

Supporting Information

Calcium Carbide as the Acetylide Source: Transition-Metal-Free Synthesis of Substituted Pyrazoles via [1,5]-Sigmatropic Rearrangements

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A. General Methods

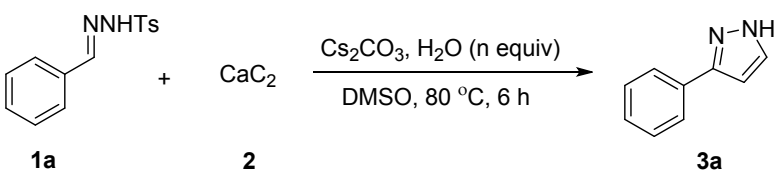
^1H and ^{13}C NMR spectra were recorded using a Bruker DRX-400 spectrometer using CDCl_3 as solvent. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively. Mass spectra were recorded on a Thermo Scientific ISQ gas chromatograph-mass spectrometer. The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker TENSOR 27 spectrometer. Melting points were determined with a Büchi Melting Point B-545 instrument.

B. General Procedure for the Preparation of **3** and **5**

In a Schlenk tube, a mixture of *N*-tosylhydrazones (0.5 mmol), CaC_2 (2 mmol) and Cs_2CO_3 (0.5 mmol) was stirred in DMSO (2 mL). Then H_2O (2.5 mmol) was added by using a microliter syringe. The mixture was allowed to stir at 80 °C for 6 h. After completion of the reaction (monitored by TLC), water (10 mL) was added to the reaction mixture, and the resulting mixture was extracted with ethyl acetate. The combined organic layers were then dried over MgSO_4 , filtered, and then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give **3** or **5**.

C. Optimization of the Reaction Conditions

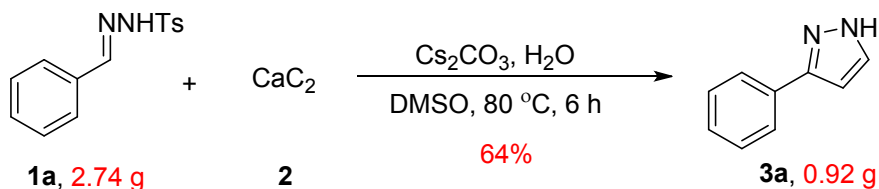
Table S1. Screening of the Amount of Water for Reaction^a



Entry	n (equiv)	Yield of 3a ^b (%)
1	1	59
2	4	71
3	5	86
4	6	84
5	10	79

^a Reaction conditions: All reactions were performed with **1a** (0.5 mmol), **2a** (2 mmol), base (0.5 mmol) and 2.0 mL solvent at 80 °C for 6 h unless otherwise noted. ^b Yields were analyzed by GC-MS using *n*-dodecane as an internal standard.

D. Gram-Scale Experiment

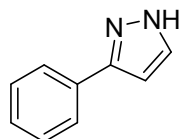


Scheme S1. Gram-scale synthesis of **3a** from **1a** and CaC_2 .

In a 200 mL two-necked round-bottom flask with a reflux condenser, a mixture of *N*-tosylhydrazone **1a** (2.74 g, 10 mmol), CaC_2 (2.56 g, 40 mmol) and Cs_2CO_3 (3.26 g, 10 mmol) were added in DMSO (40 mL). The flask was then sealed with a wizened balloon and a rubber plug, respectively. After stirring at room temperature for 5 min, water (0.9 mL, 50 mmol) was added using an injector. The mixture was allowed to stir at 80 °C for 6 h. After completion of the reaction (monitored by TLC), water (100×3 mL) was added to the reaction mixture, and the resulting mixture was extracted with ethyl acetate for 3 times. The combined organic layers were then dried over MgSO_4 , filtered, and then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give **3a** as a yellow oil.

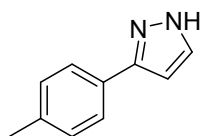
E. Analytical Data

3-Phenyl-1H-pyrazole (3a)



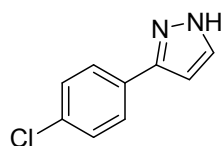
Yellow oil (56.9 mg, 79%); IR (KBr): 3172, 2964, 1456, 758, 693 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 10.08 (s, 1H), 7.77 (d, $J = 7.7$ Hz, 2H), 7.61 (s, 1H), 7.40 (t, $J = 7.5$ Hz, 2H), 7.37-7.30 (m, 1H), 6.62 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 149.0, 133.3, 132.1, 128.8, 128.0, 125.8, 102.6; MS (EI, 70 eV) m/z : 144.07, 115.07, 90.07, 77.06; HRMS ESI (m/z): calcd for $\text{C}_9\text{H}_9\text{N}_2$ [$\text{M} + \text{H}$] $^+$: 145.0760, found: 145.0763.

3-(*p*-Tolyl)-1H-pyrazole (3b)



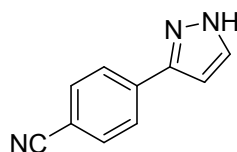
Light yellow oil (57.0 mg, 72%); IR (KBr): 3173, 2924, 1515, 1454, 821 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 10.14 (s, 1H), 7.65 (d, $J = 8.1$ Hz, 2H), 7.60 (d, $J = 2.1$ Hz, 1H), 7.21 (d, $J = 8.0$ Hz, 2H), 6.58 (d, $J = 2.1$ Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 148.7, 137.8, 133.7, 129.4, 129.1, 125.7, 102.3, 21.2; MS (EI, 70 eV) m/z : 158.25, 130.19, 90.07, 77.15; HRMS ESI (m/z): calcd for $\text{C}_{10}\text{H}_{11}\text{N}_2$ [$\text{M} + \text{H}$] $^+$: 159.0917, found: 159.0922.

3-(4-Chlorophenyl)-1H-pyrazole (3c)



Light yellow solid (63.2 mg, 71%), mp 83.0-84.0 $^{\circ}\text{C}$; IR (KBr): 3173, 2957, 1499, 1489, 1094, 829, 767 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 11.49 (s, 1H), 7.69-7.64 (m, 2H), 7.57 (d, $J = 2.2$ Hz, 1H), 7.36-7.31 (m, 2H), 6.57 (d, $J = 2.1$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 148.7, 133.8, 132.6, 130.8, 128.9, 127.1, 102.7; MS (EI, 70 eV) m/z : 178.02, 151.01, 115.06, 89.05; HRMS ESI (m/z): calcd for $\text{C}_9\text{H}_8\text{ClN}_2$ [$\text{M} + \text{H}$] $^+$: 179.0371, found: 179.0373.

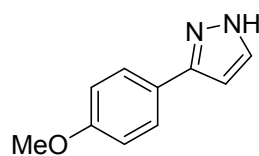
4-(1H-Pyrazol-3-yl)benzonitrile (3d)



Yellow solid (49.9 mg, 59%), mp 141.8-143.2 $^{\circ}\text{C}$; IR (KBr): 3308, 2959, 2227, 1608, 1410, 843, 771 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 9.56 (s, 1H), 7.87 (d, $J = 7.8$ Hz, 2H), 7.66 (d, $J = 9.1$ Hz, 3H), 6.69 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 148.9, 137.1, 132.5, 131.5, 126.1, 118.8, 111.0, 103.5; MS (EI, 70 eV) m/z : 169.05, 142.06, 115.07, 102.05;

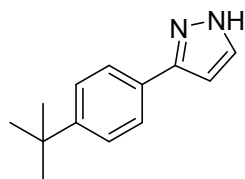
HRMS ESI (*m/z*): calcd for C₁₀H₇N₃Na [M + Na]⁺: 192.0532, found: 192.0535.

3-(4-Methoxyphenyl)-1*H*-pyrazole (3e)



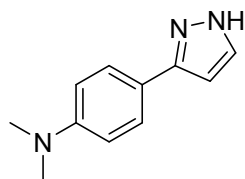
White solid (72.2 mg, 83%), mp 98.1-99.7 °C; IR (KBr): 3123, 2914, 2836, 1612, 1250, 837, 781 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ ppm 10.88 (s, 1H), 7.64 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 1.7 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.49 (d, *J* = 1.7 Hz, 1H), 3.79 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 159.4, 148.4, 133.6, 127.1, 124.7, 114.1, 102.0, 55.2; MS (EI, 70 eV) *m/z*: 174.06, 159.04, 131.07, 103.07; HRMS ESI (*m/z*): calcd for C₁₀H₁₁N₂O [M + H]⁺: 175.0866, found: 175.0868.

3-(4-(*tert*-Butyl)phenyl)-1*H*-pyrazole (3f)



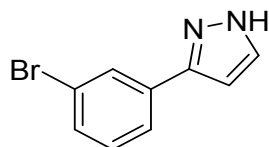
Light yellow solid (66.0 mg, 66%), mp 77.6-78.7 °C; IR (KBr): 3177, 2959, 1516, 1460, 836, 776 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ ppm 11.75 (s, 1H), 7.75-7.69 (m, 2H), 7.61 (d, *J* = 2.1 Hz, 1H), 7.49-7.41 (m, 2H), 6.60 (d, *J* = 2.1 Hz, 1H), 1.37 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 151.1, 148.5, 133.8, 129.1, 125.7, 125.6, 102.4, 34.6, 31.3; MS (EI, 70 eV) *m/z*: 200.12, 185.10, 157.09, 115.07; HRMS ESI (*m/z*): calcd for C₁₃H₁₇N₂ [M + H]⁺: 201.1386, found: 201.1386.

N,N-Dimethyl-4-(1*H*-pyrazol-3-yl)aniline (3g)



Brown solid (74.8 mg, 80%), mp 153.6-155.4 °C; IR (KBr): 3144, 2922, 1613, 1519, 1213, 817, 770 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ ppm 10.11 (s, 1H), 7.58 (dd, *J* = 8.4, 5.1 Hz, 3H), 6.70 (d, *J* = 8.7 Hz, 2H), 6.45 (d, *J* = 1.4 Hz, 1H), 2.94 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 150.3, 147.9, 135.0, 126.7, 119.7, 112.4, 101.3, 40.4; MS (EI, 70 eV) *m/z*: 187.10, 158.09, 143.08, 115.06; HRMS ESI (*m/z*): calcd for C₁₁H₁₄N₃ [M + H]⁺: 188.1182, found: 188.1183.

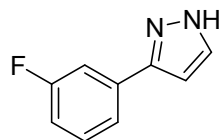
3-(3-Bromophenyl)-1*H*-pyrazole (3h)



Light yellow oil (68.8 mg, 62%); IR (KBr): 3172, 2929, 1566, 880, 767, 682 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ ppm 8.04 (d, *J* = 83.0 Hz, 2H), 7.73-7.58 (m, 2H),

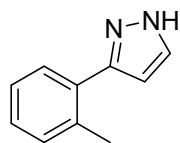
7.45 (d, $J = 7.9$ Hz, 1H), 7.26 (t, $J = 7.9$ Hz, 1H), 6.62 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 148.8, 134.6, 132.1, 130.9, 130.3, 128.8, 124.4, 122.9, 103.0; MS (EI, 70 eV) m/z : 221.97, 143.08, 116.10, 89.08; HRMS ESI (m/z): calcd for $\text{C}_9\text{H}_8\text{BrN}_2$ $[\text{M} + \text{H}]^+$: 222.9865, found: 222.9867.

3-(3-Fluorophenyl)-1H-pyrazole (3i)



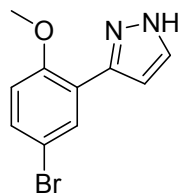
Light yellow oil (52.7 mg, 65%); IR (KBr): 3178, 2932, 1590, 859, 771, 682 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 11.18 (s, 1H), 7.61 (s, 1H), 7.54 (d, $J = 7.7$ Hz, 1H), 7.48 (d, $J = 10.0$ Hz, 1H), 7.35 (dd, $J = 14.3, 7.6$ Hz, 1H), 7.02 (td, $J = 8.2, 1.5$ Hz, 1H), 6.61 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 163.1 ($J = 243.9$ Hz), 149.0, 134.7 ($J = 8.1$ Hz), 132.3, 130.3 ($J = 8.3$ Hz), 121.5 ($J = 2.6$ Hz), 114.7 ($J = 21.1$ Hz), 112.7 ($J = 22.6$ Hz), 103.0; MS (EI, 70 eV) m/z : 162.08, 133.07, 108.08, 95.06; HRMS ESI (m/z): calcd for $\text{C}_9\text{H}_8\text{FN}_2$ $[\text{M} + \text{H}]^+$: 163.0666, found: 163.0669.

3-(*o*-Tolyl)-1H-pyrazole (3j)



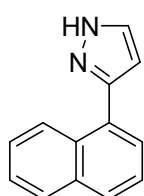
Yellow oil (51.4 mg, 65%); IR (KBr): 3174, 2946, 1455, 943, 759 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 10.70 (s, 1H), 7.52 (d, $J = 2.0$ Hz, 1H), 7.45 (d, $J = 7.3$ Hz, 1H), 7.27-7.18 (m, 3H), 6.40 (d, $J = 2.0$ Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 147.0, 136.1, 134.2, 131.5, 130.8, 129.2, 128.2, 125.9, 105.4, 20.8; MS (EI, 70 eV) m/z : 158.24, 130.21, 103.17, 77.15; HRMS ESI (m/z): calcd for $\text{C}_{10}\text{H}_{11}\text{N}_2$ $[\text{M} + \text{H}]^+$: 159.0917, found: 159.0914.

3-(5-Bromo-2-methoxyphenyl)-1H-pyrazole (3k)



Yellow solid (74.3 mg, 59%), mp 119.2-120.9 $^\circ\text{C}$; IR (KBr): 3177, 2929, 1588, 1466, 1251, 1031, 765 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 9.92 (s, 1H), 7.81 (d, $J = 2.3$ Hz, 1H), 7.62 (d, $J = 1.1$ Hz, 1H), 7.36 (dd, $J = 8.8, 2.3$ Hz, 1H), 6.86 (d, $J = 8.8$ Hz, 1H), 6.65 (s, 1H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 154.9, 140.2, 138.0, 131.5, 130.5, 120.3, 113.6, 113.3, 103.7, 56.0; MS (EI, 70 eV) m/z : 251.94, 224.97, 144.09, 102.05; HRMS ESI (m/z): calcd for $\text{C}_{10}\text{H}_{10}\text{BrN}_2\text{O}$ $[\text{M} + \text{H}]^+$: 252.9971, found: 252.9969.

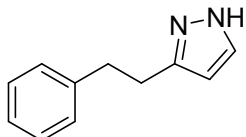
3-(Naphthalen-1-yl)-1H-pyrazole (3l)



Yellow solid (55.3 mg, 57%), mp 113.7-115.2 $^\circ\text{C}$; IR (KBr): 3161, 3053, 1516, 1384, 777 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 11.95 (s, 1H), 8.33-8.22 (m, 1H), 7.83 (dd, $J = 7.4,$

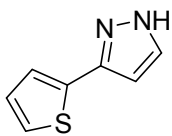
1.9 Hz, 1H), 7.78 (d, $J = 8.2$ Hz, 1H), 7.54 (dd, $J = 7.1, 1.2$ Hz, 1H), 7.47-7.34 (m, 3H), 7.28 (d, $J = 2.1$ Hz, 1H), 6.48 (d, $J = 2.1$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 147.5, 133.8, 132.7, 131.4, 130.3, 128.5, 128.3, 127.1, 126.4, 125.9, 125.7, 125.2, 106.0; MS (EI, 70 eV) m/z : 194.08, 166.09, 139.06, 96.93; HRMS ESI (m/z): calcd for $\text{C}_{13}\text{H}_{11}\text{N}_2$ $[\text{M} + \text{H}]^+$: 195.0917, found: 195.0921.

3-Phenethyl-1H-pyrazole (3m)



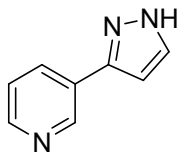
Light yellow oil (36.1mg, 42%); IR (KBr): 3191, 2928, 1590, 1453, 1360, 757, 700 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.55 (d, $J = 61.9$ Hz, 2H), 7.27 (t, $J = 7.4$ Hz, 2H), 7.19 (t, $J = 8.6$ Hz, 3H), 6.07 (s, 1H), 3.03-2.94 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 147.7, 141.2, 134.2, 128.4, 128.3, 126.1, 103.7, 35.6, 28.7; MS (EI, 70 eV) m/z : 172.09, 157.07, 91.05, 81.03; HRMS ESI (m/z): calcd for $\text{C}_{11}\text{H}_{13}\text{N}_2$ $[\text{M} + \text{H}]^+$: 173.1073, found: 173.1075.

3-(Thiophen-2-yl)-1H-pyrazole (3n)



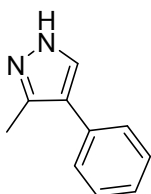
Brown oil (38.3 mg, 51%); IR (KBr): 3175, 2927, 1520, 1048, 838, 767, 698 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 10.23 (s, 1H), 7.62 (s, 1H), 7.34 (s, 1H), 7.26 (d, $J = 4.7$ Hz, 1H), 7.06 (s, 1H), 6.54 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 145.5, 135.7, 131.5, 127.6, 124.6, 124.1, 102.7; MS (EI, 70 eV) m/z : 150.00, 121.00, 96.00, 78.07; HRMS ESI (m/z): calcd for $\text{C}_7\text{H}_7\text{N}_2\text{S}$ $[\text{M} + \text{H}]^+$: 151.0324, found: 151.0326.

3-(1H-Pyrazol-3-yl)pyridine (3o)



Light yellow oil (53.0 mg, 73%); IR (KBr): 3167, 2913, 1579, 1416, 1040, 766 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 9.03 (s, 1H), 8.50 (s, 1H), 8.05 (d, $J = 7.7$ Hz, 1H), 7.60 (s, 1H), 7.28 (d, $J = 4.5$ Hz, 1H), 6.60 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 148.1, 146.7, 146.6, 133.2, 131.8, 128.9, 123.7, 102.6; MS (EI, 70 eV) m/z : 145.23, 119.20, 91.17, 78.15; HRMS ESI (m/z): calcd for $\text{C}_8\text{H}_8\text{N}_3$ $[\text{M} + \text{H}]^+$: 146.0713, found: 146.0715.

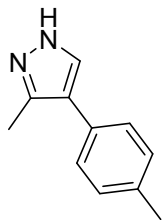
3-Methyl-4-phenyl-1H-pyrazole (5a)



Brown oil (60.9 mg, 77%); IR (KBr): 3215, 2931, 1603, 1443, 760, 697 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.62 (d, $J = 3.3$ Hz, 1H), 7.38-7.27 (m, 6H), 1.72 (s, 3H); ^{13}C NMR

(100 MHz, CDCl₃) δ ppm 146.0, 142.7, 135.5, 128.7, 128.0, 126.4, 98.5, 21.6; MS (EI, 70 eV) m/z : 158.24, 130.21, 103.19, 89.18; HRMS ESI (m/z): calcd for C₁₀H₁₁N₂ [M + H]⁺: 159.0917, found: 159.0919.

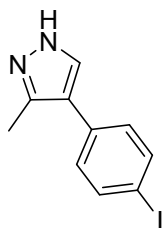
3-Methyl-4-(*p*-tolyl)-1*H*-pyrazole (5b)



Brown oil (68.0mg, 79%); IR (KBr): 3208, 2927, 1515, 1444, 814, 707 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.59 (d, J = 3.2 Hz, 1H), 7.28-7.21 (m, 3H), 7.13 (d, J = 7.9 Hz, 2H), 2.31 (s, 3H), 1.70 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 146.2, 143.5, 137.8, 132.5, 129.4, 126.3, 98.3, 21.5, 20.9; MS (EI, 70 eV) m/z : 172.10, 130.08, 103.07, 77.06; HRMS

ESI (m/z): calcd for C₁₁H₁₃N₂ [M + H]⁺: 173.1073, found: 173.1074.

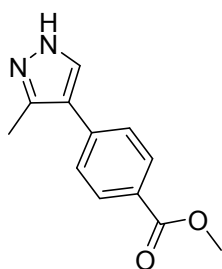
4-(4-Iodophenyl)-3-methyl-1*H*-pyrazole (5c)



Brown oil (99.4 mg, 70%); IR (KBr): 3670, 1420, 1344, 1251, 805 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.66-7.62 (m, 2H), 7.60 (d, J = 3.3 Hz, 1H), 7.23 (d, J = 3.3 Hz, 1H), 7.12-7.07 (m, 2H), 1.67 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 145.3, 142.9, 137.7, 135.3, 128.3, 97.9, 93.6, 21.5; MS (EI, 70 eV) m/z : 283.92, 157.08, 130.07, 103.07; HRMS

ESI (m/z): calcd for C₁₀H₁₀IN₂[M + H]⁺: 284.9883, found: 284.9880.

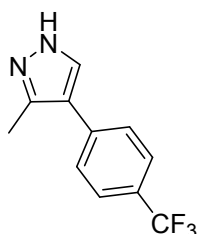
Methyl 4-(3-Methyl-1*H*-pyrazol-4-yl)benzoate (5d)



Brown oil (62.7 mg, 58%); IR (KBr): 3099, 2951, 1720, 1609, 1283, 1112, 772 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ ppm 8.00 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 3.3 Hz, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 3.3 Hz, 1H), 3.90 (s, 3H), 1.74 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 166.4, 145.3, 143.0, 140.5, 129.9, 129.7, 126.4, 98.2, 52.0, 21.6; MS (EI, 70 eV) m/z : 216.06, 185.04, 130.07, 103.06; HRMS ESI (m/z): calcd for

C₁₂H₁₃N₂O₂ [M + H]⁺: 217.0972, found: 217.0970.

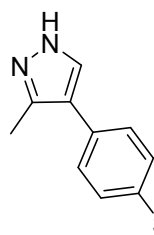
3-Methyl-4-(4-(trifluoromethyl)phenyl)-1*H*-pyrazole (5e)



Brown oil 65.6 mg, 58%); IR (KBr): 2987, 2934, 1618, 1327, 1124, 843, 785 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.65 (d, J = 3.3 Hz, 1H), 7.59 (d, J = 8.3 Hz, 2H), 7.50

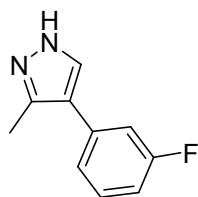
(d, $J = 8.3$ Hz, 2H), 7.29 (d, $J = 3.3$ Hz, 1H), 1.73 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 145.1, 143.2, 139.7 ($J = 1.0$ Hz), 130.3 ($J = 32.4$ Hz), 126.9, 125.7 ($J = 7.5$ Hz), 123.9 ($J = 270.6$ Hz), 98.1, 21.8; MS (EI, 70 eV) m/z : 226.06, 198.04, 157.07, 130.09; HRMS ESI (m/z): calcd for $\text{C}_{11}\text{H}_{10}\text{F}_3\text{N}_2$ $[\text{M} + \text{H}]^+$: 227.0791, found: 227.0787.

3-Methyl-4-(4-(methylthio)phenyl)-1H-pyrazole (5f)



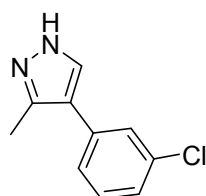
Brown oil (73.5 mg, 72%); IR (KBr): 3211, 2925, 1582, 1434, 1099, 848, 817 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.61 (d, $J = 3.3$ Hz, 1H), 7.26 (dd, $J = 9.2, 5.9$ Hz, 3H), 7.21 (d, $J = 8.4$ Hz, 2H), 2.46 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 145.8, 142.7, 138.6, 132.1, 126.9, 126.7, 98.1, 21.5, 15.7; MS (EI, 70 eV) m/z : 204.03, 189.03, 174.04, 102.05; HRMS ESI (m/z): calcd for $\text{C}_{11}\text{H}_{12}\text{N}_2\text{NaS}$ $[\text{M} + \text{Na}]^+$: 227.0613, found: 227.0614.

4-(3-Fluorophenyl)-3-methyl-1H-pyrazole (5g)



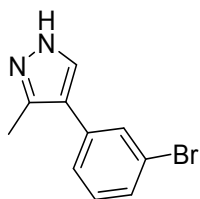
Brown oil (58.1 mg, 66%); IR (KBr): 3082, 2929, 1592, 1439, 1259, 782, 693 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.63 (d, $J = 3.3$ Hz, 1H), 7.28 (ddd, $J = 13.0, 7.5, 4.8$ Hz, 2H), 7.15-7.08 (m, 2H), 6.99 (td, $J = 8.3, 2.5$ Hz, 1H), 1.71 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 162.7 ($J = 245.1$ Hz), 145.4, 143.0, 137.8 ($J = 7.4$ Hz), 130.2 ($J = 8.2$ Hz), 122.1 ($J = 3.0$ Hz), 115.0 ($J = 20.9$ Hz), 113.8 ($J = 22.8$ Hz), 97.8, 21.6; MS (EI, 70 eV) m/z : 176.06, 148.05, 121.05, 107.03; HRMS ESI (m/z): calcd for $\text{C}_{10}\text{H}_{10}\text{FN}_2$ $[\text{M} + \text{H}]^+$: 177.0823, found: 177.0824.

4-(3-Chlorophenyl)-3-methyl-1H-pyrazole (5h)



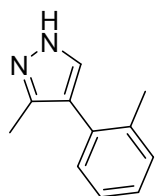
Brown oil (72.0 mg, 75%); IR (KBr): 3092, 2984, 1582, 1431, 784, 692 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.63 (d, $J = 3.3$ Hz, 1H), 7.36 (d, $J = 1.2$ Hz, 1H), 7.29-7.24 (m, 4H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 145.3, 143.4, 137.4, 134.5, 129.9, 128.2, 126.7, 124.6, 97.9, 21.5; MS (EI, 70 eV) m/z : 192.01, 157.07, 130.07, 103.06; HRMS ESI (m/z): calcd for $\text{C}_{10}\text{H}_{10}\text{ClN}_2$ $[\text{M} + \text{H}]^+$: 193.0527, found: 193.0529.

4-(3-Bromophenyl)-3-methyl-1H-pyrazole (5i)



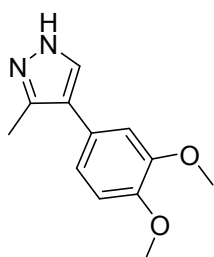
Brown oil (83.8 mg, 71%); IR (KBr): 3093, 1573, 1432, 1072, 897, 782, 698 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.61 (d, $J = 3.3$ Hz, 1H), 7.50 (t, $J = 1.7$ Hz, 1H), 7.41 (d, $J = 7.9$ Hz, 1H), 7.29 (d, $J = 7.9$ Hz, 1H), 7.24 (d, $J = 3.3$ Hz, 1H), 7.18 (t, $J = 7.9$ Hz, 1H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 145.2, 143.1, 137.7, 131.1, 130.2, 129.6, 125.1, 122.7, 97.8, 21.6; MS (EI, 70 eV) m/z : 235.96, 157.06, 130.07, 103.06; HRMS ESI (m/z): calcd for $\text{C}_{10}\text{H}_{10}\text{BrN}_2$ [$\text{M} + \text{H}$] $^+$: 237.0022, found: 237.0017.

3-Methyl-4-(*o*-tolyl)-1H-pyrazole (5j)



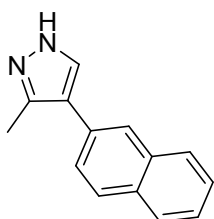
Brown oil (53.3 mg, 62%); IR (KBr): 3213, 2930, 1601, 1447, 1353, 757 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.64 (d, $J = 3.4$ Hz, 1H), 7.51 (dd, $J = 6.1, 3.3$ Hz, 1H), 7.39 (d, $J = 3.4$ Hz, 1H), 7.23-7.14 (m, 3H), 2.46 (s, 3H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 145.6, 142.2, 136.8, 134.8, 132.3, 128.0, 127.8, 126.2, 99.1, 21.9, 21.2; MS (EI, 70 eV) m/z : 172.08, 157.07, 130.07, 103.05; HRMS ESI (m/z): calcd for $\text{C}_{11}\text{H}_{13}\text{N}_2$ [$\text{M} + \text{H}$] $^+$: 173.1073, found: 173.1075

4-(3,4-Dimethoxyphenyl)-3-methyl-1H-pyrazole (5k)



Yellow oil (98.2 mg, 90%); IR (KBr): 3339, 2940, 1586, 1514, 1251, 1149, 1024 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.61 (d, $J = 3.3$ Hz, 1H), 7.27 (d, $J = 3.3$ Hz, 1H), 6.93-6.88 (m, 2H), 6.81 (d, $J = 8.9$ Hz, 1H), 3.86 (d, $J = 3.7$ Hz, 6H), 1.71 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 149.0, 148.9, 146.1, 142.5, 127.9, 118.7, 111.2, 110.0, 98.1, 55.9, 55.9, 21.7; MS (EI, 70 eV) m/z : 218.26, 203.24, 175.22, 131.19; HRMS ESI (m/z): calcd for $\text{C}_{12}\text{H}_{15}\text{N}_2\text{O}_2$ [$\text{M} + \text{H}$] $^+$: 219.1128, found: 219.1130.

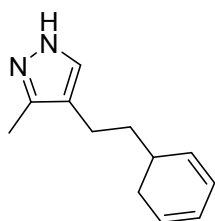
3-Methyl-4-(naphthalen-2-yl)-1H-pyrazole (5l)



Brown solid (79.1 mg, 76%), mp 150.6-151.9 $^{\circ}\text{C}$; IR (KBr): 3199, 2931, 1746, 1601, 1245, 816, 748 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.87 (s, 1H), 7.81 (d, $J = 8.1$

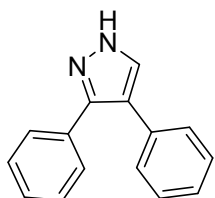
Hz, 3H), 7.68 (d, $J = 3.3$ Hz, 1H), 7.51-7.46 (m, 2H), 7.42 (dd, $J = 8.6, 1.5$ Hz, 1H), 7.37 (d, $J = 3.3$ Hz, 1H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 146.1, 142.8, 133.3, 133.0, 132.8, 128.4, 127.9, 127.5, 126.3, 126.3, 125.2, 124.4, 98.6, 21.5; MS (EI): m/z (%) = 208.09, 180.07, 166.07, 139.07; HRMS ESI (m/z): calcd for $\text{C}_{14}\text{H}_{13}\text{N}_2$ $[\text{M} + \text{H}]^+$: 209.1073, found: 209.1075.

3-Methyl-4-phenethyl-1H-pyrazole (5m)



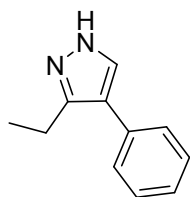
Brown oil (42.8 mg, 46%); IR (KBr): 2931, 2860, 1600, 1448, 1245, 759, 701 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.58 (d, $J = 3.3$ Hz, 1H), 7.25 (t, $J = 7.4$ Hz, 2H), 7.17 (t, $J = 7.3$ Hz, 1H), 7.09 (d, $J = 7.2$ Hz, 2H), 6.92 (d, $J = 3.3$ Hz, 1H), 2.38-2.19 (m, 4H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 145.6, 142.9, 141.1, 128.4, 128.2, 126.1, 96.1, 36.5, 30.8, 18.9; MS (EI, 70 eV) m/z : 186.08, 115.05, 95.06, 91.01; HRMS ESI (m/z): calcd for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 209.1049, found: 209.1053.

3,4-Diphenyl-1H-pyrazole (5n)



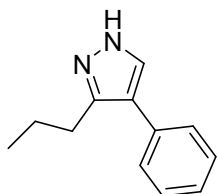
Light yellow solid (75.9 mg, 69%), mp 156.8-158.6 $^\circ\text{C}$; IR (KBr): 3159, 2934, 1603, 949, 762, 695 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 12.22 (s, 1H), 7.57 (s, 1H), 7.50-7.43 (m, 2H), 7.34-7.18 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 143.8, 134.7, 133.1, 131.4, 128.5, 128.5, 128.4, 128.3, 128.1, 126.5, 119.8; MS (EI, 70 eV) m/z : 220.08, 205.06, 165.06, 89.03; HRMS ESI (m/z): calcd for $\text{C}_{15}\text{H}_{13}\text{N}_2$ $[\text{M} + \text{H}]^+$: 221.1073, found: 221.1076.

3-Ethyl-4-phenyl-1H-pyrazole (5o)



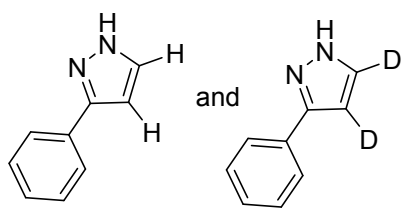
Light yellow solid (64.5 mg, 75%), mp 71.2-73.4 $^\circ\text{C}$; IR (KBr): 3170, 2966, 1762, 1243, 768, 698 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 11.59 (s, 1H), 7.59 (d, $J = 7.5$ Hz, 2H), 7.42 (t, $J = 7.4$ Hz, 3H), 7.35 (t, $J = 7.2$ Hz, 1H), 2.67 (q, $J = 7.4$ Hz, 2H), 1.23 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 144.5, 133.5, 132.3, 128.5, 127.6, 127.6, 120.1, 17.5, 15.0; MS (EI, 70 eV) m/z : 172.08, 157.04, 130.07, 103.06; HRMS ESI (m/z): calcd for $\text{C}_{11}\text{H}_{13}\text{N}_2$ $[\text{M} + \text{H}]^+$: 173.1073, found: 173.1074.

4-Phenyl-3-propyl-1H-pyrazole (5p)



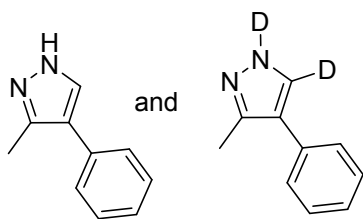
Light yellow solid (67.0 mg, 72%), 101.9-103.6 °C; IR (KBr): 3161, 2927, 1762, 1445, 768, 697 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 11.30 (s, 1H), 7.58 (d, $J = 7.3$ Hz, 2H), 7.39 (tt, $J = 14.5, 7.2$ Hz, 4H), 2.67-2.59 (m, 2H), 1.63 (dd, $J = 15.1, 7.5$ Hz, 2H), 0.97 (t, $J = 7.3$ Hz, 3H).; ^{13}C NMR (100 MHz, CDCl_3) δ ppm 144.6, 134.1, 132.3, 128.5, 127.7, 127.6, 118.3, 26.3, 23.8, 14.0; MS (EI, 70 eV) m/z : 186.10, 157.07, 130.07, 103.09; HRMS ESI (m/z): calcd for $\text{C}_{12}\text{H}_{15}\text{N}_2$ [$\text{M} + \text{H}$] $^+$: 187.1230, found: 187.1231.

3a and [D₂]-3a



Yellow oil (54.8 mg, 75%); IR (KBr): 3170, 2936, 1454, 767, 692 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 9.20 (s, 1H), 7.77 (d, $J = 7.2$ Hz, 2H), 7.61 (s, 0.18H), 7.40 (t, $J = 7.4$ Hz, 2H), 7.36-7.31 (m, 1H), 6.61 (s, 0.18H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 148.9, 133.2, 132.0, 128.7, 128.0, 125.8, 102.5; MS (EI, 70 eV) m/z : 146.09, 117.10, 91.09, 77.07; HRMS ESI (m/z): calcd for $\text{C}_9\text{H}_7\text{D}_2\text{N}_2$ [$\text{M} + \text{H}$] $^+$: 147.0886, found: 147.0889.

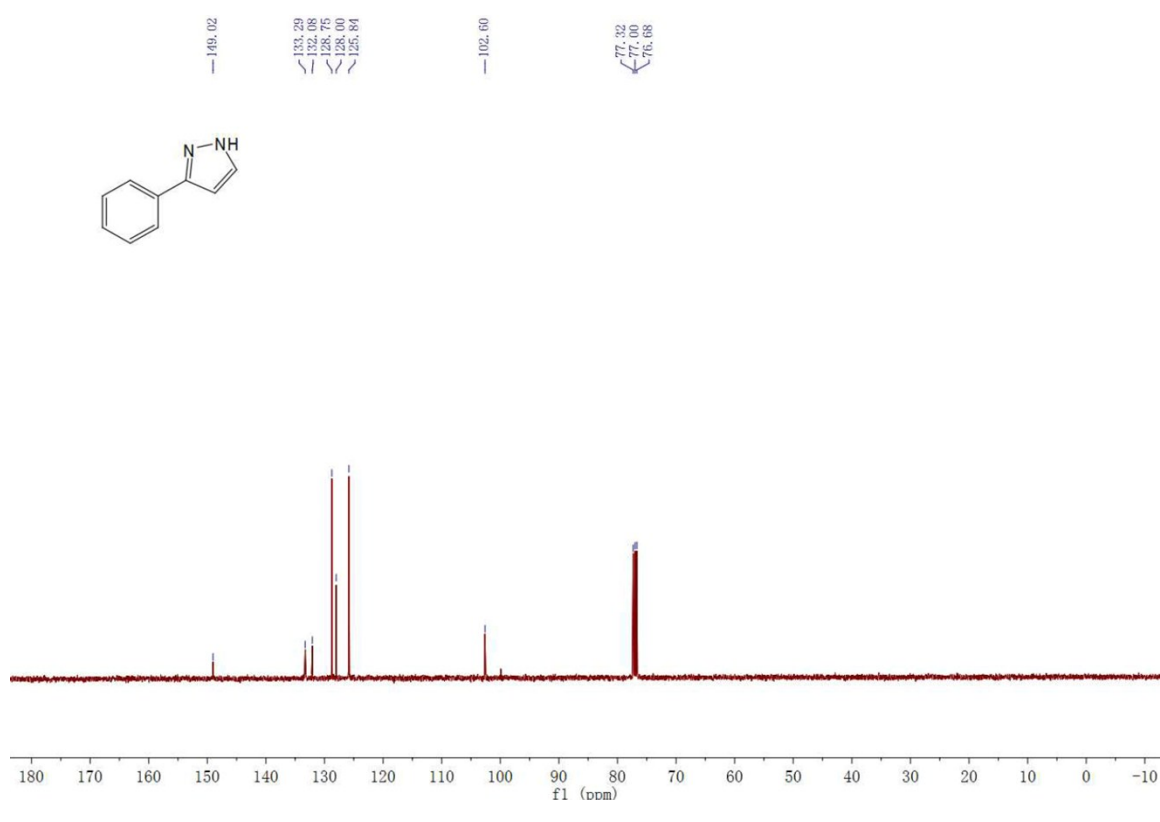
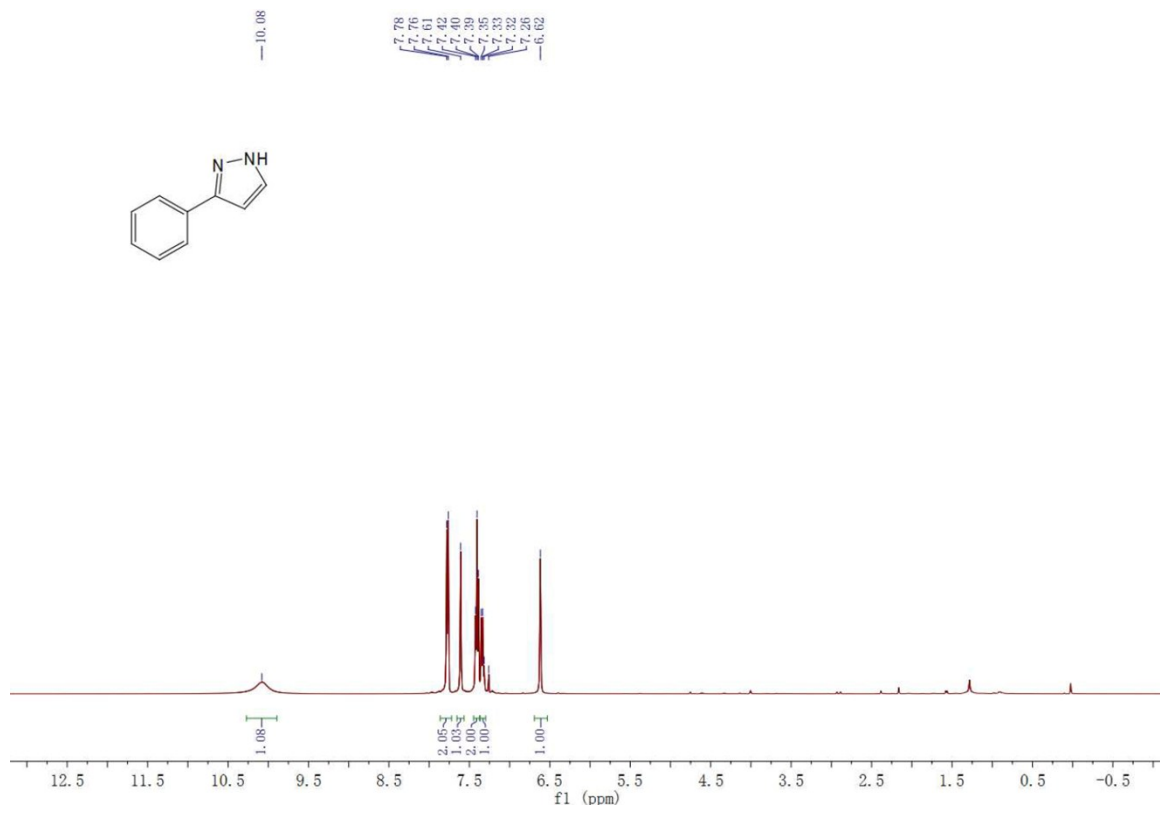
5a and [D₂]-5a



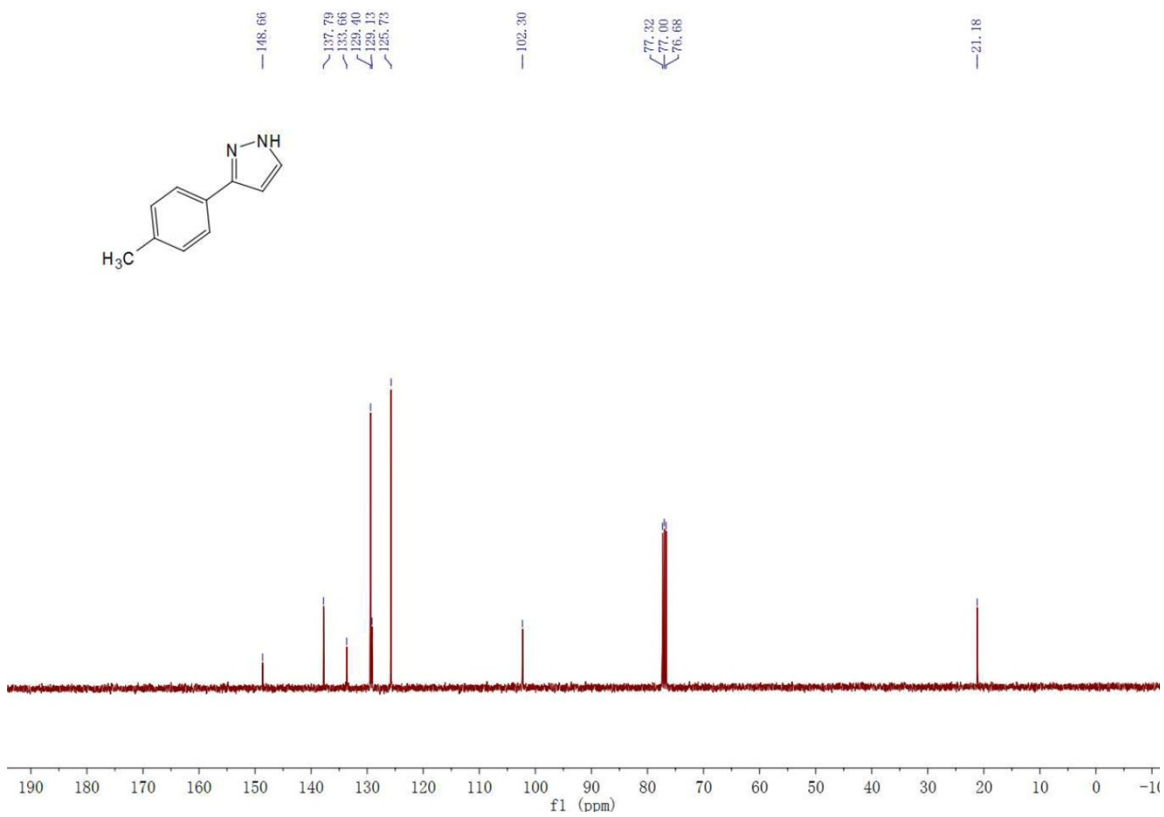
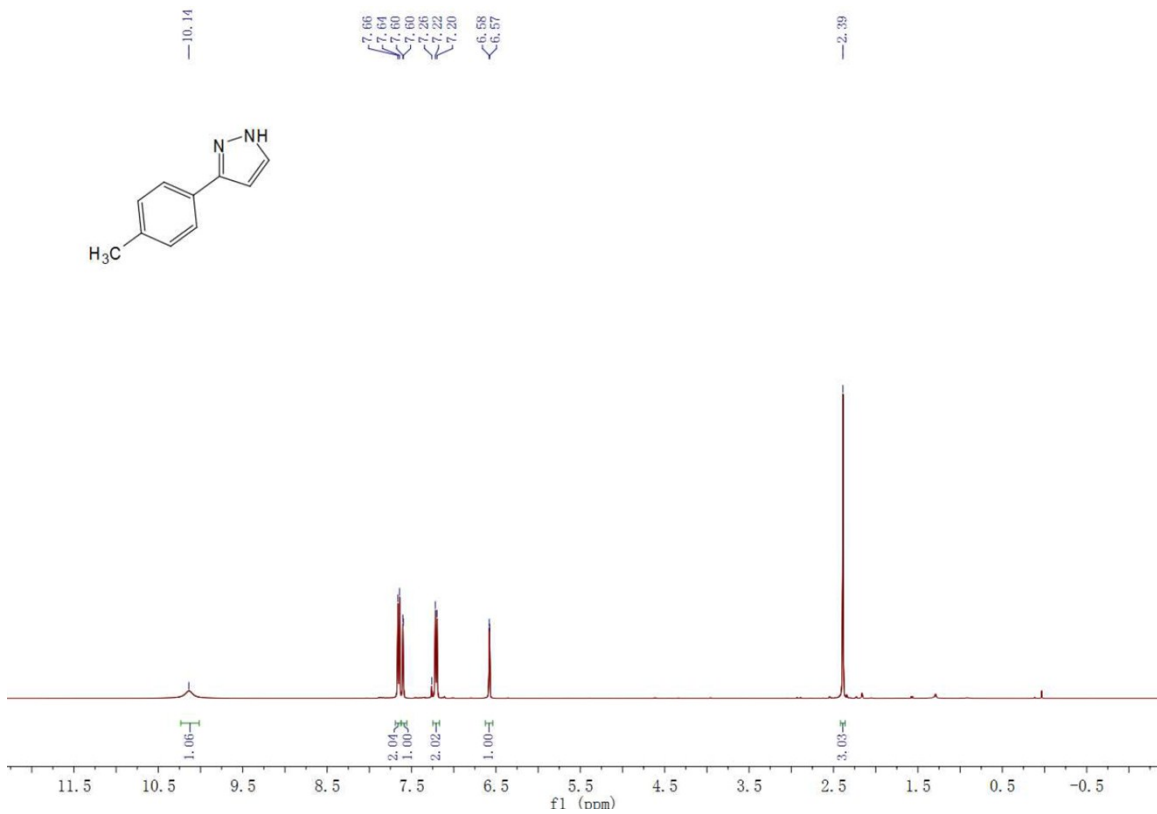
Brown oil (64.0 mg, 80%); IR (KBr): 3199, 2930, 1601, 1441, 764, 698 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.61 (s, 0.12H), 7.31 (dt, $J = 16.0, 7.5$ Hz, 5.16H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 145.9, 142.6, 135.5, 128.7, 128.0, 126.4, 98.4, 21.6; MS (EI, 70 eV) m/z : 160.11, 131.11, 117.09, 77.07; HRMS ESI (m/z): calcd for $\text{C}_{10}\text{H}_9\text{D}_2\text{N}_2$ [$\text{M} + \text{H}$] $^+$: 161.1042, found: 161.1041.

F. NMR Spectra

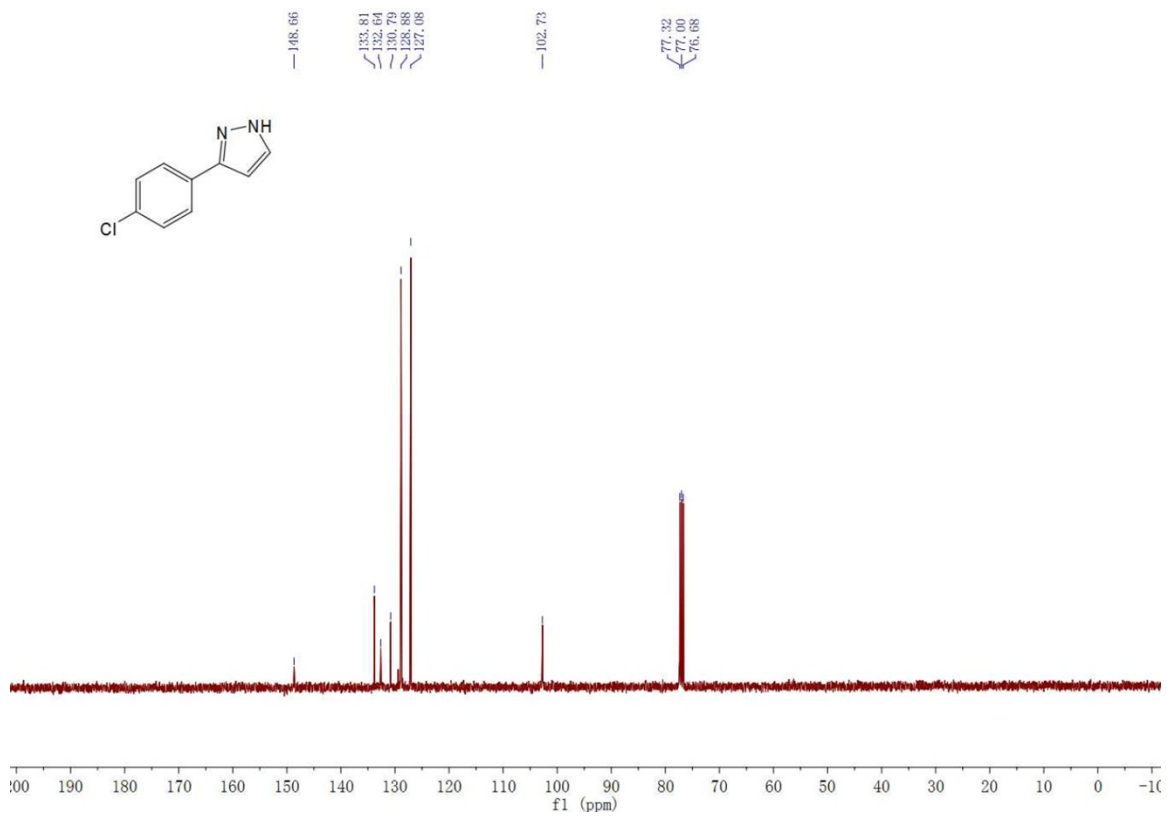
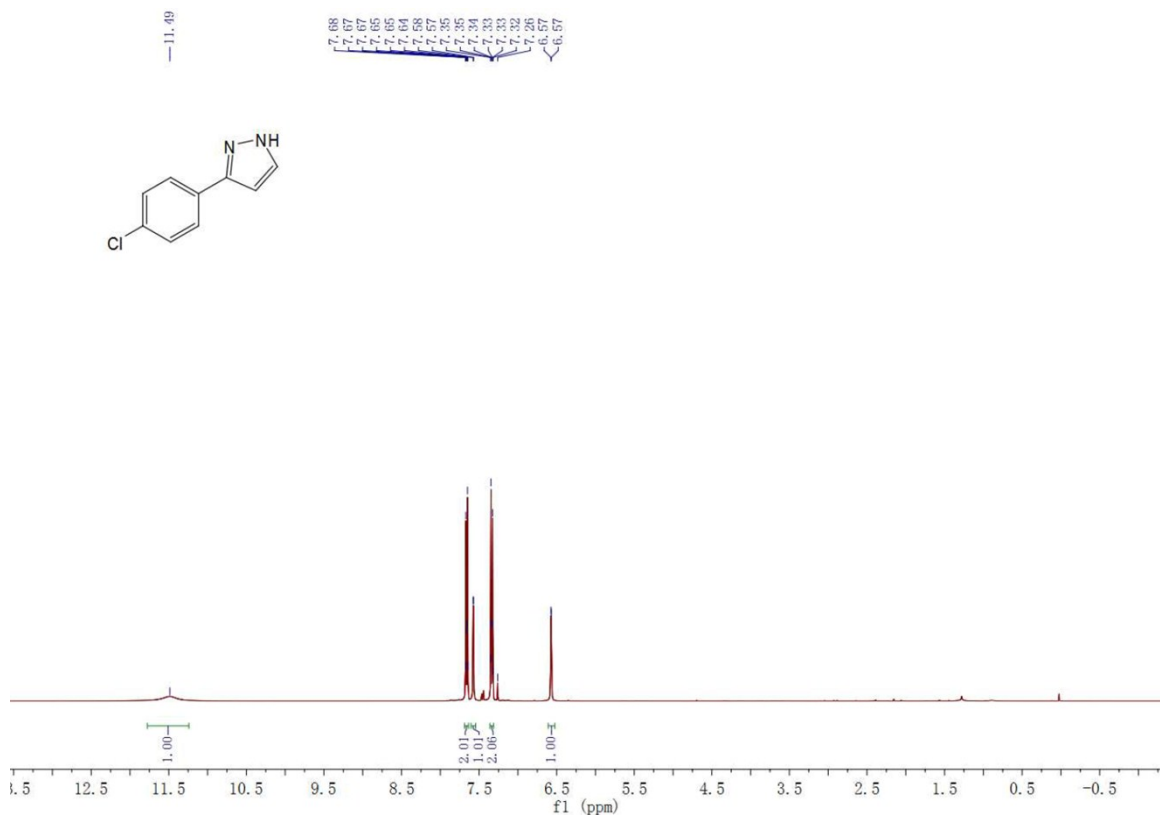
3a



3b

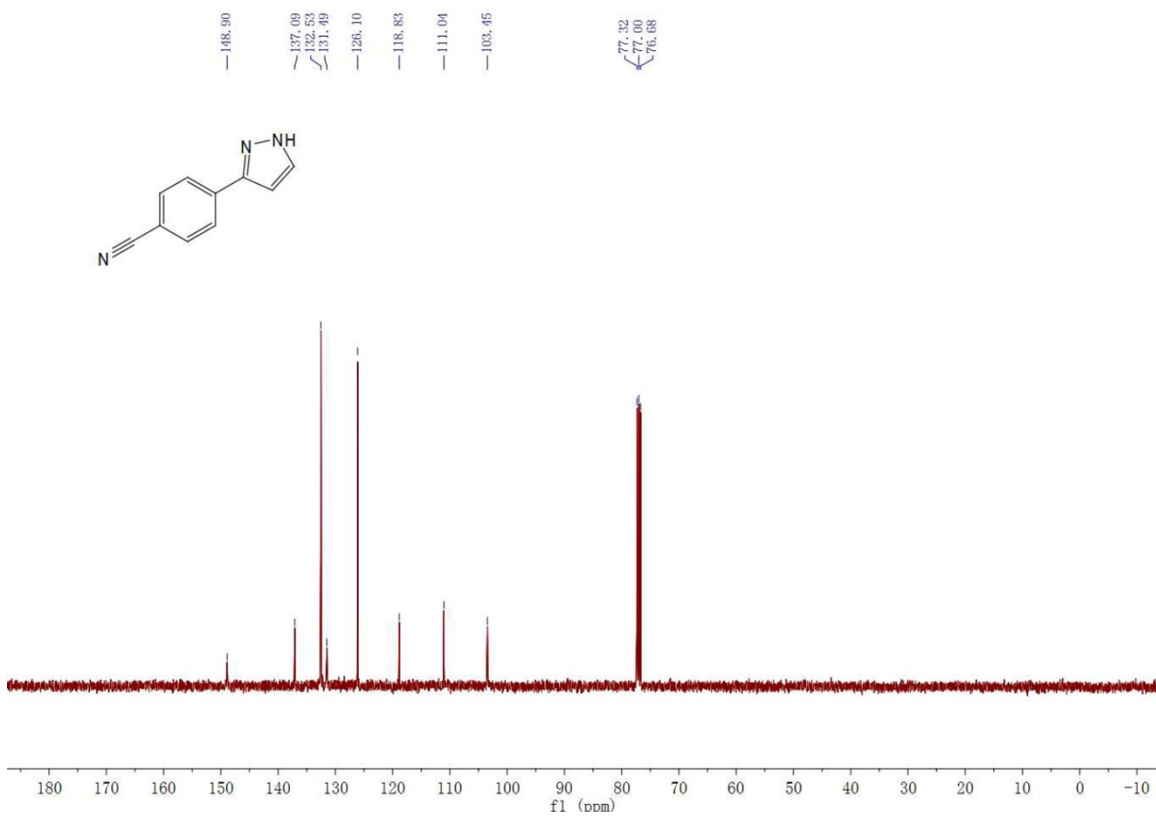
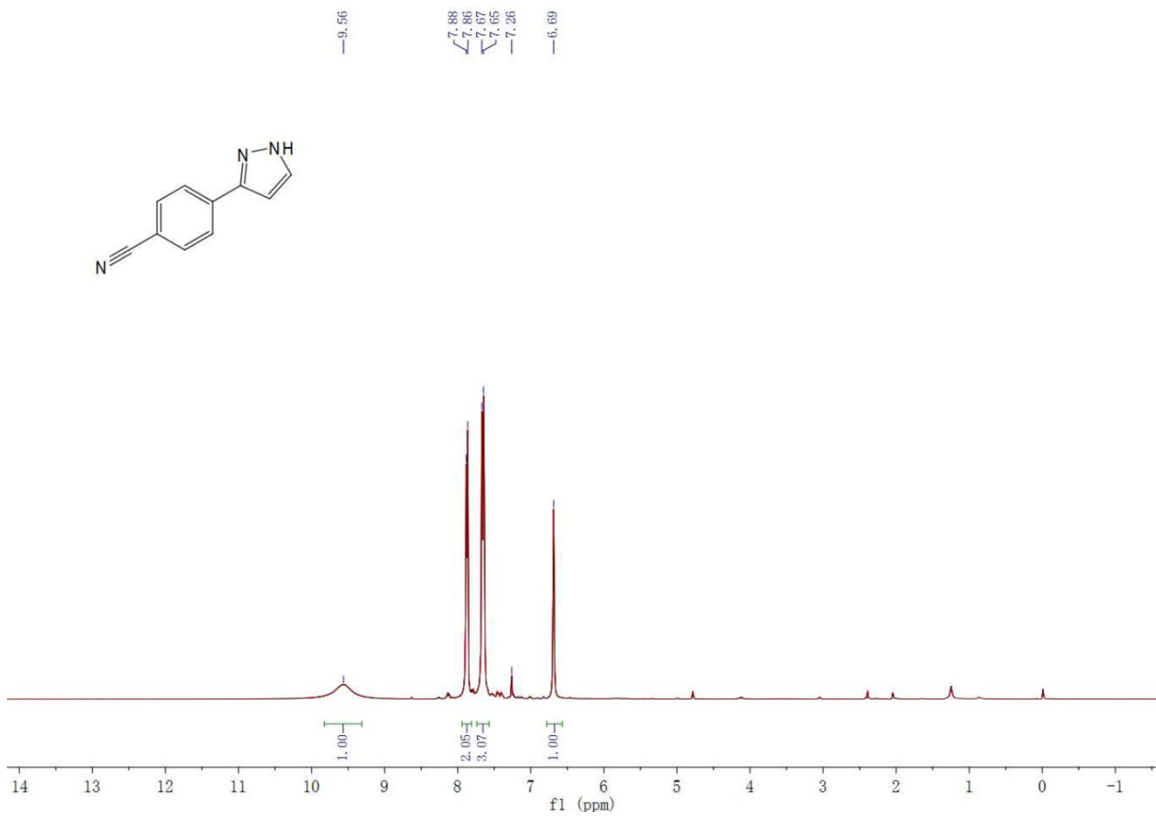


3c

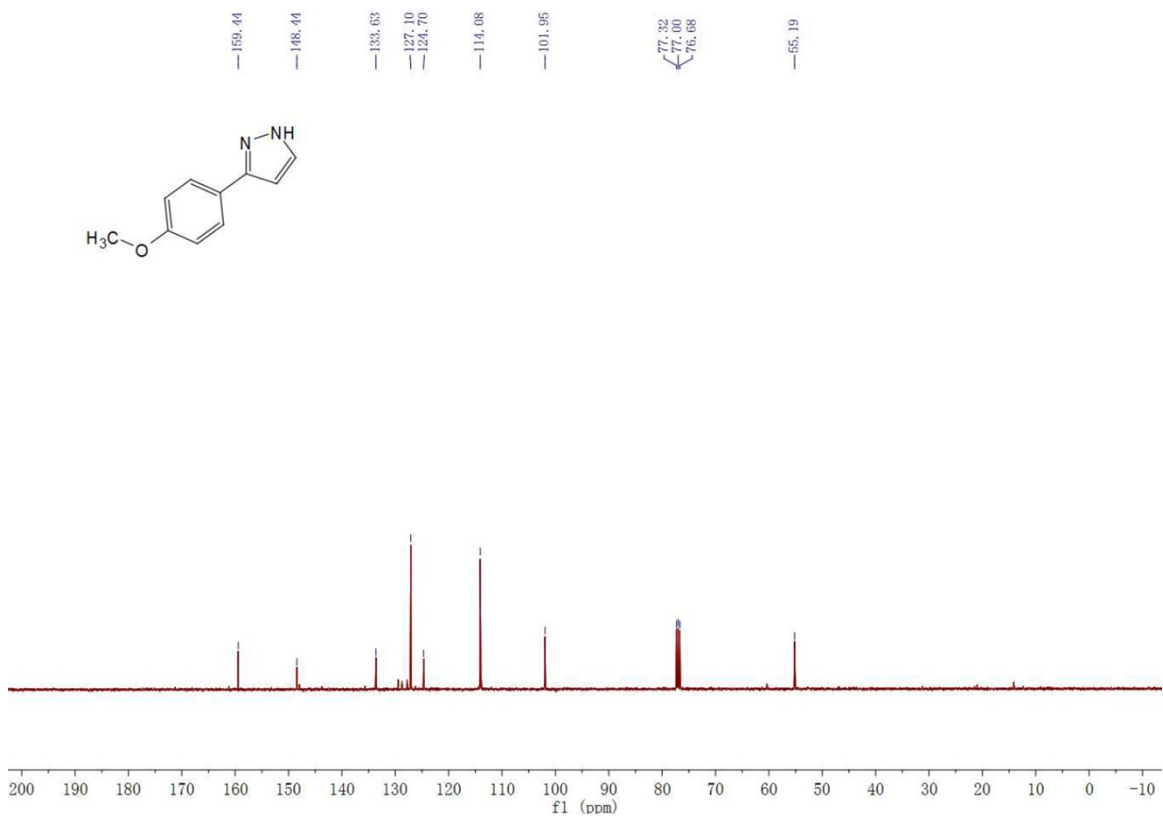
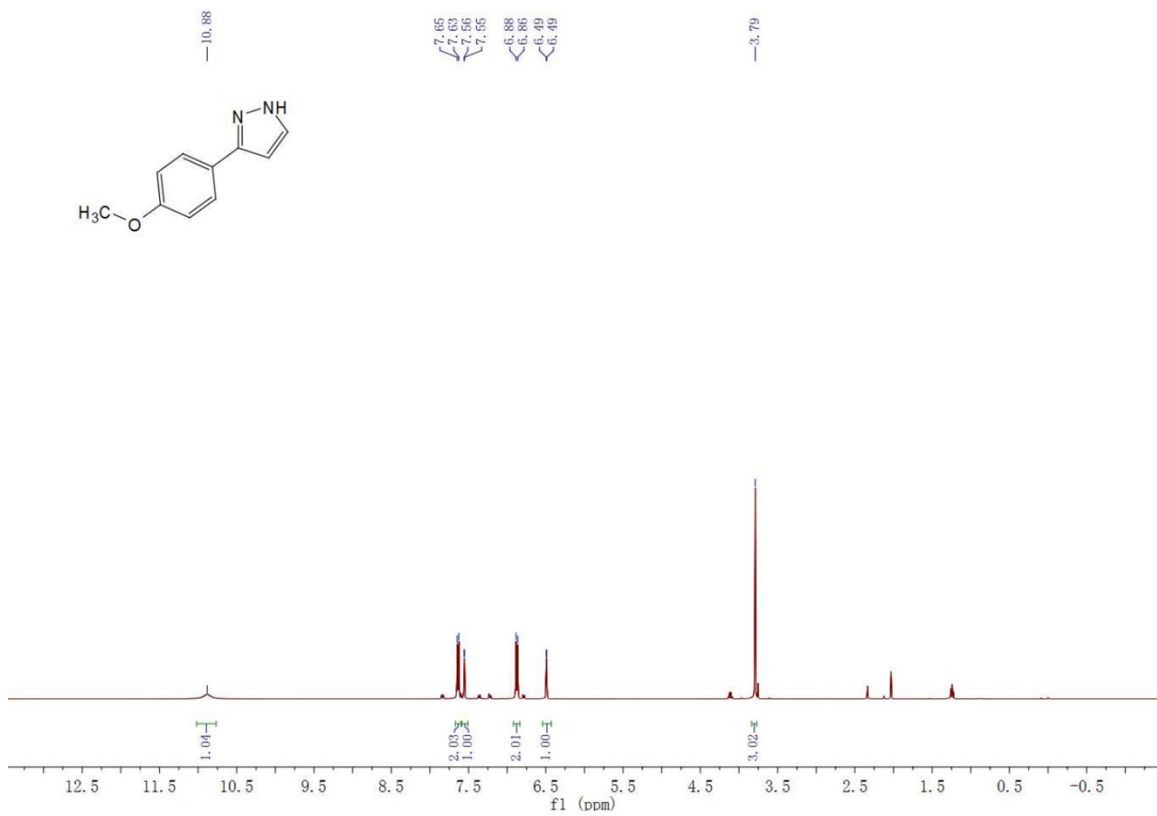


3d

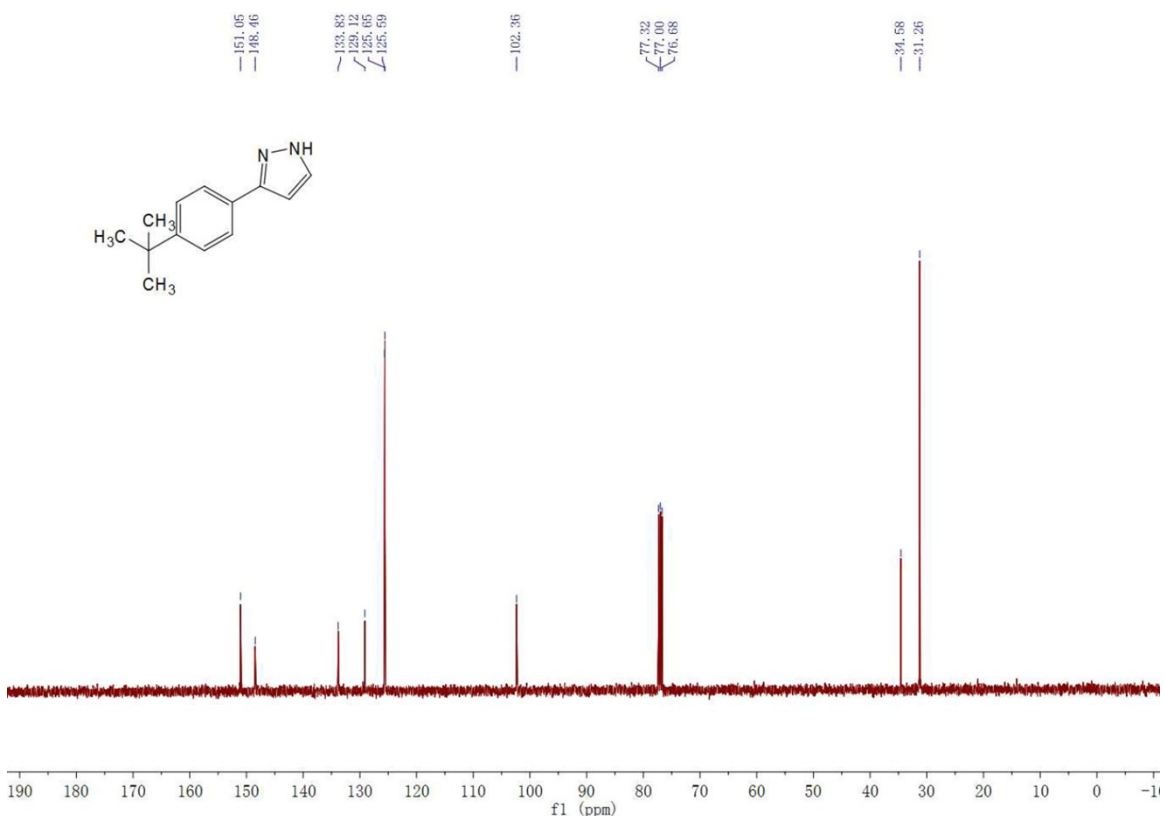
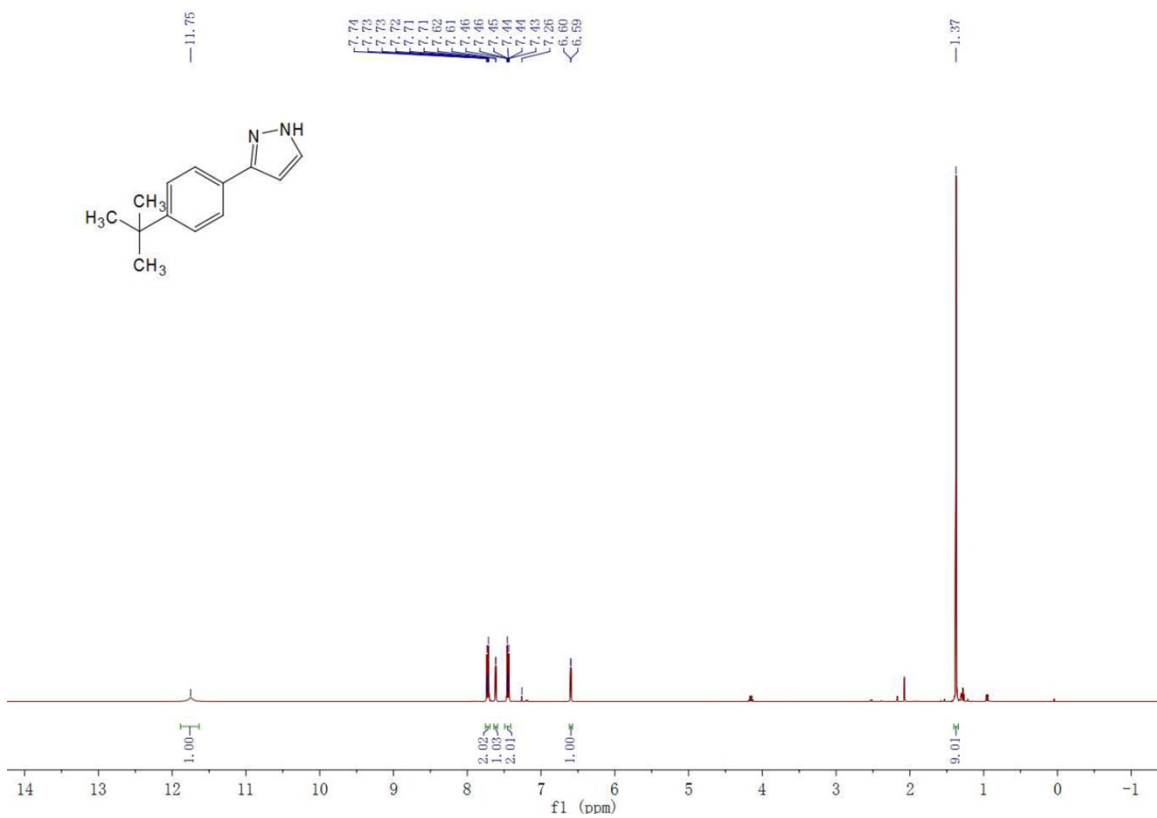
S15



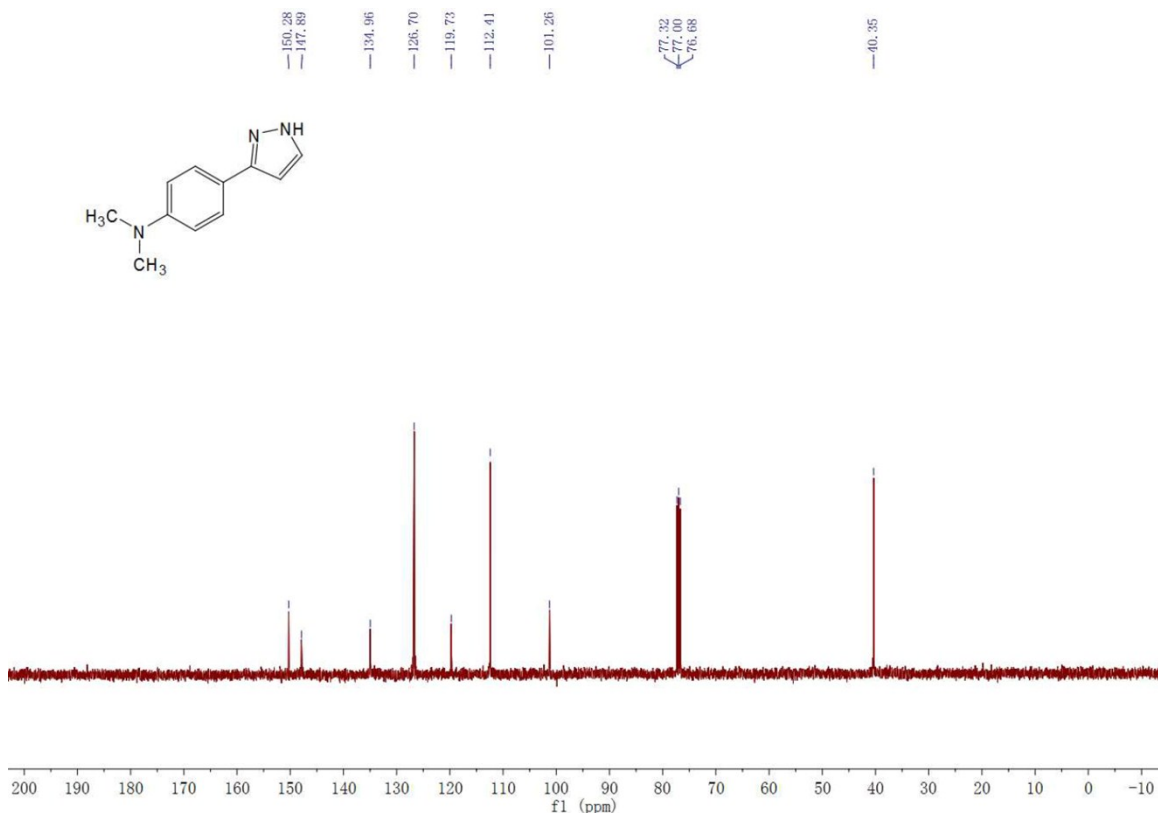
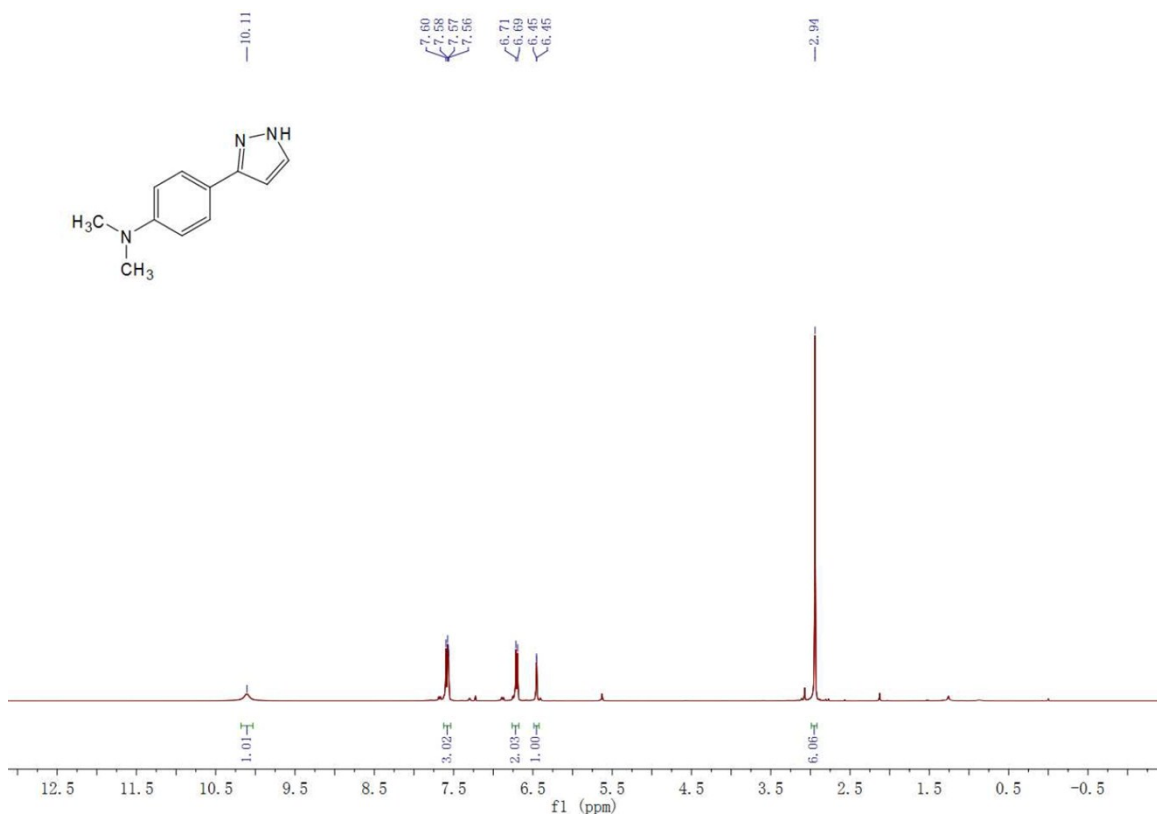
3e



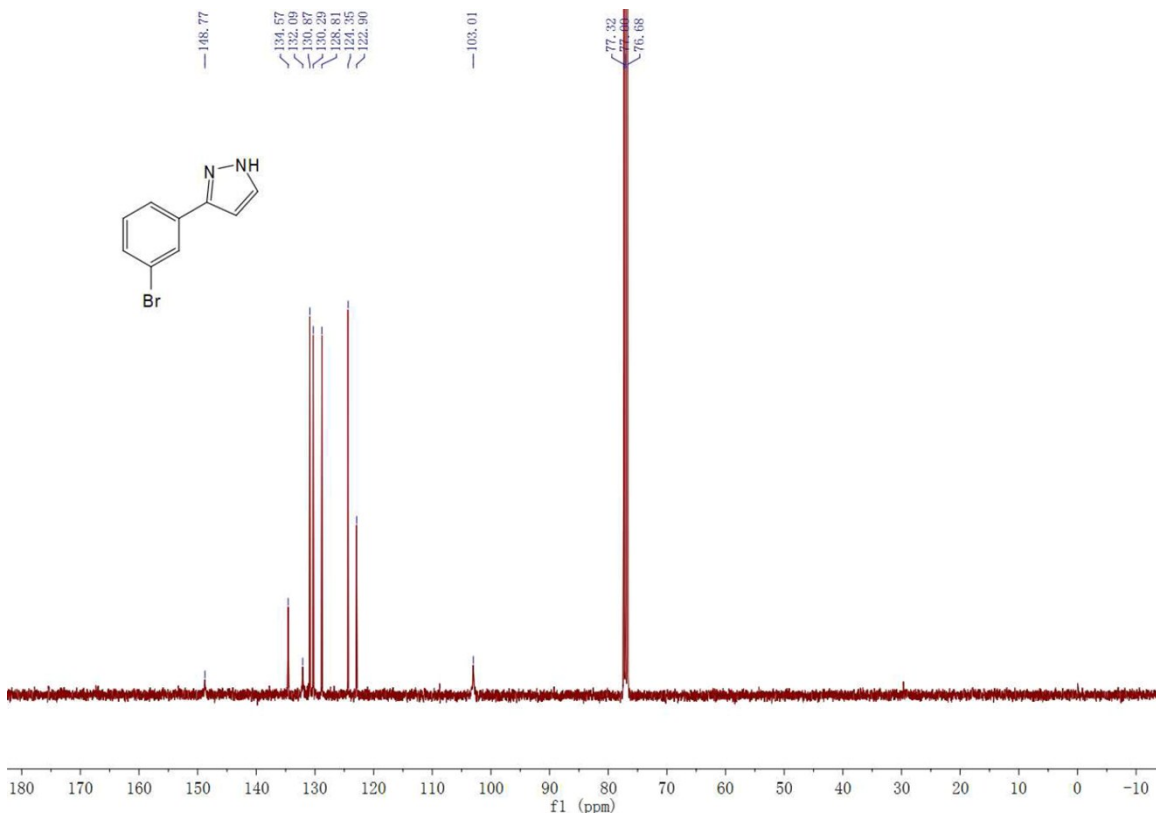
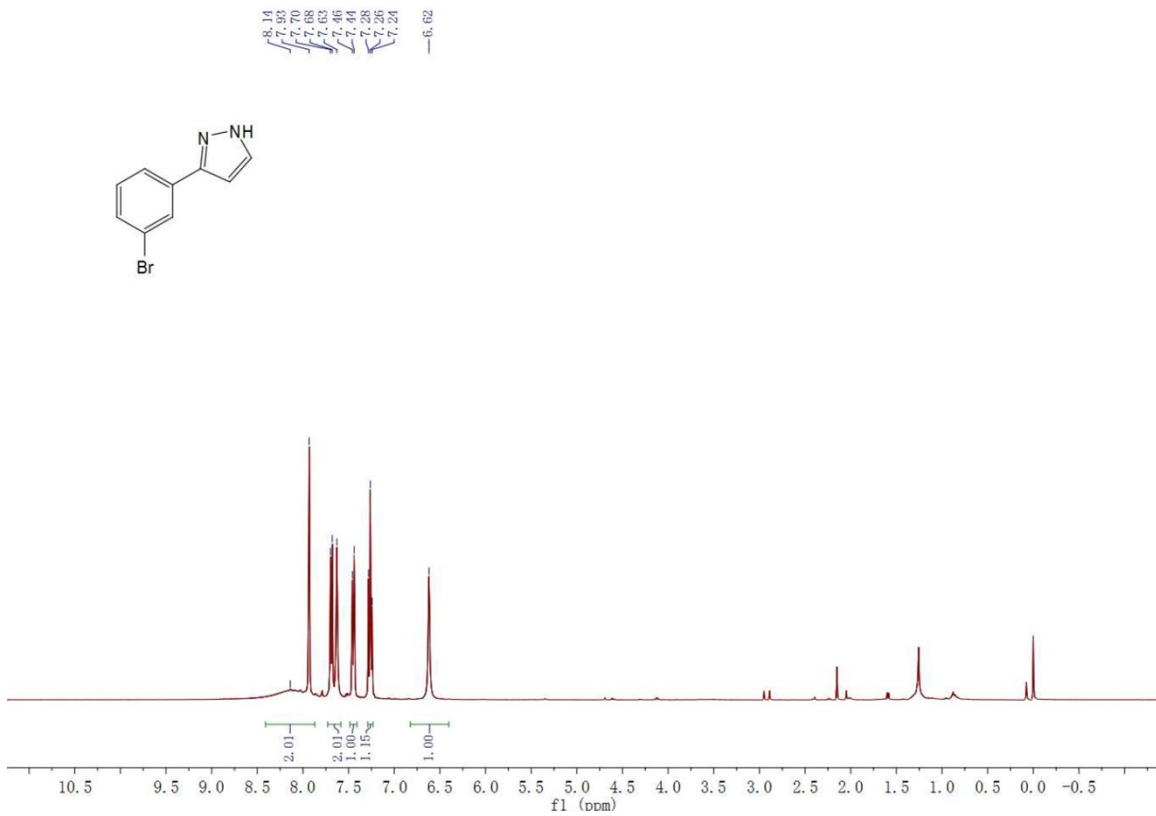
3f



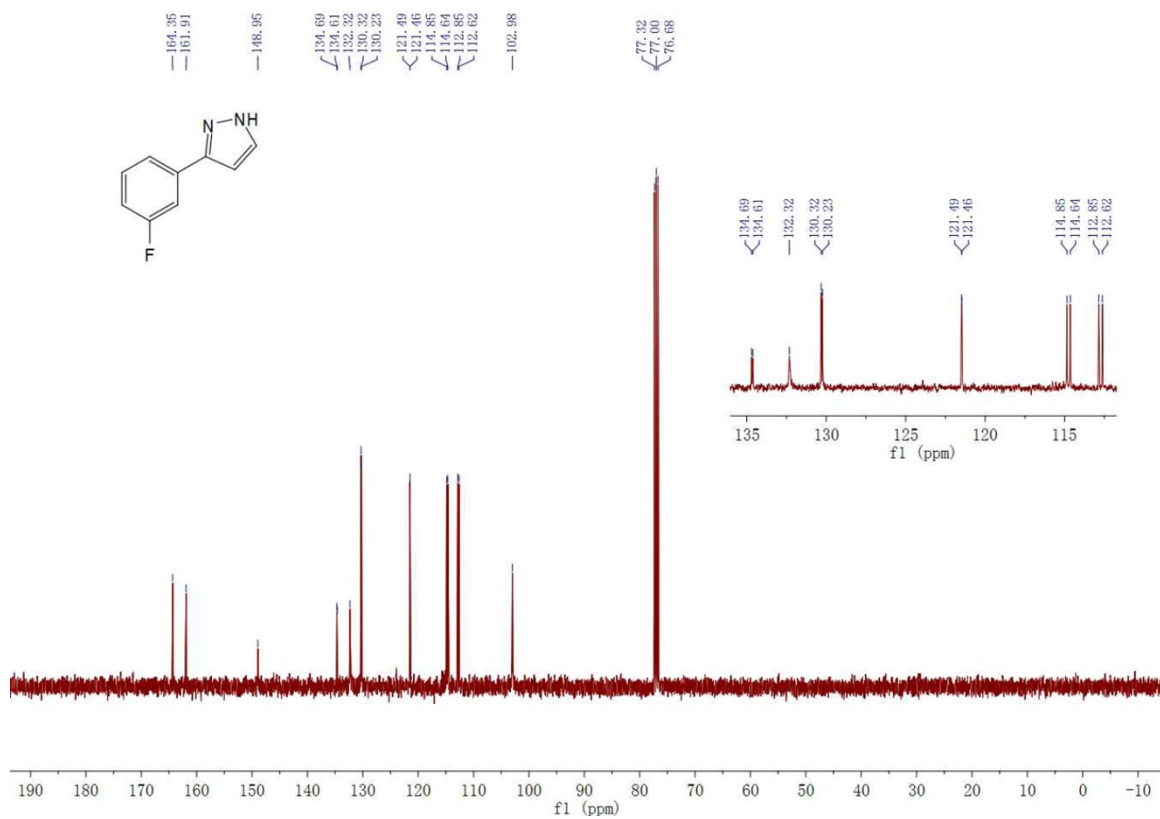
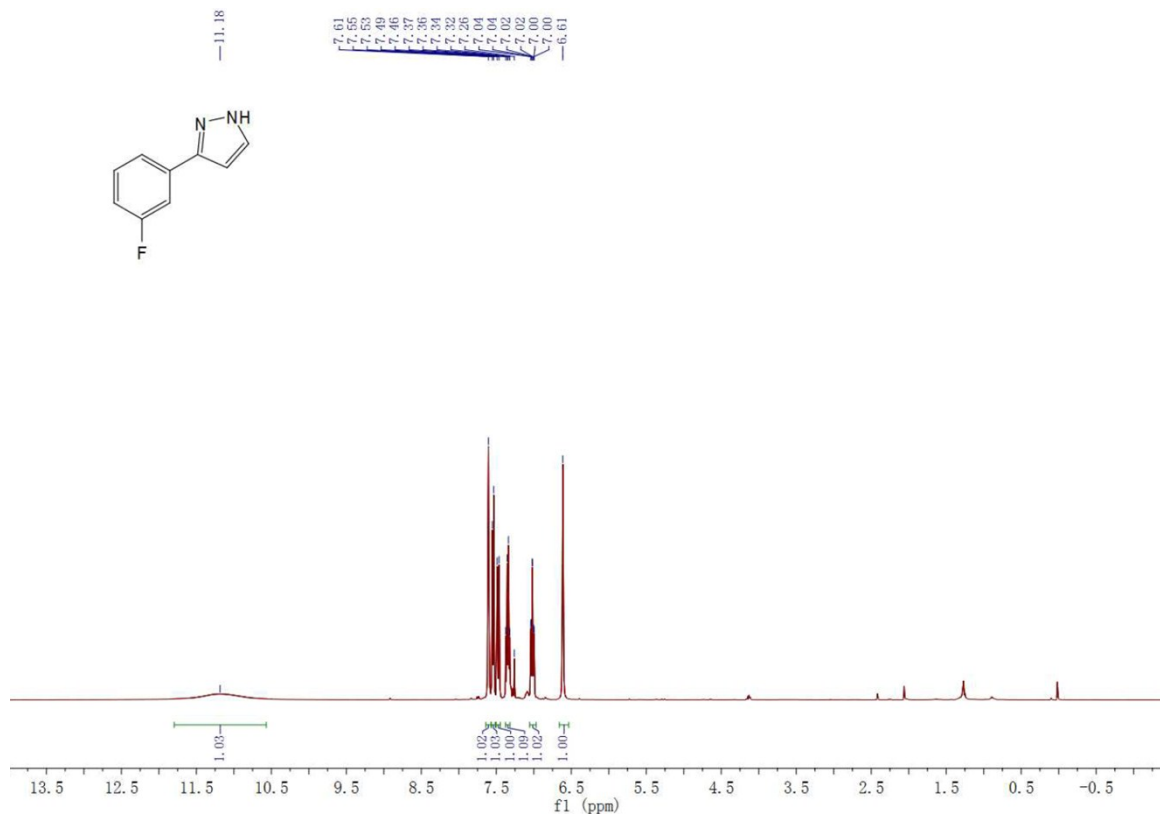
3g



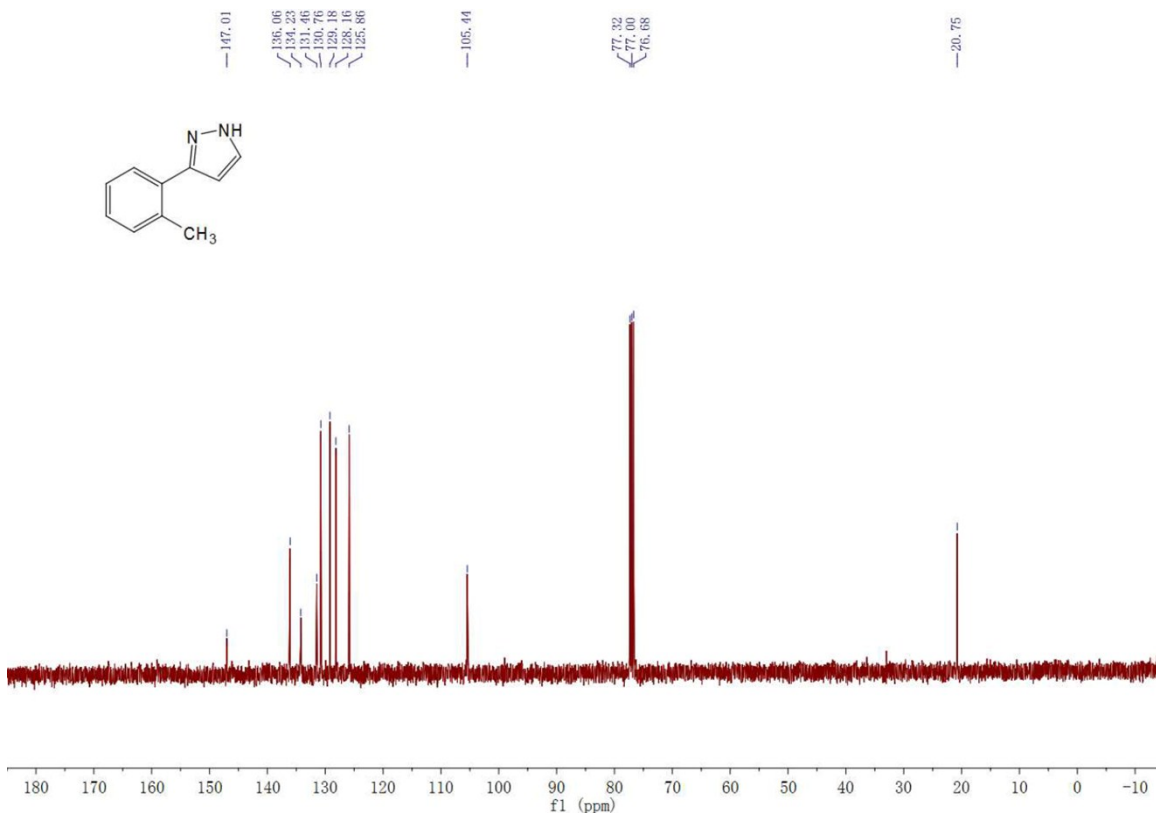
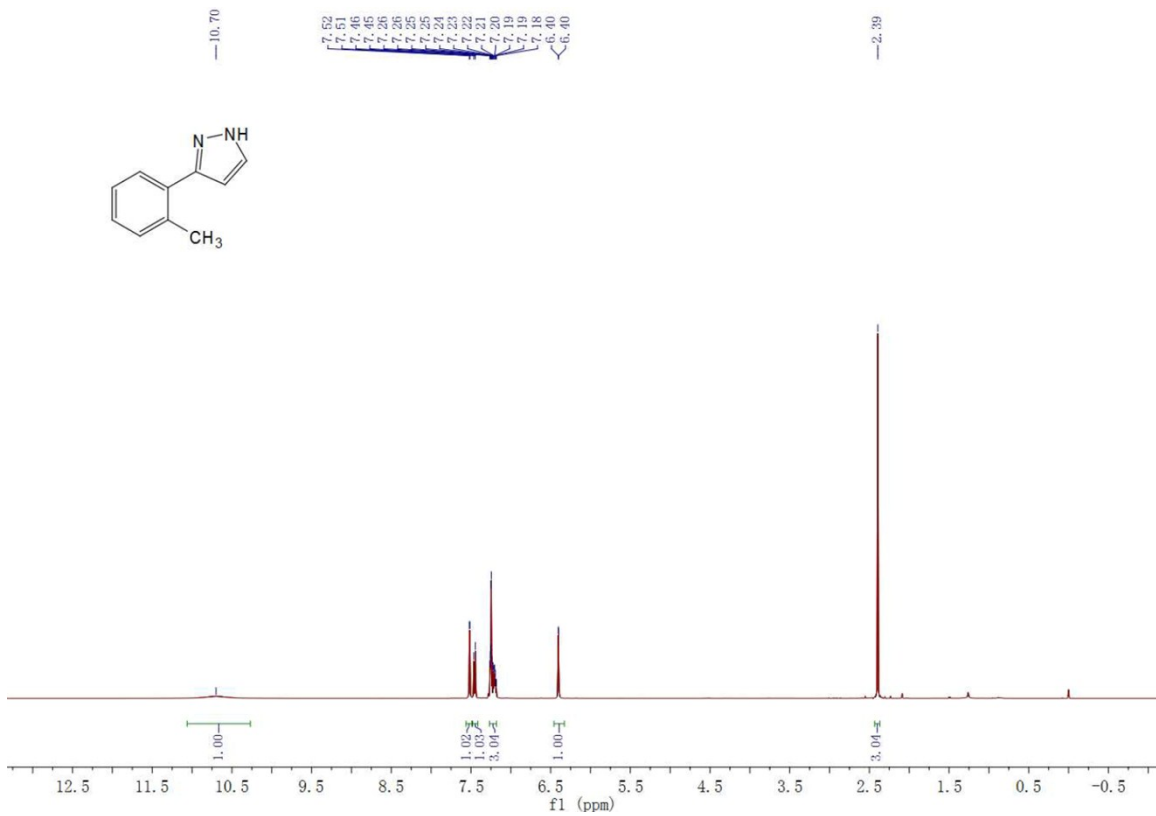
3h



3i

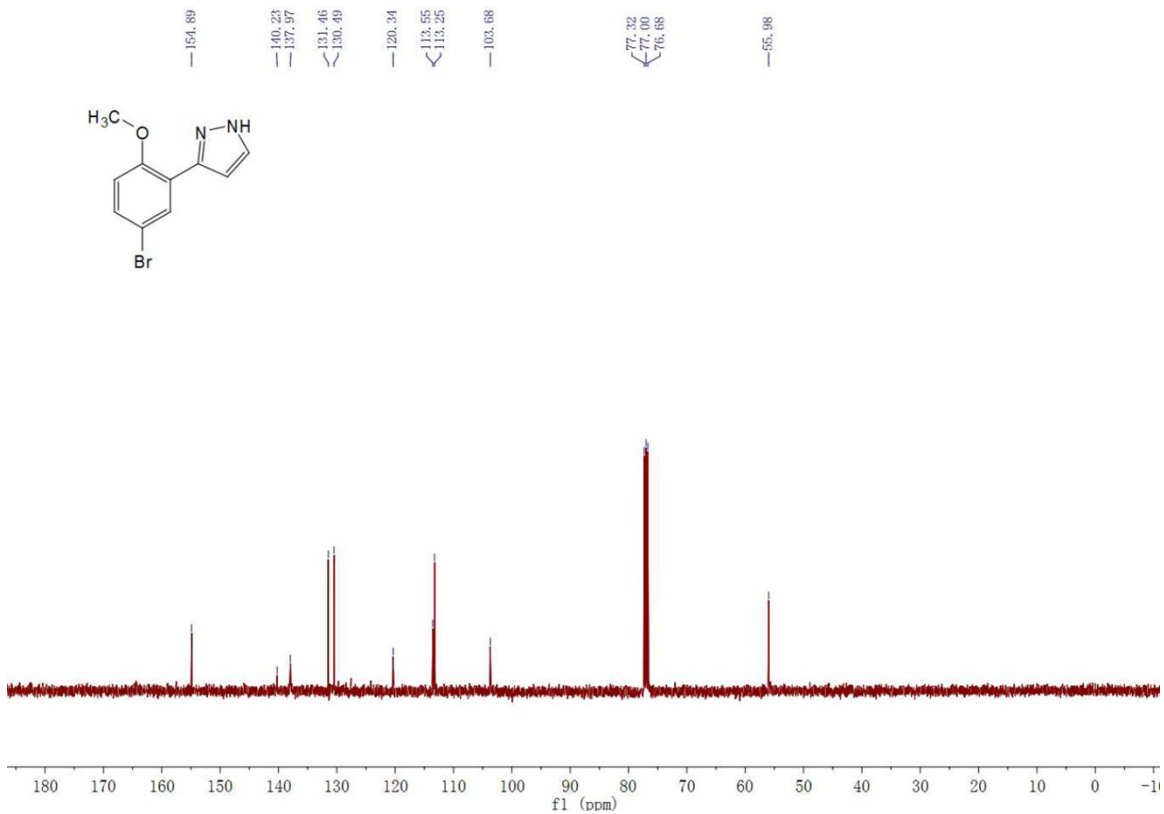
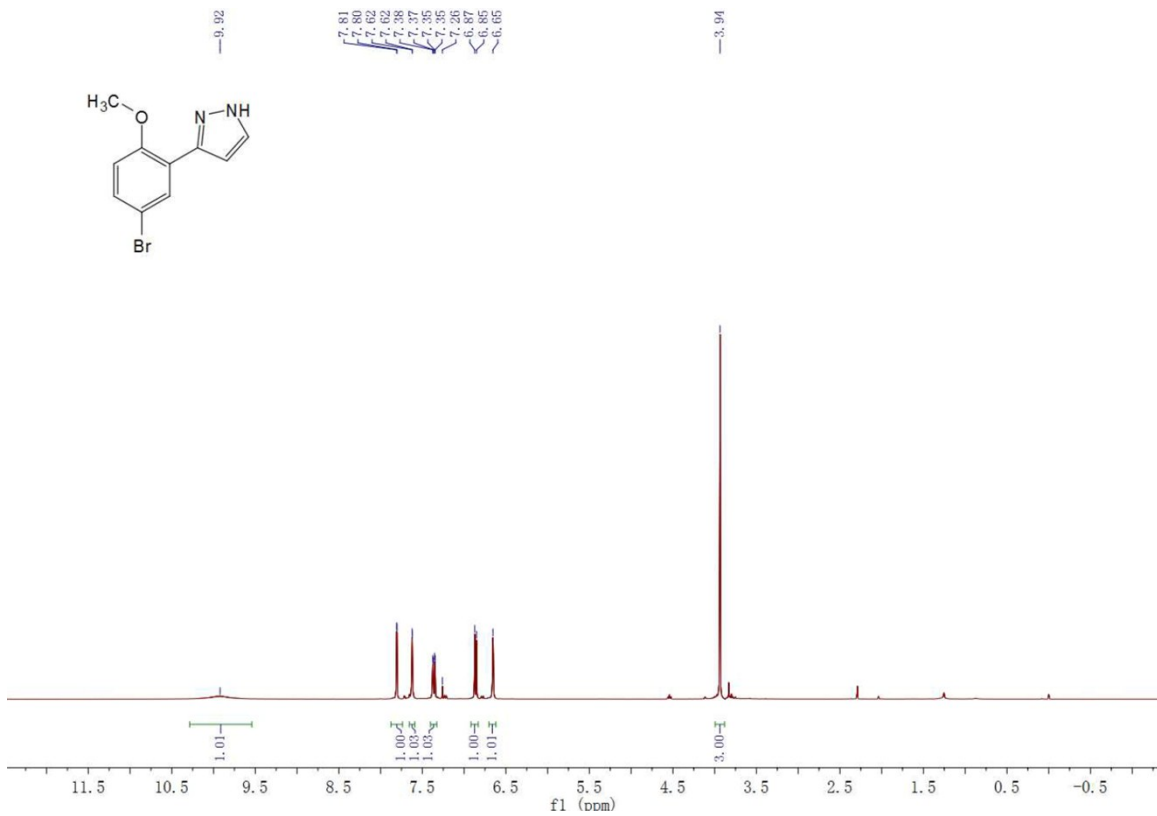


3j

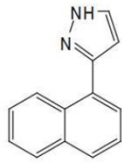


3k

S22

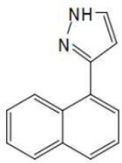
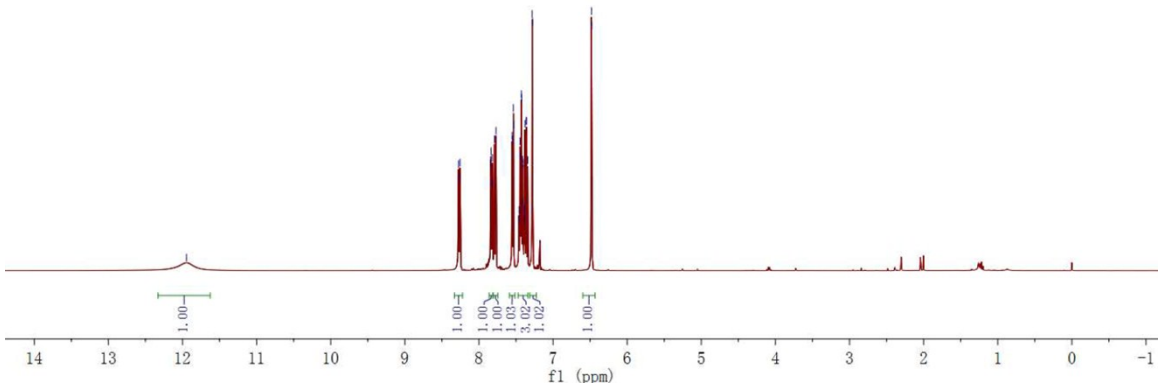


31

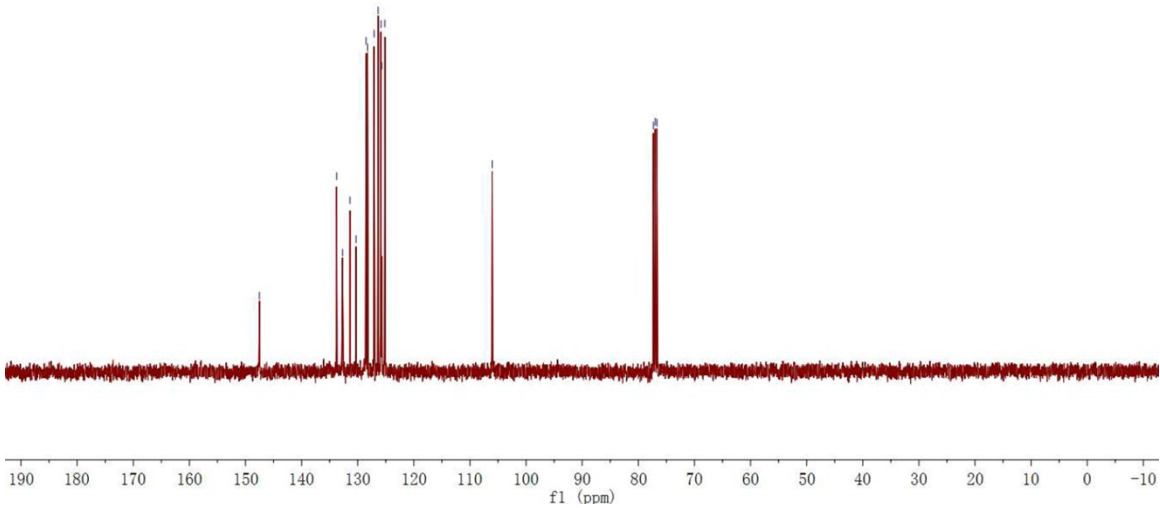


—11.95

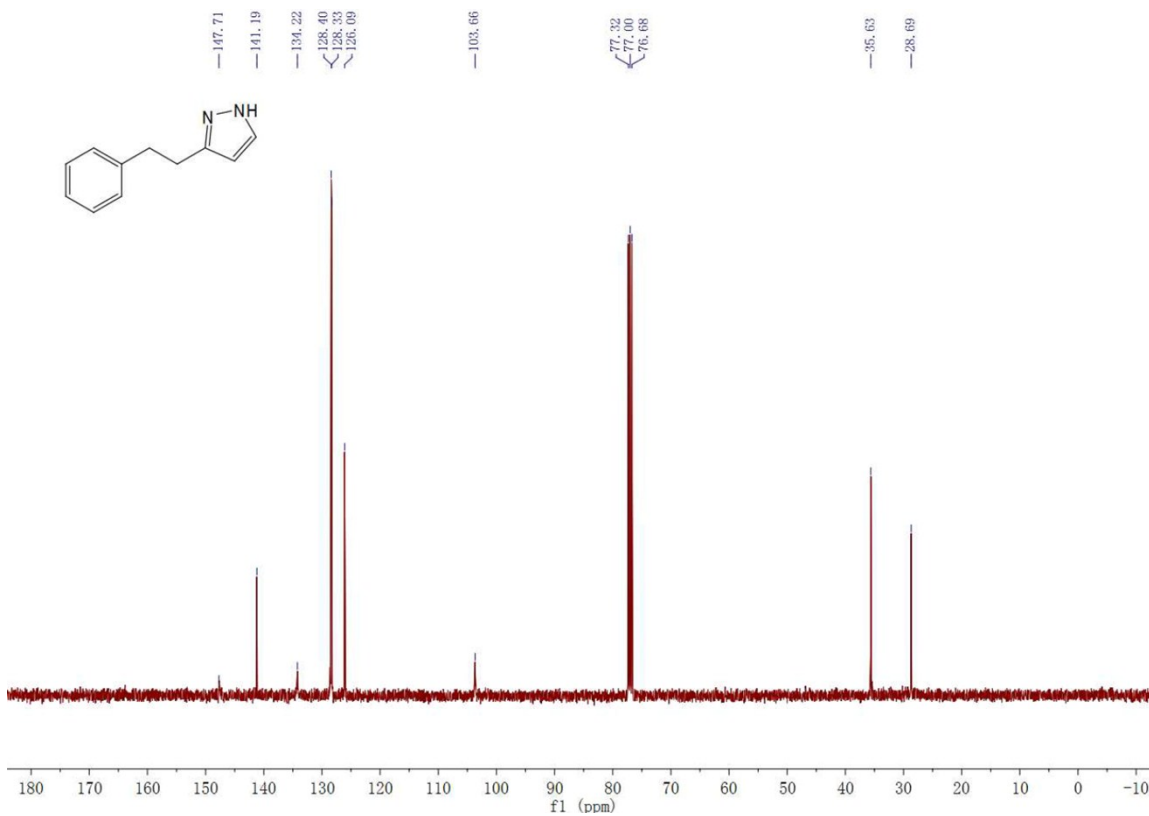
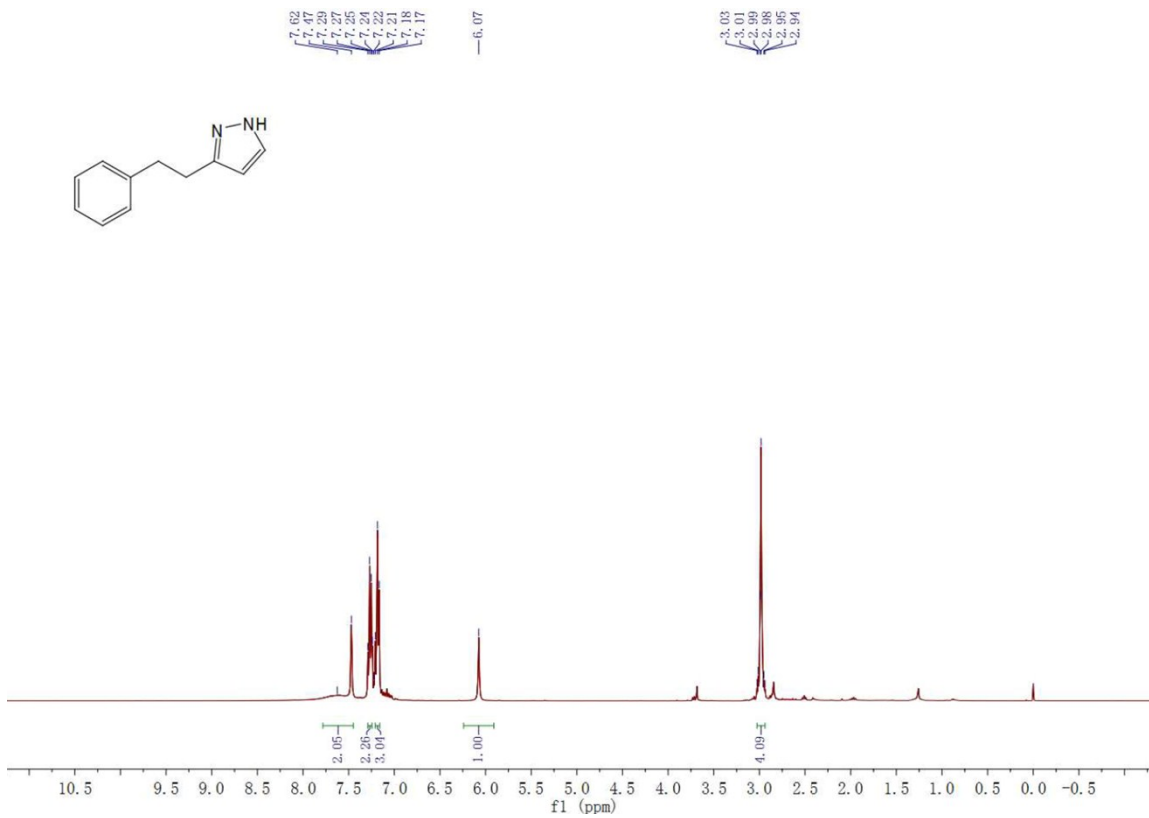
8.28
8.25
8.25
7.54
7.53
7.52
7.52
7.52
7.28
7.28
6.68



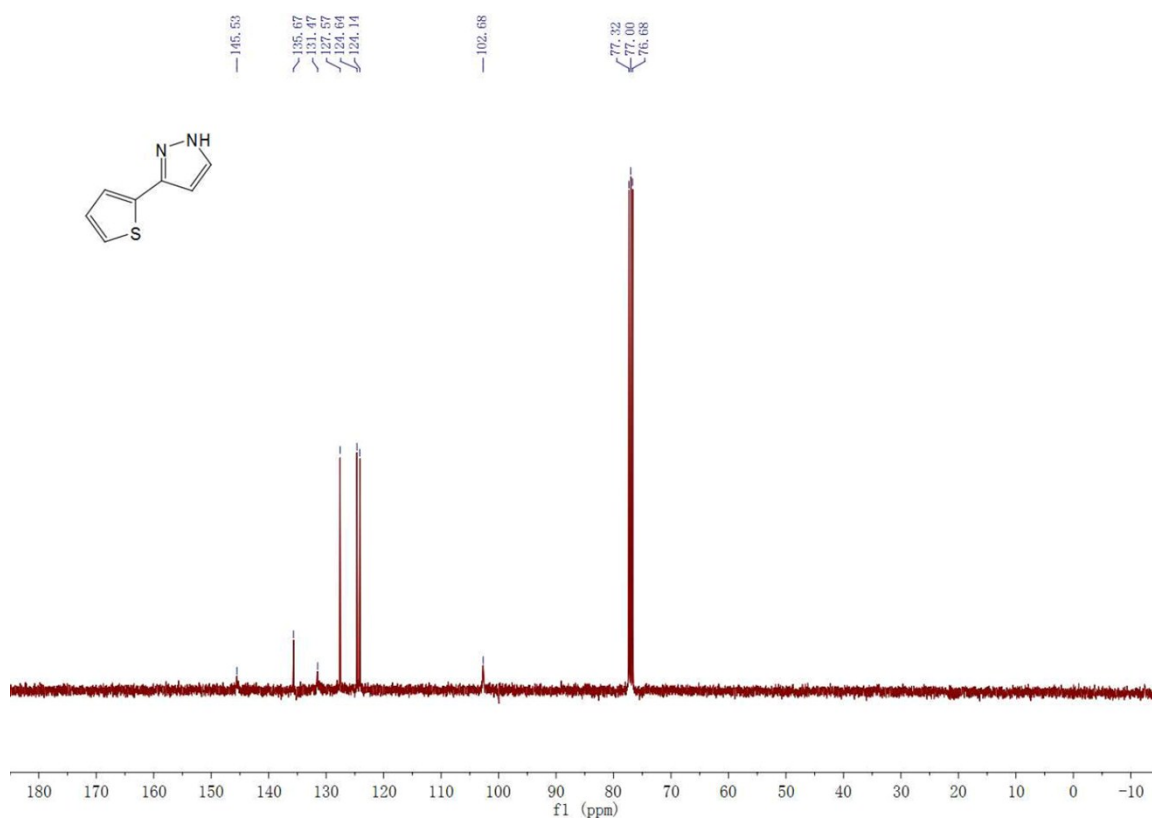
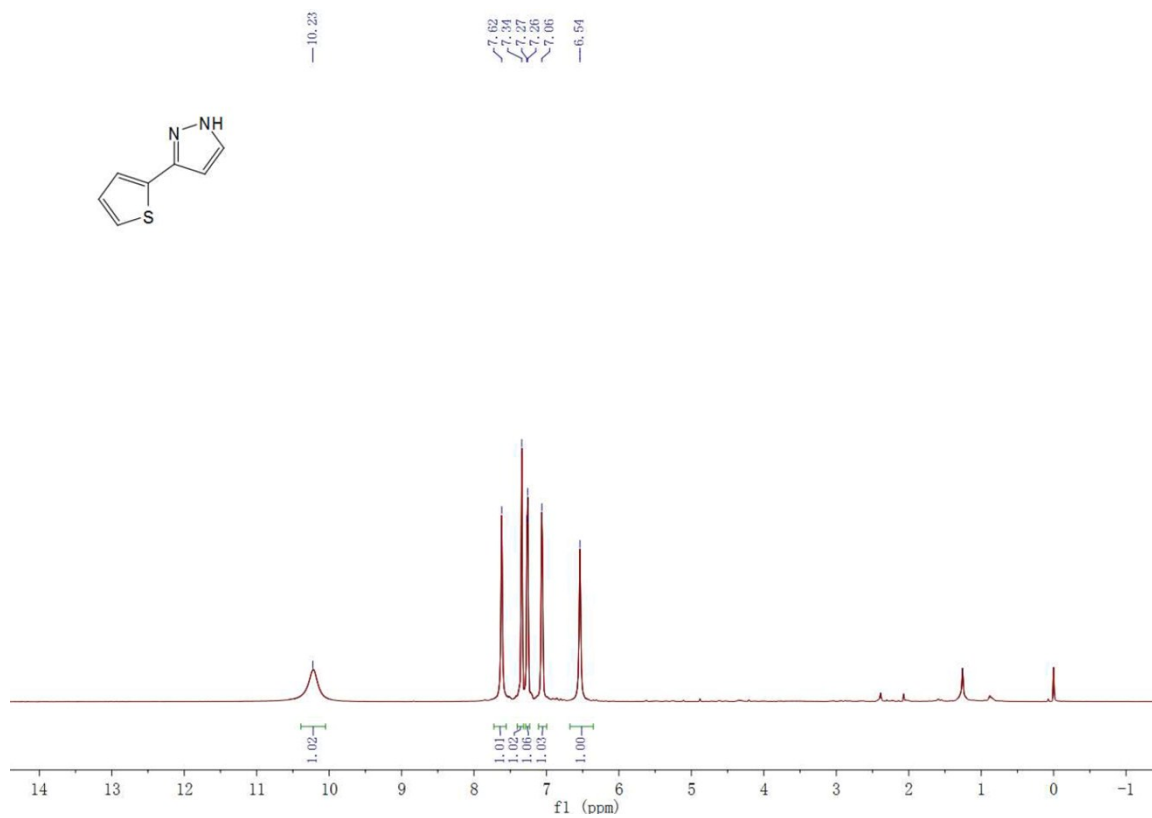
147.52
133.76
132.71
131.38
130.30
128.51
127.68
126.36
125.86
125.73
125.16
106.03
77.32
77.00
76.68



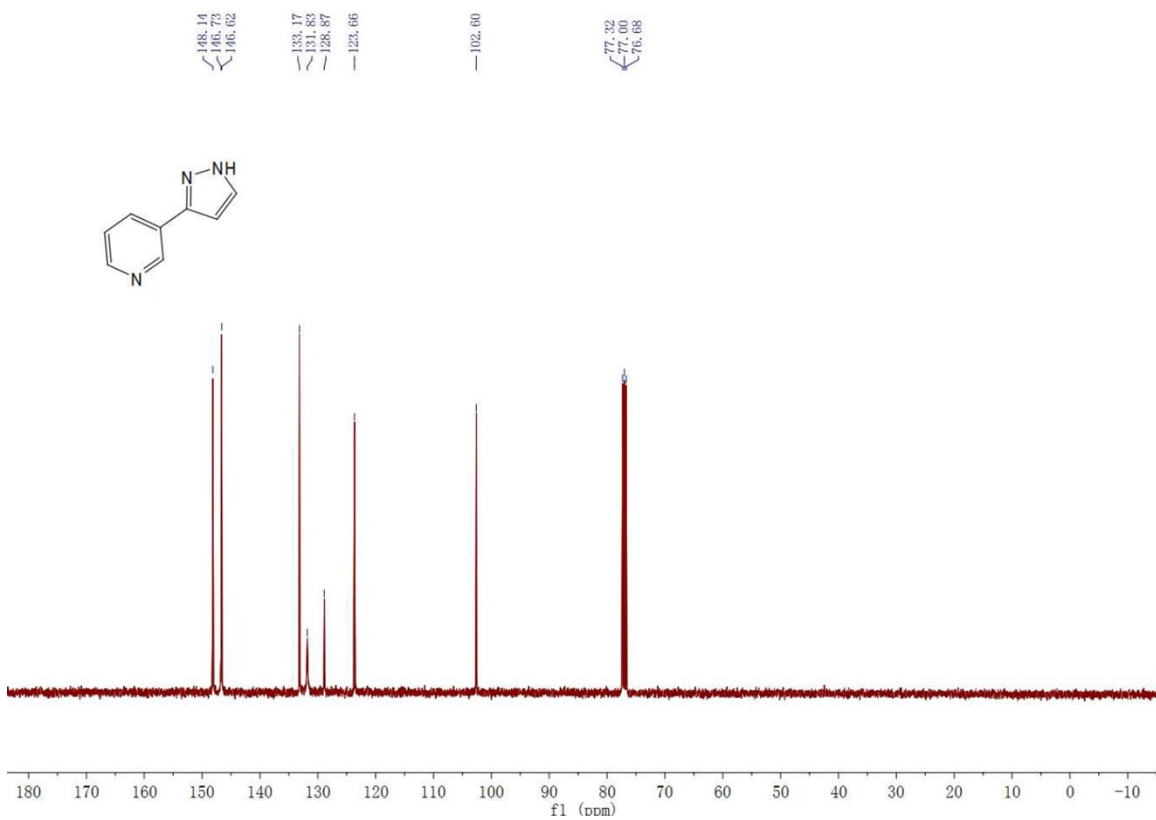
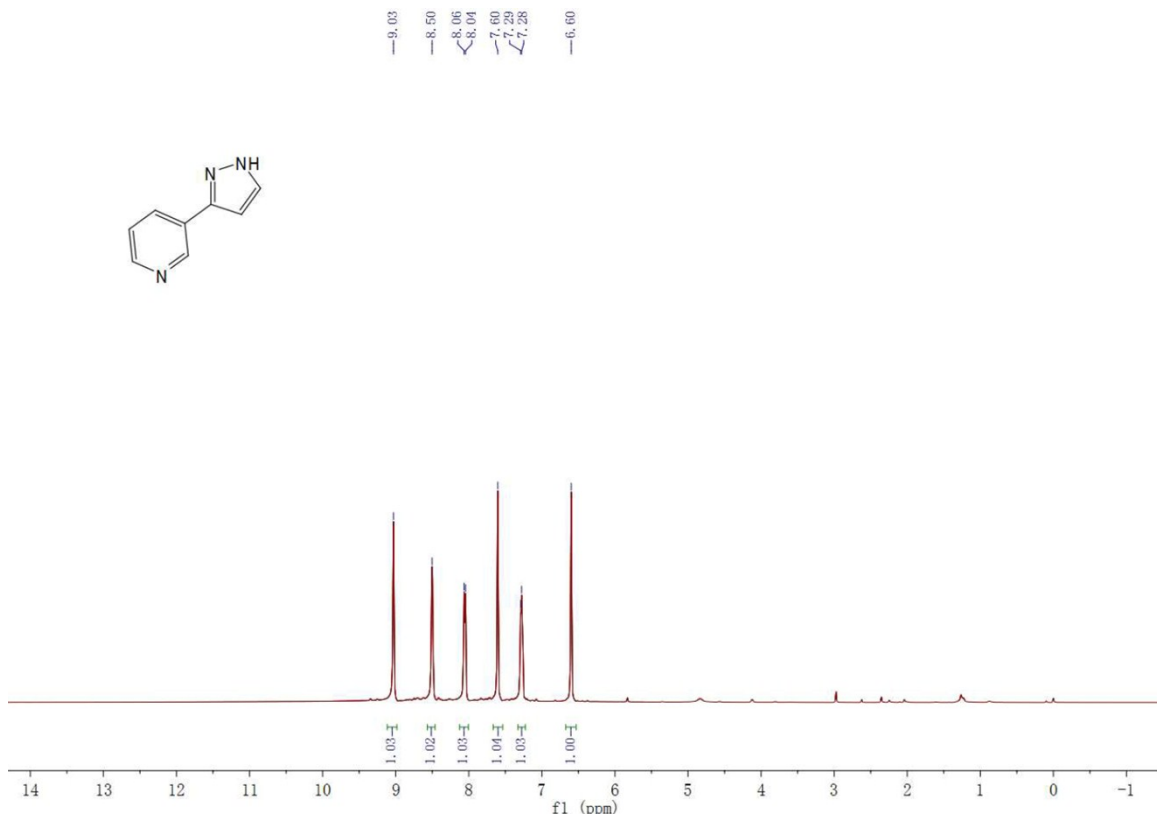
3m



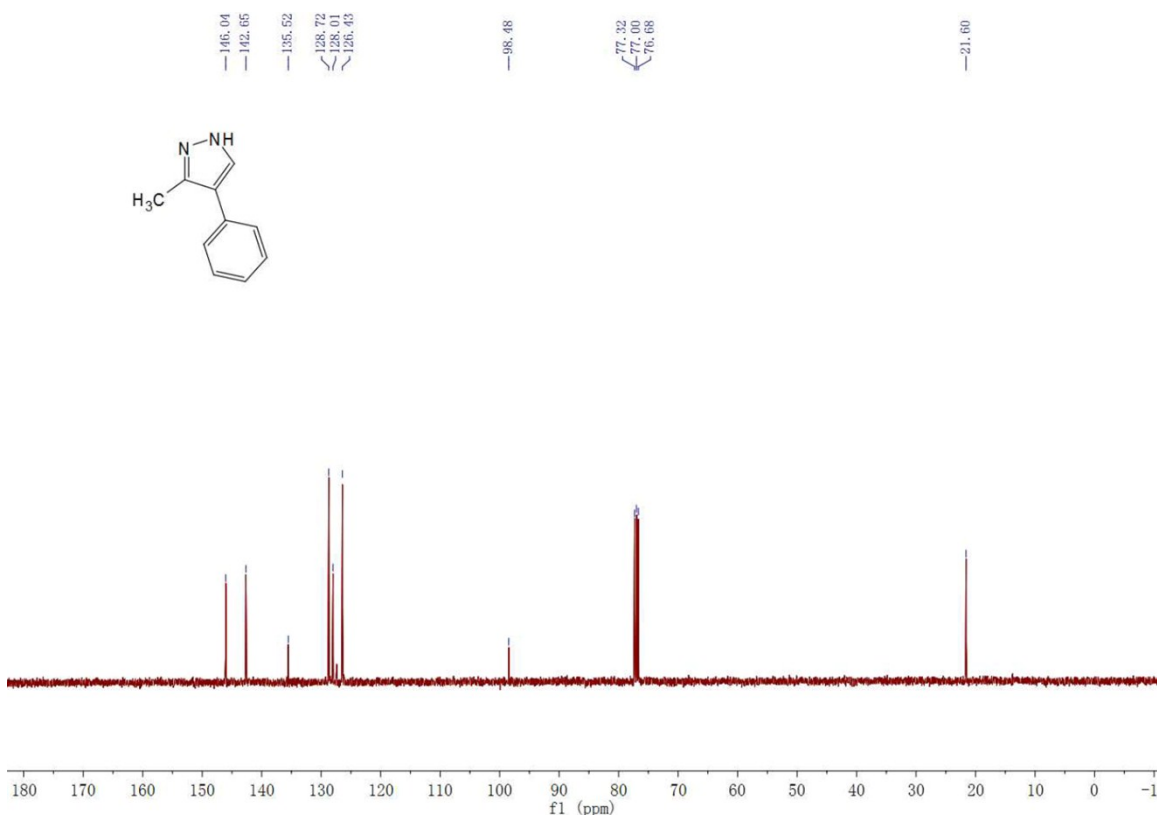
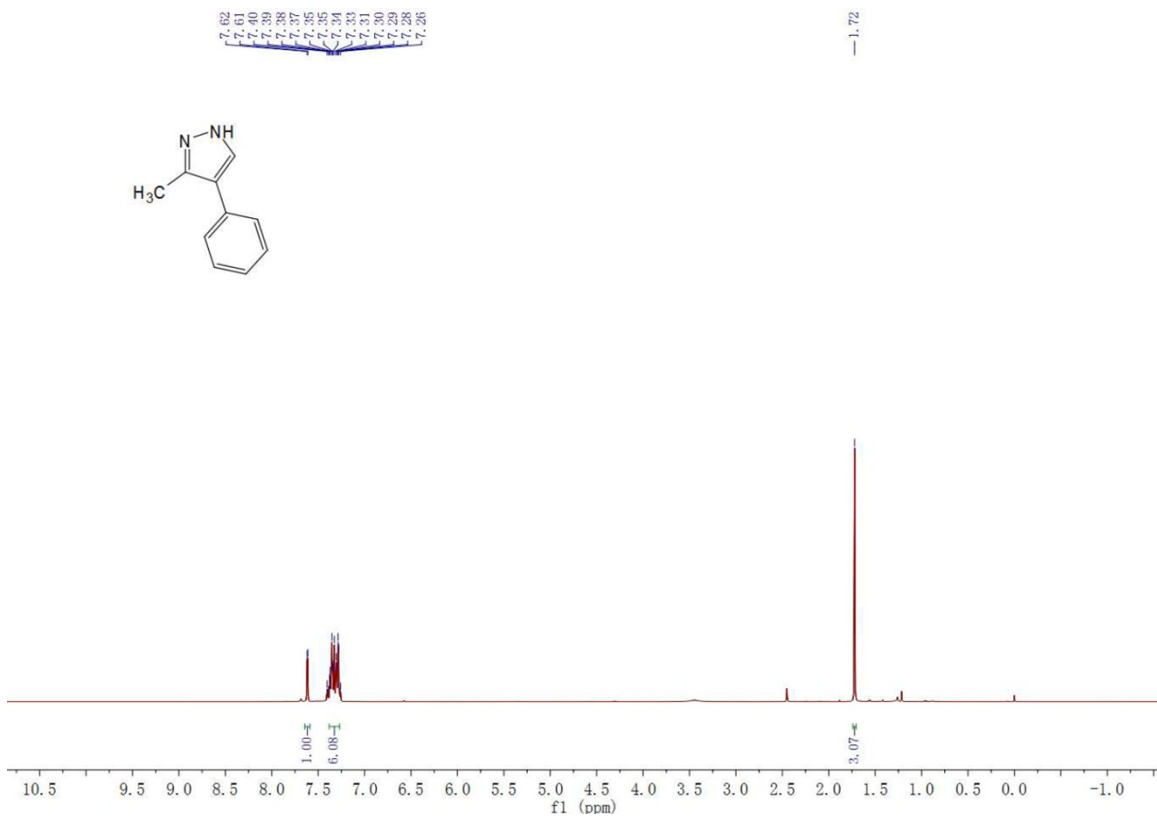
3n



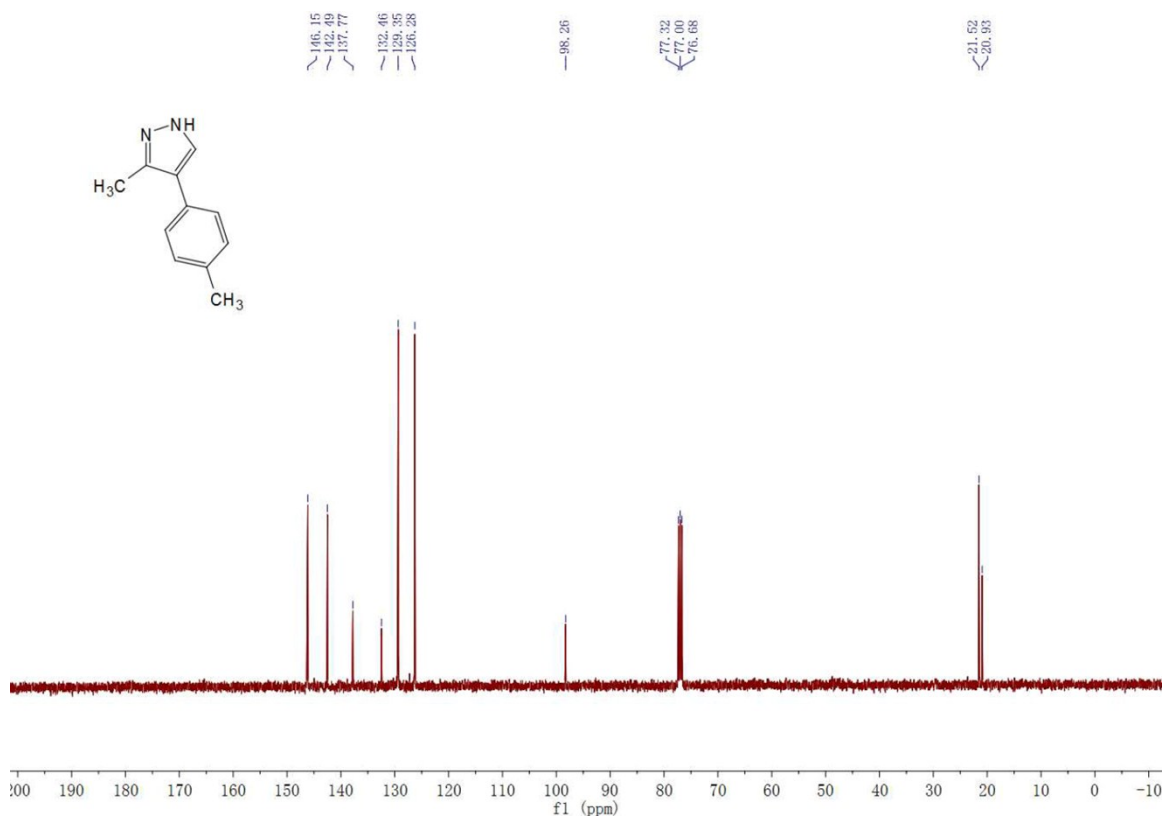
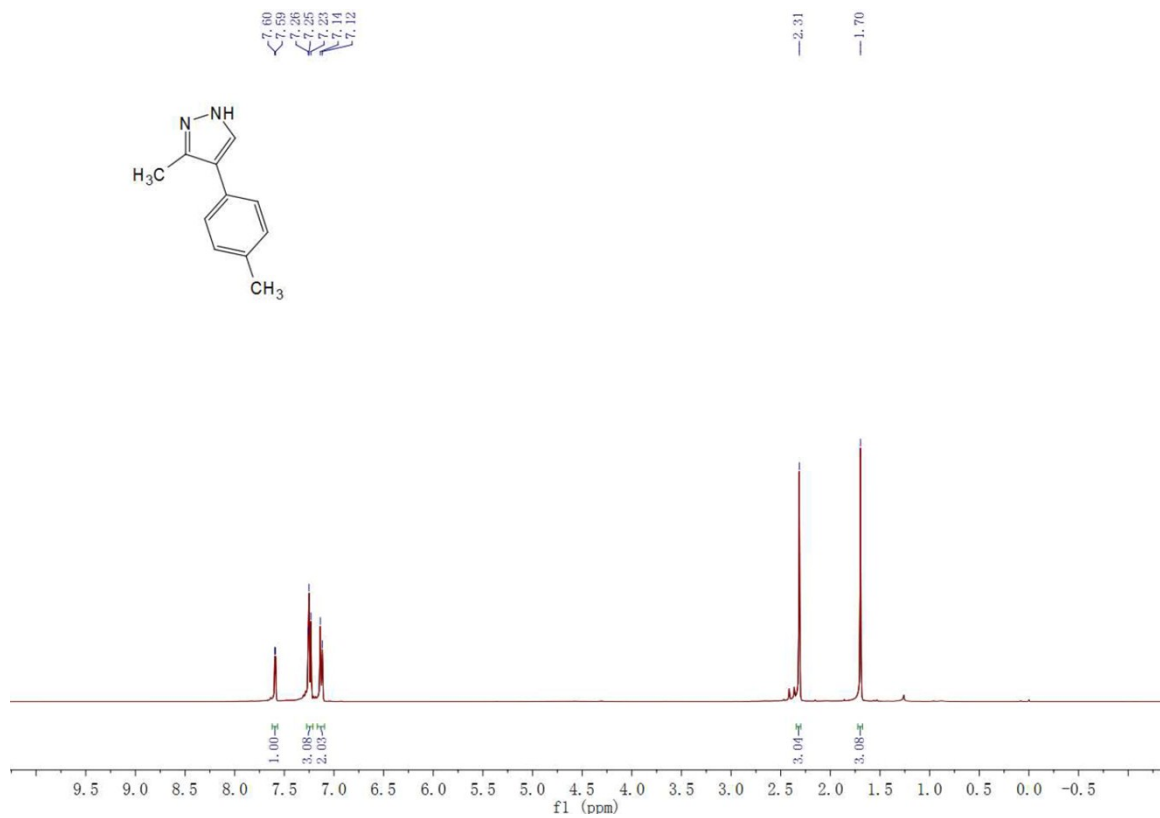
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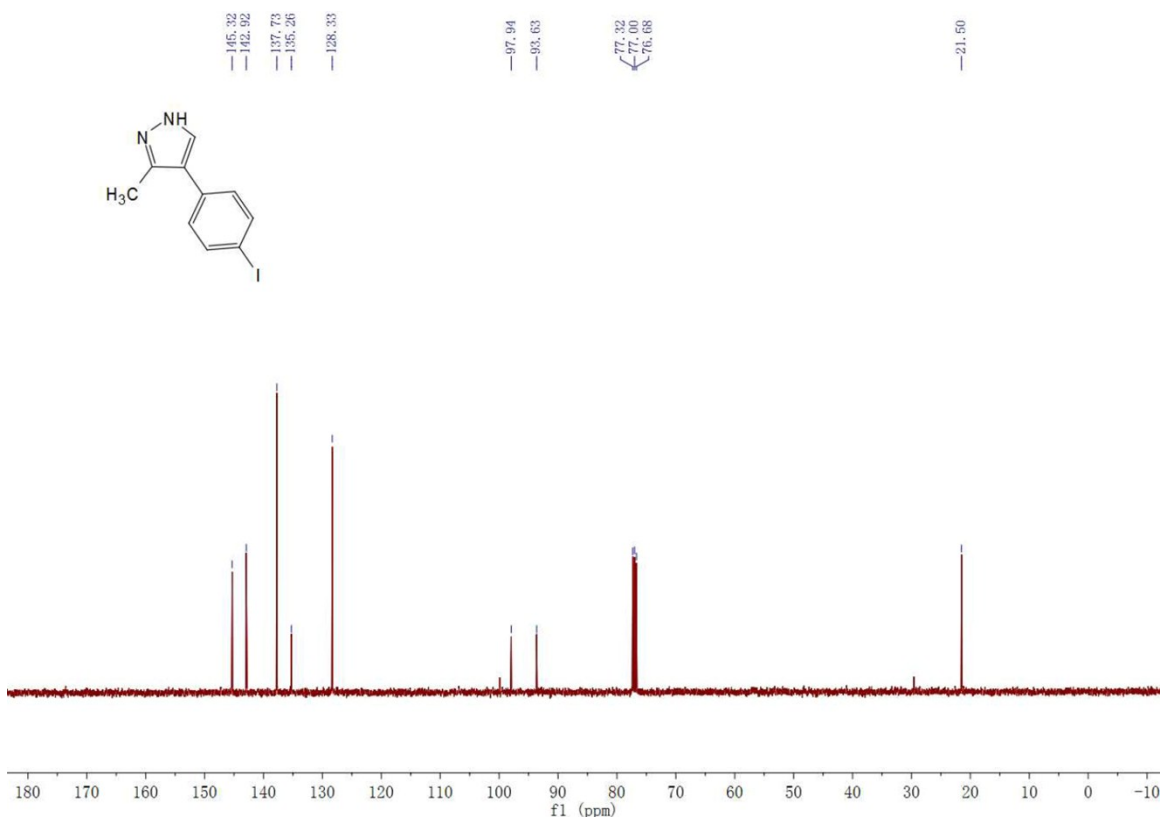
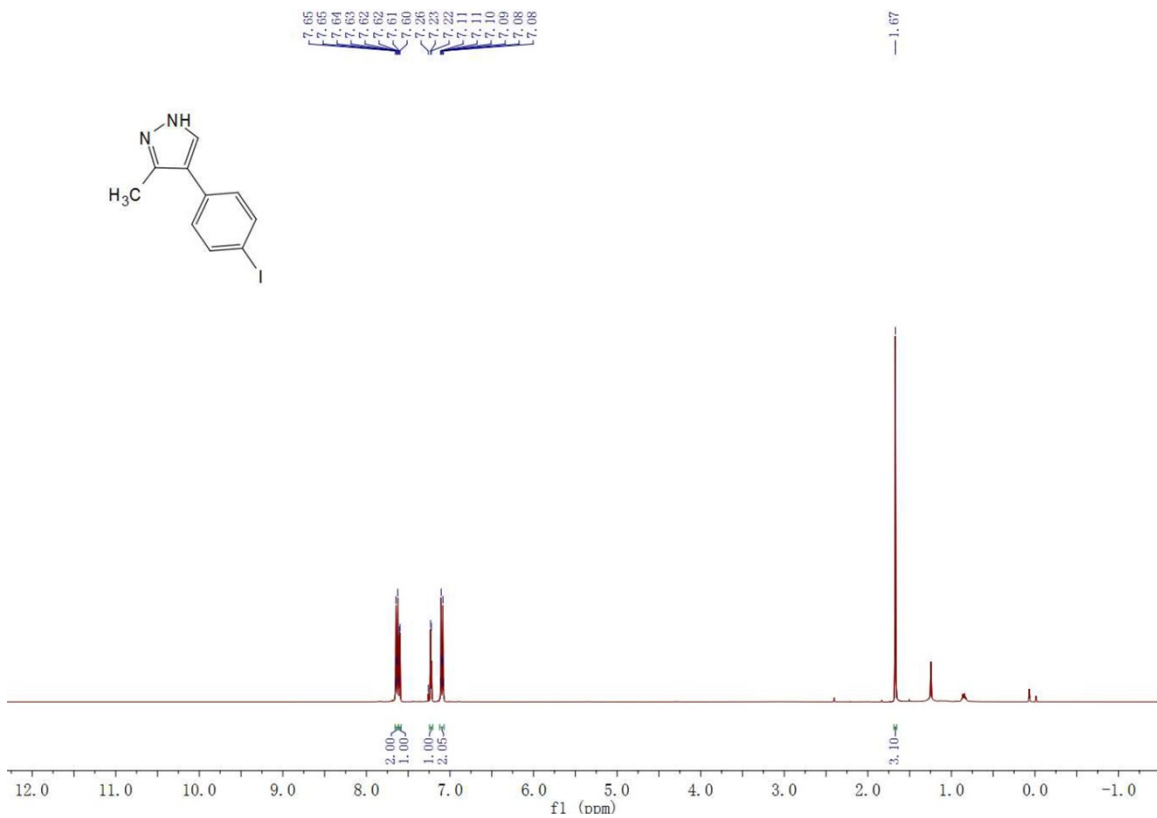
5a



5b

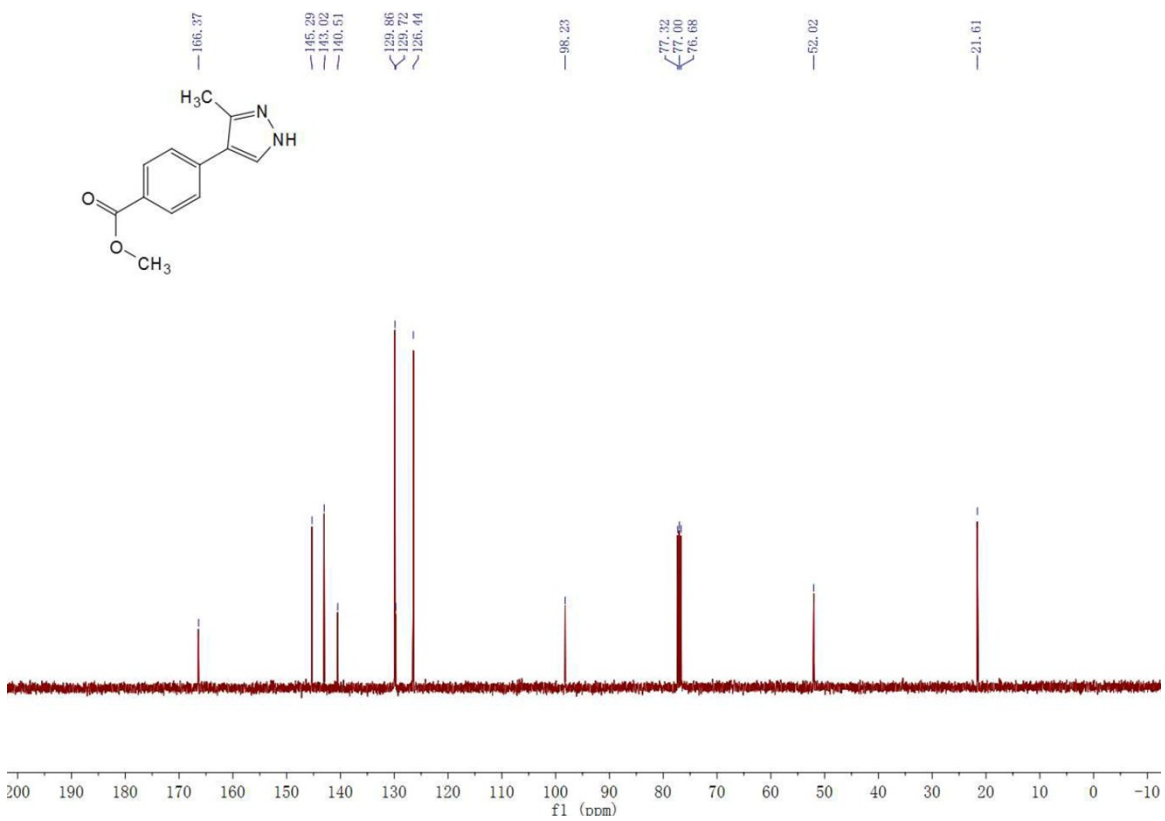
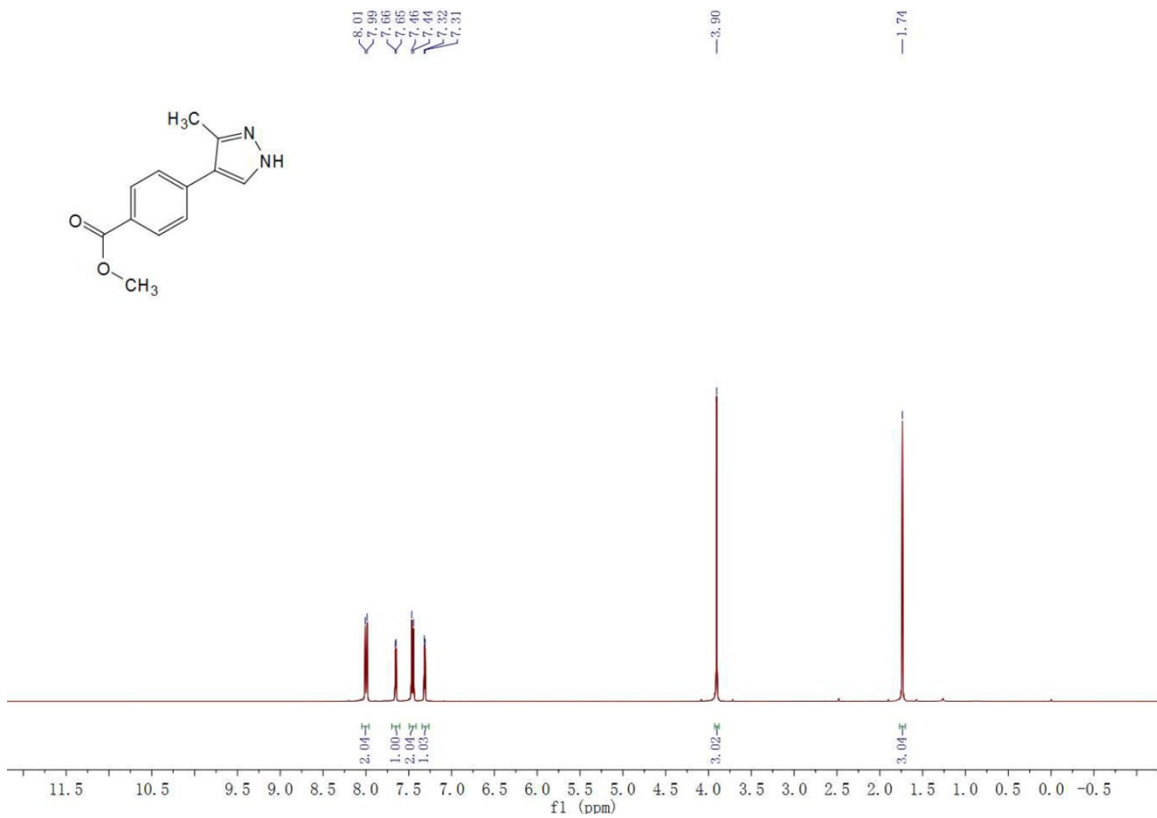


5c

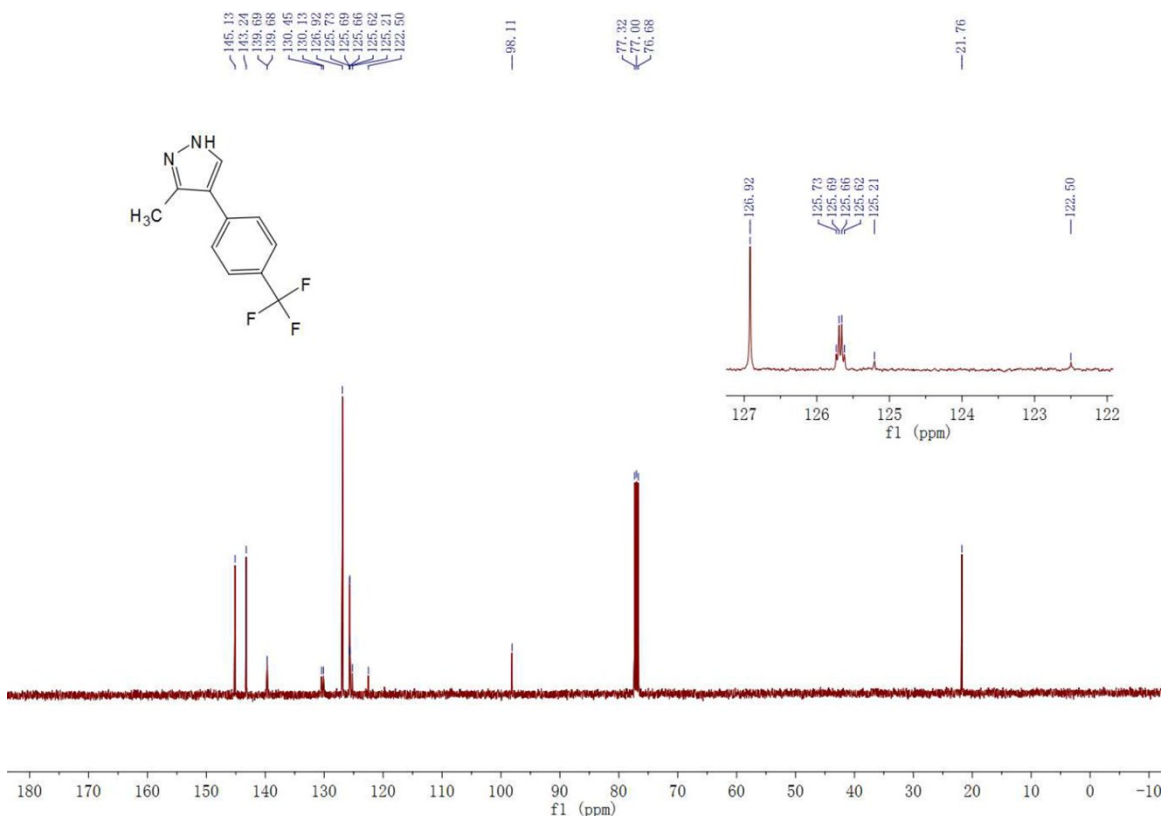
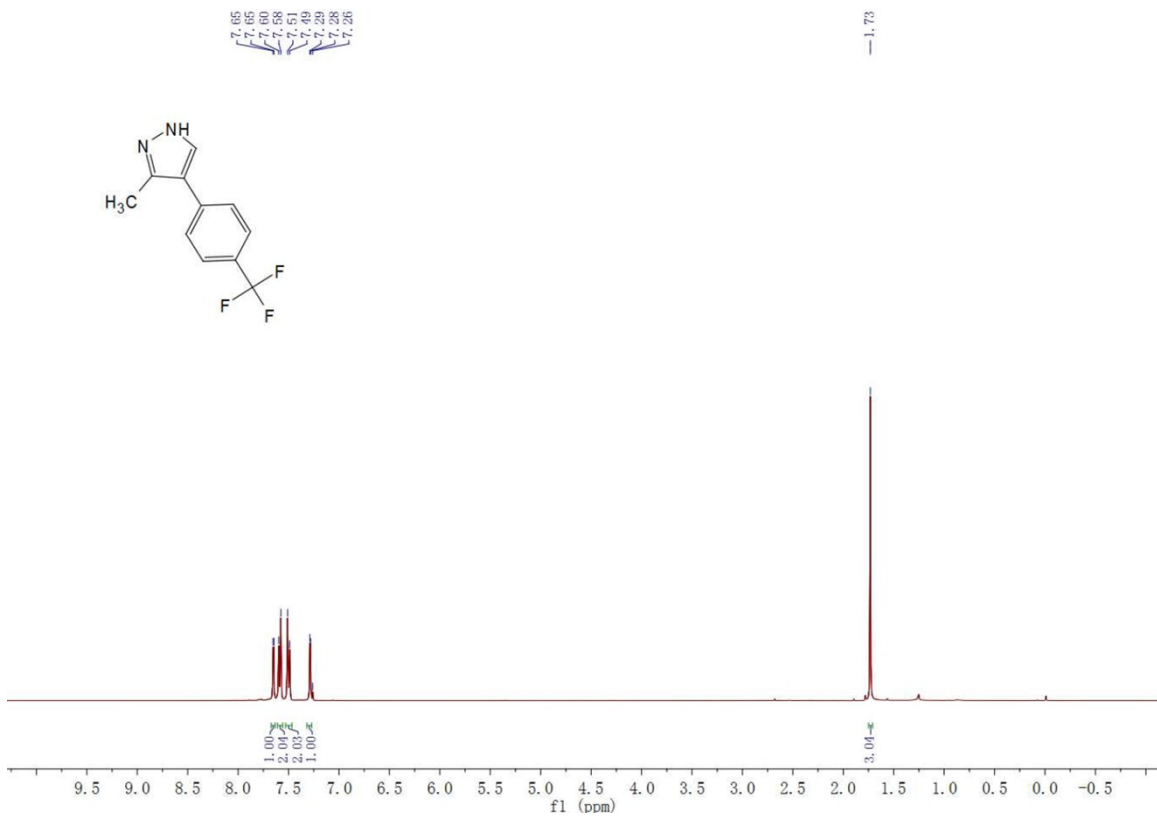


5d

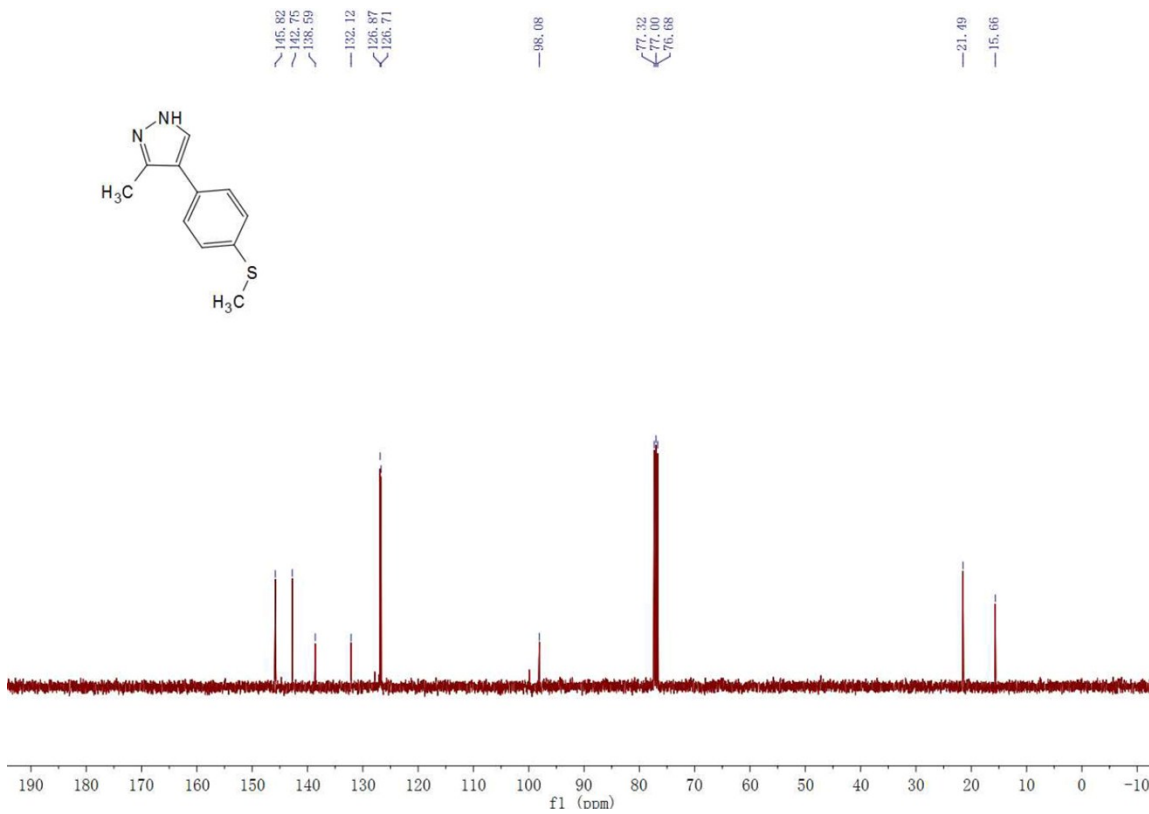
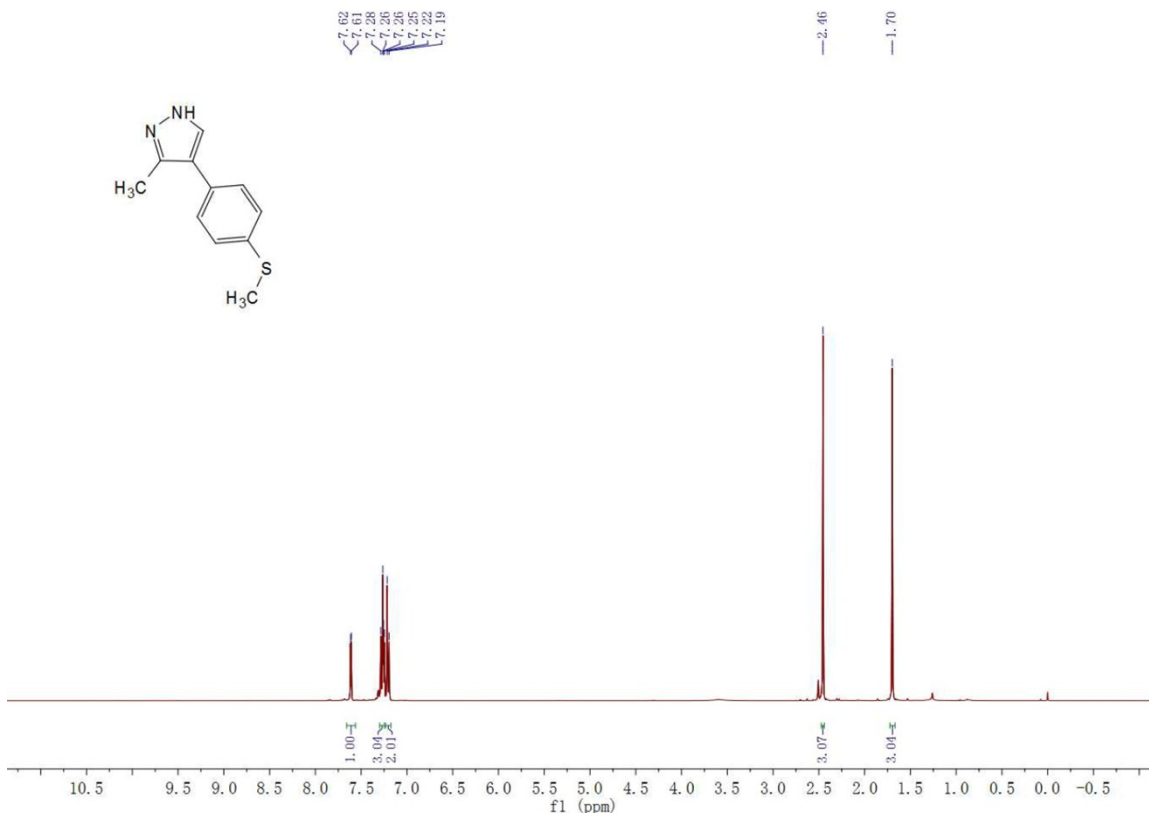
S30



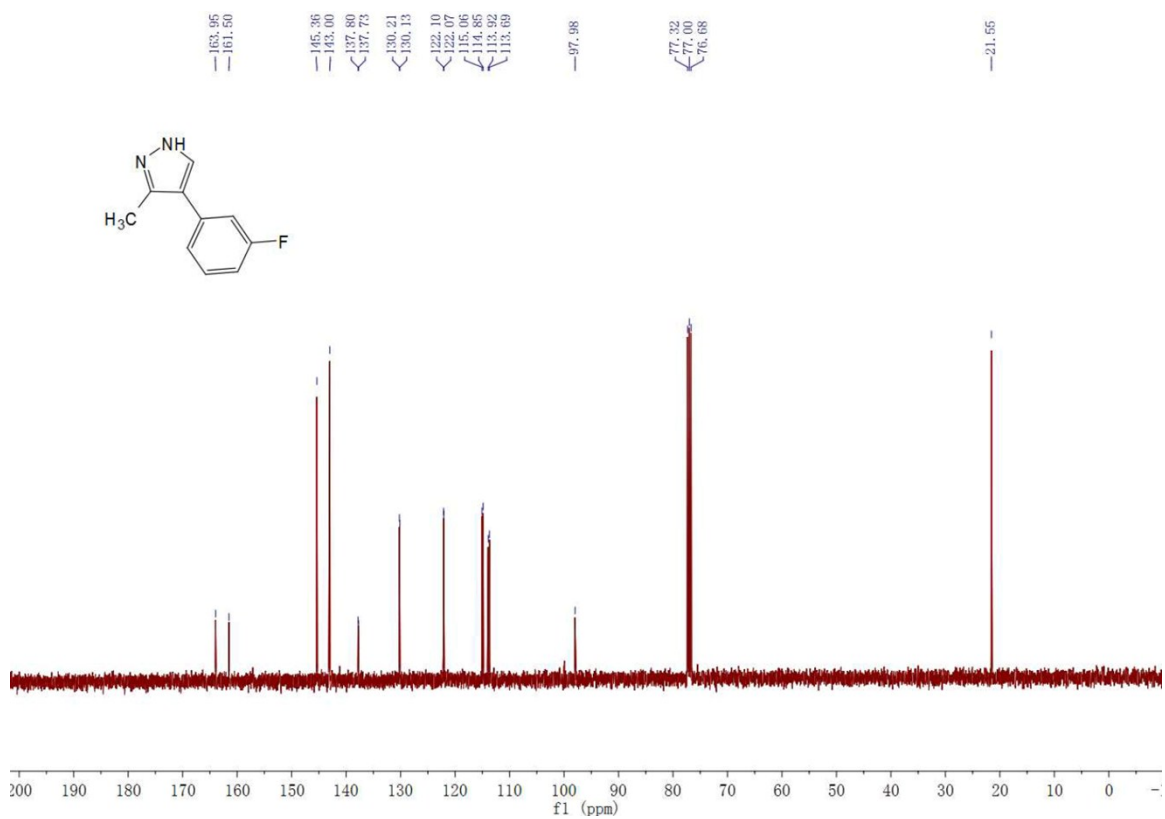
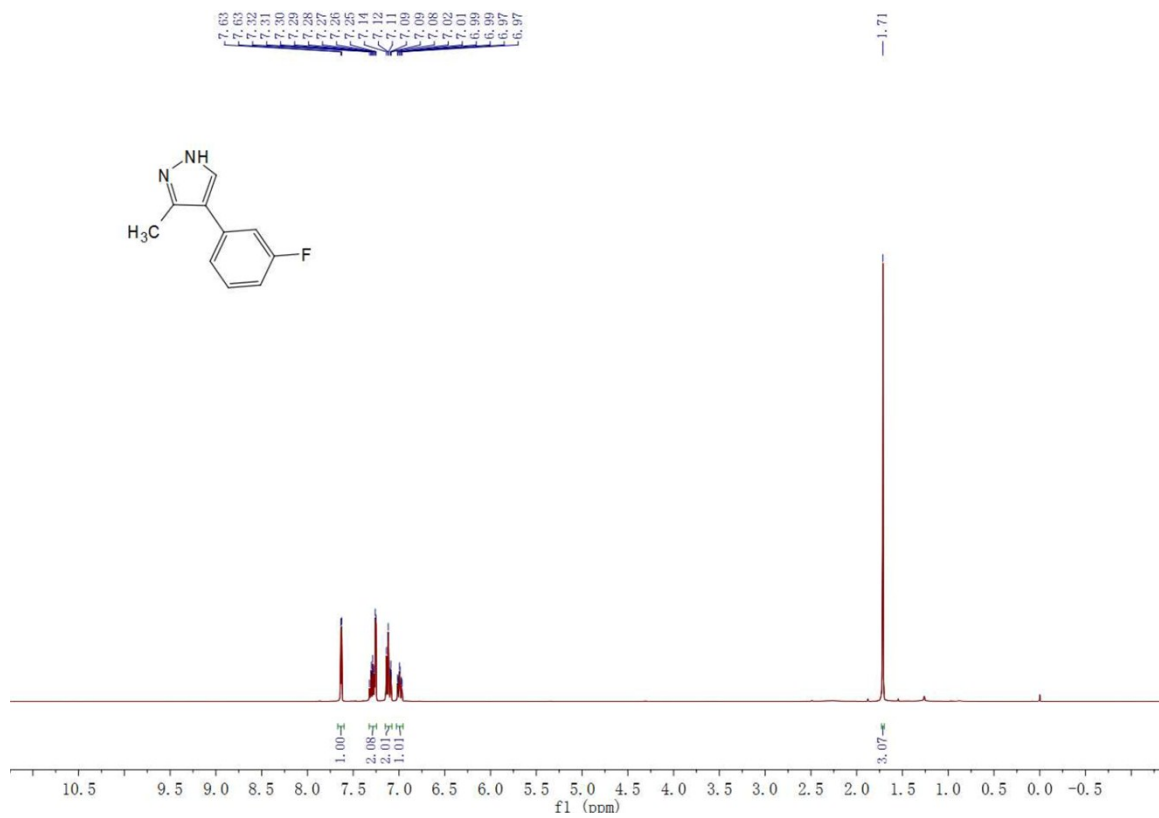
5e



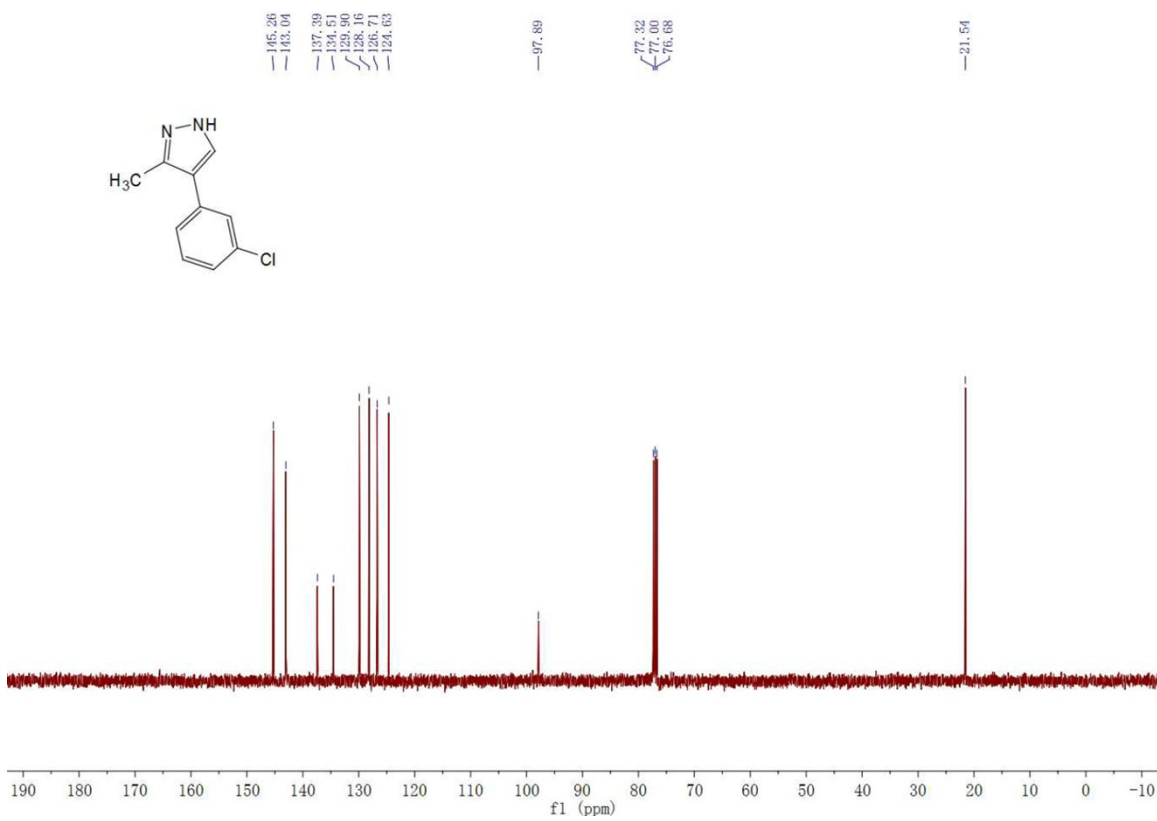
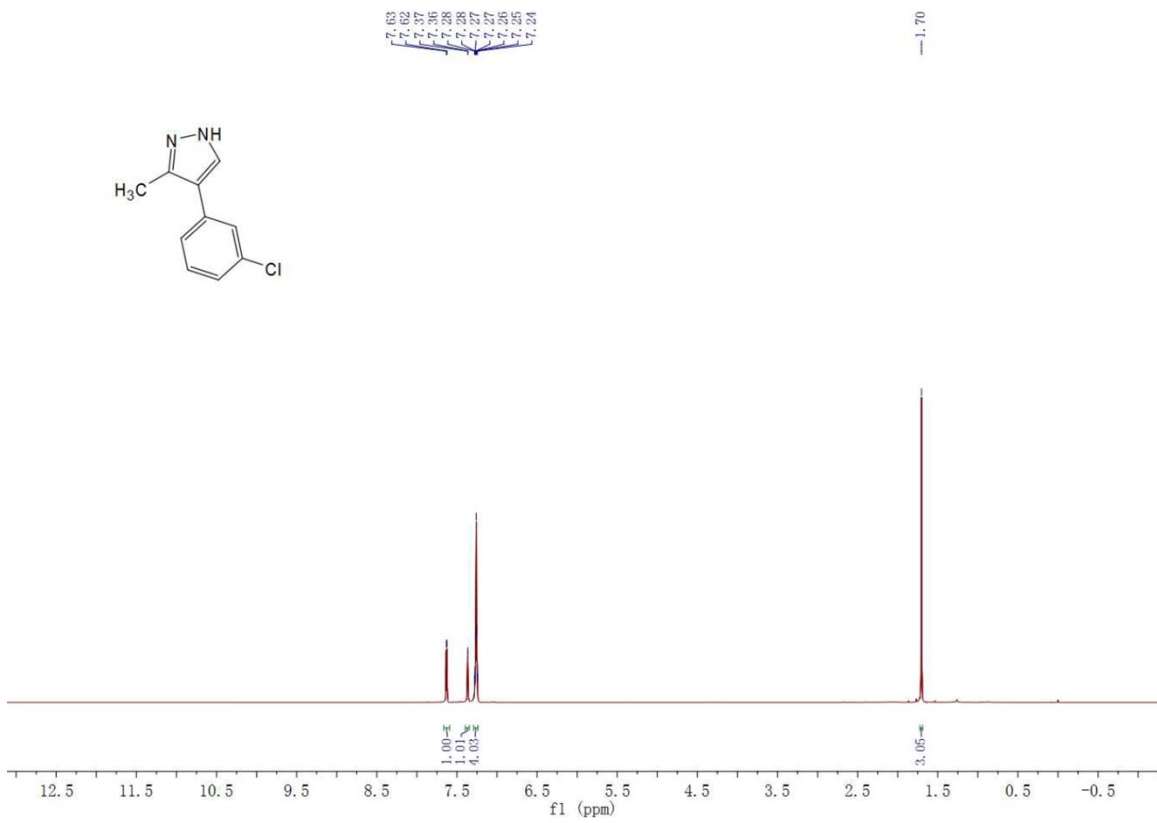
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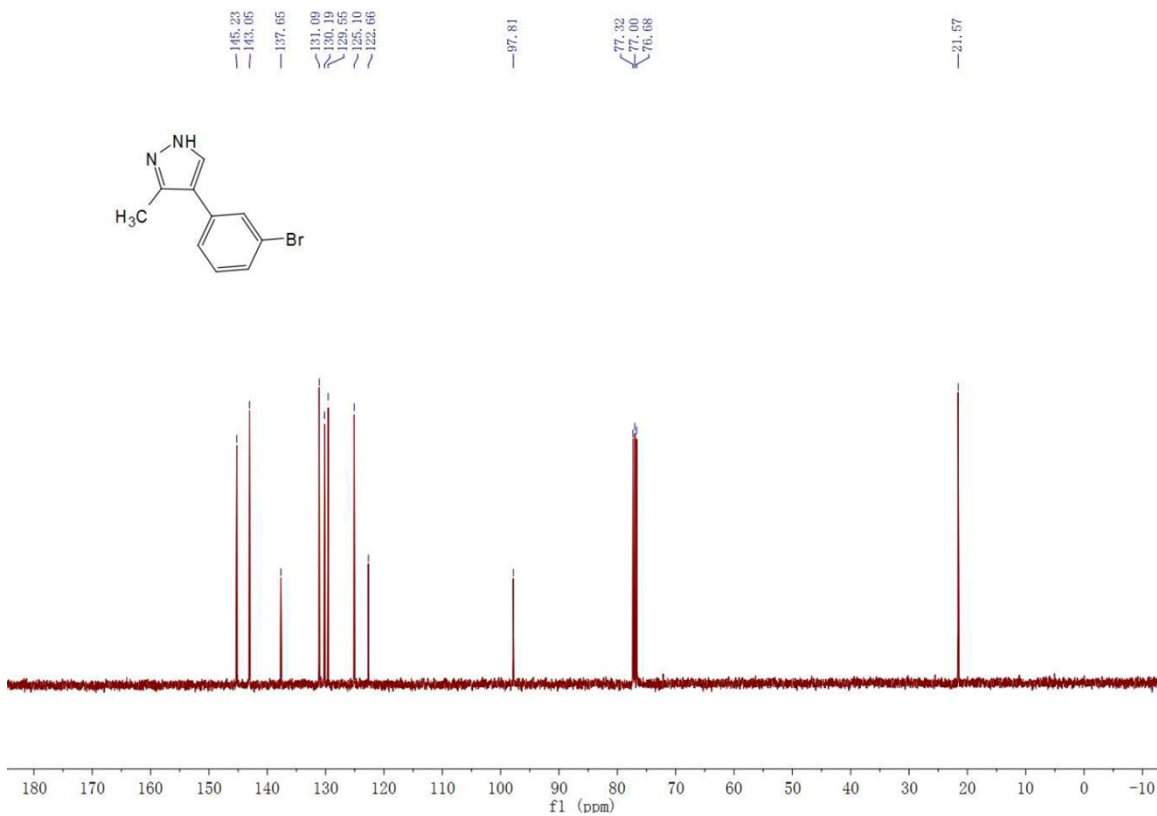
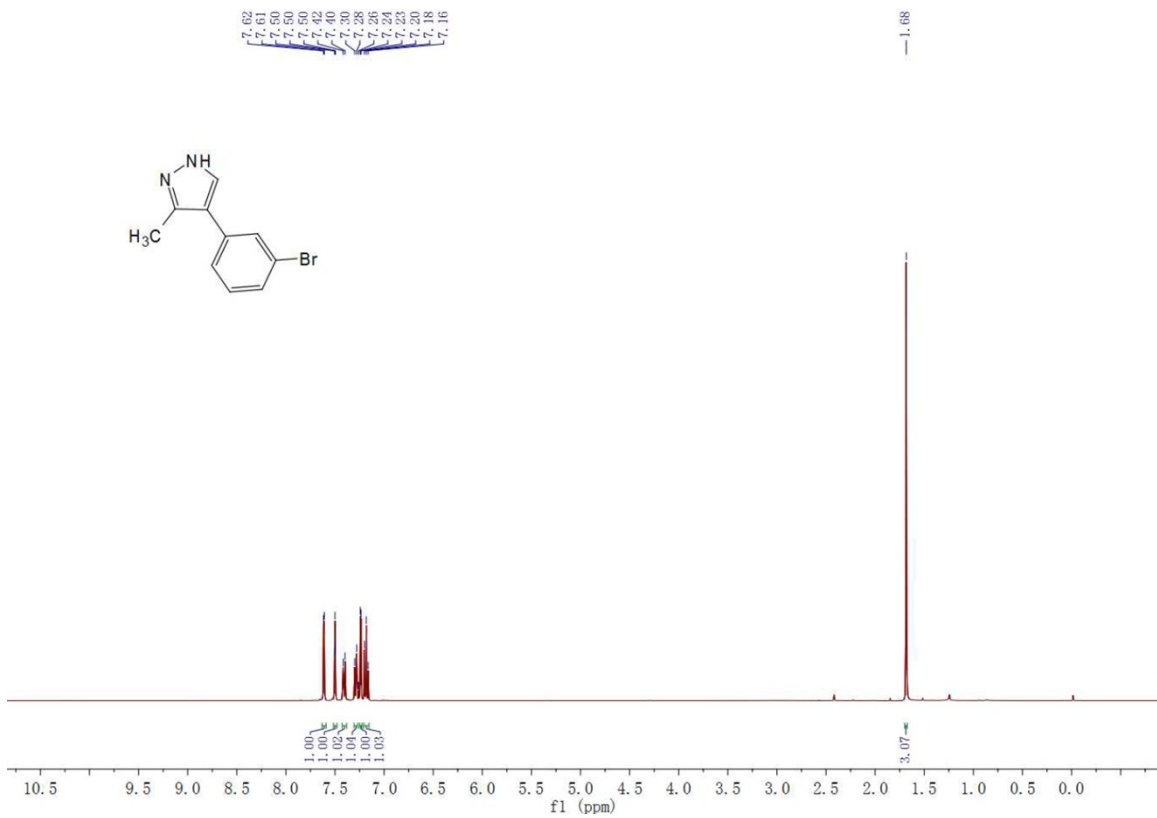
5g



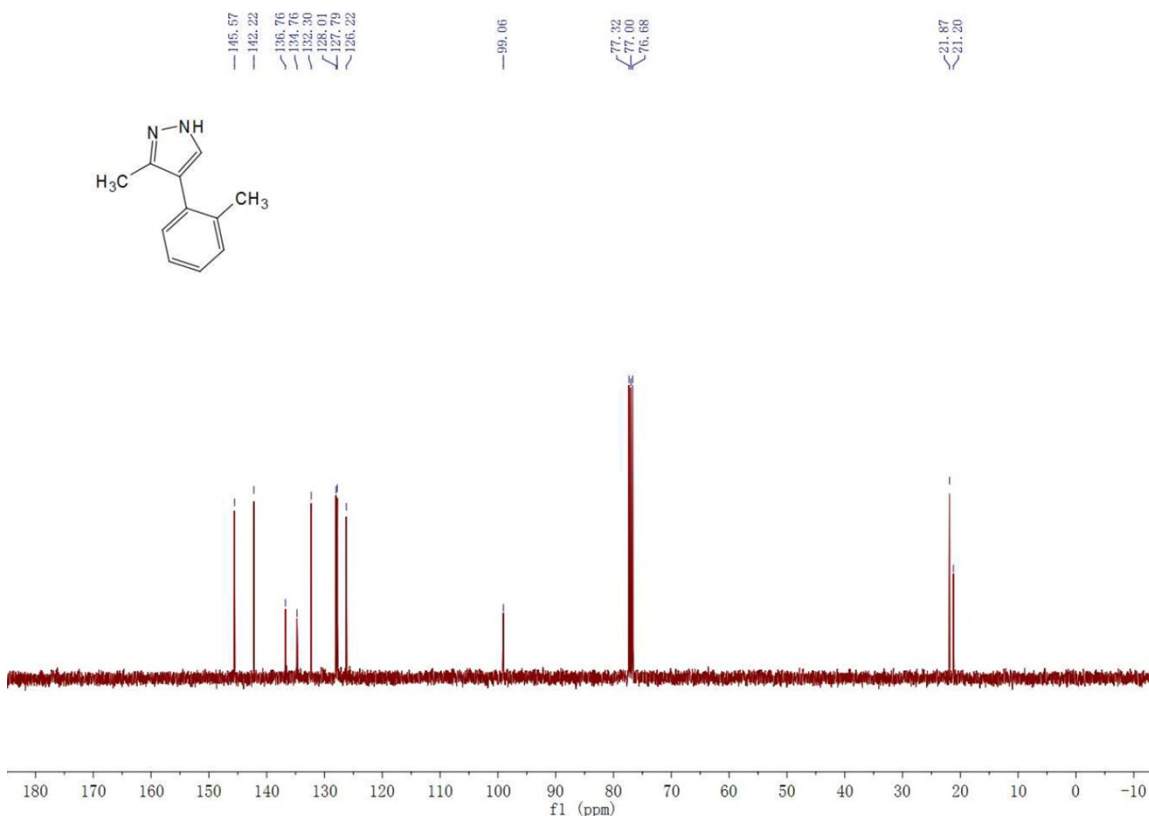
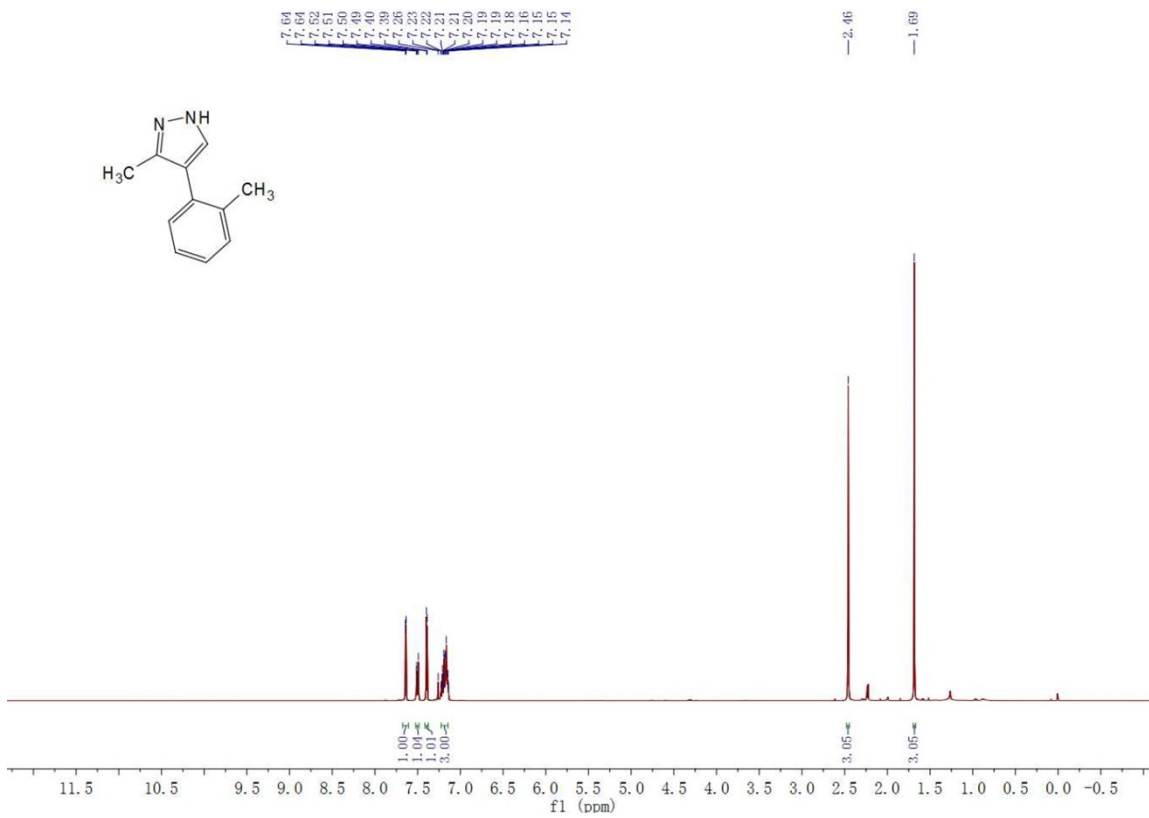
5h



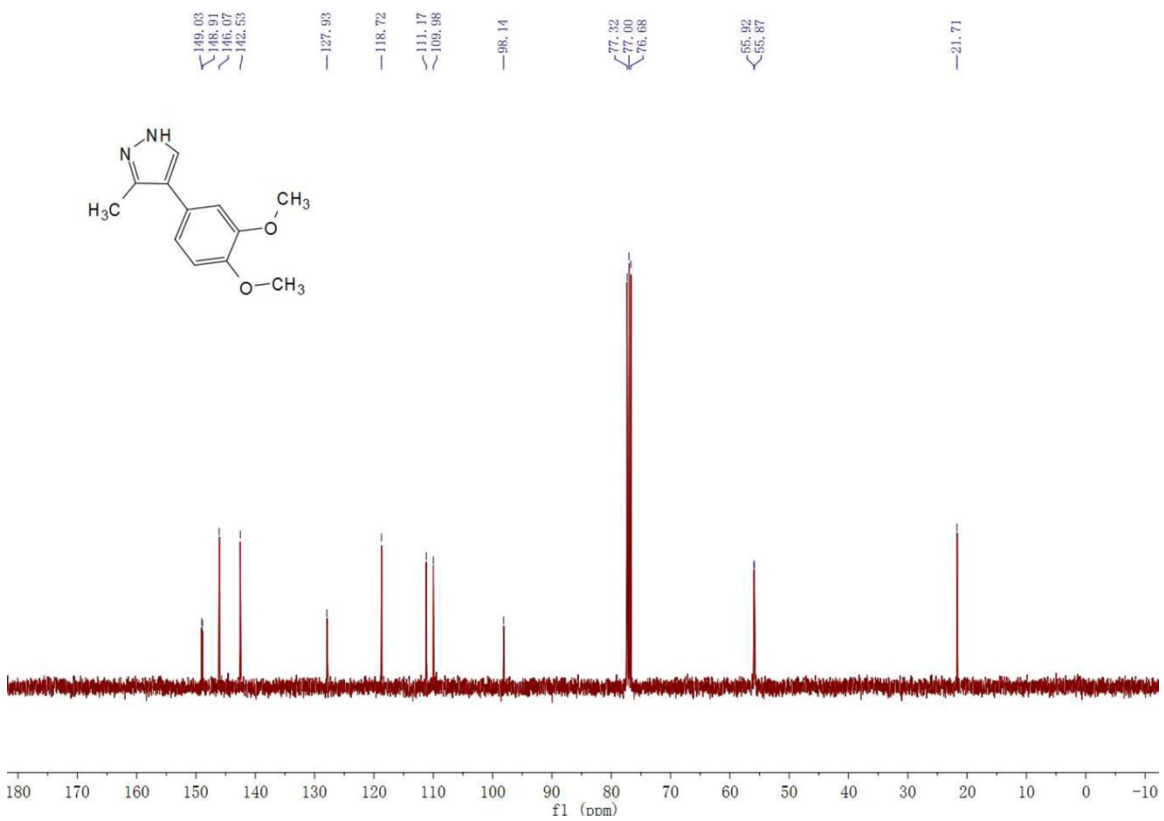
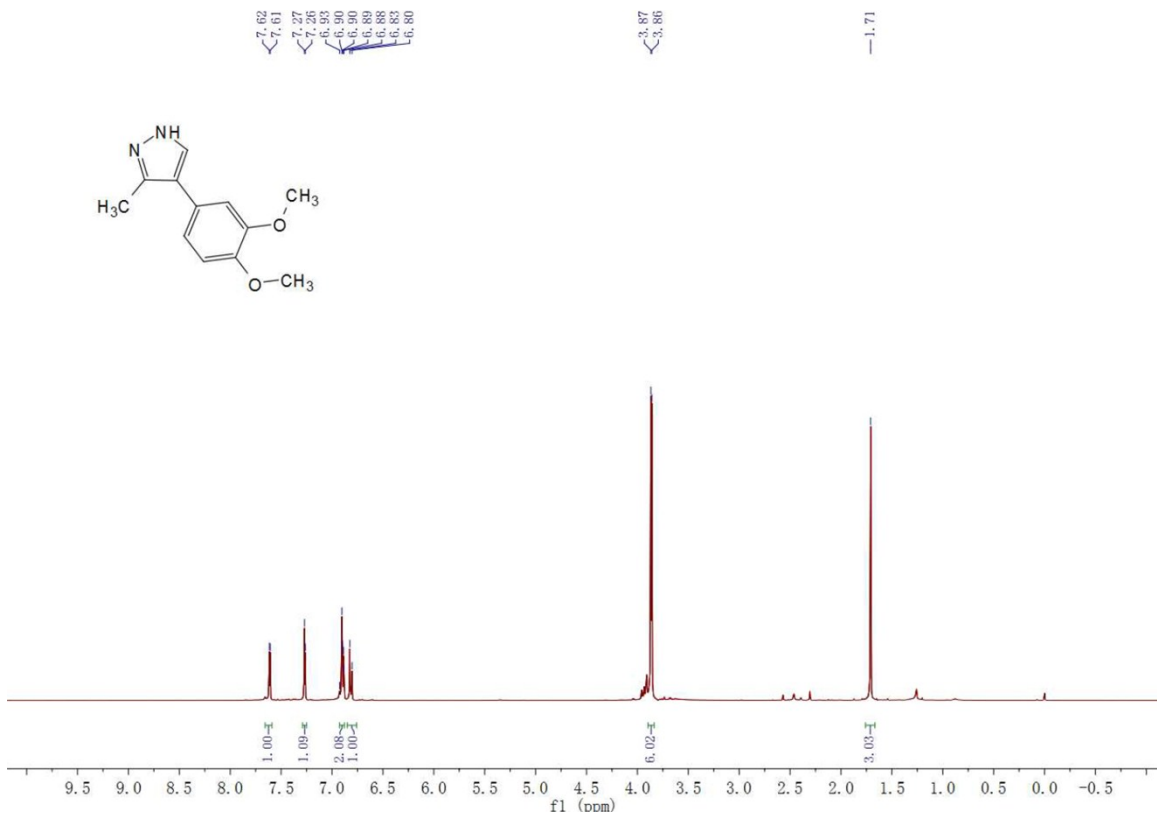
5i

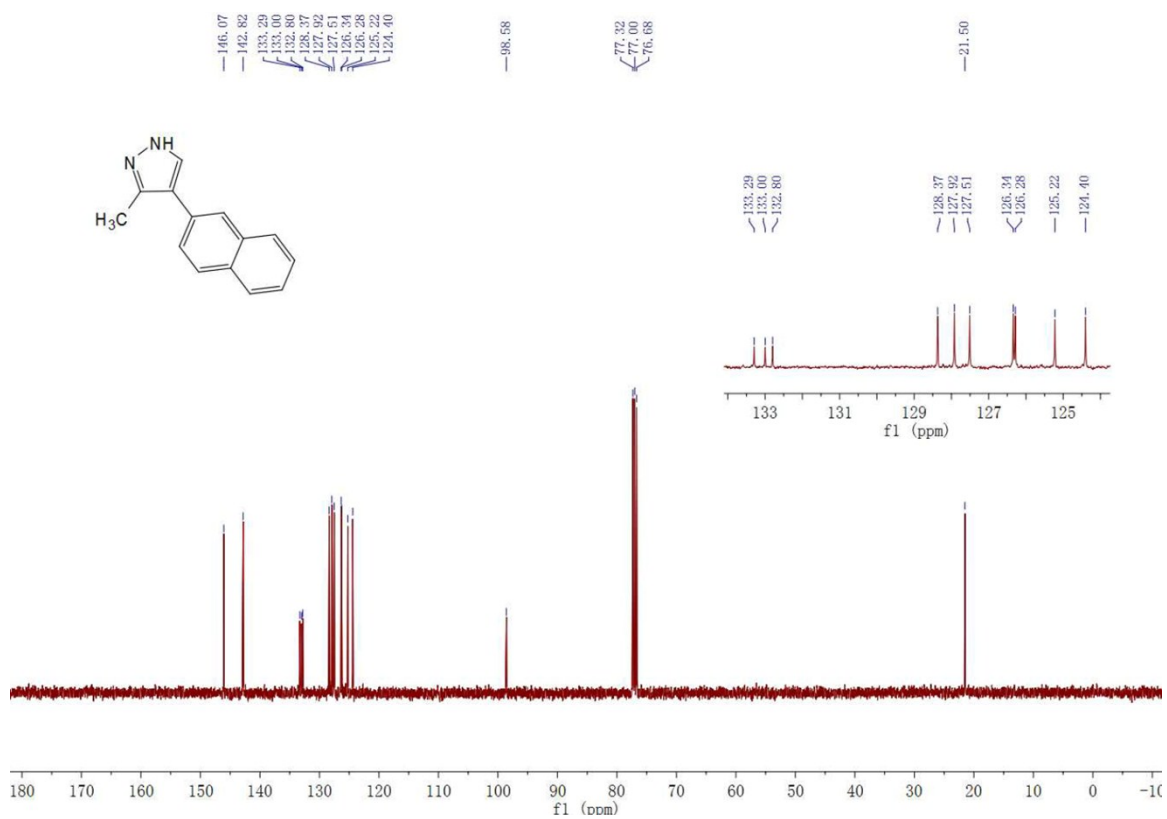
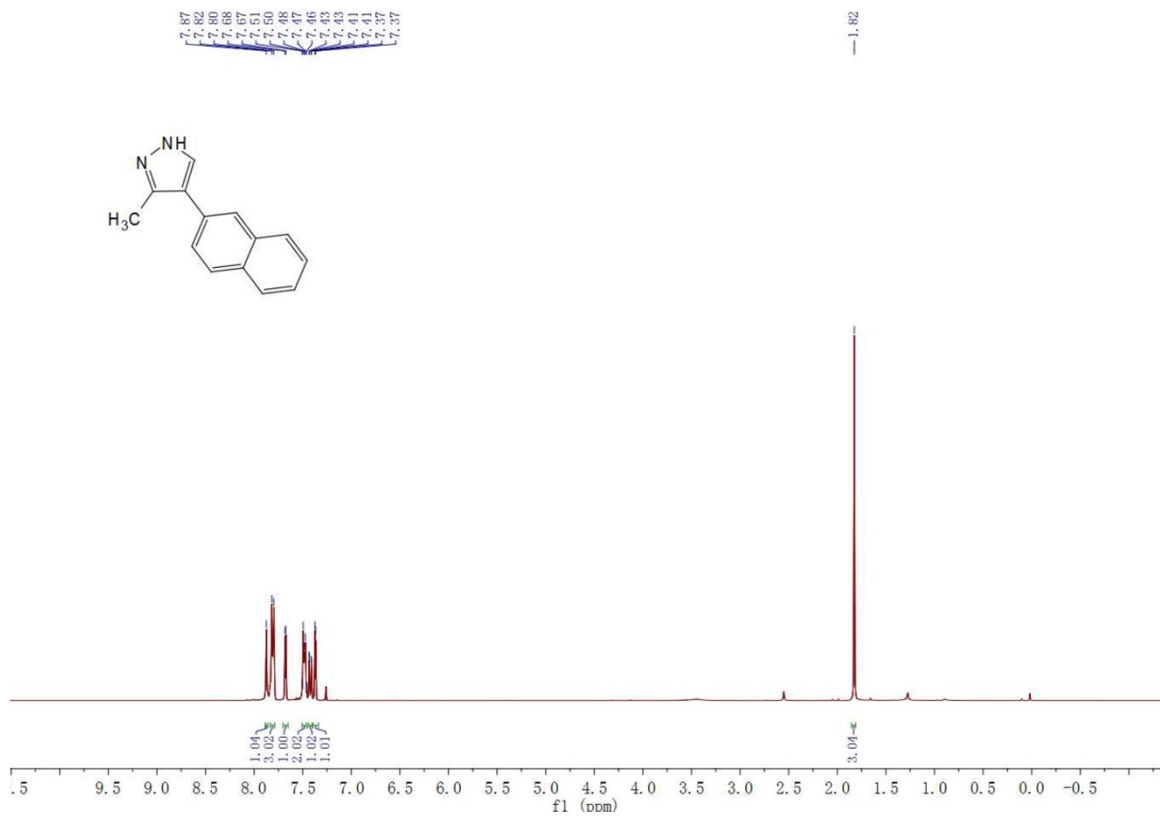


5j

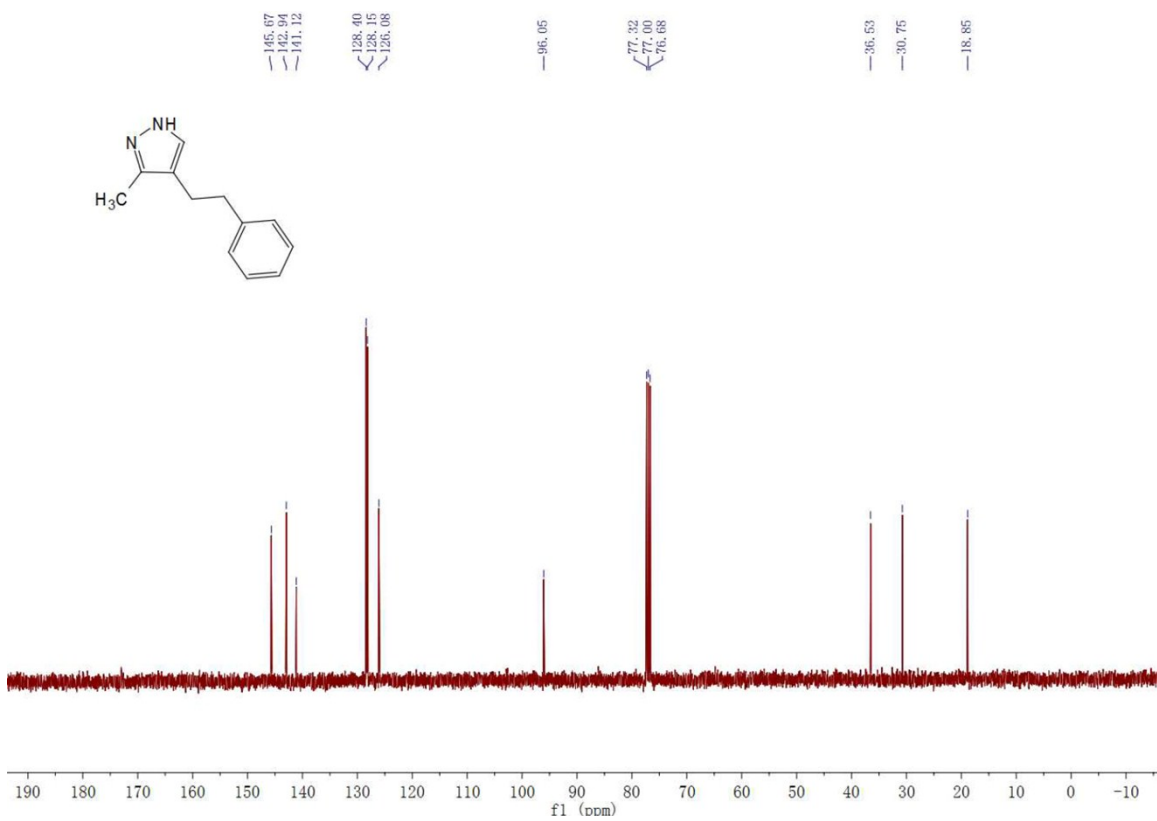
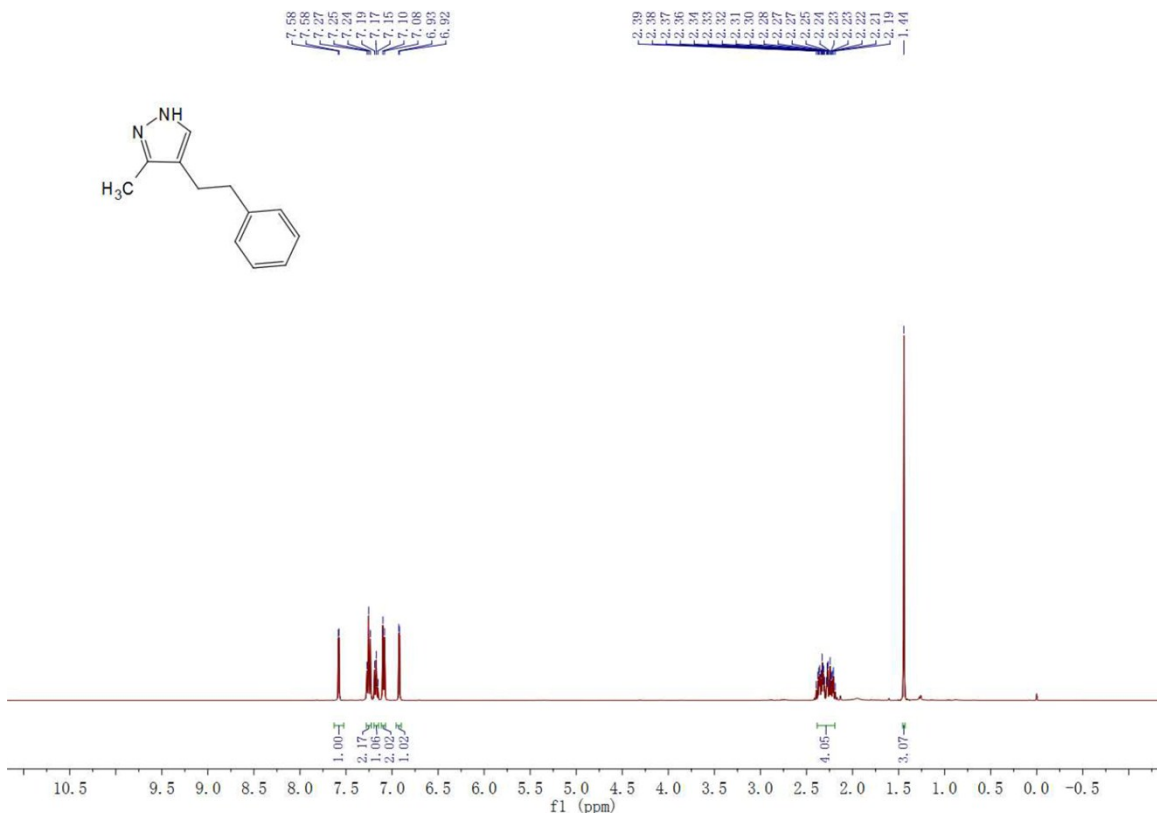


5k



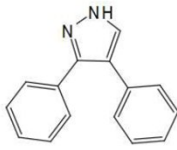


5m

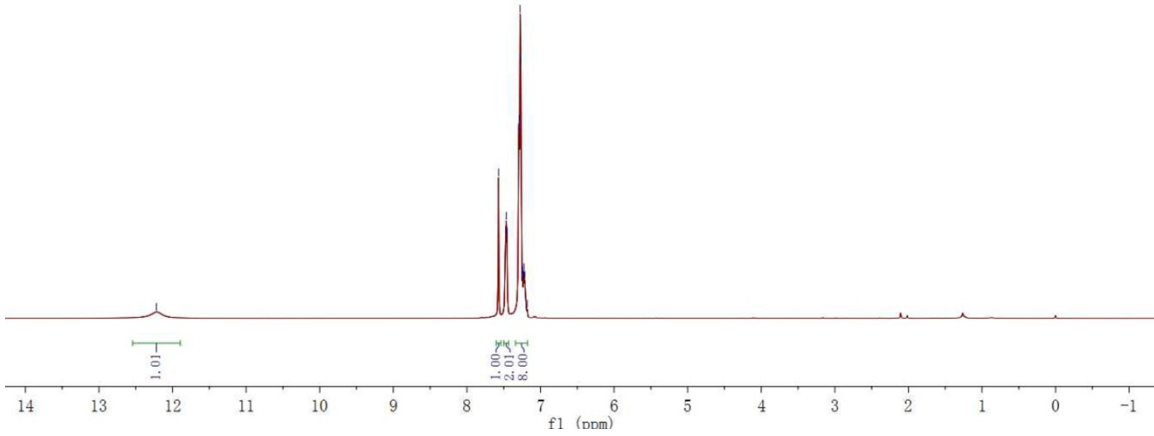


5n

—12.22

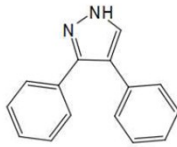


7.57
7.46
7.46
7.30
7.29
7.27
7.24
7.23
7.21
7.18

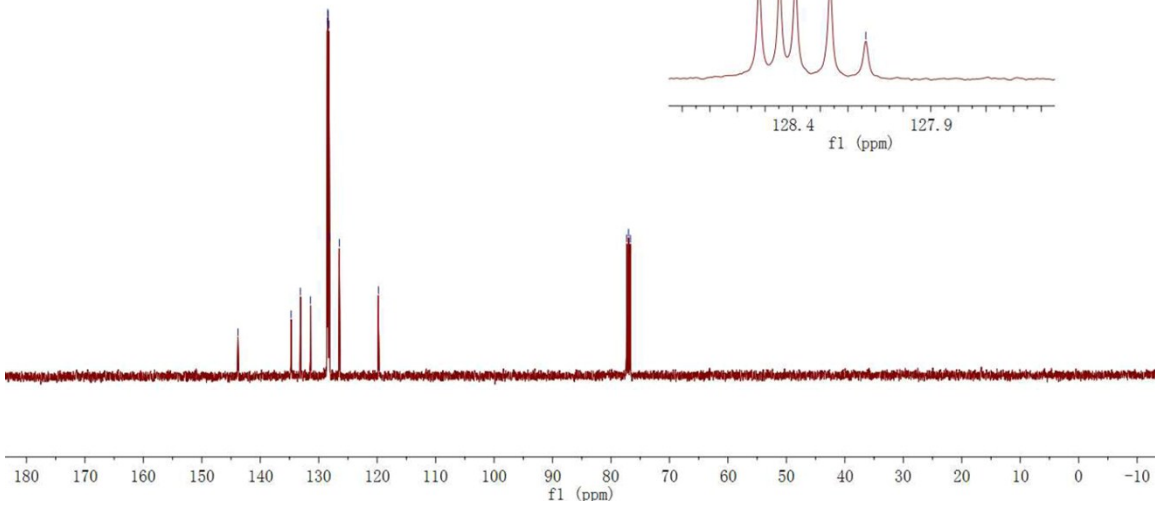


143.81
134.72
134.71
131.41
128.52
128.45
128.39
128.26
128.14
126.48
119.78

77.32
77.00
76.68

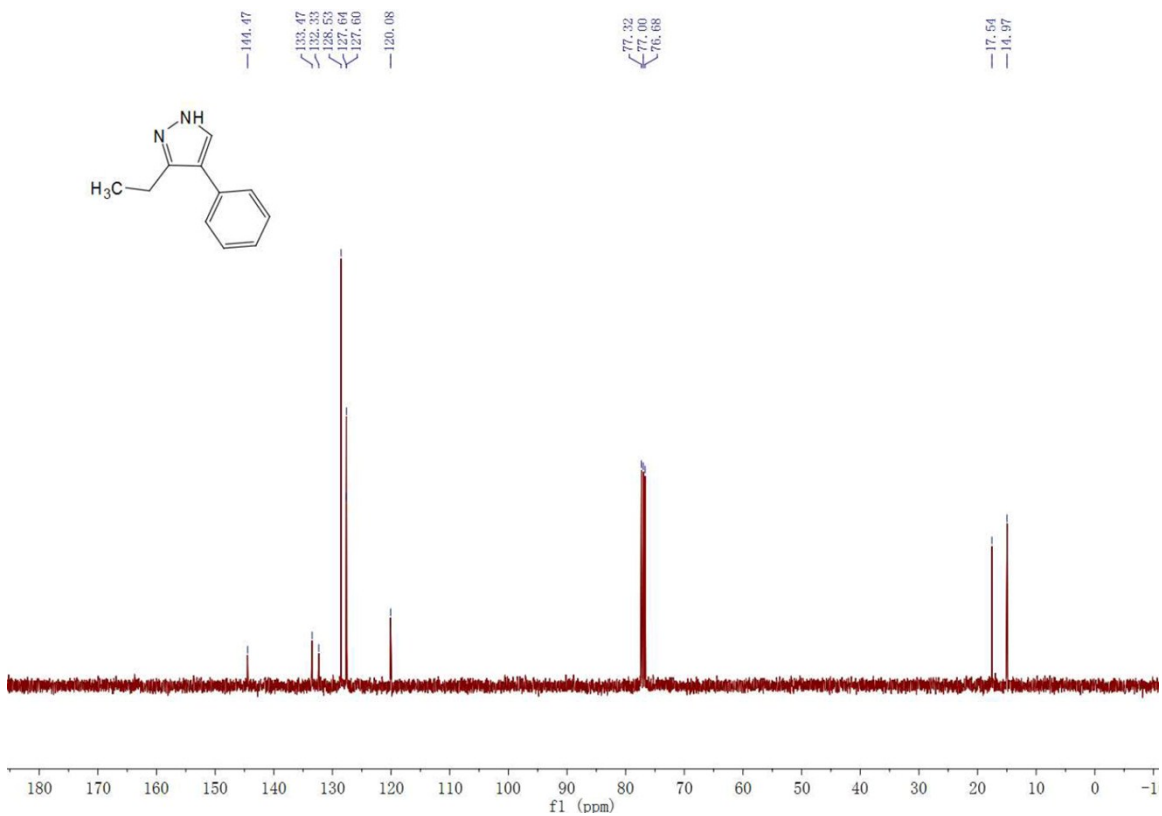
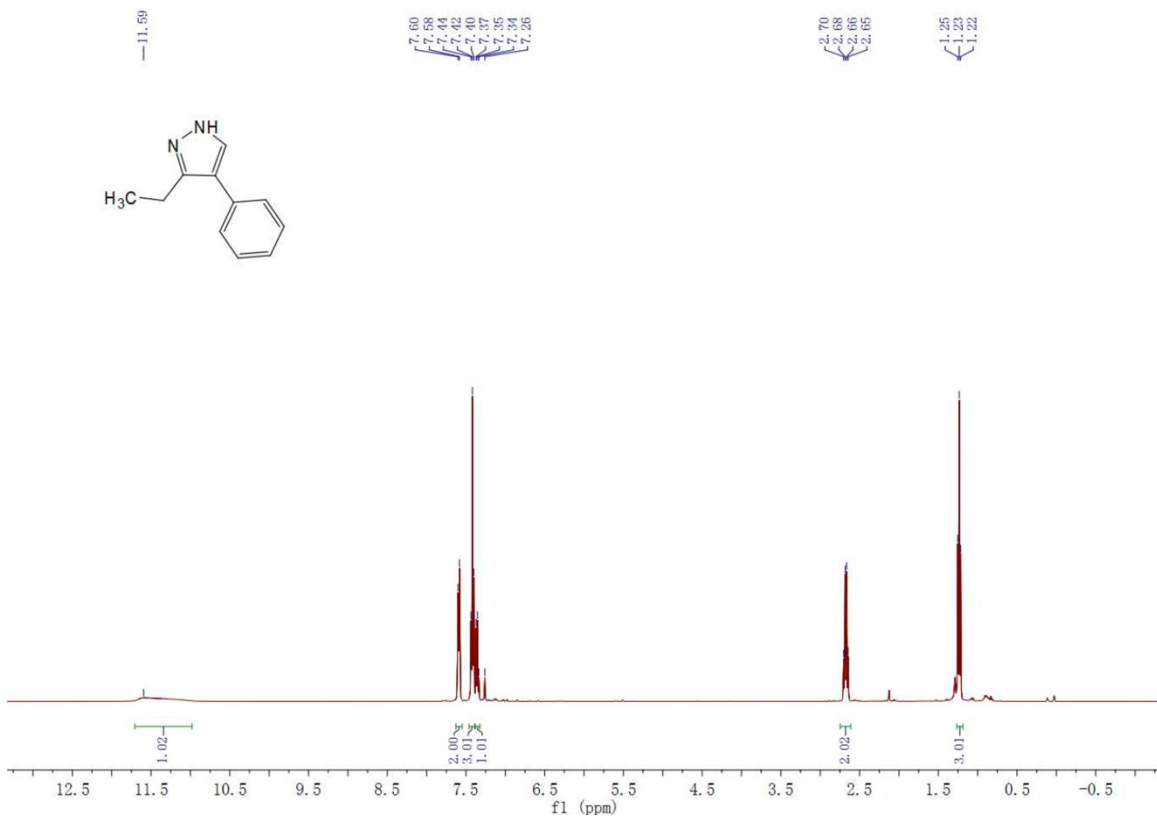


128.52
128.45
128.39
128.26
128.14



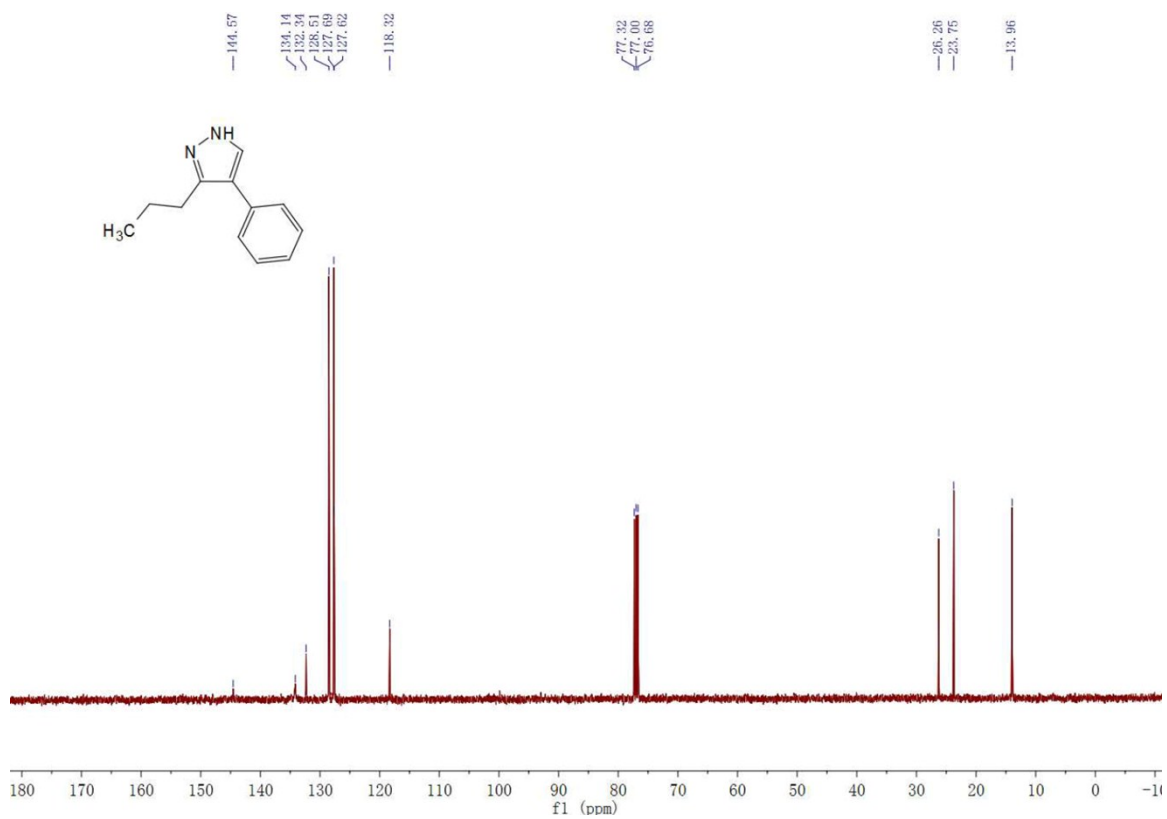
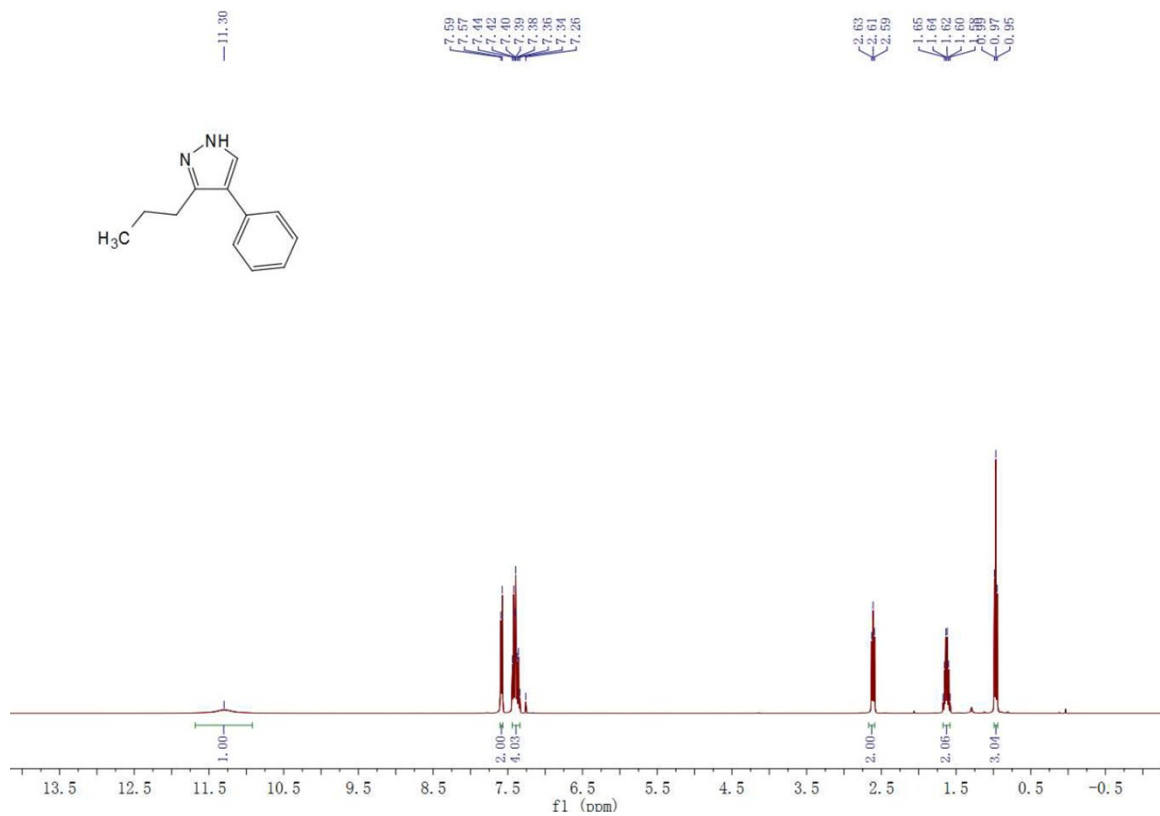
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S41

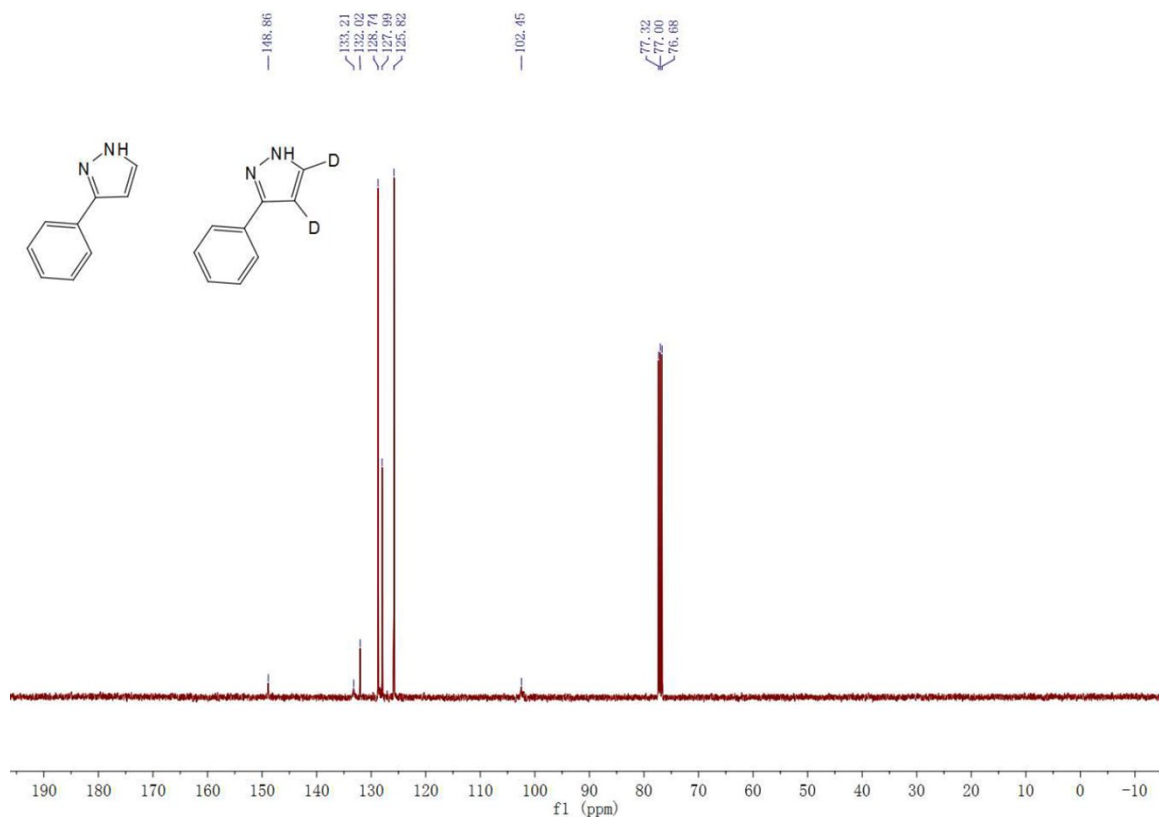
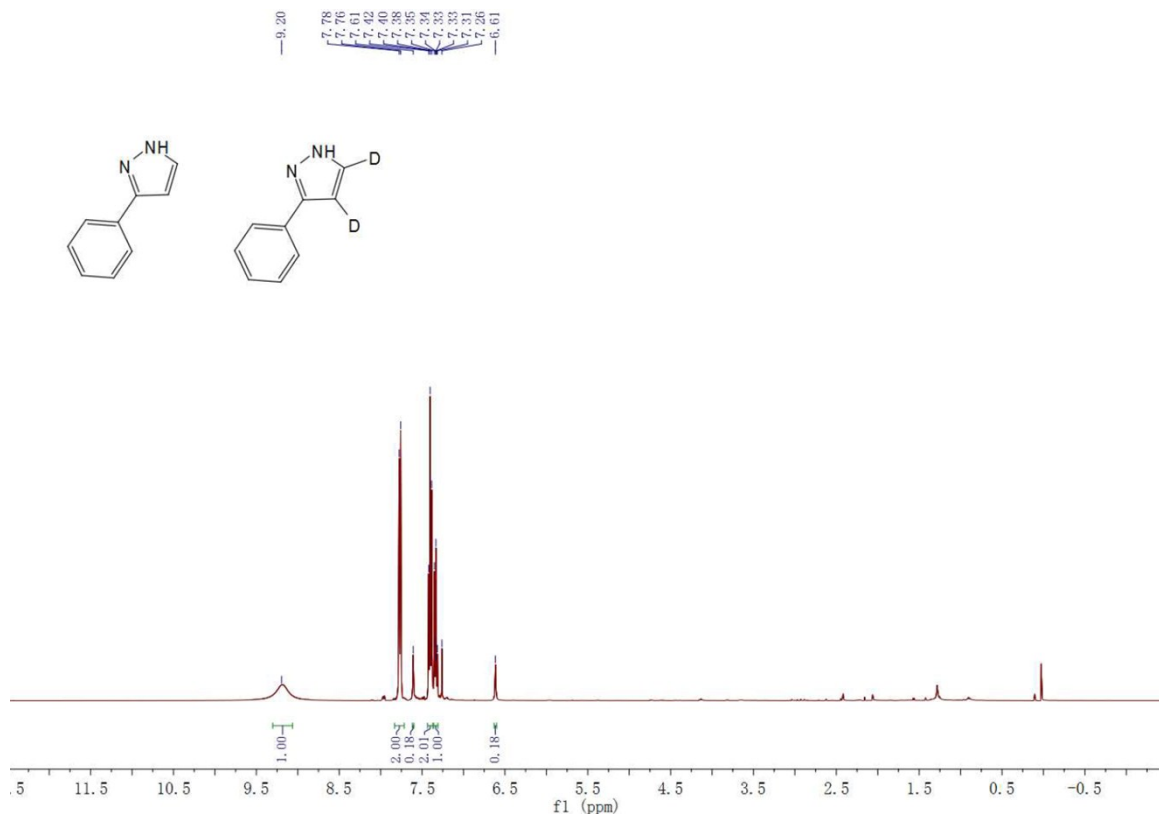


5p

S42



3a and [D₂]-3a



5a and [D₂]-5a

