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Electronic Supplementary Information for:

Radical-triggered base-free 1,3-C→C migrations:

chemodivergent synthesis of cyclic imines from *N*-allyl enamines

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Qun Liu and Ling Pan*

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I. General information

All reagents and catalysts were purchased from commercial sources and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Tsingdao silica gel plates (GF-254) using UV light as visualizing agent. Tsingdao silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography. NMR spectra were recorded on a Brüker Advance 600 (^{1}H: 600 MHz, ^{13}C: 150 MHz, ^{19}F NMR: 565 MHz) and Brüker Advance 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) at ambient temperature. Data were reported as chemical shifts in ppm relative to TMS (0 ppm) for ^{1}H NMR and $CDCl_3$ (77.0 ppm) for ^{13}C NMR. All ^{1}H NMR spectra were reported in delta (d) units, parts per million (ppm) downfield from the internal standard. Coupling constants are reported in Hertz (Hz). High-resolution mass spectra (HRMS) were obtained using a Bruker micro TOF II focusspectrometer (ESI).

Blue LEDs (5 W, λ = 465 nm) was purchased from Wattecs (parallel light reactor, WP-TEC-1020HC). Quartz tube (20 mL) was used as the irradiation vessel and the Blue LEDs irradiated at the bottom with a 1–1.5 cm distance. Blue LEDs (15 W, λ = 465–470 nm) was purchased from Merck (SynLEDZ742680). Airtight glass tube (15 mL) was used as the irradiation vessel and the Blue LEDs irradiated at the bottom with a 1–1.5 cm distance. Blue LEDs (40 W, λ = 456 nm) was purchased from Kessil (PR160) with flask (35 mL) as the irradiation vessel with a 5–6 cm distance.

Varian cary50 was used for UV-*vis* absorption analysis; spectrofluorometer (Edinburgh FS5) was used for Stern-Volmer fluorescence quenching experiments; and CH Instruments (CHI 660E) was used for Cyclic voltammetry experiments.

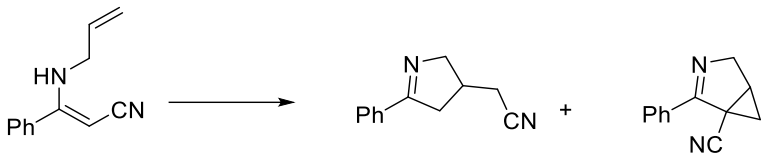
Abbreviations:

PE: Petroleum ether;
EA: Ethyl acetate;

Explain for the multiplicities:
s: singlet;
d: doublet;
t: triplet;
q: quartet;
dd: doublet of doublet;
m: multiplet.

II. Additional optimizations of reaction conditions

Table S1. Optimization for 1,3-C→C cyano migration[a]

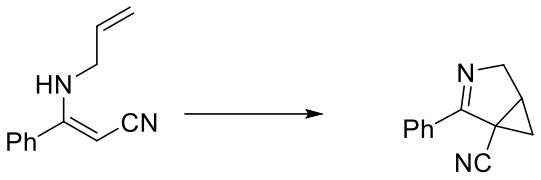


3a **4a** **5a**

Entry	Catalyst (mol%)	Light source	Solvent (mL)	Yield (%)	
				4a[b]	**5a**[b]
1	$Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (3)+ $Co(dmgH)_2PyCl$ (8)	Blue LEDs (5 W)	DCE (2)	8	12
2	$Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (3)	Blue LEDs (5 W)	DCE (2)	48	N.O.
3	$Ir(ppy)_3$ (3)	Blue LEDs (5 W)	DCE (2)	6	trace
4	$[Ir(ppy)_2(bpy)]PF_6$ (3)	Blue LEDs (5 W)	DCE (2)	N.O.	N.O.
5	$[Ir(dtbbpy)(ppy)_2][PF_6]$ (3)	Blue LEDs (5 W)	DCE (2)	N.O.	N.O.
6	$Ru(bpy)_3Cl_2$ (3)	Blue LEDs (5 W)	DCE (2)	N.O.	N.O.
7	Acr^+-Mes ClO_4^- (3)	Blue LEDs (5 W)	DCE (2)	N.O.	N.O.
8	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (5)	Blue LEDs (5 W)	DCE (2)	63	N.O.
9	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (8)	Blue LEDs (5 W)	DCE (2)	19	N.O.
10	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (5)	Blue LEDs (15 W)	DCE (2)	53	N.O.
11	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (5)	Blue LEDs (40 W)	DCE (2)	30	N.O.
12	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (5)	Blue LEDs (15 W)	1,4-Dioxane (2)	41	N.O.
13	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (5)	Blue LEDs (15 W)	EtOAc (2)	47	N.O.
14	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (5)	Blue LEDs (15 W)	EtOH (2)	33	N.O.
15[c]	***$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (5)***	***Blue LEDs (15 W)***	***DCE (2)***	***85***	***N.O.***
16[c]	-	Blue LEDs (15 W)	DCE (2)	N.R.	N.O.
17[c]	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (3)	-	DCE (2)	N.R.	N.O.
18	Acr^+-Mes ClO_4^- (3) + $Co(dmgH)_2PyCl$ (8)	Blue LEDs (5 W)	DCE (3)	N.O.	72

[a]Reaction scale: 0.3 mmol; [b]Isolated yields; [c]Nitrogen atmosphere.

Table S2. Optimization for the formation of 5a[a]



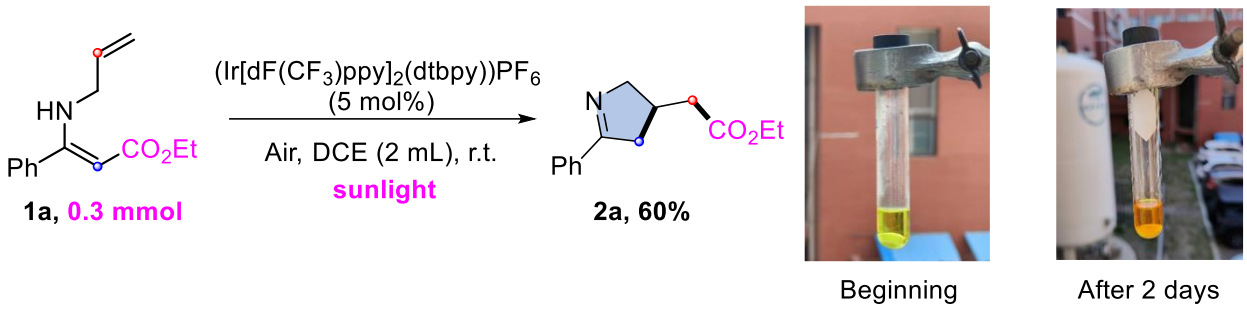
3a **5a**

Entry	Photosensitizer (mol%)	Catalyst (mol%)	Light source	Solvent (mL)	Yield of **5a** (%)[b]
1	Acr^+-Mes-Ph ClO_4^- (5)	$Co(dmgH)_2PyCl$ (10)	Blue LEDs (5 W)	DCE (2)	43
2	Acr^+-Mes-Ph BF_4^- (5)	$Co(dmgH)_2PyCl$ (10)	Blue LEDs (10 W)	DCE (2)	35
3	Acr^+-Mes-Ph Cl^- (5)	$Co(dmgH)_2PyCl$ (10)	Blue LEDs (10 W)	DCE (2)	19
4	Acr^+-Mes-dMe-Ph BF_4^- (5)	$Co(dmgH)_2PyCl$ (10)	Blue LEDs (10 W)	DCE (2)	44
5	Acr^+-Mes-Ph ClO_4^- (3)	$Co(dmgH)_2PyCl$ (10)	Blue LEDs (5 W)	DCE (2)	44
6	Acr^+-Mes-Ph ClO_4^- (8)	$Co(dmgH)_2PyCl$ (10)	Blue LEDs (5 W)	DCE (2)	40
7	Acr^+-Mes-Ph ClO_4^- (3)	$Co(dmgH)_2PyCl$ (8)	Blue LEDs (5 W)	DCE (2)	54
8	Acr^+-Mes-Ph ClO_4^- (3)	$Co(dmgH)_2$ (4-CO_2MePy)Cl (8)	Blue LEDs (5 W)	DCE (2)	44
9	Acr^+-Mes-Ph ClO_4^- (3)	$CoCl_2 \cdot 6H_2O$ (8)	Blue LEDs (5 W)	DCE (2)	24
10	Acr^+-Mes-Ph ClO_4^- (3)	$Co(dmgH)_2PyCl$ (8)	Blue LEDs (5 W)	DCE (1)	36
11	Acr^+-Mes-Ph ClO_4^- (3)	$Co(dmgH)_2PyCl$ (8)	Blue LEDs (5 W)	DCE (3)	61
12[c]	***Acr^+-Mes-Ph ClO_4^- (3)***	***$Co(dmgH)_2PyCl$ (8)***	***Blue LEDs (5 W)***	***DCE (3)***	***72***
13	-	$Co(dmgH)_2PyCl$ (8)	Blue LEDs (5 W)	DCE	N.R.
14	Acr^+-Mes-Ph ClO_4^- (3)	-	Blue LEDs (5 W)	DCE	N.R.
15	Acr^+-Mes-Ph ClO_4^- (3)	$Co(dmgH)_2PyCl$ (8)	-	DCE	N.R.

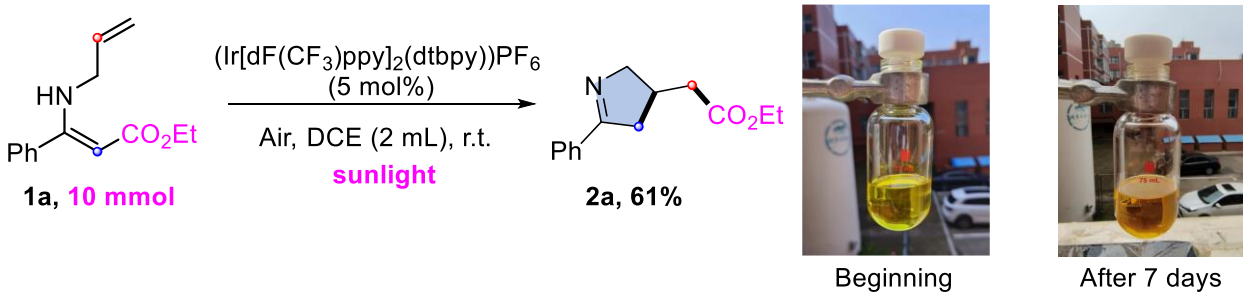
[a]Reaction scale: 0.3 mmol, ambient atmosphere; [b]Isolated yields; [c]Reaction scale: 0.2 mmol.

III. Procedures for solar synthesis

0.3 mmol-scale synthesis: To a flask (15 mL) equipped with a stir-bar was added *N*-allyl enamine **1a** (69.3 mg, 0.3 mmol), $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (16.8 mg, 0.015 mmol), and DCE (2 mL). The reaction mixture was exposed to sunlight for 2 days at ambient atmosphere. After the completion of the reaction as indicated by TLC, the solution was concentrated *in vacuo*. Then the residue was purified by silica gel flash column chromatography (PE/EA = 4/1) to afford product **2a** (41.6 mg, 60%).



Gram-scale synthesis: To a flask (75 mL) equipped with a stir-bar was added *N*-allyl enamine **1a** (2.31 g, 10 mmol), $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (0.56 g, 0.5 mmol), and DCE (40 mL). The reaction mixture was exposed to sunlight for 7 days at ambient atmosphere. After the completion of the reaction as indicated by TLC, the solution was concentrated *in vacuo*. Then the residue was purified by silica gel flash column chromatography (PE/EA = 4/1) to afford product **2a** (1.41 g, 61%).



IV. Mechanistic studies

1) UV-*vis* absorption spectra

UV-*vis* spectra were carried out using the DCE solution of *N*-allyl enamine **1a** (1×10^{-5} mol, 2×10^{-4} M in DCE), $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (5×10^{-6} mol, 1×10^{-4} M in DCE) respectively, and their mixture. It was shown that $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ has strongest ultraviolet absorption at the reaction wavelength and is the best photosensitizer.

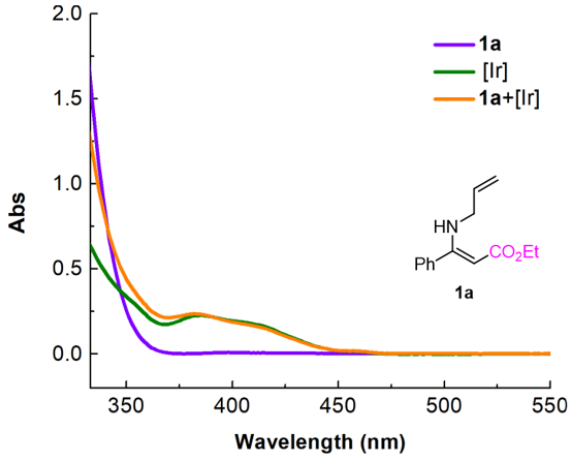


Figure S1. UV-*vis* spectra of *N*-allyl enamine **1a**, $[Ir(dtbbpy)(ppy)_2][PF_6]$ respectively and their mixture.

UV-*vis* spectra were carried out using the DCE solution of *N*-allyl enamine **3a** (1×10^{-5} mol, 2×10^{-4} M in DCE), $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (5×10^{-6} mol, 1×10^{-4} M in DCE) respectively, and their mixture. It was shown that $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ has strongest ultraviolet absorption at the reaction wavelength and is the best photosensitizer.

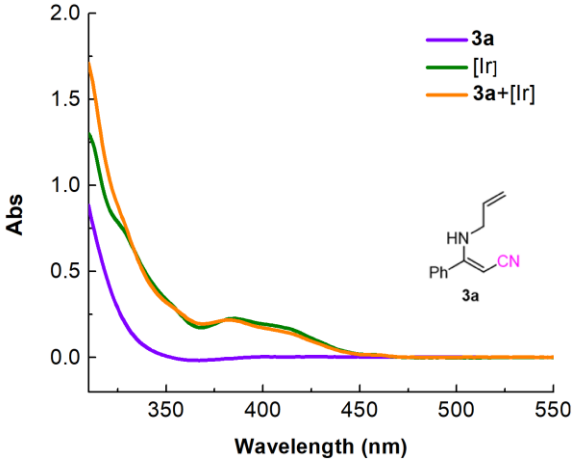


Figure S2. UV-*vis* spectra of *N*-allyl enamine **3a**, $[Ir(dtbbpy)(ppy)_2][PF_6]$ respectively and their mixture.

UV-*vis* spectra were carried out using the DCE solution of *N*-allyl enamine **3a** (1×10^{-5} mol, 2×10^{-4} M in DCE), Acr^{+}-Mes-Ph ClO_4^{-} (5×10^{-6} mol, 1×10^{-4} M in DCE), $Co(dmgH)_2PyCl$ (5×10^{-6} mol, 1×10^{-4} M in DCE) respectively, and their mixture. It was shown that Acr^{+}-Mes-Ph ClO_4^{-} has strongest ultraviolet absorption at the reaction wavelength and is the best photosensitizer.

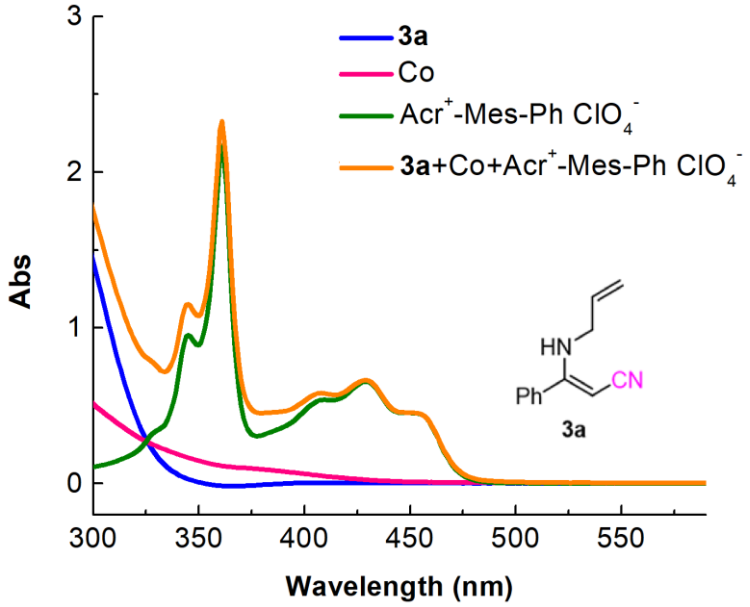


Figure S3. UV-*vis* spectra of *N*-allyl enamine **3a**, Acr^{+}-Mes-Ph ClO_4^{-}, $Co(dmgH)_2PyCl$ respectively and their mixture.

2) Emission quenching studies

Emission intensities were recorded by spectrofluorometer (Edinburgh FS5) at ambient temperature. The DCE solution of $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ were excited at 355 nm and the emission intensity at 467 and 496 nm was observed. Firstly, the emission spectrum of a 5×10^{-5} M solution of $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ in DCE was collected. Then, appropriate amount of quencher was added to the measured solution and the emission spectrum of the sample was collected. The Stern-Volmer emission quenching studies tell that the *N*-allyl enamines **1a** and **3a** both can quench the excited $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$.

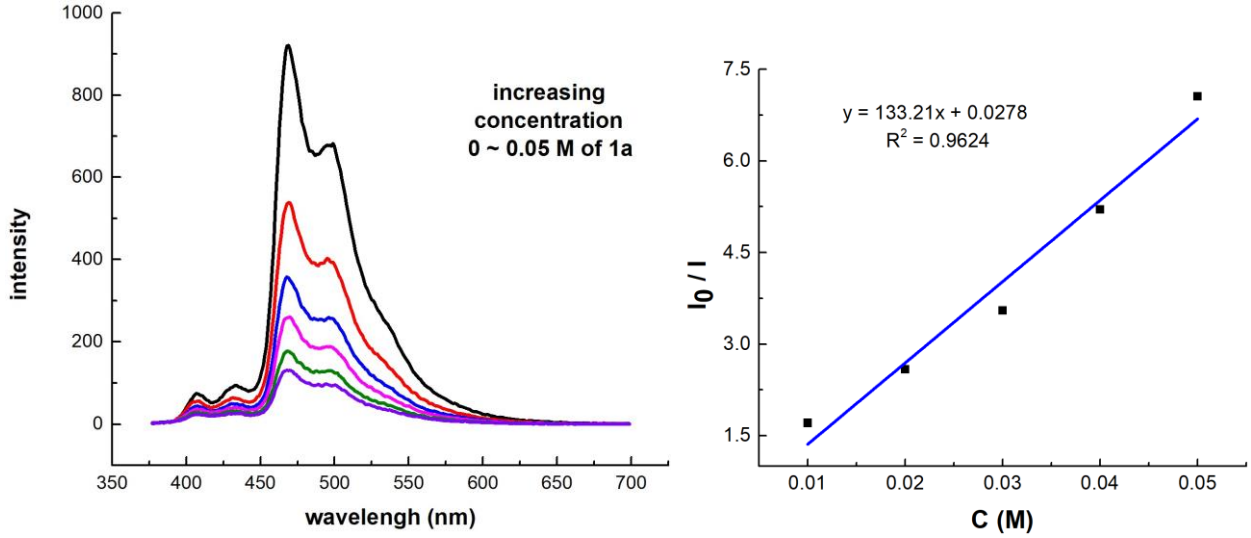


Figure S4. $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ emission quenching by *N*-allyl enamine **1a.**

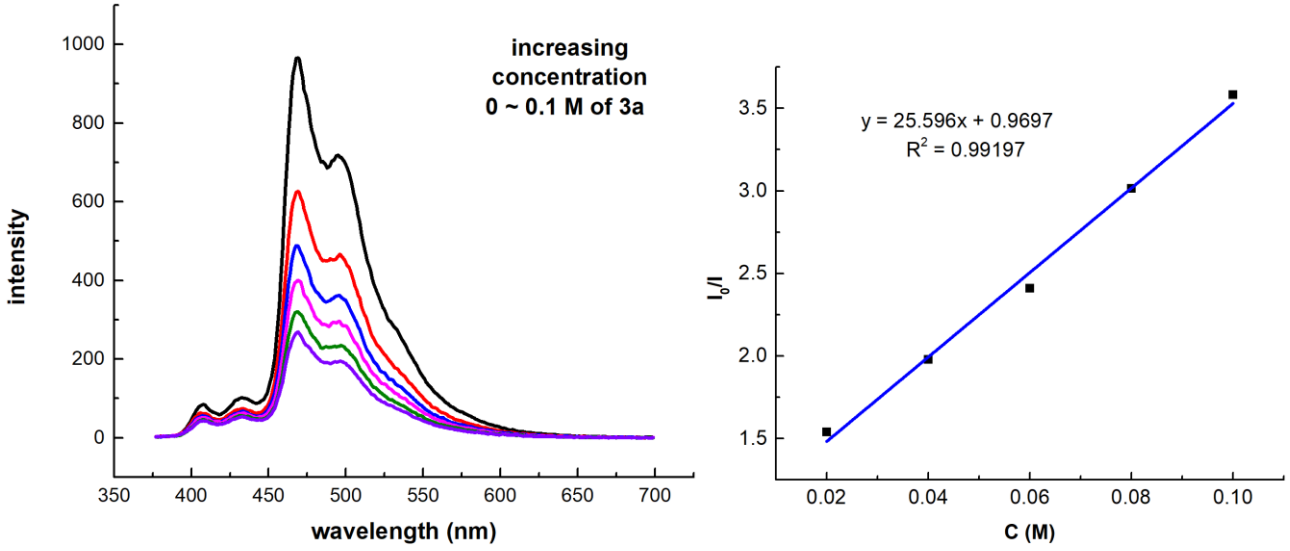


Figure S5. $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ emission quenching by *N*-allyl enamine **3a.**

Emission intensities were recorded by spectrofluorometer (Edinburgh FS5) at ambient temperature. The DCE solution of Acr^+-Mes-Ph ClO_4^- were excited at 462 nm and the emission intensity at 516 nm was observed. Firstly, the emission spectrum of a 5×10^{-5} M solution of Acr^+-Mes-Ph ClO_4^- in DCE was collected. Then, appropriate amount of quencher was added to the measured solution and the emission spectrum of the sample was collected. The Stern-Volmer emission quenching studies tell that the *N*-allyl enamine **3a** can quench the excited Acr^+-Mes-Ph ClO_4^-.

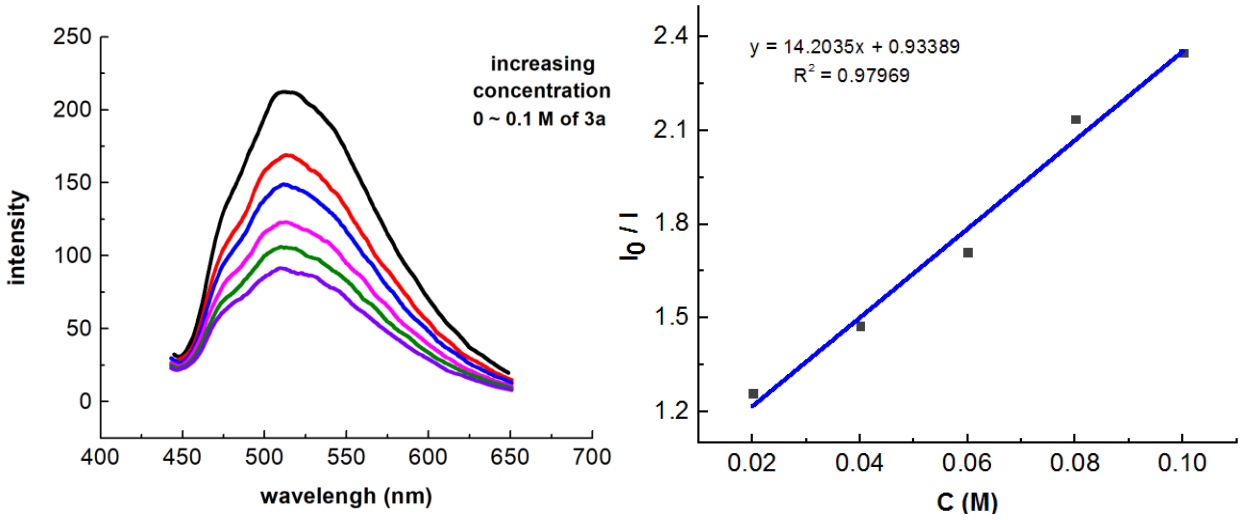


Figure S6. Acr^+-Mes-Ph ClO_4^- emission quenching by *N*-allyl enamine **3a.**

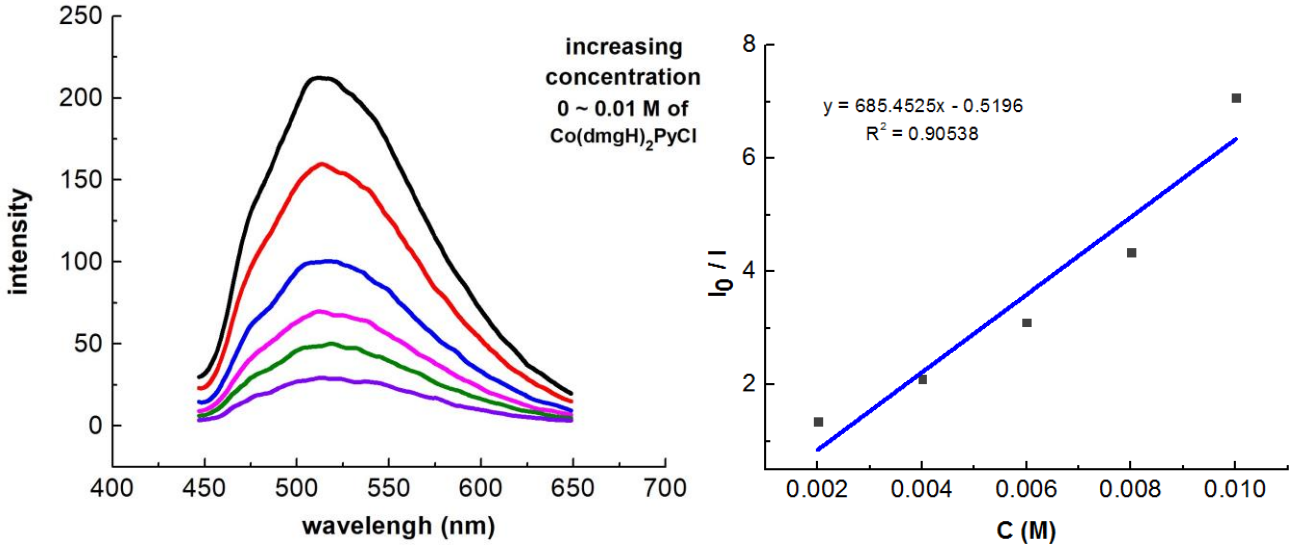


Figure S7. Acr^+-Mes-Ph ClO_4^- emission quenching by $Co(dmgH)_2PyCl$**.**

3) Cyclic voltammetry experiments

For the electrochemical measurements, a three-electrode system connected to an electrochemical station was used: A reference electrode, Ag/AgCl in 0.1 M KCl; A glassy carbon electrode as the working electrode; and a Pt wire as the counter electrode. All electrochemical measurements were performed in degassed DMF under dry N_2 atmosphere.

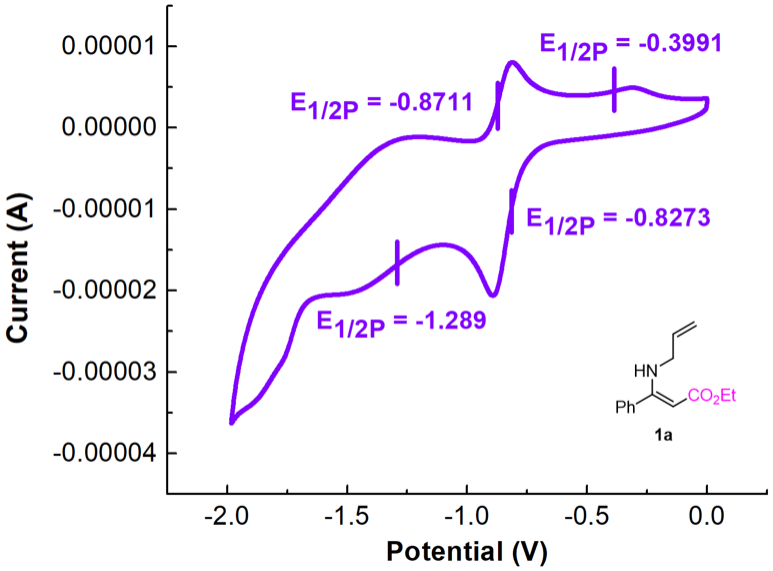


Figure S8. CV spectra of *N*-allyl enamine **1a** (3 mM) in 0.1 M NBu_4PF_6 in degassed DMF (20 mL) with scan rate 100 mV/s.

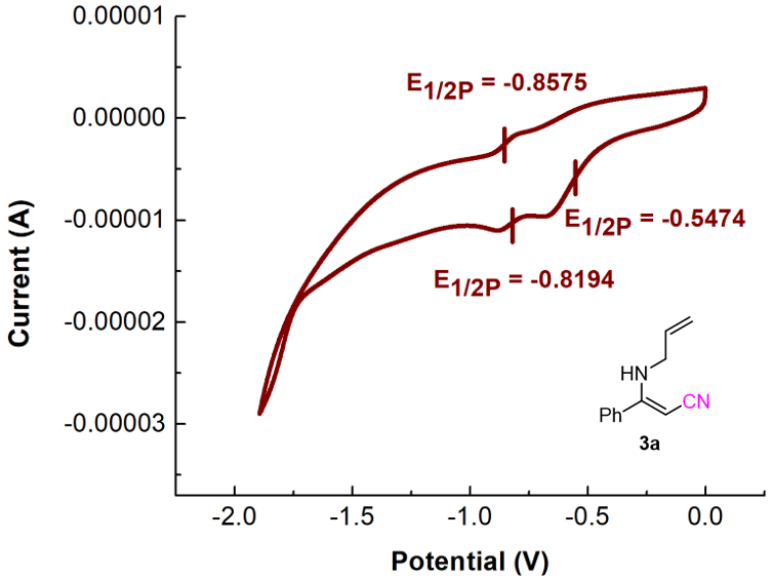
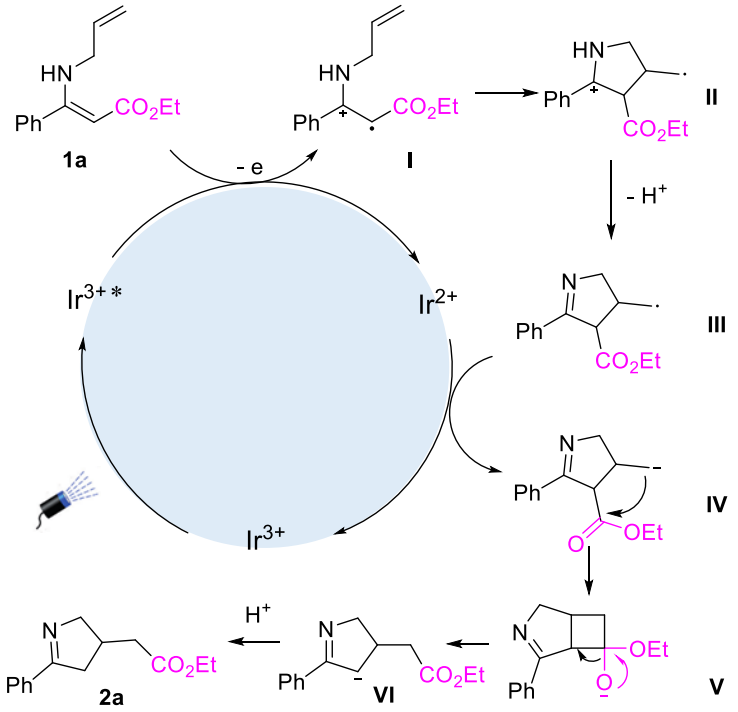


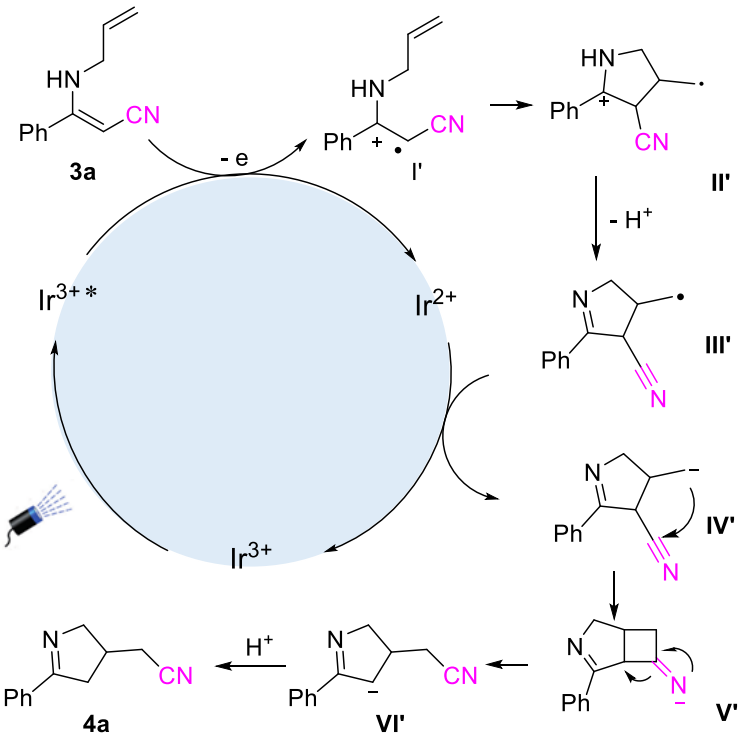
Figure S9. CV spectra of *N*-allyl enamine **3a** (3 mM) in 0.1 M NBu_4PF_6 in degassed DMF (20 mL) with scan rate 100 mV/s.

4) Plausible mechanisms

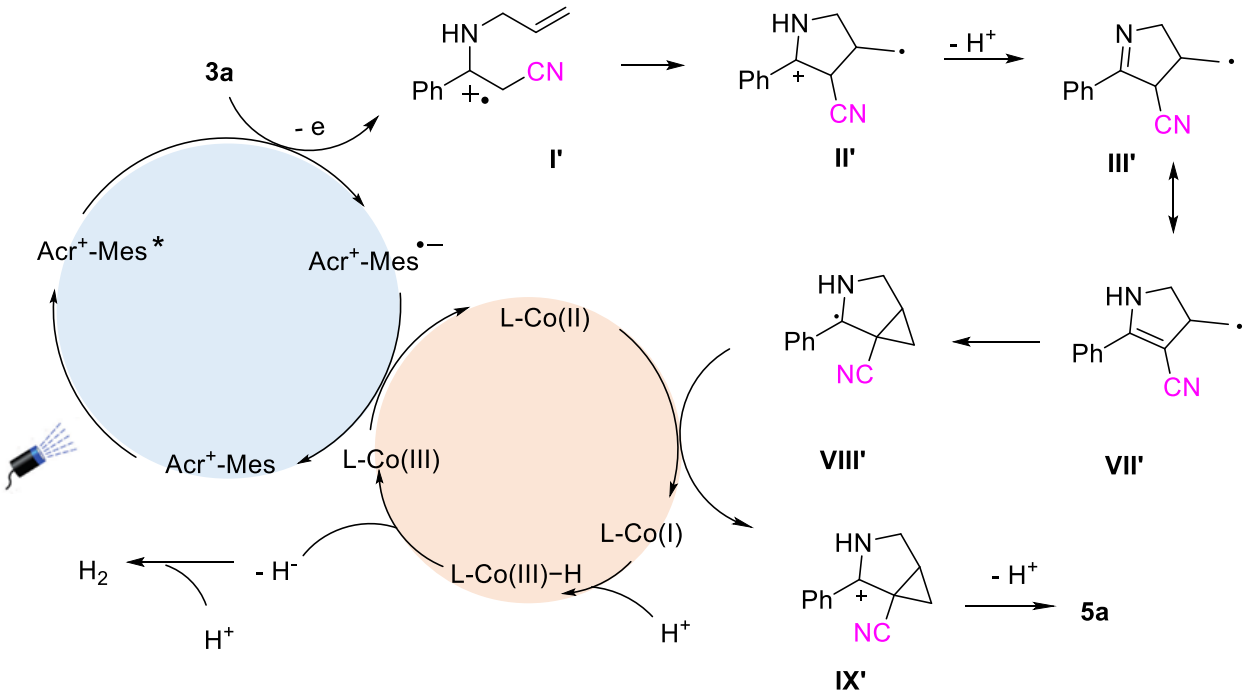
i) Mechanism for 1,3-C→C acyl migration



ii) Mechanism for 1,3-C→C cyano migration

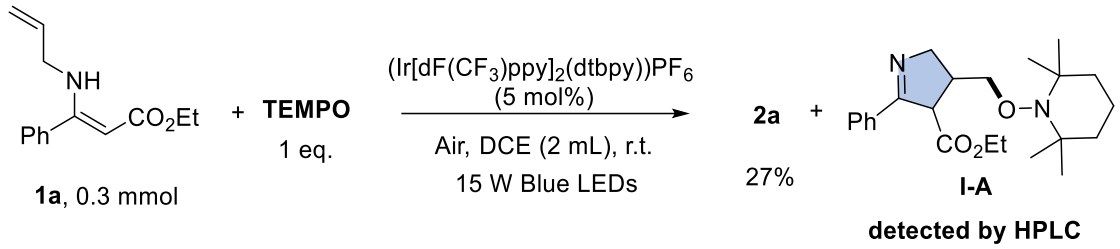


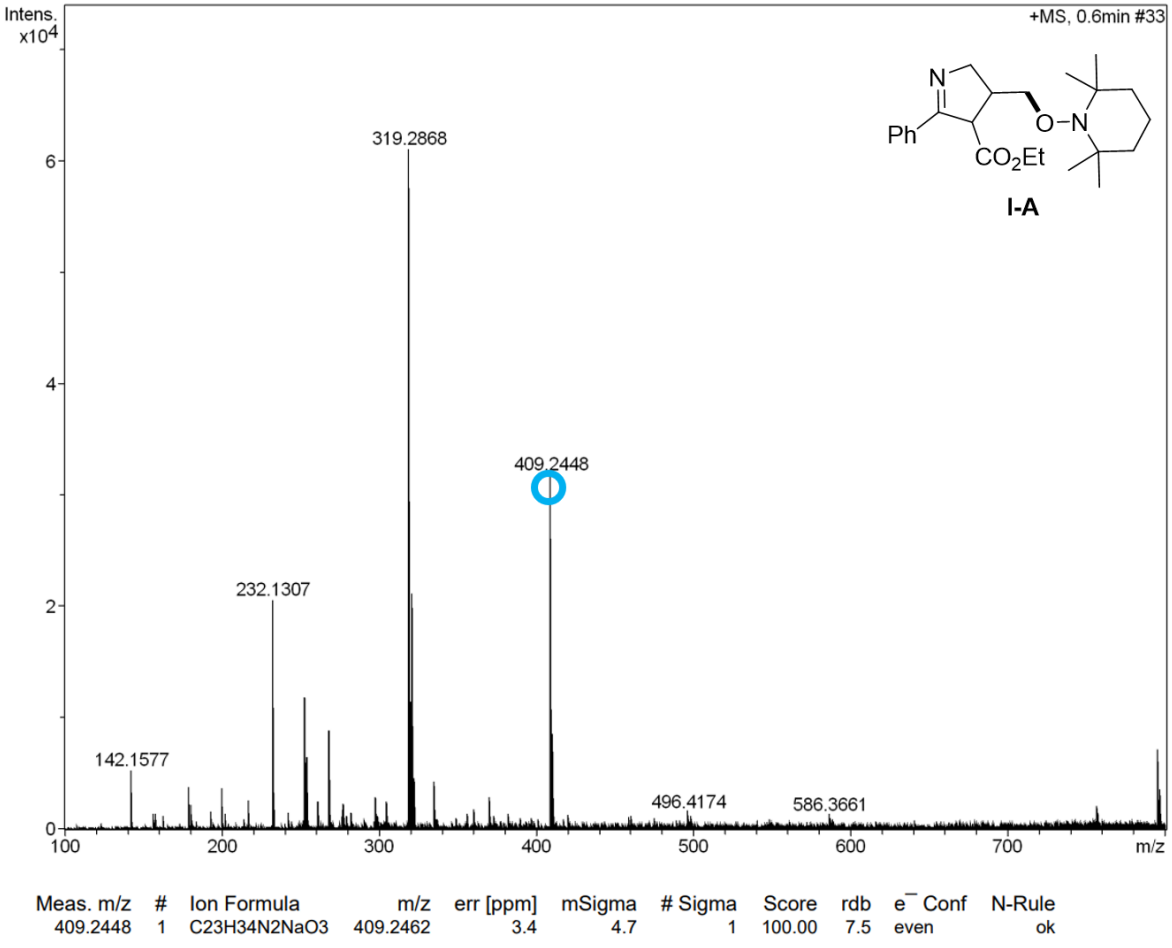
iii) Mechanism for cyclization reaction



5) Radical trapping experiments

To a flask (15 mL) equipped with a stir-bar was added *N*-allyl enamine **1a** (69.3 mg, 0.3 mmol), $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (16.8 mg, 0.015 mmol), TEMPO (46.8 mg, 0.3 mmol) and DCE (2 mL). The reaction mixture was stirred under the irradiation of blue LED light (15 W) at ambient atmosphere in a parallel light reactor. After the completion of the reaction as indicated by TLC, 3 uL of mixture was extracted from the system and intermediate **I-A** was detected by the HPLC analysis. The remaining solution was concentrated *in vacuo.* Then the residue was purified by silica gel flash column chromatography to afford product **2a** (18.7 mg, 27%).





Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
409.2448	1	C23H34N2NaO3	409.2462	3.4	4.7	1	100.00	7.5	even	ok

The TEMPO-trapping product **I-A** has been isolated as a mixture and analyzed by ^{1}H NMR spectrum (Figure S10). It was calculated that the ratio of two isomers is 10:1. The major isomer was isolated and further analyzed by ^{1}H NMR (Figure S11) and ^{1}H-^{1}H NOE spectra (Figure S12), while the minor one could not be isolated. As a result, *cis*-**I-A** was deduced as the major isomer since H_a and H_b has a strong interaction, indicating the same orientation of H_a and H_b, while H_b nearly has no interaction with H_e and H_f in Figure S12. Furthermore, compared to the formation of **2a**, the formation of **I-A** didn't undergo the formation of the highly strained four-membered ring intermediates, thus the formation of trans-**I-A** is unavoidable.

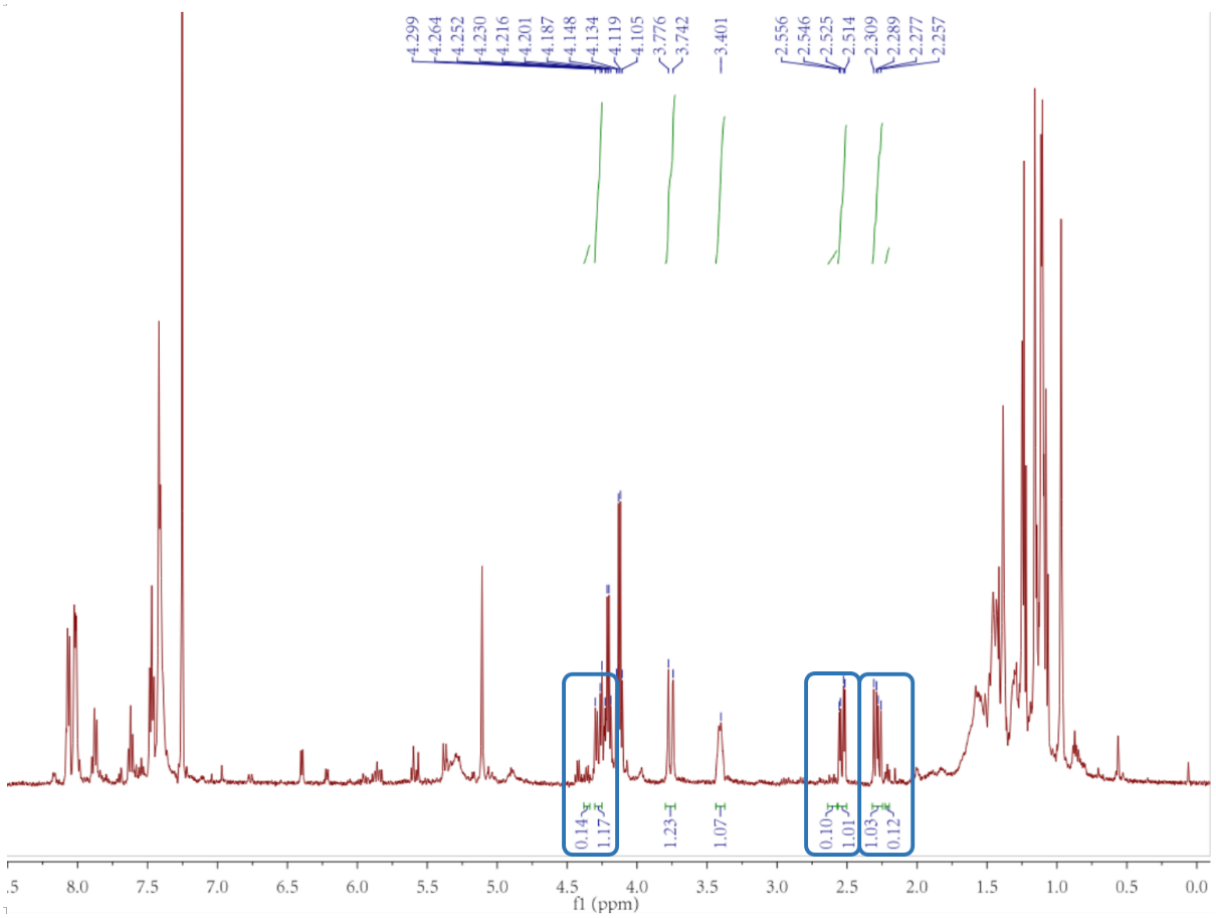


Figure S10. ^{1}H NMR of mixed **I-A**

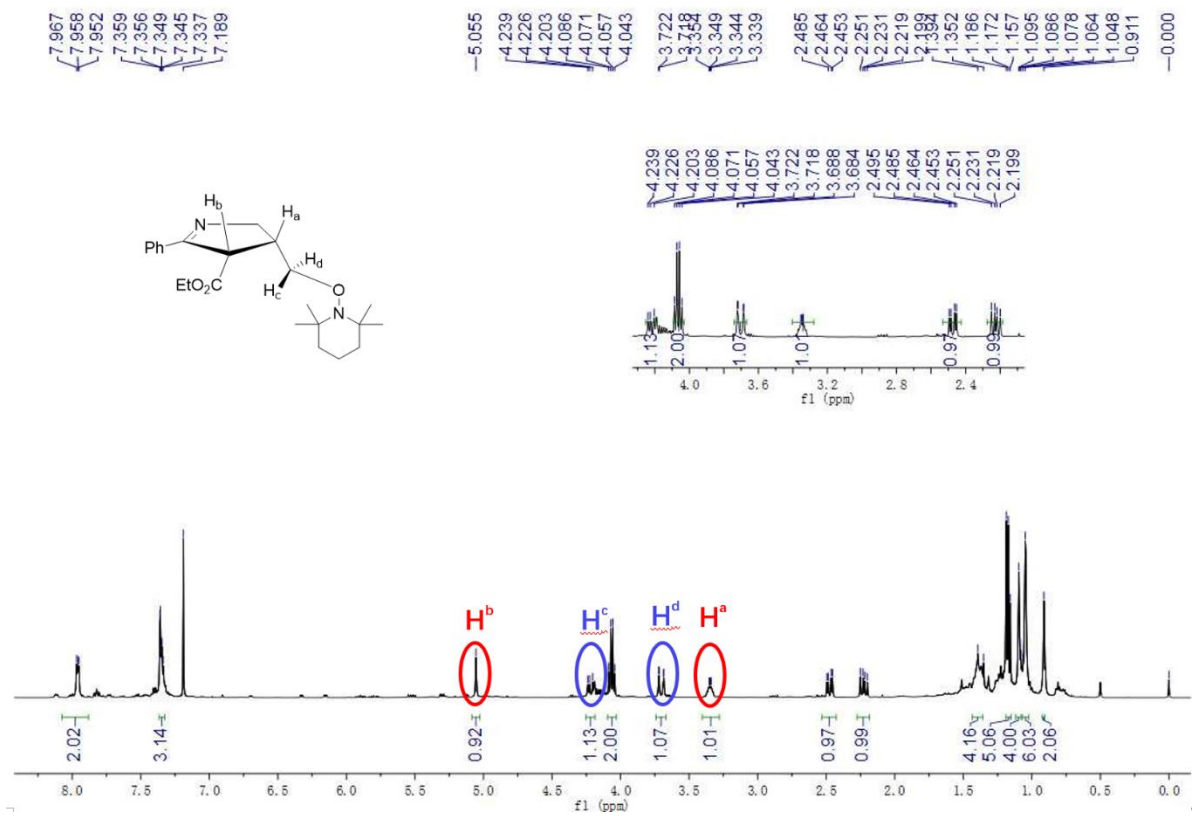


Figure S11. ^{1}H NMR of *cis*-**I-A**

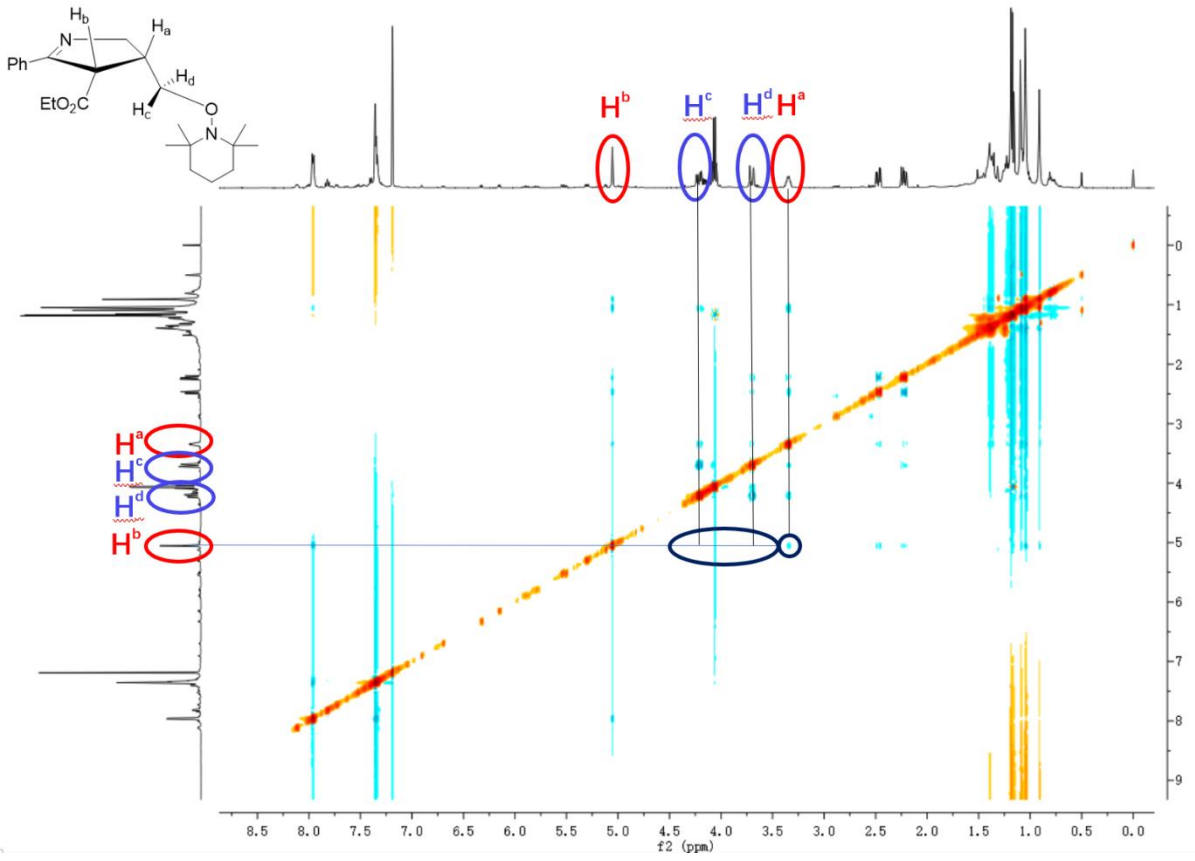
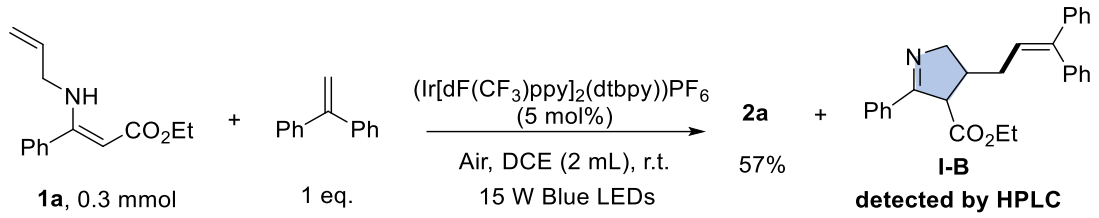
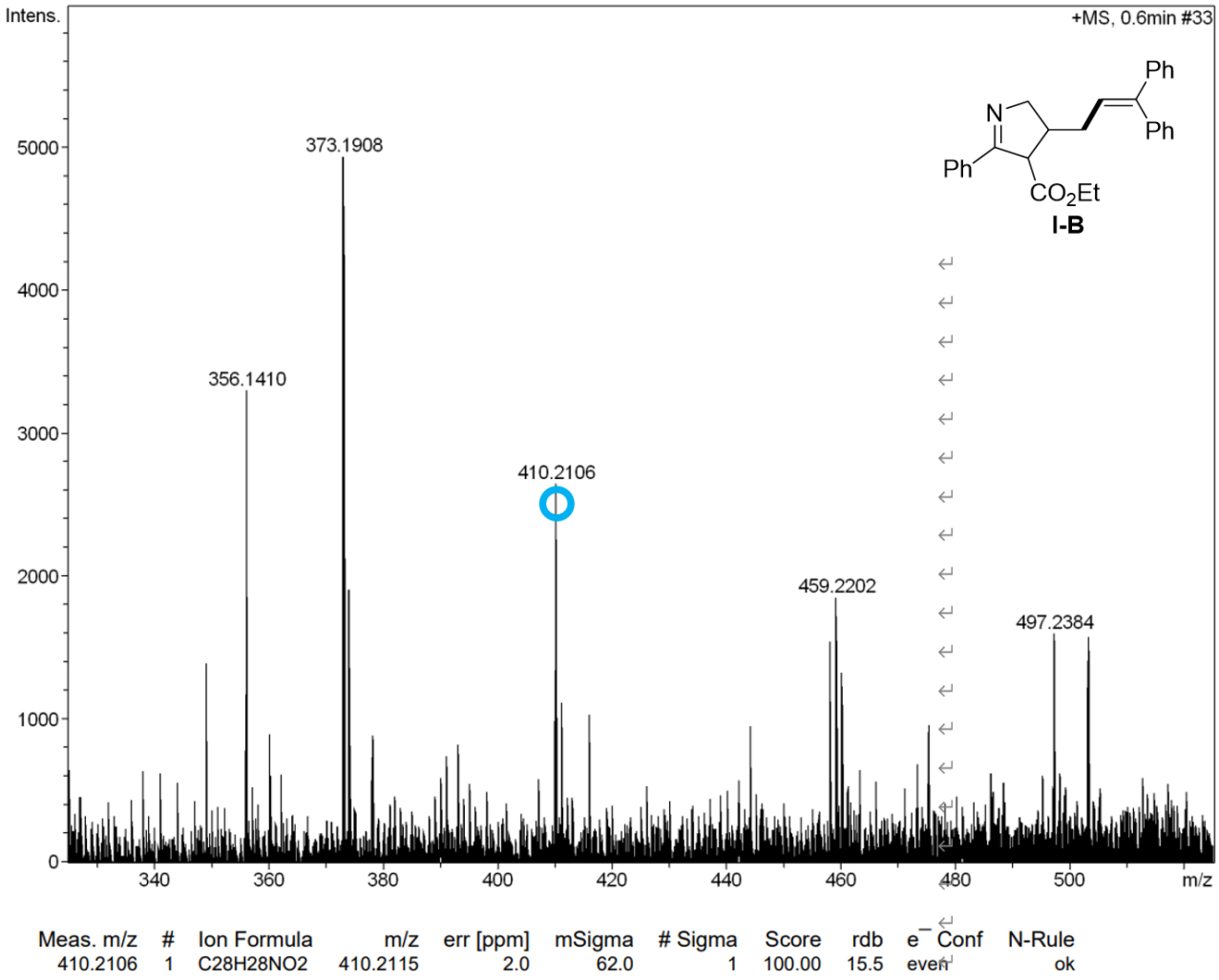


Figure S12. ^{1}H-^{1}H NOE spectra of *cis*-**I-A**

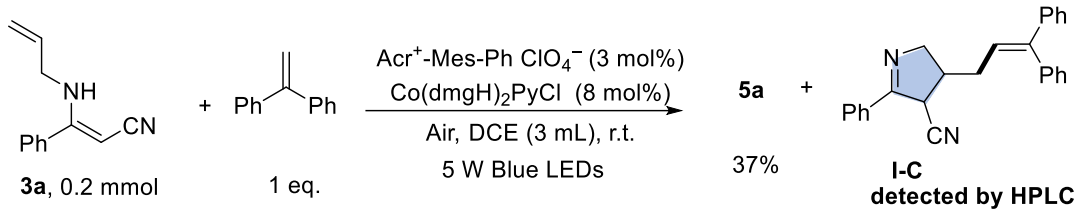
To a flask (15 mL) equipped with a stir-bar was added *N*-allyl enamine **1a** (69.3 mg, 0.3 mmol), $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (16.8 mg, 0.015 mmol), 1,1-diphenylethylene (53 μL, 0.3 mmol) and DCE (2 mL). The reaction mixture was stirred under the irradiation of blue LED light (15 W) at ambient atmosphere in a parallel light reactor. After the completion of the reaction as indicated by TLC, 3 uL of mixture was extracted from the system and intermediate **I-B** was detected by the HPLC analysis. The remaining solution was concentrated *in vacuo.* Then the residue was purified by silica gel flash column chromatography to afford product **2a** (39.5 mg, 57%).

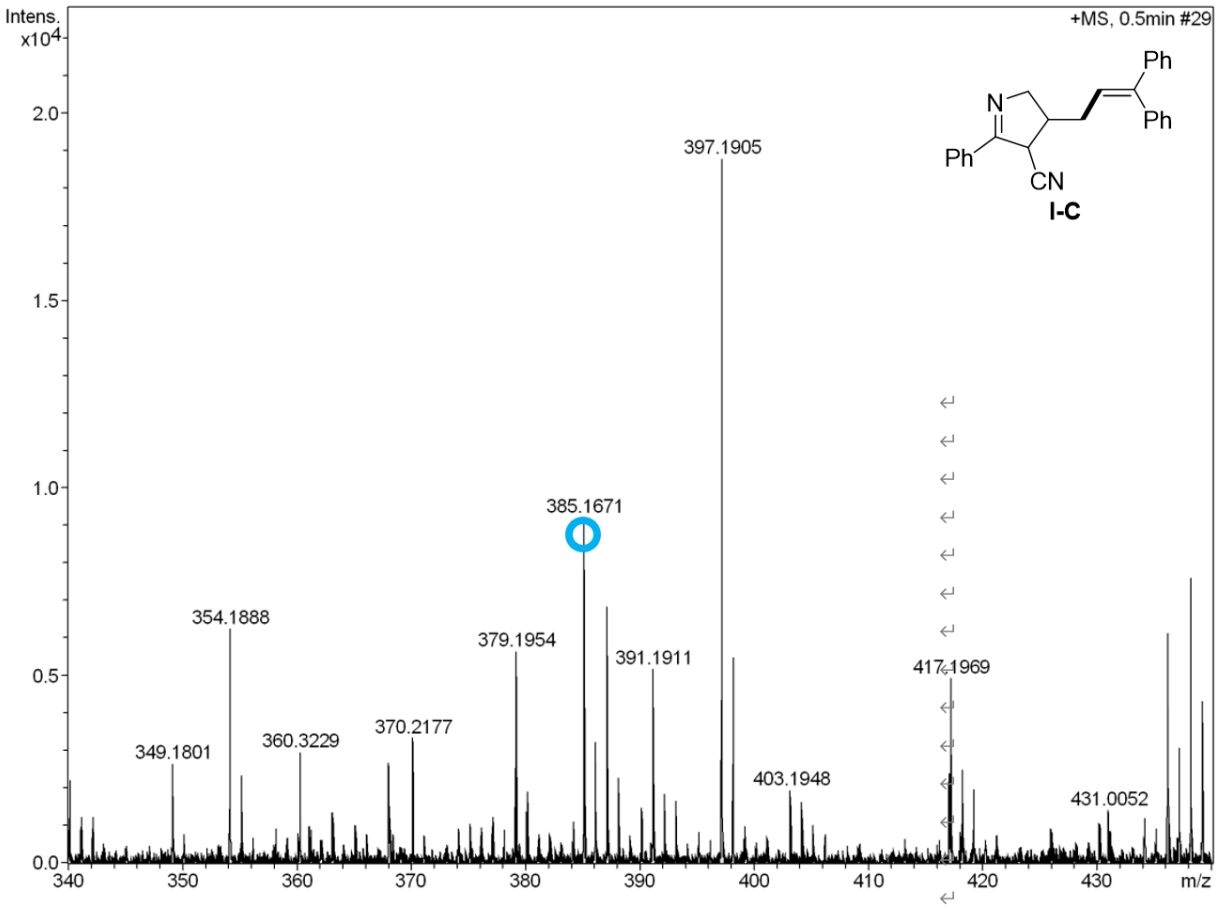




Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
410.2106	1	C28H28NO2	410.2115	2.0	62.0	1	100.00	15.5	even	ok

To a flask (20 mL) equipped with a stir-bar was added *N*-allyl enamine **3a** (36.8 mg, 0.2 mmol), Acr^+-Mes-Ph ClO_4^- (2.5 mg, 0.06 mmol), $Co(dmgH)_2PyCl$ (6.5 mg, 0.016 mmol), 1,1-diphenylethylene (53 μL, 0.3 mmol) and DCE (3 mL). The reaction mixture was stirred under the irradiation of blue LED light (5 W) at ambient atmosphere in a parallel light reactor. After the completion of the reaction as indicated by TLC, 3 uL of mixture was extracted from the system and intermediate **I-C** was detected by the HPLC analysis. The remaining solution was concentrated *in vacuo*. Then the residue was purified by silica gel flash column chromatography to afford product **5a** (13.5 mg, 37%).

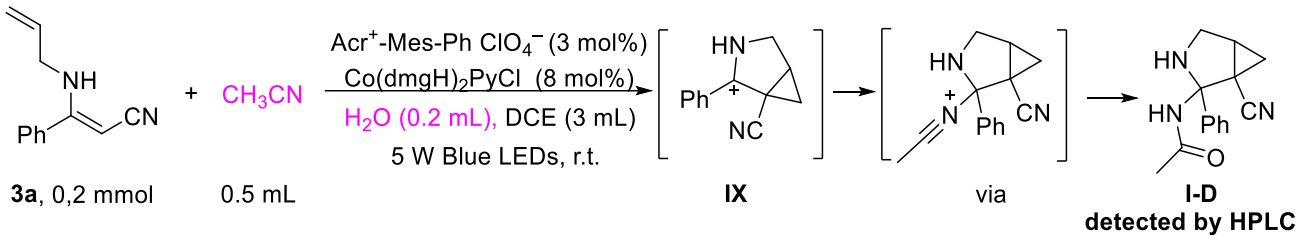


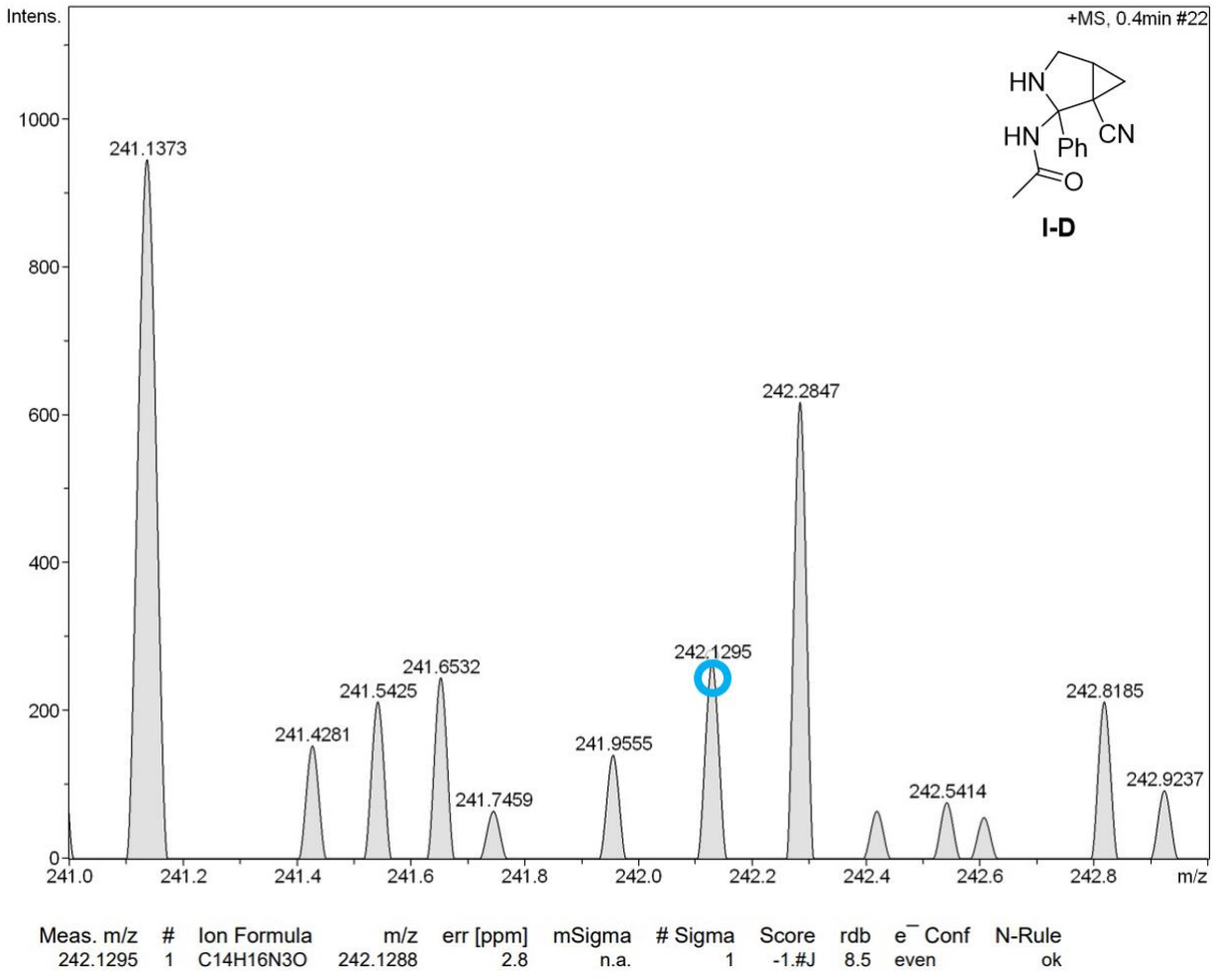


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
363.1833	1	C10H23N10O5	363.1847	3.8	491.3	1	-1.#J	4.5	even	ok
	1	C9H27N6O9	363.1834	0.2	504.9	1	-1.#J	-0.5	even	ok
385.1671	1	C26H22N2Na	385.1675	1.2	372.9	1	100.00	16.5	even	ok

6) Carbocation trapping experiments

To a flask (20 mL) equipped with a stir-bar was added *N*-allyl enamine **3a** (36.8 mg, 0.2 mmol), Acr^+-Mes-Ph ClO_4^- (2.5 mg, 0.06 mmol), $Co(dmgH)_2PyCl$ (6.5 mg, 0.016 mmol), 1,1-diphenylethylene (53 μL, 0.3 mmol), CH_3CN (0.5 mL), H_2O (0.2 mL) and DCE (3 mL). The reaction mixture was stirred under the irradiation of blue LED light (5 W) at ambient atmosphere in a parallel light reactor for 24 hours, 3 uL of mixture was extracted from the system and intermediate **I-D** was detected by the HPLC analysis.



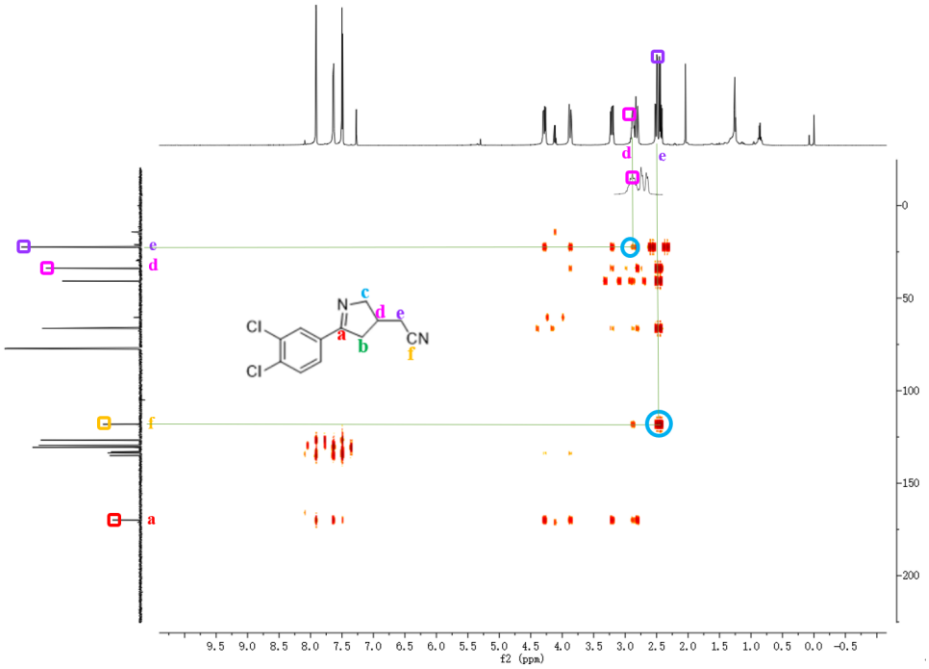


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
242.1295	1	C14H16N3O	242.1288	2.8	n.a.	1	-1.#J	8.5	even	ok

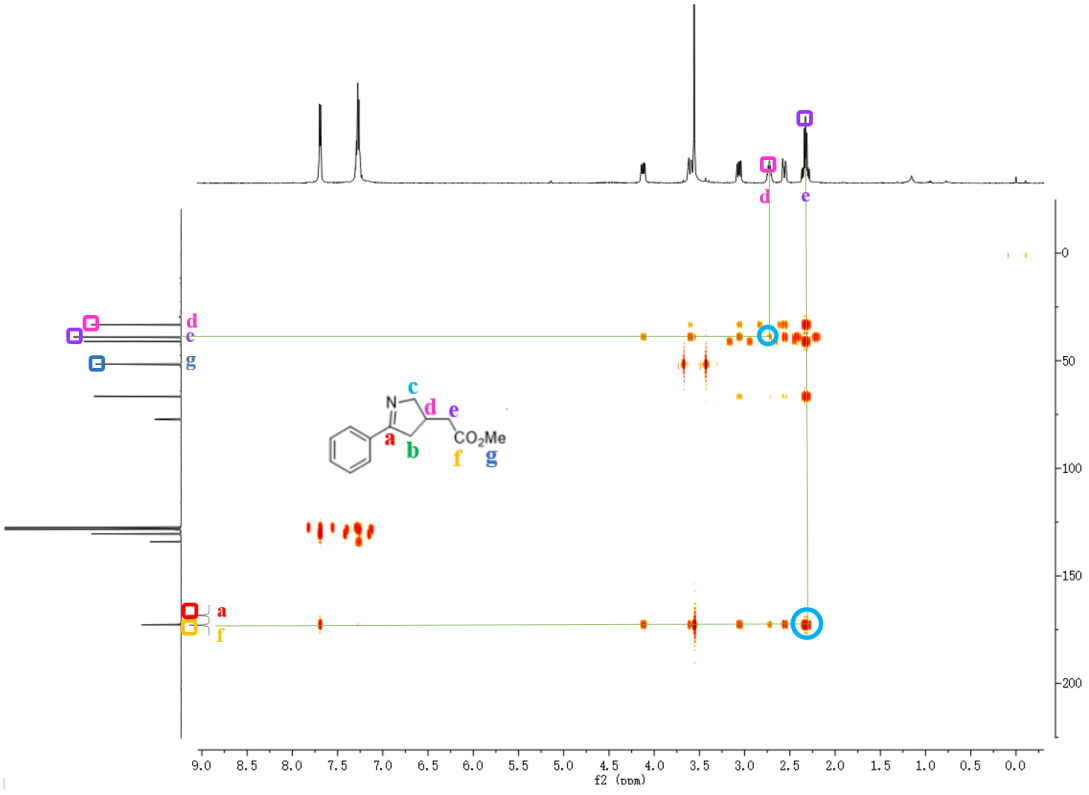
7) HMBC spectra analyses

The structure of the products (**4r, 2s, 2d, 2u**) were further verified through HMBC spectra analysis. The site e is associated with d and f, respectively.

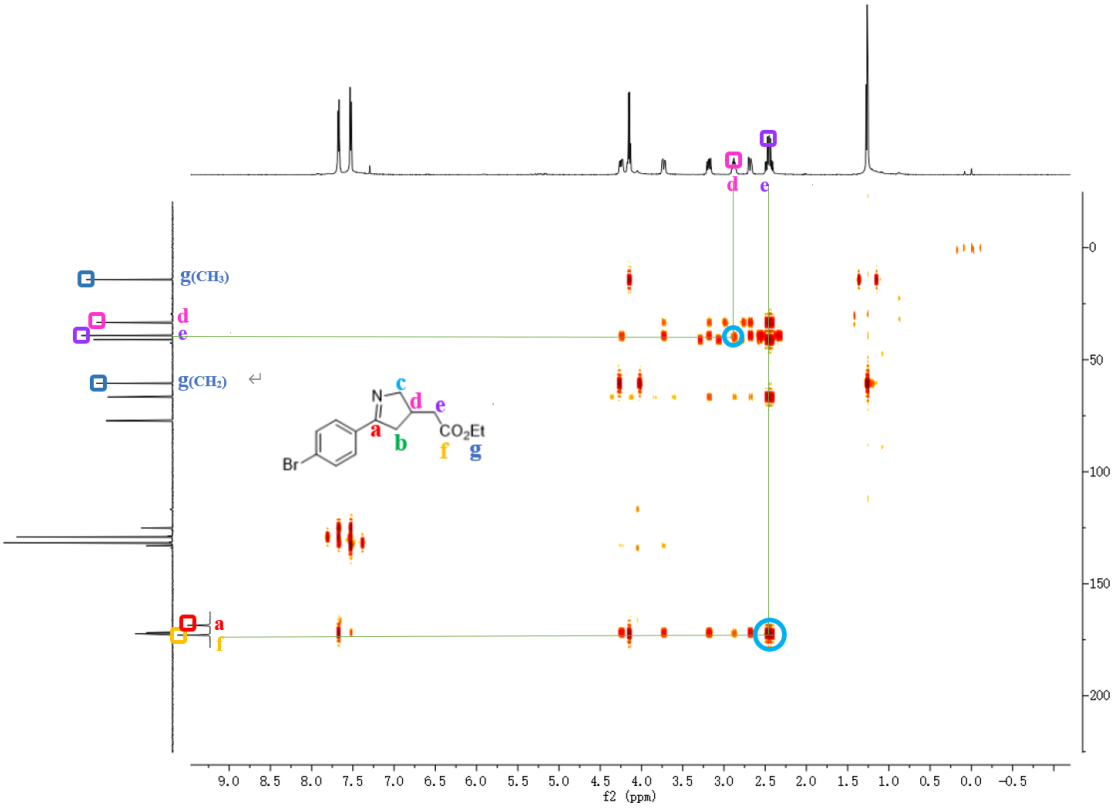
HMBC spectrum of 4r



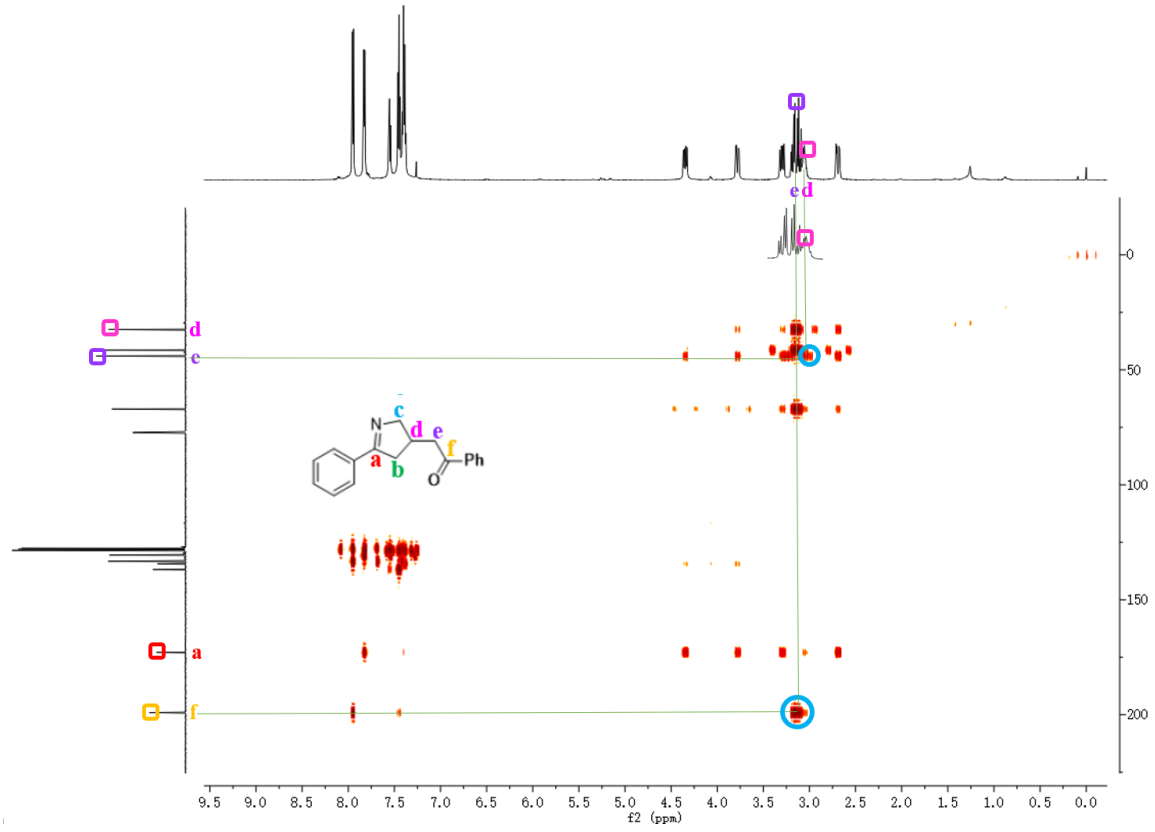
HMBC spectrum of 2s



HMBC spectrum of 2d

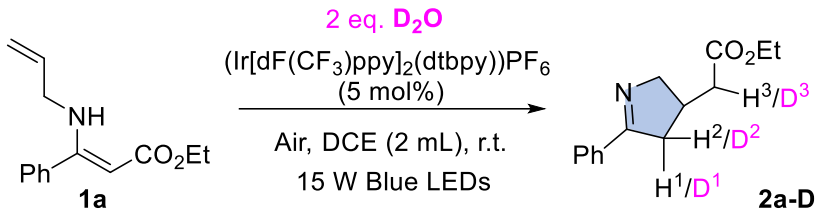


HMBC spectrum of 2u



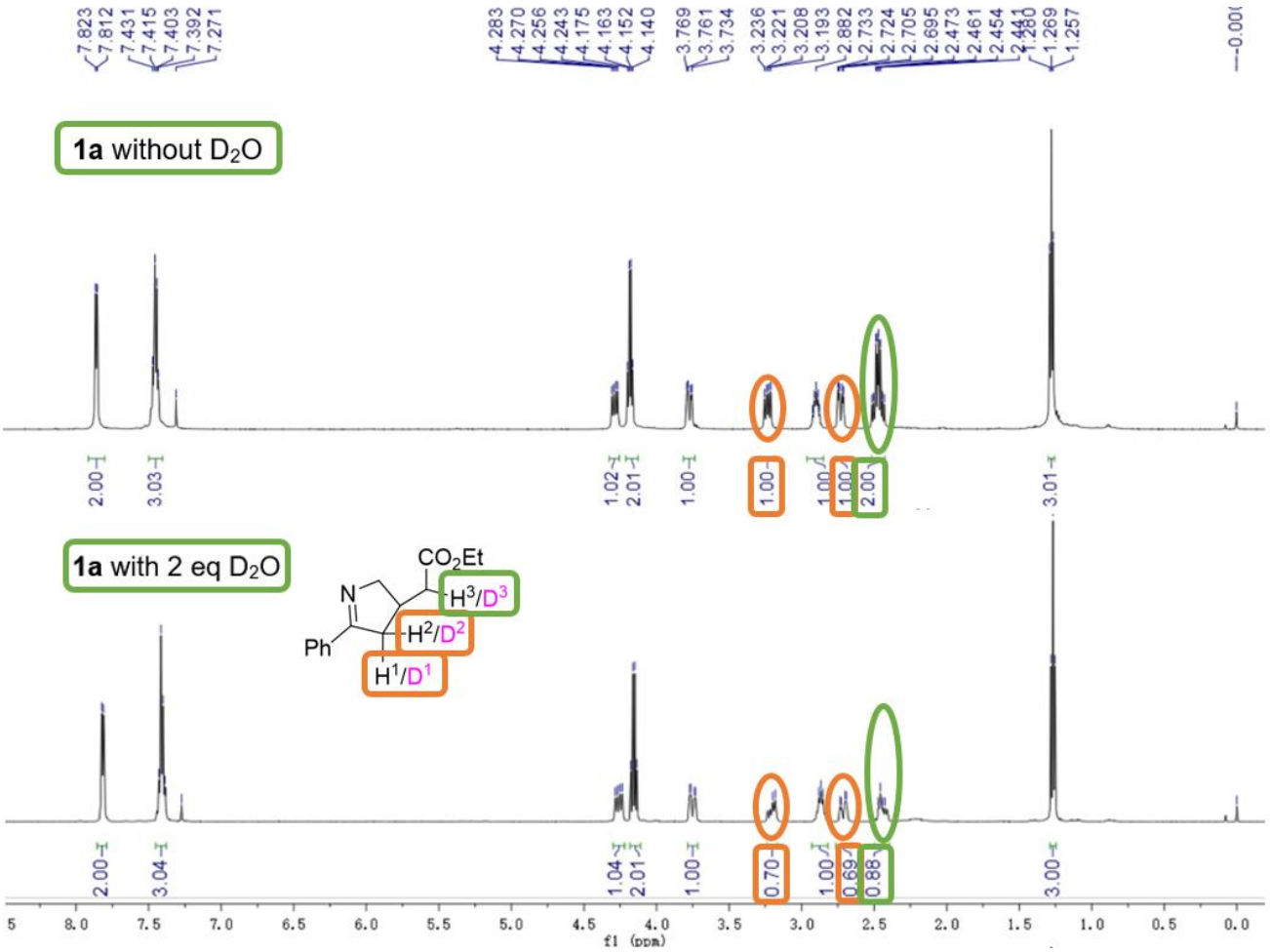
8) Hydrogen-deuterium-exchange experiments

To a flask (15 mL) equipped with a stir-bar was added *N*-allyl enamine **1a** (69.3 mg, 0.3 mmol), (Ir[dF(CF$_3$)ppy]$_2$(dtbpy))PF$_6$ (16.8 mg, 0.015 mmol), D$_2$O (11 μL, 0.6 mmol) and DCE (2 mL). The reaction mixture was stirred under the irradiation of blue LED light (15 W) at ambient atmosphere in a parallel light reactor. After the completion of the reaction as indicated by TLC, the solution was concentrated *in vacuo*. Then the residue was purified by silica gel flash column chromatography to afford product **2a-D** and characterized by **^{1}H NMR.** The results showed that carbanion may be involved in the crucial 1,3-acyl migration step.

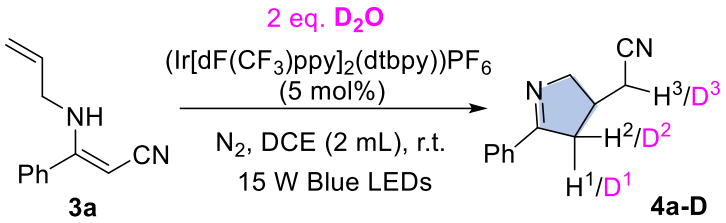


H^1/D^1 or H^2/D^2 = 0.7/0.3

H^3/D^3 = 0.4/0.6

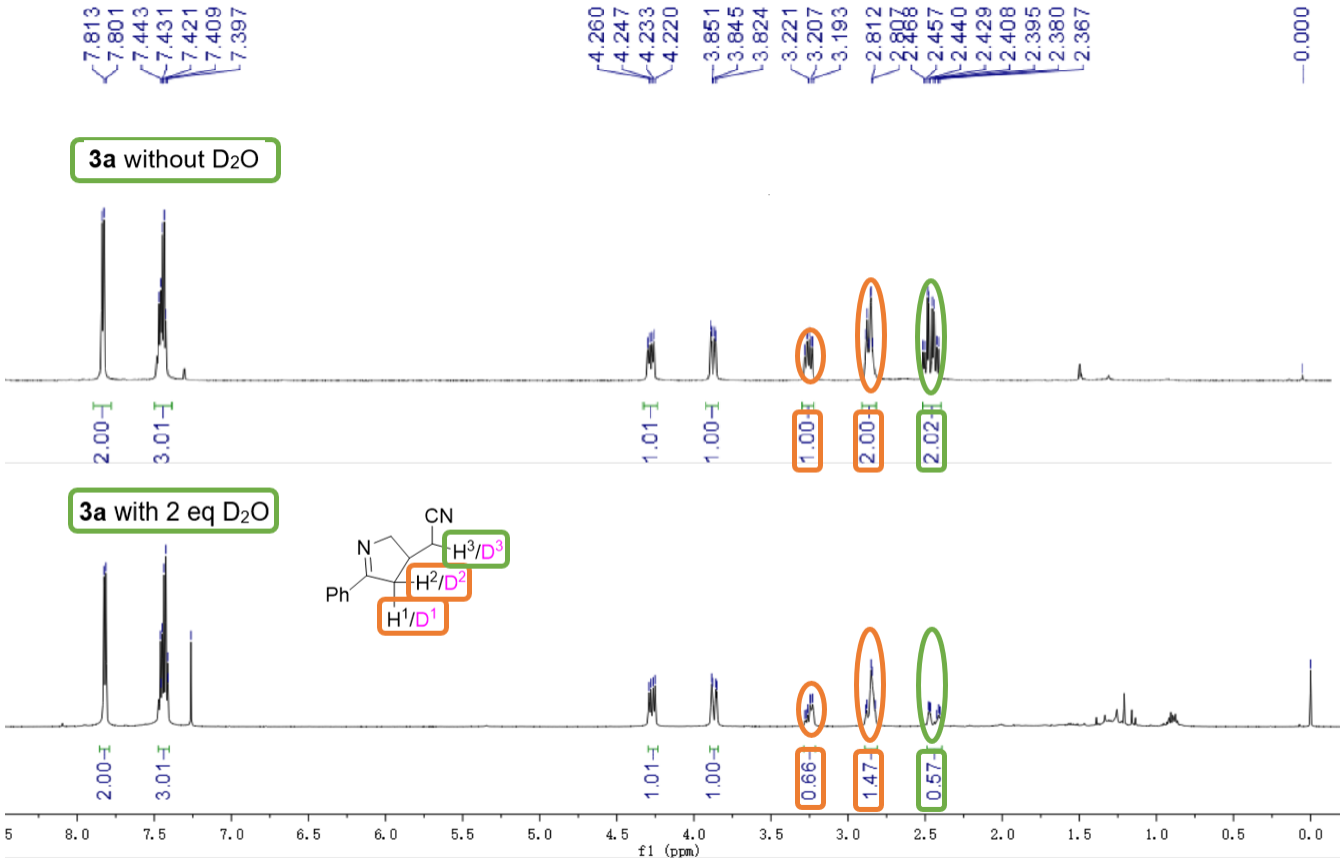


To a flask (15 mL) equipped with a stir-bar was added *N*-allyl enamine **3a** (55.2 mg, 0.3 mmol), (Ir[dF(CF$_3$)ppy]$_2$(dtbpy))PF$_6$ (16.8 mg, 0.015 mmol), D$_2$O (11 μL, 0.6 mmol) and DCE (2 mL) under nitrogen atmosphere. The reaction mixture was stirred under the irradiation of blue LED light (15 W) at ambient atmosphere in a parallel light reactor. After the completion of the reaction as indicated by TLC, the solution was concentrated *in vacuo*. Then the residue was purified by silica gel flash column chromatography to afford product **4a-D** and characterized by **^{1}H NMR.** The results showed that carbanion may be involved in the crucial 1,3-cyano migration step.

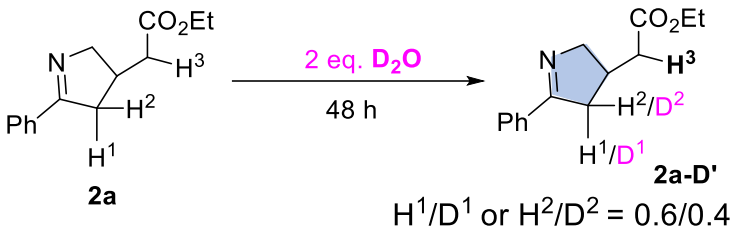


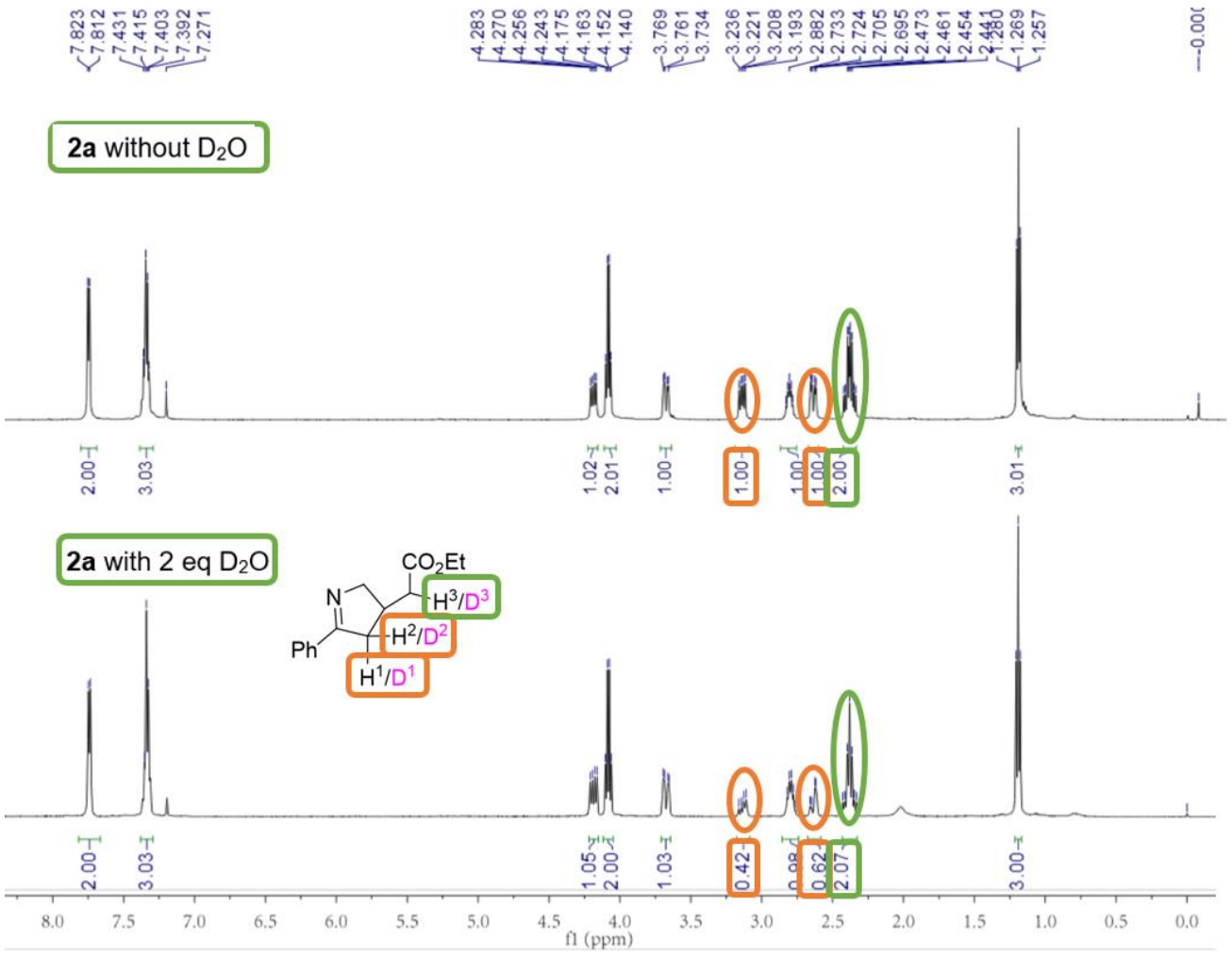
H^1/D^1 or H^2/D^2 = 0.7/0.3 or 0.5/0.5

H^3/D^3 = 0.3/0.7



To a flask (15 mL) equipped with a stir-bar was added 1,3-C→C migration product **2a** (69.3 mg, 0.3 mmol), D_2O (11 μL, 0.6 mmol) and DCE (2 mL). The reaction mixture was stirred at ambient atmosphere for 48 h, then the solution was concentrated *in vacuo* and the residue was tested by **^{1}H NMR**. The results showed that the 1,3-C→C acyl migration process was proposed to be triggered by the carbanion **IV** but not radical **III**, since H^3 of **2a-D'** in the hydrogen-deuterium-exchange investigation of **2a** could not be exchanged while H^3 of **2a-D** from **1a** was exchanged.





To a flask (20 mL) equipped with a stir-bar was added *N*-allyl enamine **3a** (36.8 mg, 0.2 mmol), Acr^+-Mes-Ph ClO_4^- (2.5 mg, 0.06 mmol), $Co(dmgH)_2PyCl$ (6.5 mg, 0.016 mmol), D_2O (7 μL, 0.6 mmol) and DCE (3 mL). The reaction mixture was stirred under the irradiation of blue LED light (5 W) at ambient atmosphere in a parallel light reactor. After the completion of the reaction as indicated by TLC, the solution was concentrated *in vacuo*. Then the residue was purified by silica gel flash column chromatography to afford product **5a** without any deuterium substitution and characterized by **^{1}H NMR.** The results showed that with the mediation of $Co(dmgH)_2PyCl$, carbanion may not be involved as the key intermediate in the formation of **5a**.

No H/D exchange phenomenon

V. Computational details

All calculations in this work were performed using Gaussian 09 program package.[1] Full geometry optimizations were performed to locate all the stationary points, using the B3LYP-D3 functional[2,3] with the 6-311+G**[4–5] basis set in gas phase model. The intrinsic reaction coordinate (IRC) path was traced to check the energy profiles connecting each transition state to two associated minima of the proposed mechanism.[6] Harmonic vibrational frequency was performed at the same level to guarantee that there is no imaginary frequency in the molecules, i.e. they locate on the minima of potential energy surface. Convergence parameters of the default threshold were retained (maximum force within 4.5×10^{-4} Hartrees/Bohr and root mean square (RMS) force within 3.0×10^{-4} Hartrees/Radian) to obtain the optimized structure. The optimal structure was identified given that all calculations for structural optimization were successfully converged within the convergence threshold of no imaginary frequency, during the process of vibration analysis.

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(6) C. Gonzalez and H. B. Schlegel, An improved Algorithm for Reaction Path Following. *J. Chem. Phys.*, 1989, **90**, 2154–2161.

Cartesian coordinates of all stationary points

Date: 1

Zero-point correction=	0.283004(Hartree/Particle)
Thermal correction to Energy=	0.300213
Thermal correction to Enthalpy=	0.301157
Thermal correction to Gibbs Free Energy=	0.236468
Sum of electronic and zero-point Energies=	-748.060508
Sum of electronic and thermal Energies=	-748.043298
Sum of electronic and thermal Enthalpies=	-748.042354
Sum of electronic and thermal Free Energies=	-748.107043

Standard orientation:

Center Number	Coordinates (Angstroms) X	Y	Z
C	-0.53173400	0.05618200	0.31577900
C	-2.00275100	0.01959600	0.04886700
C	-2.62193700	-1.16155700	-0.39869900
C	-2.80157300	1.16306400	0.23681600
C	-3.99584600	-1.20001200	-0.64172600
H	-2.01047900	-2.04947100	-0.57201600
C	-4.17653500	1.12452400	-0.00584600
H	-2.34872700	2.08592600	0.60842900
C	-4.77861000	-0.05733800	-0.44687900
H	-4.45727100	-2.12580100	-0.99474000
H	-4.78153200	2.01963400	0.15968800
H	-5.85391000	-0.08777900	-0.63974900
N	0.09241600	1.22508000	-0.07194300
H	-0.48900800	1.84597900	-0.62230300
C	1.21515600	1.88211700	0.59946700
H	0.82666900	2.75231700	1.16794000
H	1.64637000	1.20012700	1.34130800
C	2.28113600	2.36954600	-0.34837300

H	1.93453500	3.02519800	-1.15885300
C	3.58319100	2.09546500	-0.23848700
H	4.31320000	2.51496200	-0.93676300
H	3.96516500	1.43773000	0.54821700
C	0.06673100	-1.01302300	0.92336300
H	-0.59089400	-1.74482700	1.39473200
C	1.49945100	-1.23671200	1.22774100
O	2.41520700	-1.07572000	0.22867600
O	1.89413500	-1.57708000	2.31748800
C	2.06231600	-1.19053300	-1.15550200
H	1.35854300	-2.02907000	-1.28755700
H	1.55950000	-0.27082600	-1.49467800
C	3.33786200	-1.42856000	-1.94115700
H	3.10728900	-1.53906200	-3.01288100
H	4.03205100	-0.58263100	-1.82268200
H	3.84569700	-2.34211800	-1.59597500

Date: TS1

Zero-point correction=	0.276078(Hartree/Particle)
Thermal correction to Energy=	0.288959
Thermal correction to Enthalpy=	0.289904
Thermal correction to Gibbs Free Energy=	0.235860
Sum of electronic and zero-point Energies=	-748.034851
Sum of electronic and thermal Energies=	-748.017641
Sum of electronic and thermal Enthalpies=	-748.016697
Sum of electronic and thermal Free Energies=	-748.081386

Standard orientation:

Center	Coordinates (Angstroms)		
Number	X	Y	Z

C	-1.73820000	1.33480000	-1.25500000
C	-3.00960000	1.28320000	-0.55450000
C	-3.91240000	0.22420000	-0.81220000
C	-3.35960000	2.25770000	0.38950000
C	-5.14630000	0.16440000	-0.14730000
H	-3.67900000	-0.51990000	-1.51660000
C	-4.59350000	2.19870000	1.05740000
H	-2.69750000	3.04330000	0.61110000
C	-5.49070000	1.15210000	0.78830000
H	-5.81560000	-0.61940000	-0.35320000
H	-4.84610000	2.93830000	1.76010000
H	-6.41540000	1.10890000	1.28550000
N	-1.02110000	2.54050000	-1.47640000
H	-1.45610000	3.45030000	-1.36170000
C	0.42180000	2.40640000	-1.56960000
H	0.79690000	2.95170000	-2.42090000
H	0.87030000	2.75300000	-0.64810000
C	0.82360000	1.00630000	-1.83160000
H	0.66280000	0.59750000	-2.77540000
C	1.72260000	0.28770000	-0.93220000
H	2.64700000	0.40590000	-1.34420000
H	1.60000000	0.21390000	0.10820000
C	-0.97910000	0.10500000	-1.21700000
H	-0.71590000	-0.23740000	-0.26580000
C	-1.01200000	-0.90970000	-2.27730000
O	-1.52760000	-0.74840000	-3.51240000
O	-0.83730000	-2.03510000	-1.86200000
C	-1.81770000	0.42350000	-4.21200000
H	-2.68640000	0.91230000	-3.77050000
H	-0.96640000	1.10450000	-4.18840000
C	-2.13550000	0.07600000	-5.68350000
H	-2.36510000	0.98980000	-6.23370000
H	-1.27490000	-0.41170000	-6.14360000
H	-2.99560000	-0.59370000	-5.72830000

Date: 2

Zero-point correction=	0.278022(Hartree/Particle)
Thermal correction to Energy=	0.290471
Thermal correction to Enthalpy=	0.291415
Thermal correction to Gibbs Free Energy=	0.239255
Sum of electronic and zero-point Energies=	-748.0719819
Sum of electronic and thermal Energies=	-748.0547719
Sum of electronic and thermal Enthalpies=	-748.0538279
Sum of electronic and thermal Free Energies=	-748.1185169

Standard orientation:

Center Number	Coordinates (Angstroms) X	Y	Z
C	-1.71140000	1.34420000	-1.25700000
C	-3.00620000	1.27270000	-0.55460000
C	-3.91010000	0.22380000	-0.81260000
C	-3.35930000	2.25720000	0.38920000
C	-5.14630000	0.16430000	-0.14750000
H	-3.67830000	-0.51960000	-1.51650000
C	-4.59380000	2.19860000	1.05740000
H	-2.69750000	3.04330000	0.61110000
C	-5.49070000	1.15230000	0.78840000
H	-5.81570000	-0.61930000	-0.35320000
H	-4.84620000	2.93840000	1.76020000
H	-6.41560000	1.10900000	1.28550000
N	-1.03090000	2.55950000	-1.47580000
H	-1.45620000	3.45070000	-1.36170000
C	0.40480000	2.39490000	-1.56820000
H	0.80200000	2.94190000	-2.42340000
H	0.87100000	2.74990000	-0.64790000
C	0.60720000	0.86410000	-1.75030000
H	0.78000000	0.66440000	-2.81080000
C	1.79720000	0.35590000	-0.97540000

H	2.75560000	0.47580000	-1.39290000
H	1.72530000	0.26530000	0.07060000
C	-0.73040000	0.19550000	-1.30300000
H	-0.62490000	-0.18810000	-0.28440000
C	-1.12200000	-0.94020000	-2.22400000
O	-1.64470000	-0.80840000	-3.47380000
O	-0.95600000	-2.09160000	-1.81800000
C	-1.93380000	0.36490000	-4.17260000
H	-2.80310000	0.85400000	-3.73070000
H	-1.08330000	1.04620000	-4.14890000
C	-2.25230000	0.01780000	-5.64390000
H	-2.48180000	0.93160000	-6.19380000
H	-1.39170000	-0.47010000	-6.10380000
H	-3.11240000	-0.65200000	-5.68860000

Date: 3

Zero-point correction=	0.265835(Hartree/Particle)
Thermal correction to Energy=	0.279358
Thermal correction to Enthalpy=	0.280302
Thermal correction to Gibbs Free Energy=	0.224587
Sum of electronic and zero-point Energies=	-748.0794719
Sum of electronic and thermal Energies=	-748.0622619
Sum of electronic and thermal Enthalpies=	-748.0613179
Sum of electronic and thermal Free Energies=	-748.1260069

Standard orientation:

Center		Coordinates (Angstroms)	
Number	X	Y	Z

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C	-3.67660000	2.32280000	-0.50350000
C	-4.77340000	-0.09100000	0.40930000
H	-2.84250000	-0.90490000	0.07950000
C	-5.02410000	2.26770000	-0.10840000
H	-3.28320000	3.23440000	-0.84970000
C	-5.57540000	1.05940000	0.34640000
H	-5.18150000	-0.99680000	0.75230000
H	-5.62060000	3.13180000	-0.15640000
H	-6.58340000	1.01660000	0.64060000
N	-0.81450000	2.35350000	-0.97450000
C	0.56950000	2.20100000	-1.38520000
H	0.78840000	2.85090000	-2.23240000
H	1.22380000	2.44810000	-0.54810000
C	0.70170000	0.70740000	-1.78790000
H	0.72830000	0.63850000	-2.87810000
C	1.95420000	0.07260000	-1.23870000
H	2.85320000	0.19290000	-1.77240000
H	2.01760000	-0.12590000	-0.20710000
C	-0.59980000	0.04990000	-1.24430000
H	-0.38490000	-0.49170000	-0.31920000
C	-1.21570000	-0.90150000	-2.24970000
O	-2.01220000	-0.54960000	-3.29560000
O	-1.10610000	-2.10940000	-2.03310000
C	-2.19470000	0.71130000	-3.86670000
H	-3.06660000	1.18940000	-3.41730000
H	-1.32070000	1.34350000	-3.71720000
C	-2.43360000	0.55130000	-5.38440000
H	-2.56090000	1.53400000	-5.84050000
H	-1.57840000	0.05280000	-5.84300000
H	-3.33220000	-0.04250000	-5.55750000

Date: 4

Zero-point correction=	0.95105 (Hartree/Particle)
Thermal correction to Energy=	1.01578
Thermal correction to Enthalpy=	1.017669
Thermal correction to Gibbs Free Energy=	0.817128
Sum of electronic and zero-point Energies=	-3687.399506
Sum of electronic and thermal Energies=	-3687.334775
Sum of electronic and thermal Enthalpies=	-3687.332886
Sum of electronic and thermal Free Energies=	-3687.533428

Standard orientation:

Center Number	Coordinates (Angstroms) X	Y	Z
C	-4.48540000	0.83070000	4.15470000
C	-3.62550000	0.19520000	3.24070000
C	-2.33510000	-0.17090000	3.66050000
C	-1.96240000	0.13560000	4.98010000
C	-2.88660000	0.77070000	5.82550000
N	-4.09720000	1.08980000	5.39370000
H	-3.92550000	0.01050000	2.25200000
H	-0.99830000	-0.09090000	5.33180000
H	-2.58610000	1.00760000	6.80110000
C	-1.34400000	-0.77450000	2.69260000
H	-1.87500000	-1.40450000	1.97530000
H	-0.63420000	-1.39900000	3.23970000
C	-0.57720000	0.34230000	1.93630000
H	-0.05200000	0.97030000	2.65990000
H	-1.29260000	0.96110000	1.38860000
C	0.45060000	-0.25110000	0.93780000
H	1.17650000	-0.86000000	1.48200000
H	-0.06860000	-0.88470000	0.21550000
C	1.20490000	0.86320000	0.17350000
H	1.74290000	1.50090000	0.87670000

H	1.92030000	0.41210000	-0.51570000
H	0.49890000	1.47010000	-0.39520000
C	-7.68380000	2.39490000	4.69600000
C	-8.35510000	2.32840000	3.46440000
C	-7.71610000	1.73120000	2.36470000
C	-6.42980000	1.19910000	2.56010000
C	-5.83190000	1.31140000	3.82790000
N	-6.45940000	1.90830000	4.82880000
H	-8.16840000	2.85380000	5.50440000
H	-9.31670000	2.74150000	3.36750000
H	-5.92000000	0.75290000	1.75840000
C	-8.36350000	1.72080000	1.00020000
H	-9.39380000	1.37200000	1.10870000
H	-7.84110000	1.01780000	0.34750000
C	-8.38490000	3.12150000	0.32720000
H	-8.94660000	3.82260000	0.94830000
H	-8.92310000	3.01440000	-0.61960000
C	-6.98110000	3.70850000	0.00600000
H	-6.29100000	2.90380000	-0.25610000
H	-7.08140000	4.36390000	-0.86370000
C	-6.37880000	4.55300000	1.15750000
H	-6.16520000	3.93190000	2.02560000
H	-5.44680000	5.00900000	0.81860000
H	-7.07260000	5.34450000	1.44430000
C	-5.77250000	4.87830000	6.35860000
C	-5.59040000	6.19700000	5.90180000
C	-4.65350000	6.45020000	4.88880000
C	-3.91660000	5.37820000	4.35910000
C	-4.12620000	4.10400000	4.91670000
N	-5.03940000	3.89160000	5.85320000
H	-4.52120000	7.42910000	4.53200000
H	-6.15130000	6.99470000	6.28320000
H	-3.55460000	3.30380000	4.55520000
C	-7.68400000	2.50560000	8.49840000
C	-8.56600000	3.33110000	9.21300000

C	-8.54190000	4.72150000	9.01340000
C	-7.64590000	5.29970000	8.09590000
C	-6.76160000	4.47420000	7.37440000
C	-6.78620000	3.08690000	7.58920000
H	-7.69990000	1.46780000	8.64960000
H	-9.20220000	5.33580000	9.55380000
C	-2.88900000	5.57580000	3.26810000
F	-1.52660000	5.65080000	3.86740000
F	-3.14480000	6.82590000	2.49530000
F	-2.92630000	4.43320000	2.30810000
F	-7.67650000	6.74140000	7.94280000
F	-9.49780000	2.74830000	10.16040000
C	-5.24040000	-0.05050000	8.41860000
C	-5.49230000	-1.29960000	9.01530000
C	-6.36510000	-2.19800000	8.38320000
C	-6.95630000	-1.83070000	7.16280000
C	-6.66970000	-0.54970000	6.65660000
N	-5.83260000	0.27100000	7.27280000
H	-6.57120000	-3.12760000	8.82720000
H	-5.05260000	-1.57510000	9.92500000
H	-7.13750000	-0.24360000	5.76970000
C	-3.54530000	3.25470000	8.58230000
C	-2.81000000	3.20440000	9.77670000
C	-2.85250000	2.04860000	10.57440000
C	-3.62840000	0.93940000	10.19060000
C	-4.36610000	0.98830000	8.99140000
C	-4.31040000	2.14420000	8.19790000
H	-3.52480000	4.11570000	7.98800000
H	-2.30110000	2.01420000	11.46860000
C	-7.94930000	-2.73080000	6.46450000
F	-7.85050000	-2.57710000	4.98320000
F	-9.32940000	-2.36790000	6.89800000
F	-7.70210000	-4.16590000	6.78960000
F	-3.62790000	-0.21760000	11.06520000
F	-2.00930000	4.34350000	10.18500000

Ir	-5.42070000	2.05410000	6.50730000
C	-0.35040000	9.43790000	7.49040000
C	-0.33930000	10.91070000	7.56260000
C	-1.39600000	11.67880000	7.03510000
C	0.74220000	11.57430000	8.17550000
C	-1.36800000	13.08170000	7.11120000
H	-2.22320000	11.21270000	6.58550000
C	0.77170000	12.97680000	8.25390000
H	1.54380000	11.02480000	8.57640000
C	-0.28340000	13.73300000	7.72000000
H	-2.16190000	13.64460000	6.71370000
H	1.58490000	13.46000000	8.71200000
H	-0.26260000	14.78210000	7.77770000
N	0.39000000	8.70990000	8.25420000
C	0.19940000	7.28320000	8.07390000
H	1.15530000	6.79160000	7.89260000
H	-0.27030000	6.86540000	8.96520000
C	-0.72630000	7.16310000	6.83450000
H	-0.13070000	6.82920000	5.98240000
C	-1.84170000	6.17630000	7.05370000
H	-1.64080000	5.15470000	6.90260000
H	-2.63890000	6.43620000	7.68920000
C	-1.24130000	8.61130000	6.59390000
H	-2.26610000	8.70670000	6.96290000
C	-1.20270000	8.99210000	5.12830000
O	-0.08850000	9.27890000	4.40240000
O	-2.27760000	9.09420000	4.53530000
C	1.24710000	9.26290000	4.80680000
H	1.46190000	10.15470000	5.39690000
H	1.46470000	8.37510000	5.39950000
C	2.15460000	9.26010000	3.55660000
H	3.20150000	9.25390000	3.86340000
H	1.95320000	8.37270000	2.95460000
H	1.96300000	10.15190000	2.95790000

Date: 5

Zero-point correction=	0.930157 (Hartree/Particle)
Thermal correction to Energy=	1.145340
Thermal correction to Enthalpy=	1.084124
Thermal correction to Gibbs Free Energy=	0.822141
Sum of electronic and zero-point Energies=	-3687.395137
Sum of electronic and thermal Energies=	-3687.331054
Sum of electronic and thermal Enthalpies=	-3687.330014
Sum of electronic and thermal Free Energies=	-3687.530878

Standard orientation:

Center Number	Coordinates (Angstroms) X	Y	Z
C	-4.63620000	0.68030000	4.11410000
C	-3.77690000	0.07310000	3.18080000
C	-2.51280000	-0.37010000	3.60630000
C	-2.16350000	-0.16320000	4.95160000
C	-3.08560000	0.45110000	5.81480000
N	-4.27170000	0.84380000	5.37610000
H	-4.05980000	-0.04000000	2.17620000
H	-1.21950000	-0.45270000	5.31190000
H	-2.80480000	0.60920000	6.81200000
C	-1.52690000	-0.96070000	2.62530000
H	-2.06940000	-1.52140000	1.86090000
H	-0.86060000	-1.64950000	3.14890000
C	-0.69120000	0.16030000	1.95270000
H	-0.14140000	0.70800000	2.72200000
H	-1.36450000	0.85300000	1.44160000
C	0.31340000	-0.42290000	0.92480000
H	0.98790000	-1.11800000	1.42990000
H	-0.23350000	-0.96440000	0.14950000
C	1.15240000	0.69330000	0.25770000
H	1.72270000	1.23520000	1.01380000
H	1.84540000	0.24880000	-0.45830000

H	0.49760000	1.39000000	-0.26760000
C	-7.82440000	2.24890000	4.69170000
C	-8.47520000	2.26280000	3.44740000
C	-7.82000000	1.73110000	2.32390000
C	-6.54050000	1.17990000	2.50940000
C	-5.96470000	1.20940000	3.79200000
N	-6.60460000	1.74830000	4.81770000
H	-8.32520000	2.65650000	5.51670000
H	-9.43360000	2.68490000	3.36030000
H	-6.02110000	0.77640000	1.69140000
C	-8.44250000	1.80610000	0.95020000
H	-9.47640000	1.45740000	1.01790000
H	-7.91130000	1.14040000	0.26580000
C	-8.44390000	3.24440000	0.36090000
H	-9.01530000	3.91060000	1.01090000
H	-8.96260000	3.19690000	-0.60140000
C	-7.03070000	3.84070000	0.10410000
H	-6.33900000	3.04820000	-0.18880000
H	-7.10880000	4.54540000	-0.72850000
C	-6.44930000	4.61380000	1.31490000
H	-6.26020000	3.94330000	2.15130000
H	-5.50680000	5.07990000	1.02280000
H	-7.14380000	5.39390000	1.62980000
C	-5.90310000	4.60030000	6.54550000
C	-5.66200000	5.94480000	6.20680000
C	-4.61940000	6.25520000	5.32040000
C	-3.83050000	5.21280000	4.80660000
C	-4.14950000	3.89880000	5.19410000
N	-5.15080000	3.63800000	6.02150000
H	-4.43690000	7.25590000	5.05870000
H	-6.24380000	6.72380000	6.59570000
H	-3.57020000	3.11290000	4.81230000
C	-7.94550000	2.12250000	8.43130000
C	-8.87330000	2.91100000	9.12990000
C	-8.84250000	4.30950000	8.99940000

C	-7.89110000	4.93280000	8.17210000
C	-6.95950000	4.14490000	7.46810000
C	-6.99500000	2.74830000	7.60960000
H	-7.97350000	1.07840000	8.52390000
H	-9.54080000	4.89520000	9.52330000
C	-2.69370000	5.45910000	3.84140000
F	-1.45800000	4.78040000	4.33050000
F	-2.39420000	6.91190000	3.68380000
F	-3.05160000	4.90070000	2.50540000
F	-7.92110000	6.38020000	8.08480000
F	-9.86450000	2.28100000	9.98230000
C	-5.49180000	-0.42100000	8.33780000
C	-5.77320000	-1.69290000	8.86930000
C	-6.63510000	-2.55220000	8.17150000
C	-7.18580000	-2.12380000	6.95210000
C	-6.87140000	-0.82470000	6.51210000
N	-6.04580000	-0.04250000	7.19060000
H	-6.86240000	-3.49910000	8.56620000
H	-5.36190000	-2.01520000	9.77720000
H	-7.30770000	-0.47330000	5.62580000
C	-3.71940000	2.83270000	8.67940000
C	-3.02230000	2.71300000	9.89220000
C	-3.12260000	1.53060000	10.64390000
C	-3.91520000	0.45970000	10.19360000
C	-4.61750000	0.57770000	8.97830000
C	-4.51300000	1.76380000	8.23500000
H	-3.64480000	3.71520000	8.11930000
H	-2.59960000	1.44660000	11.55200000
C	-8.16660000	-2.98140000	6.18680000
F	-8.02170000	-2.76550000	4.71700000
F	-9.55490000	-2.62050000	6.59520000
F	-7.94530000	-4.43210000	6.45730000
F	-3.96860000	-0.73040000	11.02060000
F	-2.20240000	3.80970000	10.37080000

Ir	-5.59500000	1.76870000	6.52190000
C	0.70540000	8.80310000	7.89030000
C	1.49040000	9.81240000	8.62660000
C	0.98640000	10.42640000	9.79030000
C	2.76960000	10.18180000	8.16470000
C	1.74250000	11.39290000	10.47480000
H	0.03990000	10.16640000	10.16540000
C	3.52730000	11.14830000	8.84710000
H	3.16870000	9.74200000	7.29690000
C	3.01400000	11.75650000	10.00360000
H	1.35570000	11.84400000	11.34180000
H	4.47860000	11.41750000	8.49040000
H	3.57970000	12.47970000	10.51490000
N	1.23480000	8.02890000	7.00740000
C	0.30560000	7.09080000	6.40700000
H	0.24900000	7.26220000	5.33170000
H	0.63830000	6.07050000	6.59940000
C	-1.06210000	7.38580000	7.08100000
H	-1.77710000	7.71480000	6.32440000
C	-1.61470000	6.16140000	7.76800000
H	-2.09910000	5.43610000	7.18170000
H	-1.17720000	5.84530000	8.67130000
C	-0.76730000	8.53730000	8.08580000
H	-0.91380000	8.18240000	9.10940000
C	-1.65570000	9.74250000	7.85210000
O	-1.46960000	10.70170000	6.90470000
O	-2.56080000	9.94840000	8.66250000
C	-0.64290000	10.66050000	5.78140000
H	0.39680000	10.80030000	6.07900000
H	-0.74980000	9.70670000	5.26430000
C	-1.03780000	11.79990000	4.81600000
H	-0.39850000	11.76860000	3.93270000
H	-2.07800000	11.68230000	4.50940000
H	-0.91520000	12.76430000	5.31150000

Date: 6

Zero-point correction=	0.268904 (Hartree/Particle)
Thermal correction to Energy=	0.282852
Thermal correction to Enthalpy=	0.283796
Thermal correction to Gibbs Free Energy=	0.228454
Sum of electronic and zero-point Energies=	-748.0848901
Sum of electronic and thermal Energies=	-748.0676801
Sum of electronic and thermal Enthalpies=	-748.0667361
Sum of electronic and thermal Free Energies=	-748.1314251

Standard orientation:

Center Number	Coordinates (Angstroms) X	Y	Z
C	0.15160000	-0.74980000	-0.32950000
C	1.55880000	-0.34040000	-0.15290000
C	2.03380000	0.21840000	1.05470000
C	2.47980000	-0.49940000	-1.21600000
C	3.37270000	0.59060000	1.19280000
H	1.34230000	0.37580000	1.88520000
C	3.81090000	-0.11610000	-1.07590000
H	2.10590000	-0.93820000	-2.14310000
C	4.27230000	0.43050000	0.13110000
H	3.71580000	1.01730000	2.14040000
H	4.50360000	-0.24810000	-1.91380000
H	5.31840000	0.73160000	0.23990000
N	-0.24280000	-1.33130000	-1.41860000
C	-1.60930000	-1.77070000	-1.29370000
H	-2.24850000	-1.24190000	-2.02960000
H	-1.69310000	-2.84440000	-1.55830000
C	-2.12180000	-1.57790000	0.17110000
H	-3.02370000	-0.93940000	0.18880000
C	-2.38340000	-2.85020000	0.84770000
H	-2.97110000	-2.80980000	1.77760000

H	-1.52550000	-3.54140000	0.90460000
C	-0.87600000	-0.63820000	0.77250000
H	-0.50750000	-1.14970000	1.67640000
C	-1.25780000	0.72040000	1.27210000
O	-1.80160000	1.66810000	0.43500000
O	-1.18440000	1.03610000	2.44510000
C	-1.80120000	1.59350000	-0.98280000
H	-0.77540000	1.45980000	-1.36390000
H	-2.39790000	0.73680000	-1.33200000
C	-2.39770000	2.89100000	-1.50410000
H	-2.42340000	2.88830000	-2.60620000
H	-3.42560000	3.02350000	-1.13030000
H	-1.80190000	3.75480000	-1.16890000

Date: TS2

Zero-point correction=	0.268863 (Hartree/Particle)
Thermal correction to Energy=	0.279615
Thermal correction to Enthalpy=	0.280559
Thermal correction to Gibbs Free Energy=	0.232079
Sum of electronic and zero-point Energies=	-748.0573208
Sum of electronic and thermal Energies=	-748.0401108
Sum of electronic and thermal Enthalpies=	-748.0391668
Sum of electronic and thermal Free Energies=	-748.1038558

Standard orientation:

Center		Coordinates (Angstroms)	
Number	X	Y	Z

C	0.22900000	-1.36150000	-0.40290000
C	1.41770000	-0.51780000	-0.51090000
C	1.90360000	0.15900000	0.63420000

C	2.11770000	-0.38810000	-1.72050000
C	3.05360000	0.95580000	0.54890000
H	1.40240000	0.06290000	1.54740000
C	3.27370000	0.40640000	-1.80550000
H	1.78130000	-0.88200000	-2.59100000
C	3.74180000	1.08660000	-0.65960000
H	3.40060000	1.45850000	1.40940000
H	3.79440000	0.50170000	-2.71430000
H	4.60450000	1.68480000	-0.72060000
N	0.07150000	-2.47110000	-1.05490000
C	-1.19960000	-3.12700000	-0.75330000
H	-1.62840000	-3.64090000	-1.59840000
H	-1.11780000	-3.78500000	0.10860000
C	-2.00580000	-1.86420000	-0.38550000
H	-2.08320000	-1.24840000	-1.29710000
C	-3.09720000	-1.64400000	0.40260000
H	-3.25880000	-2.56020000	0.90110000
H	-3.92420000	-1.38020000	-0.19310000
C	-0.94470000	-1.23810000	0.52960000
H	-0.73620000	-1.83240000	1.40800000
C	-1.79590000	-0.23720000	0.94350000
O	-2.15570000	0.75590000	0.12400000
O	-1.95930000	0.18550000	2.24720000
C	-1.38850000	1.83490000	0.40990000
H	-1.71530000	2.20250000	1.38440000
H	-0.37610000	1.44030000	0.48200000
C	-1.40920000	2.94260000	-0.64220000
H	-0.69720000	3.69400000	-0.30270000
H	-1.10260000	2.53030000	-1.60250000
H	-2.41340000	3.35380000	-0.69420000

Date: 7

Zero-point correction=	0.264422 (Hartree/Particle)
Thermal correction to Energy=	0.277290
Thermal correction to Enthalpy=	0.278234
Thermal correction to Gibbs Free Energy=	0.225805
Sum of electronic and zero-point Energies=	-748.0834559
Sum of electronic and thermal Energies=	-748.0662459
Sum of electronic and thermal Enthalpies=	-748.0653019
Sum of electronic and thermal Free Energies=	-748.1299909

Standard orientation:

Center Number	Coordinates (Angstroms) X	Y	Z
C	0.21390000	-1.33860000	-0.44890000
C	1.42280000	-0.51170000	-0.51610000
C	1.90170000	0.15610000	0.62710000
C	2.12420000	-0.38660000	-1.73020000
C	3.05350000	0.95670000	0.55300000
H	1.39970000	0.06320000	1.54630000
C	3.27940000	0.40980000	-1.80420000
H	1.78220000	-0.88080000	-2.59310000
C	3.74210000	1.08650000	-0.66400000
H	3.39960000	1.45890000	1.40900000
H	3.79640000	0.50150000	-2.71450000
H	4.60360000	1.68530000	-0.71990000
N	0.07490000	-2.47940000	-1.06200000
C	-1.20610000	-3.14510000	-0.73120000
H	-1.62490000	-3.66100000	-1.59220000
H	-1.12090000	-3.80090000	0.13300000
C	-1.93910000	-1.83340000	-0.43900000
H	-2.02930000	-1.24500000	-1.36090000
C	-3.03040000	-1.36750000	0.54350000
H	-3.93400000	0.06310000	-1.00500000

H	-3.21200000	-2.07410000	1.35030000
C	-0.88420000	-1.22660000	0.56380000
H	-0.68830000	-1.88780000	1.41310000
C	-2.01020000	-0.21590000	0.92990000
O	-2.14770000	0.91350000	0.04850000
O	-2.08530000	0.08840000	2.32490000
C	-1.28470000	2.00490000	0.41050000
H	-1.59420000	2.42810000	1.36800000
H	-0.25120000	1.67220000	0.48280000
C	-1.37380000	3.09970000	-0.67490000
H	-0.70640000	3.92370000	-0.41920000
H	-1.07800000	2.68670000	-1.64050000
H	-2.39640000	3.47380000	-0.74070000

Date: TS3

Zero-point correction=	0.265790 (Hartree/Particle)
Thermal correction to Energy=	0.279732
Thermal correction to Enthalpy=	0.280676
Thermal correction to Gibbs Free Energy=	0.224511
Sum of electronic and zero-point Energies=	-748.0614642
Sum of electronic and thermal Energies=	-748.0442542
Sum of electronic and thermal Enthalpies=	-748.0433102
Sum of electronic and thermal Free Energies=	-748.1079992

Standard orientation:

Center	Coordinates (Angstroms)		
Number	X	Y	Z

C	0.50400000	-1.66240000	-0.42760000
C	1.66300000	-0.77560000	-0.53480000
C	1.99870000	0.02710000	0.58420000
C	2.25450000	-0.48000000	-1.77530000

C	3.05130000	0.94870000	0.52260000
H	1.44480000	-0.03690000	1.48020000
C	3.31770000	0.43850000	-1.84570000
H	1.88290000	-0.92380000	-2.65680000
C	3.76080000	1.11300000	-0.68540000
H	3.34280000	1.46910000	1.37160000
H	3.81230000	0.58110000	-2.74050000
H	4.60890000	1.70810000	-0.71470000
N	0.11880000	-2.68620000	-1.13820000
C	-1.25730000	-3.08290000	-0.76200000
H	-1.83310000	-3.49290000	-1.58230000
H	-1.19780000	-3.78390000	0.06190000
C	-1.80500000	-1.67260000	-0.34150000
H	-1.85470000	-1.03360000	-1.22300000
C	-3.04490000	-1.34890000	0.53330000
H	-3.87550000	-1.01780000	-0.11760000
H	-3.40120000	-2.19660000	1.12030000
C	-0.58420000	-1.29570000	0.44430000
H	-0.37700000	-1.69960000	1.40300000
C	-2.16320000	-0.58130000	1.32620000
O	-2.13130000	0.78720000	1.20200000
O	-2.08700000	-0.89950000	2.68990000
C	-1.41180000	1.69810000	2.02180000
H	-1.56080000	1.48050000	3.08160000
H	-0.33700000	1.65640000	1.81160000
C	-1.90410000	3.13540000	1.72260000
H	-1.42230000	3.83150000	2.41240000
H	-1.65610000	3.42450000	0.69810000
H	-2.98530000	3.17890000	1.86400000

Date: 8

Zero-point correction=	0.269465 (Hartree/Particle)
Thermal correction to Energy=	0.282685
Thermal correction to Enthalpy=	0.283629
Thermal correction to Gibbs Free Energy=	0.227181
Sum of electronic and zero-point Energies=	-748.090149
Sum of electronic and thermal Energies=	-748.072939
Sum of electronic and thermal Enthalpies=	-748.071995
Sum of electronic and thermal Free Energies=	-748.136684

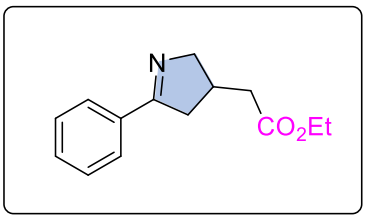
Standard orientation:

Center Number	Coordinates (Angstroms) X	Y	Z
C	0.79210000	-1.18120000	-0.84600000
C	2.21560000	-0.80970000	-0.83070000
C	2.68930000	0.22900000	-0.00470000
C	3.13260000	-1.49520000	-1.65220000
C	4.05010000	0.57920000	-0.00420000
H	2.03220000	0.75260000	0.62600000
C	4.49350000	-1.14630000	-1.65370000
H	2.80530000	-2.27460000	-2.27780000
C	4.95470000	-0.10730000	-0.82970000
H	4.39190000	1.35580000	0.61600000
H	5.16740000	-1.66340000	-2.27290000
H	5.97240000	0.15410000	-0.82970000
N	0.32000000	-2.22090000	-1.44400000
C	-1.12830000	-2.35420000	-1.32550000
H	-1.57930000	-2.42500000	-2.31570000
H	-1.36340000	-3.24980000	-0.74940000
C	-1.61020000	-1.06350000	-0.59670000
H	-2.13700000	-0.42020000	-1.30470000
C	-2.50360000	-1.35420000	0.63740000
H	-3.42860000	-1.83070000	0.30500000

H	-1.98290000	-2.03780000	1.31220000
C	-0.29620000	-0.43020000	-0.22700000
H	-0.21290000	0.57120000	0.07050000
C	-2.85630000	-0.09030000	1.38470000
O	-3.28480000	0.99550000	0.68910000
O	-2.68640000	-0.04500000	2.60410000
C	-3.43690000	2.28610000	1.20290000
H	-4.50050000	2.49560000	1.33030000
H	-2.93730000	2.38880000	2.16780000
C	-2.82800000	3.30250000	0.21080000
H	-2.94460000	4.31370000	0.60340000
H	-1.76580000	3.09400000	0.07190000
H	-3.33660000	3.23100000	-0.75160000

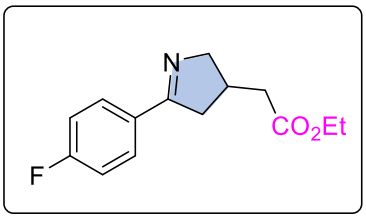
VI. Experimental procedures and analytical data

General Procedure for the synthesis of 2 and 4 (with 2a as an example) To a flask (15 mL) equipped with a stir-bar was added *N*-allyl enamine **1a** (69.3 mg, 0.3 mmol), $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (16.8 mg, 0.015 mmol), and DCE (2 mL). The reaction mixture was stirred under the irradiation of blue LED light (15 W) at ambient atmosphere in a parallel light reactor. After the completion of the reaction as indicated by TLC, the solution was concentrated *in vacuo*. Then the residue was purified by silica gel flash column chromatography (PE/EA = 4/1) to afford product **2a** (50.6 mg, 73%).



2a: ethyl 2-(5-phenyl-3,4-dihydro-2H-pyrrol-3-yl)acetate

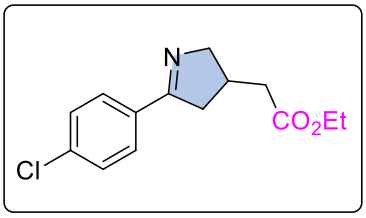
Brown oil. 50.6 mg (73%). **^{1}H NMR** (600 MHz, $CDCl_3$) 7.82 (d, *J* = 6.6 Hz, 2H), 7.43 – 7.39 (m, 3H), 4.26 (dd, *J* = 16.2, 7.8 Hz, 1H), 4.16 (q, *J* = 6.6 Hz, 2H), 3.75 (dd, *J* = 16.2, 4.8 Hz, 1H), 3.21 (dd, *J* = 16.8, 9.0 Hz, 1H), 2.91 – 2.86 (m, 1H), 2.71 (dd, *J* = 16.8, 5.4 Hz, 1H), 2.50 – 2.41 (m, 2H), 1.27 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.5, 172.4, 134.2, 130.4, 128.4, 127.5, 66.7, 60.4, 41.0, 39.3, 33.3, 14.2. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{14}H_{18}NO_2^+$ 232.1332; Found 232.1335.



2b: ethyl 2-(5-(4-fluorophenyl)-3,4-dihydro-2H-pyrrol-3-yl)acetate

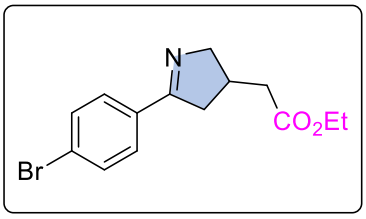
Brown oil. 52.3 mg (70%). **^{1}H NMR** (500 MHz, $CDCl_3$) 7.81 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.09 (t, *J* = 8.5 Hz, 2H), 4.25 (dd, *J* = 16.5, 8.0 Hz, 1H), 4.16 (q, *J* = 7.0 Hz, 2H), 3.74 (dd, *J* = 16.0, 5.0 Hz, 1H), 3.19 (dd, *J* = 17.0, 9.5 Hz, 1H), 2.92 – 2.84 (m, 1H), 2.69 (dd, *J* = 17.0, 5.5 Hz, 1H), 2.51 – 2.41 (m, 2H), 1.27 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.3, 171.4, 164.1 (d, *J* = 249.2

Hz), 130.5 (d, *J* = 3.2 Hz), 129.5 (d, *J* = 8.6 Hz), 115.4 (d, *J* = 21.5 Hz), 66.6, 60.5, 41.1, 39.3, 33.4, 14.1. **^{19}F NMR** (565 MHz, $CDCl_3$): -109.8. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{14}H_{17}FNO_2^+$ 250.1238; Found 250.1239.



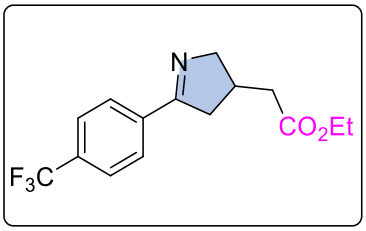
2c: ethyl 2-(5-(4-chlorophenyl)-3,4-dihydro-2H-pyrrol-3-yl)acetate

Yellow oil. 53.3 mg (67%). **^{1}H NMR** (600 MHz, $CDCl_3$) 7.67 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 4.18 (dd, *J* = 16.8, 8.4 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.66 (dd, *J* = 16.2, 4.8 Hz, 1H), 3.11 (dd, *J* = 16.8, 9.0 Hz, 1H), 2.83 – 2.79 (m, 1H), 2.60 (dd, *J* = 16.8, 6.0 Hz, 1H), 2.42 – 2.33 (m, 2H), 1.19 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.3, 171.4, 136.5, 132.7, 128.8, 128.6, 66.7, 60.5, 41.0, 39.2, 33.4, 14.2. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{14}H_{17}ClNO_2^+$ 266.0942; Found 266.0945.



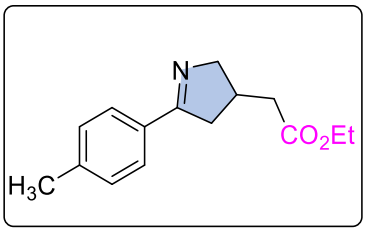
2d: ethyl 2-(5-(4-bromophenyl)-3,4-dihydro-2H-pyrrol-3-yl)acetate

Brown oil. 58.4 mg (63%). **^{1}H NMR** (500 MHz, $CDCl_3$) 7.68 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 4.25 (dd, *J* = 16.5, 8.0 Hz, 1H), 4.16 (q, *J* = 7.0 Hz, 2H), 3.73 (dd, *J* = 16.0, 5.0 Hz, 1H), 3.18 (dd, *J* = 17.0, 9.5 Hz, 1H), 2.91 – 2.86 (m, 1H), 2.68 (dd, *J* = 17.0, 5.5 Hz, 1H), 2.51 – 2.41 (m, 2H), 1.27 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.2, 171.6, 133.0, 131.6, 129.0, 125.0, 66.7, 60.4, 40.9, 39.2, 33.3, 14.1. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{14}H_{17}BrNO_2^+$ 310.0437; Found 310.0432.



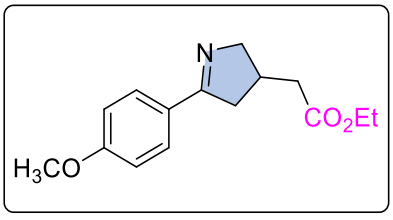
2e: ethyl 2-(5-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2H-pyrrol-3-yl)acetate

Brown oil. 76.3 mg (85%). **^{1}H NMR** (600 MHz, $CDCl_3$) 7.84 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 4.22 (dd, *J* = 16.8, 7.8 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.71 (dd, *J* = 16.2, 4.8 Hz, 1H), 3.15 (dd, *J* = 17.4, 9.0 Hz, 1H), 2.86 – 2.81 (m, 1H), 2.65 (m, *J* = 16.8, 5.4 Hz, 1H), 2.44 – 2.35 (m, 2H), 1.19 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.2, 171.4, 137.4, 132.0 (q, *J* = 32.4 Hz), 127.8, 125.3 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 270.6 Hz), 66.9, 60.5, 41.1, 39.2, 33.4, 14.1. **^{19}F NMR** (565 MHz, $CDCl_3$): -62.8. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{15}H_{17}F_3NO_2^+$ 300.1206. Found 300.1208.



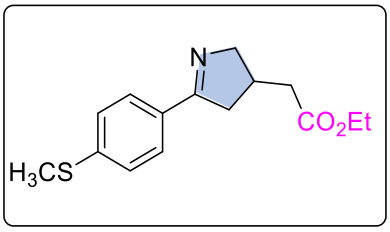
2f: ethyl 2-(5-(p-tolyl)-3,4-dihydro-2H-pyrrol-3-yl)acetate

Brown oil. 44.1 mg (60%). **^{1}H NMR** (600 MHz, $CDCl_3$) 7.63 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 4.17 (dd, *J* = 16.2, 8.4 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.65 (dd, *J* = 16.2, 5.4 Hz, 1H), 3.12 (dd, *J* = 16.8, 9.0 Hz, 1H), 2.81 – 2.77 (m, 1H), 2.62 (dd, *J* = 16.8, 6.0 Hz, 1H), 2.41– 2.33 (m, 2H), 2.30 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.4, 172.4, 140.7, 131.5, 129.1, 127.5, 66.5, 60.4, 41.0, 39.3, 33.3, 21.4, 14.2. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{15}H_{20}NO_2^+$ 246.1489; Found 246.1490.



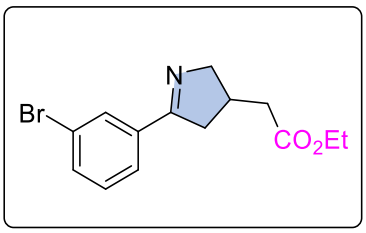
2g: ethyl 2-(5-(4-methoxyphenyl)-3,4-dihydro-2H-pyrrol-3-yl)acetate

Yellow solid. 52.5 mg (67%). mp: 64−65 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 7.77 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 9.0 Hz, 2H), 4.23 (dd, *J* = 15.6, 7.8 Hz, 1H), 4.17 (q, *J* = 6.6 Hz, 2H), 3.84 (s, 3H), 3.72 (dd, *J* = 16.2, 5.4 Hz, 1H), 3.18 (dd, *J* = 16.8, 9.0 Hz, 1H), 2.89 – 2.84 (m, 1H), 2.68 (dd, *J* = 17.4, 6.0 Hz, 1H), 2.50 – 2.42 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.5, 171.8, 161.5, 129.1, 127.2, 113.8, 66.6, 60.4, 55.3, 41.0, 39.4, 33.4, 14.2. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{15}H_{20}NO_3^+$ 262.1438; Found 262.1427.



2h: ethyl 2-(5-(4-(methylthio)phenyl)-3,4-dihydro-2H-pyrrol-3-yl)acetate

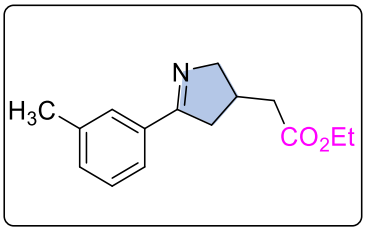
Brown solid. 45.7 mg (55%). mp: 49−50 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 7.72 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 4.24 (dd, *J* = 16.8, 8.4 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.73 (dd, *J* = 16.2, 5.4 Hz, 1H), 3.18 (dd, *J* = 16.8, 9.0 Hz, 1H), 2.89 – 2.84 (m, 1H), 2.67 (dd, *J* = 17.4, 6.0 Hz, 1H), 2.50 (s, 3H), 2.49 – 2.41 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.4, 171.9, 141.9, 130.8, 127.8, 125.5, 66.6, 60.4, 40.9, 39.3, 33.3, 15.1, 14.2. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{15}H_{20}NO_2S^+$ 278.1209; Found 278.1202.



2i: ethyl 2-(5-(3-bromophenyl)-3,4-dihydro-2H-pyrrol-3-yl)acetate

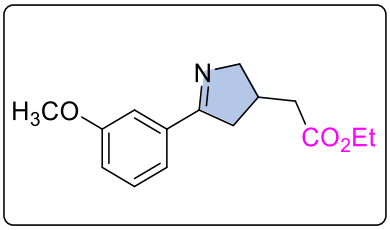
Brown oil. 78.8 mg (85%). **^{1}H NMR** (500 MHz, $CDCl_3$) 7.97 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 4.27 (dd, *J* = 16.5, 8.0 Hz, 1H), 4.16 (q, *J* = 7.5 Hz, 2H), 3.75 (dd, *J* = 16.5, 5.5 Hz, 1H), 3.18 (dd, *J* = 17.0, 9.0 Hz, 1H), 2.91 – 2.86 (m, 1H), 2.68 (dd, *J* = 17.0, 6.0 Hz, 1H), 2.51 – 2.41 (m, 2H), 1.27 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$)

172.2, 171.3, 136.2, 133.3, 130.5, 129.9, 126.0, 122.6, 66.7, 60.5, 41.0, 39.2, 33.3, 14.1. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{14}H_{17}BrNO_2^+$ 310.0437; Found 310.0431.



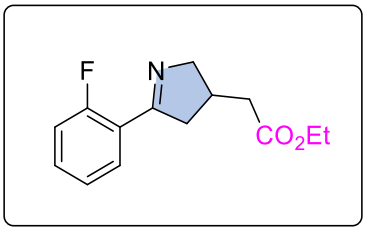
2j: ethyl 2-(5-(m-tolyl)-3,4-dihydro-2H-pyrrol-3-yl)acetate

Brown oil. 43.4 mg (59%). **^{1}H NMR** (600 MHz, $CDCl_3$) 7.60 (s, 1H), 7.50 (d, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 4.18 (dd, *J* = 16.2, 7.8 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.66 (dd, *J* = 16.2, 5.4 Hz, 1H), 3.13 (dd, *J* = 17.4, 9.0 Hz, 1H), 2.82 – 2.77 (m, 1H), 2.63 (dd, *J* = 16.8, 6.0 Hz, 1H), 2.42 – 2.33 (m, 2H), 2.30 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.7, 172.4, 138.1, 134.1, 131.2, 128.3, 128.0, 124.7, 66.6, 60.4, 41.1, 39.3, 33.3, 21.2, 14.2. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{15}H_{20}NO_2^+$ 246.1489; Found 246.1496.



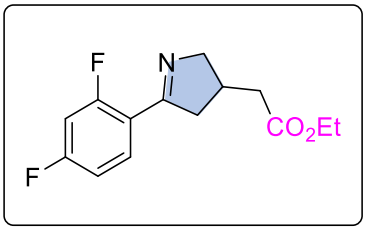
2k: ethyl 2-(5-(3-methoxyphenyl)-3,4-dihydro-2H-pyrrol-3-yl)acetate

Brown oil. 47.8 mg (61%). **^{1}H NMR** (500 MHz, $CDCl_3$) 7.43 (s, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 4.26 (dd, *J* = 16.5, 8.0 Hz, 1H), 4.16 (q, *J* = 7.5 Hz, 2H), 3.85 (s, 3H), 3.75 (dd, *J* = 16.5, 5.5 Hz, 1H), 3.21 (dd, *J* = 17.0, 9.0 Hz, 1H), 2.91 – 2.85 (m, 1H), 2.70 (dd, *J* = 17.0, 5.5 Hz, 1H), 2.50 – 2.41 (m, 2H), 1.27 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) 172.5, 172.4, 159.6, 135.6, 129.4, 120.3, 117.1, 111.6, 66.6, 60.4, 55.3, 41.2, 39.3, 33.3, 14.2. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{15}H_{20}NO_3^+$ 262.1438; Found 262.1427.



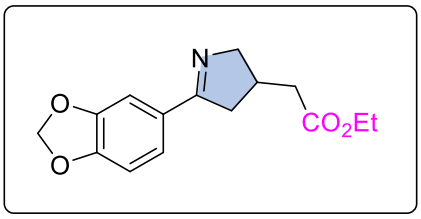
2l: ethyl 2-(5-(2-fluorophenyl)-3,4-dihydro-2H-pyrrol-3-yl)acetate

Brown oil. 45.6 mg (61%). **^{1}H NMR** (600 MHz, $CDCl_3$) 7.93 (t, *J* = 7.8 Hz, 1H), 7.39 (dd, *J* = 13.8, 6.6 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.08 (dd, *J* = 11.4, 8.4 Hz, 1H), 4.21 (dd, *J* = 16.2, 7.8 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.71 (dd, *J* = 16.8, 5.4 Hz, 1H), 3.26 (dd, *J* = 17.4, 9.0 Hz, 1H), 2.89 – 2.84 (m, 1H), 2.78 (dd, *J* = 18.0, 2.4 Hz, 1H), 2.45 (d, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.3, 169.7 (d, *J* = 2.9 Hz), 161.3 (d, *J* = 251.1 Hz), 131.9 (d, *J* = 8.7 Hz), 129.9 (d, *J* = 3.5 Hz), 124.1 (d, *J* = 3.3 Hz), 122.5 (d, *J* = 11.6 Hz), 116.2 (d, *J* = 22.8 Hz), 65.8, 60.4, 43.9 (d, *J* = 6.8 Hz), 39.2, 33.5, 14.1. **^{19}F NMR** (565 MHz, $CDCl_3$): -112.6. **HRMS** (ESI) m/z: $(M+Na)^+$ Calcd for $C_{14}H_{16}FNNaO_2^+$ 272.1057; Found 272.1067.



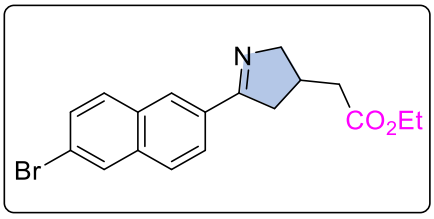
2m: ethyl 2-(5-(2,4-difluorophenyl)-3,4-dihydro-2H-pyrrol-3-yl)acetate

Brown oil. 48.9 mg (61%). **^{1}H NMR** (600 MHz, $CDCl_3$) 7.89 (dd, *J* = 15.6, 9.0 Hz, 1H), 6.84 (t, *J* = 8.4 Hz, 1H), 6.76 (t, *J* = 11.4 Hz, 1H), 4.12 (dd, *J* = 16.2, 7.8 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.62 (dd, *J* = 16.2, 5.4 Hz, 1H), 3.16 (dd, *J* = 17.4, 8.4 Hz, 1H), 2.82 – 2.77 (m, 1H), 2.68 (dd, *J* = 18.0, 2.4 Hz, 1H), 2.37 (m, 2H), 1.19 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.3, 168.7 (d, *J* = 2.7 Hz), 164.2 (dd, *J* = 251.6, 12.2 Hz), 161.7 (dd, *J* = 253.8, 12.0 Hz), 131.3 (q, *J* = 4.8 Hz), 118.9 (q, *J* = 7.95 Hz), 111.8 (dd, *J* = 21.2, 3.5 Hz), 104.3 (dd, *J* = 26.3, 25.4 Hz), 65.6, 60.5, 43.7 (d, *J* = 6.6 Hz), 39.2, 33.5, 14.2. **^{19}F NMR** (565 MHz, $CDCl_3$): -106.5, 108.4. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{14}H_{16}F_2NO_2^+$ 268.1144; Found 268.1153.



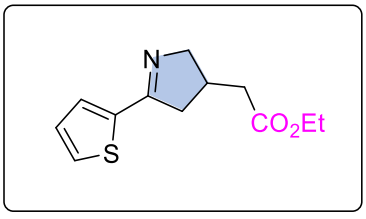
2n: ethyl 2-(5-(benzo[d][1,3]dioxol-5-yl)-3,4-dihydro-2H-pyrrol-3-yl)acetate

Brown solid. 41.3 mg (50%). mp: 46−47 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 7.40 (s, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.00 (s, 2H), 4.22 (dd, *J* = 16.2, 8.4 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.70 (dd, *J* = 16.2, 4.8 Hz, 1H), 3.15 (dd, *J* = 16.8, 9.6 Hz, 1H), 2.88 – 2.82 (m, 1H), 2.66 (dd, *J* = 16.8, 6.0 Hz, 1H), 2.49 – 2.40 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.4, 171.7, 149.5, 147.9, 128.8, 122.6, 107.8, 107.2, 101.3, 66.4, 60.4, 41.1, 39.3, 33.4, 14.2. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{15}H_{18}NO_4^+$ 276.1230; Found 276.1225.



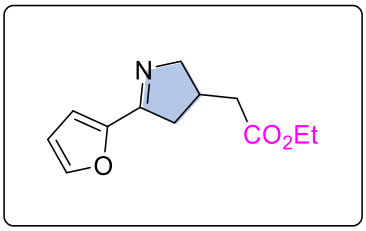
2o: ethyl 2-(5-(6-bromonaphthalen-2-yl)-3,4-dihydro-2H-pyrrol-3-yl)acetate

Yellow solid. 73.2 mg (68%). mp: 72−73 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) 8.09 (s, 1H), 8.08 (d, *J* = 7.5 Hz, 1H), 8.00 (s, 1H), 7.74 (t, *J* = 9.5 Hz, 2H), 7.57 (d, *J* = 9.0 Hz, 1H), 4.32 (dd, *J* = 16.5, 8.0 Hz, 1H), 4.17 (q, *J* = 7.0 Hz, 2H), 3.80 (dd, *J* = 16.0, 5.0 Hz, 1H), 3.32 (dd, *J* = 17.0, 9.0 Hz, 1H), 2.96 – 2.90 (m, 1H), 2.82 (dd, *J* = 16.5, 5.5 Hz, 1H), 2.51 – 2.47 (m, 2H), 1.28 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) 172.4, 172.2, 135.3, 132.2, 131.3, 130.2, 129.8, 129.8, 128.0, 127.2, 125.4, 121.2, 66.9, 60.5, 41.0, 39.3, 33.4, 14.2. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{18}H_{19}BrNO_2^+$ 360.0594; Found 360.0594.



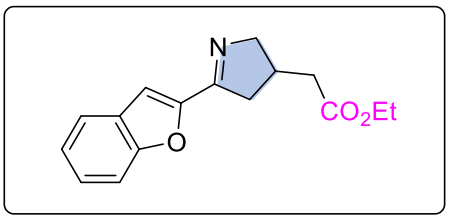
2p: ethyl 2-(5-(thiophen-2-yl)-3,4-dihydro-2H-pyrrol-3-yl)acetate

Brown oil. 51.2 mg (72%). **^{1}H NMR** (500 MHz, $CDCl_3$) 7.42 (d, *J* = 5.0 Hz, 1H), 7.30 (d, *J* = 3.5 Hz, 1H), 7.06 (dd, *J* = 4.5, 3.5 Hz, 1H), 4.22 (dd, *J* = 16.5, 8.0 Hz, 1H), 4.16 (q, *J* = 7.0 Hz, 2H), 3.71 (dd, *J* = 16.5, 5.5 Hz, 1H), 3.20 (dd, *J* = 16.5, 9.0 Hz, 1H), 2.92 – 2.86 (m, 1H), 2.70 (dd, *J* = 16.5, 5.5 Hz, 1H), 2.51 –2.41 (m, 2H), 1.27 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.3, 167.1, 139.3, 129.2, 129.2, 127.4, 66.5, 60.5, 41.6, 39.2, 33.7, 14.2. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{12}H_{16}NO_2S^+$ 238.0896; Found 238.0897.



2q: ethyl 2-(5-(furan-2-yl)-3,4-dihydro-2H-pyrrol-3-yl)acetate

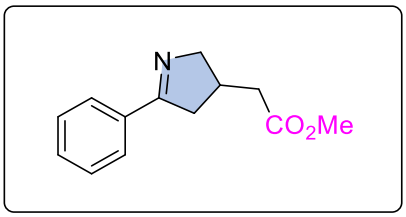
Brown oil. 46.4 mg (70%). **^{1}H NMR** (600 MHz, $CDCl_3$) 7.45 (s, 1H), 6.73 (s, 1H), 6.41 (s, 1H), 4.17 (dd, *J* = 15.6, 7.2 Hz, 1H), 4.08 (dd, *J* = 12.6, 6.0 Hz, 2H), 3.66 (d, *J* = 16.2, 3.6 Hz, 1H), 3.05 (dd, *J* = 15.6, 9.0 Hz, 1H), 2.79 – 2.77 (m, 1H), 2.57 (d, *J* = 16.8, 4.2 Hz, 1H), 2.40 – 2.33 (m, 2H), 1.19 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.3, 163.3, 149.9, 144.5, 112.9, 111.5, 66.8, 60.5, 40.9, 39.1, 33.1, 14.2. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{12}H_{16}NO_3^+$ 222.1125; Found 222.1115.



2r: ethyl 2-(5-(benzofuran-2-yl)-3,4-dihydro-2H-pyrrol-3-yl)acetate

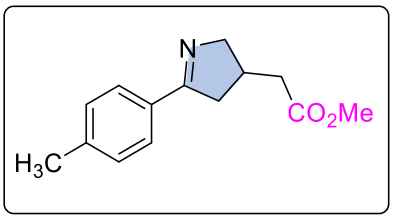
Brown oil. 39.9 mg (49%). **^{1}H NMR** (500 MHz, $CDCl_3$) 7.62 (d, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.37 (t, *J* = 7.0 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.10 (s, 1H), 4.34 (dd, *J* = 16.5, 8.0 Hz, 1H), 4.17 (q, *J* = 7.0 Hz, 2H), 3.82 (dd, *J* = 17.0, 5.5 Hz, 1H), 3.23 (dd, *J* = 17.0, 9.0 Hz, 1H), 2.94 – 2.89 (m, 1H), 2.74 (dd, *J* = 17.0, 5.5 Hz, 1H), 2.53 – 2.43 (m, 2H), 1.28 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) 172.2, 163.9, 155.4, 150.8, 127.7, 126.3, 123.2, 121.9, 111.8, 109.5,

67.1, 60.5, 41.0, 39.1, 33.2, 14.1. **HRMS** (ESI) m/z: $(M+Na)^+$ Calcd for $C_{16}H_{17}NNaO_3^+$ 294.1101; Found 294.1093.



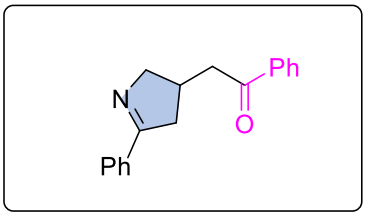
2s: methyl 2-(5-phenyl-3,4-dihydro-2H-pyrrol-3-yl)acetate

Brown oil. 46.9 mg (72%). **^{1}H NMR** (600 MHz, $CDCl_3$) 7.82 (d, *J* = 6.6 Hz, 2H), 7.42 – 7.39 (m, 3H), 4.26 (dd, *J* = 16.8, 8.4 Hz, 1H), 3.74 (dd, *J* = 16.2, 4.8 Hz, 1H), 3.69 (s, 3H), 3.21 (dd, *J* = 16.8, 9.0 Hz, 1H), 2.90 – 2.85 (m, 1H), 2.70 (dd, *J* = 16.8, 5.4 Hz, 1H), 2.51 – 2.42 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.8, 172.4, 134.2, 130.4, 128.3, 127.4, 66.7, 51.5, 41.0, 39.0, 33.2. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{13}H_{16}NO_2^+$ 218.1176; Found 218.1175.



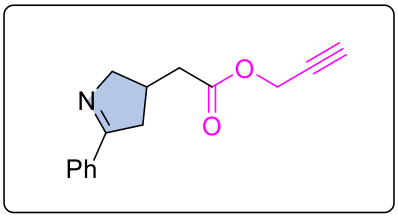
2t: methyl 2-(5-(p-tolyl)-3,4-dihydro-2H-pyrrol-3-yl)acetate

Yellow solid. 52.7 mg (76%). mp: 109−110 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) 7.63 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 4.16 (dd, *J* = 16.0, 7.5 Hz, 1H), 3.64 (dd, *J* = 16.0, 5.5 Hz, 1H), 3.61 (s, 3H), 3.11 (dd, *J* = 17.0, 9.0 Hz, 1H), 2.80 – 2.77 (m, 1H), 2.60 (dd, *J* = 17.0, 5.0 Hz, 1H), 2.43 – 2.33 (m, 2H), 2.30 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.8, 172.3, 140.7, 131.5, 129.1, 127.4, 66.5, 51.6, 41.0, 39.0, 33.2, 21.3. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{14}H_{18}NO_2^+$ 232.1332; Found 232.1337.



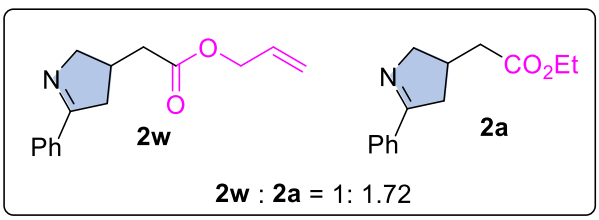
2u: 1-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-3-yl)ethan-1-one

Brown solid. 57.6 mg (73%). mp: 76−73 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) 7.96 (d, *J* = 7.5 Hz, 2H), 7.83 (d, *J* = 6.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.43 – 7.38 (m, 3H), 4.36 (dd, *J* = 16.5, 8.0 Hz, 1H), 3.79 (dd, *J* = 16.5, 5.0 Hz, 1H), 3.32 (dd, *J* = 17.0, 9.0 Hz, 1H), 3.23 – 3.10 (m, 2H), 3.10 – 3.06 (m, 1H), 2.70 (dd, *J* = 17.0, 5.5 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 199.0, 172.7, 136.7, 134.3, 133.2, 130.4, 128.6, 128.4, 127.9, 127.5, 67.0, 43.9, 41.4, 32.4. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{18}H_{18}NO^+$ 264.1383; Found 264.1383.



2v: prop-2-yn-1-yl 2-(5-phenyl-3,4-dihydro-2H-pyrrol-3-yl)acetate

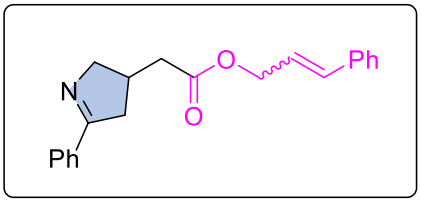
Yellow oil. 58.6 mg (81%). **^{1}H NMR** (500 MHz, $CDCl_3$) 7.81 (d, *J* = 7.0 Hz, 2H), 7.43 – 7.399 (m, 3H), 4.70 (s, 2H), 4.27 (dd, *J* = 16.5, 8.0 Hz, 1H), 3.75 (dd, *J* = 16.5, 5.0 Hz, 1H), 3.22 (dd, *J* = 17.0, 9.0 Hz, 1H), 2.92 – 2.86 (m, 1H), 2.71 (dd, *J* = 17.0, 5.5 Hz, 1H), 2.56 – 2.46 (m, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.4, 171.4, 134.1, 130.4, 128.3, 127.4, 77.4, 74.9, 66.5, 51.9, 40.9, 38.8, 33.2. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{15}H_{16}NO_2^+$ 242.1176; Found 242.1178.



2w: allyl 2-(5-phenyl-3,4-dihydro-2H-pyrrol-3-yl)acetate

Substrate **1w** was synthesized from **1a** via transesterification with a few **1a** mixed, resulting in the formation of the mixture of product **2w** and **2a**, which were difficult to be isolated (**2w : 2a =** 1: 1.72).

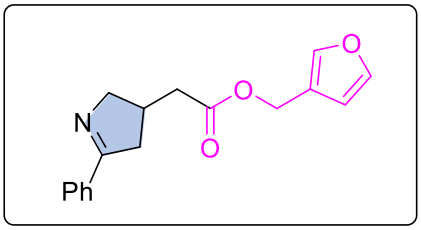
2w, 18.8 mg (70%). **^{1}H NMR** (600 MHz, $CDCl_3$) 7.73 (d, *J* = 7.8 Hz, 2H), 7.34 – 7.30 (m, 3H), 5.87 – 5.80 (m, 1H), 5.24 (d, *J* = 16.8 Hz, 1H), 5.16 (d, *J* = 10.8 Hz, 1H), 4.52 (d, *J* = 6.0 Hz, 2H), 4.18 (dd, *J* = 16.2, 7.8 Hz, 1H), 3.68 – 3.65 (m, 1H), 3.16 – 3.10 (m, 1H), 2.80 – 2.78 (m, 1H), 2.64 – 2.61 (m, 1H), 2.44 – 2.33 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$, mixed with **2a**) 172.5, 172.5, 172.3, 171.9, 134.1, 134.1, 131.9, 130.4, 130.4, 128.3, 127.4, 118.3, 66.6, 65.1, 60.4, 41.0, 39.2, 39.1, 33.2, 33.2, 14.1. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{15}H_{18}NO_2^+$ 244.1332; Found 244.1327.



2x: cinnamyl 2-(5-phenyl-3,4-dihydro-2H-pyrrol-3-yl)acetate

2x may undergo configuration transformation under the irradiation of visible light (*Z* : *E* = 1 : 2.62)[7]

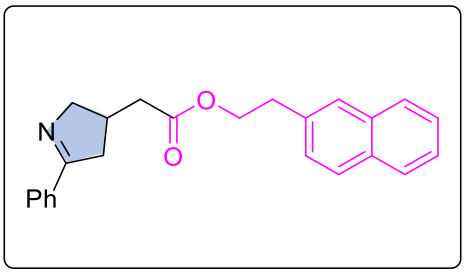
Yellow oil. 71.8 mg (75%). **^{1}H NMR** (600 MHz, $CDCl_3$) *Z*-**2x**: 7.73 (d, *J* = 6.6 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.24 – 7.14 (m, 4H), 6.59 (t, *J* = 11.4 Hz, 1H), 6.22 – 6.19 (m, 1H), 4.68 (d, *J* = 6.0 Hz, 2H), 4.19 (dd, *J* = 16.2, 8.4 Hz, 1H), 3.68 (dd, *J* = 16.2, 5.4 Hz, 1H), 3.13 (dd, *J* = 17.4, 9.0 Hz, 1H), 2.82 – 2.80 (m, 1H), 2.63 (dd, *J* = 16.8, 5.4 Hz, 1H), 2.46 – 2.37 (m, 2H). *E*-**2x**: 7.73 (d, *J* = 6.6 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.24 – 7.14 (m, 4H), 6.59 (t, *J* = 11.4 Hz, 1H), 5.75 – 5.71 (m, 1H), 4.80 (d, *J* = 6.0 Hz, 2H), 4.19 (dd, *J* = 16.2, 8.4 Hz, 1H), 3.68 (dd, *J* = 16.2, 5.4 Hz, 1H), 3.13 (dd, *J* = 17.4, 9.0 Hz, 1H), 2.82 – 2.80 (m, 1H), 2.63 (dd, *J* = 16.8, 5.4 Hz, 1H), 2.46 – 2.37 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$, mixture of *Z*-**2x** and *E*-**2x**) 172.5, 172.2, 172.1, 136.1, 135.9, 134.4, 134.2, 133.1, 130.5, 128.7, 128.6, 128.4, 128.3, 128.1, 127.5, 127.5, 126.6, 125.5, 122.9, 66.7, 65.1, 61.5, 41.0, 39.3, 33.3. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{21}H_{22}NO_2^+$ 320.1645; Found 320.1645.



(7) H. Zhang, X. He, X.-A. Yuan and S. Yu, Kinetic Resolution of 2-Cinnamylpyrrolines Enabled by Photoexcited Chiral Copper Complex-Mediated Alkene *E* → *Z* Isomerization. *ACS Catal.*, 2023, **13**, 2857−2866.

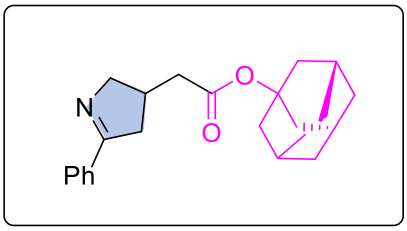
2y: furan-3-ylmethyl 2-(5-phenyl-3,4-dihydro-2H-pyrrol-3-yl)acetate

Brown oil. 58.6 mg (69%). **^{1}H NMR** (500 MHz, $CDCl_3$) 7.80 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.39 (m, 4H), 6.41 (d, *J* = 3.0 Hz, 1H), 6.36 (t, *J* = 3.0 Hz, 1H), 5.09 (s, 2H), 4.25 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.73 (dd, *J* = 16.5, 5.5 Hz, 1H), 3.19 (dd, *J* = 17.0, 9.0 Hz, 1H), 2.90 – 2.85 (m, 1H), 2.69 (dd, *J* = 17.0, 6.0 Hz, 1H), 2.54 – 2.44 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.5, 172.0, 149.3, 143.2, 134.2, 130.5, 128.4, 127.5, 110.6, 110.5, 66.6, 58.0, 41.0, 39.1, 33.3. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{17}H_{18}NO_3^+$ 284.1281; Found 284.1270.



2z: 2-(naphthalen-2-yl)ethyl 2-(5-phenyl-3,4-dihydro-2H-pyrrol-3-yl)acetate

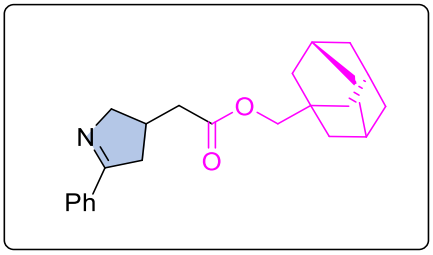
Yellow solid. 86.8 mg (81%). mp: 60–61 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 8.07 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 6.6 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.42 – 7.37 (m, 4H), 7.36 (d, *J* = 7.2 Hz, 1H), 4.45 (t, *J* = 7.2 Hz, 2H), 4.21 (dd, *J* = 16.2, 7.8 Hz, 1H), 3.69 (dd, *J* = 16.2, 5.4 Hz, 1H), 3.40 (t, *J* = 7.2 Hz, 2H), 3.07 (dd, *J* = 16.8, 9.0 Hz, 1H), 2.82 – 2.77 (m, 1H), 2.61 (dd, *J* = 16.8, 5.4 Hz, 2H), 2.46 – 2.36 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.4, 172.3, 134.2, 133.8, 133.5, 132.0, 130.4, 128.8, 128.3, 127.5, 127.4, 126.9, 126.1, 125.6, 125.4, 123.4, 66.7, 64.4, 41.0, 39.3, 33.2, 32.1. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{24}H_{24}NO_2^+$ 358.1802; Found 358.1807.



2aa: adamantan-1-yl 2-(5-phenyl-3,4-dihydro-2H-pyrrol-3-yl)acetate

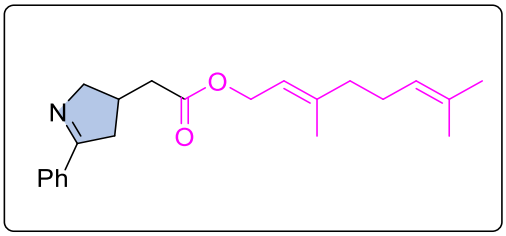
Yellow oil. 40.5 mg (40%). **^{1}H NMR** (600 MHz, $CDCl_3$) 7.82 (d, *J* = 7.2 Hz, 2H), 7.43 – 7.39 (m, 3H), 4.25 (dd, *J* = 16.2, 7.8 Hz, 1H), 3.75 (dd, *J* = 16.2, 4.8 Hz, 1H), 3.19 (dd, *J* = 16.8, 9.0 Hz, 1H), 2.85 – 2.81 (m, 1H), 2.71 (dd, *J* = 16.8, 5.4 Hz, 1H), 2.42 – 2.33 (m, 2H), 2.17 (s, 3H), 2.12 (s, 6H), 1.66 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.6, 171.5, 134.4, 130.4, 128.4, 127.5, 80.7, 66.7,

41.4, 41.0, 40.8, 36.1, 33.5, 30.8. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{22}H_{28}NO_2^+$ 338.2115; Found 338.2124.



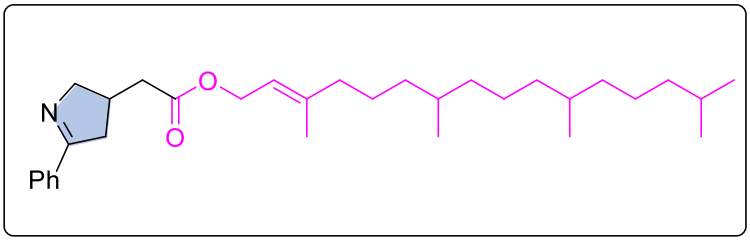
2ab: (adamantan-1-yl)methyl 2-(5-phenyl-3,4-dihydro-2H-pyrrol-3-yl)acetate

Yellow oil. 67.4 mg (64%). **^{1}H NMR** (600 MHz, $CDCl_3$) 7.82 (*J* = 7.8 Hz, 2H), 7.43 – 7.39 (m, 3H), 4.28 (dd, *J* = 16.2, 7.8 Hz, 1H), 3.77 (dd, *J* = 16.2, 5.4 Hz, 1H), 3.73 – 3.69 (m, 2H), 3.22 (dd, *J* = 16.8, 9.0 Hz, 1H), 2.91 – 2.87 (m, 1H), 2.72 (dd, *J* = 16.8, 6.0 Hz, 1H), 2.53 – 2.45 (m, 2H), 1.98 (s, 3H), 1.73 (d, *J* = 12.6 Hz, 3H), 1.64 (d, *J* = 12.0 Hz, 3H), 1.54 (d, *J* = 2.4 Hz, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.5, 172.4，134.2, 130.4, 128.4, 127.4, 74.1, 66.8, 41.1, 39.4, 39.2, 36.8, 33.3, 33.1, 27.9. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{23}H_{30}NO_2^+$ 352.2271; Found 352.2262.



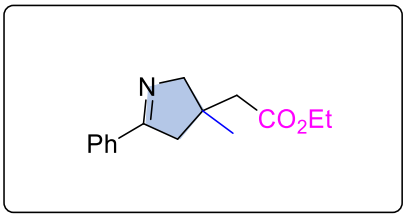
2ac: 3,7-dimethylocta-2,6-dien-1-yl 2-(5-phenyl-3,4-dihydro-2H-pyrrol-3-yl)acetate

Brown oil. 66.1 mg (65%). **^{1}H NMR** (600 MHz, $CDCl_3$) 7.81 (d, *J* = 7.2 Hz, 2H), 7.42 – 7.38 (m, 3H), 5.35 (t, *J* = 7.2 Hz, 1H), 5.10 (t, *J* = 6.6 Hz, 1H), 4.59 (d, *J* = 7.2 Hz, 2H), 4.26 (dd, *J* = 16.2, 7.8 Hz, 1H), 3.74 (dd, *J* = 16.2, 5.4 Hz, 1H), 3.20 (dd, *J* = 16.8, 9.0 Hz, 1H), 2.90 – 2.85 (m, 1H), 2.70 (dd, *J* = 16.8, 5.4 Hz, 1H), 2.50 – 2.42 (m, 2H), 2.12 – 2.10 (m, 2H), 2.10 – 2.07 (m, 2H), 1.77 (s, 3H), 1.68 (s, 3H), 1.60 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.4, 172.3, 142.7, 134.3, 132.1, 130.4, 128.4, 127.5, 123.5, 119.0, 66.7, 61.1, 41.0, 39.3, 33.3, 32.1, 26.6, 25.6, 23.4, 17.6. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{22}H_{30}NO_2^+$ 340.2271; Found 340.2280.



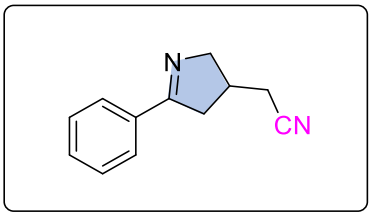
2ad: 3,7,11,15-tetramethylhexadec-2-en-1-yl 2-(5-phenyl-3,4-dihydro-2H-pyrrol-3-yl)acetate

Yellow oil. 85.2 mg (59%). **^{1}H NMR** (600 MHz, $CDCl_3$) 7.81 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.38 (m, 3H), 5.34 (t, *J* = 6.6 Hz, 1H), 4.62 (d, *J* = 7.2 Hz, 2H), 4.26 (dd, *J* = 16.2, 8.4 Hz, 1H), 3.74 (dd, *J* = 16.2, 4.8 Hz, 1H), 3.20 (dd, *J* = 16.8, 9.0 Hz, 1H), 2.90 – 2.85 (m, 1H), 2.70 (dd, *J* = 17.4, 6.0 Hz, 1H), 2.50 – 2.42 (m, 2H), 2.02 – 1.99 (m, 2H), 1.70 (s, 3H), 1.53 – 1.51 (m, 1H), 1.38 –1.34 (m, 4H), 1.32 – 1.18 (m, 8H), 1.15 –1.09 (m, 2H), 1.09 – 1.04 (m, 4H), 0.87 – 0.84 (m, 12H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.4, 172.3, 142.9, 134.3, 130.4, 128.4, 127.4, 117.8, 66.7, 61.4, 41.0, 39.8, 39.3, 39.3, 37.3, 37.3, 37.2, 36.5, 33.3, 32.7, 32.6, 27.9, 25.0, 24.7, 24.4, 22.6, 22.6, 19.7, 19.6, 16.3. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{32}H_{52}NO_2^+$ 482.3993; Found 482.4006.



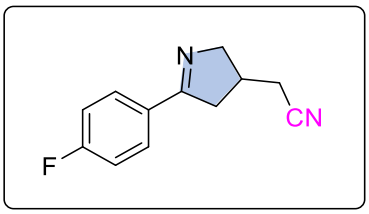
2ae: ethyl 2-(3-methyl-5-phenyl-3,4-dihydro-2H-pyrrol-3-yl)acetate

Yellow oil. 32.4 mg (44%). **^{1}H NMR** (500 MHz, $CDCl_3$) 7.81 (d, *J* = 8.0 Hz, 2H), 7.43 – 7.37 (m, 3H), 4.13 (q, *J* = 7.5 Hz, 2H), 3.98 (d, *J* = 16.0 Hz, 1H), 3.88 (d, *J* = 16.5 Hz, 1H), 3.10 (d, *J* = 17.0 Hz, 1H), 2.85 (d, *J* = 17.0 Hz, 1H), 2.49 (s, 2H), 1.25 (t, *J* = 7.5 Hz, 3H), 1.23 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.8, 171.8, 134.2, 130.7, 128.5, 127.6, 72.9, 60.4, 48.1, 44.6, 40.4, 26.1, 14.2. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{15}H_{20}NO_2^+$ 246.1489; Found 246.1487.



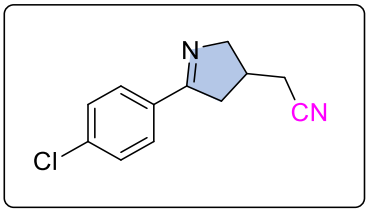
4a: 2-(5-phenyl-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

Brown oil. 49.2 mg (89%). **^{1}H NMR** (600 MHz, $CDCl_3$) 7.81 (d, *J* = 7.2 Hz, 2H), 7.44 – 7.40 (m, 3H), 4.24 (dd, *J* = 16.2, 7.8 Hz, 1H), 3.83 (dd, *J* = 16.2, 3.6 Hz, 1H), 3.21 (dd, *J* = 18.0, 9.6 Hz, 1H), 2.84 – 2.80 (m, 2H), 2.47– 2.37 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 171.7, 133.6, 130.7, 128.4, 127.4, 118.3, 66.0, 40.6, 33.5, 22.1. **HRMS** (ESI) m/z: $(M+Na)^+$ Calcd for $C_{12}H_{12}N_2Na^+$ 207.0893; Found 207.0896.



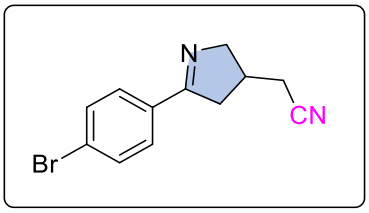
4b: 2-(5-(4-fluorophenyl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

Brown solid. 50.9 mg (84%). mp: 48−49 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 7.81 (dd, *J* = 8.4, 5.4 Hz, 2H), 7.10 (t, *J* = 8.4 Hz, 2H), 4.26 (dd, *J* = 16.2, 6.0 Hz, 1H), 3.85 (dd, *J* = 16.8, 3.6 Hz, 1H), 3.23 (dd, *J* = 18.0, 9.6 Hz, 1H), 2.88 – 2.81 (m, 2H), 2.51– 2.40 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 170.6, 165.1 (d, *J* = 249.8 Hz), 130.0 (d, *J* = 3.3 Hz), 129.6 (d, *J* = 8.7 Hz), 118.3, 115.6 (d, *J* = 21.6 Hz), 66.1, 40.8, 33.7, 22.3. **^{19}F NMR** (565 MHz, $CDCl_3$): -109.1. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{12}H_{12}FN_2^+$ 203.0979; Found 203.0970.



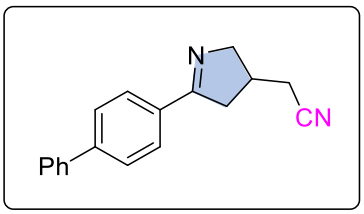
4c: 2-(5-(4-chlorophenyl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

Brown solid. 49.1 mg (75%). mp: 59−60 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 7.75 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 4.27 (dd, *J* = 16.8, 6.6 Hz, 1H), 3.86 (dd, *J* = 16.2, 3.0 Hz, 1H), 3.23 (dd, *J* = 16.2, 7.8 Hz, 1H), 2.87 – 2.81 (m, 2H), 2.51 – 2.04 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 170.9, 137.0, 132.2, 128.9, 128.8, 118.2, 66.2, 40.7, 33.8, 22.3. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{12}H_{12}ClN_2^+$ 219.0684; Found 219.0674.



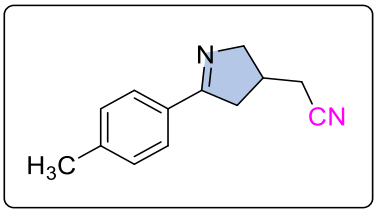
4d: 2-(5-(4-bromophenyl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

Yellow solid. 65.2 mg (83%). mp: 65−66 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 7.68 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 4.26 (dd, *J* = 16.2, 7.8 Hz, 1H), 3.85 (dd, *J* = 16.2, 3.0 Hz, 1H), 3.22 (dd, *J* = 16.8, 8.4 Hz, 1H), 2.88 – 2.81 (m, 2H), 2.52 – 2.41 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 170.9, 132.6, 131.8, 129.1, 125.4, 118.3, 66.2, 40.7, 33.7, 22.3. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{12}H_{12}BrN_2^+$ 263.0178; Found 263.0169.



4e: 2-(5-([1,1'-biphenyl]-4-yl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

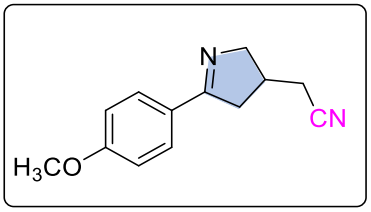
Yellow solid. 55.4 mg (71%). mp: 122−123 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 7.88 (d, *J* = 7.8 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 4.27 (dd, *J* = 15.6, 6.6 Hz, 1H), 3.87 (dd, *J* = 16.2, 2.4 Hz, 1H), 3.25 (dd, *J* = 15.6, 7.8 Hz, 1H), 2.87 – 2.85 (m, 2H), 2.49 – 2.38 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 171.5, 143.4, 140.0, 132.5, 128.8, 128.0, 127.8 127.1, 127.0, 118.4, 66.1, 40.8, 33.7, 22.2. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{18}H_{17}N_2^+$ 261.1386; Found 261.1367.



4f: 2-(5-(p-tolyl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

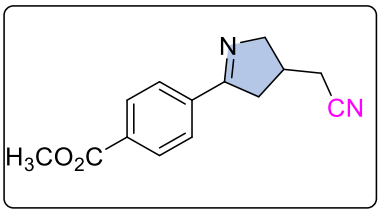
Yellow solid. 41.0 mg (69%). mp: 49−50 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 7.70 (d, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 4.24 (dd, *J* = 16.8, 7.8 Hz, 1H), 3.84 (dd, *J* = 16.2, 3.6 Hz, 1H), 3.22

(dd, *J* = 18.0, 10.2 Hz, 1H), 2.84 – 2.82 (m, 2H), 2.52 – 2.40 (m, 2H), 2.39 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) 171.8, 141.2, 131.0, 129.2, 127.5, 118.4, 66.0, 40.7, 33.7, 22.3, 21.4. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{13}H_{15}N_2^+$ 199.1230; Found 199.1239.



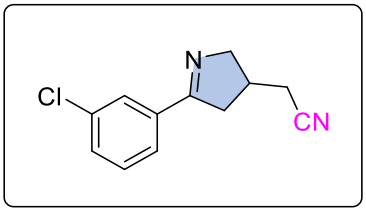
4g: 2-(5-(4-methoxyphenyl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

Brown solid. 42.4 mg (66%). mp: 50−51 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 7.69 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 4.15 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.77 (s, 3H), 3.74 (dd, *J* = 16.2, 4.2 Hz, 1H), 3.14 (dd, *J* = 18.0, 10.2, 1H), 2.77 – 2.73 (m, 2H), 2.42 – 2.31 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 171.2, 161.7, 129.2, 126.4, 118.5, 113.8, 65.8, 55.3, 40.7, 33.7, 22.3. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{13}H_{15}N_2O^+$ 215.1179; Found 215.1184.



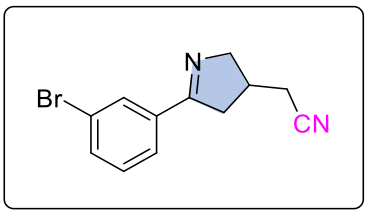
4h: methyl 4-(3-(cyanomethyl)-3,4-dihydro-2H-pyrrol-5-yl)benzoate

Yellow solid. 66.8 mg (92%). mp: 101−102 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) 8.08 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 8.5 Hz, 2H), 4.31 (dd, *J* = 17.0, 8.0 Hz, 1H), 3.94 (s, 3H), 3.90 (dd, *J* = 17.0, 4.5 Hz, 1H), 3.28 (dd, *J* = 18.5, 10.0 Hz, 1H), 2.89 – 2.87 (m, 2H), 2.54 – 2.43 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) 171.2, 166.4, 137.5, 131.9, 129.7, 127.4, 118.2, 66.2, 52.2, 40.8, 33.6, 22.2. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{14}H_{15}N_2O_2^+$ 243.1128; Found 243.1132.



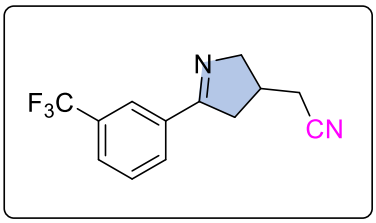
4i: 2-(5-(3-chlorophenyl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

Yellow solid. 60.8 mg (93%). mp: 95−96 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 7.82 (s, 1H), 7.67 (d, *J* = 7.2 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 4.28 (dd, *J* = 16.2, 7.8 Hz, 1H), 3.87 (dd, *J* = 16.8, 3.6 Hz, 1H), 3.22 (dd, *J* = 16.8, 8.4 Hz, 1H), 2.87 – 2.80 (m, 2H), 2.51 – 2.41 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 170.6, 135.4, 134.6, 130.7, 129.8, 127.5, 125.6, 118.2, 66.1, 40.7, 33.6, 22.2. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{12}H_{12}ClN_2^+$ 219.0684; Found 219.0677.



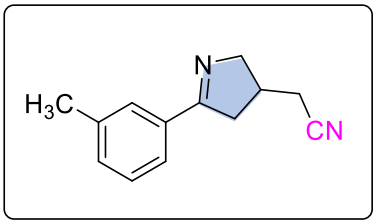
4j: 2-(5-(3-bromophenyl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

Yellow solid. 59.0 mg (75%). mp: 96−97 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 7.99 (s, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 4.28 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.88 (dd, *J* = 16.2, 3.0 Hz, 1H), 3.22 (dd, *J* = 16.8, 8.4 Hz, 1H), 2.88 – 2.81 (m, 2H), 2.52 – 2.41 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 170.6, 135.7, 133.7, 130.6, 130.1, 126.1, 122.8, 118.2, 66.2, 40.7, 33.7, 22.3. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{12}H_{12}BrN_2^+$ 263.0178; Found 263.0178.



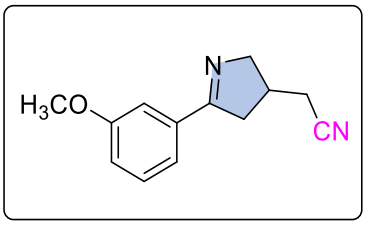
4k: 2-(5-(3-(trifluoromethyl)phenyl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

Brown oil. 62.8 mg (83%). **^{1}H NMR** (600 MHz, $CDCl_3$) 8.10 (s, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 4.32 (dd, *J* = 16.8, 7.2 Hz, 1H), 3.91 (dd, *J* = 16.8, 3.6 Hz, 1H), 3.28 (dd, *J* = 18.6, 10.2 Hz, 1H), 2.92 – 2.87 (m, 2H), 2.48 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 170.6, 134.5, 131.2 (q, *J* = 32.4 Hz), 130.7, 129.1, 127.3 (q, *J* = 3.6 Hz), 124.4 (q, *J* = 3.9 Hz), 123.8 (q, *J* = 270.9 Hz), 118.2, 66.3, 40.8, 33.8, 22.3. **^{19}F NMR** (565 MHz, $CDCl_3$) -62.8. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{13}H_{12}F_3N_2^+$ 253.0947; Found 253.0949.



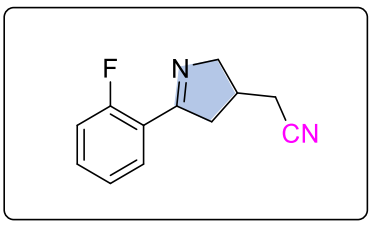
4l: 2-(5-(m-tolyl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

Yellow solid. 50.5 mg (85%). mp: 53−54 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 7.67 (s, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 4.26 (dd, *J* = 15.0, 6.6 Hz, 1H), 3.86 (dd, *J* = 16.2, 3.6 Hz, 1H), 3.24 (dd, *J* = 18.0, 9.6 Hz, 1H), 2.88 – 2.83 (m, 2H), 2.50 – 2.41 (m, 2H), 2.39 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.1, 138.3, 133.6, 131.7, 128.4, 128.1, 124.8, 118.4, 66.0, 40.8, 33.7, 22.3, 21.3. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{13}H_{15}N_2^+$ 199.1230; Found 199.1222.



4m: 2-(5-(3-methoxyphenyl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

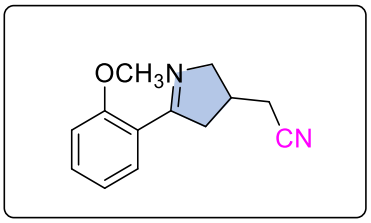
Brown oil. 46.9 mg (73%). **^{1}H NMR** (600 MHz, $CDCl_3$) 7.43 (s, 1H), 7.33 – 7.32 (m, 2H), 7.02 – 7.00 (m, 1H), 4.27 (dd, *J* = 16.2, 7.8 Hz, 1H), 3.86 (dd, *J* = 18.6, 3.6 Hz, 1H), 3.85 (s, 3H), 3.24 (dd, *J* = 18.0, 9.6 Hz, 1H), 2.85 – 2.83 (m, 2H), 2.50 – 2.40 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 171.8, 159.6, 135.0, 129.5, 120.3, 118.4, 117.4, 111.7, 66.0, 55.3, 40.9, 33.7, 22.3. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{13}H_{15}N_2O^+$ 215.1179; Found 215.1169.



4n: 2-(5-(2-fluorophenyl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

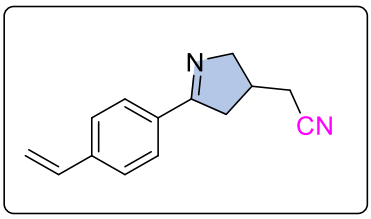
Brown oil. 44.3 mg (73%). **^{1}H NMR** (600 MHz, $CDCl_3$) 7.95 (t, *J* = 7.8 Hz, 1H), 7.42 (dd, *J* = 15.0, 7.8 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.10 (dd, *J* = 11.4, 8.4 Hz, 1H), 4.22 (dd, *J* = 16.2, 7.8 Hz,

1H), 3.83 (dd, *J* = 16.2, 4.2 Hz, 1H), 3.31 (dd, *J* = 17.4, 9.0 Hz, 1H), 2.91 (dd, *J* = 18.0, 1.8 Hz, 1H), 2.85 – 2.81 (m, 1H), 2.49 – 2.41 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 169.0 (d, *J* = 2.7 Hz), 161.2 (d, *J* = 251.1 Hz), 132.3 (d, *J* = 8.7 Hz), 129.8 (d, *J* = 3.2 Hz), 124.2 (d, *J* = 3.3 Hz), 121.8 (d, *J* = 11.4 Hz), 118.4, 116.2 (d, *J* = 22.7 Hz), 65.1, 43.5 (d, *J* = 7.1 Hz), 33.7, 22.1. **^{19}F NMR** (565 MHz, $CDCl_3$): -112.5. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{12}H_{12}FN_2^+$ 203.0979; Found 203.0984.



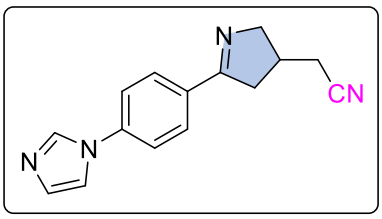
4o: 2-(5-(2-methoxyphenyl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

Brown solid. 44.3 mg (69%). mp: 36−37 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 7.77 (d, *J* = 7.2, 1H), 7.40 (t, *J* = 8.4, 1H), 6.99 (t, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 4.15 (dd, *J* = 16.2, 7.8 Hz, 1H), 3.87 (s, 3H), 3.78 (dd, *J* = 16.2, 4.2 Hz, 1H), 3.31 (dd, *J* = 18.0, 9.0 Hz, 1H), 2.97 (dd, *J* = 18.0, 4.8 Hz, 1H), 2.81 – 2.77 (m, 1H), 2.47 – 2.38 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.6, 158.2, 131.8, 129.9, 123.5, 120.7, 118.6, 111.2, 64.7, 55.4, 44.1, 34.1, 22.1. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{13}H_{15}N_2O^+$ 215.1179; Found 215.1184.



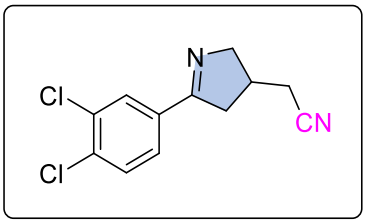
4p: 2-(5-(4-vinylphenyl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

Yellow oil. 27.7 mg (44%). **^{1}H NMR** (600 MHz, $CDCl_3$) 7.71 (d, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 6.67 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.76 (d, *J* = 17.4 Hz, 1H), 5.27 (d, *J* = 11.4 Hz, 1H), 4.23 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.79 (dd, *J* = 16.2, 4.2 Hz, 1H), 3.17 (dd, *J* = 18.0, 9.6 Hz, 1H), 2.79 – 2.77 (m, 2H), 2.44 – 2.33 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 171.6, 140.0, 136.1, 133.0, 127.9, 126.3, 118.4, 115.5, 66.1, 40.8, 33.7, 22.3. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{14}H_{15}N_2^+$ 211.1230; Found 211.1230.



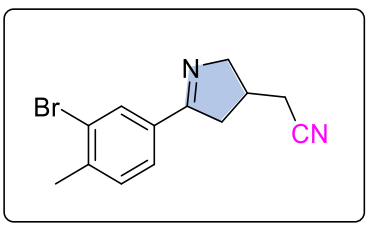
4q: 2-(5-(4-(1H-imidazol-1-yl)phenyl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

Yellow solid. 48.8 mg (65%). mp: 130−131 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 7.86 (d, *J* = 9.0 Hz, 2H), 7.85 (s, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.27 (s, 1H), 7.16 (s, 1H), 4.23 (dd, *J* = 16.8, 6.6 Hz, 1H), 3.82 (dd, *J* = 16.8, 4.2 Hz, 1H), 3.20 (dd, *J* = 18.6, 10.2 Hz, 1H), 2.84 – 2.79 (m, 2H), 2.47 – 2.37 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 170.5, 138.9, 135.3, 132.7, 130.8, 129.2, 120.9, 118.2, 117.7, 66.2, 40.7, 33.7, 22.2. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{15}H_{15}N_4^+$ 251.1291; Found 251.1284.



4r: 2-(5-(3,4-dichlorophenyl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

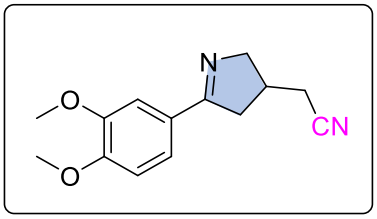
Yellow solid. 49.9 mg (66%). mp: 100−101 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 7.91 (s, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 4.28 (dd, *J* = 16.8, 7.8 Hz, 1H), 3.87 (dd, *J* = 16.8, 4.2 Hz, 1H), 3.21 (dd, *J* = 16.8, 8.4 Hz, 1H), 2.89 – 2.85 (m, 1H), 2.81 (dd, *J* = 16.8, 4.8 Hz, 1H), 2.52 – 2.42 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 169.8, 134.9, 133.6, 132.9, 130.5, 129.4, 126.6, 118.1, 66.2, 40.6, 33.7, 22.2. **HRMS** (ESI) m/z: $(M+Na)^+$ Calcd for $C_{12}H_{10}Cl_2N_2Na^+$ 275.0113; Found 275.0109.



4s: 2-(5-(3-bromo-4-methylphenyl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

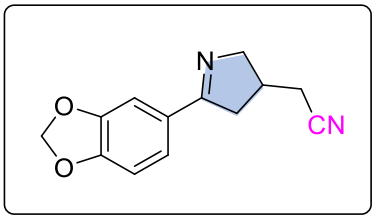
Yellow solid. 53.0 mg (64%). mp: 36−37 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 7.99 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 4.26 (dd, *J* = 16.8, 7.8 Hz, 1H), 3.85 (dd, *J* = 16.8, 3.6 Hz,

1H), 3.20 (dd, *J* = 16.8, 8.4 Hz, 1H), 2.86 – 2.79 (m, 2H), 2.50 – 2.40 (m, 5H). **^{13}C NMR** (150 MHz, $CDCl_3$) 170.5, 140.8, 133.1, 131.3, 130.8, 126.3, 125.1, 118.2, 66.0, 40.7, 33.6, 22.9, 22.2. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{13}H_{14}BrN_2^+$ 277.0335; Found 277.0336.



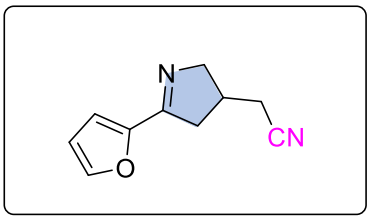
4t: 2-(5-(3,4-dimethoxyphenyl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

Brown oil. 43.2 mg (59%). **^{1}H NMR** (600 MHz, $CDCl_3$) 7.53 (s, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 4.24 (dd, *J* = 16.2, 7.8 Hz, 1H), 3.94 (s, 3H), 3.93 (s, 3H), 3.83 (dd, *J* = 16.2, 4.2 Hz, 1H), 3.23 (dd, *J* = 18.0, 9.6 Hz, 1H), 2.85 – 2.83 (m, 2H), 2.51 – 2.40 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 171.3, 151.4, 149.0, 126.7, 121.5, 118.4, 110.2, 109.2, 65.8, 55.8, 40.6, 33.8, 22.2. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{14}H_{17}N_2O_2^+$ 245.1285; Found 245.1288.



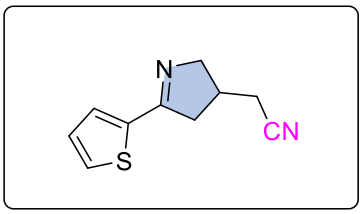
4u: 2-(5-(benzo[d][1,3]dioxol-5-yl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

Brown solid. 46.5 mg (68%). mp: 30−31 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 7.40 (s, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.01 (s, 2H), 4.22 (dd, *J* = 16.8, 7.8 Hz, 1H), 3.82 (dd, *J* = 16.8, 4.2 Hz, 1H), 3.18 (dd, *J* = 16.2, 8.4 Hz, 1H), 2.85 – 2.77 (m, 2H), 2.50 – 2.39 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 171.0, 149.8, 148.0, 128.2, 122.7, 118.4, 107.9, 107.1, 101.4, 65.8, 40.7, 33.7, 22.2. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{13}H_{13}N_2O_2^+$ 229.0972; Found 229.0963.



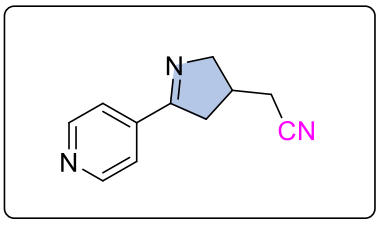
4v: 2-(5-(furan-2-yl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

Brown solid. 40.2 mg (77%). mp: 82−83 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 7.55 (s, 1H), 6.84 (d, *J* = 3.0 Hz, 1H), 6.50 (dd, *J* = 3.6, 1.8 Hz, 1H), 4.25 (dd, *J* = 16.8, 7.2 Hz, 1H), 3.86 (dd, *J* = 16.2, 3.6 Hz, 1H), 3.17 (dd, *J* = 16.8, 8.4 Hz, 1H), 2.84 – 2.77 (m, 2H), 2.50 – 2.39 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 162.5, 149.3, 144.8, 118.3, 113.4, 111.7, 66.1, 40.6, 33.5, 22.1. **HRMS** (ESI) m/z: $(M+Na)^+$ Calcd for $C_{10}H_{10}N_2NaO^+$ 197.0685; Found 197.0677.



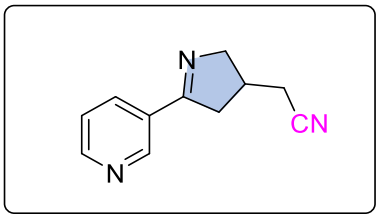
4w: 2-(5-(thiophen-2-yl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

Brown solid. 47.3 mg (83%). mp: 44−45 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 7.45 (d, *J* = 4.8 Hz, 1H), 7.33 (d, *J* = 3.6 Hz, 1H), 7.09 (dd, *J* = 4.8, 3.6 Hz, 1H), 4.23 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.81 (dd, *J* = 16.2, 3.6 Hz, 1H), 3.24 (dd, *J* = 18.0, 9.6 Hz, 1H), 2.88 – 2.83 (m, 2H), 2.51 – 2.41 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 166.4, 138.5, 129.7, 129.6, 127.5, 118.3, 65.8, 41.3, 34.0, 22.2. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{10}H_{11}N_2S^+$ 191.0637; Found 191.0633.



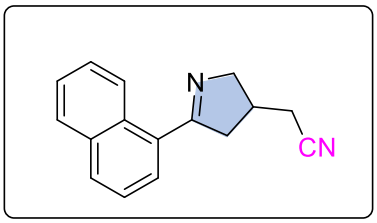
4x: 2-(5-(pyridin-4-yl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

Yellow solid. 43.3 mg (78%). mp: 111−112 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 8.72 (d, *J* = 4.8 Hz, 2H), 7.66 (d, *J* = 6.0 Hz, 2H), 4.33 (dd, *J* = 16.8, 7.8 Hz, 1H), 3.93 (dd, *J* = 16.8, 4.8 Hz, 1H), 3.25 (dd, *J* = 17.4, 9.0 Hz, 1H), 2.92 – 2.83 (m, 2H), 2.55 – 2.44 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 170.4, 150.4, 140.4, 121.3, 118.0, 66.5, 40.5, 33.5, 22.2. **HRMS** (ESI) m/z: $(M+Na)^+$ Calcd for $C_{11}H_{11}N_3Na^+$ 208.0845; Found 208.0850.



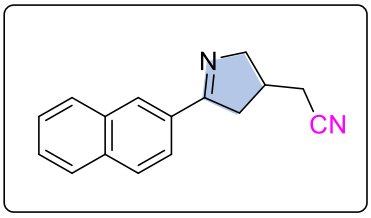
4y: 2-(5-(pyridin-3-yl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

Brown solid. 45.5 mg (82%). mp: 53−54 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 9.00 (s, 1H), 8.69 (s, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 7.38 (s, 1H), 4.31 (dd, *J* = 16.8, 7.2 Hz, 1H), 3.90 (d, *J* = 16.8 Hz, 1H), 3.27 (dd, *J* = 16.8, 9.0 Hz, 1H), 2.88 – 2.86 (m, 2H), 2.55 – 2.45 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 169.5, 151.5, 148.8, 134.5, 129.3, 123.4, 118.1, 66.1, 40.5, 33.4, 22.1. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{11}H_{12}N_3^+$ 186.1026; Found 186.1021.



4z: 2-(5-(naphthalen-1-yl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

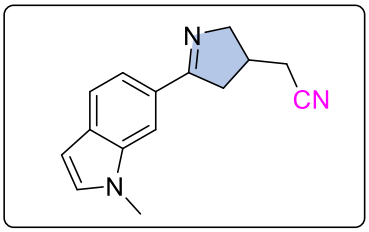
Brown oil. 56.9 mg (81%). **^{1}H NMR** (600 MHz, $CDCl_3$) 9.03 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 6.6 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 4.38 (dd, *J* = 16.8, 7.8 Hz, 1H), 4.00 (dd, *J* = 16.2, 4.2 Hz, 1H), 3.34 (dd, *J* = 17.4, 9.0 Hz, 1H), 2.93 (dd, *J* = 16.8, 4.8 Hz, 1H), 2.80 – 2.77 (m, 1H), 2.48 – 2.39 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.8, 133.9, 131.0, 130.9, 130.8, 128.3, 127.8, 127.2, 126.4, 126.1, 124.5, 118.4, 66.9, 44.0, 33.1, 22.1. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{16}H_{15}N_2^+$ 235.1230; Found 235.1227.



4aa: 2-(5-(naphthalen-2-yl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

Yellow solid. 57.6 mg (82%). mp: 36−37 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 8.10 (s, 1H), 8.05 (d, *J* = 8.4, 1H), 7.87 (d, *J* = 7.2, 1H), 7.84 (t, *J* = 9.0, 2H), 7.53 – 7.49 (m, 2H), 4.27 (dd, *J* = 16.8, 7.8 Hz,

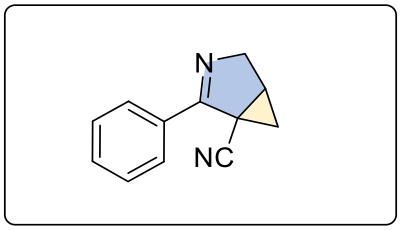
1H), 3.86 (dd, *J* = 16.8, 4.8 Hz, 1H), 3.29 (dd, *J* = 17.4, 9.0 Hz, 1H), 2.92 (dd, *J* = 17.4, 4.8 Hz, 1H), 2.84 – 2.79 (m, 1H), 2.47 – 2.36 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 171.7, 134.3, 132.7, 131.1, 128.6, 128.3, 128.2, 127.6, 127.3, 126.5, 124.0, 118.4, 66.1, 40.6, 33.6, 22.2. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{16}H_{15}N_2^+$ 235.1230; Found 235.1220.



4ab: 2-(5-(1-methyl-1H-indol-6-yl)-3,4-dihydro-2H-pyrrol-3-yl)acetonitrile

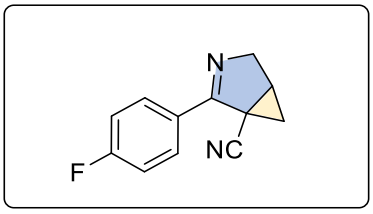
Brown solid. 42.0 mg (59%). mp: 37−38 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 7.86 (s, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 3.0 Hz, 1H), 6.49 (d, *J* = 3.0 Hz, 1H), 4.26 (dd, *J* = 16.2, 7.8 Hz, 1H), 3.85 (dd, *J* = 16.2, 3.6 Hz, 1H), 3.82 (s, 3H), 3.32 (dd, *J* = 16.8, 8.4 Hz, 1H), 2.94 (dd, *J* = 16.8, 4.2 Hz, 1H), 2.86 – 2.83 (m, 1H), 2.49 – 2.38 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) 172.8, 136.4, 131.2, 130.6, 127.1, 120.6, 119.1, 118.6, 108.8, 101.1, 65.8, 41.0, 33.8, 32.9, 22.3. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{15}H_{16}N_3^+$ 238.1339; Found 238.1333.

General Procedure for the synthesis of 5 (with 5a as an example) To a flask (20 mL) equipped with a stir-bar was added *N*-allyl enamine **3a** (36.8 mg, 0.2 mmol), Acr^+-Mes-Ph ClO_4^- (2.5 mg, 0.06 mmol), $Co(dmgH)_2PyCl$ (6.5 mg, 0.016 mmol) and DCE (3 mL). The reaction mixture was stirred under the irradiation of blue LED light (5 W) at ambient atmosphere in a parallel light reactor. After the completion of the reaction as indicated by TLC, the solution was concentrated *in vacuo*. Then the residue was purified by silica gel flash column chromatography (PE/EA = 3/1) to afford product **5a** (26.6 mg, 73%).



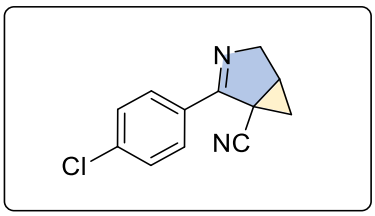
5a: 2-phenyl-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile

Brown oil. 26.6 mg (73%). **^{1}H NMR** (600 MHz, $CDCl_3$) 7.98 (d, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 4.23 (dd, *J* = 18.0, 6.0 Hz, 1H), 4.09 (d, *J* = 18.0 Hz, 1H), 2.82 (dd, *J* = 14.4, 6.0 Hz, 1H), 1.88 (dd, *J* = 8.4, 4.8 Hz, 1H), 0.99 (t, *J* = 5.4 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 168.5, 131.5, 131.4, 128.7, 128.3, 118.6, 62.0, 29.8, 24.7, 22.9. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{12}H_{11}N_2^+$ 183.0917; Found 183.0912.



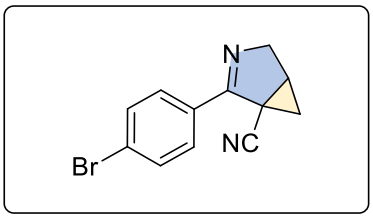
5b: 2-(4-fluorophenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile

Brown oil. 26.0 mg (65%). **^{1}H NMR** (600 MHz, $CDCl_3$) 7.99 (dd, *J* = 8.4, 5.4 Hz, 2H), 7.16 (t, *J* = 9.0 Hz, 2H), 4.22 (dd, *J* = 18.0, 6.0 Hz, 1H), 4.08 (d, *J* = 18.0 Hz, 1H), 2.83 (dd, *J* = 14.4, 7.2 Hz, 1H), 1.89 (dd, *J* = 9.0, 4.8 Hz, 1H), 1.00 (t, *J* = 5.4 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 167.3, 164.7 (d, *J* = 251.1 Hz), 130.5 (d, *J* = 8.9 Hz), 127.7 (d, *J* = 3.2 Hz), 118.5, 115.9 (d, *J* = 21.9 Hz), 62.0, 30.0, 24.7, 23.0. **^{19}F NMR** (565 MHz, $CDCl_3$) -107.7. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{12}H_{10}FN_2^+$ 201.0823; Found 201.0831



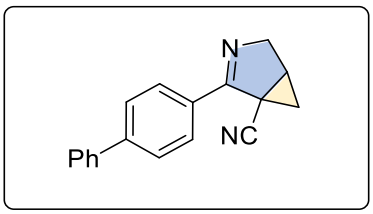
5c: 2-(4-chlorophenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile

Brown oil. 32.8 mg (76%). **^{1}H NMR** (600 MHz, $CDCl_3$) 7.92 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 4.23 (dd, *J* = 18.0, 6.0 Hz, 1H), 4.08 (d, *J* = 18.0 Hz, 1H), 2.83 (dd, *J* = 13.2, 6.0 Hz, 1H), 1.89 (dd, *J* = 9.0, 4.8 Hz, 1H), 1.00 (t, *J* = 5.4 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 167.5, 137.8, 129.9, 129.6, 129.1, 118.4, 62.1, 30.0, 24.6, 23.0. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{12}H_{10}ClN_2^+$ 217.0527; Found 217.0534.



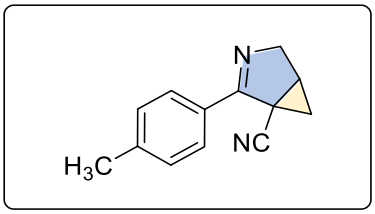
5d: 2-(4-bromophenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile

Brown solid. 38.0 mg (73%). mp: 38−39 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) 7.85 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 4.21 (dd, *J* = 18.5, 6.0 Hz, 1H), 4.08 (d, *J* = 18.0 Hz, 1H), 2.84 (dd, *J* = 13.5, 6.0 Hz, 1H), 1.88 (dd, *J* = 9.0, 5.0 Hz, 1H), 0.99 (t, *J* = 5.0 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 167.5, 132.0, 130.2, 129.7, 126.2, 118.4, 62.1, 30.0, 24.6, 22.9. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{12}H_{10}BrN_2^+$ 261.0022; Found 261.0022.



5e: 2-([1,1'-biphenyl]-4-yl)-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile

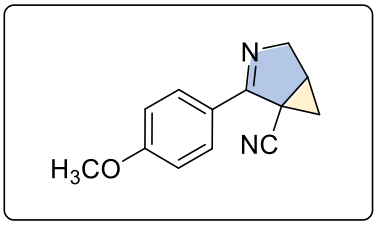
Brown solid. 33.6 mg (65%). mp: 31−32 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 7.98 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 4.18 (dd, *J* = 18.0, 6.0 Hz, 1H), 4.03 (d, *J* = 18.0 Hz, 1H), 2.76 (dd, *J* = 13.2, 6.0 Hz, 1H), 1.83 (dd, *J* = 8.4, 4.2 Hz, 1H), 0.94 (t, *J* = 4.8 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 168.2, 144.2, 140.0, 130.2, 128.9, 128.8, 128.0, 127.4, 127.1, 118.7, 62.1, 29.9, 24.7, 23.0. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{18}H_{15}N_2^+$ 259.1230; Found 259.1236.



5f: 2-(p-tolyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile

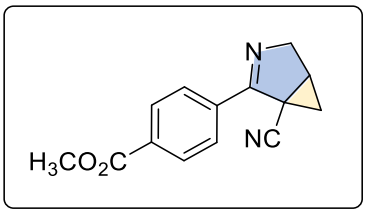
Brown oil. 27.5 mg (70%). **^{1}H NMR** (500 MHz, $CDCl_3$) 7.87 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.21 (dd, *J* = 18.0, 6.0 Hz, 1H), 4.06 (d, *J* = 18.0 Hz, 1H), 2.80 (dd, *J* = 13.5, 6.0 Hz, 1H),

2.41 (s, 3H), 1.86 (dd, *J* = 9.0, 5.0 Hz, 1H), 0.98 (t, *J* = 5.0 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 168.4, 141.9, 129.4, 128.7, 128.2, 118.8, 61.9, 29.7, 24.7, 22.9, 21.5. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{13}H_{13}N_2^+$ 197.1073; Found 197.1079.



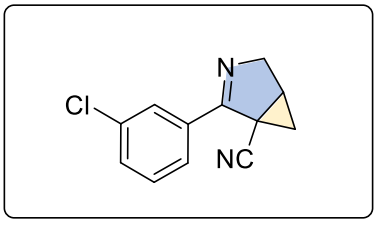
5g: 2-(4-methoxyphenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile

Brown oil. 29.3 mg (69%). **^{1}H NMR** (600 MHz, $CDCl_3$) 7.94 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 4.19 (dd, *J* = 18.0, 6.0 Hz, 1H), 4.04 (d, *J* = 18.0 Hz, 1H), 3.86 (s, 3H), 2.79 (dd, *J* = 13.2, 6.0 Hz, 1H), 1.86 (dd, *J* = 8.4, 4.2 Hz, 1H), 0.97 (t, *J* = 5.4 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 167.7, 162.2, 130.0, 124.2, 118.9, 114.1, 61.8, 55.4, 29.9, 24.6, 22.9. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{13}H_{13}N_2O^+$ 213.1022; Found 213.1020.



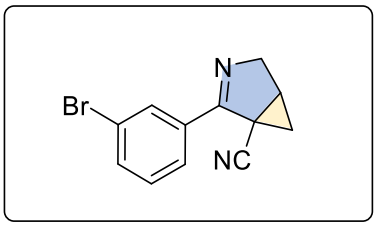
5h: methyl 4-(1-cyano-3-azabicyclo[3.1.0]hex-2-en-2-yl)benzoate

Brown oil. 37.0 mg (77%). **^{1}H NMR** (600 MHz, $CDCl_3$) 8.05 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 8.4 Hz, 2H), 4.17 (dd, *J* = 18.0, 5.4 Hz, 1H), 4.03 (d, *J* = 18.6 Hz, 1H), 3.85 (s, 3H), 2.77 (dd, *J* = 13.2, 6.0 Hz, 1H), 1.82 (dd, *J* = 9.0, 4.8 Hz, 1H), 0.93 (t, *J* = 4.8 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 167.7, 166.1, 135.1, 132.4, 129.8, 128.1, 118.2, 62.2, 52.2, 29.9, 24.7, 22.8. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{14}H_{13}N_2O_2^+$ 241.0972; Found 241.0961.



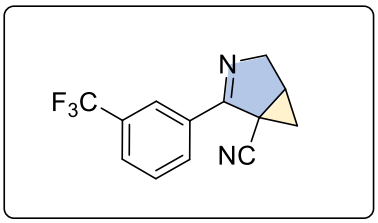
5i: 2-(3-chlorophenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile

Brown oil. 34.1 mg (79%). **^{1}H NMR** (500 MHz, $CDCl_3$) 7.96 (s, 1H), 7.86 (d, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 4.24 (dd, *J* = 18.0, 6.0 Hz, 1H), 4.10 (d, *J* = 18.0 Hz, 1H), 2.84 (dd, *J* = 14.0, 6.5 Hz, 1H), 1.90 (dd, *J* = 8.5, 4.5 Hz, 1H), 1.00 (t, *J* = 5.0 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 167.3, 134.9, 133.1, 131.5, 130.0, 128.1, 126.4, 118.2, 62.1, 30.0, 24.7, 22.9. **HRMS** (ESI) m/z: $(M+Na)^+$ Calcd for $C_{12}H_9ClN_2Na^+$ 239.0346; Found 239.0324.



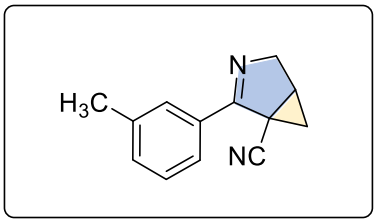
5j: 2-(3-bromophenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile

Brown oil. 38.5 mg (74%). **^{1}H NMR** (600 MHz, $CDCl_3$) 8.12 (s, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 4.24 (dd, *J* = 18.0, 6.0 Hz, 1H), 4.09 (d, *J* = 18.6 Hz, 1H), 2.84 (dd, *J* = 13.8, 6.6 Hz, 1H), 1.89 (dd, *J* = 9.0, 4.8 Hz, 1H), 0.99 (t, *J* = 5.4 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 167.2, 134.4, 133.3, 131.1, 130.2, 126.9, 122.9, 118.2, 62.1, 30.0, 24.6, 23.0. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{12}H_{10}BrN_2^+$ 261.0022; Found 261.0026.



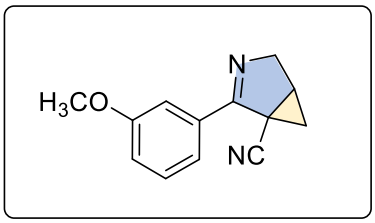
5k: 2-(3-(trifluoromethyl)phenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile

Yellow oil. 36.5 mg (73%). **^{1}H NMR** (600 MHz, $CDCl_3$) 8.26 (s, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 1H), 4.27 (dd, *J* = 18.0, 6.0 Hz, 1H), 4.13 (d, *J* = 18.6 Hz, 1H), 2.87 (dd, *J* = 13.8, 6.0 Hz, 1H), 1.93 (dd, *J* = 8.4, 4.8 Hz, 1H), 1.03 (t, *J* = 4.8 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 167.3, 132.2, 131.5, 131.4 (q, *J* = 32.6 Hz), 129.4, 128.0 (q, *J* = 3.5 Hz), 123.6 (q, *J* = 3.9 Hz), 123.7 (q, *J* = 270.8 Hz), 118.2, 62.2, 30.1, 24.7, 23.0. **^{19}F NMR** (565 MHz, $CDCl_3$) -62.8. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{13}H_{10}F_3N_2^+$ 251.0791; Found 251.0795.



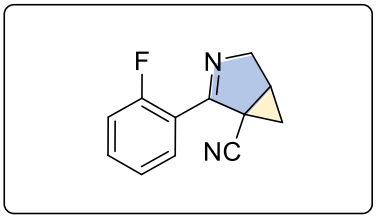
5l: 2-(m-tolyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile

Brown oil. 29.4 mg (75%). **^{1}H NMR** (500 MHz, $CDCl_3$) 7.78 (s, 1H), 7.77 (d, *J* = 6.5, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 4.22 (dd, *J* = 18.0, 6.0 Hz, 1H), 4.08 (d, *J* = 18.0 Hz, 1H), 2.81 (dd, *J* = 13.5, 6.0 Hz, 1H), 2.42 (s, 3H), 1.88 (dd, *J* = 8.5, 4.5 Hz, 1H), 0.98 (t, *J* = 5.0 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 168.7, 138.5, 132.3, 131.3, 128.7, 128.6, 125.5, 118.7, 62.0, 29.7, 24.8, 22.9, 21.3. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{13}H_{13}N_2^+$ 197.1073; Found 197.1066.



5m: 2-(3-methoxyphenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile

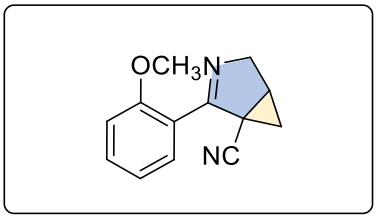
Brown oil. 33.5 mg (79%). **^{1}H NMR** (600 MHz, $CDCl_3$) 7.51 (d, *J* = 7.2 Hz, 1H), 7.42 (s, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 4.17 (dd, *J* = 18.0, 6.0 Hz, 1H), 4.02 (d, *J* = 18.0 Hz, 1H), 3.80 (s, 3H), 2.75 (dd, *J* = 13.8, 6.0 Hz, 1H), 1.82 (dd, *J* = 9.0, 4.8 Hz, 1H), 0.93 (t, *J* = 5.4 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 168.5, 159.8, 132.6, 129.8, 121.0, 118.7, 118.3, 112.4, 62.0, 55.4, 29.9, 24.9, 23.0. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{13}H_{13}N_2O^+$ 213.1022; Found 213.1025.



5n: 2-(2-fluorophenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile

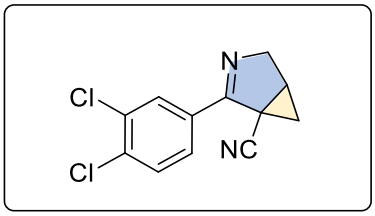
Yellow oil. 18.8 mg (47%). **^{1}H NMR** (500 MHz, $CDCl_3$) 7.76 (t, *J* = 7.0 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.26 – 7.18 (m, 2H), 4.21 (dd, *J* = 18.0, 6.0 Hz, 1H), 4.10 (d, *J* = 18.0 Hz, 1H), 2.85 (dd, *J* =

13.5, 6.5 Hz, 1H), 1.90 (dd, *J* = 8.5, 5.0 Hz, 1H), 1.07 (t, *J* = 5.0 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 165.9, 161.1 (d, *J* = 251.9 Hz), 133.3 (d, *J* = 8.6 Hz), 130.6 (d, *J* = 2.7 Hz), 124.6 (d, *J* = 3.3 Hz), 120.0 (d, *J* = 12.3 Hz), 118.1, 116.4 (d, *J* = 21.5 Hz), 62.1, 30.1, 27.6, 22.5. **^{19}F NMR** (565 MHz, $CDCl_3$) -111.0. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{12}H_{10}FN_2^+$ 201.0823; Found 201.0820.



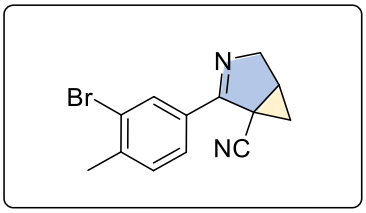
5o: 2-(2-methoxyphenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile

Brown oil. 24.6 mg (58%). **^{1}H NMR** (500 MHz, $CDCl_3$) 7.64 (d, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.0 Hz, 1H), 7.02 – 7.00 (m, 2H), 4.13 (dd, *J* = 18.0, 6.0 Hz, 1H), 4.02 (d, *J* = 18.0 Hz, 1H), 3.97 (s, 3H), 2.79 (dd, *J* = 14.0, 6.5 Hz, 1H), 1.81 (dd, *J* = 8.5, 4.5 Hz, 1H), 1.01 (t, *J* = 5.5 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 168.5, 158.3, 132.7, 130.7, 121.3, 120.9, 118.9, 111.4, 61.5, 55.6, 30.1, 28.5, 22.5. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{13}H_{13}N_2O^+$ 213.1022; Found 213.1015.



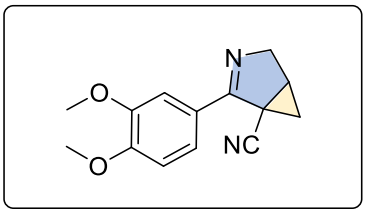
5r: 2-(3,4-dichlorophenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile

Yellow oil. 46.5 mg (93%). **^{1}H NMR** (600 MHz, $CDCl_3$) 8.00 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 4.17 (dd, *J* = 18.6, 6.0 Hz, 1H), 4.03 (d, *J* = 18.0 Hz, 1H), 2.79 (dd, *J* = 14.4, 6.0 Hz, 1H), 1.84 (dd, *J* = 9.0, 4.8 Hz, 1H), 0.93 (t, *J* = 5.4 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 166.5, 136.0, 133.3, 131.2, 130.8, 130.0, 127.3, 118.1, 62.2, 30.2, 24.6, 23.0. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{12}H_9Cl_2N_2^+$ 251.0137; Found 251.0137.



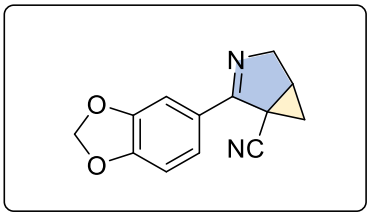
5s: 2-(3-bromo-4-methylphenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile

Brown oil. 40.0 mg (73%). **^{1}H NMR** (500 MHz, $CDCl_3$) 8.14 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 4.23 (dd, *J* = 18.0, 5.5 Hz, 1H), 4.08 (d, *J* = 18.0 Hz, 1H), 2.83 (dd, *J* = 13.5, 6.0 Hz, 1H), 2.45 (s, 3H), 1.89 (dd, *J* = 8.5, 4.5 Hz, 1H), 0.99 (t, *J* = 5.0 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 167.1, 141.7, 131.9, 130.9, 130.7, 127.1, 125.3, 118.4, 62.0, 29.9, 24.6, 23.0, 22.9. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{13}H_{12}BrN_2^+$ 275.0178; Found 275.0184.



5t: 2-(3,4-dimethoxyphenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile

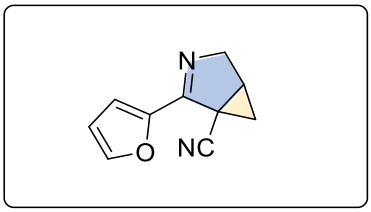
Brown oil. 32.9 mg (68%). **^{1}H NMR** (600 MHz, $CDCl_3$) 7.56 (d, *J* = 8.4 Hz, 1H), 7.43 (s, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 4.14 (dd, *J* = 18.0, 6.0 Hz, 1H), 3.98 (d, *J* = 18.0 Hz, 1H), 3.87 (s, 6H), 2.74 (dd, *J* = 13.2, 6.0 Hz, 1H), 1.81 (dd, *J* = 9.0, 4.8 Hz, 1H), 0.92 (t, *J* = 5.4 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 167.8, 152.0, 149.1, 124.3, 122.3, 118.9, 110.5, 110.1, 61.7, 55.9, 55.9, 29.9, 24.5, 23.0. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{14}H_{15}N_2O_2^+$ 243.1128; Found 243.1121.



5u: 2-(benzo[d][1,3]dioxol-5-yl)-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile

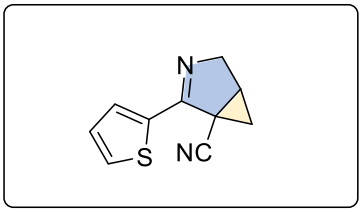
Brown oil. 21.7 mg (48%). **^{1}H NMR** (500 MHz, $CDCl_3$) 7.47 (d, *J* = 8.5 Hz, 1H), 7.35 (s, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 5.97 (s, 2H), 4.12 (dd, *J* = 18.0, 6.0 Hz, 1H), 3.98 (d, *J* = 18.0 Hz, 1H), 2.73 (dd, *J* = 14.0, 6.0 Hz, 1H), 1.80 (dd, *J* = 8.5, 4.5 Hz, 1H), 0.91 (t, *J* = 5.5 Hz, 1H). **^{13}C NMR** (150

MHz, $CDCl_3$) 167.7, 150.5, 148.2, 125.8, 123.8, 118.8, 108.2, 107.9, 101.6, 61.7, 30.0, 24.6, 22.9. **HRMS** (ESI) m/z: $(M+Na)^+$ Calcd for $C_{13}H_{10}N_2NaO_2^+$ 249.0634; Found 249.0620.



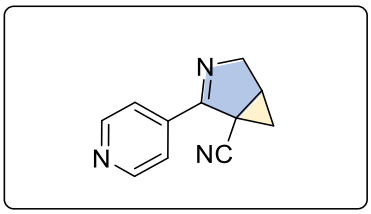
5v: 2-(furan-2-yl)-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile

Brown oil. 13.4 mg (39%). **^{1}H NMR** (500 MHz, $CDCl_3$) 7.62 (s, 1H), 7.28 (d, *J* = 4.0 Hz, 1H), 6.58 – 6.57 (m, 1H), 4.27 (dd, *J* = 18.5, 6.0 Hz, 1H), 4.08 (d, *J* = 18.0 Hz, 1H), 2.84 (dd, *J* = 13.5, 6.0 Hz, 1H), 1.84 (dd, *J* = 9.0, 5.0 Hz, 1H), 0.99 (t, *J* = 5.5 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 158.4, 146.9, 145.8, 118.1, 115.5, 112.1, 62.2, 30.0, 24.6, 23.0. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{10}H_9N_2O^+$ 173.0709; Found 173.0711.



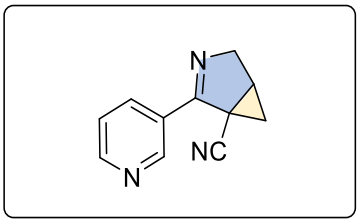
5w: 2-(thiophen-2-yl)-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile

Brown oil. 25.9 mg (69%). **^{1}H NMR** (500 MHz, $CDCl_3$) 7.89 (d, *J* = 3.5 Hz, 1H), 7.50 (d, *J* = 5.0 Hz, 1H), 7.15 (t, *J* = 4.5 Hz, 1H), 4.22 (dd, *J* = 18.5, 6.0 Hz, 1H), 4.03 (d, *J* = 18.5 Hz, 1H), 2.85 (dd, *J* = 14.0, 6.0 Hz, 1H), 1.86 (dd, *J* = 8.5, 4.5 Hz, 1H), 1.02 (t, *J* = 5.0 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 162.4, 135.9, 130.9, 130.7, 128.0, 118.5, 61.8, 30.6, 24.8, 23.0. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{10}H_9N_2S^+$ 189.0481; Found 189.0475.



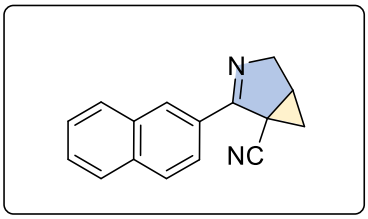
5x: 2-(pyridin-4-yl)-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile

Brown oil. 10.3 mg (28%). **^{1}H NMR** (500 MHz, $CDCl_3$) 8.79 (s, 2H), 7.85 (s, 2H), 4.31 (dd, *J* = 18.5, 5.5 Hz, 1H), 4.16 (d, *J* = 18.5 Hz, 1H), 2.90 (dd, *J* = 13.0, 6.0 Hz, 1H), 1.94 (dd, *J* = 8.0, 4.5 Hz, 1H), 1.03 (t, *J* = 5.0 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 167.0, 150.6, 138.2, 121.9, 118.0, 62.6, 30.0, 24.6, 23.0. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{11}H_{10}N_3^+$ 184.0869; Found 184.0869.



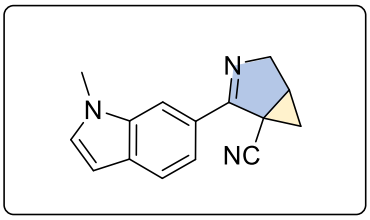
5y: 2-(pyridin-3-yl)-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile

Brown solid. 14.6 mg (40%). mp: 86−87 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 9.22 (s, 1H), 8.75 (d, *J* = 4.2 Hz, 1H), 8.27 (d, *J* = 7.8 Hz, 1H), 7.43 – 7.42 (m, 1H), 4.28 (dd, *J* = 18.0, 6.0 Hz, 1H), 4.14 (d, *J* = 18.6 Hz, 1H), 2.88 (dd, *J* = 13.8, 6.0 Hz, 1H), 1.94 (dd, *J* = 8.4, 4.8 Hz, 1H), 1.03 (t, *J* = 5.4 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 166.4, 152.2, 149.3, 135.4, 127.3, 123.5, 118.1, 62.4, 29.9, 24.7, 23.0. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{11}H_{10}N_3^+$ 184.0869; Found 184.0872.



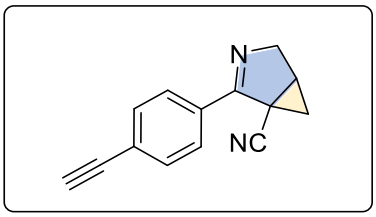
5aa: 2-(naphthalen-2-yl)-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile

Yellow oil. 39.9 mg (86%). **^{1}H NMR** (500 MHz, $CDCl_3$) 8.43 (s, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.51 – 7.46 (m, 2H), 4.21 (dd, *J* = 18.0, 6.0 Hz, 1H), 4.05 (dd, *J* = 18.0 Hz, 1H), 2.78 (dd, *J* = 13.5, 6.0 Hz, 1H), 1.87 (dd, *J* = 9.0, 5.0 Hz, 1H), 0.98 (t, *J* = 5.5 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 168.5, 134.7, 132.7, 129.3, 129.0, 128.8, 128.7, 127.8, 127.7, 126.7, 124.4, 118.8, 62.1, 30.0, 24.7, 23.0. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{16}H_{13}N_2^+$ 233.1073; Found 233.1063.



5ab: 2-(1-methyl-1H-indol-6-yl)-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile

Brown solid. 15.0 mg (32%). mp: 91−92 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) 7.99 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.18 (d, *J* = 2.5 Hz, 1H), 6.52 (d, *J* = 3.0 Hz, 1H), 4.25 (dd, *J* = 18.0, 6.0 Hz, 1H), 4.10 (d, *J* = 18.0 Hz, 1H), 3.86 (s, 3H), 2.83 (dd, *J* = 14.0, 6.0 Hz, 1H), 1.93 (dd, *J* = 8.5, 4.5 Hz, 1H), 1.05 (t, *J* = 5.0 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 169.5, 136.4, 131.7, 131.2, 124.7, 121.0, 119.6, 119.2, 109.9, 101.4, 61.7, 33.0, 29.9, 24.9, 23.1. **HRMS** (ESI) m/z: $(M+H)^+$ Calcd for $C_{15}H_{14}N_3^+$ 236.1182; Found 236.1176.



5ac: 2-(4-ethynylphenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile

Brown oil. 14.0 mg (34%). **^{1}H NMR** (500 MHz, $CDCl_3$) 7.87 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 4.18 (dd, *J* = 18.5, 6.0 Hz, 1H), 4.04 (d, *J* = 18.5 Hz, 1H), 3.15 (s, 1H), 2.77 (dd, *J* = 13.5, 6.0 Hz, 1H), 1.83 (dd, *J* = 9.0, 5.0 Hz, 1H), 0.94 (t, *J* = 5.5 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 167.8, 132.5, 131.5, 128.2, 125.4, 118.5, 82.9, 79.7, 62.2, 30.0, 24.7, 23.0. **HRMS** (ESI) m/z: $(M+Na)^+$ Calcd for $C_{14}H_{10}N_2Na^+$ 229.0736; Found 229.0740.

VII. Crystal data of compounds

Single-crystal X-ray diffraction data was collected at room temperature on a Oxford Diffraction Gemini R Ultra diffractometer, the X-ray generator using Mo-Kα (λ =0.71073 Å) radiation with a ω scan technique. The crystal structures were solved bydirect method of SHELXS-97[8] and refined by full-matrix least-squares techniques usingthe SHELXL-97 program. Drawing of the compound shows ellipsoid contour at the 30% probability level. Non-hydrogen atoms were refined anisotropic. CCDC deposition number: 2282774 (**4r**) and 2282777 (**5h**). Data can be obtained free of charge viawww.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

The single crystals of **4r, 5h** were cultivated from the mixed solvent of dichloromethane, ethyl acetate and petroleum ether via solvent volatilization, respectively.

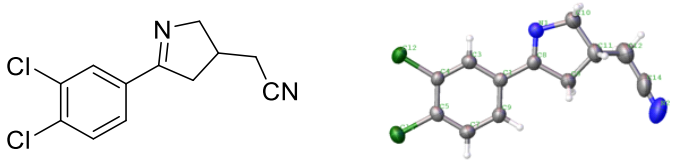


Table S3. Crystallographic data and structural refinement for **4r.**

Empirical formula	$C_{12}H_{10}Cl_2N_2$
Formula weight	253.12
Crystal system	Orthorhombic
Space group	P c a 21
a (Å)	7.8855(7)
b (Å)	13.1039(9)
c (Å)	11.2372(10)
α (deg)	90
β (deg)	90
γ (deg)	90
Volume (Å3)	1161.15(17)
Z	4
Calculated density (mg/m^3)	1.448
Absorption coefficient (mm-1)	0.530

(8) G. M. Sheldrick, *SHELXS-97, Programs for X-ray crystal Structure Solution,* University of Göttingen, Göttingen, Germany, 1997.

F(000)	520.0
Theta range for data collection (deg)	3.519 to 29.275
Reflections collected/unique	5190/2293
Goodness-of-fit on F2	1.062
Final R indices [I> 2σ(I)]	R1= 0.0390, WR2 = 0.0791
R indices (all data)	R1= 0.0574, WR2 =0.0934

Table S4. Bond lengths [Å] and angles [°] for **4r**.

Cl(1)-C(5)	1.728(4)	C(3)-C(1)-C(8)	120.7(3)
Cl(2)-C(4)	1.735(4)	C(9)-C(1)-C(3)	118.9(3)
C(1)-C(3)	1.390(5)	C(9)-C(1)-C(8)	120.4(3)
C(1)-C(8)	1.475(5)	C(8)-N(1)-C(10)	109.3(3)
C(1)-C(9)	1.390(6)	C(4)-C(3)-C(1)	120.1(4)
N(1)-C(8)	1.278(5)	C(3)-C(4)-Cl(2)	119.1(3)
N(1)-C(10)	1.475(5)	C(3)-C(4)-C(5)	120.4(4)
C(3)-C(4)	1.382(5)	C(5)-C(4)-Cl(2)	120.5(3)
C(4)-C(5)	1.394(5)	C(4)-C(5)-Cl(1)	120.3(3)
C(5)-C(7)	1.371(6)	C(7)-C(5)-Cl(1)	119.7(3)
C(6)-C(8)	1.502(6)	C(7)-C(5)-C(4)	119.9(4)
C(6)-C(11)	1.533(6)	C(8)-C(6)-C(11)	103.3(4)
C(6)-C(9)	1.391(5)	C(5)-C(7)-C(9)	119.7(4)
C(10)-C(11)	1.541(7)	C(1)-C(8)-C(6)	122.3(3)
C(11)-C(12)	1.514(6)	N(1)-C(8)-C(1)	121.9(4)
C(11)-C(14)	1.449(9)	N(1)-C(8)-C(6)	115.7(3)
C(14)-N(2)	1.136(8)	C(1)-C(9)-C(7)	120.9(4)
		N(1)-C(10)-C(11)	107.7(3)
		C(6)-C(11)-C(10)	103.7(3)
		C(12)-C(11)-C(6)	113.3(4)
		C(12)-C(11)-C(10)	114.5(4)
		C(14)-C(12)-C(11)	112.4(5)
		N(2)-C(14)-C(12)	177.3(7)

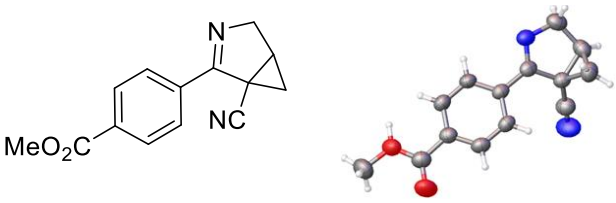


Table S5. Crystallographic data and structural refinement for **5h.**

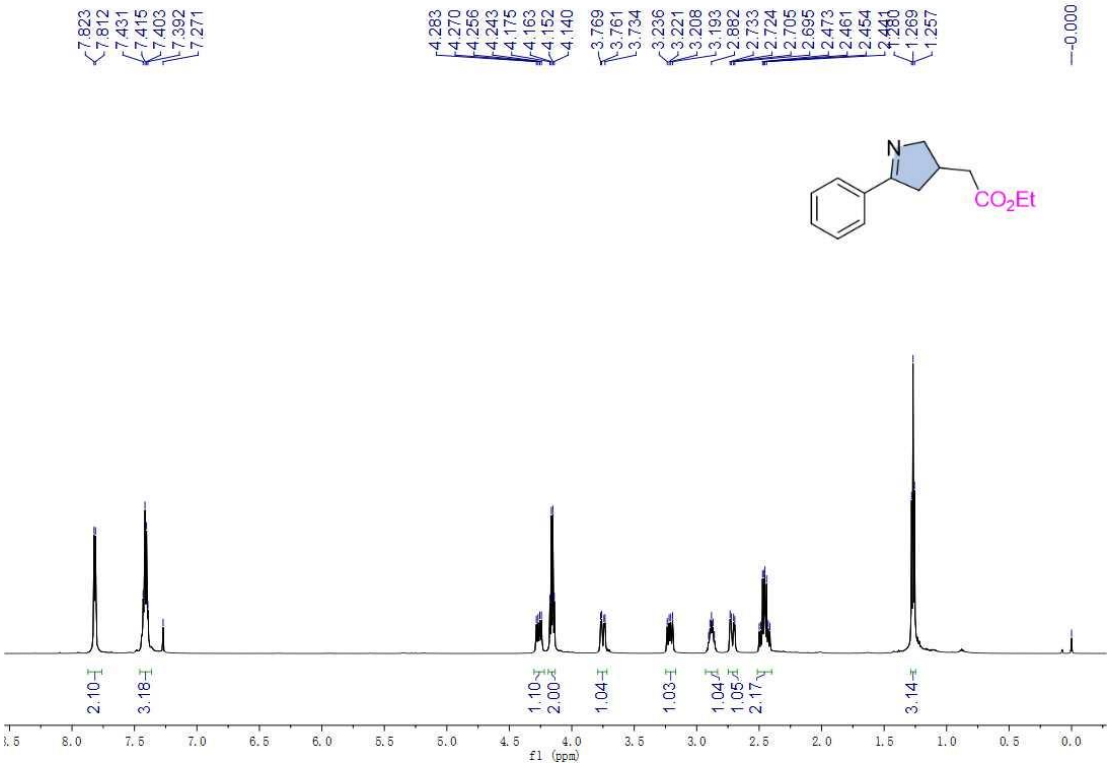
Empirical formula	$C_{14}H_{12}N_2O_2$
Formula weight	240.26
Crystal system	Triclinic
Space group	P -1
a (Å)	5.5922(6)
b (Å)	6.7269(13)
c (Å)	17.374(3)
α (deg)	87.781(16)
β (deg)	85.060(12)
γ (deg)	70.579(14)
Volume (Å3)	614.08(19)
Z	2
Calculated density (mg/m^3)	1.299
Absorption coefficient (mm-1)	0.089
F(000)	252.0
Theta range for data collection (deg)	3.408 to 29.293
Reflections collected/unique	4360/2774
Goodness-of-fit on F2	1.066
Final R indices [I> 2σ(I)]	R1= 0.0742, WR2 = 0.1224
R indices (all data)	R1= 0.1865, WR2 =0.1741

Table S6. Bond lengths [Å] and angles [°] for **5h**.

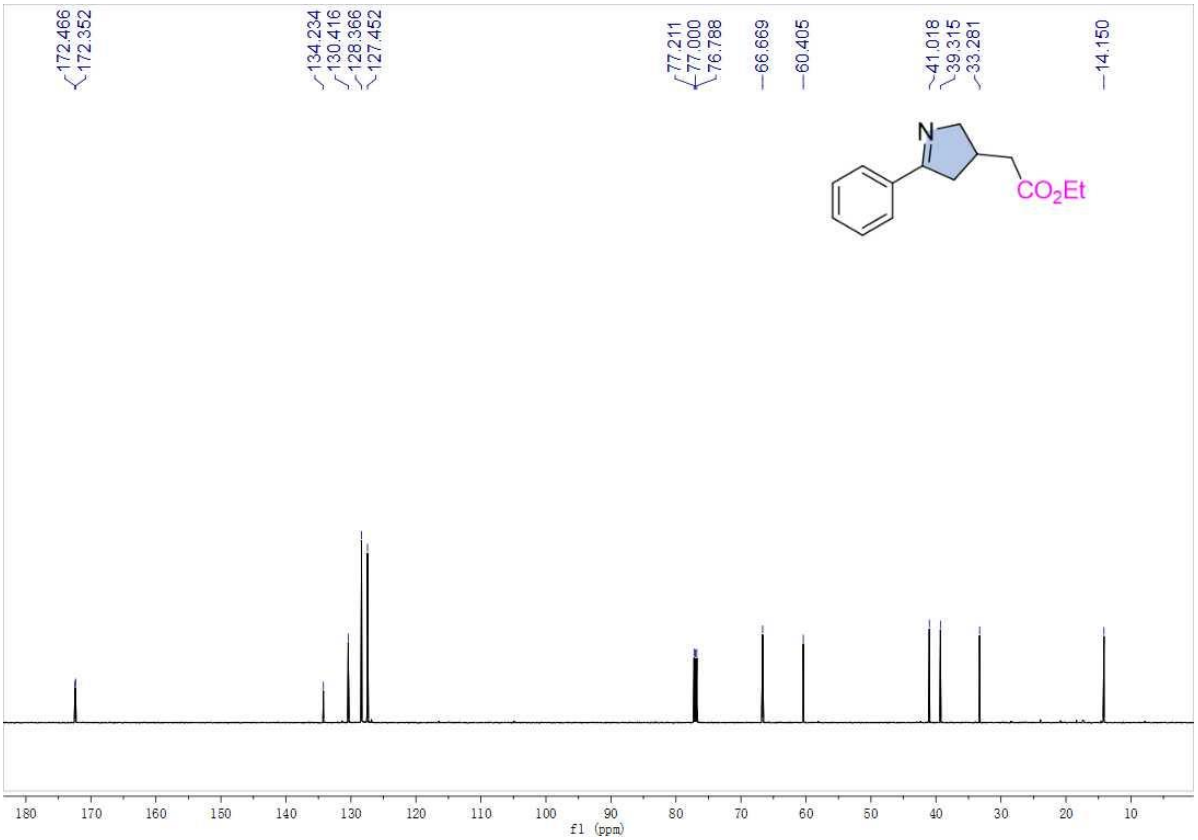
C(1)-C(3)	1.389(4)	C(3)-C(1)-C(10)	122.3(3)
C(1)-C(9)	1.382(4)	C(9)-C(1)-C(3)	118.6(3)
C(1)-C(10)	1.485(4)	C(9)-C(1)-C(10)	119.1(3)
C(2)-C(3)	1.373(4)	C(3)-C(2)-C(4)	120.2(3)
C(2)-C(4)	1.390(4)	C(2)-C(3)-C(1)	121.1(3)
C(4)-C(5)	1.383(4)	C(2)-C(4)-C(7)	120.6(3)
C(4)-C(7)	1.475(4)	C(5)-C(4)-C(2)	118.9(3)
C(5)-C(9)	1.381(4)	C(5)-C(4)-C(7)	120.5(3)
N(2)-C(7)	1.279(3)	C(9)-C(5)-C(4)	120.6(3)
N(2)-C(14)	1.463(4)	C(7)-N(2)-C(14)	109.5(3)
C(7)-C(12)	1.495(4)	C(4)-C(7)-C(12)	122.6(3)
O(2)-C(10)	1.325(3)	N(2)-C(7)-C(4)	122.7(3)
O(2)-C(18)	1.449(4)	N(2)-C(7)-C(12)	114.6(3)
C(10)-O(1)	1.202(4)	C(10)-O(8)-C(1)	117.0(3)
C(12)-C(13)	1.440(4)	C(5)-C(9)-C(1)	120.6(3)
C(12)-C(15)	1.516(4)	O(2)-C(10)-C(1)	112.5(3)
C(12)-C(16)	1.515(4)	O(1)-C(10)-C(1)	123.8(3)
C(13)-N(1)	1.143(4)	O(1)-C(10)-O(2)	123.7(3)
C(14)-C(16)	1.516(4)	C(7)-C(12)-C(15)	113.5(3)
C(15)-C(16)	1.475(4)	C(7)-C(12)-C(16)	103.6(2)
		C(13)-C(12)-C(7)	120.9(2)
		C(13)-C(12)-C(15)	121.1(2)
		C(13)-C(12)-C(16)	122.7(3)
		C(16)-C(12)-C(15)	58.22(19)
		N(1)-C(13)-C(12)	179.2(4)
		N(1)-C(14)-C(16)	107.6(3)
		C(16)-C(15)-C(12)	60.9(2)
		C(12)-C(16)-C(14)	104.2(3)
		C(15)-C(16)-C(12)	60.9(2)
		C(15)-C(16)-C(14)	117.6(3)

VIII. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra

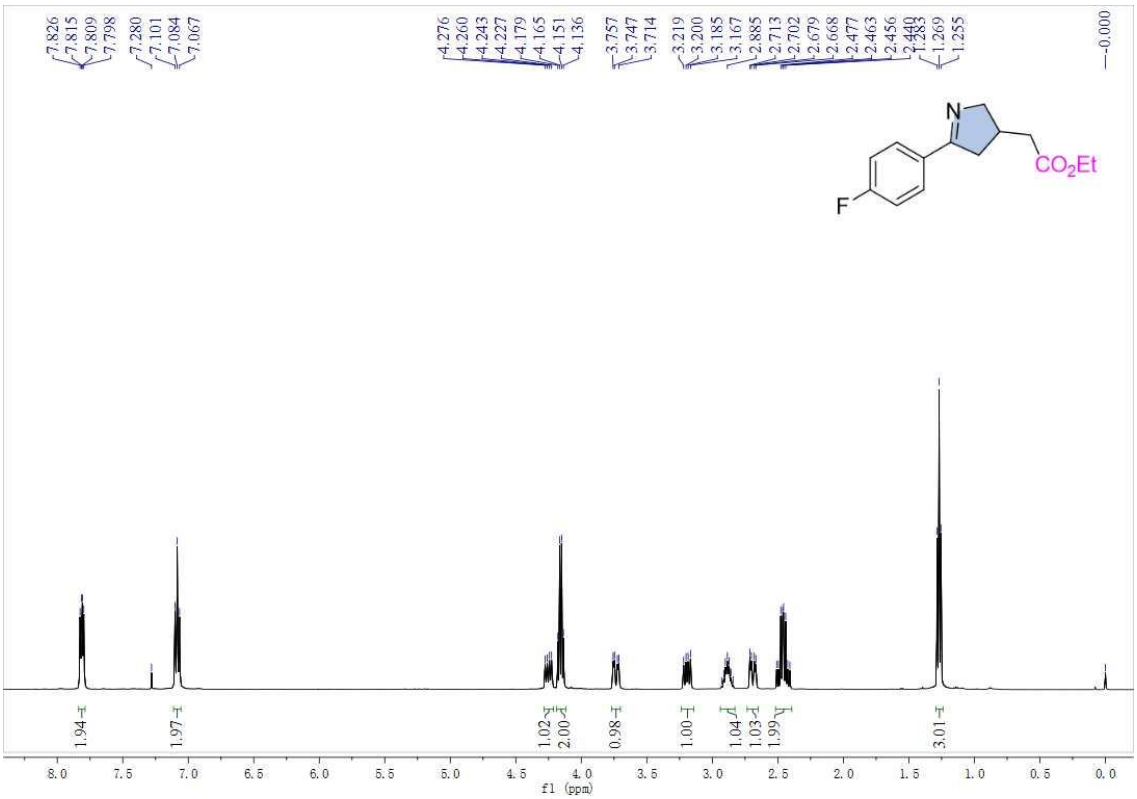
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 2a



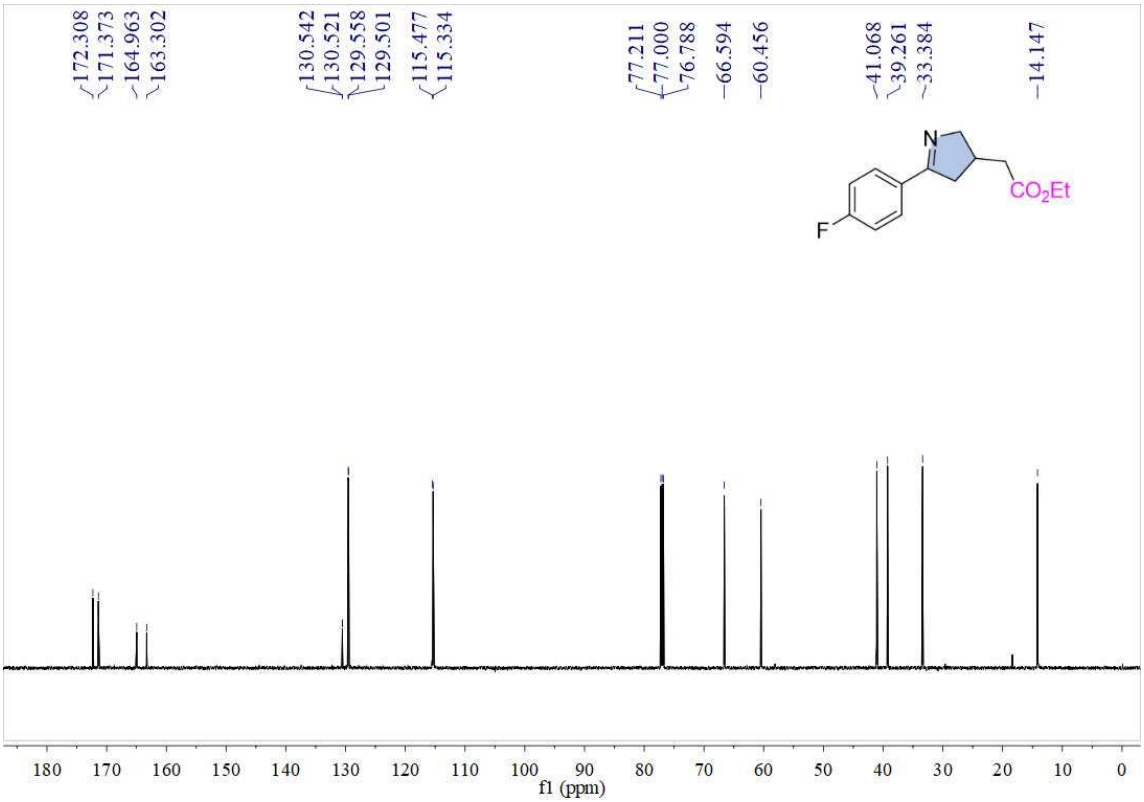
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2a



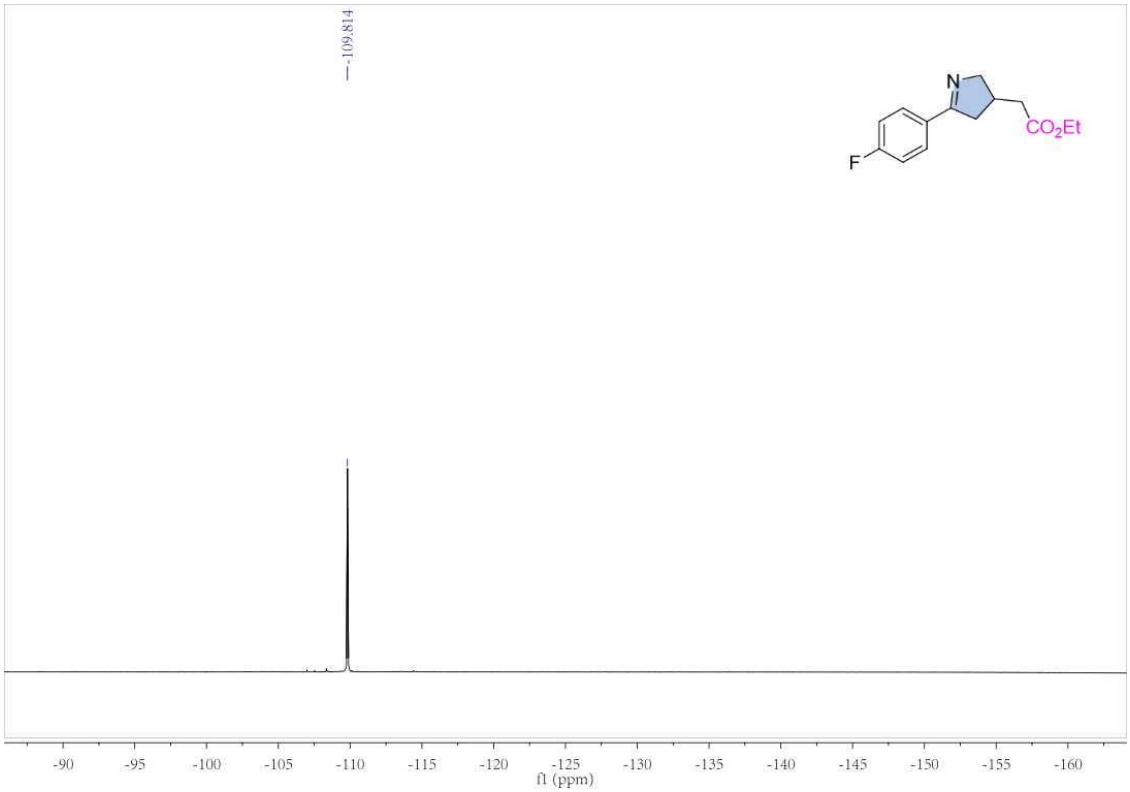
^{1}H spectrum (500 MHz, $CDCl_3$) of compound 2b



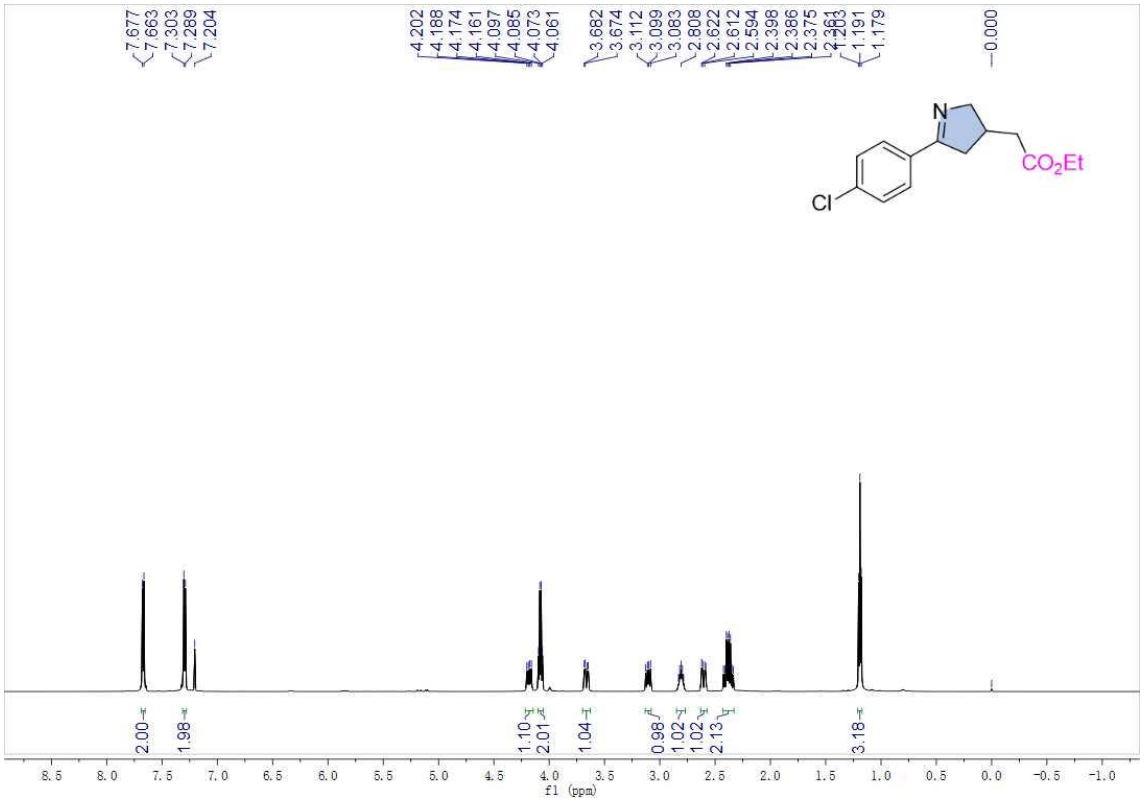
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2b



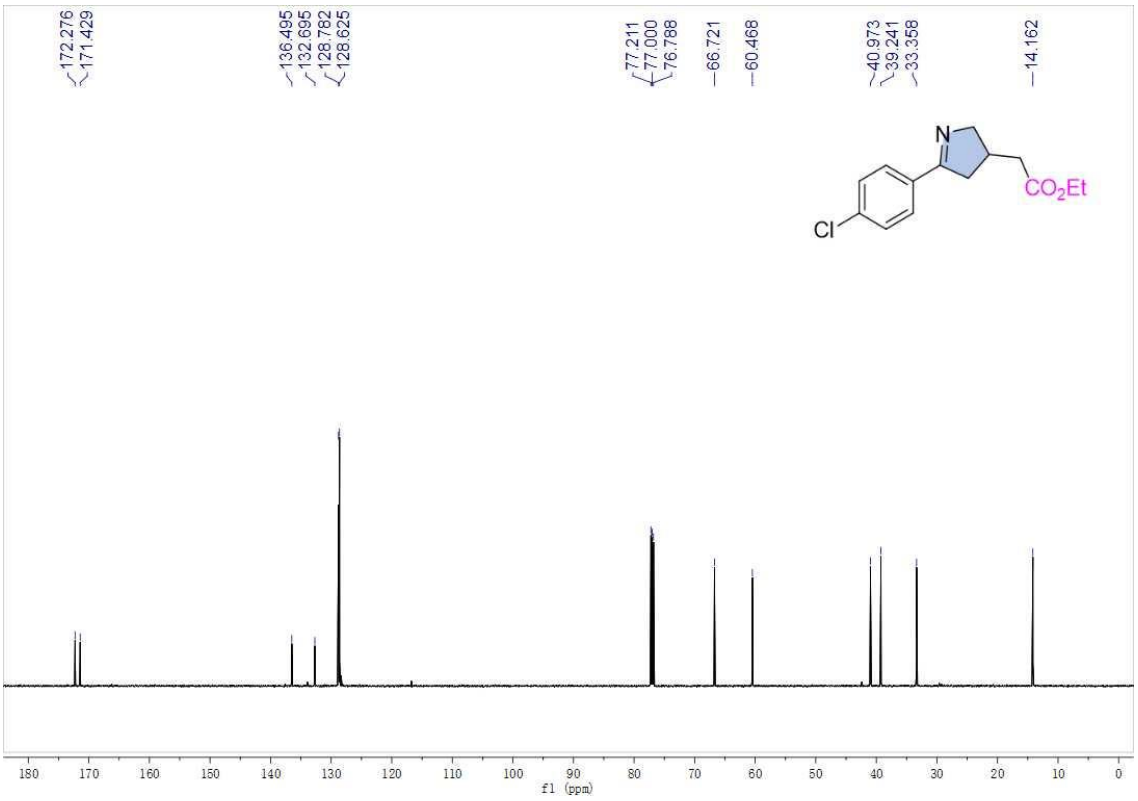
^{19}F spectrum (565 MHz, $CDCl_3$) of compound 2b



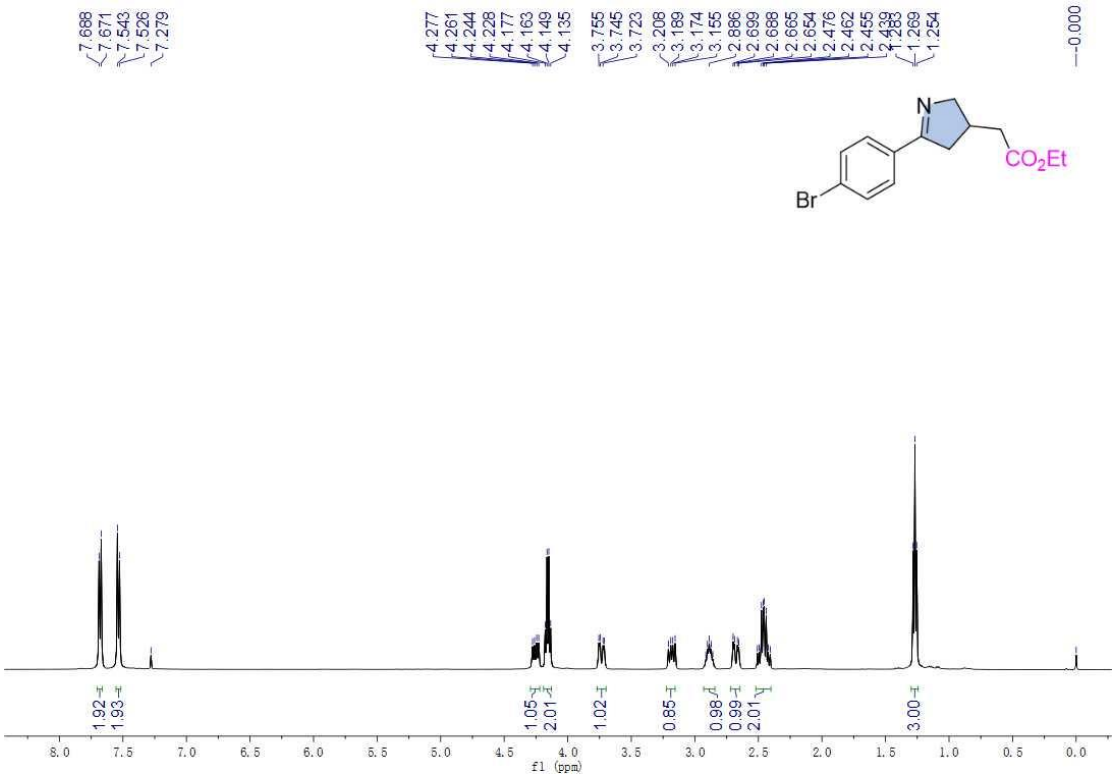
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 2c



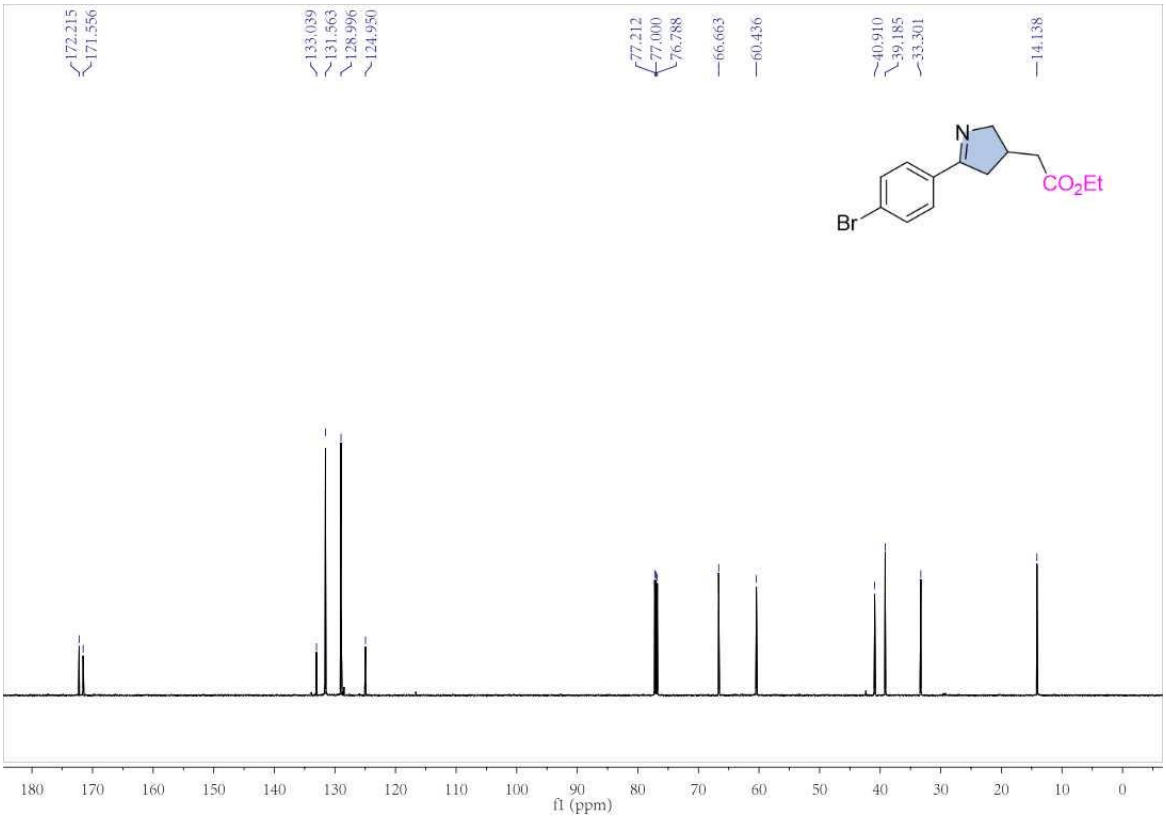
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2c



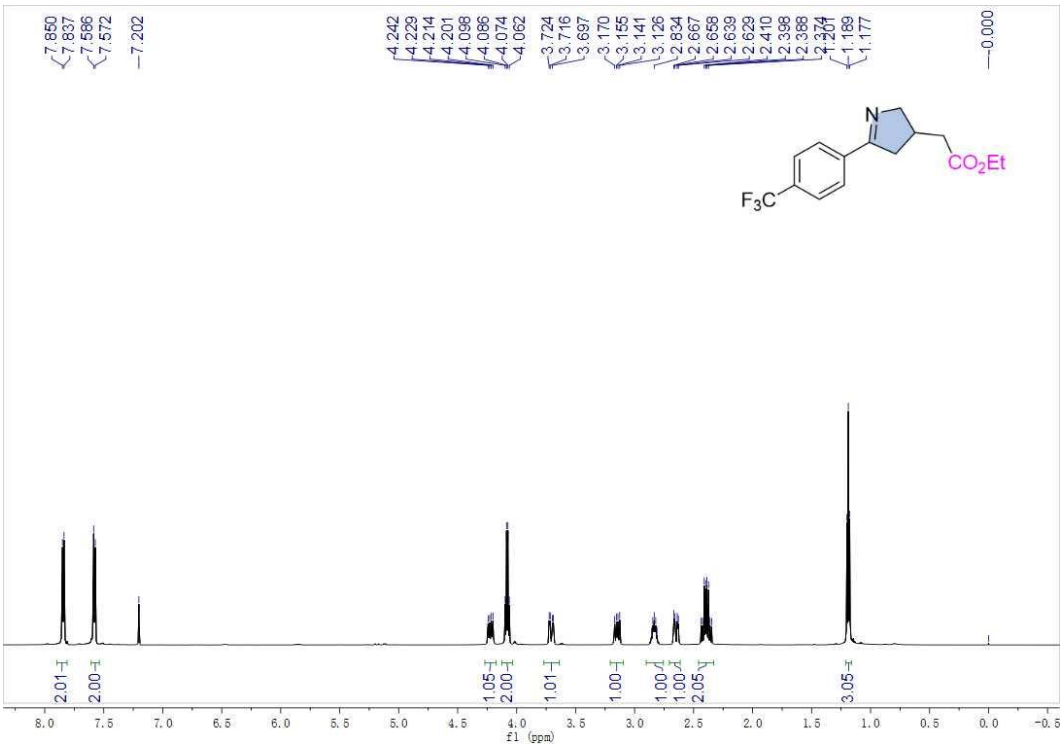
^{1}H spectrum (500 MHz, $CDCl_3$) of compound 2d



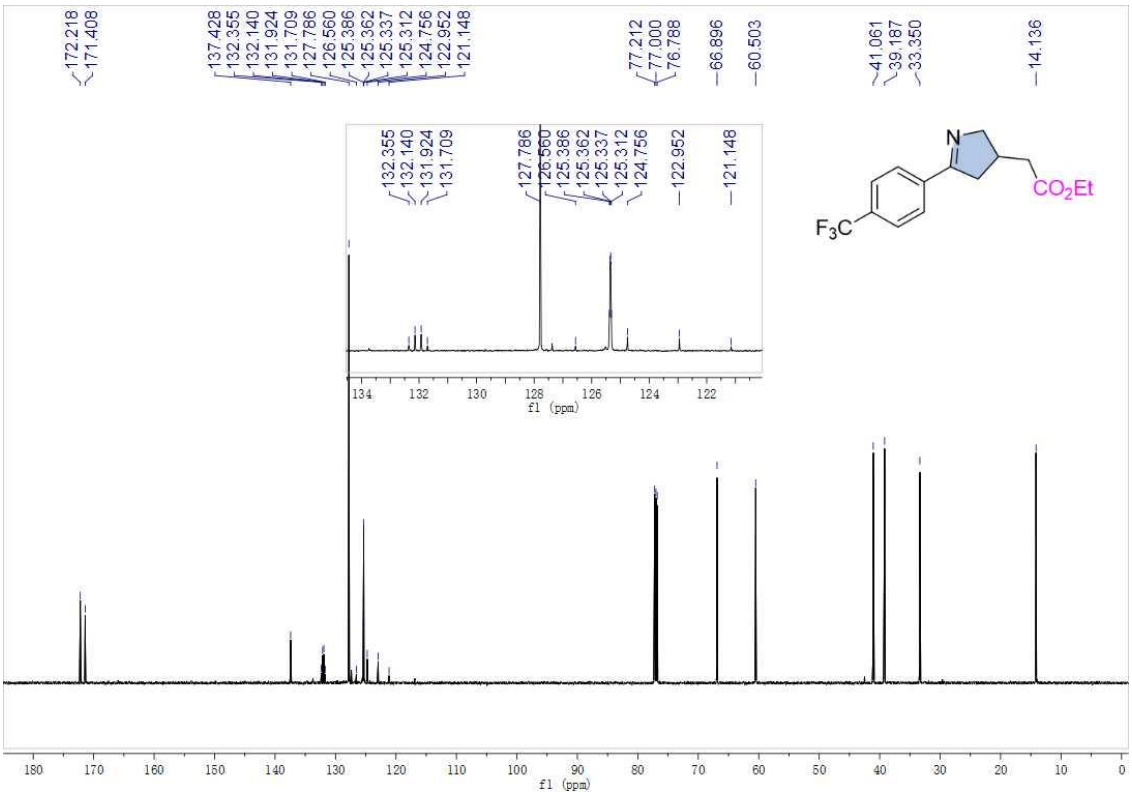
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2d



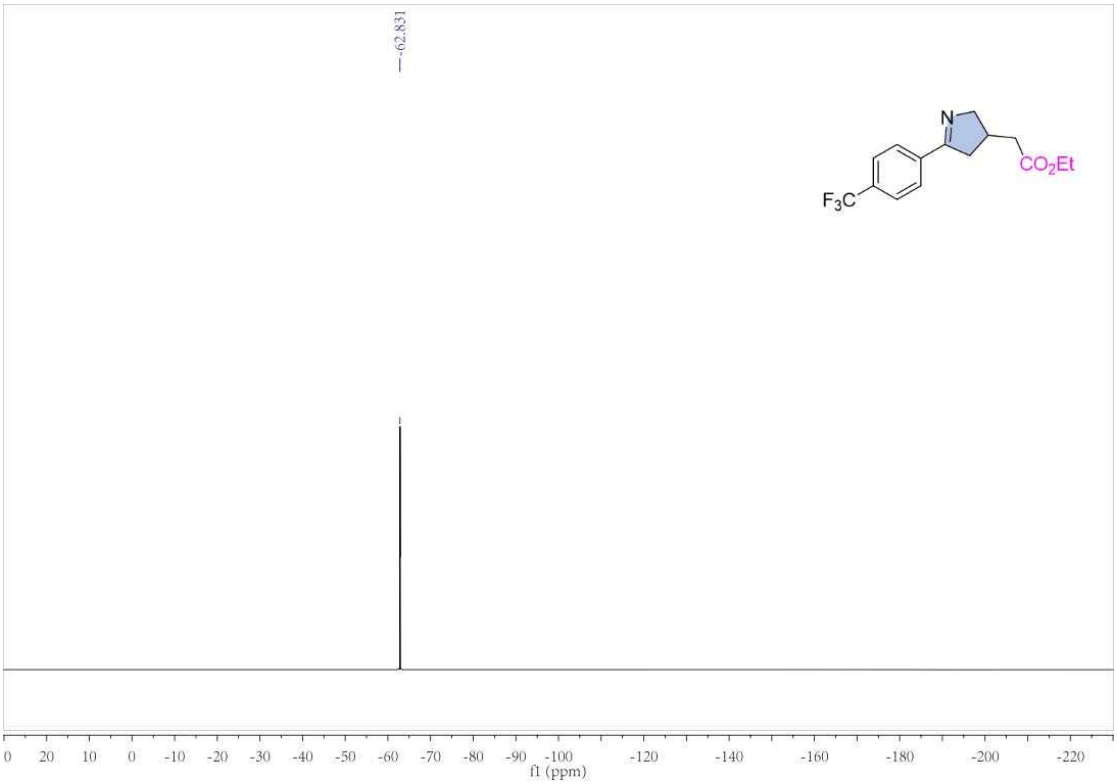
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 2e



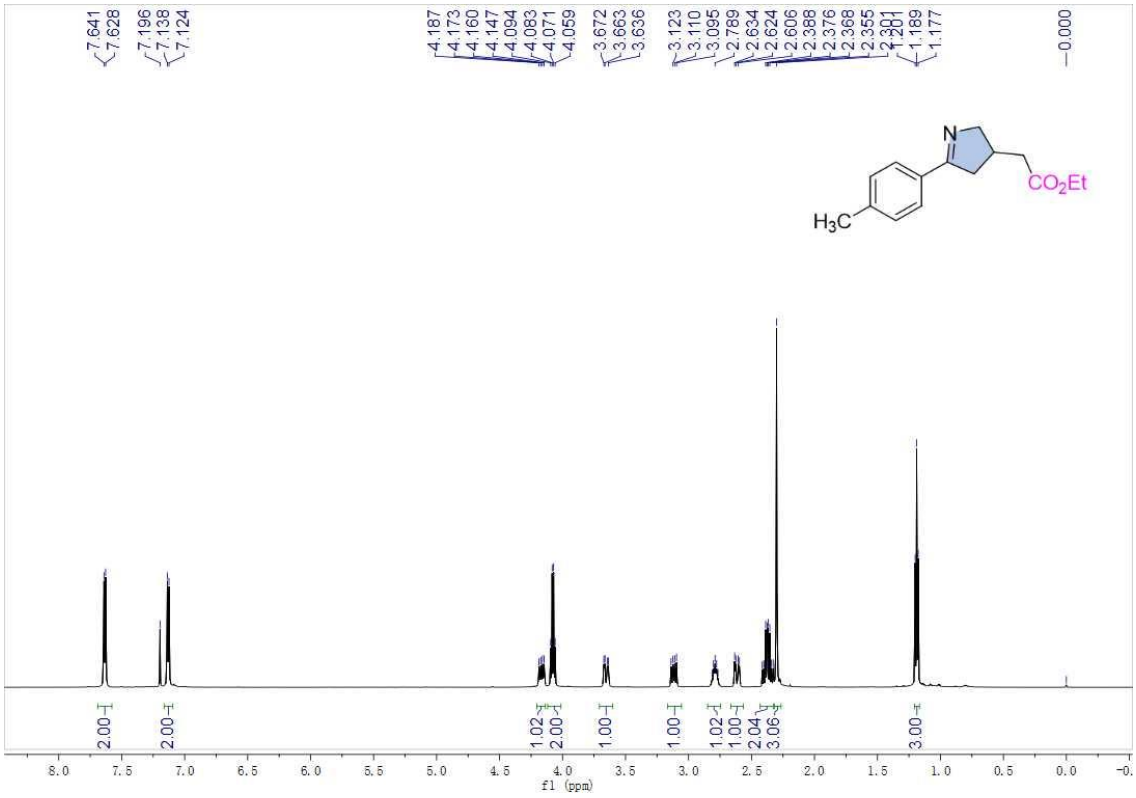
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2e



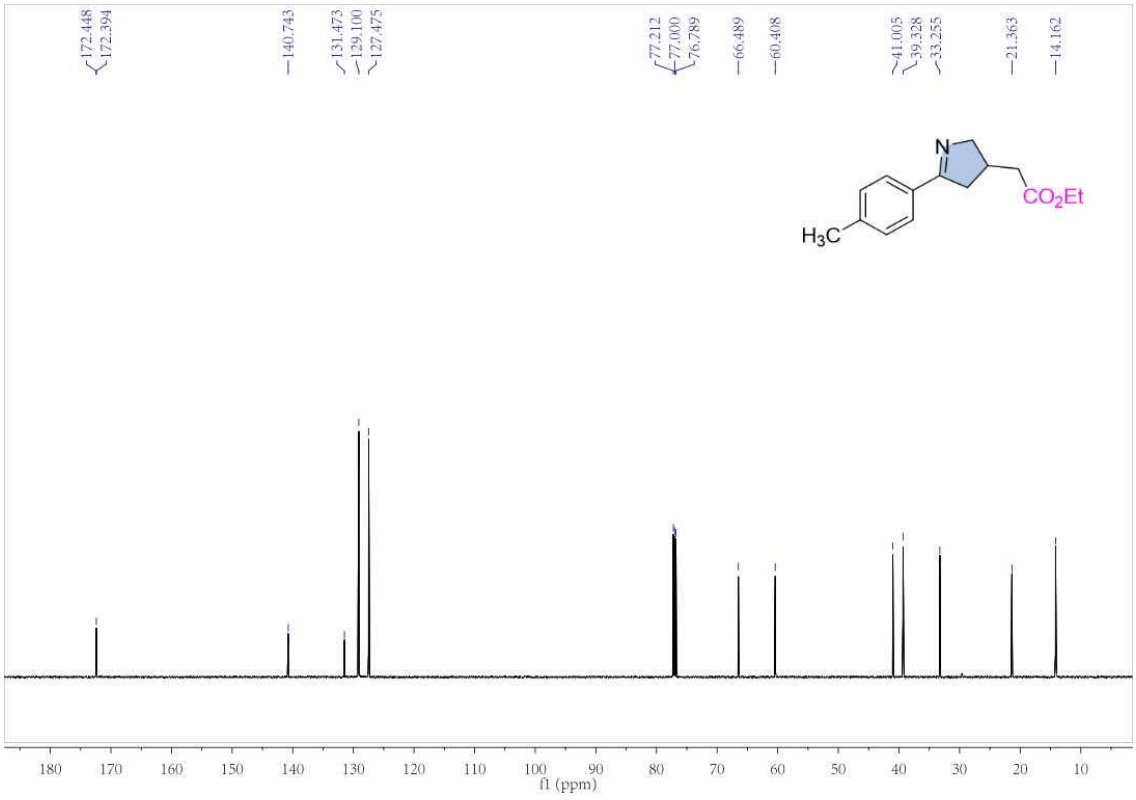
^{19}F spectrum (565 MHz, $CDCl_3$) of compound 2e



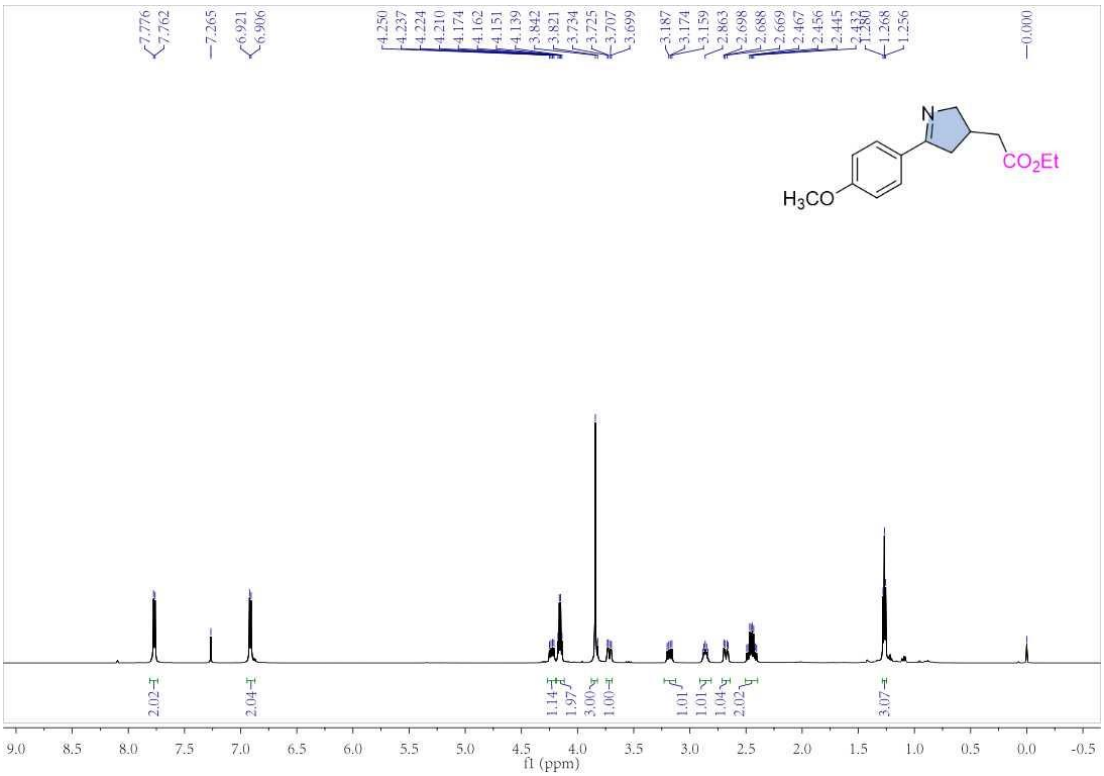
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 2f



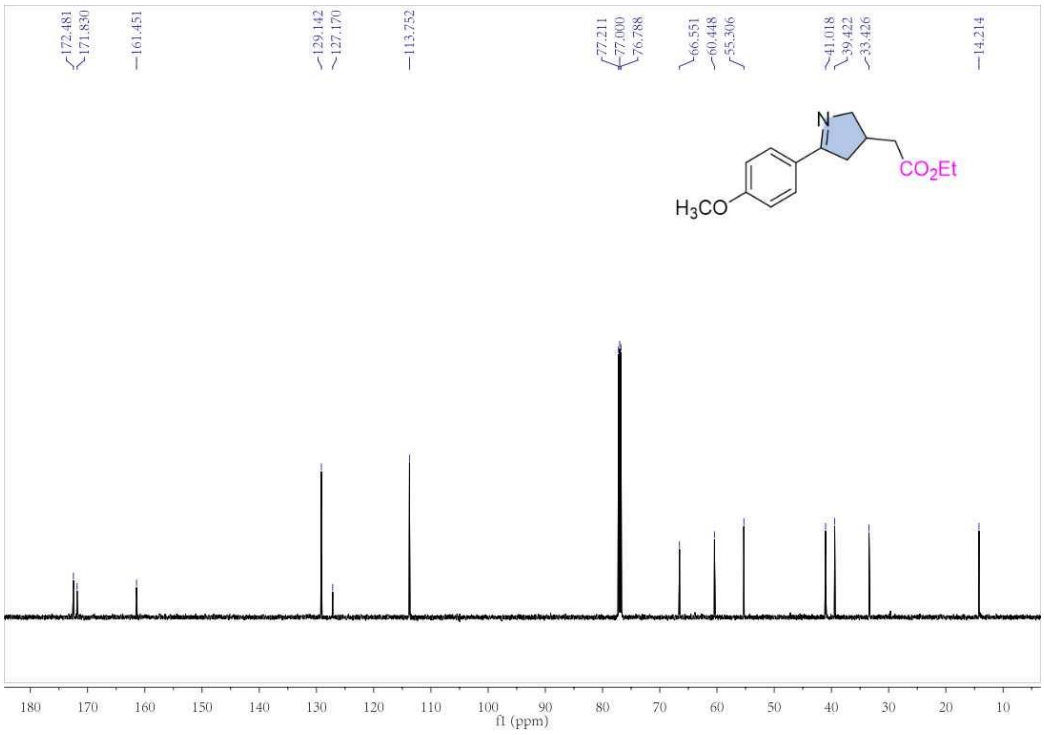
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2f



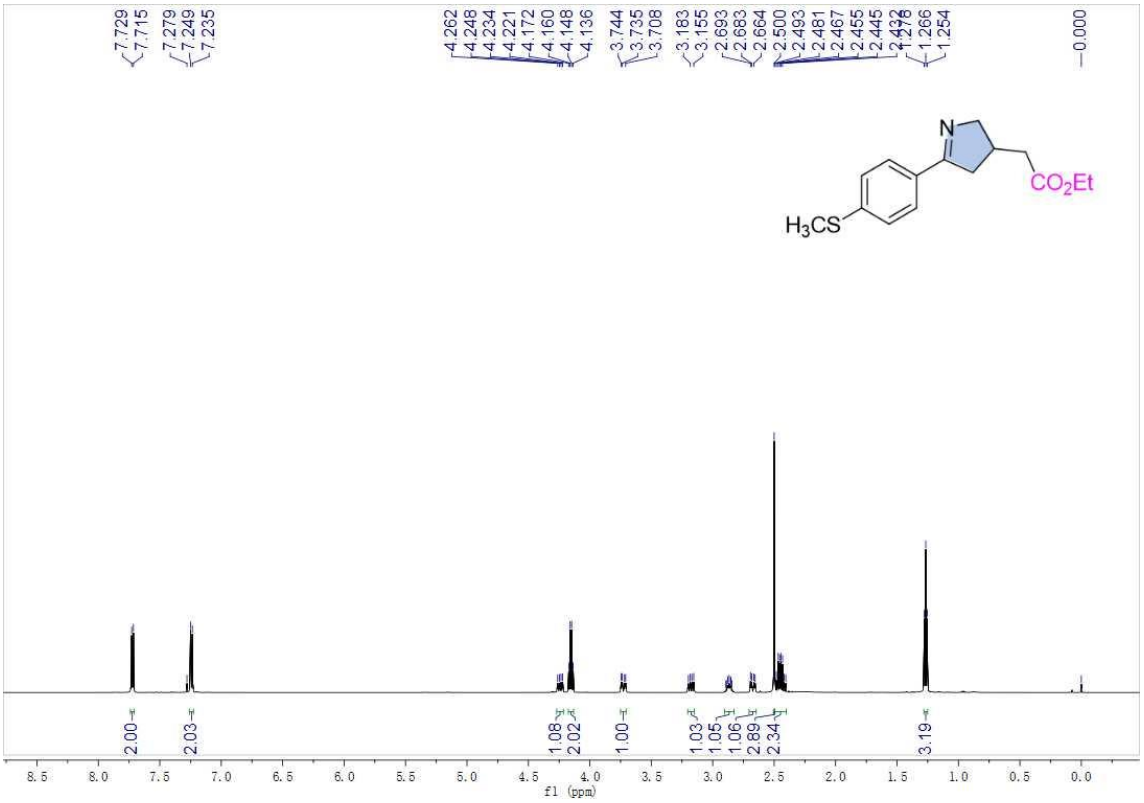
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 2g



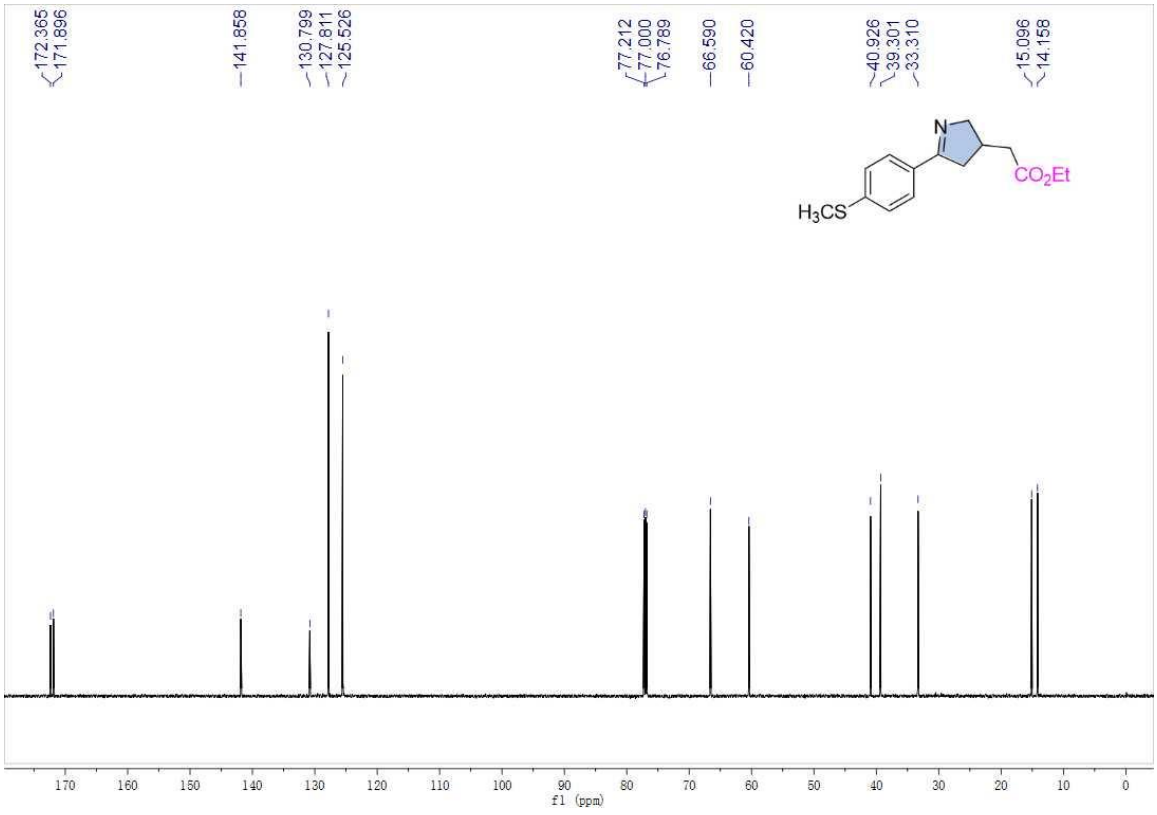
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2g



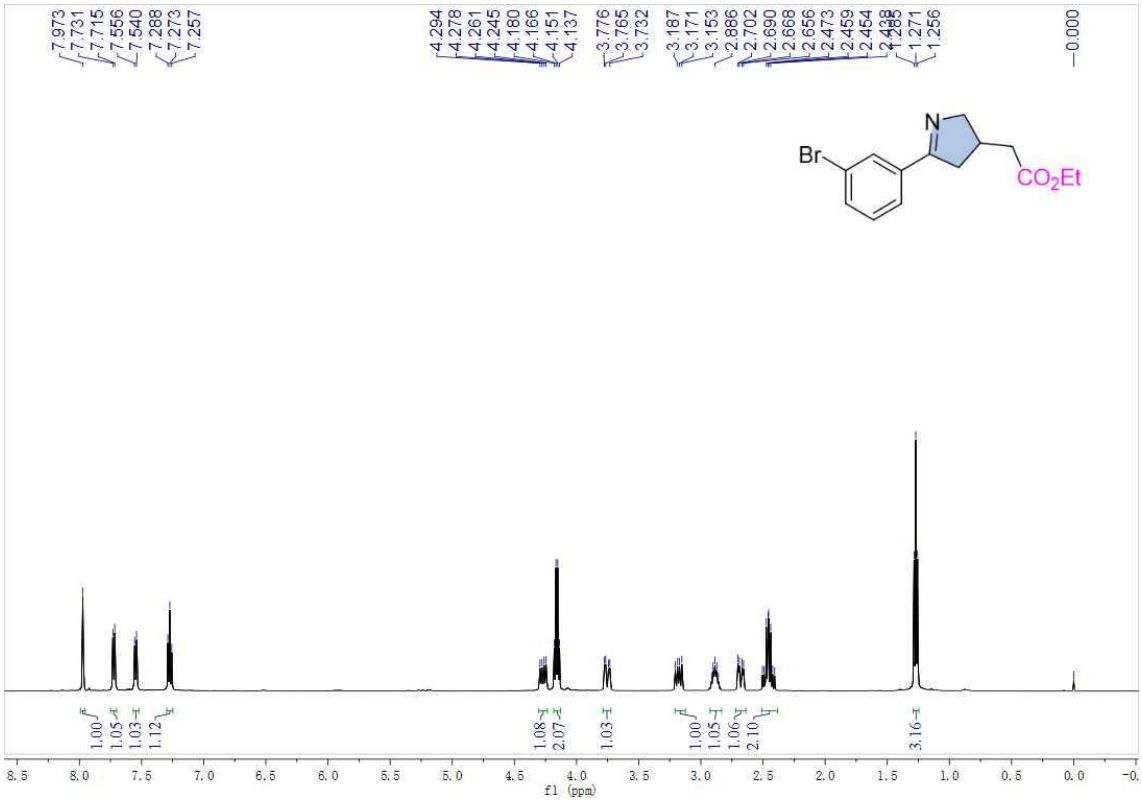
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 2h



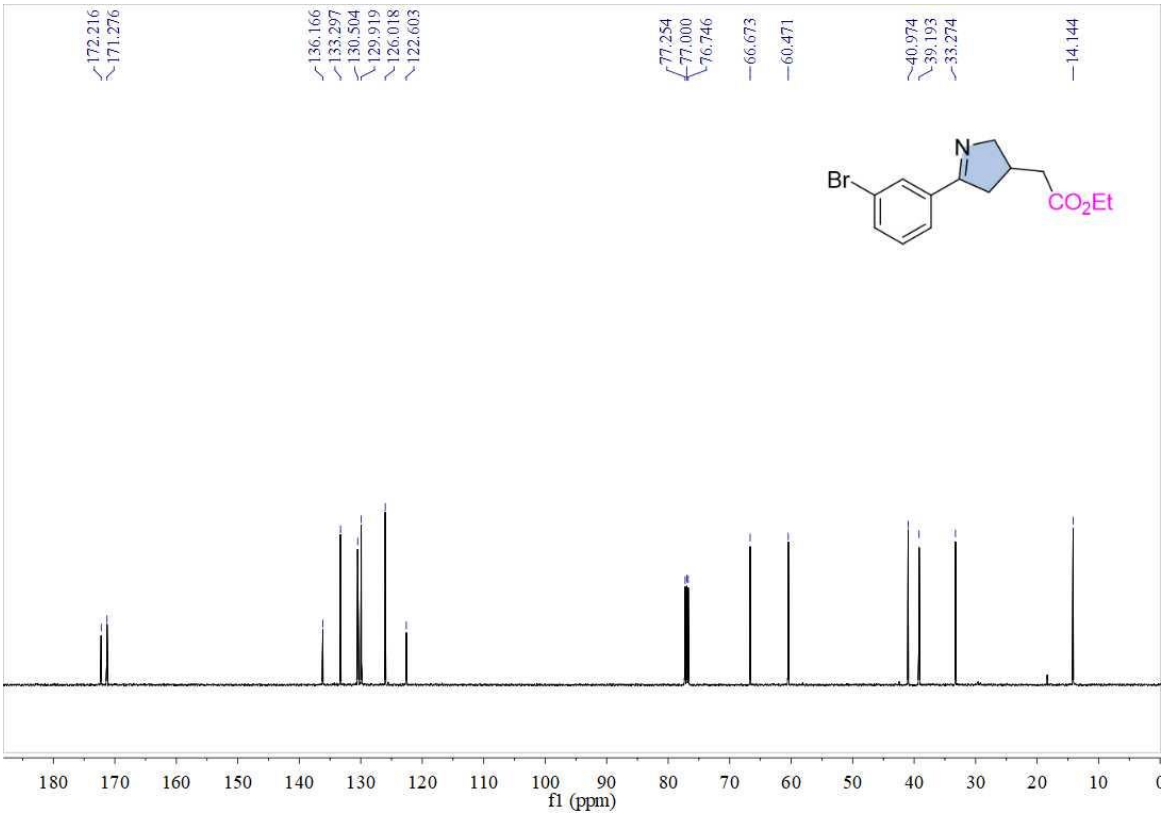
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2h



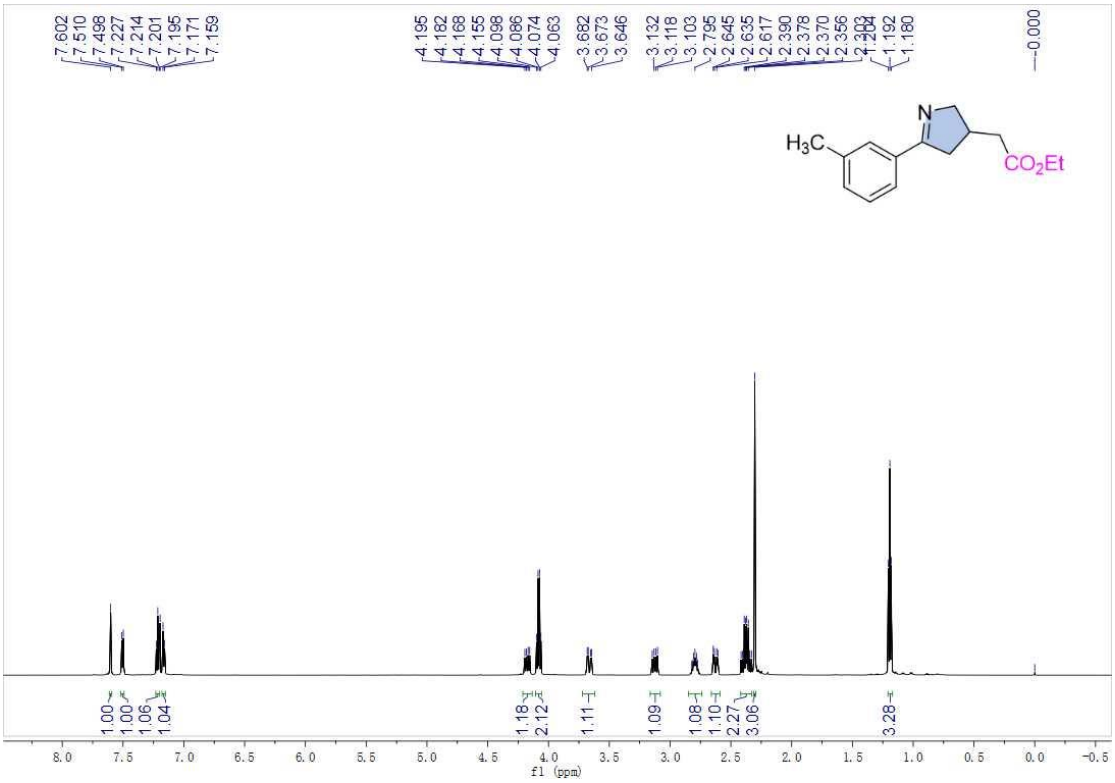
^{1}H spectrum (500 MHz, $CDCl_3$) of compound 2i



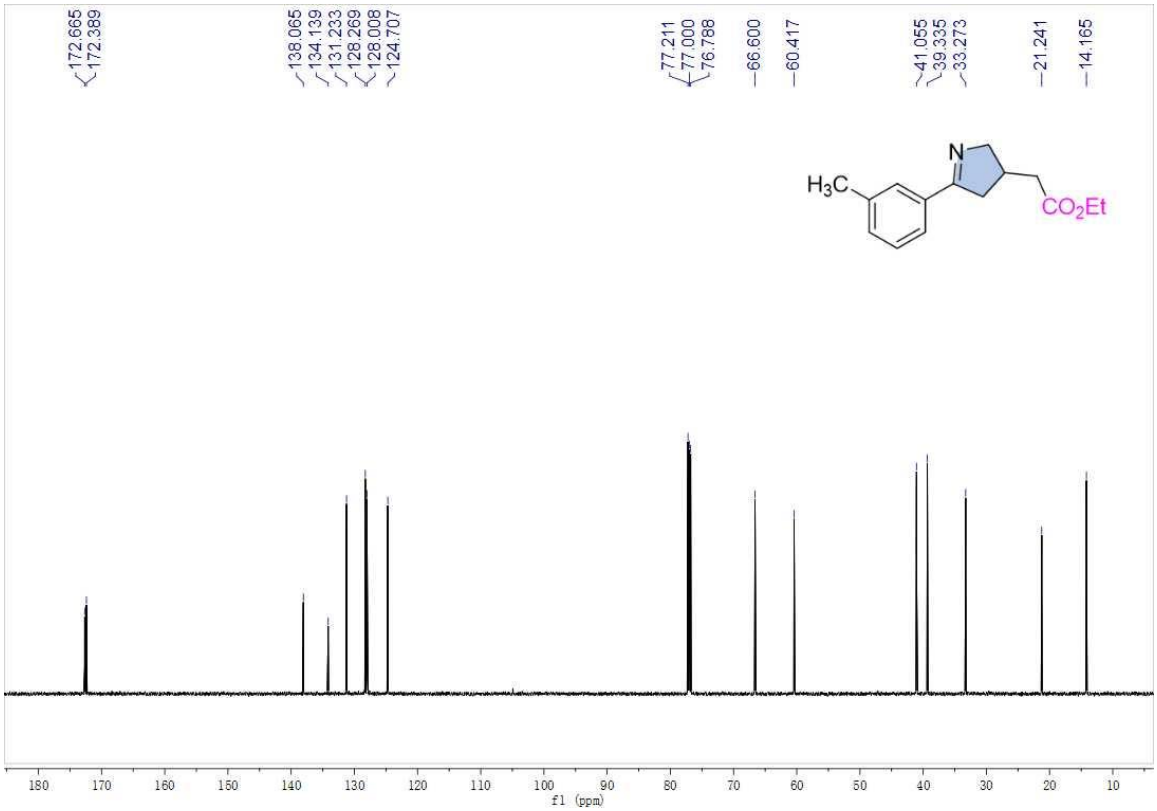
^{13}C spectrum (125 MHz, $CDCl_3$) of compound 2i



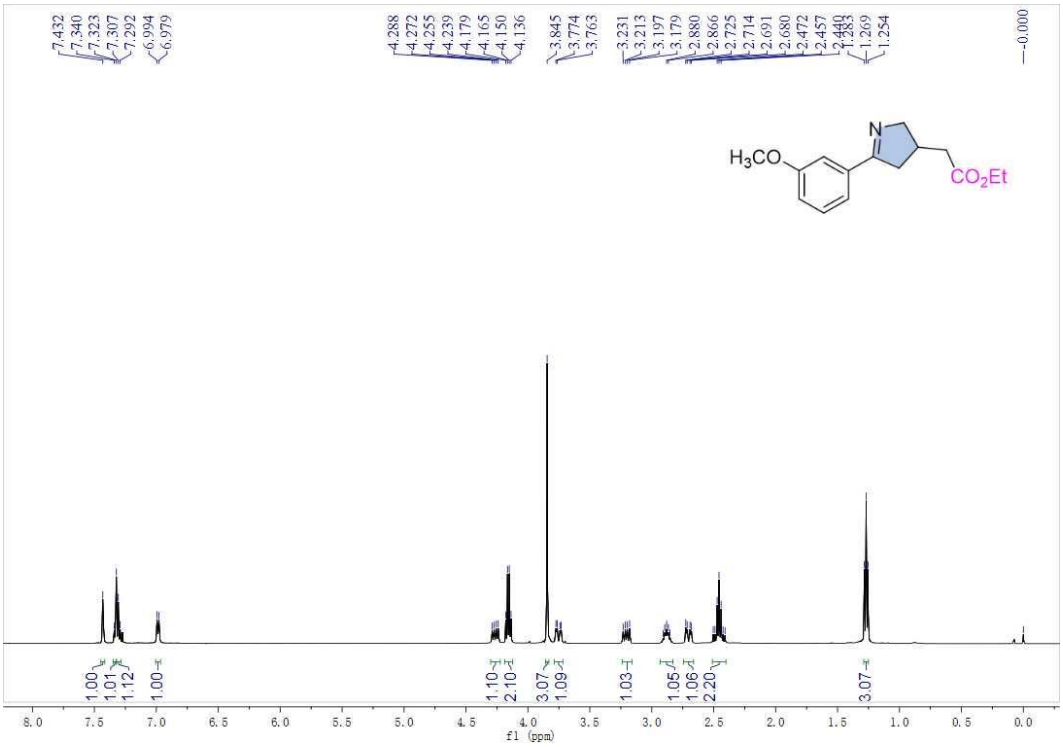
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 2j



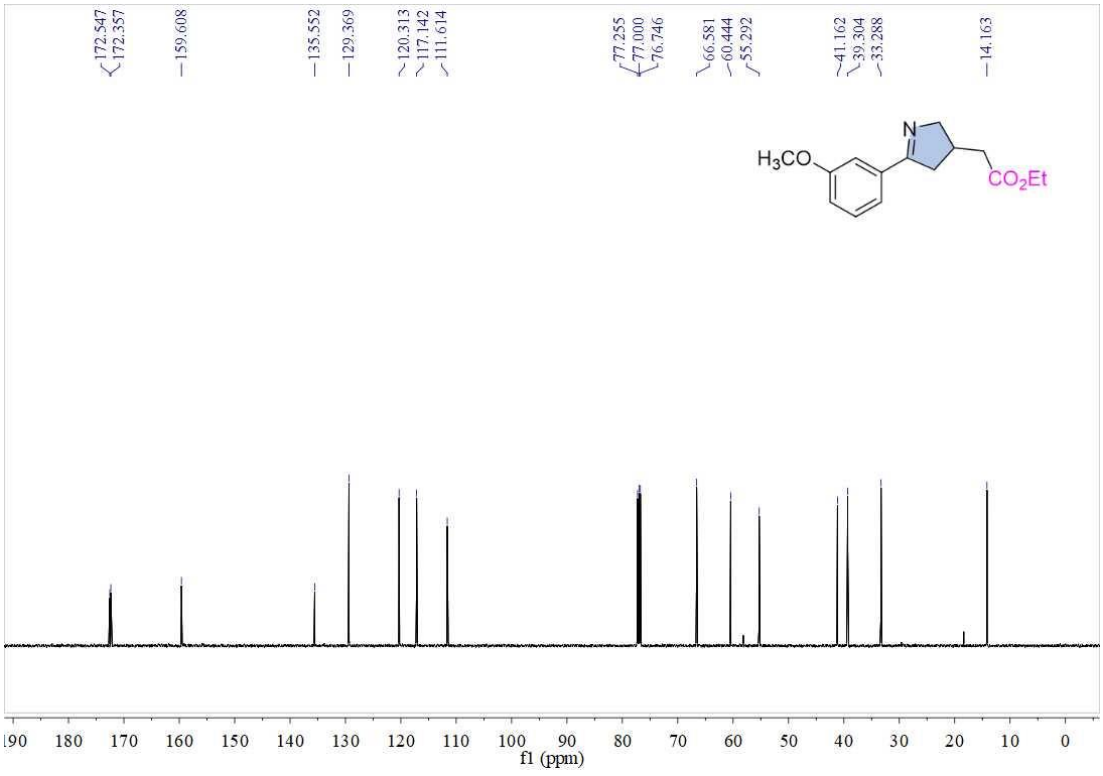
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2j



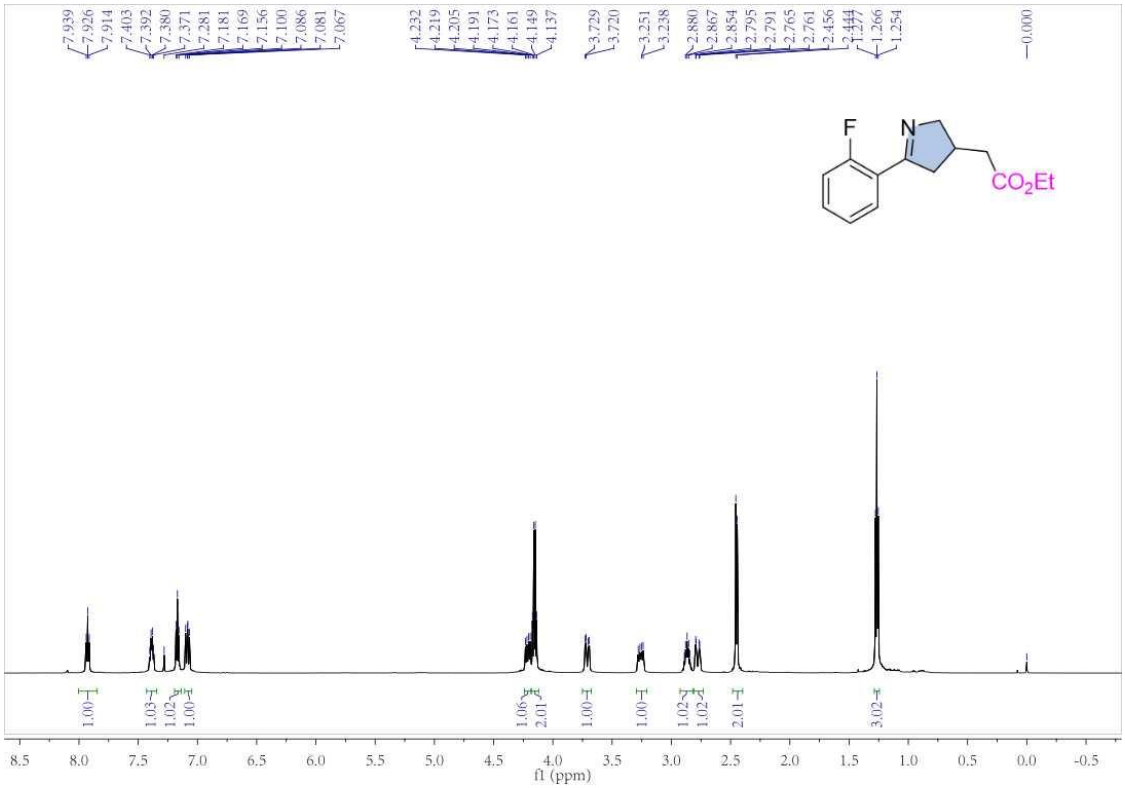
^{1}H spectrum (500 MHz, $CDCl_3$) of compound 2k



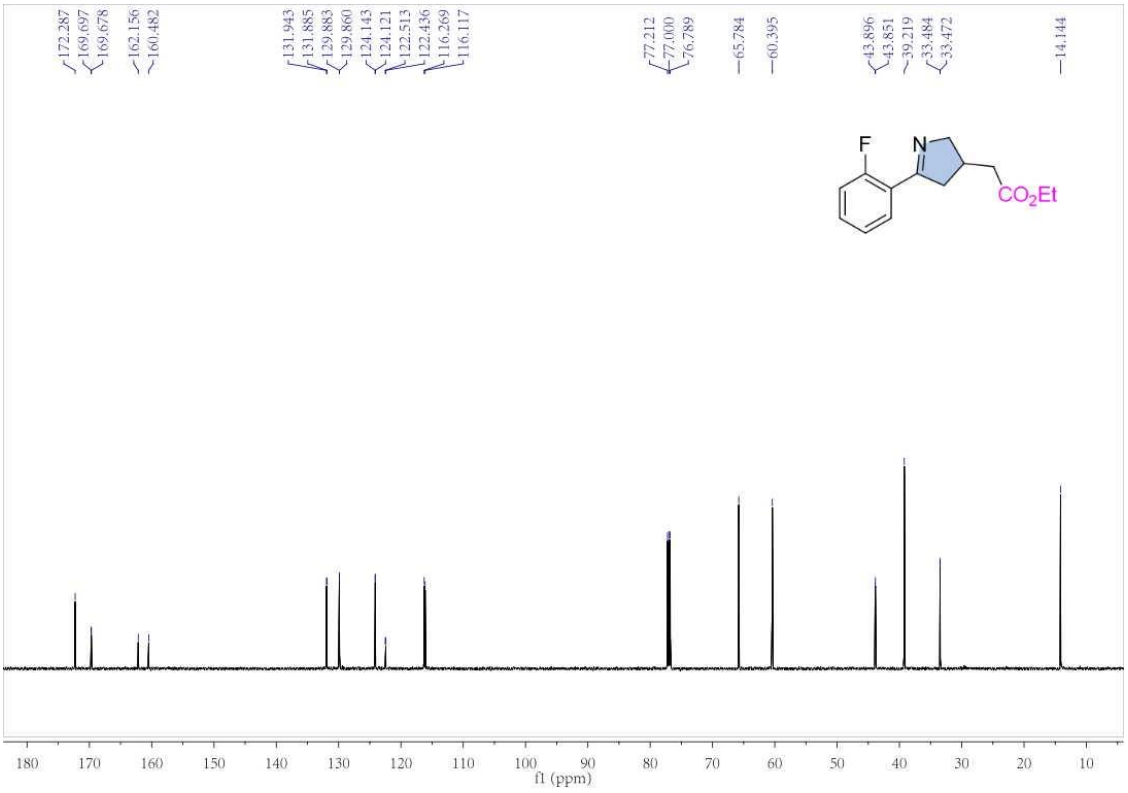
^{13}C spectrum (125 MHz, $CDCl_3$) of compound 2k



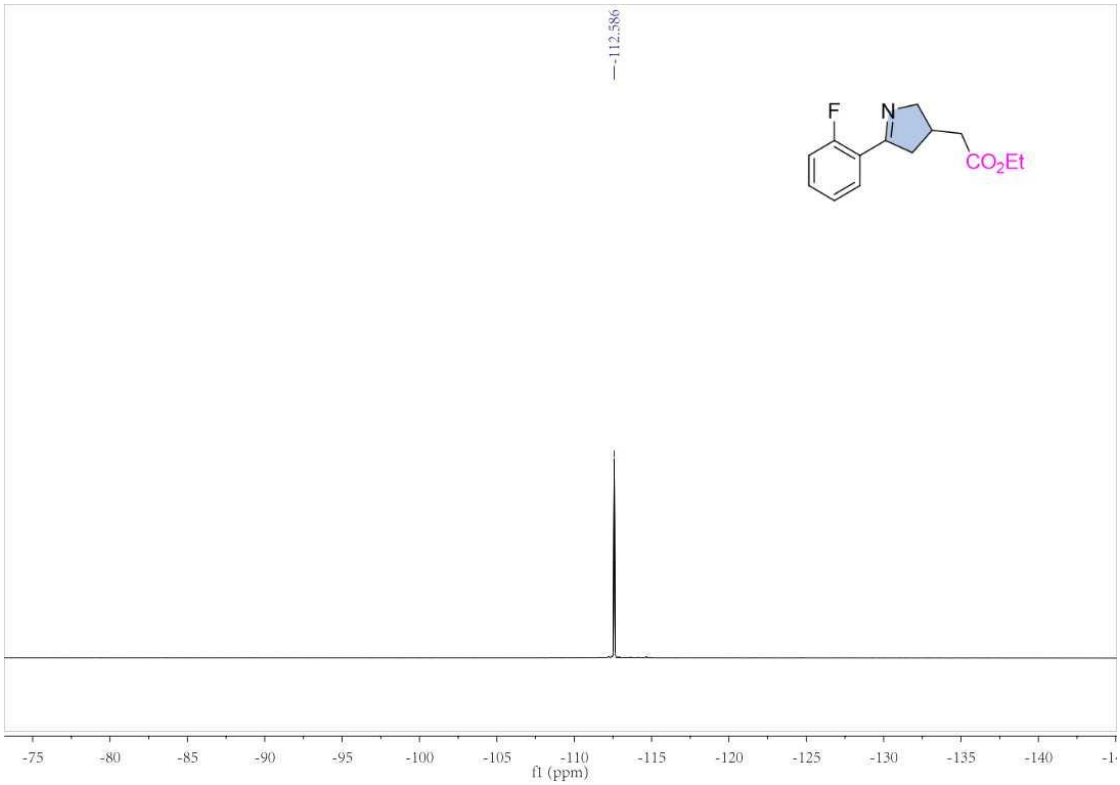
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 2l



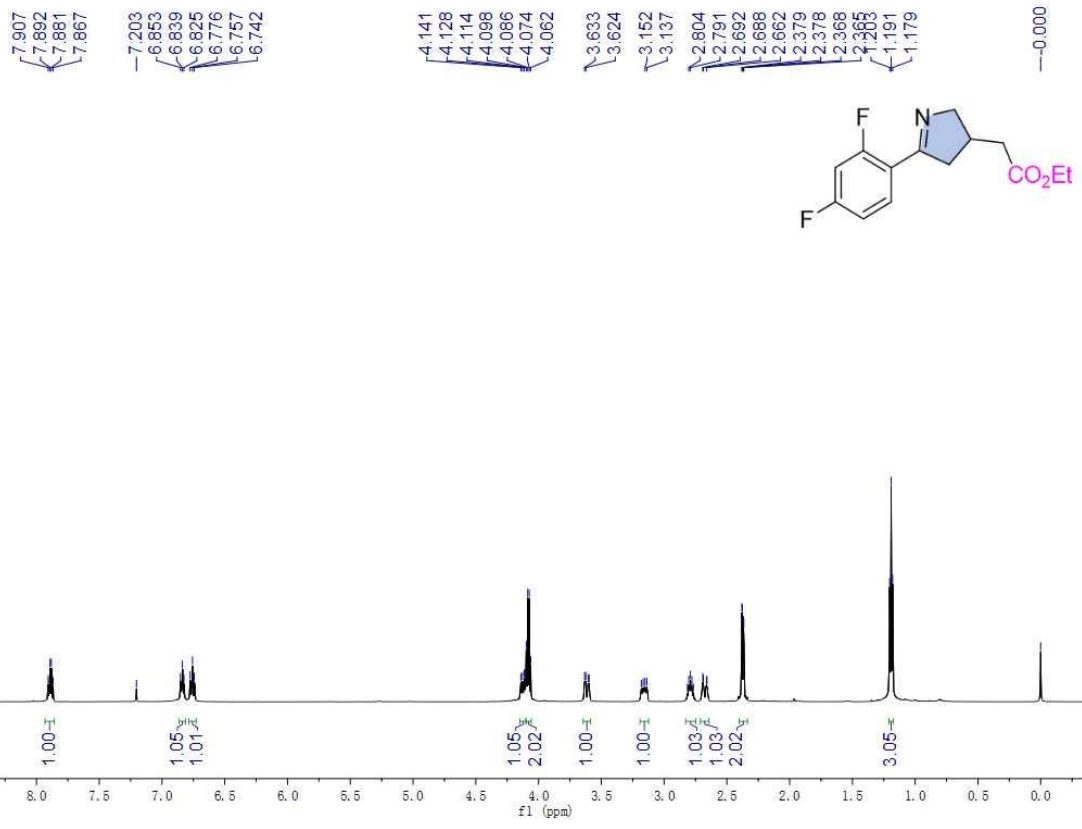
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2l



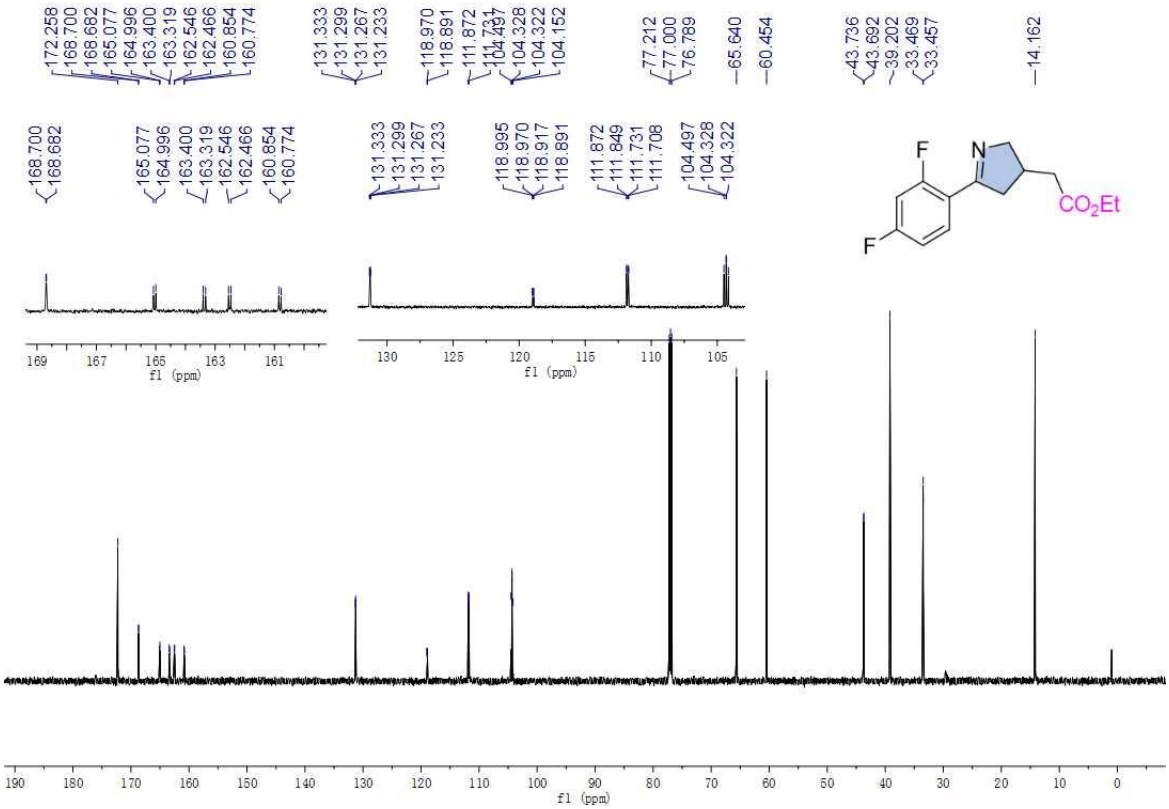
^{19}F spectrum (565 MHz, $CDCl_3$) of compound 2l



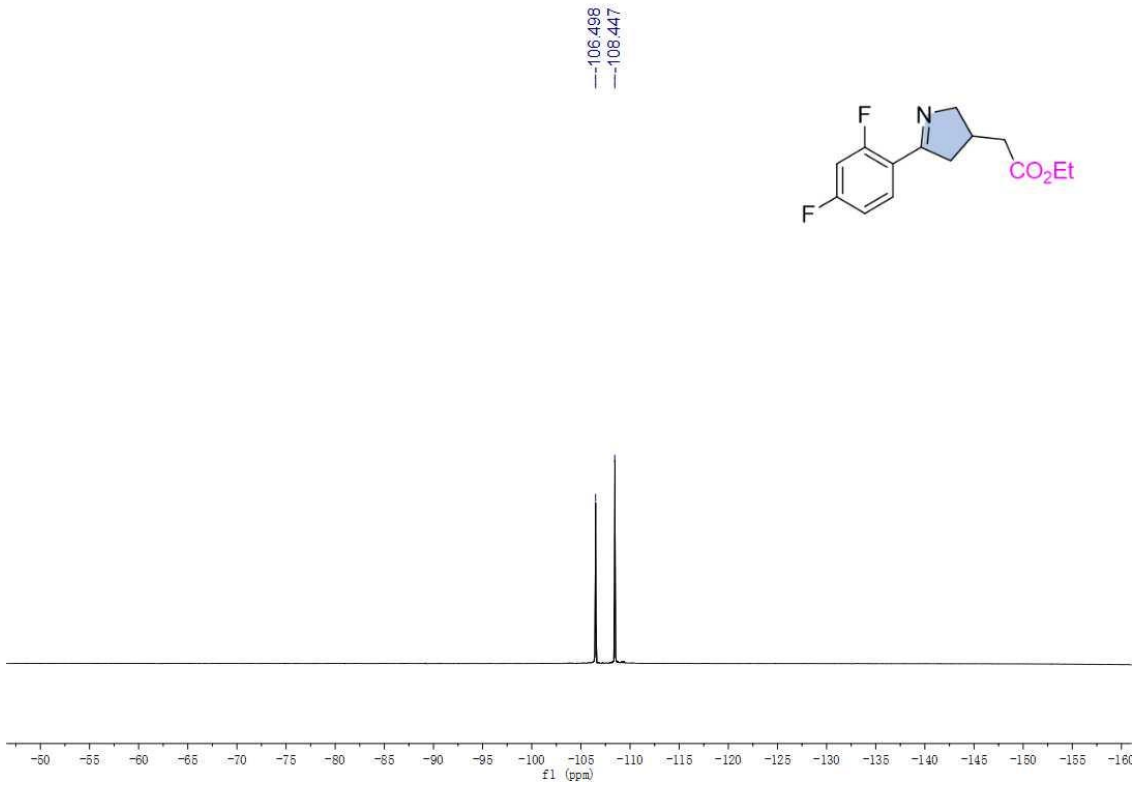
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 2m



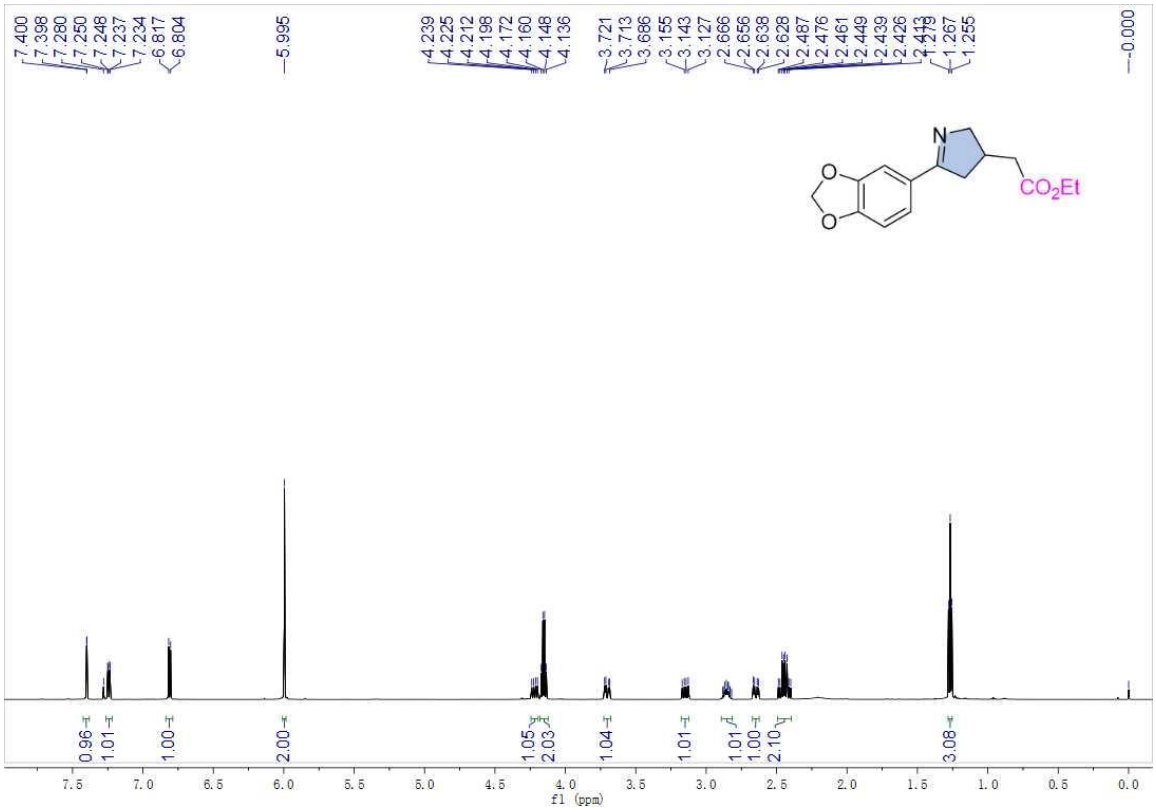
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2m



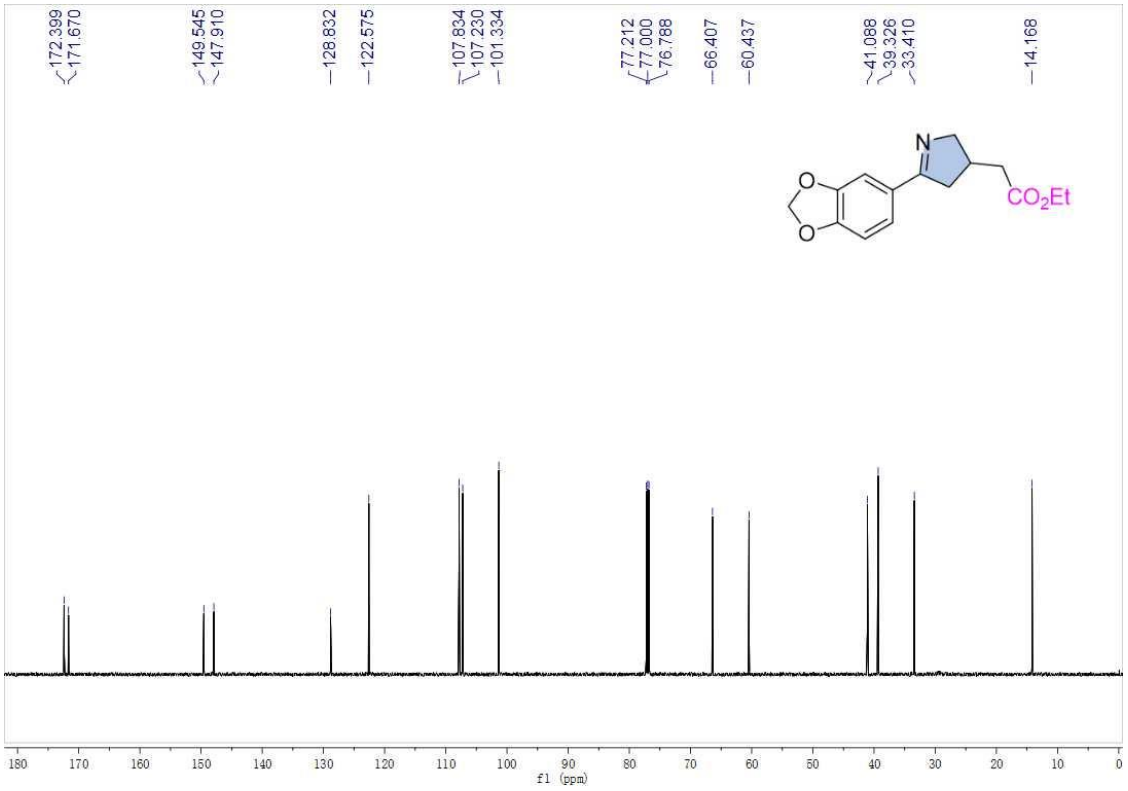
^{19}F spectrum (565 MHz, $CDCl_3$) of compound 2m



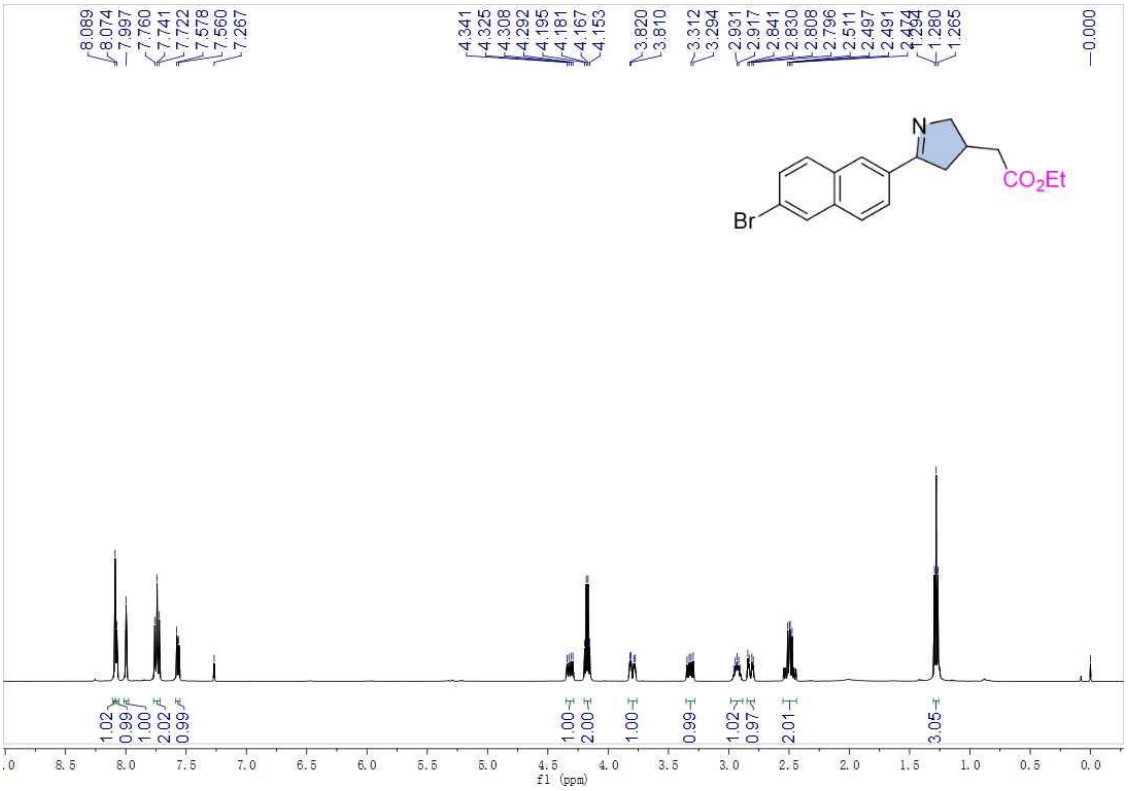
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 2n



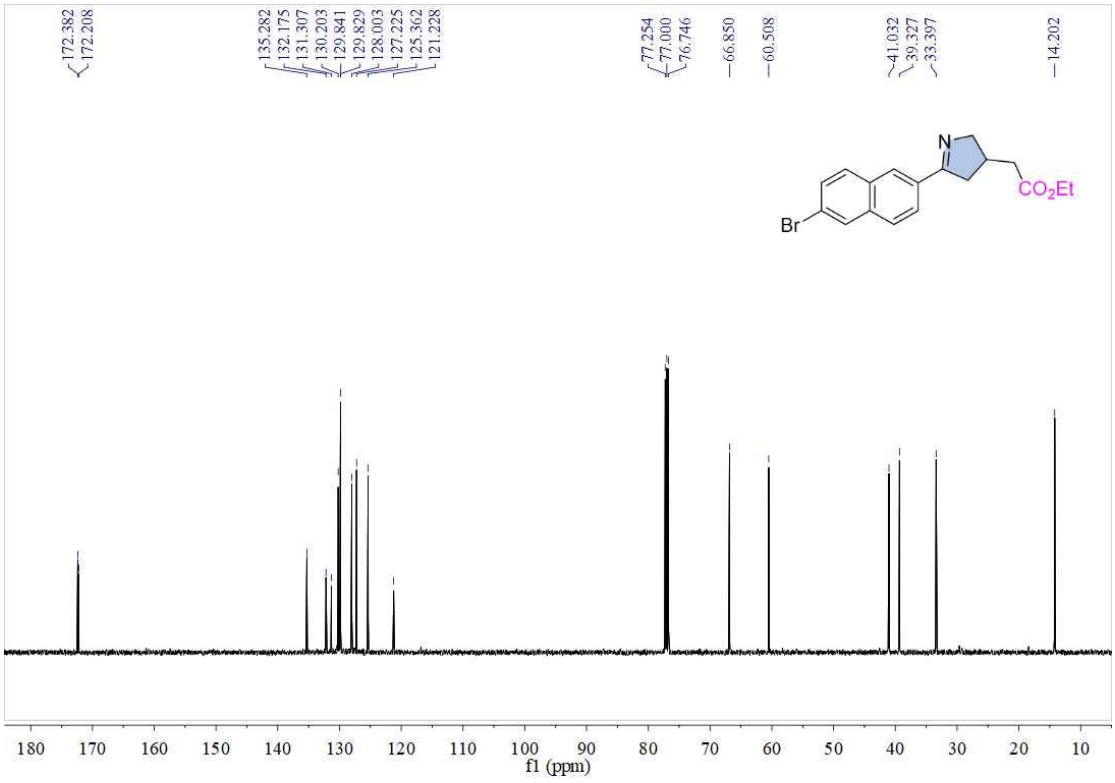
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2n



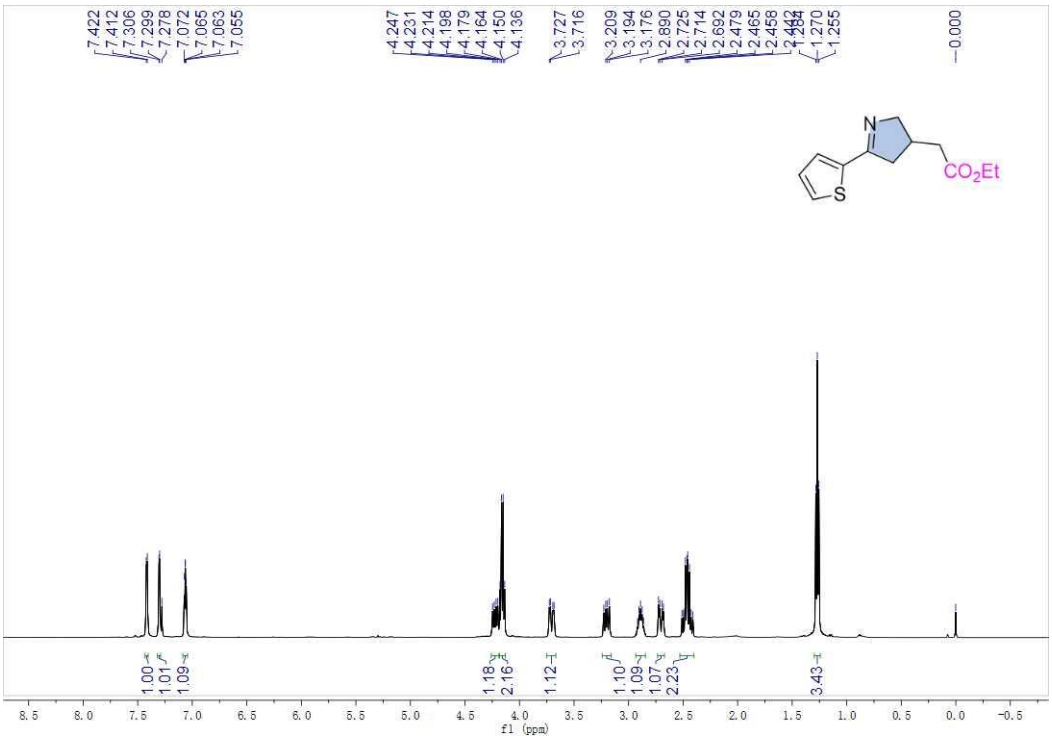
^{1}H spectrum (500 MHz, $CDCl_3$) of compound 2o



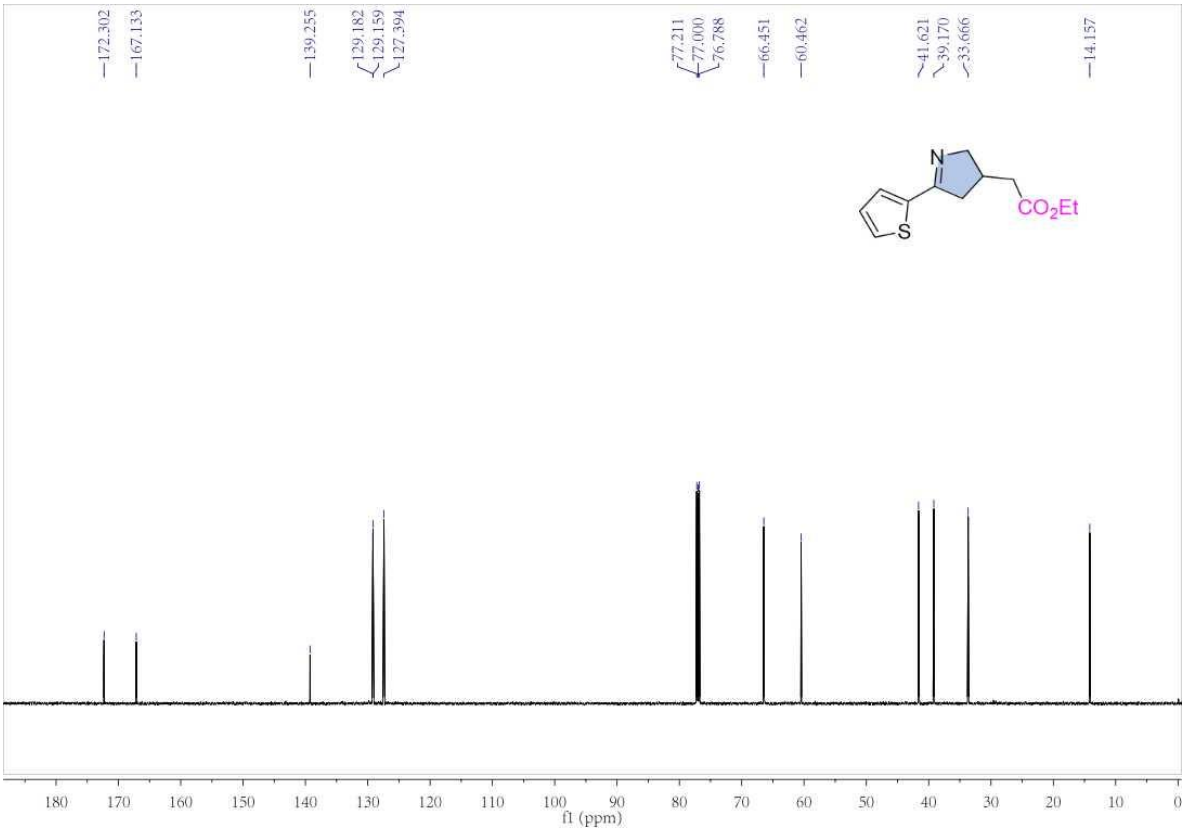
^{13}C spectrum (125 MHz, $CDCl_3$) of compound 2o



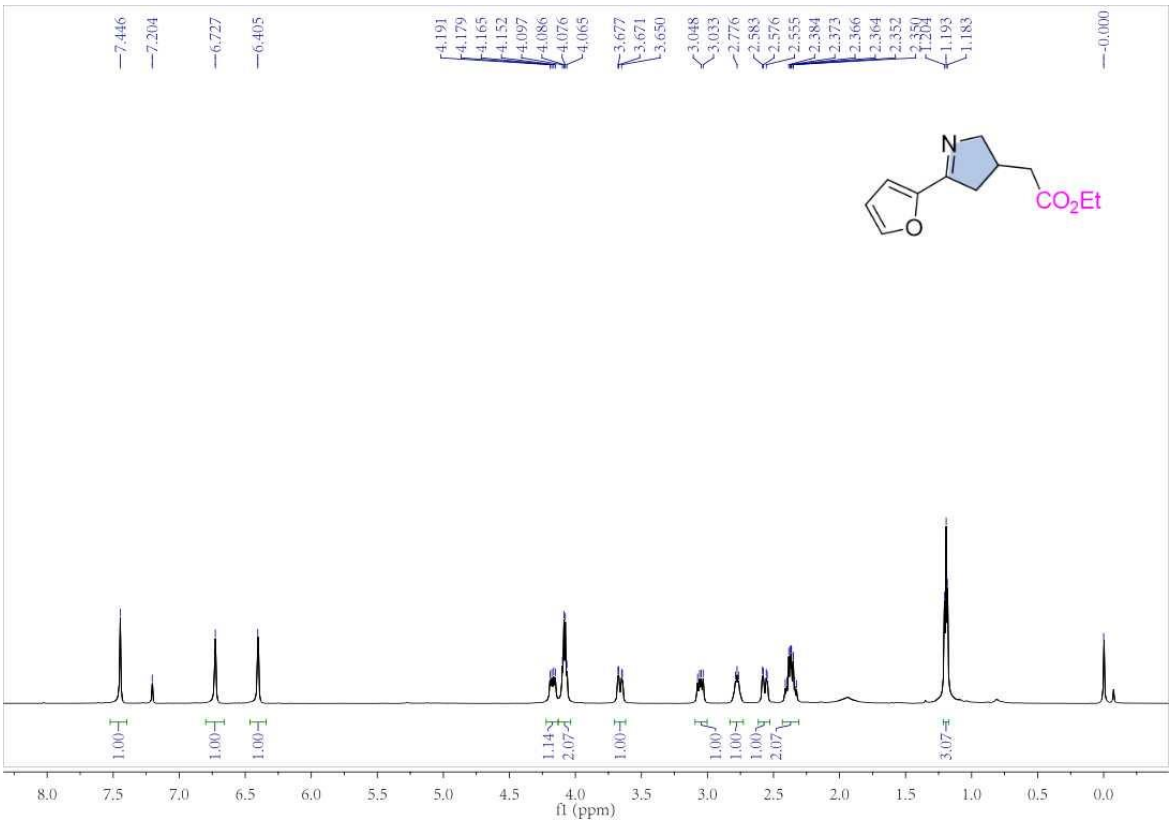
^{1}H spectrum (500 MHz, $CDCl_3$) of compound 2p



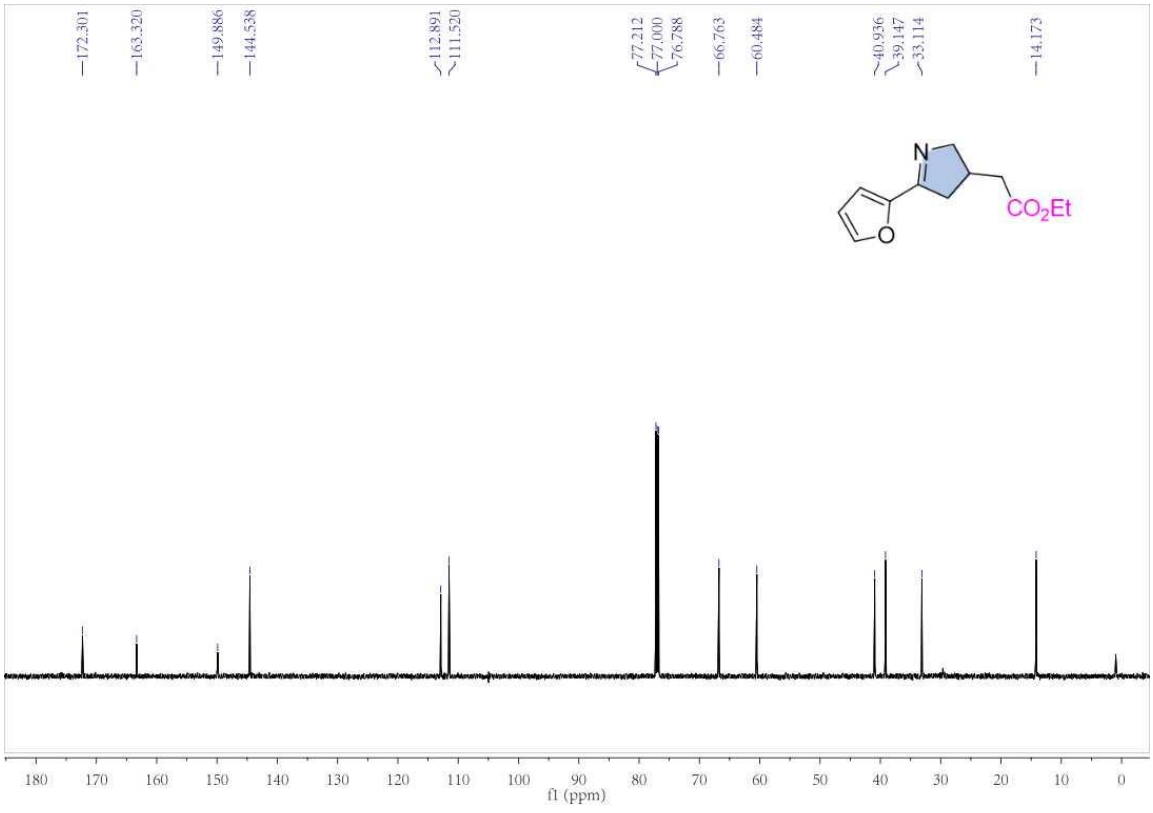
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2p



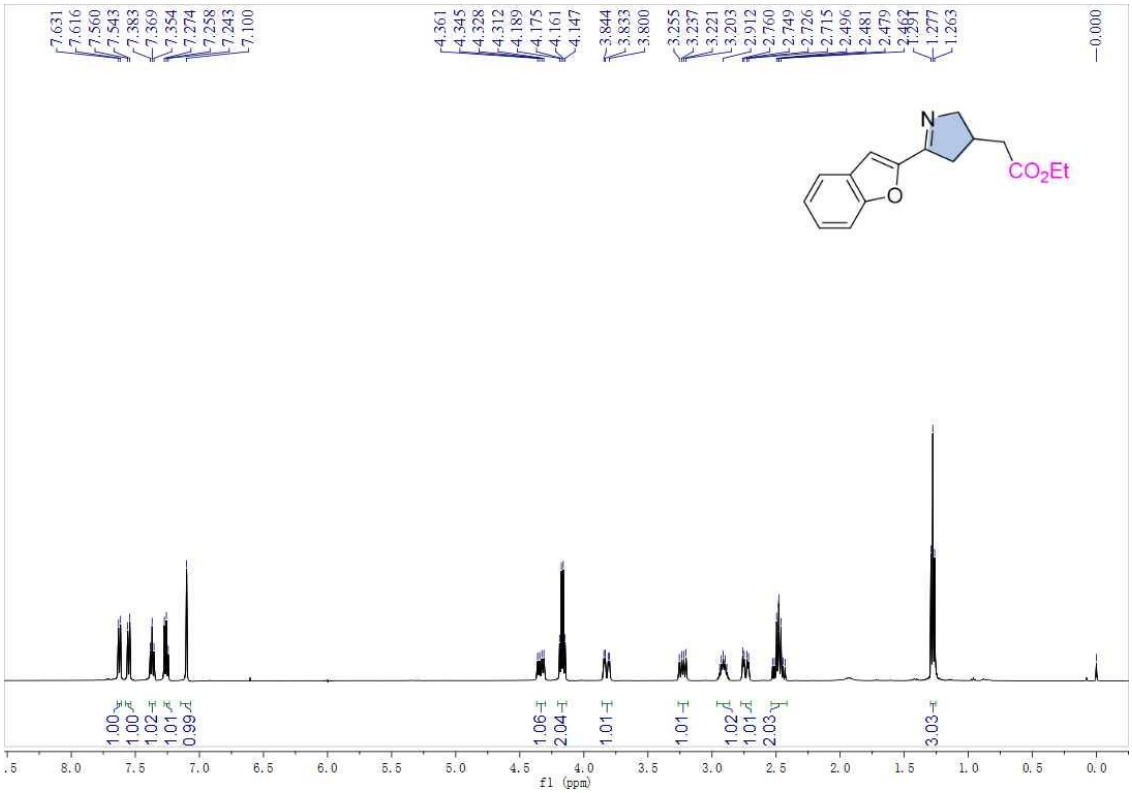
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 2q



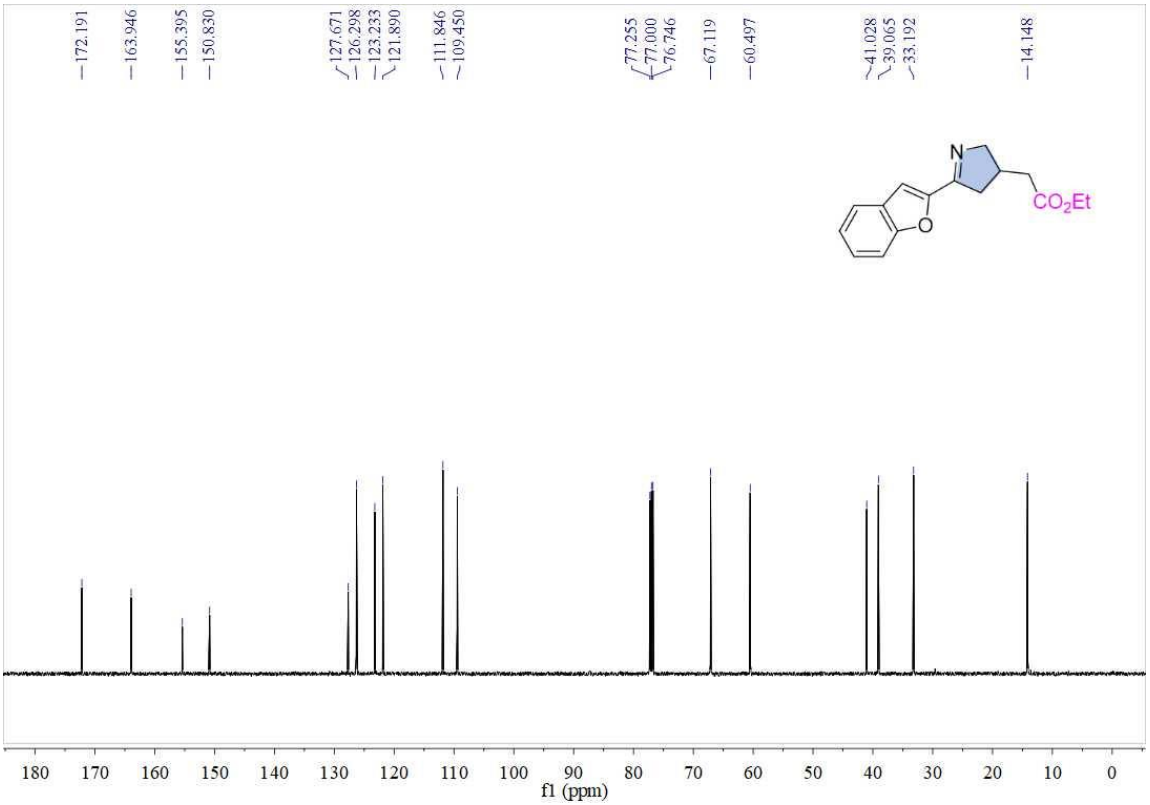
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2q



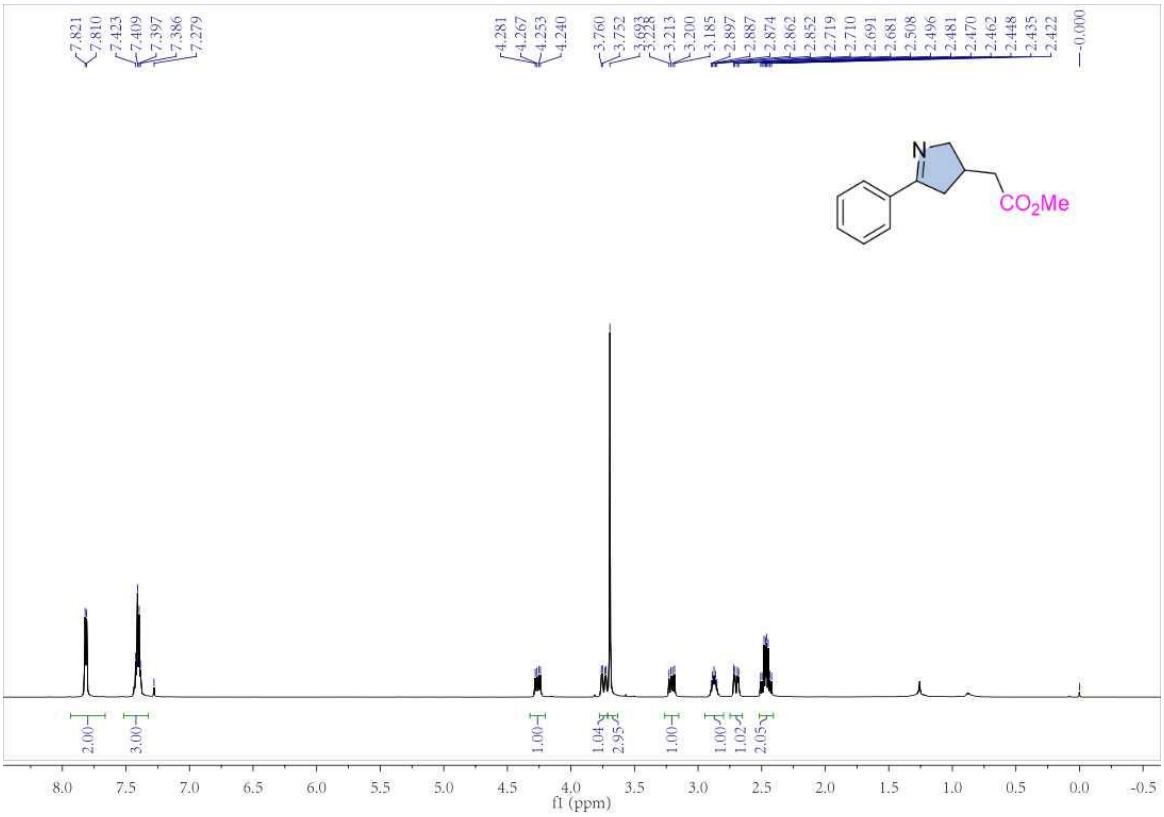
^{1}H spectrum (500 MHz, $CDCl_3$) of compound 2r



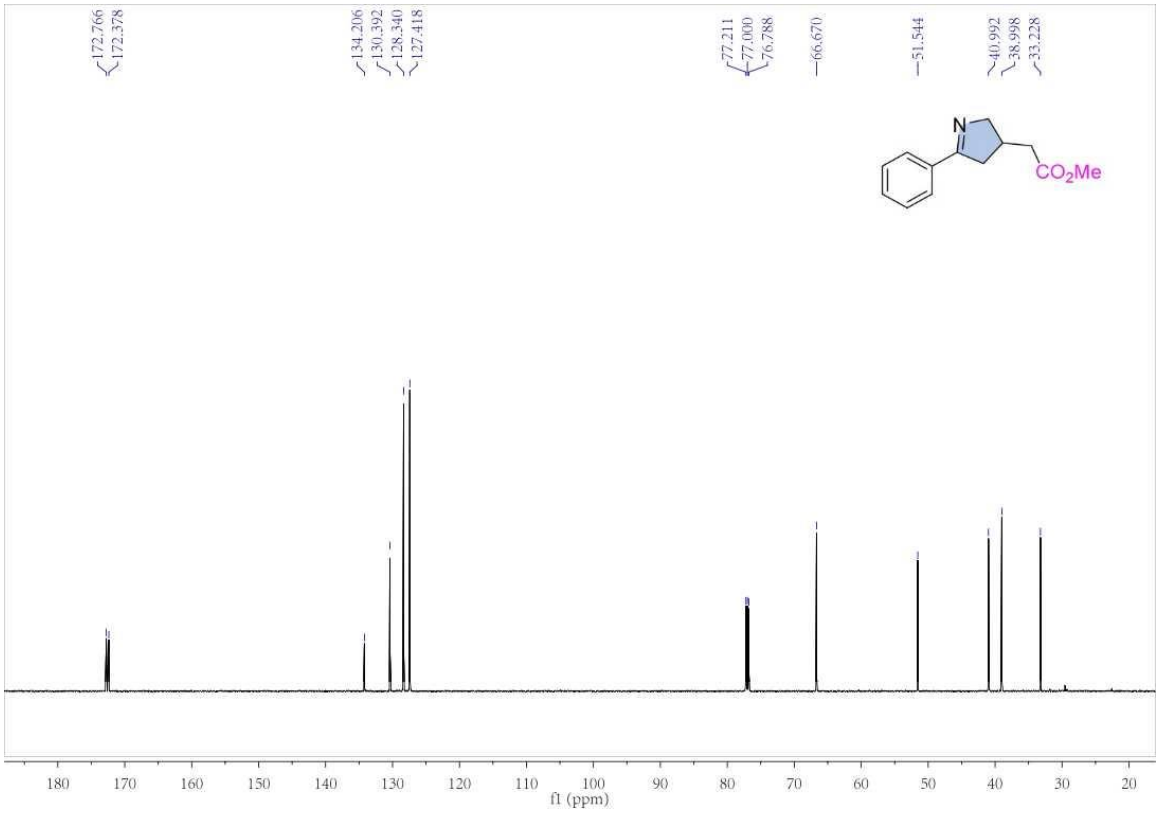
^{13}C spectrum (125 MHz, $CDCl_3$) of compound 2r



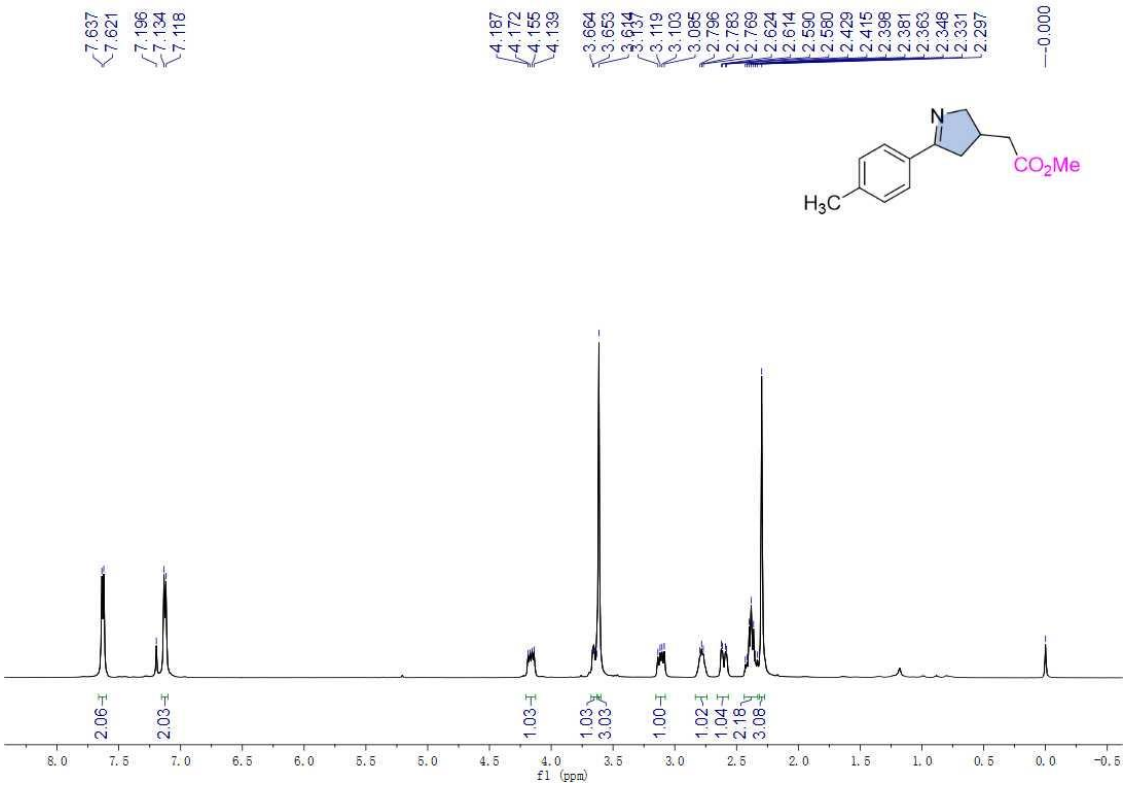
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 2s



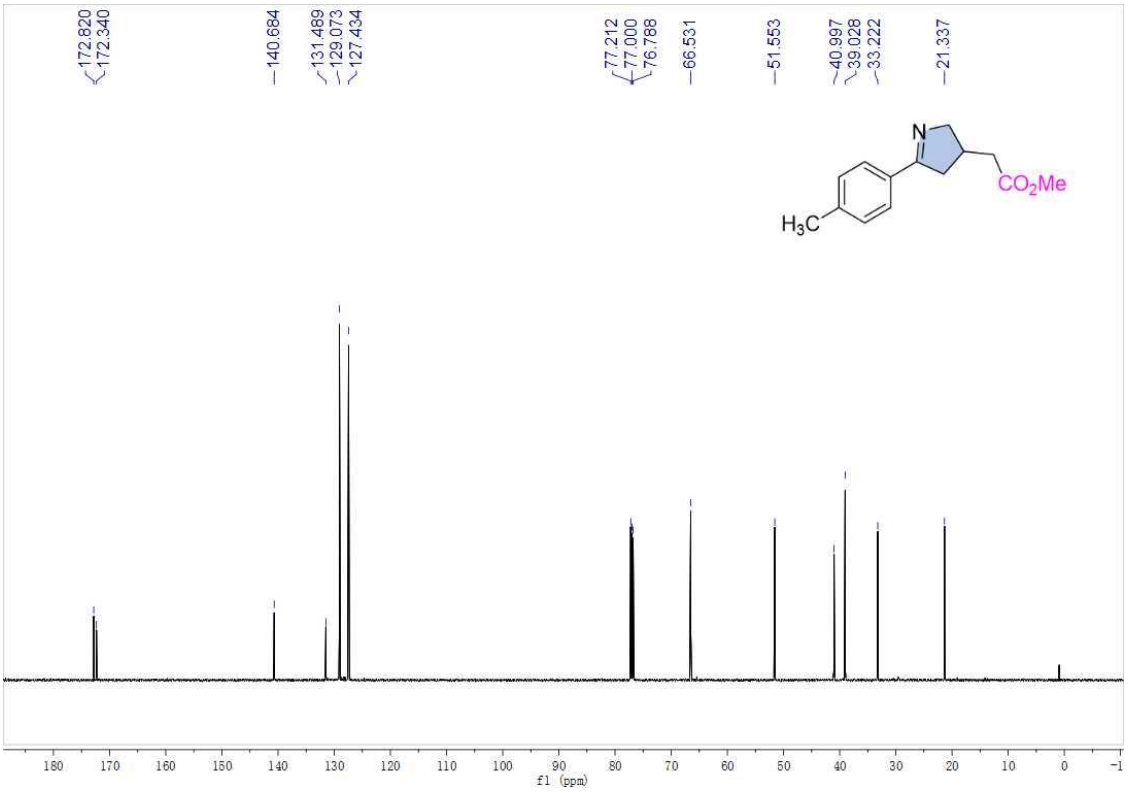
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2s



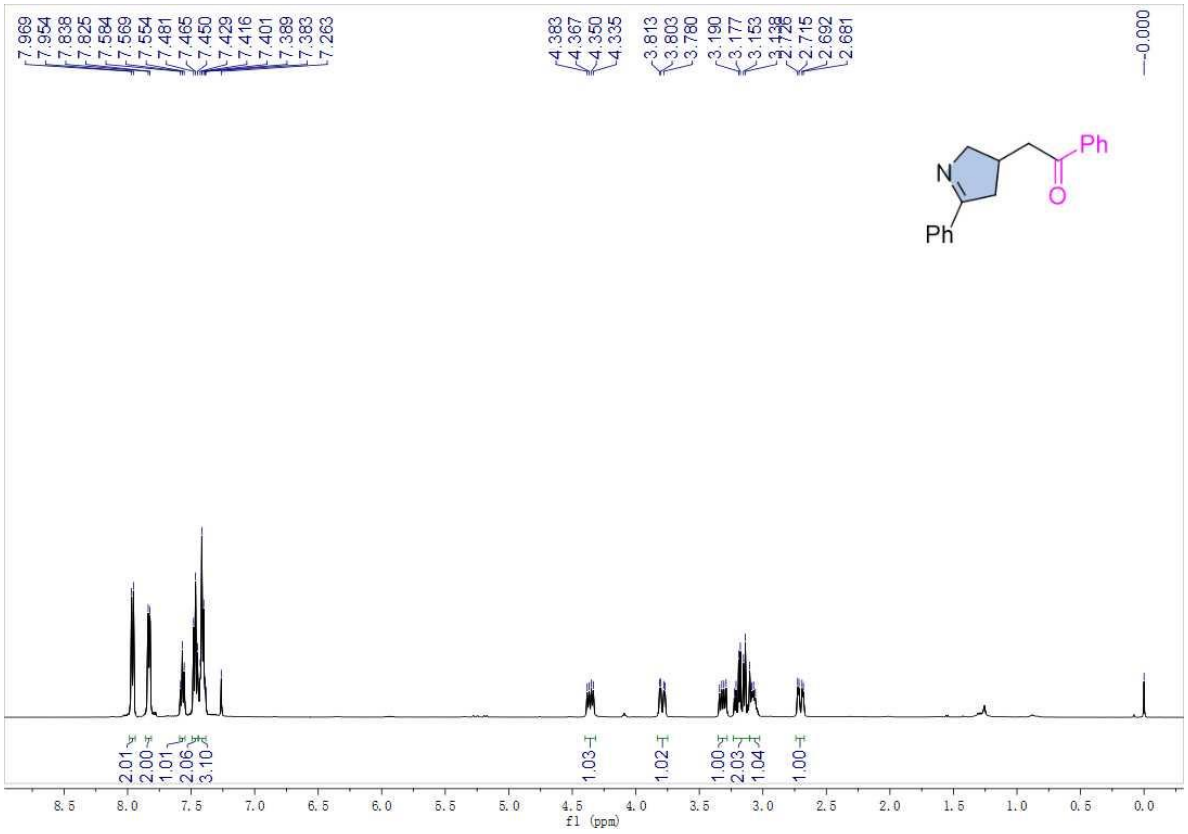
^{1}H spectrum (500 MHz, $CDCl_3$) of compound 2t



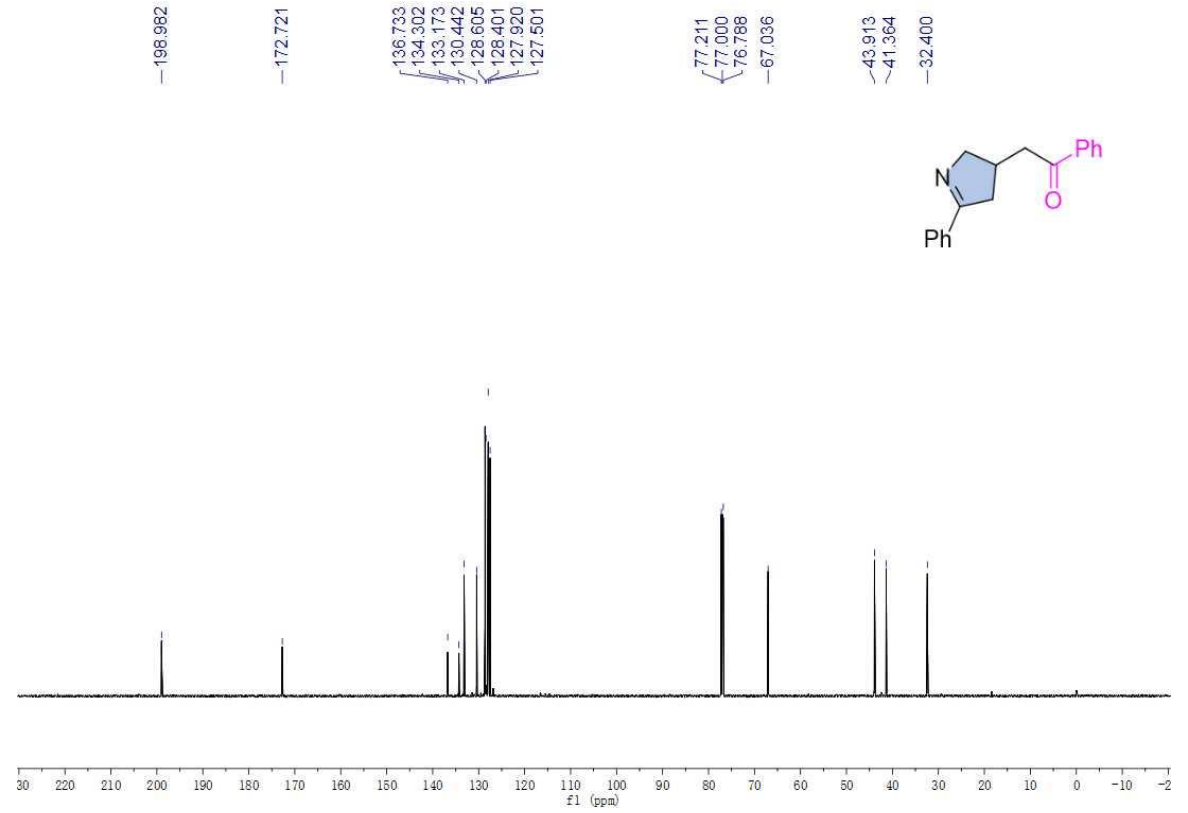
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2t



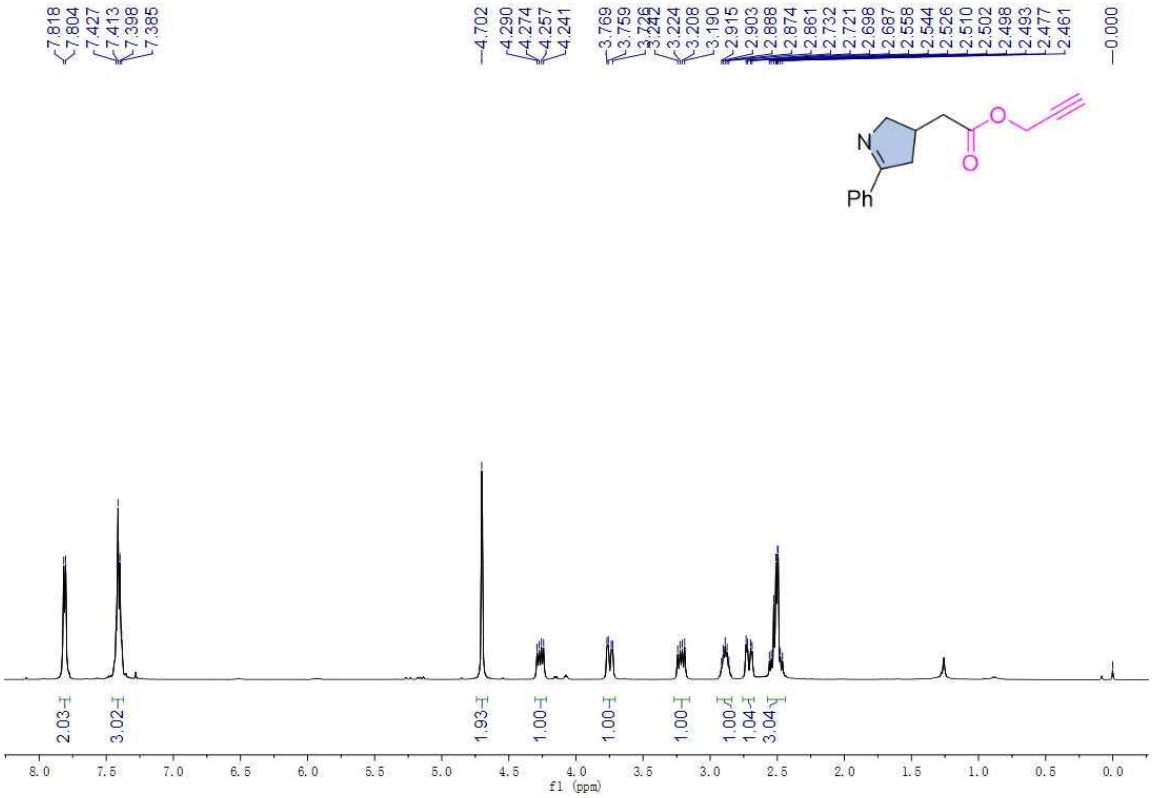
^{1}H spectrum (500 MHz, $CDCl_3$) of compound 2u



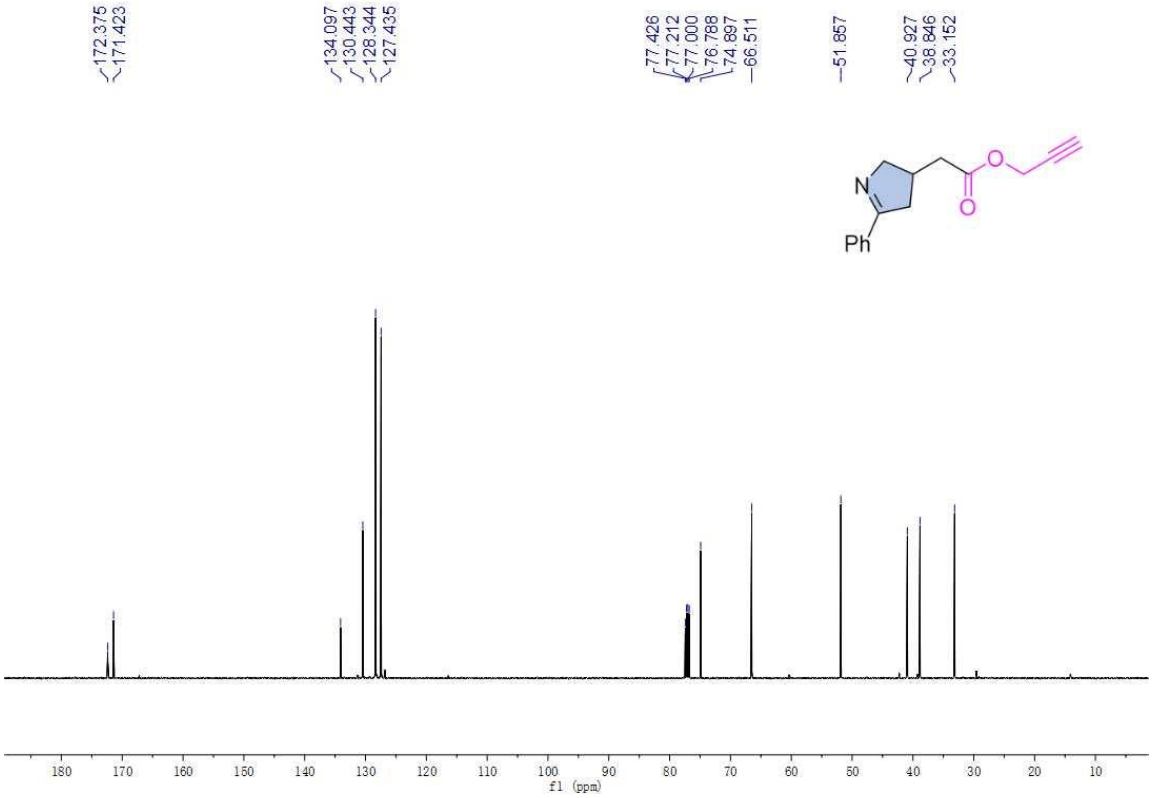
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2u



^{1}H spectrum (500 MHz, $CDCl_3$) of compound 2v

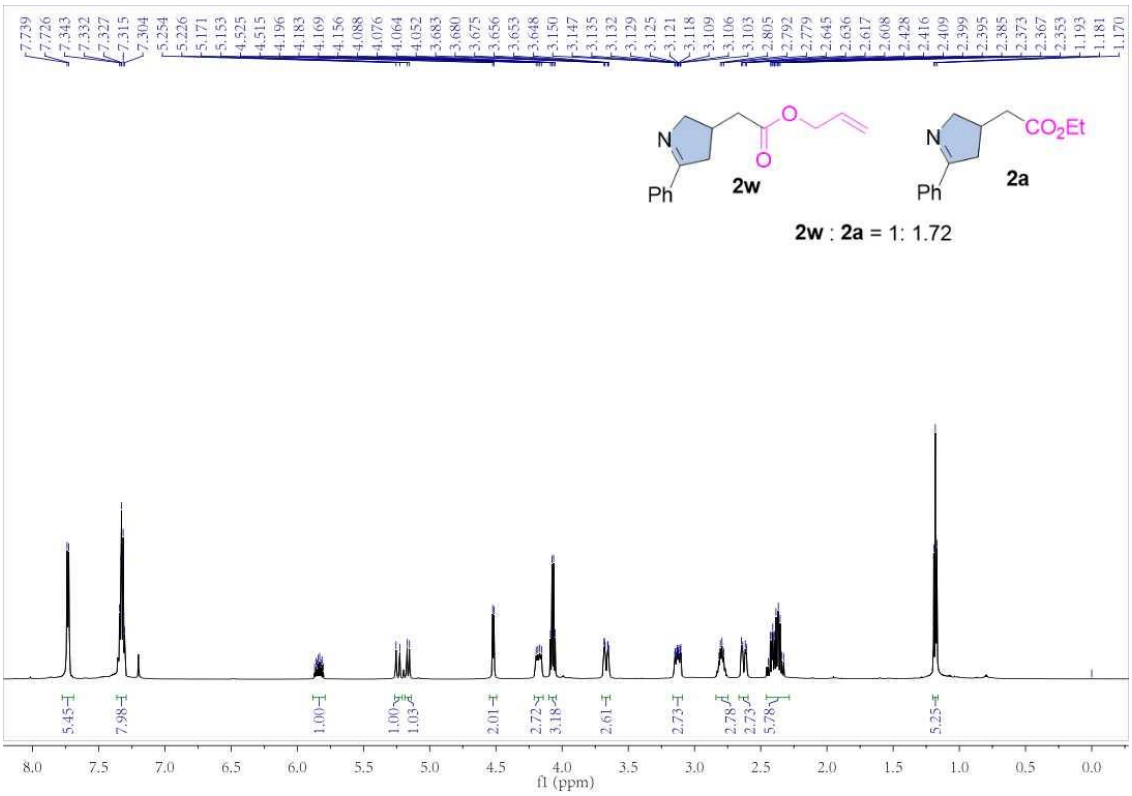


^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2v

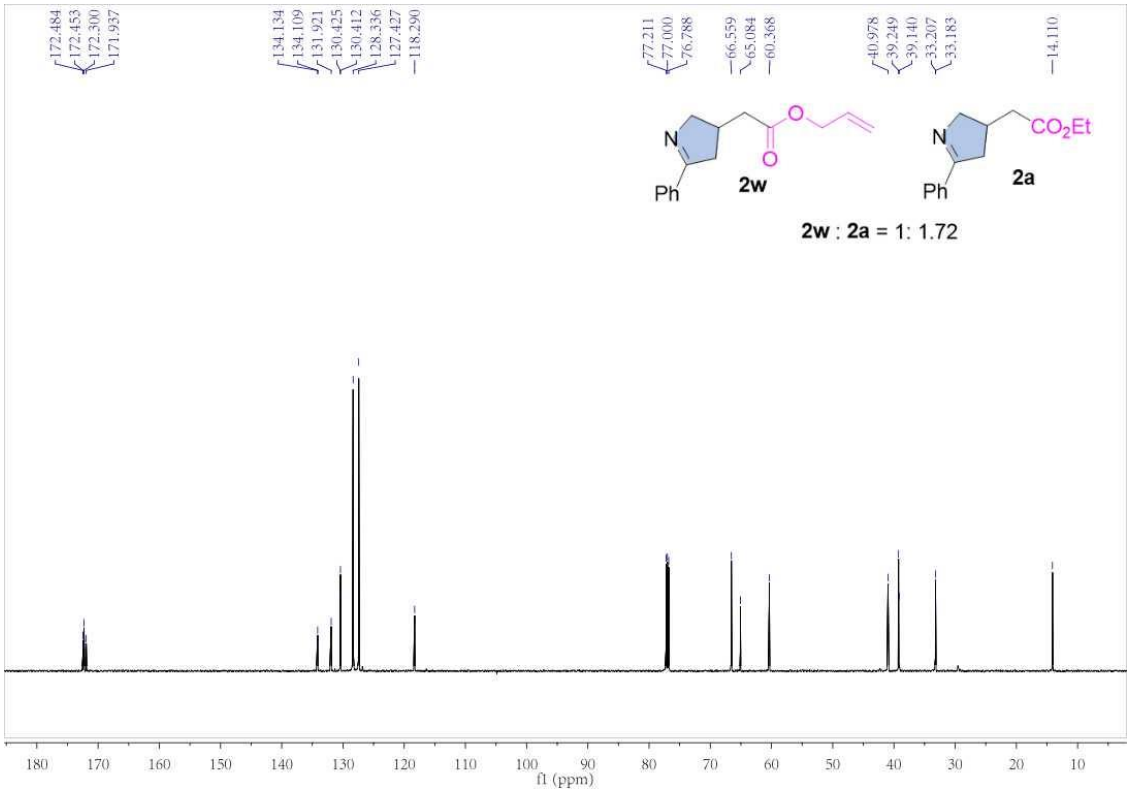


^{1}H spectrum (600 MHz, $CDCl_3$) of compound 2w and 2a

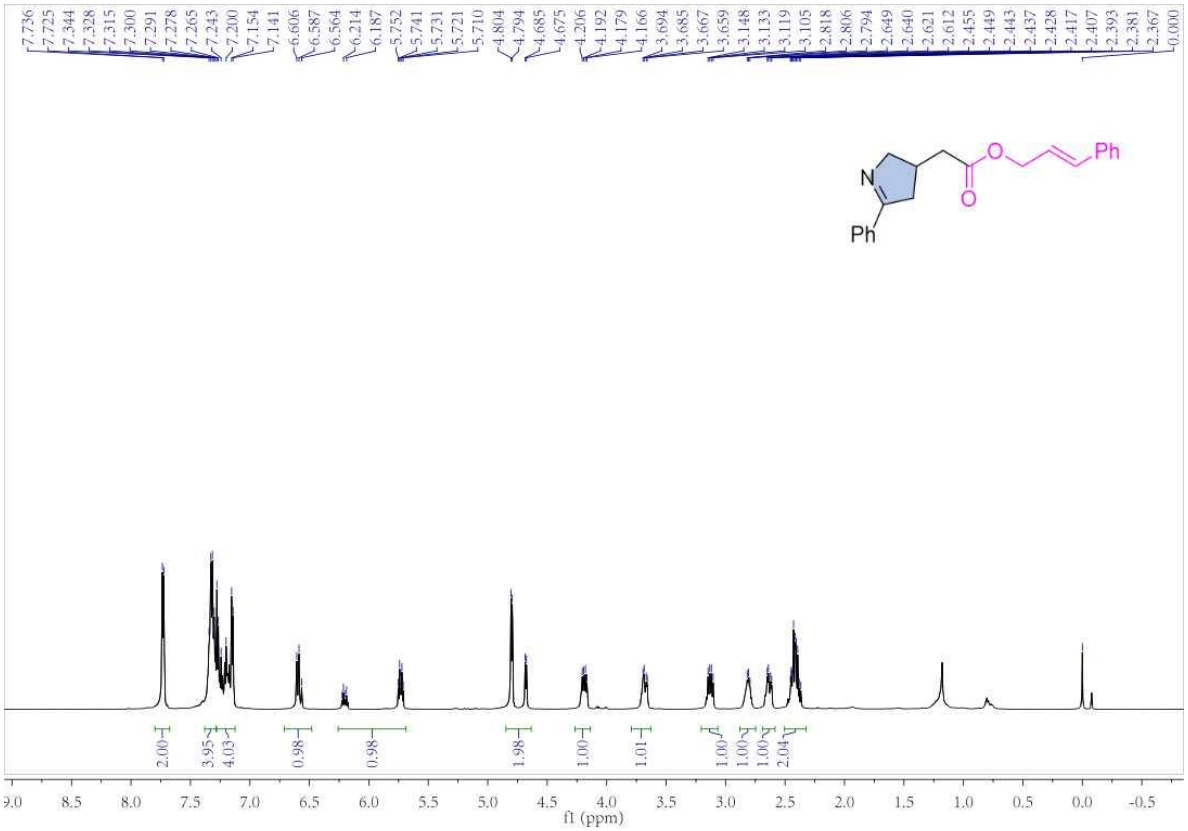
(The ratio of **2w**/**2a** is 1:1.72)



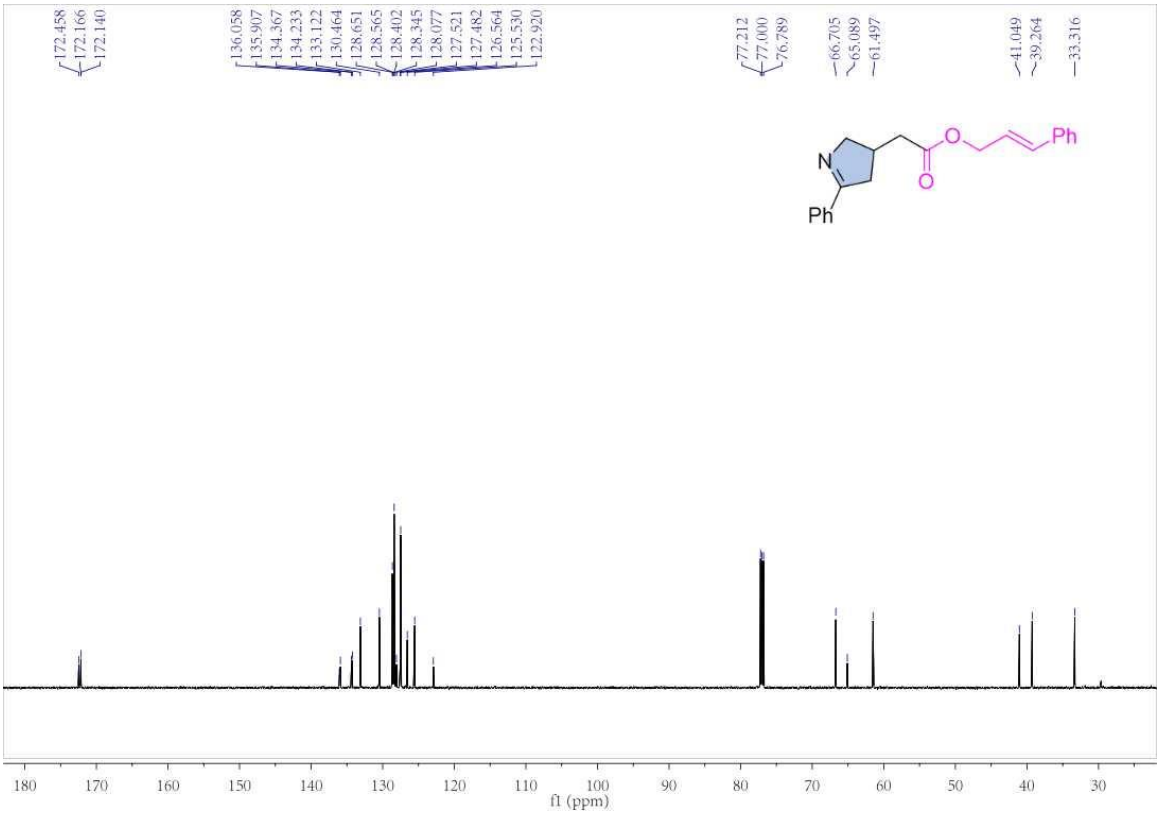
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2w and 2a



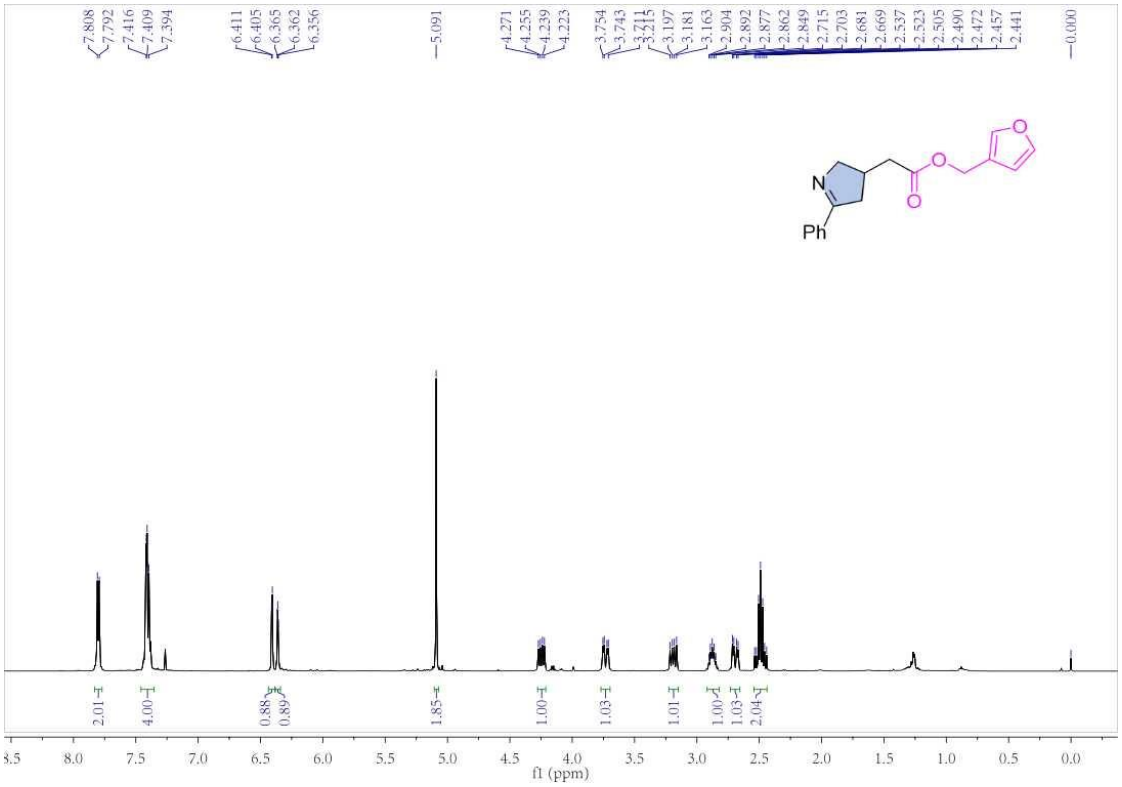
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 2x



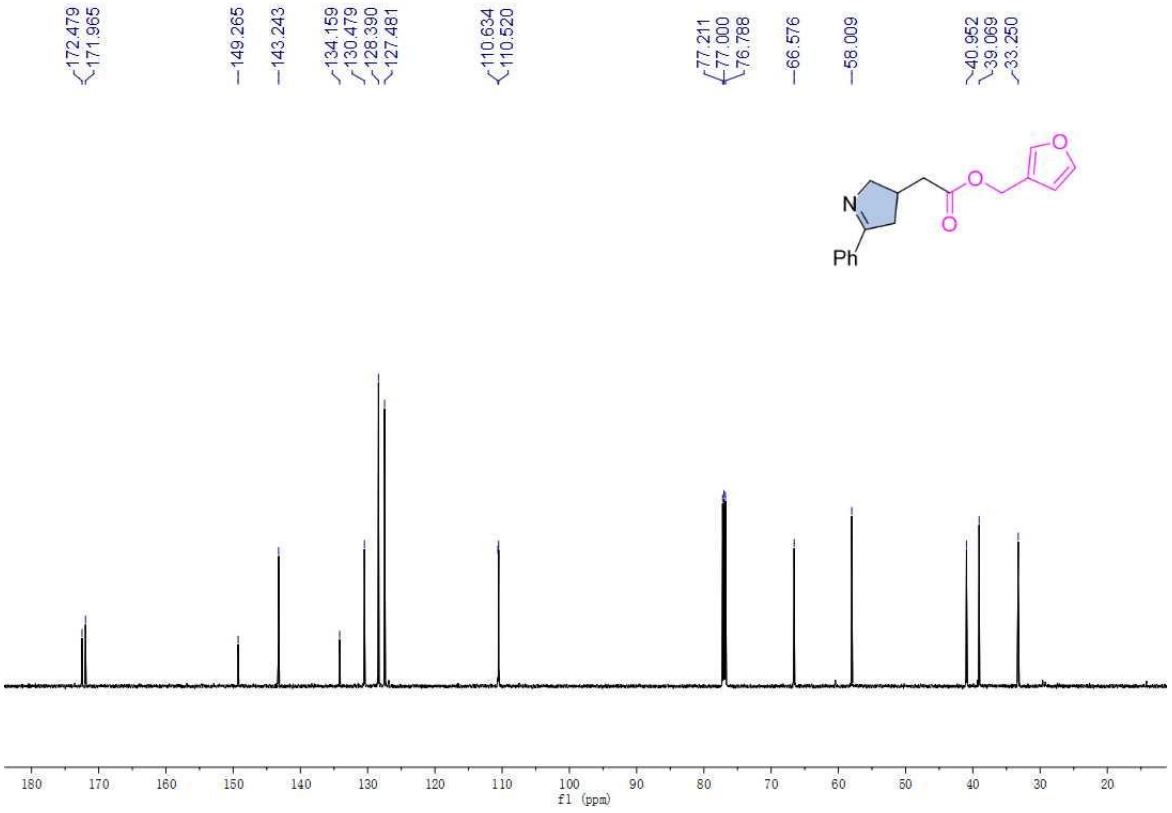
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2x



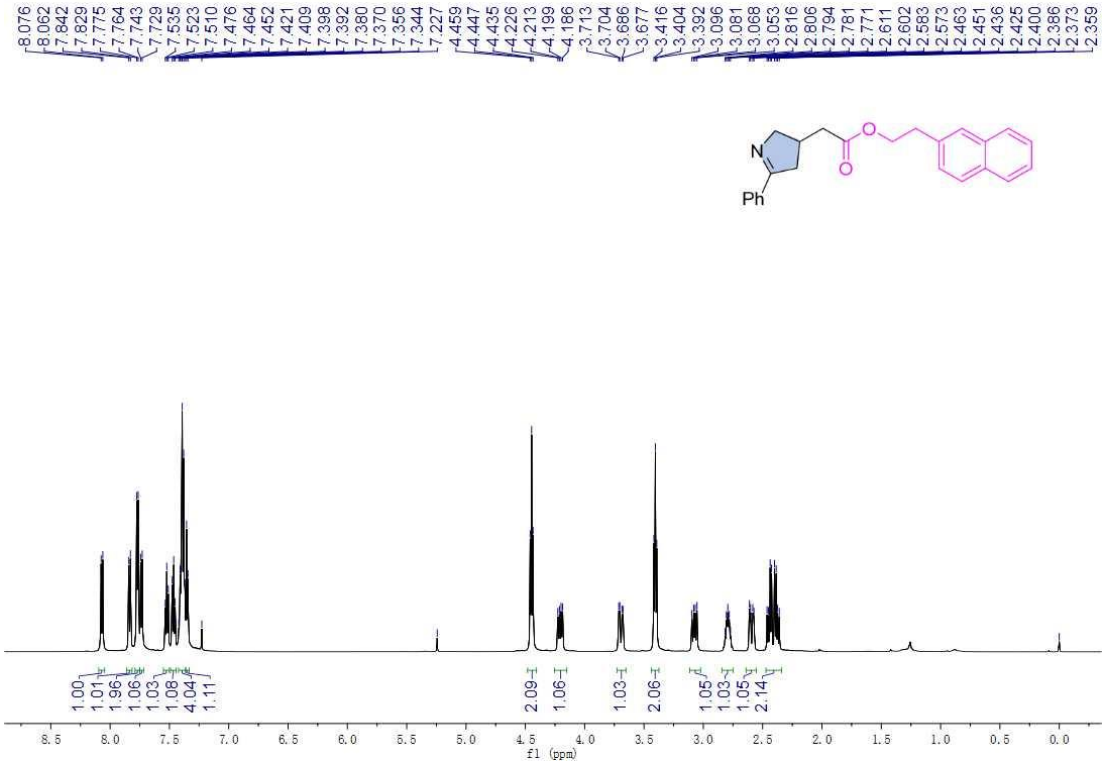
^{1}H spectrum (500 MHz, $CDCl_3$) of compound 2y



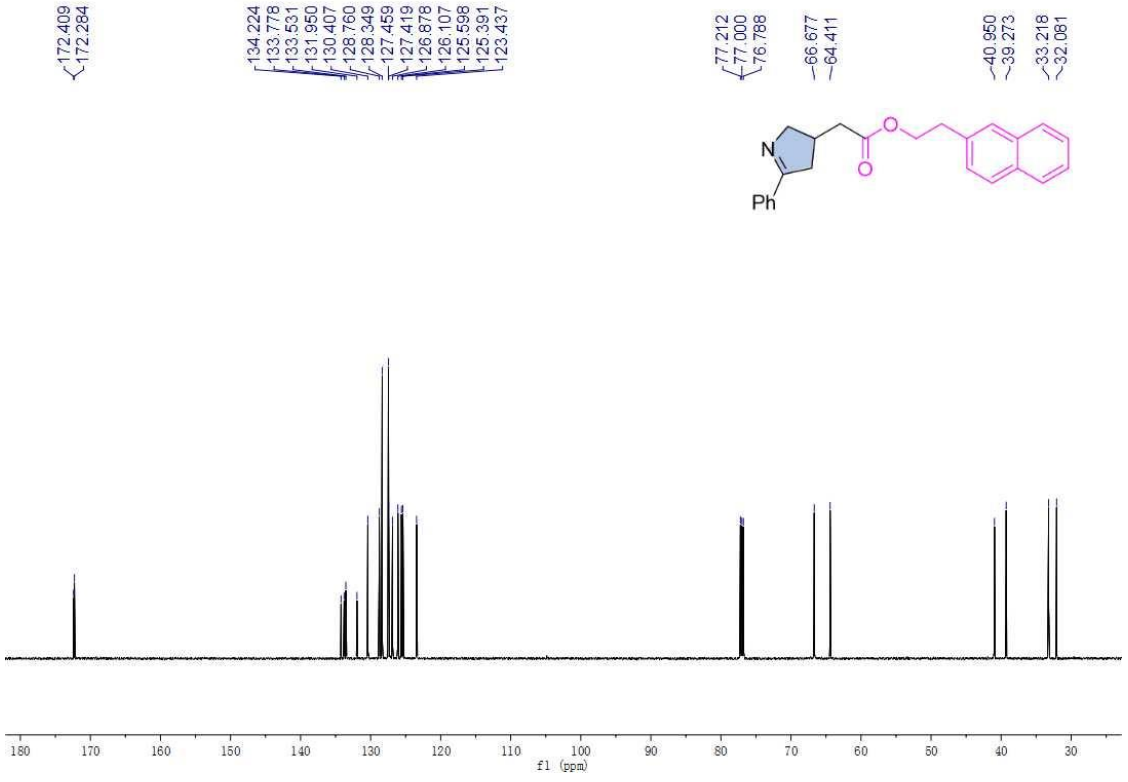
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2y



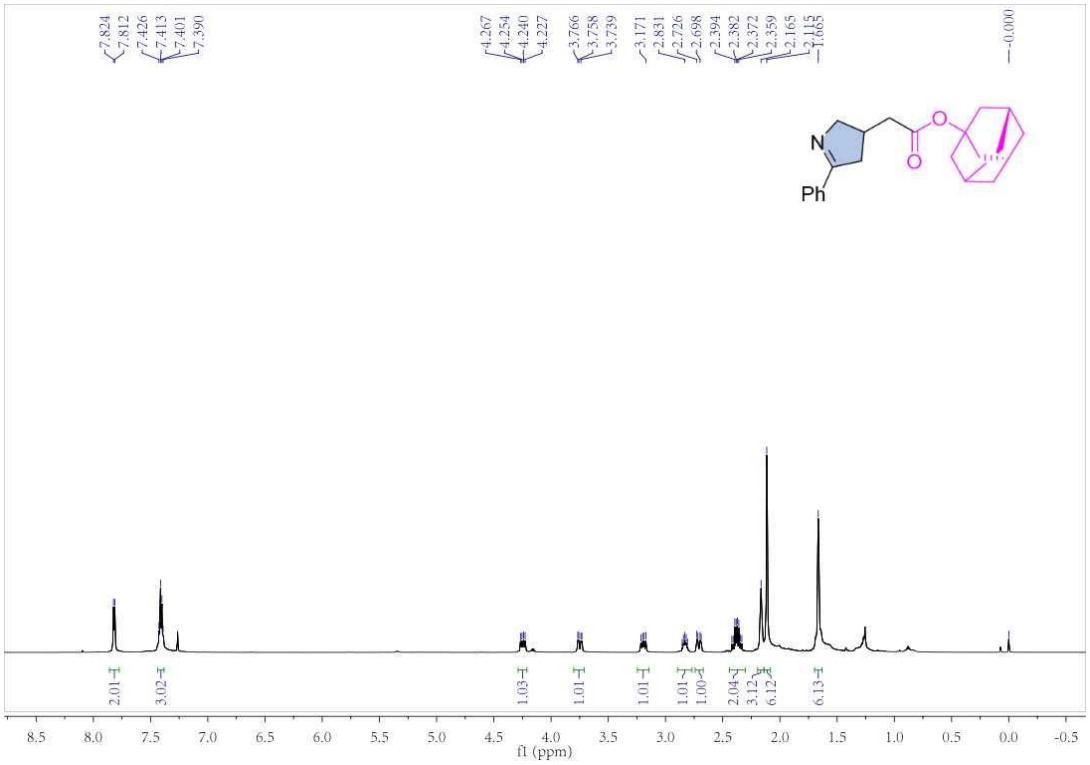
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 2z



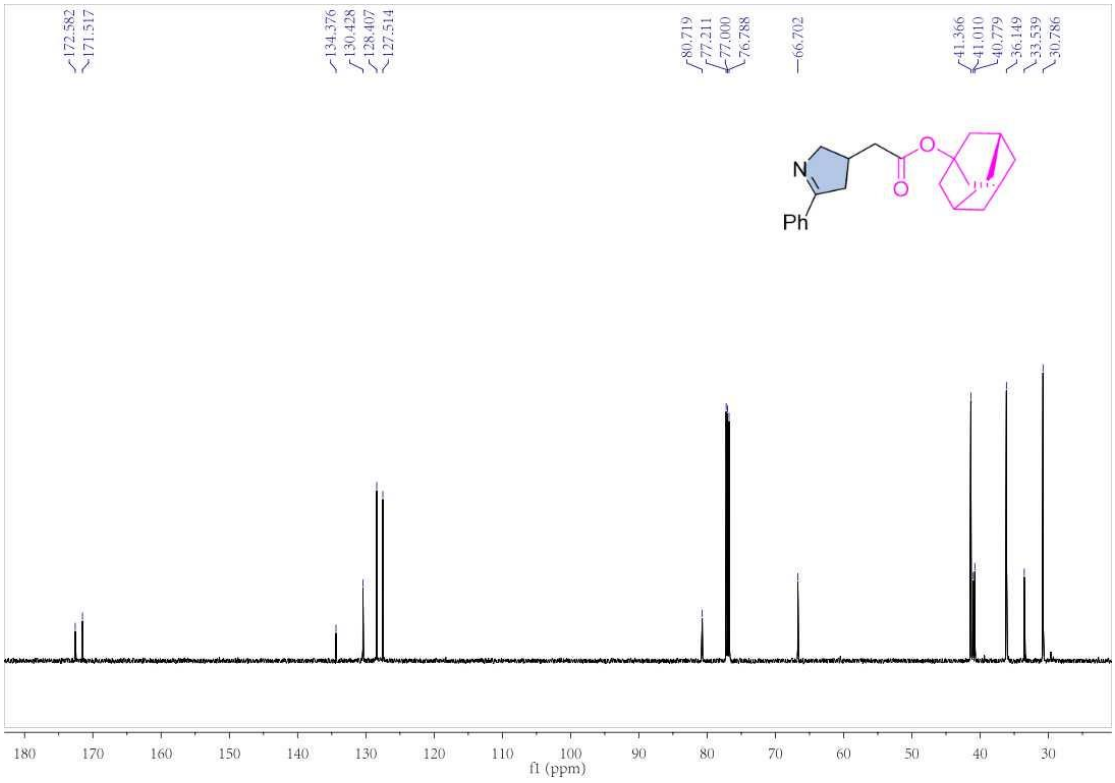
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2z



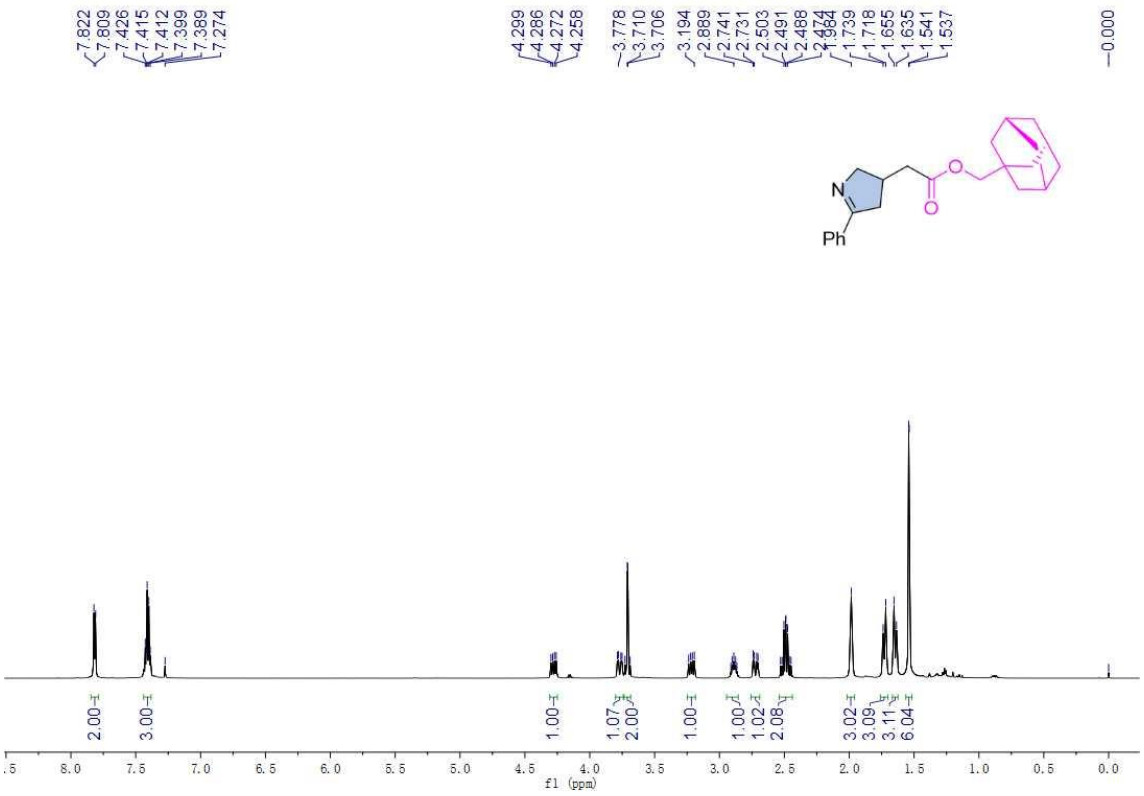
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 2aa



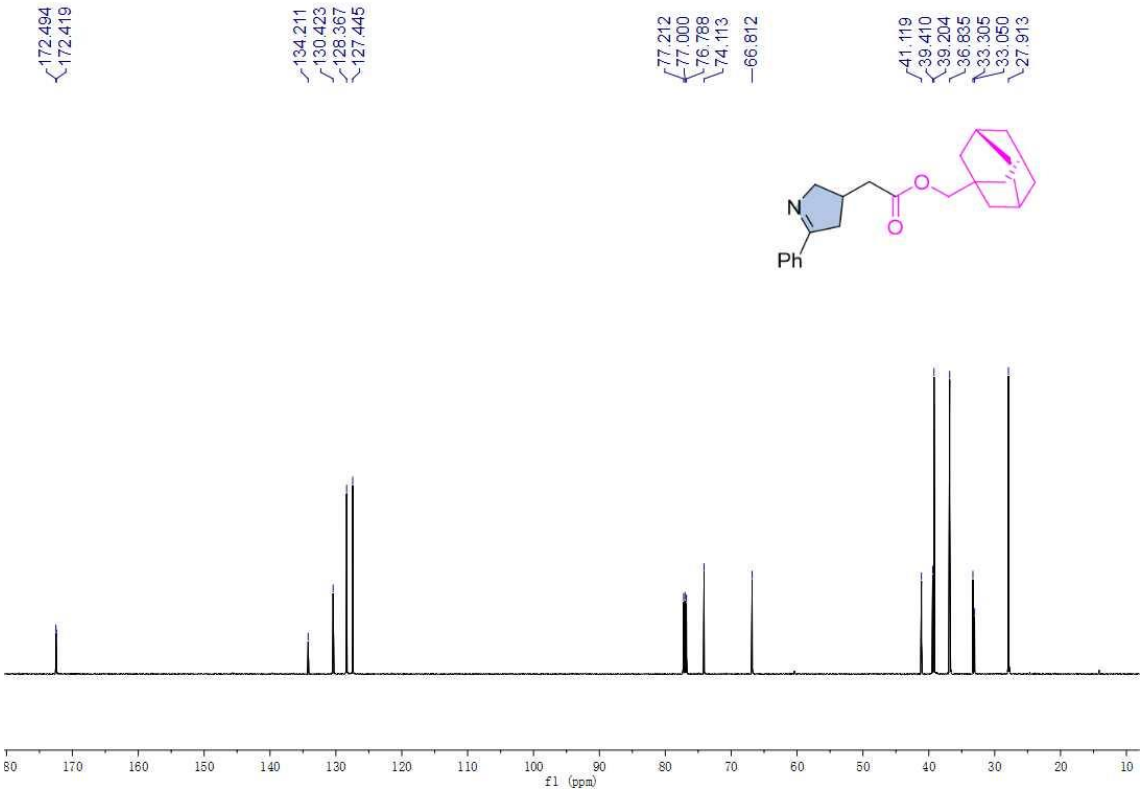
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2aa



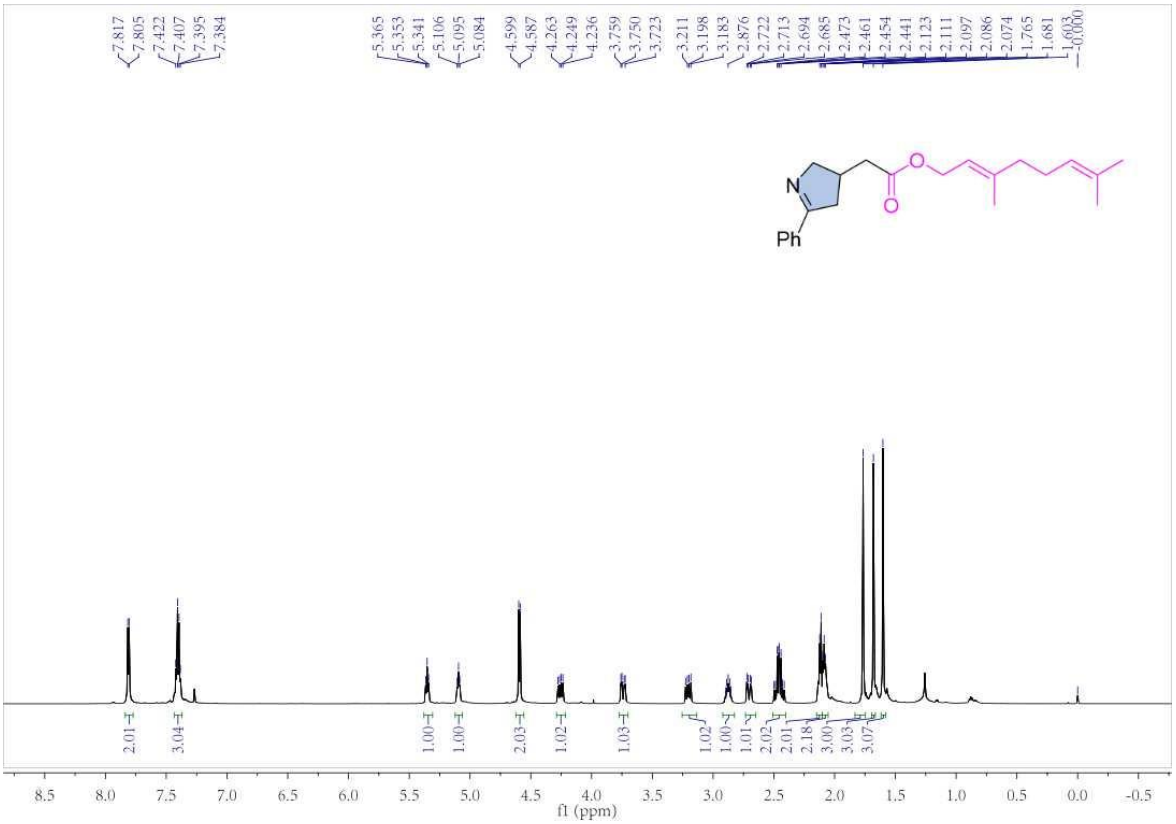
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 2ab



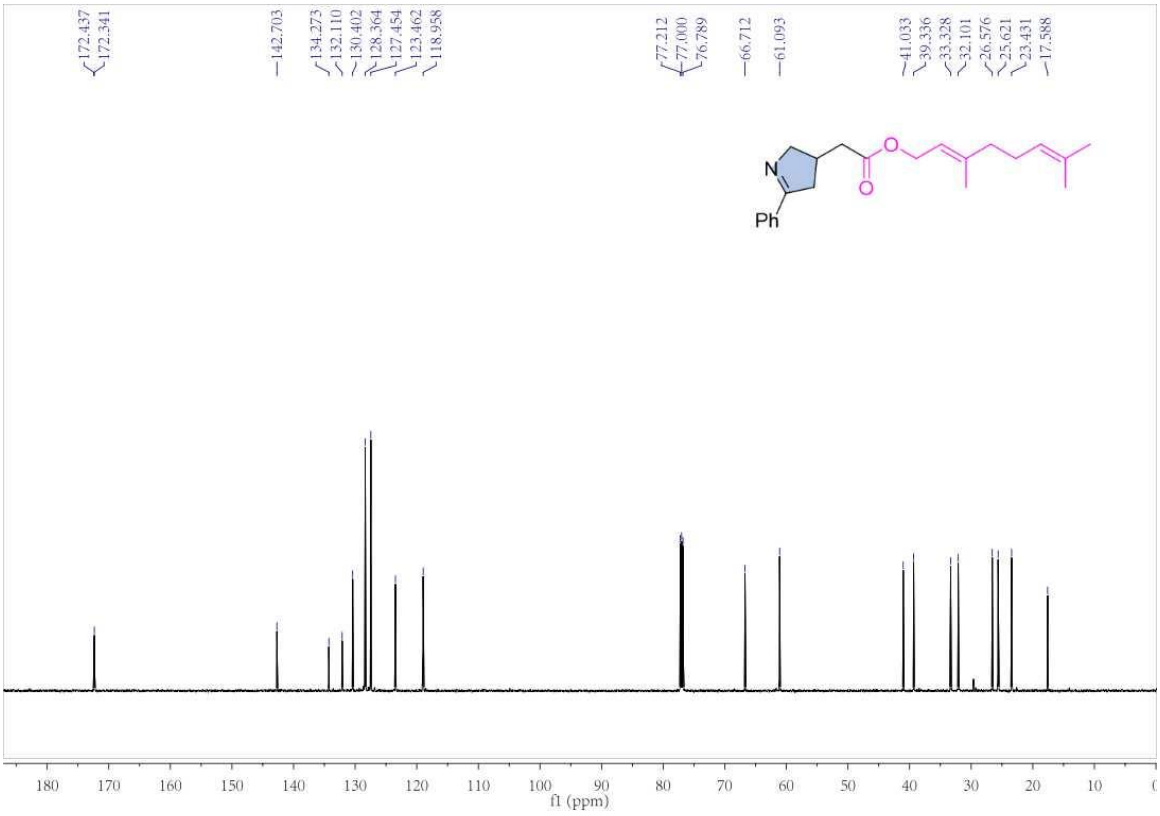
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2ab



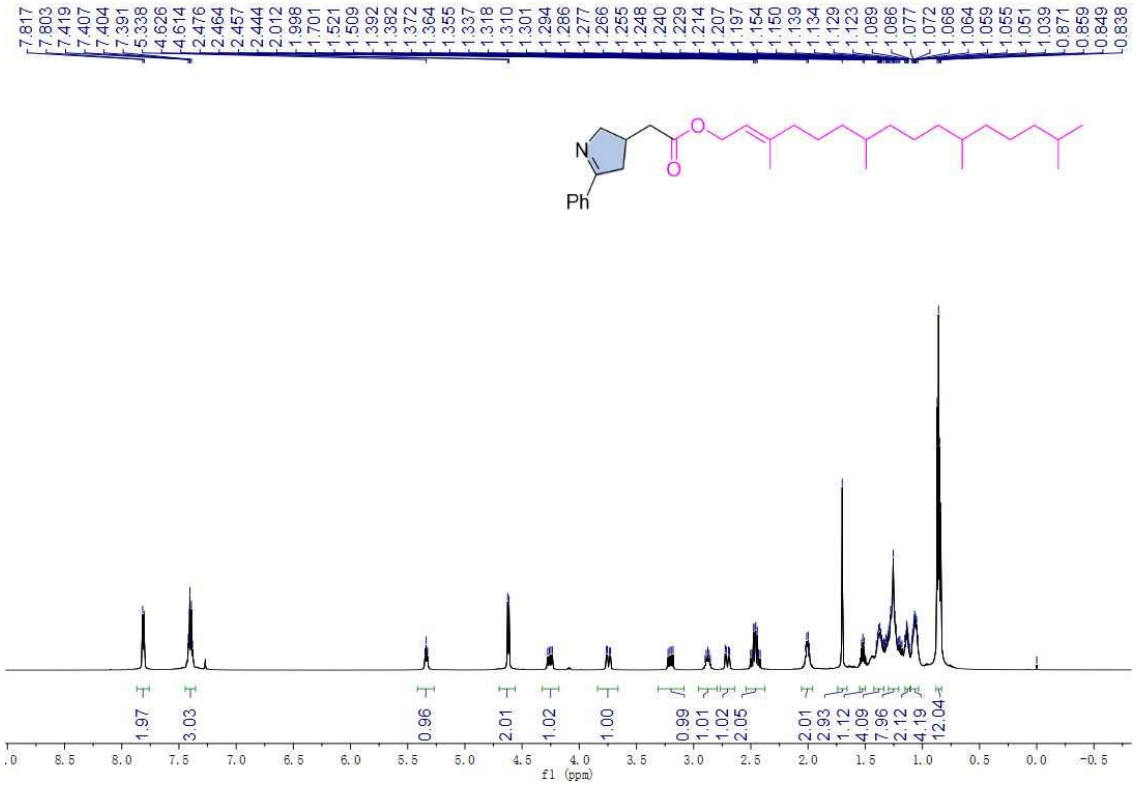
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 2ac



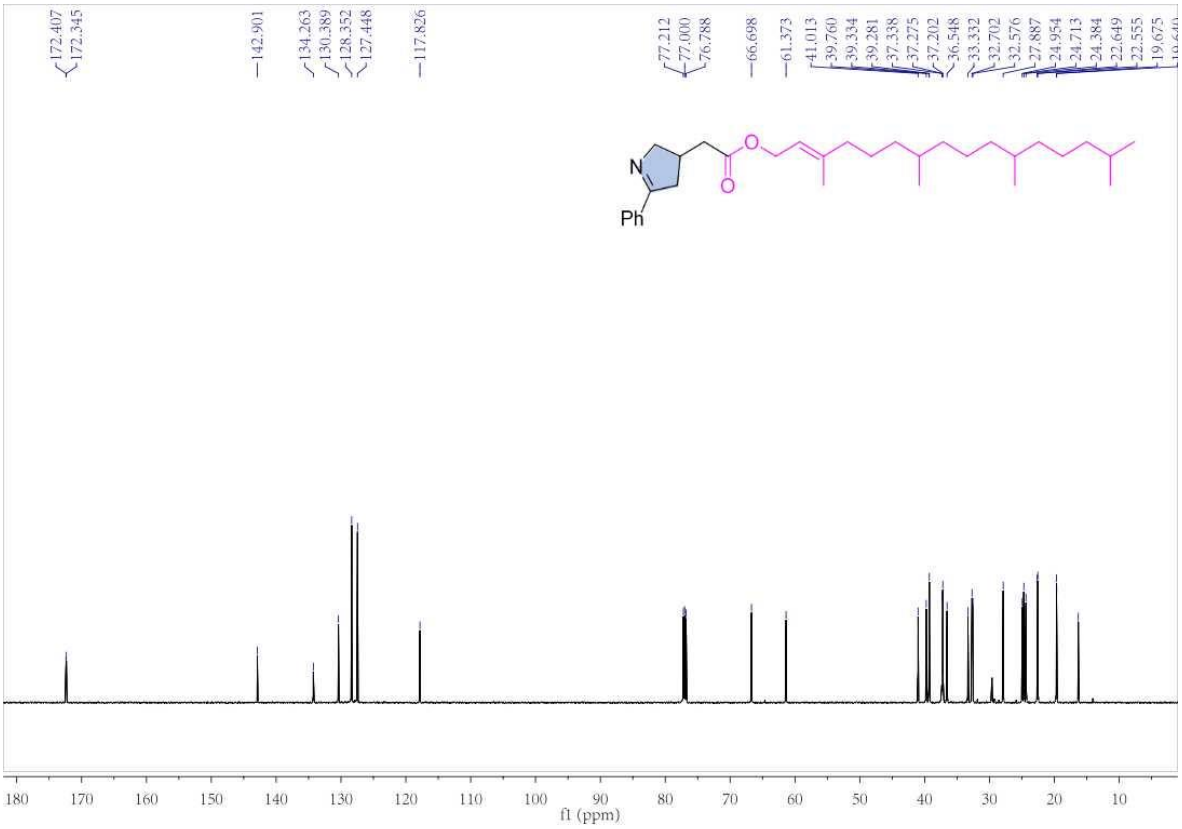
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2ac



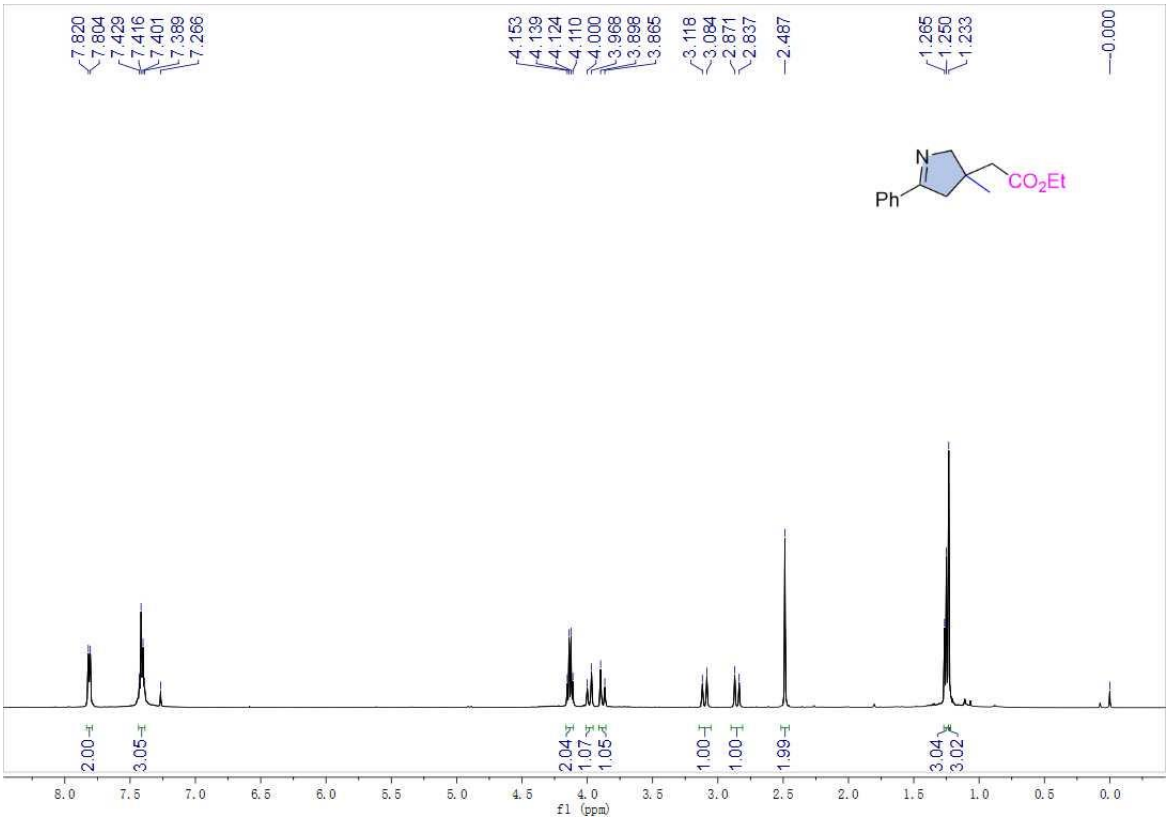
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 2ad



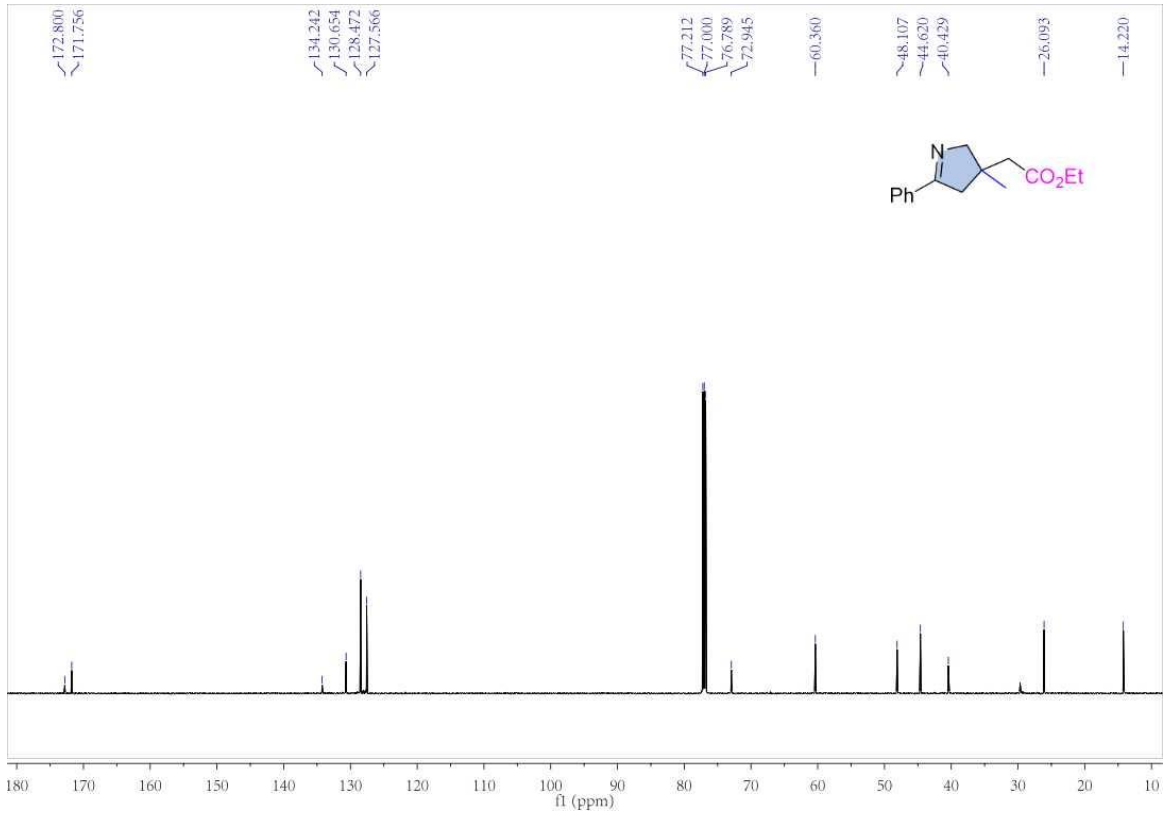
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2ad



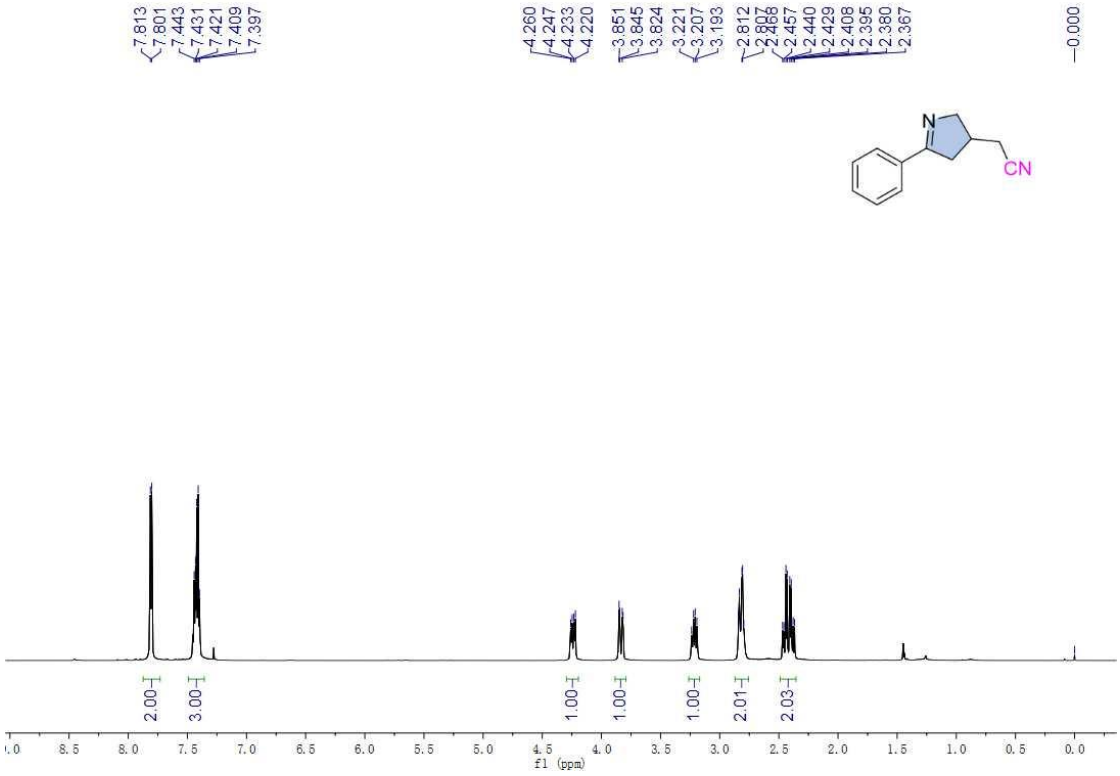
^{1}H spectrum (500 MHz, $CDCl_3$) of compound 2ae



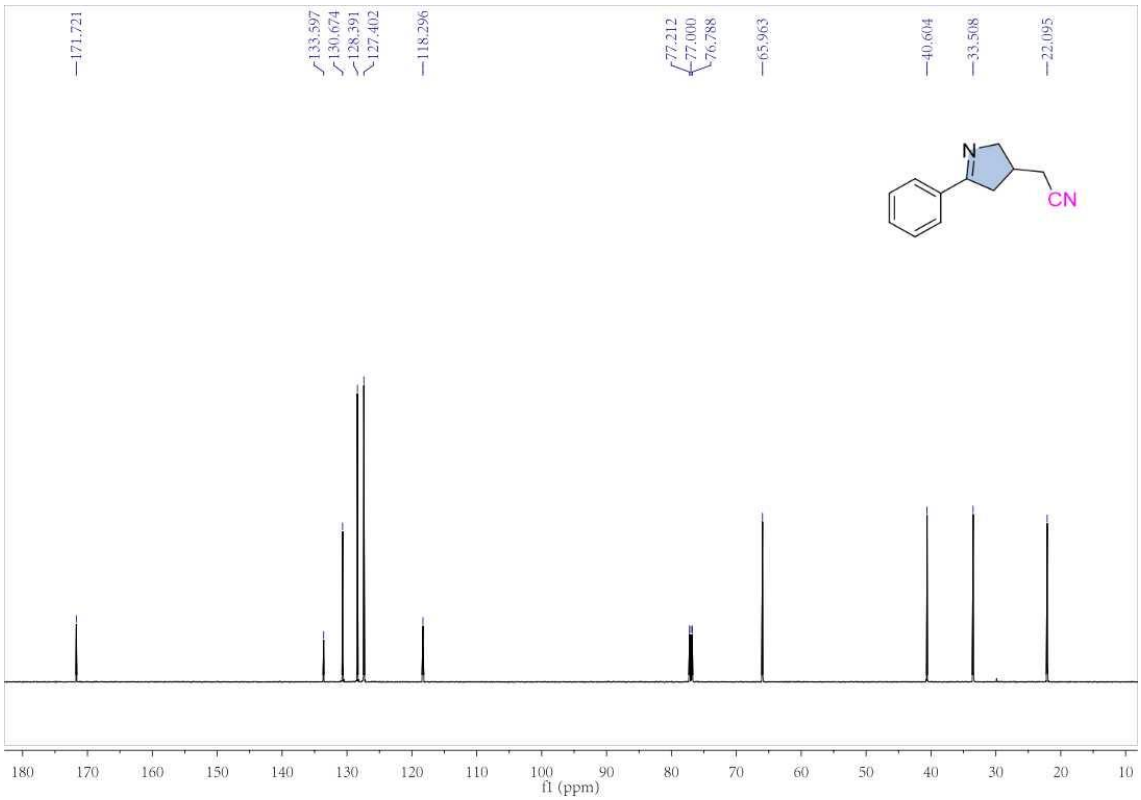
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 2ae



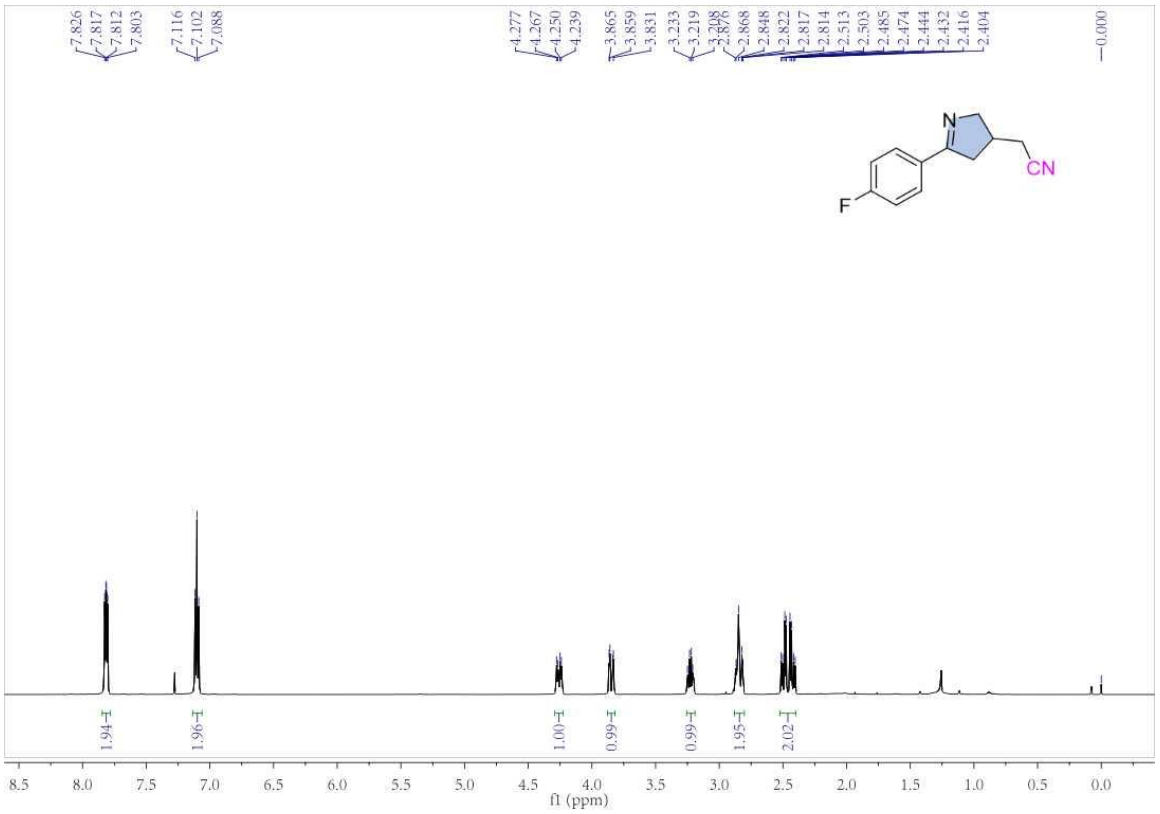
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4a



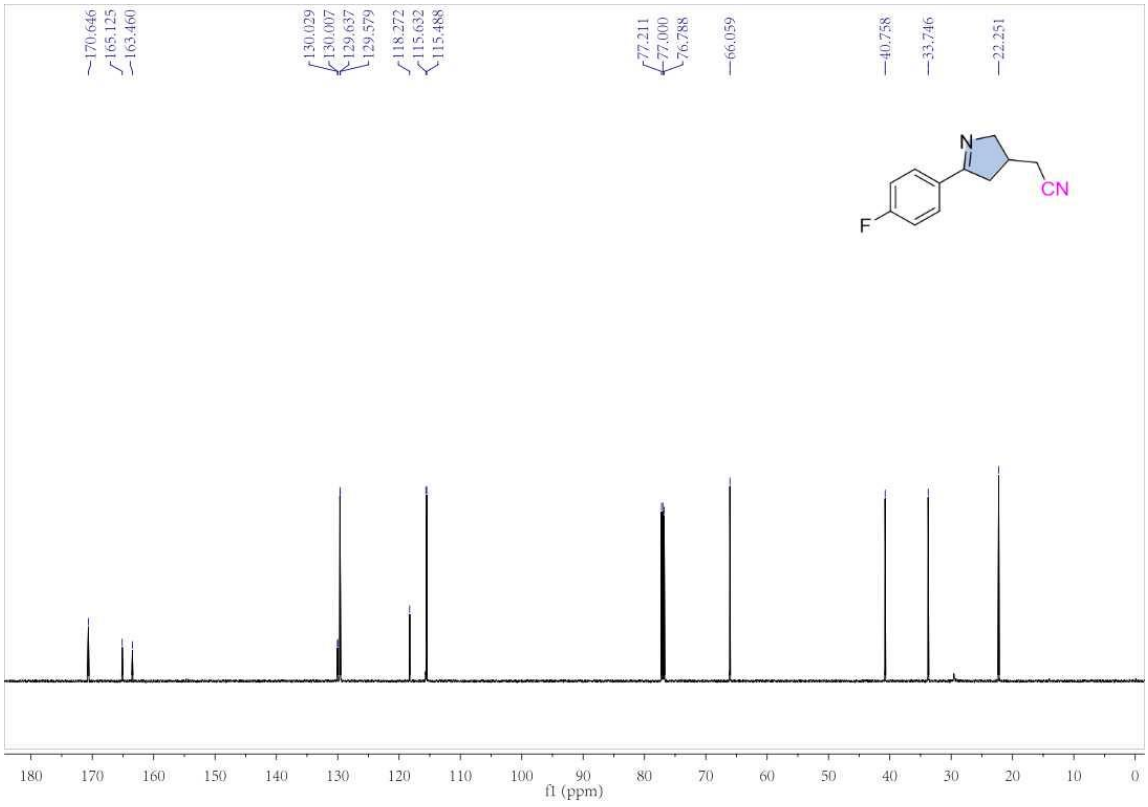
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4a



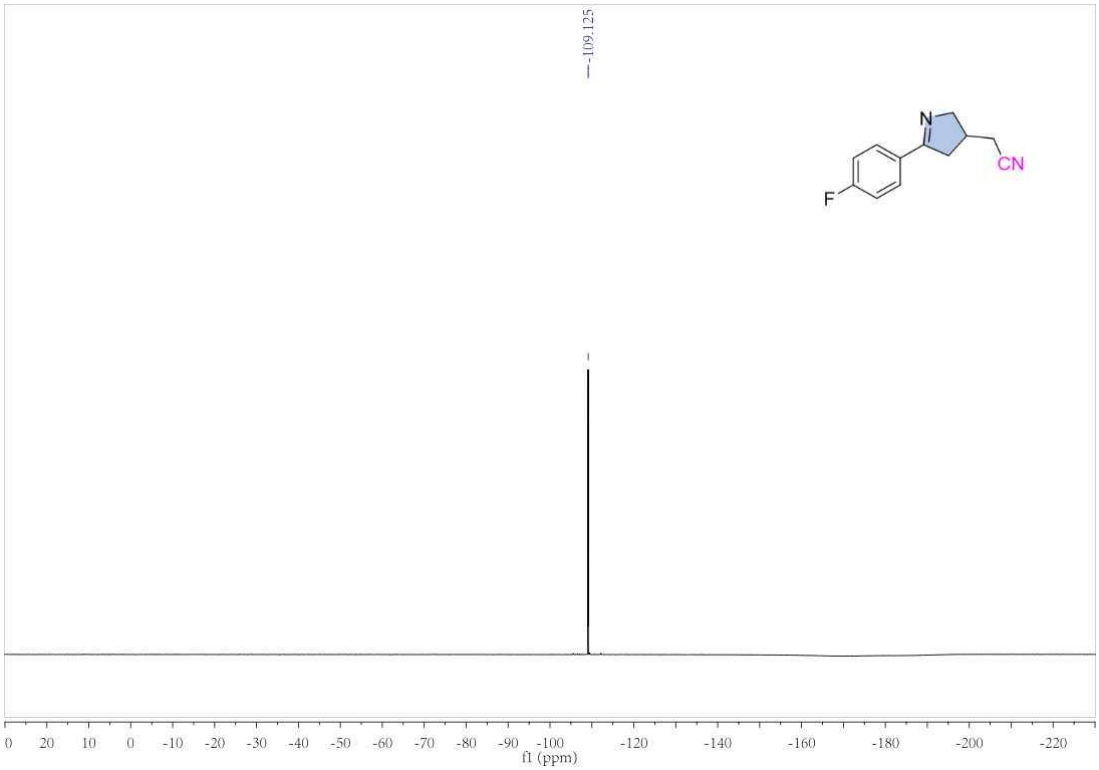
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4b



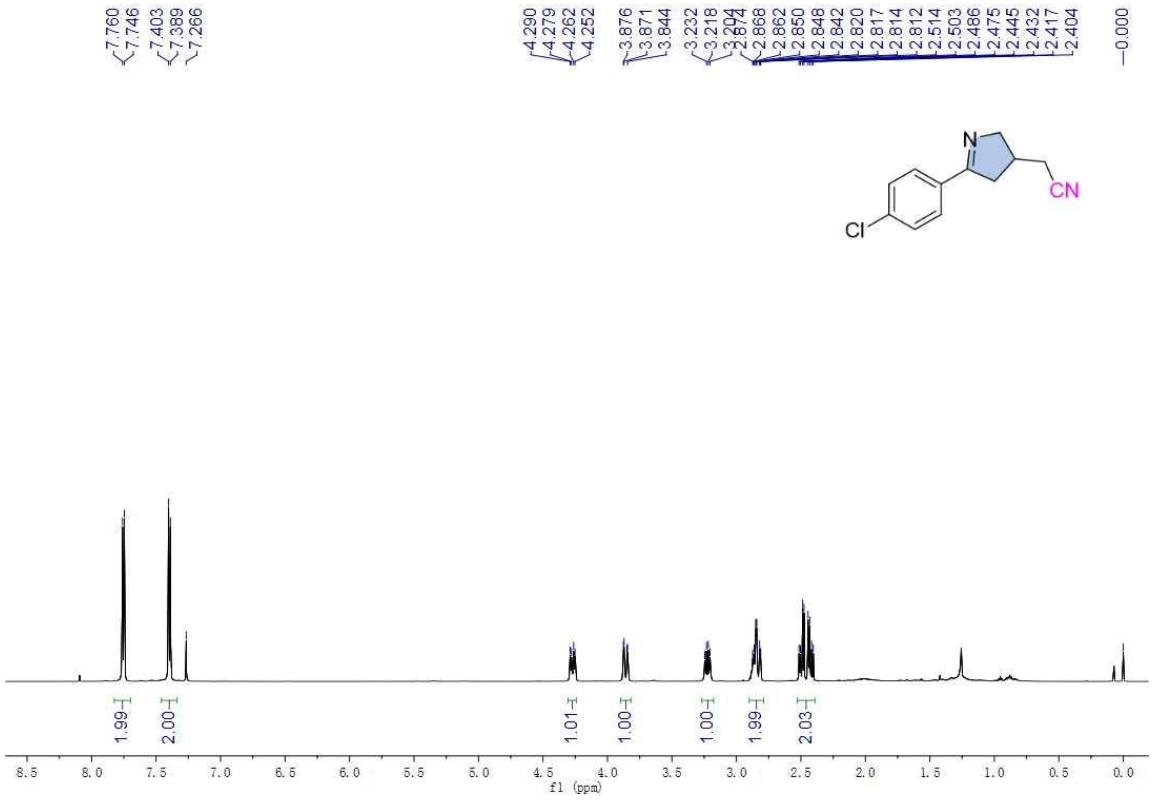
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4b



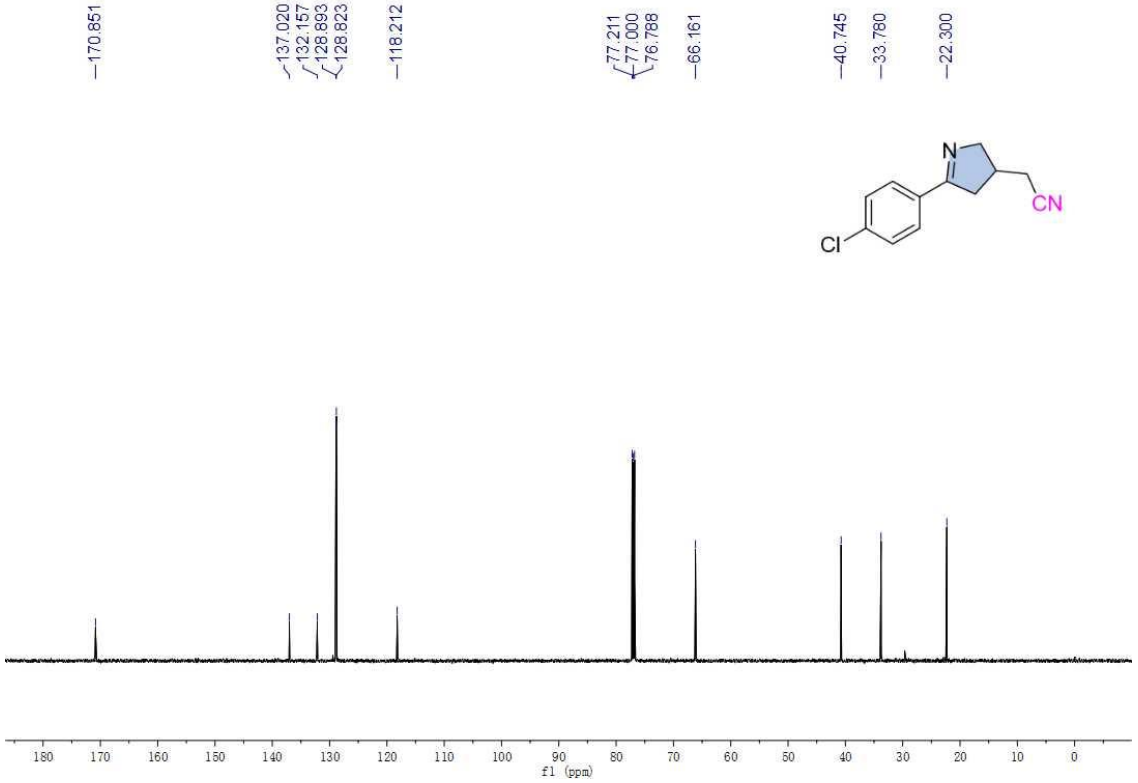
^{19}F spectrum (565 MHz, $CDCl_3$) of compound 4b



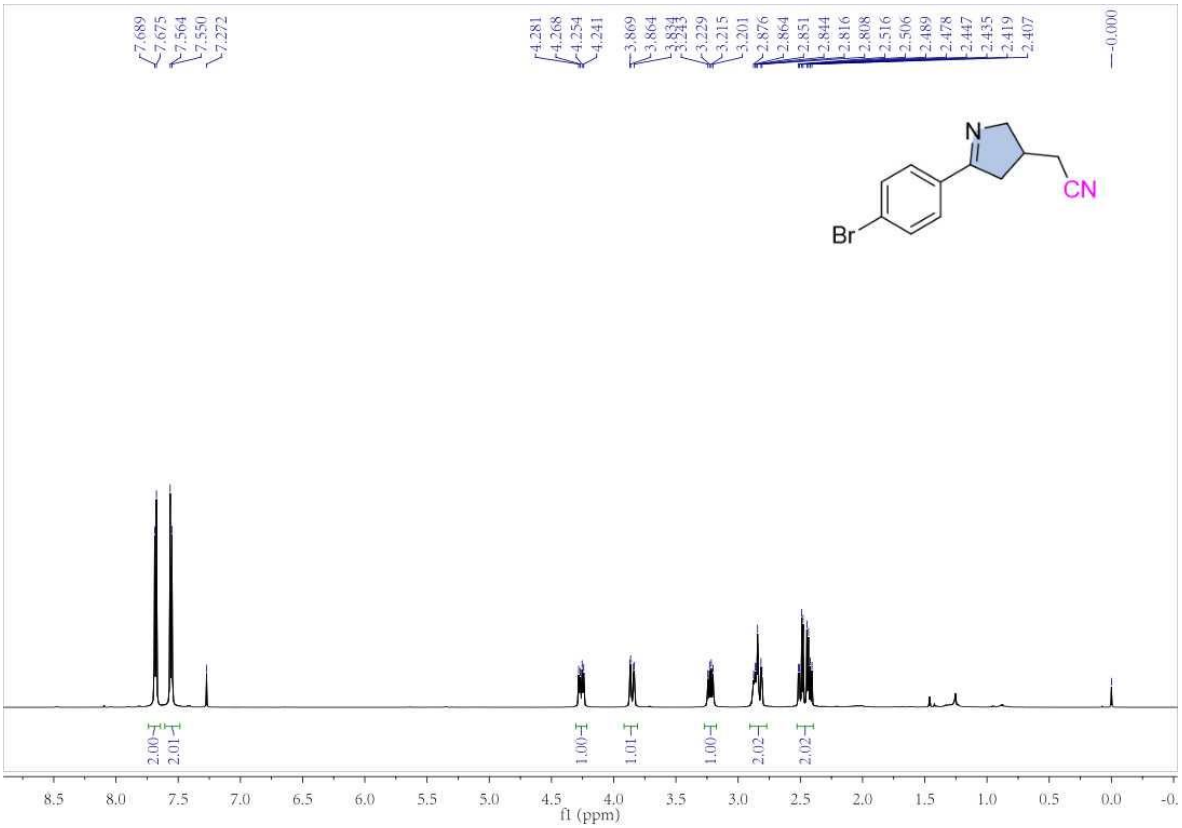
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4c



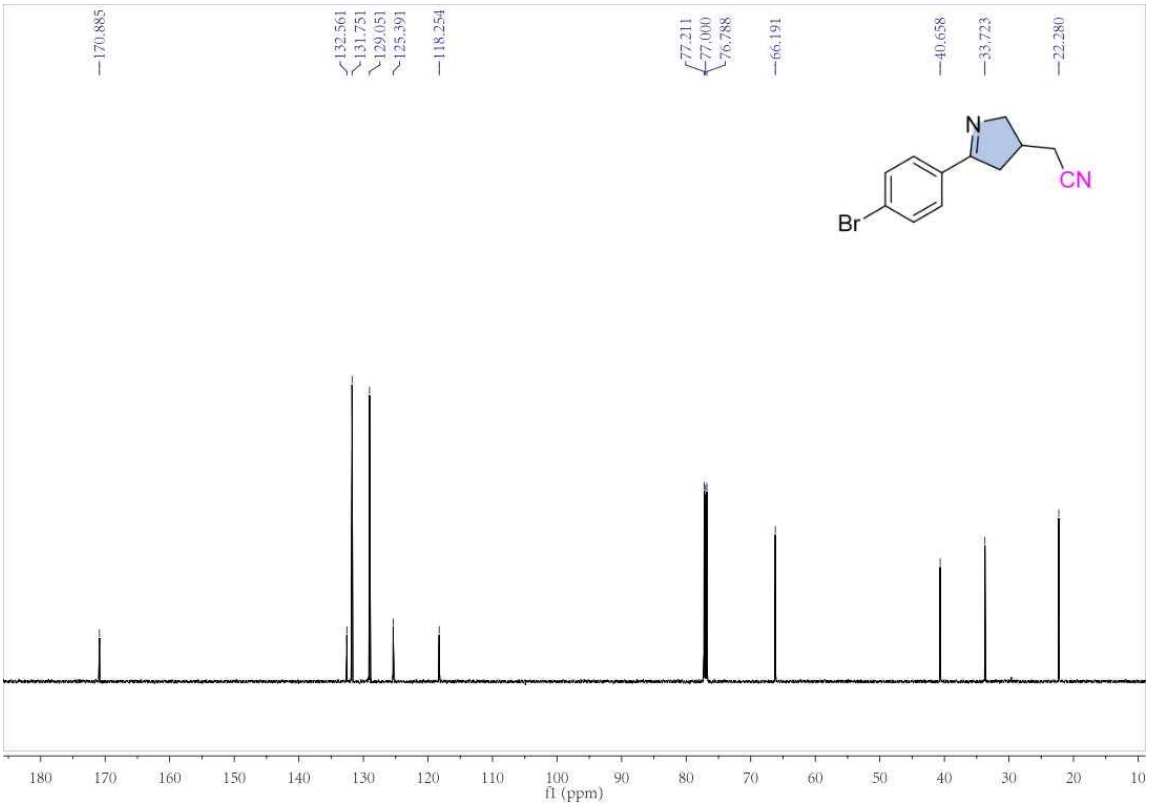
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4c



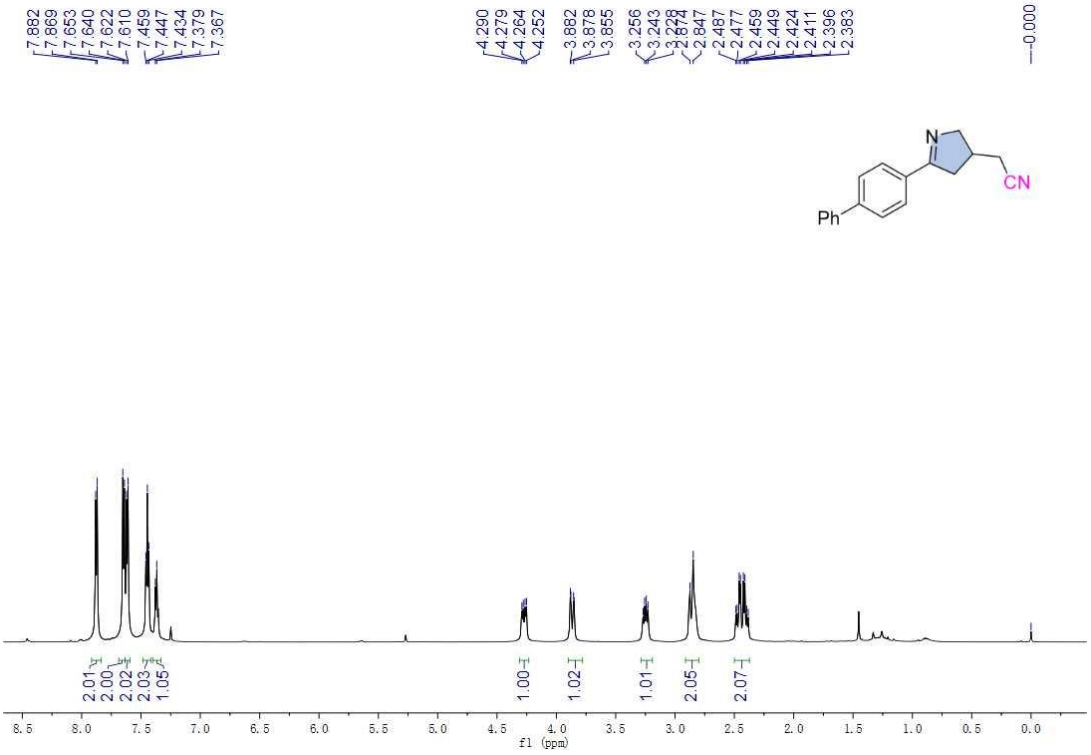
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4d



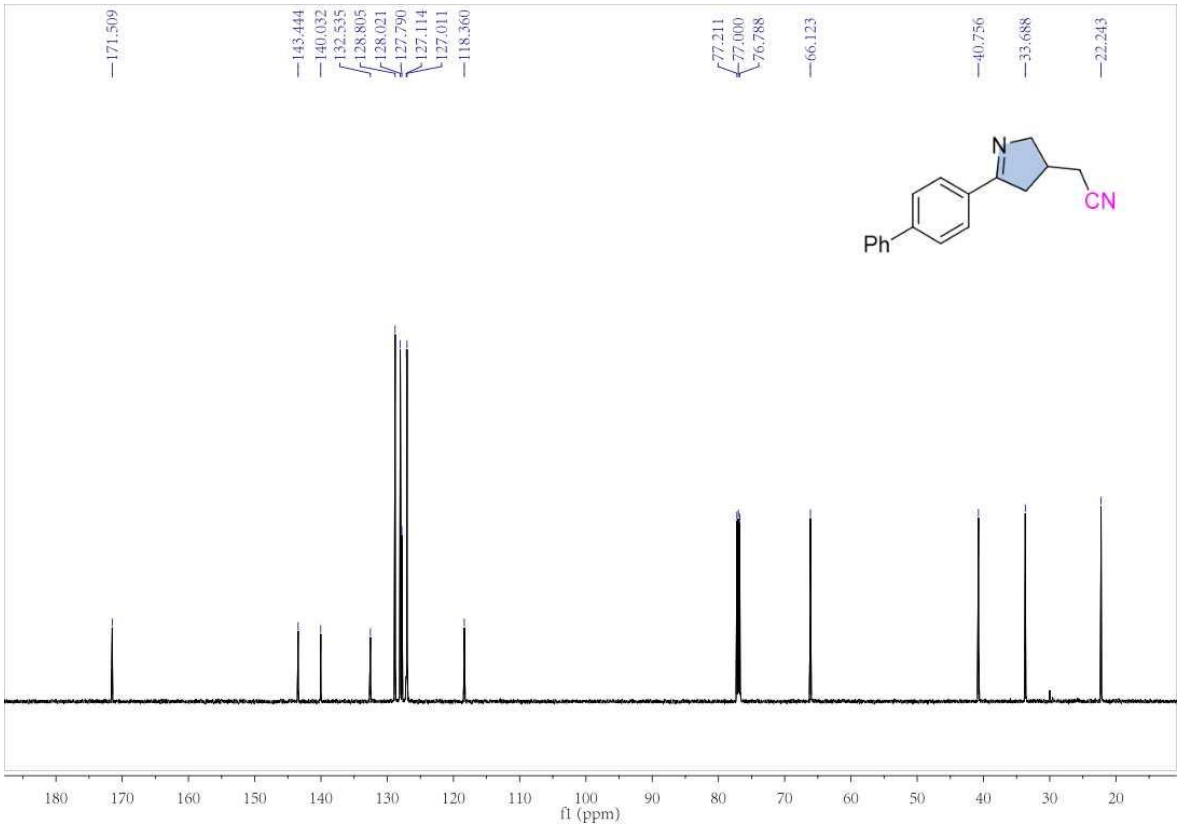
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4d



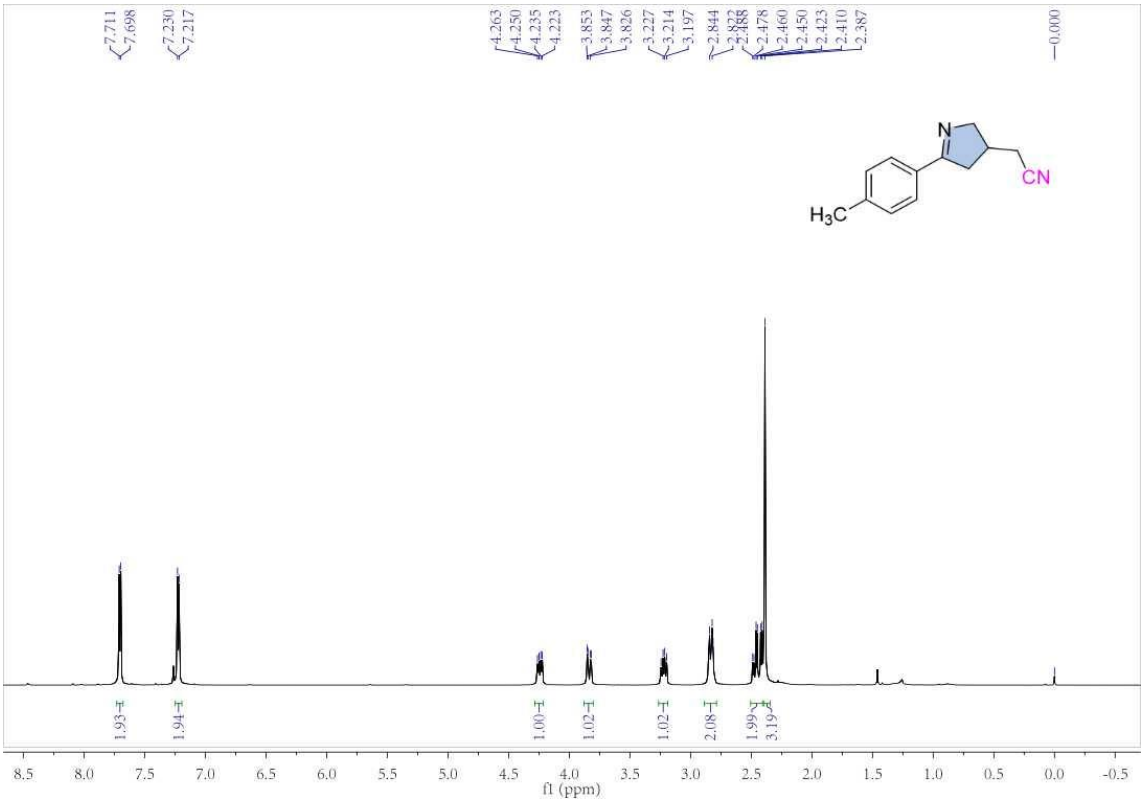
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4e



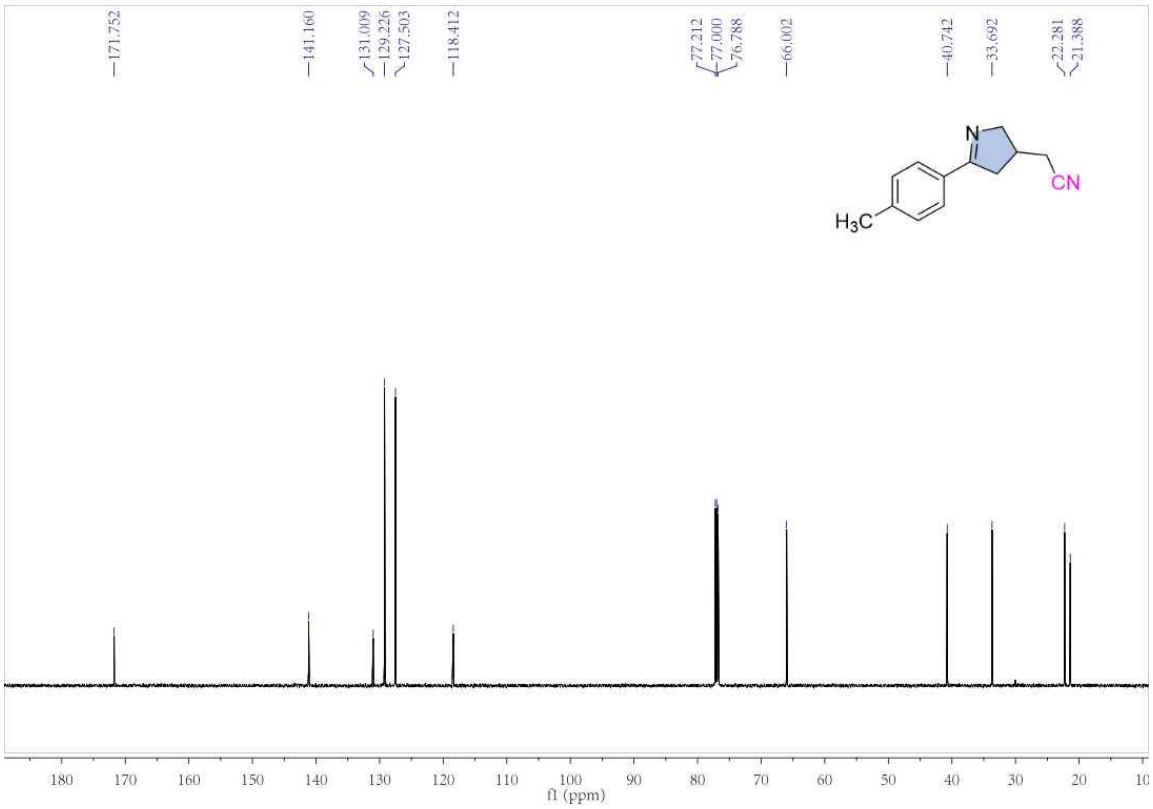
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4e



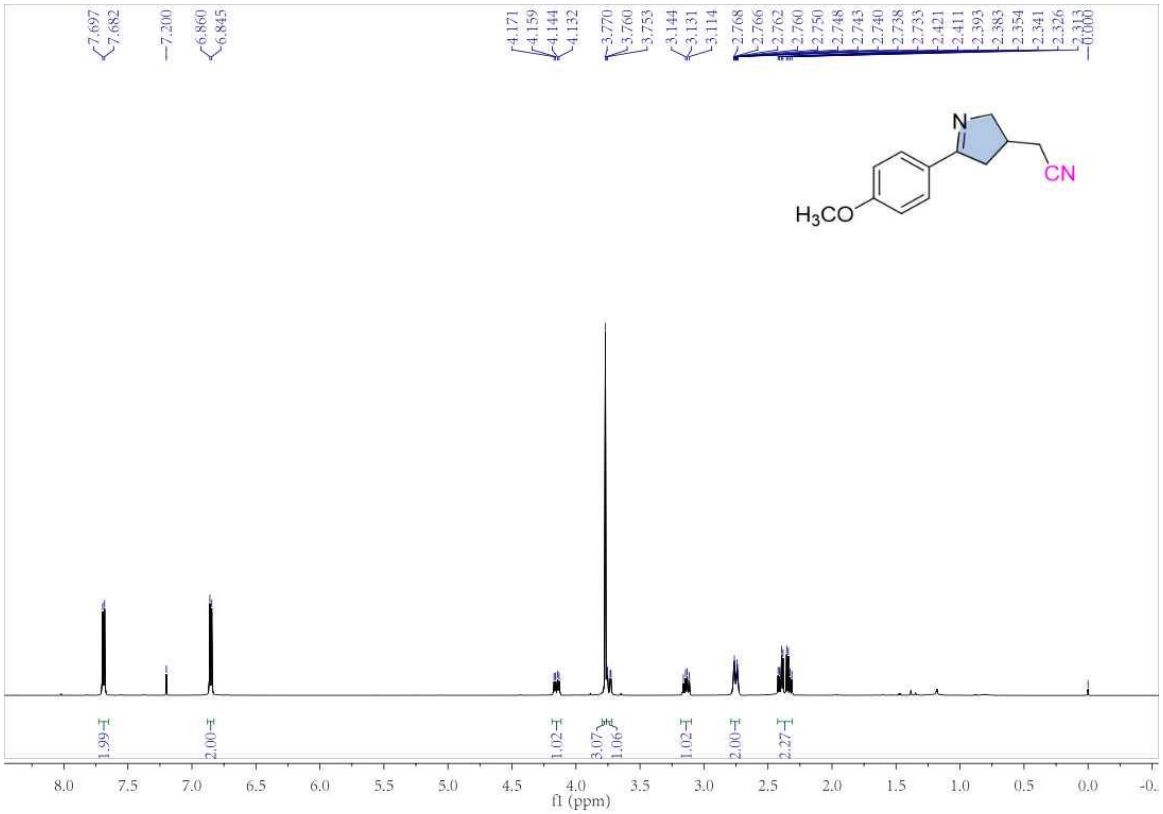
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4f



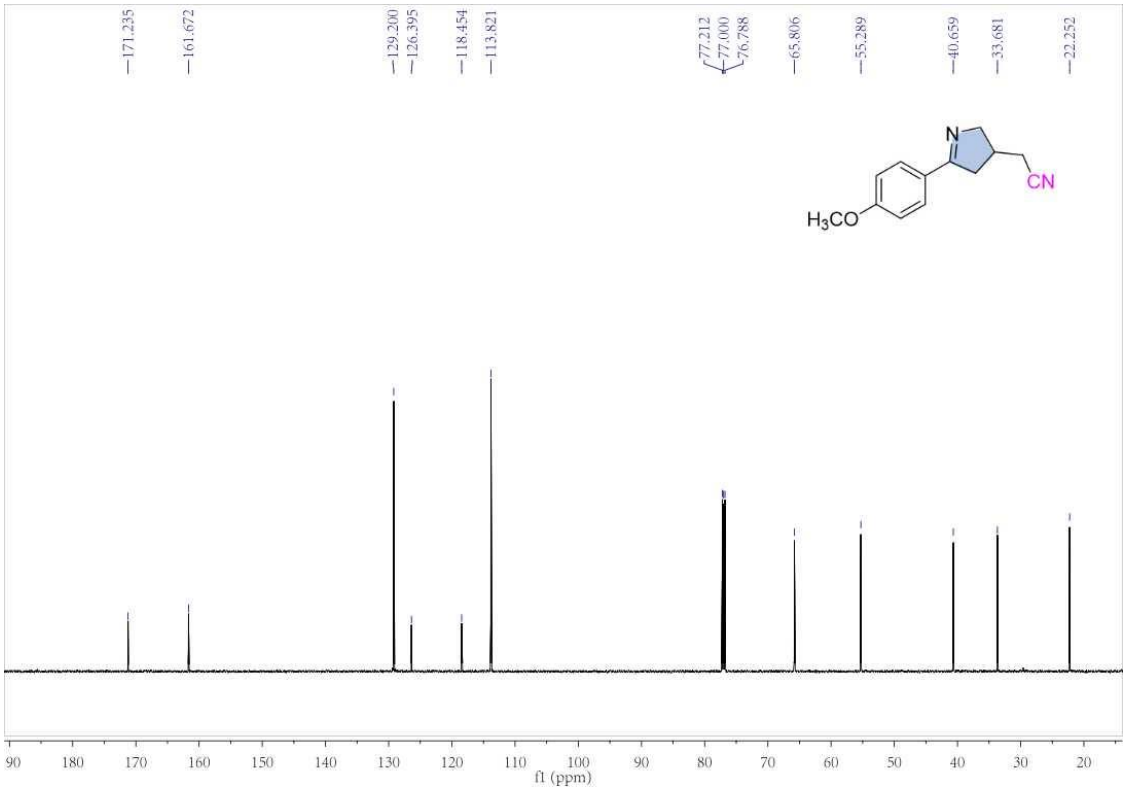
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4f



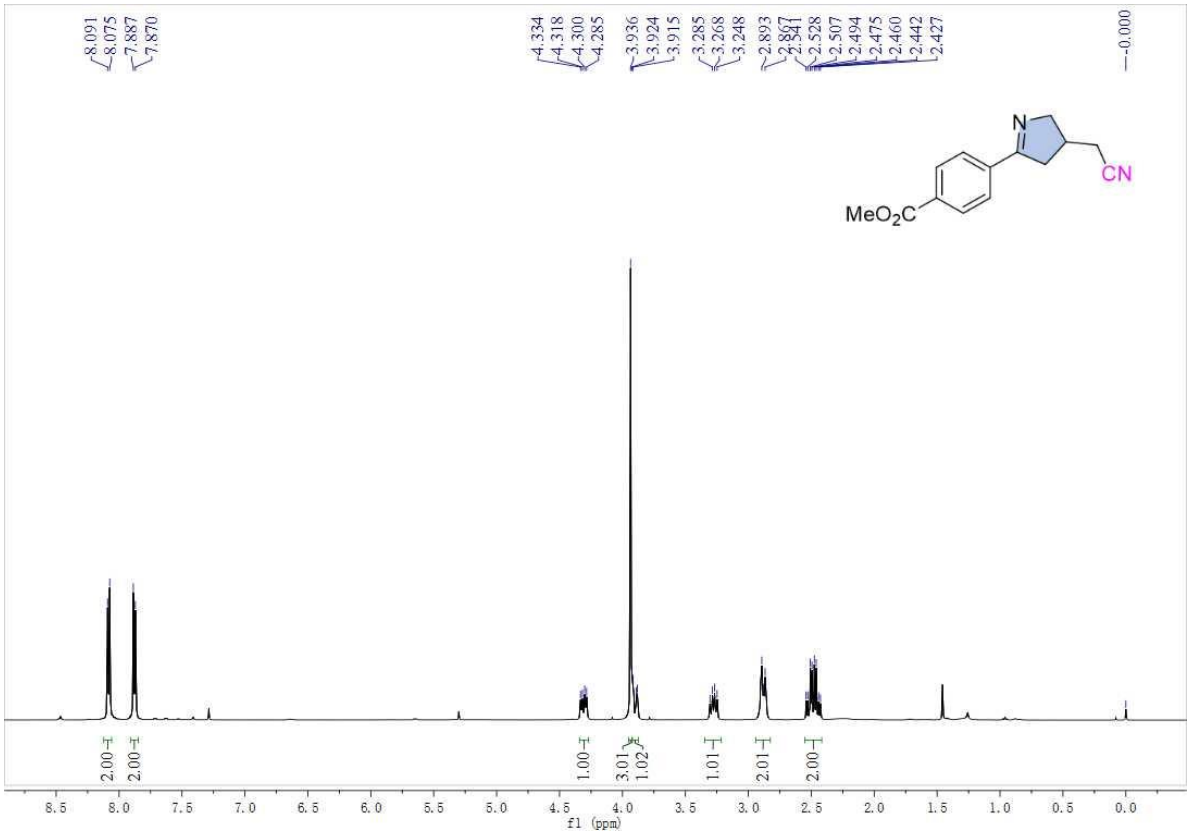
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4g



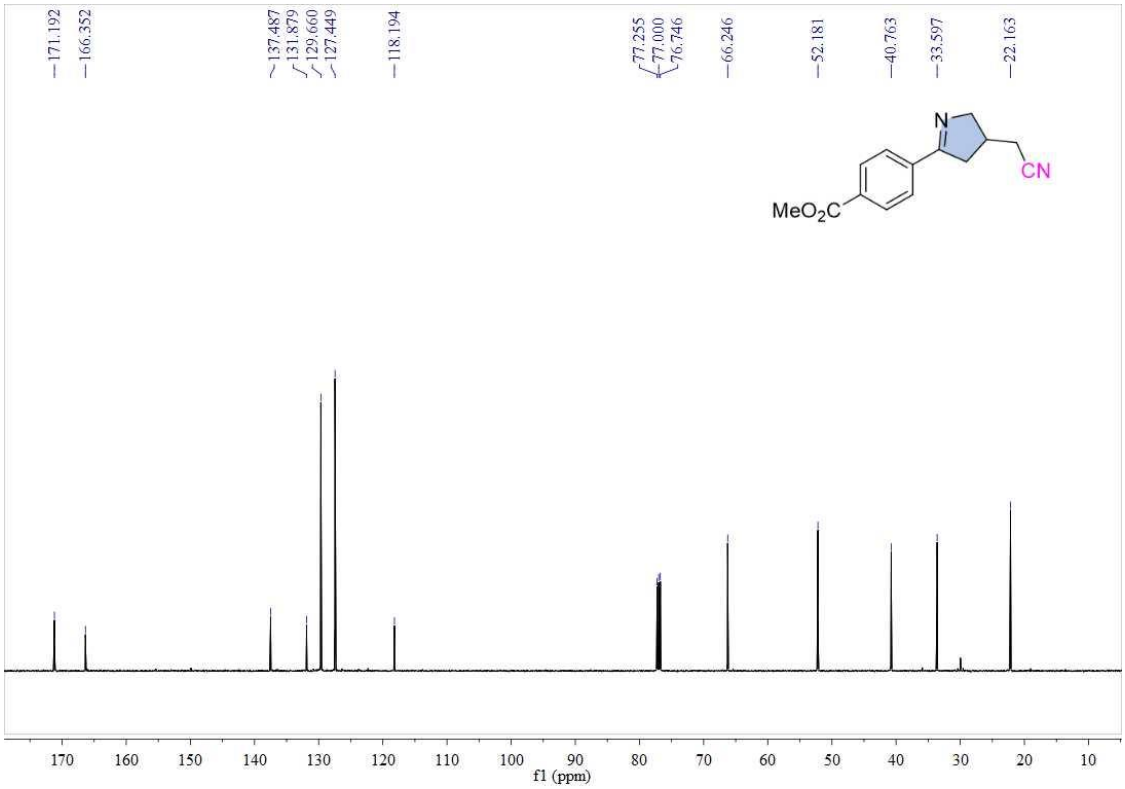
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4g



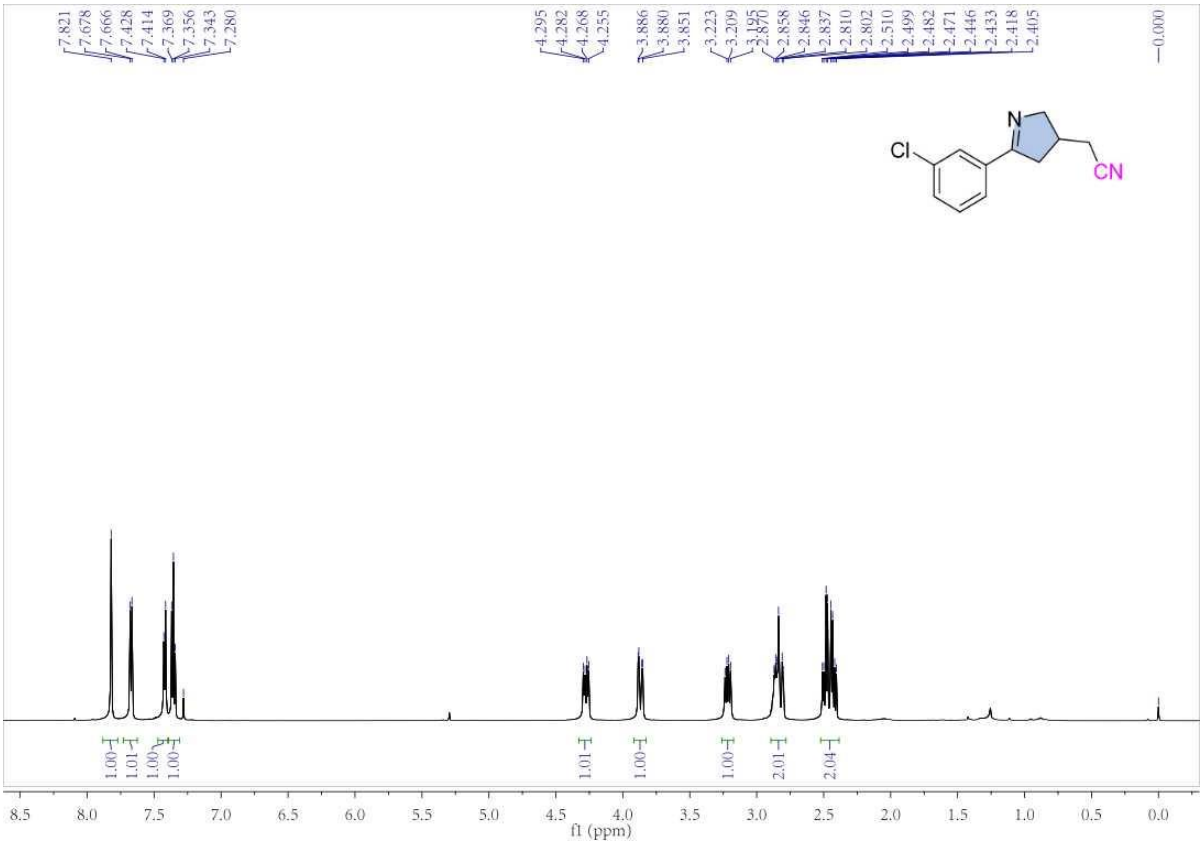
^{1}H spectrum (500 MHz, $CDCl_3$) of compound 4h



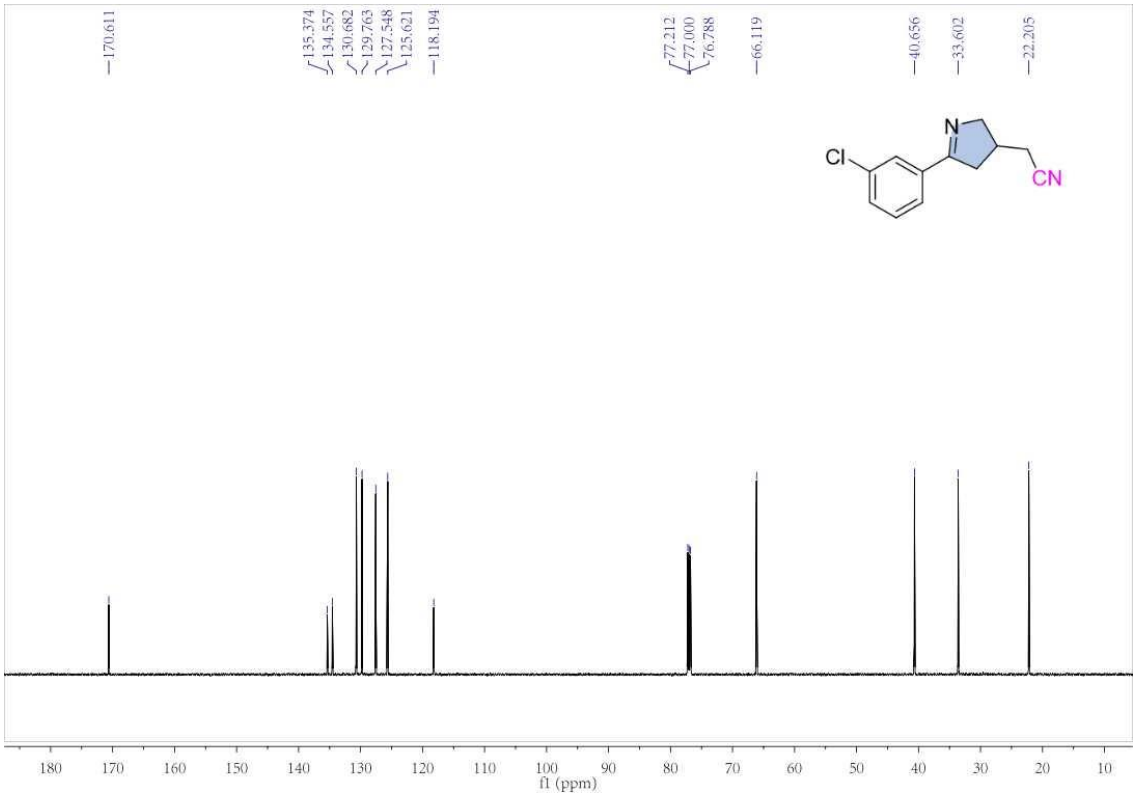
^{13}C spectrum (125 MHz, $CDCl_3$) of compound 4h



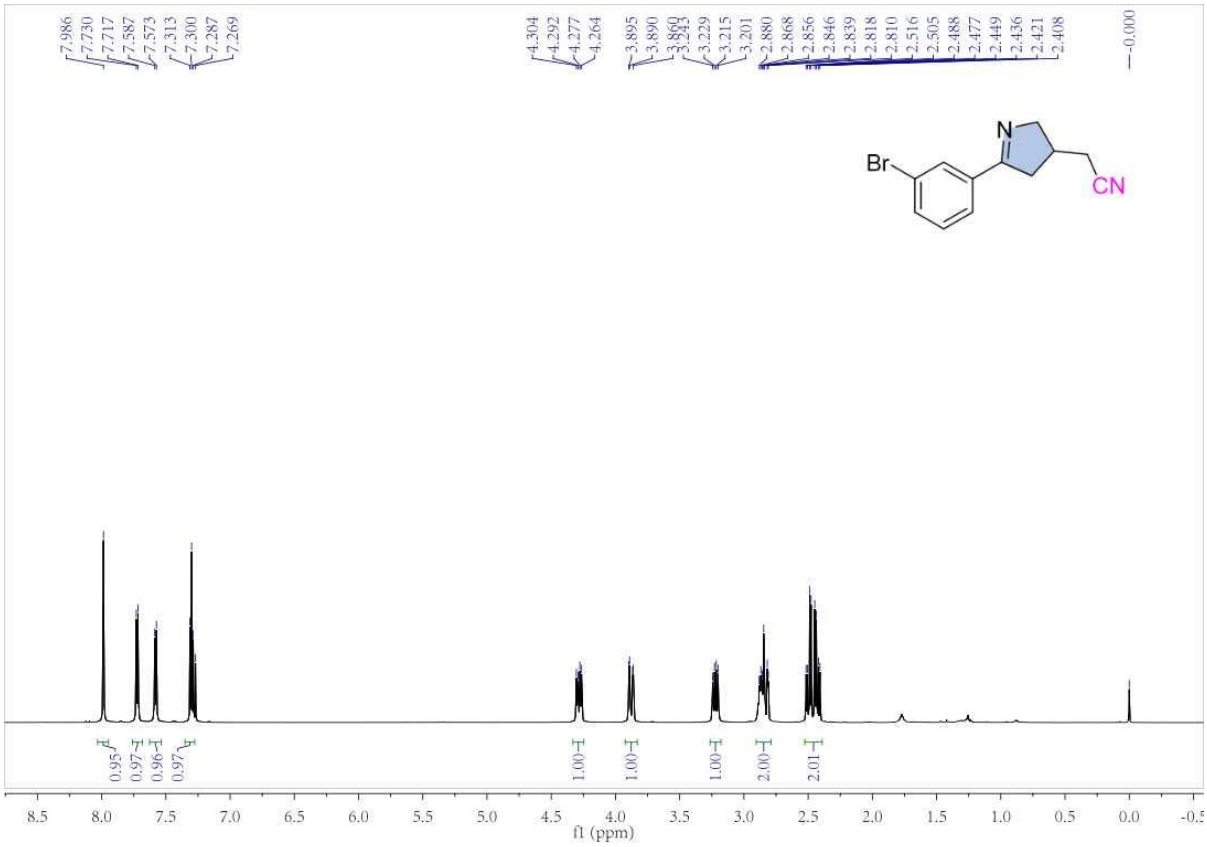
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4i



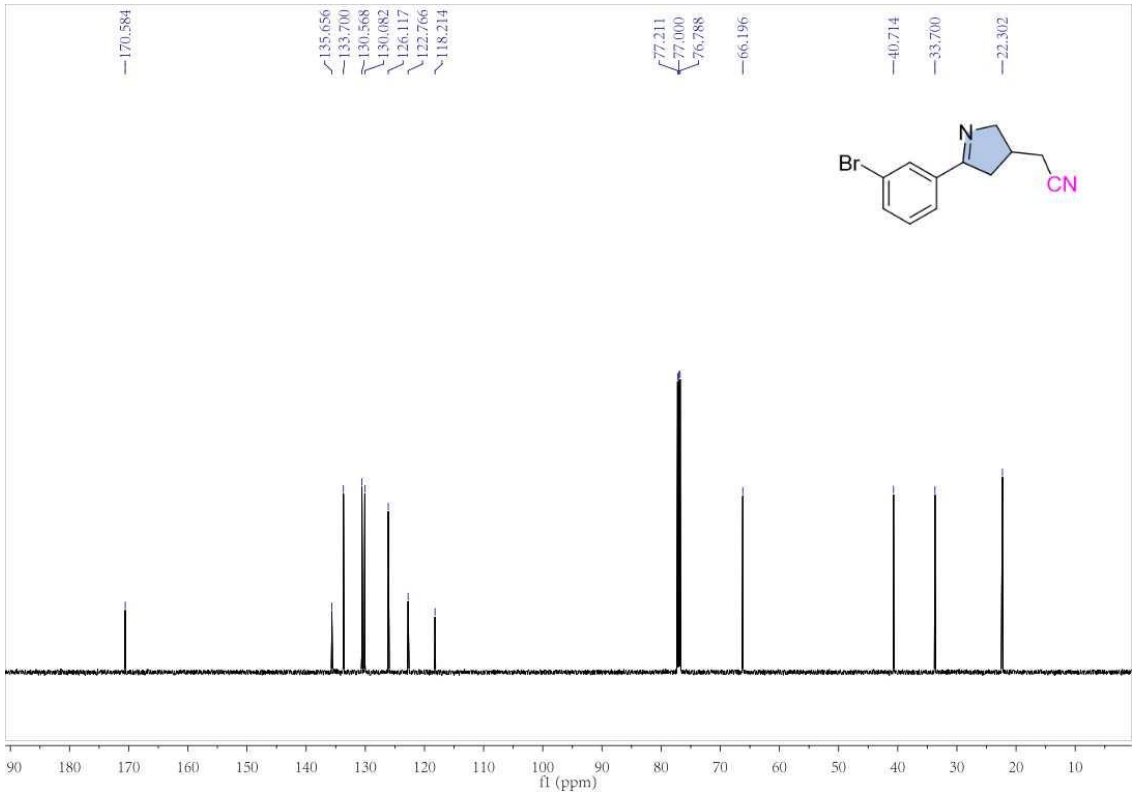
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4i



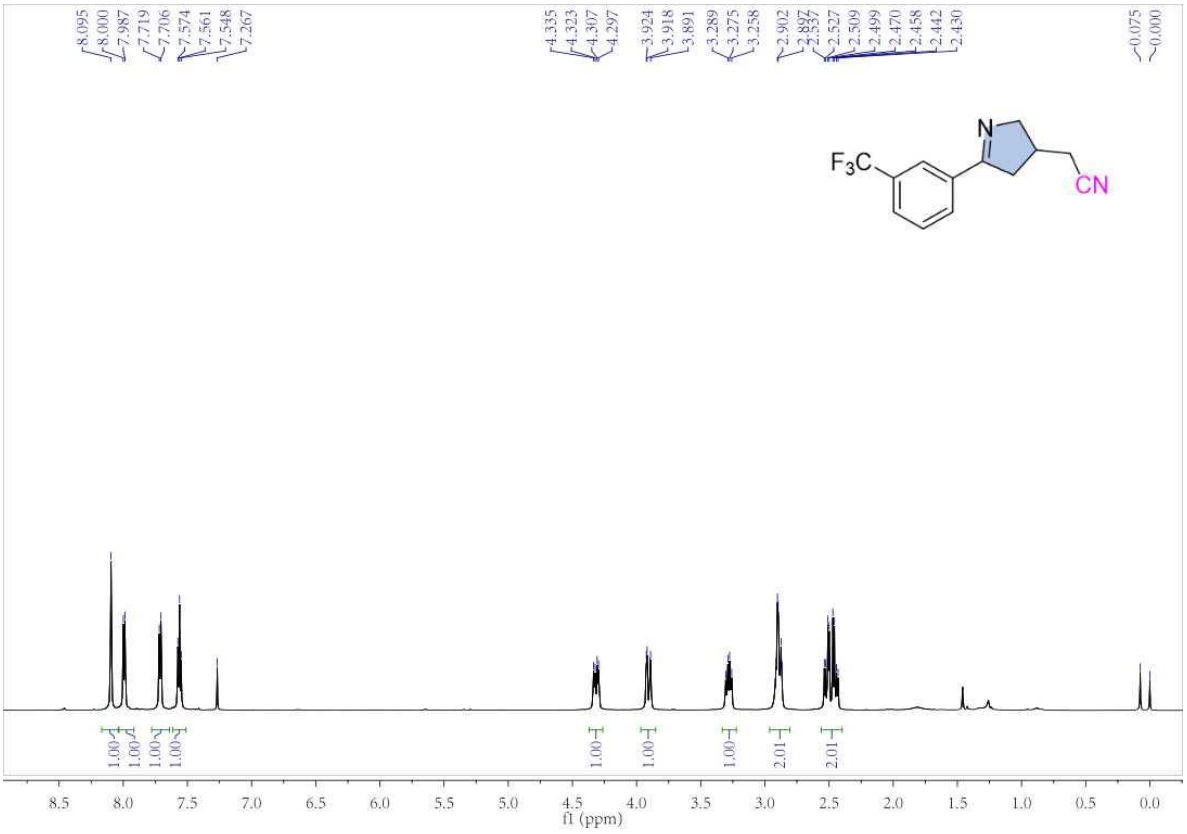
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4j



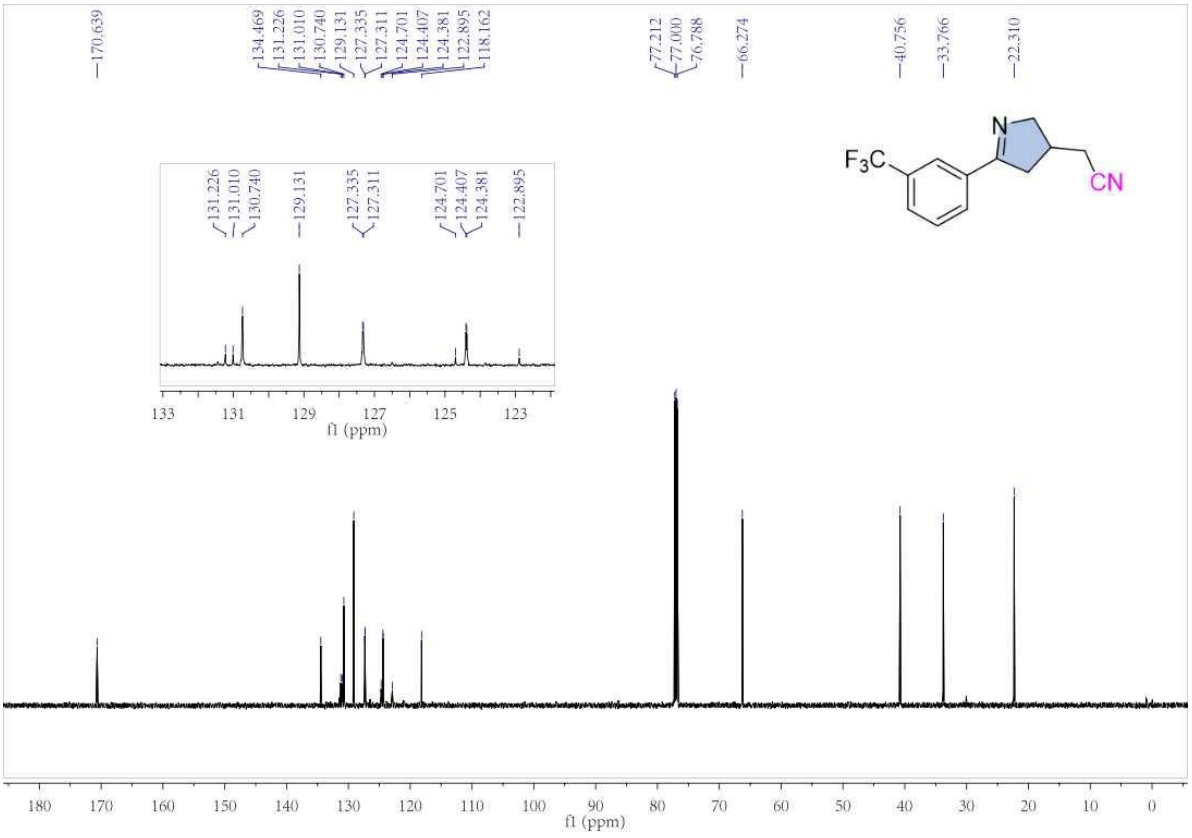
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4j



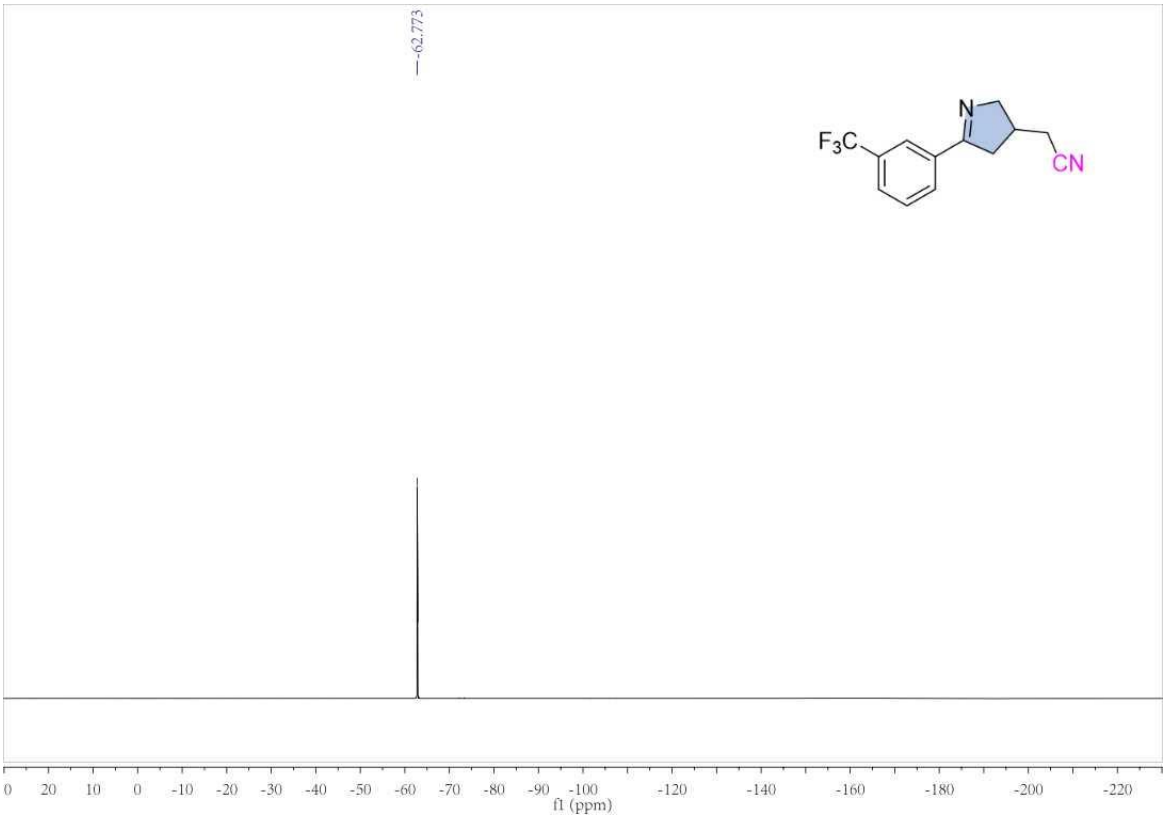
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4k



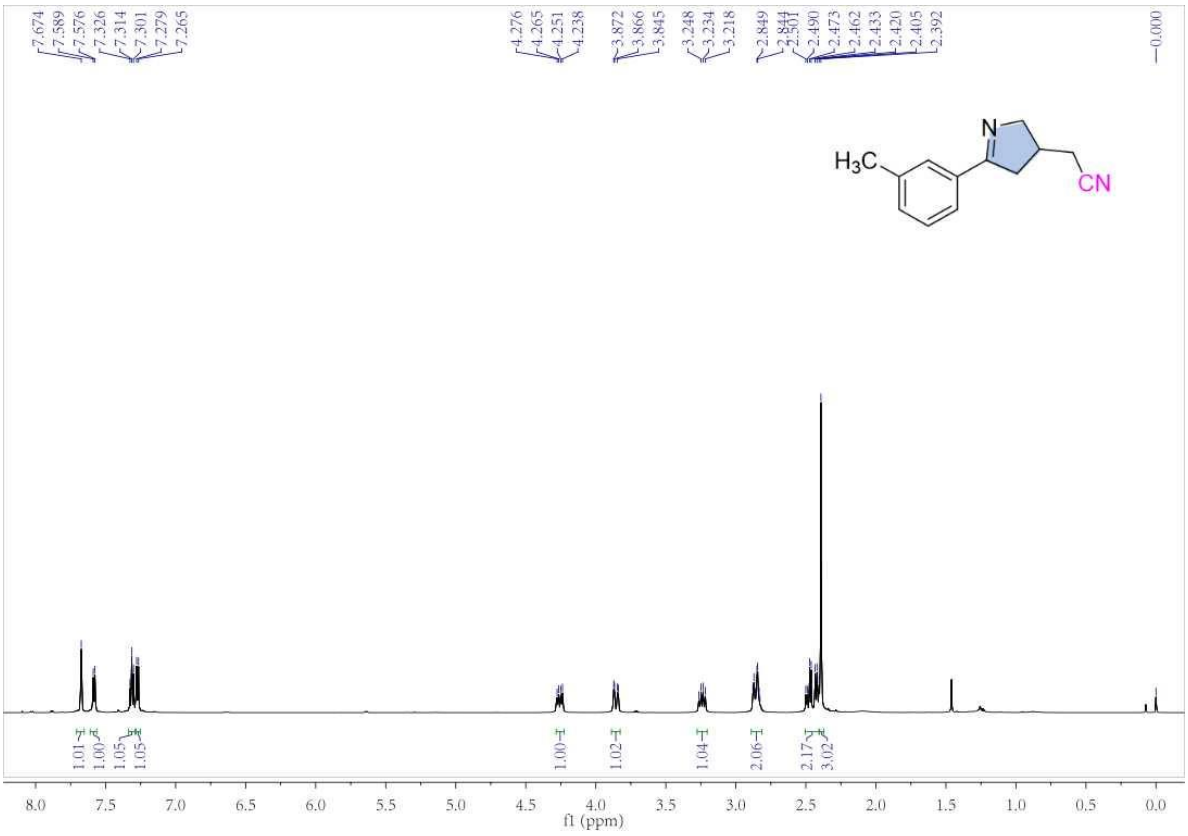
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4k



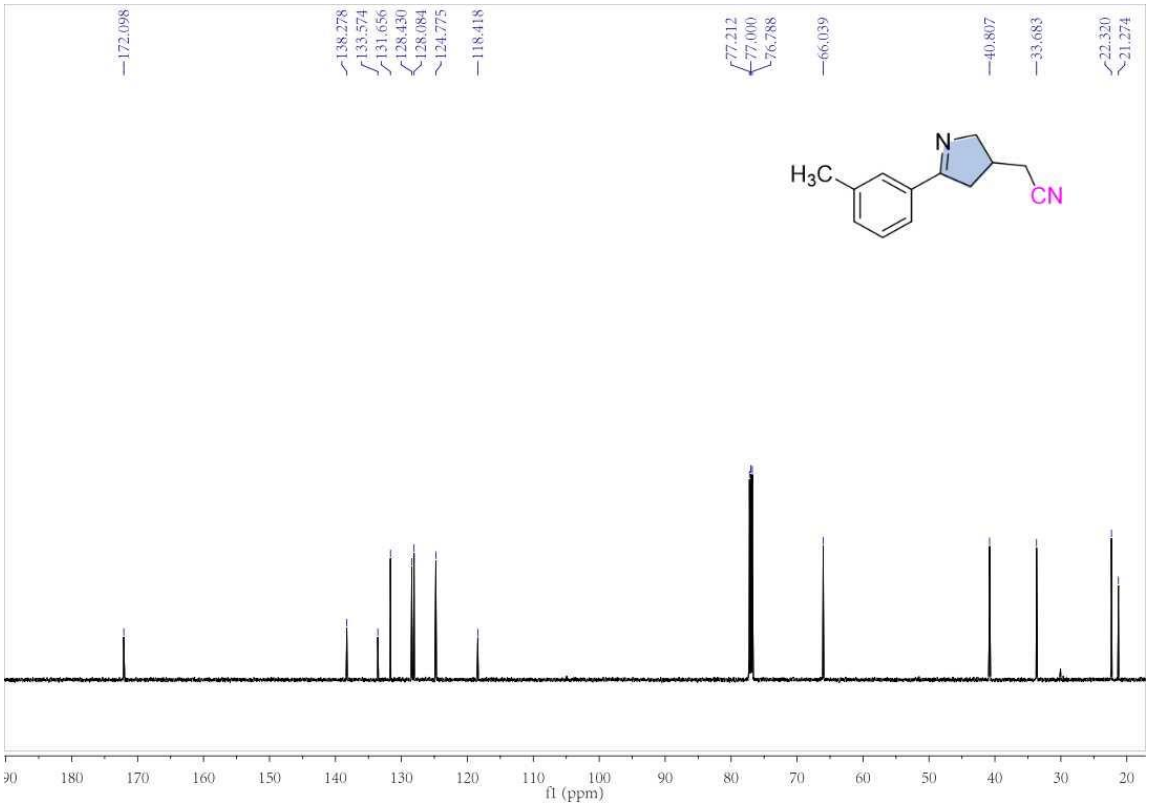
^{19}F spectrum (565 MHz, $CDCl_3$) of compound 4k



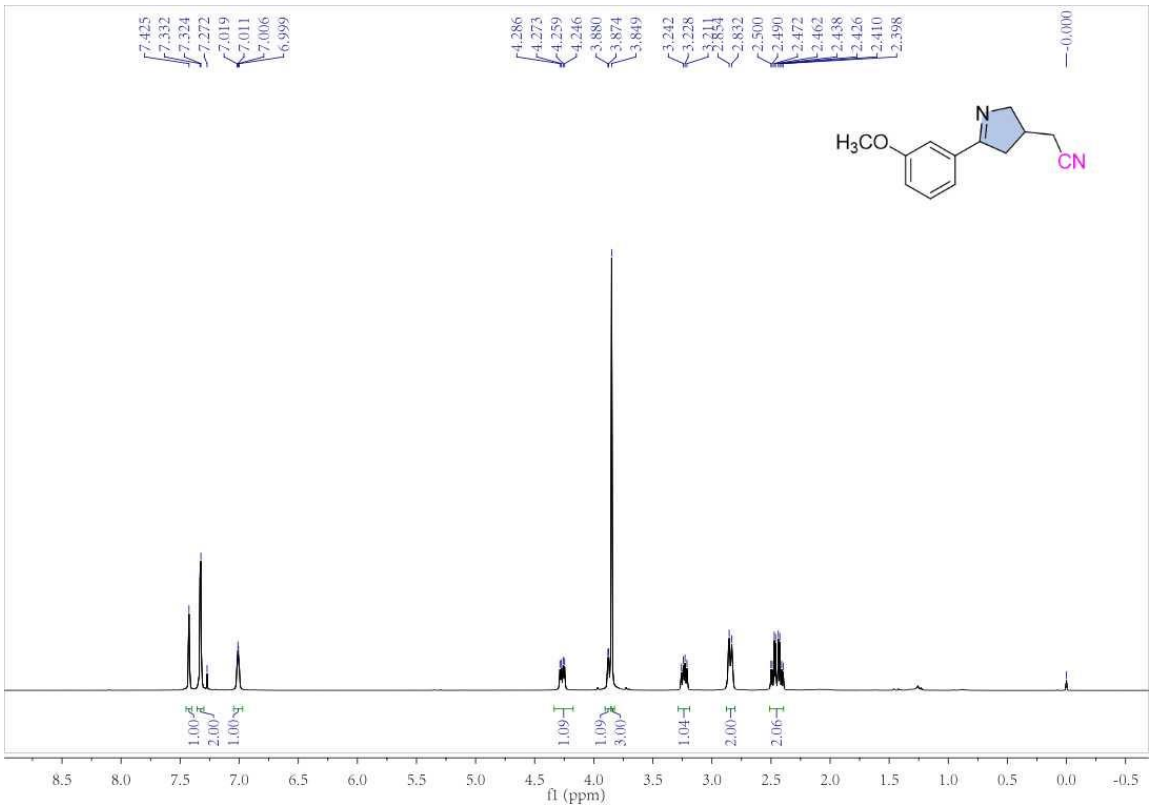
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4l



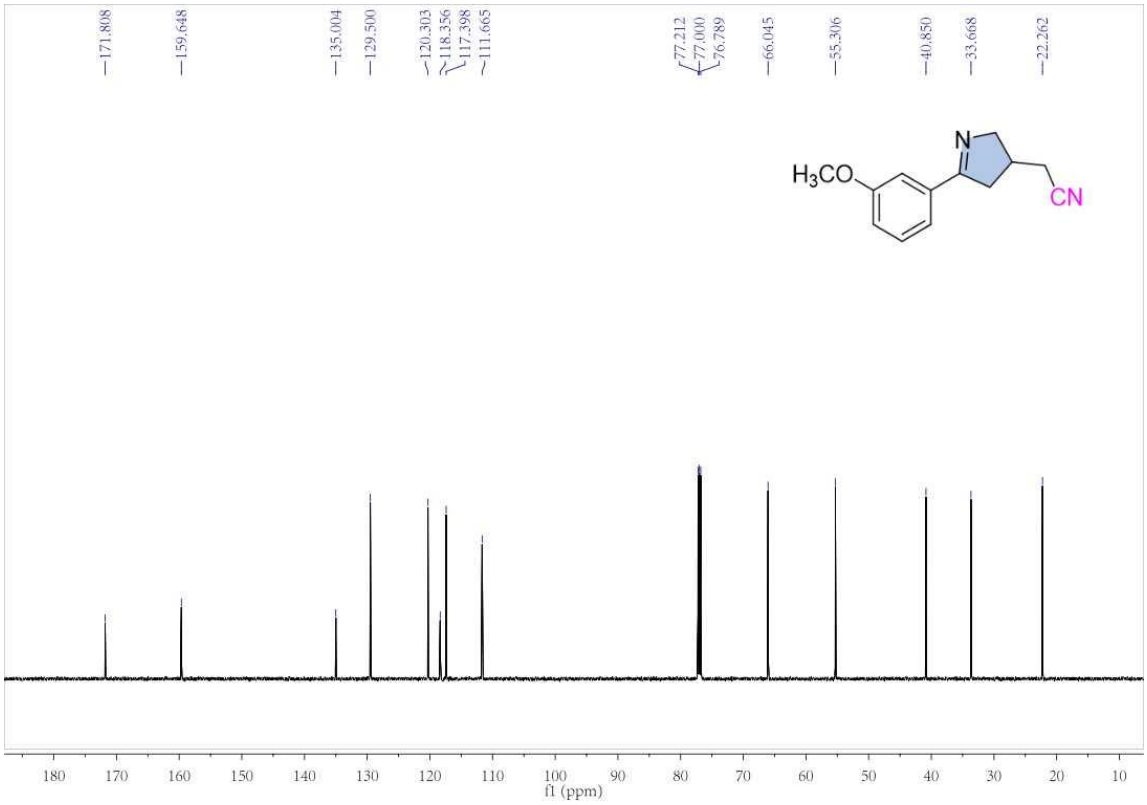
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4l



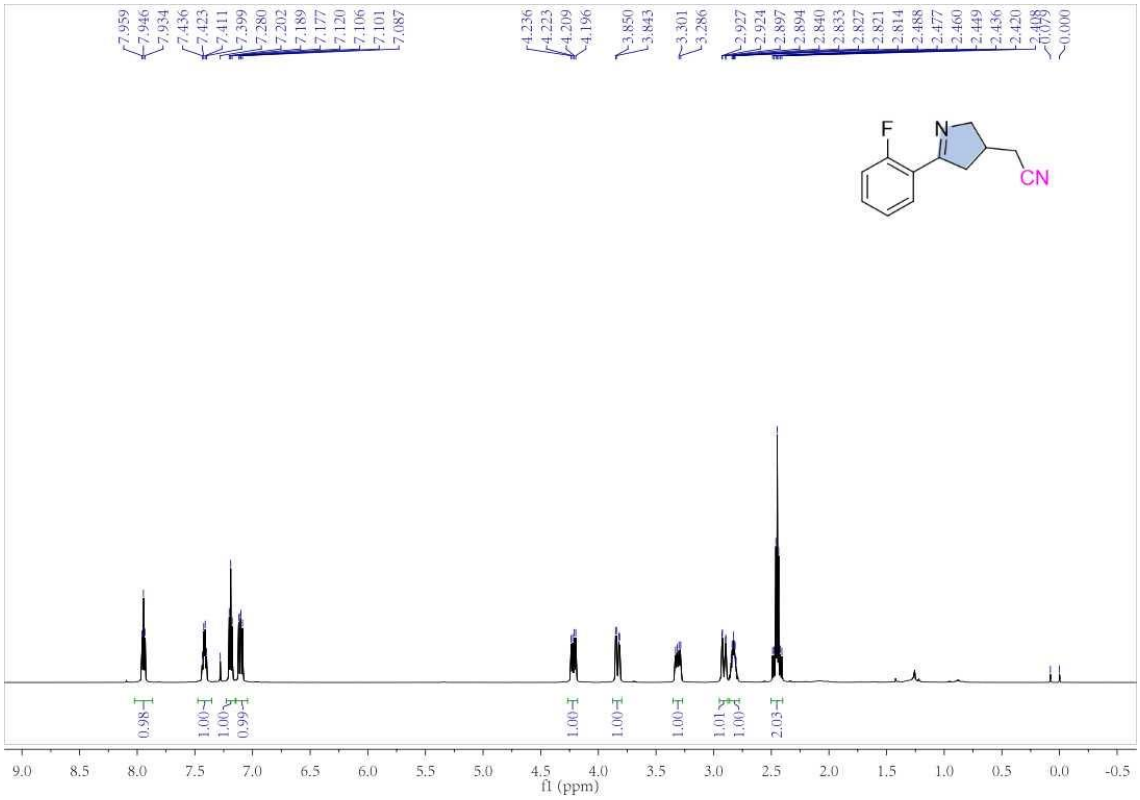
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4m



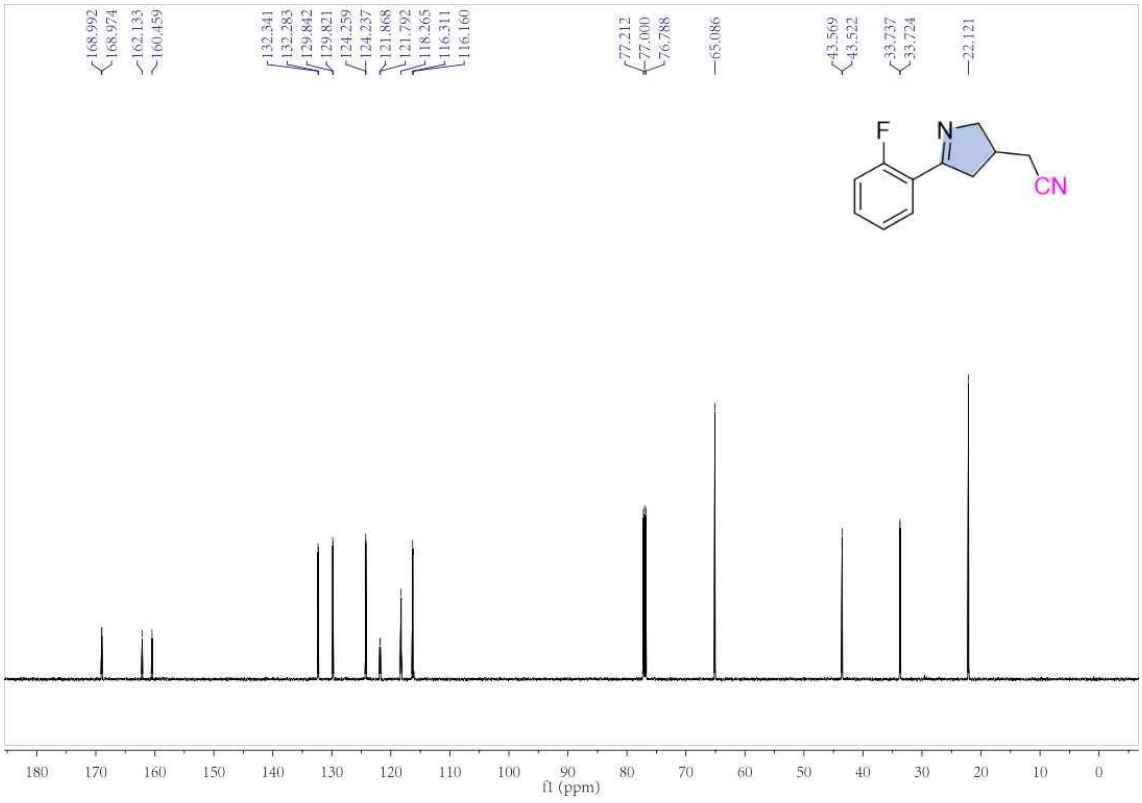
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4m



^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4n

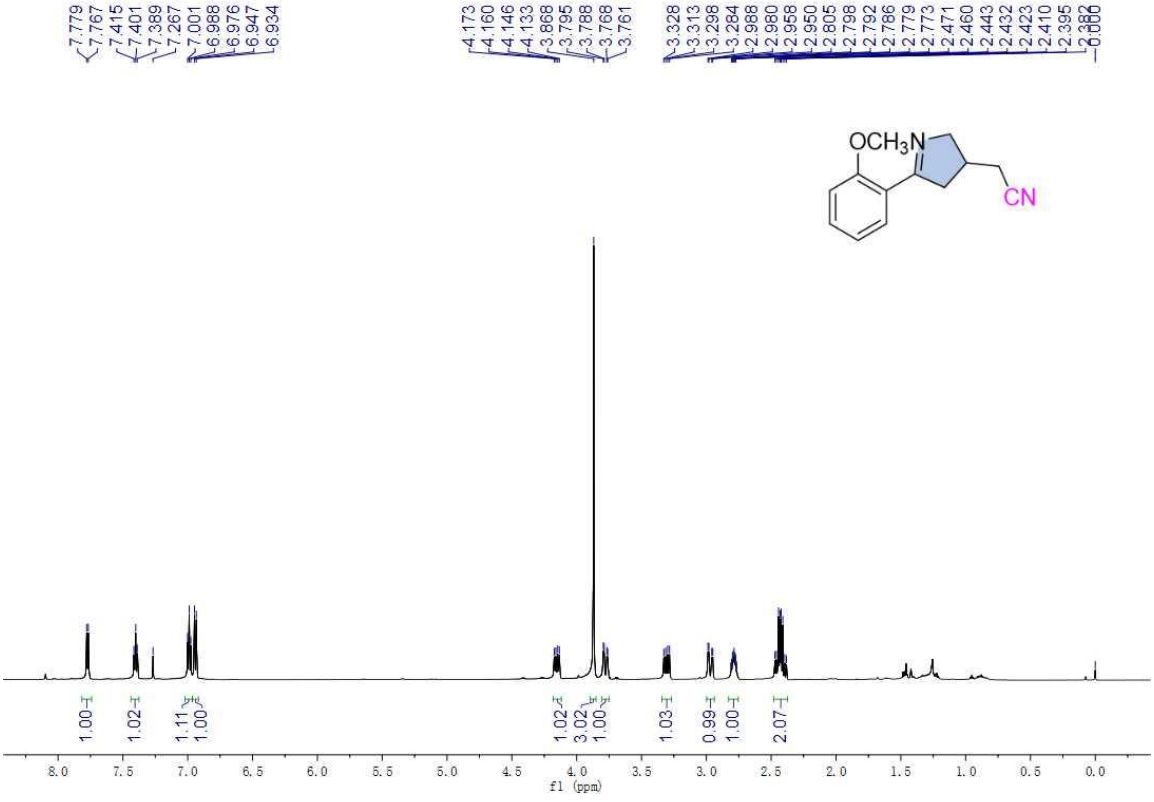


^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4n

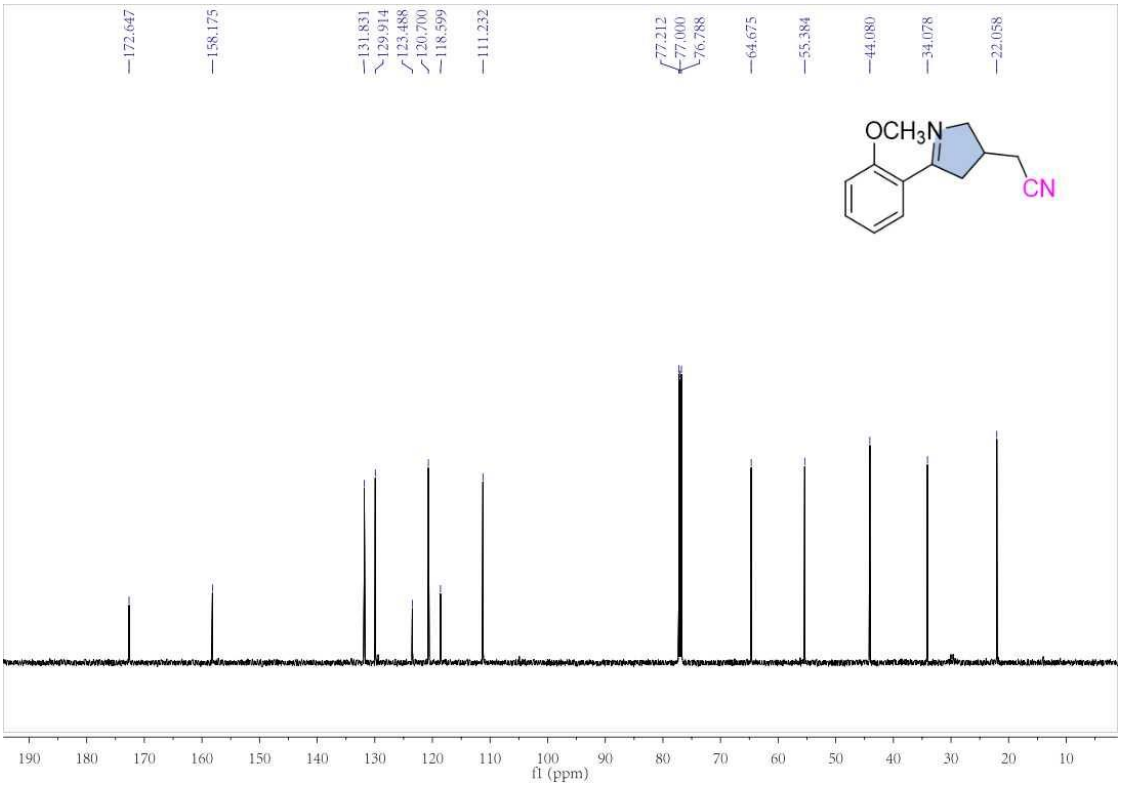


^{19}F spectrum (565 MHz, $CDCl_3$) of compound 4n

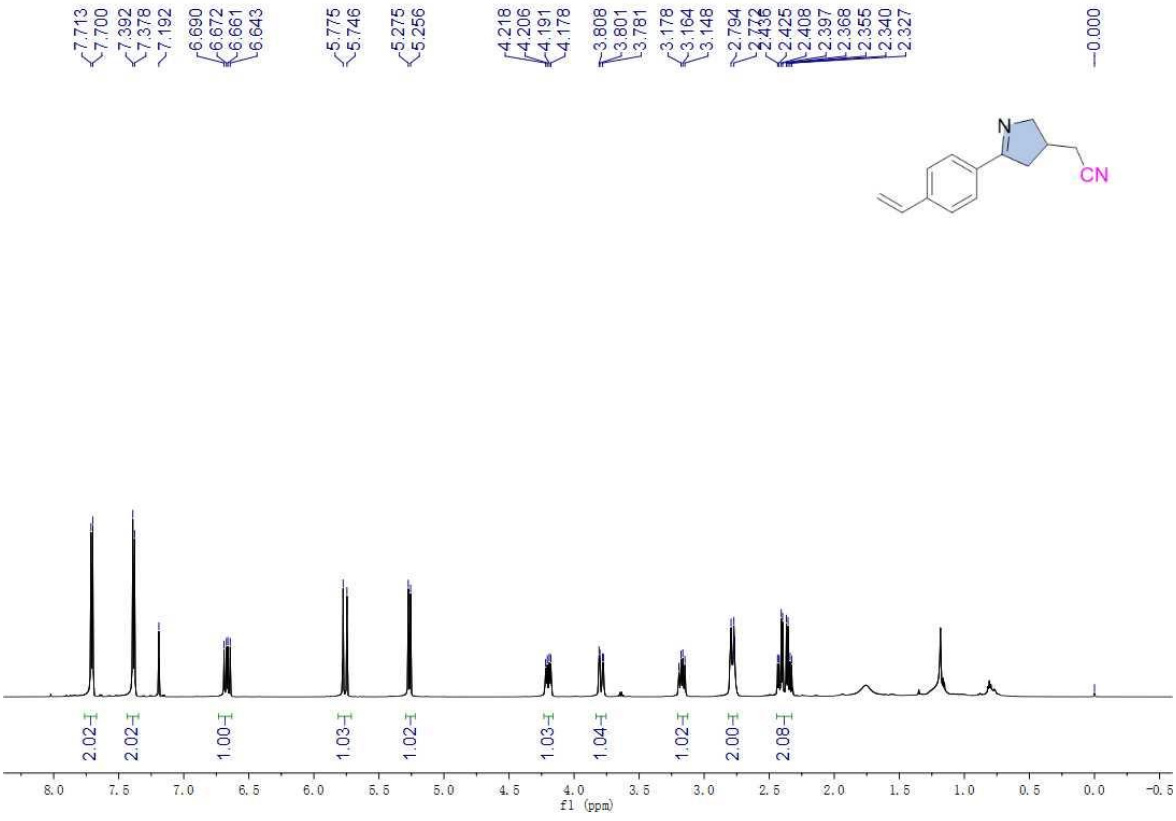
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4o



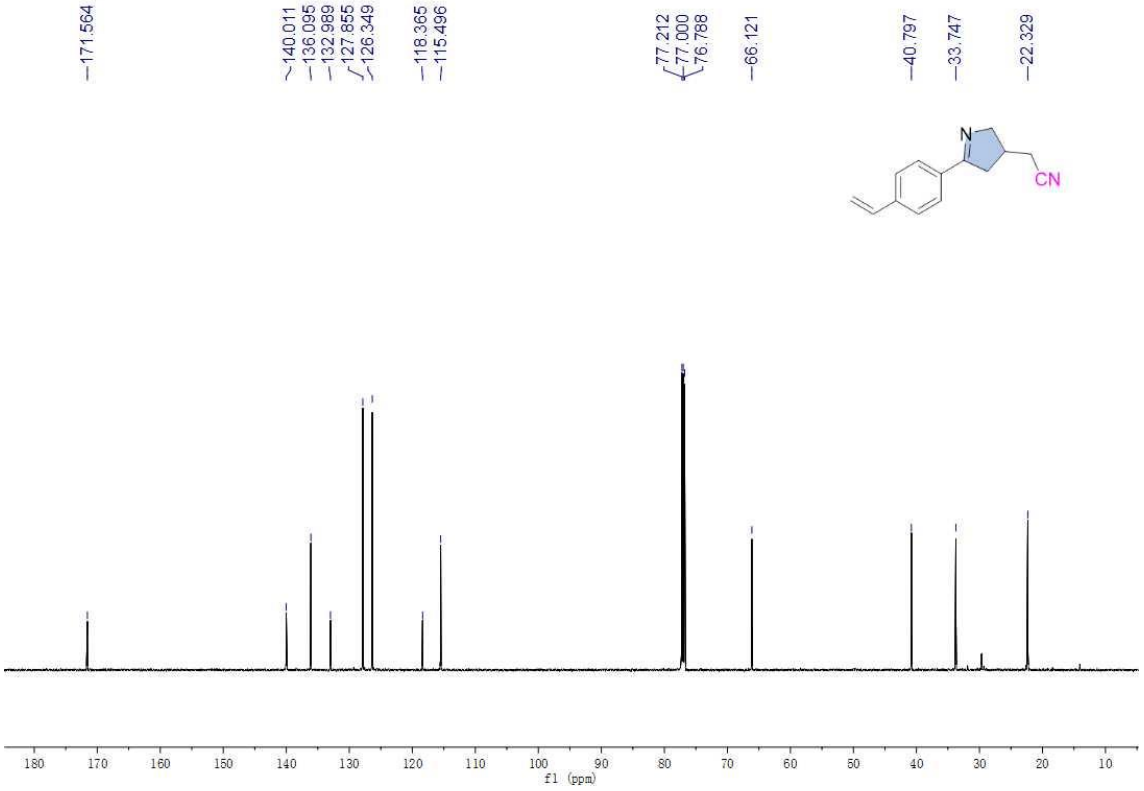
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4o



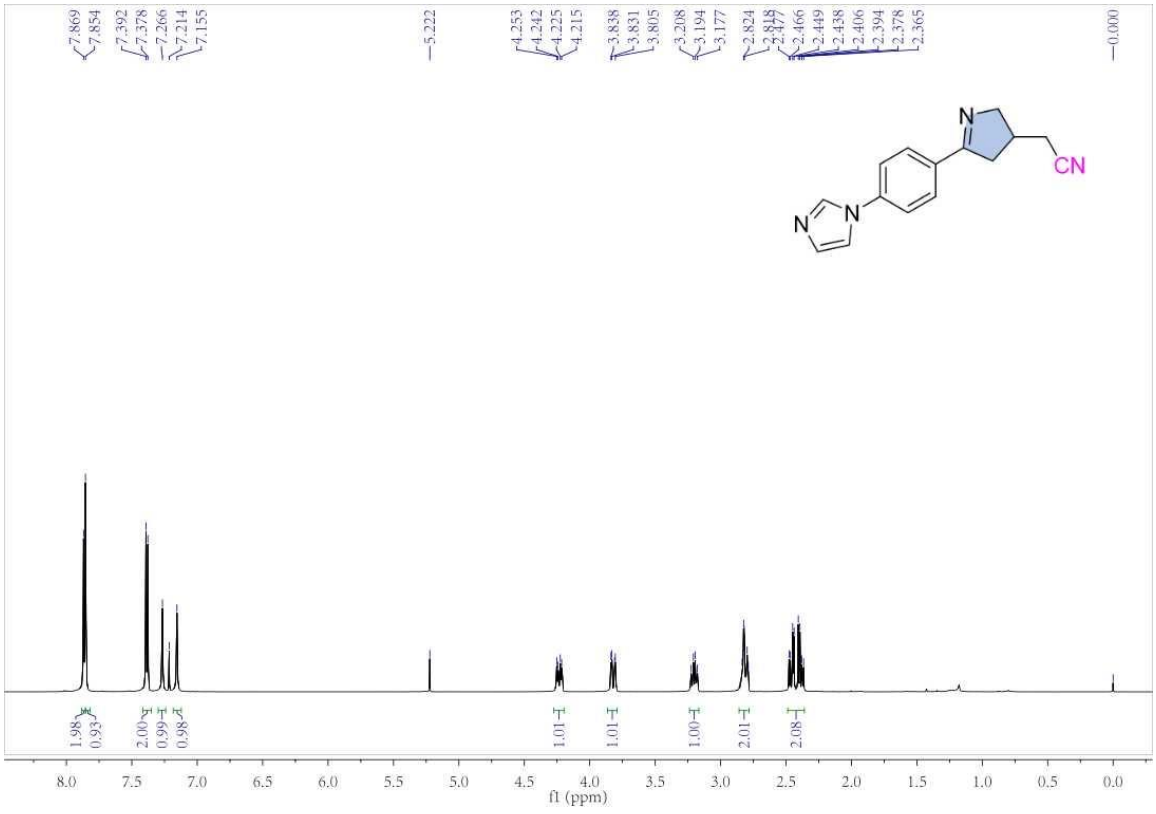
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4p



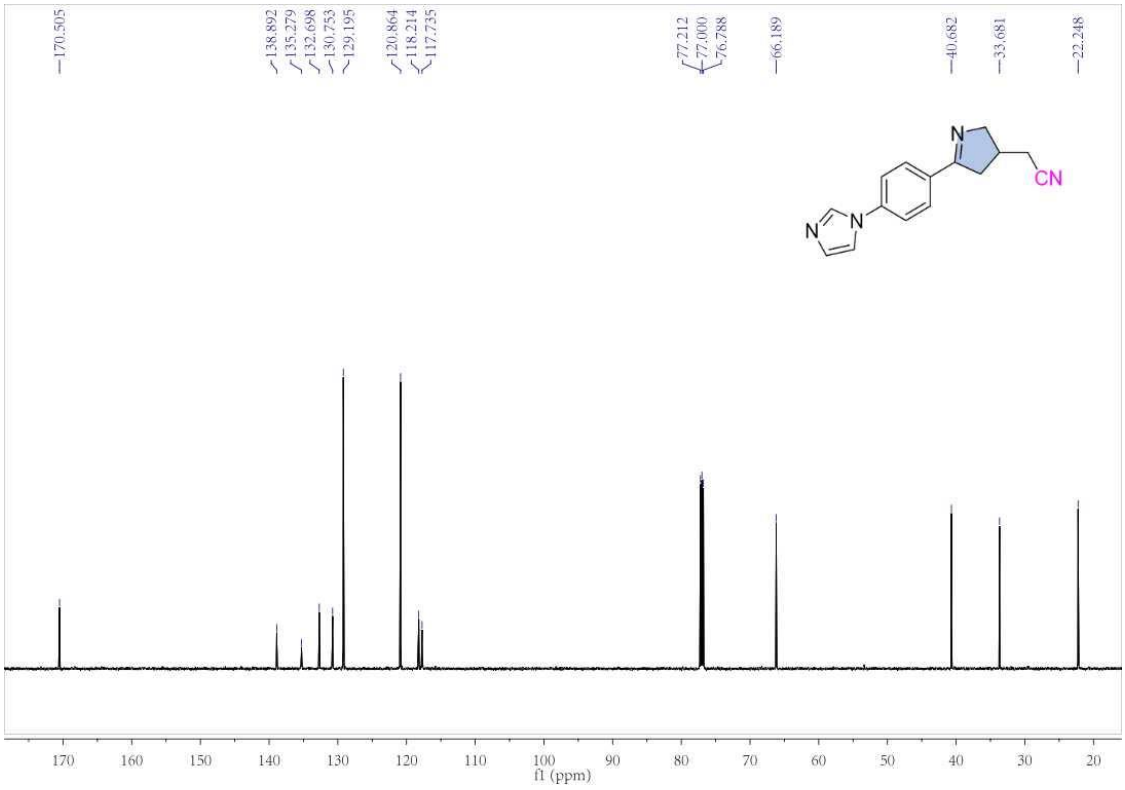
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4p



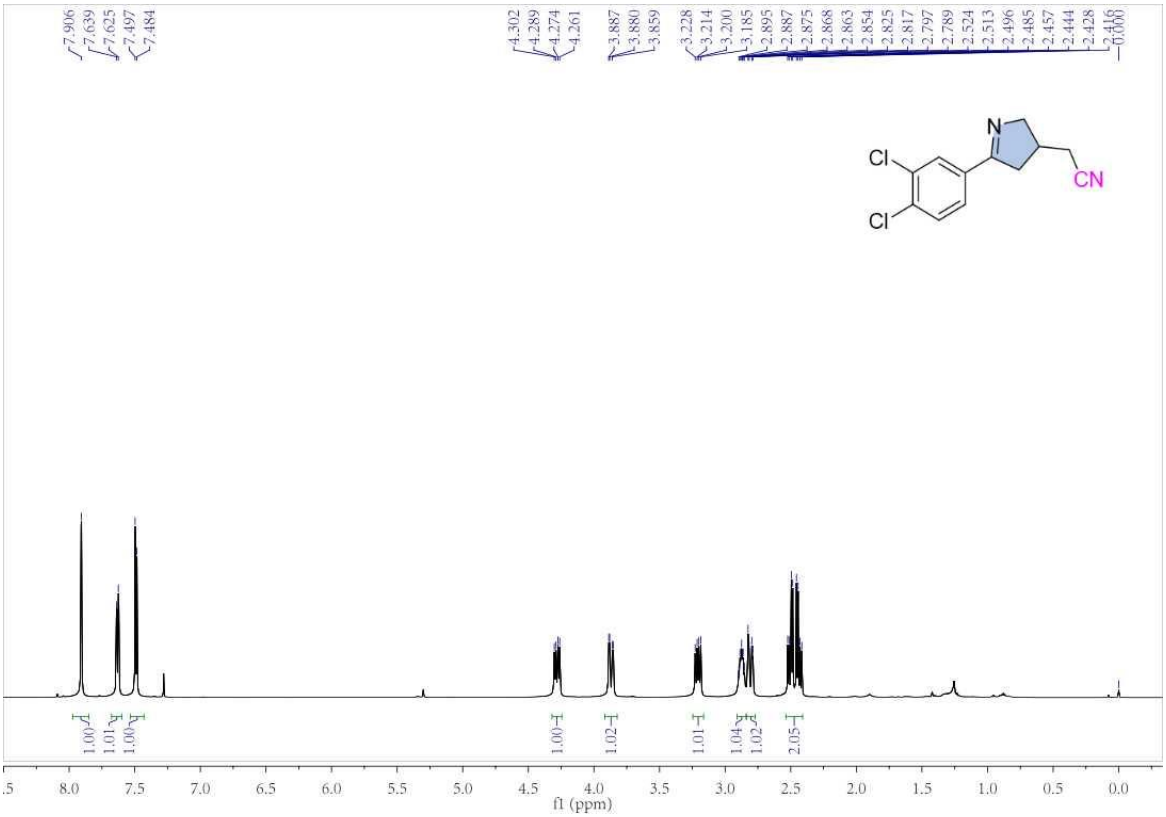
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4q



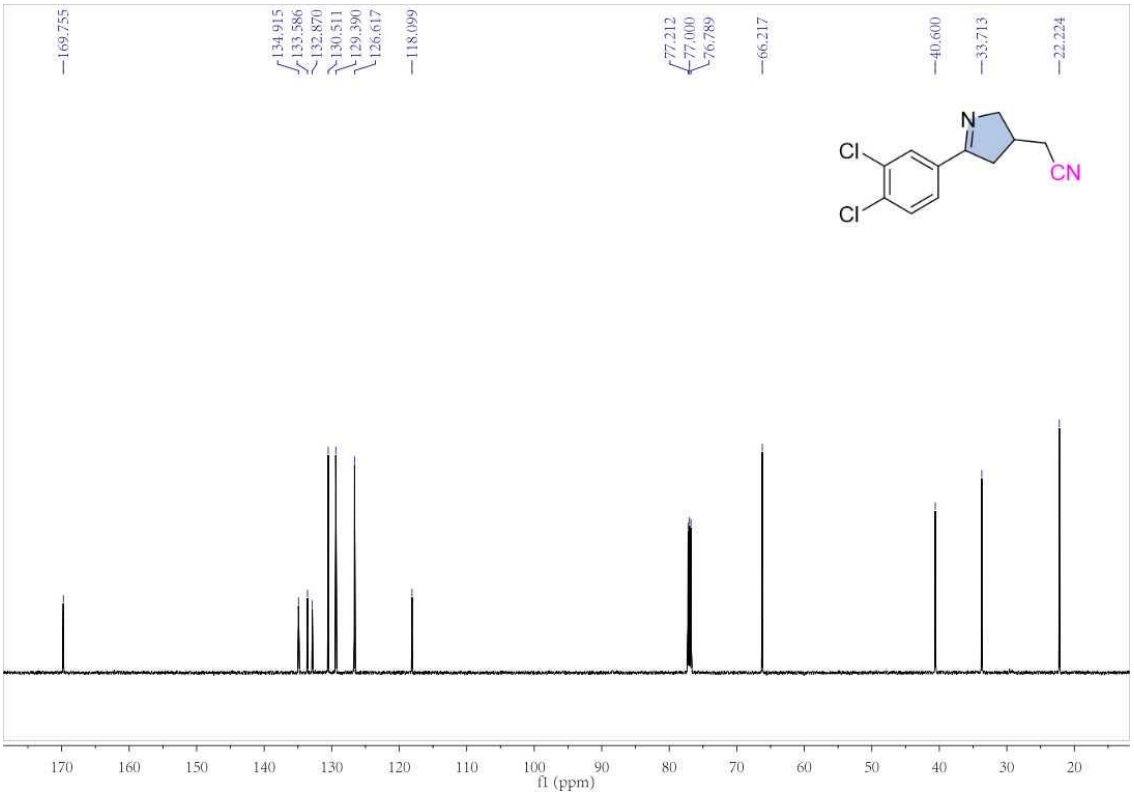
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4q



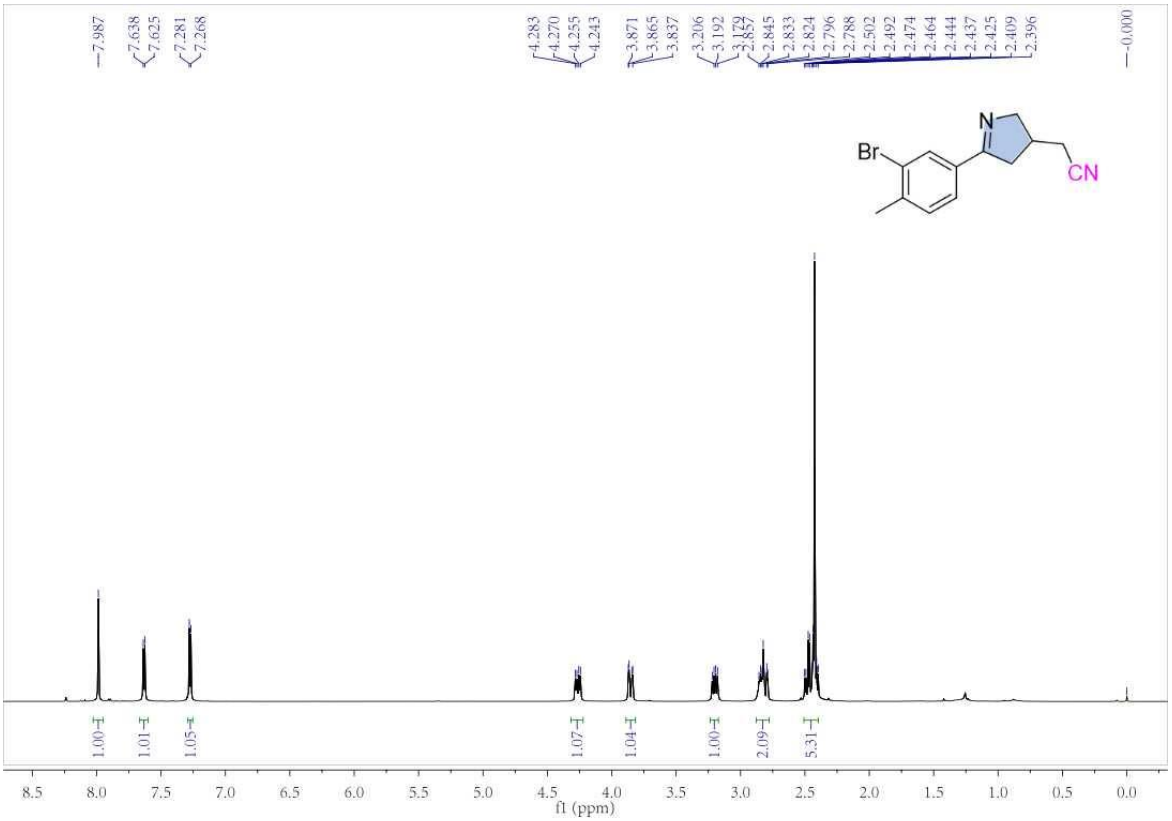
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4r



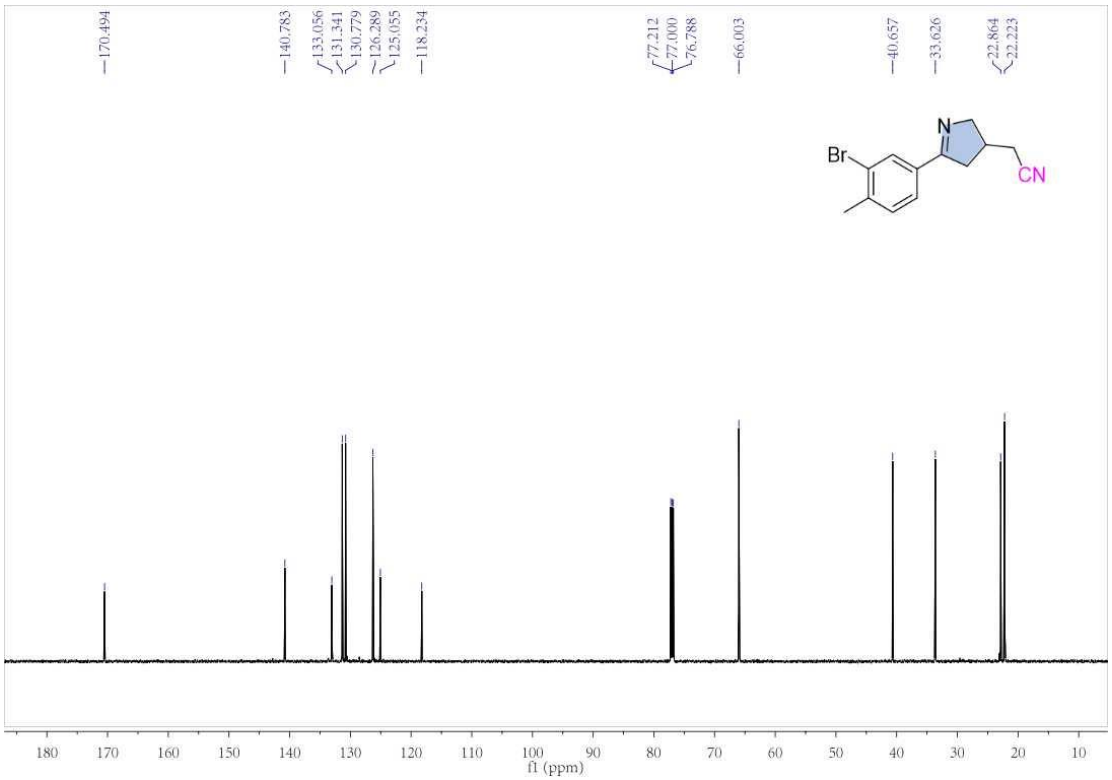
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4r



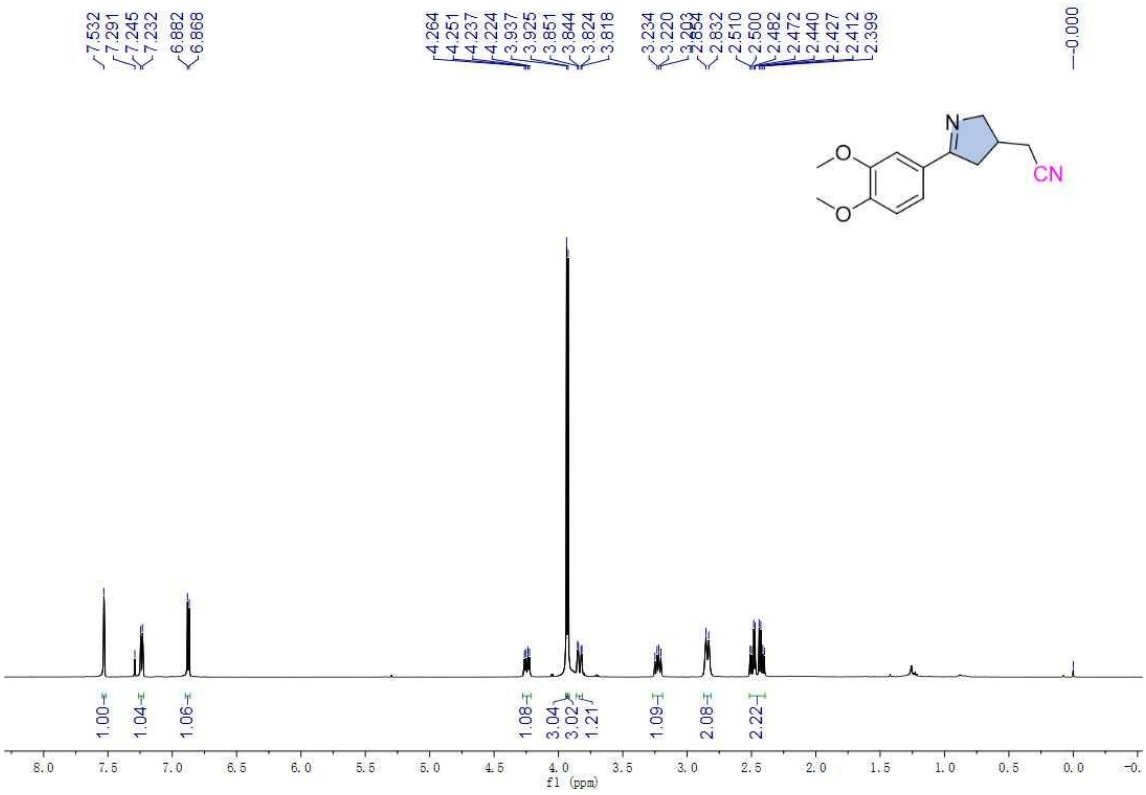
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4s



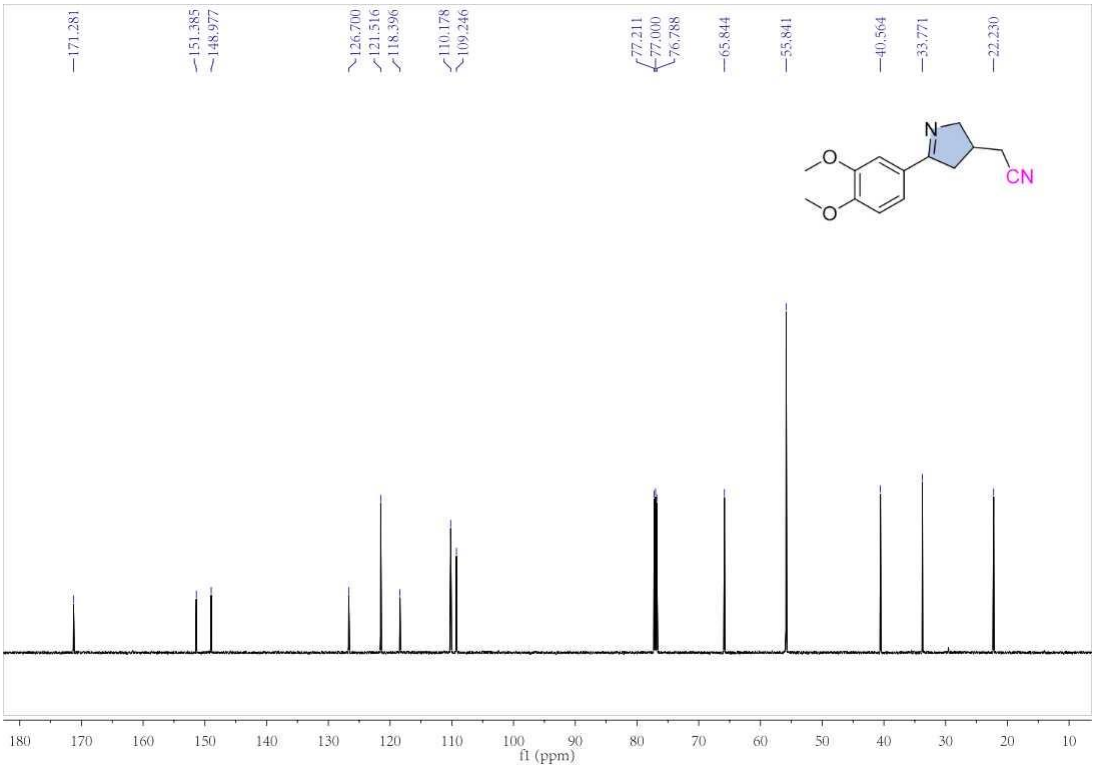
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4s



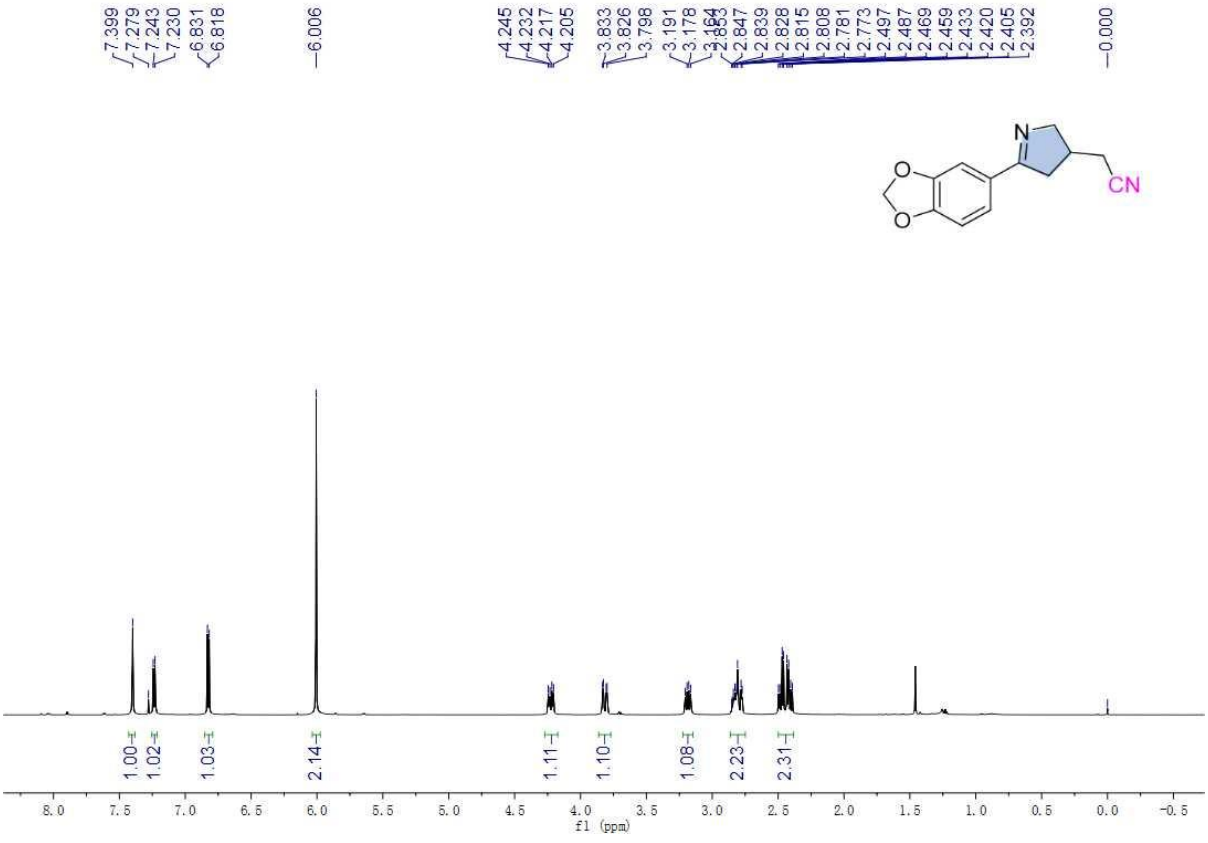
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4t



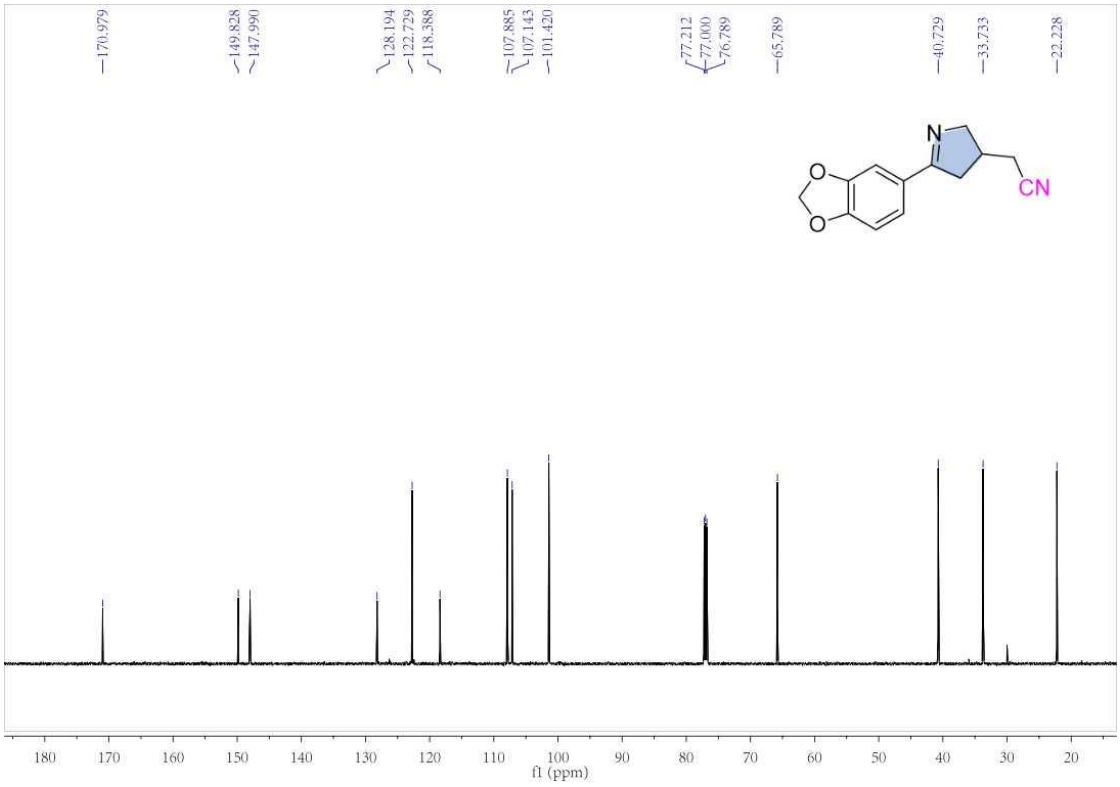
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4t



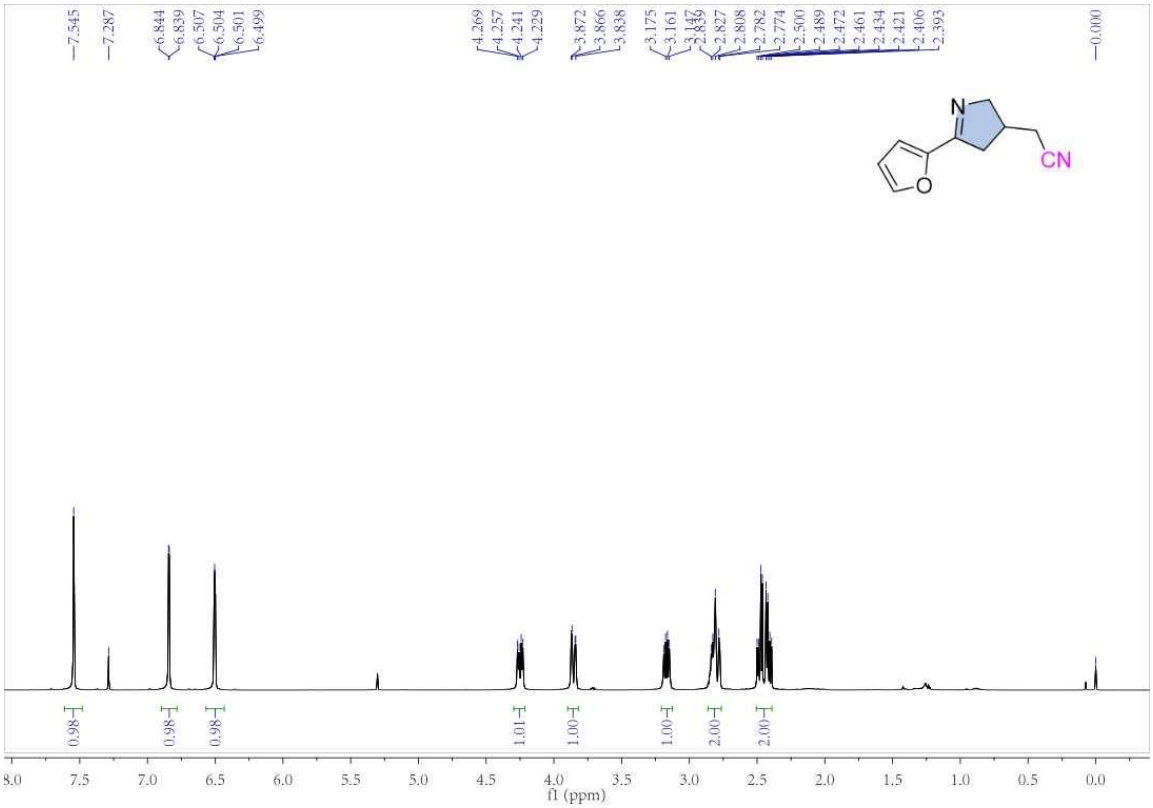
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4u



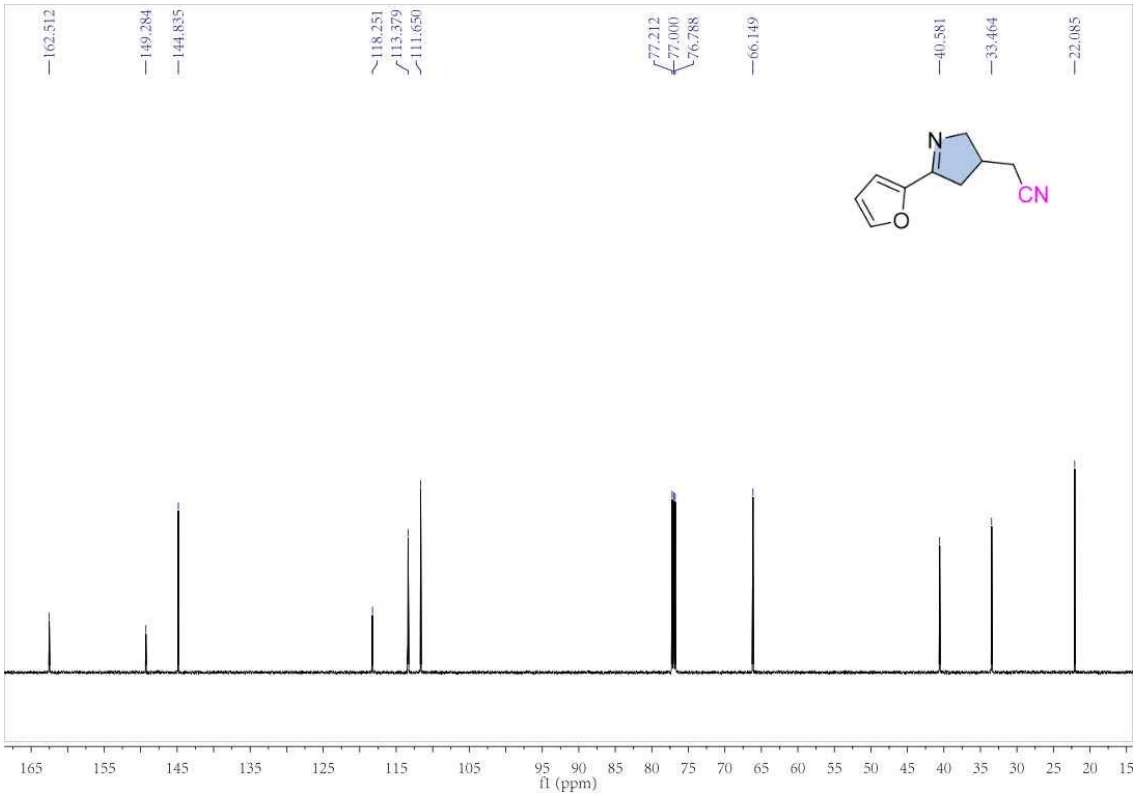
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4u



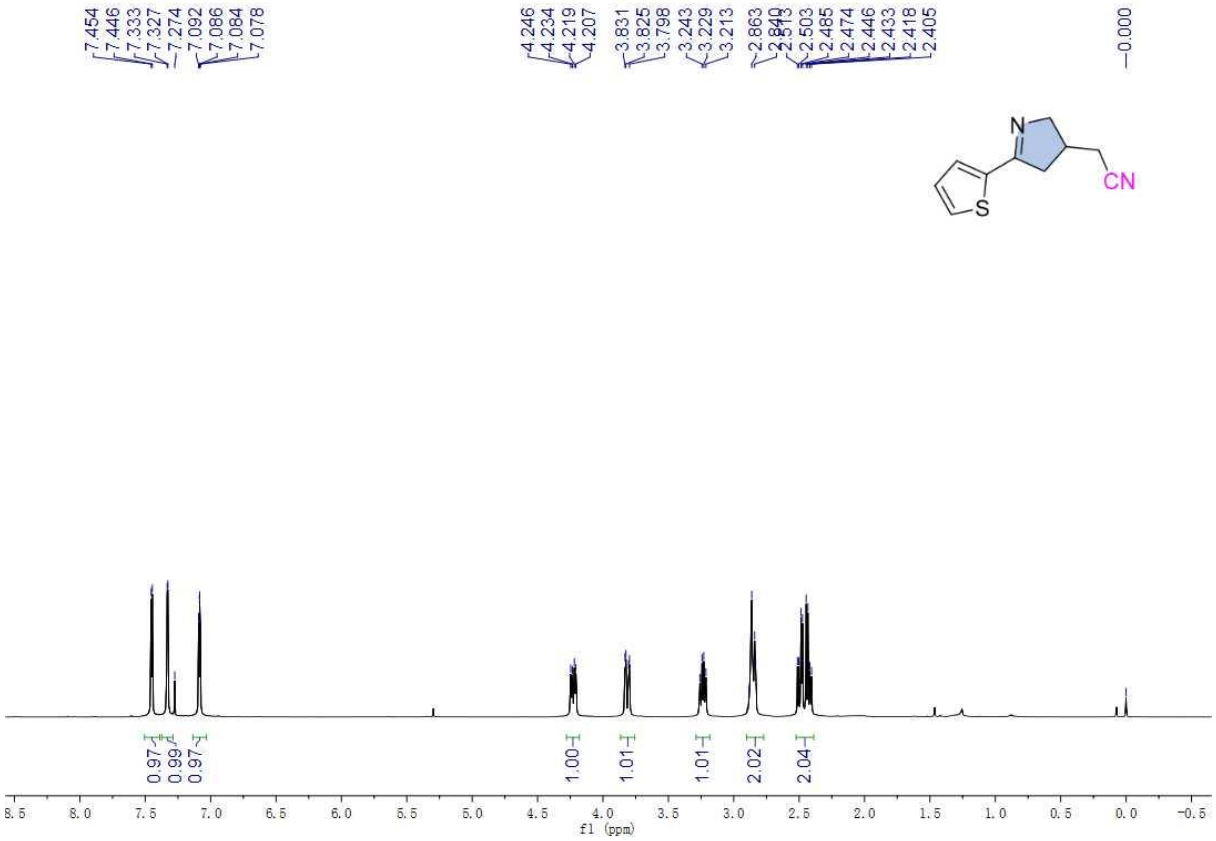
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4v



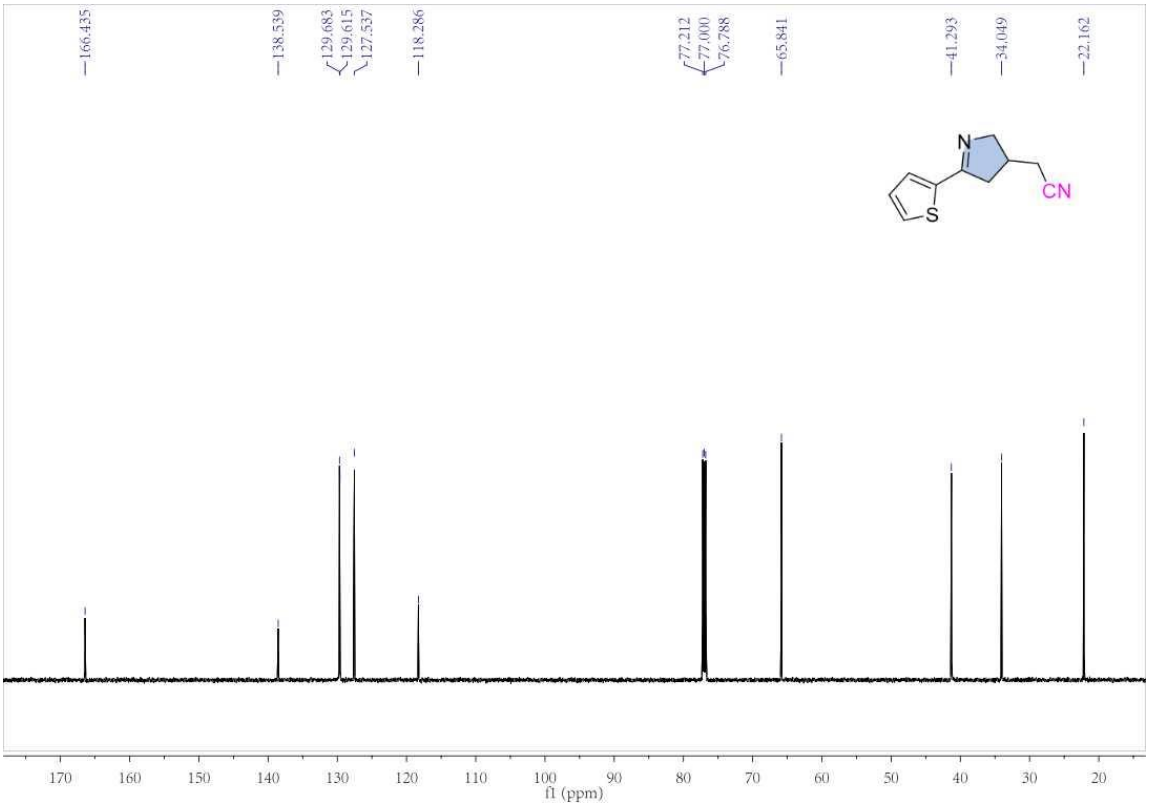
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4v



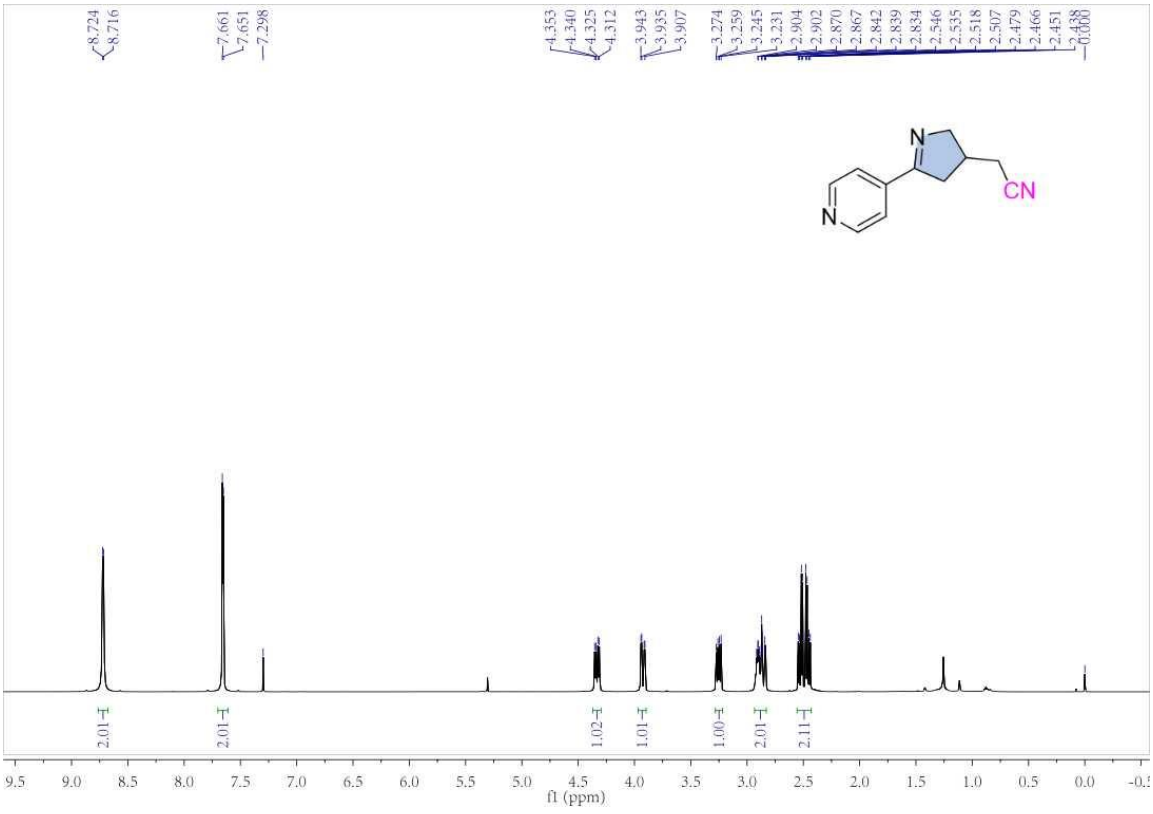
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4w



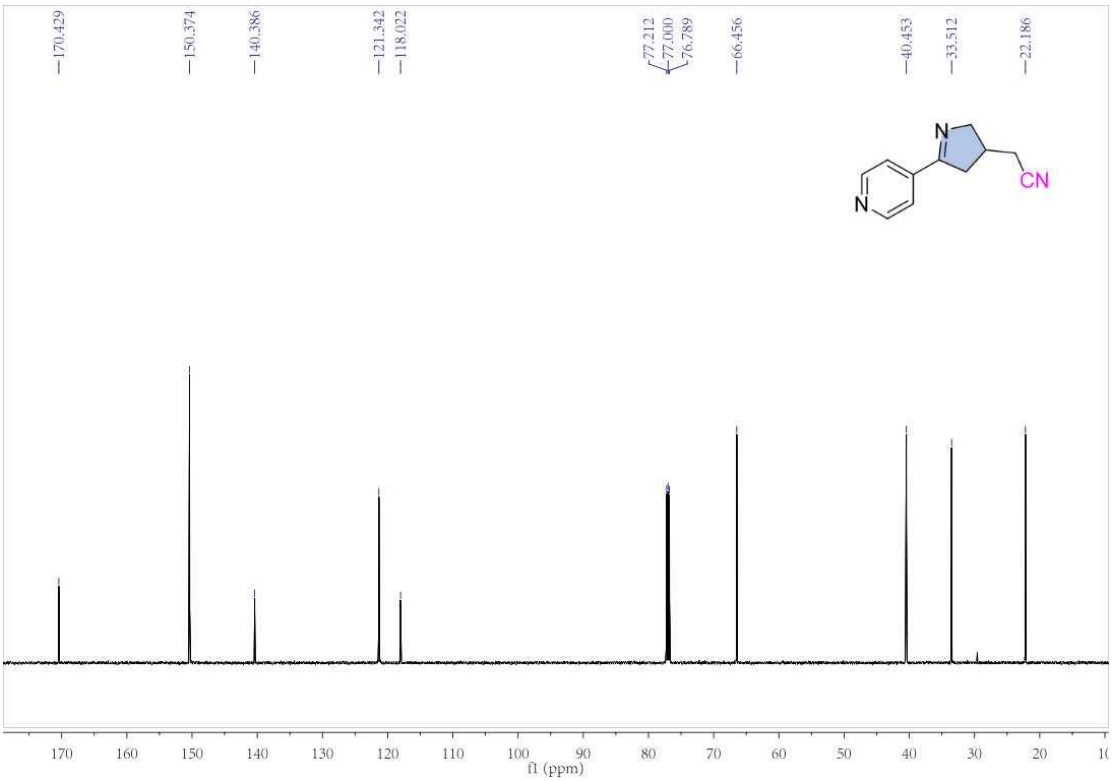
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4w



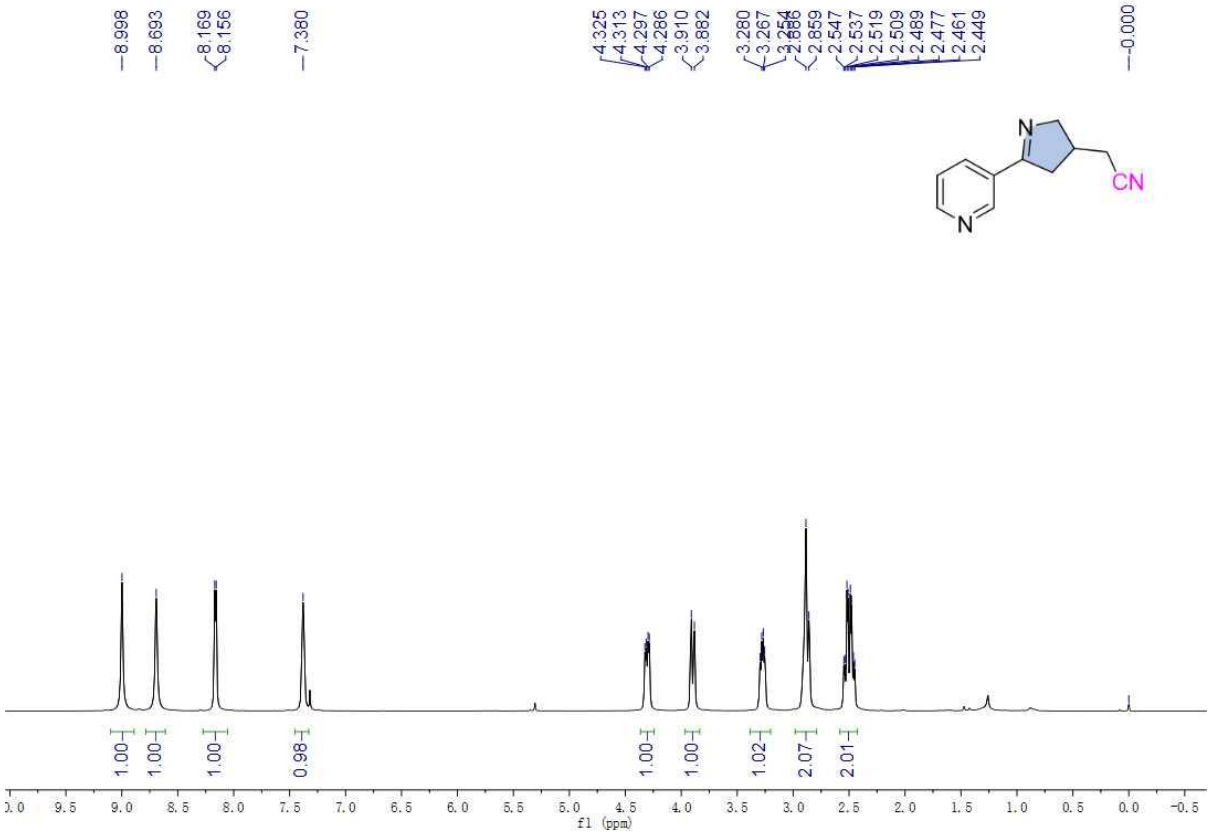
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4x



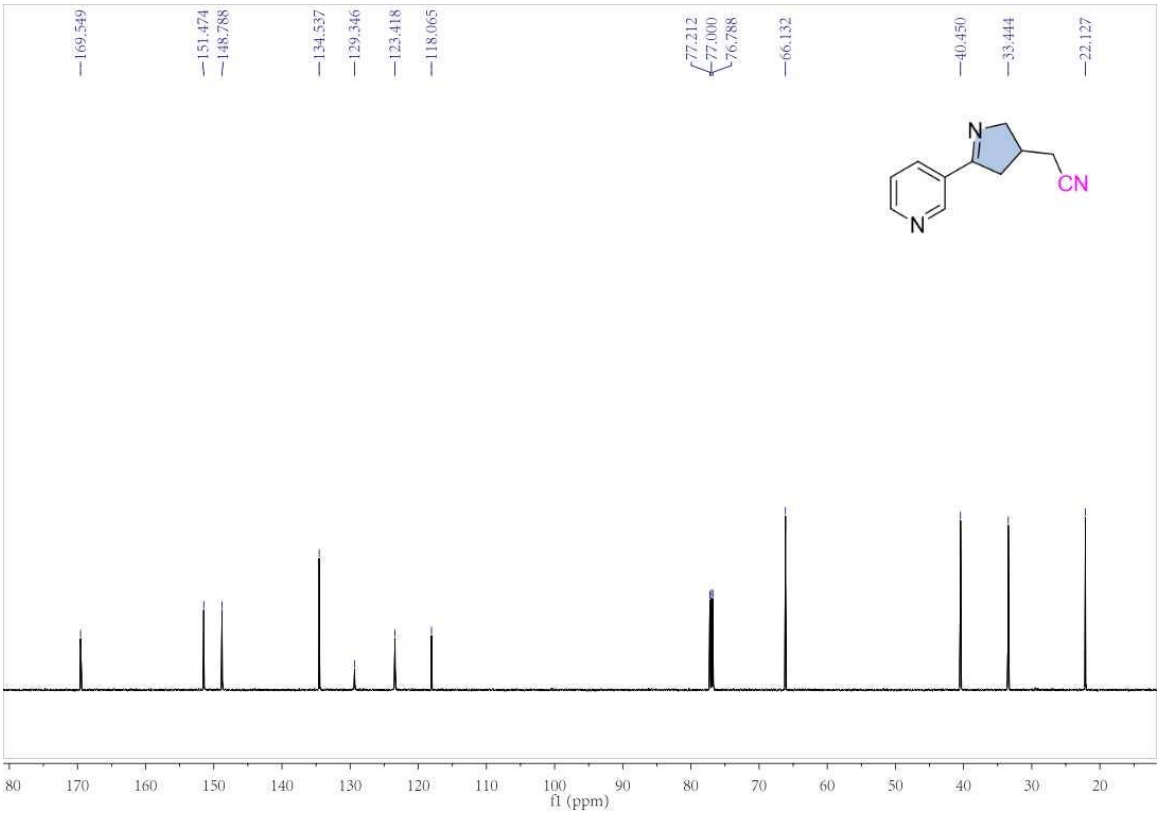
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4x



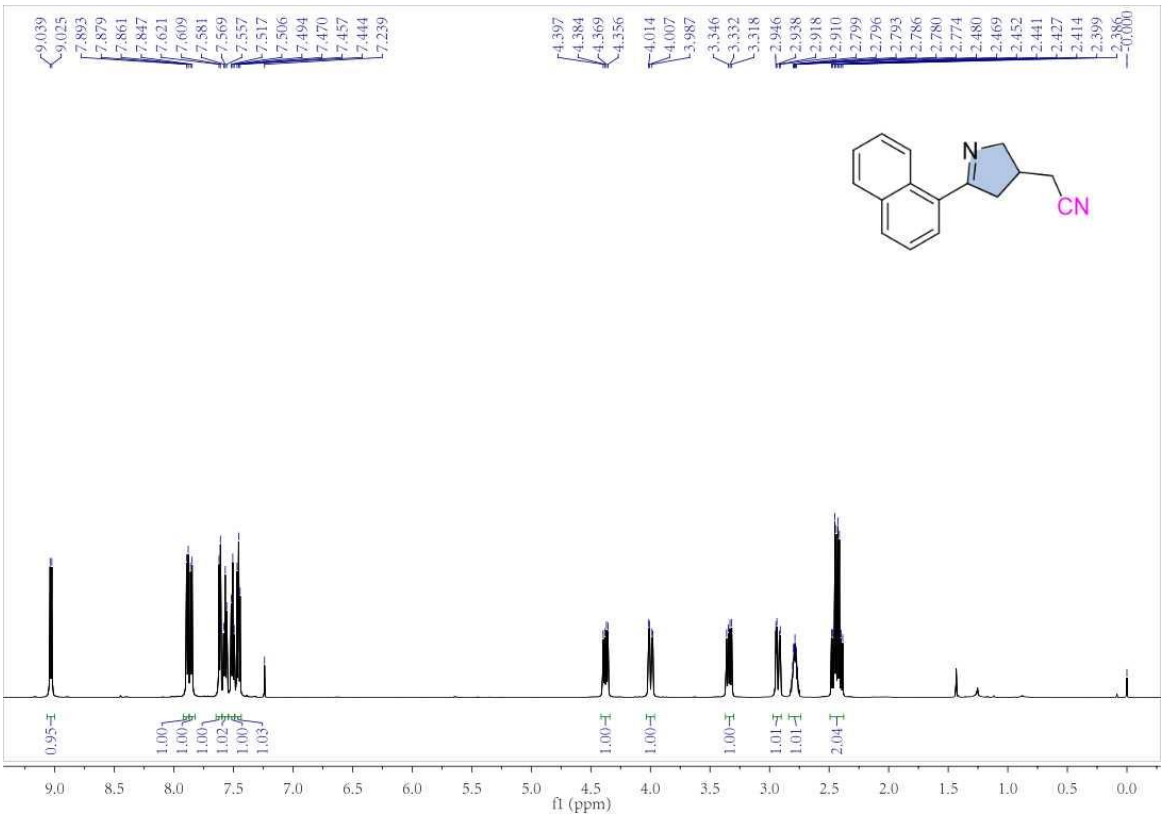
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4y



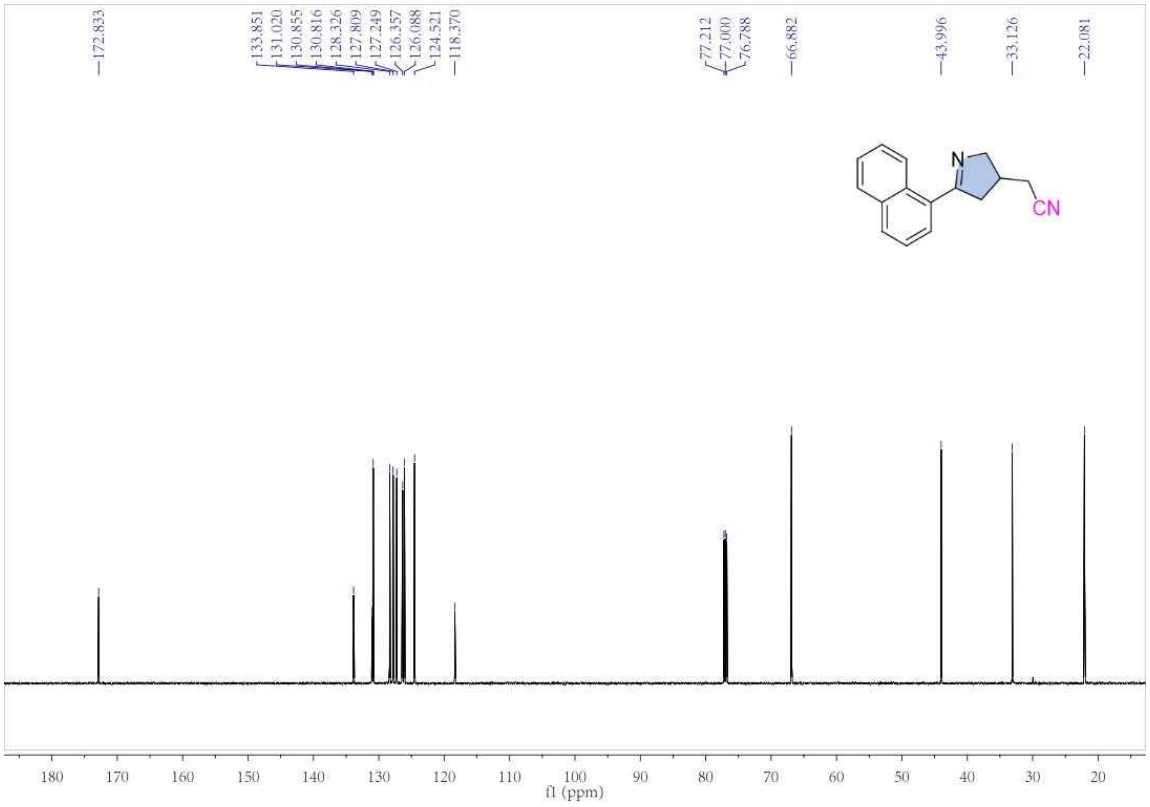
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4y



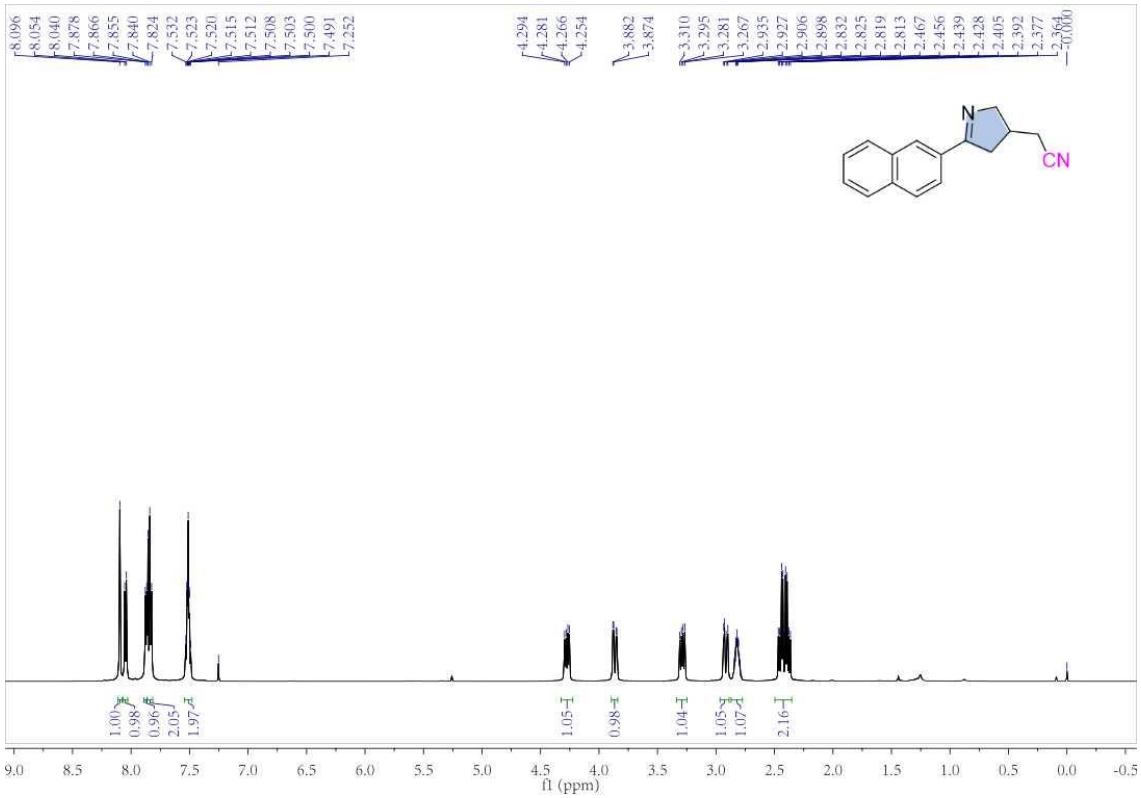
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4z



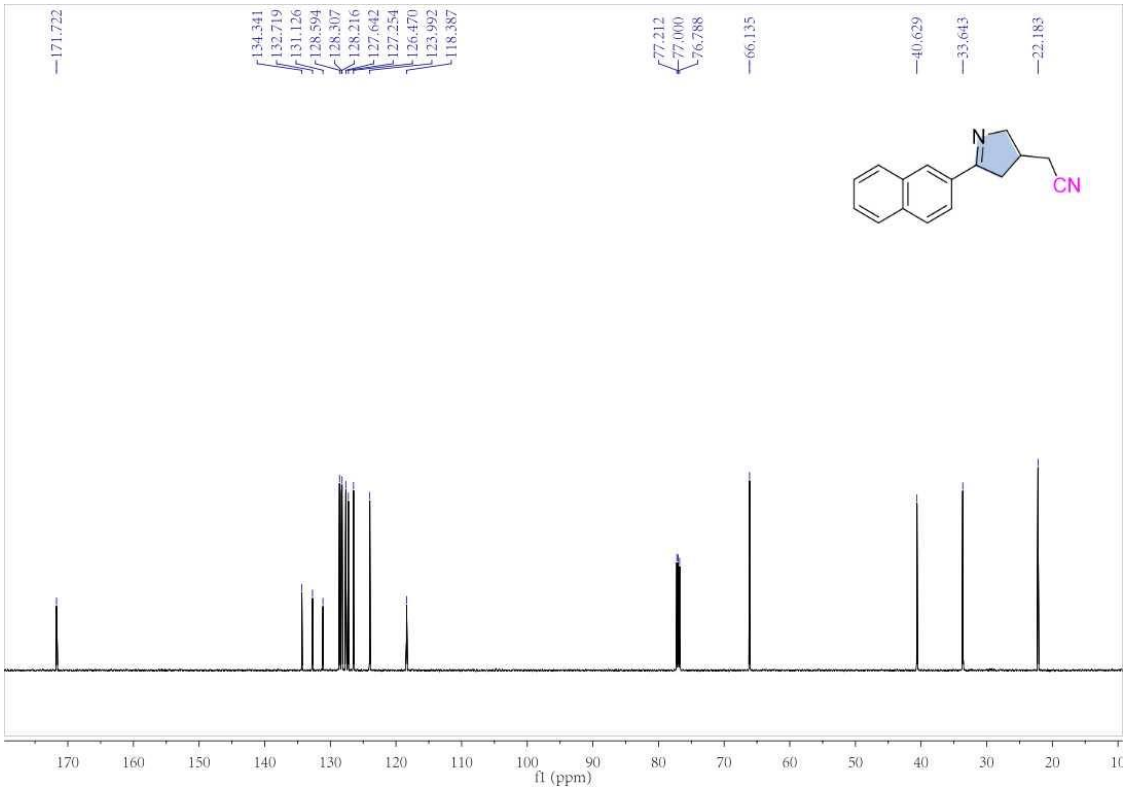
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4z



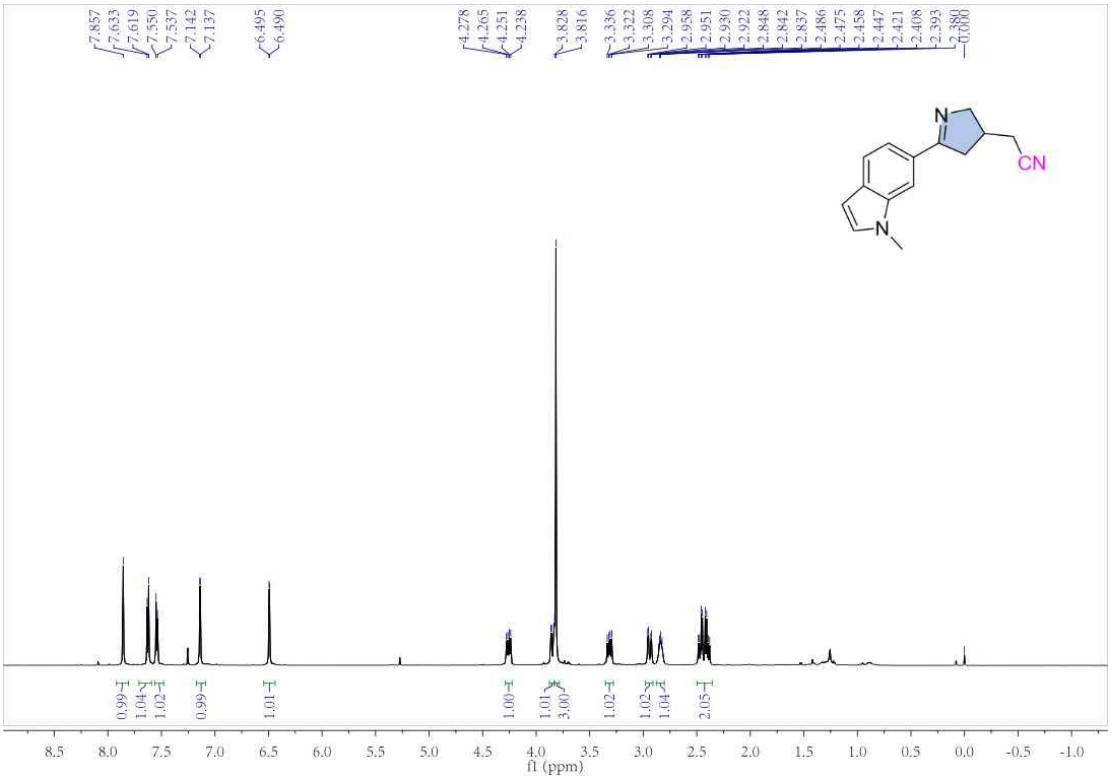
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4aa



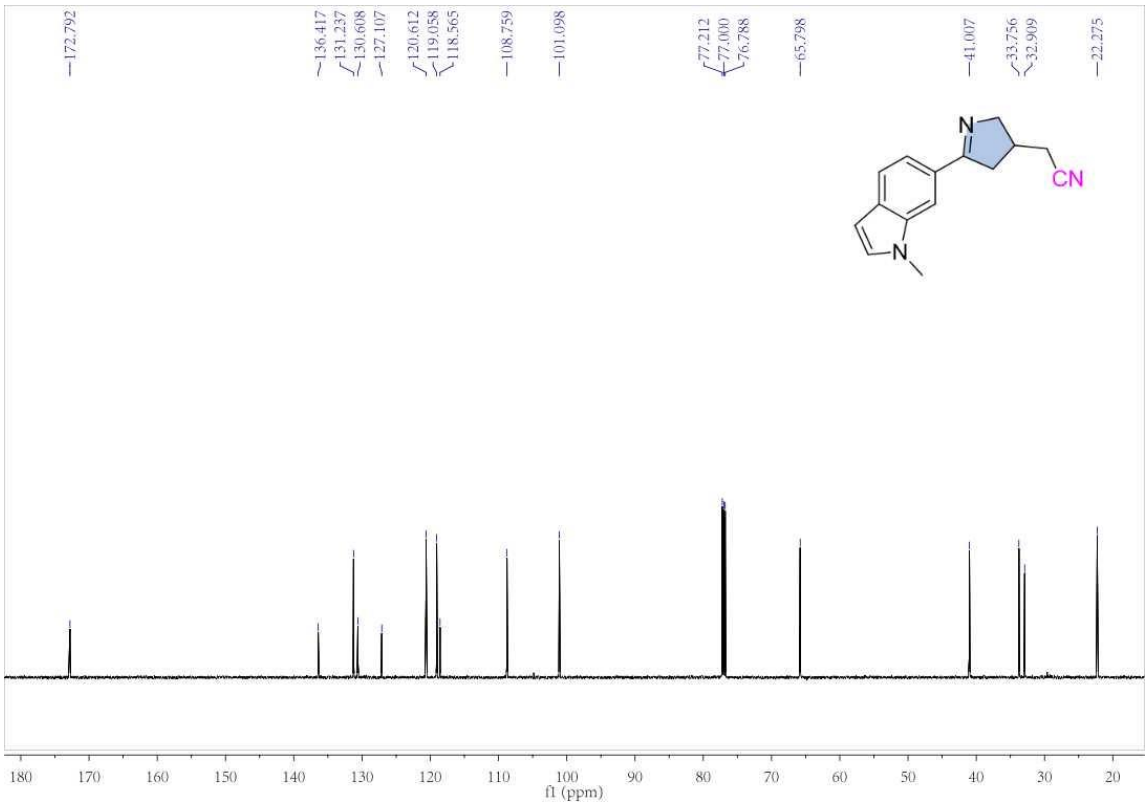
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4aa



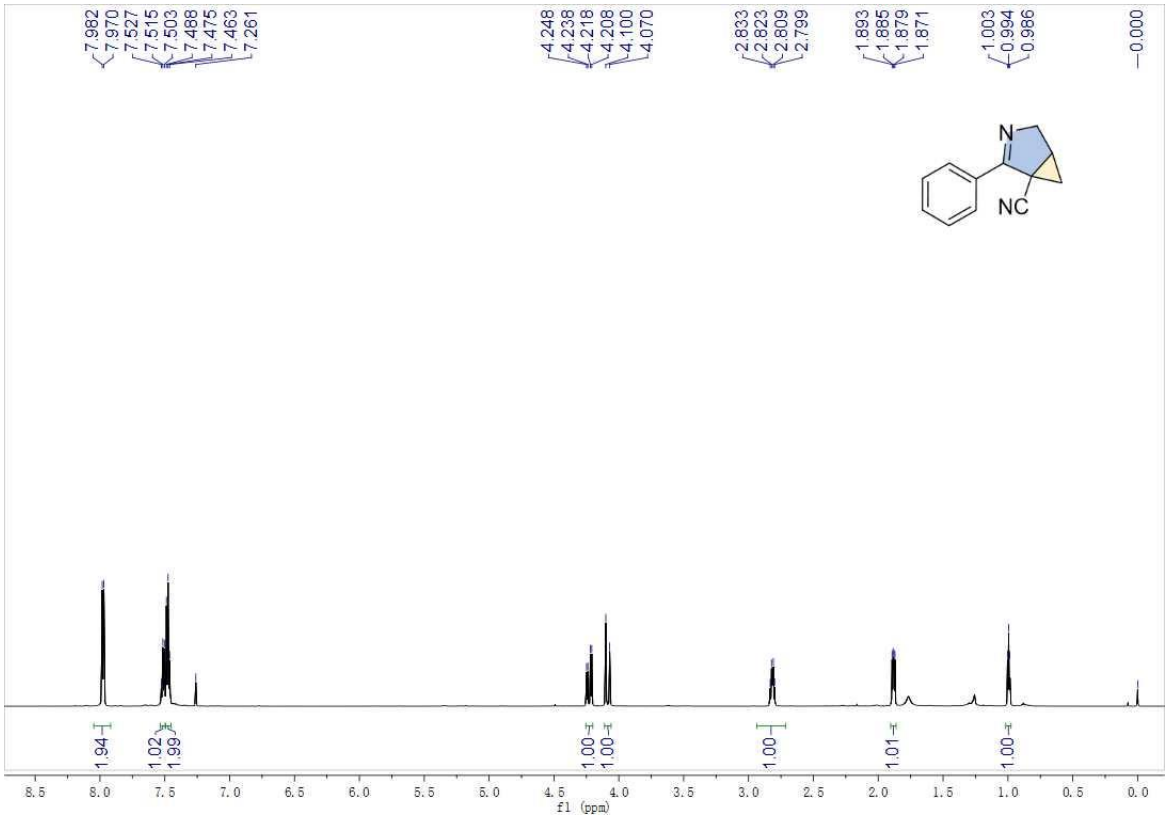
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4ab



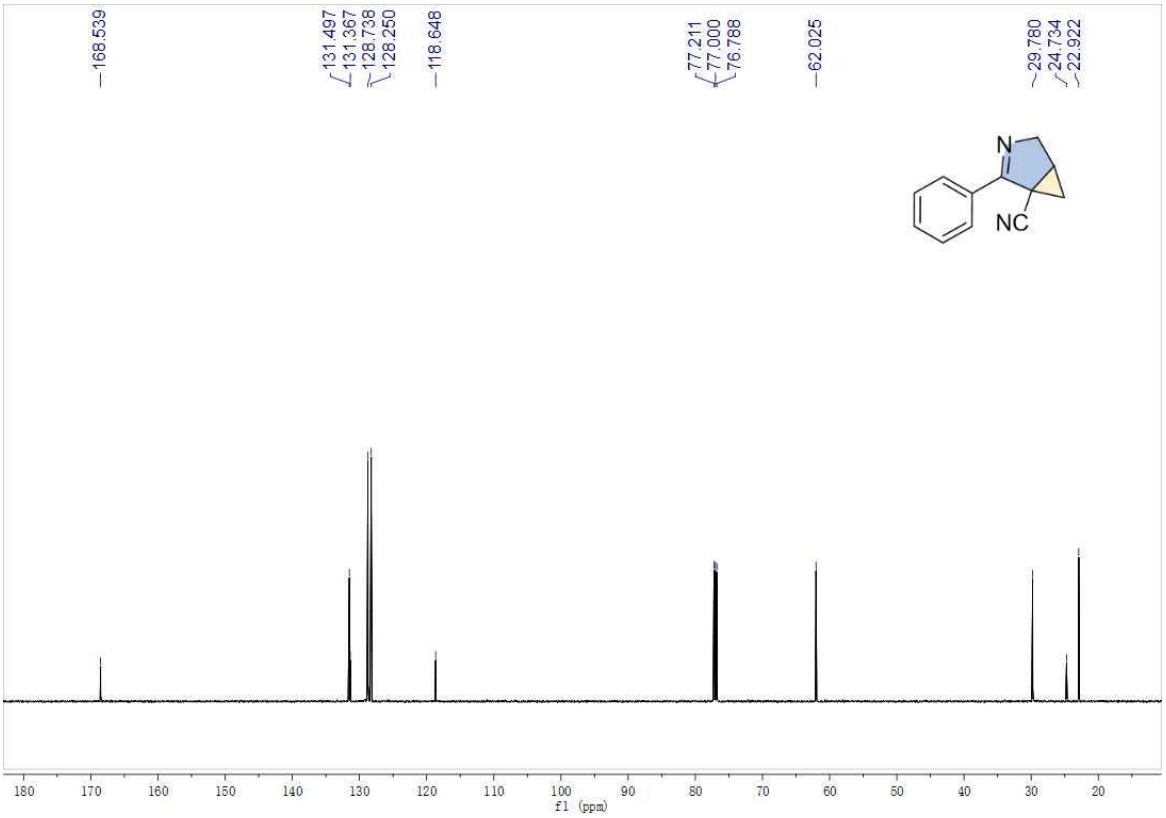
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 4ab



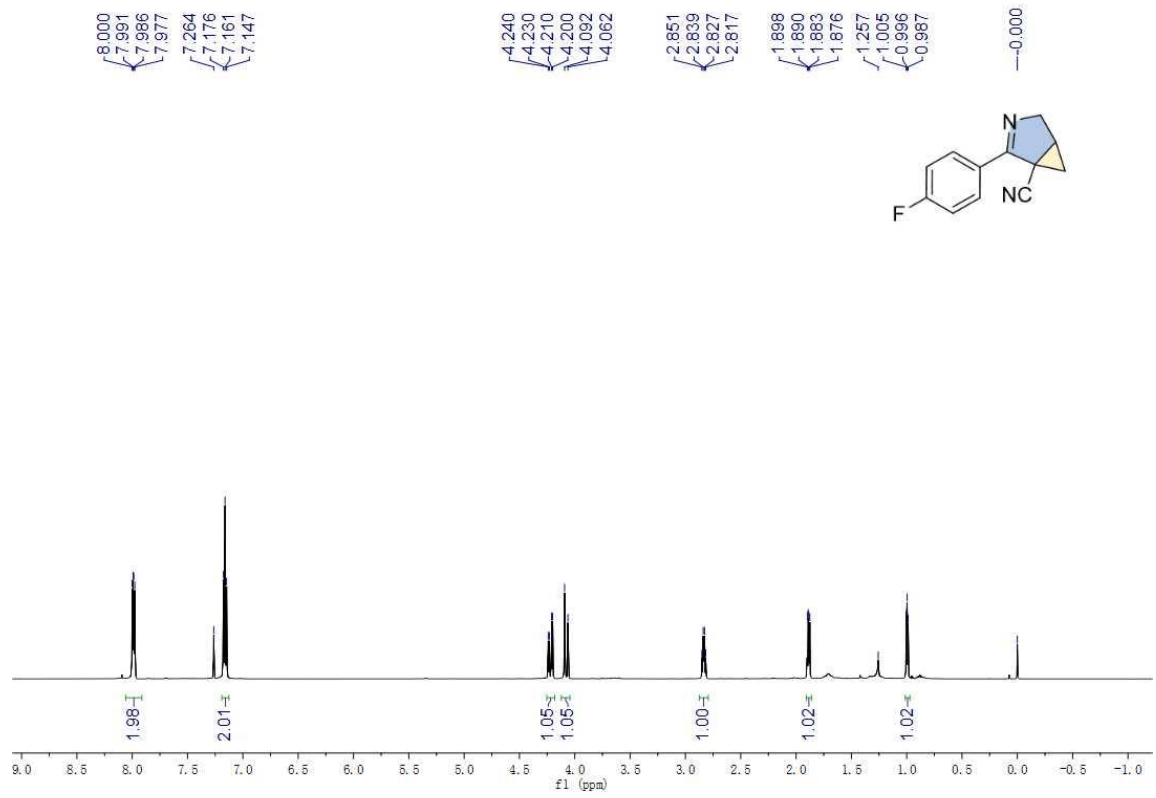
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 5a



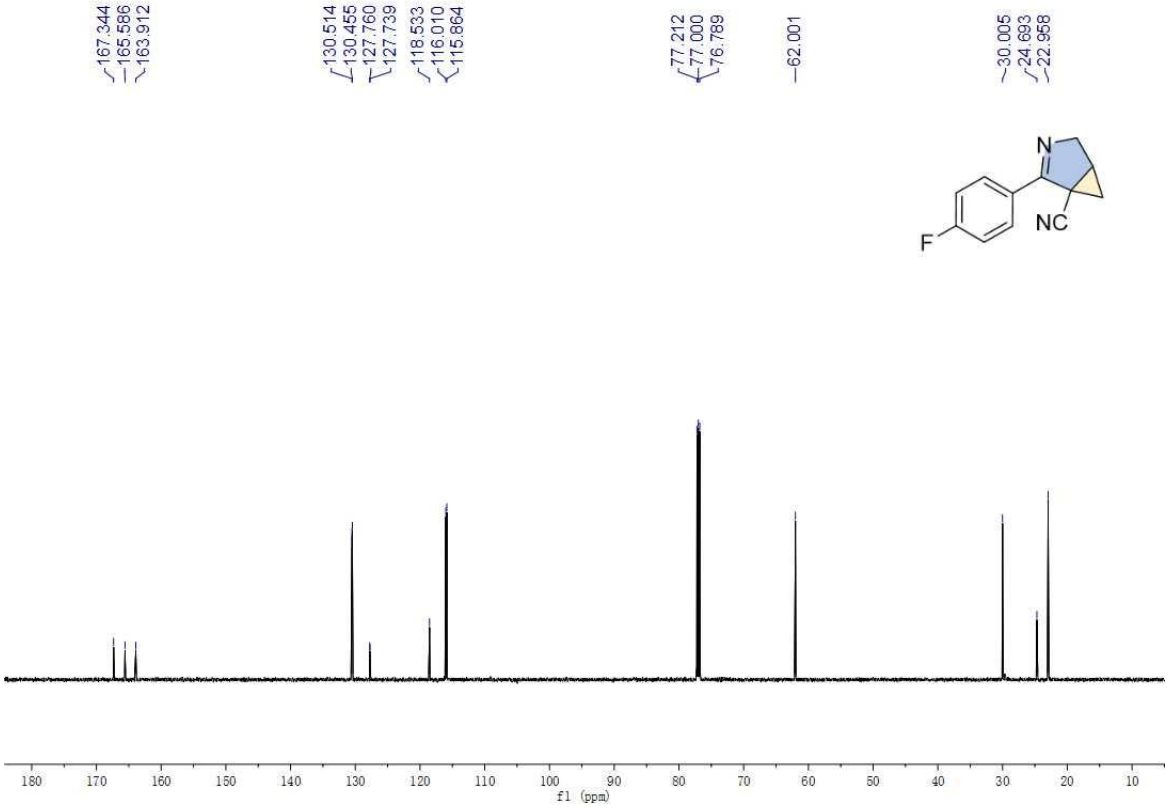
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5a



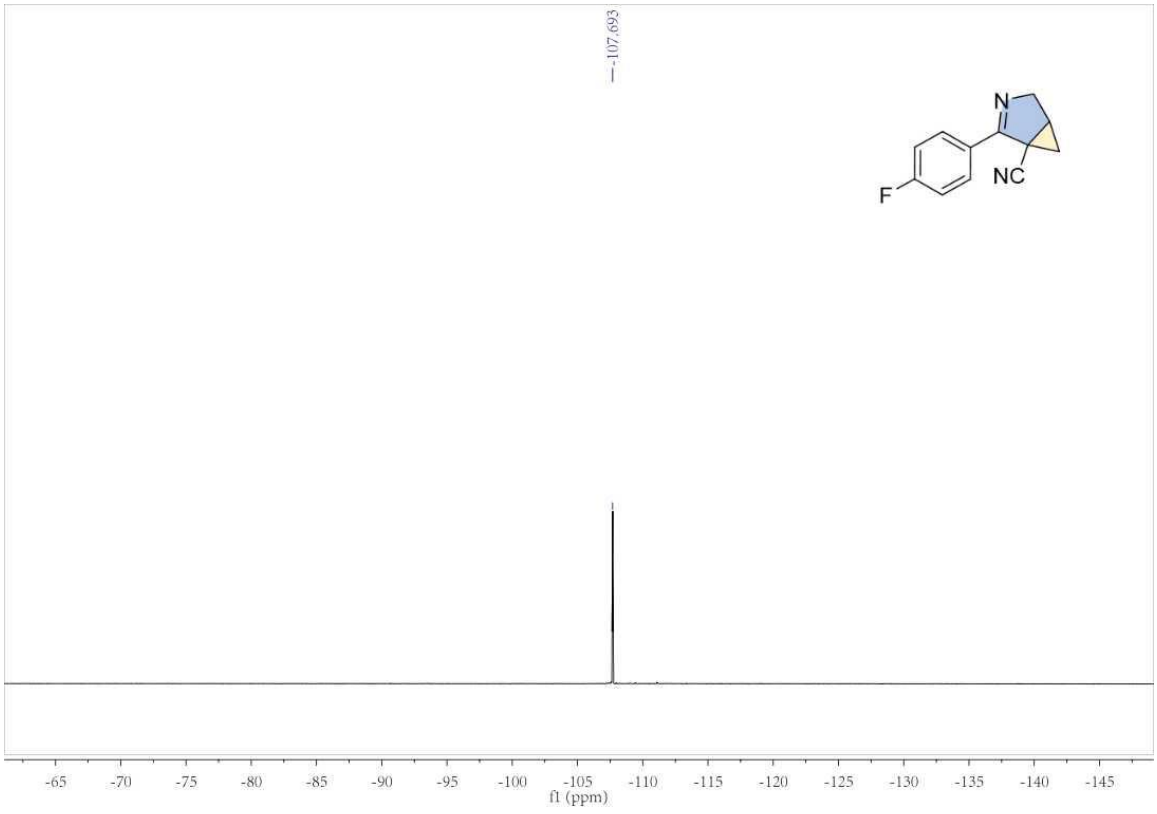
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 5b



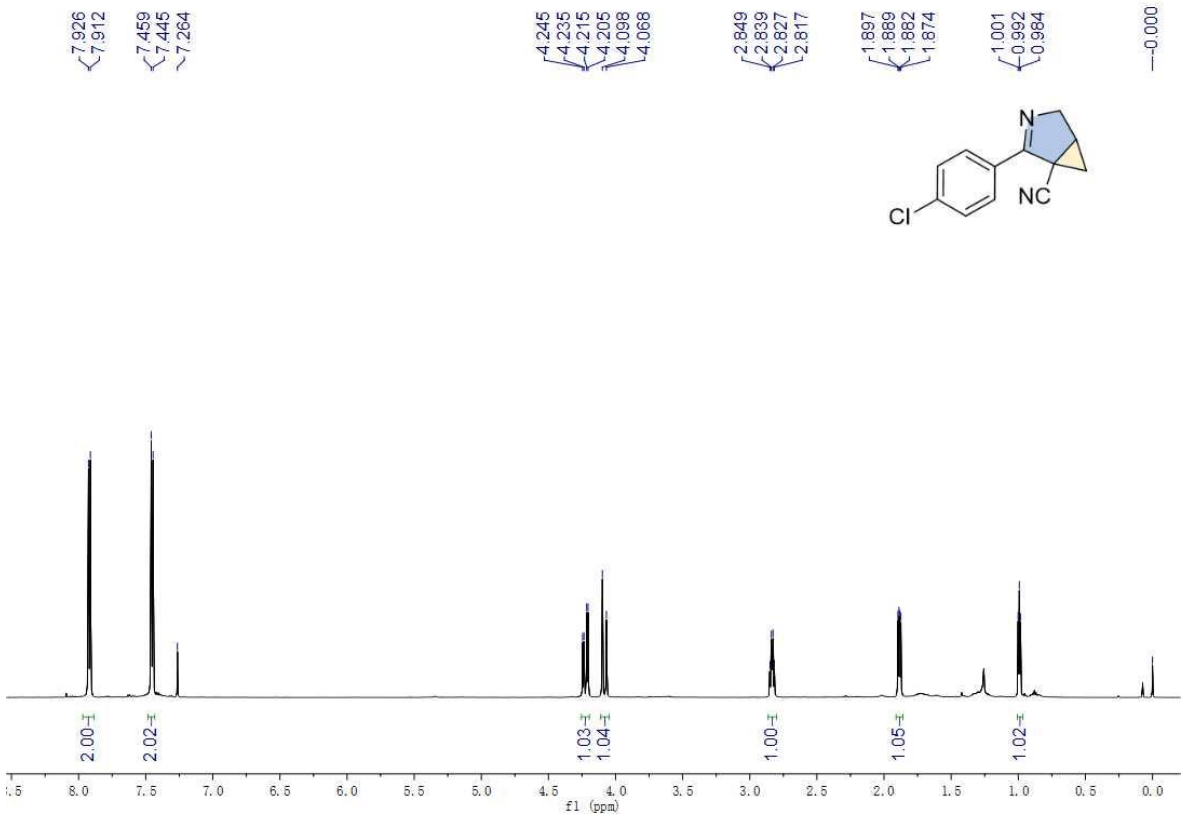
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5b



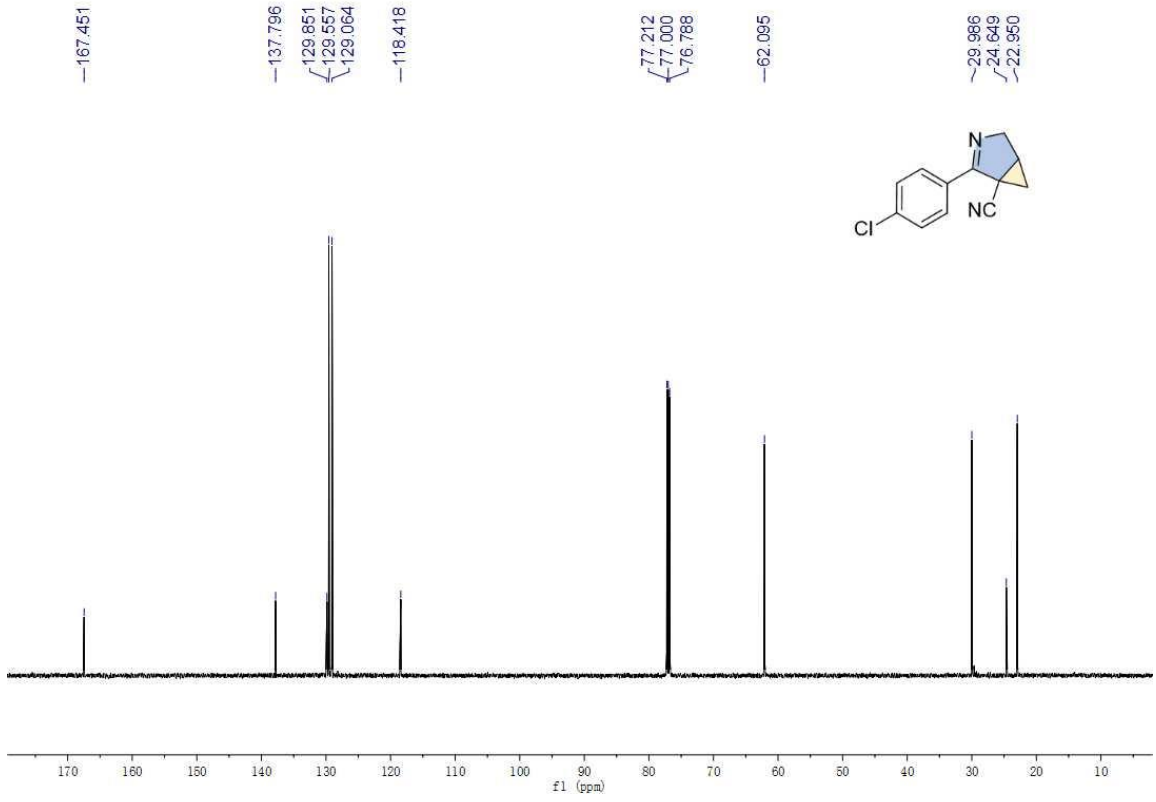
^{19}F spectrum (565 MHz, $CDCl_3$) of compound 5b



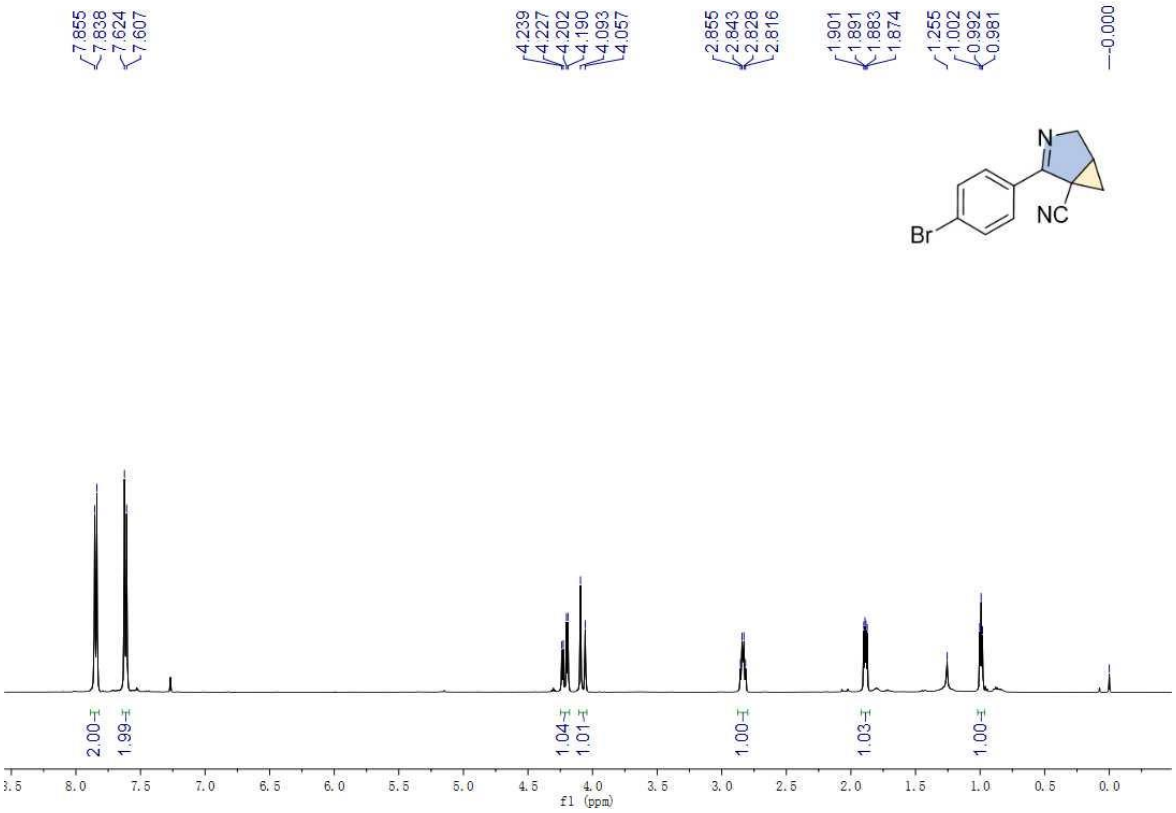
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 5c



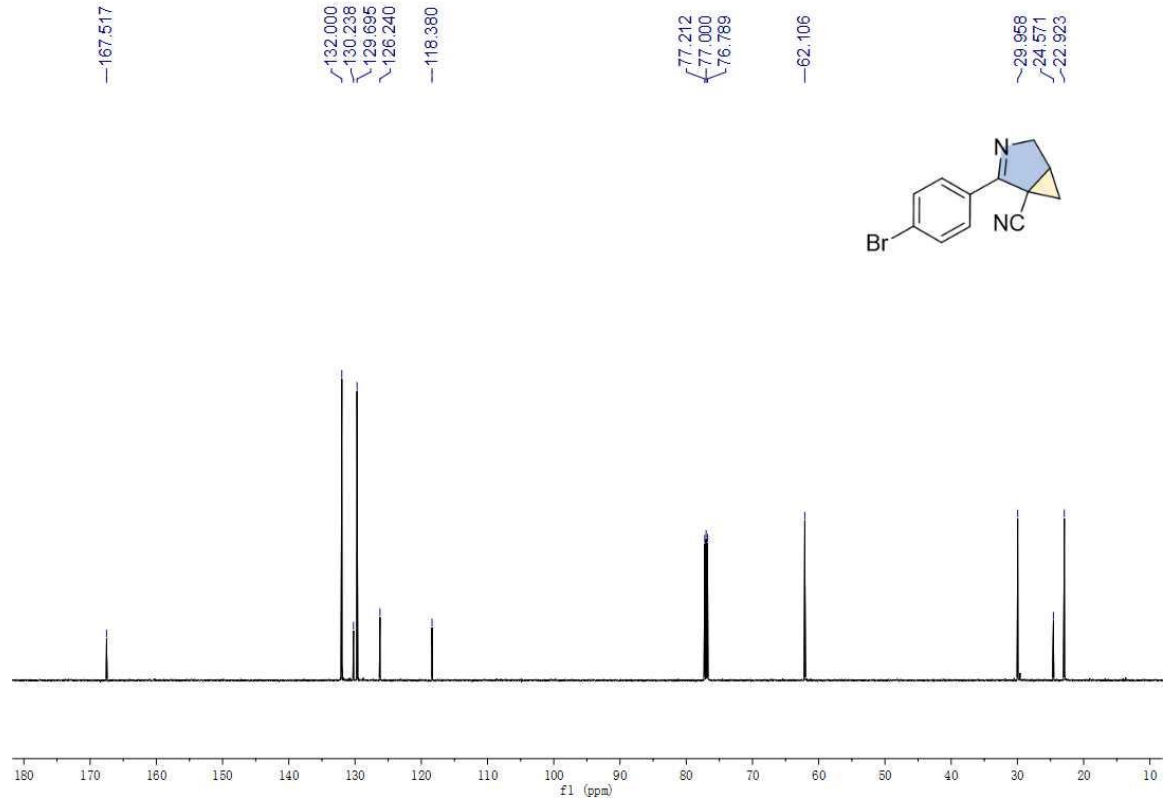
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5c



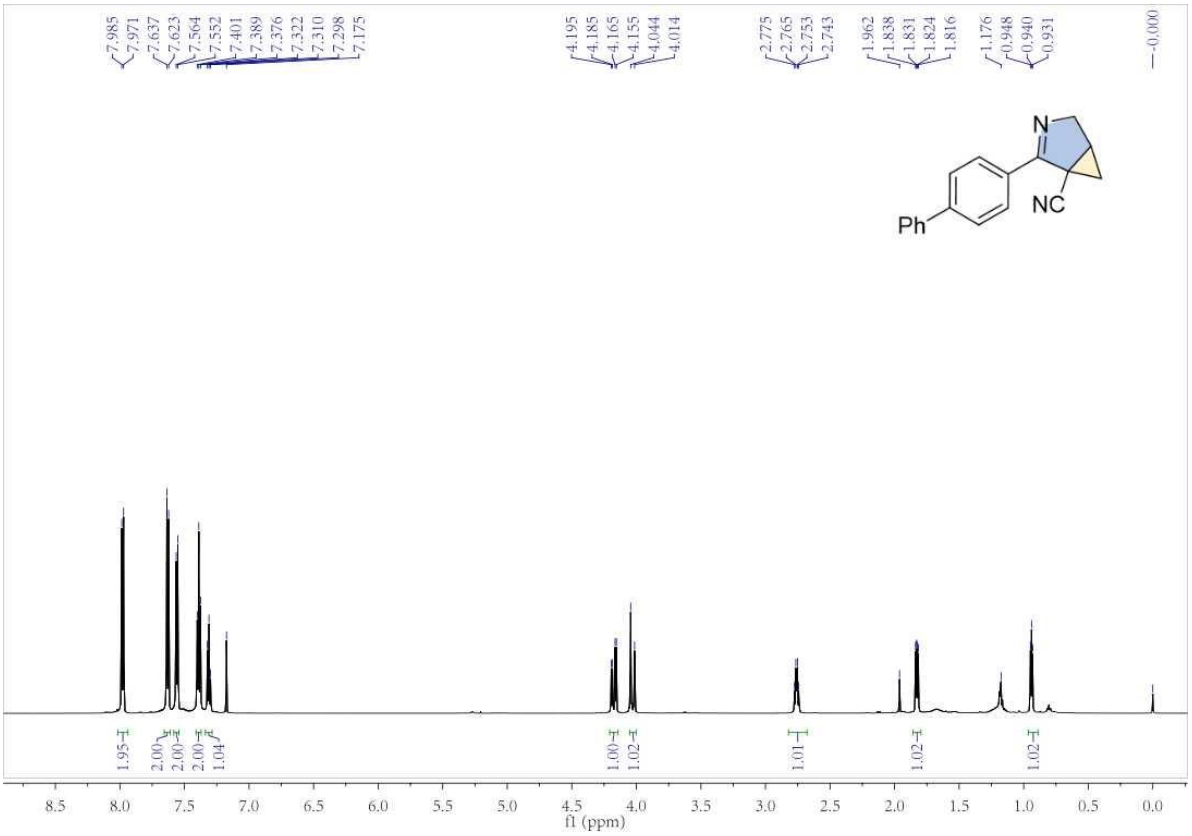
^{1}H spectrum (500 MHz, $CDCl_3$) of compound 5d



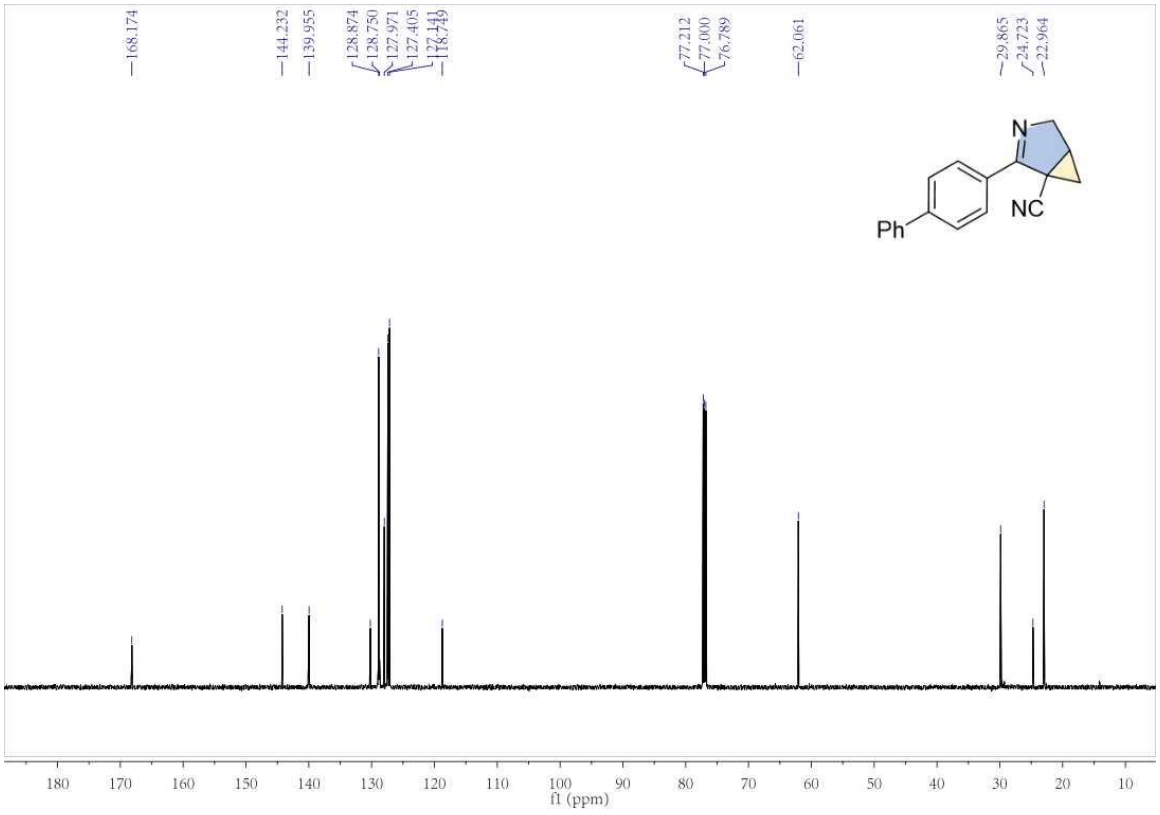
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5d



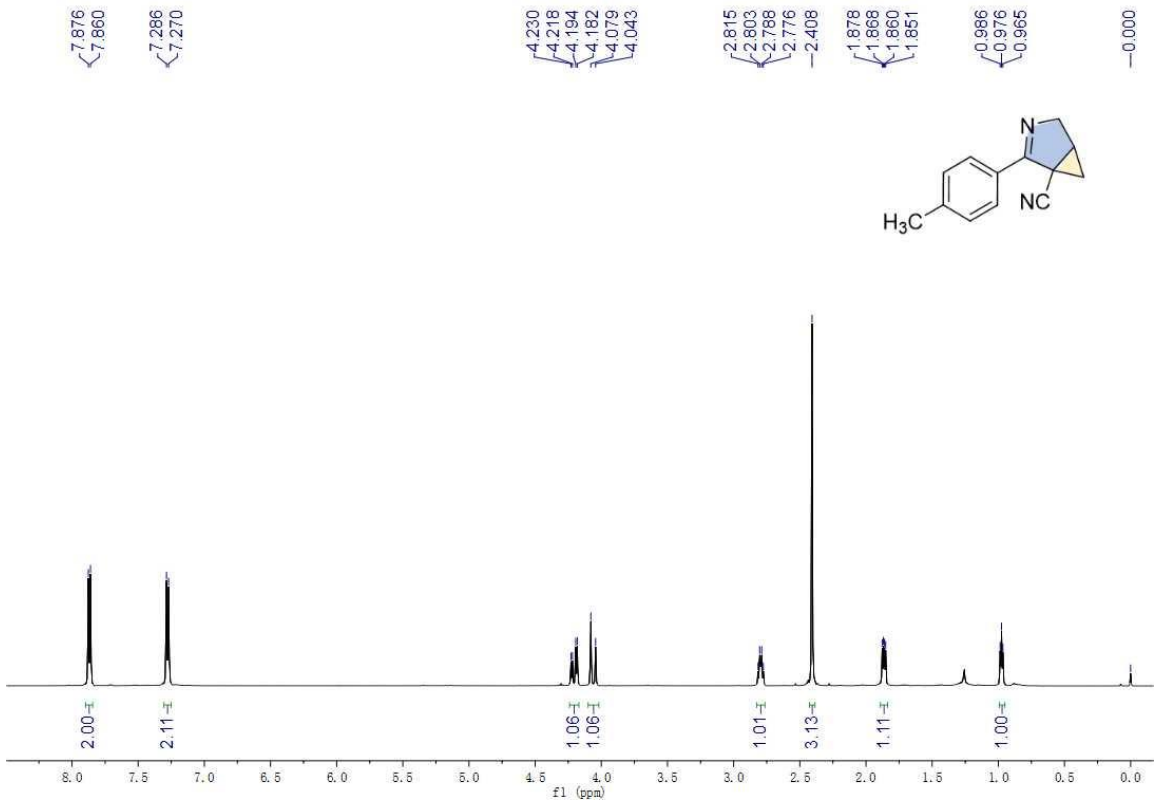
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 5e



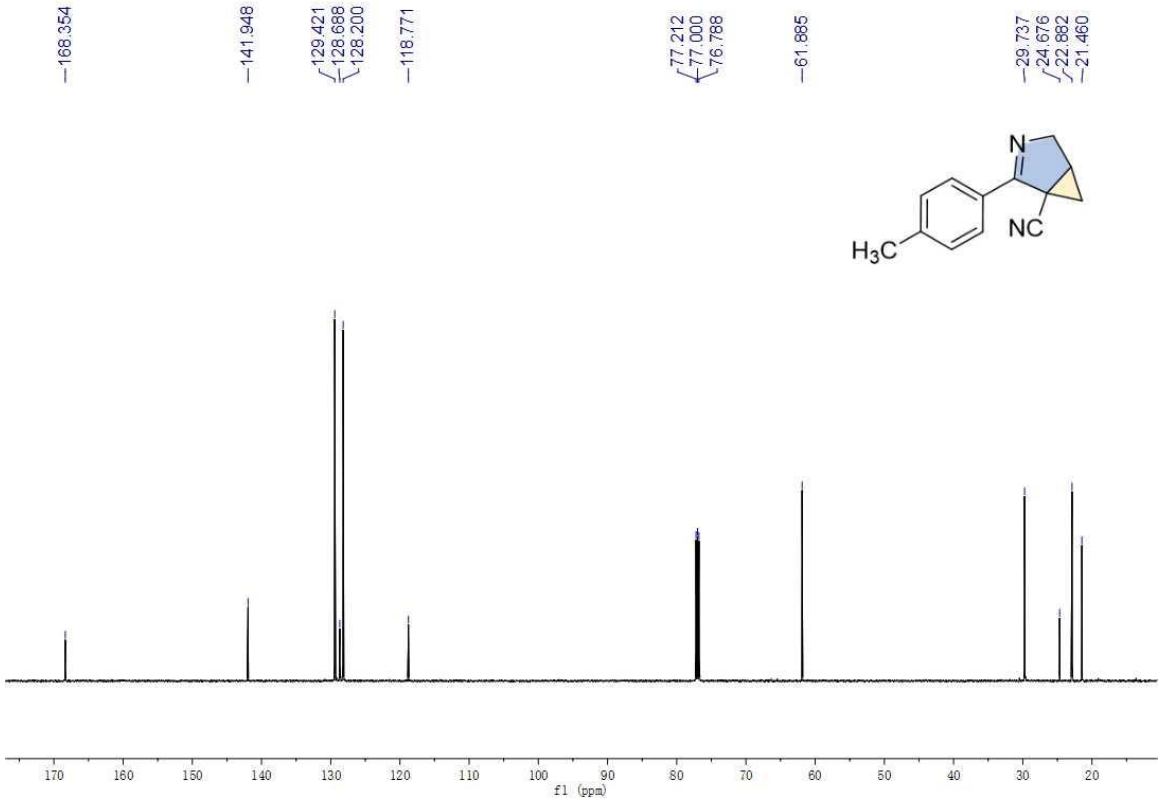
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5e



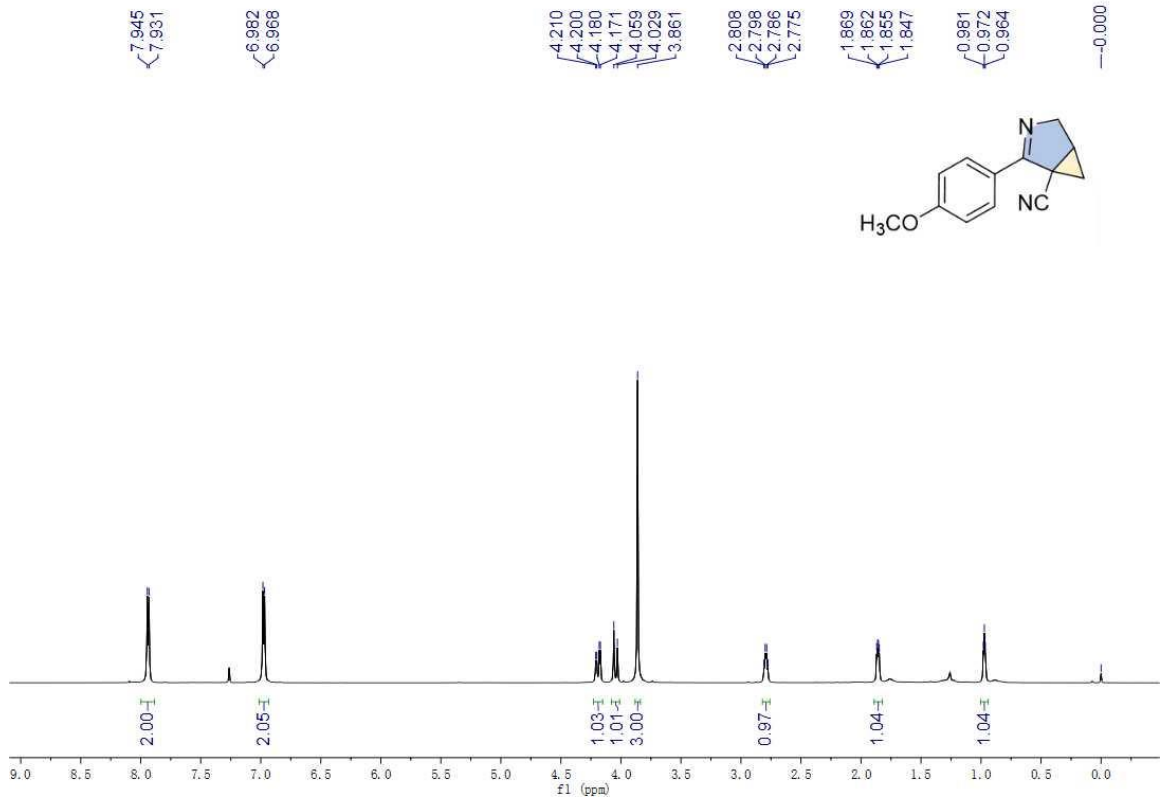
^{1}H spectrum (500 MHz, $CDCl_3$) of compound 5f



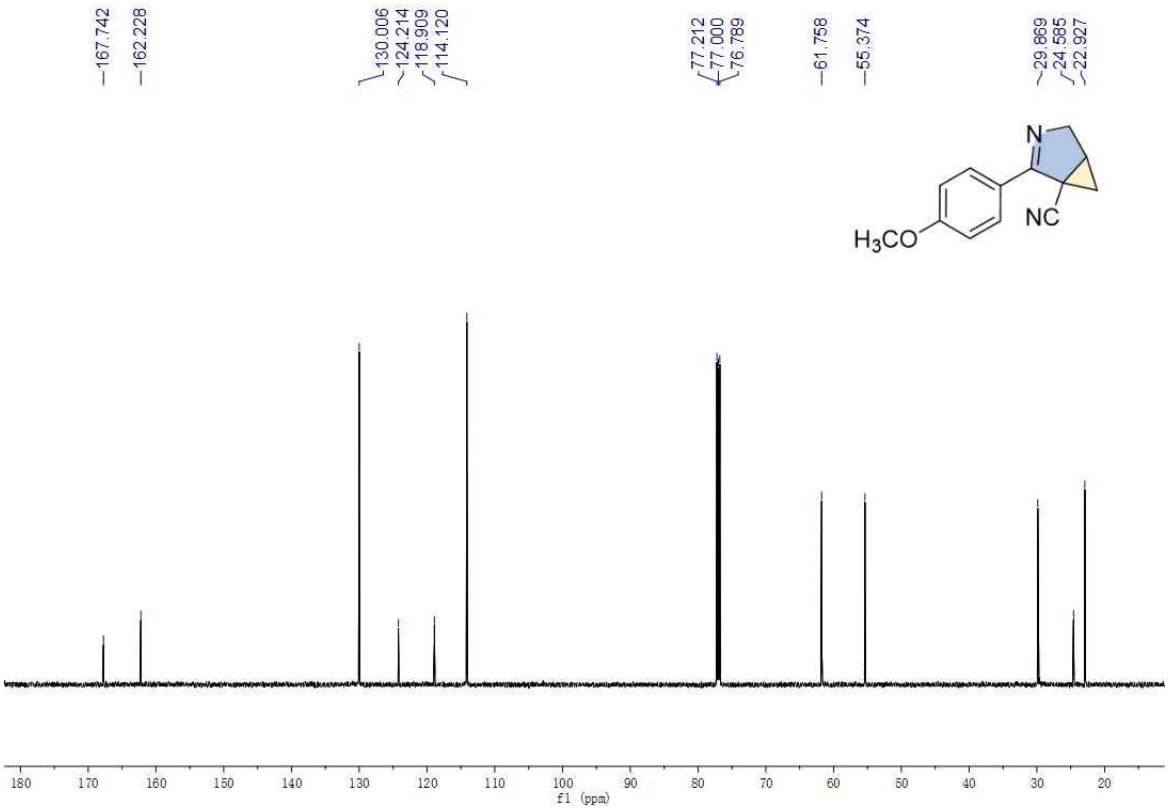
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5f



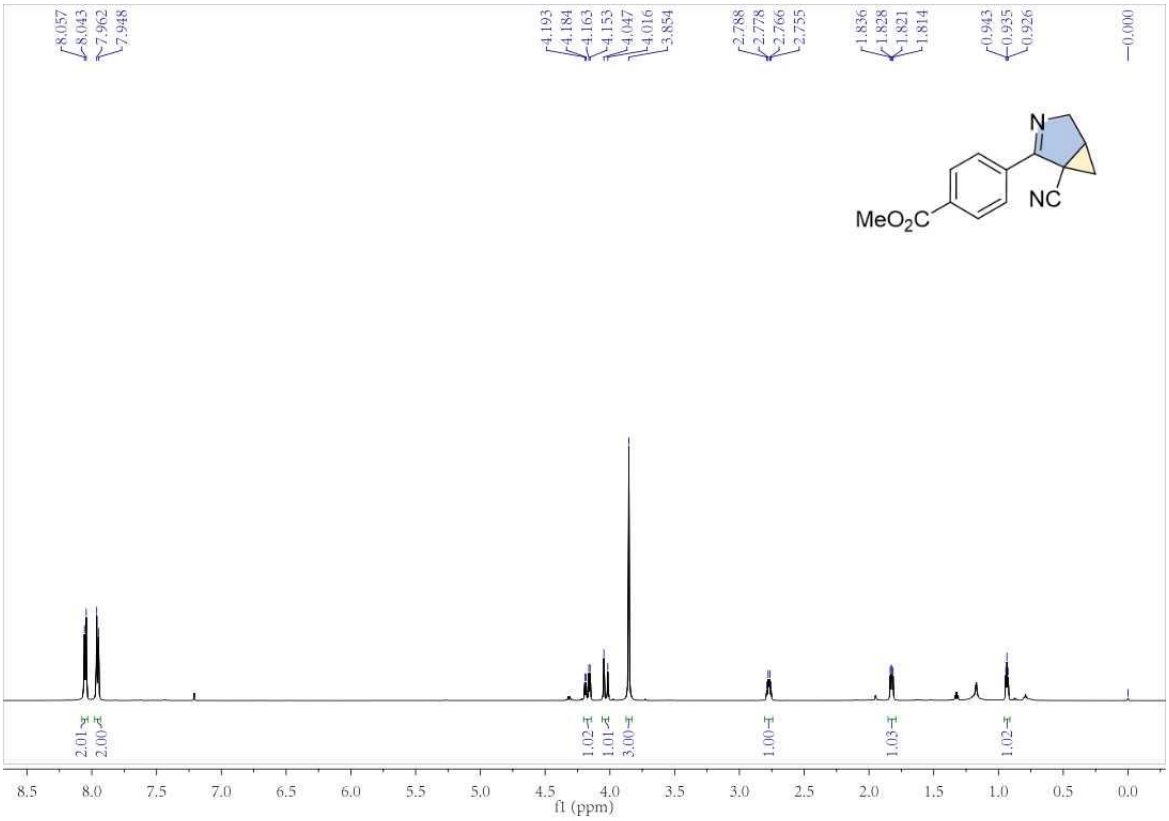
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 5g



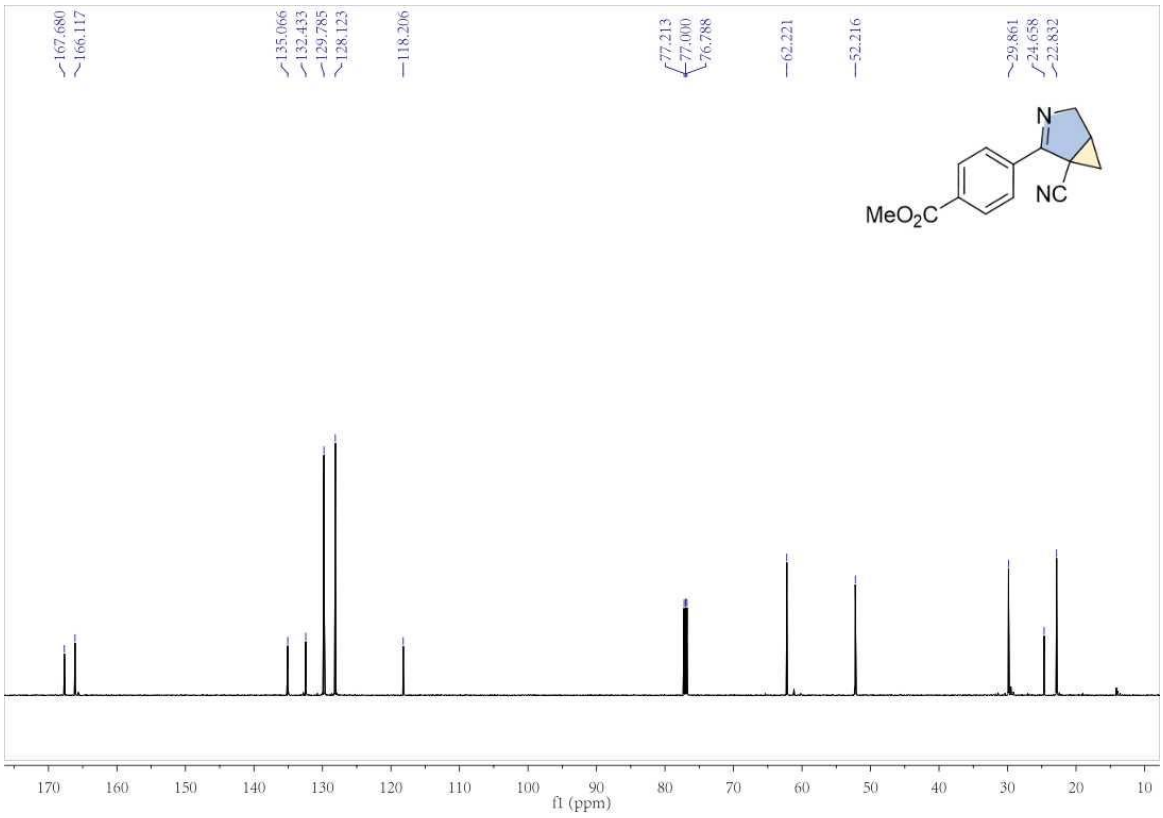
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5g



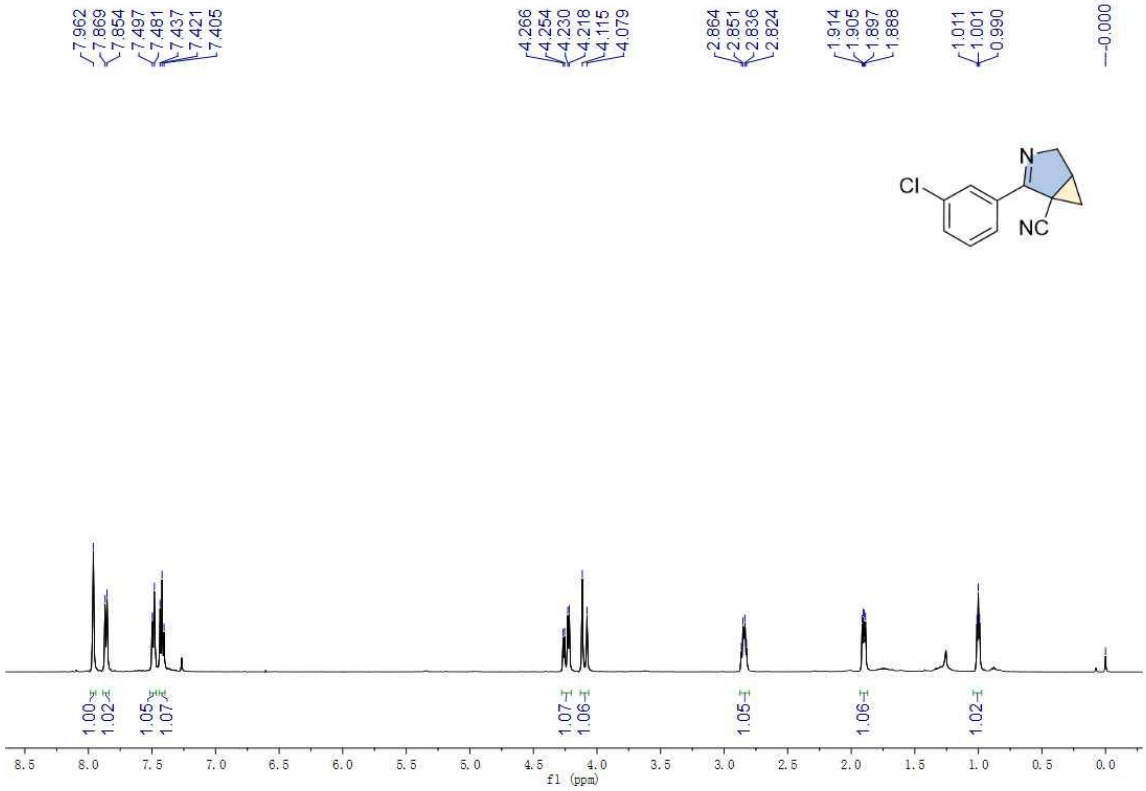
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 5h



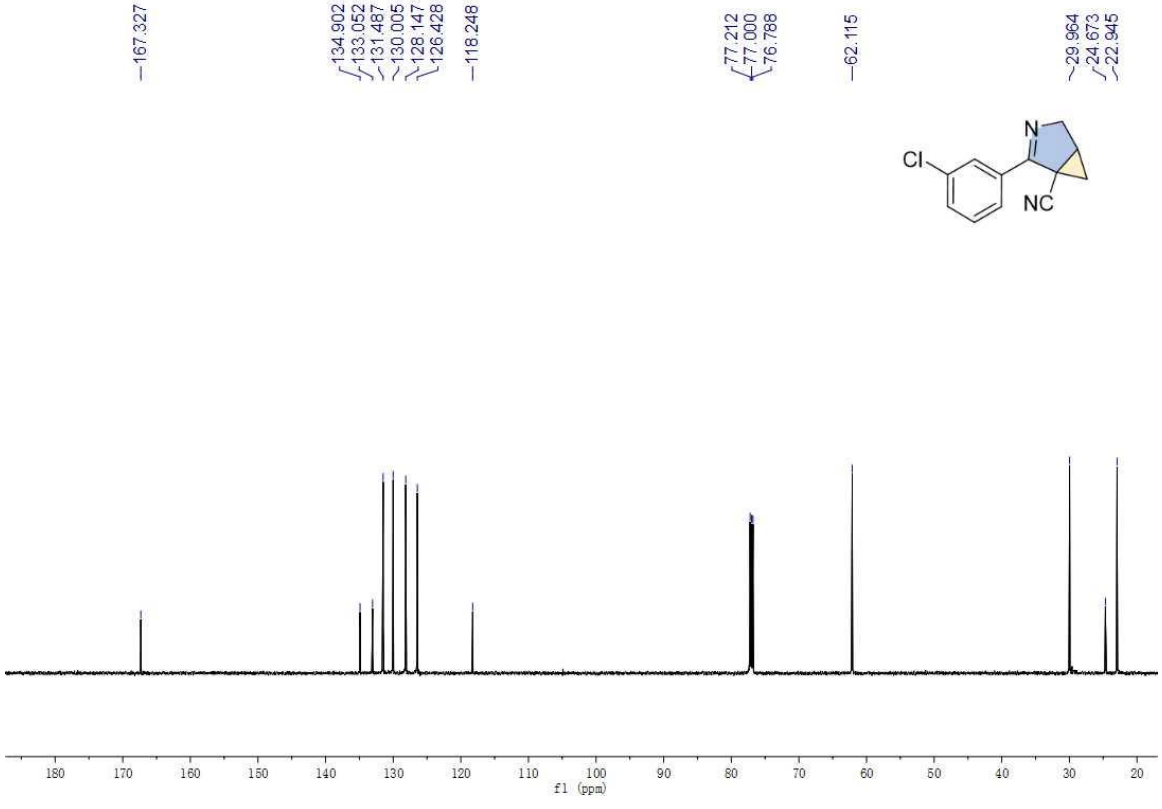
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5h



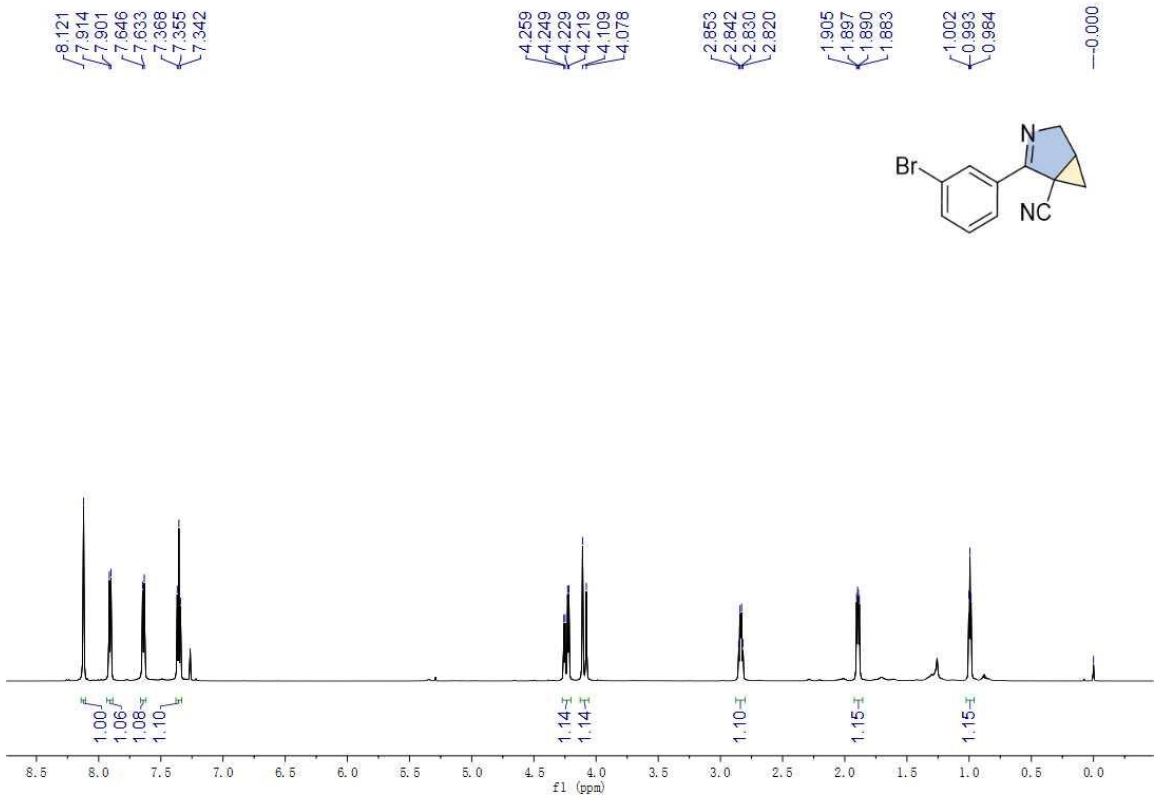
^{1}H spectrum (500 MHz, $CDCl_3$) of compound 5i



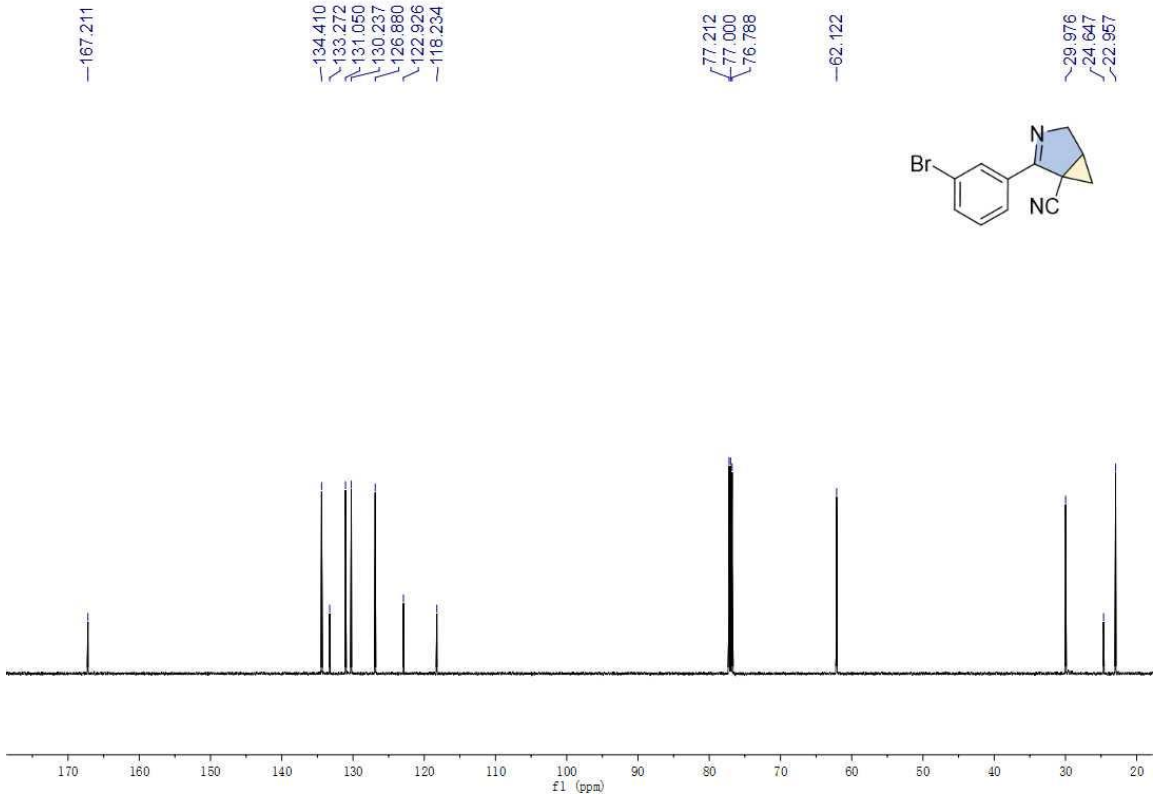
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5i



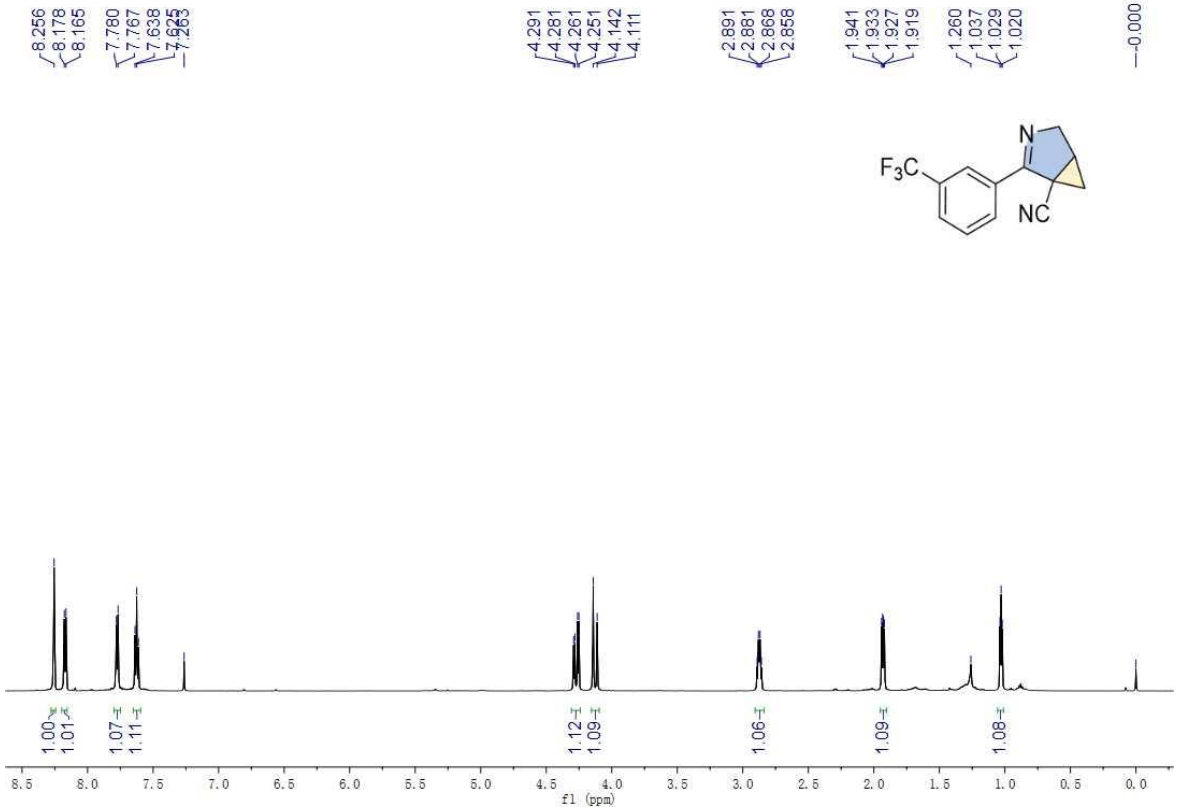
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 5j



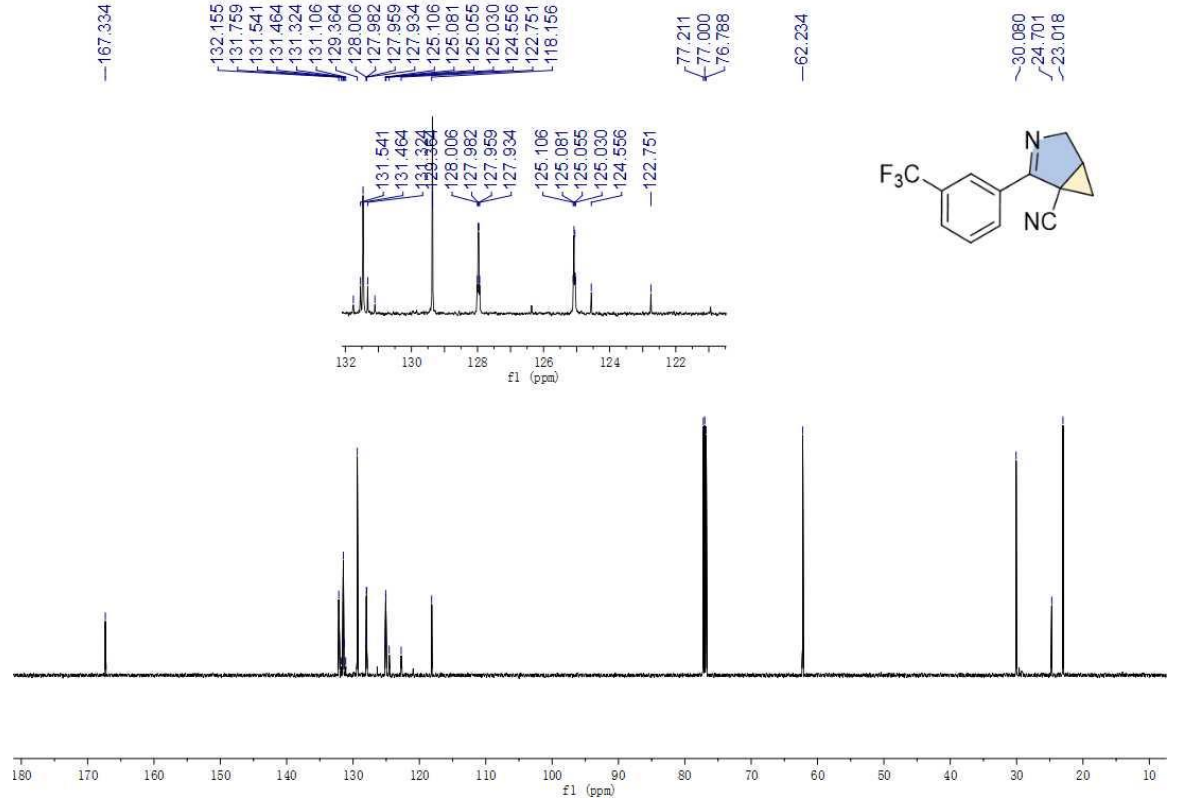
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5j



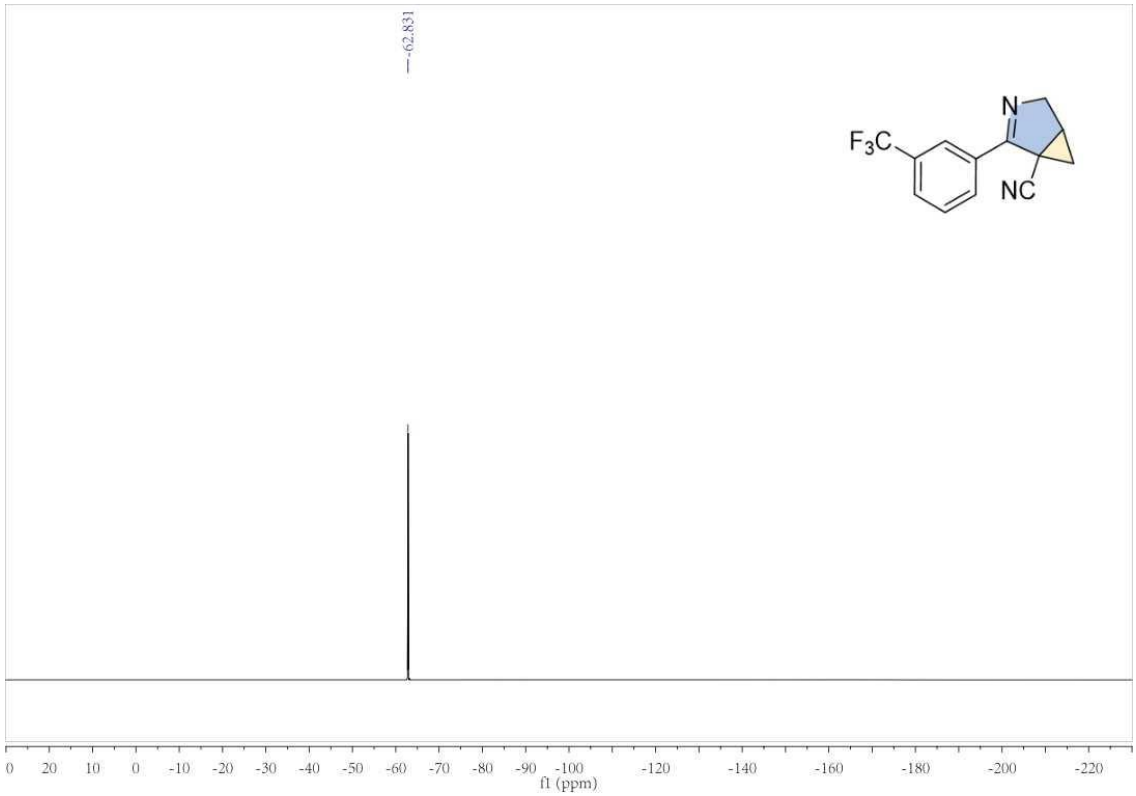
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 5k



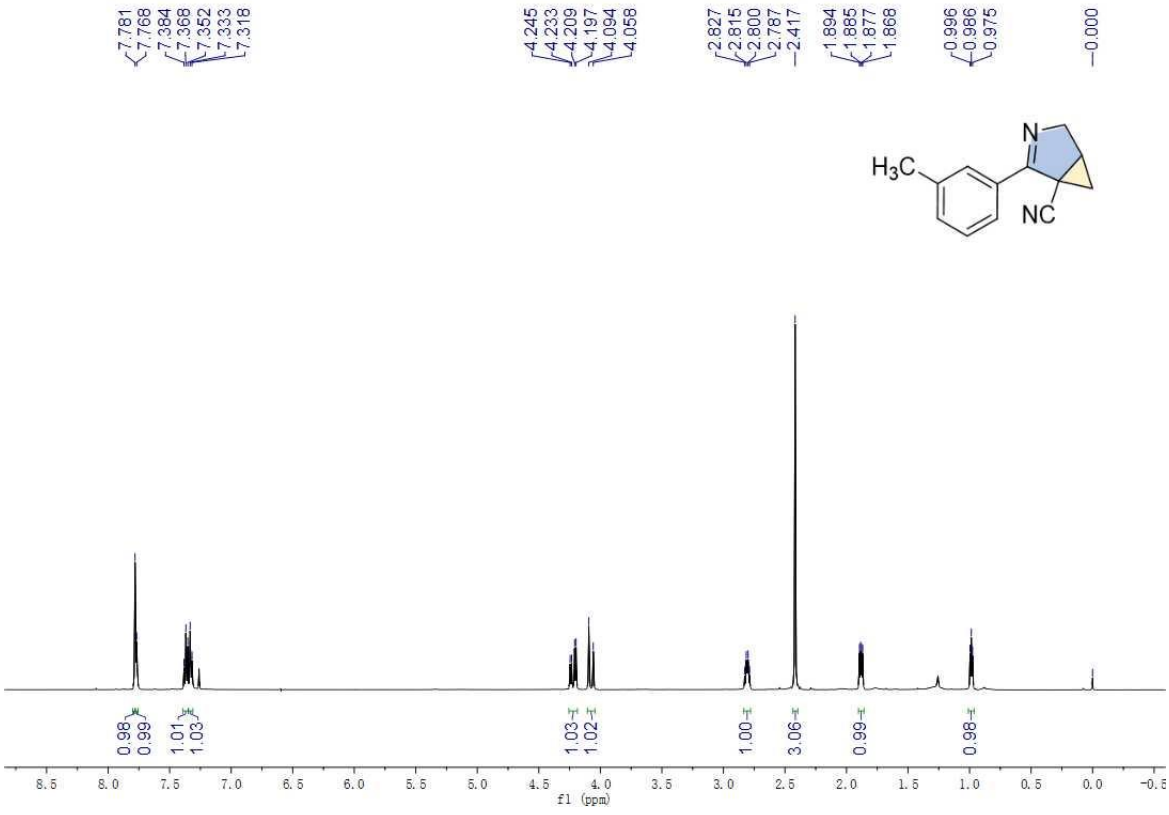
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5k



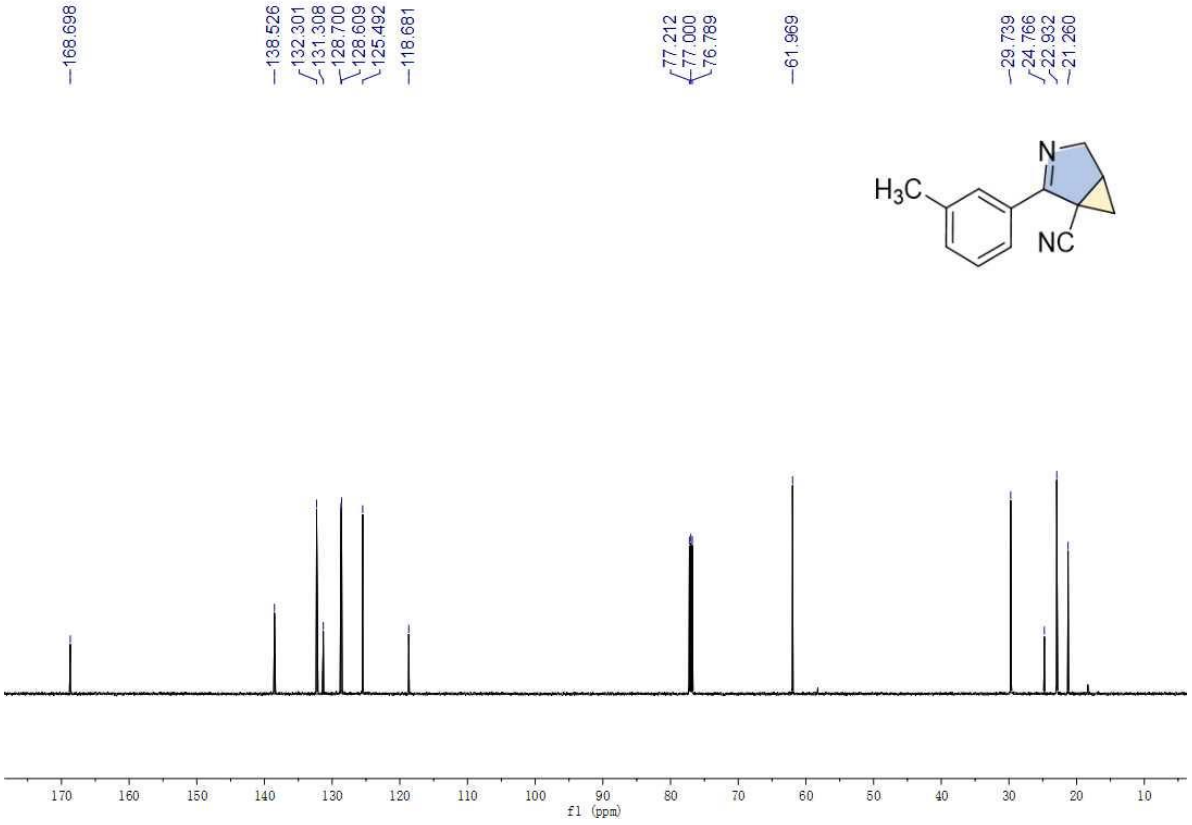
^{19}F spectrum (565 MHz, $CDCl_3$) of compound 5k



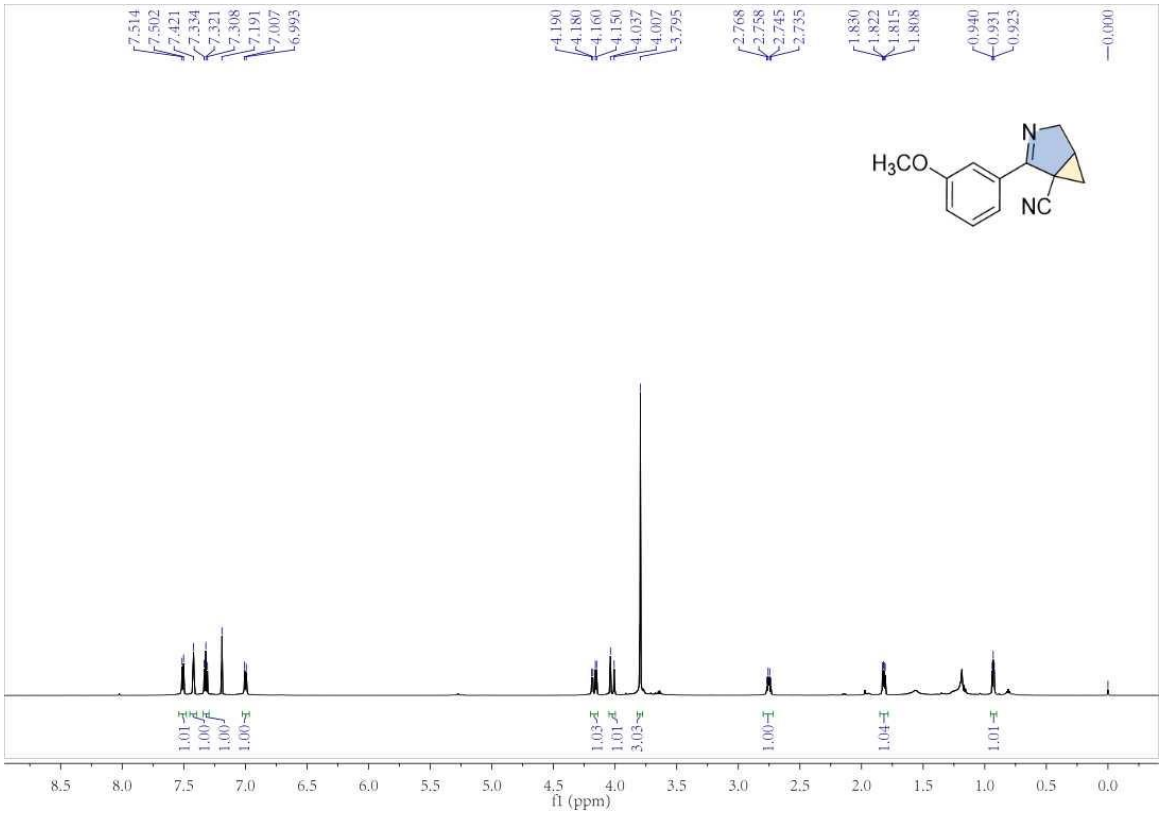
^{1}H spectrum (500 MHz, $CDCl_3$) of compound 5l



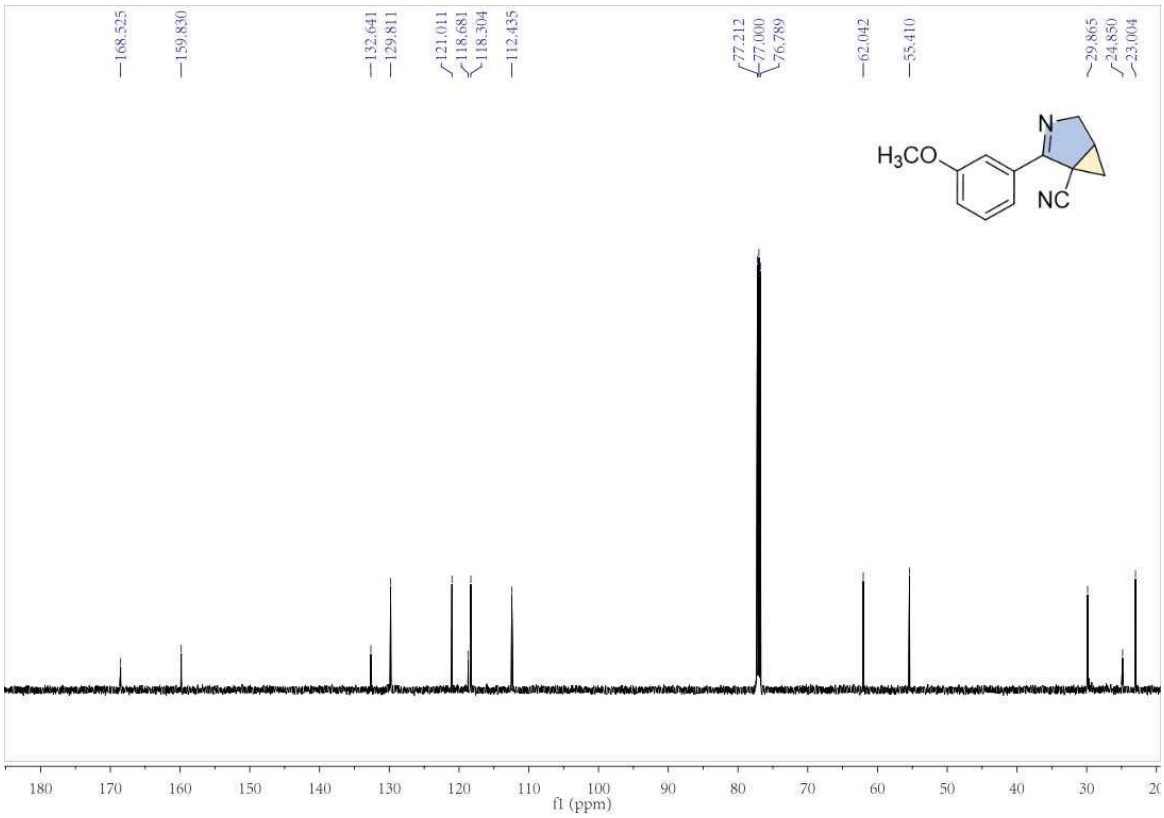
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5l



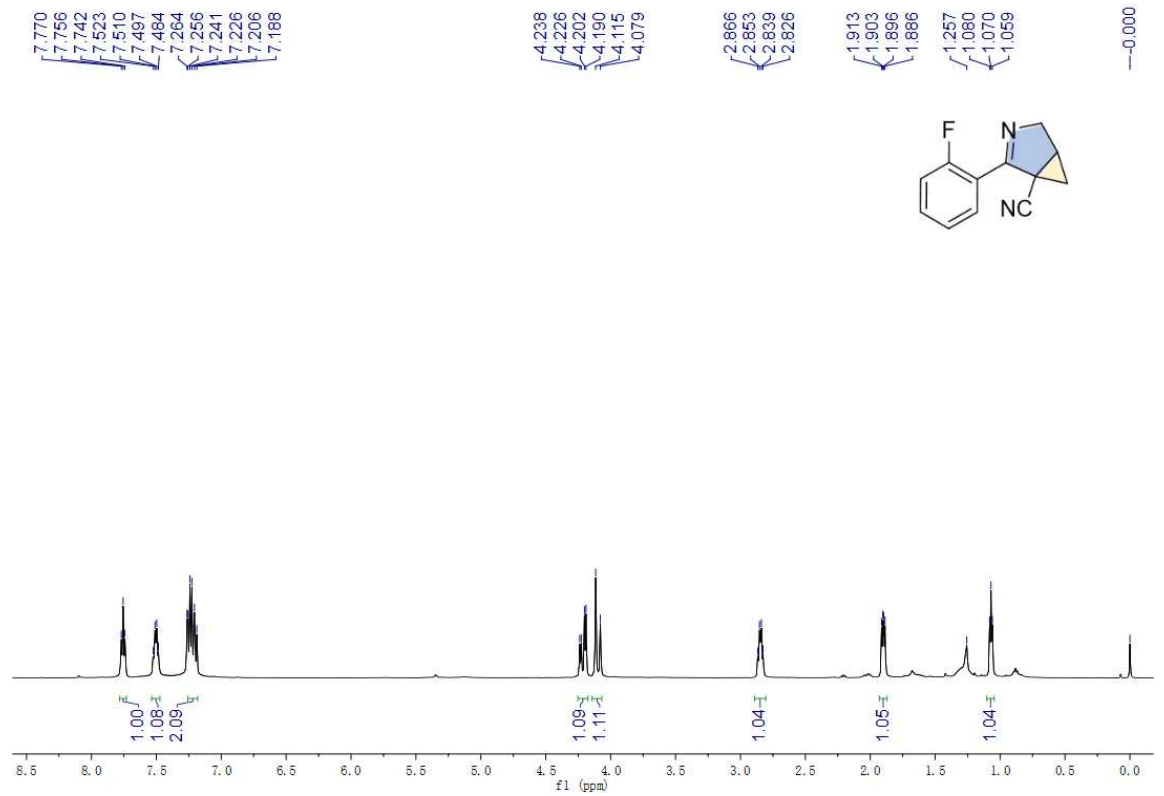
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 5m



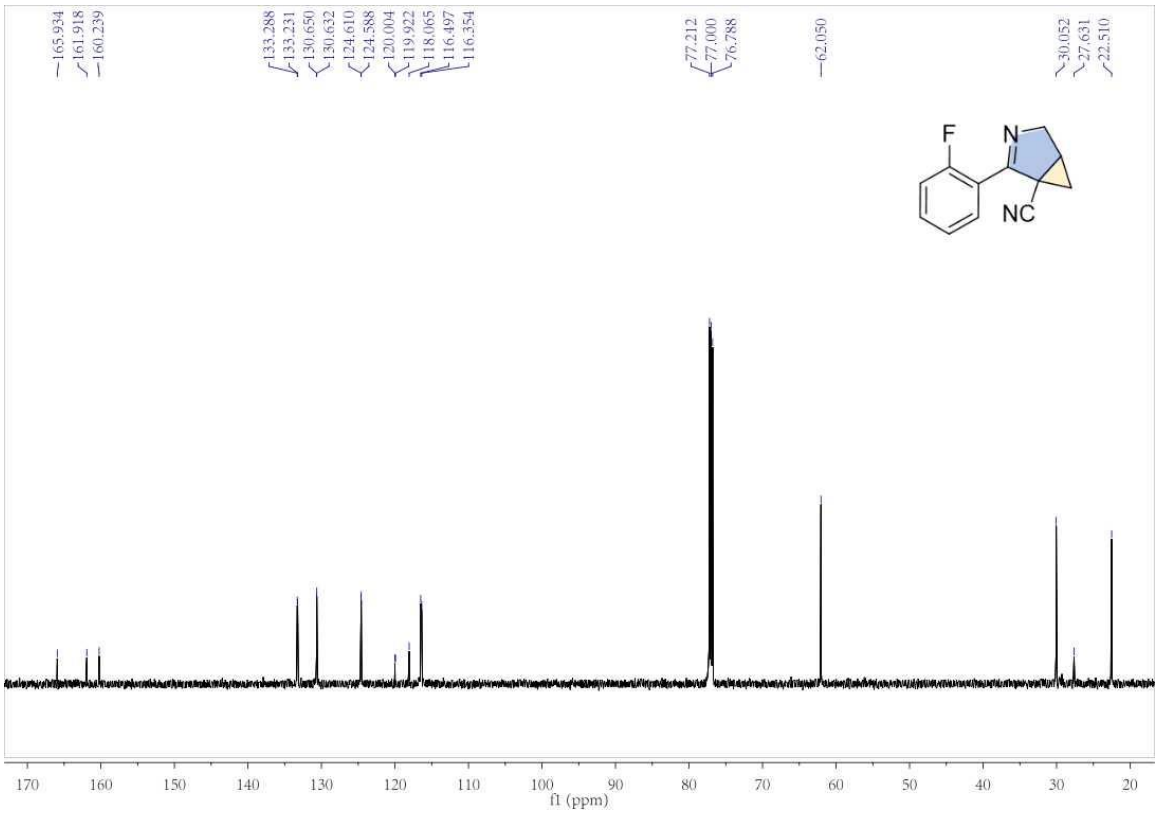
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5m



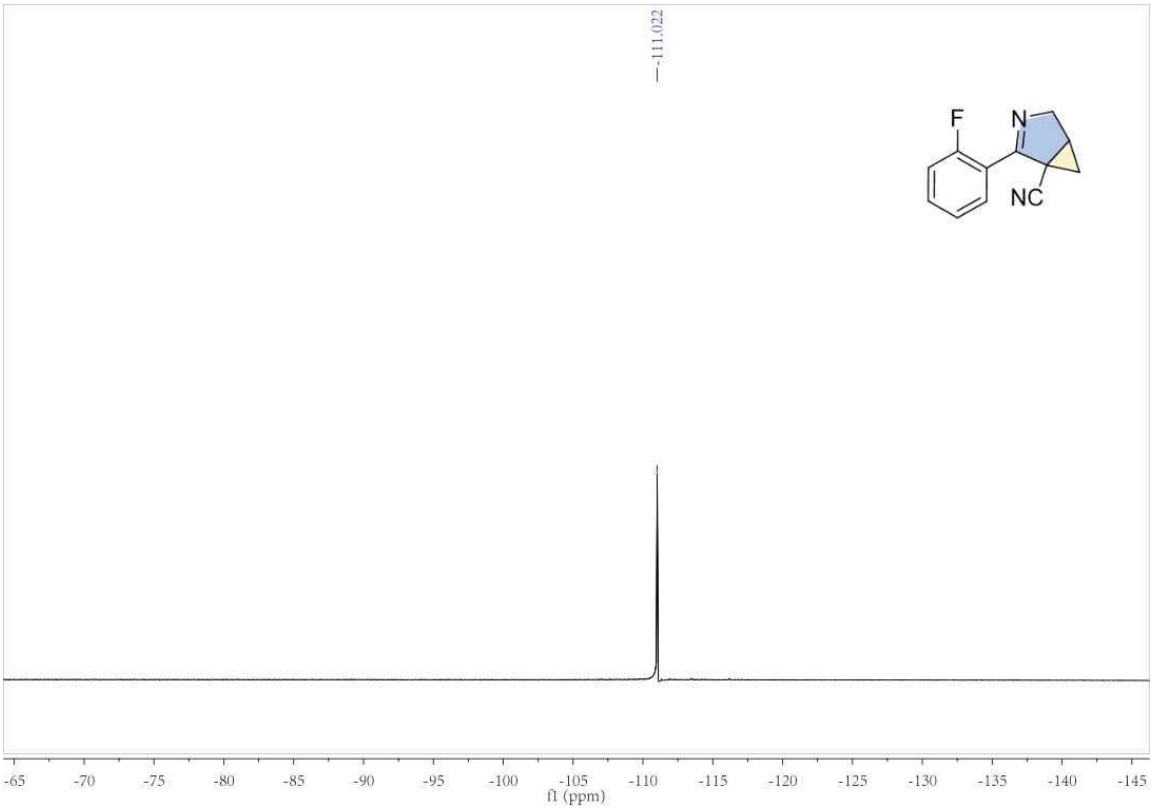
^{1}H spectrum (500 MHz, $CDCl_3$) of compound 5n



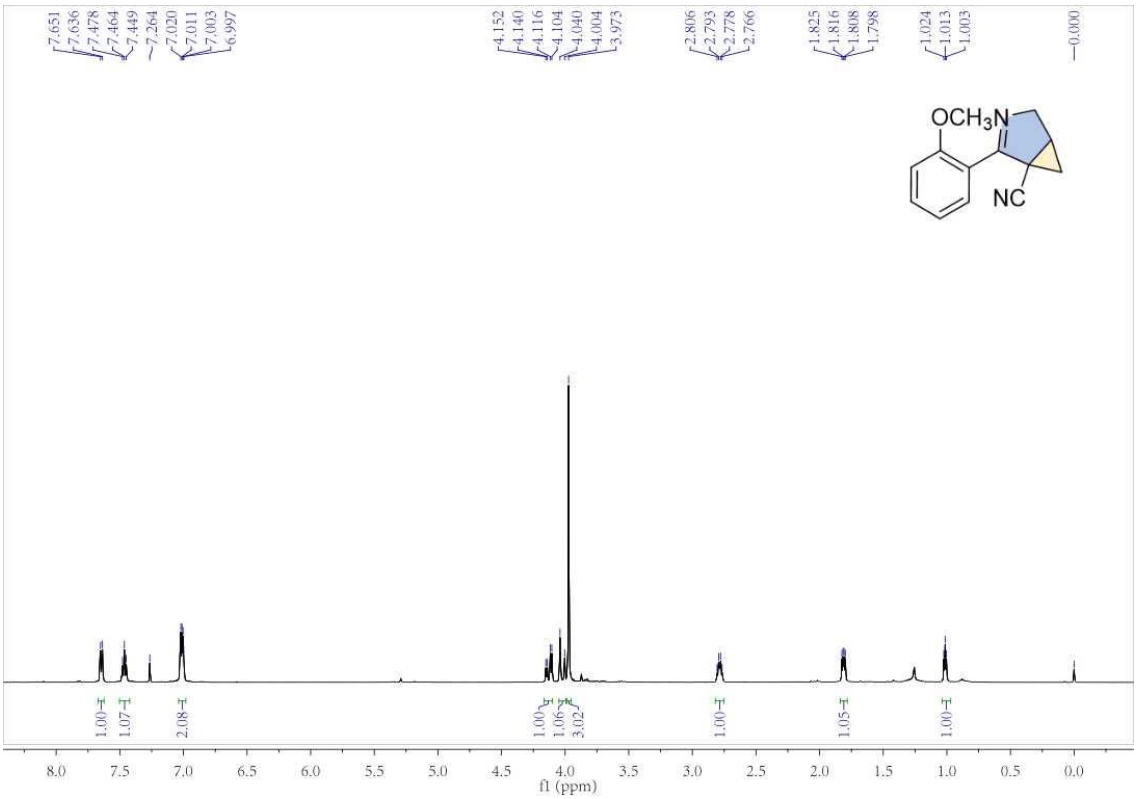
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5n



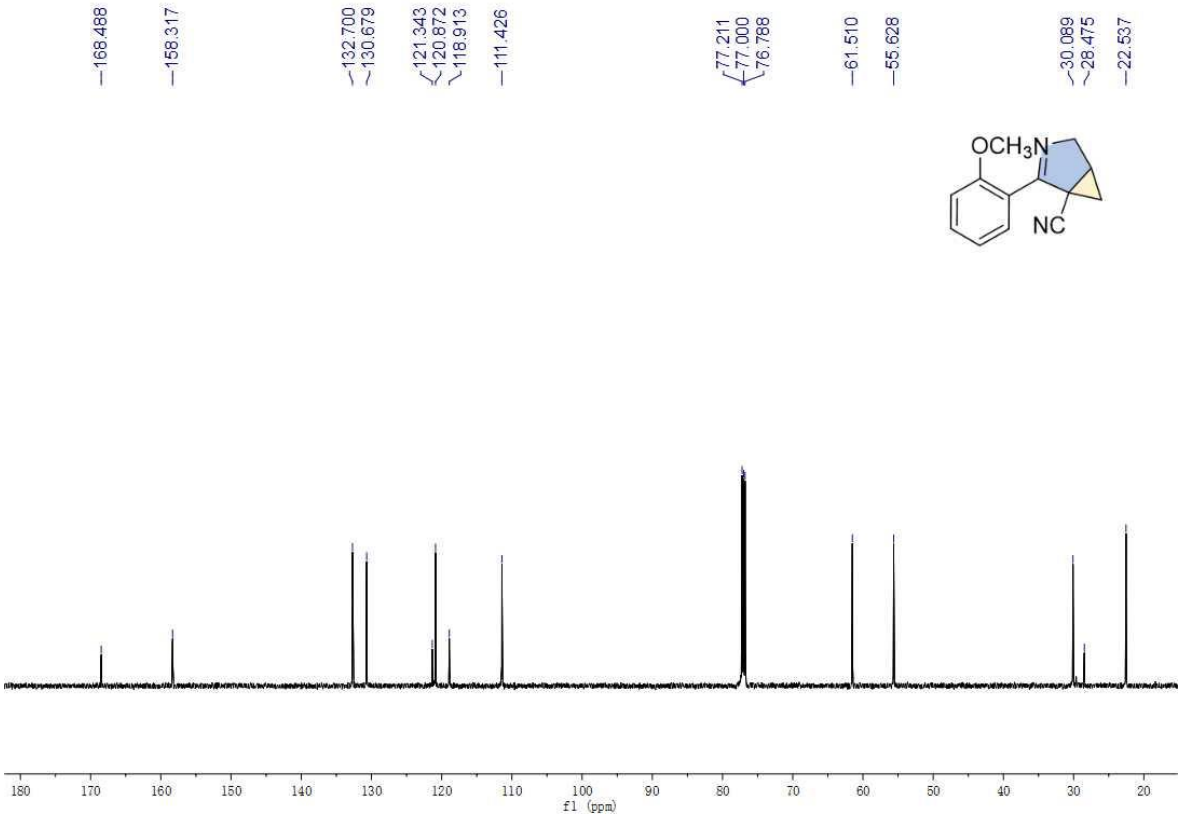
^{19}F spectrum (565 MHz, $CDCl_3$) of compound 5n



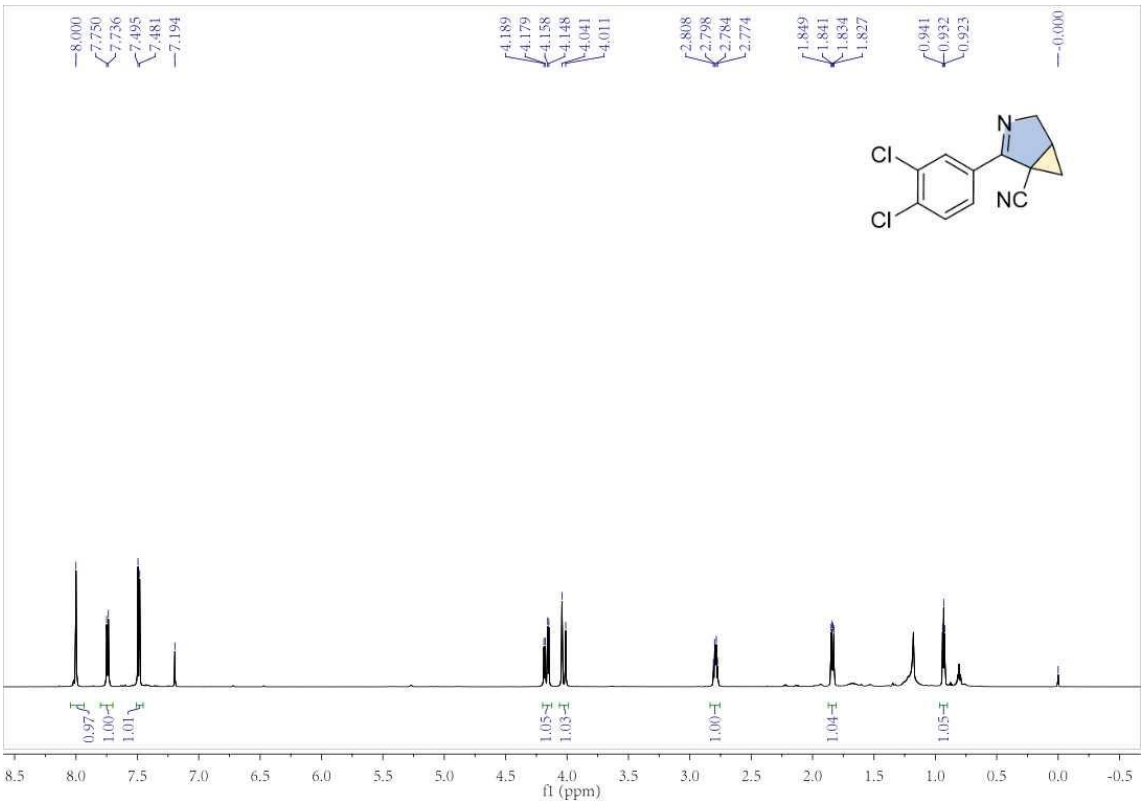
^{1}H spectrum (500 MHz, $CDCl_3$) of compound 5o



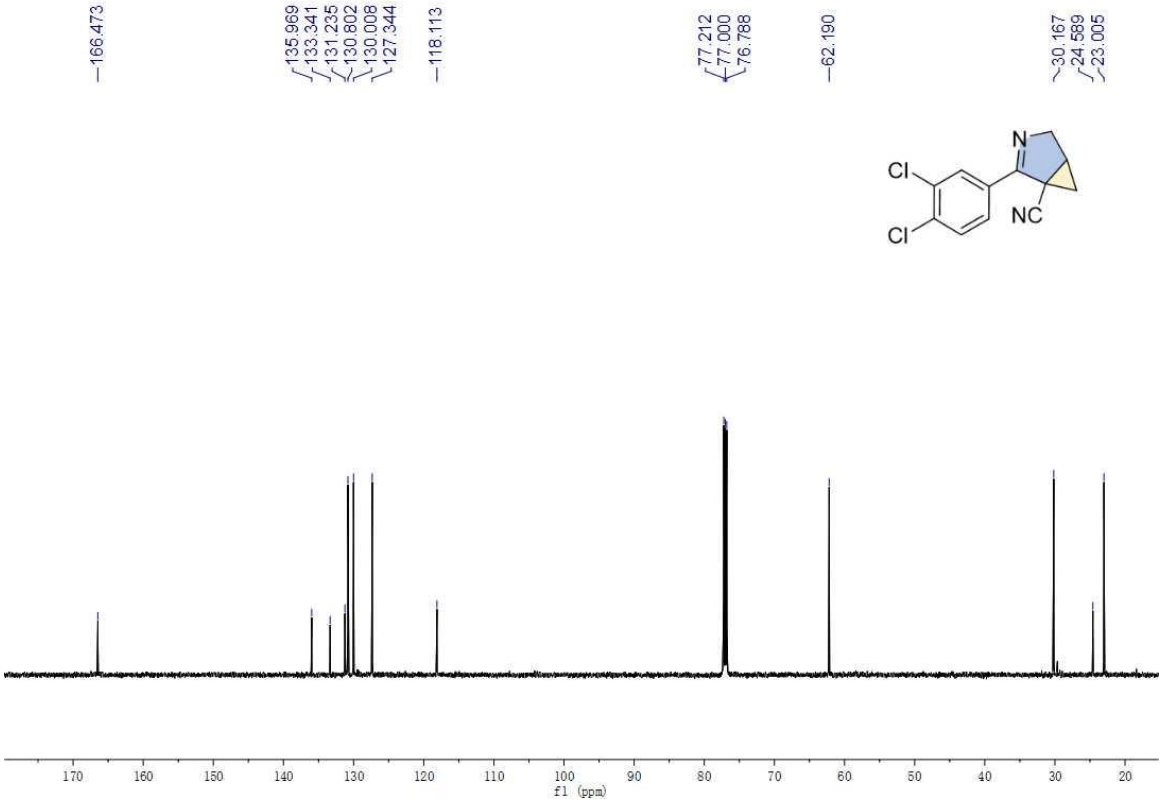
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5o



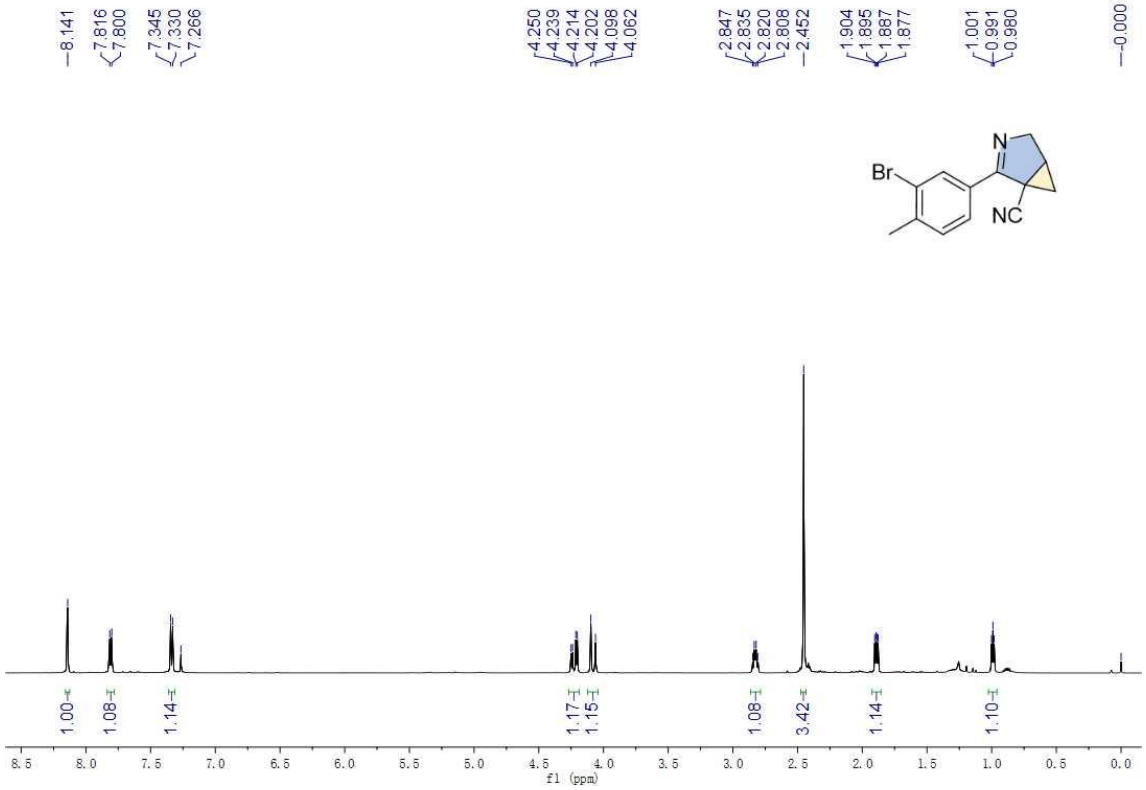
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 5r



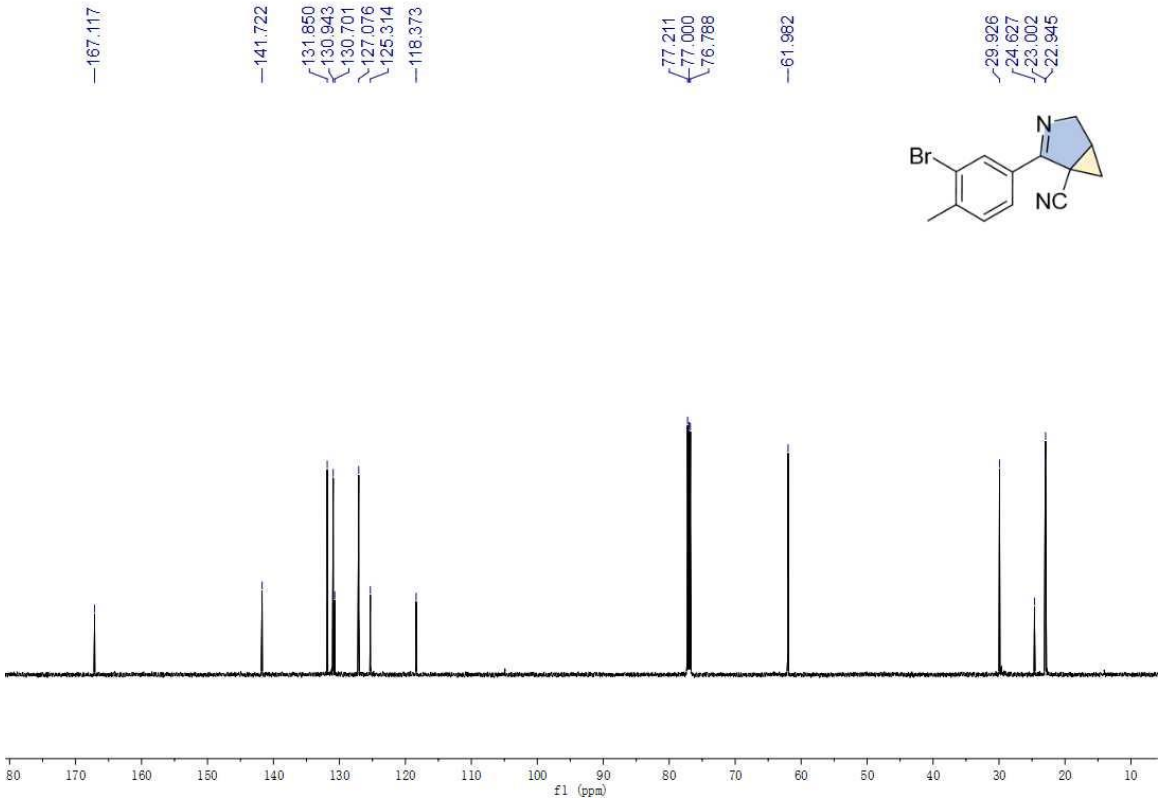
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5r



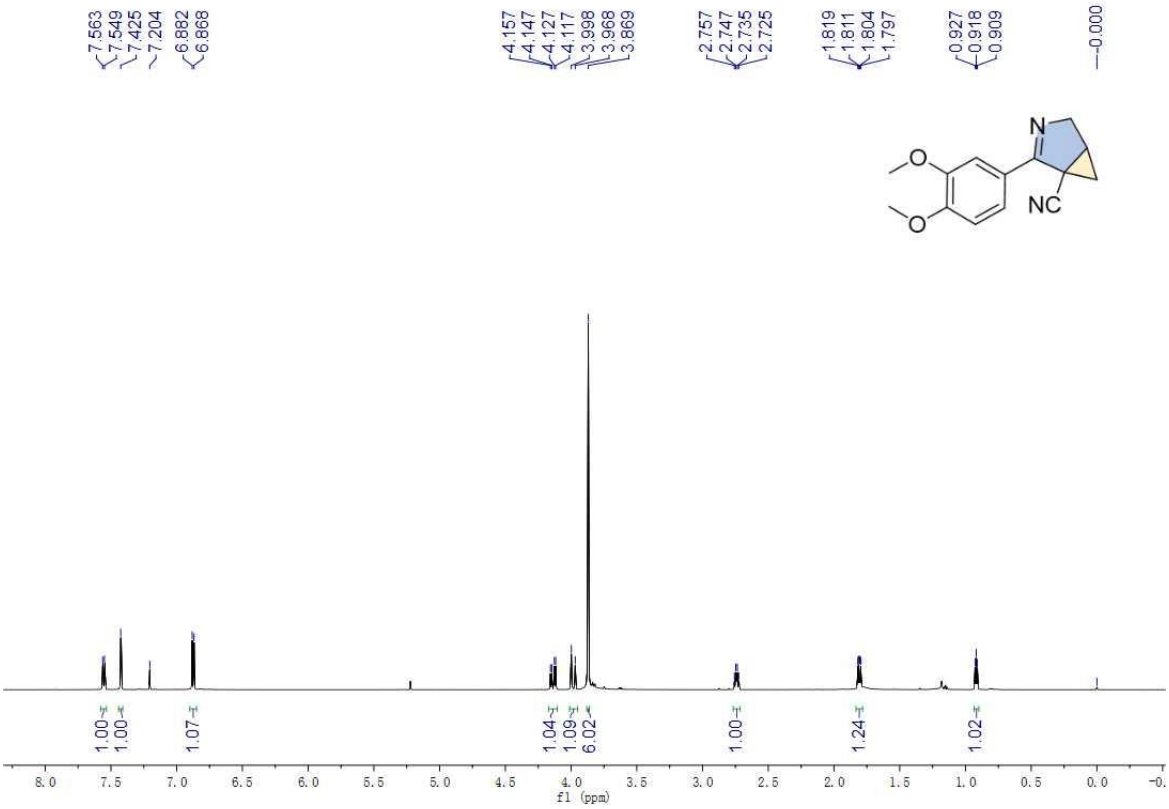
^{1}H spectrum (500 MHz, $CDCl_3$) of compound 5s



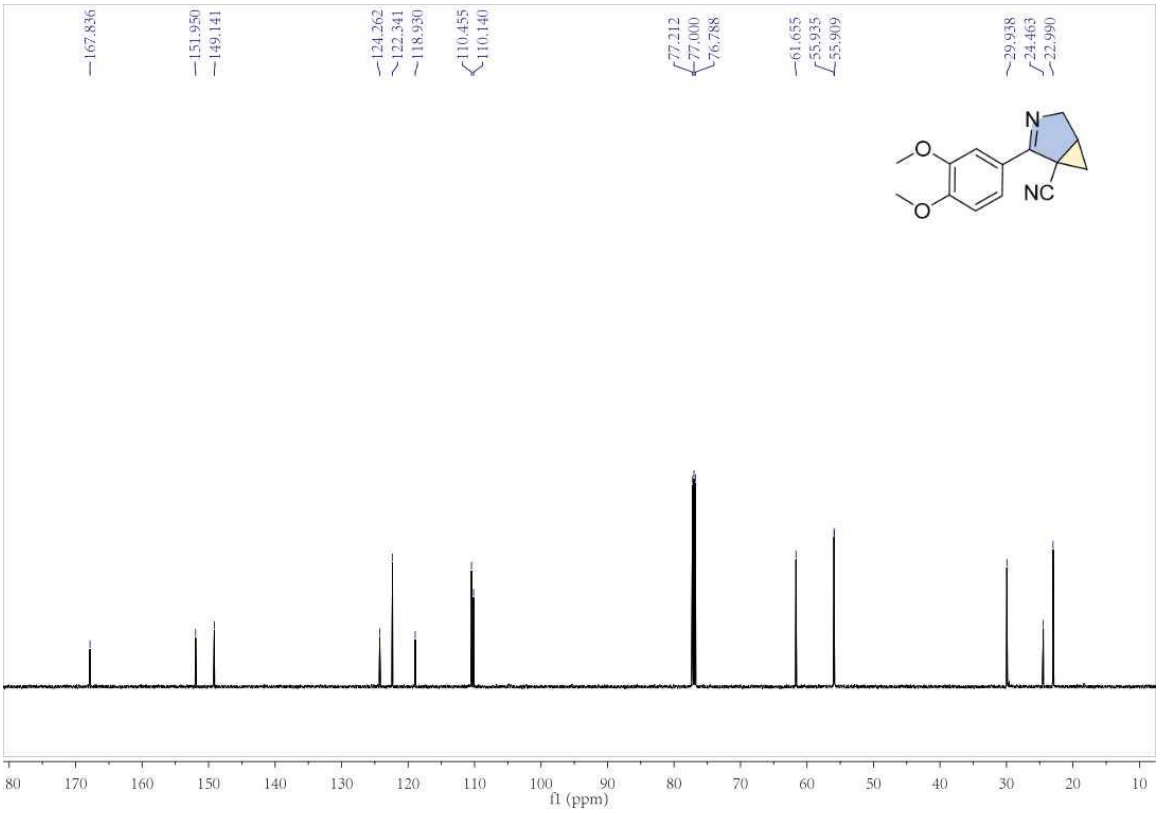
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5s



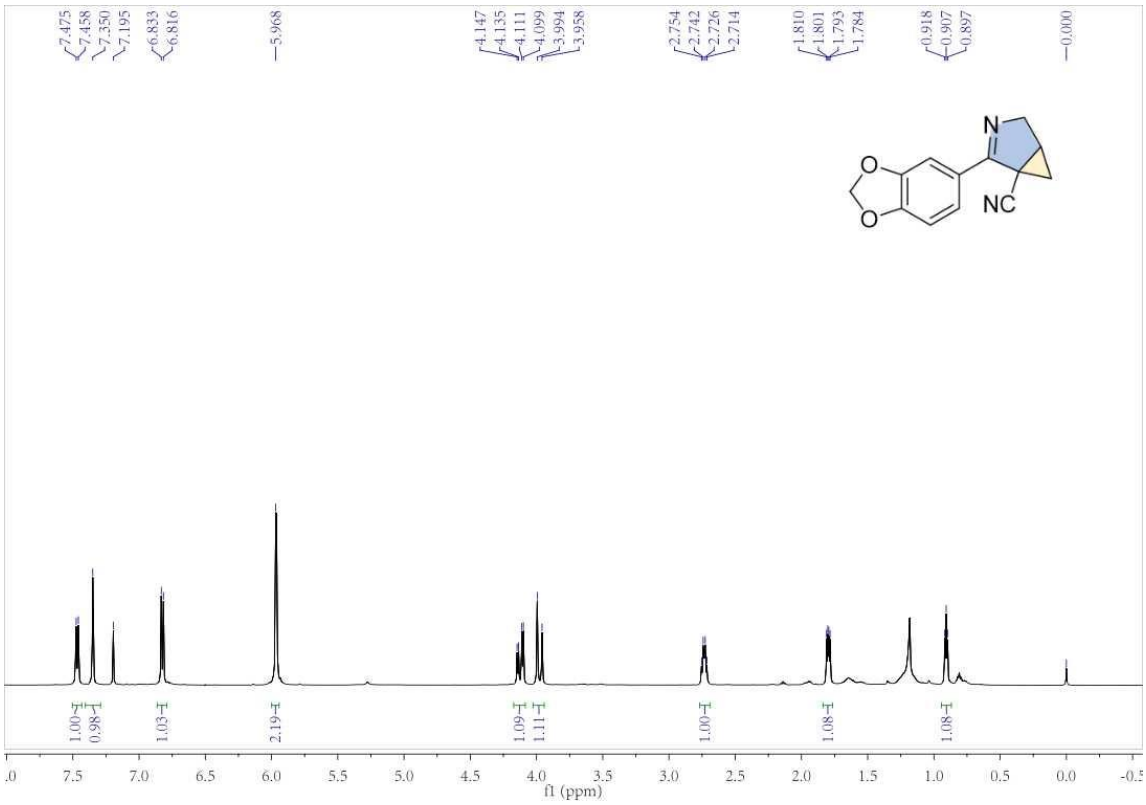
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 5t



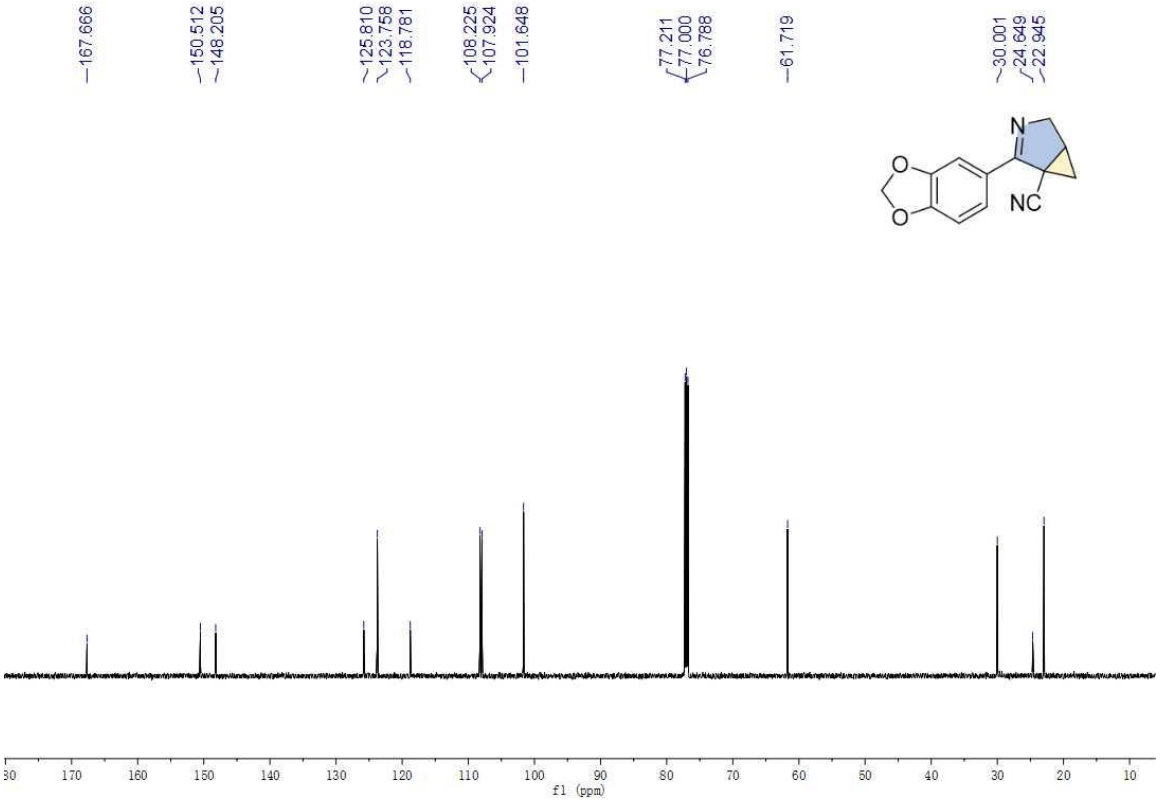
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5t



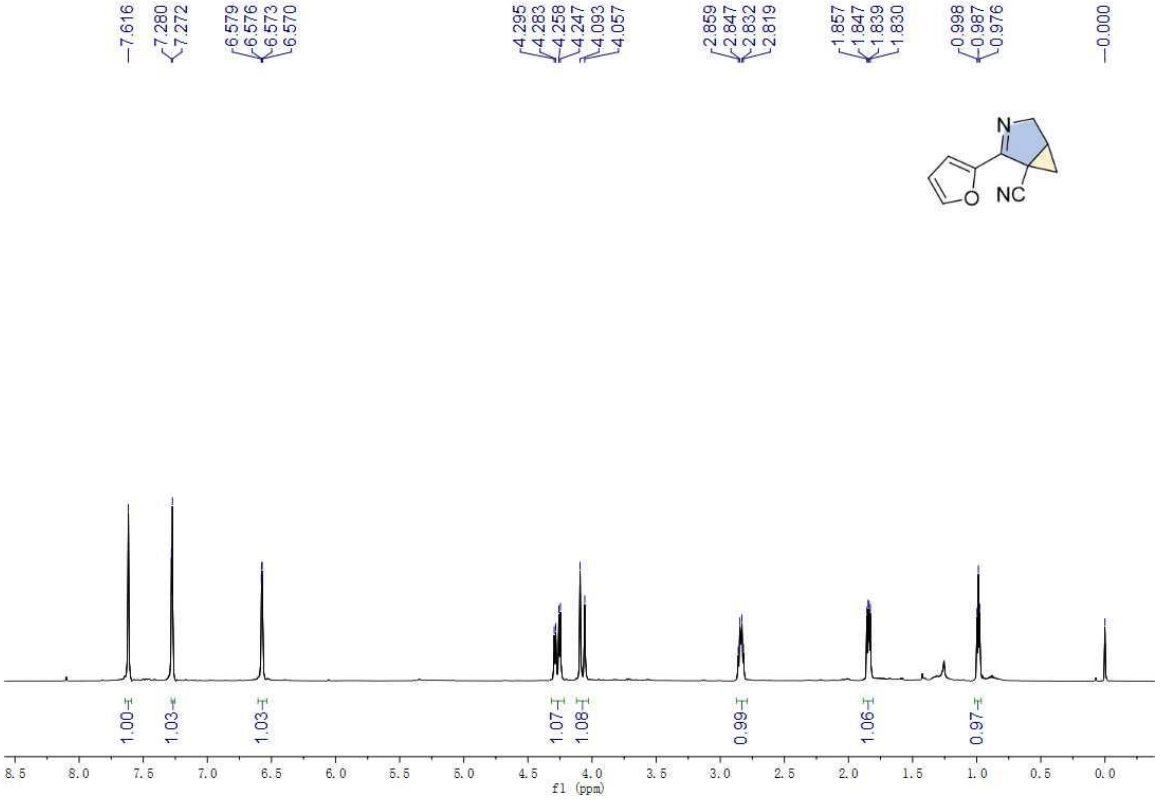
^{1}H spectrum (500 MHz, $CDCl_3$) of compound 5u



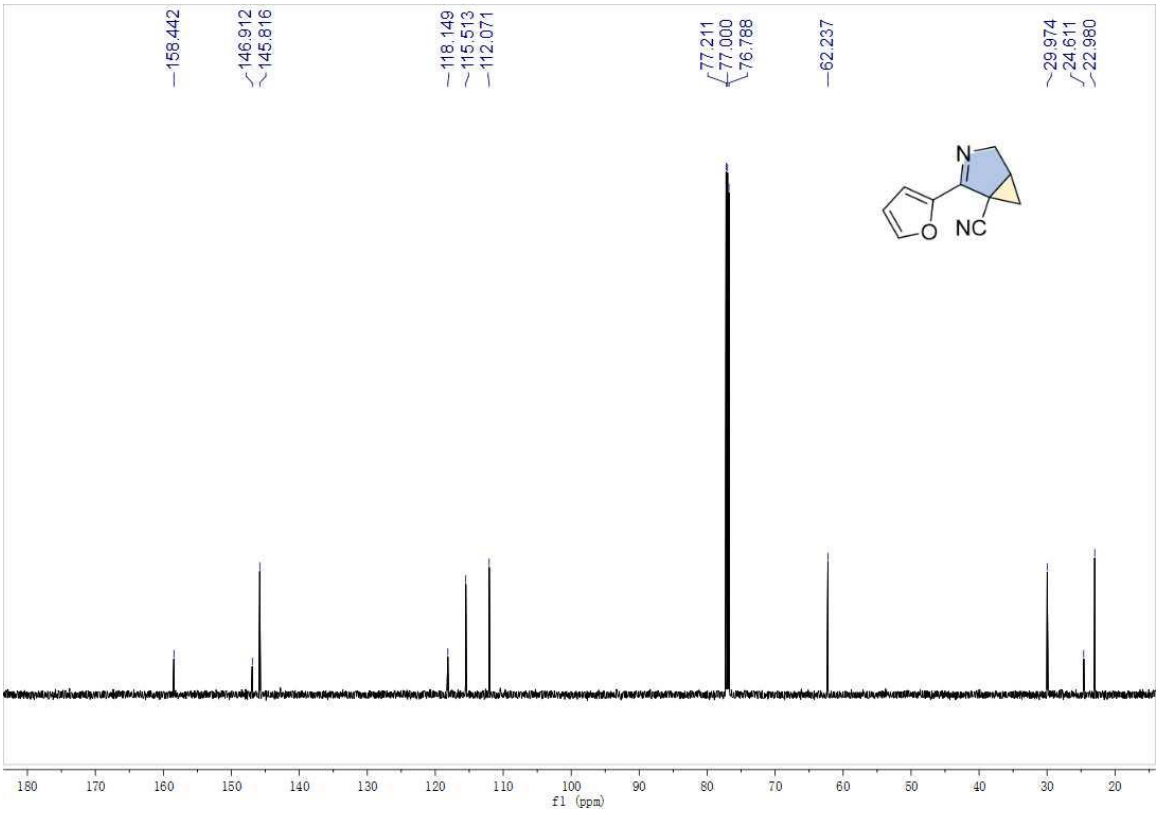
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5u



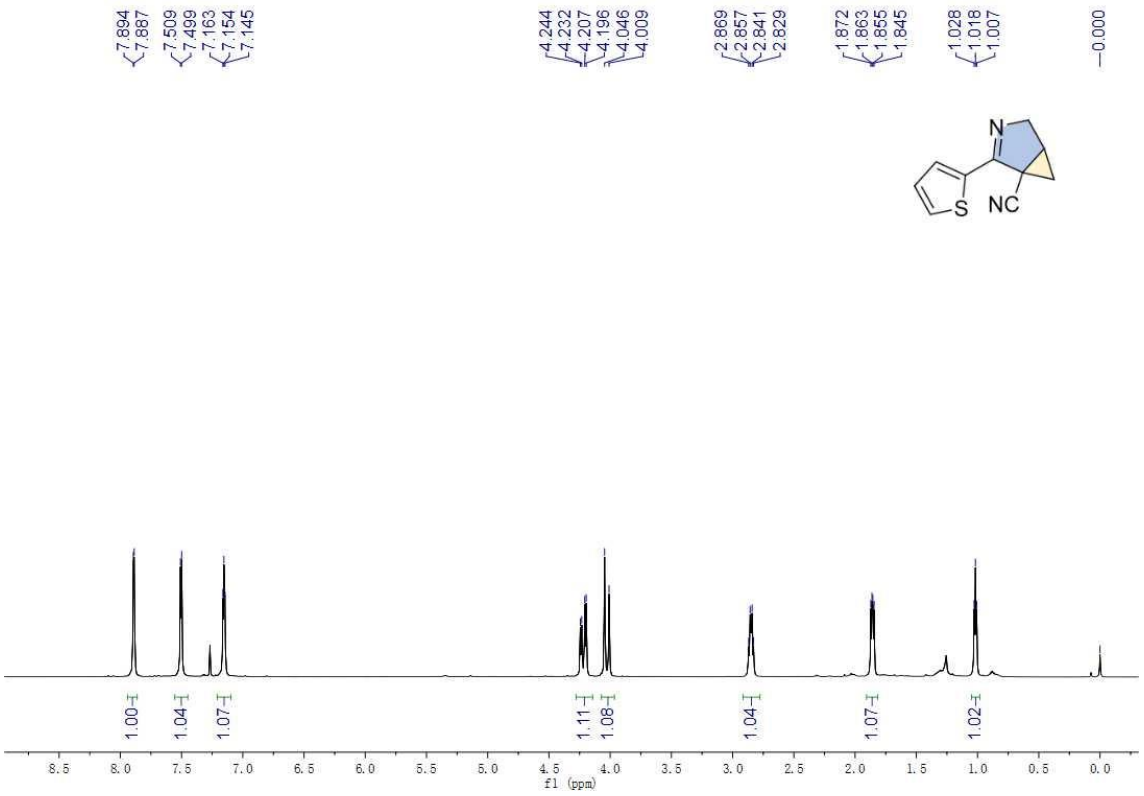
^{1}H spectrum (500 MHz, $CDCl_3$) of compound 5v



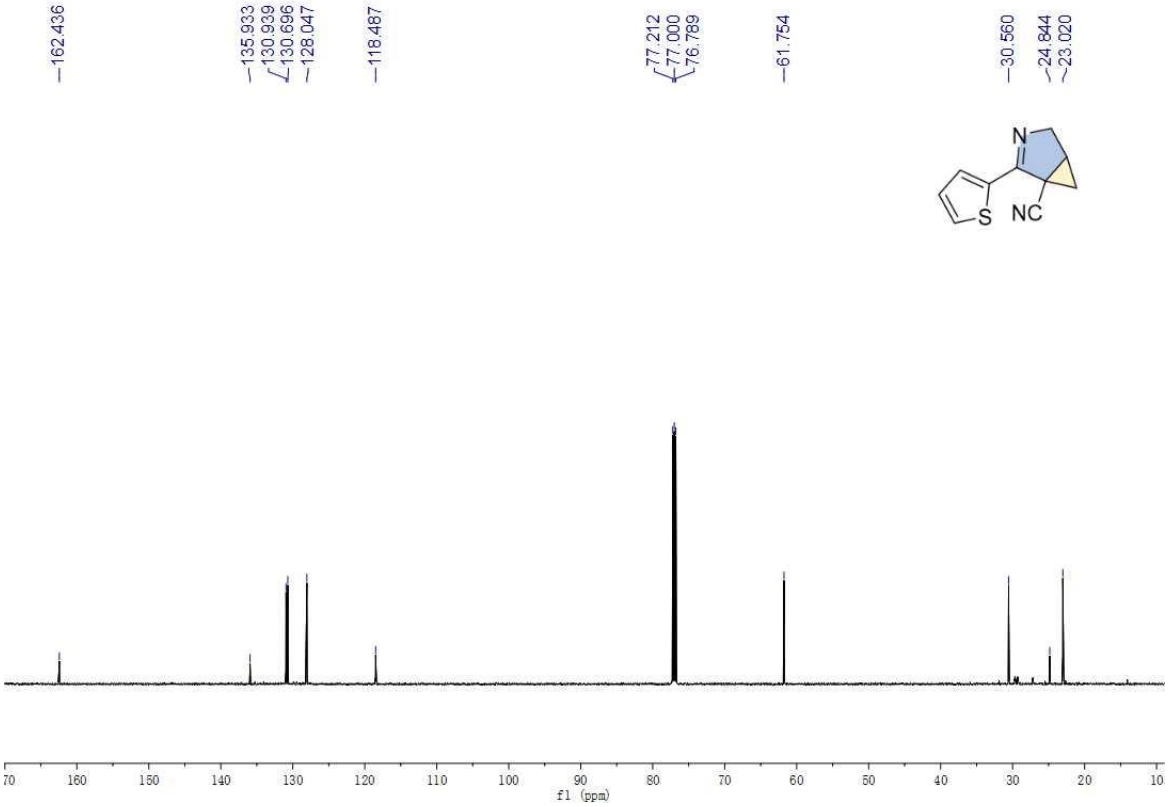
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5v



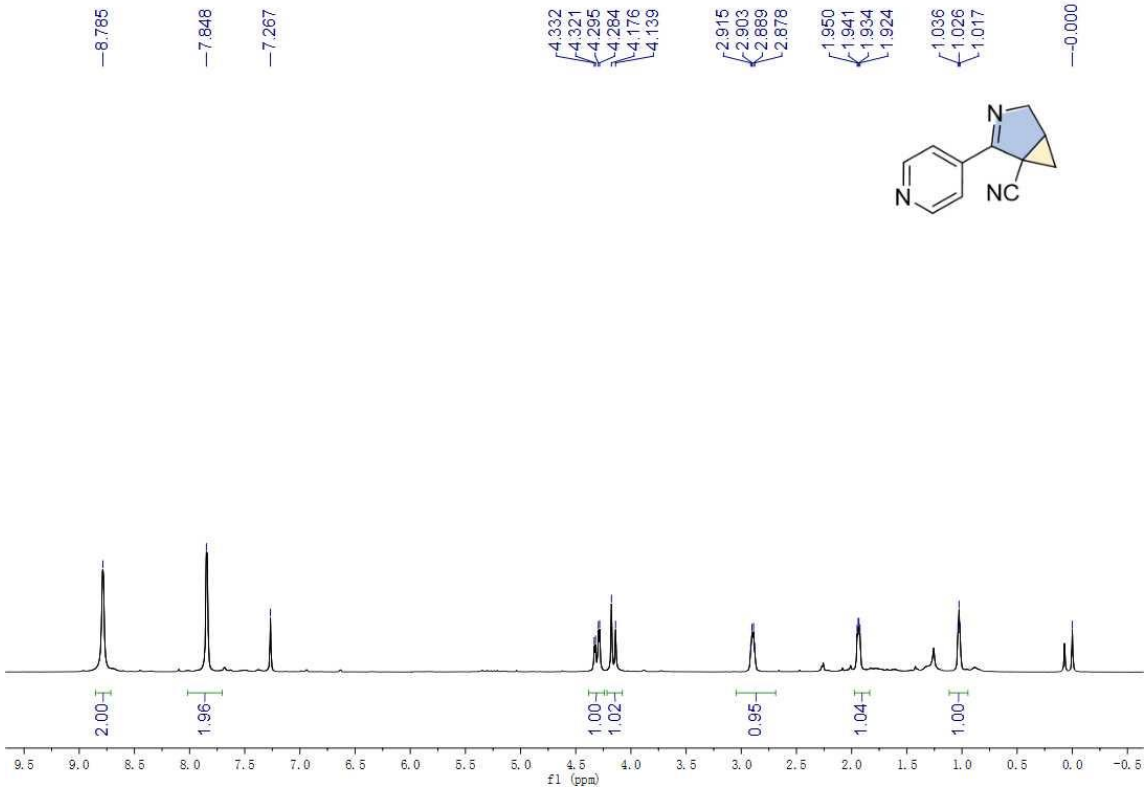
^{1}H spectrum (500 MHz, $CDCl_3$) of compound 5w



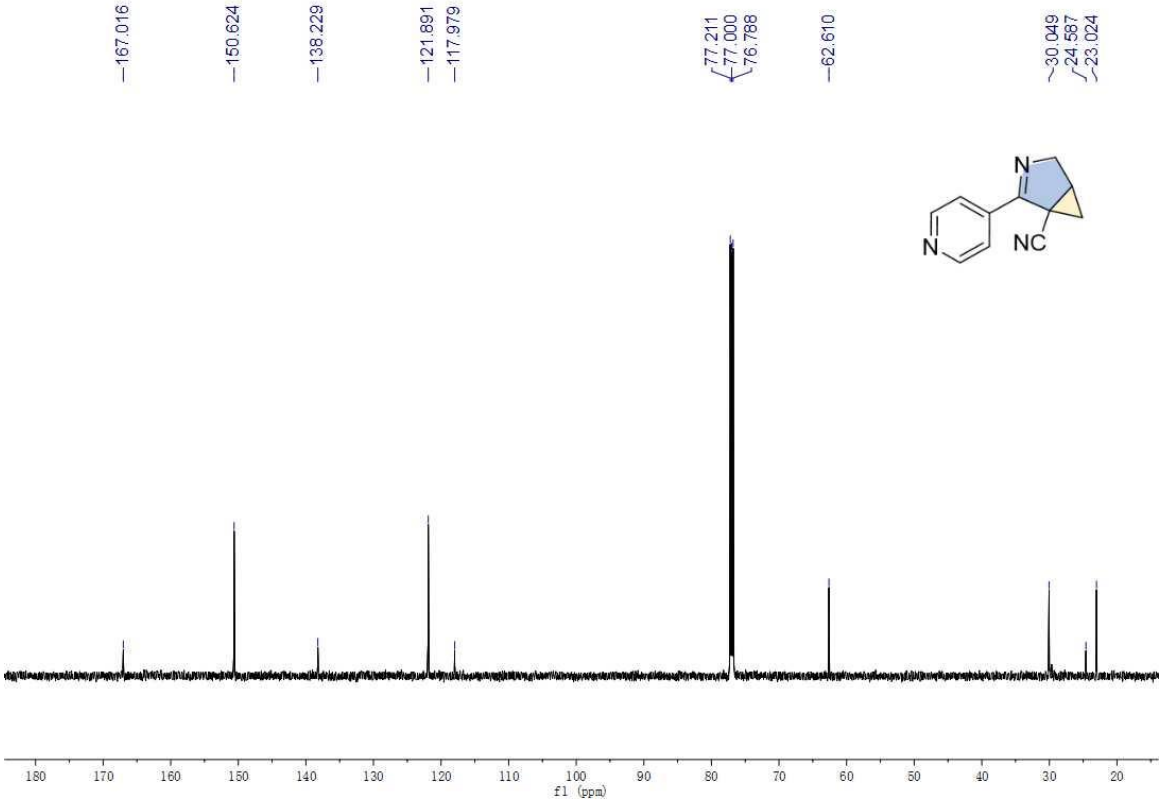
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5w



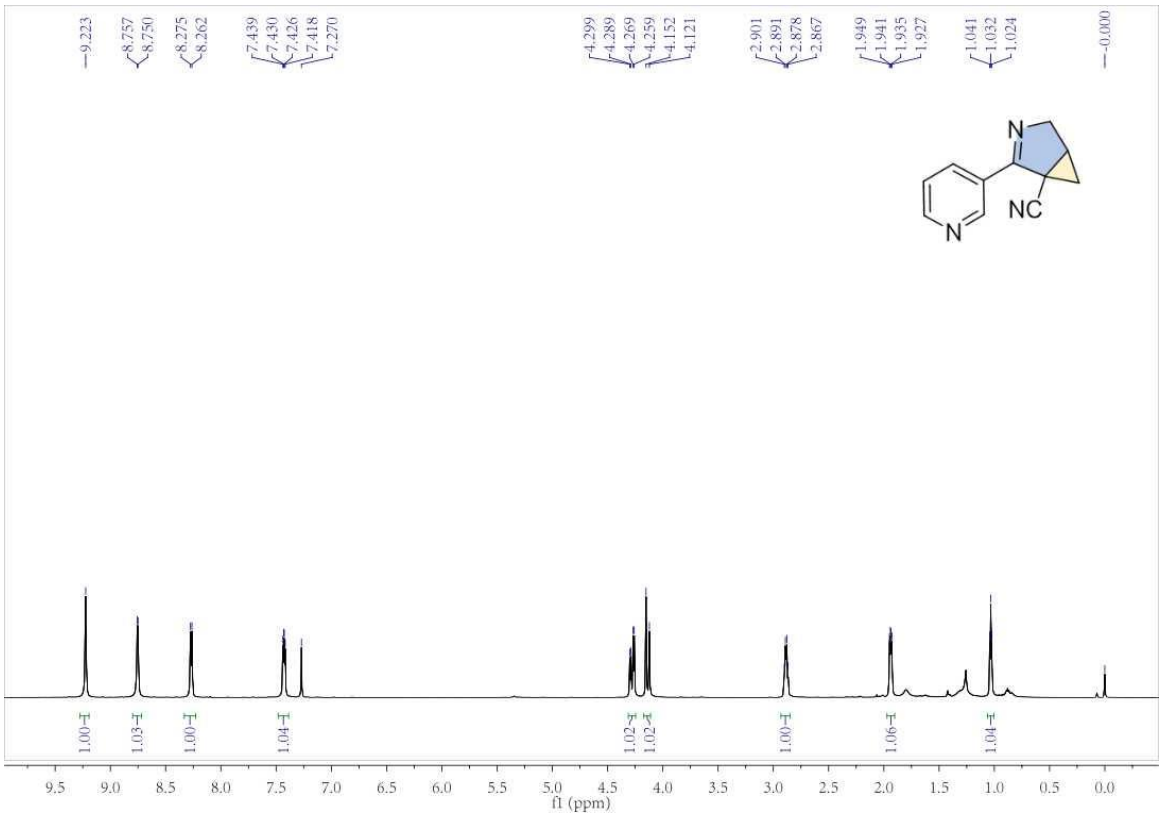
^{1}H spectrum (500 MHz, $CDCl_3$) of compound 5x



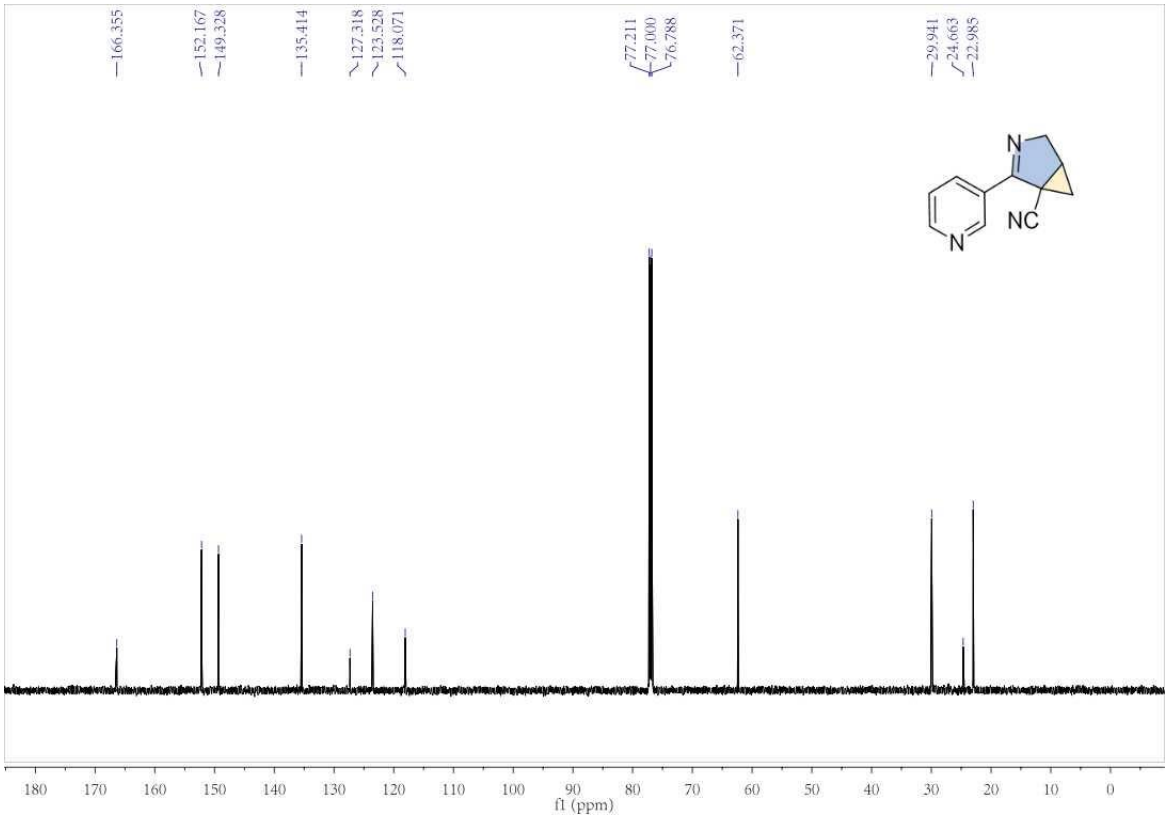
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5x



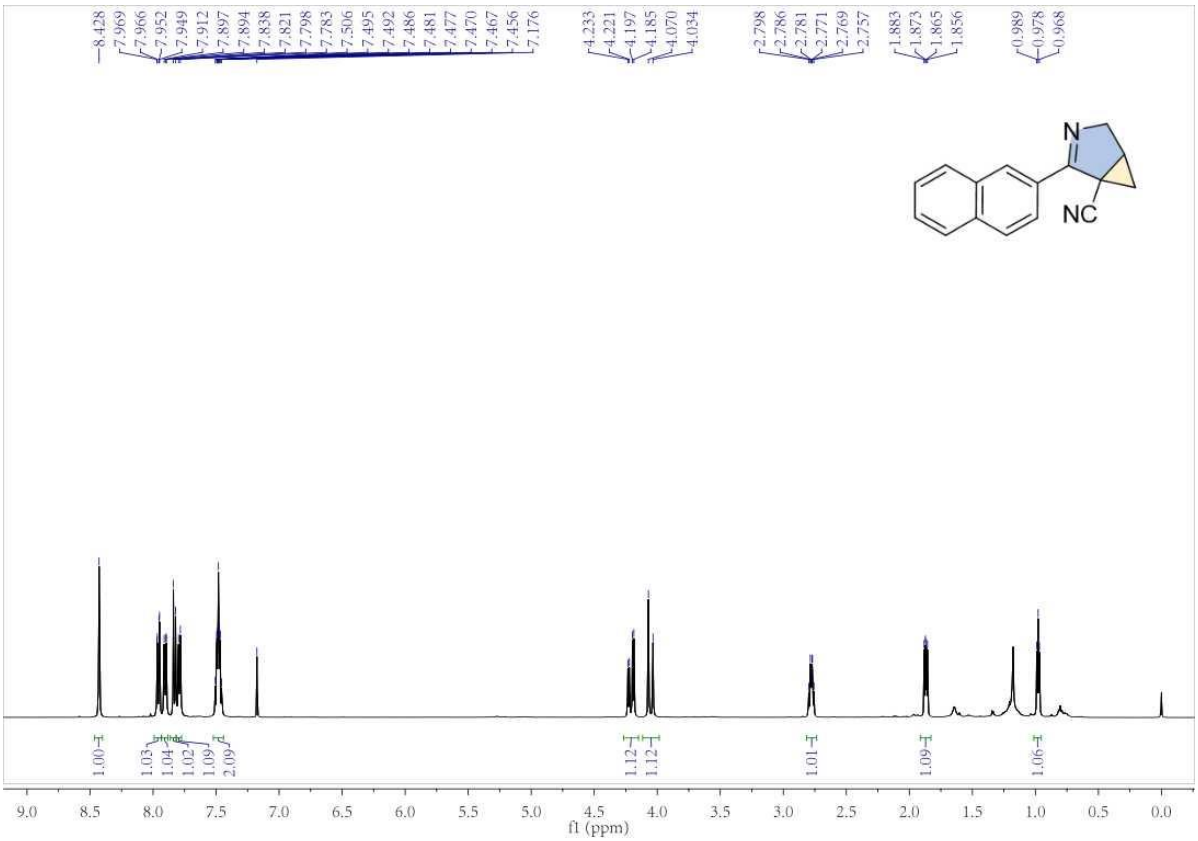
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 5y



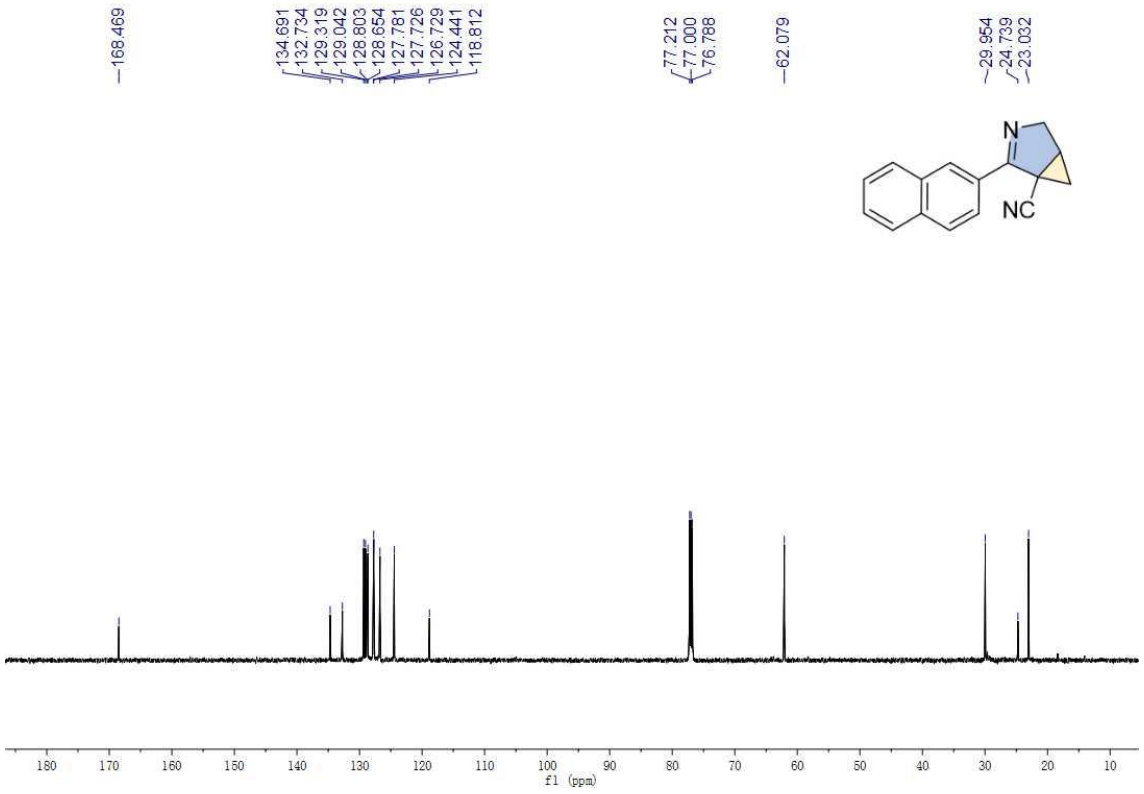
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5y



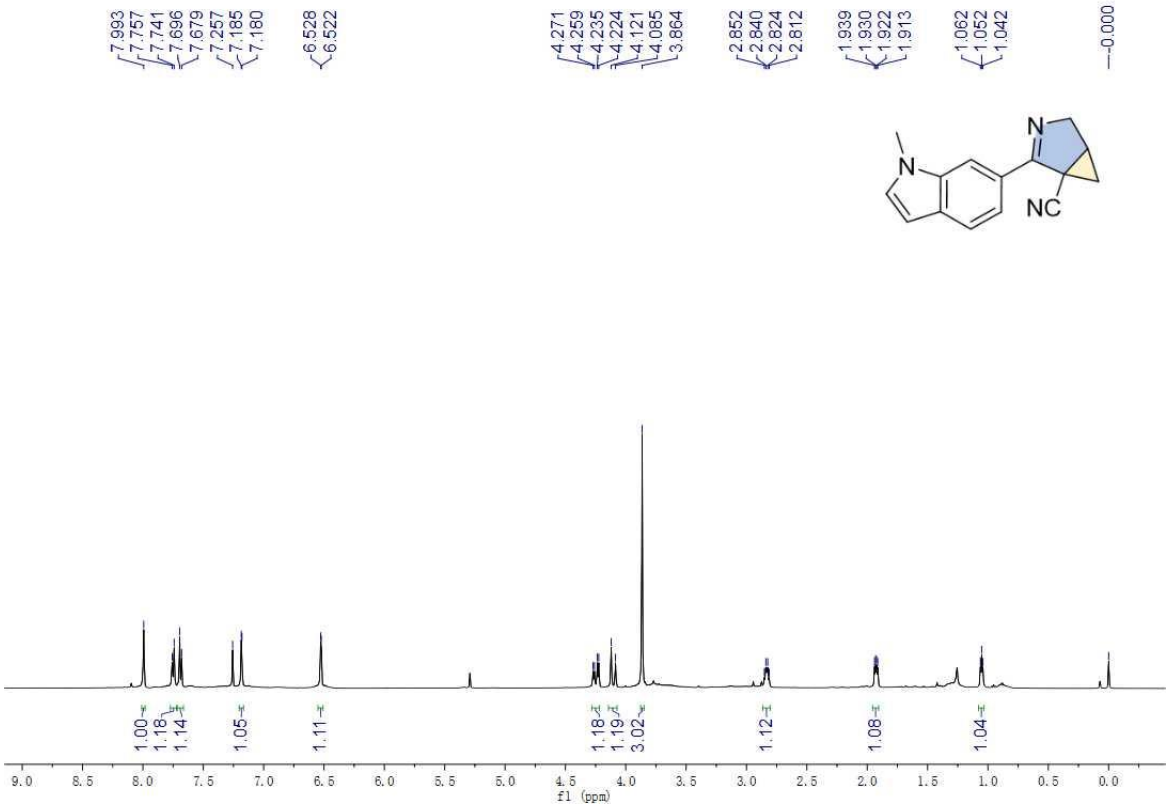
^{1}H spectrum (500 MHz, $CDCl_3$) of compound 5aa



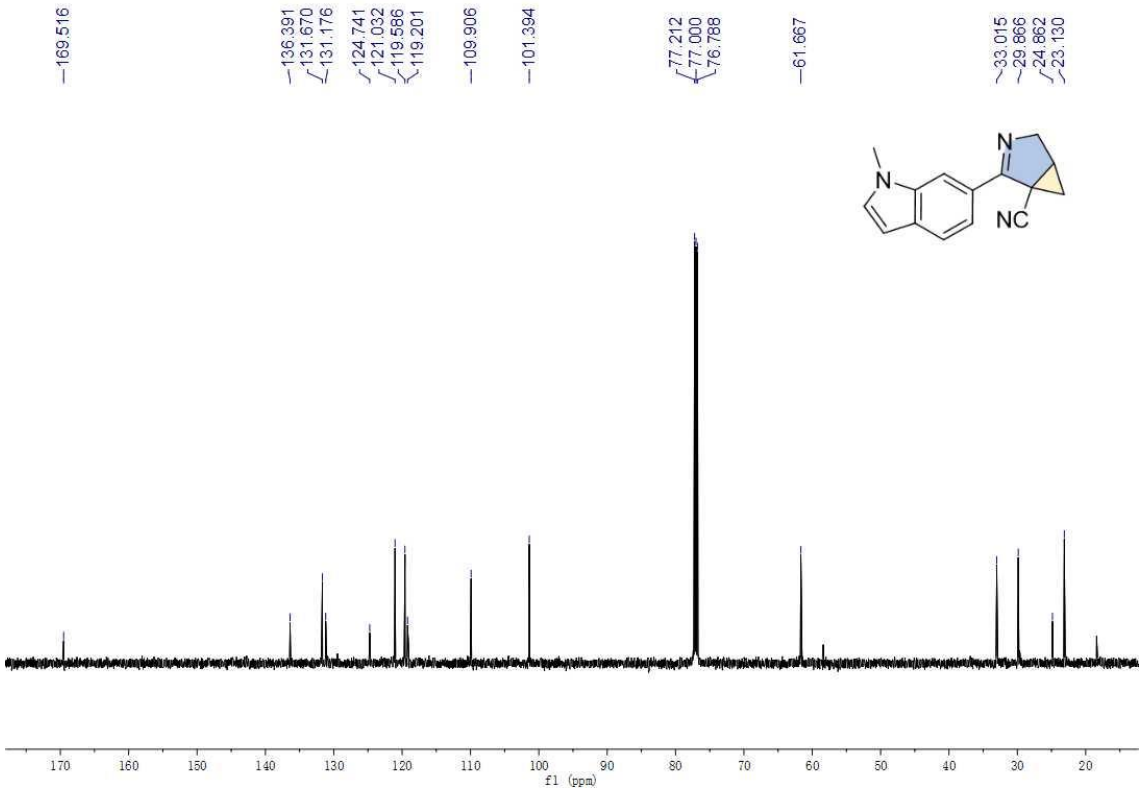
^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5aa



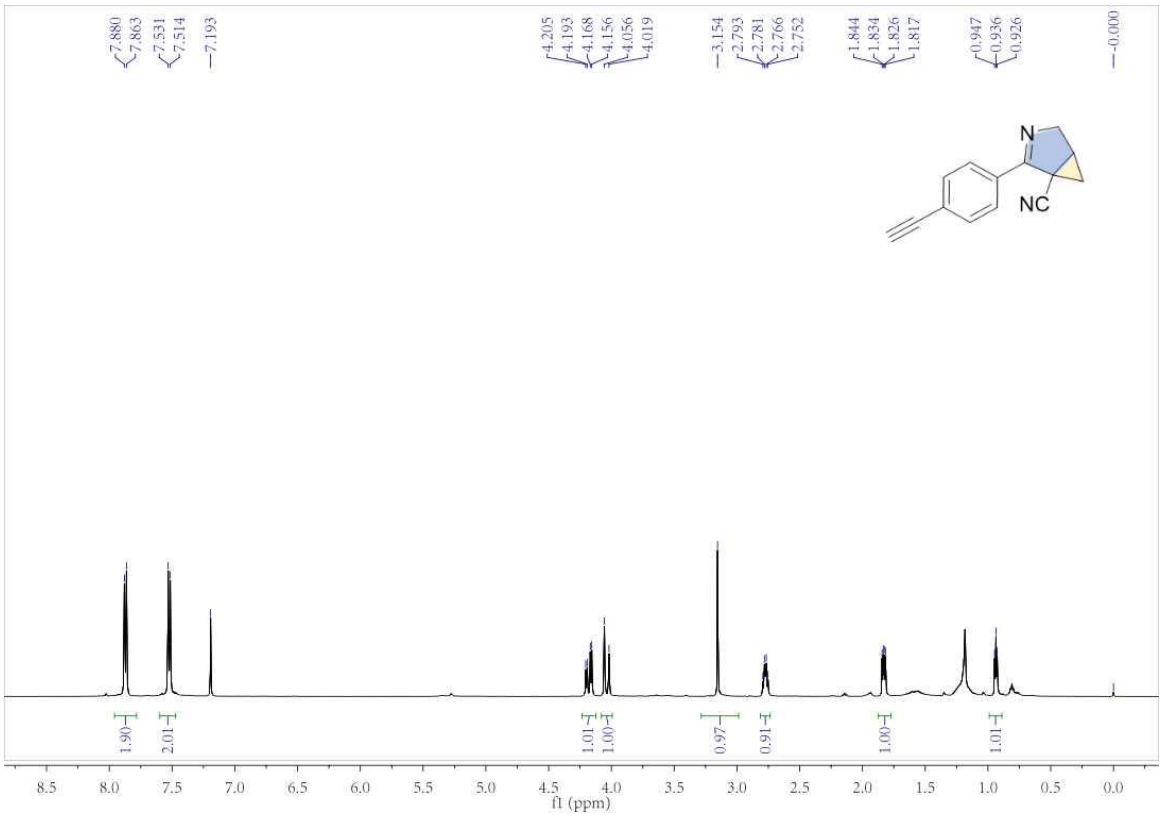
^{1}H spectrum (500 MHz, $CDCl_3$) of compound 5ab



^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5ab



^{1}H spectrum (500 MHz, $CDCl_3$) of compound 5ac



^{13}C spectrum (150 MHz, $CDCl_3$) of compound 5ac