Supporting Information

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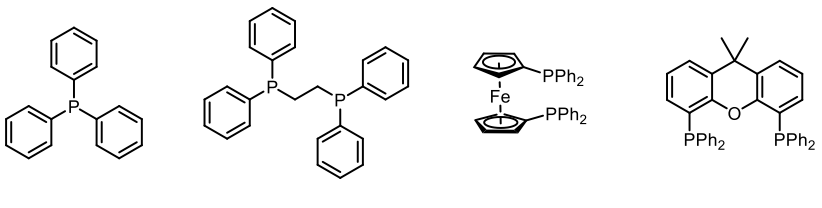
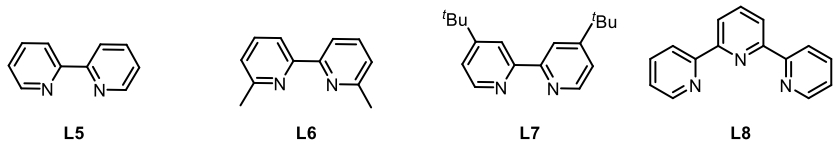
1 General remarks

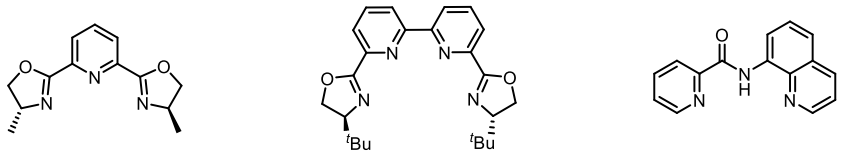
Unless otherwise noted, all reactions were carried out under carbon monoxide or nitrogen atmosphere. All reagents were from commercial sources and used as received without further purification. All solvents were dried by standard techniques and distilled prior to use. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (bp. 60~90 °C), dichloromethane and ethyl acetate as eluent. All NMR spectra were recorded at ambient temperature using Bruker Avance III 400 MHz NMR (^{1}H, 400 MHz; ^{13}C {1H}, 100 MHz, ^{19}F 376 MHz). ^{1}H NMR chemical shifts are reported relative to TMS and were referenced via residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm; DMSO-d_6: 2.50 ppm) whereas ^{13}C{1H} NMR spectra are reported relative to TMS via the carbon signals of the deuterated solvent ($CDCl_3$:77.0 ppm; DMSO-d_6: 39.5 ppm. Data for 1H are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br =broad), coupling constant (Hz), and integration. All ^{13}C NMR spectra were broad-band ^{1}H decoupled. All reactions were monitored by GC-FID or NMR analysis. HRMS data was obtained with Micromass HPLC-Q-TOF mass spectrometer (ESI) or Agilent 6540 Accurate-MS spectrometer(Q-TOF).

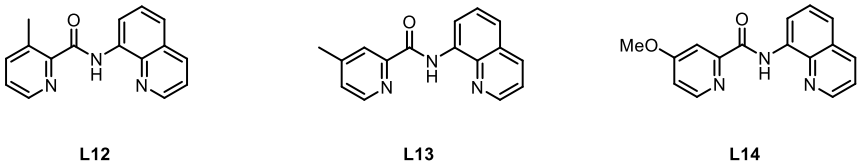
Because of the high toxicity of carbon monoxide, all the reactions should be performed in an autoclave. The laboratory should be well-equipped with a CO detector and alarm system.

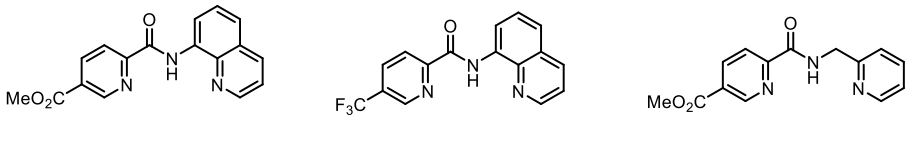
2 The ligands used in this reaction





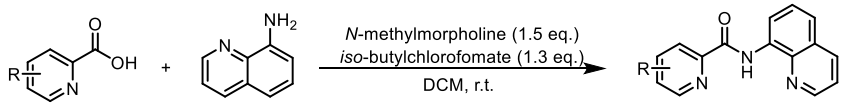






2.1 Experimental procedures and characterization data for *N,N,N*-ligands

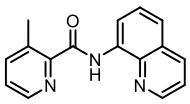
N,N,N-ligands **L11-L17** were synthesized according to the modified published procedures.[1]



To a round-bottom flask equipped with a Teflon-coated magnetic stir bar were added 2-picolinic acid (1.3 equiv.), *N*-methylmorpholine (1.5 equiv.) and DCM (0.2 M) under N_2. The reaction mixture was cooled to 0 ºC, followed by addition of *iso*-butylchloroformate (1.3 equiv.). Amine (1.0 equiv) was subsequently added into the reaction by dissolving with DCM after the reaction mixture was stirred at 0 ºC for 30 min. The reaction mixture was allowed to warm to room temperature and stirring for 24 h. Upon completion, concentrated under reduced pressure. The crude

product was purified through column chromatography on neutral alumina.

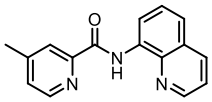
3-Methyl-N-(quinolin-8-yl)picolinamide (L12)



^{1}H NMR (400 MHz, $CDCl_3$) δ 12.32 (s, 1H), 9.08 – 8.87 (m, 2H), 8.59 (d, *J* = 4.6 Hz, 1H), 8.12 (dt, *J* = 8.3, 1.3 Hz, 1H), 7.72 – 7.48 (m, 3H), 7.42 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.32 (dd, *J* = 7.8, 4.6 Hz, 1H), 2.84 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 150.3, 148.9, 148.7, 148.4, 139.3, 136.2, 134.5, 128.1, 127.3, 127.1, 123.3, 122.0, 121.6, 116.8, 21.2.

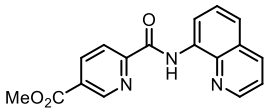
4-Methyl-*N*-(quinolin-8-yl)picolinamide (L13)



^{1}H NMR (400 MHz, $CDCl_3$) δ 12.26 (s, 1H), 9.01 (dd, *J* = 7.8, 1.6 Hz, 1H), 8.93 (q, *J* = 3.4, 1.6 Hz, 1H), 8.59 (t, *J* = 4.0 Hz, 1H), 8.27 – 8.08 (m, 2H), 7.67 – 7.54 (m, 1H), 7.54 – 7.48 (m, 1H), 7.47 – 7.39 (m, 1H), 7.29 – 7.22 (m, 1H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 150.3, 148.9, 148.7, 148.4, 139.3, 136.2, 134.5, 128.1, 127.3, 127.1, 123.3, 122.0, 121.6, 116.8, 21.2.

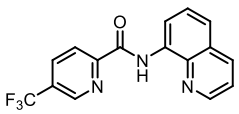
Methyl 6-(quinolin-8-ylcarbamoyl)nicotinate (L15)



^{1}H NMR (400 MHz, $CDCl_3$) δ 12.29 (s, 1H), 9.38 (s, 1H), 9.10 – 8.95 (m, 1H), 8.52 (d, *J* = 8.1 Hz, 1H), 8.43 (d, *J* = 8.1 Hz, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.50 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.01 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 153.5, 149.8, 148.8, 139.3, 138.7, 136.3, 133.9, 128.2, 127.3, 122.4, 122.1, 121.7, 117.0, 52.7.

***N*-(Quinolin-8-yl)-5-(trifluoromethyl)picolinamide (L16)**



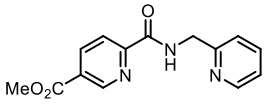
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.26 (s, 1H), 9.07 (dt, *J* = 2.0, 0.8 Hz, 1H), 9.04 – 8.93 (m, 2H), 8.49 (d, *J* = 8.4 Hz, 1H), 8.19 (td, *J* = 8.0, 2.0 Hz, 2H), 7.71 – 7.57 (m, 2H), 7.51 (dd, *J* = 8.4, 4.0

Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2, 153.6, 149.0, 145.8 (q, *J* = 4.2 Hz), 139.4, 136.4, 135.0 (q, *J* = 3.3 Hz), 134.2, 129.0 (q, *J* = 33.2 Hz), 128.2, 127.4, 123.4 (q, *J* = 271.1 Hz), 122.6, 122.3, 121.8, 117.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5.

Methyl 6-((pyridin-2-ylmethyl)carbamoyl)nicotinate (L17)

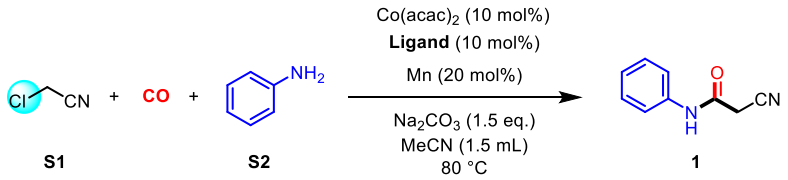


^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.19 (d, *J* = 2.1 Hz, 1H), 9.00 (t, *J* = 5.9 Hz, 1H), 8.67 – 8.59 (m, 1H), 8.45 (dd, *J* = 8.1, 2.1 Hz, 1H), 8.31 (d, *J* = 8.1 Hz, 1H), 7.68 (td, *J* = 7.7, 1.8 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.17 (m, 1H), 4.82 (d, *J* = 5.6 Hz, 2H), 3.99 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 163.5, 156.6, 152.8, 149.6, 149.4, 138.5, 136.8, 128.0, 122.4, 122.0, 121.9, 52.7, 44.8.

2. Optimization of reaction conditions

Table 1: The effect of Ligands.

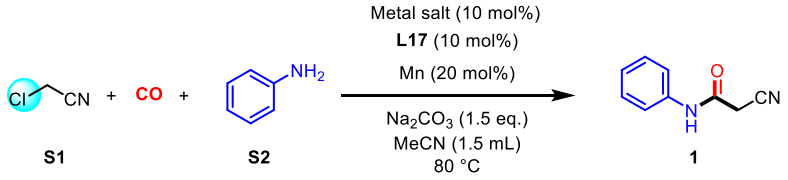


S1 S2 1

Entry	Ligand	Yield (%)[a]
1	**L1** (20 mol%)	0
2	**L2**	0
3	**L3**	0
4	**L4**	0
5	**L5**	0
6	**L6**	0
7	**L7**	0
8	**L8**	0
9	**L9**	0
10	**L10**	0
11	**L11**	0
12	***L12***	***79***
13	**L13**	19
14	**L14**	25
15	**L15**	32
16	***L16***	***78***
17	***L17***	***80***

Reaction conditions: **S1** (1.5 eq.), **S2** (0.3 mmol), $Co(acac)_2$ (10 mol%), **Ligand** (10 mol%), Mn (20 mol%), Na_2CO_3 (1.5 eq.), MeCN (1.5 mL), **CO** (30 bar), 80 °C, 12 h. [a]Yields were determined by GC with dodecane as an internal standard.

Table 2: The effect of Metal salts.

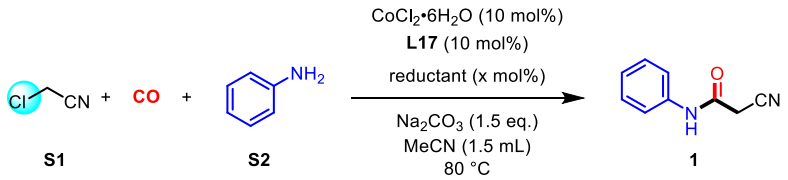


S1 S2 1

Entry	Metal salts	Yield (%)[a]
1	$Co(acac)_3$	58
2	***$CoCl_2$•$6H_2O$***	***99 (92[b])***
3	$Co(OAc)_2$•$4H_2O$	41
4	$Co(OAc)_2$	51
5	$CoCl_2$	42
6	$CoBr_2$	49
7	w/o [Co]	0
8	$Pd(OAc)_2$ (1 mol%, w/o Mn)	0
9	$Ni(acac)_2$ (w/o Mn)	0
10	$Cu(acac)_2$ (w/o Mn)	0

Reaction conditions: **S1** (1.5 eq.), **S2** (0.3 mmol), Metal salt (10 mol%), **L17** (10 mol%), Mn (20 mol%), Na_2CO_3 (1.5 eq.), MeCN (1.5 mL), **CO** (30 bar), 80 °C, 12 h. [a]Yields were determined by GC with dodecane as an internal standard. [b]Isolated yield.

Table 3: The effect of reductant.



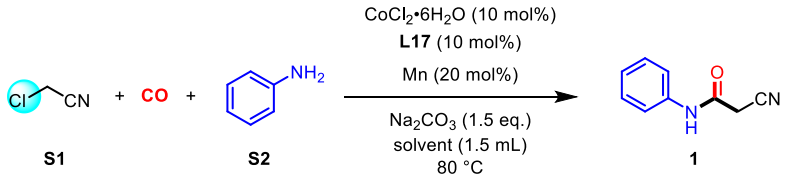
S1 S2 1

Entry	Reductant (x mol%)	Yield (%)[a]
1	w/o Mn	0
2	Mn (10 mol%)	89
3	Mn (30 mol%)	99
4	Mn (40 mol%)	99
5	Mn (60 mol%)	99
6	Zn (20 mol%)	90
7	$MeSiH(EtO)_2$ (20 mol%)	92
8	$SiH(MeO)_3$ (20 mol%)	98

Reaction conditions: **S1** (1.5 eq.), **S2** (0.3 mmol), $CoCl_2$•$6H_2O$ (10 mol%), **L17** (10 mol%), reductant (x mol%), Na_2CO_3 (1.5 eq.), MeCN (1.5 mL), **CO** (30 bar), 80 °C, 12 h. [a]Yields were

determined by GC with dodecane as an internal standard.

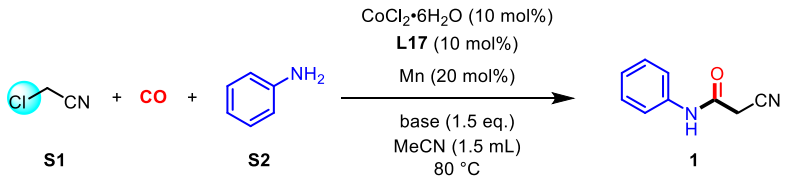
Table 4: The effect of solvents.



Entry	Reductant (x mol%)	Yield (%)[a]
1	Dioxane	0
2	THF	0
3	DMF	0
4	$PhCF_3$	0
5	DCE	0
6	DCM	0
8	DME	0

Reaction conditions: **S1** (1.5 eq.), **S2** (0.3 mmol), $CoCl_2$•$6H_2O$ (10 mol%), **L17** (10 mol%), Mn (20 mol%), Na_2CO_3 (1.5 eq.), MeCN (1.5 mL), **CO** (30 bar), 80 °C, 12 h. [a]Yields were determined by GC with dodecane as an internal standard.

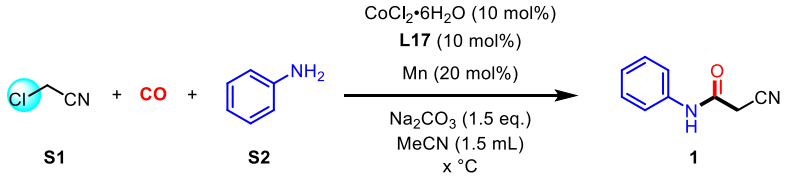
Table 5: The effect of bases.



Entry	base	Yield (%)[a]
1	K_2CO_3	85
2	K_3PO_4	86
3	Na_3PO_4	98
4	Et_3N	83
5	DBU	60
6	pyridine	91

Reaction conditions: **S1** (1.5 eq.), **S2** (0.3 mmol), $CoCl_2$•$6H_2O$ (10 mol%), **L17** (10 mol%), Mn (20 mol%), Base (1.5 eq.), MeCN (1.5 mL), **CO** (30 bar), 80 °C, 12 h. [a]Yields were determined by GC with dodecane as an internal standard.

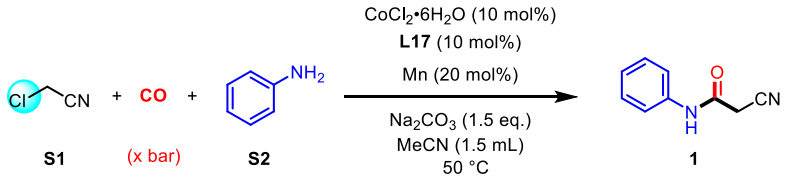
Table 6: The effect of temperature.



Entry	Temperature (°C)	Yield (%)[a]
1	60	99
2	***50***	***98***
3	40	64
4	r.t.	5

Reaction conditions: **S1** (1.5 eq.), **S2** (0.3 mmol), $CoCl_2 \cdot 6H_2O$ (10 mol%), **L17** (10 mol%), Mn (20 mol%), Na_2CO_3 (1.5 eq.), MeCN (1.5 mL), **CO** (30 bar), x °C, 12 h. [a]Yields were determined by GC with dodecane as an internal standard.

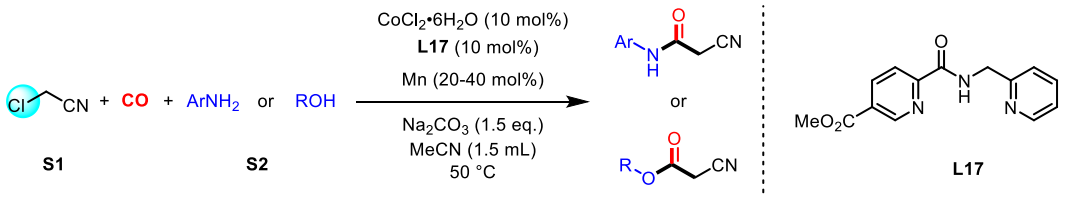
Table 7: The effect of the pressure of **CO**.



Entry	Temperature (°C)	Yield (%)[a]
1	20	98
2	10	98
3	***5***	***98***
4	1	90

Reaction conditions: **S1** (1.5 eq.), **S2** (0.3 mmol), $CoCl_2 \cdot 6H_2O$ (10 mol%), **L17** (10 mol%), Mn (20 mol%), Na_2CO_3 (1.5 eq.), MeCN (1.5 mL), **CO** (x bar), 50 °C, 12 h. [a]Yields were determined by GC with dodecane as an internal standard.

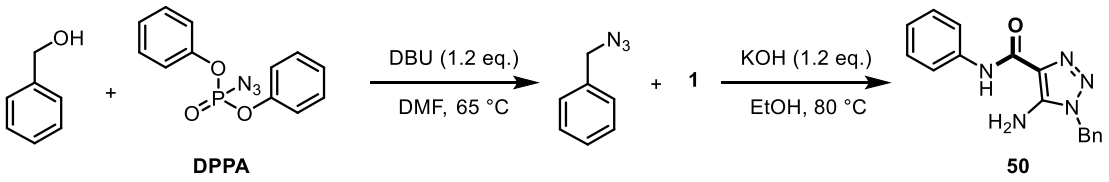
3. General procedure



A 4 mL screw-cap vial was charged with $CoCl_2$•$6H_2O$ (10 mol%, 7.2 mg), **L6** (5 mol%, 8.7 mg), Mn (20-40 mol%, 4.4-6.6 mg), Na_2CO_3 (0.45 mmol, 47.7 mg) and an oven-dried stirring bar. The vial was closed with a Teflon septum and cap and connected to the atmosphere via a needle. Then amines or alcohols (0.3 mmol), $ClCH_2CN$ (0.75 mmol, 90.0 mg), MeCN (1.5 mL) was added with a syringe under N_2 atmosphere, the vial was moved to an alloy plate and put into a Parr 4560 series autoclave (300 mL) under N_2 atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with 5 bar CO. The autoclave was placed on a heating plate equipped with a magnetic stirrer. The reaction mixture was heated to 50 ℃ for 12 h. After the reaction was completed, the crude mixture was filtered and concentrated under vacuum. The crude product was purified by column chromatography (PE/EA =2/1 to 1/1) on silica gel to afford the corresponding 2-cyanoacetate compounds.

4. Later-stage of pharmaceutical derivatives.

4.1 Synthesis of Compound 50[2]

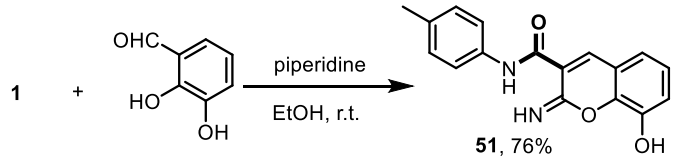


Step 1: A mixture of benzyl alcohol (4 mmol) and diphenylphosphoryl azide (**DPPA**, 1.2 eq.) were dissolved in dry solvent (7 mL). To the mixture at 0 °C, under N_2 atmosphere was added DBU (1.2 eq.). The reaction was warmed to room temperature and stirred until complete. The resulting mixture was washed with H_2O and 5% HCl. The organic phase was concentrated in vacuum and purified by silica gel chromatography using petroleum ether.

Step 2: To a 10 mL Schlenk tube (azidomethyl)benzene (0.3 mmol), **1** (0.2 mmol), KOH(1.5 eq.)

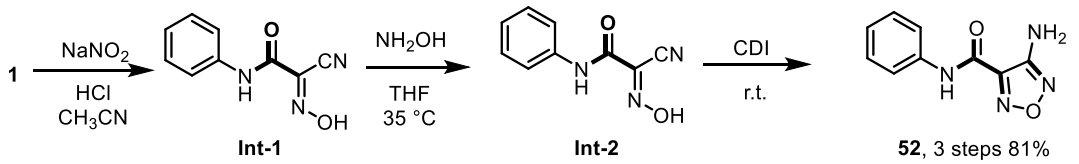
and EtOH (2 mL) were added. The mixture was stirred at 80 ℃ for 1h. The solvent of the reaction solution was removed by vacuum rotary evaporation. The solid was filtered by suction, and the filter cake was washed with ice-cold ethanol to obtain the target product (80%).

4.2 Synthesis of Compound 51[3]



To a stirred solution of **1** (0.4 mmol) in EtOH (3 mL) were added 2,3-dihydroxybenzaldehyde (0.4 mmol) and piperidine (three drops). The resulting mixture was stirred at room temperature for 24 h. The insoluble materials are collected by filtration, washed with EtOH, and dried to give rise to the corresponding amides as a pale-yellow solid.

4.3 Synthesis of Compound 52[4]



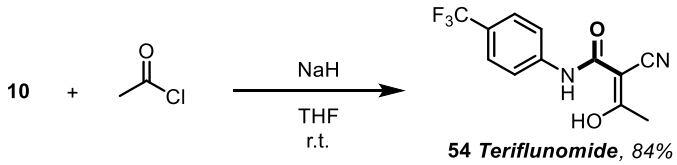
Step 1: A 100-mL round-bottomed flask equipped with a magnetic stir bar was charged with the nitrile substrate (1.0 eq) and MeCN (0.2 M). To the stirred mixture was added concentrated HCl (10.0 eq). In a separate 1 Dram vial, sodium nitrite (2.2 eq) was dissolved in H_2O (7 M with respect to sodium nitrite). The resulting aqueous solution was added dropwise to the stirred reaction mixture at room temperature and stirred for 2-12 h. Upon complete consumption of the starting material, the reaction mixture was diluted with H_2O and transferred to a separatory funnel. The aqueous layer was extracted with EtOAc (x3). The combined organics were washed with brine (x1), dried (Na_2SO_4) and concentrated in vacuo. The crude product can be directly used in the next step without purification.

Step 2: A 20-mL vial equipped with a magnetic stir bar was charged with **Int-1** (0.5 g) and THF (10 mL). To the resulting homogeneous solution was added 50 wt % aqueous hydroxylamine (0.227 mg, 3.44 mmol) and the mixture was heated at 50 ℃. Upon complete consumption of the starting material, as determined by TLC analysis, the reaction mixture was cooled to room temperature and diluted with H_2O (10 mL). The aqueous layer was extracted with DCM(x2). The combined organics

were washed with brine (x1), dried (Na_2SO_4) and concentrated in vacuo. The crude product can be directly used in the next step without purification.

Step 3: A 2-dram vial equipped with a magnetic stir bar was charged with the **Int-2** and THF (5.5 mL). To the resulting homogeneous solution was added 50 % aqueous hydroxylamine (0.129 g, 1.95 mmol). The mixture was heated at 35 ℃ until TLC analysis indicated complete consumption of the starting material (typically 12 h). The reaction mixture was cooled to rt and 1,1'-carbonyldiimidazole (0.365 g, 2.25 mmol) was added portion wise. Upon cessation of gas evolution, the reaction mixture was sampled and typically judged to be complete by TLC analysis. The reaction mixture was concentrated in vacuo and purified directly by column chromatography on silica gel using petroleum ethe/EtOAc as eluent.

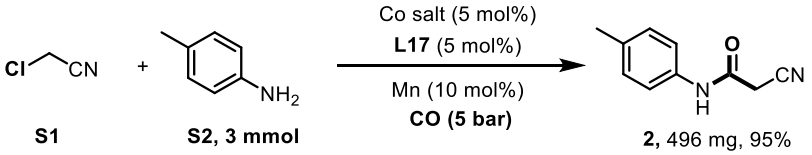
4.4 Synthesis of Compound 53[5]



54 ***Teriflunomide****, 84%*

Amide **10** (228 mg, 1.00 mmol, 1.0 eq.) in dry THF (10 mL), NaH (92.0 mg, 2.30 mmol, 2.3 eq.) and acetyl chloride (78.5 mL, 1.10 mmol, 1.1 eq.) were used to give **54** as colorless crystals (84%). Rf = 0.65 (3:2 hexanes/acetone).

5. Scale-up reaction

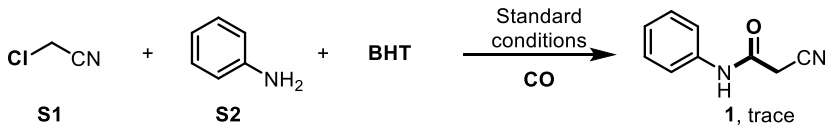


S1 **S2, 3 mmol** **2,** 496 mg, 95%

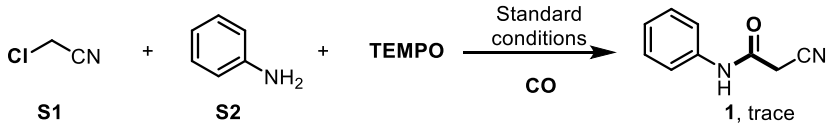
A 25 mL screw-cap vial was charged with $CoCl_2 \cdot 6H_2O$ (5 mol%), **L17** (5 mol%), Mn (10 mol%), Na_2CO_3 (4.5 mmol, 477 mg) and an oven-dried stirring bar. The vial was closed with a Teflon septum and cap and connected to the atmosphere via a needle. Then aniline (3 mmol, 279mg), $BrCH_2CN$ (7.5 mmol, 900 mg), MeCN (15 mL) was added with a syringe under N_2 atmosphere, the vial was moved to an alloy plate and put into a Parr 4560 series autoclave (300 mL) under N_2 atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with

5 bar CO. The autoclave was placed on a heating plate equipped with a magnetic stirrer. The reaction mixture was heated to 50 ℃ for 24 h. After the reaction was completed, the crude mixture was filtered and concentrated under vacuum. The crude product was purified by column chromatography (PE/EA = 2/1) on silica gel to afford **2** (95%).

6. Radical inhibition experiments



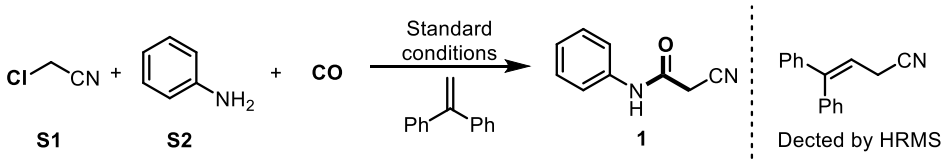
A 4 mL screw-cap vial was charged with BHT (3 equiv., 198.3 mg), $CoCl_2 \cdot 6H_2O$ (10 mol%, 7.2 mg), **L17** (10 mol%, 8.1 mg), Mn (20 mol%), Na_2CO_3 (0.45 mmol, 47.7 mg) and an oven-dried stirring bar. The vial was closed with a Teflon septum and cap and connected to the atmosphere via a needle. Then aniline (0.3 mmol, 27.9 mg), $ClCH_2CN$ (1.5 eq.), MeCN (1.5 mL) was added with a syringe under N_2 atmosphere, the vial was moved to an alloy plate and put into a Parr 4560 series autoclave (300 mL) under N_2 atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with 5 bar CO. The autoclave was placed on a heating plate equipped with a magnetic stirrer. The reaction mixture was heated to 50 ℃ for 16 h. After the reaction was completed, the crude mixture was filtered and concentrated under vacuum. Only a trace amount of the target product **1** was detected in GC-MS.



A 4 mL screw-cap vial was charged with **TEMPO** (3 equiv.), $CoCl_2 \cdot 6H_2O$ (10 mol%, 7.2 mg), **L17** (10 mol%, 8.1 mg), Mn (20 mol%), Na_2CO_3 (0.45 mmol, 47.7 mg) and an oven-dried stirring bar. The vial was closed with a Teflon septum and cap and connected to the atmosphere via a needle. Then aniline (0.3 mmol, 27.9 mg), $ClCH_2CN$ (1.5 eq.), MeCN (1.5 mL) was added with a syringe under N_2 atmosphere, the vial was moved to an alloy plate and put into a Parr 4560 series autoclave (300 mL) under N_2 atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with 5 bar CO. The autoclave was placed on a heating plate equipped with a magnetic stirrer. The reaction mixture was heated to 50 ℃ for 16 h. After the reaction was completed,

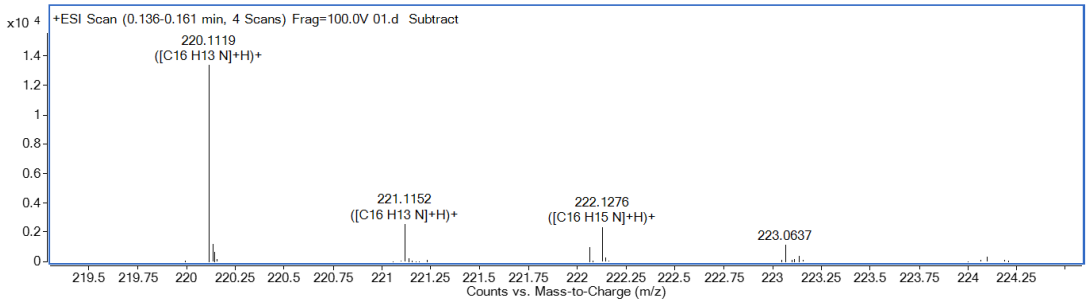
the crude mixture was filtered and concentrated under vacuum. Only a trace amount of the target product **1** was detected in GC-MS.

7. Radical capture experiment

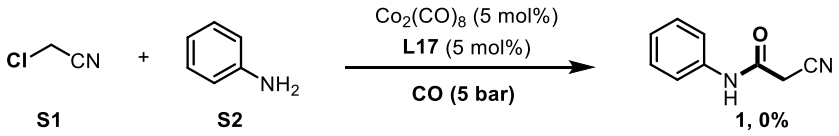


A 4 mL screw-cap vial was charged with 1,1-DPE (3 equiv., 162.2 mg), $CoCl_2 \cdot 6H_2O$ (10 mol%, 7.2 mg), **L17** (10 mol%, 8.1 mg), Mn (20 mol%), Na_2CO_3 (0.45 mmol, 47.7 mg) and an oven-dried stirring bar. The vial was closed with a Teflon septum and cap and connected to the atmosphere via a needle. Then aniline (0.3 mmol, 27.9 mg), $ClCH_2CN$ (1.5 eq.), MeCN (1.5 mL) was added with a syringe under N_2 atmosphere, the vial was moved to an alloy plate and put into a Parr 4560 series autoclave (300 mL) under N_2 atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with 5 bar CO. The autoclave was placed on a heating plate equipped with a magnetic stirrer. The reaction mixture was heated to 50 °C for 16 h. After the reaction was completed, the crude mixture was filtered and concentrated under vacuum. 4,4-diphenylbut-3-enenitrile was detected by HRMS.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{14}N$ 200.1121; found: 200.1119.



8. Reaction with $Co_2(CO)_8$

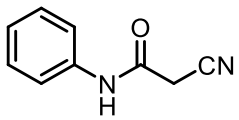


A 4 mL screw-cap vial was charged with $Co_2(CO)_8$ (10 mol%, 7.2 mg), **L17** (10 mol%, 8.1 mg),

Na_2CO_3 (0.45 mmol, 47.7 mg) and an oven-dried stirring bar. The vial was closed with a Teflon septum and cap and connected to the atmosphere via a needle. Then aniline (0.3 mmol, 27.9 mg), $ClCH_2CN$ (1.5 eq.), MeCN (1.5 mL) was added with a syringe under N_2 atmosphere, the vial was moved to an alloy plate and put into a Parr 4560 series autoclave (300 mL) under N_2 atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with 5 bar CO. The autoclave was placed on a heating plate equipped with a magnetic stirrer. The reaction mixture was heated to 50 ℃ for 16 h. After the reaction, no product **1** was detected by GC-MS.

9. Characterization data of products

2-Cyano-*N*-phenylacetamide (1)



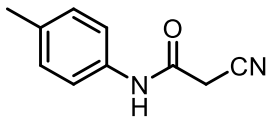
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) yield (44 mg, 92%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.29 (s, 1H), 7.81 – 7.47 (m, 2H), 7.38 – 7.28 (m, 2H), 7.09 (tt, *J* = 7.2, 1.2 Hz, 1H), 3.90 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 161.5, 138.8, 129.4, 124.4, 119.7, 116.4, 27.2.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_9H_9N_2O$ 161.0709; found: 161.0714.

2-Cyano-*N*-(*p*-tolyl)acetamide (2)



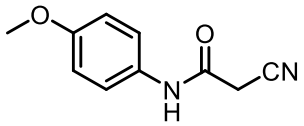
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) yield (49 mg, 94%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.20 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 3.87 (s, 2H), 2.25 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 161.2, 136.3, 133.4, 129.7, 119.7, 116.4, 27.1, 20.9.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{10}H_{11}N_2O$ 175.0866; found: 175.0868.

2-Cyano-*N*-(4-methoxyphenyl)acetamide (3)



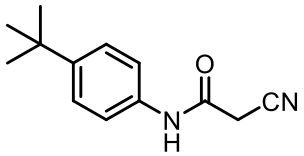
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 1:1) yield (53 mg, 93%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.15 (s, 1H), 7.46 (d, *J* = 9.0 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 1H), 3.85 (s, 2H), 3.73 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 160.9, 156.1, 131.9, 121.3, 116.5, 114.5, 55.6, 27.0.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{10}H_{11}N_2O_2$ 191.0815; found: 191.0819.

***N*-(4-(tert-butyl)phenyl)-2-cyanoacetamide (4)**



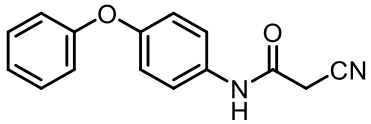
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) yield (59 mg, 92%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.22 (s, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 2H), 1.26 (s, 9H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 161.2, 146.7, 136.3, 126.0, 119.5, 116.5, 34.5, 31.6, 27.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{17}N_2O$ 217.1335; found: 217.1330.

2-Cyano-*N*-(4-phenoxyphenyl)acetamide (5)



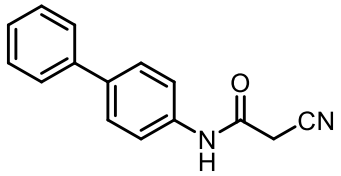
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 1:1) yield (67 mg, 89%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.34 (s, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.45 – 7.34 (m, 2H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.05 – 6.95 (m, 4H), 3.91 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 161.3, 157.6, 152.8, 134.6, 130.4, 123.6, 121.5, 119.9, 118.5, 116.4, 27.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{13}N_2O_2$ 253.0972; found: 253.0970.

***N*-([1,1'-biphenyl]-4-yl)-2-cyanoacetamide (6)**



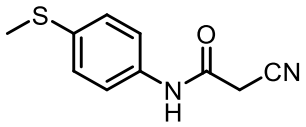
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) yield (62 mg, 88%) as a white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.43 (s, 1H), 7.74 – 7.61 (m, 6H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 3.96 (s, 2H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 161.5, 140.0, 138.3, 136.1, 129.4, 127.6, 127.6, 126.8, 120.1, 116.4, 27.3.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{13}N_2O$ 237.1022; found: 237.1020.

2-Cyano-*N*-(4-(methylthio)phenyl)acetamide (7)



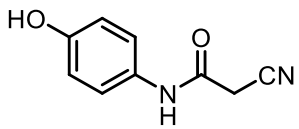
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 1:1) yield (50 mg, 81%) as a white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.30 (s, 1H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 2H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 161.3, 136.2, 133.2, 127.5, 120.4, 116.4, 27.2, 15.8.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{10}H_{11}N_2OS$ 207.0587; found: 207.0595.

2-Cyano-*N*-(4-hydroxyphenyl)acetamide (8)



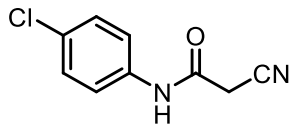
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 2:3) yield (45 mg, 87%) as a white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.03 (s, 1H), 9.28 (s, 1H), 7.33 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 2H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 160.7, 154.3, 130.4, 121.6, 116.6, 115.7, 26.9.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_9H_9N_2O_2$ 177.0659; found: 177.0655.

***N*-(4-chlorophenyl)-2-cyanoacetamide (9)**



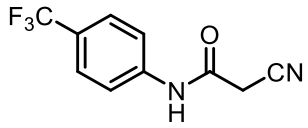
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) yield (53 mg, 92%) as a white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.44 (s, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.39 (d, *J* = 8.8 Hz, 1H), 3.93 (s, 2H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 161.7, 137.8, 129.3, 128.0, 121.3, 116.2, 27.3.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_9H_8ClN_2O$ 195.0320; found: 195.0325.

2-Cyano-*N*-(4-(trifluoromethyl)phenyl)acetamide (10)



The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) yield (57 mg, 84%) as a white solid.

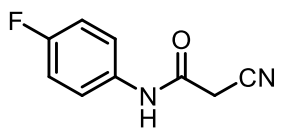
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.67 (s, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 3.99 (s, 2H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 162.3, 142.4, 126.7 (q, *J* = 3.9 Hz), 124.7 (q, *J* = 269.7 Hz), 124.4 (q, *J* = 31.9 Hz), 119.62, 116.12, 27.44.

^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -60.6.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{10}H_8F_3N_2O$ 229.0583; found: 229.0586.

2-Cyano-*N*-(4-fluorophenyl)acetamide (11)



The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) yield (51 mg, 96%) as a white solid.

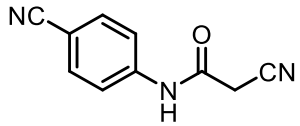
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.35 (s, 1H), 7.83 – 7.44 (m, 2H), 7.32 – 7.02 (m, 2H), 3.89 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 161.4, 158.8 (d, J = 239.0 Hz), 135.2 (d, J = 2.7 Hz), 121.6 (d, J = 7.9 Hz), 116.3, 116.0 (d, J = 22.2 Hz), 27.1.

^{19}F NMR (376 MHz, DMSO-d_6) δ -118.5.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_9H_8FN_2O$ 179.0615; found: 179.0620.

2-Cyano-*N*-(4-cyanophenyl)acetamide (12)



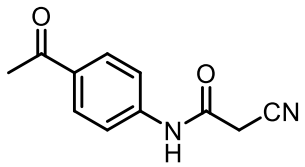
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 1:2) yield (59 mg, 92%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.73 (s, 1H), 7.81 (d, J = 8.8 Hz, 2H), 7.73 (d, J = 8.8 Hz, 2H), 3.99 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 162.5, 143.0, 133.9, 119.8, 119.3, 116.0, 106.2, 27.6.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{10}H_8N_3O$ 186.0662; found: 186.0662.

***N*-(4-acetylphenyl)-2-cyanoacetamide (13)**



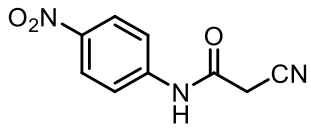
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 1:1) yield (53 mg, 88%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.63 (s, 1H), 7.96 (d, J = 8.8 Hz, 2H), 7.69 (d, J = 8.8 Hz, 2H), 3.97 (s, 2H), 2.54 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 197.0, 162.2, 143.1, 132.7, 130.0, 119.0, 116.2, 27.5, 26.9.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{11}H_{11}N_2O_2$ 203.0815; found: 203.0815.

2-Cyano-*N*-(4-nitrophenyl)acetamide (14)



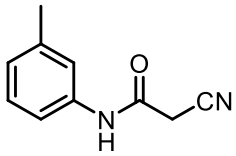
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 1:2) yield (47 mg, 77%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.90 (s, 1H), 8.25 (d, J = 9.2 Hz, 1H), 7.80 (d, J = 9.2 Hz, 1H), 4.02 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 162.7, 144.9, 143.1, 125.5, 119.5, 116.0, 27.6.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_9H_8N_3O_3$ 206.0560; found: 206.0560.

2-Cyano-*N*-(*m*-tolyl)acetamide (15)



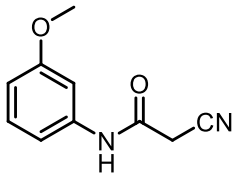
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) yield (42 mg, 81%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.21 (s, 1H), 7.39 (s, 1H), 7.35 – 7.31 (m, 1H), 7.21 (t, J = 7.6 Hz, 1H), 6.96 – 6.90 (m, 1H), 3.88 (s, 2H), 2.28 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 161.4, 138.8, 138.6, 129.2, 125.1, 120.2, 116.9, 116.4, 27.2, 21.6.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{10}H_{11}N_2O$ 175.0866; found: 175.0867.

2-Cyano-*N*-(3-methoxyphenyl)acetamide (16)



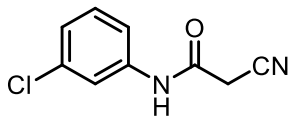
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 1:1) yield (52 mg, 92%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.27 (s, 1H), 7.24 – 7.20 (m, 2H), 7.10 – 7.05 (m, 1H), 6.73 – 6.65 (m, 1H), 3.89 (s, 2H), 3.73 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 161.5, 160.0, 140.0, 130.2, 116.3, 111.9, 109.7, 105.5, 55.5, 27.3.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{10}H_{11}N_2O_2$ 191.0815; found: 208.1088.

***N*-(3-chlorophenyl)-2-cyanoacetamide (17)**



The title compound was prepared following the general procedure, purification by column

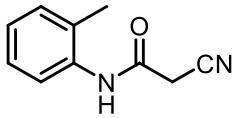
chromatography on silica gel (petroleum ether/EtOAc = 1:1) yield (52 mg, 90%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.49 (s, 1H), 7.76 (s, 1H), 7.46 – 7.34 (m, 2H), 7.22 – 7.12 (m, 1H), 3.94 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 162.0, 140.2, 133.7, 131.1, 124.1, 119.2, 118.1, 116.2, 27.3.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_9H_8ClN_2O$ 195.0320; found: 195.0325.

2-Cyano-*N*-(*o*-tolyl)acetamide (18)



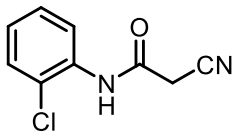
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) yield (38 mg, 73%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.65 (s, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.29 – 7.04 (m, 3H), 3.92 (s, 2H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 161.7, 136.0, 132.2, 130.9, 126.6, 126.2, 125.4, 116.6, 26.5, 18.2.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{10}H_{11}N_2O$ 175.0866; found: 175.0868.

***N*-(2-chlorophenyl)-2-cyanoacetamide (19)**



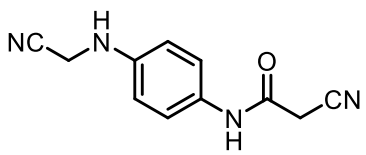
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) yield (40 mg, 69%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.95 (s, 1H), 7.72 (d, J = 1.6 Hz, 1H), 7.52 (dd, J = 8.0, 1.6 Hz, 1H), 7.41 – 7.32 (m, 1H), 7.27 – 7.17 (m, 1H), 4.01 (s, 2H).

^{13}C NMR (101 MHz, DMSO) δ 162.2, 134.6, 130.1, 128.1, 127.4, 127.1, 126.6, 116.3, 26.7.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_9H_8ClN_2O$ 195.0320; found: 195.0325.

2-Cyano-*N*-(4-((isocyanomethyl)amino)phenyl)acetamide (20)



The title compound was prepared following the general procedure, purification by column

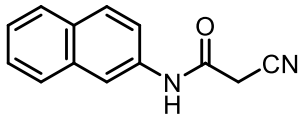
chromatography on silica gel (petroleum ether/EtOAc = 1:2) yield (59 mg, 80%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.02 (s, 1H), 7.35 (d, J = 8.8 Hz, 2H), 6.69 (d, J = 8.8 Hz, 2H), 6.15 (t, J = 6.8 Hz, 1H), 4.22 (d, J = 6.8 Hz, 2H), 3.82 (s, 2H).

^{13}C NMR (101 MHz, DMSO) δ 160.6, 143.7, 129.9, 121.4, 119.1, 116.6, 113.7, 32.2, 26.9.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{11}H_{11}N_4O$ 215.0927; found: 215.0923.

2-Cyano-*N*-(naphthalen-2-yl)acetamide (21)



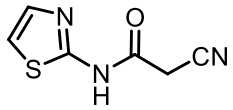
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) yield (56 mg, 89%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.54 (s, 1H), 8.29 (d, J = 2.0 Hz, 1H), 8.00 – 7.84 (m, 3H), 7.59 (dd, J = 8.8, 2.0 Hz, 1H), 7.54 – 7.47 (m, 1H), 7.46 – 7.40 (m, 1H), 4.01 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 161.8, 136.4, 133.8, 130.5, 129.1, 128.0, 127.9, 127.0, 125.4, 120.2, 116.4, 116.1, 27.4.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{11}N_2O$ 211.0866; found: 211.0880.

2-Cyano-*N*-(thiazol-2-yl)acetamide (22)



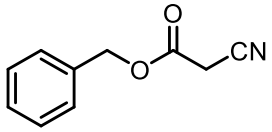
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 1:1) yield (30 mg, 60%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.45 (s, 1H), 7.50 (d, J = 3.6 Hz, 1H), 7.28 (d, J = 3.6 Hz, 1H), 4.04 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 162.2, 158.0, 138.2, 115.7, 114.6, 26.4.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_6H_6N_3OS$ 168.0226; found: 168.0229.

Benzyl 2-cyanoacetate (23)



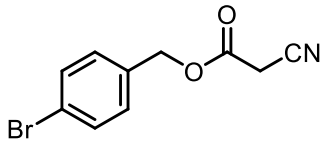
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yield (44 mg, 85%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.33 (m, 5H), 5.23 (s, 2H), 3.48 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 134.3, 128.9, 128.8, 128.6, 112.9, 68.6, 24.8.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{10}H_{10}NO_2$ 176.0706; found: 176.0708.

4-Bromobenzyl 2-cyanoacetate (24)



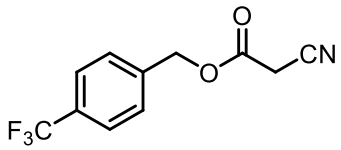
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yield (64 mg, 85%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.45 (m, 2H), 7.34 – 7.19 (m, 2H), 5.17 (s, 2H), 3.49 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 133.3, 132.0, 130.3, 123.1, 112.8, 67.7, 24.8.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{10}H_9BrNO_2$ 253.9811; found: 253.9812

4-(Trifluoromethyl)benzyl 2-cyanoacetate (25)



The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yield (59 mg, 82%) as a colorless oil.

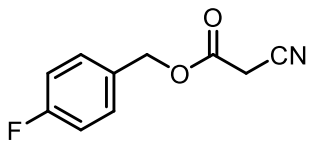
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 5.28 (s, 2H), 3.53 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 138.2 (q, J = 1.1 Hz), 131.0 (q, J = 32.4 Hz), 128.6, 125.8 (q, J = 3.8 Hz), 123.9 (q, J = 270.5 Hz), 112.7, 67.4, 24.7.

^{19}F NMR (375 MHz, $CDCl_3$) δ -62.7.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{11}H_9F_3NO_2$ 244.0580; found: 244.0583

4-Fluorobenzyl 2-cyanoacetate (26)



The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yield (45 mg, 78%) as a colorless oil.

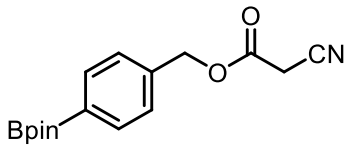
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 2H), 7.14 – 6.96 (m, 2H), 5.19 (s, 2H), 3.48 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, *J* = 246.5 Hz), 162.82, 130.8 (d, *J* = 8.4 Hz), 130.3 (d, *J* = 3.3 Hz), 115.8 (d, *J* = 21.7 Hz), 112.9, 67.8, 24.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.4.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{10}H_9FNO_2$ 194.0612; found: 194.0610

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl 2-cyanoacetate (27)



The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yield (61 mg, 68%) as a white solid.

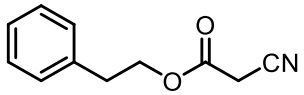
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 5.23 (s, 2H), 3.48 (s, 2H), 1.34 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 137.2, 135.2, 127.6, 112.9, 84.0, 68.4, 24.9, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.5.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{21}BNO_4$ 301.1594; found: 301.1599.

Phenethyl 2-cyanoacetate (28)



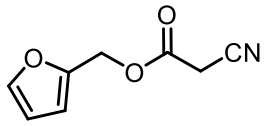
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yield (51 mg, 90%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 2H), 7.27 – 7.18 (m, 3H), 4.41 (t, *J* = 7.2 Hz, 2H), 3.40 (s, 2H), 2.98 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 136.9, 128.9, 128.7, 126.9, 113.0, 67.3, 34.8, 24.7.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{11}H_{12}NO_2$ 190.0863; found: 190.0868.

Furan-2-ylmethyl 2-cyanoacetate (29)



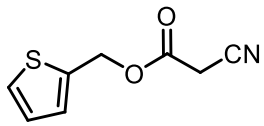
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 1:1) yield (35 mg, 70%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 1.2 Hz, 1H), 6.48 (d, *J* = 3.2 Hz, 1H), 6.38 (dd, *J* = 3.2, 1.6 Hz, 1H), 5.19 (s, 2H), 3.48 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 147.9, 143.9, 112.7, 111.9, 110.8, 60.0, 24.7.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_8H_8NO_3$ 166.0499; found: 166.0497.

Thiophen-2-ylmethyl 2-cyanoacetate (30)



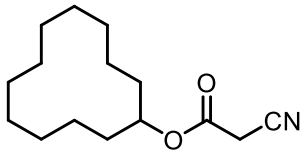
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 1:1) yield (47 mg, 86%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.14 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.00 (dd, *J* = 5.2, 3.6 Hz, 1H), 5.37 (s, 2H), 3.47 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 136.0, 129.4, 127.8, 127.1, 112.9, 62.5, 24.8.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_8H_8NO_2S$ 182.0270; found: 182.0274.

Cyclododecyl 2-cyanoacetate (31)



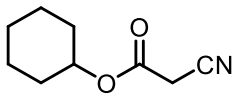
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 25:1) yield (70 mg, 93%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.26 – 4.97 (m, 1H), 3.43 (s, 2H), 2.00 – 1.71 (m, 2H), 1.61 – 1.48 (m, 2H), 1.54 – 1.19 (m, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 113.2, 75.9, 28.9, 25.0, 24.0, 23.8, 23.3, 23.1, 20.7.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{26}NO_2$ 252.1958; found: 252.1954.

Cyclohexyl 2-cyanoacetate (32)



The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yield (37 mg, 74%) as a colorless oil.

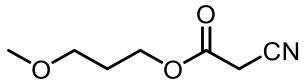
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.86 (tt, *J* = 9.2, 4.0 Hz, 1H), 3.44 (s, 2H), 1.94 – 1.84 (m, 2H), 1.79

– 1.69 (m, 2H), 1.58 – 1.39 (m, 4H), 1.37 – 1.23 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 113.2, 75.9, 31.3, 25.1, 25.1, 23.5.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_9H_{14}NO_2$ 168.1019; found: 168.1020.

3-Methoxypropyl 2-cyanoacetate (33)



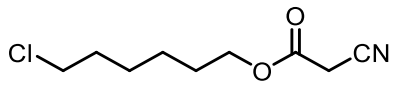
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yield (42 mg, 90%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.31 (t, *J* = 6.8 Hz, 2H), 3.49 (s, 2H), 3.46 (t, *J* = 6.4 Hz, 2H), 3.33 (s, 3H), 1.95 (p, *J* = 6.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 113.1, 68.6, 64.1, 58.7, 28.6, 24.7.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_7H_{12}NO_3$ 158.0812; found: 158.0812.

6-Chlorohexyl 2-cyanoacetate (34)



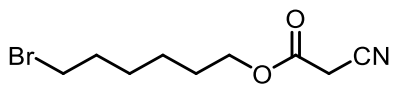
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yield (53 mg, 88%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (t, *J* = 6.8 Hz, 2H), 3.55 (t, *J* = 6.4 Hz, 2H), 3.47 (s, 2H), 1.84 – 1.75 (m, 2H), 1.71 (p, *J* = 6.8 Hz, 2H), 1.54 – 1.36 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 113.1, 66.8, 44.9, 32.3, 28.2, 26.4, 25.1, 24.7.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_9H_{15}ClNO_2$ 204.0786; found: 204.0787.

6-Bromohexyl 2-cyanoacetate (35)



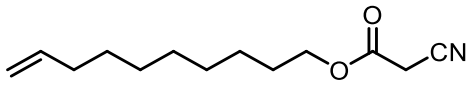
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yield (67 mg, 91%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (t, *J* = 6.8 Hz, 2H), 3.48 (s, 2H), 3.42 (t, *J* = 6.8 Hz, 2H), 1.93 – 1.83 (m, 2H), 1.78 – 1.64 (m, 2H), 1.56 – 1.45 (m, 2H), 1.45 – 1.31 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 113.1, 66.8, 33.7, 32.5, 28.1, 27.6, 24.9, 24.8.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_9H_{15}BrNO_2$ 248.0281; found: 248.0282.

Dec-9-en-1-yl 2-cyanoacetate (36)



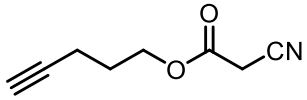
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 25:1) yield (54 mg, 81%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 – 5.74 (m, 1H), 4.99 (dq, *J* = 17.2, 1.6 Hz, 1H), 4.95 – 4.88 (m, 1H), 4.20 (t, *J* = 6.8 Hz, 2H), 3.46 (s, 2H), 2.11 – 1.96 (m, 2H), 1.76 – 1.63 (m, 2H), 1.42 – 1.24 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 139.1, 114.2, 113.1, 67.1, 33.8, 29.3, 29.1, 29.0, 28.9, 28.3, 25.7, 24.7.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{22}NO_2$ 224.1645; found: 224.1643.

Pent-4-yn-1-yl 2-cyanoacetate (37)



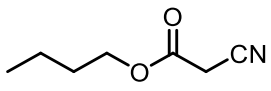
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yield (34 mg, 75%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.34 (t, *J* = 6.4 Hz, 2H), 3.47 (s, 2H), 2.33 (td, *J* = 7.2, 2.8 Hz, 2H), 2.00 (t, *J* = 2.8 Hz, 1H), 1.92 (p, *J* = 6.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 112.9, 82.4, 69.5, 65.4, 27.1, 24.7, 15.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_8H_{10}NO_2$ 152.0706; found: 152.0705.

Butyl 2-cyanoacetate (38)



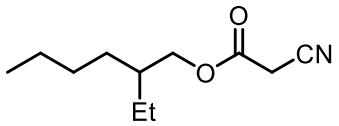
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yield (38 mg, 90%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (t, *J* = 6.4 Hz, 2H), 3.46 (s, 2H), 1.79 – 1.59 (m, 2H), 1.52 – 1.31 (m, 2H), 0.95 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 113.1, 66.8, 30.3, 24.7, 18.9, 13.6.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_7H_{12}NO_2$ 142.0863; found: 142.0863.

2-Ethylhexyl 2-cyanoacetate (39)



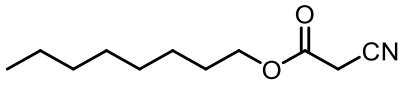
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yield (48 mg, 82%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13 (dd, *J* = 6.0, 2.8 Hz, 2H), 3.46 (s, 2H), 1.67 – 1.58 (m, 1H), 1.47 – 1.34 (m, 2H), 1.34 – 1.21 (m, 6H), 1.02 – 0.85 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 113.0, 69.4, 38.6, 30.2, 28.8, 24.7, 23.6, 22.9, 14.0, 10.9.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{11}H_{20}NO_2$ 198.1489; found: 198.1485.

Octyl 2-cyanoacetate (40)



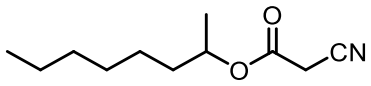
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yield (55 mg, 94%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.20 (t, *J* = 6.8 Hz, 2H), 3.46 (s, 2H), 1.75 – 1.62 (m, 2H), 1.45 – 1.22 (m, 10H), 0.89 (t, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 113.1, 67.1, 31.7, 29.1, 28.3, 25.7, 24.7, 22.6, 14.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{11}H_{20}NO_2$ 198.1489; found: 198.1485.

Octan-2-yl 2-cyanoacetate (41)



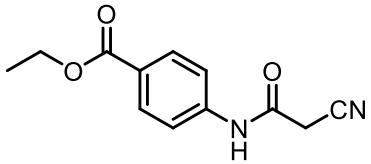
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yield (54 mg, 93%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.14 – 4.87 (m, 1H), 3.43 (s, 2H), 1.79 – 1.43 (m, 2H), 1.38 – 1.23 (m, 11H), 1.00 – 0.82 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 113.2, 74.6, 35.6, 31.6, 29.0, 25.2, 25.0, 22.5, 19.7, 14.0.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{11}H_{20}NO_2$ 198.1489; found: 198.1487.

Ethyl 4-(2-cyanoacetamido)benzoate (42)



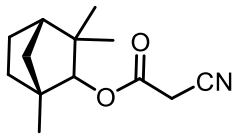
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 1:1) yield (54 mg, 78%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.63 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 2H), 4.29 (q, *J* = 6.8 Hz, 2H), 3.96 (s, 2H), 1.31 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 165.7, 162.2, 143.1, 130.8, 125.3, 119.1, 116.2, 61.0, 27.5, 14.7.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{13}N_2O_3$ 233.0921; found: 233.0924.

(1*R*,4*S*)-1,3,3-Trimethylbicyclo[2.2.1]heptan-2-yl 2-cyanoacetate (43)



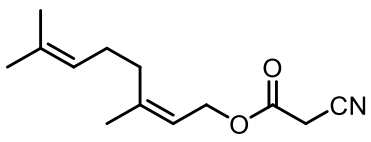
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 25:1) yield (59 mg, 75%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.45 (d, *J* = 2.0 Hz, 1H), 3.48 (s, 2H), 1.78 – 1.75 (m, 2H), 1.74 (d, *J* = 2.4 Hz, 1H), 1.63 – 1.57 (m, 1H), 1.54 – 1.43 (m, 1H), 1.29 – 1.21 (m, 1H), 1.18 – 1.13 (m, 1H), 1.11 (s, 3H), 1.07 (s, 3H), 0.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 113.1, 89.3, 48.4, 48.2, 41.3, 39.7, 29.6, 26.4, 25.7, 24.7, 20.1, 19.3.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{20}NO_2$ 222.1489; found: 222.1486.

(*Z*)-3,7-Dimethylocta-2,6-dien-1-yl 2-cyanoacetate (44)



The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 1:1) yield (55 mg, 83%) as a colorless oil.

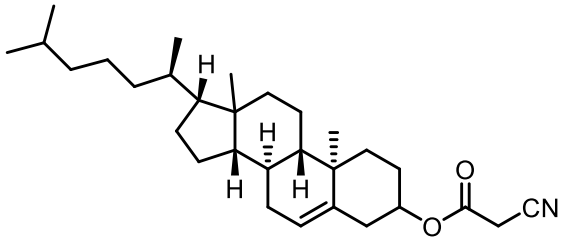
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 (td, *J* = 7.2, 1.6 Hz, 1H), 5.15 – 5.04 (m, 1H), 4.69 (d, *J* = 7.6 Hz, 2H), 3.45 (s, 2H), 2.26 – 2.02 (m, 4H), 1.78 (d, *J* = 1.5 Hz, 3H), 1.69 (s, 2H), 1.61 (d, *J* = 1.4

Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 144.4, 132.4, 123.3, 117.8, 113.1, 63.4, 32.2, 26.6, 25.7, 24.8, 23.5, 17.7.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{20}NO_2$ 222.1489; found: 222.1482.

(8S,9S,10R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-cyanoacetate (45)



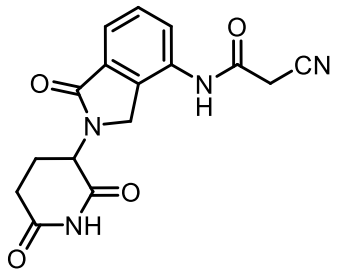
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 1:1) yield (0.2 mmol scale, 56 mg, 62%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 (d, *J* = 4.8 Hz, 1H), 4.84 – 4.54 (m, 1H), 3.43 (s, 2H), 2.59 – 2.34 (m, 2H), 2.07 – 1.95 (m, 2H), 1.92 – 1.79 (m, 3H), 1.72 – 1.62 (m, 1H), 1.58 – 1.52 (m, 2H), 1.52 – 1.41 (m, 4H), 1.39 – 1.25 (m, 4H), 1.22 – 1.07 (m, 7H), 1.05 – 0.96 (m, 6H), 0.92 (d, *J* = 6.4 Hz, 3H), 0.87 (d, *J* = 1.6 Hz, 3H), 0.86 (d, *J* = 1.6 Hz, 3H), 0.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 138.9, 123.4, 113.2, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 37.8, 36.8, 36.5, 36.2, 35.8, 31.9, 31.8, 28.2, 28.0, 27.5, 25.1, 24.3, 23.8, 22.8, 22.6, 21.0, 19.3, 18.7, 11.9.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{30}H_{48}NO_2$ 454.368; found: 454.3669.

2-Cyano-*N*-(2-(2,6-dioxopiperidin-3-yl)-1-oxoisoindolin-4-yl)acetamide (46)



The title compound was prepared following the general procedure, purification by column chromatography on silica gel (EtOAc) yield (0.2 mmol scale, 60 mg, 92%) as a white solid.

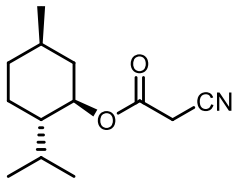
^{1}H NMR (400 MHz, DMSO-d_6) δ 11.04 (s, 1H), 10.21 (s, 1H), 7.82 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.65

– 7.51 (m, 2H), 5.18 (dd, *J* = 13.2, 5.2 Hz, 1H), 4.64 – 4.24 (m, 2H), 3.97 (s, 2H), 3.12 – 2.84 (m, 1H), 2.72 – 2.58 (m, 1H), 2.35 (qd, *J* = 13.2, 4.4 Hz, 1H), 2.15 – 1.99 (m, 1H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 173.3, 171.6, 168.1, 161.9, 134.3, 133.3, 133.3, 129.4, 125.7, 120.3, 116.3, 52.0, 46.8, 31.7, 26.8, 23.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{15}N_4O_4$ 327.1088; found: 327.1089.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 2-cyanoacetate (47)



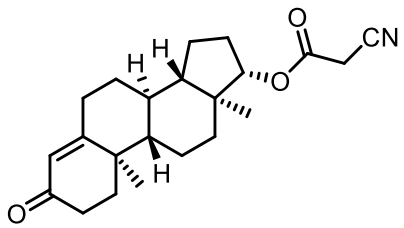
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) yield (48 mg, 72%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.77 (td, *J* = 10.8, 4.4 Hz, 1H), 3.44 (s, 2H), 2.10 – 1.98 (m, 1H), 1.93 – 1.80 (m, 1H), 1.77 – 1.66 (m, 2H), 1.58 – 1.39 (m, 2H), 1.14 – 1.00 (m, 2H), 0.96 – 0.86 (m, 6H), 0.77 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 113.2, 46.8, 40.5, 34.0, 31.4, 26.3, 25.0, 23.3, 21.9, 20.7, 16.2.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{22}NO_2$ 224.1645; found: 224.1645.

(8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 2-cyanoacetate (48)



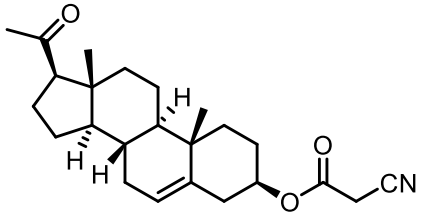
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) yield (0.2 mmol scale, 51 mg, 72%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (d, *J* = 1.6 Hz, 1H), 4.68 (t, *J* = 9.2, 7.6 Hz, 1H), 3.46 (s, 2H), 2.51 – 2.16 (m, 5H), 2.10 – 1.97 (m, 1H), 1.92 – 1.79 (m, 2H), 1.76 – 1.54 (m, 5H), 1.50 – 1.33 (m, 2H), 1.30 – 1.16 (m, 4H), 1.12 – 0.92 (m, 3H), 0.89 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 170.7, 162.8, 124.0, 113.1, 85.2, 53.6, 50.1, 42.8, 38.6, 36.5, 35.7, 35.3, 33.9, 32.7, 31.4, 27.3, 24.9, 23.4, 20.5, 17.4, 12.0.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{30}NO_3$ 356.2220; found: 356.2224.

(3*R*,8*R*,9*R*,10*S*,13*R*,14*R*,17*R*)-17-Acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-cyanoacetate (49)



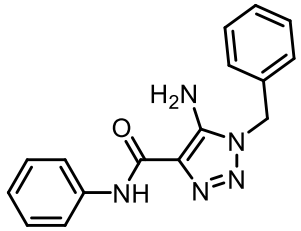
The title compound was prepared following the general procedure, purification by column chromatography on silica gel (petroleum ether/EtOAc = 1:1) yield (0.2 mmol scale, 59 mg, 64%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45 – 5.34 (m, 1H), 4.81 – 4.61 (m, 1H), 3.45 (s, 2H), 2.54 (t, *J* = 8.8 Hz, 1H), 2.42 – 2.35 (m, 2H), 2.24 – 2.16 (m, 1H), 2.13 (s, 3H), 2.09 – 1.96 (m, 2H), 1.95 – 1.86 (m, 2H), 1.76 – 1.41 (m, 8H), 1.32 – 1.10 (m, 3H), 1.05 – 0.98 (m, 4H), 0.63 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 162.3, 138.9, 123.1, 113.1, 76.9, 63.6, 56.8, 49.8, 44.0, 38.7, 37.7, 36.8, 36.5, 31.8, 31.7, 31.6, 27.5, 25.1, 24.5, 22.8, 21.0, 19.3, 13.2.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{34}NO_3$ 384.2533; found: 384.2533.

5-Amino-1-benzyl-*N*-phenyl-1*H*-1,2,3-triazole-4-carboxamide (50)

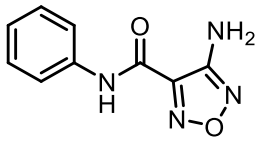


^{1}H NMR (400 MHz, DMSO-d_6) δ 10.05 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.21 (m, 7H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.61 (s, 2H), 5.49 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 161.2, 145.9, 139.5, 136.3, 129.1, 128.9, 128.2, 127.8, 123.5, 122.1, 120.4, 48.8.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{16}N_5O$ 294.1349; found: 294.1345.

4-Amino-*N*-phenyl-1,2,5-oxadiazole-3-carboxamide (51)

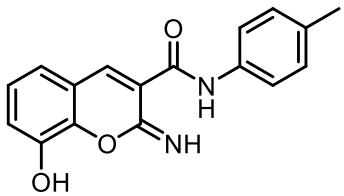


^{1}H NMR (400 MHz, DMSO-d_6) δ 10.98 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.45 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 157.0, 156.6, 141.5, 138.2, 129.2, 125.1, 121.2.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_9H_9N_4O_2$ 205.0720; found: 205.0722.

8-Hydroxy-2-imino-N-(p-tolyl)-2H-chromene-3-carboxamide (52)

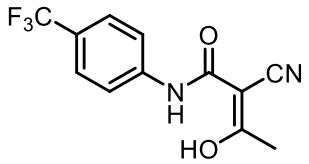


^{1}H NMR (400 MHz, DMSO-d_6) δ 12.78 (s, 1H), 10.14 (s, 1H), 9.05 (s, 1H), 8.49 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.06 (m, 5H), 2.28 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 160.0, 156.4, 144.4, 142.4, 142.4, 136.3, 133.5, 129.9, 124.5, 120.5, 120.1, 120.0, 119.9, 21.0.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{15}N_2O_3$ 295.1077; found: 295.1078.

(*Z*)-2-Cyano-3-hydroxy-*N*-(4-(trifluoromethyl)phenyl)but-2-enamide (53)



^{1}H NMR (400 MHz, DMSO-d_6) δ 13.65 (s, 1H), 10.61 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 2.31 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 187.4, 166.9, 141.8, 126.3 (q, *J* = 3.8 Hz), 124.8 (q, *J* = 32.1 Hz), 124.6 (q, *J* = 269.8 Hz), 121.76, 118.08, 81.63, 23.18.

^{19}F NMR (376 MHz, DMSO-d_6) δ -60.5.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{10}F_3N_2O_2$ 271.0689; found: 271.0688.

10. Reference

[1] Zhang, Y.-T.; Cao, Q.-H.; Xi, Y.; Wu, X.-Q.; Qu, J.-P.; Chen, Y.-F. *J. Am. Chem. Soc.* **2024**, *146*, 7971−7978.

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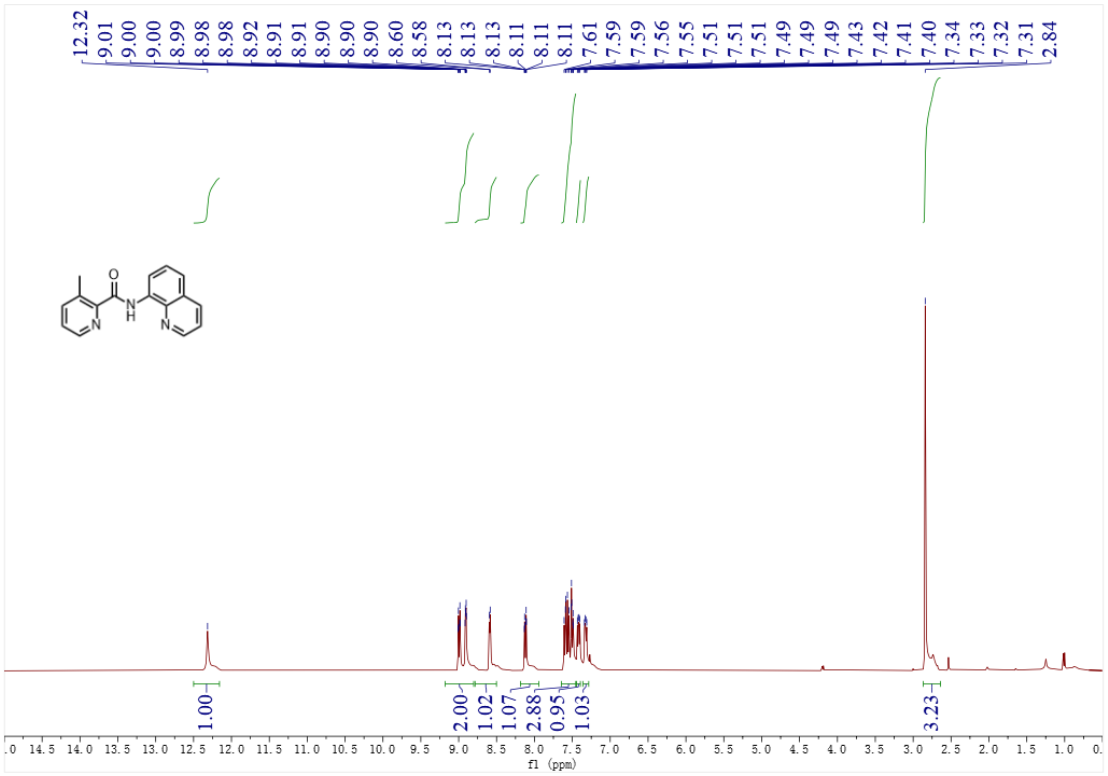
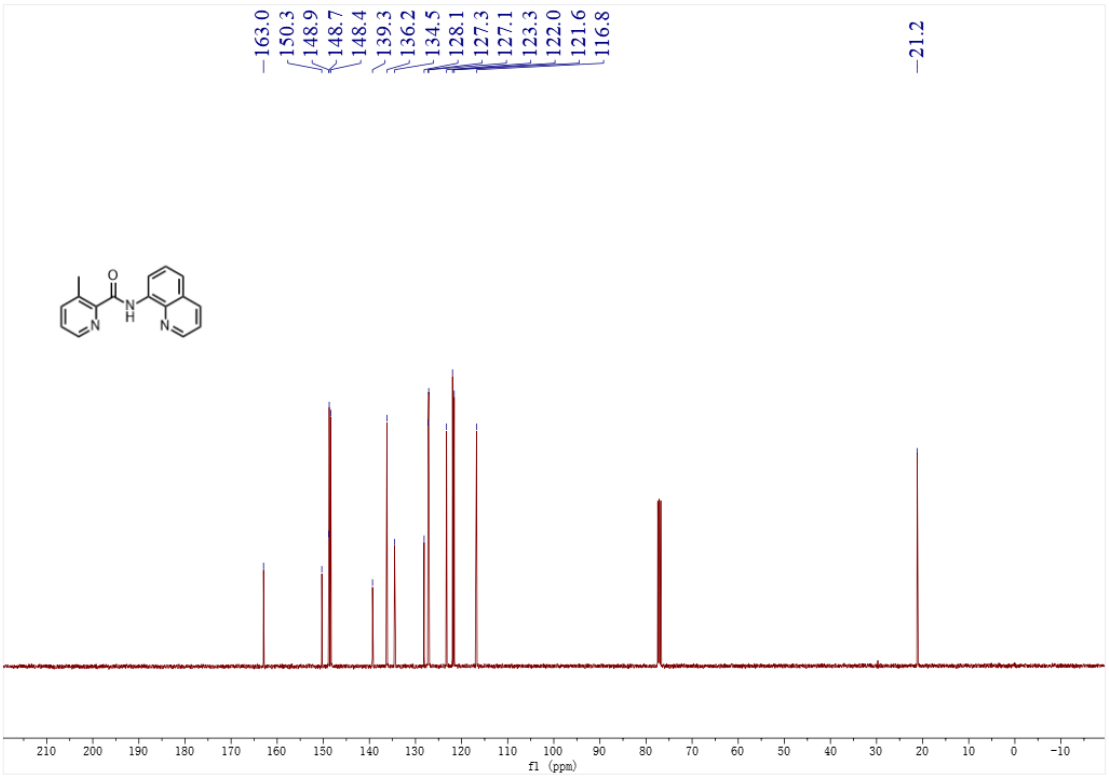
11. Spectra of compounds

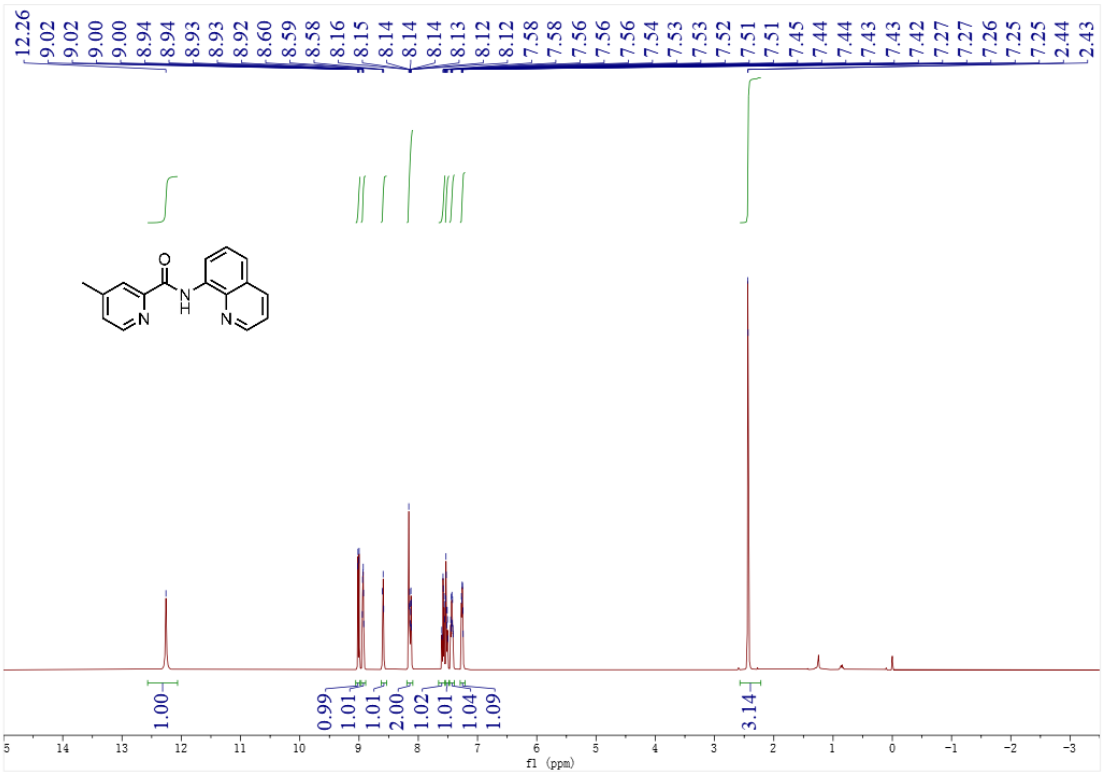
^{1}H NMR spectrum of **L12** ($CDCl_3$)



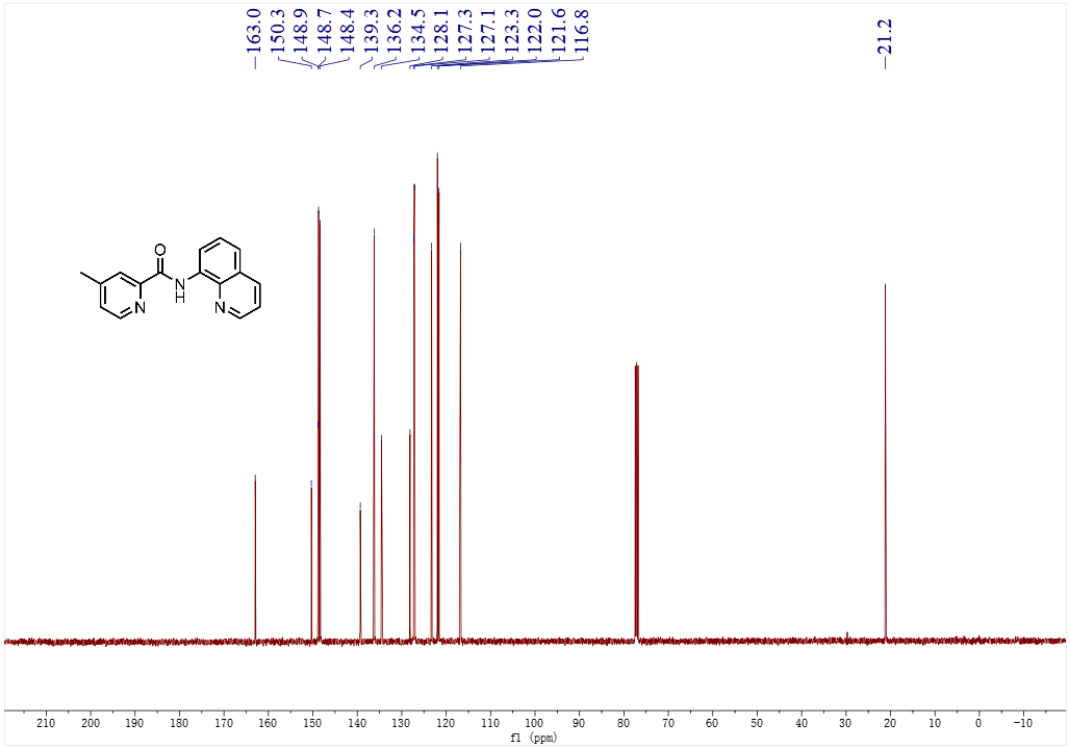
^{13}C NMR spectrum of **L12** ($CDCl_3$)



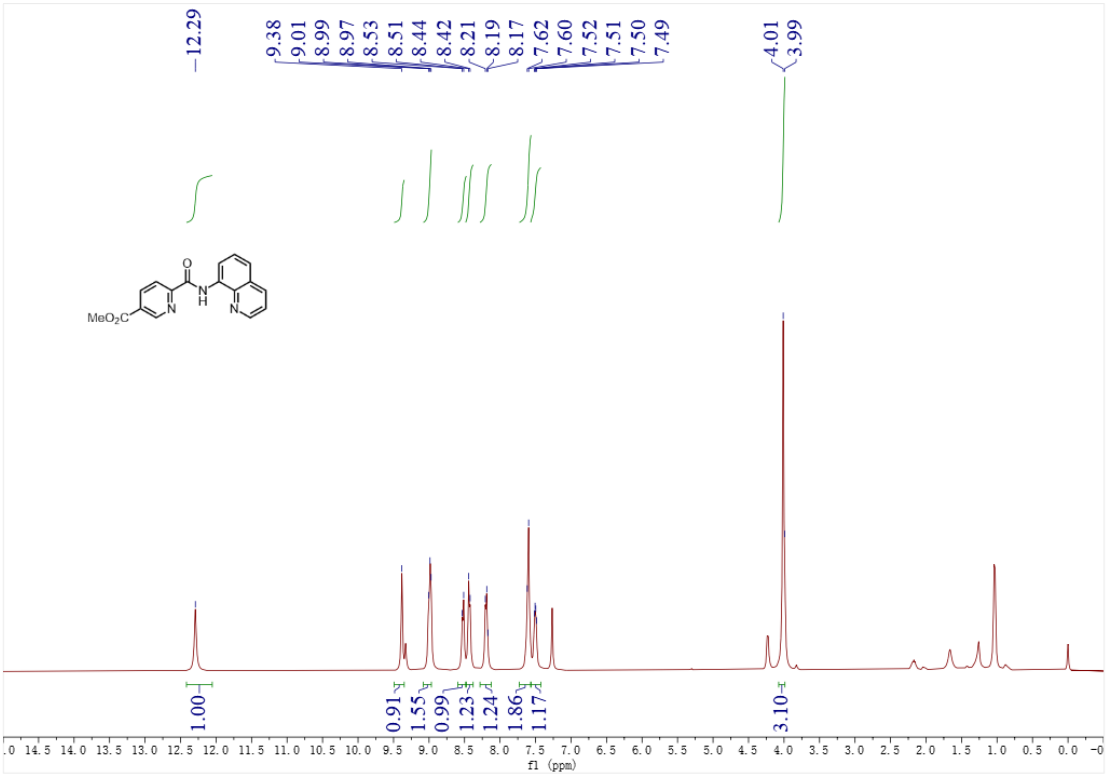
^{1}H NMR spectrum of **L13** ($CDCl_3$)



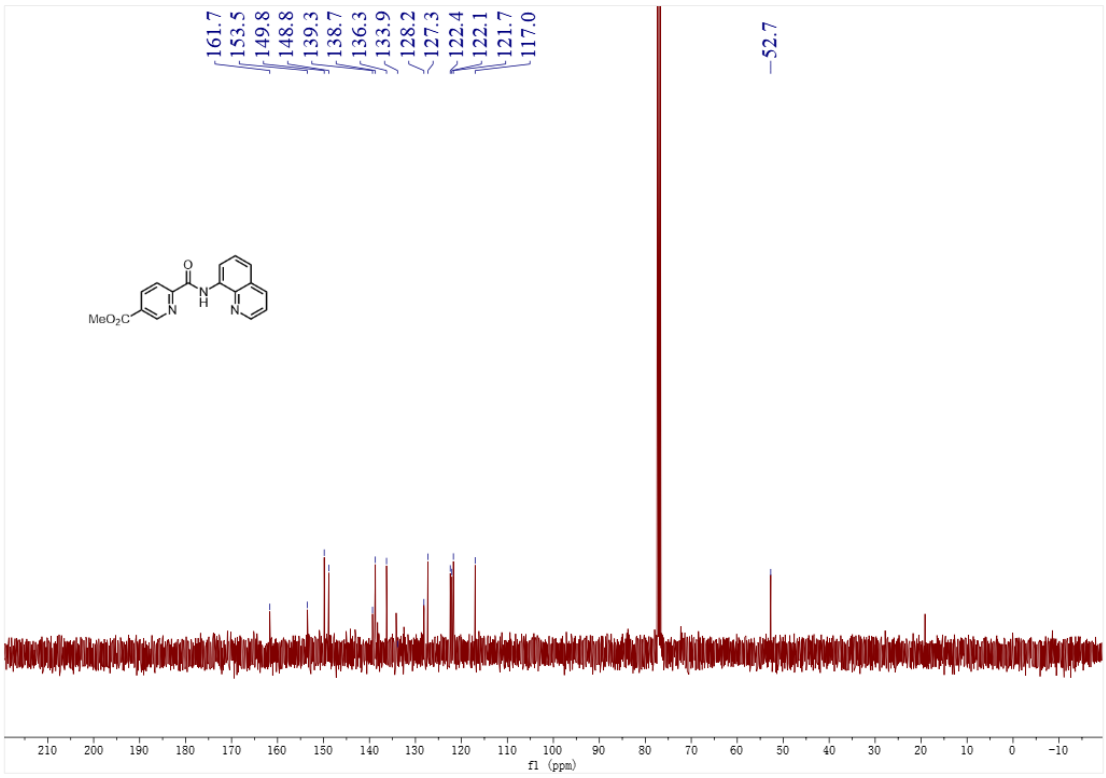
^{13}C NMR spectrum of **L13** ($CDCl_3$)



^{1}H NMR spectrum of **L15** ($CDCl_3$)



^{13}C NMR spectrum of **L15** ($CDCl_3$)



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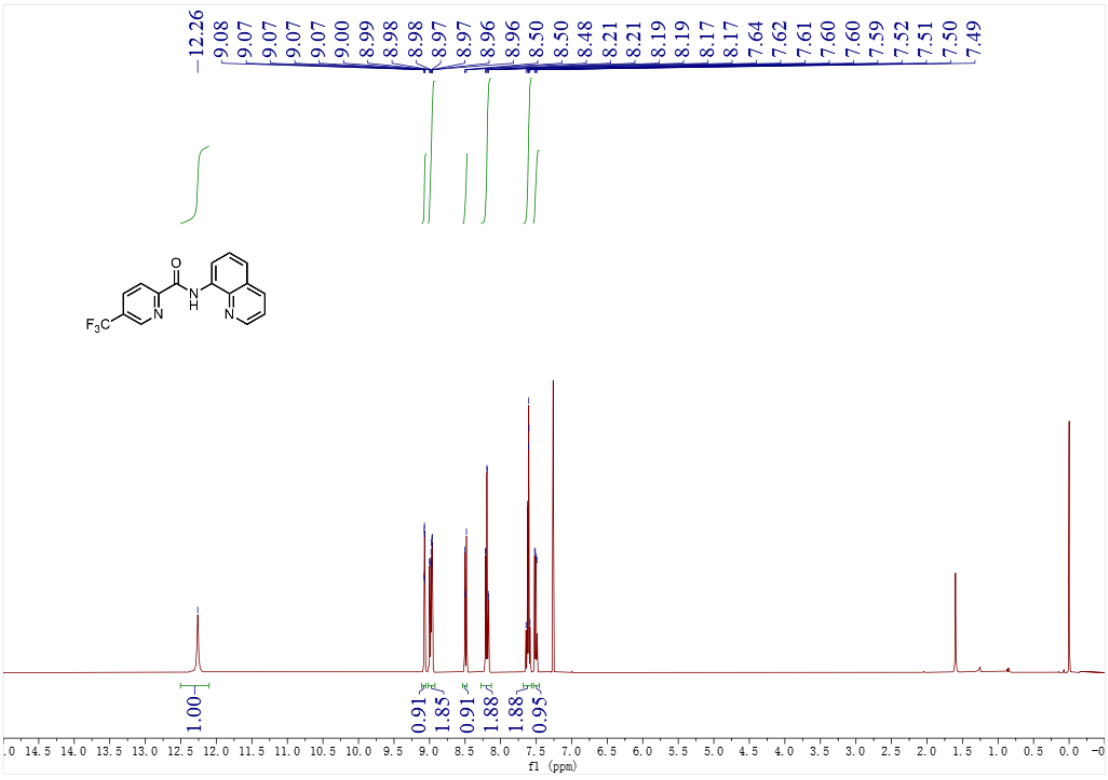

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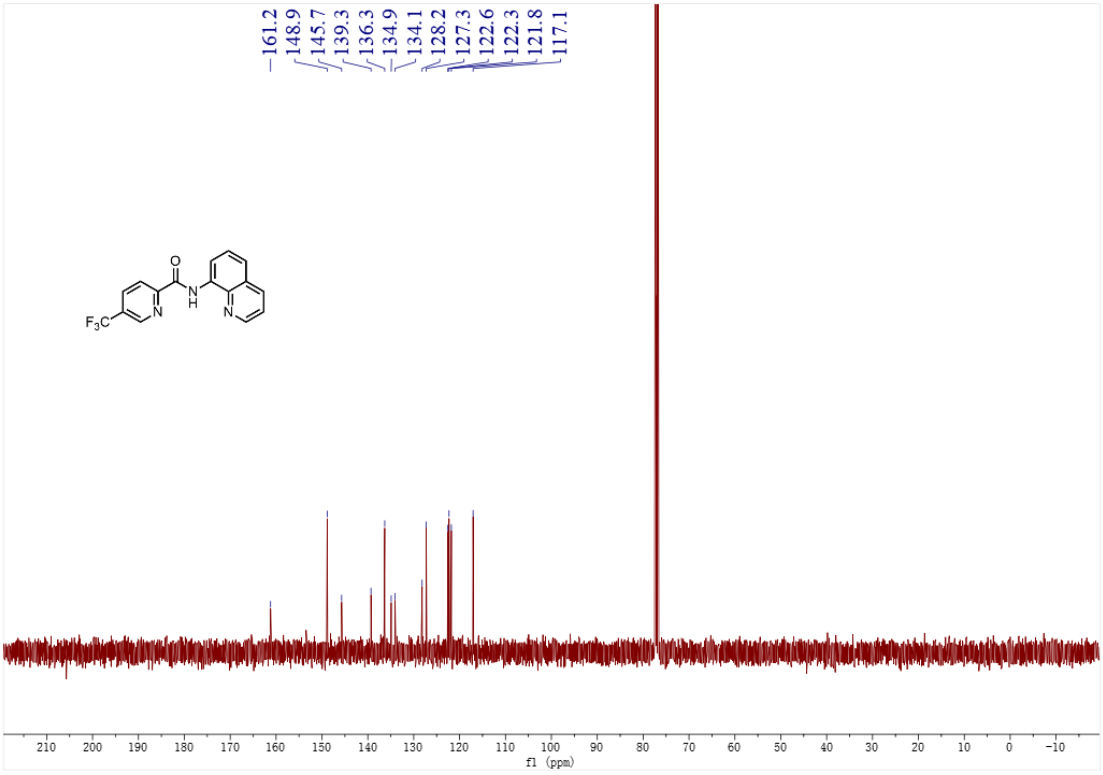
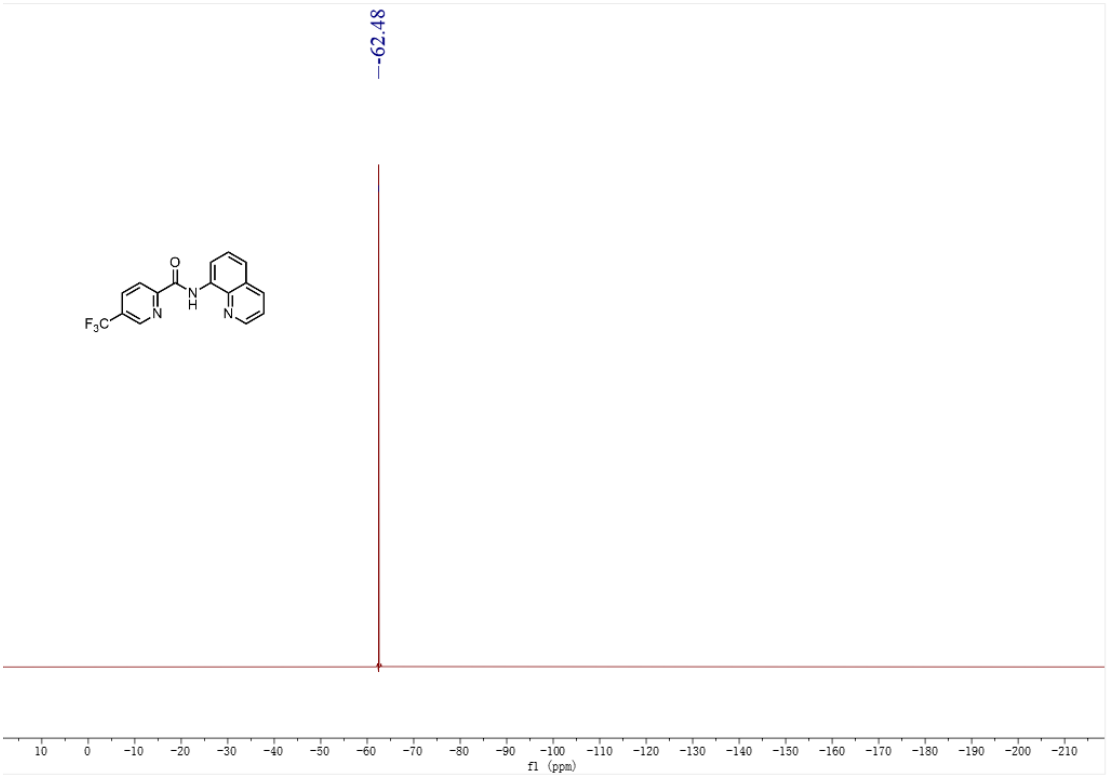


^{19}F NMR spectrum of **L16** ($CDCl_3$)



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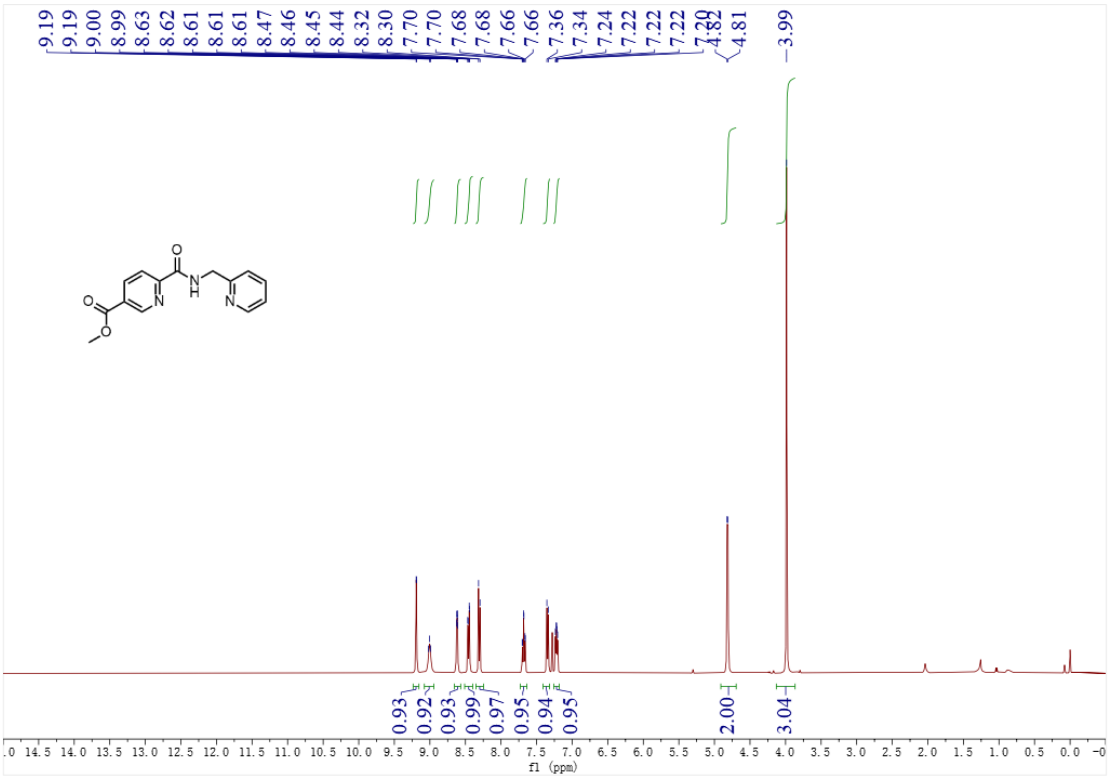
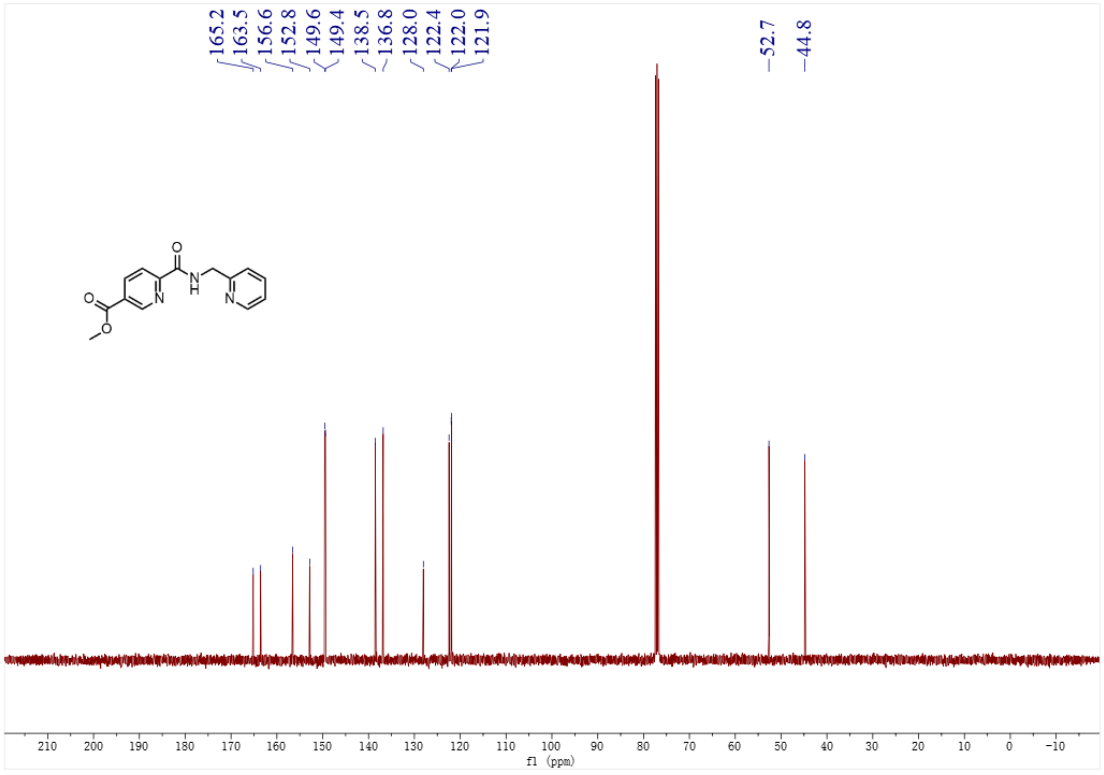
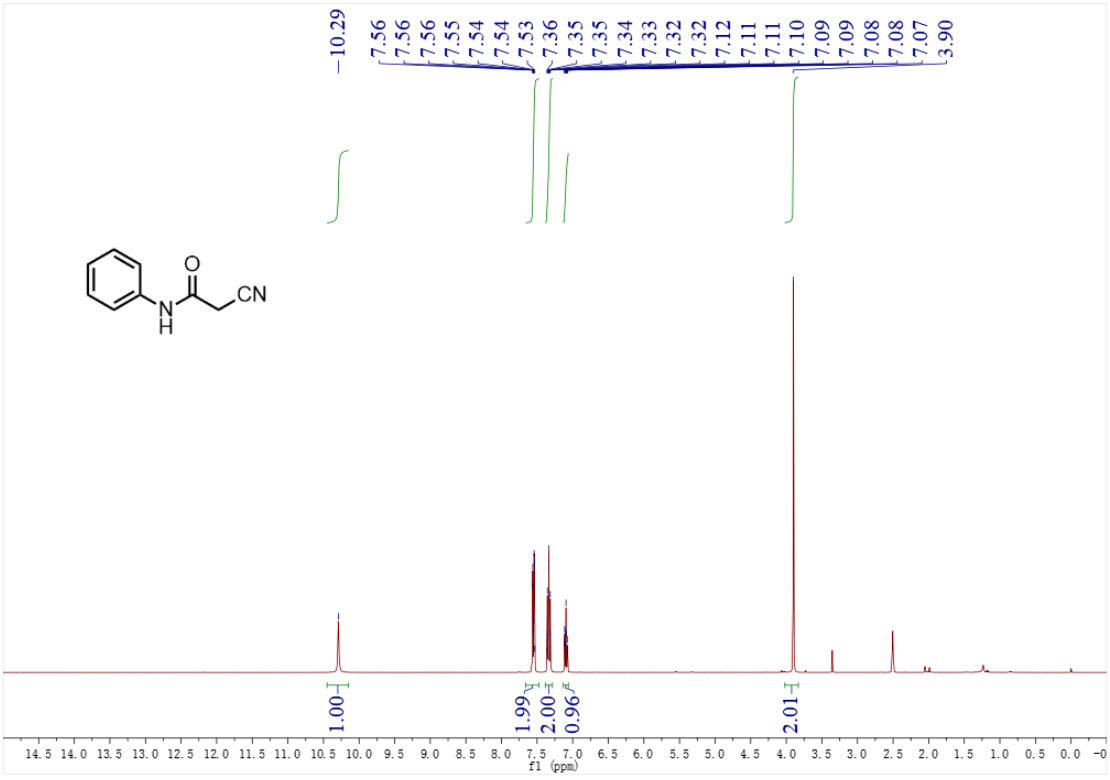


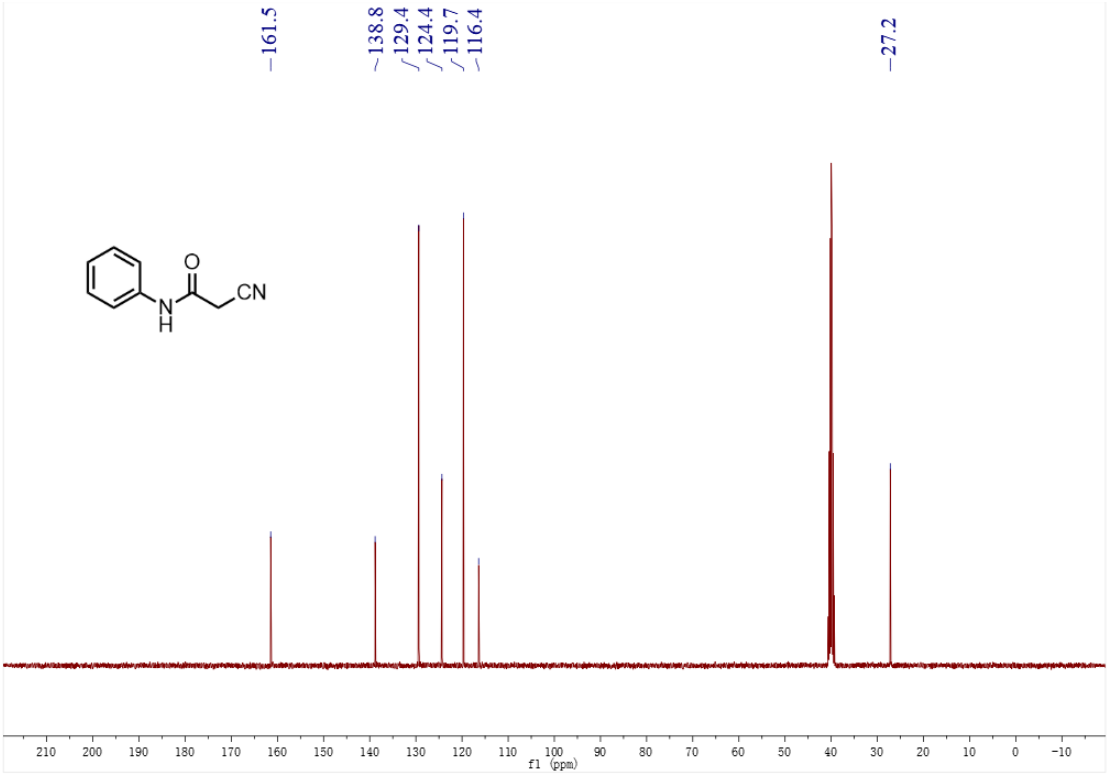
^{13}C NMR spectrum of **L17** ($CDCl_3$)



^{1}H NMR spectrum of **1** (DMSO-d_6)



^{13}C NMR spectrum of **1** (DMSO-d_6)



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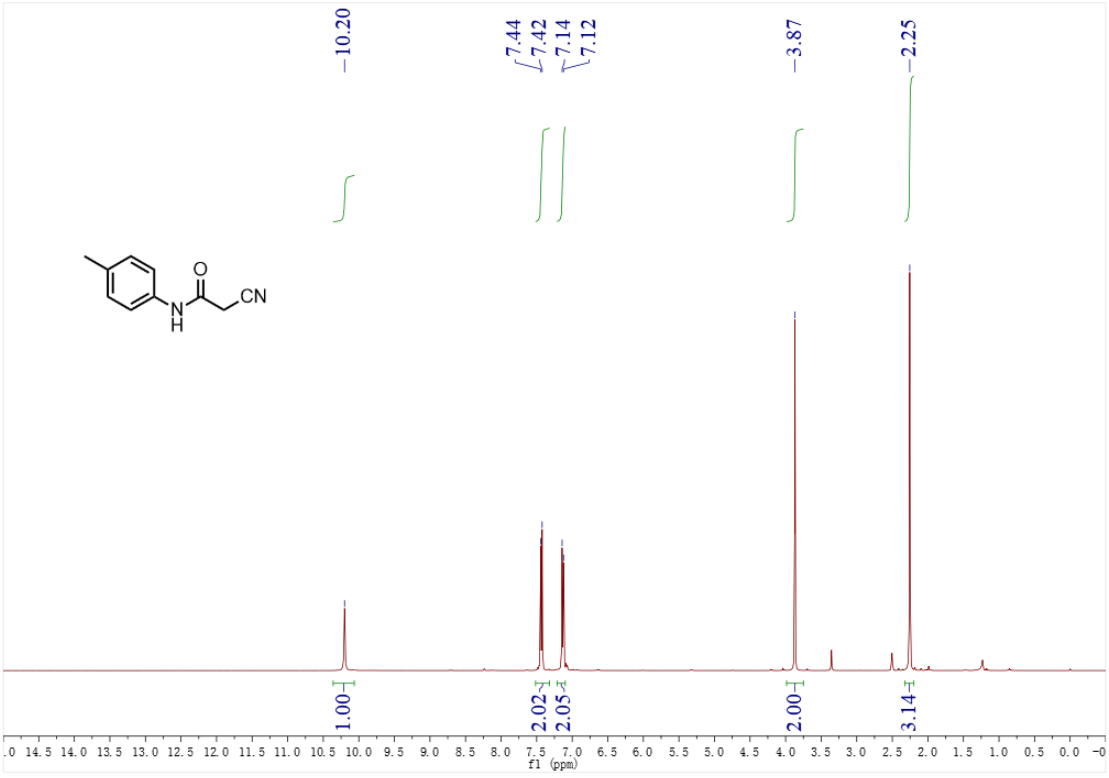
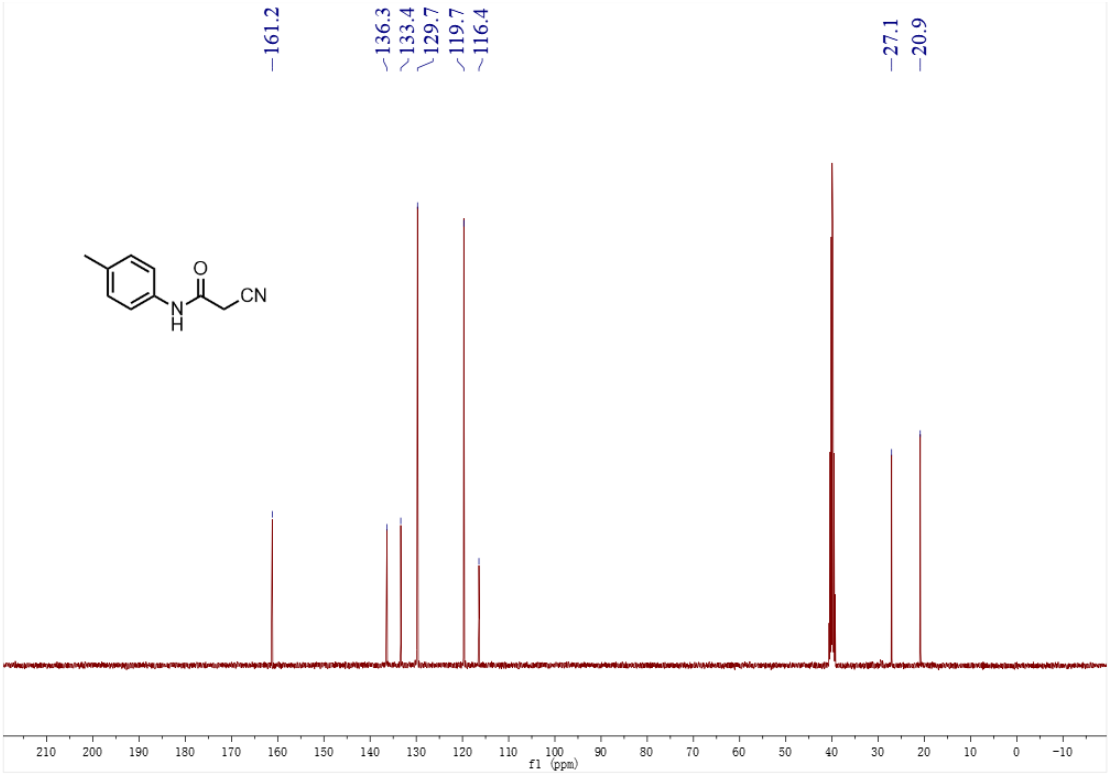
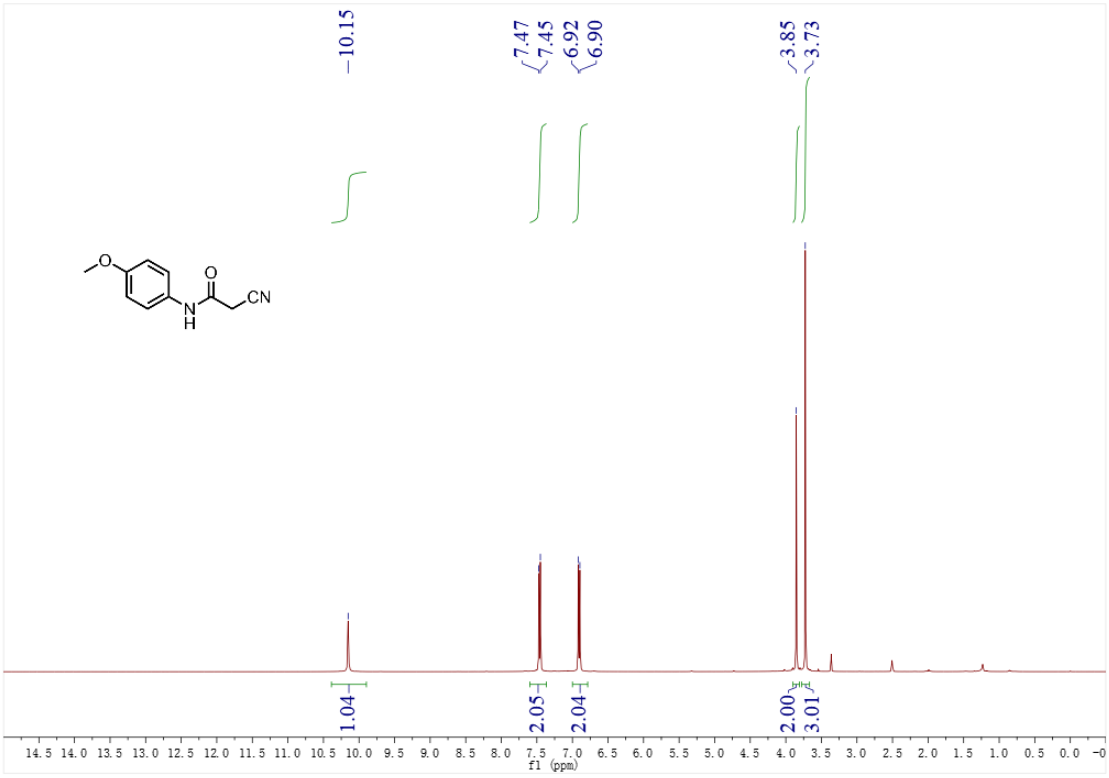


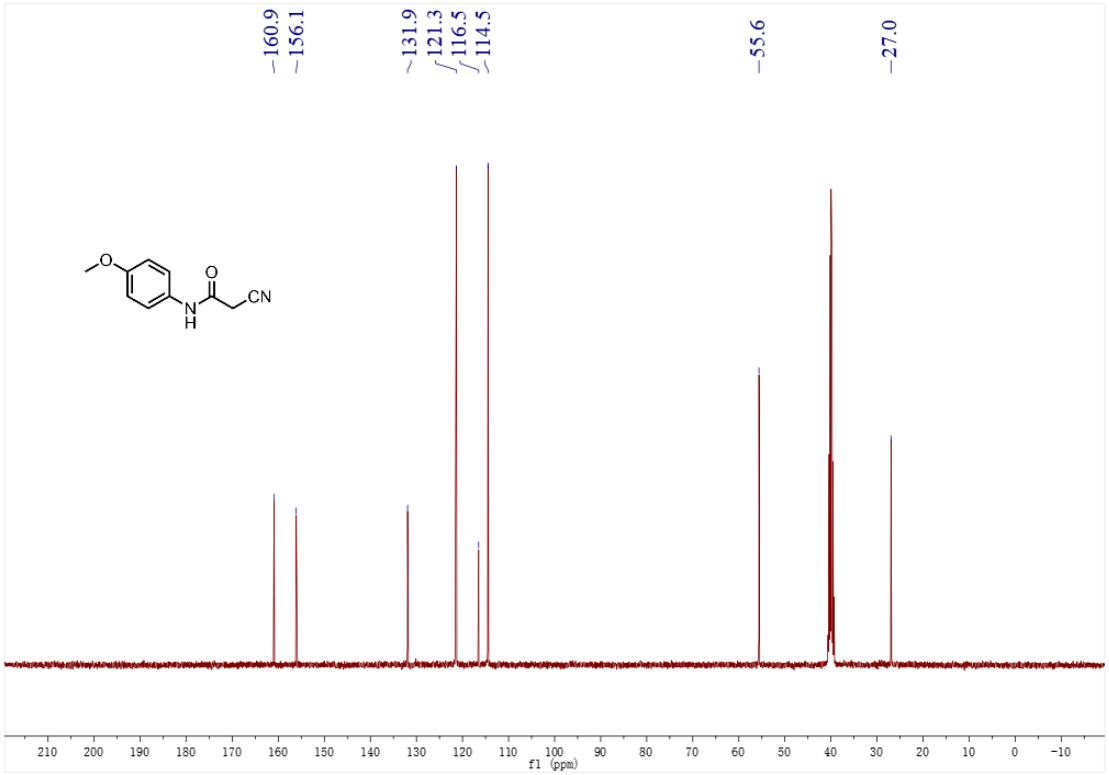
^{13}C NMR spectrum of **2** (DMSO-d_6)



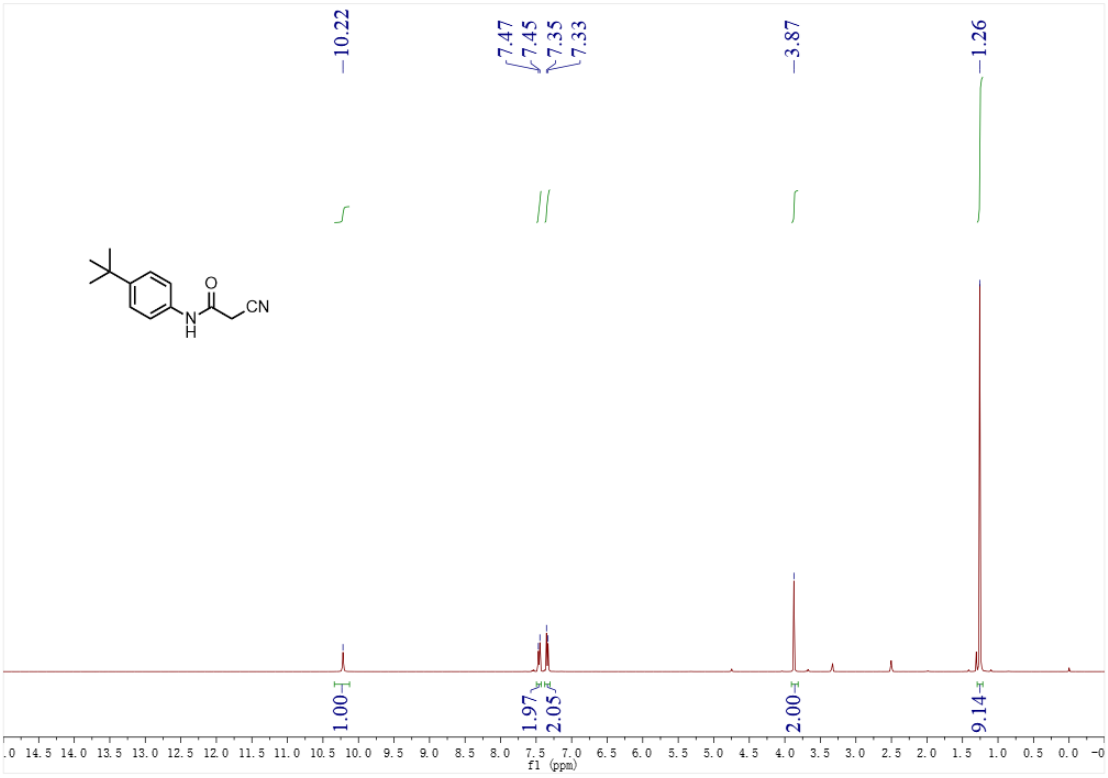
^{1}H NMR spectrum of **3** (DMSO-d_6)



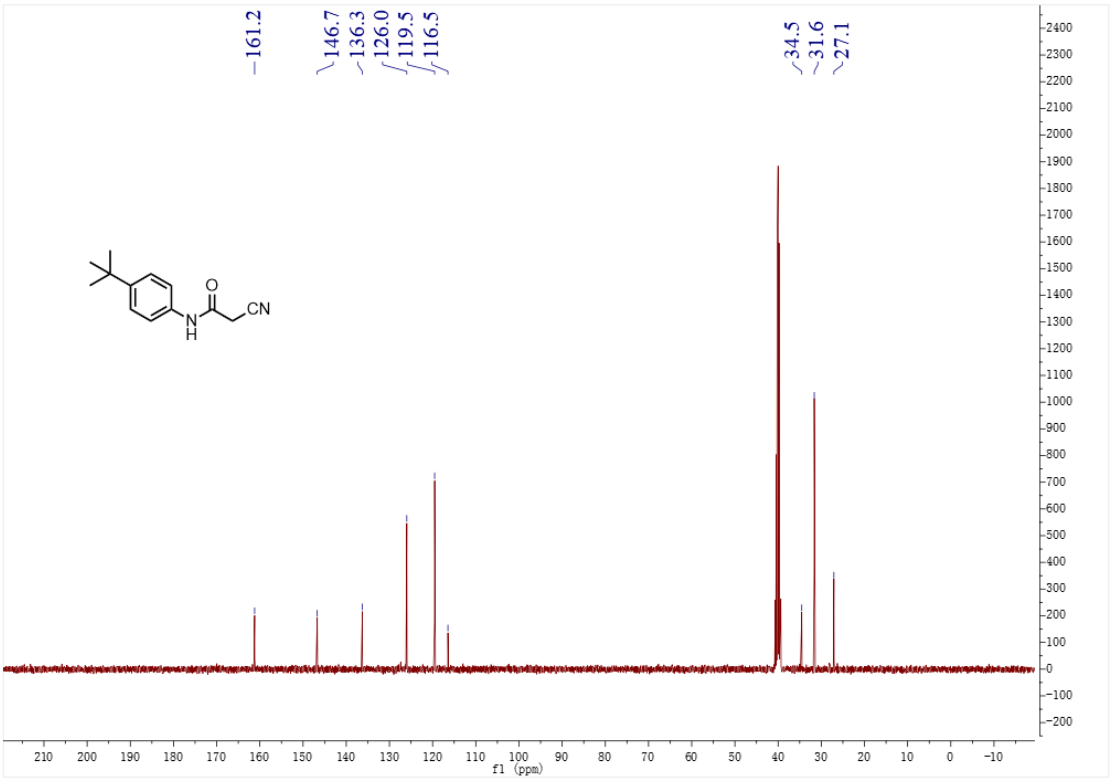
^{13}C NMR spectrum of **3** (DMSO-d_6)



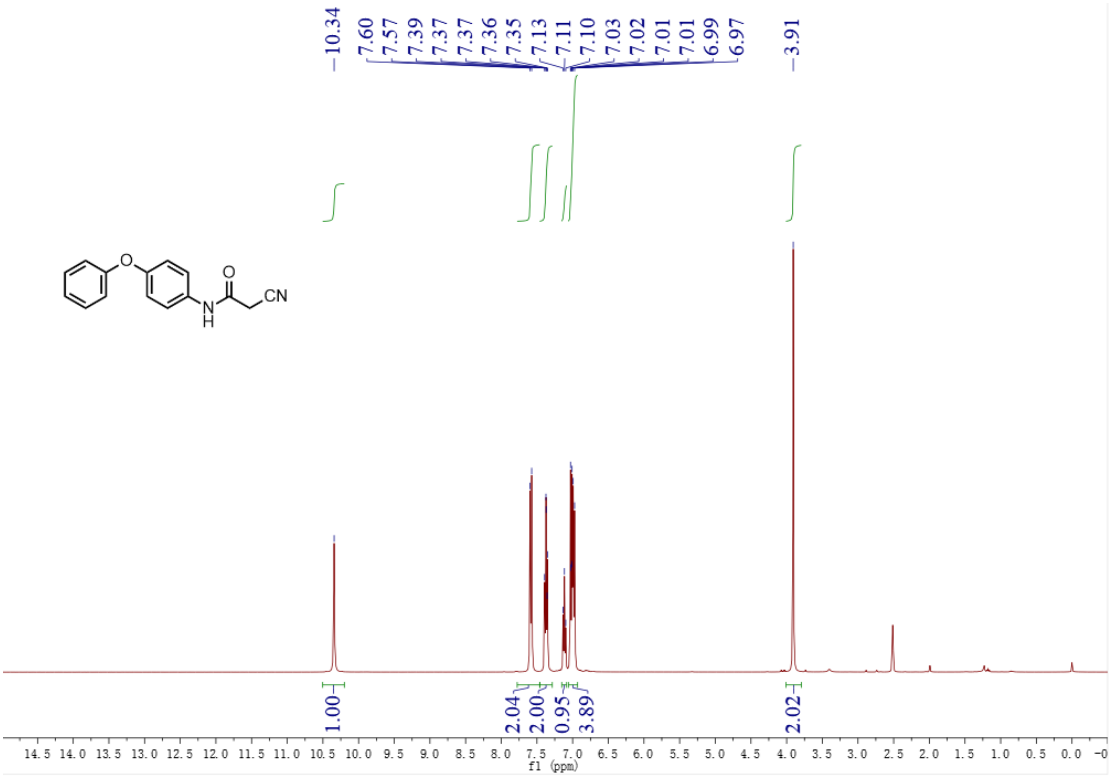
^{1}H NMR spectrum of **4** (DMSO-d_6)



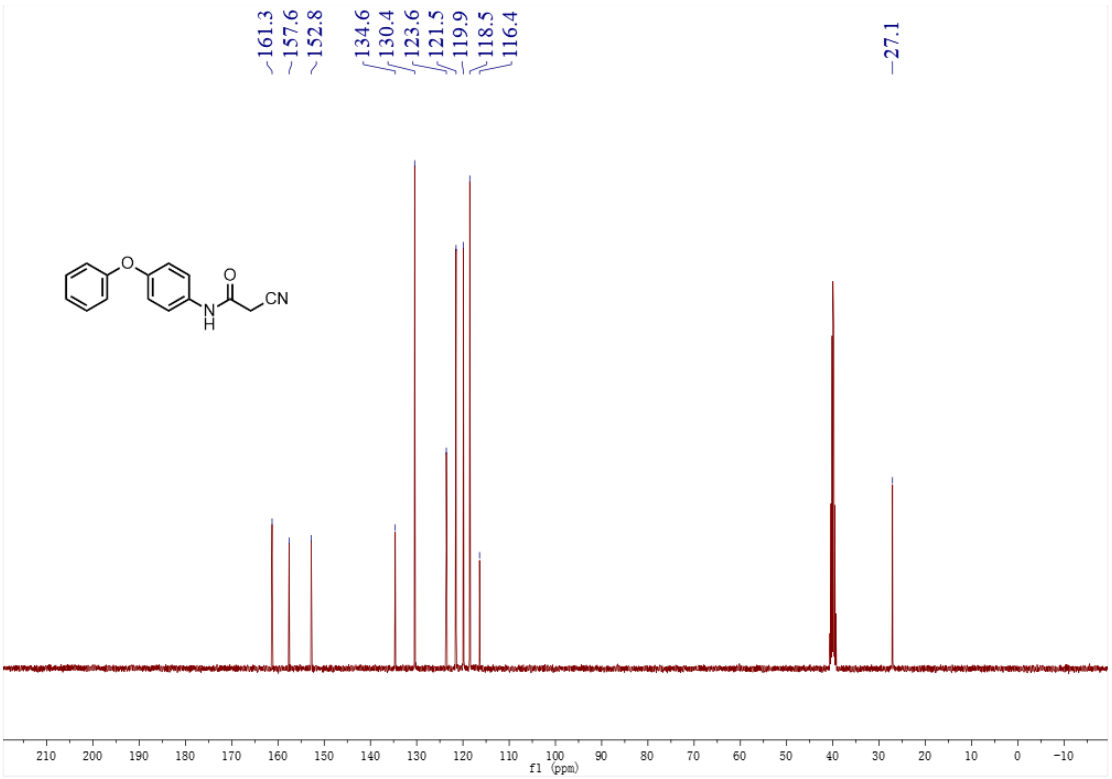
^{13}C NMR spectrum of **4** (DMSO-d_6)



^{1}H NMR spectrum of **5** (DMSO-d_6)



^{13}C NMR spectrum of **5** (DMSO-d_6)



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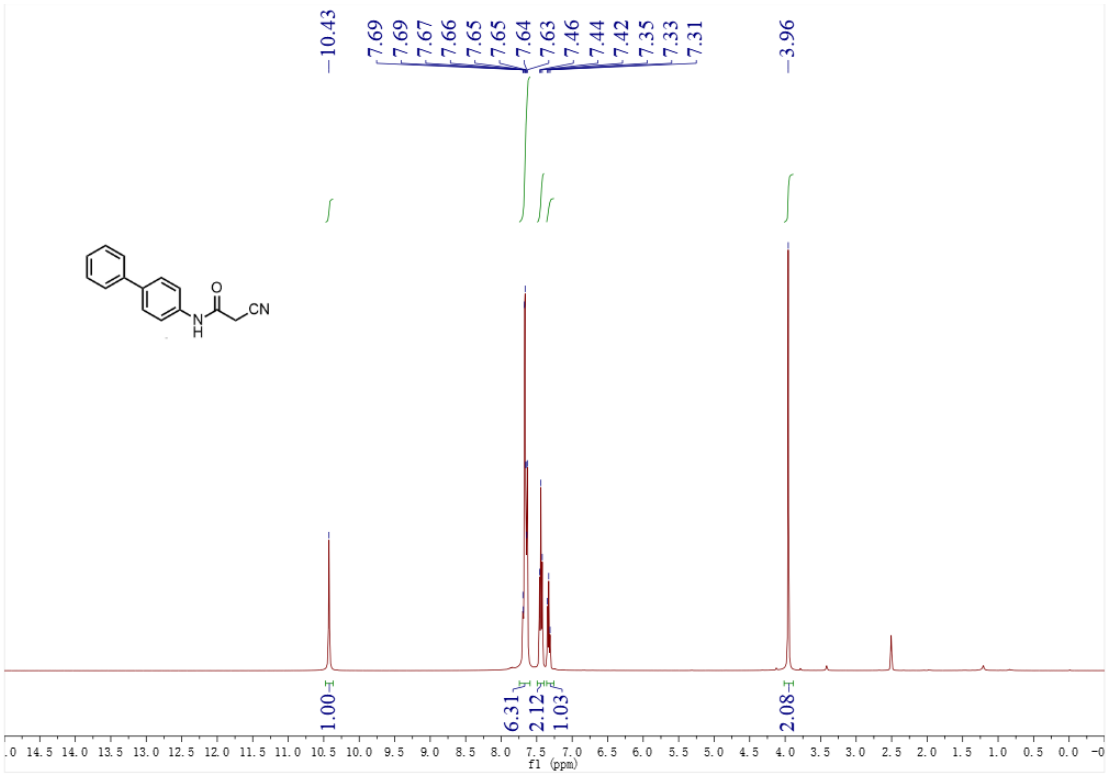
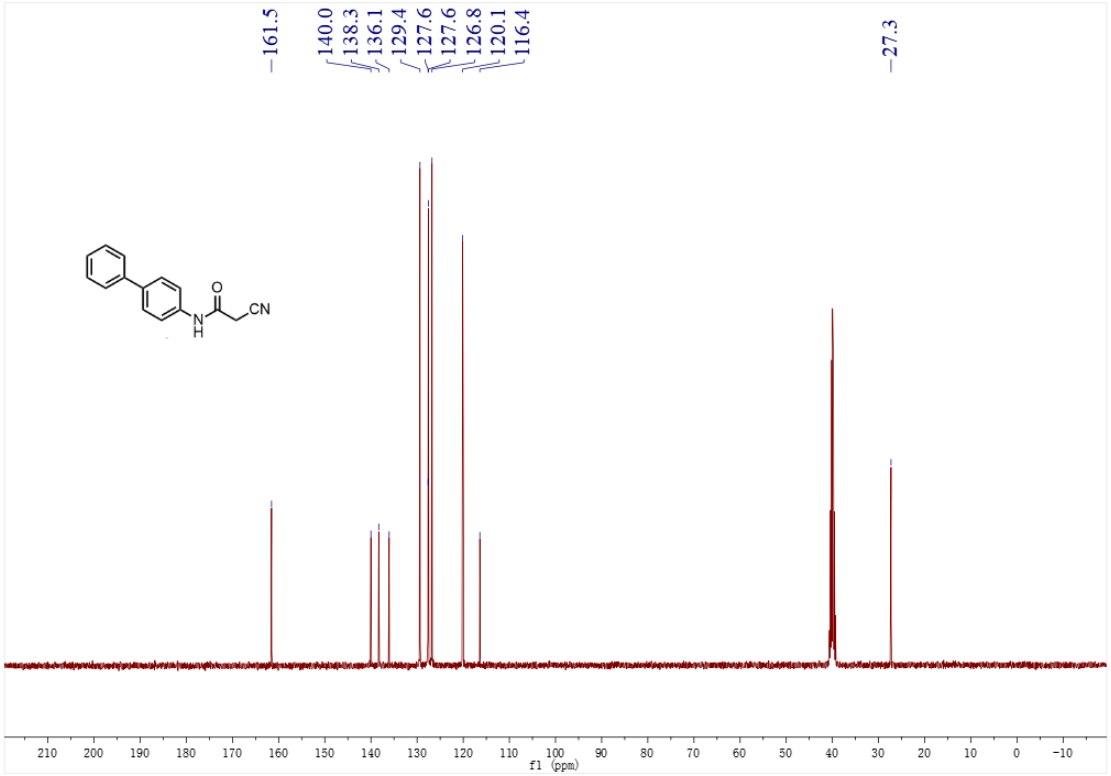


^{13}C NMR spectrum of **6** (DMSO-d_6)



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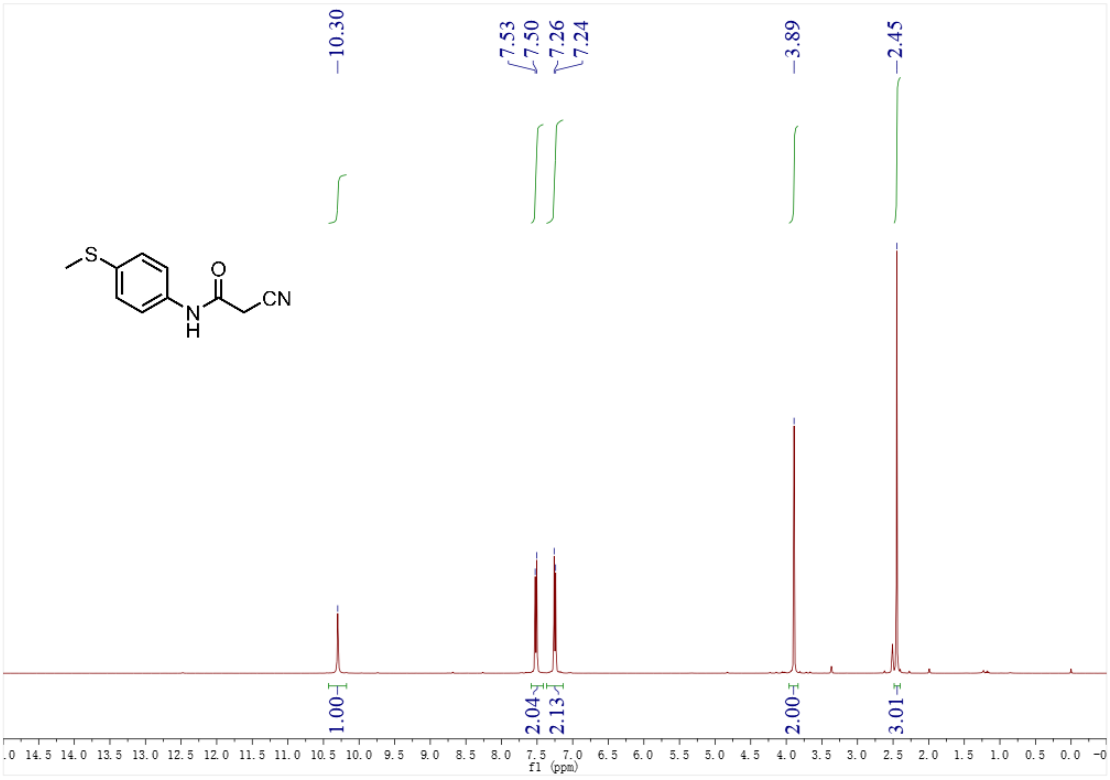
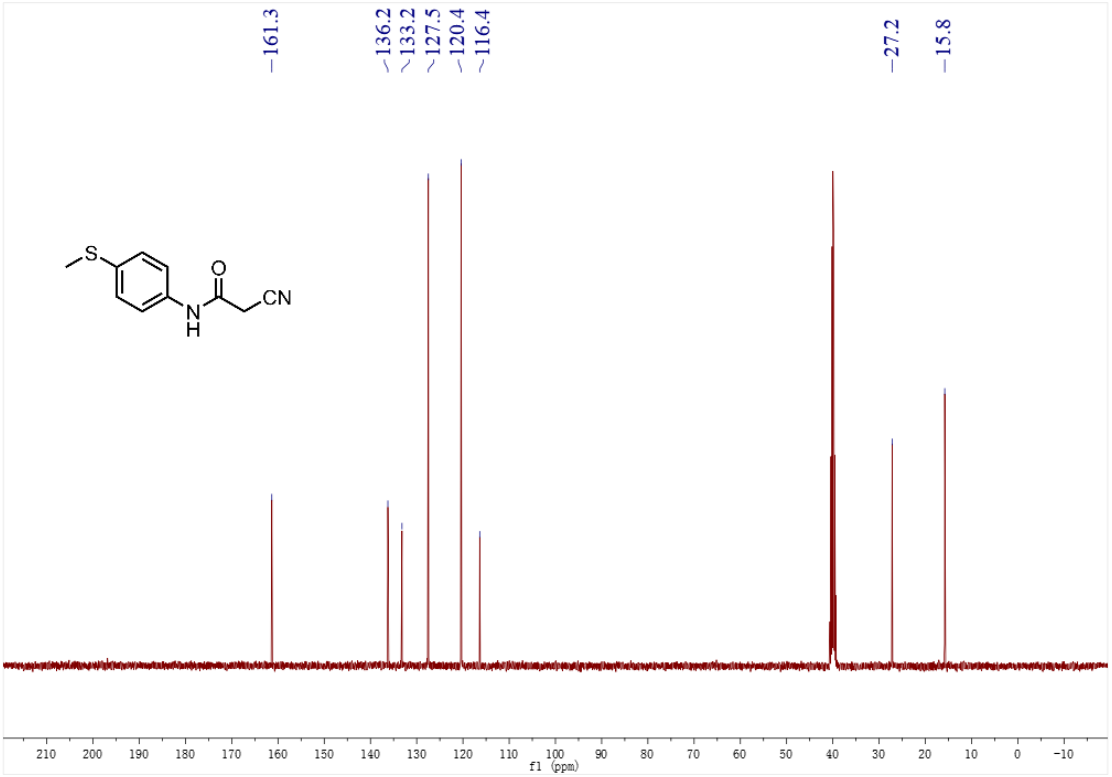
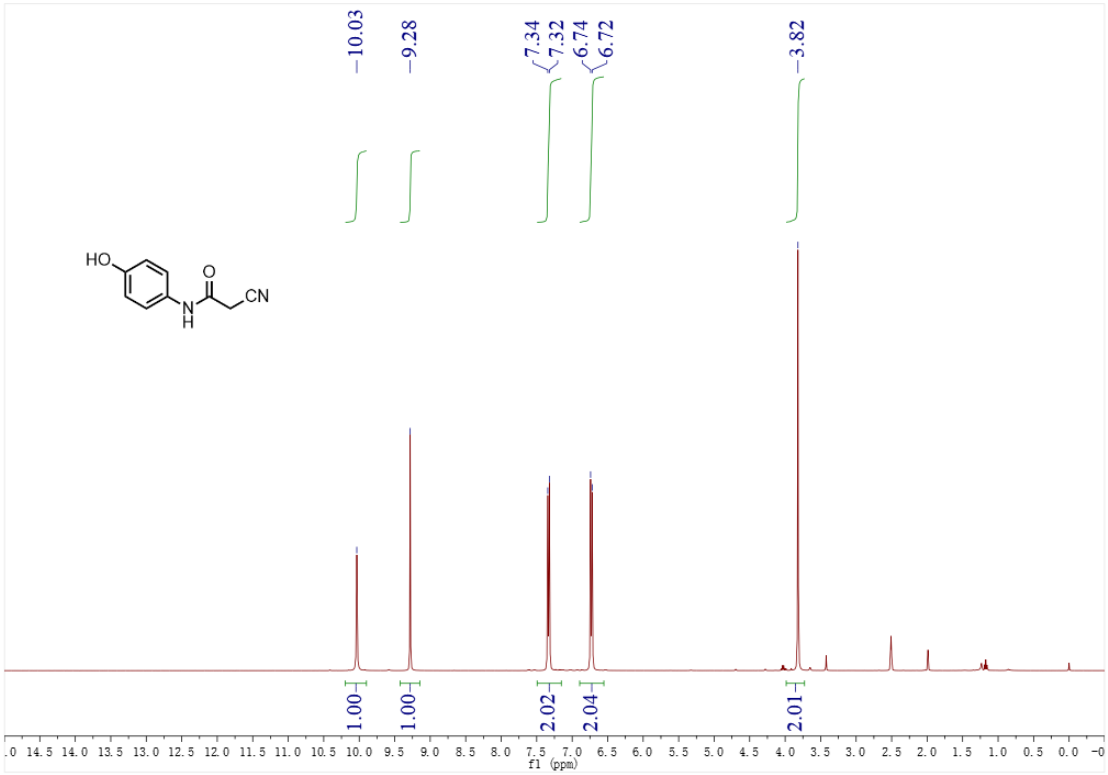


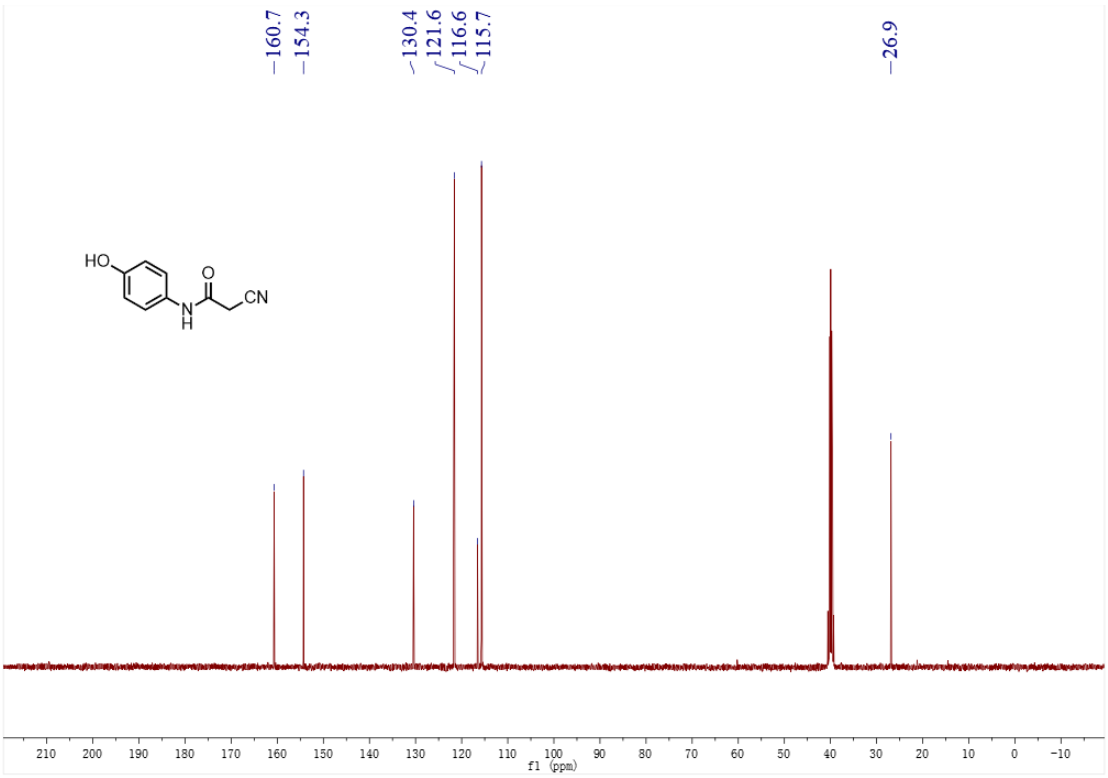
^{13}C NMR spectrum of **7** (DMSO-d_6)



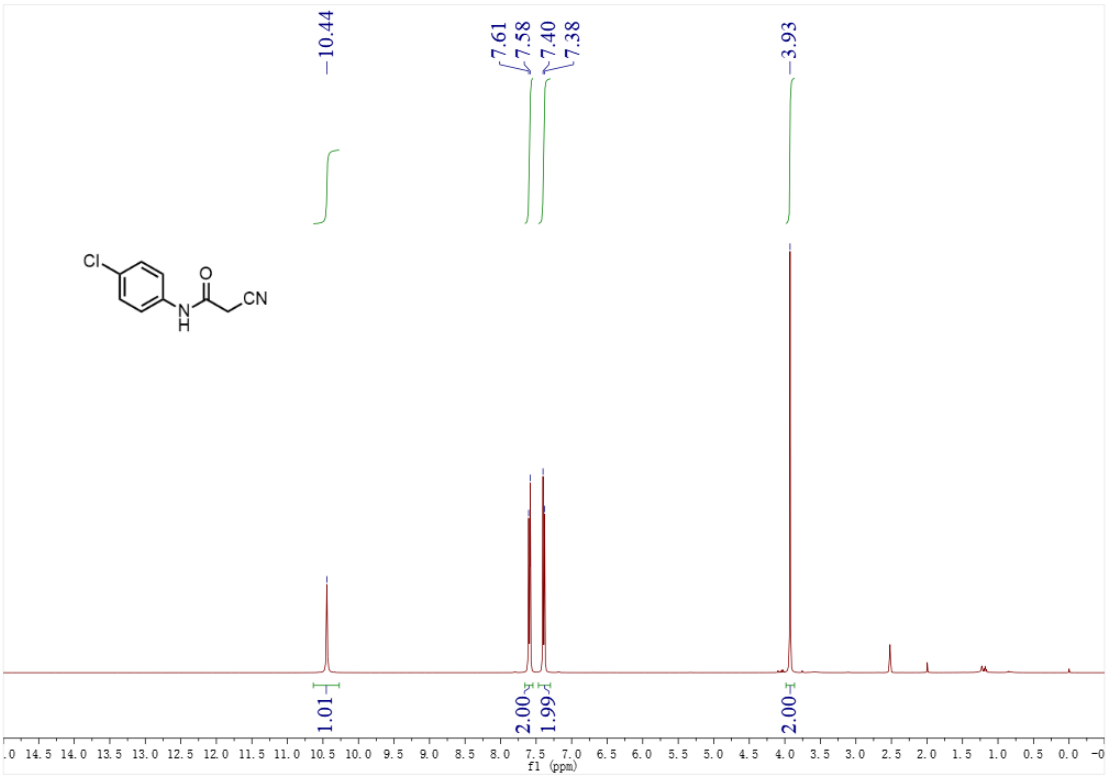
^{1}H NMR spectrum of **8** (DMSO-d_6)



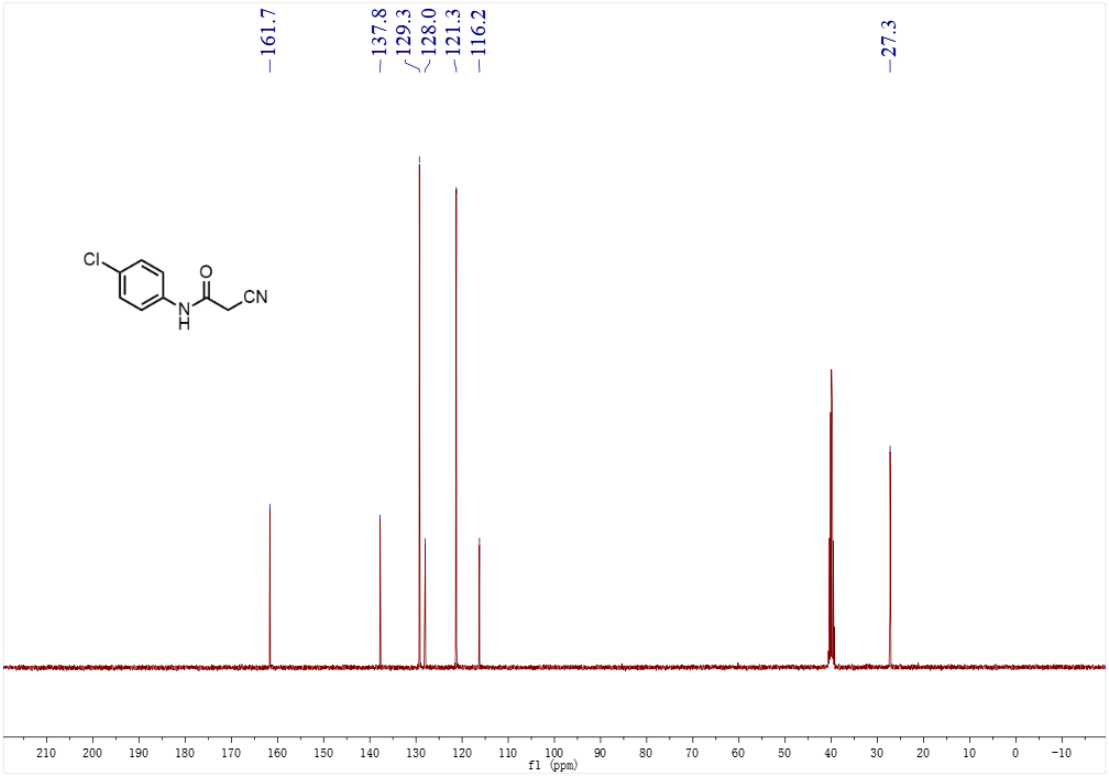
^{13}C NMR spectrum of **8** (DMSO-d_6)



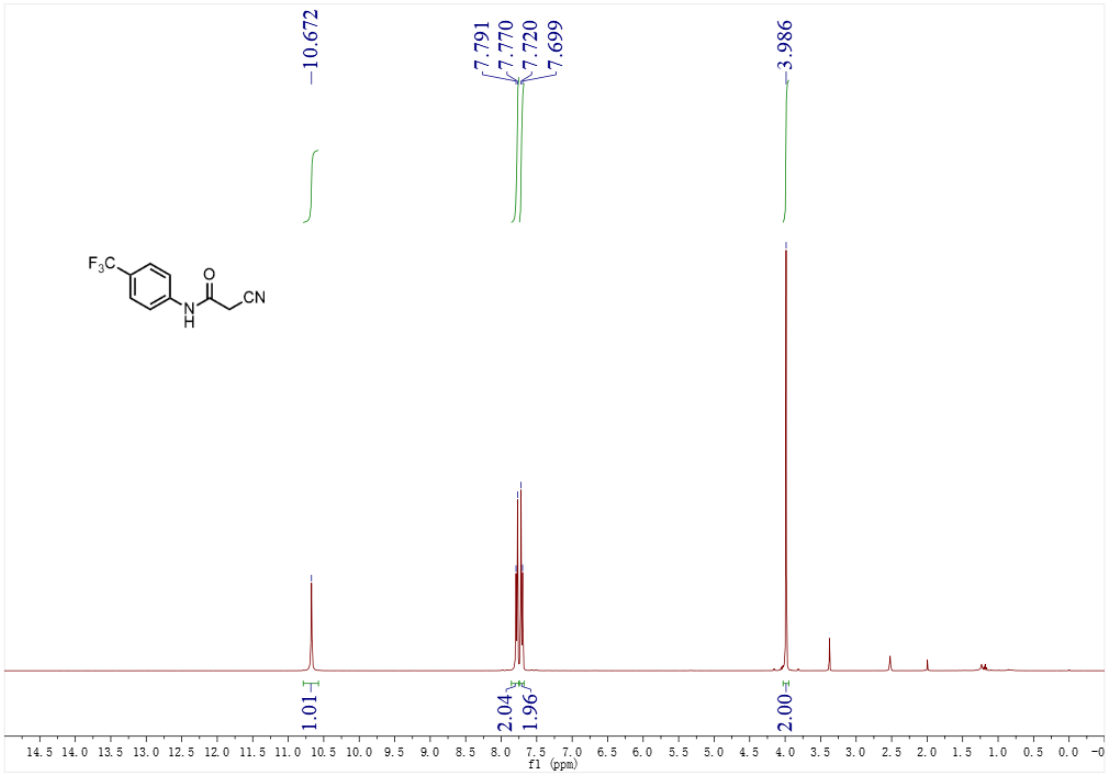
^{1}H NMR spectrum of **9** (DMSO-d_6)



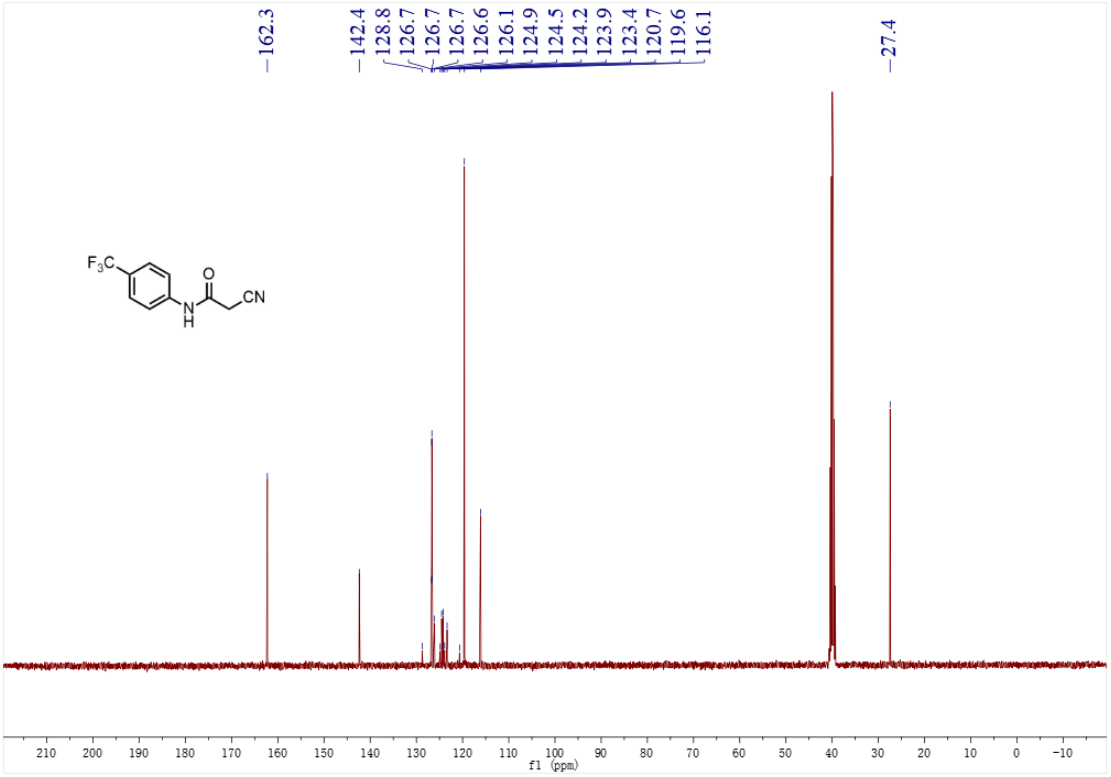
^{13}C NMR spectrum of **9** (DMSO-d_6)



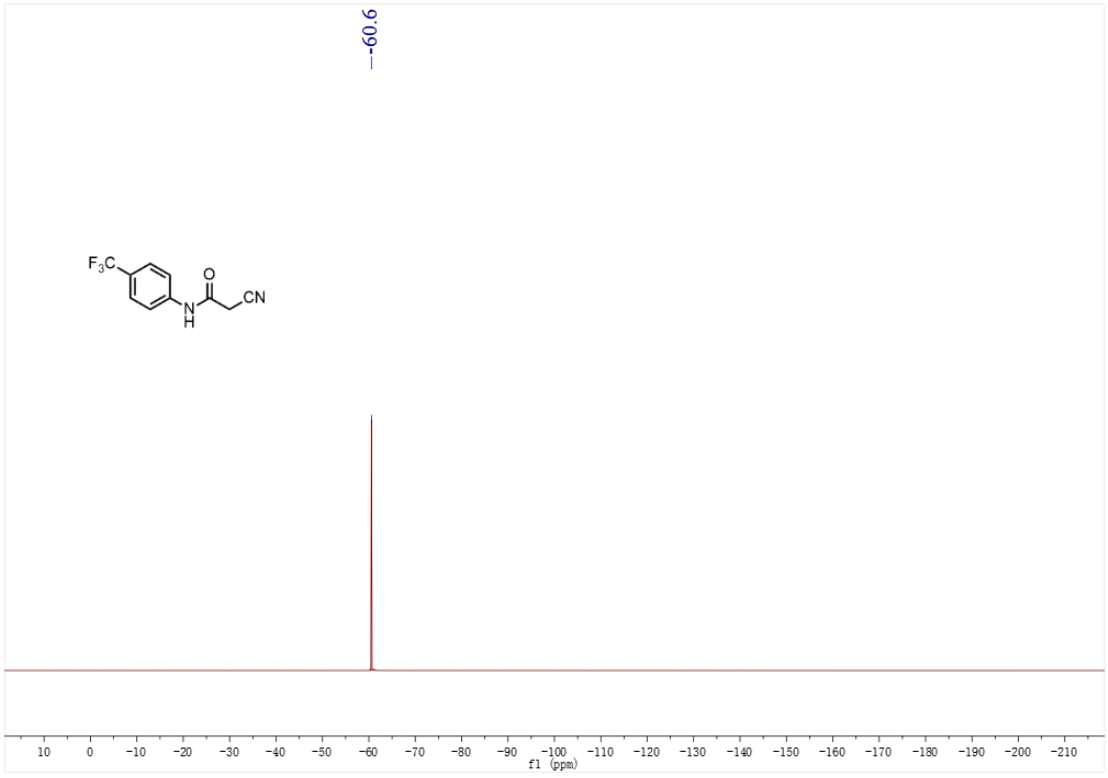
^{1}H NMR spectrum of **10** (DMSO-d_6)



^{13}C NMR spectrum of **10** (DMSO-d_6)



^{19}F NMR spectrum of **10** (DMSO-d_6)



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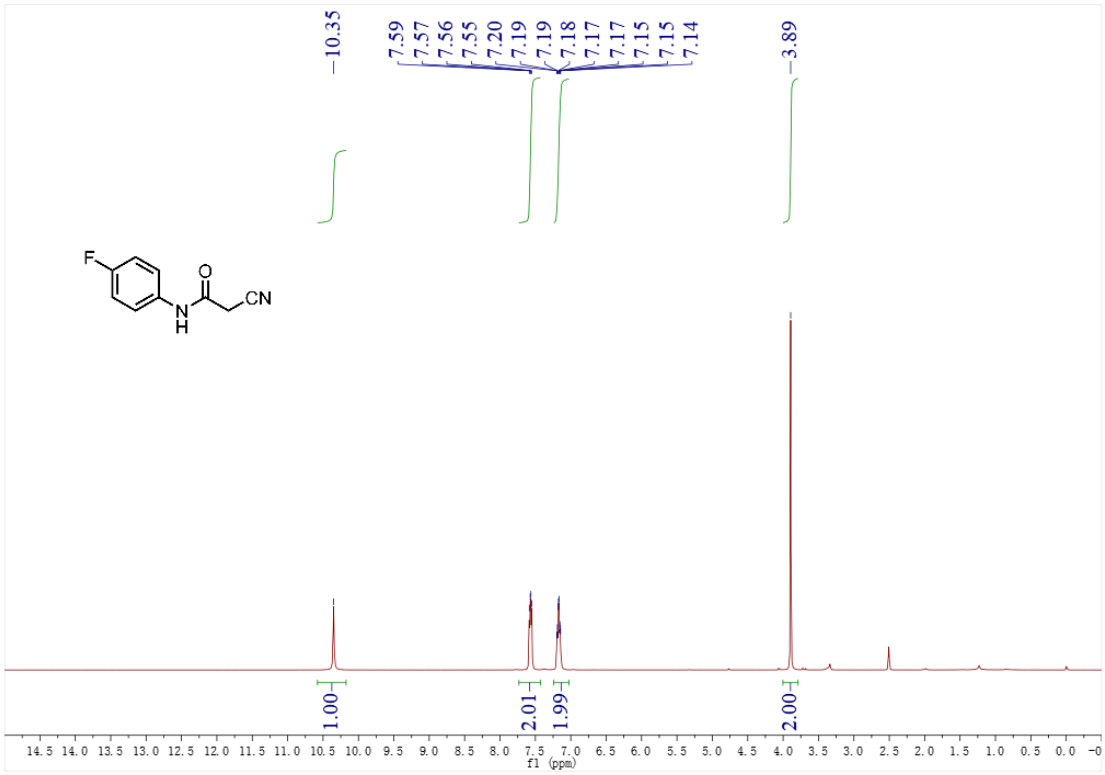

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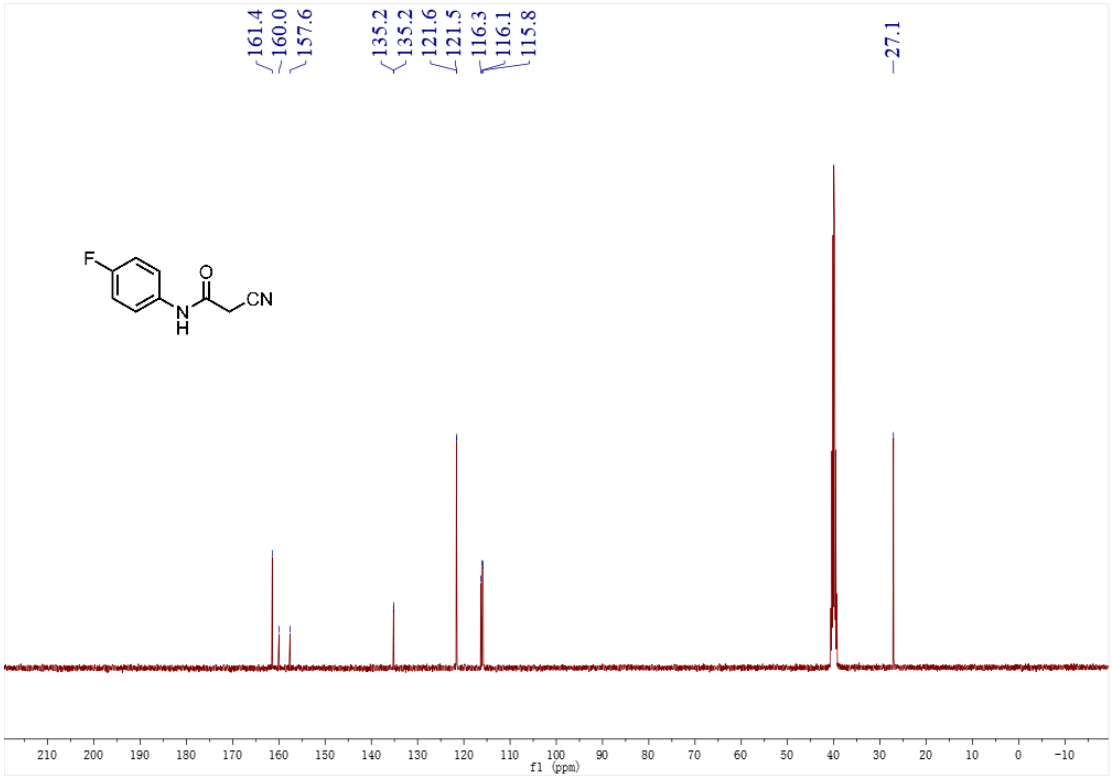

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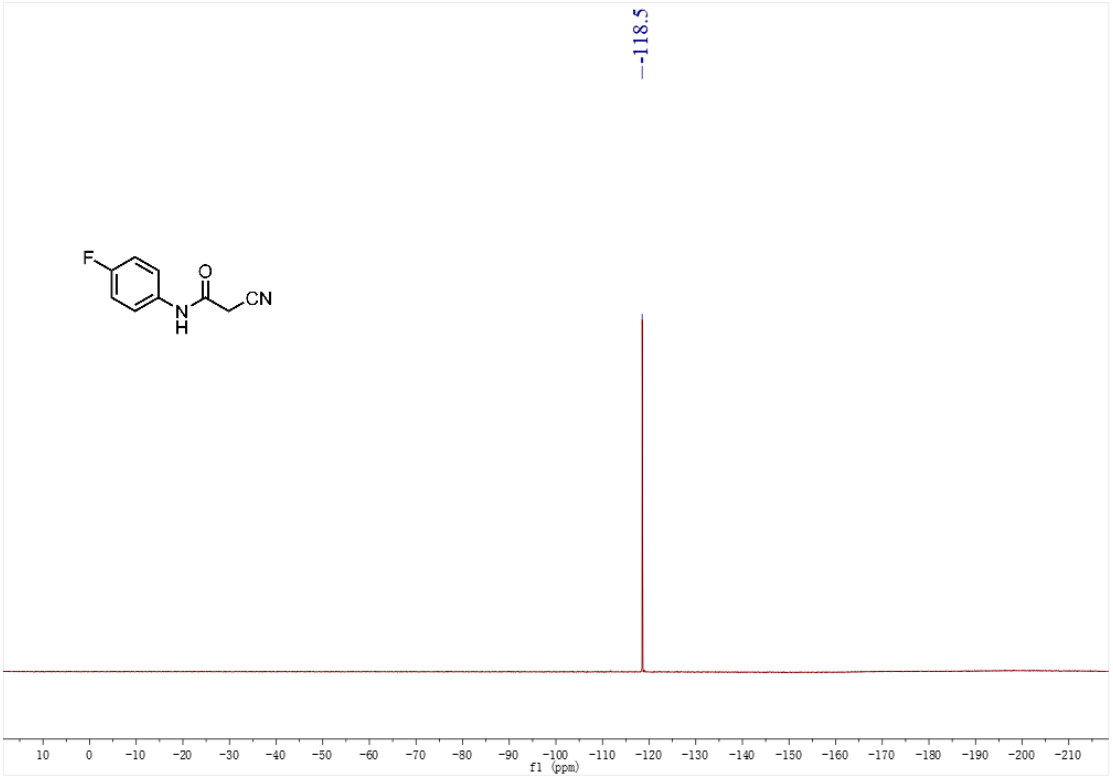

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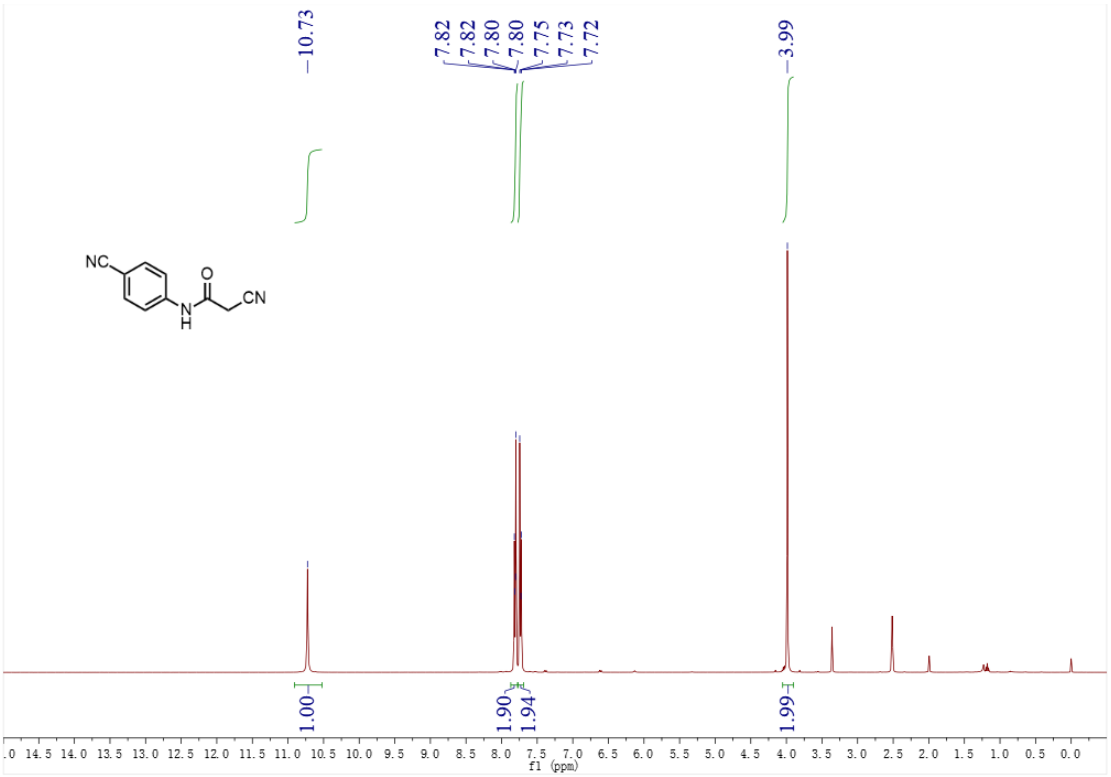

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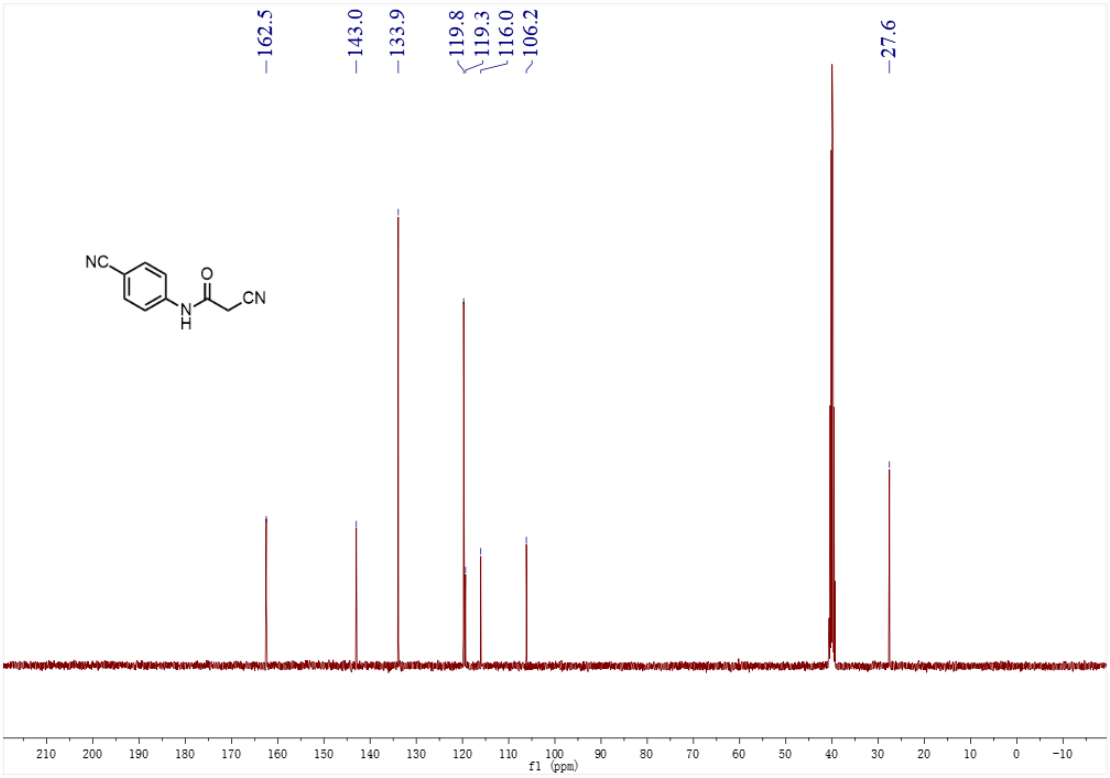

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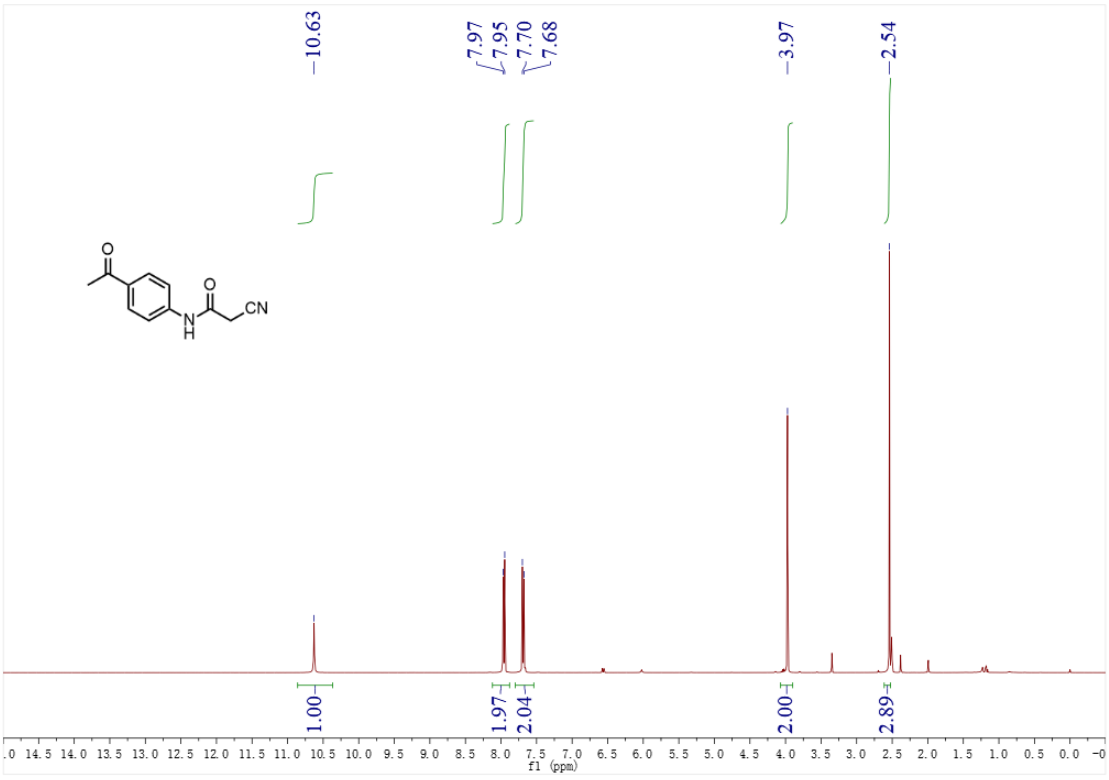

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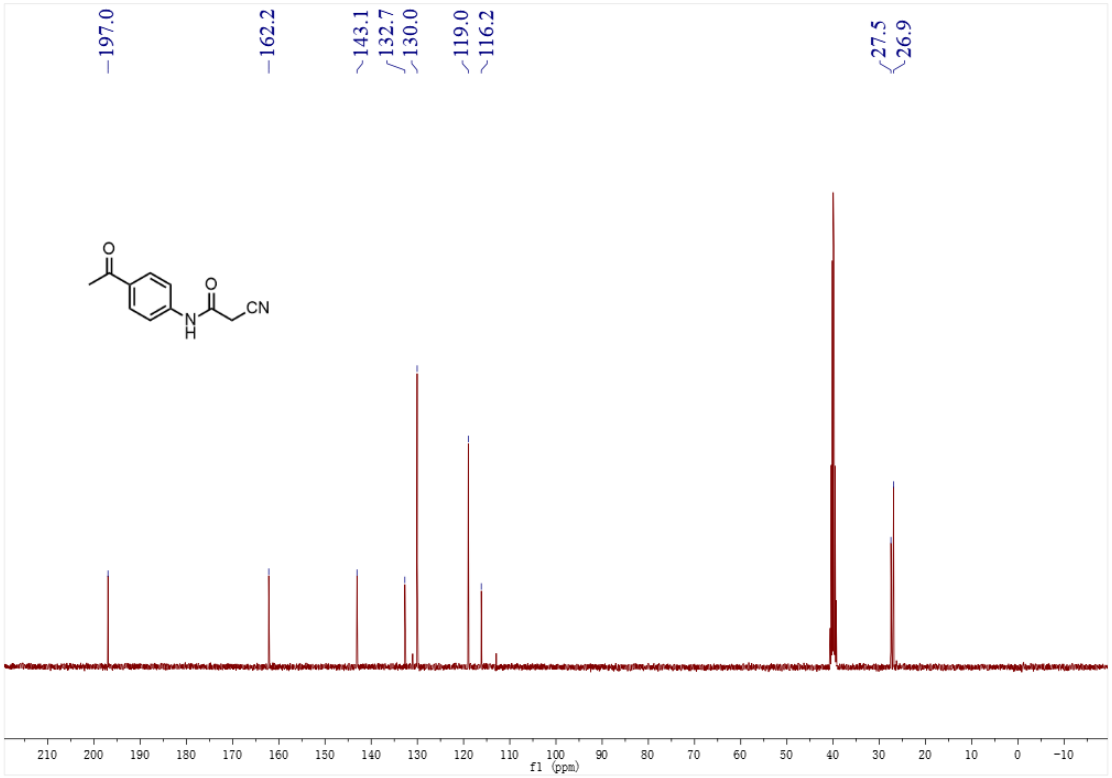

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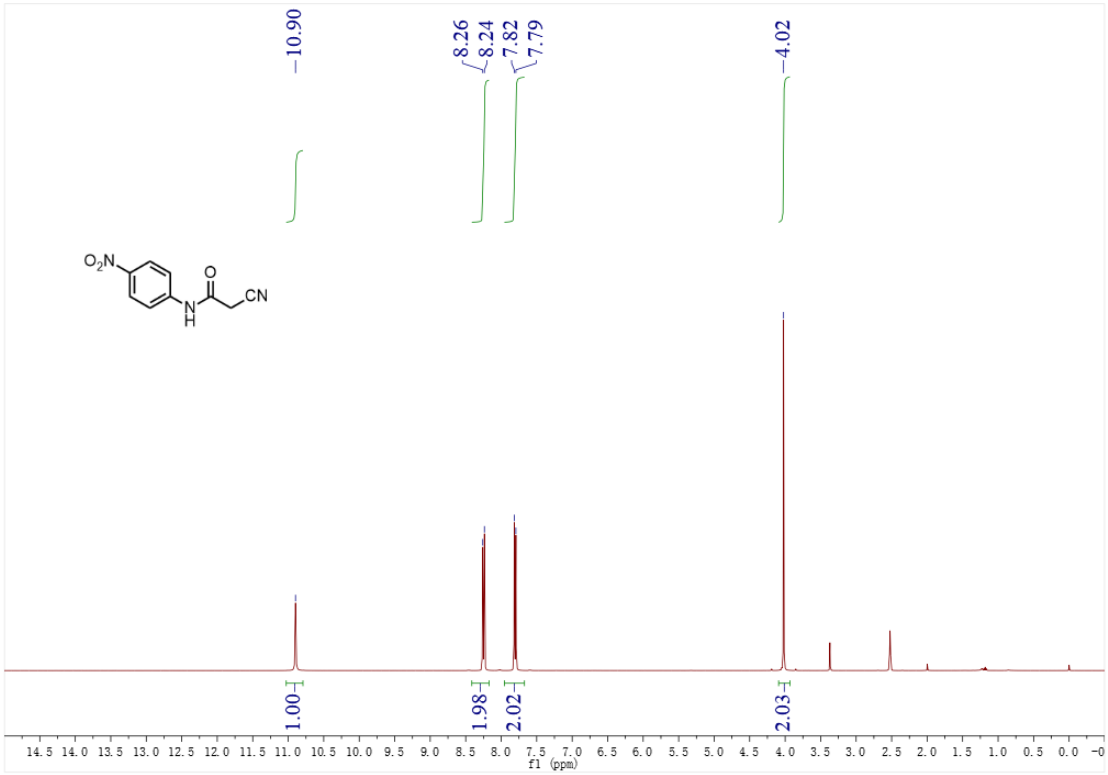
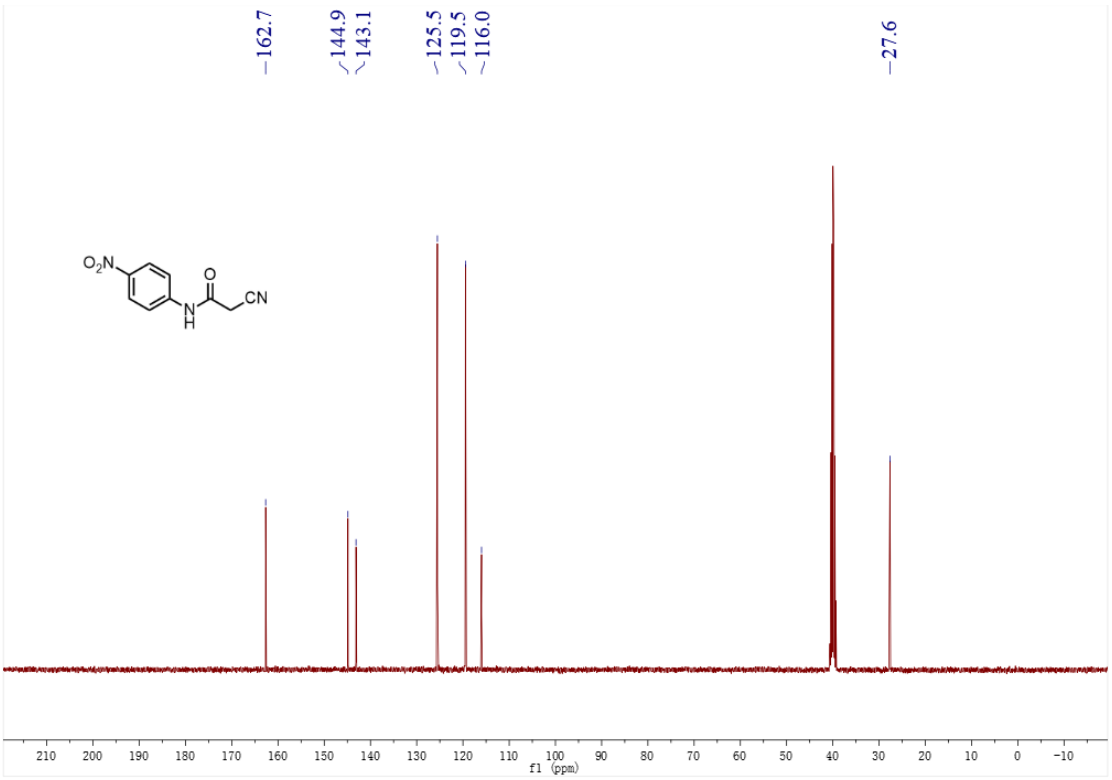
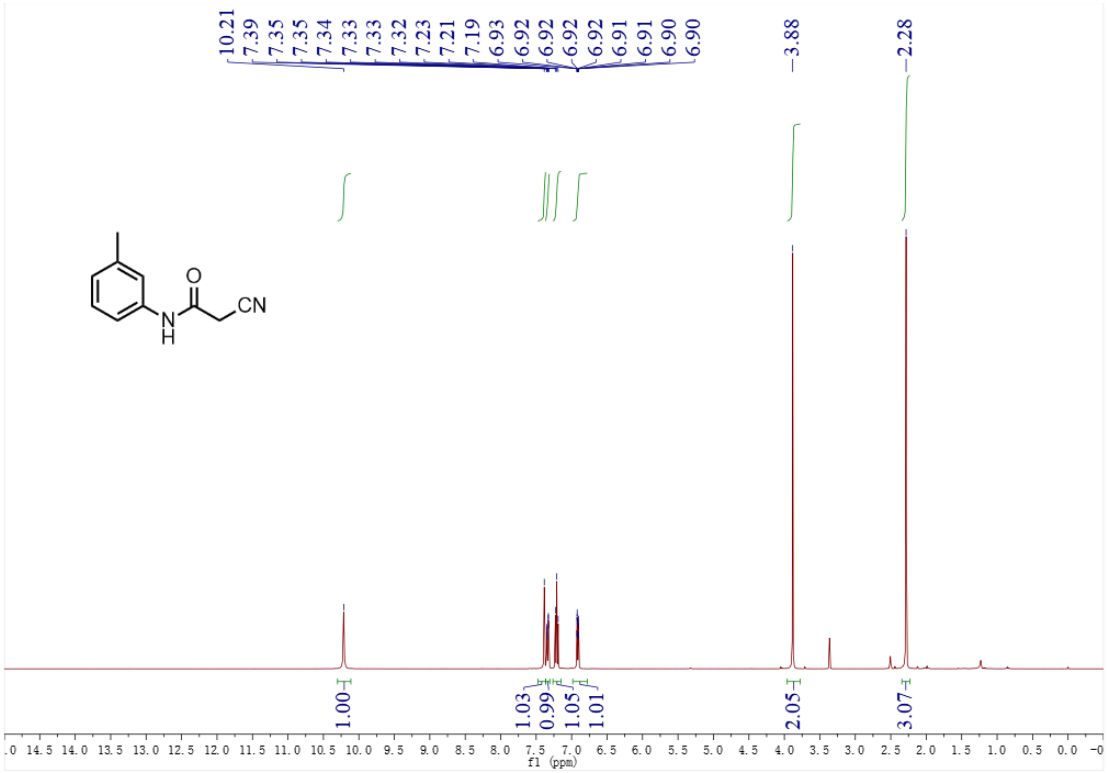


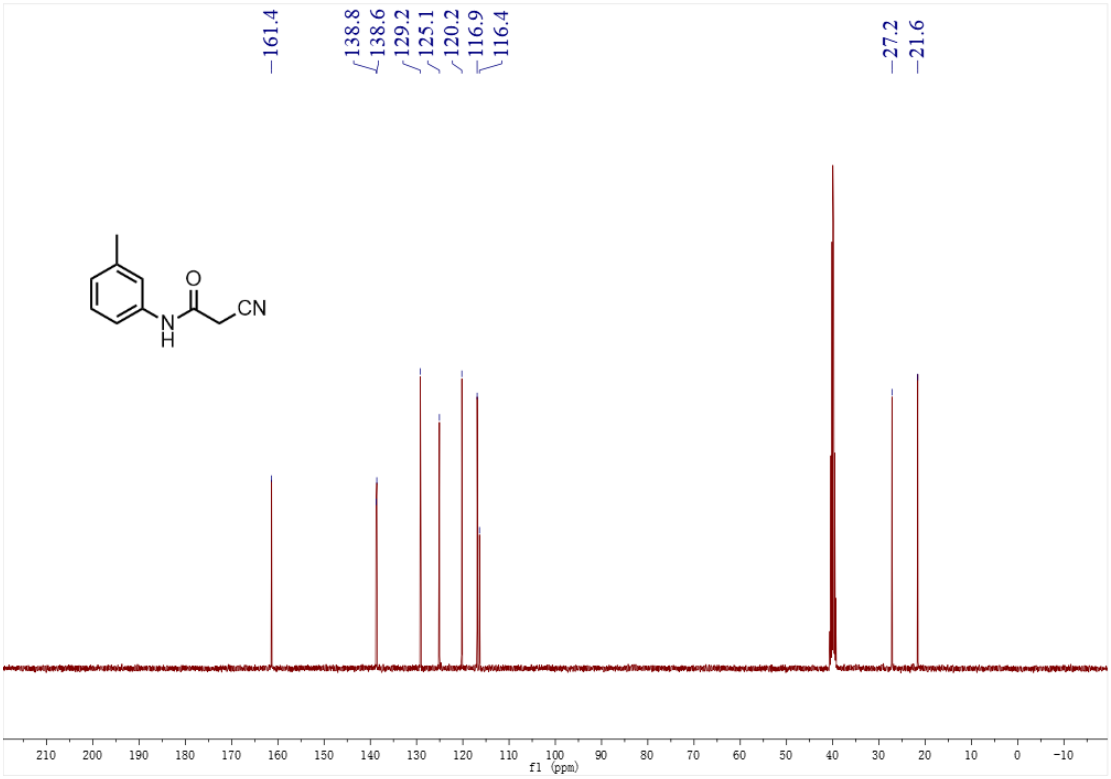
^{13}C NMR spectrum of **14** (DMSO-d_6)



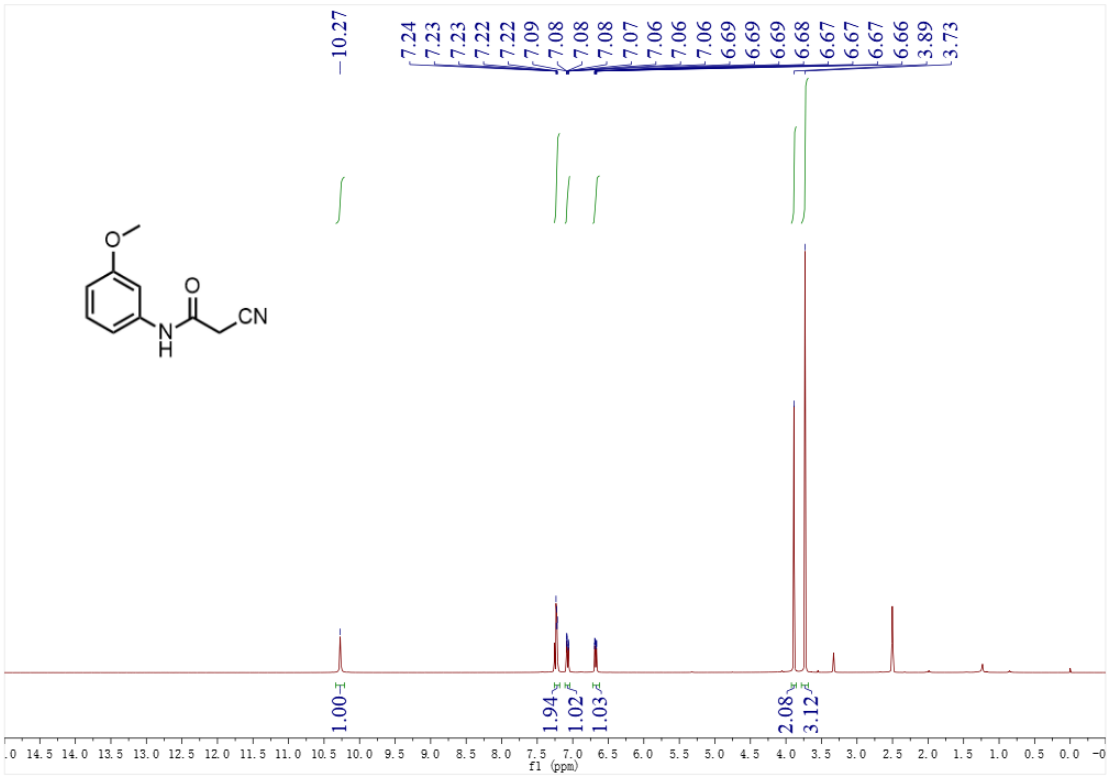
^{1}H NMR spectrum of **15** (DMSO-d_6)



^{13}C NMR spectrum of **15** (DMSO-d_6)



^{1}H NMR spectrum of **16** (DMSO-d_6)



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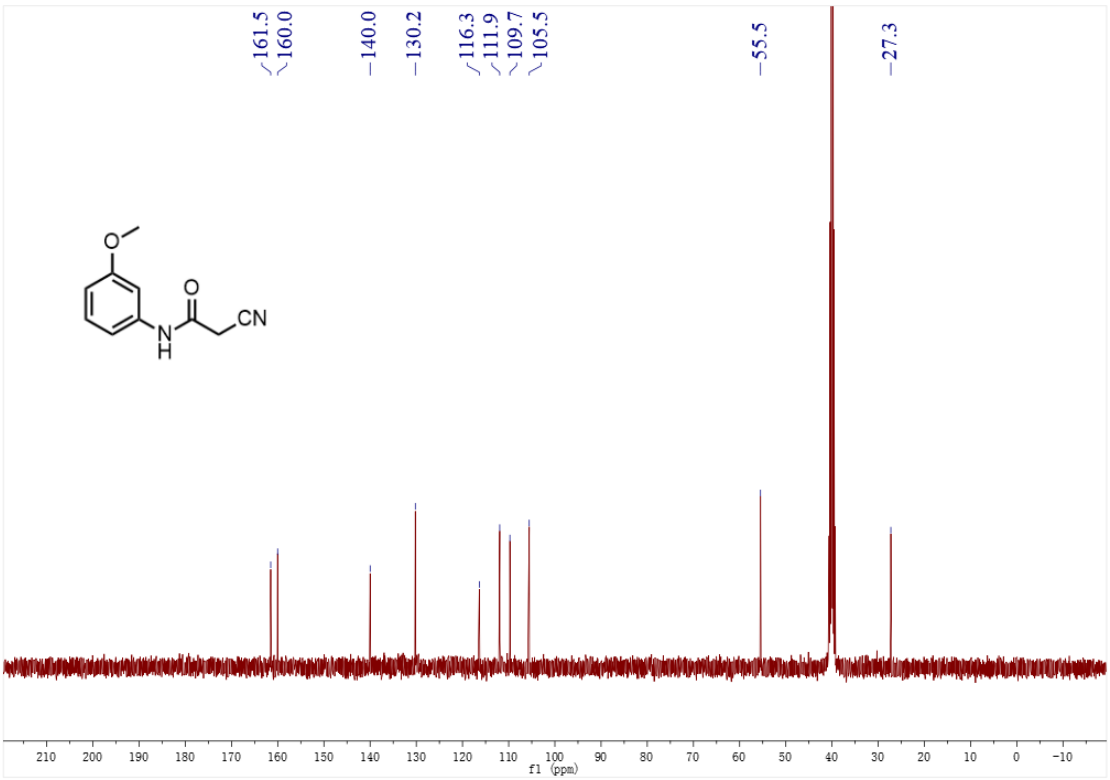
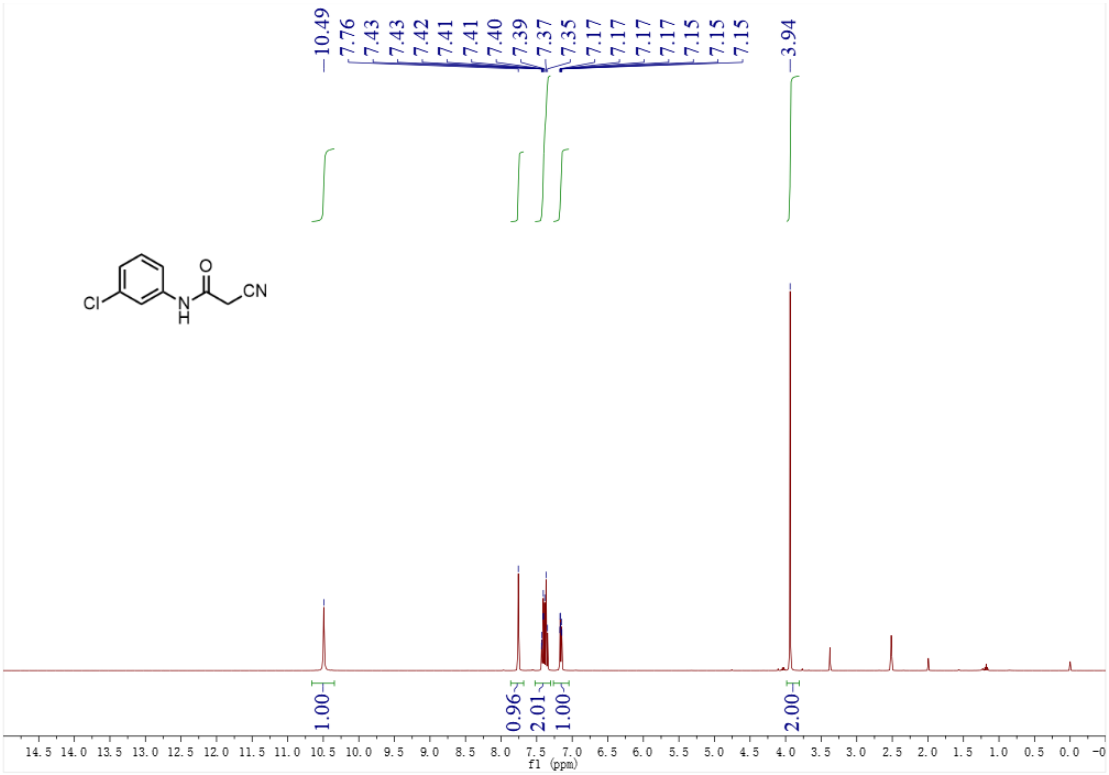
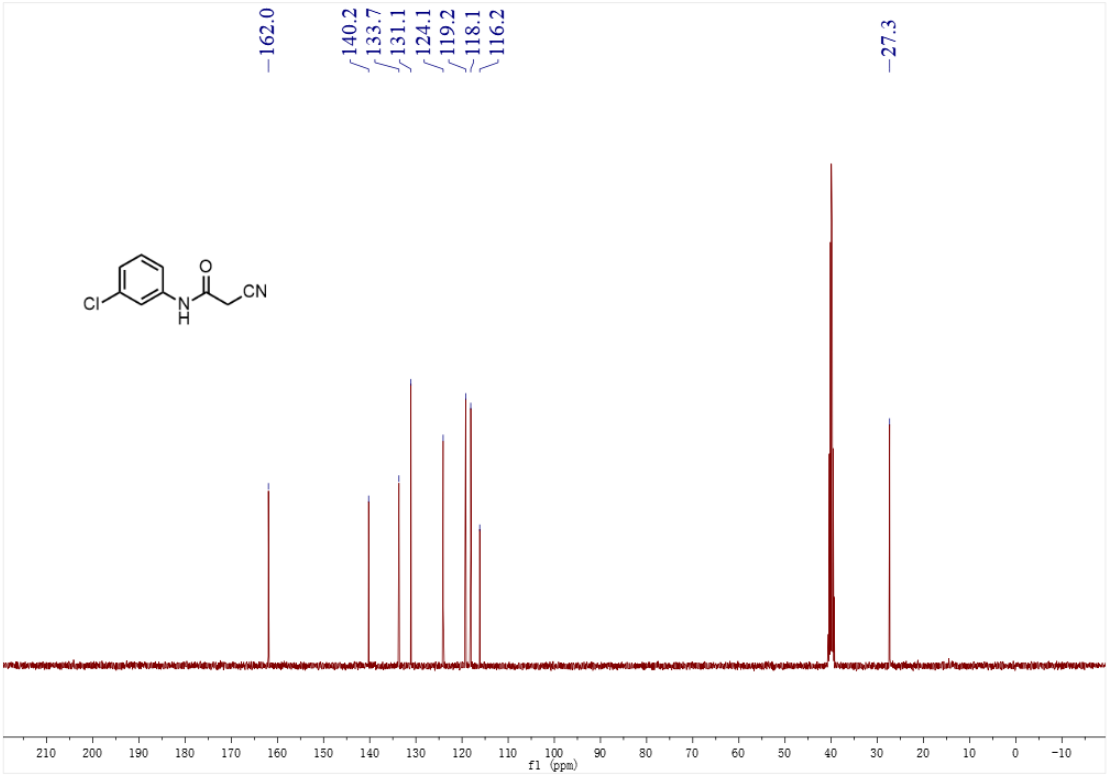


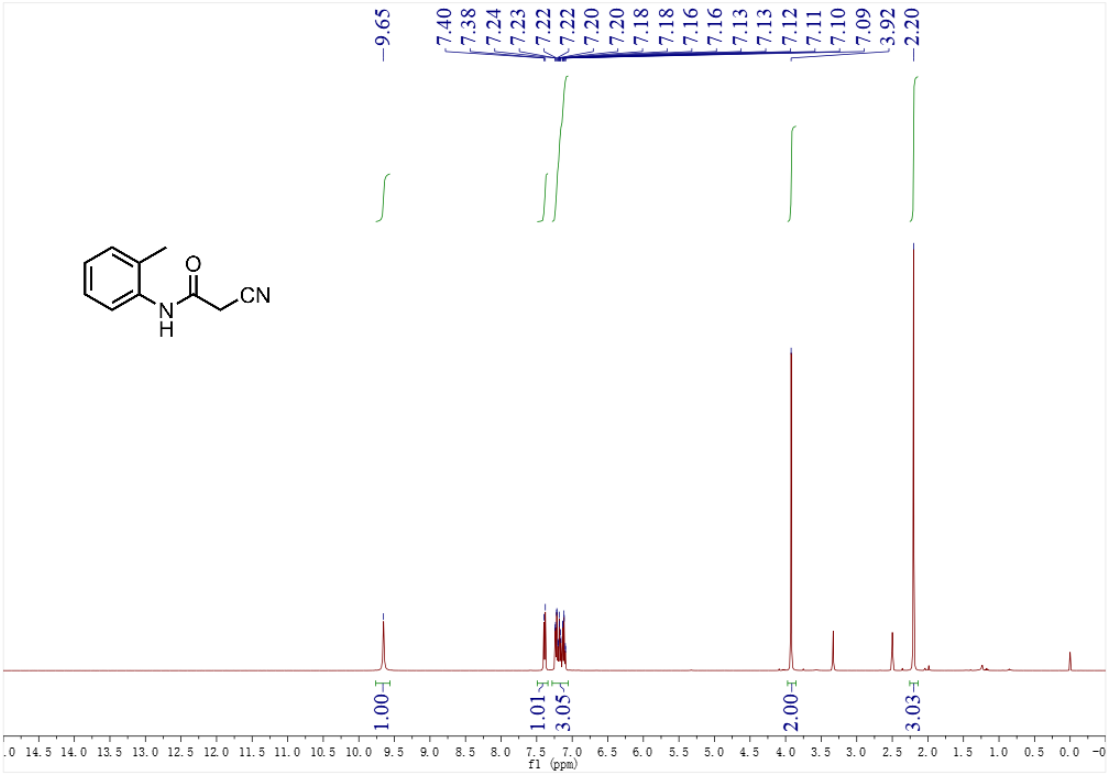
^{1}H NMR spectrum of **17** (DMSO-d_6)



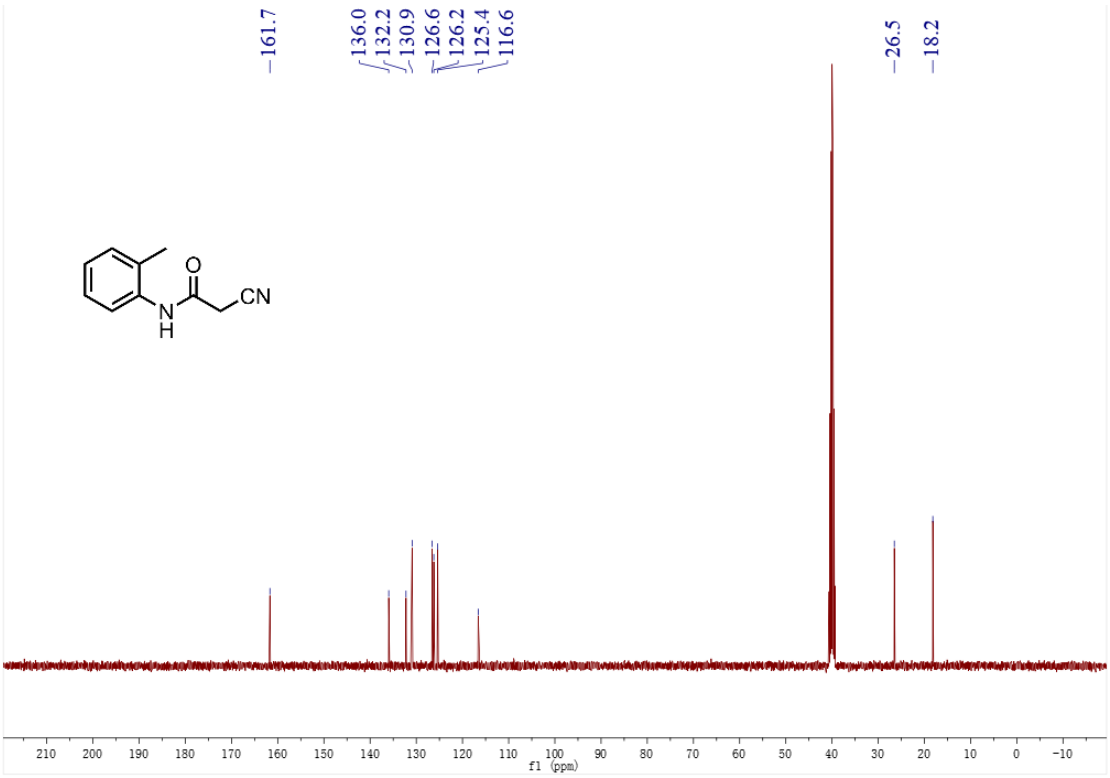
^{13}C NMR spectrum of **17** (DMSO-d_6)



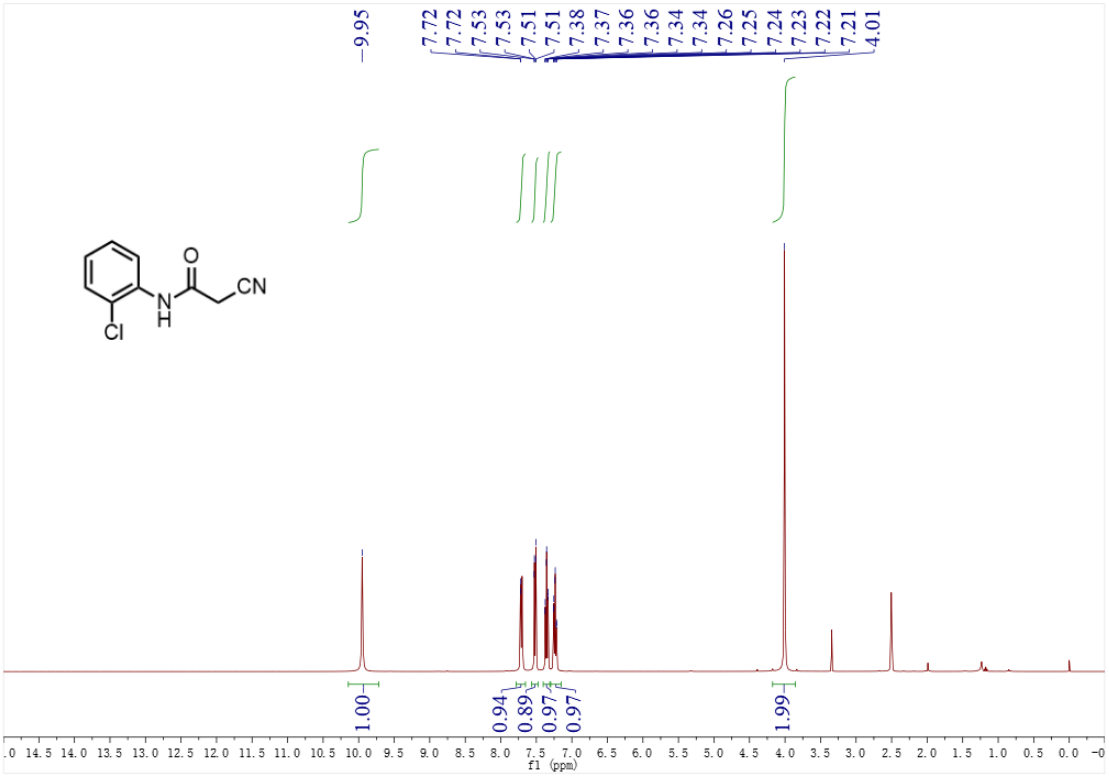
^{1}H NMR spectrum of **18** (DMSO-d_6)



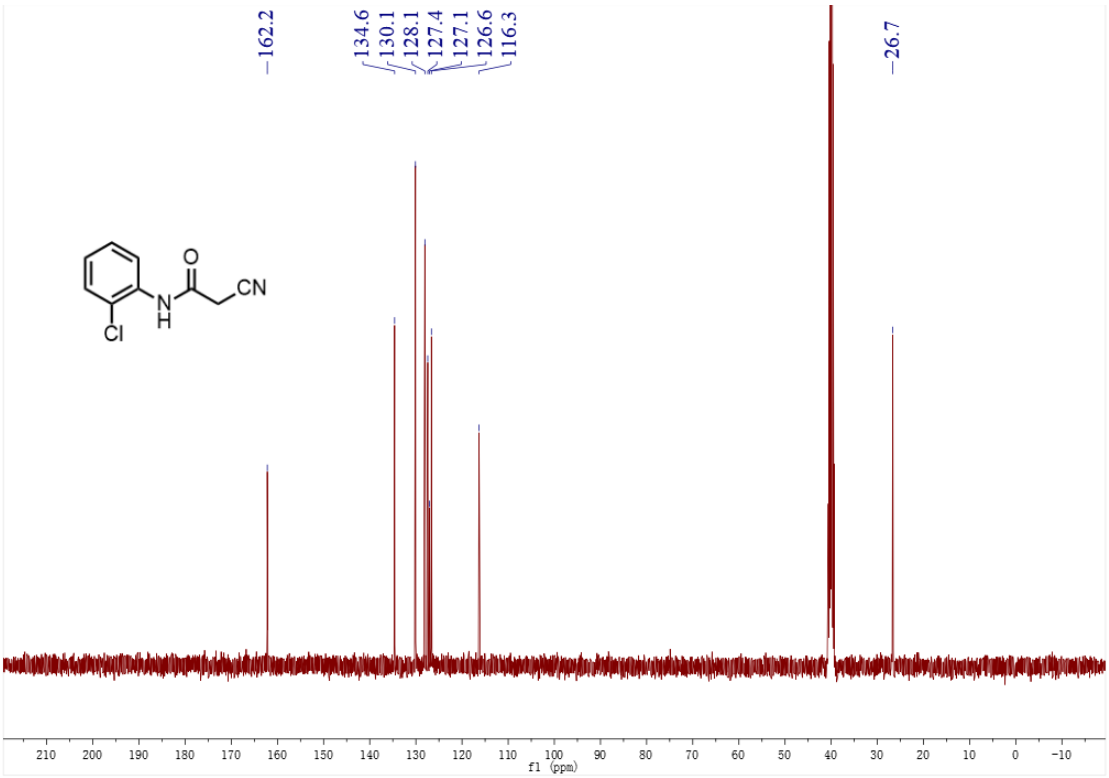
^{13}C NMR spectrum of **18** (DMSO-d_6)



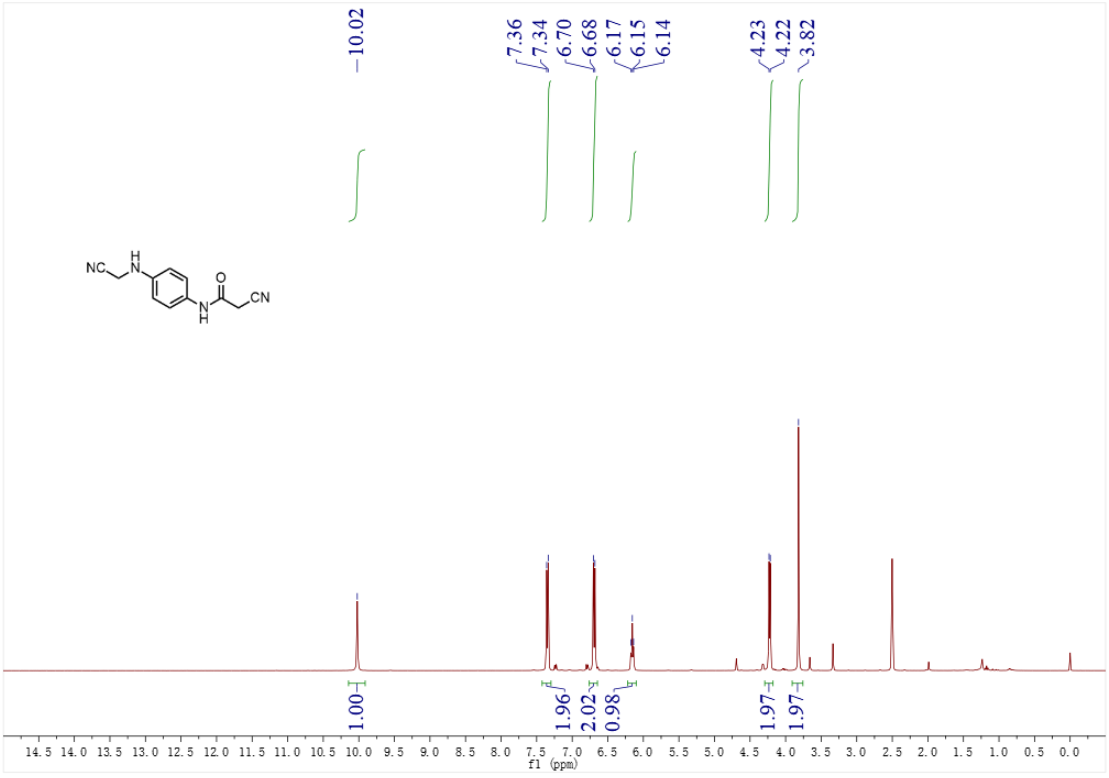
^{1}H NMR spectrum of **19** (DMSO-d_6)



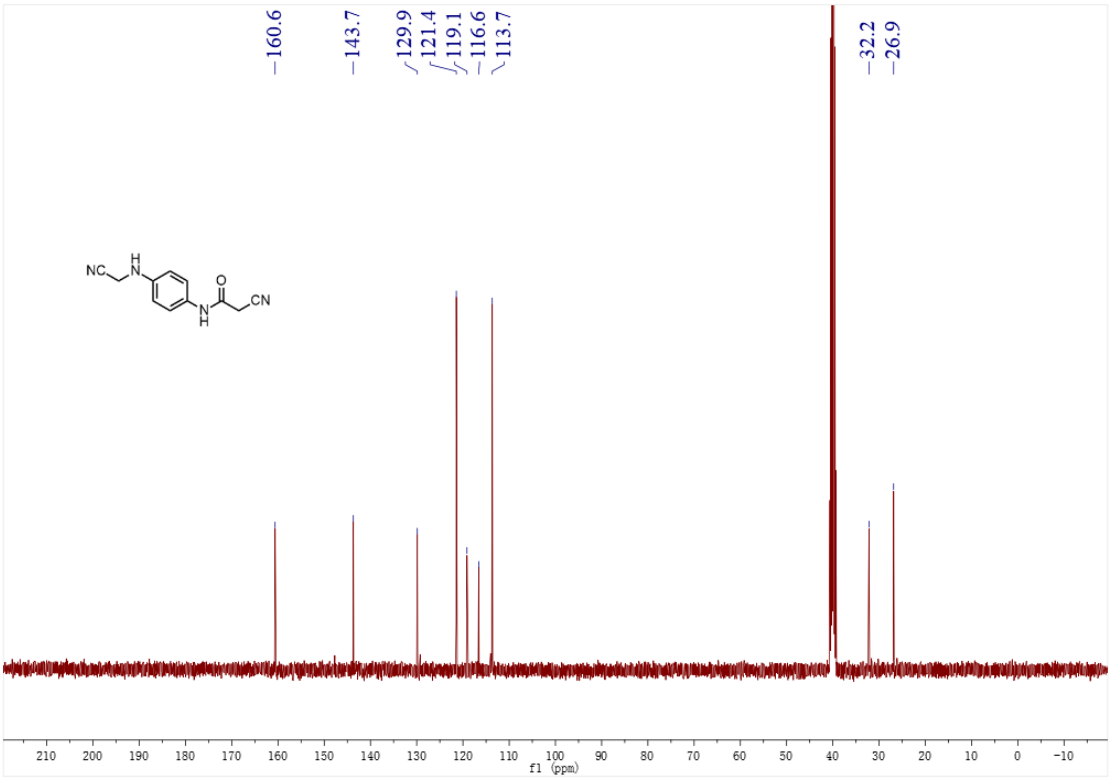
^{13}C NMR spectrum of **19** (DMSO-d_6)



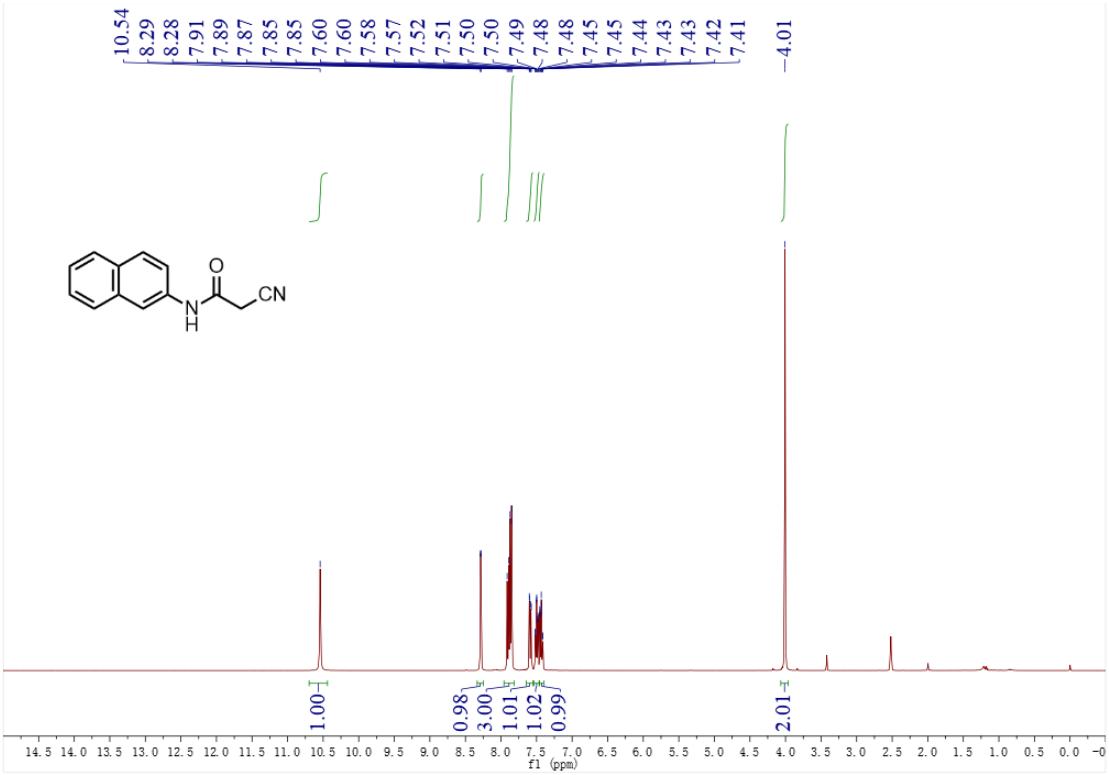
^{1}H NMR spectrum of **20** (DMSO-d_6)



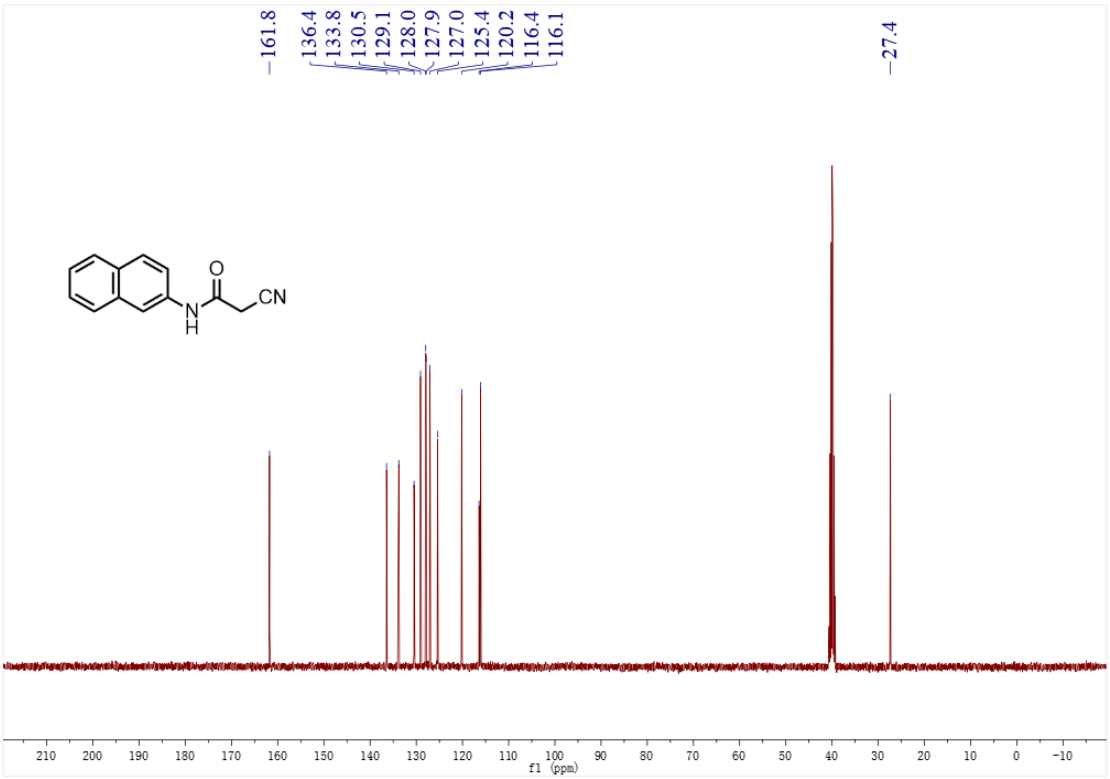
^{13}C NMR spectrum of **20** (DMSO-d_6)



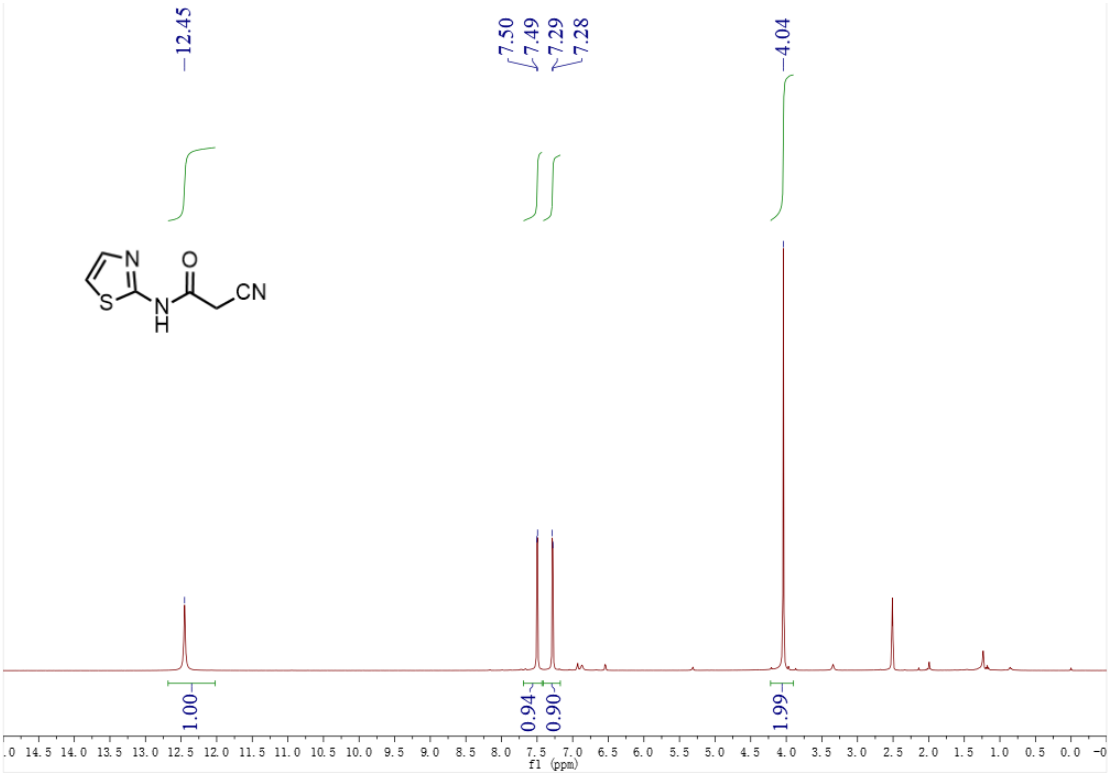
^{1}H NMR spectrum of **21** (DMSO-d_6)



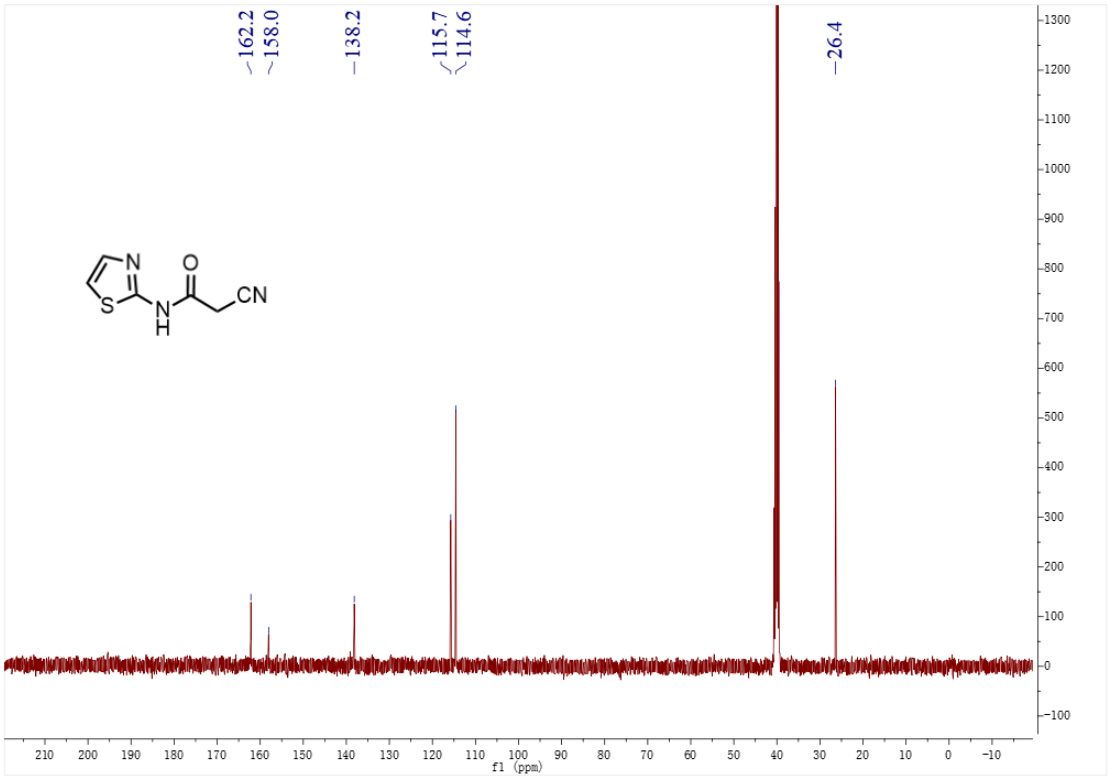
^{13}C NMR spectrum of **21** (DMSO-d_6)



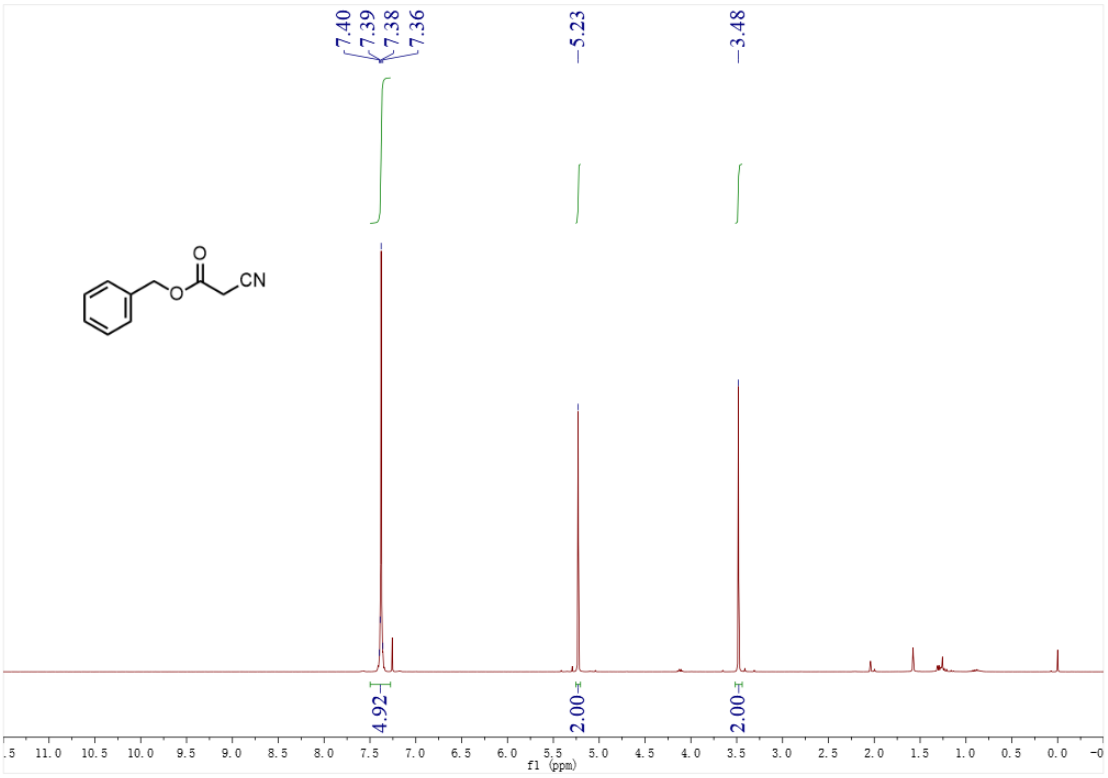
^{1}H NMR spectrum of **22** (DMSO-d_6)



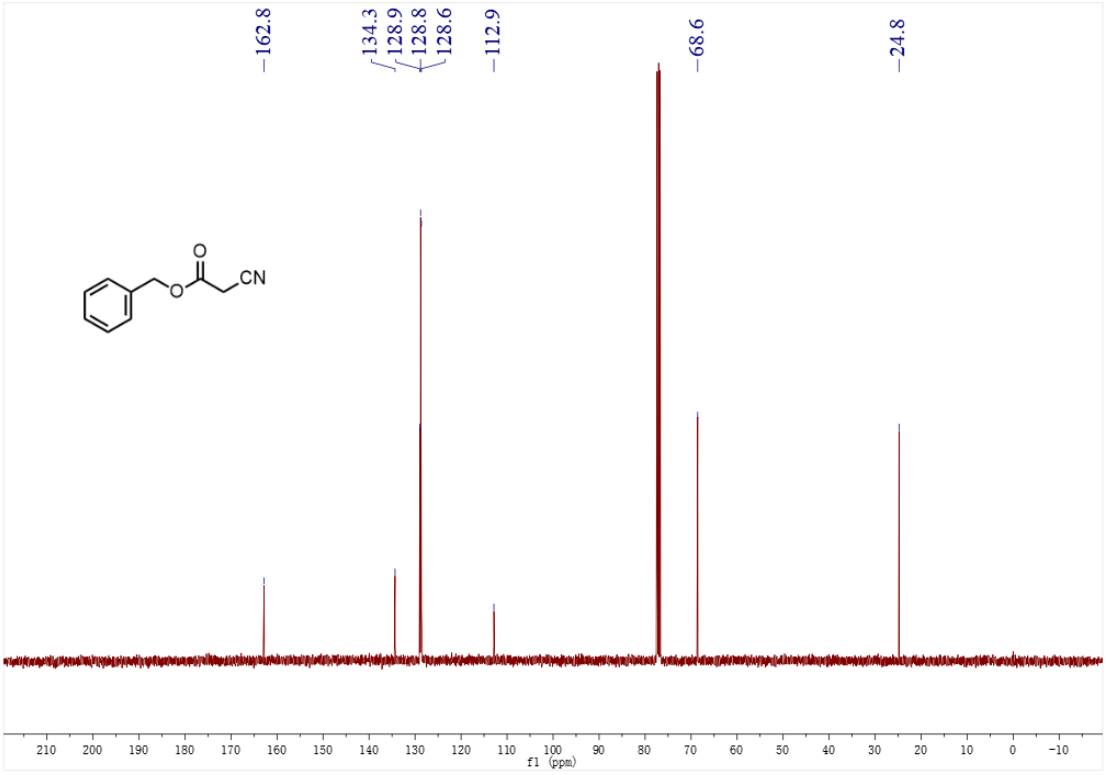
^{13}C NMR spectrum of **22** (DMSO-d_6)



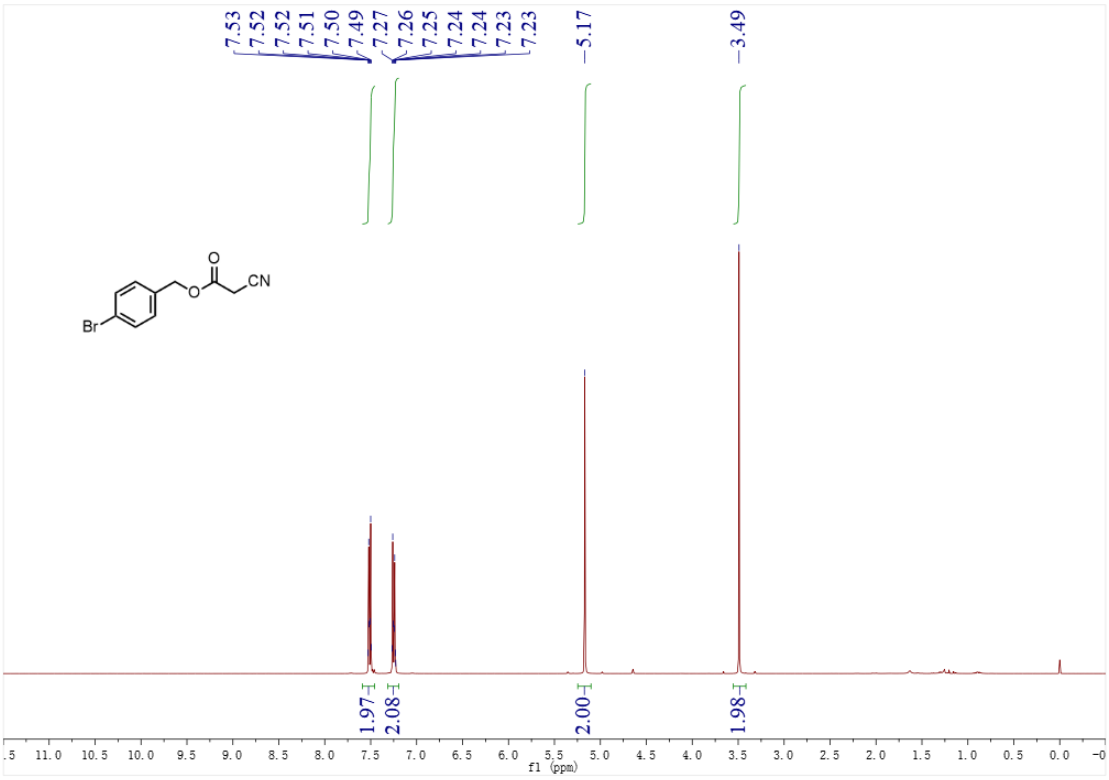
^{1}H NMR spectrum of **23** ($CDCl_3$)



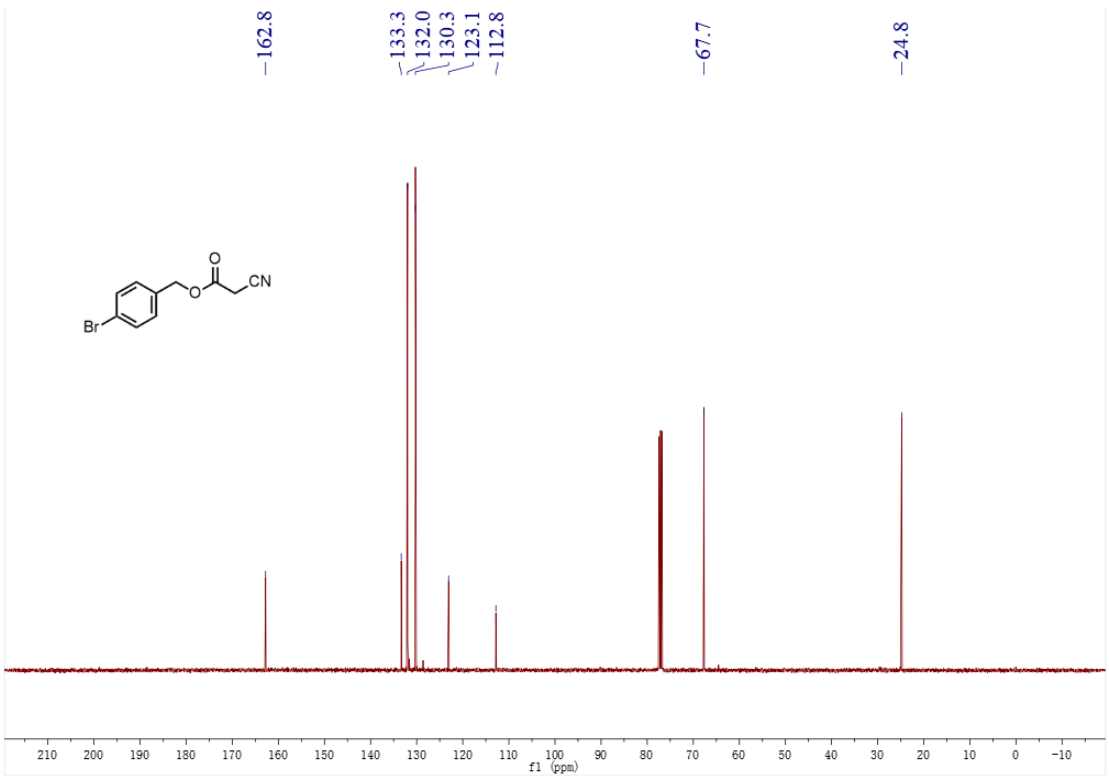
^{13}C NMR spectrum of **23** ($CDCl_3$)



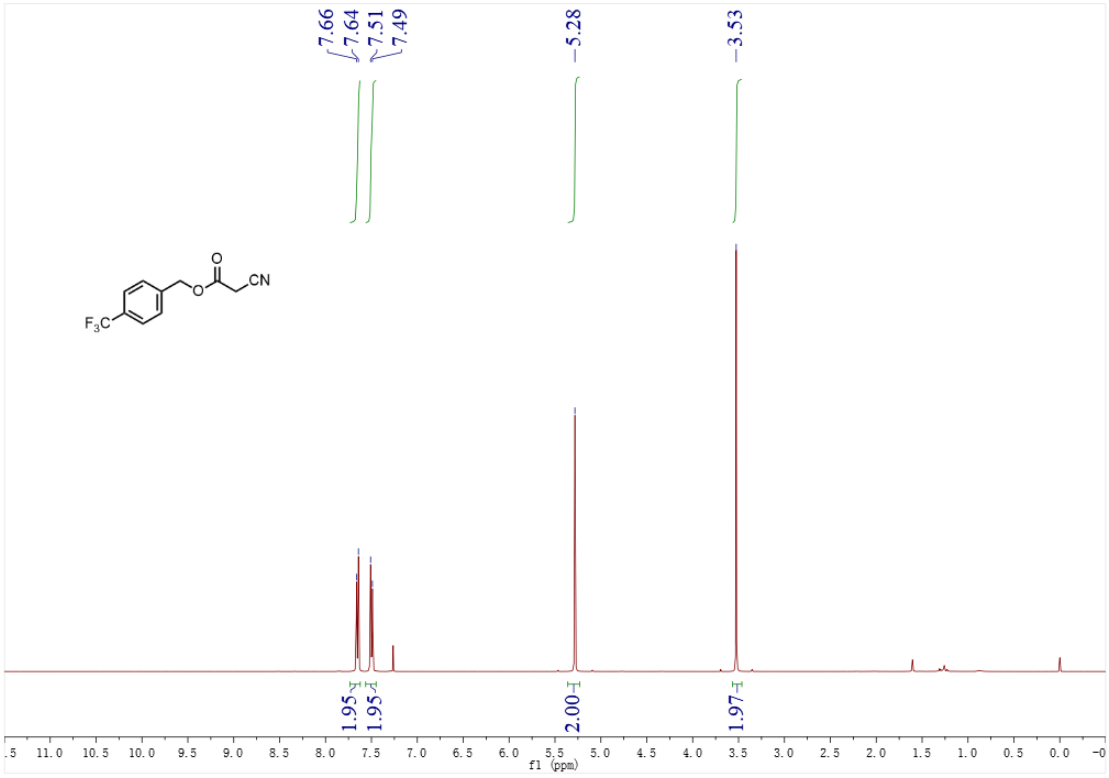
^{1}H NMR spectrum of **24** ($CDCl_3$)



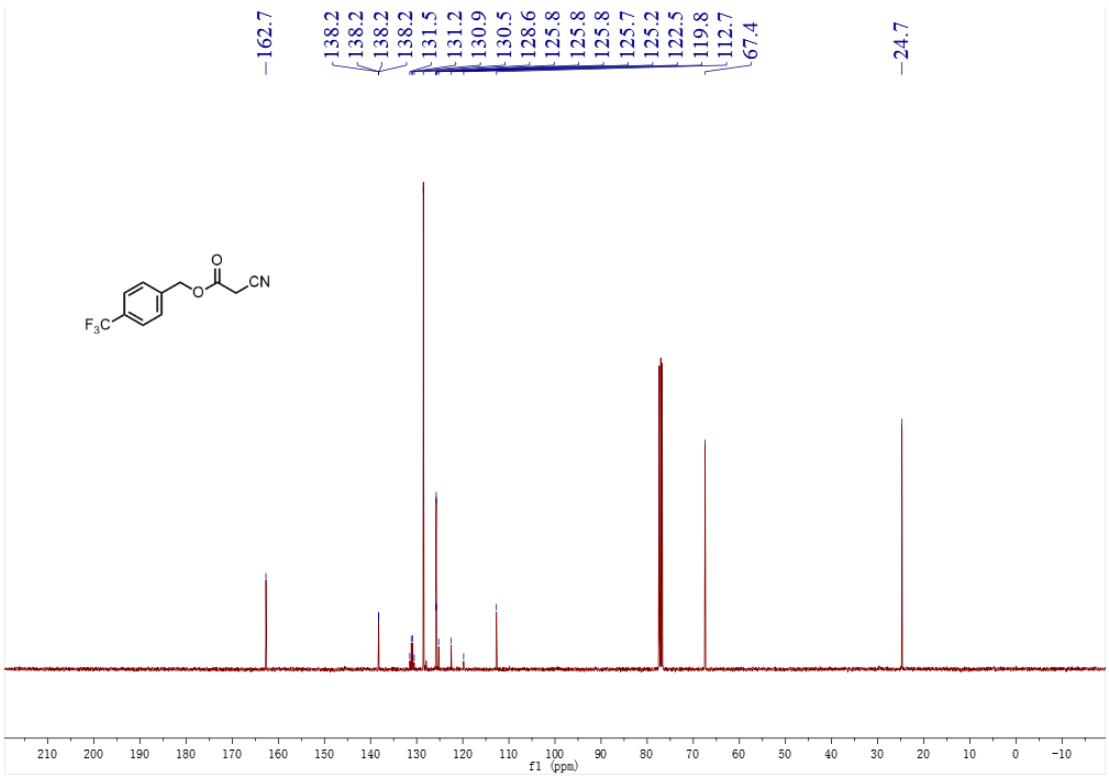
^{13}C NMR spectrum of **24** ($CDCl_3$)



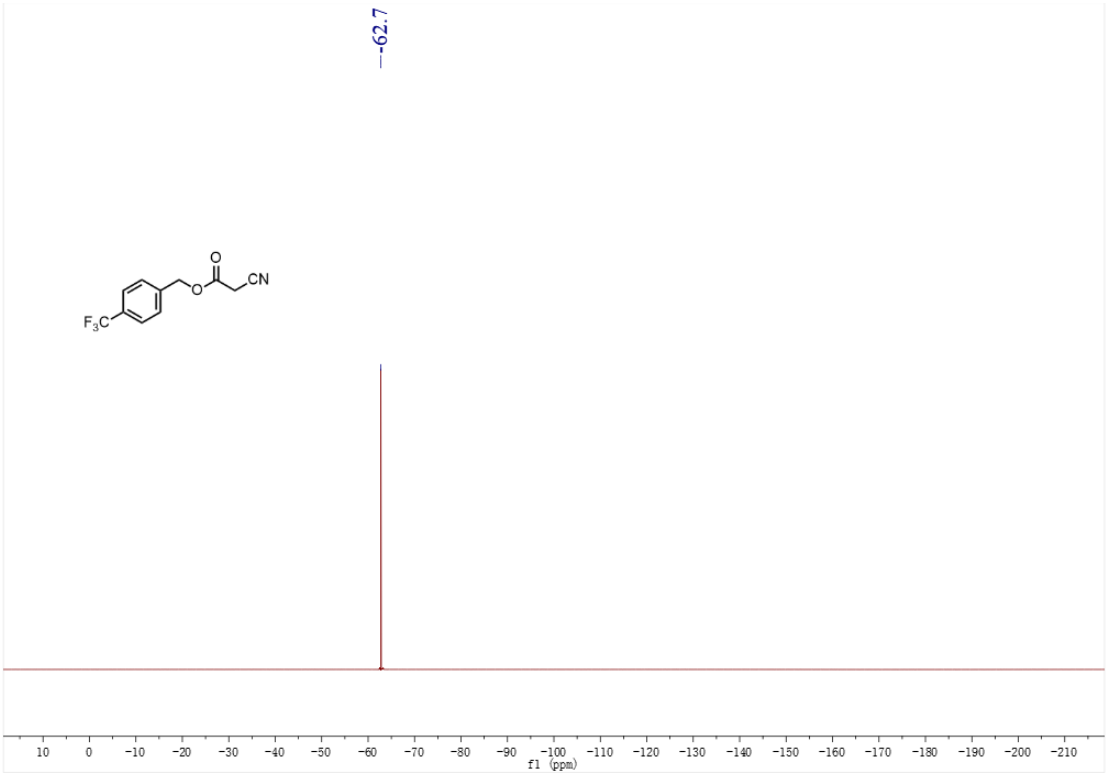
^{1}H NMR spectrum of **25**($CDCl_3$)



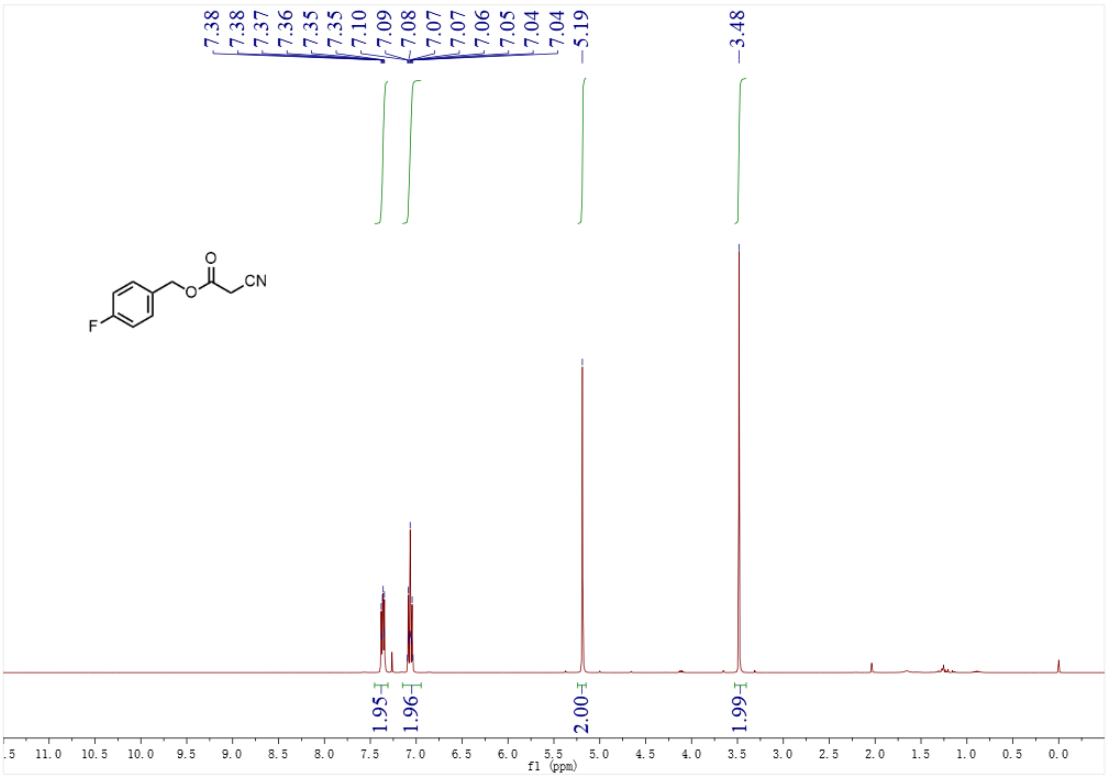
^{13}C NMR spectrum of **25** ($CDCl_3$)



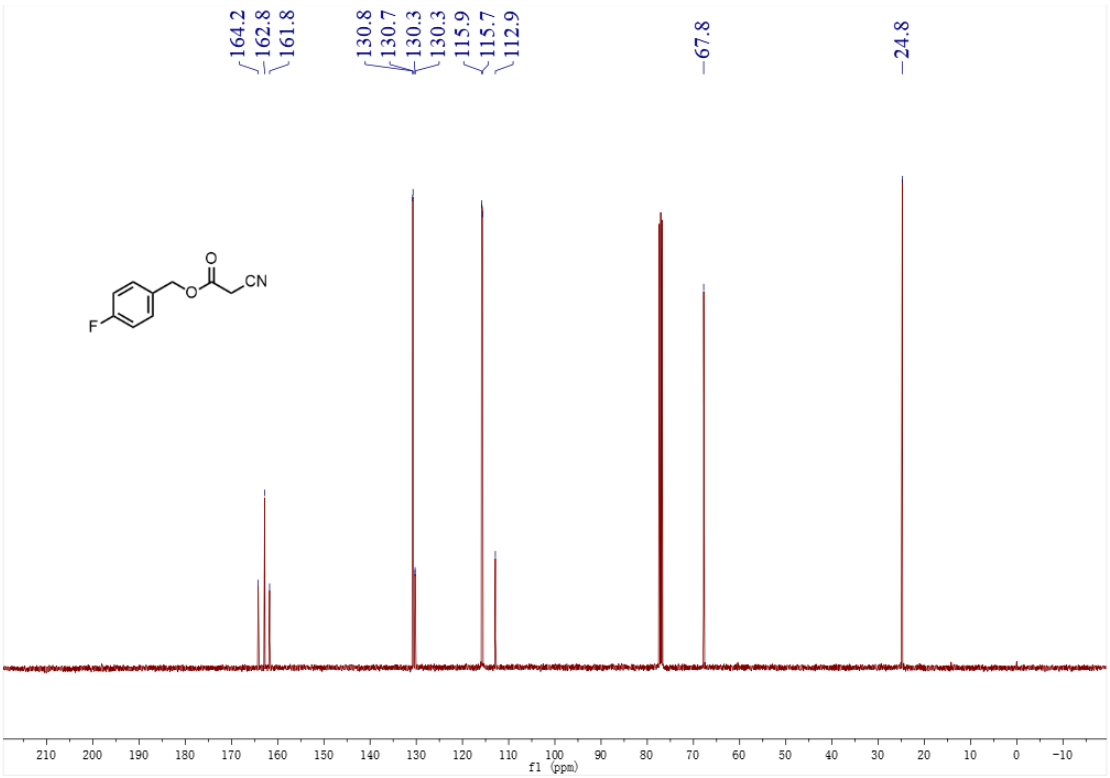
^{19}F NMR spectrum of **25** ($CDCl_3$)



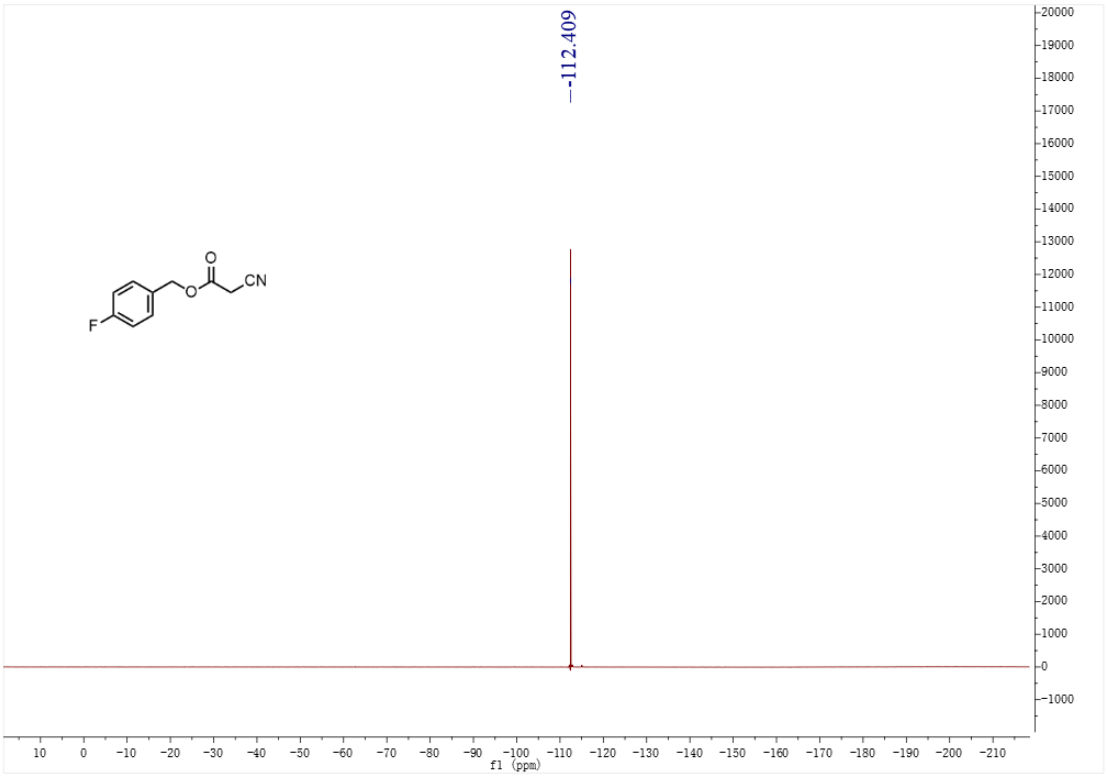
^{1}H NMR spectrum of **26** ($CDCl_3$)



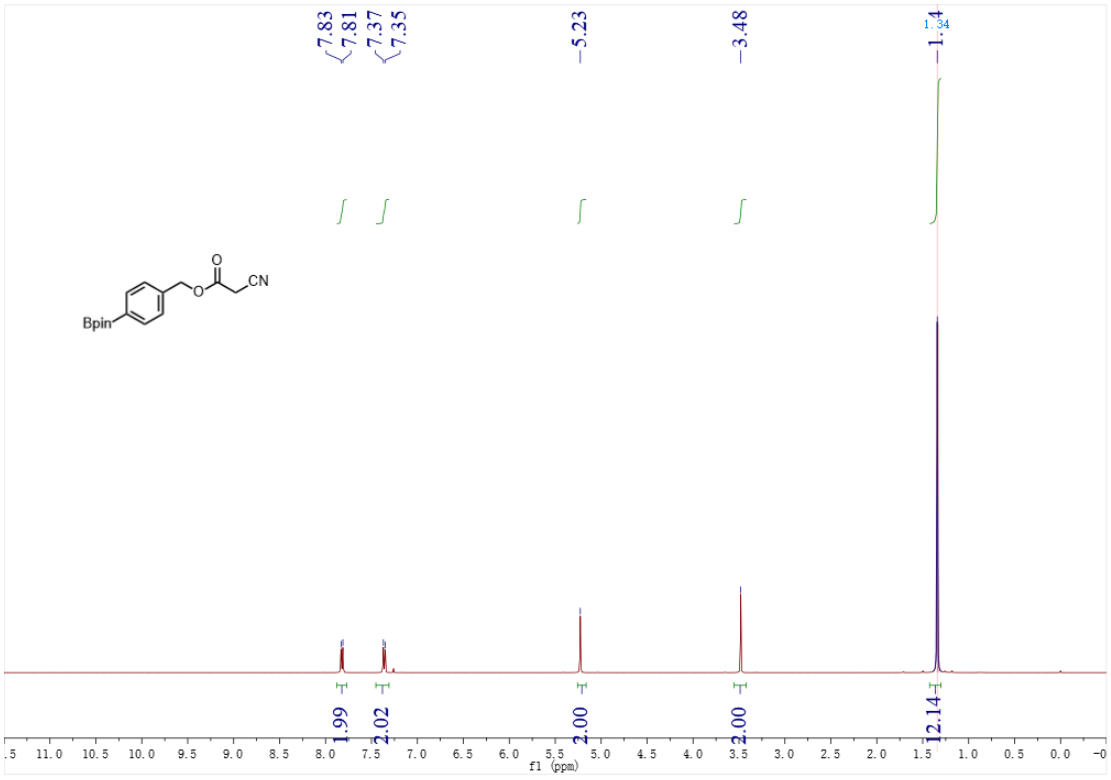
^{13}C NMR spectrum of **26** ($CDCl_3$)



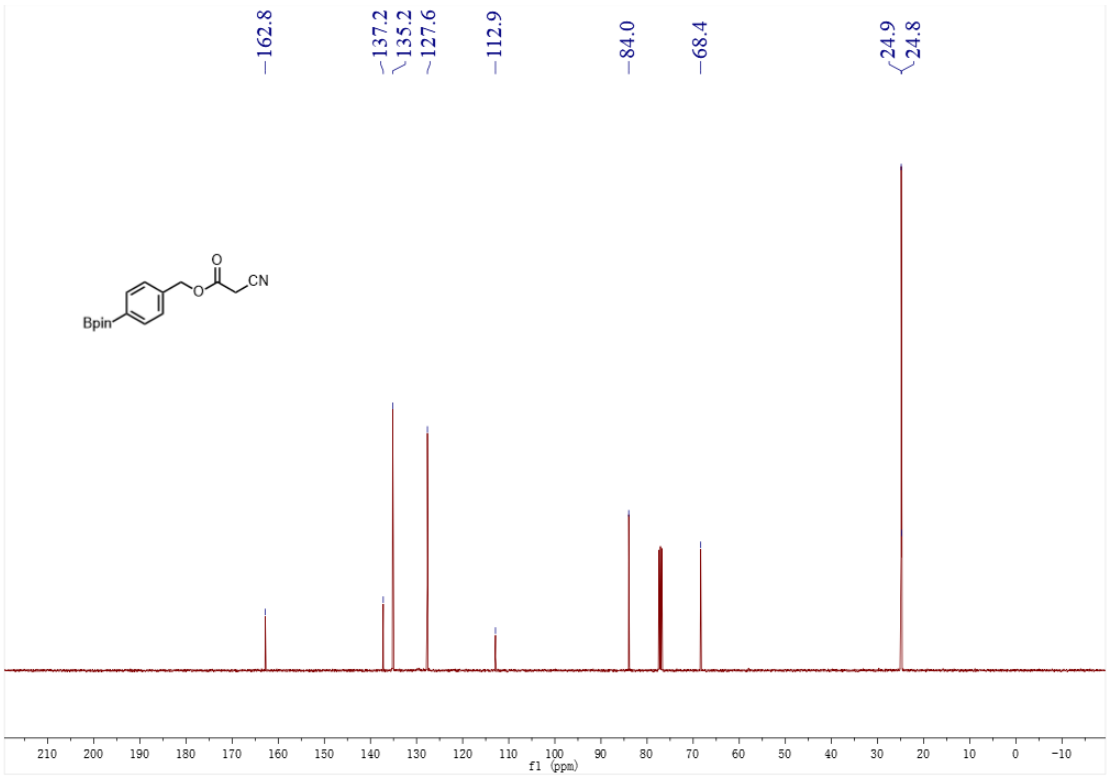
^{19}F NMR spectrum of **26** ($CDCl_3$)



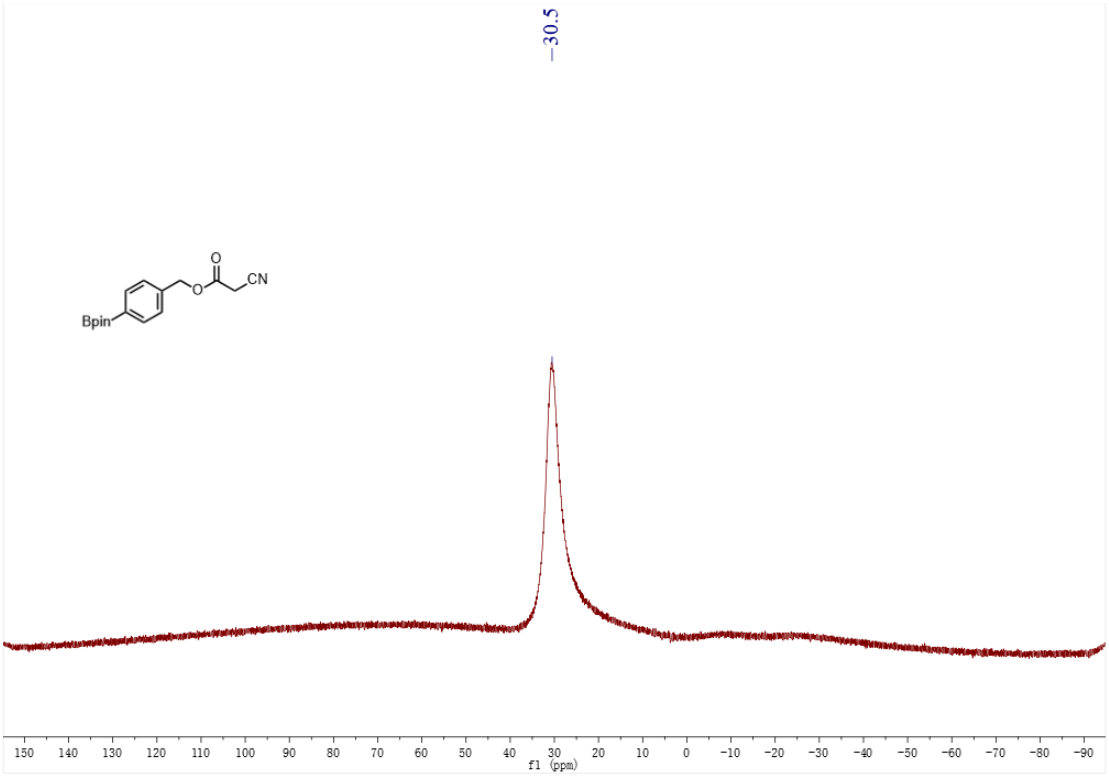
^{1}H NMR spectrum of **27** ($CDCl_3$)



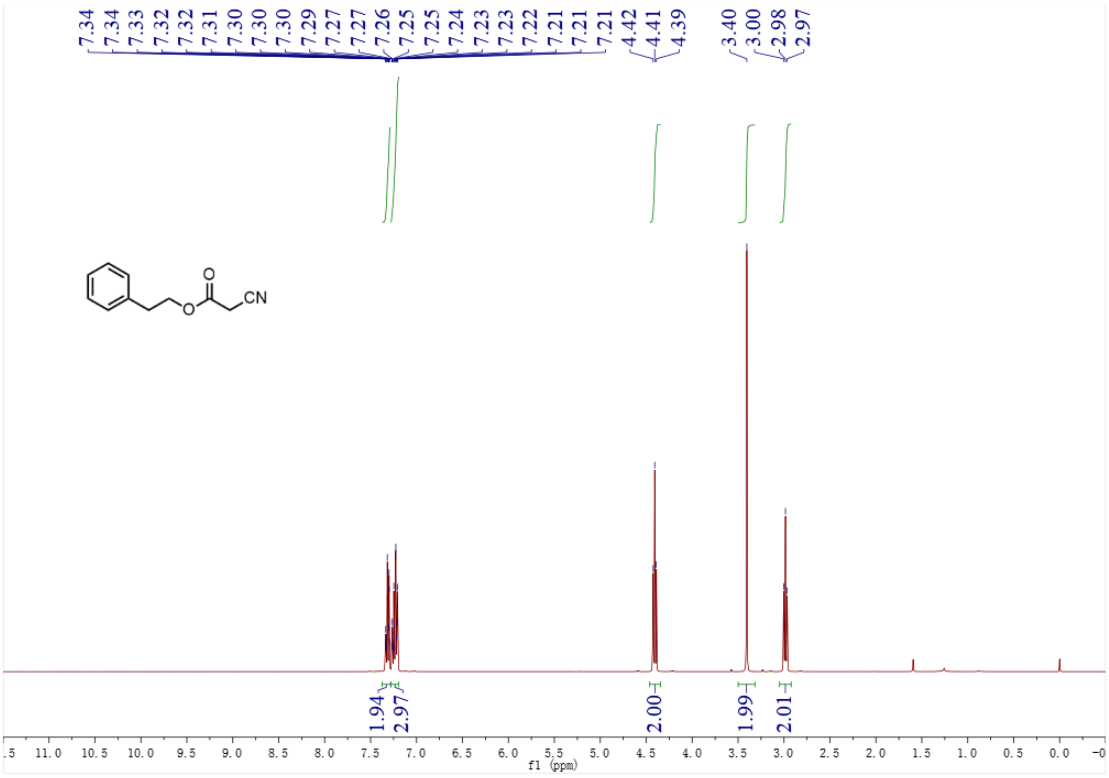
^{13}C NMR spectrum of **27** ($CDCl_3$)



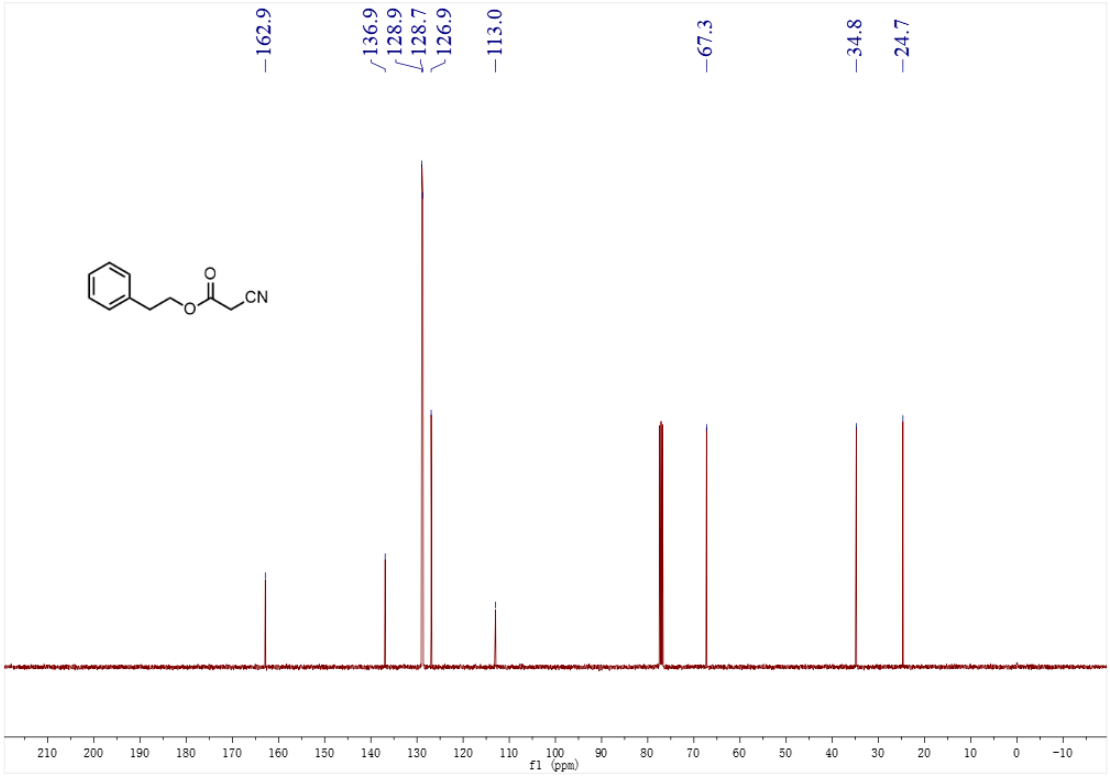
^{11}B NMR spectrum of **27** ($CDCl_3$)



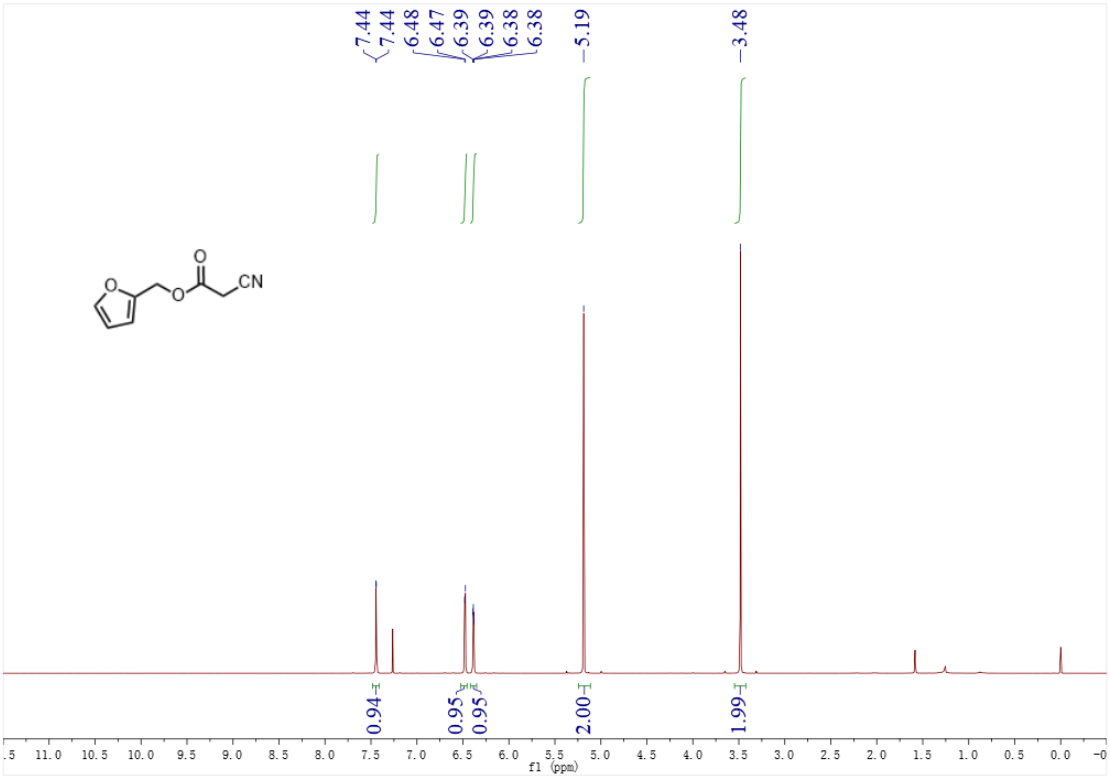
^{1}H NMR spectrum of **28** ($CDCl_3$)



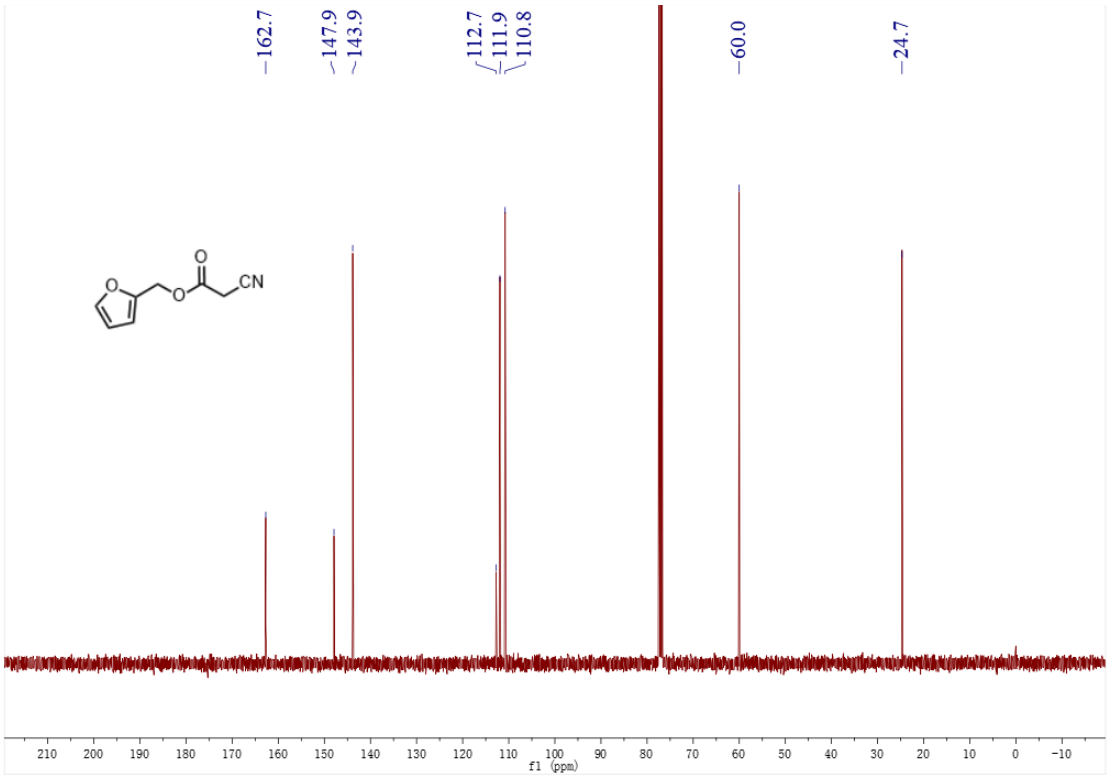
^{13}C NMR spectrum of **28** ($CDCl_3$)



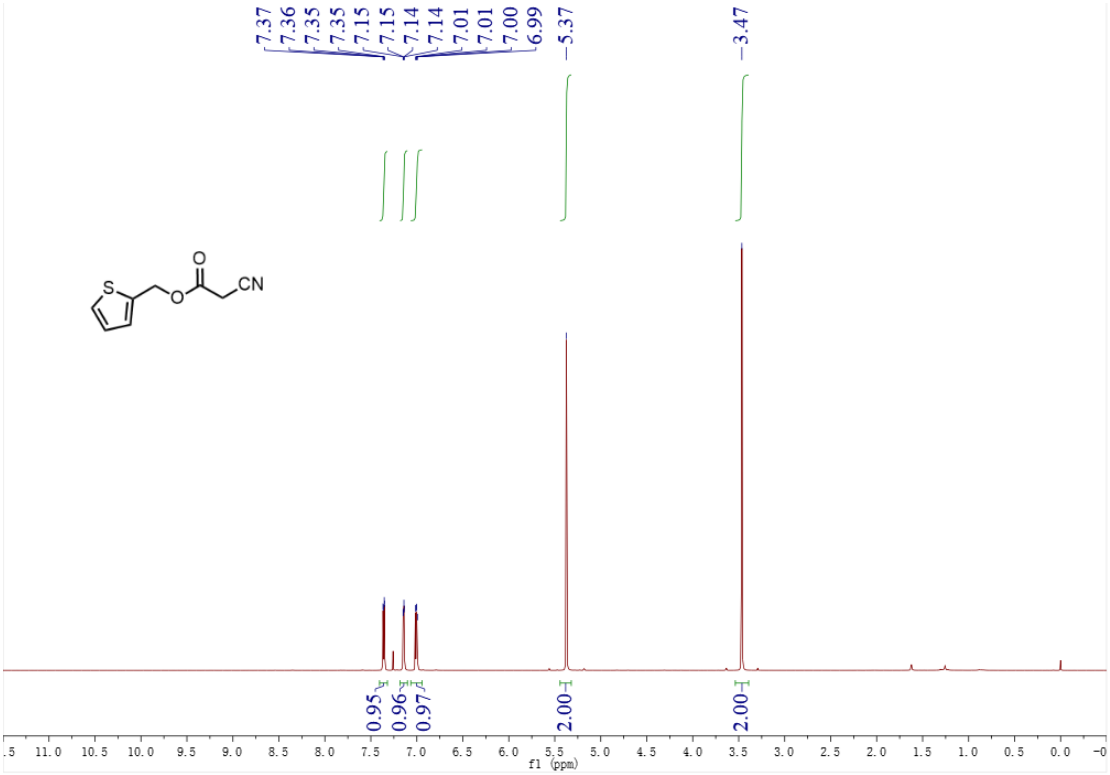
^{1}H NMR spectrum of **29** ($CDCl_3$)



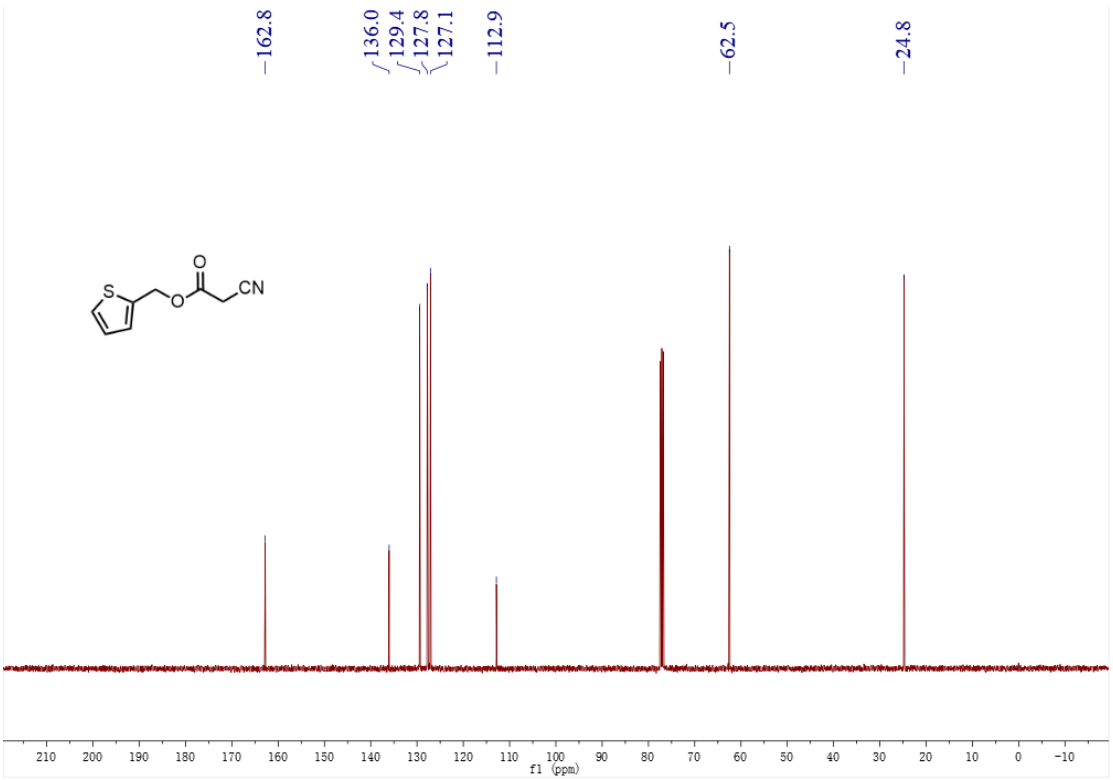
^{13}C NMR spectrum of **29** ($CDCl_3$)



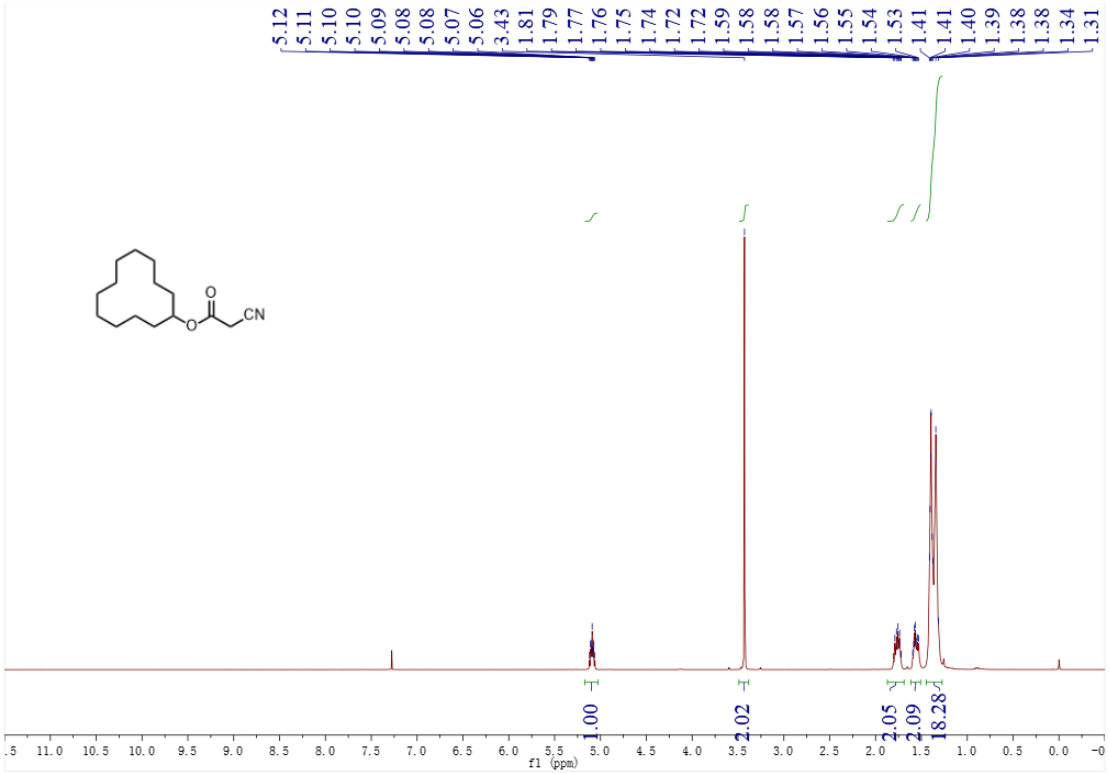
^{1}H NMR spectrum of **30** ($CDCl_3$)



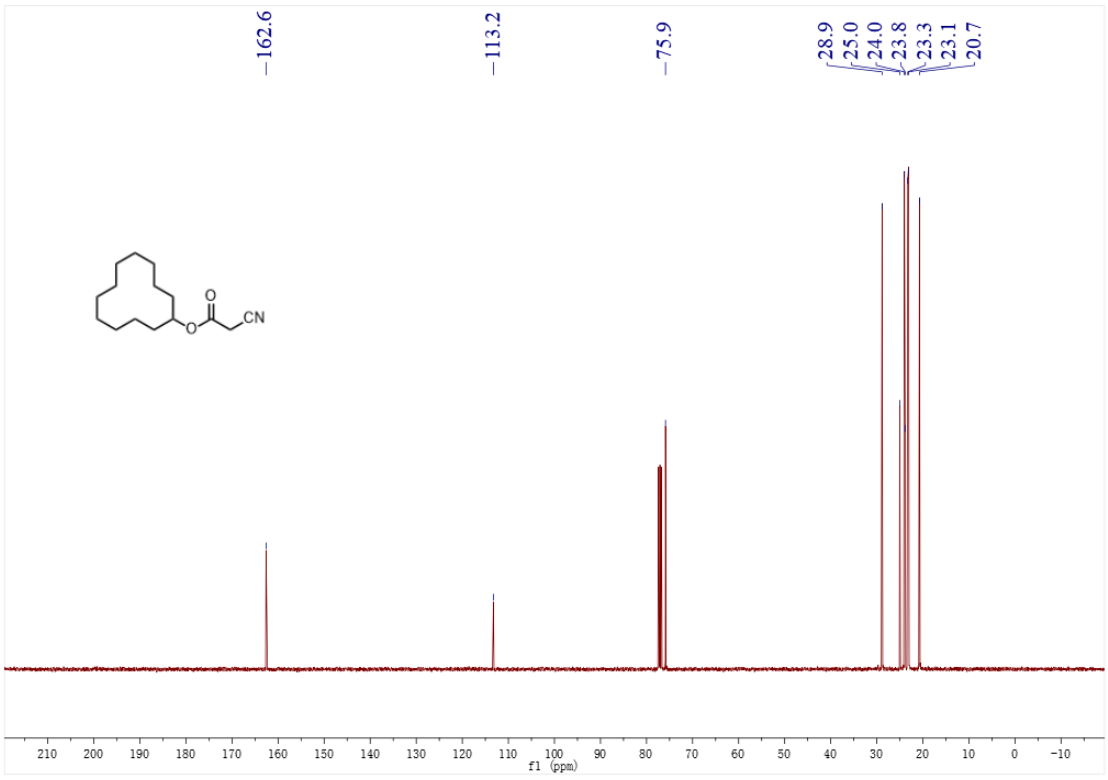
^{13}C NMR spectrum of **30** ($CDCl_3$)



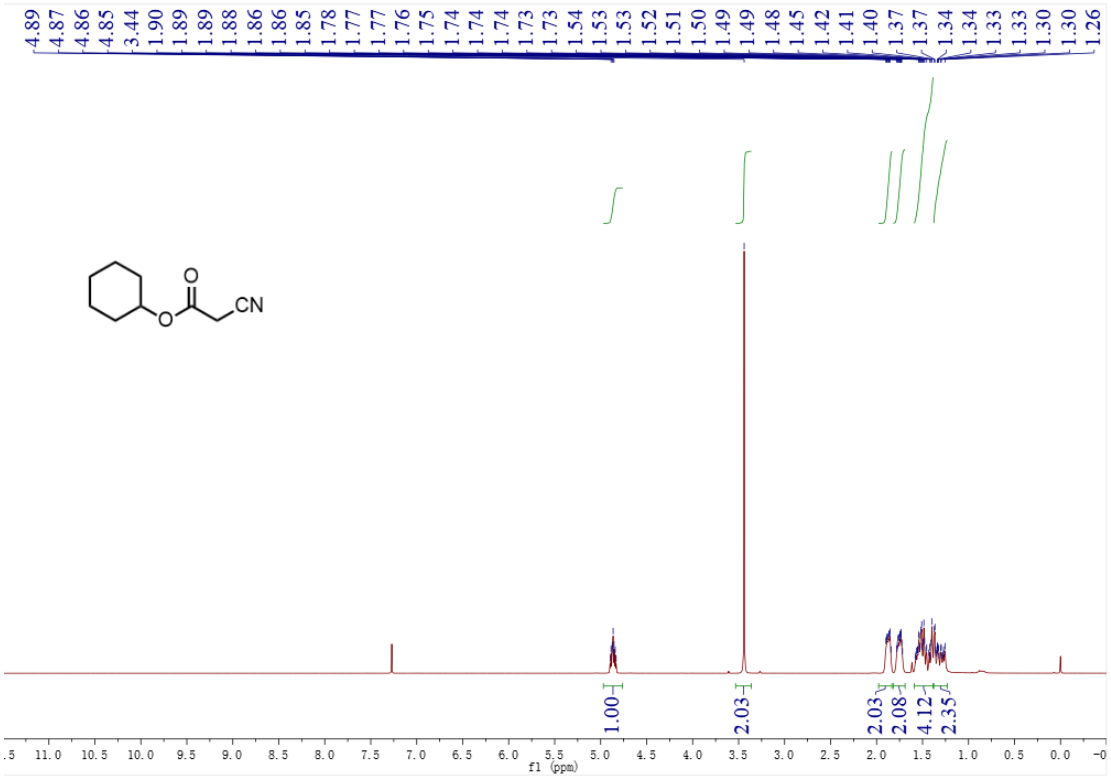
^{1}H NMR spectrum of **31** ($CDCl_3$)



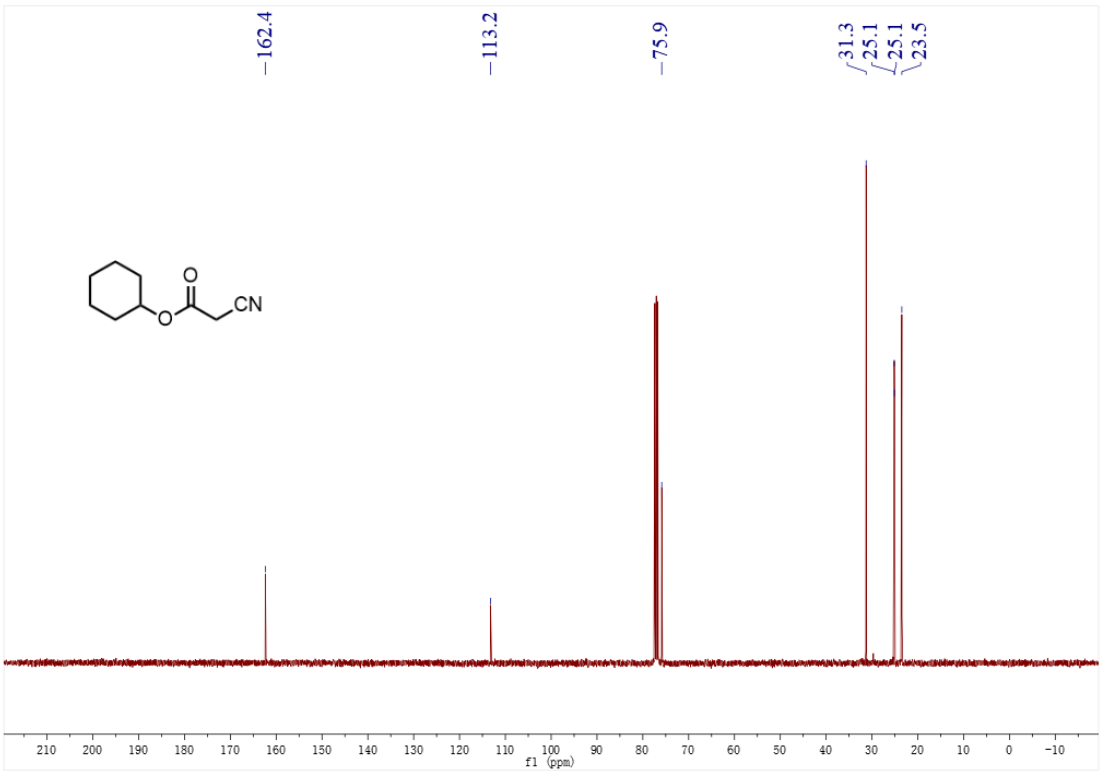
^{13}C NMR spectrum of **31** ($CDCl_3$)



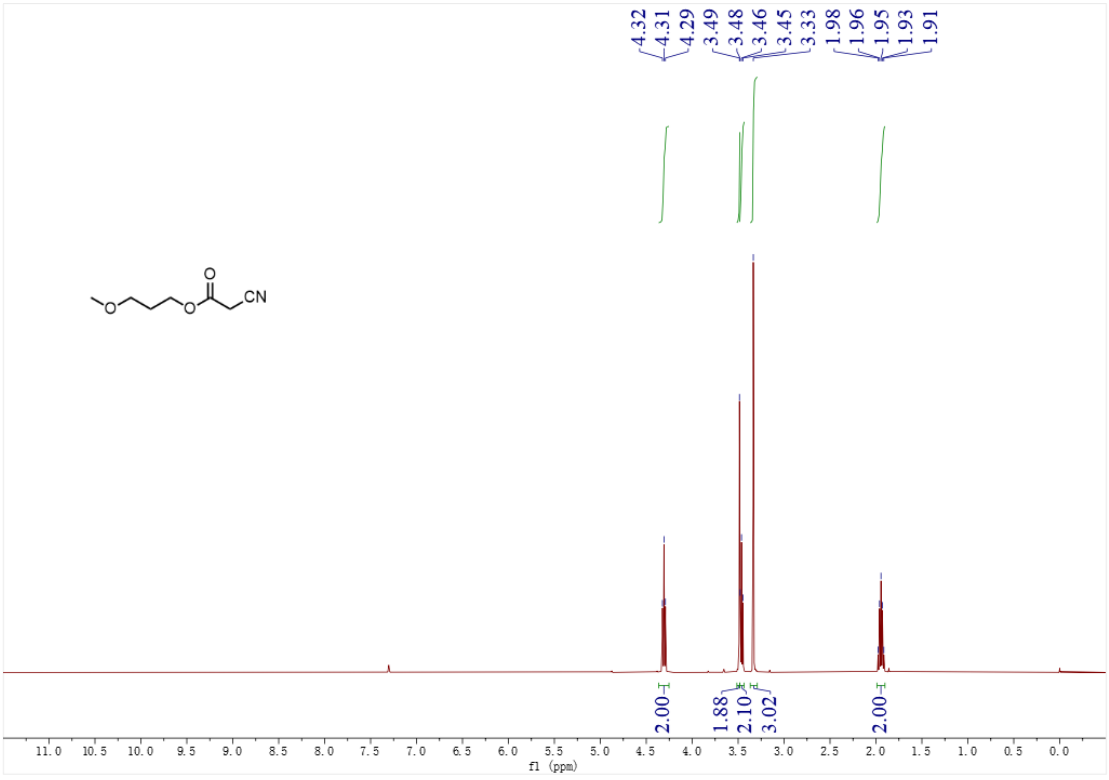
^{1}H NMR spectrum of **32** ($CDCl_3$)



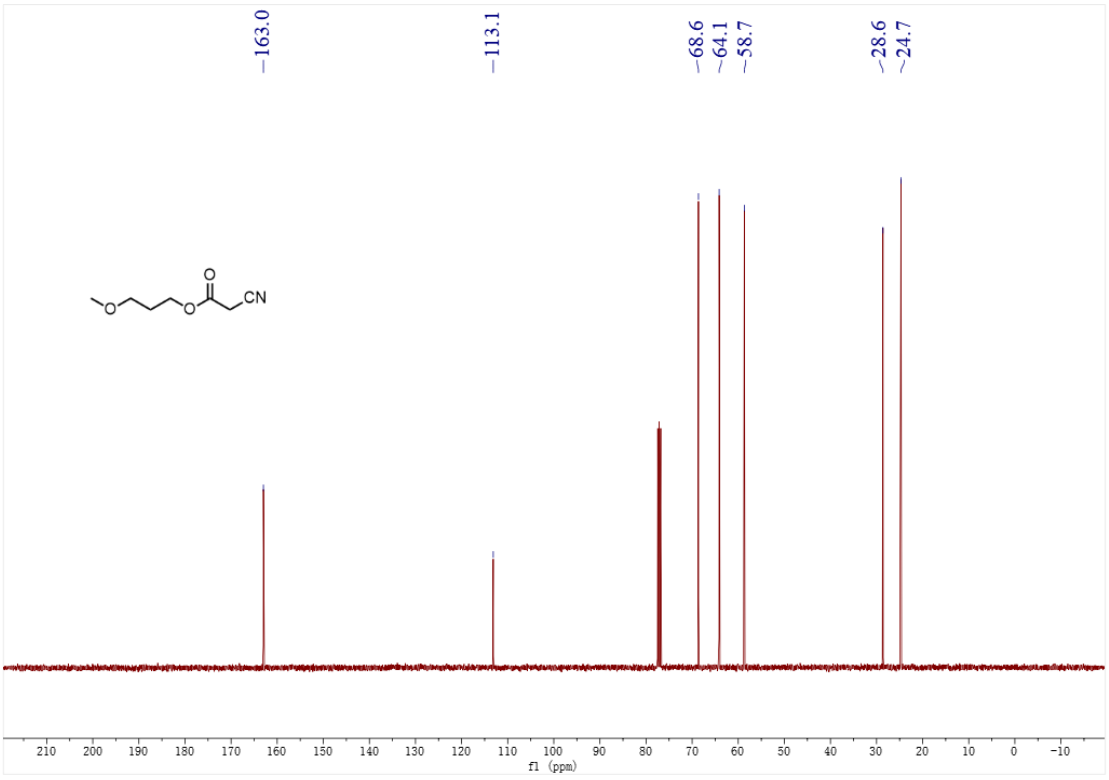
^{13}C NMR spectrum of **32** ($CDCl_3$)



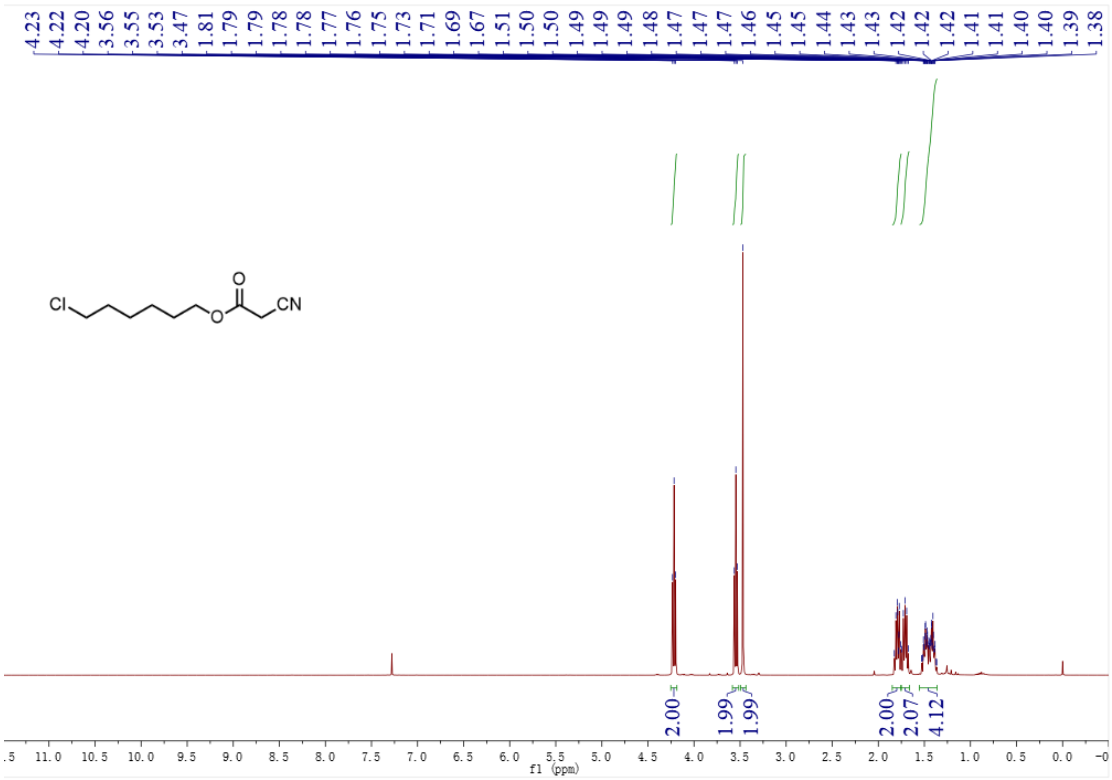
^{1}H NMR spectrum of **33** ($CDCl_3$)



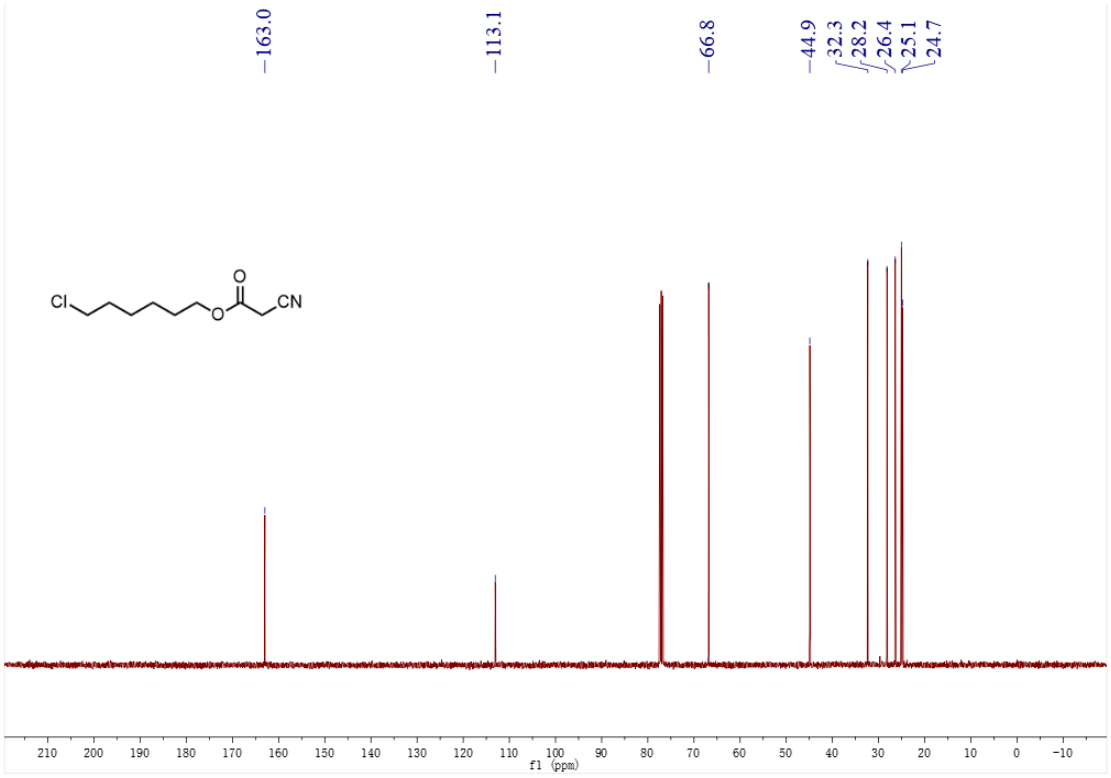
^{13}C NMR spectrum of **33** ($CDCl_3$)



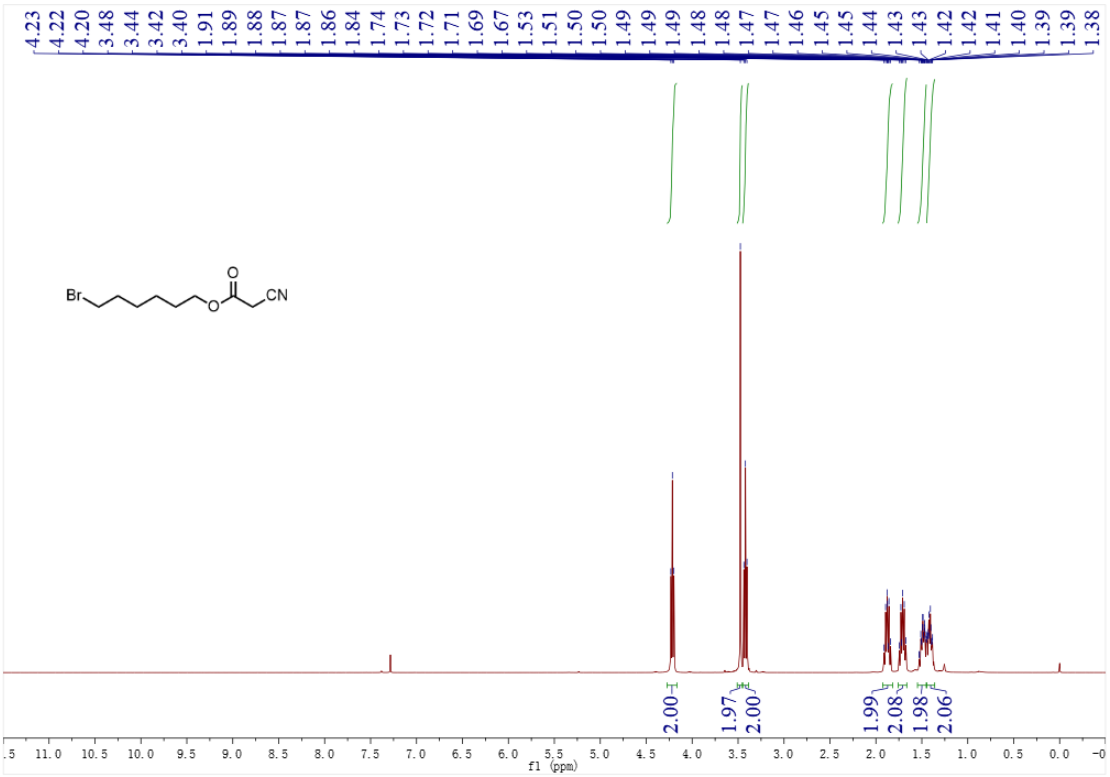
^{1}H NMR spectrum of **34** ($CDCl_3$)



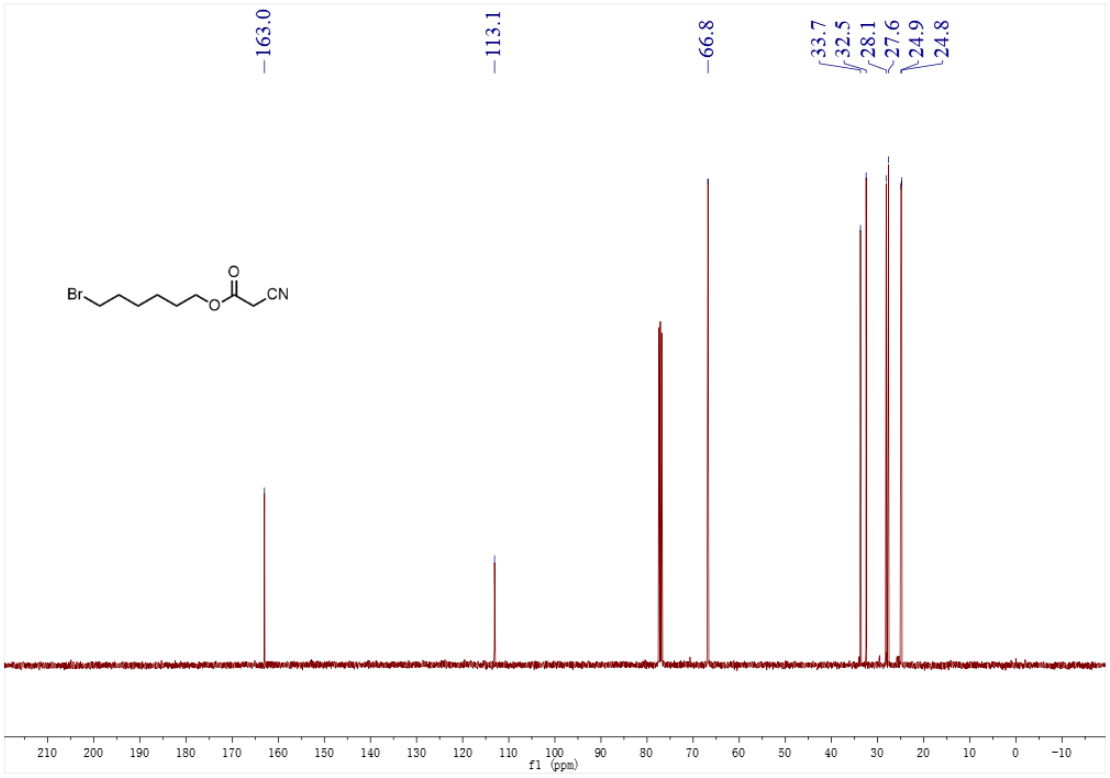
^{13}C NMR spectrum of **34** ($CDCl_3$)



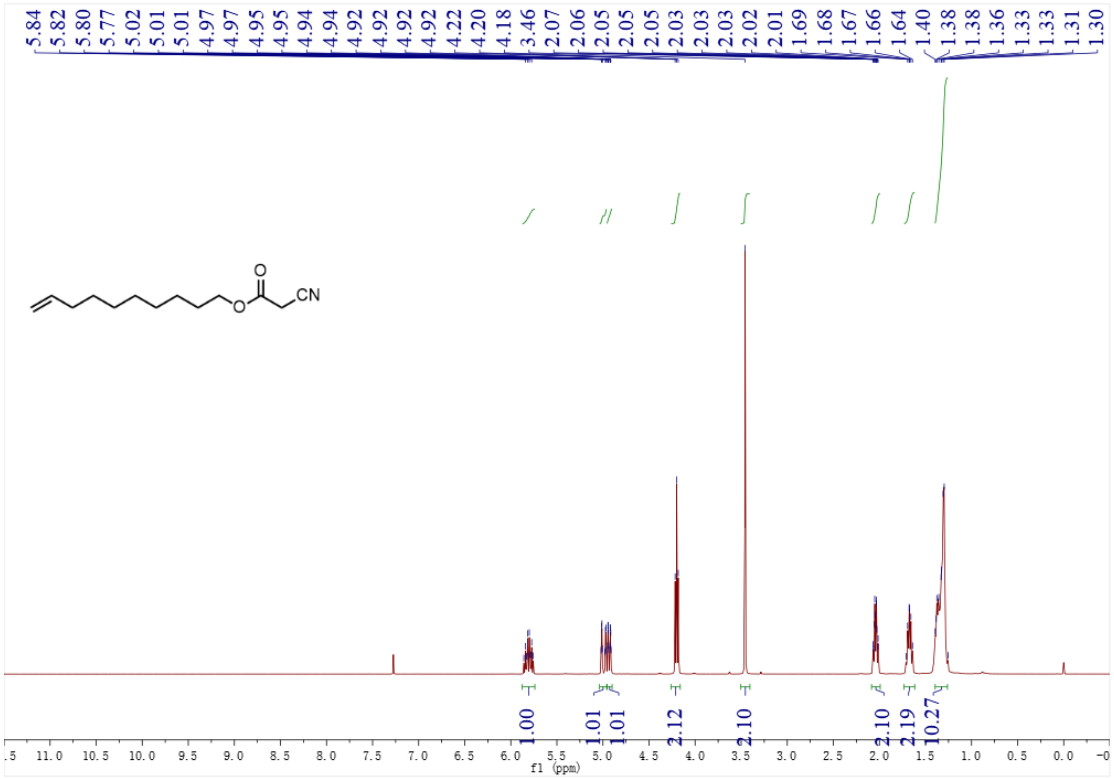
^{1}H NMR spectrum of **35** ($CDCl_3$)



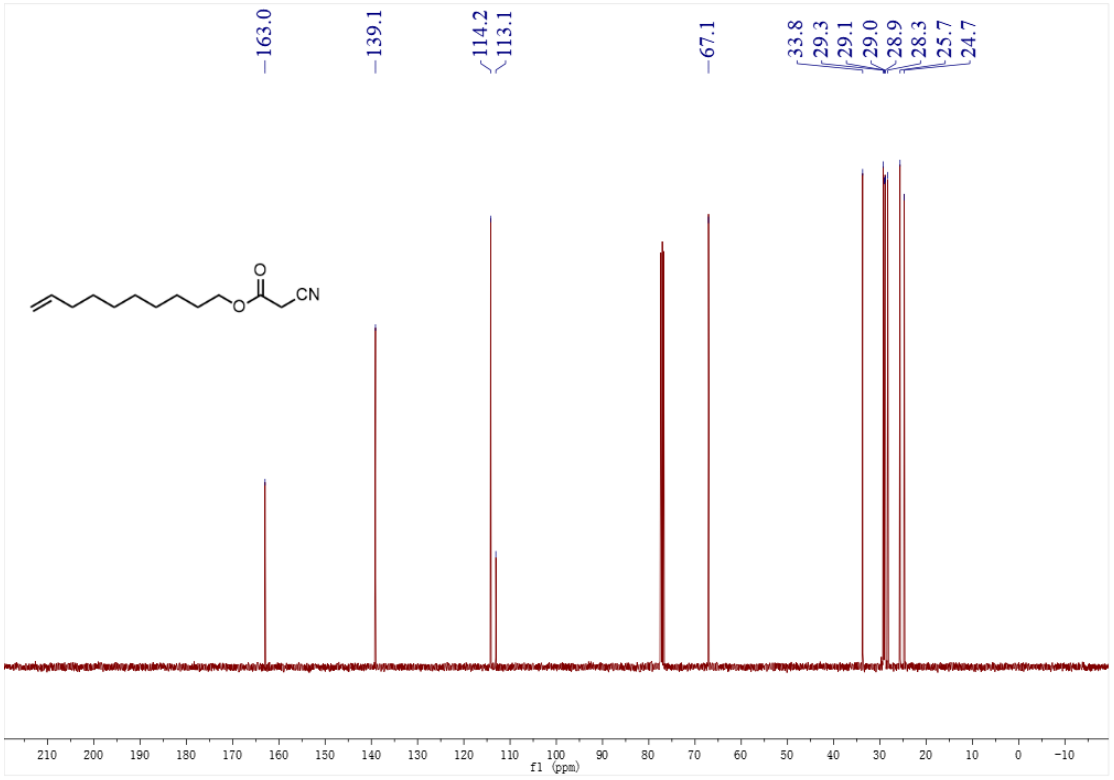
^{13}C NMR spectrum of **35** ($CDCl_3$)



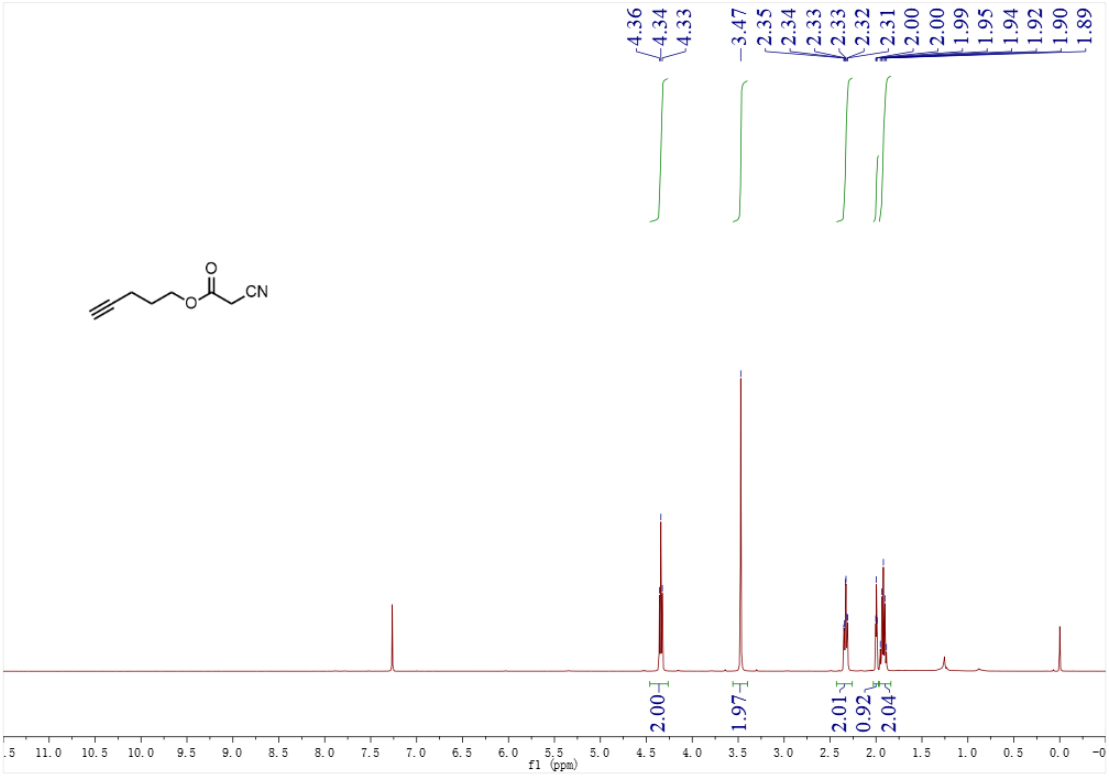
^{1}H NMR spectrum of **36** ($CDCl_3$)



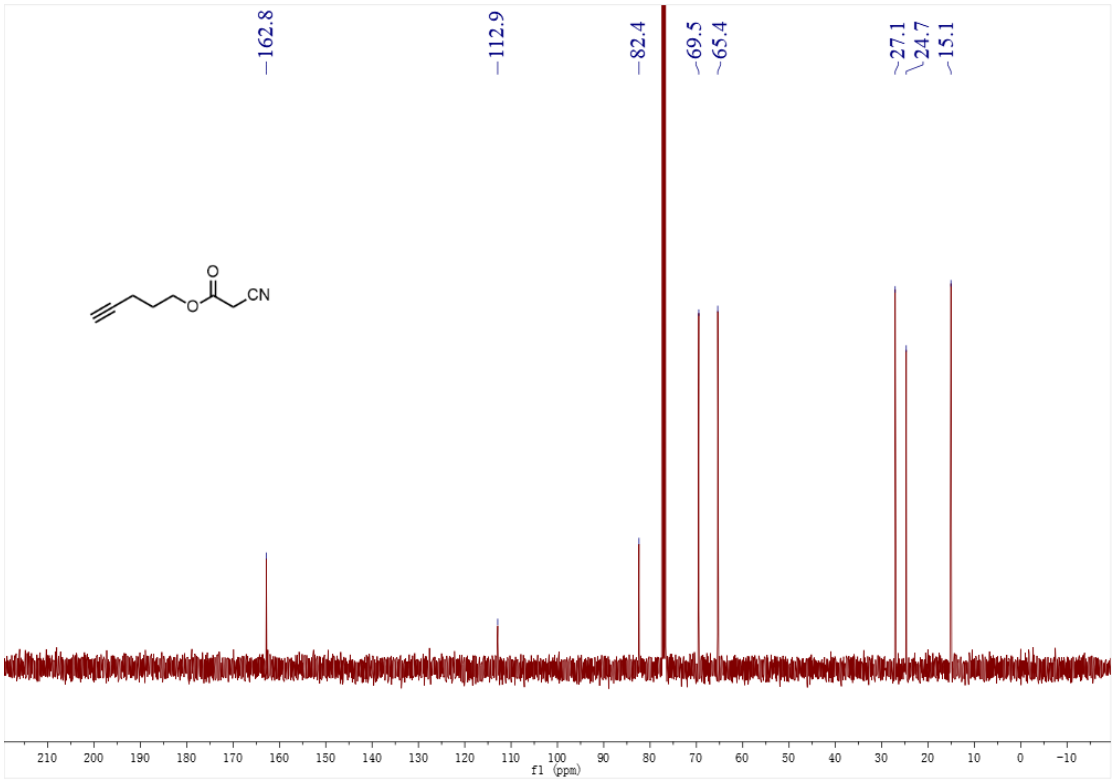
^{13}C NMR spectrum of **36** ($CDCl_3$)



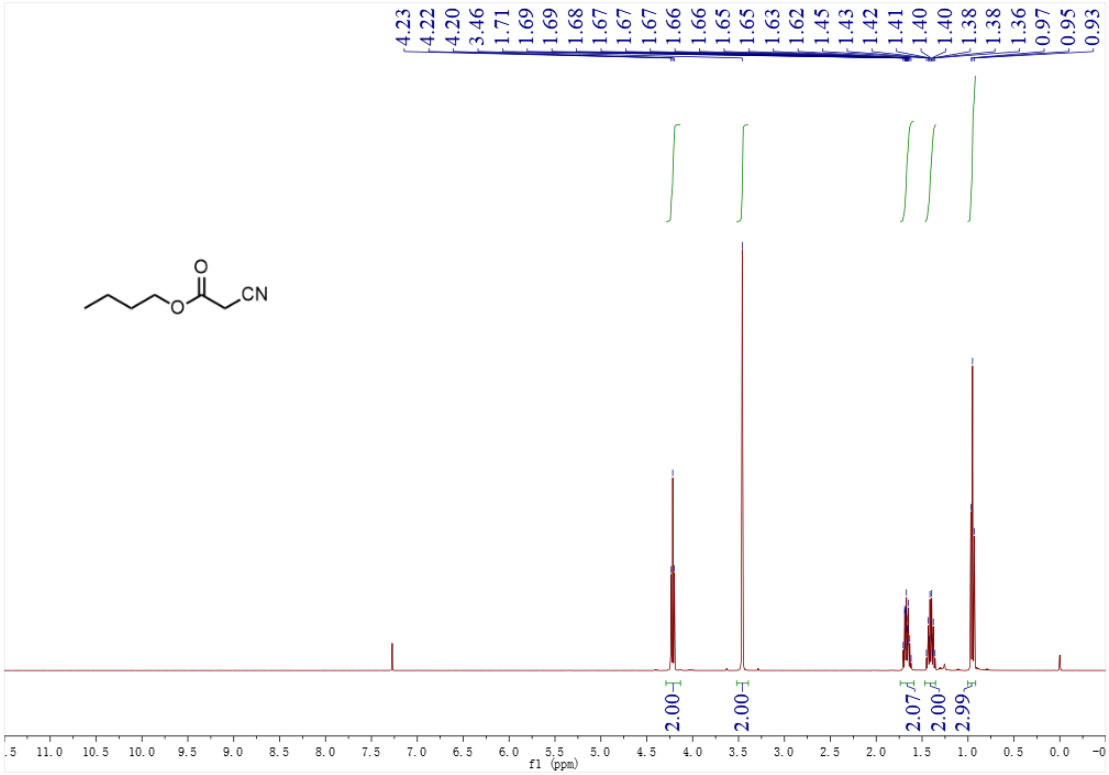
^{1}H NMR spectrum of **37** ($CDCl_3$)



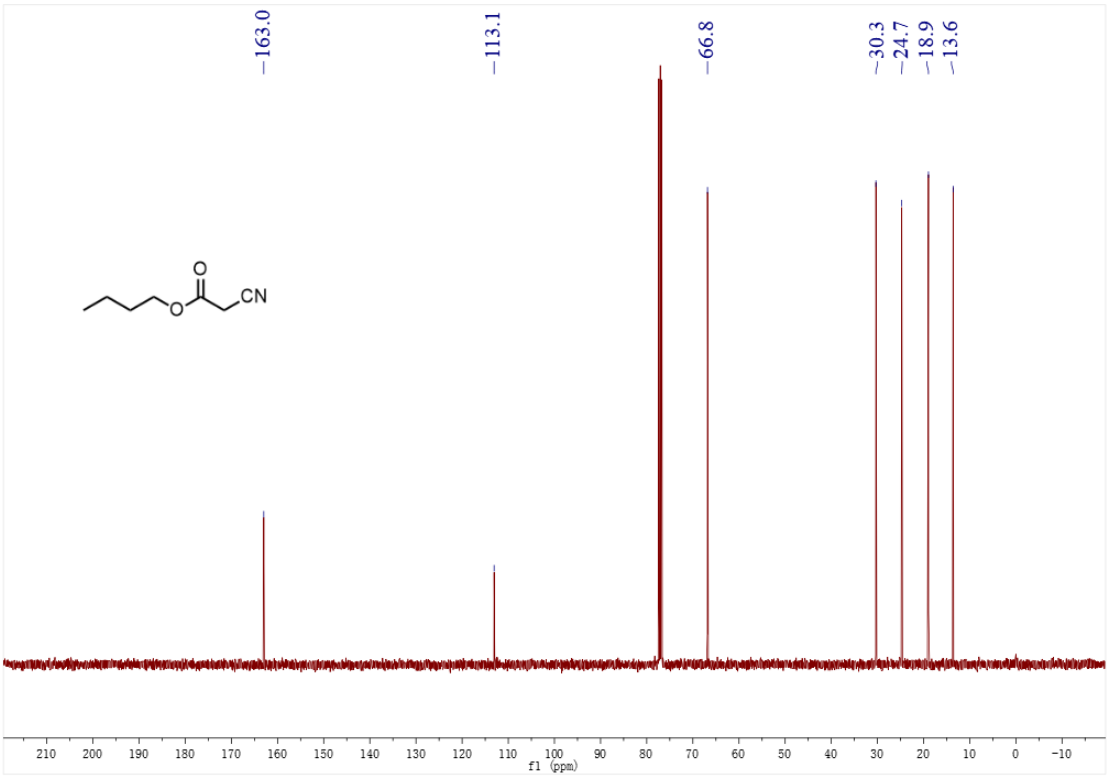
^{13}C NMR spectrum of **37** ($CDCl_3$)



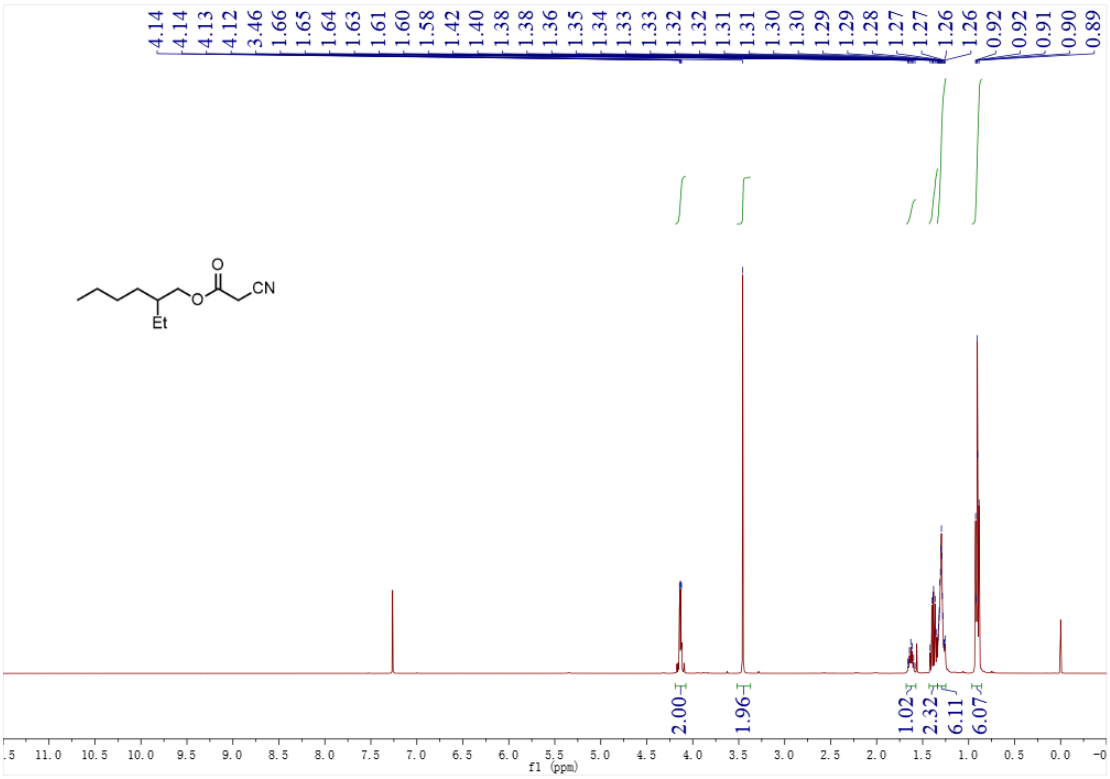
^{1}H NMR spectrum of **38** ($CDCl_3$)



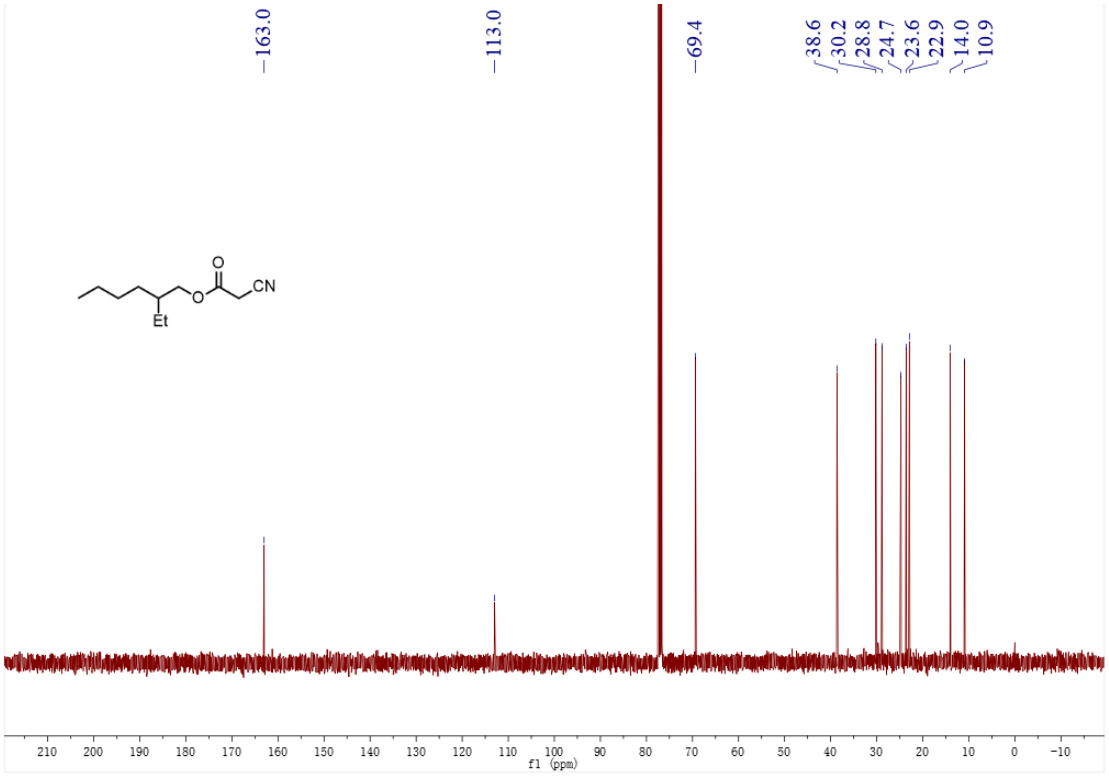
^{13}C NMR spectrum of **38** ($CDCl_3$)



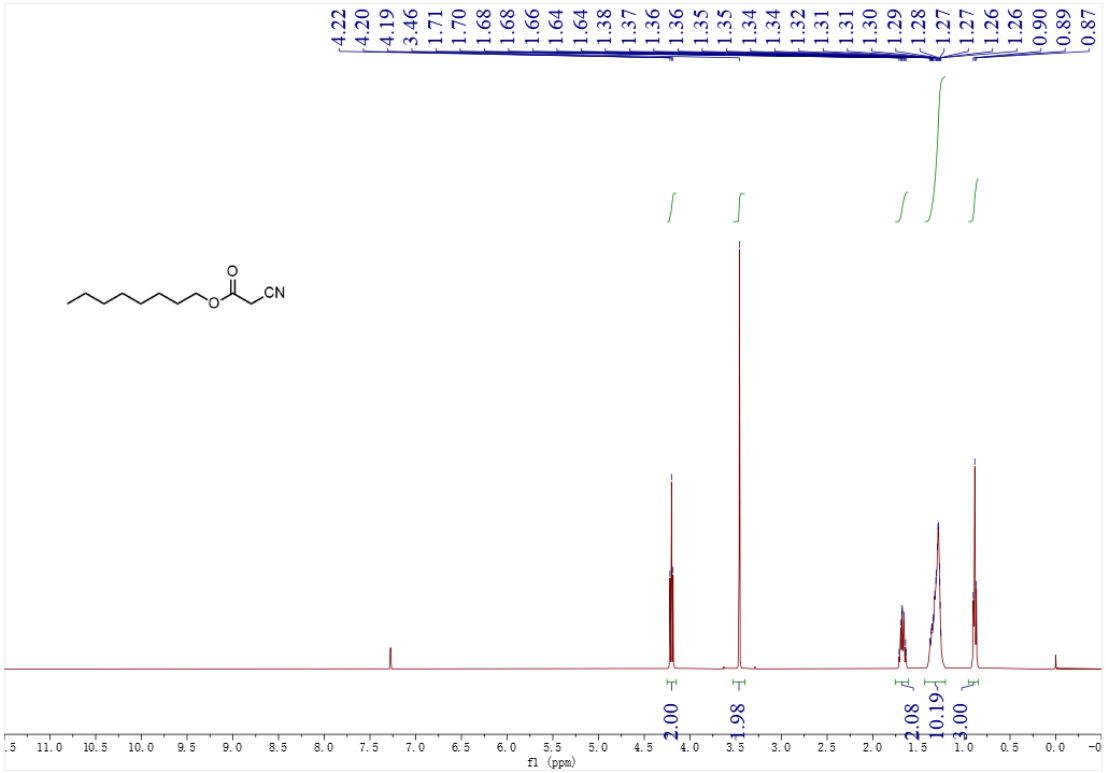
^{1}H NMR spectrum of **39** ($CDCl_3$)



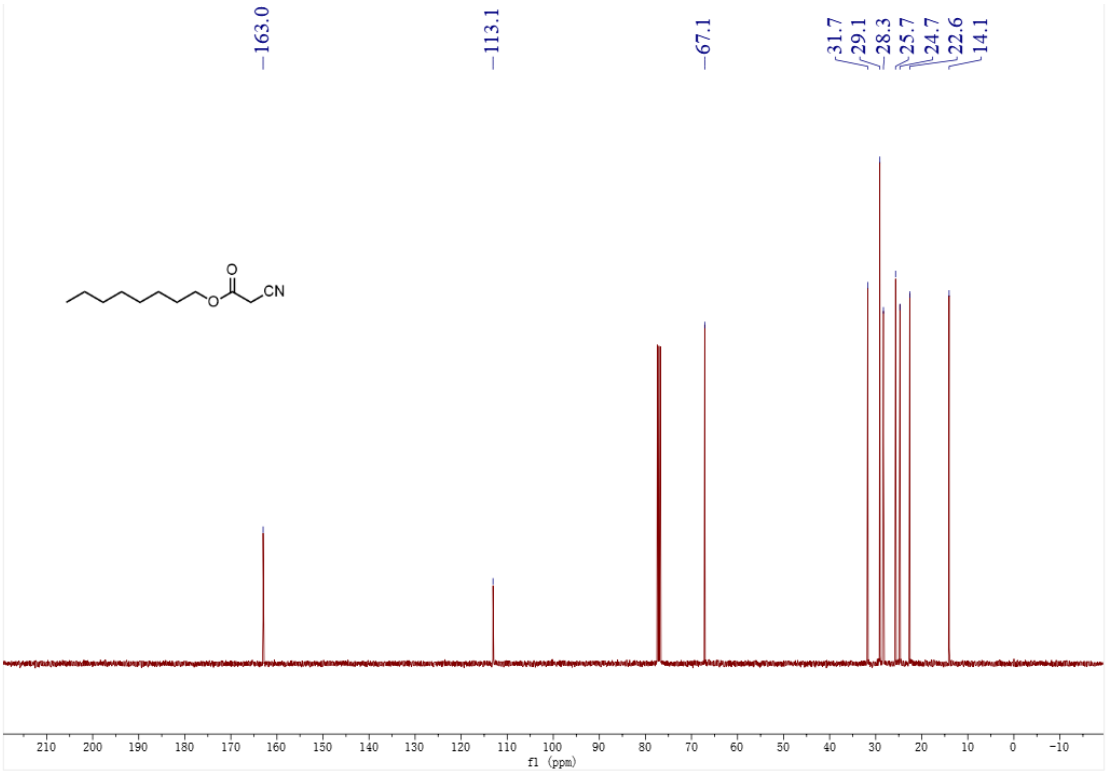
^{13}C NMR spectrum of **39** ($CDCl_3$)



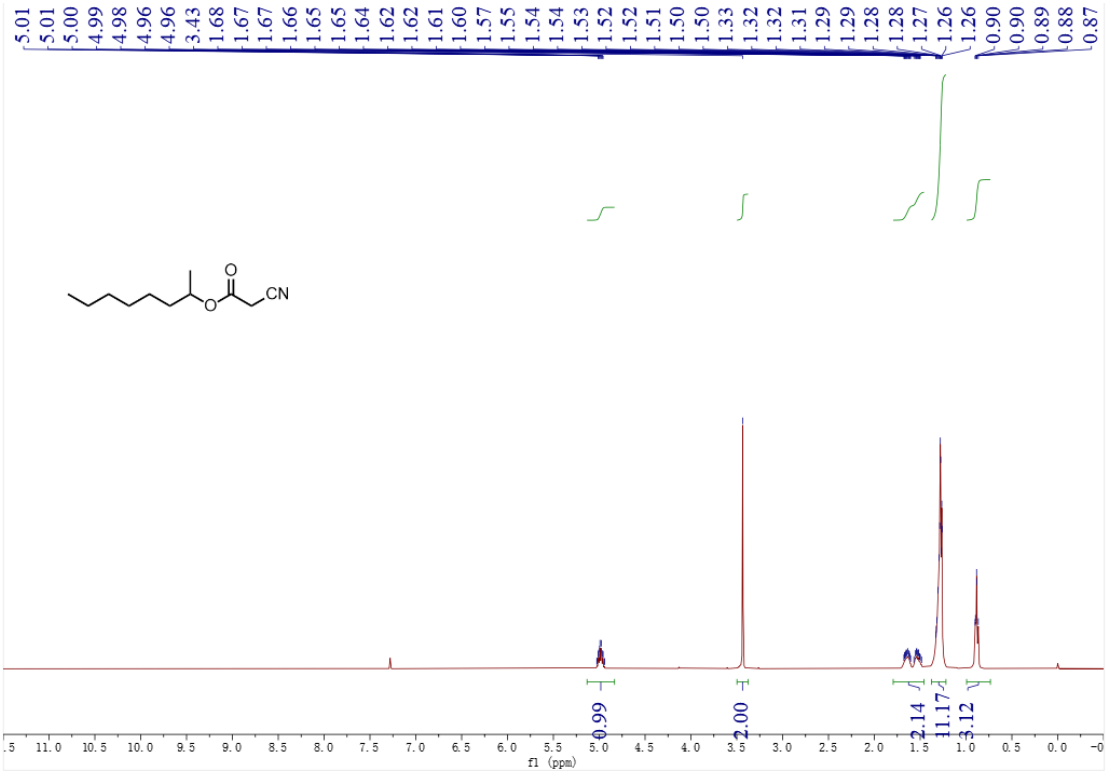
^{1}H NMR spectrum of **40** ($CDCl_3$)



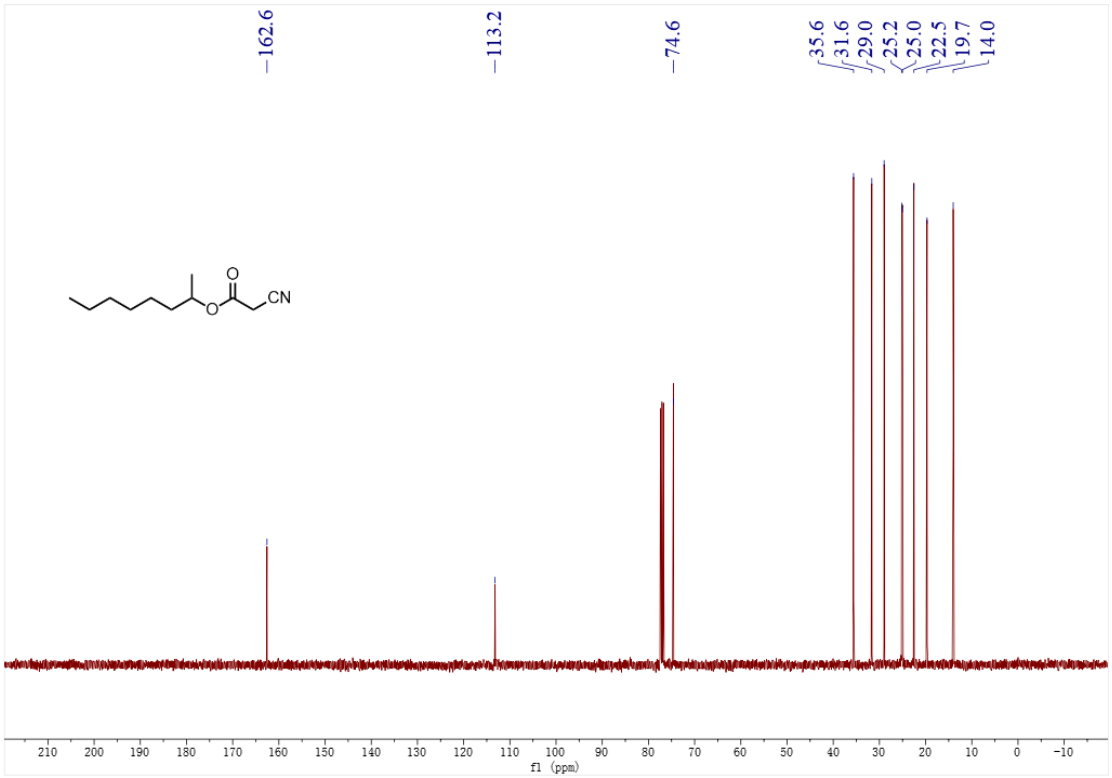
^{13}C NMR spectrum of **40** ($CDCl_3$)



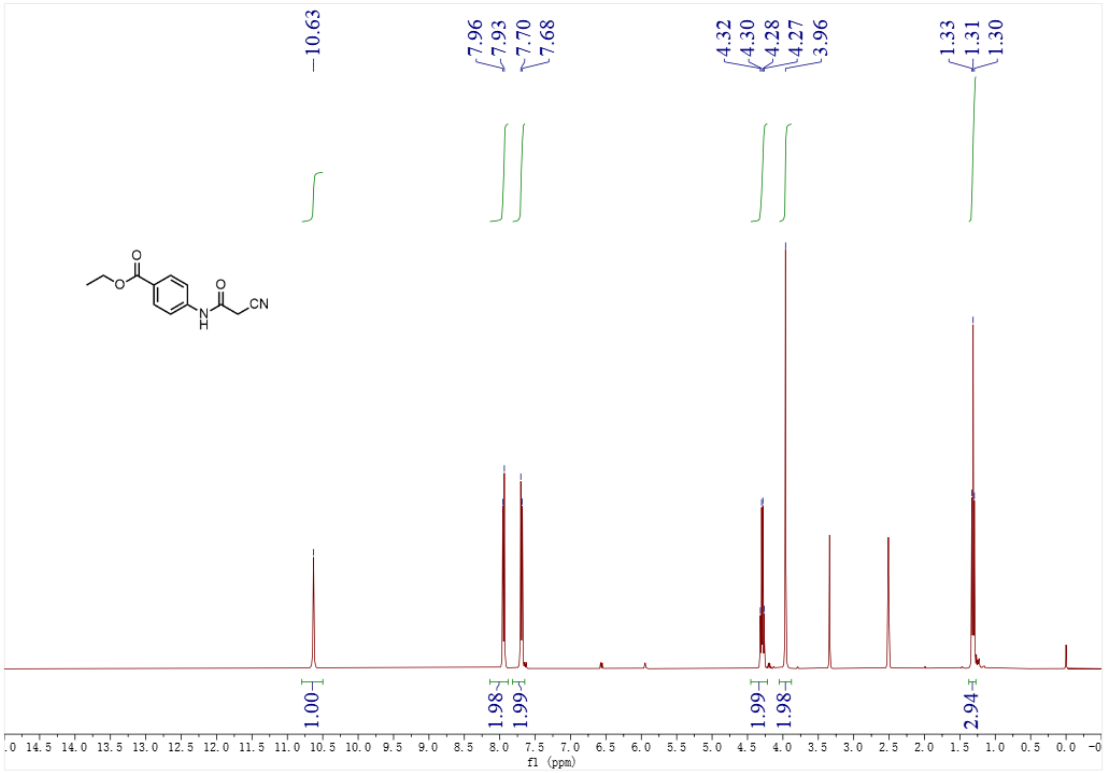
^{1}H NMR spectrum of **41** ($CDCl_3$)



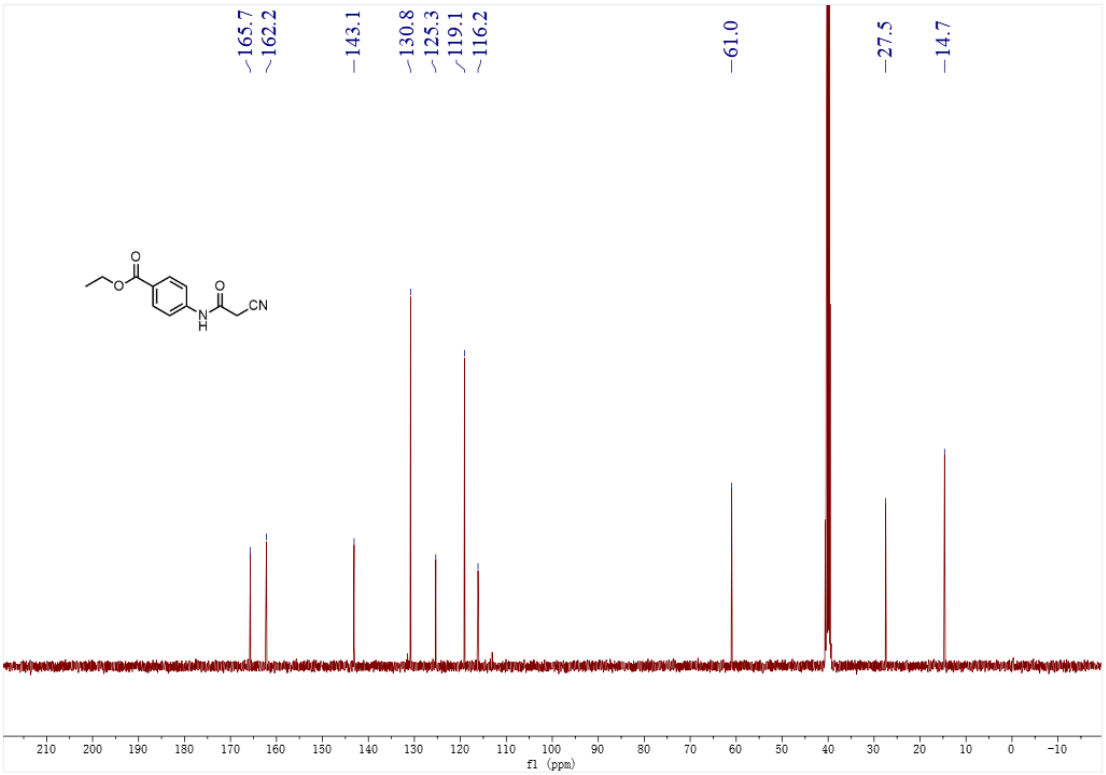
^{13}C NMR spectrum of **41** ($CDCl_3$)



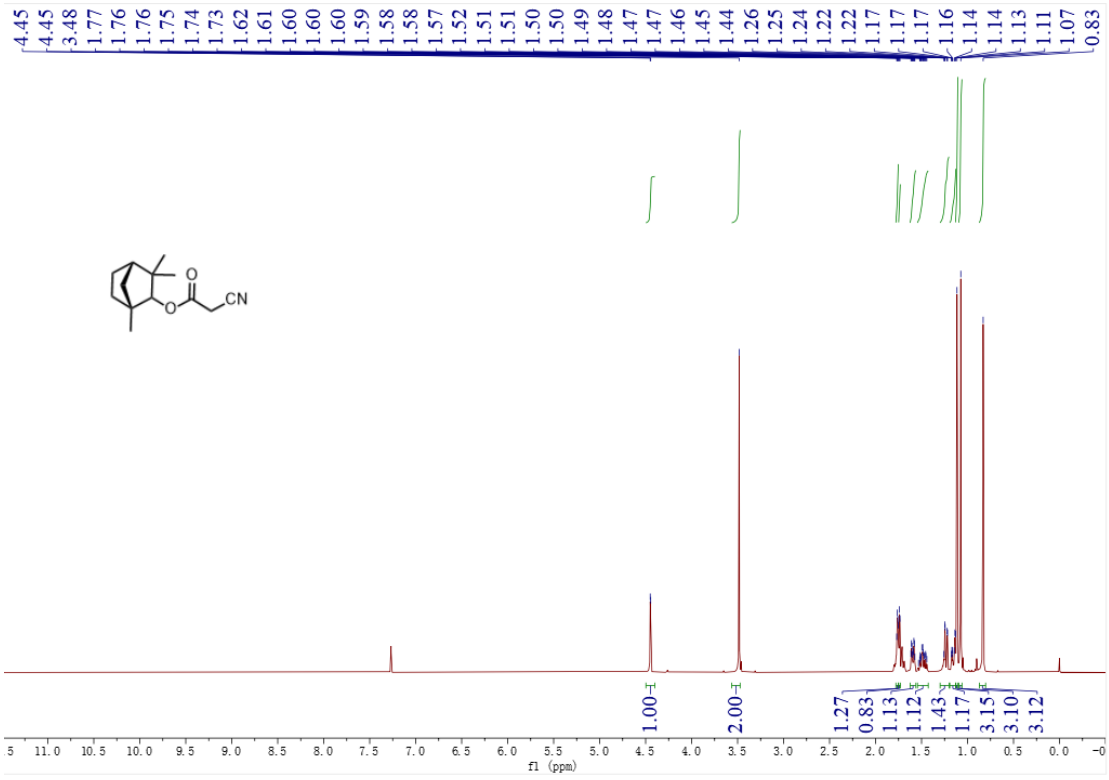
^{1}H NMR spectrum of **42** ($CDCl_3$)



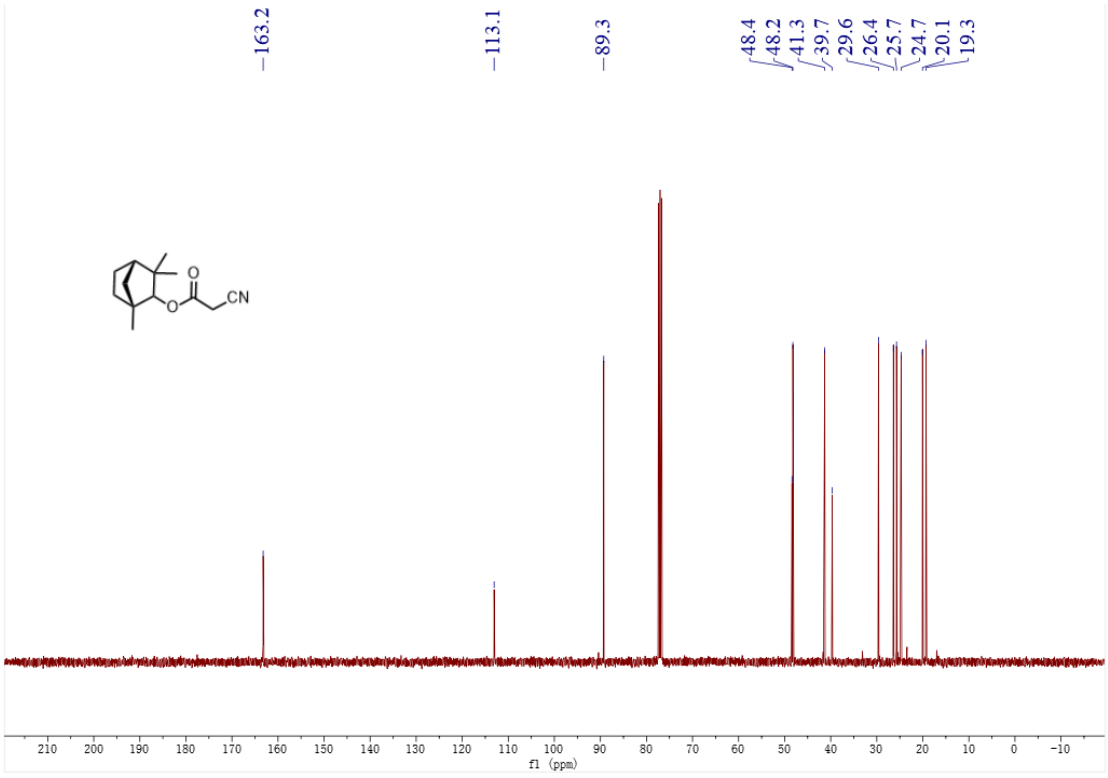
^{13}C NMR spectrum of **42** ($CDCl_3$)



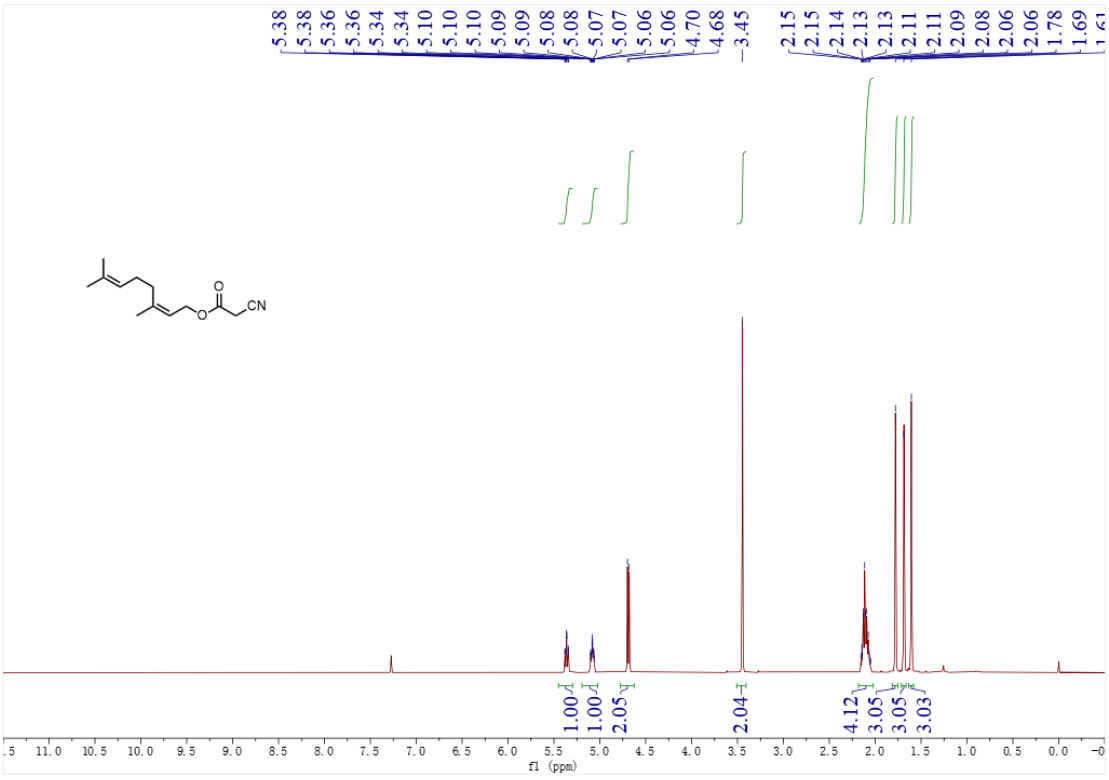
^{1}H NMR spectrum of **43** ($CDCl_3$)



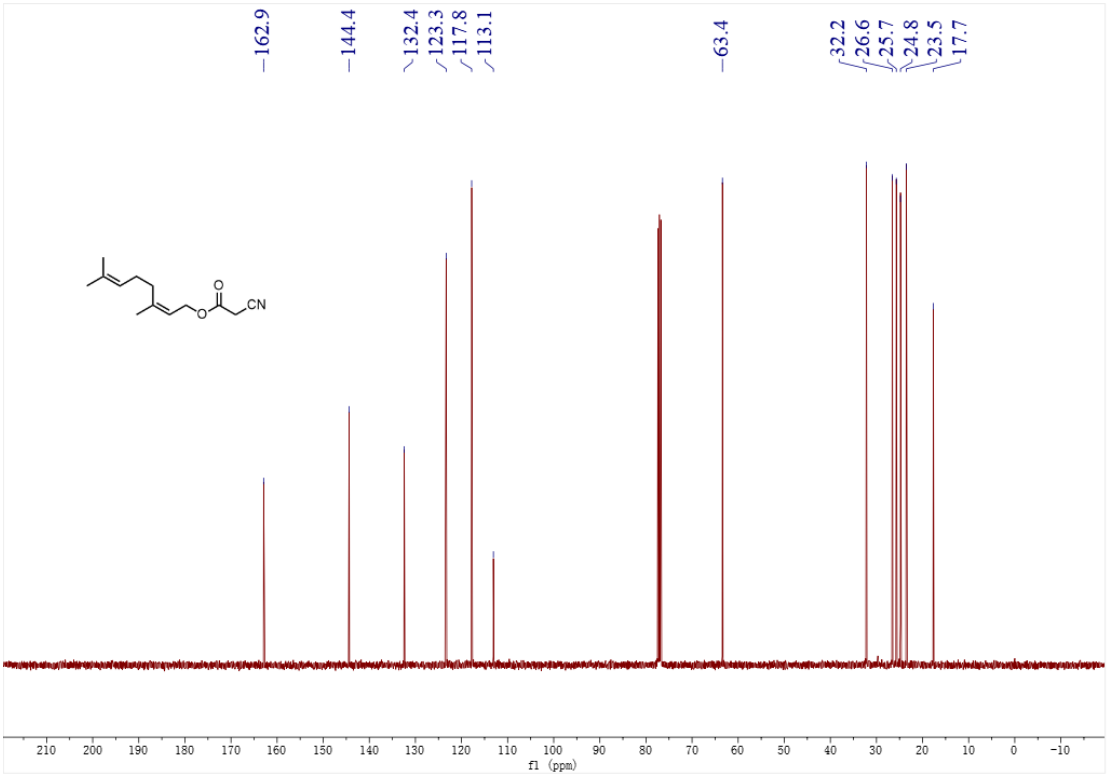
^{13}C NMR spectrum of **43** ($CDCl_3$)



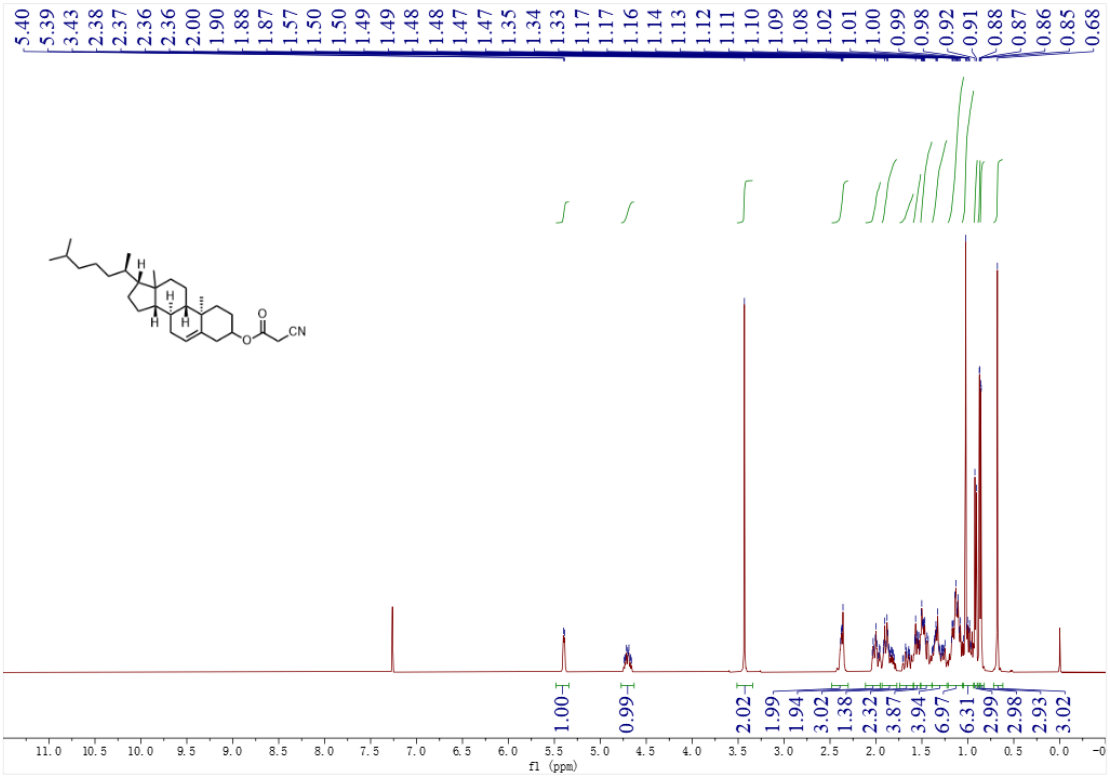
^{1}H NMR spectrum of **44** ($CDCl_3$)



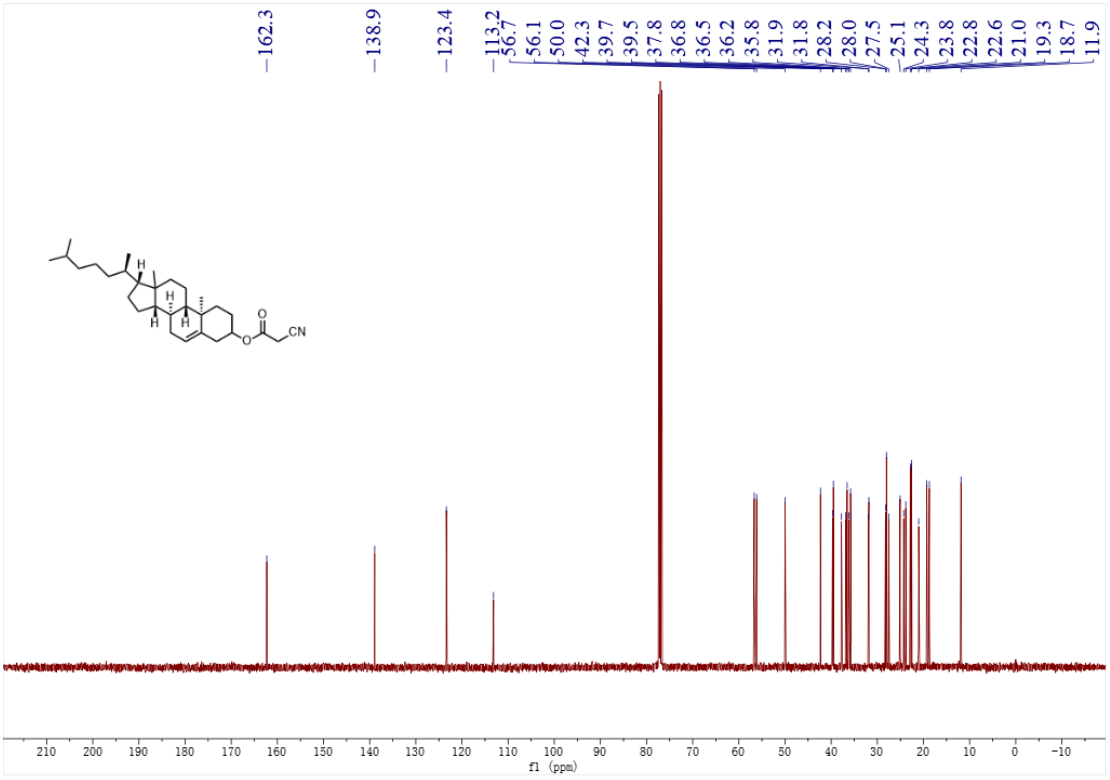
^{13}C NMR spectrum of **44** ($CDCl_3$)



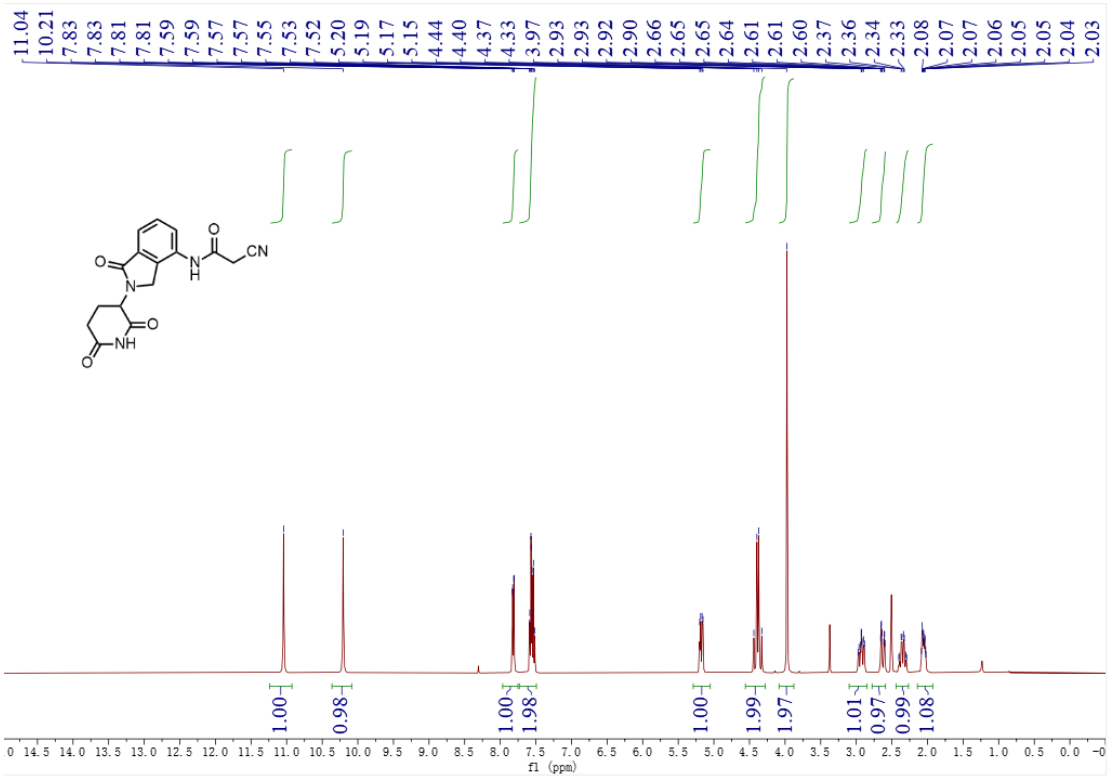
^{1}H NMR spectrum of **45** ($CDCl_3$)



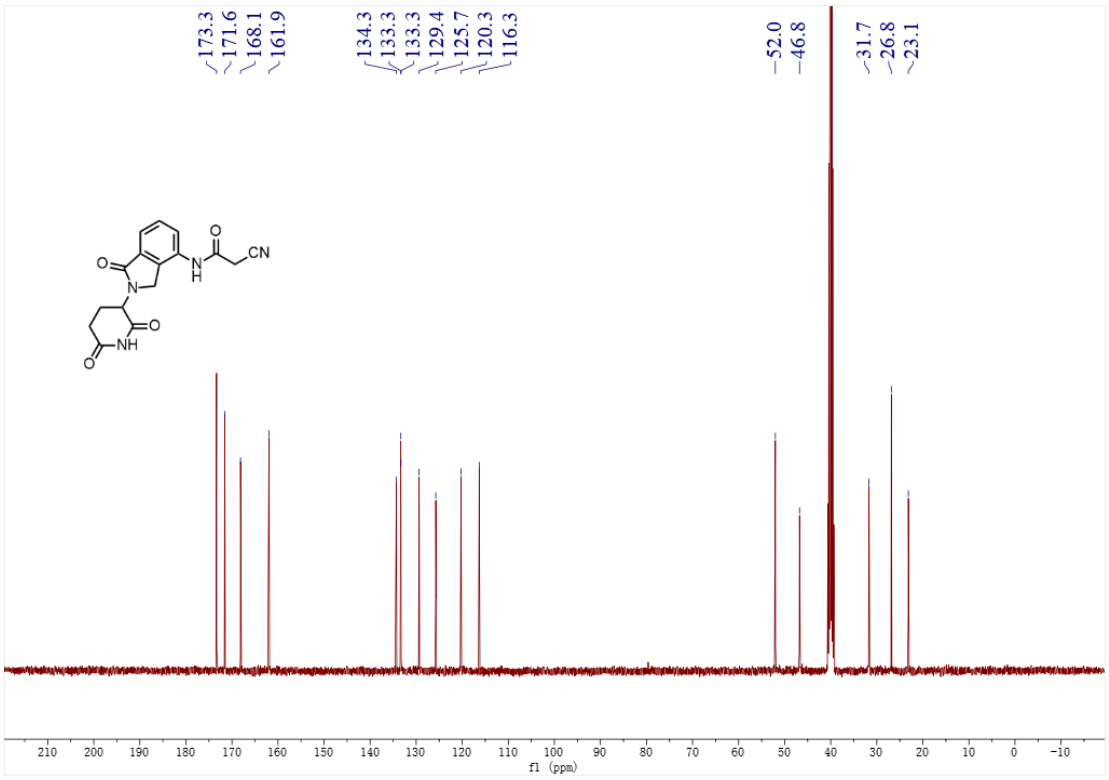
^{13}C NMR spectrum of **45** ($CDCl_3$)



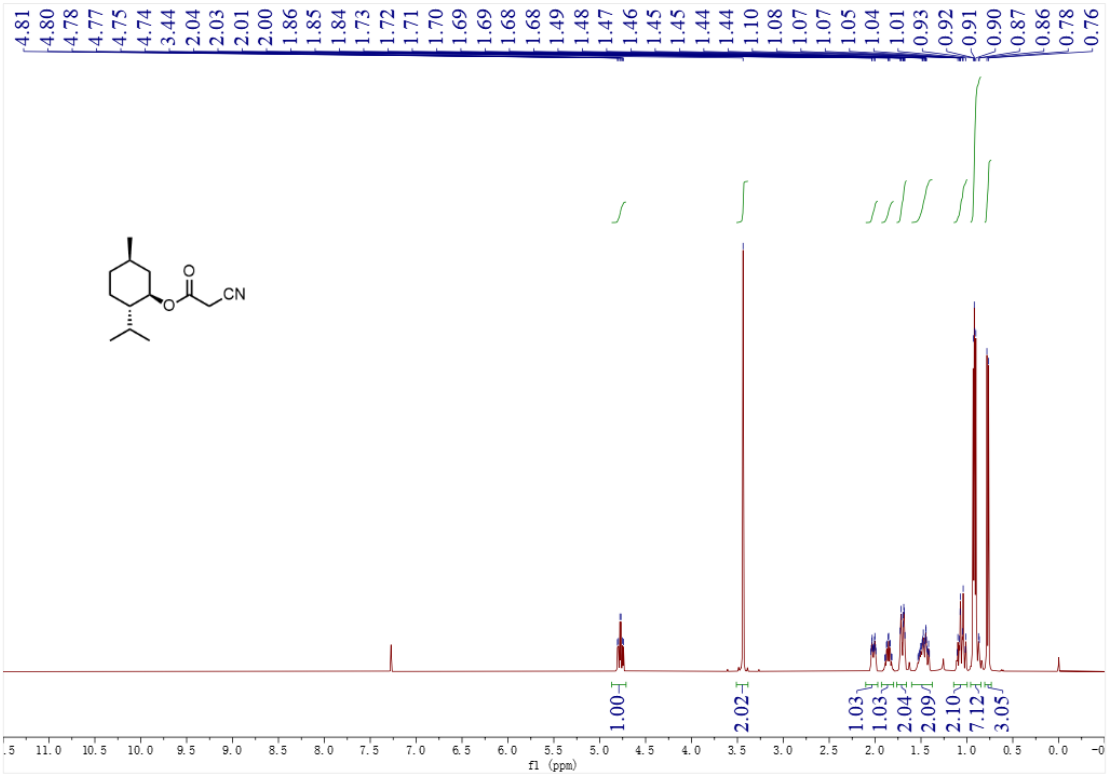
^{1}H NMR spectrum of **46** ($CDCl_3$)



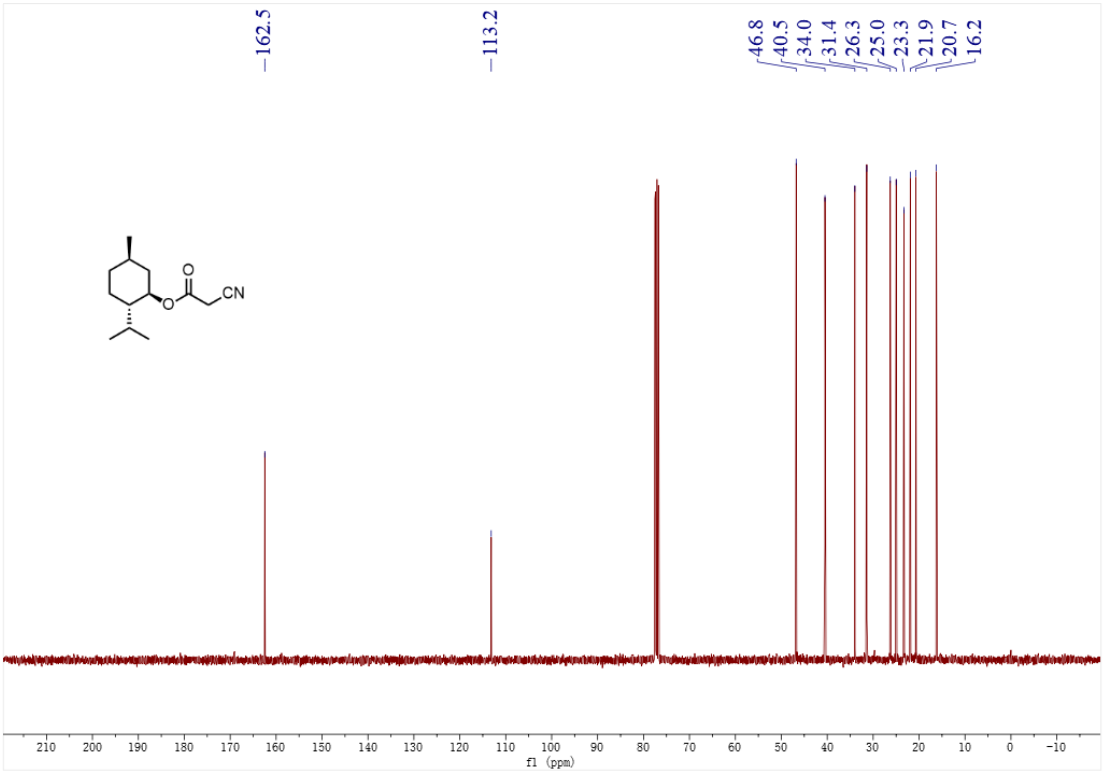
^{13}C NMR spectrum of **46** ($CDCl_3$)



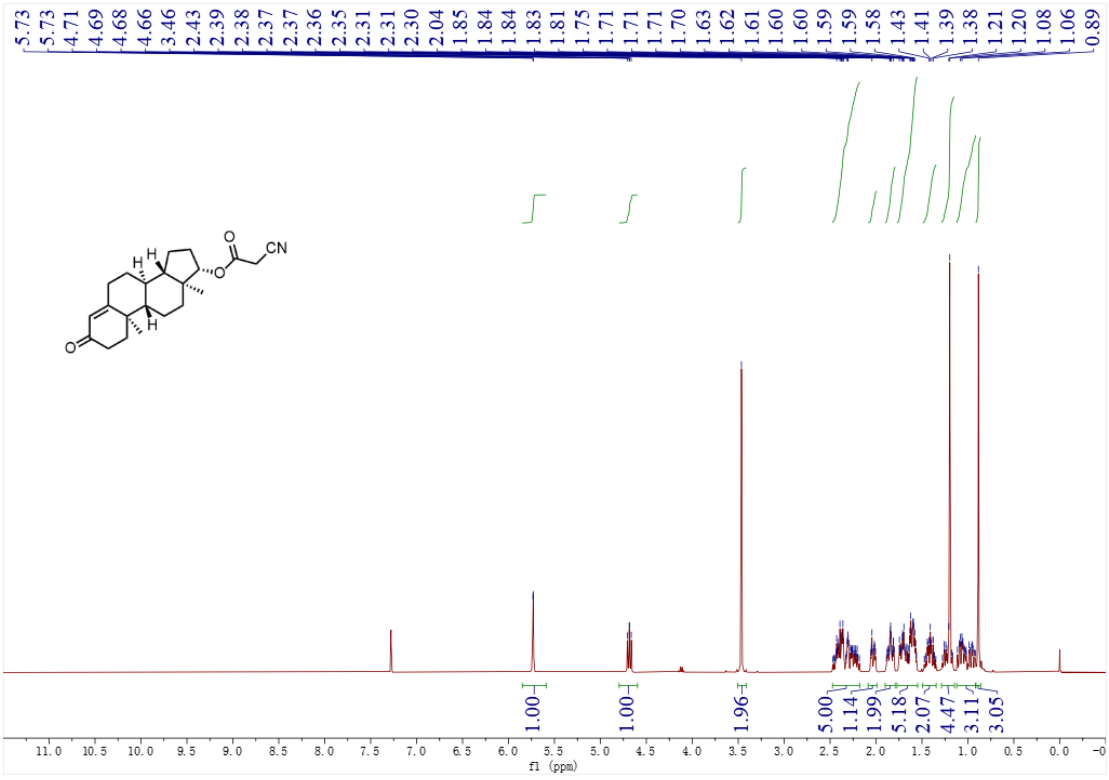
^{1}H NMR spectrum of **47** ($CDCl_3$)



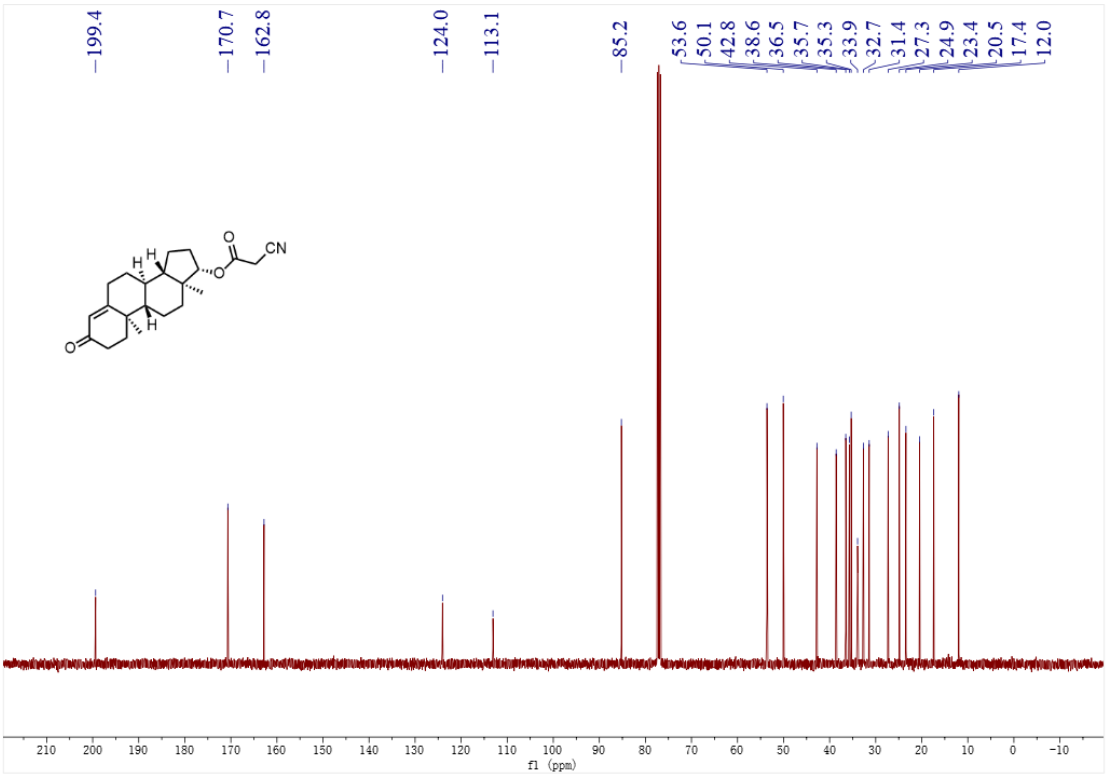
^{13}C NMR spectrum of **47** ($CDCl_3$)



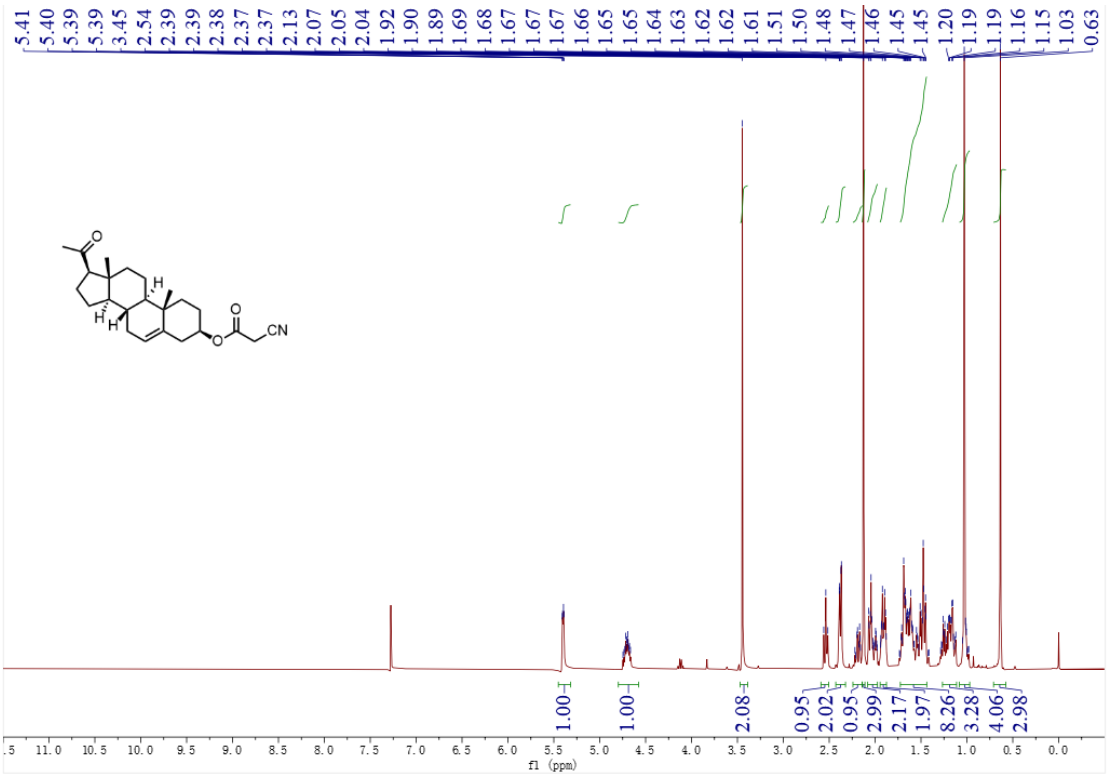
^{1}H NMR spectrum of **48** ($CDCl_3$)



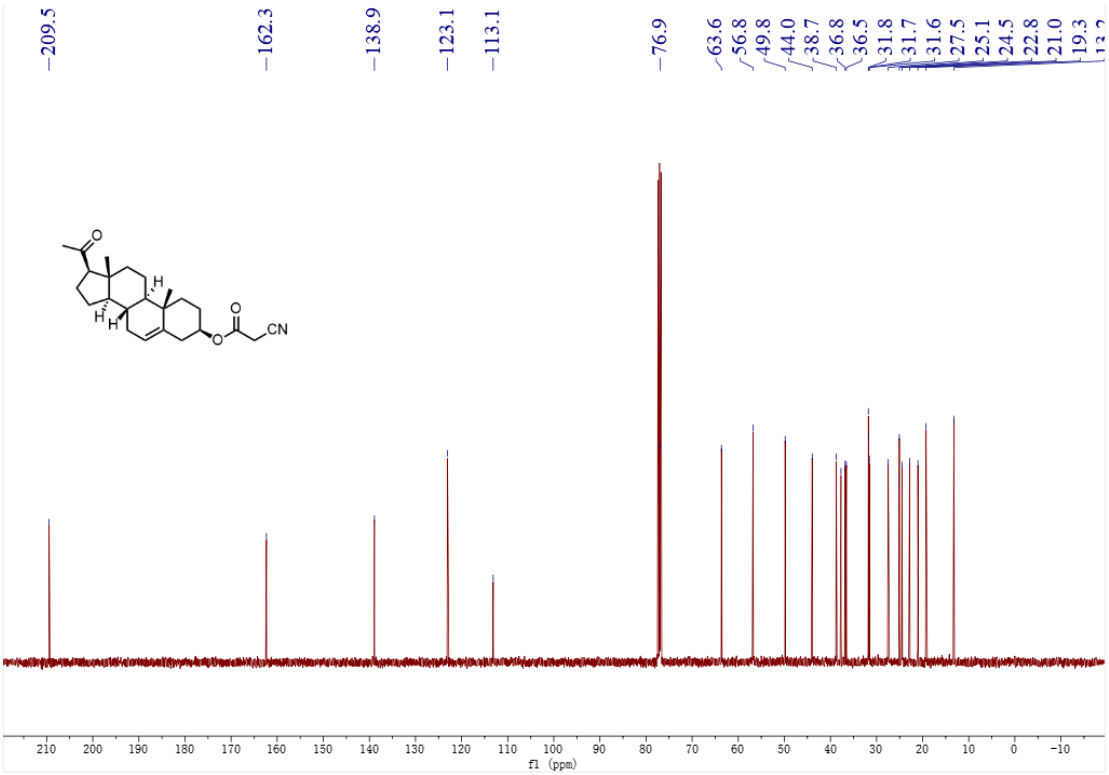
^{13}C NMR spectrum of **48** ($CDCl_3$)



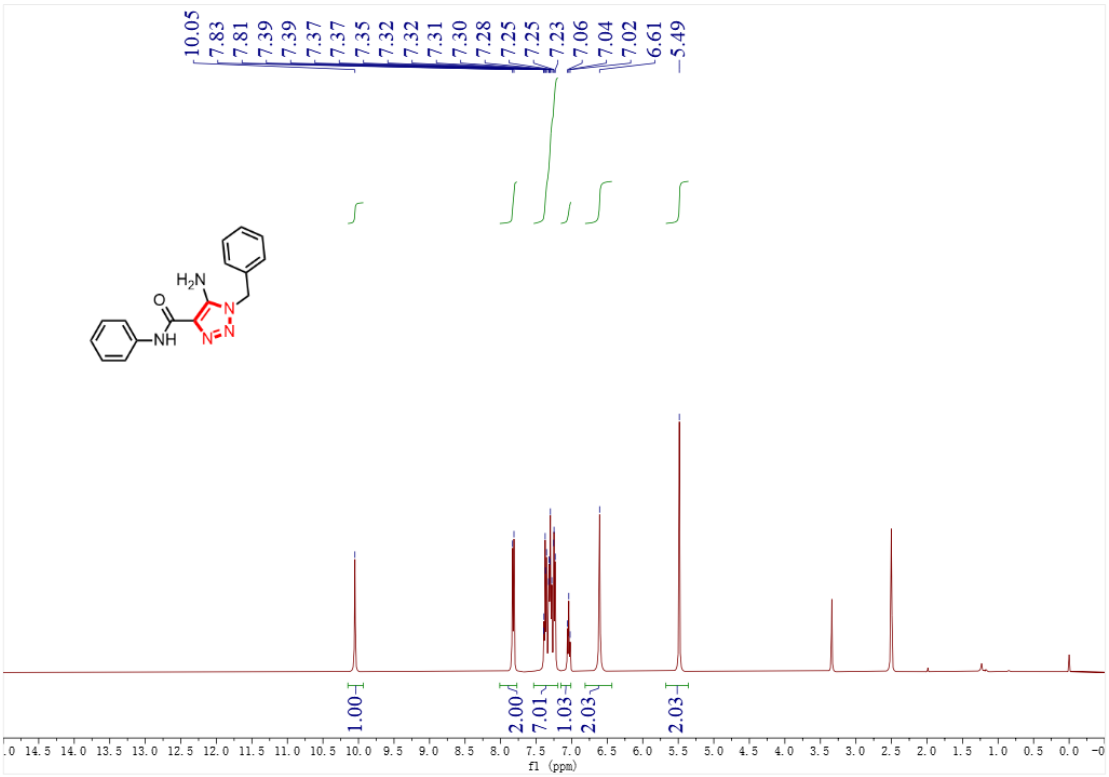
^{1}H NMR spectrum of **49** ($CDCl_3$)



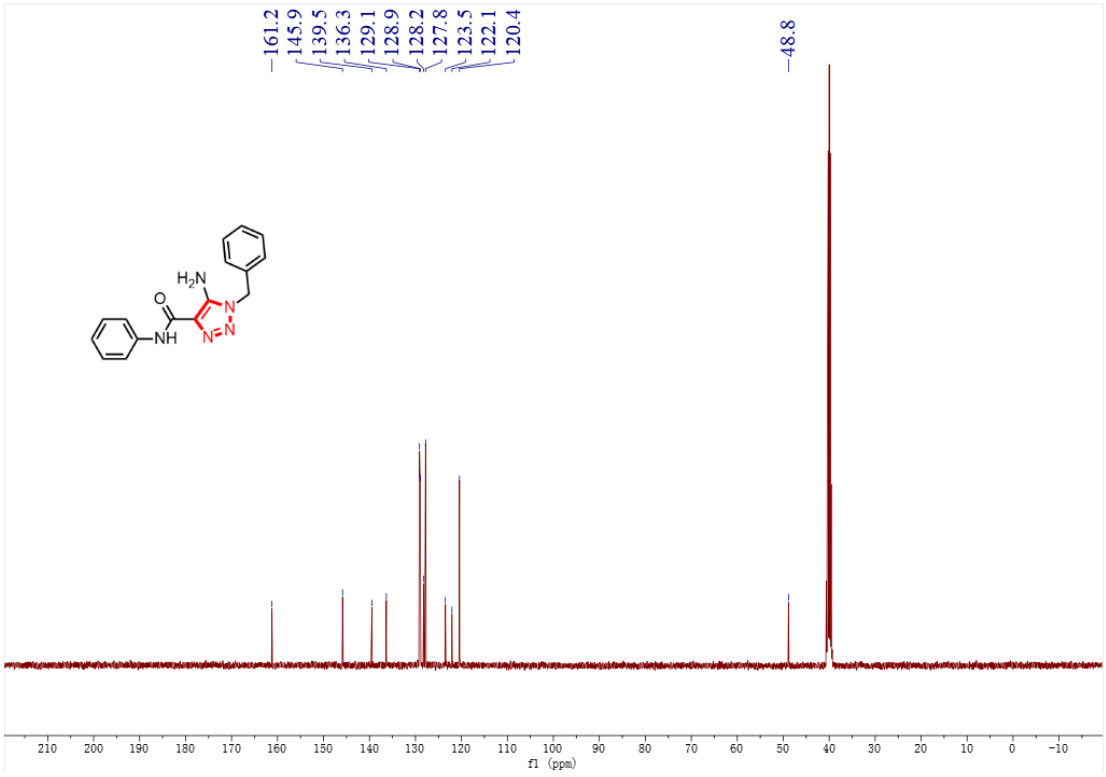
^{13}C NMR spectrum of **49** ($CDCl_3$)



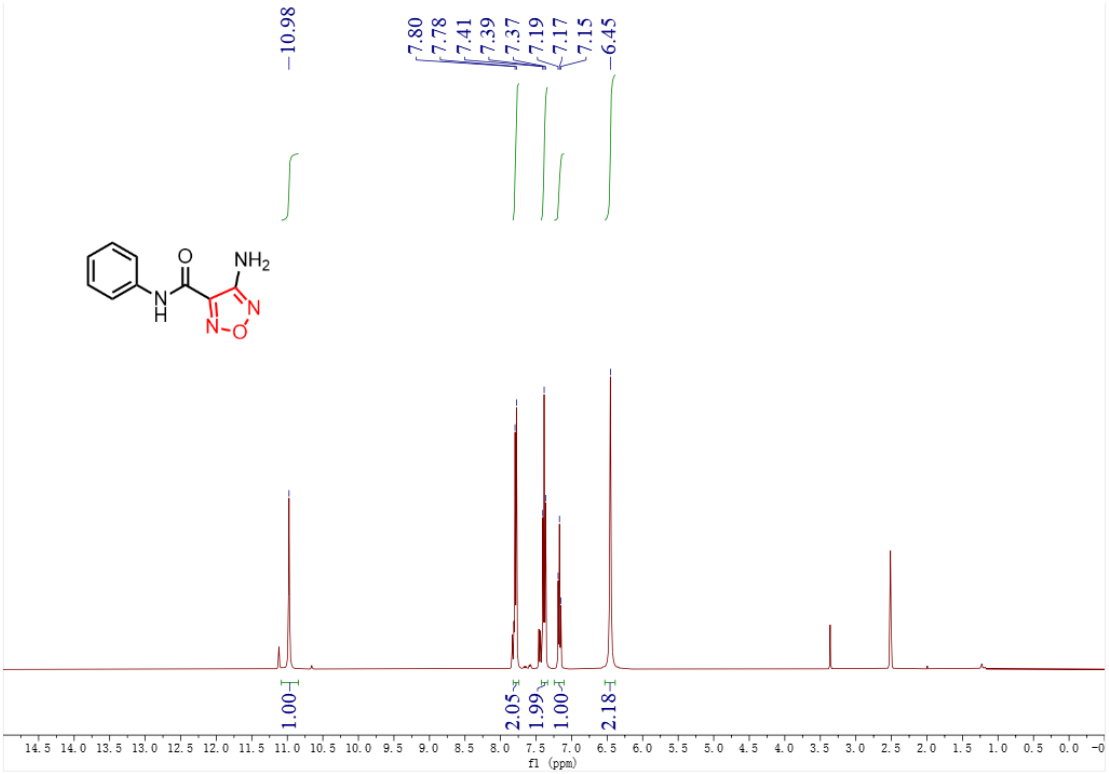
^{1}H NMR spectrum of **50** (DMSO-d_6)



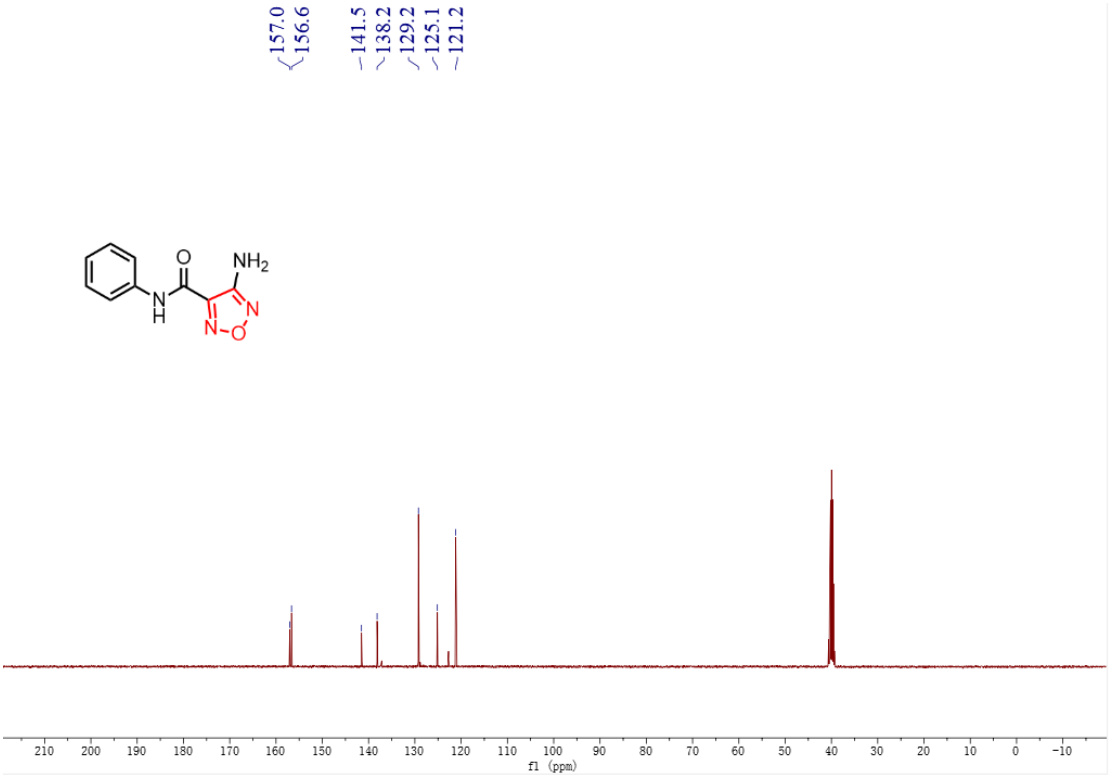
^{13}C NMR spectrum of **50** (DMSO-d_6)



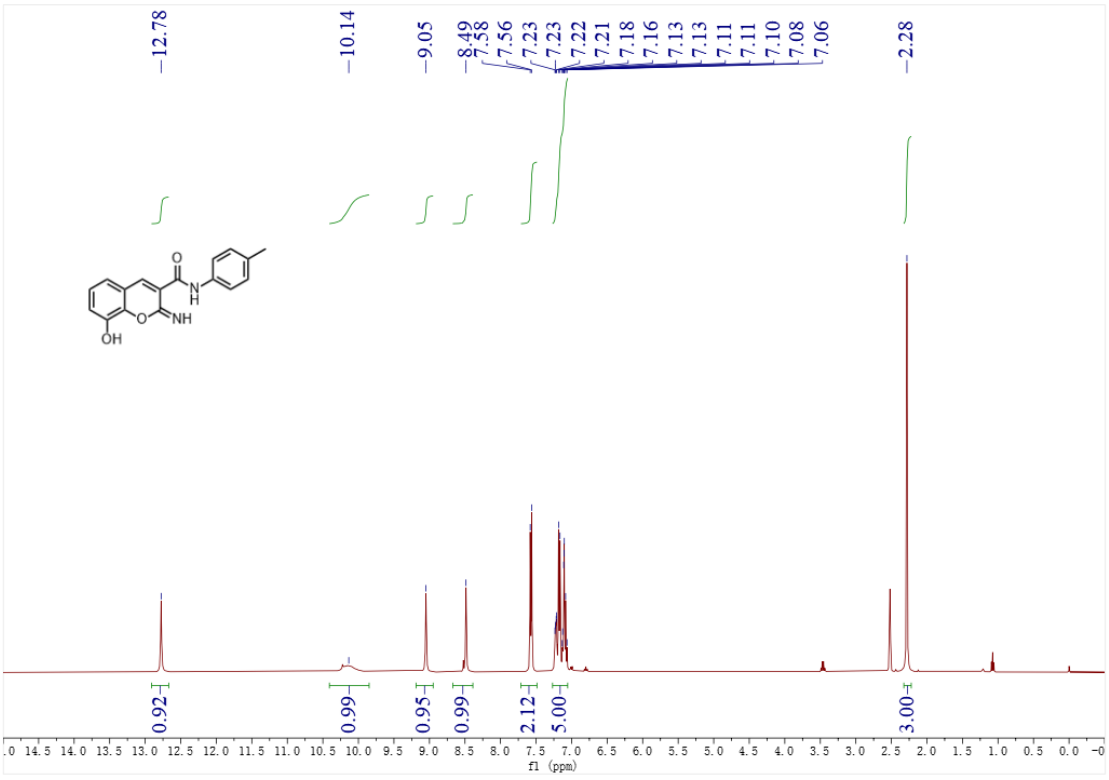
^{1}H NMR spectrum of **51** (DMSO-d_6)



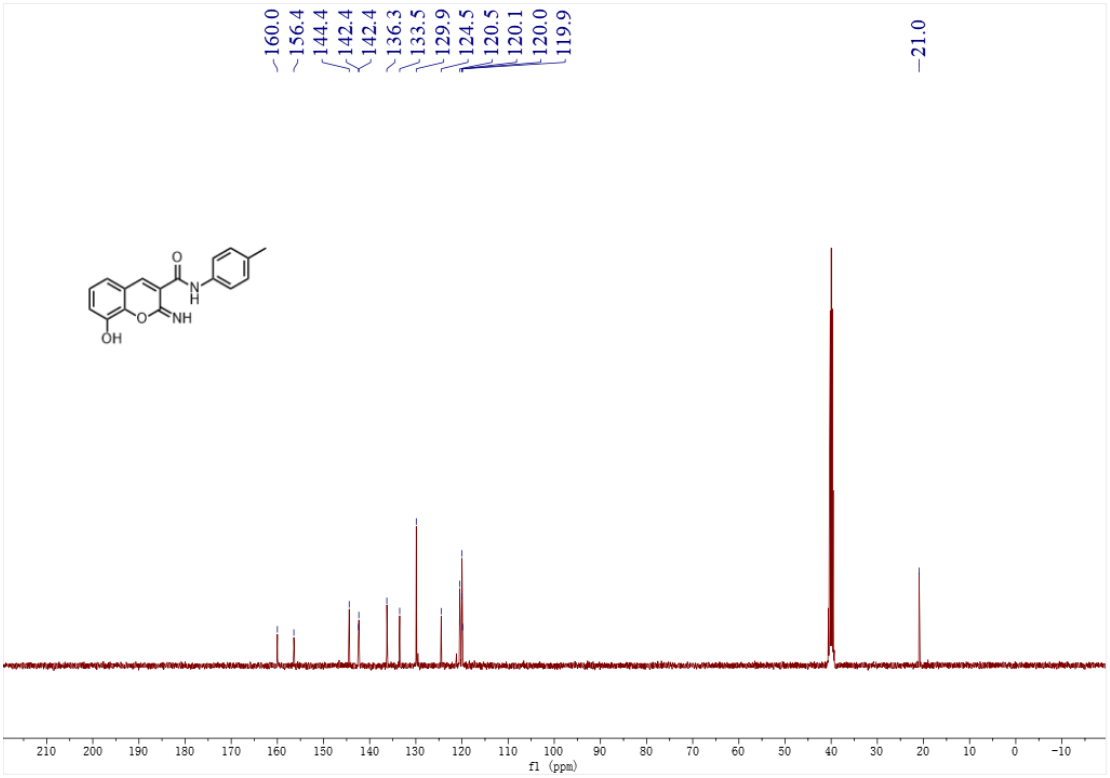
^{13}C NMR spectrum of **51** (DMSO-d_6)



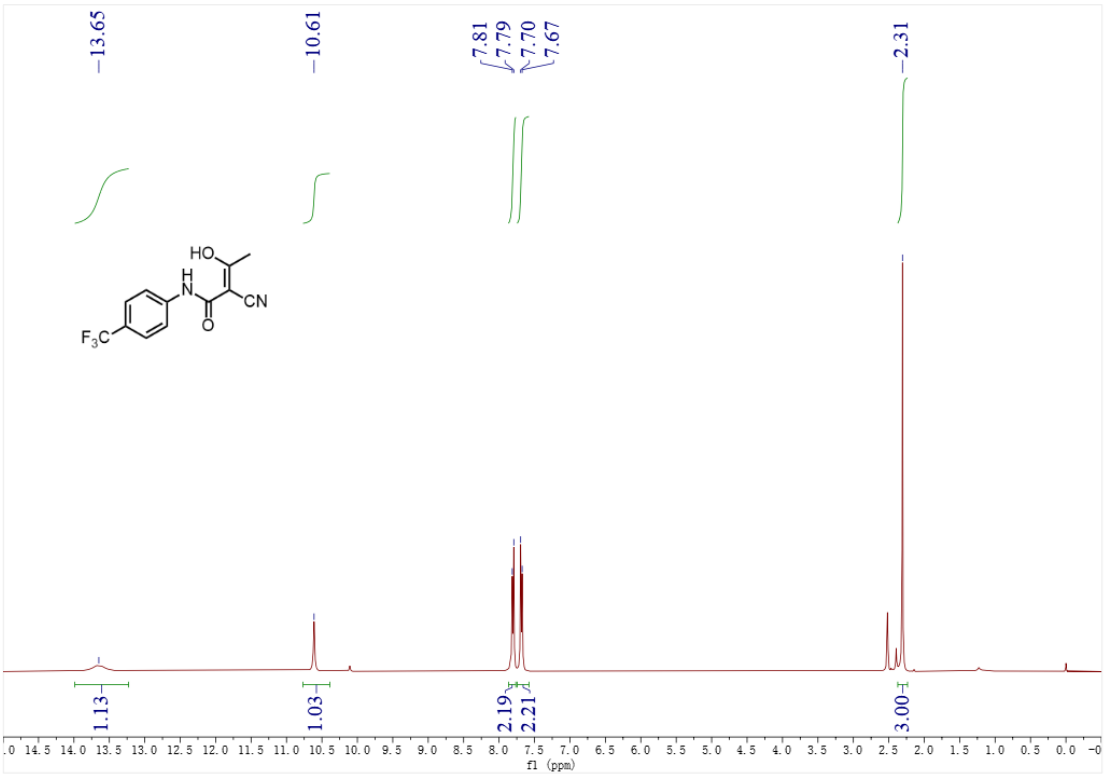
^{1}H NMR spectrum of **52** (DMSO-d_6)



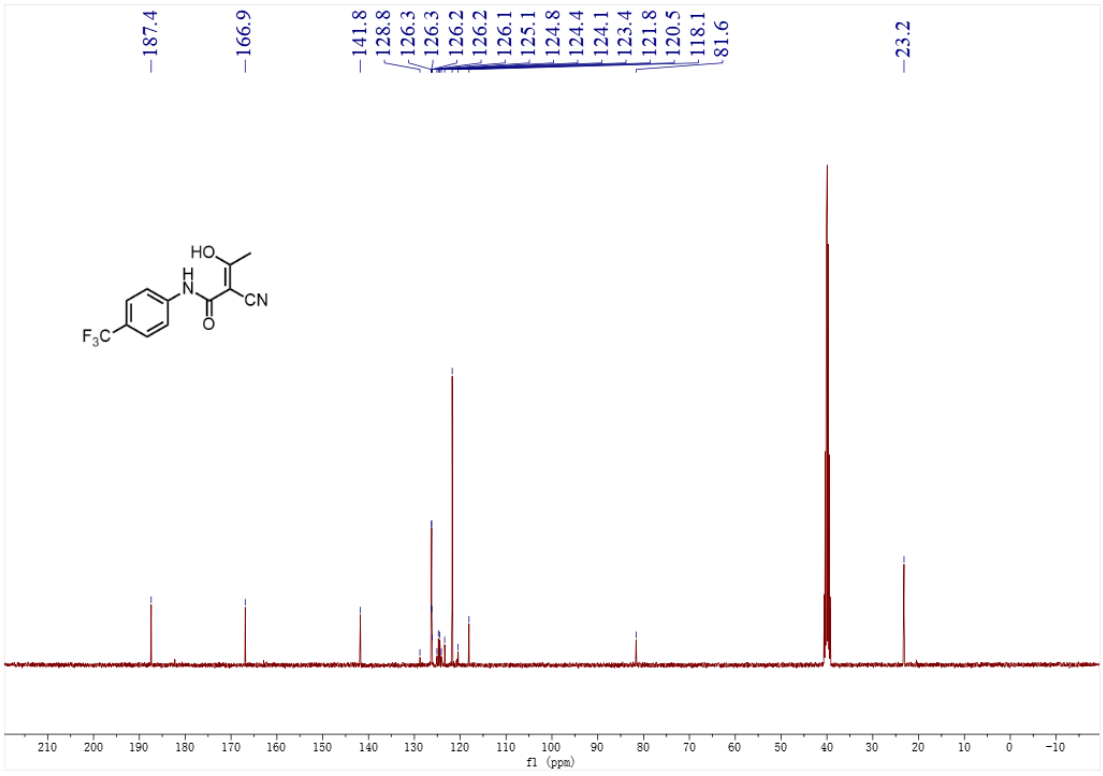
^{13}C NMR spectrum of **52** (DMSO-d_6)



^{1}H NMR spectrum of **53** (DMSO-d_6)



^{13}C NMR spectrum of **53** (DMSO-d_6)



^{19}F NMR spectrum of **53** (DMSO-d_6)