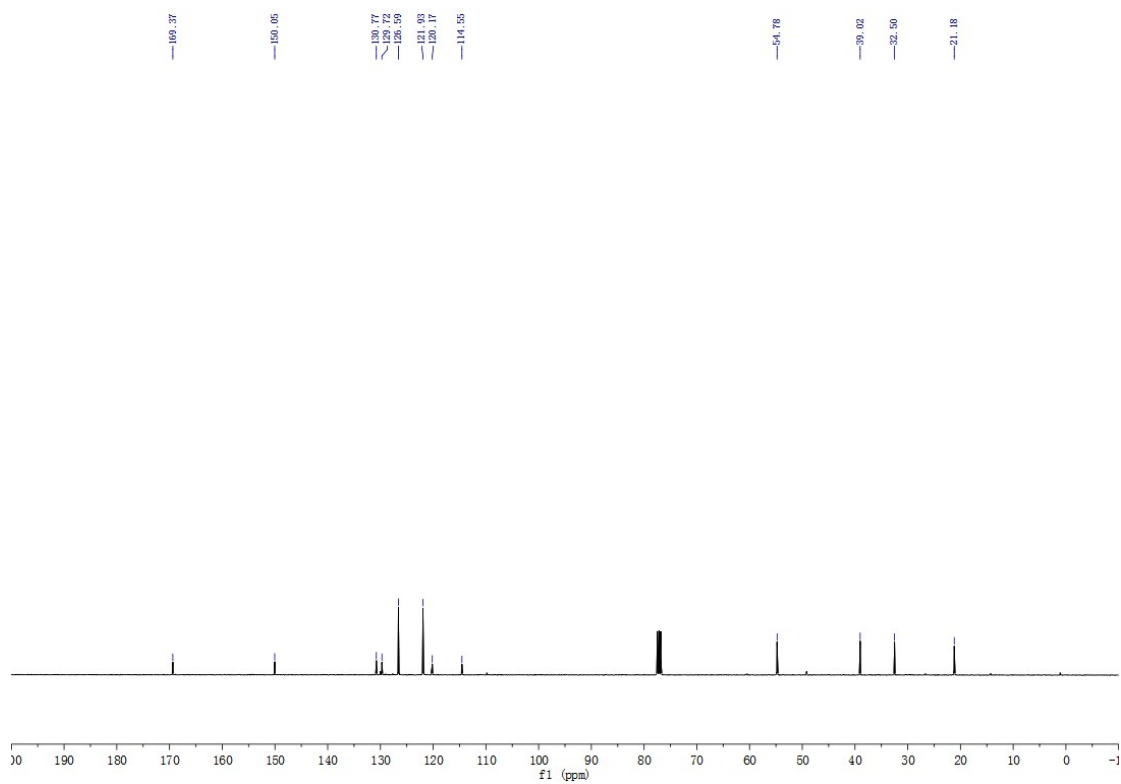
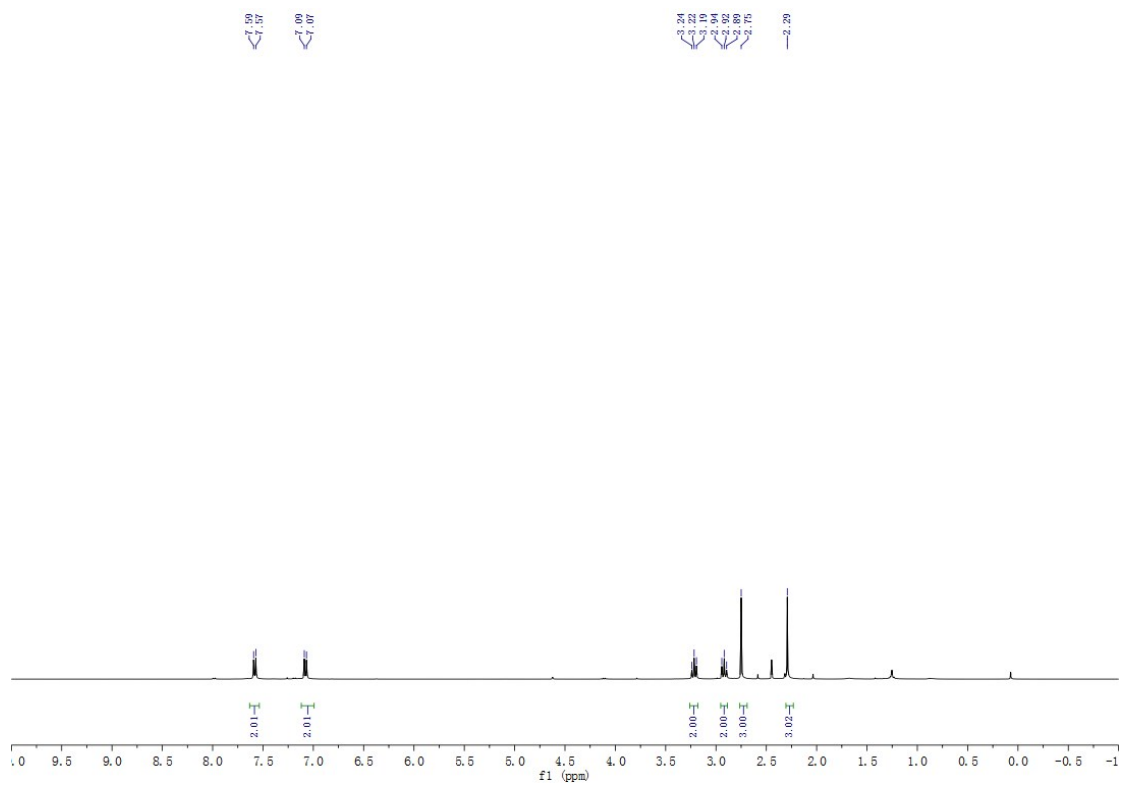
3-(4-formylphenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4k)



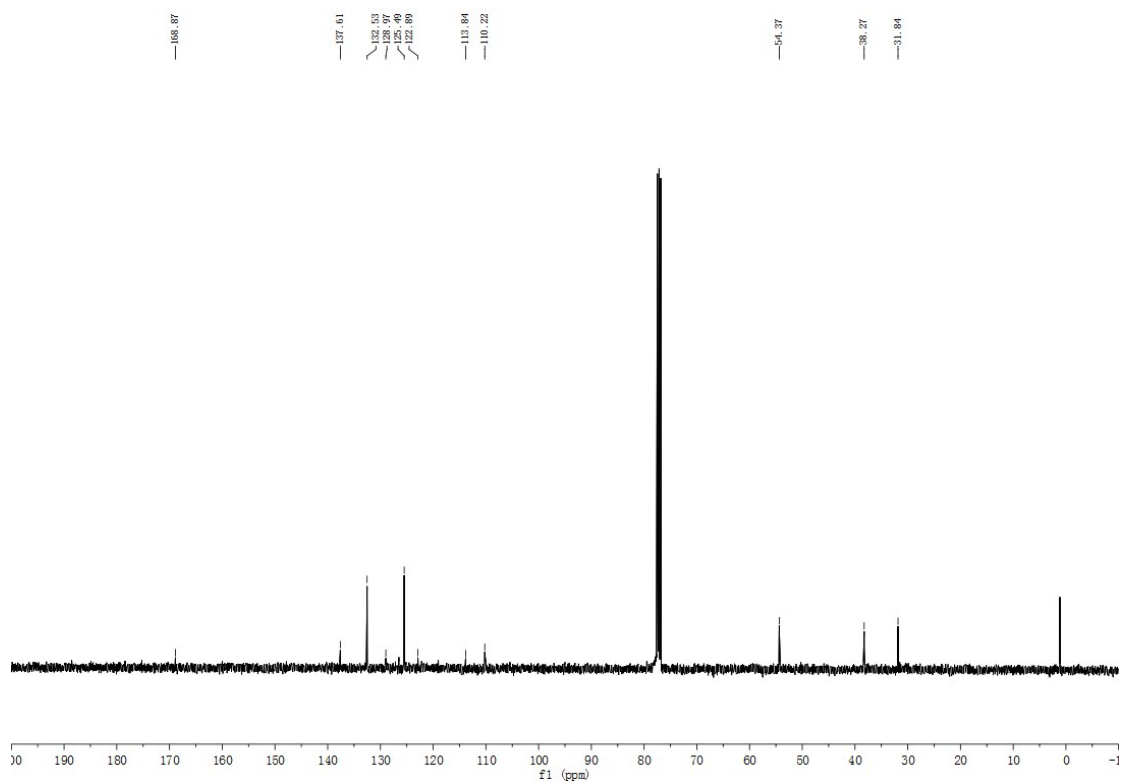
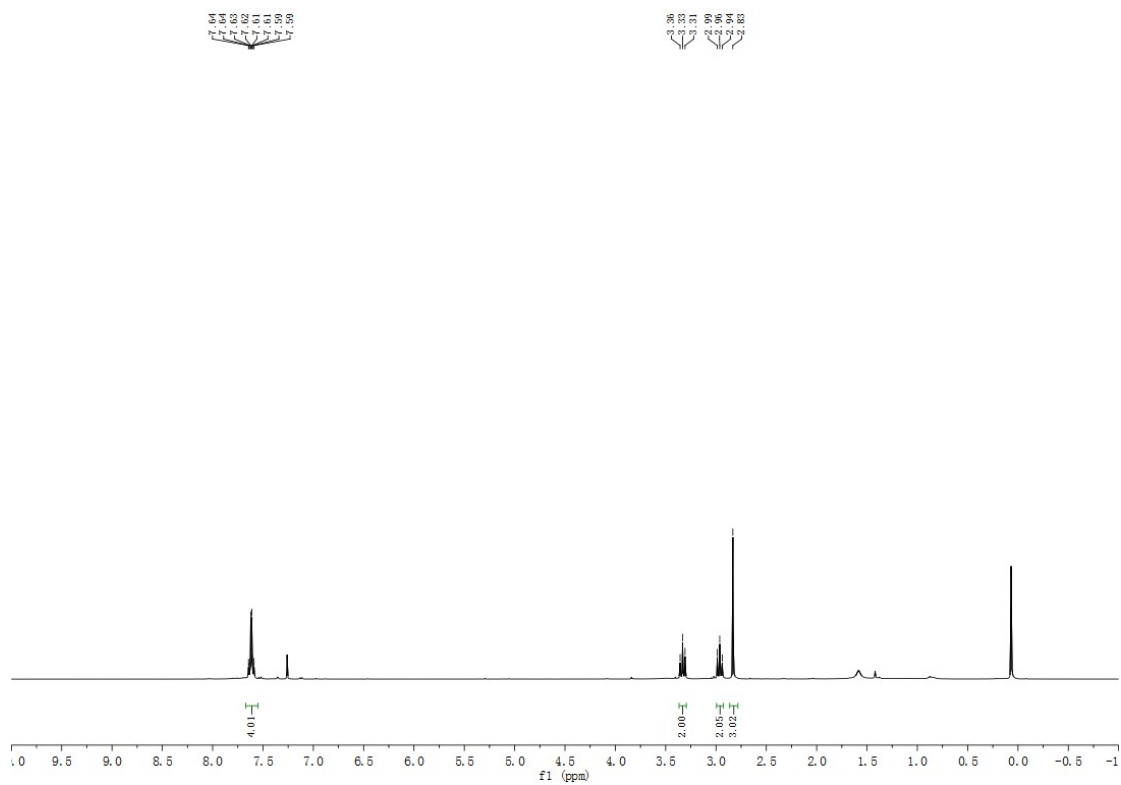
4-(2-cyano-1-methyl-4,5-dihydro-1H-pyrrol-3-yl)benzoic acid (4l)



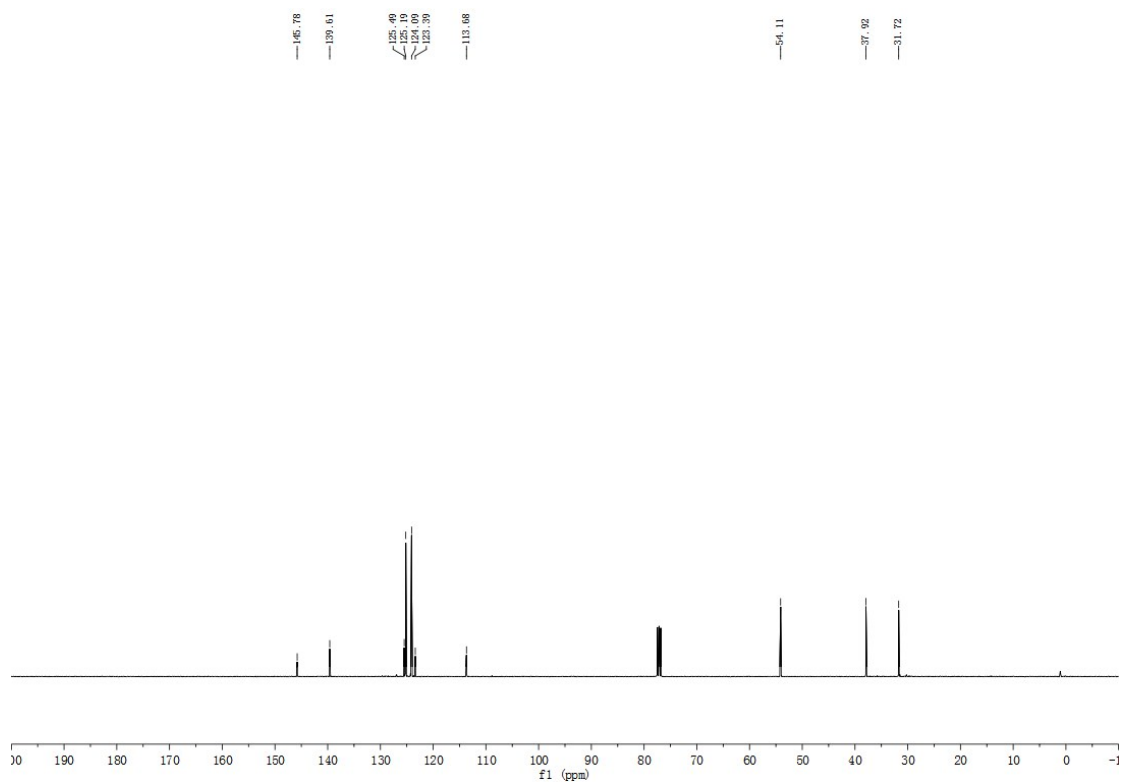
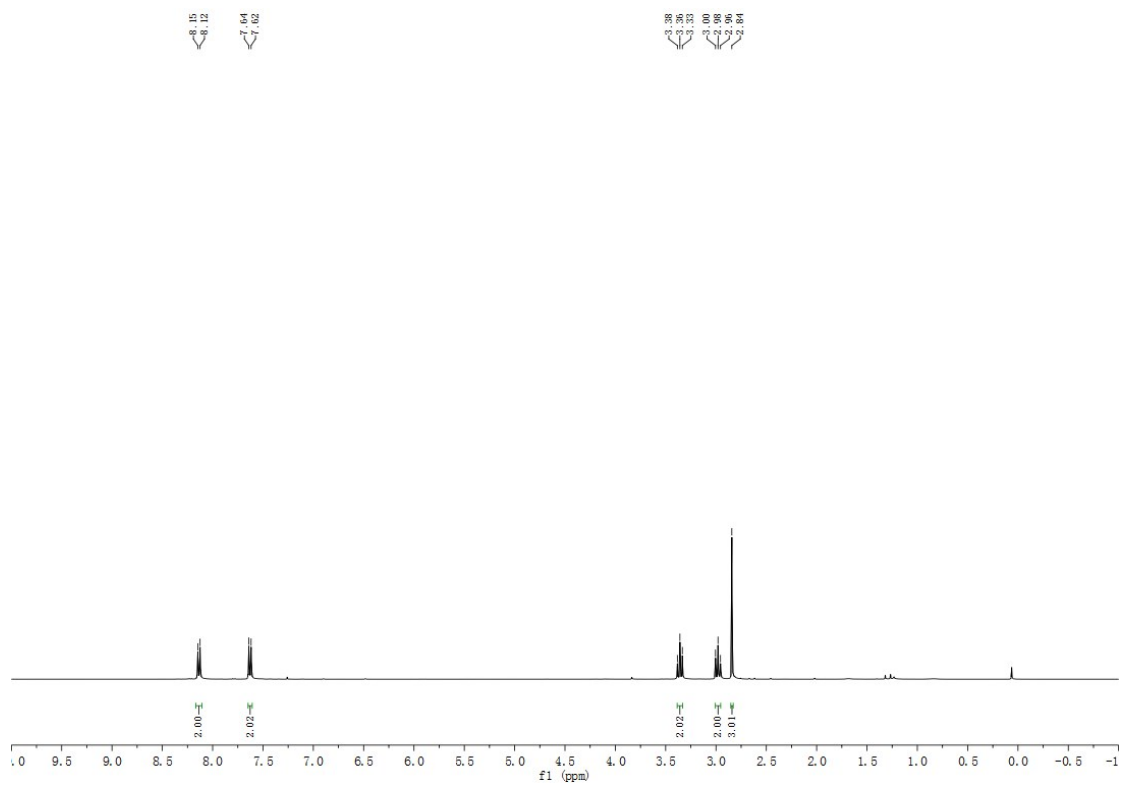
4-(2-cyano-1-methyl-4,5-dihydro-1H-pyrrol-3-yl)phenyl acetate (4m)



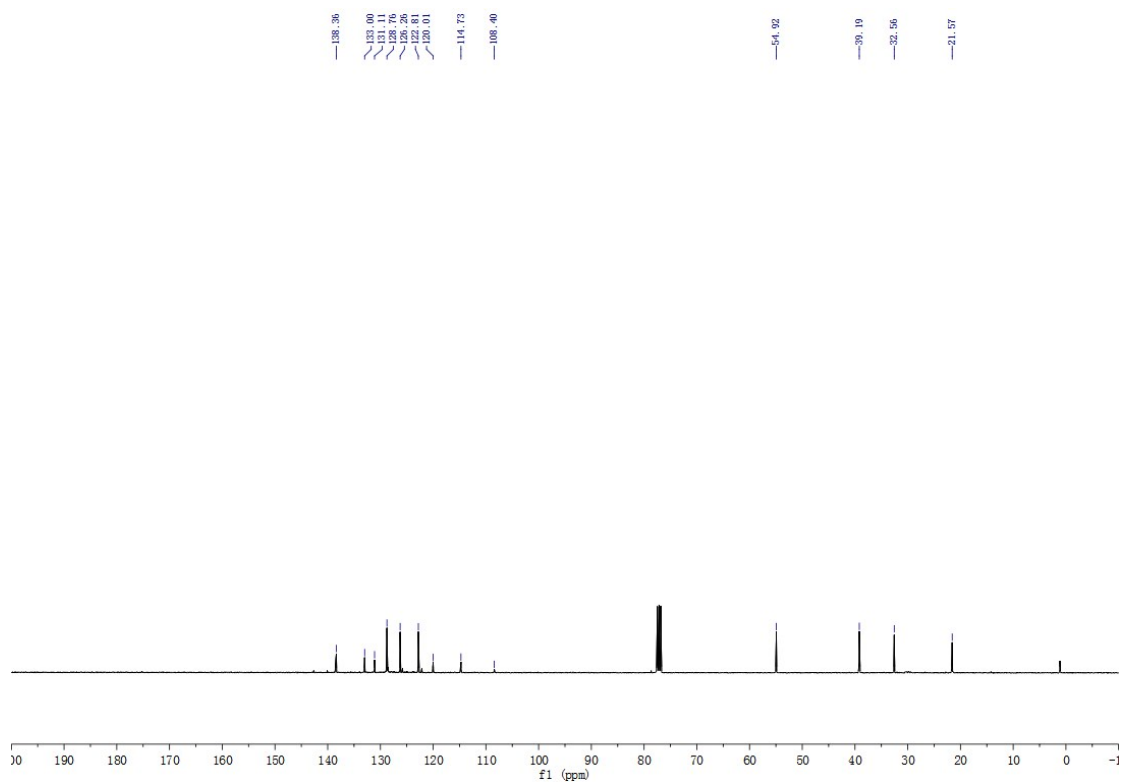
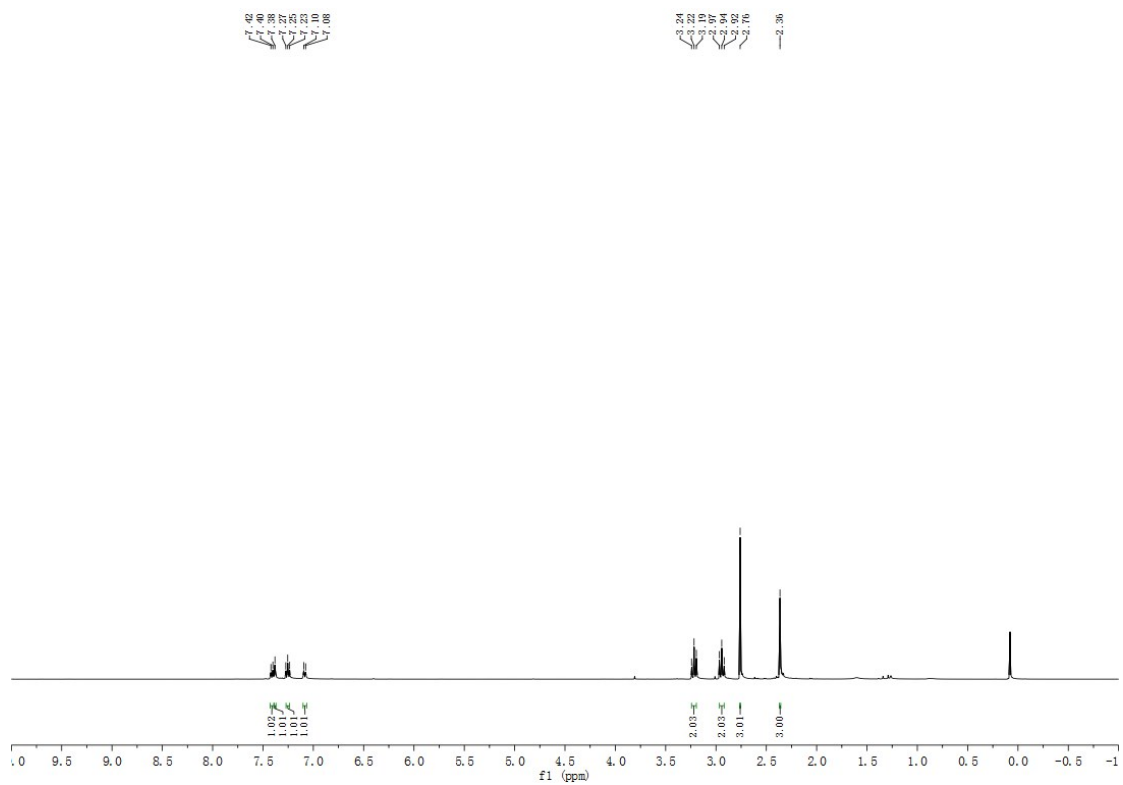
3-(4-cyanophenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4n)



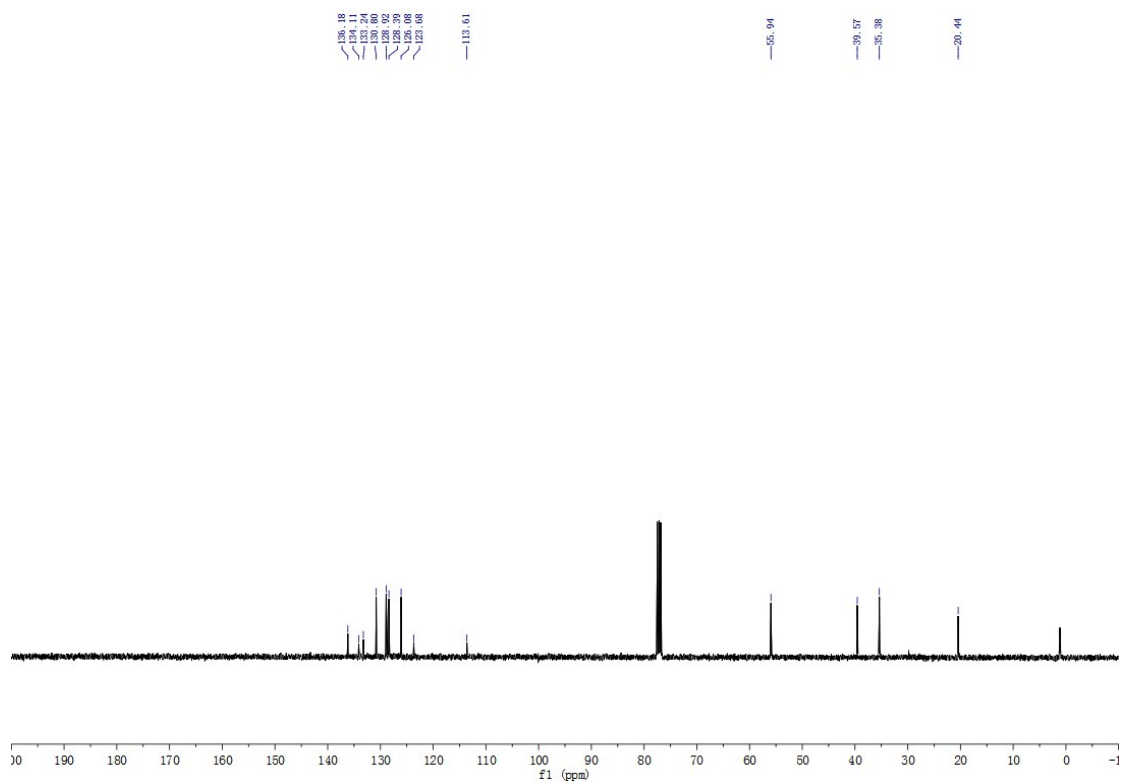
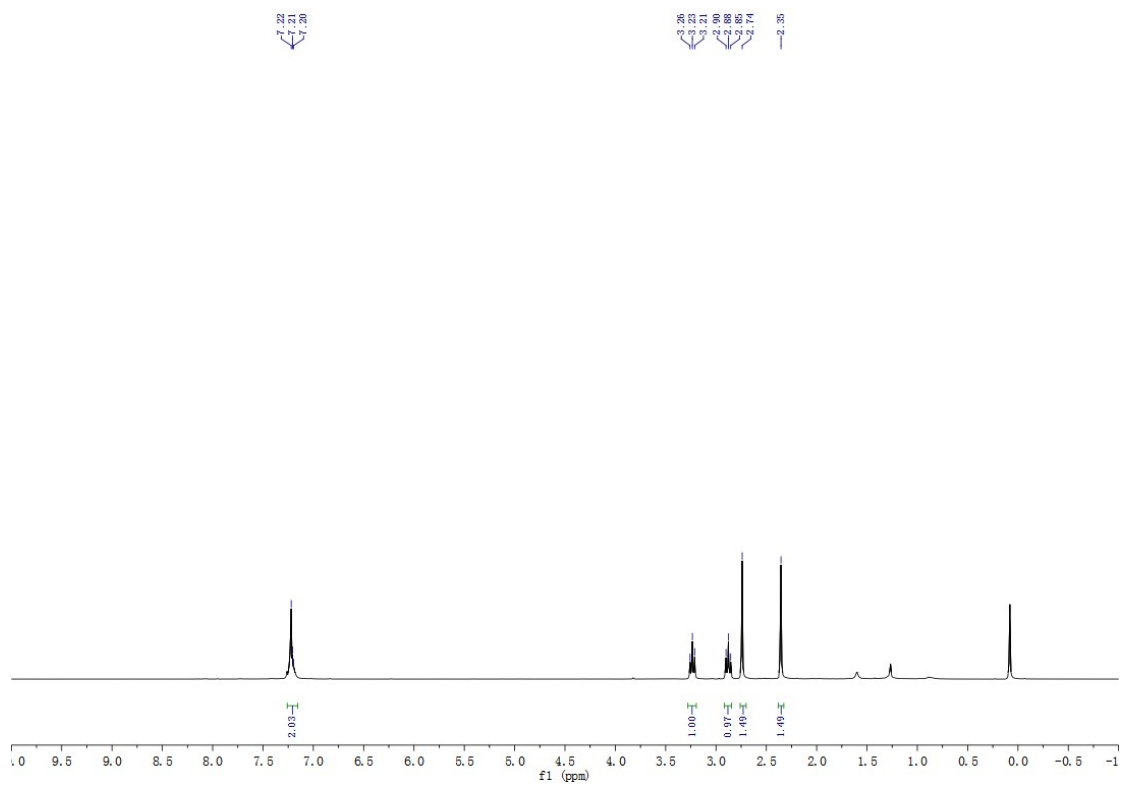
1-methyl-3-(4-nitrophenyl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4o)



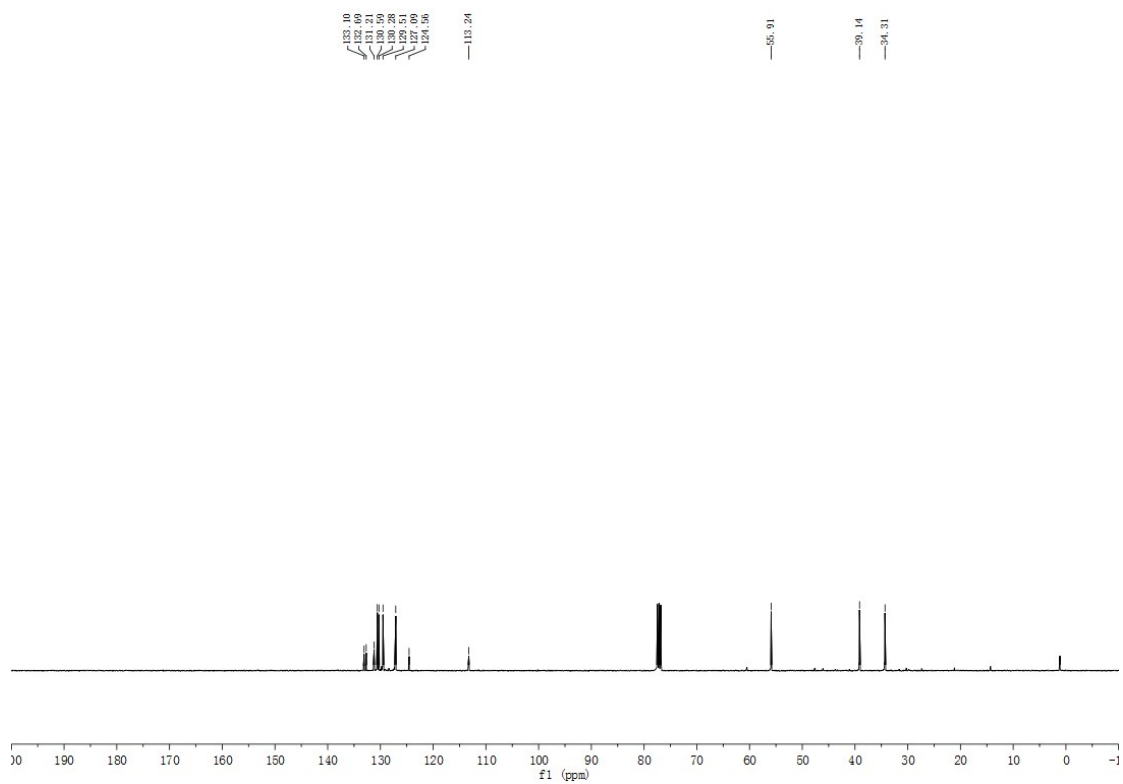
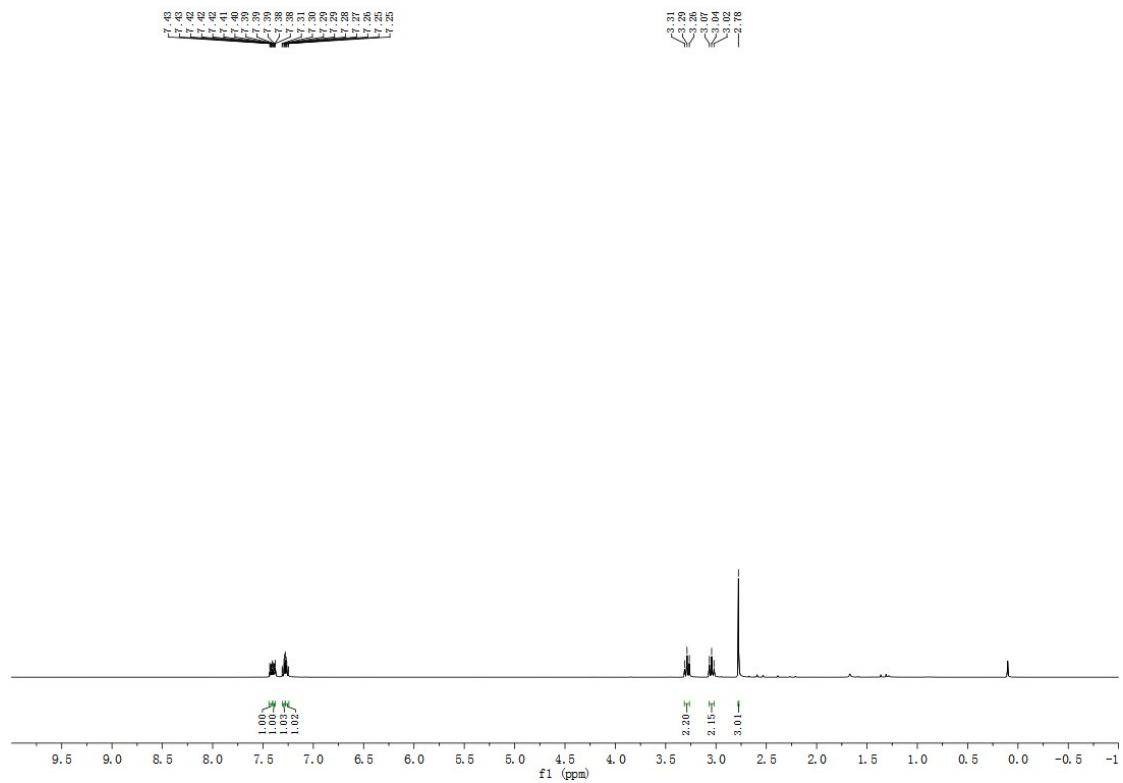
1-methyl-3-(m-tolyl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4p)



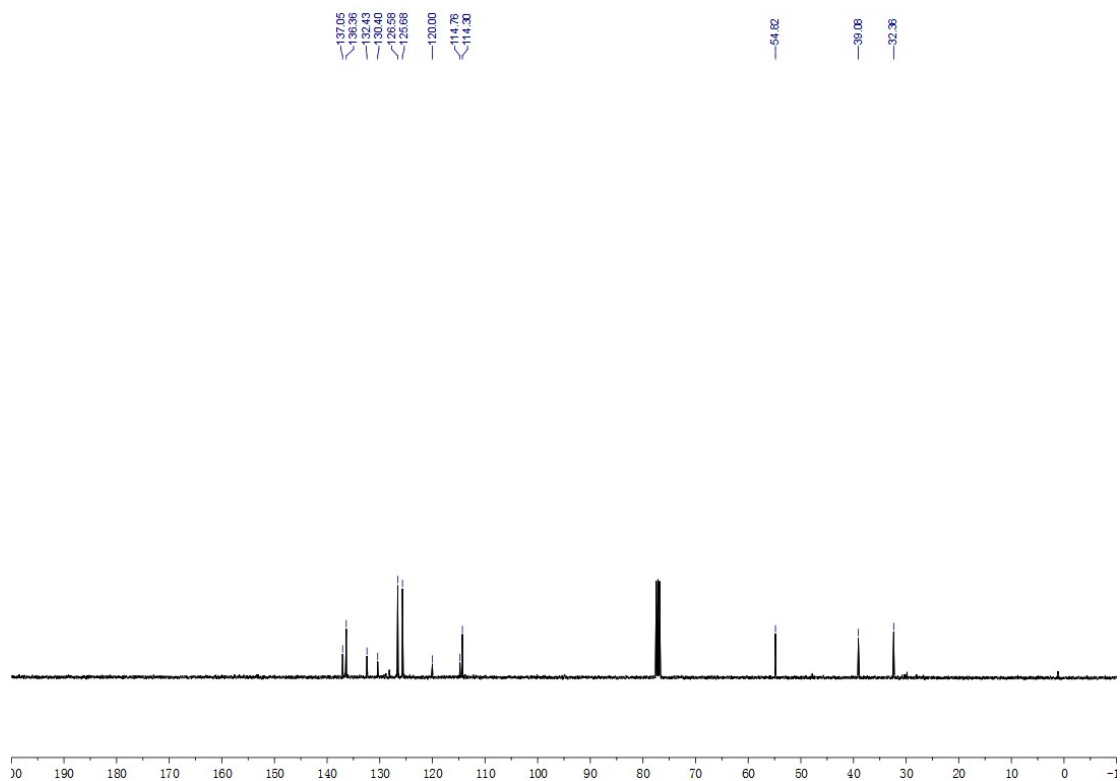
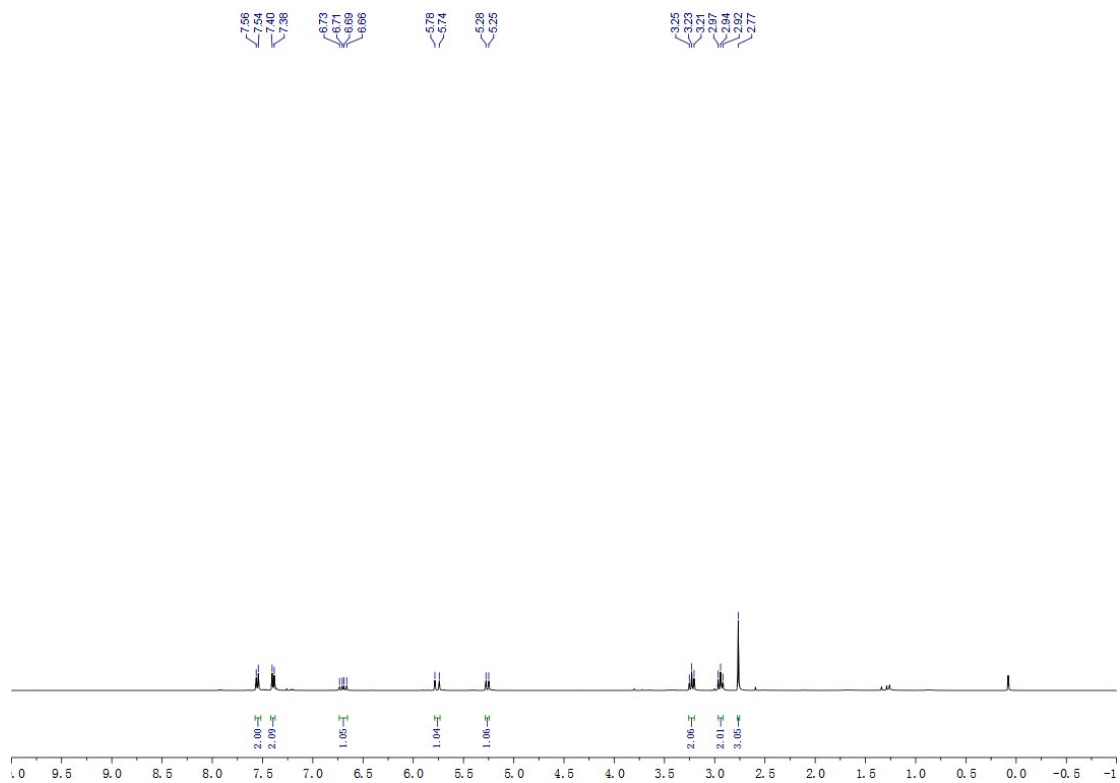
1-methyl-3-(o-tolyl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4q)



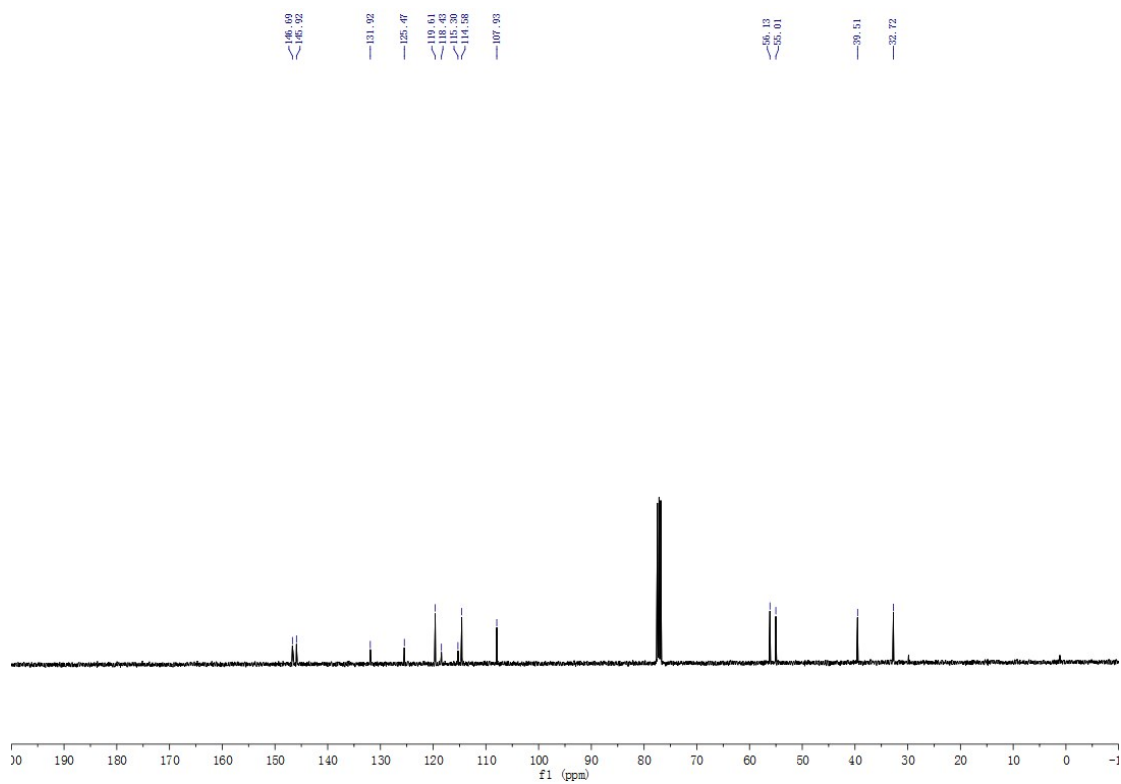
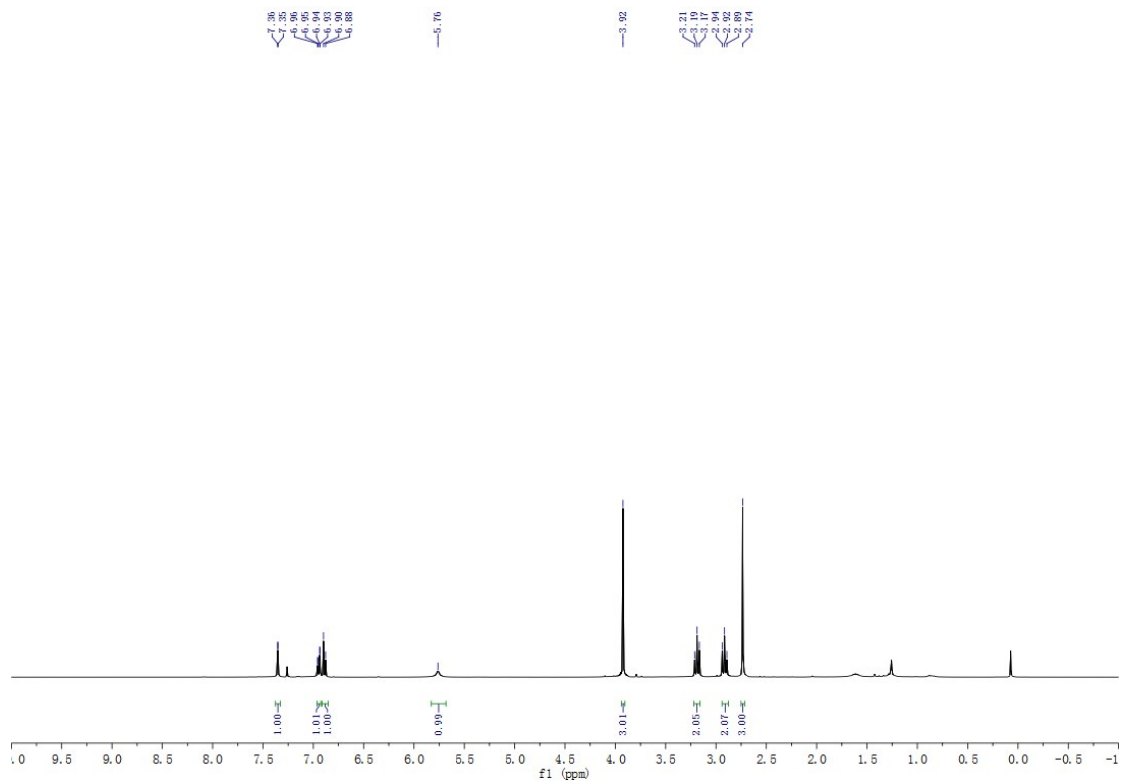
3-(2-chlorophenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4r)



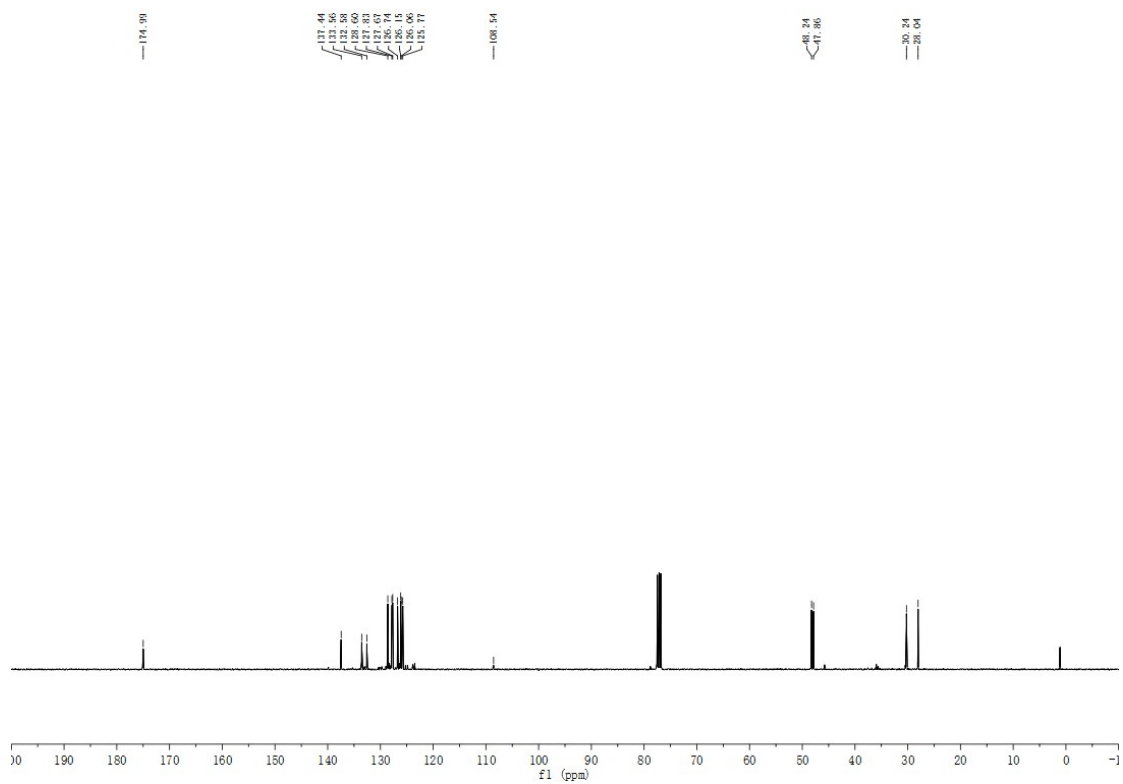
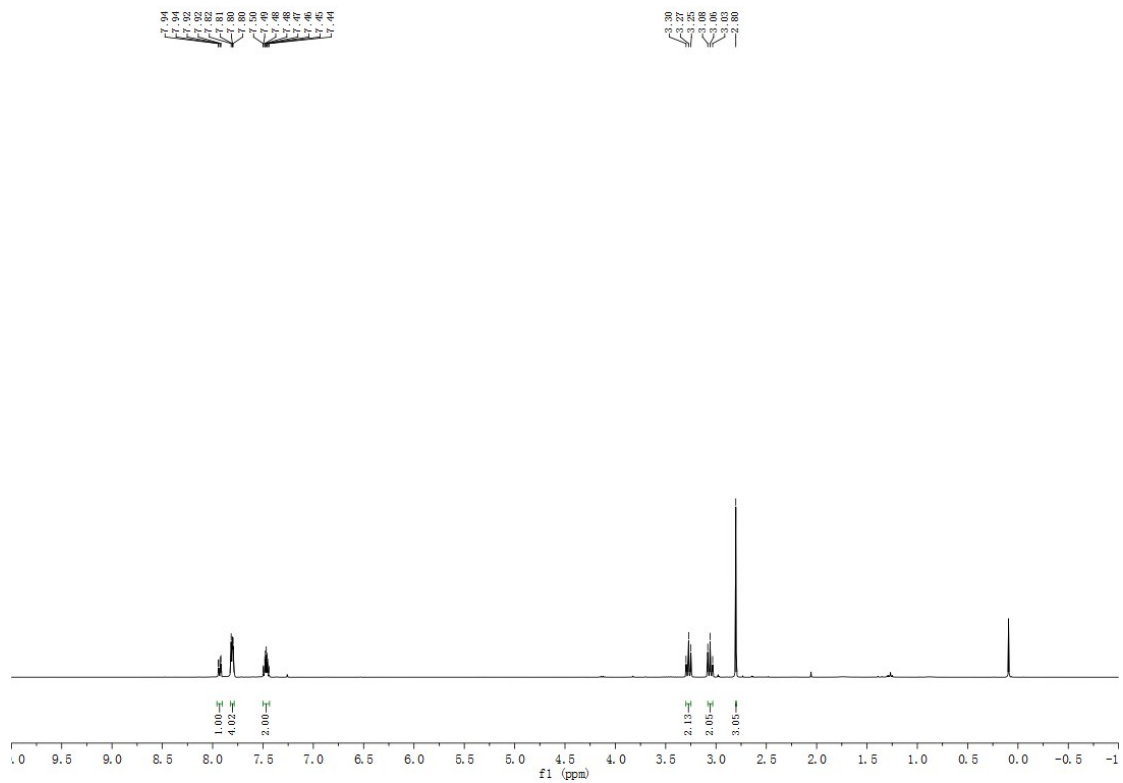
1-methyl-3-(4-vinylphenyl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4s)



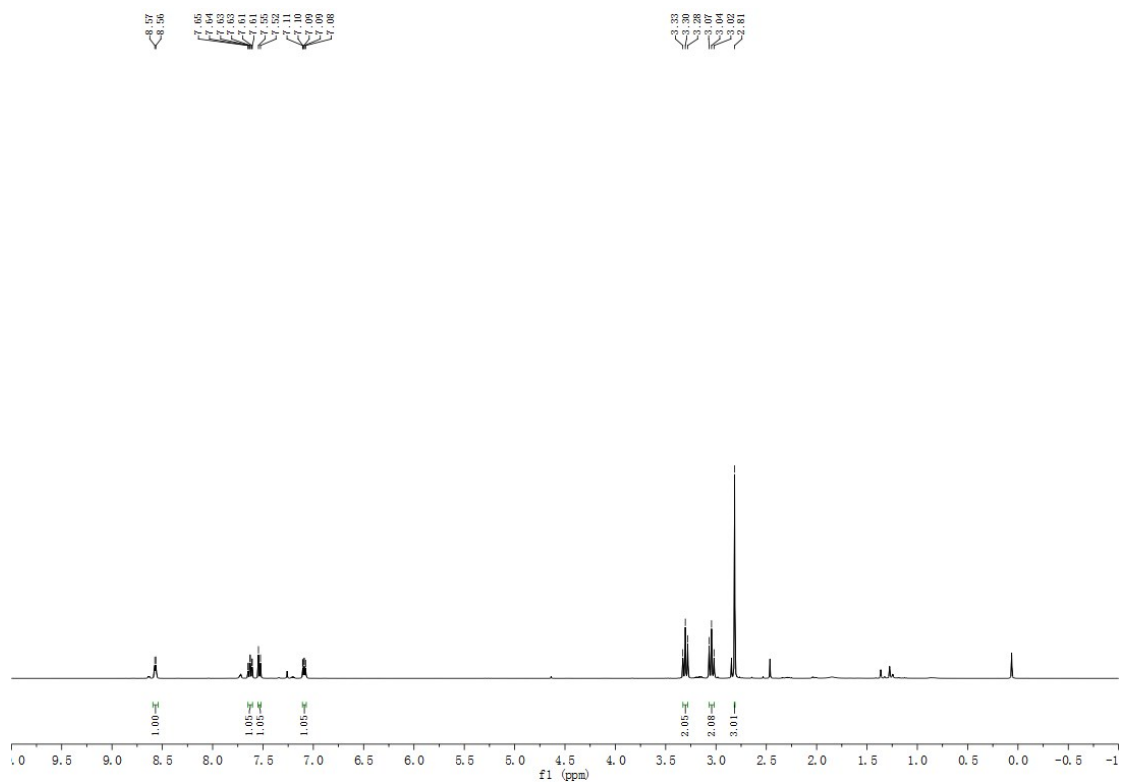
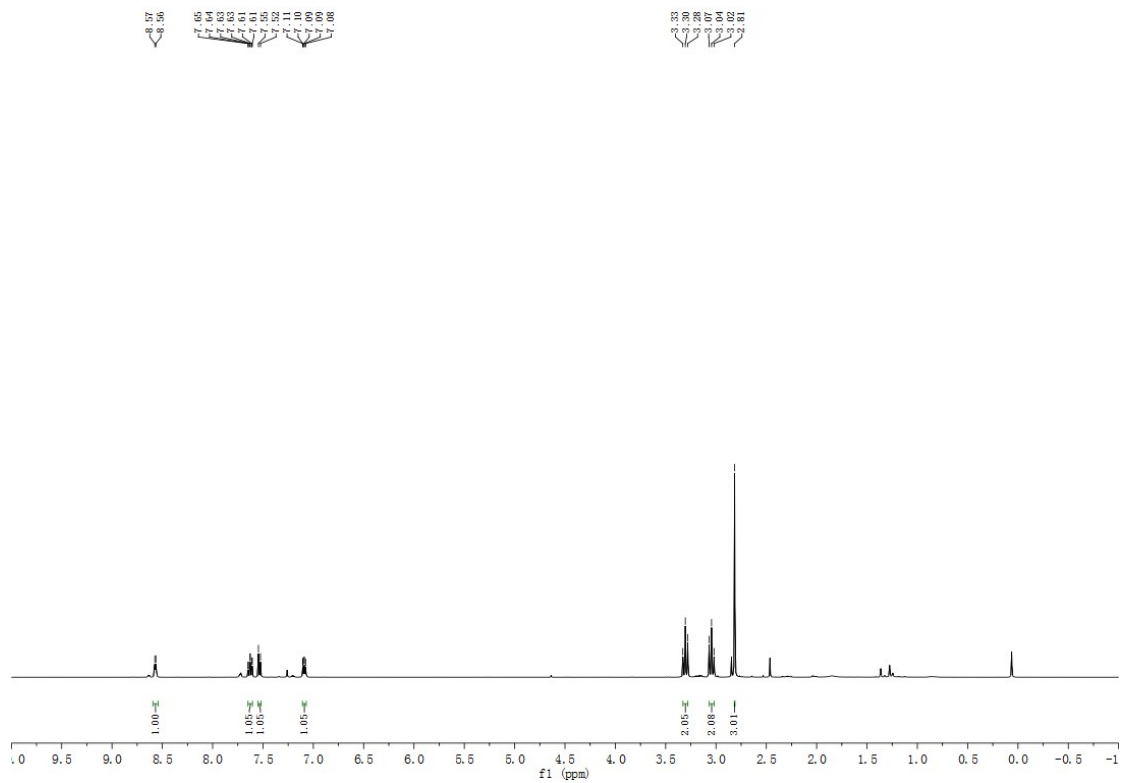
3-(4-hydroxy-3-methoxyphenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4t)



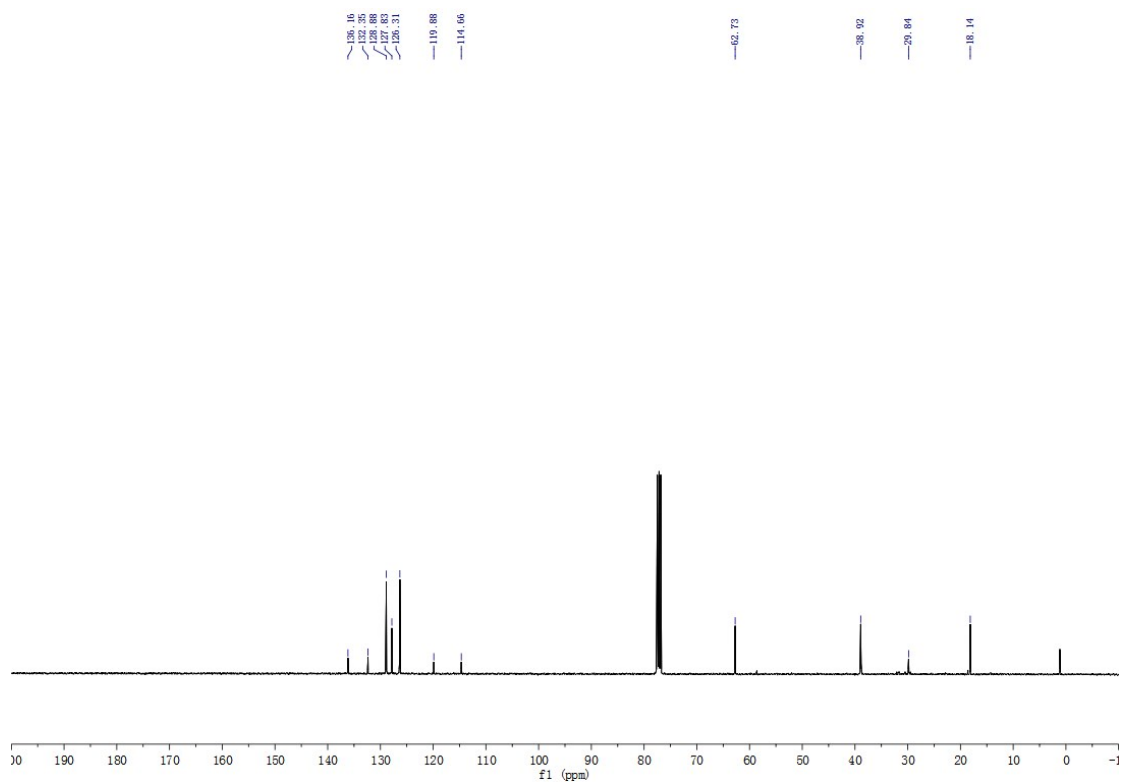
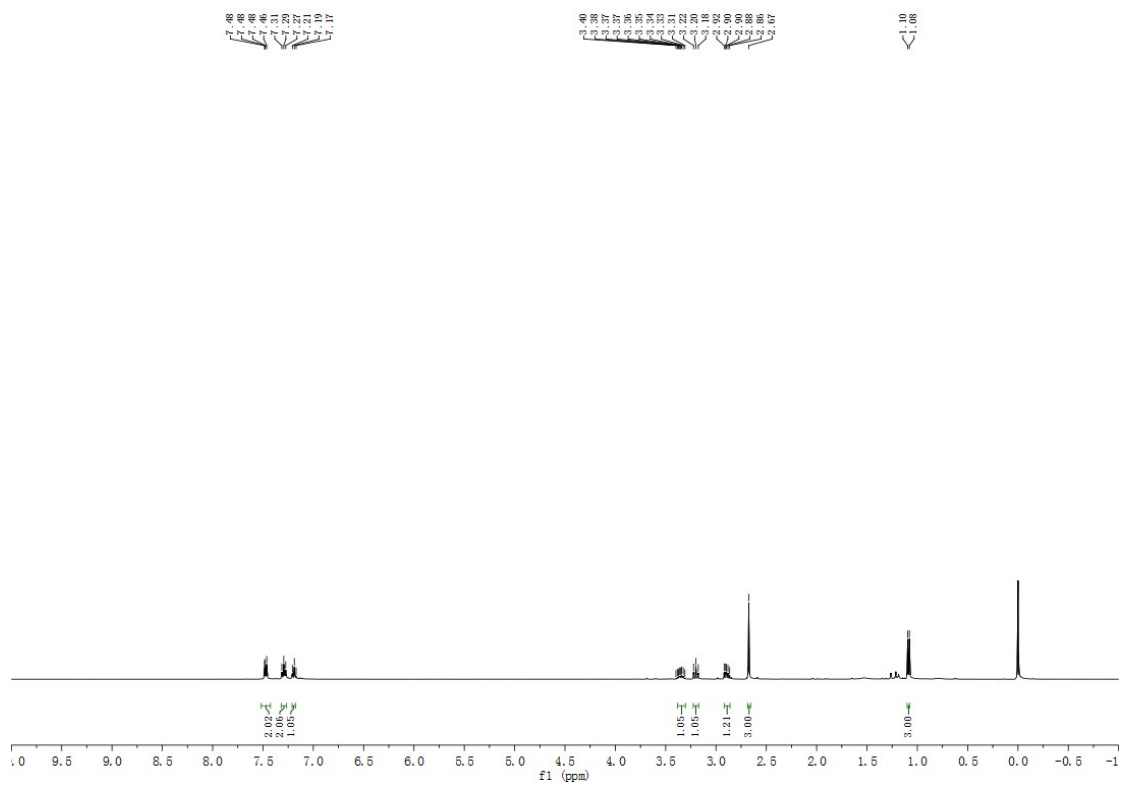
1-methyl-3-(naphthalen-2-yl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4u)



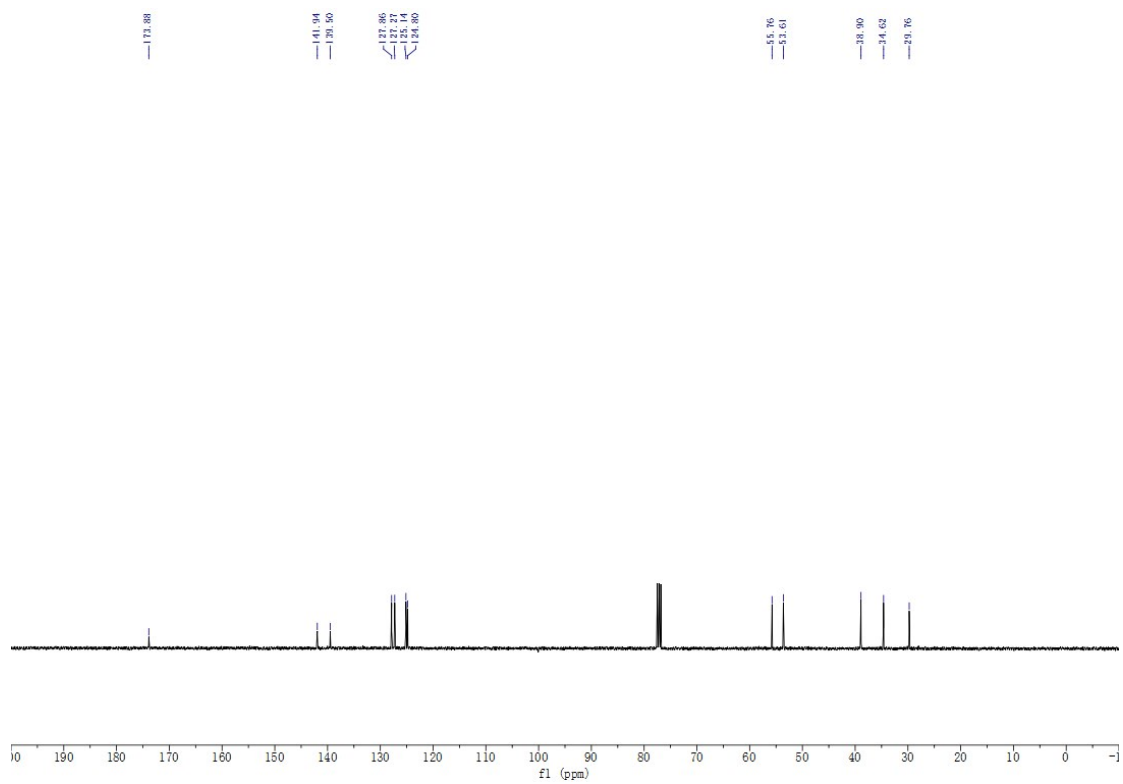
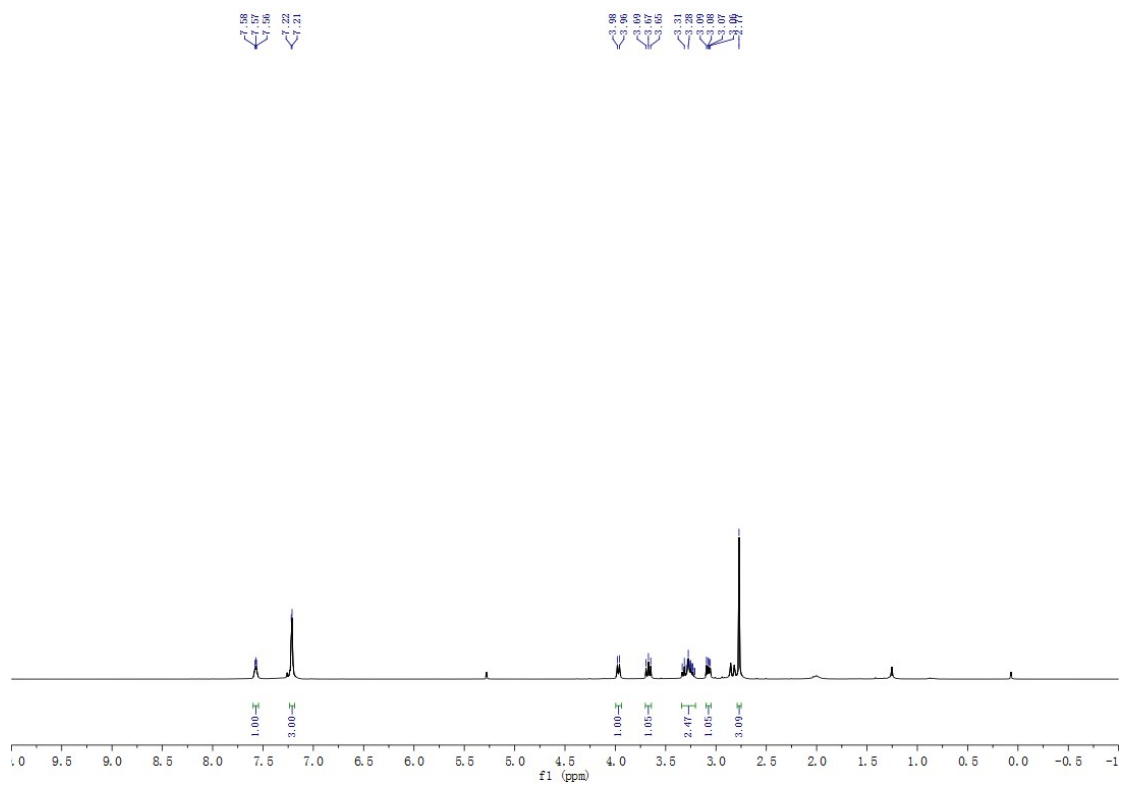
1-methyl-3-(pyridin-2-yl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4v)



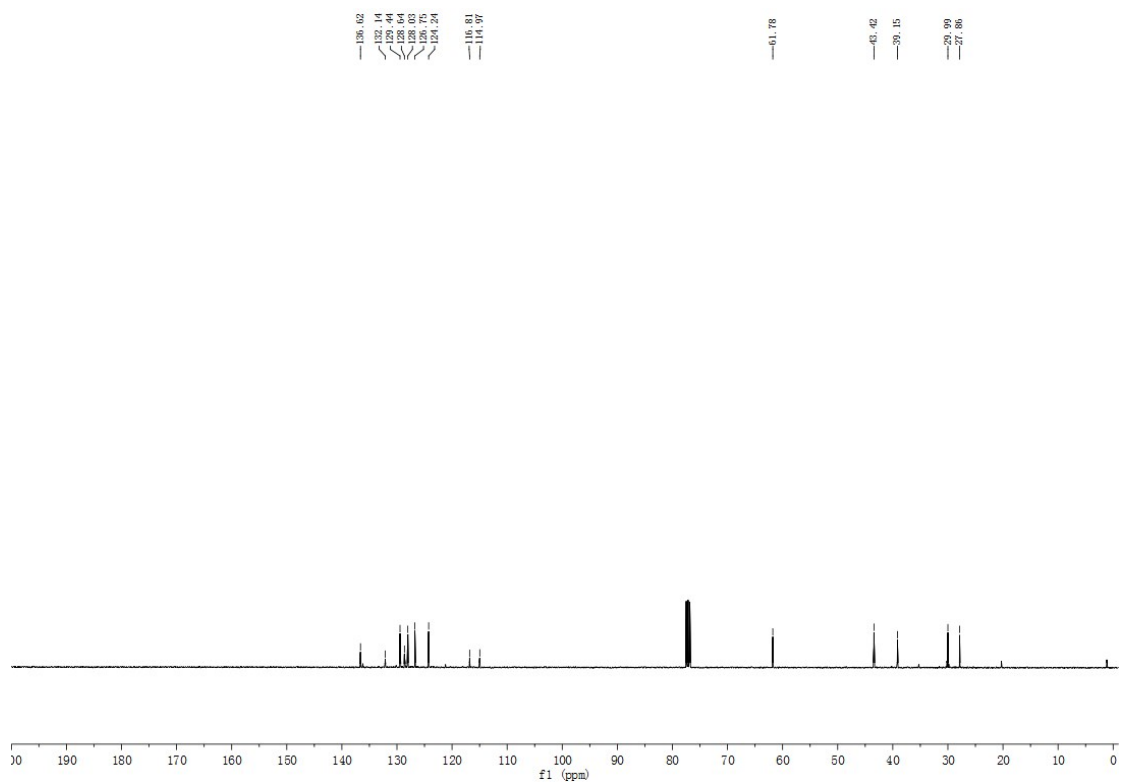
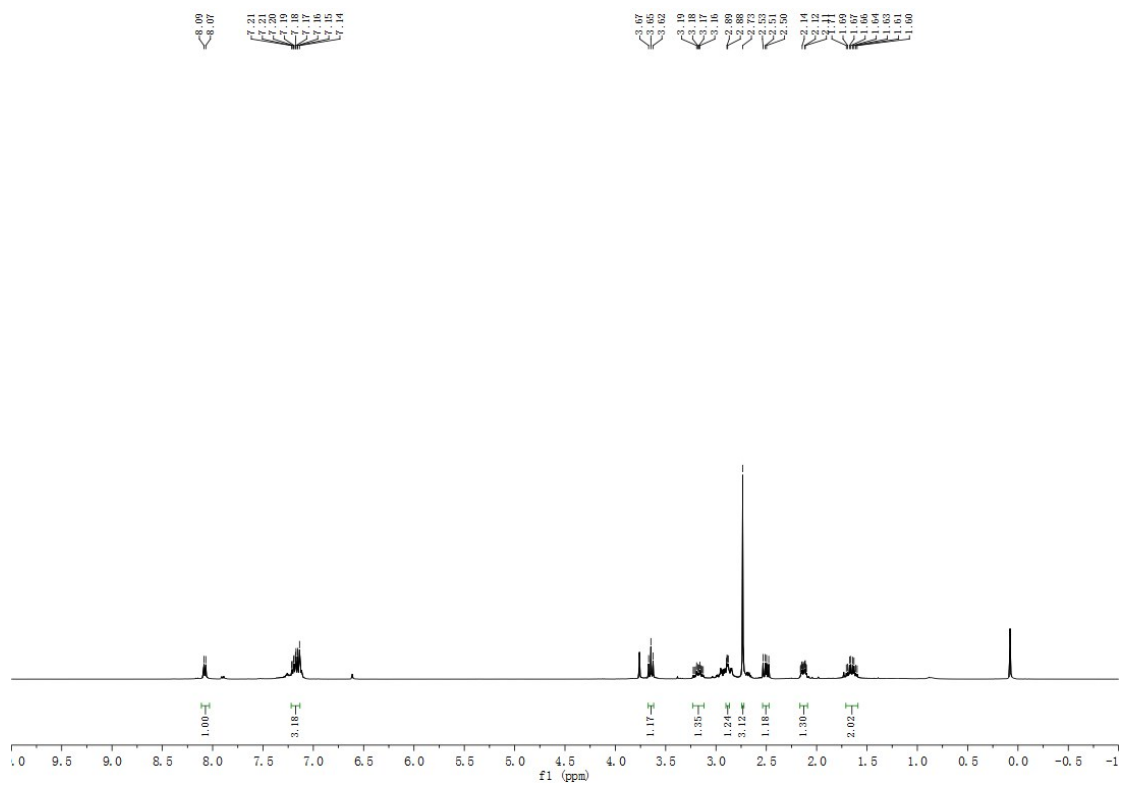
1,4-dimethyl-3-phenyl-1H-pyrrole-2-carbonitrile (4w)



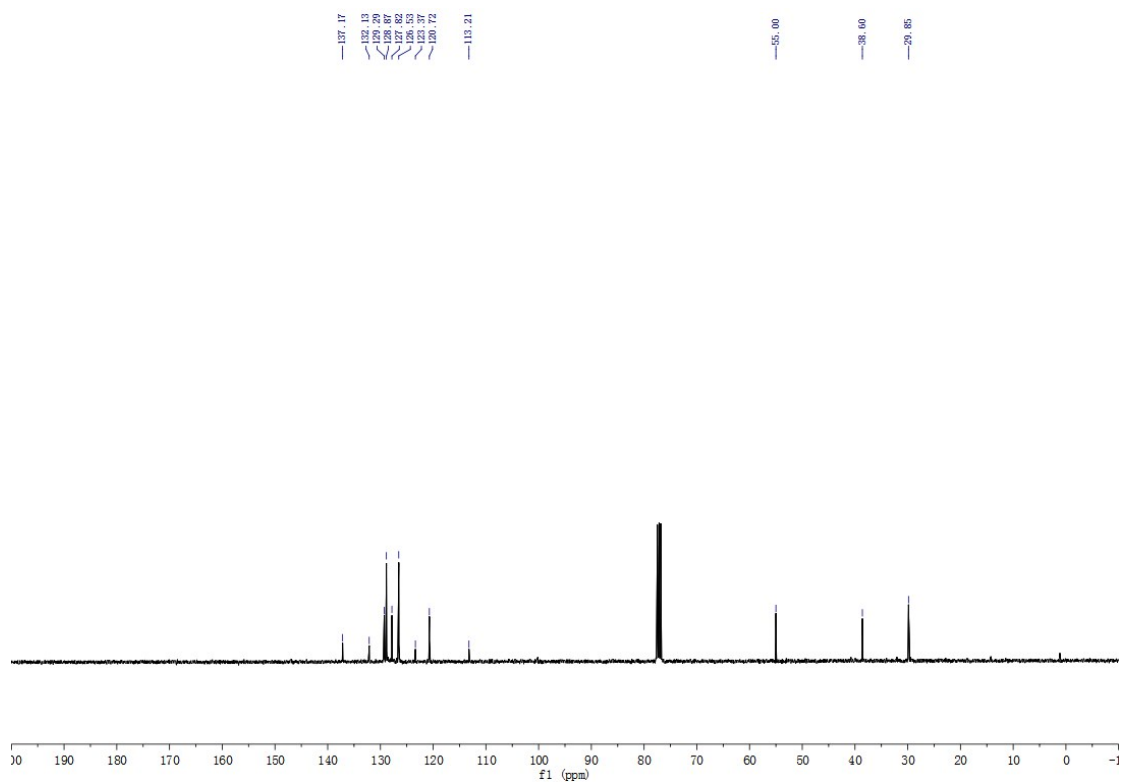
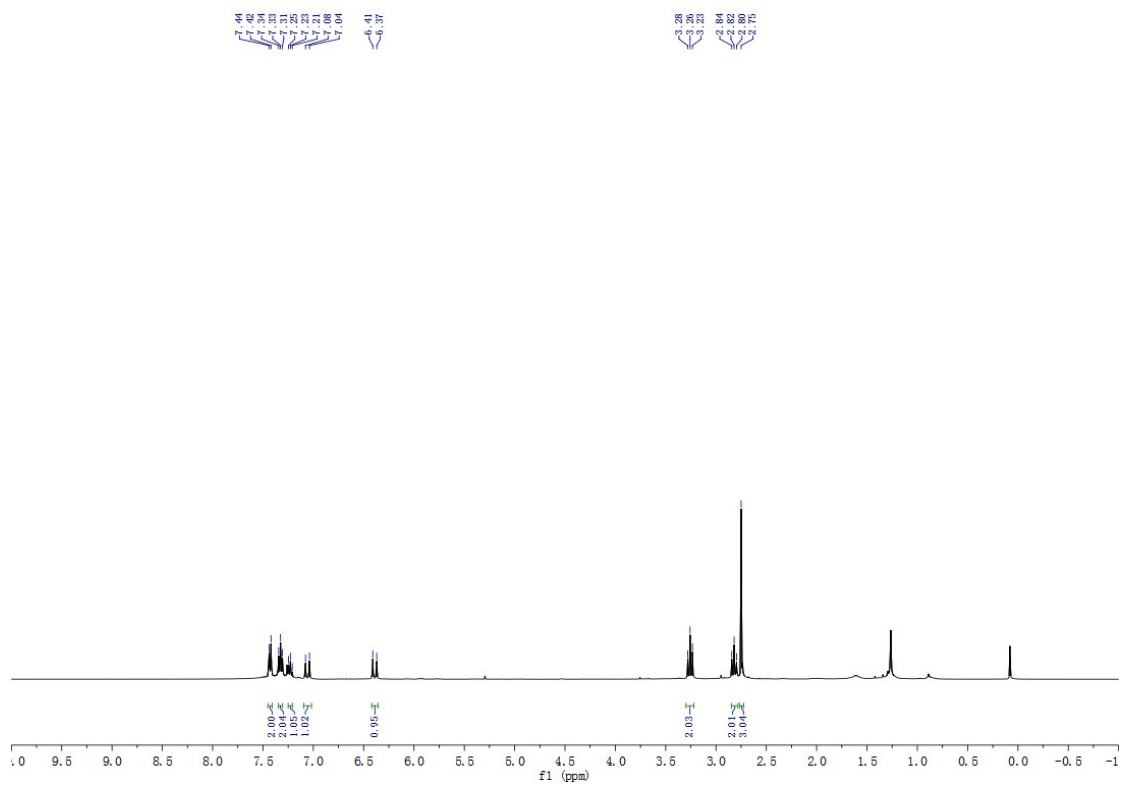
2-methyl-1,2,8,8a-tetrahydroindeno[1,2-c]pyrrole-3-carbonitrile (4x)



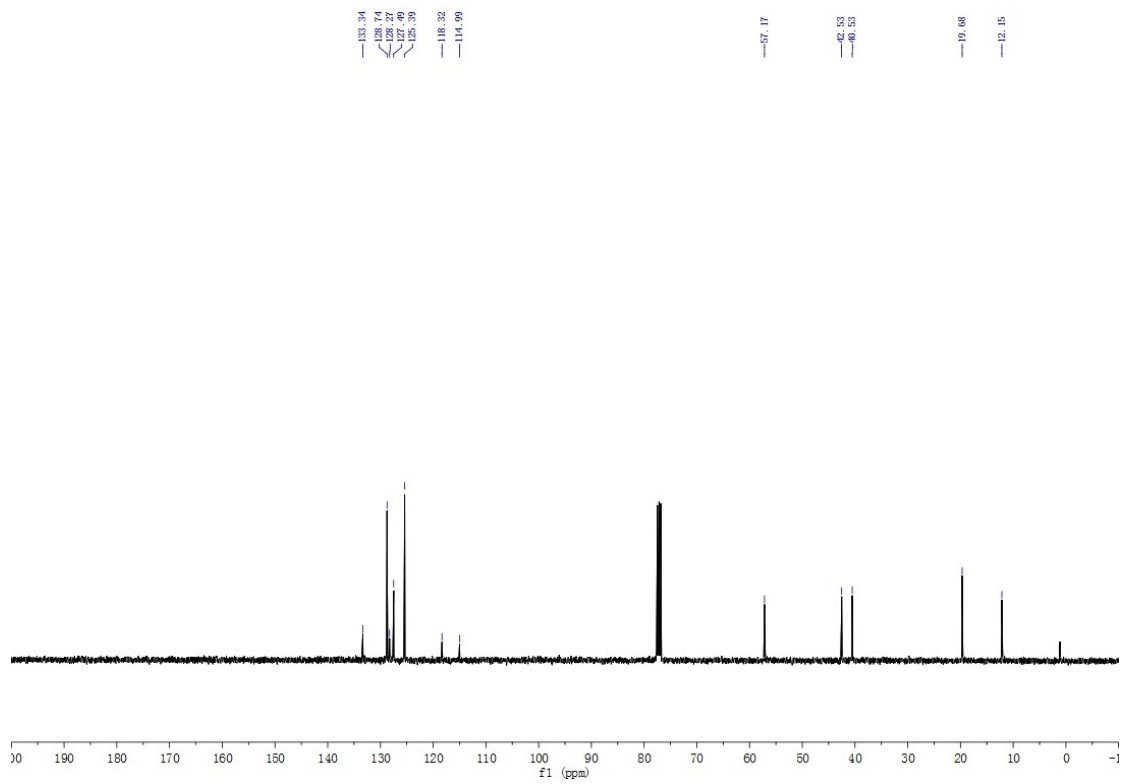
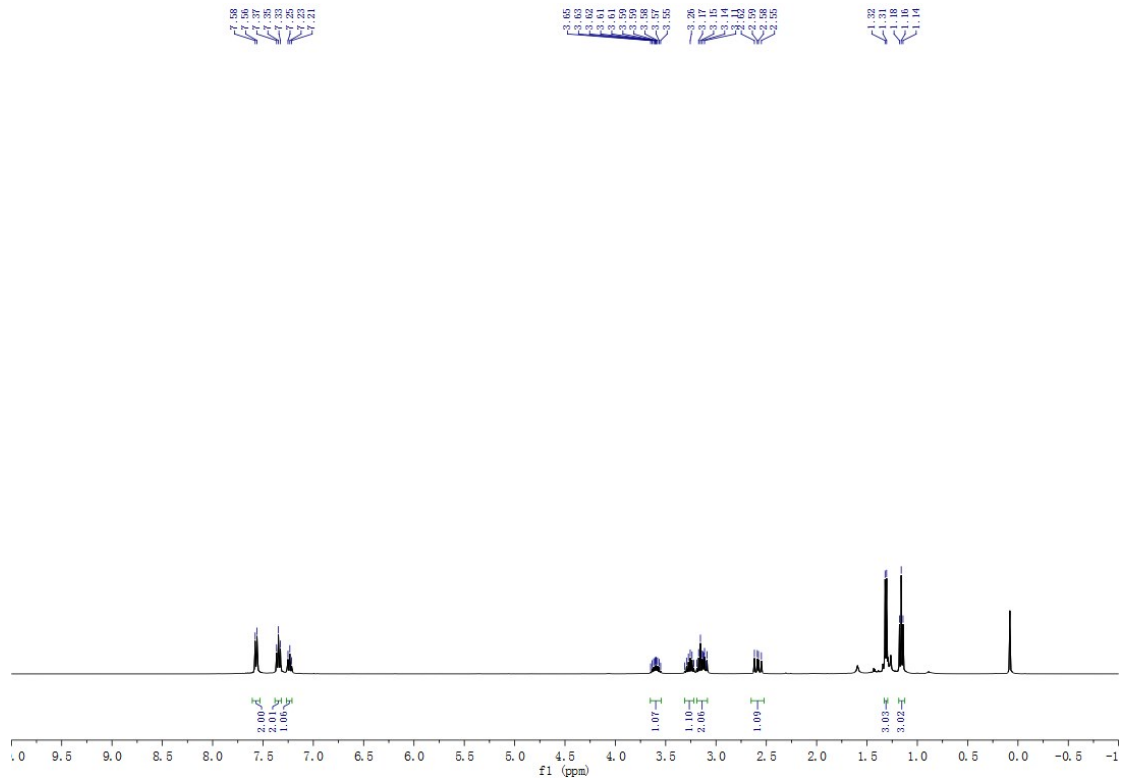
2-methyl-3,3a,4,5-tetrahydro-2H-benzof[e]isoindole-1-carbonitrile (4y)



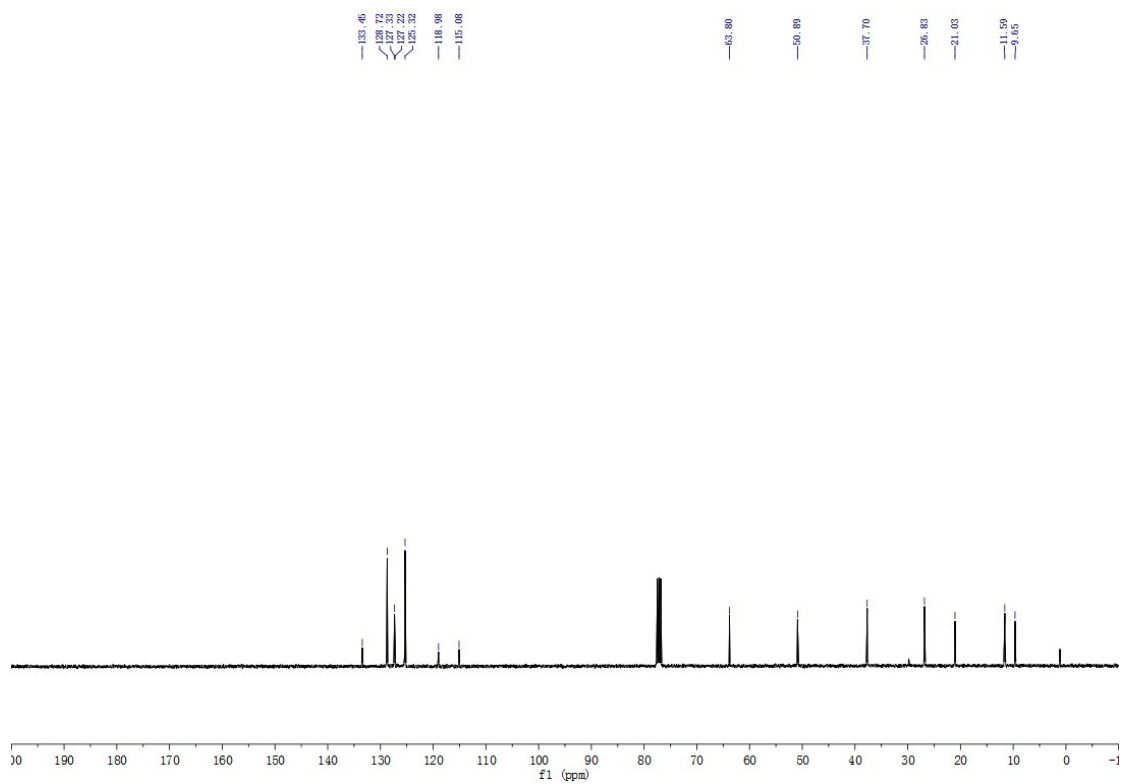
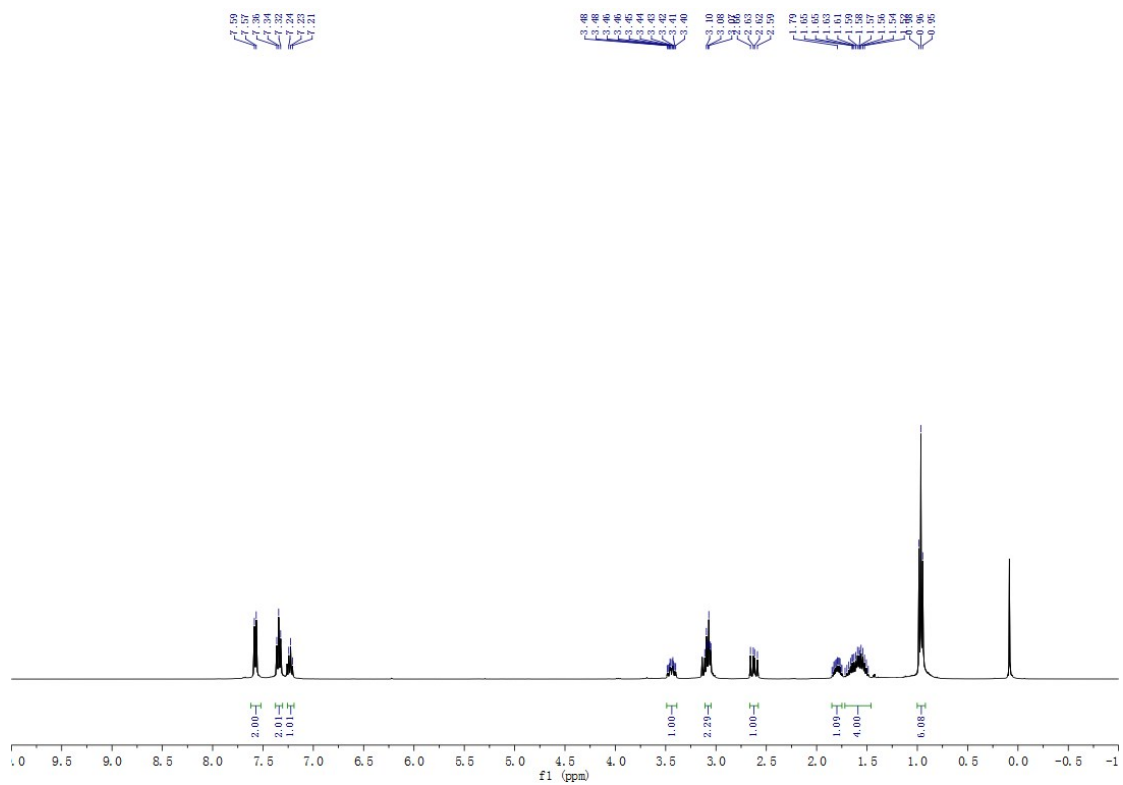
(E)-1-methyl-3-styryl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4z)



1-ethyl-5-methyl-3-phenyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4aa)



5-ethyl-3-phenyl-1-propyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4ab)



2-phenyl-1,5,6,7,8a-hexahydroindolizine-3-carbonitrile (4c)

