Supporting Information for

One-step Synthesis of Cyanated Pyrazolo[1, 5–*a*]pyridines Utilizing *N*-Aminopyridines as 1,3-Dipole and Nitrogen Source

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1. General considerations

Unless otherwise noted, commercial reagents were purchased from Adamas, Alfa, Aladdin, TCI, *J&K* or Macklin and used without further purification. All reactions were carried out using oven-dried glassware and all reactions proceeded without special care. Column chromatography was performed on 200-300 mesh silica gel (Huanghai, China).

^{1}H, ^{19}F and ^{13}C{^{1}H} NMR spectra were recorded on an Bruker Ascend 400 MHz spectrometer at ambient temperature. ^{1}H NMR spectra are referred to the residual solvent signal (δ = 7.26 ppm) and ^{13}C NMR spectra are referred to the residual solvent signal (δ = 77.16 ppm). Data for ^{1}H NMR are reported as follows: chemical shifts (δ ppm), multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz), integration.

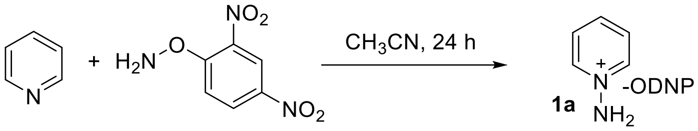
The data of HRMS was carried out on a waters G2-XS high-resolution mass spectrometer (HR-ESI-MS), or Thermo Fisher Scientific LTQ FTICR-MS, or Agilent 7250 GC/QTOF. Melting point were recorded using a SGW X-4 Melting Point Apparatus. X-ray diffraction data were collected on SuperNova, Dual, Cu at zero, AtlasS2.

2. Experimental procedures and characterization data

2.1 Experimental procedures

The synthesis of compounds 1, 5, and 7 according to the following procedure:

The substrates **1**, **5**, and **7** are known and were prepared according to the procedures in the literature.[1-3] As exemplified for **1a**:

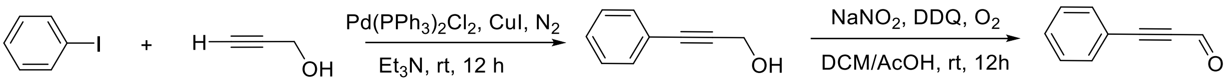


1a

To a solution of pyridine (0.47 g, 6.0 mmol) in acetonitrile (25 mL) was added *O*-(2,4-dinitrophenyl) hydroxylamine (1.3 g, 6.6 mmol). The reaction flask was sealed with rubber plug, and the reaction mixture was stirred for 24 h at room temperature, then upon filtering off the solvent. The orange solid **1a** was obtained in 80% yield (1.33 g), which was carried out to the next step without further purification.

The synthesis of compounds 2 according to the following procedure:

The substrates **2** are known and were prepared according to the procedures in the literature.[4] As exemplified for **2a**:



2a

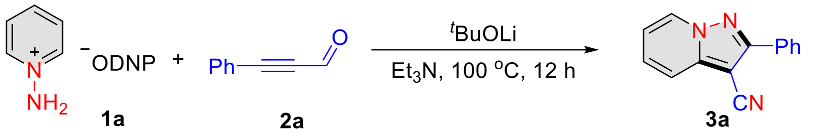
Step 1: To a mixture of iodobenzene (816 mg, 4 mmol) and prop-2-yn-1-ol (336 mg, 6 mmol), $Pd(PPh_3)_2Cl_2$ (140 mg, 5 mol %) and CuI (76 mg, 10 mol %) were added, followed by 8 mL Et_3N, and the reaction was allowed to stir at room temperature under N_2 for 12 h. The solvent was removed, and the mixture was purified by column chromatography (eluted with petroleum ether/ethyl acetate = 4:1) to give 2-phenylethyn-1-ol (brown oil) in 87% yield (459.9 mg).

Step 2: To a solution of 2-phenylethyn-1-ol in 6 mL of mixed solvent (DCM/AcOH = 10:1), $NaNO_2$ (24 mg) and DDQ (79 mg) were added, and the mixture reacted at room temperature under O_2 for 12 h. The solvent was removed, and the mixture was purified by column chromatography (eluted with petroleum ether/ethyl acetate = 8:1) to give **2a** (brown oil) in 73% yield (330.4 mg).

The synthesis of products 3, 4, and 6 according to the following procedure:

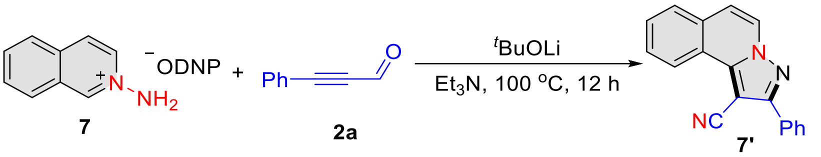
The compounds **3a**, **3b**, **3e**, **3k**, **4a**, **4b**, **4d-4f**, **4h**, **4i**, **4m**, and **4n** were known compounds and their NMR data were in agreement with the literature.[5]

As exemplified for **3a**:



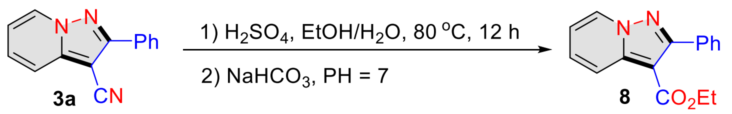
A pressure tube was charged with **1a** (166.8 mg, 0.60 mmol, 2.0 equiv), **2a** (39.0 mg, 0.30 mmol, 1.0 equiv), ^{t}BuOLi (24 mg, 0.30 mmol, 1.0 equiv), Et_3N (3.0 mL). The mixtures were heated with a heating mantle at 100 °C for 12 h, then cooled to room temperature. The solution was concentrated in vacuo, and the residue was purified by flash column chromatography (petroleum ether: ethyl acetate = 7: 1) to give product **3a** in 85% yield (55.9 mg).

The synthesis of products 7' according to the following procedure:



A pressure tube was charged with **7** (196.8 mg, 0.60 mmol, 2.0 equiv), **2a** (39.0 mg, 0.30 mmol, 1.0 equiv), ^{t}BuOLi (24 mg, 0.30 mmol, 1.0 equiv), Et_3N (3.0 mL). The mixtures were heated with a heating mantle at 100 °C for 12 h, then cooled to room temperature. The solution was concentrated in vacuo, and the residue was purified by flash column chromatography (petroleum ether: ethyl acetate = 7: 1) to give product **7'** in 60% yield (48.4 mg).

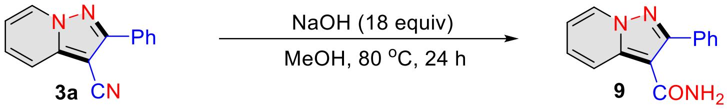
The synthesis of products 8 according to the following procedure:



To a solution of 4N H_2SO_4 (1 mL) and ethanol (2 mL) was added **3a** (65.7 mg, 0.30 mmol, 1.0 equiv). The reaction mixture was stirred at 80 °C for 12 h. The mixture was cooled to room temperature and alkalized by $NaHCO_3$ to PH = 7, and then extracted with 10 mL ethyl acetate. The organic layer was washed with brine and dried over Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by flash column chromatography (petroleum ether: ethyl acetate = 7: 1) to give product **8** in

55% yield (43.9 mg). **8** were known compounds and its NMR data were in agreement with the literature.[6]

The synthesis of products 9 according to the following procedure:

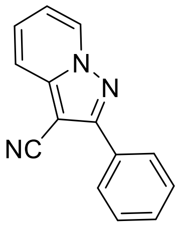


3a   9

To a solution of NaOH (215.9 mg, 5.40 mmol, 18 equiv) and methanol (3 mL) was added **3a** (65.7 mg, 0.30 mmol, 1.0 equiv). The reaction mixture was stirred at 80 °C for 24 h. then cooled to room temperature. The solution was concentrated in vacuo, and the residue was purified by flash column chromatography (petroleum ether: ethyl acetate = 7: 1) to give product **9** in 45% yield (32.0 mg).

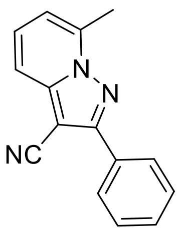
2.2 Characterization data

2-Phenylpyrazolo[1,5-*a*]pyridine-3-carbonitrile (3a)



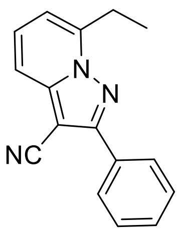
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **3a**. Yellow solid (55.9 mg, 85%), mp 121.2-123.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 6.9 Hz, 1H), 8.14 (d, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.53 – 7.43 (m, 4H), 7.03 (t, *J* = 6.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 144.6, 130.5, 130.2, 129.6, 129.1, 127.9, 127.6, 117.1, 115.1, 114.7, 79.6. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{14}H_9N_3$, 219.0796; found 219.0788.

7-Methyl-2-phenylpyrazolo[1,5-*a*]pyridine-3-carbonitrile (3b)



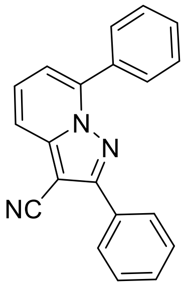
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **3b**. Yellow solid (58.0 mg, 83%), mp 130.1-131.2 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 6.7 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.38 (t, 1H), 6.86 (d, *J* = 7.0 Hz, 1H), 2.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 145.0, 139.9, 130.9, 130.0, 129.0, 127.8, 127.6, 114.5, 114.0, 79.5, 17.9. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{15}H_{11}N_3$, 233.0953; found 233.0943.

7-Ethyl-2-phenylpyrazolo[1,5-*a*]pyridine-3-carbonitrile (3c)



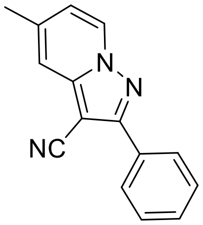
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **3c**. Yellow solid (59.3 mg, 80%), mp 132.8-133.4 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.9 Hz, 2H), 7.63 (d, *J* = 8.7 Hz, 1H), 7.54 – 7.44 (m, 3H), 7.40 (t, 1H), 6.85 (d, *J* = 7.1 Hz, 1H), 3.26 (q, *J* = 7.4 Hz, 2H), 1.46 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 145.0, 144.9, 131.0, 129.9, 129.0, 127.9, 127.6, 115.6, 114.3, 111.9, 79.3, 24.3, 10.9. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{16}H_{13}N_3$, 247.1109; found 247.1099.

2,7-Diphenylpyrazolo[1,5-*a*]pyridine-3-carbonitrile (3d)



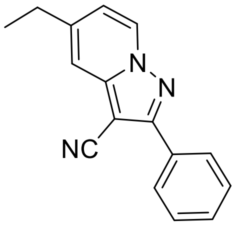
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **3d**. Yellow solid (55.8 mg, 63%), mp 136.2-137.0 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 5.8 Hz, 2H), 7.97 – 7.93 (m, 2H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.57 – 7.53 (m, 3H), 7.51 – 7.44 (m, 4H), 7.06 (d, *J* = 7.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 145.7, 141.7, 132.1, 130.7, 130.1, 130.0, 129.4, 128.9, 128.4, 128.0, 127.5, 115.5, 115.3, 115.2, 79.5. HRMS (GC/QTOF) m/z: [M] $^+$ calcd for $C_{20}H_{13}N_3$, 295.1109; found 295.1101.

5-Methyl-2-phenylpyrazolo[1,5-*a*]pyridine-3-carbonitrile (3e)



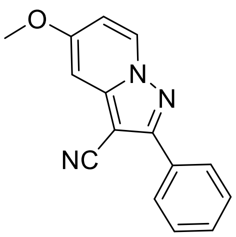
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **3e**. Yellow solid (55.9 mg, 80%), mp 129.8-130.9 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 7.0 Hz, 1H), 8.12 (d, *J* = 7.9 Hz, 2H), 7.53 – 7.46 (m, 4H), 6.82 (d, *J* = 7.1 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 144.8, 139.5, 130.7, 130.1, 129.0, 128.7, 127.5, 117.1, 115.6, 115.4, 78.3, 21.5. HRMS (GC/QTOF) m/z: [M] $^+$ calcd for $C_{15}H_{11}N_3$, 233.0953; found 233.0958.

5-Ethyl-2-phenylpyrazolo[1,5-*a*]pyridine-3-carbonitrile (3f)



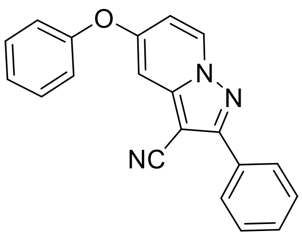
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **3f**. Yellow solid (60.8 mg, 82%), mp 134.5-135.6 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 7.3 Hz, 1H), 8.13 (d, *J* = 8.2 Hz, 2H), 7.56 – 7.46 (m, 4H), 6.87 (d, *J* = 6.9 Hz, 1H), 2.79 (q, *J* = 7.6 Hz, 2H), 1.34 (t, *J* = 7.6 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 145.4, 144.9, 130.7, 130.0, 129.0, 128.8, 127.5, 116.2, 114.1, 78.5, 28.5, 14.2. HRMS (GC/QTOF) m/z: [M] $^+$ calcd for $C_{16}H_{13}N_3$, 247.1109; found 247.1099.

5-Methoxy-2-phenylpyrazolo[1,5-*a*]pyridine-3-carbonitrile (3g)



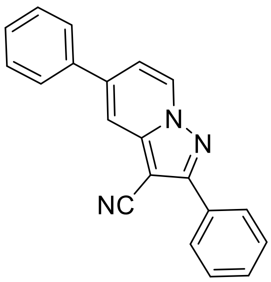
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **3g**. Yellow solid (58.3 mg, 78%), mp 110.4-111.5 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.5 Hz, 1H), 8.12 – 8.08 (m, 2H), 7.53 – 7.47 (m, 3H), 6.95 (d, *J* = 2.6 Hz, 1H), 6.66 (dd, *J* = 7.6, 2.7 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 156.2, 146.4, 130.7, 130.3, 130.1, 129.0, 127.4, 115.7, 109.1, 94.4, 78.4, 56.3.HRMS (GC/QTOF) m/z: [M] $^+$ calcd for $C_{15}H_{11}N_3O$, 249.0902; found 249.0893.

5-Phenoxy-2-phenylpyrazolo[1,5-*a*]pyridine-3-carbonitrile (3h)



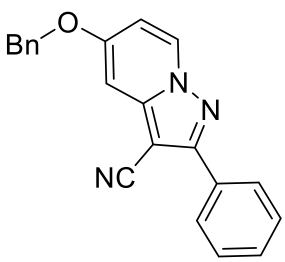
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **3h**. Yellow solid (56.9 mg, 61%), mp 137.2-138.0 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 7.3 Hz, 1H), 8.09 (d, *J* = 6.1 Hz, 2H), 7.52 – 7.46 (m, 5H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 7.7 Hz, 2H), 6.88 – 6.80 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 156.7, 153.9, 146.1, 130.9, 130.7, 130.6, 130.2, 129.1, 127.5, 126.2, 120.9, 115.4, 109.0, 99.4, 78.9. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{20}H_{13}N_3O$, 311.1059; found 311.1053.

2,5-Diphenylpyrazolo[1,5-*a*]pyridine-3-carbonitrile (3i)



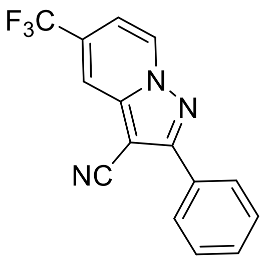
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **3i**. Yellow solid (57.5 mg, 65%), mp 136.5-137.6 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.0 Hz, 1H), 8.16 (d, *J* = 6.5 Hz, 2H), 7.92 (s, 1H), 7.70 (d, *J* = 6.9 Hz, 2H), 7.56 – 7.47 (m, 6H), 7.29 (dd, *J* = 7.2, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 144.9, 141.2, 137.4, 130.6, 130.2 (2C), 129.4 (2C), 129.1, 127.6, 127.1, 115.3, 114.4, 113.7, 79.7. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{15}H_{11}N_3O$, 249.0902; found 249.0893.

5-(Benzyloxy)-2-phenylpyrazolo[1,5-*a*]pyridine-3-carbonitrile (3j)



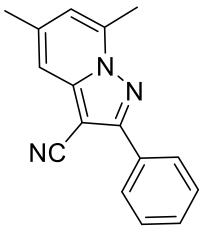
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **3j**. Yellow solid (43.8 mg, 45%), mp 142.6-143.7 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 7.5 Hz, 1H), 8.11 (d, *J* = 6.3 Hz, 2H), 7.54 – 7.44 (m, 8H), 7.05 (d, *J* = 2.7 Hz, 1H), 6.74 (dd, *J* = 7.6, 2.6 Hz, 1H), 5.18 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 146.3, 134.9, 130.7, 130.5, 130.1, 129.1, 129.0, 128.9, 127.9, 127.4, 115.7, 109.3, 95.6, 78.6, 71.1, 29.8. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{15}N_3ONa$, 348.1113; found 348.1119.

2-Phenyl-5-(trifluoromethyl)pyrazolo[1,5-*a*]pyridine-3-carbonitrile (3k)



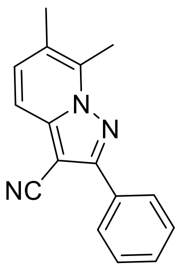
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **3k**. Yellow solid (66.3 mg, 77%), mp 138.2-139.4 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 7.2 Hz, 1H), 8.17 – 8.11 (m, 2H), 8.07 (s, 1H), 7.56 – 7.49 (m, 3H), 7.18 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 143.2, 130.7, 130.4, 130.0, 129.8, 129.7, 129.2, 127.6, 122.6 (q, *J* = 273.0 Hz), 115.0 (q, *J* = 4.7 Hz), 114.0, 110.5 (q, *J* = 2.9 Hz), 82.4. HRMS (ESI) m/z: [M+H] $^+$ calcd for $C_{15}H_9F_3N_3$, 288.0749; found 288.0754.

5,7-Dimethyl-2-phenylpyrazolo[1,5-*a*]pyridine-3-carbonitrile (3l)



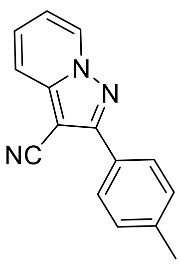
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **3l**. Yellow solid (54.8 mg, 74%), mp 132.6-132.7 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 6.7 Hz, 2H), 7.52 – 7.45 (m, 3H), 7.37 (s, 1H), 6.65 (s, 1H), 2.76 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 145.0, 139.3, 138.9, 131.0, 129.8, 128.9, 127.5, 116.5, 115.8, 113.2, 78.2, 21.4, 17.6. HRMS (GC/QTOF) m/z: [M] $^+$ calcd for $C_{16}H_{13}N_3$, 247.1109; found 247.1101.

6,7-Dimethyl-2-phenylpyrazolo[1,5-*a*]pyridine-3-carbonitrile (3m)



Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **3m**. Yellow solid (51.9 mg, 70%), mp 130.3-131.4 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.2 Hz, 2H), 7.52 – 7.44 (m, 4H), 7.23 (d, *J* = 8.9 Hz, 1H), 2.76 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 143.4, 137.3, 131.2, 131.1, 129.8, 128.9, 127.4, 121.7, 115.7, 113.2, 78.7, 18.0, 14.1. HRMS (GC/QTOF) m/z: [M] $^+$ calcd for $C_{16}H_{13}N_3$, 247.1109; found 247.1100.

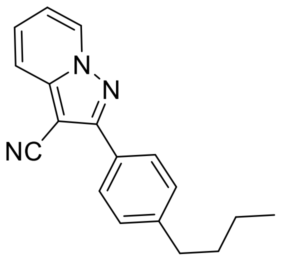
2-(*p*-Tolyl)pyrazolo[1,5-*a*]pyridine-3-carbonitrile (4a)



Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **4a**. Yellow solid (50.3 mg, 72%), mp 130.3-131.4 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 7.0 Hz, 1H), 8.04 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 8.9 Hz, 1H), 7.44 (t, 1H), 7.33 (d, *J*

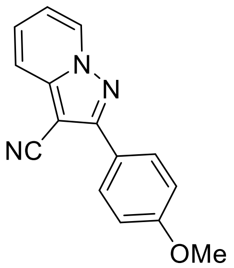
= 8.0 Hz, 2H), 7.01 (t, *J* = 6.2 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 144.6, 140.4, 129.8, 129.5, 127.8, 127.7, 127.5, 117.0, 115.3, 114.5, 79.3, 21.6. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{15}H_{11}N_3$, 233.0953; found 233.0958.

2-(4-Butylphenyl)pyrazolo[1,5-*a*]pyridine-3-carbonitrile (4b)



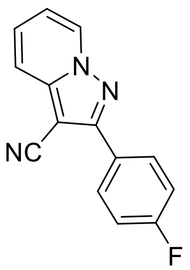
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **4b**. Yellow solid (62.7 mg, 76%), mp 133.4-134.5 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 6.9 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.9 Hz, 1H), 7.37 (d, *J* = 8.7 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 2H), 6.93 (t, *J* = 7.0 Hz, 1H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.66 – 1.58 (m, 2H), 1.41 – 1.32 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 145.2, 144.4, 129.3, 129.0, 127.7, 127.6, 127.3, 116.7, 115.1, 114.4, 79.0, 35.5, 33.4, 22.3, 13.9. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{18}H_{17}N_3$, 275.1422; found 275.1413.

2-(4-Methoxyphenyl)pyrazolo[1,5-*a*]pyridine-3-carbonitrile (4c)



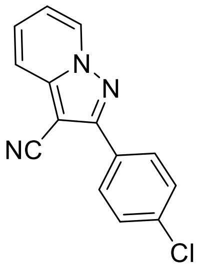
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **4c**. Yellow solid (55.3 mg, 74%), mp 132.5-133.6 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 6.9 Hz, 1H), 8.11 (d, *J* = 8.7 Hz, 2H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.44 (t, 1H), 7.06 – 6.97 (m, 3H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 155.8, 144.7, 132.3, 129.5, 129.0, 127.7, 123.1, 116.9, 115.4, 114.5, 114.4, 113.5, 78.9, 55.5. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{15}H_{11}N_3O$, 249.0902; found 249.0894.

2-(4-Fluorophenyl)pyrazolo[1,5-*a*]pyridine-3-carbonitrile (4d)



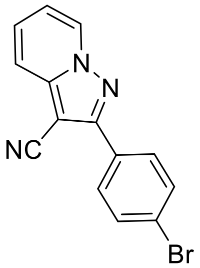
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **4d**. Yellow solid (49.8 mg, 70%), mp 135.8-136.9 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 7.1 Hz, 1H), 8.18 – 8.09 (m, 2H), 7.76 (d, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.21 (t, *J* = 8.7 Hz, 2H), 7.04 (t, *J* = 7.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 144.6, 129.6, 129.5, 128.0, 126.8, 117.1, 116.3, 116.1, 115.1, 114.8, 79.4. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{14}H_8FN_3$, 237.0702; found 237.0692.

2-(4-Chlorophenyl)pyrazolo[1,5-*a*]pyridine-3-carbonitrile (4e)



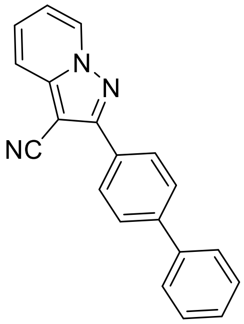
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **4e**. Yellow solid (50.9 mg, 67%), mp 138.2-139.3 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 6.9 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.9 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 3H), 7.05 (t, *J* = 6.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 144.6, 136.3, 129.6, 129.4, 129.0, 128.8, 128.0, 117.1, 114.9, 114.9, 79.5. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{14}H_8ClN_3$, 253.0407; found 253.0403.

2-(4-Bromophenyl)pyrazolo[1,5-*a*]pyridine-3-carbonitrile (4f)



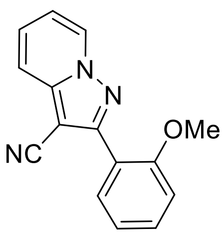
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **4f**. Yellow solid (61.5 mg, 69%), mp 138.4-139.5 ºC. ^{1}H NMR (400 MHz, DMSO-d6) δ 8.98 (t, *J* = 6.8 Hz, 1H), 8.04 – 7.89 (m, 3H), 7.84 – 7.77 (m, 2H), 7.67 (q, *J* = 7.3 Hz, 1H), 7.27 (q, *J* = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d6) δ 153.5, 143.8, 132.3, 130.3, 129.4, 129.3, 128.9, 123.7, 116.6, 115.8, 114.6, 78.0. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{14}H_8BrN_3$, 296.9902; found 296.9893.

2-([1,1'-Biphenyl]-4-yl)pyrazolo[1,5-*a*]pyridine-3-carbonitrile (4g)



Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **4g**. Yellow solid (68.2 mg, 77%), mp 139.3-140.4 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 6.9 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 3H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.51 – 7.35 (m, 4H), 7.02 (t, *J* = 6.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 144.6, 142.9, 140.3, 129.5, 129.4, 129.0, 127.9, 127.9, 127.8, 127.7, 127.2, 117.0, 114.7, 79.5. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{20}H_{13}N_3$, 295.1109; found 295.1111.

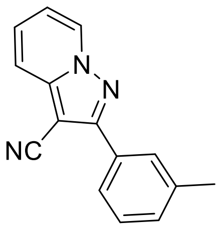
2-(2-Methoxyphenyl)pyrazolo[1,5-*a*]pyridine-3-carbonitrile (4h)



Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **4h**. Yellow solid (50.8 mg, 68%), mp 136.5-137.6 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 7.0 Hz, 1H), 7.72 (d, *J* = 8.9 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* =

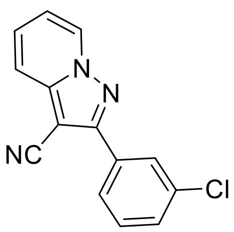
7.9 Hz, 1H), 7.38 (t, 1H), 7.10 – 7.01 (m, 2H), 6.94 (t, *J* = 6.9 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 154.2, 143.8, 131.4, 130.9, 129.3, 127.4, 120.8, 119.4, 116.8, 114.6, 114.1, 111.4, 82.9, 55.2. HRMS (GC/QTOF) m/z: [M] $^+$ calcd for $C_{15}H_{11}N_3O$, 249.0902; found 249.0893.

2-(*m*-Tolyl)pyrazolo[1,5-*a*]pyridine-3-carbonitrile (4i)



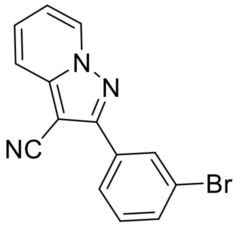
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **4i**. Yellow solid (52.4 mg, 75%), mp 134.8-135.9 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 7.0 Hz, 1H), 7.95 – 7.90 (m, 2H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.40 (q, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 1H), 6.98 (t, *J* = 6.9 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 13C NMR (101 MHz, Chloroform-d) δ 155.9, 144.5, 138.7, 130.9, 130.3, 129.4, 128.9, 128.0, 127.7, 124.6, 116.9, 115.1, 114.5, 79.4, 21.5. HRMS (GC/QTOF) m/z: [M] $^+$ calcd for $C_{15}H_{11}N_3$, 233.0953; found 233.0944.

2-(3-Chlorophenyl)pyrazolo[1,5-*a*]pyridine-3-carbonitrile (4j)



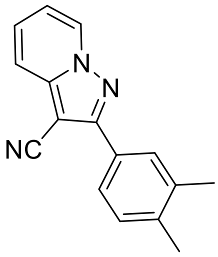
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **4j**. Yellow solid (53.9 mg, 71%), mp 137.1-138.2 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 6.8 Hz, 1H), 8.12 (s, 1H), 8.08 – 8.02 (m, 1H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.51 – 7.42 (m, 3H), 7.10 – 7.02 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 144.5, 135.1, 132.2, 130.4, 130.2, 129.6, 128.1, 127.5, 125.6, 117.2, 115.0, 114.7, 79.7. HRMS (GC/QTOF) m/z: [M] $^+$ calcd for $C_{14}H_8ClN_3$, 253.0407; found 253.0396.

2-(3-Bromophenyl)pyrazolo[1,5-*a*]pyridine-3-carbonitrile (4k)



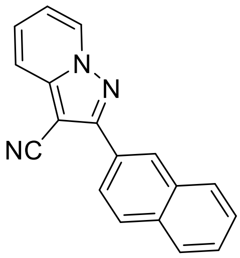
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **4k**. Yellow solid (65.0 mg, 73%), mp 139.7-140.8 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 6.9 Hz, 1H), 8.24 (s, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.03 (t, *J* = 7.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 144.5, 133.0, 132.4, 130.5, 130.2, 129.5, 128.0, 126.0, 123.1, 117.1, 114.9, 114.7, 79.6. HRMS (GC/QTOF) m/z: [M] $^+$ calcd for $C_{14}H_8BrN_3$, 296.9902; found 296.9895.

2-(3,4-Dimethylphenyl)pyrazolo[1,5-a]pyridine-3-carbonitrile (4l)



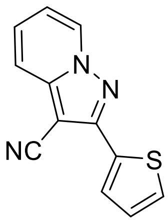
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **4l**. Yellow solid (51.9 mg, 70%), mp 131.6-132.7 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 6.9 Hz, 1H), 7.91 – 7.84 (m, 2H), 7.70 (d, *J* = 8.9 Hz, 1H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.24 (s, 1H), 6.96 (t, *J* = 6.7 Hz, 1H), 2.34 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 144.5, 139.0, 137.3, 130.2, 129.3, 128.4, 127.9, 127.6, 124.9, 116.8, 115.2, 114.4, 79.1, 19.8, 19.8. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{16}H_{13}N_3$, 247.1109; found 247.1099.

2-(Naphthalen-2-yl)pyrazolo[1,5-*a*]pyridine-3-carbonitrile (4m)



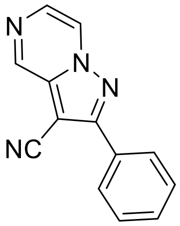
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **4m**. Yellow solid (60.5 mg, 75%), mp 133.5-134.6 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 6.9 Hz, 1H), 8.35 – 8.29 (m, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.97 – 7.92 (m, 1H), 7.88 – 7.81 (m, 2H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.57 – 7.49 (m, 3H), 7.09 (t, *J* = 6.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 143.8, 134.0, 131.2, 130.5, 129.7, 129.0, 128.6, 128.0, 127.7, 127.2, 126.4, 125.6, 125.3, 117.2, 114.7, 114.5, 83.1. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{18}H_{11}N_3$, 269.0953; found 269.0949.

2-(Thiophen-2-yl)pyrazolo[1,5-*a*]pyridine-3-carbonitrile (4n)



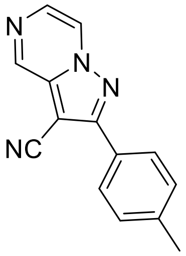
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **4n**. Yellow solid (47.9 mg, 71%), mp 128.7-129.8 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 7.0 Hz, 1H), 7.99 (d, *J* = 3.7 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.19 (t, 1H), 7.01 (t, *J* = 6.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 144.3, 132.6, 129.5, 128.4, 128.3, 128.2, 128.1, 116.9, 114.7, 114.7, 78.7. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{12}H_{17}N_3S$, 225.0361; found 225.0351.

2-Phenylpyrazolo[1,5-*a*]pyrazine-3-carbonitrile (6a)



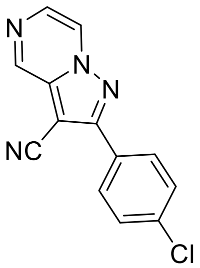
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **6a**. Yellow solid (42.9 mg, 65%), mp 121.4-122.6 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.49 (d, *J* = 4.6 Hz, 1H), 8.19 – 8.14 (m, 3H), 7.58 – 7.52 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 143.3, 139.0, 132.5, 130.9, 129.6, 129.3, 127.8, 122.1, 113.5, 81.0. HRMS (GC/QTOF) m/z: [M] $^{+}$ calcd for $C_{13}H_8N_4$, 220.0749; found 220.0745.

2-(*p*-Tolyl)pyrazolo[1,5-*a*]pyrazine-3-carbonitrile (6b)



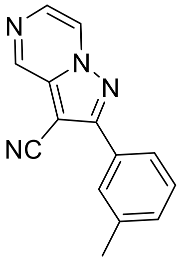
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **6b**. Yellow solid (42.1 mg, 60%), mp 123.5-124.8 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (s, 1H), 8.48 (d, *J* = 4.6 Hz, 1H), 8.17 (s, 1H), 8.06 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 143.1, 141.3, 132.4, 130.0, 127.6, 126.8, 122.1, 113.6, 80.7, 21.68. HRMS (GC/QTOF) m/z: [M] $^{+}$ calcd for $C_{14}H_{10}N_4$, 234.0905; found 234.0902.

2-(4-Chlorophenyl)pyrazolo[1,5-*a*]pyrazine-3-carbonitrile (6c)



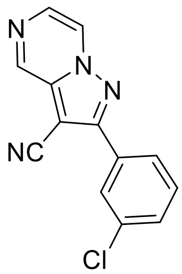
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **6c**. Yellow solid (41.9 mg, 55%), mp 131.2-133.6 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.48 (s, 1H), 8.20 (s, 1H), 8.15 – 8.07 (m, 2H), 7.55 – 7.46 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 143.3, 138.9, 137.1, 132.7, 129.6, 129.0, 128.1, 122.1, 113.3, 80.9. HRMS (GC/QTOF) m/z: [M] $^{+}$ calcd for $C_{13}H_7ClN_4$, 254.0359; found 254.0351.

2-(*m*-Tolyl)pyrazolo[1,5-*a*]pyrazine-3-carbonitrile (6d)



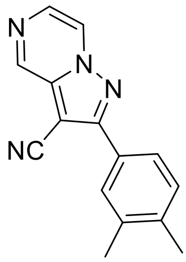
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **6d**. Yellow solid (40.0 mg, 57%), mp 126.7-127.9 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.48 (d, *J* = 4.7 Hz, 1H), 8.17 (d, *J* = 4.7 Hz, 1H), 7.96 (s, 2H), 7.44 (t, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 143.3, 139.1, 132.5, 131.7, 129.5, 129.2, 128.3, 124.9, 122.1, 113.5, 81.0, 21.6. HRMS (GC/QTOF) m/z: [M] $^{+}$ calcd for $C_{14}H_{10}N_4$, 234.0905; found 234.0902.

2-(3-Chlorophenyl)pyrazolo[1,5-*a*]pyrazine-3-carbonitrile (6e)



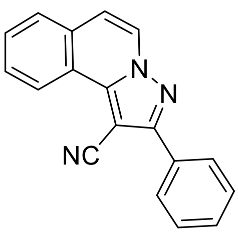
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **6e**. Yellow solid (44.2 mg, 58%), mp 133.4-134.9 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (s, 1H), 8.53 – 8.46 (m, 1H), 8.23 – 8.19 (m, 1H), 8.15 (s, 1H), 8.10 – 8.05 (m, 1H), 7.52 – 7.48 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 143.4, 135.4, 132.8, 131.3, 130.9, 130.6, 127.7, 125.8, 113.1, 81.2. HRMS (GC/QTOF) m/z: [M] $^+$ calcd for $C_{13}H_{17}ClN_4$, 254.0359; found 254.0358.

2-(3,4-Dimethylphenyl)pyrazolo[1,5-*a*]pyrazine-3-carbonitrile (6f)



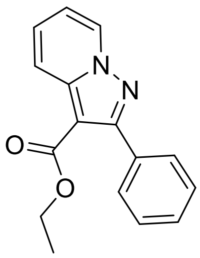
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **6f**. Yellow solid (39.4 mg, 53%), mp 136.3-137.2 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (s, 1H), 8.47 (d, *J* = 4.6 Hz, 1H), 8.15 (d, *J* = 4.6 Hz, 1H), 7.95 – 7.87 (m, 2H), 7.31 (d, *J* = 7.8 Hz, 1H), 2.38 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 143.1, 140.0, 139.0, 137.8, 132.4, 130.5, 128.7, 127.1, 125.2, 122.1, 113.6, 80.7, 20.0. HRMS (GC/QTOF) m/z: [M] $^+$ calcd for $C_{15}H_{12}N_4$, 248.1062; found 248.1056.

2-Phenylpyrazolo[5,1-*a*]isoquinoline-1-carbonitrile (7')



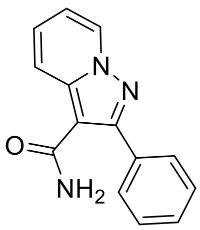
Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **7'**. Yellow solid (48.4 mg, 60%), mp 142.3-144.2 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 – 8.86 (m, 1H), 8.32 (d, *J* = 7.4 Hz, 1H), 8.17 (d, *J* = 6.7 Hz, 2H), 7.86 – 7.82 (m, 1H), 7.75 – 7.71 (m, 2H), 7.57 – 7.46 (m, 3H), 7.24 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 141.7, 130.6, 130.2, 130.1, 130.0, 129.1, 128.9, 127.7, 127.5, 126.1, 124.1, 123.3, 116.7, 115.1, 81.6. HRMS (GC/QTOF) m/z: [M] $^+$ calcd for $C_{18}H_{11}N_3$, 269.0953; found 269.0943.

Ethyl 2-phenylpyrazolo[1,5-*a*]pyridine-3-carboxylate (8)



Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **8**. Yellow solid (43.9 mg, 55%), mp 145.1-146.4 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 6.9 Hz, 1H), 8.09 (d, *J* = 8.9 Hz, 1H), 7.71 – 7.68 (m, 2H), 7.37 – 7.32 (m, 3H), 7.29 – 7.23 (m, 1H), 6.80 (t, *J* = 6.8 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 156.9, 142.6, 132.5, 129.9, 128.8, 128.7, 127.7, 127.2, 119.7, 113.8, 100.7, 59.8, 14.2. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{18}H_{11}N_3$, 266.1055, found 266.1051.

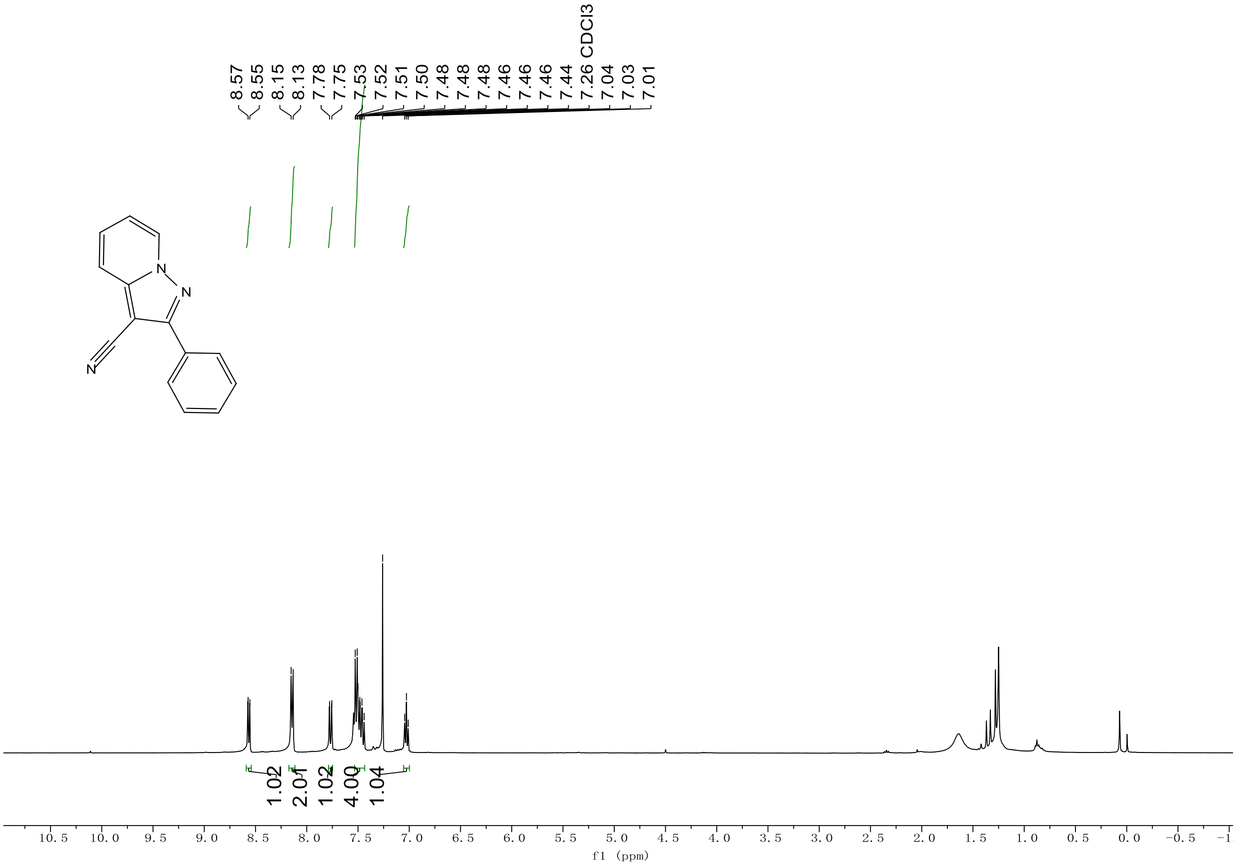
2-Phenylpyrazolo[1,5-*a*]pyridine-3-carboxamide (9)

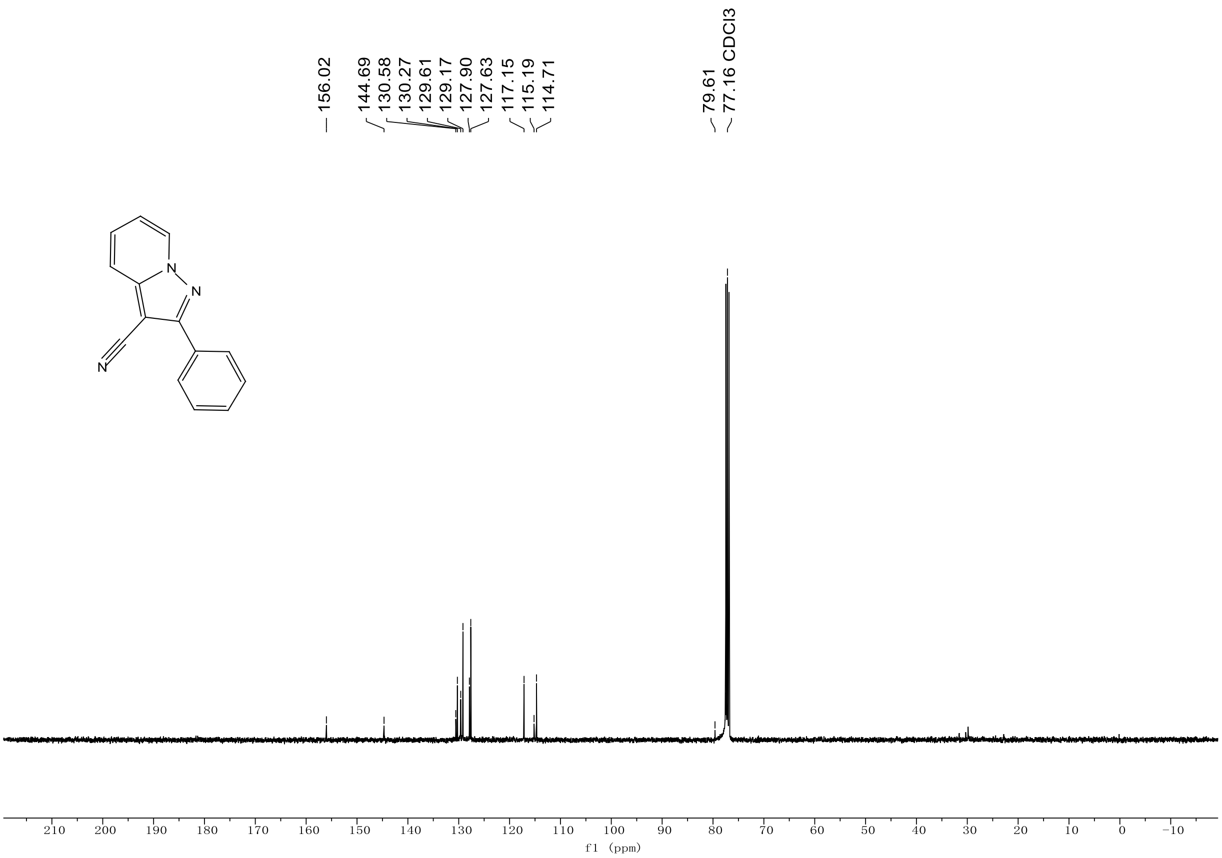


Flash column chromatography on silica gel (eluent: PE/EA = 7/1, v/v) to afford **9**. Yellow solid (32.0 mg, 45%), mp 145.1-146.4 ºC. ^{1}H NMR (400 MHz, DMSO-d6) δ 8.77 (d, *J* = 6.9 Hz, 1H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.81 (d, *J* = 7.2 Hz, 2H), 7.53 – 7.40 (m, 5H), 7.05 (t, *J* = 6.9 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d6) δ 165.1, 152.0, 140.4, 132.5, 128.9, 128.8, 128.5, 126.0, 118.3, 113.7, 105.4. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{14}H_{11}N_3O$, 237.0902; found 237.0893.

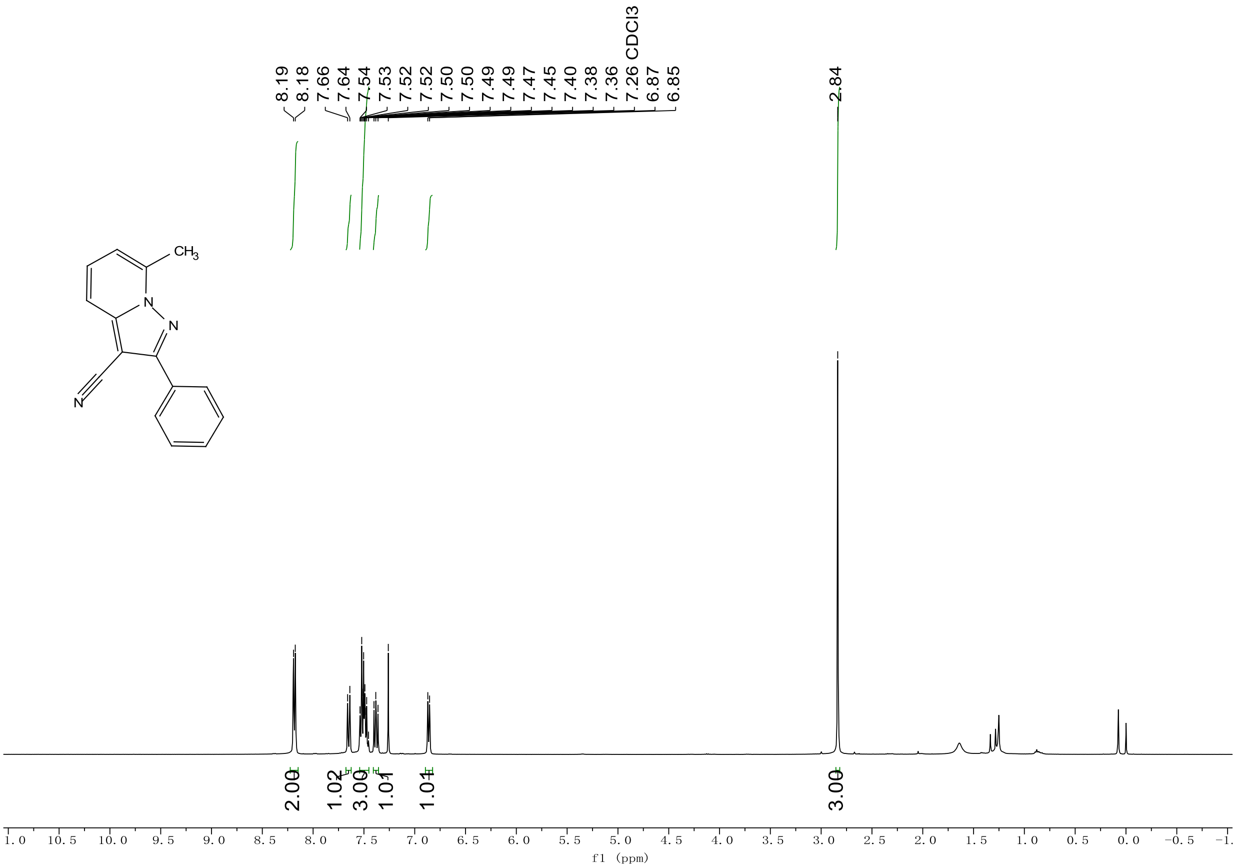
3. NMR spectra for new compounds

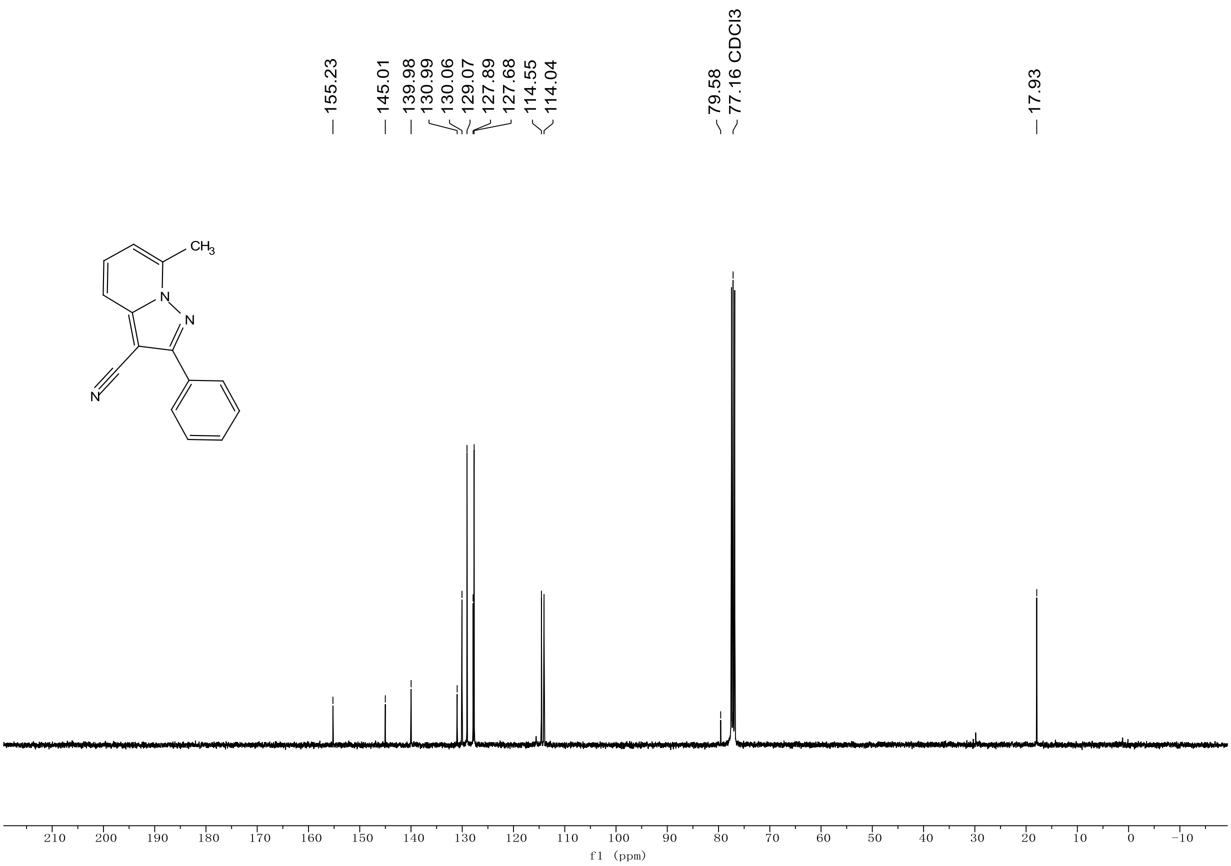
[1]H NMR (400 MHz, $CDCl_3$) and [13]C NMR (100 MHz, $CDCl_3$) spectrum of compound **3a**



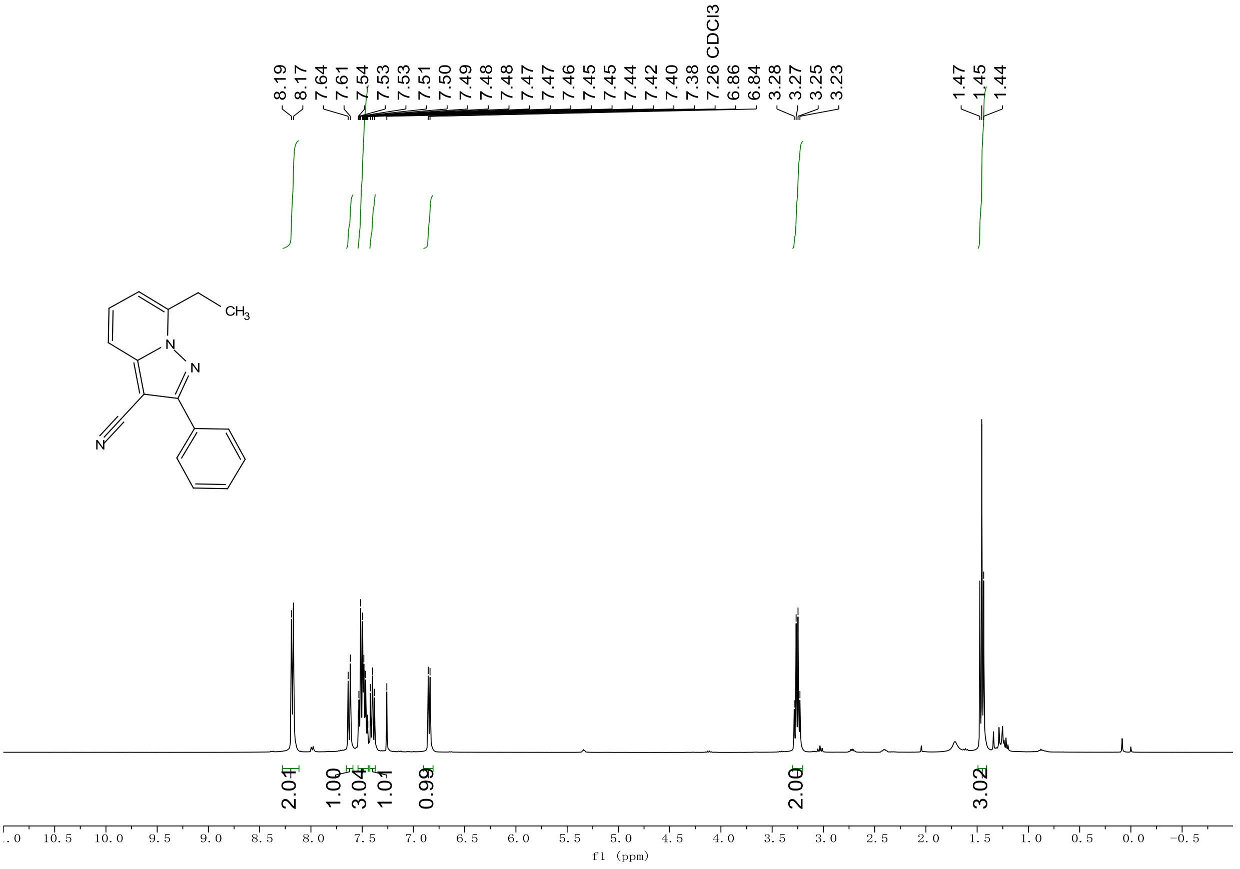


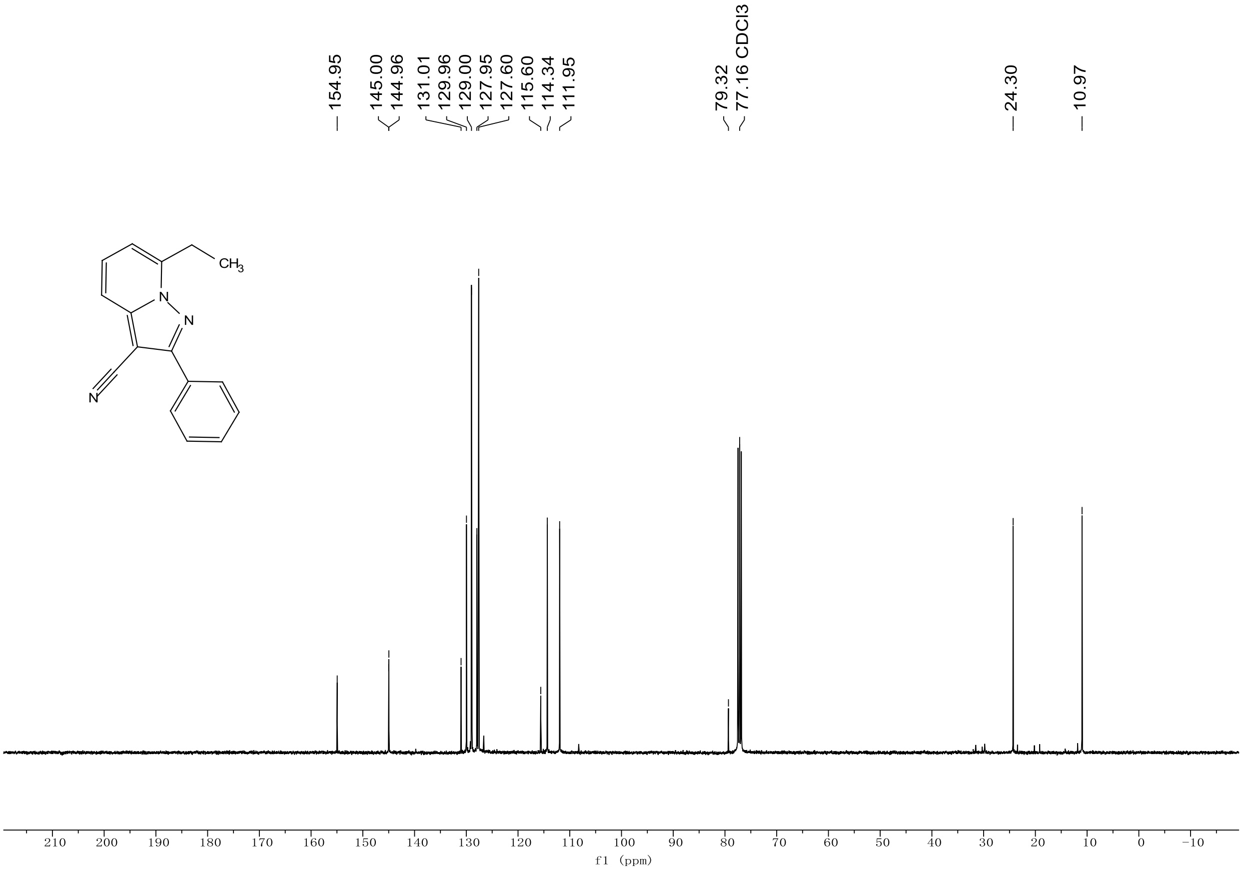
[1]H NMR (400 MHz, $CDCl_3$) and [13]C NMR (100 MHz, $CDCl_3$) spectrum of compound **3b**



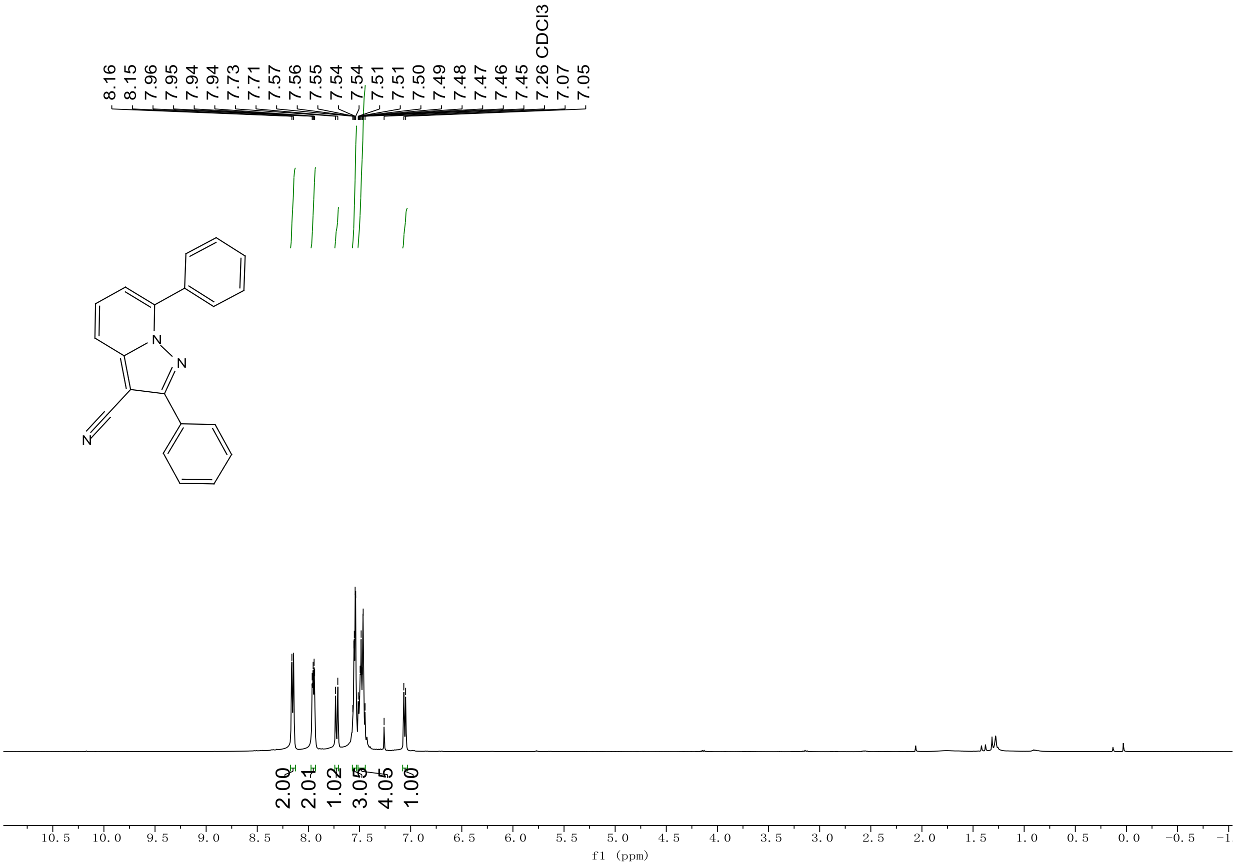


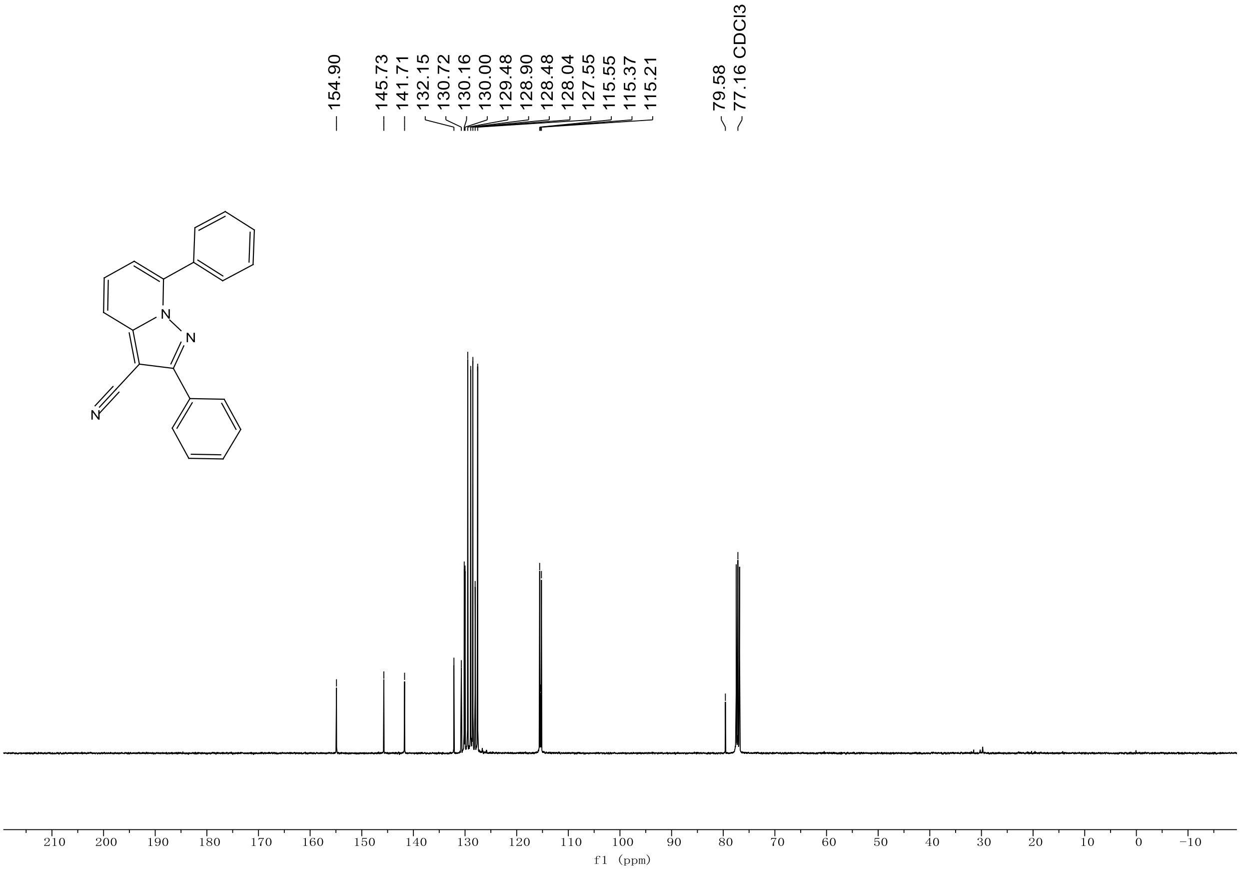
[1]H NMR (400 MHz, $CDCl_3$) and [13]C NMR (100 MHz, $CDCl_3$) spectrum of compound **3c**



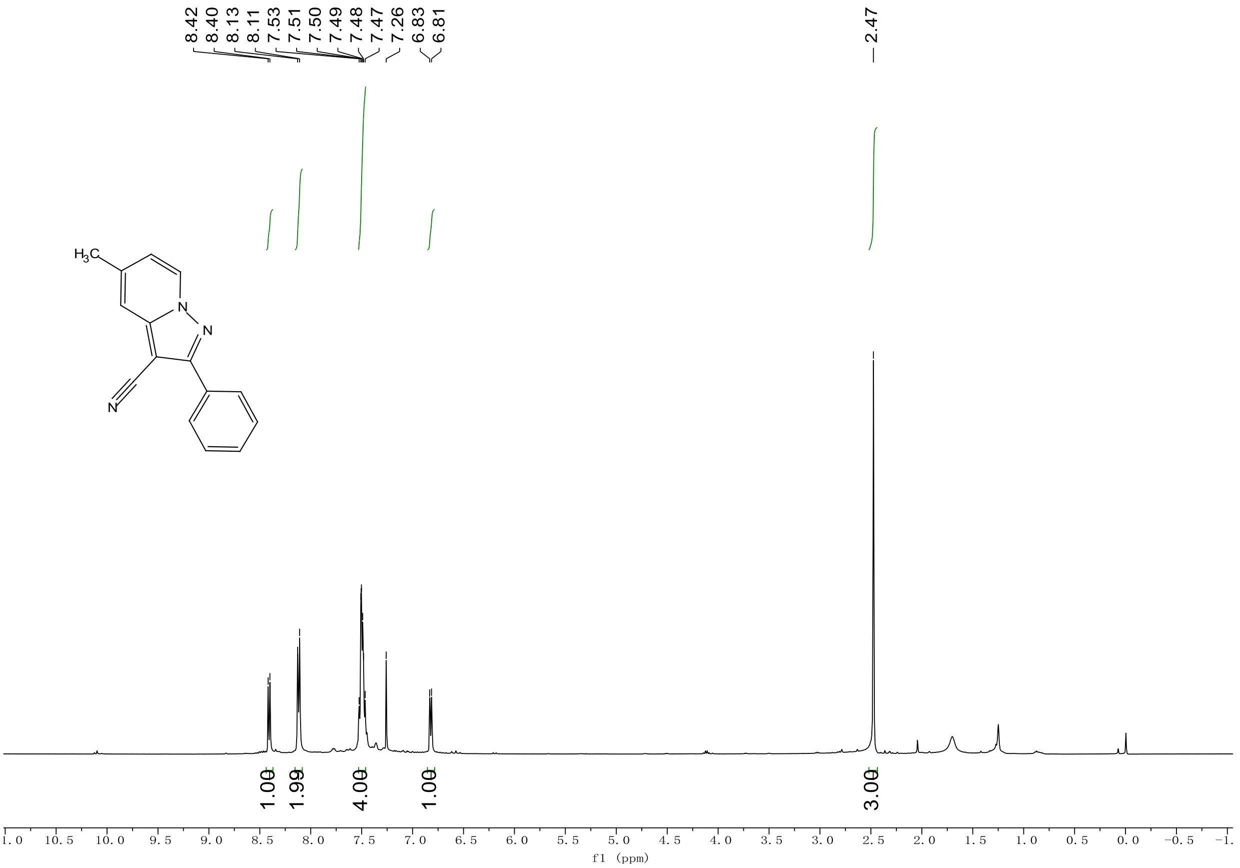


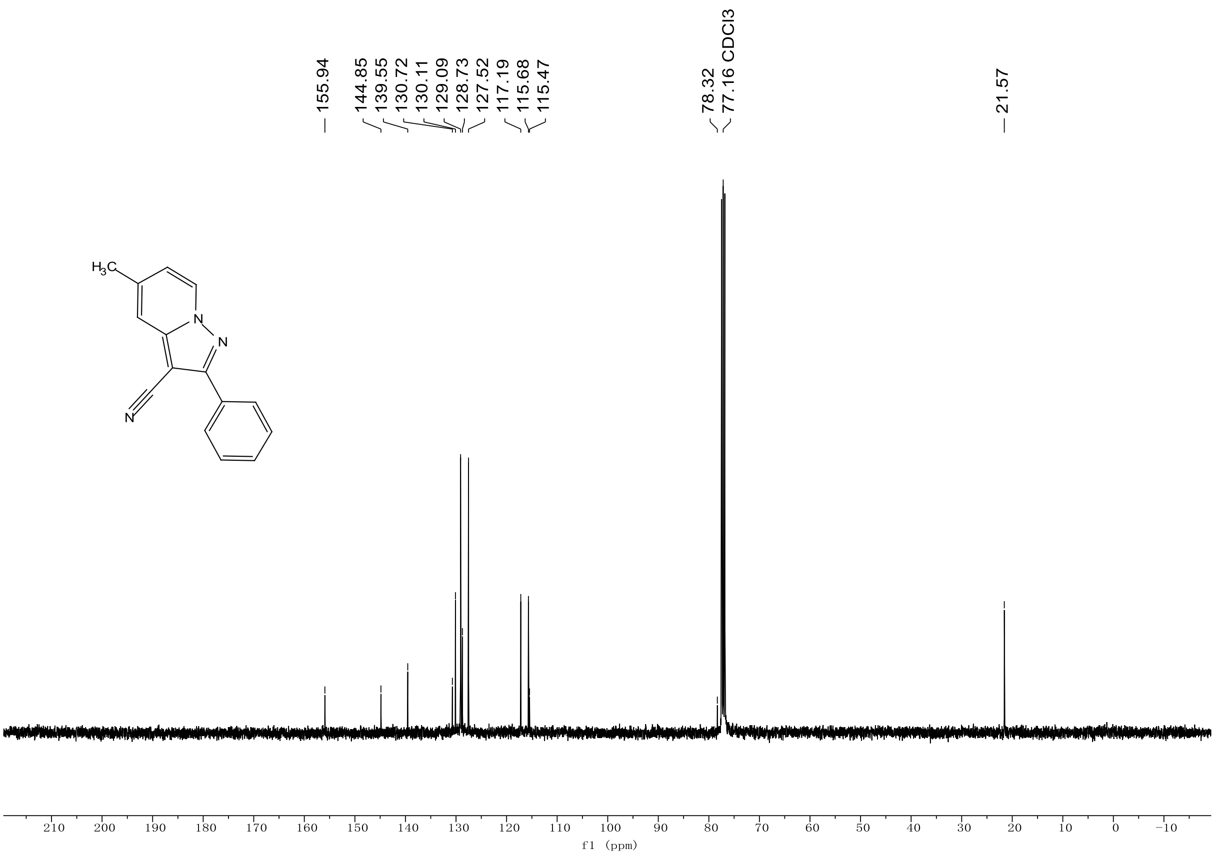
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3d**



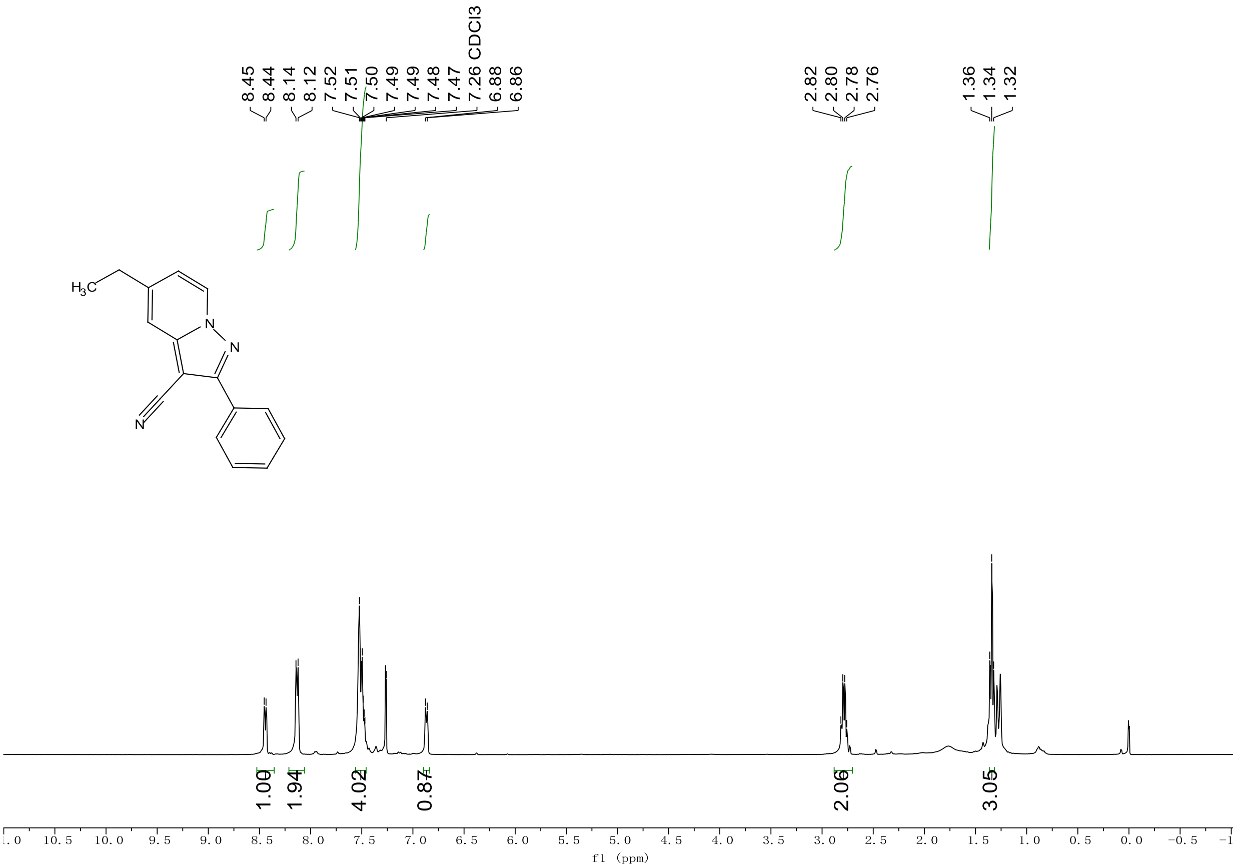


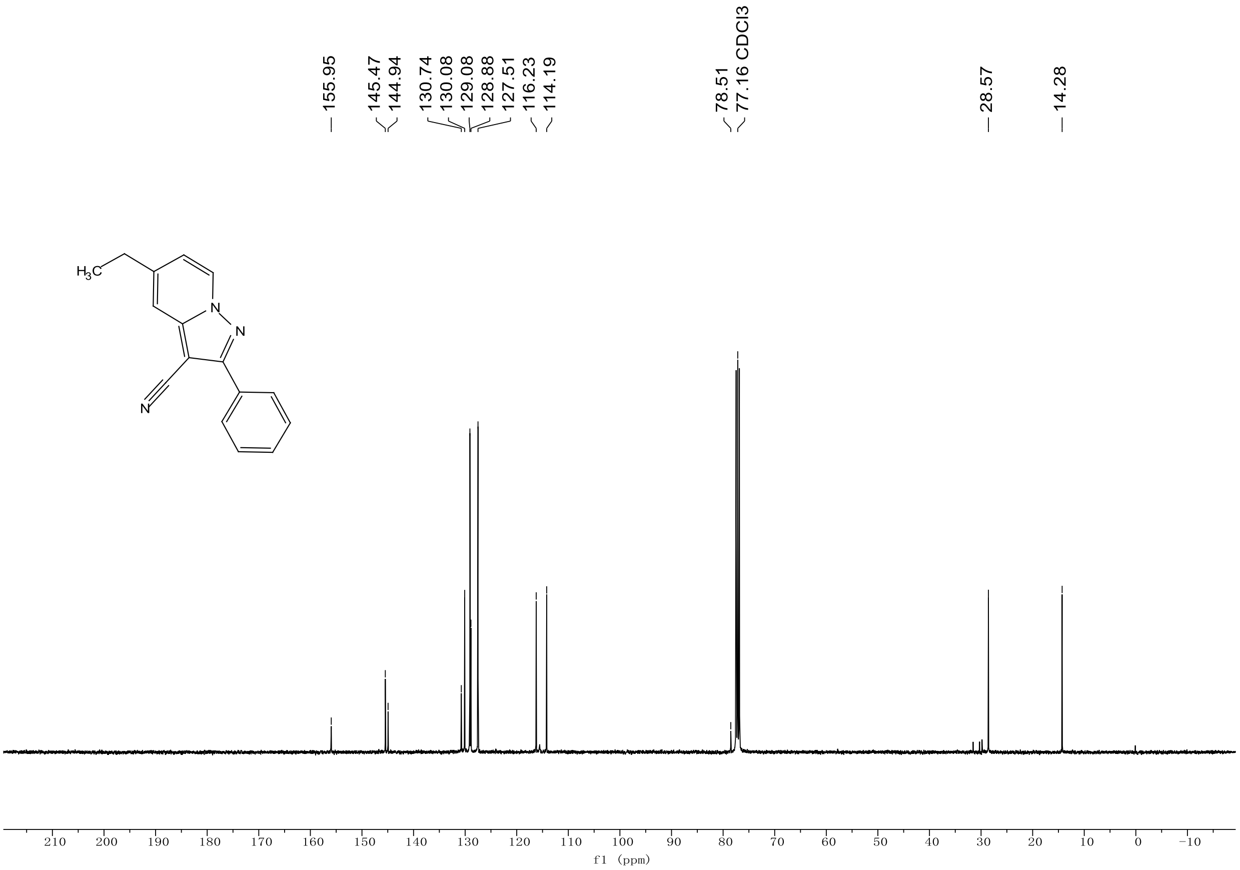
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3e**



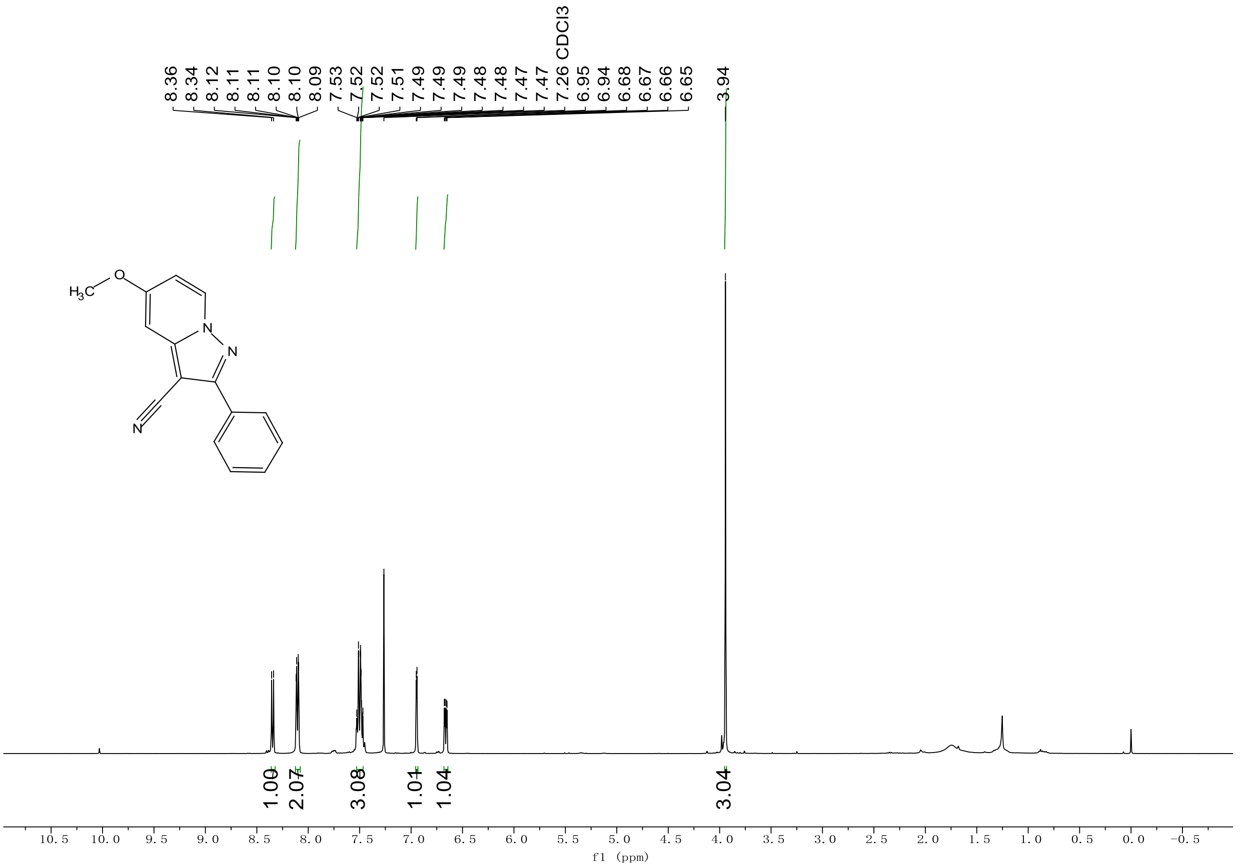


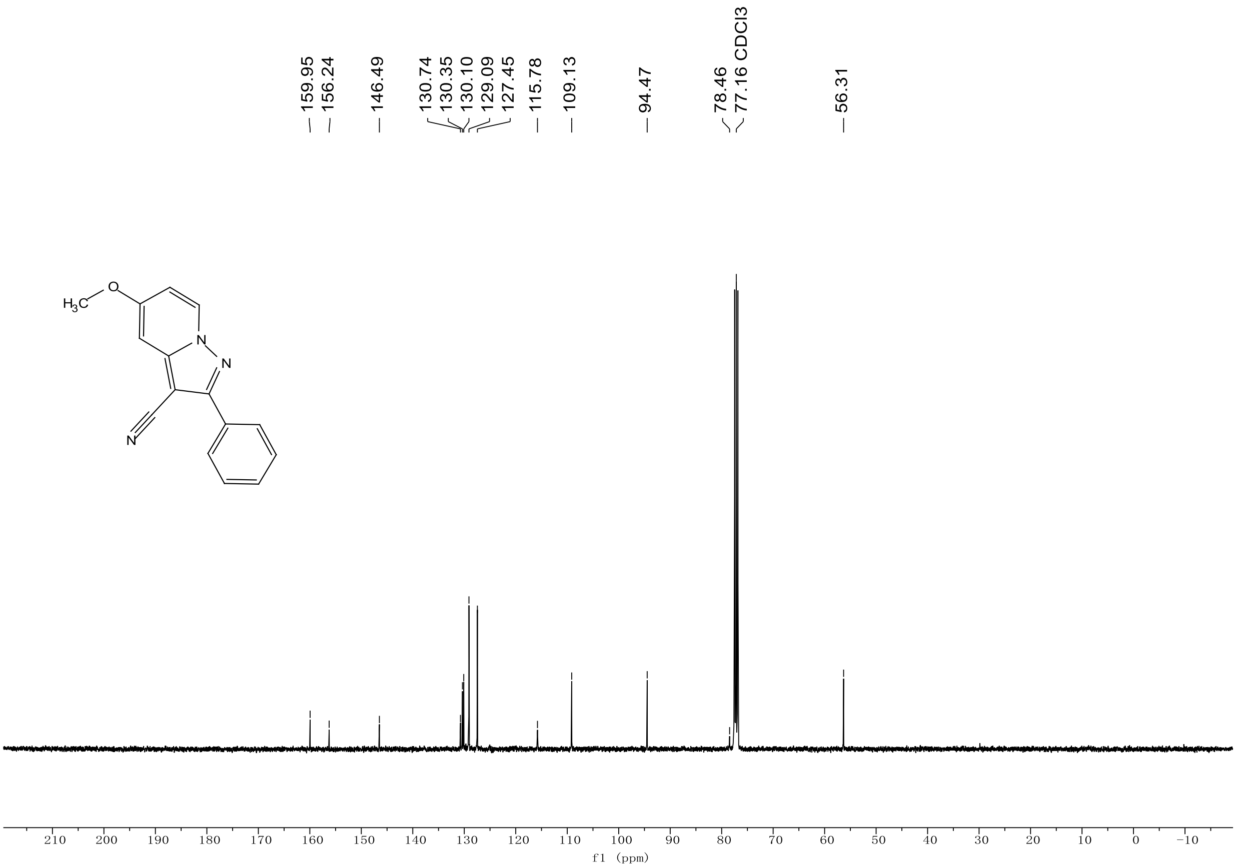
[1]H NMR (400 MHz, $CDCl_3$) and [13]C NMR (100 MHz, $CDCl_3$) spectrum of compound **3f**



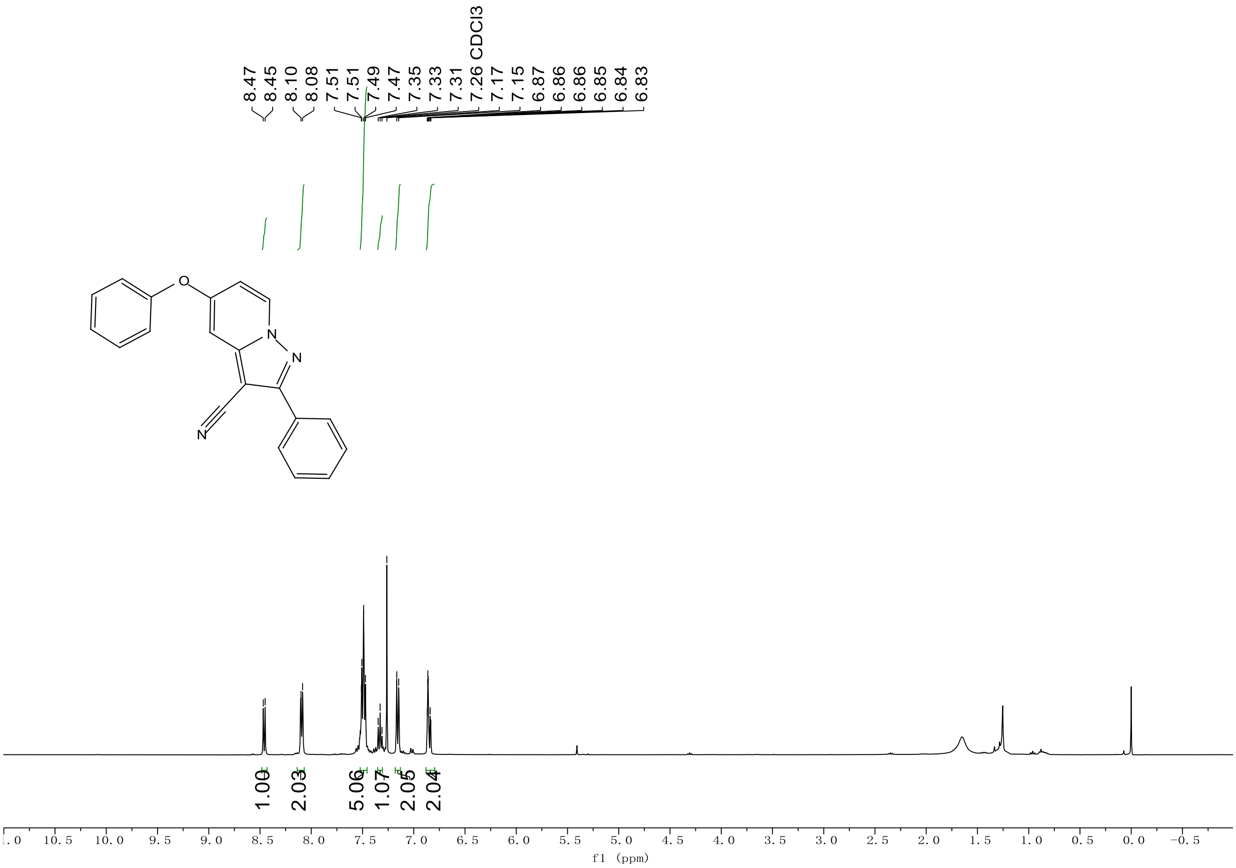


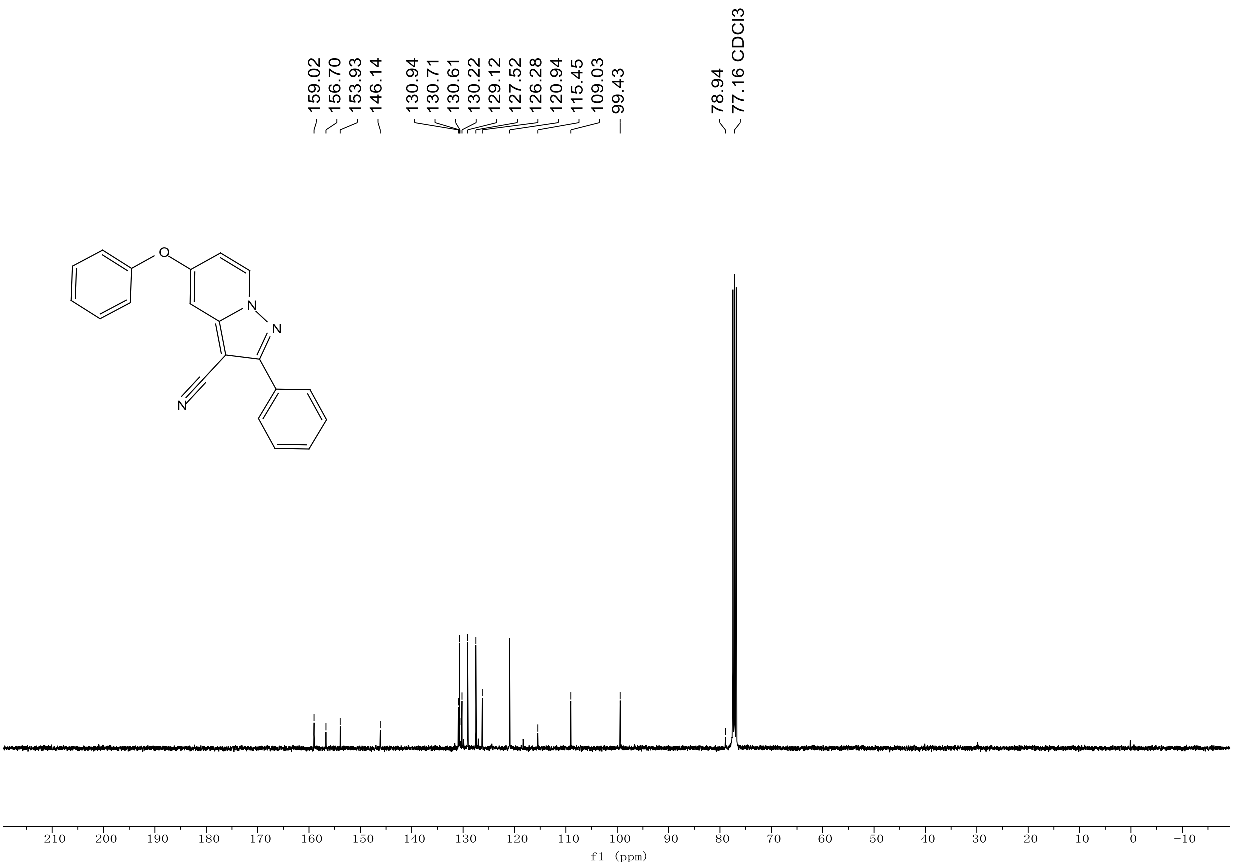
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3g**



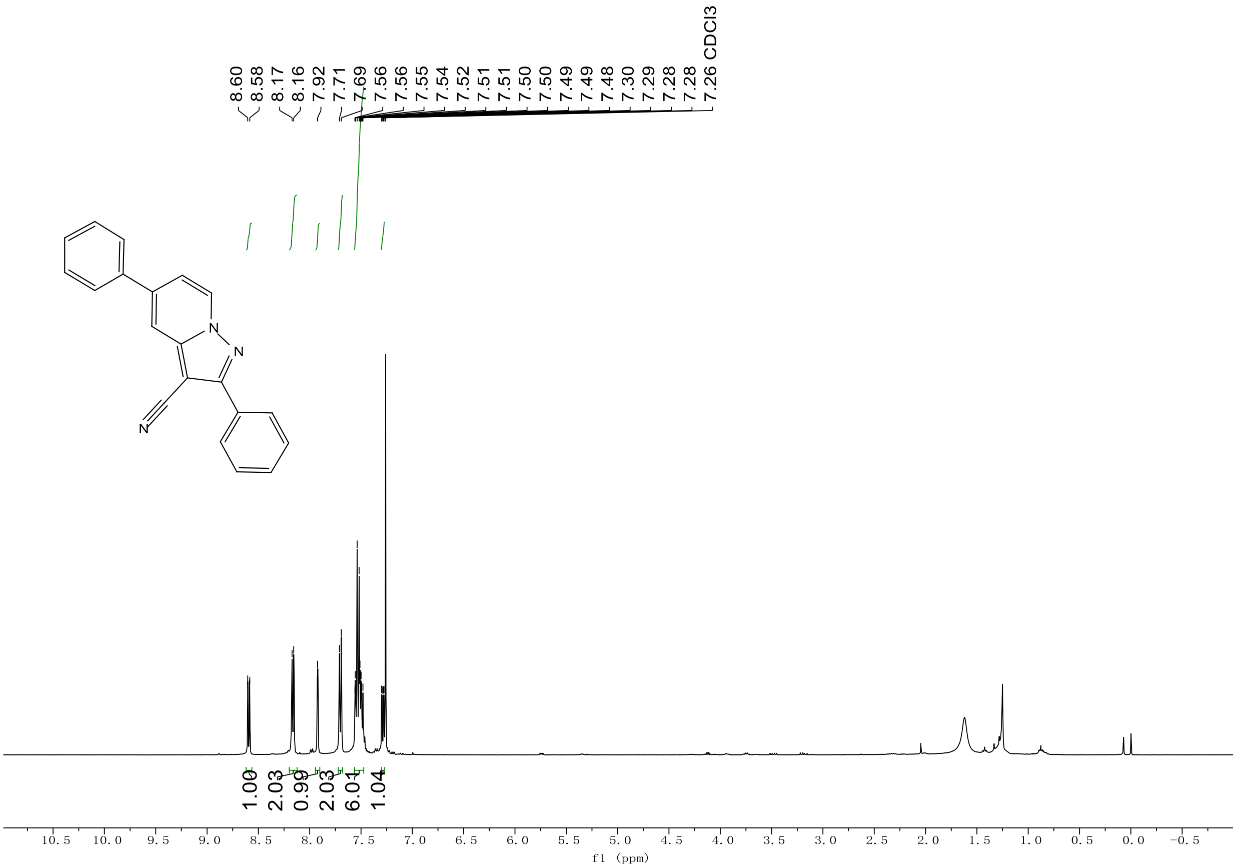


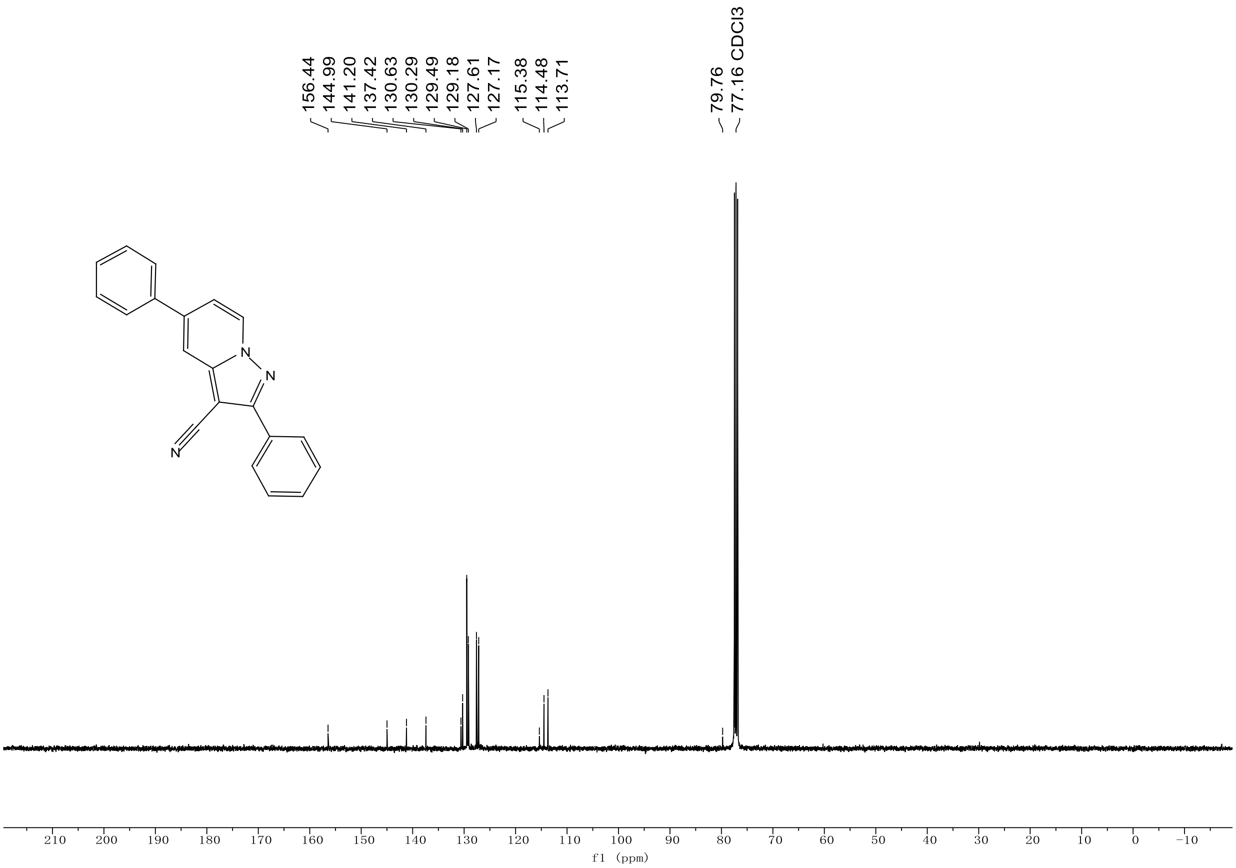
[1]H NMR (400 MHz, $CDCl_3$) and [13]C NMR (100 MHz, $CDCl_3$) spectrum of compound **3h**



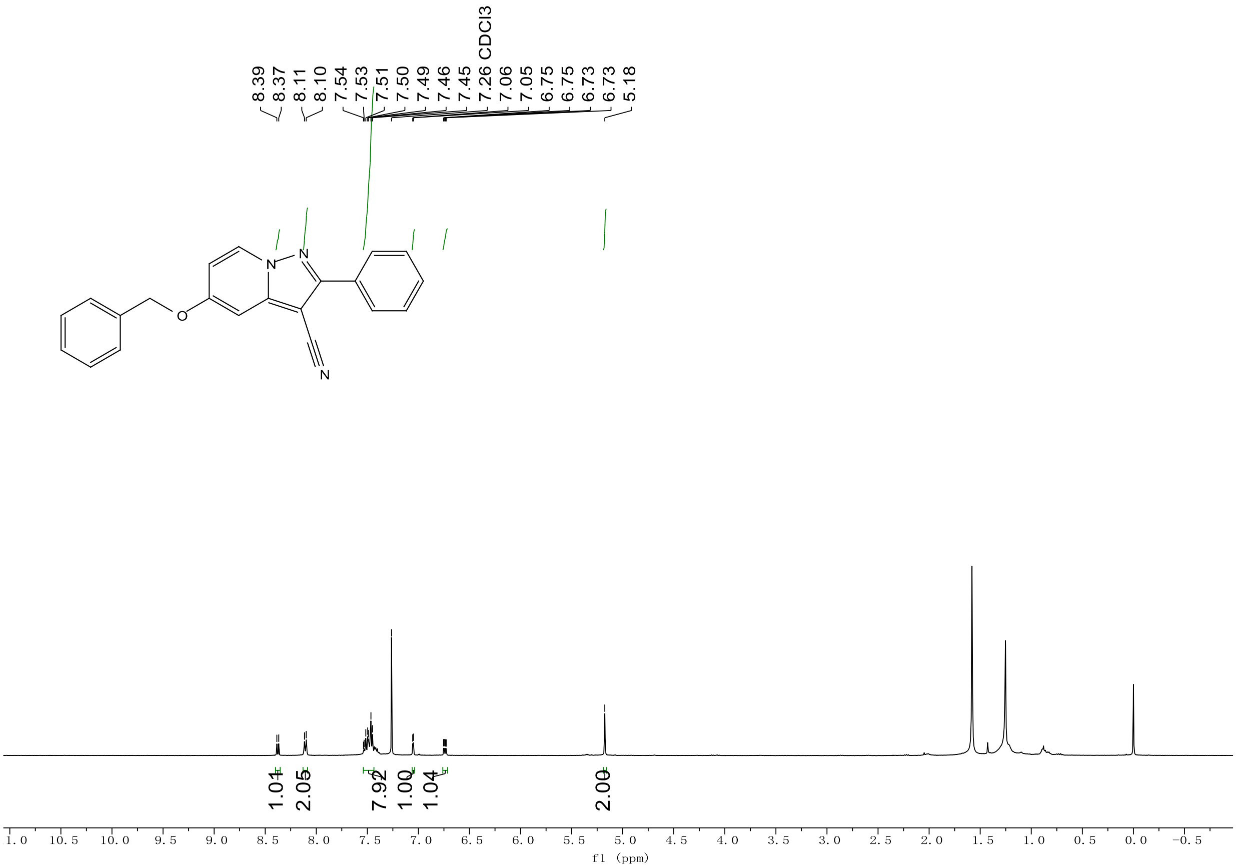


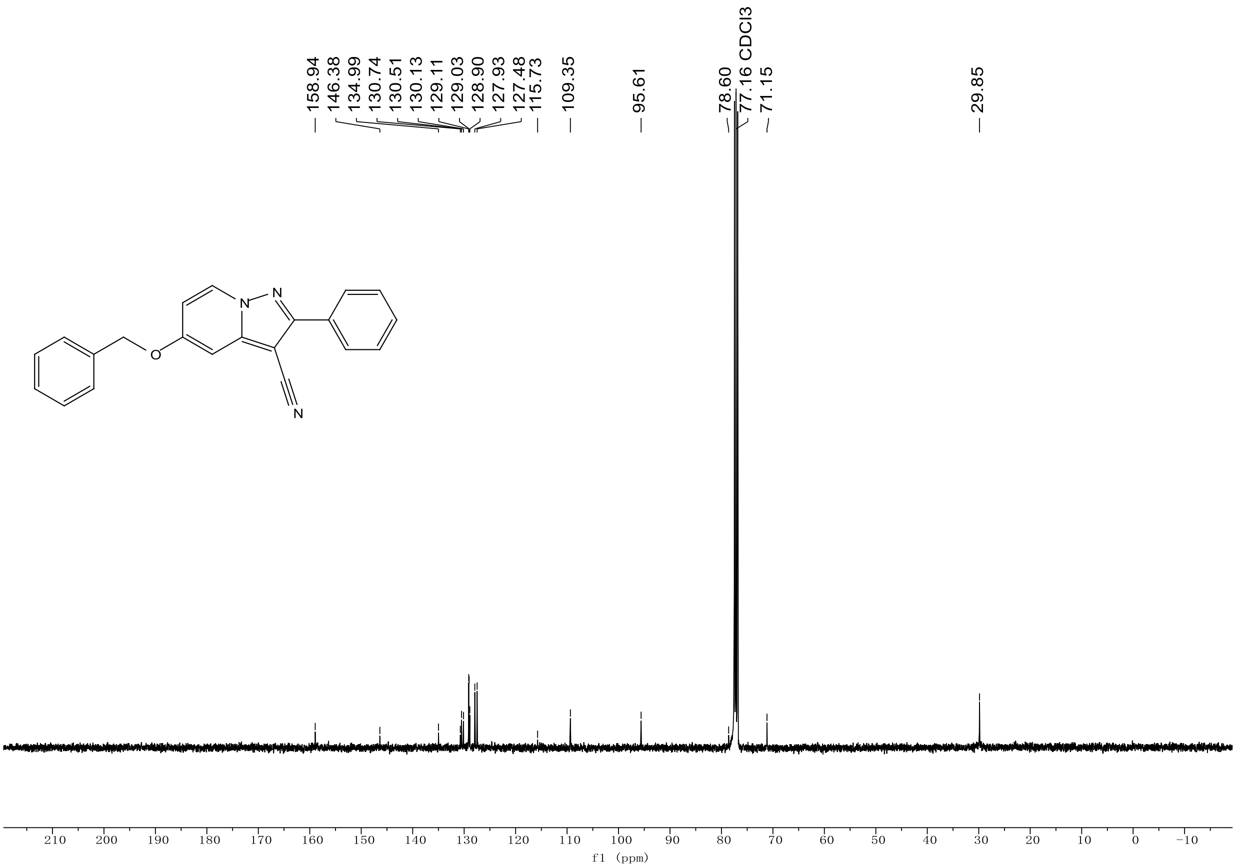
[1]H NMR (400 MHz, $CDCl_3$) and [13]C NMR (100 MHz, $CDCl_3$) spectrum of compound **3i**



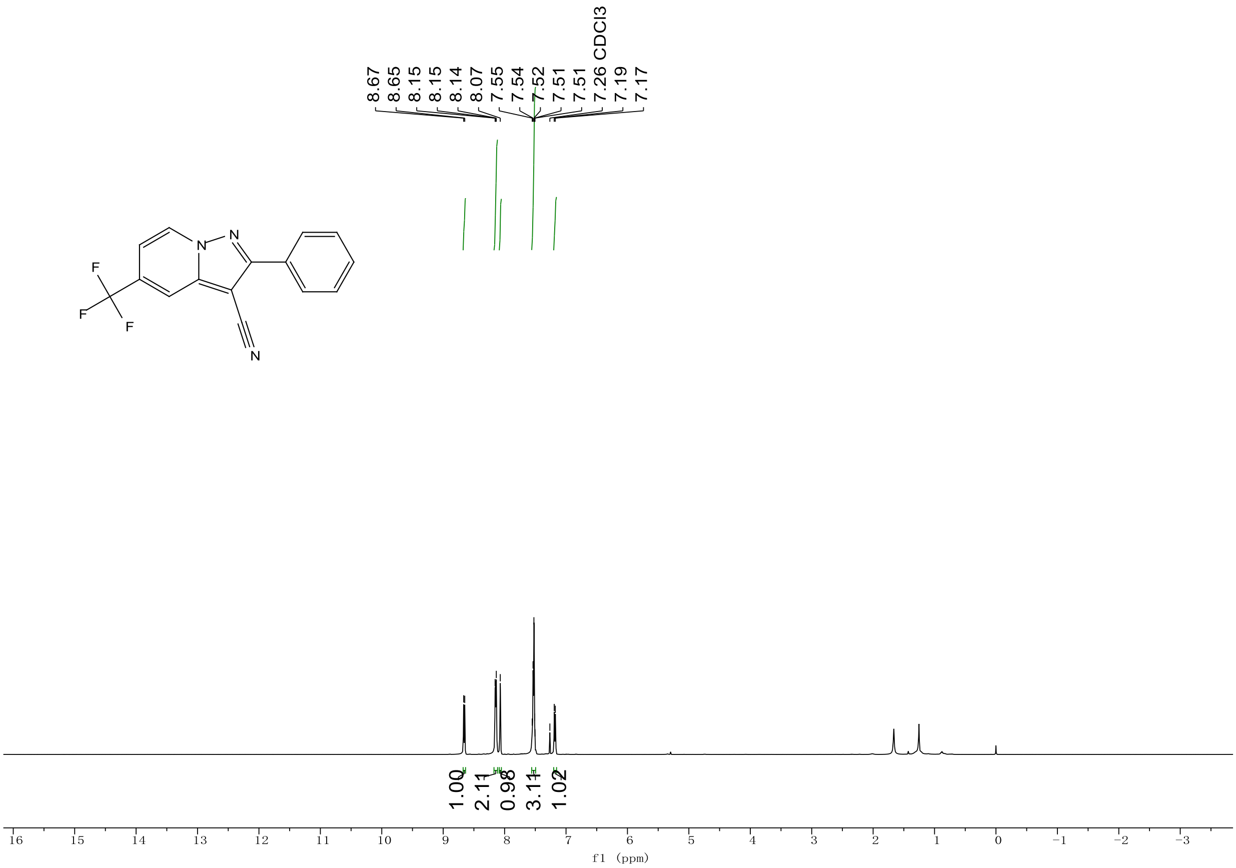


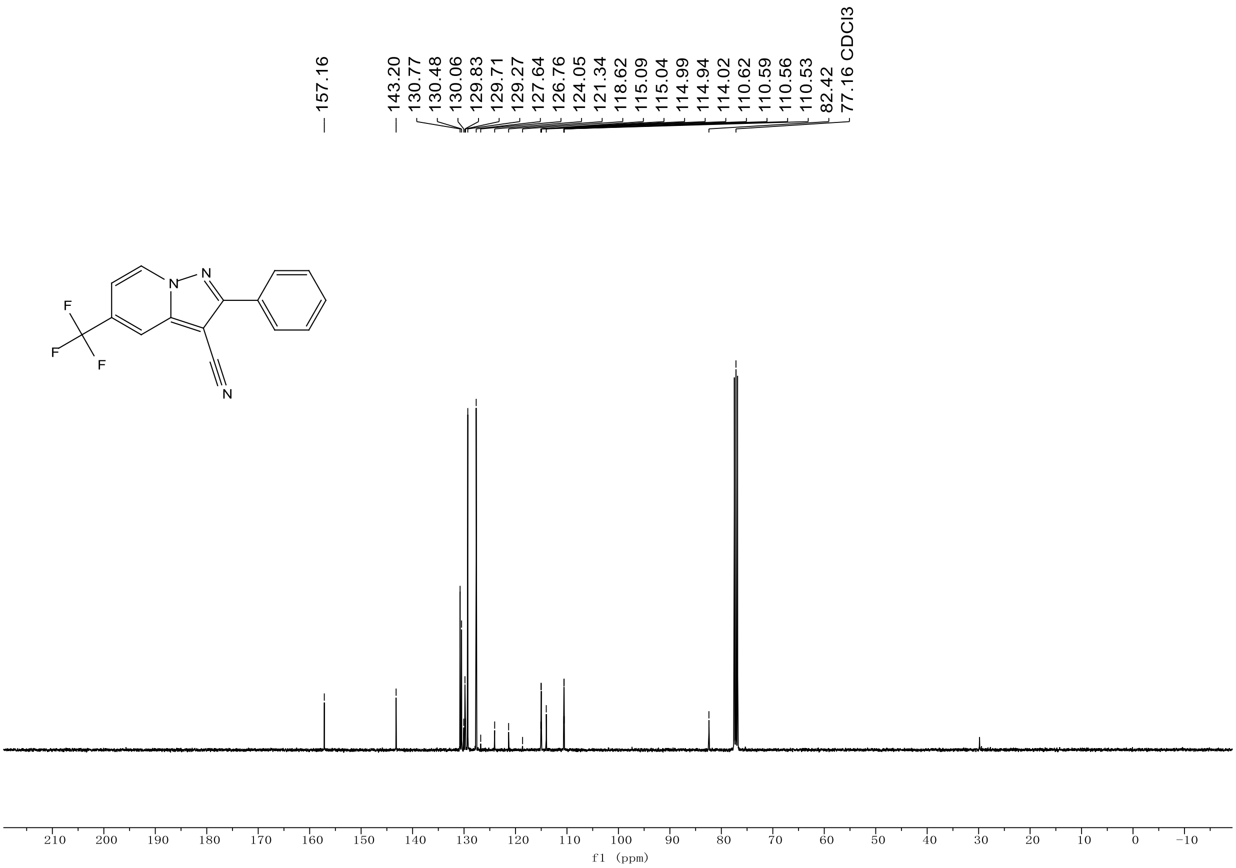
[1]H NMR (400 MHz, $CDCl_3$) and [13]C NMR (100 MHz, $CDCl_3$) spectrum of compound **3j**



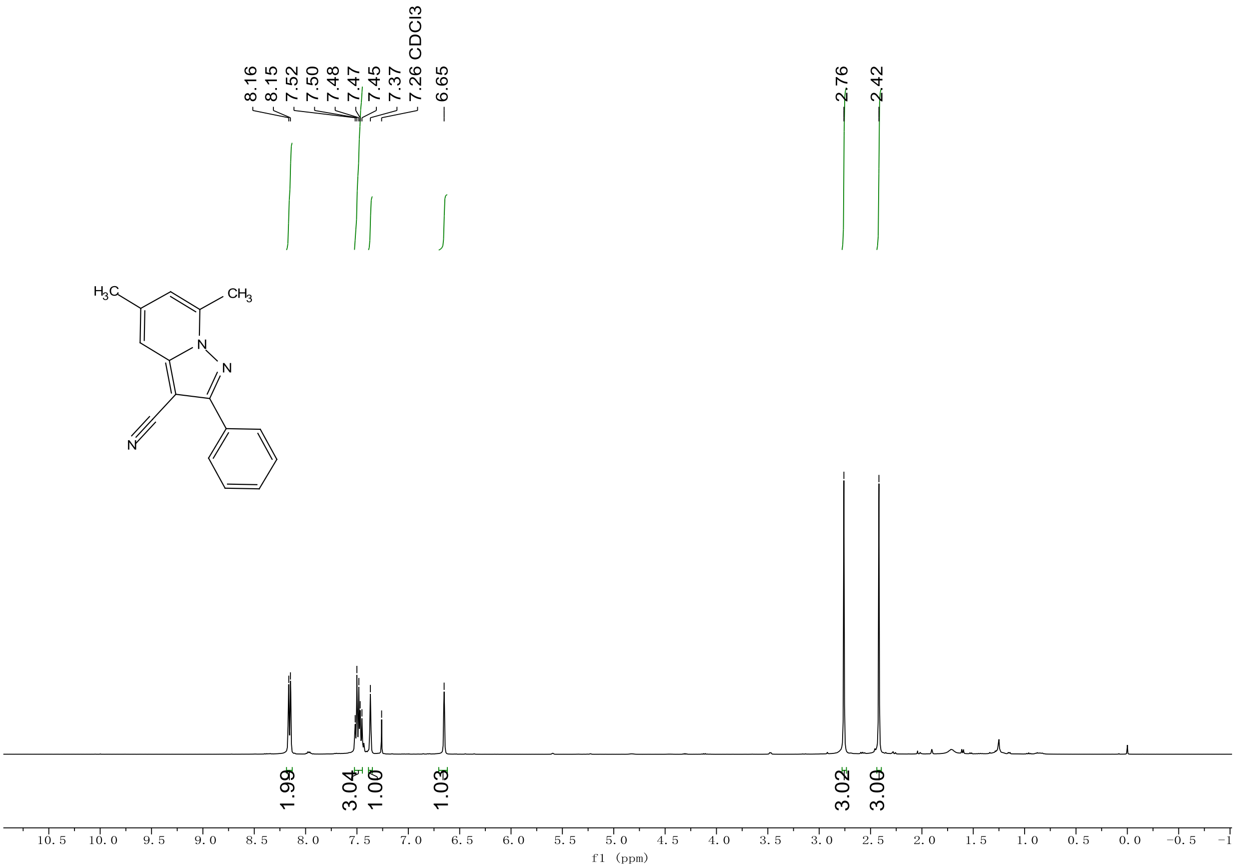


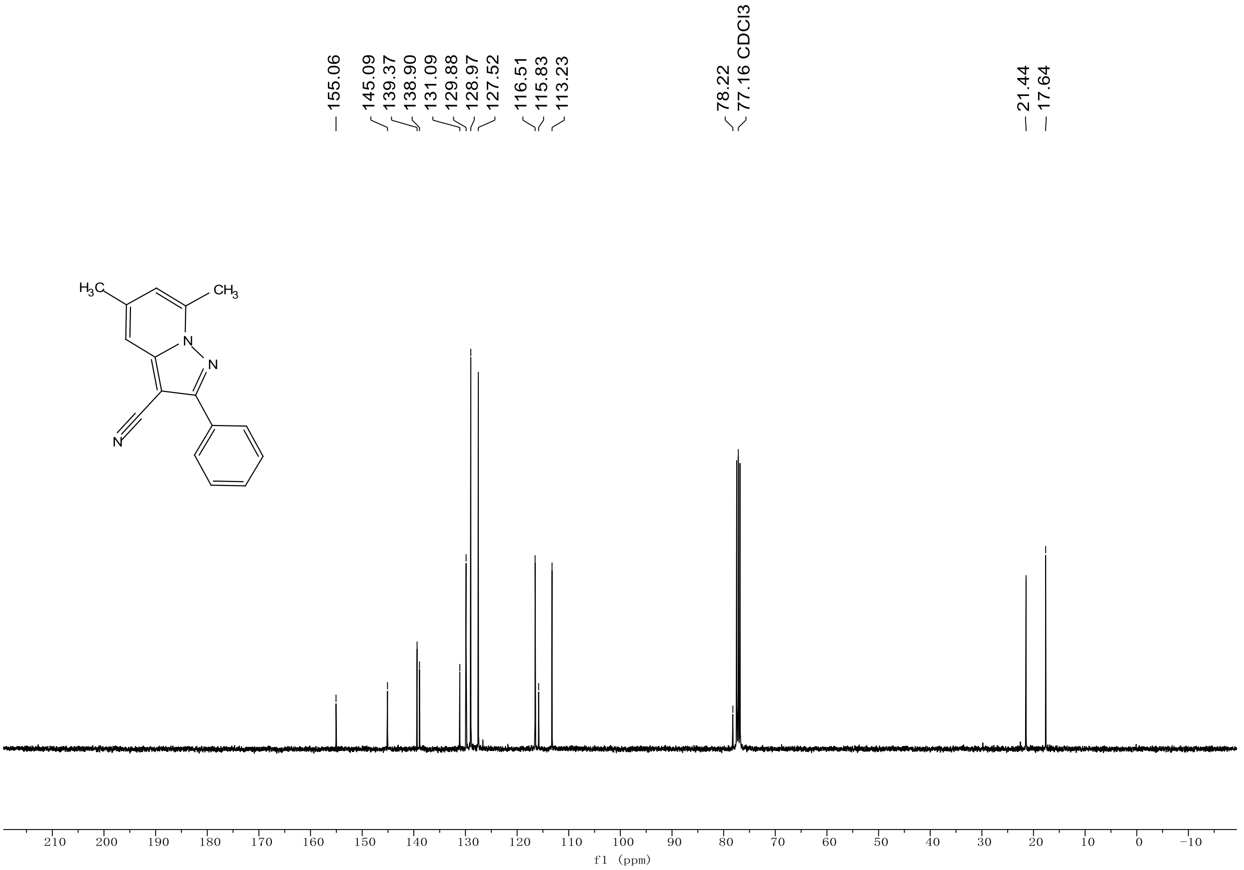
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3k**



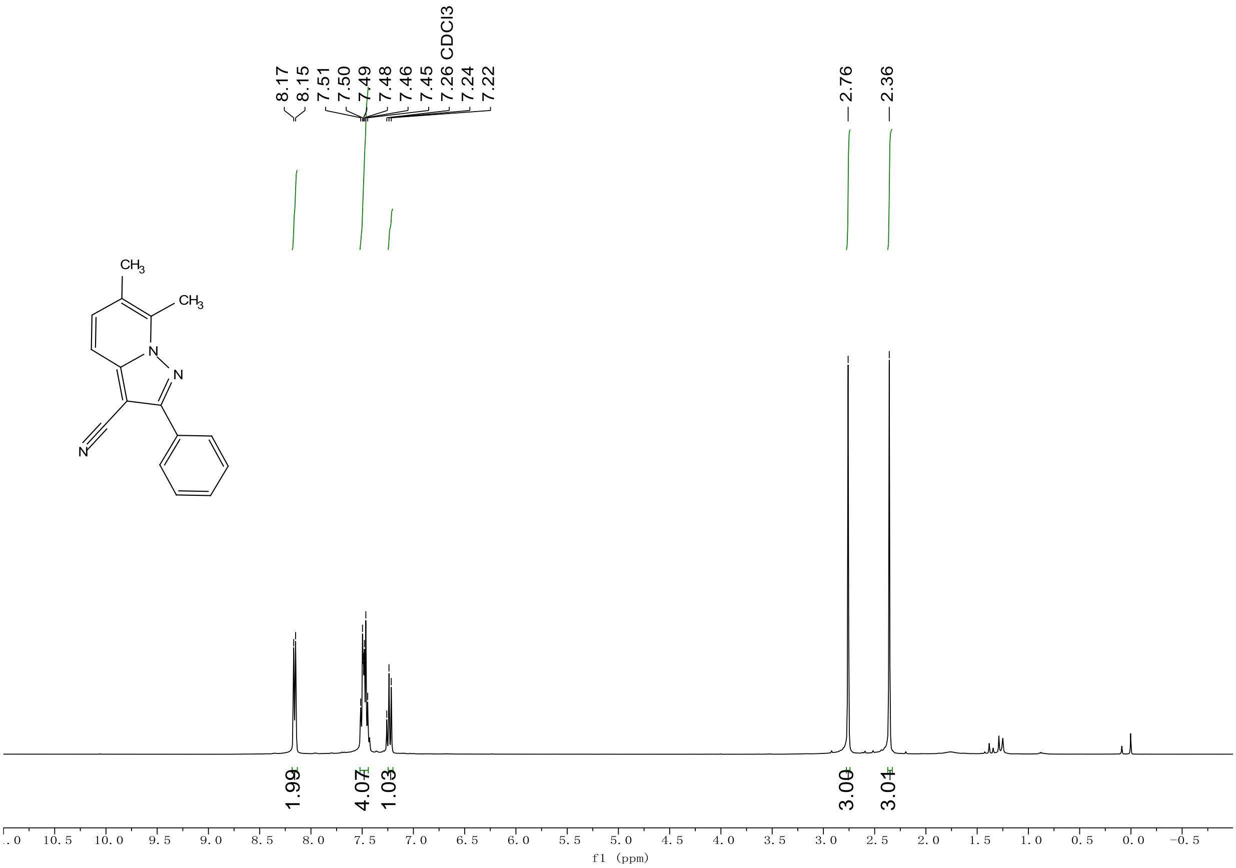


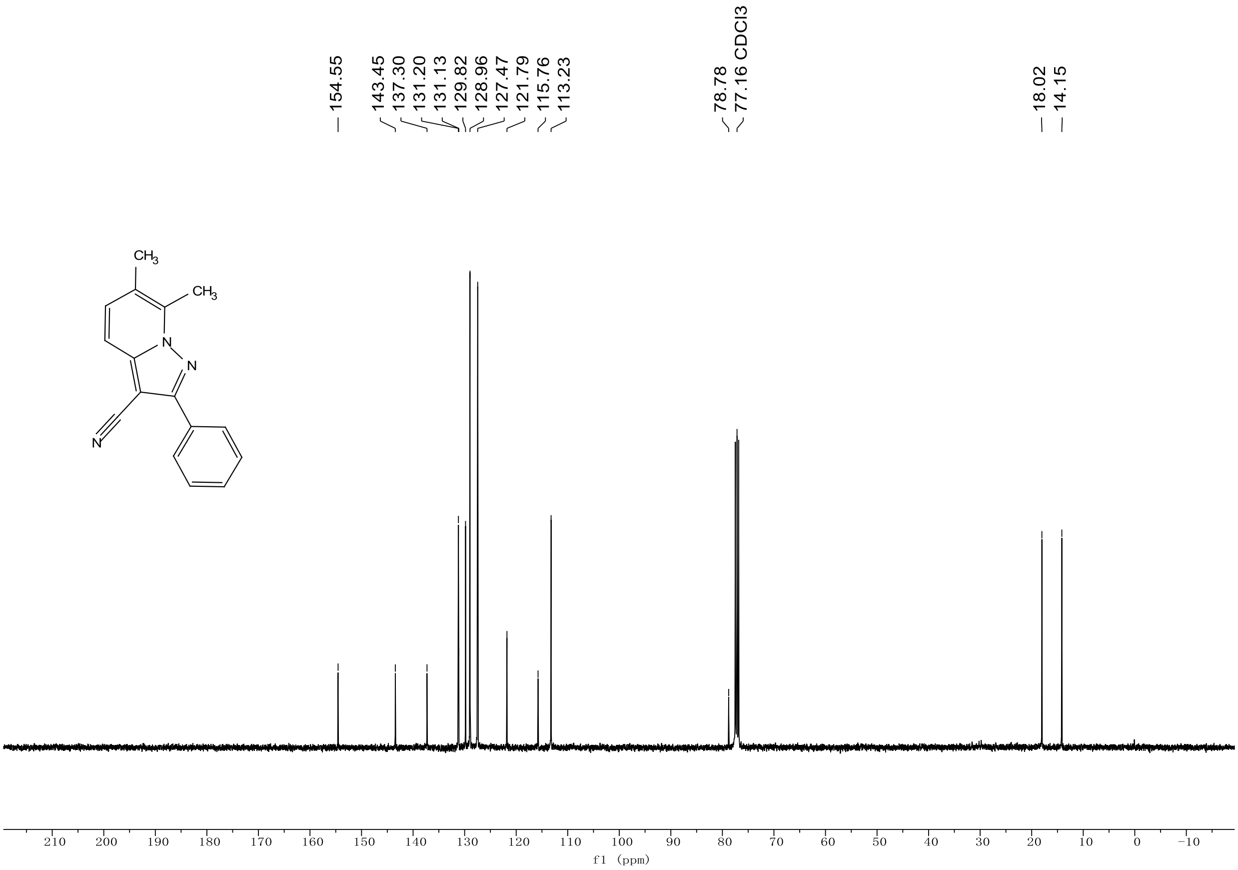
[1]H NMR (400 MHz, $CDCl_3$) and [13]C NMR (100 MHz, $CDCl_3$) spectrum of compound **3l**



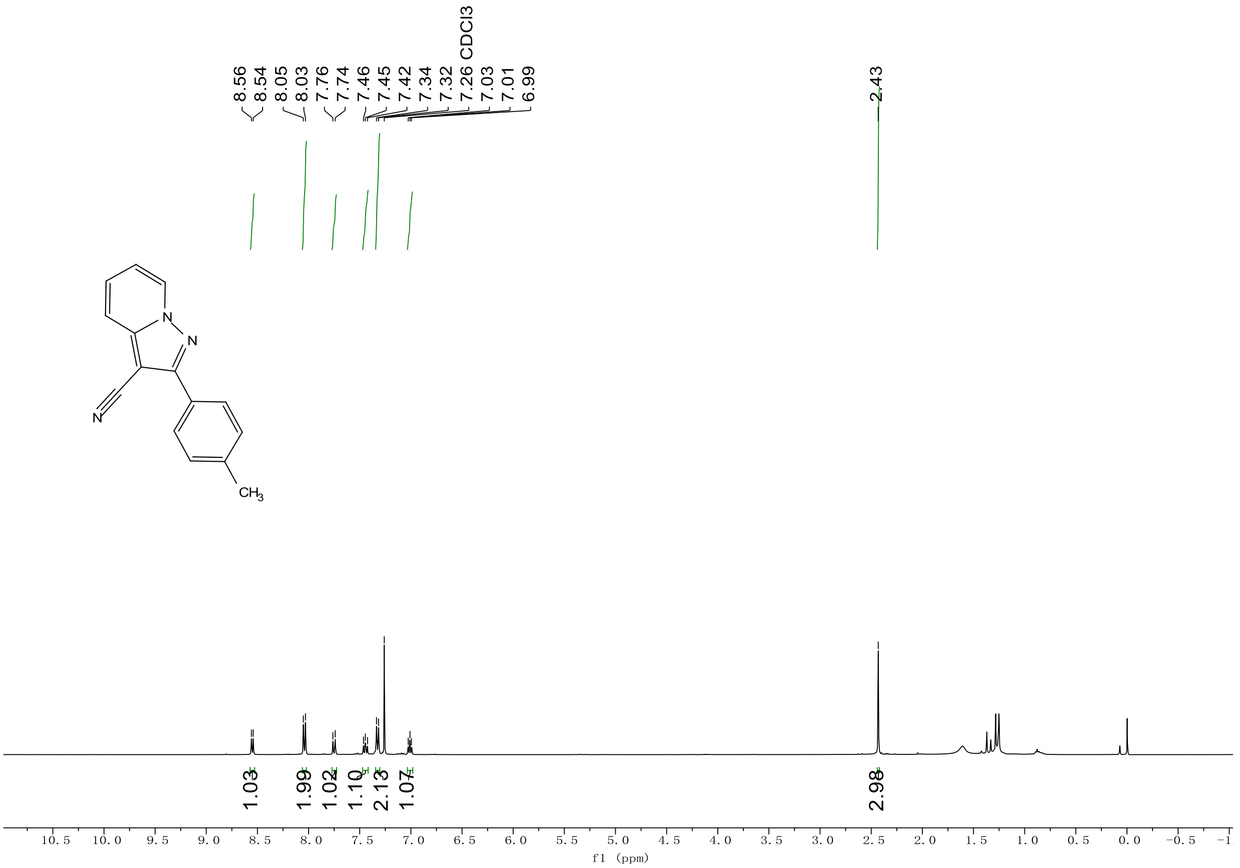


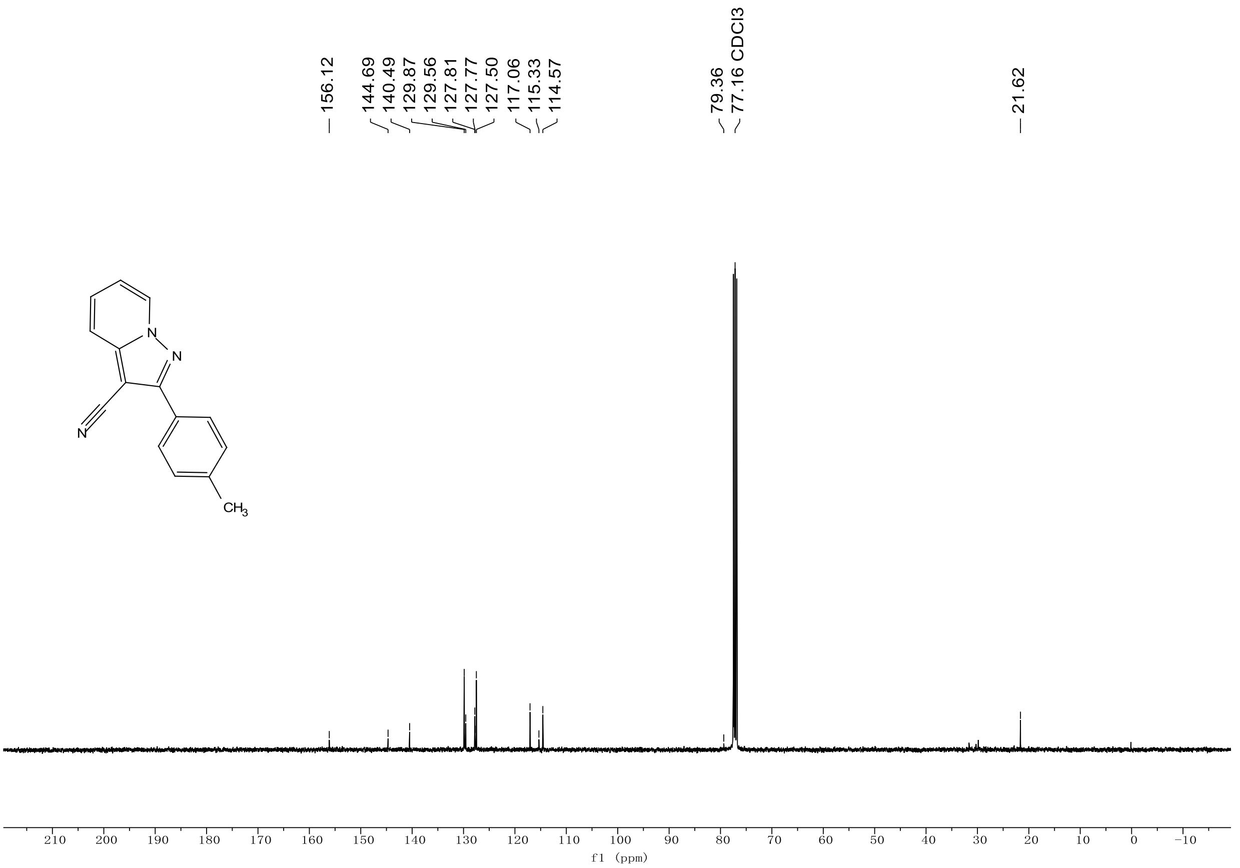
[1]H NMR (400 MHz, $CDCl_3$) and [13]C NMR (100 MHz, $CDCl_3$) spectrum of compound **3m**



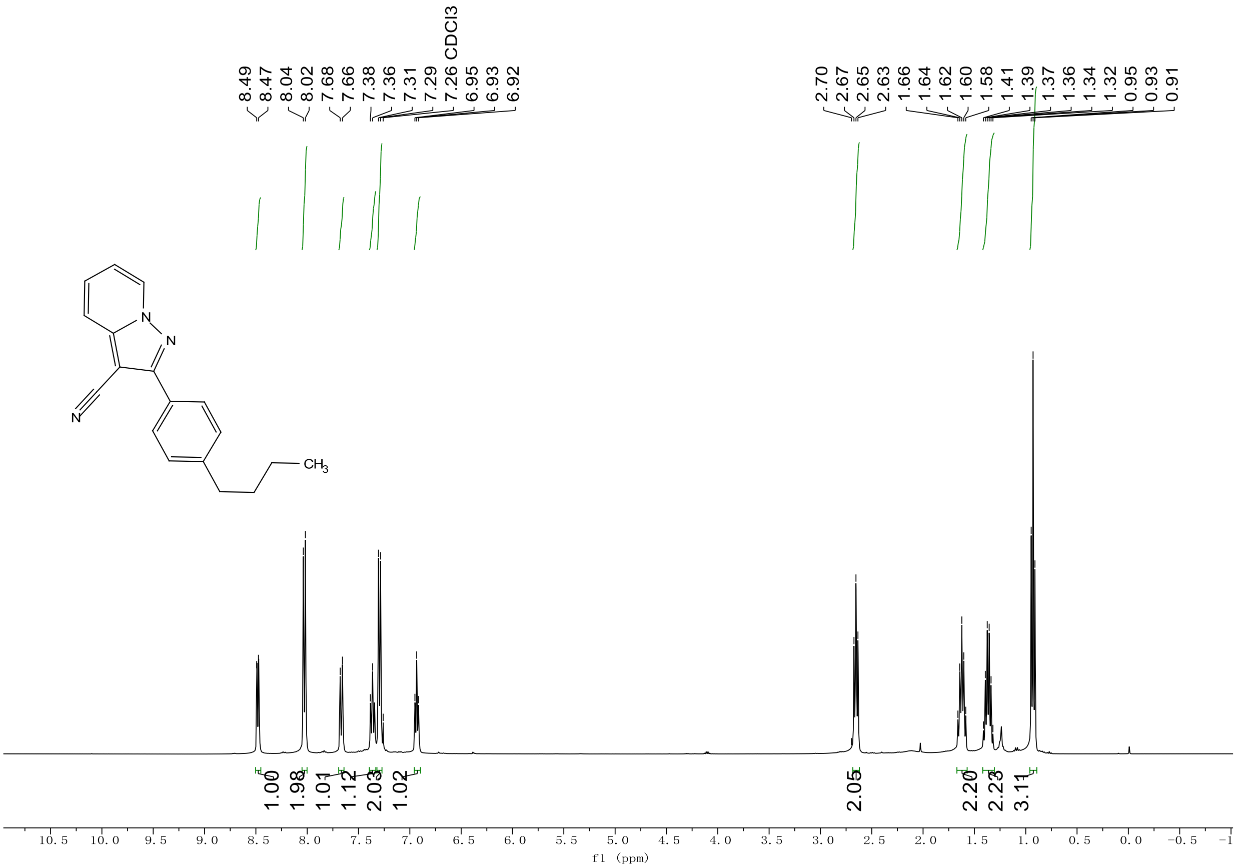


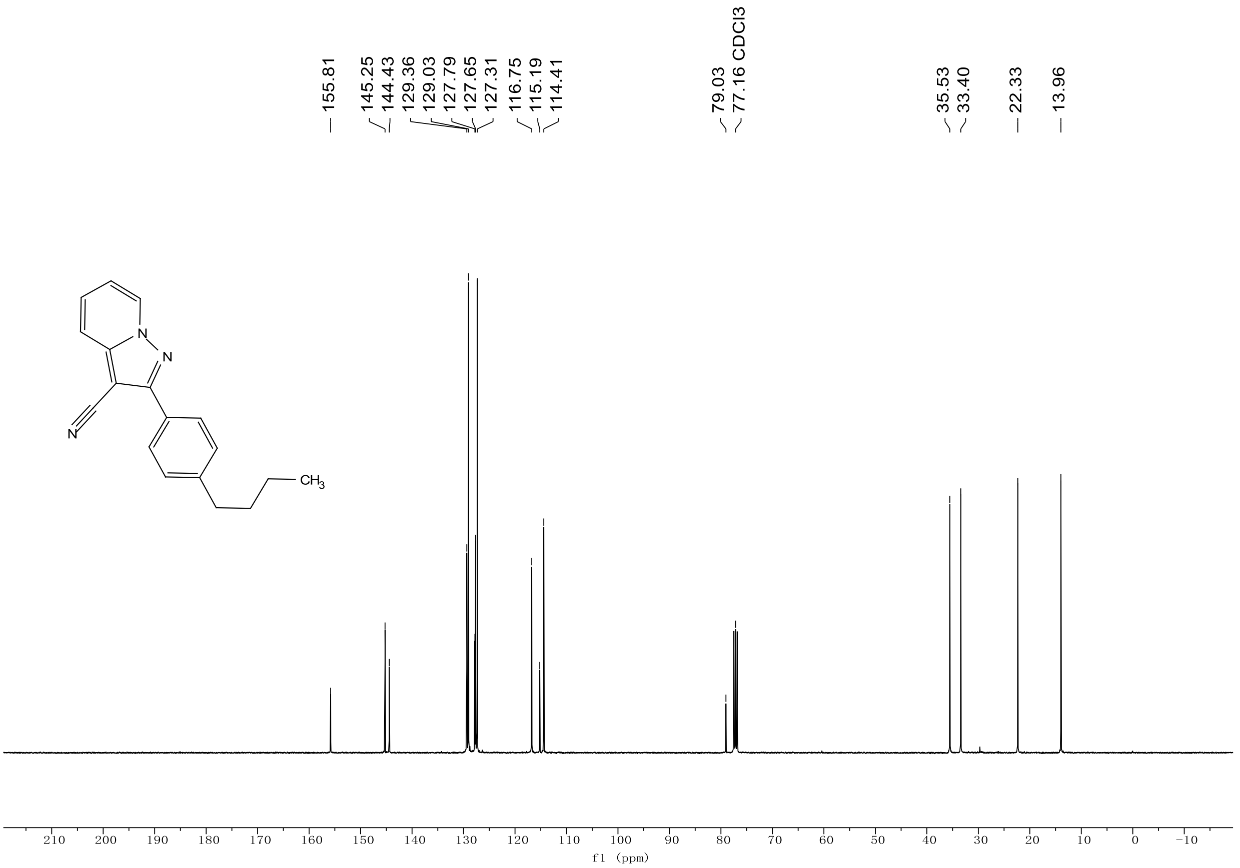
[1]H NMR (400 MHz, $CDCl_3$) and [13]C NMR (100 MHz, $CDCl_3$) spectrum of compound **4a**



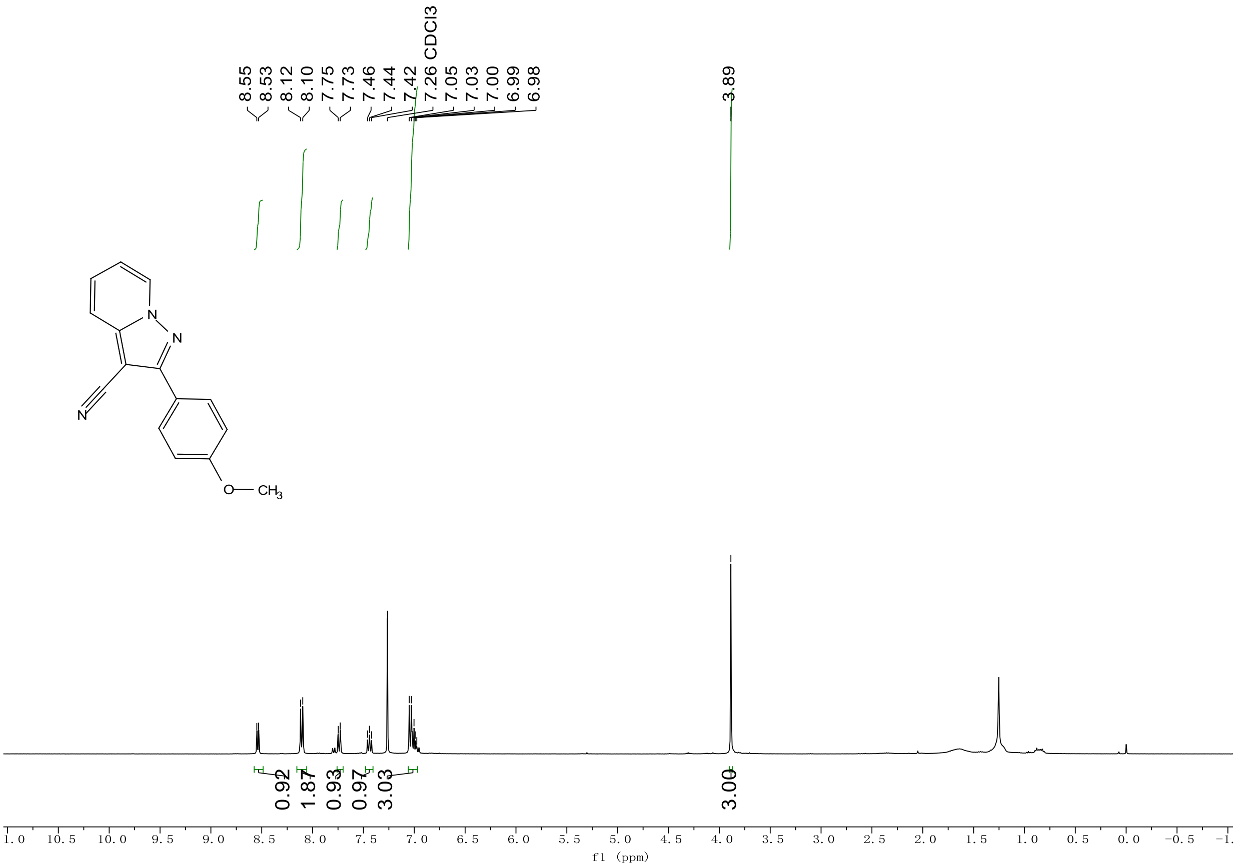


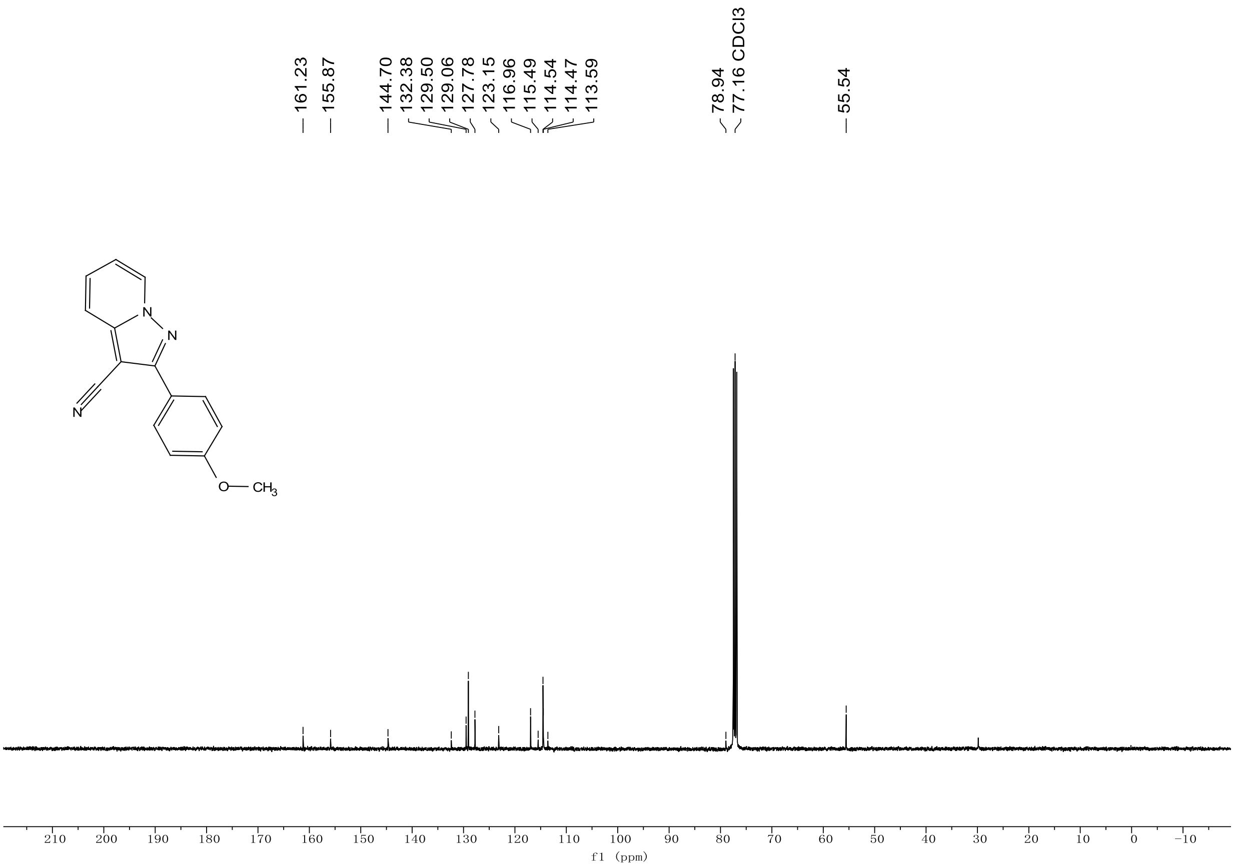
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4b**



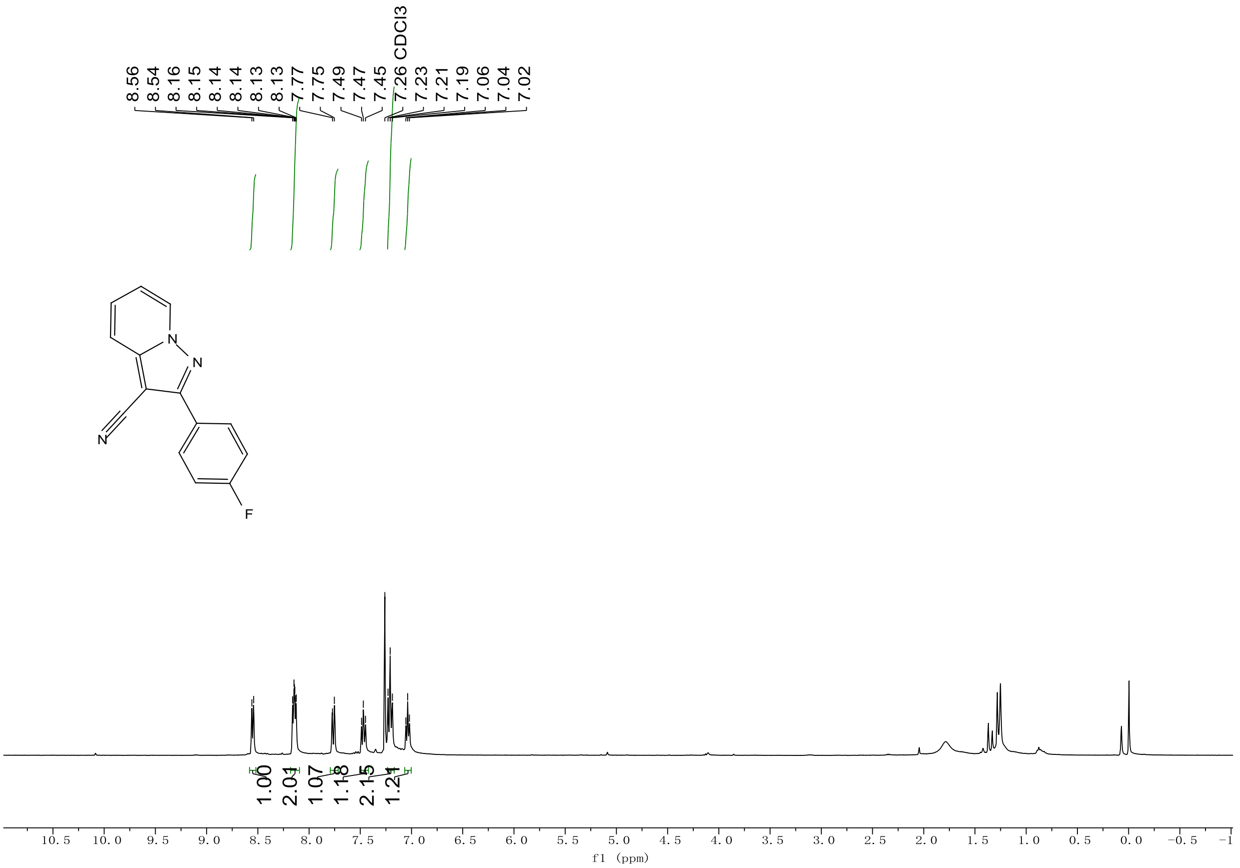


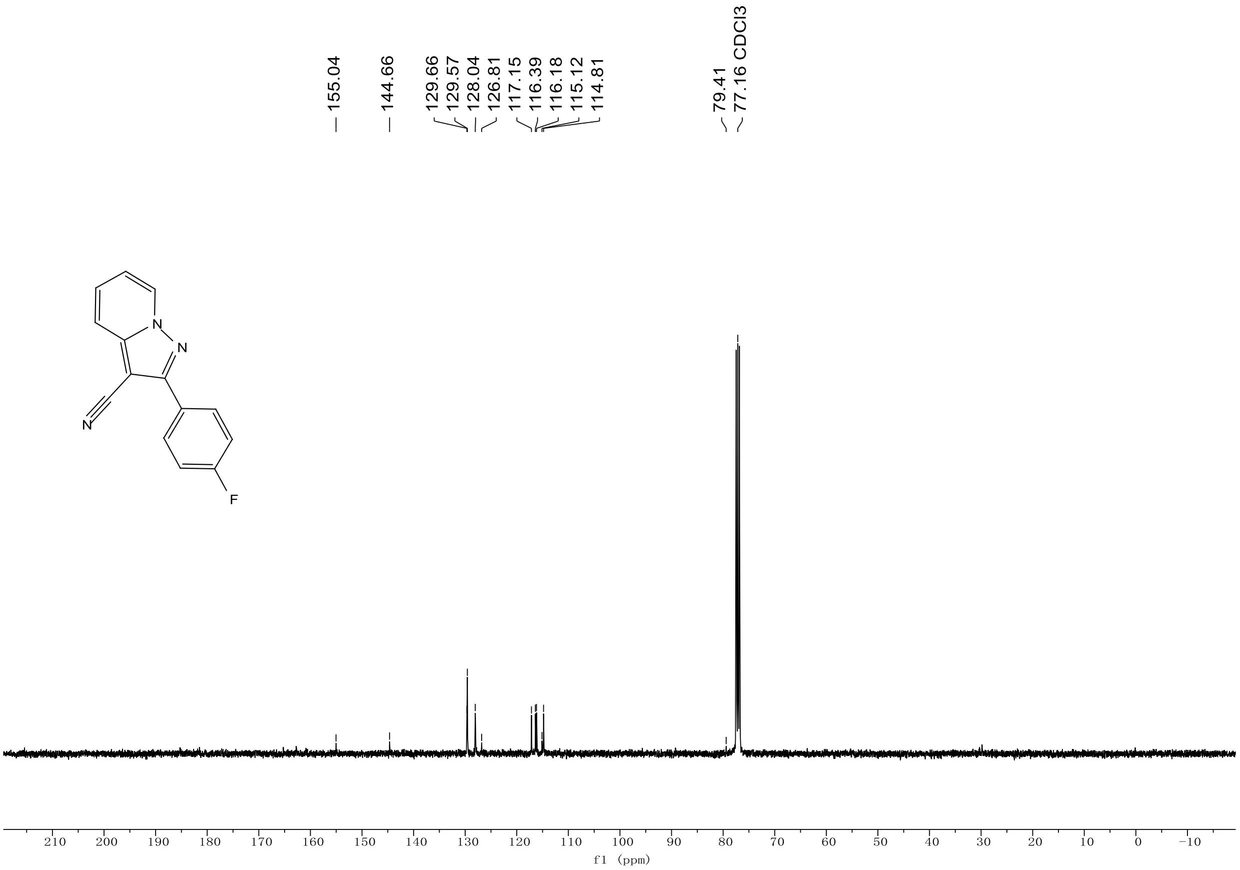
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4c**



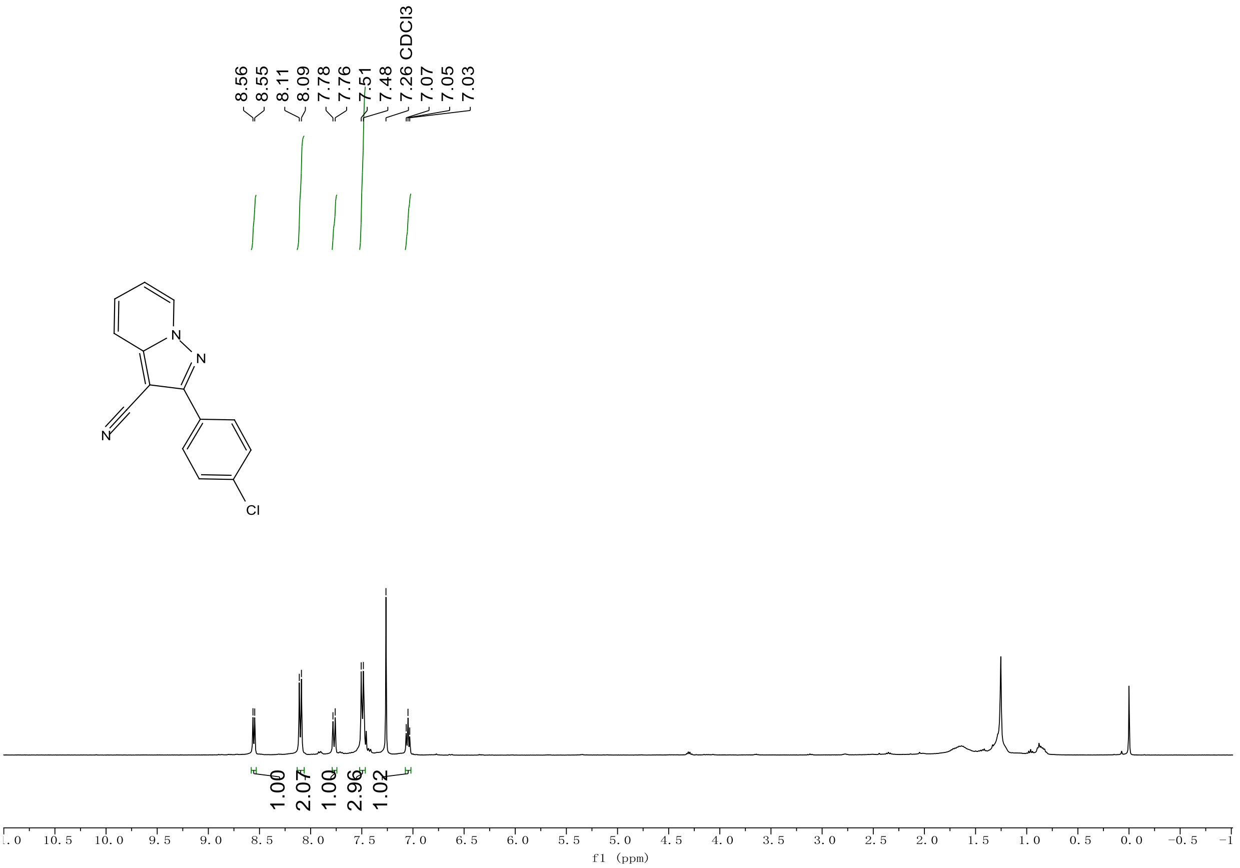


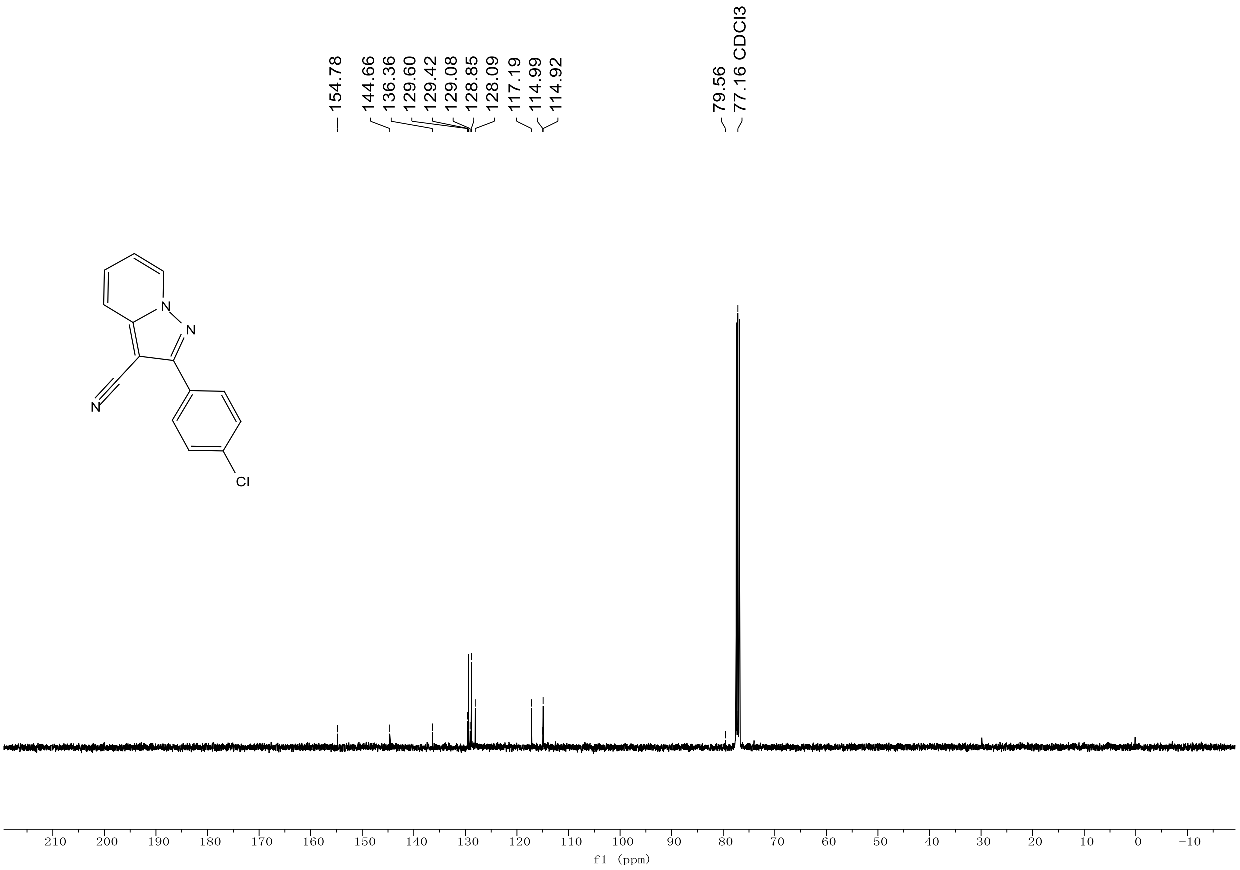
[1]H NMR (400 MHz, $CDCl_3$) and [13]C NMR (100 MHz, $CDCl_3$) spectrum of compound **4d**



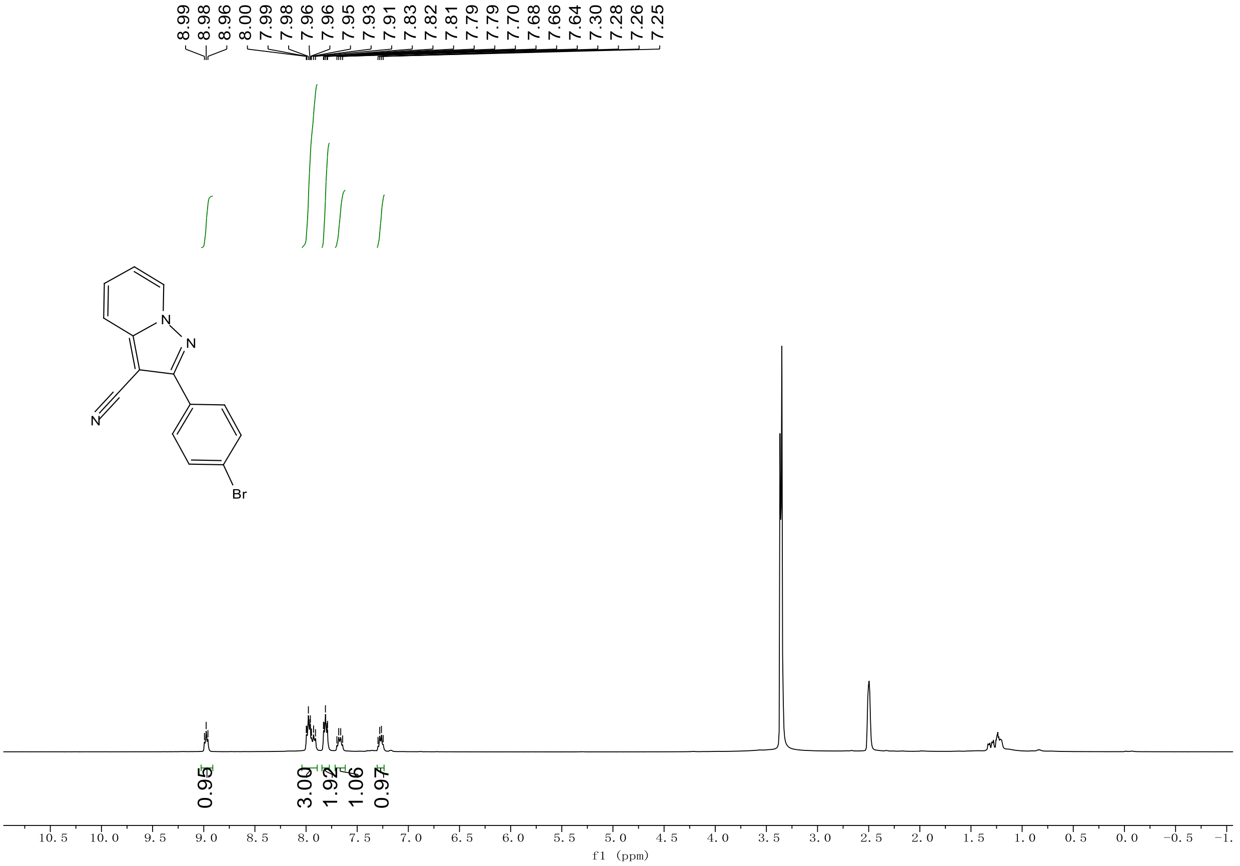


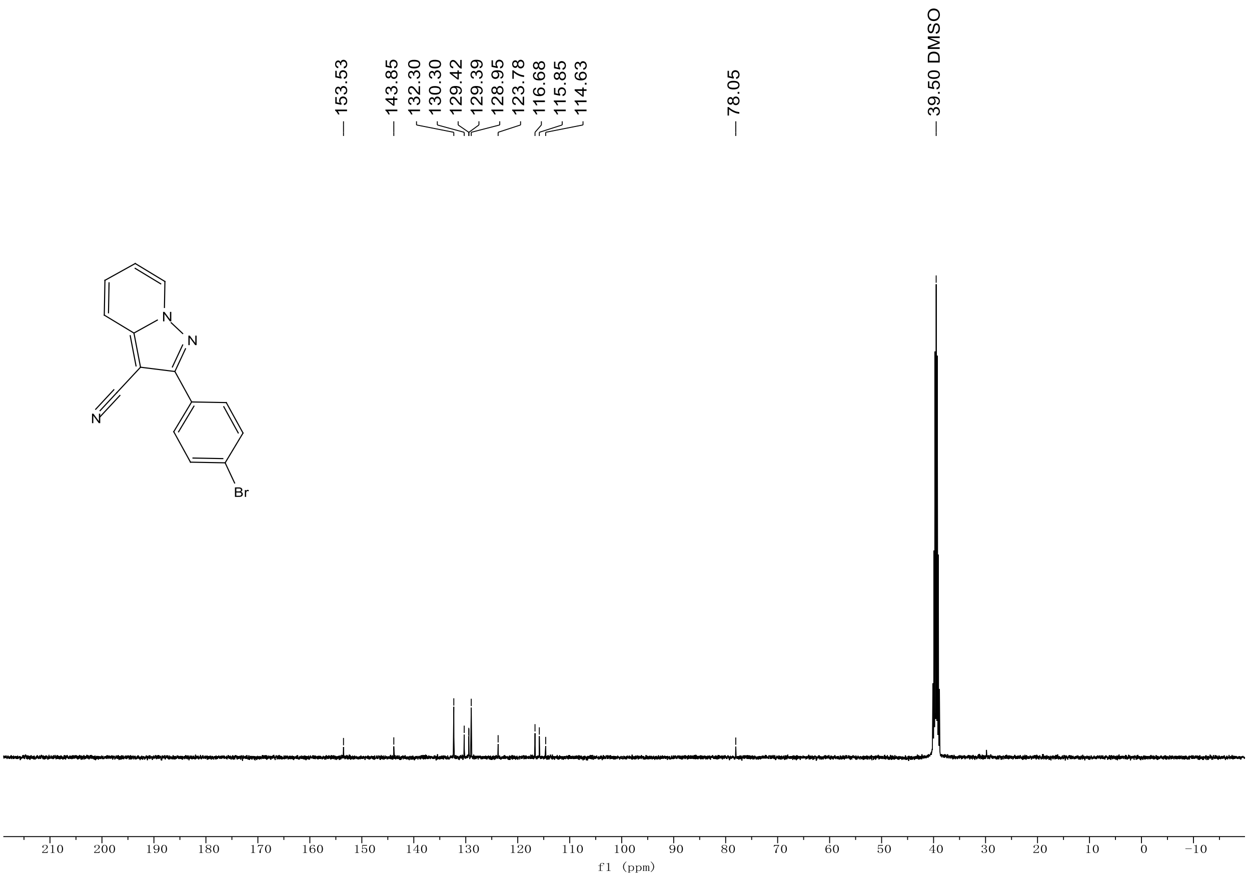
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4e**



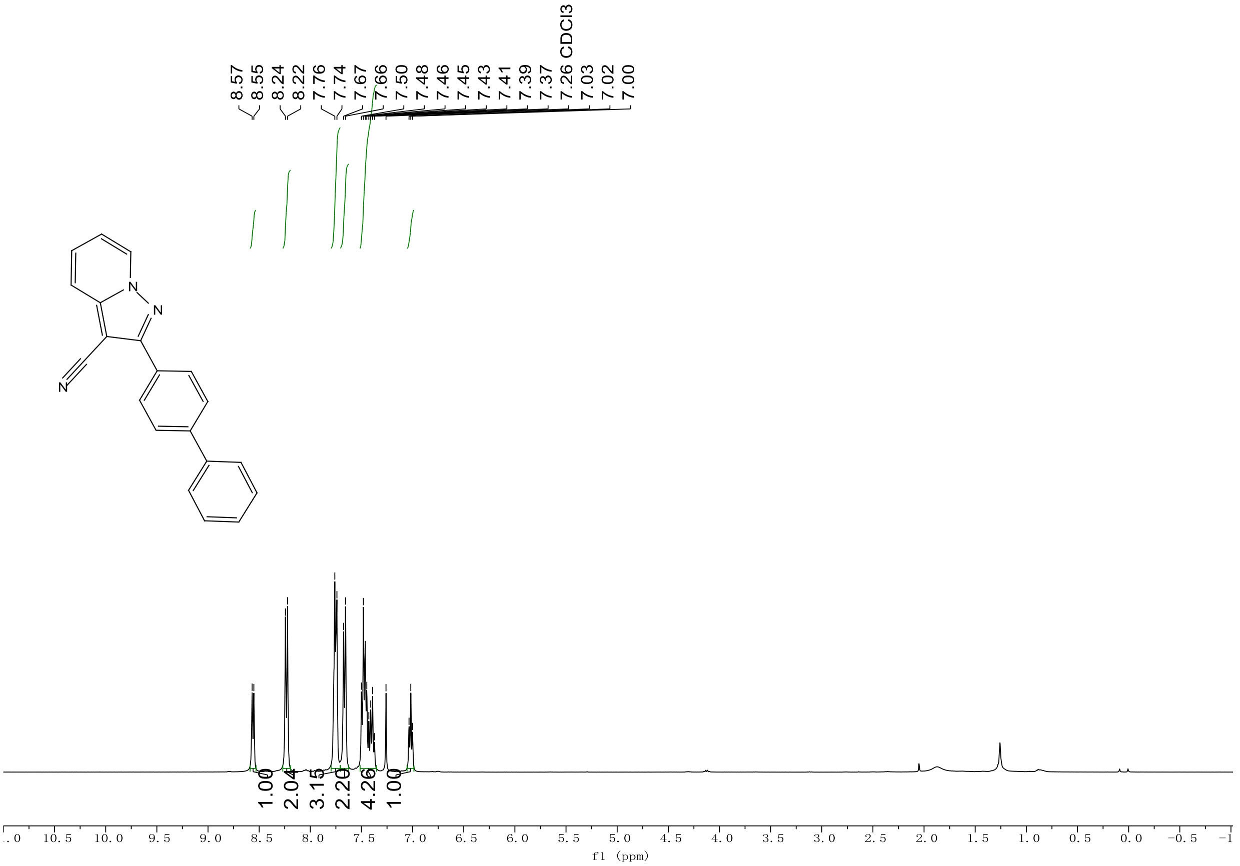


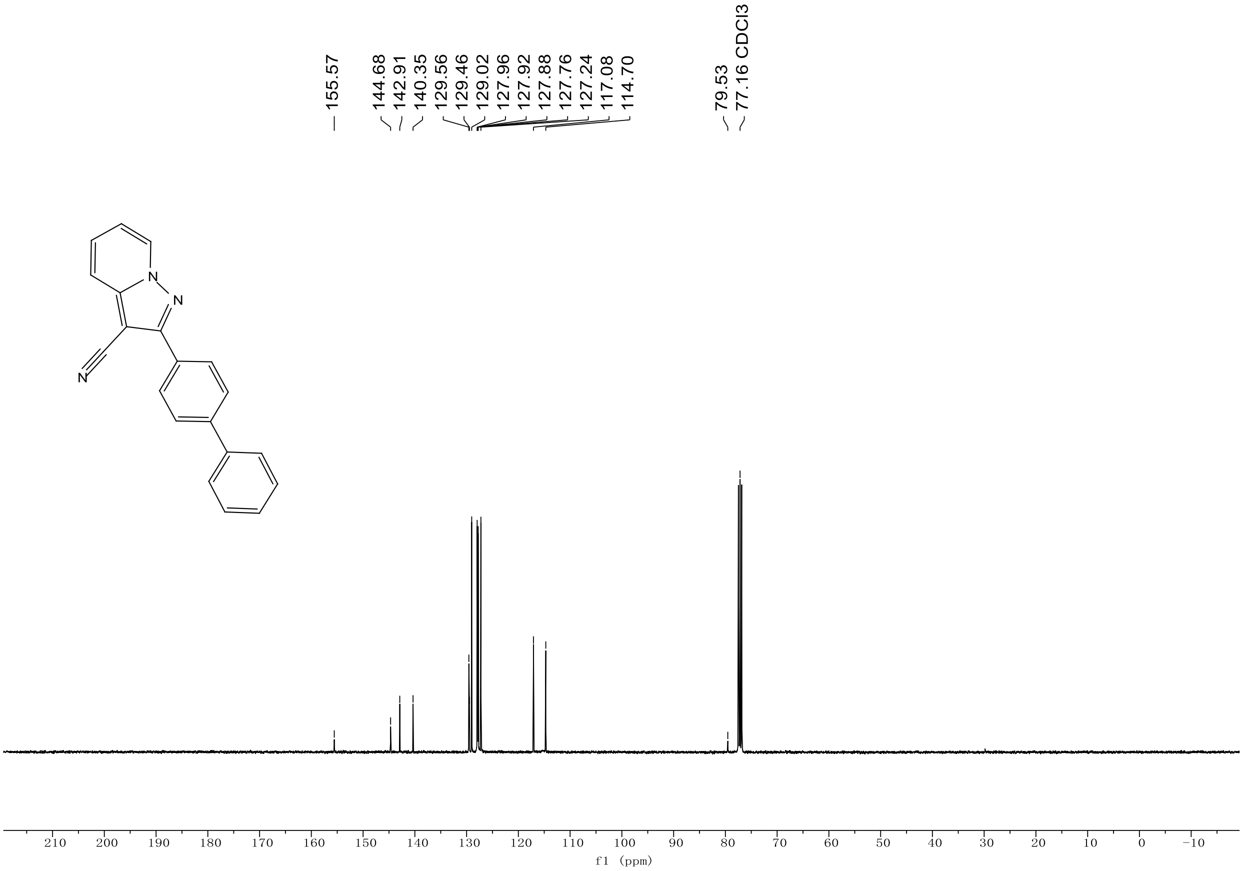
[1]H NMR (400 MHz, DMSO-d6) and [13]C NMR (100 MHz, DMSO-d6) spectrum of compound **4f**



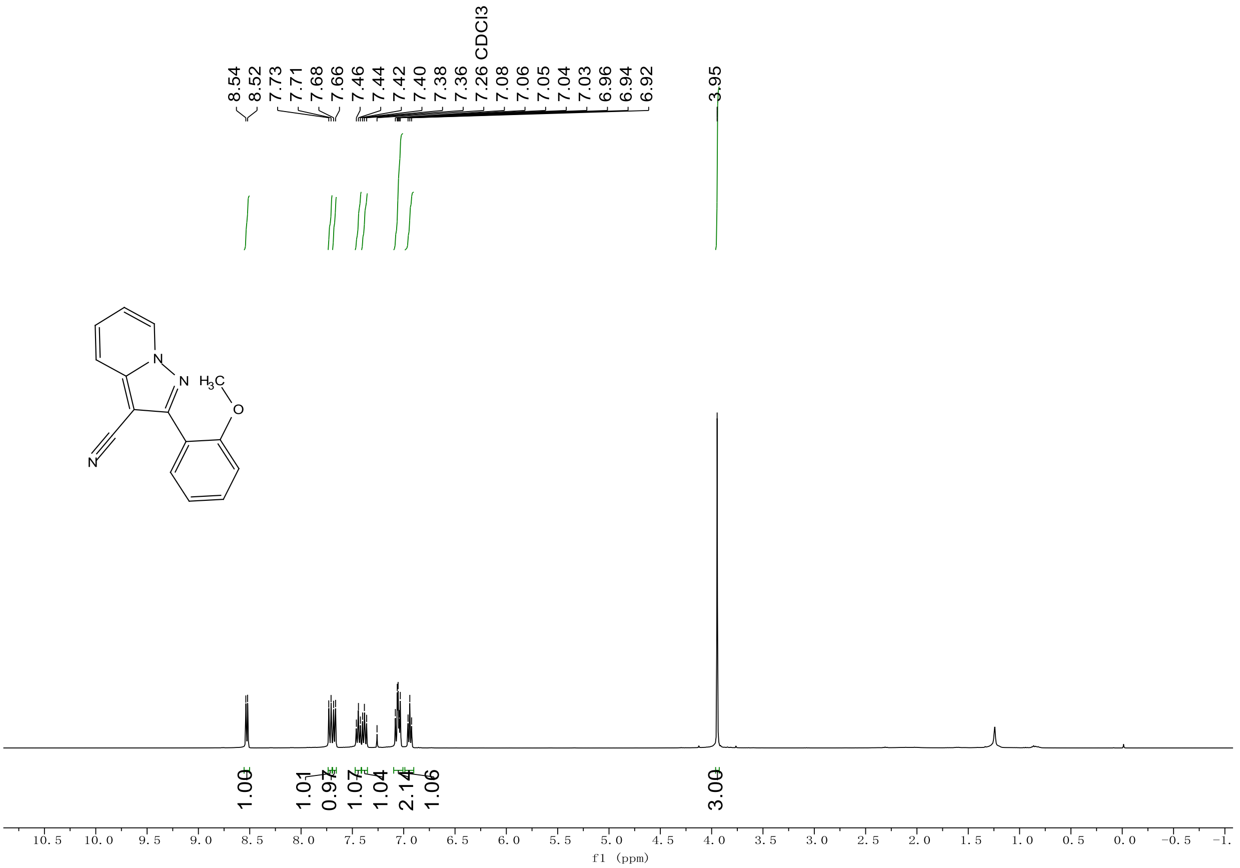


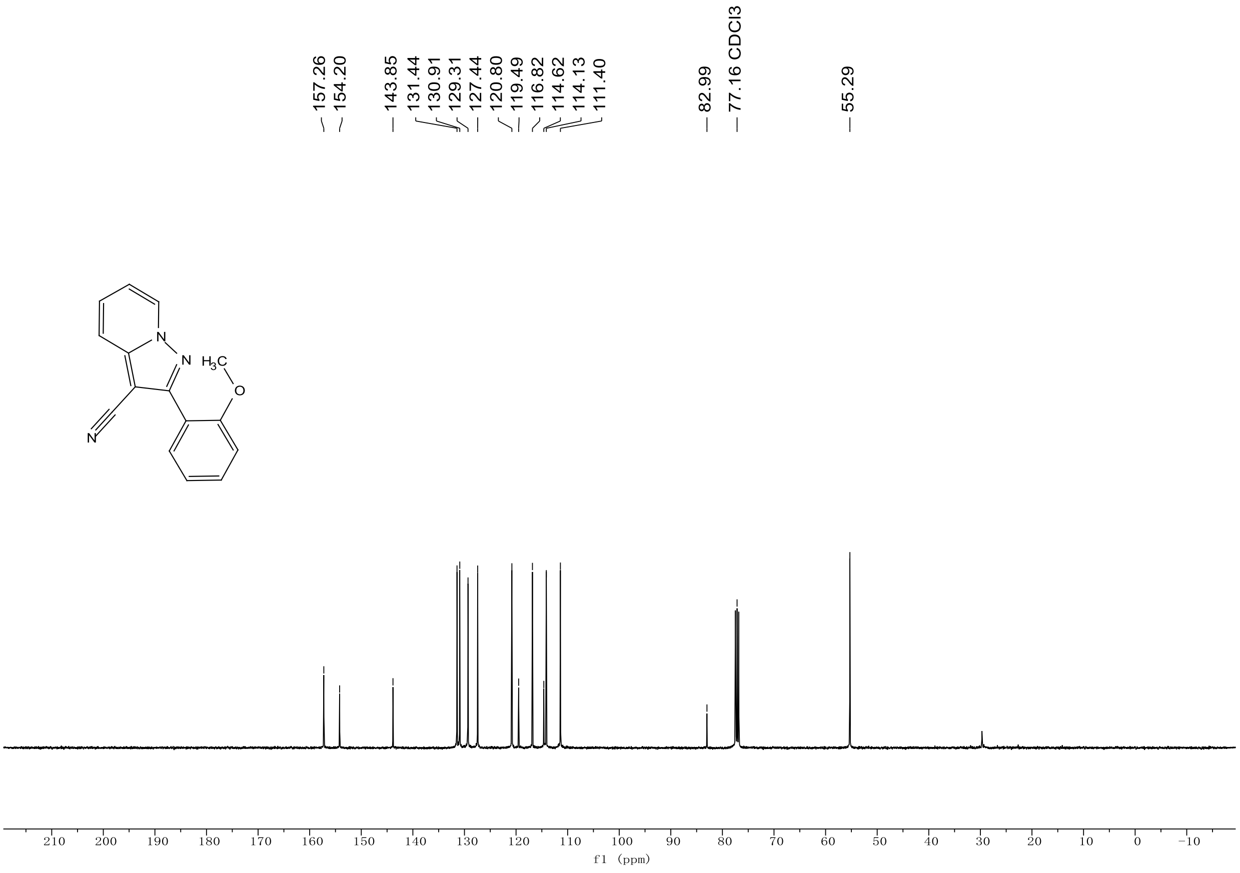
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4g**



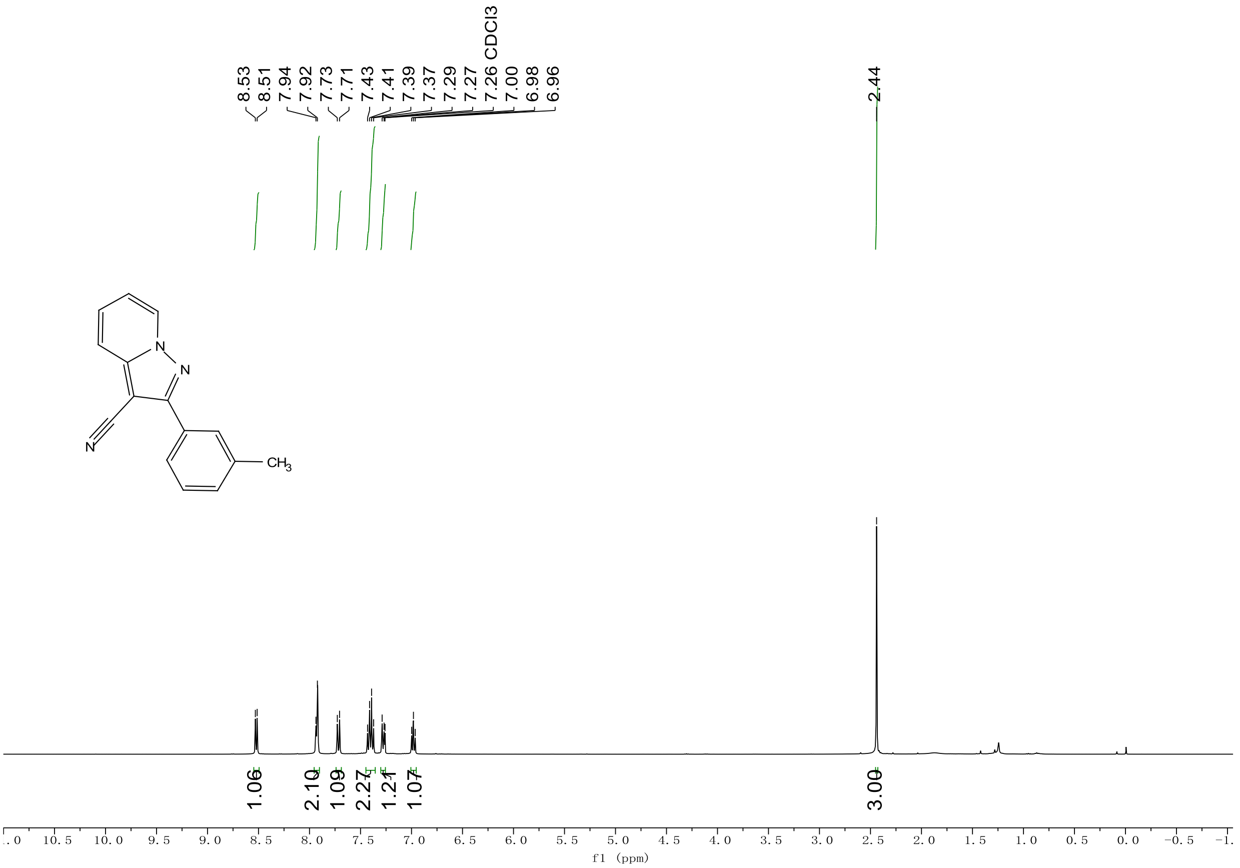


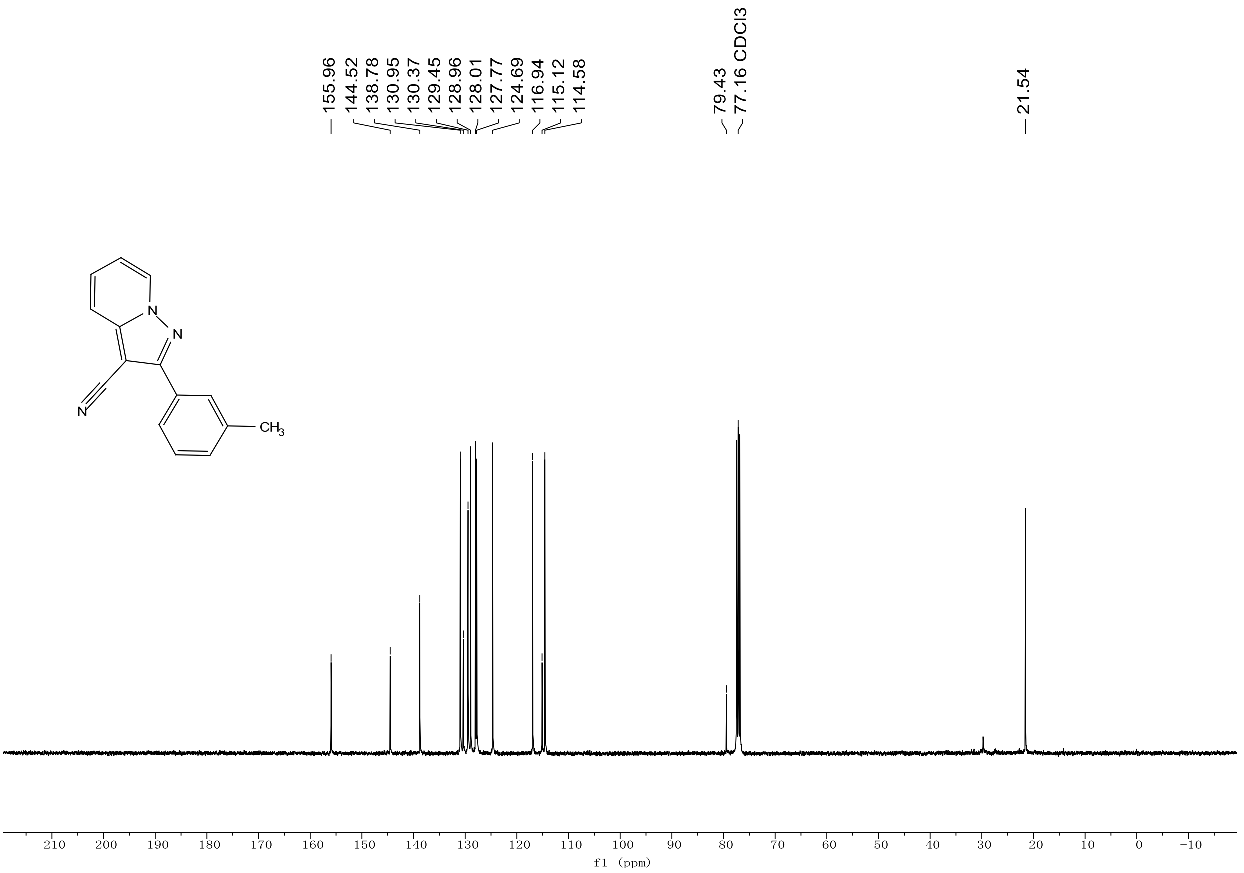
[1]H NMR (400 MHz, $CDCl_3$) and [13]C NMR (100 MHz, $CDCl_3$) spectrum of compound **4h**



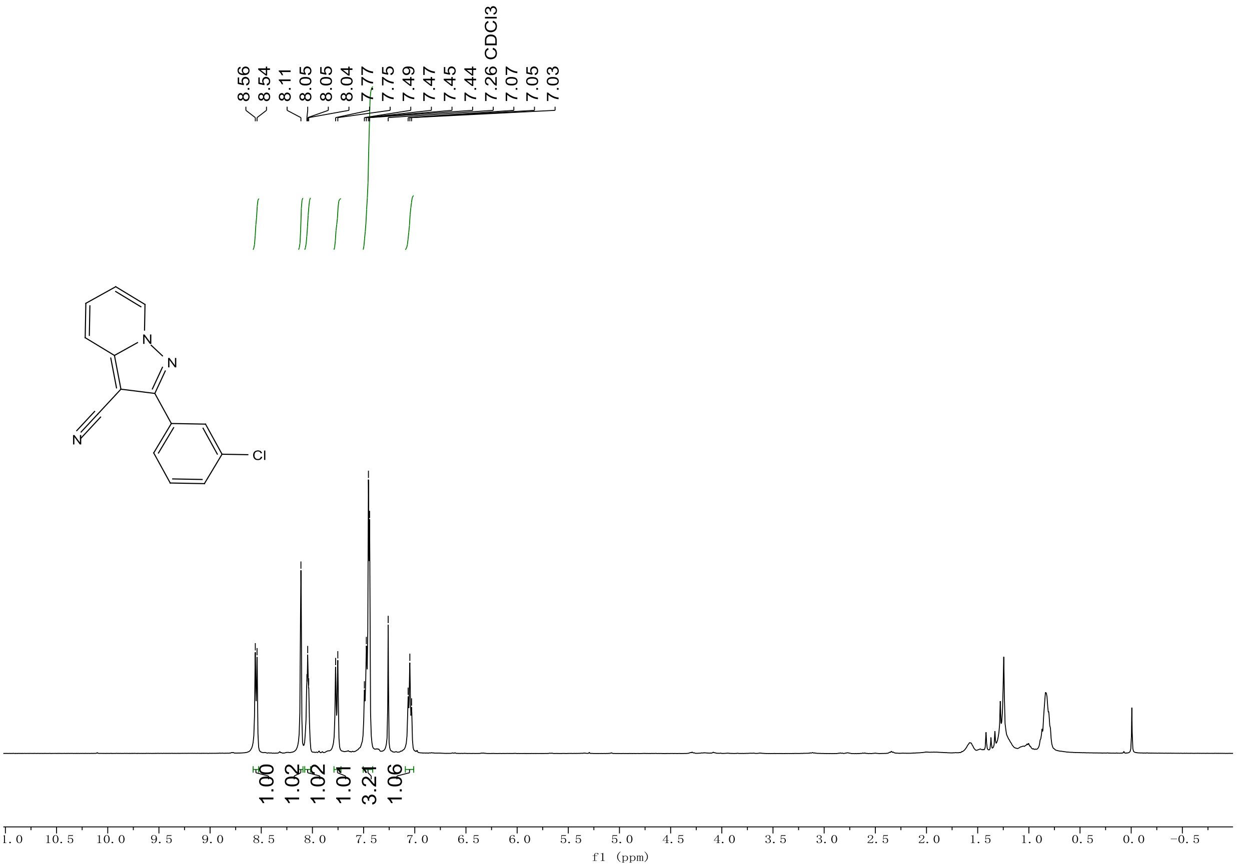


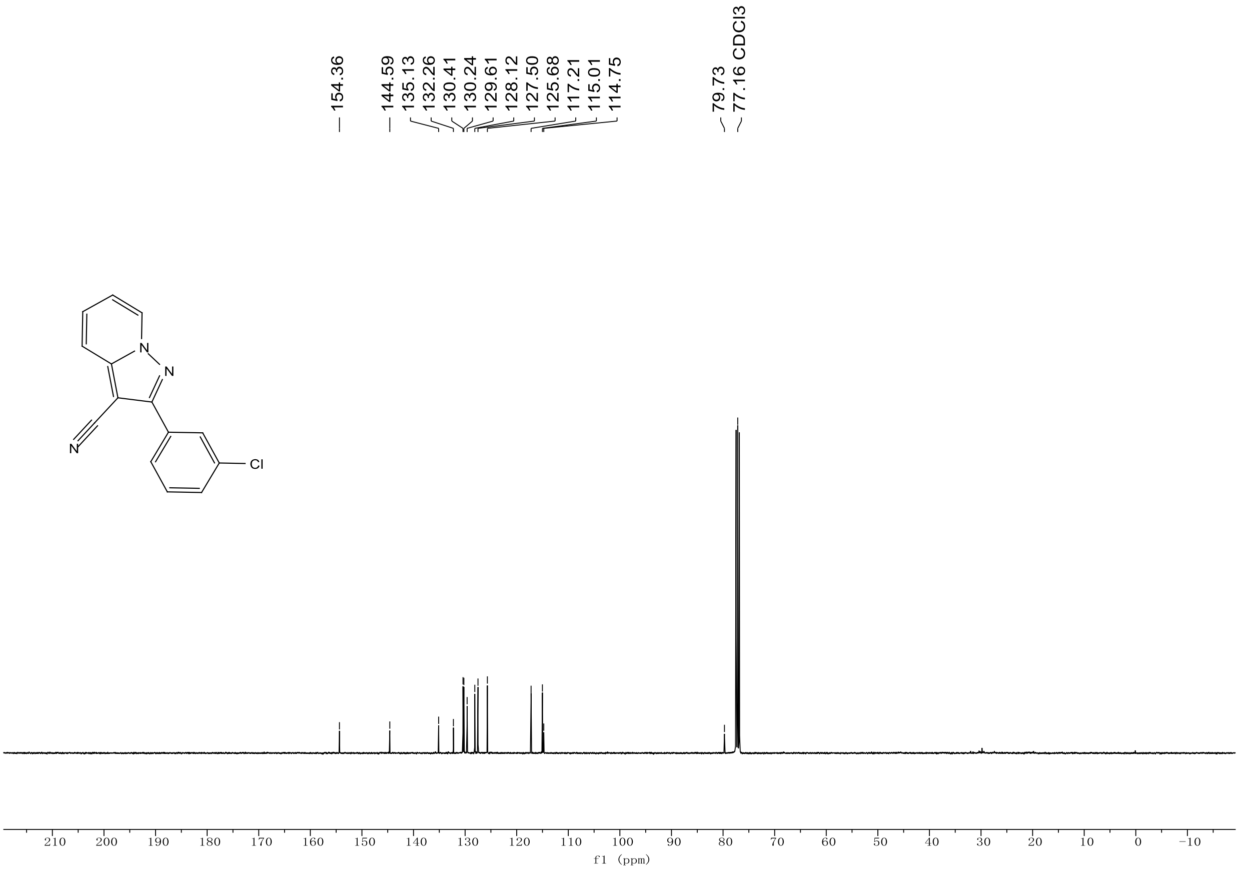
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4i**



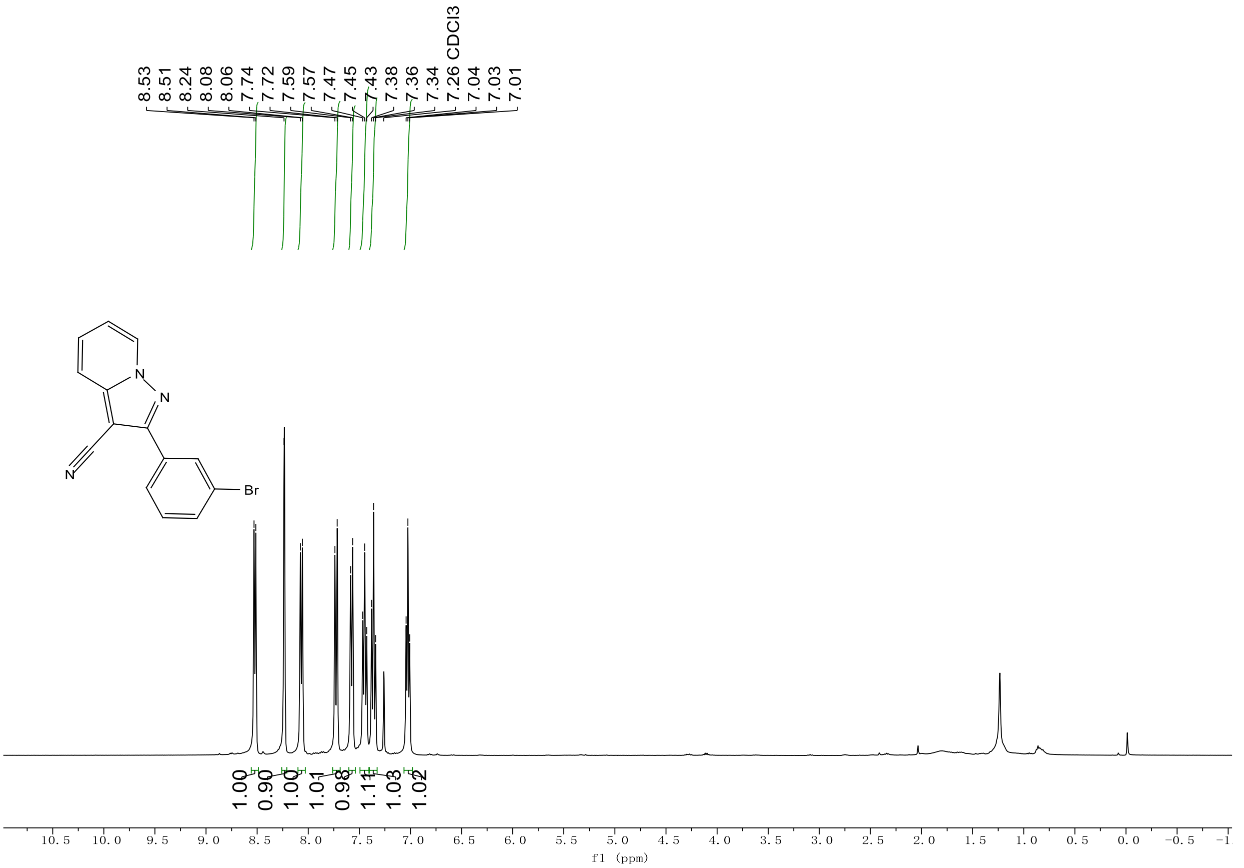


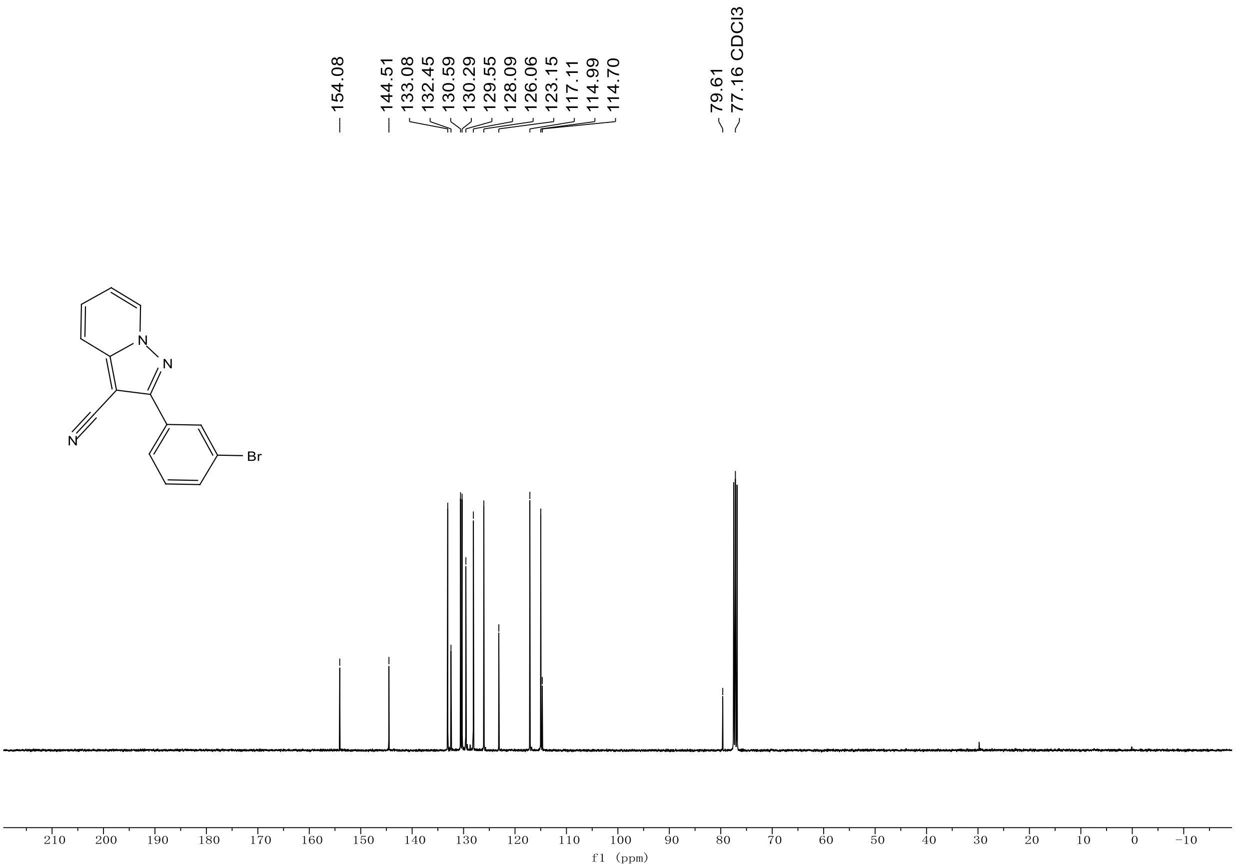
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4j**



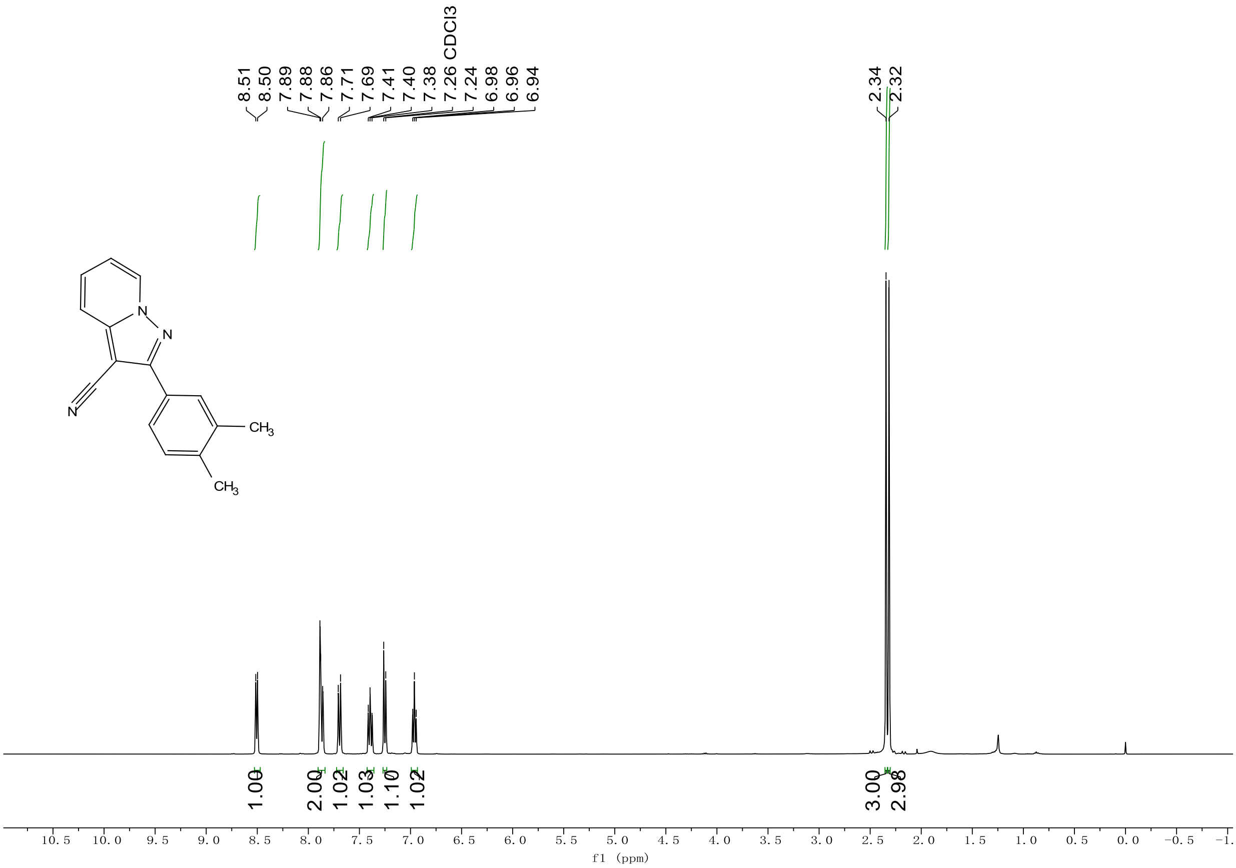


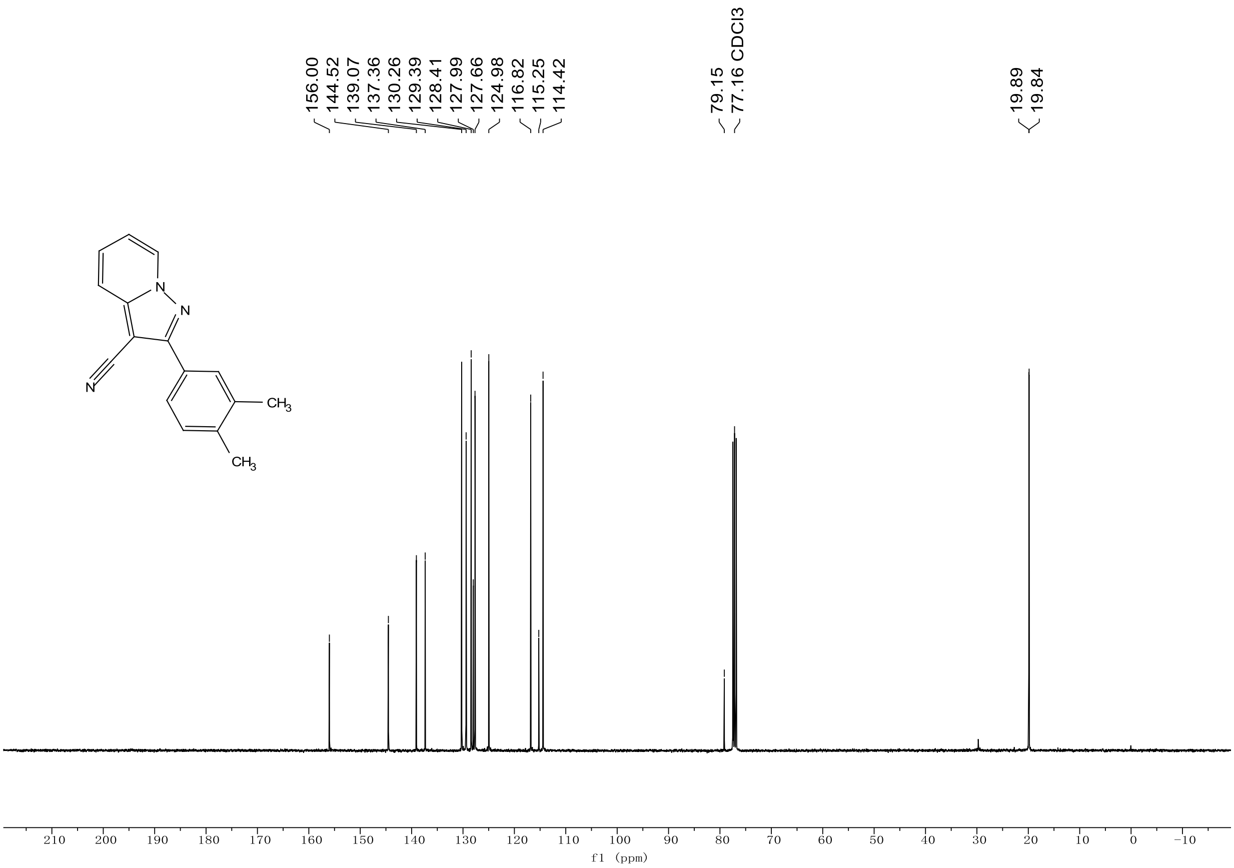
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4k**



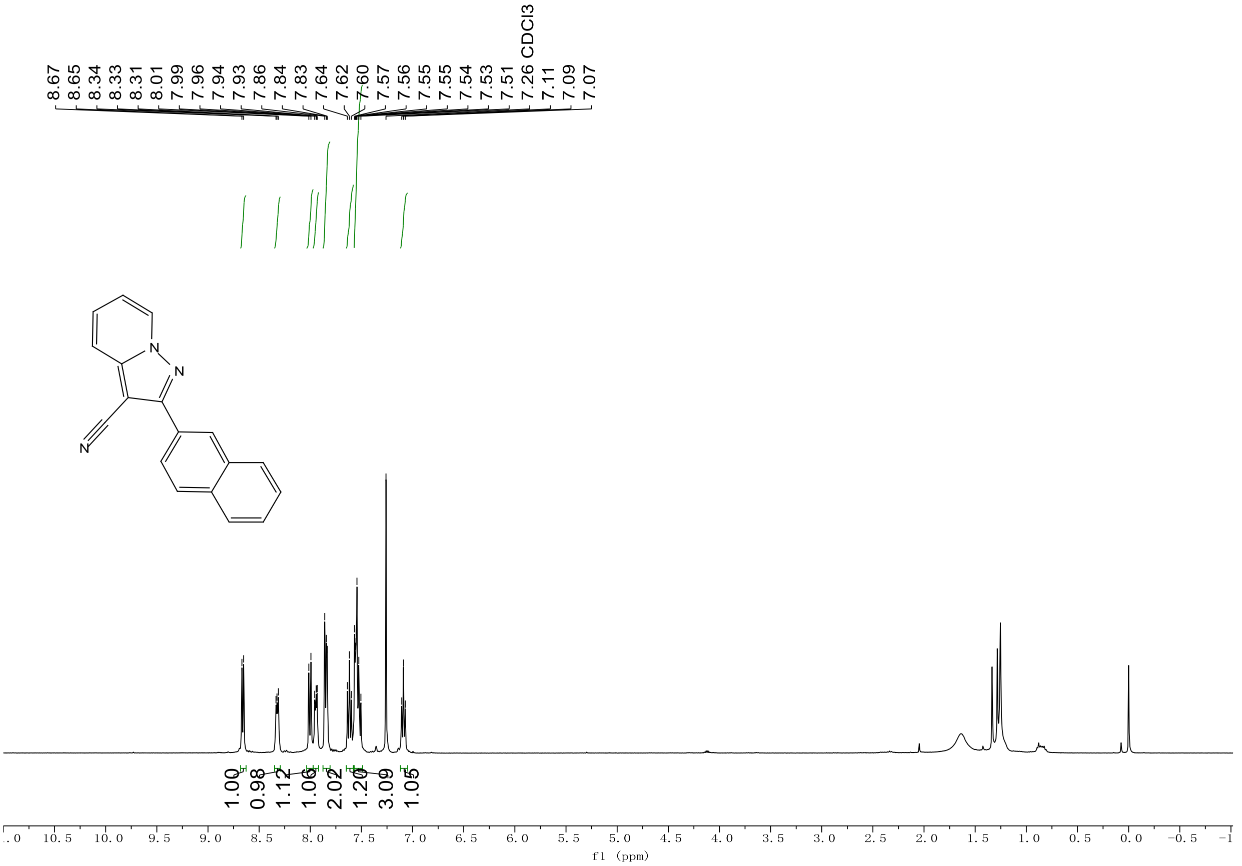


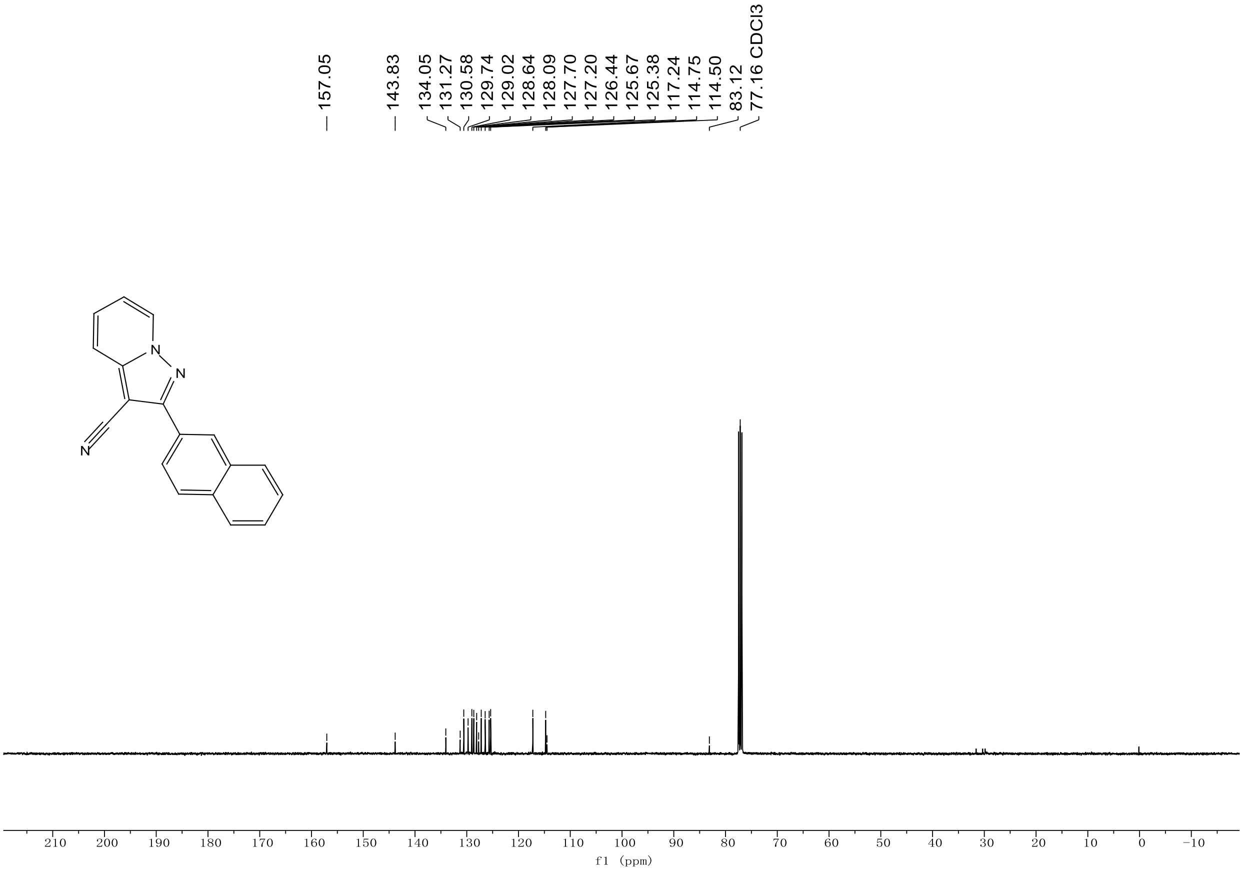
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4l**



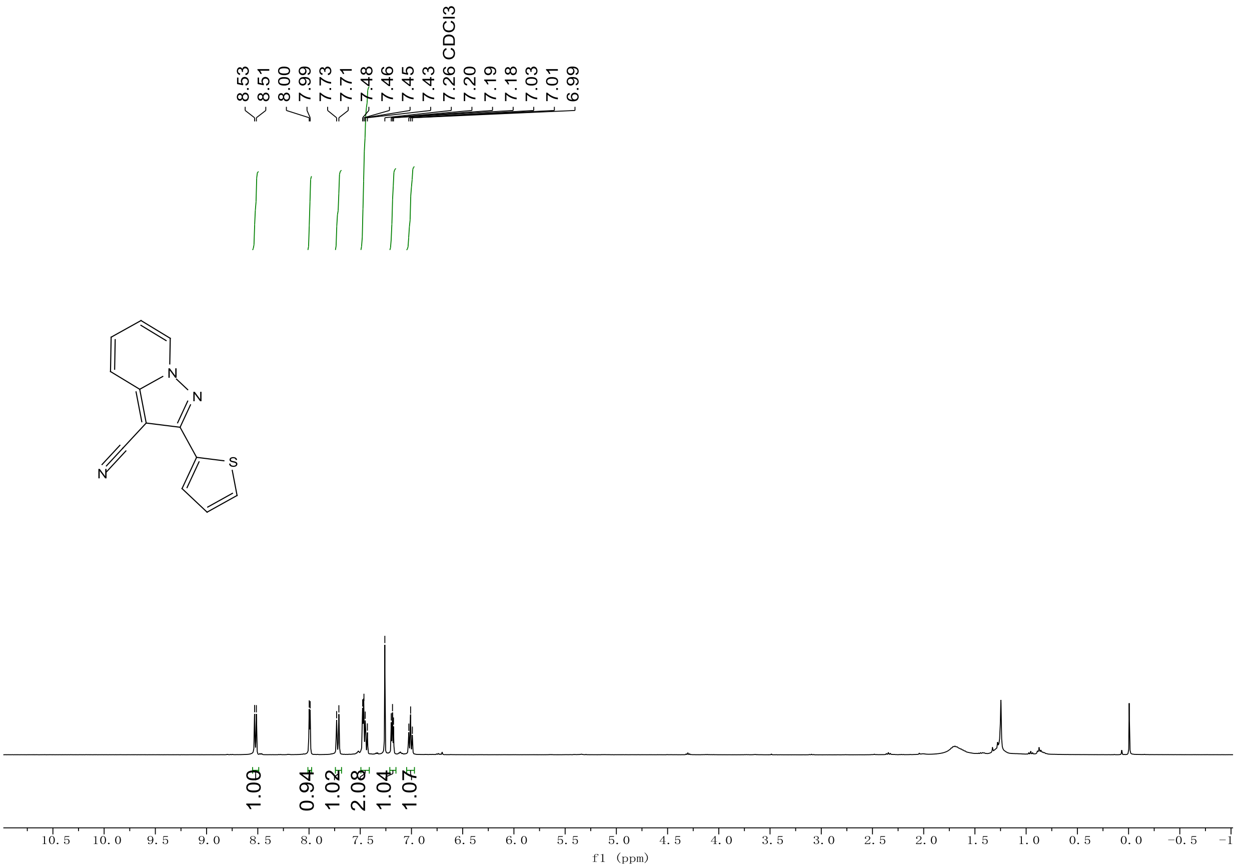


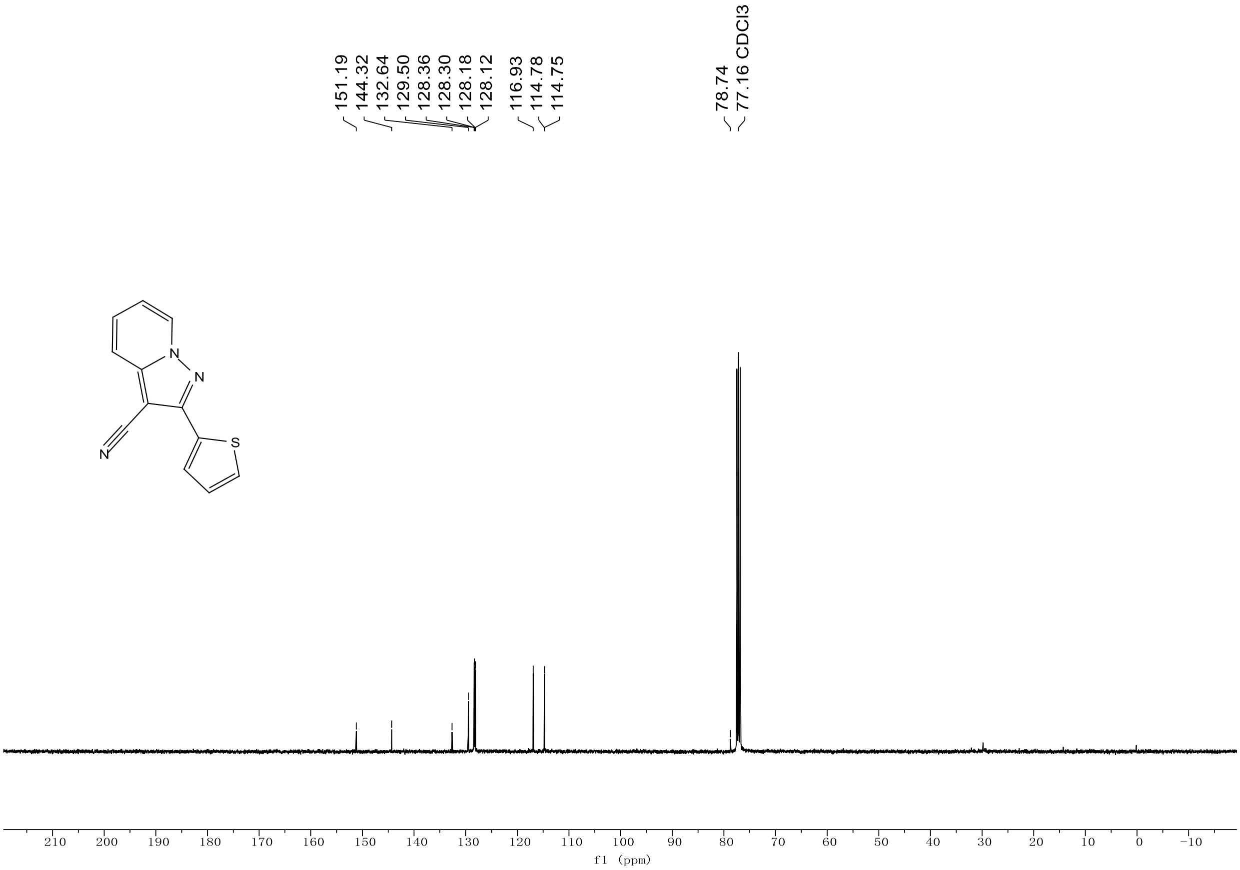
[1]H NMR (400 MHz, $CDCl_3$) and [13]C NMR (100 MHz, $CDCl_3$) spectrum of compound **4m**



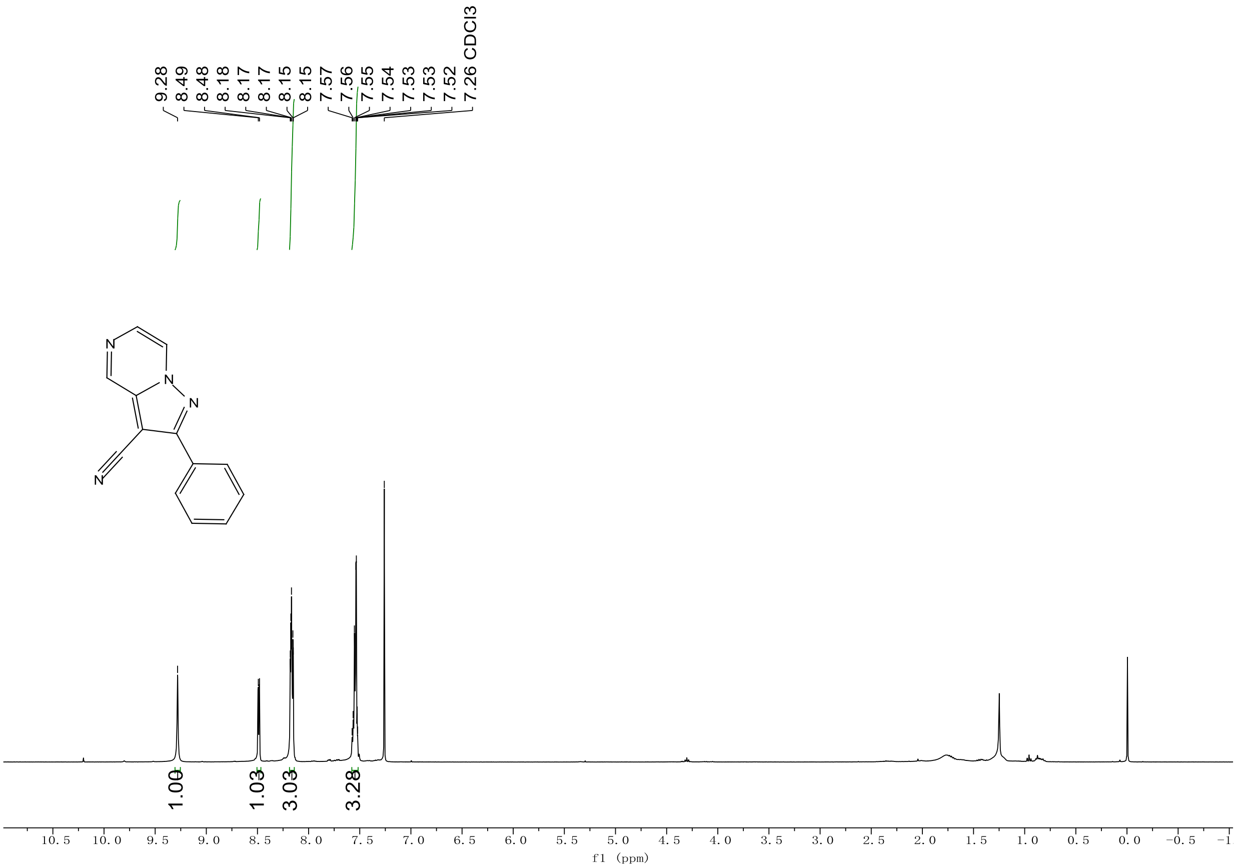


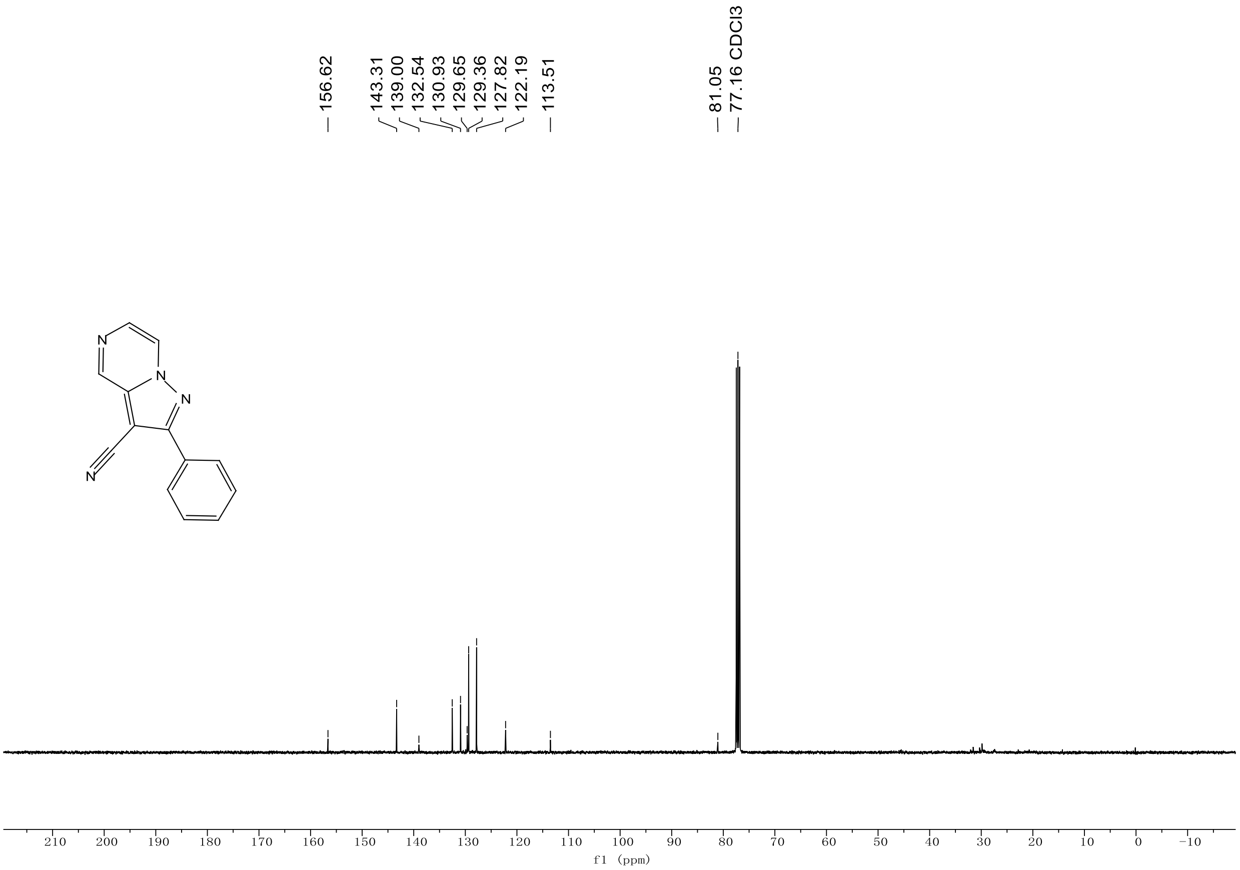
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4n**



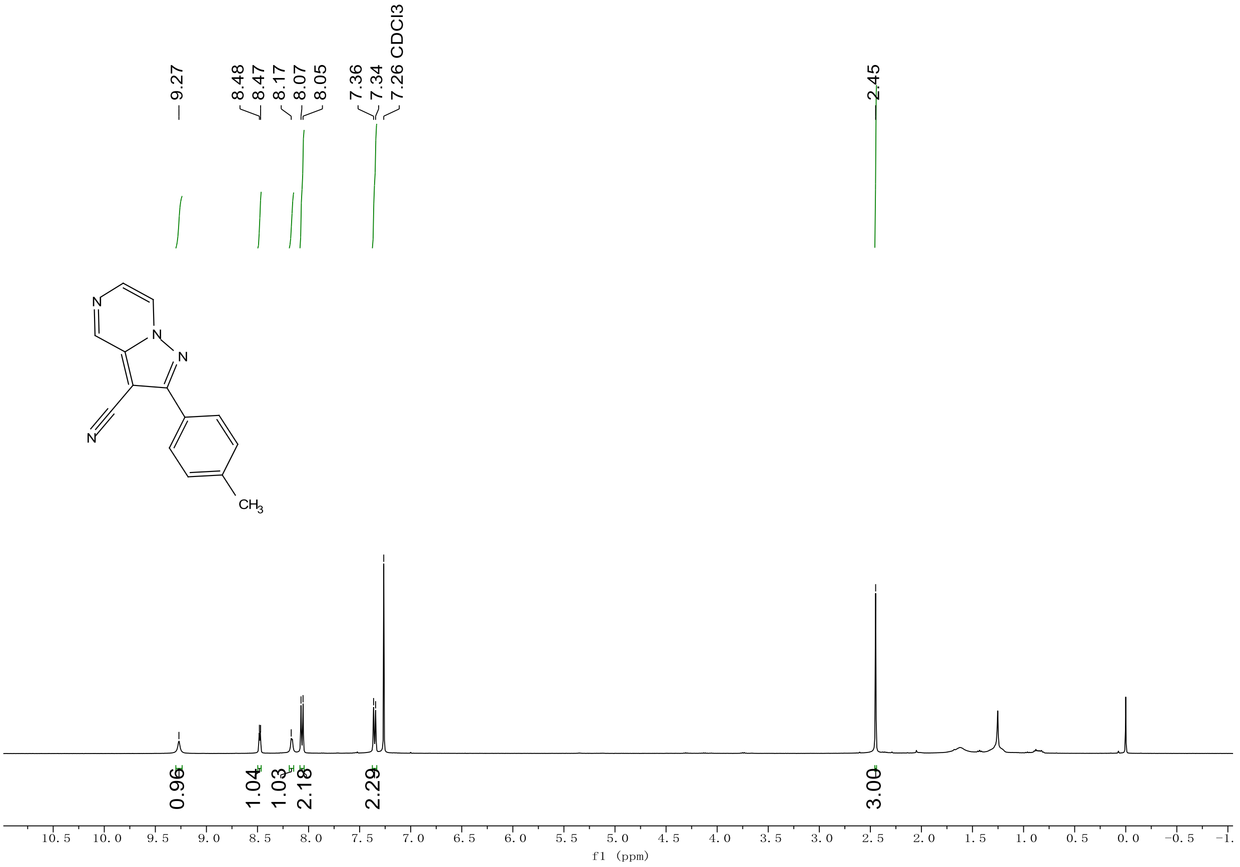


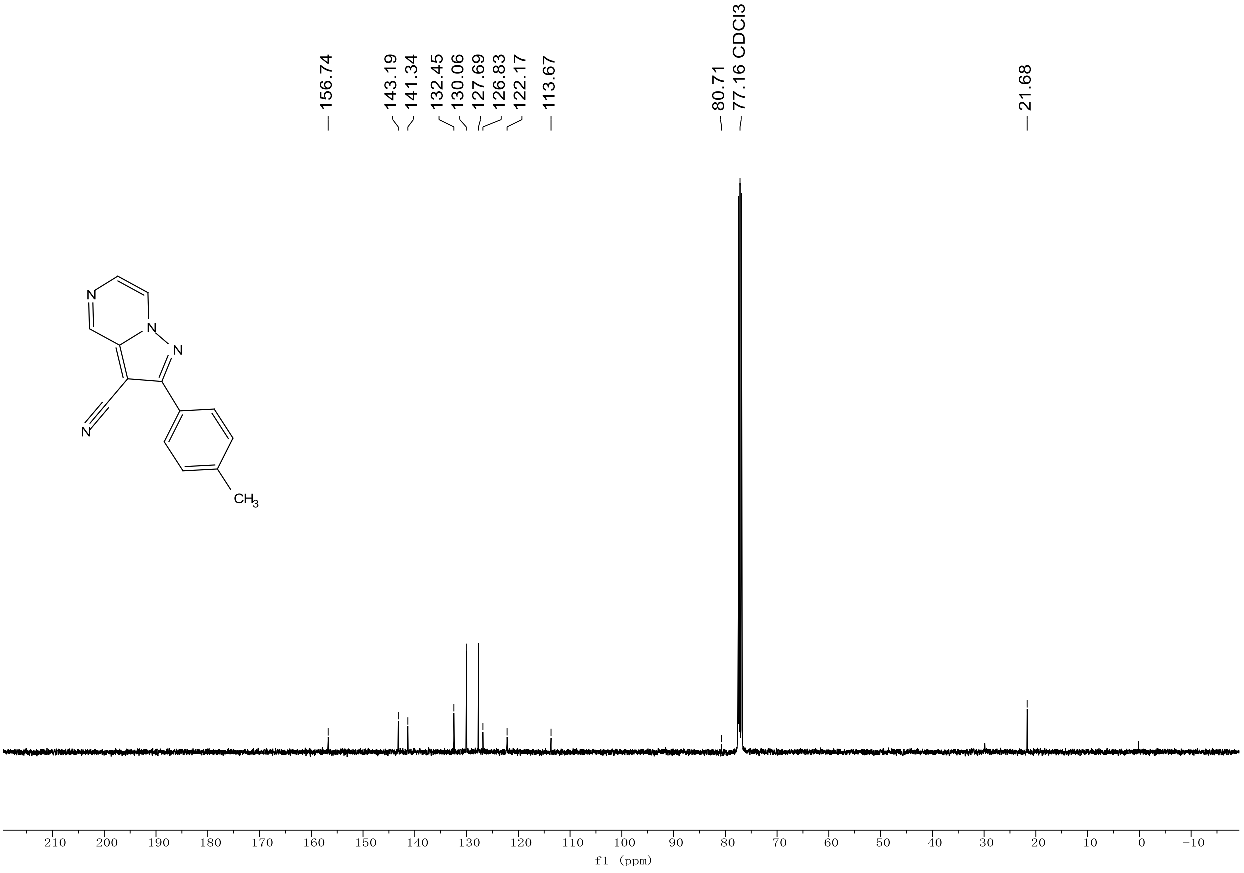
[1]H NMR (400 MHz, $CDCl_3$) and [13]C NMR (100 MHz, $CDCl_3$) spectrum of compound **6a**



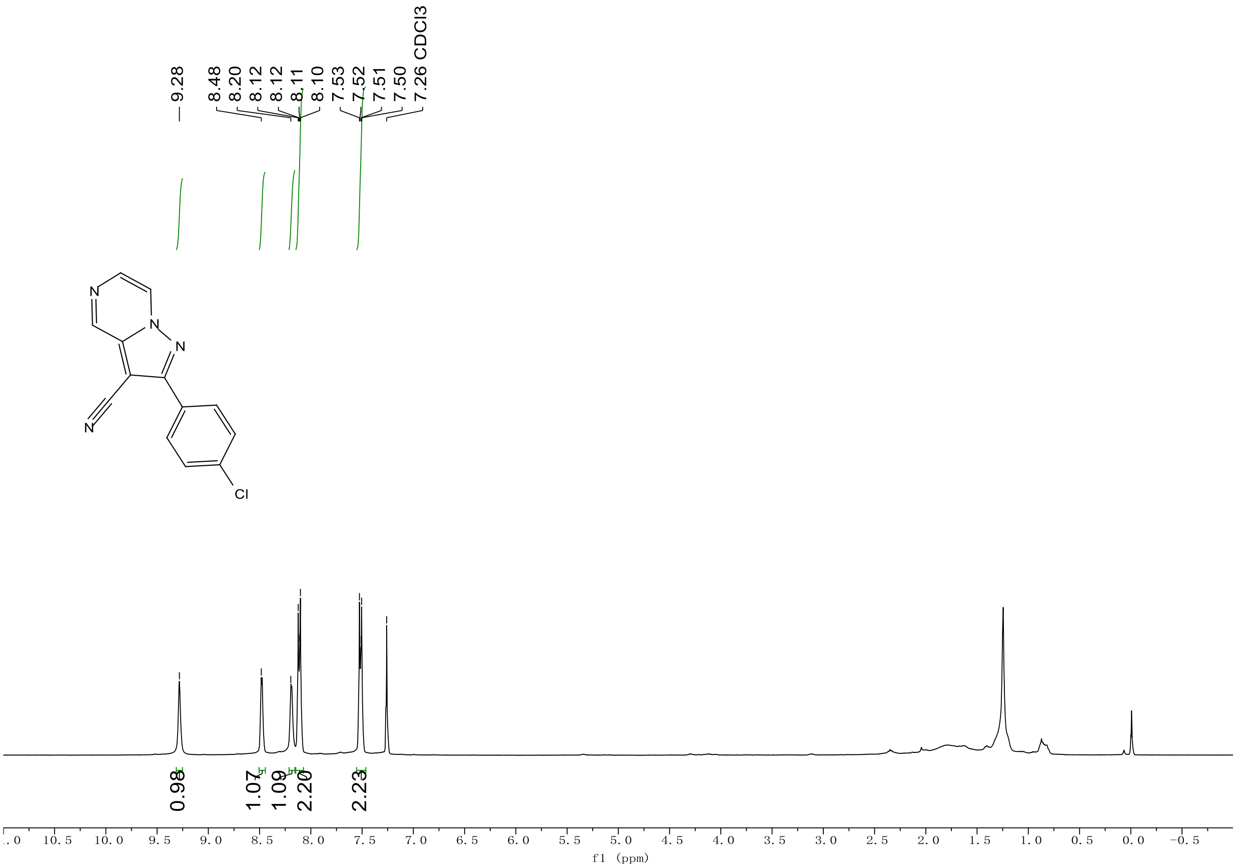


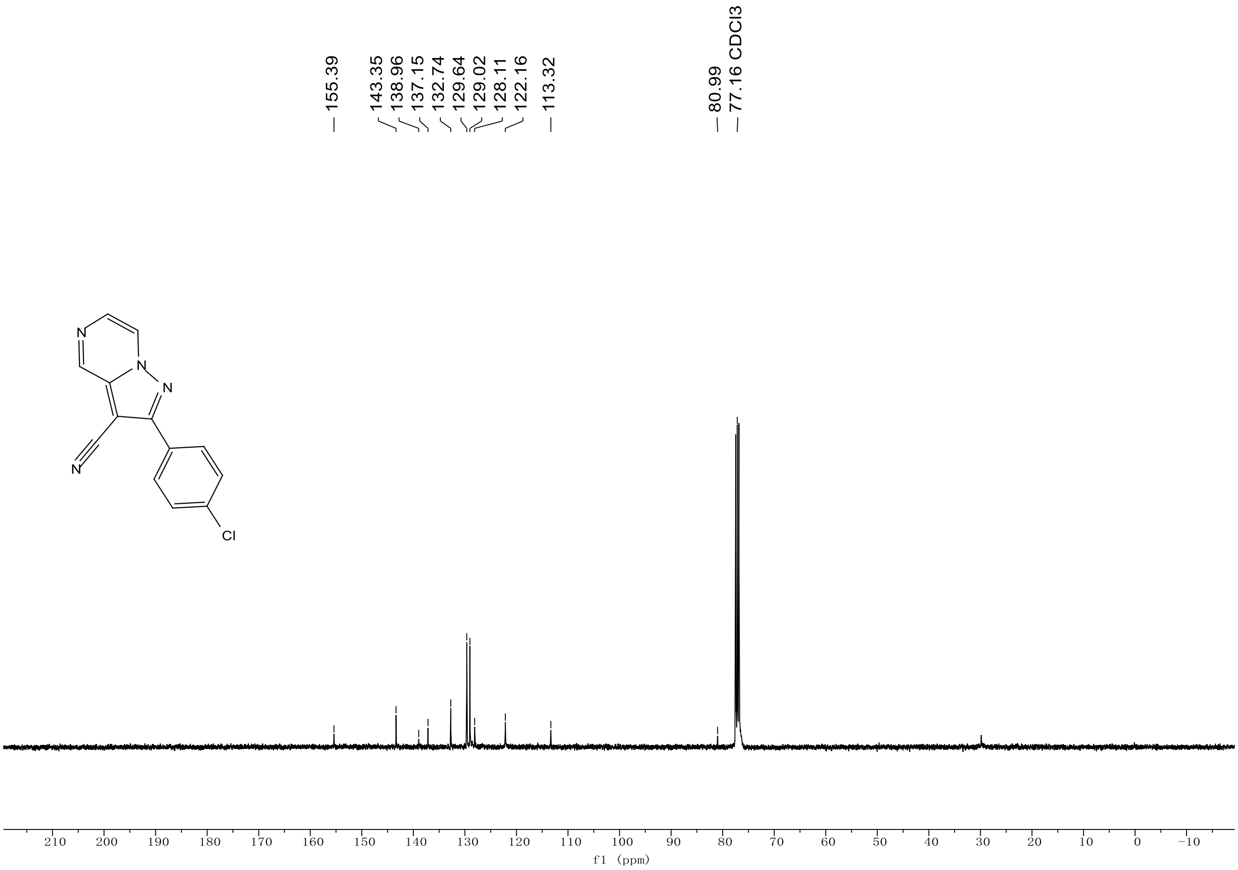
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6b**



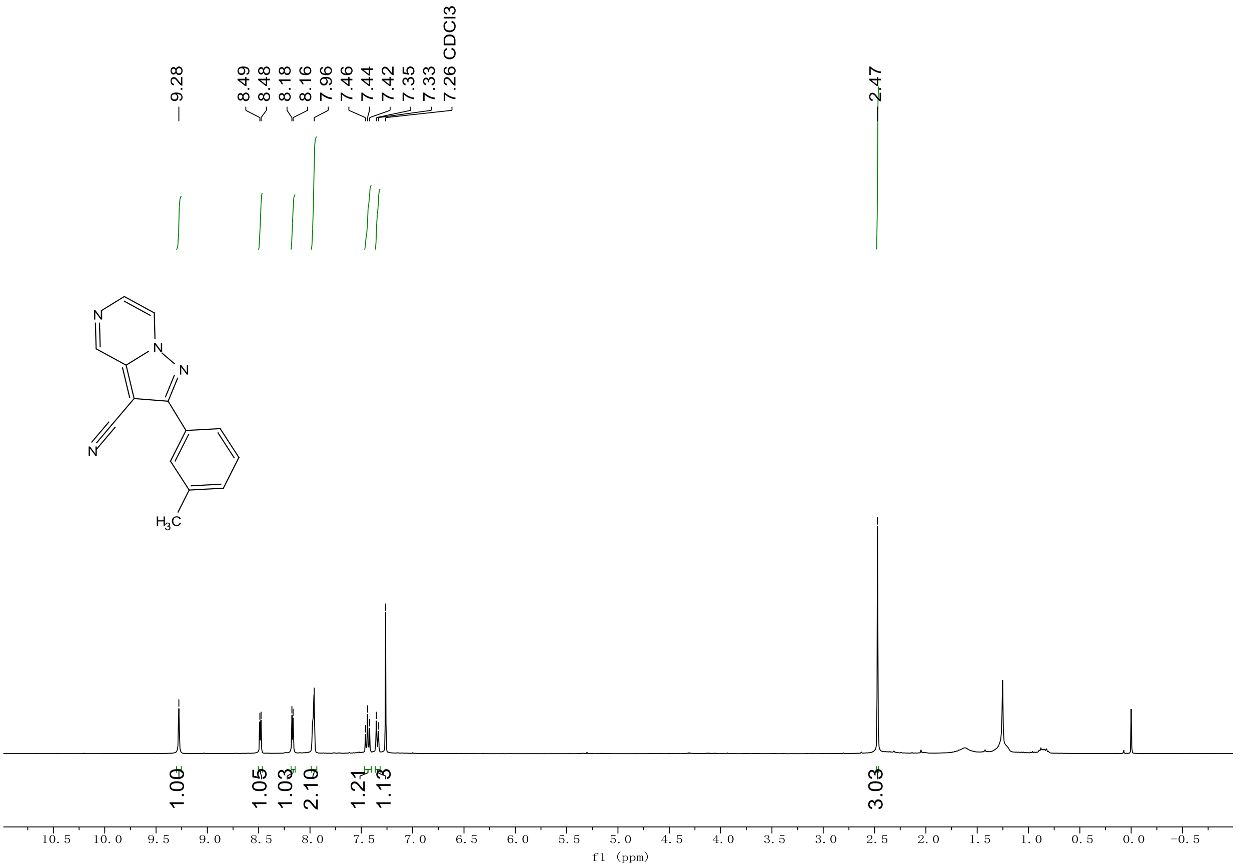


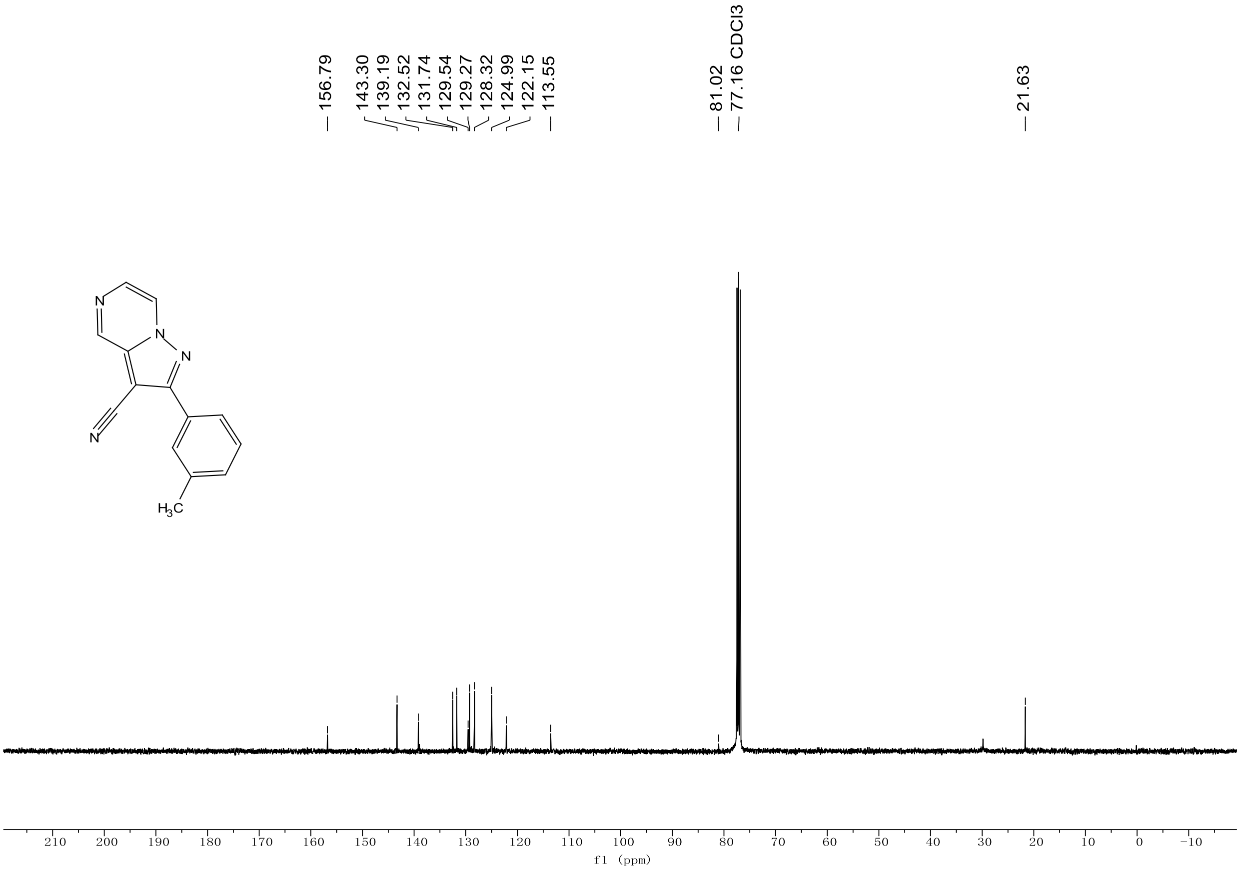
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6c**



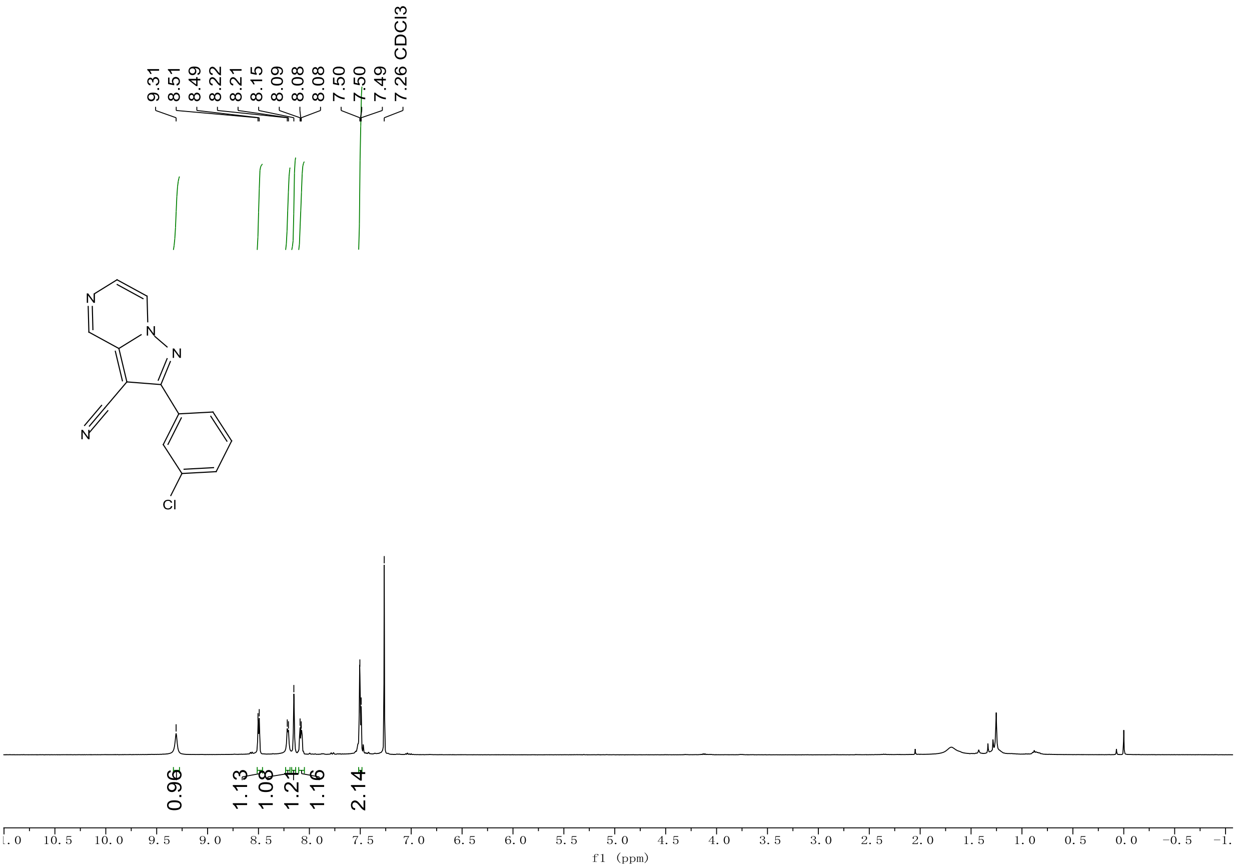


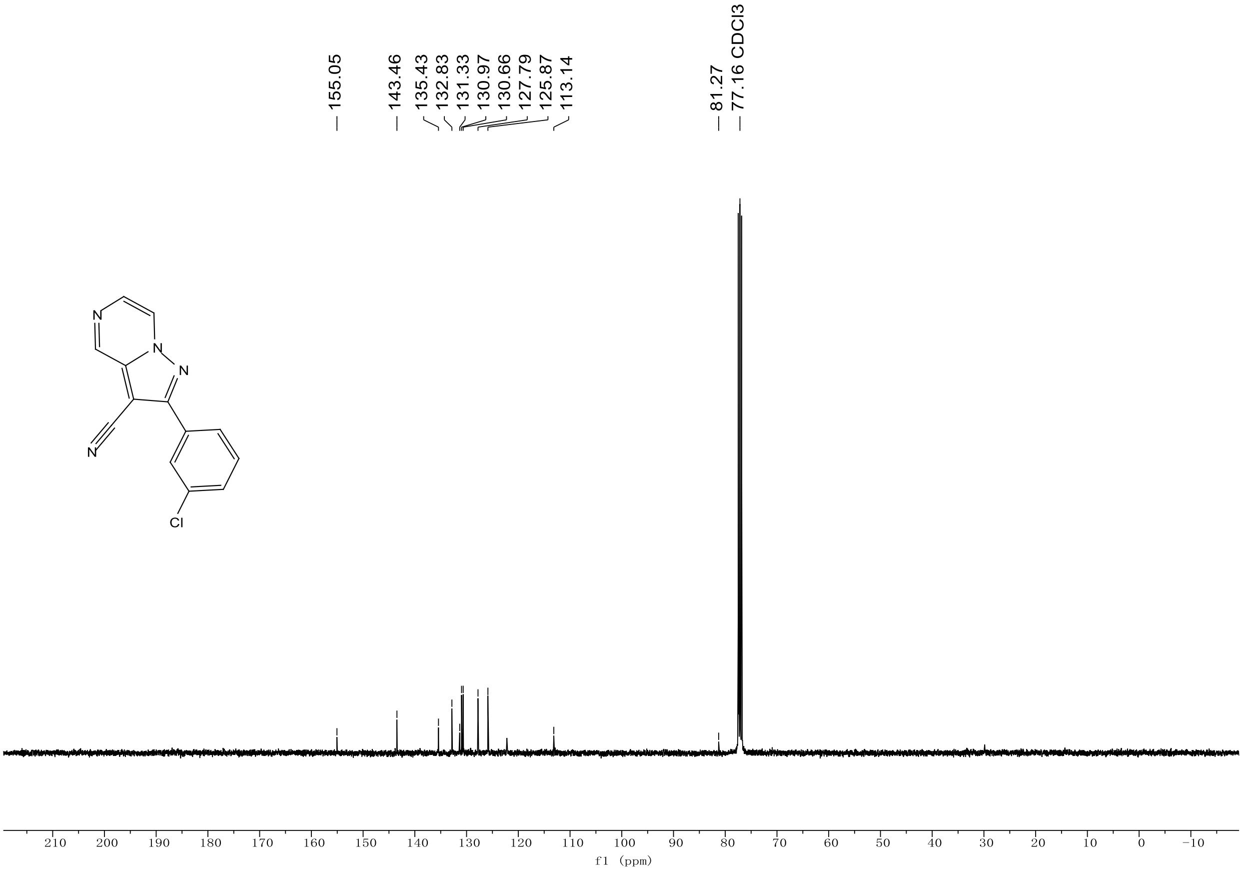
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6d**



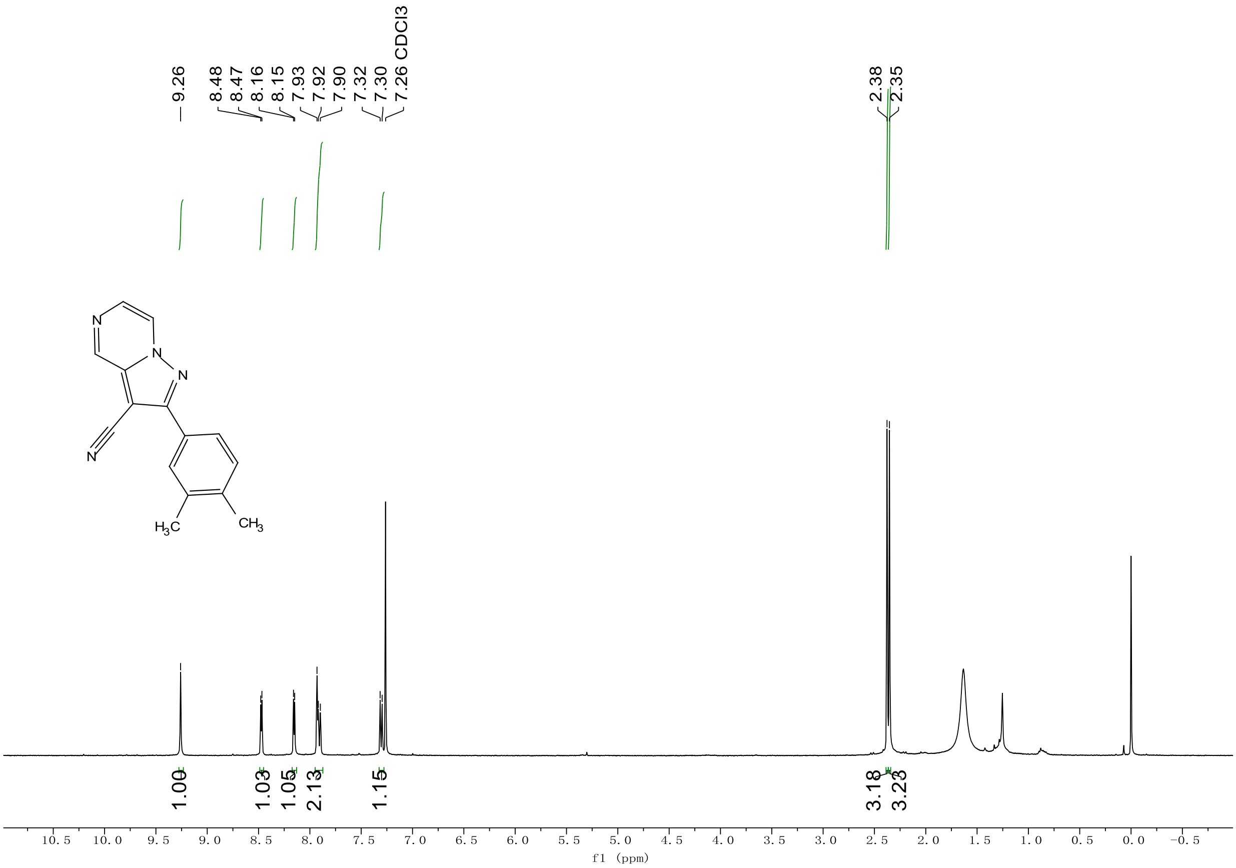


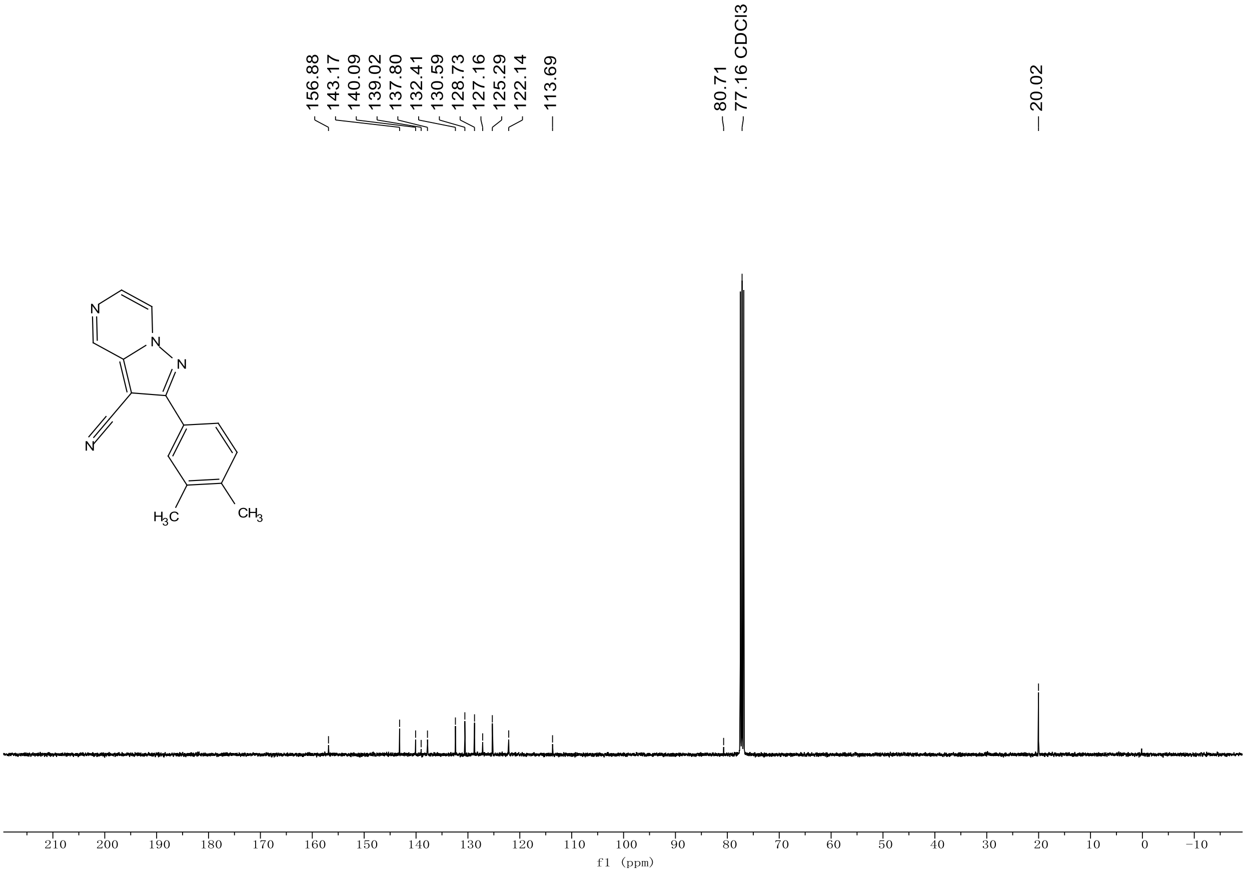
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6e**



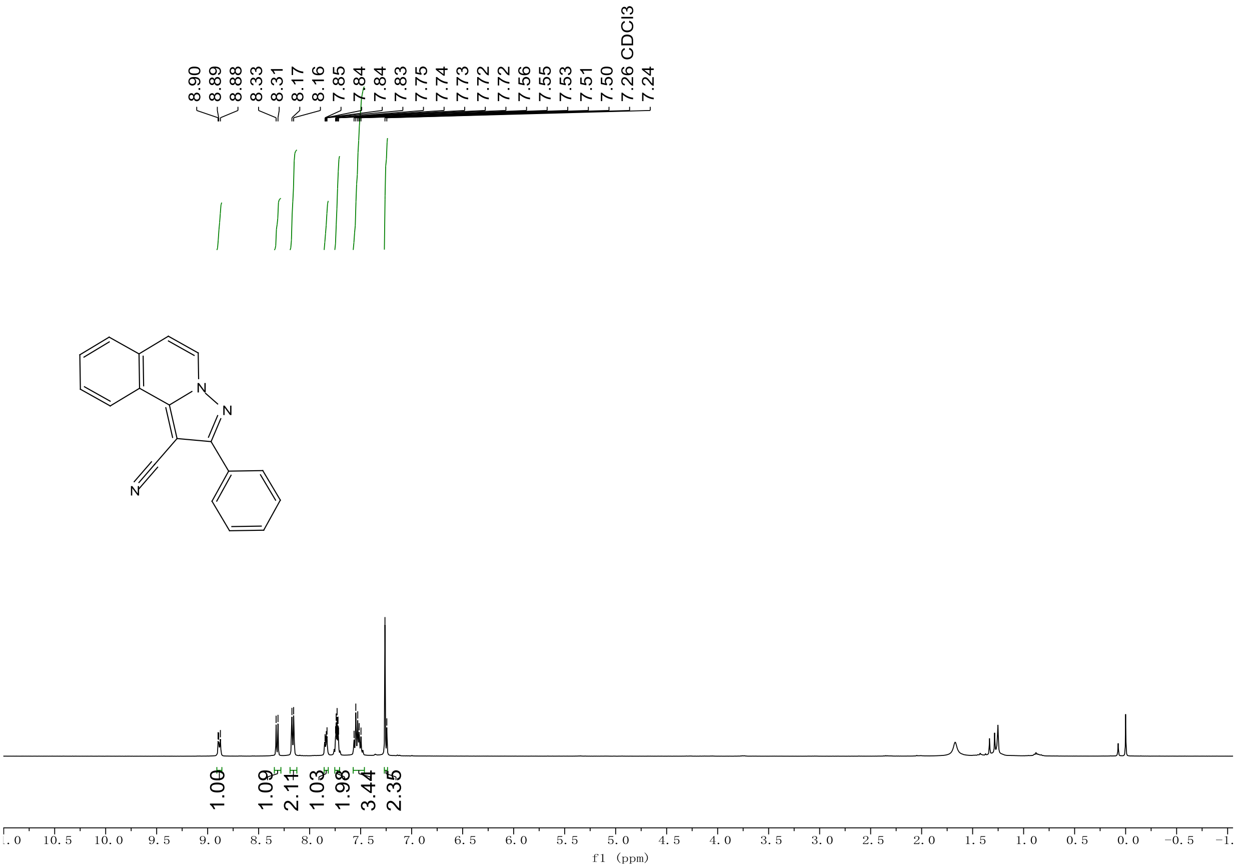


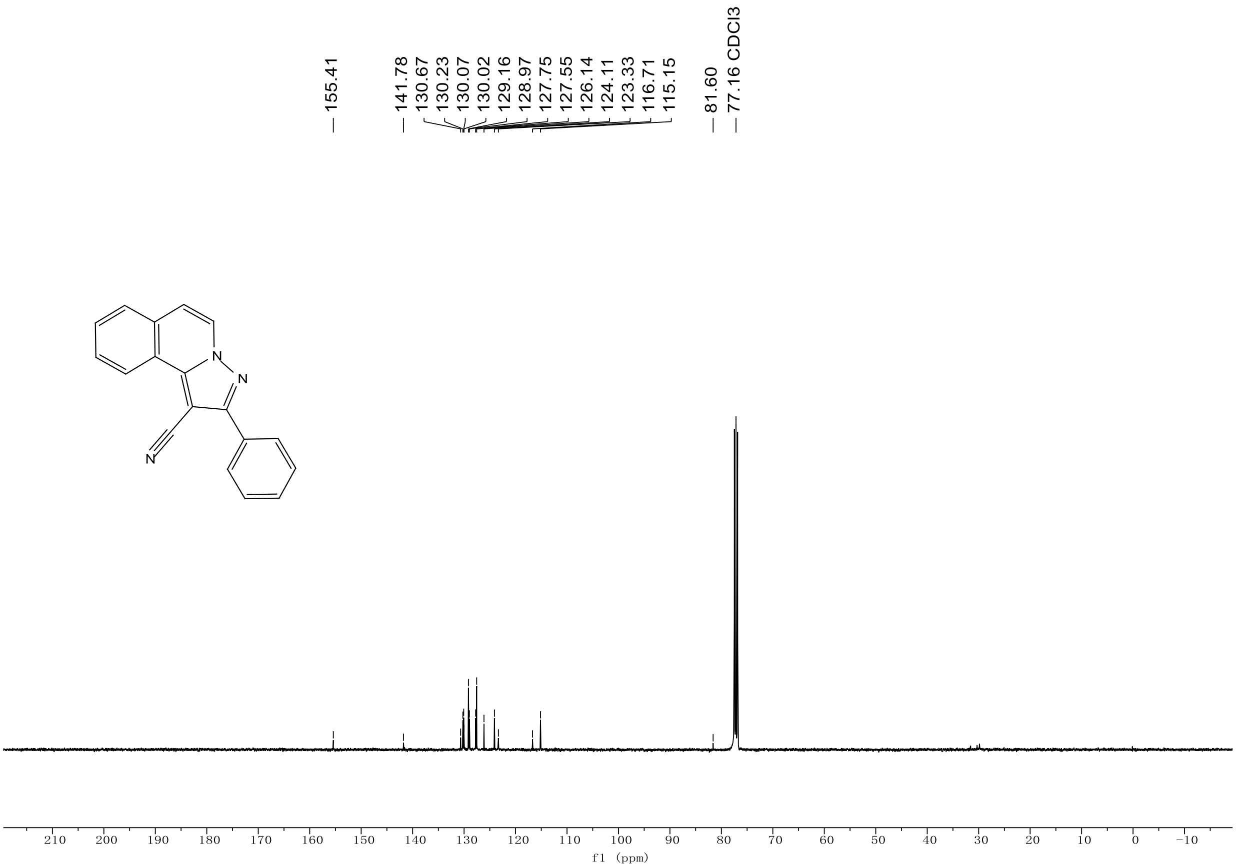
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6f**



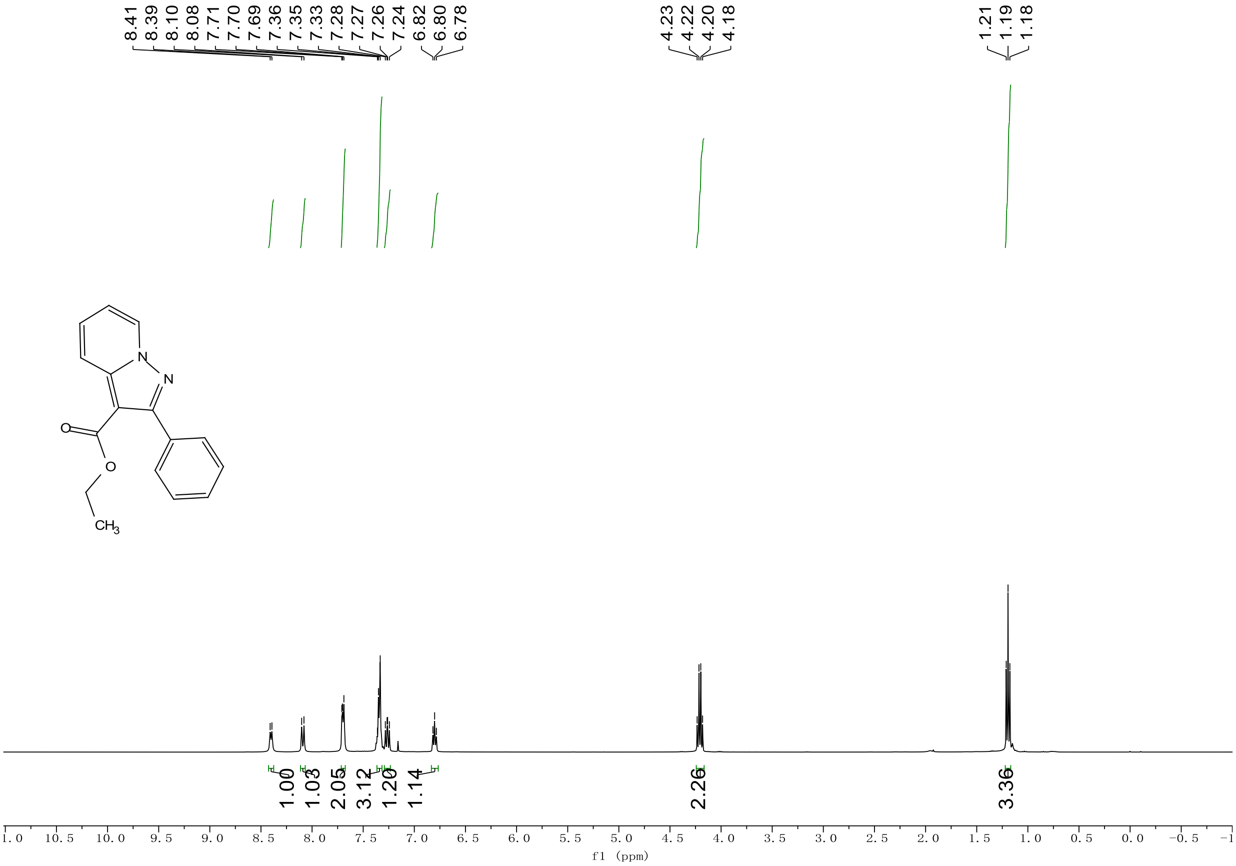


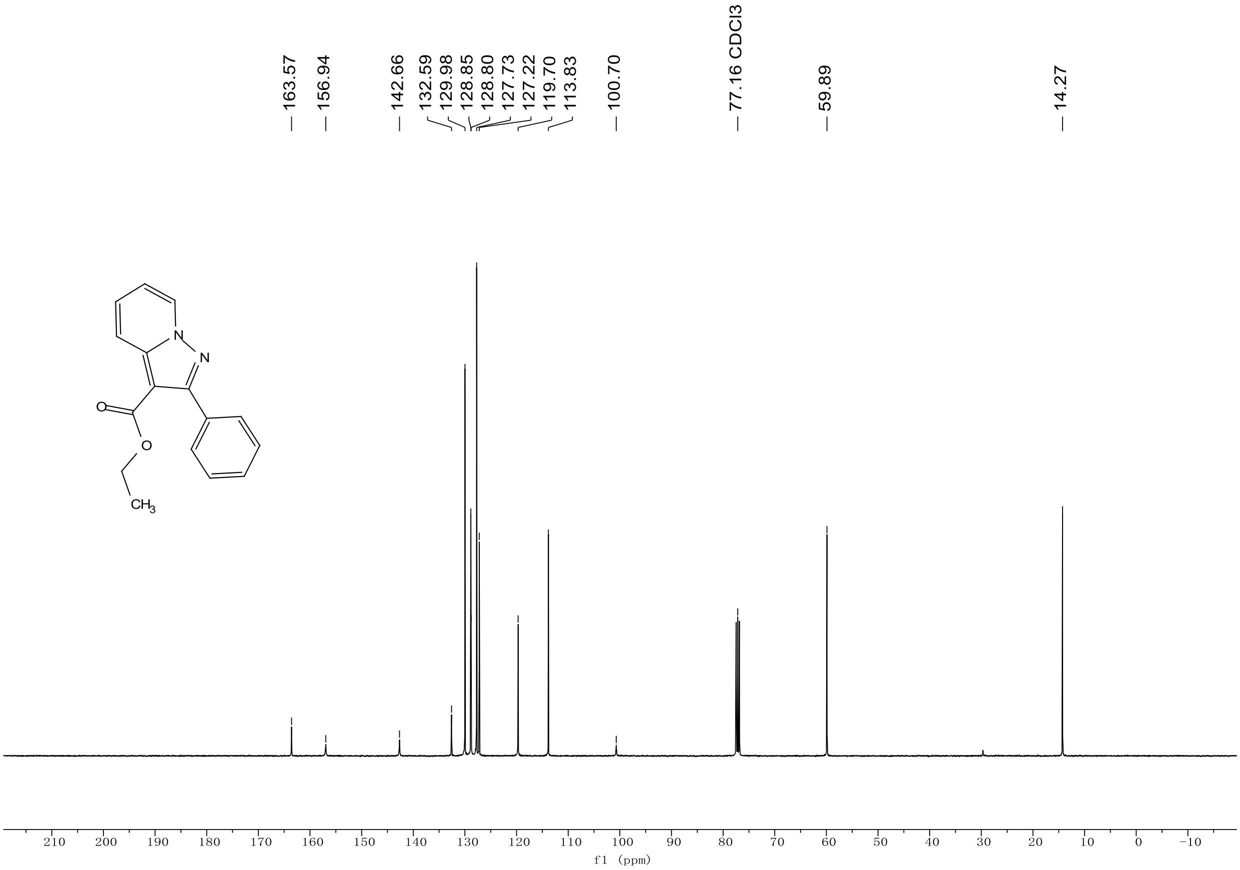
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **7’**



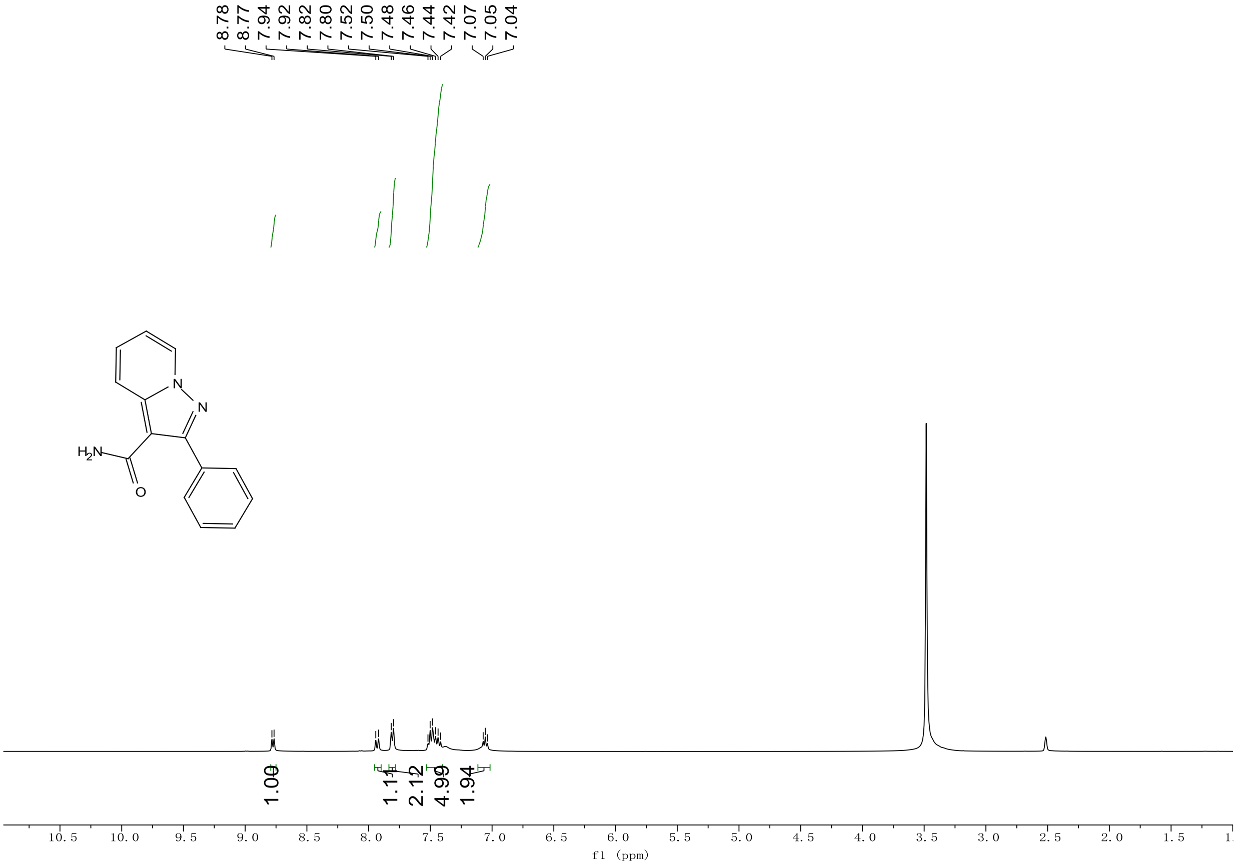


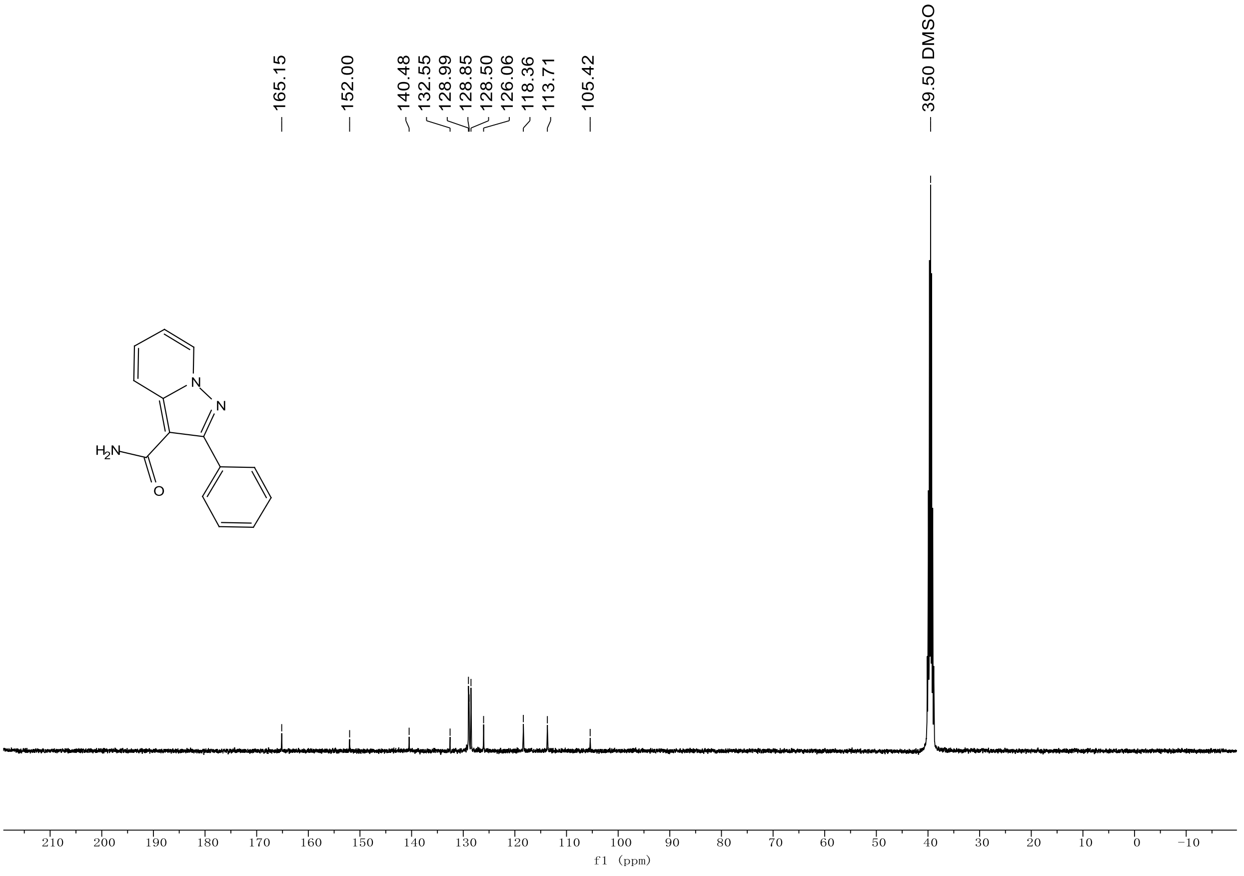
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **8**





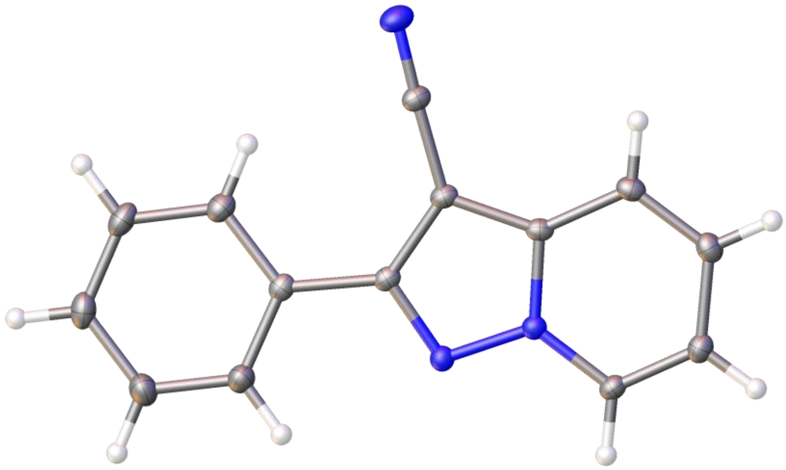
[1]H NMR (400 MHz, DMSO-d6) and [13]C NMR (100 MHz, DMSO-d6) spectrum of compound **9**





4. X-ray crystallographic data

Figure S1 X-ray single crystal structure of **3a**



Single crystals of **3a** were grown by slow evaporation of its EA/PE solution. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC 2242824).

Table S1 Crystal data and structure refinement for **3a.**

Identification code	gy1115
Empirical formula	$C_{14}H_9N_3$
Formula weight	219.24
Temperature/K	200.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	5.5109(5)
b/Å	9.7172(8)
c/Å	19.8992(17)
α/°	90
β/°	89.678(8)
γ/°	90
Volume/Å^3	1065.60(16)
Z	4
ρ_{calc}g/cm^3	1.367
μ/mm^{-1}	0.085
F(000)	456.0
Crystal size/mm^3	0.15 × 0.12 × 0.11
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.094 to 49.998
Index ranges	$-6 \leq h \leq 6$, $-11 \leq k \leq 8$, $-23 \leq l \leq 23$
Reflections collected	5024
Independent reflections	1890 [R_{int} = 0.1229, R_{sigma} = 0.1080]
Data/restraints/parameters	1890/0/155
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0666, wR_2 = 0.1593
Final R indexes [all data]	R_1 = 0.0814, wR_2 = 0.1805
Largest diff. peak/hole / e Å^{-3}	0.35/-0.33

Table S2 Bond Lengths for **3a**

Atom	Atom	Length/Å
N1	C14	1.148(3)
N2	N3	1.364(2)
N2	C9	1.379(3)
N2	C13	1.357(2)
N3	C7	1.336(2)
C1	C2	1.387(3)
C1	C6	1.392(3)
C1	C7	1.472(3)
C2	C3	1.383(3)
C3	C4	1.386(4)
C4	C5	1.372(3)
C5	C6	1.380(3)
C7	C8	1.417(3)
C8	C9	1.395(3)
C8	C14	1.417(3)
C9	C10	1.406(3)
C10	C11	1.348(3)
C11	C12	1.414(3)
C12	C13	1.349(3)

Table S3 Bond Angles for **3a**

Atom	**Atom**	**Atom**	**Angle/°**
N3	N2	C9	112.63(15)
C13	N2	N3	124.07(16)
C13	N2	C9	123.29(17)
C7	N3	N2	105.18(16)
C2	C1	C6	118.0(2)
C2	C1	C7	122.8(2)
C6	C1	C7	119.19(19)
C3	C2	C1	120.7(2)
C2	C3	C4	120.8(2)
C5	C4	C3	118.7(2)
C4	C5	C6	120.9(3)
C5	C6	C1	120.9(2)
N3	C7	C1	119.00(19)
N3	C7	C8	111.10(17)
C8	C7	C1	129.90(18)
C7	C8	C14	130.35(19)
C9	C8	C7	105.87(17)
C9	C8	C14	123.8(2)
N2	C9	C8	105.22(18)
N2	C9	C10	118.00(18)
C8	C9	C10	136.79(19)

C11	C10	C9	118.96(19)
C10	C11	C12	121.1(2)
C13	C12	C11	120.03(19)
C12	C13	N2	118.59(19)
N1	C14	C8	178.4(2)

Table S4 checkCIF/PLATON report

Bond precision	C-C = 0.0031 A	Wavelength = 0.71073	
Cell	a=5.5109(5)	b=9.7172(8)	c=19.8992(17)
	alpha=90	beta=89.678(8)	gamma=90
Temperature	200 K	1.379(3)	
	Calculated	Reported	
Volume	1065.60(16)	1065.60(16)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C14 H9 N3	C14 H9 N3	
Sum formula	C14 H9 N3	C14 H9 N3	
Mr	219.24	219.24	
Dx,g cm-3	1.367	1.367	
Z	4	4	
Mu (mm-1)	0.085	0.085	
F000	456.0	456.0	
F000’	456.15		
h,k,lmax	6,11,23	6,11,23	
Nref	1889	1890	
Tmin,Tmax	0.988,0.991		
Correction method	Not given		
Data completeness	1.001		
Theta(max)	24.999		
R(reflections)	0.0666(1427)		
wR2(reflections)	0.1805(1890)		
S	1.053		
Npar	155		

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C
RINTA01_ALERT_3_C The value of Rint is greater than 0.12
Rint given 0.123
PLAT157_ALERT_4_C Non-standard Monoclinic Beta Angle less 90 Deg 89.68

Degree Alert level G
PLAT020_ALERT_3_G The Value of Rint is Greater Than 0.12 .... 0.123 Report

PLAT158_ALERT_4_G The Input Unitcell is NOT Standard/Reduced ..... Please Check
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still 49% Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ....
2.7 Low PLAT967_ALERT_5_G Note: Two-Theta Cutoff Value in Embedded .res .. 50.0 Degree
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 2 Info
0 **ALERT level A** = Most likely a serious problem **-** resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
2 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
6 **ALERT level G** = General information/check it is not something unexpected
0 **ALERT type 1** CIF construction/syntax error, inconsistent or missing data
1 **ALERT type 2** Indicator that the structure model may be wrong or deficient
4 **ALERT type 3** Indicator that the structure quality may be low
2 **ALERT type 4** Improvement, methodology, query or suggestion
1 **ALERT type 5** Informative message, check

5. References

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(c) Wang, A.; Liu, Y.-Z.; Shen, Z.; Qiao Z.; Ma, X. *Org. Lett.*, **2022**, *24*, 1454-1459.
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