Supporting Information

Developing Multi-Functional Anthraquinone Based Conjugated Porous Polymers for Near-Infrared-Light-Driven High Selective Cyanation of α-Amino C(sp^3)−H Bonds

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1. General information

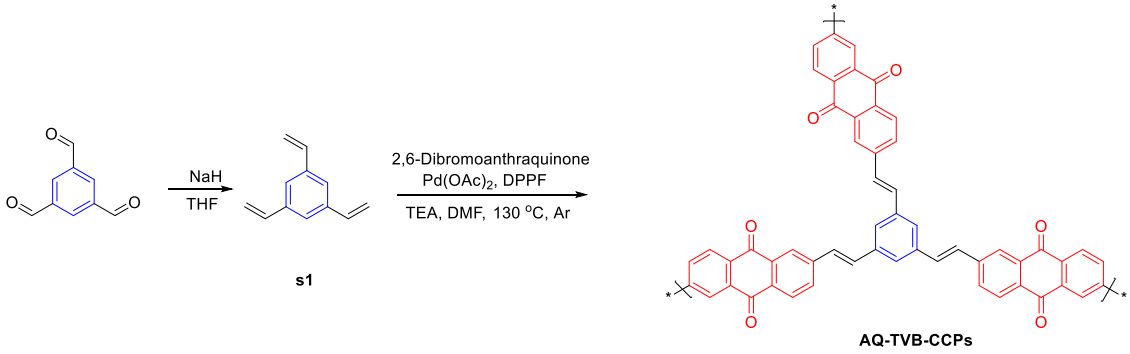
Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification. Column chromatography on silica gel (300-400 mesh) was carried out using technical grade 60-90 ℃ petroleum ether (distillated prior to use) and analytical grade EtOAc (without further purification). ^{1}H and ^{13}C spectra were recorded on a 400 or 500 spectrometer. Chemical shifts were reported in ppm. ^{1}H NMR spectra were referenced to $CDCl_3$ (7.26 ppm), and ^{13}C NMR spectra were referenced to $CDCl_3$ (77.2 ppm). Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and *J*, coupling constant in Hz. LC-MS spectra were recorded on Agilent 6545 Q-TOF LC/MS using electron spray ionization (ESI) source. Solid state ^{1}H NMR spectra were recorded on a Bruker Avance III 400 MHz NMR spectrometer. Nitrogen sorption isotherms at the temperature of liquid nitrogen were performed on a Quantachrome Autosorb-1 system, and the samples were degassed for 10 h at 393 K before the measurements were obtained. The specific surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) methods. Scanning electron microscopy (SEM) was performed using a SU8020. X-ray diffraction (XRD) measurements were conducted with a scanning step of 2°/min in the 2θ range of 5-90 °(D/MAX2200pc). Thermogravimetric analysis (TGA) was carried out using a thermal analyzer (NETZSCH STA 449 F3), during which the sample was heated at the rate of 10 $Kmin^{-1}$ from room temperature up to 1073 K under a nitrogen atmosphere. FT-IR spectra were recorded on a Thermo-Nicolet 6700 spectrometer between 4000-500 cm^{-1}. The EPR spectra were monitored using an MS5000 spectrometer (Bruker, Germany). Measurement settings were as follows: modulation frequency, 100 kHz; modulation width, 0.2 mT; magnetic field, 330−340 mT; sweep time, 60 s; microwave power, 10 mW; microwave frequency, 9.46 GHz. UV-vis diffuse reflectance spectra (DRS) were performed on a Perkin Elmer Lambda 750 in the 400~1200 nm range, with $BaSO_4$ as the reference substance. The NIR LED light devices were purchased from Beijing Roger tech Ltd (www.rogertech.cn). Dependent density functional theory (DFT) calculations were carried out at the M062X-def2svp SMD(solvent=methanol).

Photoelectrochemical measurements

The photoelectrochemical measurements were conducted on an electrochemical workstation (CHI660E, CH Instruments Inc., Shanghai) with standard three electrodes in 0.1 M Na_2SO_4 electrolyte solution: Indium-doped tin oxide (ITO) conductive glass was employed as the working electrode, the Pt mesh and Ag/AgCl served as counter electrode and reference electrode, respectively. The working electrode was prepared as follows: 6 mg photocatalyst was dispersed in mixed solution of ethanol (3 mL) and nafion (20 μL) and followed by ultrasonic treatment. The slurry was evenly applied to Indium-doped tin oxide (ITO) conductive glass by spin coating, while the side part was previously protected by Teflon tape. For electrochemical impedance spectra (EIS) measurements, the frequency spanned from 100 kHz to 10 MHz and the perturbation signal was 5 mV. In photocurrent response measurements, light from a 15 W LEDs was irradiated from the backside of the working electrode to minimize the influence of sample thickness. The Mott-Schottky measurements were performed at 1000 Hz, 1500Hz and 2000Hz. The exposed area under illumination was 0.8×1 cm^2.

2. General Experiment

2.1 Preparation of AQ-TVB-CPPs



NaH (16.5 mmol, 3.3 equiv.) and THF (0.33 M) were added to a round bottom flask under nitrogen, and the mixture was stirred for over 30 min at 0 ℃. Next, a solution of 1,3,5-Triethenylbenzene (5.0 mmol, 1.0 equiv.) in THF (10 mL) was slowly added to the solution at 0 ℃ over 30 min followed by stirring at room temperature 3 days. The reaction was quenched by water, and the mixture was extracted with CH_2Cl_2. The organic layer was washed with brines and dried over Mg_2SO_4. After filtration and concentration, the residue was purified by silica gel column chromatography with petroleum ether as eluent to afford **s1**[1]. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.93 – 6.78 (m, 3H), 6.64 – 6.62 (m, 3H), 5.76 (dd, 3H), 5.21 (dd, 3H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ136.3, 134.9, 122.3, 114.3.

2,6-Dibromoanthraquinone (1.0 mmol, 1.0 equiv.), **s1** (2.0 mmol, 2.0 equiv.), $Pd(OAc)_2$ (10 mmol%), 1,1'-Bis(diphenylphosphino)-ferrocene (DPPF, 10 mmol%), TEA (4.0 mmol, 4.0 equiv.) and DMF (5 mL) were added to a round bottom flask under nitrogen. This mixture was refluxed at 130 ℃ for 48 hours. Subsequently, filter the mixture and wash the solid with water and ethanol to obtain AQ-TVB-CPPs.

2.2 Photothermal experiment

Add AQ-TVB-CPPs (10 mg), methanol (2 mL), and a stirrer to two dry quartz tubes, and place the reaction tubes under 760 nm, 15 W LED lights and 455 nm, 15 W LED lights, respectively. Stir the mixture and align the thermal imager with the substrate of the quartz tube. Simultaneously turn on the LED light and thermal imaging device to record the temperature changes of the mixture under two different lighting conditions.

2.3 Consumption rate experiment

4-Methoxy-*N*, *N*-dimethylaniline (0.2 mmol), TMSCN (0.4 mmol), AQ-TVB-CPPs (10 mg), 1,3,5-trimethoxybenzene (0.2 mmol) and methanol (2 mL) were added to 2 dry quartz tubes, and One quartz tube was placed under a 760 nm, 15 W LED light for 8 hours of reaction, while the

other quartz tube was placed under a 455 nm, 15 W LED light for 8 hours of reaction. During the reaction process, take 5uL of the reaction solution every hour, add chromatographic methanol (1 mL), filter the membrane, and quantify the solution using LC-MS.

2.4 Synthesis of α-Phenylglycine

A solution of **3v** (0.2 mmol) and NaOH (0.9 mmol) in ethanol (4 mL) was refluxed at 90 ℃ for 5 h. The reaction mixture was acidified by adding 2 M HCl aqueous solution and extracted with ether (10 mL × 2). The combined organic layer was dried over Na_2SO_4. α-phenylglycine (75%).

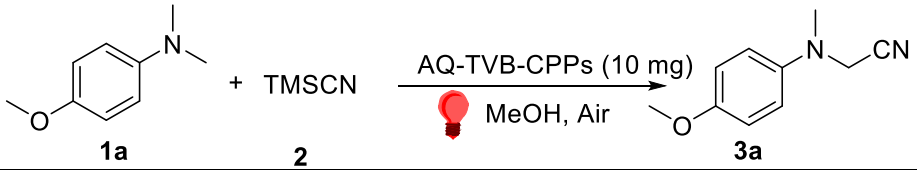
2.5 General procedures I: Cyanation of α-C-H bond of amine

A dried quartz tube was charged with amine **1** (0.2 mmol, 1.0 equiv.), TMSCN (0.4 mmol, 2.0 equiv.), the catalyst (10 mg), and methanol (2 mL). The reaction mixture was stirred for 8 hours under 760 nm, 15 W light irradiation. Upon completion of the reaction (monitored by TLC), the solution was filtered and washed with EtOAc. The filtrate was evaporated under vacuum. The crude product was purified directly by silica gel column chromatography (PE: EA = 10:1) to yield the corresponding product **3** or **4**.

2.6 General procedures II: Quenching experiment

A dried Quartz tube charged with 4-methoxy-*N*,*N*-dimethylaniline (0.2 mmol, 1.0 equiv.), TMSCN (0.4 mmol, 2.0 equiv.), AQ-TVB-CPPs (10 mg), quencher (0.4 mmol, 2.0 equiv.) and methanol (2 mL). The reaction mixture was stirred for 8 hours under 760 nm 15 W light irradiation. After the reaction is complete, add 1,3,5-trimethylbenzene (0.1 mmol) and determine the yield of the reaction by ^{1}H NMR.

Table S1. Control experiments: the effect of various scavengers on the photocatalysis process (under standard condition).



760 nm		455 nm	
Additive (2.0 equiv.)	Yield (%)	Additive (2.0 equiv.)	Yield (%)
$^1O_2$ scavenger (NaN_3)	29	$^1O_2$ scavenger (NaN_3)	64
hole scavenger (KI)	Trace	hole scavenger (KI)	60
$HO^{\bullet}$ scavenger (*i*-PrOH)	83	$HO^{\bullet}$ scavenger (*i*-PrOH)	56
$O_2^{\bullet-}$ scavenger (*p*-BQ)	81	$O_2^{\bullet-}$ scavenger (*p*-BQ)	17

2.7 General procedures III: Cyclic experiment

A dried Quartz tube charged with 4-methoxy-*N*,*N*-dimethylaniline (0.2 mmol, 1.0 equiv.), TMSCN (0.4 mmol, 2.0 equiv.), AQ-TVB-CPPs (10 mg) and methanol (2 mL). The reaction mixture was stirred for 8 hours under 760 nm 15 W light irradiation. When the reaction was completed

(monitored by TLC), the solution was filtered and washed with EtOAc. The catalyst was collected and dried under vacuum for the next catalytic cycle. The filtrate was evaporated with addition of 1,3,5-trimethylbenzene (0.1 mmol, 0.5 equiv.) under vacuum. The yield was further determined by ^{1}H NMR.

3. Supplementary tables and figures

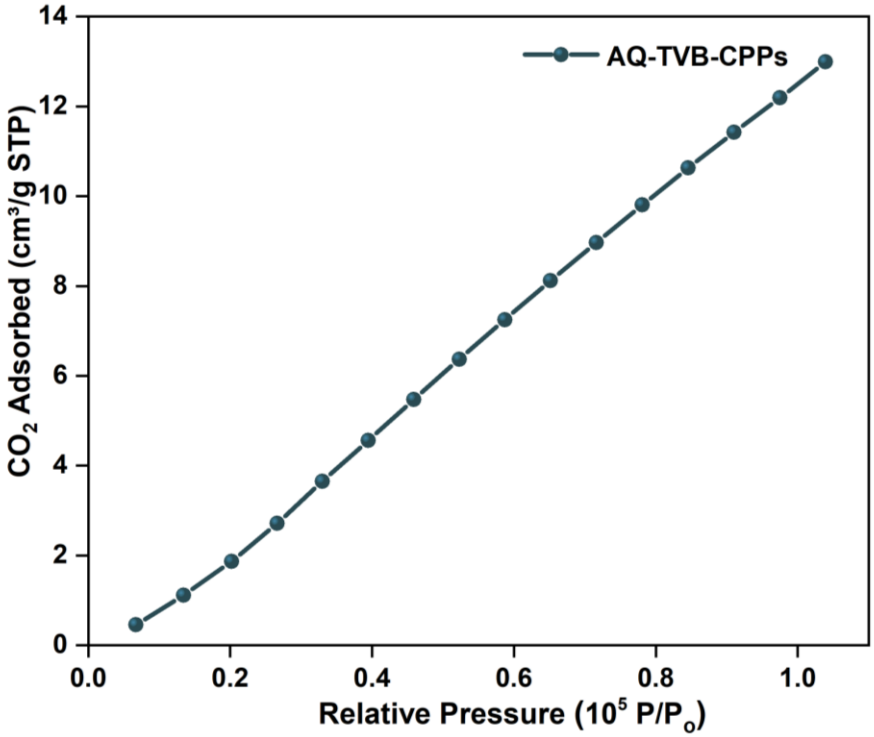


Figure S1. CO_2 adsorption curve of AQ-TVB-CPPs.

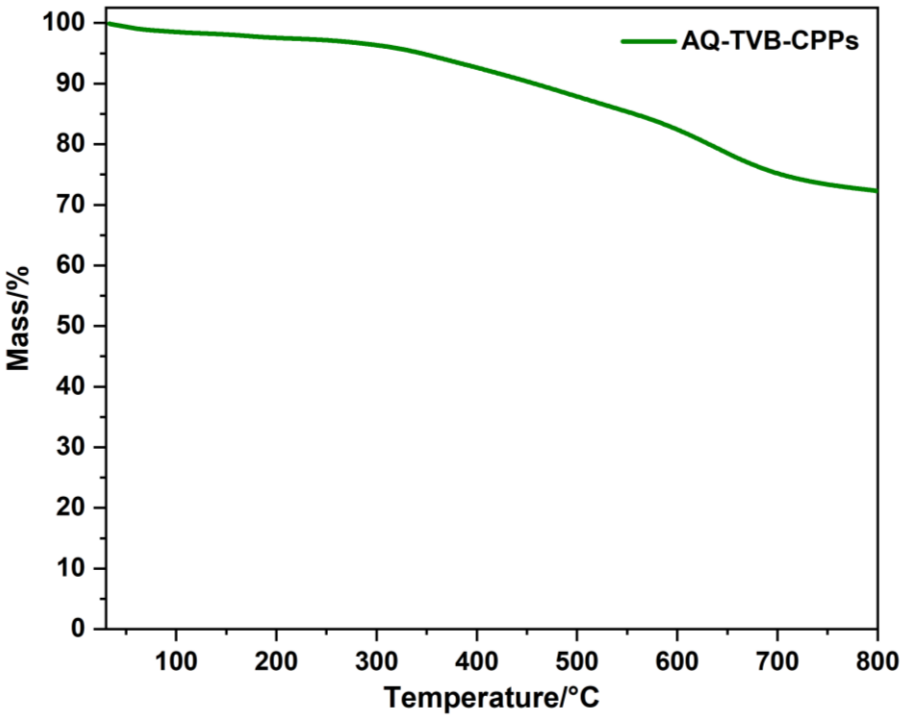


Figure S2. TGA spectrum of AQ-TVB-CPPs.

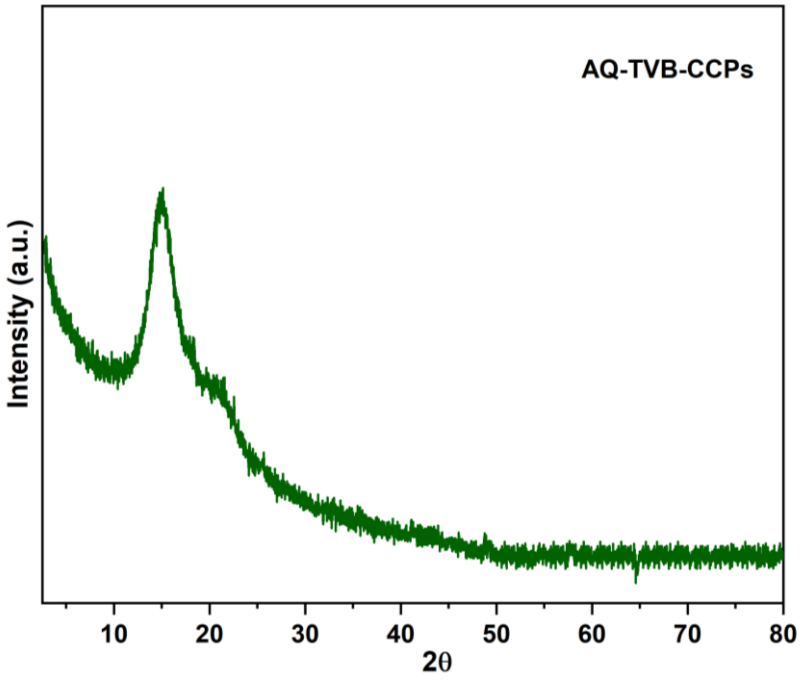


Figure S3. XRD analysis catalysis of AQ-TVB-CPPs.

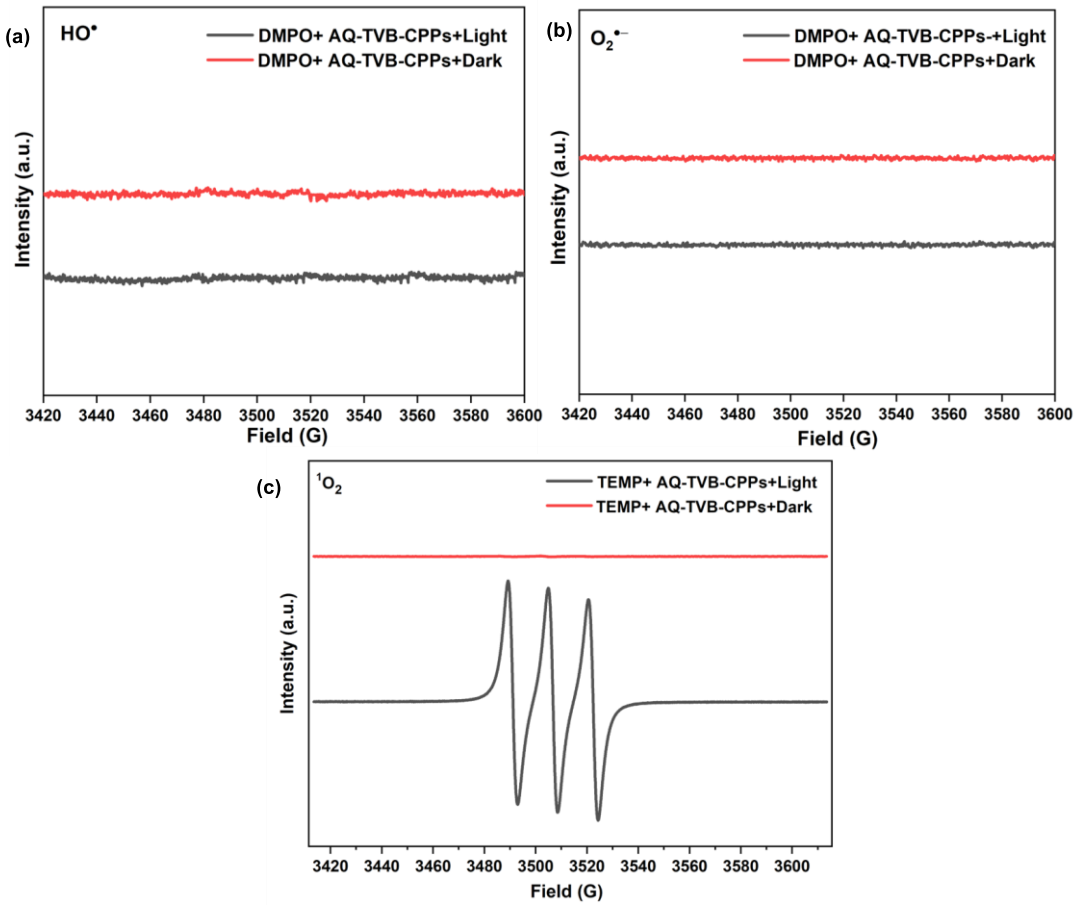


Figure S4. EPR spectra (a) DMPO-$O_2^{\bullet-}$, (b) DMPO-$^{\bullet}OH$, (c) TEMP-$^1O_2$ spectra of AQ-TVB-CPPs under NIR light irradiation and dark.

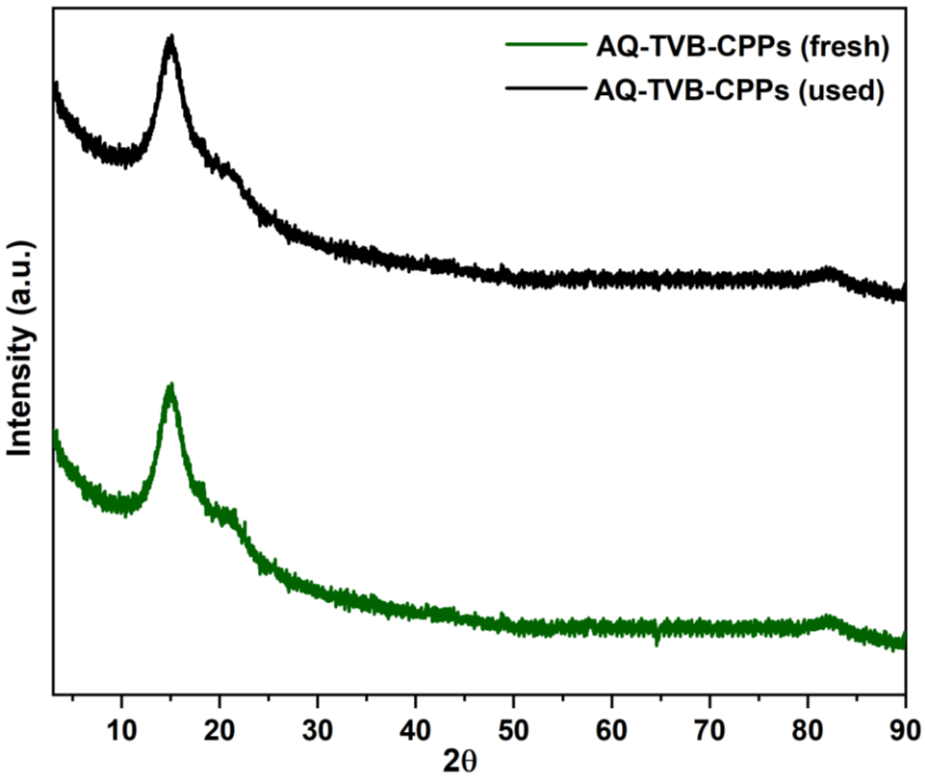


Figure S5. XRD analysis fresh and used catalysis of AQ-TVB-CPPs.

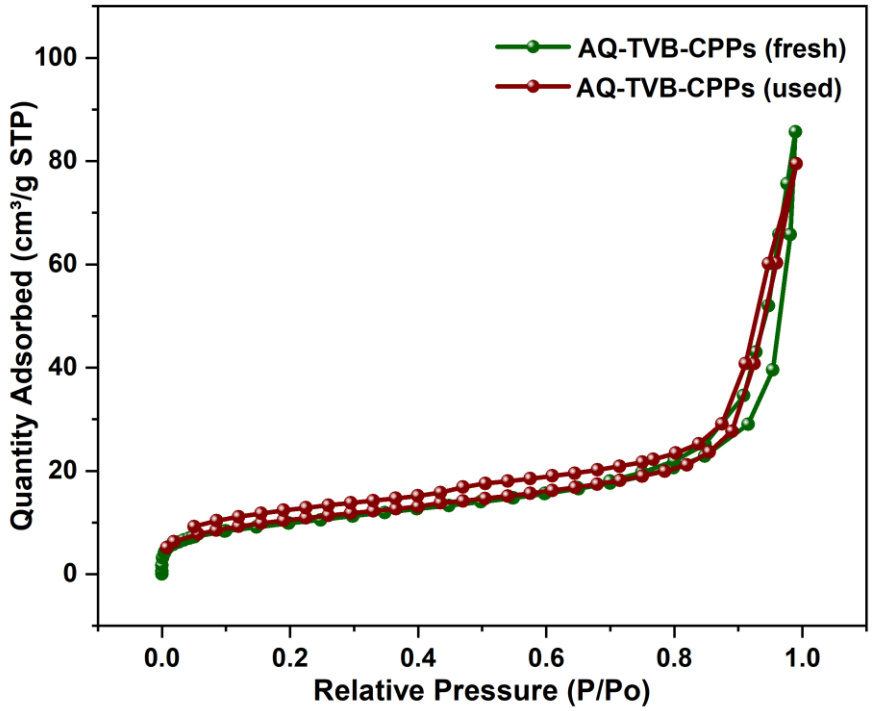


Figure S6. N_2-physisorption isotherm analysis fresh and used catalysis of AQ-TVB-CCPs.

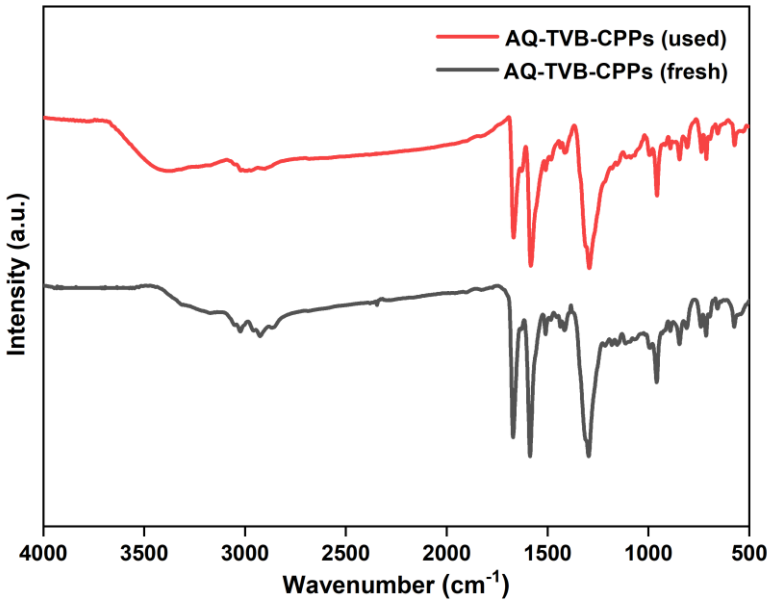


Figure S7. FT-IR spectra of fresh and used AQ-TVB-CPPs.

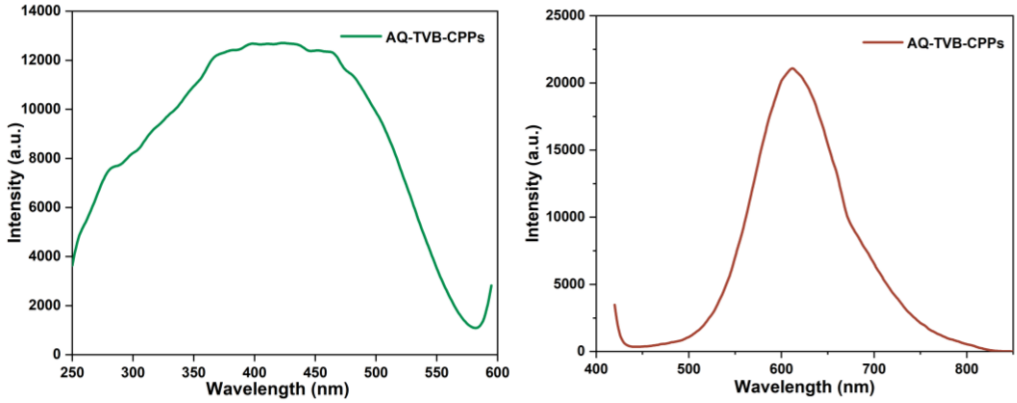


Figure S8. Excitation spectrum of AQ-TVB-CPPs (lfet) and Emission spectrum of AQ-TVB-CPPs (right).

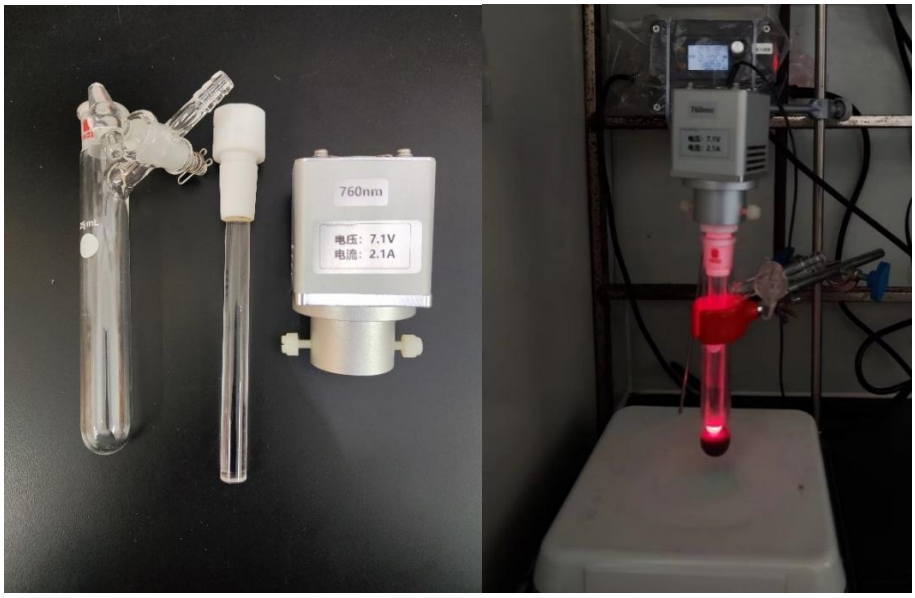


Figure S9. Photoreactor setup used in this study.

Figure S10. Photoreactor setup used in this gram-scale reaction.

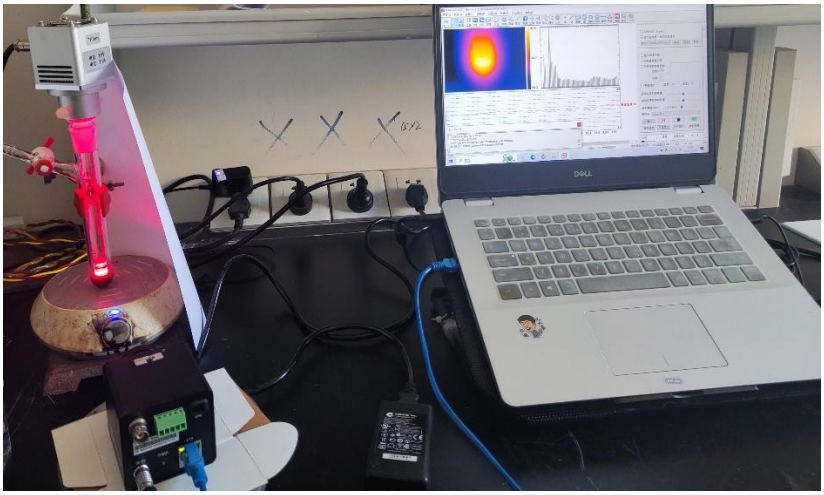


Figure S11. Photothermal experimental apparatus.

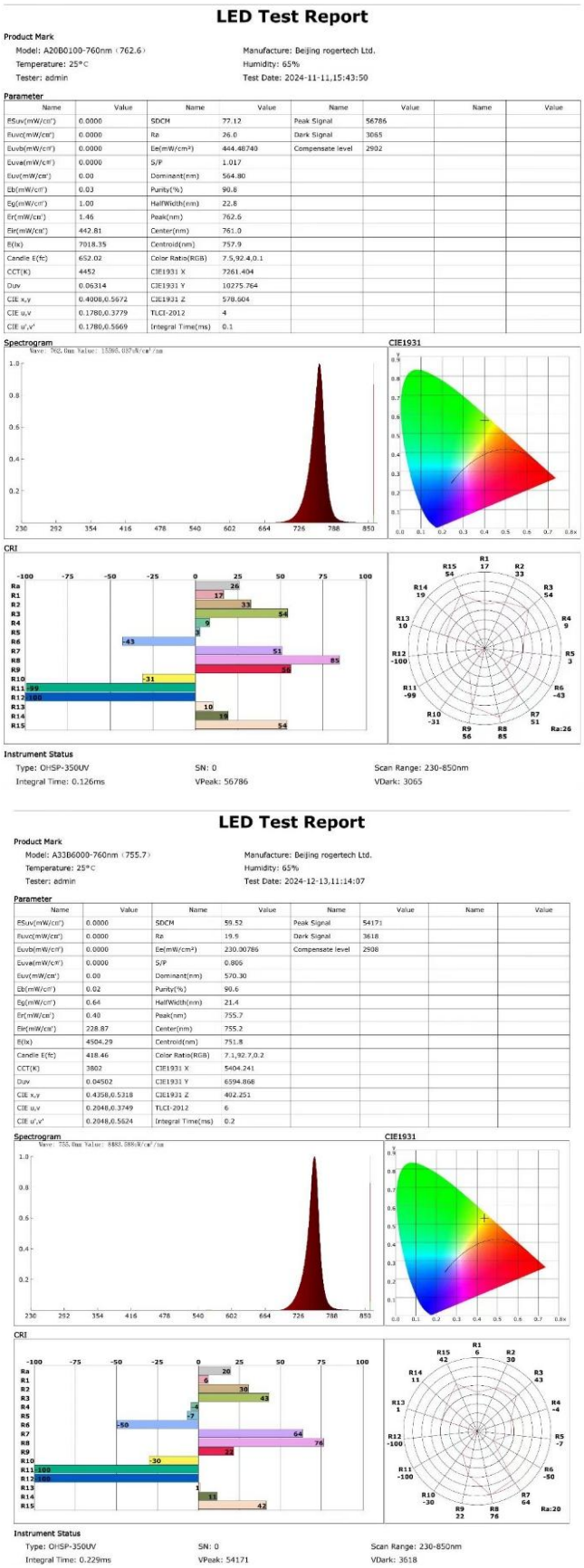
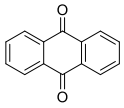


Figure S12. Detailed information on two types of NIR light sources.

4. Calculation of HOMO and LUMO



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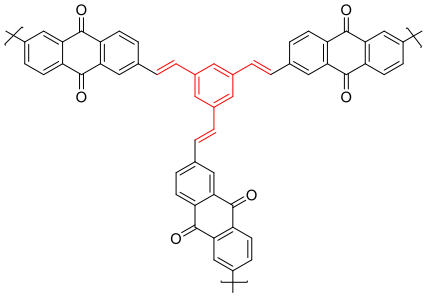

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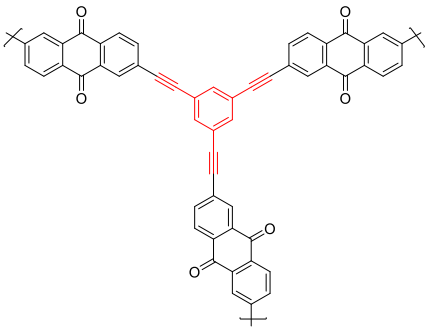

AQ-TrE-CPPs
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AQ-TrE-CPPs

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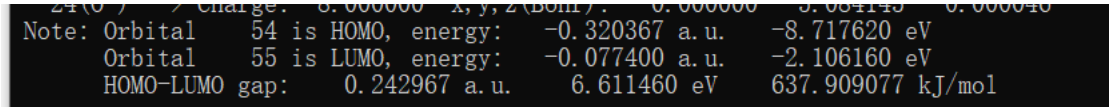

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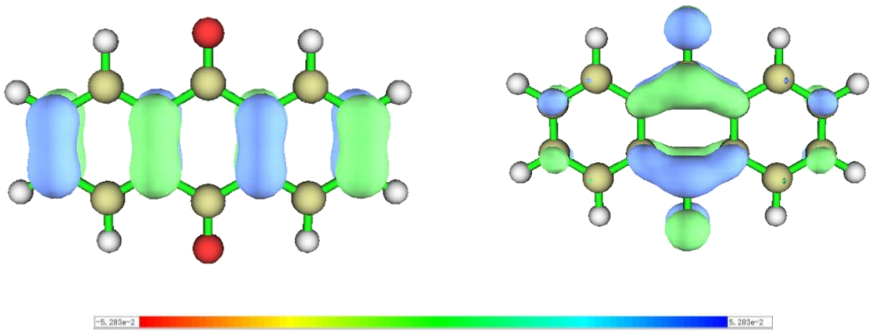

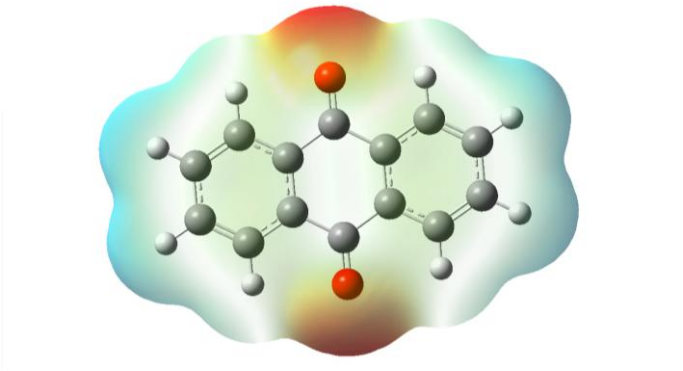

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Note: Orbital   201 is HOMO, energy:   -0.263343 a.u.    -7.165935 eV
      Orbital   202 is LUMO, energy:   -0.082140 a.u.    -2.235146 eV
      HOMO-LUMO gap:    0.181203 a.u.     4.930789 eV    475.748893 kJ/mol
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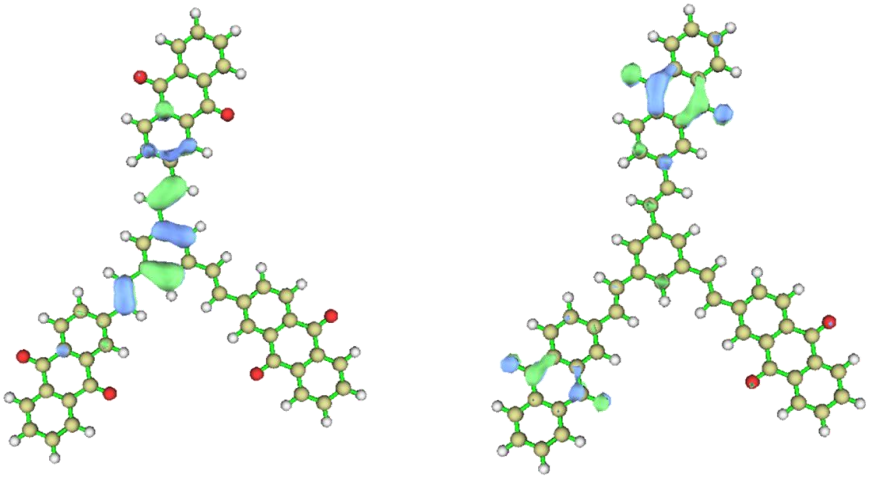
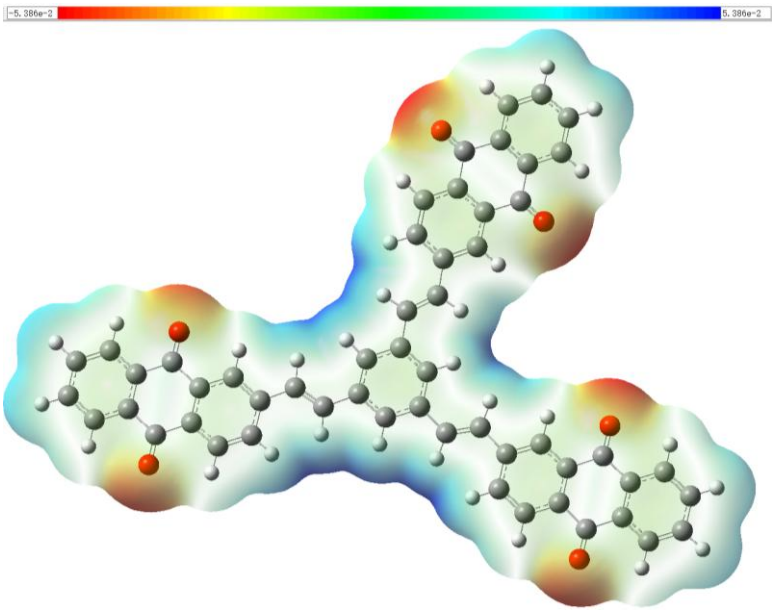
HOMO LUMO





AQ-TrE-CPPs:

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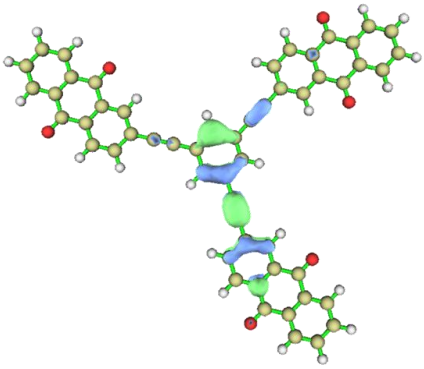
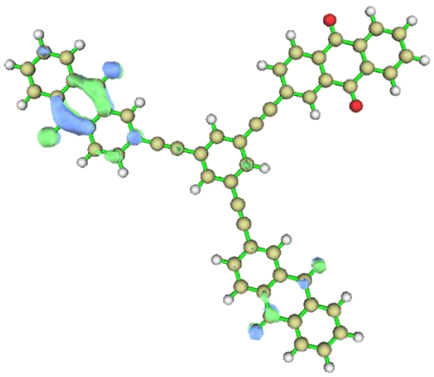
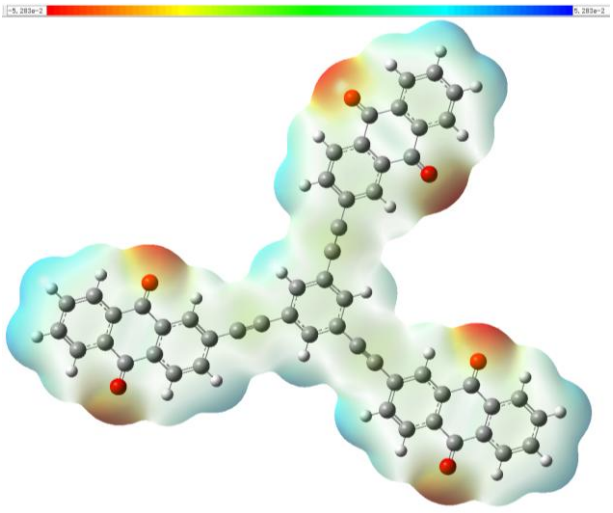
HOMO

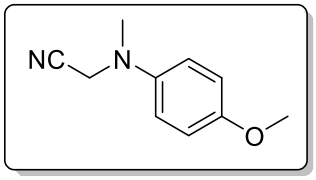


LUMO

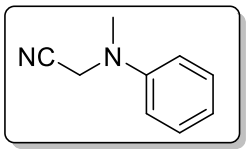




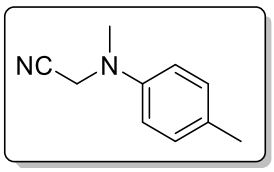
5. Characterization data of all products obtained based on General procedures I



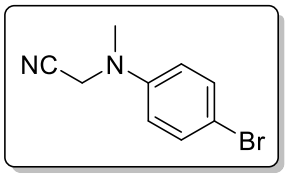
2-((4-methoxyphenyl)(methyl)amino)acetonitrile (**3a**). Yellow oil; Yield = 90%, 31.7 mg (PE/EA = 10:1) **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.88 (d, 4H), 4.07 (s, 2H), 3.77 (s, 3H), 2.92 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.4, 142.2, 117.8, 115.5, 114.8, 55.6, 44.0, 40.0; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{10}H_{13}N_2O]^+$ 177.1022, found 177.1019.



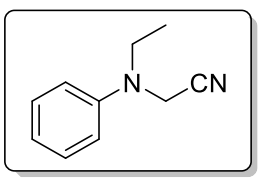
2-(methyl(phenyl)amino)acetonitrile (**3b**). Yellow oil; Yield = 85%, 24.8 mg (PE/EA = 10:1); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.35 – 7.32 (m, 2H), 6.95 – 6.93 (m, 1H), 6.89 – 6.88 (m, 2H), 4.17 (s, 2H), 3.01 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 147.8, 129.5, 120.2, 115.6, 114.9, 42.3, 39.3. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_9H_{11}N_2]^+$ 147.0917, found 147.0915.



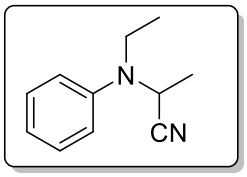
2-(methyl(p-tolyl)amino)acetonitrile(**3c**). Yellow oil; Yield = 87%, 27.9 mg (PE/EA = 10:1); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.14 – 7.12 (m, 2H), 6.82 – 6.80 (m, 2H), 4.14 (s, 2H), 2.97 (s, 3H), 2.30 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 145.8, 130.1, 130.0, 116.6, 115.2, 43.0, 39.6, 20.5. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{10}H_{13}N_2]^+$ 161.1073, found 161.1071.



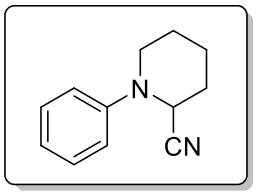
2-((4-bromophenyl)(methyl)amino)acetonitrile(**3d**). Yellow oil; Yield = 76%, 34.0 mg (PE/EA = 10:1); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.42 – 7.38 (m, 2H), 6.74 – 6.73 (m, 2H), 4.15 (s, 2H), 3.00 (s, 3H).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ 146.9, 132.4, 116.6, 115.2, 112.8, 42.3, 39.5. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_9H_{10}BrN_2]^+$ 225.0022, found 225.0019.



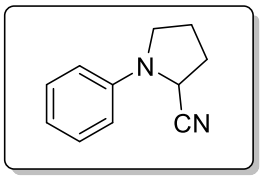
2-(ethyl(phenyl)amino)acetonitrile(**3e**). Yellow oil; Yield = 62%, 19.8 mg (PE/EA = 10:1); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.33 – 7.30 (m, 2), 6.92 – 6.86 (m, 3H), 4.15 (s, 2H), 3.47 – 3.43 (m, 2H), 1.25 (t, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 147.0, 129.7, 120.0, 116.5, 115.1, 46.4, 39.7, 12.4. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{10}H_{13}N_2]^+$ 161.1073, found 161.1068.



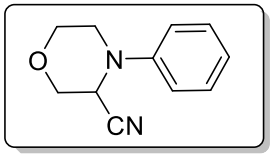
2-(ethyl(phenyl)amino)propanenitrile(**3f**). Yellow oil; Yield = 66%, 23.0 mg (PE/EA = 10:1); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.33 – 7.30 (m, 2H), 7.01 – 6.97 (m, 3H), 4.50 – 4.46 (m, 1H), 3.40 – 3.31 (m, 2H), 1.57 (d, 3H), 1.19 (t, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 146.9, 129.5, 121.9, 119.6, 119.1, 48.4, 43.7, 18.6, 14.0. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{11}H_{15}N_2]^+$ 175.1230, found 175.1228.



1-phenylpiperidine-2-carbonitrile(**3g**). Yellow oil; Yield = 73%, 27.2 mg (PE/EA = 10:1); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.34 – 7.20 (m, 2H), 7.03 – 6.99 (m, 3H), 4.63 (t, 1H), 3.47 – 3.44 (t, 1H), 3.07 – 3.02 (m, 1H), 2.07 – 2.00 (m, 2H), 1.88 – 1.84 (m, 2H), 1.75 – 1.68 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 149.8, 129.5, 122.4, 118.5, 117.3, 52.2, 46.8, 29.4, 25.2, 20.3. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{12}H_{15}N_2]^+$ 187.1230, found 187.1233.

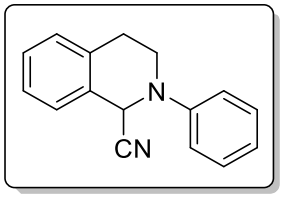


1-phenylpyrrolidine-2-carbonitrile(**3h**). Yellow oil; Yield = 67%, 23.1 mg (PE/EA = 10:1); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.32 – 7.29 (m, 2H), 6.84 (m, 1H), 6.71 – 6.69 (m, 2H), 4.46 – 4.44 (m, 1H), 349 – 3.45 (m, 1H), 3.40 – 3.35 (m, 1H), 2.44 – 2.41 (m, 1H), 2.34 – 2.18 (m, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 145.3, 129.6, 119.4, 118.4, 112.8, 49.2, 47.6, 31.7, 24.1. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{11}H_{13}N_2]^+$ 173.1073, found 173.1067.

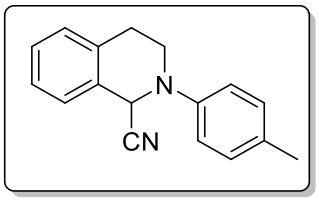


4-phenylmorpholine-3-carbonitrile(**3i**). Yellow oil; Yield = 63%, 23.7 mg (PE/EA = 10:1); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.37 – 7.34 (m, 2H), 7.06 – 7.03 (m, 1H), 7.00 – 6.98 (m, 2H), 4.43 (t, 1H), 4.18 – 4.15 (m, 1H), 4.11 – 4.09 (m, 1H), 3.93 – 3.91 (m, 1H), 3.78 – 3.73 (m, 1H), 3.31 – 3.28 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.0, 129.3, 122.4, 117.0, 115.7,

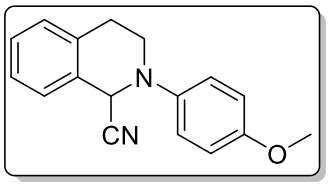
67.8, 66.6, 50.8, 45.2. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{11}H_{13}N_2O]^+$ 189.1022, found 189.1025.



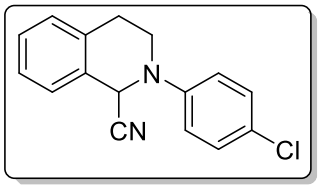
2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(**3j**). Yellow oil; Yield = 95%, 44.5 mg (PE/EA = 10:1); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.41 – 7.38 (m, 2H), 7.36 – 7.30 (m, 3H), 7.29 – 7.27 (m, 1H), 7.13 – 7.11 (m, 2H), 7.07 – 7.04 (m, 1H), 5.55 (s, 1H), 3.82 – 3.78 (m, 1H), 3.54 – 3.49 (m, 1H), 3.22 – 3.15 (m, 1H), 3.02 – 2.97 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.5, 134.7, 129.7, 129.7, 129.5, 128.9, 127.2, 127.0, 122.0, 117.9, 117.7, 53.3, 44.3, 28.6. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{16}H_{15}N_2]^+$ 235.1230, found 235.1227.



2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(**3k**). Yellow oil; Yield = 91%, 45.2 mg (PE/EA = 10:1); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.36-7.30 (m, 3H), 7.29-7.27 (m, 1H), 7.22-7.20 (m, 2H), 7.06-7.04 (m, 2H), 5.50 (s, 1H), 3.76 – 3.72 (m, 1H), 3.51-3.45 (m, 1H), 3.23-3.16 (m, 1H), 3.01-2.96 (m, 1H), 2.36 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 146.4, 134.6, 131.9, 130.2, 129.7, 129.5, 128.8, 127.2, 126.9, 118.4, 117.8, 54.2, 44.5, 28.7, 20.7. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{17}H_{17}N_2]^+$ 249.1386, found 249.1383.

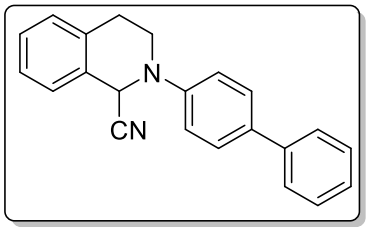


2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(**3l**). Yellow oil; Yield = 90%, 47.5 mg (PE/EA = 10:1); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.35 – 7.26 (m, 4H), 7.14 – 7.11 (m, 2H), 6.97 – 6.94 (m, 2H), 5.40 (s, 1H), 3.84(s, 3H), 3.64 – 3.60 (m, 1H), 3.51 – 3.45 (m, 1H), 3.24 – 3.17 (m, 1H), 3.00 – 2.95 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 155.8, 142.7, 134.5, 129.8, 129.6, 128.8, 127.2, 126.8, 121.2, 117.7, 114.9, 55.8, 55.7, 45.0, 28.8. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{17}H_{17}N_2O]^+$ 265.1335, found 265.1331.

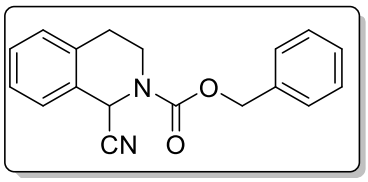


2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(**3m**). Yellow oil; Yield = 87%, 47.5 mg (PE/EA = 10:1); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.37 – 7.31 (m, 5H), 7.30 – 7.27 (m, 1H), 7.05 – 7.02 (m, 2H), 5.48 (s, 1H), 3.76 – 3.71 (m, 1H), 3.51 – 3.46 (m, 1H), 3.21 – 3.14 (m, 1H), 3.00 – 2.98 (m, 1H).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ 147.1, 134.5, 129.6, 129.5,

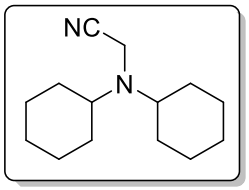
129.3, 129.0, 127.2, 127.1, 127.1, 119.0, 117.6, 53.3, 44.4, 28.6. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{16}H_{14}ClN_2]^+$ 269.0840, found 269.0842.



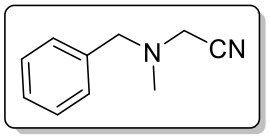
2-([1,1'-biphenyl]-4-yl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(**3n**). Yellow oil; Yield = 83%, 51.5 mg (PE/EA = 10:1); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.62 – 7.57 (m, 4H), 7.45 – 7.42 (m, 2H), 7.34 –7.31 (m, 4H), 7.27 –7.26 (m, 1H), 7.17 – 7.15 (m, 2H), 5.58 (s, 1H), 3.86 – 3.82 (m, 1H), 3.56 –3.51 (m, 1H), 3.23 –3.16 (m, 1H), 3.03 –2.99 (m, 1H).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ 147.7, 140.8, 134.7, 134.7, 129.6, 129.5, 129.0, 128.9, 128.3, 127.2, 127.1, 127.0, 126.8, 117.9, 117.7, 53.1, 44.3, 28.7. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{22}H_{19}N_2]^+$ 311.1543, found 311.1540.



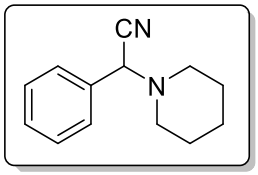
benzyl 1-cyano-3,4-dihydroisoquinoline-2(1H)-carboxylate(**3o**). Yellow oil; Yield = 43%, 25.1 mg (PE/EA = 5:1); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.23 – 8.21 (m, 1H), 7.54 – 7.51 (m, 3H), 7.44 – 7.36 (m, 5H), 7.27 – 7.25 (m, 1H), 5.41 (s, 2H), 4.14 – 4.12 (m, 2H), 3.07 – 3.05 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 163.9, 154.7, 139.7, 135.6, 133.3, 129.93, 129.2, 128.8, 128.5, 128.2, 127.5, 127.4, 68.9, 44.9, 28.4. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{18}H_{17}N_2O_2]^+$ 293.1285, found 293.1283.



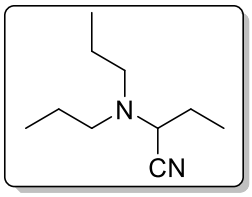
2-(dicyclohexylamino)acetonitrile(**3p**). Colorless oil; Yield = 78%, 44.0 mg (PE/EA = 10:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 3.59 (s, 2H), 2.77 – 2.70 (m, 2H), 1.85 – 1.76 (m, 9H), 1.63 – 1.59 (m, 3H), 1.30 – 1.23 (m, 8H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 119.7, 57.8, 34.3, 31.1, 26.1, 25.9. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{14}H_{25}N_2]^+$ 221.2012, found 221.2013.



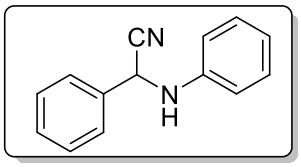
2-(benzyl(methyl)amino)acetonitrile(**3q**). Colorless oil, Yield = 79%, 25.1 mg (PE/EA = 5:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.37 – 7.27 (m, 5H), 3.61 (s, 2H), 3.45 (s, 2H), 2.44 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 137.1, 129.1, 128.8, 128.0, 114.7, 60.24, 44.3, 42.5. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{10}H_{13}N_2]^+$ 161.1073, found 161.1069.



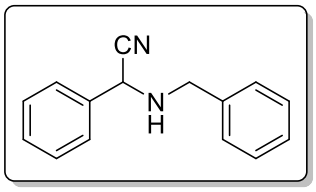
2-phenyl-2-(piperidin-1-yl)acetonitrile(**3r**). Colorless oil, Yield = 68%, 27.2 mg (PE/EA = 20:1); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.56 – 7.53 (m, 2H), 7.42 – 7.35 (m, 3H), 4.84 (s, 1H), 2.55 – 2.51 (m, 4H), 1.66 – 1.56 (m, 4H), 1.51 – 1.49 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 129.0, 128.9, 128.8, 128.7, 128.0, 115.7, 63.1, 25.9, 24.0. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{13}H_{17}N_2]^+$ 201.1386, found 201.1381.



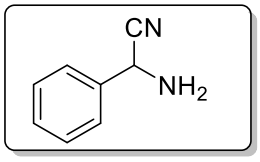
2-(dipropylamino)butanenitrile(**3s**). Colorless oil, Yield = 69%, 27.2 mg (PE/EA = 10:1); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 3.47 (t, *J* = 7.8 Hz, 1H), 2.53 – 2.47 (m, 2H), 2.38 – 2.33 (m, 2H), 1.82 – 1.70 (m, 2H), 1.51 – 1.41 (m, 4H), 1.04 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 118.7, 56.5, 53.7, 25.5, 21.3, 11.8, 10.9. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{10}H_{21}N_2]^+$ 169.1699, found 169.1700.



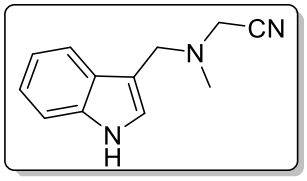
2-phenyl-2-(phenylamino)acetonitrile(**3t**). Colorless oil, Yield = 81%, 33.7 mg (PE/EA = 10:1); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.63 – 7.61 (m, 2H), 7.50 –7.45 (m, 3H), 7.31 –7.26 (m, 2H), 6.94 – 6.90 (m, 1H), 6.81 –6.78 (m, 2H), 5.45 (s, 1H), 4.06 (s, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 144.8, 134.1, 129.7, 129.7, 129.5, 127.4, 120.4, 118.3, 114.3, 50.4. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{14}H_{13}N_2]^+$ 209.1073, found 209.1073.



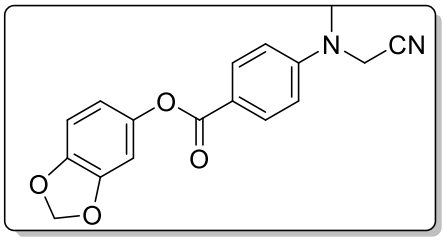
2-(benzylamino)-2-phenylacetonitrile(**3u**). Colorless oil, Yield = 77%, 34.2 mg (PE/EA = 20:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.56 – 7.54 (m, 2H), 7.44 – 7.38 (m, 5H), 7.36 – 7.34 (m, 2H), 7.32 – 7.30 (m, 1H), 4.76 (s, 1H), 4.07 (d, 1H), 3.97 (d, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 138.2, 134.9, 129.2, 129.1, 128.8, 128.6, 127.8, 127.4, 118.9, 53.6, 51.4. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{15}H_{15}N_2]^+$ 223.1230, found 223.1230.



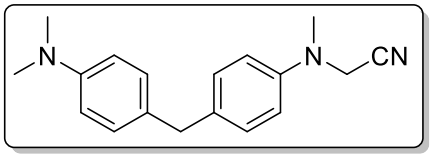
2-amino-2-phenylacetonitrile(**3v**). Colorless oil, Yield = 77%, 16.1 mg (PE/EA = 20:1); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.55 – 7.53 (m, 2H), 7.44 – 7.39 (m, 3H), 4.92 (s, 1H), 1.94 (s, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 136.4, 129.2, 129.2, 126.8, 121.0, 47.4. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_8H_9N_2]^+$ 133.0760, found 133.0761.



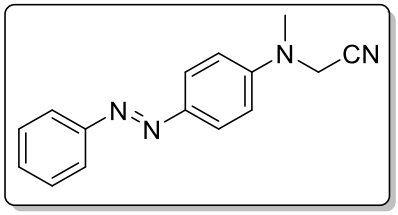
2-(((1H-indol-3-yl)methyl)(methyl)amino)acetonitrile(**3w**). Yellow oil, Yield = 54%, 21.5 mg (DCM/MeOH = 10:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.18 (s, 1H), 7.75 – 7.73 (m, 1H), 7.39 – 7.37 (m, 1H), 7.26 – 7.21 (m, 1H), 7.18 – 7.13 (m, 2H), 3.82 (s, 2H), 3.46 (s, 2H), 2.51 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 136.6 127.3, 124.2, 122.6, 120.0, 119.6, 115.0, 111.8, 111.3, 51.3, 43.7, 42.5. **HRMS**(ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{12}H_{14}N_3]^+$ 200.1182, found 200.1186.



benzo[d][1,3]dioxol-5-yl 4-((cyanomethyl)(methyl)amino)benzoate (**3x**). Yellow oil, Yield = 45%, 27.9 mg (PE/EA = 8:1); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.91 – 7.88 (m, 2H), 6.94 – 6.90 (m, 2H), 6.80 – 6.79 (m, 1H), 6.55 – 6.53 (m, 2H), 5.96 (s, 2H), 5.20 (s, 2H), 2.87 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 166.8, 153.1, 147.9, 147.5, 131.8, 130.6, 122.1, 118.2, 111.2, 109.0, 108.3, 101.2, 66.0, 30.3. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{17}H_{15}N_2O_4]^+$ 311.1026, found 311.1030.

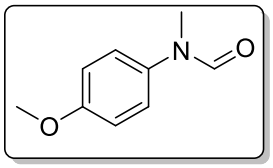


2-((4-(4-(dimethylamino)benzyl)phenyl)(methyl)amino)acetonitrile(**3y**). Yellow oil; Yield = 63%, 35.2 mg (PE/EA = 8:1); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.14 – 7.12 (m, 2H), 7.07 – 7.05 (m, 2H), 6.81 – 6.79 (m, 2H), 6.73 – 6.72 (m, 2H), 4.13 (s, 2H), 3.84 (s, 2H), 2.97 (s, 3H), 2.92 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 146.1, 134.2, 129.9, 129.6, 115.6, 115.5, 113.4, 42.8, 41.2, 40.1, 39.6. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{18}H_{22}N_3]^+$ 280.1808, found 280.1804.

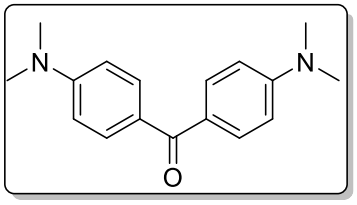


(*E*)-2-(methyl(4-(phenyldiazenyl)phenyl)amino)acetonitrile (**3z**). Yellow oil, Yield = 57%, 28.5 mg (PE/EA = 5:1); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.97 – 7.94 (m, 2H), 7.89 – 7.87 (m,

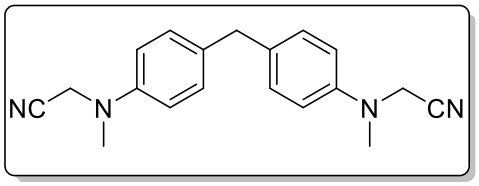
2H), 7.52 – 7.48 (m, 2H), 7.45 – 7.43 (m, 1H), 6.95 – 6.92 (m, 2H), 4.29 (s, 2H), 3.15 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 153.0, 149.9, 146.1, 130.4, 129.2, 125.0, 122.6, 113.9, 41.7, 39.5. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $[C_{15}H_{15}N_4]^+$ 251.1291, found 251.1292.



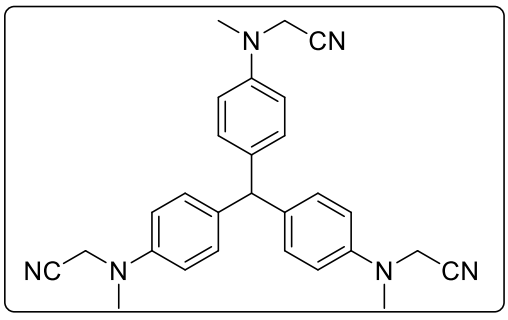
N-(4-methoxyphenyl)-*N*-methylformamide (**3aa**). White solid; Yield = 17%,5.6 mg (PE/EA = 5:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.34 (s, 1H), 7.12 – 7.06 (m, 2H), 6.95 – 6.90 (m, 2H), 3.82 (s, 3H), 3.27 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 162.6, 124.8, 114.9, 55.7, 32.9. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_9H_{12}NO_2]^+$ 166.0863, found 166.0861.



bis(4-(dimethylamino)phenyl)methanone (**3ya**). White solid; Yield = 43%, 23.1 mg (PE/EA = 5:1); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.18 (d, 4H), 6.69 (d, 4H), 2.94 (s, 12H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 190.4, 150.3, 128.5, 124.3, 112.8, 40.6. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{17}H_{20}N_2O]^+$ 269.1648, found 269.1650.

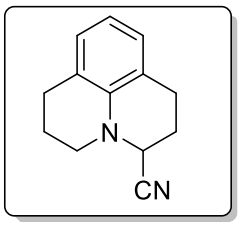


2,2'-((methylenebis(4,1-phenylene))bis(methylazanediyl))diacetonitrile (**3yb**). Yellow oil, Yield = 11%, 6.9 mg (PE/EA = 2:1); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.14 – 7.12 (m, 4H), 6.82 – 6.80 (m, 4H), 4.13 (s, 4H), 3.87 (s, 2H), 2.97 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 146.2, 133.4, 129.9, 115.6, 115.3, 42.6, 40.0, 39.4. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{19}H_{21}N_4]^+$ 305.1761, found 305.1763.



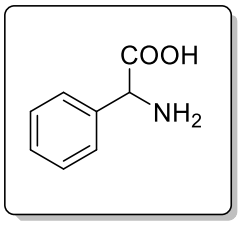
2,2',2''-((methanetriyltris(benzene-4,1-diyl))tris(methylazanediyl))triacetonitrile (**4a**). Purple solid, Yield = 44%, 39.4 mg (PE/EA = 5:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.05 – 7.01 (m, 6H), 6.81 – 6.77 (m, 6H), 5.37 (s, 1H), 4.15 (s, 6H), 2.99 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 146.2, 136.4, 130.4, 115.7, 115.0, 54.3, 42.6, 39.5. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for

$[C_{28}H_{29}N_6]^+$ 449.2448, found 449.2446.



2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline-3-carbonitrile (**4b**). Yellow solid, Yield = 43%,

17.0 mg (PE/EA = 10:1); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.86 – 6.83 (m, 2H), 6.65 (t, *J* = 7.4 Hz, 1H), 4.19 (td, *J* = 3.8, 1.4 Hz, 1H), 3.39 – 3.34 (m, 1H), 3.17 – 3.10 (m, 2H), 2.88 – 2.72 (m, 3H), 2.29 – 2.23 (m, 2H), 2.07 – 2.00 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 139.5, 127.8, 127.2, 123.4, 120.9, 118.6, 118.4, 50.9, 49.4, 27.4, 25.3, 24.3, 22.0. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{13}H_{15}N_2]^+$ 199.1230, found 199.1233.



2-amino-2-phenylacetic acid (**3va**). White solid, Yield = 75%, 22.7 mg; **^{1}H NMR** (400 MHz, Trifluoroacetic acid-*d*) δ 7.53 – 7.37 (m, 5H), 5.32 (s, 1H). **^{13}C NMR** (101 MHz, Trifluoroacetic acid-*d*) δ 165.1, 133.9, 132.3, 130.9, 129.9, 60.3. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_8H_{10}NO_2]^+$ 152.0706, found 152.0708.

6. References

[1] Cao J, Lv D-Q, Yu F, Chiou M-F, Li Y-J, Bao H-L. *Org. Lett*. **2021**, *23*, 3184–3189.

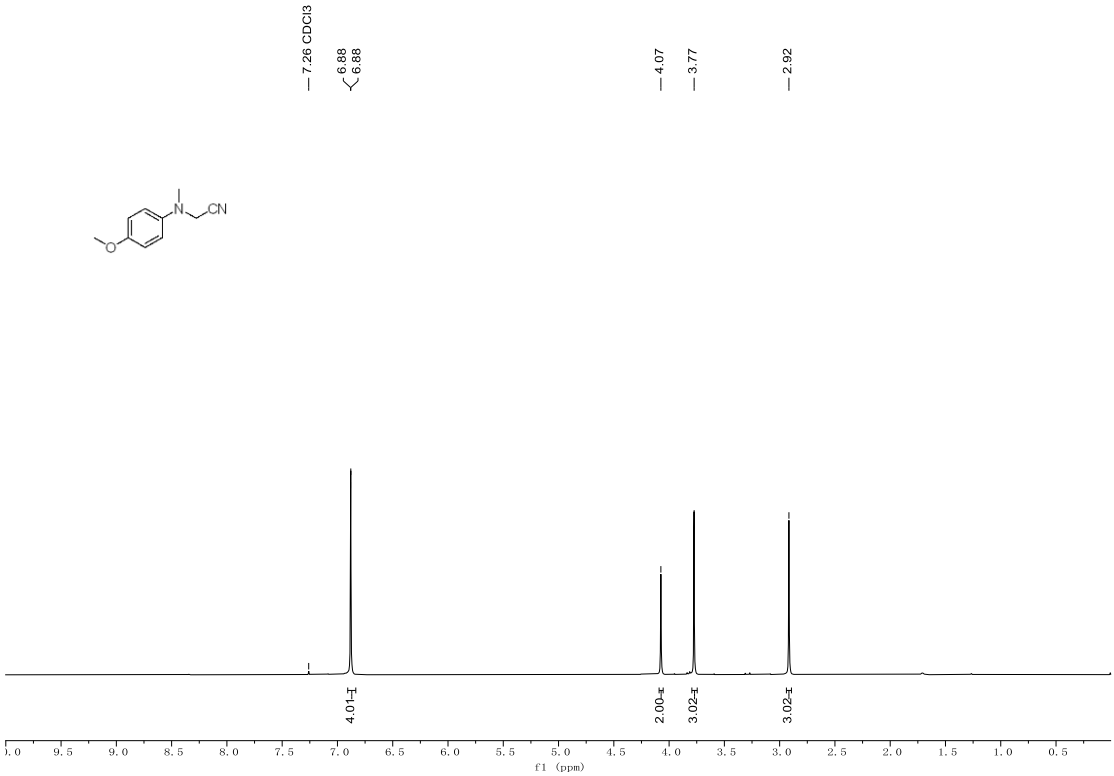
[2] Han W, Ofial AR. *Chem. Commun*. **2009**, 5024–5026.

[3] Wagner A, Han W, Mayer P, Ofial AR. *Adv. Synth. Catal*. **2013**, *355*, 3058–3070.

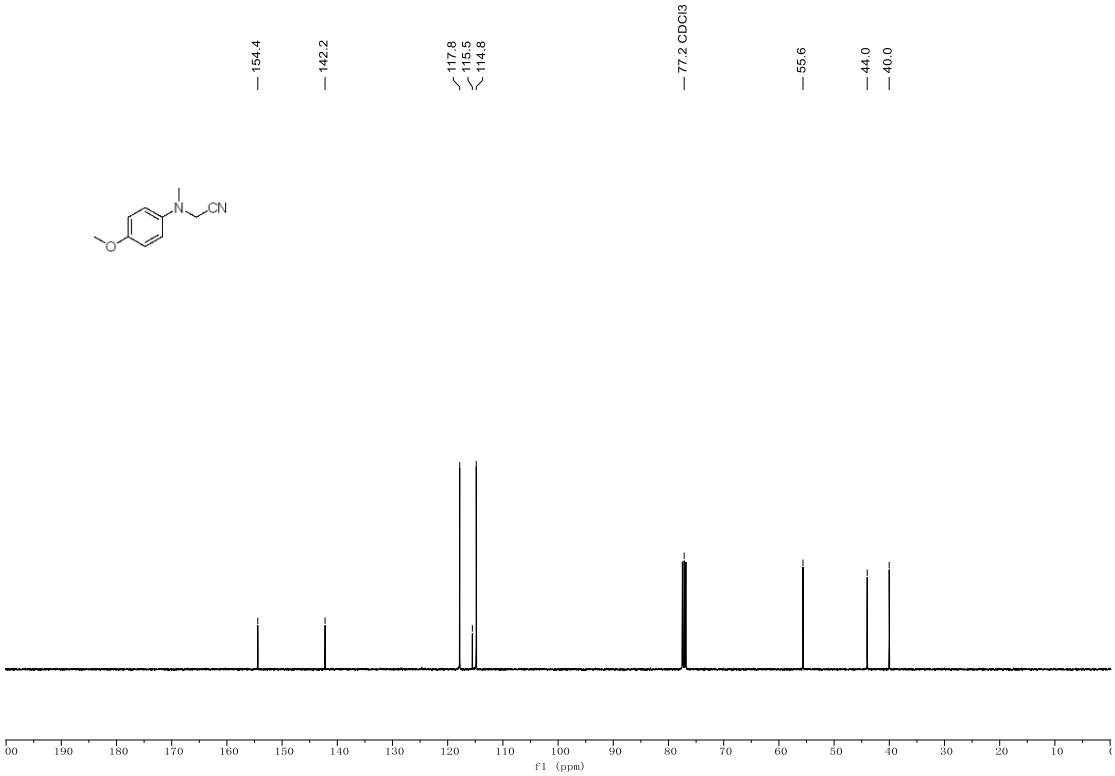
[4] Pacheco JCO, Lipp A, Nauth AM, Acke F, Dietz J-P, Opatz T. *Chem. Eur. J*. **2016**, *22*, 5409–5415.

[5] Ushakov DB, Gilmore K, Kopetzki D, McQuade DT, Seeberger PH. *Angew. Chem. Int. Ed*. **2014**, *53*, 557–561.

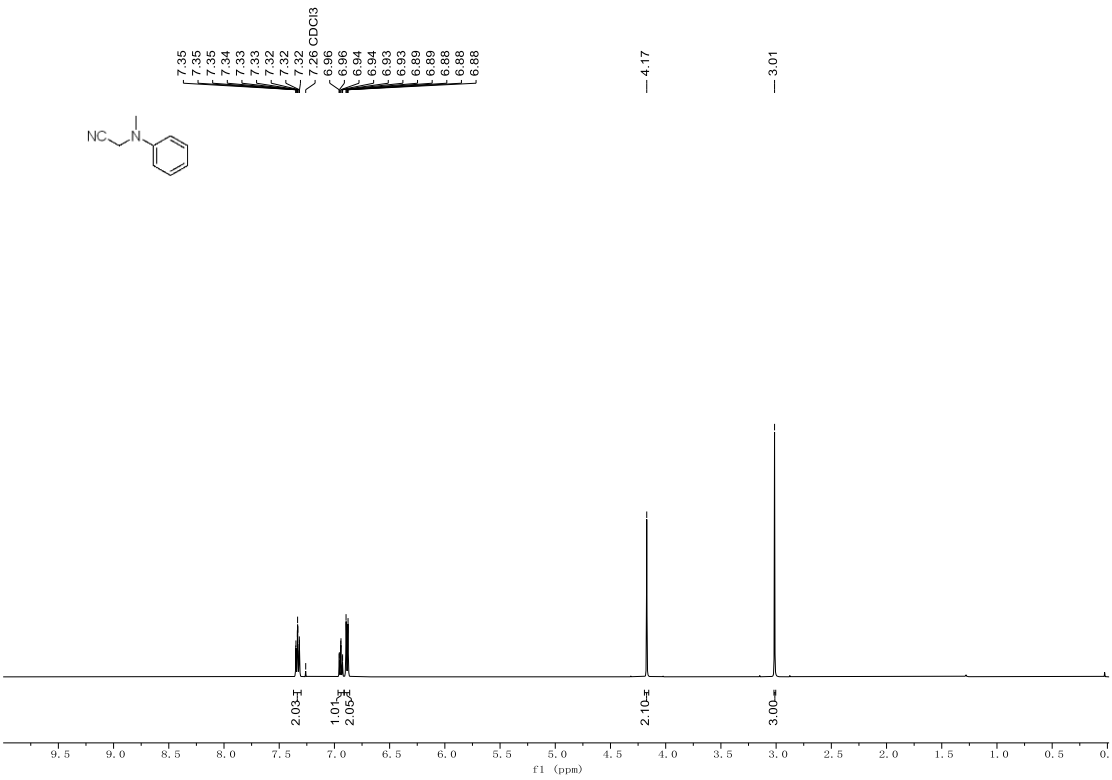
7. Copies of ^{1}H and ^{13}C NMR spectra of all products



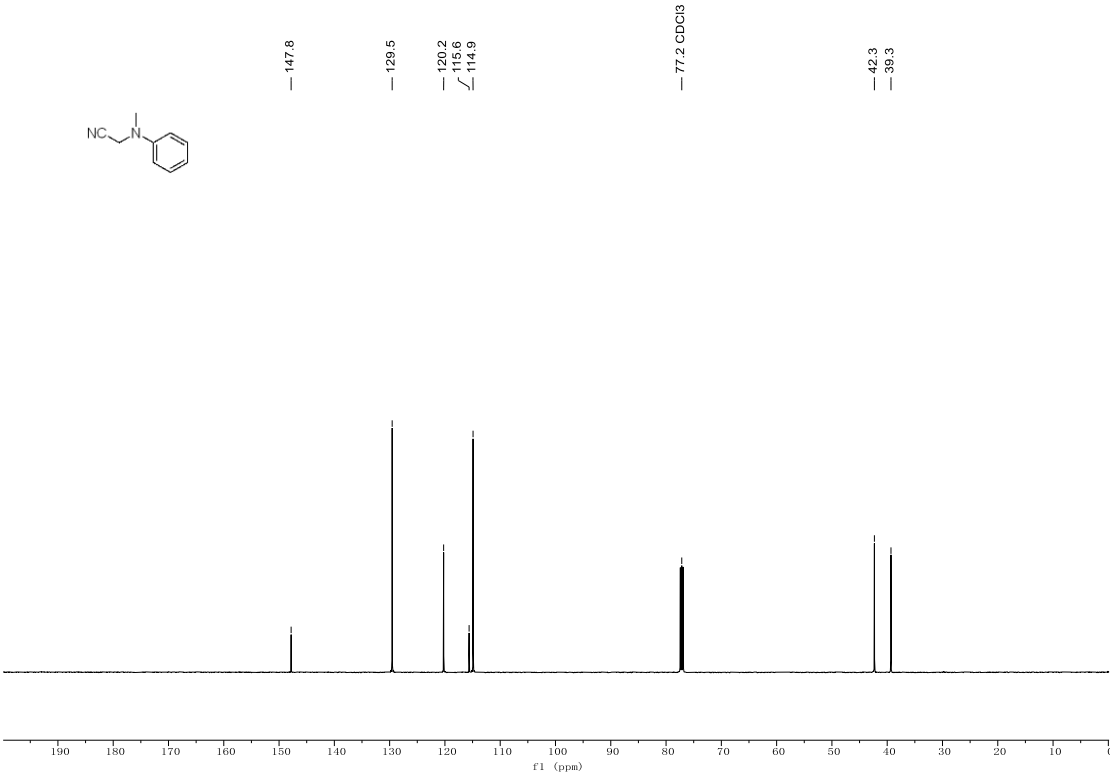
^{1}H NMR of **3a** (400 MHz, Chloroform-*d*).



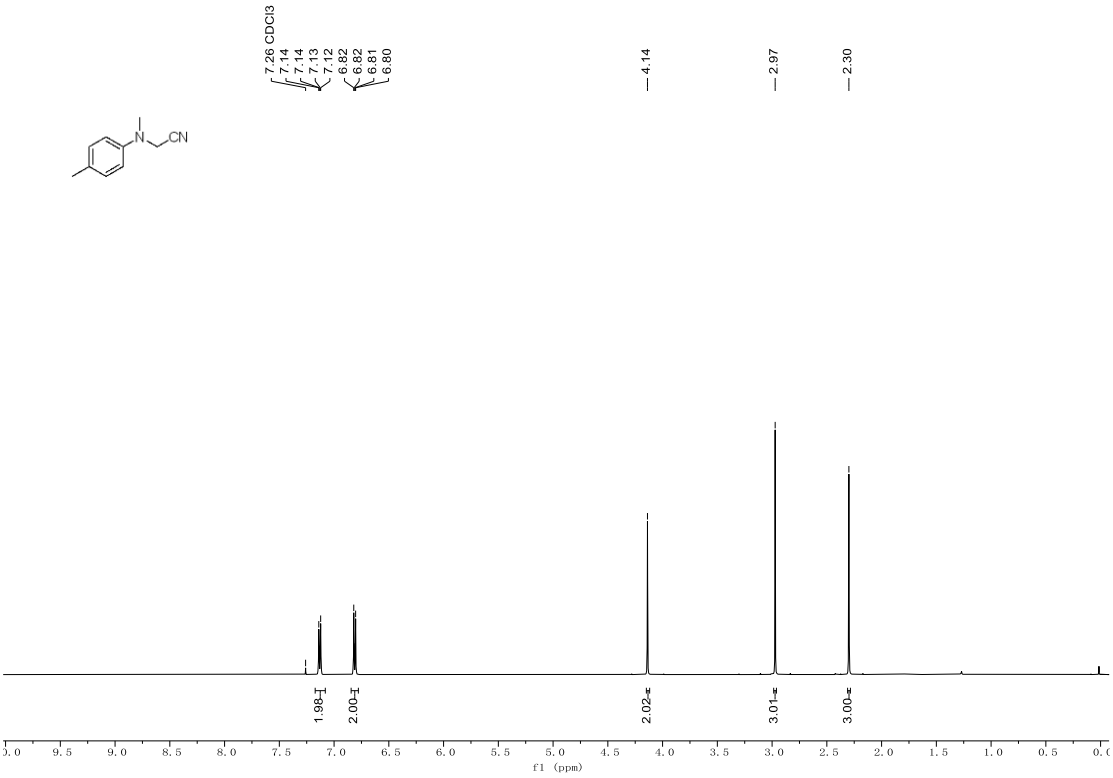
^{13}C NMR of **3a** (101 MHz, Chloroform-*d*).



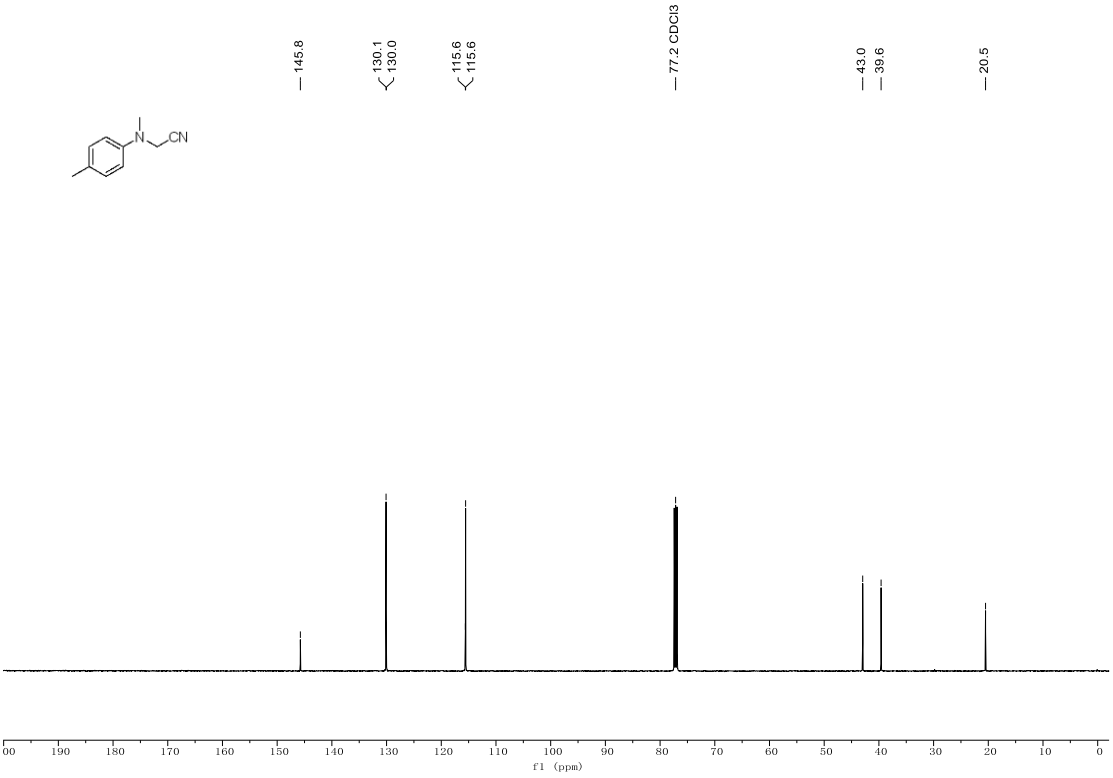
^{1}H NMR of **3b** (500 MHz, Chloroform-*d*).



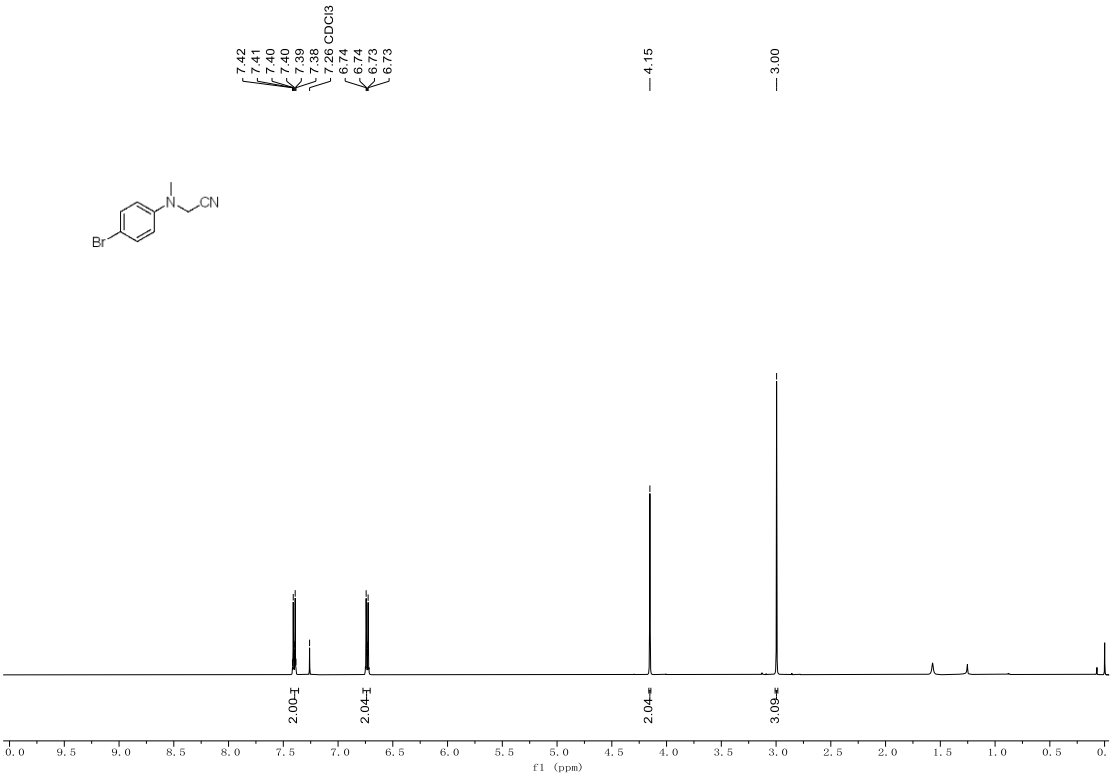
^{13}C NMR of **3b** (126 MHz, Chloroform-*d*).



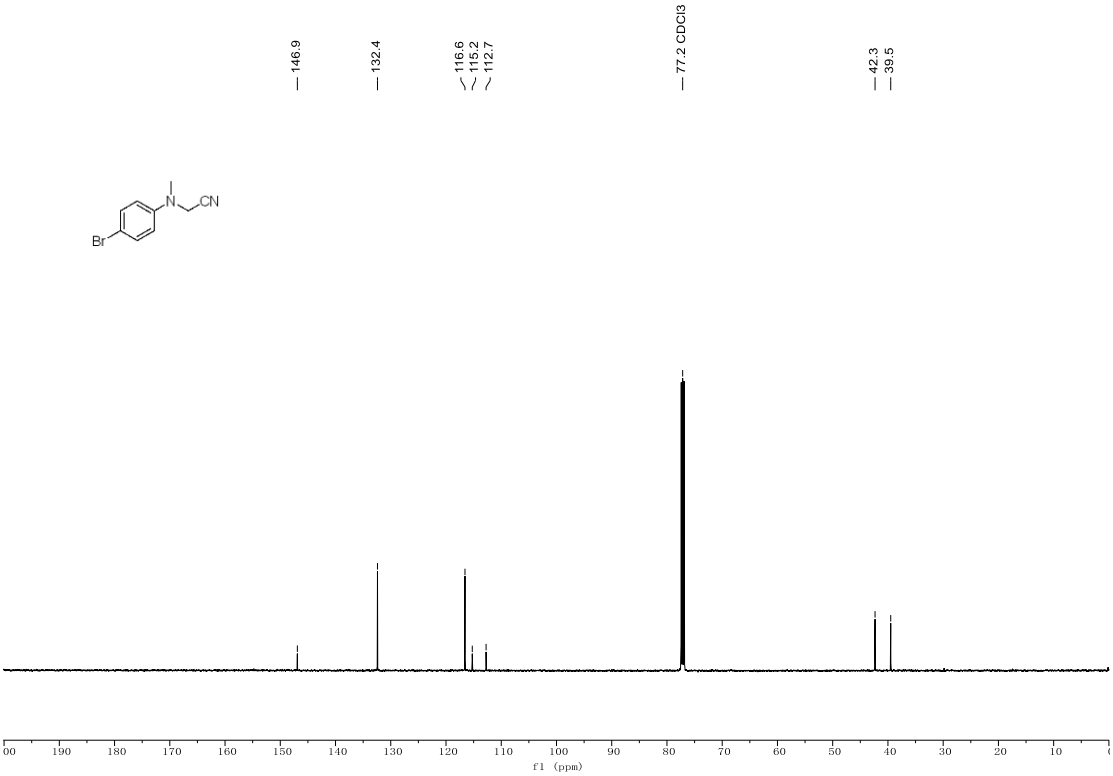
^{1}H NMR of **3c** (500 MHz, Chloroform-*d*).



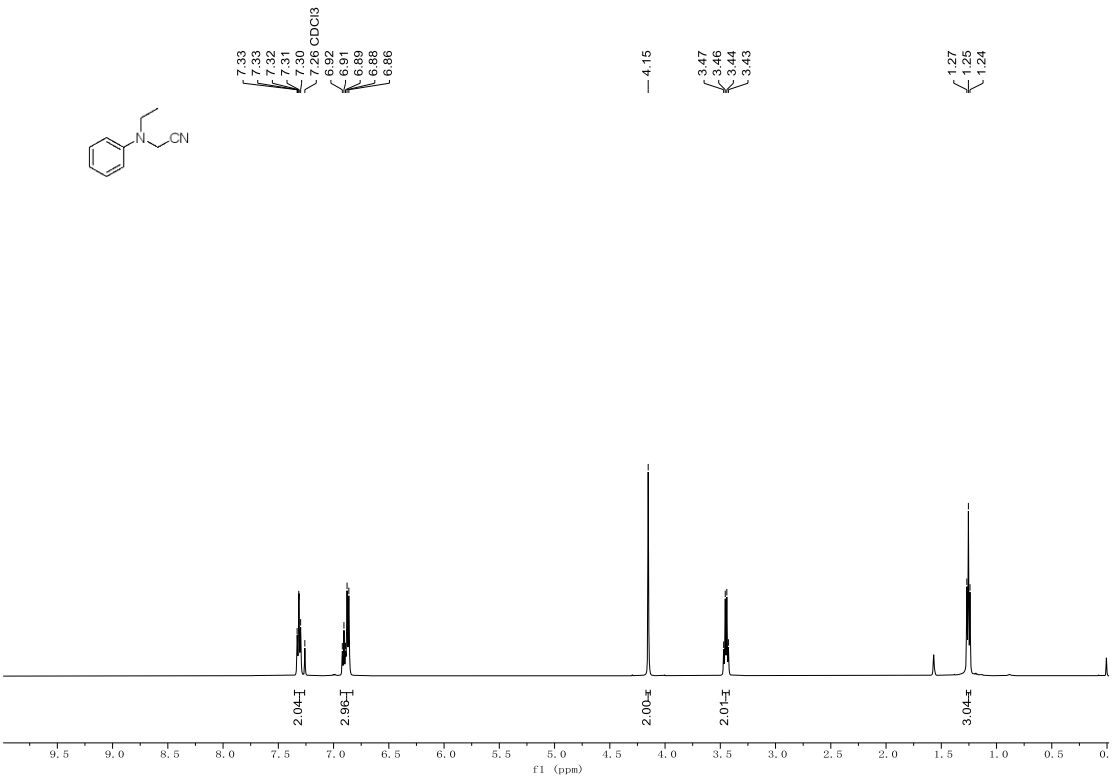
^{13}C NMR of **3c** (126 MHz, Chloroform-*d*).



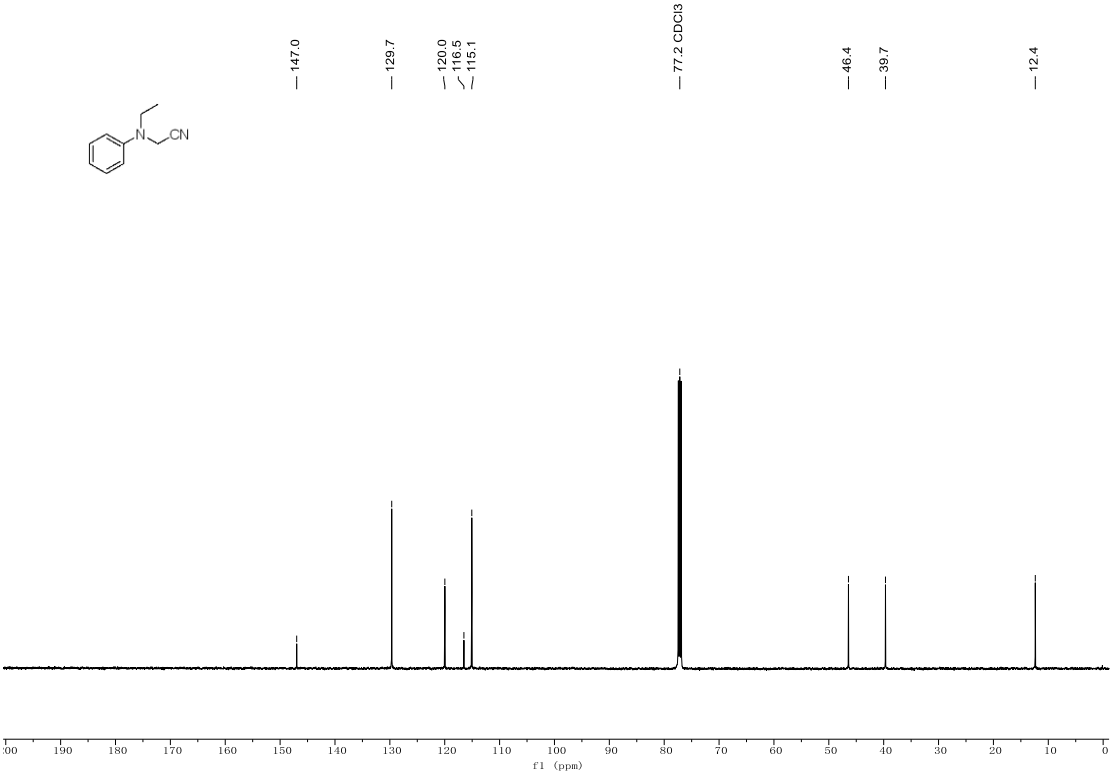
^{1}H NMR of **3d** (500 MHz, Chloroform-*d*).



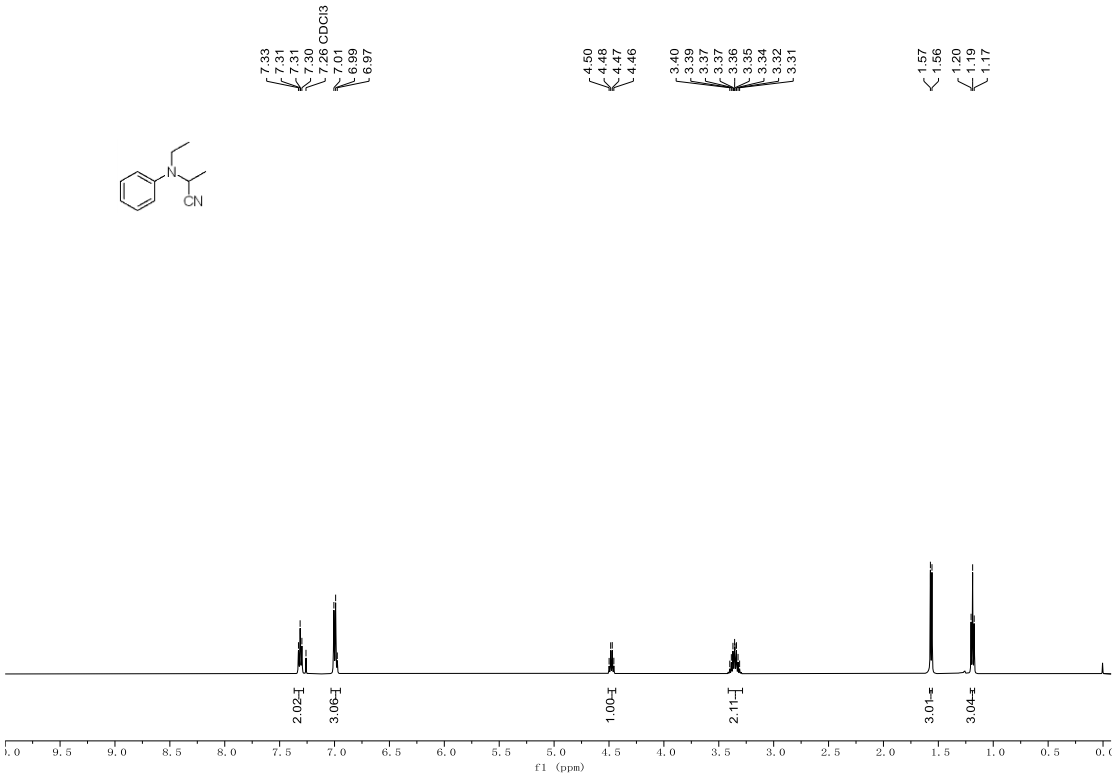
^{13}C NMR of **3d** (126 MHz, Chloroform-*d*).



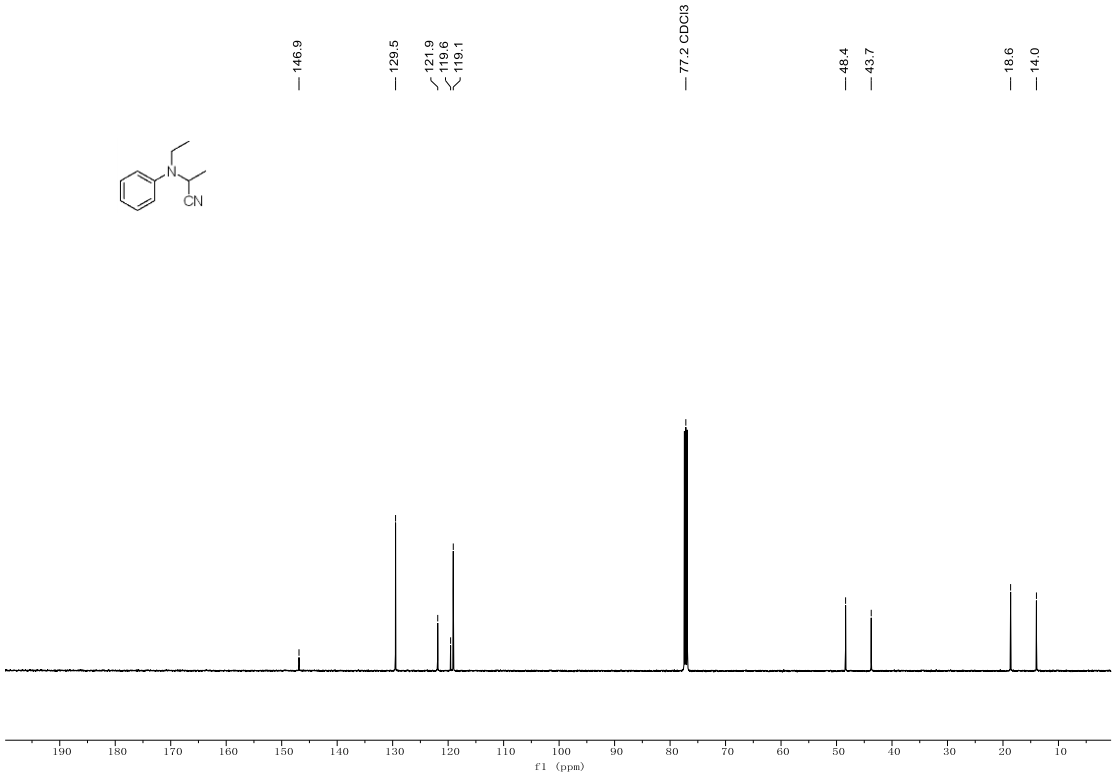
^{1}H NMR of **3e** (500 MHz, Chloroform-*d*).



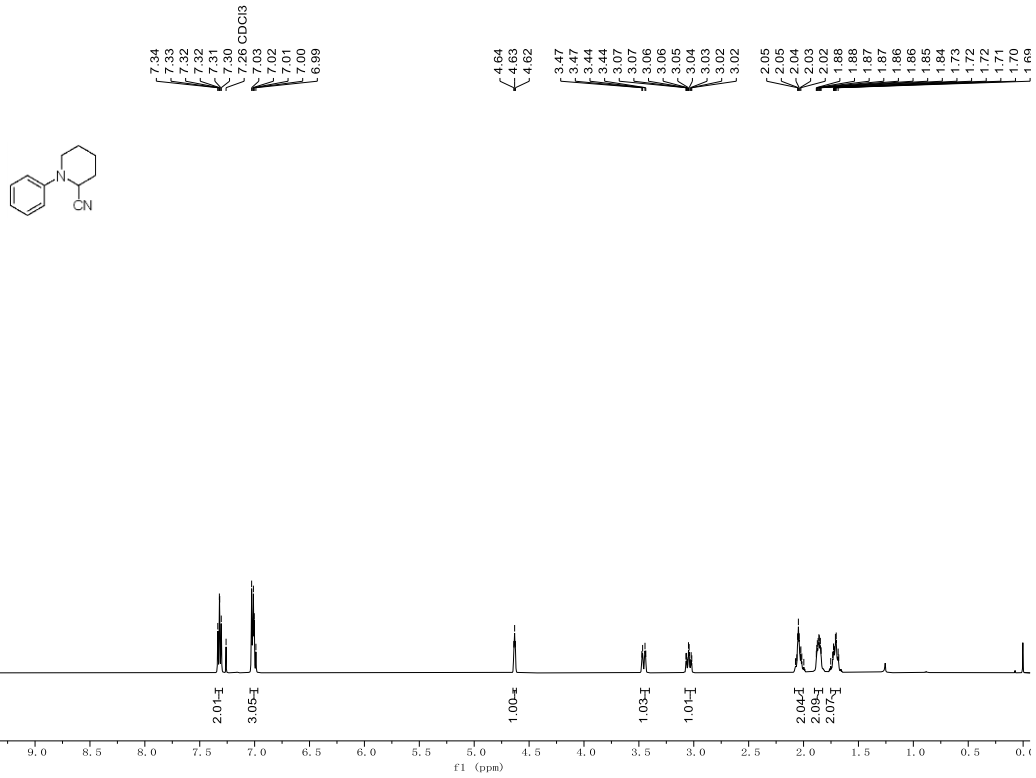
^{13}C NMR of **3e** (126 MHz, Chloroform-*d*).



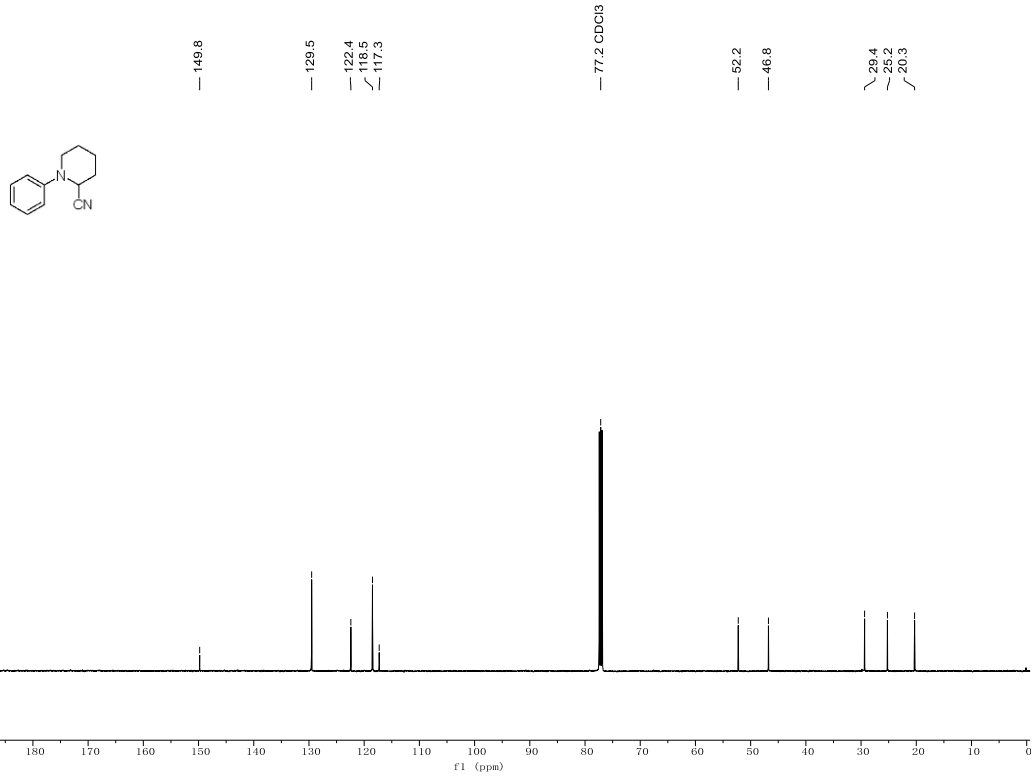
^{1}H NMR of **3f** (500 MHz, Chloroform-*d*)



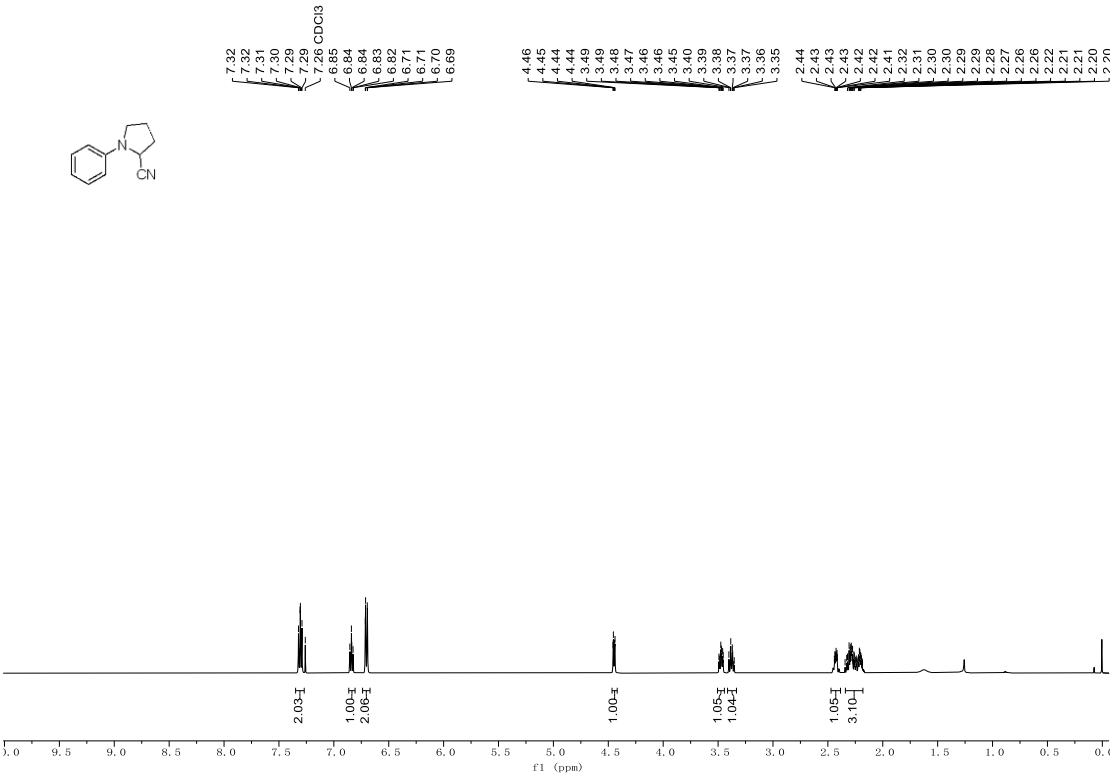
^{13}C NMR of **3f** (126 MHz, Chloroform-*d*)



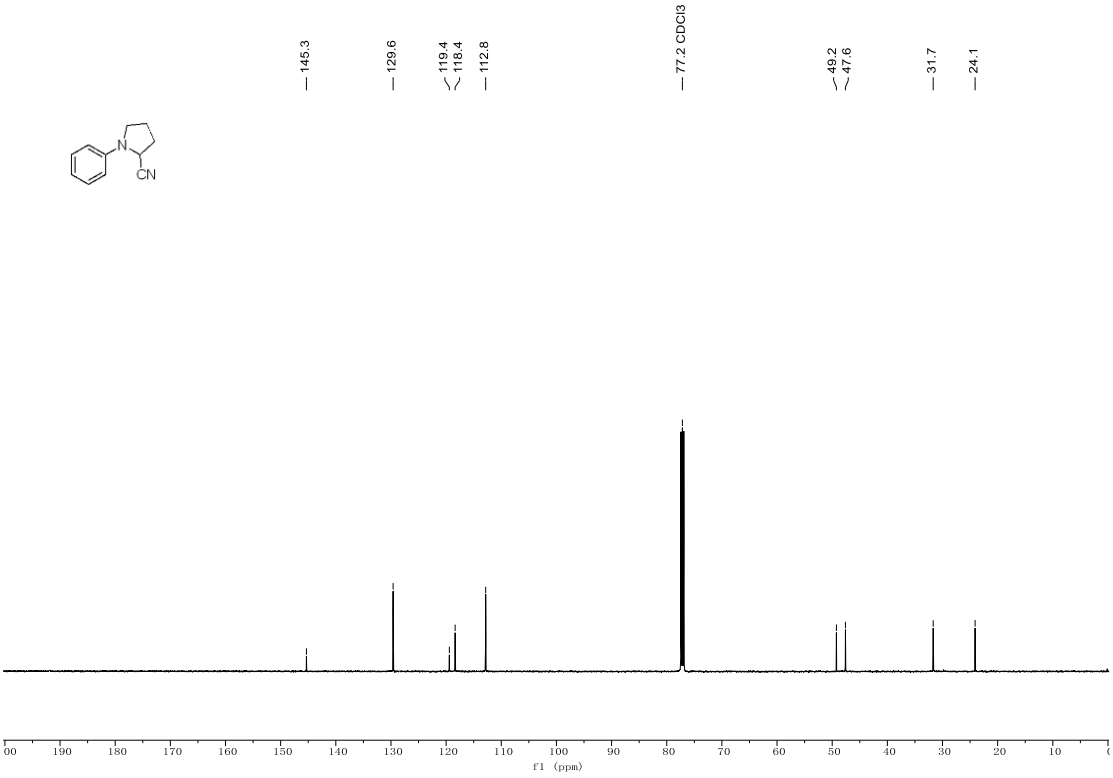
^{1}H NMR of **3g** (500 MHz, Chloroform-*d*).



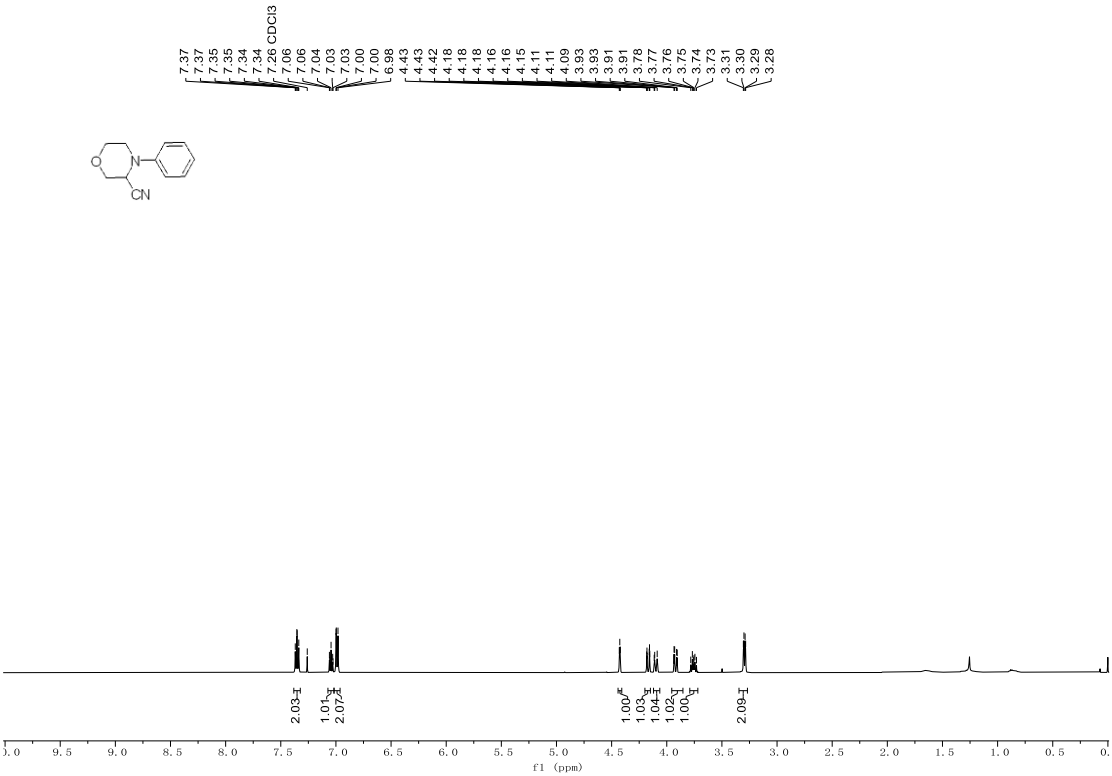
^{13}C NMR of **3g** (126 MHz, Chloroform-*d*).



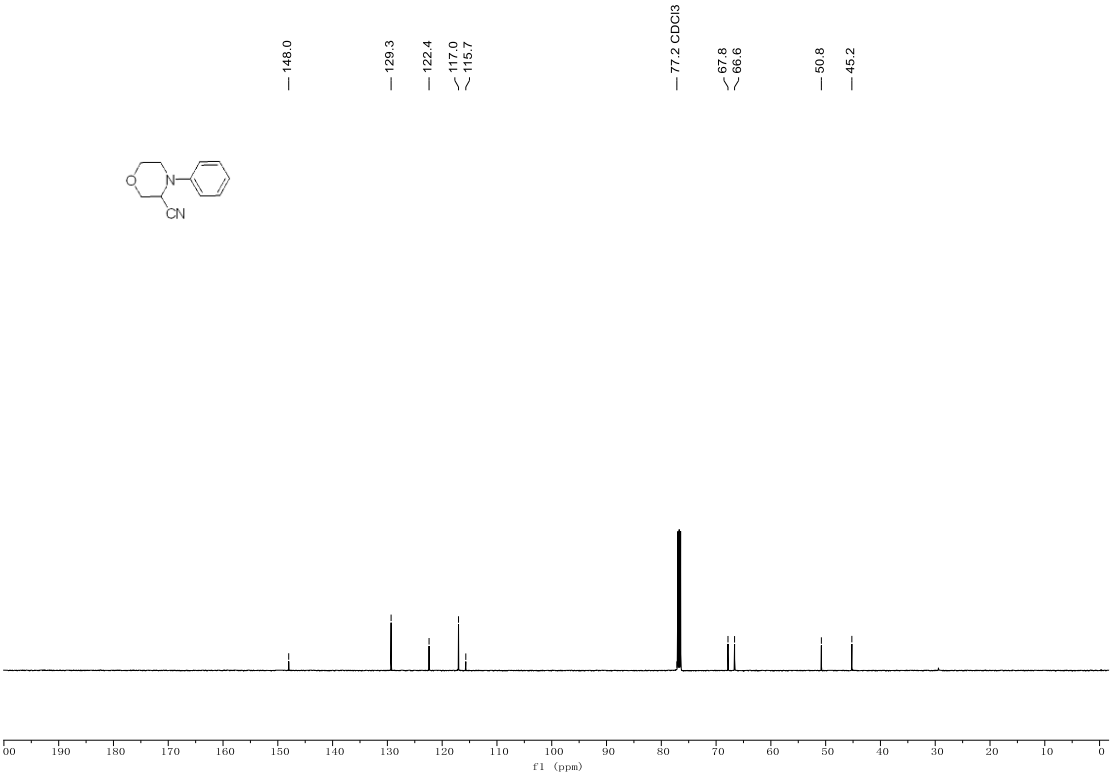
^{1}H NMR of **3h** (500 MHz, Chloroform-*d*)



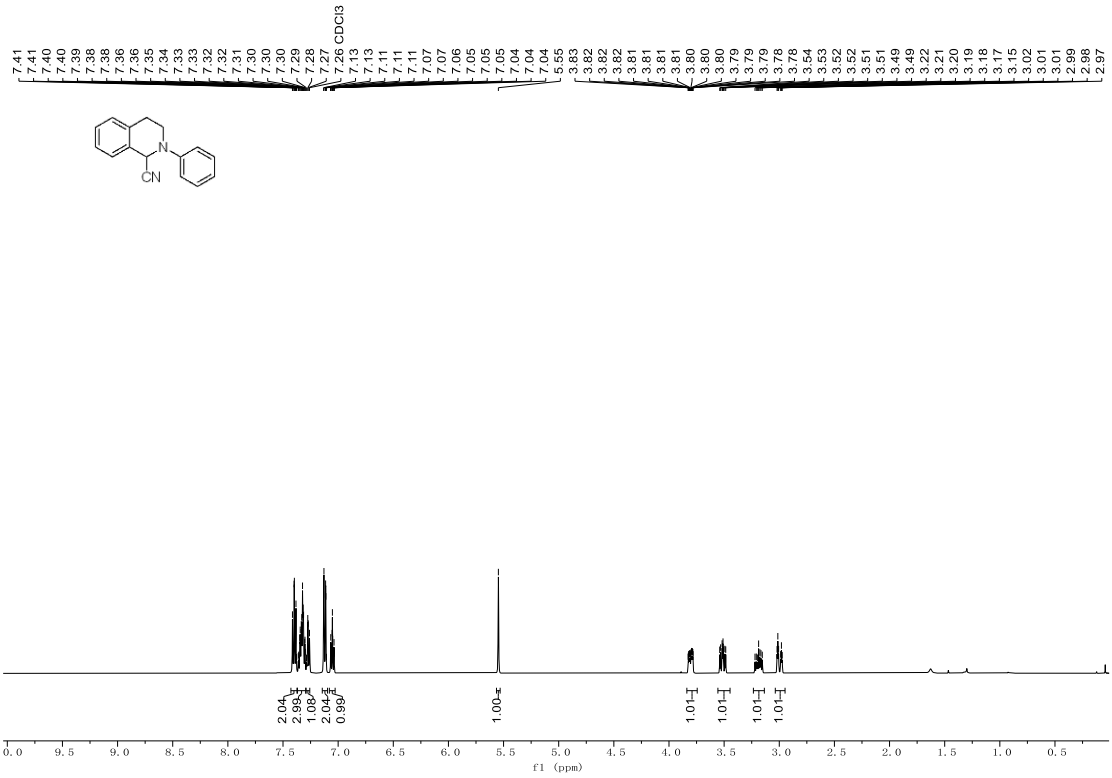
^{13}C NMR of **3h** (126 MHz, Chloroform-*d*).



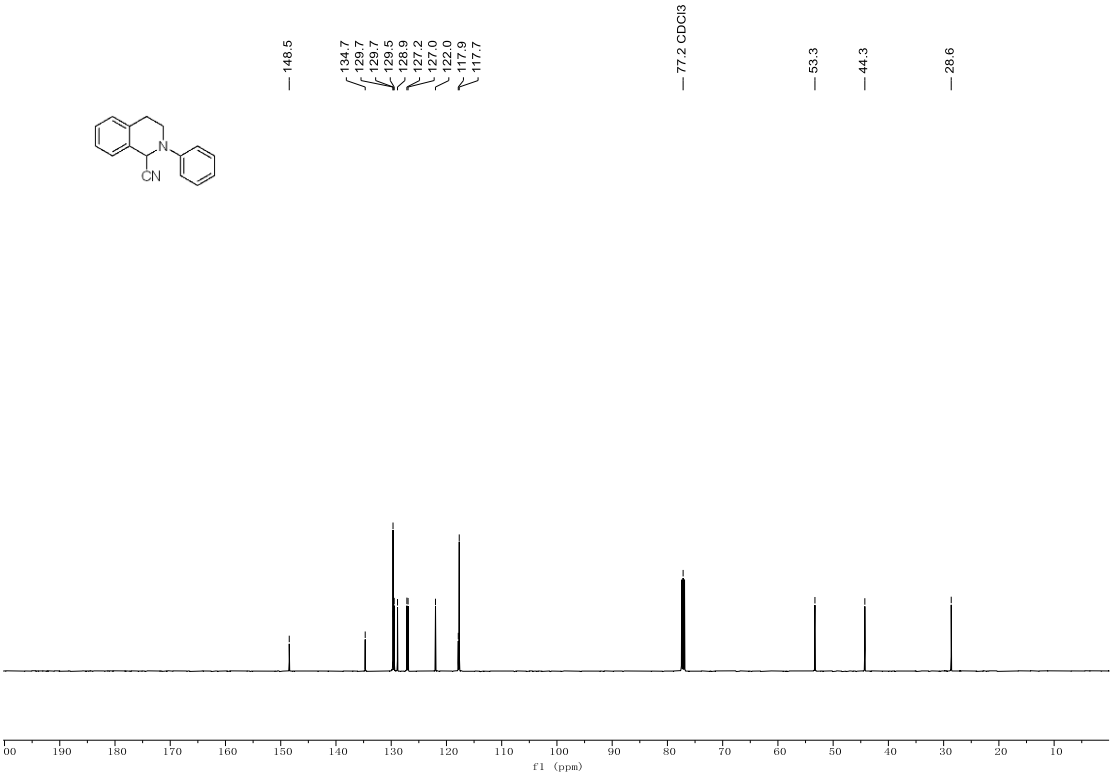
^{1}H NMR of **3i** (500 MHz, Chloroform-*d*).



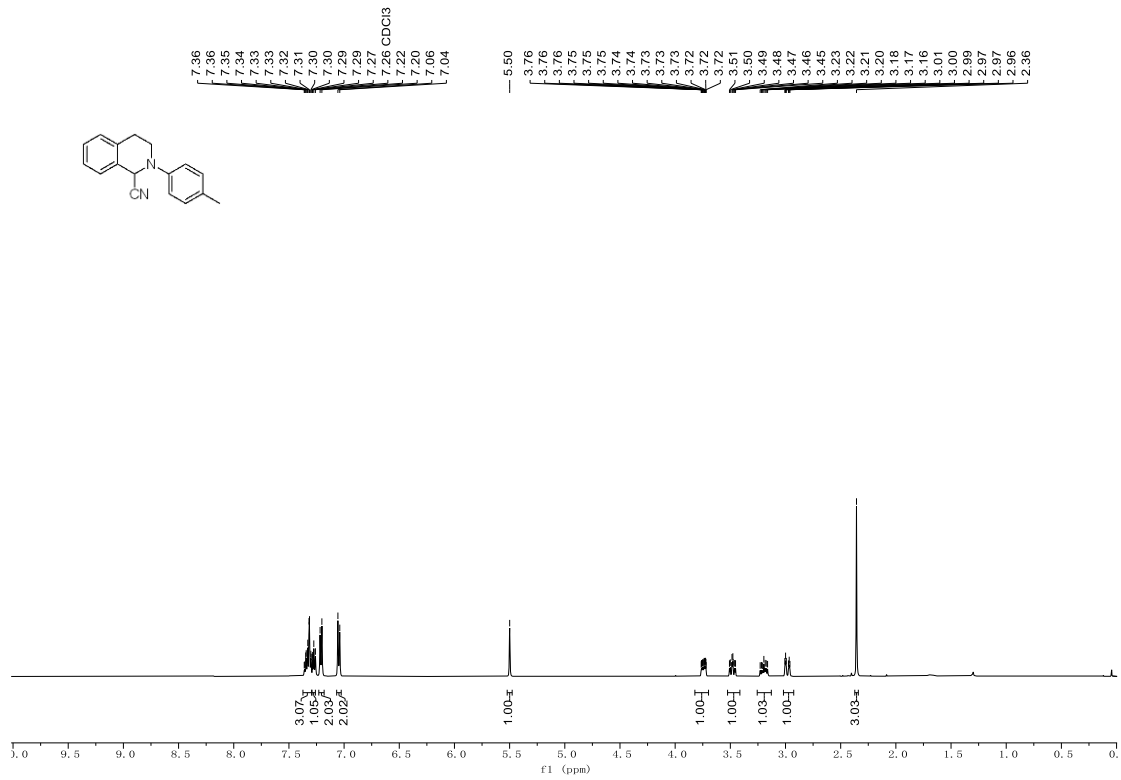
^{13}C NMR of **3i** (126 MHz, Chloroform-*d*).



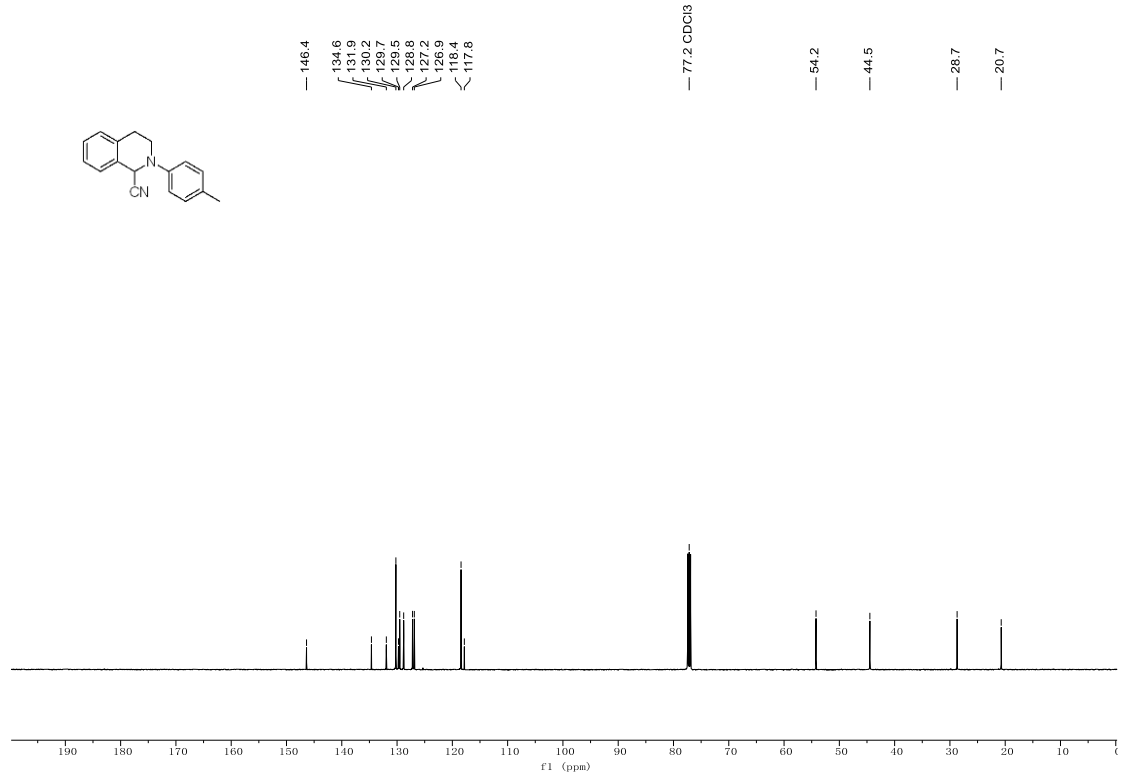
^{1}H NMR of **3j** (500 MHz, Chloroform-*d*).



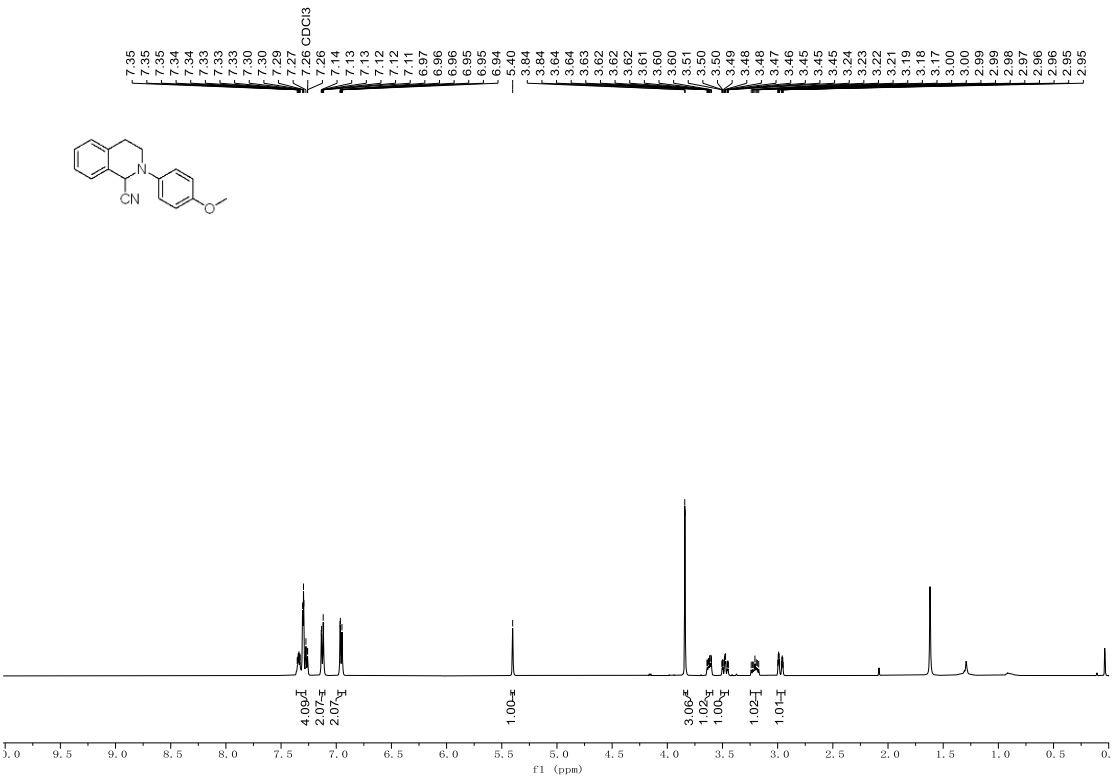
^{13}C NMR of **3j** (126 MHz, Chloroform-*d*).



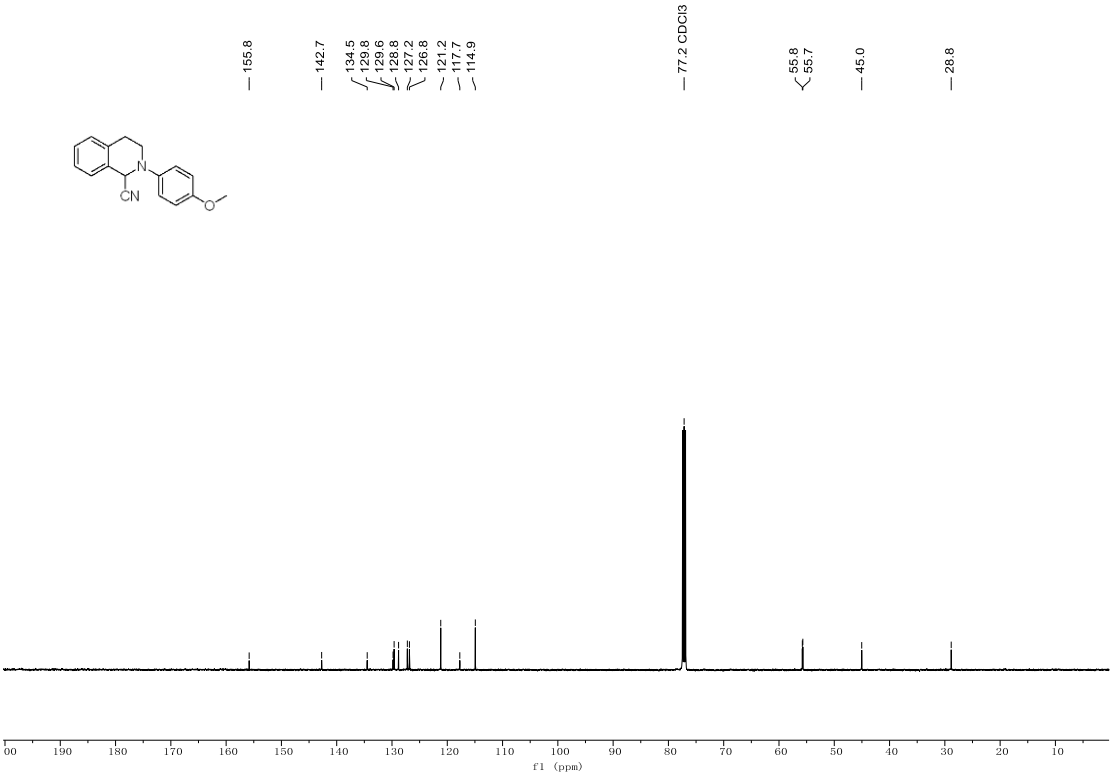
^{1}H NMR of **3k** (500 MHz, Chloroform-*d*).



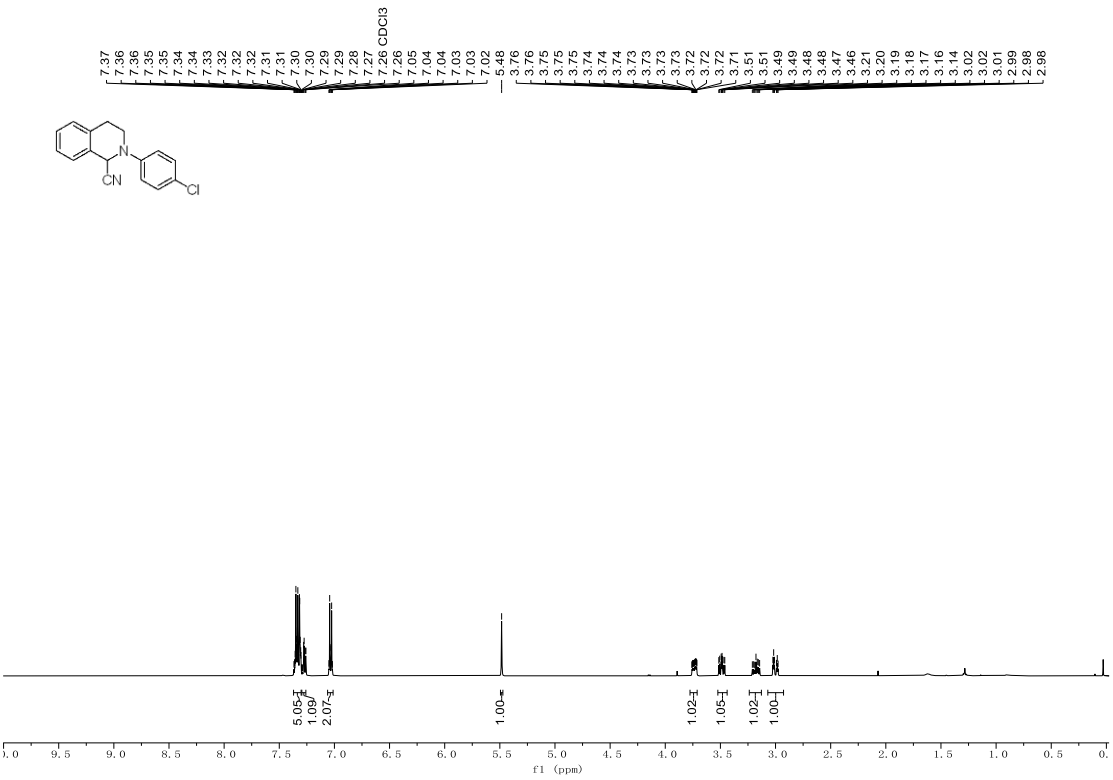
^{13}C NMR of **3k** (126 MHz, Chloroform-*d*).



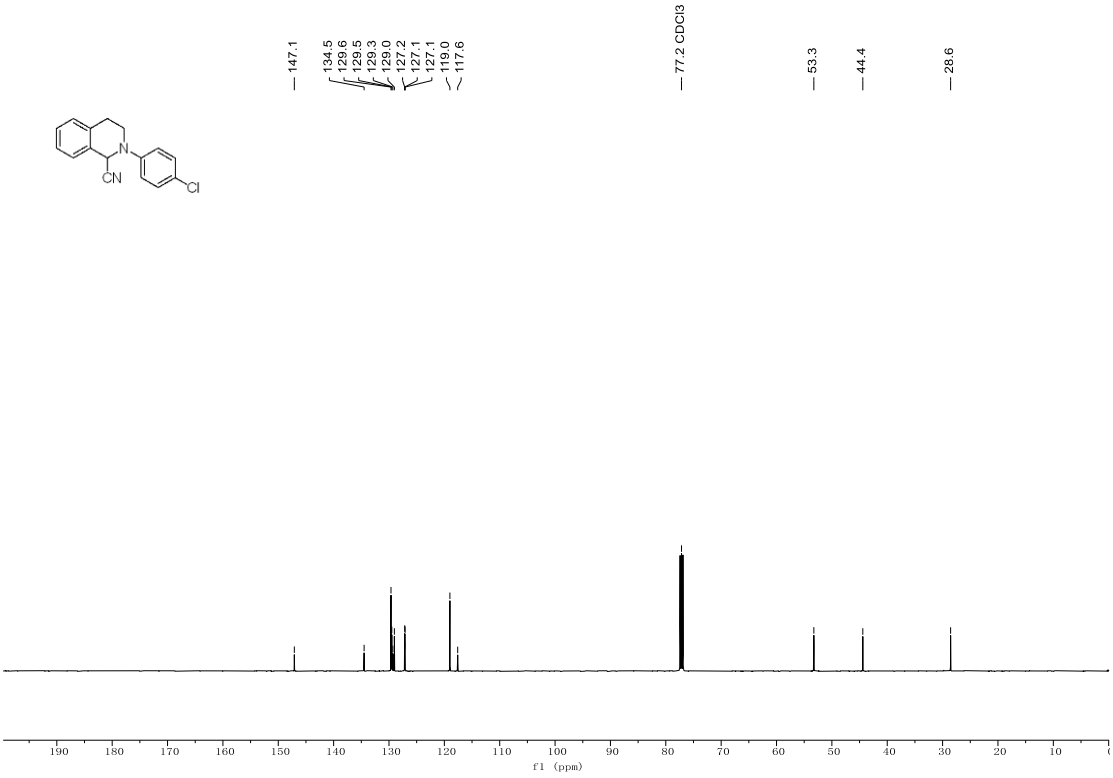
^{1}H NMR of **3l** (500 MHz, Chloroform-*d*).



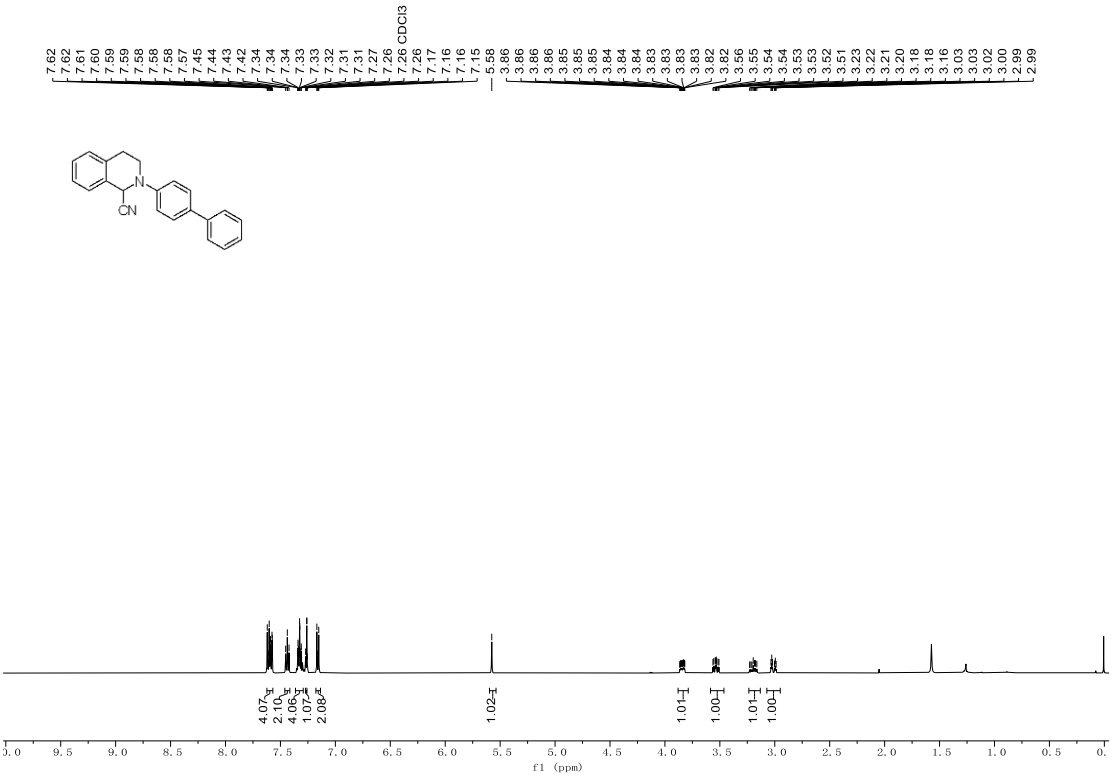
^{13}C NMR of **3l** (126 MHz, Chloroform-*d*).



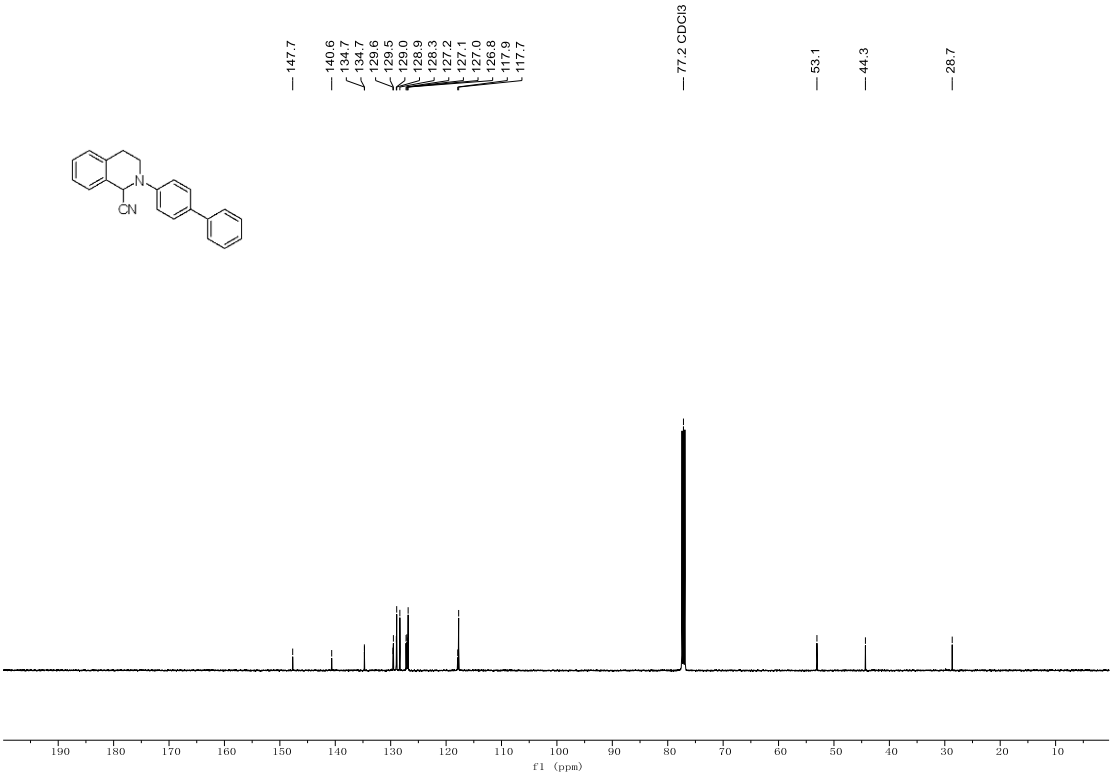
^{1}H NMR of **3m** (500 MHz, Chloroform-*d*).



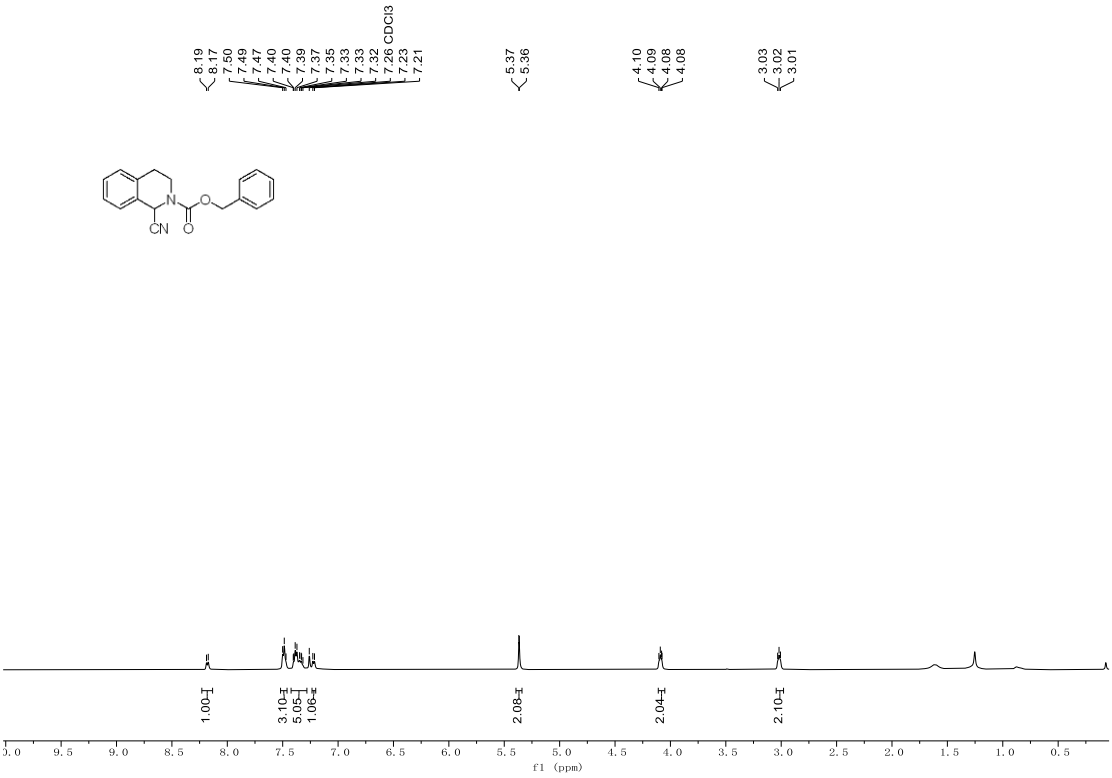
^{13}C NMR of **3m** (126 MHz, Chloroform-*d*).



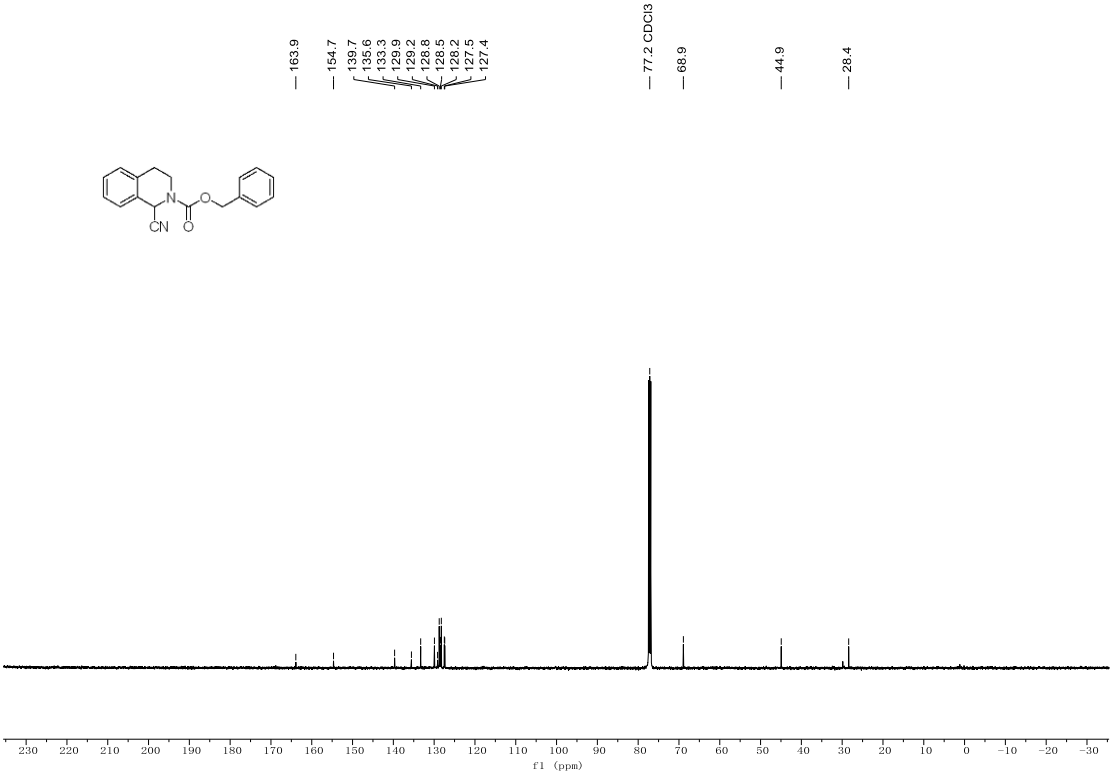
^{1}H NMR of **3n** (500 MHz, Chloroform-*d*).



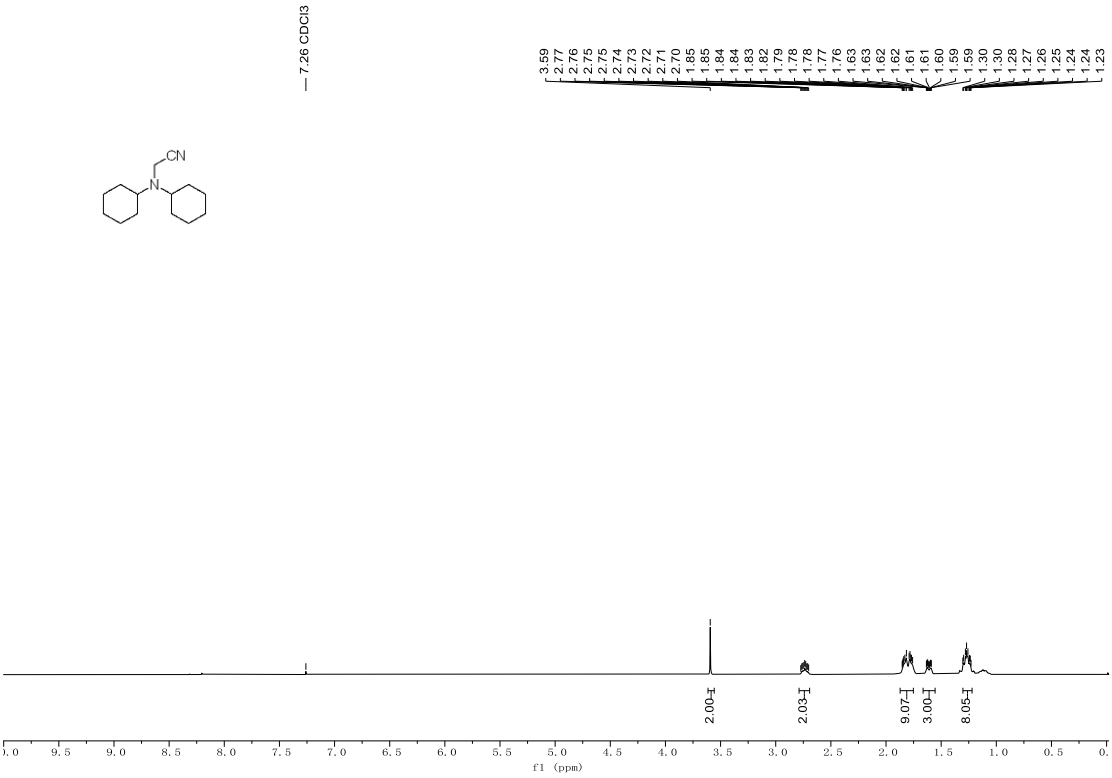
^{13}C NMR of **3n** (126 MHz, Chloroform-*d*).



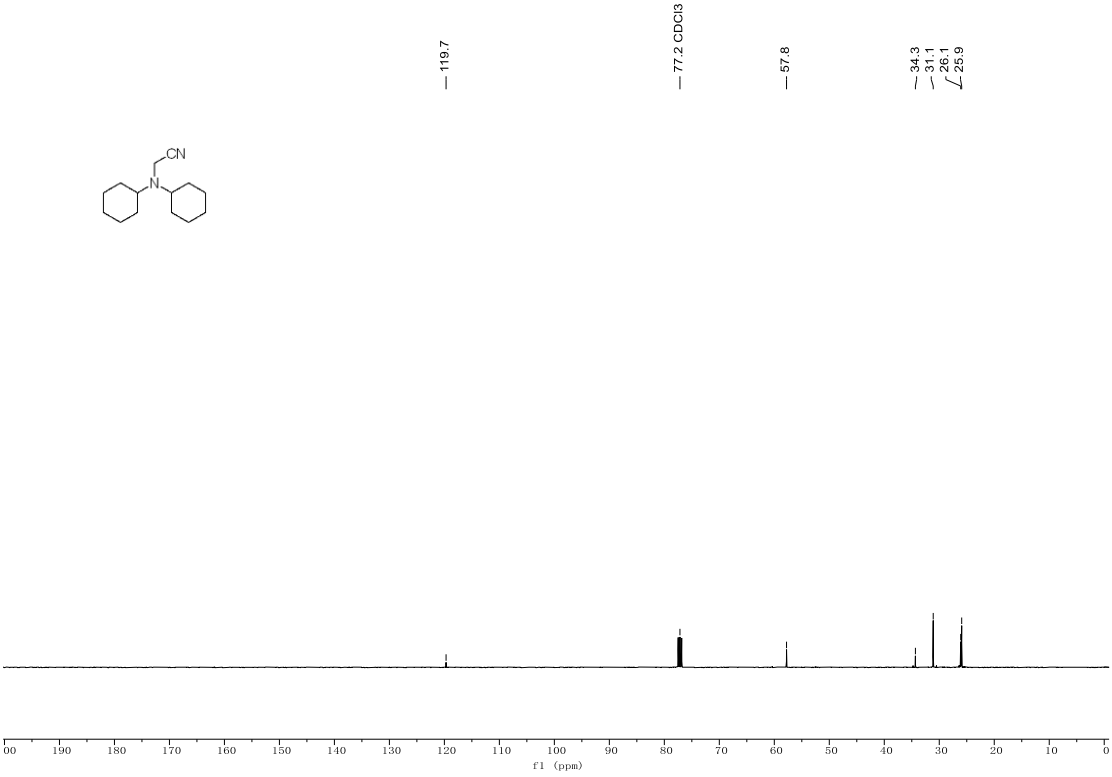
^{1}H NMR of **3o** (500 MHz, Chloroform-*d*).



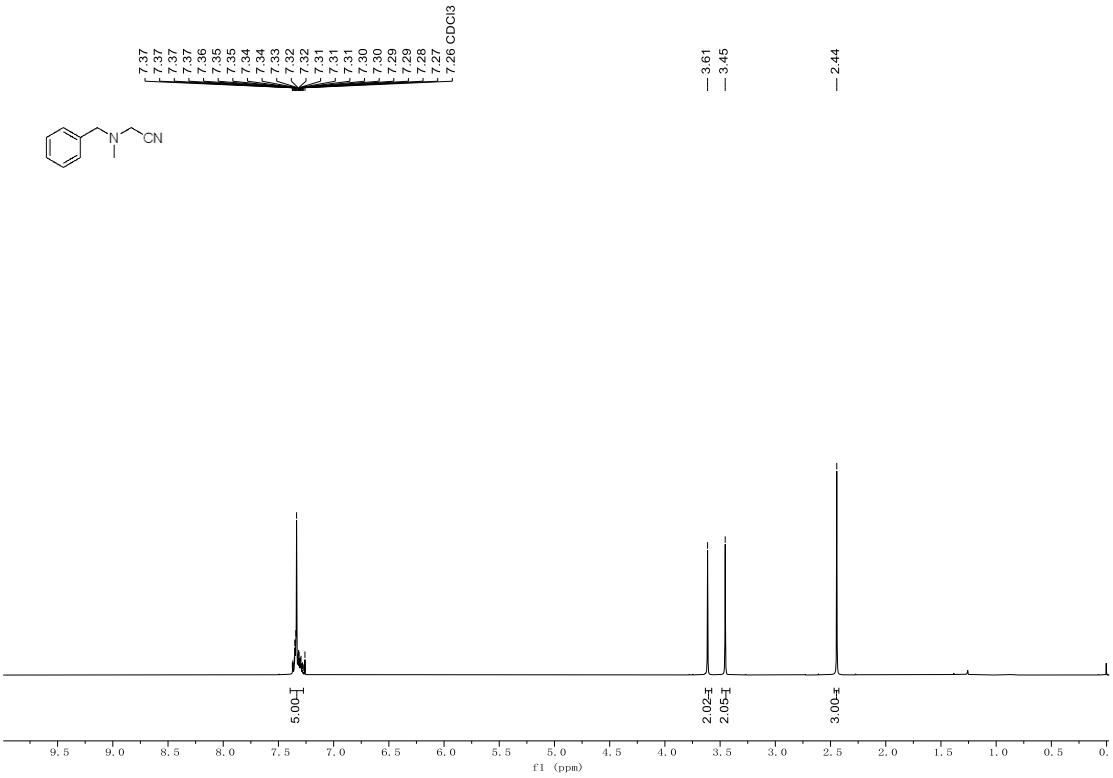
^{13}C NMR of **3o** (126 MHz, Chloroform-*d*).



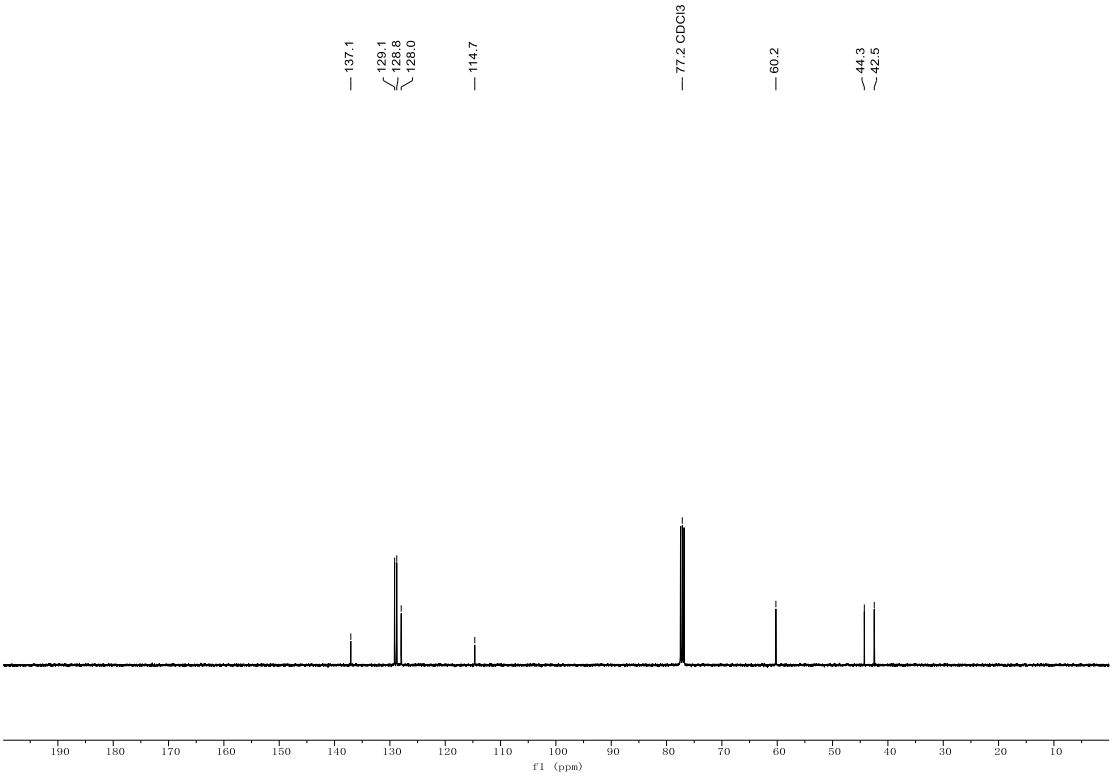
^{1}H NMR of **3p** (400 MHz, Chloroform-*d*).



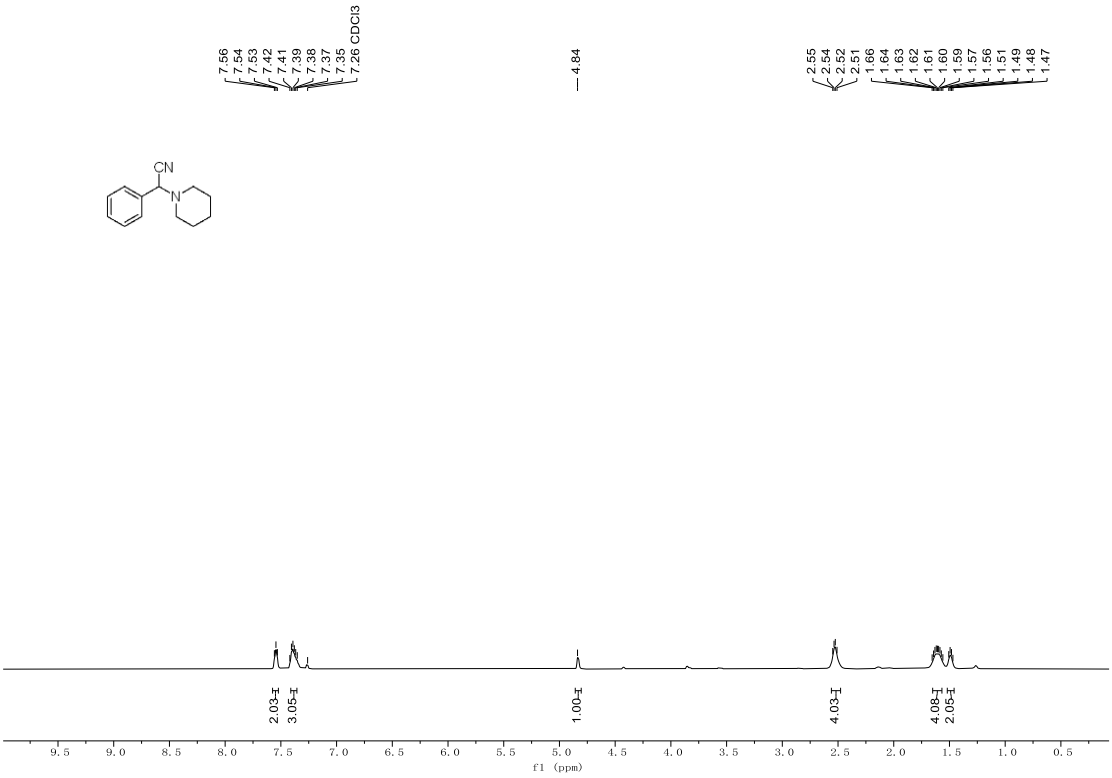
^{13}C NMR of **3p** (101 MHz, Chloroform-*d*).



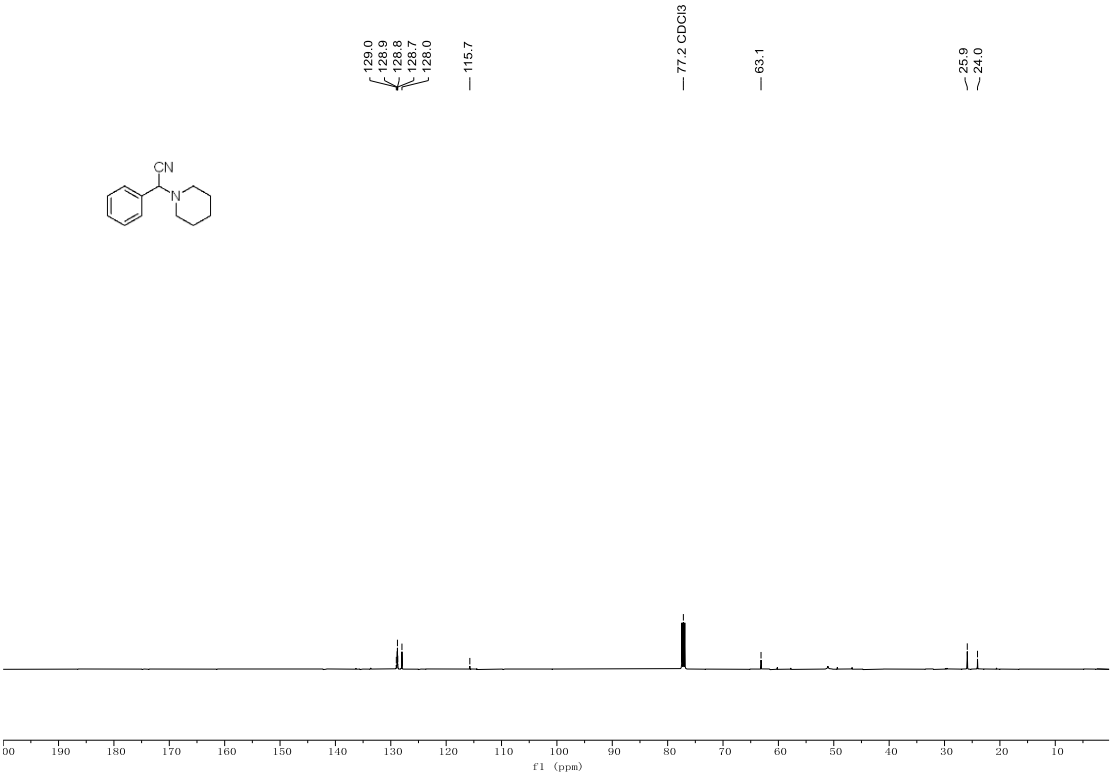
^{1}H NMR of **3q** (400 MHz, Chloroform-*d*).



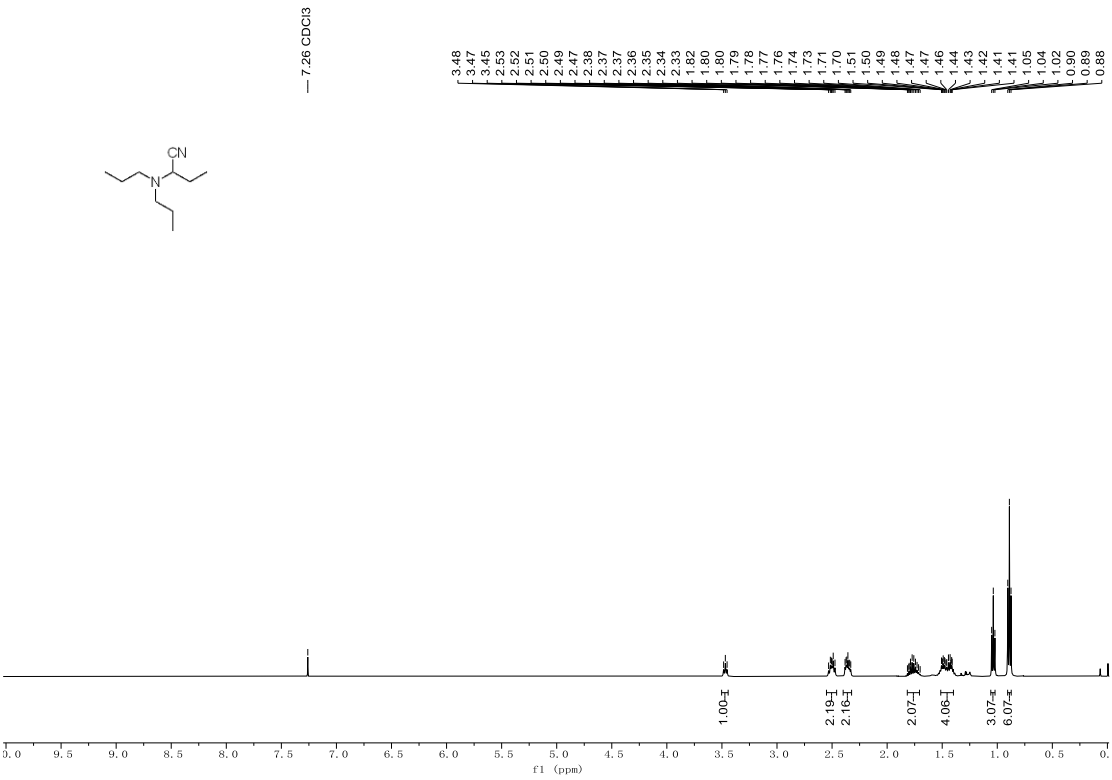
^{13}C NMR of **3q** (101 MHz, Chloroform-*d*).



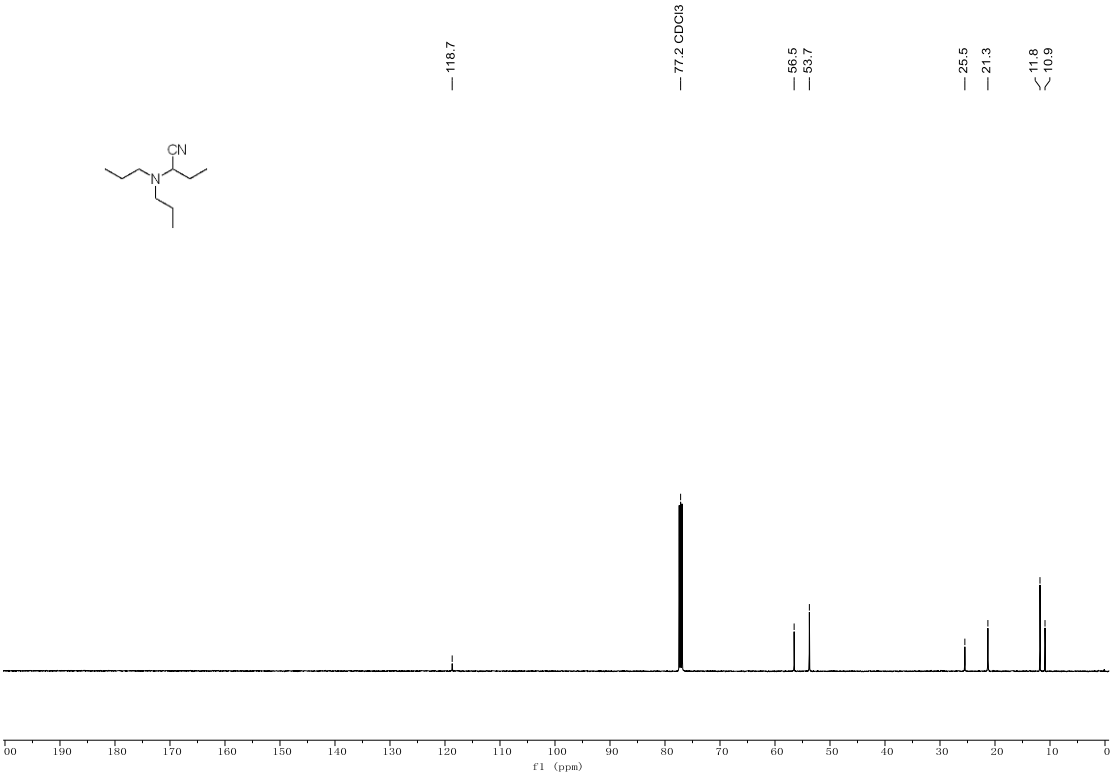
^{1}H NMR of **3r** (500 MHz, Chloroform-*d*).



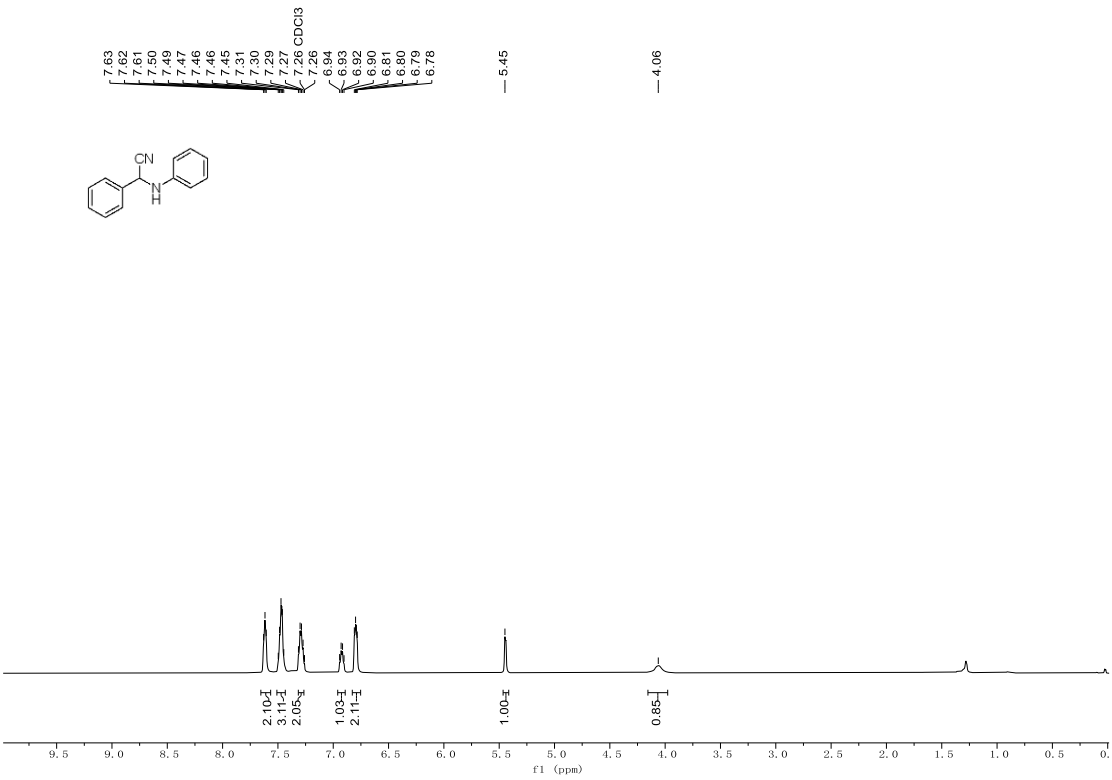
^{13}C NMR of **3r** (126 MHz, Chloroform-*d*).



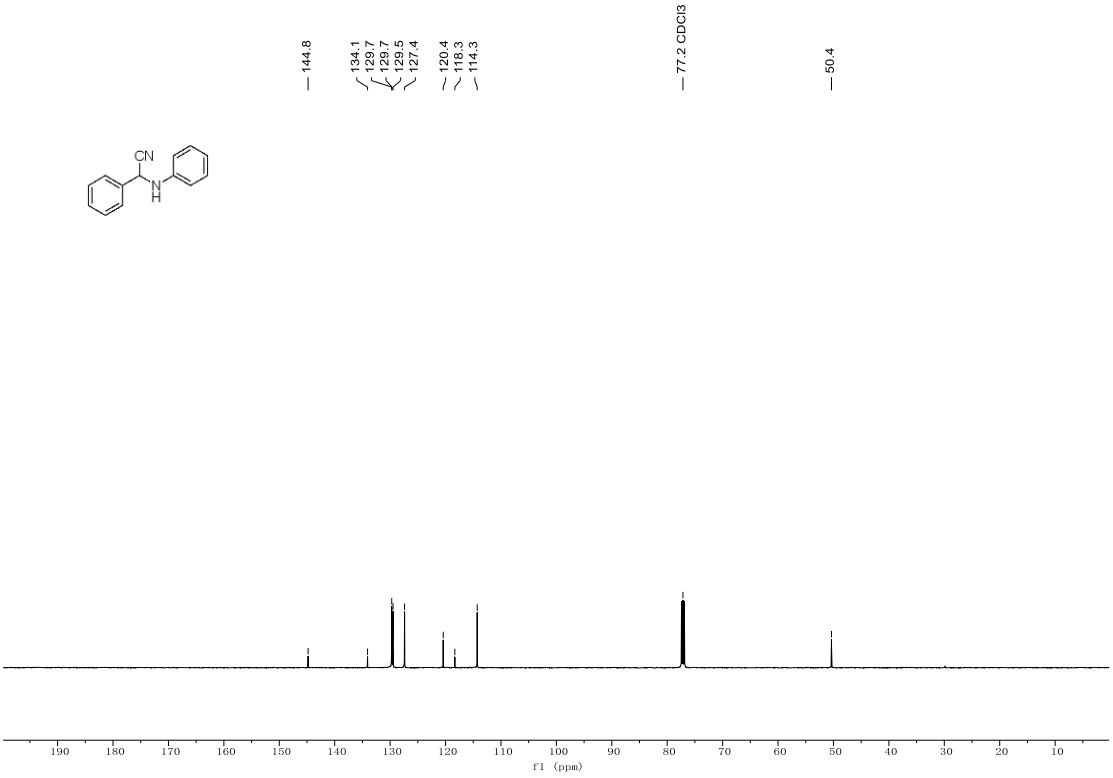
^{1}H NMR of **3s** (500 MHz, Chloroform-*d*).



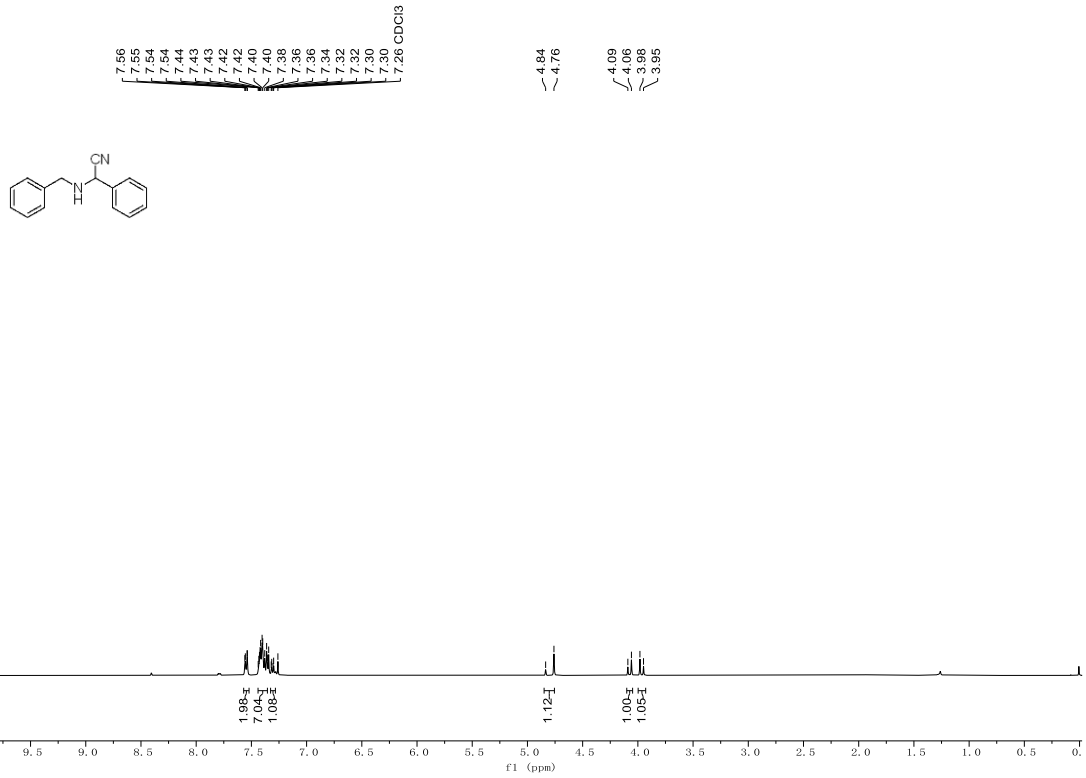
^{13}C NMR of **3s** (126 MHz, Chloroform-*d*).



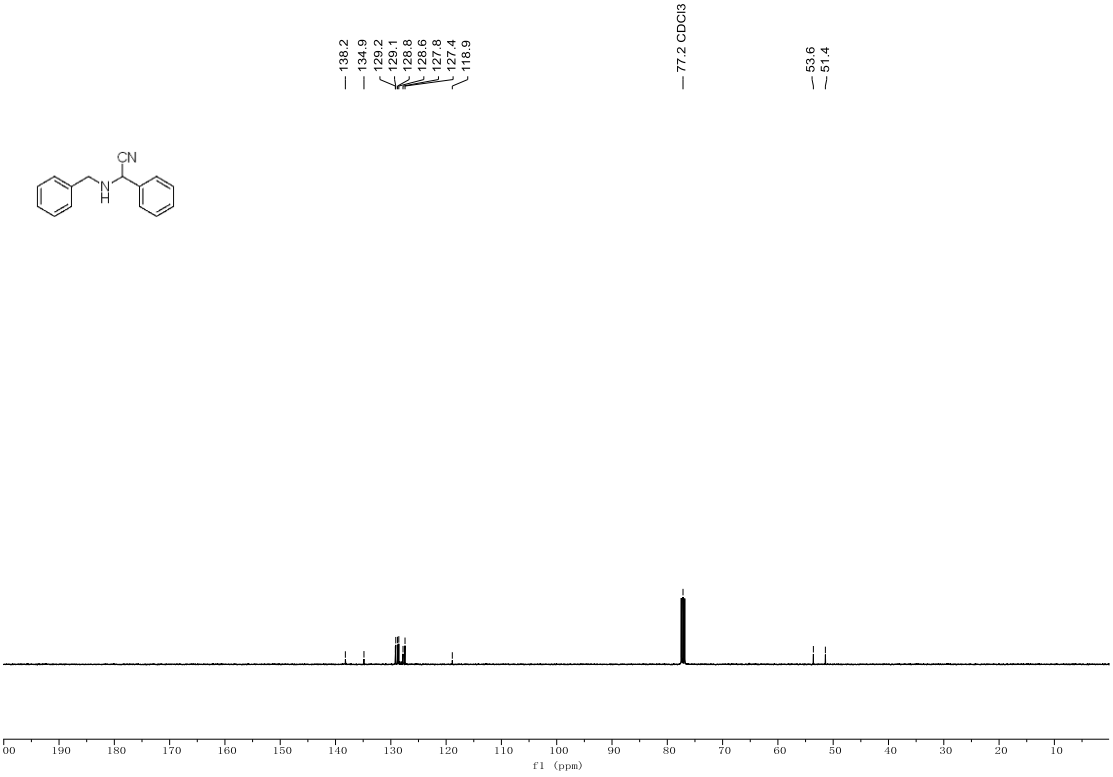
^{1}H NMR of **3t** (500 MHz, Chloroform-*d*).



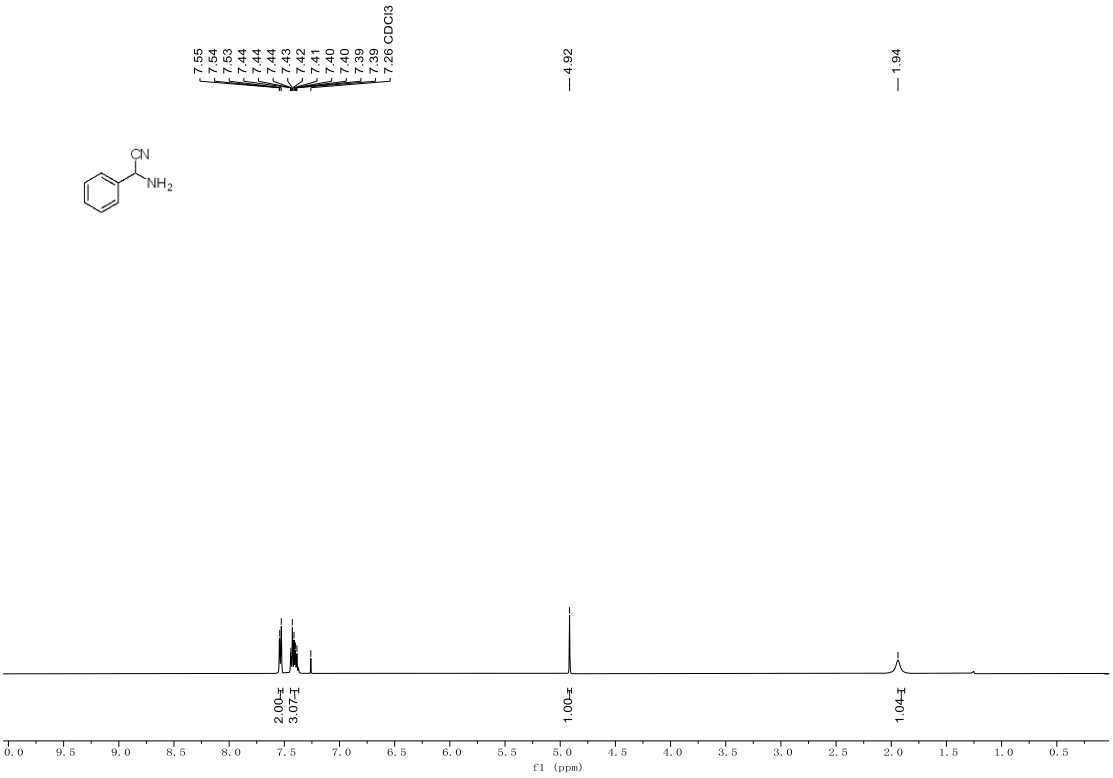
^{13}C NMR of **3t** (126 MHz, Chloroform-*d*).



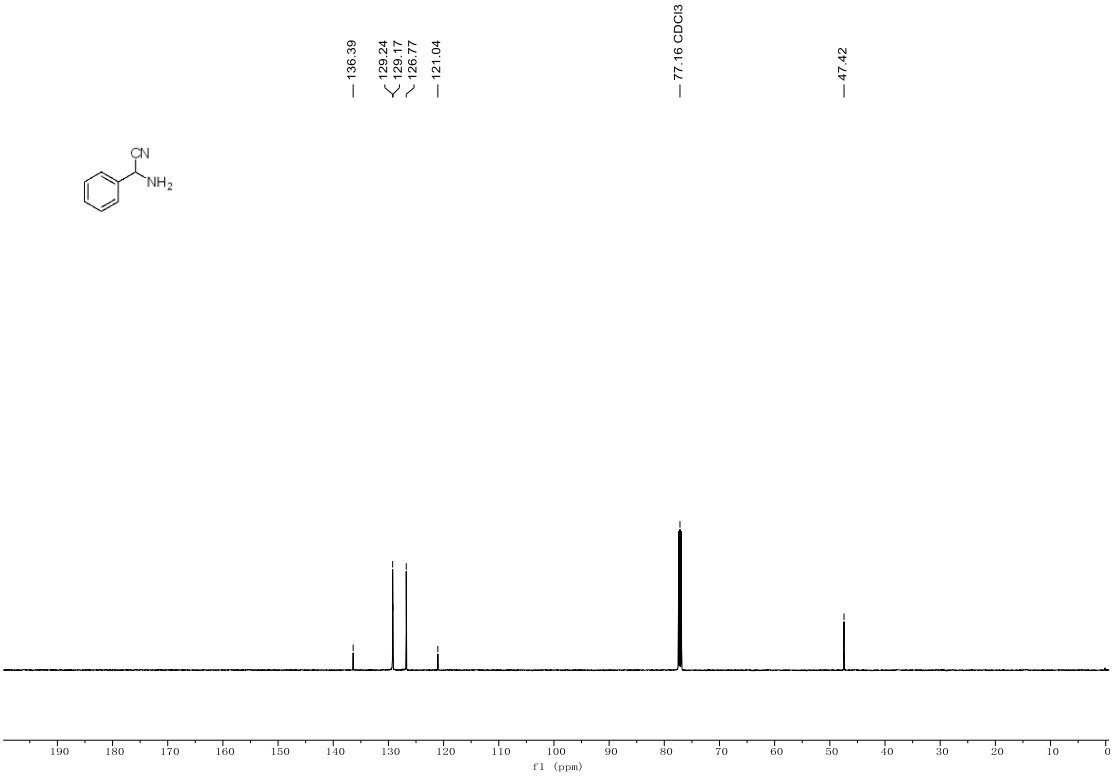
^{1}H NMR of **3u** (400 MHz, Chloroform-*d*).



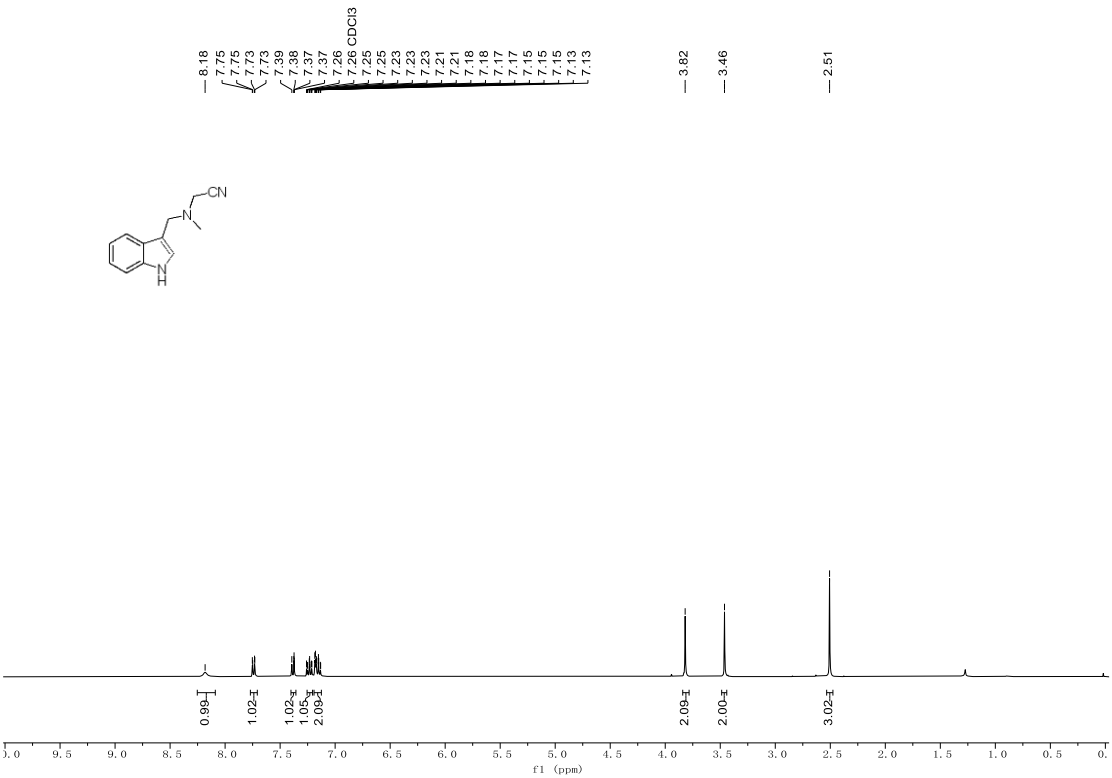
^{13}C NMR of **3u** (101 MHz, Chloroform-*d*).



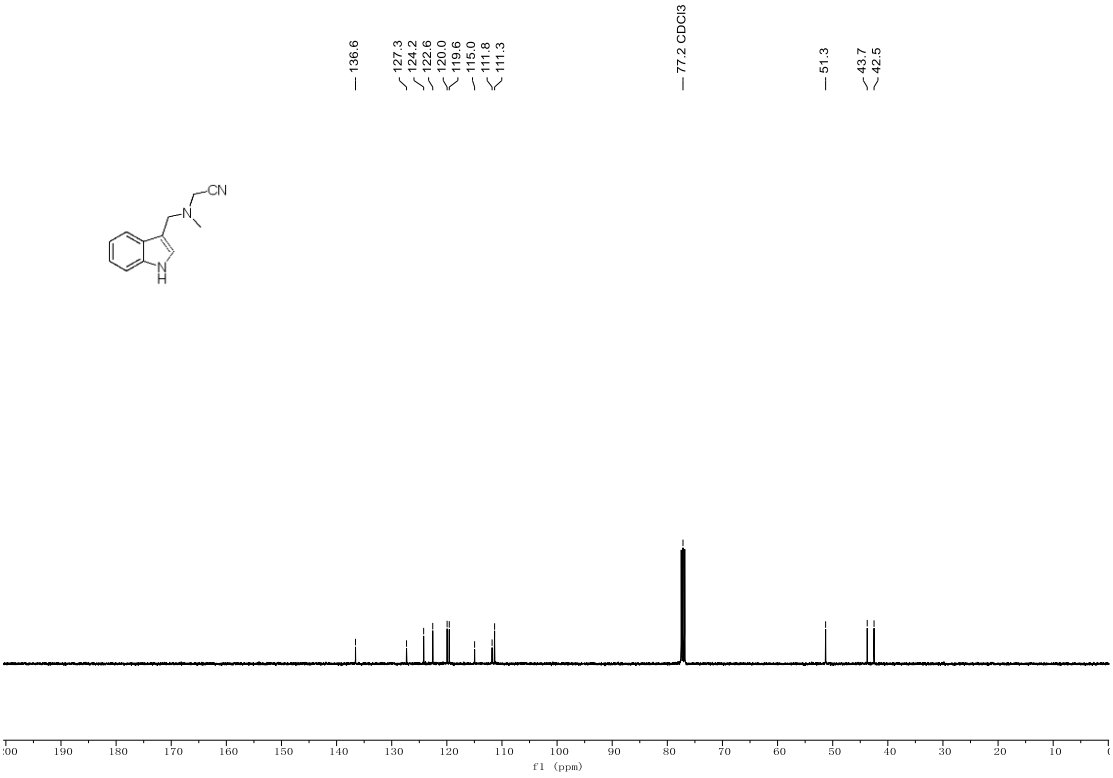
^{1}H NMR of **3v** (500 MHz, Chloroform-*d*).



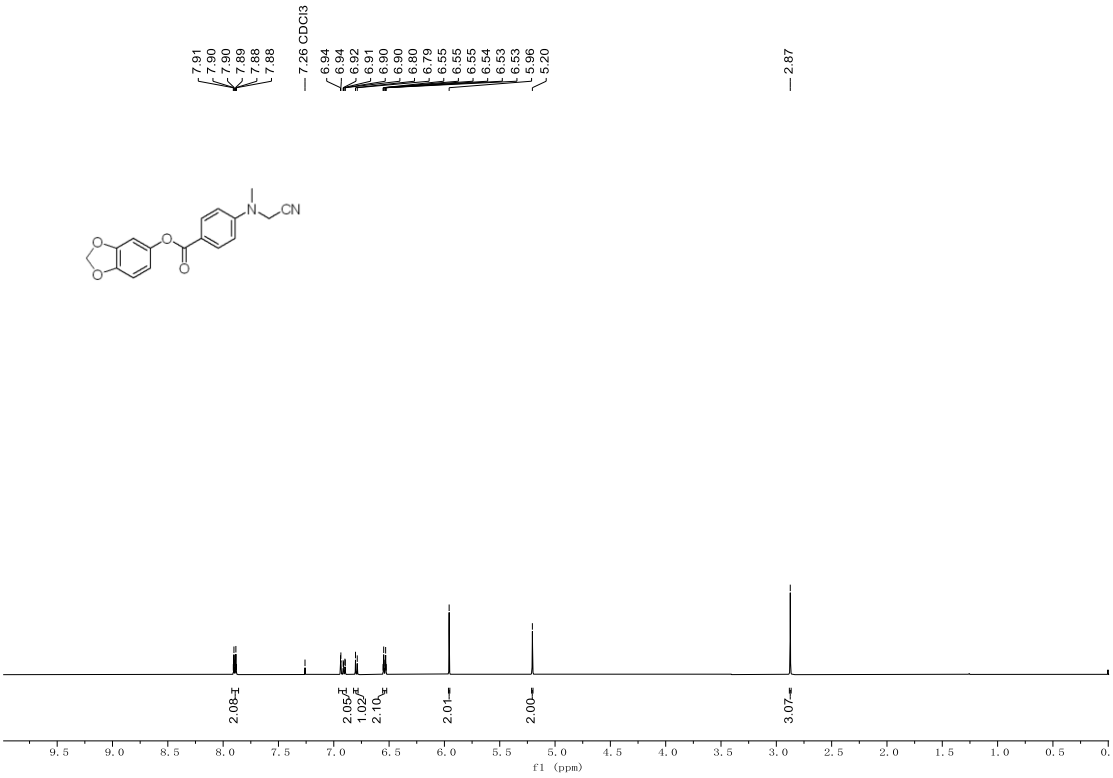
^{13}C NMR of **3v** (126 MHz, Chloroform-*d*).



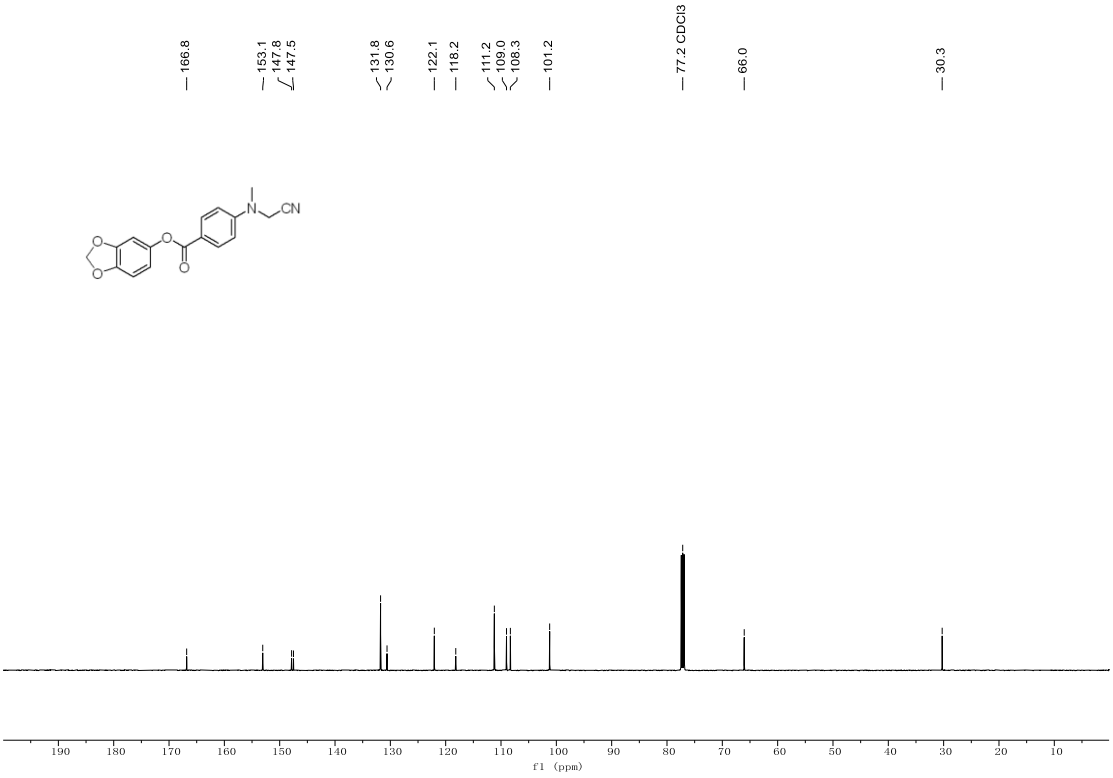
^{1}H NMR of **3w** (400 MHz, Chloroform-*d*).



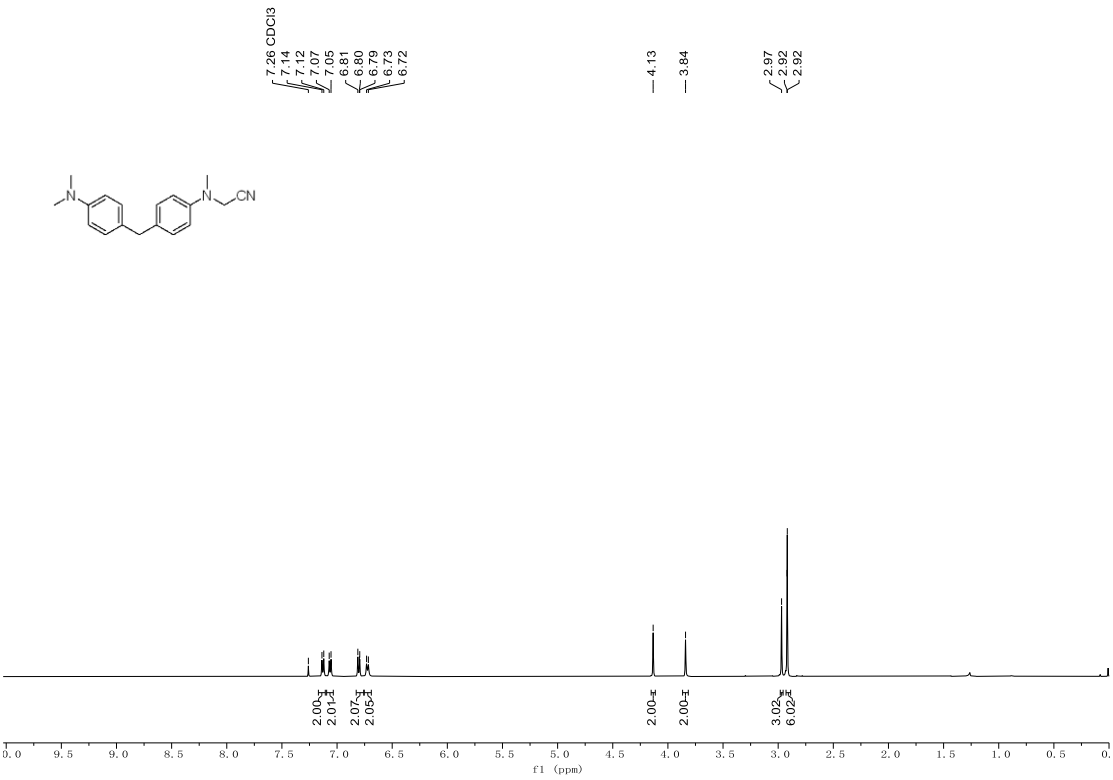
^{13}C NMR of **3w** (101 MHz, Chloroform-*d*).



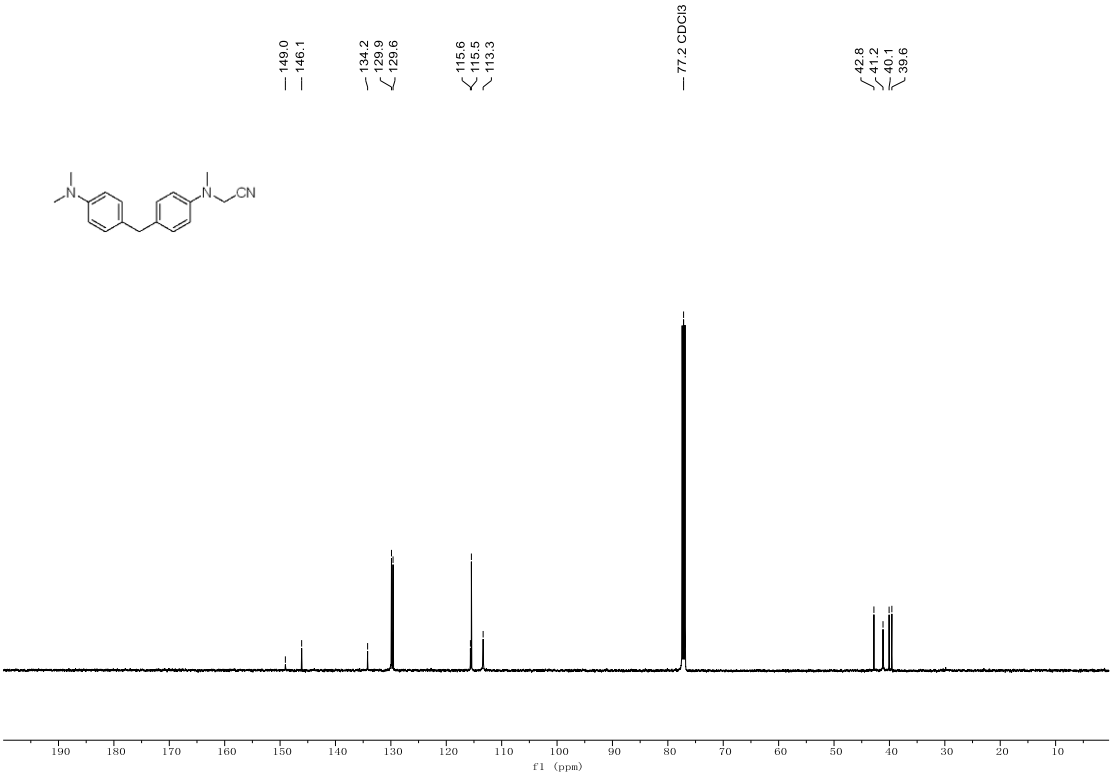
^{1}H NMR of **3x** (400 MHz, Chloroform-*d*).



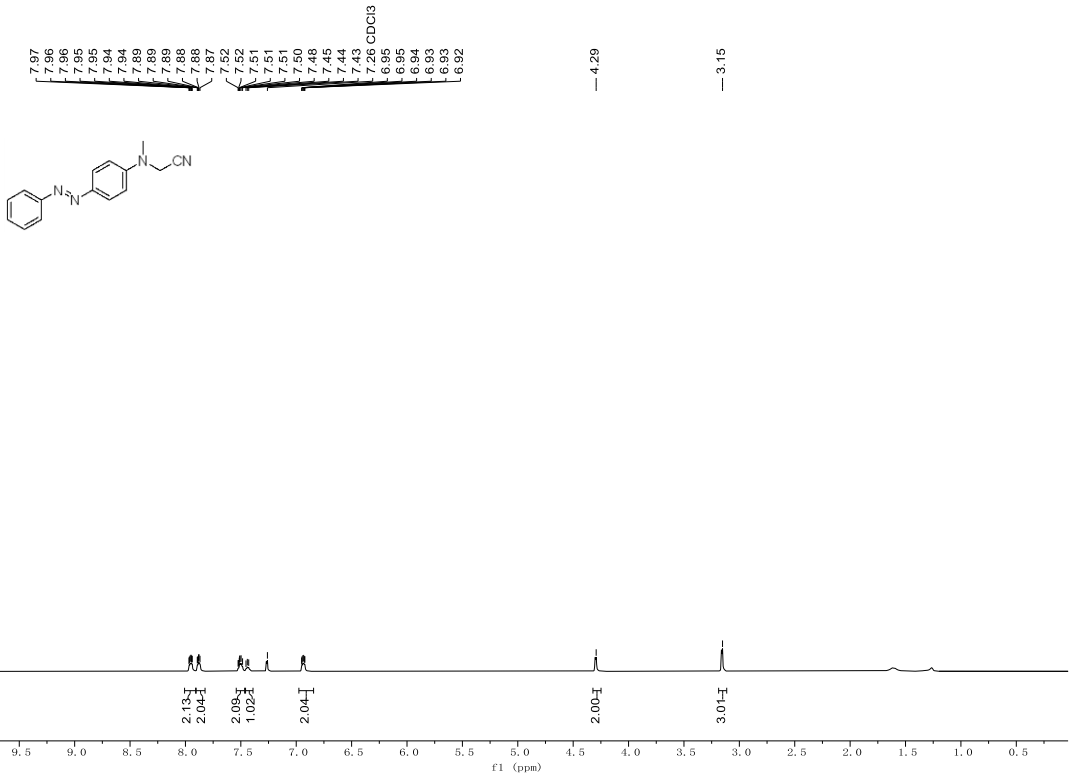
^{13}C NMR of **3x** (126 MHz, Chloroform-*d*).



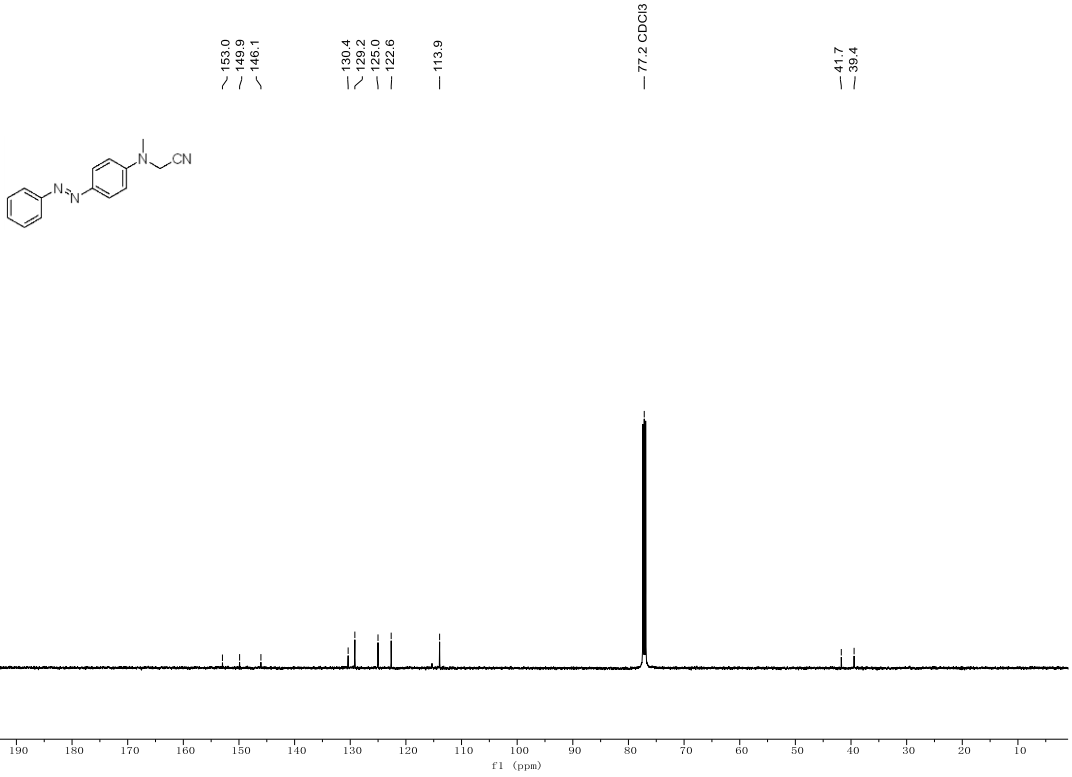
^{1}H NMR of **3y** (400 MHz, Chloroform-*d*).



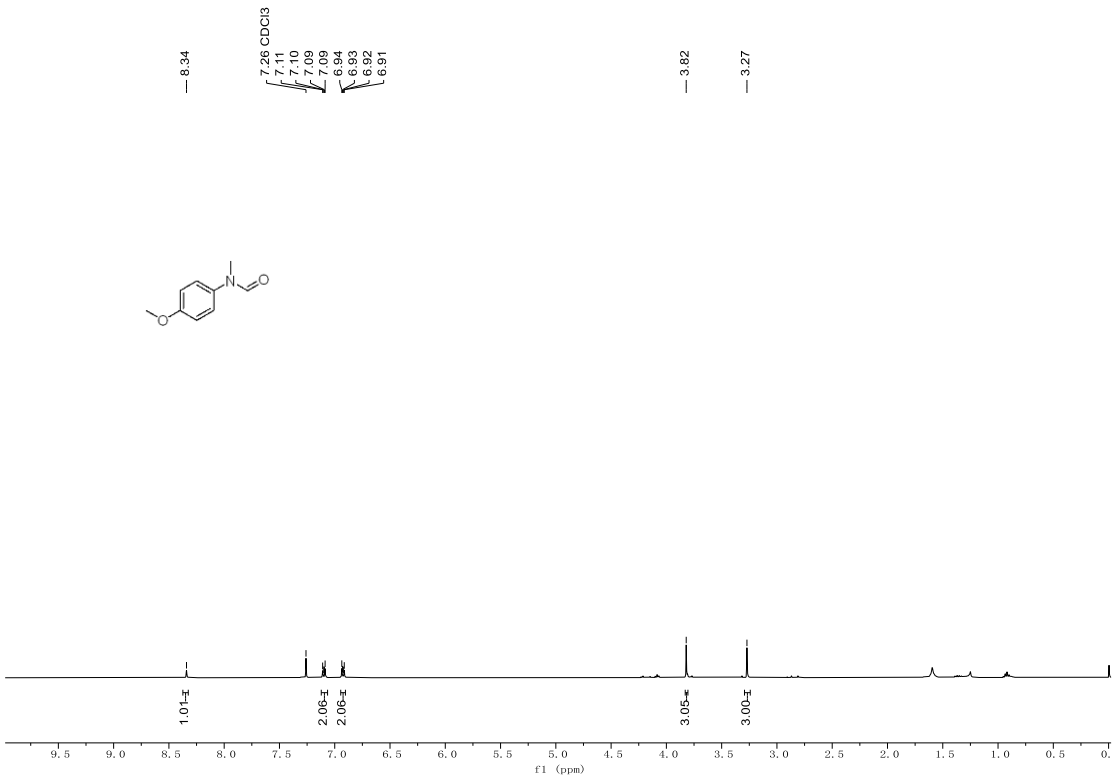
^{13}C NMR of **3y** (126 MHz, Chloroform-*d*).



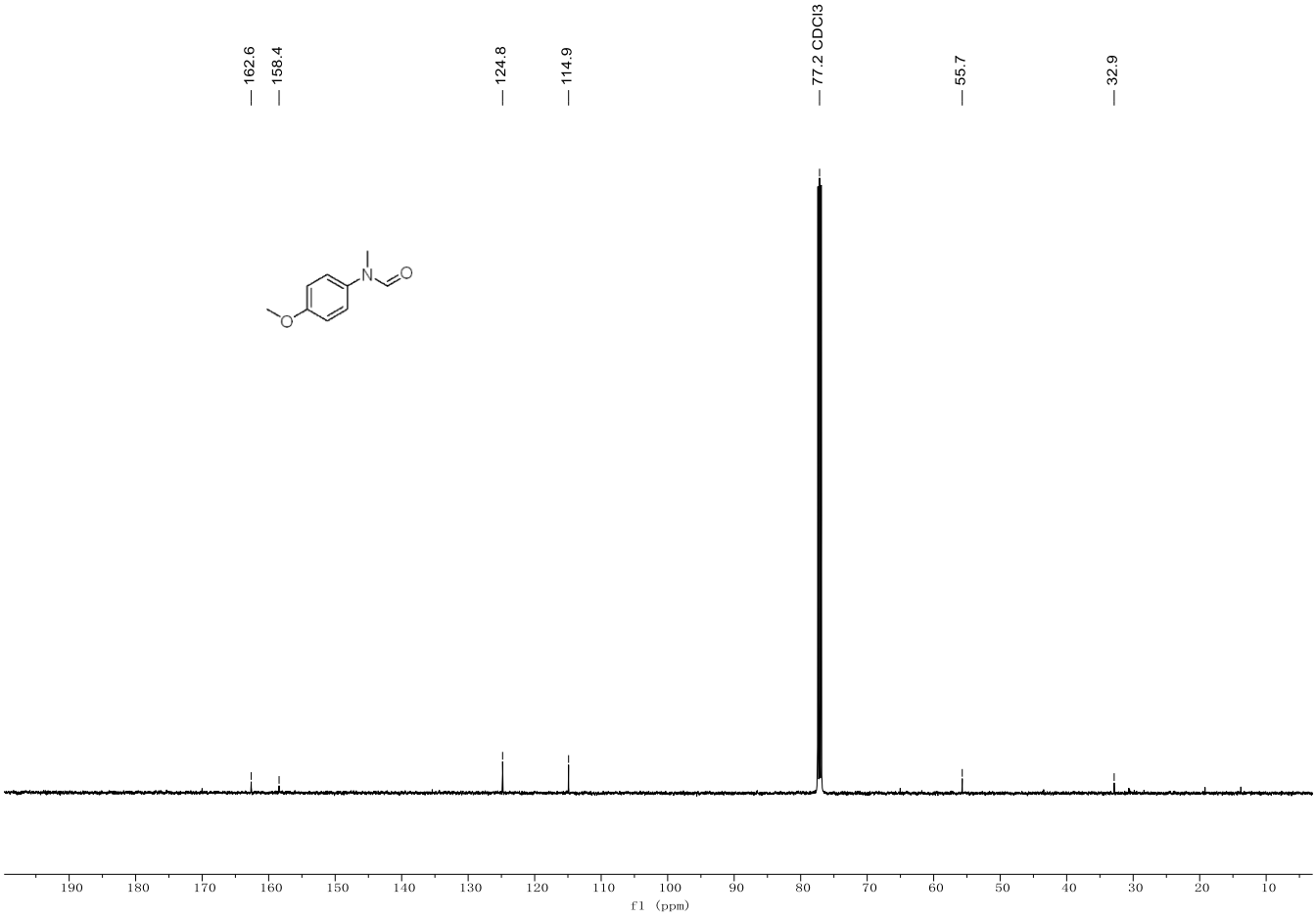
^{1}H NMR of **3z** (400 MHz, Chloroform-*d*).



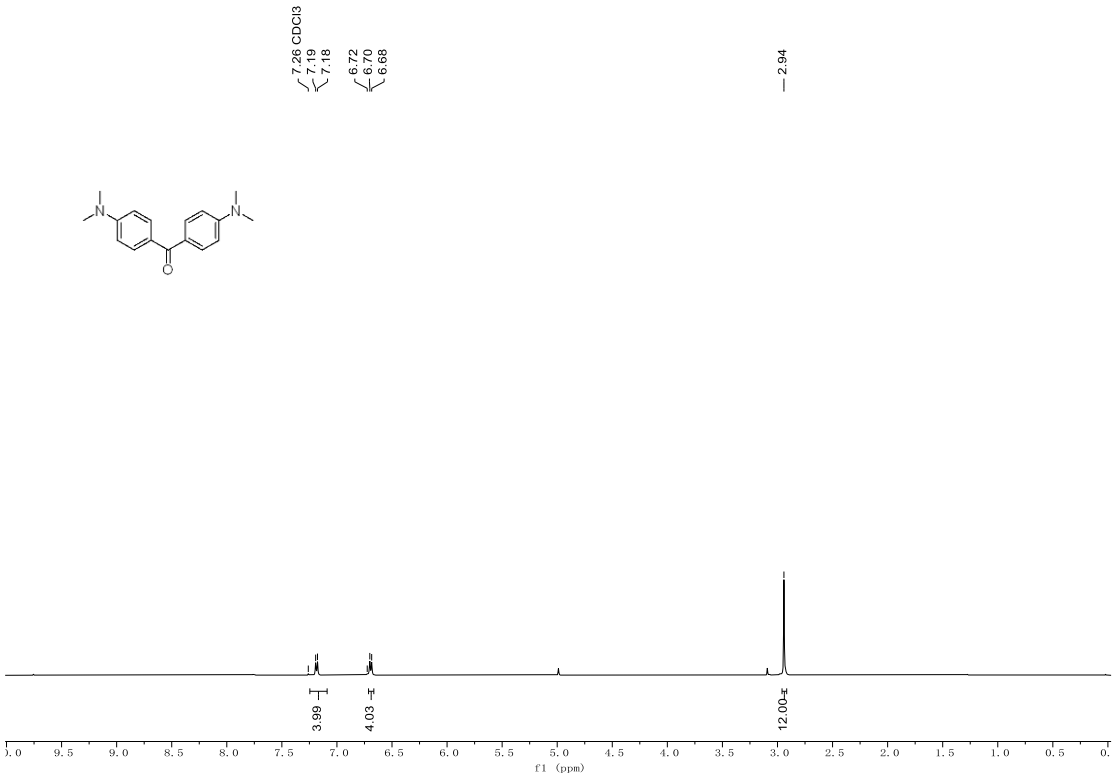
^{13}C NMR of **3z** (126 MHz, Chloroform-*d*).



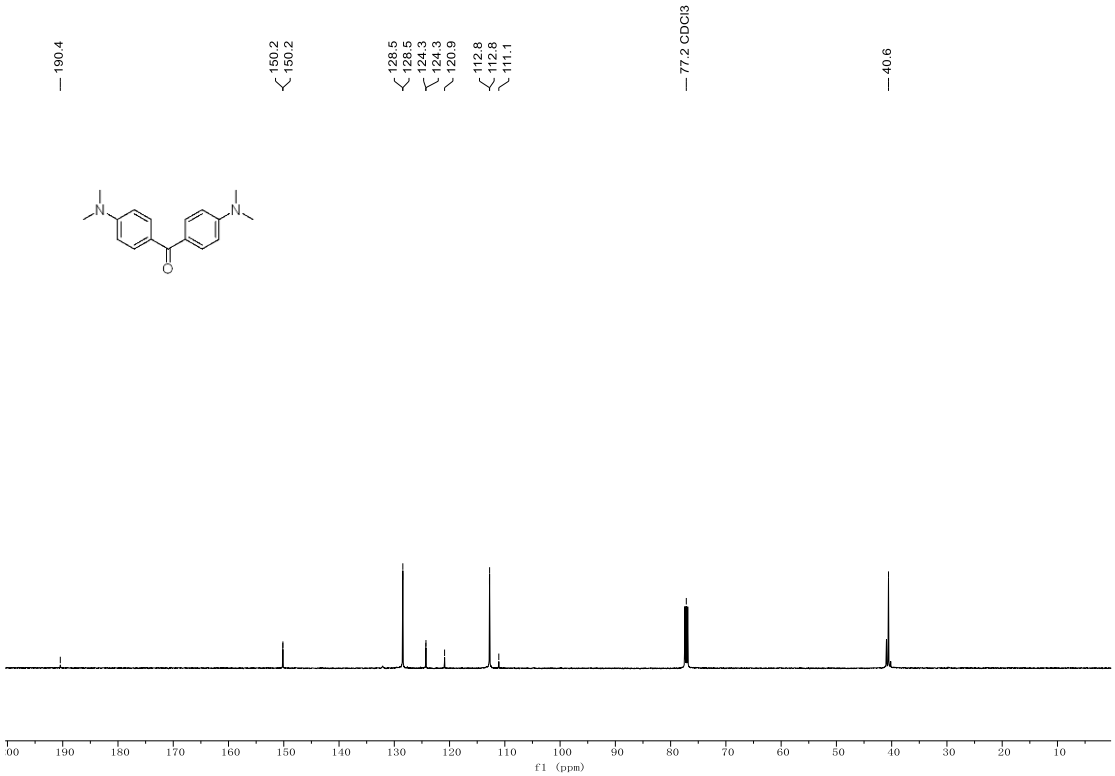
^{1}H NMR of **3aa** (400 MHz, Chloroform-*d*).



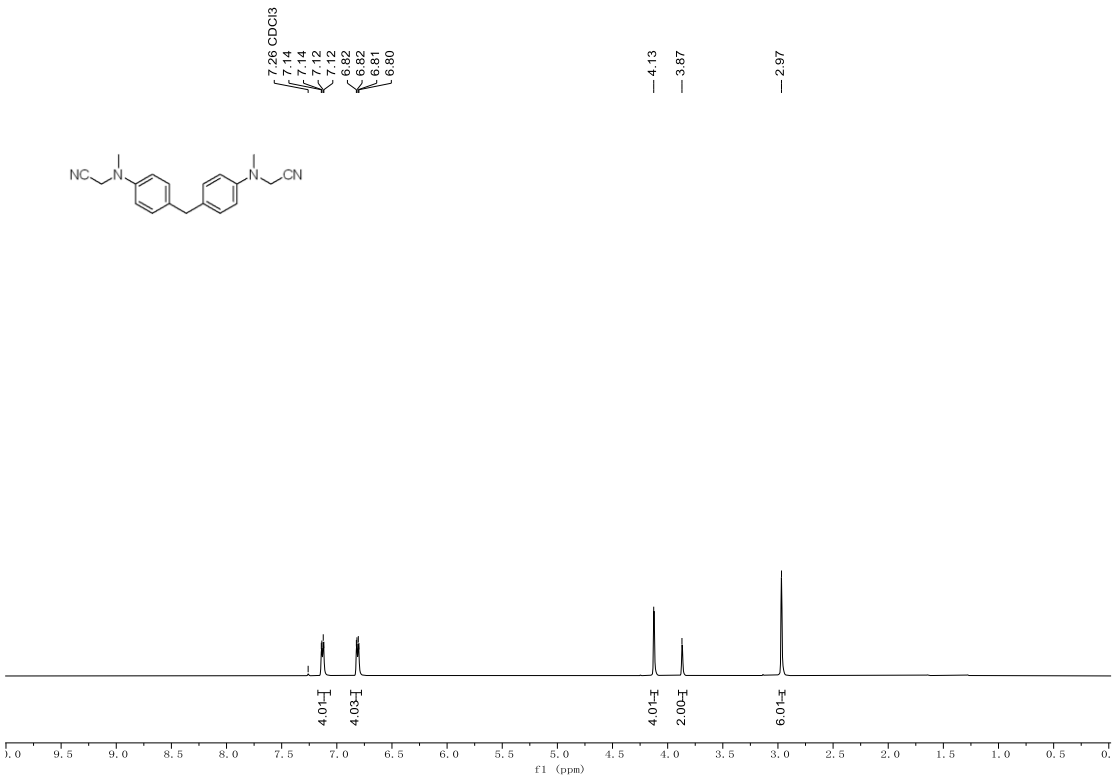
^{13}C NMR of **3aa** (101 MHz, Chloroform-*d*).



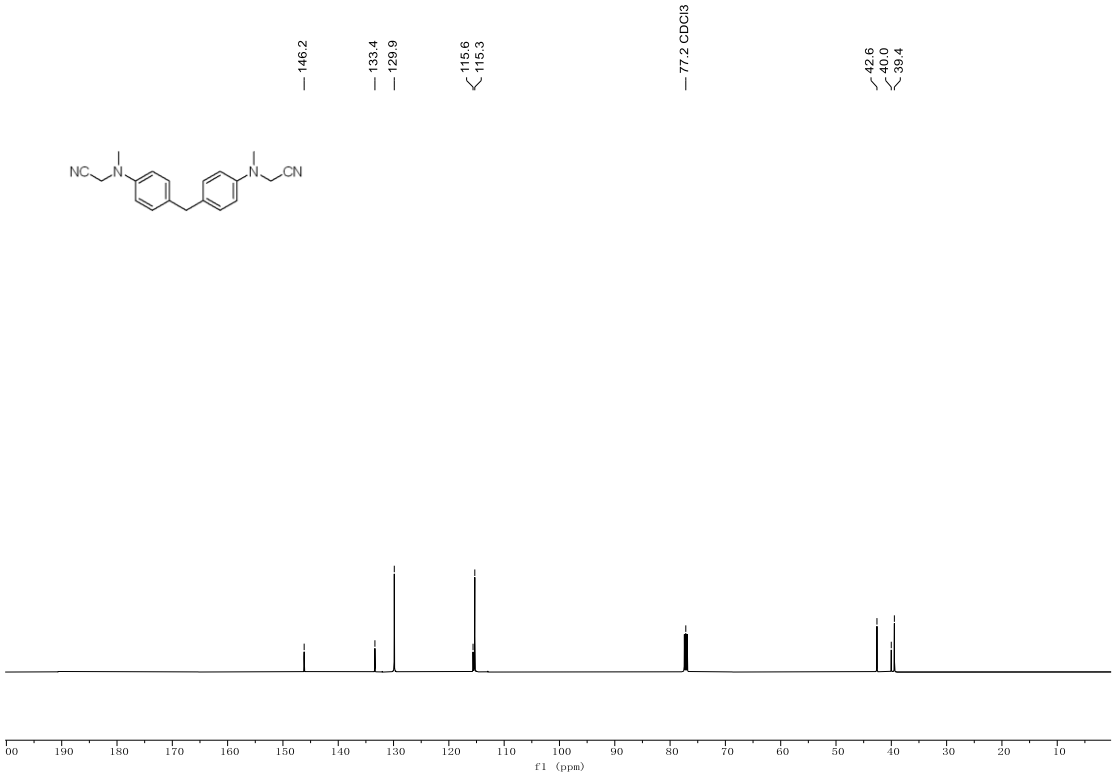
^{1}H NMR of **3ya** (400 MHz, Chloroform-*d*).



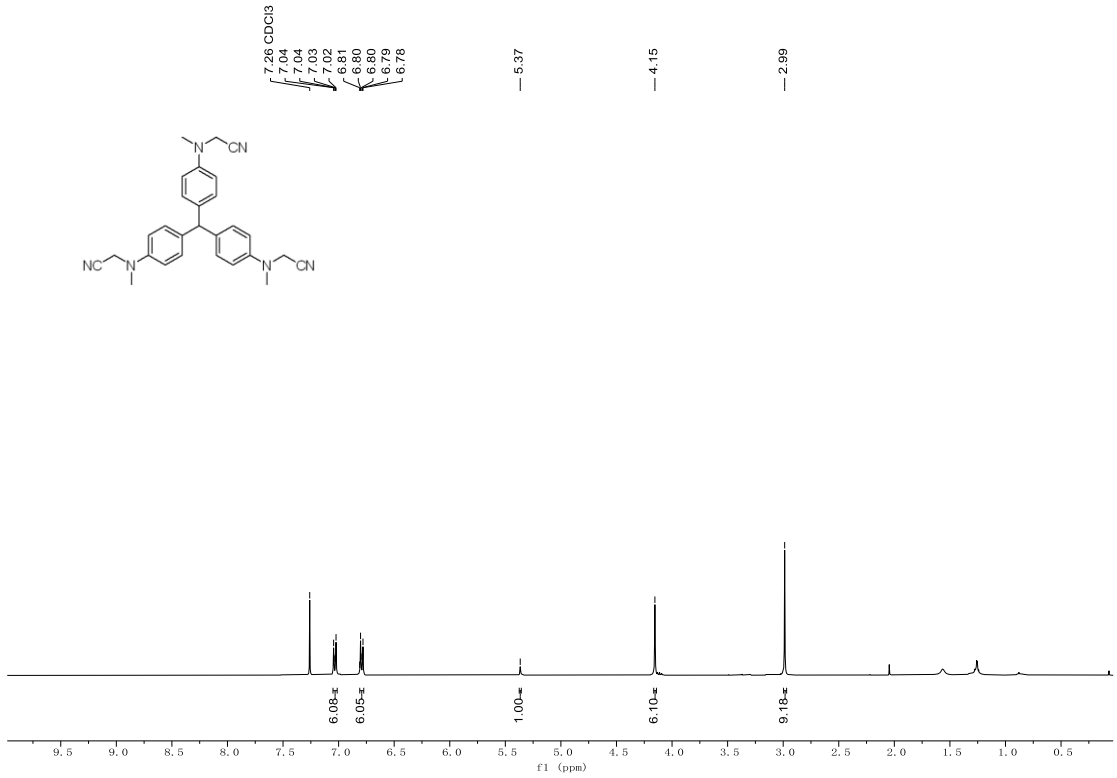
^{13}C NMR of **3ya** (126 MHz, Chloroform-*d*).



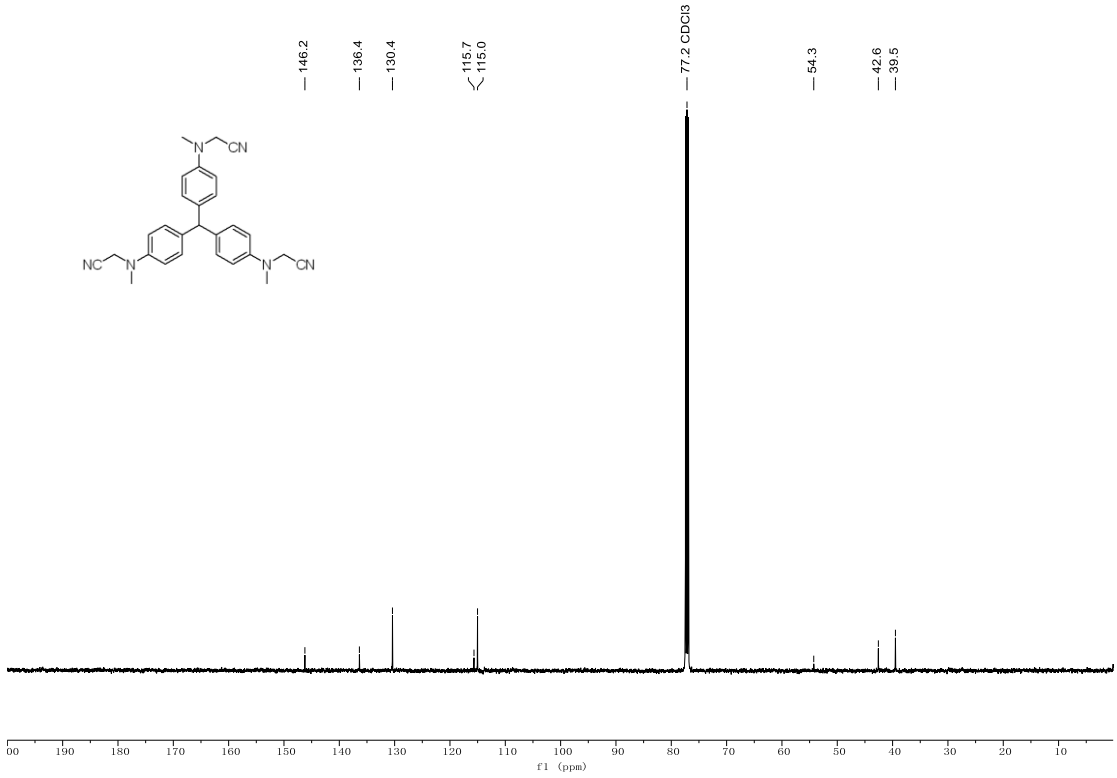
^{1}H NMR of **3yb** (500 MHz, Chloroform-*d*).



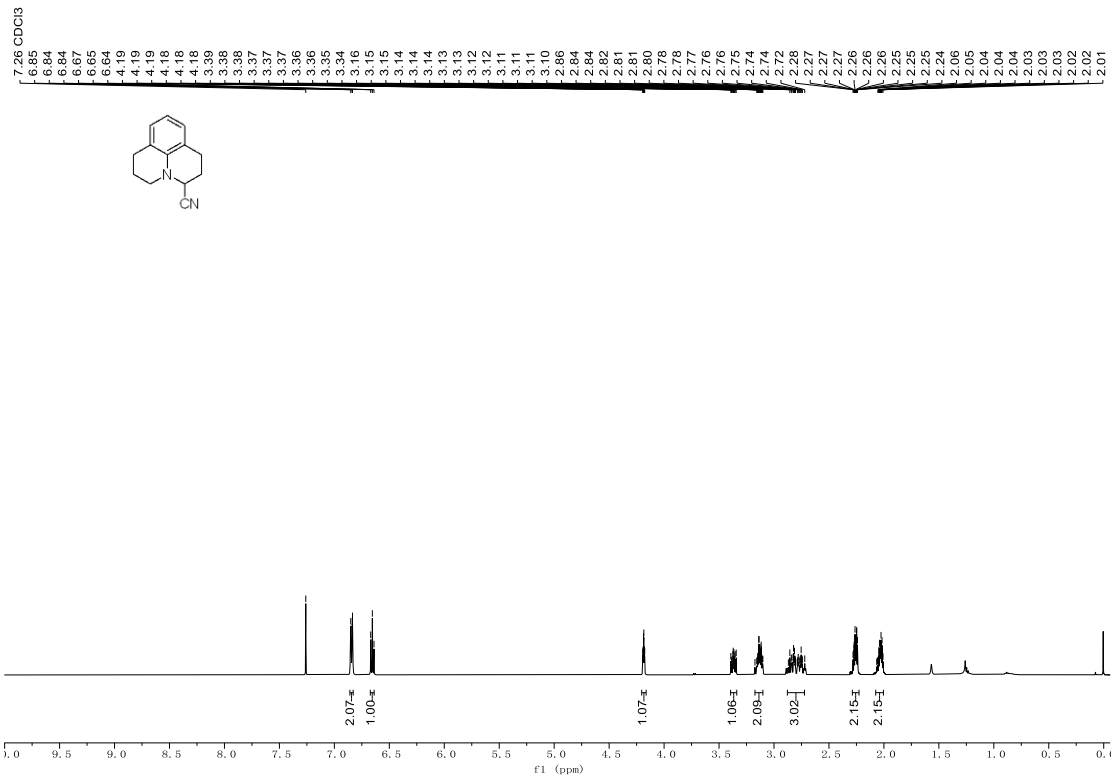
^{13}C NMR of **3yb** (126 MHz, Chloroform-*d*).



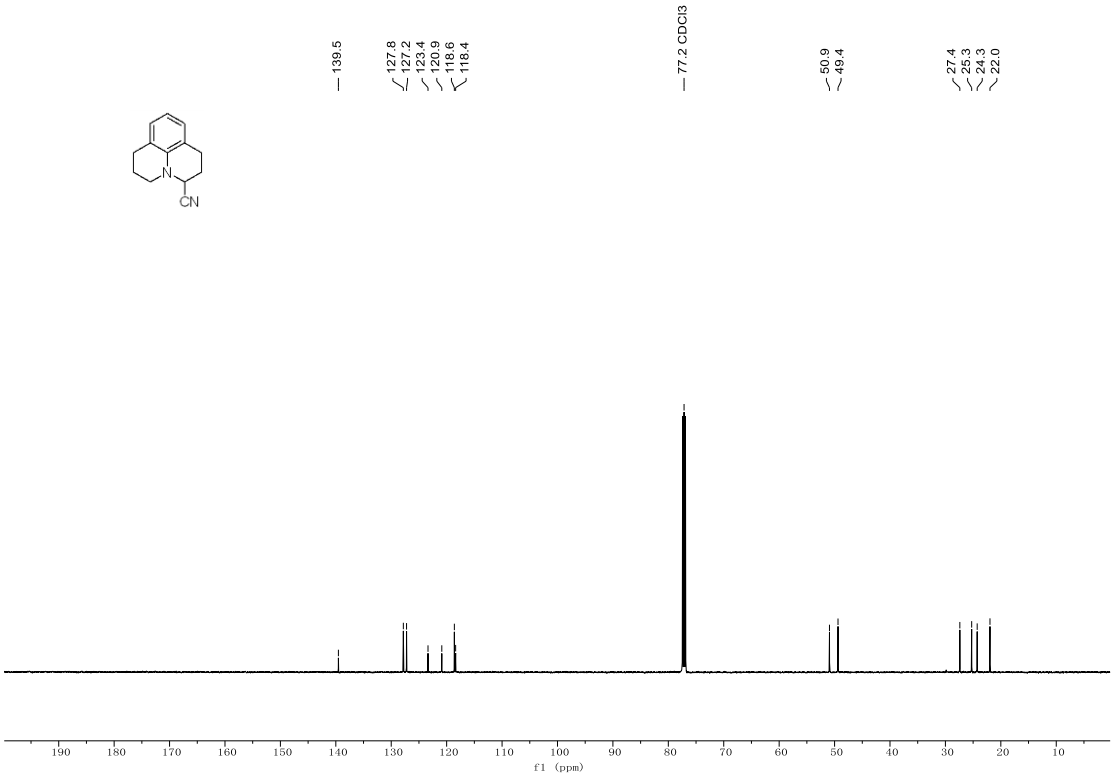
^{1}H NMR of **4a** (400 MHz, Chloroform-*d*).



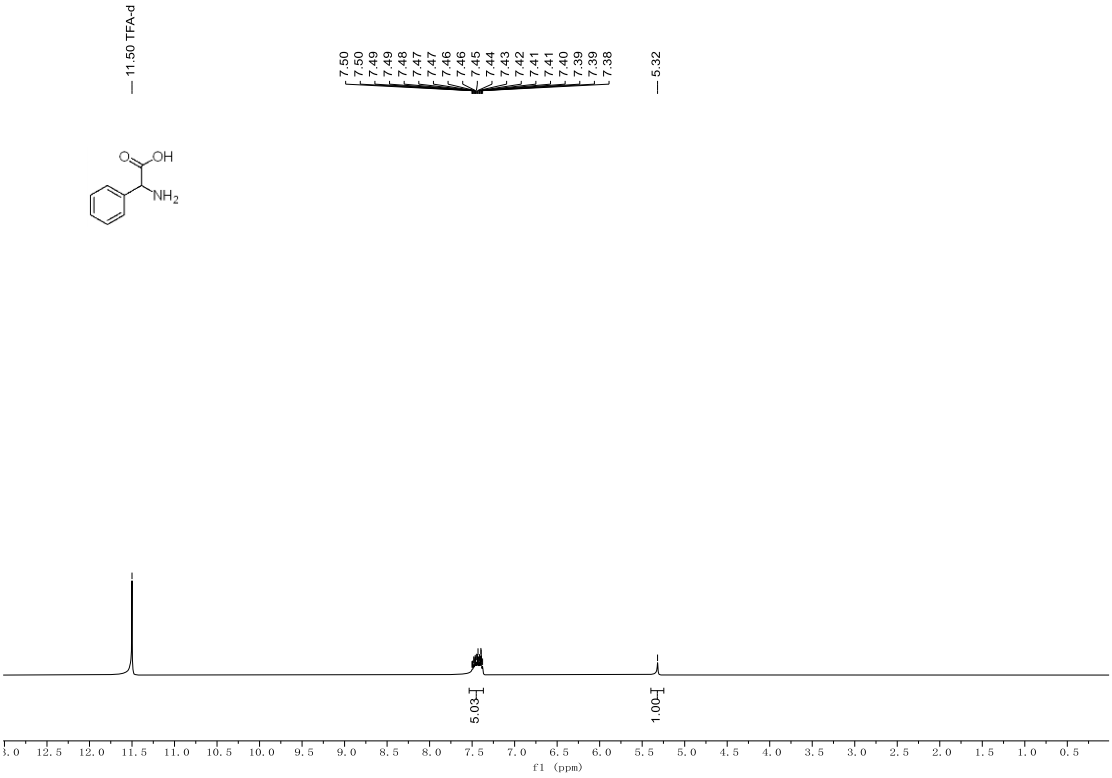
^{13}C NMR of **4a** (126 MHz, Chloroform-*d*).



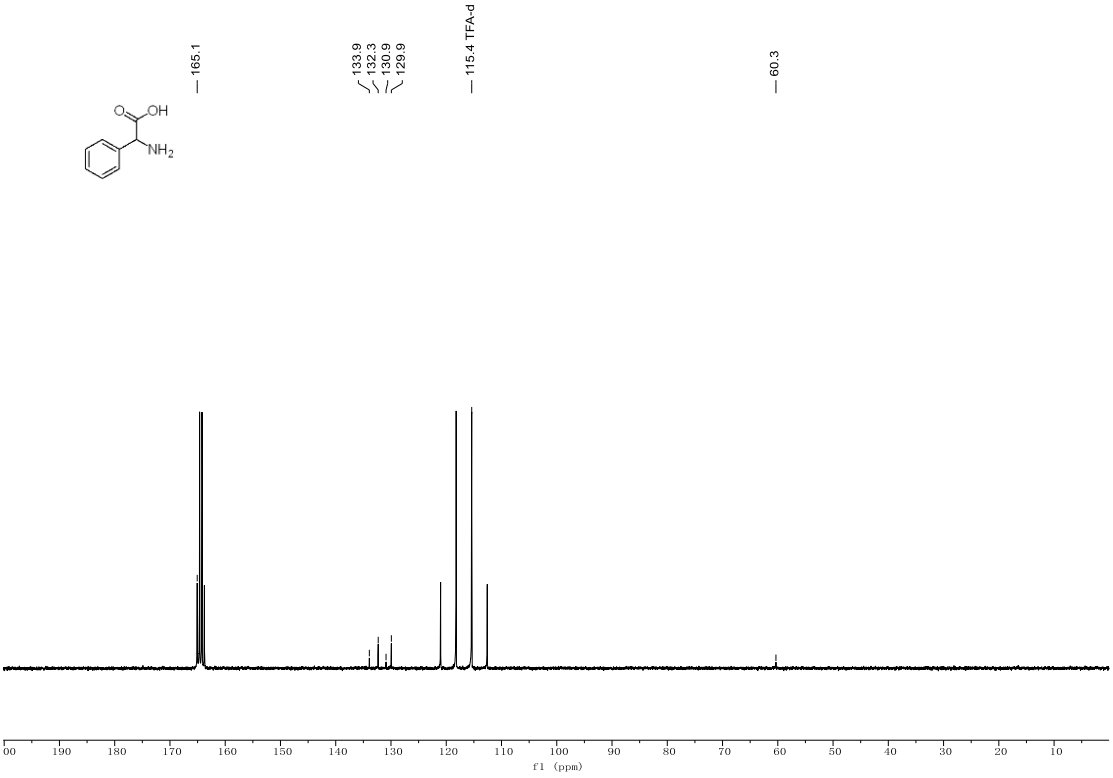
^{1}H NMR of **4b** (500 MHz, Chloroform-*d*).



^{13}C NMR of **4b** (126 MHz, Chloroform-*d*).



^{1}H NMR of **3va** (400 MHz, Trifluoroacetic acid-*d*).



^{13}C NMR of **3va** (101 MHz, Trifluoroacetic acid-d).