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Palladium-Catalyzed Dehydrogenation of α-Cyclohexene-Substituted Nitriles to α-Aryl Nitriles

Yinglin Zhao, Zhida Zhang, Zehuan Qi and Renhua Liu

Y. Zhao, Z. Zhang, Z. Qi, Prof. R. Liu

Engineering Research Centre of Pharmaceutical Process Chemistry, Ministry of Education

School of Pharmacy, East China University of Science and Technology

130 Meilong Road, Shanghai 200237, P. R. China

E-mail: liurh@ecust.edu.cn.

Abstract: The development of a practical, inexpensive, and cyanide-free method for synthesizing α-aryl nitriles remains a challenging goal in synthetic chemistry. Here, we report an approach for synthesizing α-aryl nitriles toward achieving this goal, which involves the condensation of cyclohexanones with cyanoacetic acid to the acetonitrile-substituted cyclohexenes, and the dehydrogenation of acetonitrile-substituted cyclohexenes to α-aryl nitriles. In addition, similarly, α-(1-cyclohexenyl) alkenyl nitriles are also dehydrogenated to form substituted α-aryl nitriles by this catalytic dehydrogenation system. This synthetic strategy bypasses the toxicity challenge caused by the use of cyanides in conventional approaches. The wide substrate range, facile preparation of the substrates, and the use of commercially available and recovered catalysts, all of which make the approach inherently practical and inexpensive.

Table of Contents

1. General information

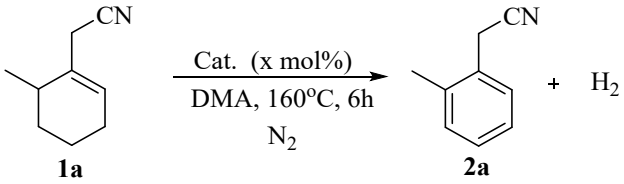
10% Pd/C was firstly washed with acetone and then was dried under reduced pressure at 100 ^{o}C before used. 5% Pd/Asbestos and 5% Pd/Al_2O_3 were obtained from the commercial sources without further processing. Solvents obtained from commercial suppliers and used without further purification. All the other chemical reagents were obtained from commercial sources and used without further purification. The purification of compounds was accomplished by chromatography with petroleum ether and ethyl acetate as eluents. Visualization was achieved under a UV lamp (254 nm and 365 nm).

All new compounds were fully characterized. ^{1}H NMR (400 MHz) spectra were recorded on a Bruker Avance 400 spectrometer in deuterated solvents [using $CDCl_3$ (for ^{1}H, δ = 7.26, DMSO-d_6 (for ^{1}H, δ = 2.50) as the internal standard]. ^{13}C NMR (100 MHz) spectra on a Bruker DRX-400 NMR spectrometer in deuterated solvents [using $CDCl_3$ (for ^{13}C, δ = 77.16), DMSO-d_6 (for ^{13}C, δ = 39.52) as internal standard]. HRMS analyses were made by East China University Of Science and Technology by means of ESI or EI.

2. General procedure for the reaction condition optimization

2.1 The reaction condition optimization of α-aryl nitriles

Table S1. The effect of the catalyst and the amount of catalyst on the reaction

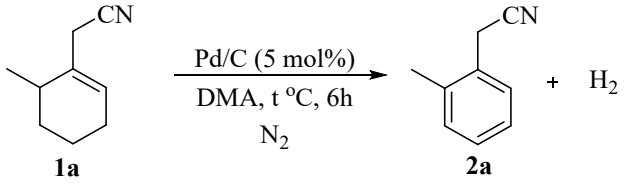


1a **2a**

Entry[a]	Cat.	Equiv.	Yield[b] (%)
1	**Pd/C**	**0.10**	**72**
2	Pd/Al_2O_3	0.10	65
3	Pd/Asbestos	0.10	45
4	Cu/C	0.10	--
5	Pt/C	0.10	--
6	Pd/C	0.01	43
7	Pd/C	0.02	63
8	**Pd/C**	**0.05**	**75**
9[c]	Pd/C	0.05	45
10[d]	Pd/C	0.05	37

[a] Reaction conditions: Unless noted, a mixture of **1a** (0.20 mmol), **Cat.** (**x** mol%), in DMA (1.0 mL) was stirred at **160** °C, in a N_2 atmosphere, for 6h. [b] Isolated yield. [c] air instead of N_2. [d] O_2 instead of N_2.

Table S2. The effect of the temperature on the reaction

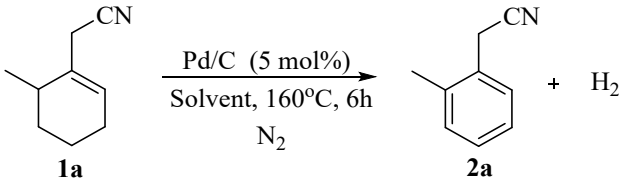


1a **2a**

Entry[a]	T (°C)	Yield[b] (%)
1	**160**	**75**
2	reflux	72
3	110	< 2
4	120	< 2
5	130	< 2
6	140	< 2
7	150	13
8[c]	180	57

[a] Reaction conditions: Unless noted, a mixture of **1a** (0.20 mmol), **Cat.** (**x** mol%), in DMA (1.0 mL) was stirred at **160** °C, in a N_2 atmosphere, for 6h. [b] Isolated yield. [c] NMP instead of DMA.

Table S3 The effect of the solvents on the reaction

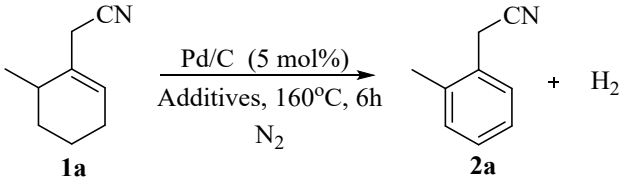


1a **2a**

Entry[a]	Solvent	Yield[b] (%)
1	**DMA**	**75**
2	NMP	68
3[c]	DMF	25
4	DMSO	< 2
5[d]	1,4-dioxane	< 10
6[d]	toluene	< 10
7[e]	dimethylbenzene	< 10
8	*tert*-butylbenzene	31

[a] Reaction conditions: Unless noted, a mixture of **1a** (0.20 mmol), Pd/C (5 mol%), in **solvent** (1.0 mL) was stirred at 160 °C, in a N_2 atmosphere, for 6h. [b] Isolated yield. [c]153°C instead of 160 °C. [d]110°C instead of 160 °C. [e]135°C instead of 160 °C.

Table S4 The effect of the additives on the reaction



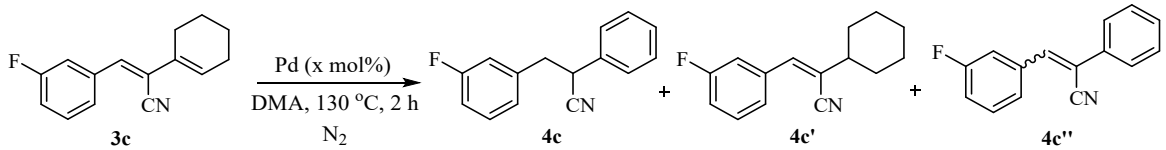
1a **2a**

Entry[a]	Additives	Yield[b] (%)
1	Cs_2CO_3	43
2	K_2CO_3	39
3	**--**	**75**
4	CH_3COOH	65
5	H_3PO_4	46
6	TfOH	71
7	*p*-TSOH	68

[a] Reaction conditions: Unless noted, a mixture of **1a** (0.20 mmol), **additives** (20 mol%), Pd/C (5 mol%), in DMA (1.0 mL) was stirred at 160 °C, in a N_2 atmosphere, for 6h. [b] Isolated yield.

2.2 The reaction condition optimization of substituted α-aryl nitriles

Table S5. The reaction condition optimization of α-arylalkyl nitriles



3c **4c** **4c'** **4c''**

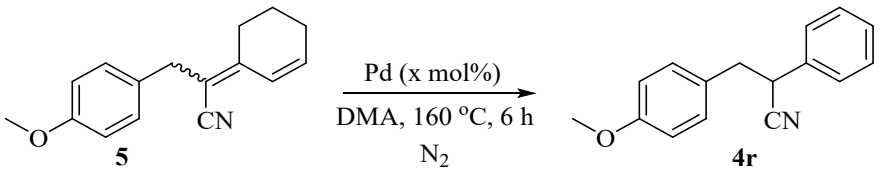
Entry[a]	Pd.	Equiv.	**4c/4c`/4c``**Yield[b] (%)
1	Pd/C	0.10	45/35/<5

2	Pd/Al_2O_3	0.10	53/32/<5
3	Pd/Asbestos	0.10	37/31/<5
4	Pd/Al_2O_3	0.010	47/31/<5
5	**Pd/Al_2O_3**	**0.025**	**65/25/**<5
6	Pd/Al_2O_3	0.05	64/26/<5
7[c]	Pd/Al_2O_3	0.025	57/20/<5
8[d]	Pd/Al_2O_3	0.025	62/30/<5
9[e]	Pd/Al_2O_3	0.025	60/35/<5

[a] Reaction conditions: Unless noted, a mixture of **3c** (0.20 mmol), **Pd.** (**x** mol%), in DMA (1.0 mL) was stirred at **130** °C, in a N_2 atmosphere, for 2h. [b] Isolated yield. [c] air instead of N_2. [d] 150 °C instead of 130 °C. [e] 6 h instead of 2 h.

2.3 The reaction condition optimization of substituted α-aryl nitriles

Table S6. The reaction condition optimization of α-arylalkyl nitriles

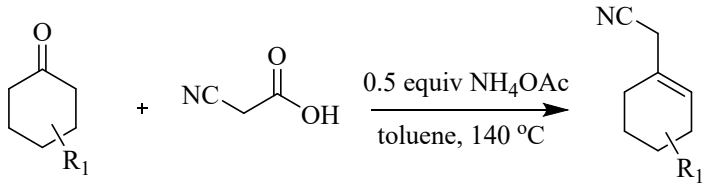


Entry[a]	Pd.	Equiv.	Yield[b] (%)
1	Pd/C	0.10	60
2	Pd/Al_2O_3	0.10	39
3	Pd/Asbestos	0.10	37
4	Pd/C	0.010	--
5	Pd/C	0.025	29
6	**Pd/C**	**0.05**	**65**
7[c]	Pd/C	0.025	57
8[d]	Pd/C	0.025	60

[a] Reaction conditions: Unless noted, a mixture of **5** (0.20 mmol), **Pd.** (**x** mol%), in DMA (1.0 mL) was stirred at **160** °C, in a N_2 atmosphere, for 6h. [b] Isolated yield. [c] air instead of N_2. [d] 150 °C instead of 130 °C.

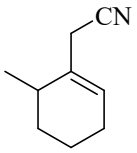
3.General procedure for synthesis of substrates

3.1 General scheme for the synthesis of the α-cyclohexenyl acetonitriles.



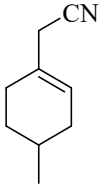
Procedure: Ketone (20 mmol) was refluxed with cyanoacetic acid (20 mmol) and ammonium acetate (10 mmol) in toluene (100 mL), at 140 °C, in oil bath for 4 h, incorporating a Dean-Stark Apparatus to remove water. After removal of toluene, the resulting residues were collected. The crude reaction mixture was purified by column chromatography on silica gel to get the desired product.

1a: 2-(6-methylcyclohex-1-en-1-yl)acetonitrile



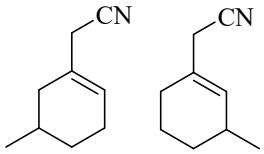
1a-1 were purchased from commercial sources.

1b: 2-(4-methylcyclohex-1-en-1-yl)acetonitrile



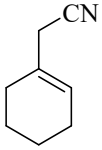
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.74 (s, 1H), 2.99 (s, 2H), 2.36 – 1.89 (m, 3H), 1.73-1.67 (m, 3H), 1.40 – 1.18 (m, 1H), 0.96 (d, *J* = 6.2 Hz, 3H).

1c：2-(3-methylcyclohex-1-en-1-yl)acetonitrile and 2-(5-methylcyclohex-1-en-1-yl)acetonitrile



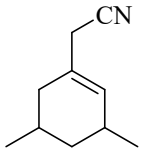
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.77-5.62 (m, 1H), 2.99 (d, 2H), 2.18 – 1.88 (m, 3H), 1.85–1.60 (m,3H), 1.18-1.10 (m, 1H), 1.04 – 0.88 (m, 3H). (Two isomers on the spectrum)

1d: 2-(cyclohex-1-en-1-yl)acetonitrile



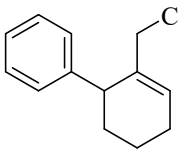
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.78 (t, *J* = 3.9 Hz, 1H), 2.99 (s, 2H), 2.06-1,98 (m, 4H), 1.68-1.58 (m, 4H).

1e: 2-(3,5-dimethylcyclohex-1-en-1-yl)acetonitrile



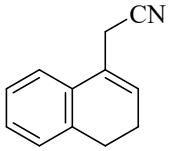
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.57 (t, *J* = 4.0 Hz, 1H), 2.99 (s, 2H), 2.30-2.22 (m, 1H), 1.98 (ddd, *J* = 15.7, 4.8, 2.4 Hz, 1H), 1.81 – 1.55 (m, 4H), 1.02 – 0.95 (m, 6H).

1f: 2-(1,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)acetonitrile



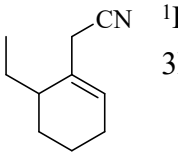
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 2H), 6.11 (t, *J* = 4.7 Hz, 1H), 3.38 (t, *J* = 6.0 Hz, 1H), 2.90 – 2.69 (m, 2H), 2.22-2.16 (m, 2H), 2.08 – 1.96 (m, 1H), 1.74 – 1.51 (m, 3H).

1g: 2-(3,4-dihydronaphthalen-1-yl)acetonitrile



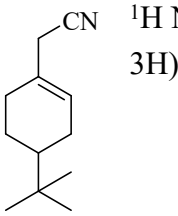
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.14 (m, 3H), 7.10 (d, *J* = 8.3 Hz, 1H), 6.26 (t, *J* = 4.5 Hz, 1H), 3.48 (s, 2H), 2.80 (t, *J* = 8.1 Hz, 2H), 2.36 (tdd, *J* = 7.8, 4.4, 2.1 Hz, 2H).

1h: 2-(6-ethylcyclohex-1-en-1-yl)acetonitrile



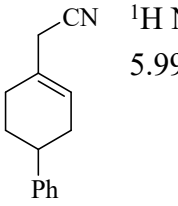
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.81 (t, *J* = 3.8 Hz, 1H), 3.03 (s, 2H), 2.08 – 1.95 (m, 3H), 1.78 – 1.44 (m, 5H), 1.32-1.26 (m, 1H), 0.91 (t, *J* = 7.5 Hz, 3H).

1i: 2-(4-(*tert*-butyl)cyclohex-1-en-1-yl)acetonitrile



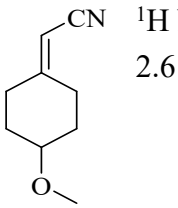
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.77 (t, *J* = 3.7 Hz, 1H), 2.99 (s, 2H), 2.14 – 2.03 (m, 3H), 1.90 – 1.74 (m, 2H), 1.27 – 1.16 (m, 2H), 0.86 (s, 9H).

1j: 2-(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)acetonitrile



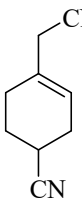
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.28 – 7.13 (m, 3H), 5.99 – 5.72 (m, 1H), 3.06 (s, 2H), 7.82 -7.76(m, 1H), 2.50 – 1.92 (m, 5H), 1.83 (m, 1H).

1k: 2-(4-methoxycyclohex-1-en-1-yl)acetonitrile



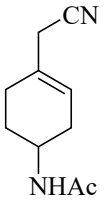
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.09 (s, 1H), 3.48 – 3.42 (m, 1H), 3.36 (s, 3H), 2.71 – 2.61 (m, 1H), 2.53 – 2.42 (m, 2H), 2.24 – 2.13 (m,1H), 1.85 – 1.74 (m, 4H).

1l: 4-(cyanomethyl)cyclohex-3-ene-1-carbonitrile



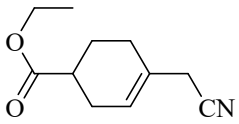
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.75 (t, *J* = 3.8 Hz, 1H), 3.03 (s, 2H), 2.82 (dtd, *J* = 8.5, 6.1, 3.5 Hz, 1H), 2.47 – 2.31 (m, 2H), 2.29 – 2.07 (m, 2H), 2.00 – 1.90 (m, 2H).

1m: *N*-(4-(cyanomethyl)cyclohex-3-en-1-yl)acetamide



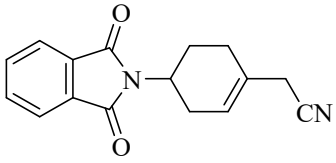
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.87 (d, *J* = 8.0 Hz, 1H), 5.69 (t, *J* = 4.0 Hz, 1H), 4.01 (ddt, *J* = 13.2, 10.9, 5.8 Hz, 1H), 2.99 (s, 2H), 2.39 (d, *J* = 17.2 Hz, 1H), 2.11 (tdd, *J* = 17.9, 11.8, 6.9 Hz, 2H), 1.92 (m, 5H), 1.67 – 1.53 (m, 1H).

1n: ethyl 4-(cyanomethyl)cyclohex-3-ene-1-carboxylate



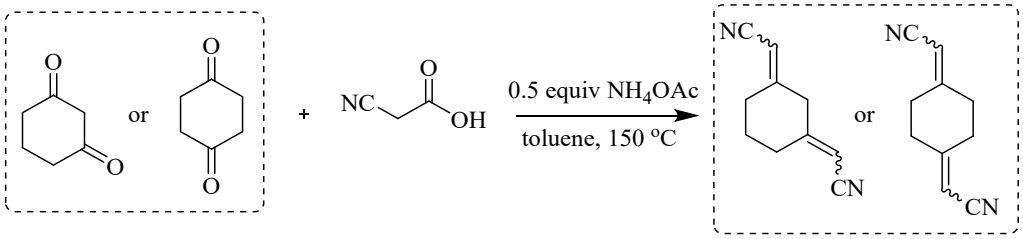
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.76 (t, *J* = 3.0 Hz, 1H), 4.16 – 4.10 (m, 2H), 2.99 (s, 2H), 2.50 (m, 1H), 2.29 (dq, *J* = 5.8, 2.7 Hz, 2H), 2.13 – 2.01 (m, 3H), 1.73 (dtd, *J* = 12.0, 6.0, 2.2 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H).

1o: 2-(4-(1,3-dioxoisoindolin-2-yl)cyclohex-1-en-1-yl)acetonitrile



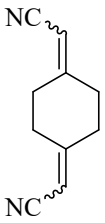
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.1 Hz, 2H), 5.87 – 5.77 (m, 1H), 4.49 – 4.30 (m, 1H), 3.08 (s, 2H), 3.00-2.90 (m, 1H), 2.68-2.52 (m, 1H), 2.48 – 2.15 (m, 3H), 1.93 – 1.84 (m, 1H).

3.2 General Scheme for the Synthesis of 2,2'-(cyclohexane-1,4-diylidene) diacetonitrile.



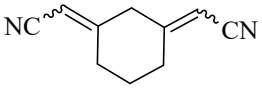
Procedure: Ketone (20 mmol) was refluxed with cyanoacetic acid (20 mmol) and ammonium acetate (10 mmol) in toluene (100 mL), at 150 °C, in oil bath for 6 h, incorporating a Dean-Stark Apparatus to remove water.. After removal of toluene, the resulting residues were collected. The crude reaction mixture was purified by column chromatography on silica gel to get the desired product.

1p: 2,2'-(cyclohexane-1,4-diylidene)diacetonitrile



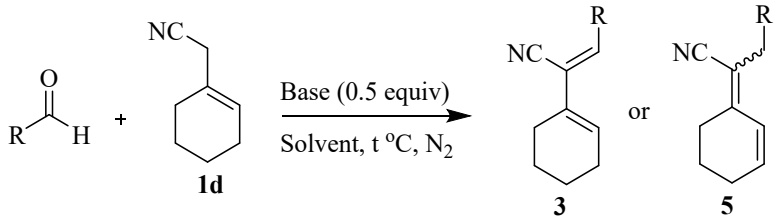
The ^{1}H NMR was messy and a variety of isomers coexisted, but the product obtained by dehydrogenation was the target product and was verified by raw material mass spectrometry. HRMS (EI): *m/z* cacld for $C_{10}H_{10}N_2^{+\circ}$ $[M]^{+\circ}$: 158.0844; found 158.0843

1q: 2,2'-(cyclohexane-1,3-diylidene)diacetonitrile



^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.33 (s, 1H), 5.14 (s, 1H), 3.23 (s, 2H), 2.72 – 2.54 (m, 2H), 2.28 – 2.21 (m, 2H), 1.92-1.82 (m, 2H). (Two isomers on the spectrum, the data represent only one group). HRMS (EI): *m/z* cacld for $C_{10}H_{10}N_2^{+\circ}$ $[M]^{+\circ}$: 158.0844; found 158.0843.

3.3 General Scheme for condensation of α-cyclohexenyl acetonitriles and aldehydes.

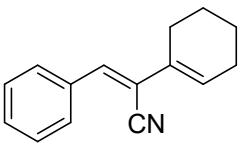


Procedure: Method **A:** Aldehyde (10 mmol) was refluxed with **1d** (10 mmol) and *t*-BuOK or KOH (5 mmol) in toluene (50 mL) at 130 °C, in oil bath for 5 h, incorporating a Dean-Stark Apparatus to remove water.. After removal of toluene, the resulting residues were collected. The crude reaction mixture was purified by column chromatography on silica gel to get the desired product [1].

Method **B:** Aromatic aldehyde (10 mmol) was reacted with **1d** (10 mmol) and NaOH (5 mmol) in EtOH (10 mL) at 25-35 °C in oil bath for 6-20 h. After removal of solvent, the resulting residues were collected. The crude reaction mixture was purified by column chromatography on silica gel to get the desired product [2].

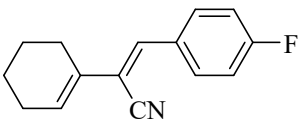
Method **C:** Aromatic aldehyde (10 mmol) was reacted with **1d** (10 mmol) and NaOH (5 mmol) in DMA (10 mL) at 60 °C in oil bath for 2 h. After removal of solvent, the resulting residues were collected. The crude reaction mixture was purified by column chromatography on silica gel to get the desired product.

3a: 2-(cyclohex-1-en-1-yl)-3-phenylacrylonitrile



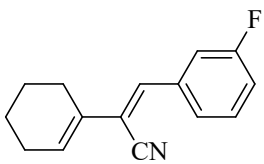
Method **B:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.8 Hz, 2H), 7.28 (dq, *J* = 12.9, 8.0, 7.4 Hz, 3H), 6.90 (s, 1H), 6.40 (t, *J* = 3.8 Hz, 1H), 2.16 (m, 4H), 1.71 – 1.62 (m, 2H), 1.58 – 1.52 (m, 2H).

3b: 2-(cyclohex-1-en-1-yl)-3-(4-fluorophenyl)acrylonitrile



Method **B:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.09 (t, *J* = 8.7 Hz, 2H), 6.95 (s, 1H), 6.50 (t, *J* = 2.9 Hz, 1H), 2.30-2.22 (m, 4H), 1.81 – 1.72 (m, 2H), 1.69 – 1.61 (m, 2H).

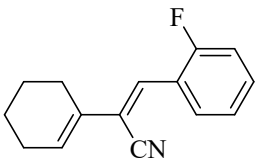
3c: 2-(cyclohex-1-en-1-yl)-3-(3-fluorophenyl)acrylonitrile



Method **B:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.8 Hz, 1H), 7.48 (dt, *J* = 10.1, 2.0 Hz, 1H), 7.37 (td, *J* = 8.0, 6.0 Hz, 1H), 7.06 (td, *J* = 8.3, 2.5 Hz,

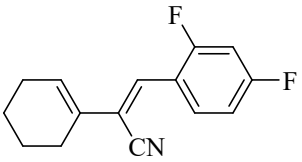
1H), 6.94 (s, 1H), 6.54 (t, *J* = 4.0 Hz, 1H), 2.31-2.24 (m, 4H), 1.82–1.73 (m, 2H), 1.70 – 1.61 (m, 2H).

3d：2-(cyclohex-1-en-1-yl)-3-(2-fluorophenyl)acrylonitrile



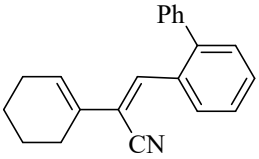
Method **B:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (t, *J* = 7.9 Hz, 1H), 7.45 – 7.31 (m, 1H), 7.25 (d, *J* = 9.2 Hz, 2H), 7.12 (t, *J* = 9.5 Hz, 1H), 6.57 (q, *J* = 3.2 Hz, 1H), 2.32 (d, *J* = 6.2 Hz, 4H), 1.86 – 1.76 (m, 2H), 1.73 – 1.65 (m, 2H).

3e: 2-(cyclohex-1-en-1-yl)-3-(2,4-difluorophenyl)acrylonitrile

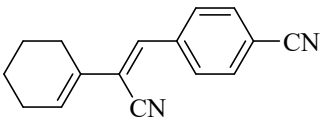


Method **B:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (td, *J* = 8.7, 6.2 Hz, 1H), 7.11 (s, 1H), 6.96 (td, *J* = 9.0, 2.7 Hz, 1H), 6.90 – 6.80 (m, 1H), 6.53 (t, *J* = 4.0 Hz, 1H), 2.32 – 2.24 (m, 4H), 1.82 – 1.73 (m, 2H), 1.70 – 1.61 (m, 2H).

3f: 3-([1,1'-biphenyl]-2-yl)-2-(cyclohex-1-en-1-yl)acrylonitrile



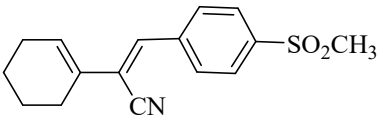
Method **A:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (dd, *J* = 5.4, 3.7 Hz, 1H), 7.51 – 7.41 (m, 6H), 7.39 – 7.33 (m, 2H), 6.95 (s, 1H), 6.53 (t, *J* = 4.3 Hz, 1H), 2.29 (q, *J* = 2.7 Hz, 2H), 2.05 – 1.97 (m, 2H), 1.73 – 1.62 (m, 4H).



3g: 4-(2-cyano-2-(cyclohex-1-en-1-yl)vinyl)benzonitrile

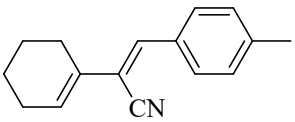
Method **B:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 6.3 Hz, 2H), 7.69 (d, *J* = 6.6 Hz, 2H), 6.97 (s, 1H), 6.61 (t, *J* = 4.2 Hz, 1H), 2.38 – 2.23 (m, 4H), 1.87 – 1.74 (m, 2H), 1.72 – 1.62 (m, 2H).

3h: 2-(cyclohex-1-en-1-yl)-3-(4-(methylsulfonyl)phenyl)acrylonitrile



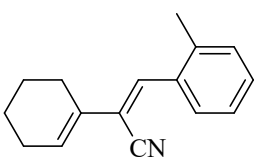
Method **B:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.5 Hz, 2H), 7.91 (d, *J* = 8.5 Hz, 2H), 7.03 (s, 1H), 6.62 (t, *J* = 3.5 Hz, 1H), 3.08 (s, 3H), 2.33-2.27 (m, 4H), 1.83 – 1.75 (m, 2H), 1.71 – 1.64 (m, 2H).

3i: 2-(cyclohex-2-en-1-ylidene)-3-(*p*-tolyl)propanenitrile



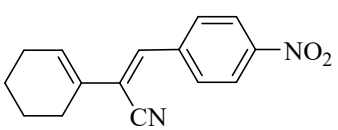
Method **B:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 6.97 (s, 1H), 6.54 – 6.40 (m, 1H), 2.38 (s, 3H), 2.27 (t, *J* = 5.9 Hz, 4H), 1.82 – 1.73 (m, 2H), 1.70 – 1.61 (m, 2H).

3j: 2-(cyclohex-2-en-1-ylidene)-3-(*o*-tolyl)propanenitrile



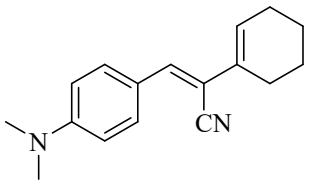
Method **B:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.66 (m, 1H), 7.20 – 7.15 (m, 2H), 7.14 – 7.09 (m, 2H), 6.42 (t, *J* = 4.1 Hz, 1H), 2.23 (s, 3H), 2.21 – 2.15 (m, 4H), 1.72 – 1.66 (m, 2H), 1.59 – 1.53 (m, 2H).

3k: 2-(cyclohex-1-en-1-yl)-3-(2-nitrophenyl)acrylonitrile



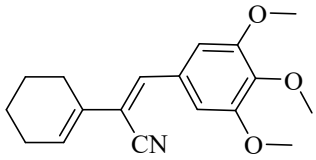
Method B: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.72 (t, *J* = 8.1 Hz, 1H), 7.56 (t, *J* = 8.5 Hz, 1H), 7.47 (s, 1H), 6.57 (t, *J* = 3.8 Hz, 1H), 2.34-2.27 (m, 4H), 1.82-1.77 (m, 2H), 1.72 – 1.63 (m, 2H).

3l: 2-(cyclohex-1-en-1-yl)-3-(4-(dimethylamino)phenyl)acrylonitrile



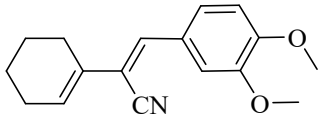
Method **C:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 9.0 Hz, 2H), 6.89 (s, 1H), 6.69 (d, *J* = 9.0 Hz, 2H), 6.36 (t, *J* = 4.1 Hz, 1H), 3.02 (s, 6H), 2.32 – 2.17 (m, 4H), 1.80 – 1.71 (m, 2H), 1.63 (m, 2H).

3m: 2-(cyclohex-1-en-1-yl)-3-(3,4,5-trimethoxyphenyl)acrylonitrile



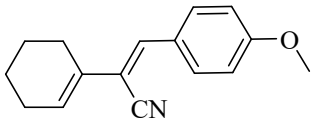
Method **A:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.06 (s, 2H), 6.90 (s, 1H), 6.48 (t, *J* = 3.9 Hz, 1H), 3.89 (d, 9H), 2.27 (d, *J* = 4.8 Hz, 4H), 1.82 – 1.72 (m, 2H), 1.65 (dt, *J* = 8.5, 2.4 Hz, 2H).

3n: 2-(cyclohex-1-en-1-yl)-3-(3,4-dimethoxyphenyl)acrylonitrile



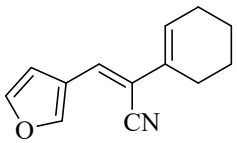
Method **A:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 2.1 Hz, 1H), 7.23 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.91 (s, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.43 (t, *J* = 3.9 Hz, 1H), 3.91 (d , 6H), 2.28 – 2.22 (m, 4H), 1.78 – 1.72 (m, 2H), 1.64 (dt, *J* = 11.6, 4.3 Hz, 2H).

3o: 2-(cyclohex-1-en-1-yl)-3-(4-methoxyphenyl)acrylonitrile



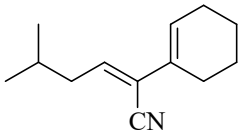
Method **A:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.6 Hz, 2H), 6.95 – 6.88 (m, 3H), 6.43 (t, *J* = 3.9 Hz, 1H), 3.83 (d, *J* = 0.9 Hz, 3H), 2.24 (d, *J* = 5.0 Hz, 4H), 1.75 (dd, *J* = 7.6, 4.0 Hz, 2H), 1.66 – 1.59 (m, 2H).

3p: 2-(cyclohex-1-en-1-yl)-3-(furan-3-yl)acrylonitrile



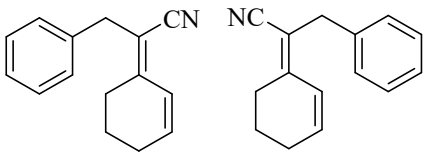
Method **A:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.50 (d, *J* = 1.9 Hz, 1H), 7.17 (d, *J* = 2.1 Hz, 1H), 6.88 (s, 1H), 6.44 (s, 1H), 2.31 – 2.26 (m, 4H), 1.82 – 1.77 (m, 2H), 1.68 (dd, *J* = 5.8, 2.2 Hz, 2H).

3q: 2-(cyclohex-1-en-1-yl)-5-methylhex-2-enenitrile

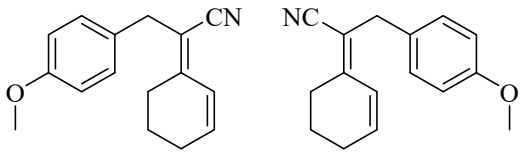


Method **A:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.27 (dd, *J* = 14.9, 6.5 Hz, 2H), 2.38 (t, *J* = 7.3 Hz, 2H), 2.22 (d, *J* = 5.0 Hz, 2H), 2.14 (ddd, *J* = 6.4, 4.4, 2.2 Hz, 2H), 1.81 (dt, *J* = 13.4, 6.7 Hz, 1H), 1.76 – 1.70 (m, 2H), 1.66 – 1.62 (m, 2H), 0.99 (s, 3H), 0.97 (s, 3H).

5a: 2-(cyclohex-2-en-1-ylidene)-3-phenylpropanenitrile



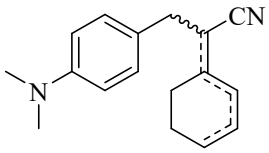
Method **A:** ^{1}H NMR (400 MHz, Chloroform-*d*) (Many isomers on the spectrum, the product data prove that the substrate is correct). HRMS(EI): *m/z* calcd for $C_{15}H_{15}N$ $[M]^{+\bullet}$: 209.1204; found: 209.1207.



5r: 2-(cyclohex-2-en-1-ylidene)-3-(4-methoxyphenyl)propanenitrile

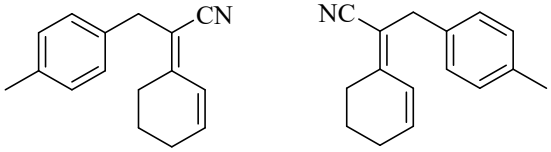
Method **A:** ^{1}H NMR (400 MHz, Chloroform-*d*) (Many isomers on the spectrum, the product data prove that the substrate is correct). HRMS(EI): *m/z* calcd for $C_{16}H_{17}NO$ $[M]^{+\bullet}$: 239.1310; found: 239.1313.

5s：2-(cyclohex-2-en-1-ylidene)-3-(4-(dimethylamino)phenyl) propanenitrile



Method **A:** HRMS(ESI): *m/z* calcd for $C_{17}H_{16}N_2$ $[M]^{+\bullet}$: 248.1313; found: 248.1315（This substrate may involve the double bond moving completely into the ring, resulting in multiple isomers, and therefore only showing high resolution）

1i: 2-(cyclohex-2-en-1-ylidene)-3-(*p*-tolyl)propanenitrile



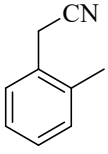
Method **A:** ^{1}H NMR (400 MHz, Chloroform-*d*) (Many isomers on the spectrum, the product data prove that the substrate is correct). HRMS(ESI): *m/z* calcd for $C_{16}H_{17}N$ $[M]^{+\bullet}$: 223.1361; found: 223.1362.

4 . General procedure for synthesis of products

4.1 General procedure for synthesis of α-aryl nitriles

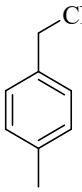
1 (0.20 mmol), **Pd/C** (**5** mol%) were added to a 25 mL Schlenk tube with a magnetic bar under N_2. DMA (1.0 mL) was added and then the mixture was heated at 160 °C with vigorous stirring for an 6 h. The solution was diluted with ethyl acetate (10 mL), and then filtered. The resulting filtrate is washed with water (2*5 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel to get the desired product.

2a: 2-(*o*-tolyl)acetonitrile [3].



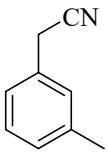
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (d, 1H), 7.28 – 7.16 (m, 3H), 3.65 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.21, 130.82, 128.77, 128.63, 128.58, 126.90, 117.74, 22.01, 19.43.

2b: 2-(*p*-tolyl)acetonitrile [4]



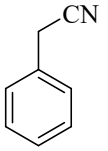
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.12 (m, 4H), 3.70 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.03, 129.95, 127.98, 127.02, 118.25, 23.39, 21.22.

2c: 2-(*m*-tolyl)acetonitrile [4]



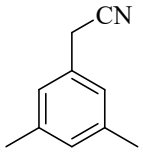
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (t, *J* = 7.6 Hz, 1H), 7.18 – 7.03 (m, 3H), 3.70 (s, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.03, 129.82, 129.02, 128.78, 128.63, 124.97, 118.01, 23.51, 21.31.

2d: 2-phenylacetonitrile [3].



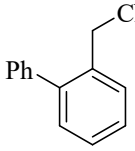
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.27 (m, 5H), 3.75 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 129.93, 129.16, 128.07, 127.94, 117.84, 23.63.

2e: 2-(3,5-dimethylphenyl)acetonitrile [3].



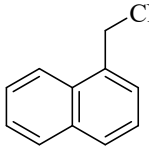
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.95 (s, 1H), 6.93 (s, 2H), 3.66 (s, 2H), 2.31 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.88, 129.62, 125.72, 118.17, 23.42, 21.21.

2f: 2-([1,1'-biphenyl]-2-yl)acetonitrile [4]



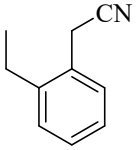
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.52 (m, 1H), 7.52 – 7.34 (m, 5H), 7.32 – 7.26 (m, 3H), 3.63 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.98, 140.02, 130.56, 129.04, 128.80, 128.33, 127.89, 127.85, 118.36, 22.15.

2g: 2-(naphthalen-1-yl)acetonitrile [3].



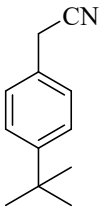
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 7.9 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.68 – 7.53 (m, 3H), 7.48 (t, *J* = 7.7 Hz, 1H), 4.14 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.77, 130.81, 129.15, 129.09, 127.09, 126.49, 126.39, 125.81, 125.49, 122.41, 117.66, 21.72.

2h: 2-(2-ethylphenyl)acetonitrile [6]



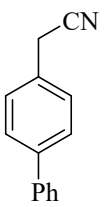
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.1 Hz, 1H), 7.26 – 7.19 (m, 2H), 3.70 (s, 2H), 2.66 (q, *J* = 7.5 Hz, 2H), 1.26 (t, *J* = 7.5 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.76, 128.88, 128.78, 128.62, 127.77, 126.65, 117.94, 25.62, 21.28, 14.39.

2i: 2-(4-(*tert*-butyl)phenyl)acetonitrile [3].



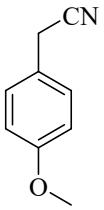
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 3.71 (s, 2H), 1.32 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.16, 127.65, 126.85, 126.07, 118.07, 34.55, 31.26, 23.12.

2j: 2-([1,1'-biphenyl]-4-yl)acetonitrile [3].



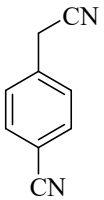
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (dd, *J* = 9.7, 7.7 Hz, 4H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.42-7.36 (m, *J* = 7.9 Hz, 3H), 3.80 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.30, 140.40, 129.07, 129.02, 128.55, 128.02, 127.83, 127.26, 118.02, 23.50.

2k: 2-(4-methoxyphenyl)acetonitrile [3].



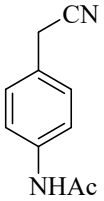
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.16 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 3.74 (s, 3H), 3.61 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.36, 129.11, 121.78, 118.25, 114.53, 55.37, 22.84.

2l: 4-(cyanomethyl)benzonitrile [3]



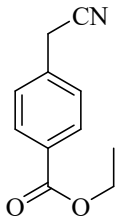
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 3.85 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.15, 132.94, 128.79, 118.09, 116.52, 112.42, 23.82.

2m: *N*-(4-(cyanomethyl)phenyl)acetamide [3]



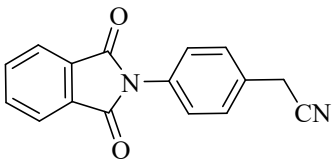
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (s, 1H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 3.70 (s, 2H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.68, 137.95, 128.54, 125.41, 120.47, 117.97, 24.48, 23.08.

2n: ethyl 4-(cyanomethyl)benzoate [4]



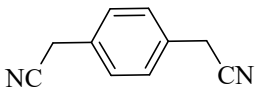
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.91, 134.69, 130.50, 130.37, 127.94, 117.13, 61.21, 23.67, 14.30.

2o: 2-(4-(1,3-dioxoisoindolin-2-yl)phenyl)acetonitrile [7]



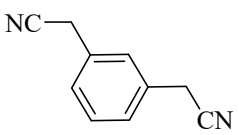
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.81 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.50 (s, 4H), 3.82 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.06, 134.58, 131.69, 131.67, 129.71, 128.72, 127.16, 123.89, 117.36, 23.40.

20: 2,2'-(1,4-phenylene)diacetonitrile [8]



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (s, 4H), 3.75 (s, 4 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 129.99, 128.74, 117.59, 23.26.

2q: 2,2'-(1,3-phenylene)diacetonitrile [8]



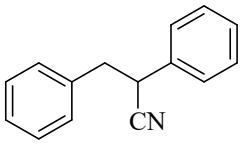
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.30 (m, 1H), 7.27 – 7.21 (m, 3H), 3.70 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 130.10, 128.99, 126.71, 126.51, 116.49, 22.44.

4.2 General procedure for synthesis of substituted α-aryl nitriles

Method A: 3 (0.20 mmol), **Pd/Al_2O_3** (2.5 mol%) were added to a 25 mL Schlenk tube with a magnetic bar under N_2. DMA (1.0 mL) was added and then the mixture was heated at 130 °C with vigorous stirring for an 2 h. The solution was diluted with ethyl acetate (10 mL), and then filtered. The resulting filtrate is washed with water (2*5 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel to get the desired product.

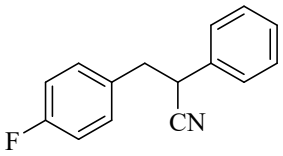
Method B: 3 (0.20 mmol), **Pd/C** (5 mol%) were added to a 25 mL Schlenk tube with a magnetic bar under N_2. DMA (1.0 mL) was added and then the mixture was heated at 160 °C with vigorous stirring for an 6 h. The solution was diluted with ethyl acetate (10 mL), and then filtered. The resulting filtrate is washed with water (2*5 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel to get the desired product.

4a: 2,3-diphenylpropanenitrile [3]



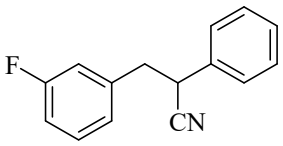
Method A: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.24 (m, 8H), 7.16 – 7.10 (m, 2H), 3.99 (dd, *J* = 8.3, 6.4 Hz, 1H), 3.16 (qd, *J* = 13.6, 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.27, 135.22, 129.21, 129.01, 128.62, 128.20, 127.48, 127.38, 120.36, 42.20, 39.80.

4b: 3-(4-fluorophenyl)-2-phenylpropanenitrile [5]



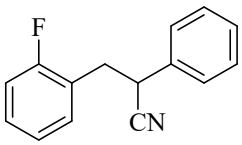
Method A: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.29 (m, 3H), 7.23 (dt, *J* = 7.4, 1.9 Hz, 2H), 7.12 – 7.03 (m, 2H), 7.02 – 6.91 (m,2H), 3.98 (dd, *J* = 7.8, 6.6 Hz, 1H), 3.18 – 2.78 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ162.14 (d, *J* = 245.6 Hz), 134.86, 131.88 (d, *J* = 4.0 Hz), 130.85 (d, *J* = 8.2 Hz), 129.06, 128.29, 127.47, 120.19, 115.48 (d, *J* = 22.2 Hz) , 41.26, 39.77. ^{19}F NMR (400 MHz, Chloroform-*d*) δ -115.05.

4c: 3-(3-fluorophenyl)-2-phenylpropanenitrile (CAS: 1266753-73-4)



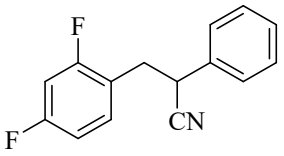
Method A: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.30 (m, 3H), 7.30 – 7.20 (m, 3H), 7.00 – 6.88 (m, 2H), 6.82 (dt, *J* = 9.6, 2.1 Hz, 1H), 4.00 (dd, *J* = 8.2, 6.5 Hz, 1H), 3.23 – 3.07 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.66(d, *J* = 245.5 Hz), 134.37, 131.39(d, *J* = 4.0 Hz), 130.36(d, *J* = 8.4 Hz), 128.57, 127.81, 126.99, 119.70, 114.99(d, *J* = 22.3 Hz), 40.78, 39.29. ^{19}F NMR (400 MHz, Chloroform-*d*) δ -112.74.

4d: 3-(2-fluorophenyl)-2-phenylpropanenitrile (CAS: 1226034-18-9)



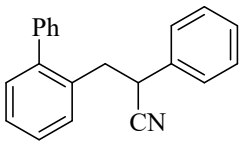
Method A: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.28 (m, 5H), 7.28 – 7.22 (m, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.11 – 6.98 (m, 2H), 4.07 (dd, *J* = 8.6, 6.8 Hz, 1H), 3.26 – 3.13 (m, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 162.21(d, *J* = 246.1 Hz), 135.17, 131.62(d, *J* = 4.5 Hz), 129.46(d, *J* = 9.1 Hz), 129.08, 128.34, 127.36, 124.34, 123.54(d, *J* = 15.1 Hz), 120.20, 115.51(d, *J* = 22.7 Hz), 38.34, 35.99. ^{19}F NMR (400 MHz, Chloroform-*d*) δ -118.25.

4e: 3-(2,4-difluorophenyl)-2-phenylpropanenitrile



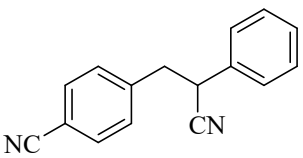
Method A: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (td, *J* = 8.3, 5.4 Hz, 3H), 7.32 – 7.27 (m, 2H), 7.12 (td, *J* = 8.2, 6.1 Hz, 1H), 6.82 (t, *J* = 8.5 Hz, 2H), 4.04 (dd, *J* = 8.4, 6.9 Hz, 1H), 3.26 – 3.10 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.64 (dd, *J* = 251 Hz, 11 Hz), 161.32 (dd, *J* = 243 Hz, 10 Hz), 134.94, 132.37, 129.23, 128.54, 127.47, 120.10, 119.47(d, *J* = 15 Hz), 111.58 (d, *J* = 21 Hz), 104.13 (t, *J* = 26 Hz), 38.44, 35.45. ^{19}F NMR (400 MHz, Chloroform-*d*) δ -110.43, -113.72. HRMS(EI): *m/z* calcd for $C_{15}H_{11}F_2N$ $[M]^{+\cdot}$: 243.0860; found: 243.0862

4f: 3-([1,1'-biphenyl]-2-yl)-2-phenylpropanenitrile



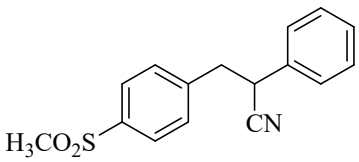
Method A: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 (q, *J* = 7.4, 6.8 Hz, 3H), 7.45 – 7.40 (m, 3H), 7.37 – 7.28 (m, 6H), 6.99 (dd, *J* = 6.5, 3.0 Hz, 2H), 3.72 (dd, *J* = 9.8, 5.9 Hz, 1H), 3.33 (dd, *J* = 13.7, 5.9 Hz, 1H), 3.17 (dd, *J* = 13.8, 9.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.36, 141.02, 135.55, 134.14, 130.41, 130.39, 129.17, 128.99, 128.61, 128.02, 127.91, 127.58, 127.47, 127.14, 120.40, 40.27, 38.82. HRMS(EI): *m/z* calcd for $C_{21}H_{17}N$ $[M]^{+\cdot}$: 283.1357; found: 283.1359

4g: 4-(2-cyano-2-phenylethyl)benzonitrile (CAS: 71947-06-3)



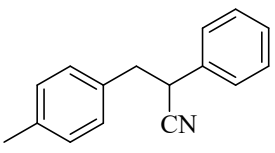
Method A: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 6.4 Hz, 2H), 7.34 – 7.25 (m, 3H), 7.18 – 7.09 (m, 4H), 3.98 (t, *J* = 7.1 Hz, 1H), 3.26 – 3.05 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.38, 134.23, 132.39, 130.17, 129.25, 128.62, 127.43, 119.68, 118.57, 111.55, 41.92, 39.06.

4h: 3-(4-(methylsulfonyl)phenyl)-2-phenylpropanenitrile (CAS:2577543-06-5)



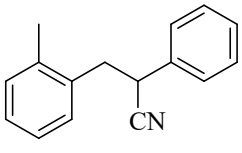
Method B: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.70 (m, 2H), 7.26 – 7.17 (m, 5H), 7.14 – 7.10 (m, 2H), 3.94 (t, *J* = 7.2 Hz, 1H), 3.12 (d, *J* = 7.3 Hz, 2H), 2.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.43, 139.71, 134.30, 130.36, 129.28, 128.63, 127.75, 127.42, 119.74, 44.53, 41.74, 39.14.

4i: 2-phenyl-3-(*p*-tolyl)propanenitrile [5]



Method A: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.29 (m, 3H), 7.28 (d, *J* = 6.2 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 3.98 (dd, *J* = 8.3, 6.5 Hz, 1H), 3.25 – 3.02 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.99, 135.32, 133.22, 129.29, 129.06, 128.98, 128.13, 127.48, 120.45, 41.82, 39.94, 21.09.

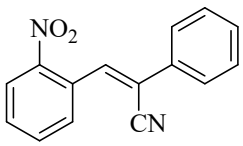
4j: 2-phenyl-3-(*o*-tolyl)propanenitrile [5]



Method A: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 – 7.31 (m, 3H), 7.29 – 7.26 (m, 2H), 7.19 – 7.13 (m, 4H), 3.96 (dd, *J* = 8.7, 6.5 Hz, 1H), 3.23 (dd, *J* = 13.9, 8.8 Hz, 1H), 3.13 (dd, *J* = 13.9, 6.5 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (151 MHz,

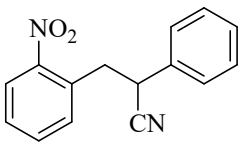
$CDCl_3$) δ 136.30, 135.48, 134.71, 130.61, 130.08, 129.09, 128.26, 127.57, 127.42, 126.31, 120.51, 39.52, 38.79, 19.26.

4ka: 3-(2-nitrophenyl)-2-phenylacrylonitrile



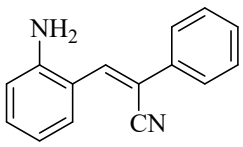
Method B: HRMS(ESI): *m/z* calcd for $C_{15}H_{10}N_2O_2S^+[M+Na]^+$: 273.0742; found: 273.1.

4kb: 3-(2-nitrophenyl)-2-phenylpropanenitrile



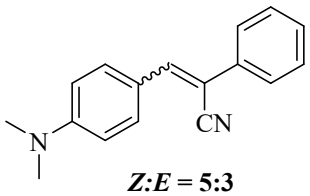
Method B: HRMS(ESI): *m/z* calcd for $C_{15}H_{12}N_2O_2S^+[M+Na]^+$: 275.0742; found: 275.1

4kc: 3-(2-aminophenyl)-2-phenylacrylonitrile (CAS: 2378164-26-0)



Method B: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (s, 1H), 7.71 – 7.68 (m, 1H), 7.64 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.53 – 7.43 (m, 5H), 7.30 – 7.24 (m, 2H), 5.03 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.20, 147.14, 137.62, 137.35, 129.75, 129.23, 128.97, 128.32, 127.57, 125.64, 125.10, 124.28, 122.90.

4l: 3-(4-(dimethylamino)phenyl)-2-phenylacrylonitrile

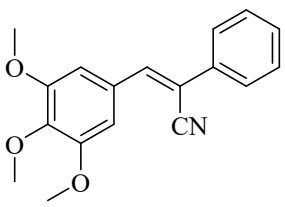


***Z*:*E* = 5:3**

Method A: HRMS(EI): *m/z* calcd for $C_{17}H_{16}N_2$ $[M]^{+\cdot}$: 248.1313; found: 248.1315

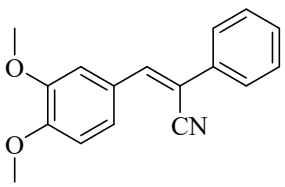
(Isomers on the spectrum).

4m: 2-phenyl-3-(3,4,5-trimethoxyphenyl)acrylonitrile (CAS: 49581-04-6)



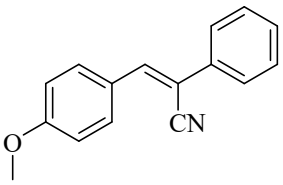
Method B: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.64 (m, 2H), 7.49 – 7.37 (m, 4H), 7.20 (s, 2H), 3.94 (s, 6H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.28, 142.23, 140.13, 134.52, 129.13, 129.10, 125.94, 118.39, 110.46, 106.61, 61.07, 56.27.

4n: 3-(3,4-dimethoxyphenyl)-2-phenylacrylonitrile (CAS: 37629-65-5)



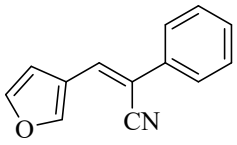
Method B: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 1.7 Hz, 1H), 7.70 (d, *J* = 7.3 Hz, 2H), 7.52 – 7.45 (m, 3H), 7.42 (t, *J* = 6.9 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 1H), 4.02 (s, 3H), 3.99 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.24, 149.14, 142.17, 134.88, 129.07, 128.83, 126.82, 125.84, 124.46, 118.70, 111.03, 110.86, 108.75, 56.07.

4o: 3-(4-methoxyphenyl)-2-phenylacrylonitrile (CAS: 5432-07-5)



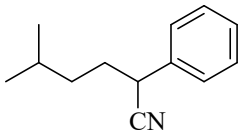
Method B: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.6 Hz, 2H), 7.69 (d, *J* = 5.7 Hz, 2H), 7.54 – 7.44 (m, 3H), 7.44 – 7.35 (m, 1H), 7.01 (d, *J* = 8.7 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.49, 141.93, 134.90, 131.28, 129.08, 128.81, 126.58, 125.83, 118.64, 114.46, 108.66, 55.49.

4p: 3-(furan-3-yl)-2-phenylacrylonitrile (CAS: 1958821-33-4)



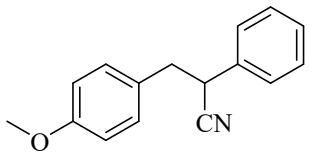
Method B: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.92 (m, 1H), 7.65 – 7.60 (m, 2H), 7.52 (t, *J* = 1.9 Hz, 1H), 7.46 – 7.41 (m, 3H), 7.40 – 7.36 (m, 1H), 7.24 (d, *J* = 2.0 Hz, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ 145.98, 144.41, 133.95, 132.06, 129.08, 128.96, 125.61, 121.91, 118.26, 110.28, 108.78.

4q: 5-methyl-2-phenylhexanenitrile (CAS: 5558-34-9)



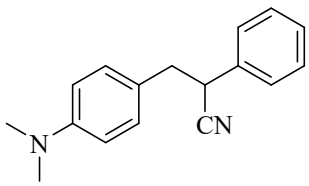
Method B: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.35 (m, 2H), 7.33 (d, *J* = 7.0 Hz, 3H), 3.81 – 3.69 (m, 1H), 1.96 – 1.83 (m, 2H), 1.43 – 1.26 (m, 3H), 0.89 (dd, *J* = 6.7, 2.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.15, 129.09, 128.03, 127.27, 120.97, 37.71, 36.11, 33.97, 27.69, 22.50, 22.28.

4r: 3-(4-methoxyphenyl)-2-phenylpropanenitrile [5]



Method B: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (q, *J* = 8.3, 7.4 Hz, 3H), 7.22 – 7.18 (m, 2H), 7.00 (d, *J* = 8.3 Hz, 2H), 6.78 (d, *J* = 8.3 Hz, 2H), 3.96 – 3.86 (m, 1H), 3.74 (s, 3H), 3.14 – 2.95 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.66, 135.05, 130.10, 128.78, 128.10, 127.94, 127.31, 120.27, 113.78, 55.03, 41.20, 39.86.

4s: 3-(4-(dimethylamino)phenyl)-2-phenylpropanenitrile (CAS: 72035-45-1)



Method B: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.30 (m, 3H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.65 (d, *J* = 8.7 Hz, 2H), 3.93 (dd, *J* = 8.3, 6.4 Hz, 1H), 3.16 – 2.93 (m, 2H), 2.92 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.86, 135.65, 129.93, 128.96, 128.04, 127.57, 124.10, 120.76, 112.66, 41.51, 40.63, 40.33.

4.3 General procedure for a gram-scale experiment

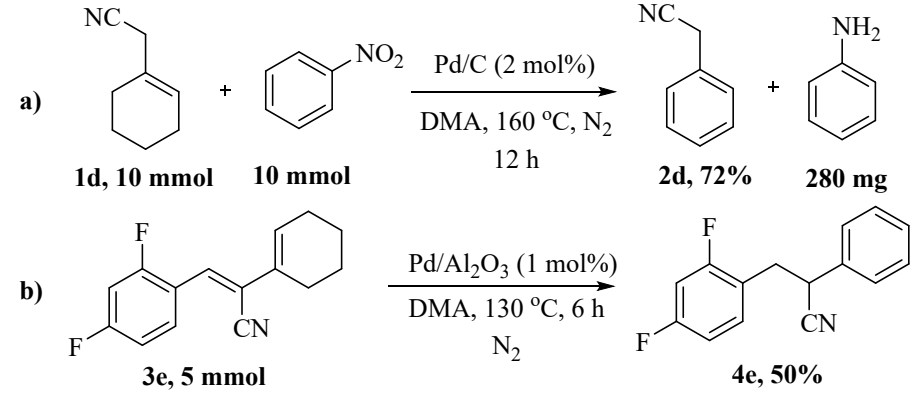


Fig S1. Gram-scale experiment

a): 1d (10 mmol), **$PhNO_2$** (10 mmol) and **Pd/C** (0.2 mmol) were added to a 50 mL Schlenk tube with a magnetic bar under N_2. DMA (20 mL) was added and then the mixture was heated at 160 °C with vigorous stirring for an 12 h. The solution was evaporated under vacuum, dissolved with ethyl acetate (100 mL), and then filtered. The resulting filtrate was evaporated under vacuum, and the crude reaction mixture was purified by column chromatography on silica gel to get the desired product.

b): 3e (5 mmol), **Pd/Al_2O_3** (0.05 mmol) were added to a 25 mL Schlenk tube with a magnetic bar under N_2. DMA (10 mL) was added and then the mixture was heated at 160 °C with vigorous stirring for an 6 h. The solution was evaporated under vacuum, dissolved with ethyl acetate (50 mL), and then filtered. The resulting filtrate was evaporated under vacuum, and the crude reaction mixture was purified by column chromatography on silica gel to get the desired product.

4.4 Further Studies

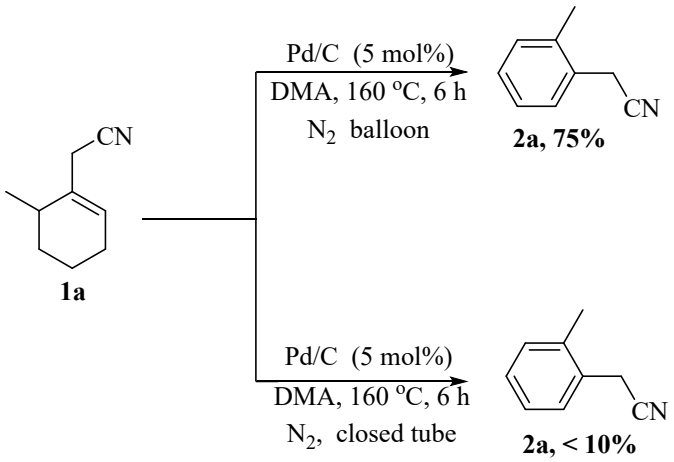


Fig S2. Control experiments

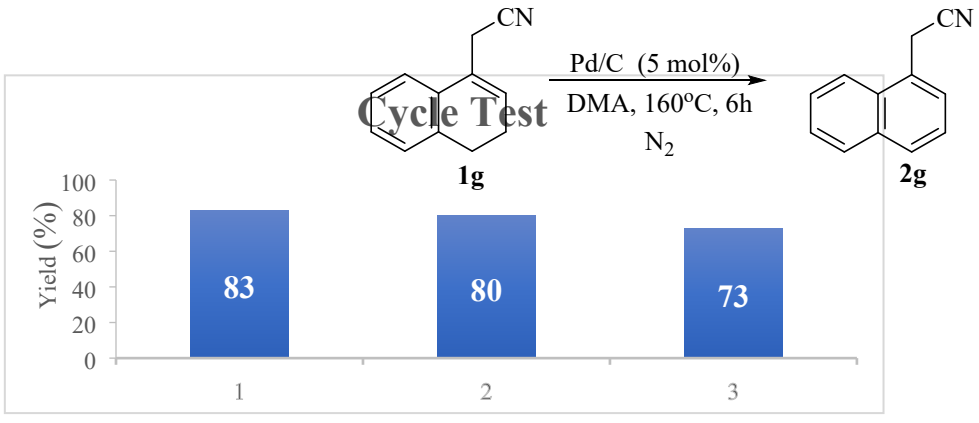


Fig S3. Cycle test experiment

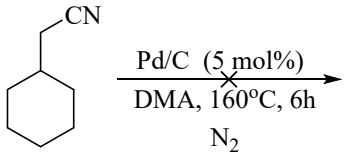
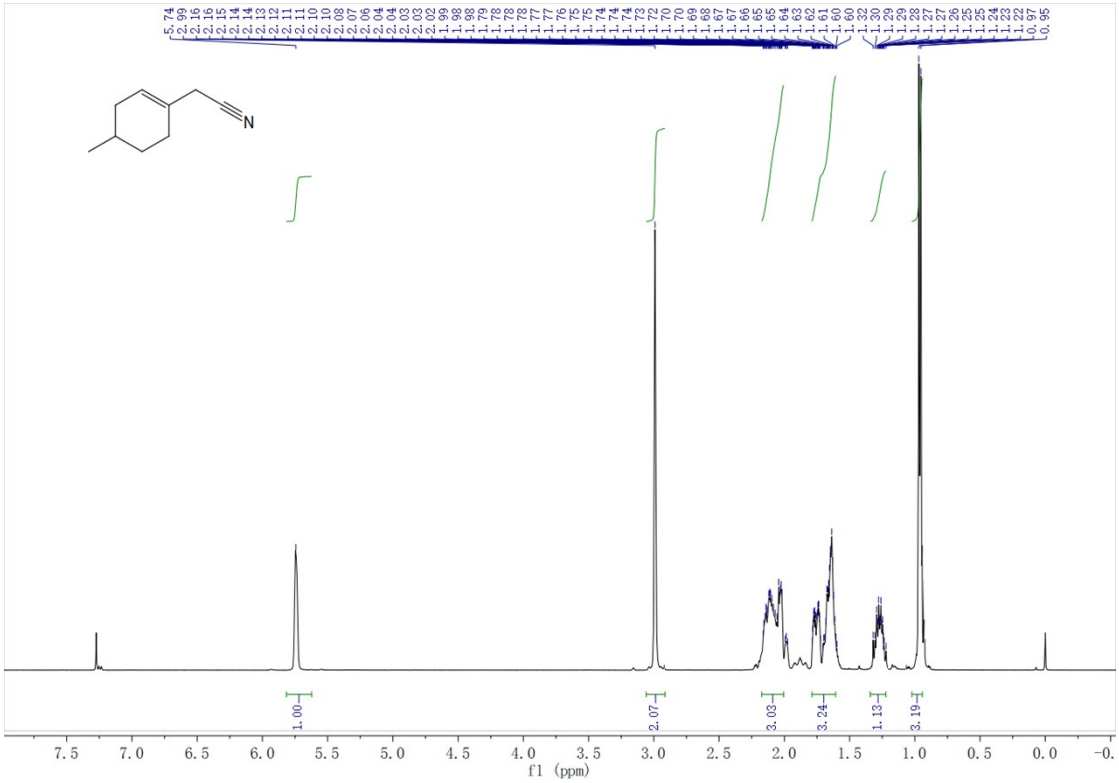


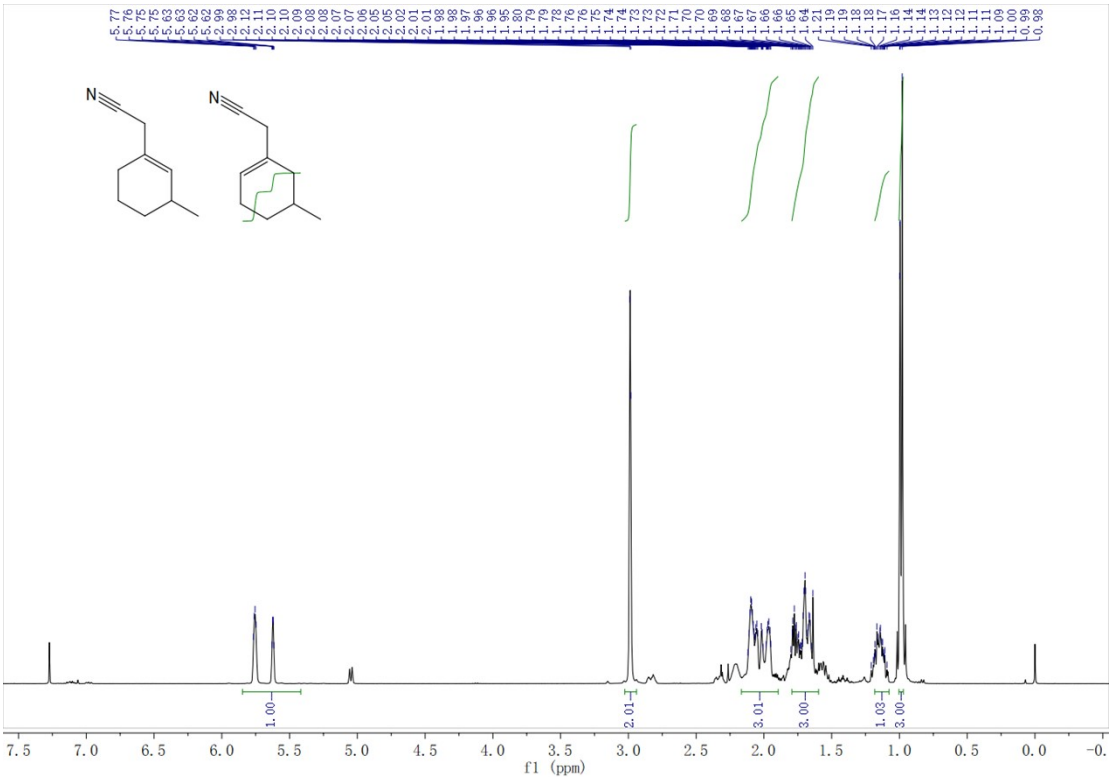
Fig S4. The acetonitrile-substituted cyclohexane as substrate

5. NMR spectra

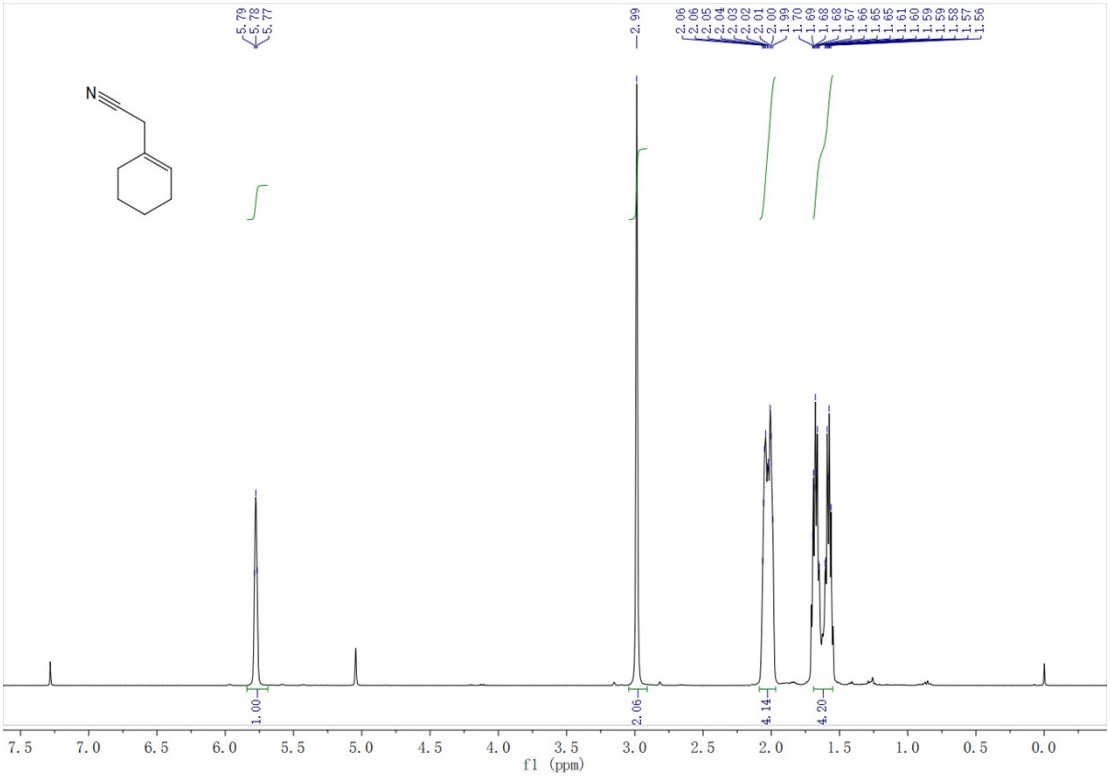
5.1 NMR spectra of substrates (The substrate spectra contain trace amounts of double-bond shift products)



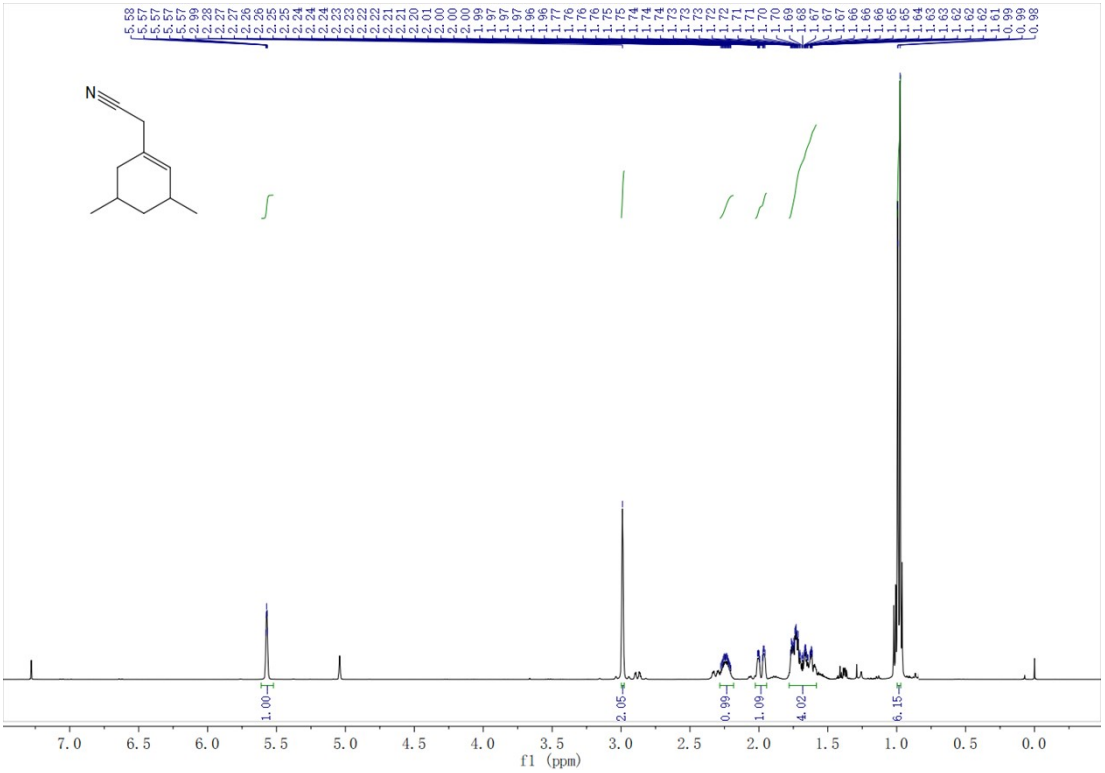
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1b**



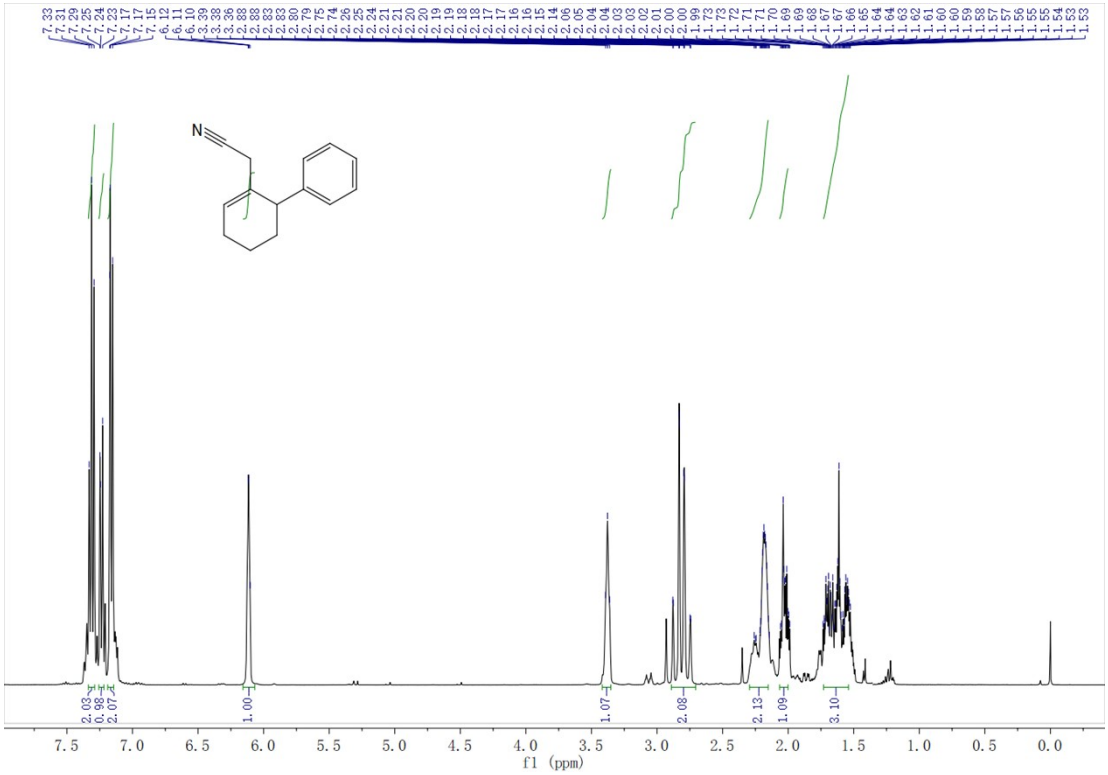
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1c**



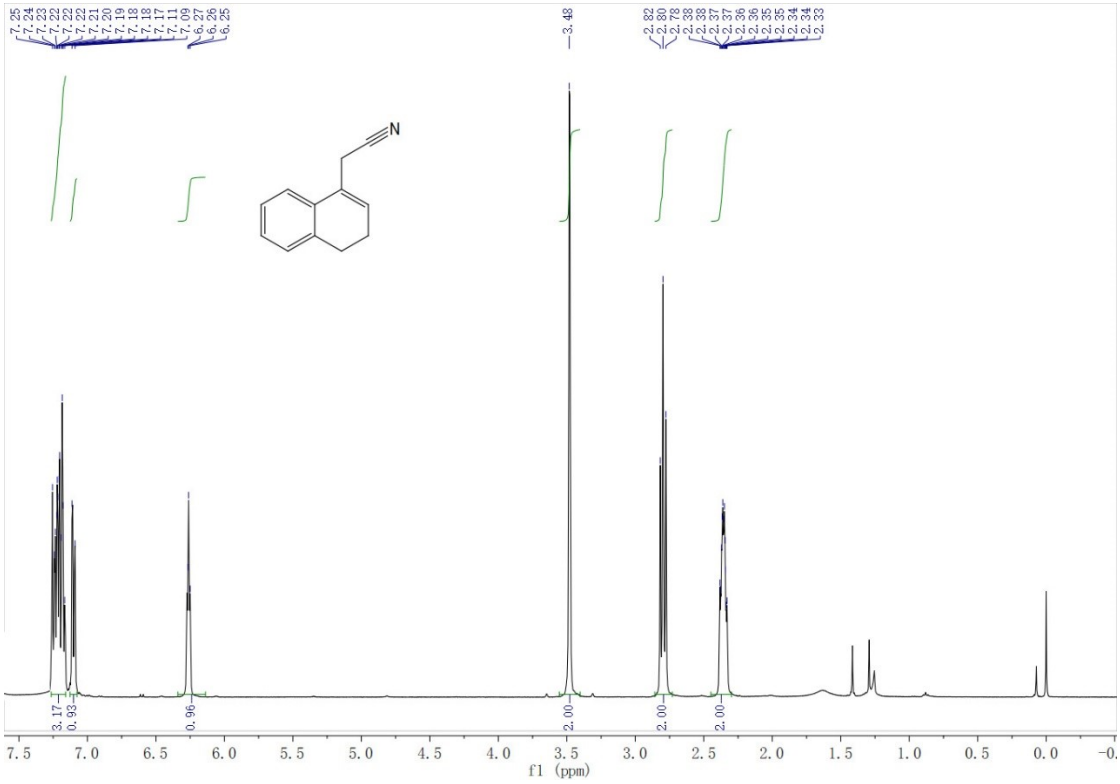
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1d**



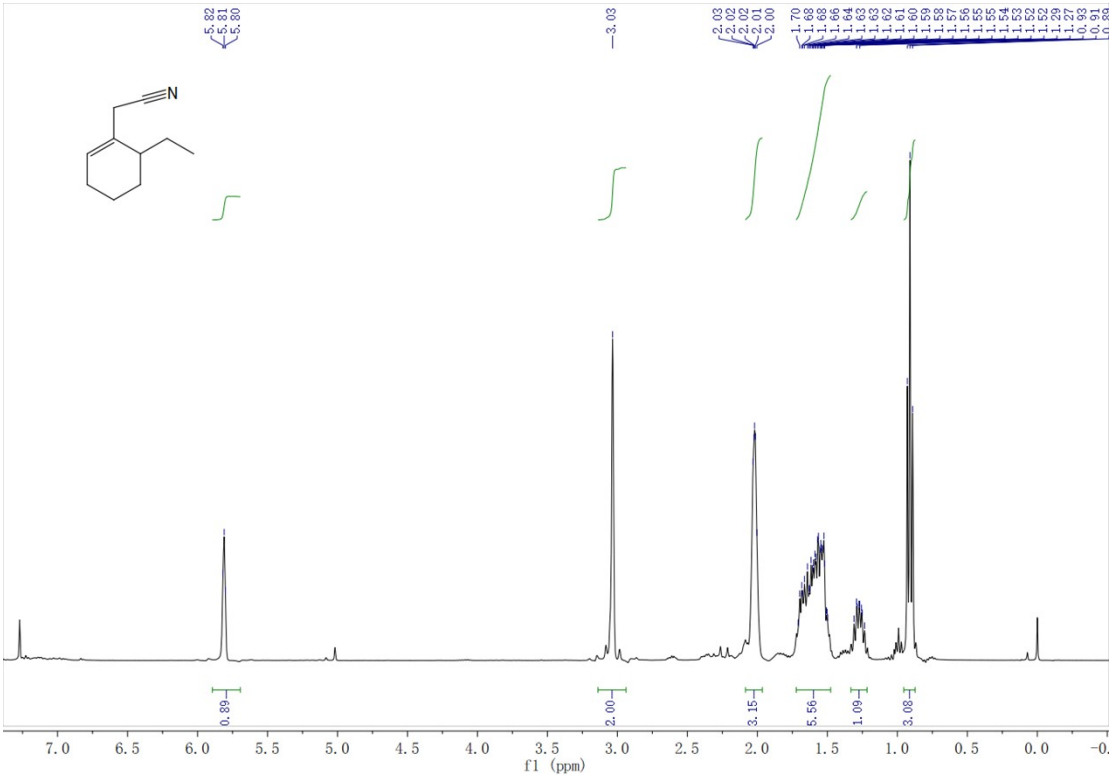
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1e**



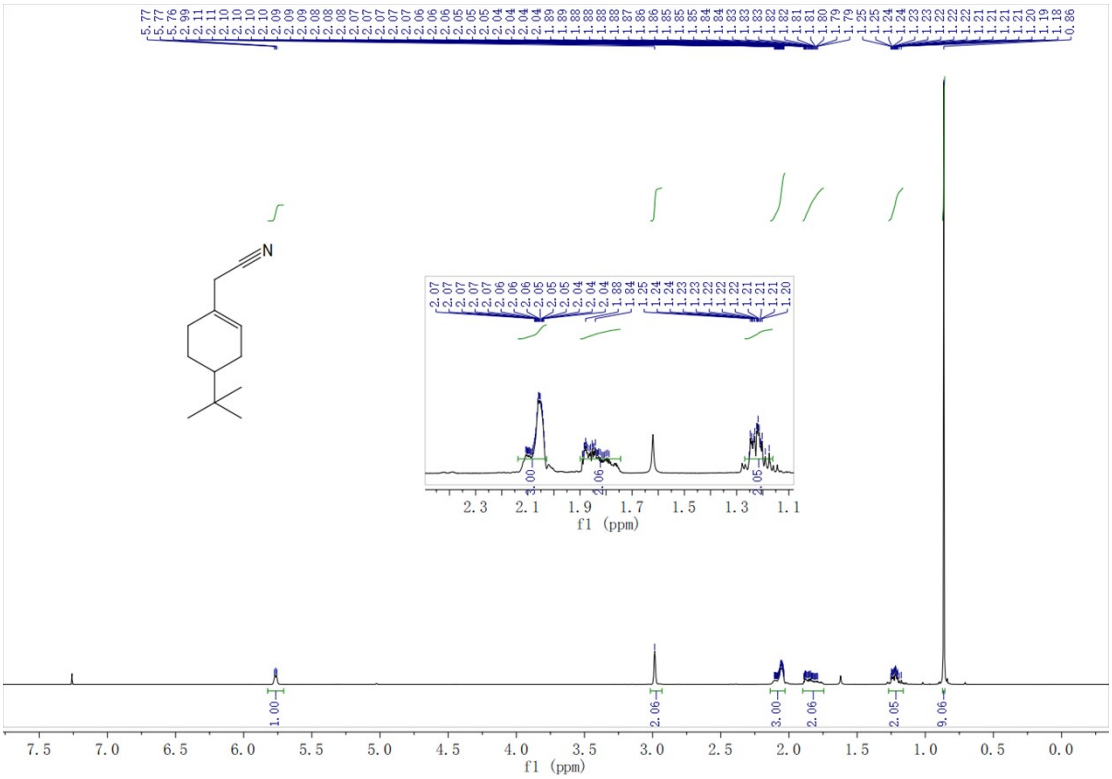
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1f**



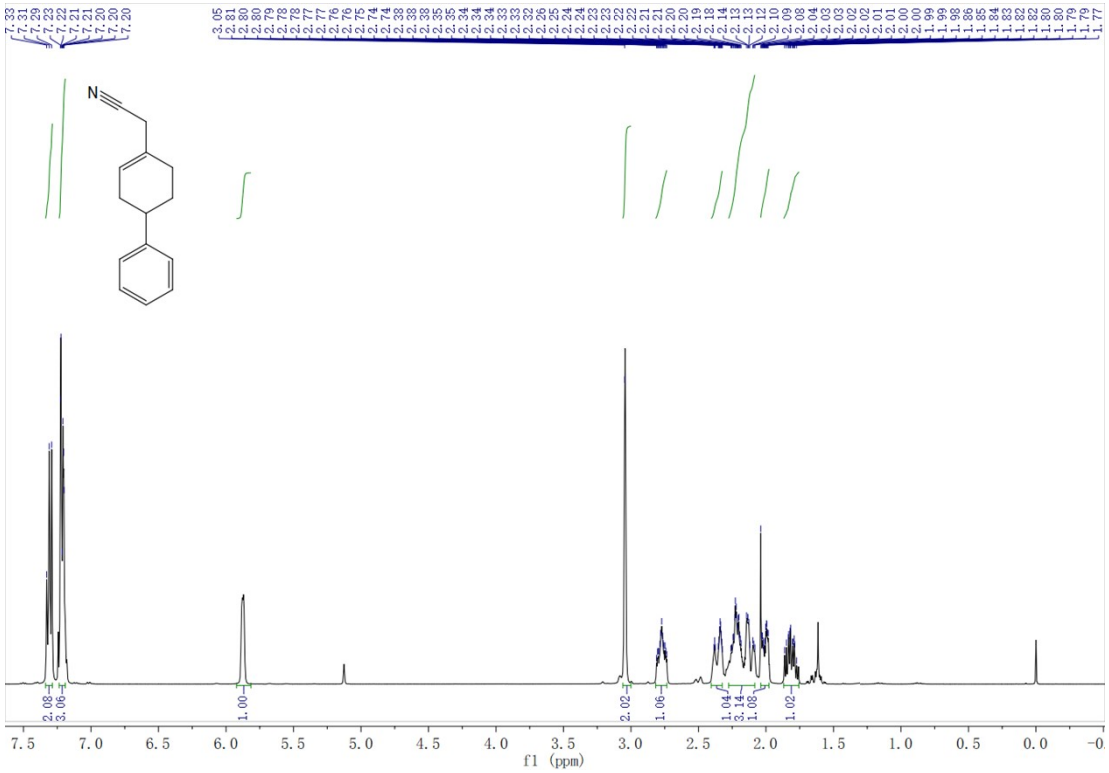
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1g**



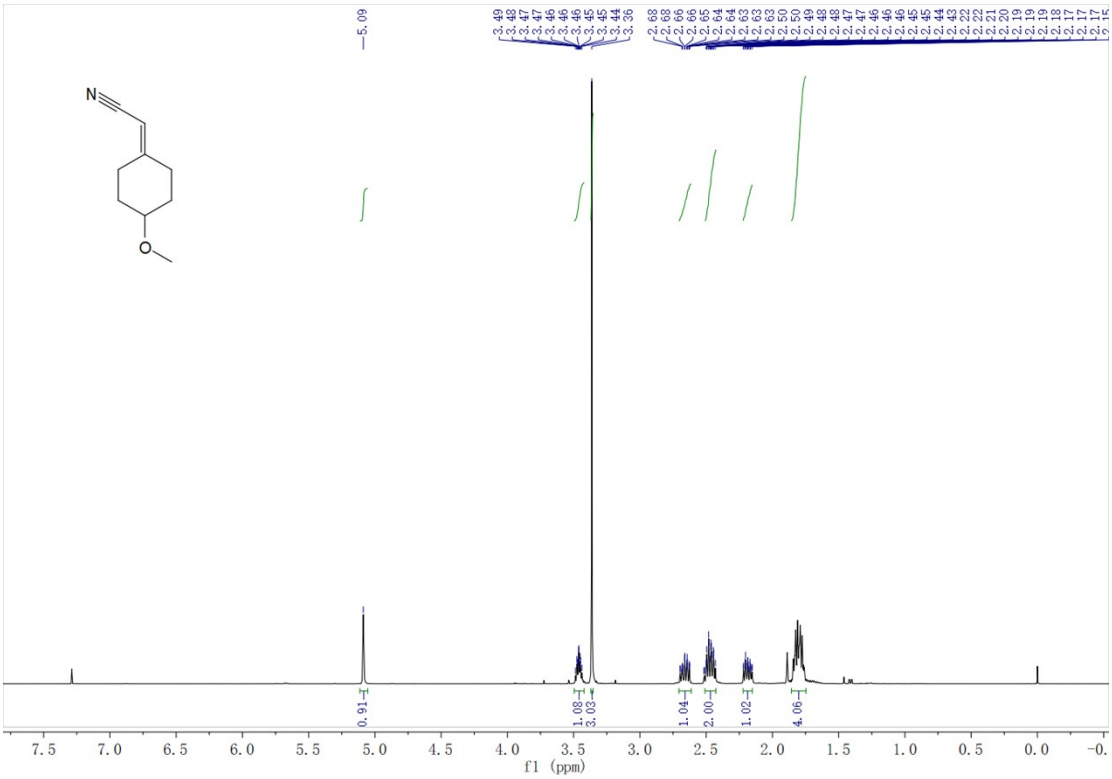
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1h**



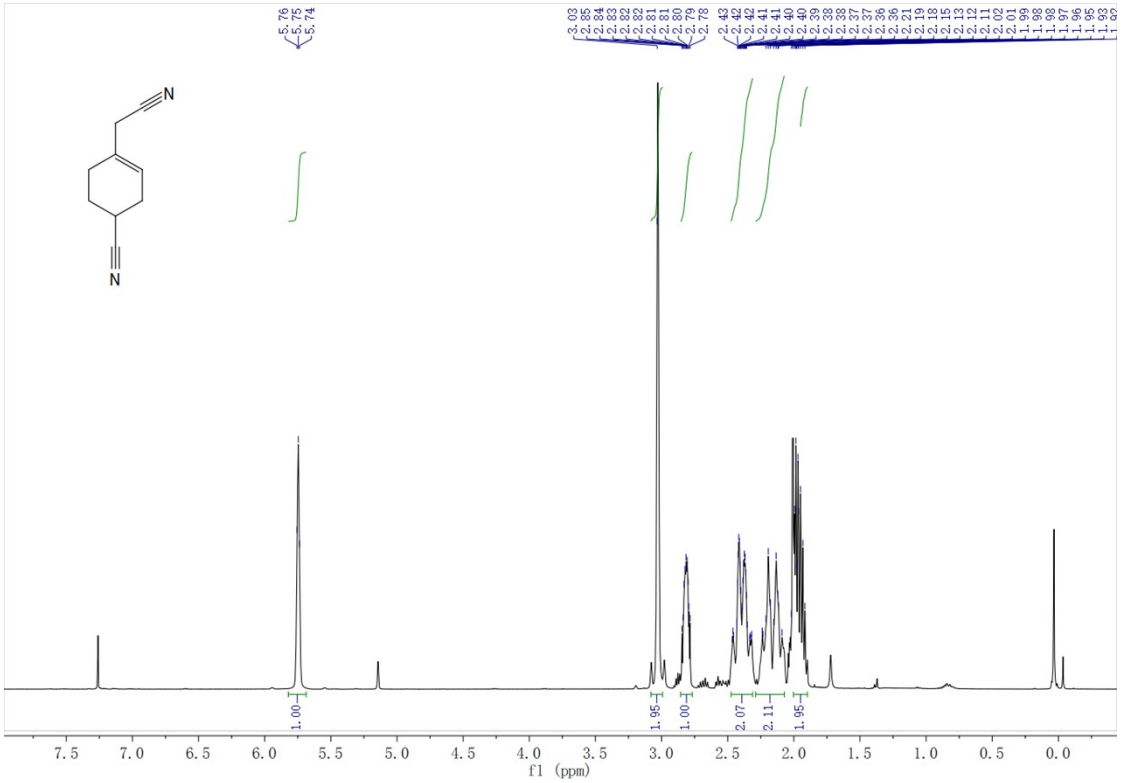
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1i**



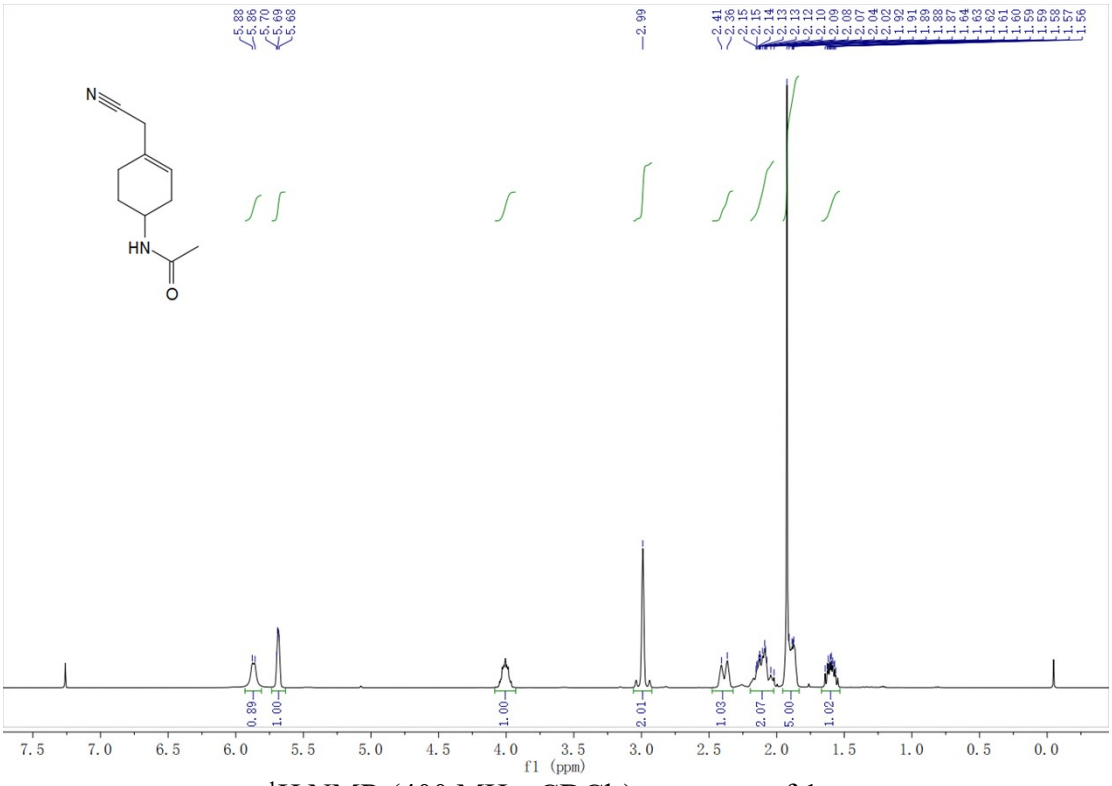
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1j**



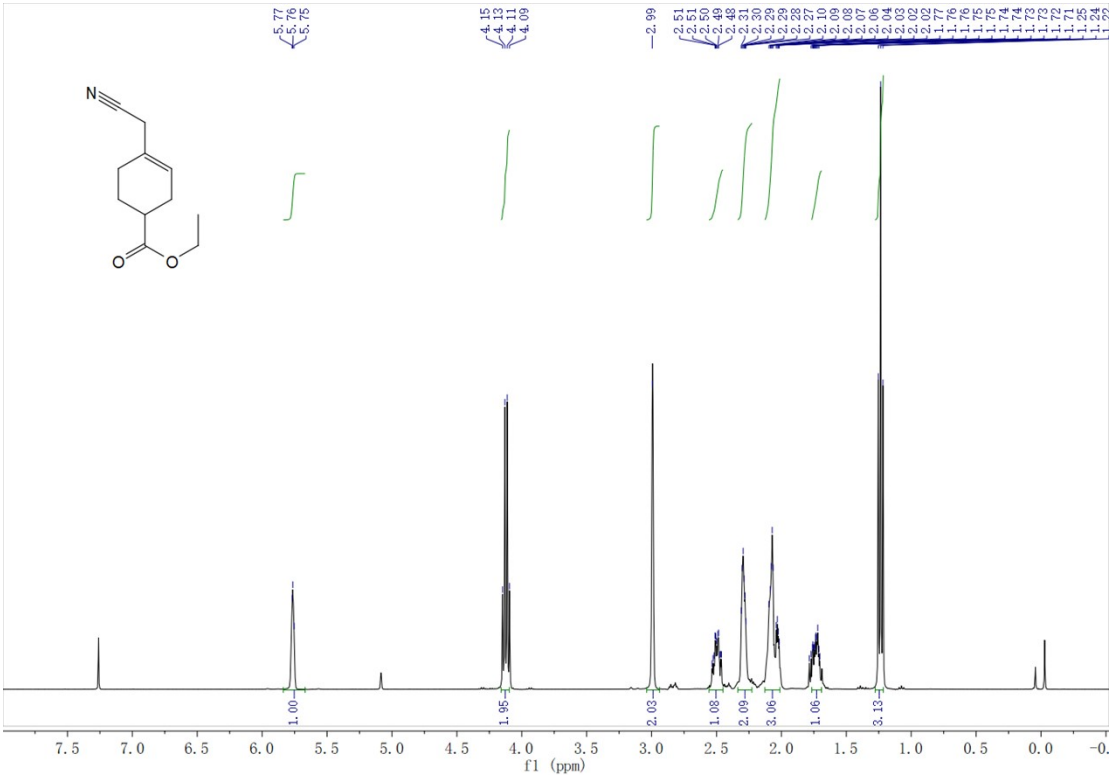
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1k**



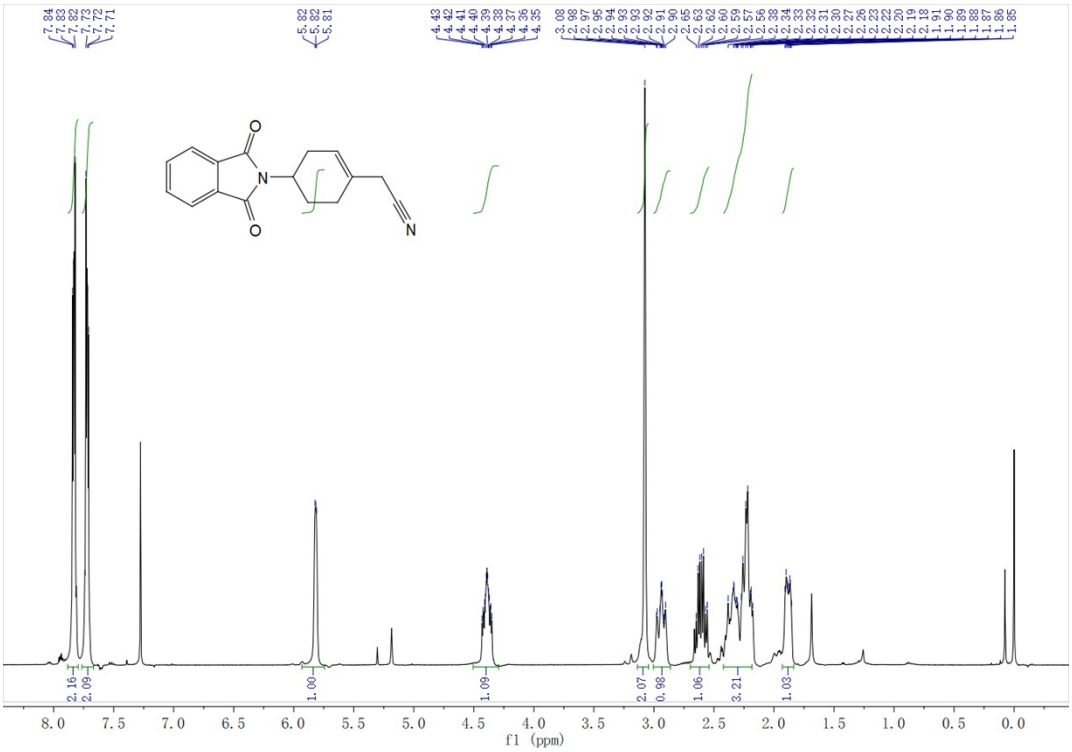
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1l**



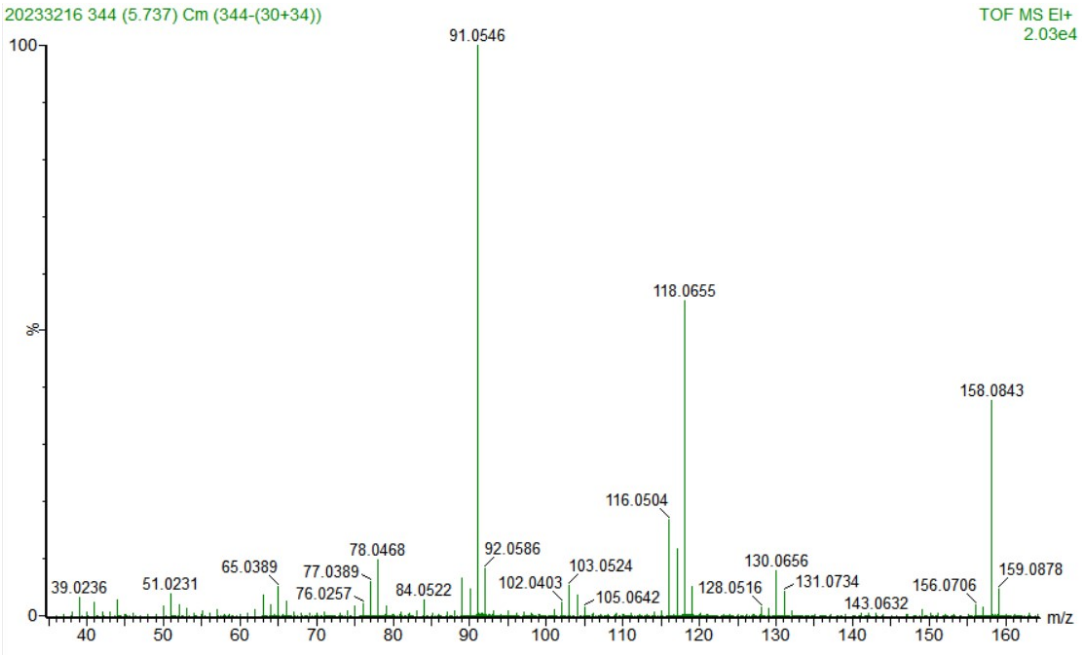
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1m**



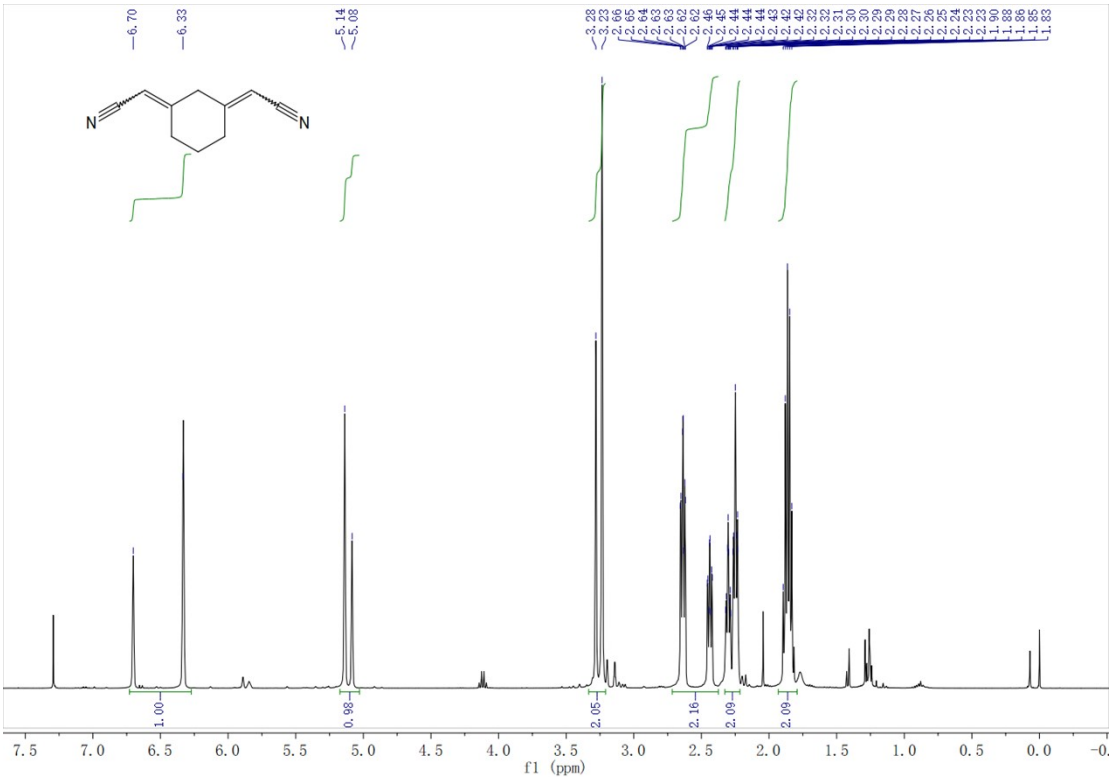
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1n**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1o**

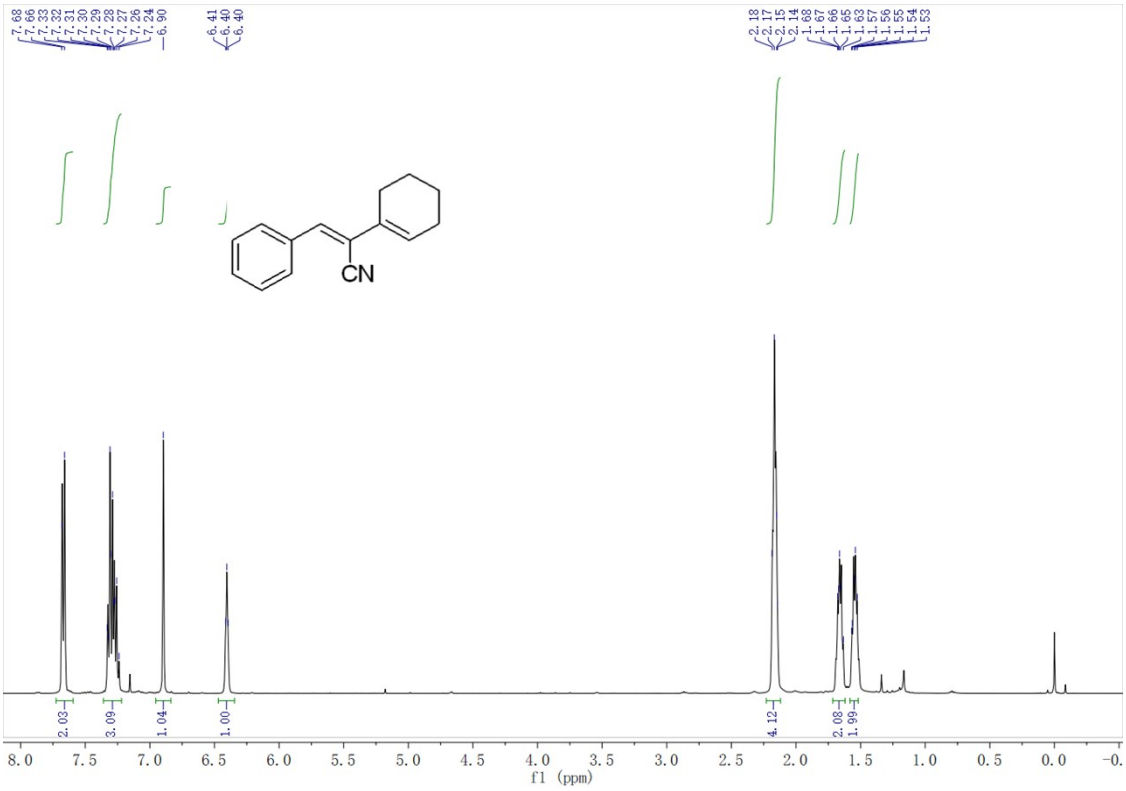


Mass spectrum of **1p**

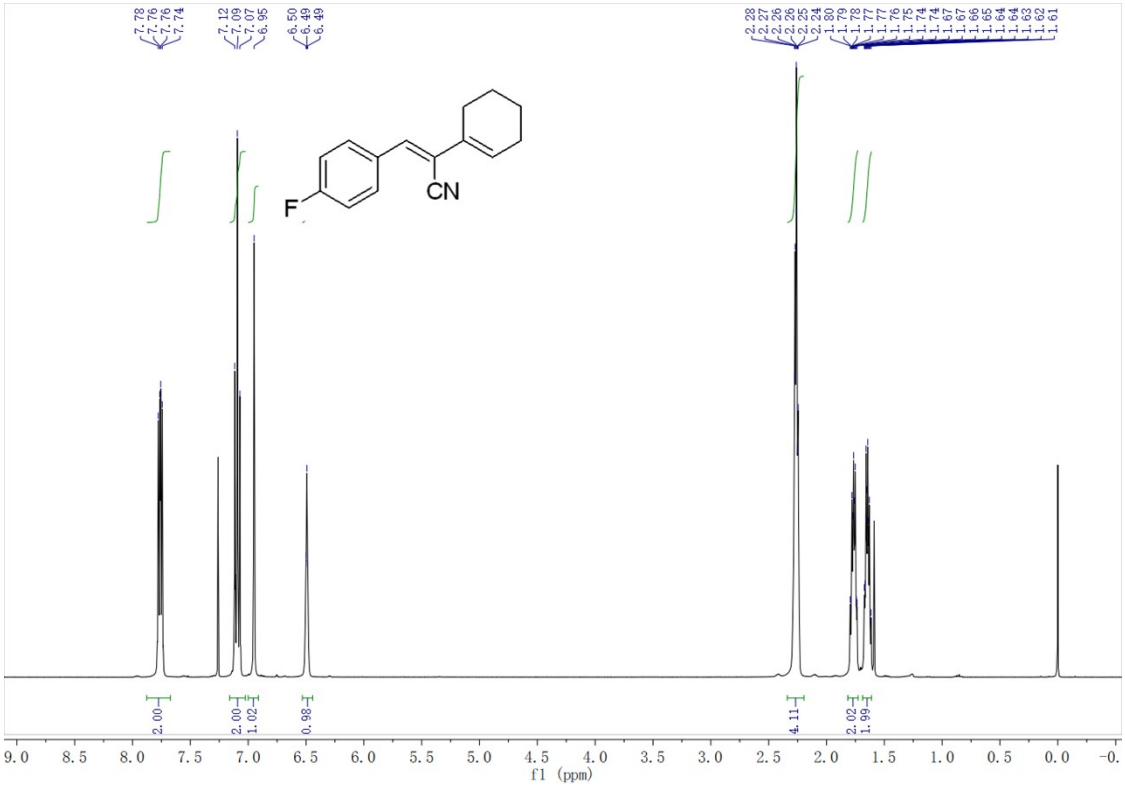


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1q**

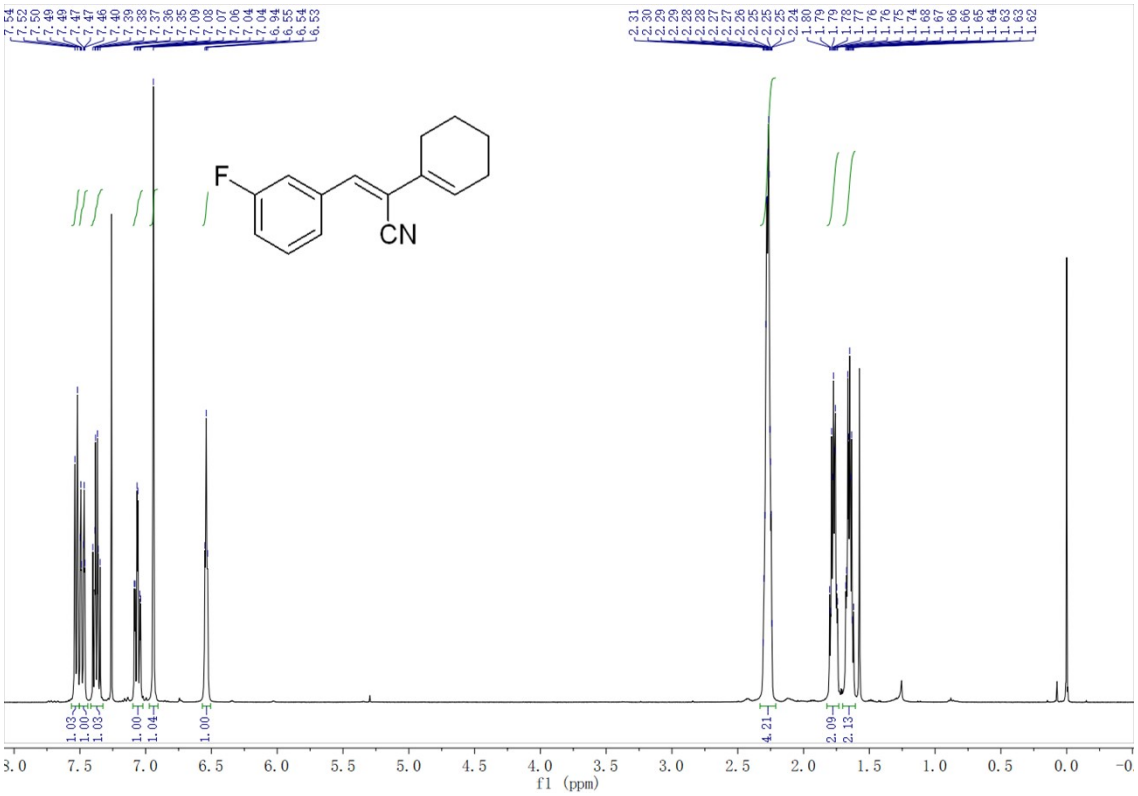
Mass spectrum of **1q**



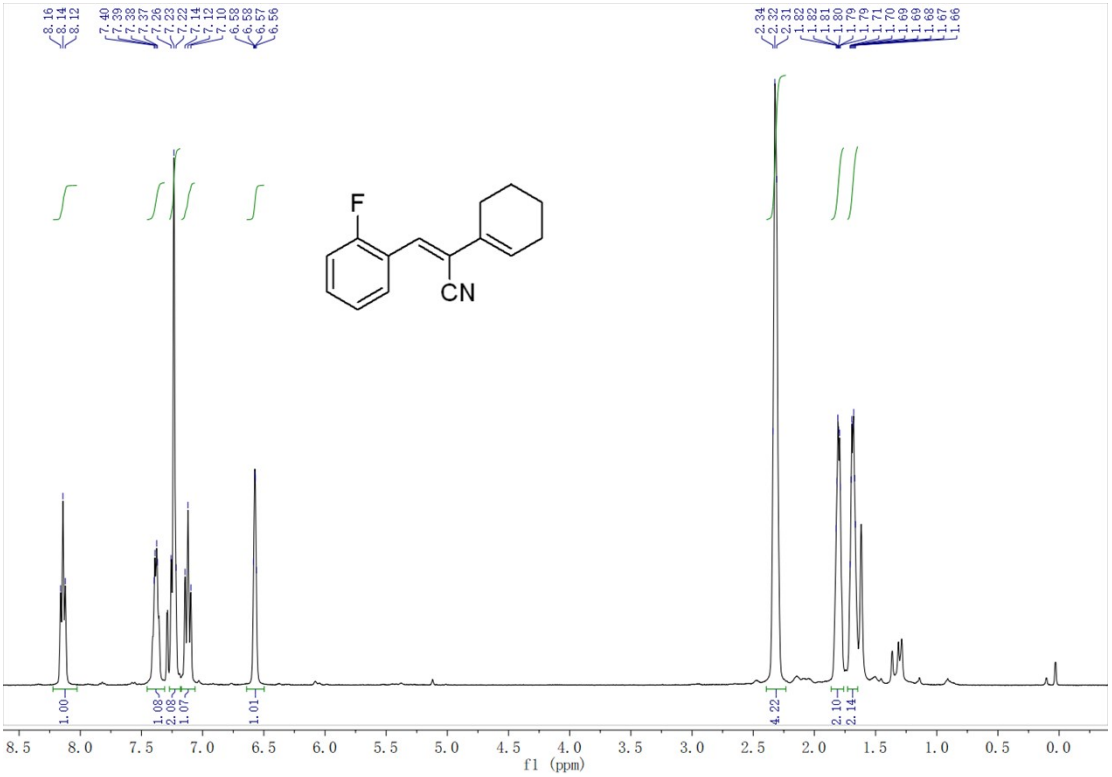
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3a**



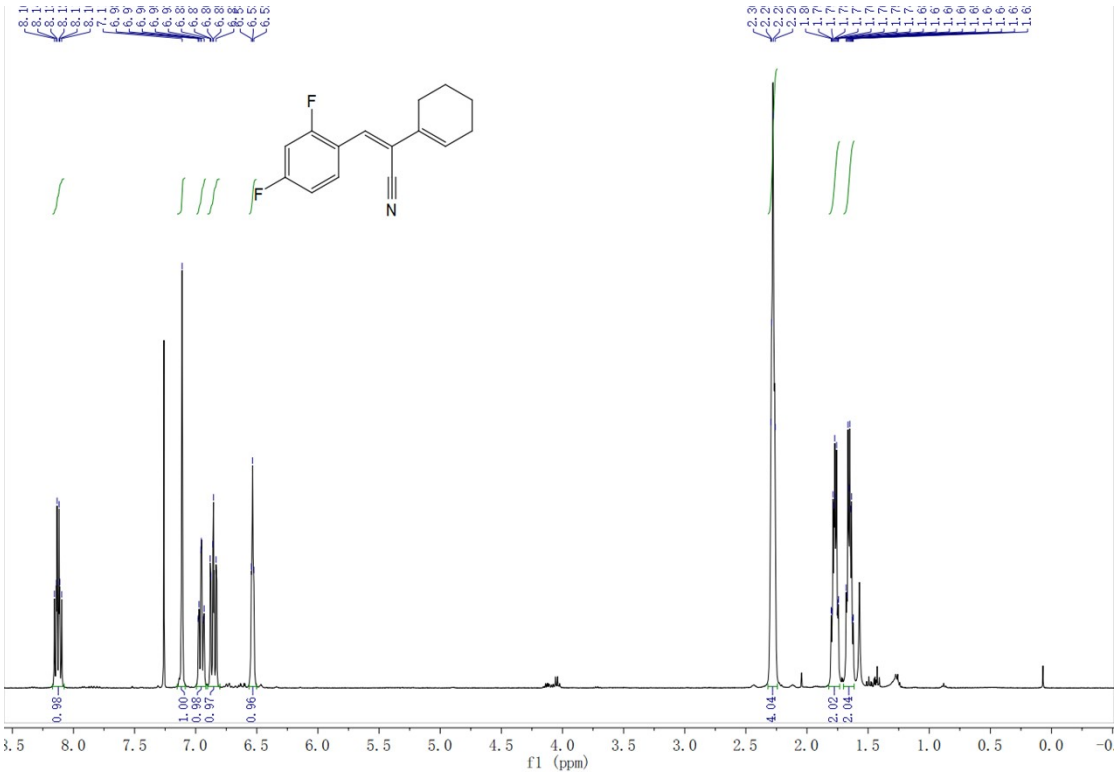
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3b**



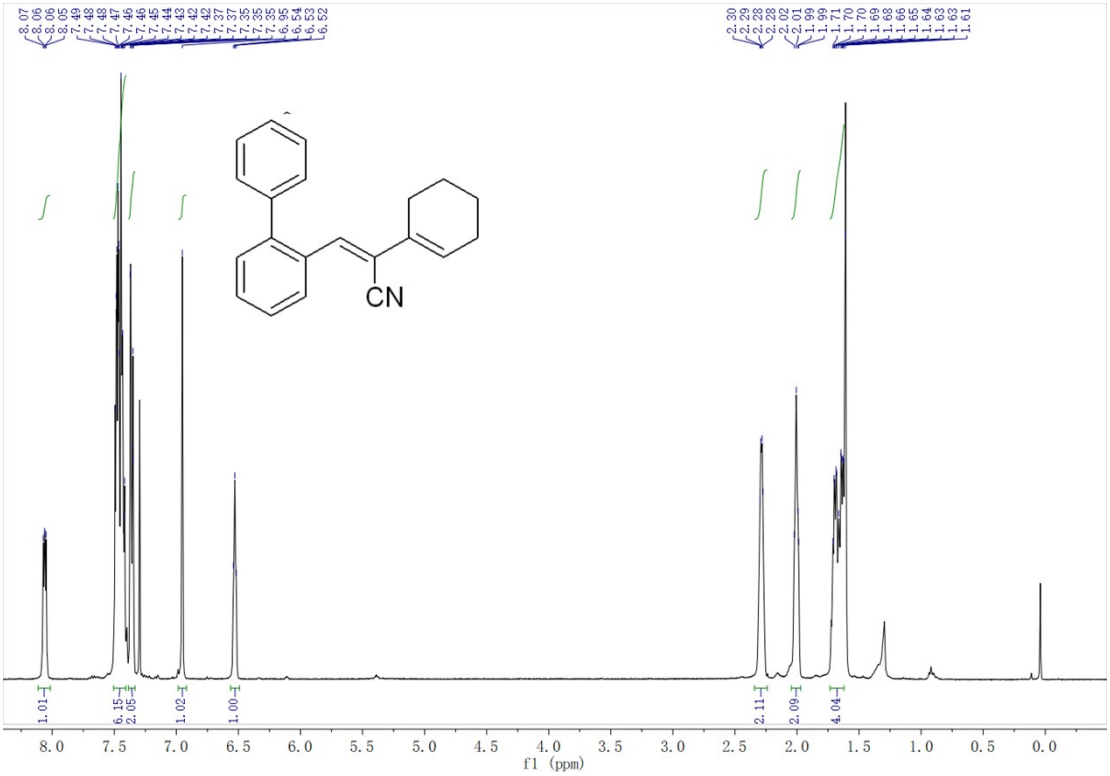
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3c**



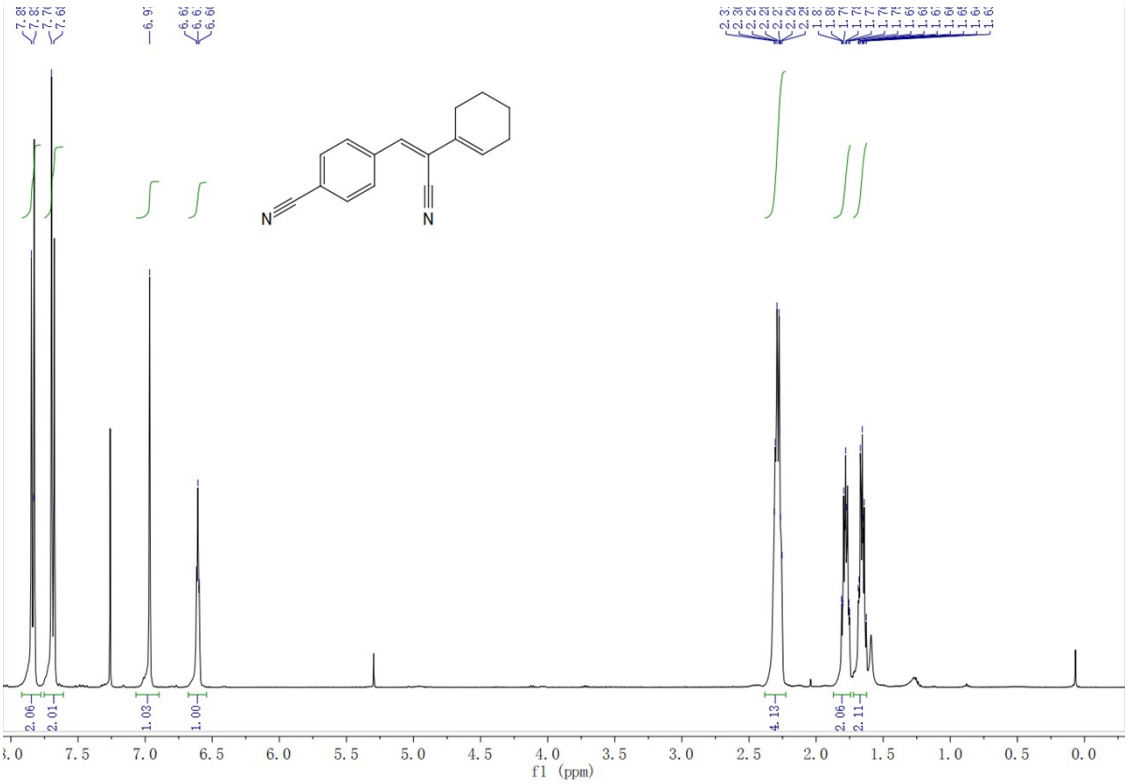
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3d**



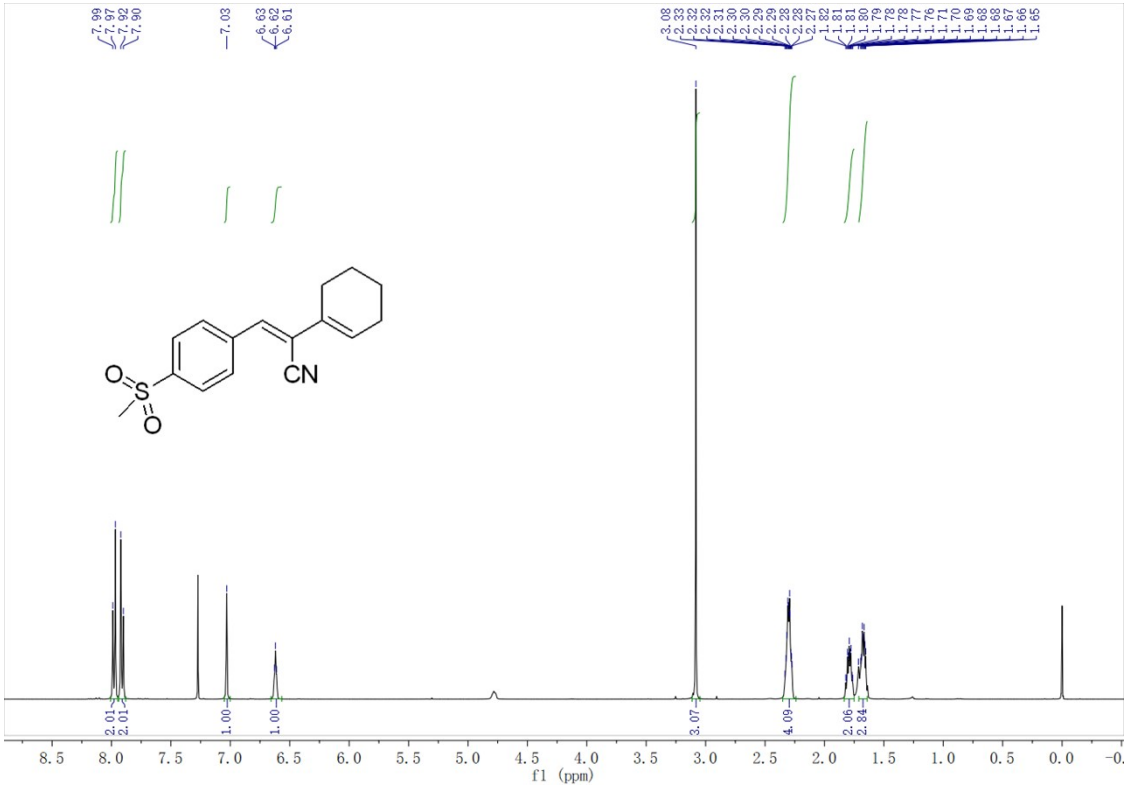
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3e**



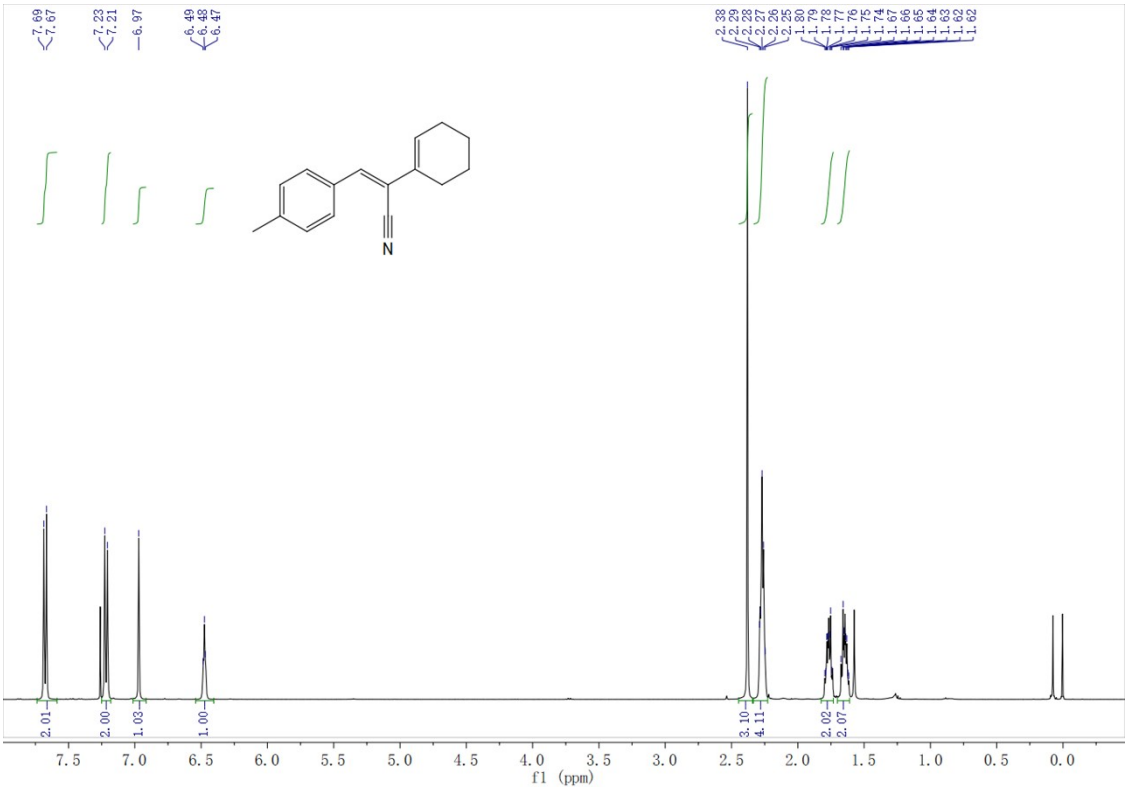
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3f**



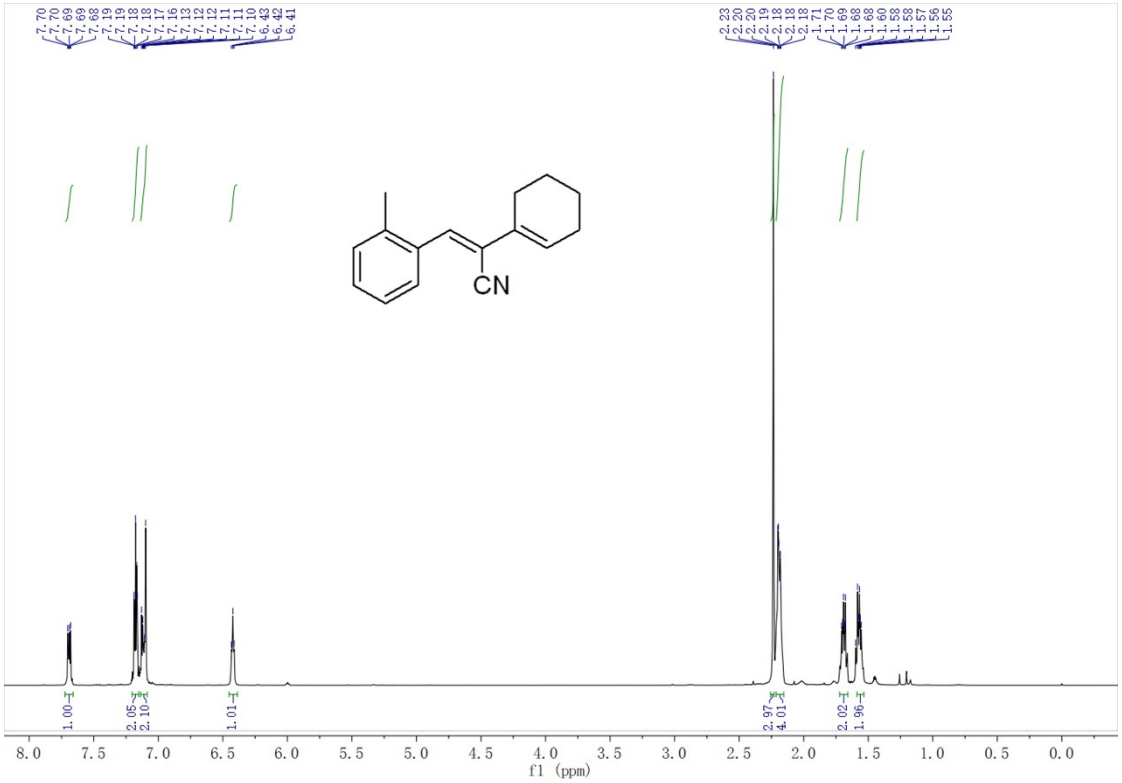
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3g**



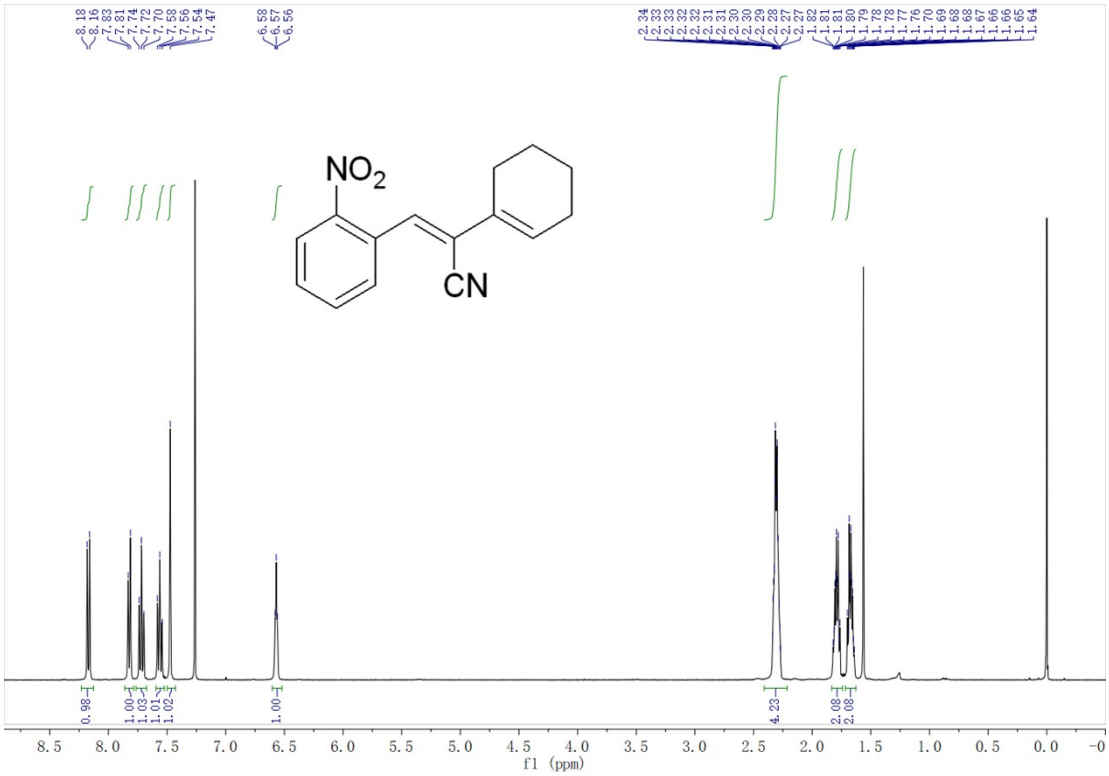
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3h**



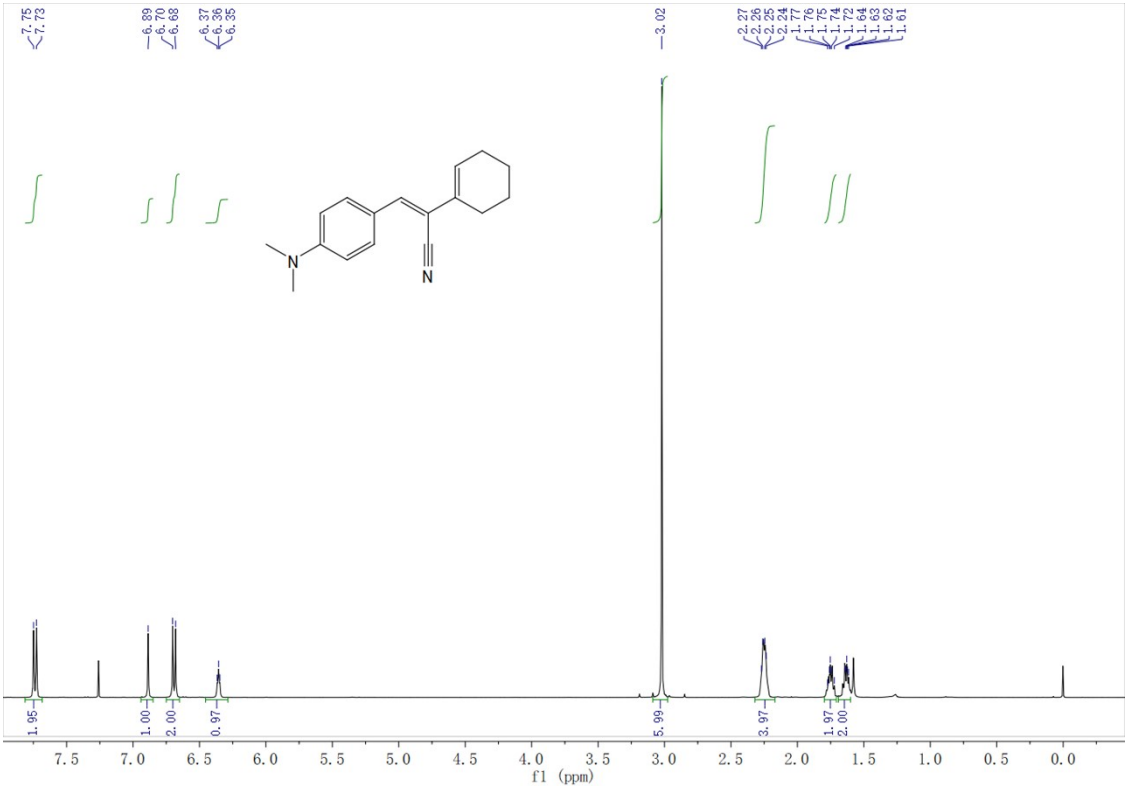
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3i**



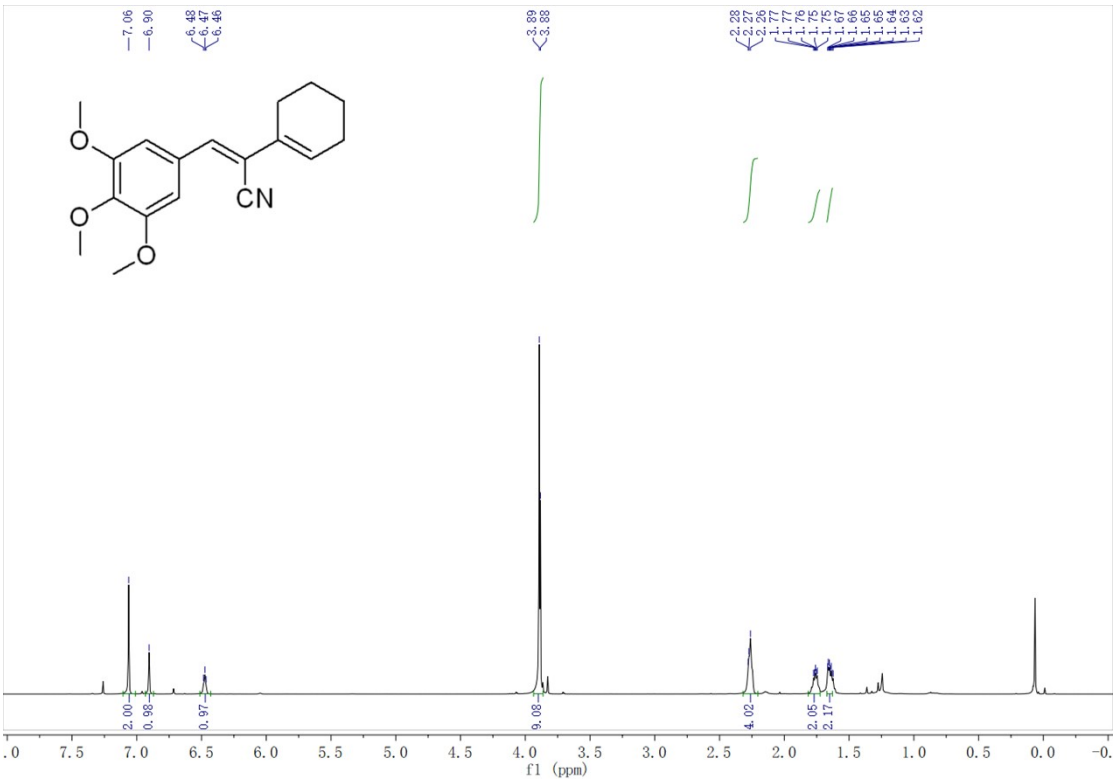
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3j**



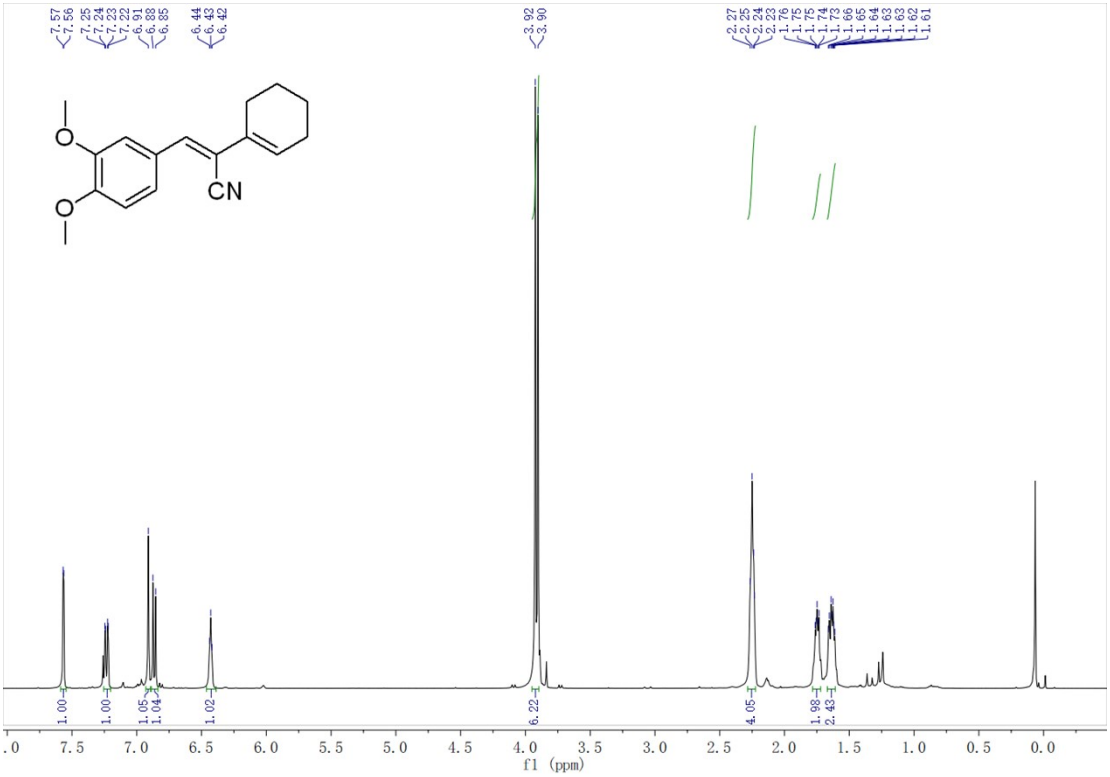
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3k**



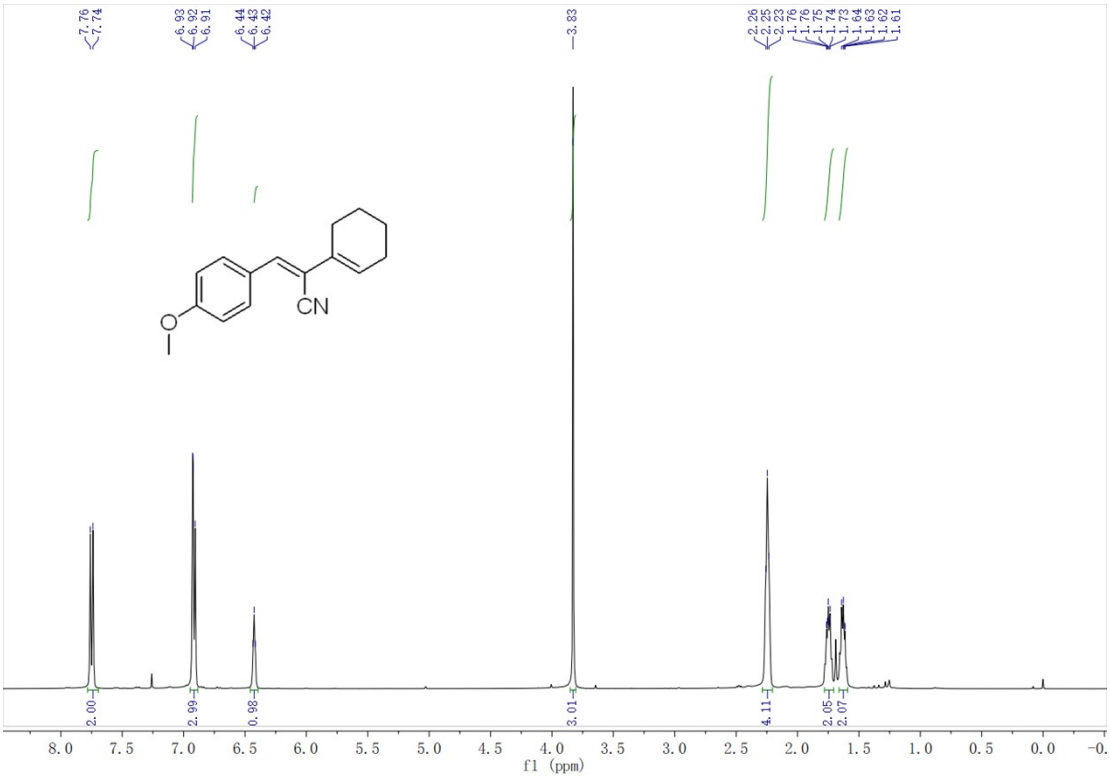
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3l**



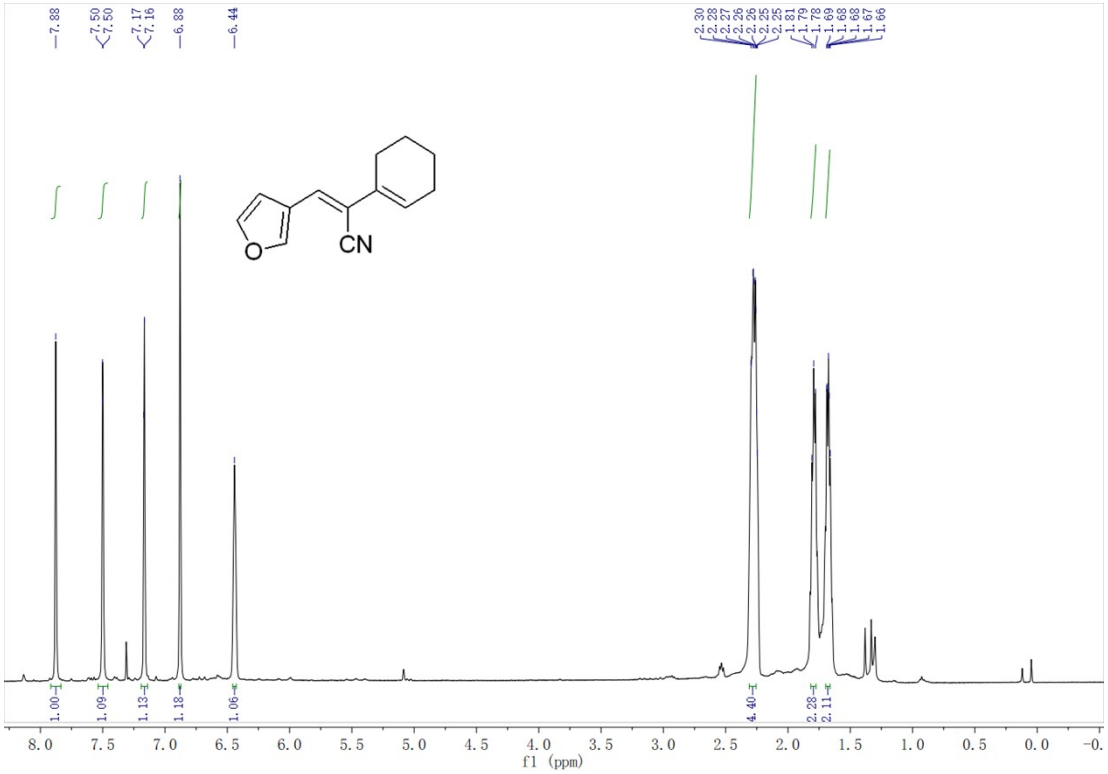
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3m**



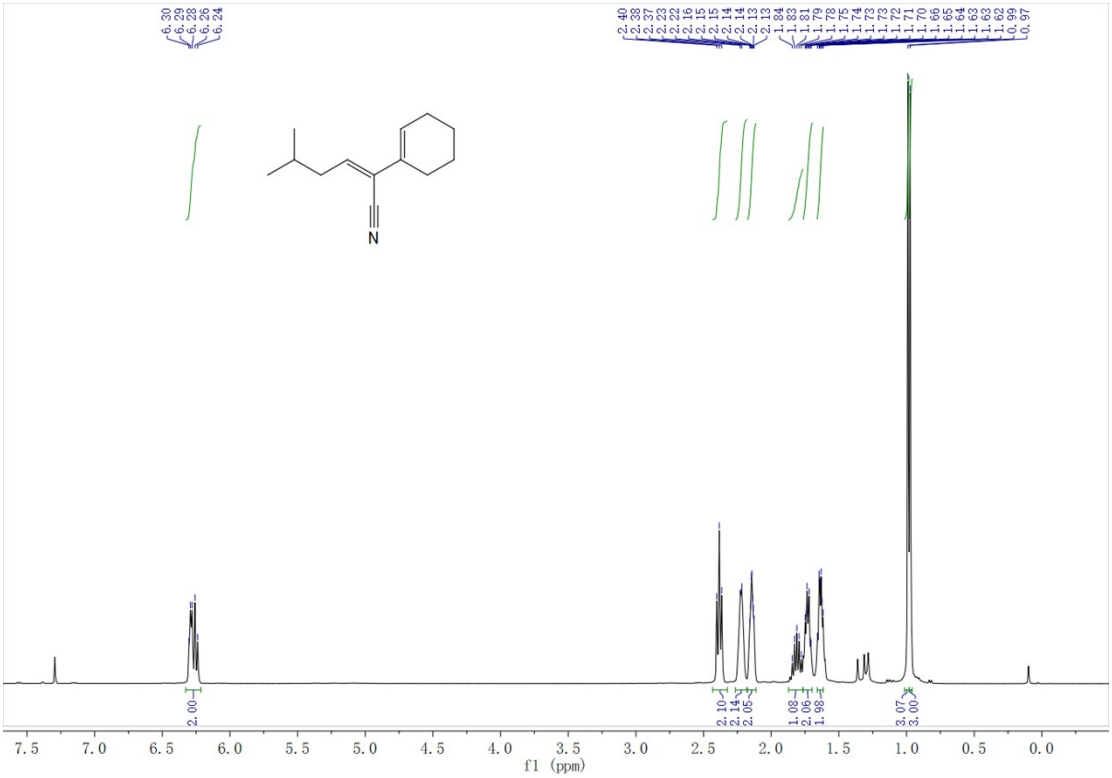
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3n**



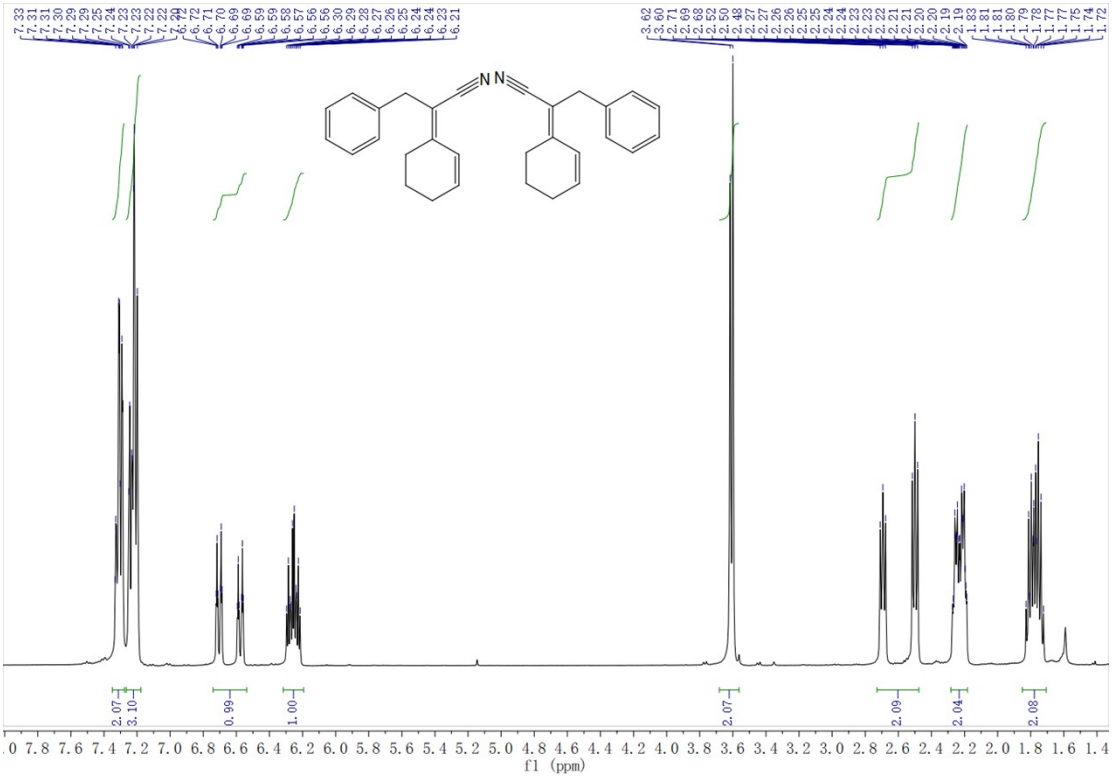
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3o**



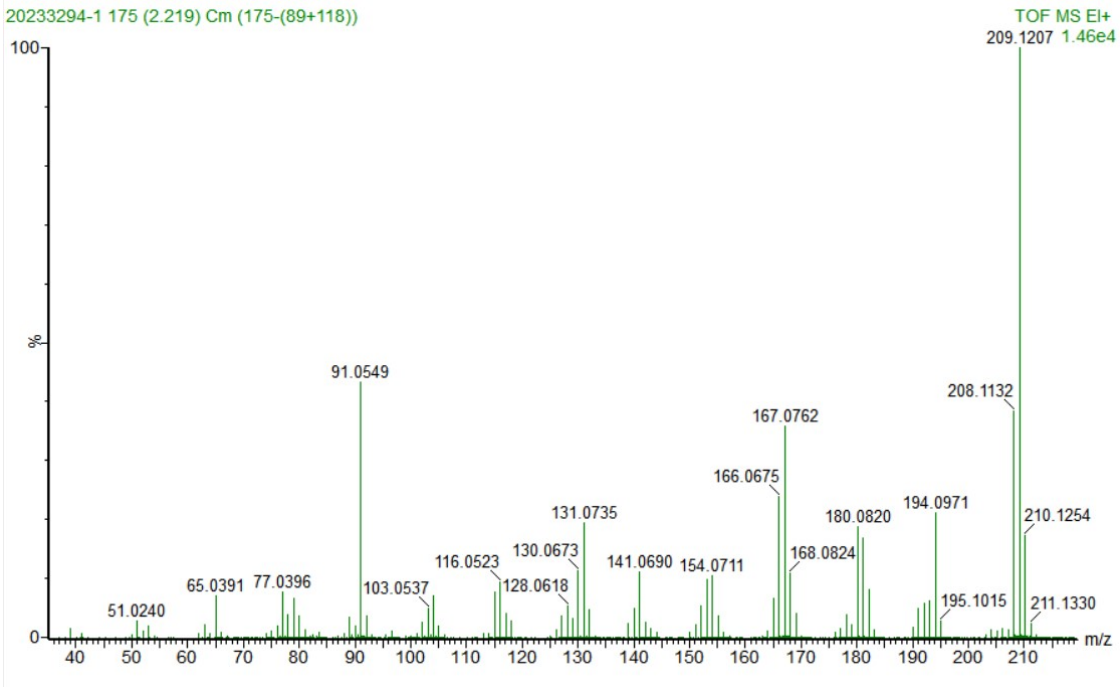
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3p**



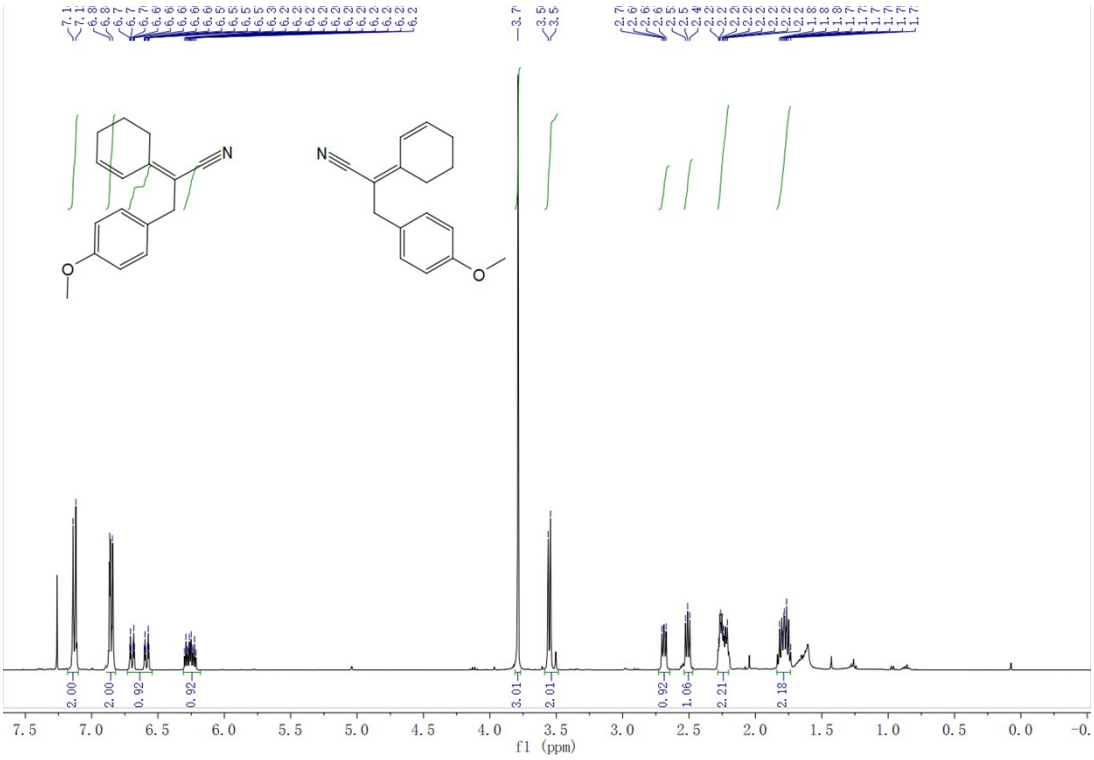
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3q**



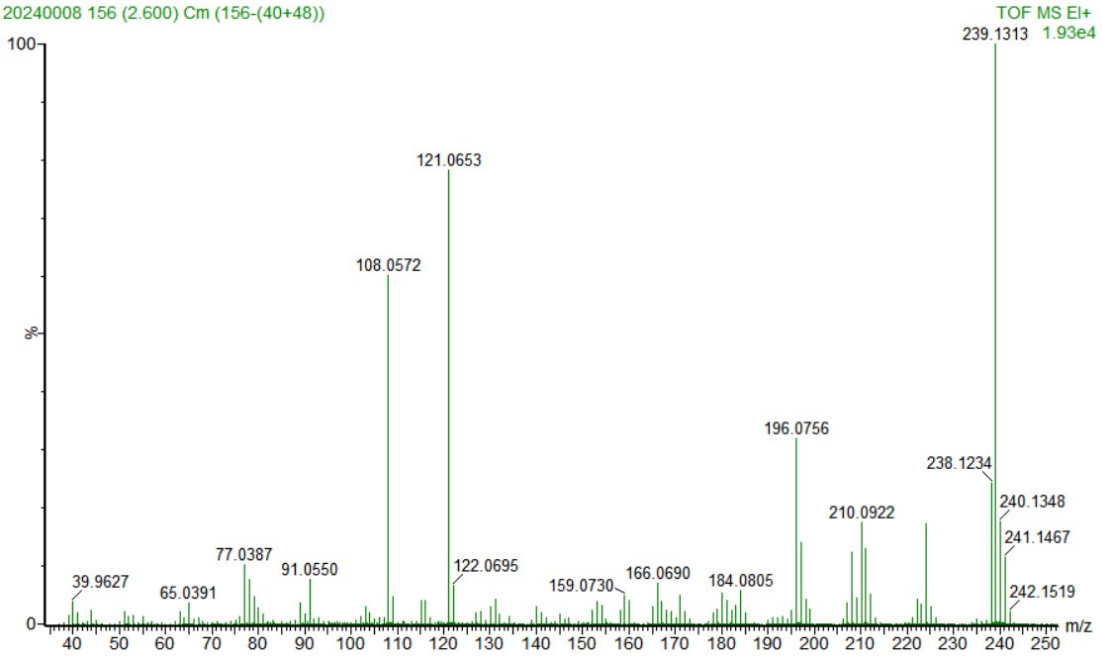
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5a**



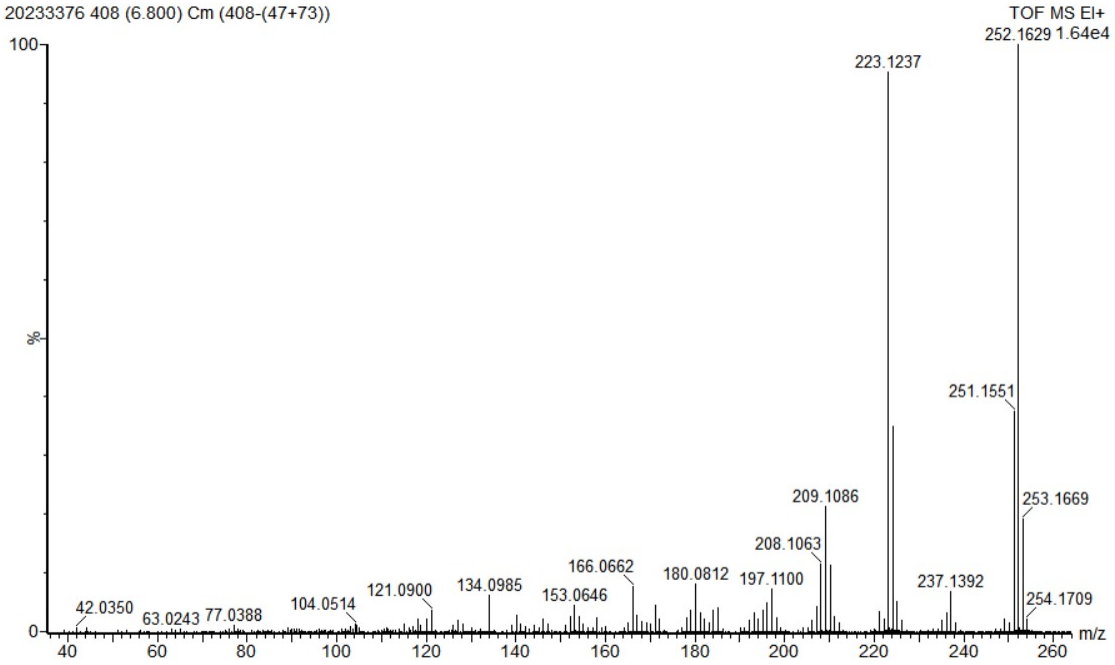
Mass spectrum of **5a**



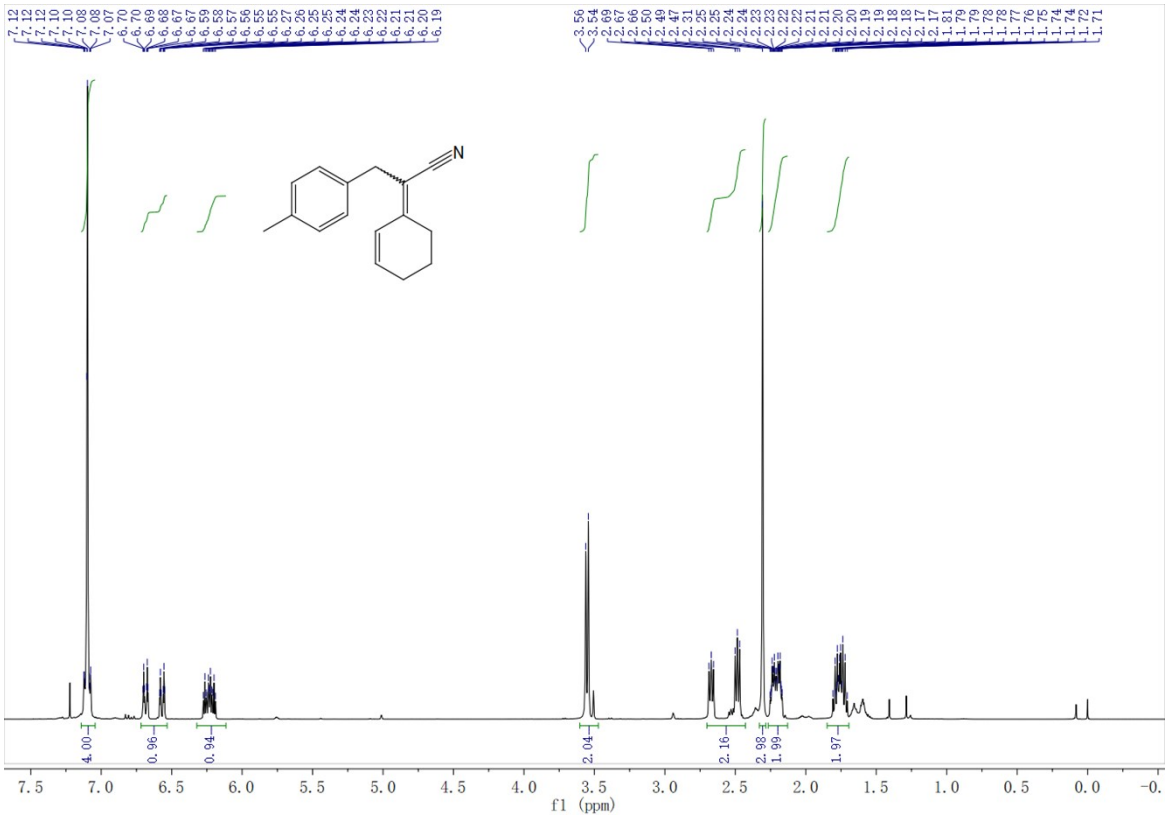
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5r**



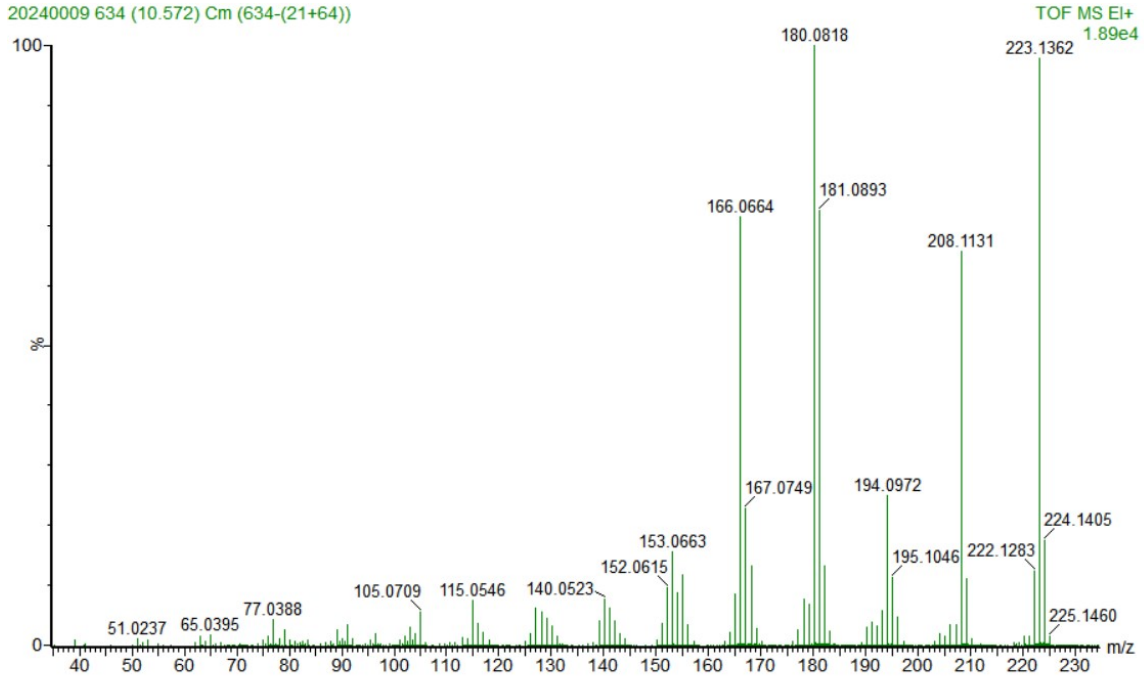
Mass spectrum of **5r**



Mass spectrum of **5s**

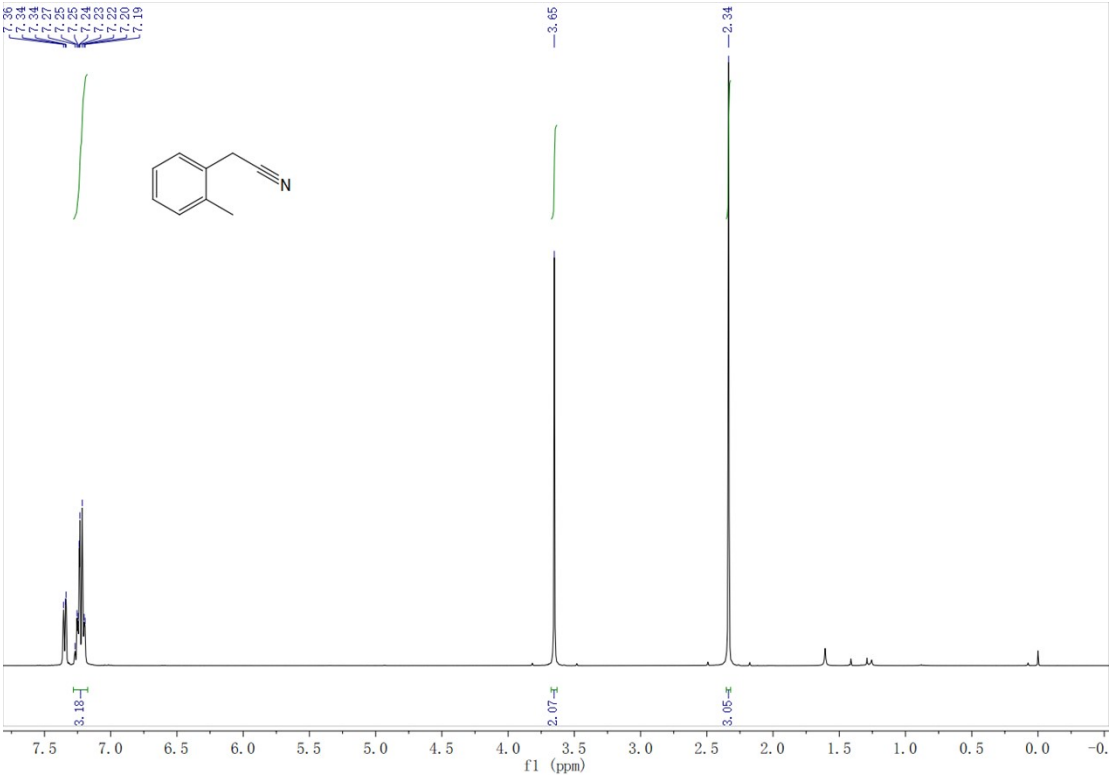


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5i**

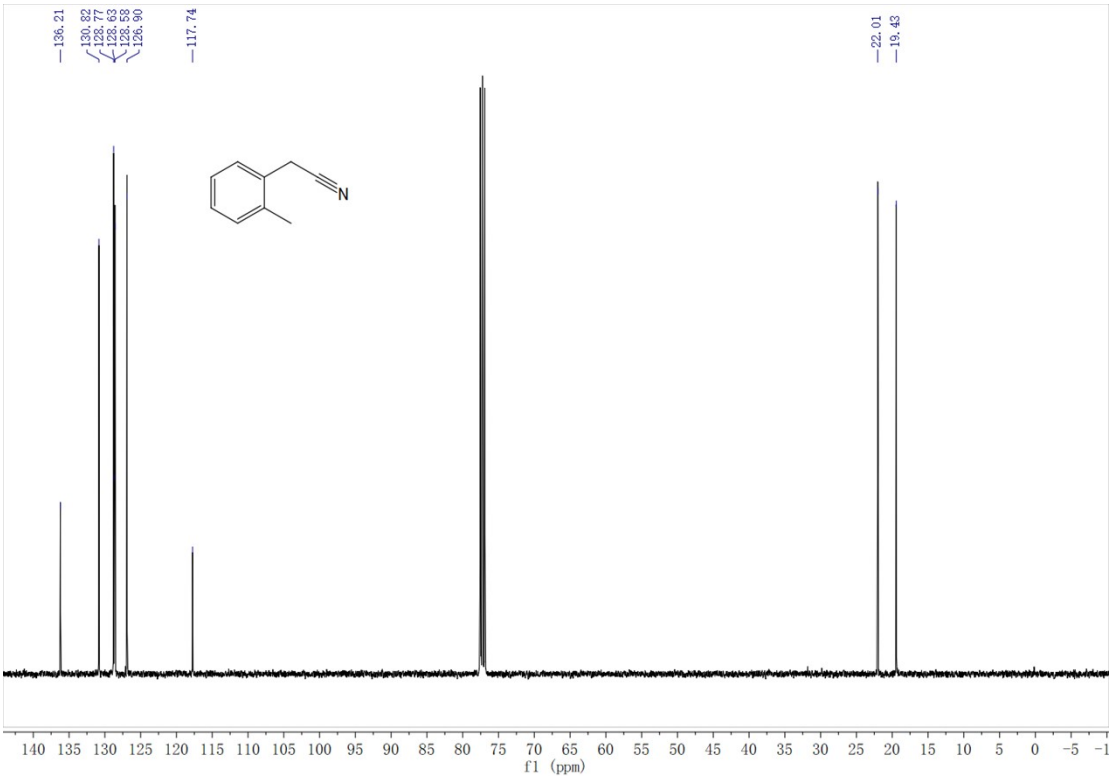


Mass spectrum of **5i**

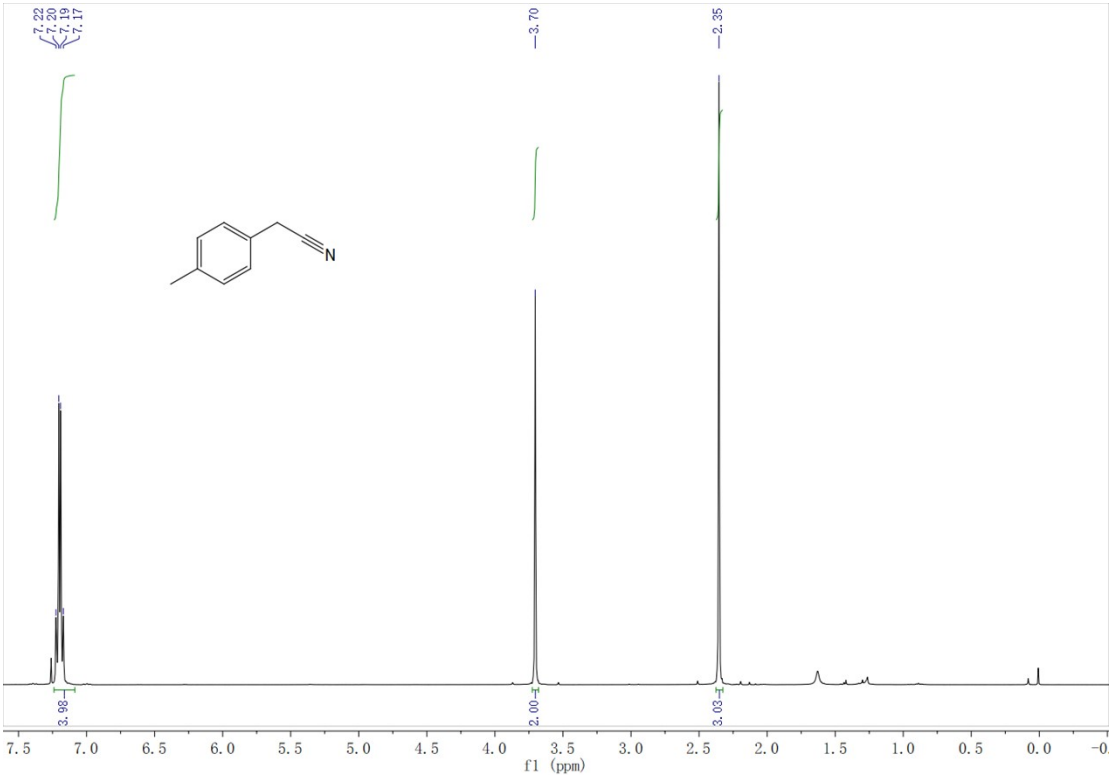
5.2 NMR spectra of products



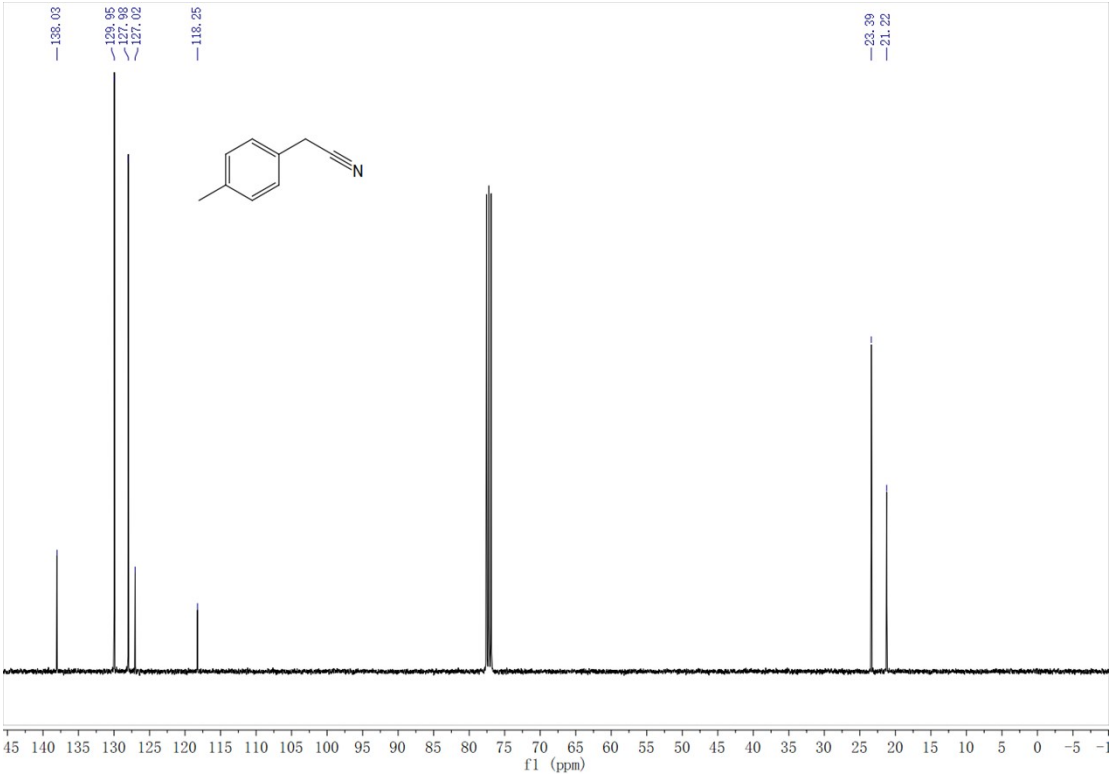
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2a**



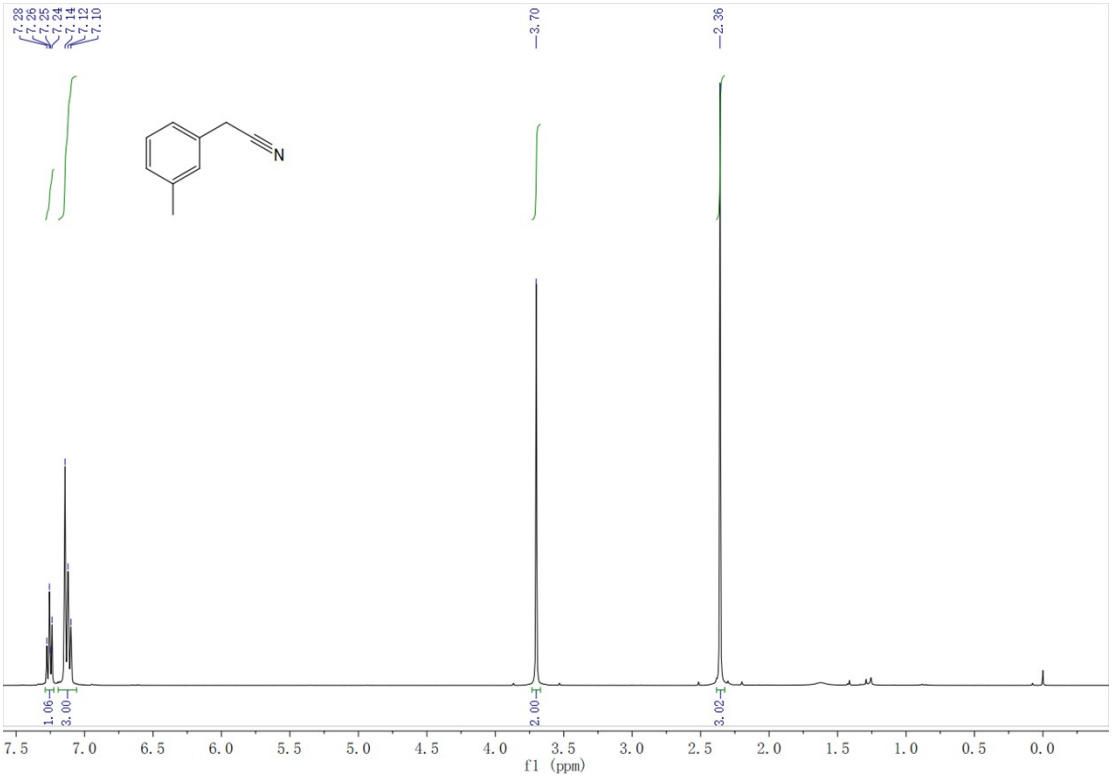
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **2a**



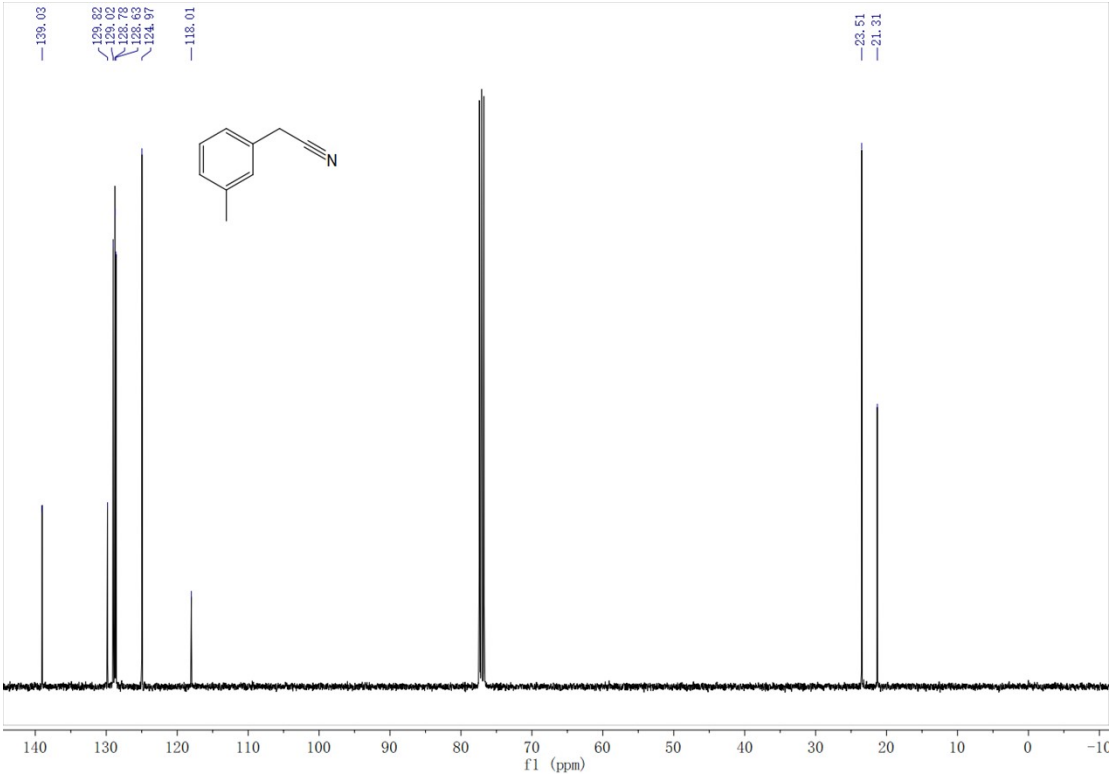
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2b**



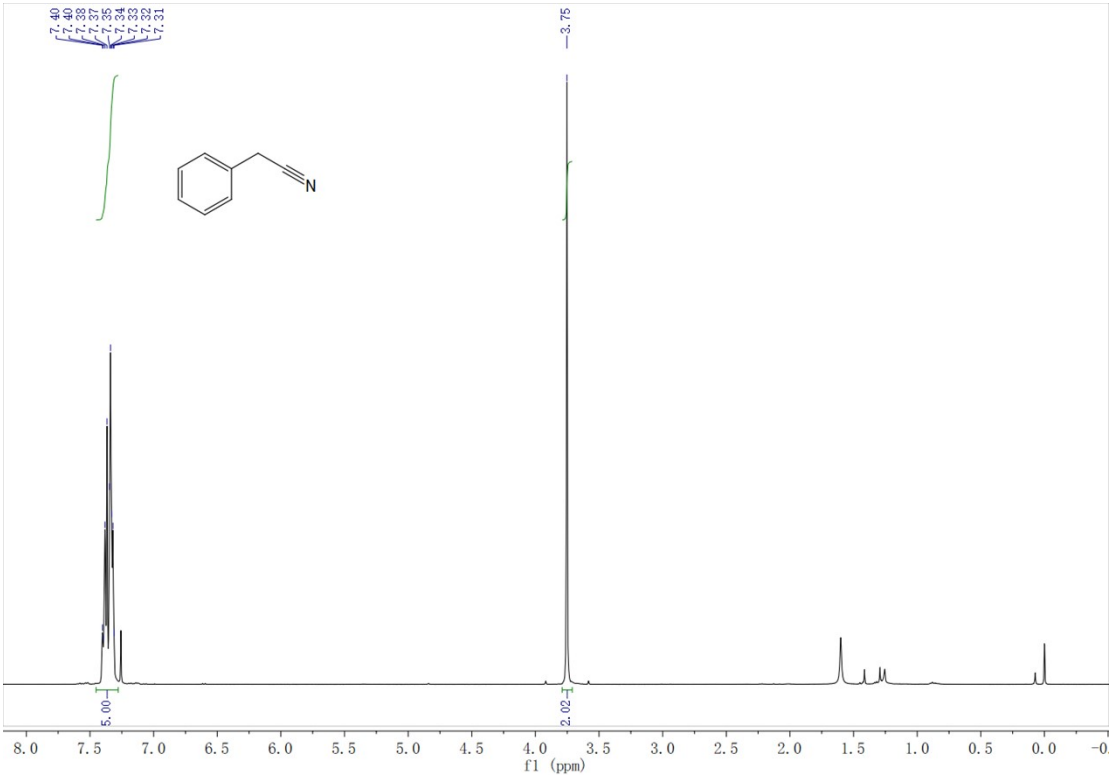
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **2b**



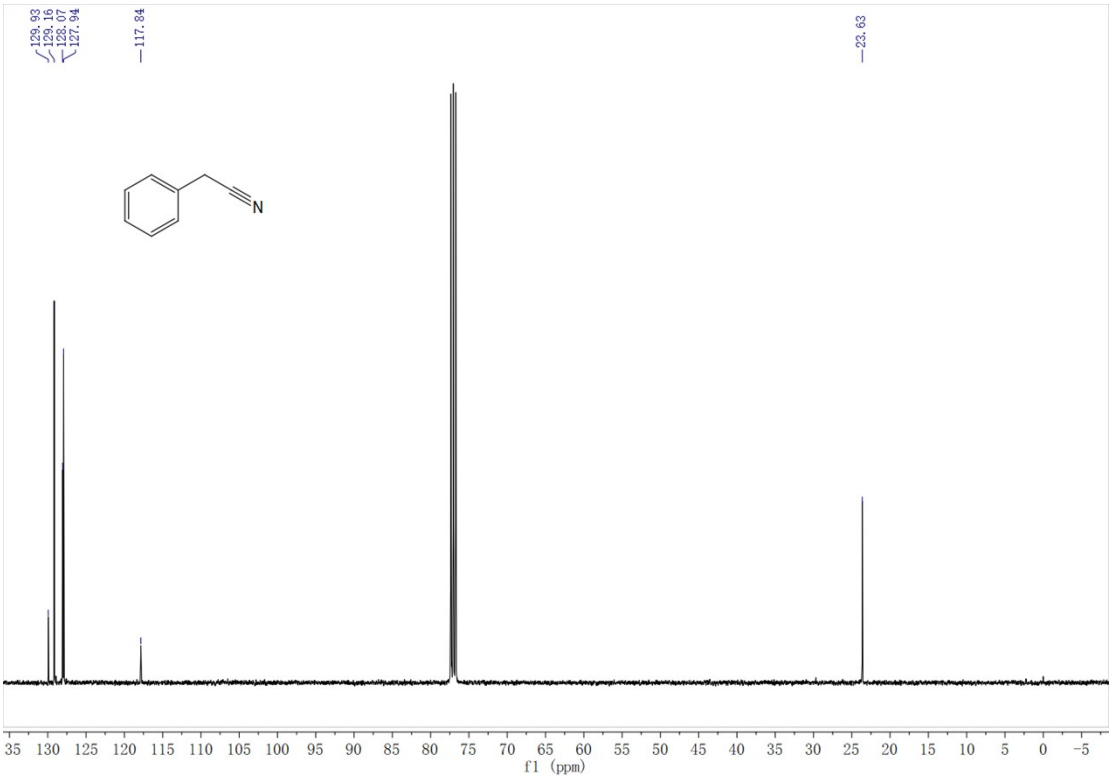
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2c**



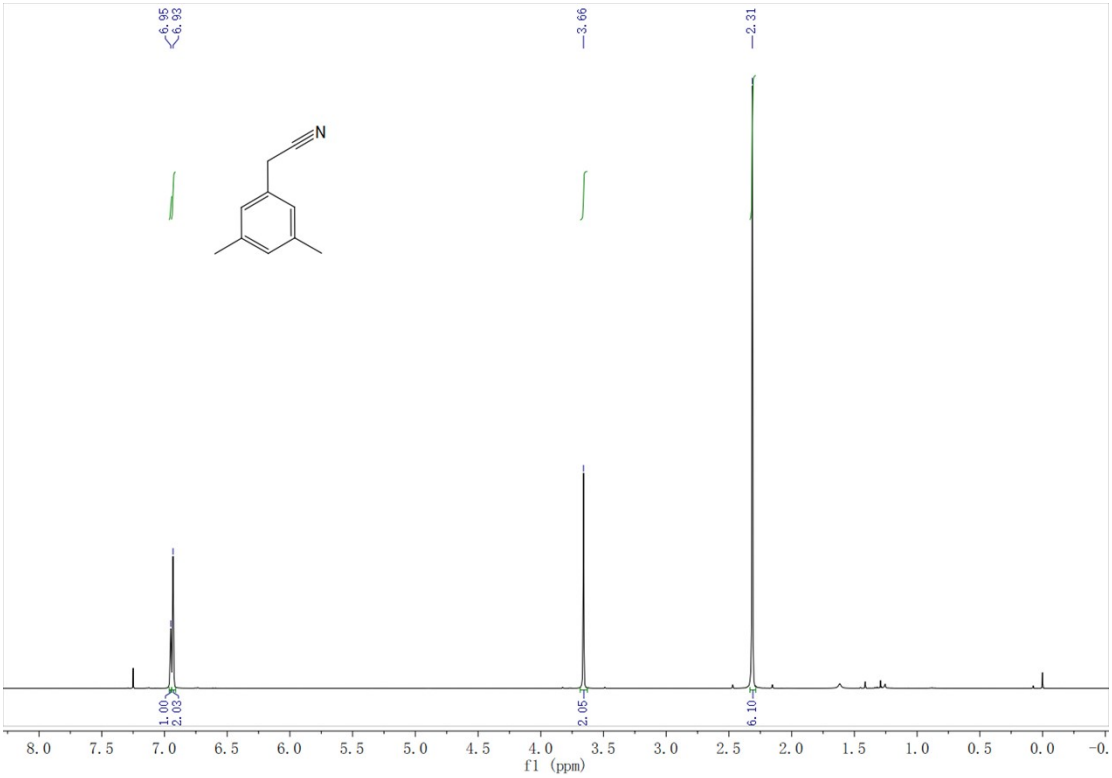
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **2c**



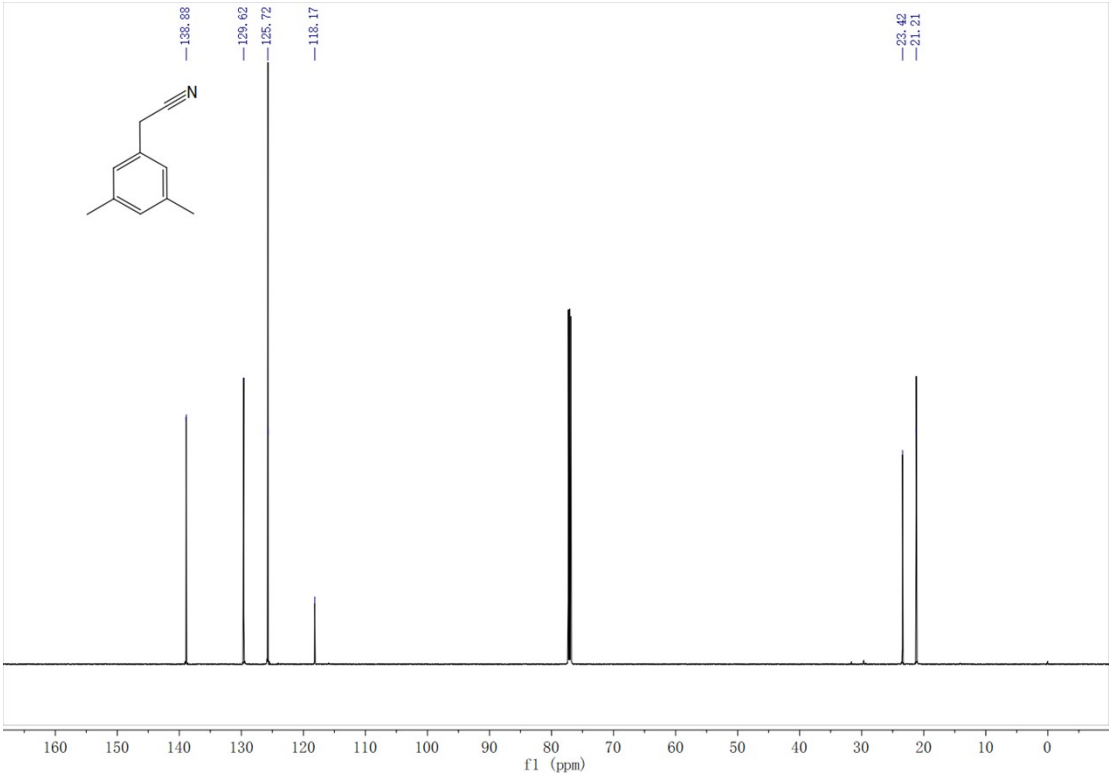
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2d**



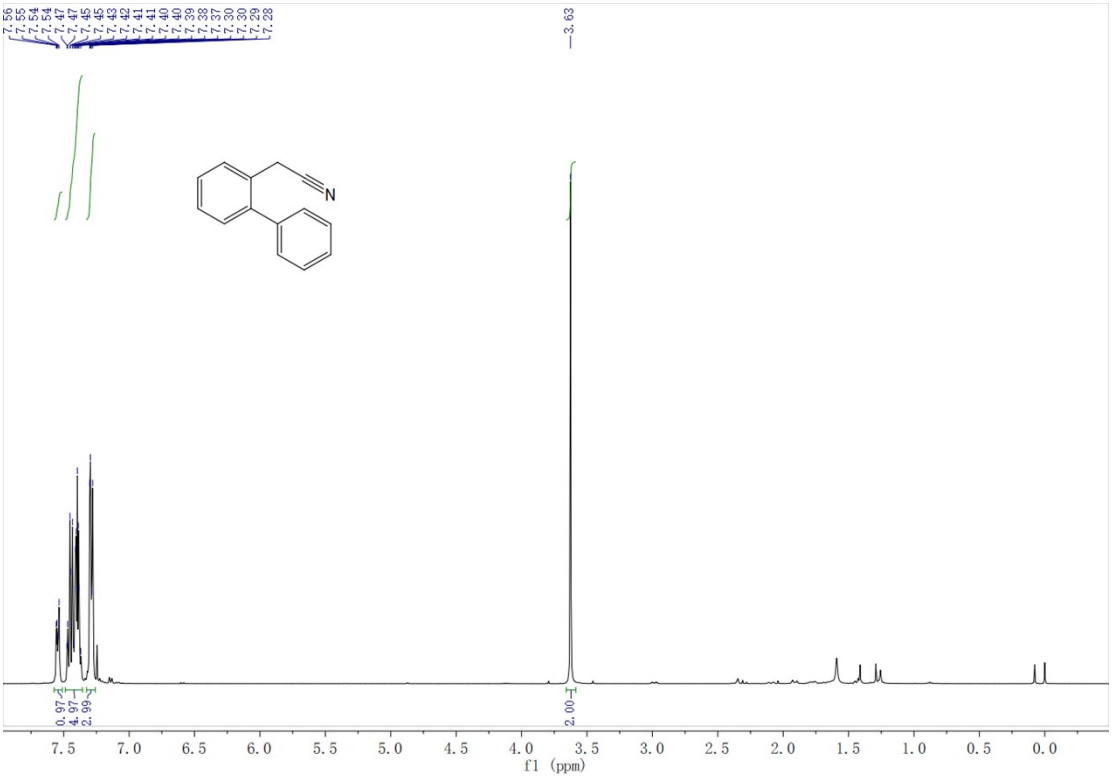
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **2d**



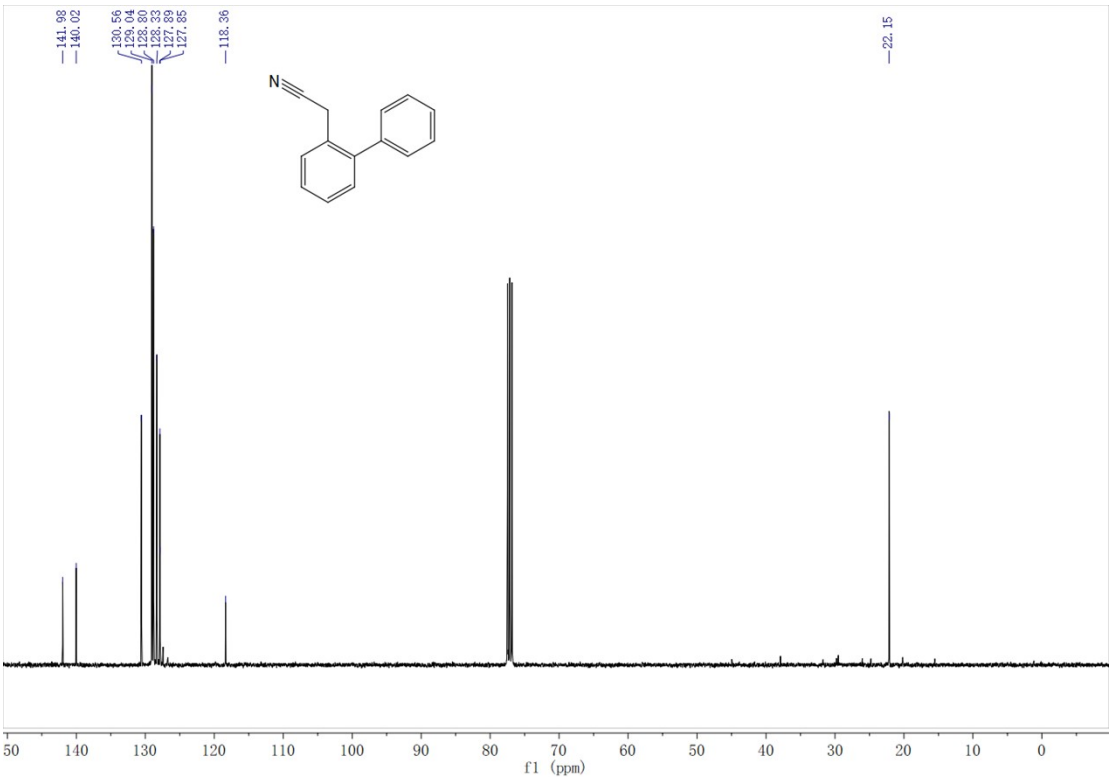
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2e**



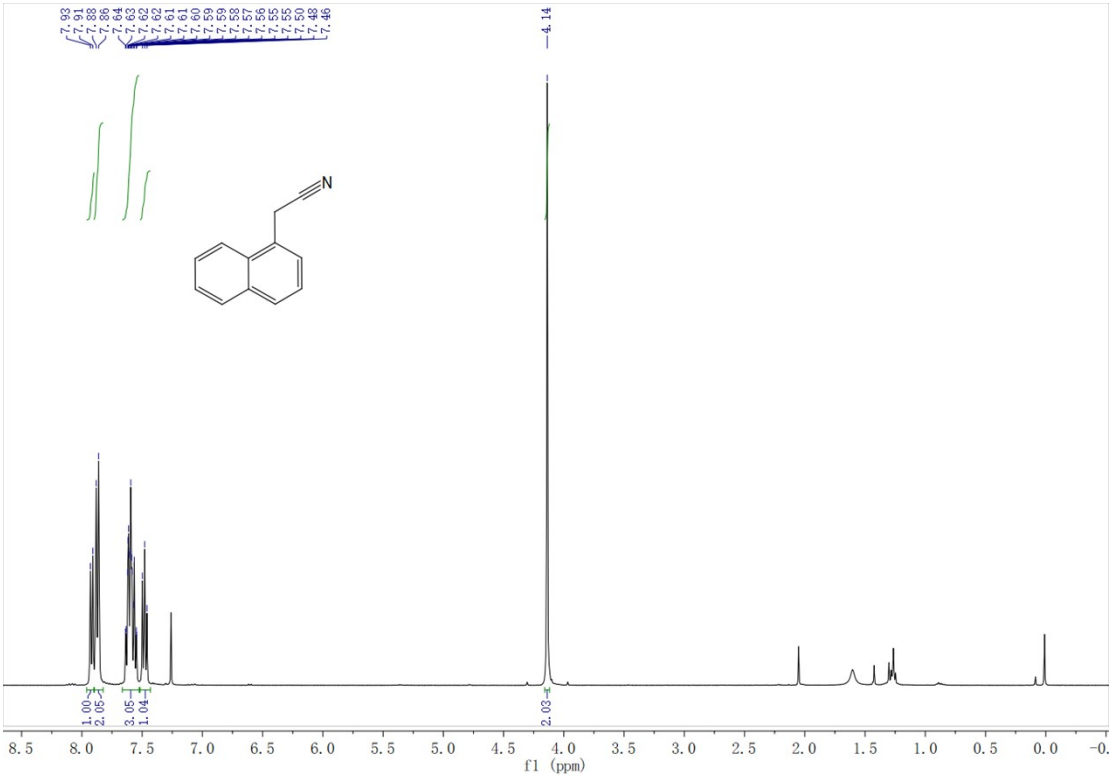
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **2e**



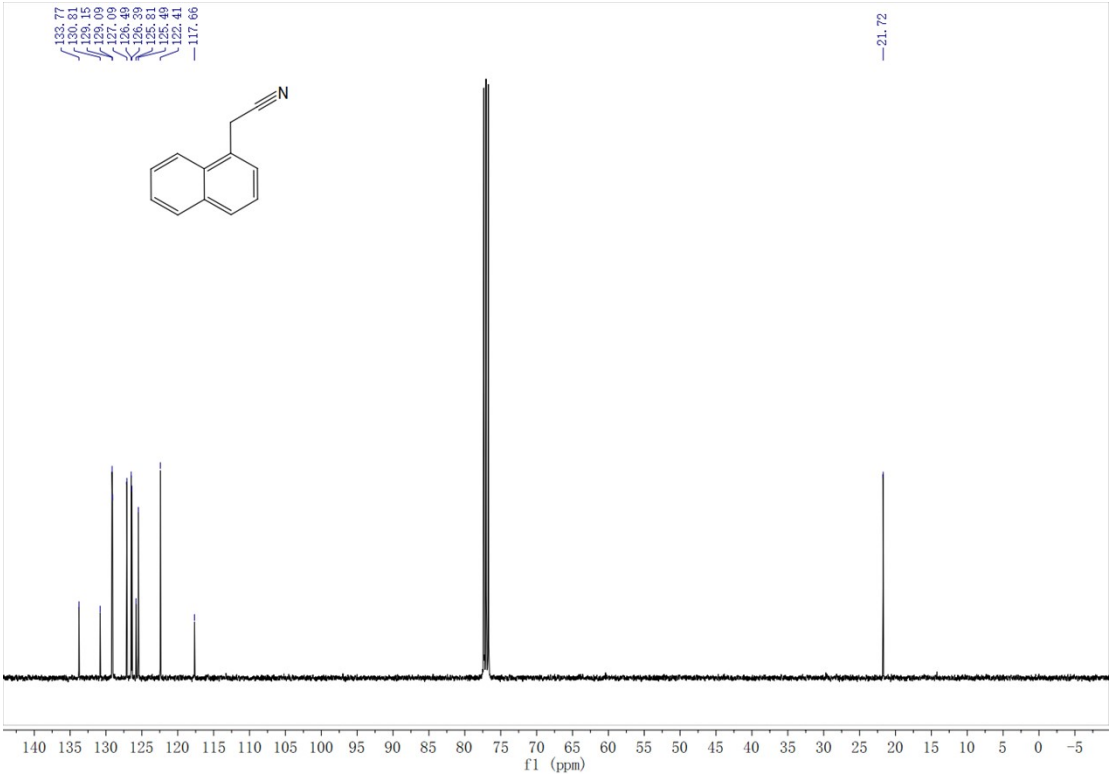
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2f**



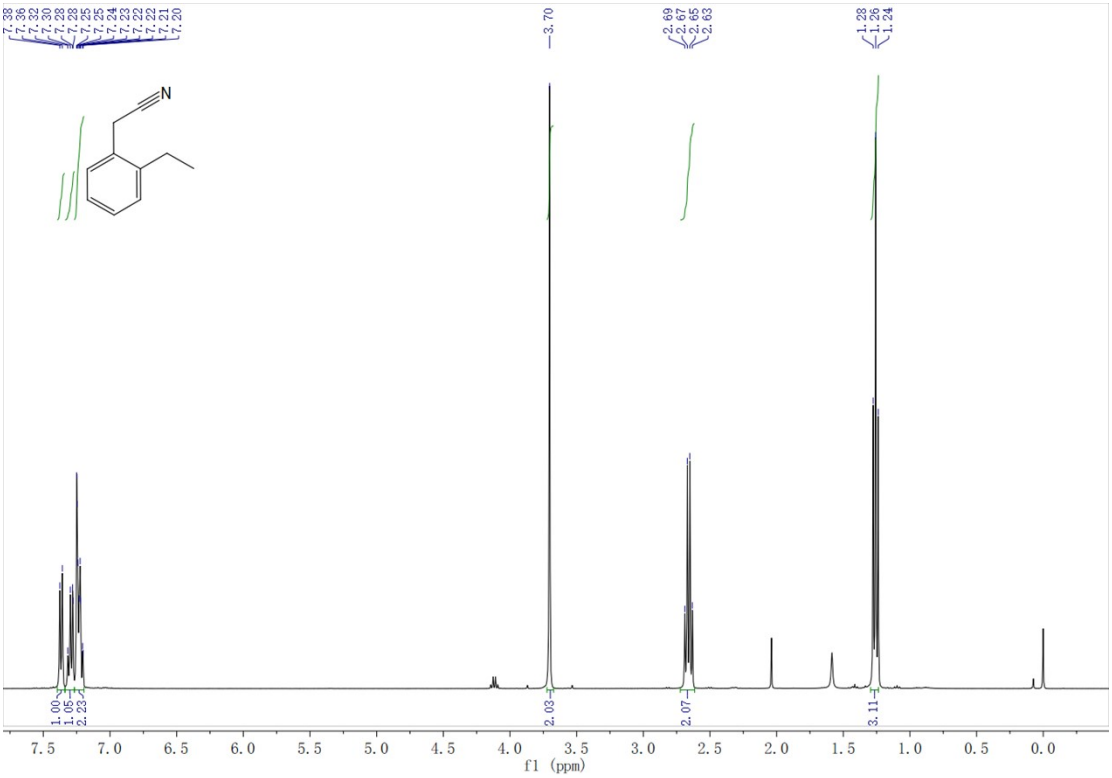
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **2f**



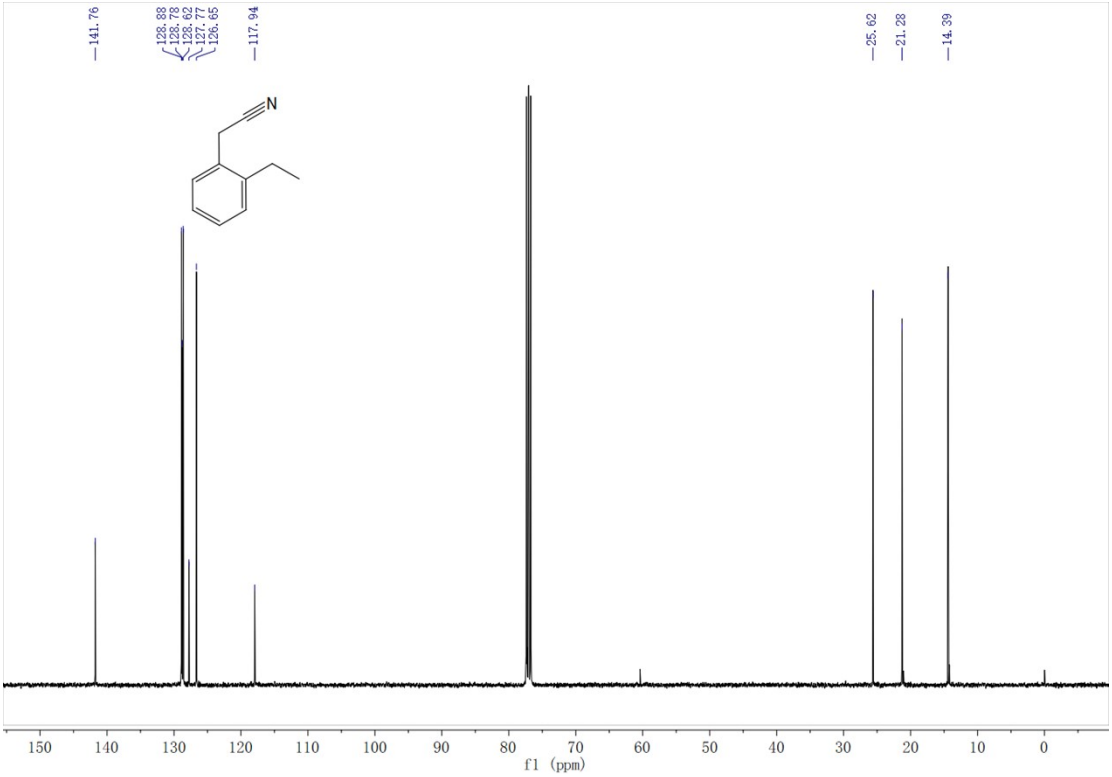
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2g**



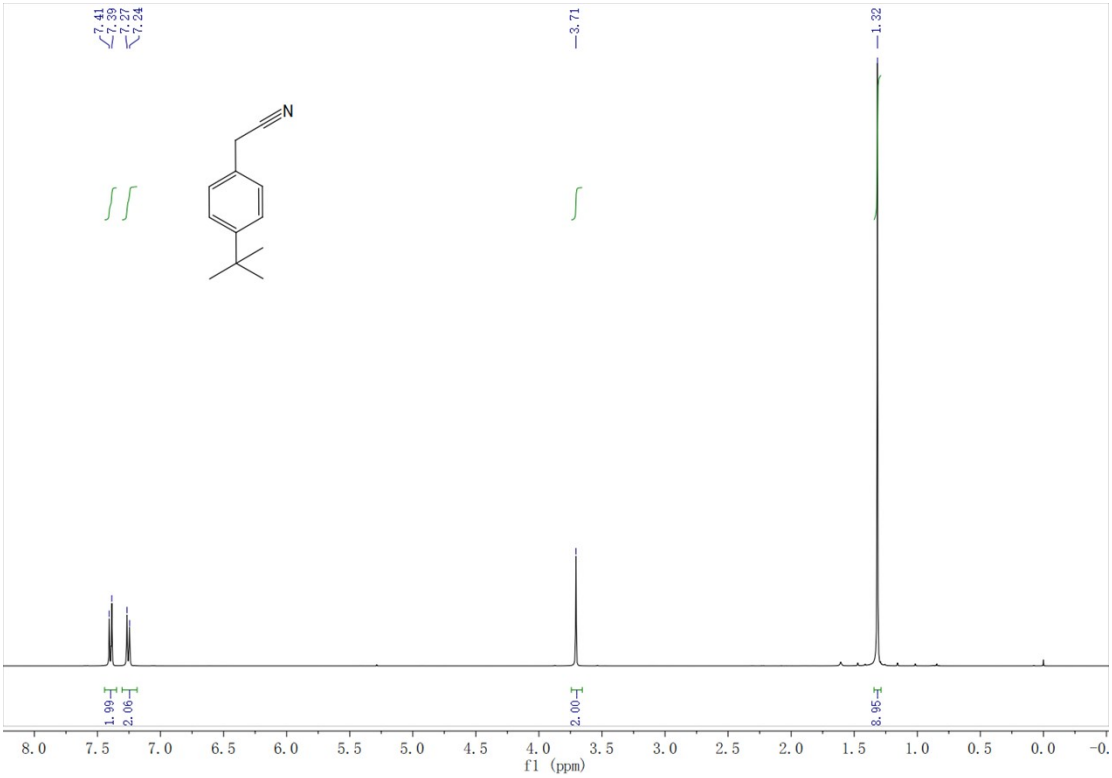
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **2g**



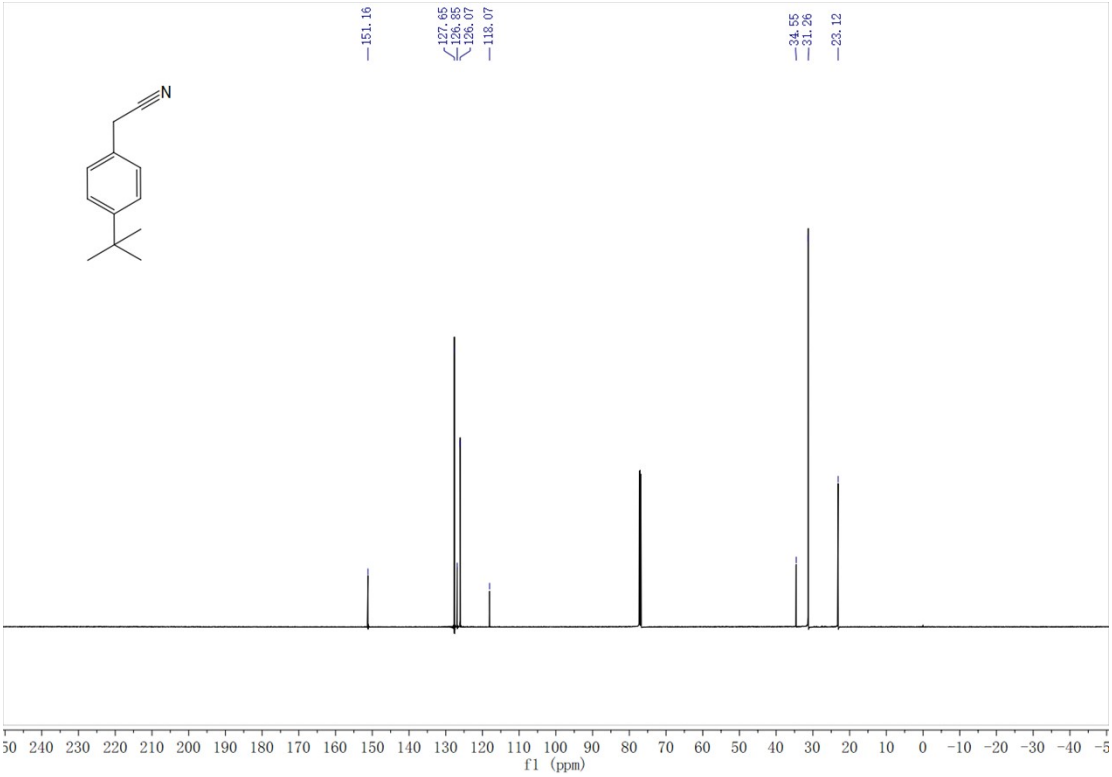
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2h**



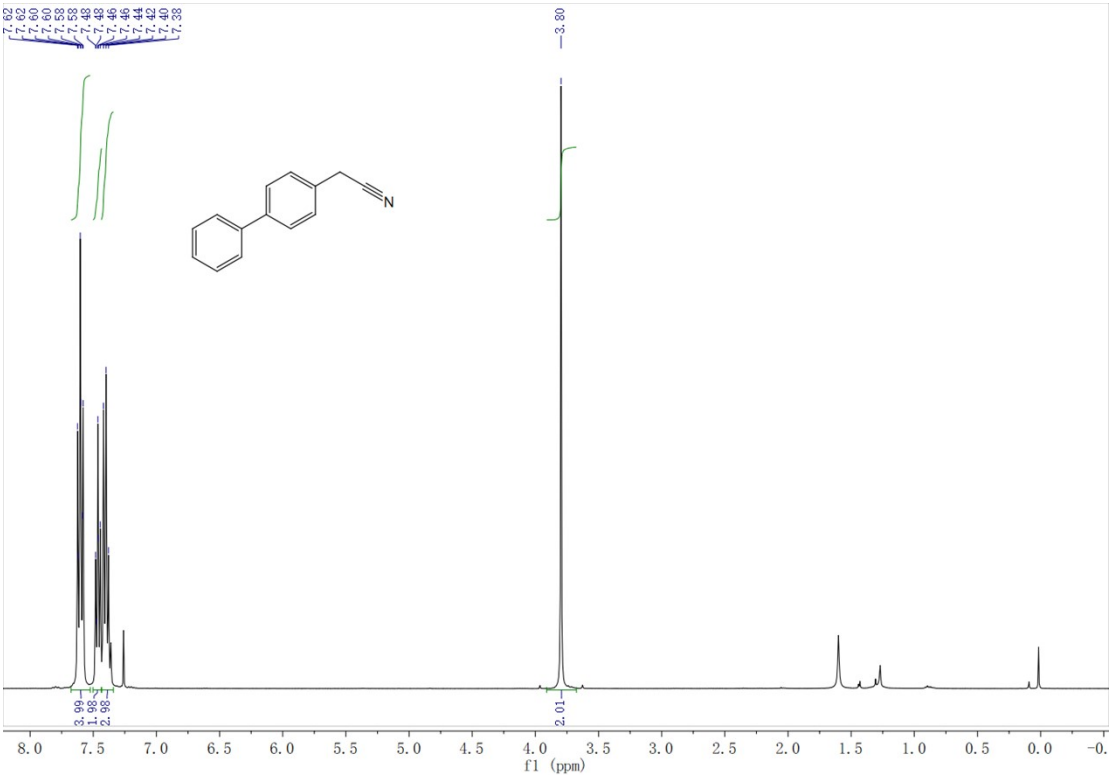
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **2h**



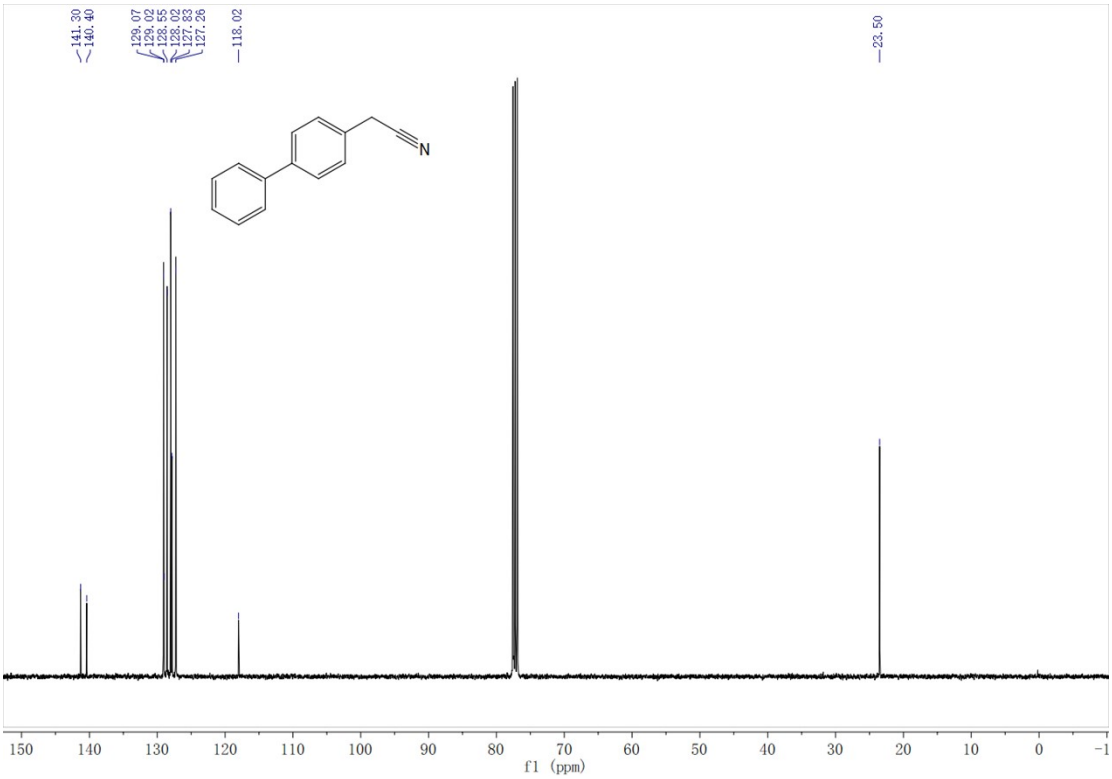
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2i**



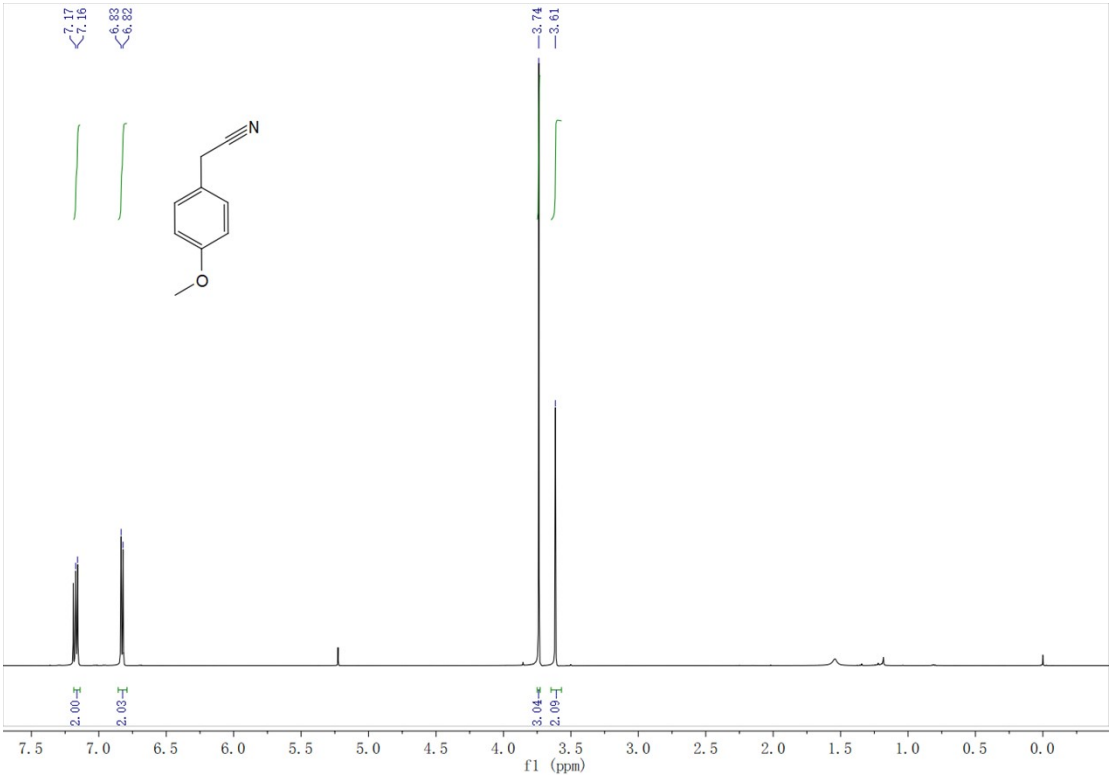
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **2i**



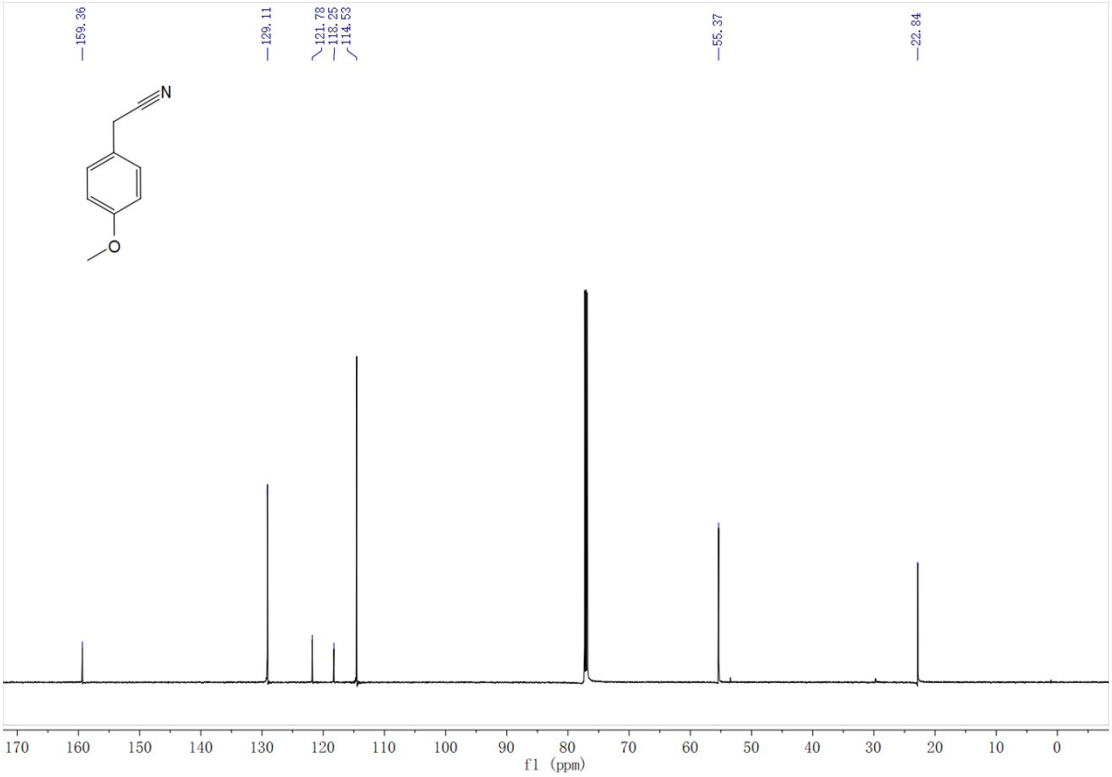
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2j**



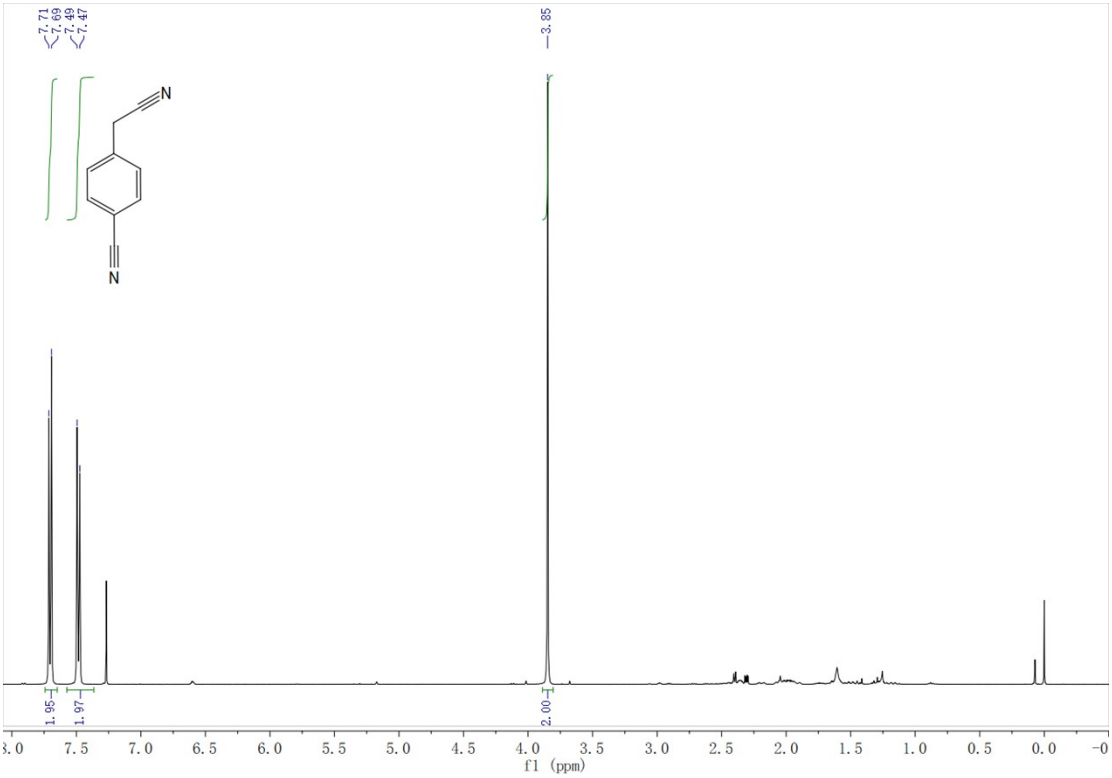
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **2j**



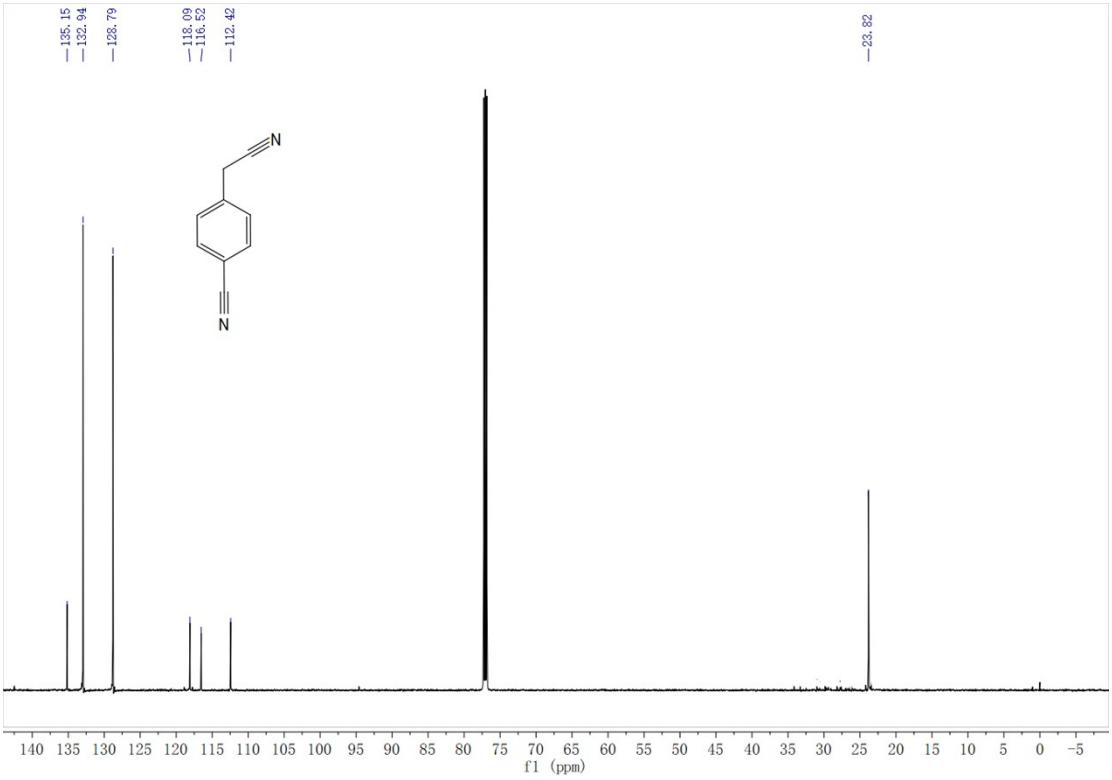
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2k**



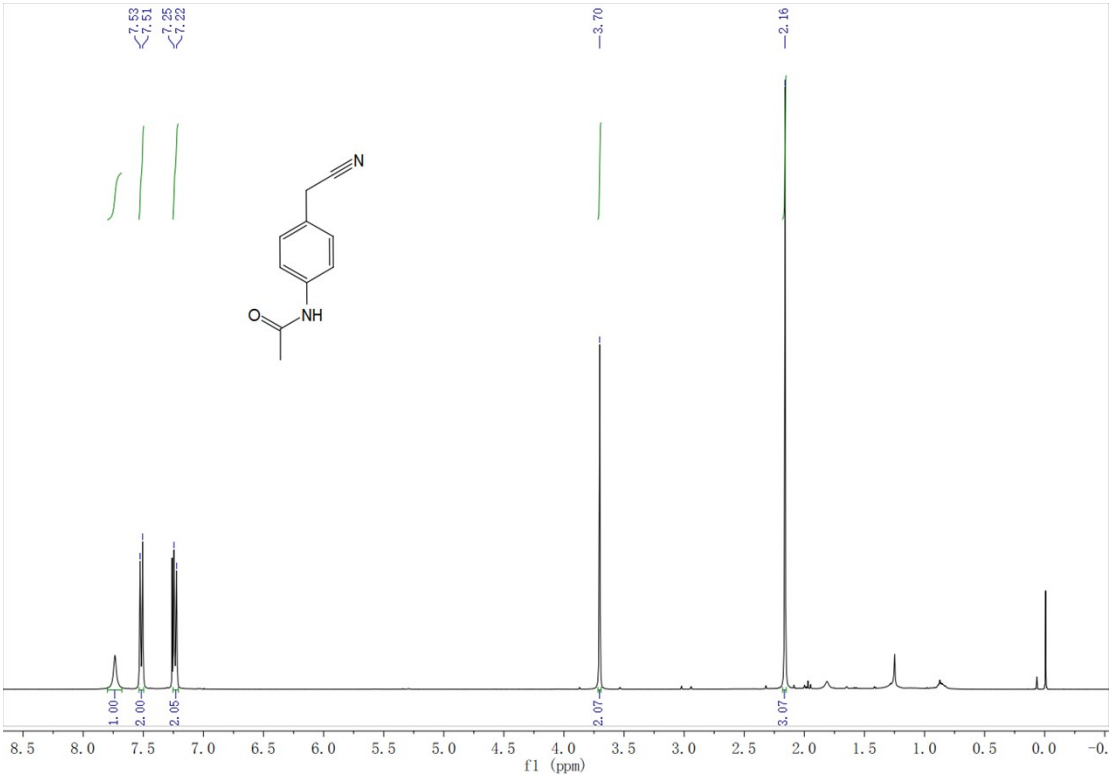
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **2k**



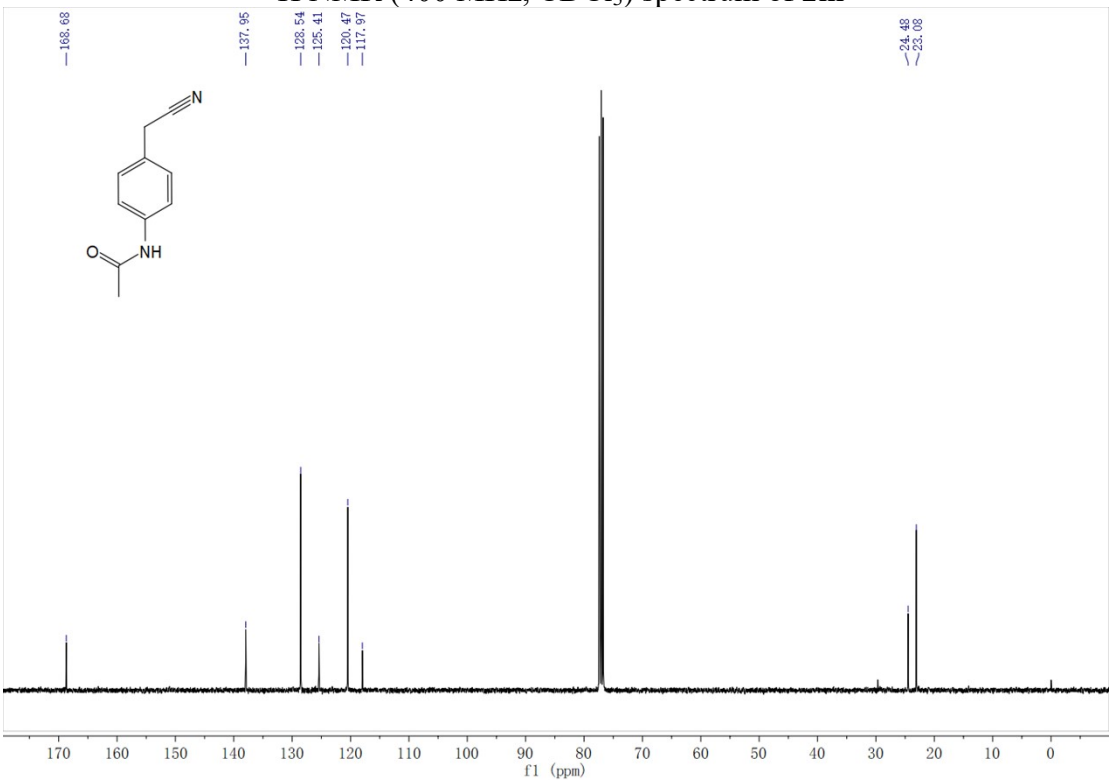
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2l**



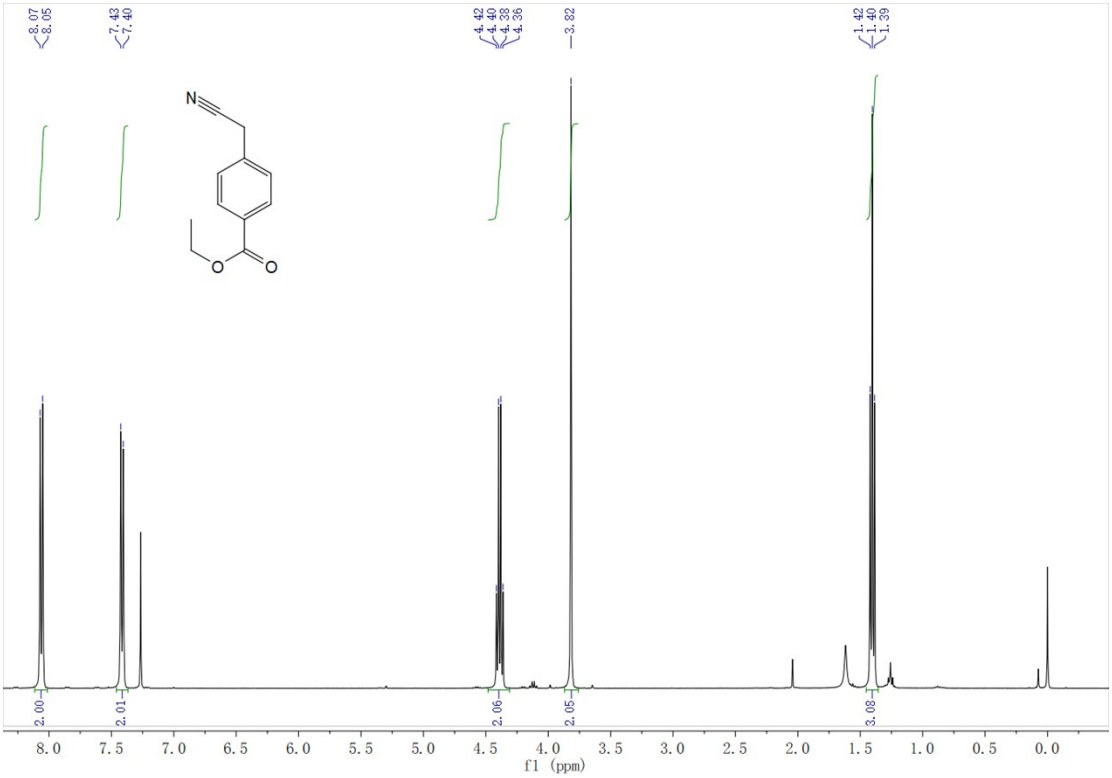
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **2l**



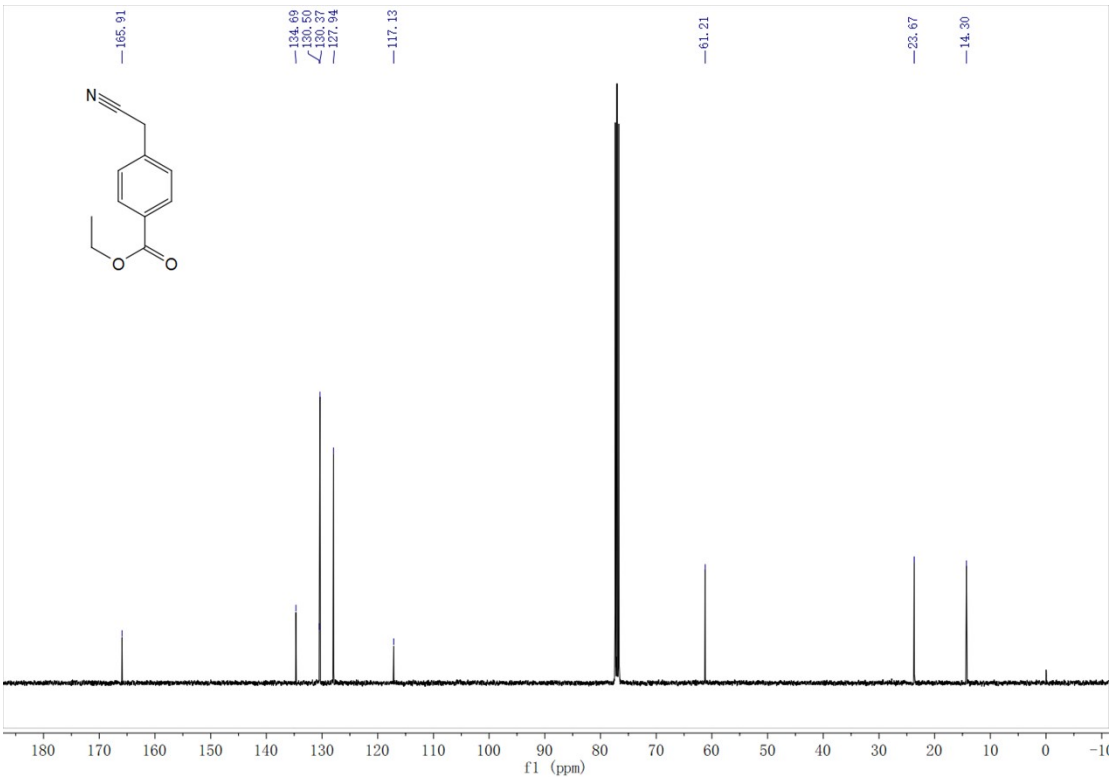
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2m**



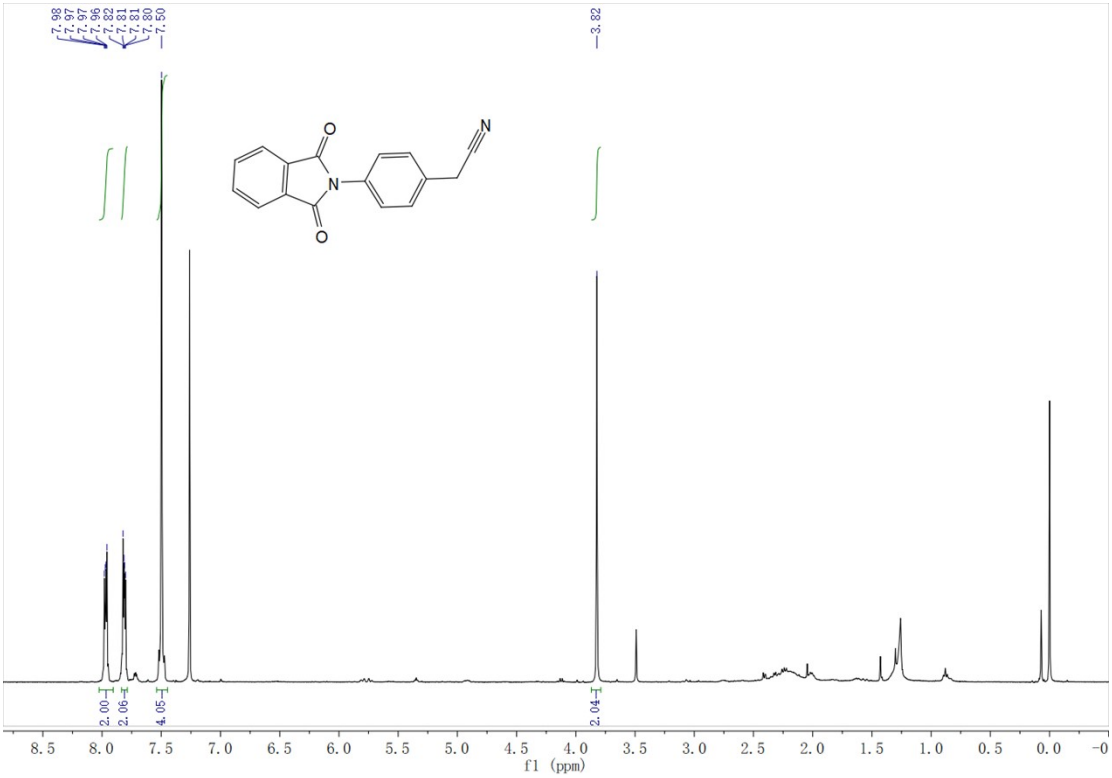
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **2m**



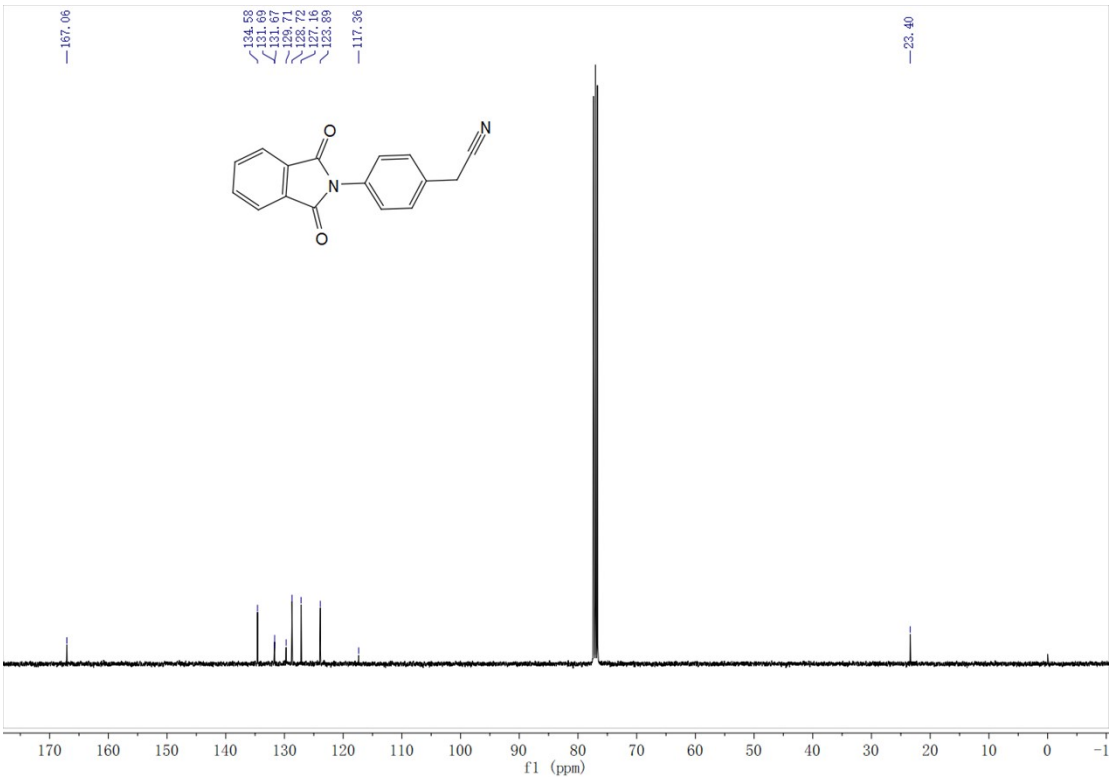
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2n**



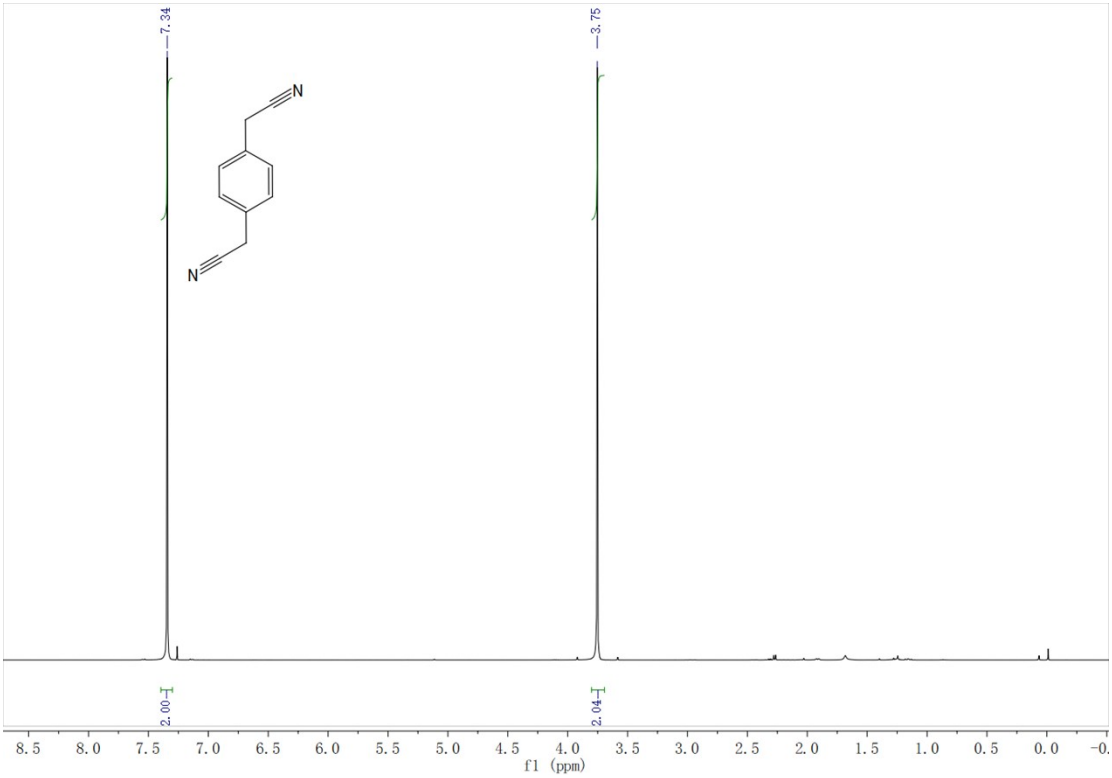
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **2n**



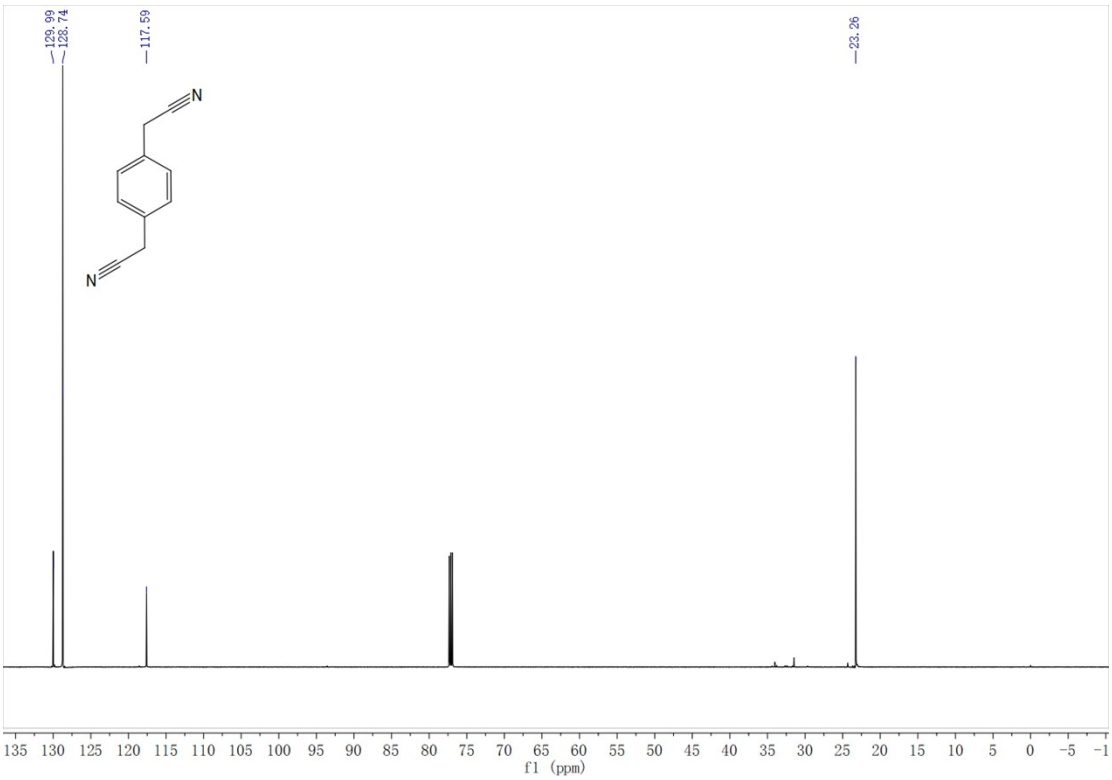
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2o**



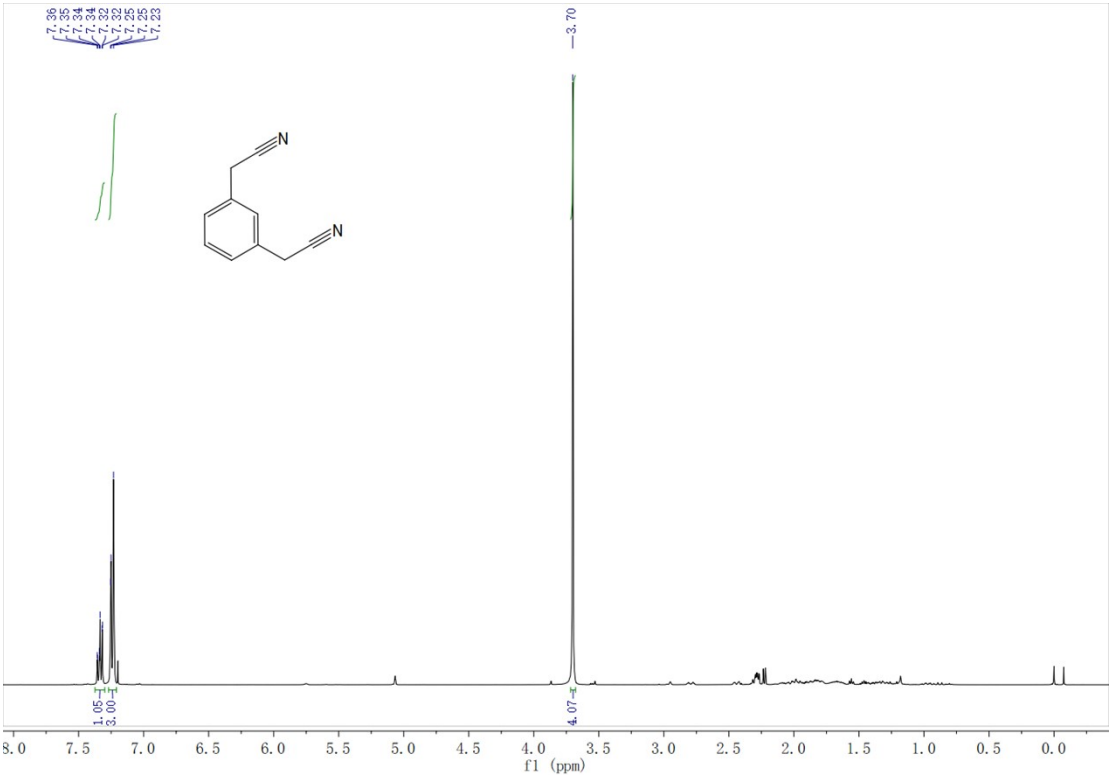
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **2o**



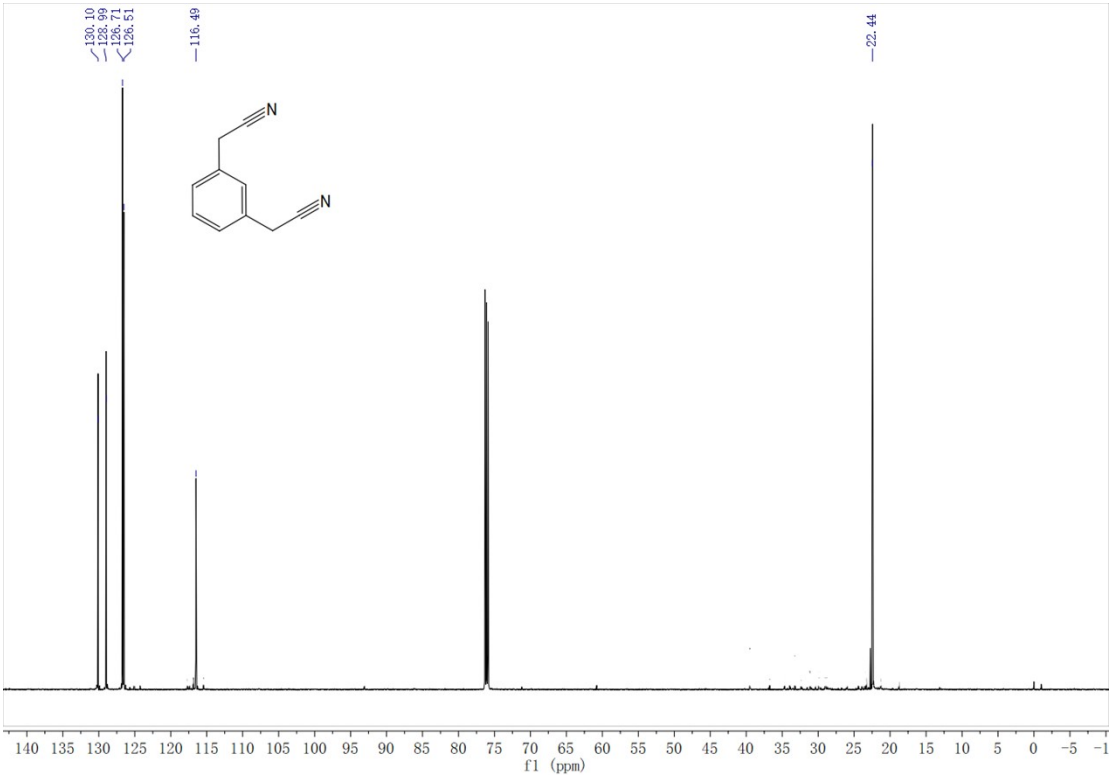
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2p**



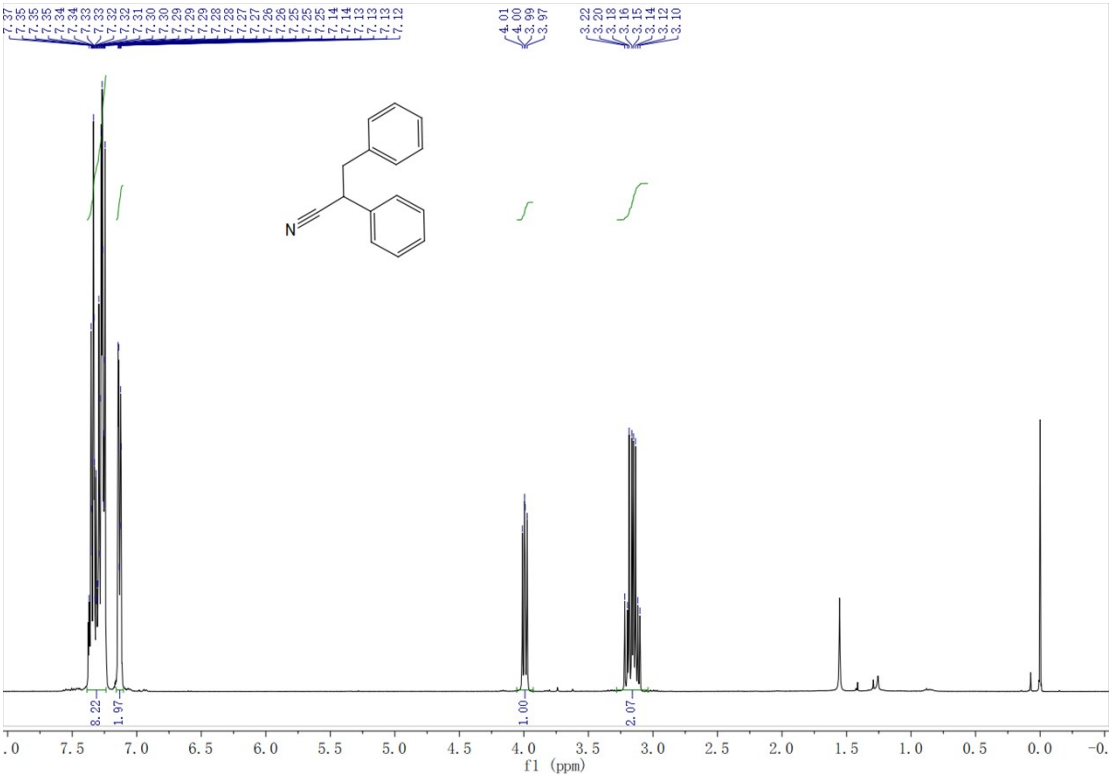
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **2p**



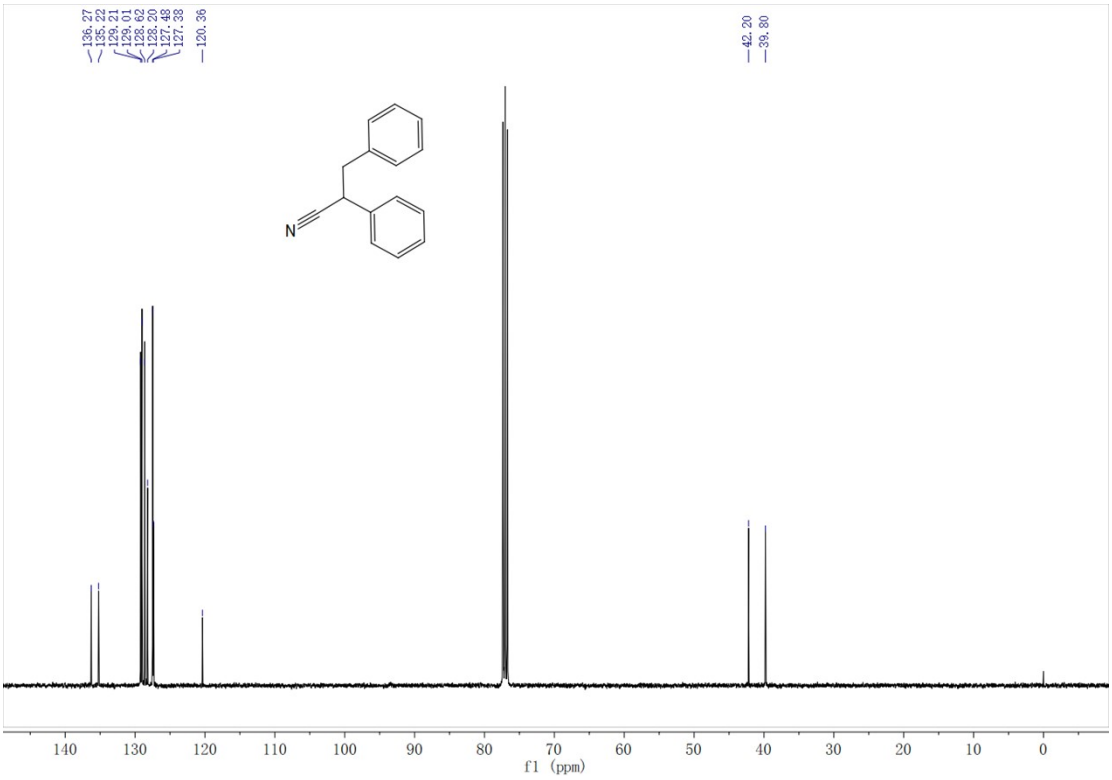
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2q**



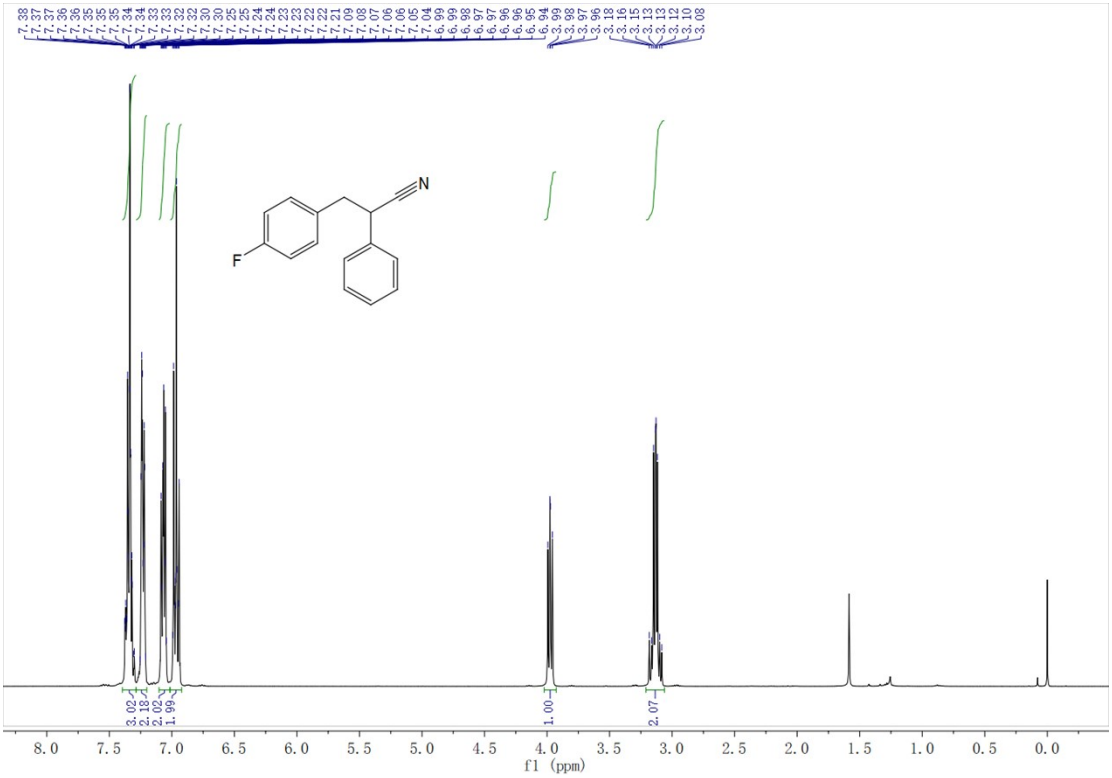
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **2q**



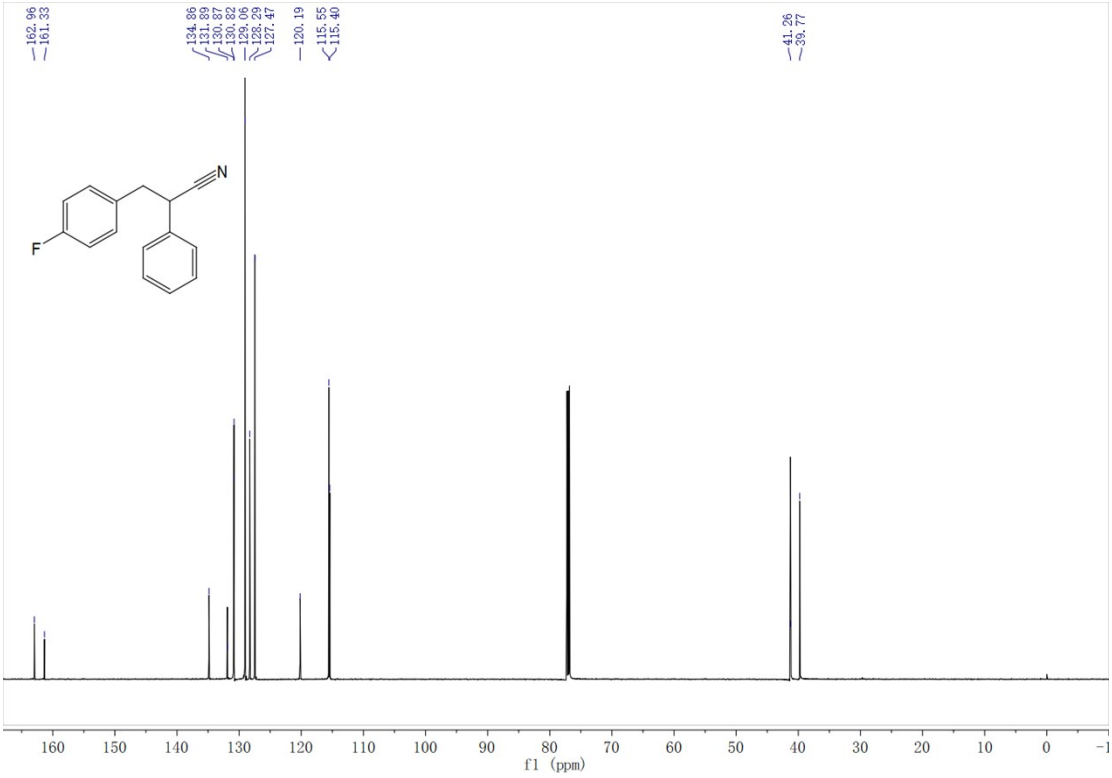
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4a**



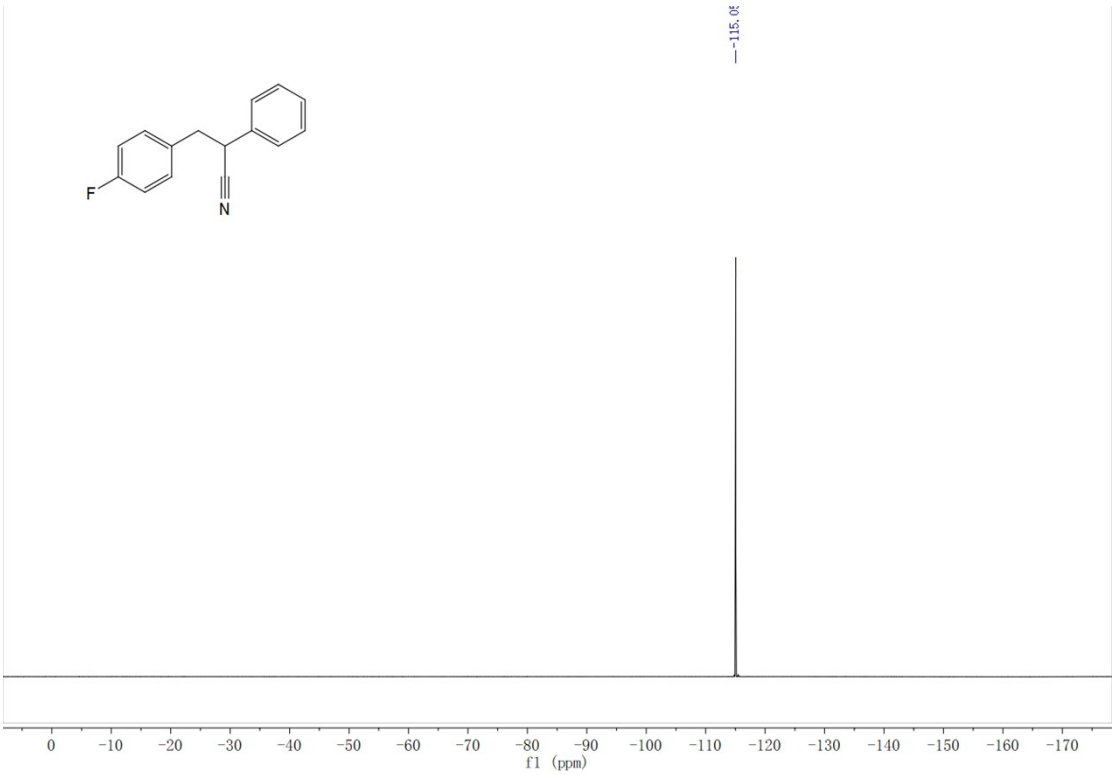
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **4a**



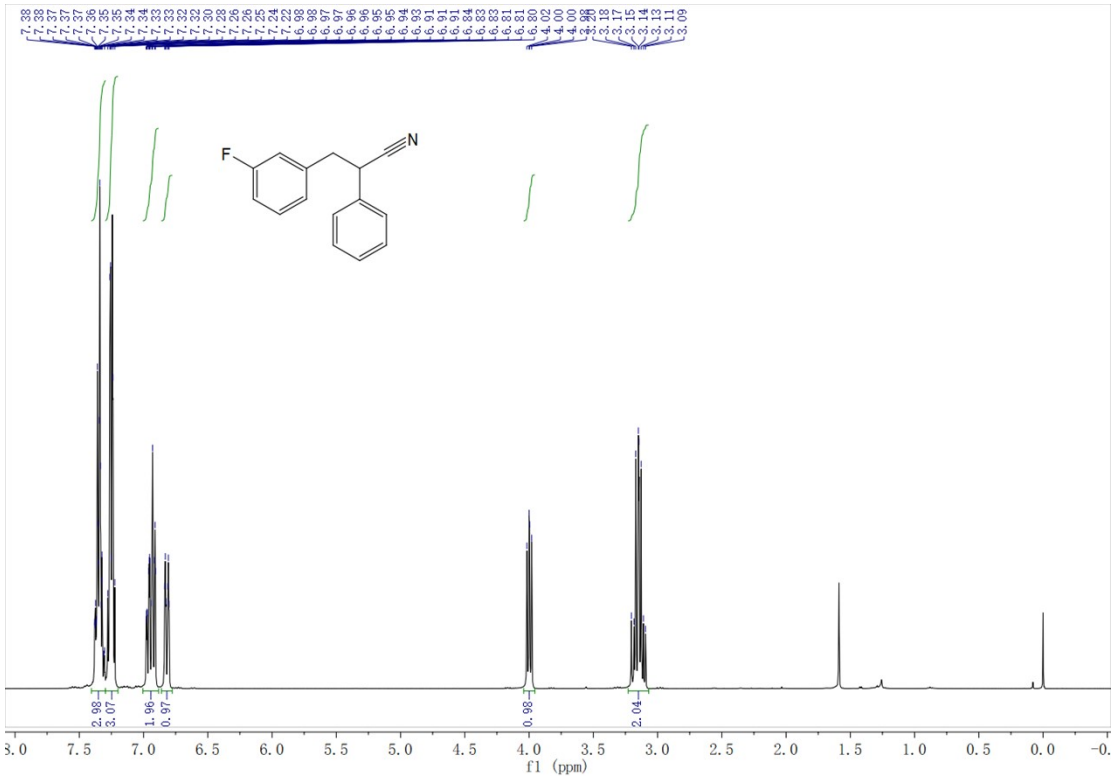
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4b**



^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **4b**

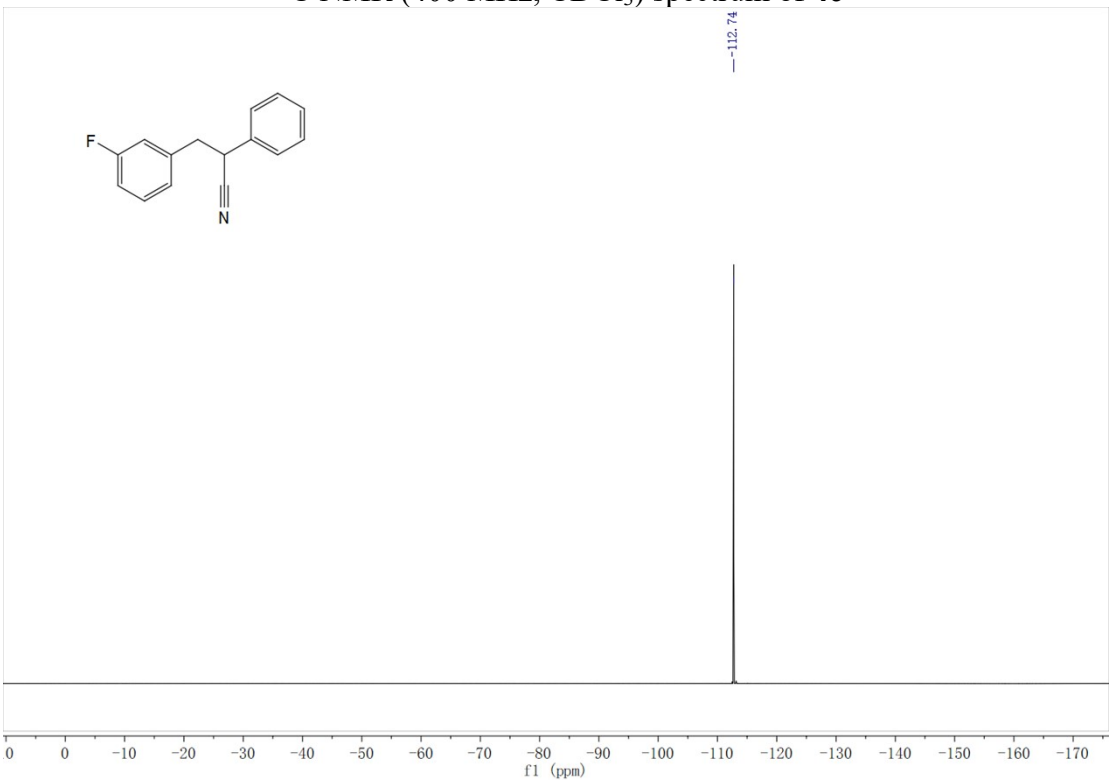


^{19}F NMR (400 MHz, $CDCl_3$) spectrum of **4b**

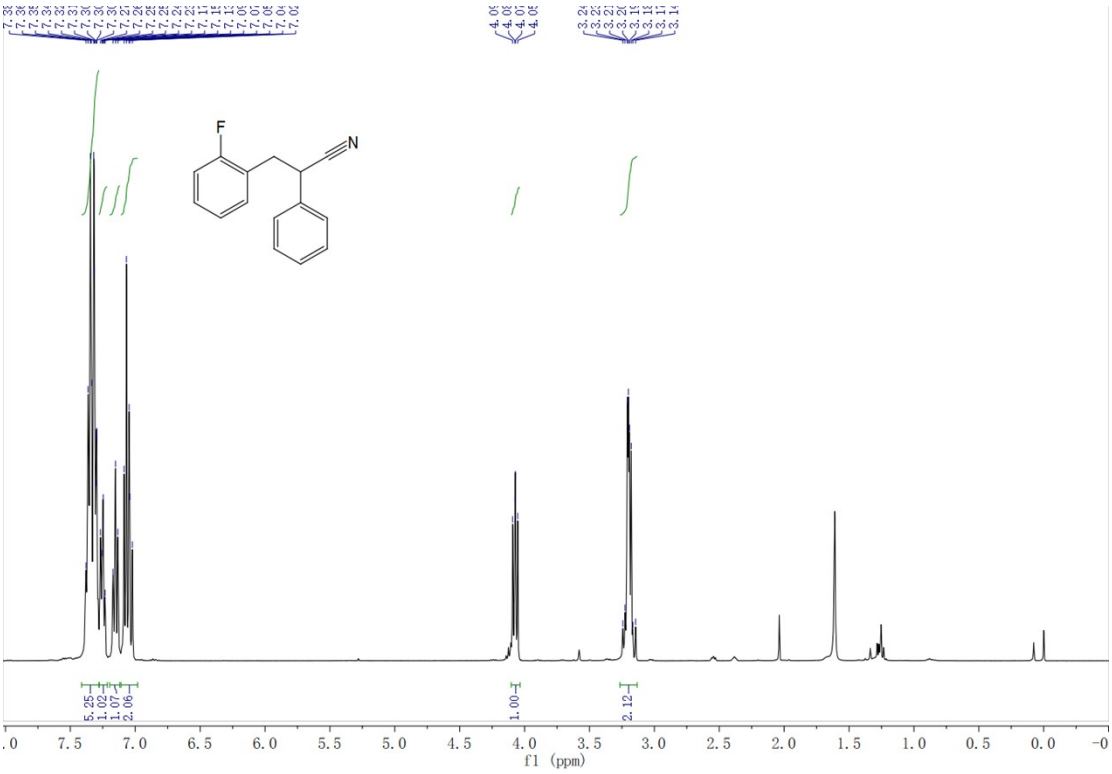


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4c**

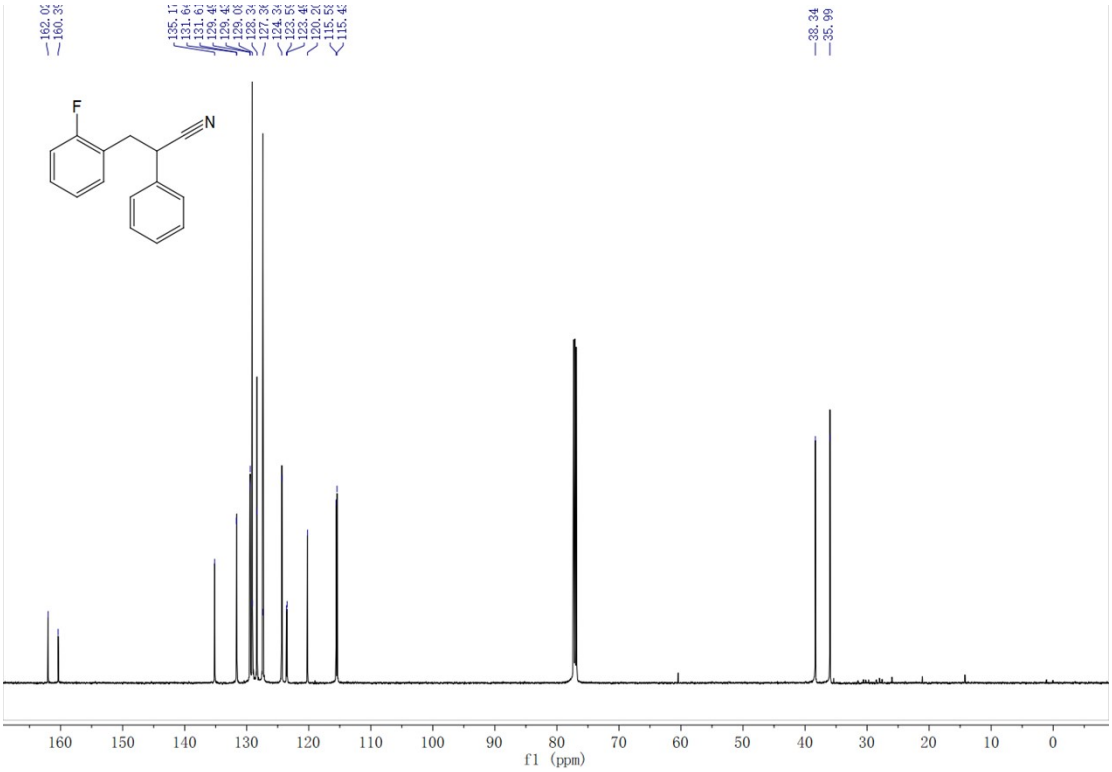
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **4c**



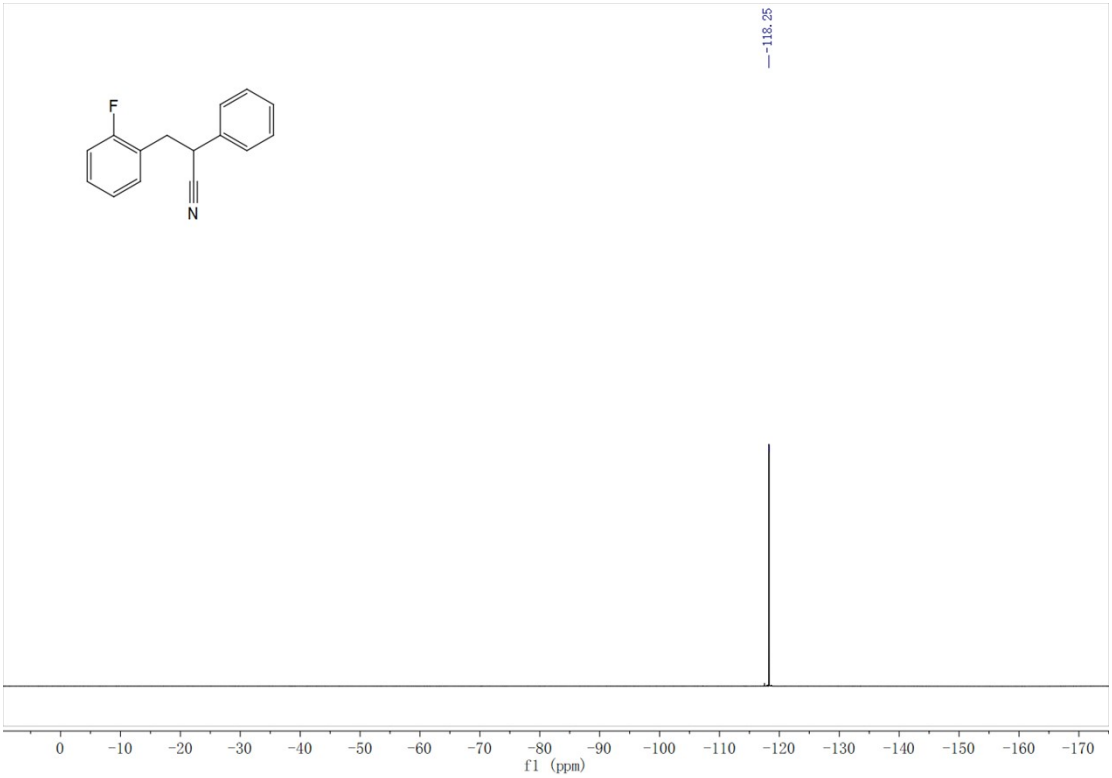
^{19}F NMR (400 MHz, $CDCl_3$) spectrum of **4c**



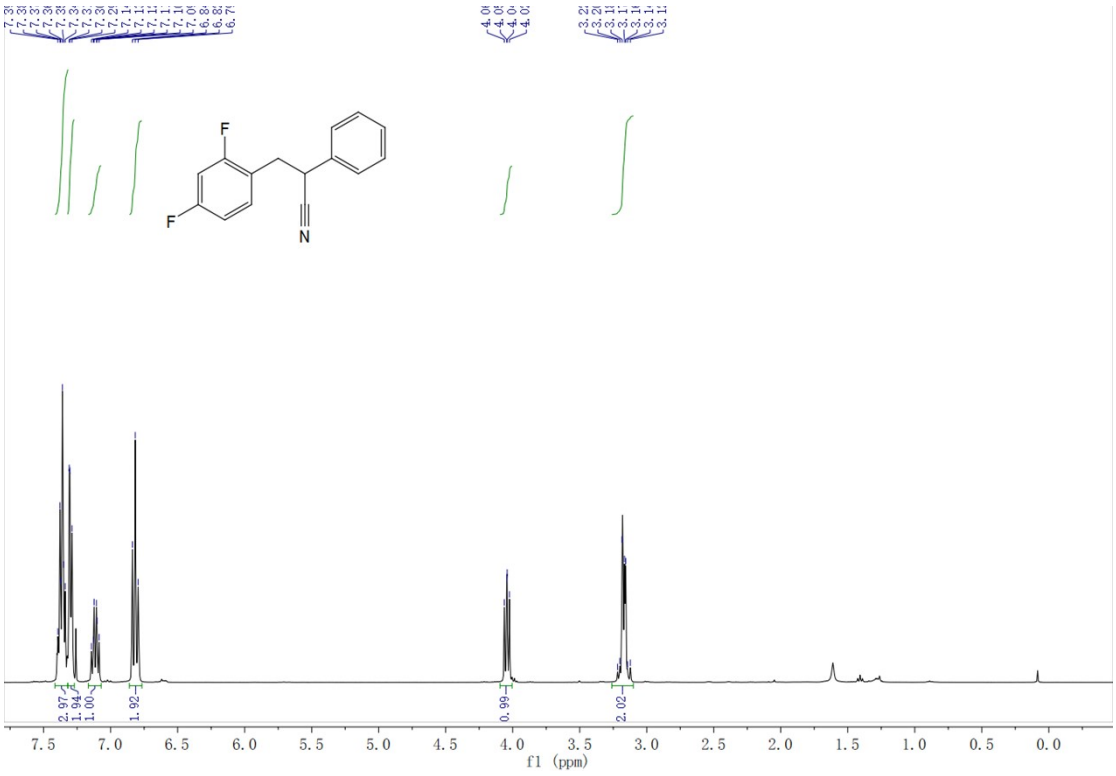
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4d**



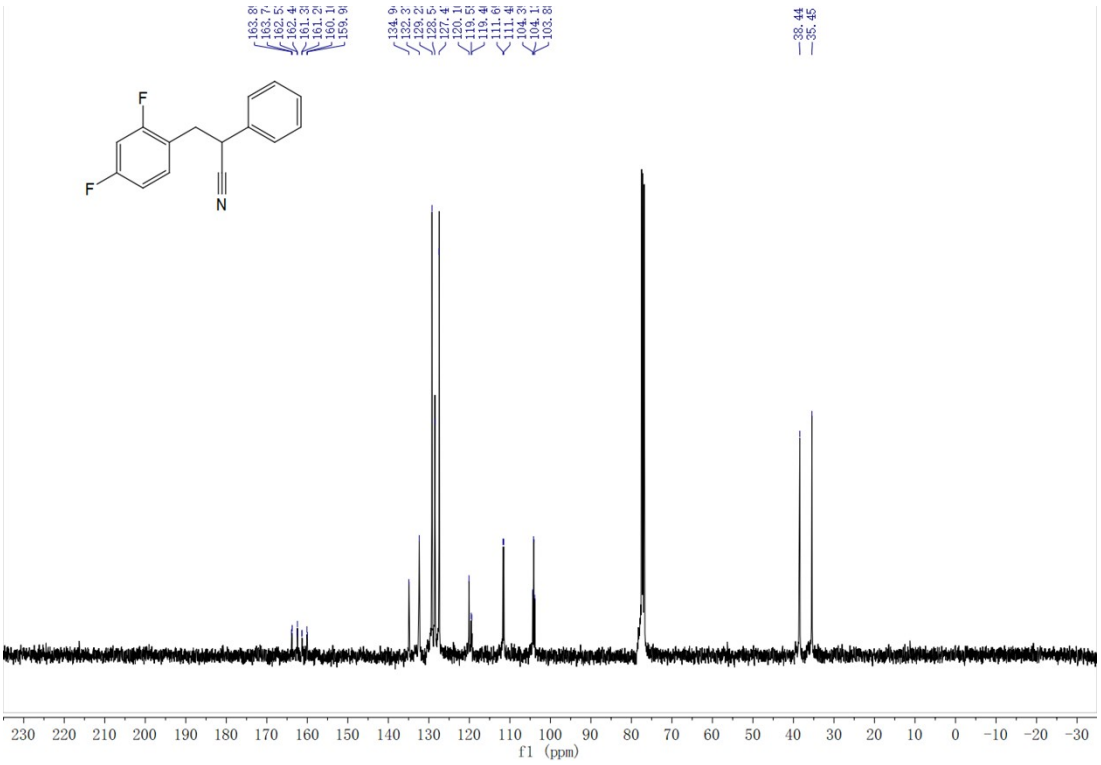
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **4d**



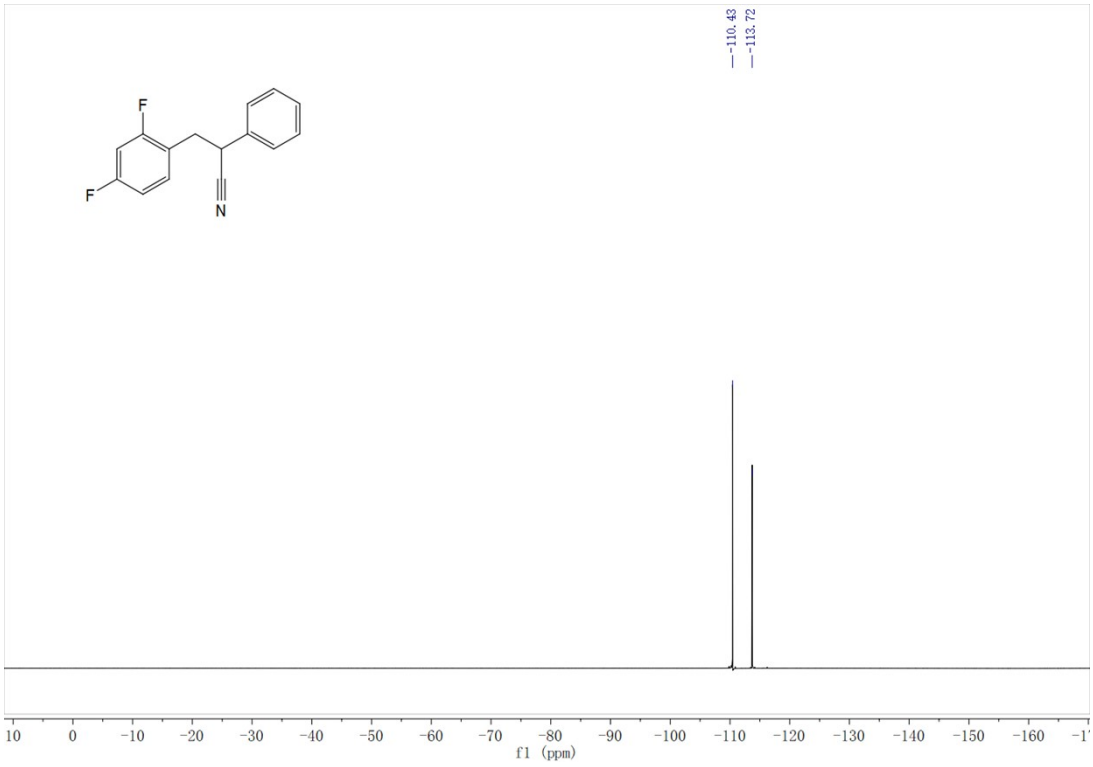
^{19}F NMR (400 MHz, $CDCl_3$) spectrum of **4d**



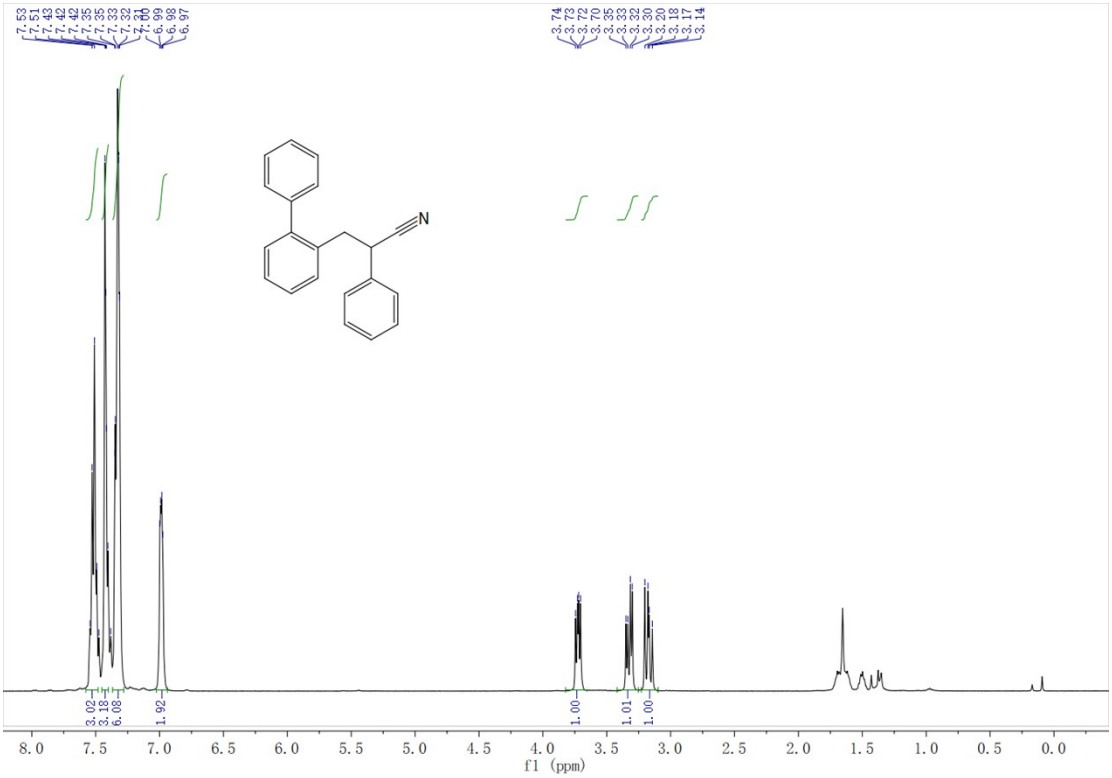
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4e**



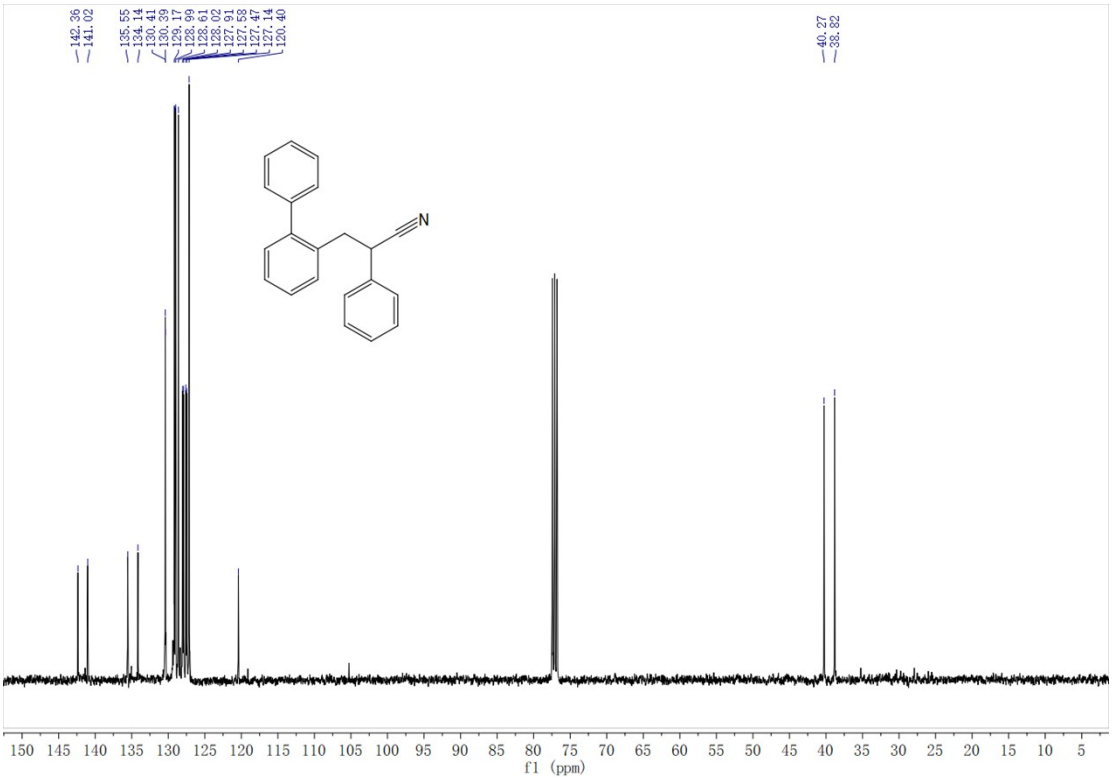
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **4e**



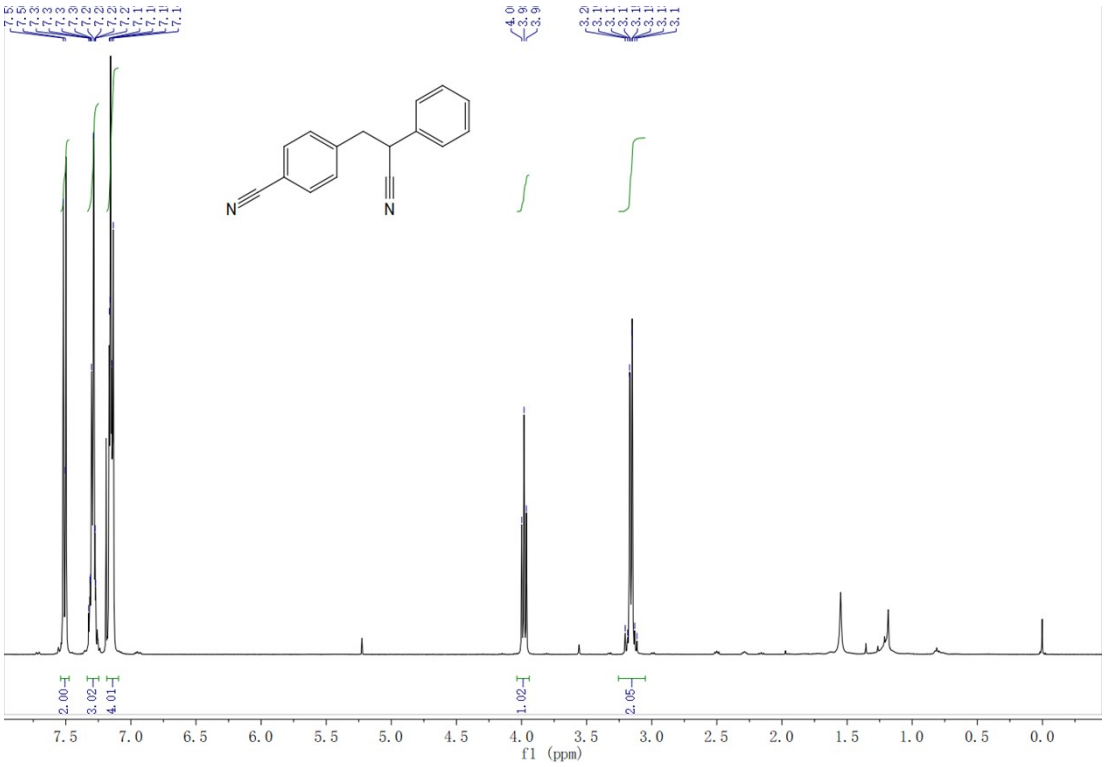
^{19}F NMR (400 MHz, $CDCl_3$) spectrum of **4e**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4f**

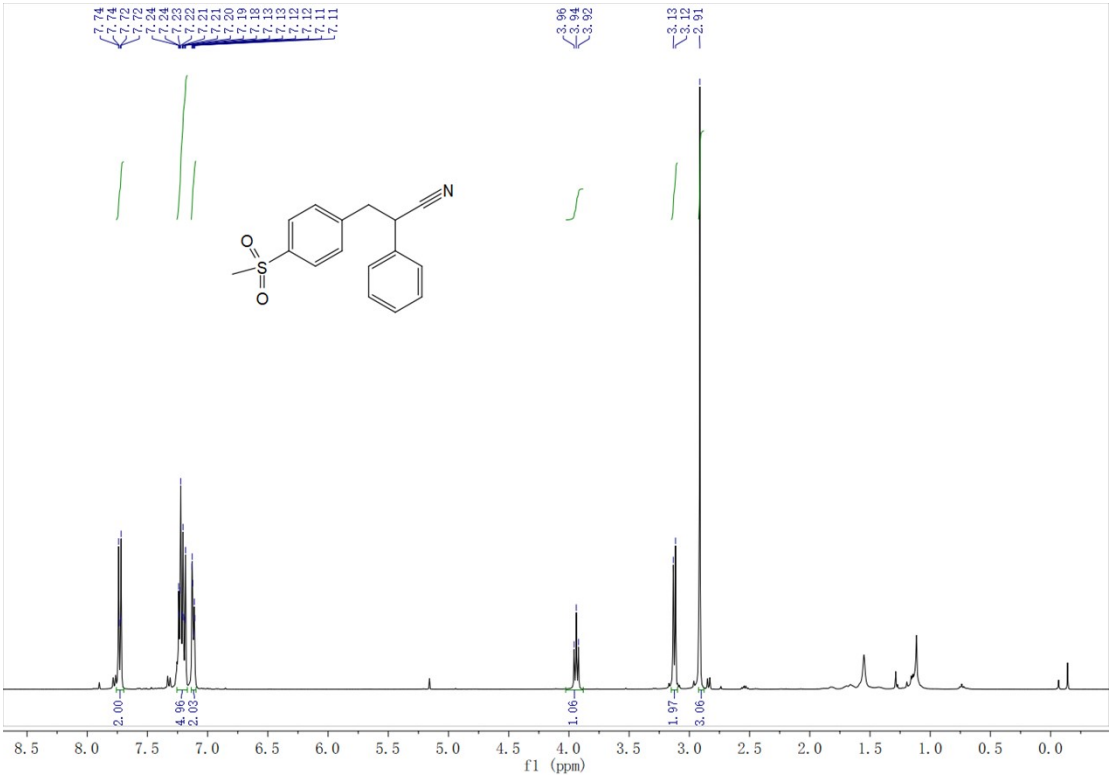


^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **4f**

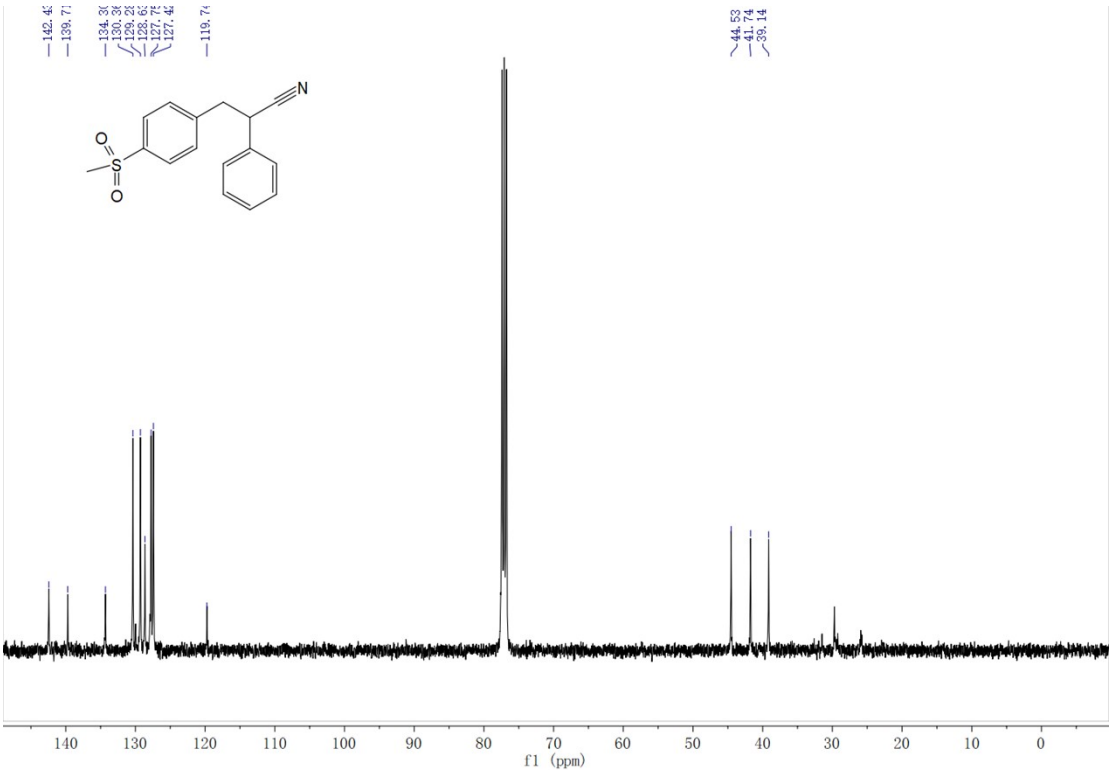


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4g**

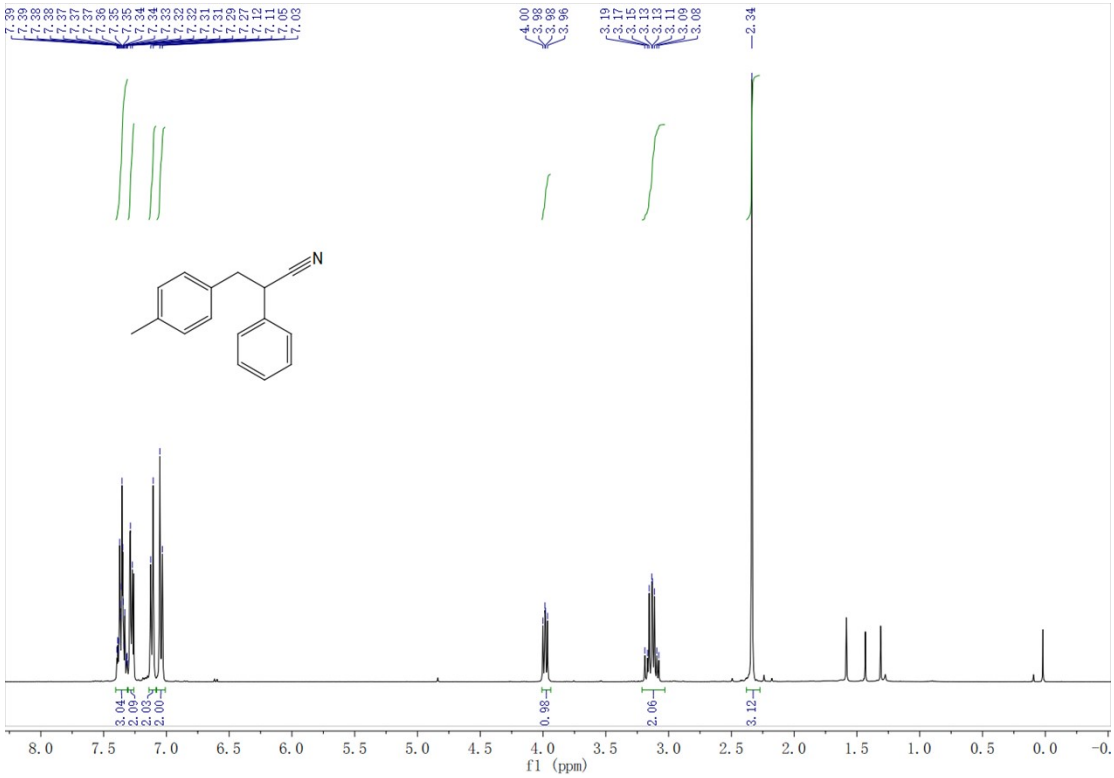
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **4g**



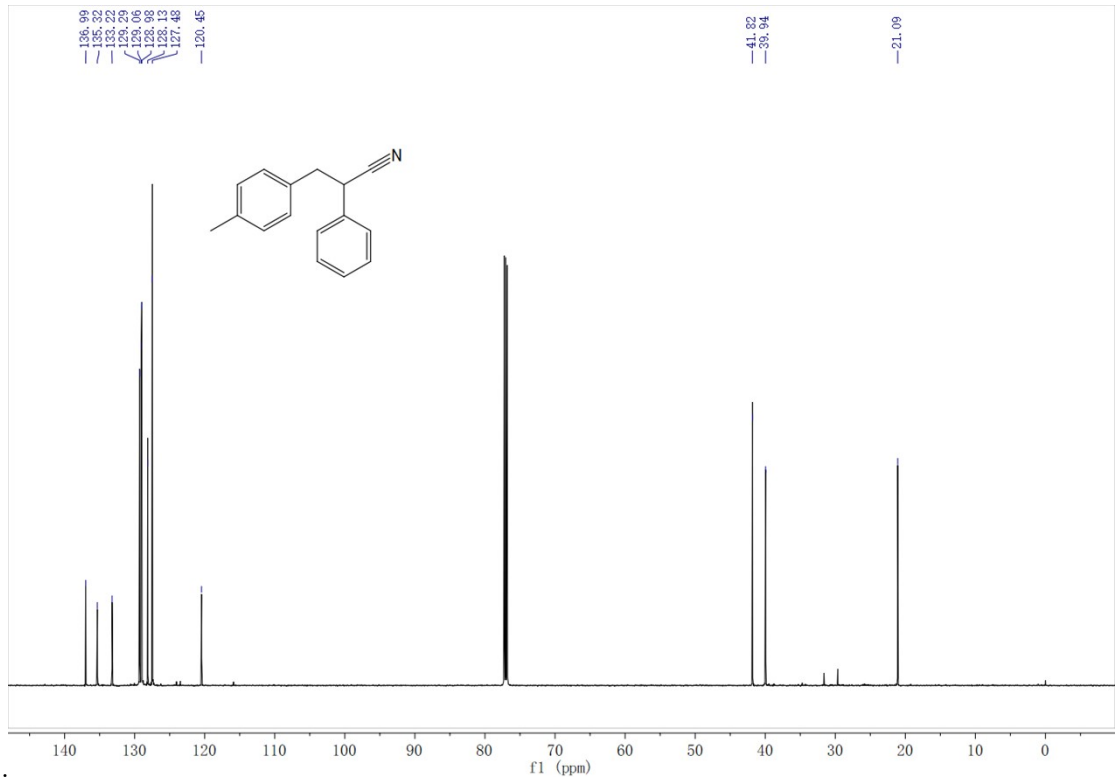
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4h**



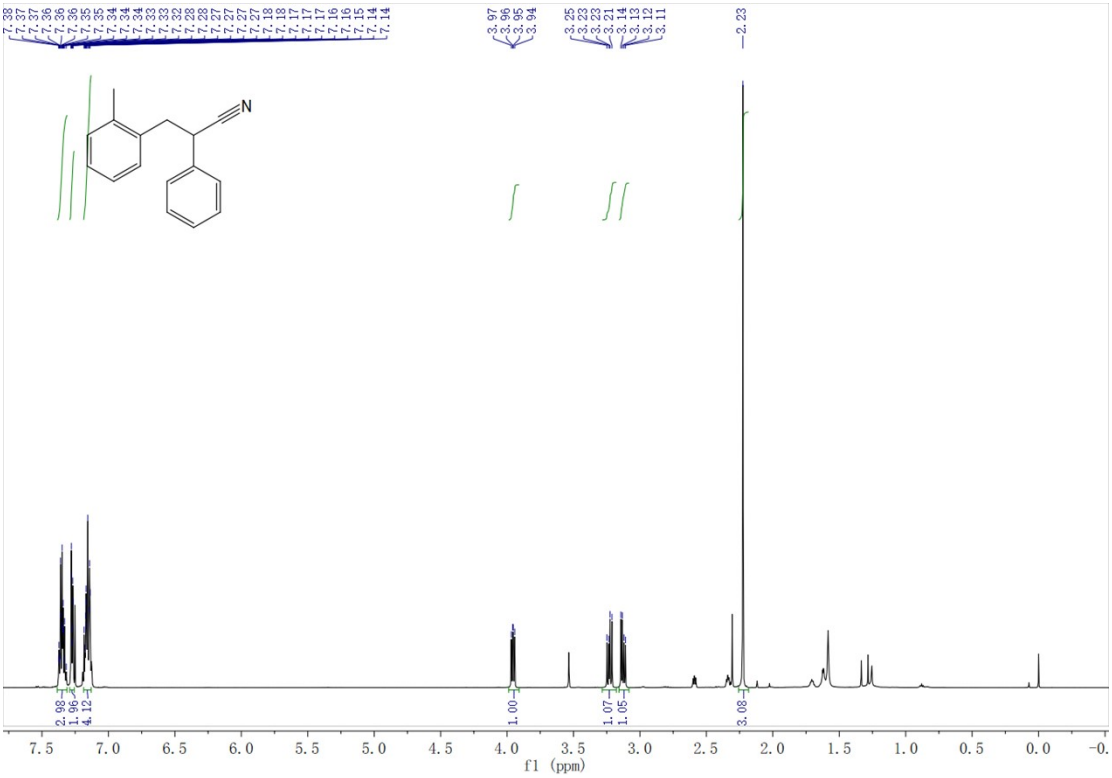
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **4h**



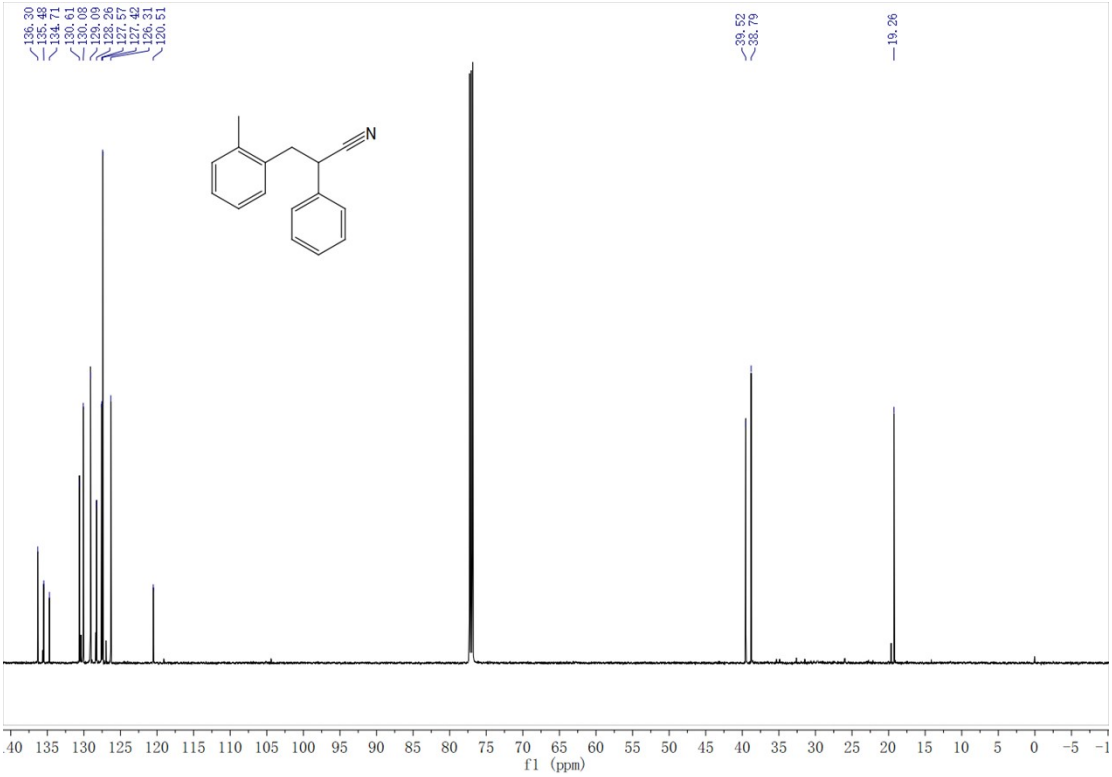
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4i**



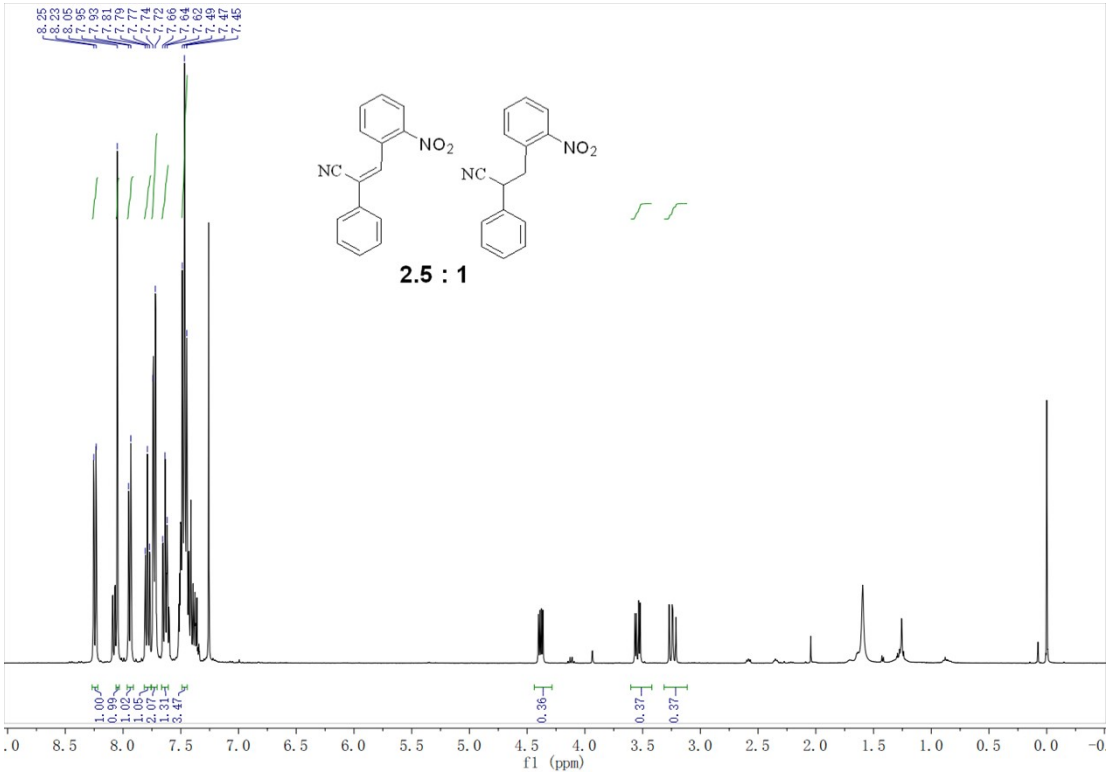
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **4i**



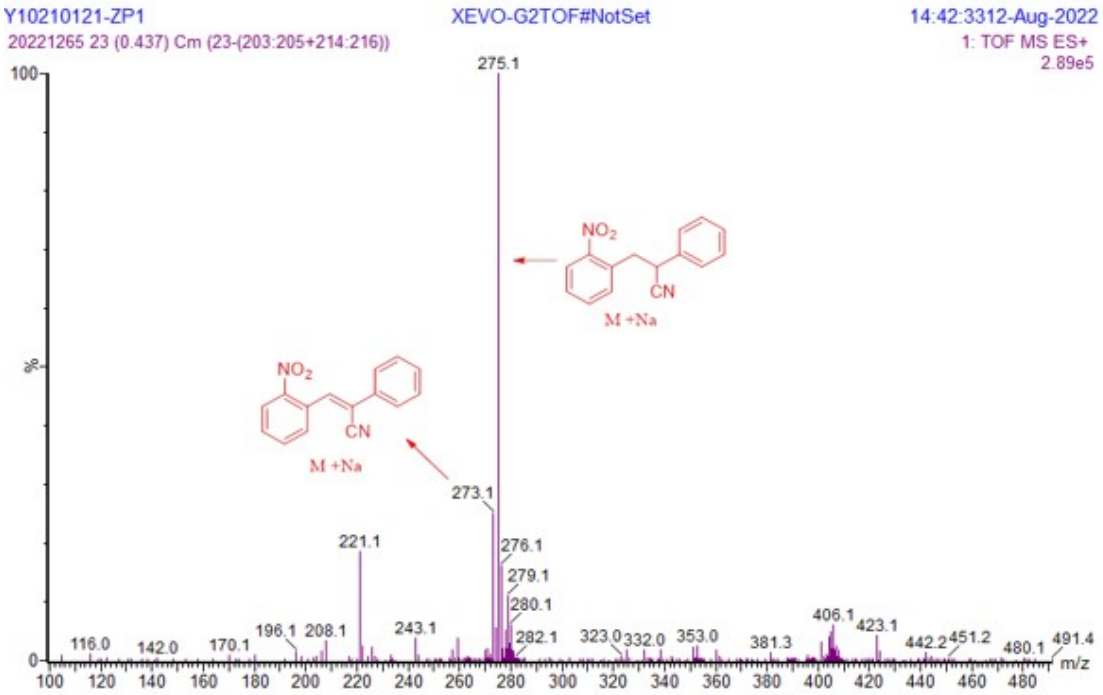
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4j**



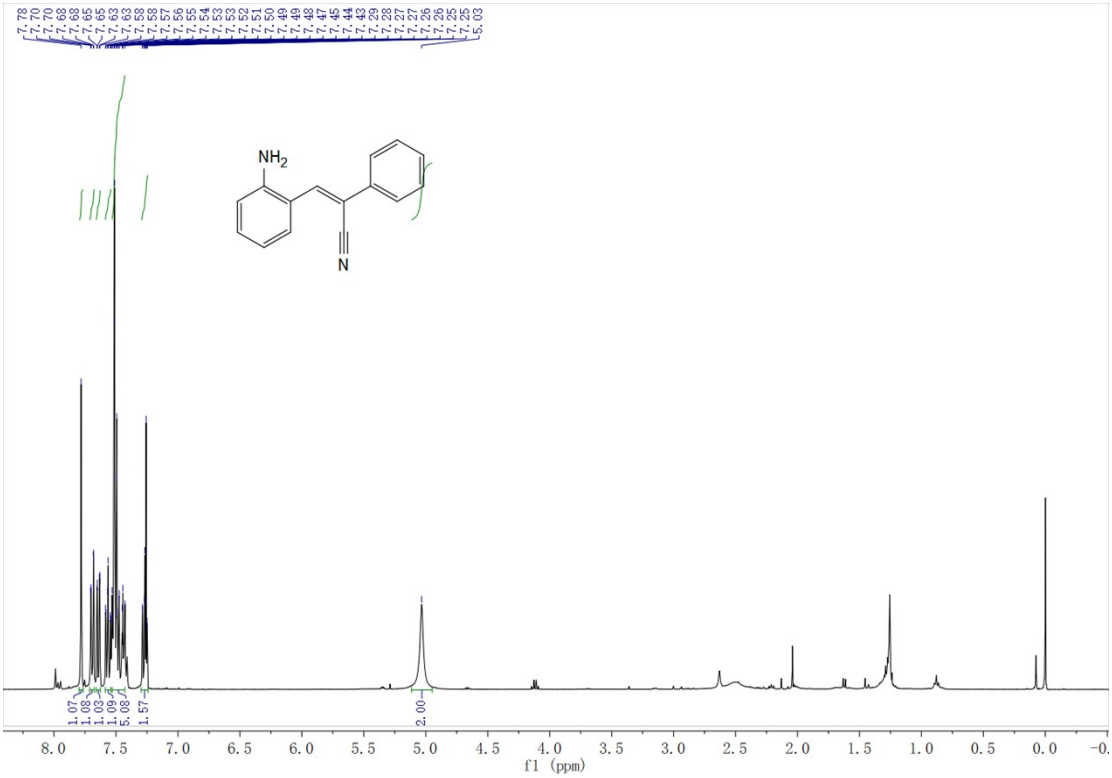
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **1e-104j**



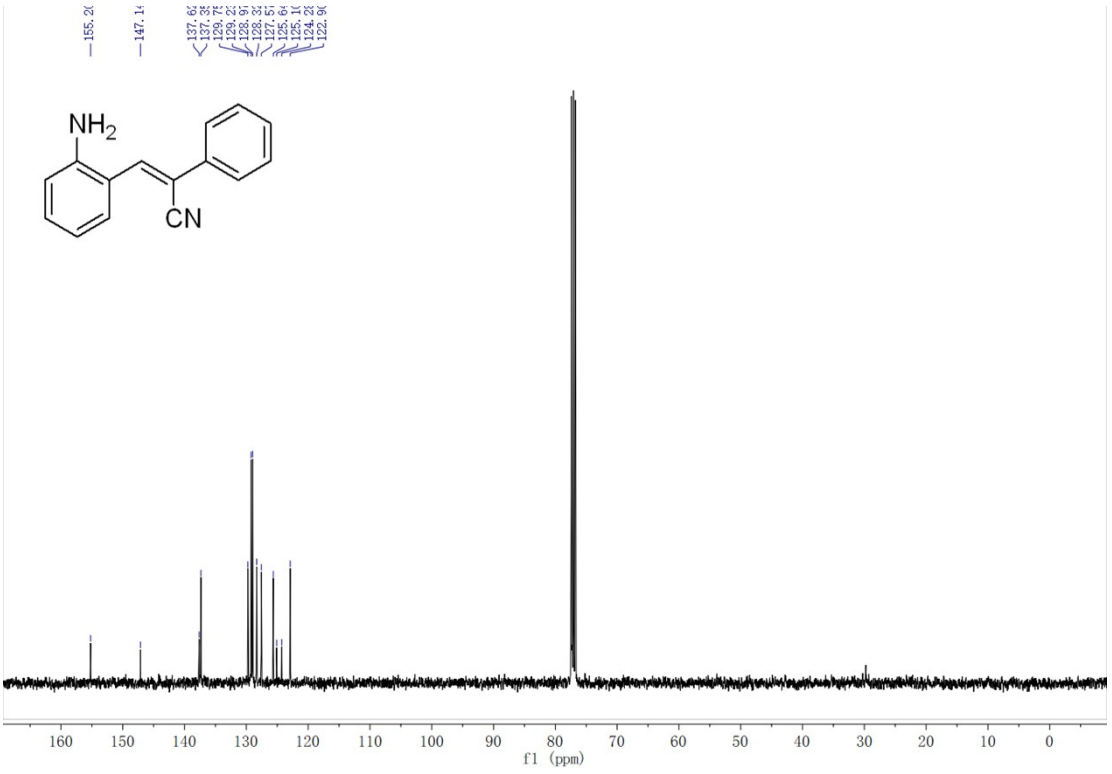
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4ka and 4kb**



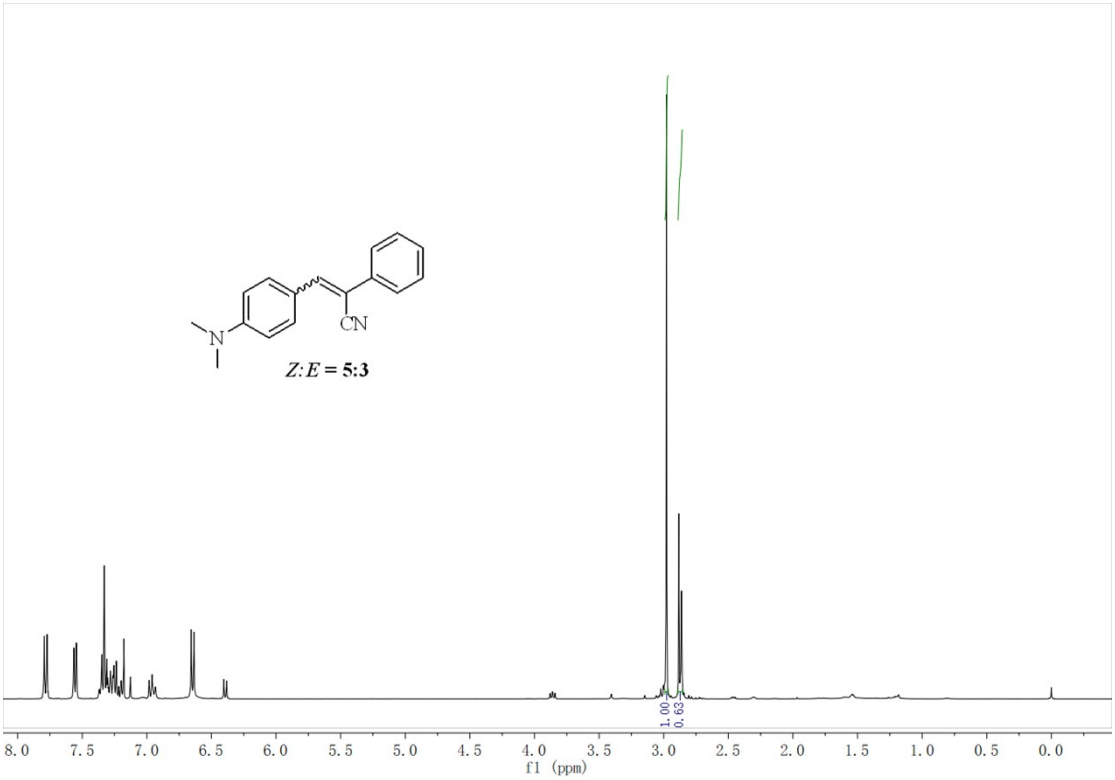
MASS spectrometry of **4ka and 4kb**



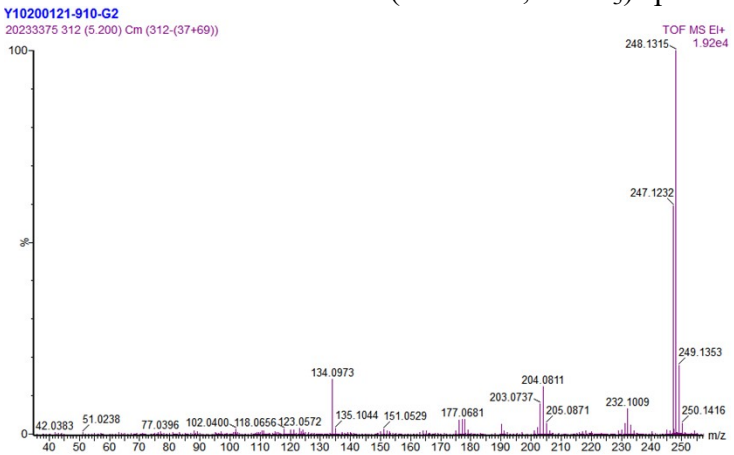
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4kc**



^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **4kc**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4l**



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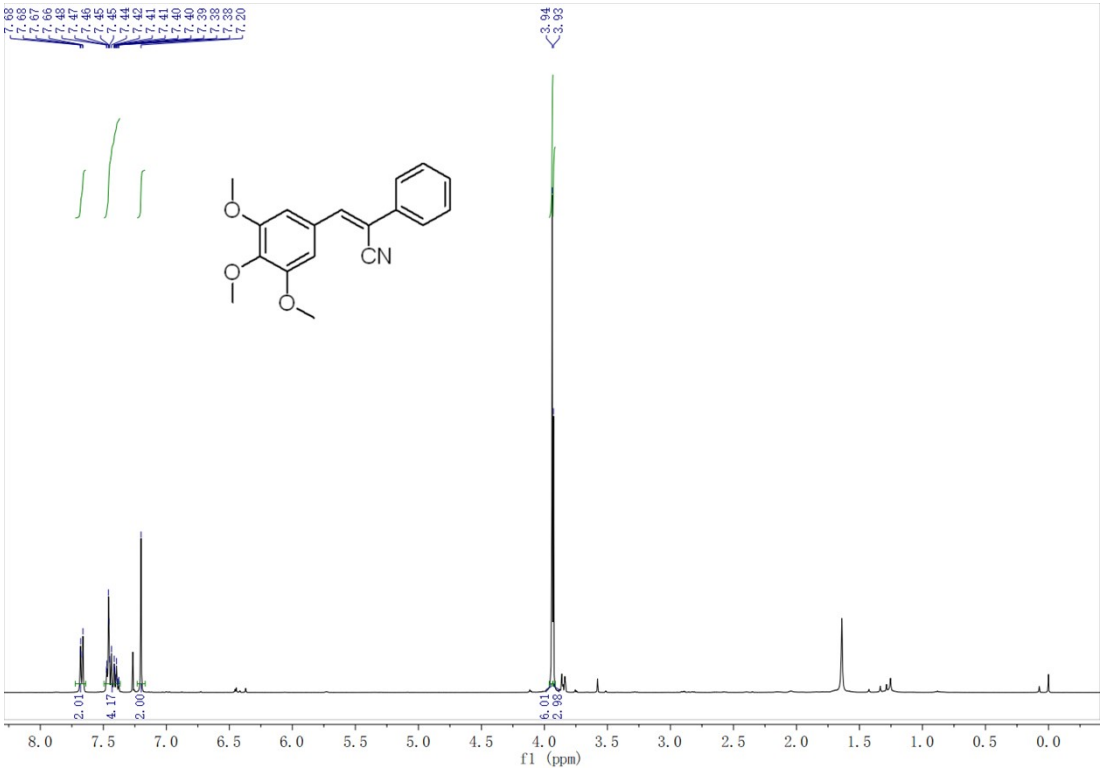
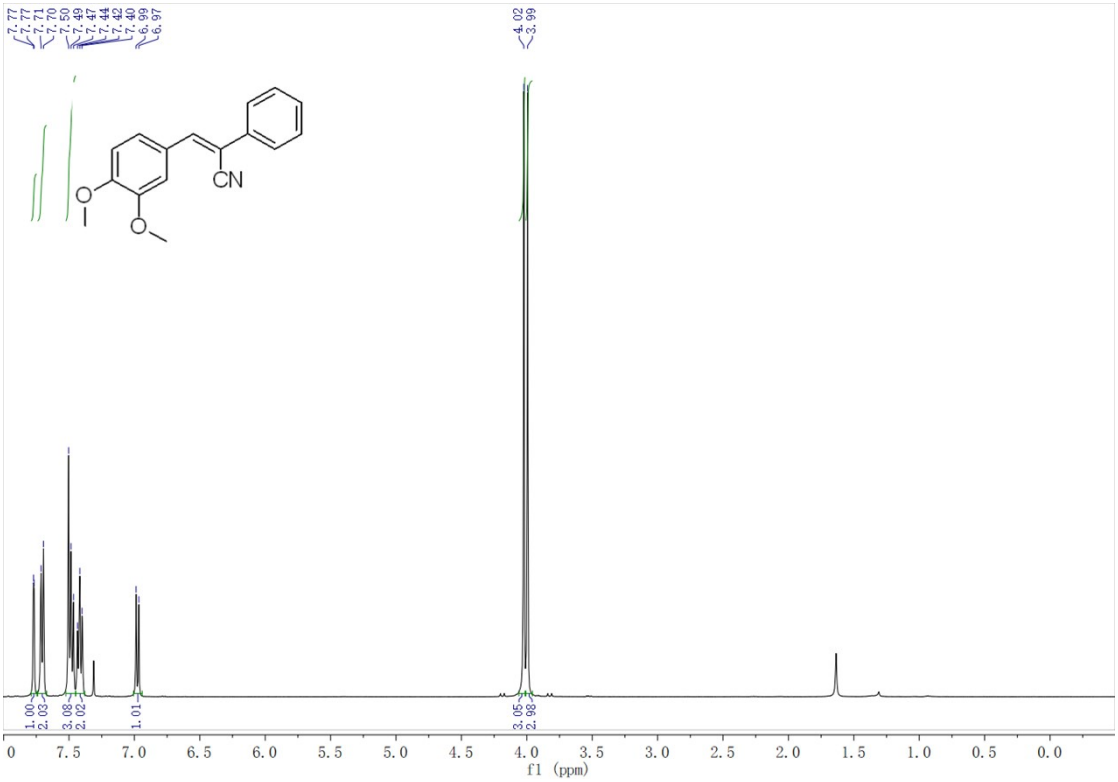


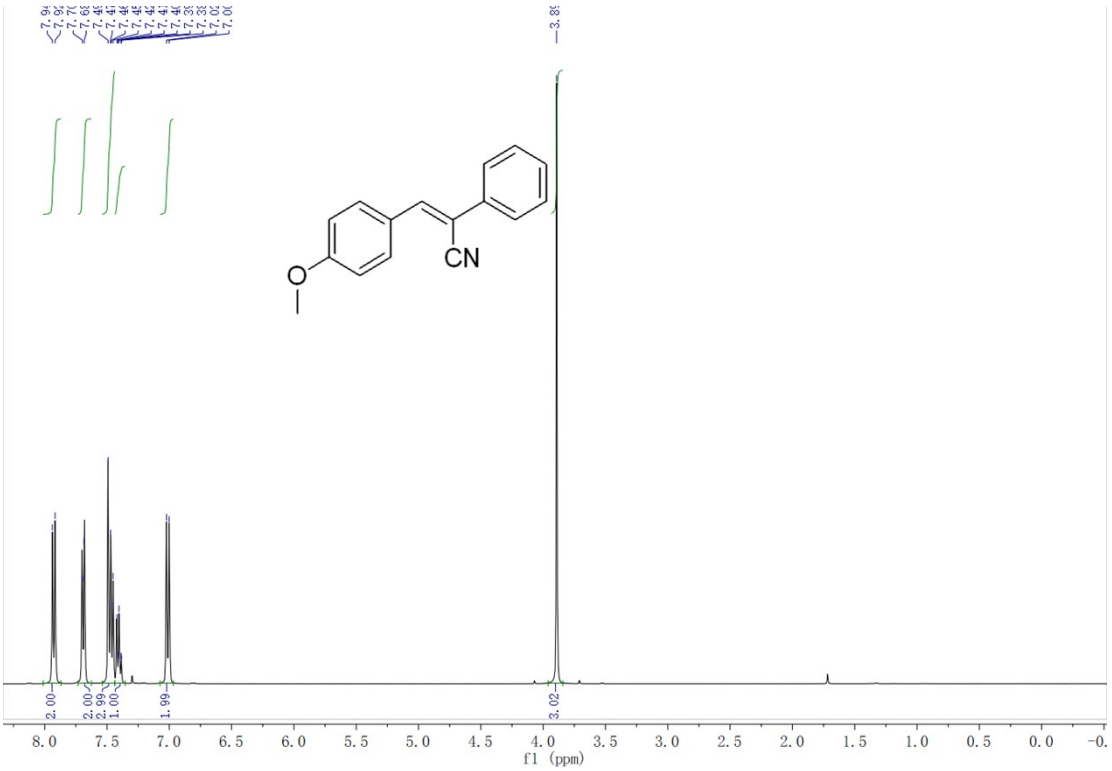
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4m**

^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **4m**

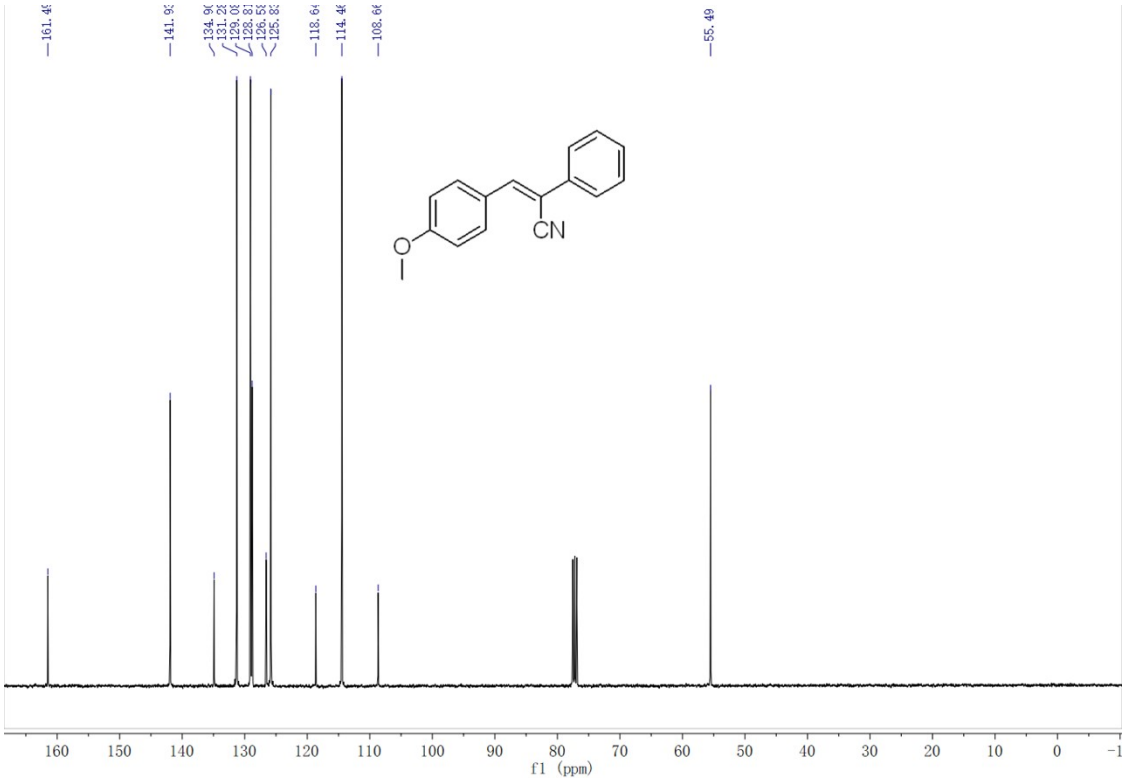


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4n**

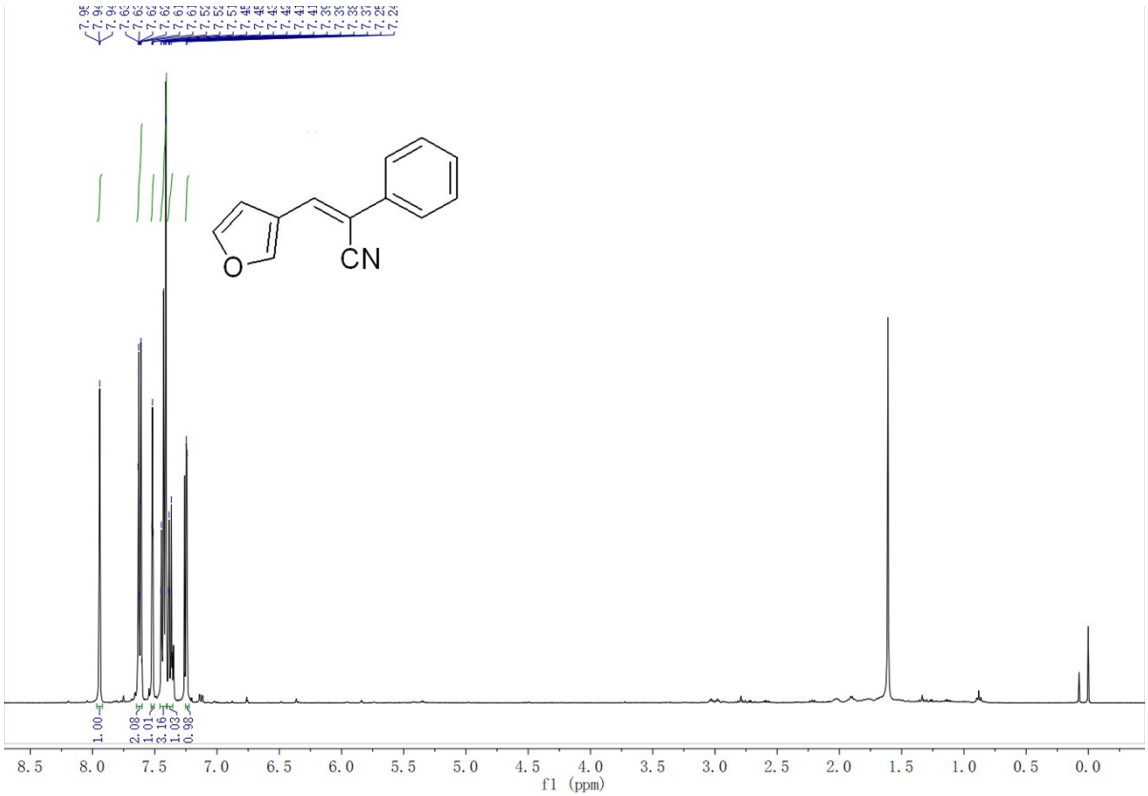
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **4n**



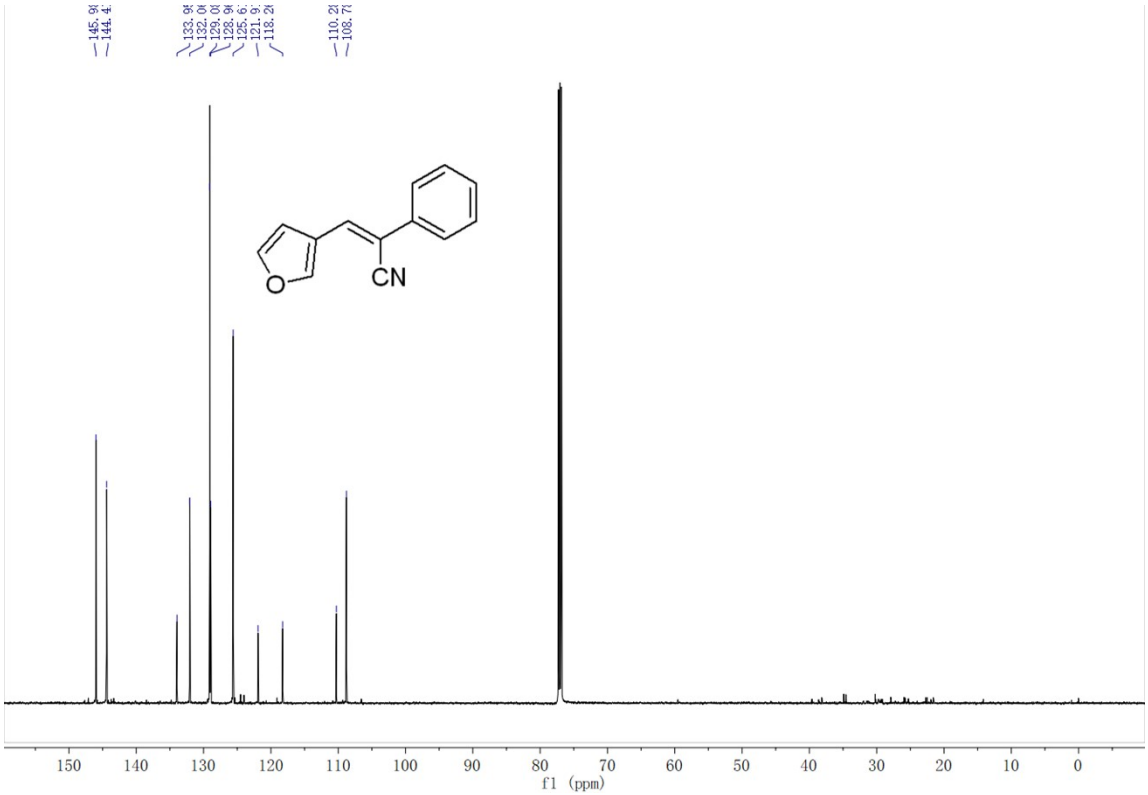
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4o**



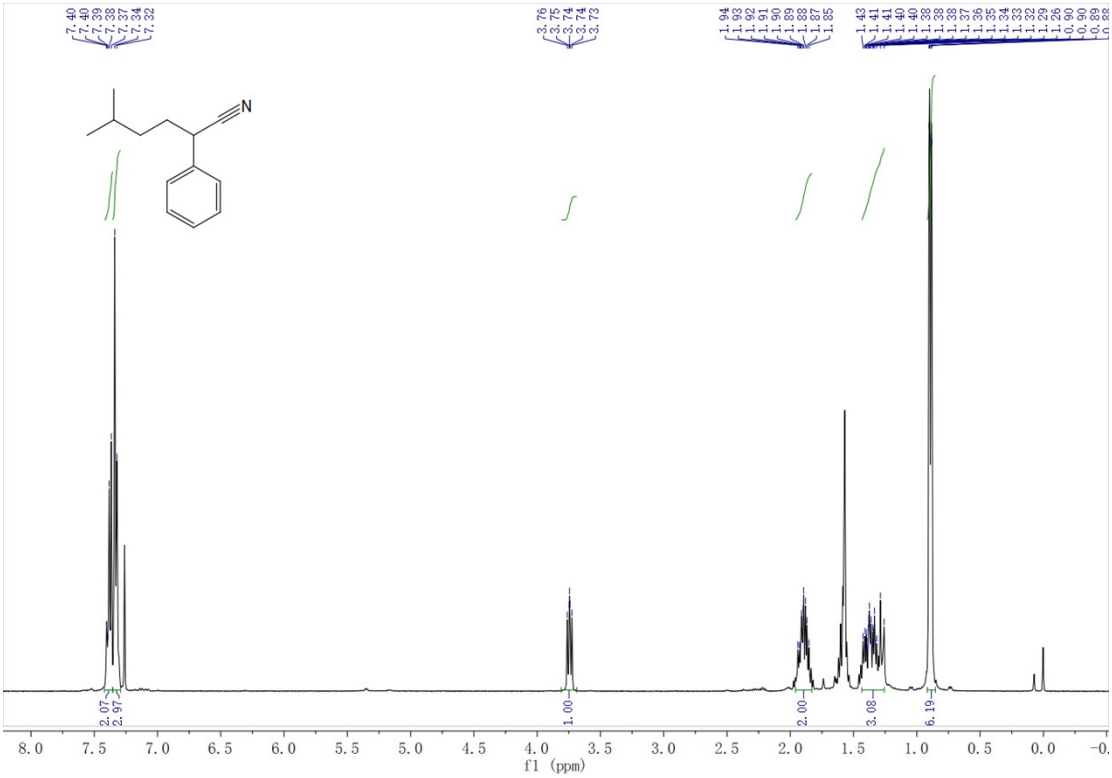
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **4o**



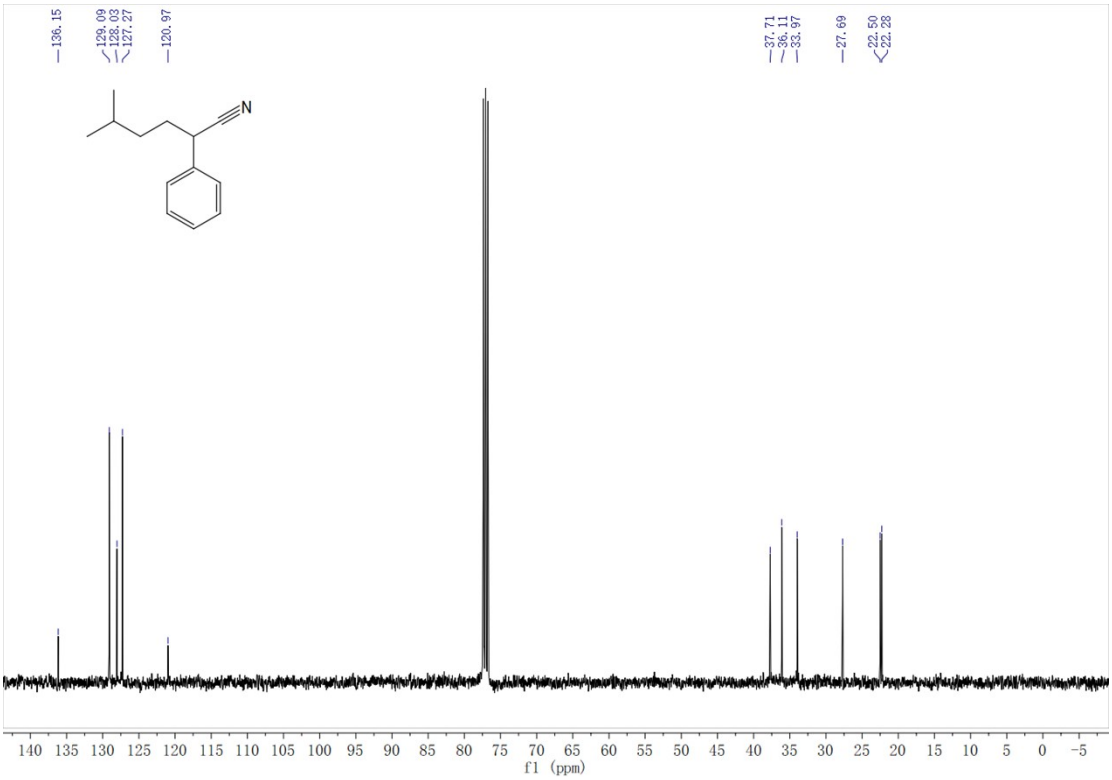
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4p**



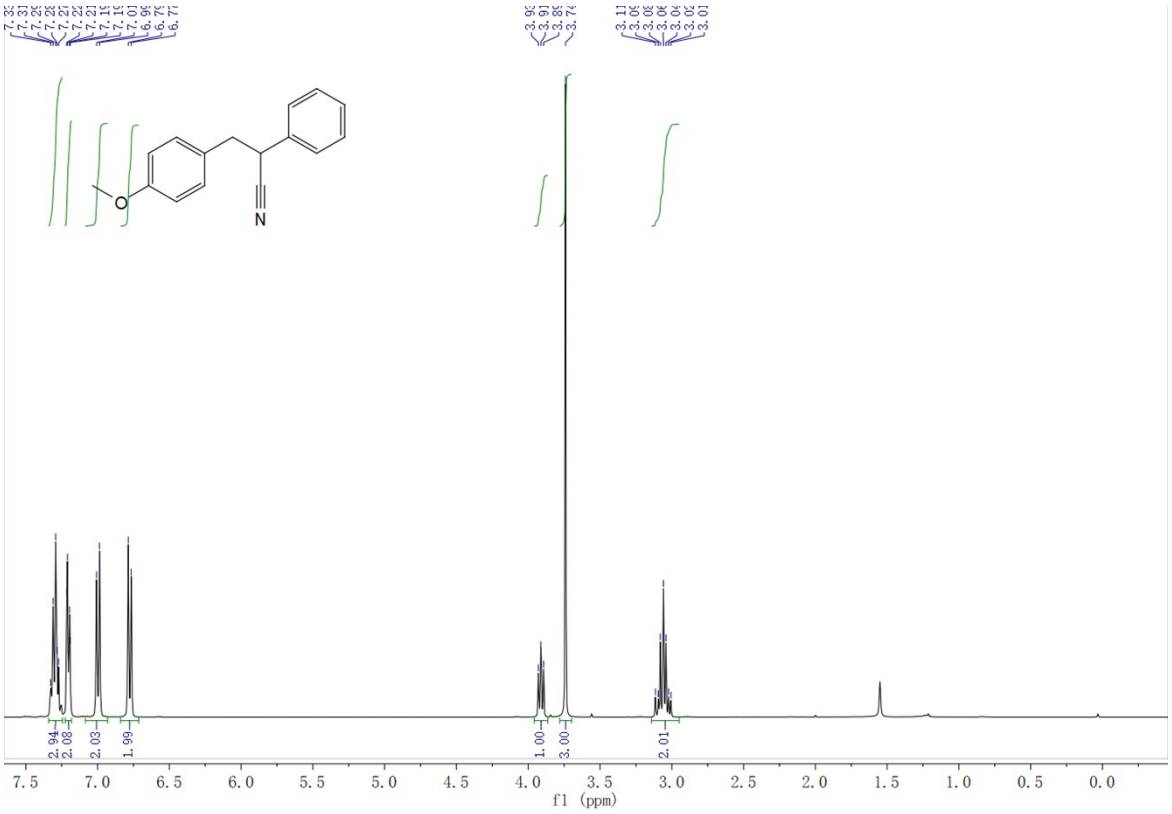
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **4p**



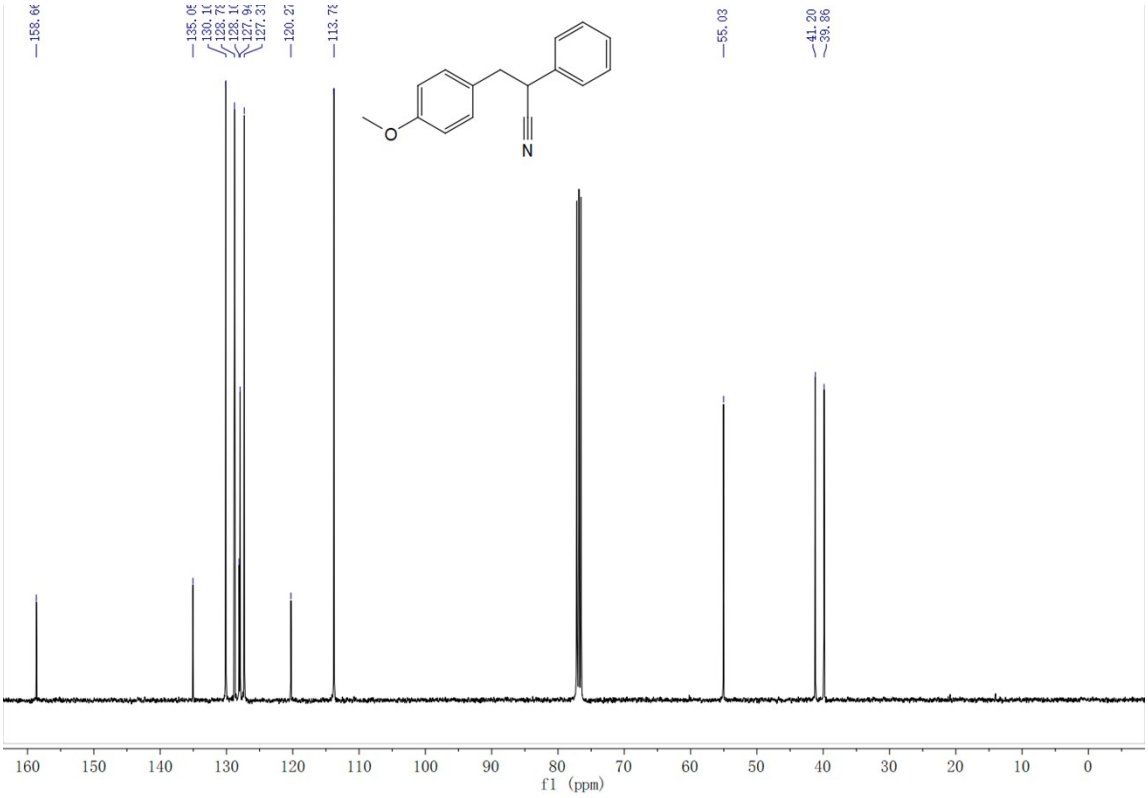
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4q**



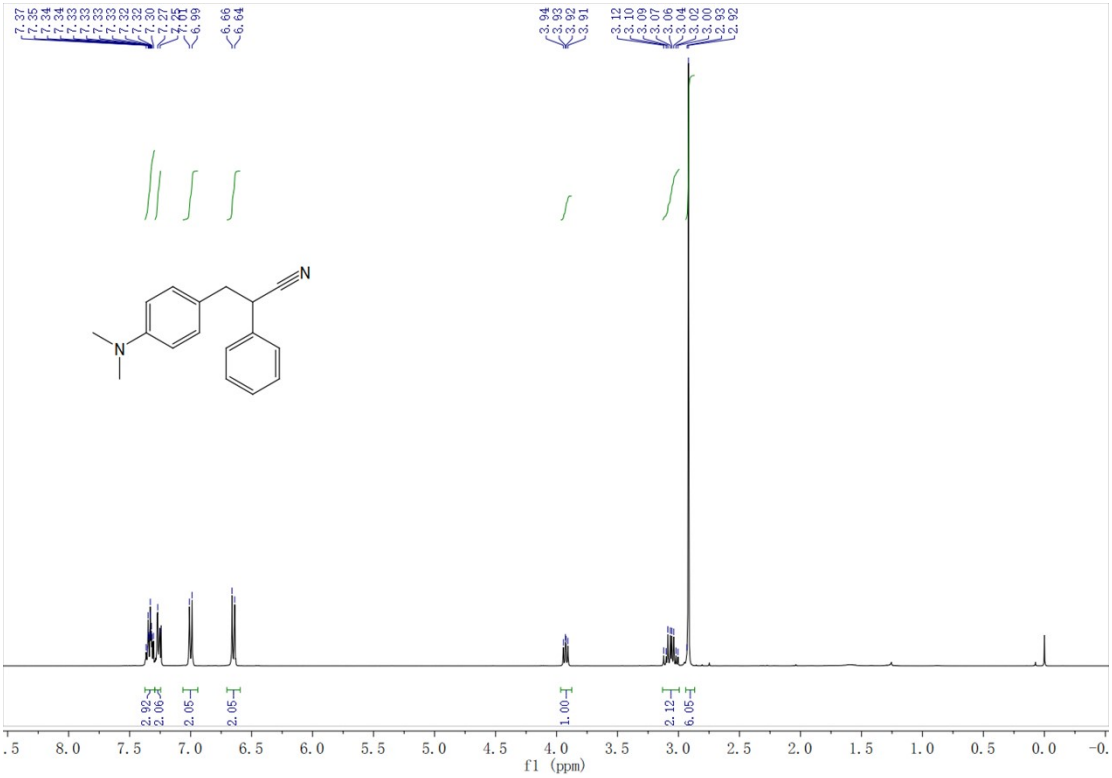
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **4q**



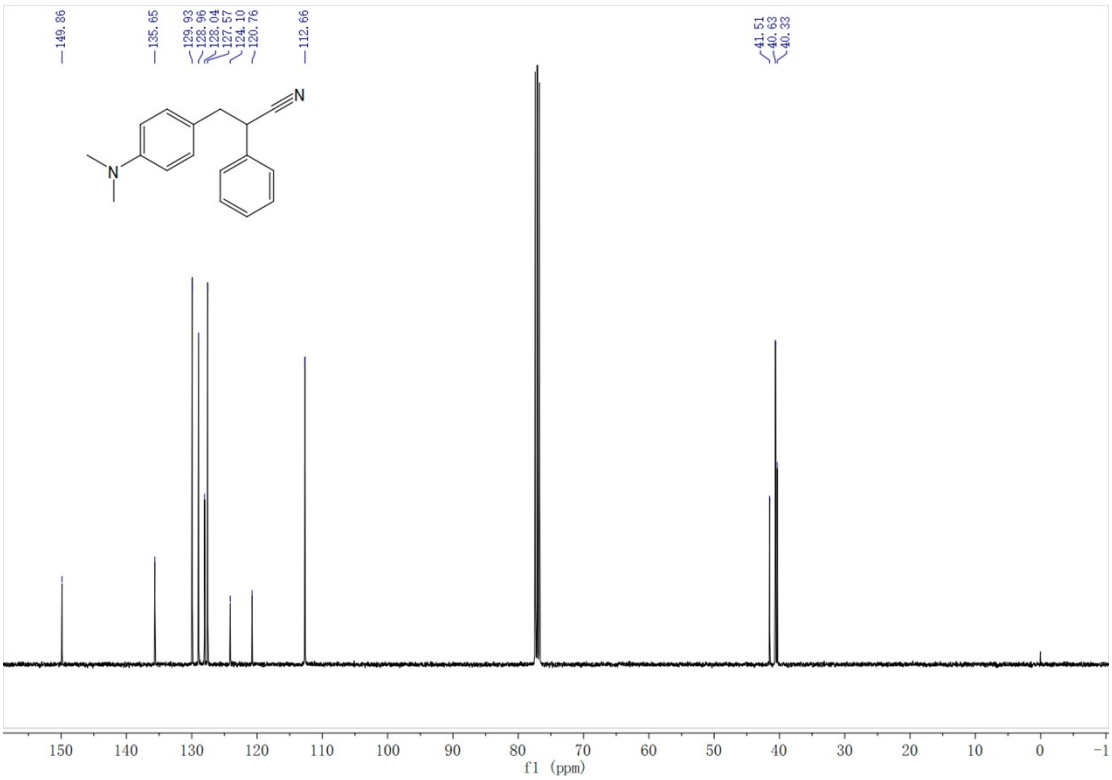
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4r**



^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **4r**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4s**



^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **4s**

6. References

[1] K. Paudel, S. Xu, K. Ding. *J. Org. Chem.* **2020**, 85, 23, 14980–14988

[2] Patent Number: US493553

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