Water-promoted deconstructive amination of alkenes through single-carbon deletion: access to fully substituted pyrroles

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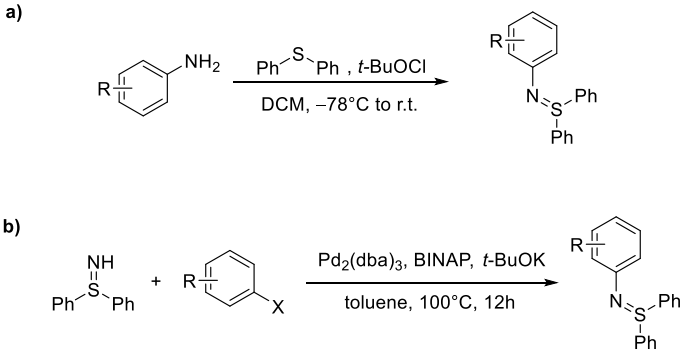
Supplementary Information

Contents

1. General information

Unless otherwise noted, all reactions were carried out under an atmosphere of argon. Commercial reagents and solvents were purchased from Adamas-Beta, Macklin, Alfa Aesar, Bidepharm, Energy Chemical, and Leyan, and used without further purification. Dienes **1**[1] and sulfilimines **2**[2] were synthesized according to literature procedures. Oil baths were used as the heat source. Thin-layer chromatography (TLC) was performed on glass-backed silica plates, and products were visualized under UV light (λ = 254 nm). Flash column chromatography was carried out on silica gel (200–300 mesh) using ethyl acetate (EA) and petroleum ether (PE) as eluents. Nuclear magnetic resonance (NMR) spectra were recorded at 25 °C on Bruker 600 or 700 MHz, or JEOL 600 MHz instruments. ^{1}H NMR chemical shifts (δ) were reported in ppm relative to residual non-deuterated solvent signals ($CDCl_3$: δ = 7.26 ppm). ^{13}C NMR chemical shifts were referenced to $CDCl_3$ (δ = 77.2 ppm), and ^{19}F NMR spectra were recorded where applicable. High-resolution mass spectra (HRMS) were obtained on an Agilent P/N G1969-90010 and reported for $[M+H]^+$ or $[M+Na]^+$ ions. Melting points were measured using a BUCHI Melting Point M-565 instrument. X-ray diffraction data were collected on a Bruker D8 QUEST and deposited at the Cambridge Crystallographic Data Centre.

2. General procedure for the synthesis of *S*,*S*-diphenyl-*N*-arylsulfilimines



S,*S*-diphenyl-*N*-arylsulfilimines **2a**, **2b**, **2c**, **2f**, **2h**, **2j**, **2k**, **2l**, and **2n** were prepared following procedure a from the literature.[3]

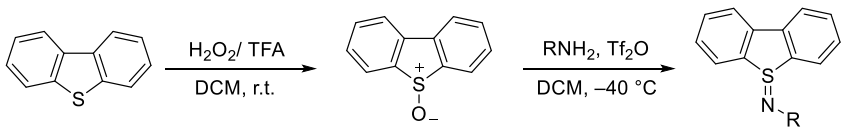
Procedure a:

Under N_2, *t*-BuOCl (2.3 g, 21.0 mmol) was slowly added to a mixture of substituted aniline (20.0 mmol) and diphenyl sulfide (0.8 mL, 22.0 mmol) in 80 mL of DCM at −78 °C. The mixture was stirred at this temperature for 1 h and then for an additional hour at room temperature. After adding NEt_3 (4.16 mL, 30 mmol), the mixture was stirred for 10 min. The solvent was evaporated to yield crude products, which can be purified through flash column chromatography with EA and petroleum ether as the eluent, resulting in 15%-79% yields of *S*,*S*-diphenyl-*N*-arylsulfilimines.

S,*S*-diphenyl-*N*-arylsulfilimines **2d, 2e, 2g, 2i, 2m, 2o, 2p,** and **2q** were prepared following procedure b from the literature.[3]

Procedure b: To a vial, diphenyl-λ-sulfanimine (110 mg, 0.5 mmol), substituted iodobenzene (1.0 mmol; for **2o**, **2p**, and **2q**, X = Br), $Pd_2(dba)_3$ (23 mg, 5 mol%), BINAP (31 mg, 10 mol%), and *t*-BuOK (112 mg, 1.0 mmol) were added, followed by 2 mL of anhydrous toluene. The mixture was stirred at 100 °C for 12 hours. After evaporating the solvent, the residue was purified by column chromatography with EA and petroleum ether as eluent, yielding the corresponding *S*,*S*-diphenyl-*N*-arylsulfilimines in 72-89% yields.

3. General procedure for the synthesis of cyclic dibenzothiophene sulfilimine

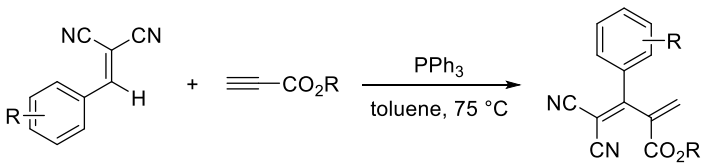


2s and **2t** were prepared following procedure from the literature.[4]

In a nitrogen-filled oven-dried vial, benzothiophene (1.0 mmol), DCM (2.2 mL), and TFA (2.2 mL) were combined. At room temperature, H_2O_2 (30% aq., 102 μL, 1.1 mmol) was added, and the reaction was monitored by TLC (10% EA in DCM). Additional H_2O_2 was added until the starting material was completely consumed. The reaction was quenched with saturated aqueous $NaHCO_3$ at 0 ºC, and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$ and concentrated in *vacuo*. The crude mixture was purified by column chromatography (20% EA in DCM) to yield benzothiophene *S*-oxide.[5]

Under nitrogen, dibenzothiophene-*S*-oxide (1.0 g, 5.0 mmol, 1.0 equiv.) and 40 mL of dry DCM (*c* = 0.13) were placed in a 100 mL two-necked round-bottom flask. The mixture was stirred at –40 °C for 5 min before adding triflic anhydride (0.85 mL, 1.4 g, 5.1 mmol, 1.0 equiv.). After stirring at –40 °C for 1 hour, a solution of corresponding amine (13 mmol, 2.5 equiv.) in DCM (10 mL) was added dropwise over 10 minutes. The reaction mixture was then warmed to 25 °C, and 20 mL of saturated aqueous sodium carbonate solution was added, stirring for 5 min. The mixture was transferred to a separatory funnel, and the organic layer was separated. The aqueous layer was extracted with DCM (2 × 40 mL). The combined organic layers were dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography using DCM/MeOH to obtain **2s** or **2t**.

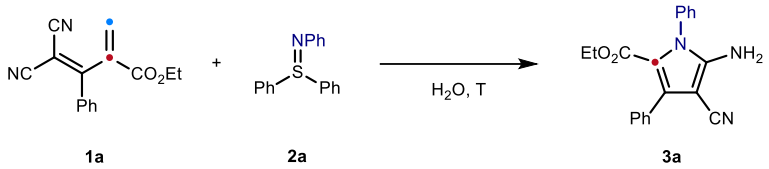
4. General procedure for the synthesis of dicyano-2-methylenebut-3-enoates



The corresponding dicyano-2-methylenebut-3-enoates were prepared according to the literature procedure.[6] Under an argon atmosphere, arylidenemalononitrile (2.0 mmol) and triphenylphosphine (PPh_3, 20.0 mol %) were dissolved in toluene (25 mL) in three-necked flask. Ethyl propionate (2.4 mmol) was diluted with toluene (40 mL) and added dropwise to the reaction mixture at 75 °C for 3 hours. Once the addition was finished, the reaction mixture was cooled down to room temperature. Then the mixture was directly purified by column chromatography on silica gel using a petroleum ether/ethyl acetate solvent system (20:1) to dicyano-2-methylenebut-3-enoates.

5. Optimization of reaction conditions

Table S1. Screening of reaction temperatures.

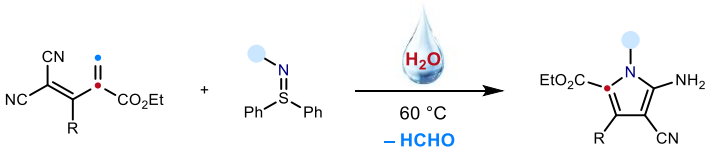


1a 2a 3a

Entry[a]	T (°C)	*t* (h)	Yield[b] (%)
1	R.T.	72 h	41
2	50 °C	9 h	75
3	60 °C	4 h	81
4	70 °C	4 h	75
5	80 °C	2 h	71

[a]Reaction conditions: **1a** (0.12 mmol), **2a** (0.10 mmol) in water (1.0 mL) under Ar for the indicated time; [b]Isolated yield.

6. General procedure for the synthesis of 3



1 2 3

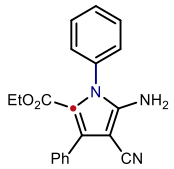
In a 10 mL Schlenk tube, diene 1 (0.12 mmol, 1.2 equiv.), sulfilimine 2 (0.10 mmol, 1.0 equiv.), and H_2O (1.0 mL) were combined and stirred at 60 °C for 4 h. Reaction progress was monitored by TLC by dissolving a small aliquot of the reaction mixture in EA. Completion was confirmed by the disappearance of sulfilimine **2** and aziridine **4**. Upon completion, the mixture was worked up by column chromatography (method A) or filtration (method B):

Method A: The reaction mixture was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford product **3**. The isolated product was dried under vacuum and characterized by ^{1}H NMR, ^{13}C NMR, *etc*.

Method B: The mixture was filtered under reduced pressure through a Büchner funnel. The solid was

washed with water (3 × 5 mL), dried, and characterized by ^{1}H NMR, ^{13}C NMR, *etc*.

Ethyl 5-amino-4-cyano-1,3-diphenyl-1*H*-pyrrole-2-carboxylate (3a)



3a

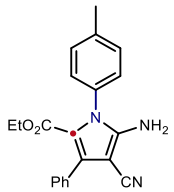
Prepared according to the general procedure, the crude product was purified by filtration to afford **3a** (27.0 mg, 81% yield, white solid, m.p.: 201.1 – 201.3 ℃).

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.49 – 7.44 (m, 5H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 6.6 Hz, 2H), 4.35 (s, 2H), 3.82 (q, *J* = 7.2 Hz, 2H), 0.75 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 159.9, 148.4, 136.3, 135.1, 132.5, 129.83, 129.80, 129.4, 128.1, 127.8, 127.7, 115.8, 114.4, 76.9, 59.9, 13.5.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{17}N_3NaO_2^+$ 354.1218; found: 354.1216.

Ethyl 5-amino-4-cyano-3-phenyl-1-(p-tolyl)-1*H*-pyrrole-2-carboxylate (3b)



3b

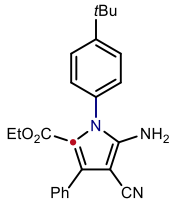
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 5:1) to afford **3b** (27.8 mg, 80% yield, white solid, m.p.: 212.5 – 212.7 ℃).

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.44 (d, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.2 Hz 2H), 7.31 (d, *J* = 7.2 Hz 1H), 7.28 (d, *J* = 6.6 Hz, 2H), 7.16 (d, *J* = 6.6 Hz, 2H), 4.33 (s, 2H), 3.84 (q, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 0.78 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 160.0, 148.5, 148.4, 139.6, 134.84, 134.82, 133.5, 132.58, 132.56, 130.4, 129.8, 128.1, 127.8, 127.4, 115.9, 114.4, 76.8, 59.9, 21.3, 13.5.

HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{21}H_{20}N_3O_2^+$ 346.1556; found 346.1564.

Ethyl 5-amino-1-(4-(tert-butyl)phenyl)-4-cyano-3-phenyl-1*H*-pyrrole-2-carboxylate (3c)



3c

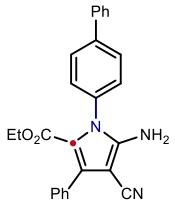
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1) to afford **3c** (29.1 mg, 75% yield, white solid, m.p.: 221.1 – 221.3 ℃).

^{1}H NMR (700 MHz, Chloroform-*d*) δ (ppm): 7.51 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 7.0 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 4.34 (s, 2H), 3.84 (q, *J* = 7.7 Hz, 2H), 1.374(s, 9H), 0.75 (t, *J* = 7.7 Hz, 3H).

^{13}C NMR (175 MHz, Chloroform-*d*) δ (ppm): 159.9, 152.6, 148.5, 135.0, 133.5, 132.5, 129.8, 128.1, 127.8, 127.1, 126.7, 115.9, 114.5, 76.8, 59.8, 34.9, 31.3, 13.4.

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{24}H_{25}N_3NaO_2^+$ 410.1844; found 410.1853.

Ethyl 1-([1,1'-biphenyl]-4-yl)-5-amino-4-cyano-3-phenyl-1*H*-pyrrole-2-carboxylate (3d)



3d

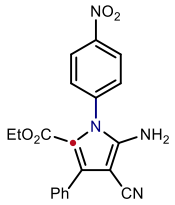
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1) to afford **3d** (31.0 mg, 76% yield, white solid, m.p.: 195.1 – 195.9 ℃).

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): δ 7.67 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.45 – 7.40 (m, 4H), 7.35 – 7.30 (m, 6H), 4.40 (s, 2H), 3.84 (q, *J* = 7.2 Hz, 2H), 0.77 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 160.0, 148.53, 148.51, 142.4, 139.7, 135.3, 135.2, 132.5, 129.8, 129.0, 128.4, 128.2, 128.0, 127.8, 127.2, 115.9, 114.4, 77.0, 60.0, 13.5.

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{26}H_{21}N_3NaO_2^+$ 430.1531; found 430.1539.

Ethyl 5-amino-4-cyano-1-(4-nitrophenyl)-3-phenyl-1*H*-pyrrole-2-carboxylate (3e)



3e

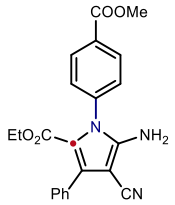
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 5:1) to afford **3e** (28.7 mg, 77% yield, yellow solid, m.p.: 138.4 – 138.8 ℃).

^{1}H NMR (700 MHz, Chloroform-*d*) δ (ppm): 8.38 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 7 Hz, 2H), 7.40 – 7.36 (m, 3H), 4.41 (s, 2H), 3.87 (q, *J* = 7.0 Hz, 2H), 0.84 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (175 MHz, Chloroform-*d*) δ (ppm): 159.8, 148.04, 147.95, 141.8, 135.9, 131.9, 129.8, 129.0, 128.5, 127.9, 125.1, 115.2, 114.2, 78.0, 60.3, 13.6.

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{20}H_{16}N_4NaO_4^+$ 399.1069; found 399.1077.

Ethyl-5-amino-4-cyano-1-(4-(methoxycarbonyl)phenyl)-3-phenyl-1*H*-pyrrole-2-carboxylate (3f)



3f

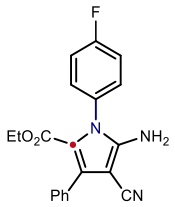
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1) to afford **3f** (30.9 mg, 79% yield, white solid, m.p.: 201.7 – 202.0 ℃).

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 8.09 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 7.2 Hz, 2H), 7.31–7.25 (m, 5H), 4.37 (s, 2H), 3.84 (s, 3H), 3.76 (q, *J* = 6.6 Hz, 2H), 0.71 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 165.9, 159.8, 148.3, 140.3, 135.6, 132.2, 131.1, 131.0, 129.8, 128.3, 127.83, 127.81, 115.6, 114.2, 77.3, 60.1, 52.5, 13.5.

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{21}H_{19}N_3NaO_4^+$ 412.1273; found 412.1282.

Ethyl 5-amino-4-cyano-1-(4-fluorophenyl)-3-phenyl-1*H*-pyrrole-2-carboxylate (3g)



3g

Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 5:1) to afford **3g** (28.0 mg, 80% yield, yellow solid, m.p.: 201.3 – 201.6 °C).

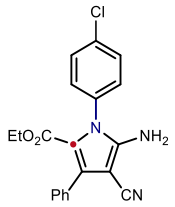
^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.50 (d, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.39 (d, *J* = 6.6 Hz, 1H), 7.36 – 7.34 (m, 2H), 7.25 (t, *J* = 8.4 Hz, 2H), 4.42 (s, 2H), 3.91 (q, *J* = 7.2 Hz, 2H), 0.87 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 162.8 (d, *J* = 250.7 Hz), 159.9, 148.5, 135.2, 132.4, 132.1 (d, *J* = 3.3 Hz), 129.8, 129.7 (d, *J* = 8.6 Hz), 128.2, 127.8, 116.9 (d, *J* = 22.8 Hz), 115.7, 114.4, 77.0, 60.0, 13.5.

^{19}F NMR (564 MHz, Chloroform-*d*) δ (ppm): -110.66 – 110.72 (m, 1F).

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{20}H_{16}FN_3NaO_2^+$ 372.1124; found 372.1133.

Ethyl 5-amino-1-(4-chlorophenyl)-4-cyano-3-phenyl-1*H*-pyrrole-2-carboxylate (3h)



3h

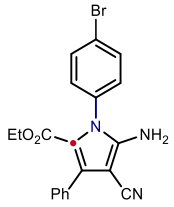
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1) to afford **3h** (24.5 mg, 68% yield, white solid, m.p.: 246.5 – 249.6 °C).

^{1}H NMR (700 MHz, Chloroform-*d*) δ (ppm): 7.47 (d, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 7.0 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 7.0 Hz, 1H), 7.25 (d, *J* = 78.4 Hz, 2H), 4.32 (s, 2H), 3.85 (q, *J* = 7.0 Hz, 2H), 0.81 (t, *J* = 7.0, 3H).

^{13}C NMR (175 MHz, Chloroform-*d*) δ (ppm): 159.8, 148.2, 134.6, 132.3, 130.08, 130.05, 129.8, 129.7, 129.2, 128.5, 128.3, 127.8, 114.3, 77.3, 60.0, 13.5.

HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{20}H_{17}ClO_2^+$ 366.1009; found 366.1008.

Ethyl 5-amino-1-(4-bromophenyl)-4-cyano-3-phenyl-1*H*-pyrrole-2-carboxylate (3i)



3i

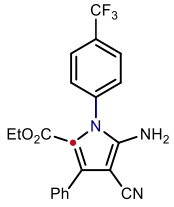
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1) to afford **3i** (27.5 mg, 67% yield, white solid, m.p.: 196.8 – 197.4 ℃).

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.46 – 7.43 (m, 5H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 6.6 Hz, 2H), 4.38 (s, 2H), 3.80 (q, *J* = 7.2 Hz, 2H), 0.75 (t, *J* = 6.6 Hz, 3H);

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 159.6, 148.5, 136.1, 133.7, 131.5, 131.4, 131.0, 129.8, 129.5, 127.7, 122.4, 115.6, 114.4, 76.6, 60.0, 13.5.

HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{20}H_{17}BrN_3O_2^+$ 410.0504; found 410.0500.

Ethyl 5-amino-4-cyano-3-phenyl-1-(4-(trifluoromethyl)phenyl)-1*H*-pyrrole-2-carBoxylate (3j)



3j

Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1) to afford **3j** (17.8 mg, 45% yield, white solid, m.p.: 174.4 – 174.8 ℃).

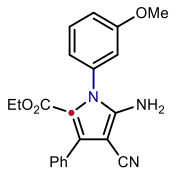
^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.48 (d, *J* = 6.6 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.37 (d, *J* = 6.6 Hz, 1H), 7.34 – 7.21 (m, 2H), 7.22 (t, *J* = 8.4 Hz, 2H), 4.40 (s, 2H), 3.89 (q, *J* = 7.2 Hz, 2H), 0.85 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 163.7, 162.0, 159.9, 148.5, 135.2, 132.4, 132.1(d, *J* = 3.3 Hz), 129.8, 129.7(d, *J* = 88.7 Hz), 128.2, 127.8, 116.9(d, *J* = 22.7 Hz), 115.7, 114.4, 77.06, 60.0, 13.5;

^{19}F NMR (564 MHz, Chloroform-*d*) δ (ppm): -62.0, (s, 3F).

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{21}H_{16}F_3N_3NaO_2^+$422.1092; found 422.1084.

Ethyl-5-amino-4-cyano-1-(3-methoxyphenyl)-3-phenyl-1*H*-pyrrole-2-carboxylate (3k)



3k

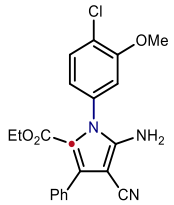
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1) to afford **3k** (29.7 mg, 82% yield, white solid, m.p.:185.9 – 186.2℃).

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.53 – 7.45 (m, 3H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 6.0 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 4.42 (s, 2H), 3.88 (q, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 0.83 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 159.9, 159.6, 148.47, 148.45, 136.5, 135.1, 131.2, 129.8, 129.3, 127.74, 127.70, 124.6, 116.1, 114.2, 113.3, 76.8, 59.8, 55.3, 13.6.

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{21}H_{19}N_3NaO_3^+$ 384.1324; found 384.1331.

Ethyl 5-amino-1-(4-chloro-3-methoxyphenyl)-4-cyano-3-phenyl-1*H*-pyrrole-2-carboxylate (3l)



3l

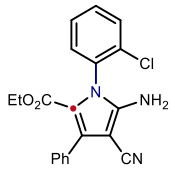
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1) to afford **3l** (29.8 mg, 75% yield, white solid, m.p.: 182.7 – 183.4 ℃).

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.49 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.43–7.36 (m, 3H), 6.88(dd, *J* = 8.4, 2.4 Hz, 1H), 6.86 (d, *J* = 2.4 Hz, 1H), 4.37 (s, 2H), 3.90 – 3.87 (m, 5H), 0.84 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 159.8, 156.0, 148.3, 135.6, 135.1, 132.2, 131.0, 129.8, 128.3, 127.8, 124.0, 120.3, 115.5, 114.4, 111.7, 77.1, 60.0, 56.5, 13.6.

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{21}H_{18}ClN_3NaO_3^+$ 418.0934; found 418.0943.

Ethyl-5-amino-1-(2-chlorophenyl)-4-cyano-3-phenyl-1*H*-pyrrole-2-carboxylate (3m)



3m

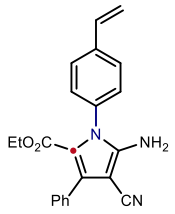
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1) to afford **3m** (18.0 mg, 49% yield, white solid, m.p.: 190.8 – 191.1 ℃).

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.59 (d, *J* = 6.6 Hz, 1H), 7.50 (d, *J* = 6.6 Hz, 2H), 7.49 – 7.44 (m, 2H), 7.42 – 7.35 (m, 4H) , 4.27 (s, 2H), 3.91 – 3.85 (m, 2H), 0.83 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 159.7, 147.9, 135.1, 134.2, 133.3, 132.2, 131.0, 130.7, 129.89, 129.87, 128.2, 128.1, 127.8, 115.6, 114.1, 77.6, 59.9, 13.5.

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{20}H_{16}ClN_3NaO_2^+$ 388.0829; found 388.0838.

Ethyl 5-amino-4-cyano-3-phenyl-1-(4-vinylphenyl)-1*H*-pyrrole-2-carboxylate (3n)



3n

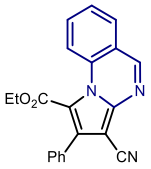
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1) to afford **3n** (32.1 mg, 87% yield, white solid, m.p.: 222.1 – 222.3 ℃).

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.52 (d, *J* = 9.0 Hz, 2H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.33 – 7.31 (m, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.73 (dd, *J* = 18.0, 10.8 Hz, 1H), 5.79 (d, *J* = 17.4 Hz, 1H), 5.34 (d, *J* = 10.8 Hz, 1H), 4.3 (s, 2H), 3.85 (q, *J* = 7.2 Hz, 2H), 0.79 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 158.9, 147.32, 147.31, 137.8, 134.5, 134.3, 134.0, 131.4, 128.8, 127.1, 126.8, 126.7, 126.4, 114.9, 113.4, 76.0, 58.9, 12.5.

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{22}H_{19}N_3NaO_2^+$ 380.1375; found 380.1382.

Ethyl 3-cyano-2-phenylpyrrolo[1,2-a]quinazoline-1-carboxylate (3o)



3o

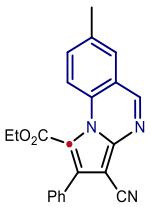
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 10:1) to afford **3o** (26.0 mg, 76% yield, white solid, m.p.: 183.2 – 183.5℃).

^{1}H NMR (700 MHz, Chloroform-*d*) δ (ppm): 8.89 (s, 1H), 8.05 (d, *J* = 9.1 Hz, 1H), 7.95 (dd, *J* = 7.7 Hz, 1.4 Hz, 1H), 7.80 (t, *J* = 7.0 Hz, 1H), 7.58 (t, *J* = 7.0 Hz, 1H), 7.54 (d, *J* = 7.0 Hz, 2H), 7.43 – 7.38 (m, 3H), 4.21 (q, *J* = 7.0 Hz, 2H), 1.00 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (175 MHz, Chloroform-*d*) δ (ppm): 162.2, 153.4, 144.4, 137.8, 134.8, 133.8, 131.4, 129.8, 129.5, 128.8, 128.2, 126.4, 120.1, 117.8, 115.4, 114.3, 88.9, 62.1, 13.6.

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{22}H_{15}N_3NaO_2^+$ 364.1062; found 364.1065.

Ethyl 3-cyano-7-methyl-2-phenylpyrrolo[1,2-a]quinazoline-1-carboxylate (3p)



3p

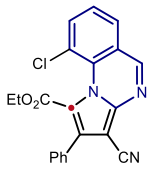
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 10:1) to afford **3p** (15.9 mg, 45% yield, white solid, m.p.: 188.9 – 190.3 ℃).

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 8.89 (s, 1H), 8.00 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.77 (s, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.53 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.48 – 7.44 (m, 3H), 4.26 (q, *J* = 7.2 Hz, 2H), 2.56 (s, 3H), 1.06 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 162.2, 153.3, 144.3, 137.7, 136.5, 135.2, 133.0, 131.5, 129.8, 128.8, 128.7, 128.2, 120.2, 117.6, 115.1, 114.3, 88.6, 61.9, 21.0, 13.6.

HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{21}H_{18}N_3O_2^+$ 356.1399; found 356.1400.

Ethyl 9-chloro-3-cyano-2-phenylpyrrolo[1,2-a]quinazoline-1-carboxylate (3q)



3q

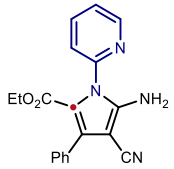
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 10:1) to afford **3q** (8.8 mg, 23% yield, white solid, m.p.: 195.8 – 197.7 ℃).

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 9.41(s, 1H), 8.01 (d, *J* = 9.0 Hz, 1H), 7.76 (t, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.53 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.51 – 7.46 (m, 3H), 4.27 (q, *J* = 7.2 Hz, 2H), 1.06 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 162.0, 149.8, 144.2, 138.5, 136.0, 134.5, 133.5, 131.1, 129.8, 128.9, 128.3, 127.1, 117.7, 116.7, 115.7, 113.9, 89.5, 62.2, 13.6;

HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{21}H_{15}ClN_3O_2^+$ 376.0853 found 376.0855.

Ethyl 5-amino-4-cyano-3-phenyl-1-(pyridin-2-yl)-1*H*-pyrrole-2-carboxylate (3r)



3r

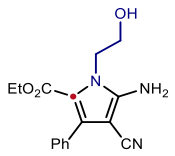
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 5:1) to afford **3r** (19.0 mg, 57% yield, yellow solid, m.p.: 138.7 – 138.9 ℃)

^{1}H NMR (700 MHz, Chloroform-*d*) δ (ppm): 8.46 (d, *J* = 4.2 Hz, 1H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.42 (d, *J* = 7.0 Hz, 2H), 7.31 – 7.25 (m, 4H), 7.15 (s, 1H), 5.38 (s, 2H), 3.83 (q, *J* = 7.0 Hz, 2H), 0.76 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (175 MHz, Chloroform-*d*) δ (ppm): 160.1, 150.8, 149.7, 148.4, 138.5, 136.9, 131.9, 130.0, 128.5, 127.8, 123.0, 121.4, 115.7, 112.9, 77.6, 60.3, 13.6.

HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{19}H_{17}N_4O_2^+$ 333.1352; found 333.1361.

Ethyl 5-amino-4-cyano-1-(2-hydroxyethyl)-3-phenyl-1*H*-pyrrole-2-carboxylate (3s)



3s

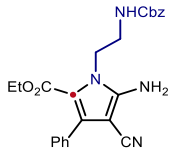
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 1:1) to afford **3s** (25.3 mg, 85% yield, yellow solid, m.p.: 151.6 – 151.9℃)

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.37 – 7.33 (m, 5H), 4.97 (s, 2H), 4.28 (t, *J* = 4.8 Hz, 2H), 4.06 (t, *J* = 4.8 Hz, 2H), 4.02 (q, *J* = 7.2 Hz, 2H), 2.58 (s, 1H), 0.96 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 161.1, 150.4, 135.1, 133.2, 129.7, 127.9, 127.7, 116.2, 113.7, 78.3, 63.5, 60.1, 47.7, 13.7.

HRMS (ESI-TOF) m/z [M+Na]$^+$ Calcd for $C_{16}H_{17}N_3NaO_3^+$ 322.1168; found 322.1177.

Ethyl 5-amino-1-(2-(((benzyloxy)carbonyl)amino)ethyl)-4-cyano-3-phenyl-1*H*-pyrrole-2-carboxylate (3t)



3t

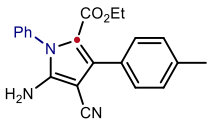
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 5:1) to afford **3t** (27.9 mg, 67% yield, yellow solid, m.p.: 164.7 – 165.2℃)

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.30 – 7.22 (m, 10H), 5.19 (t, *J* = 6.0 Hz, 1H), 5.03 (s, 2H), 4.99 (s, 2H), 4.17 (t, *J* = 7.2 Hz, 2H), 3.90 (q, *J* = 7.2 Hz, 2H), 3.42 (q, *J* = 6.6 Hz, 2H), 0.84 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 161.1, 157.7, 149.1, 135.9, 135.2, 133.1, 129.7, 128.7, 128.5, 128.3, 127.9, 127.6, 115.8, 112.6, 77.6, 67.4, 60.0, 43.5, 41.0, 13.6.

HRMS (ESI-TOF) m/z [M+Na]$^+$ Calcd for $C_{24}H_{24}N_4NaO_3^+$ 455.1695; found 455.1703.

Ethyl 5-amino-4-cyano-1-phenyl-3-(p-tolyl)-1*H*-pyrrole-2-carboxylate (3u)



3u

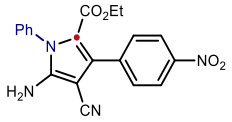
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1) to afford **3u** (28.8 mg, 83% yield, yellow solid, m.p.: 213.9 – 214.5 ℃)

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.45 – 7.41 (m, 3H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 6.6 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 4.32 (s, 2H), 3.79 (q, *J* = 7.2 Hz, 2H), 2.30 (s, 3H), 0.73 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 159.9, 148.4, 138.0, 136.4, 135.3, 129.8, 129.7, 129.37, 129.35, 128.5, 127.7, 116.0, 114.3, 59.8, 21.4, 13.5.

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{21}H_{19}N_3NaO_2^+$ 368.1375; found 368.1385.

Ethyl 5-amino-4-cyano-3-(4-nitrophenyl)-1-phenyl-1*H*-pyrrole-2-carboxylate (3v)



3v

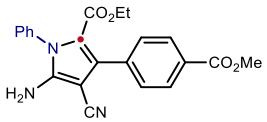
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1) to afford **3v** (27.0 mg, 72% yield, yellow solid, m.p.: 199.5 – 199.8℃)

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 8.26 (d, *J* = 6 Hz, 2H), 7.67 (d, *J* = 6 Hz, 2H), 7.32 (d, *J* = 6 Hz, 2H), 4.43 (s, 2H), 3.87 (q, *J* = 6 Hz, 2H), 0.79 (t, *J* = 6 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 159.3, 148.6, 147.6, 139.5, 135.9, 132.3, 131.0, 130.0, 129.9, 127.7, 123.1, 115.2, 115.0, 76.6, 60.3, 13.6.

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{20}H_{16}ClN_3NaO_2^+$ 388.0829; found 388.0839.

Ethyl 5-amino-4-cyano-3-(4-(methoxycarbonyl)phenyl)-1-phenyl-1*H*-pyrrole-2-carboxylate (3w)



3w

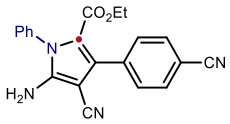
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 5:1) to afford **3w** (18.5 mg, 57% yield, white solid, m.p.: 175.9 – 176.2℃)

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 8.09 (d, *J* = *8.4* Hz, 2H), 7.37 (d, *J* = 6.6 Hz, 2H) ,7.31 – 7.25 (m, 5H), 4.38 (s, 2H), 3.84 (s, 3H), 3.76 (q, *J* = 7.2 Hz, 2H), 0.71 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 159.8, 159.0, 148.3, 136.2, 134.7, 133.7, 129.8, 129.5, 128.8, 127.7, 122.3, 115.8, 115.3, 114.5, 114.0, 59.9, 55.3, 13.5.

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{22}H_{19}N_3NaO_4^+$ 412.1273; found 412.1270

Ethyl 5-amino-4-cyano-3-(4-cyanophenyl)-1-phenyl-1*H*-pyrrole-2-carboxylate (3x)



3x

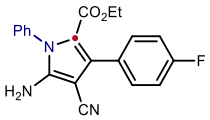
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1) to afford **3x** (20.0 mg, 56% yield, yellow solid, m.p.: 223.0 – 223.3°C)

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.63 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.50 – 7.46 (m, 3H), 7.26 (d, *J* = 7.8 Hz, 2H), 4.42 (s, 2H), 3.80 (q, *J* = 7.2 Hz, 2H), 0.73 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 159.3, 148.7, 137.5, 135.9, 132.7, 131.6, 130.7, 129.9, 129.7, 127.7, 118.8, 115.3, 114.7, 111.8, 76.4, 60.2, 13.5.

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{21}H_{16}N_4NaO_2^+$ 379.1171; found 379.1177.

Ethyl 5-amino-4-cyano-3-(4-fluorophenyl)-1-phenyl-1*H*-pyrrole-2-carboxylate (3y)



3y

Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1) to afford **3y** (26.1 mg, 85% yield, yellow solid, m.p.: 207.4 – 215.1°C)

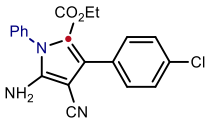
^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.52 – 7.48 (m, 3H), 7.46-7.44 (m, 2H), 7.29 (d, *J* = 6.6 Hz, 2H), 7.07 (t, *J* = 8.4 Hz, 2H), 4.34 (s, 2H), 3.84 (q, *J* = 7.2 Hz, 2H), 0.79 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 162.7 (d, J_{FC} = 246.0 Hz), , 159.7, 148.3, 136.2, 134.0, 131.6 (d, J_{FC} = 3.3 Hz), 129.8, 129.5, 128.4 (d, J_{FC} = 3.5 Hz) 127.7, 115.7, 114.8 (d, J_{FC} = 21.6 Hz), 114.5 76.9, 59.9, 13.5.

^{19}F NMR (564 MHz, Chloroform-*d*) δ (ppm): -113.69 – -113.74 (m, 1F).

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{20}H_{16}FN_3NaO_2^+$ 350.1305; found 350.1311.

Ethyl 5-amino-3-(4-chlorophenyl)-4-cyano-1-phenyl-1*H*-pyrrole-2-carboxylate (3aa)



3aa

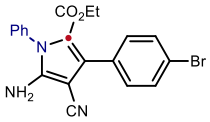
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1) to afford **3aa** (23.0 mg, 63% yield, yellow solid, m.p.: 216.0 – 221.5 ℃)

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm):7.56 – 7.52 (m, 3H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 6.6 Hz, 2H), 4.38 (s, 2H), 3.88 (q, *J* = 7.2 Hz, 2H), 0.83 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 159.6, 148.3, 136.1, 134.2, 133.7, 131.2, 130.9, 129.9, 129.6, 128.1, 127.7, 115.6, 114.5, 76.8, 60.0, 13.5.

HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{20}H_{17}N_3O_2^+$ 366.1009; found 366.1007.

Ethyl 5-amino-3-(4-bromophenyl)-4-cyano-1-phenyl-1*H*-pyrrole-2-carboxylate (3ab)



3ab

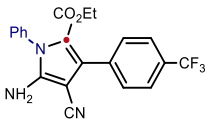
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1) to afford **3ab** (25.6 mg, 62% yield, yellow solid, m.p.: 162.3 – 162.5 ℃)

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.47 – 7.43 (m, 5H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 6.6 Hz, 2H), 4.38 (s, 2H), 3.80 (q, *J* = 7.2 Hz, 2H), 0.75 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 159.6, 148.4, 136.1, 133.7, 131.5, 131.4, 131.0, 129.9, 129.6, 127.7, 122.4, 115.6, 114.4, 76.6, 60.0, 13.5.

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{20}H_{16}BrN_3NaO_2^+$ 432.0324; found 432.0332.

Ethyl 5-amino-4-cyano-1-phenyl-3-(4-(trifluoromethyl)phenyl)-1*H*-pyrrole-2-carboxylate (3ac)



3ac

Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 5:1) to afford **3ac** (20.8 mg, 63% yield, yellow solid, m.p.: 186.6-186.6 ℃)

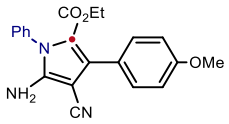
^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.60 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.50 – 7.45 (m, 3H), 7.27 (d, *J* = 6.0 Hz, 2H), 4.35 (s, 2H), 3.80 (q, *J* = 7.2 Hz, 2H), 0.72 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 158.5, 147.4, 135.2, 135.0, 132.3, 129.3, 129.3, 128.9, 128.6, 126.6, 123.74 (q, J_{FC} = 3.6 Hz), 123.15(q, J_{FC} = 270.4 Hz), 114.4, 113.7, 75.7, 59.0, 12.4.

^{19}F NMR (564 MHz, Chloroform-*d*) δ (ppm): -62.6 (s, 3F).

HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{21}H_{17}F_3N_3O_2^+$ 400.1273; found 400.1271.

Ethyl 5-amino-4-cyano-3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrrole-2-carboxylate (3ad)



3ad

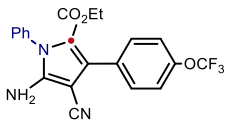
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1) to afford **3ad** (27.4 mg, 76% yield, yellow solid, m.p.: 190.1 – 190.3 ℃)

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.46 – 7.41 (m, 3H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 2H), 6.86 (d, *J* = 9.0 Hz, 2H), 4.34 (s, 2H), 3.80 (q, *J* = 7.2 Hz, 2H), 3.76 (s, 3H), 0.75 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 159.9, 159.6, 148.47, 148.45, 136.5, 135.1, 131.2, 129.8, 129.3, 127.7, 124.6, 116.1, 114.2, 113.3, 76.8, 59.8, 55.3, 13.6;

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{21}H_{19}N_3NaO_2^+$ 384.1324; found 384.1333.

Ethyl 5-amino-4-cyano-1-phenyl-3-(4-(trifluoromethoxy)phenyl)-1*H*-pyrrole-2-carboxylate (3ae)



3ae

Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 5:1) to afford **3ae** (16.5 mg, 48% yield, white solid, m.p.: 221.8 – 222.1 ℃)

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.48 – 7.45 (m, 4H), 7.26 (d, *J* = 6.6 Hz, 2H), 7.19 (t, *J* =

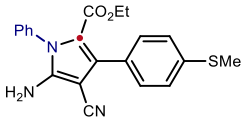
8.4 Hz, 3H), 4.31 (s, 2H), 3.80 (q, J = 7.2 Hz, 2H), 0.73 (t, J = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 158.6, 148.0, 147.4, 135.1, 132.5, 130.4, 130.1, 128.8, 128.6, 126.6, 119.5 (q, J_{FC} = 257.6 Hz), 119.2, 114.5, 113.6, 75.7, 59.0, 12.3;

^{19}F NMR (564 MHz, Chloroform-*d*) δ (ppm): -57.7 (s, 3F).

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{21}H_{16}F_3N_3NaO_3^+$ 483.1040; found 483.1050.

Ethyl 5-amino-4-cyano-3-(4-(methylthio)phenyl)-1-phenyl-1*H*-pyrrole-2-carboxylate (3af)



3af

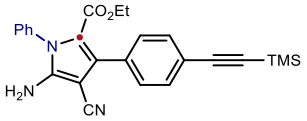
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 5:1) to afford **3al** (19.0 mg, 60% yield, yellow solid, m.p.: 201.1 – 201.3 °C)

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.48 – 7.44 (m, 3H), 7.38 (d, J = 7.8 Hz, 2H), 7.26 (d, J = 6.6 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 4.28 (s, 2H), 3.82 (q, J = 7.2 Hz, 2H), 2.45 (s, 3H), 0.77 (t, J = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 158.8, 147.3, 137.7, 135.3, 133.5, 129.2, 128.8, 128.4, 127.9, 126.6, 124.7, 114.8, 113.3, 76.0, 58.9, 14.6, 12.5.

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{21}H_{19}N_3NaO_2S^+$ 400.1096; found 400.1104.

Ethyl 5-amino-4-cyano-1-phenyl-3-(4-((trimethylsilyl)ethynyl)phenyl)-1*H*-pyrrole-2-carboxylate (3ag)



3ag

Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1) to afford **3ag** (40.1 mg, 94% yield, white solid, m.p.: 195.7 – 196.9 °C)

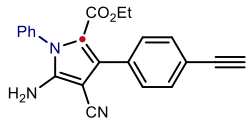
^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.56 – 7.50 (m, 5H), 7.44 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 6.6 Hz, 2H), 4.35 (s, 2H), 3.89 (q, J = 7.2 Hz, 2H), 0.85 (t, J = 7.2 Hz, 3H), 0.26 (s, 9H);

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 159.7, 148.37, 148.35, 136.1, 134.0, 132.7, 131.4, 129.9,

129.8, 127.7, 124.6, 116.1, 114.2, 113.3, 76.8, 59.8, 55.3, 13.6;

HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{25}H_{26}N_3O_2^+$ 428.1794; found 428.1790.

Ethyl 5-amino-4-cyano-1-phenyl-3-(4-((trimethylsilyl)ethynyl)phenyl)-1*H*-pyrrole-2-carboxylate (3ah)



3ah

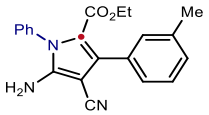
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1) to afford **3ah** (29.8 mg, 84% yield, white solid, m.p.: 176.1 – 176.5 ℃)

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.56 – 7.45 (m, 5H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.28 - 7.26(m, 2H), 4.28 (s, 2H), 3.82 (q, *J* = 7.2 Hz, 2H), 3.05 (s, 1H), 0.77 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 158.7, 147.3, 135.1, 132.9, 132.0, 130.6, 128.9, 128.8, 128.6, 126.7, 120.8, 114.5, 113.5, 82.6, 76.7, 59.0, 28.7, 12.5;

HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{22}H_{18}N_3O_2^+$ 356.1399; found 356.1396.

Ethyl 5-amino-4-cyano-1-phenyl-3-(o-tolyl)-1*H*-pyrrole-2-carboxylate (3ai)



3ai

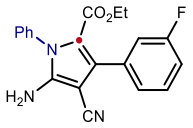
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 5:1) to afford **3ai** (31.0 mg, 90% yield, white solid, m.p.: 170.1 – 173.6 ℃).

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.48 – 7.43 (m, 3H), 7.27– 7.22 (m, 5H), 7.11– 7.10 (m, 1H), 4.26 (s, 2H), 3.81 (q, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 0.76 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 159.9, 148.3, 148.2, 137.2, 136.3, 135.1, 132.2, 130.5, 129.8, 129.4, 128.9, 127.7, 126.9, 115.8, 114.4, 77.0, 59.8, 21.5, 13.5;

HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{21}H_{20}N_3O_2^+$ 346.1556; found 346.1556.

Ethyl 5-amino-4-cyano-3-(3-fluorophenyl)-1-phenyl-1*H*-pyrrole-2-carboxylate (3aj)



3aj

Prepared according to the general procedure, the crude product was purified by filtration to afford **3aj** (29.7 mg, 86% yield, yellow solid, m.p.: 189.6 – 189.9℃).

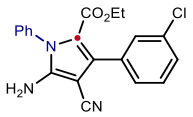
^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.47 – 7.41 (m, 3H), 7.30-7.23 (m, 1H), 7.24 (d, *J* = 7.2 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 10.2 Hz, 1H), 6.98 (t, *J* = 8.4 Hz, 1H), 4.38 (s, 2H), 3.80 (q, *J* = 7.2 Hz, 2H), 0.75 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 162.2 (d, *J* = 243.8 Hz) 159.7, 148.6, 136.2, 134.7 (d, J_{FC} = 8.4 Hz), 133.5, 129.9, 129.6, 129.4 (d, J_{FC} = 8.4 Hz), 127.8, 125.6 (d, J_{FC} = 3.5 Hz), 117.2 (d, J_{FC} = 22.4 Hz), 115.6, 115.1 (d, J_{FC} = 21.2 Hz), 114.6, 76.7, 60.1, 13.5.

^{19}F NMR (564 MHz, Chloroform-*d*) δ (ppm): -114.01 – 114.06 (m, 1F).

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{20}H_{16}FN_3NaO_2^+$ 372.1124; found 372.1131.

Ethyl 5-amino-3-(3-chlorophenyl)-4-cyano-1-phenyl-1*H*-pyrrole-2-carboxylate (3ak)



3ak

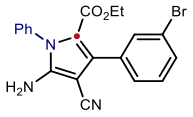
Prepared according to the general procedure, the crude product was purified by filtration to afford **3ak** (31.0 mg, 85% yield, yellow solid, m.p.: 158.8 – 159.0 ℃).

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.50 – 7.45 (m, 3H), 7.45 (s, 1H), 7.33 (d, *J* = 4.8 Hz, 1H), 7.29 – 7.26 (m, 4H), 4.39 (s, 2H), 3.84 (q, *J* = 7.2 Hz, 2H), 0.81 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 159.7, 148.6, 136.1, 134.4, 133.6, 133.3, 130.3, 129.9, 129.6, 129.2, 128.3, 128.0, 127.8, 115.5, 114.7, 76.8, 60.1, 13.5.

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{20}H_{16}ClN_3NaO_2^+$ 388.0829; found 388.0839.

Ethyl 5-amino-3-(3-bromophenyl)-4-cyano-1-phenyl-1*H*-pyrrole-2-carboxylate (3al)



3al

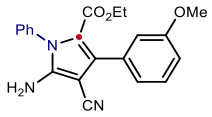
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1) to afford **3al** (34.0 mg, 83% yield, yellow solid, m.p.: 132.6 – 132.8 ℃).

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.52 – 7.48 (m, 5H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 6.6 Hz, 2H), 4.37 (s, 2H), 3.85 (q, *J* = 7.2 Hz, 2H), 0.80 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 159.7, 148.5, 136.2, 133.8, 131.6, 131.5, 131.1, 129.9, 129.6, 127.7, 122.5, 115.6, 114.5, 76.8, 60.1, 13.6;

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{20}H_{16}BrN_3NaO_2^+$ 432.0324; found 432.0332.

Ethyl 5-amino-4-cyano-3-(3-methoxyphenyl)-1-phenyl-1*H*-pyrrole-2-carboxylate (3am)



3am

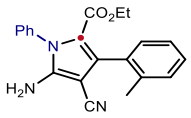
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 5:1) to afford **3am** (31.0 mg, 86% yield, white solid, m.p.: 181.1 – 181.3 ℃).

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.51 – 7.45 (m, 3H), 7.37 (d, *J* = 6.6 Hz, 2H), 7.30 – 7.29 (m, 2H), 7.18 (d, *J* = 6.6 Hz, 2H), 4.31 (s, 2H), 3.84 (q, *J* = 6.0 Hz, 2H), 2.35 (s, 3H), 0.79 (t, *J* = 6.0 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 159.9, 148.3, 138.0, 136.4, 135.2, 129.8, 129.7, 129.4, 129.3, 128.6, 128.5, 127.73, 127.70, 115.9, 114.3, 77.0, 59.8, 21.4, 13.5;

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{21}H_{19}N_3NaO_3^+$ 384.1324; found 384.1334.

Ethyl 5-amino-4-cyano-1-phenyl-3-(o-tolyl)-1*H*-pyrrole-2-carboxylate (3an)



3an

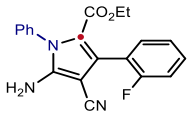
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 5:1) to afford **3an** (22.0 mg, 64% yield, white solid, m.p.: 197.5 – 197.8 ℃).

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.51 – 7.45 (m, 3H), 7.30 (d, *J* = 6.6 Hz, 2H), 7.21 – 7.15 (m, 4H), 4.36 (s, 2H), 3.77 – 3.73 (m, 2H), 2.22 (s, 3H), 0.66 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 159.8, 148.2, 136.6, 136.1, 134.9, 132.8, 129.8, 129.7, 129.6, 129.5, 128.1, 127.7, 125.2, 115.6, 114.9, 77.3, 59.7, 20.0, 13.3.

HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{21}H_{20}N_3O_2^+$ 346.1556; found 346.1556.

Ethyl 5-amino-4-cyano-1-phenyl-3-(o-tolyl)-1*H*-pyrrole-2-carboxylate (3ao)



3ao

Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 5:1) to afford **3ao** (32.3 mg, 92% yield, white solid, m.p.: 191.2 – 192.4 ℃).

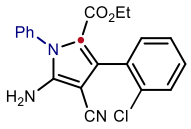
^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.50 – 7.45 (m, 3H), 7.38 (td, *J* = 7.8, 1.8 Hz, 1H), 7.33 – 7.29 (m, 3H), 7.15 (td, *J* = 7.2, 1.2 Hz, 1H), 7.07 (t, *J* = 9.0 Hz, 1H), 4.32 (s, 2H), 3.83 (q, 2H), 0.76 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 160.0 (d, *J* = 246.7 Hz), 159.6, 148.3, 136.0, 131.5 (d, *J* = 2.9 Hz), 130.0 (d, *J* = 8.1 Hz), 129.8, 129.6, 127.8, 127.5, 123.7 (d, *J* = 3.6 Hz), 120.9 (d, *J* = 15.2 Hz), 115.6, 115.4 (d, *J* =22.2 Hz), 115.4, 77.0, 60.0, 13.4;

^{19}F NMR (564 MHz, Chloroform-*d*) δ (ppm): -113 (s, 1F).

HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{20}H_{17}N_3O_2^+$ 350.1305; found 350.1299.

Ethyl 5-amino-3-(2-chlorophenyl)-4-cyano-1-phenyl-1*H*-pyrrole-2-carboxylate (3ap)



3ap

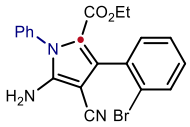
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1) to afford **3ap** (22.3 mg, 61% yield, yellow solid, m.p.: 210.2 – 214.7 ℃).

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.50 – 7.46 (m, 3H), 7.41 – 7.39 (m, 1H), 7.34 – 7.32 (m, 2H), 7.27 – 7.24 (m, 3H), 4.29 (s, 2H), 3.82 – 3.76 (m, 2H), 1.52 – 1.51 (m, 3H);

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.5, 148.0, 135.8, 133.9, 132.4, 131.4, 131.3, 129.8, 129.6, 129.4, 129.3, 127.9, 126.4, 115.6, 115.2, 77.2, 59.9, 13.3;

HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{20}H_{17}ClN_3O_2^+$ 366.1009; found 366.1007.

Ethyl 5-amino-3-(2-bromophenyl)-4-cyano-1-phenyl-1*H*-pyrrole-2-carboxylate (3aq)



3aq

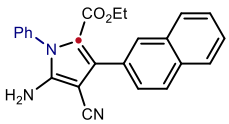
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1) to afford **3aq** (34.8 mg, 71% yield, white solid, m.p.: 222.2 – 223.4 °C).

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.54 (d, *J* = 7.8 Hz, 1H), 7.56 – 7.51 (m, 3H), 7.37 – 7.34 (m, 3H), 7.36 (s, 1H), 7.24 – 7.21 (m, 1H), 4.34 (s, 2H), 3.89 – 3.78 (m, 2H), 0.74 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 159.4, 147.9, 135.8, 134.5, 133.2, 132.4, 131.1, 129.8, 129.6, 129.5, 128.0, 126.9, 124.1, 115.4, 115.1, 77.2, 59.9, 13.3;

HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{20}H_{17}BrN_3O_2^+$ 410.0504; found 410.0500.

Ethyl 5-amino-4-cyano-3-(naphthalen-2-yl)-1-phenyl-1*H*-pyrrole-2-carboxylate (3ar)



3ar

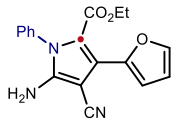
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 5:1) to afford **3ar** (28.0 mg, 73% yield, yellow solid, m.p.: 264.6 - 265.0 °C).

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.93 (s, 1H), 7.82 – 7.78 (m, 3H), 7.53 (d, *J* = 9.0 Hz, 1H), 7.47 – 7.41 (m, 5H), 7.26 (d, *J* = 6.6 Hz, 2H), 4.37 (s, 2H), 3.79 (q, *J* = 7.2 Hz, 2H), 0.68 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 159.9, 148.53, 148.51, 136.3, 134.91, 133.1, 133.0, 132.97, 130.0, 129.8, 129.5, 128.9, 128.3, 128.0, 127.74, 127.66, 127.2, 126.3, 126.1, 115.9, 114.6, 77.1, 59.9, 13.6.

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{24}H_{19}N_3NaO_2^+$ 404.1375; found 404.1382.

Ethyl 5-amino-4-cyano-3-(furan-2-yl)-1-phenyl-1*H*-pyrrole-2-carboxylate (3as)



3as

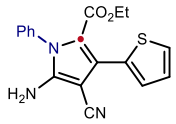
Prepared according to the general procedure, the crude product was purified by filtration to afford **3as** (27.0 mg, 84% yield, yellow solid, m.p.: 173.2 – 173.5 ℃).

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.51 – 7.46 (m, 4H), 7.26 (d, *J* = 6.6 Hz, 2H), 7.09 (s, 1H), 6.47 (s, 1H), 4.33 (s, 2H), 3.94 (q, *J* = 7.2 Hz, 2H), 0.86 (t, *J* = 6.6 Hz,3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 159.6, 148.8, 146.0, 142.7, 136.5, 129.9, 129.5, 127.7, 123.5, 116.1, 113.9, 112.2, 111.5, 74.7, 60.2, 13.7.

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{18}H_{15}N_3NaO_3^+$ 344.1011; found 344.1020.

Ethyl 5-amino-4-cyano-1-phenyl-3-(thiophen-2-yl)-1*H*-pyrrole-2-carboxylate (3at)



3at

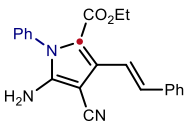
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 5:1) to afford **3at** (22.0 mg, 65% yield, yellow solid, m.p.: 201.7 – 202.0 ℃).

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.48 – 7.42 (m, 3H), 7.33 (dd, *J* = 10.8, 1.8 Hz, 2H), 7.24 (d, *J* = 7.8Hz, 2H), 7.01 (t, *J* = 4.8 Hz, 1H), 4.36 (s, 2H), 3.87 (q, *J* = 7.2 Hz, 2H), 0.88 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 159.7, 148.6, 136.3, 132.5, 129.9, 129.6, 129.0, 127.7, 127.1, 126.8, 126.7, 115.9, 115.1, 60.2, 13.6;

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{18}H_{15}N_3NaO_2S^+$ 360.0783; found 360.0785.

Ethyl (E)-5-amino-4-cyano-1-phenyl-3-styryl-1*H*-pyrrole-2-carboxylate (3au)



3au

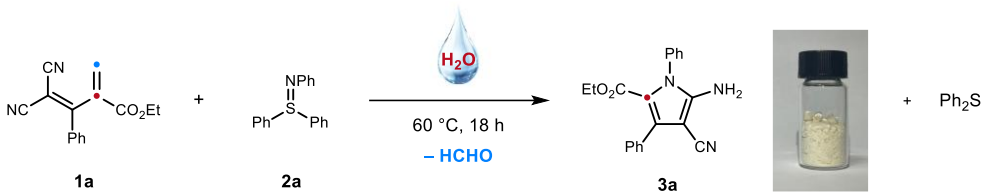
Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 5:1) to afford **3au** (12.0 mg, 34% yield, yellow solid, m.p.: 168.5 – 168.8 ℃).

^{1}H NMR (700 MHz, Chloroform-*d*) δ (ppm):8.35 (d, *J* = 16.8 Hz, 1H), 8.08 – 8.05 (m, 3H), 8.03 – 8.00 (m, 3H), 7.86 (t, *J* = 7.7 Hz, 2H), 7.78 – 7.77 (m, 3H), 4.56 (s, 2H), 4.88 (q, *J* = 7.0 Hz, 2H), 1.55 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (175 MHz, Chloroform-*d*) δ (ppm): 160.1, 149.7, 137.3, 136.4, 132.6, 130.7, 129.8, 129.4, 128.7, 128.1, 127.7, 126.8, 119.6, 116.9, 115.6, 72.3, 60.1, 13.9.

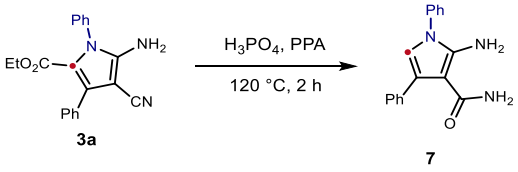
HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{22}H_{19}N_3NaO_2^+$ 380.1375; found 380.1385.

7. Scale-up synthesis



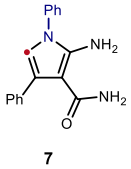
A 50 mL reaction tube was charged with **1a** (2.4 mmol, 1.2 equiv., 605.4 mg), **2a** (2.0 mmol, 1.0 equiv., 554.8 mg), and H_2O (20.0 mL). The mixture was stirred at 60 °C for 18 h and monitored by TLC. Upon completion, the reaction mixture was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) to afford byproduct Ph_2S (339.0 mg, 91%) and product **3a** (521.0 mg, 79%).

8. Synthetic transformations of the products



A 10 mL reaction tube was charged with **3a** (0.10 mmol, 1.0 equiv., 33.1 mg), polyphosphoric acid (PPA, 0.01 mmol, 0.1 equiv., 3.4 mg), and H_3PO_4 (1.0 mL). The mixture was stirred at 120 °C for 2 h and monitored by TLC. Upon completion, the reaction was cooled to room temperature, placed in an ice bath, and neutralized to pH 7 with aqueous ammonium hydroxide, resulting in the formation of a precipitate. The solid was collected by filtration to afford compound **7** (23.6 mg, 85%).

Ethyl 5-acetamido-4-cyano-1,3-diphenyl-1*H*-pyrrole-2-carboxylate (7)



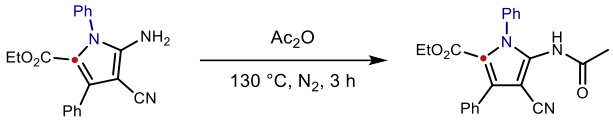
White solid, m.p.: 145.2 – 145.5 °C.

^{1}H NMR (700 MHz, Chloroform-*d*) δ (ppm): 7.86 (t, *J* = 7.7 Hz, 2H), 7.84 – 7.82 (m, 4H), 7.80 – 7. 74 (m, 3H), 7.69 (t, *J* = 7.7 Hz, 1H), 6.62 (s, 2H), 5.90 (s, 1H), 5.55 (s, 2H)

^{13}C NMR (175 MHz, Chloroform-*d*) δ (ppm): 168.5, 145.6, 137.3, 135.2, 129.9, 129.5, 128.8, 127.8,

127.4, 125.1, 122.8, 113.8, 94.4;

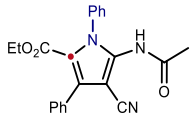
HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{15}N_3NaO^+$ 300.1113; found 300.1114.



3a **8**

3a (0.10 mmol, 1.0 equiv., 33.1 mg) and Ac_2O (4.1 mmol, 41.0 equiv., 5 mL) were added to a Schlenk tube under argon. The solution was stirred at 130 °C for 3 h and monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and poured into ice water. Aqueous ammonium hydroxide was added until a red precipitate formed. The solid was collected by vacuum filtration and recrystallized from diethyl ether to afford **8** (29.8 mg, 80%).

<u>Ethyl 5-acetamido-4-cyano-1,3-diphenyl-1*H*-pyrrole-2-carboxylate (8)</u>



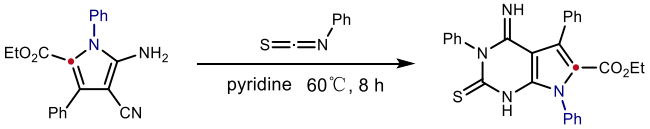
8

White solid, m.p.: 169.1 – 171.0 ℃.

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.40 – 7.36 (m, 5H), 7.34 – 7.30 (m, 3H), 7.20 (s, 2H), 7.16 (s, 1H), 3.82 (q, J = 7.2 Hz, 2H), 1.85 (s, 3H), 0.73 (t, J = 7.2 Hz, 3H);

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 169.5, 159.6, 136.3, 135.4, 133.7, 131.7, 129.8, 129.5, 129.1, 128.4, 128.0, 127.5, 120.0, 114.2, 93.1, 60.7, 22.8, 13.4;

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{19}N_3NaO_3^+$ 396.1324; found 396.1331.

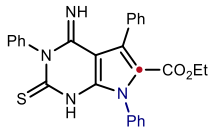


3a **9**

3a (0.10 mmol, 1.0 equiv., 33.1 mg) and phenyl isothiocyanate (0.11 mmol, 1.1 equiv., 13.6 mg) were added to a Schlenk tube, followed by pyridine (2.0 mL) under argon. The mixture was stirred at 60 °C for

8 h and monitored by TLC. Upon completion, the reaction mixture was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1 to 3:1) to afford product 9 (27.9 mg, 59%).

Ethyl 4-imino-3,5,7-triphenyl-2-thioxo-2,3,4,7-tetrahydro-1*H*-pyrrolo[2,3-d]pyrimidine-6-carboxylate (9)



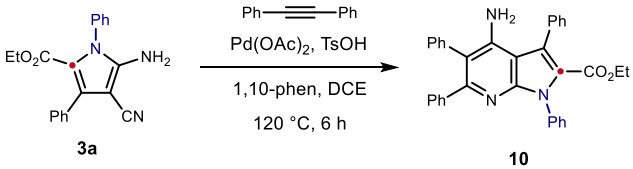
9

White solid, m.p.: 220.4 – 220.7 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.54 – 7.50 (m, 5H), 7.44 – 7.41 (m, 3H), 7.35 (dd, *J* = 15.0, 6.0 Hz, 4H), 7.03 (t, *J* = 7.2 Hz, 2H), 6.87 (t, *J* = 6.0 Hz, 1H), 6.73 (s, 1H), 3.93 (q, *J* = 6.0 Hz, 2H), 0.78 (t, *J* = 6.0 Hz, 3H);

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 166.4, 160.7, 154.7, 152.3, 138.5, 136.6, 133.7, 130.2, 128.8, 128.7, 128.6, 128.0, 127.6, 123.6, 123.0, 122.7, 119.5, 101.0, 60.6, 13.4.

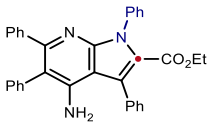
HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{22}N_4NaO_2S^+$ 489.1361; found 489.1365.



3a **10**

3a (0.10 mmol, 1.0 equiv., 33.1 mg), diphenylacetylene (0.15 mmol, 1.5 equiv., 26.7 mg), $Pd(OAc)_2$ (0.01 mmol, 10 mol%, 2.25 mg), TsOH (0.01 mmol, 10 mol%, 1.7 mg), and 1,10-phenanthroline (0.01 mmol, 10 mol%, 1.8 mg) were added to a Schlenk tube, followed by DCE (1.0 mL) under argon. The mixture was stirred at 120 °C for 6 h and monitored by TLC. Upon completion, the reaction mixture was diluted with ethyl acetate (10 mL), washed with saturated sodium bicarbonate solution (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford product **10** (39.8 mg, 78%).[4]

Ethyl 4-amino-1,3,5,6-tetraphenyl-1*H*-pyrrolo[2,3-b]pyridine-2-carboxylate (10)



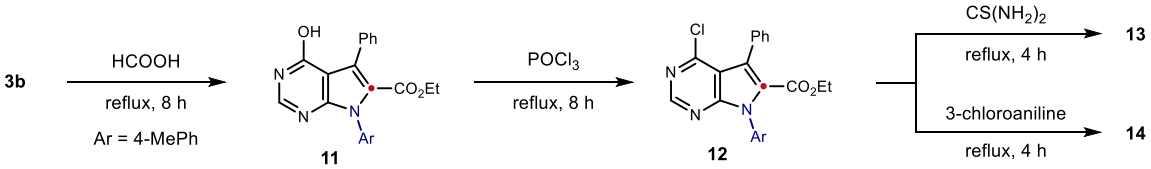
10

White solid, 178.1 – 178.2 °C.

^{1}H NMR (700 MHz, Chloroform-*d*) δ (ppm): 7.58 – 7.55 (m, 4H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.46 (t, *J* = 7.0 Hz, 2H), 7.42 – 7.39 (m, 2H), 7.29 – 7.26 (m, 4H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 7.0 Hz, 2H), 7.11 – 7.07 (m, 3H), 4.30 (s, 2H), 3.96 (q, *J* = 7.0 Hz, 2H), 0.80 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (175 MHz, Chloroform-*d*) δ (ppm): 161.4, 156.3, 148.9, 147.2, 141.3, 137.9, 136.7, 135.1, 131.6, 130.29, 130.26, 128.9, 128.5, 128.2, 128.0, 127.9, 127.3, 127.2, 127.12, 127.06, 124.1, 105.0, 60.4, 13.4;

HRMS (ESI-TOF) m/z [M + Na]+ Calcd for $C_{34}H_{27}N_3NaO_2$ 532.2001; found 532.2001.



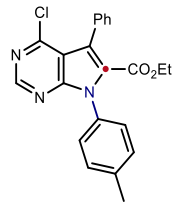
Step 1. Synthesis of 11

A 10 mL reaction tube was charged with **3b** (0.10 mmol, 1.0 equiv., 34.5 mg) and formic acid (20 mL). The reaction mixture was refluxed at 100 °C for 8 h and monitored by TLC. Upon completion, the mixture was cooled to room temperature, placed in an ice bath, and a yellow solid precipitated. The solid was collected by filtration, dried, and recrystallized from ethanol to afford compound **11**.

Step 2. Synthesis of 12

A 10 mL reaction tube was charged with **11** (0.10 mmol, 1.0 equiv., 37.4 mg) and $POCl_3$ (30 mL). The reaction mixture was refluxed at 110 °C for 8 h and monitored by TLC. Upon completion, the mixture was cooled to room temperature and poured into ice water. The aqueous phase was extracted with DCM (3 × 20 mL), and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1 to 10:1) to afford compound **12** (17.0 mg, 43%).[5]

Ethyl 4-chloro-5-phenyl-7-(p-tolyl)-7*H*-pyrrolo[2,3-d]pyrimidine-6-carboxylate (12)



12

White solid, m.p.: 178.1 – 178.2 ℃.

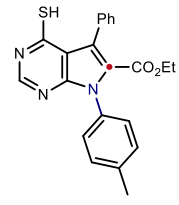
^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): δ 8.71 (s, 1H), 7.46 – 7.43 (m, 5H), 7.37 – 7.32(m, 4H), 3.99 (q, *J* = 7.2 Hz, 2H), 2.46 (s, 3H), 0.82 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 160.6, 155.1, 153.5, 152.3, 139.1, 133.3, 131.9, 130.9, 129.9, 128.8, 128.0, 127.5, 127.2, 122.4, 115.3, 61.4, 21.4, 13.3;

HRMS (ESI-TOF) m/z [M + H]+ Calcd for $C_{22}H_{19}ClN_3O_2$ 392.1166; found 392.1172.

A 10 mL reaction tube was charged with **12** (0.10 mmol, 1.0 equiv., 39.3 mg) and thiourea (0.20 mmol, 2.0 equiv., 15.2 mg) in dry ethanol (30 mL). The mixture was refluxed at 80 °C for 4 h and monitored by TLC. Upon completion, the reaction mixture was poured into ice water and extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) to afford compound **13** (33.2 mg, 85%).[10]

Ethyl 5-phenyl-4-thioxo-7-(p-tolyl)-4,7-dihydro-3*H*-pyrrolo[2,3-d]pyrimidine-6-carboxylate (13)



13

White solid, m.p.: 204.8 – 205.1 ℃.

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 12.62 (s, 1H), 7.80 (s, 1H), 7.46 – 7.44 (m, 2H), 7.42 – 7.40 (m, 3H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.27 (s, 1H), 7.25 (s, 1H), 3.92 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 0.77 (t, *J* = 7.2 Hz, 3H);

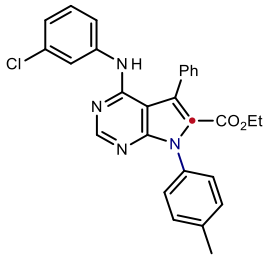
^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 178.8, 160.6, 145.7, 144.4, 139.2, 133.4, 132.9, 130.8,

129.8, 128.7, 127.7, 127.3, 127.2, 126.4, 117.4, 61.0, 21.4, 13.3;

HRMS (ESI-TOF) m/z [M + H]+ Calcd for $C_{22}H_{20}N_3O_2S$ 390.1276; found 390.1280.

A 10 mL reaction tube was charged with **12** (0.10 mmol, 1.0 equiv., 39.3 mg) and 3-chloroaniline (0.12 mmol, 1.2 equiv., 15.2 mg) in dry ethanol (2 mL). The mixture was refluxed at 80 °C for 4 h and monitored by TLC. Upon completion, the reaction mixture was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 80:1 to 50:1) to afford compound **14** (37.1 mg, 77%).[7]

Ethyl 4-((3-chlorophenyl)amino)-5-phenyl-7-(p-tolyl)-7*H*-pyrrolo[2,3-d]pyrimidine-6-carboxylate (14)



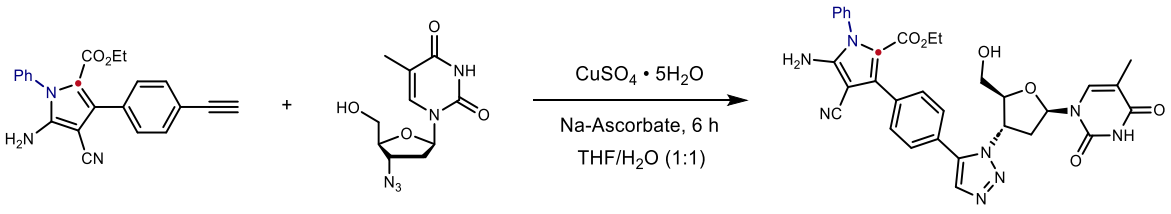
14

White solid, m.p.: 197.4 – 198.0 ℃.

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 8.48 (s, 1H), 7.61 (t, *J* = 1.8 Hz, 1H), 7.52 – 7.50 (m, 5H), 7.25 (dd, *J* = 7.8 Hz, 2.4 Hz, 4H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.97 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.90 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.70 (s, 1H), 3.90 (q, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 0.74 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 159.5, 153.95, 153.87, 150.6, 138.6, 137.3, 133.4, 132.8, 132.7, 129.0, 128.6, 128.5, 127.63, 127.61, 126.2, 122.8, 122.0, 121.3, 118.6, 116.5, 101.8, 59.6, 20.1, 12.2.;

HRMS (ESI-TOF) m/z [M + H]$^+$ Calcd for $C_{28}H_{24}ClN_4O_2$ 483.1588; found 483.1598.

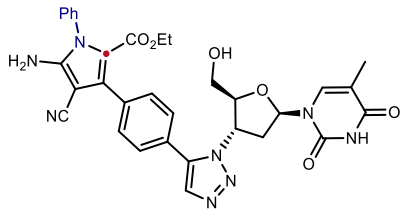


3ah Zidovudine 91%

To a solution of **3ah** (35.5 mg, 0.10 mmol) in THF (1.0 mL) were added Zidovudine (26.7 mg, 0.10 mmol), and a freshly prepared aqueous solution of $CuSO_4·5H_2O$ (25.0 mg, 0.10 mmol) and sodium

ascorbate (19.8 mg, 0.10 mmol) in H_2O (1.0 mL). The mixture was stirred until completion, as monitored by TLC, then concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) to afford compound **15** as a white solid (56.4 mg, 91%).

Ethyl 5-amino-4-cyano-3-(4-(1-((2S,3S,5R)-2-(hydroxymethyl)-5-(5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)tetrahydrofuran-3-yl)-1*H*-1,2,3-triazol-5-yl)phenyl)-1-phenyl-1*H*-pyrrole-2-carboxylate (15)



15

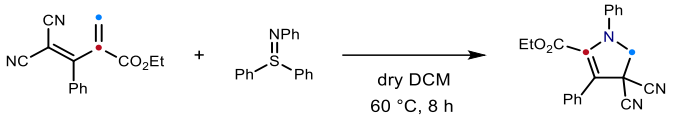
White solid, m.p.: 249.1 – 253.5°C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 8.46 (s, 1H), 7.86 (s, 1H), 7.81 (d, *J* = 7.8 Hz, 2H), 7.48 – 7.41 (m, 5H), 7.25 (d, *J* = 7.2 Hz, 2H), 6.45 (t, *J* = 6.6 Hz, 1H), 5.43 – 5.40 (m, 1H), 4.48 (s, 3H), 4.47 – 4.35 (m, 1H), 3.85 (dd, *J* = 12.0, 3.0 Hz, 1H), 3.76 – 3.70 (m, 3H), 2.91 – 2.87 (m, 1H), 2.72 – 2.67 (m, 1H), 1.83 (s, 3H), 1.19 (s, 1H), 1.06 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 165.0, 160.0, 151.0, 150.5, 147.4, 136.9, 136.7, 135.1, 133.1, 130.2, 129.7, 129.3, 128.8, 127.7, 124.7, 120.9, 115.6, 113.8, 110.4, 85.4, 85.0, 74.9, 60.8, 59.9, 59.5, 37.7, 12.5, 11.1;

HRMS (ESI-TOF) m/z [M + H]+ Calcd for $C_{32}H_{31}N_8O_6$ 623.2367; found 623.2358.

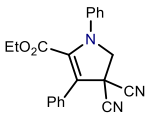
9. Mechanistic experiments



1a **2a** **5a**

In a 10 mL reaction tube, **1a** (0.12 mmol, 1.2 equiv., 30.3 mg) and aniline **2a** (0.10 mmol, 1.0 equiv., 33.2 mg) were dissolved in dry DCM (1.0 mL, water≤30 ppm from Adamas-Beta) and stirred at 60℃ for 8 h. monitored by TLC. Upon completion, the reaction mixture concentrated in *vacuo*. Then the crude material was purified by column chromatography on silica gel using petroleum ether and ethyl acetate (20/1) as eluents to yield product **5a** (14.4 mg, 42% yield).

Ethyl 5-amino-4-cyano-1,3-diphenyl-1*H*-pyrrole-2-carboxylate (5a)



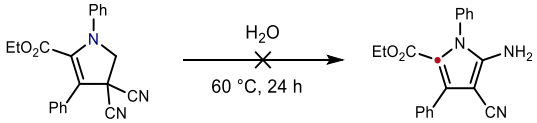
5a

Prepared according to the general procedure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 20//1) to afford **5a** (34.3 mg, 99.9% yield, yellow solid, m.p.: 176.3 - 176.6 ℃).

^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.46 – 7.39 (m, 5H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 7.2 Hz, 2H), 4.52 (s, 2H), 4.07 (q, *J* = 7.2 Hz, 2H), 0.95 (t, *J* = 7.2 Hz, 3H).

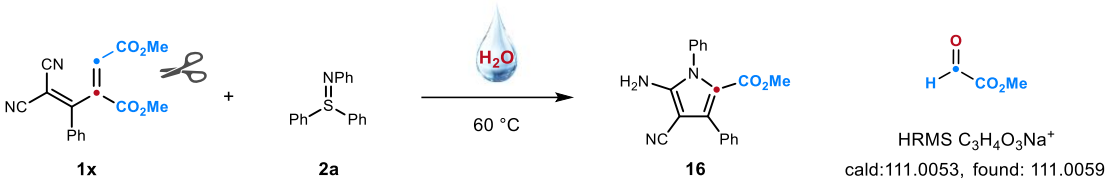
^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 161.1, 142.9, 141.1, 129.8, 129.6, 129.2, 128.9, 128.2, 125.8, 121.6, 115.2, 113.8, 63.5, 62.3, 41.5, 13.5.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{17}N_3NaO_2^+$ 344.1399; found: 344.1394.



5a **3a**

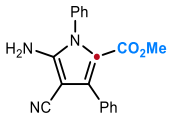
In a 10 mL reaction tube, **5a** (0.10 mmol, 1.0 equiv., 34.3 mg) were dissolved in H_2O (1.0 mL) and stirred at 60℃ over 12 h. monitored by TLC, no generation of **3a** was observed.



In a 10 mL reaction tube, **1x** (0.12 mmol, 1.2 equiv., 35.6 mg) and **2a** (0.10 mmol, 1.0 equiv., 27.7 mg) were dissolved in H_2O (1.0 mL) and stirred at 60℃ for 4h. monitored by TLC. Upon completion, the reaction mixture concentrated in vacuo. Then the crude mixture was purified by column chromatography on silica gel using petroleum ether and ethyl acetate (5/1) as eluents to yield product **16** (26.0 mg, 82% yield), the generation of methyl glyoxylate was observed by HRMS analysis.

Methyl 5-amino-4-cyano-1,3-diphenyl-1*H*-pyrrole-2-carboxylate (16)

White solid, m.p.: 197.6 – 197.9 ℃.



16

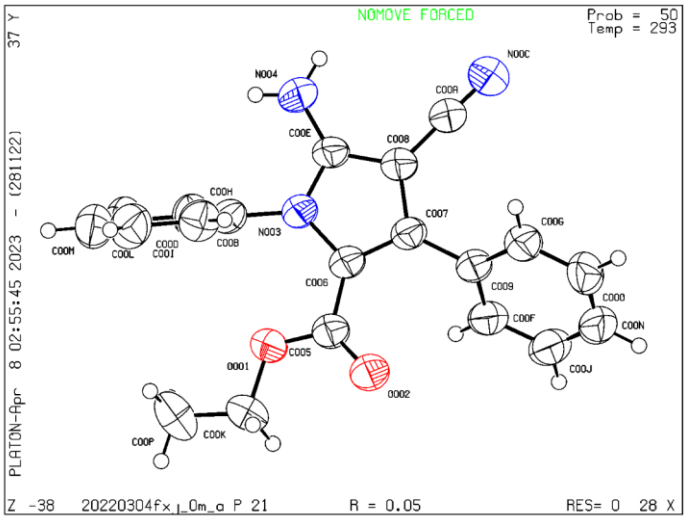
^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm): 7.56 – 7.51 (m, 3H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 6.6 Hz, 2H), 4.40 (s, 2H), 3.40 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ (ppm): 160.5, 148.6, 136.1, 135.1, 132.4, 129.9, 129.7, 129.5, 128.2, 127.9, 127.7, 115.8, 114.0, 77.0, 50.9.

HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{19}H_{15}N_3NaO_2^+$ 340.1062; found 340.1071.

10. Single crystal X-ray diffraction analysis and crystal data

To a 5 mL tube containing **3a** (20.0 mg), a 5:1 mixture of *n*-hexane (5 mL) and dichloromethane (1 mL) was added. The mixture was sonicated to give a clear solution and left at room temperature to yield crystals of **3a**, which were characterized by X-ray diffraction (Bruker D8 QUEST). CCDC 2466191 (**3a**) contains the supplementary crystallographic data for this work and is available free of charge at www.ccdc.cam.ac.uk/data_request/cif.



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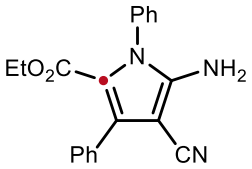


3a

(Ellipsoid contour probability 50%)

Identification code	20220304fxj	
Chemical formula	$C_{20}H_{17}N_3O_2$	
Formula weight	331.36 g/mol	
Temperature	293(2) K	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 6.9335(4) Å	α = 90°
	b = 15.0785(7) Å	β = 101.786(4)°
	c = 8.7254(5) Å	γ = 90°
Volume	892.98(8) $Å^3$	
Z	2	
Density (calculated)	1.232 g/cm^3	
Absorption coefficient	0.658 mm^{-1}	

F(000)	348	
Theta range for data collection		5.18 to 68.57°
Index ranges		-8<=h<=7, -17<=k<=18, -10<=l<=10
Reflections collected	9432	
Independent reflections	3188 [R(int) = 0.0602]	
Coverage of independent reflections	99.1%	
Absorption correction	Multi-Scan	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	3188 / 1 / 227	
Goodness-of-fit on F2	1.009	
Final R indices	2362 data; I>2σ(I)	R1 = 0.0532, wR2 = 0.1289
	all data	R1 = 0.0749, wR2 = 0.1525
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0651P)^2+0.2490P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	-0.3(2)	
Largest diff. peak and hole	0.154 and -0.197 eÅ^{-3}	
R.M.S. deviation from mean	0.044 eÅ^{-3}	

11. Density functional theory (DFT) studies

8.1 Computational methods

All density functional theory (DFT) calculations were carried out with Gaussian 16 program software.[7] The SMD model[8] was employed to simulate the solvent effect of DCM and aqueous solution for all calculations. Full geometry optimizations were operated to locate all of the stationary points, using M06-2X density functional theory method with def2-SVP basis set[9] for all atoms in DCM or aqueous solution, under experimental temperature and pressure (333.15 K and 1 atm). In the meantime, the stability of the DFT wave-function of the auxiliary Kohn–Sham determinant was examined.[10] Harmonic vibrational frequency calculations were implemented at the same level of theory to characterize all stationary points. Herein, minima have zero imaginary frequencies, and transition states (TS) have one imaginary vibrational frequency. Intrinsic reaction coordinate (IRC) method was implemented to track minimum energy paths connecting each transition state structure to two corresponding minima. To get more accurate energies, single-point energies of all stationary points were calculated with the same functional and at a larger basis set of def2-TZVPP in the DCM or aqueous solution under experimental temperature and pressure (333.15 K and 1 atm). Unless otherwise noted, the Gibbs free energies of formation (ΔG, kcal mol^{-1}) are relative to the initial reactants obtained at the M06-2X/Def2-TZVPP/SMD(solvent)//M06-2X/def2-SVP/SMD(solvent) level. All DFT-optimized structures were visualized by *CYLview* 2.0 program.[11]

8.2 Computational results

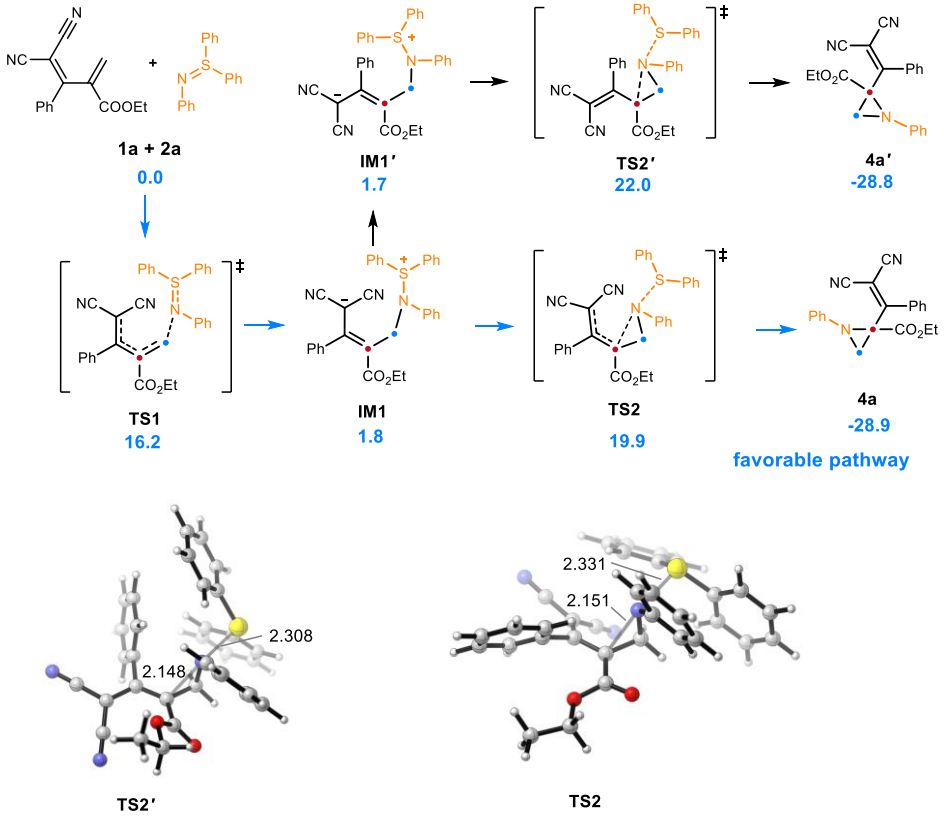


Figure S1. Comparison of alternative pathways for the formation of **4a** in aqueous solution.

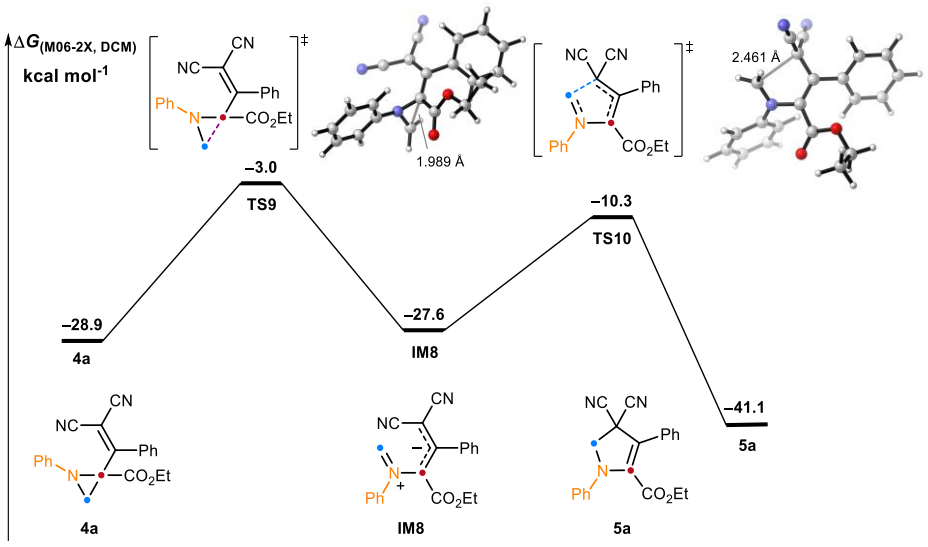


Figure S2. Energy profile of the conversion of **4a** to **5a** in DCM solution.

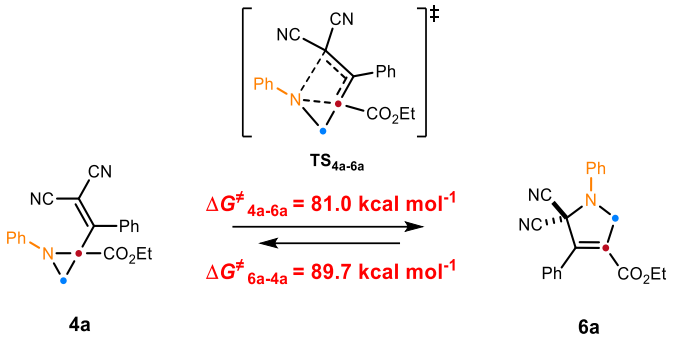


Figure S3. Exclusion of the possibility of isomerization of 4a to 6a in aqueous solution by calculations.

8.3 Data of energies

Table S2. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree) , single-point energies (SP-E, hartree), total energies (E_c, hartree) corrected by the addition of *ZPE* and SP-E, sum of electronic and thermal free energies (G_c, hartree) with the addition of SP-E as well as *ZPE* and thermal corrections, and relative energies (ΔE, kcal mol^{-1}) and relative Gibbs free energies (ΔG, kcal mol^{-1}) of various species for the formation of **3a** at the M06-2X/Def2-TZVPP/SMD(H_2O)//M06-2X/def2-SVP/SMD(H_2O) level under experimental temperature and pressure (333.15 K and 1 atm). IF represents imaginary frequencies (cm^{-1}).

Species	*ZPE*	G_0	SP-E	E_c(ZPE + SP-E)	ΔE	G_c (G_0 + SP-E)	ΔG	IF
1a	0.23769	0.18176	-838.70995	-838.47226		-838.52819		
2a	0.28058	0.22479	-1147.79048	-1147.50991		-1147.56569		
H_2O	0.02131	0.00037	-76.44136	-76.42005		-76.44098		
1a + **2a** + 3H_2O	0.58220	0.40767	-2215.82450	-2215.24231	0.0	-2215.41684	0.0	
TS1	0.51951	0.43609	-1986.50423	-1985.98472		-1986.06814		232.23*i*
TS1+ 3H_2O	0.58344	0.43721	-2215.82830	-2215.24486	-1.6	-2215.39109	16.2	
IM1	0.52280	0.44082	-1986.53186	-1986.00905		-1986.09103		
IM1 + 3H_2O	0.58673	0.44194	-2215.85593	-2215.26920	-16.9	-2215.41399	1.8	
TS2	0.52079	0.43948	-1986.50159	-1985.98080		-1986.06211		391.05*i*
TS2 + 3H_2O	0.58472	0.44060	-2215.82566	-2215.24094	0.9	-2215.38506	19.9	
4a	0.33705	0.27291	-1125.09478	-1124.75773		-1124.82187		
Ph_2S	0.18405	0.13920	-861.45721	-861.27315		-861.31800		
4a + Ph_2S + 3H_2O	0.58503	0.41323	-2215.87605	-2215.29102	-30.6	-2215.46282	-28.9	
IM1'	0.52298	0.44174	-1986.53298	-1986.01000		-1986.09124		
IM1' + 3H_2O	0.58691	0.44286	-2215.85705	-2215.27014	-17.5	-2215.41419	1.7	
TS2'	0.52051	0.43945	-1986.49826	-1985.97775		-1986.05880		455.44*i*
TS2' + 3H_2O	0.58444	0.44057	-2215.82233	-2215.23789	2.8	-2215.38176	22.0	
4a'	0.33698	0.27215	-1125.09393	-1124.75695		-1124.82178		
4a' + Ph_2S + 3H_2O	0.58496	0.41247	-2215.87521	-2215.29025	-30.1	-2215.46274	-28.8	
TS3	0.52068	0.43817	-1986.48721	-1985.96653		-1986.04903		285.32*i*
TS3 + 3H_2O	0.58461	0.43929	-2215.81128	-2215.22667	9.8	-2215.37199	28.1	
6a	0.33807	0.27413	-1125.10985	-1124.77178		-1124.83573		
6a + Ph_2S + 3H_2O	0.58605	0.41445	-2215.89113	-2215.30508	-39.4	-2215.47669	-37.6	
TS$_{4a-6a}$	0.33393	0.27005	-1124.96285	-1124.62891		-1124.69279		684.15*i*
TS$_{4a-6a}$ + Ph_2S + 3H_2O	0.58191	0.41037	-2215.74412	-2215.16221	50.3	-2215.33375	52.1	
TS4	0.36060	0.29519	-1201.50983	-1201.14924		-1201.21465		1069.35*i*
TS4 + Ph_2S + 2H_2O	0.58727	0.43513	-2215.84975	-2215.26249	-12.7	-2215.41462	1.4	
IM2	0.36647	0.30171	-1201.54633	-1201.17987		-1201.24462		
IM2 + Ph_2S + 2H_2O	0.59314	0.44166	-2215.88626	-2215.29312	-31.9	-2215.44460	-17.4	

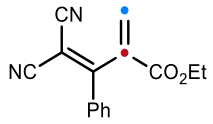
Continued Table S2.

Species	*ZPE*	G_0	SP-E	E_c(ZPE + SP-E)	Δ*E*	G_c (G_0 + SP-E)	Δ*G*	IF
TS5	0.36129	0.29762	-1201.48972	-1201.12844		-1201.19211		1384.33*i*
TS5 + Ph_2S + $2H_2O$	0.58796	0.43756	-2215.82965	-2215.24169	0.4	-2215.39208	15.5	
IM3	0.33169	0.26941	-1087.01819	-1086.68650		-1086.74878		
HCHO	0.02724	0.00256	-114.50282	-114.47558		-114.50026		
IM3 + HCHO + Ph_2S + $2H_2O$	0.58560	0.41192	-2215.86093	-2215.27533	-20.7	-2215.44901	-20.2	
IM4	0.35624	0.28870	-1163.46395	-1163.10771		-1163.17525		
IM4 + HCHO + Ph_2S + H_2O	0.58884	0.43083	-2215.86533	-2215.27649	-21.4	-2215.43450	-11.1	
TS6	0.35227	0.28882	-1163.42114	-1163.06886		-1163.13232		1254.05*i*
TS6 + HCHO + Ph_2S + H_2O	0.58488	0.43096	-2215.82252	-2215.23764	2.9	-2215.39156	15.9	
TS6′	0.37664	0.30990	-1239.87931	-1239.50268		-1239.56941		909.01*i*
TS6′ + HCHO + Ph2S	0.58793	0.45167	-2215.83933	-2215.25141	-5.7	-2215.38767	18.3	
IM5	0.33495	0.27200	-1087.05156	-1086.71662		-1086.77957		
IM5 + HCHO + Ph_2S+$2H_2O$	0.58886	0.41451	-2215.89430	-2215.30544	-39.6	-2215.47980	-39.5	
TS7	0.35368	0.28861	-1163.45550	-1163.10182		-1163.16690		1133.01*i*
TS7 + HCHO + Ph_2S + H_2O	0.58628	0.43074	-2215.85688	-2215.27060	-17.8	-2215.42614	-5.8	
TS7′	0.37985	0.31380	-1239.91416	-1239.53431		-1239.60036		1320.48*i*
TS7′ + HCHO + Ph_2S	0.59114	0.45556	-2215.87418	-2215.28304	-25.6	-2215.41862	-1.1	
IM6	0.35508	0.28847	-1163.46683	-1163.11175		-1163.17836		
IM6 + HCHO + Ph_2S + H_2O	0.58768	0.43061	-2215.86821	-2215.28053	-24.0	-2215.43760	-13.0	
TS8	0.35724	0.29356	-1163.45973	-1163.10249		-1163.16617		117.11*i*
TS8 + HCHO + Ph_2S + H_2O	0.58984	0.43569	-2215.86111	-2215.27127	-18.2	-2215.42541	-5.4	
IM7	0.35750	0.28906	-1163.52246	-1163.16496		-1163.23340		
IM7 + HCHO + Ph_2S + H_2O	0.59010	0.43120	-2215.92384	-2215.33374	-57.4	-2215.49264	-47.6	
3a	0.33346	0.27162	-1087.09102	-1086.75756		-1086.81940		
3a + HCHO + Ph_2S + $2H_2O$	0.58737	0.41412	-2215.93376	-2215.34638	-65.3	-2215.51963	-64.5	

Table S3. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree) , single-point energies (SP-E, hartree), total energies (E_c, hartree) corrected by the addition of *ZPE* and SP-E, sum of electronic and thermal free energies (G_c, hartree) with the addition of SP-E as well as *ZPE* and thermal corrections, and relative energies (ΔE, kcal mol^{-1}) and relative Gibbs free energies (ΔG, kcal mol^{-1}) of various species for the conversion of **4a** to **5a** at the M06-2X/Def2-TZVPP/SMD(DCM)//M06-2X/def2-SVP/SMD(DCM) level under experimental temperature and pressure (333.15 K and 1 atm). IF represents imaginary frequencies (cm^{-1}).

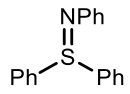
Species	*ZPE*	G_0	SP-E	E_c (ZPE + SP-E)	ΔE	G_c(G_0 + SP-E)	ΔG	IF
4a	0.33703	0.27300	-1125.10827	-1124.77125	0.0	-1124.83528	0.0	
TS9	0.33440	0.26978	-1125.06385	-1124.72945	26.2	-1124.79407	25.9	627.65*i*
IM8	0.33635	0.27184	-1125.10511	-1124.76876	1.6	-1124.83328	1.3	
TS10	0.33638	0.27238	-1125.07797	-1124.74159	18.6	-1124.80559	18.6	197.20*i*
5a	0.33853	0.27403	-1125.12882	-1124.79030	-12.0	-1124.85480	-12.2	

8.3 Cartesian coordinates of DFT-computed structure



1a

8	-0.134692	5.537878	5.663082
8	0.387508	5.523589	3.488783
7	1.253266	10.626184	4.168673
6	0.509463	5.958274	4.731651
6	1.537058	7.047527	4.846643
6	2.419637	7.322432	3.687518
6	2.598973	8.605149	3.254867
6	3.102973	6.171771	3.060597
6	3.572591	8.968794	2.261077
7	4.356996	9.308630	1.482180
6	1.845430	9.711517	3.781163
6	3.219052	6.065941	1.666423
1	2.803748	6.840642	1.019869
6	3.573006	5.129577	3.875268
1	3.469214	5.199171	4.960235
6	3.816647	4.943115	1.099878
6	4.303818	3.920783	1.915774
6	4.181502	4.016063	3.303427
1	4.556822	3.216396	3.943154
1	3.891293	4.861404	0.014804
1	4.771464	3.042351	1.468525
6	-0.457545	4.386757	3.244100
6	-0.090060	3.845558	1.885538
1	-1.505073	4.716413	3.295459
1	-0.287717	3.649850	4.040757
1	-0.716471	2.974316	1.652728
1	-0.245512	4.605399	1.107156
1	0.964772	3.533250	1.871337
6	1.657266	7.692396	6.013463
1	1.004334	7.427603	6.847997
1	2.411533	8.467491	6.164089

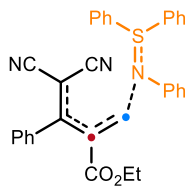


2a

16	1.527348	-1.009272	-0.147112
6	0.611485	0.524184	0.181364
6	-0.604058	0.445934	0.855966
6	1.167974	1.739096	-0.209157
6	-1.296422	1.628746	1.123115
1	-1.005655	-0.519548	1.171898
6	0.468657	2.911922	0.067461
1	2.135514	1.754454	-0.716054
6	-0.761388	2.855192	0.728871
1	-2.251483	1.589478	1.648550
1	0.885006	3.874704	-0.232213
1	-1.303201	3.777215	0.944717
6	1.087111	-1.244984	-1.873093
6	-0.251779	-1.514999	-2.160453
6	2.061292	-1.205883	-2.864029
6	-0.621661	-1.730725	-3.485466
1	-1.000248	-1.552114	-1.365206
6	1.673404	-1.425840	-4.187524
1	3.097400	-1.006654	-2.594833
6	0.339606	-1.685244	-4.498314
1	-1.664850	-1.939307	-3.725746
1	2.424283	-1.394264	-4.978300
1	0.045399	-1.857139	-5.534591
7	3.100214	-0.638340	-0.252115
6	3.786737	-0.617905	0.951647
6	5.199319	-0.548001	0.881516
6	3.207064	-0.627862	2.241238
6	5.979579	-0.509422	2.028834
1	5.663719	-0.529470	-0.106202
6	4.002432	-0.597752	3.388275
1	2.120832	-0.650142	2.360222
6	5.391253	-0.538170	3.299180
1	7.066280	-0.459384	1.932240
1	3.517581	-0.611871	4.366766
1	6.006747	-0.508679	4.198929

H_2O

8	0.110436	-0.443668	0.000000
1	1.074696	-0.385103	0.000000
1	-0.156244	0.484842	0.000000



TS1

8	3.588622	4.593504	3.581443
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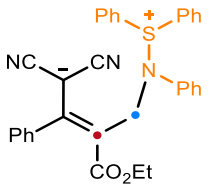
7	5.611054	9.218332	0.235635
6	3.500609	4.889665	2.405669
6	4.457401	5.794195	1.706625
6	4.618181	5.752229	0.269921
6	5.143809	6.780237	-0.496211
6	4.281030	4.482434	-0.431665
6	5.505791	6.584532	-1.869690
7	5.828570	6.473251	-2.977105
6	5.394750	8.114307	-0.042120
6	3.436256	4.487597	-1.548372
1	3.024596	5.431375	-1.912326
6	4.777769	3.265572	0.055463
1	5.428202	3.259564	0.933198
6	3.095320	3.288870	-2.172479
6	3.601559	2.080561	-1.692094
6	4.445242	2.071390	-0.578923
1	4.844023	1.128755	-0.201487
1	2.426366	3.299290	-3.034160
1	3.335729	1.143214	-2.183311
6	1.606977	3.493687	2.190215
6	0.712292	3.026506	1.069965
1	1.040781	3.960561	3.010285
1	2.202074	2.669804	2.610915
1	0.002661	2.278777	1.448390
1	0.143105	3.868432	0.650266
1	1.309750	2.568503	0.267595
6	5.129082	6.661625	2.536759
1	5.131897	6.426497	3.602601
1	5.920836	7.318413	2.177778
16	3.947203	8.619534	4.559284
6	5.648854	9.164411	4.541191
6	6.445416	8.793273	5.621078
6	6.131256	9.931312	3.481033
6	7.776757	9.213131	5.639842
1	6.040116	8.183644	6.430957
6	7.463997	10.332230	3.511981
1	5.482020	10.184331	2.641841
6	8.282061	9.977043	4.588945
1	8.418629	8.932758	6.475603
1	7.866346	10.924954	2.689301
1	9.324779	10.297206	4.604740
6	3.080116	10.158989	4.927200
6	2.844204	10.455562	6.268097
6	2.668747	10.994600	3.892299
6	2.188019	11.646000	6.579569
1	3.166836	9.773554	7.058026
6	2.007766	12.177222	4.221797
1	2.859502	10.718407	2.853561
6	1.771572	12.502227	5.559045
1	1.996132	11.899296	7.622868
1	1.674373	12.846794	3.427962
1	1.252766	13.429116	5.807675
7	3.707146	8.358977	2.941796
6	2.453312	7.845395	2.609582
6	2.142165	7.812483	1.233466
6	1.505823	7.315128	3.510537
6	0.945217	7.267769	0.779092
1	2.856388	8.243459	0.529914
6	0.308444	6.773859	3.045673
1	1.700134	7.310558	4.585836
6	0.017812	6.740744	1.680680
1	0.734883	7.259146	-0.292290
1	-0.406510	6.372040	3.766333
1	-0.922477	6.316812	1.325698



IM1

8	3.656760	4.255932	3.465206
8	2.451606	4.464165	1.600249
7	5.080349	9.565498	0.794315
6	3.483277	4.787350	2.381665
6	4.319274	5.883440	1.848431
6	4.586836	6.006706	0.501372
6	5.164199	7.160549	-0.130614
6	4.297843	4.851889	-0.404287
6	5.751147	7.071915	-1.418841

7	6.247237	7.022169	-2.471277
6	5.126427	8.466897	0.410043
6	3.515306	5.031917	-1.551939
1	3.141340	6.028528	-1.796895
6	4.769051	3.570209	-0.092653
1	5.386472	3.426938	0.797168
6	3.190339	3.944332	-2.360719
6	3.654496	2.667452	-2.038615
6	4.447878	2.483536	-0.904929
1	4.821309	1.489655	-0.653077
1	2.567343	4.093413	-3.244069
1	3.400495	1.816558	-2.672813
6	1.683763	3.312361	1.962273
6	0.686242	3.073933	0.856453
1	1.192981	3.500846	2.929468
1	2.367258	2.458612	2.088834
1	0.073110	2.193349	1.089841
1	0.021531	3.942371	0.740609
1	1.205693	2.897138	-0.097309
6	4.801581	6.829128	2.903453
1	5.046339	6.238952	3.803456
1	5.704623	7.362305	2.581589
16	3.989647	8.593512	4.763812
6	5.721718	9.000172	4.727111
6	6.511485	8.338107	5.667527
6	6.248723	9.905037	3.804402
6	7.882491	8.591989	5.678596
1	6.067891	7.636714	6.376507
6	7.619894	10.139724	3.828804
1	5.614648	10.400822	3.069183
6	8.431374	9.487424	4.761979
1	8.518337	8.087036	6.406146
1	8.057088	10.837990	3.114397
1	9.504442	9.683285	4.773430
6	3.137873	10.143622	4.539193
6	2.633249	10.727792	5.700329
6	2.986226	10.717586	3.276597
6	1.968290	11.948032	5.591121
1	2.753906	10.243502	6.671300
6	2.311474	11.933137	3.190775
1	3.388556	10.227134	2.387528
6	1.808007	12.545441	4.340956
1	1.567221	12.424564	6.485991
1	2.178279	12.403728	2.216100
1	1.279887	13.496416	4.259650
7	3.753939	7.859377	3.233916
6	2.378417	7.455409	3.053671
6	1.775771	7.769219	1.832380
6	1.684103	6.717133	4.015687
6	0.486644	7.315712	1.562476
1	2.338905	8.347554	1.096857
6	0.386079	6.282050	3.745710
1	2.162685	6.450570	4.960875
6	-0.209999	6.573211	2.518624
1	0.022507	7.546966	0.602710
1	-0.154099	5.701916	4.495227
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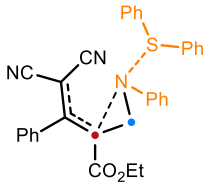

TS2

8	3.567190	4.376450	2.536294
8	3.354858	4.259421	0.316093
7	6.439339	8.880969	0.501673
6	3.538220	4.938251	1.453787
6	3.770491	6.370075	1.252082
6	3.455946	7.022748	0.030283
6	4.104697	8.198930	-0.376370
6	2.349193	6.516876	-0.827357
6	3.569857	9.058926	-1.382286
7	3.153029	9.794621	-2.177448
6	5.381161	8.588110	0.124782
6	1.126881	6.161731	-0.238534
1	1.003074	6.264549	0.842029
6	2.511562	6.377025	-2.211219
1	3.467956	6.631624	-2.672795
6	0.081619	5.683792	-1.024086
6	0.251452	5.540996	-2.403535
6	1.468319	5.884289	-2.993973
1	1.608574	5.764431	-4.069250
1	-0.868844	5.418878	-0.558522
1	-0.565528	5.159302	-3.018030
6	2.942742	2.893309	0.416460
6	2.584720	2.433090	-0.975321
1	2.083305	2.831895	1.100557

1	3.762536	2.300753	0.848679
1	2.255137	1.385930	-0.948966
1	1.768881	3.047182	-1.385335
1	3.452904	2.508626	-1.644900
6	4.207126	7.143382	2.460845
1	4.670411	6.500033	3.218292
1	4.861999	7.995311	2.254977
16	3.191227	9.506908	4.077798
6	4.283226	8.844211	5.292875
6	3.681409	8.562351	6.527060
6	5.606126	8.455437	5.037839
6	4.408153	7.893436	7.510078
1	2.648694	8.863466	6.714312
6	6.321761	7.797993	6.034522
1	6.076976	8.658343	4.075283
6	5.726833	7.512516	7.266344
1	3.938494	7.673850	8.469618
1	7.352671	7.498585	5.841709
1	6.296014	6.991492	8.037295
6	4.131407	10.498997	2.957108
6	5.334841	11.130121	3.296064
6	3.527672	10.724490	1.712169
6	5.943181	11.968325	2.366295
1	5.784738	10.986301	4.278556
6	4.142984	11.582568	0.800521
1	2.580067	10.243079	1.461310
6	5.353152	12.195133	1.120143
1	6.881617	12.460157	2.625981
1	3.671574	11.761392	-0.167022
1	5.835510	12.859281	0.401816
7	2.867582	7.613770	2.757405
6	2.063064	6.873087	3.632401
6	0.671152	7.060114	3.504843
6	2.557712	6.052853	4.667015
6	-0.206688	6.414710	4.363390
1	0.305216	7.721403	2.717439
6	1.669644	5.420748	5.532416
1	3.630309	5.920331	4.807678
6	0.293058	5.591716	5.379146
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1	2.056237	4.791631	6.335256
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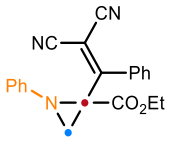

4a

6	2.651778	-0.503629	0.570183
6	2.203429	0.770339	0.402494
6	0.778794	1.053368	0.055930
6	-0.230210	1.327228	1.139847
1	-0.996586	2.066769	0.888362
1	0.103043	1.287028	2.179019
6	3.085529	1.947862	0.535487
6	4.361439	1.947576	-0.051146
6	2.622527	3.106687	1.178643
6	5.167259	3.079399	0.026307
1	4.707291	1.073023	-0.605102
6	3.440825	4.230457	1.265995
1	1.630072	3.126822	1.630022
6	4.711835	4.219494	0.691111
1	6.151679	3.074274	-0.443259
1	3.080020	5.120614	1.782576
1	5.346089	5.105089	0.752131
6	0.557285	1.827951	-1.228163
8	-0.481219	2.371893	-1.509635
8	1.619210	1.787166	-2.010077
6	1.553742	2.511550	-3.254686
6	2.926296	2.469552	-3.874330
1	1.227829	3.537890	-3.037001
1	0.792746	2.032700	-3.886936
1	2.912916	3.012248	-4.828623
1	3.663789	2.944709	-3.212124
1	3.235598	1.433115	-4.066618
7	-0.228804	0.089165	0.426606
6	-1.255792	-0.298056	-0.462527
6	-2.593105	-0.214767	-0.065085
6	-0.928122	-0.824111	-1.718344
6	-3.597419	-0.665164	-0.921194
1	-2.839258	0.200754	0.913909
6	-1.940267	-1.265707	-2.567143
1	0.119496	-0.873589	-2.026120
6	-3.277993	-1.192434	-2.172777
1	-4.639752	-0.598513	-0.605082
1	-1.679358	-1.669475	-3.546772
1	-4.067108	-1.541112	-2.840022

6	3.975265	-0.792524	1.056610
6	1.876851	-1.679933	0.271642
7	5.019620	-1.070085	1.468334
7	1.354714	-2.679436	0.015016

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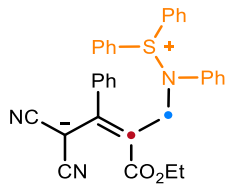
16	1.619531	-1.082346	-0.387353
6	0.856883	0.464748	0.058440
6	0.775311	0.753281	1.427628
6	0.382744	1.391831	-0.875839
6	0.226507	1.960642	1.854089
1	1.137896	0.028899	2.160282
6	-0.174018	2.593475	-0.436080
1	0.446350	1.181955	-1.944638
6	-0.253994	2.885413	0.925293
1	0.167898	2.174284	2.922670
1	-0.544546	3.309177	-1.172014
1	-0.689456	3.827252	1.261461
6	1.140010	-1.272719	-2.093480
6	-0.175562	-1.622502	-2.419809
6	2.093933	-1.107230	-3.100710
6	-0.535172	-1.789811	-3.755310
1	-0.913195	-1.757263	-1.626411
6	1.730158	-1.289481	-4.436283
1	3.116631	-0.832102	-2.837885
6	0.417442	-1.626360	-4.764095
1	-1.562014	-2.057328	-4.009284
1	2.476602	-1.161515	-5.221681
1	0.133996	-1.763897	-5.808707



IM1'

8	2.769912	4.236212	2.557083
8	1.579438	4.996257	0.829059
7	3.176999	3.561152	-1.289676
6	2.609445	5.062656	1.677055
6	3.457045	6.257628	1.486812
6	3.862031	6.723822	0.254013
6	3.727118	6.066034	-1.015313
6	4.615074	8.019920	0.205849
6	4.041608	6.751555	-2.214475
7	4.290752	7.303074	-3.209991
6	3.407307	4.695510	-1.159828
6	6.004139	8.023929	0.023713
1	6.532057	7.076333	-0.105507
6	3.939009	9.232490	0.364434
1	2.854963	9.228530	0.492768
6	6.707829	9.227652	0.022337
6	6.028232	10.437707	0.184572
6	4.642874	10.438772	0.349722
1	4.104415	11.380954	0.473666
1	7.791280	9.221740	-0.108093
1	6.579712	11.379267	0.180471
6	0.764296	3.819972	0.894228
6	-0.280675	3.925448	-0.187622
1	0.313949	3.760538	1.896867
1	1.408379	2.939161	0.756432
1	-0.939828	3.047817	-0.152902
1	-0.894099	4.826930	-0.048856
1	0.193050	3.966982	-1.178598
6	3.995731	6.857112	2.754348
1	4.378199	6.060932	3.415501
1	4.822876	7.525963	2.516195
16	3.482087	8.862204	4.559688
6	5.249838	8.752180	4.728554
6	5.707134	8.179261	5.915638
6	6.119814	9.173723	3.717092
6	7.081753	8.020335	6.089939
1	5.006953	7.865598	6.692457
6	7.486420	9.008149	3.910880
1	5.739943	9.617537	2.792876
6	7.964004	8.433053	5.092690
1	7.459420	7.576890	7.011411
1	8.179821	9.327651	3.131872
1	9.038145	8.308088	5.236038
6	3.205957	10.379577	3.636556
6	3.982890	11.505994	3.908186
6	2.091734	10.429759	2.802262
6	3.650250	12.706270	3.281233
1	4.834841	11.462504	4.588181
6	1.772952	11.640293	2.189300
1	1.488593	9.539556	2.621680
6	2.550923	12.774235	2.424764
1	4.256653	13.592457	3.471031

1	0.910241	11.691659	1.524208
1	2.297853	13.717830	1.939666
7	2.977873	7.638705	3.523392
6	1.895562	6.847837	4.059176
6	0.703975	6.791104	3.336166
6	2.066985	6.081037	5.214208
6	-0.317027	5.940160	3.761730
1	0.595926	7.390285	2.430416
6	1.037533	5.247053	5.642975
1	3.011437	6.124884	5.763402
6	-0.150367	5.169172	4.912122
1	-1.245329	5.882770	3.191210
1	1.167434	4.646806	6.544380
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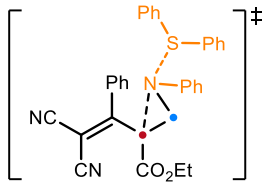

TS2'

8	3.019471	3.937088	2.627140
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6	2.850177	4.798311	1.786728
6	3.725698	5.978186	1.621584
6	4.015972	6.577048	0.390405
6	3.850056	5.983873	-0.877568
6	4.642844	7.938763	0.378517
6	4.118382	6.727311	-2.062177
7	4.325973	7.317794	-3.040892
6	3.526394	4.613042	-1.080569
6	6.022613	8.073096	0.180556
1	6.640568	7.179488	0.068113
6	3.846940	9.081063	0.512223
1	2.771490	8.974127	0.664116
6	6.600315	9.341516	0.123484
6	5.803018	10.480672	0.251269
6	4.426715	10.348756	0.443505
1	3.797802	11.235892	0.545385
1	7.676576	9.439436	-0.027522
1	6.254746	11.472773	0.201137
6	0.879007	3.714621	1.084230
6	-0.234044	3.951054	0.095764
1	0.507626	3.661345	2.119463
1	1.433015	2.788417	0.870227
1	-0.957568	3.126913	0.149775
1	-0.758197	4.890811	0.321008
1	0.162359	4.001145	-0.928254
6	4.210957	6.576749	2.910663
1	4.364085	5.820761	3.694216
1	5.109007	7.181583	2.771536
16	3.586793	8.914940	4.729357
6	5.351732	8.819561	4.738821
6	5.932228	8.172663	5.834502
6	6.134561	9.259880	3.663371
6	7.312471	7.974234	5.854657
1	5.311951	7.830704	6.665180
6	7.510609	9.061554	3.701857
1	5.670846	9.736316	2.797128
6	8.101115	8.419607	4.794525
1	7.770317	7.472621	6.707968
1	8.123135	9.402606	2.865434
1	9.180577	8.264504	4.816129
6	3.209014	10.418932	3.856965
6	4.019964	11.553654	3.961262
6	2.008735	10.460220	3.142592
6	3.634926	12.724783	3.311180
1	4.941648	11.531793	4.543946
6	1.631986	11.641499	2.505729
1	1.371791	9.578084	3.080750
6	2.445394	12.772150	2.582593
1	4.269435	13.608953	3.385190
1	0.697311	11.672064	1.944362
1	2.150537	13.693266	2.078144
7	3.039454	7.415421	3.062153
6	1.885843	6.787125	3.598145
6	0.664486	7.047736	2.955896
6	1.919890	5.926676	4.708384
6	-0.502912	6.434011	3.399874
1	0.658151	7.699355	2.080005
6	0.744831	5.338722	5.163181
1	2.863279	5.732945	5.223017
6	-0.464715	5.583011	4.506458
1	-1.444488	6.620504	2.881746
1	0.771355	4.681816	6.033449
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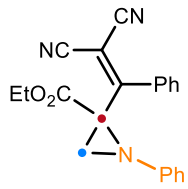

4a'

6	2.971372	1.868714	0.697397
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1	-1.013792	2.278995	0.660473
1	0.014207	1.630296	2.075141
6	2.521237	-0.566873	0.880586
6	3.190012	-0.859739	2.077751
6	2.231464	-1.597552	-0.026866
6	3.569066	-2.170607	2.358256
1	3.386581	-0.066781	2.801582
6	2.630950	-2.900512	0.250421
1	1.717239	-1.364991	-0.960305
6	3.296367	-3.188810	1.444482
1	4.076095	-2.397083	3.296961
1	2.419520	-3.695613	-0.465493
1	3.598157	-4.213776	1.665235
6	0.618885	1.720723	-1.340401
8	-0.388516	2.250494	-1.737540
8	1.724575	1.588527	-2.048526
6	1.747017	2.222281	-3.343721
6	3.119961	2.018228	-3.928043
1	1.509311	3.286156	-3.200984
1	0.958062	1.769501	-3.960111
1	3.168147	2.491406	-4.917514
1	3.886594	2.473469	-3.285963
1	3.339660	0.947992	-4.042160
7	-0.327439	0.228097	0.474767
6	-1.382277	-0.175228	-0.380581
6	-2.703985	0.004347	0.040772
6	-1.122742	-0.805617	-1.602909
6	-3.755199	-0.453913	-0.751450
1	-2.901763	0.500461	0.992883
6	-2.180865	-1.256937	-2.389150
1	-0.093550	-0.929070	-1.946285
6	-3.500868	-1.087529	-1.968183
1	-4.782460	-0.310169	-0.412493
1	-1.967644	-1.741997	-3.343045
1	-4.325564	-1.442723	-2.587215
6	4.343153	1.741929	1.102104
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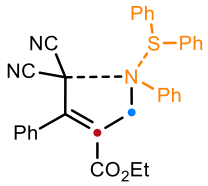
7	5.455479	1.675861	1.411182
7	2.136612	4.242690	0.069341



TS3

8	3.360889	3.698127	3.765347
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6	3.720129	3.950948	2.630076
6	3.903366	5.322221	2.111733
6	3.742958	5.674514	0.798974
6	4.190526	6.993107	0.382090
6	2.999134	4.847356	-0.185605
6	3.422068	7.764881	-0.518549
7	2.747524	8.413158	-1.211864
6	5.442124	7.509944	0.790039
6	1.799423	4.220884	0.185809
1	1.413037	4.356550	1.199733
6	3.464437	4.709675	-1.499822
1	4.390566	5.206851	-1.796359
6	1.097088	3.444456	-0.732276
6	1.582135	3.289206	-2.033233
6	2.764004	3.925543	-2.415420
1	3.142358	3.811640	-3.432391
1	0.163965	2.963601	-0.434622
1	1.032180	2.680267	-2.752557
6	3.577400	1.666123	2.045377
6	3.799216	0.832541	0.808150
1	2.516975	1.690949	2.338926
1	4.159806	1.299321	2.902797
1	3.482058	-0.201798	0.995780
1	3.214839	1.230979	-0.034628
1	4.861988	0.826358	0.529416
6	4.194378	6.394908	3.137447
1	3.819741	6.044765	4.111893
1	5.279012	6.560845	3.235308
16	4.141089	8.989749	4.782310

6	5.884531	8.725215	4.903094
6	6.260078	7.497031	5.469485
6	6.859216	9.658673	4.531003
6	7.609446	7.194092	5.627449
1	5.499410	6.780578	5.787429
6	8.205760	9.340084	4.695964
1	6.580561	10.632945	4.131137
6	8.585789	8.110254	5.234012
1	7.895978	6.236264	6.063430
1	8.963489	10.068646	4.404599
1	9.642642	7.870173	5.356510
6	3.895879	10.426005	3.789754
6	2.855059	11.277503	4.172327
6	4.576728	10.620109	2.579714
6	2.500981	12.342026	3.341763
1	2.321471	11.106088	5.108997
6	4.224214	11.695150	1.770459
1	5.352742	9.921872	2.263570
6	3.185598	12.553419	2.146665
1	1.686837	13.005669	3.635374
1	4.751256	11.853015	0.828438
1	2.908942	13.387708	1.500505
7	3.602149	7.685732	2.756751
6	2.239546	7.727419	2.704213
6	1.659469	8.874024	2.090946
6	1.386568	6.688018	3.171151
6	0.284892	8.971556	1.948580
1	2.321098	9.649617	1.703335
6	0.014683	6.801840	3.017722
1	1.802236	5.807281	3.661575
6	-0.536890	7.938308	2.411289
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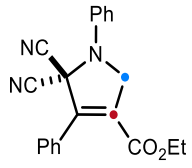

6a

6	0.488078	0.434916	-0.748932
6	0.958828	1.862232	-0.406368
6	-0.068288	2.512339	0.153735
6	-1.300024	1.674162	0.260293
1	-2.170492	2.159744	-0.208094
1	-1.550066	1.482492	1.318760
6	2.377075	2.254605	-0.549557
6	3.115428	2.536732	0.608779
6	2.995121	2.337022	-1.803807
6	4.455162	2.903535	0.512235
1	2.627816	2.468682	1.583844
6	4.337130	2.706100	-1.893715
1	2.425014	2.137046	-2.711980
6	5.067607	2.988282	-0.739640
1	5.023055	3.122929	1.417600
1	4.811180	2.778582	-2.873422
1	6.117297	3.276112	-0.815275
6	-0.073856	3.886844	0.721633
8	-0.889196	4.228105	1.547750
8	0.869190	4.667870	0.224676
6	1.014031	5.984239	0.792544
6	1.799678	5.925411	2.083244
1	0.015533	6.415350	0.939505
1	1.541911	6.558469	0.023442
1	1.934295	6.943066	2.474637
1	1.268201	5.331906	2.840040
1	2.791632	5.483945	1.912539
7	-0.918278	0.457255	-0.445192
6	-1.705266	-0.695029	-0.413058
6	-3.007297	-0.626768	0.115352
6	-1.240998	-1.925842	-0.910480
6	-3.815356	-1.760086	0.139292
1	-3.393737	0.314338	0.505151
6	-2.064000	-3.050463	-0.876621
1	-0.242033	-2.030978	-1.334654
6	-3.354020	-2.980872	-0.353940
1	-4.822192	-1.681623	0.552953
1	-1.680387	-3.993884	-1.268421
1	-3.991306	-3.865269	-0.331313
6	1.268594	-0.511004	0.106550
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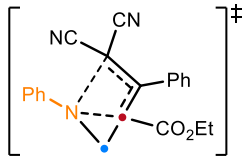

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6	1.513579	-0.282061	-0.165421
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6	0.618596	1.421204	0.946855
6	0.246878	0.471142	2.056142
1	-0.650807	0.651744	2.655860
1	1.049237	-0.091288	2.536825
6	3.015374	1.838537	-0.172243
6	3.191787	3.196920	0.201111
6	4.069492	1.225852	-0.899224
6	4.318612	3.907276	-0.192532
1	2.431784	3.691402	0.808392
6	5.181038	1.957160	-1.306223
1	4.024303	0.157548	-1.125610
6	5.318151	3.304736	-0.964726
1	4.421093	4.951151	0.111783
1	5.966331	1.456660	-1.876489
1	6.200452	3.868573	-1.269648
6	-0.232559	2.666579	0.784096
8	-1.168334	2.910149	1.504729
8	0.130010	3.378488	-0.262410
6	-0.599345	4.594963	-0.528878
6	-0.099056	5.721263	0.346157
1	-1.668439	4.397796	-0.377182
1	-0.417704	4.794821	-1.590257
1	-0.643384	6.642351	0.096987
1	-0.265028	5.498654	1.409153
1	0.972796	5.894817	0.177677
7	-0.048743	0.125411	0.665927
6	-1.351894	-0.091356	0.133716
6	-2.233287	-0.945616	0.795926
6	-1.689621	0.526153	-1.074455
6	-3.487712	-1.177289	0.236116
1	-1.935471	-1.415477	1.734833
6	-2.947183	0.284064	-1.620280
1	-0.974313	1.187559	-1.569759
6	-3.843283	-0.565088	-0.967011
1	-4.190407	-1.839301	0.743216
1	-3.228327	0.762290	-2.559074
1	-4.827522	-0.750111	-1.399263
6	1.916832	-1.433326	0.656130
6	1.486150	-0.633110	-1.578071
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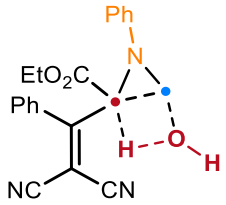

TS4

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7	-2.410598	2.226537	-1.544830
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6	-0.061899	-0.625750	-0.595467
6	0.539362	0.629812	-0.243448
6	-0.110930	1.847650	-0.415025
6	1.909349	0.672598	0.344698
6	0.486177	3.072785	0.017719
7	0.932880	4.084628	0.366268
6	-1.391632	2.008430	-1.034452
6	2.154157	0.071575	1.586452
1	1.345276	-0.441635	2.111846
6	2.950247	1.314945	-0.332482
1	2.758925	1.779829	-1.301985
6	3.427541	0.123166	2.147010
6	4.468424	0.757830	1.464650
6	4.228994	1.348465	0.224197
1	5.039737	1.841482	-0.314020
6	-2.369211	-0.699325	0.326114
6	-3.748578	-0.870825	0.102634
6	-1.916350	-0.536541	1.649228
6	-4.640283	-0.860829	1.174571
1	-4.136079	-1.024421	-0.904371
6	-2.820870	-0.531213	2.706056
1	-0.851172	-0.420440	1.848407
6	-4.190513	-0.688233	2.482309
1	-5.704847	-0.996614	0.975015
1	-2.444036	-0.403041	3.722394
1	-4.893441	-0.682927	3.315857
1	3.609702	-0.339379	3.118121

1	5.467828	0.789909	1.901339
6	2.607951	-3.108257	-0.055025
6	4.070542	-2.846568	-0.313384
1	2.246743	-3.997497	-0.591067
1	2.399072	-3.247739	1.016597
1	4.667412	-3.699079	0.036954
1	4.256228	-2.708917	-1.387680
1	4.401333	-1.943677	0.220973
1	-0.020165	-0.559652	-2.091669
6	-1.962523	-0.897042	-2.088774
1	-2.249597	-1.941731	-2.284415
1	-2.781896	-0.209465	-2.335371
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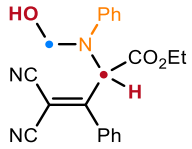
1	-0.643174	-1.228432	-3.589801



IM2

8	0.084949	-2.411284	-0.889893
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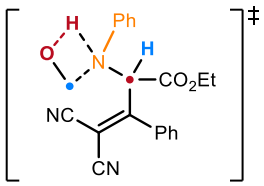
7	1.664799	-0.861326	0.909598
7	2.727050	1.755324	2.344076
6	-0.451383	-1.735559	-0.049452
6	0.251500	-0.669945	0.803433
6	-0.197442	0.759640	0.503638
6	0.536929	1.811409	0.954893
6	-1.489213	1.006513	-0.184696
6	0.144539	3.168987	0.679721
7	-0.128810	4.271625	0.463793
6	1.754951	1.707820	1.718205
6	-1.730808	0.521165	-1.479473
1	-0.963084	-0.040838	-2.015960
6	-2.495401	1.716137	0.484563
1	-2.318736	2.078390	1.499267
6	-2.956488	0.756999	-2.095301
6	-3.957502	1.460789	-1.422191
6	-3.726195	1.935656	-0.131727
1	-4.506673	2.479240	0.402167
6	2.538180	-0.688366	-0.161906
6	3.889093	-1.079938	-0.047343
6	2.131058	-0.103558	-1.379420
6	4.783730	-0.873806	-1.097124
1	4.256440	-1.567545	0.853125
6	3.035364	0.092147	-2.417728
1	1.099686	0.203121	-1.537961
6	4.373434	-0.284075	-2.289778
1	5.820257	-1.192215	-0.971368
1	2.679274	0.547850	-3.343339
1	5.077469	-0.127492	-3.107465
1	-3.130655	0.384515	-3.105596
1	-4.920105	1.635930	-1.904932
6	-2.566437	-2.673518	-0.523223
6	-3.991769	-2.415845	-0.107345
1	-2.268194	-3.721000	-0.375262
1	-2.390755	-2.409945	-1.576732
1	-4.669333	-3.028560	-0.716433
1	-4.142535	-2.673986	0.949818
1	-4.248759	-1.356320	-0.254988
1	-0.168689	-0.832742	1.810400
6	2.223777	-1.367029	2.176083
1	2.516908	-2.424792	2.066245
1	3.121780	-0.771206	2.394734
8	1.339848	-1.197130	3.239545
1	0.805875	-1.997989	3.338730



TS5

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7	1.677430	-0.758872	0.761934
7	1.949545	1.287778	3.734328
6	-0.714288	-1.469027	0.541273
6	0.278699	-0.487382	1.157375
6	-0.143287	0.963392	0.940405
6	0.363299	1.906904	1.777478
6	-1.092216	1.328108	-0.133526
6	0.149181	3.316958	1.588021
7	0.021257	4.457912	1.455381
6	1.239376	1.562980	2.864763
6	-0.923446	0.860744	-1.446881
1	-0.079186	0.221898	-1.708538
6	-2.197769	2.138161	0.173914

1	-2.360742	2.468255	1.201480
6	-1.825703	1.235477	-2.439678
6	-2.916826	2.047427	-2.130118
6	-3.106194	2.490190	-0.819991
1	-3.967807	3.109507	-0.567880
6	2.108059	-0.344410	-0.559134
6	2.051926	-1.218565	-1.645807
6	2.593379	0.955705	-0.710482
6	2.451141	-0.766101	-2.902521
1	1.678785	-2.232874	-1.512376
6	2.979910	1.400672	-1.973984
1	2.669672	1.612441	0.158060
6	2.902062	0.543901	-3.071643
1	2.404417	-1.444029	-3.755735
1	3.351947	2.418709	-2.095195
1	3.205269	0.893266	-4.059521
1	-1.675086	0.883002	-3.460730
1	-3.626190	2.329232	-2.909570
6	-3.009942	-2.055118	0.544421
6	-3.497180	-1.513346	-0.779480
1	-3.778177	-1.980635	1.321335
1	-2.677150	-3.098152	0.466407
1	-4.392597	-2.069603	-1.089314
1	-3.760856	-0.449063	-0.687631
1	-2.731883	-1.626214	-1.559829
1	0.240369	-0.681347	2.243708
6	2.218823	-2.100713	1.341276
1	1.353516	-2.729672	1.622309
1	2.780785	-2.594727	0.526688
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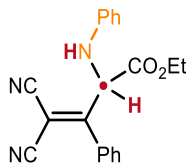

IM3

8	-0.076162	-2.486111	-0.927737
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7	1.649126	-1.036279	0.765768
7	2.707766	1.569754	2.365983
6	-0.543530	-1.802981	-0.052634
6	0.243686	-0.768353	0.760198
6	-0.179001	0.674400	0.446959
6	0.578921	1.713295	0.889628
6	-1.465549	0.951952	-0.239085
6	0.236832	3.078541	0.585106
7	0.006307	4.185740	0.344653
6	1.764438	1.581909	1.697158
6	-1.741094	0.448504	-1.519998
1	-1.001326	-0.153782	-2.050705
6	-2.438564	1.712661	0.424753
1	-2.239572	2.086994	1.430877
6	-2.963404	0.718274	-2.128678
6	-3.929259	1.474738	-1.461653
6	-3.666295	1.966833	-0.183686
1	-4.419846	2.550293	0.346800
6	2.546432	-0.681304	-0.233351
6	3.922239	-0.712618	0.064309
6	2.148971	-0.290917	-1.521222
6	4.864510	-0.376035	-0.900159
1	4.238134	-1.002075	1.069164
6	3.104679	0.050588	-2.478834
1	1.095326	-0.264879	-1.793235
6	4.465654	0.010827	-2.182697
1	5.924858	-0.411526	-0.643445
1	2.769291	0.349164	-3.473670
1	5.205960	0.277375	-2.937616
1	-3.162367	0.331309	-3.128874
1	-4.889435	1.676834	-1.938647
6	-2.718039	-2.645862	-0.428939
6	-4.111266	-2.293249	0.024530
1	-2.482009	-3.708300	-0.274912
1	-2.558119	-2.407114	-1.490671
1	-4.844049	-2.870725	-0.554365
1	-4.245930	-2.526147	1.089698
1	-4.305991	-1.221883	-0.133054
1	-0.115527	-0.919656	1.792570
1	2.058173	-1.143517	1.686680

HCHO

6	0.002975	-0.194723	-0.000000
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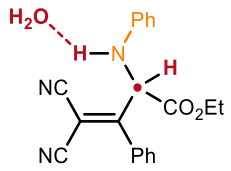

IM4

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7	0.624775	-0.174057	1.933244
7	2.462381	2.419702	2.047714
6	-0.809582	-1.139972	0.186968
6	-0.515085	0.059996	1.111884
6	-0.573268	1.385172	0.363401
6	0.354632	2.365074	0.538364
6	-1.758370	1.632235	-0.490357
6	0.196750	3.662086	-0.071297
7	0.107779	4.721984	-0.524729
6	1.517343	2.309264	1.389301
6	-3.046384	1.401328	0.014083
1	-3.185387	1.067267	1.043674
6	-1.601096	2.070246	-1.813254
1	-0.598925	2.218151	-2.220136
6	-4.160274	1.629008	-0.791247
6	-3.999177	2.064130	-2.106763
6	-2.717970	2.280244	-2.616812
1	-2.586175	2.609743	-3.648239
6	1.844464	-0.651173	1.489267
6	2.857550	-0.878964	2.442439
6	2.131664	-0.900539	0.135309
6	4.100841	-1.361920	2.054540
1	2.648119	-0.658145	3.490559
6	3.383456	-1.394737	-0.237259
1	1.401308	-0.687113	-0.646214
6	4.375887	-1.633473	0.710577
1	4.866339	-1.529163	2.814645
1	3.580396	-1.582590	-1.294416
1	5.351314	-2.016394	0.409216
1	-5.159681	1.463407	-0.386907
1	-4.873543	2.232935	-2.737026
6	-0.887306	-3.487253	0.103396
6	-0.649951	-4.644052	1.038667
1	-0.174378	-3.478297	-0.733685
1	-1.905121	-3.488195	-0.310872
1	-0.780508	-5.587669	0.492829
1	0.371535	-4.612481	1.442061
1	-1.363277	-4.622668	1.873784
1	-1.393123	0.082996	1.783787
8	1.046623	1.148696	4.516581
1	1.810757	1.548038	4.073191
1	0.591961	0.169790	2.894154
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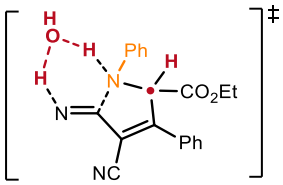

TS6

8	-0.333944	-1.121125	-0.746250
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7	1.810921	2.640232	2.564202
6	-0.536681	-1.020180	0.437524
6	-0.502693	0.300181	1.201589
6	-0.696515	1.517985	0.310640
6	0.225352	2.453387	0.626538
6	-1.815985	1.602271	-0.632442
6	0.319544	3.789602	0.136967
7	0.432699	4.882812	-0.225420
6	1.109707	2.037625	1.749253
6	-2.956931	0.807597	-0.427090
1	-3.013866	0.131988	0.429033
6	-1.771341	2.457650	-1.745914
1	-0.879237	3.051848	-1.946896
6	-4.037640	0.887605	-1.300455
6	-3.988426	1.748445	-2.397714
6	-2.851692	2.527407	-2.620624
1	-2.802528	3.189561	-3.485976
6	1.899521	-0.309661	1.313529
6	2.174087	-1.532245	1.929523
6	2.624038	0.099263	0.192583
6	3.173472	-2.356535	1.413065
1	1.597225	-1.835142	2.805671
6	3.623068	-0.729652	-0.314687
1	2.409769	1.054480	-0.288790
6	3.897217	-1.957242	0.289790
1	3.386210	-3.311706	1.895221
1	4.189220	-0.411894	-1.191173
1	4.679329	-2.601548	-0.113996

1	-4.921299	0.273260	-1.123656
1	-4.833892	1.806441	-3.084857
6	-0.647982	-3.355030	0.684702
6	-0.783309	-4.349491	1.807755
1	0.331536	-3.420495	0.188225
1	-1.430564	-3.475692	-0.077284
1	-0.708780	-5.367320	1.402929
1	0.015989	-4.210327	2.549007
1	-1.755706	-4.243709	2.307679
1	-1.283981	0.275132	1.977439
8	1.495379	0.762475	4.184512
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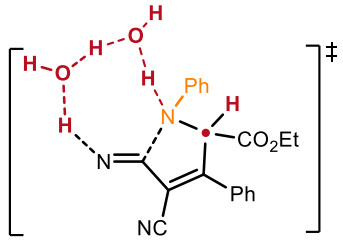
1	2.264762	0.186318	4.310522



TS6′

8	-0.825767	0.060779	1.659546
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7	0.944078	-0.398529	-1.055683
7	1.325680	-2.570977	-2.183524
1	1.545358	0.172134	-2.076270
6	-0.302386	0.712247	0.789978
6	-0.301757	0.325429	-0.687048
6	-1.442967	-0.614558	-1.024367
6	-0.946922	-1.741838	-1.574593
6	-2.832474	-0.212270	-0.774246
6	-1.661870	-2.854508	-2.109115
7	-2.189787	-3.778430	-2.564353
6	0.543097	-1.762587	-1.686598
6	-3.879119	-1.150161	-0.744320
1	-3.675049	-2.211058	-0.886998
6	-3.131457	1.141193	-0.536448
1	-2.341386	1.894891	-0.543828
6	-5.186851	-0.740317	-0.503926
6	-5.473921	0.608391	-0.286259
6	-4.442131	1.546848	-0.300094
1	-4.656491	2.601747	-0.124620
6	1.946576	-0.530305	-0.015180
6	1.837557	-1.539045	0.945075
6	2.999020	0.384565	0.038521
6	2.786180	-1.628255	1.962110
1	1.005613	-2.244368	0.898912
6	3.942280	0.292658	1.062191
1	3.070432	1.173603	-0.711610
6	3.838182	-0.712653	2.023686
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1	4.761988	1.011305	1.105155
1	4.578202	-0.784376	2.822042
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1	-6.500614	0.926068	-0.098517
6	0.693112	2.143553	2.365923
6	1.592588	3.351966	2.362021
1	1.179289	1.265885	2.819622
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1	1.838964	3.625865	3.396311
1	2.527944	3.138309	1.825721
1	1.094680	4.206825	1.884365
8	2.227968	0.510595	-2.984497
1	1.702024	0.411450	-3.794109
1	2.920573	-0.308983	-2.972675
8	3.607475	-1.508828	-2.716328
1	2.727246	-2.037447	-2.432877
1	3.867063	-1.899499	-3.563385
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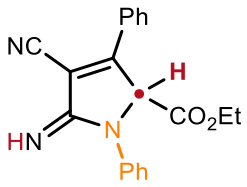

IM5

8	0.965516	-1.332706	-1.100363
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7	2.827956	2.612825	0.057911
6	0.204924	-1.107294	-0.193994
6	0.320932	0.115898	0.722543
6	-0.449800	1.264792	0.102210
6	0.436529	2.242391	-0.192112
6	-1.897667	1.225076	-0.125744
6	0.174234	3.530837	-0.744181
7	-0.007015	4.585941	-1.182800

6	1.812177	1.854903	0.201519
6	-2.735774	0.517329	0.752368
1	-2.314494	-0.002153	1.613592
6	-2.461457	1.886865	-1.229514
1	-1.819846	2.407450	-1.942124
6	-4.110710	0.489218	0.537689
6	-4.663527	1.154203	-0.558053
6	-3.836595	1.849400	-1.441707
1	-4.263306	2.358503	-2.306718
6	2.745378	-0.254824	1.147742
6	2.617962	-1.049526	2.292818
6	3.900367	-0.347787	0.360808
6	3.645189	-1.920066	2.652502
1	1.716021	-0.982195	2.902898
6	4.930140	-1.205955	0.741391
1	3.985377	0.237546	-0.555534
6	4.808095	-1.995050	1.885706
1	3.536493	-2.536755	3.545896
1	5.828478	-1.268646	0.125394
1	5.614012	-2.670696	2.174901
1	-4.753865	-0.055215	1.230288
1	-5.741062	1.125891	-0.726811
6	-1.158047	-2.945744	-0.756845
6	-2.465612	-3.532117	-0.292219
1	-0.332579	-3.669140	-0.703544
1	-1.217221	-2.563028	-1.785196
1	-2.738402	-4.376126	-0.939232
1	-2.383915	-3.896791	0.740787
1	-3.265475	-2.779863	-0.342434
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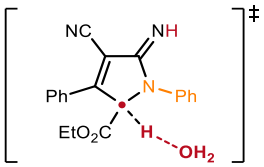
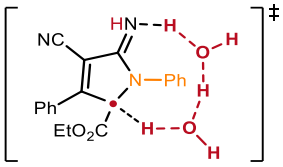


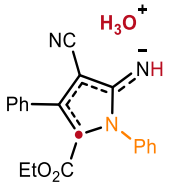
TS7

8	0.637632	6.036322	6.120349
8	0.965462	4.963205	4.188116
7	0.861264	8.549621	4.834685
7	1.714050	10.791519	4.405376
1	1.092749	11.099094	5.159365
6	0.838089	6.068391	4.919028
6	0.911469	7.295360	4.109761
6	1.970832	7.491677	3.132572
6	2.364385	8.804011	3.165043
6	2.506166	6.488561	2.186457
6	3.259117	9.460918	2.280303
7	3.982871	10.020979	1.576524
6	1.634562	9.524228	4.214368
6	1.653706	5.632628	1.470612
1	0.574071	5.696520	1.617767
6	3.893457	6.400435	1.983187
1	4.562719	7.048360	2.552686
6	2.180389	4.718633	0.564276
6	3.563341	4.631296	0.373145
6	4.417729	5.468669	1.089366
1	5.499157	5.407745	0.947660
6	-0.082607	8.837613	5.843049
6	-1.364869	8.244856	5.822721
6	0.252542	9.690511	6.902625
6	-2.285294	8.540566	6.817550
1	-1.628060	7.531638	5.022982
6	-0.680455	9.988415	7.893404
1	1.259645	10.108492	6.968565
6	-1.956838	9.423872	7.854006
1	-3.279938	8.074449	6.784048
1	-0.391396	10.666196	8.708129
1	-2.686400	9.650945	8.639247
1	1.510939	4.063998	0.004023
1	3.978007	3.901417	-0.327564
6	0.894258	3.700308	4.860865
6	1.005154	2.622309	3.802849
1	-0.053869	3.648708	5.407861
1	1.713336	3.639250	5.584740
1	0.848803	1.638343	4.270132
1	0.236041	2.768060	3.031433
1	1.995133	2.639215	3.334123
8	-0.964199	7.679948	2.339934
1	-0.929225	8.665014	2.286291
1	-1.870066	7.450607	2.643286
1	-0.166657	7.358973	3.175619



TS7′

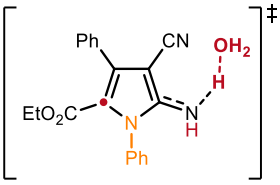
8	0.858749	6.099714	6.023988
8	1.146156	5.143682	4.021599
7	1.094743	8.668953	4.935297
7	1.802882	10.969447	4.610920
1	1.127093	11.197025	5.342107
6	1.063208	6.196297	4.832593
6	1.199897	7.483815	4.110006
6	2.303474	7.750688	3.202265
6	2.661984	9.067893	3.356969
6	2.857877	6.846342	2.180530
6	3.531555	9.825803	2.528676
7	4.221496	10.473775	1.859178
6	1.849983	9.698018	4.398270
6	2.017819	6.043225	1.394029
1	0.942539	6.044789	1.574898
6	4.239949	6.834775	1.940592
1	4.901890	7.446601	2.556455
6	2.553900	5.246639	0.386049
6	3.931424	5.234172	0.157134
6	4.772755	6.026561	0.937953
1	5.850214	6.016210	0.767918
6	0.032658	8.888198	5.845147
6	-1.242862	8.360793	5.606959
6	0.266818	9.633018	7.007654
6	-2.268092	8.583744	6.523274
1	-1.434132	7.777660	4.705600
6	-0.770584	9.864955	7.909513
1	1.268112	10.014865	7.212832
6	-2.041159	9.341069	7.673630
1	-3.256817	8.164551	6.330132
1	-0.575128	10.448058	8.810770
1	-2.849483	9.516236	8.384648
1	1.891895	4.631421	-0.224969
1	4.348454	4.604618	-0.630429
6	1.007744	3.838658	4.608477
6	-0.447761	3.485508	4.819561
1	1.572105	3.811197	5.549664
1	1.483592	3.161754	3.889410
1	-0.523997	2.460247	5.207074
1	-0.915410	4.165936	5.543901
1	-0.999288	3.539846	3.870693
8	-0.562026	8.301449	2.369000
1	-0.472573	7.868898	1.503592
1	-0.226139	9.260684	2.243122
1	0.209508	7.733780	3.144484
8	0.291631	10.715361	2.057630
1	0.771043	11.022466	2.855769
1	0.972212	10.704990	1.367038



IM6

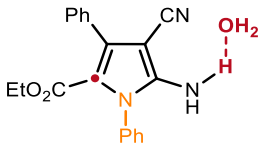
8	-1.130852	6.025592	5.067797
8	0.799551	5.025004	4.530215
7	0.305195	8.566343	5.076821
7	1.065914	10.876890	4.989141
1	0.316393	11.035131	5.663432
6	0.036536	6.103492	4.730521
6	0.758439	7.352054	4.510044
6	1.794478	7.613606	3.640498
6	2.029338	9.025392	3.696000
6	2.490880	6.702244	2.708541
6	2.934052	9.755377	2.941799
7	3.687972	10.385870	2.318524
6	1.103373	9.639363	4.631782
6	1.778646	5.829912	1.871043
1	0.687857	5.808849	1.919328
6	3.889469	6.740086	2.615739
1	4.455330	7.413874	3.262880
6	2.453089	5.002164	0.976994
6	3.847617	5.036331	0.901077
6	4.562952	5.908680	1.720611
1	5.652256	5.942125	1.666987
6	-0.482134	8.654576	6.251573
6	-1.533402	9.574393	6.317498
6	-0.196407	7.844620	7.357570
6	-2.287232	9.687570	7.486215
1	-1.765157	10.190512	5.447215
6	-0.965251	7.949777	8.513408
1	0.631058	7.133804	7.303597
6	-2.009664	8.874716	8.584439
1	-3.105059	10.408514	7.530096
1	-0.740411	7.311077	9.369066
1	-2.605787	8.958973	9.494100
1	1.886300	4.329764	0.330767

1	4.373844	4.386975	0.199647
6	0.131028	3.757797	4.489641
6	1.160254	2.708956	4.149438
1	-0.669444	3.806841	3.735989
1	-0.336504	3.570600	5.466887
1	0.682547	1.720874	4.113976
1	1.615057	2.912505	3.169412
1	1.954246	2.684482	4.908630
8	5.310731	11.698848	1.001829
1	4.568033	11.086876	1.614515
1	5.722865	11.116085	0.338740
1	6.032417	11.994680	1.585519



TS8

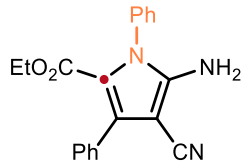
8	-1.028786	6.032162	5.074117
8	0.803951	4.890852	4.478292
7	0.520814	8.486290	4.782230
7	1.401568	10.738361	4.470066
1	0.713177	10.999230	5.176198
6	0.112760	6.023084	4.648353
6	0.877185	7.208660	4.285853
6	1.872242	7.351274	3.338967
6	2.172888	8.743750	3.270431
6	2.469638	6.340487	2.441298
6	3.066155	9.435047	2.461479
7	3.776137	10.128082	1.844993
6	1.341438	9.474658	4.208398
6	1.672913	5.431666	1.728066
1	0.588178	5.455529	1.850857
6	3.858486	6.319707	2.249627
1	4.489333	7.023192	2.797674
6	2.256097	4.509931	0.862271
6	3.642254	4.485260	0.689922
6	4.440674	5.394239	1.383052
1	5.523851	5.383670	1.251979
6	-0.184744	8.707852	5.990836
6	-1.170900	9.697575	6.049228
6	0.120640	7.962106	7.136111
6	-1.839080	9.945038	7.248948
1	-1.419822	10.263358	5.149996
6	-0.563863	8.201713	8.324379
1	0.897248	7.195803	7.087305
6	-1.541846	9.197299	8.387456
1	-2.605819	10.720460	7.286568
1	-0.324201	7.612876	9.211217
1	-2.071062	9.387093	9.322277
1	1.624098	3.809704	0.313391
1	4.097038	3.762074	0.011139
6	0.071677	3.664017	4.586675
6	1.020032	2.536146	4.264189
1	-0.778290	3.697910	3.888369
1	-0.332435	3.579211	5.605590
1	0.492953	1.576141	4.344097
1	1.411521	2.635784	3.241687
1	1.865442	2.528365	4.966102
8	4.306442	12.470664	2.645961
1	4.214737	11.514027	2.210634
1	5.166053	12.512193	3.109252
1	3.613850	12.513879	3.338228



IM7

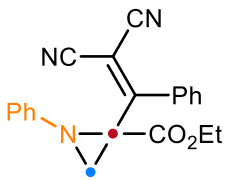
8	-0.716899	6.256373	5.097125
8	1.014299	5.032717	4.379448
7	0.987215	8.611621	4.786797
7	1.925119	10.792494	4.610651
1	1.248844	11.176947	5.259400
6	0.395830	6.187164	4.614972
6	1.211564	7.340094	4.227478
6	2.197985	7.452148	3.268282
6	2.603163	8.825754	3.259609
6	2.713907	6.431332	2.332793
6	3.553839	9.429047	2.407107
7	4.337805	9.934908	1.714740
6	1.838703	9.513414	4.226195
6	1.840520	5.613956	1.599541
1	0.762309	5.722939	1.733711
6	4.095584	6.300768	2.135435
1	4.784882	6.930011	2.702609
6	2.341543	4.674584	0.702043

6	3.720206	4.542275	0.519524
6	4.594673	5.358420	1.236130
1	5.672621	5.261049	1.098374
6	0.178399	8.899643	5.930081
6	-0.871032	9.811868	5.820010
6	0.460686	8.276088	7.146894
6	-1.639551	10.109272	6.945792
1	-1.082762	10.280773	4.857330
6	-0.322704	8.566319	8.260868
1	1.287025	7.565110	7.208609
6	-1.370104	9.485060	8.163180
1	-2.458931	10.824680	6.864617
1	-0.109588	8.076853	9.212137
1	-1.977494	9.714146	9.039849
1	1.651770	4.045567	0.136917
1	4.110925	3.806039	-0.184642
6	0.238141	3.835290	4.532126
6	1.107272	2.674959	4.117034
1	-0.662223	3.920226	3.905844
1	-0.083316	3.754211	5.580157
1	0.545876	1.737414	4.224223
1	1.419129	2.777700	3.067844
1	2.004715	2.617680	4.748343
8	3.703393	12.581547	3.136342
1	3.130394	12.659042	2.359631
1	4.358156	11.928106	2.848528
1	2.563752	11.427134	4.121480



3a

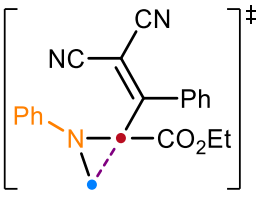
8	-0.754061	6.141669	5.057685
8	0.991186	4.897025	4.414853
7	0.987549	8.475579	4.803076
7	1.894567	10.672568	4.591035
1	1.449401	10.965765	5.455483
1	2.730598	11.184894	4.329139
6	0.375507	6.057674	4.620661
6	1.216776	7.201774	4.256583
6	2.235211	7.300210	3.328762
6	2.653025	8.669942	3.329978
6	2.772031	6.268874	2.417007
6	3.641253	9.269450	2.514238
7	4.450629	9.775186	1.853227
6	1.861877	9.363285	4.262687
6	1.914812	5.453006	1.663243
1	0.833867	5.572561	1.761802
6	4.158002	6.124942	2.264571
1	4.834489	6.752918	2.848354
6	2.435587	4.501931	0.789640
6	3.818081	4.356109	0.652071
6	4.676778	5.170779	1.389143
1	5.757611	5.062767	1.286439
6	0.139835	8.780017	5.914663
6	-0.886642	9.711520	5.762098
6	0.364725	8.153246	7.141590
6	-1.692963	10.023496	6.856974
1	-1.050463	10.184478	4.792497
6	-0.455674	8.459582	8.224078
1	1.175666	7.428367	7.236059
6	-1.482162	9.396321	8.084400
1	-2.495299	10.753671	6.743751
1	-0.287923	7.968672	9.183608
1	-2.118841	9.637761	8.936636
1	1.758459	3.874215	0.208013
1	4.224221	3.610512	-0.033265
6	0.196397	3.708188	4.540097
6	1.068566	2.536793	4.164769
1	-0.676571	3.800948	3.877212
1	-0.168295	3.635111	5.574422
1	0.492020	1.606337	4.251298
1	1.424499	2.632303	3.129032
1	1.938308	2.471088	4.832916



4a (DCM solvent)

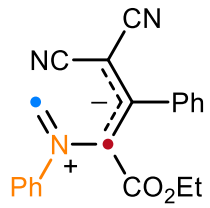
6	2.657573	-0.496996	0.635587
6	2.227715	0.779117	0.429206
6	0.803941	1.071878	0.085928
6	-0.209009	1.268076	1.187882
1	-0.978967	2.017955	0.978504

1	0.125207	1.162619	2.223107
6	3.112209	1.956081	0.554976
6	4.417786	1.933378	0.038788
6	2.622918	3.139698	1.132351
6	5.225280	3.063544	0.124685
1	4.791071	1.040975	-0.465967
6	3.440506	4.263156	1.226720
1	1.606183	3.179665	1.525699
6	4.741852	4.227168	0.725381
1	6.234787	3.037497	-0.287984
1	3.056407	5.171889	1.692143
1	5.378108	5.111120	0.793551
6	0.567224	1.913120	-1.156429
8	-0.436127	2.542551	-1.354818
8	1.574867	1.807301	-2.007214
6	1.461958	2.540857	-3.240005
6	2.741527	2.344123	-4.011822
1	1.281707	3.598093	-2.998241
1	0.584376	2.162540	-3.784465
1	2.680786	2.886019	-4.965248
1	3.600761	2.730344	-3.445890
1	2.907753	1.279389	-4.226770
7	-0.193591	0.082633	0.395681
6	-1.212413	-0.291043	-0.503143
6	-2.551816	-0.251518	-0.104645
6	-0.873041	-0.764444	-1.776970
6	-3.545586	-0.686420	-0.980401
1	-2.807843	0.116134	0.890824
6	-1.875365	-1.190578	-2.645028
1	0.176760	-0.793133	-2.079576
6	-3.214731	-1.156260	-2.251768
1	-4.589602	-0.653915	-0.663660
1	-1.604962	-1.554680	-3.637808
1	-3.996405	-1.493245	-2.933957
6	3.971204	-0.793250	1.148301
6	1.870315	-1.673225	0.357966
7	5.006814	-1.070109	1.577189
7	1.343832	-2.671917	0.114798



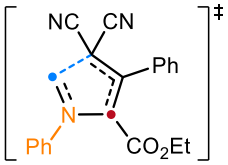
TS9 (DCM solvent)

6	2.208826	-0.391610	1.107395
6	2.003478	0.774829	0.375386
6	0.728461	1.154764	-0.134049
6	-0.847282	1.435475	1.046515
1	-1.826288	1.914067	0.903426
1	-0.242209	1.677274	1.923914
6	3.128221	1.740199	0.241608
6	4.364622	1.329310	-0.269996
6	2.945115	3.078371	0.616331
6	5.403345	2.248001	-0.409923
1	4.506968	0.291799	-0.579004
6	3.988992	3.990694	0.486410
1	1.980149	3.400507	1.014810
6	5.219091	3.577919	-0.030065
1	6.360686	1.922226	-0.819603
1	3.842219	5.028544	0.789841
1	6.035236	4.294716	-0.136108
6	0.499763	2.168807	-1.196575
8	-0.560007	2.718360	-1.394258
8	1.566911	2.337136	-1.968658
6	1.504446	3.375967	-2.953074
6	2.884781	3.521531	-3.543707
1	1.164898	4.302219	-2.465876
1	0.755709	3.101339	-3.710619
1	2.880682	4.310274	-4.308347
1	3.610968	3.792692	-2.763448
1	3.208281	2.581973	-4.013343
7	-0.449630	0.446192	0.250742
6	-1.270718	-0.340819	-0.578574
6	-2.530950	-0.721021	-0.108643
6	-0.812786	-0.760342	-1.830972
6	-3.346938	-1.511211	-0.914526
1	-2.852107	-0.423494	0.891671
6	-1.634469	-1.563269	-2.617599
1	0.172455	-0.451463	-2.186206
6	-2.902803	-1.935381	-2.167855
1	-4.331157	-1.810929	-0.551309
1	-1.281766	-1.893401	-3.595883
1	-3.542283	-2.560948	-2.792038
6	3.429347	-0.629989	1.816850
6	1.250372	-1.450597	1.201472
7	4.398794	-0.847422	2.410199
7	0.510547	-2.337102	1.281151



IM8 (DCM solvent)

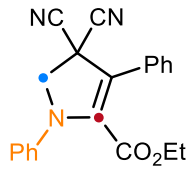
6	0.509227	2.035257	0.024371
6	0.722610	0.728688	-0.487066
6	-0.180966	-0.011968	-1.246828
6	-1.251070	1.639001	-2.599340
6	2.059625	0.122374	-0.207212
6	2.527520	-0.002523	1.105162
6	2.859555	-0.314886	-1.270248
6	3.776160	-0.570801	1.351671
1	1.903656	0.333298	1.936103
6	4.112590	-0.870643	-1.022481
1	2.493979	-0.215255	-2.295104
6	4.571621	-1.003199	0.289655
1	4.129383	-0.675390	2.378811
1	4.733751	-1.201204	-1.856689
1	5.551681	-1.442448	0.484196
6	-0.108394	-1.455576	-1.539271
8	-0.659419	-1.962088	-2.491799
8	0.581840	-2.151274	-0.640098
6	0.867318	-3.516263	-0.957488
6	1.770040	-4.053931	0.125244
1	1.345664	-3.556855	-1.948266
1	-0.078870	-4.073716	-1.021054
1	2.012277	-5.105749	-0.079346
1	2.706799	-3.479232	0.167142
1	1.277642	-3.993625	1.106076
7	-1.330219	0.583448	-1.869139
6	-2.627655	-0.002923	-1.598461
6	-3.509991	-0.228328	-2.651697
6	-2.954050	-0.318810	-0.281693
6	-4.763740	-0.766483	-2.371598
1	-3.204946	-0.011793	-3.677009
6	-4.213087	-0.854062	-0.016586
1	-2.236905	-0.135543	0.520164
6	-5.116184	-1.076123	-1.057058
1	-5.462212	-0.956674	-3.187461
1	-4.488155	-1.095393	1.010889
1	-6.098073	-1.500873	-0.843217
6	1.572118	2.812786	0.566715
6	-0.759618	2.666662	-0.014456
7	2.417393	3.471430	1.009796
7	-1.817097	3.139786	-0.096954
1	-2.166842	2.118824	-2.950600
1	-0.265154	2.048306	-2.833432



TS10 (DCM solvent)

6	1.055347	0.164017	0.061435
6	1.107038	1.632781	0.168577
6	0.172069	2.287523	0.937235
6	2.079109	2.362917	-0.681708
6	3.383792	1.871178	-0.830246
6	1.695073	3.510456	-1.393830
6	4.297154	2.534431	-1.647459
1	3.685589	0.971940	-0.288863
6	2.605891	4.166508	-2.215589
1	0.667987	3.876117	-1.317880
6	3.910874	3.682801	-2.338700
1	5.313462	2.150299	-1.746898
1	2.295066	5.052278	-2.771791
1	4.624479	4.197157	-2.984748
6	0.187265	3.720602	1.370014
8	-0.805984	4.330141	1.676543
8	1.417387	4.204524	1.442277
6	1.566777	5.585764	1.807809
6	1.539870	5.759842	3.310476
1	0.772976	6.168467	1.320922
1	2.536015	5.878445	1.386100
1	1.728544	6.813079	3.561286
1	0.560788	5.476221	3.719756
1	2.318473	5.145427	3.783855
6	1.675157	-0.634465	1.064261
6	1.097394	-0.388022	-1.258092
7	2.167599	-1.263662	1.906325
7	1.079302	-0.828243	-2.330314
7	-1.002924	1.569882	1.255862
6	-2.266699	2.028520	0.741611

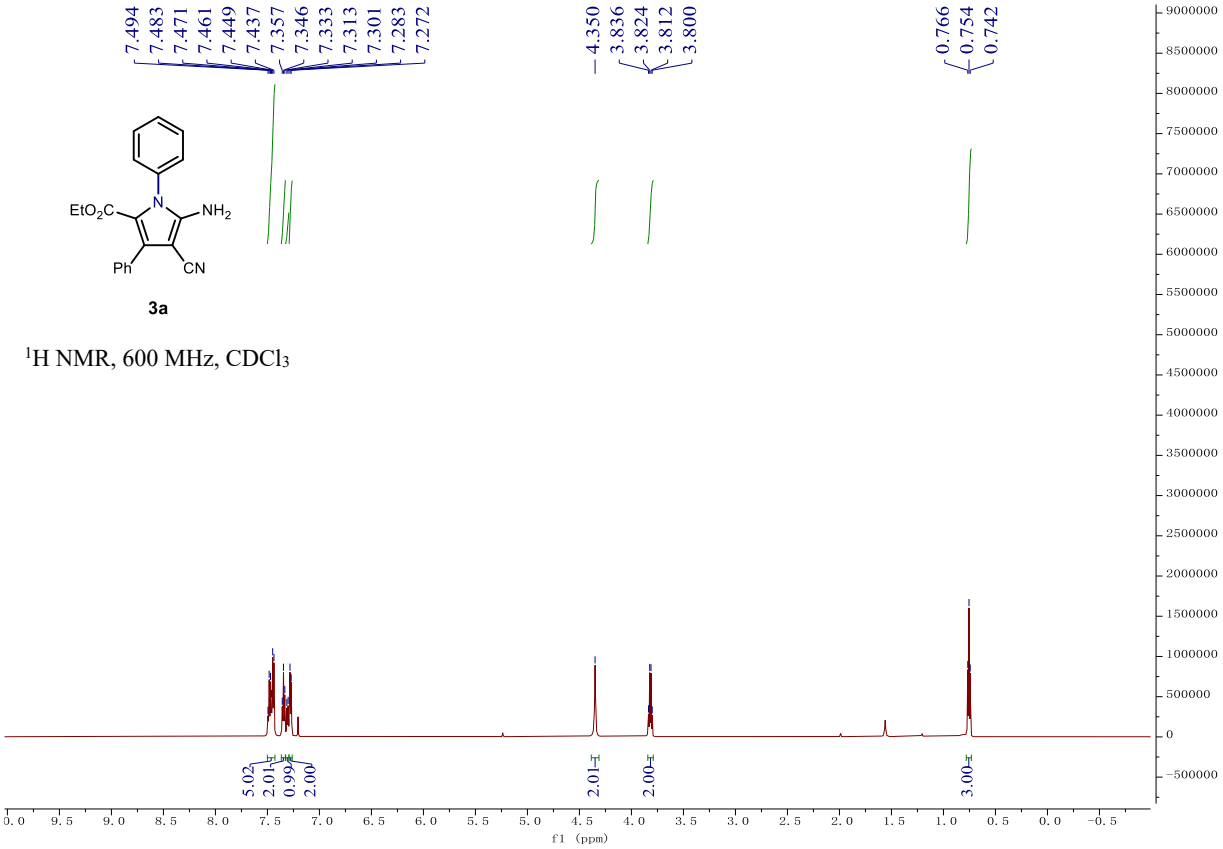
6	-2.331498	2.620180	-0.520261
6	-3.411295	1.831528	1.511769
6	-3.570608	3.020030	-1.013148
1	-1.422826	2.751529	-1.109832
6	-4.646690	2.229411	1.003550
1	-3.326728	1.389014	2.505806
6	-4.727267	2.825382	-0.254959
1	-3.633522	3.479104	-2.000696
1	-5.547543	2.082167	1.600847
1	-5.694887	3.141473	-0.647416
6	-0.851796	0.313887	1.609748
1	-1.690840	-0.370998	1.464944
1	-0.046131	0.047820	2.289084



5a (DCM solvent)

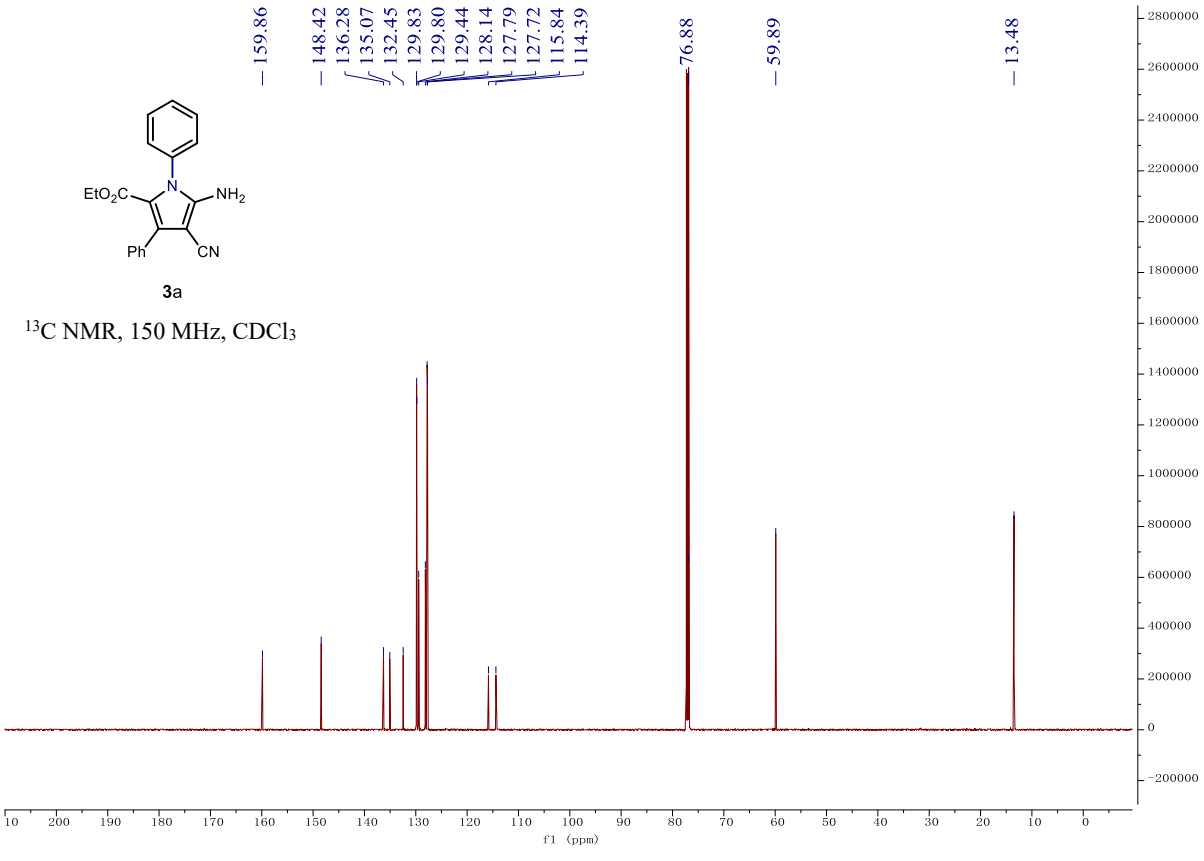
6	0.526824	0.304242	-0.483713
6	0.950321	1.770648	-0.278476
6	-0.035194	2.353863	0.439954
6	2.325651	2.248115	-0.518183
6	3.096891	2.731193	0.550463
6	2.892424	2.206961	-1.801520
6	4.398357	3.181884	0.337210
1	2.674549	2.736779	1.558499
6	4.197510	2.649568	-2.009212
1	2.303613	1.844570	-2.645973
6	4.952113	3.140678	-0.942796
1	4.985145	3.556682	1.177804
1	4.624494	2.616758	-3.012917
1	5.973528	3.487250	-1.108915
6	0.054071	3.696521	1.108398
8	-0.232770	3.863631	2.263020
8	0.475375	4.632564	0.274734
6	0.656834	5.957119	0.811363
6	1.977112	6.080688	1.538458
1	-0.191343	6.185004	1.470924
1	0.617247	6.614857	-0.064440
1	2.100134	7.114315	1.891629
1	2.010065	5.413893	2.411403
1	2.814478	5.840075	0.868690
6	1.278778	-0.525703	0.486347
6	0.759935	-0.217184	-1.841057
7	1.861940	-1.133314	1.272753
7	0.924027	-0.606501	-2.912773
7	-1.121540	1.536579	0.693366
6	-2.429761	2.023119	0.943192
6	-2.848154	3.277446	0.482827
6	-3.327315	1.203313	1.637322
6	-4.144036	3.717599	0.748573
1	-2.169687	3.905842	-0.098633
6	-4.627074	1.641681	1.877436
1	-2.993045	0.228559	1.997156
6	-5.038345	2.902959	1.442564
1	-4.459124	4.700187	0.393286
1	-5.319623	0.996533	2.420612
1	-6.054159	3.247955	1.640665
6	-0.990703	0.344674	-0.146791
1	-1.556994	0.483540	-1.082433
1	-1.329317	-0.567693	0.356848

12. NMR and HPLC spectra



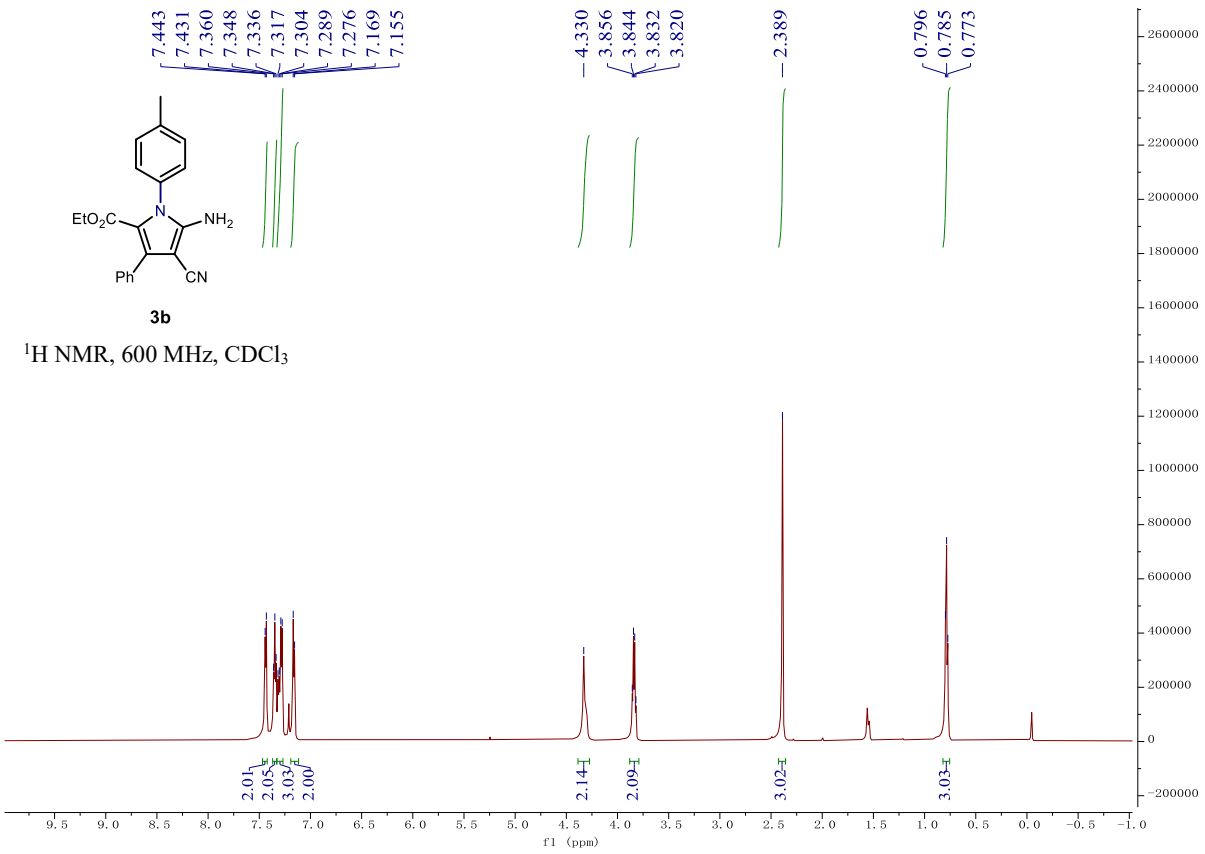
3a

^{1}H NMR, 600 MHz, $CDCl_3$



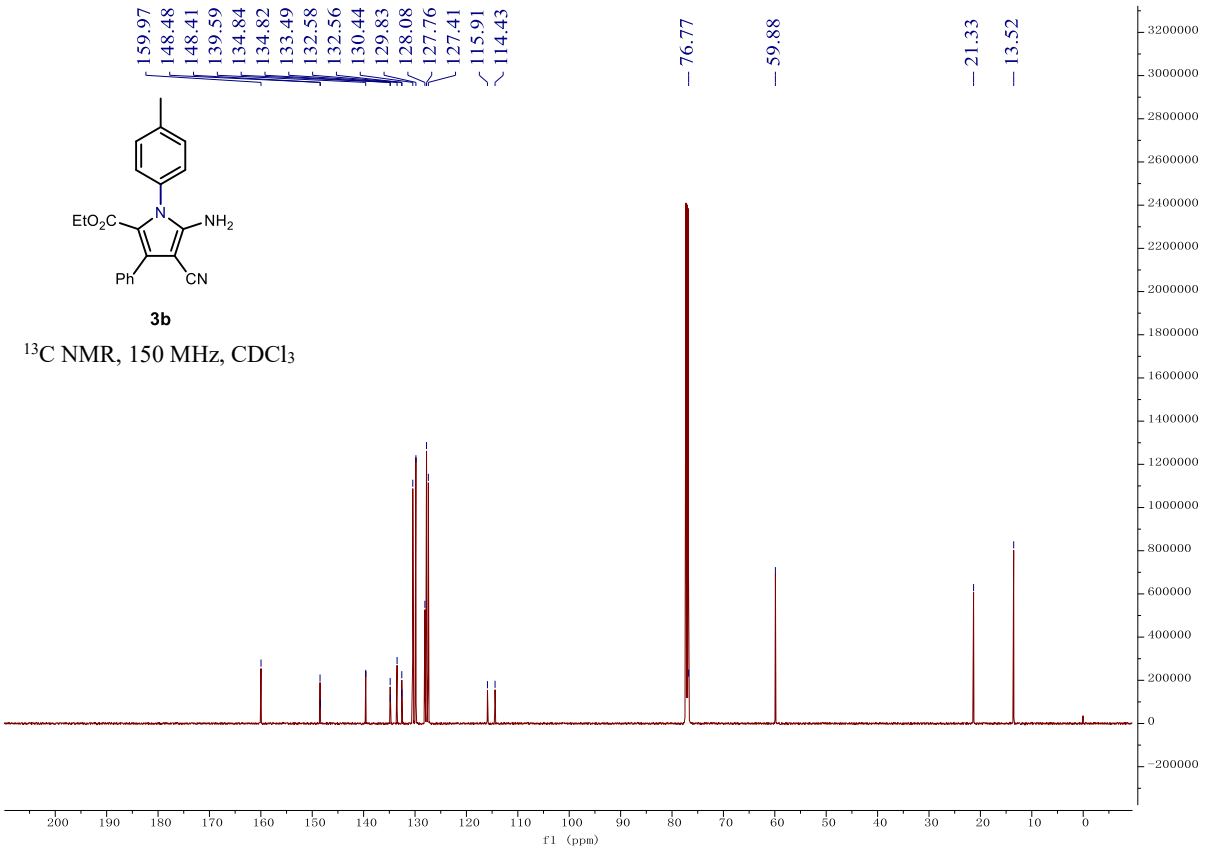
3a

^{13}C NMR, 150 MHz, $CDCl_3$



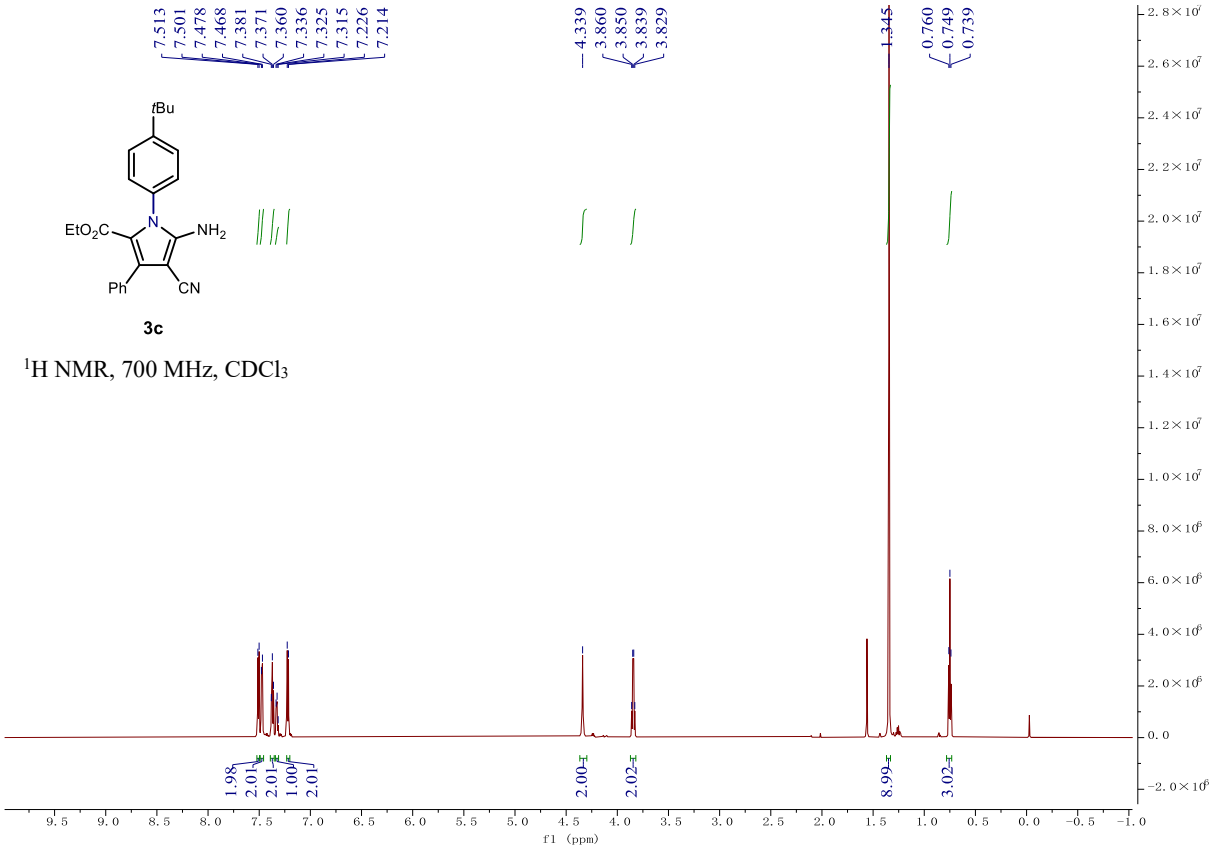
3b

^{1}H NMR, 600 MHz, $CDCl_3$



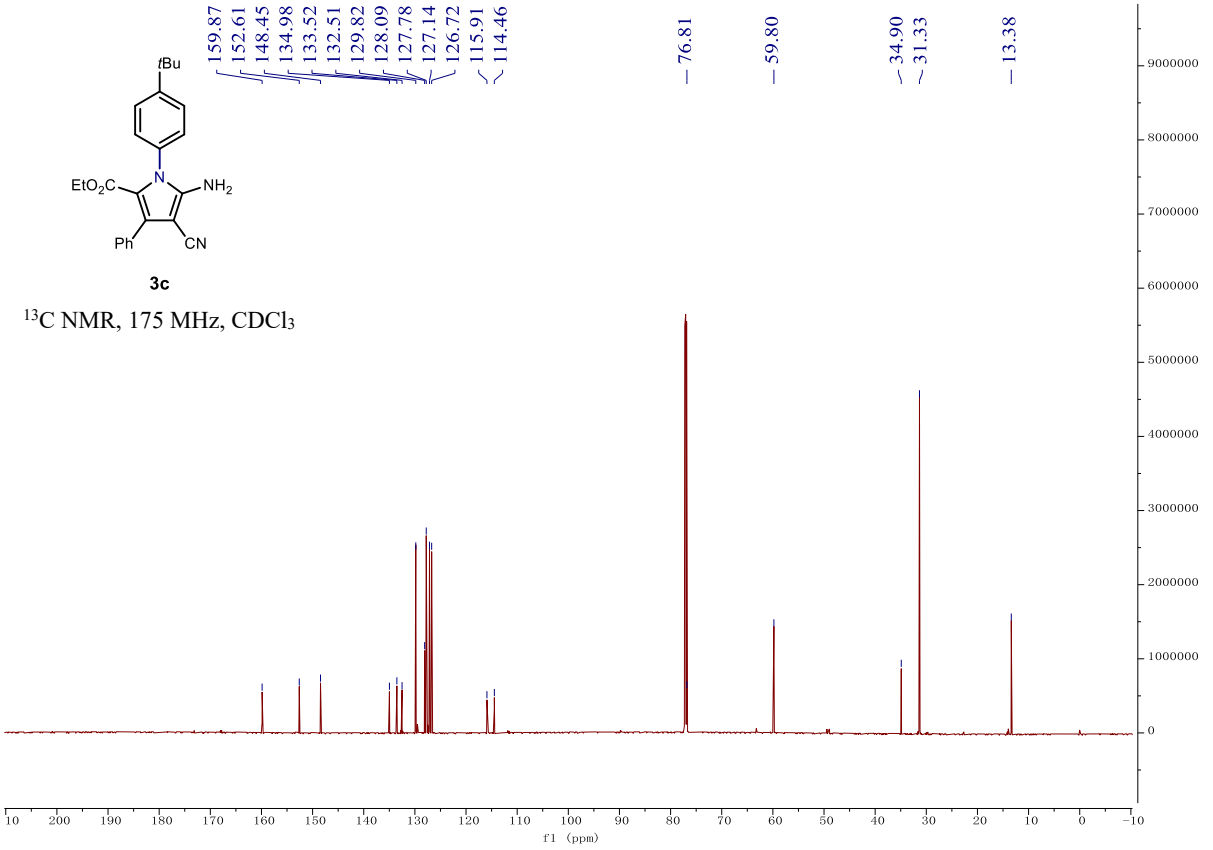
3b

^{13}C NMR, 150 MHz, $CDCl_3$



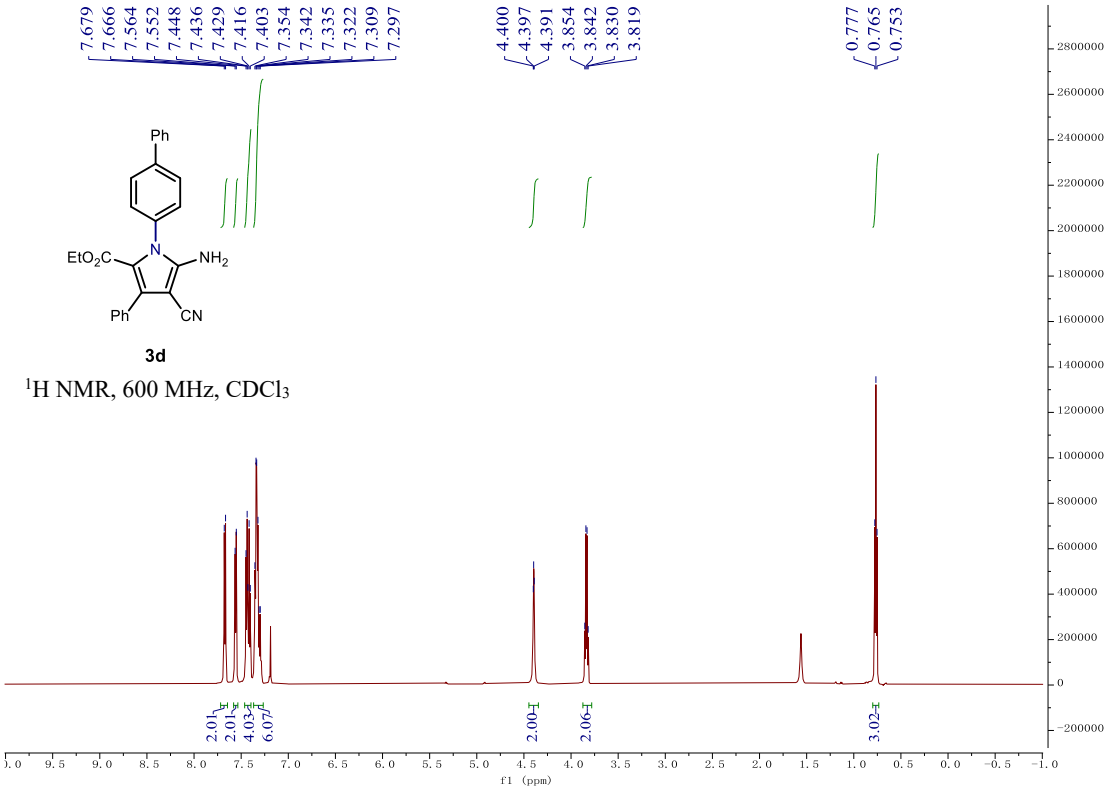
3c

^{1}H NMR, 700 MHz, $CDCl_3$



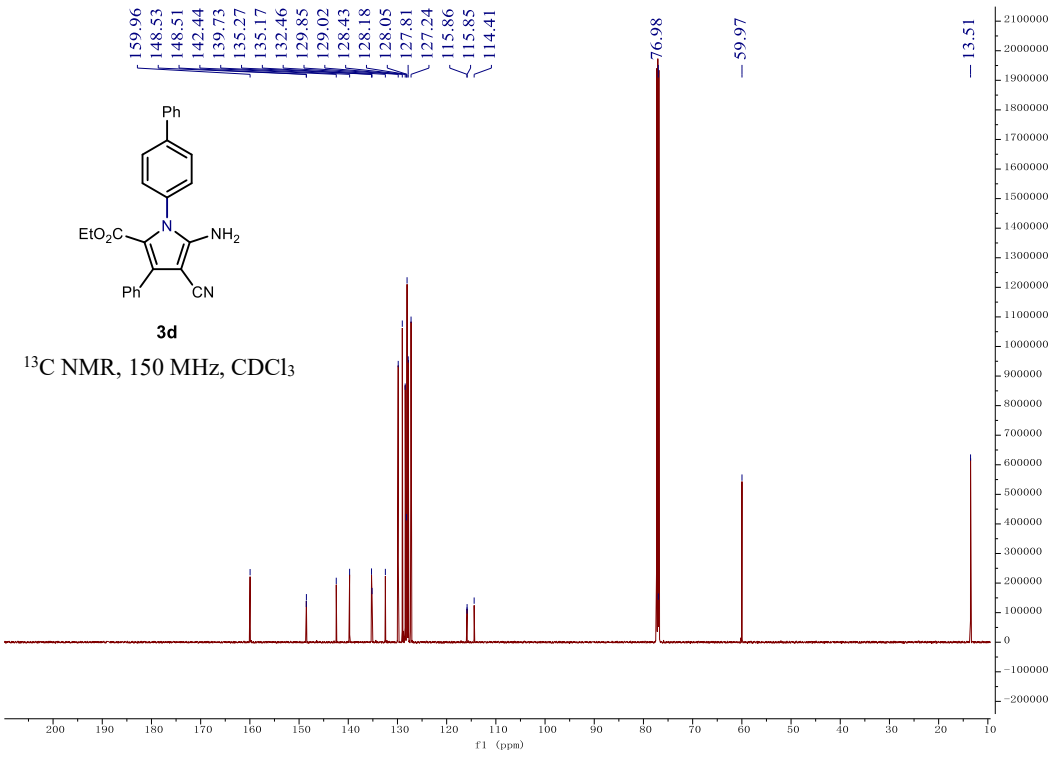
3c

^{13}C NMR, 175 MHz, $CDCl_3$



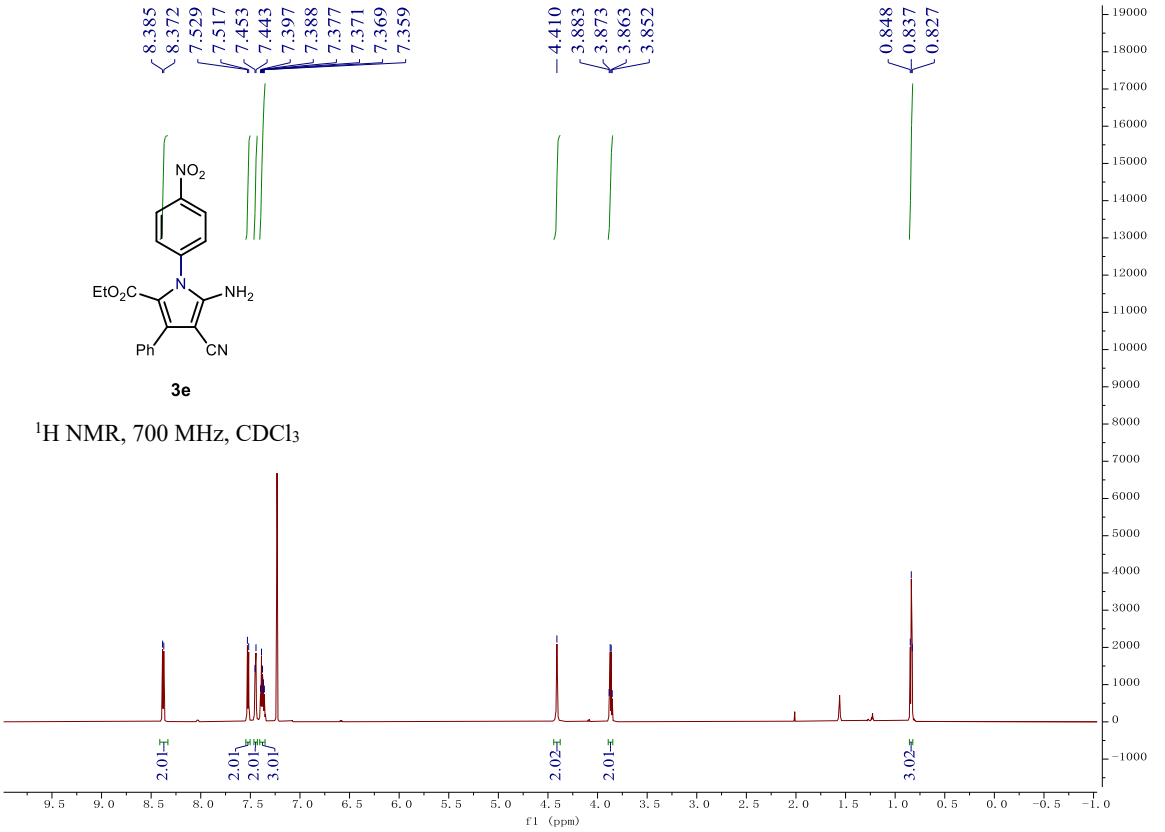
3d

^{1}H NMR, 600 MHz, $CDCl_3$



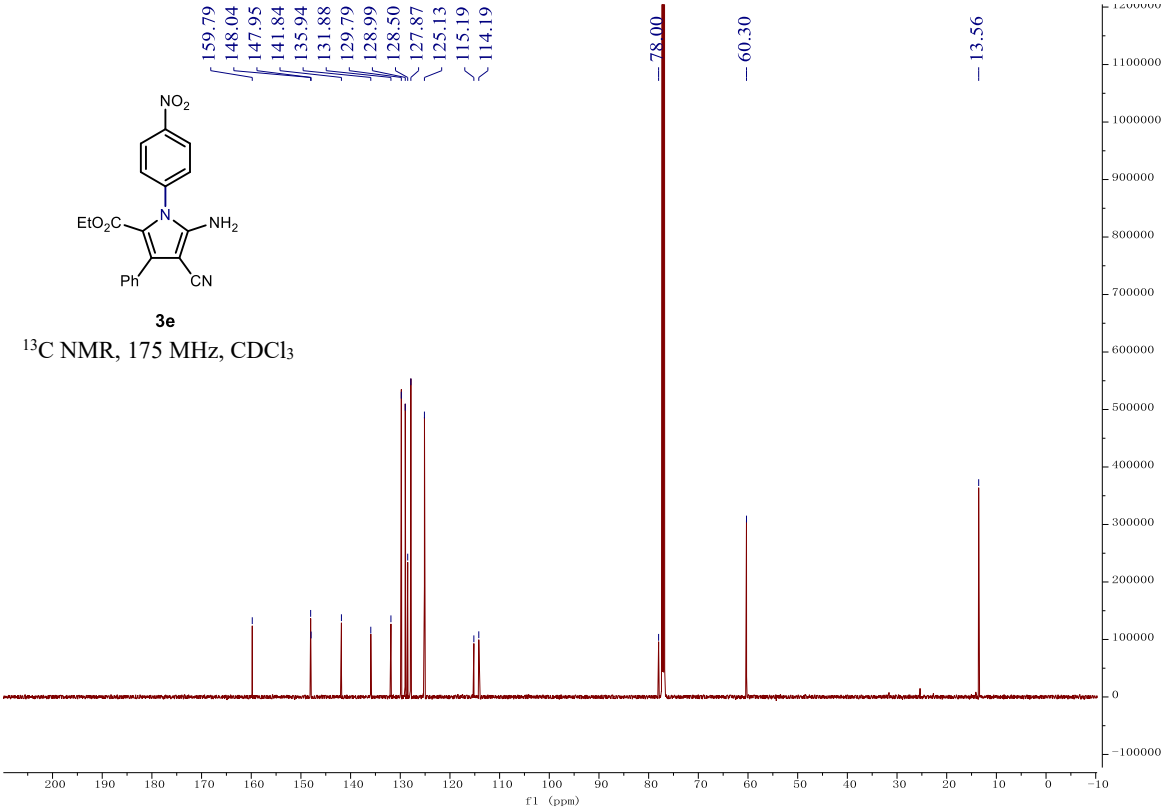
3d

^{13}C NMR, 150 MHz, $CDCl_3$



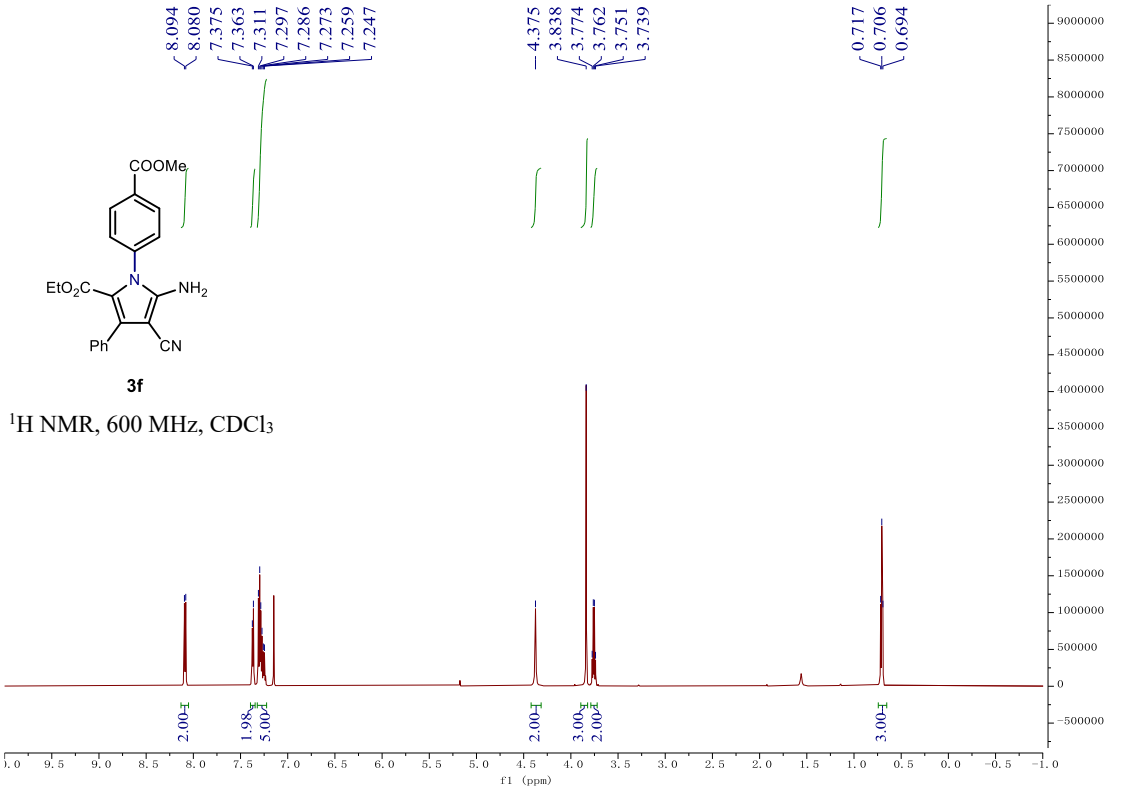
3e

^{1}H NMR, 700 MHz, $CDCl_3$



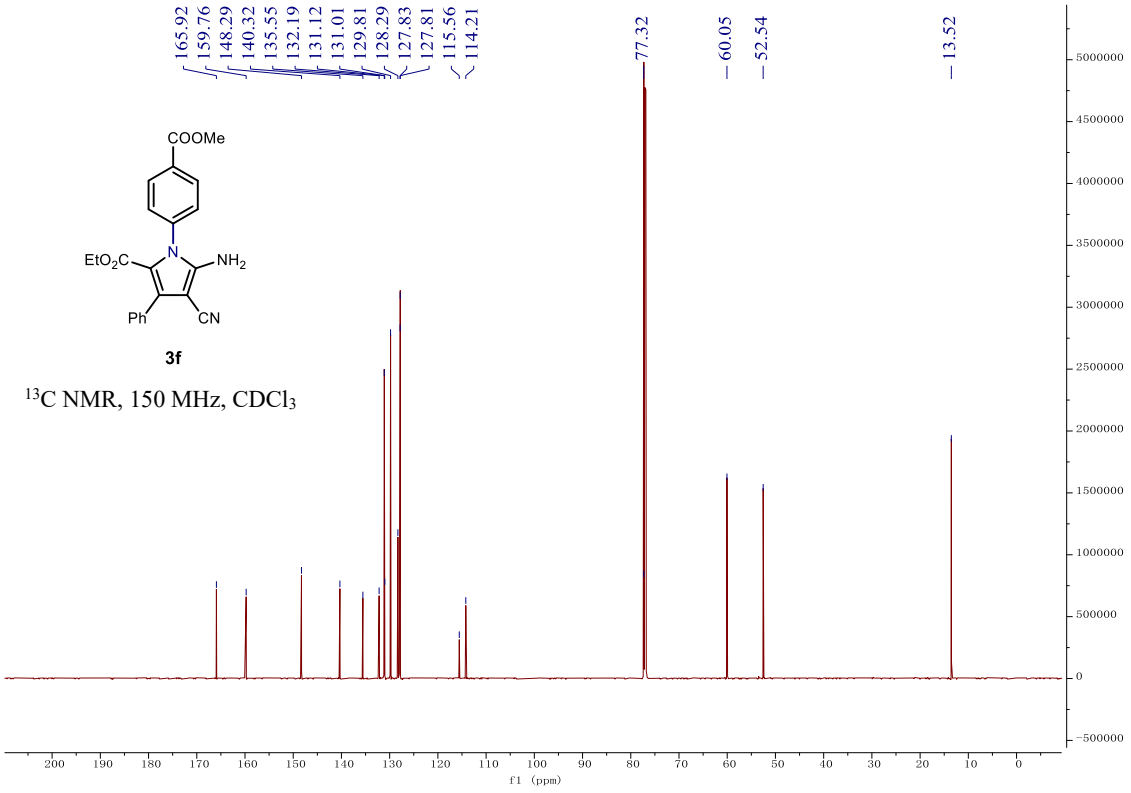
3e

^{13}C NMR, 175 MHz, $CDCl_3$



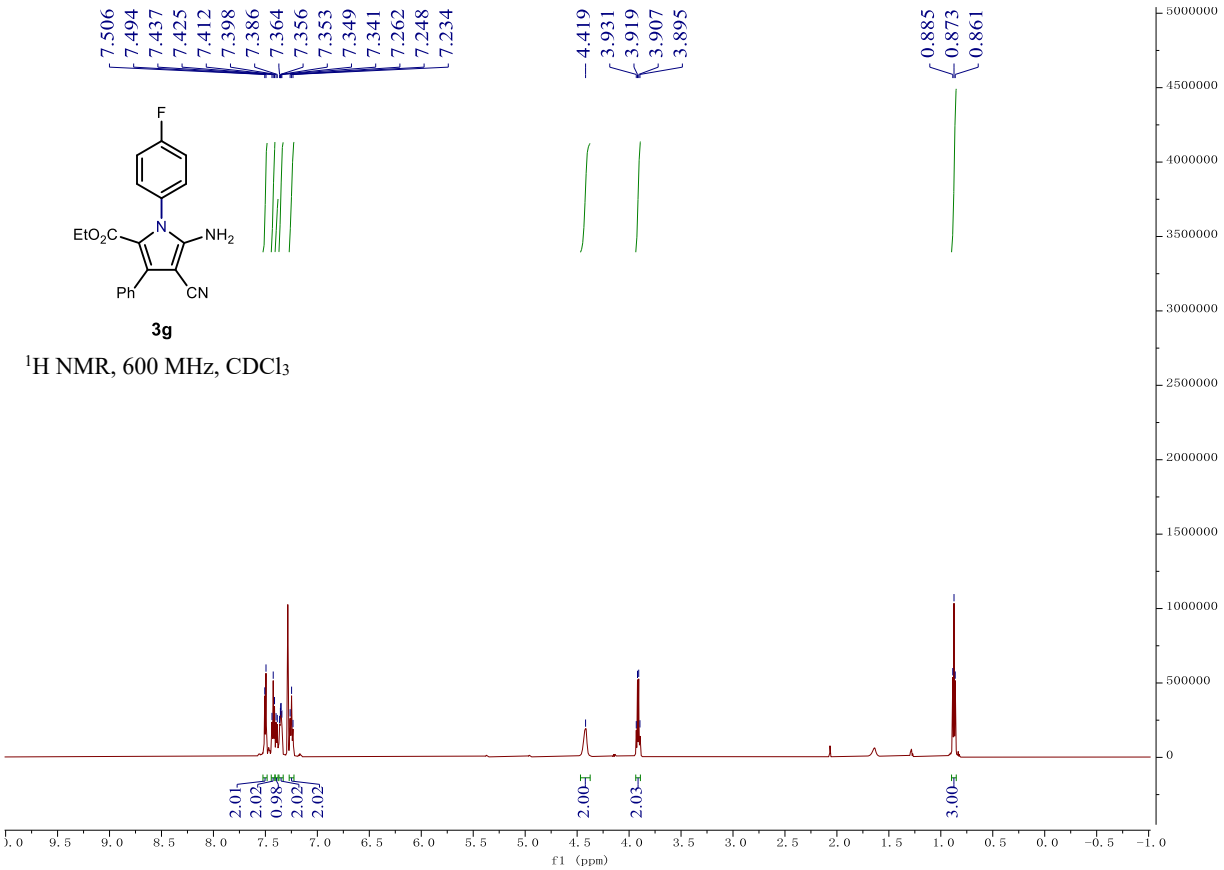
3f

^{1}H NMR, 600 MHz, $CDCl_3$



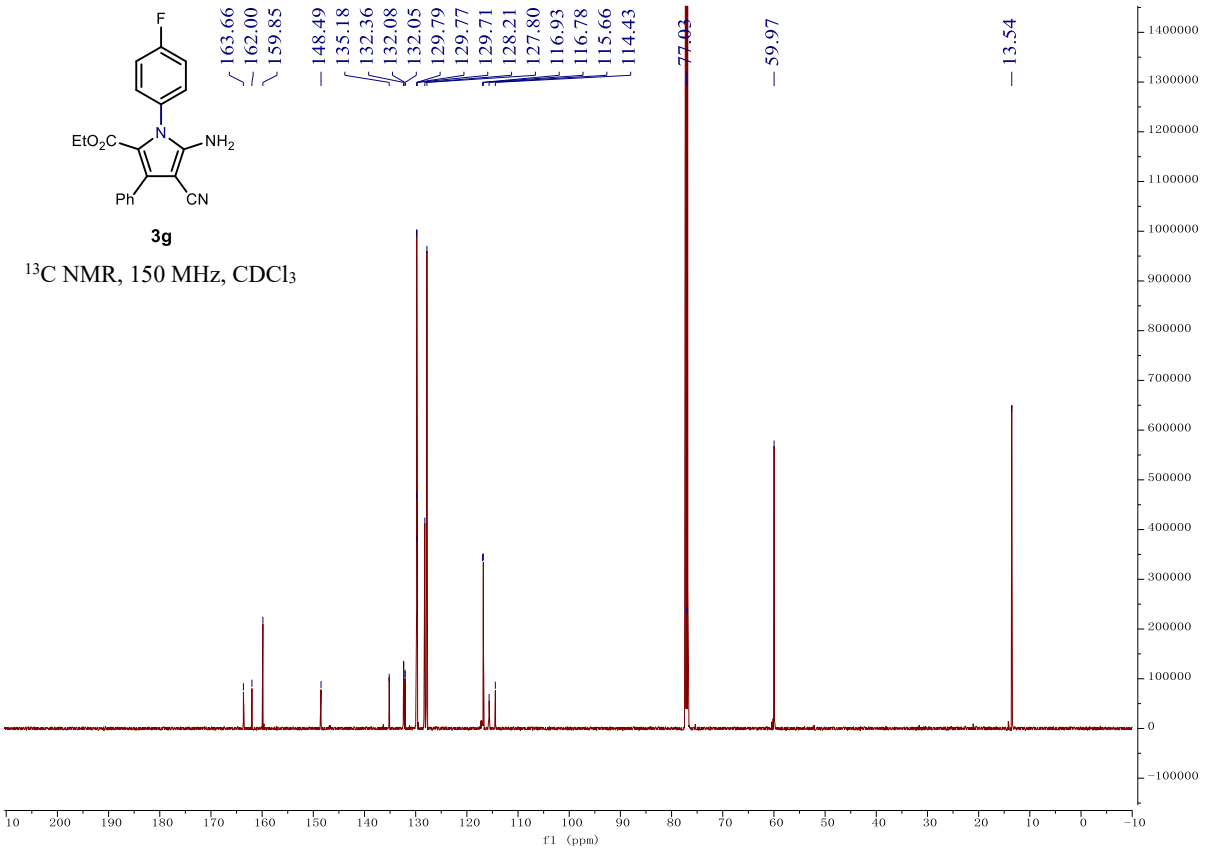
3f

^{13}C NMR, 150 MHz, $CDCl_3$



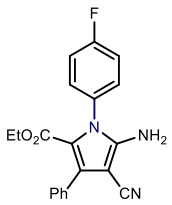
3g

^{1}H NMR, 600 MHz, $CDCl_3$



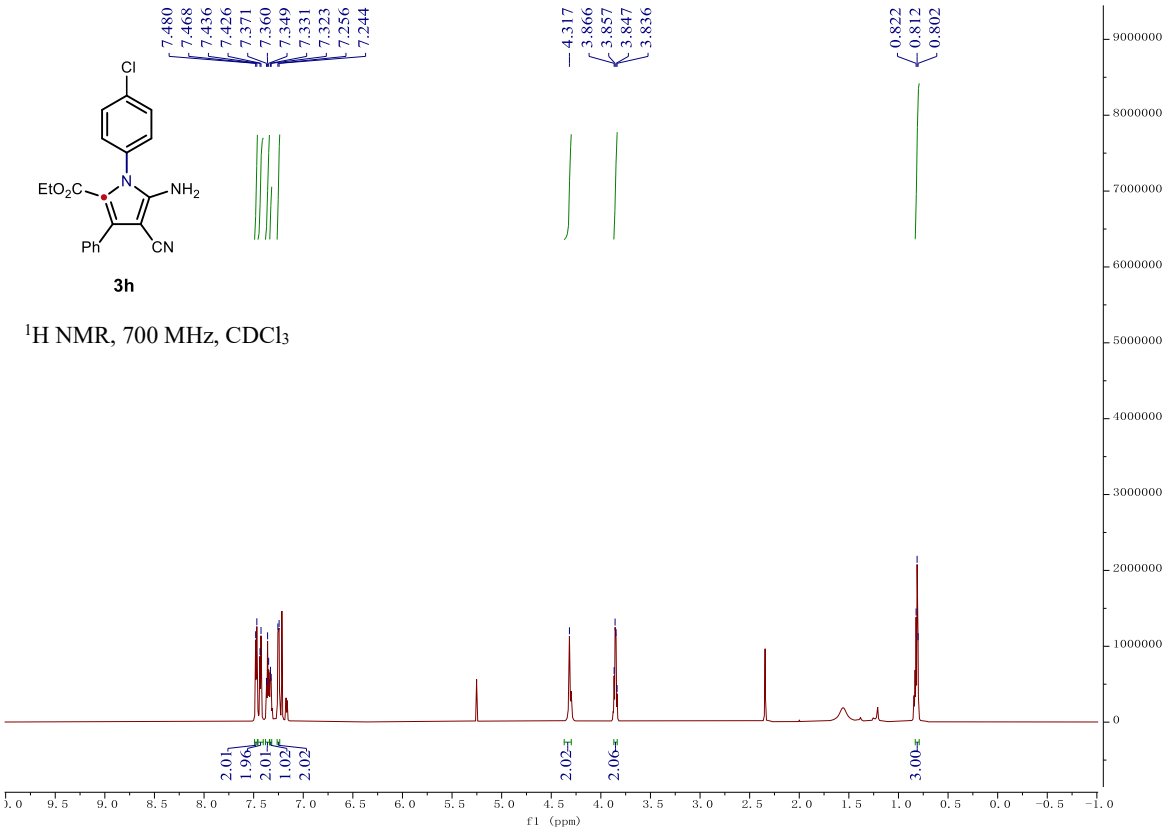
3g

^{13}C NMR, 150 MHz, $CDCl_3$



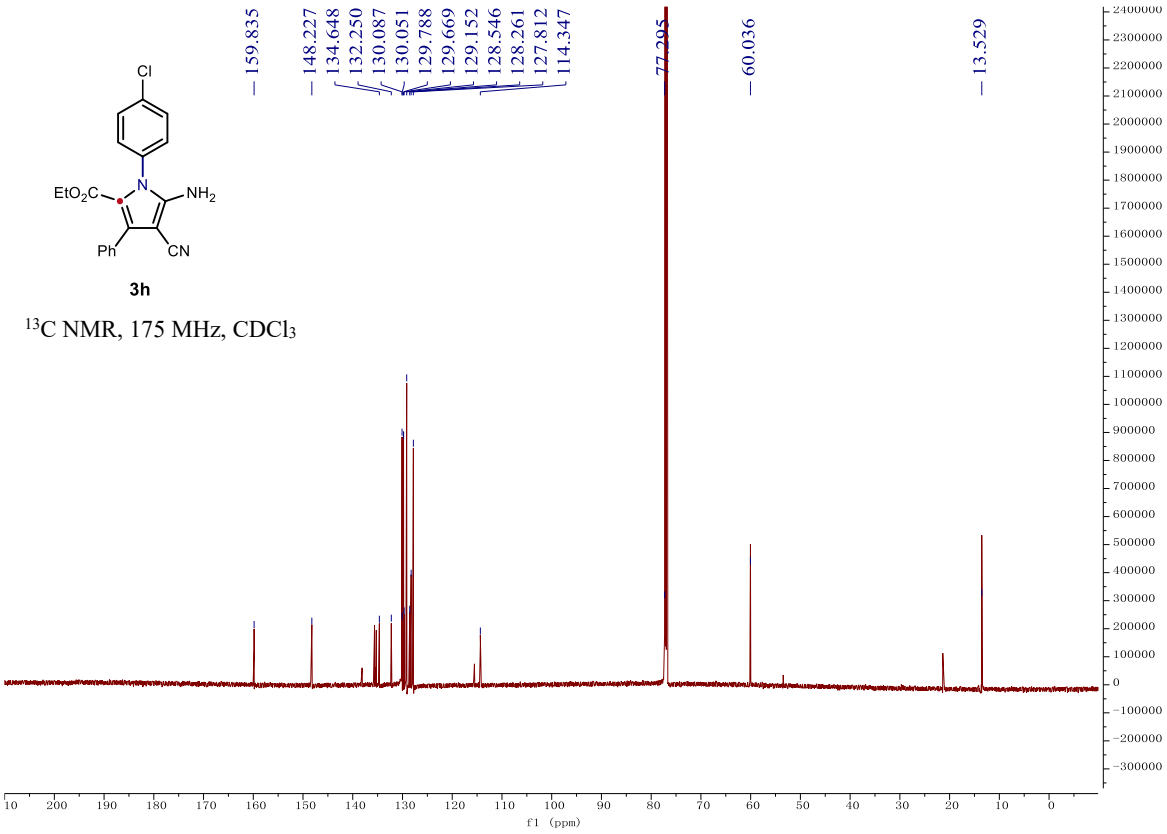
3g

^{19}F NMR, 600 MHz, $CDCl_3$



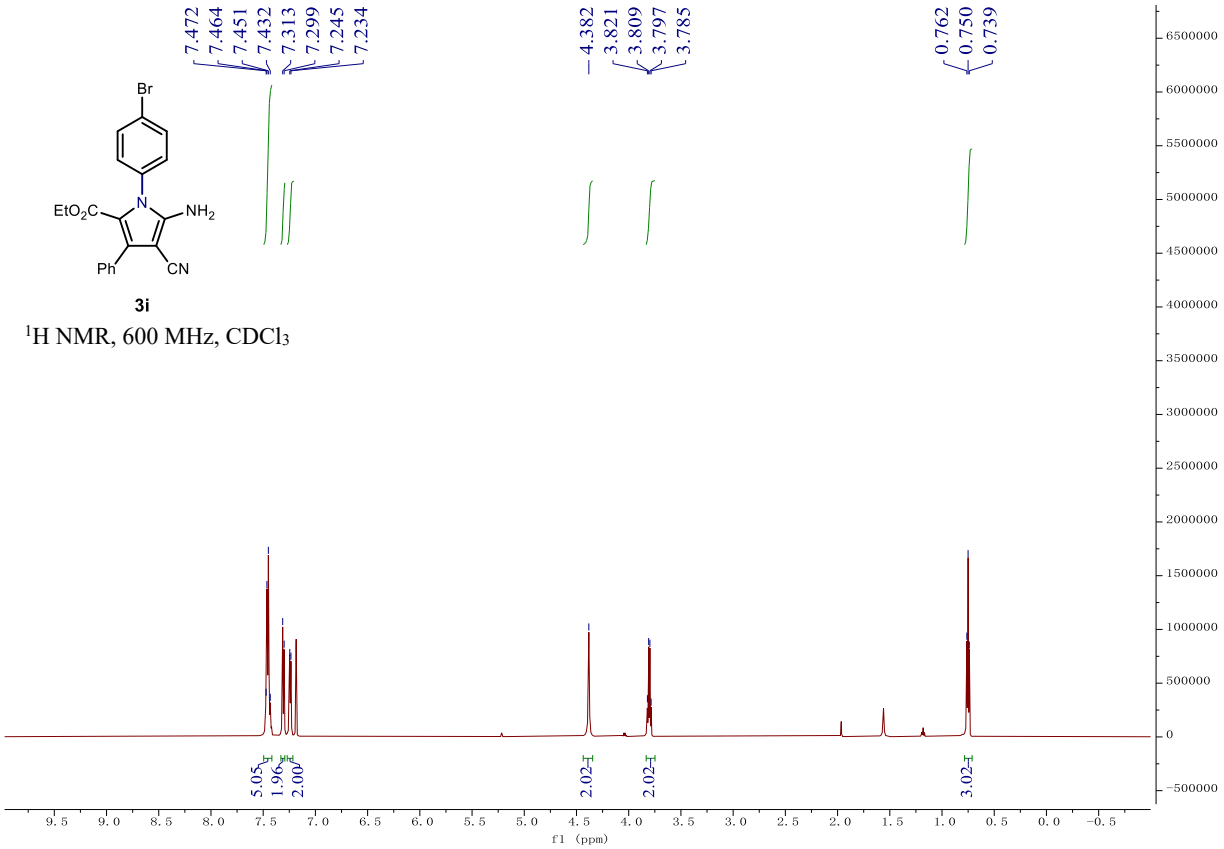
3h

^{1}H NMR, 700 MHz, $CDCl_3$



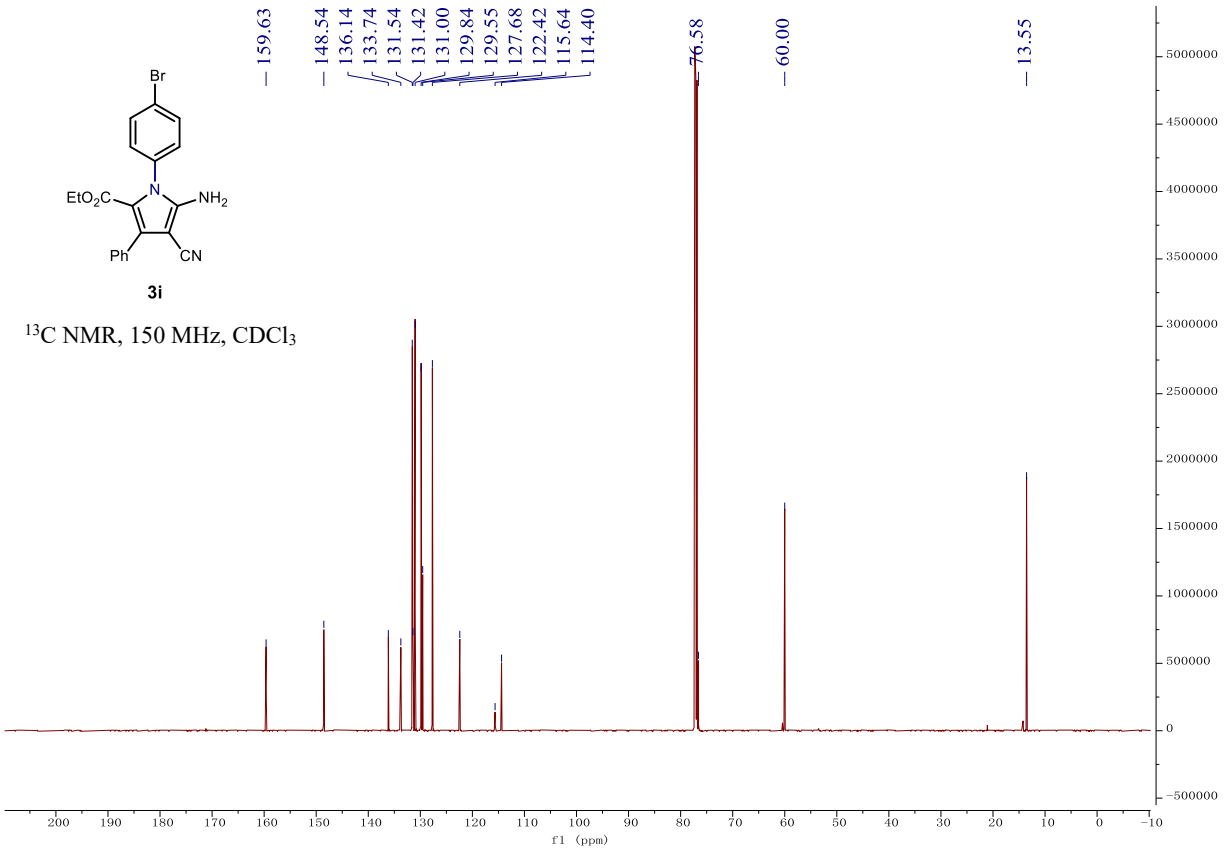
3h

^{13}C NMR, 175 MHz, $CDCl_3$



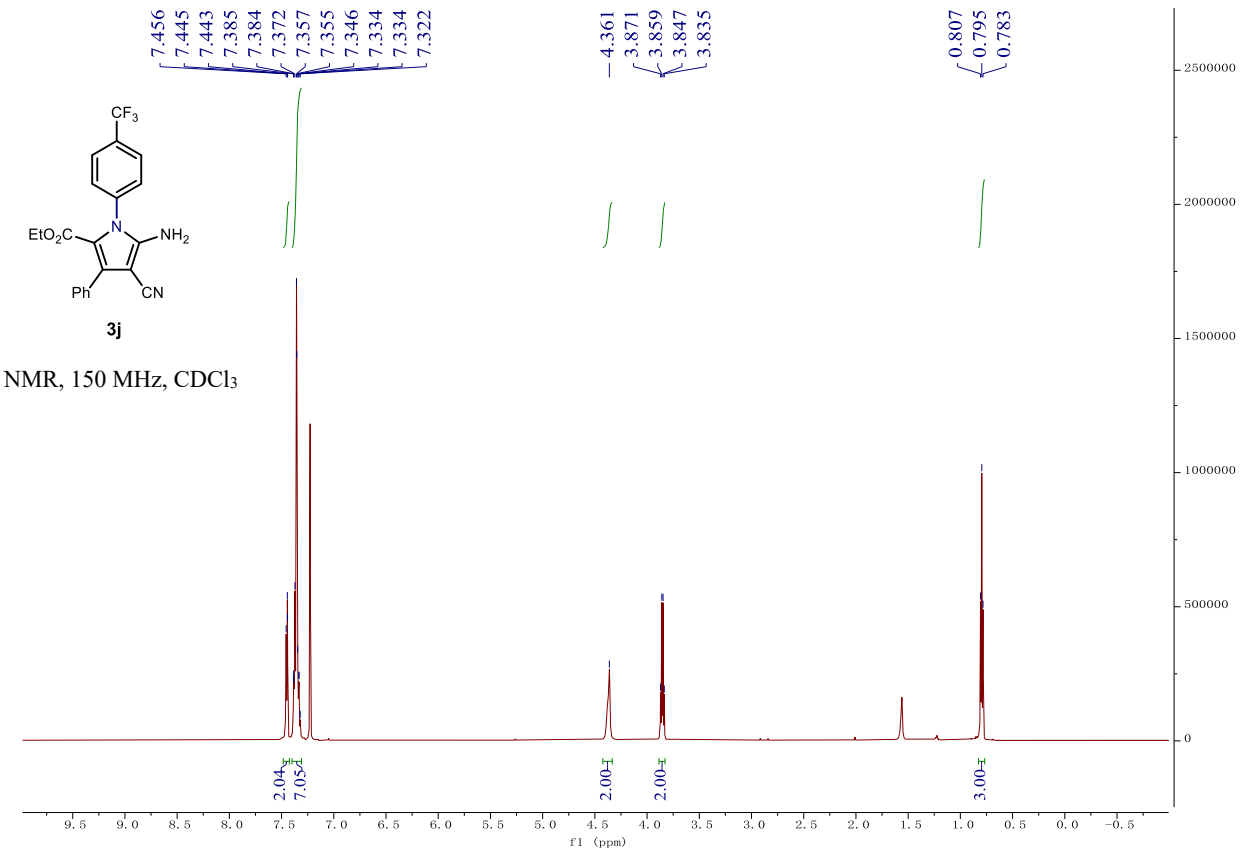
3i

^{1}H NMR, 600 MHz, $CDCl_3$



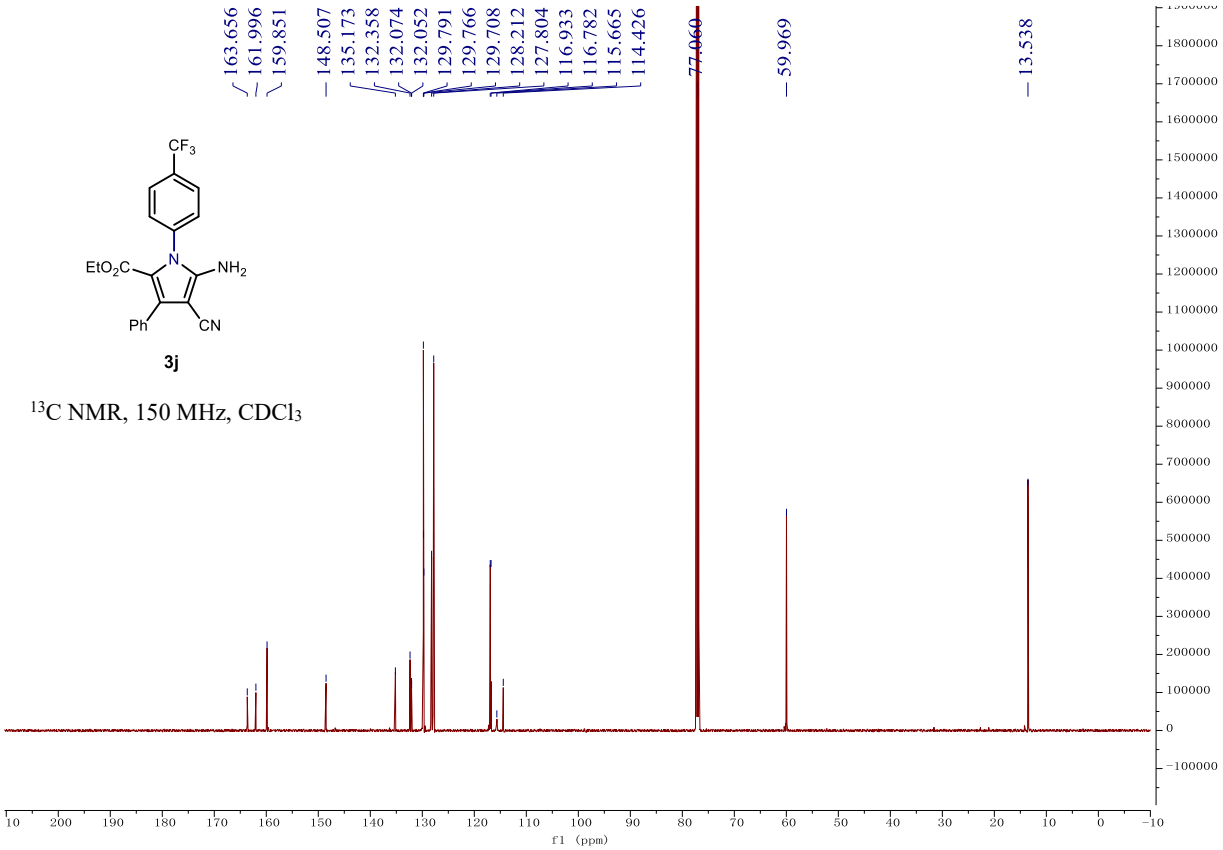
3i

^{13}C NMR, 150 MHz, $CDCl_3$



3j

^{1}H NMR, 150 MHz, $CDCl_3$



3j

^{13}C NMR, 150 MHz, $CDCl_3$

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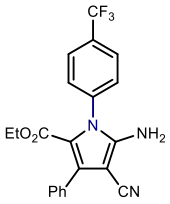
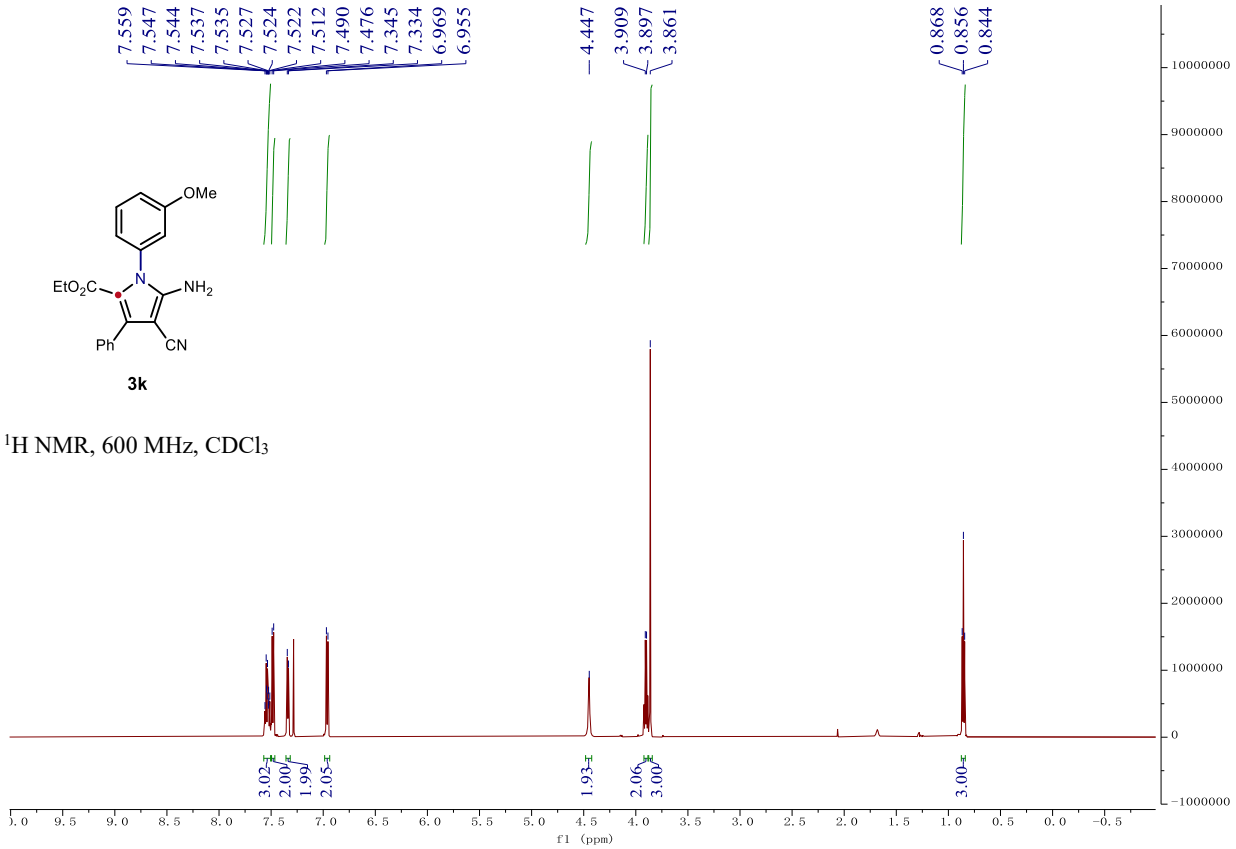
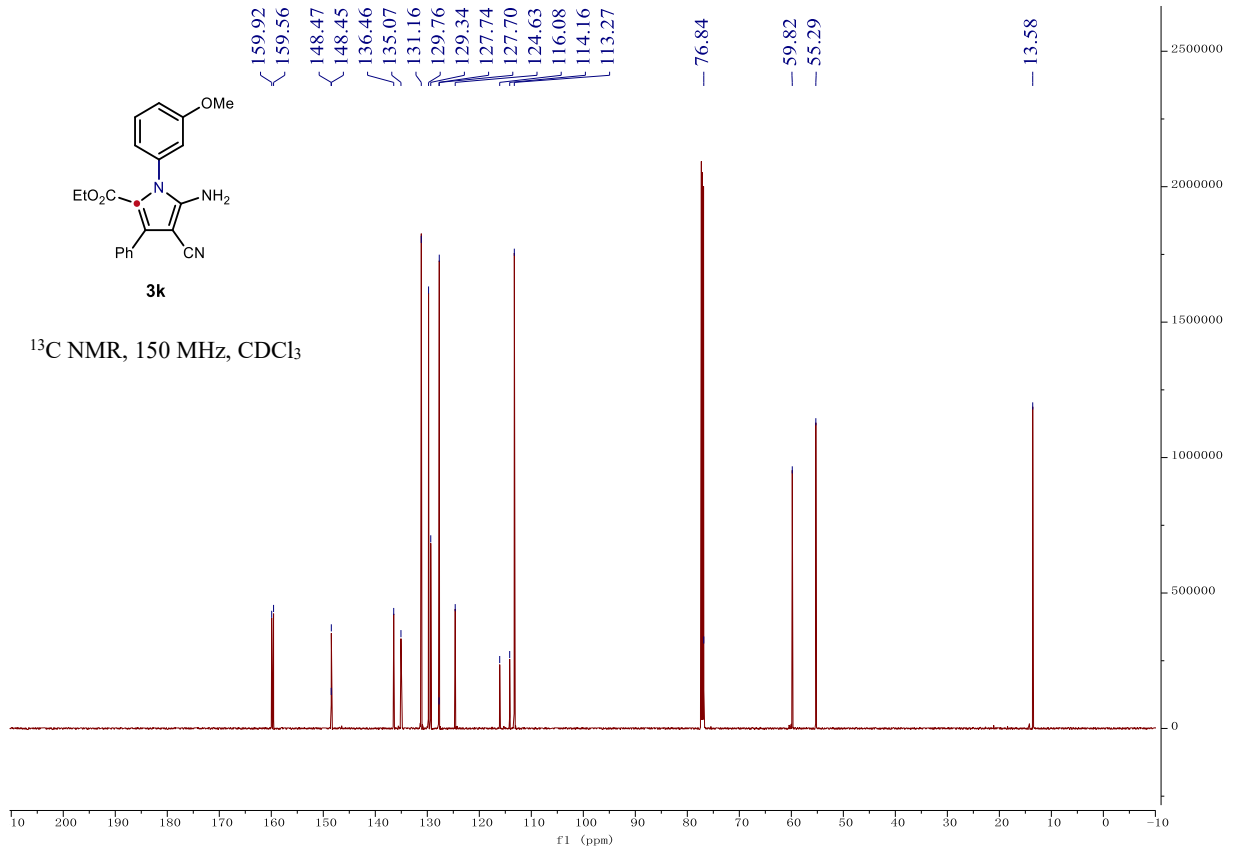


3j

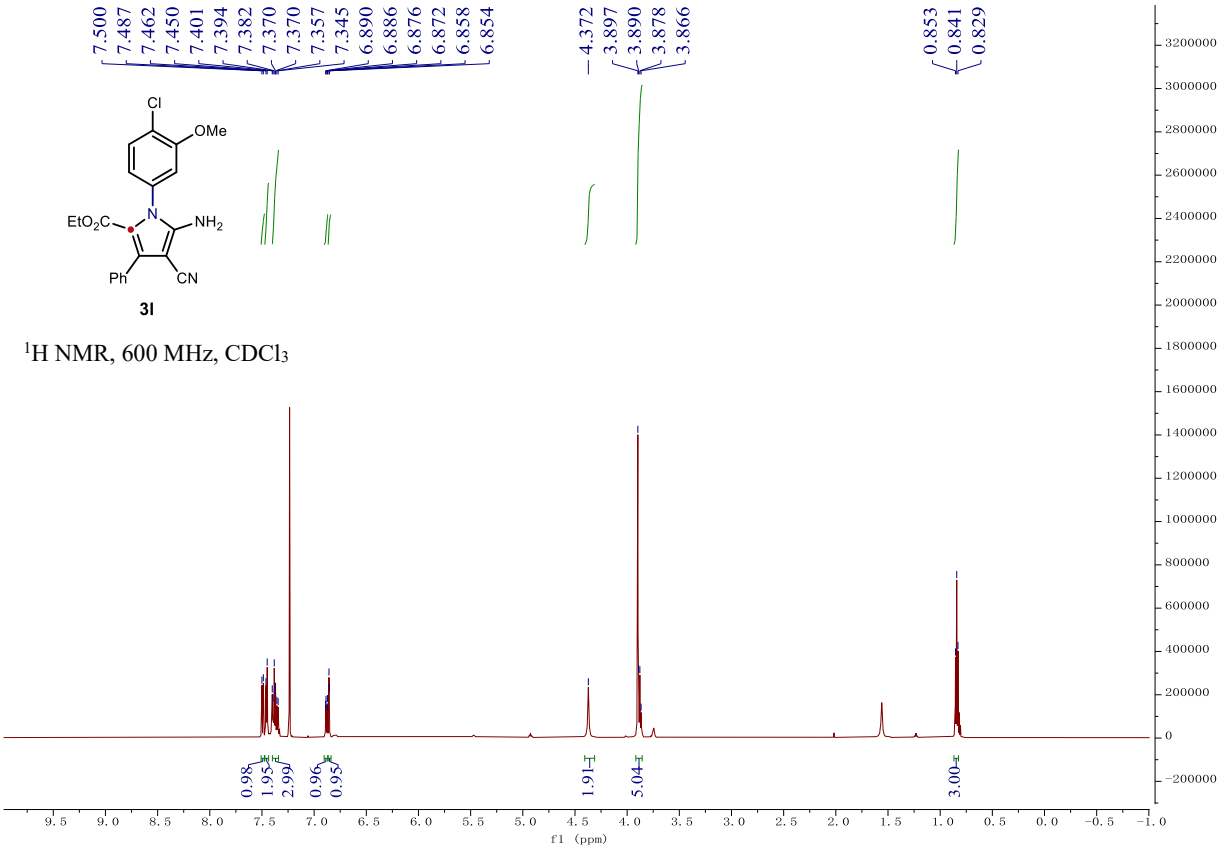
^{19}F NMR, 564 MHz, $CDCl_3$



^{1}H NMR, 600 MHz, $CDCl_3$

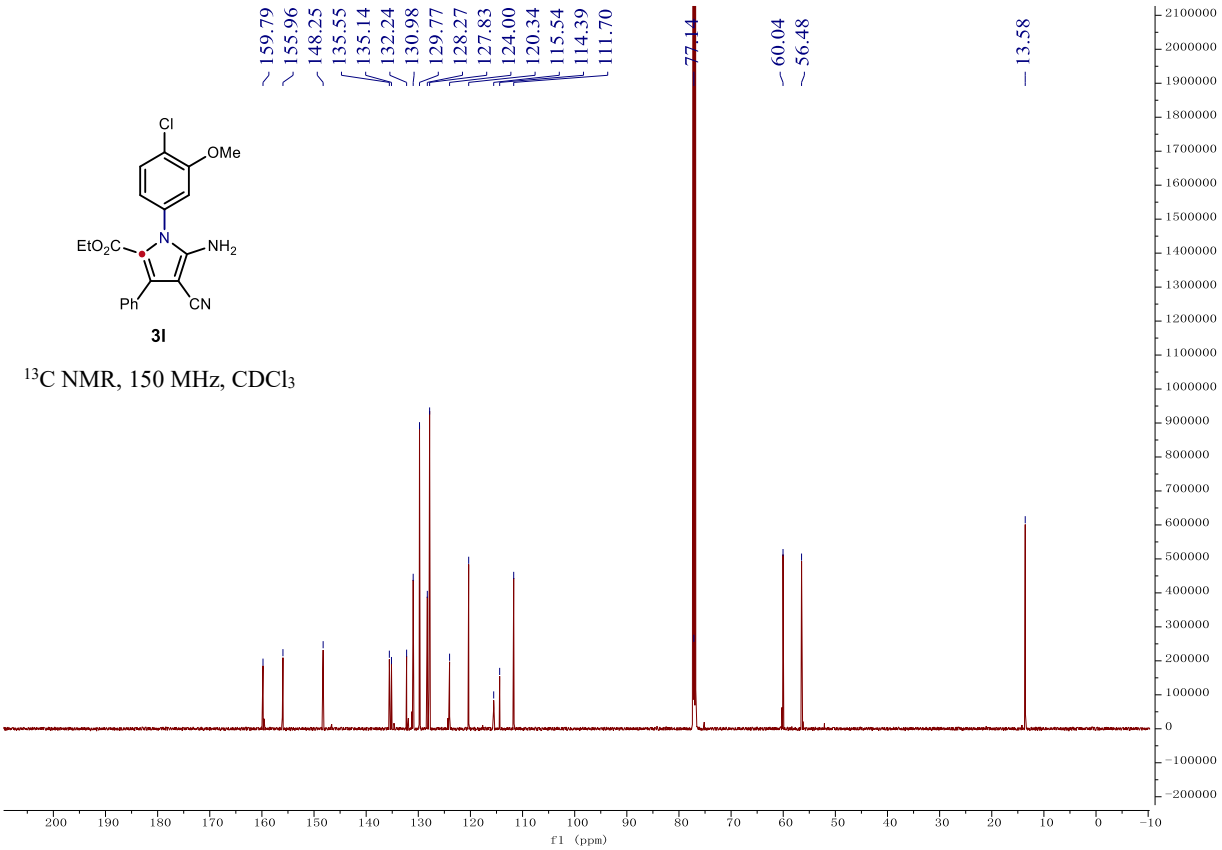


^{13}C NMR, 150 MHz, $CDCl_3$



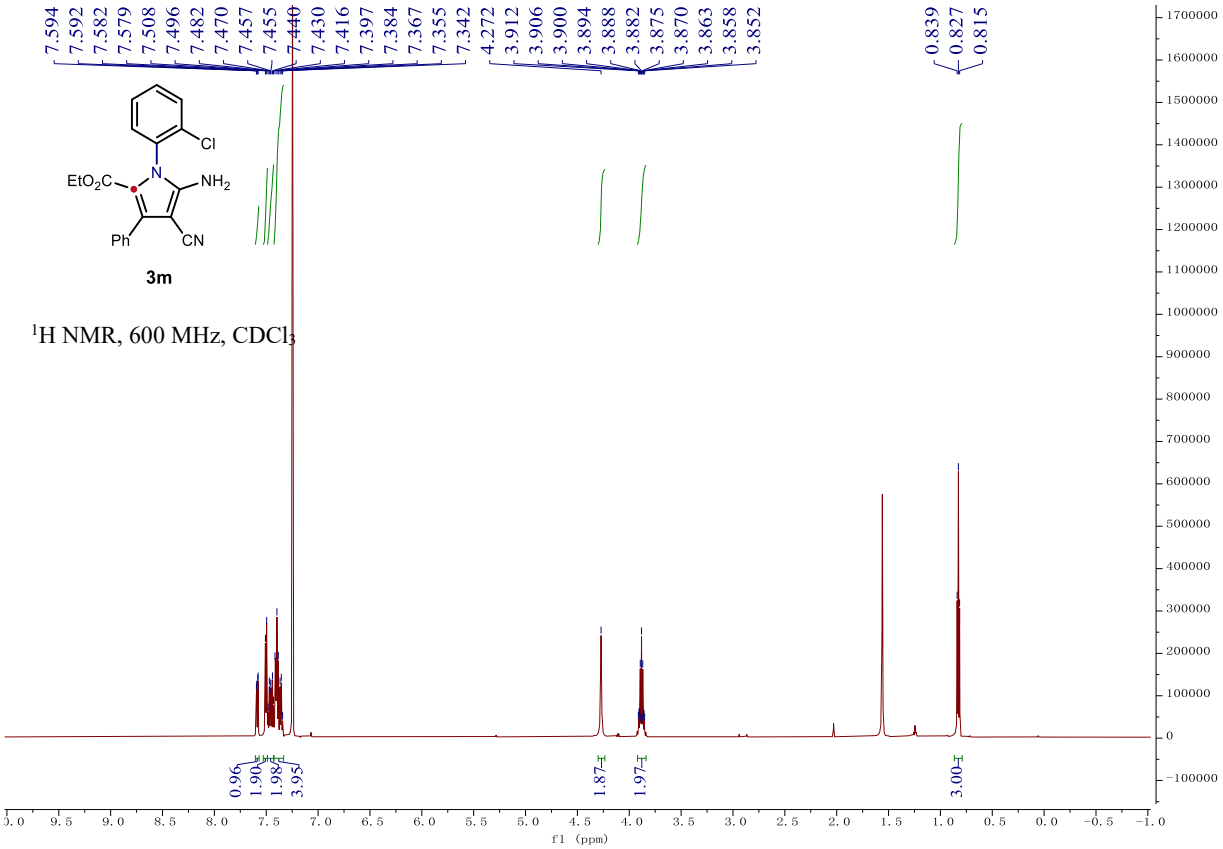
3l

^{1}H NMR, 600 MHz, $CDCl_3$



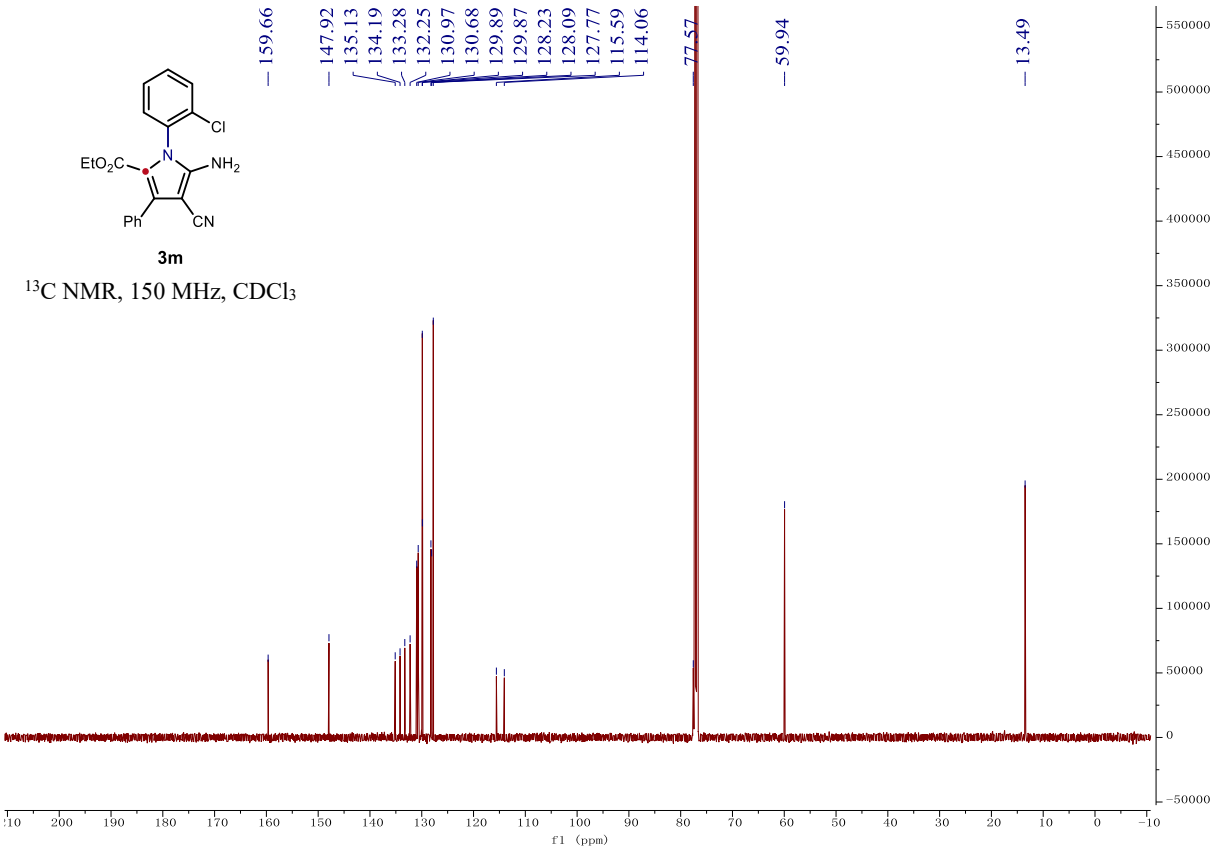
3l

^{13}C NMR, 150 MHz, $CDCl_3$



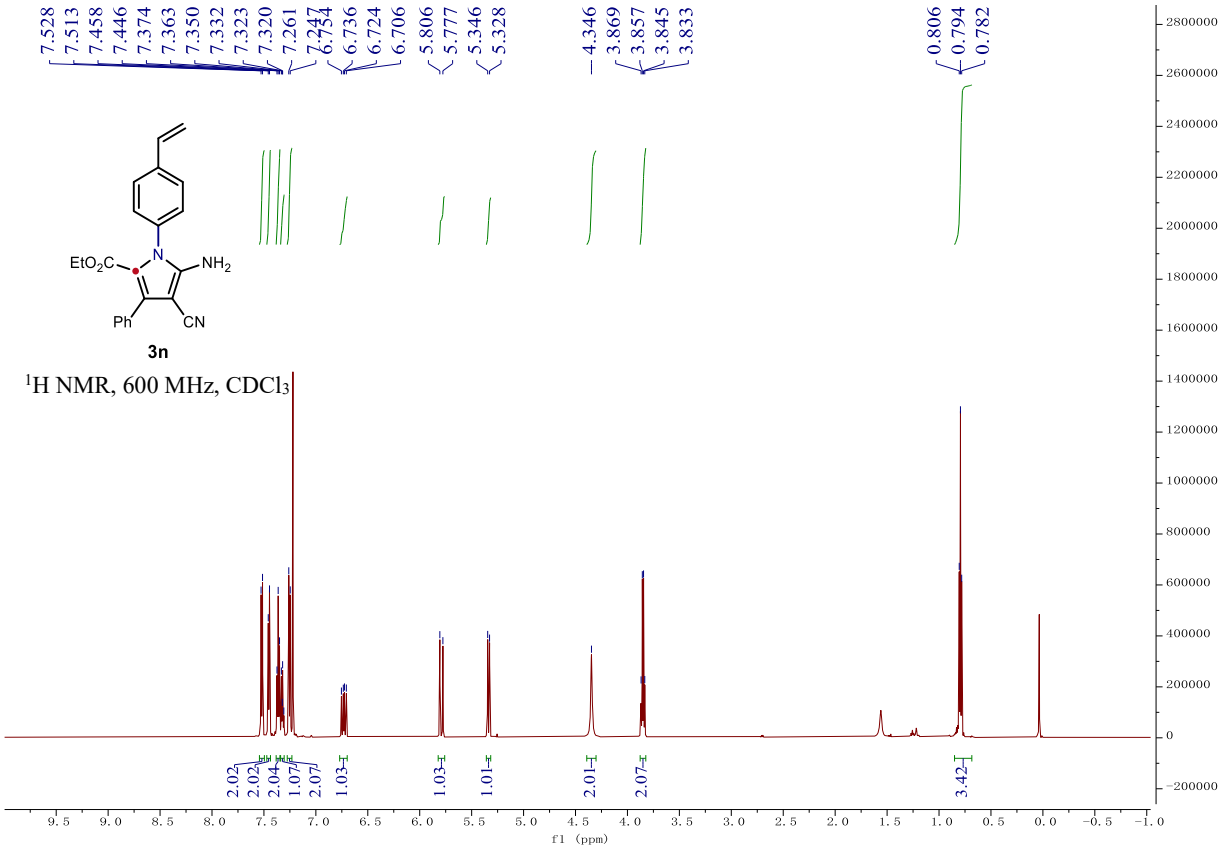
3m

^{1}H NMR, 600 MHz, $CDCl_3$



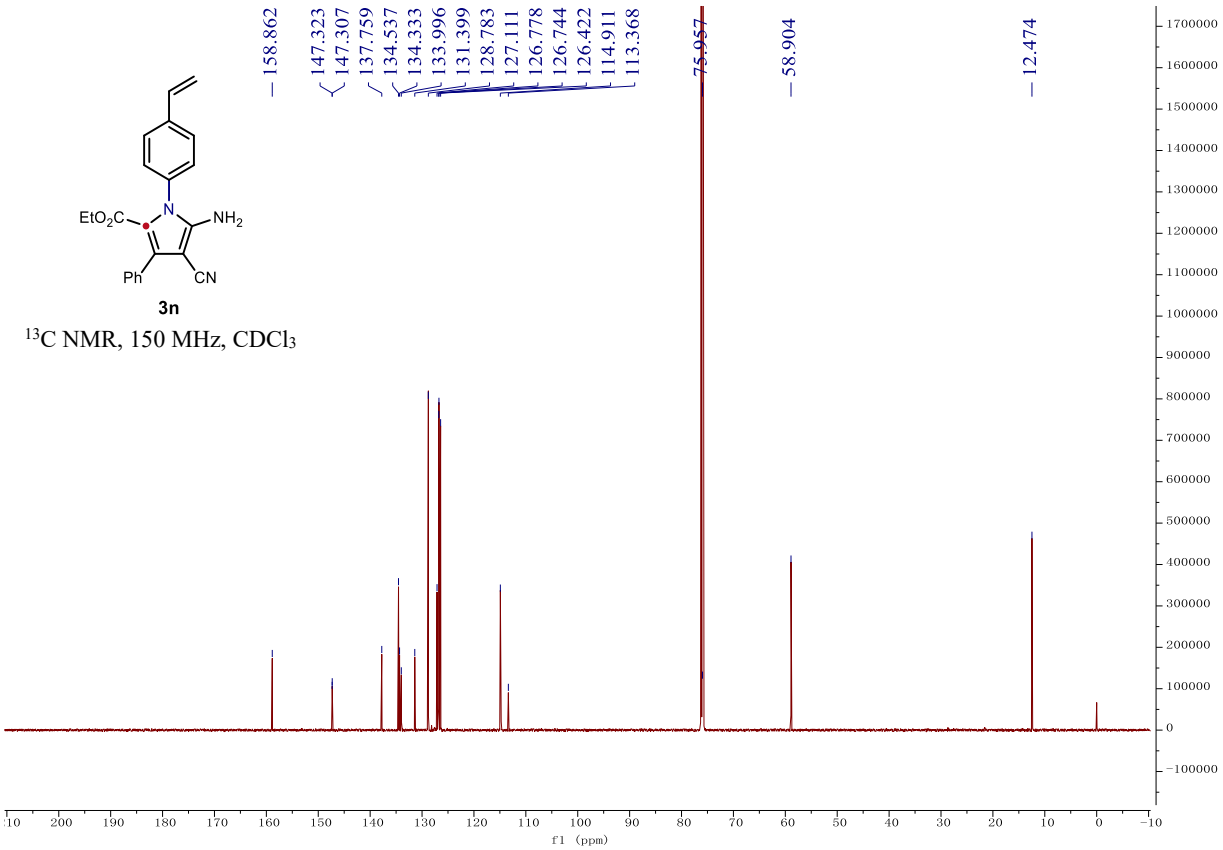
3m

^{13}C NMR, 150 MHz, $CDCl_3$



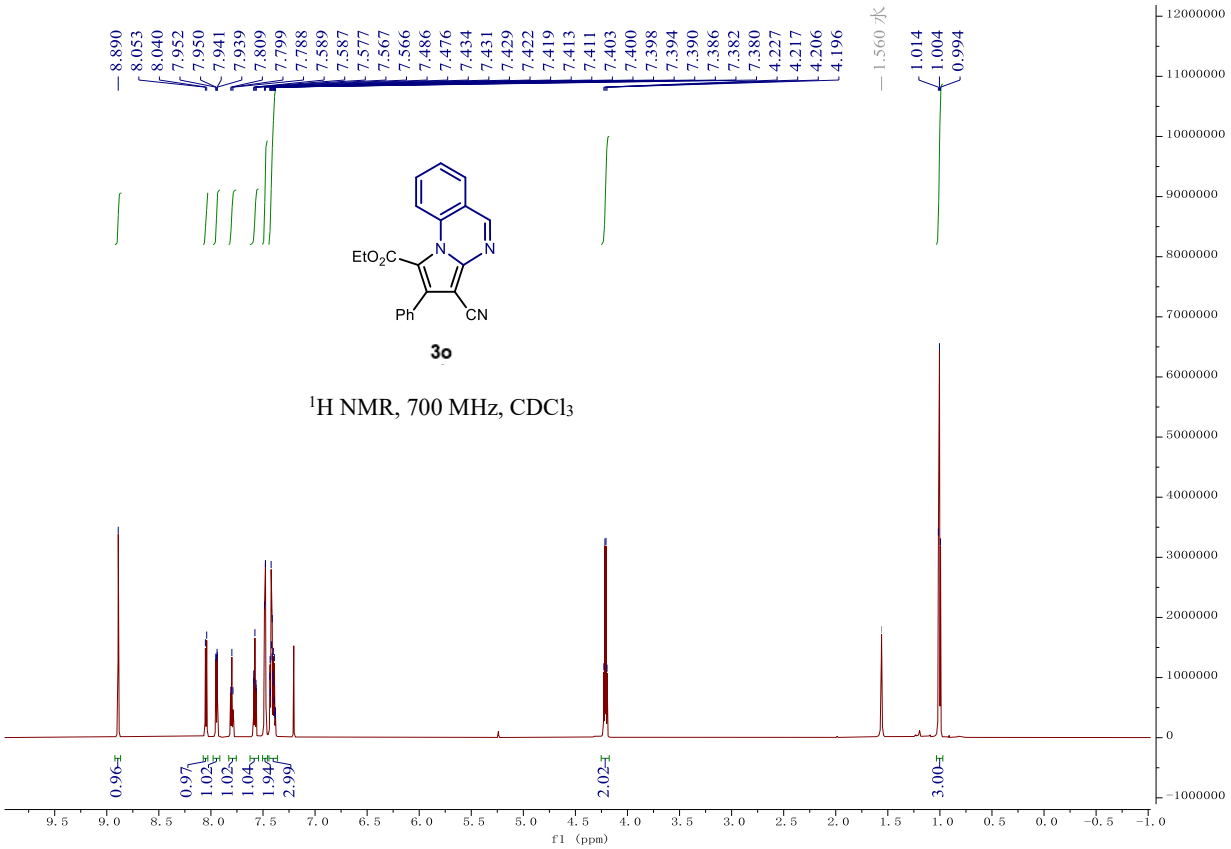
3n

^{1}H NMR, 600 MHz, $CDCl_3$



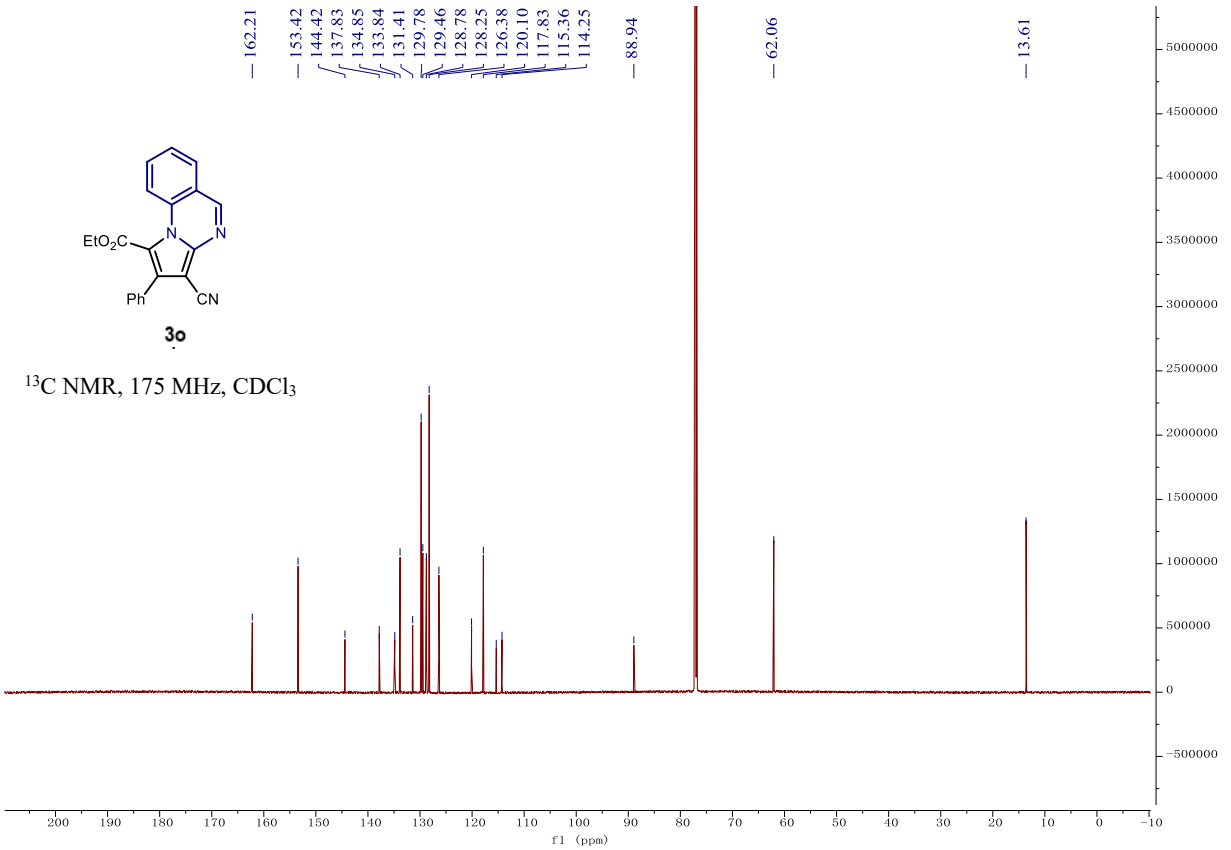
3n

^{13}C NMR, 150 MHz, $CDCl_3$



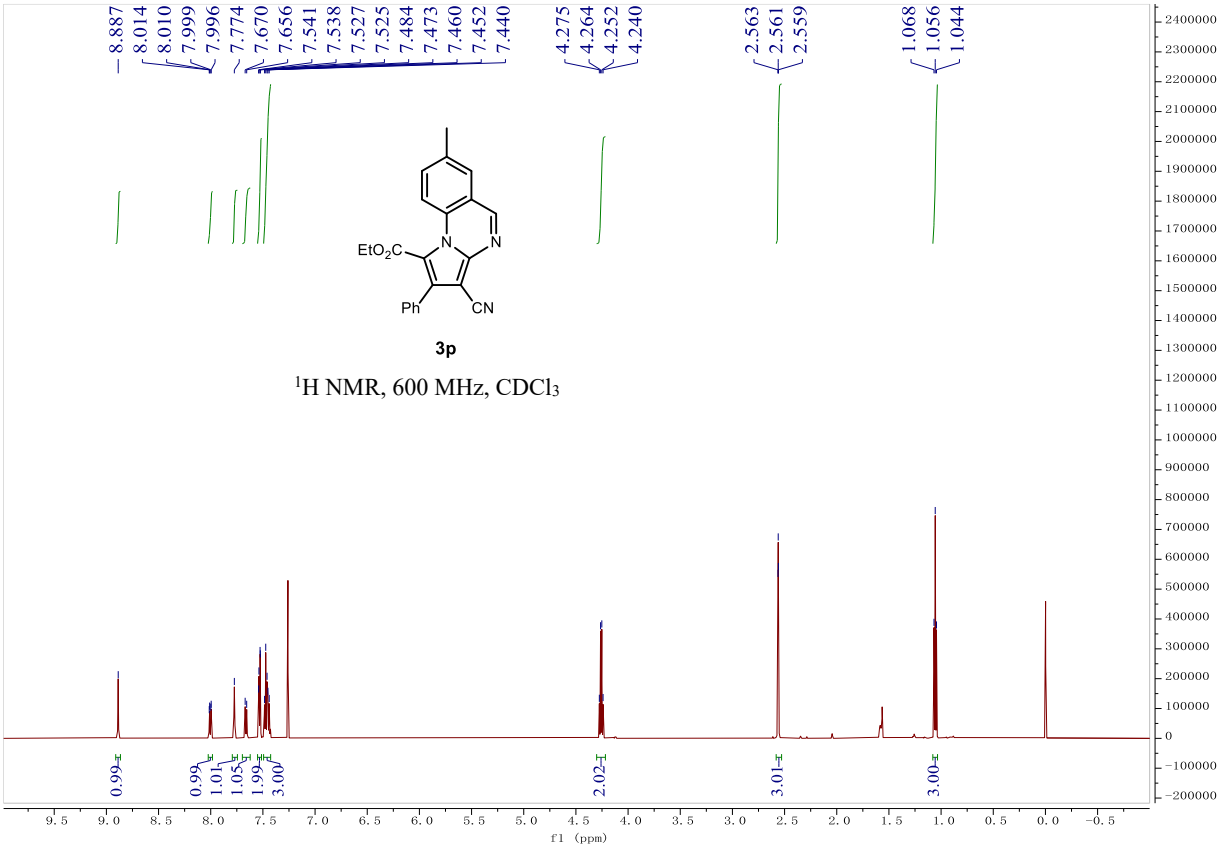
3o

^{1}H NMR, 700 MHz, $CDCl_3$



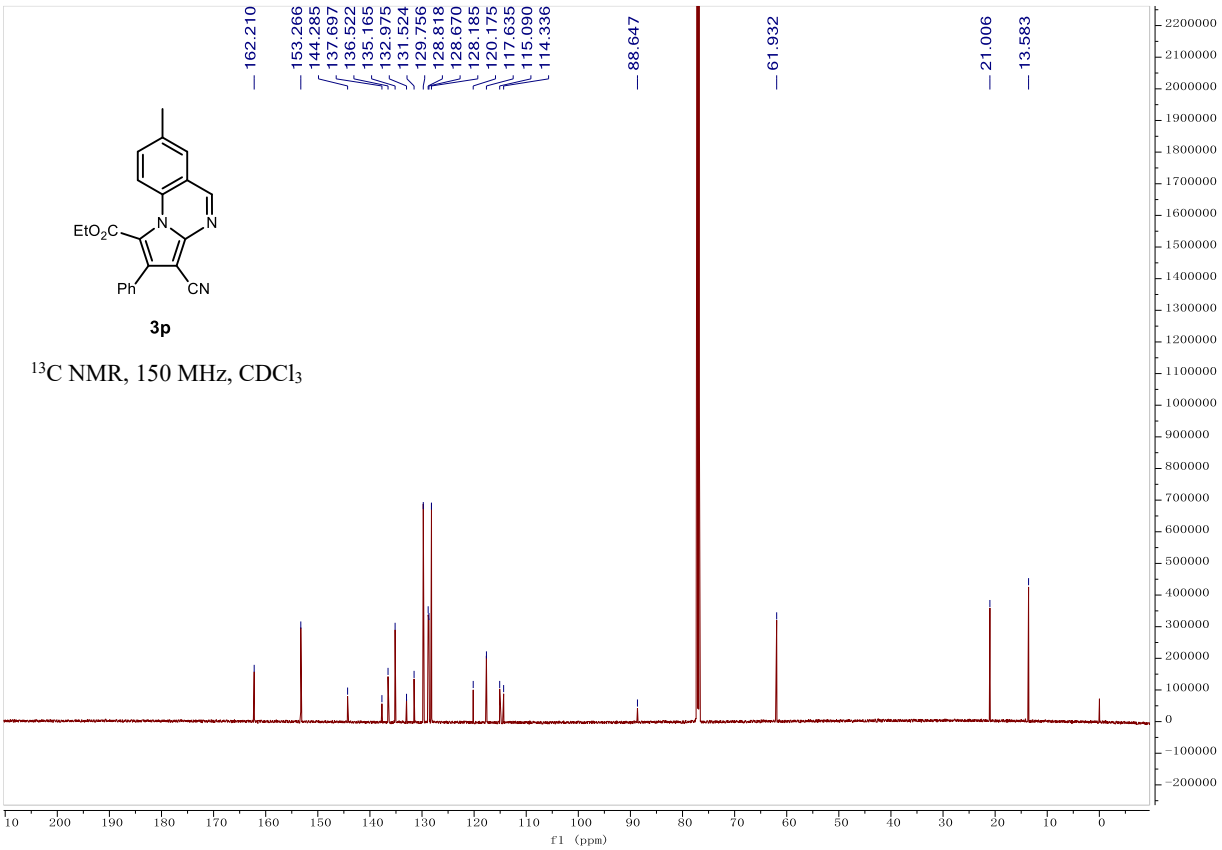
3o

^{13}C NMR, 175 MHz, $CDCl_3$



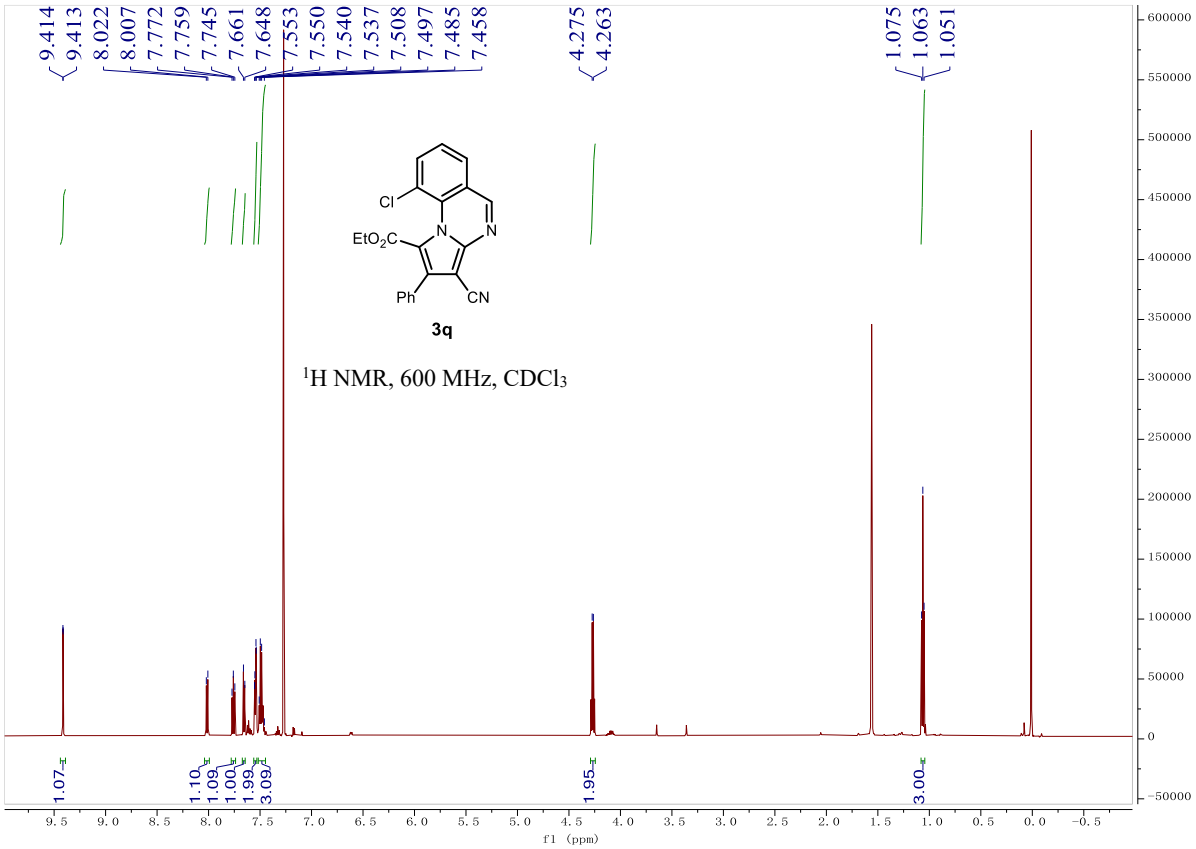
3p

^{1}H NMR, 600 MHz, $CDCl_3$



3p

^{13}C NMR, 150 MHz, $CDCl_3$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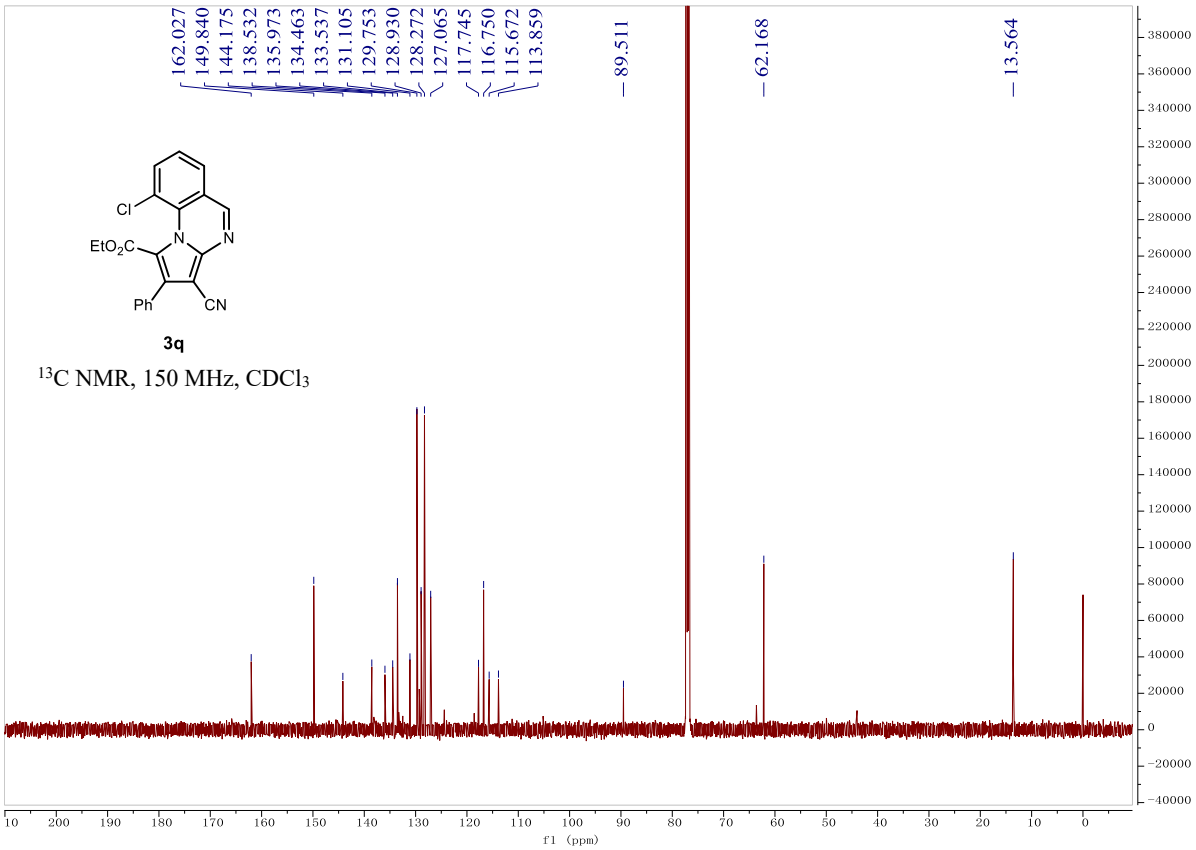
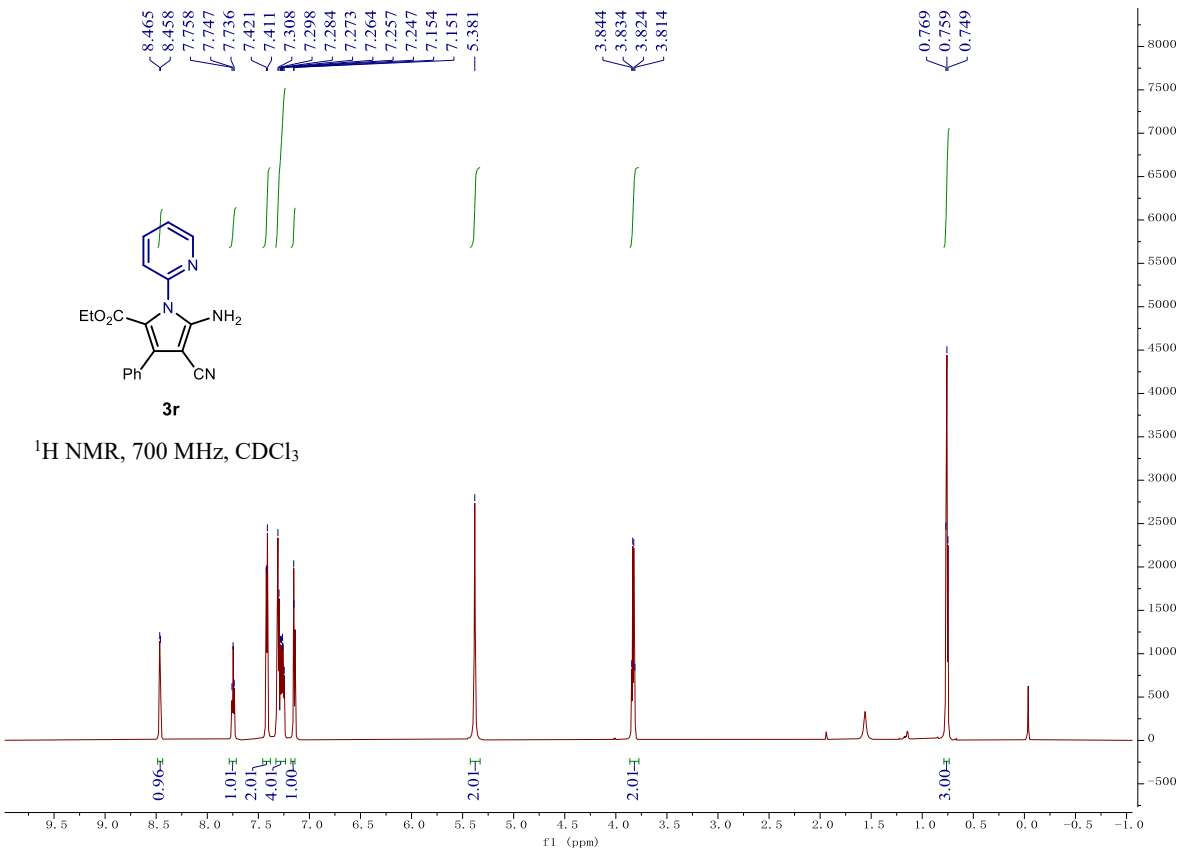
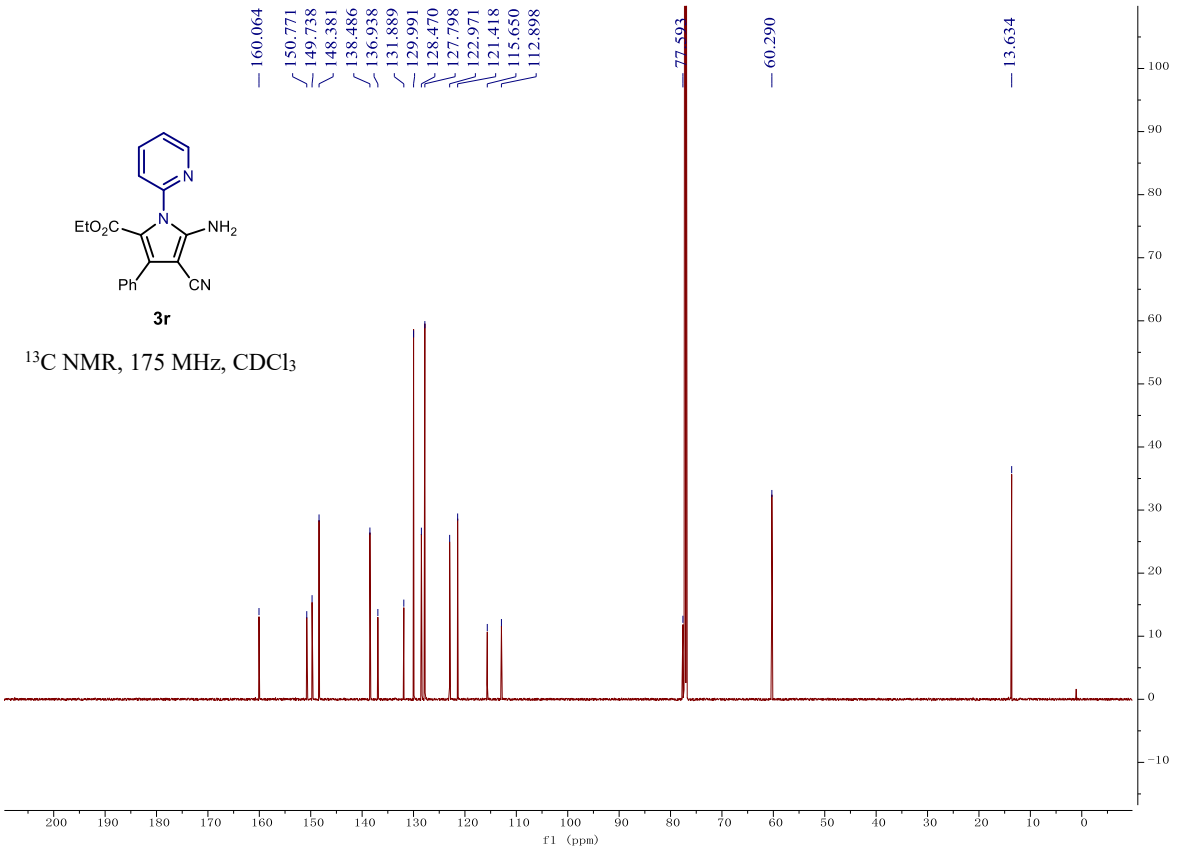
9.413
8.022
8.007
7.772
7.759
7.745
7.661
7.648
7.553
7.550
7.540
7.537
7.508
7.497
7.485
7.458
4.275
4.263
1.075
1.063
1.051
Cl
EtO2C
N
N
Ph
CN
3q
1H NMR, 600 MHz, CDCl3
1.07
1.10
1.09
1.00
1.99
3.09
1.95
3.00
f1 (ppm)


162.027
149.840
144.175
138.532
135.973
134.463
133.537
131.105
129.753
128.930
128.272
127.065
117.745
116.750
115.672
113.859
89.511
62.168
13.564
Cl
EtO2C
N
N
Ph
CN
3q
13C NMR, 150 MHz, CDCl3
f1 (ppm)



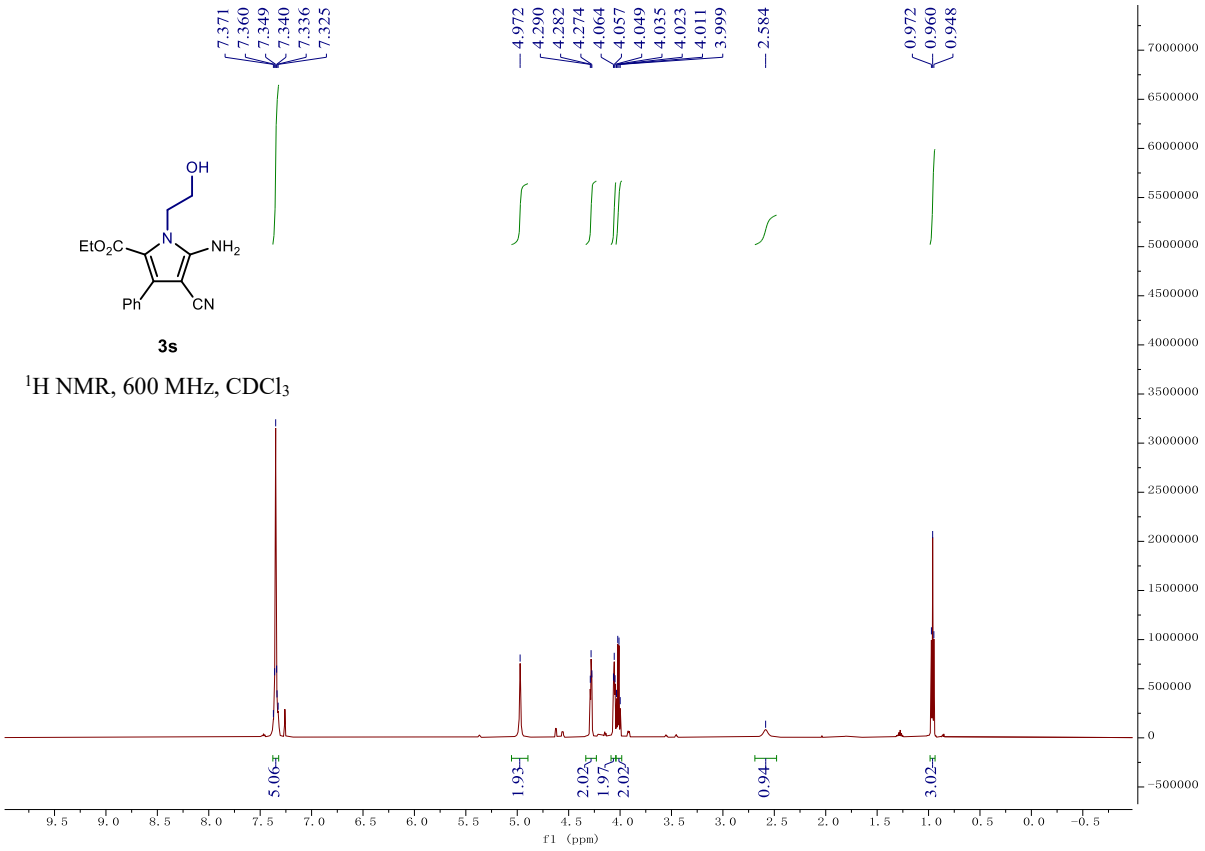
3r

^{1}H NMR, 700 MHz, $CDCl_3$



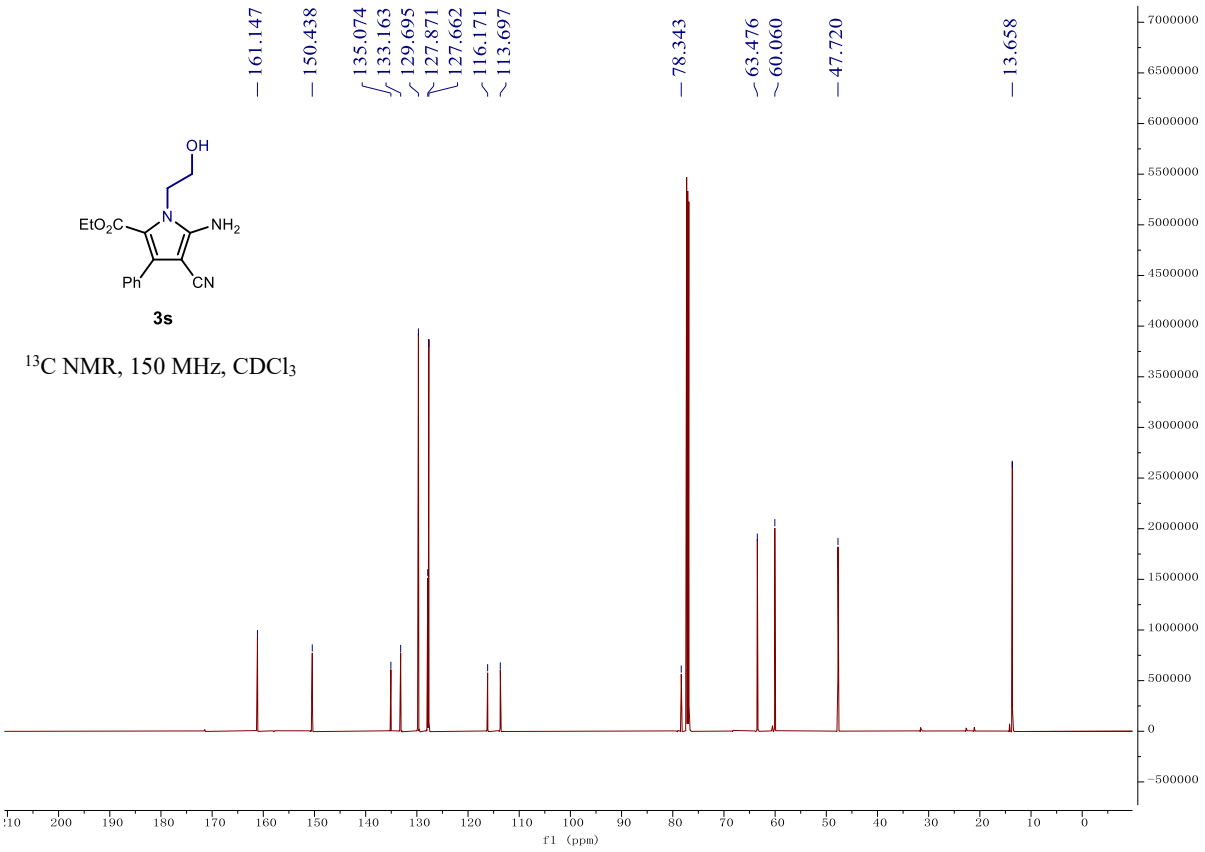
3r

^{13}C NMR, 175 MHz, $CDCl_3$



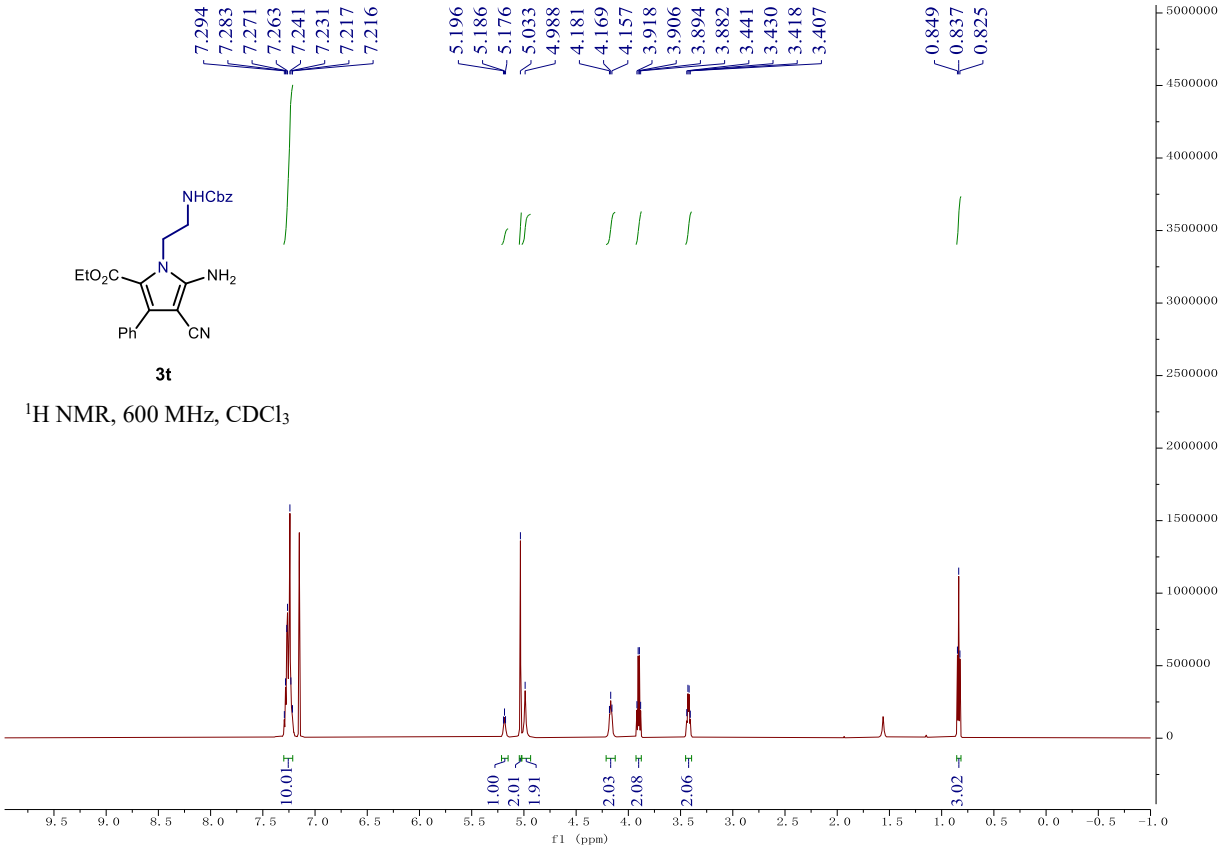
3s

^{1}H NMR, 600 MHz, $CDCl_3$



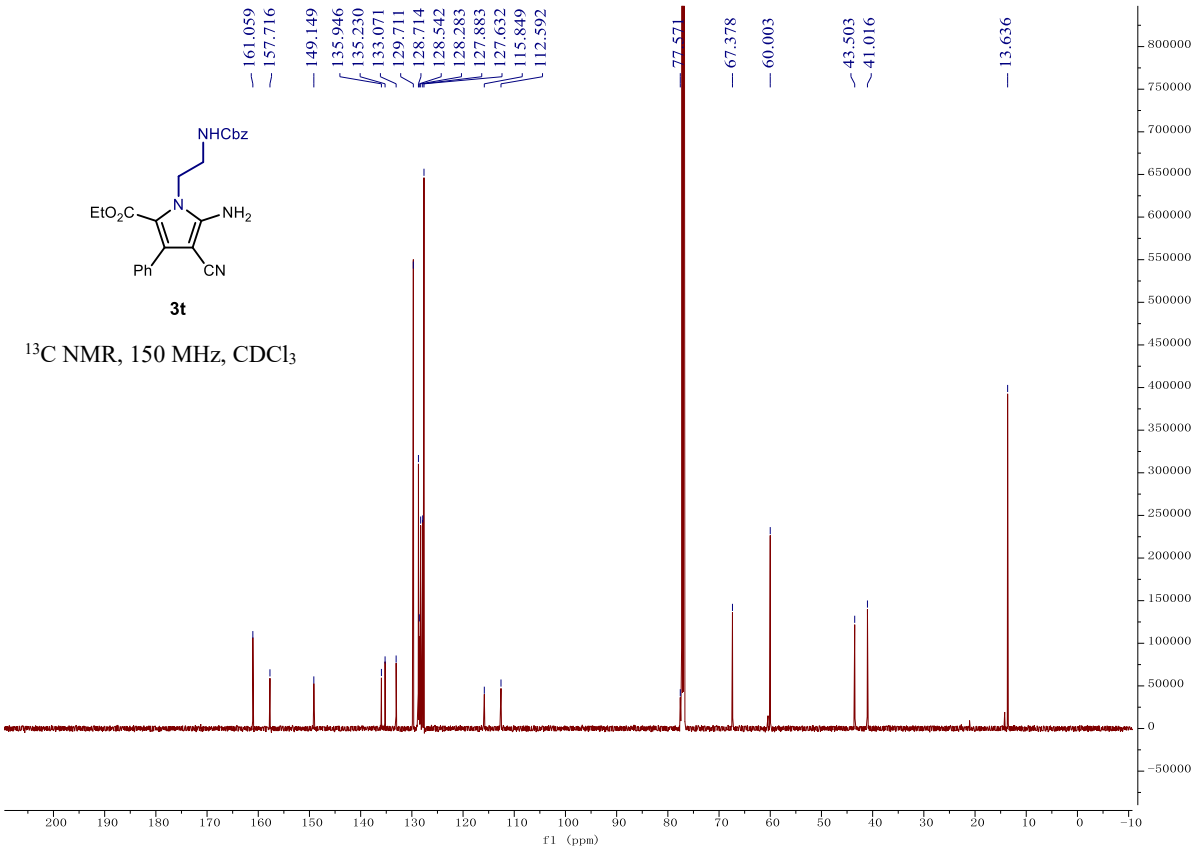
3s

^{13}C NMR, 150 MHz, $CDCl_3$



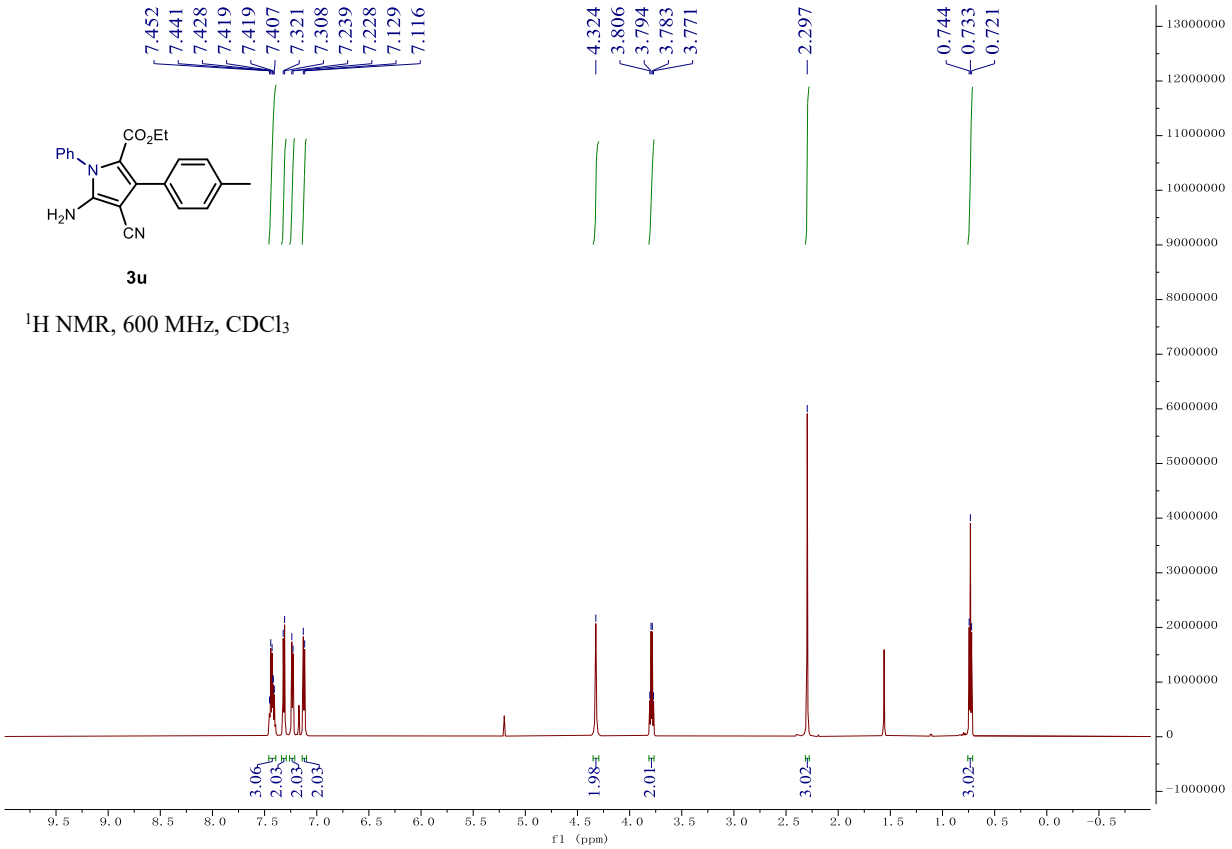
3t

^{1}H NMR, 600 MHz, $CDCl_3$



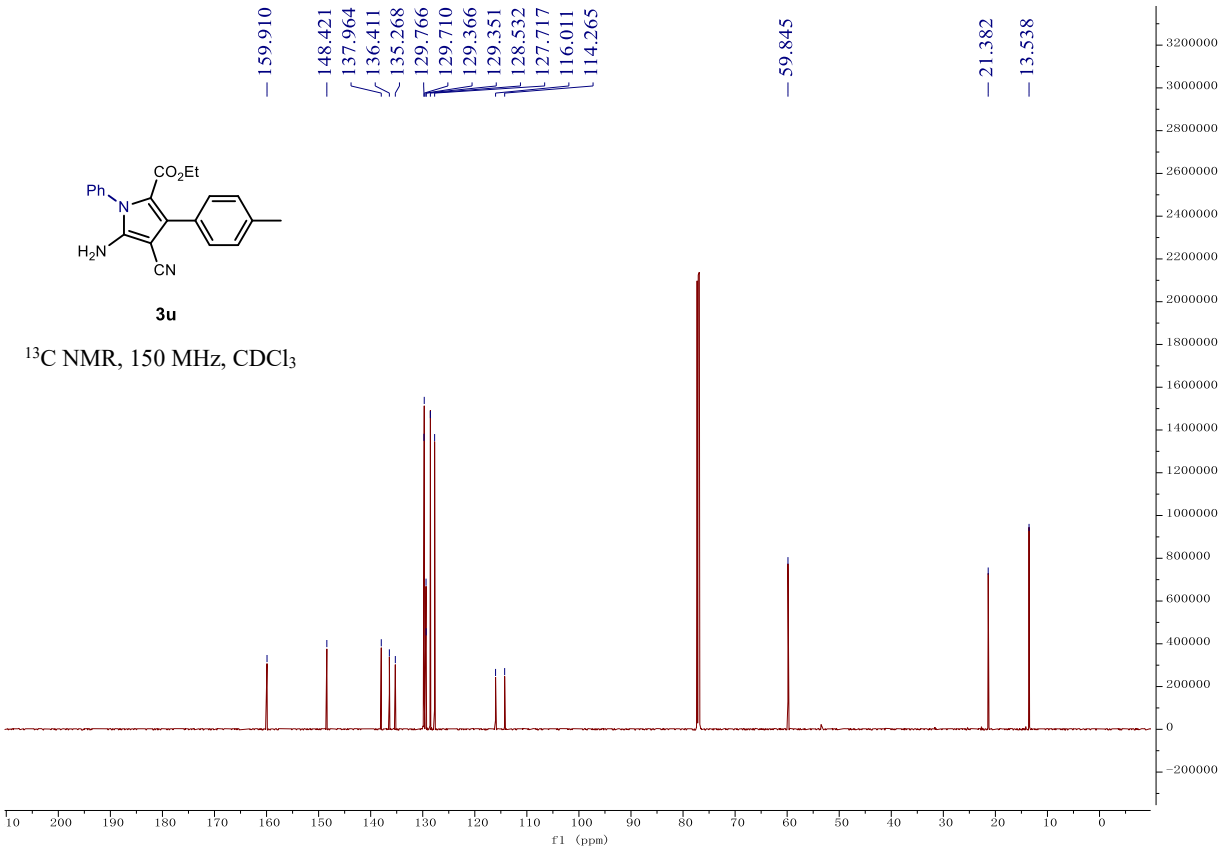
3t

^{13}C NMR, 150 MHz, $CDCl_3$



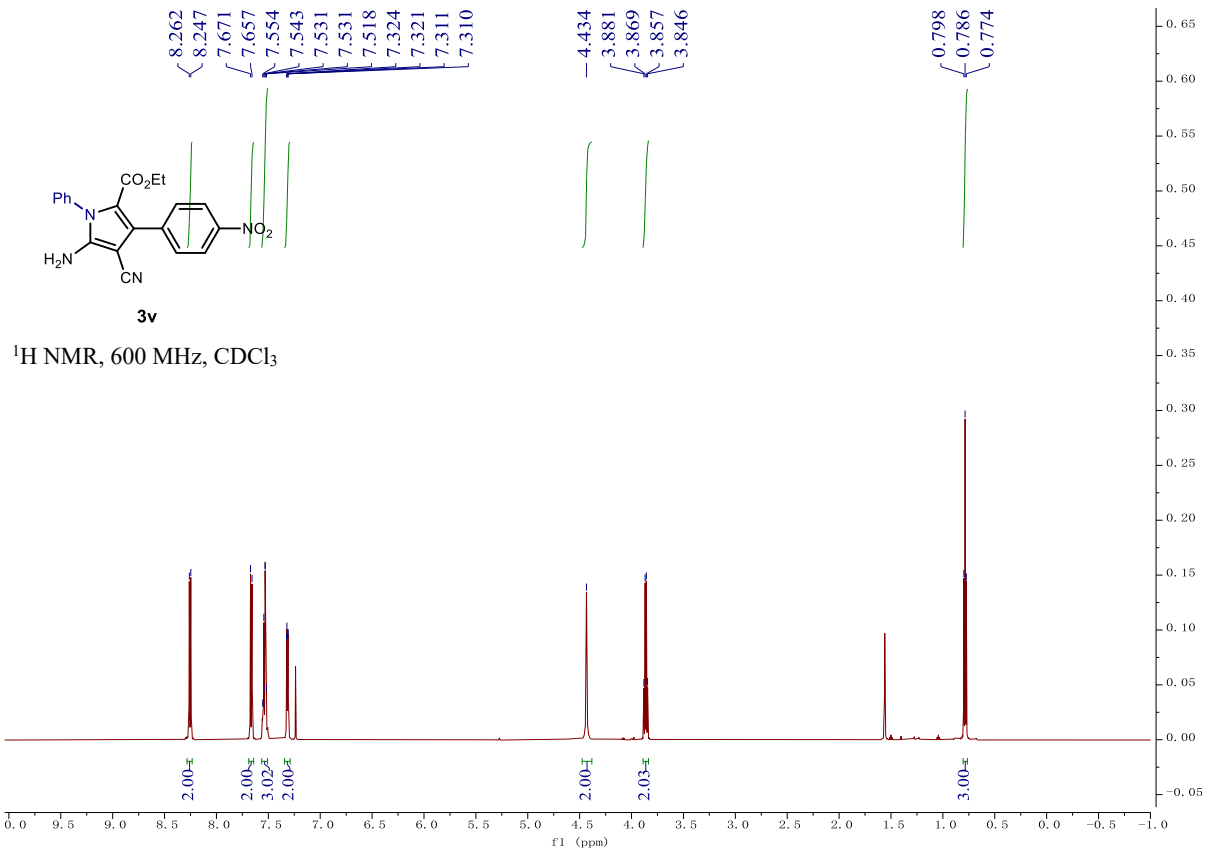
3u

^{1}H NMR, 600 MHz, $CDCl_3$



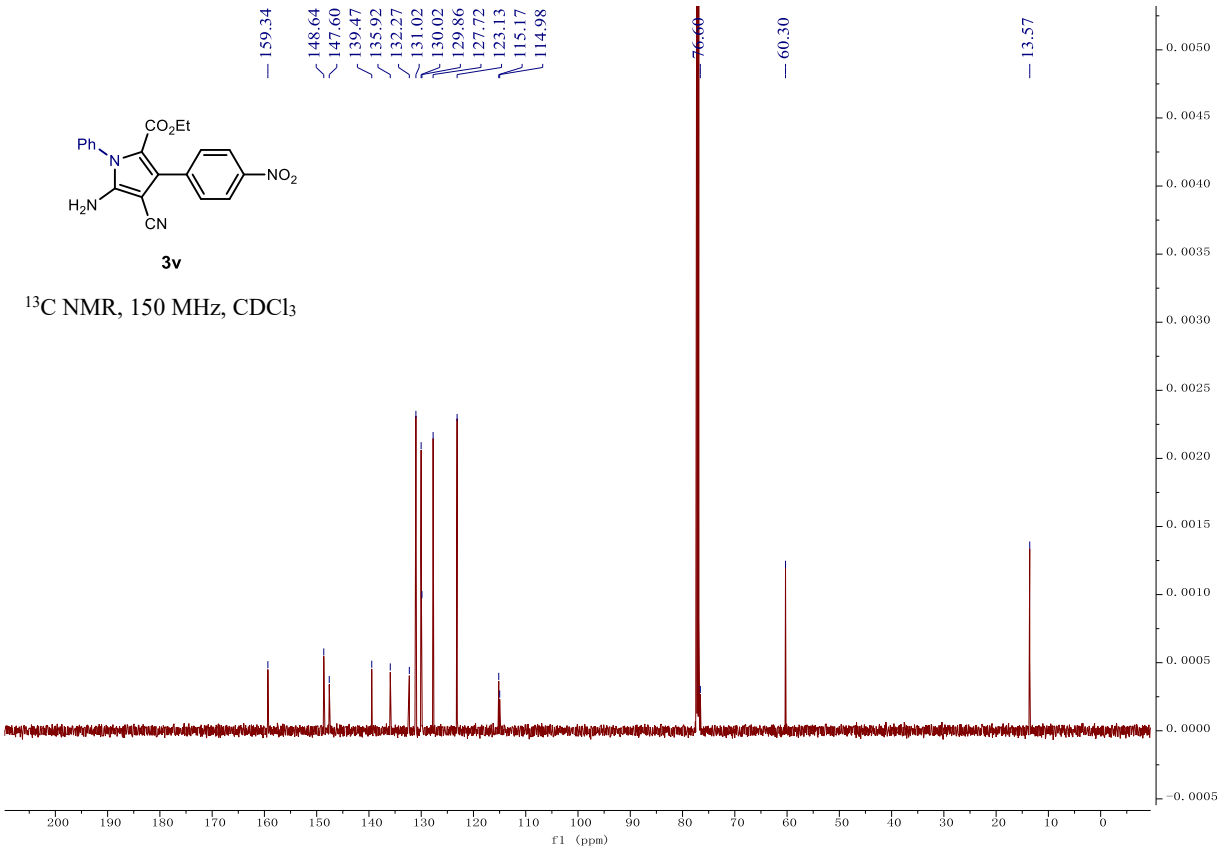
3u

^{13}C NMR, 150 MHz, $CDCl_3$



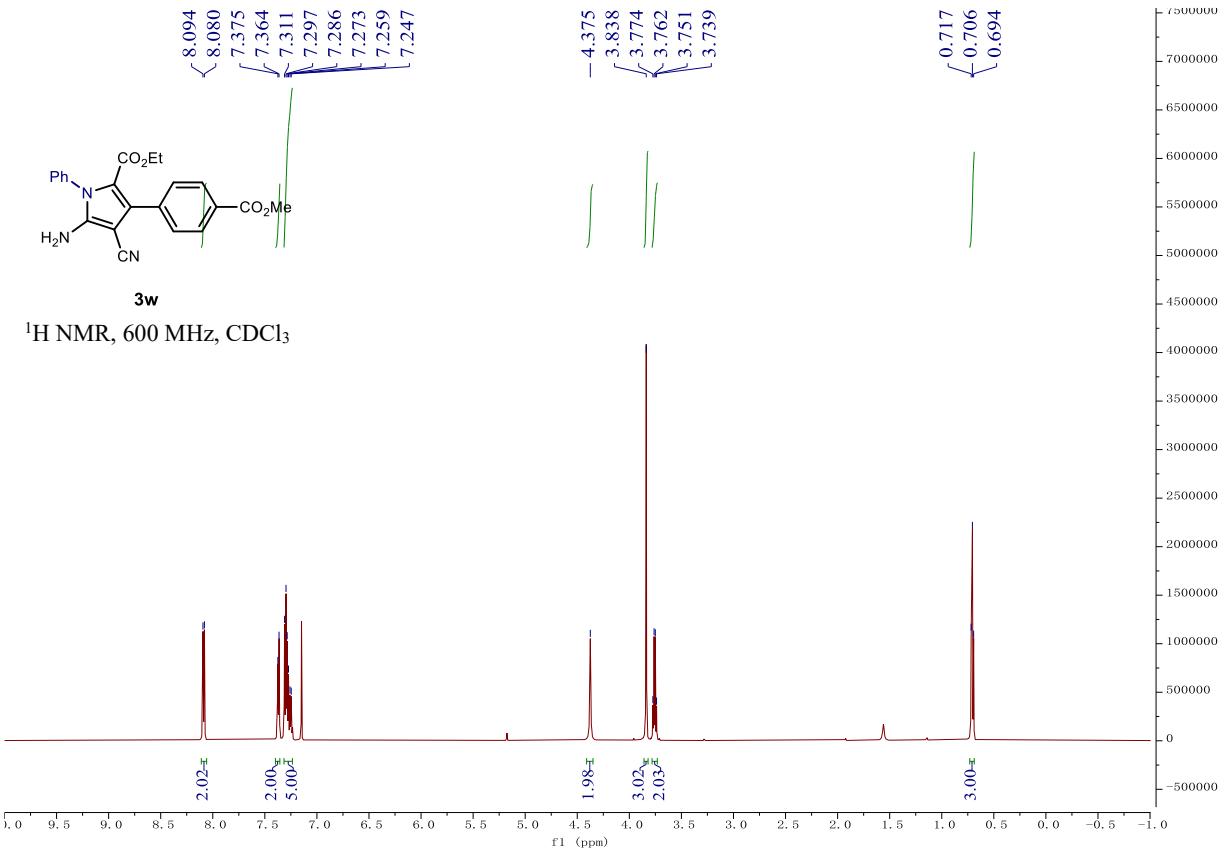
3v

^{1}H NMR, 600 MHz, $CDCl_3$



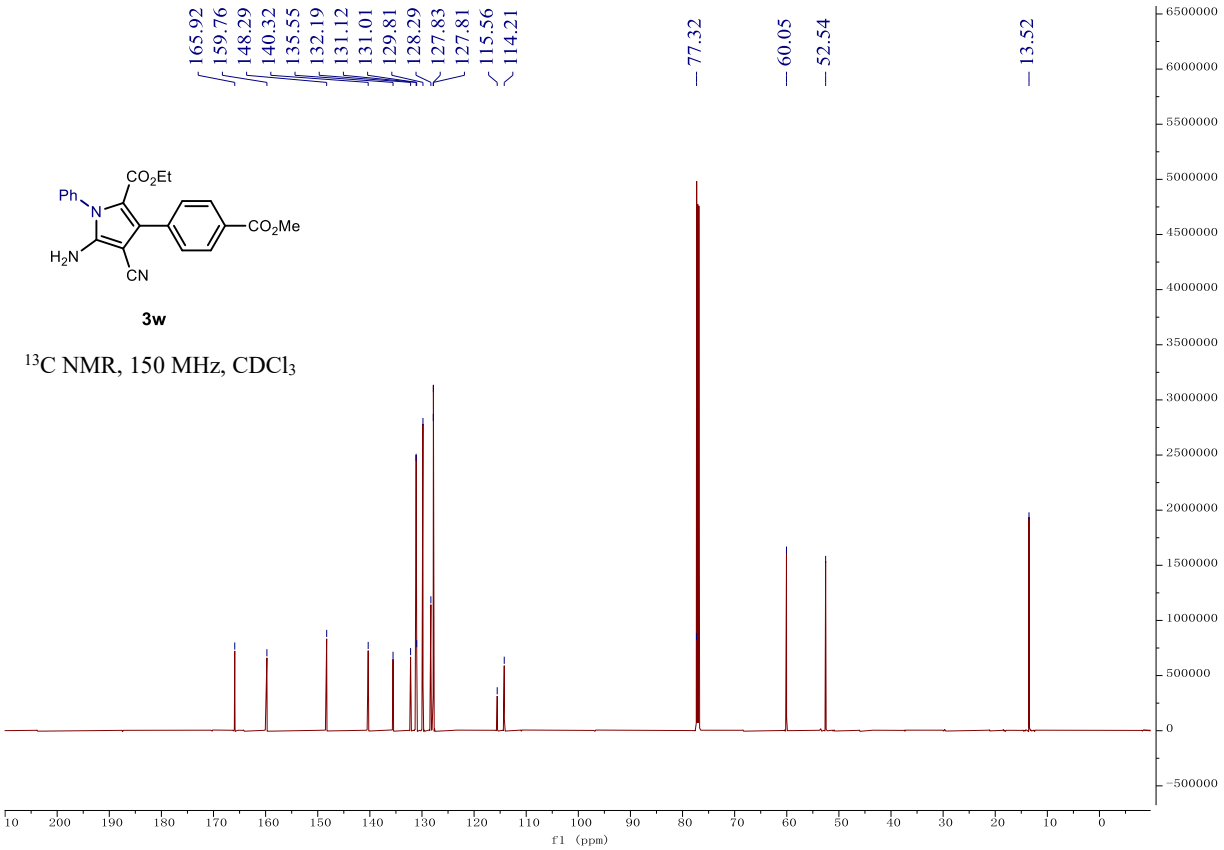
3v

^{13}C NMR, 150 MHz, $CDCl_3$



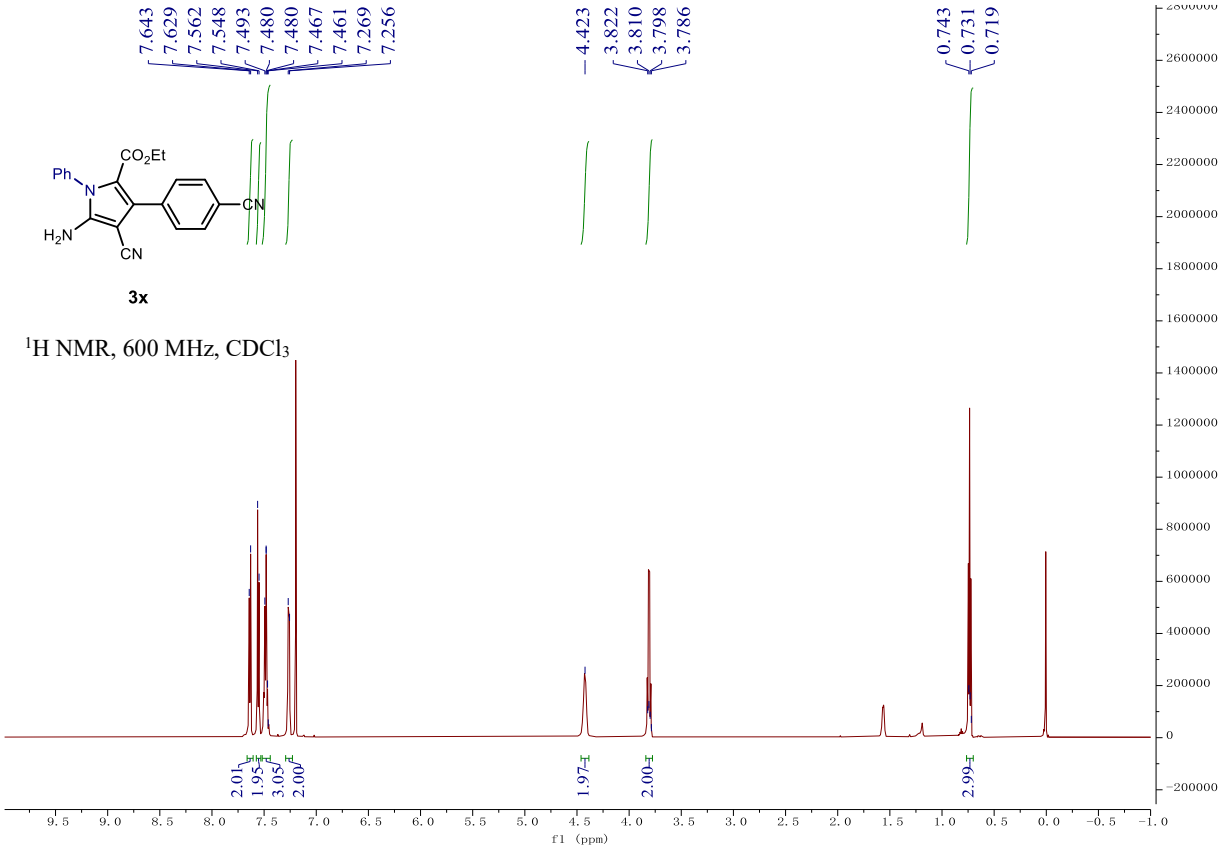
3w

^{1}H NMR, 600 MHz, $CDCl_3$



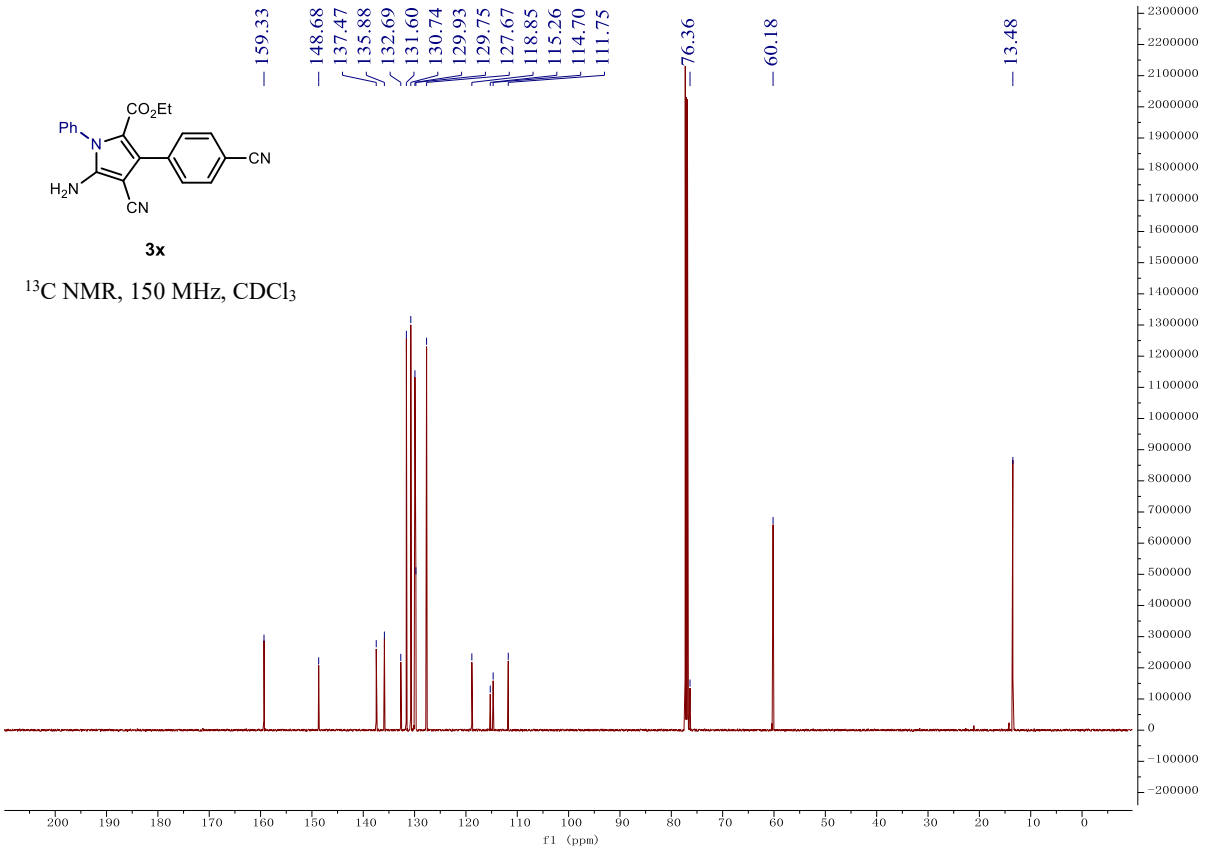
3w

^{13}C NMR, 150 MHz, $CDCl_3$



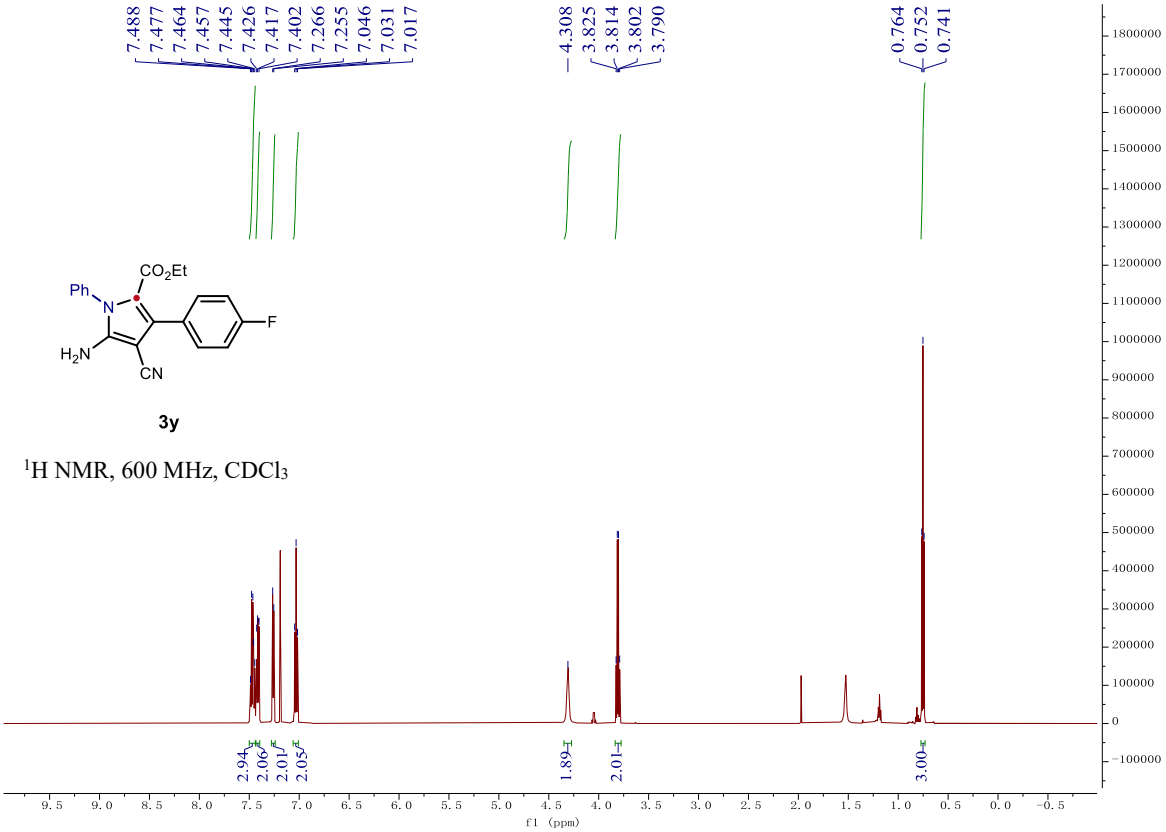
3x

^{1}H NMR, 600 MHz, $CDCl_3$



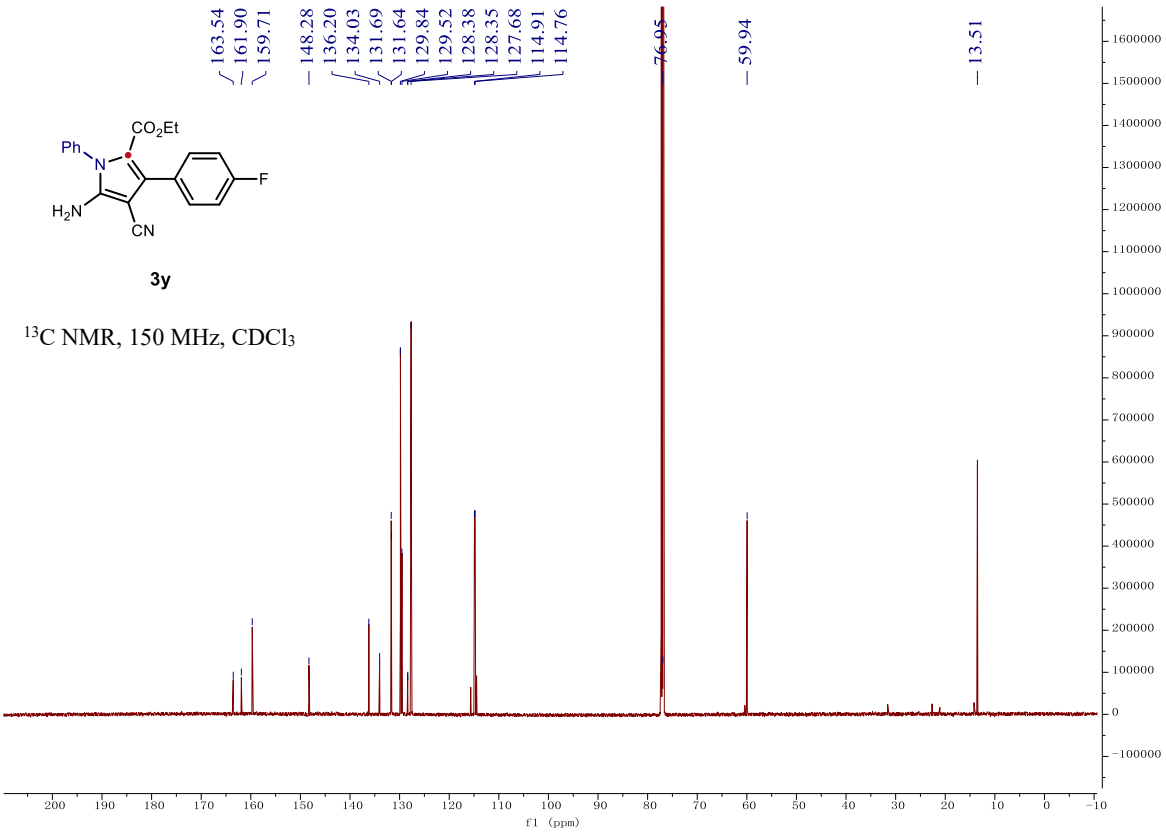
3x

^{13}C NMR, 150 MHz, $CDCl_3$



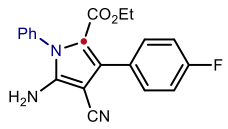
3y

^{1}H NMR, 600 MHz, $CDCl_3$



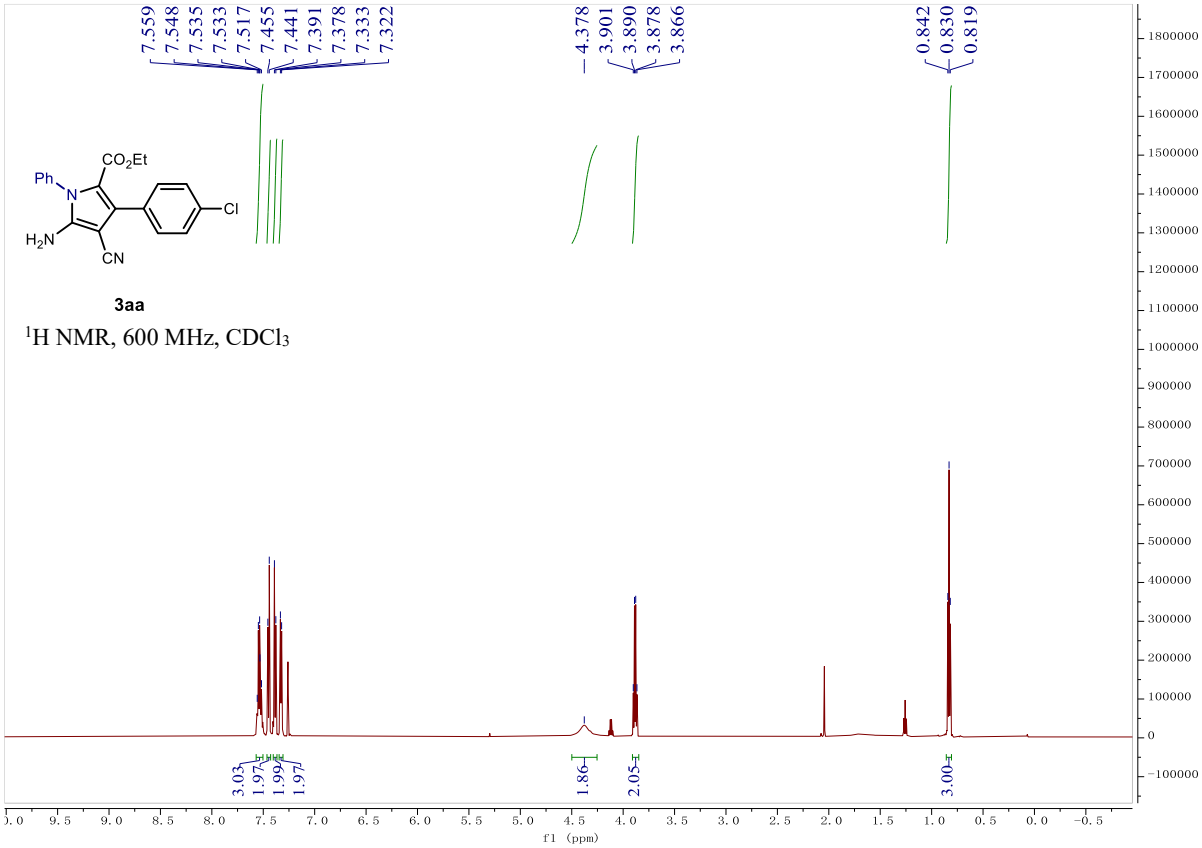
3y

^{13}C NMR, 150 MHz, $CDCl_3$



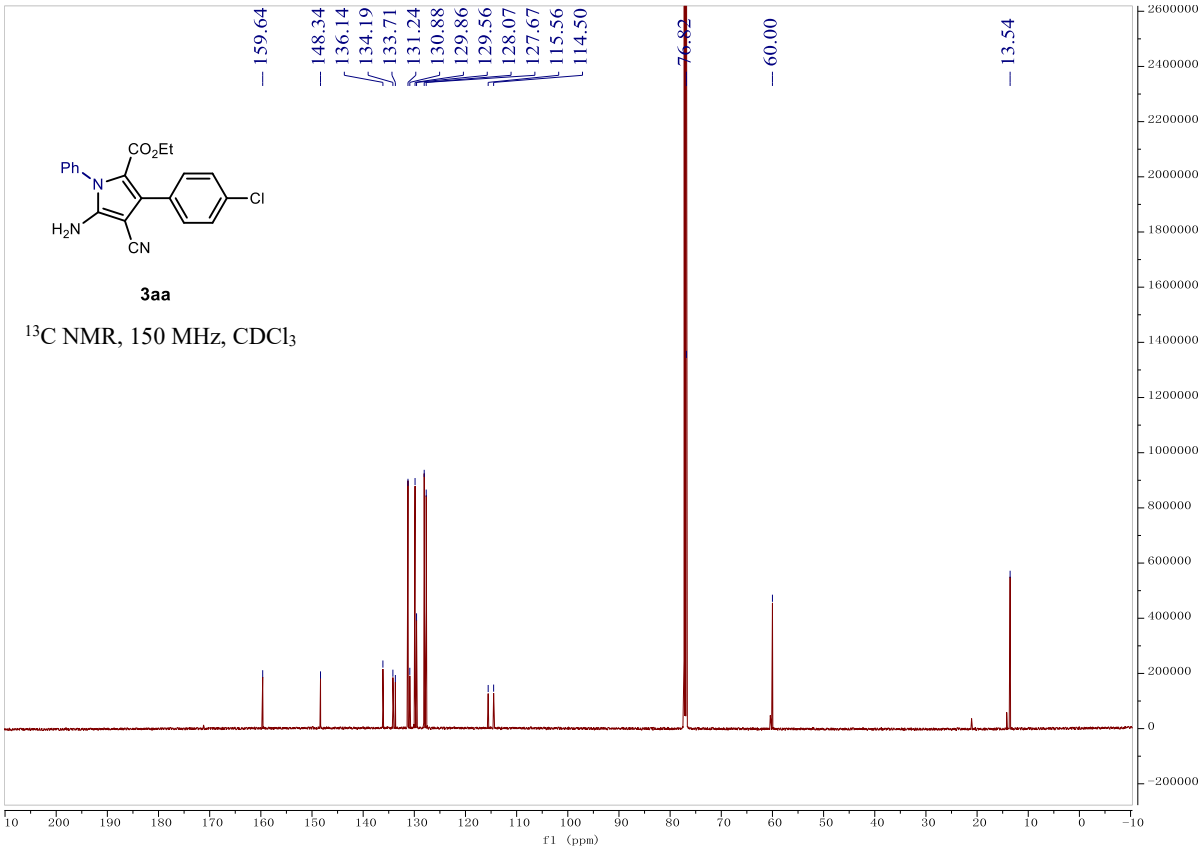
3y

^{19}F NMR, 564 MHz, $CDCl_3$



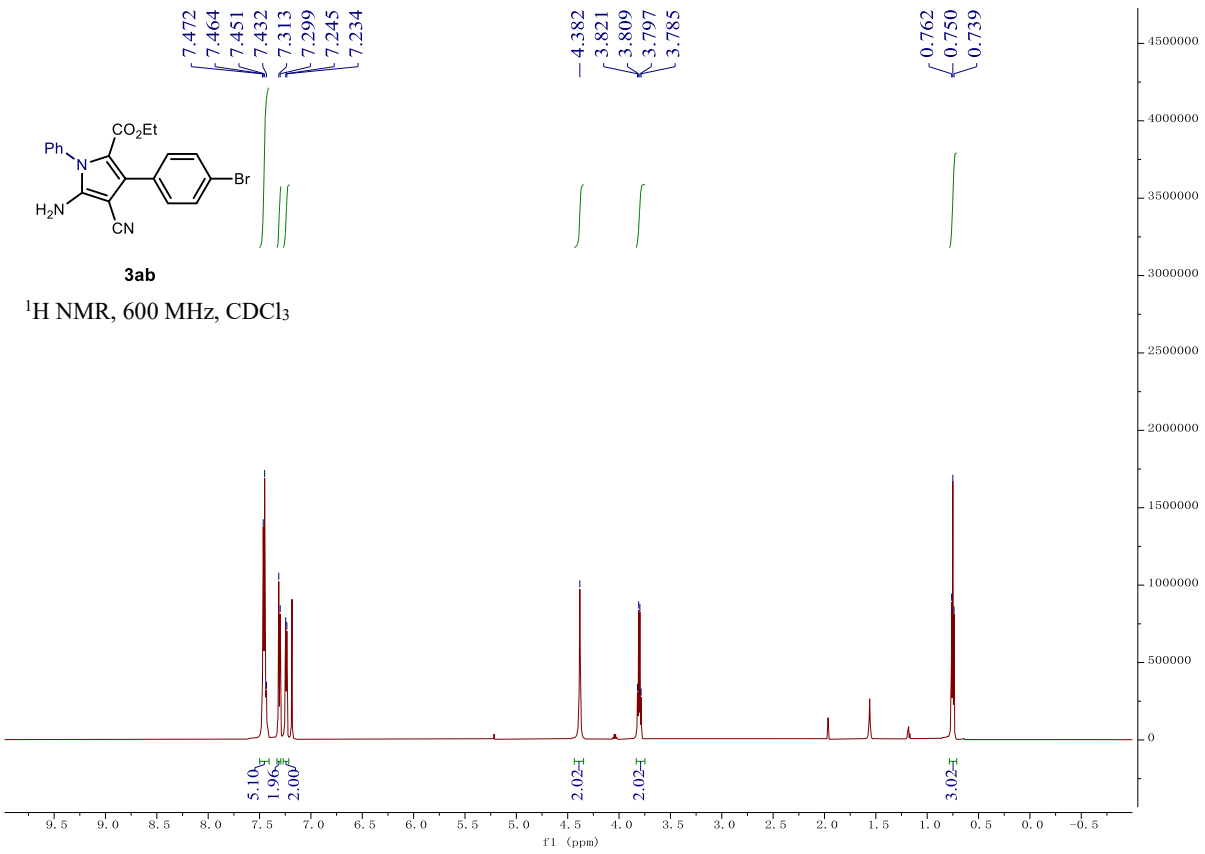
3aa

^{1}H NMR, 600 MHz, $CDCl_3$



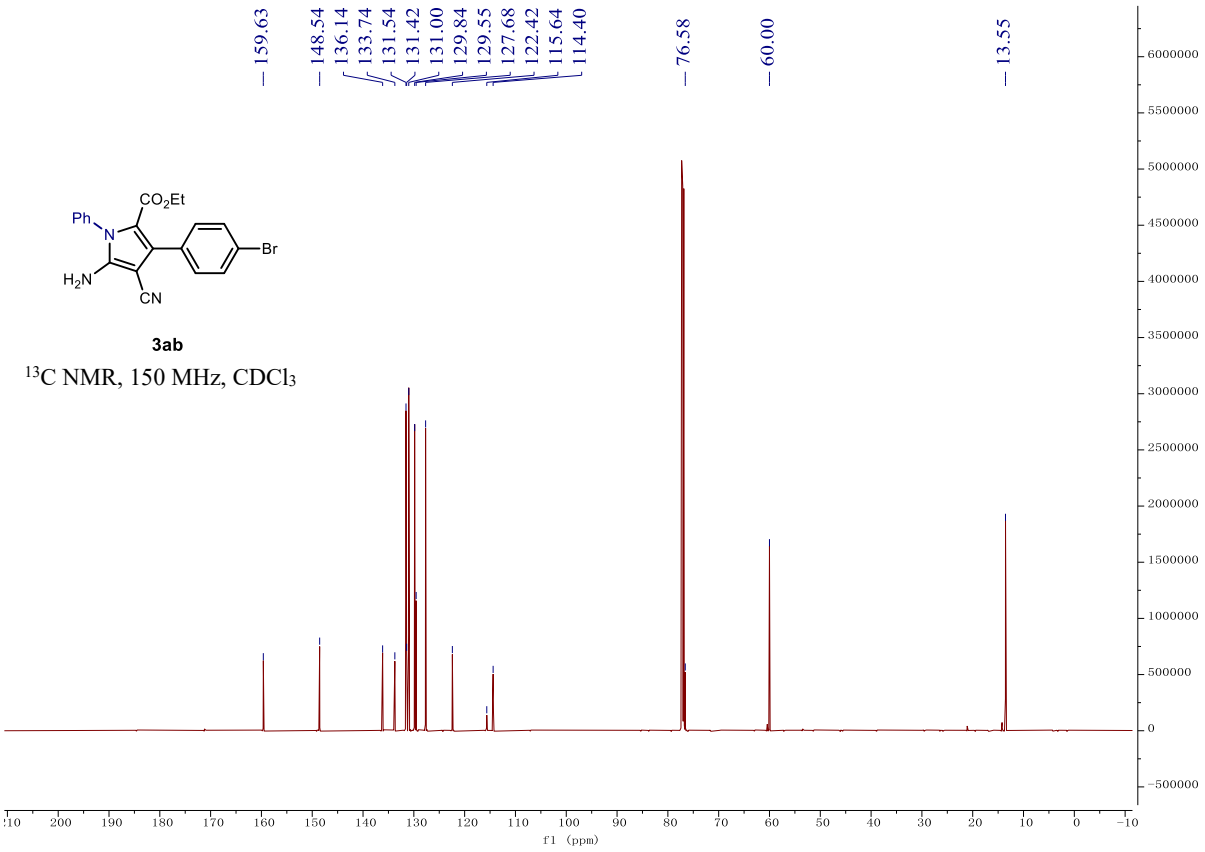
3aa

^{13}C NMR, 150 MHz, $CDCl_3$



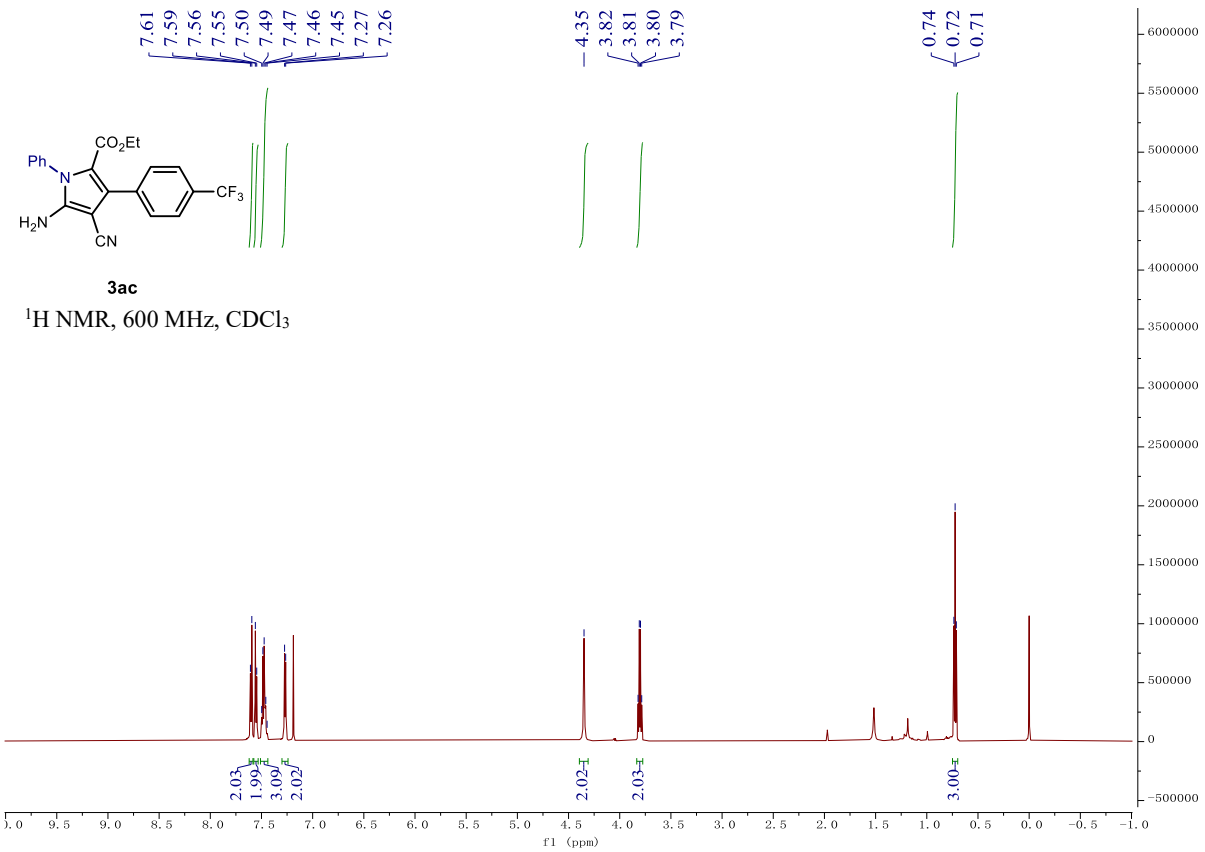
3ab

^{1}H NMR, 600 MHz, $CDCl_3$



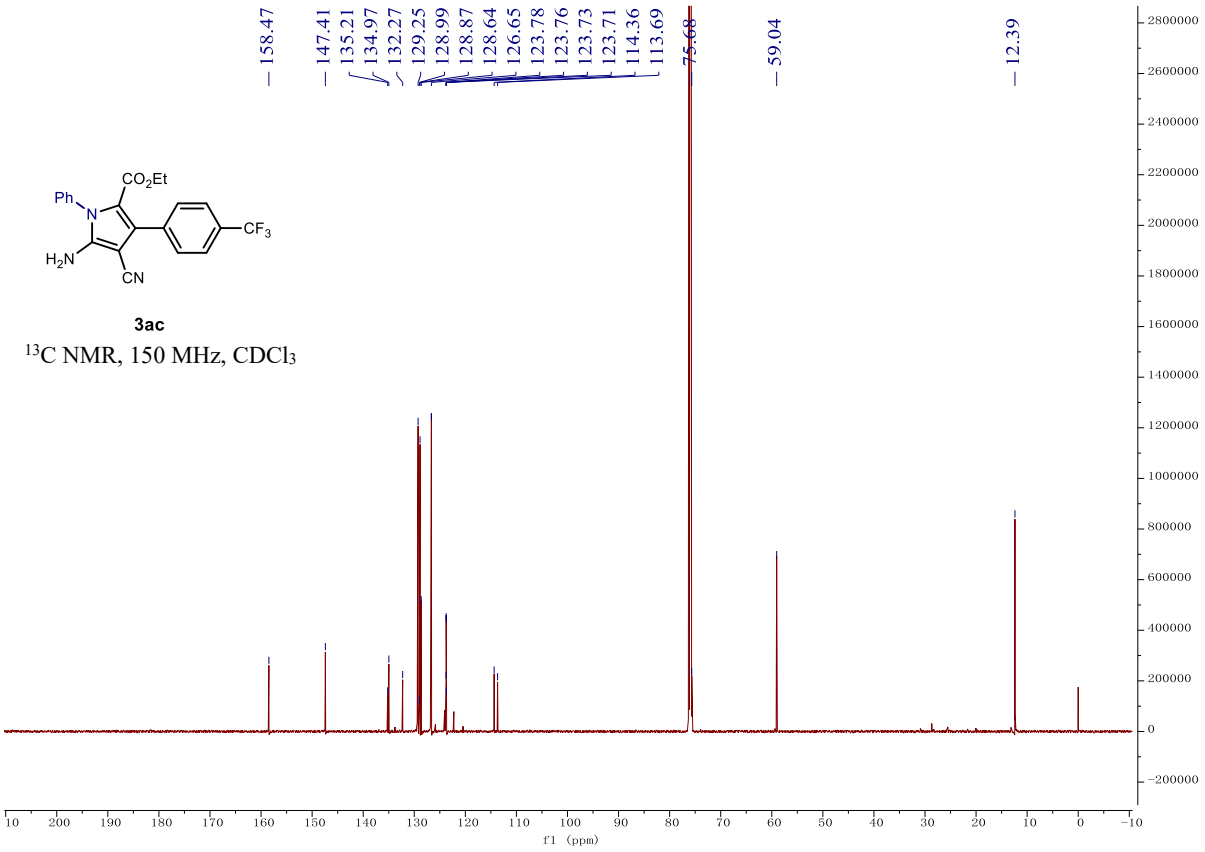
3ab

^{13}C NMR, 150 MHz, $CDCl_3$



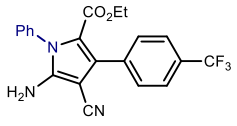
3ac

^{1}H NMR, 600 MHz, $CDCl_3$



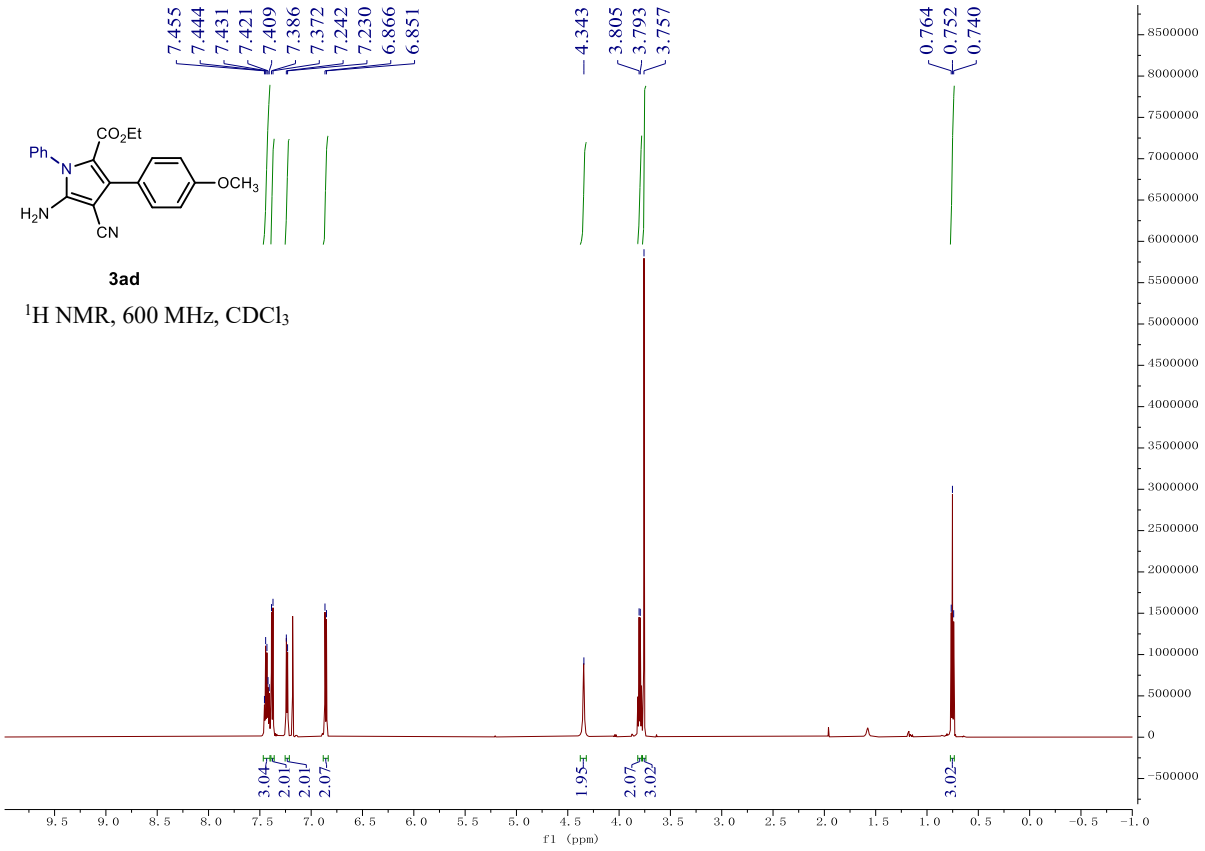
3ac

^{13}C NMR, 150 MHz, $CDCl_3$



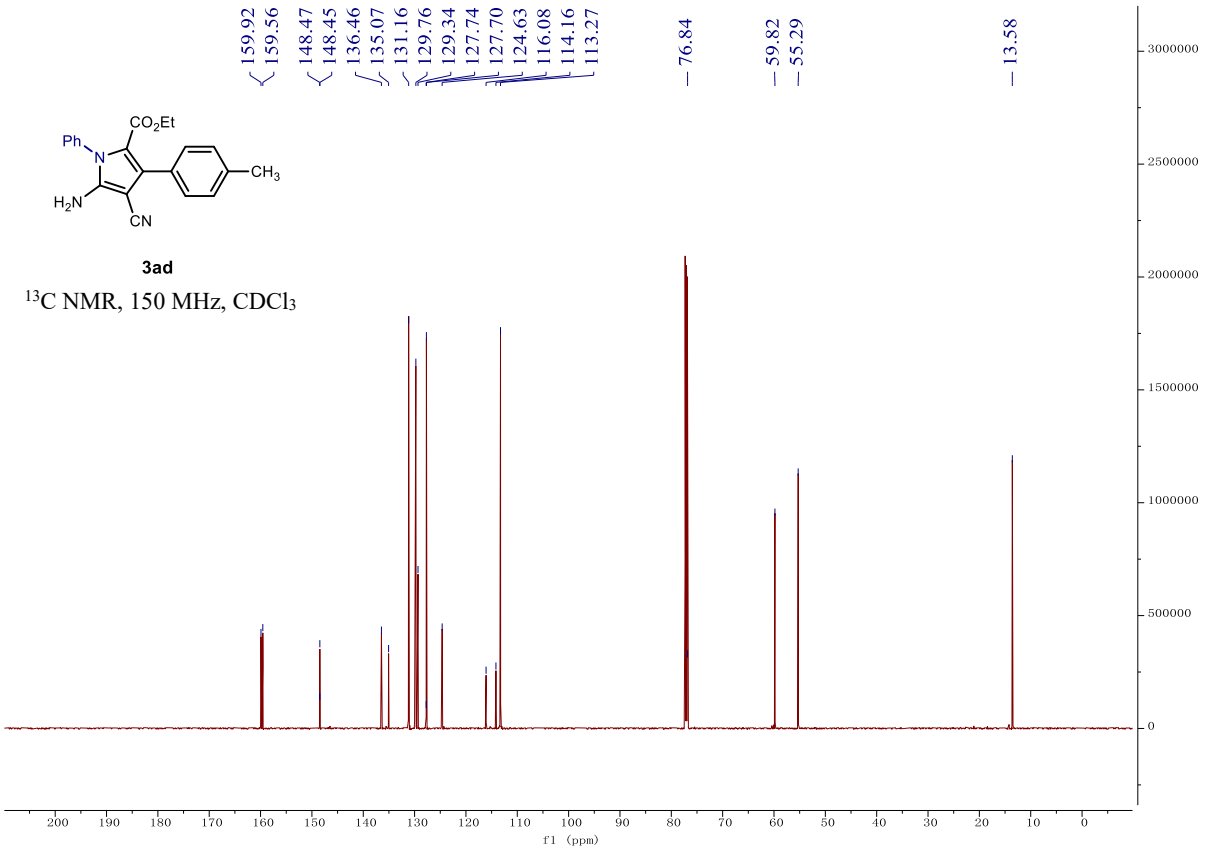
3ac

^{19}F NMR, 564 MHz, $CDCl_3$



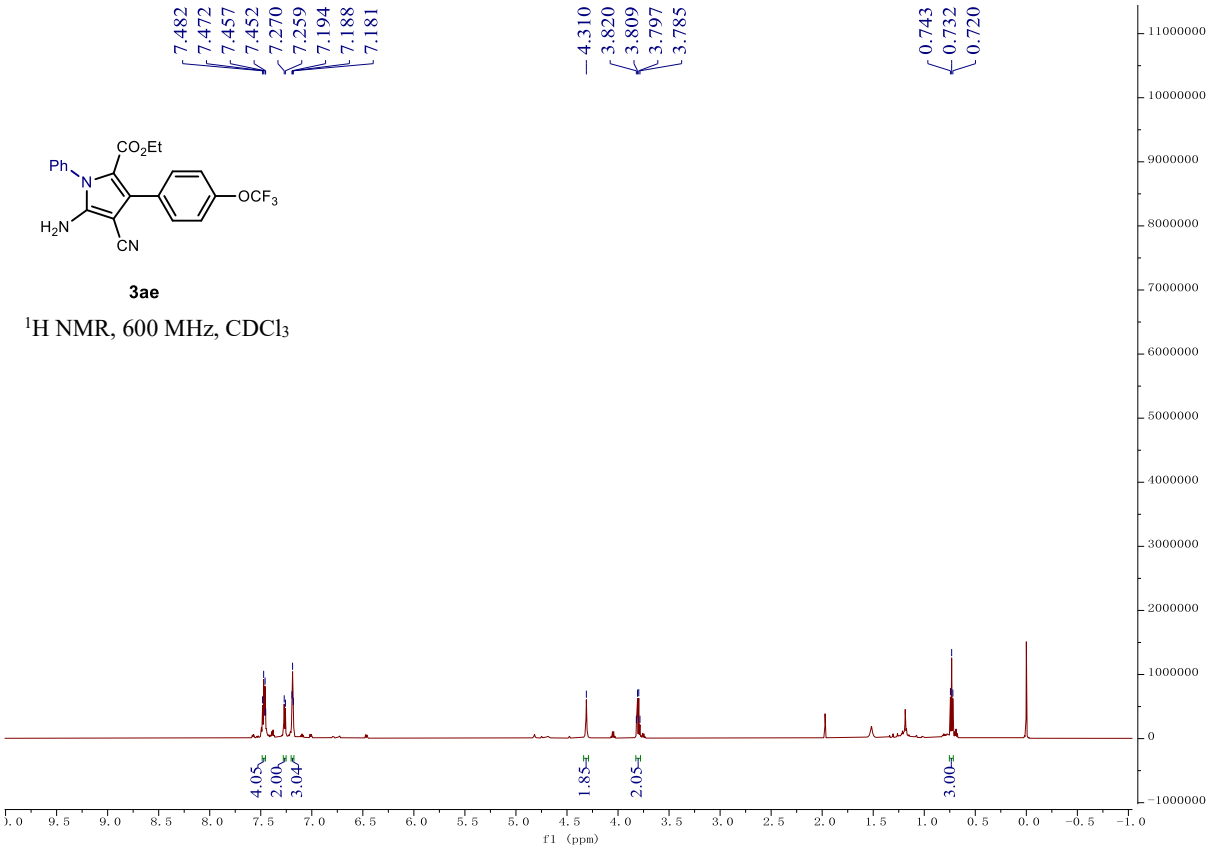
3ad

^{1}H NMR, 600 MHz, $CDCl_3$



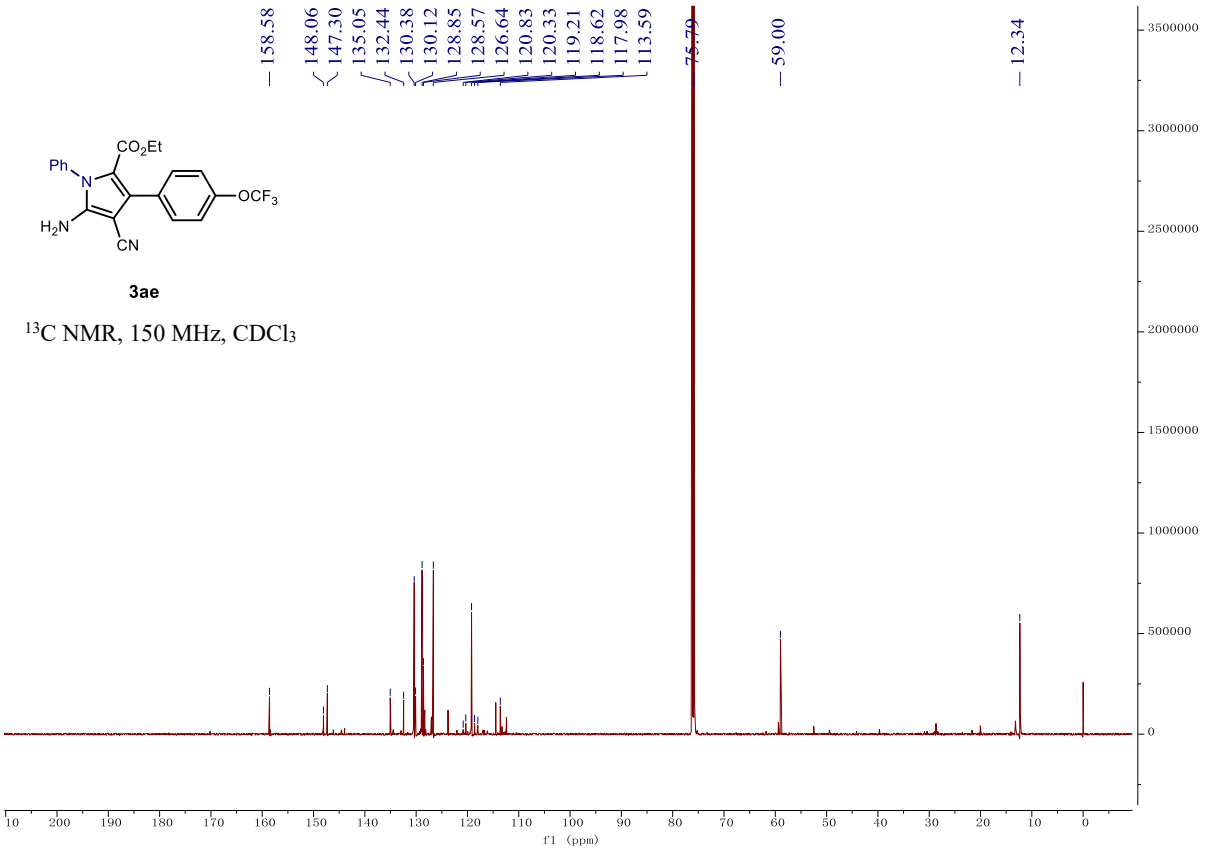
3ad

^{13}C NMR, 150 MHz, $CDCl_3$



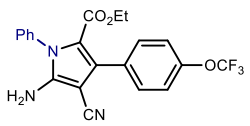
3ae

^{1}H NMR, 600 MHz, $CDCl_3$



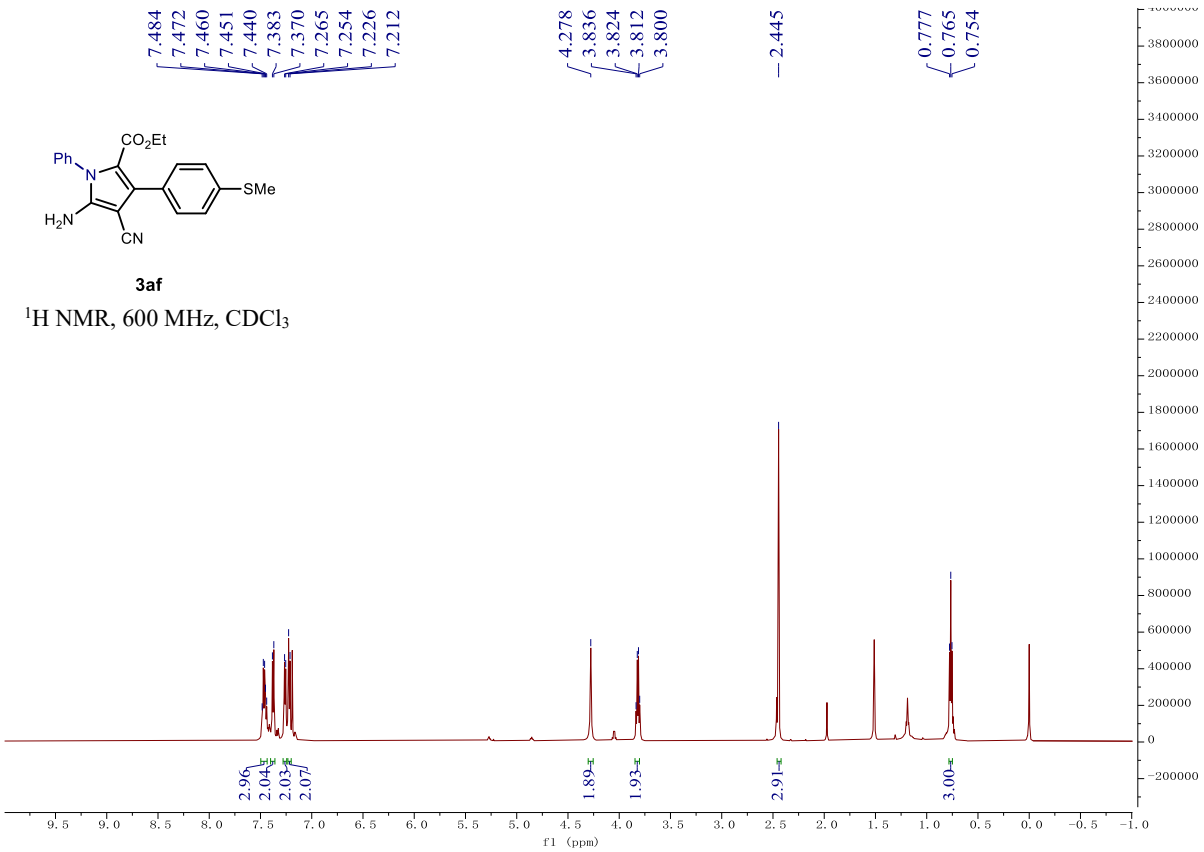
3ae

^{13}C NMR, 150 MHz, $CDCl_3$



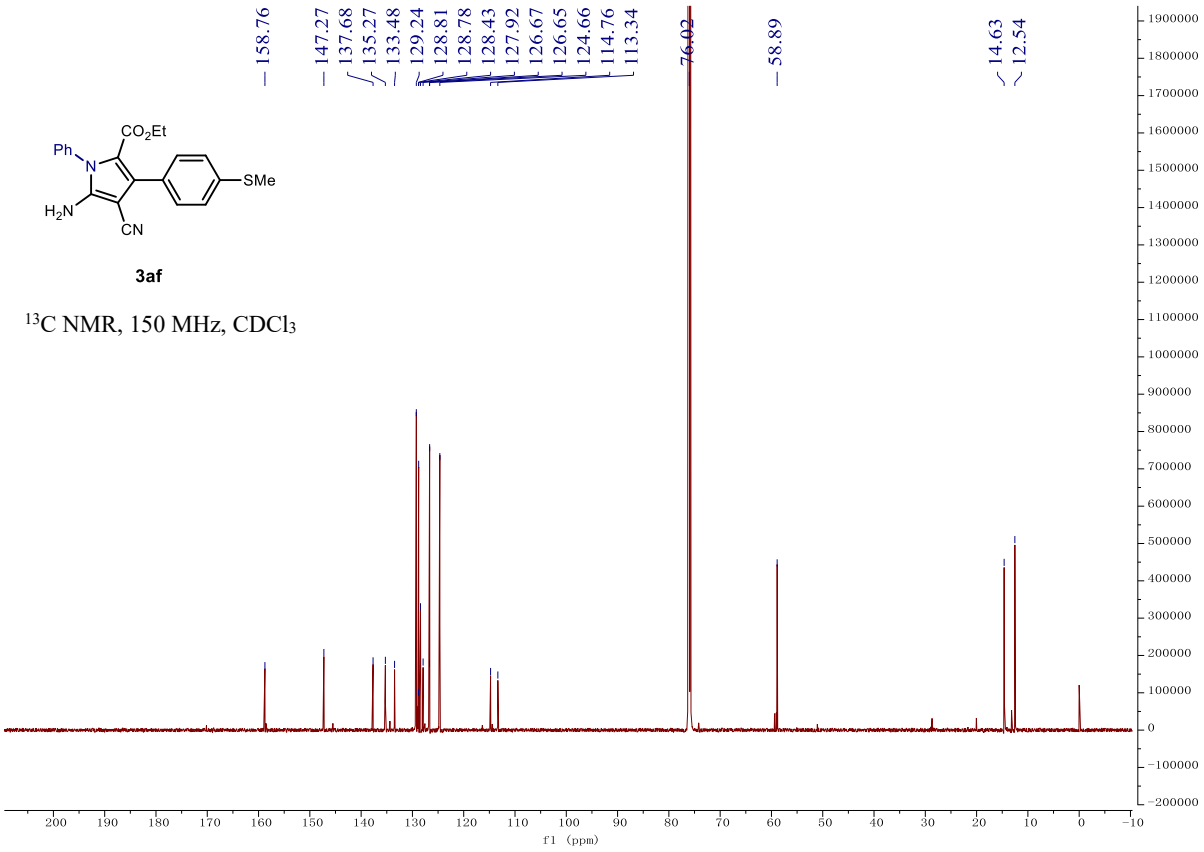
3ae

^{1}H NMR, 564 MHz, $CDCl_3$



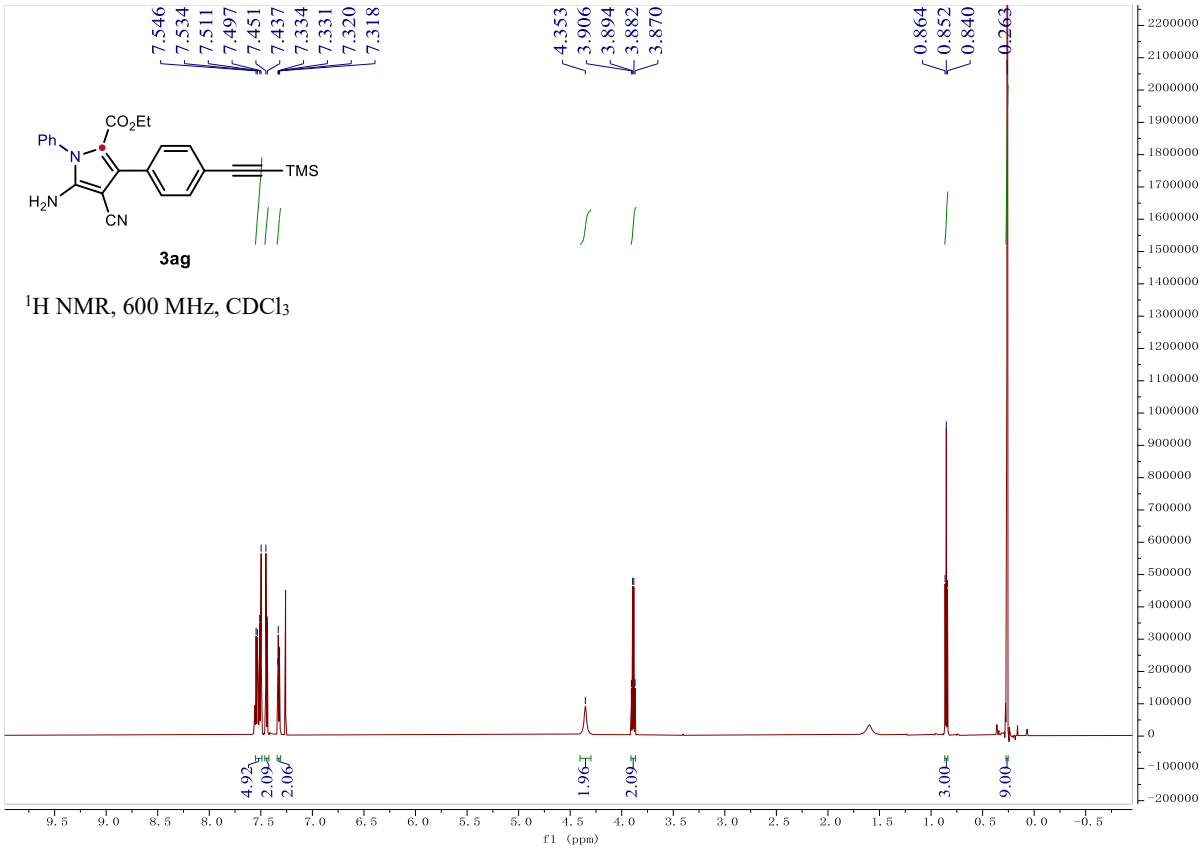
3af

^{1}H NMR, 600 MHz, $CDCl_3$



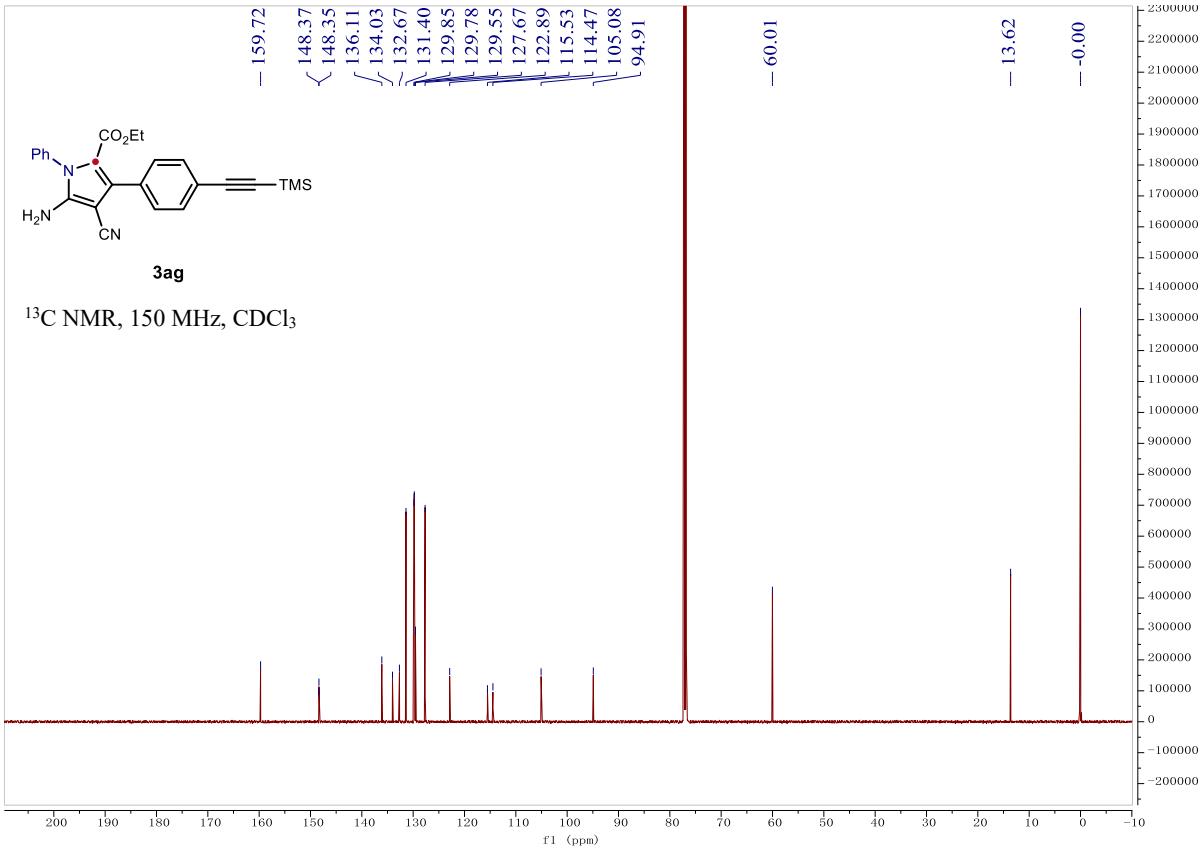
3af

^{13}C NMR, 150 MHz, $CDCl_3$



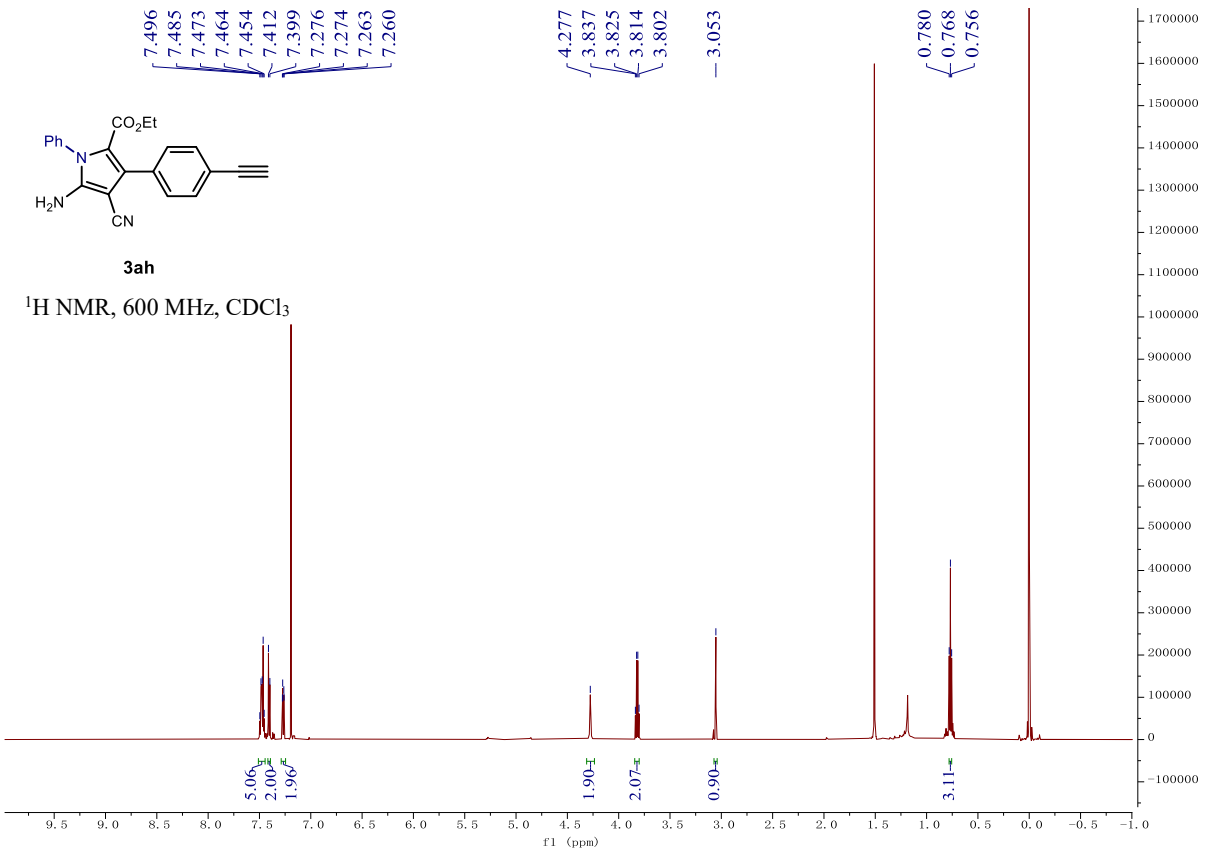
3ag

^{1}H NMR, 600 MHz, $CDCl_3$



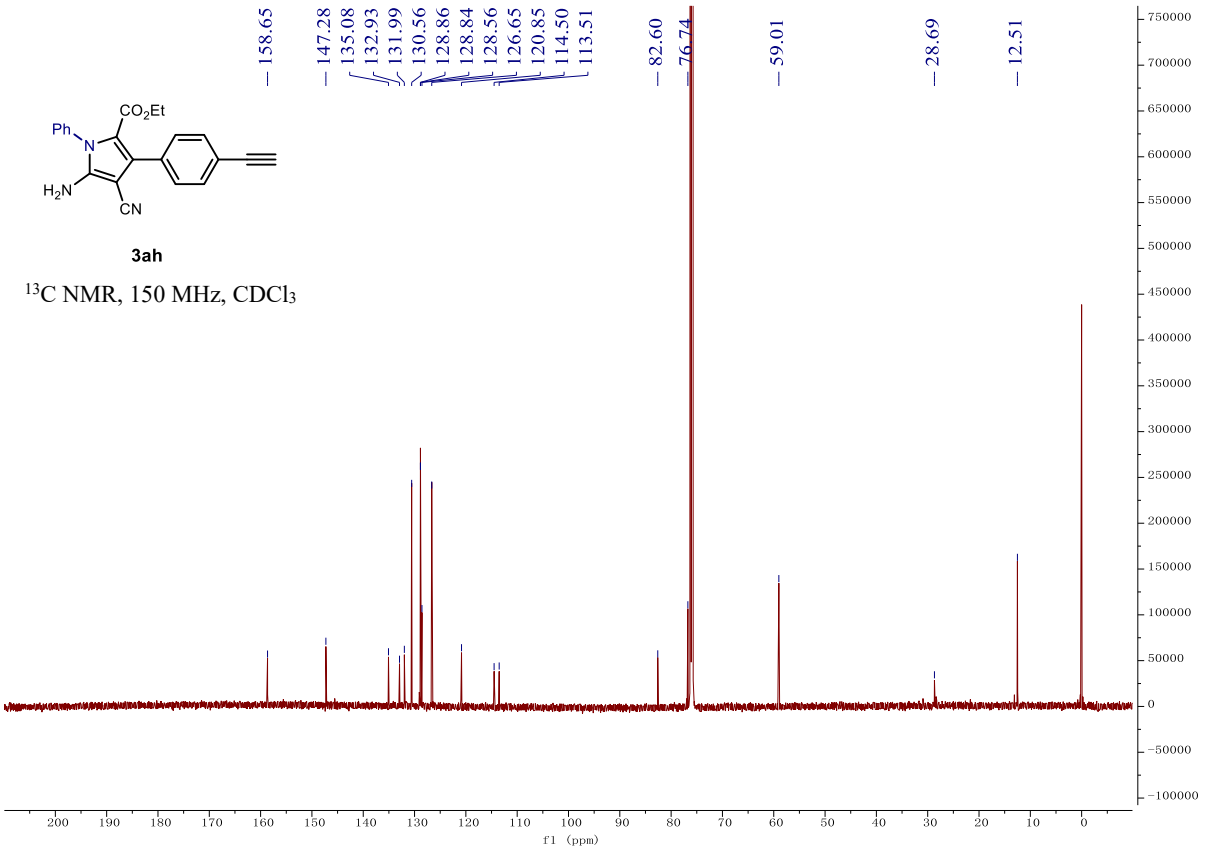
3ag

^{13}C NMR, 150 MHz, $CDCl_3$



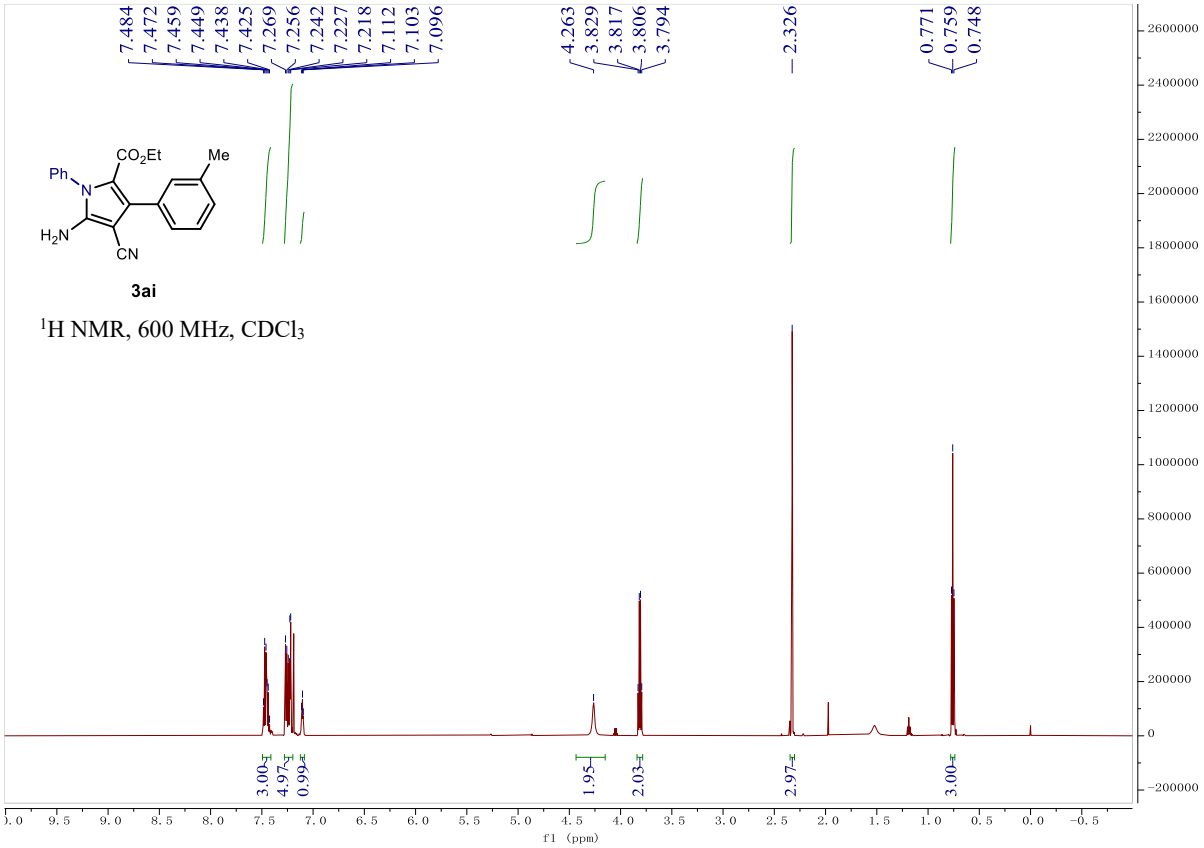
3ah

^{1}H NMR, 600 MHz, $CDCl_3$



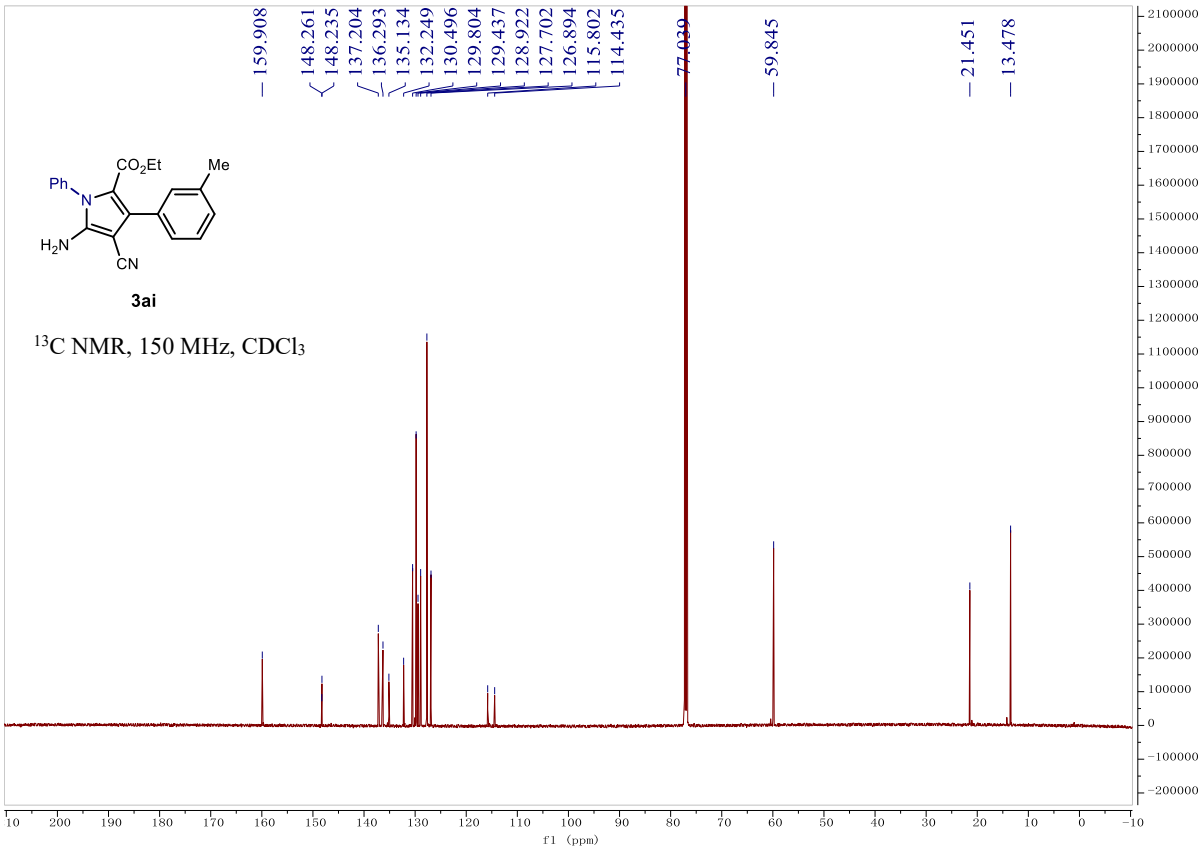
3ah

^{13}C NMR, 150 MHz, $CDCl_3$



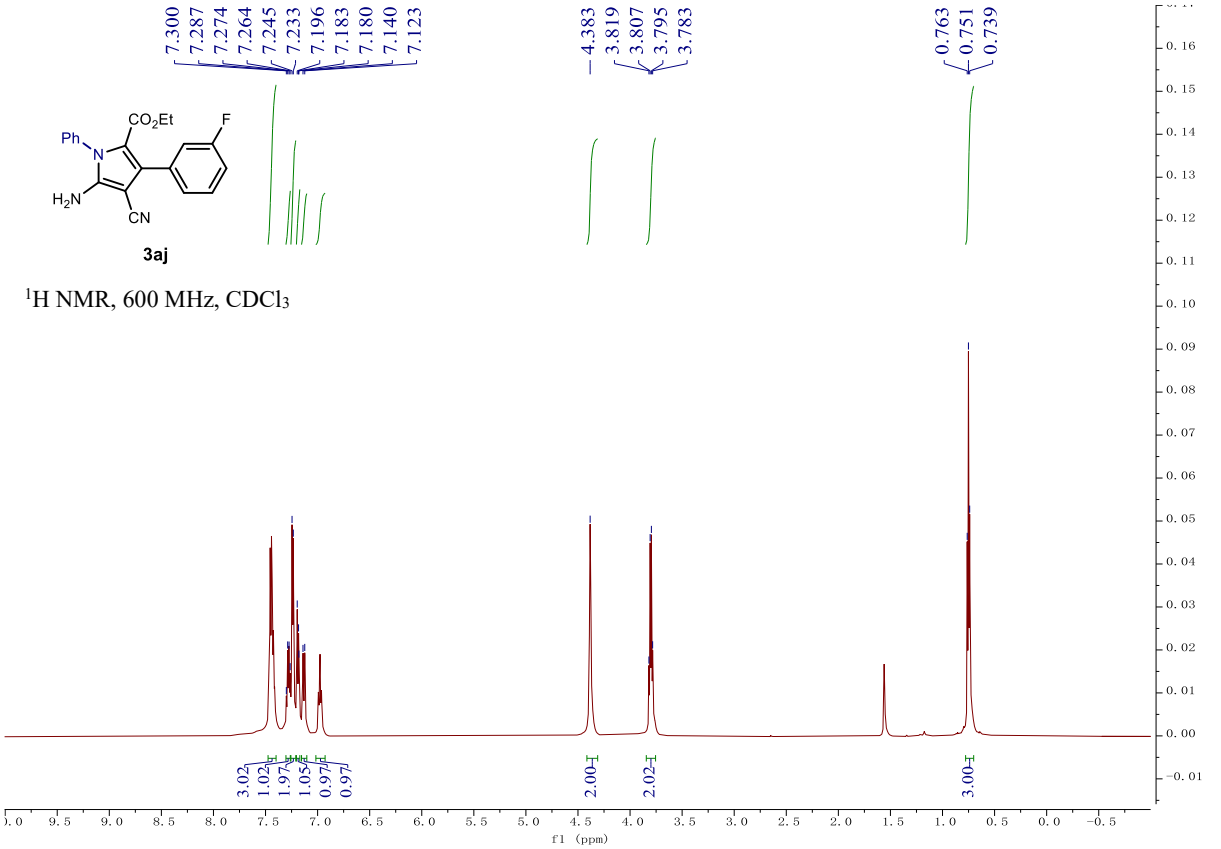
3ai

^{1}H NMR, 600 MHz, $CDCl_3$



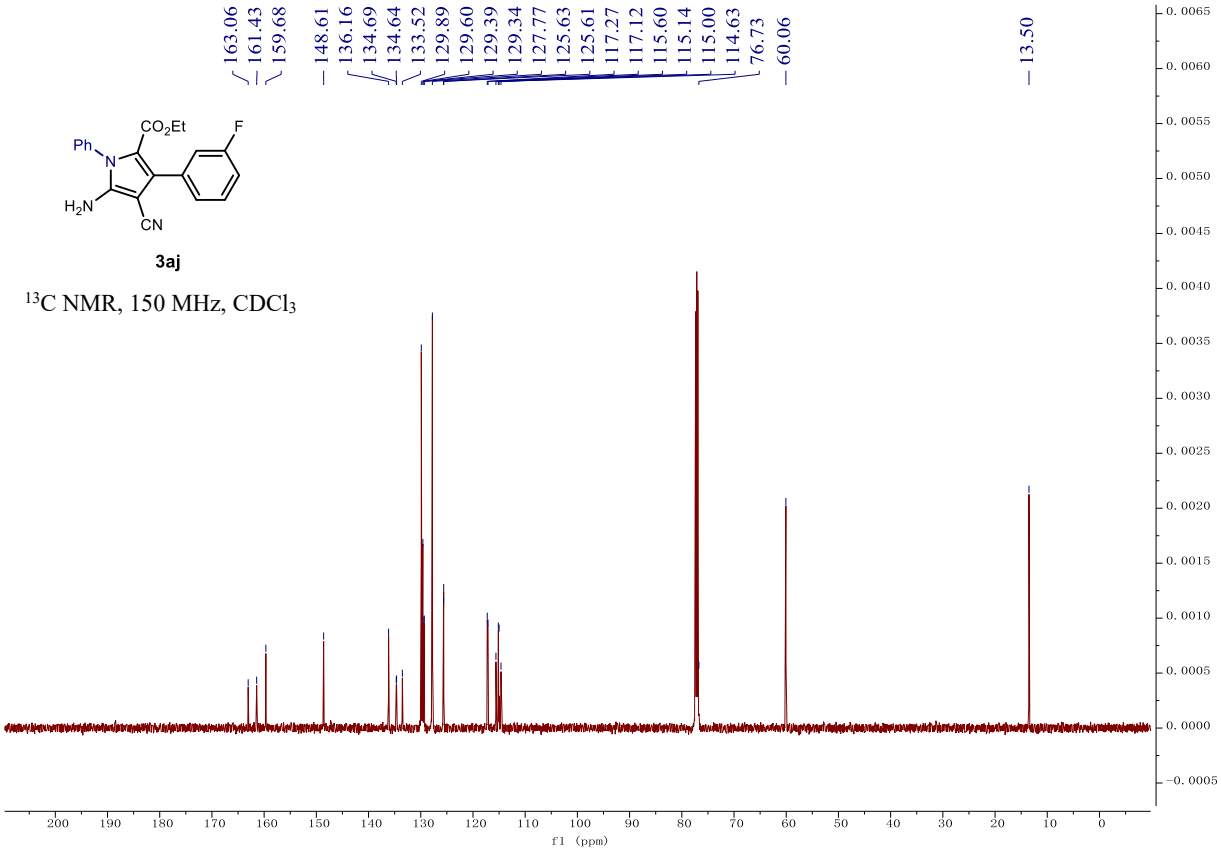
3ai

^{13}C NMR, 150 MHz, $CDCl_3$



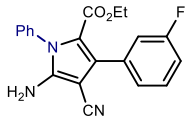
3aj

^{1}H NMR, 600 MHz, $CDCl_3$



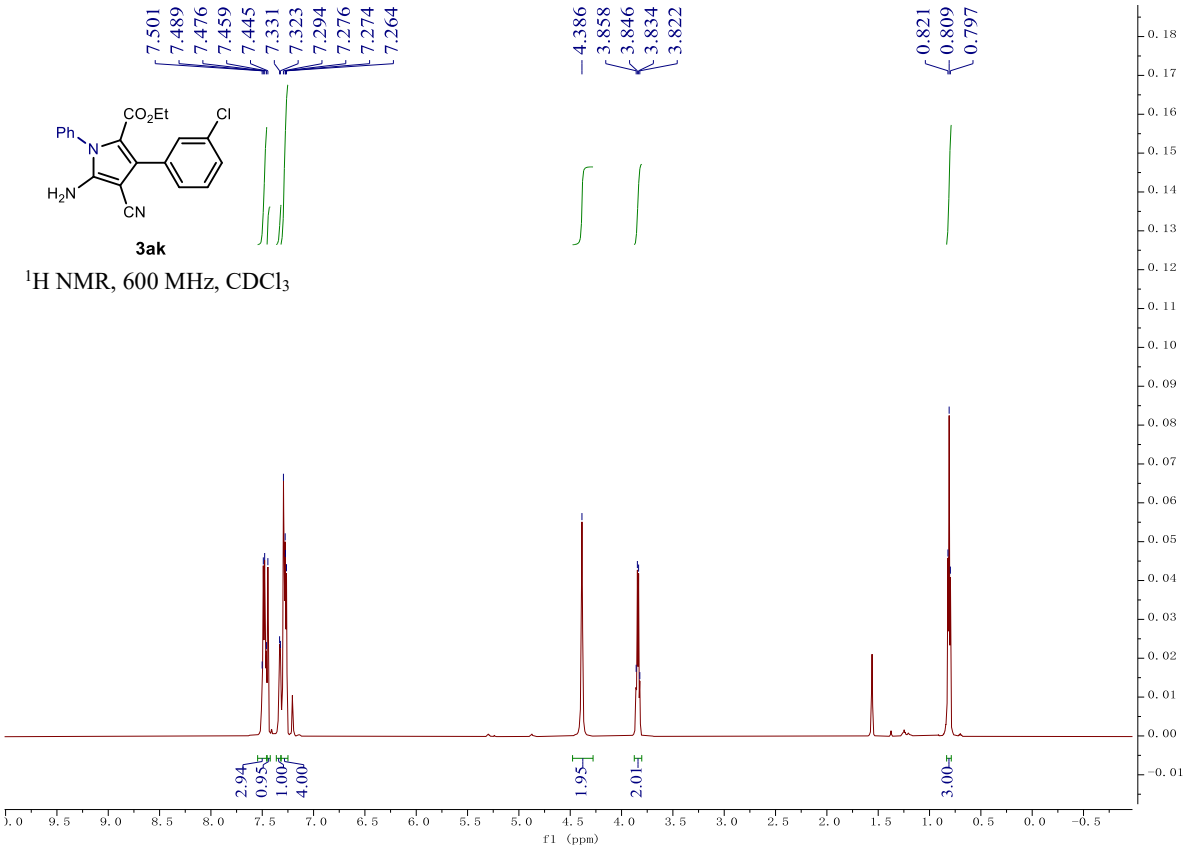
3aj

^{13}C NMR, 150 MHz, $CDCl_3$



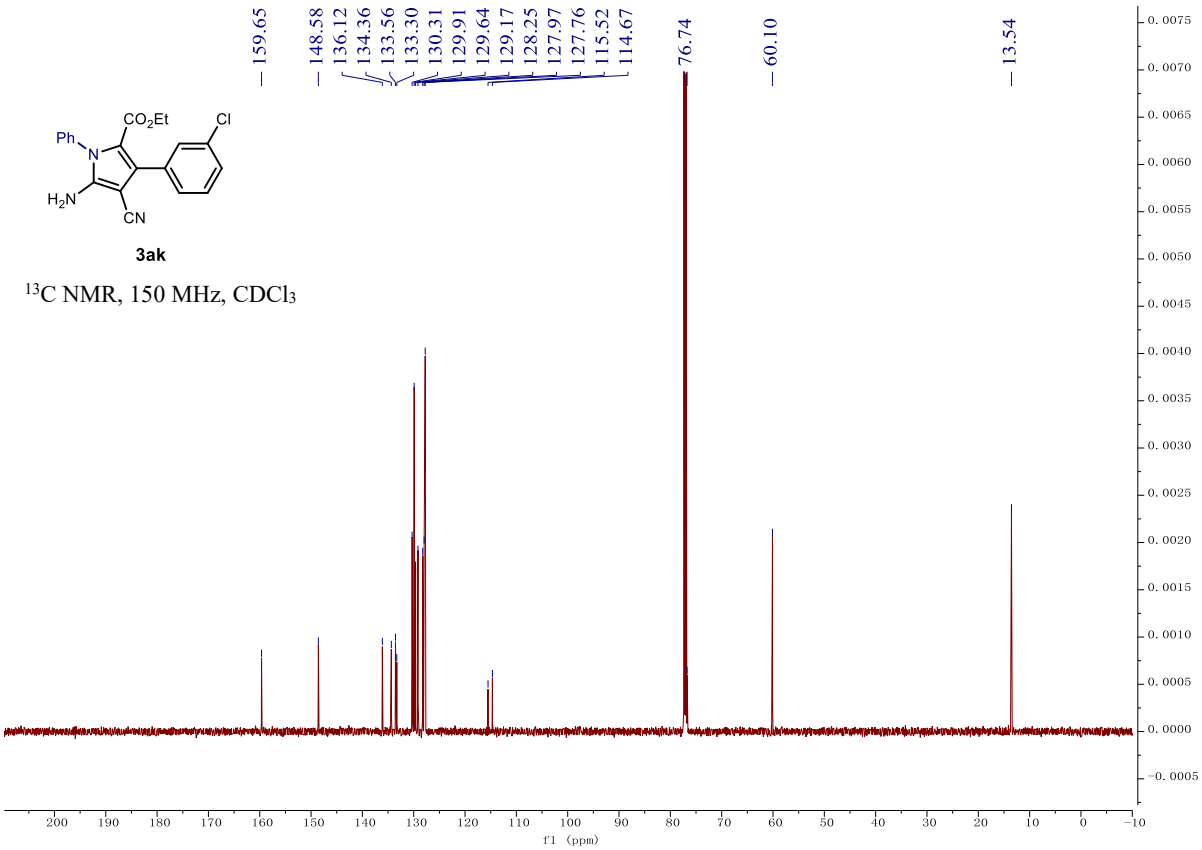
3aj

^{19}F NMR, 564 MHz, $CDCl_3$



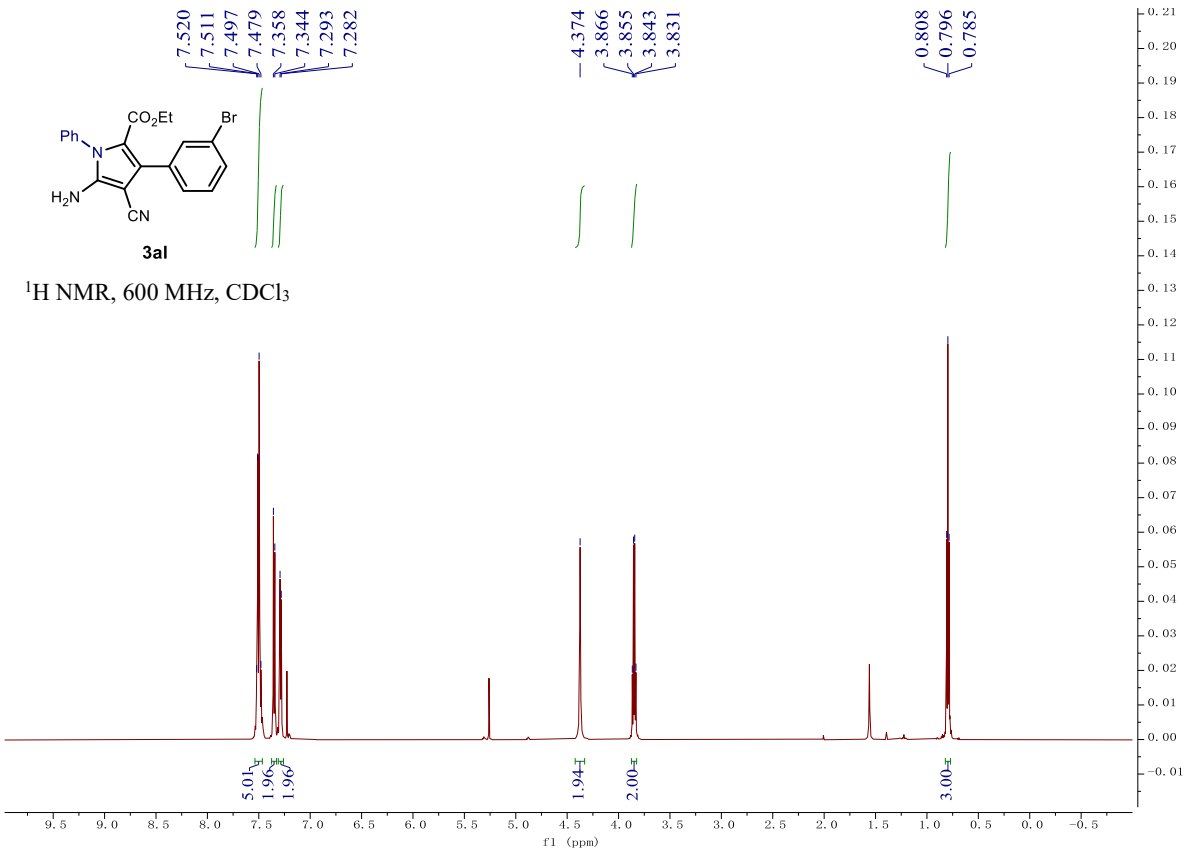
3ak

^{1}H NMR, 600 MHz, $CDCl_3$



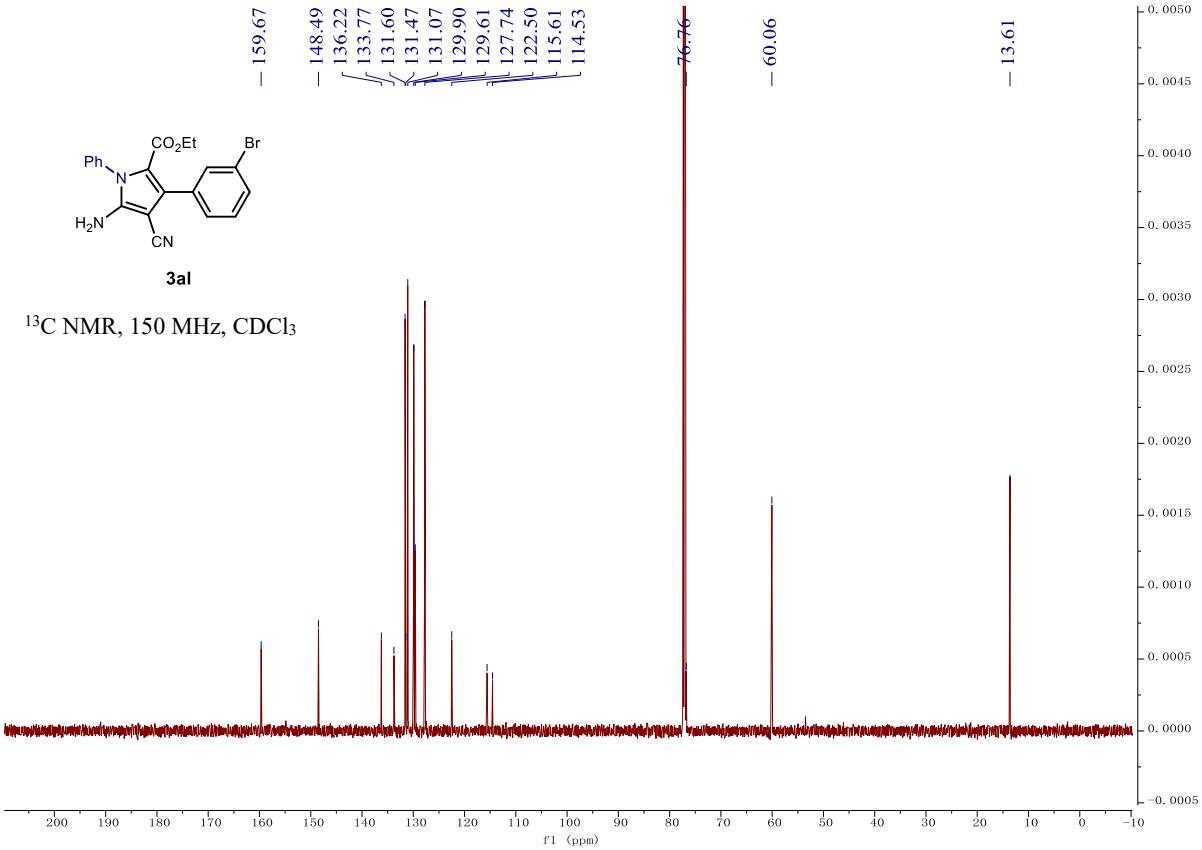
3ak

^{13}C NMR, 150 MHz, $CDCl_3$



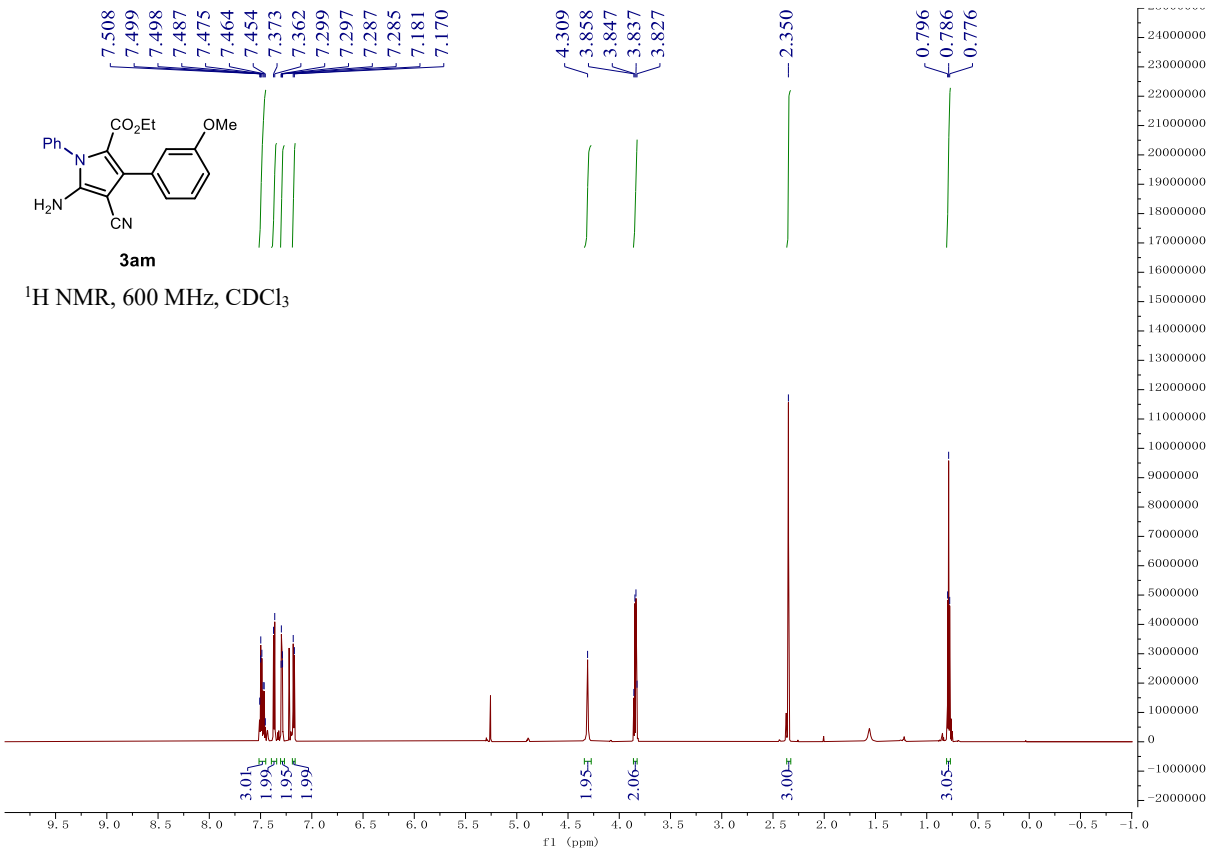
3al

^{1}H NMR, 600 MHz, $CDCl_3$



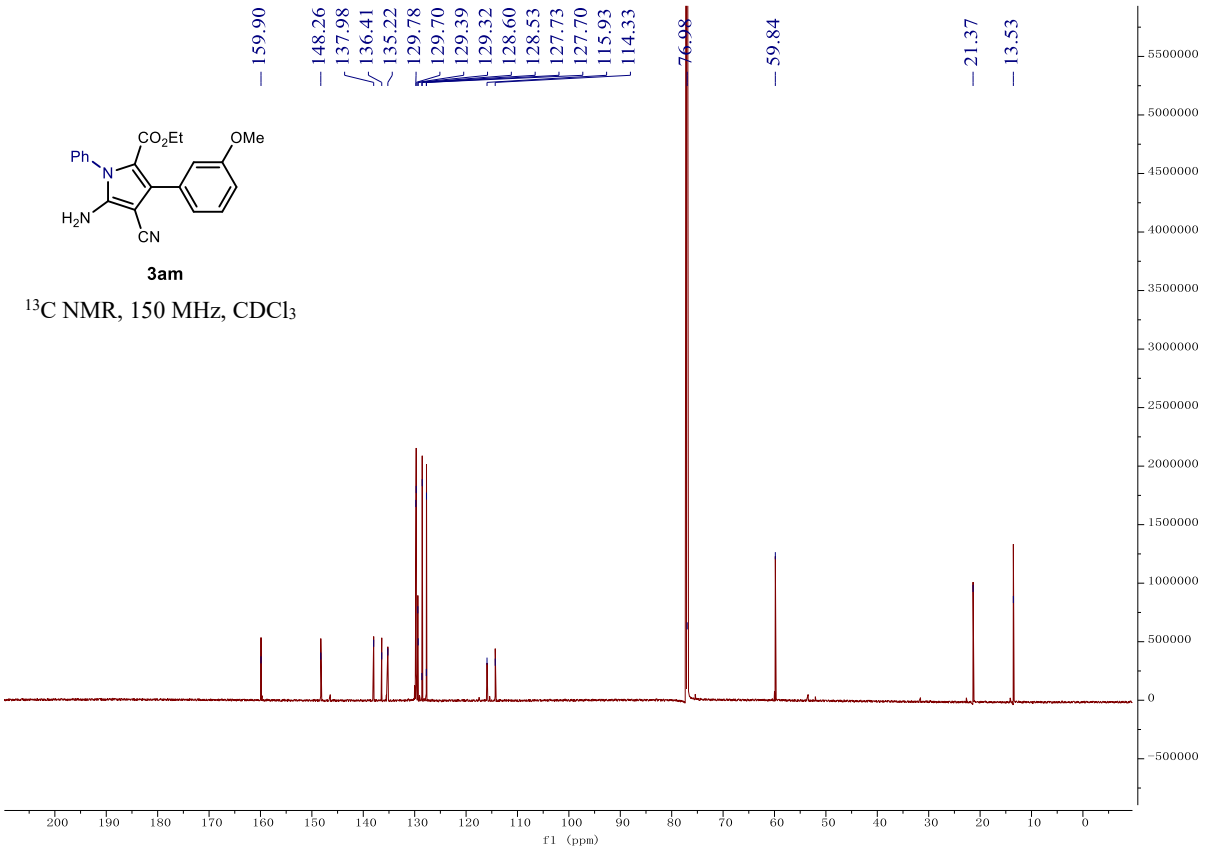
3al

^{13}C NMR, 150 MHz, $CDCl_3$



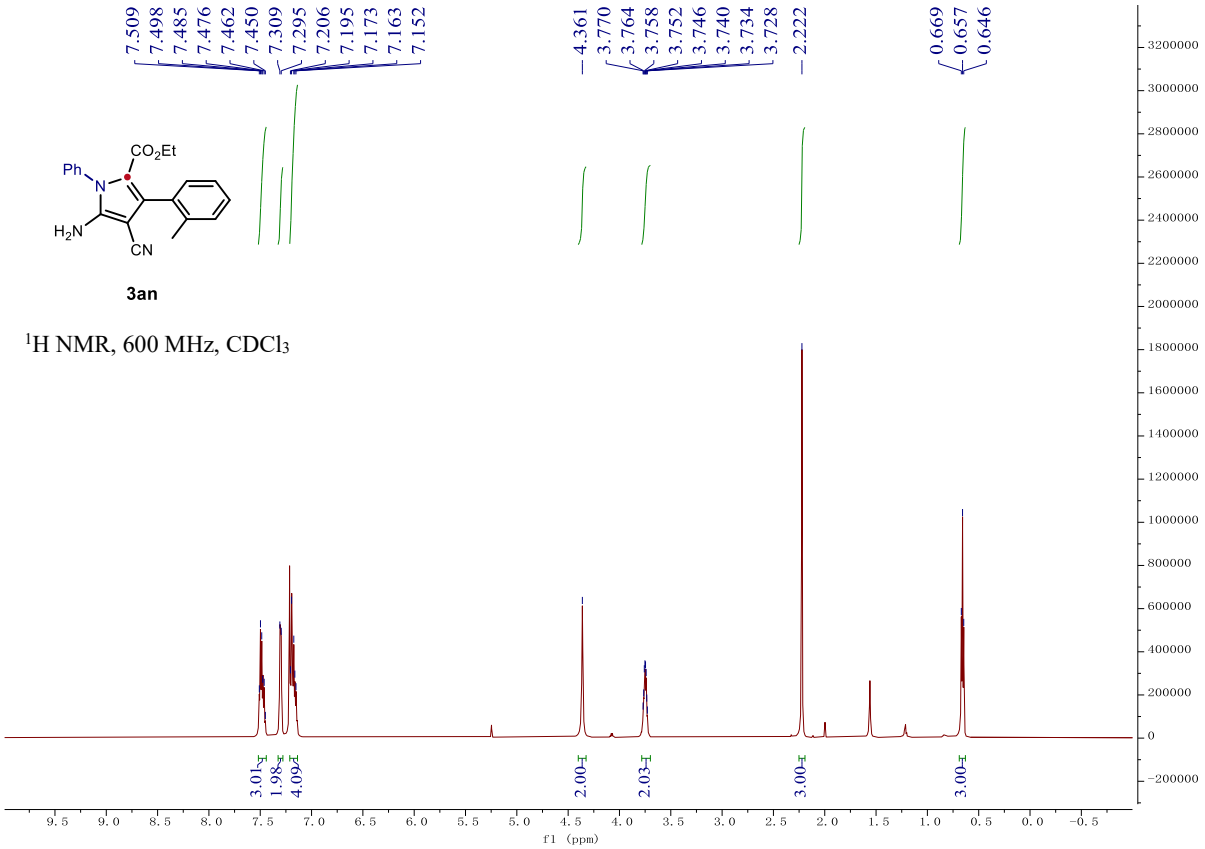
3am

^{1}H NMR, 600 MHz, $CDCl_3$



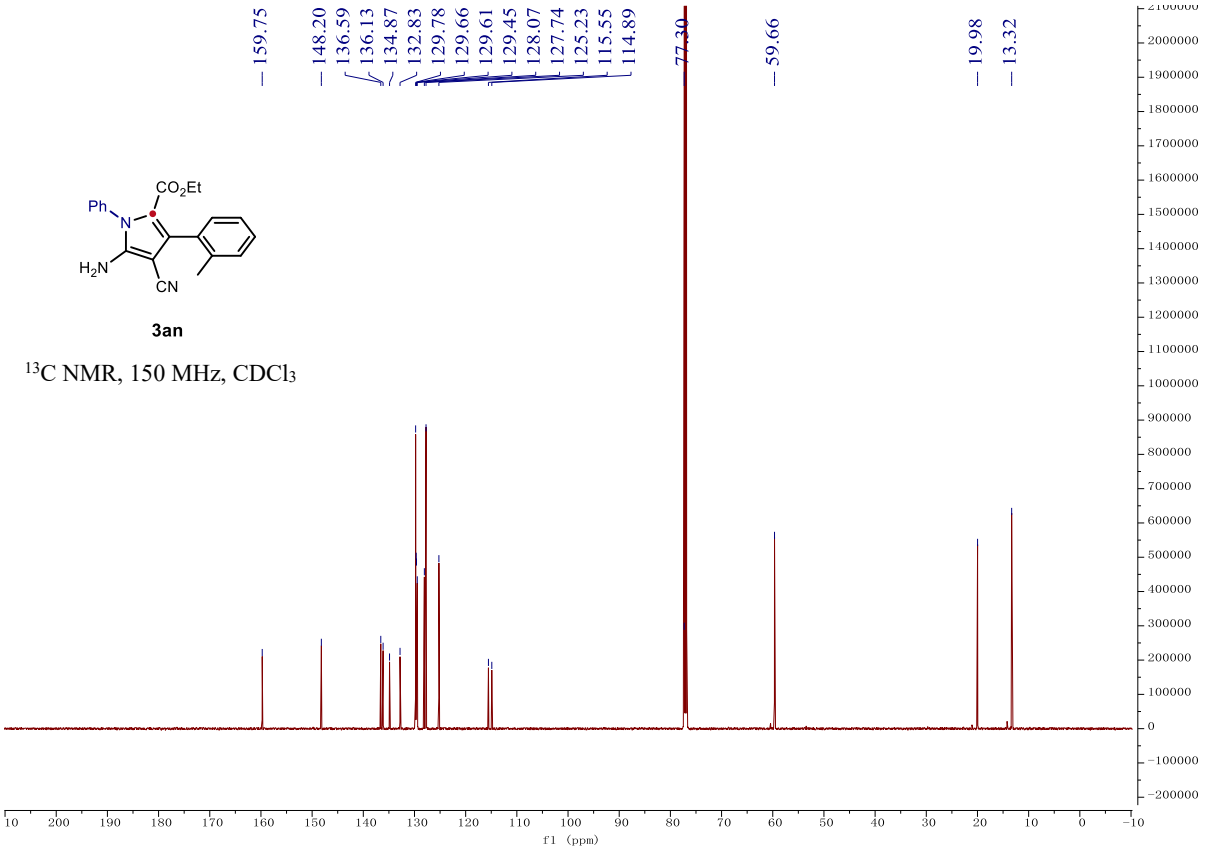
3am

^{13}C NMR, 150 MHz, $CDCl_3$



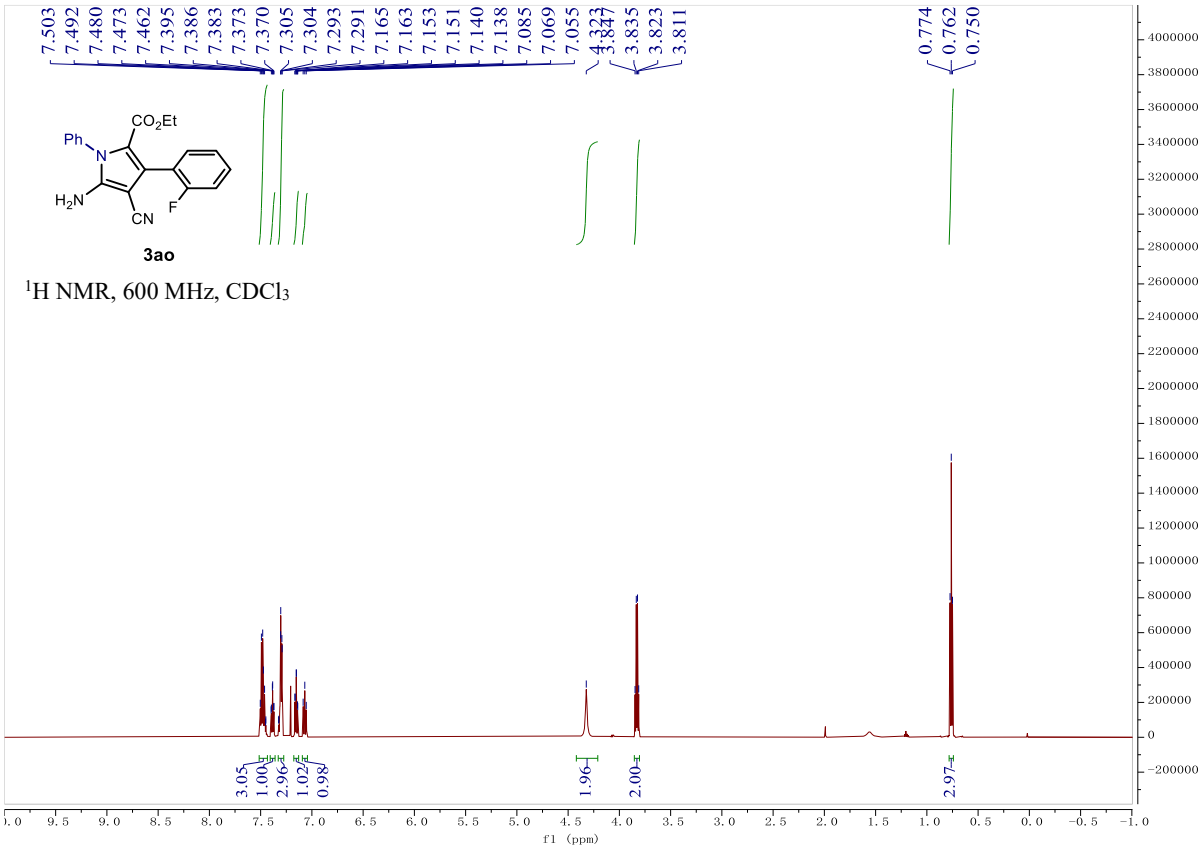
3an

^{1}H NMR, 600 MHz, $CDCl_3$



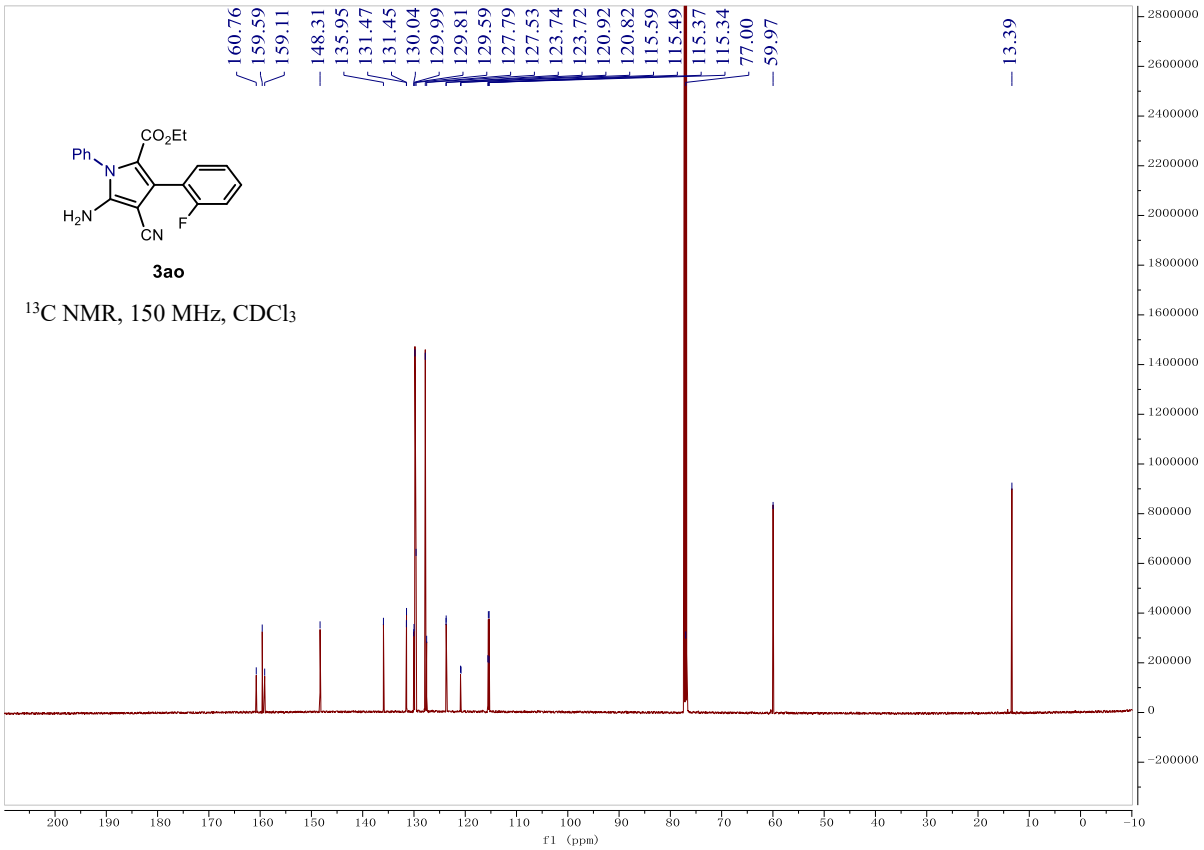
3an

^{13}C NMR, 150 MHz, $CDCl_3$



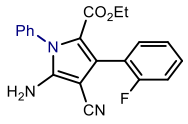
3ao

^{1}H NMR, 600 MHz, $CDCl_3$



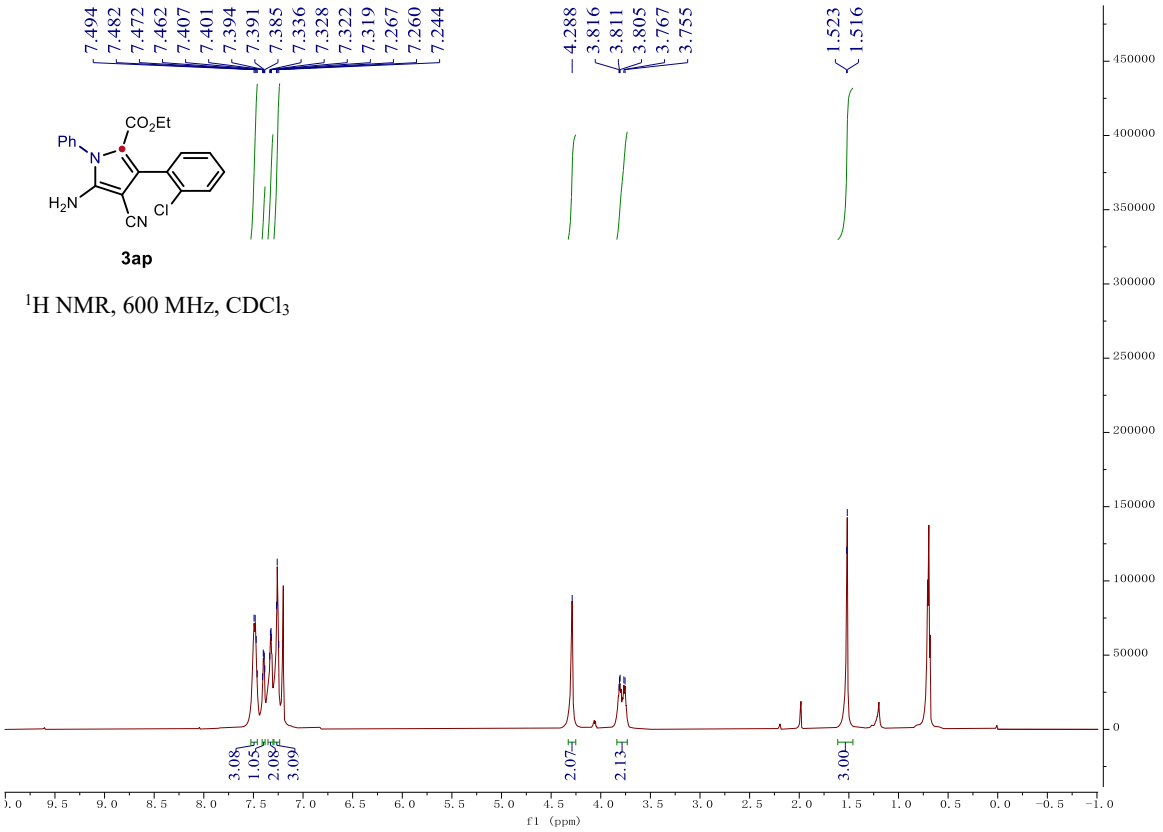
3ao

^{13}C NMR, 150 MHz, $CDCl_3$



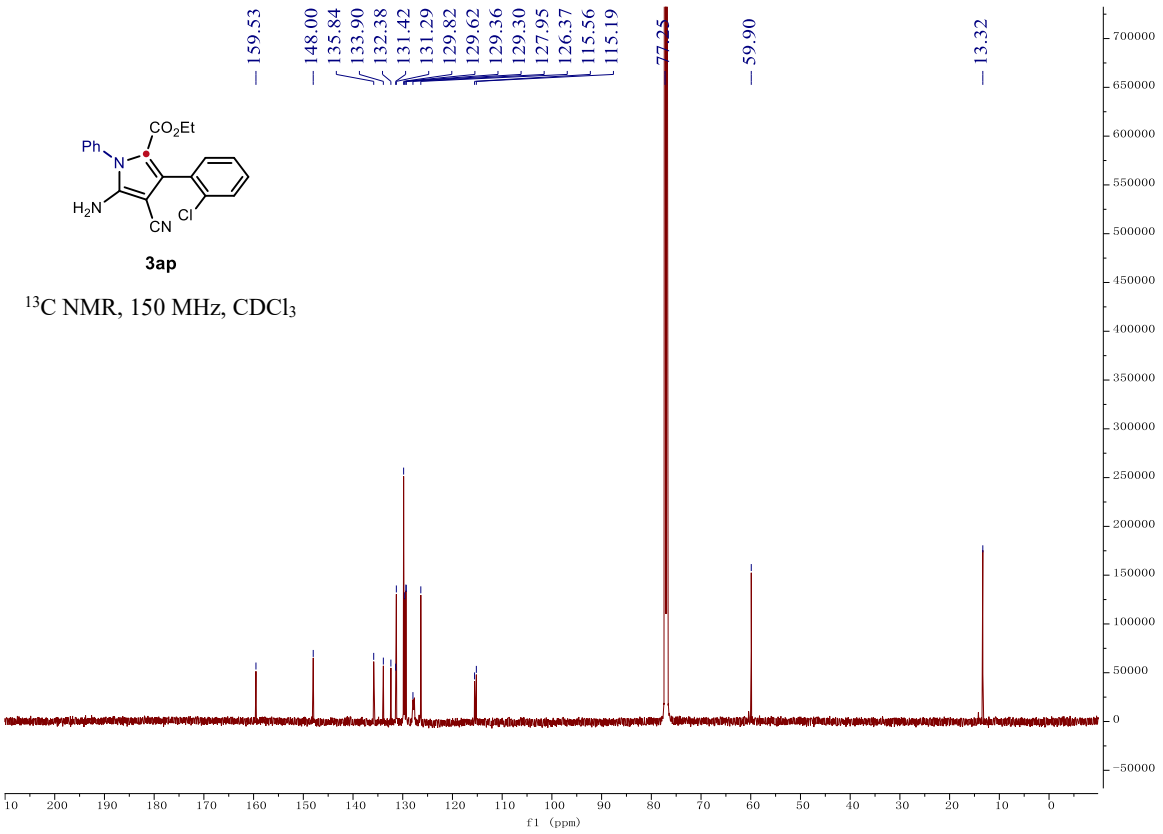
3ao

^{19}F NMR, 564 MHz, $CDCl_3$



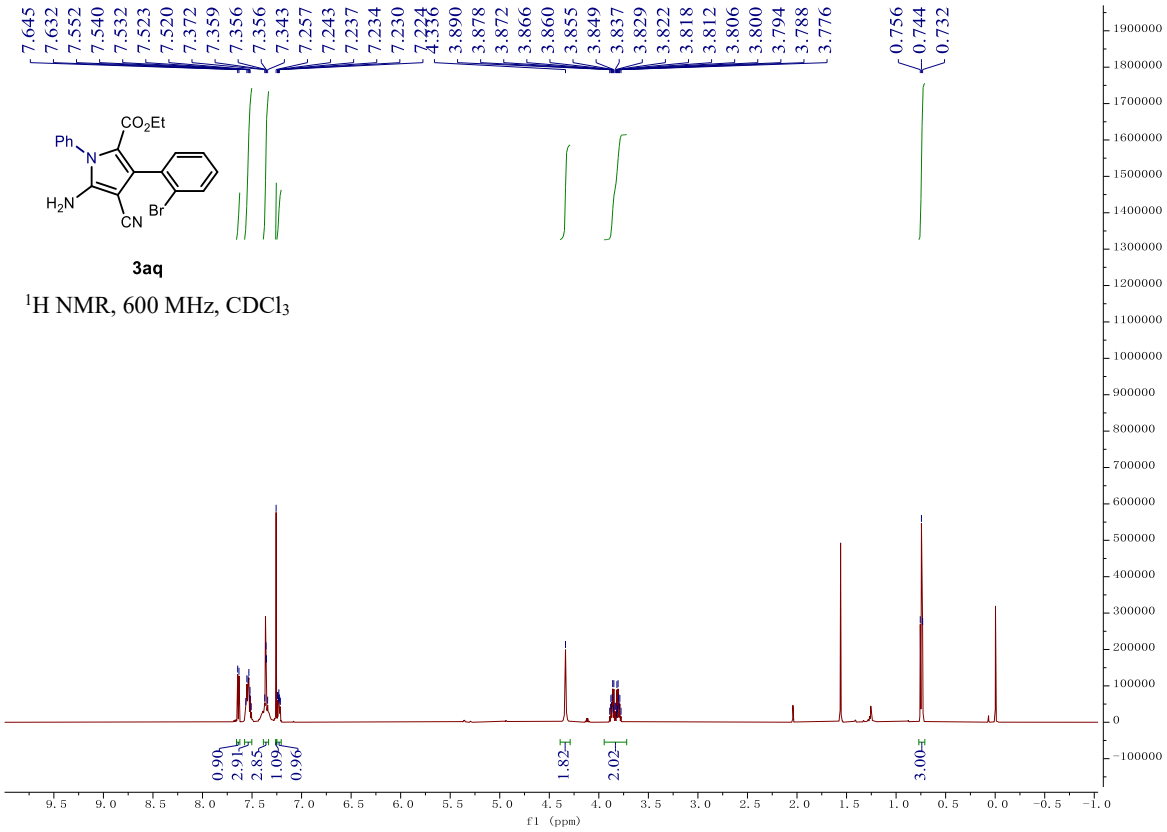
3ap

^{1}H NMR, 600 MHz, $CDCl_3$



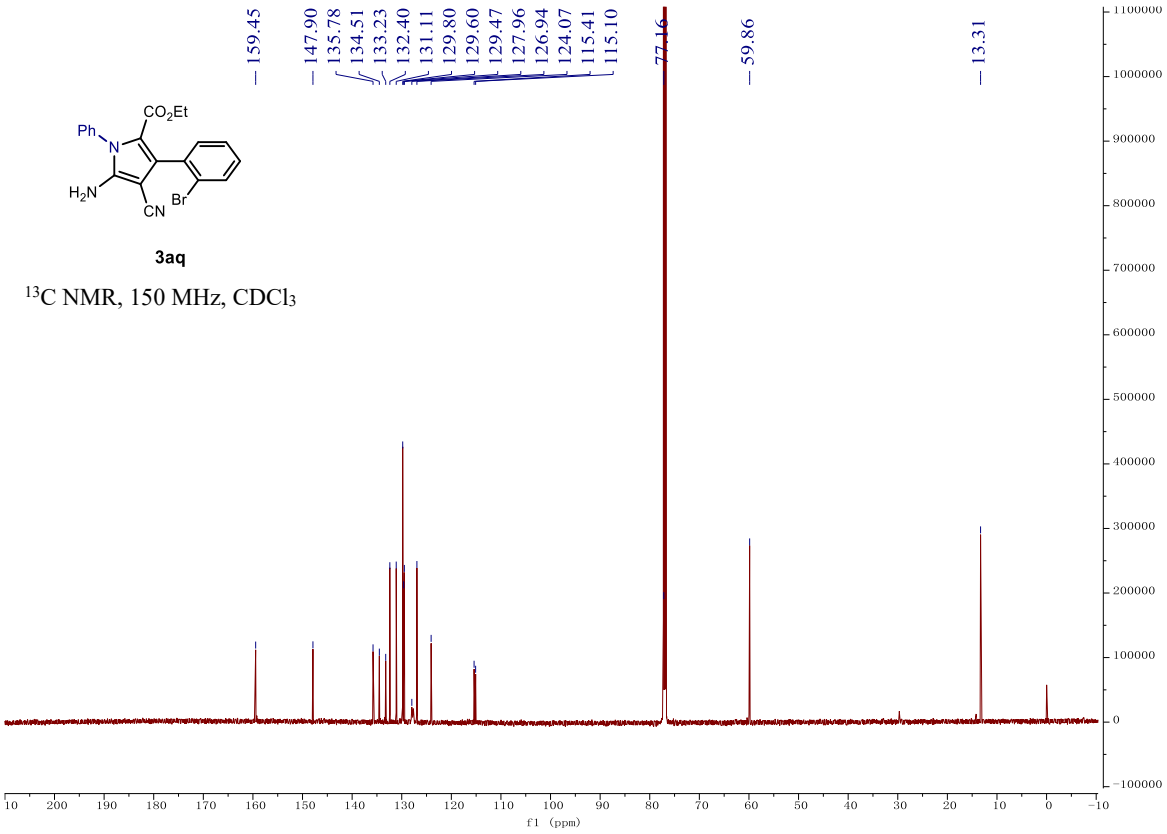
3ap

^{13}C NMR, 150 MHz, $CDCl_3$



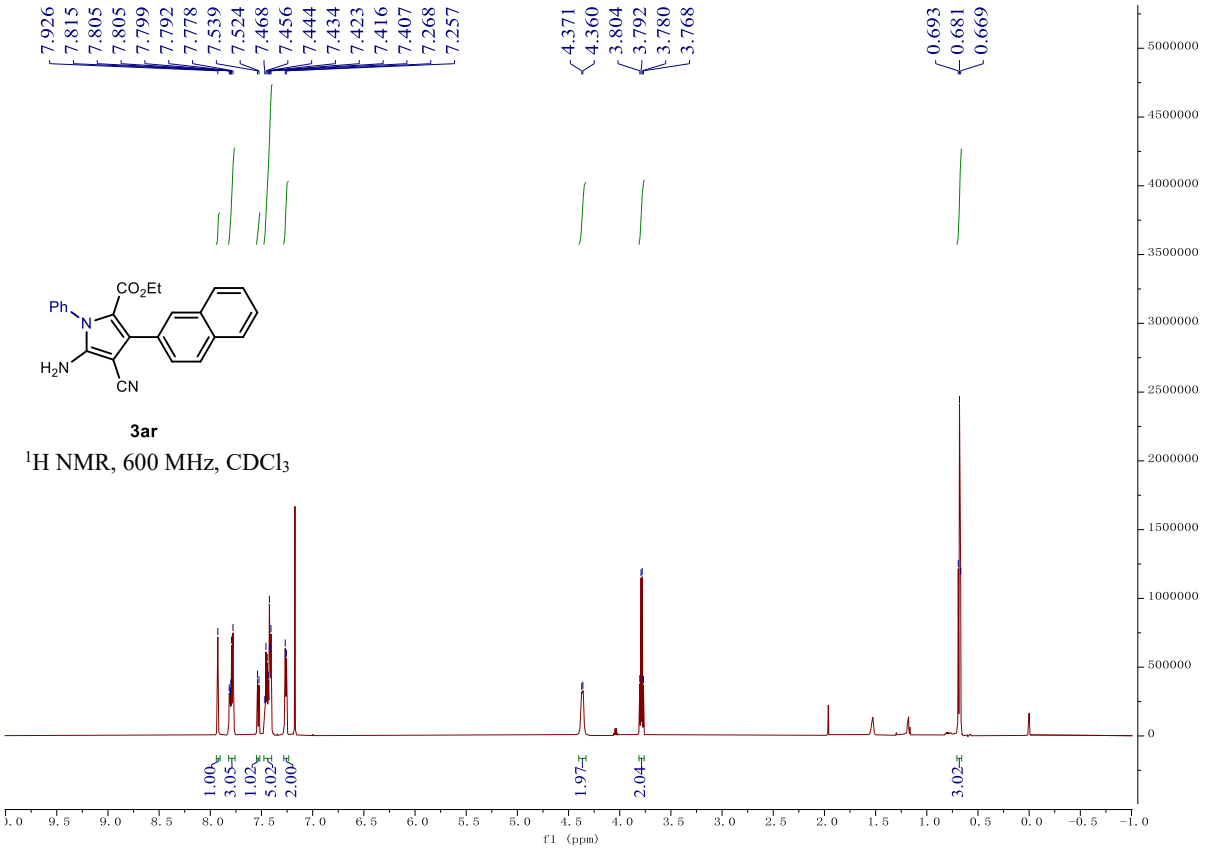
3aq

^{1}H NMR, 600 MHz, $CDCl_3$



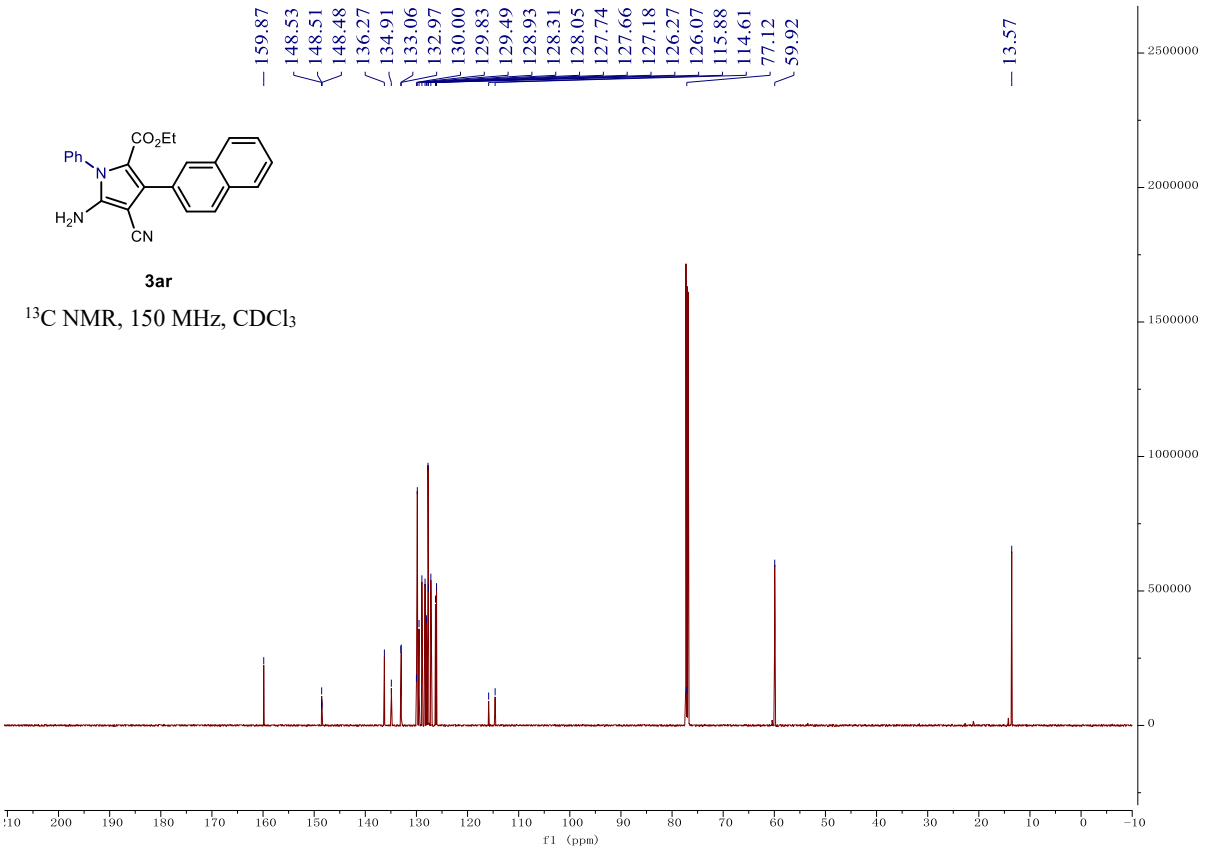
3aq

^{13}C NMR, 150 MHz, $CDCl_3$



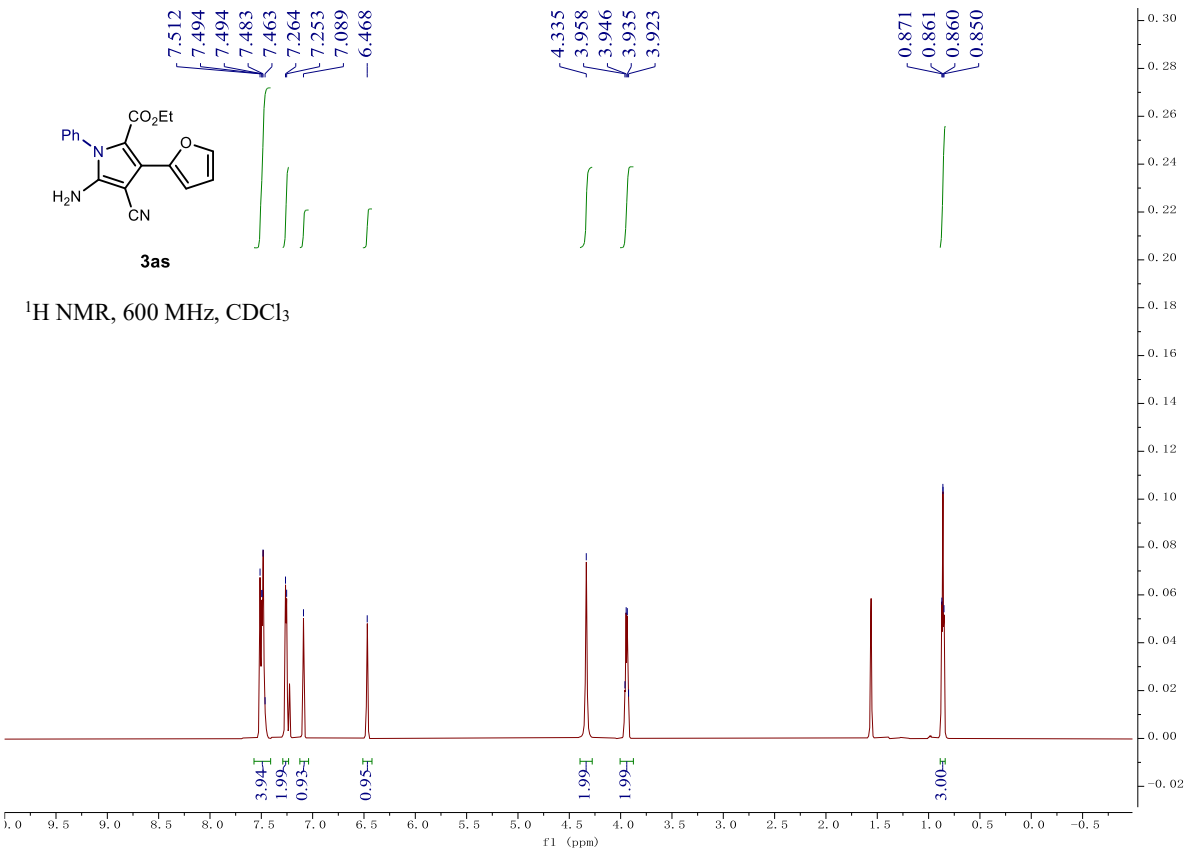
3ar

^{1}H NMR, 600 MHz, $CDCl_3$



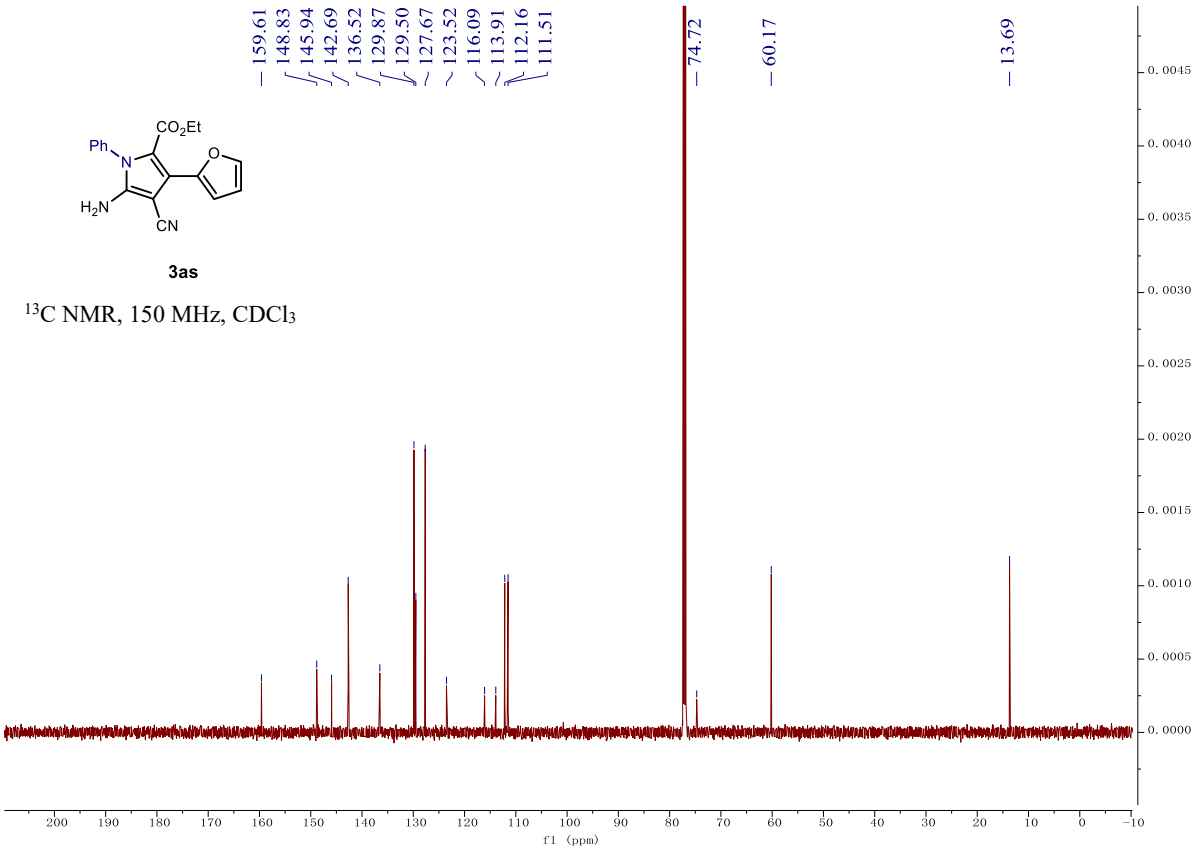
3ar

^{13}C NMR, 150 MHz, $CDCl_3$



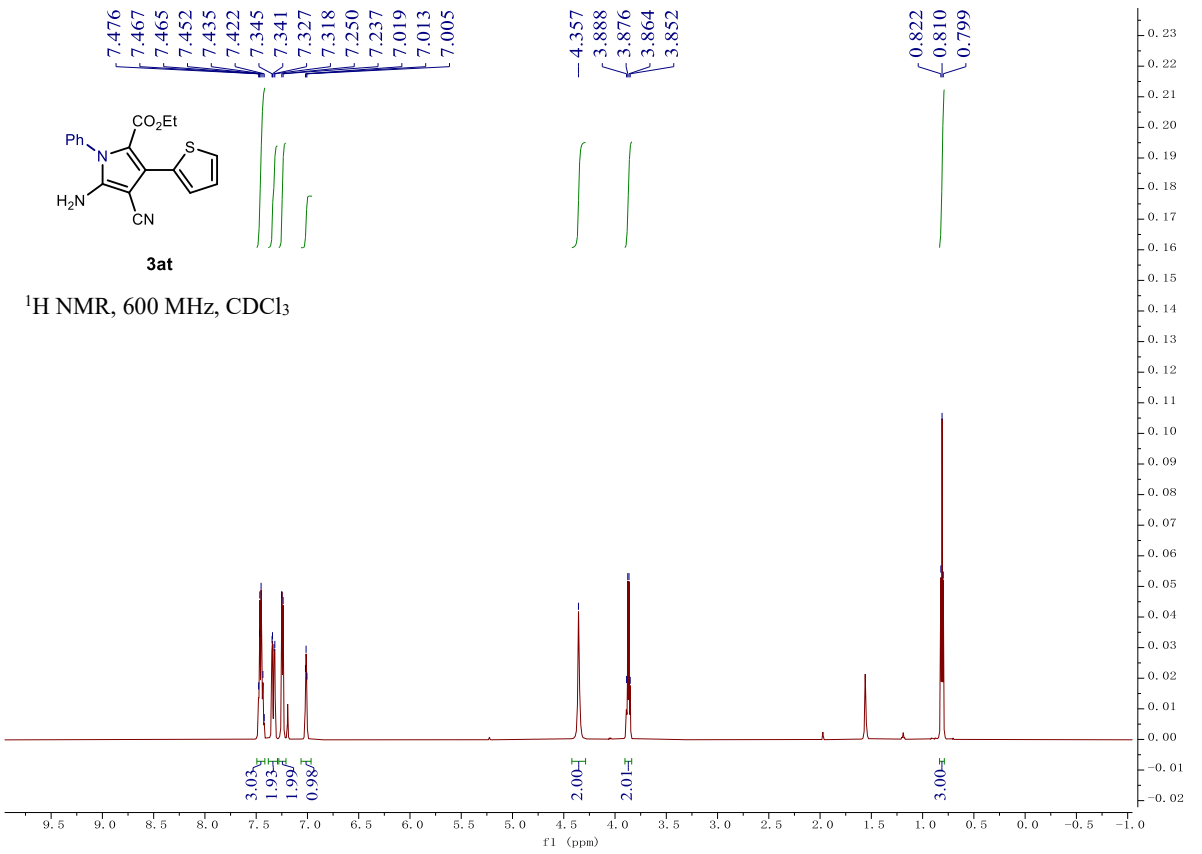
3as

^{1}H NMR, 600 MHz, $CDCl_3$



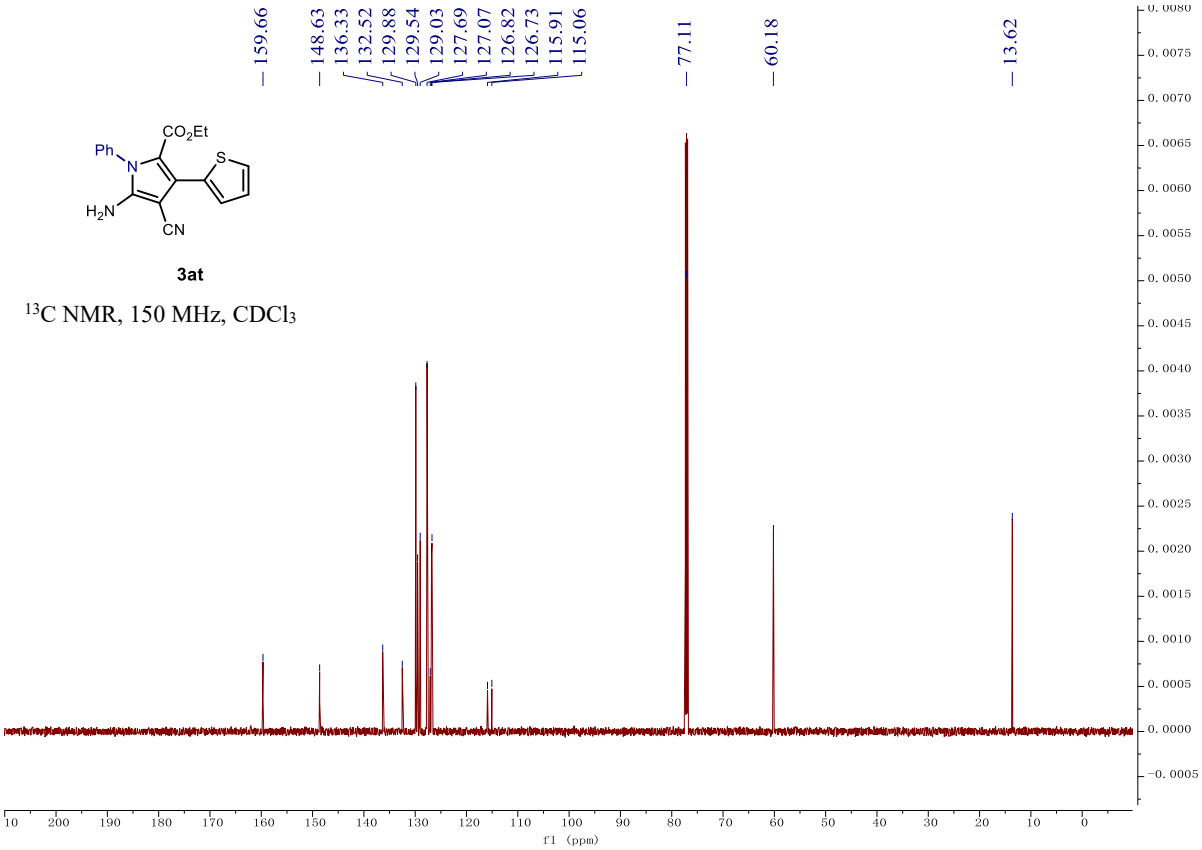
3as

^{13}C NMR, 150 MHz, $CDCl_3$



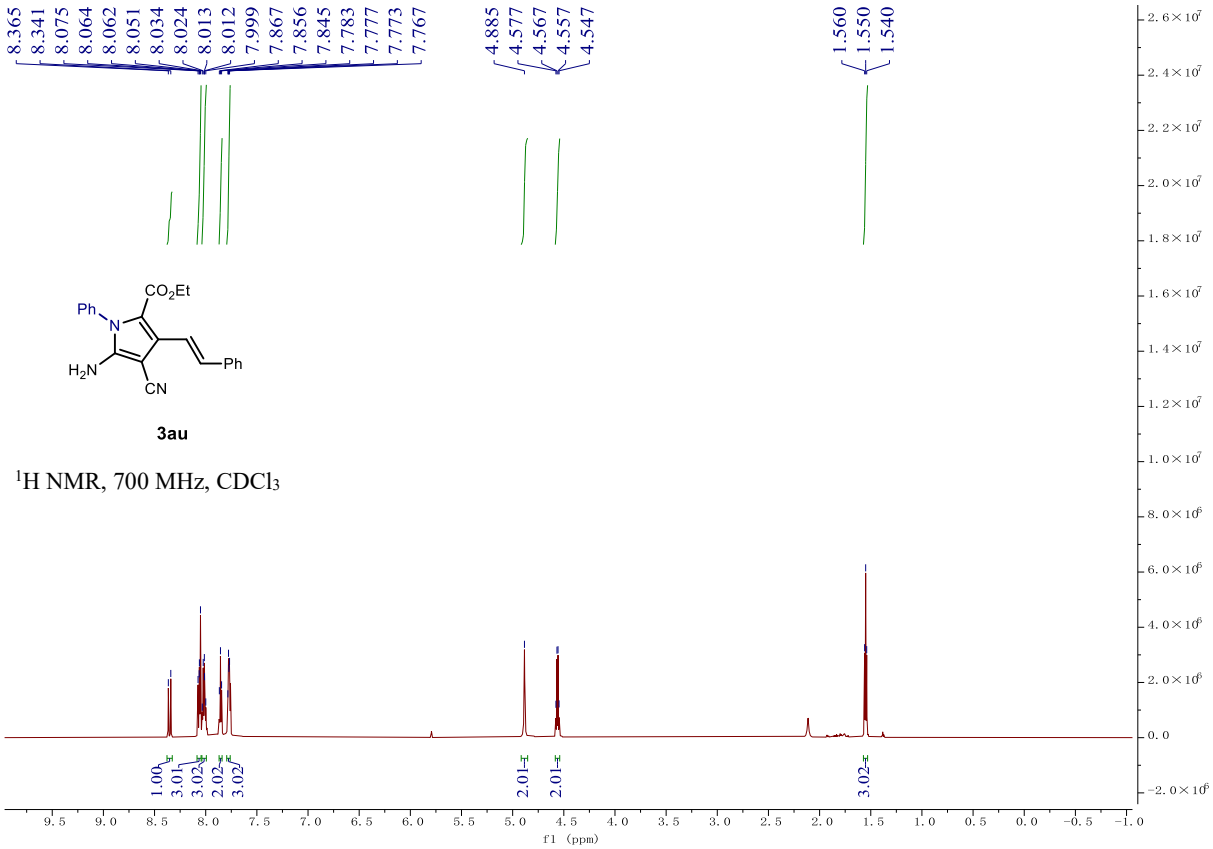
3at

^{1}H NMR, 600 MHz, $CDCl_3$



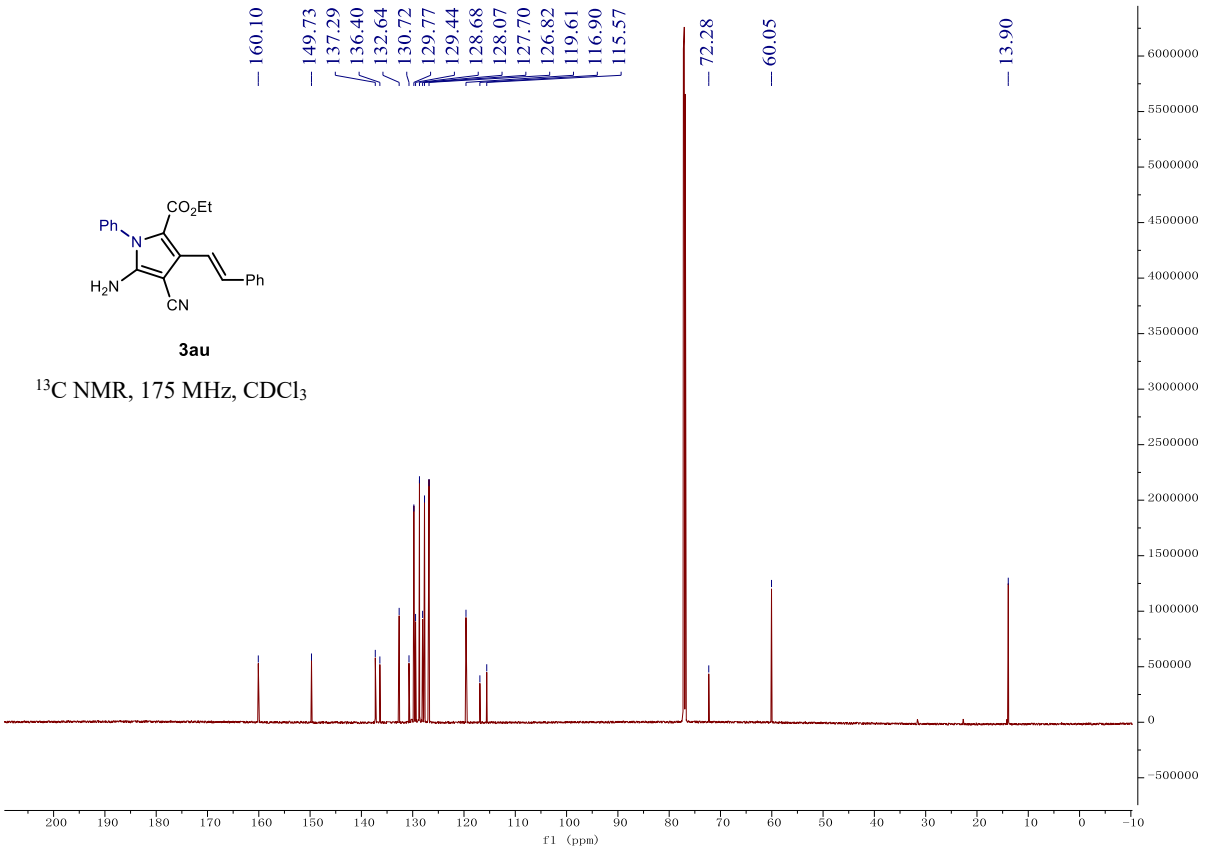
3at

^{13}C NMR, 150 MHz, $CDCl_3$



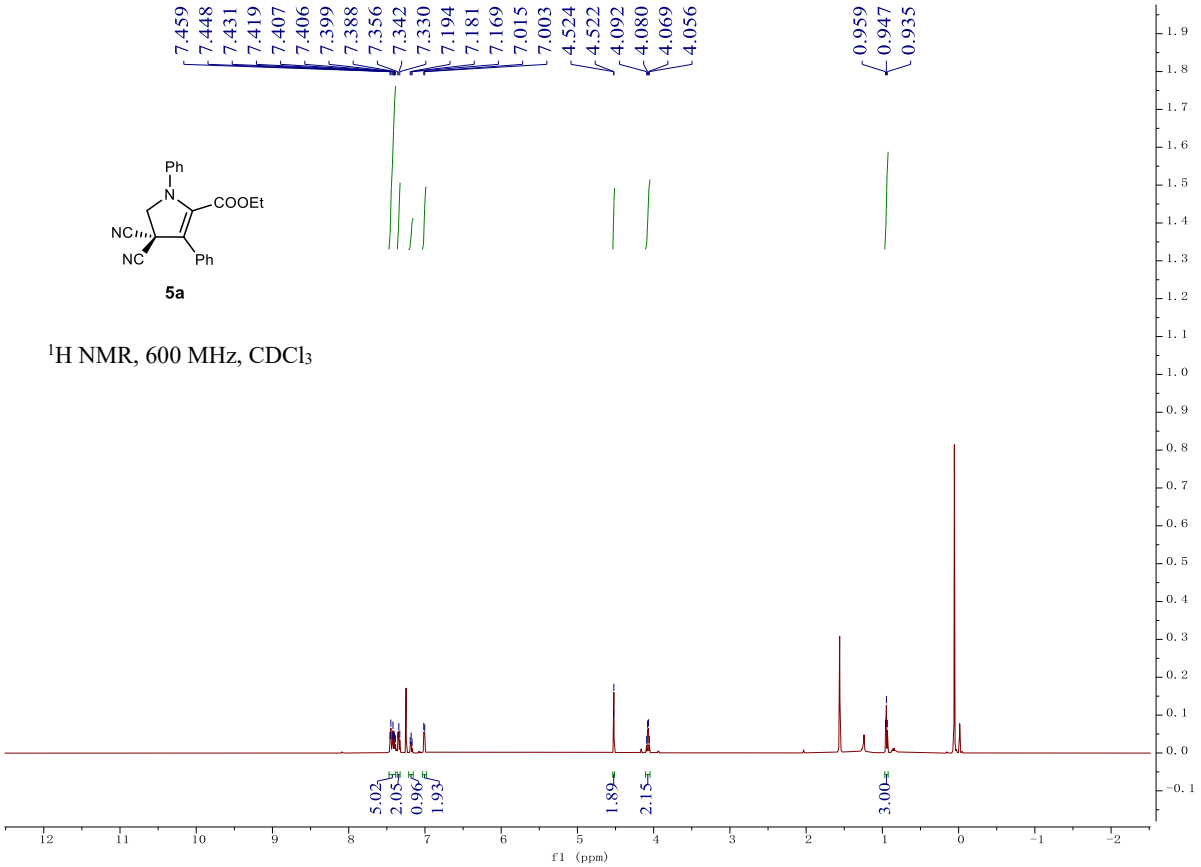
3au

^{1}H NMR, 700 MHz, $CDCl_3$



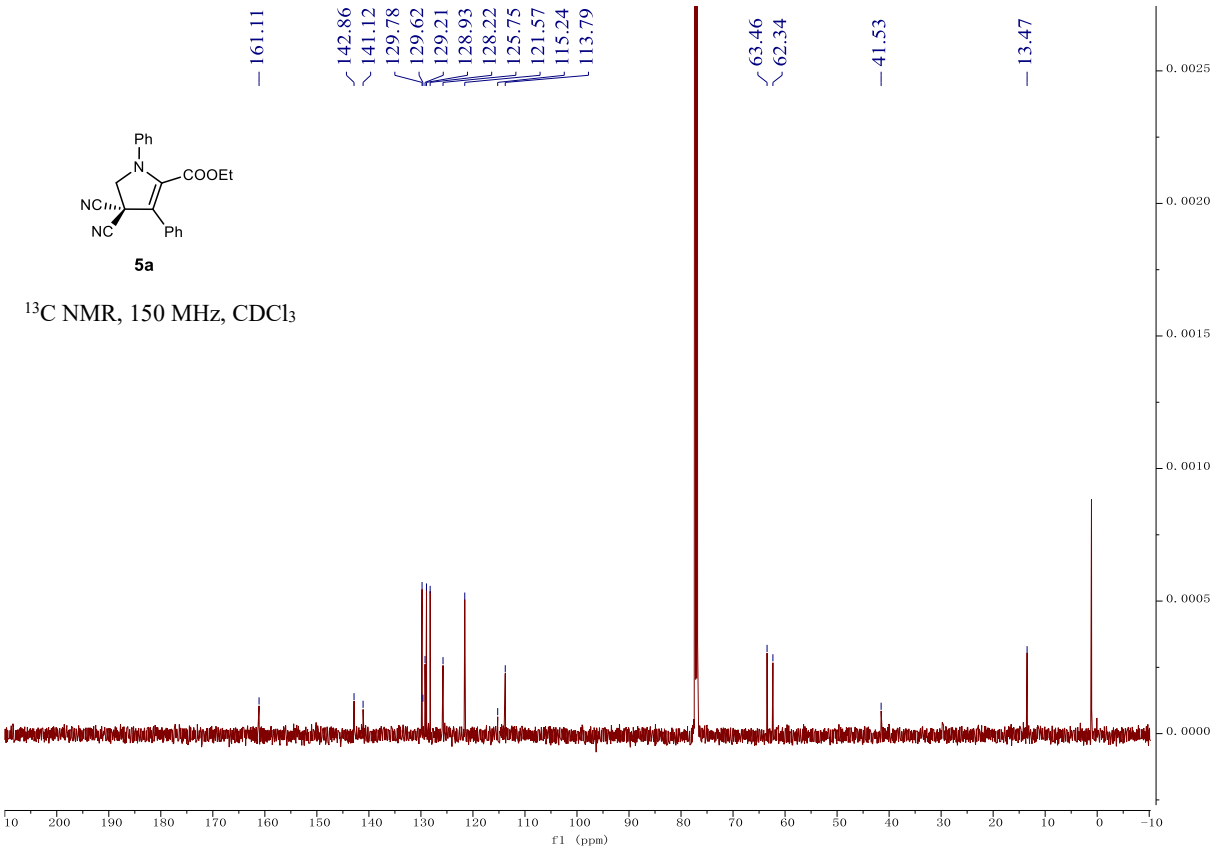
3au

^{13}C NMR, 175 MHz, $CDCl_3$



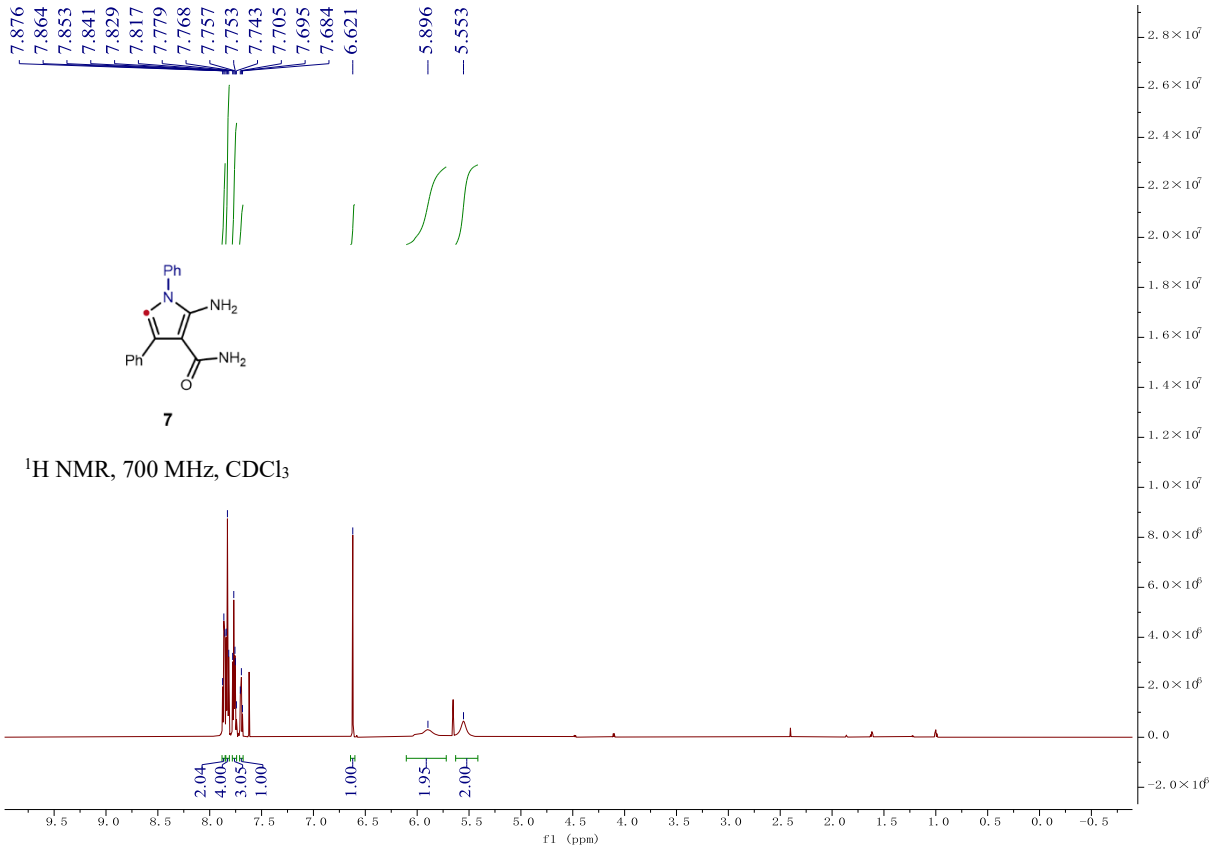
5a

^{1}H NMR, 600 MHz, $CDCl_3$



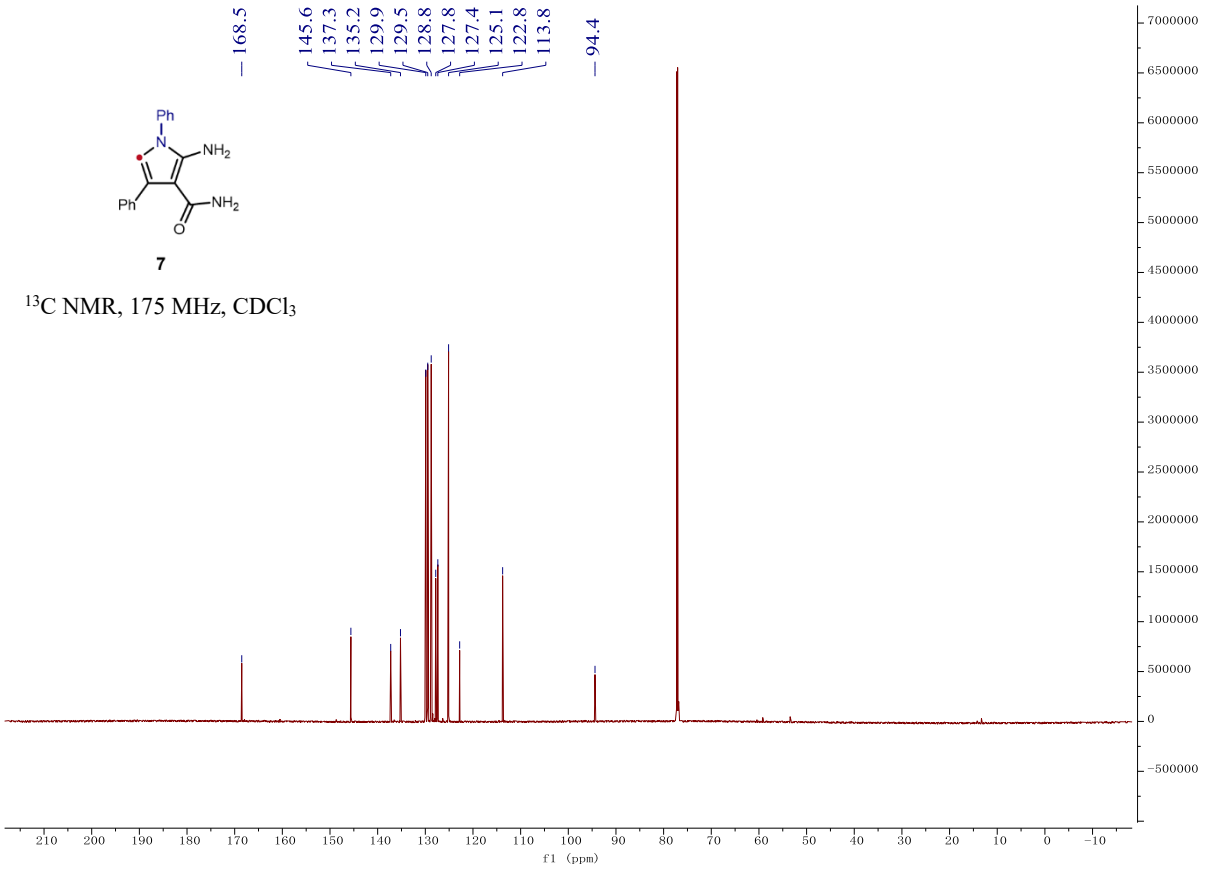
5a

^{13}C NMR, 150 MHz, $CDCl_3$



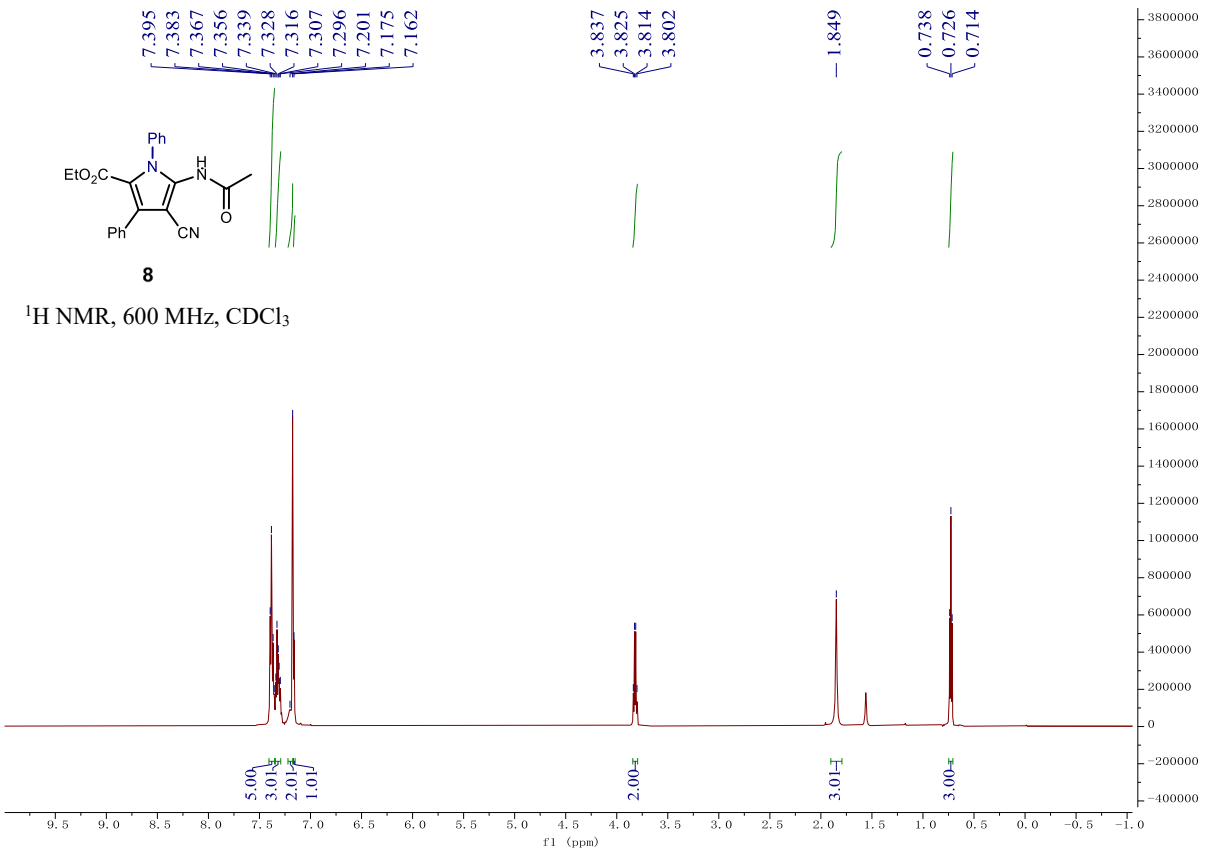
7

^{1}H NMR, 700 MHz, $CDCl_3$



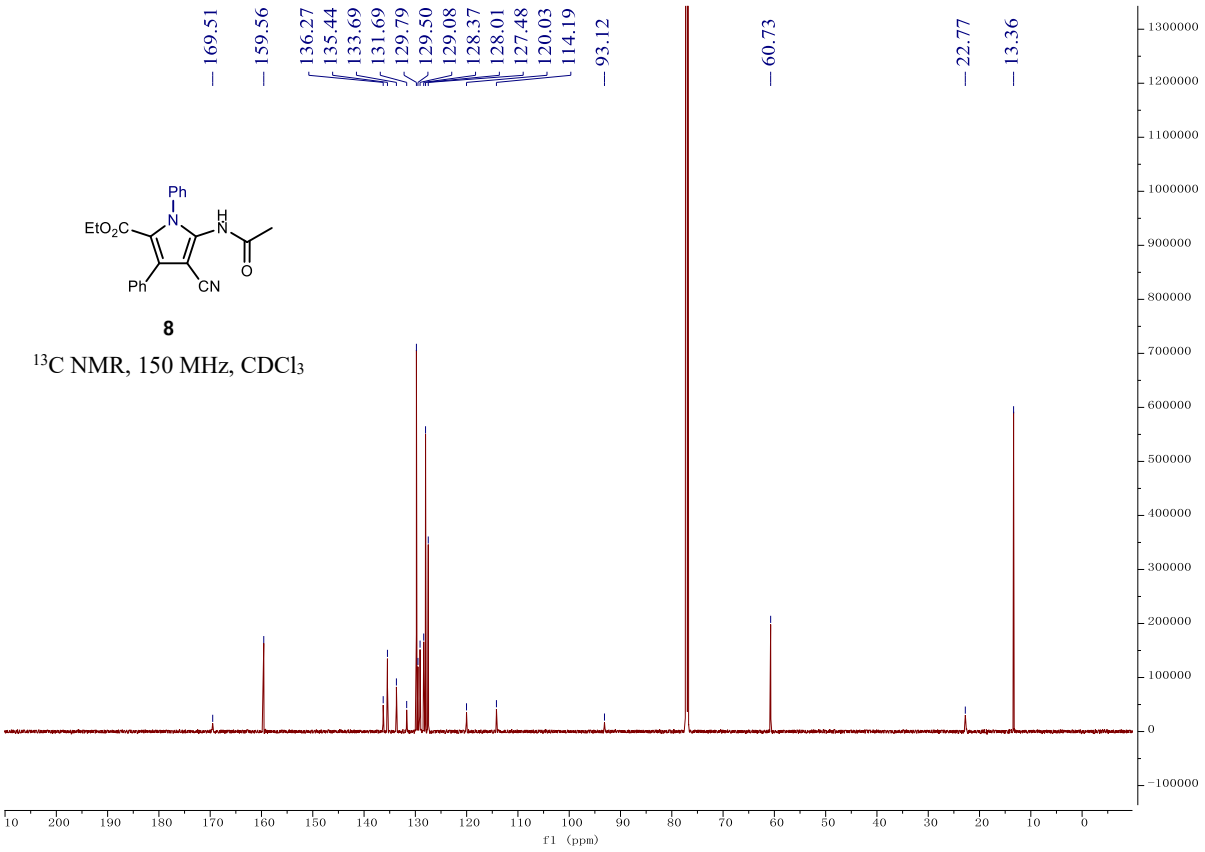
7

^{13}C NMR, 175 MHz, $CDCl_3$



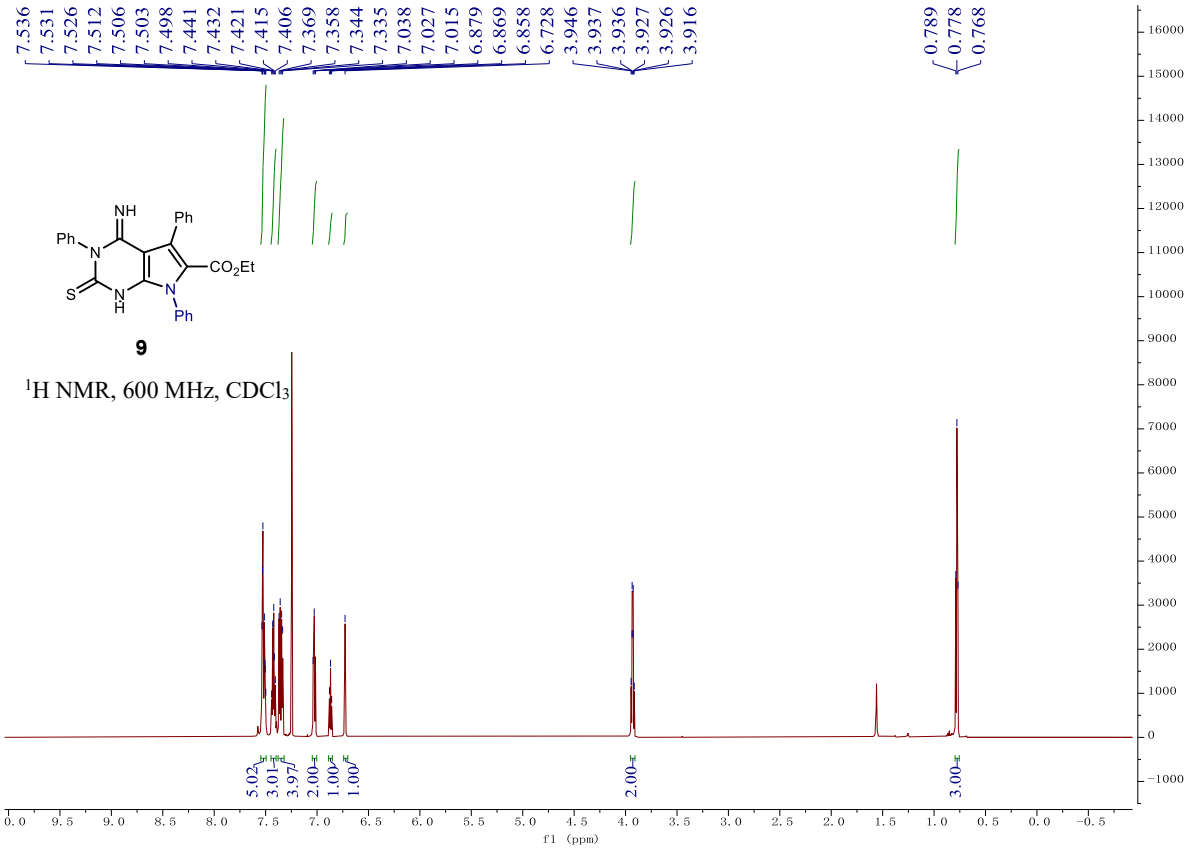
8

^{1}H NMR, 600 MHz, $CDCl_3$



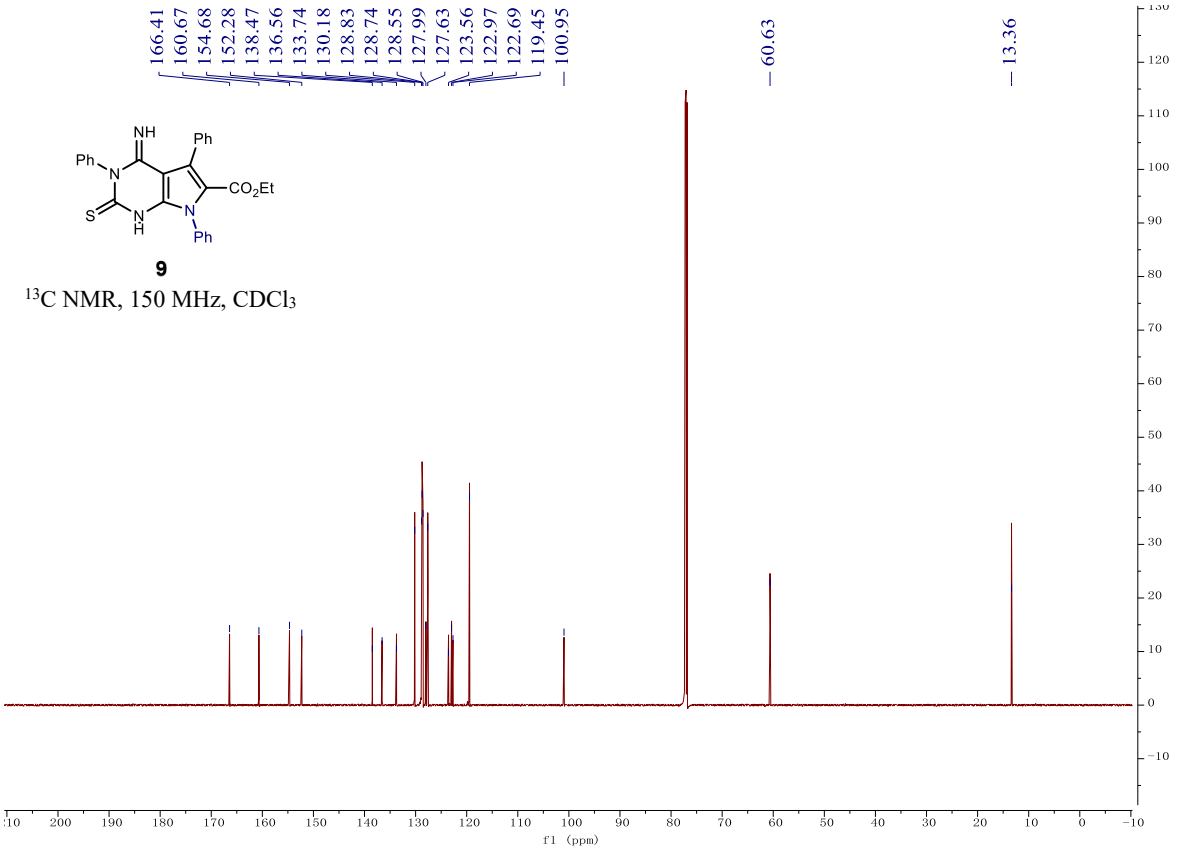
8

^{13}C NMR, 150 MHz, $CDCl_3$



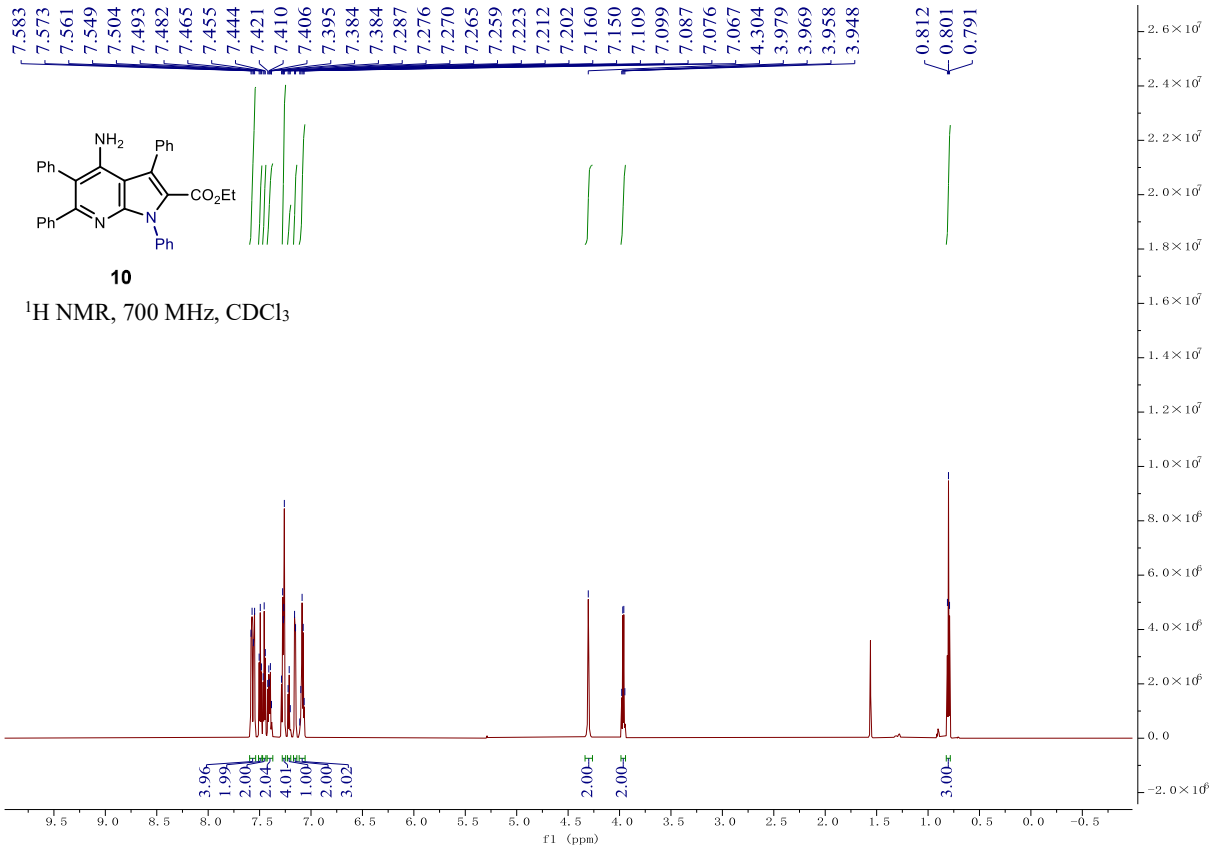
9

^{1}H NMR, 600 MHz, $CDCl_3$



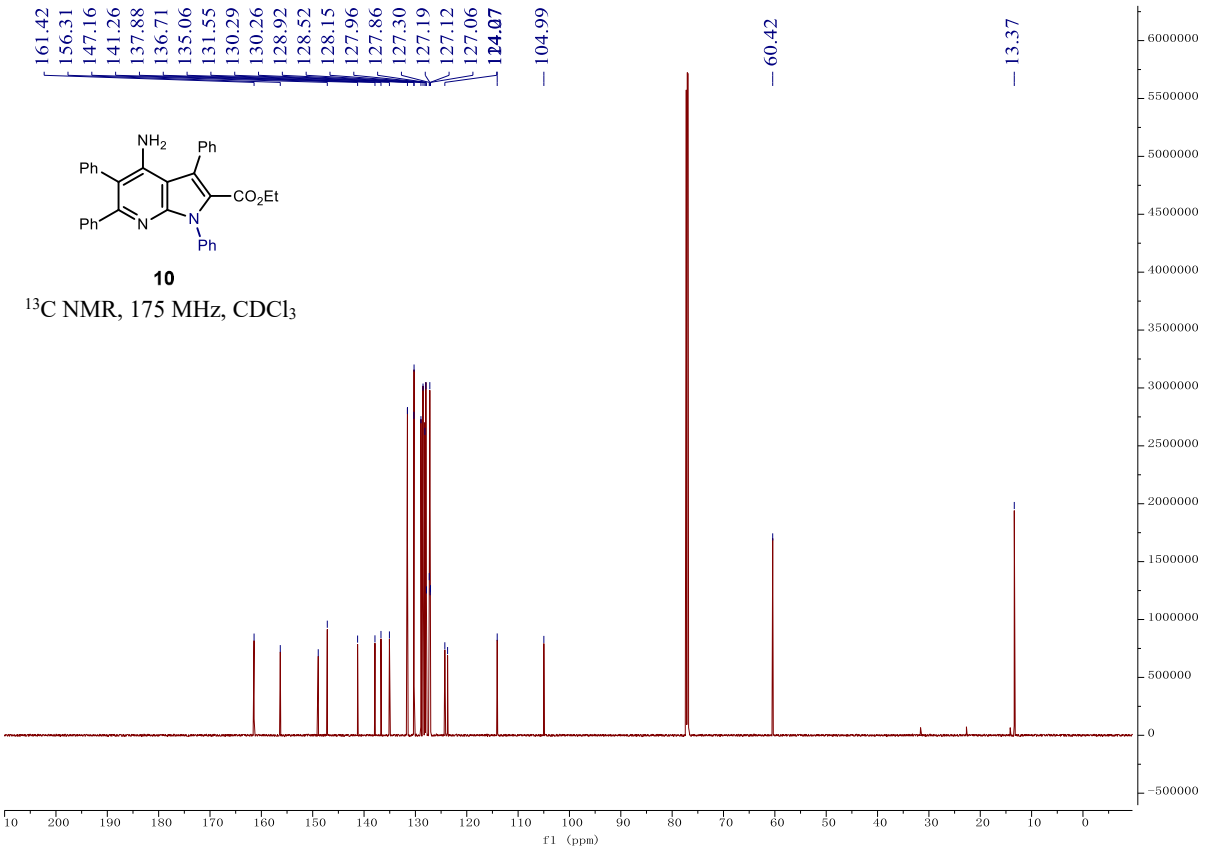
9

^{13}C NMR, 150 MHz, $CDCl_3$



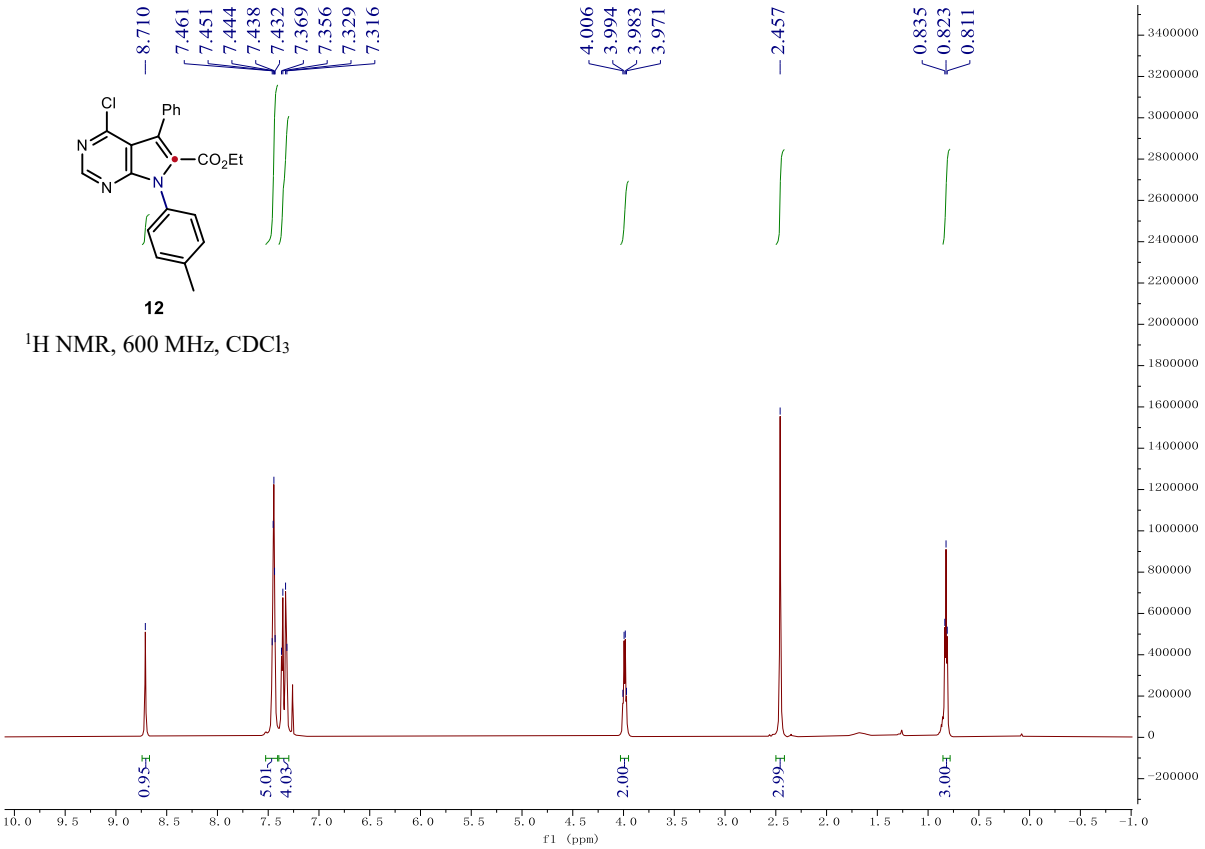
10

^{1}H NMR, 700 MHz, $CDCl_3$



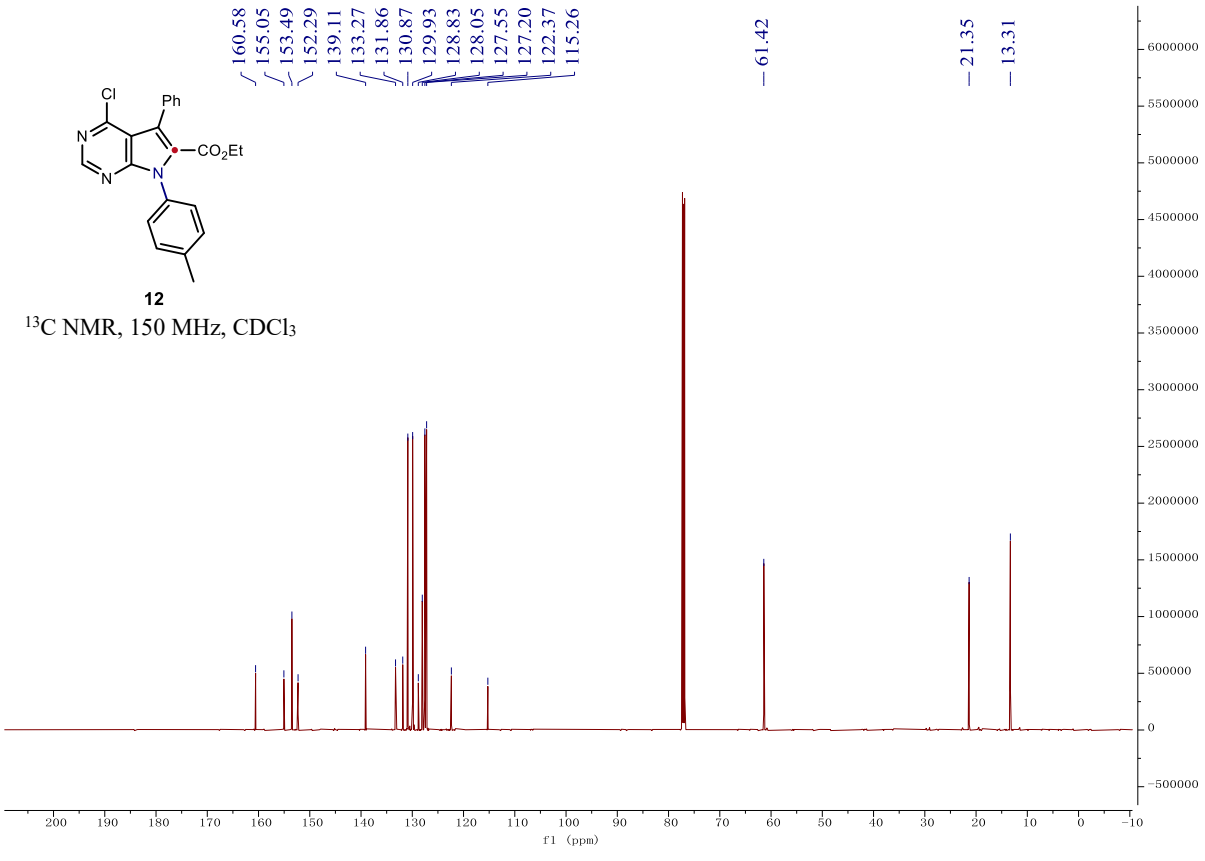
10

^{13}C NMR, 175 MHz, $CDCl_3$



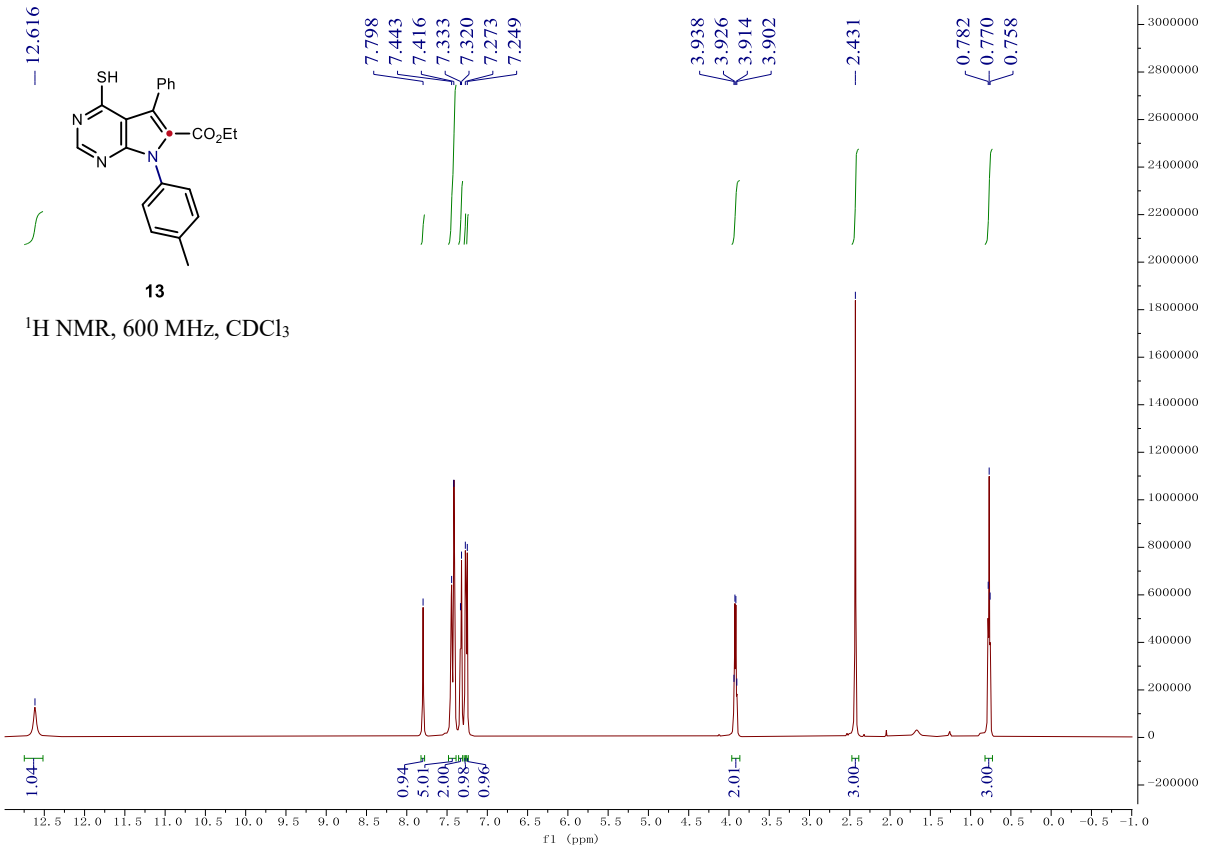
12

^{1}H NMR, 600 MHz, $CDCl_3$



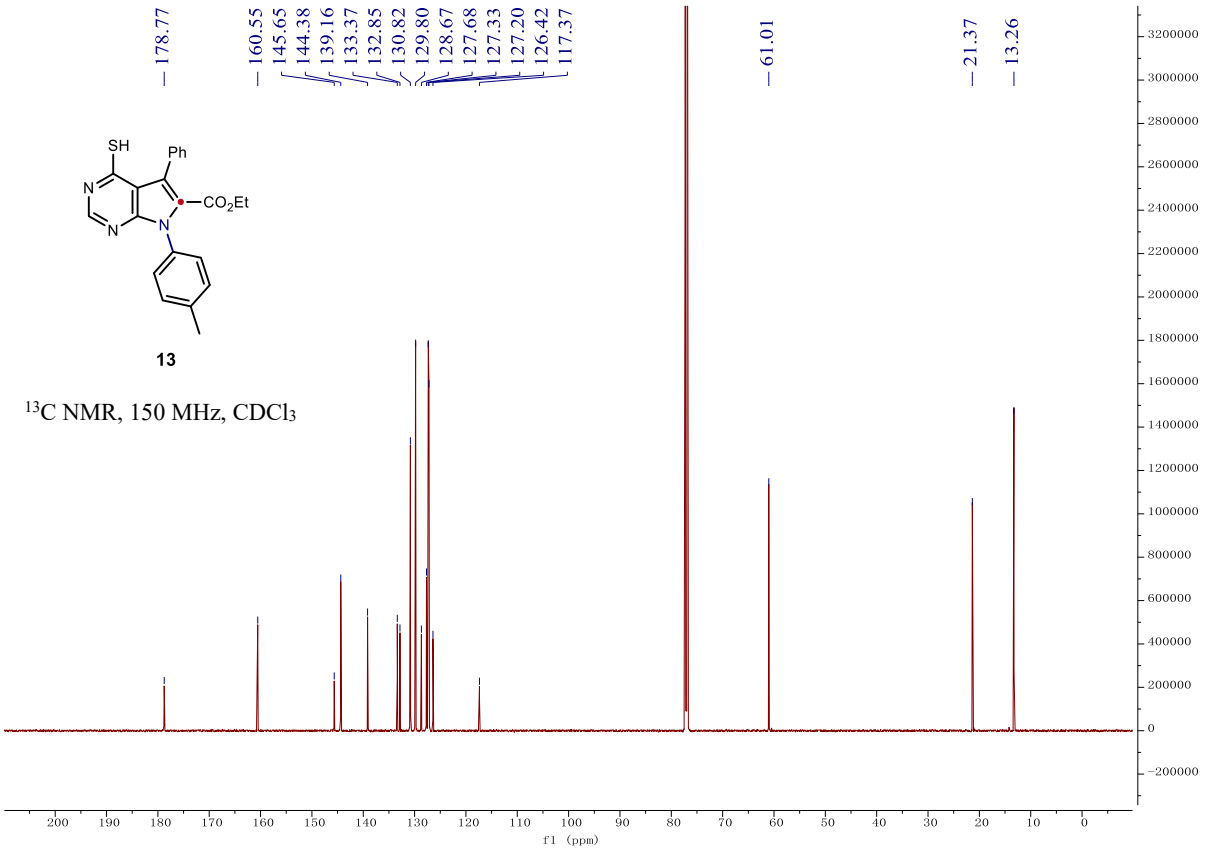
12

^{13}C NMR, 150 MHz, $CDCl_3$



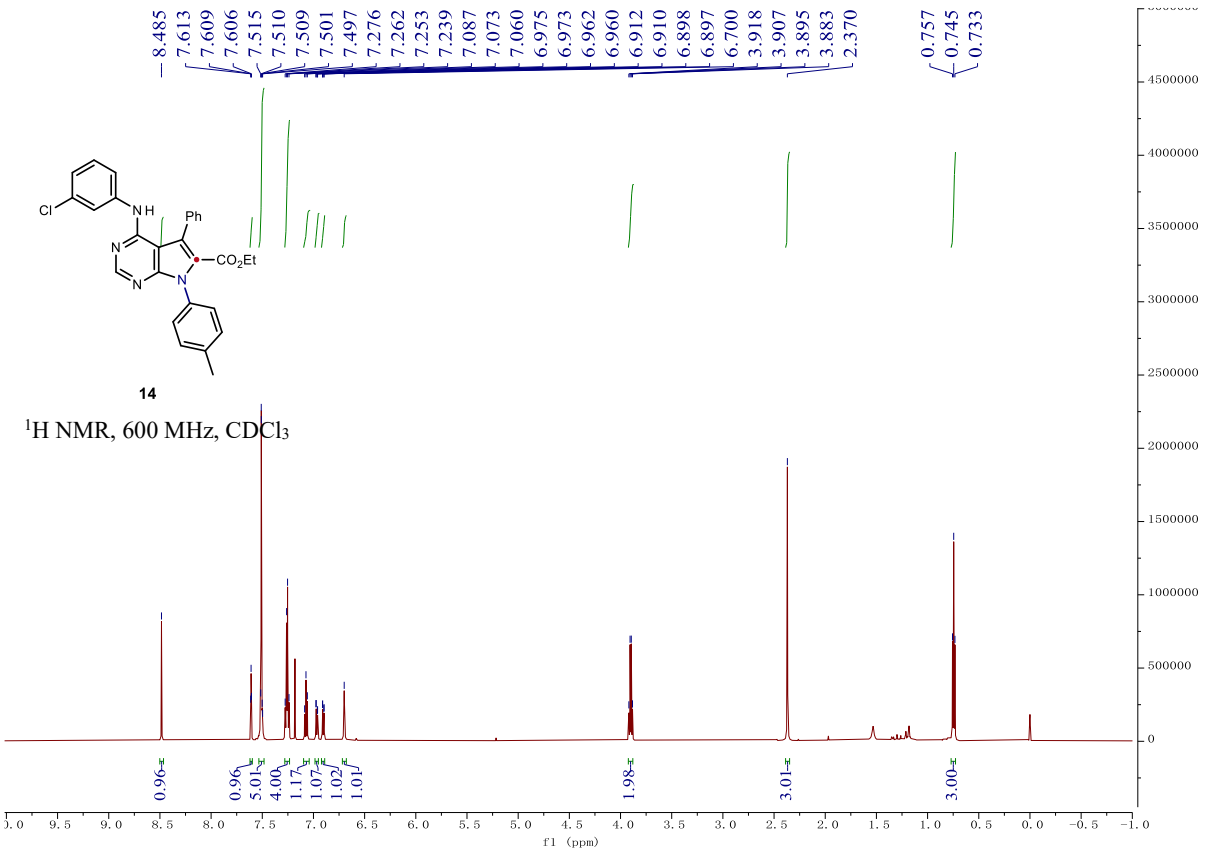
13

^{1}H NMR, 600 MHz, $CDCl_3$



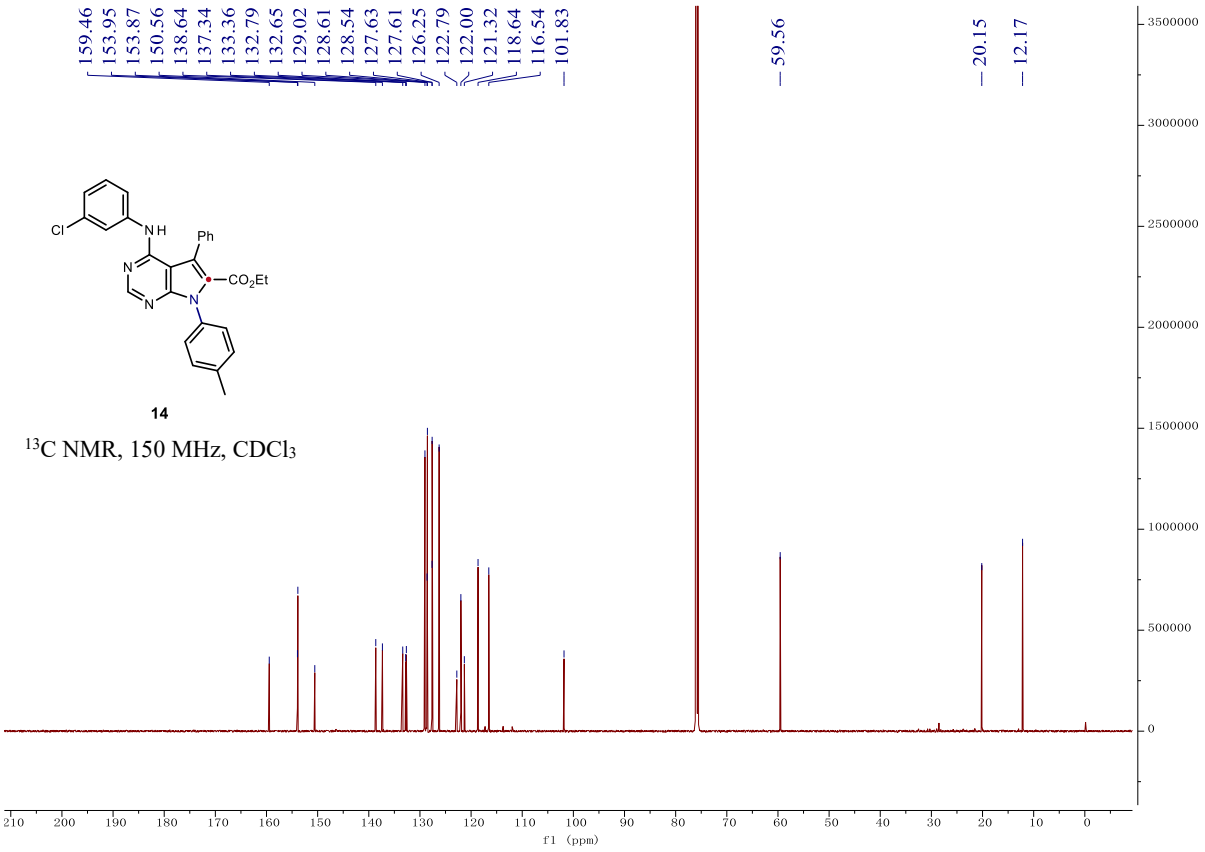
13

^{13}C NMR, 150 MHz, $CDCl_3$



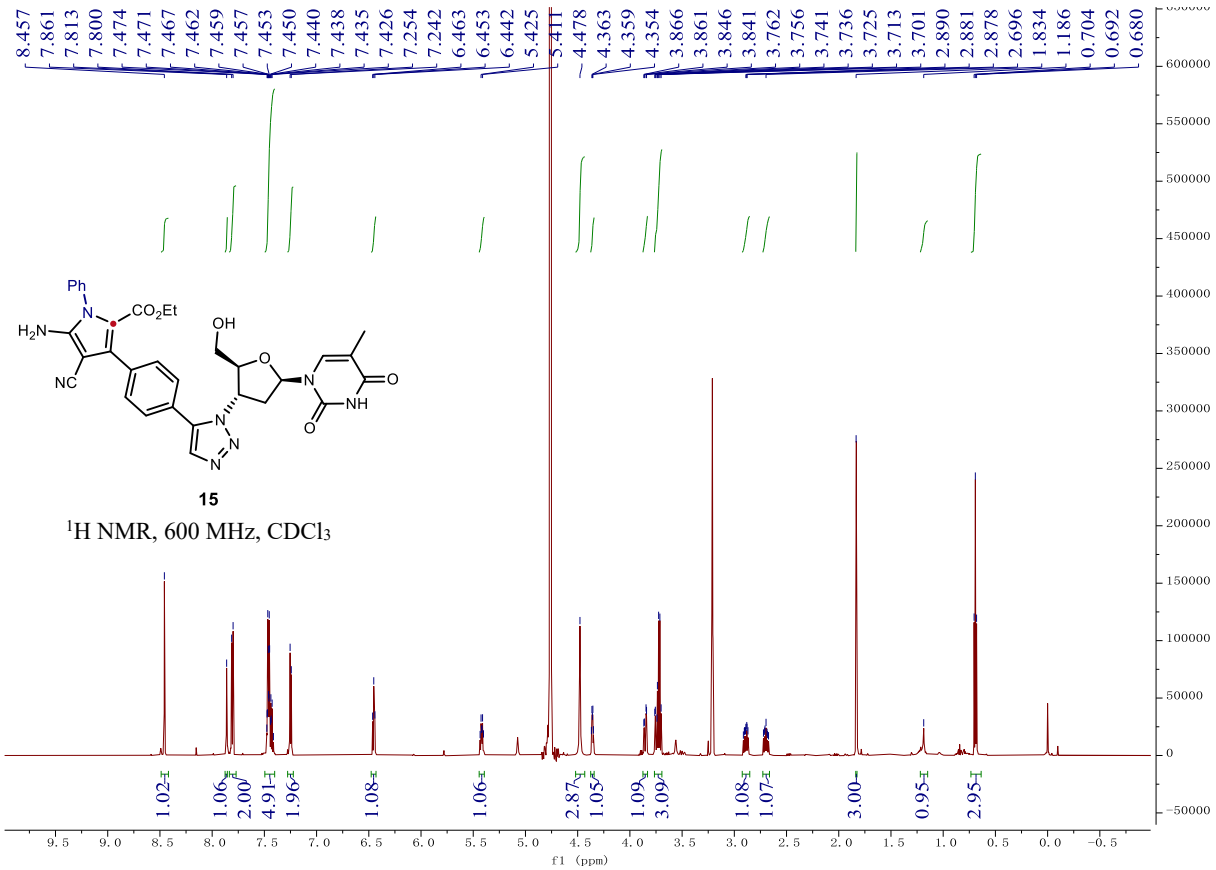
14

^{1}H NMR, 600 MHz, $CDCl_3$



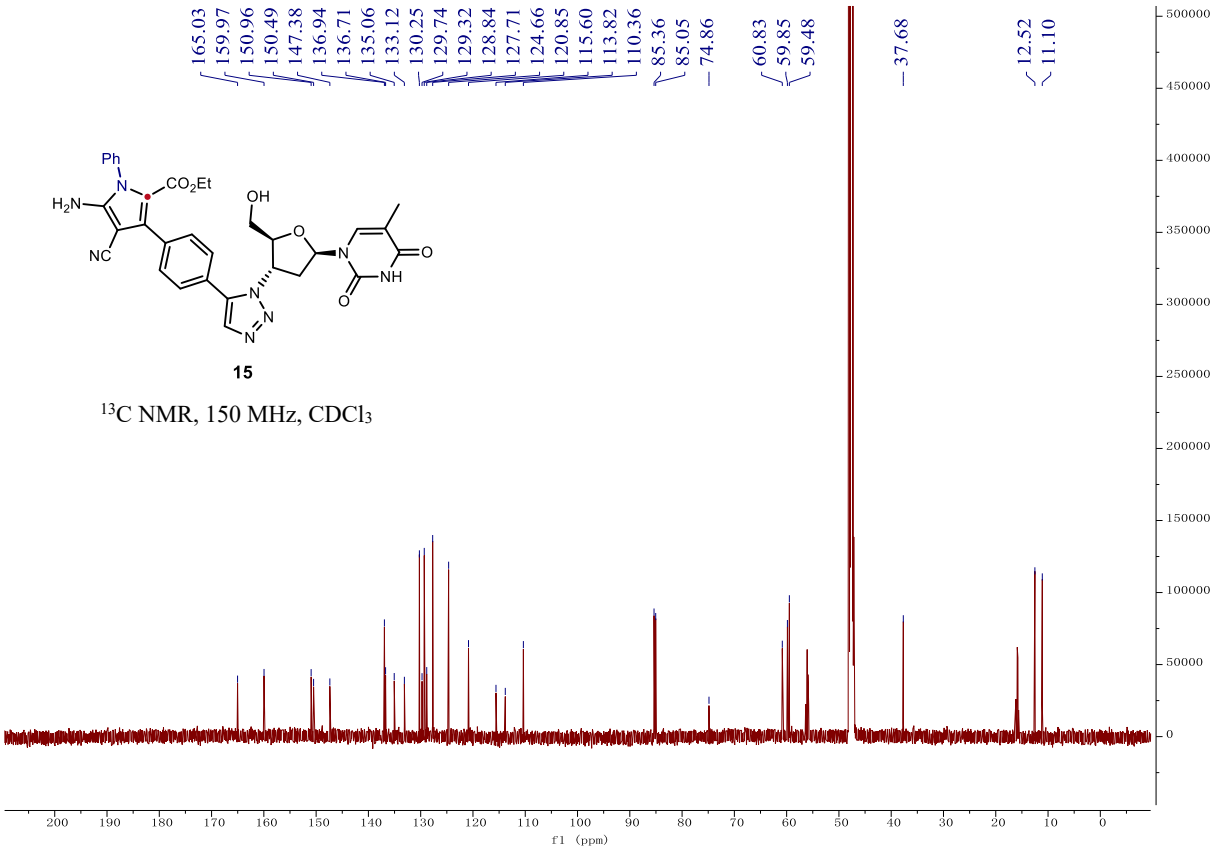
14

^{13}C NMR, 150 MHz, $CDCl_3$



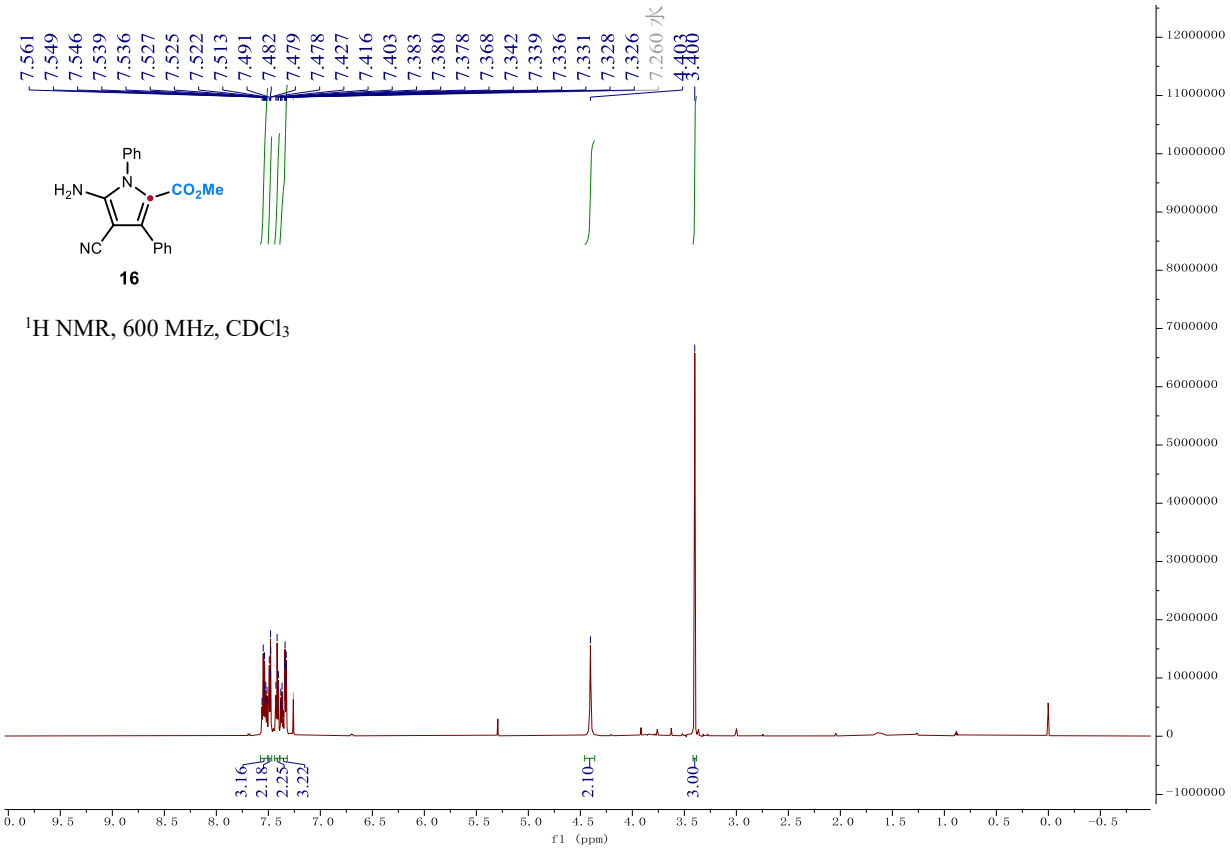
15

^{1}H NMR, 600 MHz, $CDCl_3$

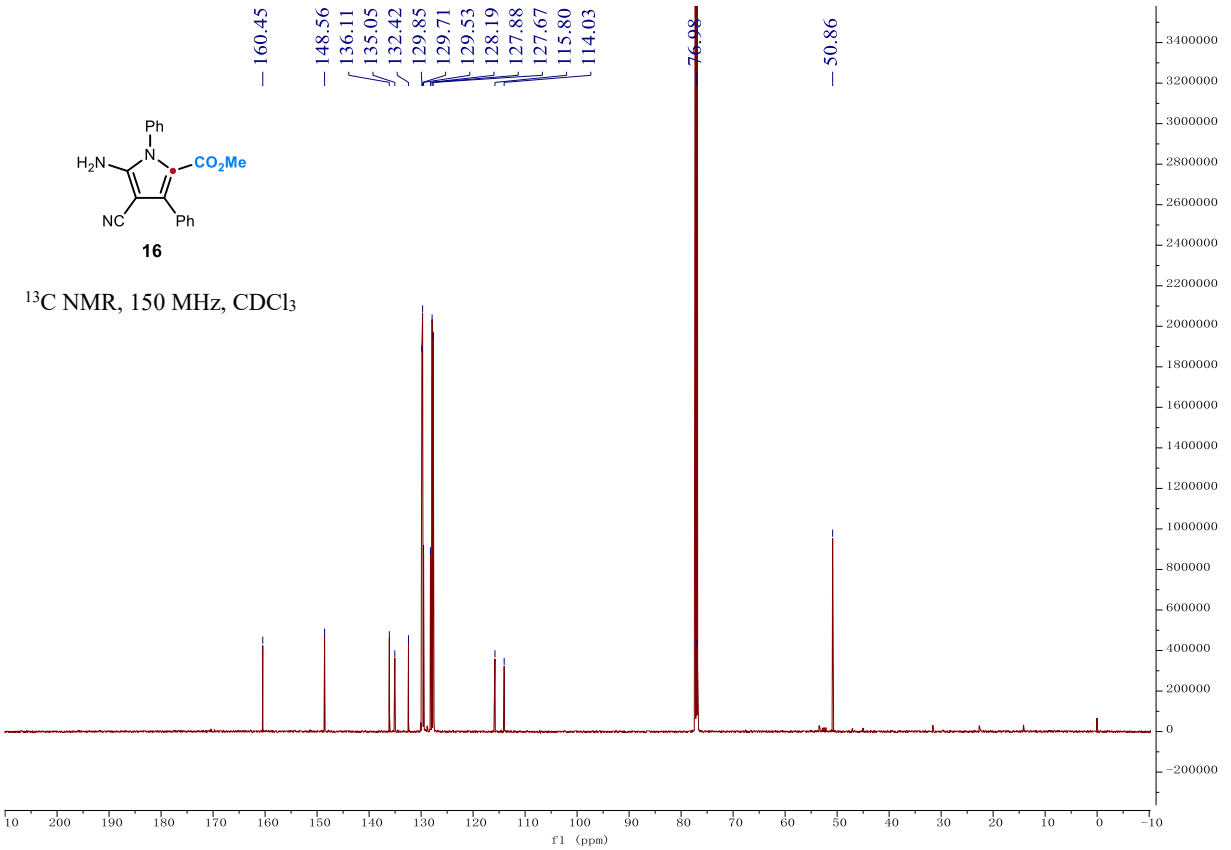


15

^{13}C NMR, 150 MHz, $CDCl_3$



^{1}H NMR, 600 MHz, $CDCl_3$



^{13}C NMR, 150 MHz, $CDCl_3$

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