Supplementary Information

Radical Transformation of Aliphatic C-H Bonds to Oxime Ethers via HAT

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content

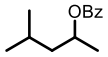
1. General information S2
2. Preparation of starting materials..... S2
3. Optimization of condition B..... S8
4. General procedure for synthesis 3a-3oo and 4a-4f..... S8
5. Synthetic applications..... S22
6. Investigation of the mechanism..... S24
7. Reference..... S27
8. NMR Spectrum..... S28

1. General information

Reagents were purchased from commercial sources and were used as received. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 400 Ultrashield NMR spectrometers. ^{19}F NMR spectra were recorded on a Varian 400 instrument spectrometer. Chemical shifts (δ) were given in parts per million (ppm) and were measured downfield from internal tetramethylsilane. High-resolution mass spectrometry (HRMS) data were obtained on an FTICR-MS instrument (Ionspec 7.0 T, ESI/ Quadrupole Mass Analyzer, ESI-QMA). The melting points were determined on an X-4 microscope melting point apparatus and are uncorrected. Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography was performed over silica gel (100-200 mesh). When heating is needed for reaction, we use heating mantle as heat source.

2. Preparation of starting materials

5-methylhexan-2-yl benzoate (1z)

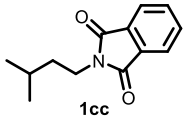


1z

1z was synthesized according to previous literature.[1] To a solution of 4-methylpetan-2-ol (1.16 g, 10.0 mmol, 1.00 equiv), DMAP (4-dimethylaminepyridine) (24.4 mg, 2.00 mmol, 0.200 equiv) and Et_3N (2.00 mL, 15.0 mmol, 1.50 equiv) in CH_2Cl_2 (50.0 mL) at 0 °C was added benzoyl chloride (1.68 g, 12.0 mmol, 1.20 equiv). The reaction mixture was warmed to 23 °C and stirred for 6 hours before quenched with H_2O (10.0 mL) and extracted 3 times with CH_2Cl_2 (20.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 50:1 (v/v) to afford **1z** as a colourless oil (1.78g, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 5.27 (dq, *J* = 12.4, 6.1 Hz, 1H), 1.76 (dt, *J* = 13.3, 5.9 Hz, 2H), 1.47 – 1.38 (m, 1H), 1.36 (d, *J* = 6.2 Hz, 3H), 0.96 (dd, *J* = 6.2, 4.1 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 132.8, 131.1, 129.6, 128.4, 70.3, 45.4, 24.9, 23.1, 22.5, 20.7.
The data are in accord with the previous literature.[1]

2-isopentylisoindoline-1,3-dione (1cc)

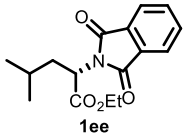


1cc

1cc was synthesized according to previous literature.[2] The 3-methylbutan-1-amine (10.0 mmol, 1.00 equiv) and phthalic anhydride (10.0 mmol, 1.00 equiv) were heated at 120 °C in a sealed tube equipped with a stir bar for 2 h. After cooling to room temperature, the mixture was dissolved in ethyl acetate, washed with water and dried over anhydrous MgSO4. The solvent was evaporated and the residue was purified by flash column chromatography (petroleum ether/EtOAc = 4:1, v:v) to afford **1cc** as a colourless oil (1.84 g, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.77 (m, 2H), 7.75 – 7.64 (m, 2H), 3.70 (dd, *J* = 13.4, 6.3 Hz, 2H), 1.69 – 1.50 (m, 3H), 0.96 (t, *J* = 5.8 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 133.9, 132.4, 123.3, 37. 5, 36.6, 26.0, 22.5.
The data are in accord with the previous literature.[2]

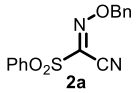
Ethyl (S)-2-(1,3-dioxoisoindolin-2-yl)-4-methylpentanoate (1ee)



1ee

1ee was synthesized according to previous literature.[2] Ethyl L-leucinate hydrochloride (10.0 mmol, 1.00 equiv), triethylamine (20.0 mmol, 2.00 equiv) and phthalic anhydride (10.0 mmol, 1.00 equiv) were heated at 120 °C in a sealed tube equipped with a stir bar for 2 h. After cooling to room temperature, the mixture was dissolved in ethyl acetate, washed with water and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was purified by flash column chromatography (petroleum ether/EtOAc = 3:1, v:v) to afford **1ee** as a colourless oil (2.51g, 87% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H), 7.77 – 7.69 (m, 2H), 4.96 – 4.88 (m, 1H), 4.26 – 4.12 (m, 2H), 2.38 – 2.25 (m, 1H), 2.01 – 1.88 (m, 1H), 1.55 – 1.41 (m, 1H), 1.26 – 1.17 (m, 3H), 0.99 – 0.88 (m, 5H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 167.9, 134.3, 131.9, 123.6, 61.9, 50.9, 37.4, 25.2, 23.3, 21.1, 14.2.
The data are in accord with the previous literature.[2]

***N*-(benzyloxy)-1-(phenylsulfonyl)methanimidoyl cyanide (2a)**



2a

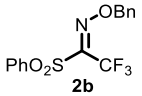
2a was synthesized according to previous literature.[3] A solution of NaOEt in EtOH (prepared fresh from 400 mg, 17.39 mmol, 1.2 equiv. of Na and 10 ml of EtOH) was added to the suspension of *(Phenylsulfonyl)acetonitrile* (2.62 g, 14.5 mmol, 1 equiv.) in EtOH (10 ml) at RT. To the resulting clear solution isoamyl nitrite (2.4 ml, 17.40 mmol, 1.2 equiv.) was added. The mixture was stirred at RT for 2 hours upon which a yellow solid precipitated. The mixture was cooled in an ice-bath, the solid was filtered and washed with cold EtOH and then with Et_2O. Drying under high vacuum afforded the sodium salt of *N-hydroxy-1-(phenylsulfonyl)methanimidoyl cyanide* as yellow powder that was used directly in the next step.

To the suspension of the sodium salt of *N-hydroxy-1-(phenylsulfonyl)methanimidoyl cyanide* (1 g, 4.307 mmol, 1 equiv.) in EtOH (10 ml) was added benzyl bromide (0.63 ml, 5.168 mmol, 1.2 equiv.) and the mixture was heated to reflux. A clear solution resulted within 2 minutes. After 1 hour the mixture was cooled to RT and concentrated under reduced pressure. EtOAc (80 ml) was added to the residue and was subsequently washed with sat. NH_4Cl (30 ml) and water (30 ml). The organic phase was dried over Na_2SO_4 and the solvent removed under

reduced pressure. The crude product was recrystallized from hexane and EtOAc to afford *N-(benzyloxy)-1-(phenylsulfonyl)methanimidoyl cyanide* (**2a**) (0.94 g, 67 %) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.8 Hz, 2H), 7.76 (t, *J* = 7.4 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 2H), 7.41 – 7.35 (m, 3H), 7.34 – 7.29 (m, 2H), 5.44 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6, 135.6, 134.8, 133.8, 129.9, 129.5, 129.3, 128.9, 105.8, 81.7.
The data are in accord with the previous literature.[3]

2,2,2-trifluoro-1-(phenylsulfonyl)ethan-1-one *O*-benzyl oxime (2b)



2b

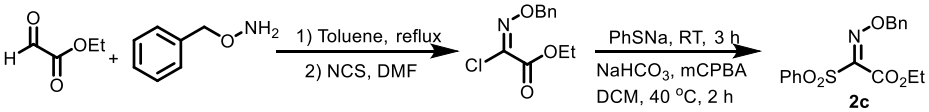
2b was synthesized according to previous literature.[4] A 100 mL round bottom flask equipped with a condenser, and a Teflon coated magnetic stir bar was charged with Ph_3P (10.4 g, 2.5 equiv), Et_3N (2.2 mL, 1 equiv), CCl_4 (6.5 mL), and CF_3COOH (1.71g, 15 mmol, 1 equiv). After the solution was stirred for about 10 min (ice bath), O-benzyl hydroxylamine (1.85 g, 1 equiv) dissolved in CCl_4 (7 mL) was added. The mixture was then refluxed under stirring (3 h). Solvent was removed under reduced pressure, and the residue was diluted with hexane and filtered. Residual solid Ph_3PO, Ph_3P, and Et_3N-HCl were washed with hexane several times. The filtrate was concentrated under reduced pressure to afford crude *N-(benzyloxy)-2,2,2-trifluoroacetimidoyl chloride* as yellow oil.

To a solution of *N-(benzyloxy)-2,2,2-trifluoroacetimidoyl chloride* (2.37 g, 10 mmol) in THF (20 mL) was added thiophenol sodium salt (1.58 g, 12 mmol). The reaction mixture was stirred for 3 h at room temperature, diluted with diethyl ether (60 mL) and washed with aqueous $NaHCO_3$ (2 × 30 mL) and brine (30 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give crude *phenyl-N-(benzyloxy)-2,2,2-trifluoroethanimidothioate* (2.4 g) as yellow oil.

To a solution of 2.4 g *phenyl-N-(benzyloxy)-2,2,2-trifluoroethanimidothioate* in CH_2Cl_2 (40mL) was added $NaHCO_3$ (1.18 g, 14 mmol) and MCPBA (5.32 g, 15.4 mmol) at 0 °C. After being stirred for 1 h, the reaction mixture was heated for 1 h at 40 °C, diluted with CH_2Cl_2 (30 mL) and washed with aqueous $NaHCO_3$ (2 ×30 mL), aqueous Na_2SO_3 (30 mL) and brine (30 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was chromatographed on a silica gel chromatography (hexane: EtOAc = 10:1) to give the product 1g (2.12 g, 62% over two steps) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 2H), 7.37 – 7.27 (m, 3H), 7.08 (d, *J* = 7.0 Hz, 2H), 5.21 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.51 (C-F, 2*JC-F*= 34.4 Hz), 138.5, 134.9, 133.8, 129.3, 129.1, 129.0, 128.8, 128.6, 118.6 (C-F, 1*JC-F* = 276.4 Hz). 81.1.
The data are in accord with the previous literature.[4]

Methyl (*E*)-2-((benzyloxy)imino)-2-(phenylsulfonyl)acetate (2c)



2c was synthesized according to previous literature with modified procedure[5]. A 100 mL round bottom flask equipped with a condenser, and a Teflon coated magnetic stir bar was charged with *glyoxylic acid ethyl ester* (2.04 g, 1.0 equiv), *N-benzyloxyamine* (2.46 g, 1.0equiv) and toluene 50 mL, The mixture was then refluxed under stirring (4 h). Solvent was removed under reduced pressure to afford *ethyl 2-((benzyloxy)imino) acetate* as yellow oil. The crude could used directly without further purification.

A mixture of *ethyl 2-((benzyloxy)imino) acetate* (1.0 eqiv), and *N-chlorosuccinimide* (3.0 equiv) in DMF was stirred at 50 °C for 2 days. The mixture was diluted with Et_2O, washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. Direct reaction to the next step does not require purification.

To a solution of *ethyl 2-((benzyloxy)imino)-2- chloroacetate* (1 equiv) in THF (20 mL) was added thiophenol sodium salt (1.2 equiv). The reaction mixture was stirred for 3 h at room temperature, diluted with diethyl ether (60 mL) and washed with aqueous $NaHCO_3$ (2 × 30 mL) and brine (30 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give crude *ethyl-2-((benzyloxy)imino)-2-(phenylthio)acetate* as yellow oil.

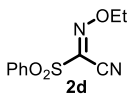
A solution of *ethyl-2-((benzyloxy)imino)-2-(phenylthio)acetate* (1.0 equiv) in CH_2Cl_2 was treated with $NaHCO_3$ (3.0 equiv), and *m*-CPBA (3.0 equiv) at 0 °C successively. After being stirred at room temperature for 4 h, the reaction mixture was diluted with CH_2Cl_2, washed with 10% $Na_2S_2O_3$ (aq), $NaHCO_3$ (aq), and brine, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (PE:EA = 10∶1) to afford **2c** as white solid (2.8 g, total 40% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.4, 1.1 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.09 (d, *J* = 6.3 Hz, 2H), 5.18 (s, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 147.4, 139.2, 134.6, 134.6, 129.3, 128.9, 128.7, 128.5, 128.5, 80.0, 63.5, 14.0.

The data are in accord with the previous literature.[5]

_N_-ethoxy-1-(phenylsulfonyl)methanimidoyl cyanide (2d)



2d was synthesized according to the procedure as **2a.** To the suspension of the sodium salt of *N-hydroxy-1-(phenylsulfonyl)methanimidoyl cyanide* (231 mg, 1 mmol, 1 equiv.) in EtOH (2 ml) was added ethyliodide (187 mg, 1.2 mmol, 1.2 equiv.) and the mixture was heated to reflux. A clear solution resulted within 2 minutes. After 1 hour the mixture was cooled to RT and

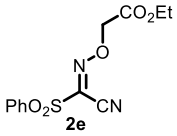
concentrated under reduced pressure. EtOAc (10 ml) was added to the residue and was subsequently washed with sat. NH_4Cl (10 ml) and water (10 ml). The organic phase was dried over Na_2SO_4 and the solvent removed under reduced pressure. The crude product was recrystallized from hexane and EtOAc to afford *N-ethoxy-1-(phenylsulfonyl)methanimidoyl cyanide* (**2d**) (176 mg, 74 %) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.98 (m, 2H), 7.77 (t, *J* = 7.5 Hz, 1H), 7.65 (t, *J* = 7.9 Hz, 2H), 4.54 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.8, 135.6, 134.3, 130.1, 129.3, 106.0, 76.0, 14.4.

HRMS(ESI-QMA) m/z: $[M+Na]^+$ Calcd for $C_{10}H_{10}N_2NaO_3S$ 261.0310; Found 261.0308.

Ethyl -2-(((cyano(phenylsulfonyl)methylene)amino)oxy)acetate (2e)



2e

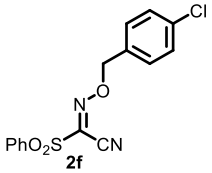
2e was synthesized according to the procedure as **2a.** To the suspension of the sodium salt of *N-hydroxy-1-(phenylsulfonyl)methanimidoyl cyanide* (231 mg, 1 mmol, 1 equiv.) in EtOH (2 ml) was added ethyl bromoacetate (200 mg, 1.2 mmol, 1.2 equiv.) and the mixture was heated to reflux. A clear solution resulted within 2 minutes. After 1 hour the mixture was cooled to RT and concentrated under reduced pressure. EtOAc (10 ml) was added to the residue and was subsequently washed with sat. NH_4Cl (10 ml) and water (10 ml). The organic phase was dried over Na_2SO_4 and the solvent removed under reduced pressure. The crude product was recrystallized from hexane and EtOAc to afford *Ethyl -2-(((cyano(phenylsulfonyl)methylene)amino)oxy)acetate* (**2e**) (239 mg, 81 %) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 2H), 4.93 (s, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 136.1, 136.0, 135.8, 130.0, 129.3, 105.4, 73.7, 61.9, 14.1.

HRMS(ESI-QMA) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{12}N_2NaO_5S$ 319.0365; Found 319.0362.

***N*-((4-chlorobenzyl)oxy)-1-(phenylsulfonyl)methanimidoyl cyanide (2f)**



2f

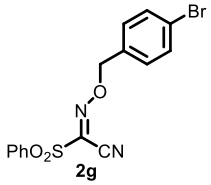
2f was synthesized according to the procedure as **2a.** To the suspension of the sodium salt of *N-hydroxy-1-(phenylsulfonyl)methanimidoyl cyanide* (231 mg, 1 mmol, 1 equiv.) in EtOH (2 ml) was added *1-(bromomethyl)-4-chlorobenzene* (243 mg, 1.2 mmol, 1.2 equiv.) and the mixture was heated to reflux. A clear solution resulted within 2 minutes. After 1 hour the mixture was cooled to RT and concentrated under reduced pressure. EtOAc (10 ml) was added to the residue and was subsequently washed with sat. NH_4Cl (10 ml) and water (10 ml). The organic phase was dried over Na_2SO_4 and the solvent removed under reduced pressure. The crude product

was recrystallized from hexane and EtOAc to afford *N-((4-chlorobenzyl)oxy)-1-(phenylsulfonyl)methanimidoyl cyanide* (**2f**) (216 mg, 71 %) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 2H), 7.80 – 7.74 (m, 1H), 7.66 – 7.59 (m, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 5.39 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 135.7, 135.6, 135.2, 132.3, 130.7, 130.0, 129.3, 129.2, 105.7, 80.6.

HRMS(ESI-QMA) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{11}ClN_2NaO_3S$ 357.0077; Found 357.0174.

***N*-((4-bromobenzyl)oxy)-1-(phenylsulfonyl)methanimidoyl cyanide(2g)**



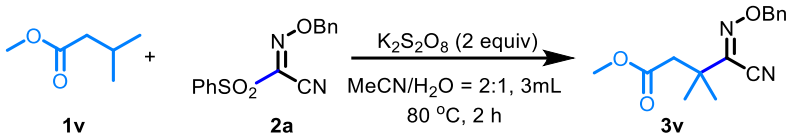
2g

2e was synthesized according to the procedure as **2a.** To the suspension of the sodium salt of *N-hydroxy-1-(phenylsulfonyl)methanimidoyl cyanide* (231 mg, 1 mmol, 1 equiv.) in EtOH (2 ml) was added 1-bromo-4-(bromomethyl)benzene (296 mg, 1.2 mmol, 1.2 equiv.) and the mixture was heated to reflux. A clear solution resulted within 2 minutes. After 1 hour the mixture was cooled to RT and concentrated under reduced pressure. EtOAc (10 ml) was added to the residue and was subsequently washed with sat. NH_4Cl (10 ml) and water (10 ml). The organic phase was dried over Na_2SO_4 and the solvent removed under reduced pressure. The crude product was recrystallized from hexane and EtOAc to afford *N-((4-bromobenzyl)oxy)-1-(phenylsulfonyl)methanimidoyl cyanide* (**2g**) (286 mg, 76 %) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.5 Hz, 2H), 7.77 (t, *J* = 7.5 Hz, 1H), 7.62 (t, *J* = 7.9 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 5.37 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 135.7, 135.2, 132.8, 132.1, 130.9, 130.0, 129.3, 123.8, 105.7, 80.6.

HRMS(ESI-QMA) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{11}BrN_2NaO_3S$ 400.9571; Found 400.9568.

3. Optimization of condition B



1v 2a 3v

entry	deviation from standard conditions	yield (%)[b]
1	none	70 (61%[c])
2	$Na_2S_2O_8$ instead of $Na_2S_2O_8$	53
3	$(NH_4)_2S_2O_8$ instead of $Na_2S_2O_8$	32
4	MeCN as solvent	n.d.
5	MeCN/H_2O (1:1, v:v) as solvent	57
6	MeCN/H_2O (3:1, v:v) as solvent	46
7	40 °C	n.d.
8	60 °C	32%
9	no $K_2S_2O_8$	n.d.

[a]Alkane (2.0 mmol), **2a** (0.2 mmol), $K_2S_2O_8$ (0.4 mmol), 2:1 (v/v) MeCN/H_2O (3.0 mL), 80 °C, 2 h. [b]Yields were determined from the ^1H NMR spectra of crude product mixtures with CH_2Br_2 as an internal standard; n.d., not detected. [c]Isolated yield.

4. General procedure for synthesis 3a-3oo and 4a-4f

Condition A: To an 8 mL vial equipped with a magnetic stir bar was added TBADT (16.8 mg, 0.008 mmol, 0.04 equiv), sulfonyl oxime (0.2 mmol, 60.2 mg), alkanes, $Na_2S_2O_8$ (0.4 mmol, 95.2 mg), 1 mL MeCN and 1 mL DCM. Then the tube was purged with Ar gas for 5 min. and sealed with PTFE cap. The tube was stirred at 25 °C for 18 h under 390 nm. Then the solvent was removed under reduced pressure and the crude product was purified by column chromatography (eluent: n-hexane/AcOEt) to provide the product (**3a-3u, 4a-4f**).

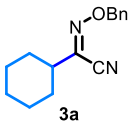
Condition B: To an 8 mL vial equipped with a magnetic stir bar was added sulfonyl oxime (0.2 mmol, 60 mg), alkanes, $K_2S_2O_8$ (0.4 mmol, 108 mg), 2 mL MeCN and 1 mL H_2O. Then the tube was purged with Ar gas for 5 min. and sealed with PTFE cap. The tube was stirred at 80 °C for 2 h. Then the solvent was removed under reduced pressure and the crude product was purified by column chromatography (eluent: n-hexane/AcOEt) to provide the product(**3v-3ee**)

Procedure for synthesis of 3a at 2.0 mmol scale

To a 20 mL vial equipped with a magnetic stir bar was added TBADT (168 mg, 0.08 mmol, 0.04 equiv), **2a** (2 mmol, 600 mg), cyclohexane (20.0 mmol, 10.0 equiv), $Na_2S_2O_8$ (4 mmol, 952 mg), 10 mL MeCN and 10 mL DCM. Then the tube was purged with Ar gas for 15 min to remove oxygen. The tube was sealed with PTFE cap and stirred at 25 °C for 18 h under 390 nm. Then the solvent was removed under reduced pressure and the crude product was purified

by column chromatography (eluent: n-hexane/AcOEt = 10: 1) to provide the product **3a** 398 mg at 82% yield.

***N*-(benzyloxy)cyclohexanecarbimidoyl cyanide (3a)**



3a

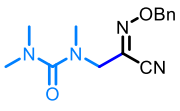
According to the *general procedure condition A*. Colorless oil, 42.7 mg, 88 % yield. Rf = 0.7 (PE: EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.29 (m, 5H), 5.23 (s, 2H), 2.43 (tt, *J* = 11.6, 3.5 Hz, 1H), 1.92 – 1.75 (m, 4H), 1.74 – 1.63 (m, 1H), 1.48 – 1.15 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.4, 136.3, 128.6, 128.5, 128.5, 110.0, 77.7, 40.9, 30.0, 25.5, 25.5.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}N_2O$ 243.1492; Found 243.1499.

***N*-(benzyloxy)-2-(1,3,3-trimethylureido)acetimidoyl cyanide (3b)**



3b

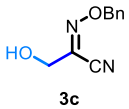
According to the *general procedure condition A*. Colorless oil, 43.3 mg, 79 % yield. Rf = 0.5 (PE: EA = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 5H), 5.26 (s, 2H), 4.11 (s, 2H), 2.85 (s, 6H), 2.79 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 135.7, 130.5, 128.6, 128.6, 128.5, 109.6, 78.3, 50.5, 38.5, 37.6.

HRMS(ESI-QMA) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{18}N_4NaO_2$ 297.1322; Found 297.1328.

***N*-(benzyloxy)-2-hydroxyacetimidoyl cyanide (3c)**



3c

According to the *general procedure condition A*. Colorless oil, 35.0 mg, 92 % yield. Rf = 0.7 (PE: EA = 20:1); E: Z = 9:5.

E isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 5H), 5.28 (s, 2H), 4.38 (s, 2H).

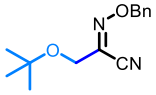
^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 131.9, 128.8, 128.8, 128.7, 109.6, 78.5, 61.2.

Z isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 5H), 5.25 (s, 2H), 4.45 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$)135.5, 130.9, 129.0, 128.8, 128.7, 113.1, 79.3, 57.3

HRMS(ESI-QMA) m/z: $[M+Na]^+$ Calcd for $C_{10}H_{10}N_2NaO_2$ 213.0634; Found 213.0638.

***N*-(benzyloxy)-2-(tert-butoxy)acetimidoyl cyanide (3d)**



3d

According to the *general procedure condition A*. Colorless oil, 40.8 mg, 83 % yield. Rf = 0.7 (PE: EA = 20:1); E: Z =3:1.

E isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.16 (m, 5H), 5.14 (s, 2H), 4.02 (s, 2H), 1.11 (s, 9H).

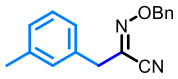
^{13}C NMR (101 MHz, $CDCl_3$) δ 135.8, 131.6, 128.6, 128.5, 128.5, 109.8, 78.2, 75.1, 60.6, 27.4.

Z isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.16 (m, 5H), 5.13 (s, 2H), 4.10 (s, 2H), 1.10 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ135.6, 131.6, 128.8, 128.7, 128.7, 113.0, 78.9, 75.1, 56.5, 27.3.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{14}H_{19}N_2O_2$ 247.1441; Found 247.1449.

N-(benzyloxy)-2-(m-tolyl)acetimidoyl cyanide (3e)



3e

According to the *general procedure condition A*. Colorless oil, 43.8 mg, 83 % yield. Rf = 0.7 (PE: EA = 20:1); E: Z = 7:3.

E isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.32 (m, 5H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.12 (d, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 5.4 Hz, 2H), 5.30 (s, 2H), 3.68 (s, 2H), 2.35 (s, 3H).

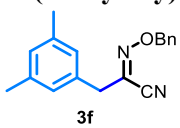
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 137.7, 136.1, 133.4, 131.9, 129.7, 128.7, 128.6, 128.4, 126.0, 110.2, 77.9, 38.1, 34.4, 21.4.

Z isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 5H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.12 (d, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 5.4 Hz, 2H), 5.32 (s, 2H), 3.78 (s, 2H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 137.7, 135.8, 133.1, 131.9, 129.8, 128.9, 128.7, 128.5, 126.1, 114.5, 78.6, 38.1, 34.4, 21.4.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}N_2O$ 265.1335; Found 265.1340.

N-(benzyloxy)-2-(3,5-dimethylphenyl)acetimidoyl cyanide (3f)



3f

According to the *general procedure condition A*. Colorless oil, 44.5 mg, 80 % yield. Rf = 0.7 (PE: EA = 20:1); E: Z = 7:3.

E isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.31 (m, 5H), 6.93 (s, 1H), 6.82 (s, 2H), 5.30 (s, 2H), 3.64 (s, 2H), 2.30 (s, 6H).

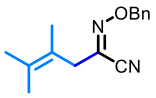
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 136.3, 133.4, 132.1, 129.6, 128.7, 128.5, 126.8, 110.4, 77.9, 38.1, 34.4, 21.3.

Z isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.31 (m, 5H), 6.93 (s, 1H), 6.82 (s, 2H), 5.32 (s, 2H), 3.73 (s, 2H), 2.29 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 137.9, 135.9, 133.1, 129.4, 128.8, 128.5, 126.9 114.64, 78.7, 38.1, 34.4, 21.3.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{18}H_{19}N_2O$ 279.1492; Found 279.1499.

N-(benzyloxy)-3,4-dimethylpent-3-enimidoyl cyanide (3g)



3g

According to the *general procedure condition A*. Colorless oil, 41.6 mg, 86 % yield. Rf = 0.7 (PE: EA = 20:1); E: Z = 4:1.

E isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.18 (m, 5H), 5.13 (s, 2H), 3.02 (s, 2H), 1.61 (s, 3H), 1.59 (s, 3H), 1.51 (s, 3H).

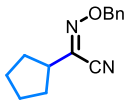
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 131.5, 131.2, 128.7, 128.6, 128.4, 119.8, 110.6, 77.7, 36.9, 21.1, 20.7, 18.1.

Z isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.17 (m, 5H), 5.14 (s, 2H), 3.11 (s, 2H), 1.56 (s, 3H), 1.56 (s, 3H), 1.55 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.0, 131.5, 131.1, 128.7, 128.6, 128.5, 119.8, 114.6, 78.5, 33.3, 20.9, 20.8, 19.1.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}N_2O$ 243.1492; Found 243.1498.

N-(benzyloxy)cyclopentanecarbimidoyl cyanide (3h)



3h

According to the *general procedure condition A*. Colorless oil, 33.2 mg, 73 % yield. Rf = 0.7 (PE: EA = 20:1); E: Z = 3:1.

E isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.17 (m, 5H), 5.10 (s, 2H), 2.75 (p, *J* = 7.9 Hz, 1H), 1.88 – 1.72 (m, 2H), 1.70 – 1.38 (m, 6H).

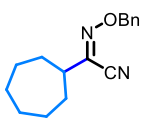
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.8, 136.2, 128.6, 128.5, 128.4, 109.9, 77.6, 42.0, 30.5, 25.2.

Z isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.18 (m, 5H), 5.12 (s, 2H), 3.23 (p, *J* = 8.46 Hz, 1H), 1.88 – 1.72 (m, 2H), 1.68 – 1.38 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.8, 136.0, 128.6, 128.5, 128.4, 109.9, 78.2, 36.9, 30.3, 25.4.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{14}H_{17}N_2O$ 229.1335; Found 229.1340.

N-(benzyloxy)cycloheptanecarbimidoyl cyanide (3i)



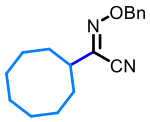
3i

According to the *general procedure condition A*. Colorless oil, 39.3 mg, 78 % yield. Rf = 0.6 (PE: EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.28 (m, 5H), 5.23 (s, 2H), 2.68 – 2.55 (m, 1H), 1.93 – 1.84 (m, 2H), 1.81 – 1.72 (m, 2H), 1.69 – 1.44 (m, 8H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 136.4, 128.6, 128.5, 128.4, 110.2, 77.7, 42.7, 31.9, 28.0, 26.1.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{16}H_{21}N_2O$ 257.1648; Found 257.1657.

***N*-(benzyloxy)cycloheptanecarbimidoyl cyanide (3j)**

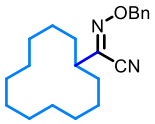


3j

According to the *general procedure condition A*. Colorless oil, 47.5 mg, 88 % yield. Rf = 0.6 (PE: EA = 20:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.29 (m, 5H), 5.23 (s, 2H), 2.68 (ddd, *J* = 13.2, 9.2, 3.8 Hz, 1H), 1.87 – 1.78 (m, 2H), 1.77 – 1.67 (m, 4H), 1.64 – 1.48 (m, 8H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 136.3, 128.5, 128.5, 128.3, 110.2, 77.6, 41.1, 29.5, 26.7, 25.9, 24.8.

HRMS(ESI-QMA) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{22}N_2NaO$ 293.1624; Found 293.1628.

***N*-(benzyloxy)cyclododecanecarbimidoyl cyanide (3k)**

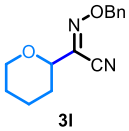


3k

According to the *general procedure condition A*. Colorless oil, 54.1 mg, 83 % yield. Rf = 0.6 (PE: EA = 20:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.18 (m, 5H), 5.12 (s, 2H), 2.54 (p, *J* = 6.6 Hz, 1H), 1.64 – 1.53 (m, 2H), 1.43 – 1.32 (m, 2H), 1.28 – 1.16 (m, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 136.2, 128.5, 128.3, 128.3, 109.9, 77.6, 37.3, 27.4, 23.7, 23.7, 23.3, 23.1, 22.1.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{21}H_{31}N_2O$ 327.2431; Found 327.2441.

***N*-(benzyloxy)tetrahydro-2*H*-pyran-2-carbimidoyl cyanide (3l)**



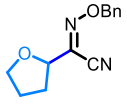
3l

According to the *general procedure condition A*. Colorless oil, 44.9 mg, 92 % yield. Rf = 0.7 (PE: EA = 20:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.16 (m, 5H), 5.15 (s, 2H), 4.01 (dd, *J* = 9.6, 3.9 Hz, 1H), 3.97 – 3.90 (m, 1H), 3.39 (td, *J* = 11.5, 2.3 Hz, 1H), 1.85 – 1.75 (m, 1H), 1.65 – 1.57 (m, 2H), 1.55 – 1.38 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.8, 133.8, 128.7, 128.6, 128.5, 109.2, 78.4, 75.4, 68.8, 29.2, 25.2, 22.5.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{14}H_{17}N_2O_2$ 245.1285; Found 245.1292.

N-(benzyloxy)tetrahydrofuran-2-carbimidoyl cyanide (3m)



3m

According to the *general procedure condition A*. Colorless oil, 41.8 mg, 91 % yield. Rf = 0.7 (PE: EA = 20:1). E: Z = 4:1

E isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.29 (m, 5H), 5.26 (s, 2H), 4.62 (t, *J* = 6.6 Hz, 1H), 4.01 – 3.85 (m, 2H), 2.25 – 2.18 (m, 1H), 2.12 – 1.96 (m, 3H).

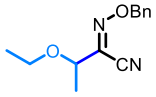
^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 134.3, 128.6, 128.6, 128.5, 109.2, 78.3, 72.5, 69.5, 30.2, 25.9.

Z isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.31 (m, 5H), 5.25 (s, 2H), 4.98 (t, *J* = 7.0 Hz 1H), 4.08 – 3.99 (m, 2H), 2.37 – 2.24 (m, 1H), 1.98 – 1.78 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 134.3, 128.7, 128.7, 128.6, 109.2, 78.9, 72.1, 69.4, 30.7, 25.8.

HRMS(ESI-QMA) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{14}N_2NaO_2$ 253.0947; Found 253.0950.

N-(benzyloxy)-2-ethoxypropanimidoyl cyanide (3n)



3n

According to the *general procedure condition A*. Colorless oil, 40.4 mg, 87 % yield. Rf = 0.7 (PE: EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.30 (m, 5H), 5.28 (s, 2H), 4.15 (q, *J* = 6.5 Hz, 1H), 3.56 – 3.29 (m, 2H), 1.43 (d, *J* = 6.6 Hz, 3H), 1.19 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.8, 135.2, 128.6, 128.5, 128.4, 108.7, 78.2, 73.4, 64.7, 19.1, 15.1.

HRMS(ESI-QMA) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{16}N_2NaO_2$ 255.1104; Found 255.1108.

N-(benzyloxy)-2-hydroxypropanimidoyl cyanide (3o)

3o

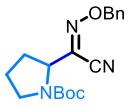
According to the *general procedure condition A*. Colorless oil, 29.8 mg, 73 % yield. Rf = 0.4 (PE: EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.30 (m, 5H), 5.26 (s, 2H), 4.58 (q, *J* = 6.5 Hz, 1H), 2.41 (s, 1H), 1.47 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.8, 135.6, 128.7, 128.6, 128.5, 108.8, 78.4, 66.8, 20.7.

HRMS(ESI-QMA) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{12}N_2NaO_2$ 227.0791; Found 227.0795.

***tert*-butyl -2-(((benzyloxy)imino)(cyano)methyl)pyrrolidine-1-carboxylate (3p)**



3p

According to the *general procedure condition A*. Colorless oil, 57.9 mg, 88 % yield. Rf = 0.7 (PE: EA = 10:1). E: Z = 2:1

E isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.34 (m, 5H), 5.26 (s, 2H), 4.50 (s, 1H), 3.62 – 3.39 (m, 2H), 2.28 – 2.18 (m, 1H), 2.10 – 1.84 (m, 3H), 1.37 (s, 9H).

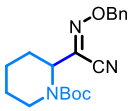
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 135.8, 134.9, 128.5, 109.2, 80.7, 78.2, 57.9, 46.6, 31.7, 28.2, 23.2.

Z isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.31 (m, 5H), 5.29 (s, 2H), 4.64 (s, 1H), 3.68 – 3.41 (m, 2H), 2.25 (m, 1H), 2.10 – 1.87 (m, 3H), 1.50 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 135.8, 134.9, 128.6, 111.8, 80.4, 78.2, 57.8, 46.9, 30.9, 28.4, 23.9.

HRMS(ESI-QMA) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{23}N_3NaO_3$ 352.1632; Found 352.1641.

***tert*-butyl -2-(((benzyloxy)imino)(cyano)methyl)piperidine-1-carboxylate (3q)**



3q

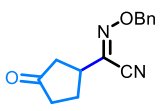
According to the *general procedure condition A*. Colorless oil, 57.6 mg, 84 % yield. Rf = 0.7 (PE: EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.17 (m, 5H), 5.15 (s, 2H), 3.86 (d, *J* = 12.2 Hz, 1H), 2.58 (t, *J* = 11.6 Hz, 1H), 2.01 (d, *J* = 13.9 Hz, 1H), 1.65 – 1.54 (m, 1H), 1.49 – 1.42 (m, 2H), 1.33 (s, 9H), 1.31 – 1.10 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 135.9, 132.5, 128.6, 128.6, 128.5, 109.5, 99.9, 80.6, 78.3, 51.9, 28.3, 26.2, 24.6, 19.2.

HRMS(ESI-QMA) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{25}N_3NaO_3$ 366.1788; Found 366.1796.

***N*-(benzyloxy)-3-oxocyclopentane-1-carbimidoyl cyanide (3r)**



3r

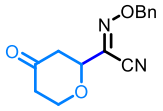
According to the *general procedure condition A*. Colorless oil, 37.7 mg, 78 % yield. Rf = 0.4 (PE: EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.29 (m, 5H), 5.24 (s, 2H), 3.33 – 3.17 (m, 1H), 2.46 (t, *J* = 8.0 Hz, 2H), 2.39 – 2.29 (m, 2H), 2.21 (dd, *J* = 18.5, 8.8 Hz, 1H), 2.12 – 2.01 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 214.7, 135.7, 133.7, 128.8, 128.6, 109.5, 99.9, 78.3, 41.3, 39.1, 37.1, 27.1.

HRMS(ESI-QMA) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{14}N_2NaO_2$ 265.0947; Found 265.0950.

***N*-(benzyloxy)-4-oxotetrahydro-2*H*-pyran-2-carbimidoyl cyanide (3s)**



3s

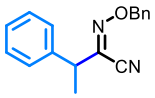
According to the *general procedure condition A*. Colorless oil, 27.8 mg, 54 % yield. Rf = 0.4 (PE: EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 5H), 5.29 (s, 2H), 4.49 (dd, *J* = 10.4, 3.5 Hz, 1H), 4.30 (ddd, *J* = 11.7, 6.9, 2.7 Hz, 1H), 3.80 (td, *J* = 11.5, 3.4 Hz, 1H), 2.74 (ddd, *J* = 14.8, 10.4, 0.9 Hz, 1H), 2.68 – 2.54 (m, 2H), 2.43 (ddd, *J* = 15.1, 5.1, 3.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.2, 135.2, 131.3, 128.8, 128.7, 128.7, 99.9, 78.9, 74.8, 66.2, 44.3, 41.7.

HRMS(ESI-QMA) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{14}N_2NaO_3$ 281.0897; Found 281.0900.

***N*-(benzyloxy)-2-phenylpropanimidoyl cyanide (3t)**



3t

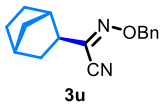
According to the *general procedure condition A*. Colorless oil, 22.7 mg, 43 % yield. Rf = 0.7 (PE: EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 5H), 7.34 (d, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 7.1 Hz, 1H), 7.24 (d, *J* = 7.1 Hz, 2H), 5.28 (s, 2H), 3.90 (q, *J* = 7.1 Hz, 1H), 1.55 (t, *J* = 7.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 136.3, 136.1, 129.0, 128.5, 128.5, 128.4, 127.8, 127.5, 109.7, 77.9, 42.5, 18.0.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}N_2O$ 265.1335; Found 265.1342.

***N*-(benzyloxy)bicyclo[2.2.1]heptane-2-carbimidoyl cyanide (3u)**



3u

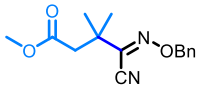
According to the *general procedure condition A*. Colorless oil, 40.1 mg, 79 % yield. Rf = 0.7 (PE: EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.29 (m, 5H), 5.23 (s, 2H), 2.53 – 2.42 (m, 2H), 2.33 (s, 1H), 1.92 – 1.81 (m, 1H), 1.67 – 1.49 (m, 3H), 1.43 (d, *J* = 10.1 Hz, 1H), 1.33 – 1.12 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 136.4, 128.6, 128.5, 128.4, 110.8, 77.8, 44.8, 41.0, 36.4 35.84, 34.2, 29.7, 28.7.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{16}H_{19}N_2O$ 255.1492; Found 255.1501.

Methyl-4-((benzyloxy)imino)-4-cyano-3,3-dimethylbutanoate (3v)



3v

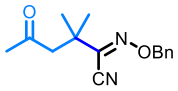
According to the *general procedure condition B*. Colorless oil, 33.4 mg, 61 % yield. Rf = 0.6 (PE: EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 -7.31 (m, 5H), 5.24 (s, 2H), 3.56 (s, 3H), 2.57 (s, 2H), 1.32 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 139.1, 136.3, 128.6, 128.6, 128.5, 109.4, 78.0, 51.7, 44.2, 38.3, 25.9.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}N_2O_3$ 275.1390; Found 275.1401.

***N*-(benzyloxy)-2,2-dimethyl-4-oxopentanimidoyl cyanide (3w)**



3w

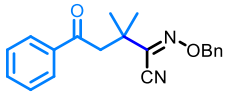
According to the *general procedure condition B*. Colorless oil, 37.2 mg, 72 % yield. Rf = 0.5 (PE: EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.18 (m, 5H), 5.12 (s, 2H), 2.59 (s, 2H), 1.94 (s, 3H), 1.19 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.4, 139.4, 136.2, 128.5, 128.3, 109.4, 99.9, 77.7, 51.9, 37.9, 31.2, 26.0.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}N_2O_2$ 259.1441; Found 259.1449.

***N*-(benzyloxy)-2,2-dimethyl-4-oxo-4-phenylbutanimidoyl cyanide (3x)**



3x

According to the *general procedure condition B*. Colorless oil, 45.4 mg, 71 % yield. Rf = 0.4 (PE: EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.33 – 7.28 (m, 5H), 5.18 (s, 2H), 3.27 (s, 2H), 1.39 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.1, 139.7, 137.4, 136.3, 133.4, 128.7, 128.5, 128.5, 128.3, 128.1, 109.6, 77.8, 47.3, 38.3, 26.5.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}N_2O_2$ 321.1598; Found 321.1607.

***N*-(benzyloxy)-3-cyano-2,2-dimethylpropanimidoyl cyanide (3y)**

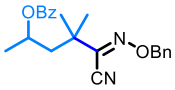
3y

According to the *general procedure condition B*. Colorless oil, 37.6 mg, 78 % yield. Rf = 0.6 (PE: EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.30 (m, 5H), 5.28 (s, 2H), 2.61 (s, 2H), 1.41 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.8, 135.4, 128.7, 128.6, 116.5, 108.6, 100.0, 78.6, 38.2, 28.2, 25.5.

HRMS(ESI-QMA) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{15}N_3NaO$ 264.1107; Found 264.1110.

6-((benzyloxy)imino)-6-cyano-5,5-dimethylhexan-2-yl benzoate (3z)



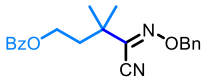
3z

According to the *general procedure condition B*. Colorless oil, 56.0 mg, 77 % yield. Rf = 0.5 (PE: EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.28 – 7.20 (m, 3H), 7.10 – 7.02 (m, 2H), 5.30 (dtd, *J* = 12.3, 6.2, 4.1 Hz, 1H), 4.86 (d, *J* = 11.9 Hz, 1H), 4.66 (d, *J* = 11.9 Hz, 1H), 2.30 (dd, *J* = 15.1, 10.4 Hz, 1H), 1.69 (dd, *J* = 15.1, 2.0 Hz, 1H), 1.30 (d, *J* = 6.2 Hz, 3H), 1.25 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 139.8, 135.8, 133.1, 130.1, 129.9, 128.4, 128.4, 128.3, 109.9, 77.5, 68.1, 46.1, 38.5, 27.7, 23.8, 21.5.

HRMS(ESI-QMA) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{24}N_2NaO_3$ 387.1679; Found 387.1685.

4-((benzyloxy)imino)-4-cyano-3,3-dimethylbutyl benzoate (3aa)



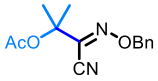
3aa

According to the *general procedure condition B*. Colorless oil, 55.3 mg, 79 % yield. Rf = 0.5 (PE: EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.99 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.28 (m, 3H), 7.28 – 7.23 (m, 2H), 5.13 (s, 2H), 4.32 (t, *J* = 6.4 Hz, 2H), 2.08 (t, *J* = 6.3 Hz, 2H), 1.31 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 139.6, 135.9, 133.1, 129.9, 129.8, 129.7, 128.6, 128.5, 128.5, 109.7, 77.9, 61.2, 38.7, 38.5, 25.7.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{21}H_{23}N_2O_3$ 351.1703; Found 351.1708.

1-((benzyloxy)imino)-1-cyano-2-methylpropan-2-yl acetate (3bb)



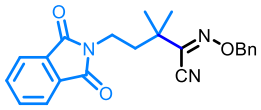
3bb

According to the *general procedure condition B*. Colorless oil, 20.3 mg, 39 % yield. Rf = 0.65 (PE: EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.30 (m, 5H), 5.28 (s, 2H), 2.06 (s, 3H), 1.63 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 136.8, 135.9, 128.7, 128.6, 128.5, 108.8, 78.5, 78.3, 25.4, 21.7.

HRMS(ESI-QMA) m/z: $[M+NH_4]^+$ Calcd for $C_{14}H_{20}N_3O_3$ 278.1499; Found 278.1508.

***N*-(benzyloxy)-4-(1,3-dioxoisoindolin-2-yl)-2,2-dimethylbutanimidoyl cyanide (3cc)**



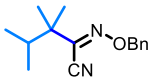
3cc

According to the *general procedure condition B*. Colorless oil, 53.3 mg, 71 % yield. Rf = 0.4 (PE: EA = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.42 – 7.29 (m, 5H), 5.24 (s, 2H), 3.77 – 3.57 (m, 2H), 2.03 – 1.89 (m, 2H), 1.30 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 138.9, 136.0, 133.9, 132.1, 128.5, 128.5, 128.4, 123.2, 109.2, 77.9, 38.5, 37.8, 33.7, 25.4.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{22}H_{22}N_3O_3$ 376.1656; Found 376.1659.

***N*-(benzyloxy)-2,2,3-trimethylbutanimidoyl cyanide (3dd)**



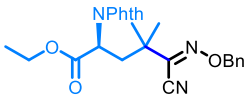
3dd

According to the *general procedure condition B*. Colorless oil, 25.8 mg, 53 % yield. Rf = 0.7 (PE: EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.19 (m, 5H), 5.13 (s, 2H), 1.80 (dt, *J* = 13.7, 6.8 Hz, 1H), 1.01 (s, 6H), 0.72 (d, *J* = 6.8 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 136.4, 128.5, 128.4, 128.3, 109.8, 77.6, 42.4, 34.8, 21.7, 17.2.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{15}H_{21}N_2O$ 245.1648; Found 245.1652.

Eethyl (*S*)-5-((benzyloxy)imino)-5-cyano-2-(1,3-dioxoisoindolin-2-yl)-4,4-dimethylpentanoate (3ee)



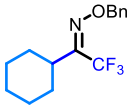
3ee

According to the *general procedure condition B*. Colorless oil, 50.2 mg, 58 % yield. Rf = 0.3 (PE: EA = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.71 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.34 – 7.29 (m, 3H), 7.23 (dd, *J* = 7.0, 2.6 Hz, 2H), 5.03 (dd, *J* = 35.3, 12.0 Hz, 2H), 4.84 (dd, *J* = 9.8, 2.8 Hz, 1H), 4.23 – 4.10 (m, 2H), 2.68 (dd, *J* = 15.4, 9.8 Hz, 1H), 2.54 (dd, *J* = 15.4, 2.9 Hz, 1H), 1.32 (s, 3H), 1.26 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 167.3, 138.5, 135.7, 134.3, 131.8, 130.8, 128.4, 128.3, 123.5, 108.9, 77.7, 62.3, 48.7, 38.7, 38.6, 26.8, 24.1, 14.1.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{25}H_{26}N_3O_5$ 448.1867; Found 448.1866.

1-cyclohexyl-2,2,2-trifluoroethan-1-one *O*-benzyl oxime (4a)



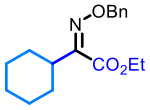
4a

According to the *general procedure condition A*. Colorless oil, 33.0 mg, 58 % yield. Rf = 0.7 (PE: EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.30 (m, 5H), 5.20 (s, 2H), 2.91 (tt, *J* = 12.0, 3.0 Hz, 1H), 1.82 – 1.71 (m, 4H), 1.70 – 1.57 (m, 3H), 1.34 – 1.13 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0(C-F, 2*JC-F* = 29.5 Hz), 136.7, 128.5, 128.2, 121.2 (C-F, *1JC-F* = 275.7 Hz), 77.5, 36.7, 27.9, 26.2, 25.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ -66.61.

HRMS(ESI-QMA) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{18}F_3NNaO$ 308.1233; Found 308.1238.

Ethyl (*Z*)-2-((benzyloxy)imino)-2-cyclohexylacetate (4b)

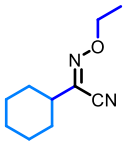


4b

According to the *general procedure condition A*. Colorless oil, 28.3 mg, 49 % yield. Rf = 0.4 (PE: EA = 20:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.30 (m, 5H), 5.23 (s, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.18 – 3.04 (m, 1H), 1.84 – 1.59 (m, 7H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.31 – 1.18 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 156.9, 137.2, 128.5, 128.1, 128.1, 77.2, 61.6, 36.9, 28.3, 26.3, 25.9, 14.3.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{17}H_{24}NO_3$ 290.1751; Found 290.1761.

Ethoxycyclohexanecarbimidoyl cyanide (4c)



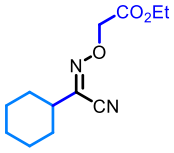
4c

According to the *general procedure condition A*. Colorless oil, 32.7 mg, 91 % yield. Rf = 0.75 (PE: EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 (q, *J* = 7.1 Hz, 2H), 2.41 (tt, *J* = 11.6, 3.5 Hz, 1H), 1.92 – 1.75 (m, 4H), 1.71 – 1.63 (m, 1H), 1.45 – 1.16 (m, 8H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 110.2, 71.7, 40.9, 30.1, 25.6, 25.5, 14.5.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for : $C_{10}H_{17}N_2O$ 181.1335; Found 181.1341.

Ethyl (Z)-2-(((cyano(cyclohexyl)methylene)amino)oxy)acetate (4d)



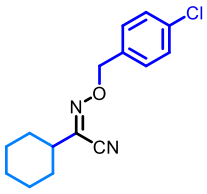
4d

According to the *general procedure condition A*. Colorless oil, 37.6 mg, 79 % yield. Rf = 0.5 (PE: EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.71 (s, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.46 (tt, *J* = 11.5, 3.5 Hz, 1H), 1.95 – 1.76 (m, 4H), 1.73 – 1.65 (m, 1H), 1.48 – 1.37 (m, 2H), 1.35 – 1.18 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 138.9, 109.5, 71.6, 61.4, 40.9, 29.9, 25.5, 25.4, 14.3.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{12}H_{19}N_2O_3$ 239.1390; Found 239.1398.

***N*-((4-chlorobenzyl)oxy)cyclohexanecarbimidoyl cyanide (4e)**



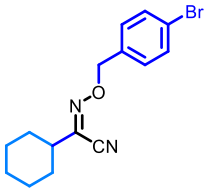
4e

According to the *general procedure condition A*. Colorless oil, 47.4 mg, 86 % yield. Rf = 0.6 (PE: EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 5.18 (s, 2H), 2.42 (tt, *J* = 11.5, 3.5 Hz, 1H), 1.93 – 1.76 (m, 4H), 1.69 (d, *J* = 11.7 Hz, 1H), 1.47 – 1.13 (m, 5H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 134.8, 134.4, 129.8, 128.8, 109.8, 76.8, 40.9, 30.0, 25.5, 25.4.

HRMS(ESI-QMA) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{17}ClN_2NaO$ 299.0922; Found 299.0925.

***N*-((4-bromobenzyl)oxy)cyclohexanecarbimidoyl cyanide (4f)**



4f

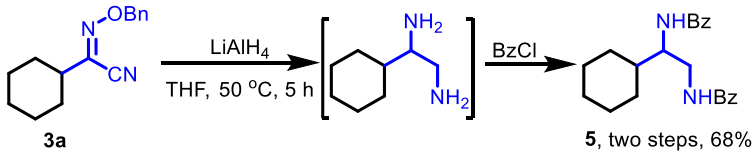
According to the *general procedure condition A*. Colorless oil, 53.8 mg, 84 % yield. Rf = 0.6 (PE: EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 5.16 (s, 2H), 2.42 (tt, *J* = 11.5, 3.5 Hz, 1H), 1.92 – 1.74 (m, 4H), 1.73 – 1.65 (m, 1H), 1.44 – 1.17 (m, 5H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 135.3, 131.8, 130.1, 122.5, 109.8, 76.8, 40.9, 30.0, 25.5, 25.4.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{15}H_{17}BrN_2NaO$ 343.0416; Found 343.0420.

5. Synthetic applications

Synthesis of 5



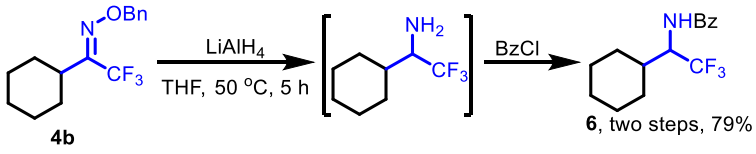
3a **5**, two steps, 68%

To the solution of *O*-benzyl oxime (**3a**) (48.6 mg, 0.2 mmol) in THF (2 mL) was added $LiAlH_4$ (38 mg, 1.0 mmol) portion-wise, refluxed for 5 h. After cooling to room temperature, H_2O (27 μL, 1.5 mmol), 15% NaOH (aq.) (27 μL, 1.5 mmol) and H_2O (81μL, 4.5 mmol) were added, the mixture was diluted with water (10 mL) and extracted with EA (3 × 10 mL). The combined extracts were washed with a saturated solution of NaCl (15 mL), dried over $MgSO_4$, and evaporated in vacuo to afford the crude amine, which was used directly in the next step.
Adding triethylamine (60.6 mg, 0.6 mmol) to a stirring solution of crude amine in 2 mL DCM. Then benzoyl chloride (67.2 mg, 2.4 equiv) in 1mL DCM was added to the solution dropwise under 0 °C. The mixture was stirred under room temperature for 4 h. then the mixture was diluted with 10 mL DCM, and the organic layer was washed with a saturated solution of $NaHCO_3$ (10 mL) and NaCl (10 mL), dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by chromatography on silica gel to afford **5** as white solid.

47.6 mg, 68%, Rf =0.2, PE: EA = 3:1
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.71 (m, 4H), 7.50 – 7.30 (m, 7H), 6.81 (d, *J* = 8.7 Hz, 1H), 4.18 (ddd, *J* = 14.9, 11.4, 3.5 Hz, 1H), 3.81 (ddd, *J* = 13.7, 11.2, 7.0 Hz, 1H), 3.46 (dt, *J* = 13.8, 3.6 Hz, 1H), 1.87 – 1.76 (m, 3H), 1.68 – 1.54 (m, 2H), 1.33 – 1.01 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 168.7, 134.2, 134.1, 131.6, 131.4, 128.6, 128.5, 127.0, 126.9, 55.2, 41.1, 40.8, 29.7, 29.2, 26.2, 26.1, 26.1.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{22}H_{27}N_2O_2$ 351.2067; Found 351.2070.

Synthesis of 6



4b **6**, two steps, 79%

To the solution of *O*-benzyl oxime (**4a**) (57.0 mg, 0.2 mmol) in THF (2 mL) was added $LiAlH_4$ (38 mg, 1.0 mmol) portion-wise, refluxed for 5 h. After cooling to room temperature, H_2O (27 μL, 1.5 mmol), 15% NaOH (aq.) (27 μL, 1.5 mmol) and H_2O (81μL, 4.5 mmol) were added, the mixture was diluted with water (10 mL) and extracted with EA (3 × 10 mL). The combined extracts were washed with a saturated solution of NaCl (15 mL), dried over $MgSO_4$, and evaporated in vacuo to afford the crude amine, which was used directly in the next step.
Adding triethylamine (30.3 mg, 0.3 mmol) to a stirring solution of crude amine in 2 mL DCM. Then benzoyl chloride (33.6 mg, 1.2 equiv) in 1mL DCM was added to the solution dropwise under 0 °C. The mixture was stirred under room temperature for 4 h. then the mixture was diluted with 10 mL DCM, and the organic layer was washed with a saturated solution of

$NaHCO_3$ (10 mL) and NaCl (10 mL), dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by chromatography on silica gel to afford **6** as white solid.

45.0 mg, 79%, Rf =0.4, PE:EA = 4:1

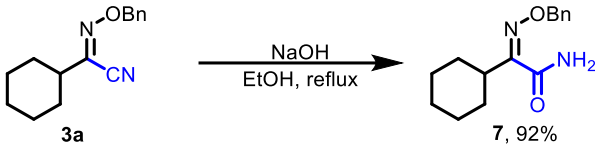
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 6.21 (s, 1H), 4.87 – 4.65 (m, 1H), 1.96 – 1.73 (m, 5H), 1.68 (d, *J* = 13.1 Hz, 1H), 1.36 – 1.22 (m, 3H), 1.18 – 1.04 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 133.7, 132.3, 128.9, 127.2, δ 125.5 (q, *JC-F* = 282.8 Hz), 54.8 (q, *JC-F* = 28.8 Hz), 37.6, 30.2, 27.6, 26.1, 25.9, 25.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -71.60, -71.63.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}F_3NO$ 286.1413; Found 286.1418.

Synthesis of 7



3a **7**, 92%

To the solution of oximonitrile (**3a**) (48.6 mg, 0.2 mmol, 1 equiv.) in EtOH (2 ml) NaOH (0.4 ml, 1M solution, 2 equiv.) was added at RT. The mixture was refluxed for 5 hours. After cooling to RT water (1 ml) and brine (1 ml) were added and extracted with EtOAc (2x15 ml). Drying over Na_2SO_4 and removal of the solvent under reduced pressure afforded the crude product, which was purified by flash chromatography (hexane:EtOAc=2:1) to give product **7** (47.8 mg, 92 %) as white solid.

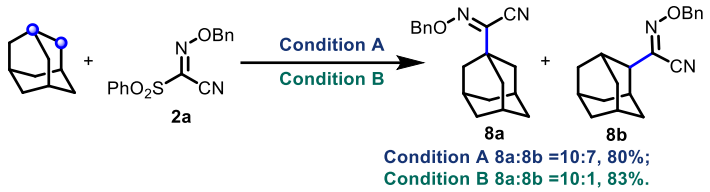
47.8 mg, 79%, Rf =0.3, PE:EA = 5:1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.32 (m, 5H), 6.68 (s, 1H), 6.43 (s, 1H), 5.16 (s, 1H), 2.70 (t, *J* = 7.0 Hz, 1H), 1.99 – 1.66 (m, 5H), 1.48 – 1.11 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 156.7, 136.8, 128.5, 128.4, 128.2 77.0, 40.2, 30.4, 26.1, 26.0.

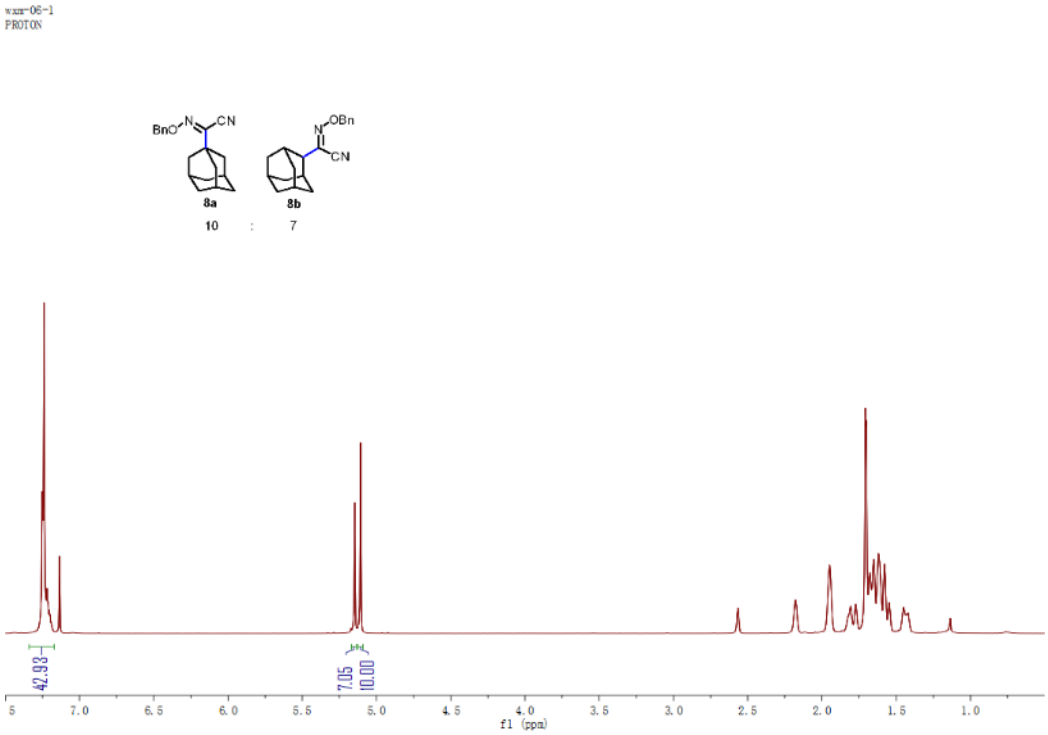
HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{15}H_{21}N_2O_2$ 261.1598; Found 261.1606.

6. Investigation of the mechanism.



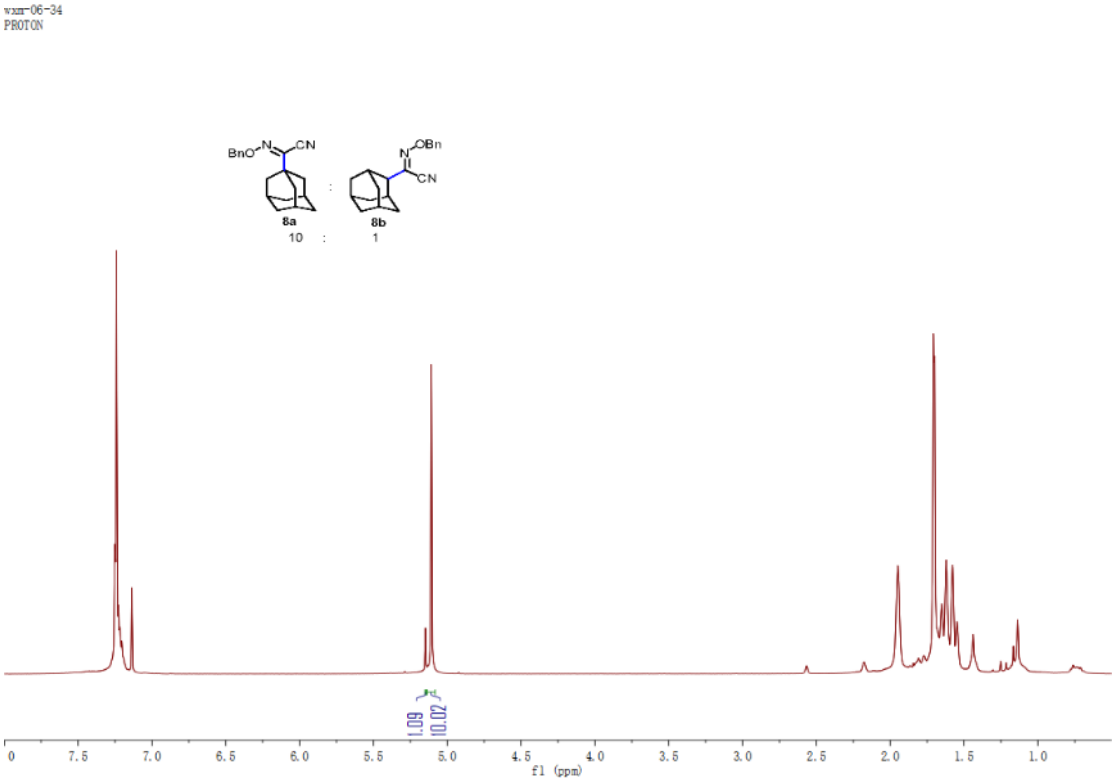
Condition A: To an 8 mL vial equipped with a magnetic stir bar was added TBADT (16.8 mg, 0.008 mmol, 0.04 equiv), sulfonyl oxime (0.2 mmol, 60.2 mg), adamantane (272 mg, 2 mmol, 10 equiv), $Na_2S_2O_8$ (0.4 mmol, 95.2 mg), 1 mL MeCN and 1 mL DCM. Then the tube was purged with Ar gas for 5 min. and sealed with PTFE cap. The tube was stirred at 25 °C for 18 h under 390 nm. Then the solvent was removed under reduced pressure and the crude product was purified by column chromatography (eluent: n-hexane/AcOEt) to provide the product **8a** and **8b** as a mixture.

8a+8b = 47.0 mg, **8a:8b** = 10:7(^{1}H NMR), Rf = 50%, PE:EA = 4:1, colorless oil.

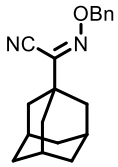


Condition B: To an 8 mL vial equipped with a magnetic stir bar was added sulfonyl oxime (0.2 mmol, 60 mg), adamantane (272 mg, 2 mmol, 10 equiv), $K_2S_2O_8$ (0.4 mmol, 108 mg), 2 mL MeCN and 1 mL H_2O. Then the tube was purged with Ar gas for 5 min. and sealed with PTFE cap. The tube was stirred at 80 °C for 2 h. Then the solvent was removed under reduced pressure and the crude product was purified by column chromatography (eluent: n-hexane/AcOEt) to provide the product **8a** and **8b** as a mixture

8a+8b = 48.8 mg, **8a:8b** = 10:1 (^{1}H NMR), Rf = 50%, PE:EA = 20:1, colorless oil.



***N*-(benzyloxy)adamantane-1-carbimidoyl cyanide (8a)**

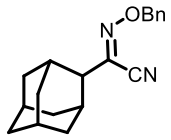


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.28 (m, 5H), 5.24 (s, 2H), 2.08 (s, 3H), 1.84 (d, *J* = 1.8 Hz, 6H), 1.73 (dd, *J* = 29.5, 12.3 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 136.3, 128.6, 128.5, 128.4, 109.4, 77.7, 39.7, 38.1, 36.3, 27.9.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{19}H_{22}N_2NaO$ 317.1630; Found 317.1628.

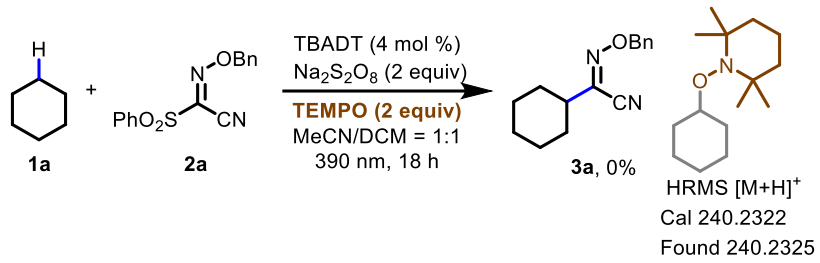
***N*-(benzyloxy)adamantane-2-carbimidoyl cyanide (8b)**



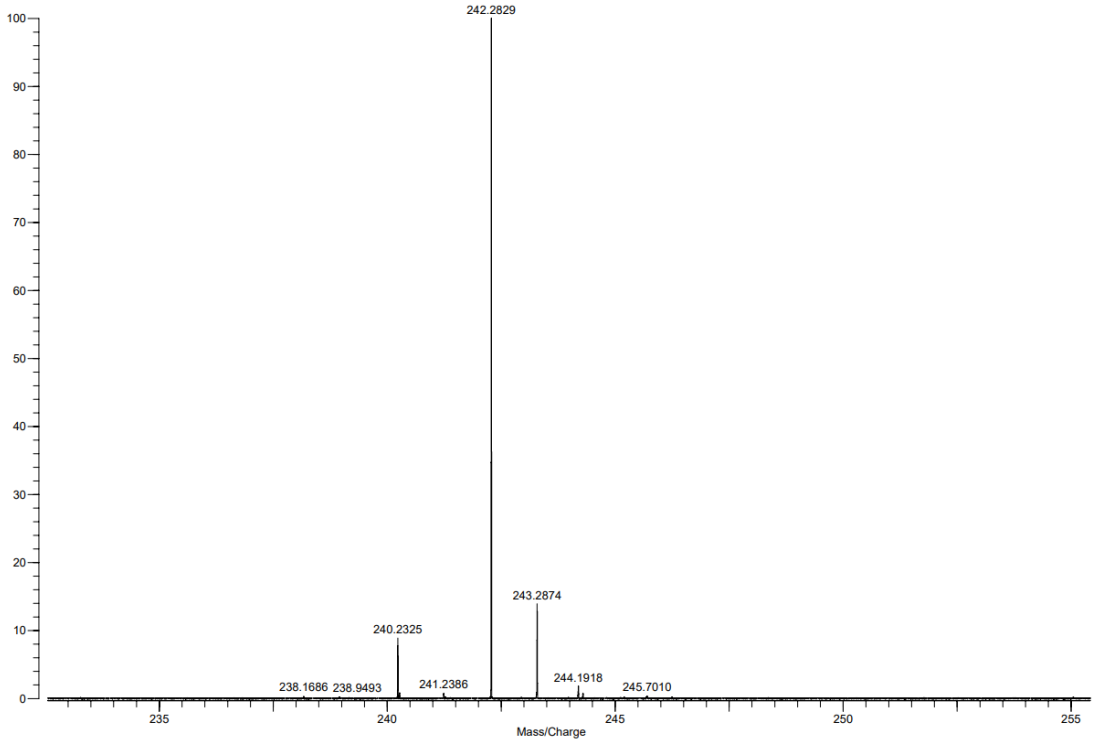
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.29 (m, 5H), 5.27 (s, 2H), 2.69 (s, 1H), 2.31 (s, 2H), 1.92 (d, *J* = 14.1 Hz, 3H), 1.79 (d, *J* = 10.2 Hz, 5H), 1.74 (s, 2H), 1.56 (d, *J* = 12.6 Hz, 2H).

^{13}C NMR (101 MHz, CDCl3) δ 136.4, 135.8, 128.5, 128.3, 110.0, 77.7, 47.0, 38.1, 37.4, 32.0, 29.7, 27.6, 27.4.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{19}H_{22}N_2NaO$ 317.1630; Found 317.1627.



To an 8 mL vial equipped with a magnetic stir bar was added TBADT (16.8 mg, 0.008 mmol, 0.04 equiv), sulfonyl oxime (60.2 mg, 0.2 mmol, 1 equiv), cyclohexane (168 mg, 2 mmol, 10 equiv), $Na_2S_2O_8$ (95.2 mg, 0.4 mmol, 2 equiv), TEMPO (62.4 mg, 0.4 mmol, 2 equiv) 1 mL MeCN and 1 mL DCM. Then the tube was purged with Ar gas for 5 min. and sealed with PTFE cap. The tube was stirred at 25 °C for 18 h under 390 nm. The reaction was completely quenched and no product **3a** detected. The coupling product of cyclohexyl radical and TEMPO was detected by HRMS.



7. Reference

1. S. Guo, X. Zhang and P. Tang, *Angew. Chem. Int. Ed.*, 2015, **54**, 4065-4069.
2. S. Mukherjee, B. Maji, A. Tlahuext-Aca and F. Glorius, *J. Am. Chem. Soc.*, 2016, **138**, 16200-16203.
3. B. Gaspar and E. M. Carreira, *J. Am. Chem. Soc.*, 2009, **131**, 13214-13215.
4. Y. Zhu, X. Wen, S. Song and N. Jiao, *ACS Catal.*, 2016, **6**, 6465-6472.
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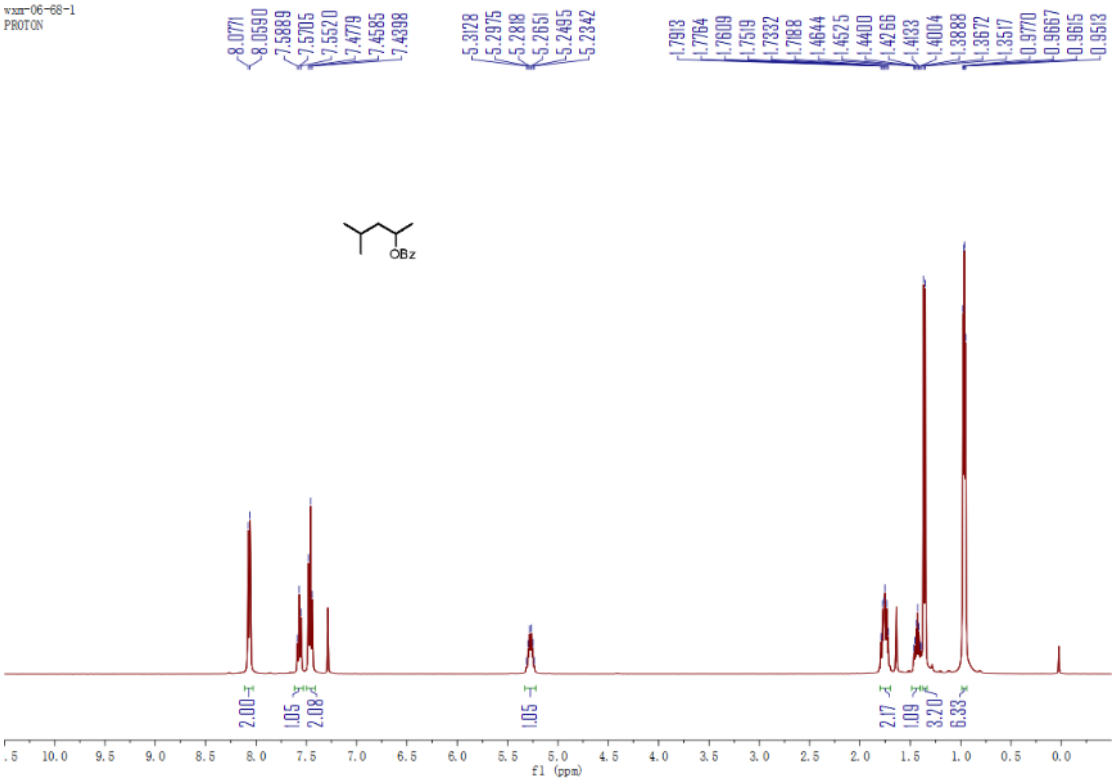
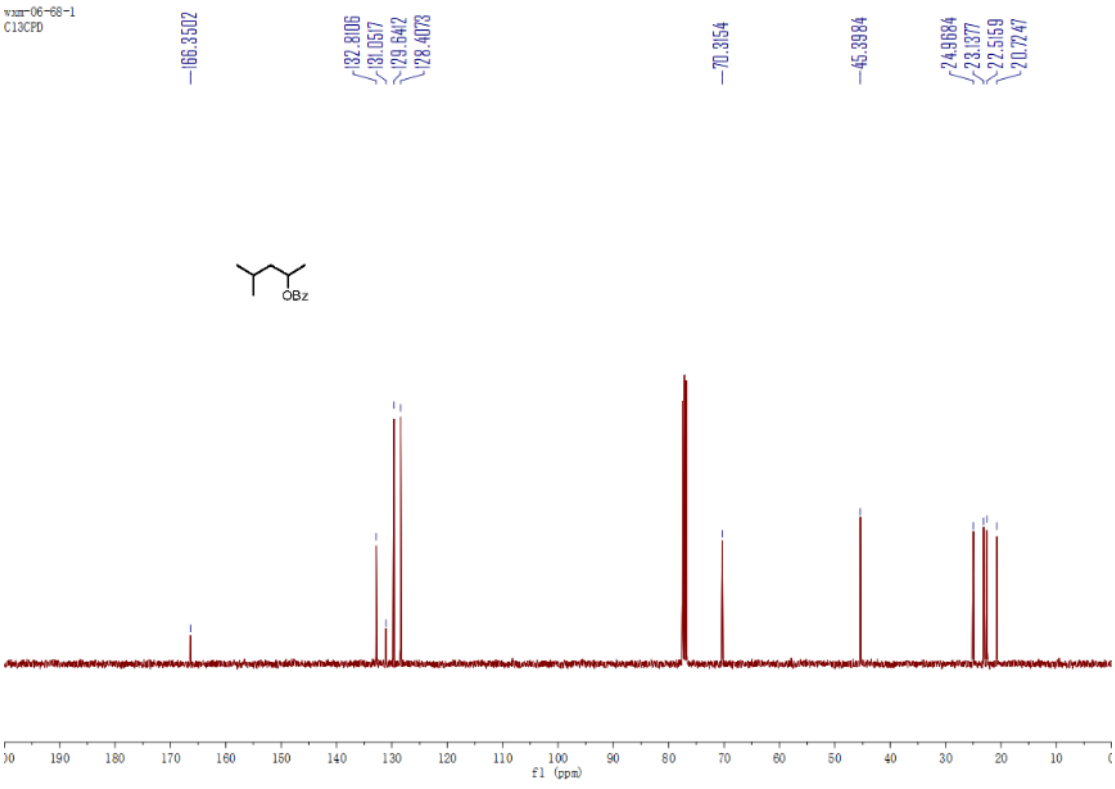
8. NMR Spectrum

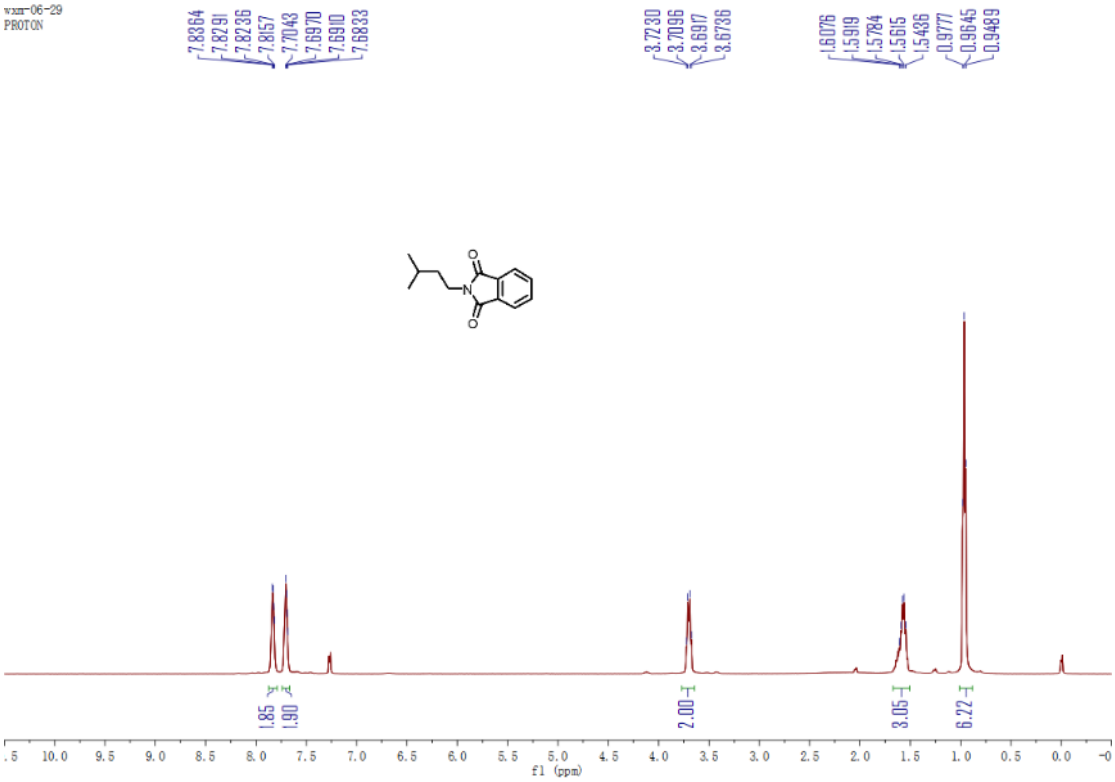
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1z**



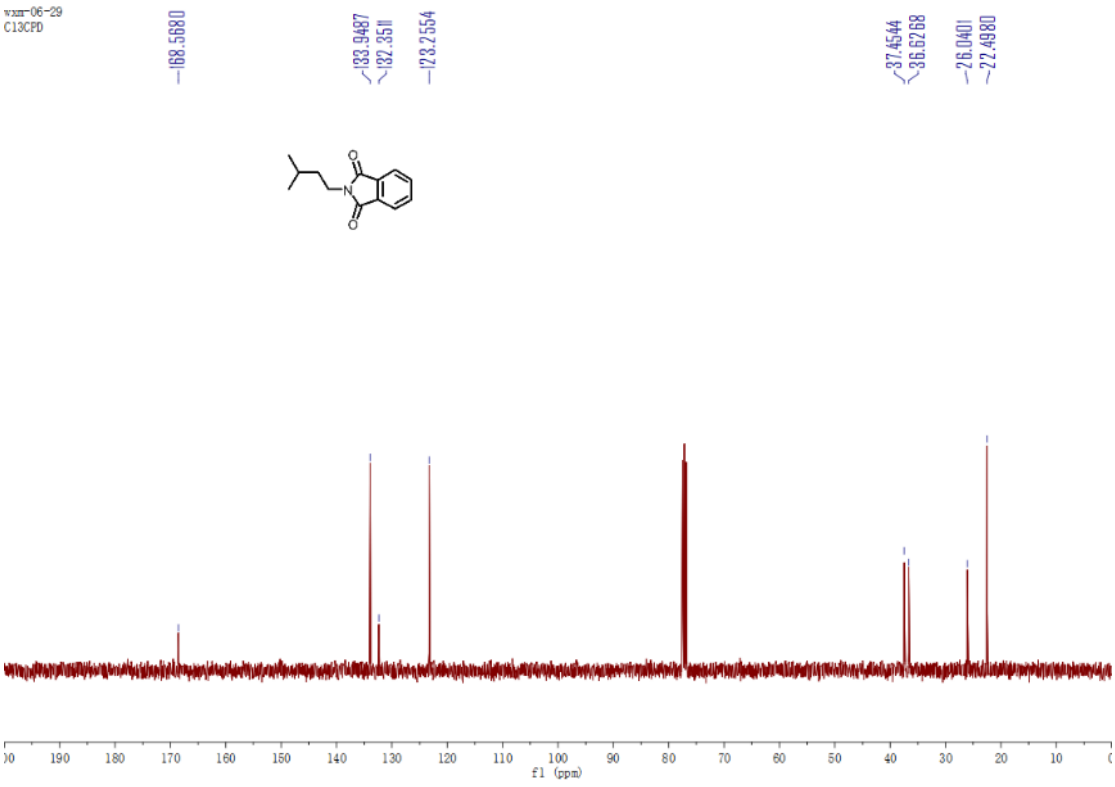
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **1z**



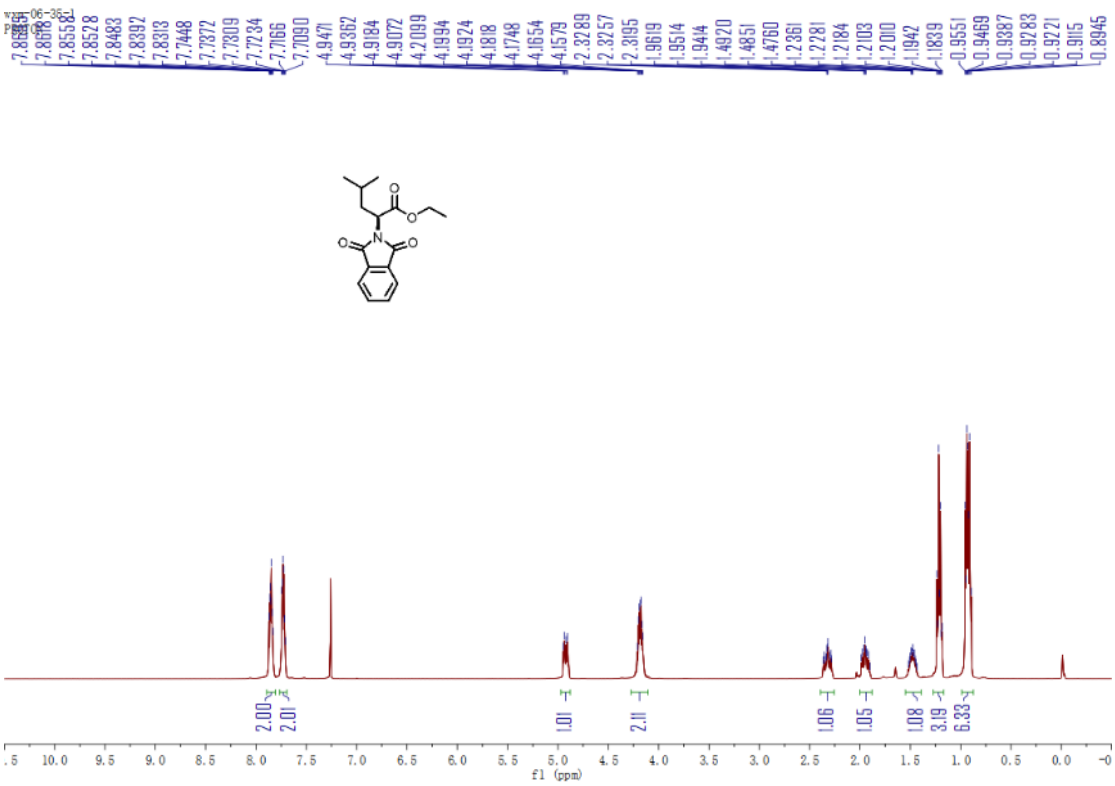
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1cc**



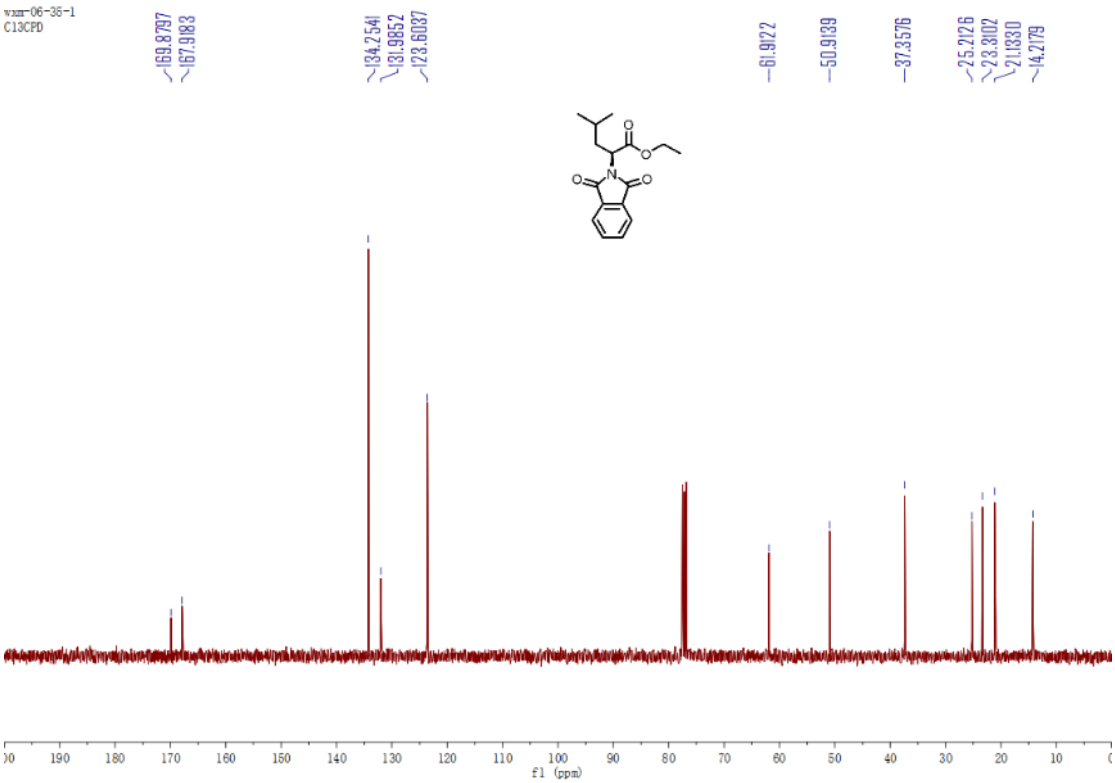
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **1cc**



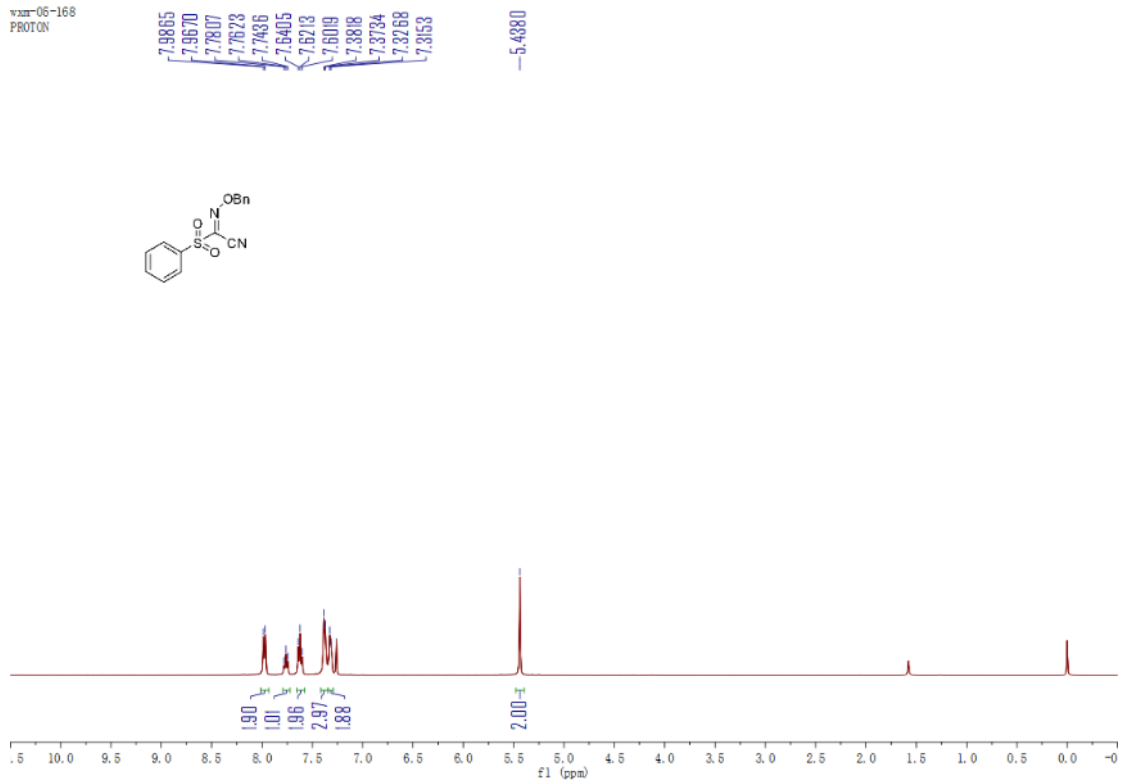
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1ee**



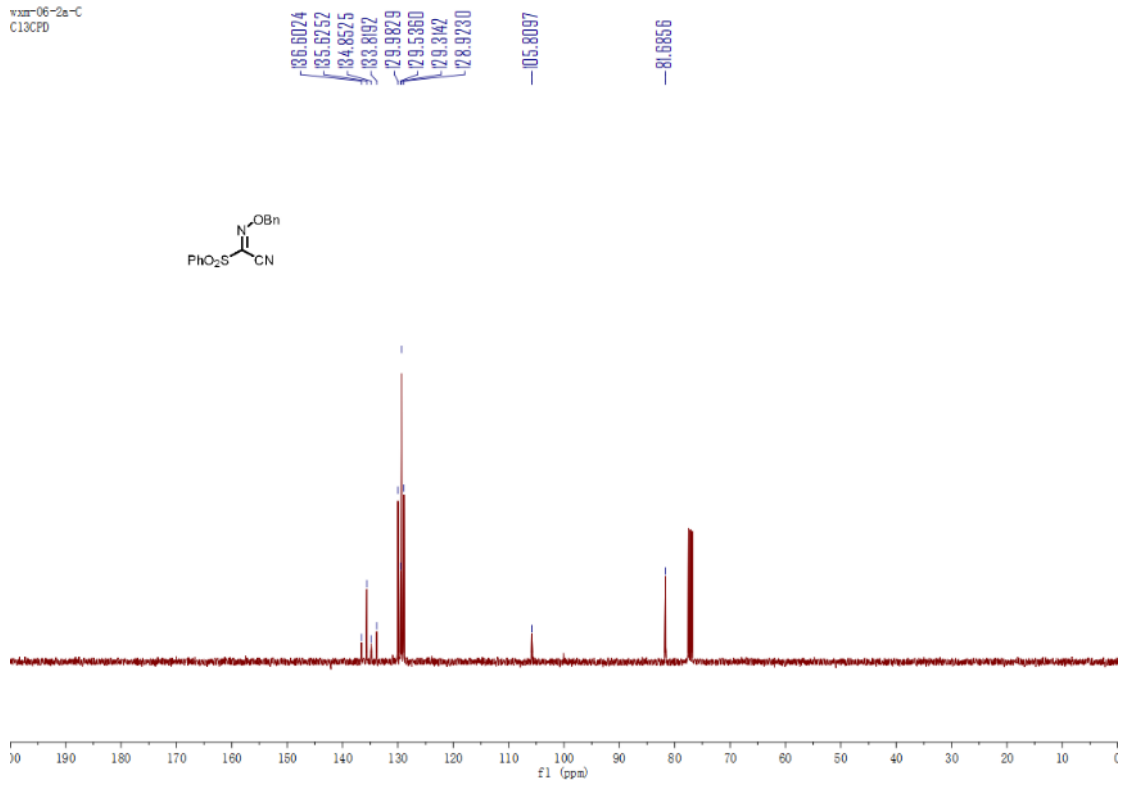
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **1ee**



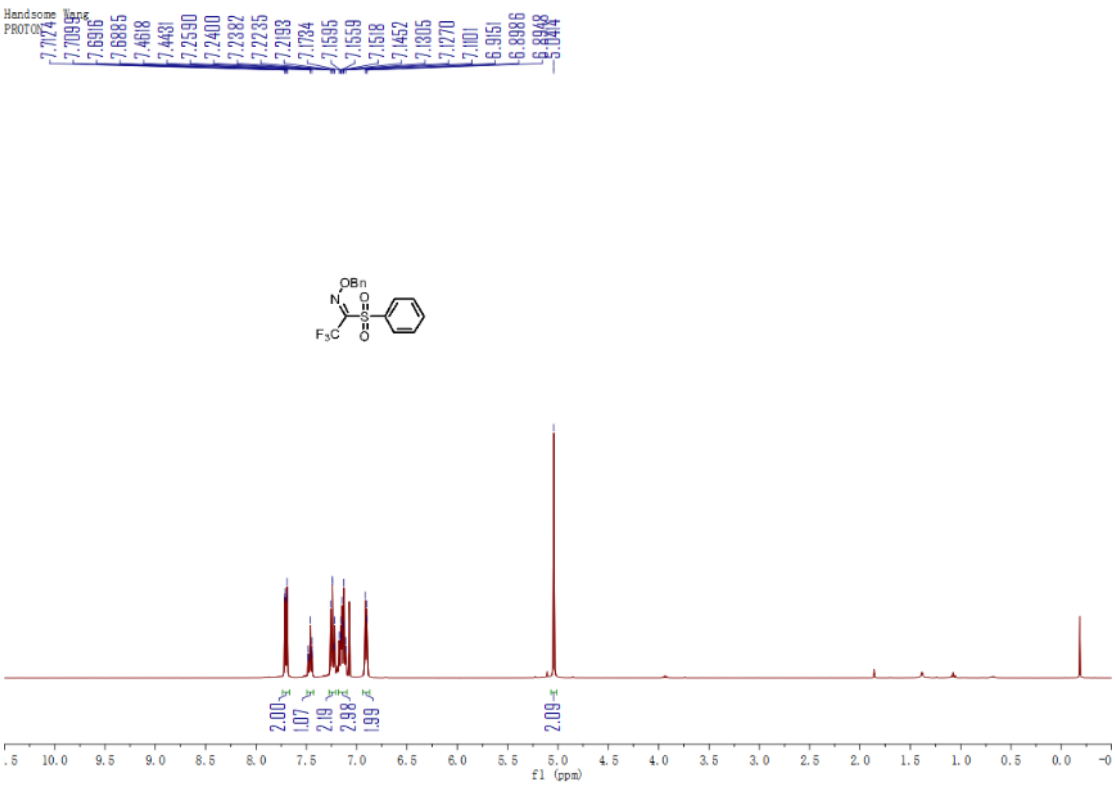
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2a**



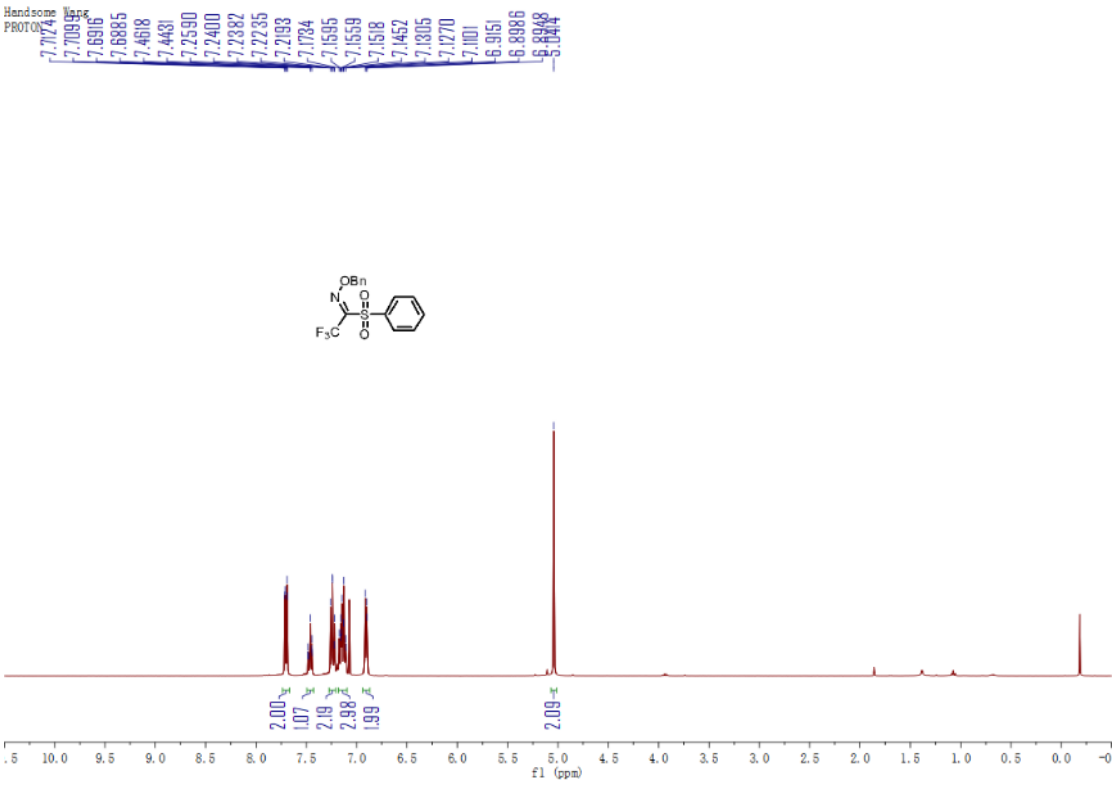
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **2a**



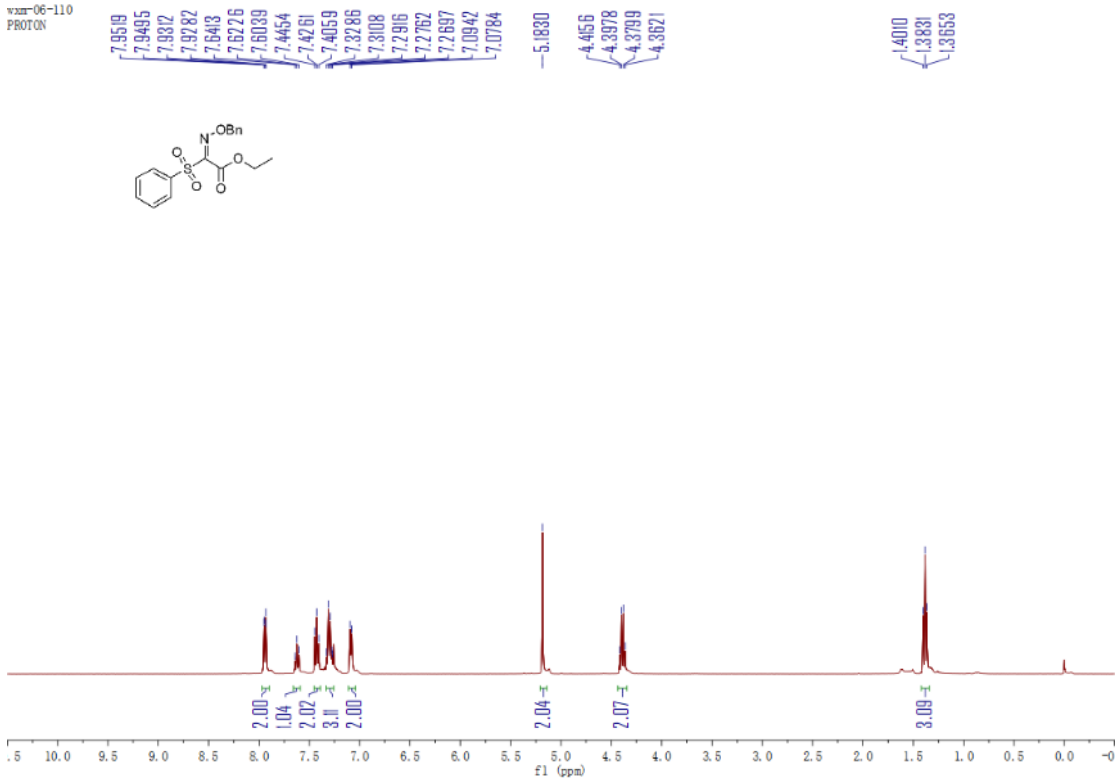
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2b**



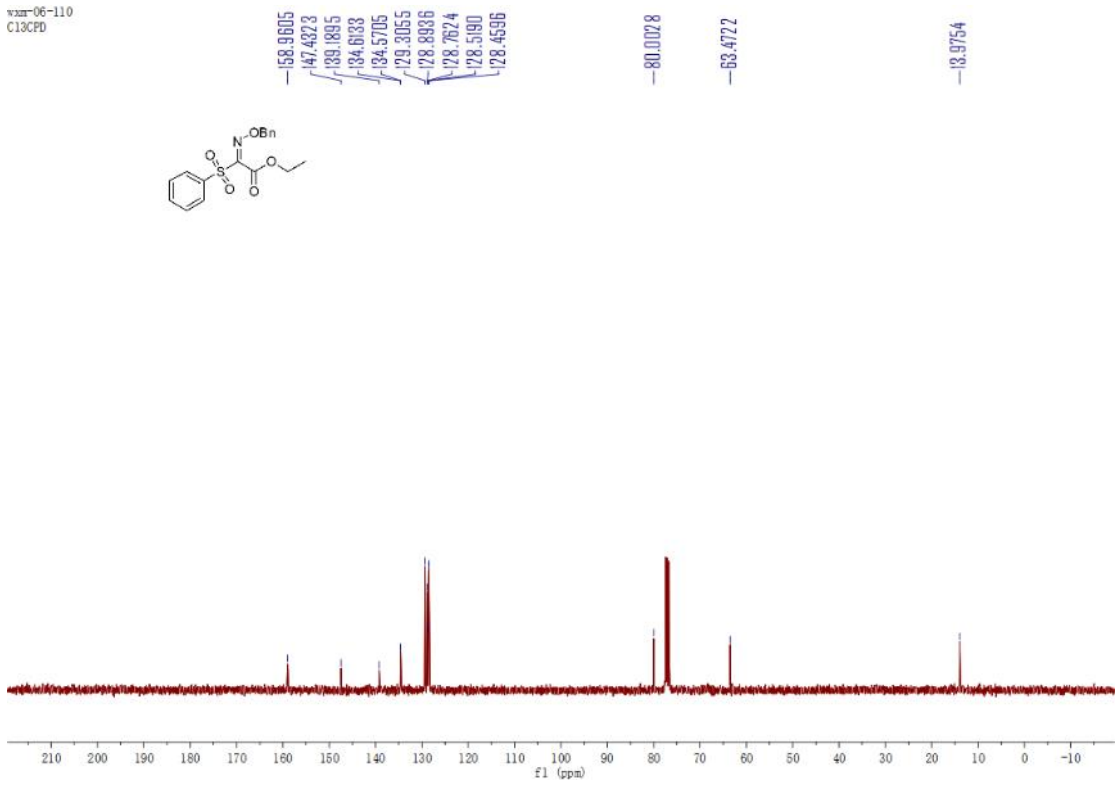
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **2b**



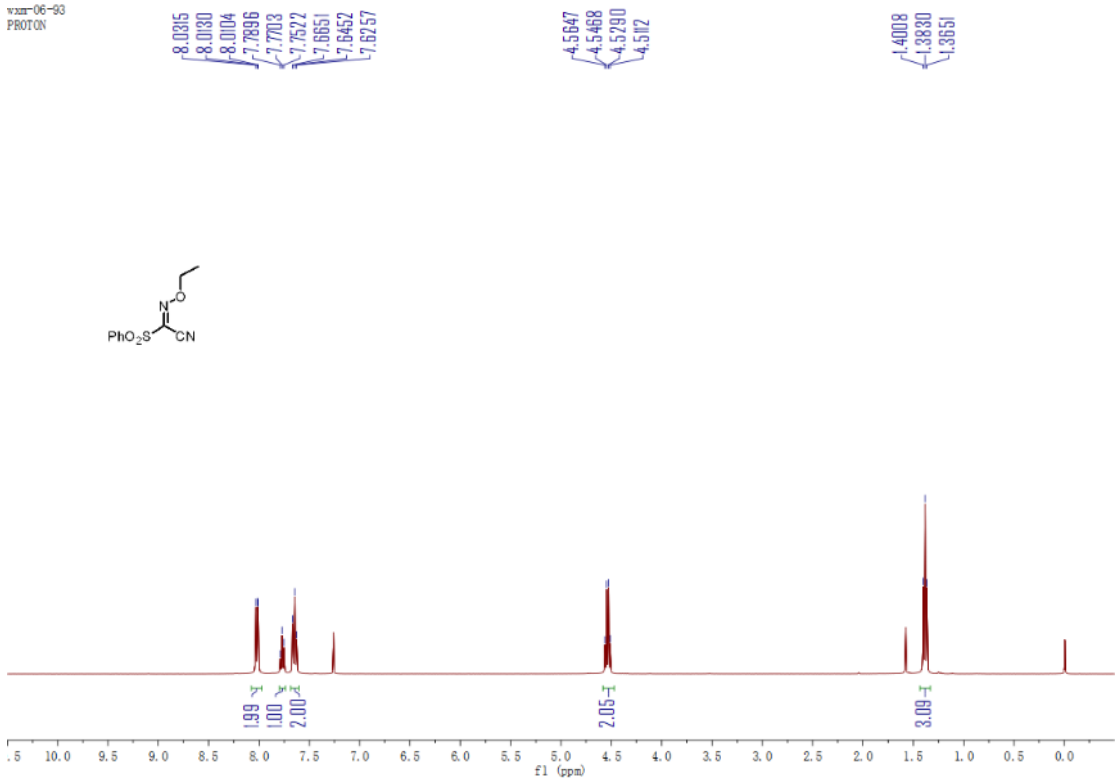
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2c**



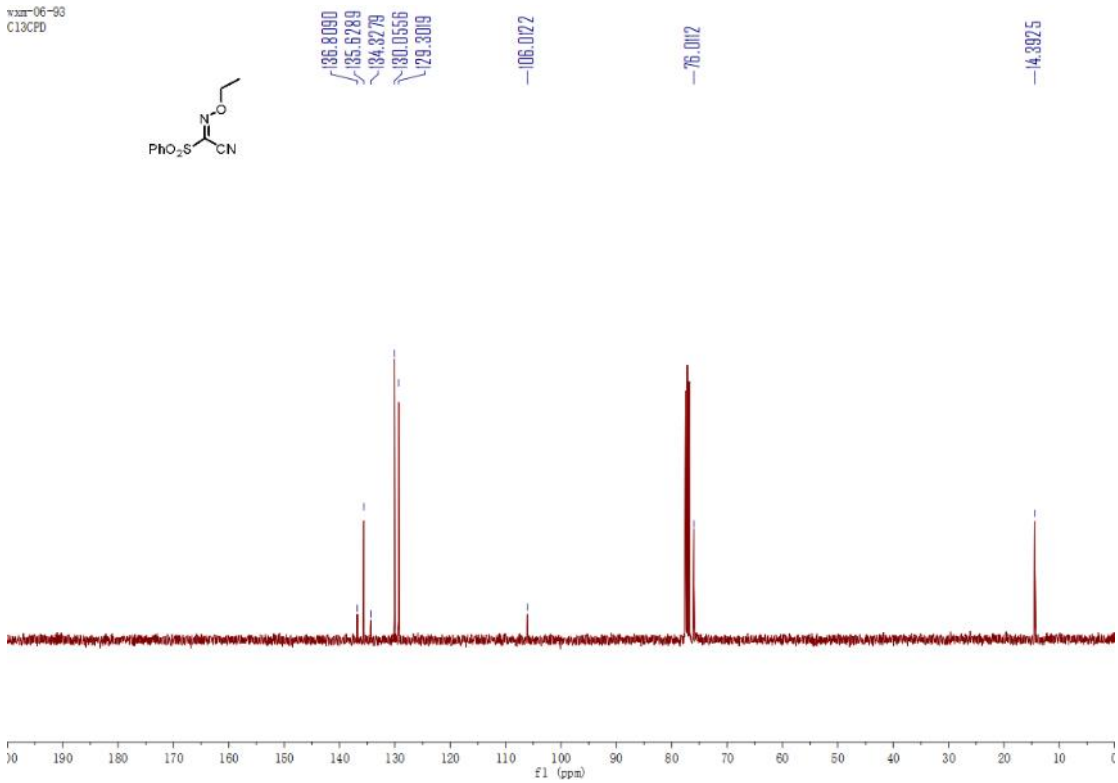
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **2c**



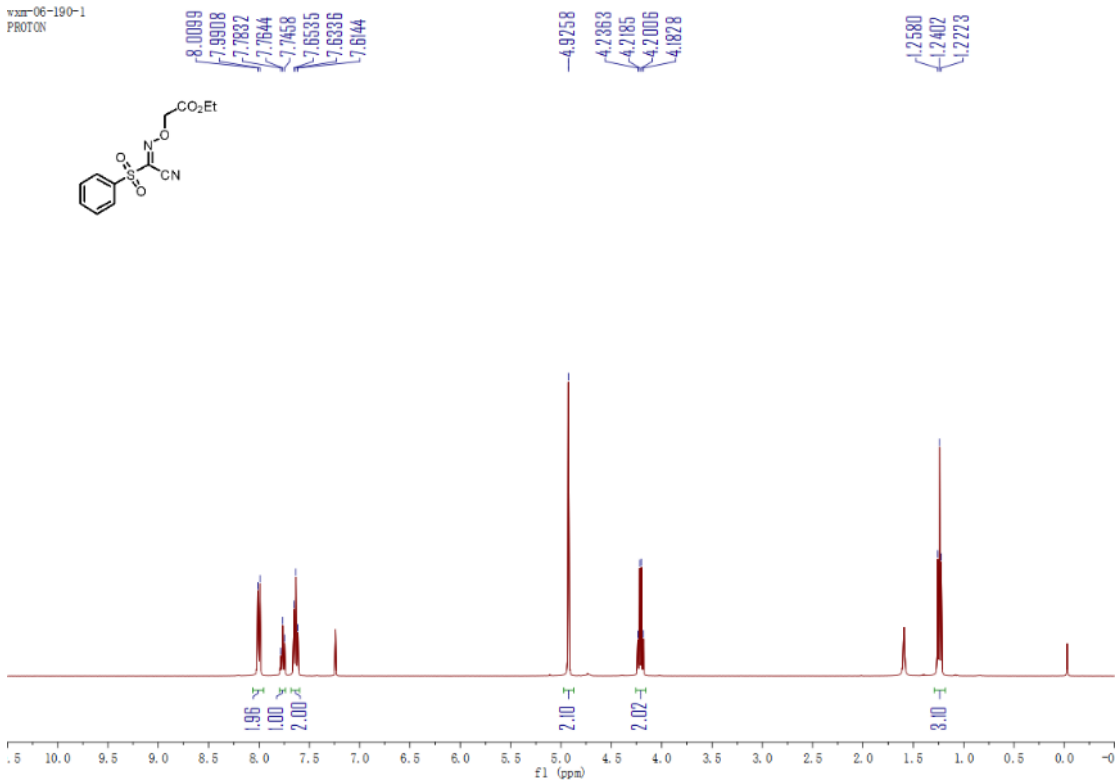
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2d**



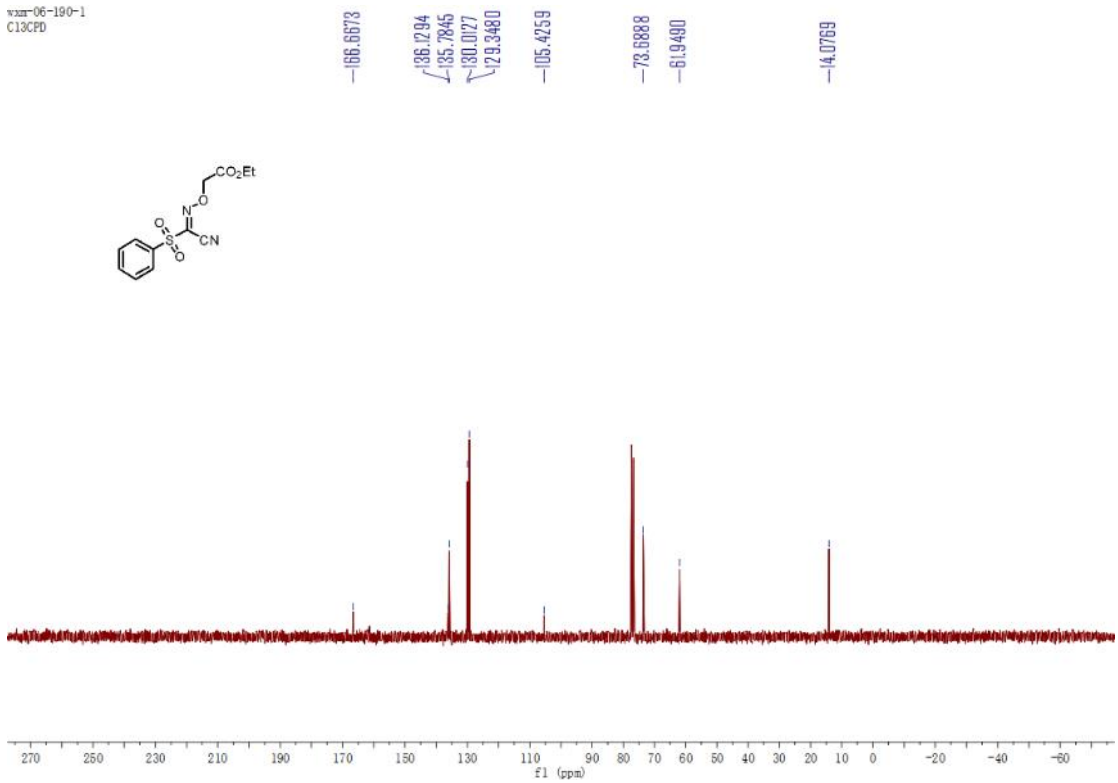
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **2d**



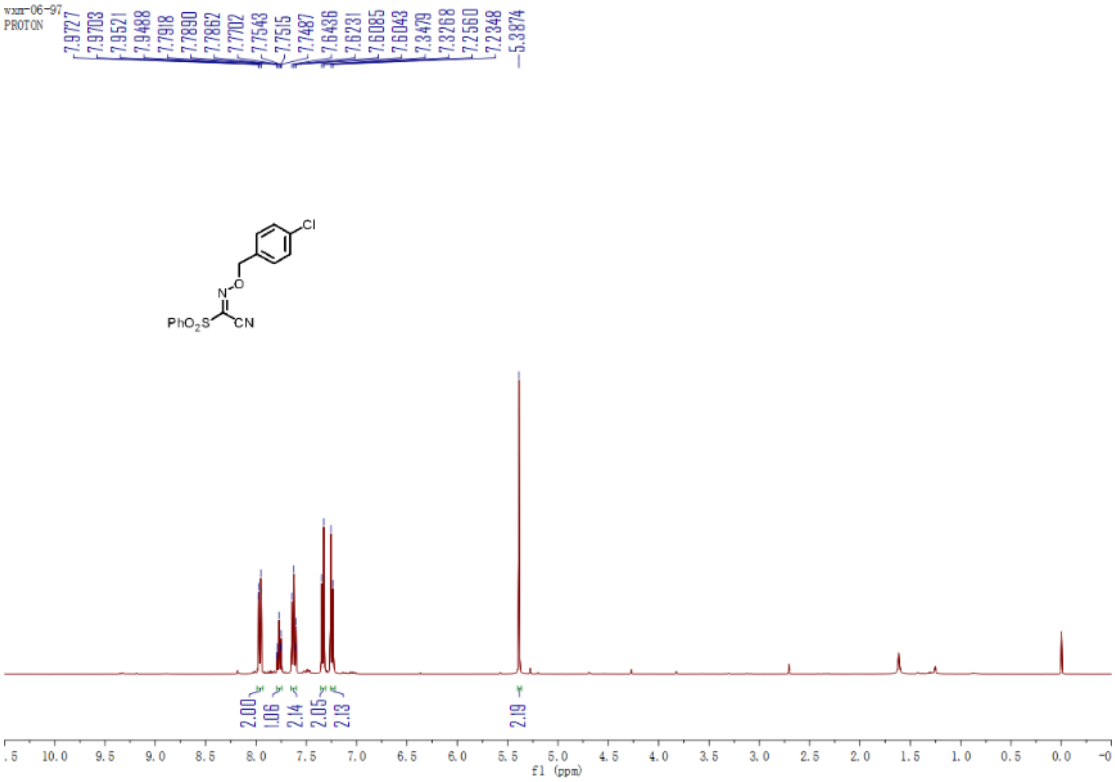
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2e**



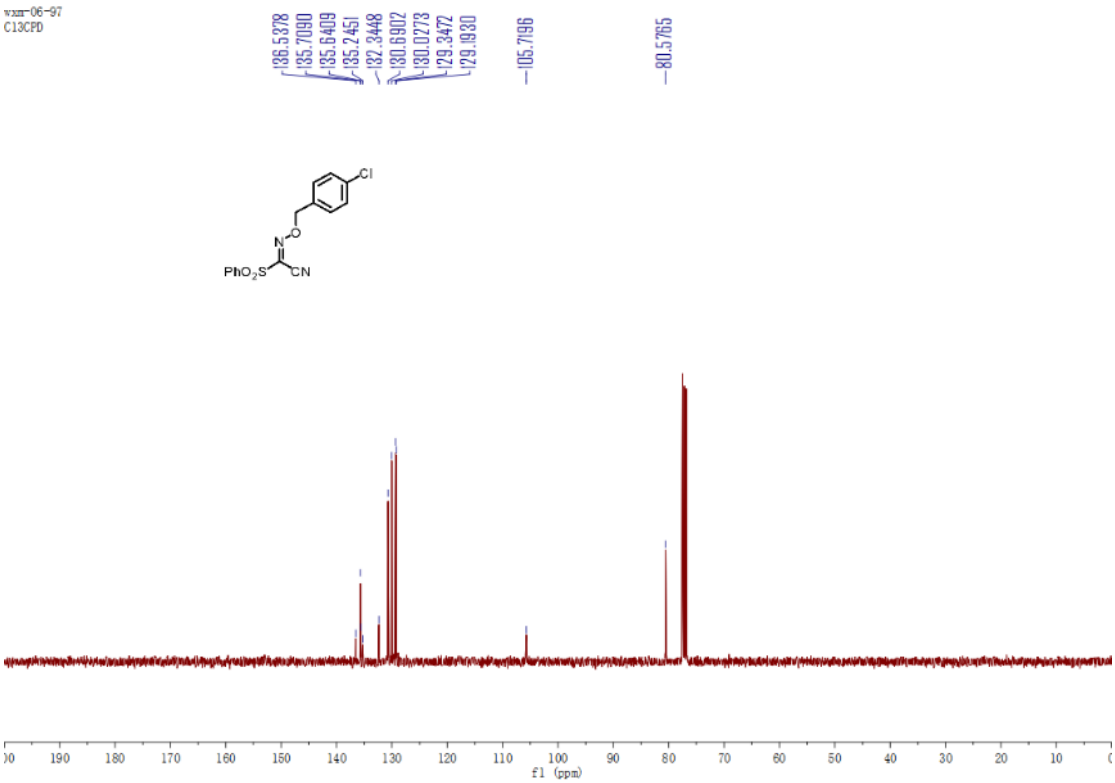
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **2e**



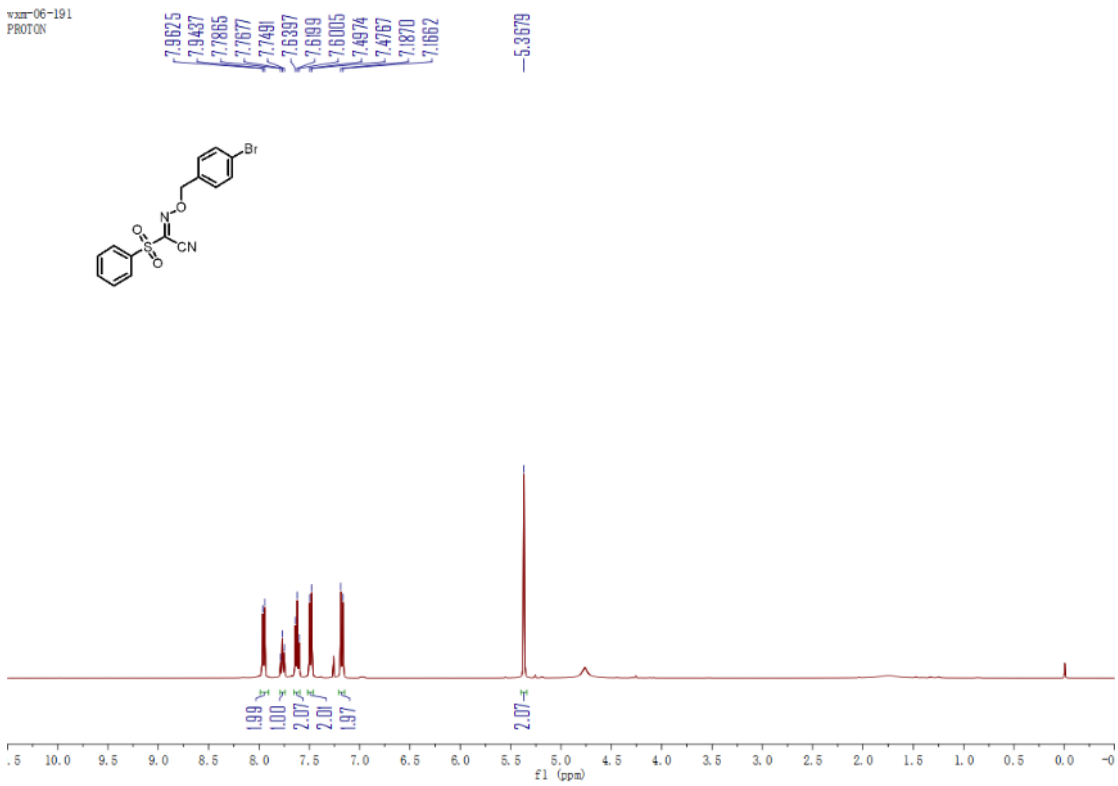
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2f**



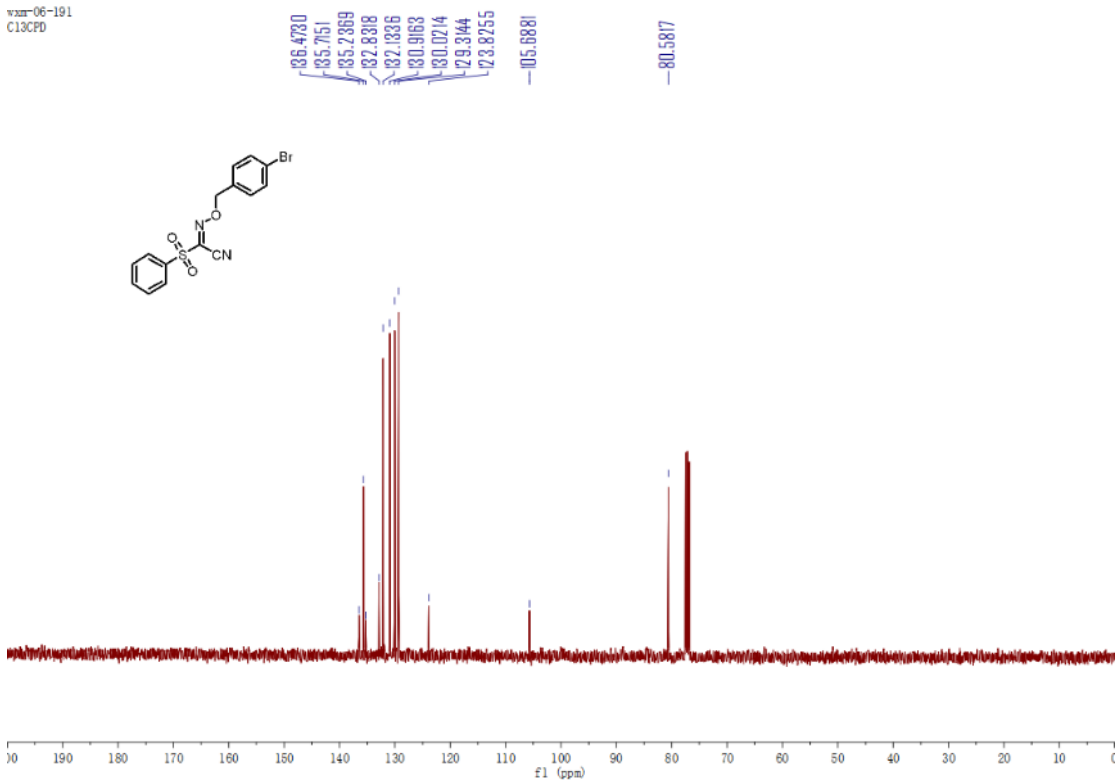
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **2f**



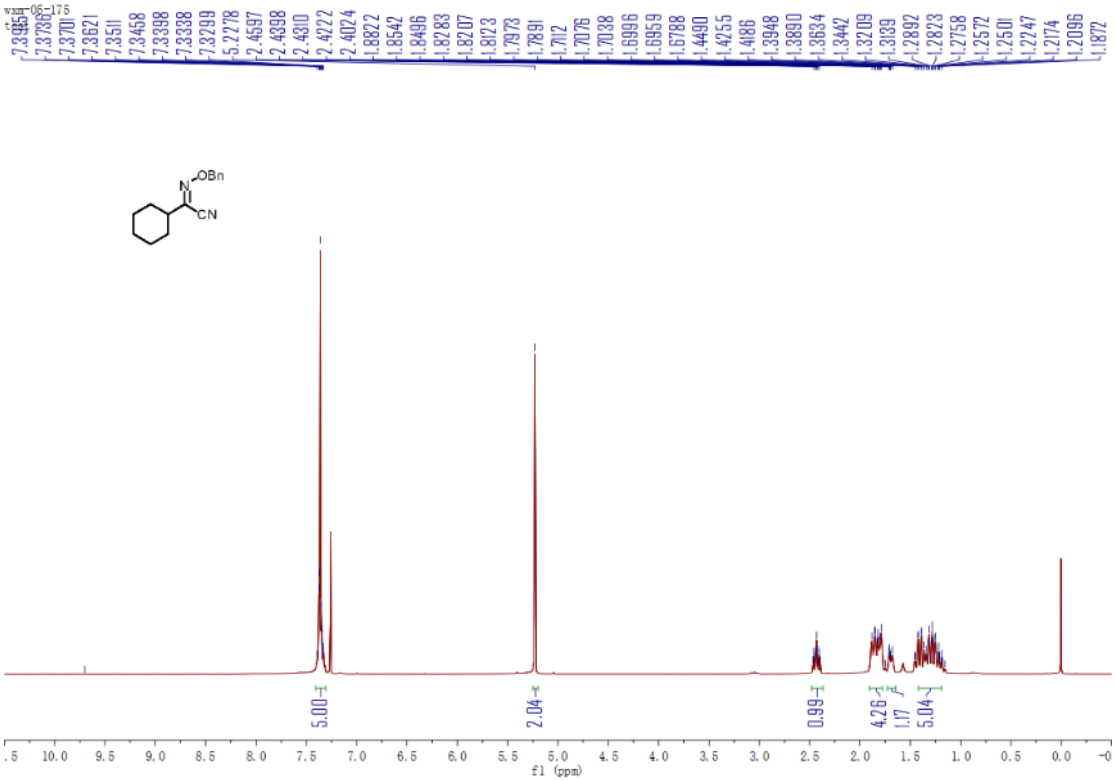
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2g**



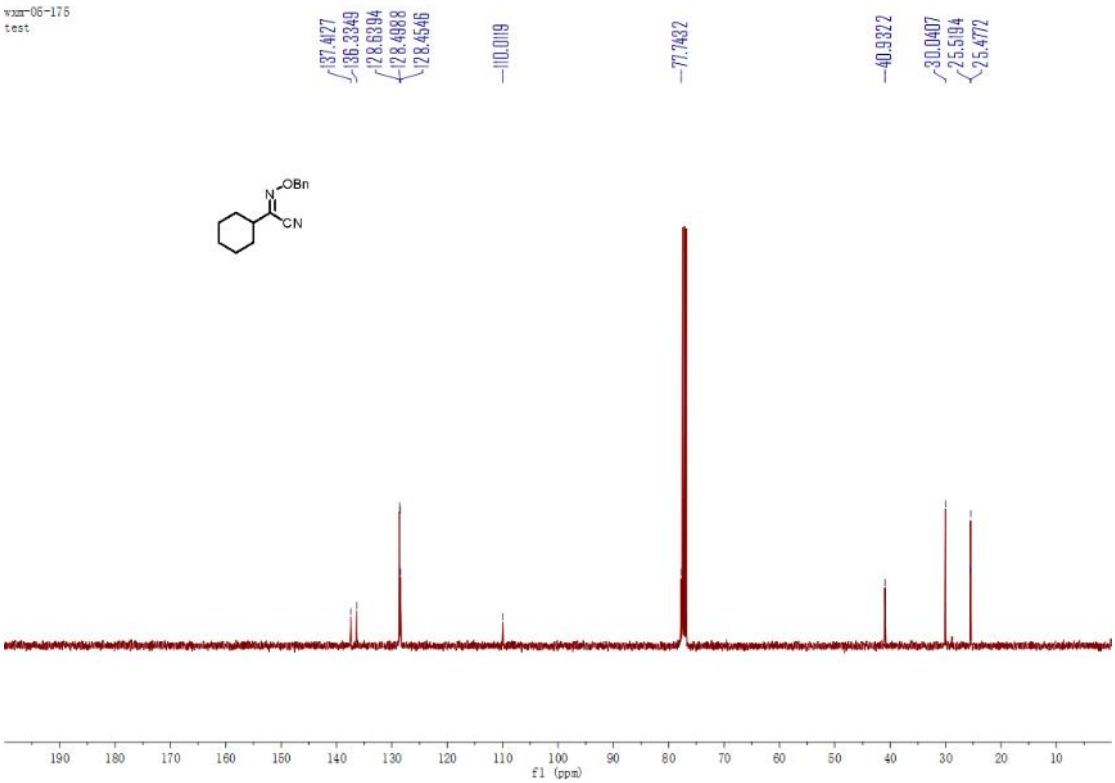
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **2g**



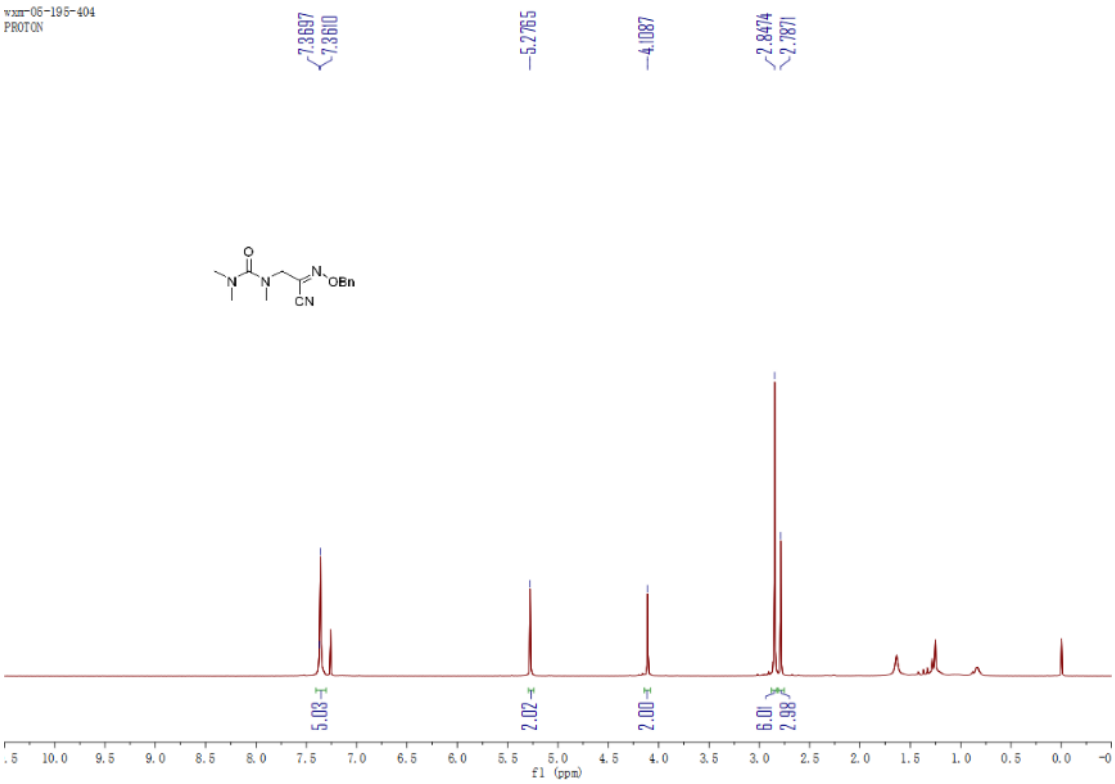
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3a**



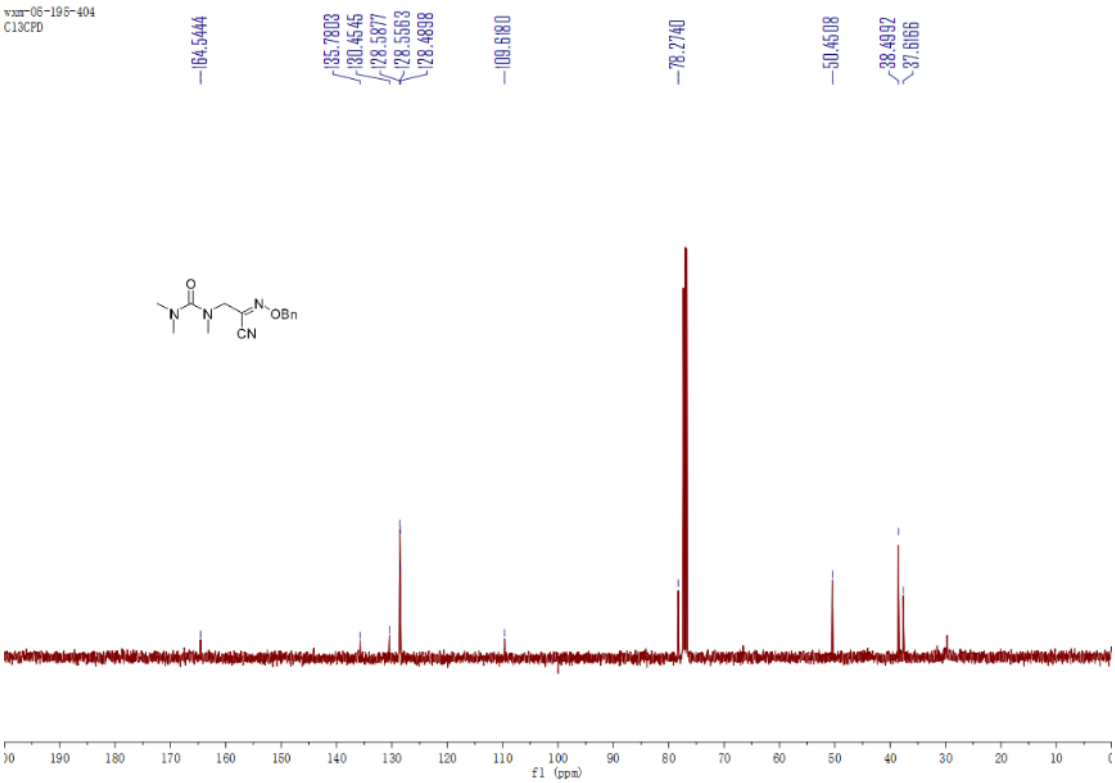
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3a**



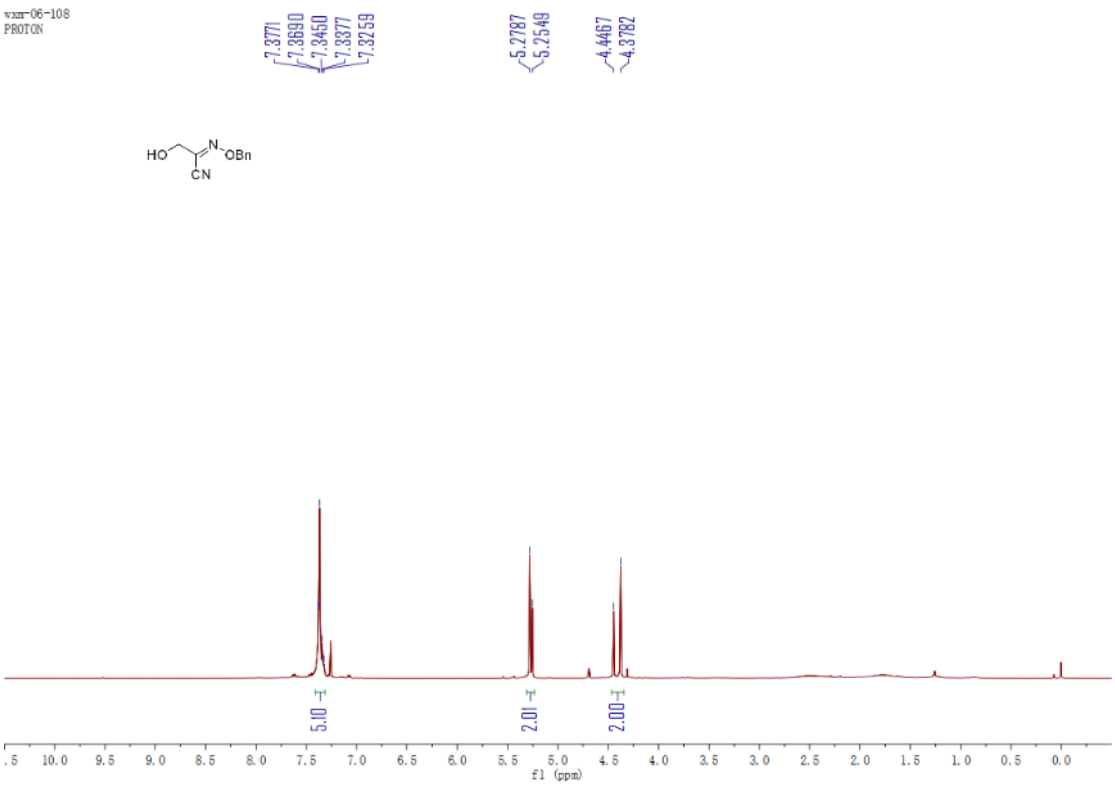
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3b**



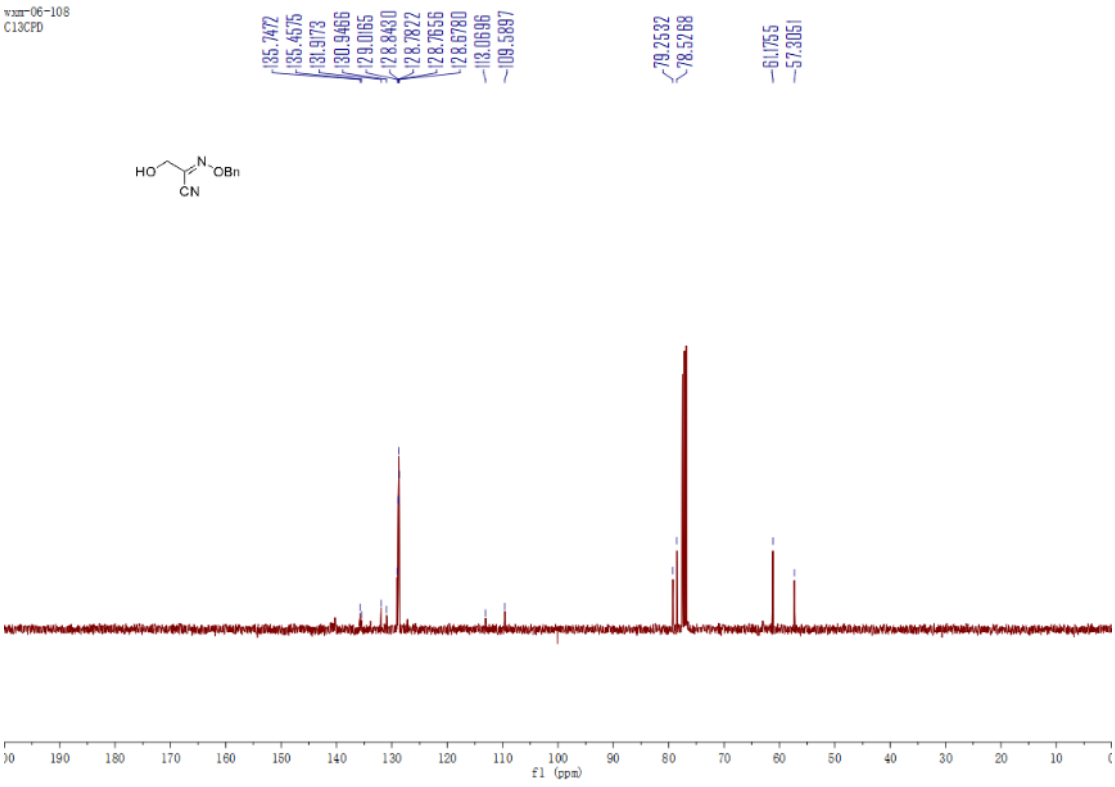
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3b**



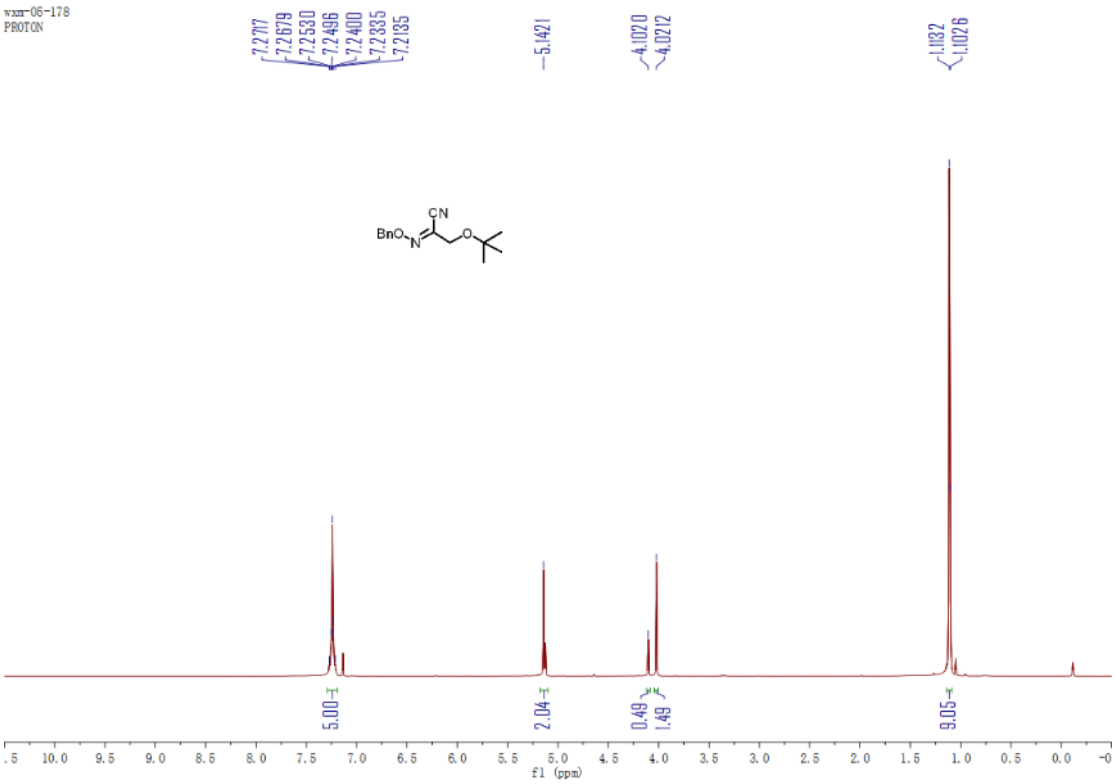
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3c**



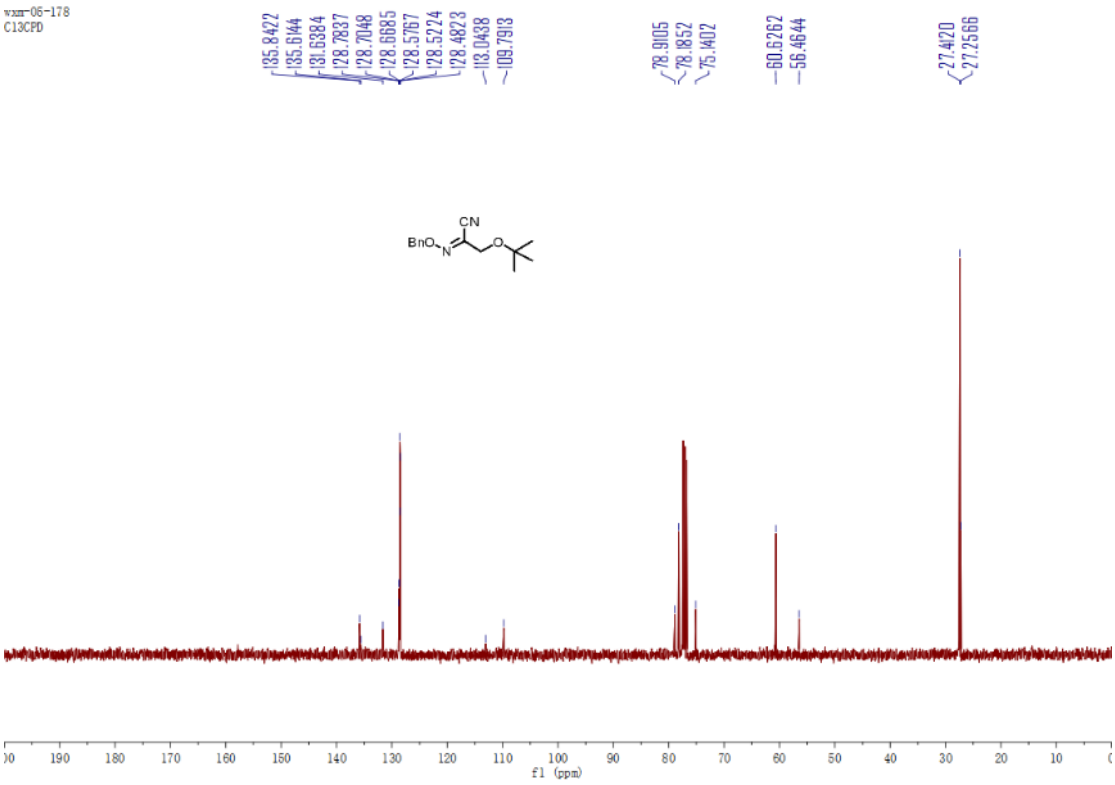
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3c**



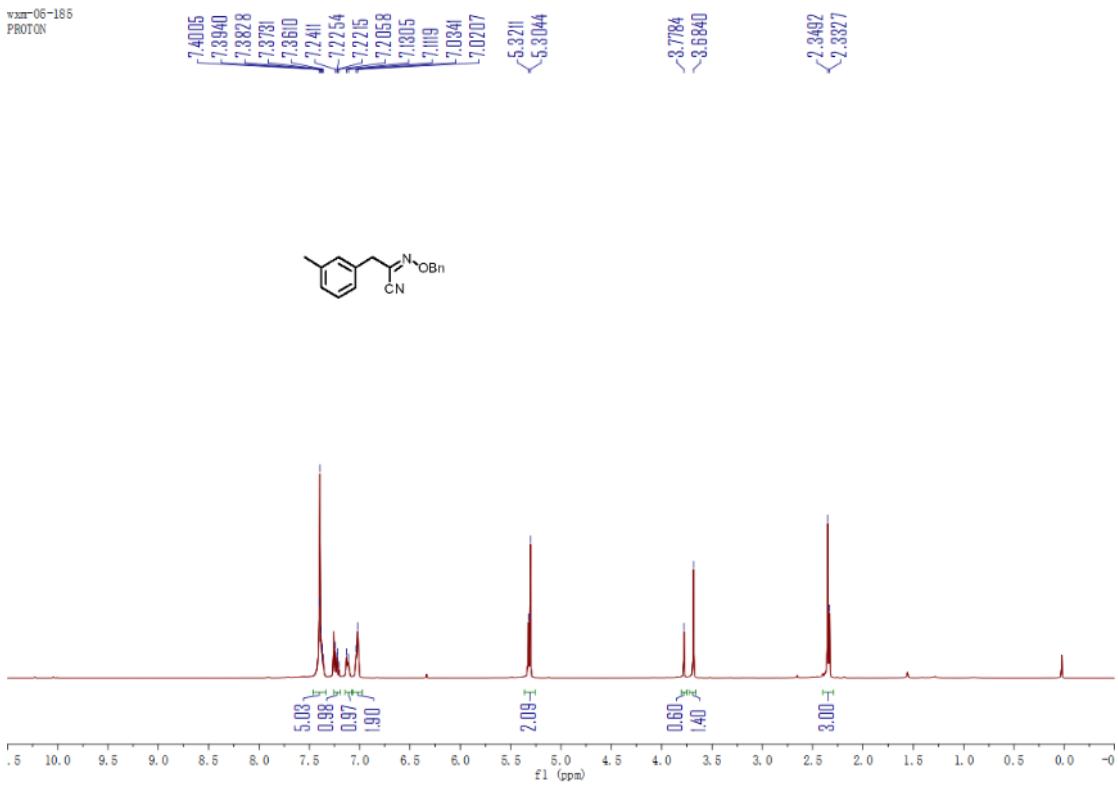
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3d**



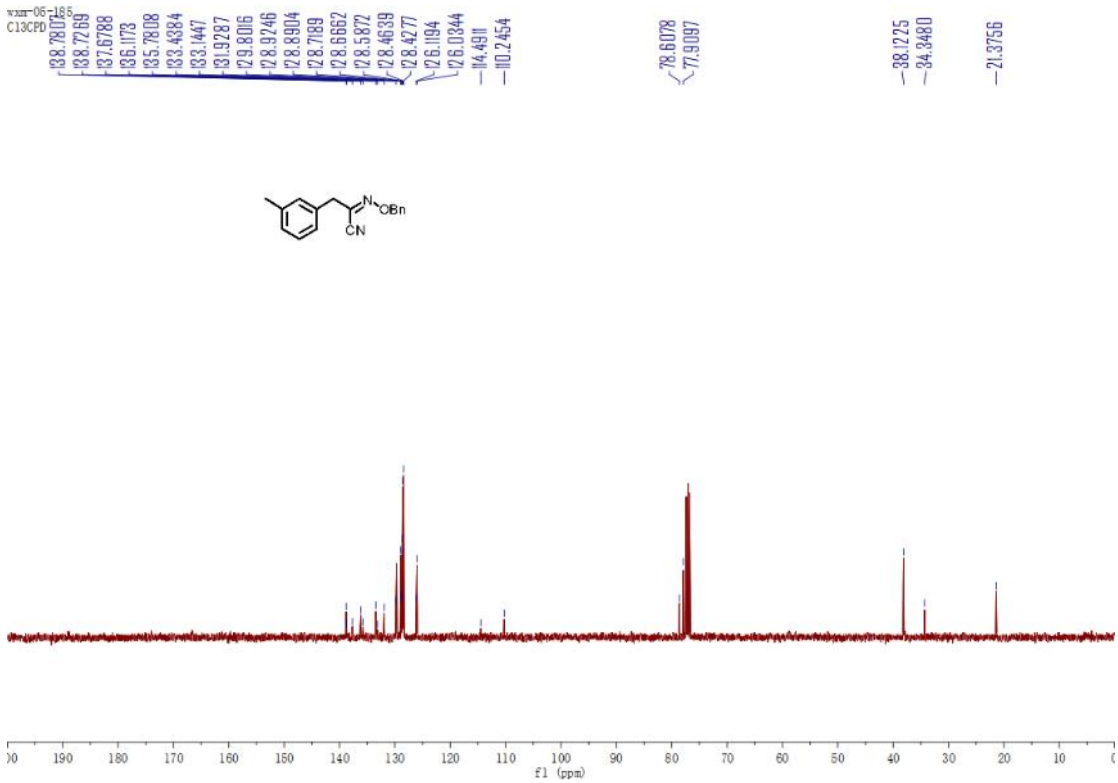
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3d**



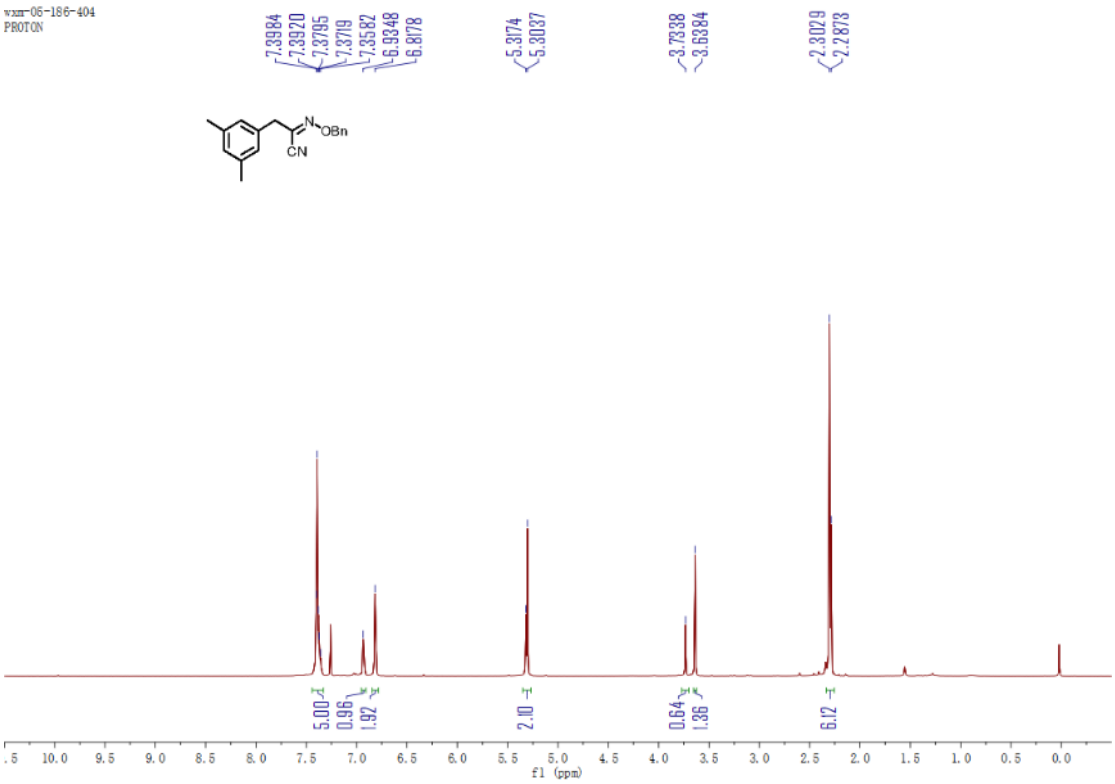
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3e**



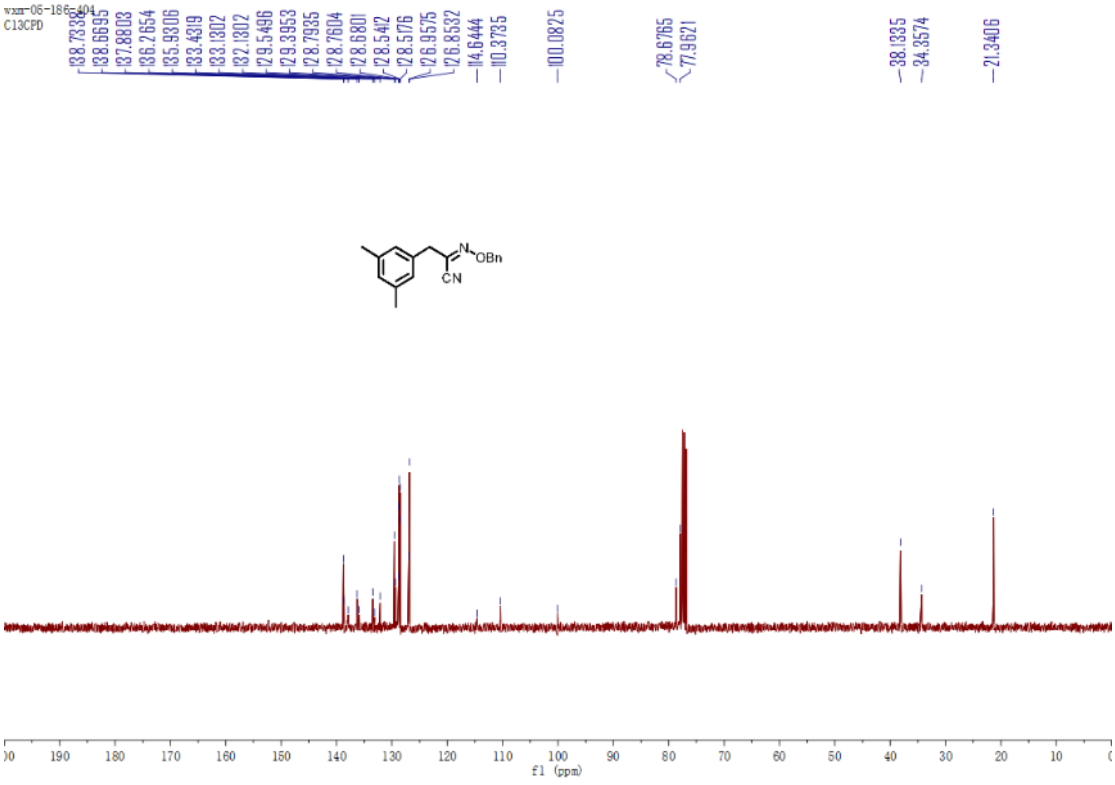
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3e**



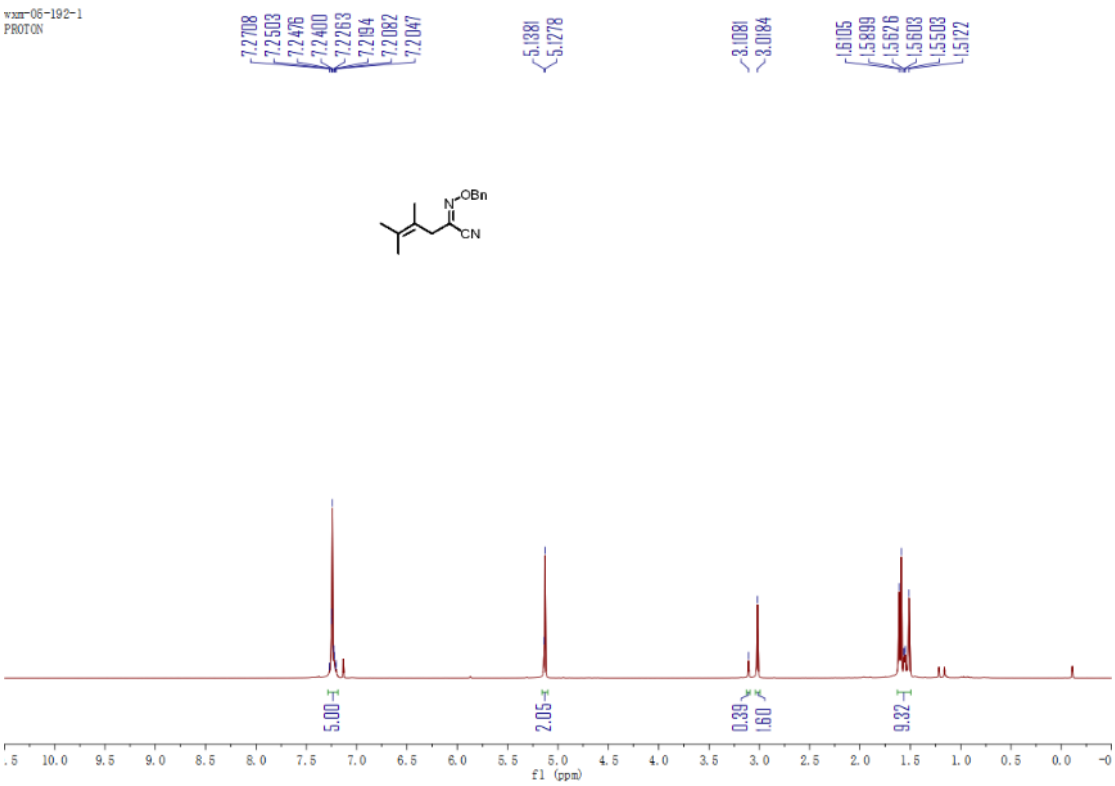
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3f**



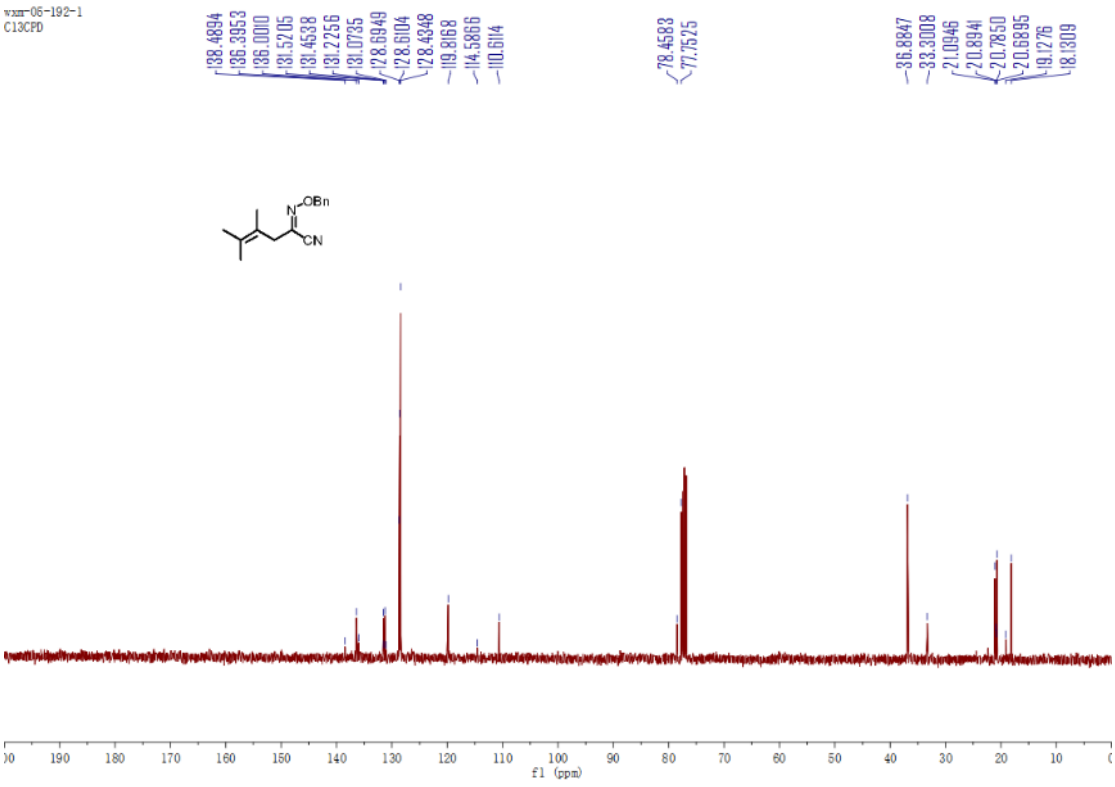
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3f**



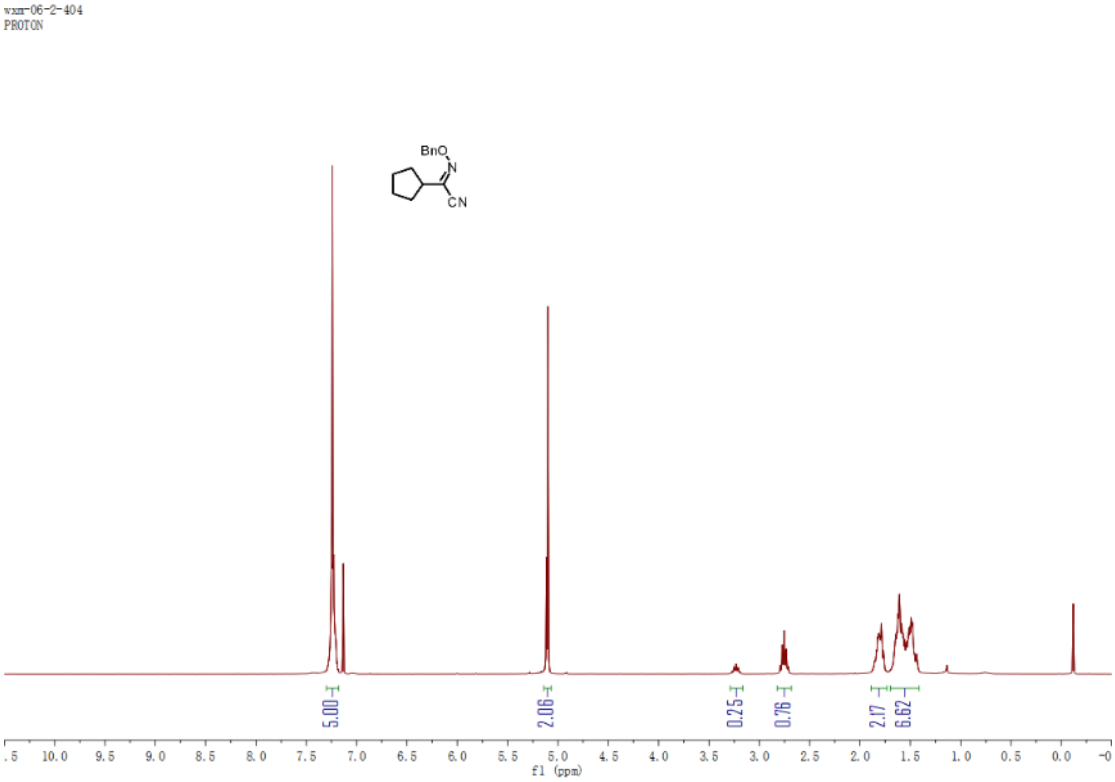
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3g**



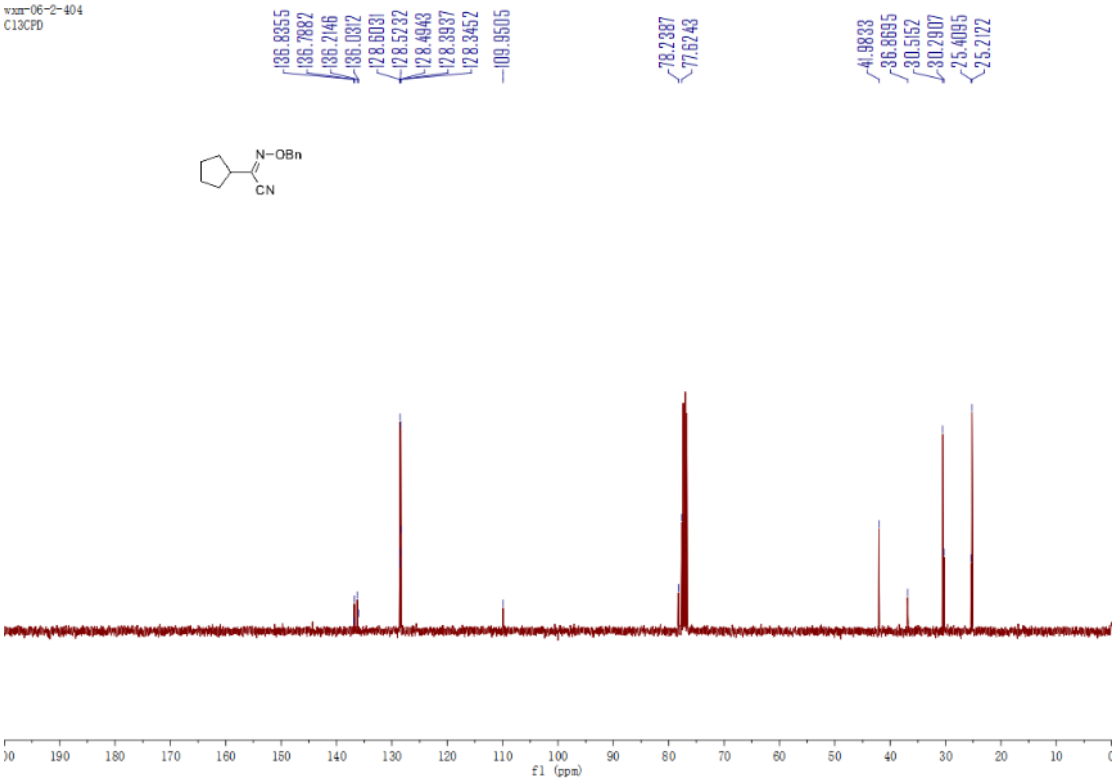
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3g**



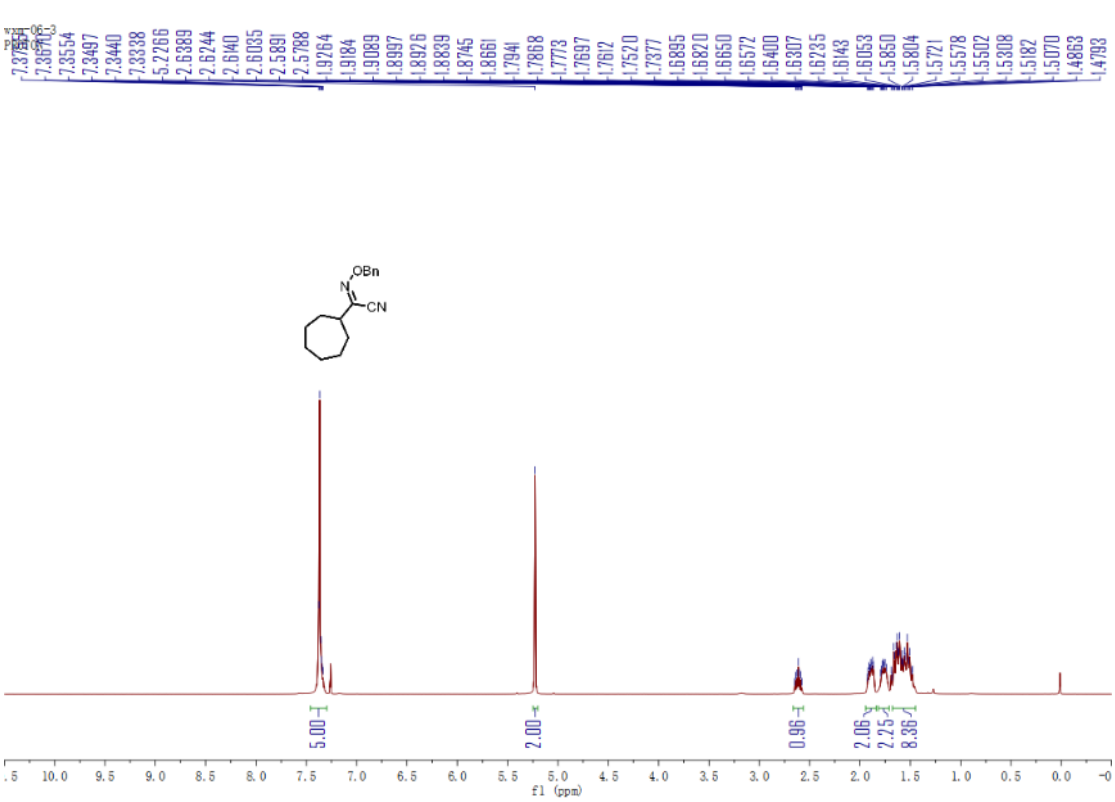
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3h**



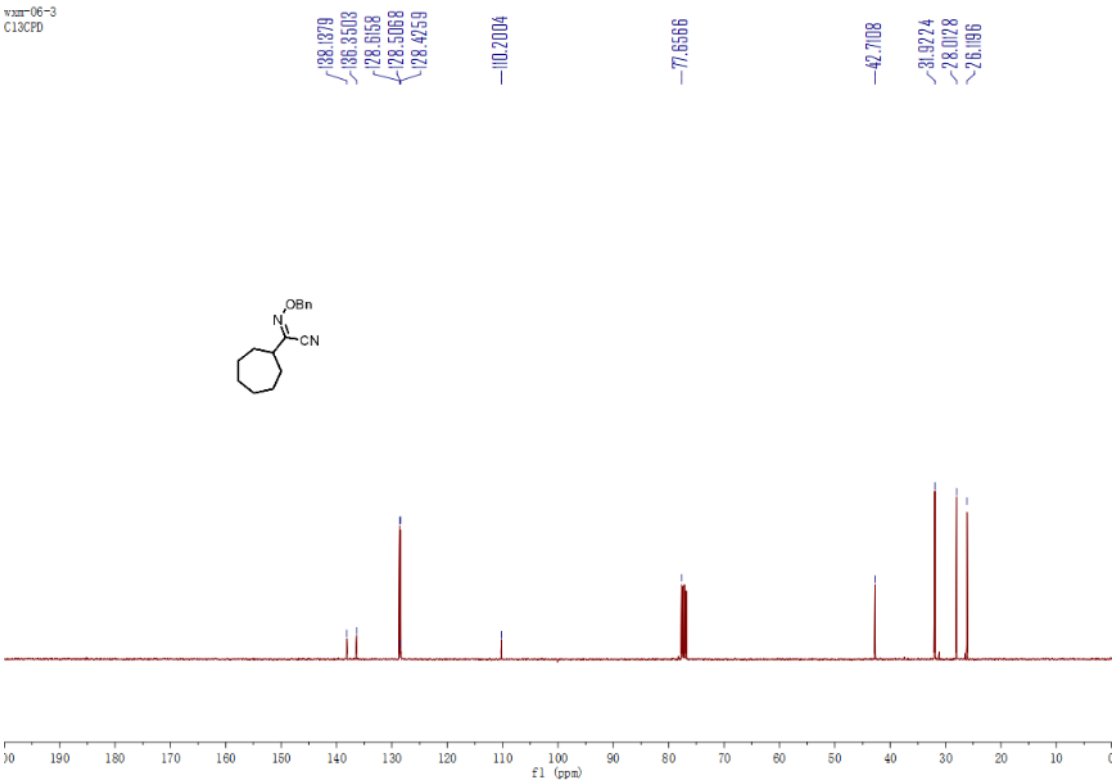
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3h**



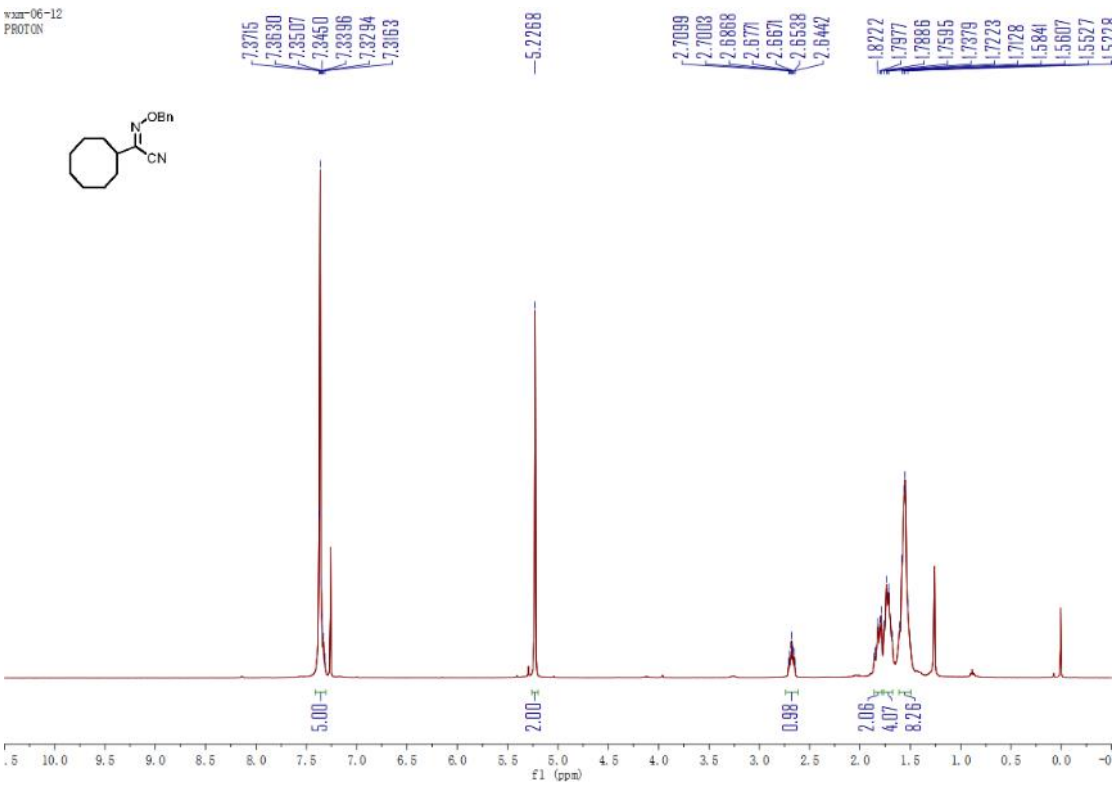
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3i**



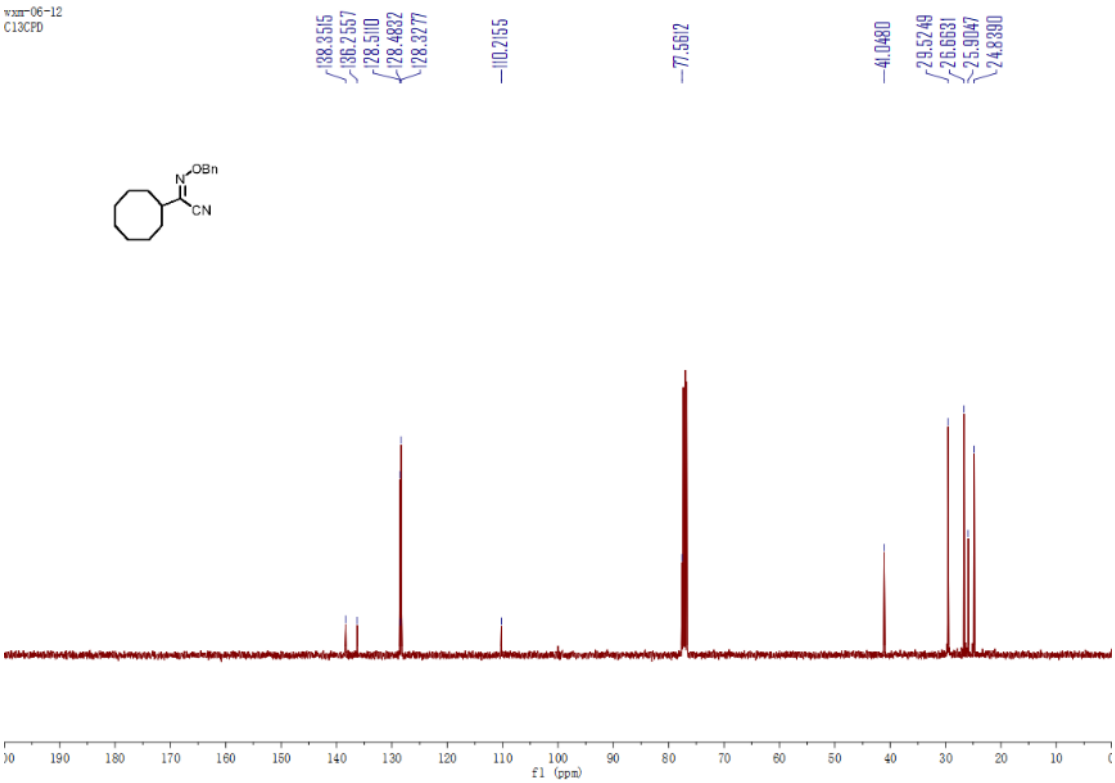
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3i**



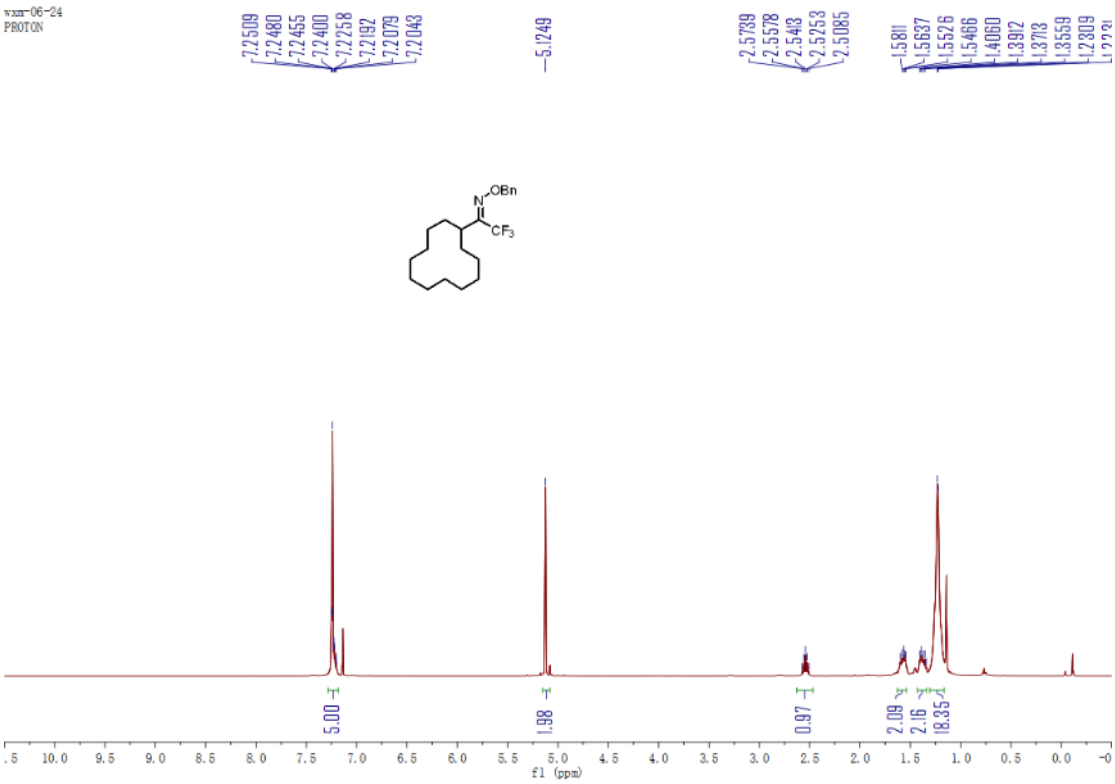
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3j**



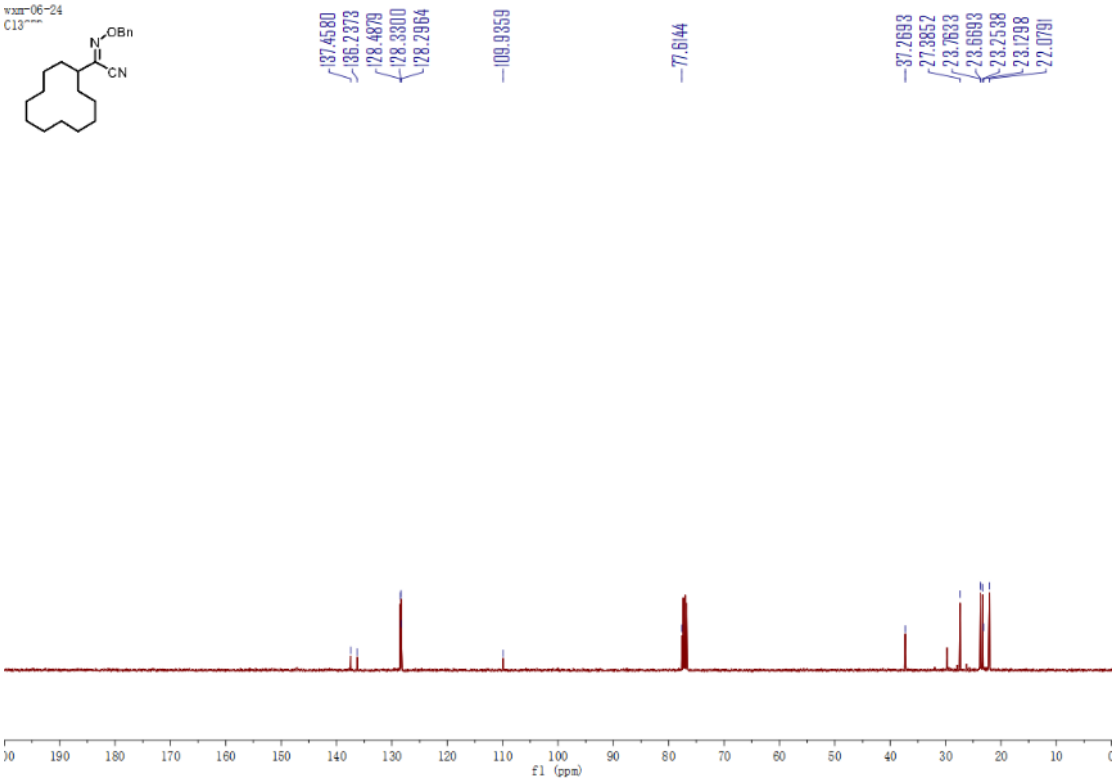
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3j**



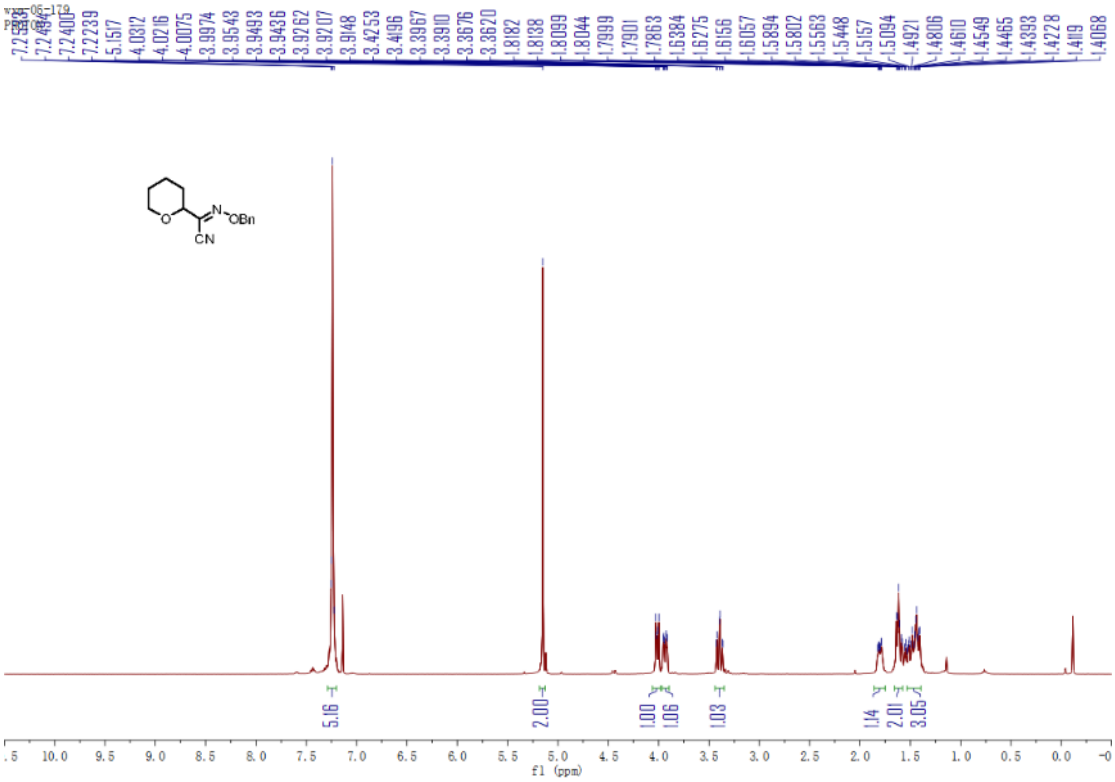
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3k**



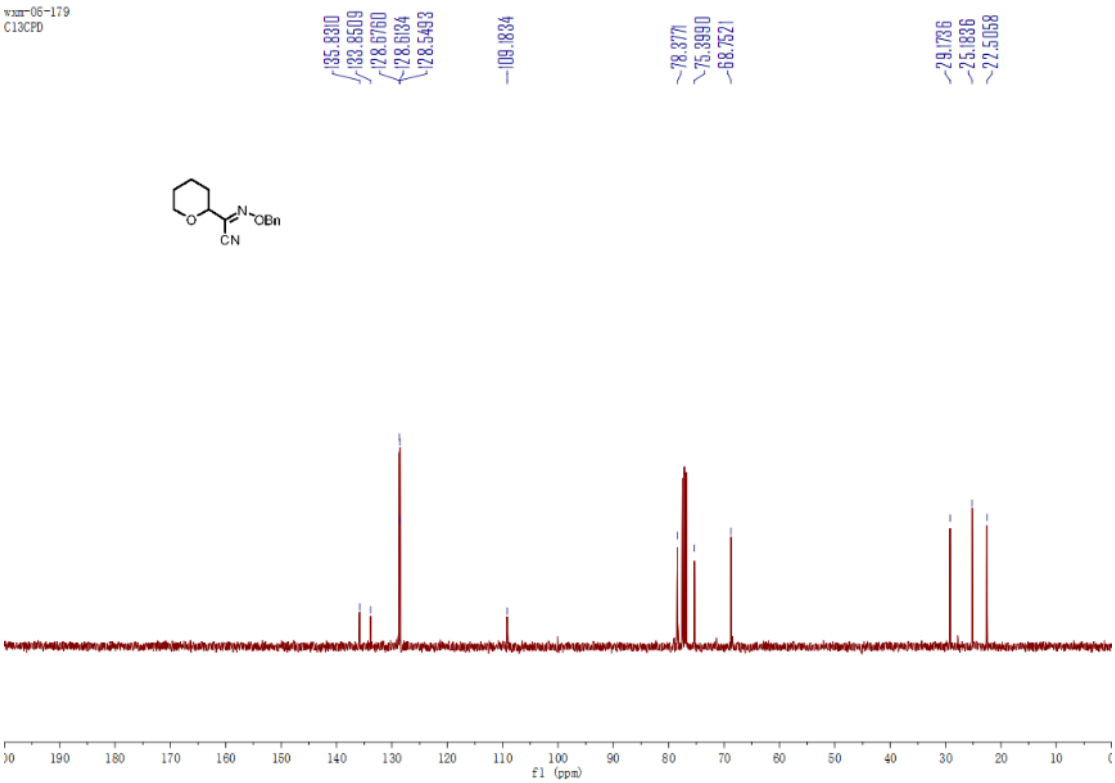
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3k**



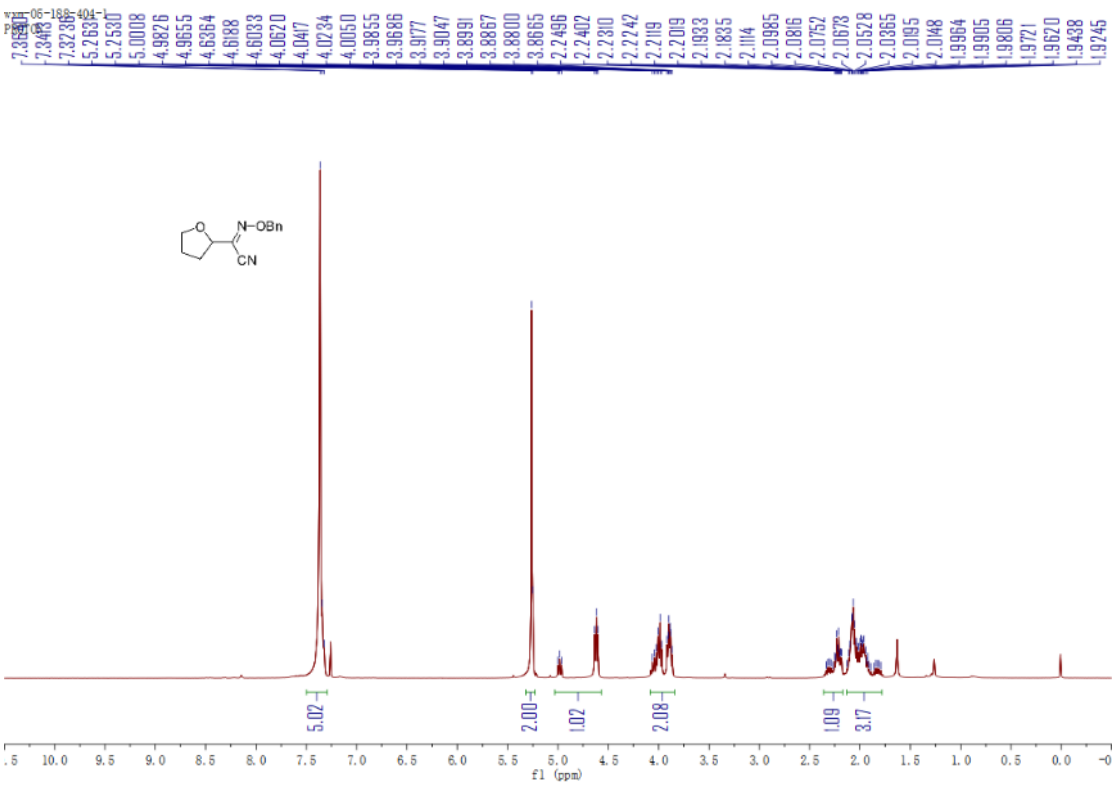
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3l**



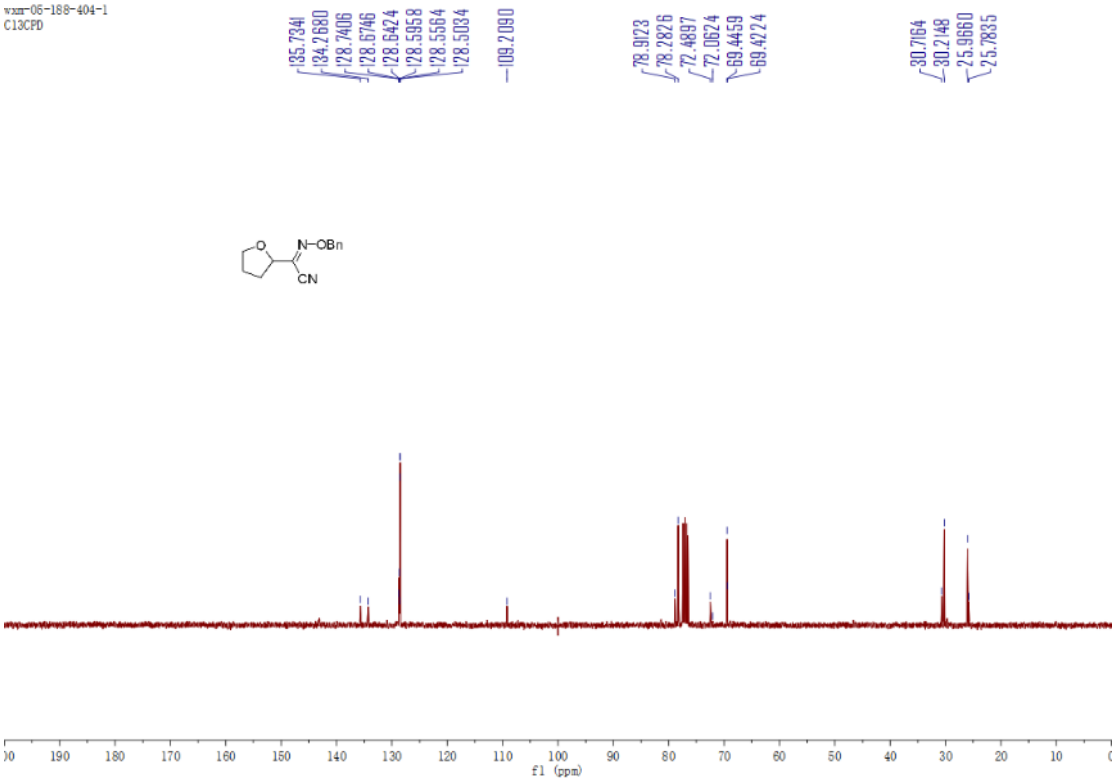
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3l**



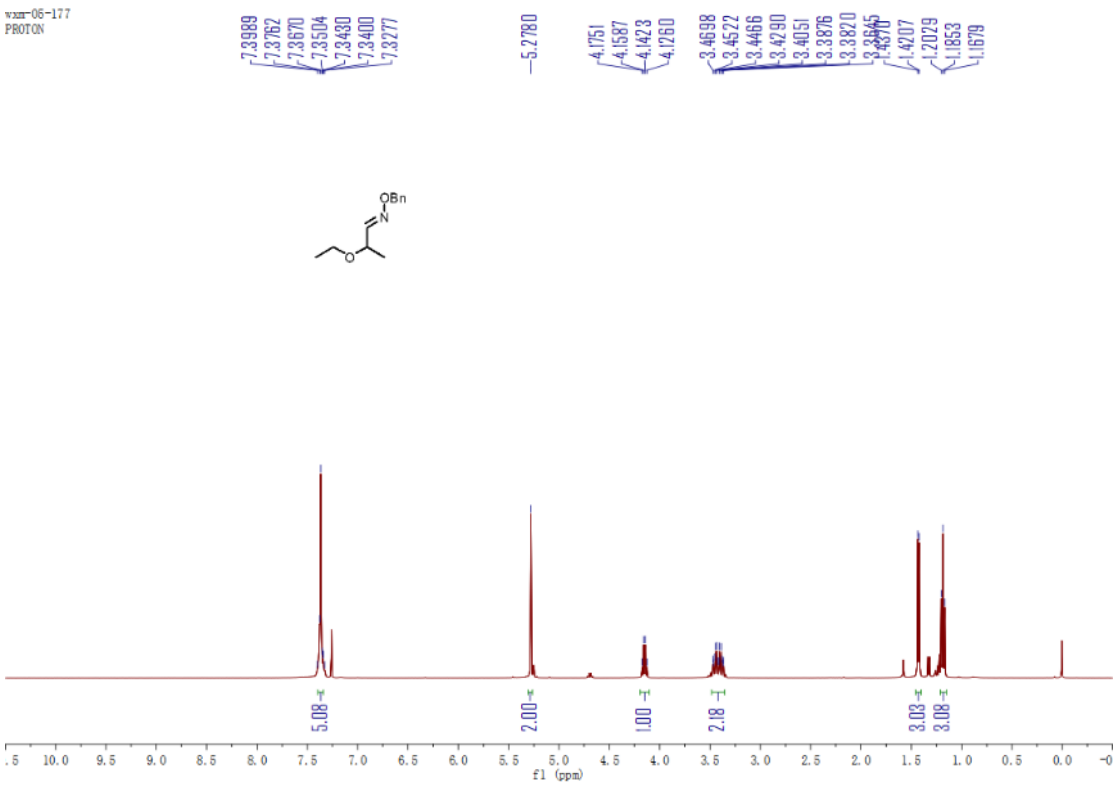
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3m**



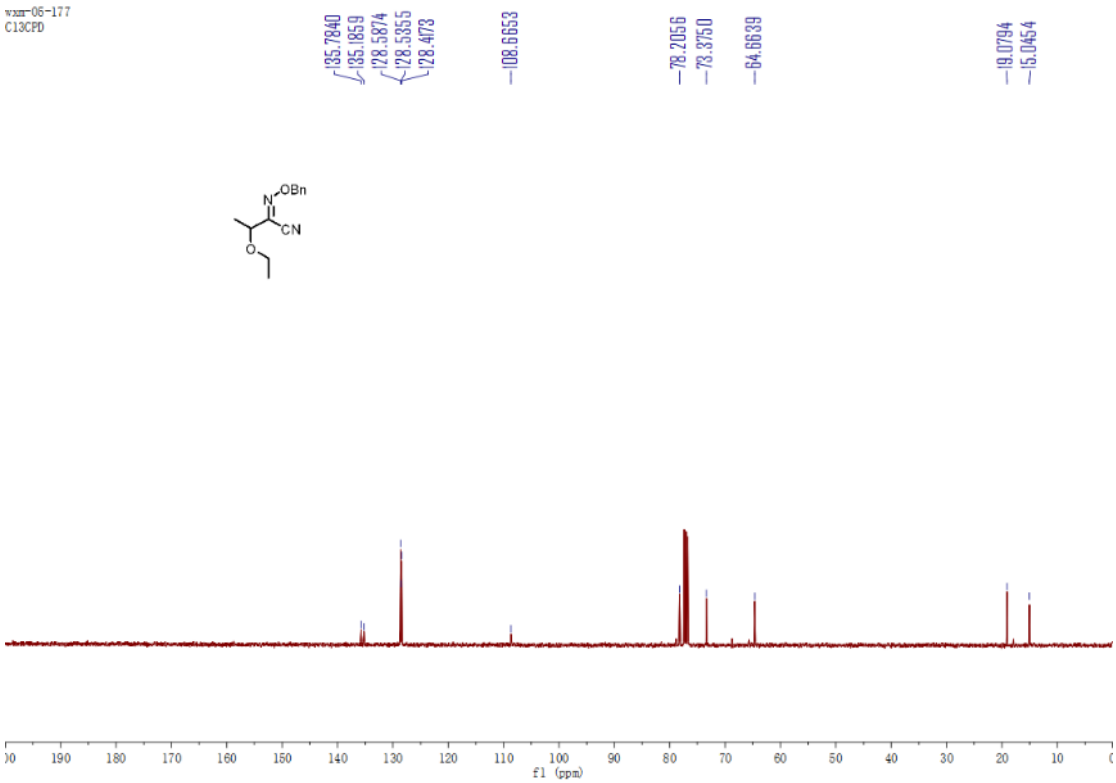
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3m**



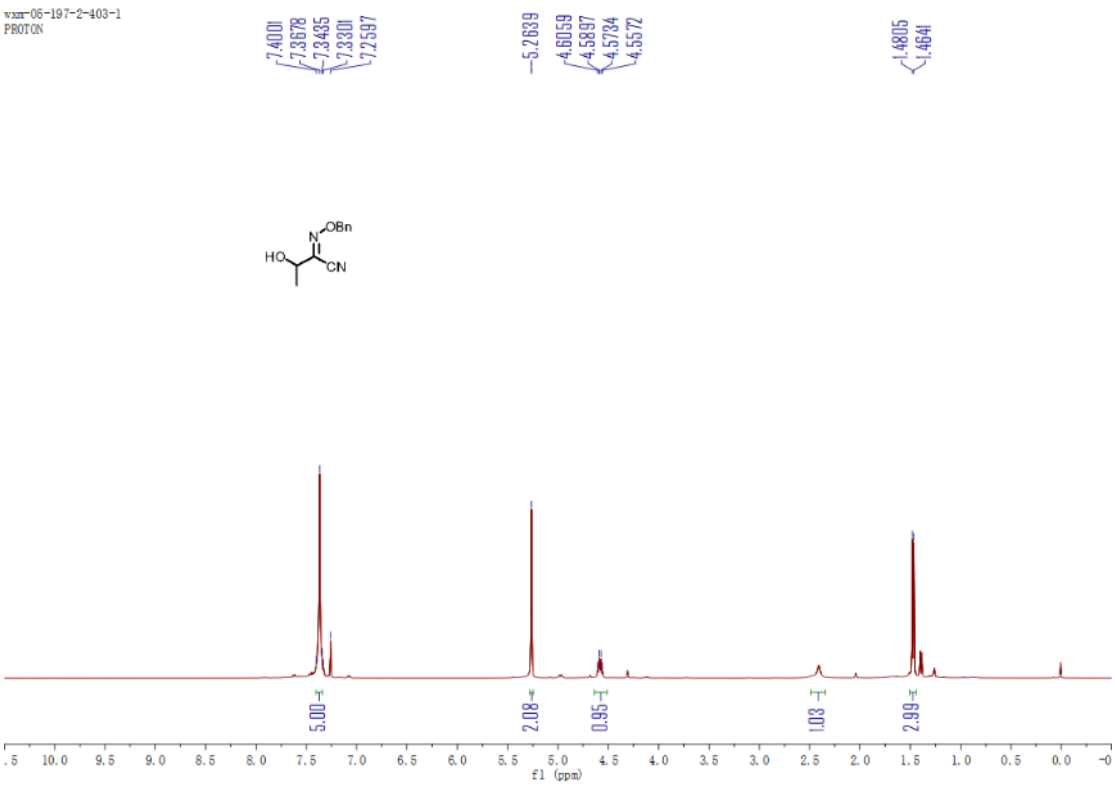
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3n**



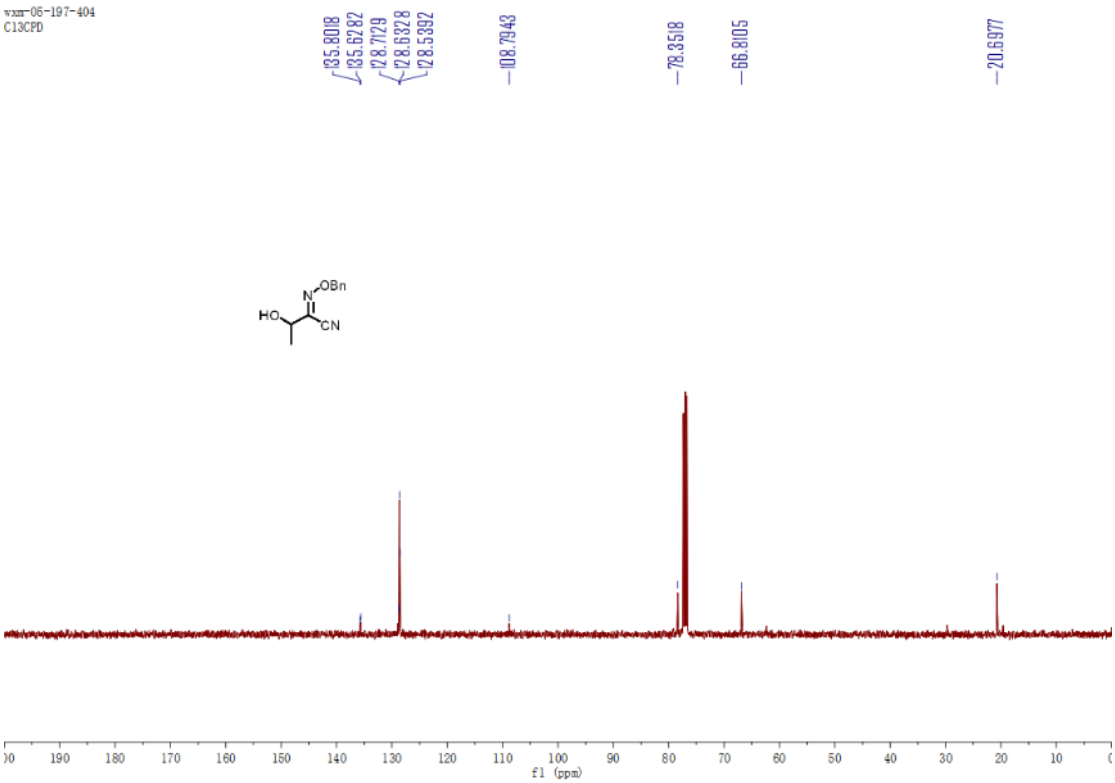
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3n**



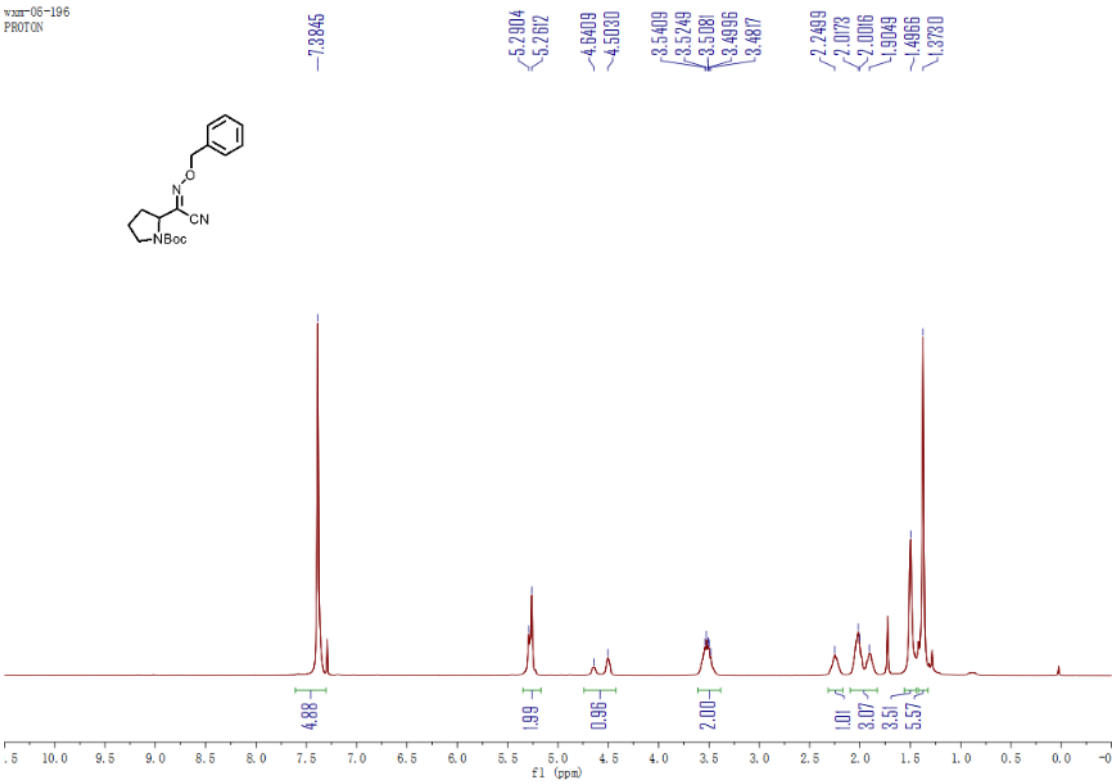
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3o**



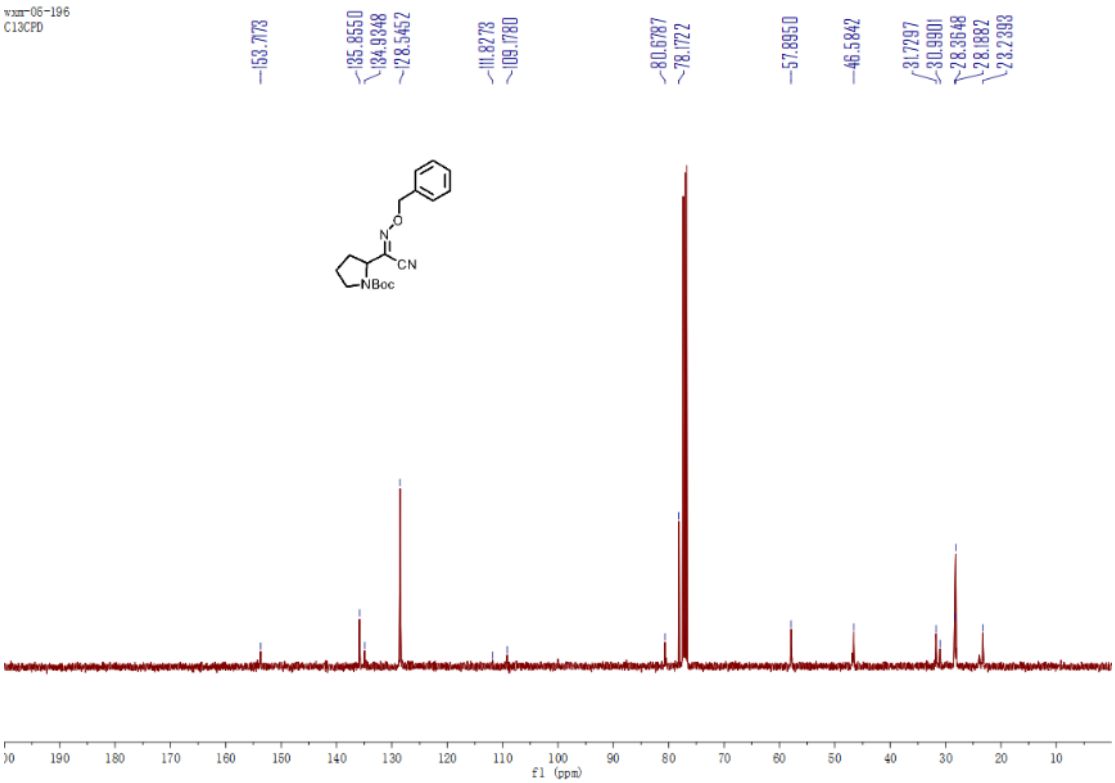
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3o**



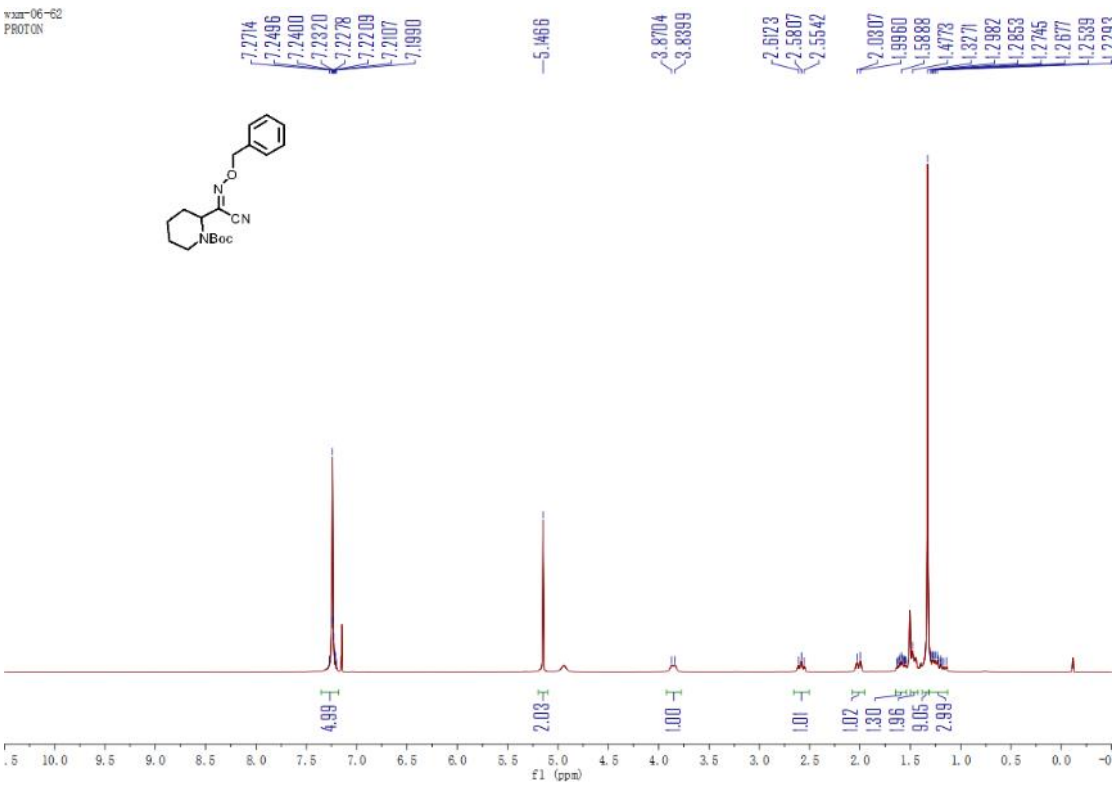
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3p**



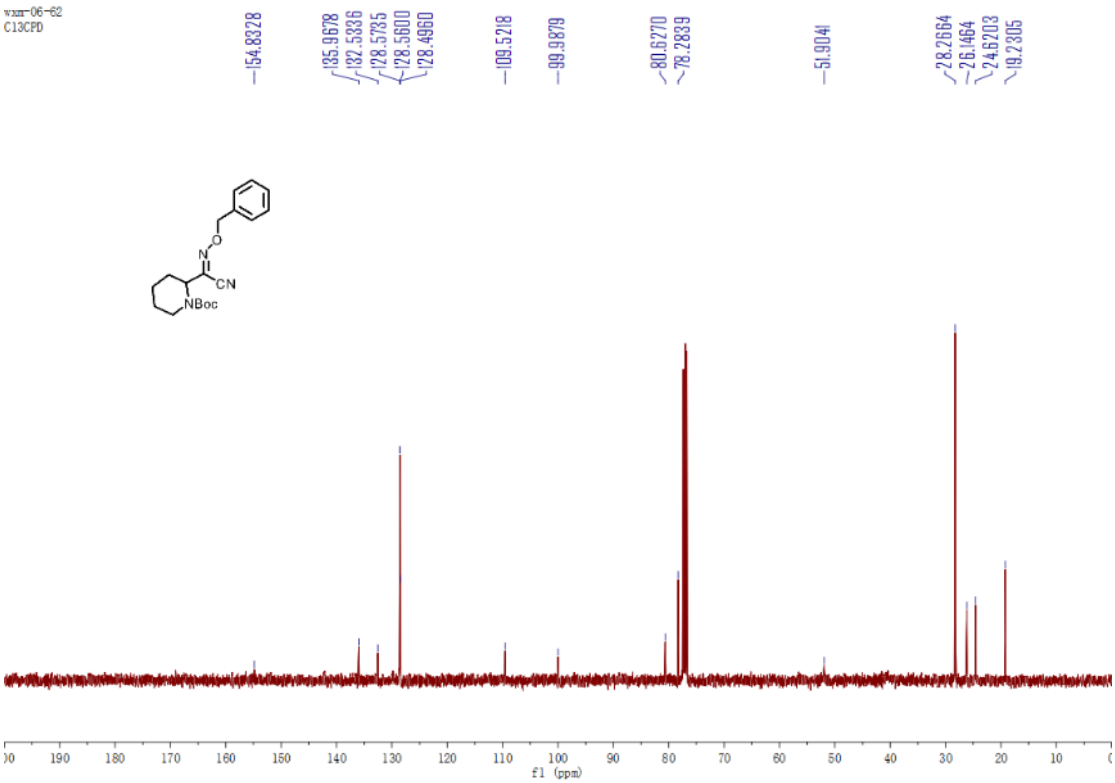
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3p**



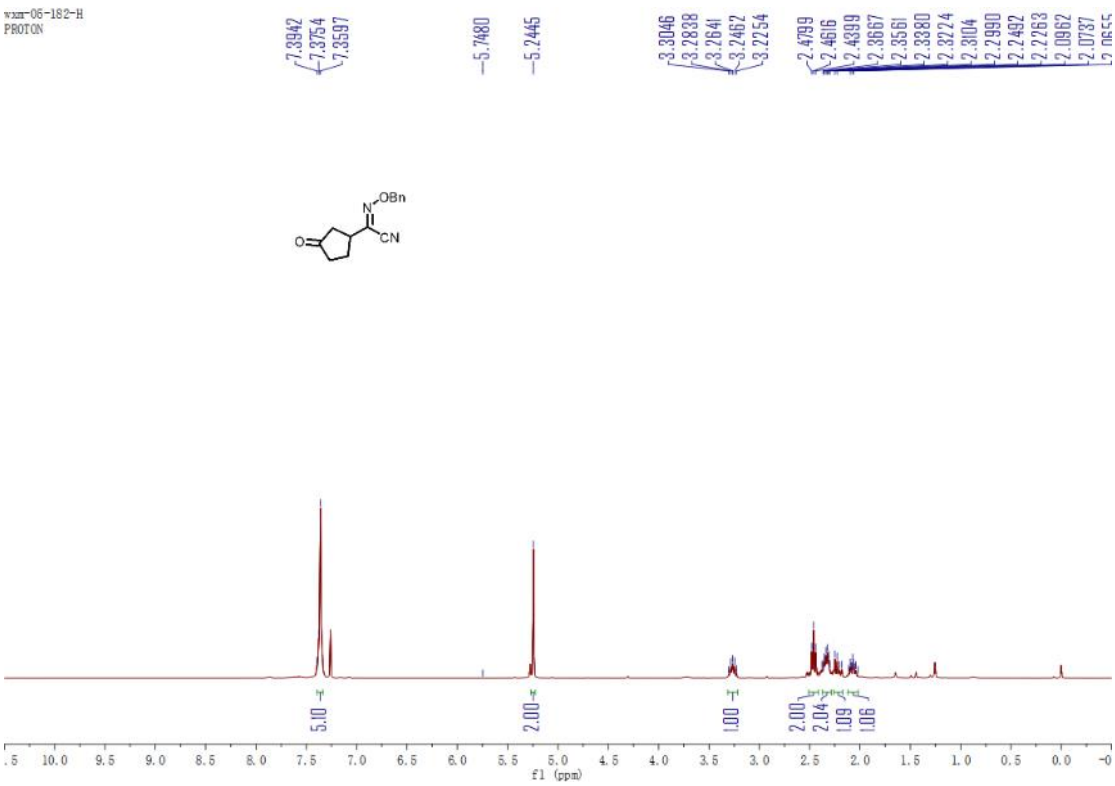
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3q**



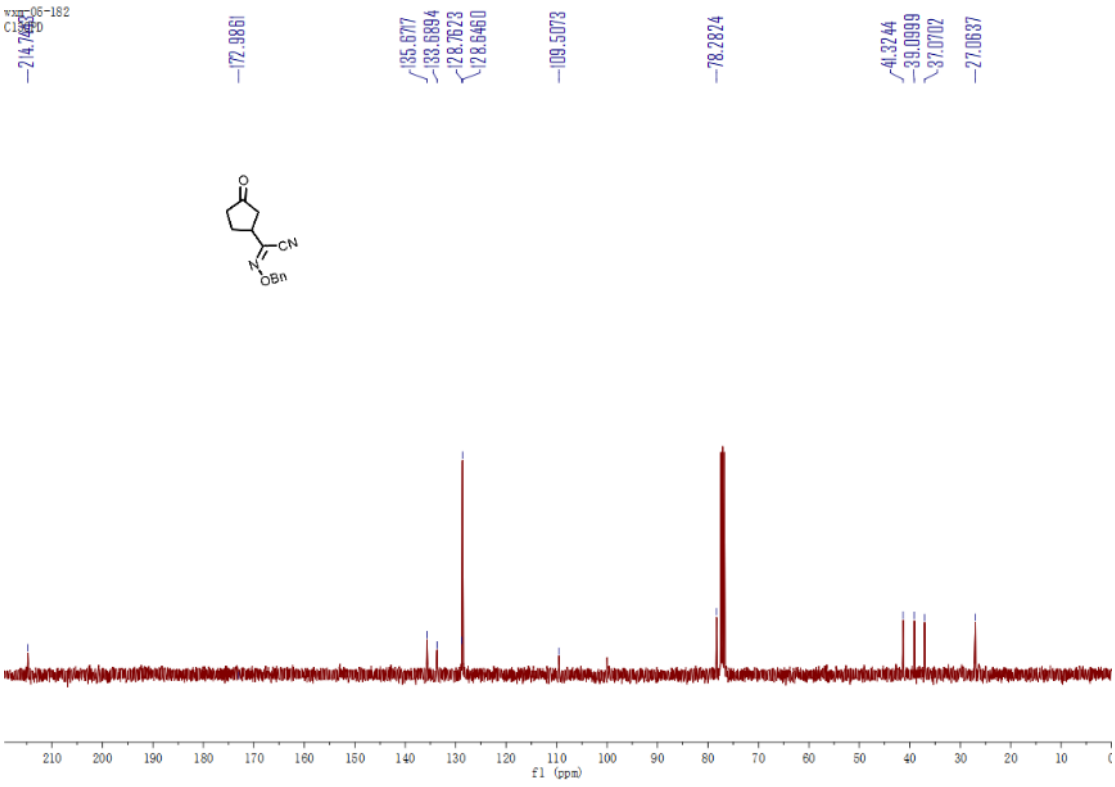
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3q**



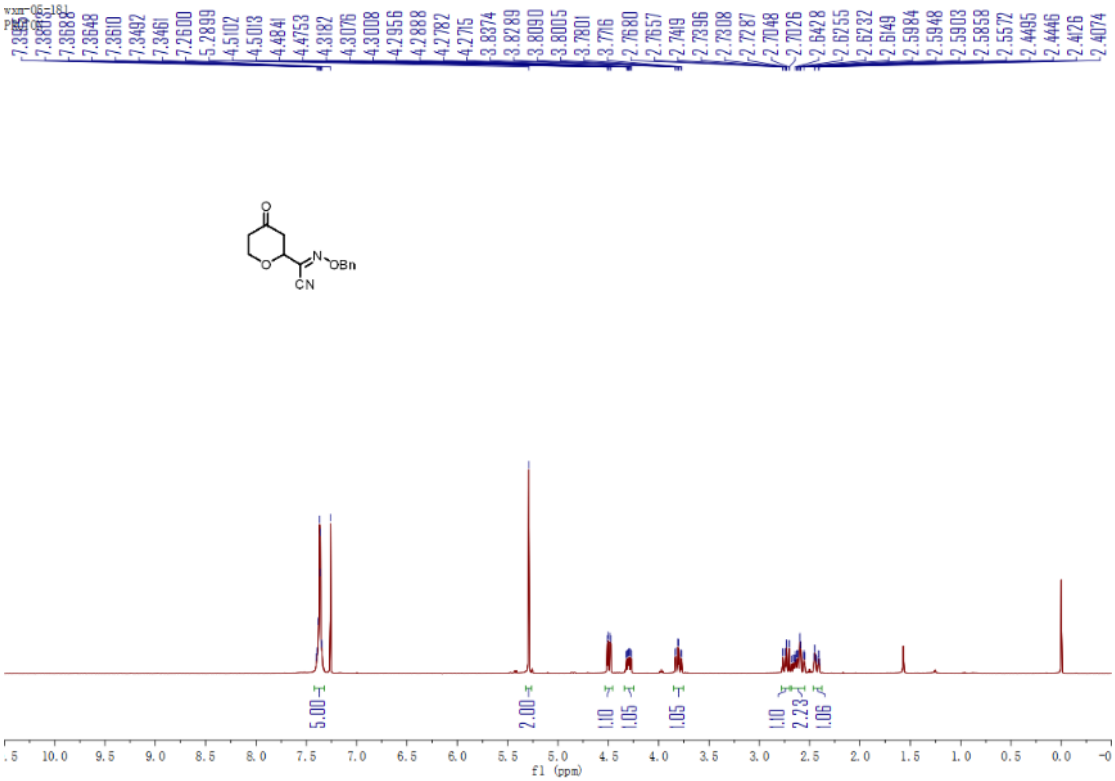
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3r**



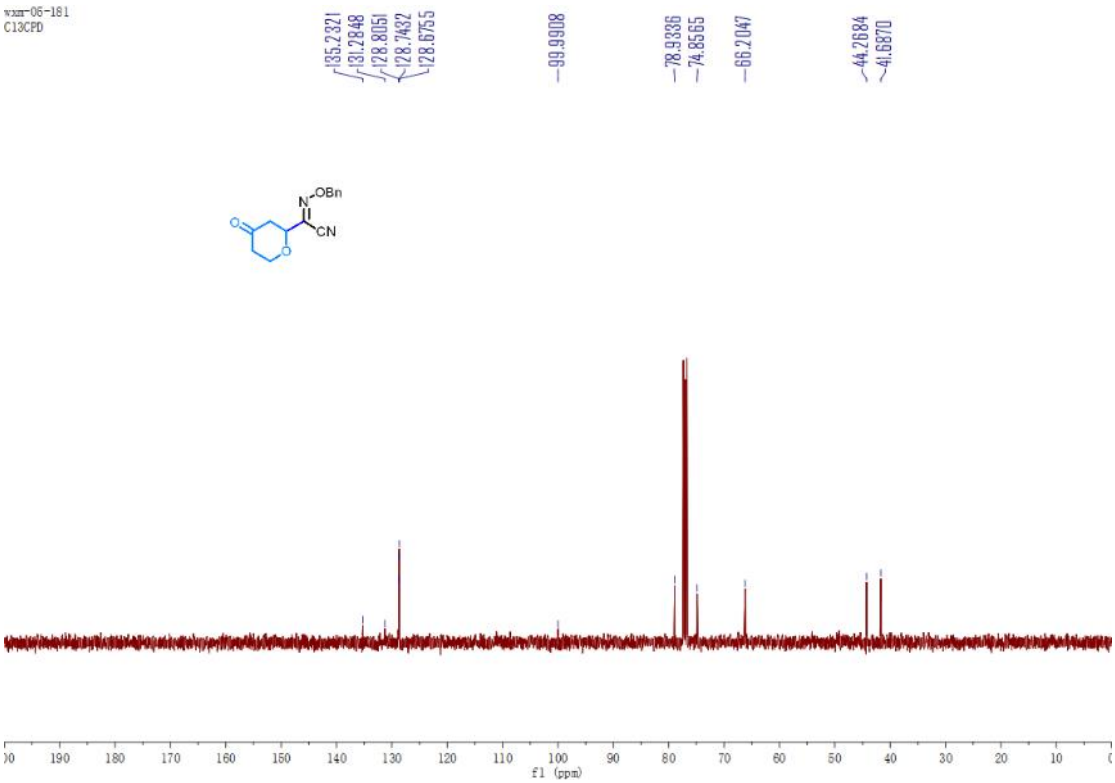
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3r**



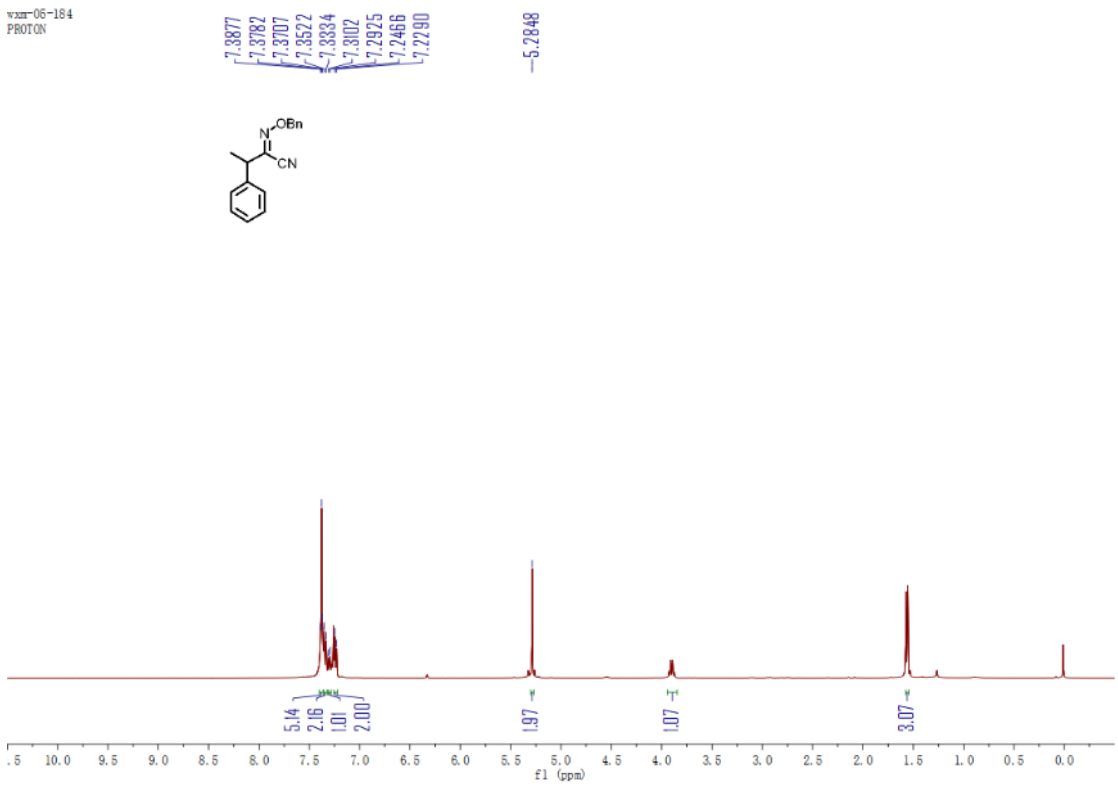
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3s**



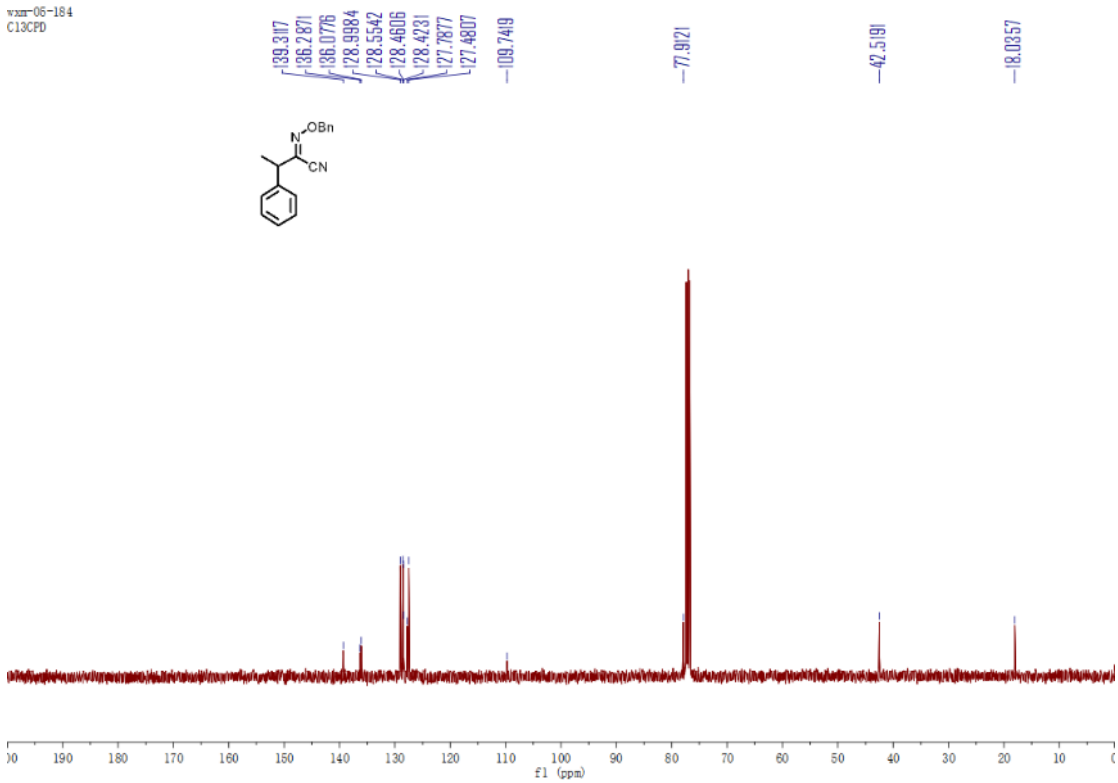
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3s**



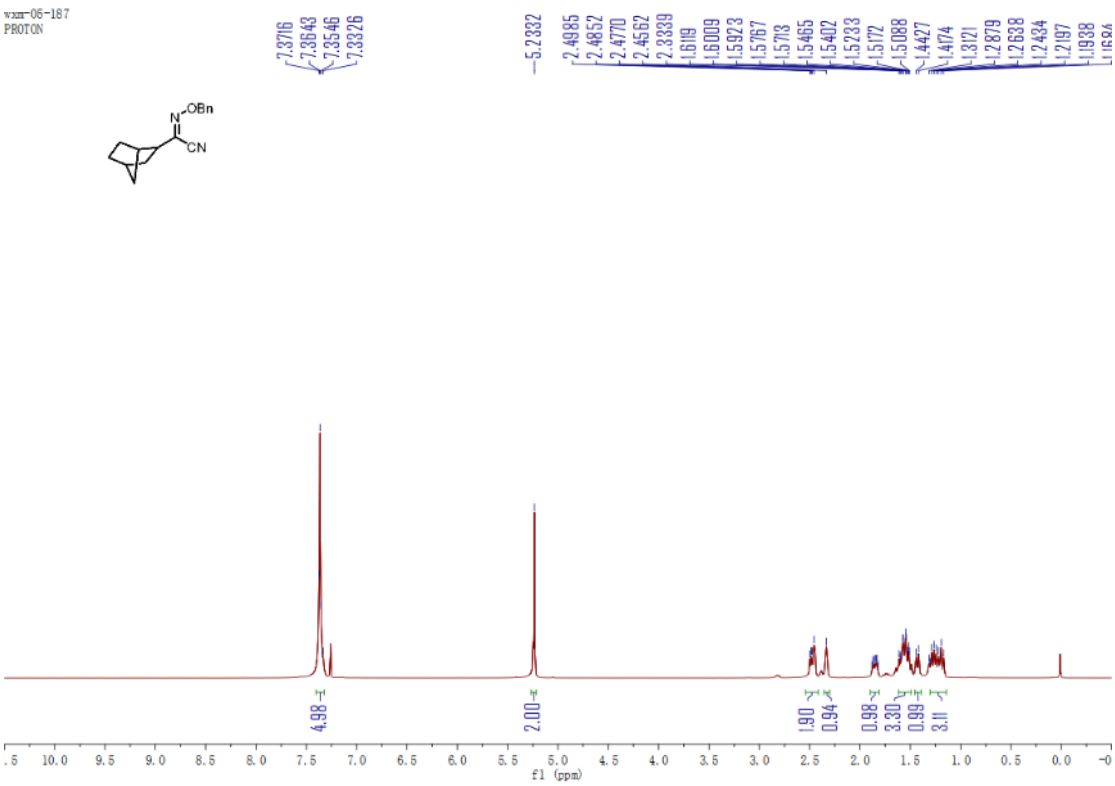
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3t**



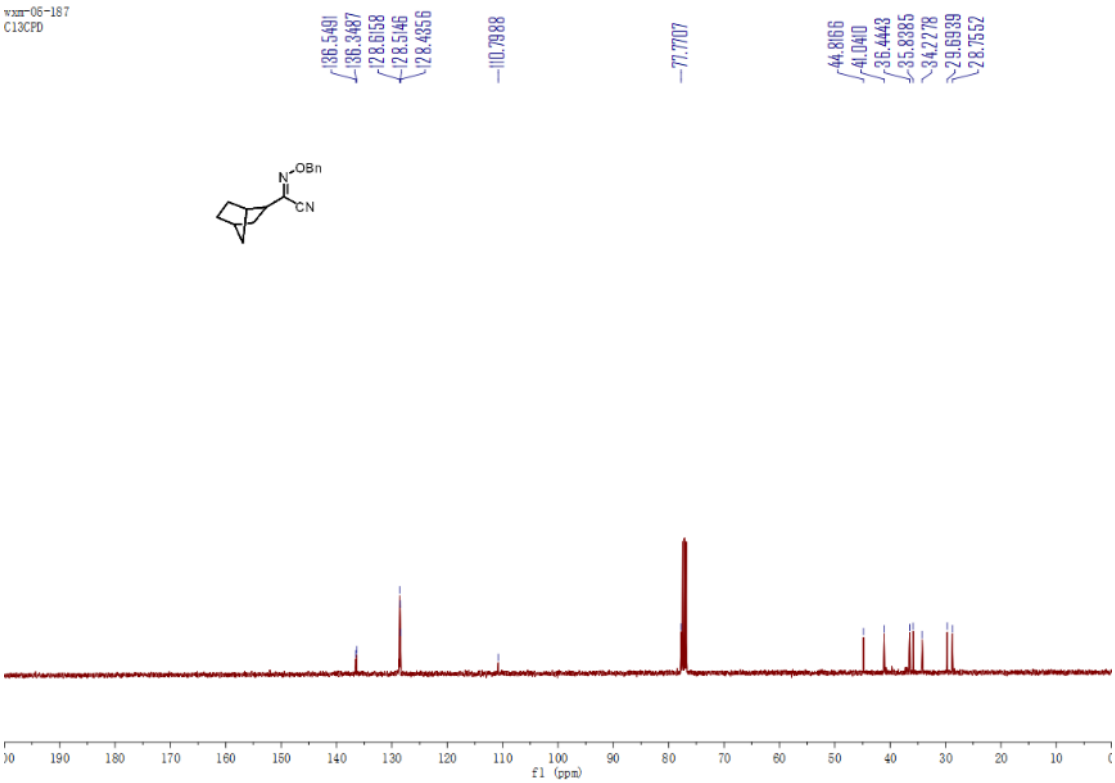
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3t**



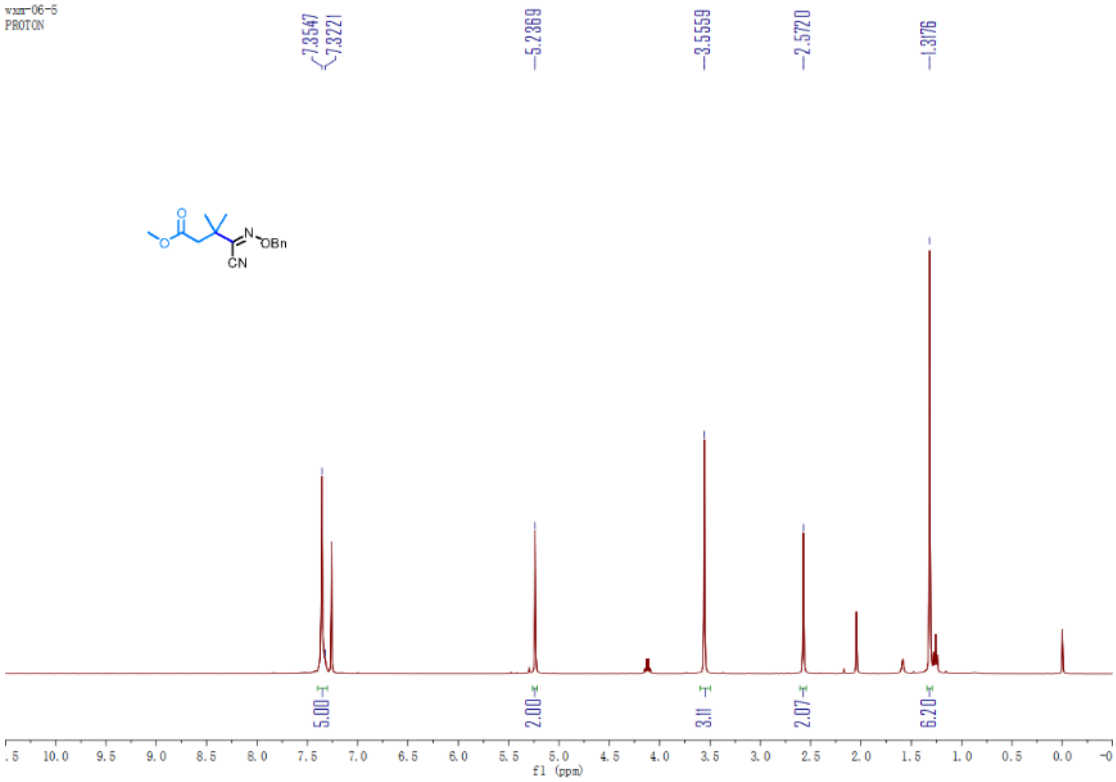
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3u**



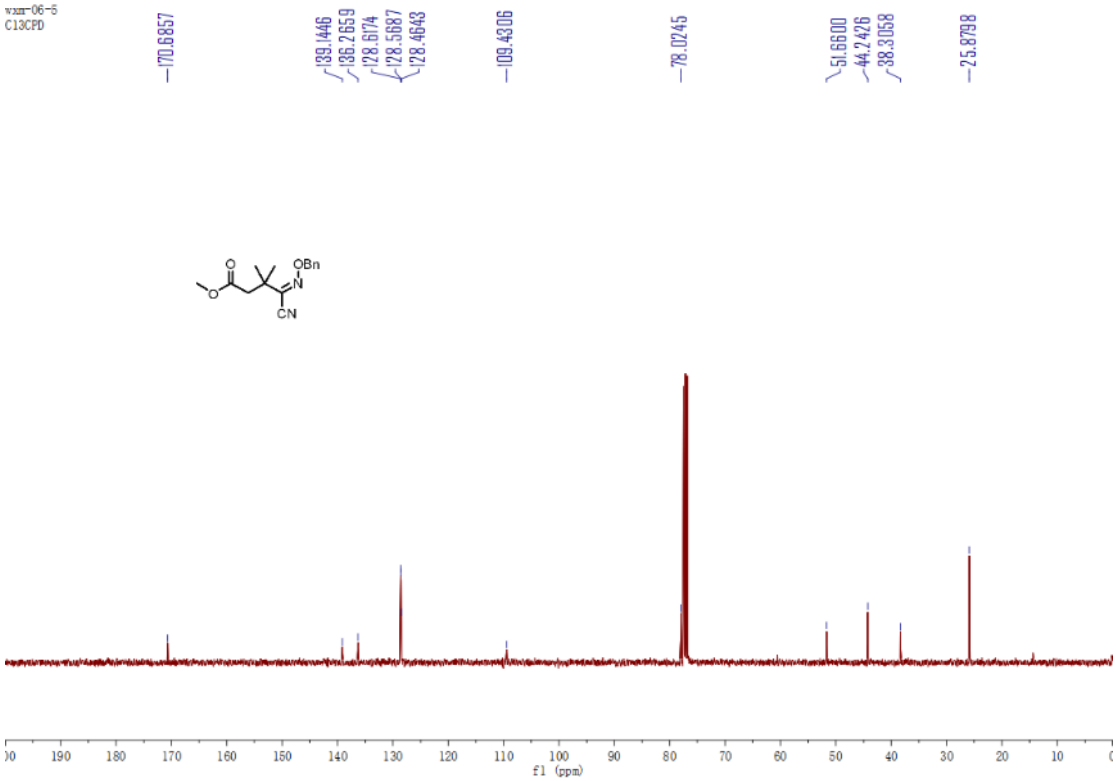
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3u**



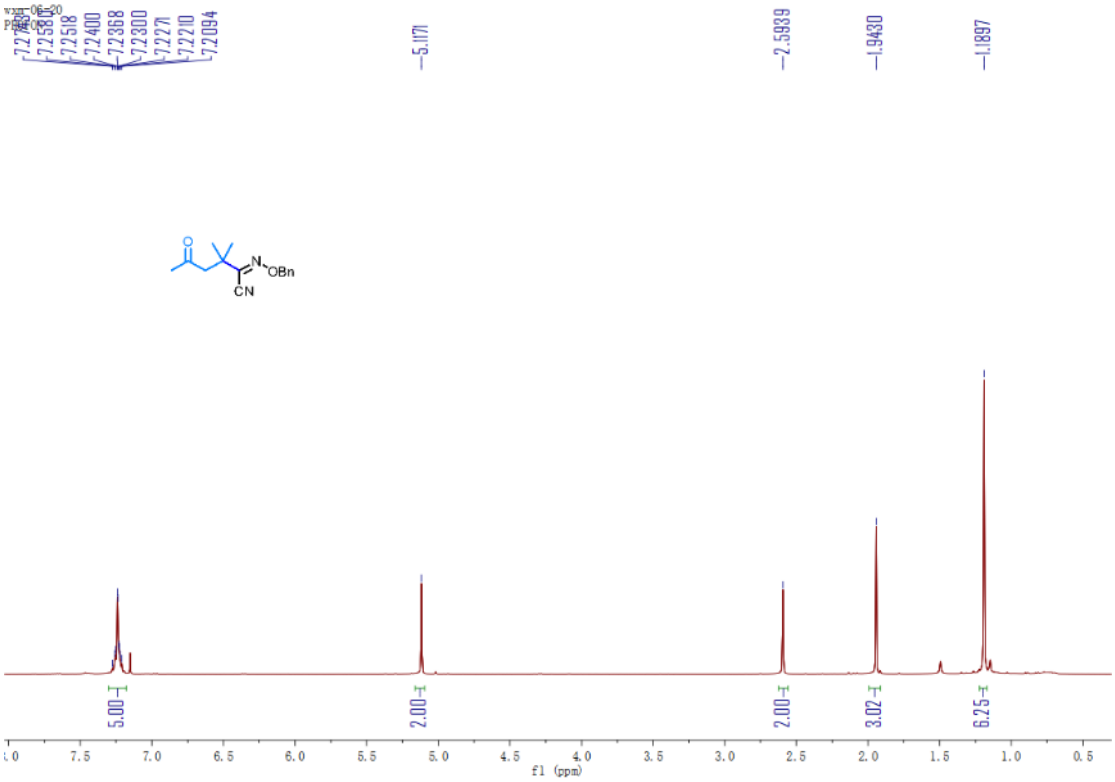
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3v**



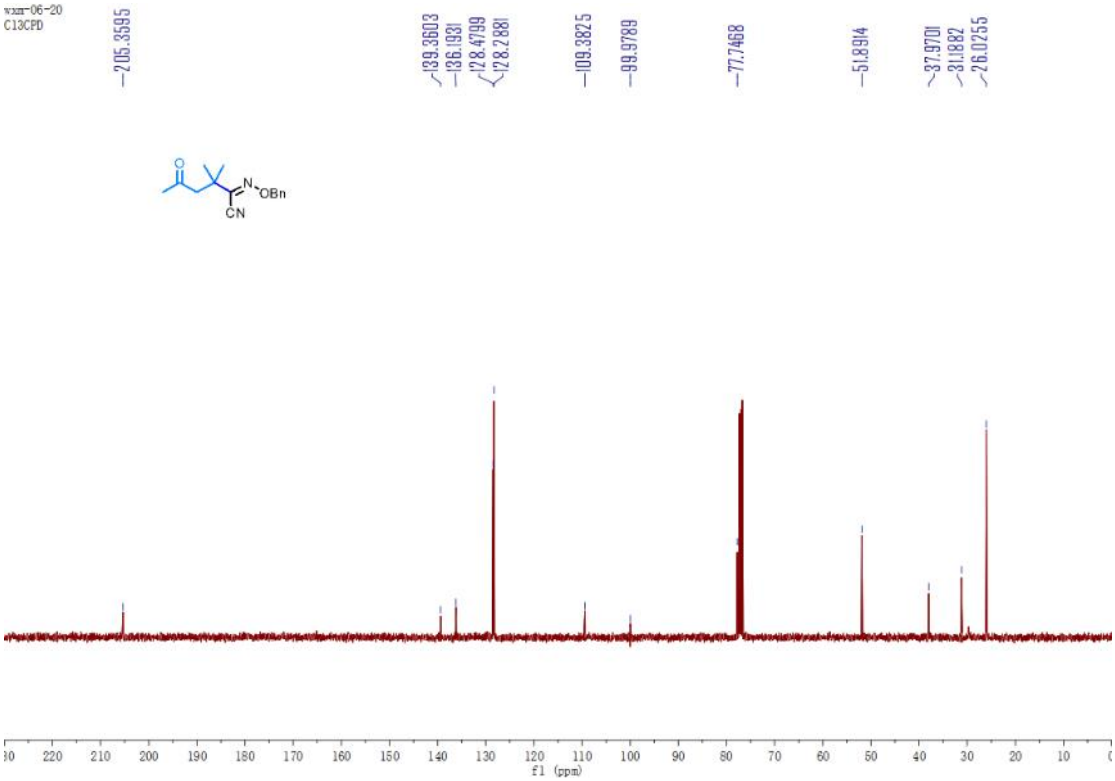
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3v**



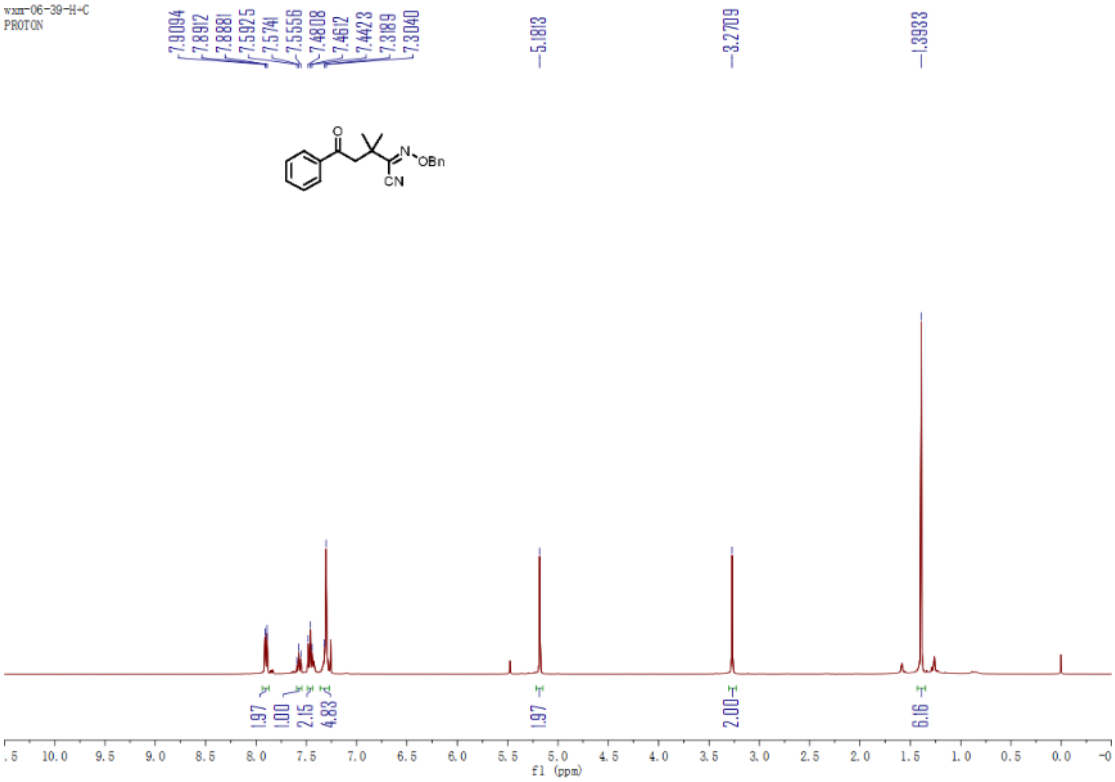
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3w**



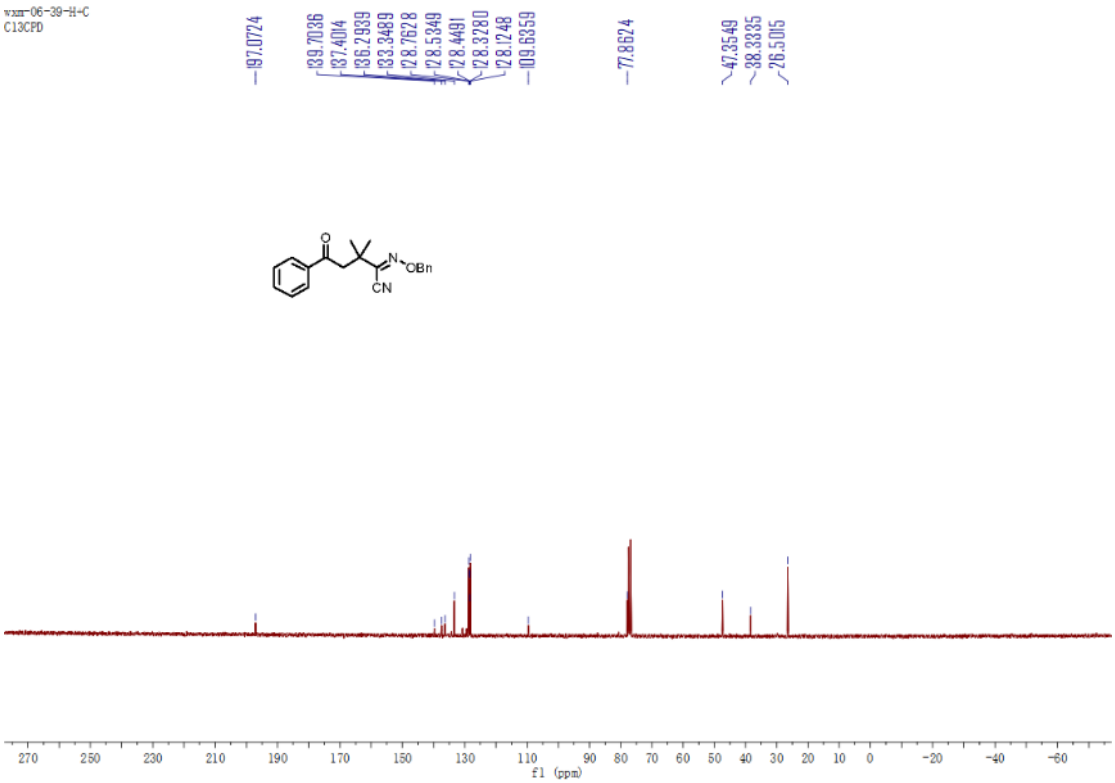
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3w**



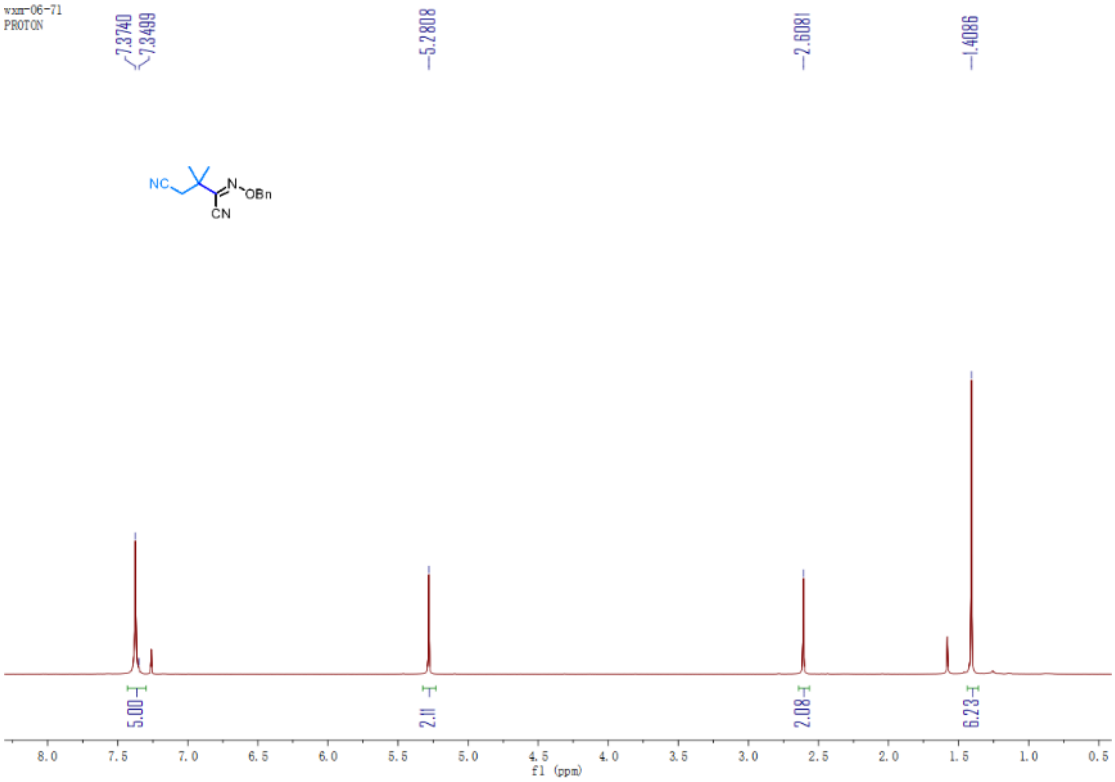
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3x**



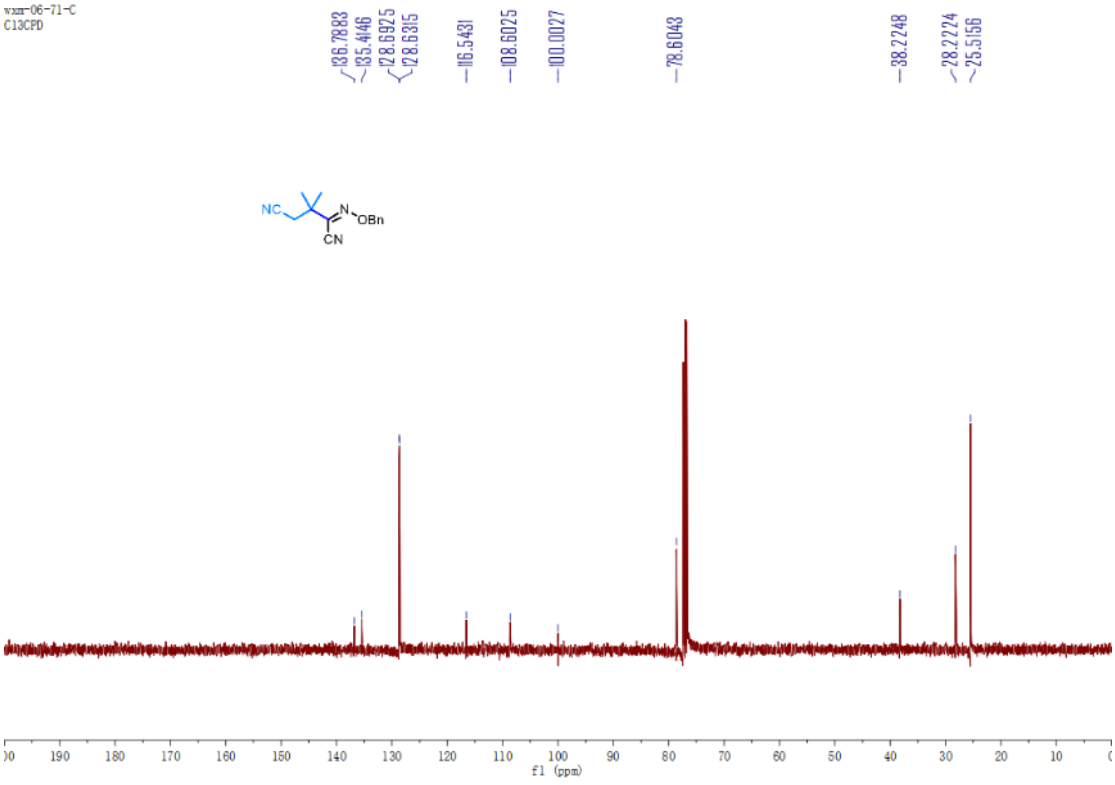
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3x**



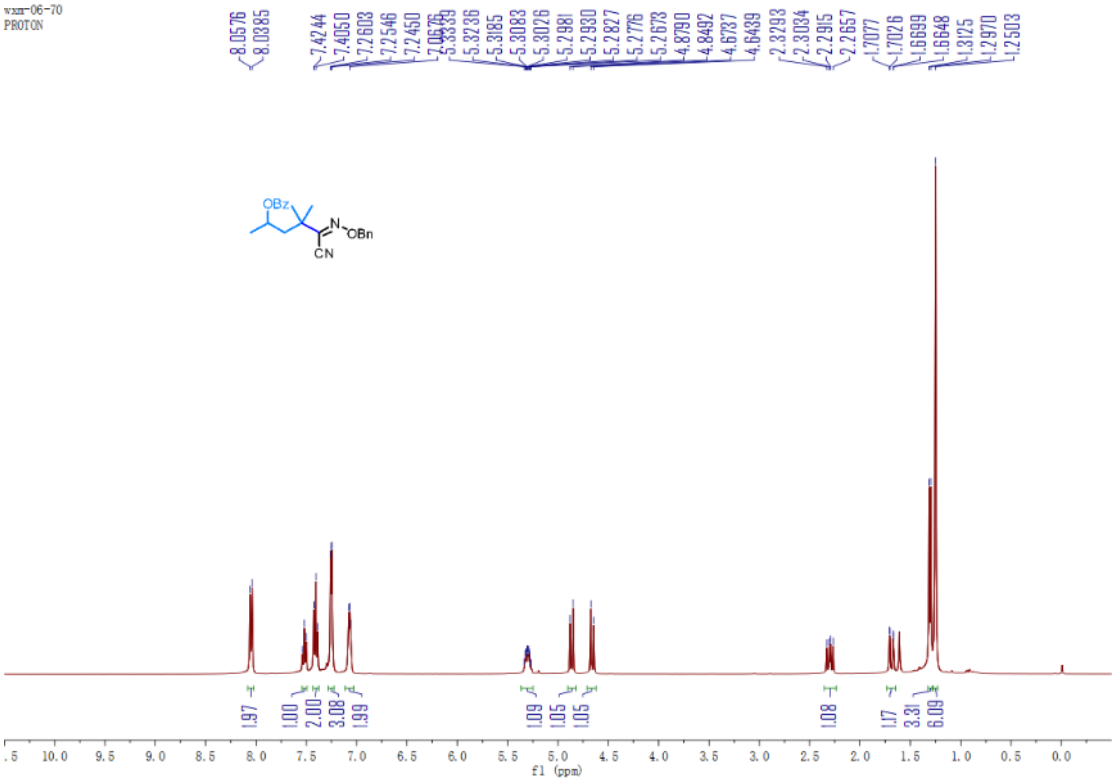
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3y**



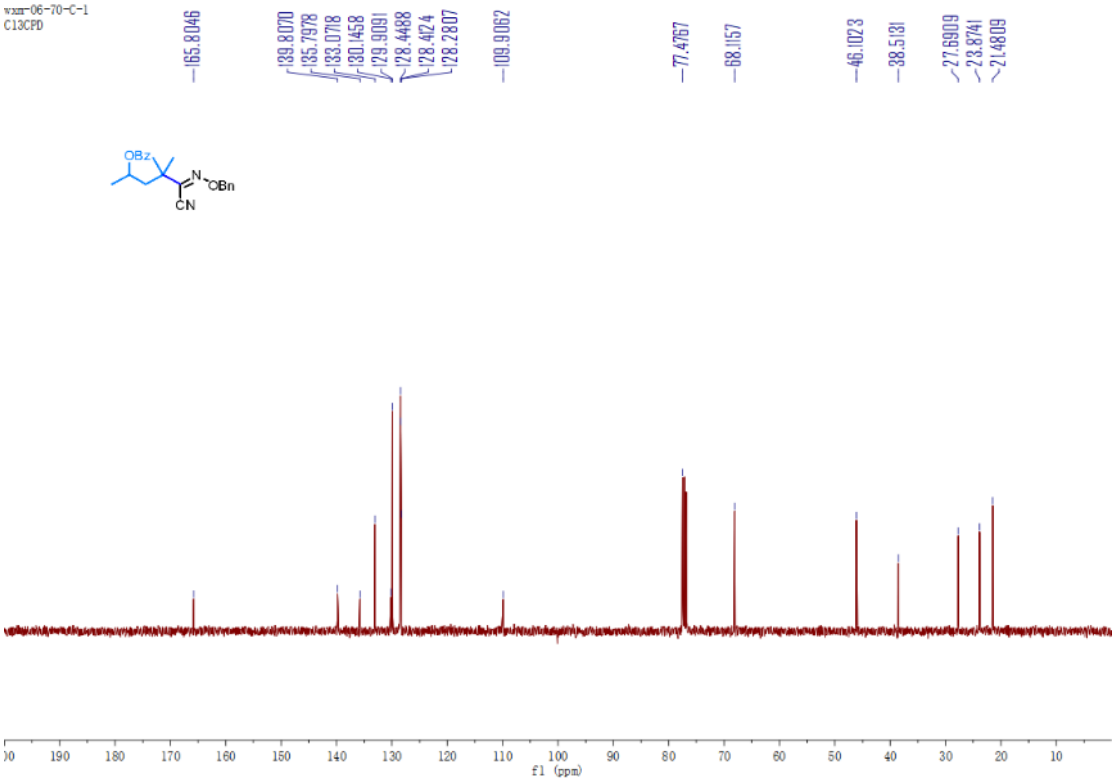
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3y**



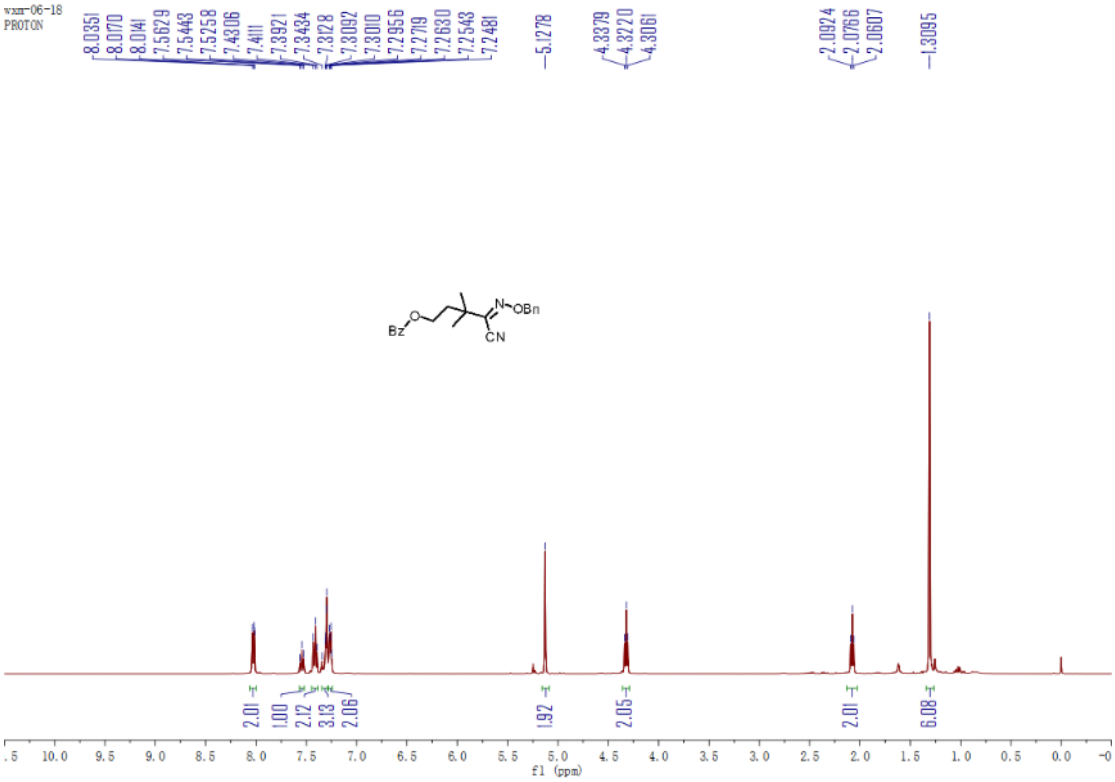
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3z**



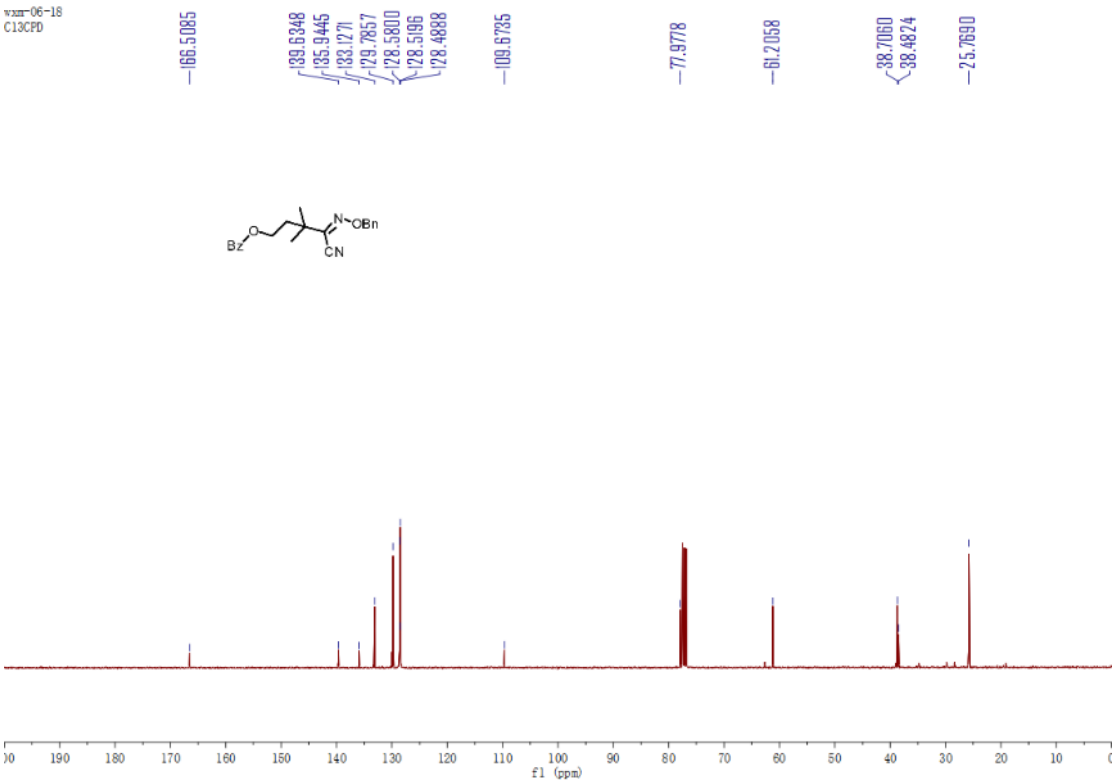
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3z**



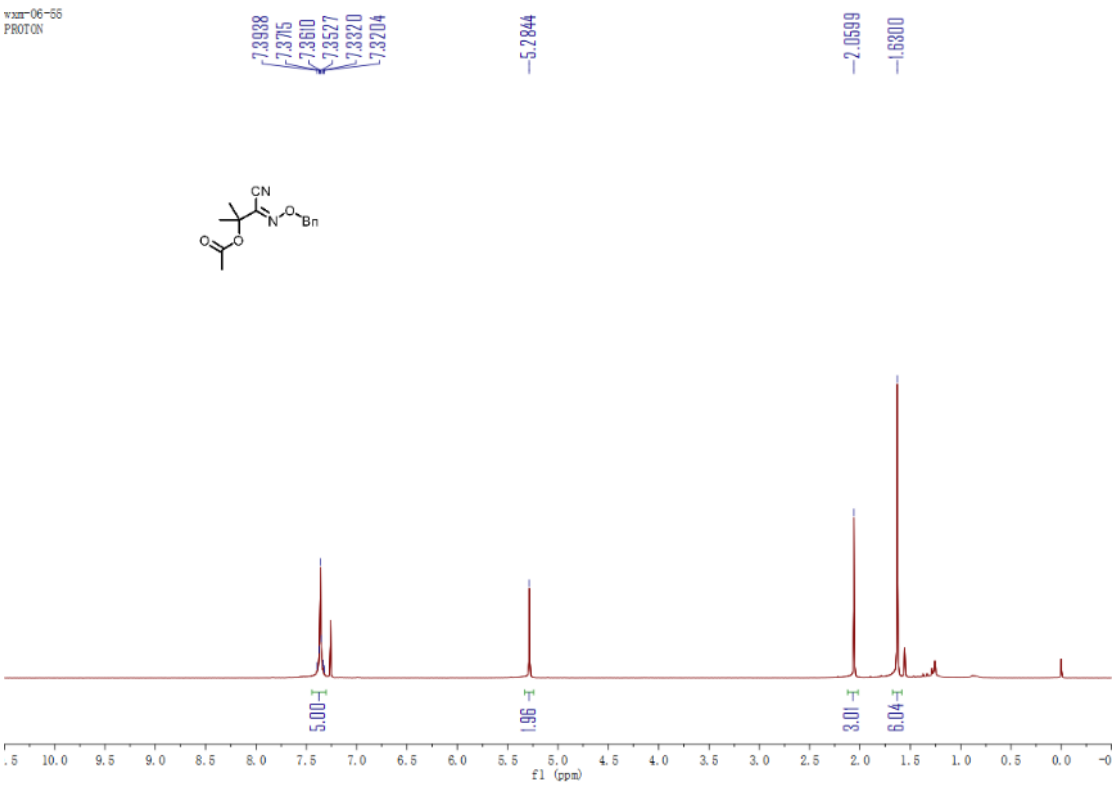
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3aa**



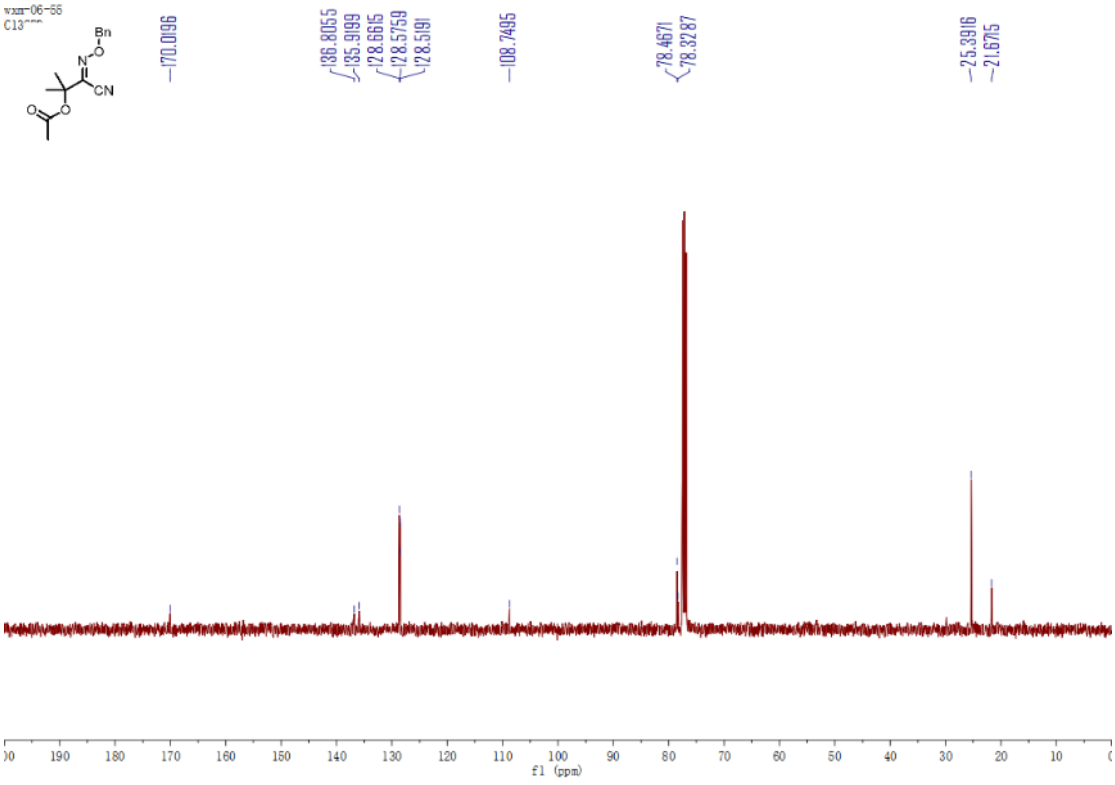
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3aa**



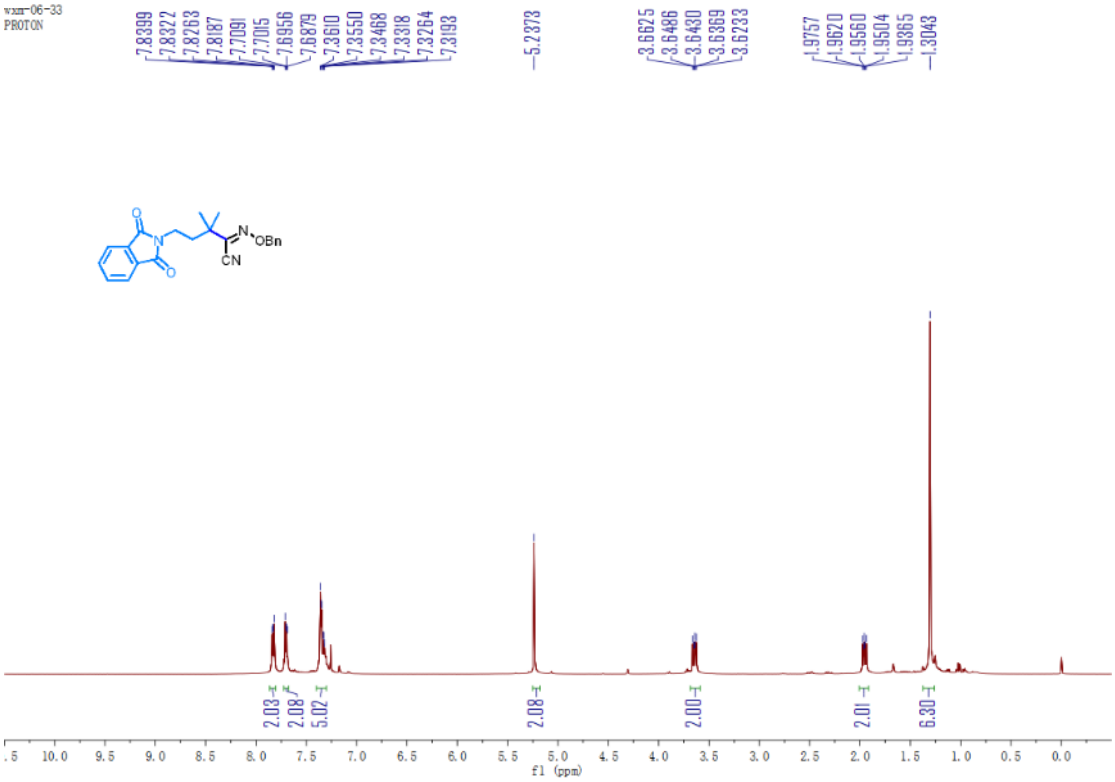
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3bb**



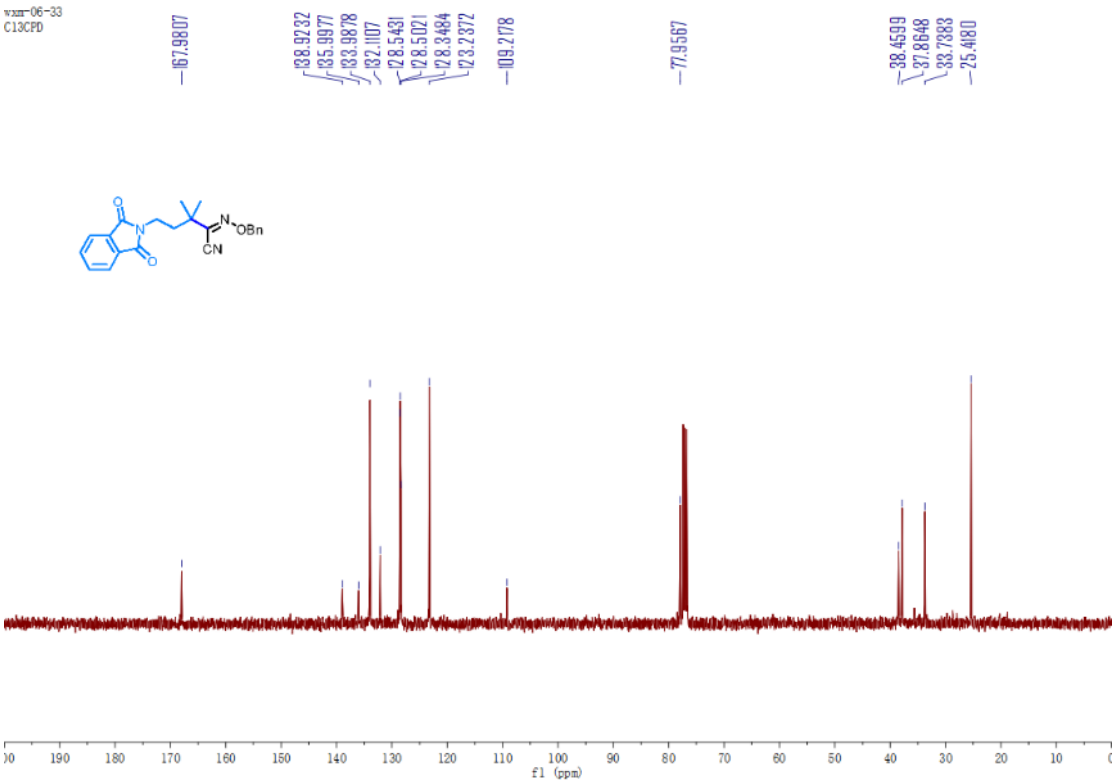
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3bb**



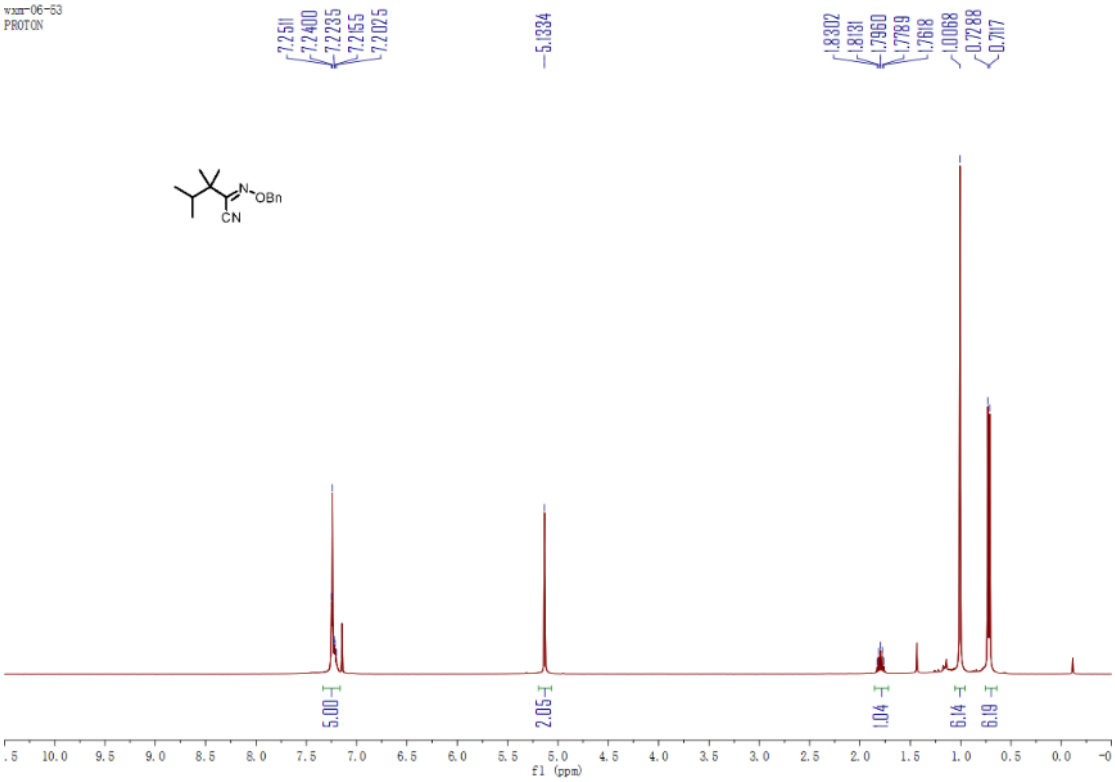
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3cc**



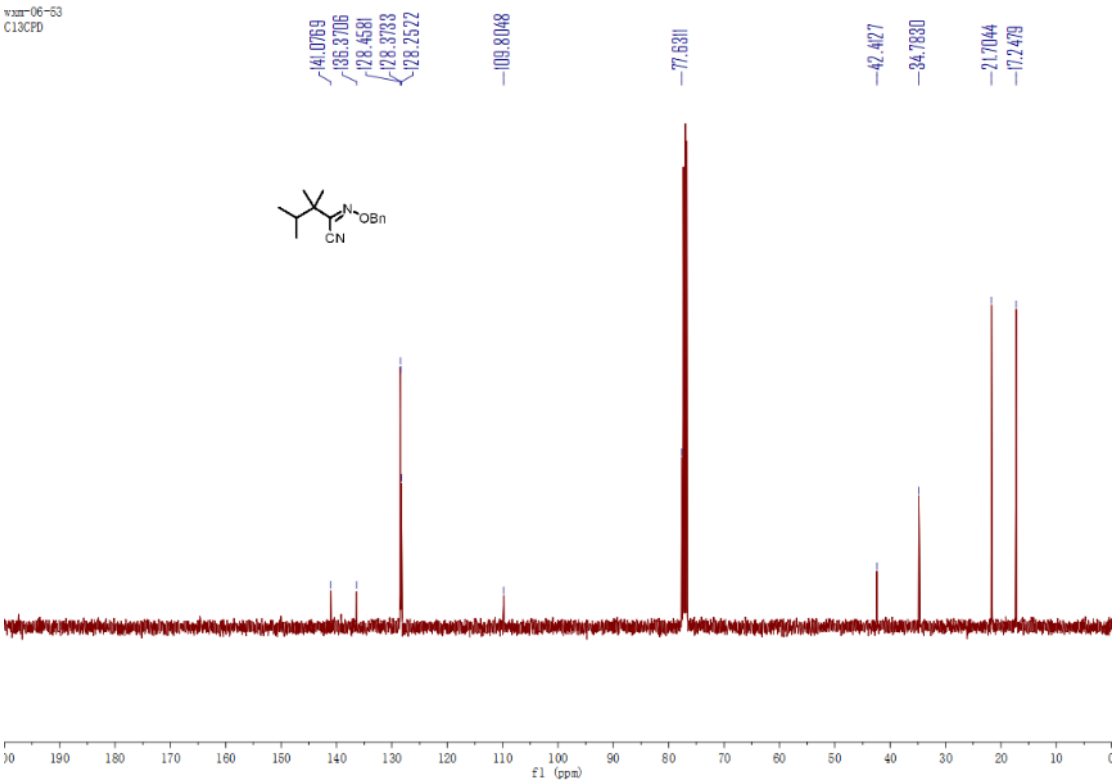
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3cc**



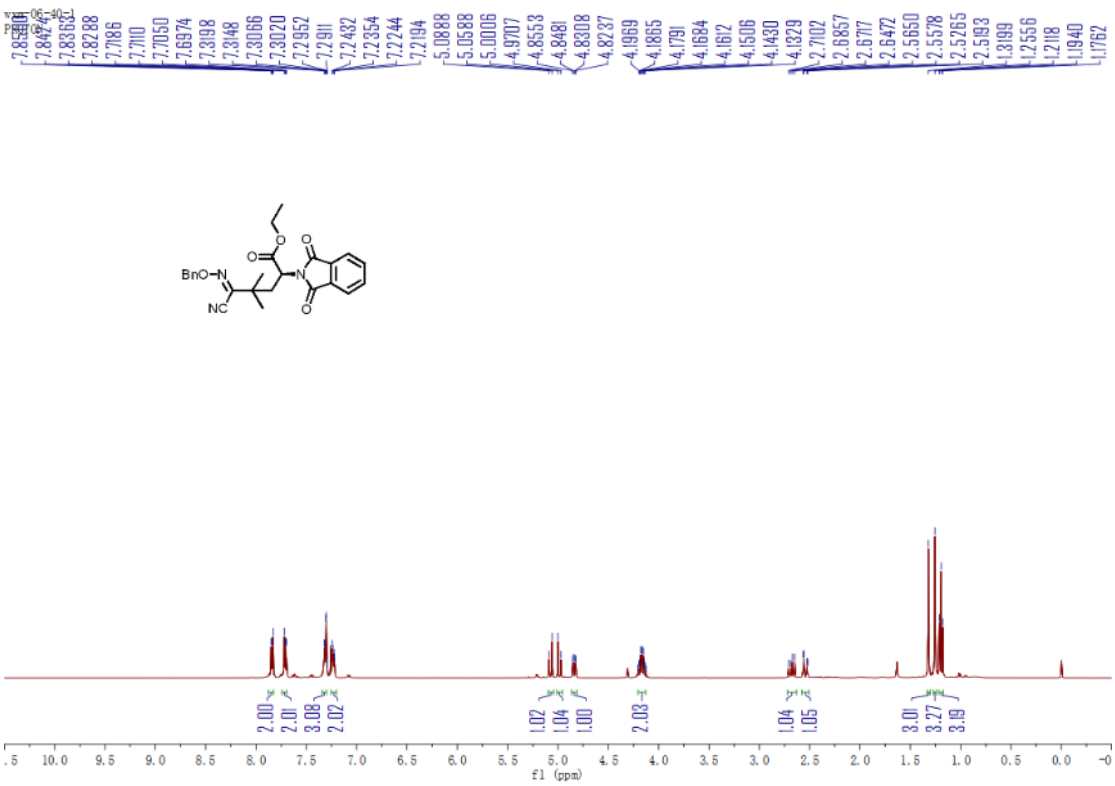
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3dd**



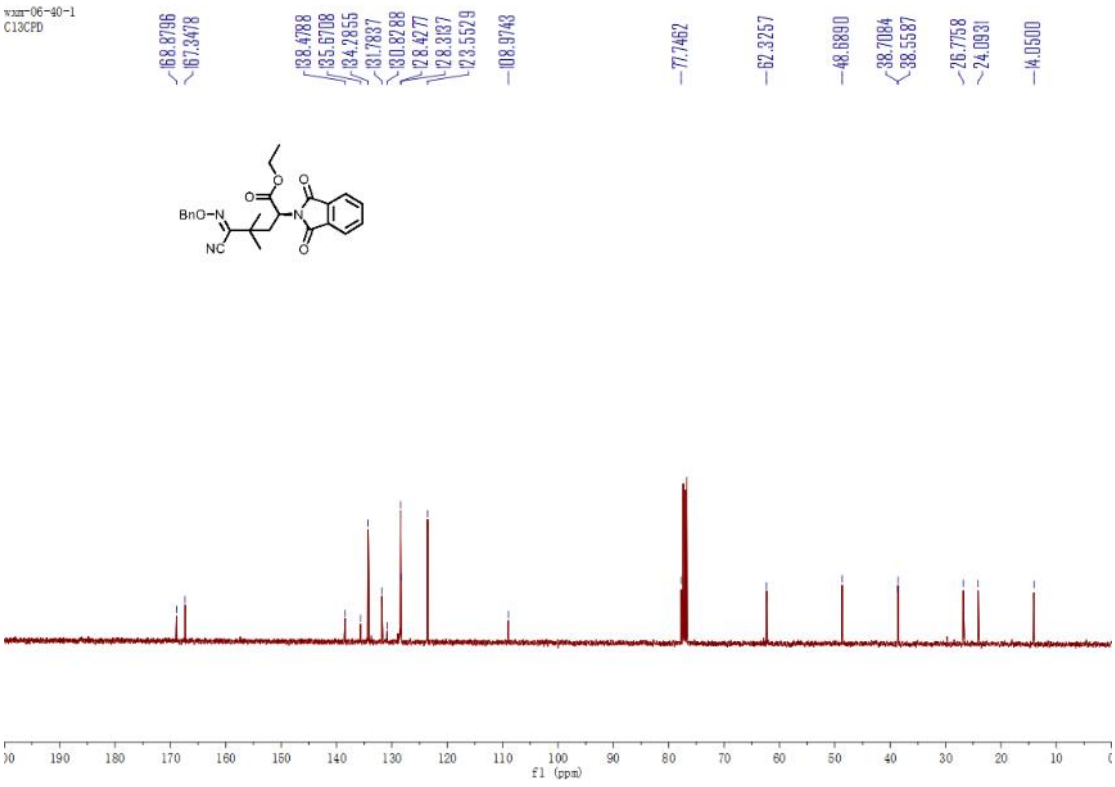
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3dd**



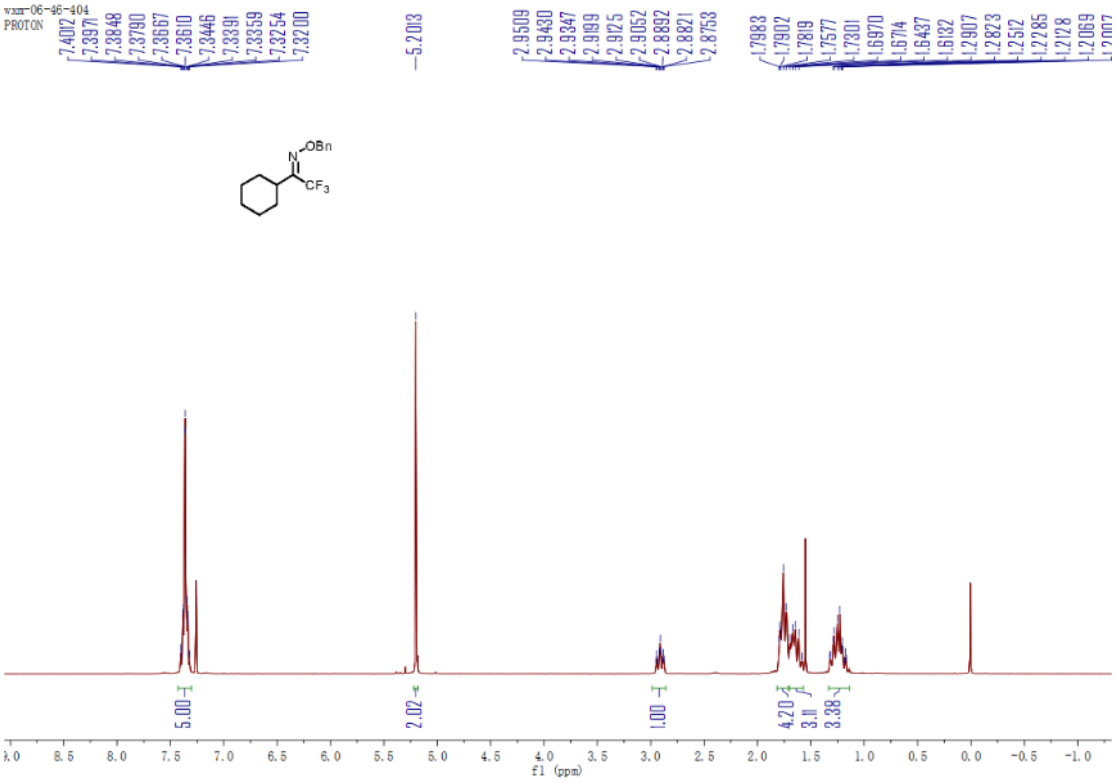
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3ee**



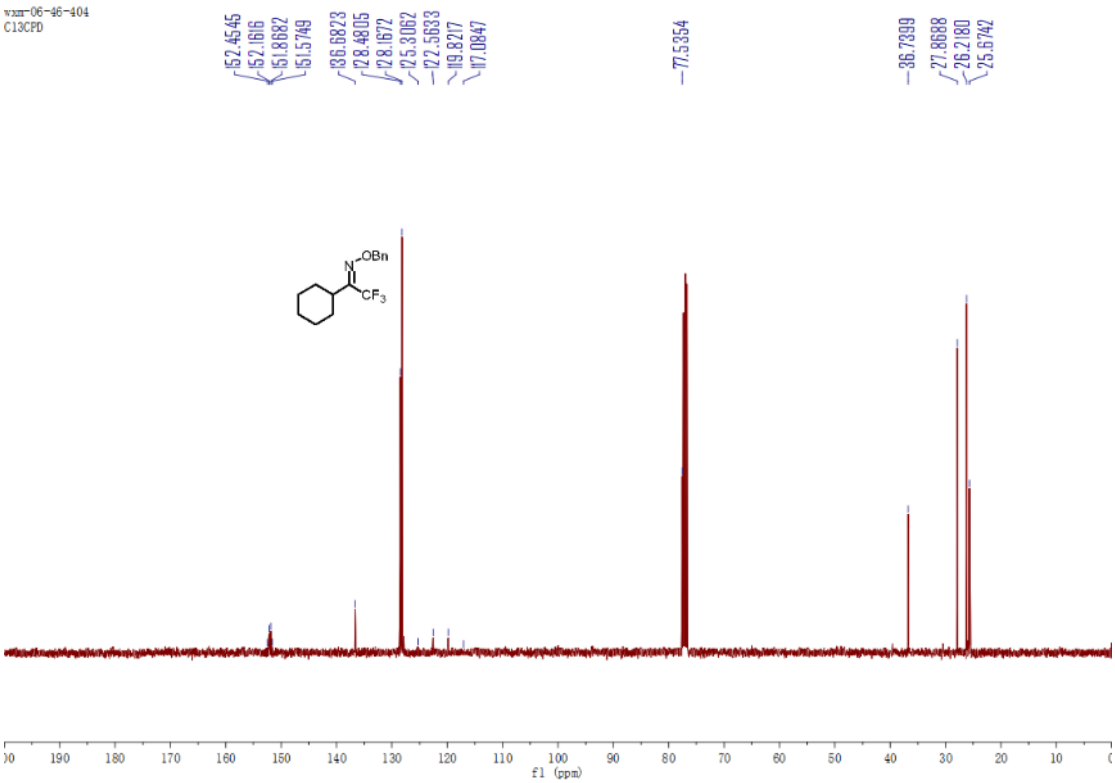
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3ee**



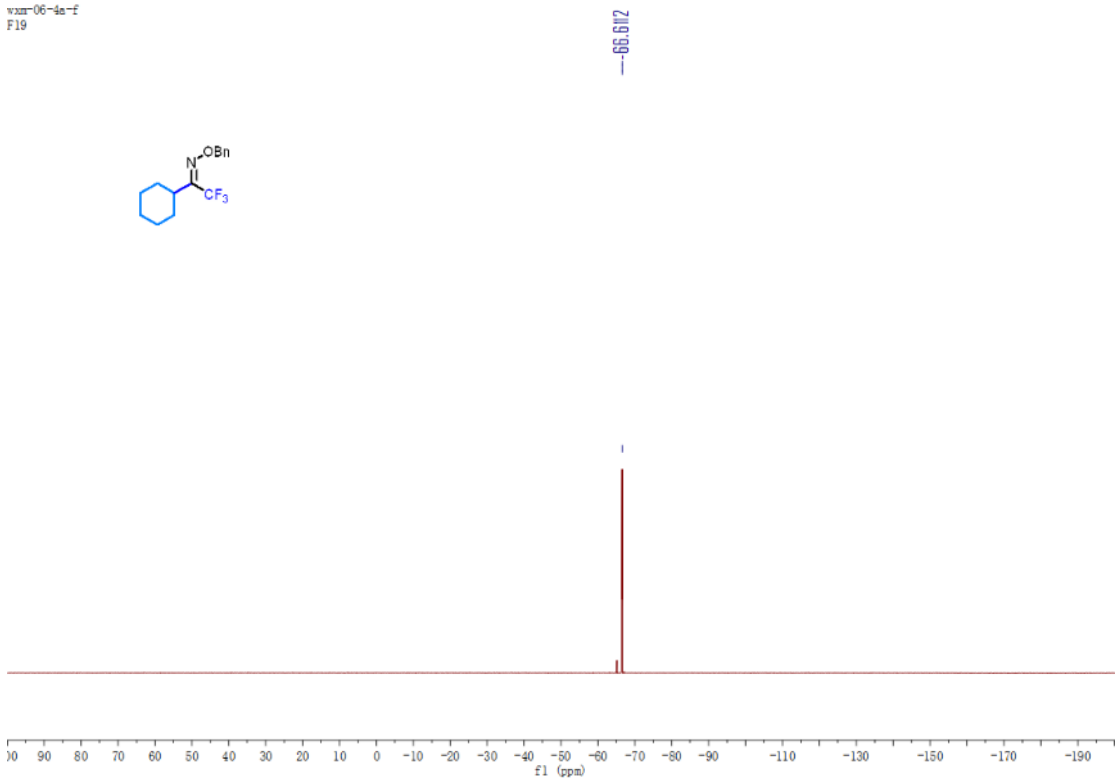
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4a**



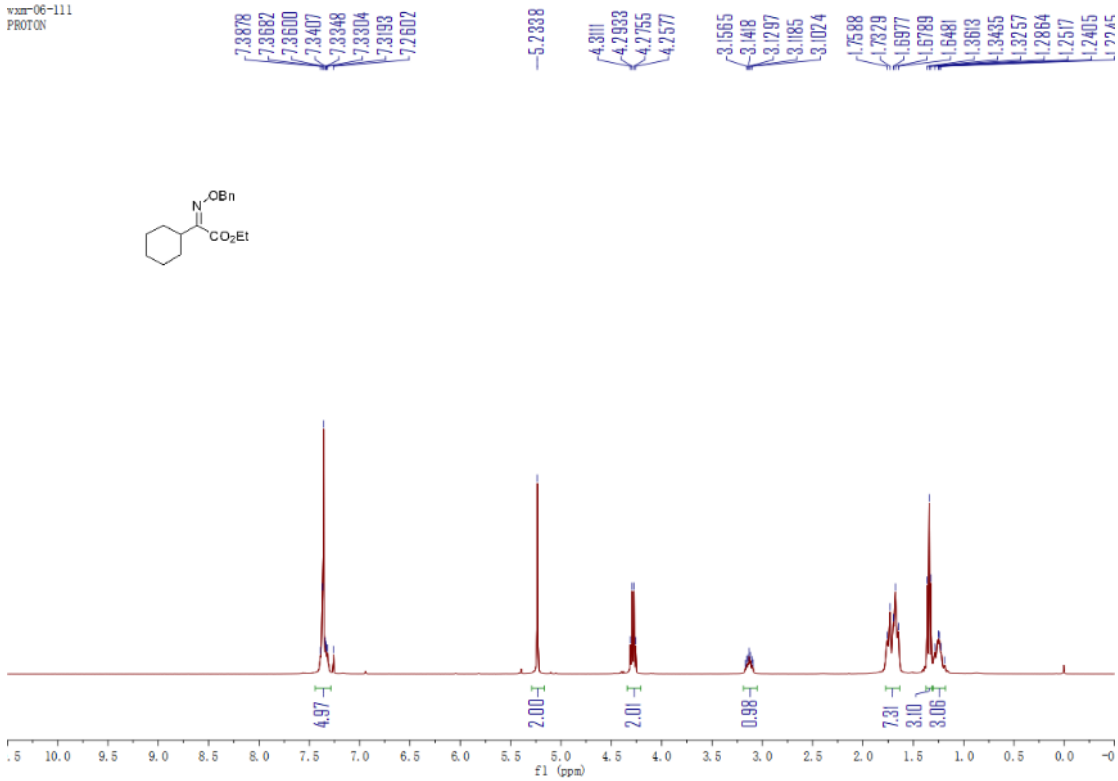
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4a**



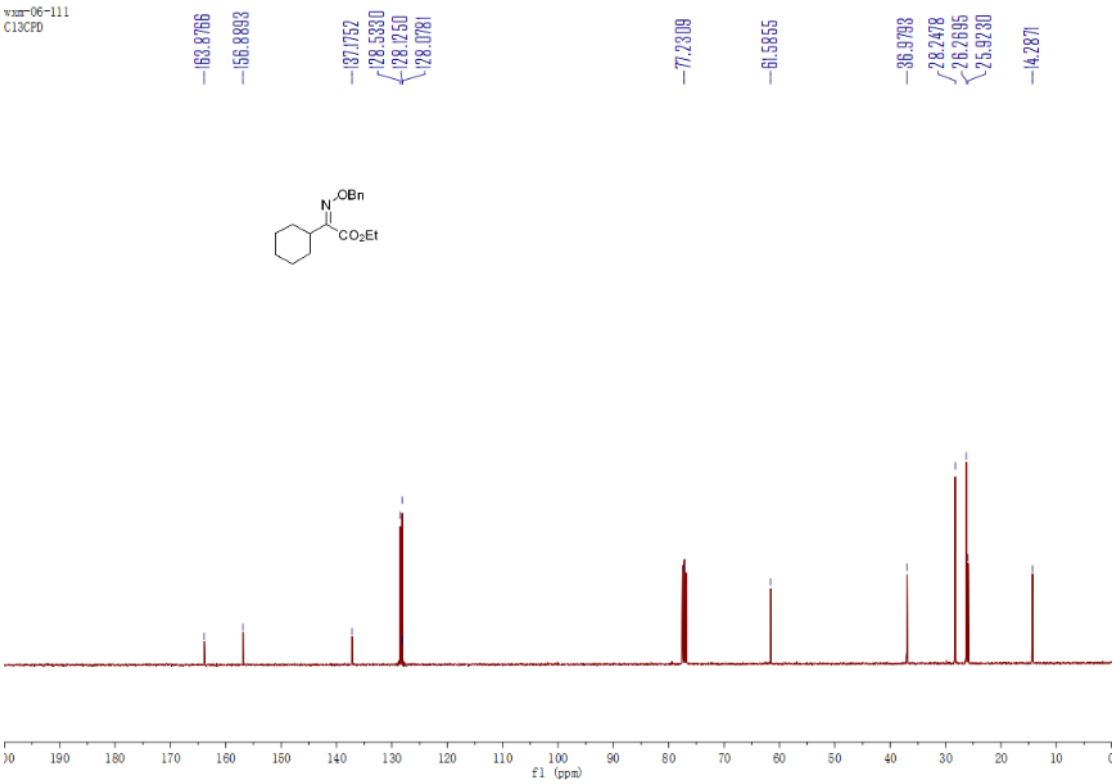
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **4a**



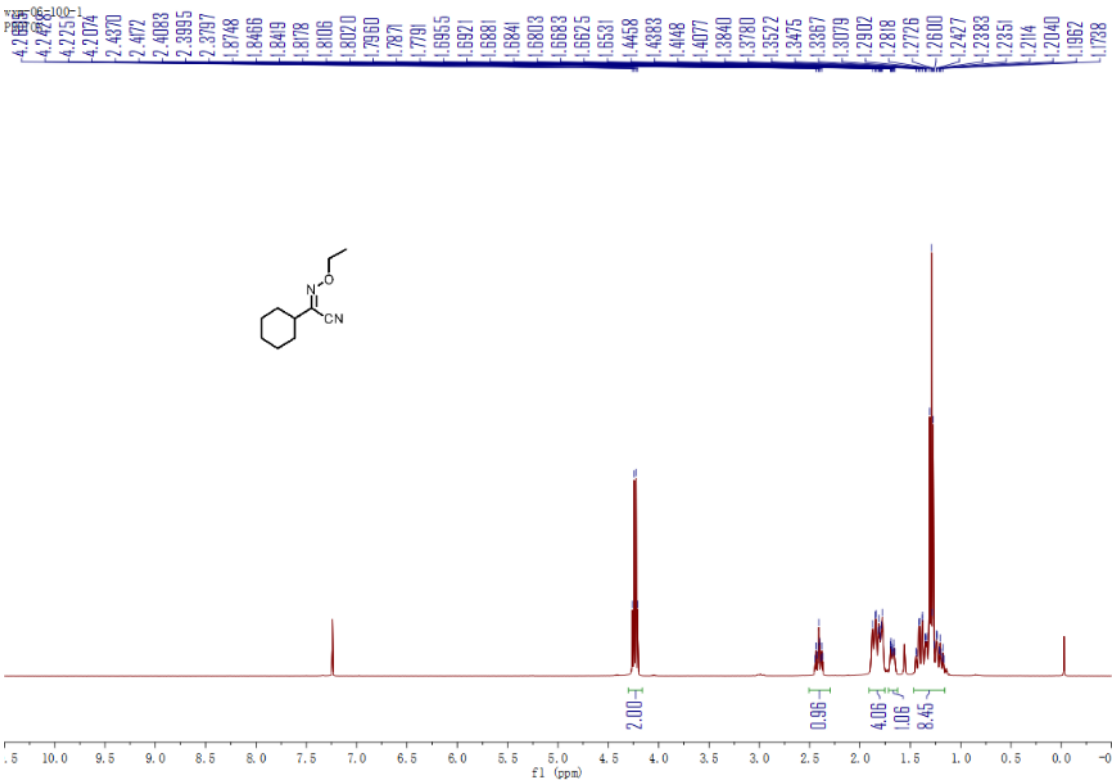
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4b**



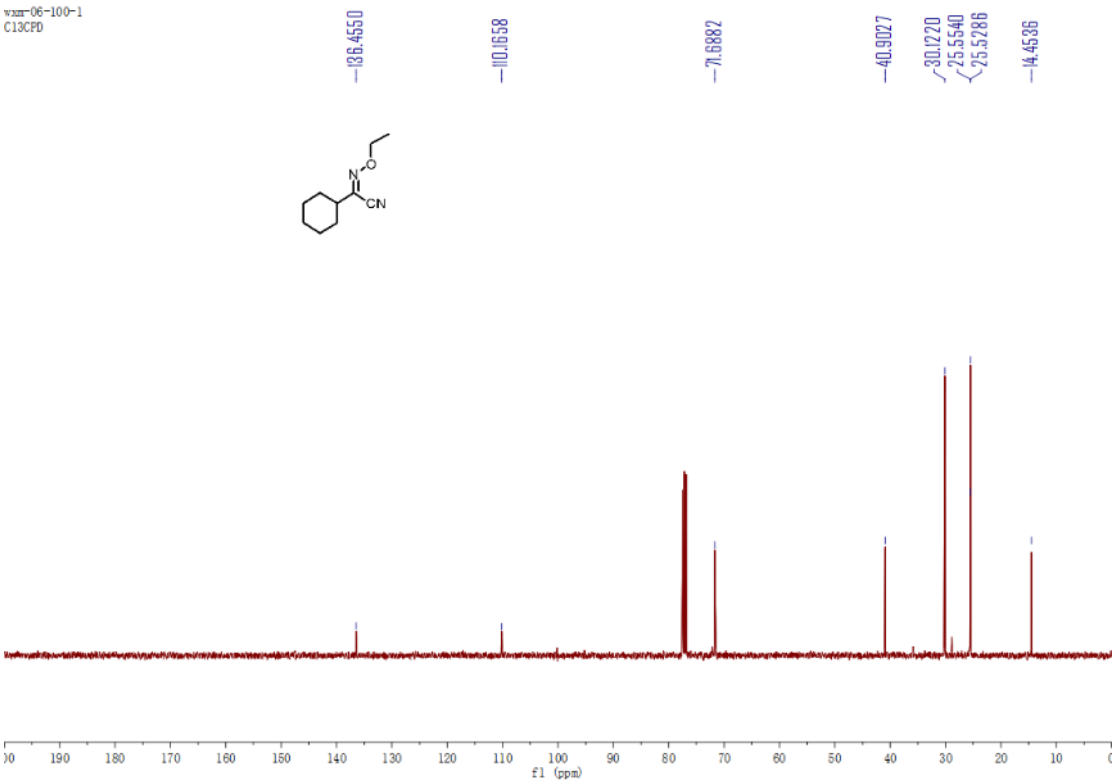
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4b**



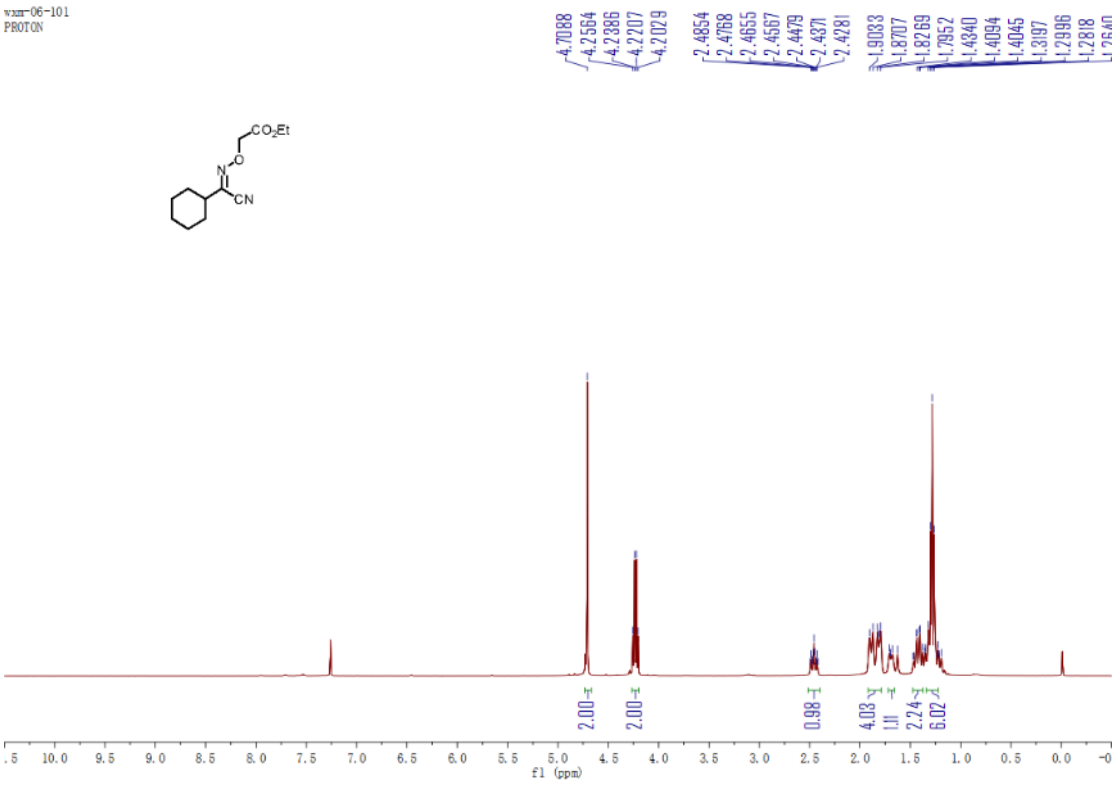
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4c**



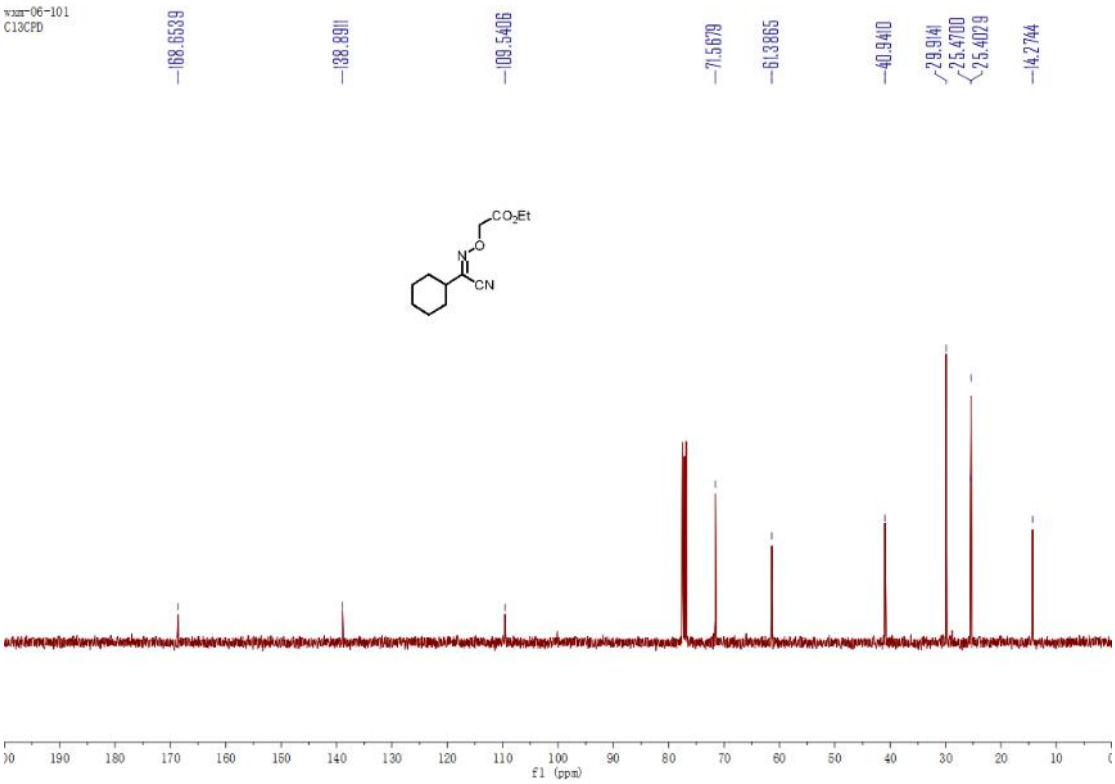
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4c**



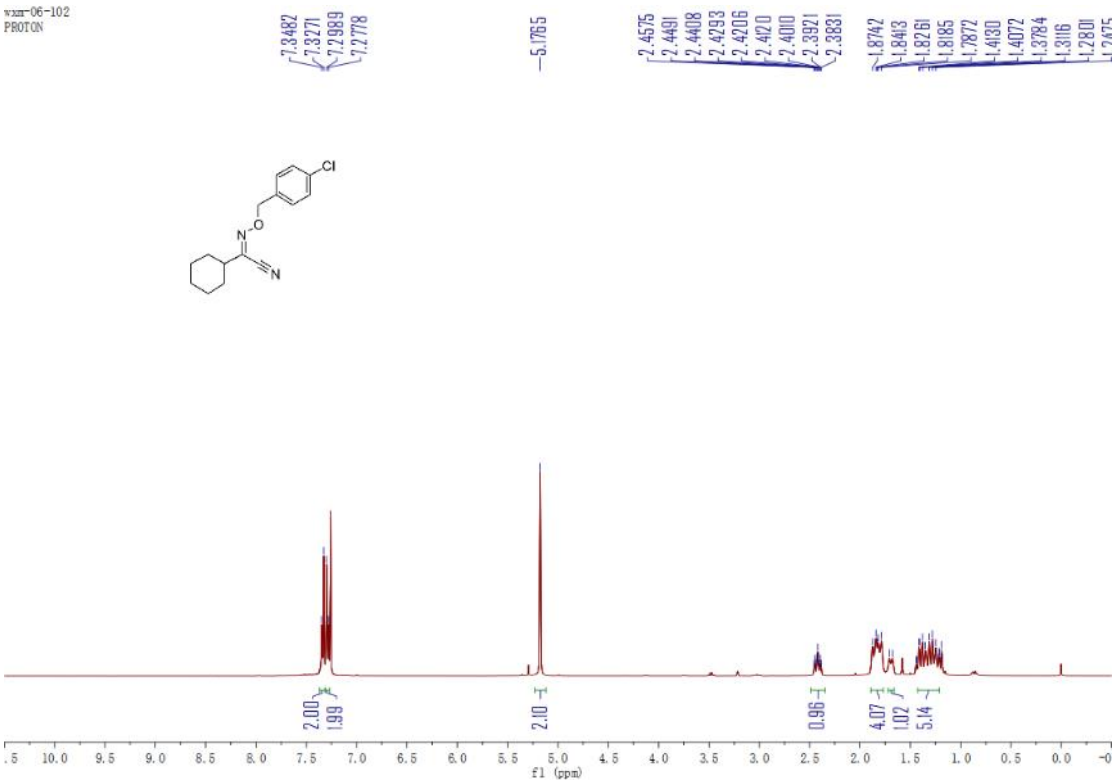
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4d**



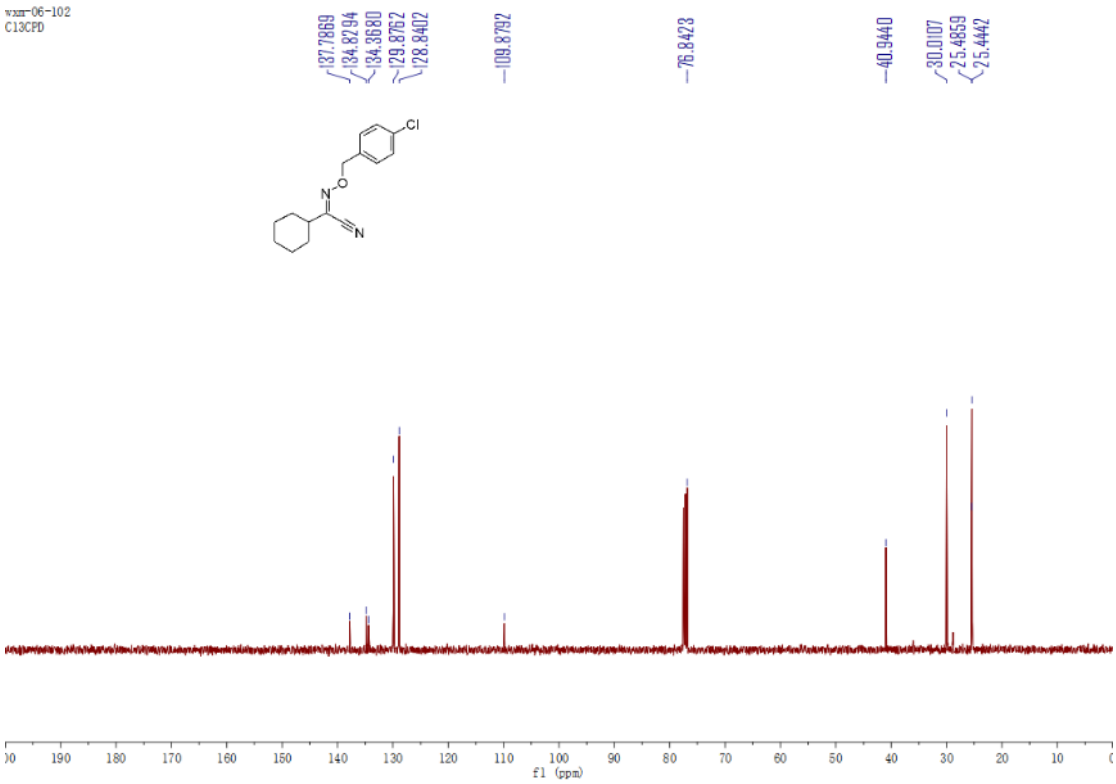
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4d**



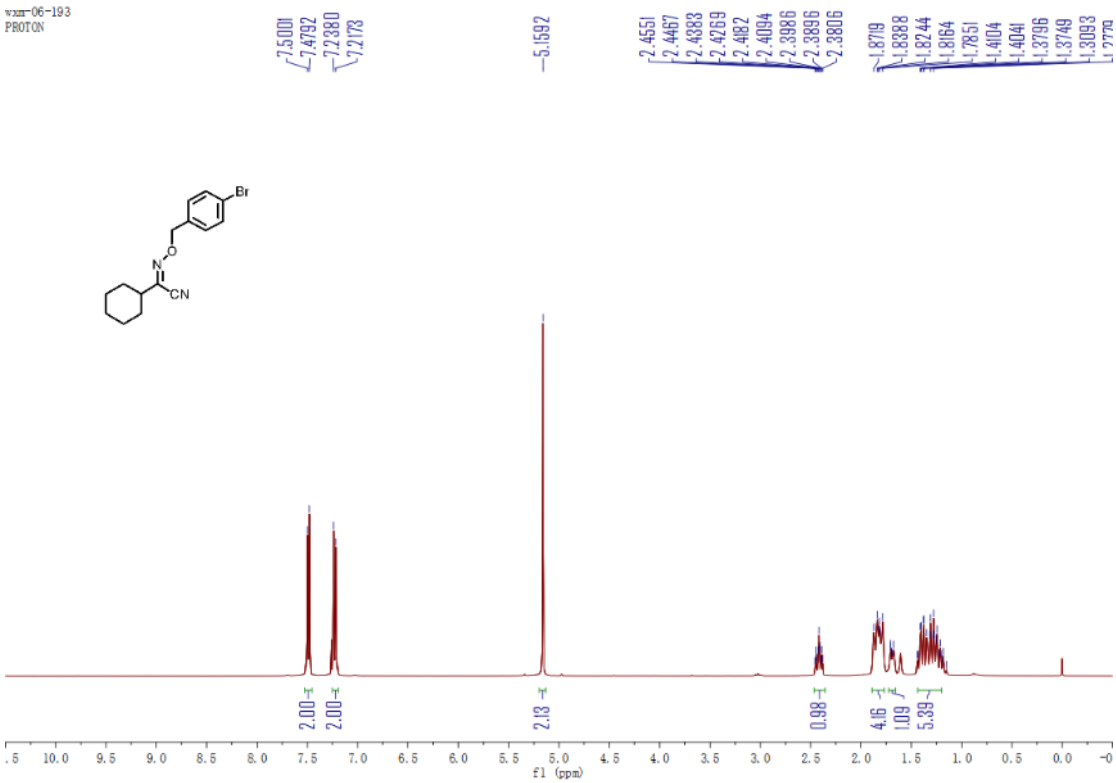
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4e**



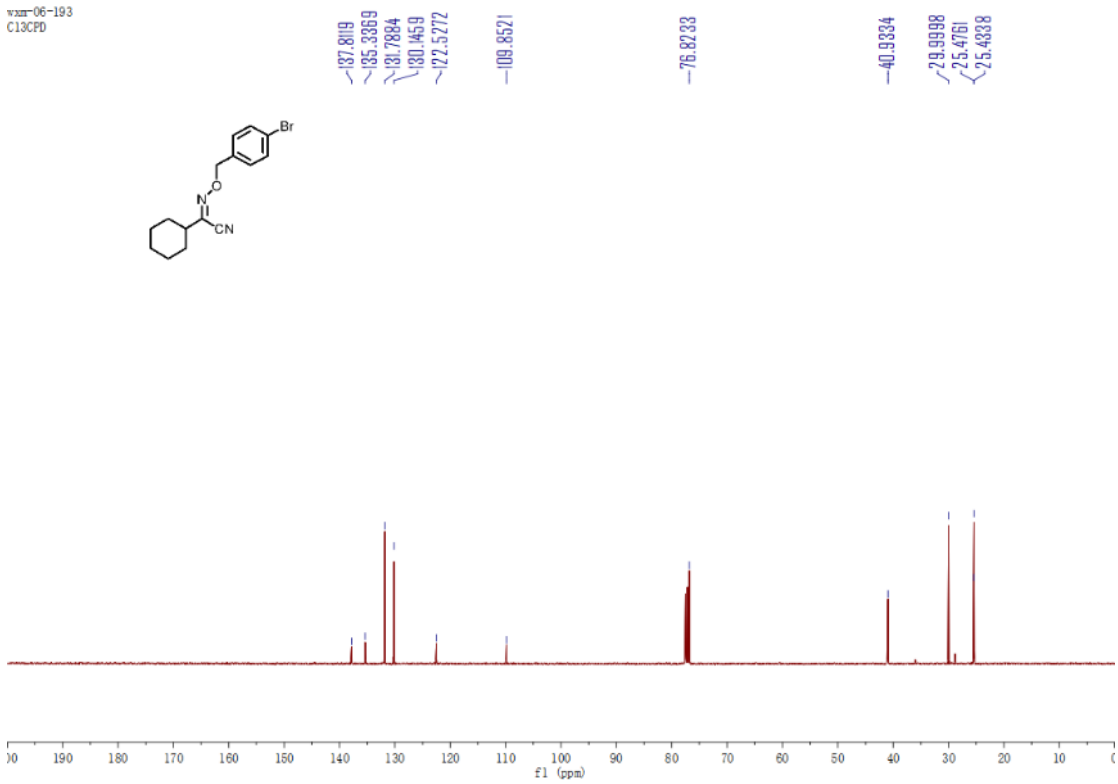
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4e**



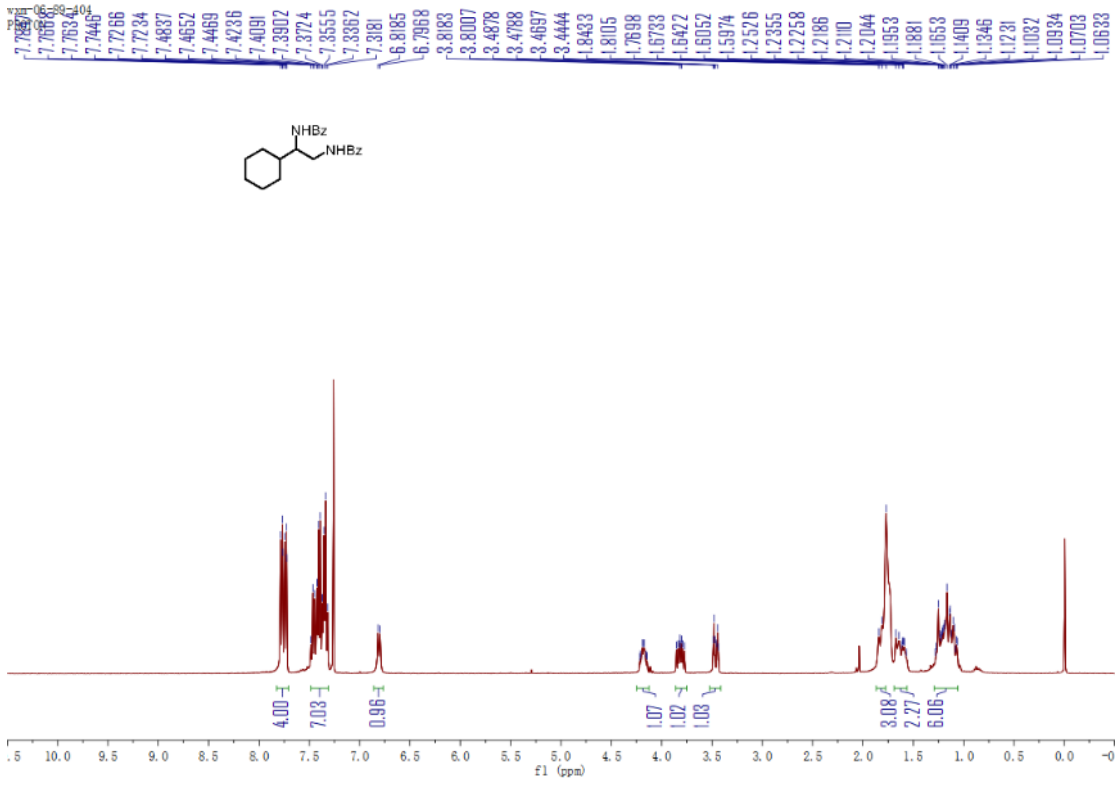
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4f**



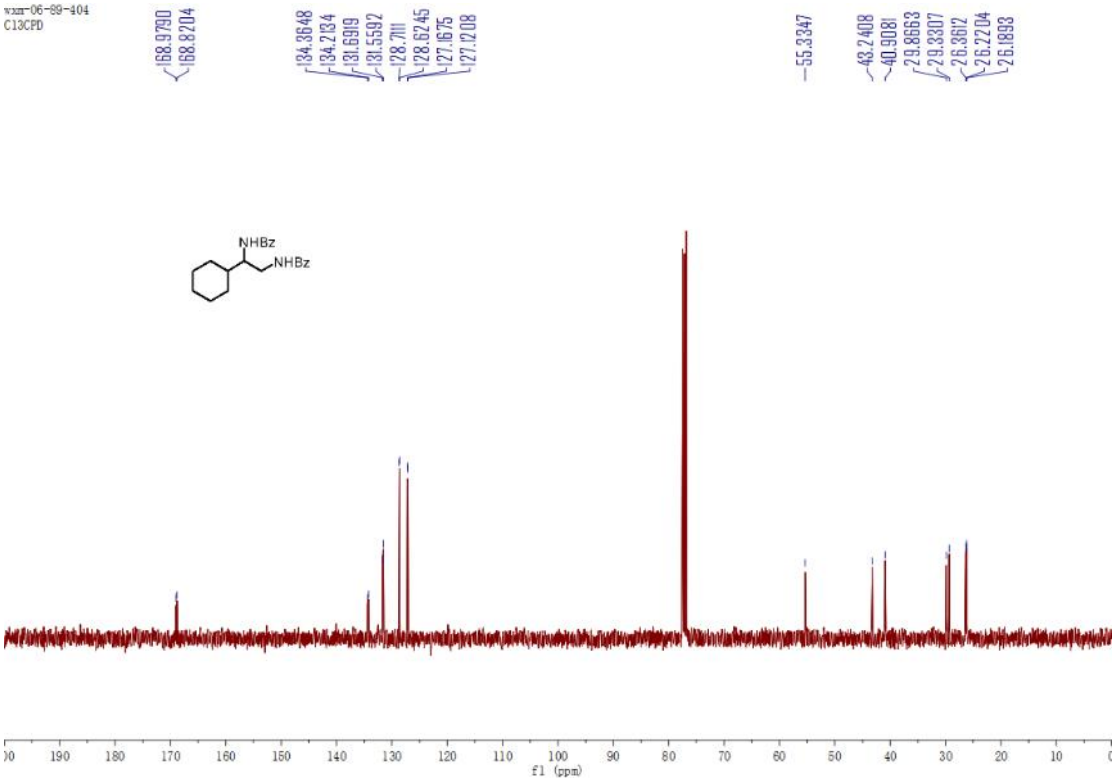
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4f**



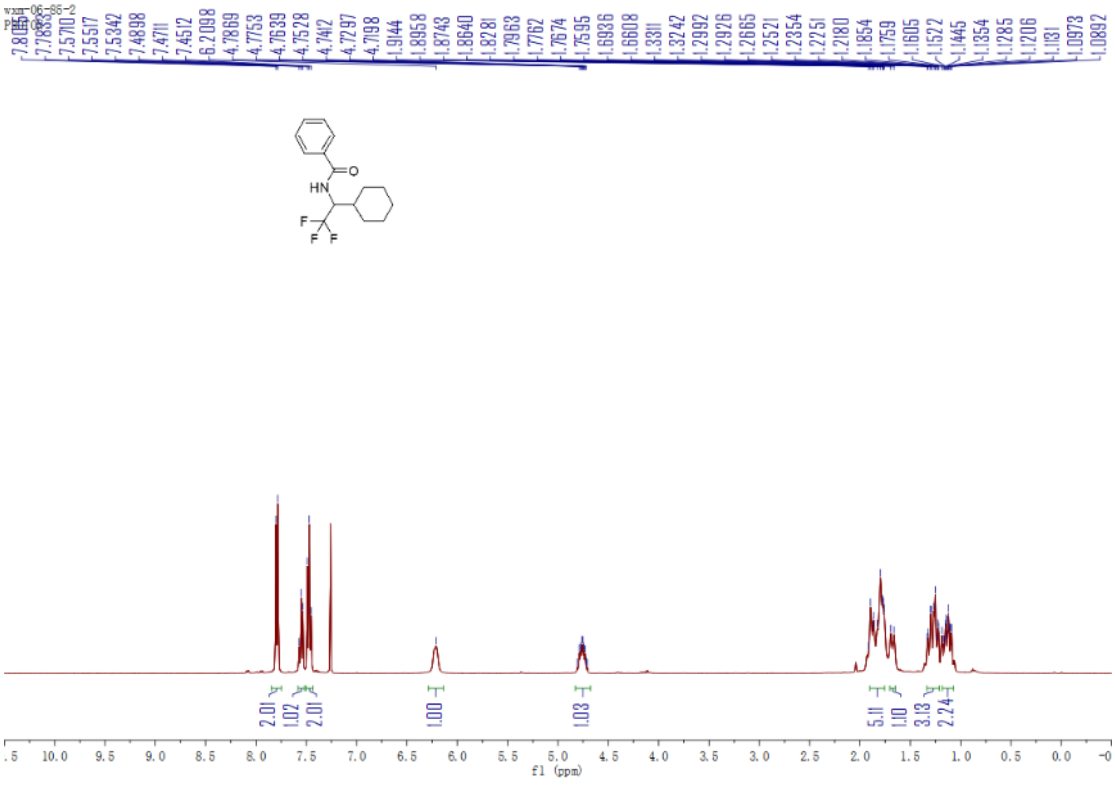
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5**



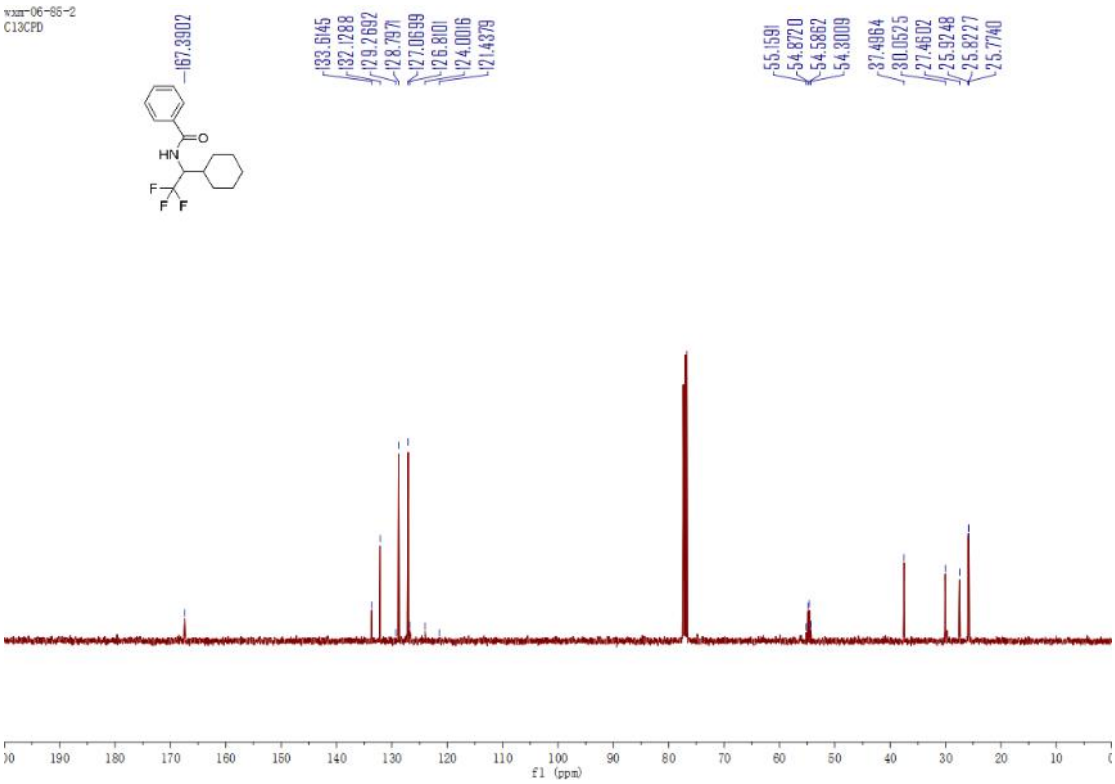
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **5**



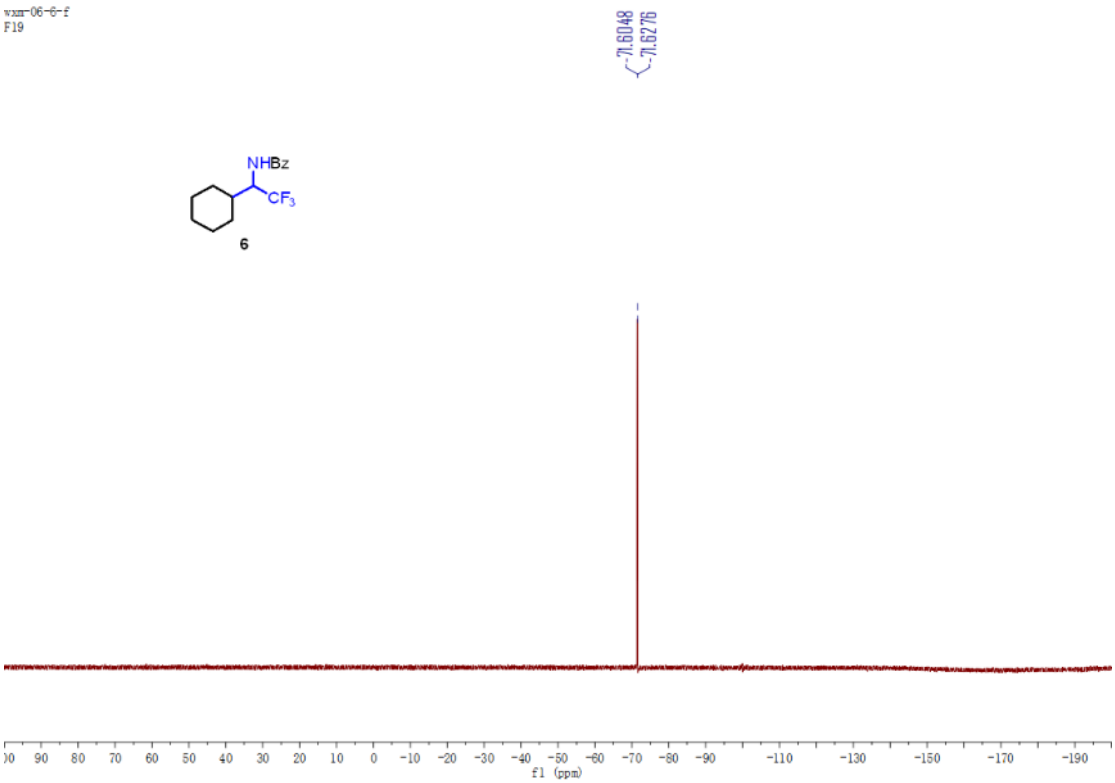
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **6**



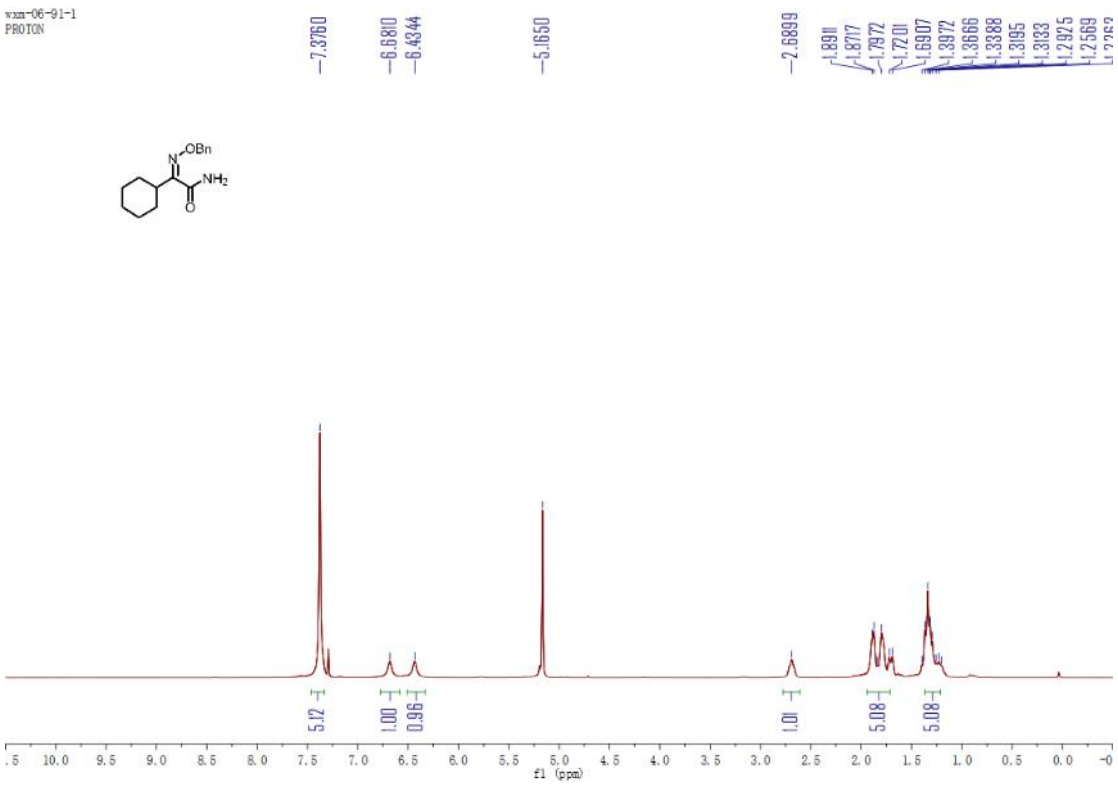
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **6**



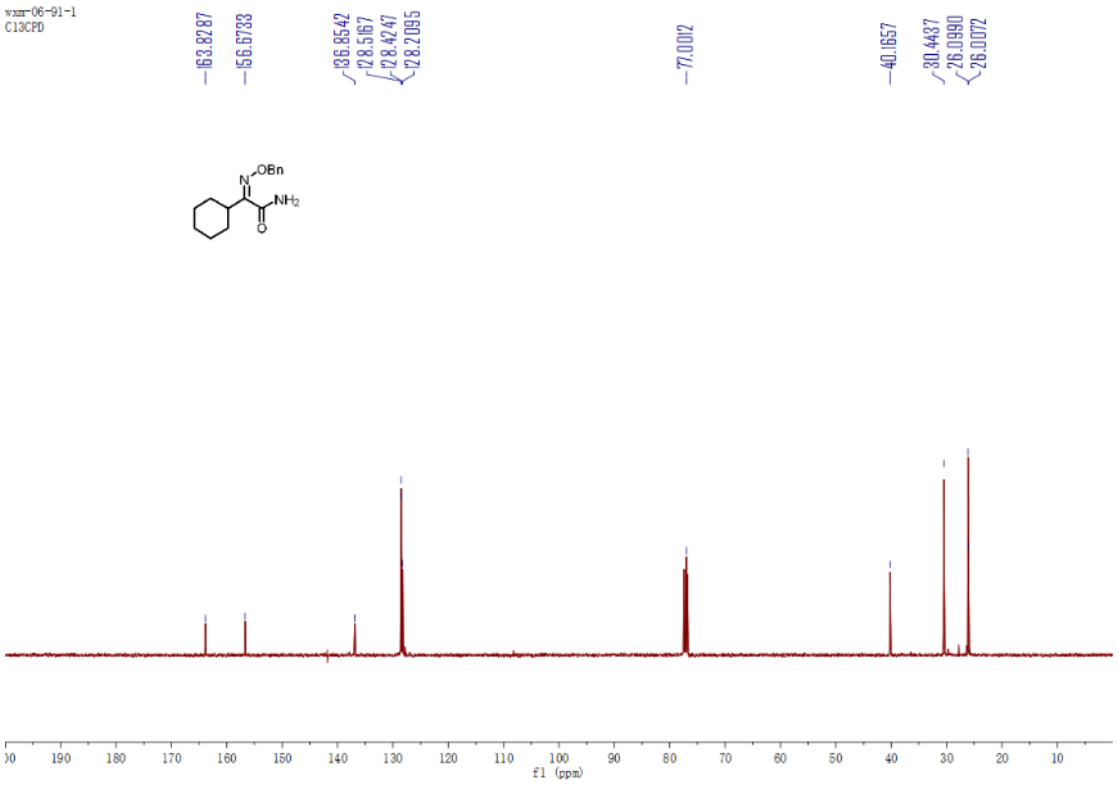
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **6**



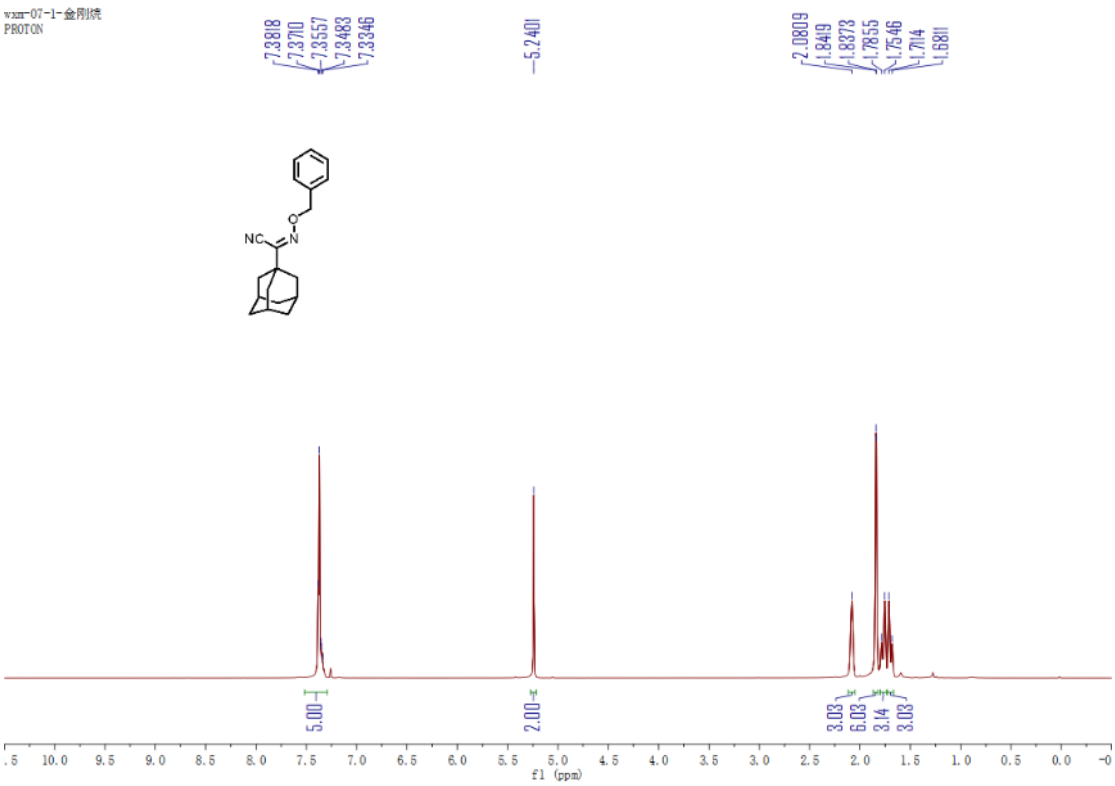
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **7**



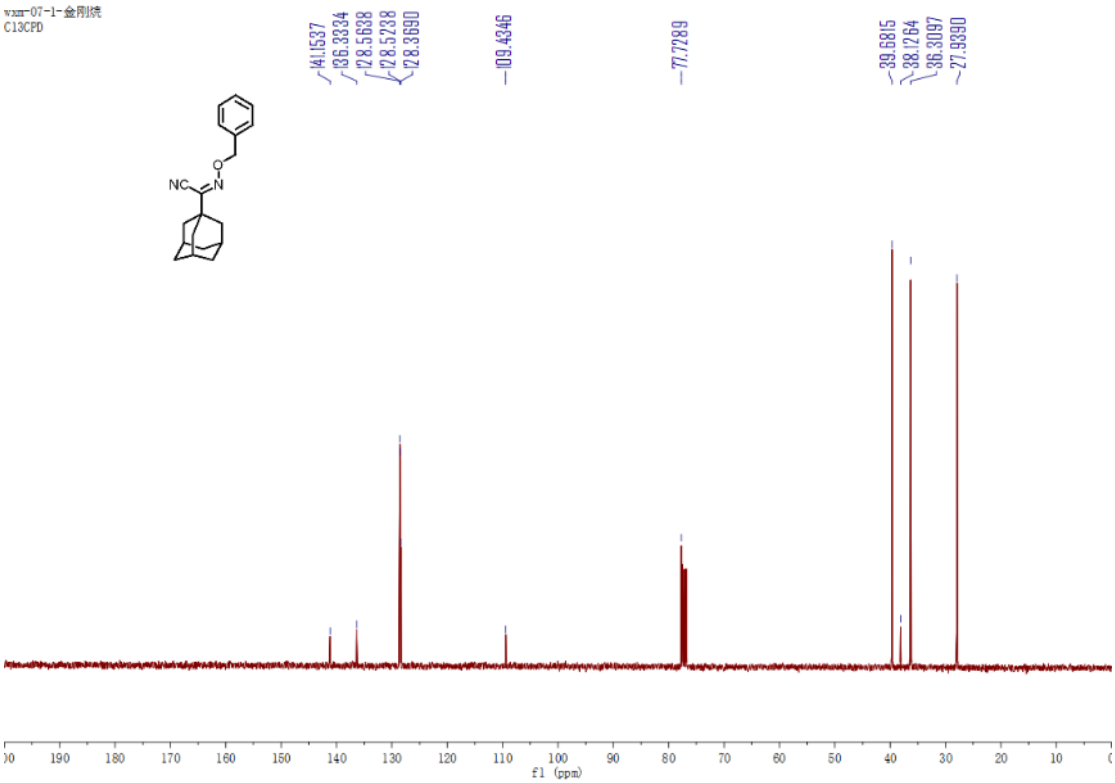
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **7**



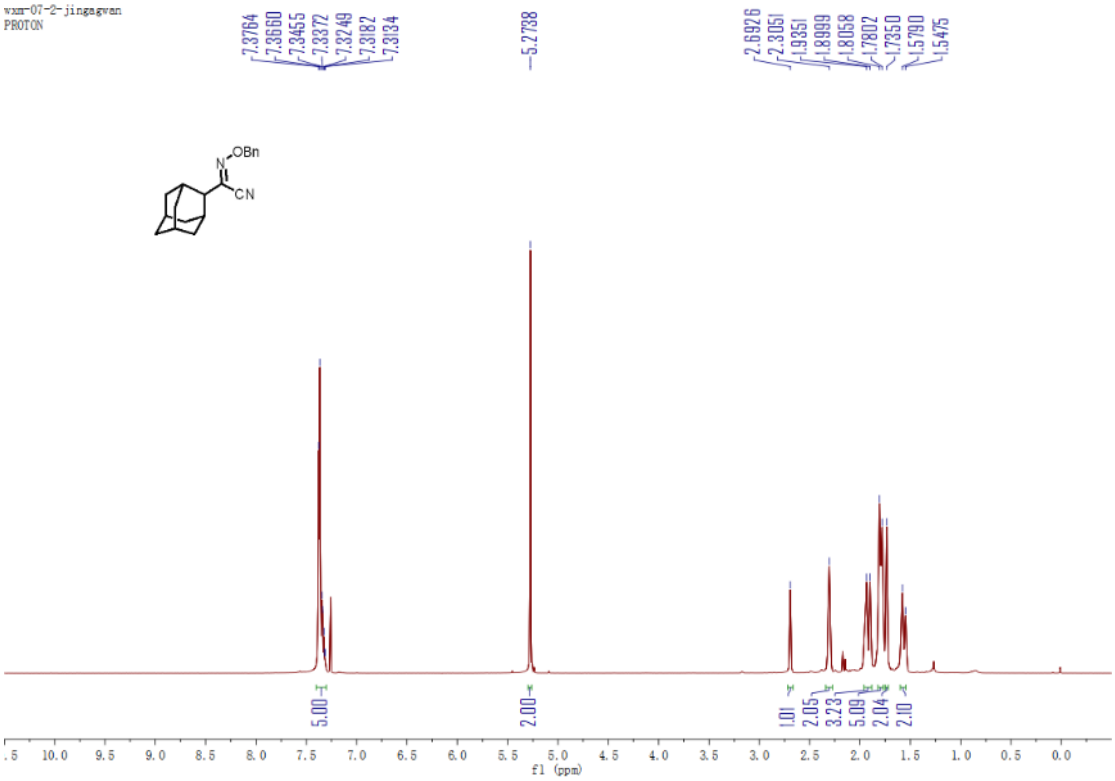
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **8a**



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **8a**



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **8b**



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **8b**