Supporting Information

Electrochemical Radical-Radical Cross-Coupling: Direct Access to *β*-Amino Nitriles from Unactivated Imines and Alkyl Nitriles

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Contents

A. General remarks

All the electrochemical reactions were performed in an undivided cell unless otherwise noted. The electrolysis instrument used is an adjustable DC regulated power supply (MS-150V 100 mA) (Dongguan Maihao Electronic Technology Co., Ltd.).

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on 600 MHz and 151 MHz NMR or 400 MHz and 101 MHz Bruker AVANCE spectrometers. ^{19}F NMR spectra were recorded on Bruker AVANCE III (376 MHz) instrument and were reported relative to $CFCl_3$ as the internal standard. The peaks were internally referenced to TMS (0.0 ppm). The NMR peak multiplicities identified as s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet; coupling constants (*J*) were reported in Hz.

All reactions were monitored by thin-layer chromatography (TLC) with Haiyang GF 254 silica gel plates (Qingdao Haiyang chemical industry Co Ltd, Qingdao, China) using UV light, vanillic aldehyde as visualizing agents. Flash column chromatography was performed using 200–300 mesh silica gel at increased pressure. Yields refer to chromatographically and spectroscopically pure materials unless otherwise stated.

High-resolution mass spectra (HRMS) were recorded on Bruker Impact II TOF mass spectrometer using ESI ionization sources.

Cyclic voltammograms were obtained on a CHI 700E potentiostat (CH Instruments, Inc.).

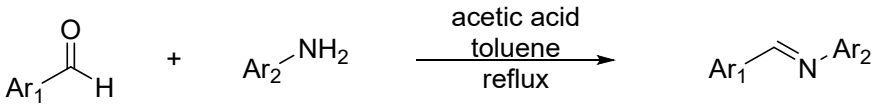
Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker EMX Nano spectrometer.

Melting points were taken on a WPX-4 apparatus (Yice instrument equipment Co Ltd, Shanghai) and were uncorrected.

All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted.

Abbreviations: BHT = 2,6-di-tert-butyl-4-methylphenol, DABCO = triethylenediamine, DCE = 1,2-dichloroethane, DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, DE =1,1-diphenylethylene, DMF = *N*, *N*-dimethylformamide, DMPO = 5,5-dimethyl-1-pyrroline-1-oxide, EA = ethyl acetate, RVC = reticulated vitreous carbon, TEMPO = 2,2,6,6-tetramethylpiperidinooxy, THF = tetrahydrofuran.

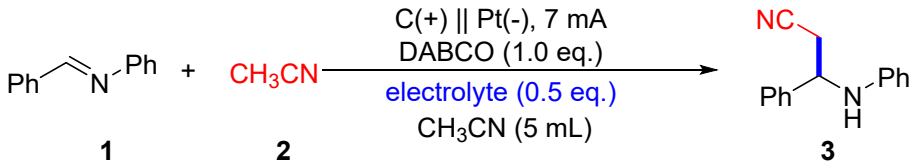
B. Synthesis of *N*,1-diarylmethanimines



In accordance with the literature known procedure,[1] the required aldehyde (50 mmol) and aniline (50 mmol) were dissolved in toluene (100 mL). To this, acetic acid (50 μL) was added, and the solution was heated to reflux for 16 hours with a Dean-Stark trap to remove water. Then the mixture was cooled to room temperature, and the solvent was removed *in vacuo* to afford the product.

C. Optimization of reaction conditions

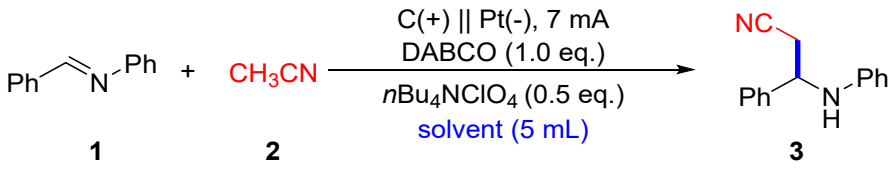
Table S1. Electrolyte screening (with DABCO as a mediator) [a]



Entry	Electrolyte	Yield (%) [b]
1	nBu$_4$NBF$_4$	27
2	nBu$_4$NPF$_6$	30
3	nBu$_4$NClO$_4$	42
4	nLiClO$_4$	N.D. [c]
5	nBu$_4$NI	N.R. [d]
6	Et$_4$NBF$_4$	11
7	Et$_4$NPF$_6$	30
8	LiBr	N.R.
9	NaI	N.R.

[a] Reaction conditions: **1** (0.3 mmol, 1.0 eq.), **2** (5.0 mL), electrolyte (0.5 eq.), DABCO (1.0 eq.), C anode (Φ = 6 mm) and Pt sheet (10 mm × 10 mm × 2 mm) cathode, constant current = 7 mA, 30 °C. Isolated yield. [b] Yield of the isolated product after chromatography on silica gel. [c] N.D. = Not Detected. [d] N.R. = No Reaction.

Table S2. Solvent screening (with DABCO as a mediator) [a]

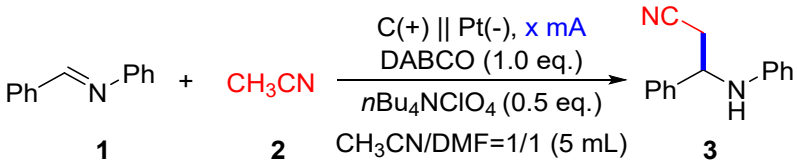


1 **2** **3**

Entry	Solvent	Yield (%) [b]
1	CH_3CN	42
2	Toluene : CH_3CN = 1:1	25
3	Acetone : CH_3CN = 1:1	N.D. [c]
4	CH_3OH : CH_3CN = 1:1	N.R. [d]
5	DCM : CH_3CN = 1:1	N.R.
6	THF : CH_3CN = 1:1	N.D.
7	EA : CH_3CN = 1:1	N.R.
8	DCE : CH_3CN =1:1	N.R.
9	DMF : CH_3CN =1:1	47

[a] Reaction conditions: **1** (0.3 mmol, 1.0 eq.), **2** (2.5 mL), solvent (2.5 mL), nBu$_4$NClO$_4$ (0.5 eq.), DABCO (1.0 eq.), C anode (Φ = 6 mm) and Pt sheet (10 mm × 10 mm × 2 mm) cathode, constant current = 7 mA, 30 °C. [b] Yield of the isolated product after chromatography on silica gel. [c] N.D. = Not Detected. [d] N.R. = No Reaction.

Table S3. Optimization of the current (with DABCO as a mediator) [a]



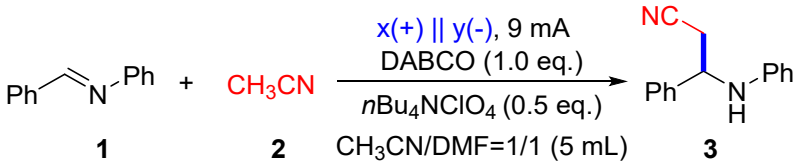
1 **2** **3**

Entry	Current	Yield (%) [b]
1	3	20
2	5	45
3	7	47
4	8	53
5	9	61
6	10	59
7	11	43
8	13	41

9	15	33

[a] Reaction conditions: **1** (0.3 mmol, 1.0 eq.), **2** (2.5 mL), DMF (2.5 mL), nBu$_4$NClO$_4$ (0.5 eq.), DABCO (1.0 eq.), C anode (Φ = 6 mm) and Pt sheet (10 mm × 10 mm × 2 mm) cathode, constant current = x mA, 30 °C. [b] Yield of the isolated product after chromatography on silica gel.

Table S4. Electrode screening (with DABCO as a mediator) [a]

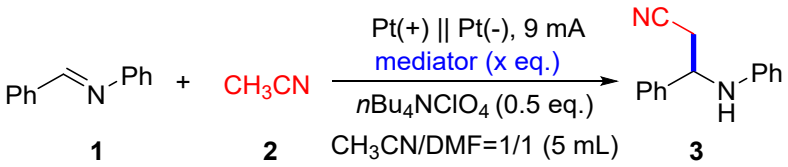


1 **2** **3**

Entry	Anode	Cathode	Yield (%) [b]
1	C	Pt	61
2	Pt	Pt	64
3	Pt	C	38
4	C	C	31
5	Pt	RVC	trace
6	Pt	Ni	31

[a] Reaction conditions: **1** (0.3 mmol, 1.0 eq.), **2** (2.5 mL), DMF (2.5 mL), nBu$_4$NClO$_4$ (0.5 eq.), DABCO (1.0 eq.), x anode and y cathode, constant current = 9 mA, 30 °C. [b] Yield of the isolated product after chromatography on silica gel.

Table S5. Mediator screening [a]



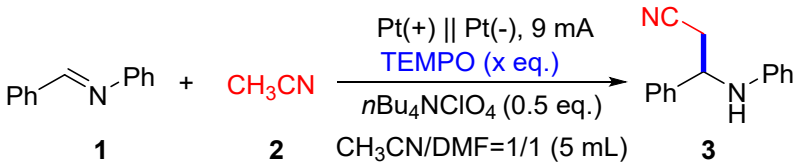
1 **2** **3**

Entry	Mediator	Yield (%) [b]
1	DABCO (1.0 eq.)	64
2	Tris (4-bromophenyl) amine (1.0 eq.)	45
3	DDQ (1.0 eq.)	N.D. [c]
4	4-Iodoanisole (1.0 eq.)	N.R. [d]
5	KI (1.0 eq.)	19
6	NH_4I (1.0 eq.)	N.R.

7	DABCO (0.5 eq.)	67
8	TEMPO (0.5 eq.)	91
9	Triphenylamine (0.5 eq.)	59
10	1,2,3,4-Tetrahydro-2-isoquinoline (0.5 eq.)	31
11	*N,N*-Diisopropylethylamine (0.5 eq.)	55
12	*N,N*-Dimethylaniline (0.5 eq.)	N.R. [c]
13	Ferrocene (0.5 eq.)	63
14	none	39

[a] Reaction conditions: **1** (0.3 mmol, 1.0 eq.), **2** (2.5 mL), DMF (2.5 mL), nBu$_4$NClO$_4$ (0.5 eq.), mediator (x eq.), Pt sheet (10 mm × 10 mm × 2 mm) anode and cathode, constant current = 9 mA, 30 °C. [b] Yield of the isolated product after chromatography on silica gel. [c] N.D. = Not Detected. [d] N.R. = No Reaction.

Table S6. Optimization of the amount of TEMPO [a]

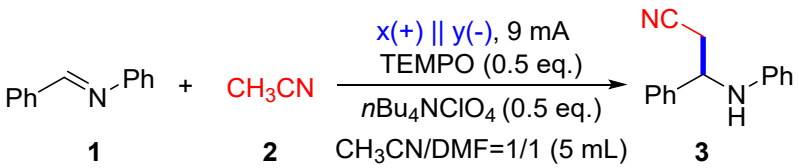


1 **2** **3**

Entry	Equivalent of TEMPO	Yield (%) [b]
1	0.25	54
2	0.5	91
3	0.75	88
4	0.85	75

[a] Reaction conditions: **1** (0.3 mmol, 1.0 eq.), **2** (2.5 mL), DMF (2.5 mL), nBu$_4$NClO$_4$ (0.5 eq.), TEMPO (x eq.), Pt sheet (10 mm × 10 mm × 2 mm) anode and cathode, constant current = 9 mA, 30 °C. [b] Yield of the isolated product after chromatography on silica gel.

Table S7. Electrode screening (with TEMPO as a mediator) [a]



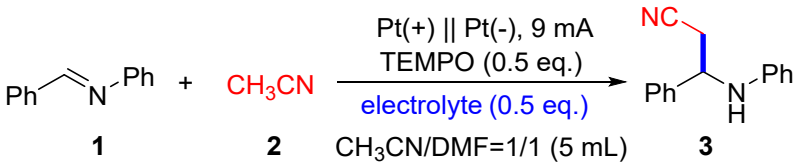
1 **2** **3**

Entry	Anode	Cathode	Yield (%) [b]

1	C	Pt	89
2	Pt	Pt	91
3	Pt	C	67
4	C	C	76

[a] Reaction conditions: **1** (0.3 mmol, 1.0 eq.), **2** (2.5 mL), DMF (2.5 mL), nBu$_4$NClO$_4$ (0.5 eq.), TEMPO (0.5 eq.), x anode and y cathode, constant current = 9 mA, 30 °C. [b] Yield of the isolated product after chromatography on silica gel.

Table S8. Electrolyte screening (with TEMPO as a mediator) [a]

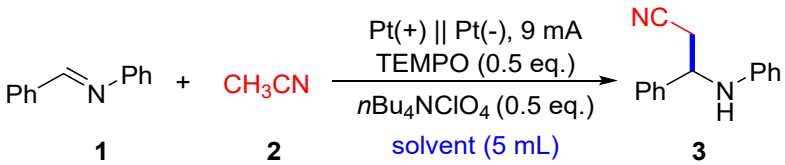


1 **2** **3**

Entry	Electrolyte	Yield (%) [b]
1	nBu$_4$NBF$_4$	85
2	nBu$_4$NPF$_6$	88
3	nBu$_4$NClO$_4$	91
4	LiClO$_4$	N.D. [c]
5	LiBr	N.R. [d]

[a] Reaction conditions: **1** (0.3 mmol, 1.0 eq.), **2** (2.5 mL), DMF (2.5 mL), electrolyte (0.5 eq.), TEMPO (0.5 eq.), Pt sheet (10 mm × 10 mm × 2 mm) anode and cathode, constant current = 9 mA, 30 °C. [b] Yield of the isolated product after chromatography on silica gel. [c] N.D. = Not Detected. [d] N.R. = No Reaction.

Table S9. Solvent screening (with TEMPO as a mediator) [a]



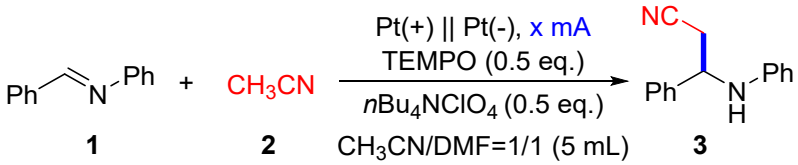
1 **2** **3**

Entry	Solvent	Yield (%) [b]
1	CH_3CN	47
2	CH_3CN : DMF = 1:1	91
3	CH_3CN : Toluene = 1:1	33
4	CH_3CN : CH_3OH = 1:1	N.R. [c]

5	CH_3CN : CH_3CH_2OH = 1:1	N.R.
6	CH_3CN : Isopropanol = 1:1	N.R.
7	CH_3CN : Isopropyl acetate = 1:1	N.R.

[a] Reaction conditions: **1** (0.3 mmol, 1.0 eq.), **2** (2.5 mL), solvent (2.5 mL), nBu$_4$NClO$_4$ (0.5 eq.), TEMPO (0.5 eq.), Pt sheet (10 mm × 10 mm × 2 mm) anode and cathode, constant current = 9 mA, 30 °C. [b] Yield of the isolated product after chromatography on silica gel. [c] N.R. = No Reaction.

Table S10. Optimization of the current (with TEMPO as a mediator) [a]

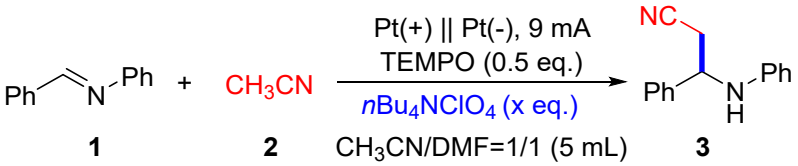


1 **2** **3**

Entry	Current	Yield (%) [b]
1	5	85
2	7	87
3	9	91
4	11	87

[a] Reaction conditions: **1** (0.3 mmol, 1.0 eq.), **2** (2.5 mL), DMF (2.5 mL), nBu$_4$NClO$_4$ (0.5 eq.), TEMPO (0.5 eq.), Pt sheet (10 mm × 10 mm × 2 mm) anode and cathode, constant current = x mA, 30 °C. [b] Yield of the isolated product after chromatography on silica gel.

Table S11. Optimization of the amount of nBu$_4$NClO$_4$ (with TEMPO as a mediator) [a]

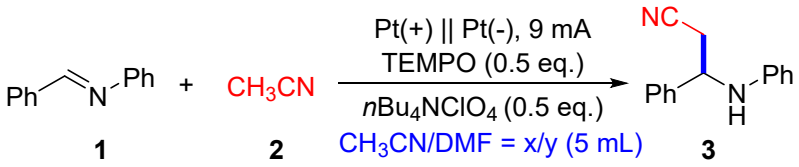


1 **2** **3**

Entry	Equivalent of nBu$_4$NClO$_4$	Yield (%) [b]
1	0	N.R. [c]
2	0.5	91
3	1.0	80
4	1.5	76
5	2.0	88

[a] Reaction conditions: **1** (0.3 mmol, 1.0 eq.), **2** (2.5 mL), DMF (2.5 mL), nBu$_4$NClO$_4$ (x eq.), TEMPO (0.5 eq.), Pt sheet (10 mm × 10 mm × 2 mm) anode and cathode, constant current = 9 mA, 30 °C. [b] Yield of the isolated product after chromatography on silica gel. [c] N.R. = No Reaction.

Table S12. Optimization of the proportion of solvents (with TEMPO as a mediator) [a]



1 **2** **3**

Entry	Proportion of solvents	Yield (%) [b]
1	CH_3CN : DMF = 2:1	75
2	CH_3CN : DMF = 1:1	91
3	CH_3CN	47
4	CH_3CN : DMF = 1:2	76

[a] Reaction conditions: **1** (0.3 mmol, 1.0 eq.), **2** (x mL), DMF (y mL), nBu$_4$NClO$_4$ (0.5 eq.), TEMPO (0.5 eq.), Pt sheet (10 mm × 10 mm × 2 mm) anode and cathode, constant current = 9 mA, 30 °C. [b] Yield of the isolated product after chromatography on silica gel.

D. General procedures for the electrolysis

D1. The materials used to make the electrolytic cell

All the materials used to make the electrolytic cell were commercially available (Figure S1). The anode and cathode used were all platinum electrodes (1.0 cm × 1.0 cm × 0.2 mm) (Gaoss Union).

Figure S1. The materials used to make the electrolytic cell for the synthesis of *β*-amino nitriles.

D2. General procedure for the electrosynthesis of *β*-amino nitriles

An undivided test tube-type electrolysis cell (10 mL) was charged with a stir bar, imine (0.3 mmol, 1.0 eq.), TEMPO (0.15 mmol, 0.5 eq.), nBu$_4$NClO$_4$ (0.15 mmol, 0.5 eq.), CH_3CN (2.5 mL) and DMF (2.5 mL), and the resulting suspension was stirred until the solids were dissolved. Then the prepared electrodes were placed into the reaction mixture. Both anode and cathode were platinum sheet electrodes (10 mm × 10 mm × 2 mm). The mixture was electrolyzed at a constant current of 9 mA at 30 °C until the imine was consumed entirely (monitored by TLC). The reaction electrodes were taken out, washed twice with ethyl acetate (20 mL) ultrasonically, and the ethyl acetate was combined with the reaction mixture. The combined mixture was washed with H_2O (10 mL × 3), brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography with ethyl acetate and petroleum ether as eluents to afford the desired product.

Note: When using nitriles other than CH_3CN, the conditions remain the same, except for nitrile (5.0 eq. to imine), DMF (5 mL).

Besides, the product could be purified by recrystallization in addition to column chromatography. Taking model reaction as an example, the operation steps are as follows:

Firstly, after the starting material imine **1** was consumed completely (monitored by TLC), the electrodes were taken out, washed twice with ethyl acetate (20 mL)

ultrasonically, and the ethyl acetate was combined with the reaction mixture. The combined mixture was washed with H_2O (10 mL × 3) and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure.

Secondly, the concentrate was dissolved in 10 mL of ethyl acetate, to which 500 mg of activated carbon powder was added. The resulting mixture was heated to reflux for 30 minutes, filtered while hot, and the filtrate was concentrated under reduced pressure to give yellow oil.

Thirdly, a small amount of ethyl acetate was added to the oil until it was completely dissolved. An appropriate amount of petroleum ether was added to the above solution until the solution was just turbid, and then ethyl acetate was added dropwise until the turbidity disappeared.

Finally, the solution was allowed to stand at -20 ºC for 1 hour, and a white solid precipitated. rinsed the solid The mother liquor was removed, and the solid was washed with ice cold petroleum ether and dried the solid in a vacuum drying oven to give pure product **3** in 58% yield.

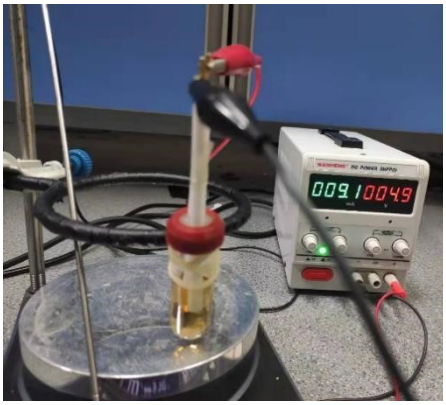


Figure S2. Reaction setup.

D3. A gram-scale experiment for the electrosynthesis of *β*-amino nitrile 3

An undivided test tube-type electrolysis cell (80 mL) was charged with a stir bar, **1** (9 mmol, 1.63 g, 1.0 eq.), TEMPO (4.5 mmol, 0.70 g, 0.5 eq.), nBu$_4$NClO$_4$ (4.5 mmol, 1.54 g, 0.5 eq.), CH_3CN (30 mL) and DMF (30 mL), and the resulting suspension was stirred until the solids were dissolved. Then the prepared electrodes were placed into the reaction mixture. Both anode and cathode were platinum sheet electrodes (30 mm × 30 mm × 2 mm each). The mixture was electrolyzed at a constant current of 81 mA

at room temperature until the imine was consumed entirely (monitored by TLC). The reaction electrodes were taken out, washed twice with ethyl acetate (60 mL) ultrasonically, and the ethyl acetate was combined with the reaction mixture. The combined mixture was washed with H_2O (30 mL × 3), brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography with ethyl acetate and petroleum ether as eluents to afford the desired product **3** in 76% yield (1.52 g).

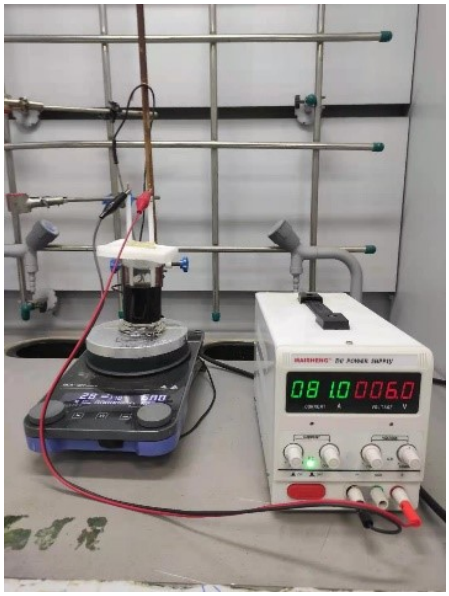


Figure S3. Gram-scale experimental setup.

E. Cyclic voltammetry experiments

The cyclic voltammetry experiments were carried out with a computer-controlled electrochemical analyzer for electrochemical measurements. The experiment was performed in a three-electrode cell (volume 15 mL) with DMF as the solvent, nBu$_4$NPF$_6$ (0.05 M) as the supporting electrolyte, the tested compound (2.0 mM), glassy carbon (diameter 3 mm) as the working electrode, Pt wire as the auxiliary electrode, and Ag/AgCl (saturated aqueous KCl) as the reference electrode. The scan speed was 100 mV/s. The potential ranges investigated were -2.2 V to +2.0 V vs Ag/AgCl (saturated aqueous KCl) for background, **1**, TEMPO, **1b** and **3**, and -3.4 V to +2.0 V vs Ag/AgCl (saturated aqueous KCl) for **A**, **B** and **C**.

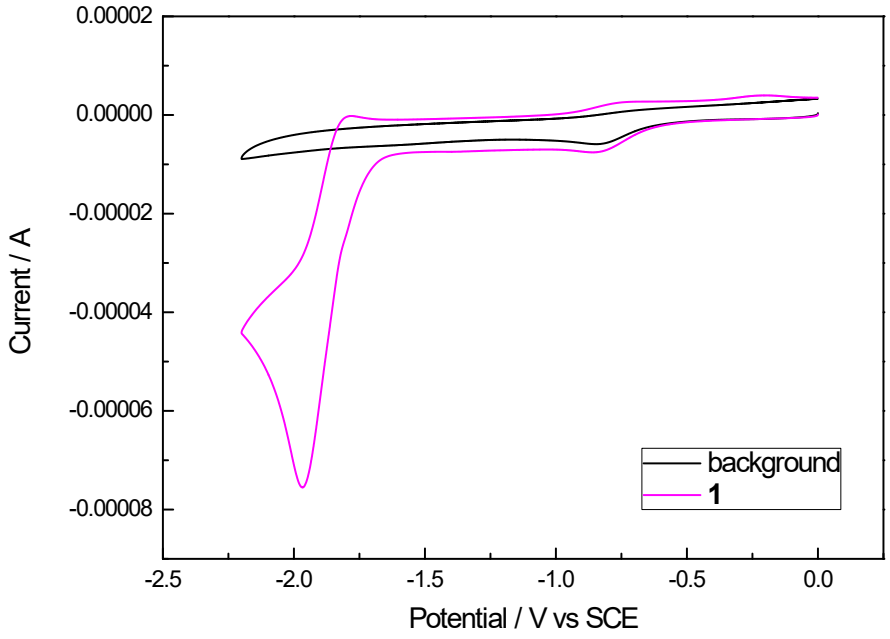


Figure S4. Cyclic voltammogram of **1** in an electrolyte of nBu$_4$NPF$_6$ (0.05 M) in DMF.

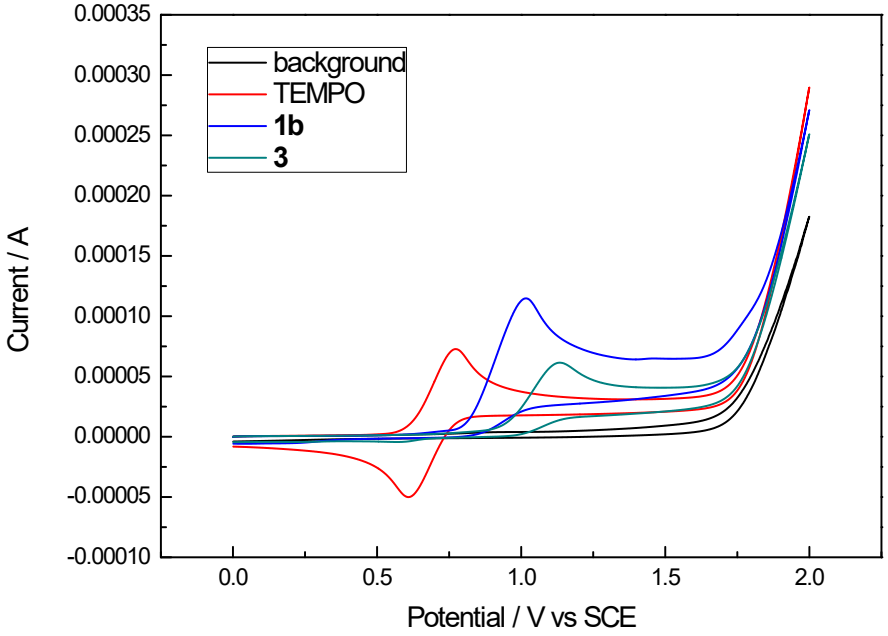


Figure S5. Cyclic voltammogram of TEMPO, **1b** and **3** in an electrolyte of nBu$_4$NPF$_6$ (0.05 M) in DMF.

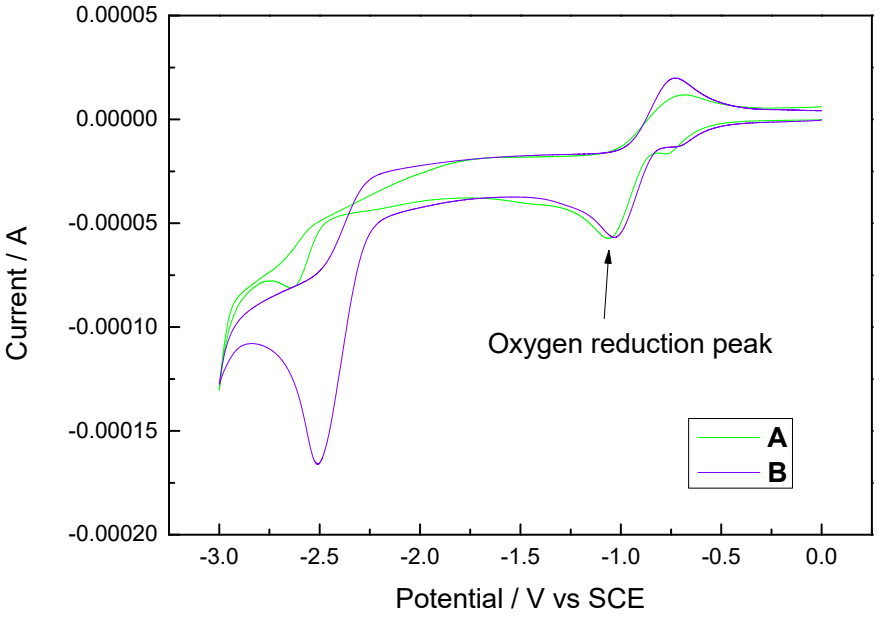


Figure S6. Cyclic voltammogram of **A and B** in an electrolyte of nBu$_4$NPF$_6$ (0.05 M) in DMF.

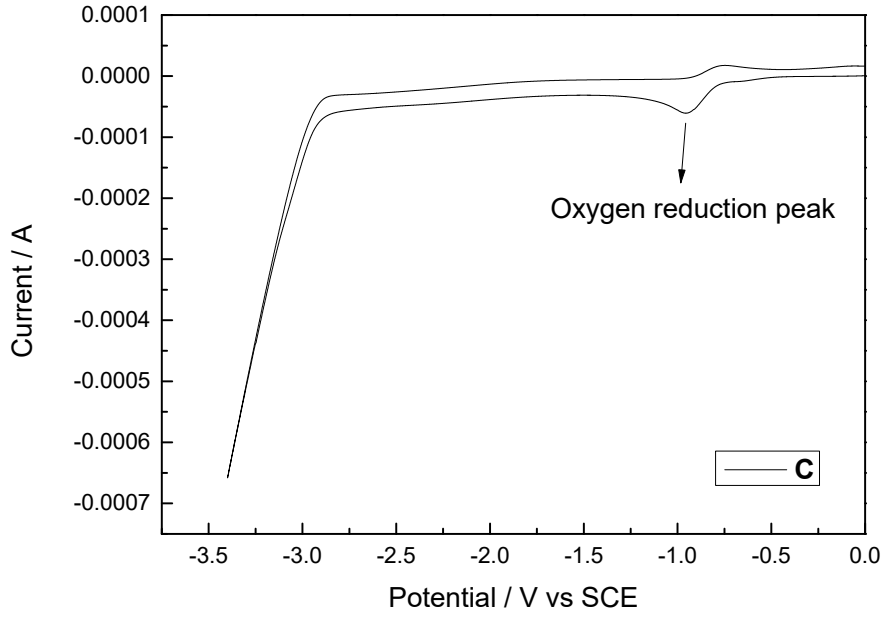


Figure S7. Cyclic voltammogram of **C** in an electrolyte of nBu$_4$NPF$_6$ (0.05 M) in DMF from -3.4 to 0 V.

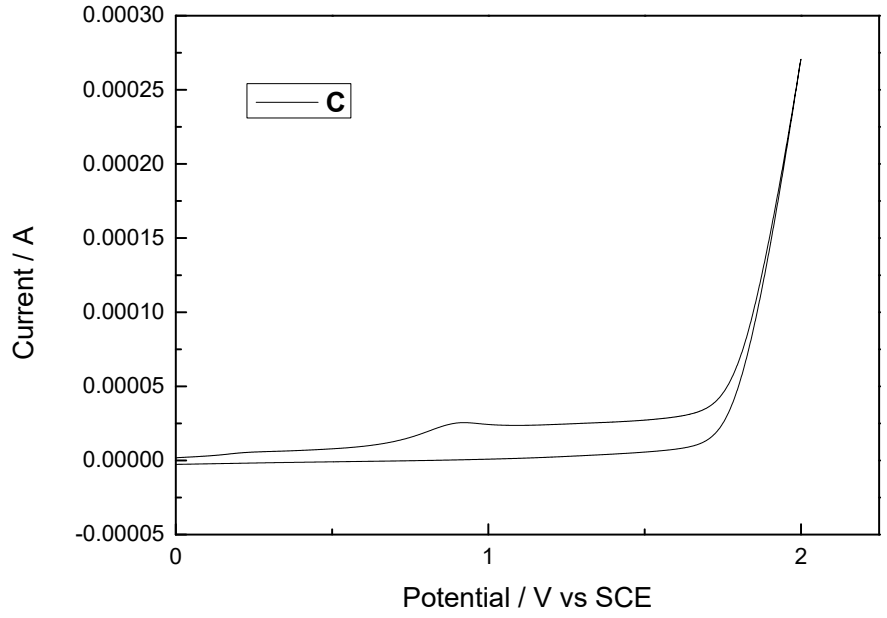


Figure S8. Cyclic voltammogram of **C** in an electrolyte of nBu$_4$NPF$_6$ (0.05 M) in DMF from 0 to +2.0 V.

F. Mechanistic experiments

F1. Electron paramagnetic resonance (EPR) experiment

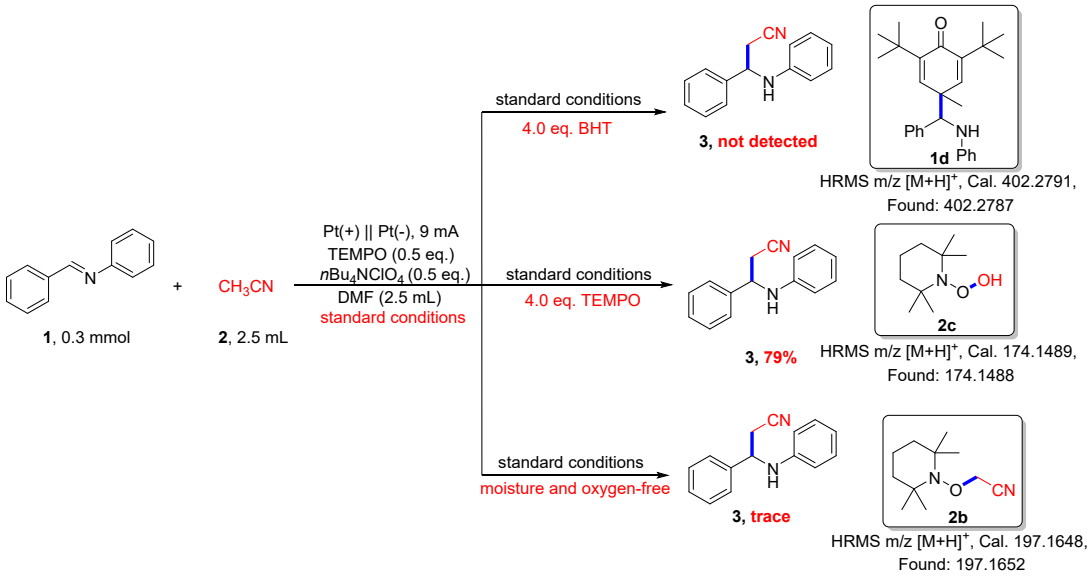
EPR spectra were recorded at 298 K on EPR spectrometer operated at 9.6403 GHz. Typical spectrometer parameters are shown as follows, scan range: 200.0 G; center fieldset: 3430.00 G; time constant: 1.28 ms; scan time: 24.02 s; modulation amplitude: 8.000 G; modulation frequency: 100.00 kHz; microwave power: 10.00 mW. g = 2.0077.

An undivided test tube-type electrolysis cell (10 mL) was charged with a stir bar, **1** (0.3 mmol, 1.0 eq.), nBu$_4$NClO$_4$ (0.15 mmol, 0.5 eq.), DMPO (40 μL), CH$_3$CN (2.5 mL), and DMF (2.5 mL), and the resulting suspension was stirred until the solids were dissolved. Then the prepared electrodes were placed into the solution. Both anode and cathode were platinum sheet electrodes (10 mm × 10 mm × 2 mm). The mixture was electrolyzed at a constant current of 9 mA. After 20 min, a capillary reaction solution was taken out and analyzed by EPR at room temperature.

F2. Radical trapping experiments

In order to confirm if the reaction undergoes a radical mechanism, radical trapping

experiments were taken.



Scheme S1. Radical trapping experiments for TEMPO as the mediator.

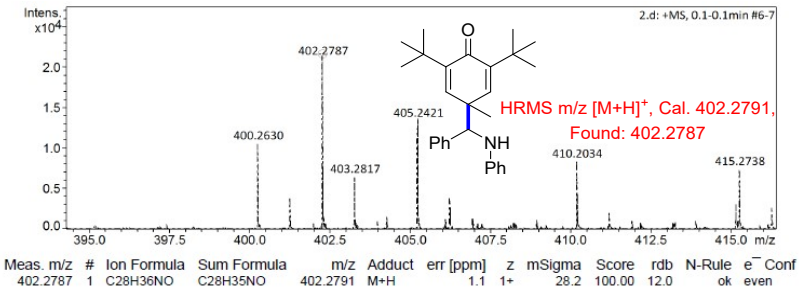


Figure S9. Mass spectrometry (HRMS) data of **1d**

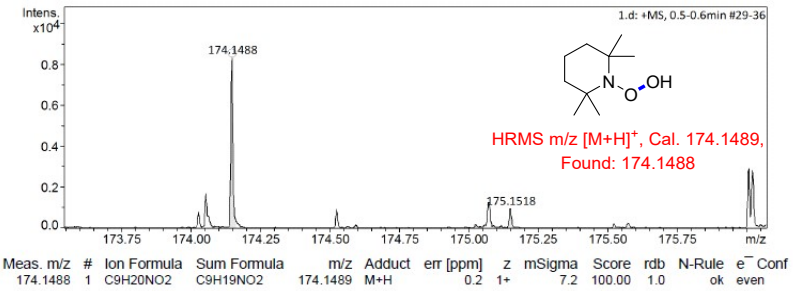


Figure S10. Mass spectrometry (HRMS) data of **2c**

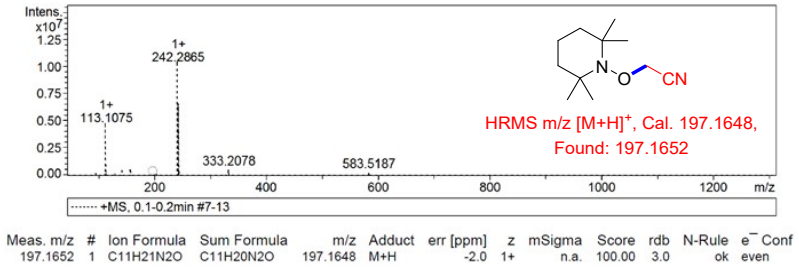
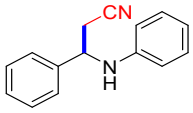


Figure S11. Mass spectrometry (HRMS) data of **2b**

F3. Experiment with sacrificial anode

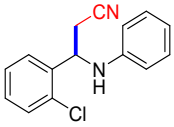
An undivided test tube-type electrolysis cell (10 mL) was charged with a stir bar, **1** (0.3 mmol, 1.0 eq.), nBu$_4$NClO$_4$ (0.15 mmol, 0.5 eq.), TEMPO (0.15 mmol, 0.5 eq.), CH_3CN (2.5 mL) and DMF (2.5 mL), and the resulting suspension was stirred until the solids were dissolved. Then the prepared electrodes (magnesium ribbon anode and platinum sheet cathode) were placed into the reaction mixture. The mixture was electrolyzed at a constant current of 9 mA for 3.5 h (**1** was completely consumed, monitored by TLC). The reaction electrodes were taken out, washed twice with ethyl acetate (20 mL) ultrasonically, and the ethyl acetate was combined with the reaction mixture. The combined mixture was washed with H_2O (10 mL ×3), brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography with ethyl acetate and petroleum ether as eluents to afford the final product **1b** in 47% yield and **3** in 47% yield.

G: Characterization data for the electrolysis products



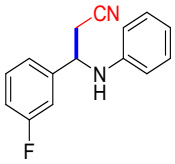
3-Phenyl-3-(phenylamino)propanenitrile (3)[2]

Yield = 91%, yellow solid. **M.p.:** 80-82 °C. **^{1}H NMR (400 MHz, Chloroform-d):** δ 7.39 – 7.34 (m, 4H), 7.32 – 7.28 (m, 1H), 7.15 – 7.11 (m, 2H), 6.73 (t, J = 7.3 Hz, 1H), 6.57 (d, J = 7.9 Hz, 2H), 4.72 (t, J = 6.1 Hz, 1H), 4.23 (brs, 1H), 2.88 – 2.78 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-d):** δ 145.9, 140.0, 129.4, 129.2, 128.5, 126.3, 118.8, 117.2, 113.9, 54.4, 26.2.



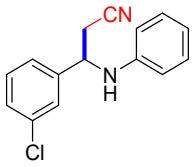
3-(2-Chlorophenyl)-3-(phenylamino)propanenitrile (4)[2]

Yield = 75%, orange oil. **^{1}H NMR (600 MHz, Chloroform-*d*):** δ 7.52 – 7.45 (m, 1H), 7.42 – 7.39 (m, 1H), 7.27 – 7.22 (m, 2H), 7.14 – 7.11 (m, 2H), 6.73 (t, J = 7.3 Hz, 1H), 6.53 (d, J = 7.7 Hz, 2H), 5.19 – 5.17 (m, 1H), 3.02 (dd, J = 17.0, 4.9 Hz, 1H), 2.87 (dd, J = 17.0, 6.3 Hz, 1H). **^{13}C NMR (151 MHz, Chloroform-*d*):** δ 145.3, 136.8, 132.6, 130.1, 129.6, 129.4, 127.7, 127.5, 119.0, 116.7, 113.9, 50.9, 24.7.



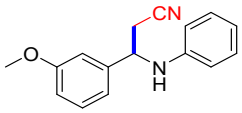
3-(3-Fluorophenyl)-3-(phenylamino)propanenitrile (5)

Yield = 83%, yellow oil. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.30 – 7.25 (m, 1H), 7.14 – 7.06 (m, 4H), 6.98 – 6.93 (m, 1H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.56 – 6.51 (m, 2H), 4.66 (t, *J* = 6.1 Hz, 1H), 4.30 (brs, 1H), 2.80 – 2.70 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*):** δ 163.7 (d, *J* = 248.6 Hz), 145.9, 143.1 (d, *J* = 6.6 Hz), 131.3 (d, *J* = 8.3 Hz), 129.9, 122.3 (d, *J* = 2.9 Hz), 119.6, 117.1, 116.0 (d, *J* = 21.3 Hz), 114.4, 113.7 (d, *J* = 22.4 Hz), 54.5, 26.7. **^{19}F NMR (376 MHz, Chloroform-*d*):** δ -111.37. **HRMS (EI):** exact mass calculated for $C_{15}H_{13}FN_2$ $[M+Na]^+$ require m/z = 263.0955, found m/z = 263.0952.



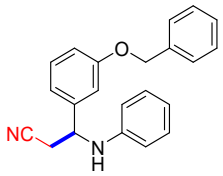
3-(3-Chlorophenyl)-3-(phenylamino)propanenitrile (6)

Yield = 79%, yellow oil. **^{1}H NMR (400 MHz, Chloroform-d):** δ 7.41 – 7.37 (m, 1H), 7.30 (m, 3H), 7.19 – 7.12 (m, 2H), 6.80 – 6.73 (m, 1H), 6.60 – 6.53 (m, 2H), 4.71 (t, J = 6.1 Hz, 1H), 2.91 – 2.79 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-d):** δ 145.4, 142.1, 135.1, 130.5, 129.5, 128.8, 126.5, 124.5, 119.2, 116.7, 114.0, 54.1, 26.2. **HRMS (EI):** exact mass calculated for $C_{15}H_{13}ClN_2$ $[M+Na]^+$ require m/z = 279.0659, found m/z = 279.0656.



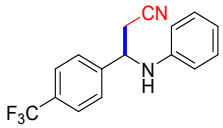
3-(3-Methoxyphenyl)-3-(phenylamino)propanenitrile (7)

Yield = 54%, brown oil. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.29 (t, *J* = 7.9 Hz, 1H), 7.17 – 7.12 (m, 2H), 6.98 (d, *J* = 7.7 Hz, 1H), 6.95 (d, *J* = 2.0 Hz, 1H), 6.84 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 2H), 4.70 (t, *J* = 6.1 Hz, 1H), 3.78 (s, 3H), 2.90 – 2.80 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*):** δ 160.2, 145.8, 141.7, 130.3, 129.4, 118.8, 118.4, 117.1, 113.9, 113.6, 112.2, 55.3, 54.4, 26.2. **HRMS (EI):** exact mass calculated for $C_{16}H_{16}N_2O$ $[M+Na]^+$ require m/z = 275.1155, found m/z = 275.1150.



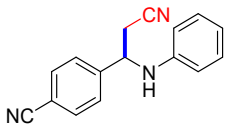
3-(3-(Benzyloxy)phenyl)-3-(phenylamino)propanenitrile (8)[2]

Yield = 73%, brown oil. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.41 – 7.33 (m, 4H), 7.33 – 7.29 (m, 1H), 7.28 – 7.24 (m, 1H), 7.14 – 7.10 (m, 2H), 7.02 – 7.00 (m, 1H), 6.97 (d, *J* = 7.7 Hz, 1H), 6.90 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 7.8 Hz, 2H), 5.01 (s, 2H), 4.66 (t, *J* = 6.1 Hz, 1H), 4.20 (brs, 1H), 2.85 – 2.73 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*):** δ 159.5, 145.9, 141.8, 136.8, 130.3, 129.4, 128.7, 128.1, 127.7, 118.8, 118.8, 117.2, 114.6, 114.0, 113.1, 70.2, 54.4, 26.2.



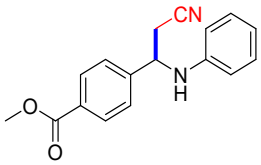
3-(Phenylamino)-3-(4-(trifluoromethyl)phenyl)propanenitrile (9)

Yield = 51%, yellow oil. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.18 – 7.11 (m, 2H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.56 (d, *J* = 7.7 Hz, 2H), 4.80 (t, *J* = 6.0 Hz, 1H), 4.30 (brs, 1H), 2.94 – 2.81 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*):** δ 145.4, 144.0, 130.8 (q, *J* = 32.7 Hz), 129.5, 126.7, 126.2 (q, *J* = 3.7 Hz), 123.9 (q, *J* = 273.3 Hz), 119.2, 116.7, 114.0, 54.0, 26.2. **^{19}F NMR (376 MHz, Chloroform-*d*):** δ -62.6. **HRMS (EI):** exact mass calculated for $C_{16}H_{13}N_2$ $[M+Na]^+$ require m/z = 313.0923, found m/z = 313.0918.



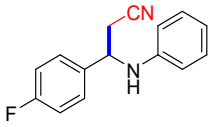
4-(2-Cyano-1-(phenylamino)ethyl)benzonitrile (10)[2]

Yield = 65%, red oil. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.14 (dd, *J* = 8.5, 7.4 Hz, 2H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.53 (d, *J* = 7.7 Hz, 2H), 4.79 (q, *J* = 5.4 Hz, 1H), 4.38 (brs, 1H), 2.96 – 2.83 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*):** δ 145.4, 145.2, 133.0, 129.5, 127.2, 119.3, 118.4, 116.5, 114.0, 112.4, 54.1, 26.2.



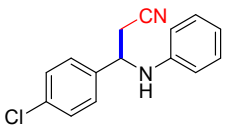
Methyl 4-(2-cyano-1-(phenylamino)ethyl)benzoate (11)

Yield = 71%, yellow solid. **m.p.**: 97-99 °C. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 8.06 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.18 – 7.11 (m, 2H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 2H), 4.81 (t, *J* = 6.0 Hz, 1H), 3.91 (s, 3H), 2.96 – 2.86 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*):** δ 166.5, 145.4, 144.9, 130.5, 130.5, 129.5, 126.3, 119.2, 116.6, 114.0, 54.3, 52.2, 26.2. **HRMS (EI):** exact mass calculated for $C_{17}H_{16}N_2O_2$ $[M+Na]^+$ require m/z = 303.1104, found m/z = 303.1101.



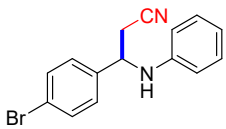
3-(4-Fluorophenyl)-3-(phenylamino)propanenitrile (12)

Yield = 34%, yellow oil. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.43 – 7.38 (m, 2H), 7.21 – 7.17 (m, 2H), 7.11 – 7.05 (m, 2H), 6.80 (t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 7.7 Hz, 2H), 4.75 (t, *J* = 6.1 Hz, 1H), 4.29 (brs, 1H), 2.85 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*):** δ 162.6 (d, *J* = 248.0 Hz), 145.7, 135.8 (d, *J* = 3.0 Hz), 129.5, 128.0 (d, *J* = 8.3 Hz), 119.0, 117.2, 116.1 (d, *J* = 21.7 Hz), 114.0, 53.8, 26.3. **^{19}F NMR (376 MHz, Chloroform-*d*):** δ -113.42. **HRMS (EI):** exact mass calculated for $C_{15}H_{13}FN_2$ $[M+H]^+$ require m/z = 241.1136, found m/z = 241.1131.



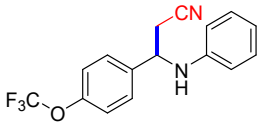
3-(4-Chlorophenyl)-3-(phenylamino)propanenitrile (13)[2]

Yield = 62%, orange oil. **m.p.:** 100-101 °C. **^{1}H NMR (600 MHz, Chloroform-d):** δ 7.35 (s, 4H), 7.15 (t, J = 7.8 Hz, 2H), 6.76 (t, J = 7.3 Hz, 1H), 6.57 (d, J = 7.9 Hz, 2H), 4.73 (t, J = 6.0 Hz, 1H), 2.93 – 2.81 (m, 2H). **^{13}C NMR (151 MHz, Chloroform-d):** δ 145.4, 138.4, 134.3, 129.4, 129.4, 127.7, 119.2, 116.7, 114.1, 53.9, 26.3.



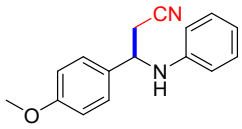
3-(4-Bromophenyl)-3-(phenylamino)propanenitrile (14)

Yield = 36%, brown oil. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.49 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.16 – 7.12 (m, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.55 (d, *J* = 7.7 Hz, 2H), 4.69 (t, *J* = 6.0 Hz, 1H), 4.21 (brs, 1H), 2.88 – 2.76 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*):** δ 145.5, 139.0, 132.3, 129.4, 128.0, 122.4, 119.1, 116.8, 114.0, 53.9, 26.2. **HRMS (EI):** exact mass calculated for $C_{15}H_{13}BrN_2$ $[M+Na]^+$ require m/z = 323.0154, found m/z = 323.0149.



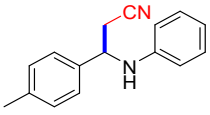
3-(Phenylamino)-3-(4-(trifluoromethoxy)phenyl)propanenitrile (15)

Yield = 53%, brown oil. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.46 – 7.42 (m, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 7.18 – 7.12 (m, 2H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 2H), 4.76 (t, *J* = 5.8 Hz, 1H), 4.23 (brs, 1H), 2.92 – 2.80 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*):** δ 149.2, 145.5, 138.6, 129.5, 127.8, 121.6, 120.4 (q, *J* = 258.2 Hz), 119.1, 116.8, 114.0, 53.8, 26.3. **^{19}F NMR (376 MHz, Chloroform-*d*):** δ -57.8. **HRMS (EI):** exact mass calculated for $C_{16}H_{13}F_3N_2O$ $[M+Na]^+$ require m/z = 329.0872, found m/z = 329.0866.



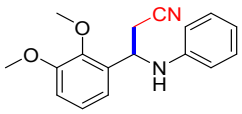
3-(4-Methoxyphenyl)-3-(phenylamino)propanenitrile (16)[3]

Yield = 44%, yellow oil. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.33 (d, *J* = 8.7 Hz, 2H), 7.18 – 7.13 (m, 2H), 6.92 – 6.89 (m, 2H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.61 – 6.58 (m, 2H), 4.72 (t, *J* = 6.0 Hz, 1H), 4.18 (brs, 1H), 3.80 (s, 3H), 2.87 (d, *J* = 6.1 Hz, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*):** δ 159.7, 145.8, 131.9, 129.4, 127.4, 118.8, 117.2, 114.58, 113.9, 55.3, 53.9, 26.2.



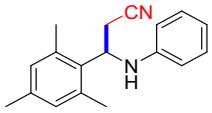
3-(Phenylamino)-3-(*p*-tolyl)propanenitrile (17)[2]

Yield = 65%, yellow oil. **^{1}H NMR (600 MHz, Chloroform-*d*):** δ 7.28 (d, J = 8.0 Hz, 2H), 7.20 – 7.12 (m, 4H), 6.74 (t, J = 7.3 Hz, 1H), 6.59 (d, J = 8.2 Hz, 2H), 4.72 (t, J = 6.0 Hz, 1H), 2.90 – 2.80 (m, 2H), 2.33 (s, 3H). **^{13}C NMR (151 MHz, Chloroform-d):** δ 145.8, 138.3, 136.9, 129.9, 129.4, 126.1, 118.8, 117.2, 114.0, 54.2, 26.2, 21.1.



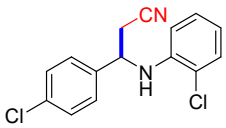
3-(2,3-Dimethoxyphenyl)-3-(phenylamino)propanenitrile (18)

Yield = 76%, brown oil. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.16 – 7.11 (m, 2H), 7.01 (t, *J* = 7.9 Hz, 1H), 6.94 (dd, *J* = 7.8, 1.3 Hz, 1H), 6.86 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.63 – 6.58 (m, 2H), 5.06 (t, *J* = 6.1 Hz, 1H), 4.35 (brs, 1H), 3.95 (s, 3H), 3.85 (s, 3H), 2.92 – 2.83 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*):** δ 152.7, 146.4, 146.0, 133.0, 129.4, 124.4, 118.8, 118.6, 117.6, 113.9, 112.6, 60.9, 55.8, 49.8, 25.1. **HRMS (EI):** exact mass calculated for $C_{17}H_{18}N_2O_2$ $[M+Na]^+$ require m/z = 305.1260, found m/z = 305.1255.



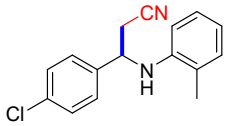
3-Mesityl-3-(phenylamino)propanenitrile (19)

Yield = 35%, yellow oil. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.23 – 7.18 (m, 2H), 6.90 (s, 2H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.62 – 6.56 (m, 2H), 5.23 (t, *J* = 7.4 Hz, 1H), 4.15 (brs, 1H), 3.07 – 2.88 (m, 2H), 2.52 (s, 6H), 2.30 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*):** δ 146.3, 137.6, 135.7, 132.6, 131.0, 129.5, 118.5, 117.7, 113.1, 51.5, 23.1, 21.1, 20.8. **HRMS (EI):** exact mass calculated for $C_{18}H_{20}N_2$ $[M+Na]^+$ require m/z = 287.1519, found m/z = 287.1514.



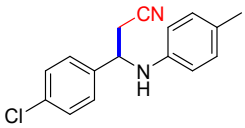
3-(4-Chlorophenyl)-3-((2-chlorophenyl)amino)propanenitrile (20)

Yield = 56%, brown oil. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.33 – 7.23 (m, 4H), 7.23 – 7.20 (m, 1H), 7.21 (dd, *J* = 7.9, 1.1 Hz, 1H), 6.64 – 6.59 (m, 1H), 6.37 (d, *J* = 8.1 Hz, 1H), 4.77 (brs, 1H), 4.70 (s, 1H), 2.84 (d, *J* = 6.1 Hz, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*):** δ 140.4, 136.9, 133.5, 128.5 (×2), 126.8, 126.5, 119.0, 118.1, 115.3, 111.7, 52.9, 25.5. **HRMS (EI):** exact mass calculated for $C_{15}H_{12}Cl_2N_2$ $[M+H]^+$ require m/z = 291.0450, found m/z = 291.0446.



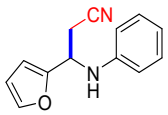
3-(4-Chlorophenyl)-3-(*o*-tolylamino)propanenitrile (21)

Yield = 23%, brown oil. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.34 (s, 4H), 7.08 (d, *J* = 7.3 Hz, 1H), 7.03 – 6.99 (m, 1H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.38 (d, *J* = 8.0 Hz, 1H), 4.76 (t, *J* = 6.0 Hz, 1H), 4.00 (brs, 1H), 2.93 – 2.82 (m, 2H), 2.23 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*):** δ 143.5, 138.6, 134.3, 130.6, 129.4, 127.6, 127.1, 123.0, 118.8, 116.8, 111.4, 53.8, 26.4, 17.5. **HRMS (EI):** exact mass calculated for $C_{16}H_{15}ClN_2$ $[M+Na]^+$ require m/z = 293.0816, found m/z = 293.0811.



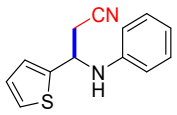
3-(4-Chlorophenyl)-3-(*p*-tolylamino)propanenitrile (22)

Yield = 47%, brown oil. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.33 (s, 4H), 6.95 (d, *J* = 8.1 Hz, 2H), 6.48 (d, *J* = 8.4 Hz, 2H), 4.68 (t, *J* = 6.0 Hz, 1H), 4.07 (brs, 1H), 2.87 – 2.78 (m, 2H), 2.21 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*):** δ 143.2, 138.6, 134.2, 129.9, 129.4, 128.4, 127.7, 116.9, 114.3, 54.2, 26.3, 20.4. **HRMS (EI):** exact mass calculated for $C_{16}H_{15}ClN_2$ $[M+Na]^+$ require m/z = 293.0816, found m/z = 293.0810.



3-(2-Furyl)-3-(phenylamino)propanenitrile (23)[2]

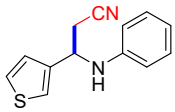
Yield = 69%, yellow oil. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.43 – 7.38 (m, 1H), 7.21 (m, 2H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.68 (d, *J* = 7.8 Hz, 2H), 6.40 – 6.30 (m, 2H), 4.92 (t, *J* = 5.8 Hz, 1H), 2.96 (d, *J* = 5.8 Hz, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*):** δ 152.0, 145.3, 142.7, 129.5, 119.4, 116.8, 114.1, 110.6, 107.6, 48.9, 23.3.



3-(Phenylamino)-3-(thiophen-2-yl)propanenitrile (24)

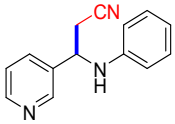
Yield = 58%, yellow oil. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.26 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.20 (m, 2H), 7.11 (d, *J* = 3.5 Hz, 1H), 6.99 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.72 – 6.64 (m, 2H), 5.07 (t, *J* = 5.7 Hz, 1H), 2.98 (d, *J* = 5.8 Hz, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*):** δ 145.2, 143.7, 129.5, 127.3, 125.3, 124.9, 119.6, 116.8, 114.3, 50.8, 26.1. **HRMS (EI):** exact mass calculated for $C_{13}H_{12}N_2S$

[M+Na]$^+$ require m/z = 251.0613, found m/z = 251.0610.



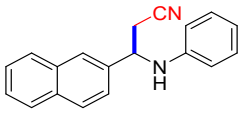
3-(Phenylamino)-3-(thiophen-3-yl)propanenitrile (25)

Yield = 73%, yellow oil. **^{1}H NMR (600 MHz, Chloroform-*d*):** δ 7.37 – 7.34 (m, 1H), 7.32 (s, 1H), 7.19 (dd, *J* = 8.2, 7.5 Hz, 2H), 7.12 (dd, *J* = 4.9, 1.0 Hz, 1H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 2H), 4.91 (s, 1H), 4.11 (brs, 1H), 2.96 – 2.88 (m, 2H). **^{13}C NMR (151 MHz, Chloroform-*d*):** δ 145.7, 141.1, 129.5, 127.2, 125.6, 122.15, 119.1, 117.2, 113.9, 50.5, 25.2. **HRMS (EI):** exact mass calculated for $C_{13}H_{12}N_2S$ [M+Na]$^+$ require m/z = 251.0613, found m/z = 251.0609.



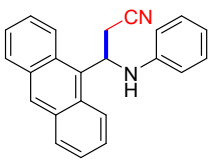
3-(3-Pyridyl)-3-(phenylamino)propanenitrile (26)[2]

Yield = 60%, brown oil. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 8.69 (s, 1H), 8.57 (d, *J* = 4.0 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.29 – 7.33 (m, 1H), 7.15 (t, J = 7.5 Hz, 2H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.58 (d, *J* = 7.7 Hz, 2H), 4.81 (t, *J* = 5.9 Hz, 1H), 4.46 (brs, 1H), 2.96 – 2.85 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*):** δ 149.8, 148.3, 145.3, 135.6, 134.1, 129.5, 124.0, 119.2, 116.6, 114.0, 52.3, 26.0.



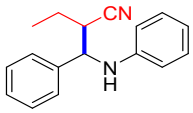
3-(Naphthalen-2-yl)-3-(phenylamino)propanenitrile (27)

Yield = 73%, yellow oil. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.83 – 7.76 (m, 4H), 7.48 – 7.42 (m, 3H), 7.11 (t, *J* = 7.6 Hz, 2H), 6.74 – 6.69 (m, 1H), 6.60 (d, *J* = 8.3 Hz, 2H), 4.84 (t, *J* = 6.2 Hz, 1H), 2.90 – 2.79 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*):** δ 145.9, 137.4, 133.4, 133.3, 129.5, 129.3, 128.1, 127.8, 126.6, 126.5, 125.4, 123.9, 118.9, 117.3, 114.1, 54.6, 26.2. **HRMS (EI):** exact mass calculated for $C_{19}H_{16}N_2$ [M+Na]$^+$ require m/z = 295.1206, found m/z = 295.1203.



3-(Anthracen-9-yl)-3-(phenylamino)propanenitrile (28)

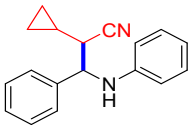
Yield = 28%, yellow solid. **m.p.:** 116-117 °C. **^{1}H NMR (600 MHz, Chloroform-*d*):** δ 8.54 (d, *J* = 8.2 Hz, 2H), 8.47 (s, 1H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.57 – 7.55 (m, 2H), 7.49 – 7.47 (m, 2H), 7.17 (t, *J* = 7.7 Hz, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 2H), 6.29 – 6.26 (m, 1H), 4.56 (brs, 1H), 3.46 – 3.37 (m, 2H). **^{13}C NMR (151 MHz, Chloroform-*d*):** δ 146.6, 131.8, 130.3, 130.1, 129.6, 129.2, 127.0, 125.2, 123.5, 119.0, 117.8, 113.4, 51.4, 24.2. **HRMS (EI):** exact mass calculated for $C_{23}H_{18}N_2$ $[M+Na]^+$ require m/z = 345.1362, found m/z = 345.1357.



Mixture of two diastereomers. d.r. = 53 : 47

2-(Phenyl(phenylamino)methyl)butanenitrile (29)

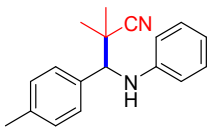
Yield = 42%, brown oil. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.48 – 7.45 (m, 1H), 7.43 – 7.30 (m, 4H), 7.20 – 7.13 (m, 2H), 6.75 (q, *J* = 7.3 Hz, 1H), 6.64 – 6.62 (m, 2H), 4.63 – 4.59 (m, 1H), 4.37 (brs, 1H), 3.15 – 3.10 (m, 0.53H), 2.95 – 2.90 (m, 0.47H), 1.91 – 1.75 (m, 1H), 1.74 – 1.66 (m, 0.53H), 1.60 – 1.52 (m, 0.47H), 1.19 – 1.12 (m, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*):** δ 146.3, 146.0, 140.0, 138.4, 129.3 (×2), 129.0, 128.9, 128.5, 128.2, 127.2, 126.5, 119.9, 119.8, 118.6, 118.5, 113.9, 113.9, 58.5, 58.4, 42.6, 40.8, 23.8, 22.8, 11.9. **HRMS (EI):** exact mass calculated for $C_{17}H_{18}N_2$ $[M+H]^+$ require m/z = 251.1543, found m/z = 251.1539.



Mixture of two diastereomers. d.r. = 54 : 46

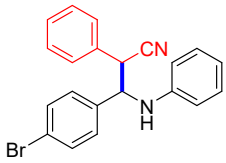
2-Cyclopropyl-3-phenyl-3-(phenylamino)propanenitrile (30)

Yield = 67%, brown oil. **^{1}H NMR (600 MHz, Chloroform-*d*):** δ 7.47 (d, *J* = 7.6 Hz, 1H), 7.38 – 7.26 (m, 4H), 7.12 – 7.09 (m, 2H), 6.70 (q, *J* = 6.9 Hz, 1H), 6.59 (dd, *J* = 14.4, 8.0 Hz, 2H), 4.70 (s, 0.54H), 4.65 (s, 0.46H), 4.46 (brs, 1H), 2.72 – 2.70 (m, 0.46H), 2.53 – 2.51 (m, 0.54H), 1.17 – 1.14 (m, 0.54H), 0.84 – 0.82 (m, 0.46H), 0.70 – 0.58 (m, 2H), 0.48 – 0.44 (m, 0.46H), 0.41 – 0.37 (m, 1H), 0.36 – 0.33 (m, 0.54H). **^{13}C NMR (151 MHz, Chloroform-*d*):** δ 146.4, 146.0, 139.9, 138.5, 129.4, 129.3, 129.0, 128.8, 128.5, 128.2, 127.4, 126.6, 118.9, 118.8, 118.6, 118.5, 114.0, 113.9, 59.5, 59.2, 45.2, 43.4, 11.5, 10.4, 5.3, 4.7, 4.1, 4.0. **HRMS (EI):** exact mass calculated for $C_{18}H_{18}N_2$ $[M+H]^+$ require m/z = 263.1543, found m/z = 263.1543.



2,2-Dimethyl-3-(phenylamino)-3-(*p*-tolyl)propanenitrile (31)

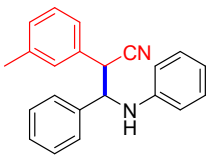
Yield = 49%, brown oil. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.28 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 7.11 – 7.06 (m, 2H), 6.69 – 6.65 (m, 1H), 6.61 – 6.54 (m, 2H), 4.39 (brs, 1H), 4.17 (s, 1H), 2.31 (s, 3H), 1.57 (s, 3H), 1.23 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*):** δ 146.5, 138.0, 135.2, 129.3, 129.2, 127.6, 123.5, 118.3, 114.0, 64.4, 38.7, 26.1, 24.6, 21.1. **HRMS (EI):** exact mass calculated for $C_{18}H_{20}N_2$ $[M+Na]^+$ require m/z = 287.1519, found m/z = 287.1513.



Mixture of two diastereomers. d.r. = 58 : 42

3-(4-Bromophenyl)-2-phenyl-3-(phenylamino)propanenitrile (32)

Yield = 53%, brown oil. **^{1}H NMR (600 MHz, Chloroform-*d*):** δ 7.36 (d, *J* = 8.3 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.28 – 7.26 (m, 2H), 7.21 – 7.14 (m, 2H), 7.11 – 7.04 (m, 4H), 6.95 (dd, *J* = 24.7, 8.3 Hz, 1H), 6.69 (dt, *J* = 21.4, 7.3 Hz, 1H), 6.51 (dd, *J* = 38.6, 7.9 Hz, 2H), 4.76 (s, 0.58H), 4.71 (s, 0.42H), 4.42 (s, 0.58H), 4.38 (d, *J* = 5.2 Hz, 0.42H), 4.34 (s, 0.42H), 4.17 (d, *J* = 5.3 Hz, 0.58H). **^{13}C NMR (151 MHz, Chloroform-*d*):** δ 145.7, 145.6, 137.8, 136.6, 132.0, 131.7, 129.5, 129.4, 129.3, 129.2, 128.9 (×3), 128.5, 128.4, 122.5, 122.4, 119.2, 119.1, 118.8, 118.6, 115.9 (×2), 114.3 (×2), 61.0, 60.8, 45.1, 44.8. **HRMS (EI):** exact mass calculated for $C_{21}H_{17}BrN_2$ $[M+Na]^+$ require m/z = 399.0467, found m/z = 399.0463.

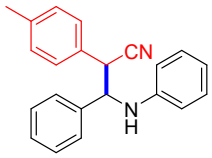


Mixture of two diastereomers. d.r. = 53 : 47

3-phenyl-3-(phenylamino)-2-(m-tolyl)propanenitrile (33)

Yield = 56%, yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.33 – 7.27 (m, 4H), 7.23 – 7.16 (m, 2H), 7.15 – 7.12 (m, 2H), 7.09 – 7.04 (m, 2H), 6.90 – 6.88 (m, 1H), 6.74 (t, *J* = 7.3 Hz, 0.47H), 6.69 (t, *J* = 7.3 Hz, 0.53H), 6.60 (d, *J* = 7.9 Hz, 0.94H), 6.51

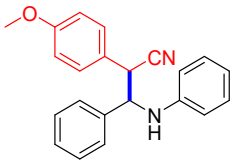
(d, J = 7.9 Hz, 1.06H), 4.80 (d, J = 4.7 Hz, 0.53H), 4.76 (d, J = 4.7 Hz, 0.47H), 4.40 (d, J = 5.5 Hz, 0.47H), 4.24 (d, J = 4.7 Hz, 0.53H), 2.37 (s, 0.47H), 2.36 (s, 0.53H), 2.31 (s, 1.59H), 2.29 (s, 1.41H). ^{13}C NMR (151 MHz, Chloroform-*d*): δ 141.2, 140.9, 134.3, 134.1, 134.0, 132.8, 127.5, 127.1, 124.6, 124.5, 124.4, 124.3, 124.2, 124.1 124.0 (× 2), 123.7 (× 2), 123.6 122.7, 122.2, 120.7, 120.5, 120.2, 114.2 114.0 (× 2), 113.8, 109.5 (× 2), 56.7 (× 2), 40.7, 40.2, 18.7, 16.5. HRMS (EI): exact mass calculated for $C_{22}H_{20}N_2$ [M+Na]+ require m/z = 335.1519, found m/z = 355.1517.



Mixture of two diastereomers. d.r. = 64 : 36

3-phenyl-3-(phenylamino)-2-(*p*-tolyl)propanenitrile (34)

Yield = 58%, colorless oil. **^{1}H NMR (600 MHz, Chloroform-*d*):** δ 7.33 – 7.26 (m, 4H), 7.18 – 6.96 (m, 7H), 6.74 – 6.68 (m, 1H), 6.58 (d, J = 7.8 Hz, 0.72H), 6.51 (d, J = 7.8 Hz, 1.28H), 4.80 (d, J = 4.4 Hz, 0.64H), 4.77 (d, J = 5.3 Hz, 0.36H), 4.38 (d, J = 5.4 Hz, 0.36H), 4.30 (brs, 1H), 4.24 (d, J = 4.7 Hz, 0.64H), 2.33 (s, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*):** δ 146.0, 145.8, 138.7, 138.6, 137.6, 129.6 (× 2), 129.3 (× 2), 129.2, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 128.2, 127.4, 126.9, 118.8, 118.7 (× 2), 114.2, 61.3 (× 2), 45.1, 44.6, 21.1, 21.0. **HRMS (EI):** exact mass calculated for $C_{22}H_{20}N_2$ $[M+H]^+$ require m/z = 313.1699, found m/z = 313.1699.

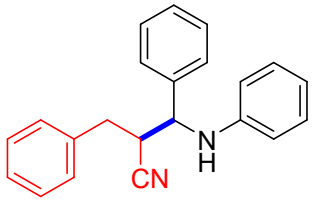


Mixture of two diastereomers. d.r. = 66 : 34

2-(4-methoxyphenyl)-3-phenyl-3-(phenylamino)propanenitrile (35)

Yield = 54%, yellow oil. **^{1}H NMR (600 MHz, Chloroform-*d*):** δ 7.33 – 7.27 (m, 3H), 7.24 – 7.12 (m, 4H), 7.10 – 7.99 (m, 2H), 6.90 – 6.81 (m, 2H), 6.74 – 6.69 (m, 1H), 6.59 (d, J = 7.9 Hz, 0.68H), 6.53 (d, J = 7.8 Hz, 1.32H), 4.79 (d, J = 4.9 Hz, 0.66H), 4.74 (d, J = 5.5 Hz, 0.34H), 4.39 (d, J = 5.5 Hz, 0.34H), 4.23 (d, J = 4.9 Hz, 0.66H), 3.79 (s, 1.98H), 3.67 (s, 1.02H). **^{13}C NMR (151 MHz, Chloroform-*d*):** δ 159.8, 159.4, 145.9, 145.8, 138.6, 137.6, 129.6, 129.5, 129.3, 129.2, 129.1, 128.7, 128.5, 128.4, 128.3, 127.4, 127.0, 124.2, 123.8, 121.8, 118.9, 118.8, 118.7, 114.6, 114.3, 114.2, 61.4,

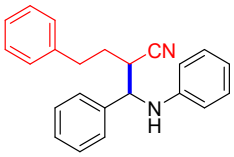
61.3, 55.3, 44.5, 44.2, 22.8. **HRMS (EI):** exact mass calculated for $C_{22}H_{20}N_2O$ $[M+Na]^+$ require m/z = 351.1468, found m/z = 351.1466.



d.r. > 20 : 1

3,4-diphenyl-4-(phenylamino)butanenitrile (36)

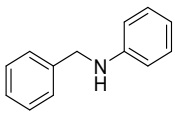
Yield = 51%, colorless oil. **^{1}H NMR (600 MHz, Chloroform-*d*):** δ 7.47 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.32 (m, 3H), 7.28 (t, *J* = 7.1 Hz, 1H), 7.21 (d, *J* = 7.4 Hz, 2H), 7.14 – 7.11 (m, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 2H), 4.57 (d, *J* = 5.4 Hz, 1H), 3.48 – 3.45 (m, 3H), 2.91 – 2.81 (m, 2H). **^{13}C NMR (151 MHz, Chloroform-*d*):** δ 145.7, 138.0, 136.5, 129.4, 129.0, 128.9 (× 2), 128.7, 127.4 (× 2), 119.6, 118.9, 114.0, 58.3, 40.7, 35.5. **HRMS (EI):** exact mass calculated for $C_{22}H_{20}N_2$ $[M+H]^+$ require m/z = 313.1699, found m/z = 313.1700, $[M+Na]^+$ require m/z = 335.1519, found m/z = 335.1518, $[M+K]^+$ require m/z = 351.1258, found m/z = 358.1261.



Mixture of two diastereomers. d.r. = 53 : 47

4-phenyl-2-(phenyl(phenylamino)methyl)butanenitrile (37)

Yield = 70%, yellow oil. **^{1}H NMR (600 MHz, Chloroform-*d*):** δ 7.40 – 7.34 (m, 2H), 7.32 – 7.24 (m, 5H), 7.22 – 7.20 (m, 1H), 7.15 – 7.08 (m, 4H), 6.69 (t, *J* = 7.0 Hz, 1H), 6.56 (d, *J* = 7.7 Hz, 1.06H), 6.52 (d, *J* = 7.6 Hz, 0.94H), 4.56 (d, *J* = 2.5 Hz, 0.53H), 4.49 (d, *J* = 4.7 Hz, 0.47H), 4.28 (brs, 1H), 3.13 – 3.10 (m, 0.47H), 2.94 – 2.86 (m, 1.53H), 2.77 – 2.67 (m, 1H), 2.19 – 2.13 (m, 0.53H), 2.03 – 1.97 (m, 0.47H), 1.92 – 1.77 (m, 1H). **^{13}C NMR (151 MHz, Chloroform-*d*):** δ 146.3, 145.9, 139.8, 139.7 (× 2), 138.3, 129.3 (× 2), 129.0 (× 2), 128.8, 128.5 (× 2), 128.4, 128.2, 127.3, 126.6, 126.5, 119.8, 119.7, 118.7 (× 2), 114.0 (× 2), 58.8, 58.5, 39.9, 38.0, 33.3, 31.8, 31.0. **HRMS (EI):** exact mass calculated for $C_{23}H_{22}N_2$ $[M+H]^+$ require m/z = 327.1856, found m/z = 327.1855, $[M+Na]^+$ require m/z = 349.1675, found m/z = 349.1673, $[M+K]^+$ require m/z = 365.1415, found m/z = 365.1415.



Benzyl-phenyl-amine (1b)[4]

Yield = 47%, yellow oil. **^{1}H NMR (600 MHz, Chloroform-*d*):** δ 7.37 (d, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.1 Hz, 1H), 7.18 (t, *J* = 7.9 Hz, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 2H), 4.33 (s, 2H). **^{13}C NMR (151 MHz, Chloroform-*d*):** δ 148.0, 139.3, 129.3, 128.6, 127.6, 127.3, 117.7, 113.0, 48.5.

H. References

[1] D. J. Dibble, R. Kurakake, A. G. Wardrip, A. Barlett, R. Lopez, J. A. Linares, M. Firstman, A. M. Schmidt, M. J. Umerani, A. A. Gorodetsky, *Org. Lett*. **2018**, *20*, 502-505.

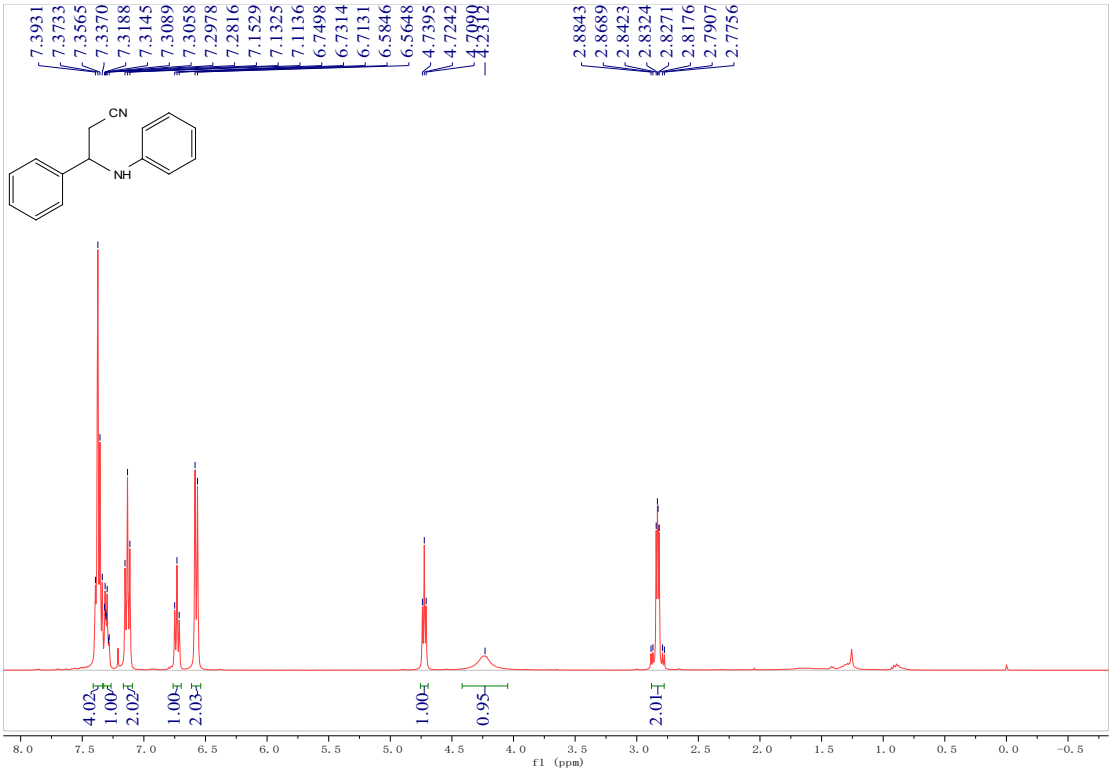
[2] T. Poisson, V. Gembus, S. Oudeyer, F. Marsais, V. Levacher, *J. Org. Chem.* **2009**, *74*, 3516-3519.

[3] K. Shibata, Y. Saito, K. Urano, M. Matsui, *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3323-3325.

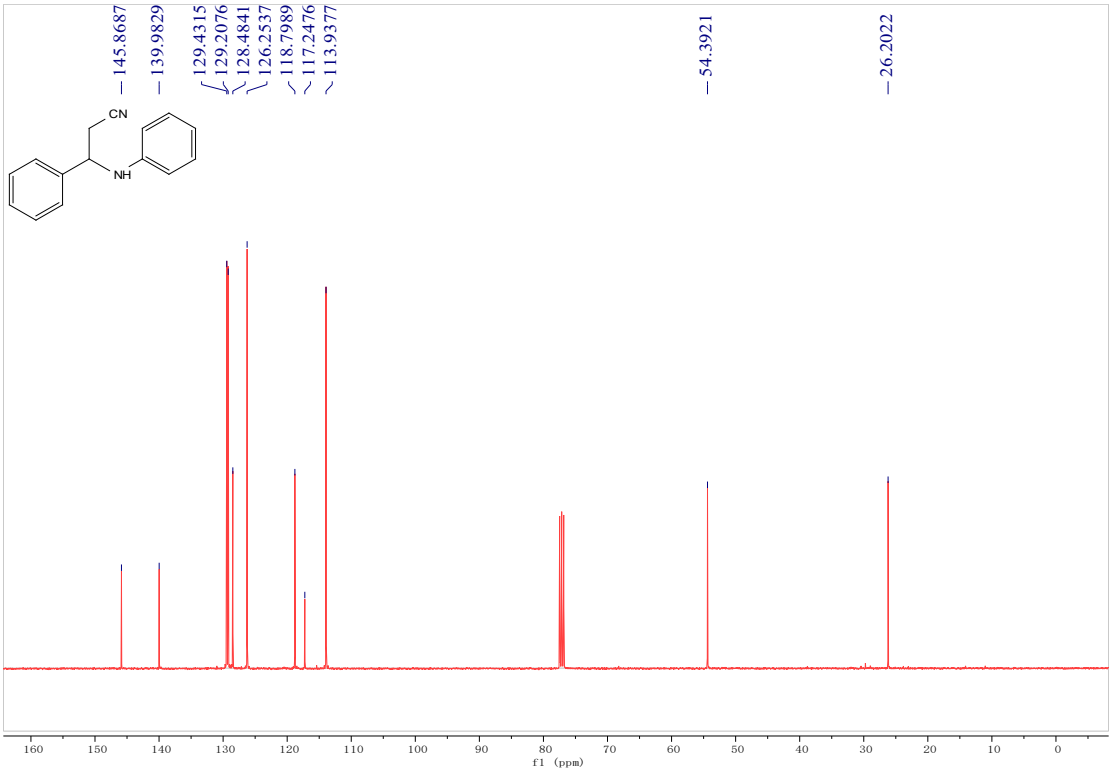
[4] W.-X. Zhang, X.-C. Dong, W.L. Zhao, *Org. Lett.* **2011**, *13*, 5386-5389.

I. NMR spectra for electrolysis products

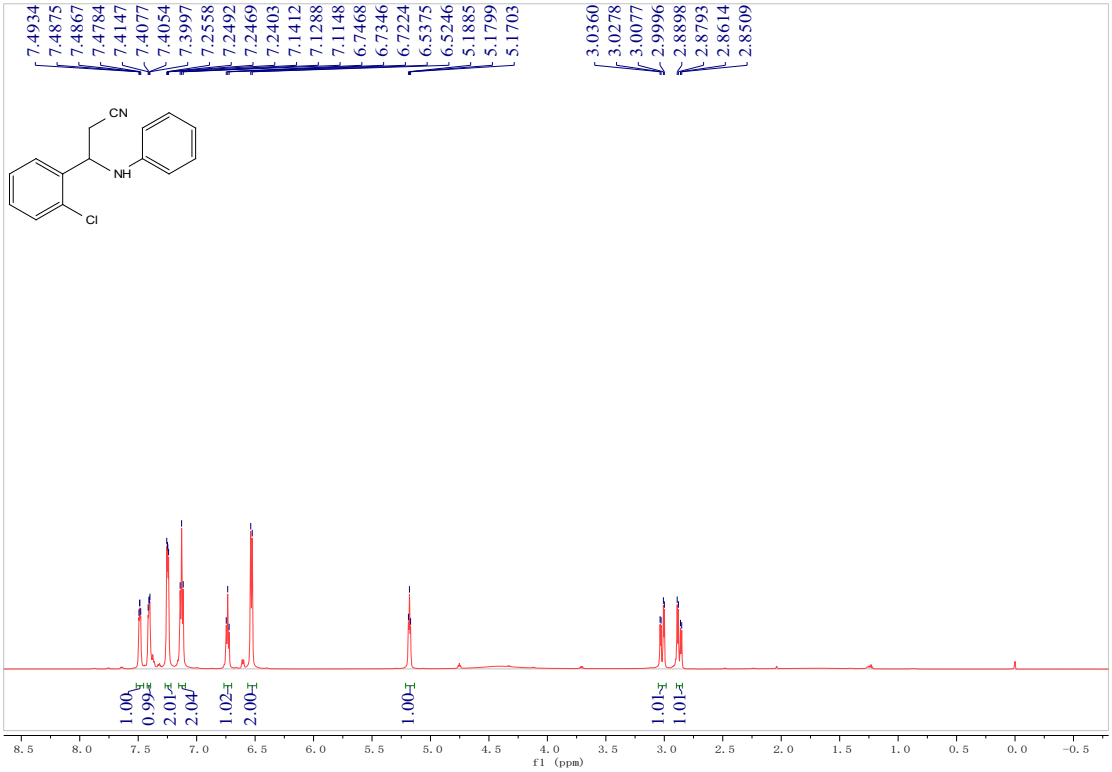
^{1}H-NMR Spectrum ($CDCl_3$) of **3**



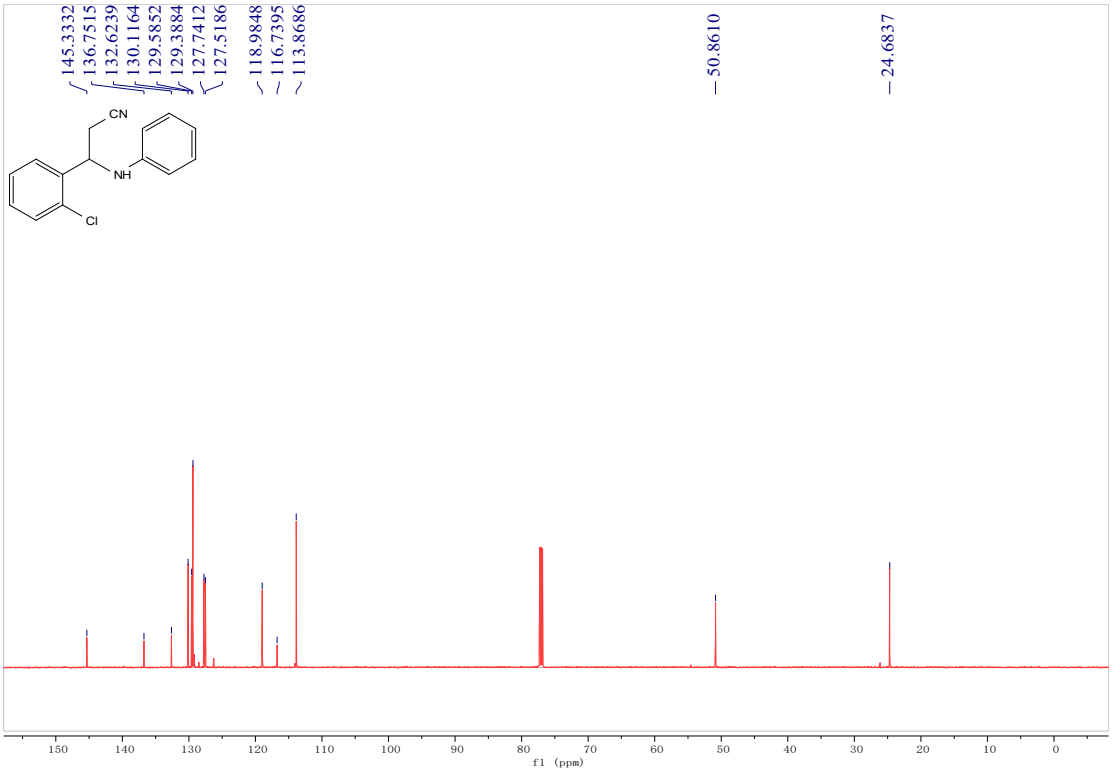
^{13}C-NMR Spectrum ($CDCl_3$) of **3**



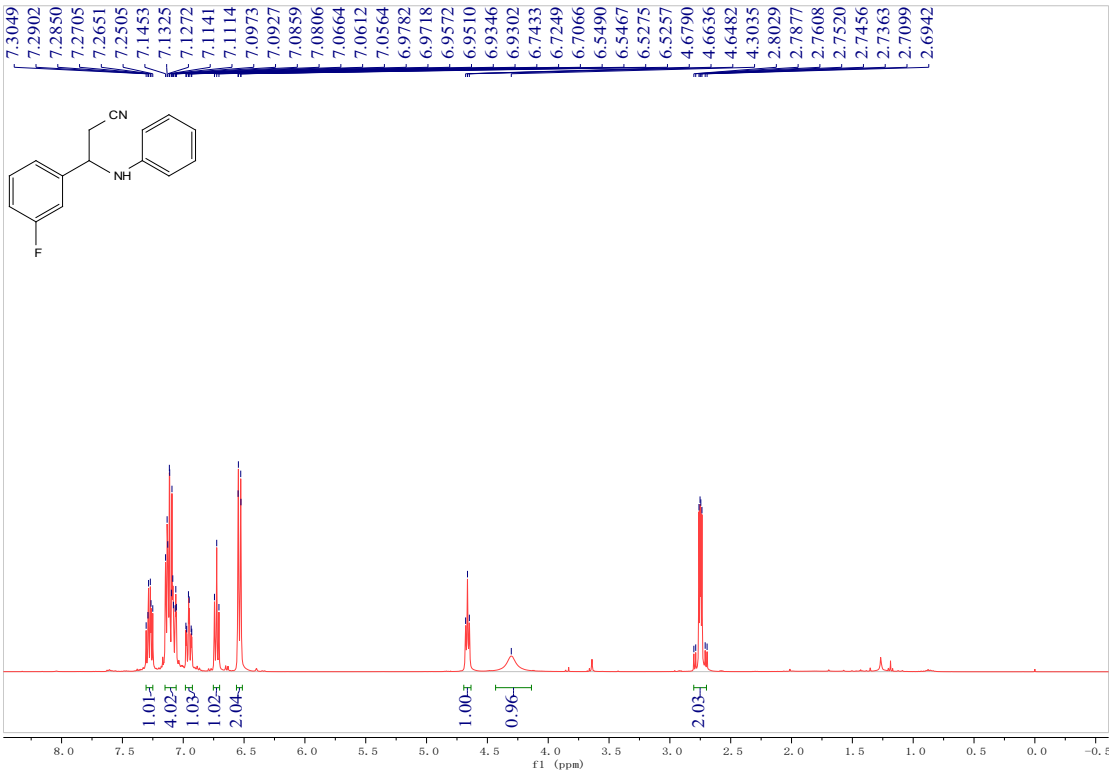
^{1}H-NMR Spectrum ($CDCl_3$) of **4**



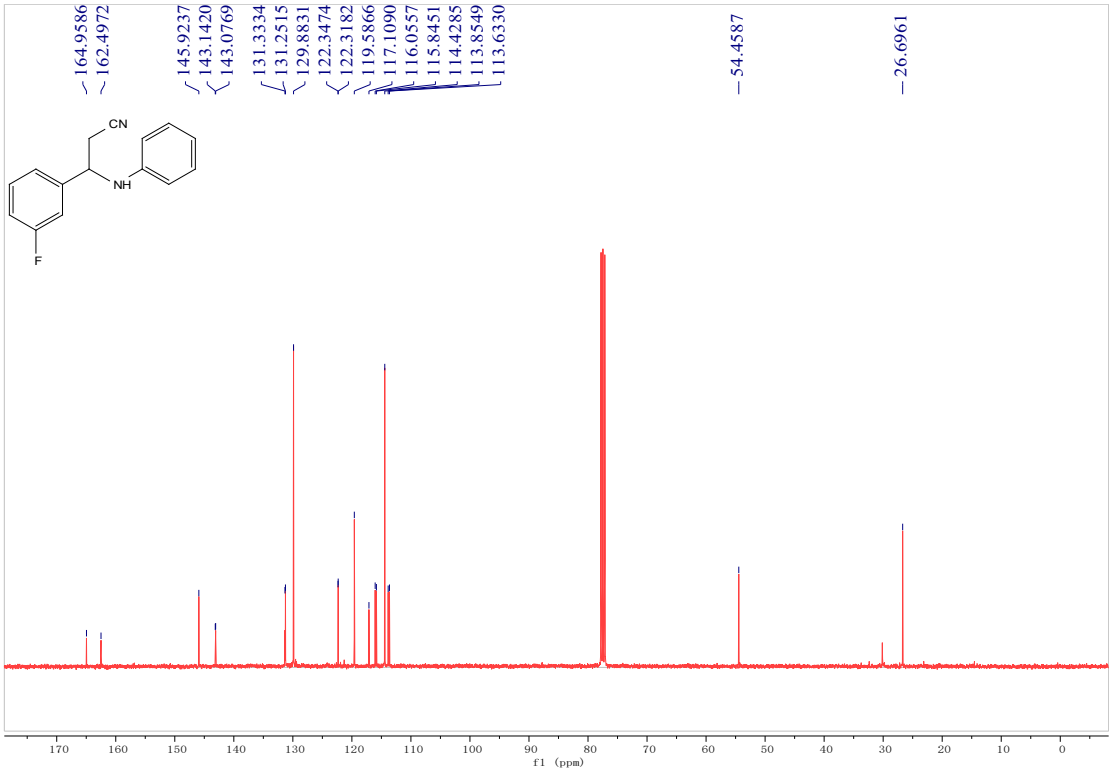
^{13}C-NMR Spectrum ($CDCl_3$) of **4**



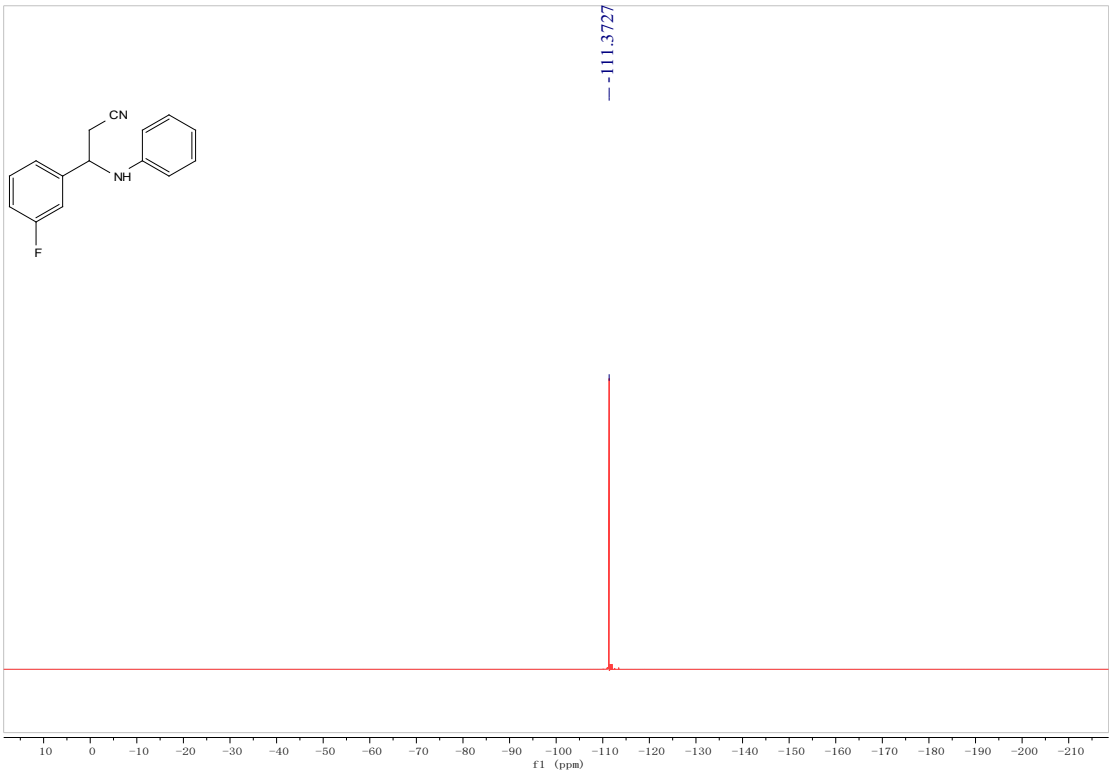
^{1}H-NMR Spectrum ($CDCl_3$) of **5**



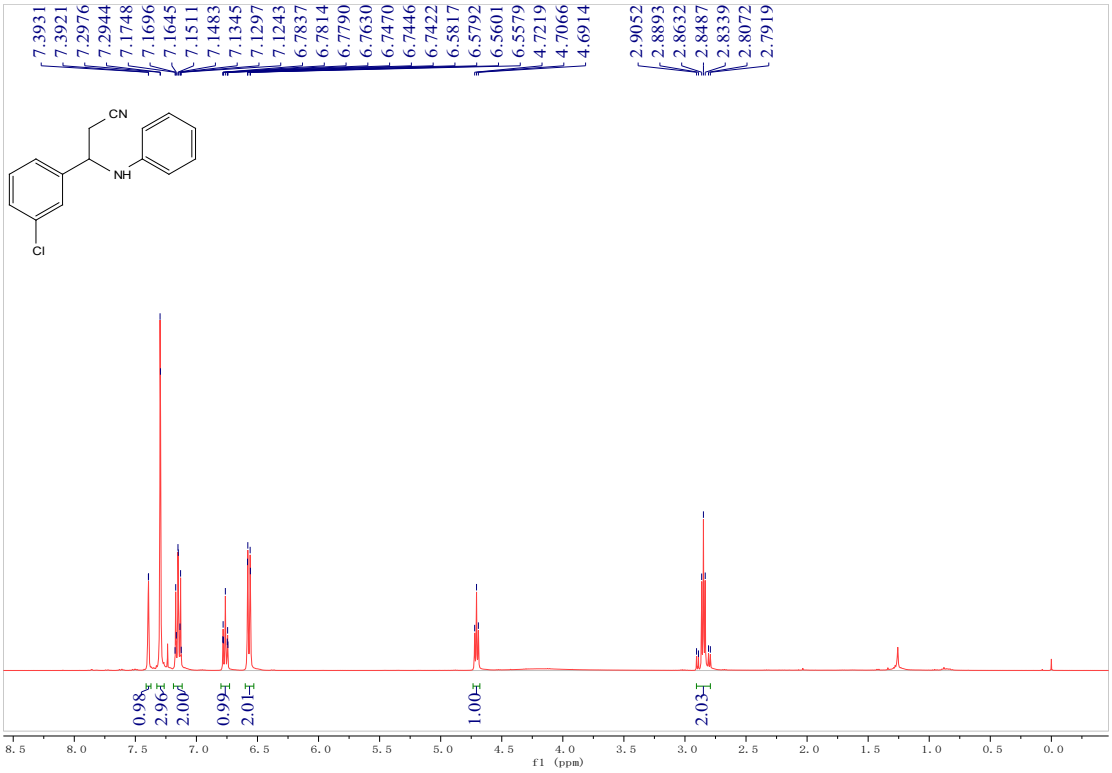
^{13}C-NMR Spectrum ($CDCl_3$) of **5**



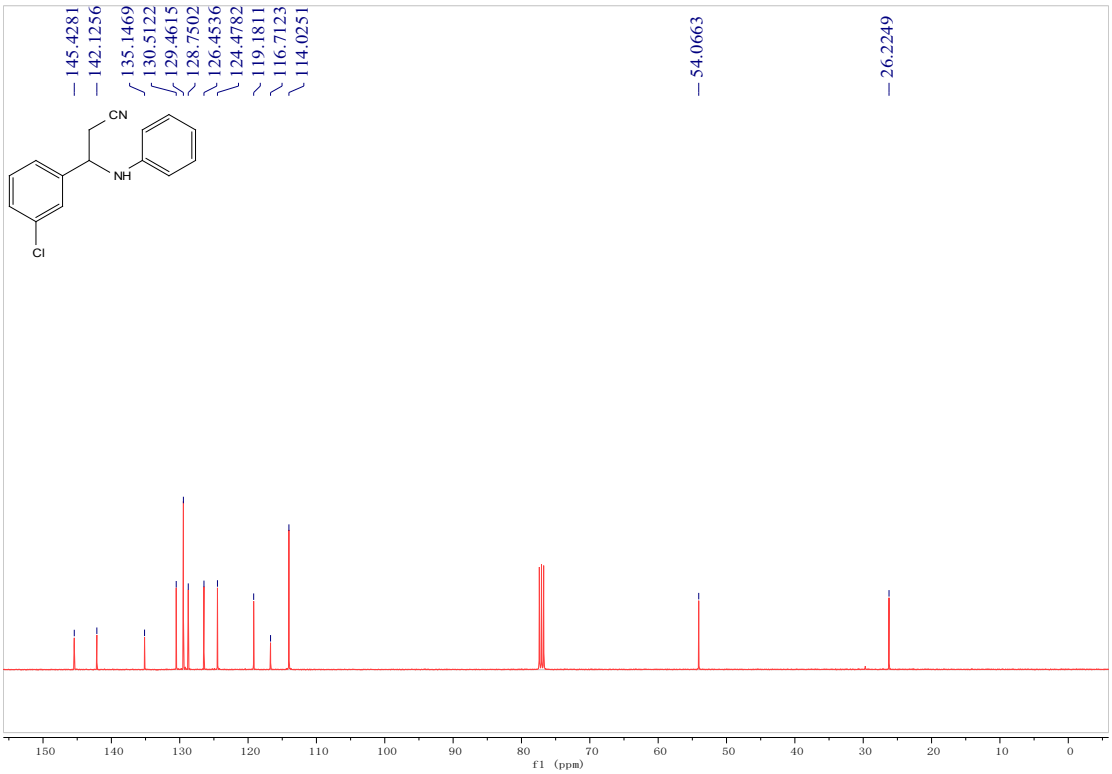
^{19}F-NMR Spectrum ($CDCl_3$) of **5**



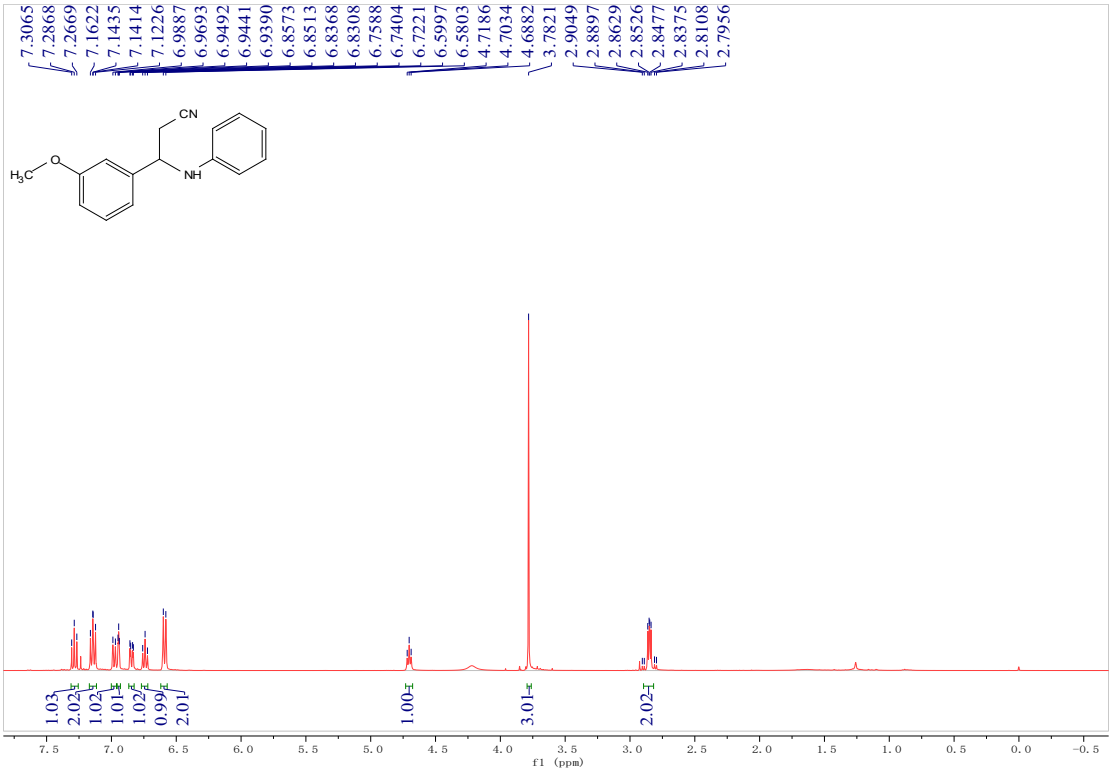
^{1}H-NMR Spectrum ($CDCl_3$) of **6**



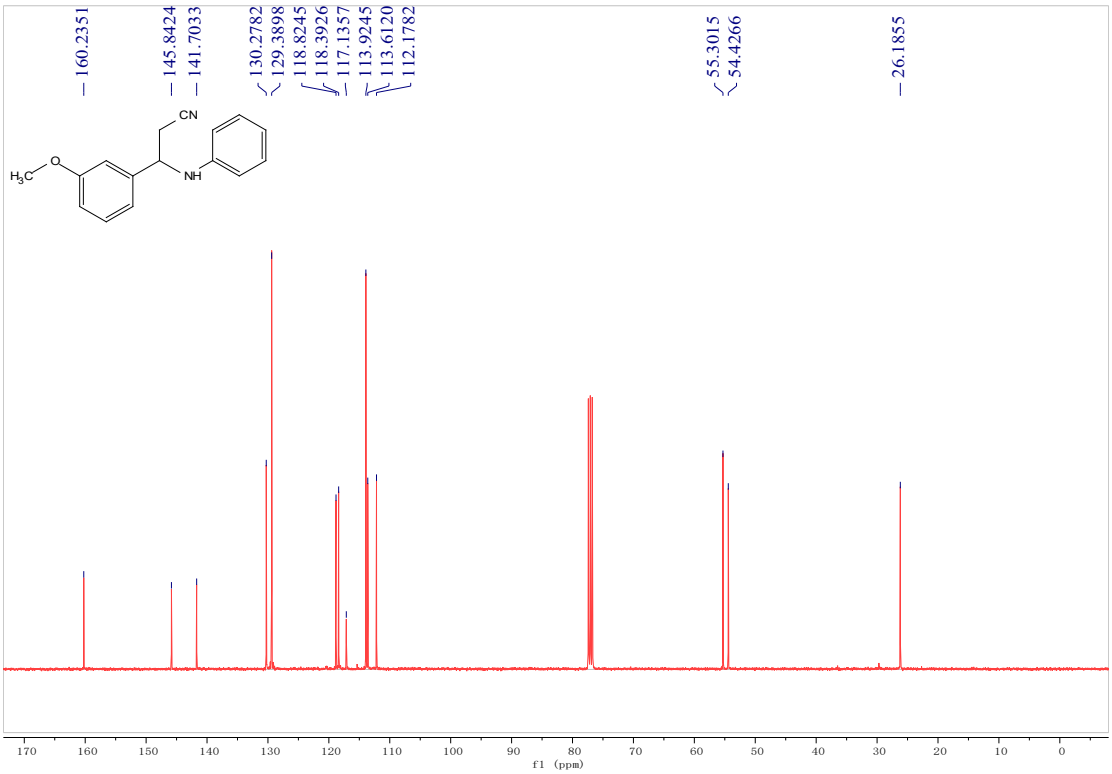
^{13}C-NMR Spectrum ($CDCl_3$) of **6**



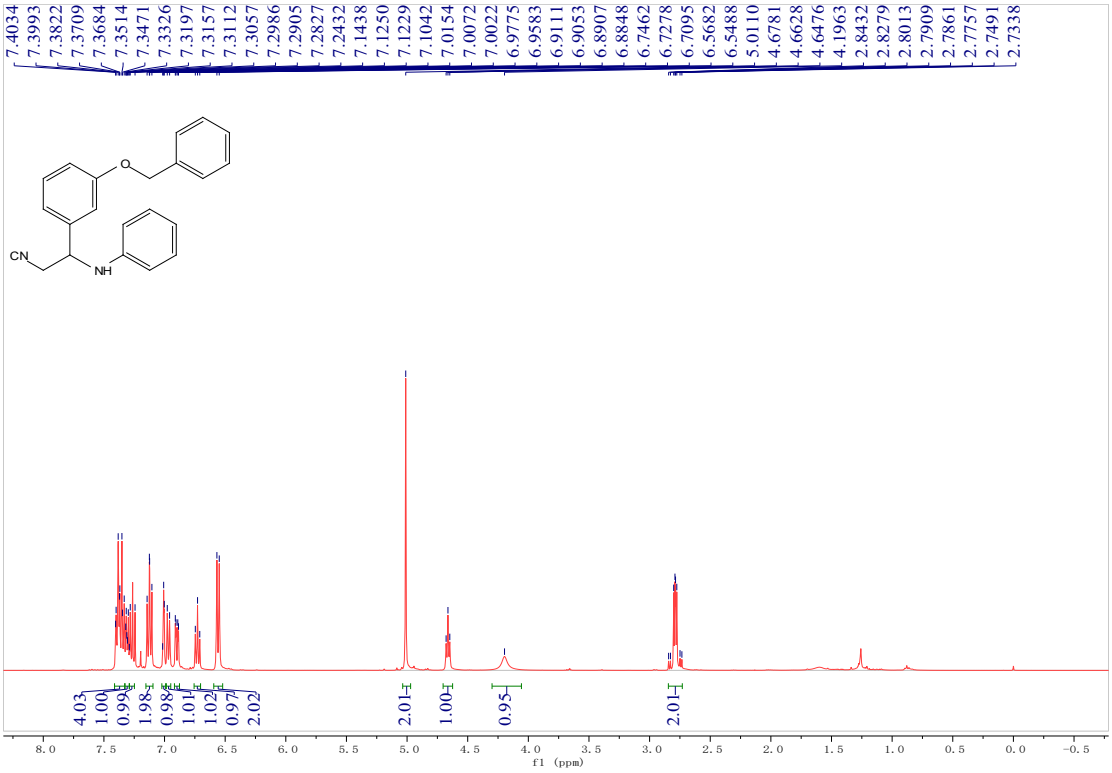
^{1}H-NMR Spectrum ($CDCl_3$) of **7**



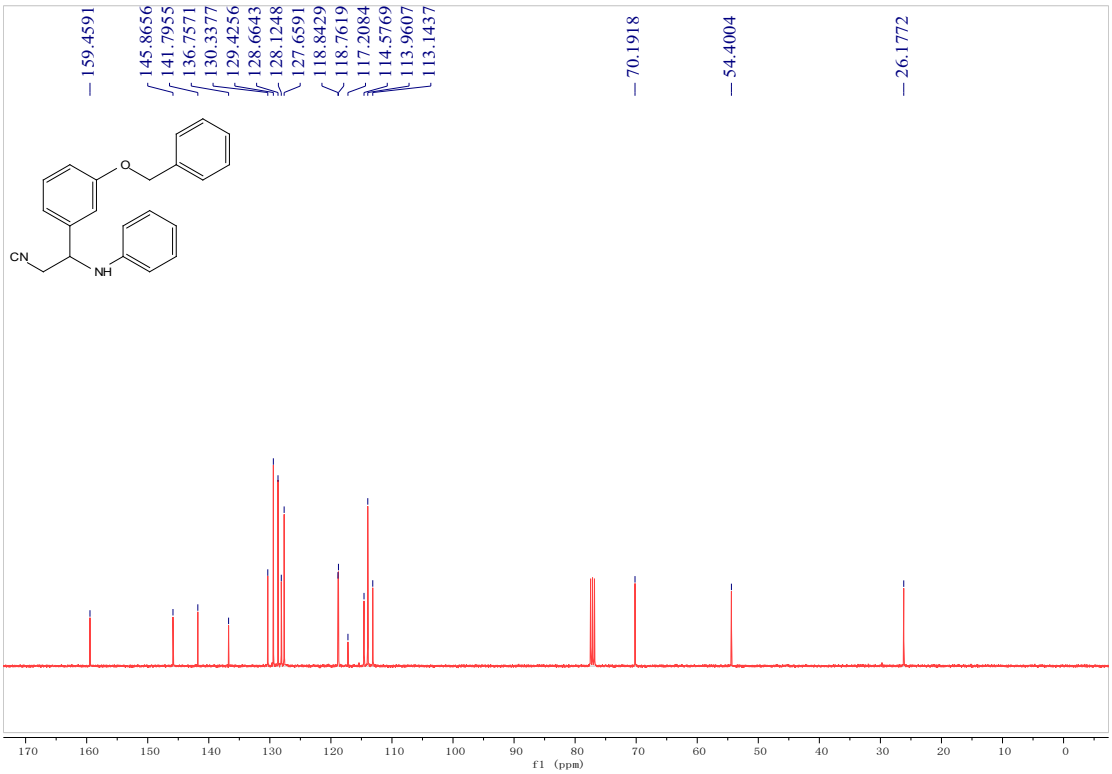
^{13}C-NMR Spectrum ($CDCl_3$) of **7**



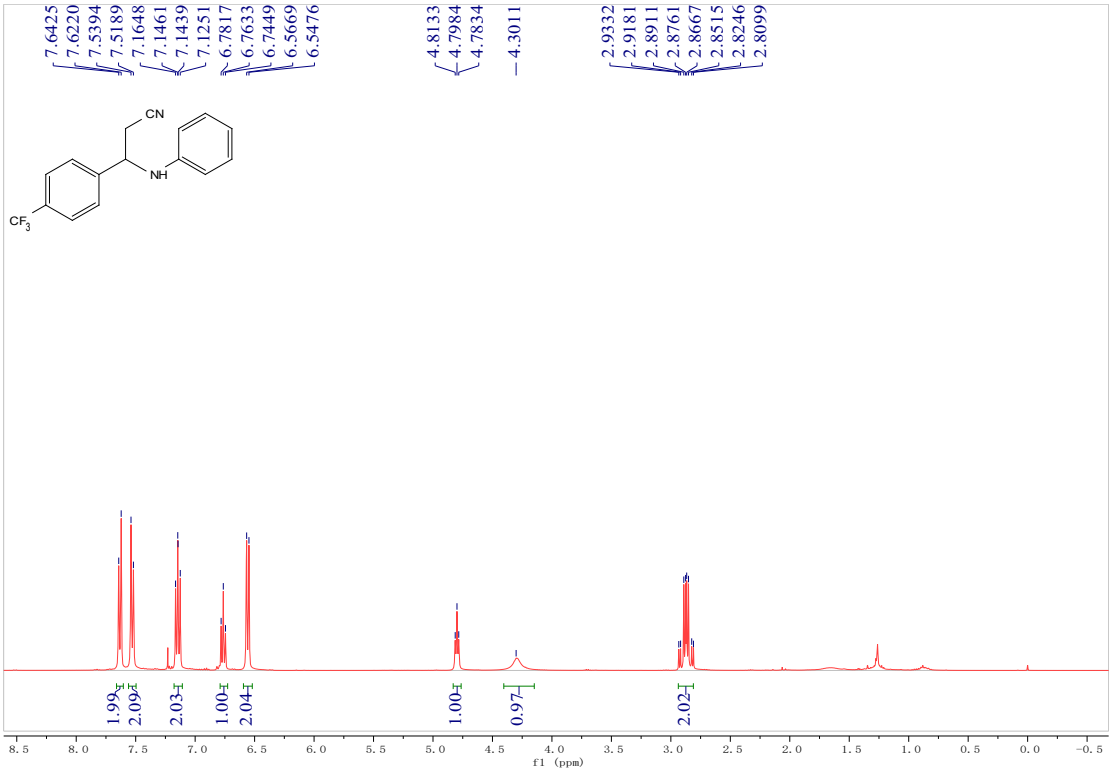
^{1}H-NMR Spectrum ($CDCl_3$) of **8**



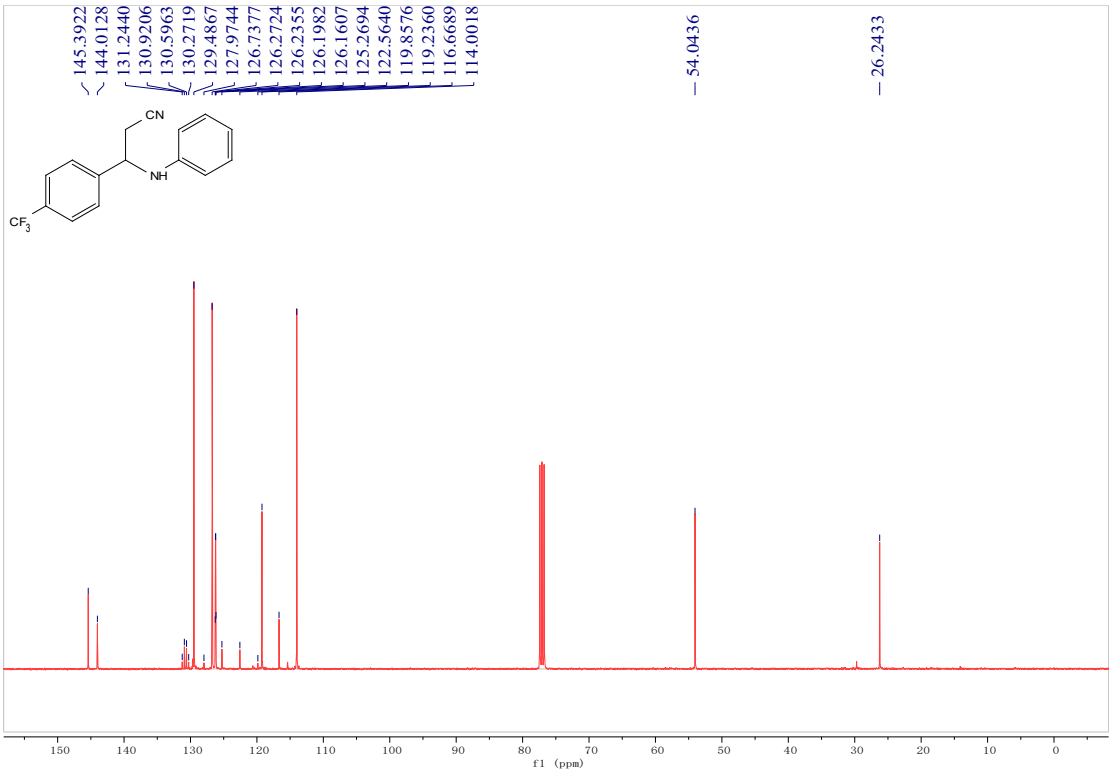
^{13}C-NMR Spectrum ($CDCl_3$) of **8**



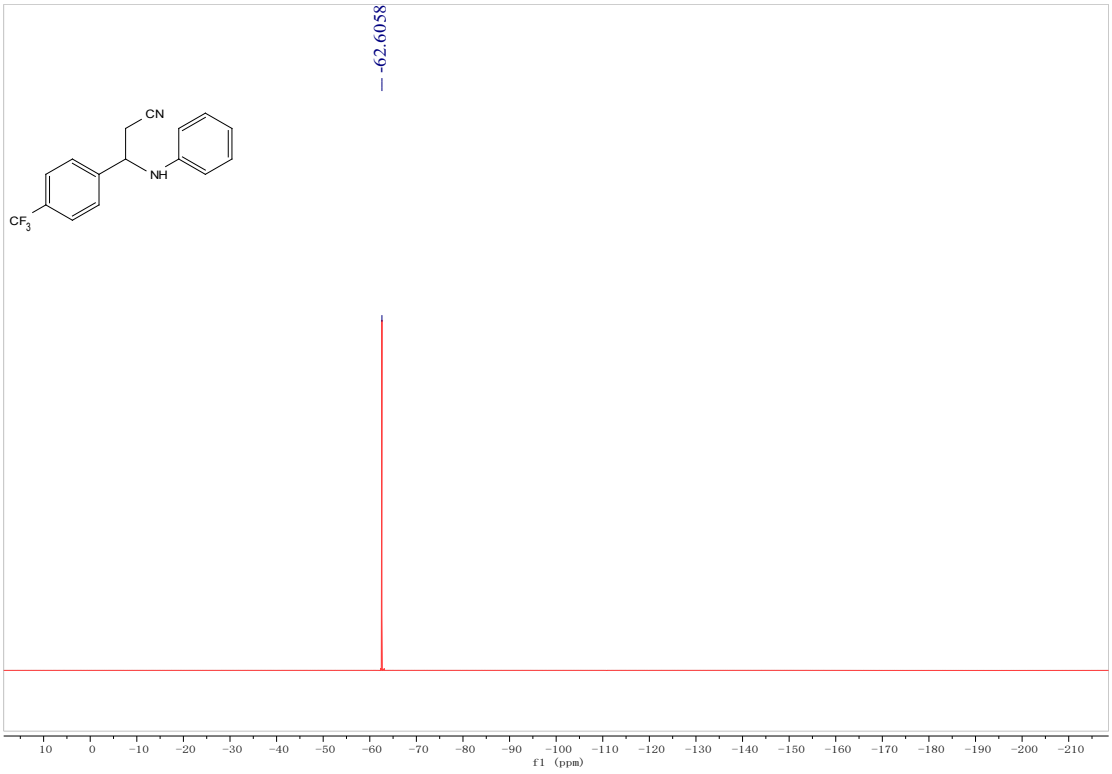
^{1}H-NMR Spectrum ($CDCl_3$) of **9**



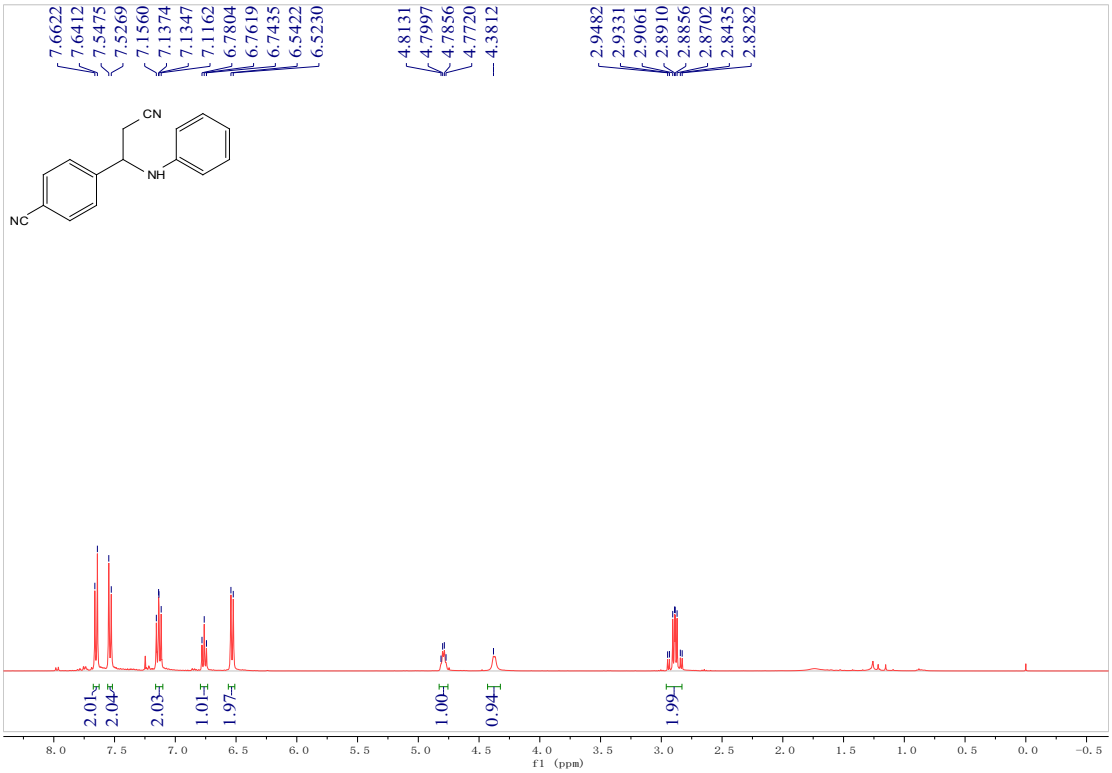
^{13}C-NMR Spectrum ($CDCl_3$) of **9**



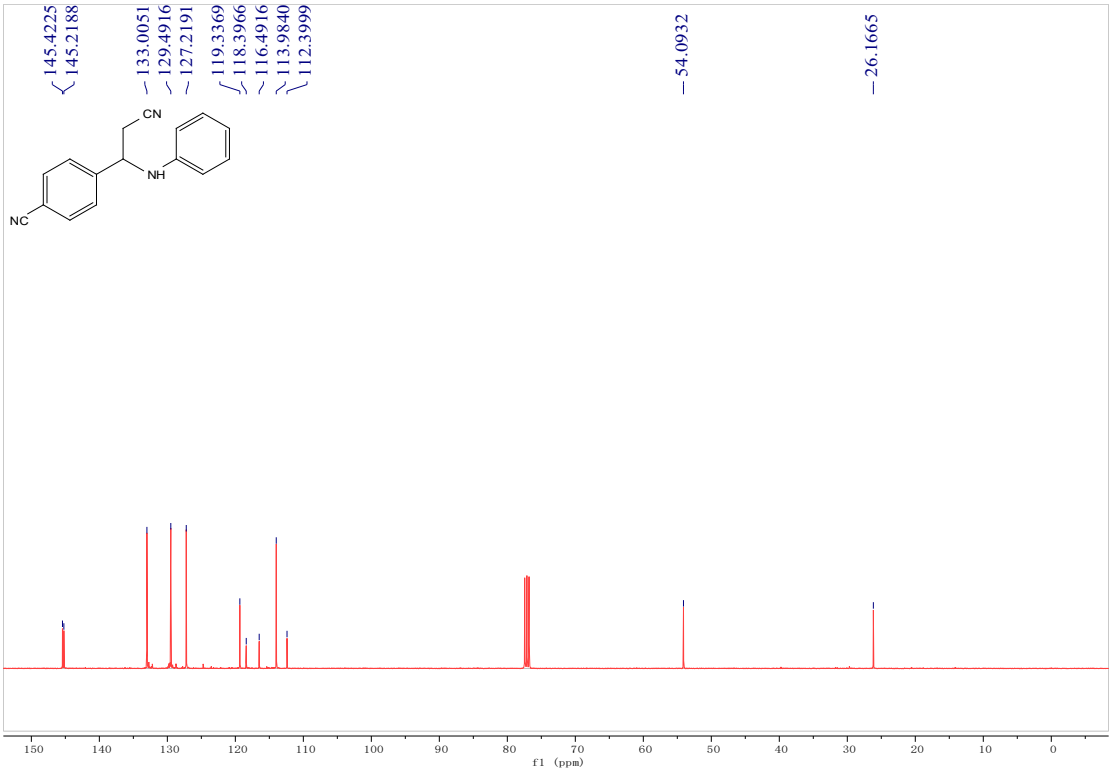
^{19}F-NMR Spectrum ($CDCl_3$) of **9**



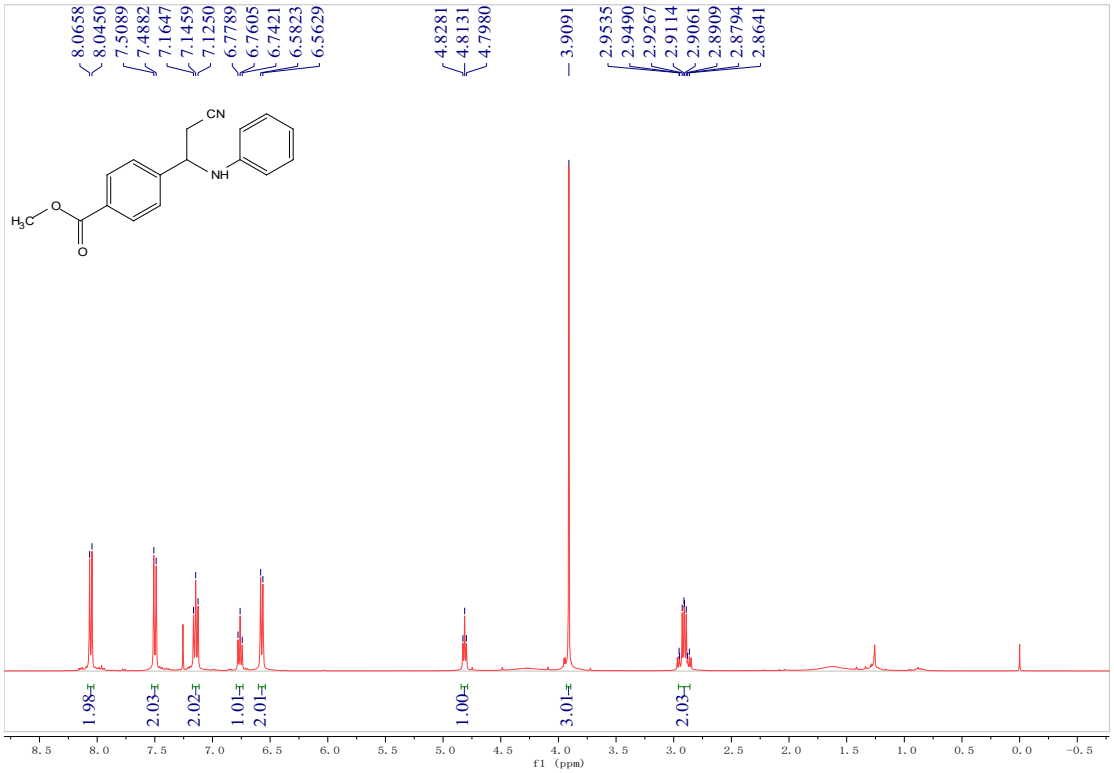
^{1}H-NMR Spectrum ($CDCl_3$) of **10**



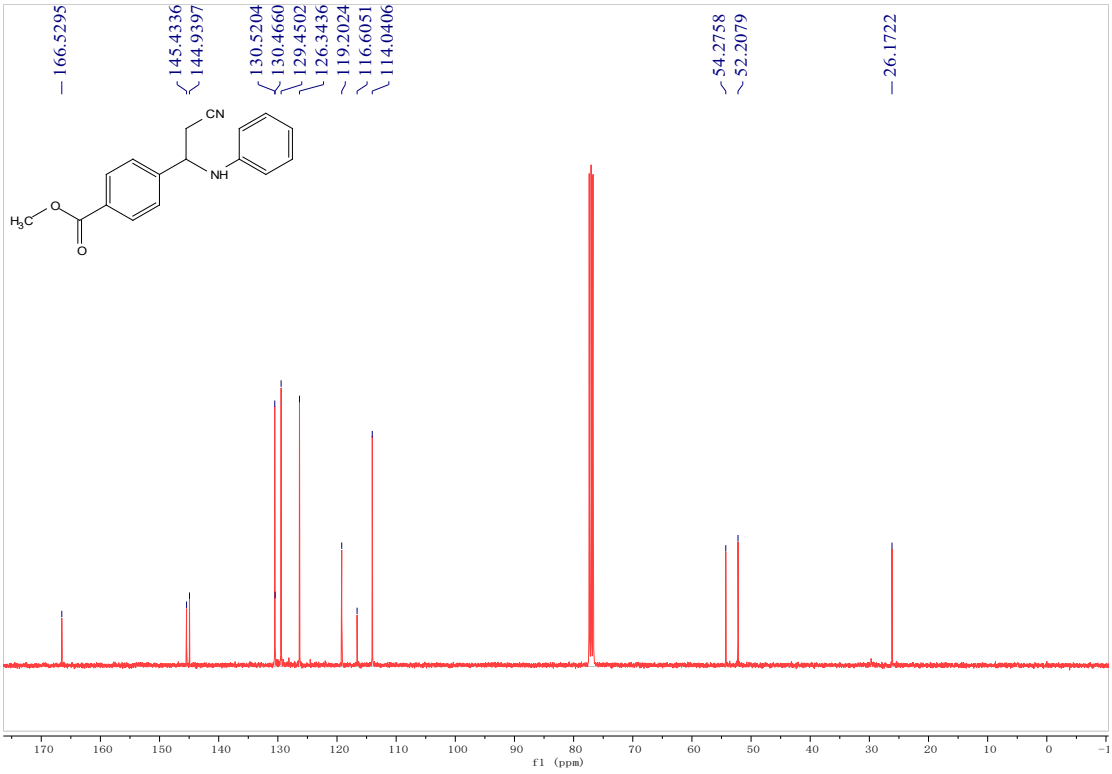
^{13}C-NMR Spectrum ($CDCl_3$) of **10**



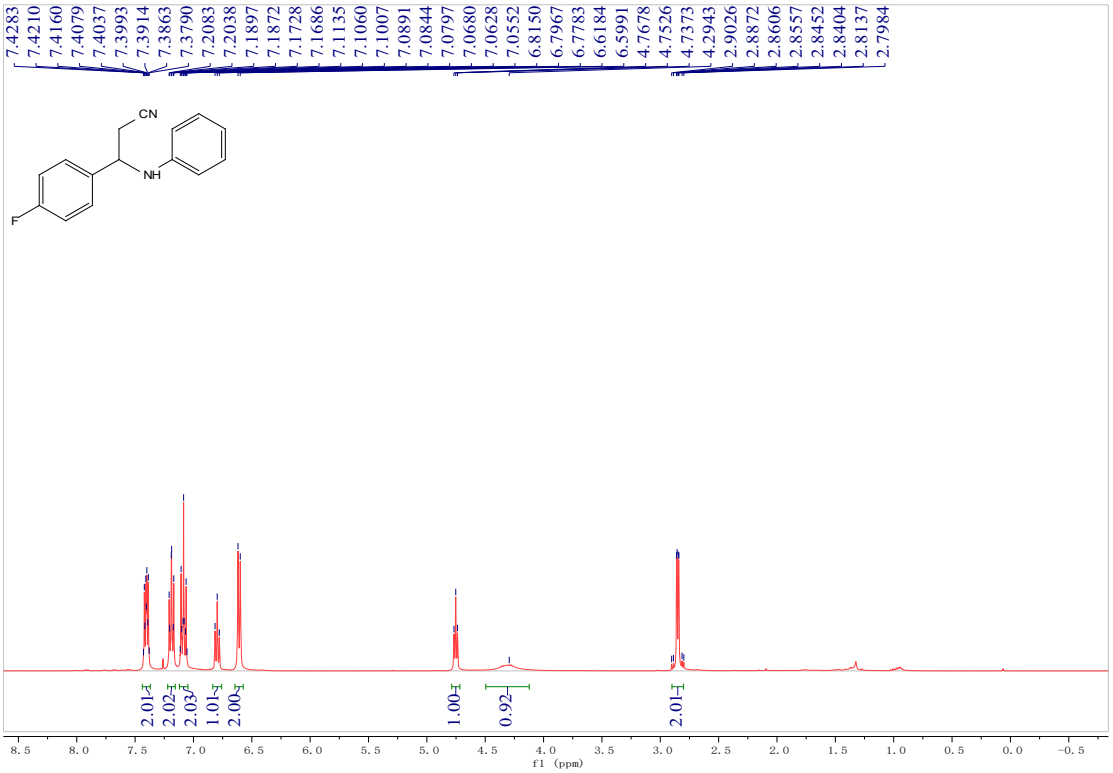
^{1}H-NMR Spectrum ($CDCl_3$) of **11**



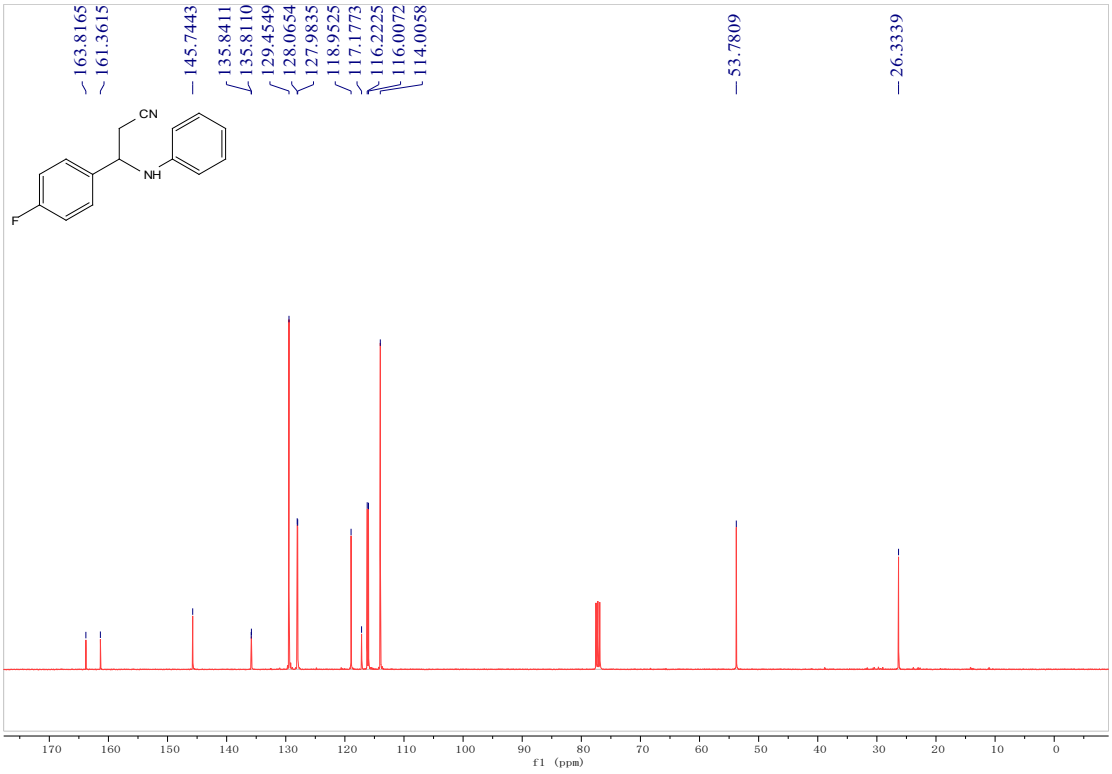
^{13}C-NMR Spectrum ($CDCl_3$) of **11**



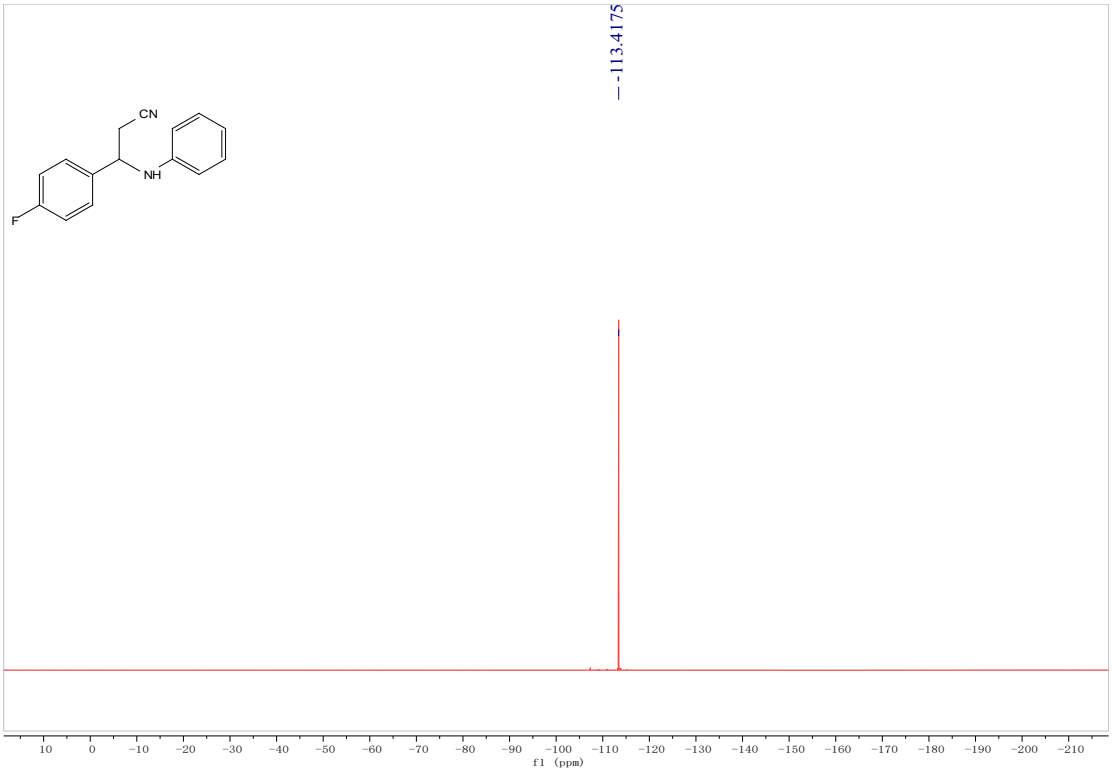
^{1}H-NMR Spectrum ($CDCl_3$) of **12**



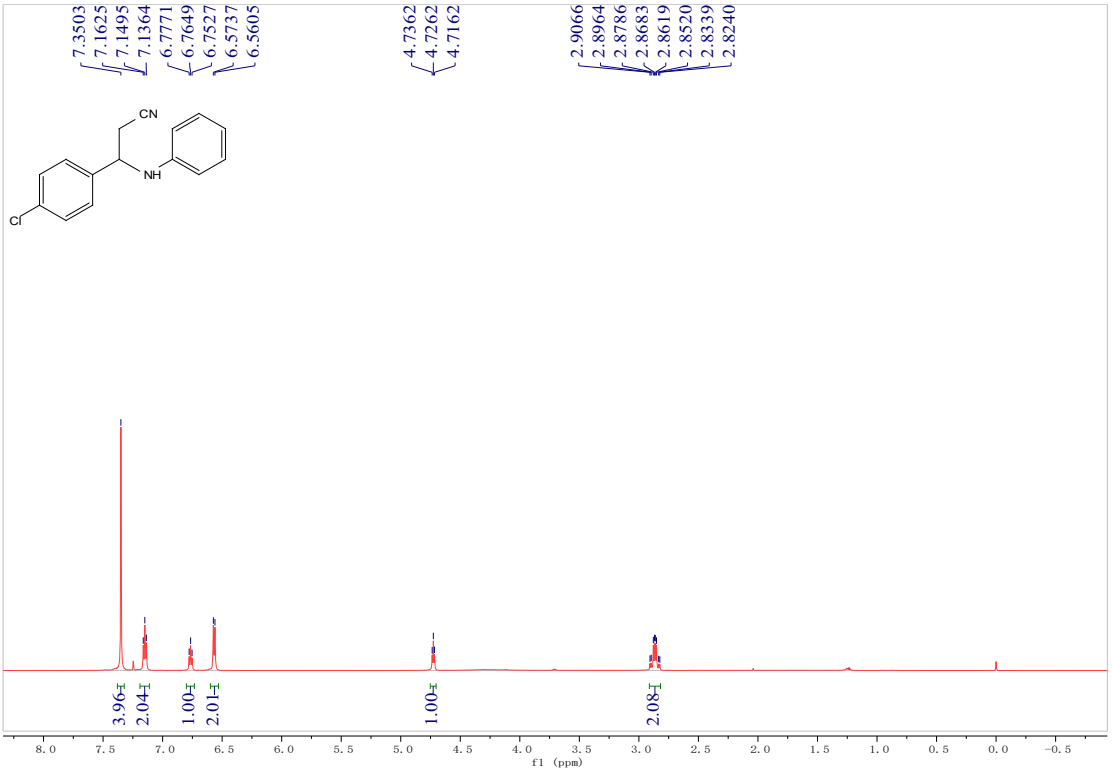
^{13}C-NMR Spectrum ($CDCl_3$) of **12**



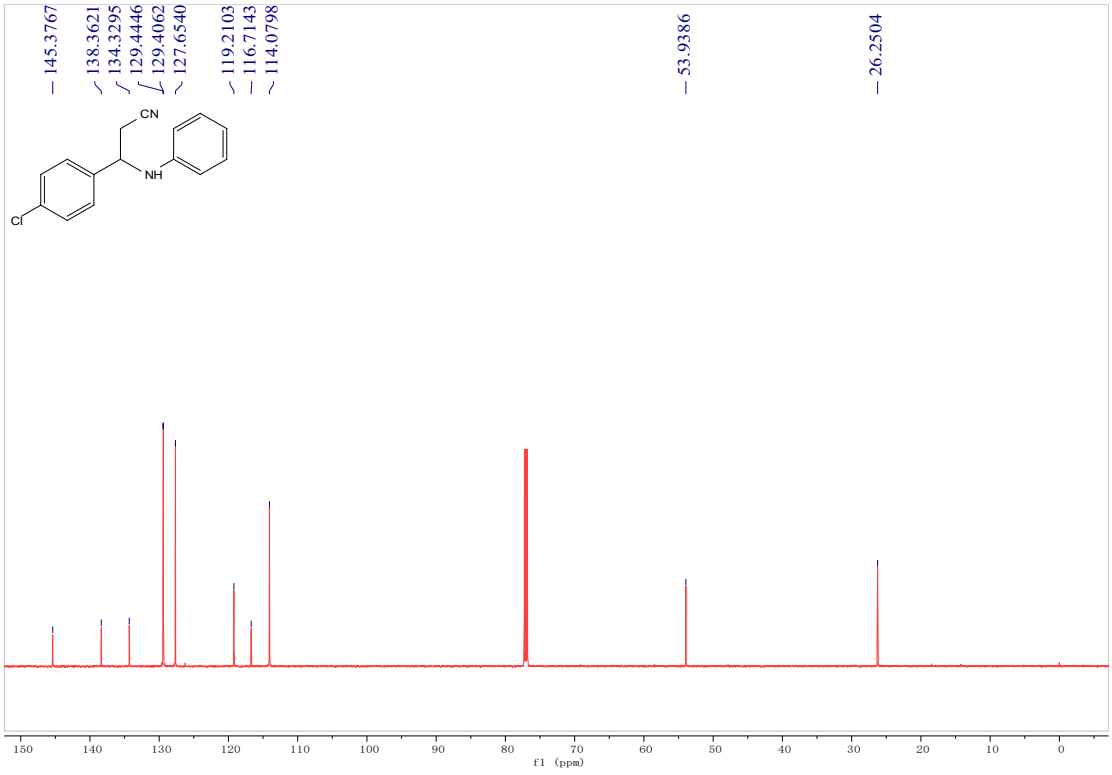
^{19}F-NMR Spectrum ($CDCl_3$) of **12**



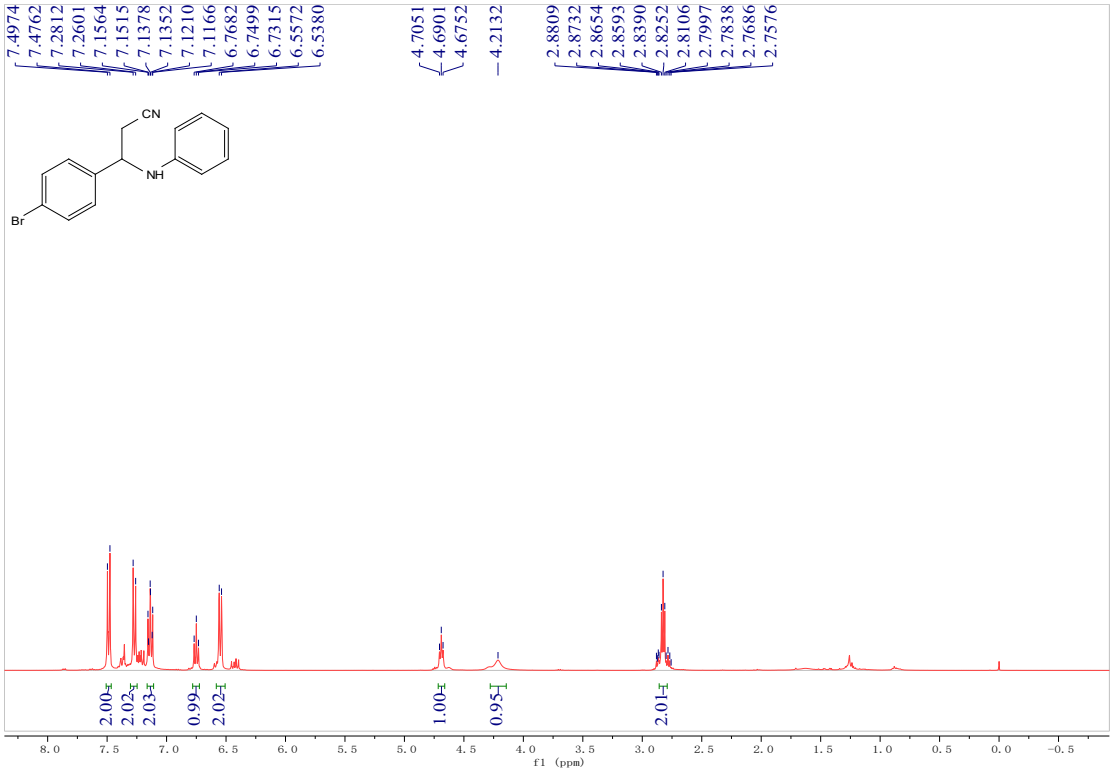
^{1}H-NMR Spectrum ($CDCl_3$) of **13**



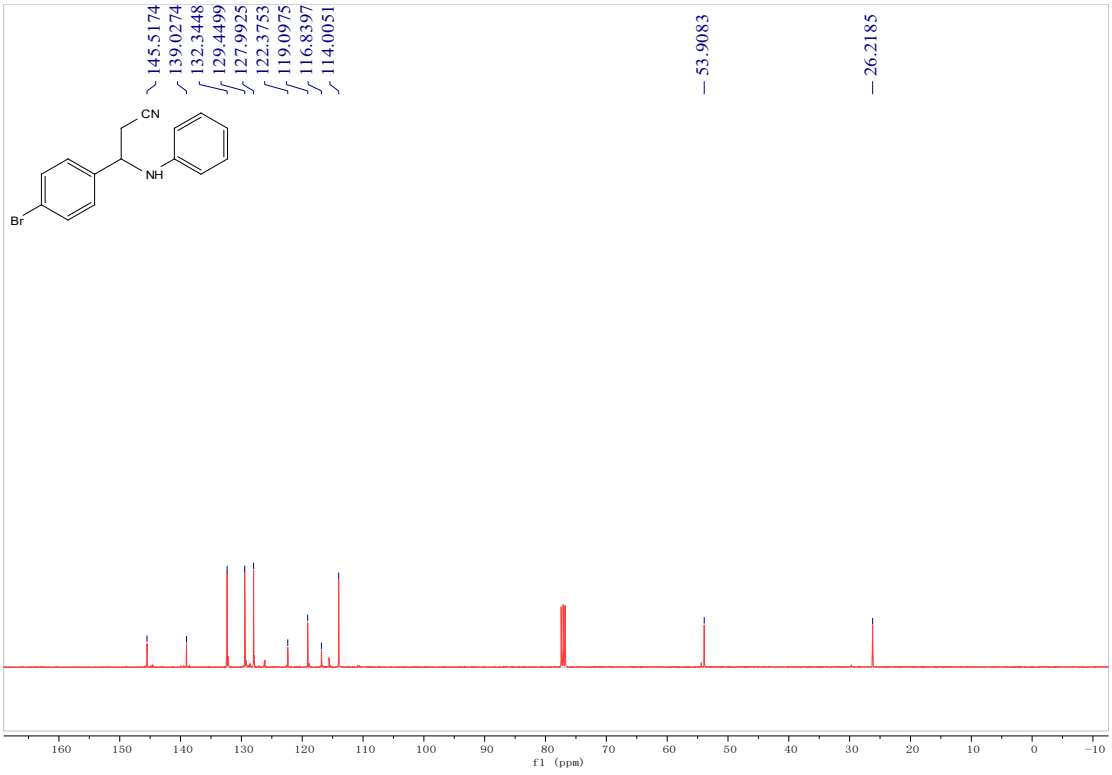
^{13}C-NMR Spectrum ($CDCl_3$) of **13**



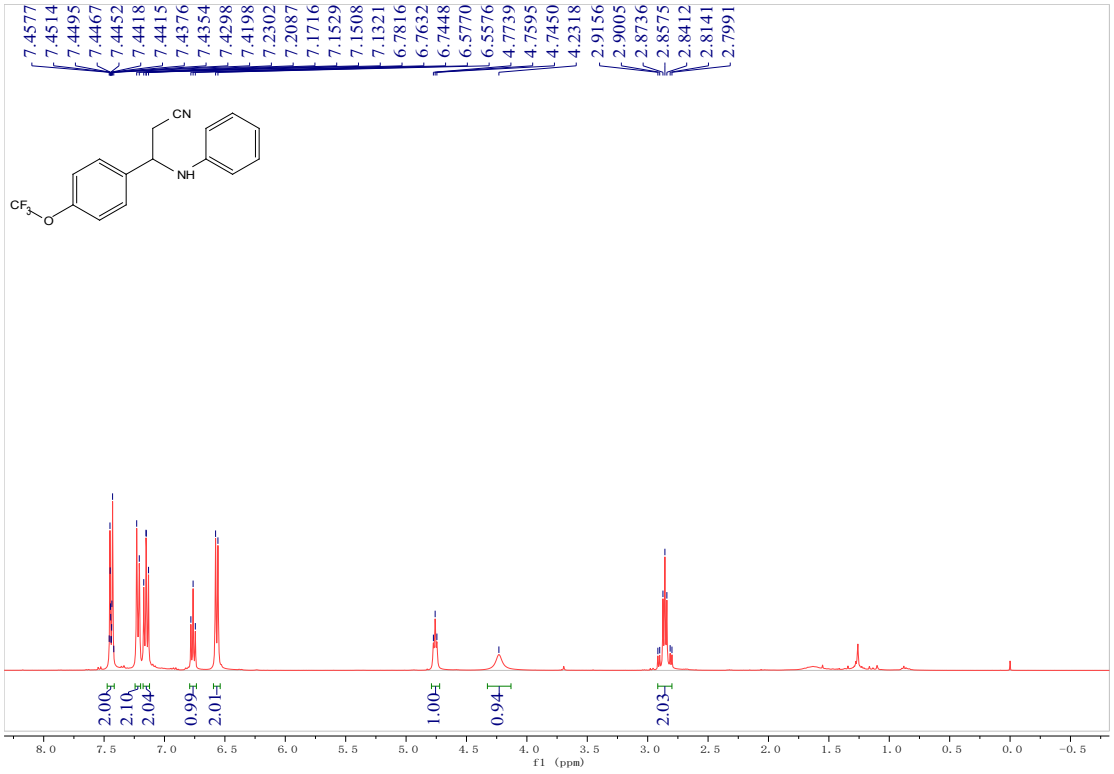
^{1}H-NMR Spectrum ($CDCl_3$) of **14**



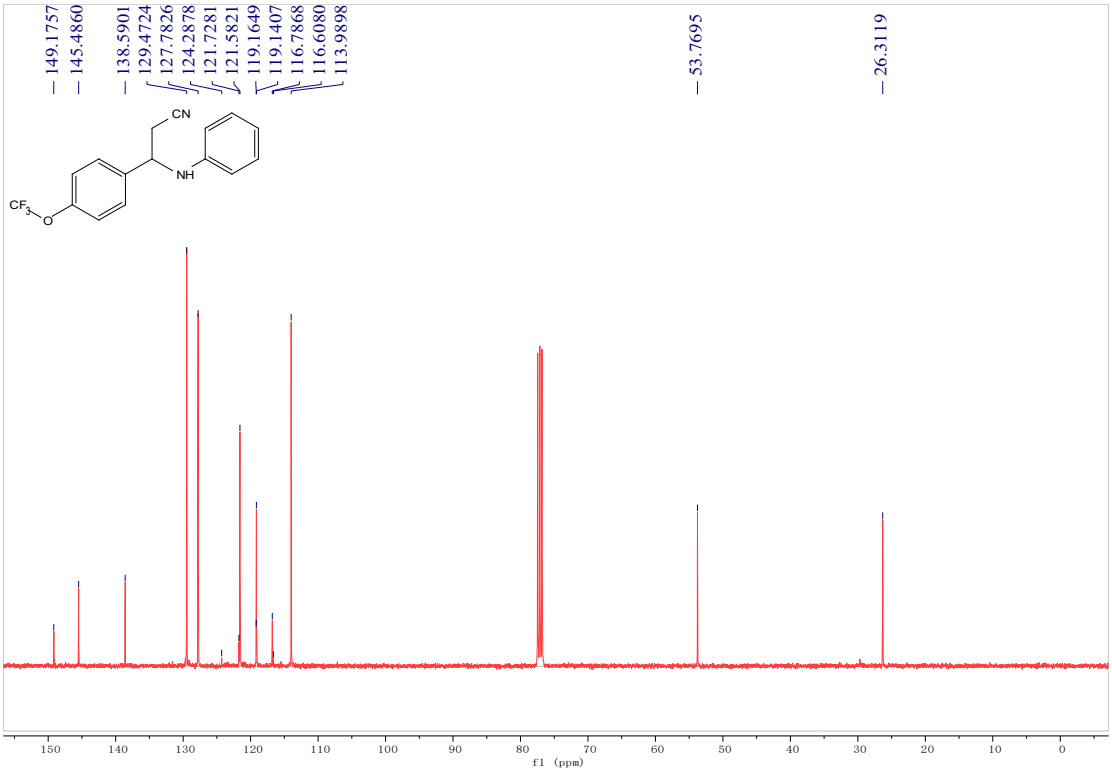
^{13}C-NMR Spectrum ($CDCl_3$) of **14**



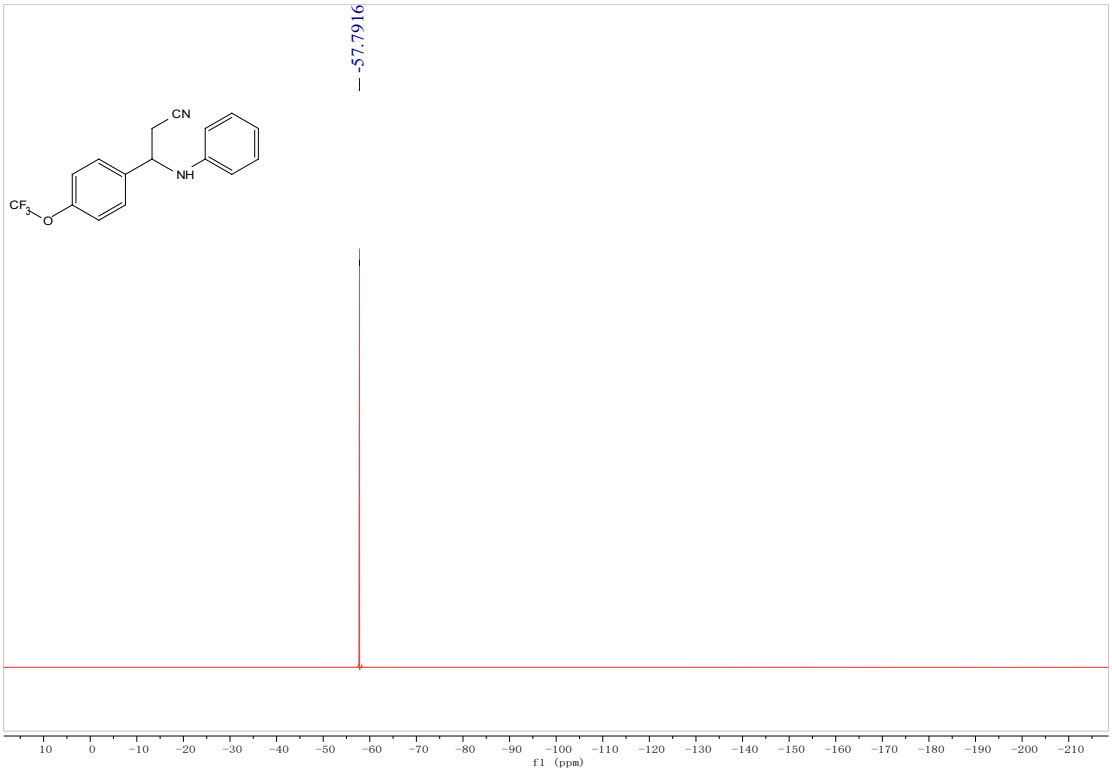
^{1}H-NMR Spectrum ($CDCl_3$) of **15**



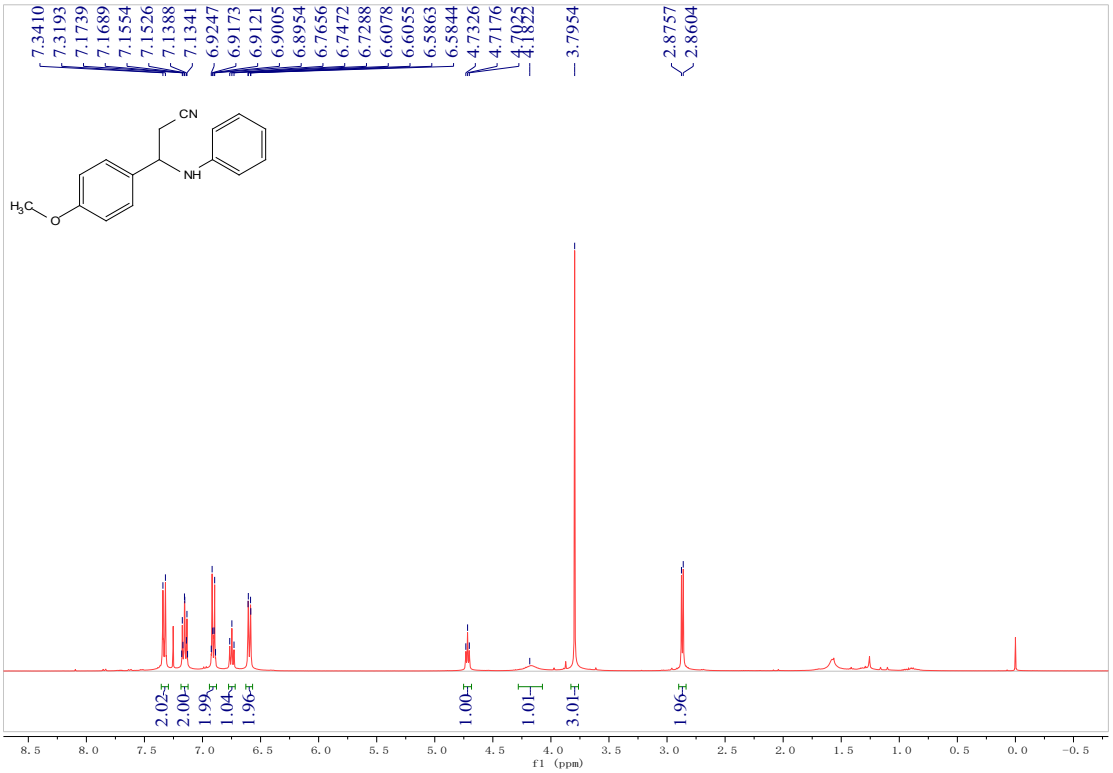
^{13}C-NMR Spectrum ($CDCl_3$) of **15**



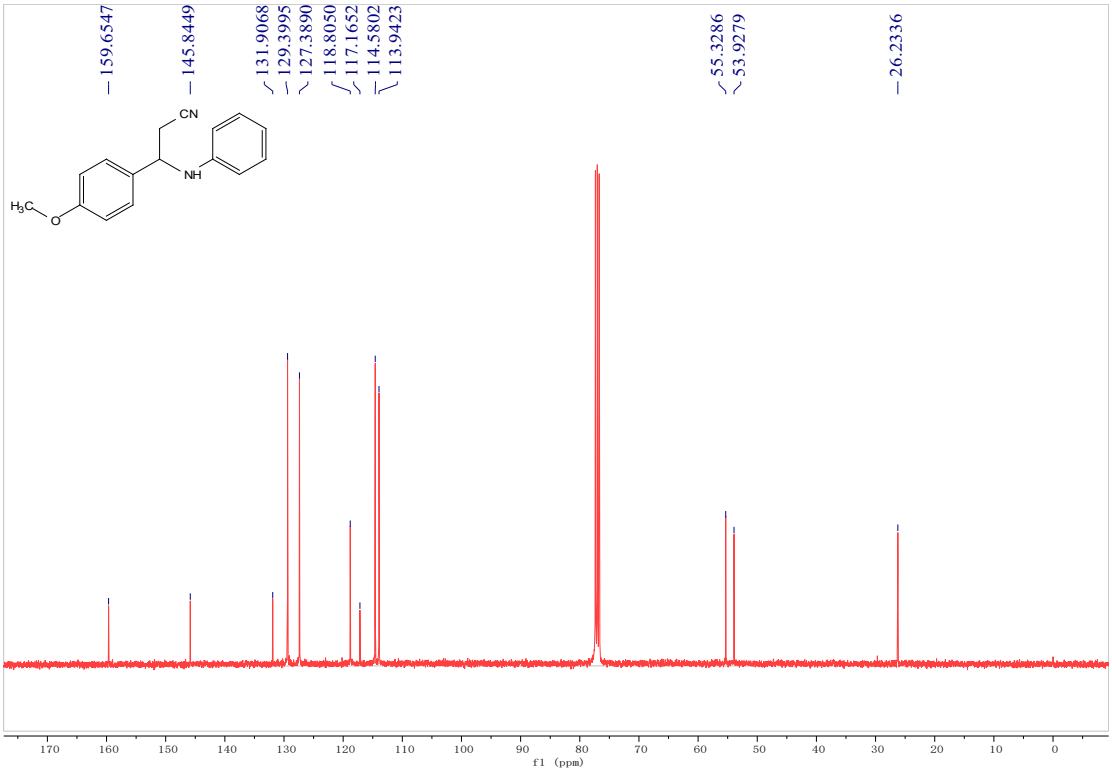
^{19}F-NMR Spectrum ($CDCl_3$) of **15**



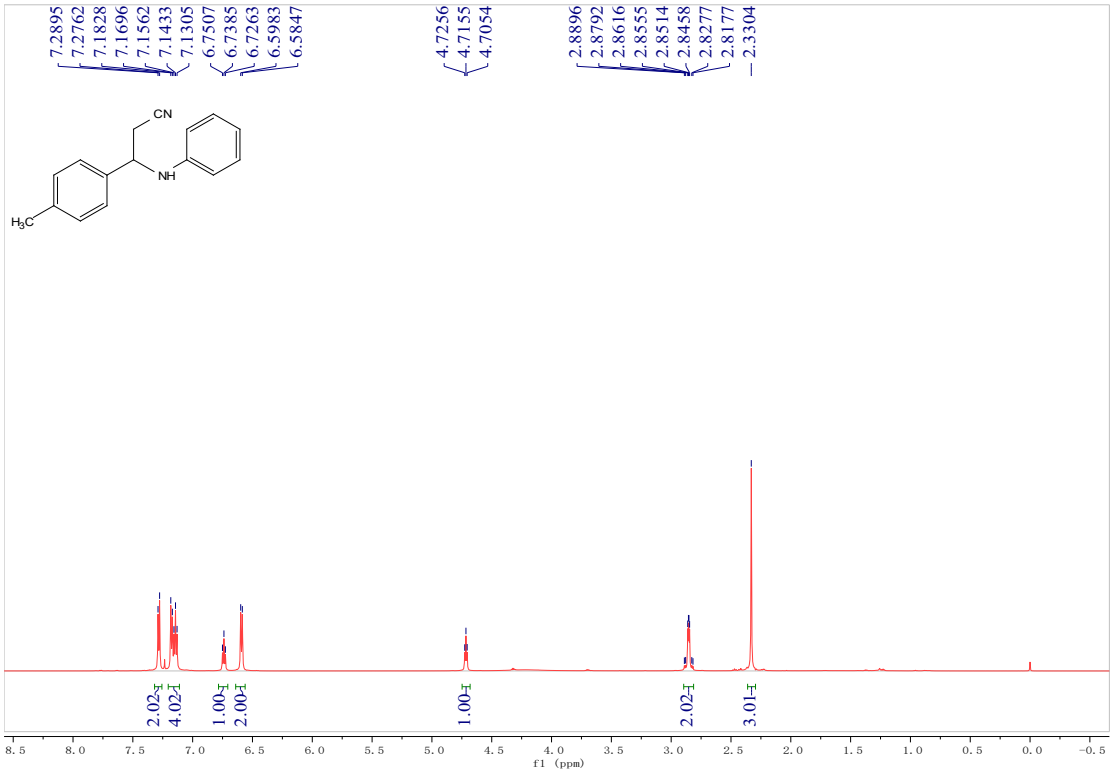
^{1}H-NMR Spectrum ($CDCl_3$) of **16**



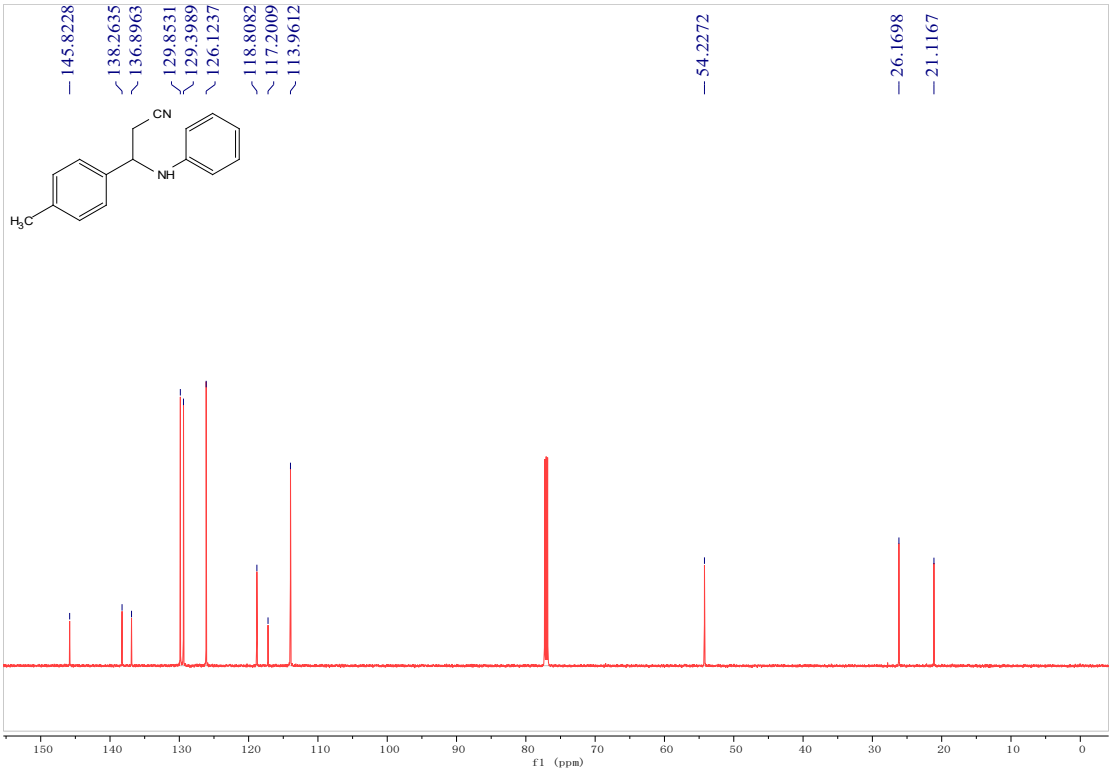
^{13}C-NMR Spectrum ($CDCl_3$) of **16**



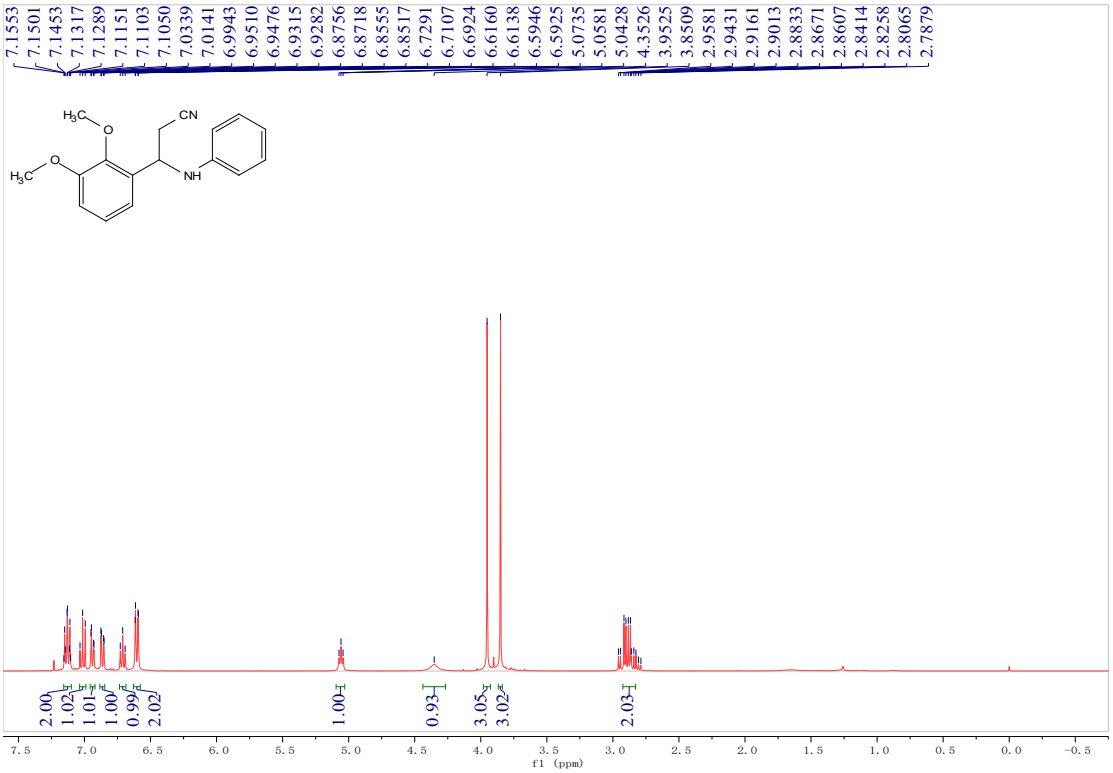
^{1}H-NMR Spectrum ($CDCl_3$) of **17**



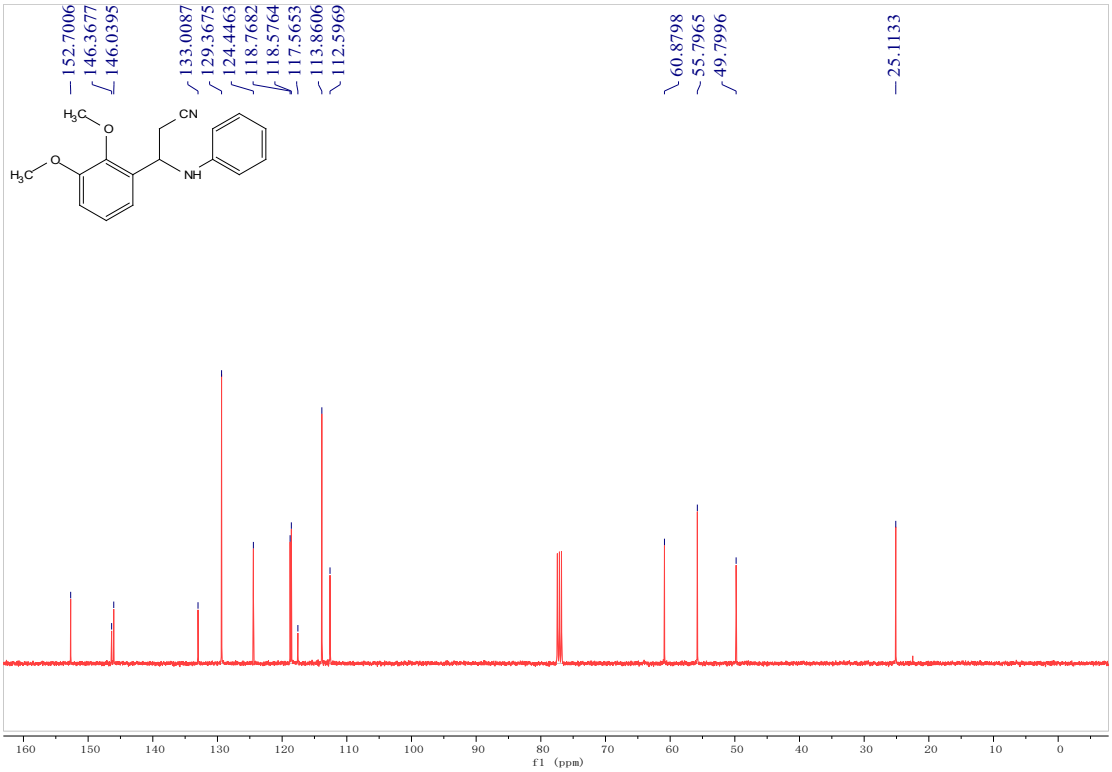
^{13}C-NMR Spectrum ($CDCl_3$) of **17**



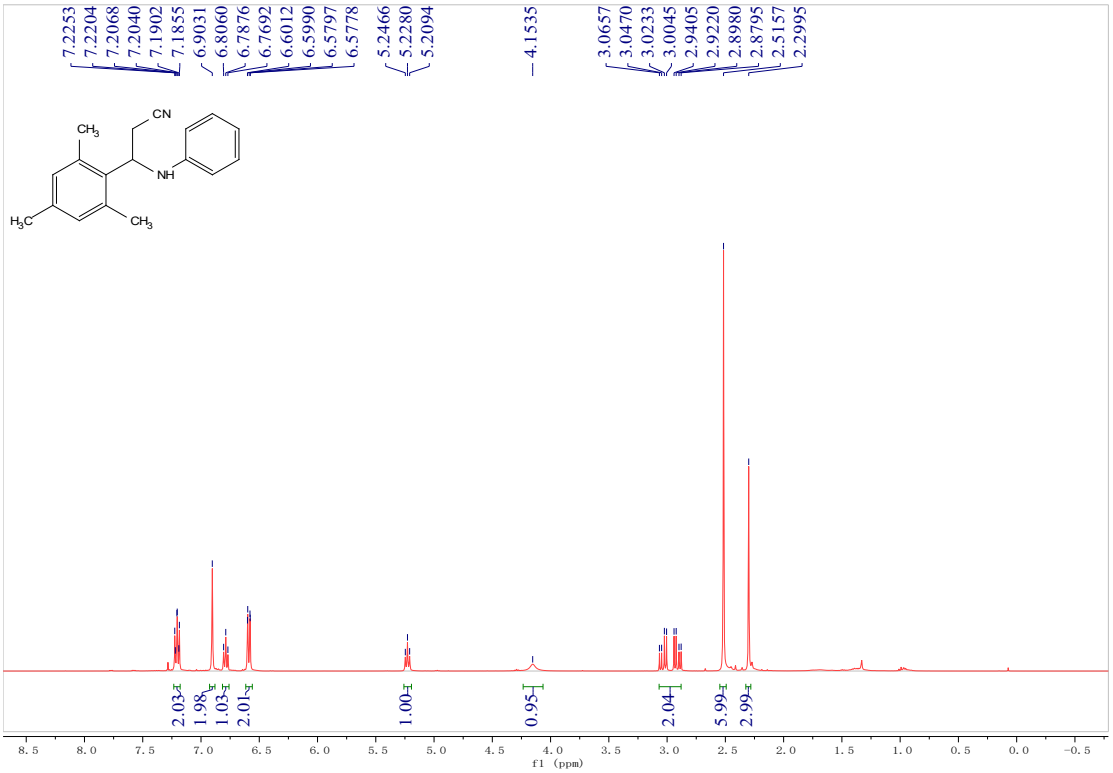
^{1}H-NMR Spectrum ($CDCl_3$) of **18**



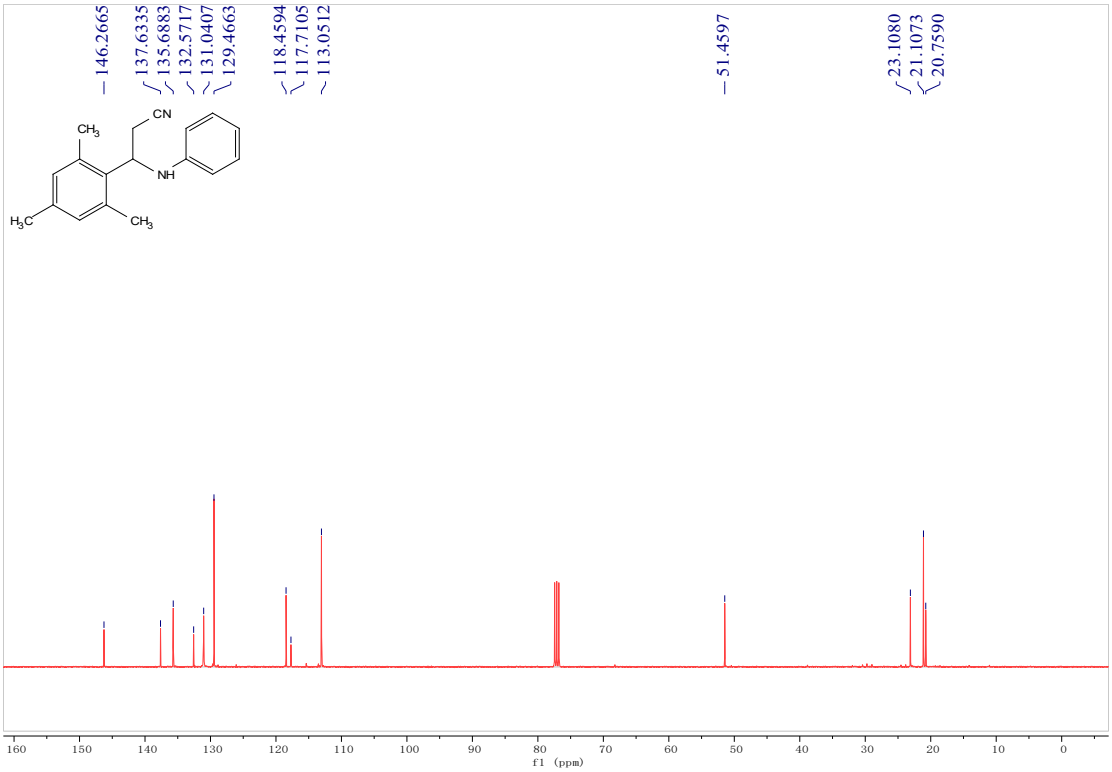
^{13}C-NMR Spectrum ($CDCl_3$) of **18**



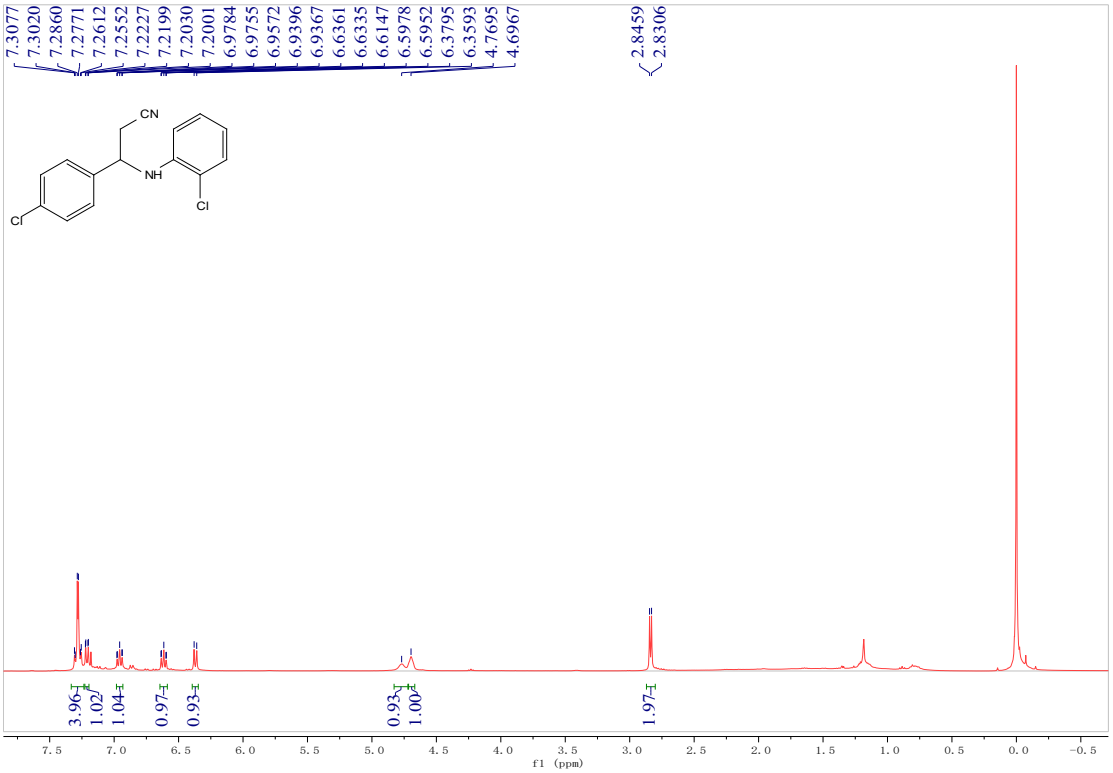
^{1}H-NMR Spectrum ($CDCl_3$) of **19**



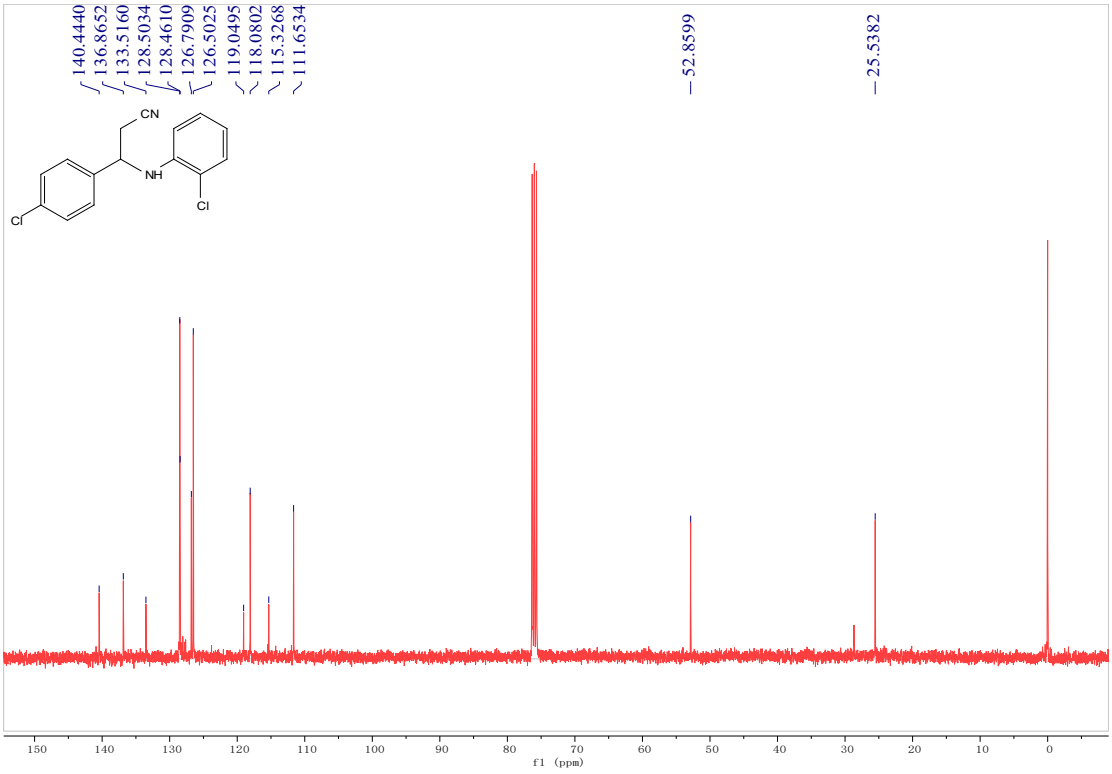
^{13}C-NMR Spectrum ($CDCl_3$) of **19**



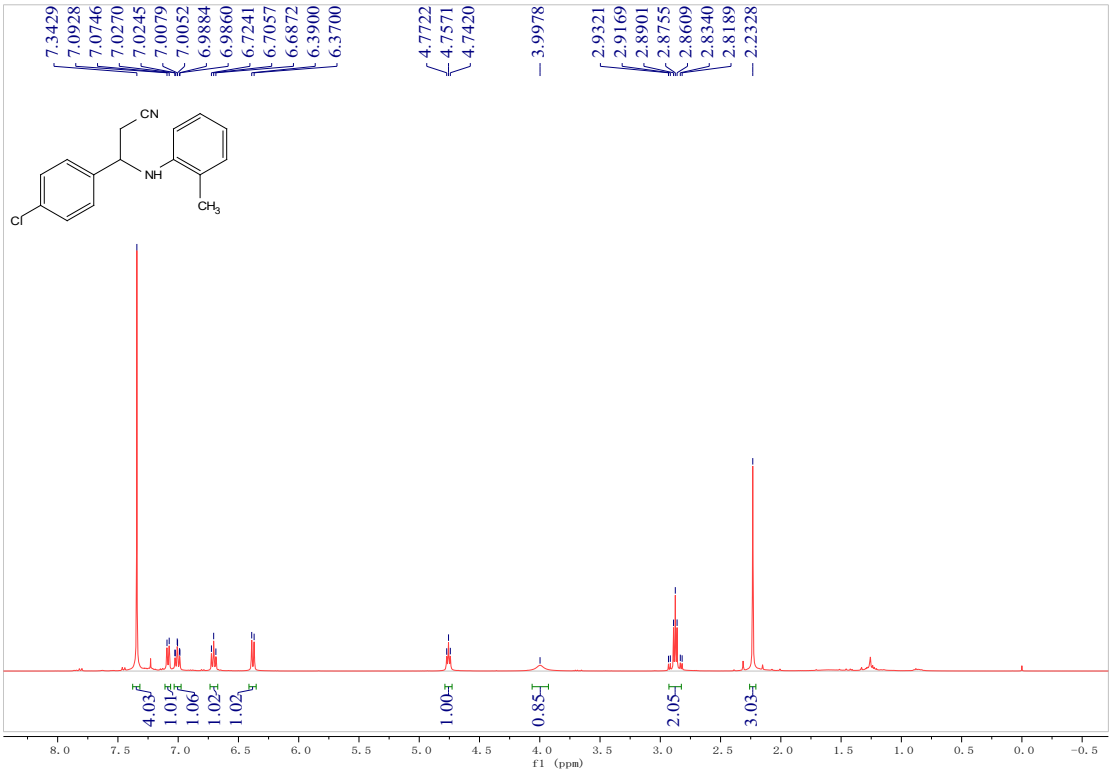
^{1}H-NMR Spectrum ($CDCl_3$) of **20**



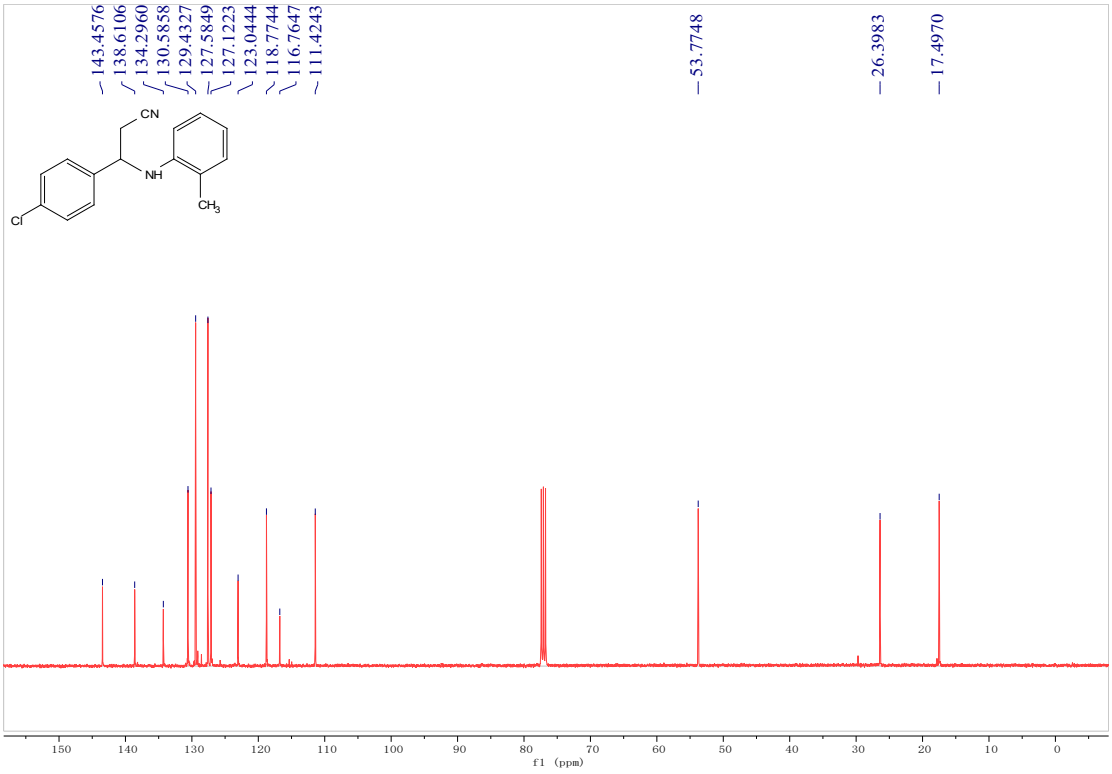
^{13}C-NMR Spectrum ($CDCl_3$) of **20**



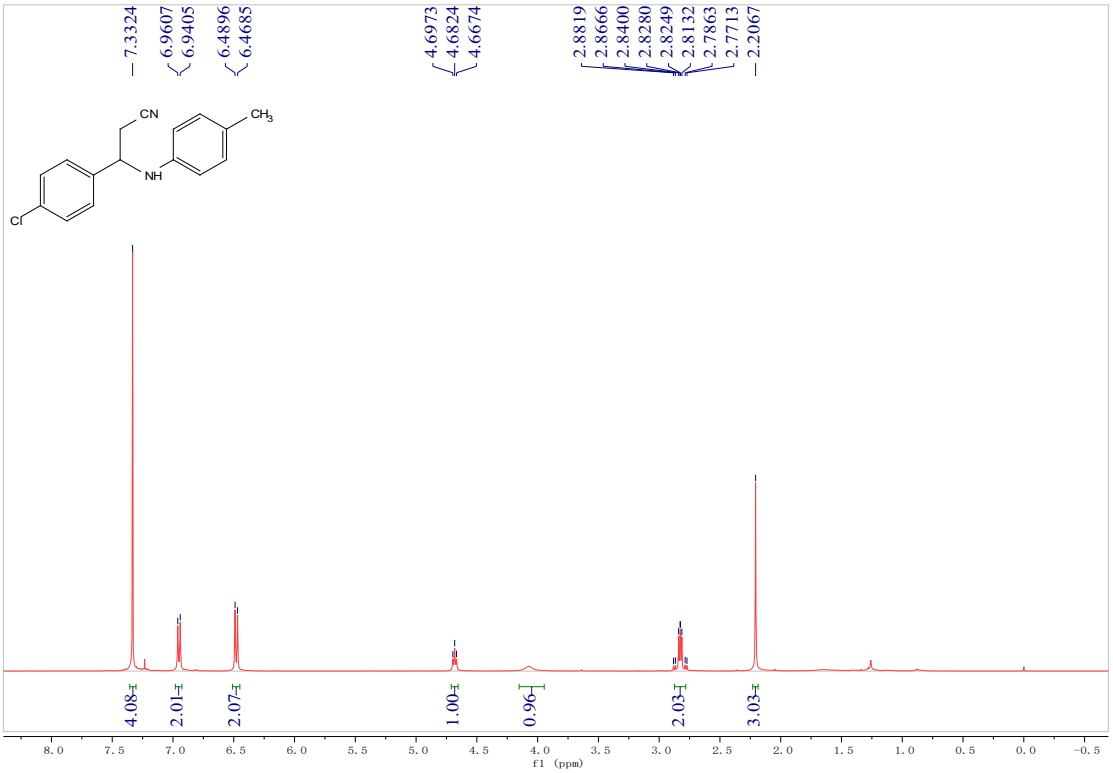
^{1}H-NMR Spectrum ($CDCl_3$) of **21**



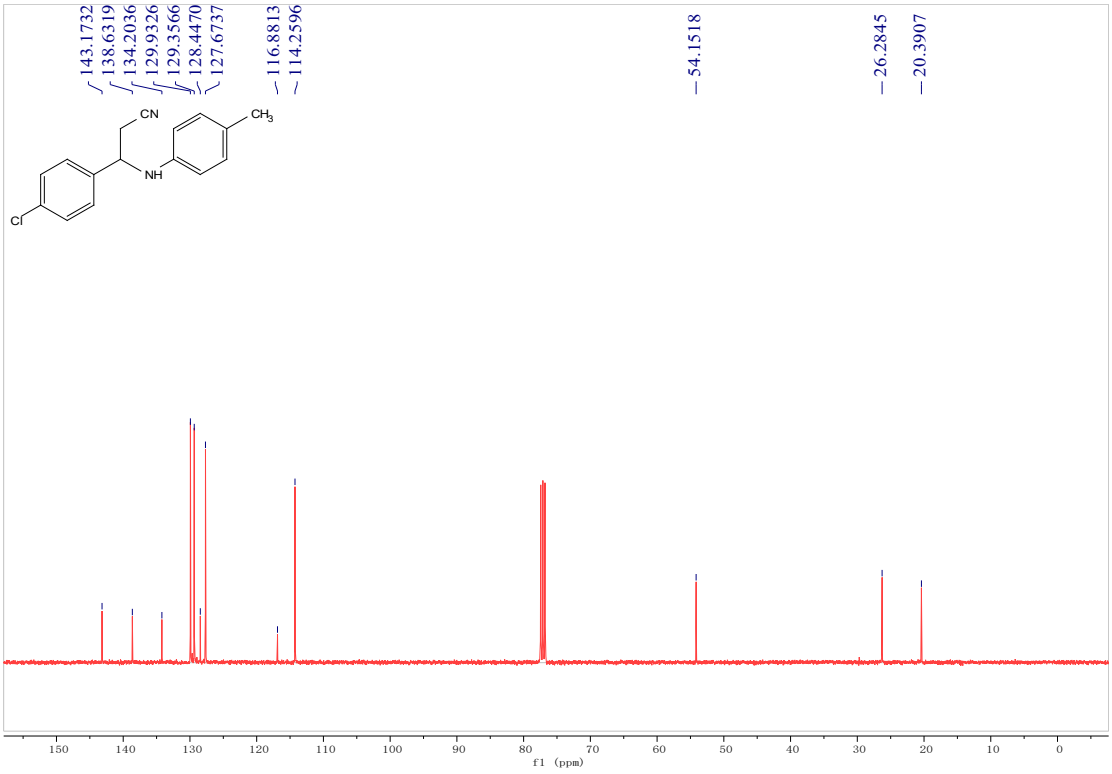
^{13}C-NMR Spectrum ($CDCl_3$) of **21**



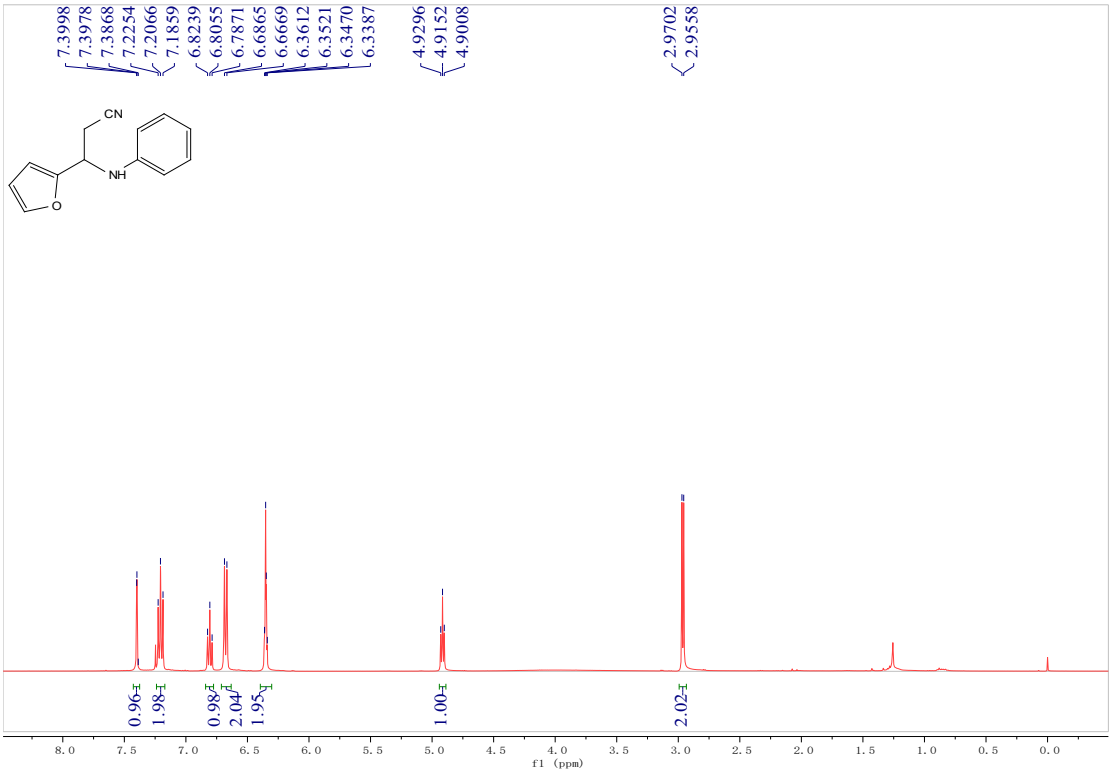
^{1}H-NMR Spectrum ($CDCl_3$) of **22**



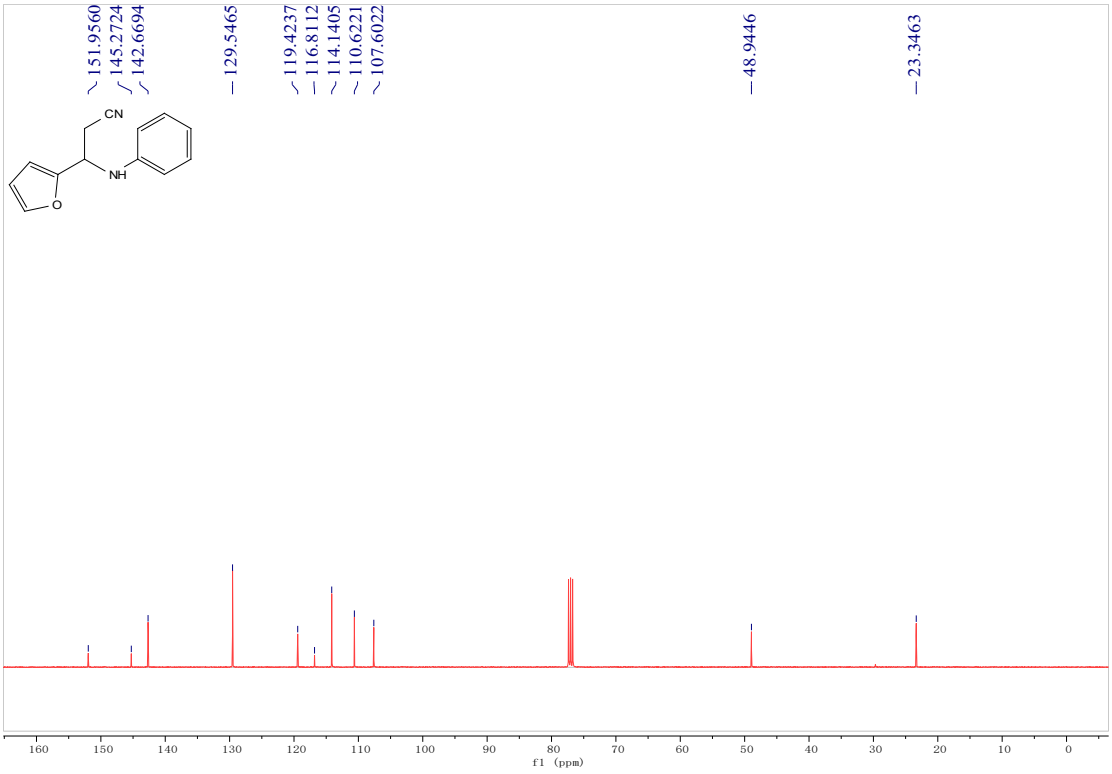
^{13}C-NMR Spectrum ($CDCl_3$) of **22**



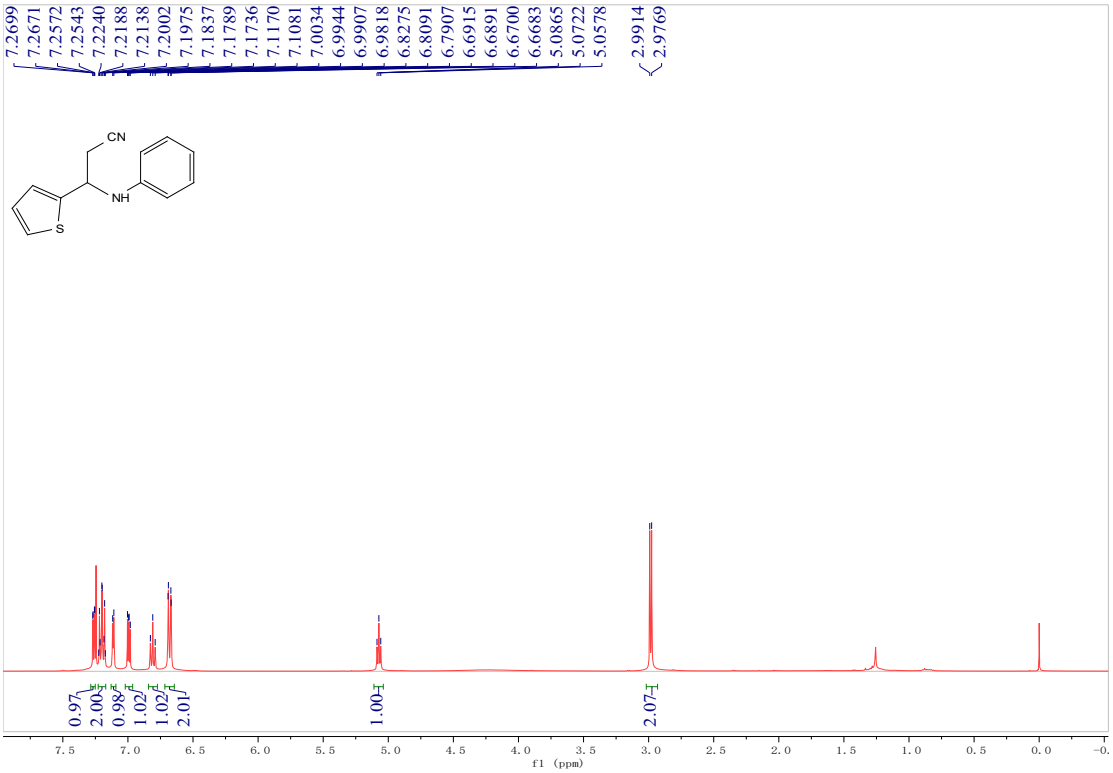
^{1}H-NMR Spectrum ($CDCl_3$) of **23**



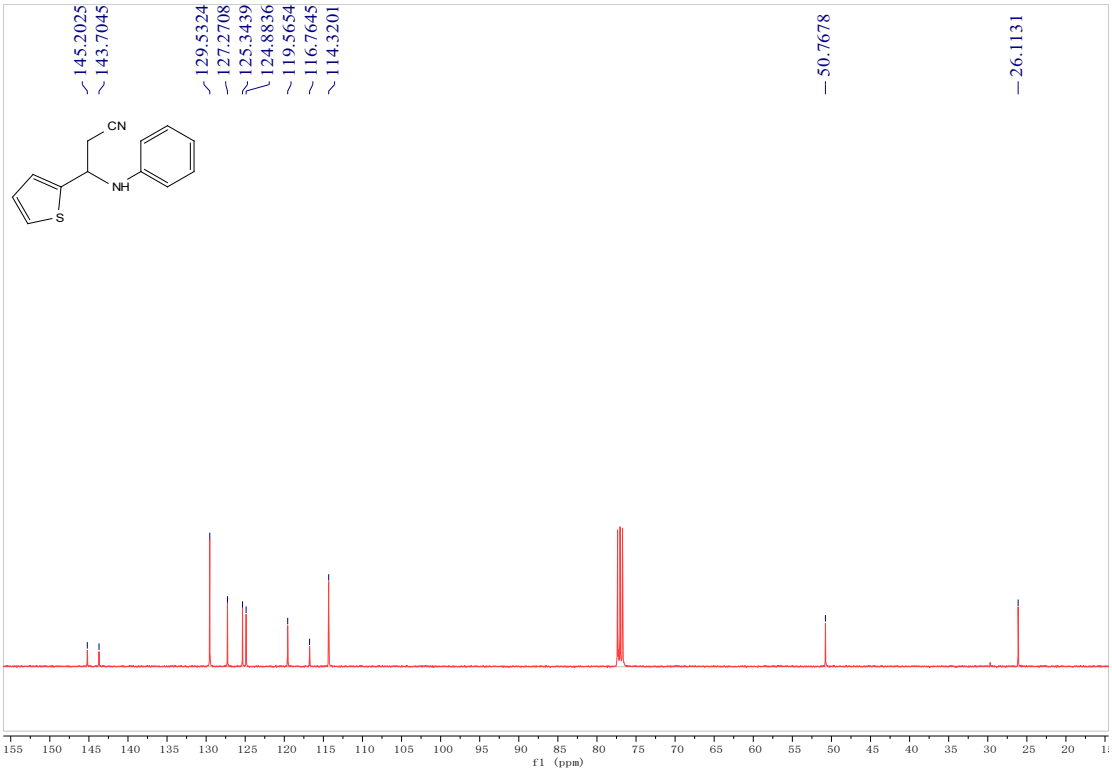
^{13}C-NMR Spectrum ($CDCl_3$) of **23**



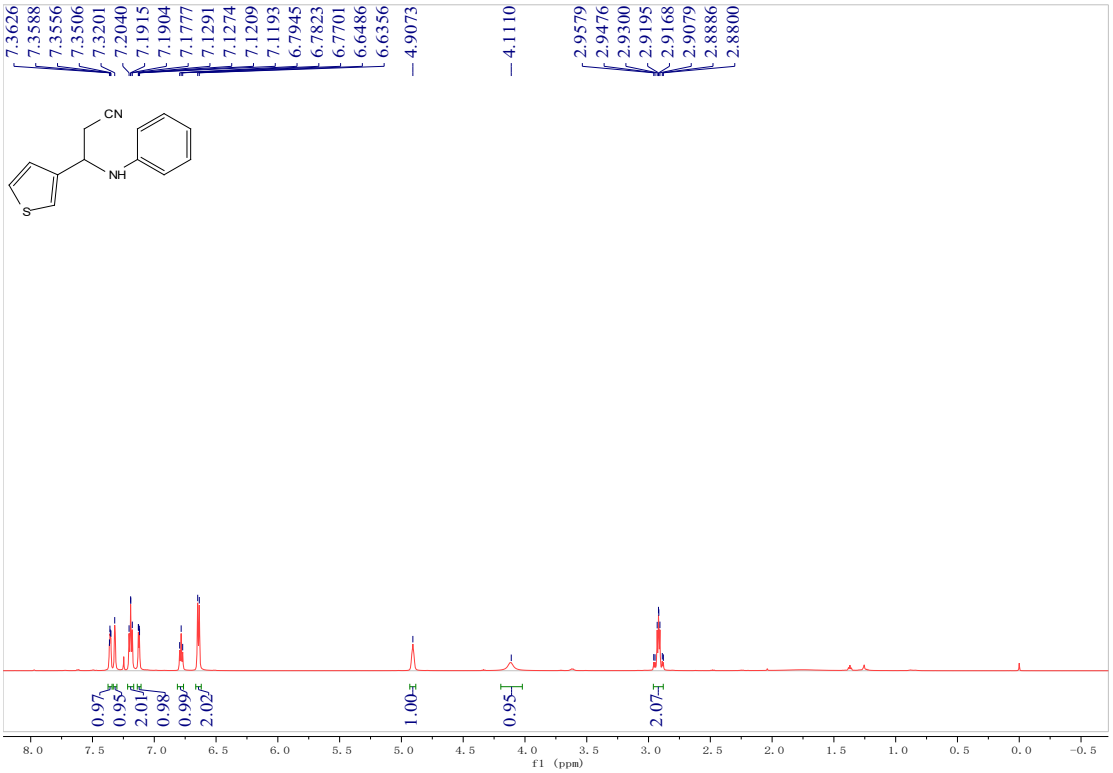
^{1}H-NMR Spectrum ($CDCl_3$) of **24**



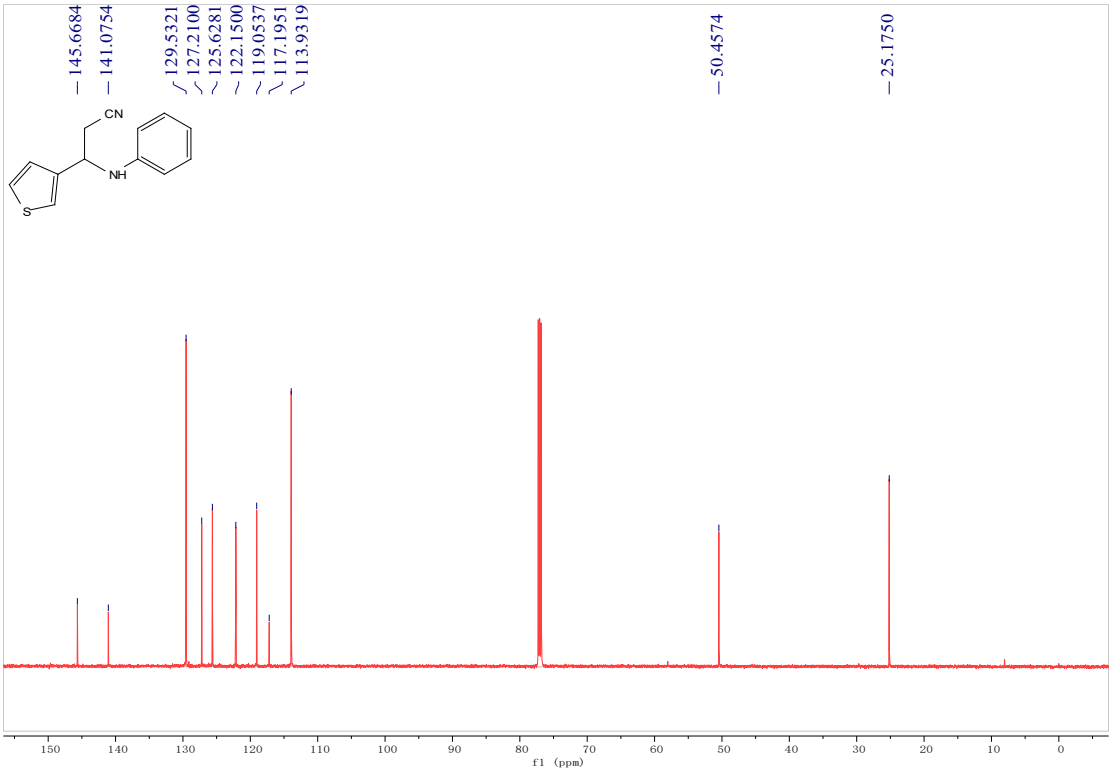
^{13}C-NMR Spectrum ($CDCl_3$) of **24**



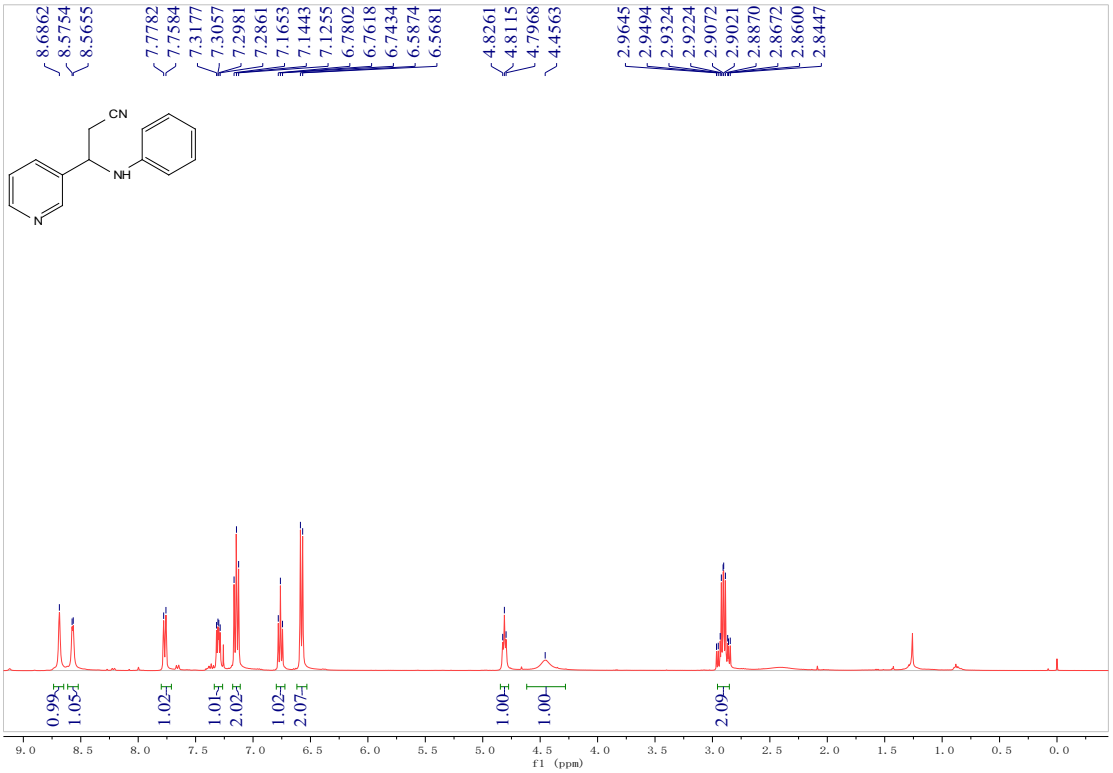
^{1}H-NMR Spectrum ($CDCl_3$) of **25**



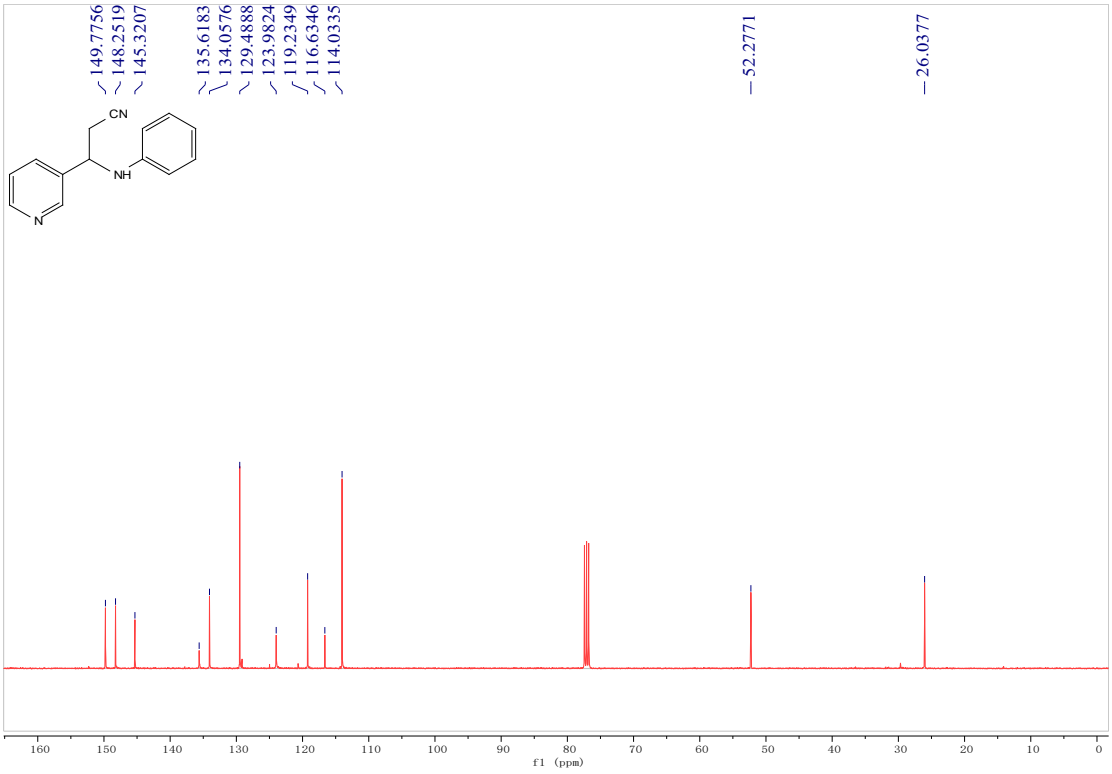
^{13}C-NMR Spectrum ($CDCl_3$) of **25**



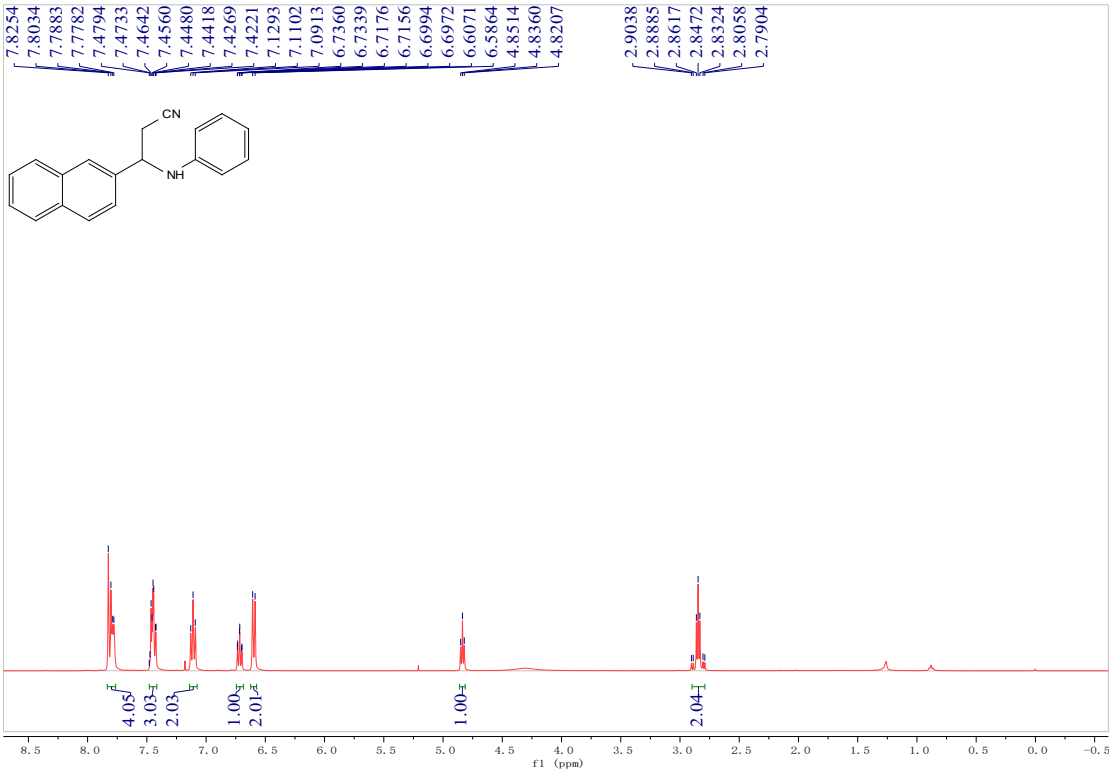
^{1}H-NMR Spectrum ($CDCl_3$) of **26**



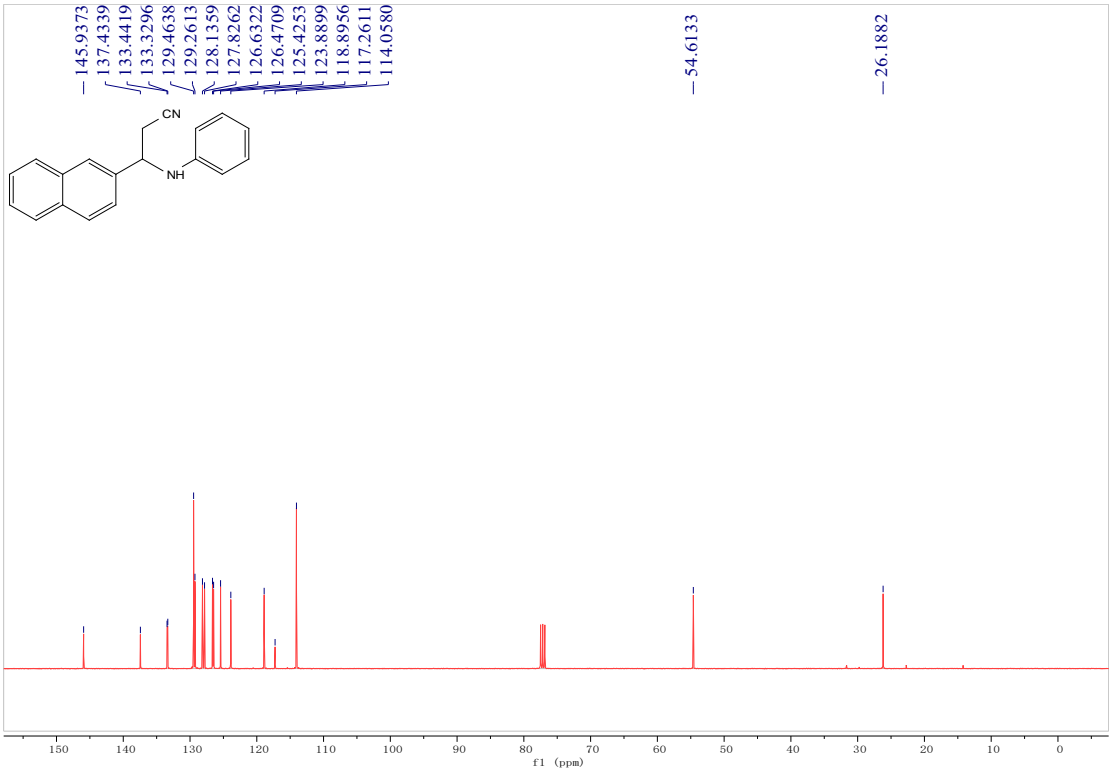
^{13}C-NMR Spectrum ($CDCl_3$) of **26**



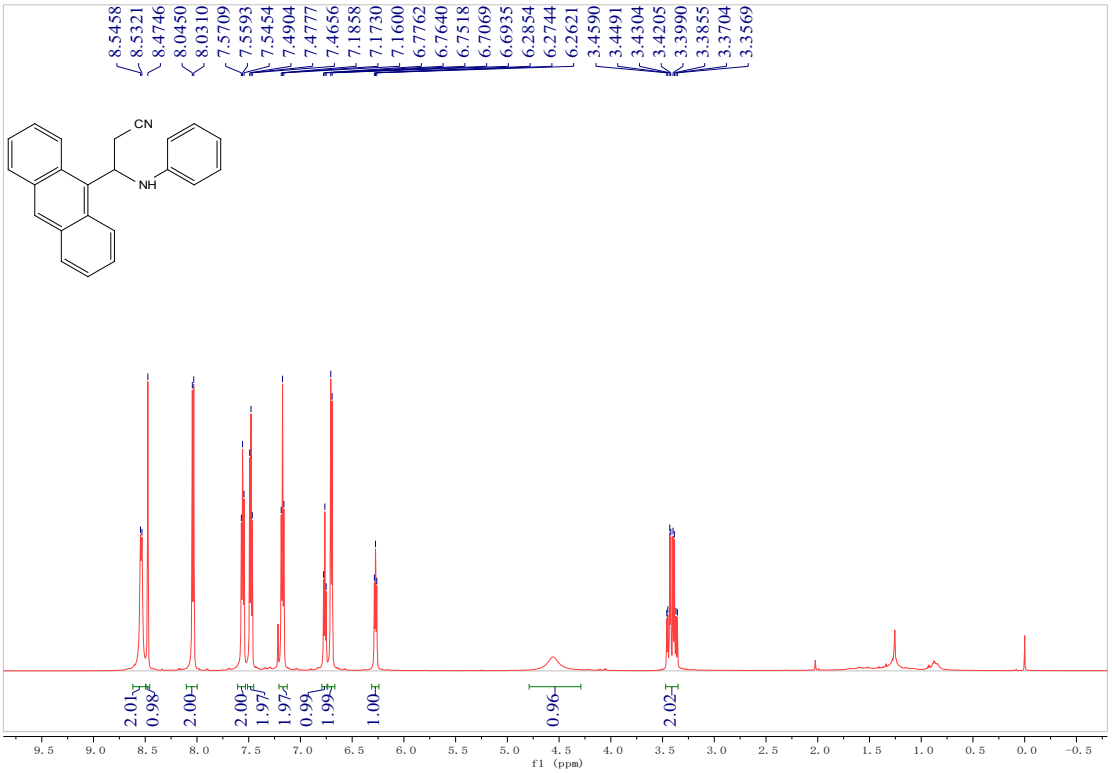
^{1}H-NMR Spectrum ($CDCl_3$) of **27**



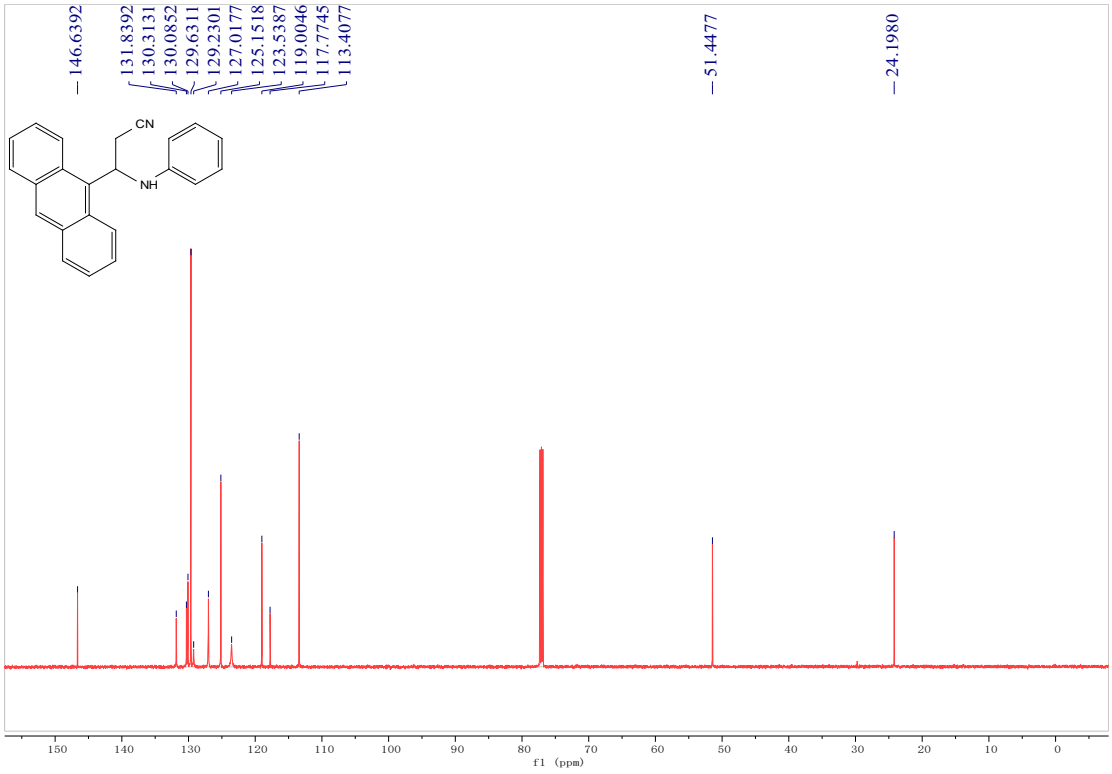
^{13}C-NMR Spectrum ($CDCl_3$) of **27**



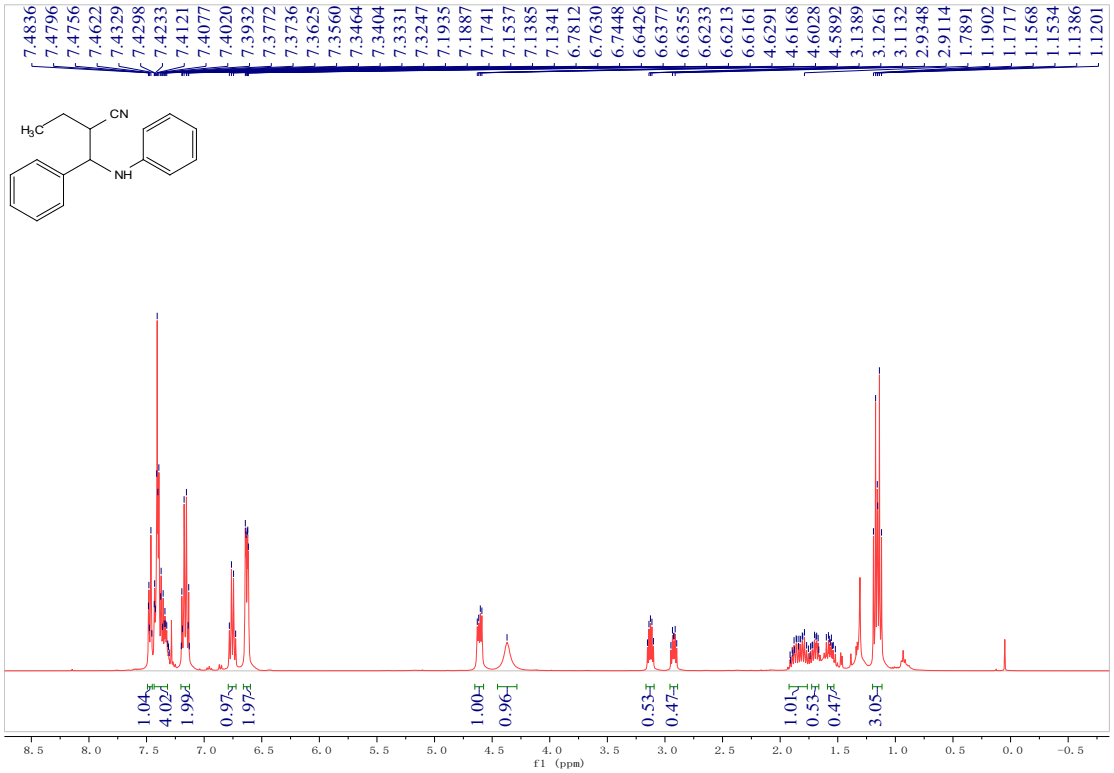
^{1}H-NMR Spectrum ($CDCl_3$) of **28**



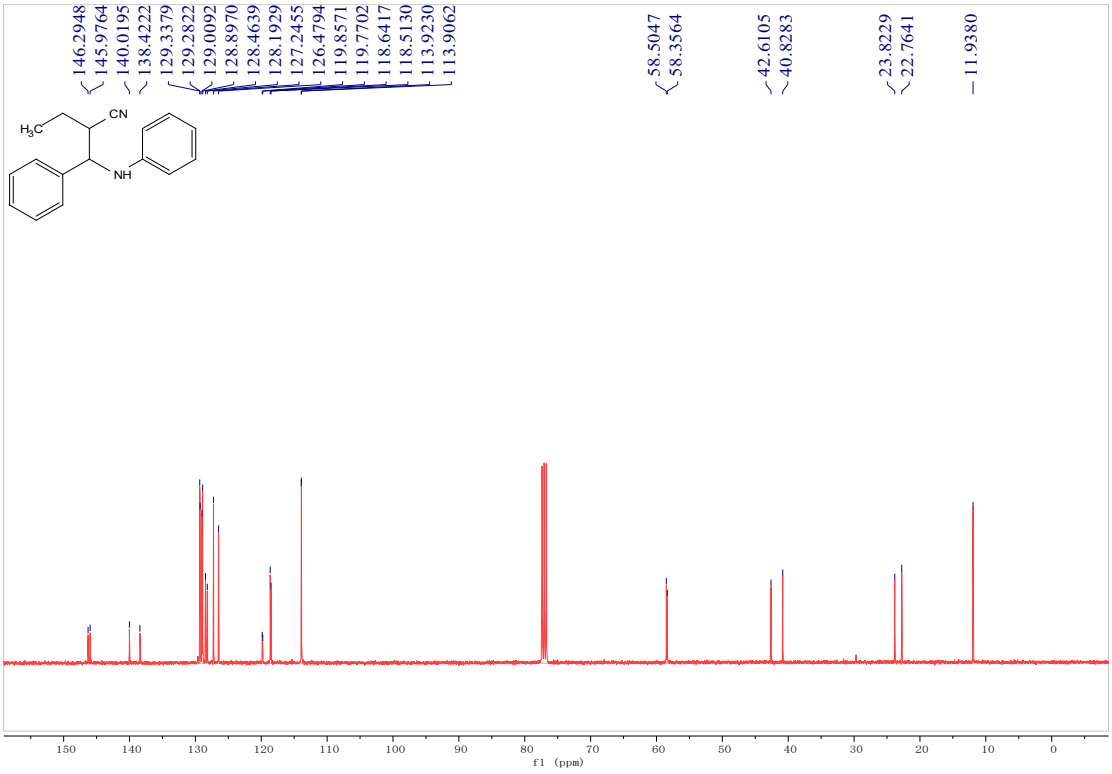
^{13}C-NMR Spectrum ($CDCl_3$) of **28**



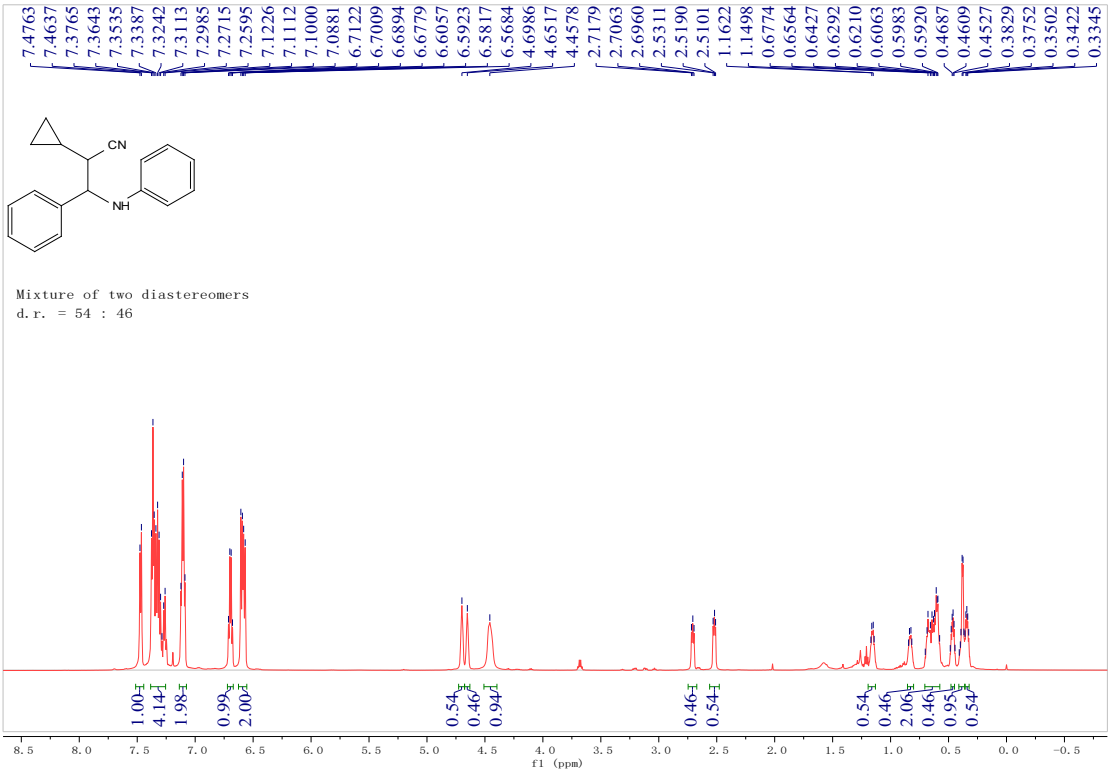
^{1}H-NMR Spectrum ($CDCl_3$) of **29**



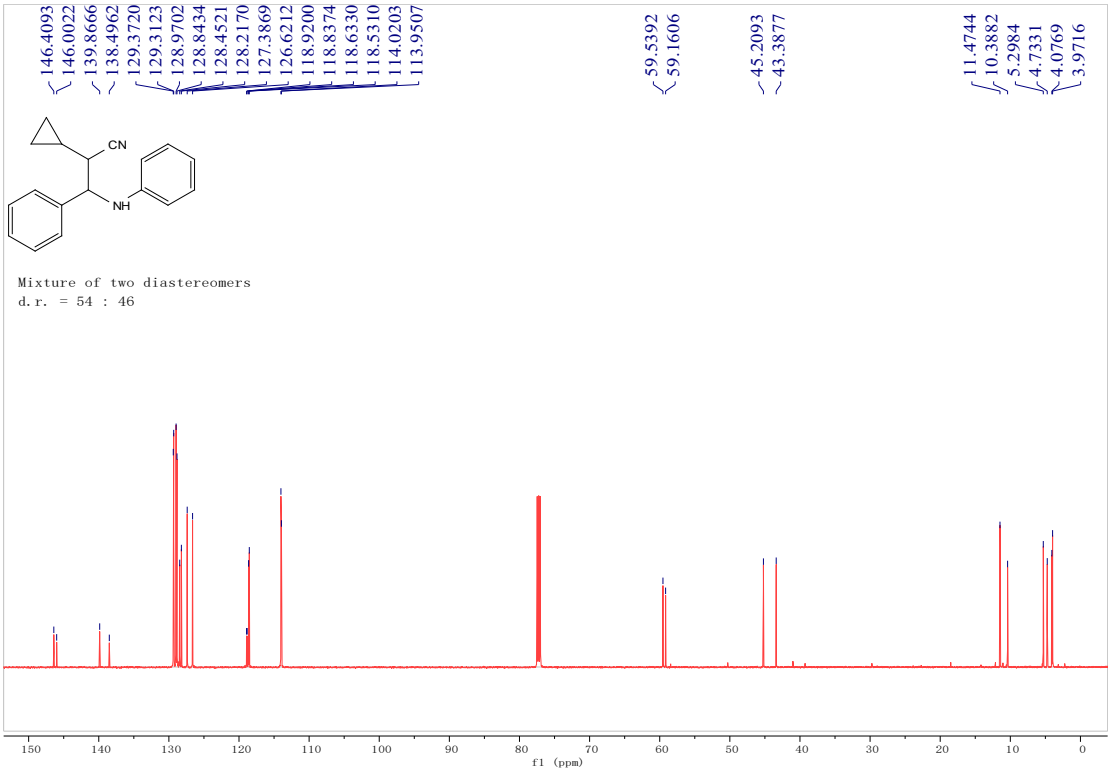
^{13}C-NMR Spectrum ($CDCl_3$) of **29**



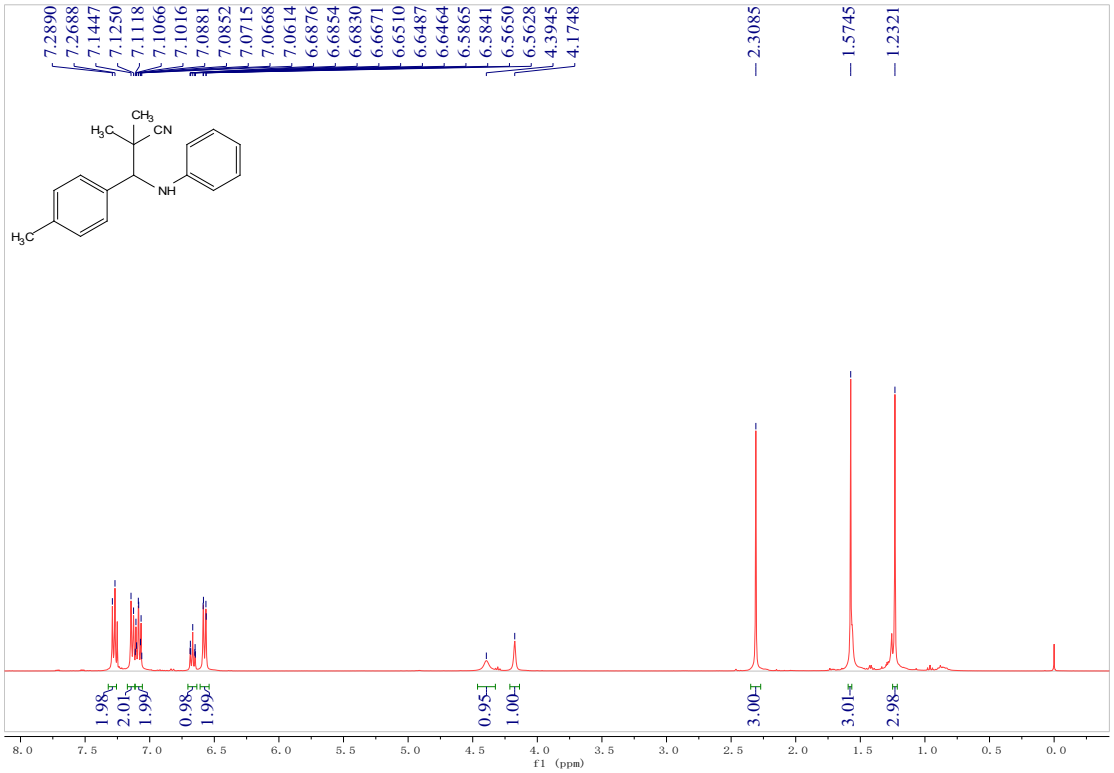
^{1}H-NMR Spectrum ($CDCl_3$) of **30**



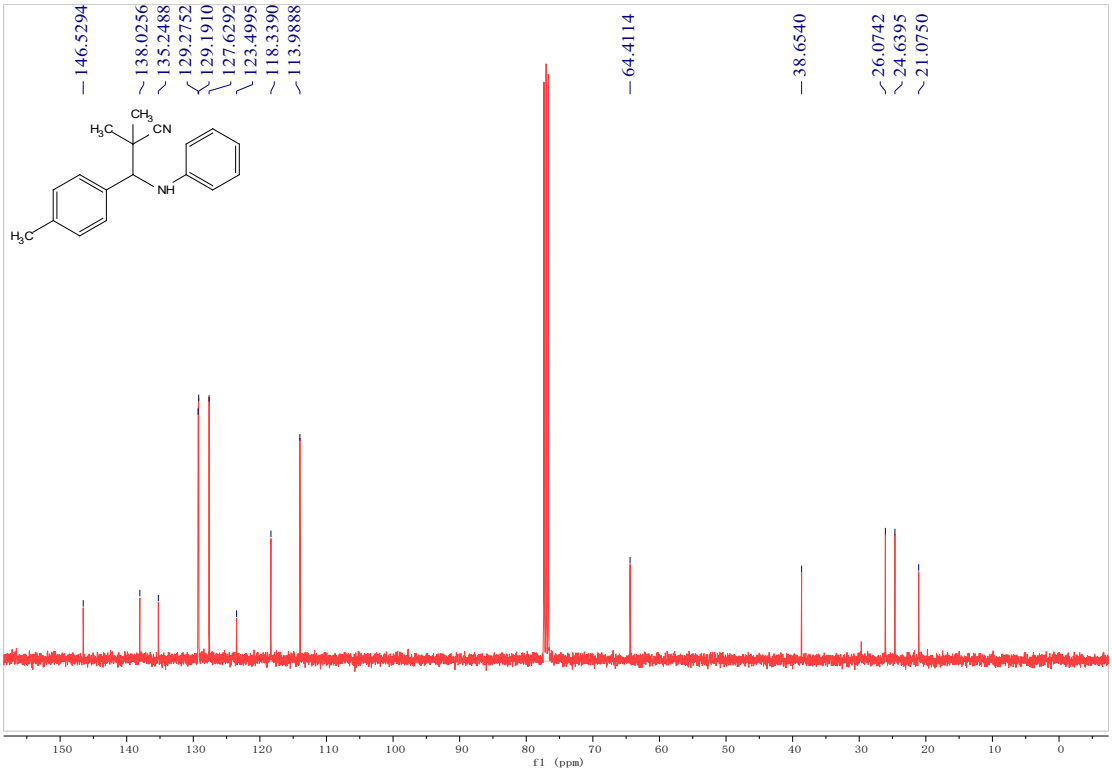
^{13}C-NMR Spectrum ($CDCl_3$) of **30**



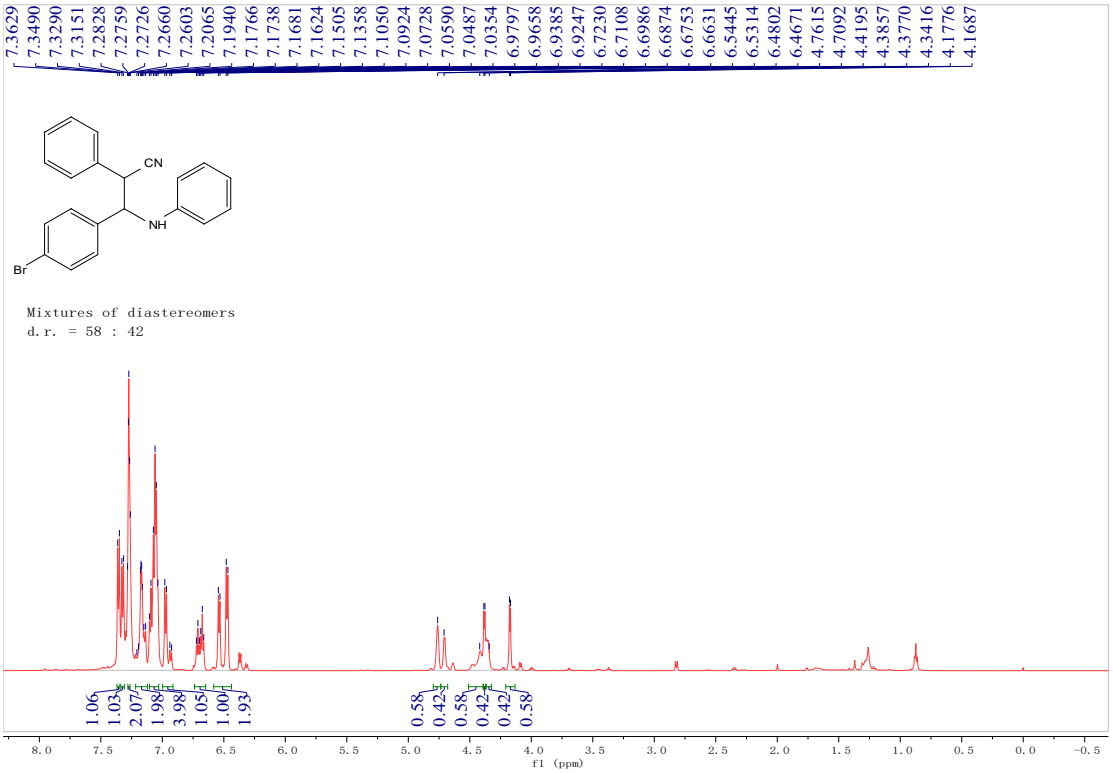
^{1}H-NMR Spectrum ($CDCl_3$) of **31**



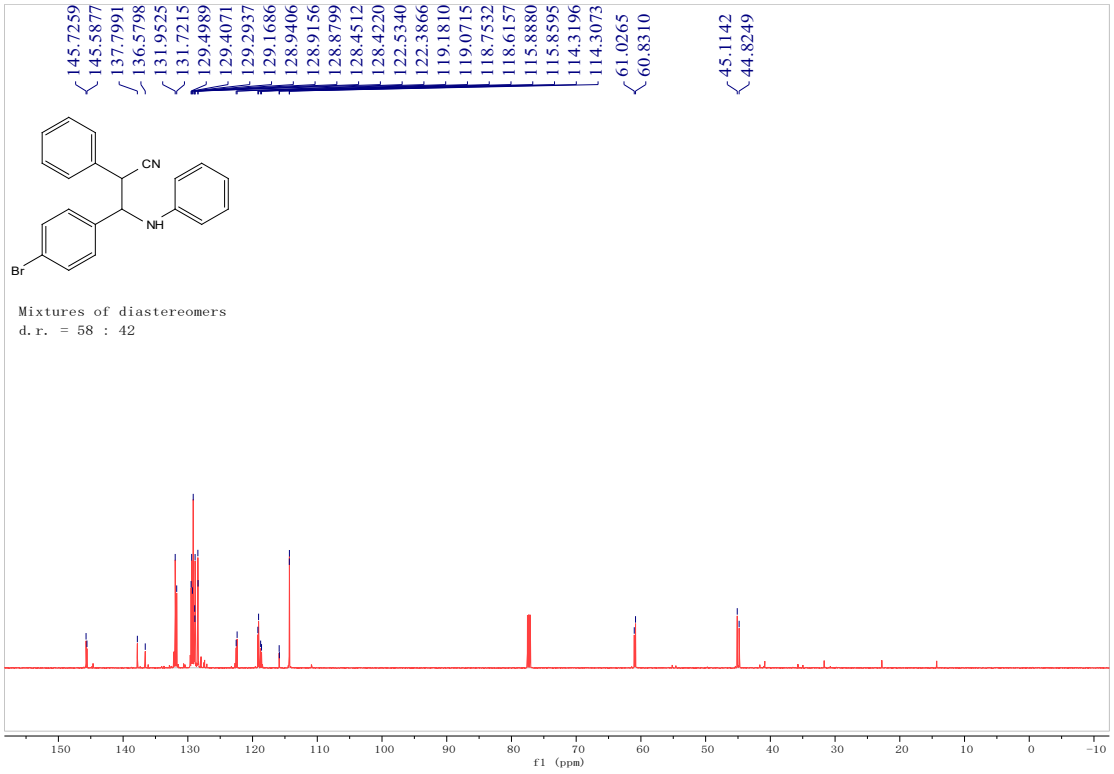
^{13}C-NMR Spectrum ($CDCl_3$) of **31**



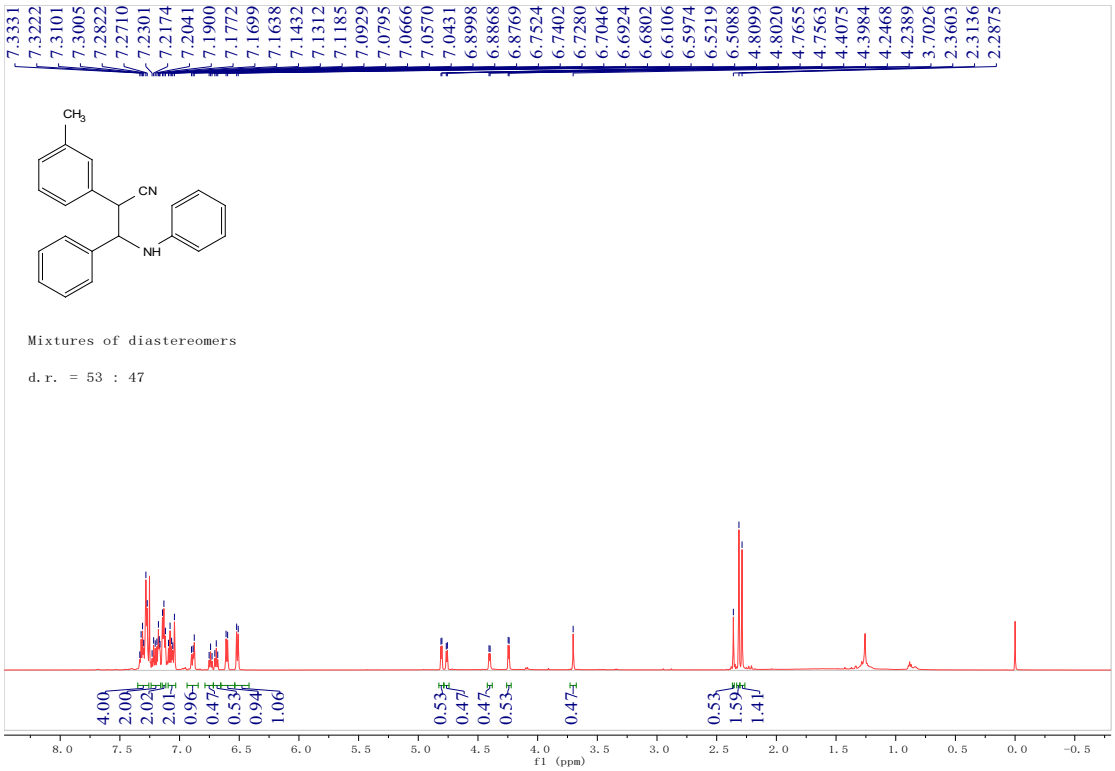
^{1}H-NMR Spectrum ($CDCl_3$) of **32**



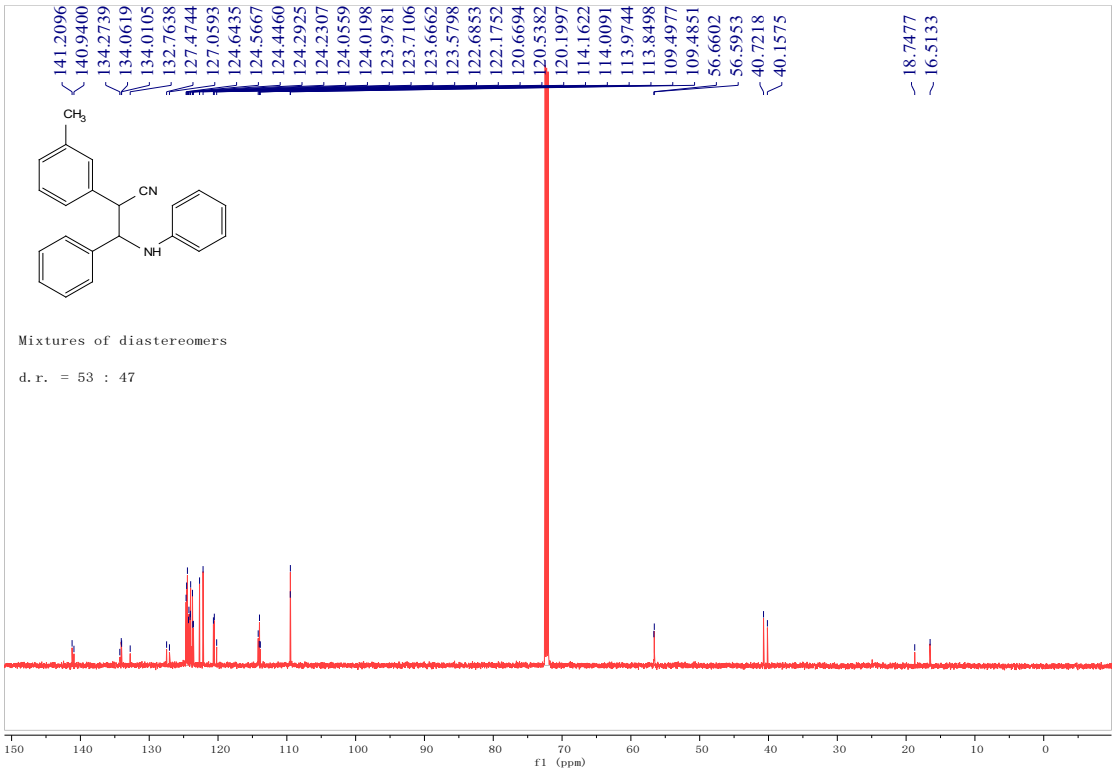
^{13}C-NMR Spectrum ($CDCl_3$) of **32**



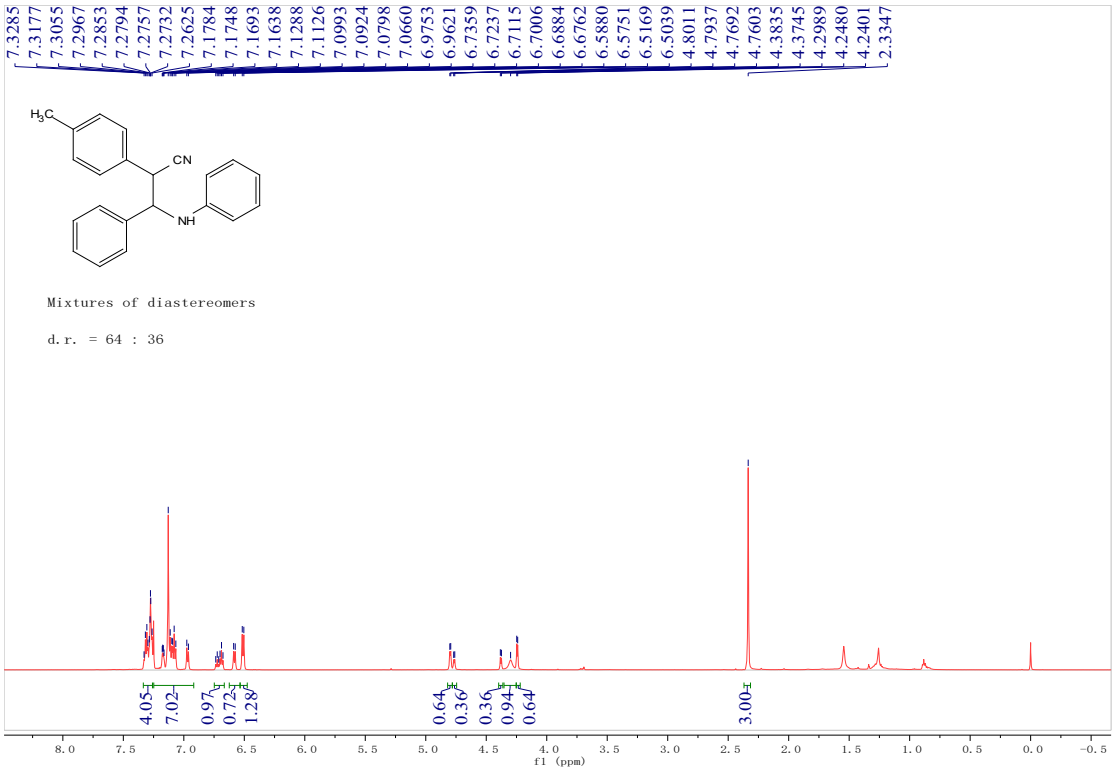
^{1}H-NMR Spectrum ($CDCl_3$) of **33**



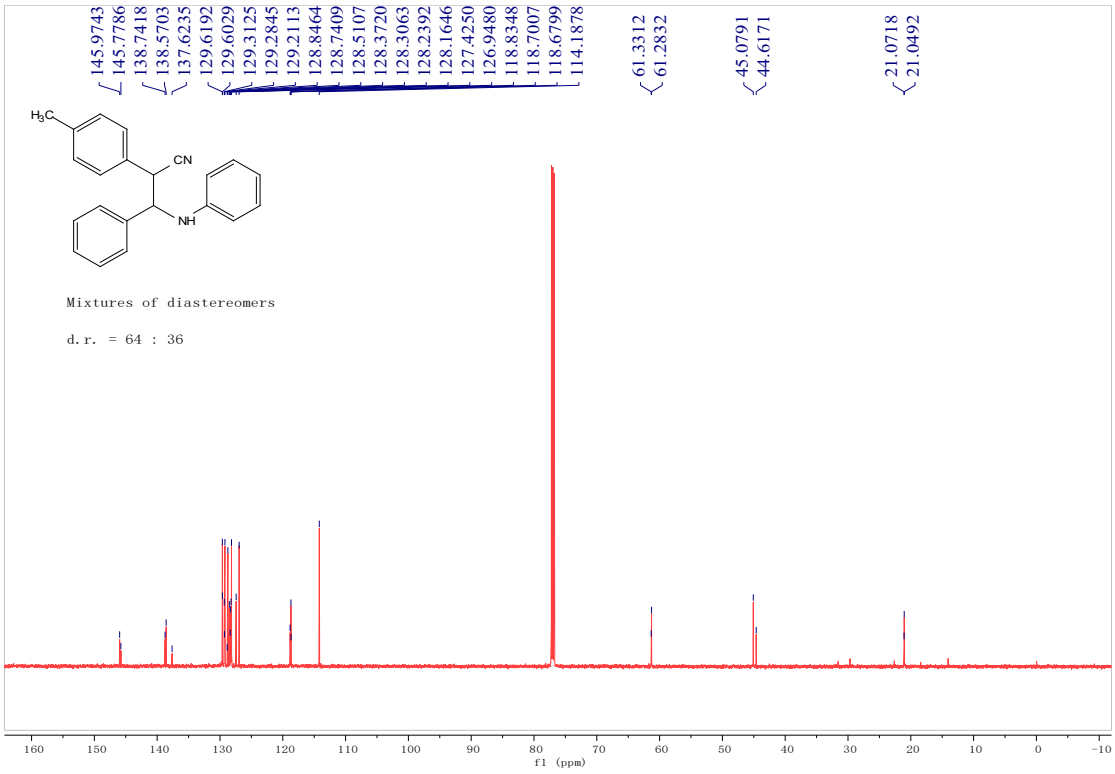
^{13}C-NMR Spectrum ($CDCl_3$) of **33**



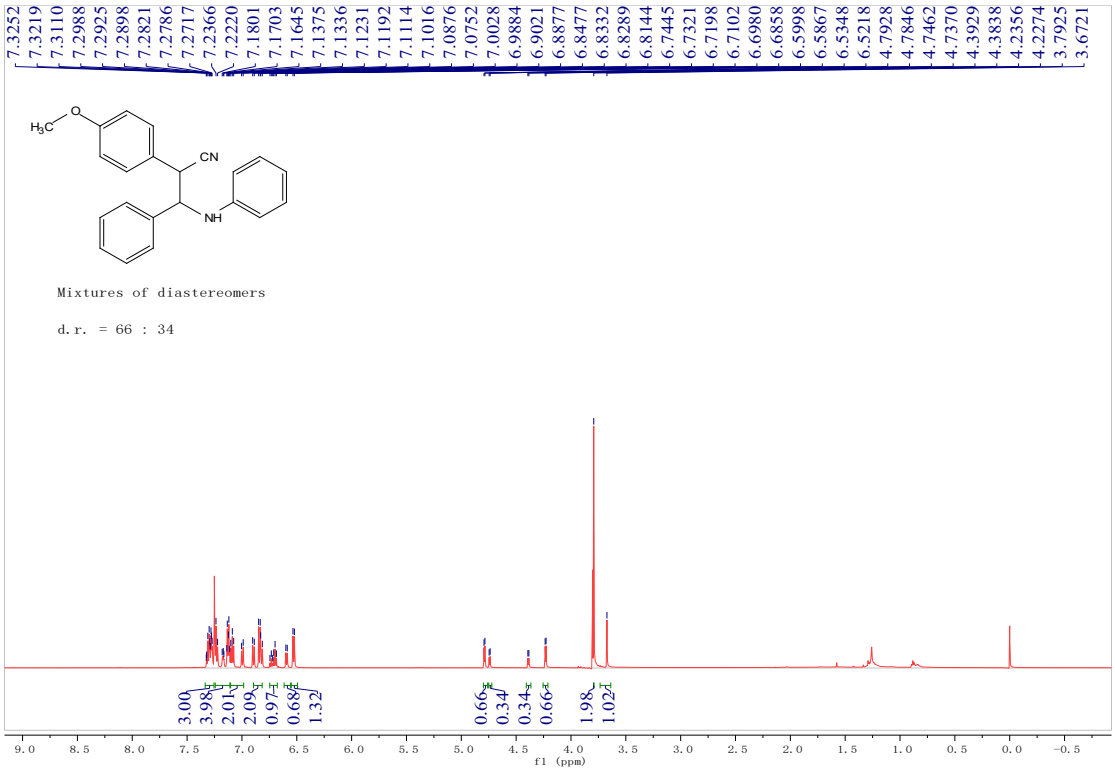
^{1}H-NMR Spectrum ($CDCl_3$) of **34**



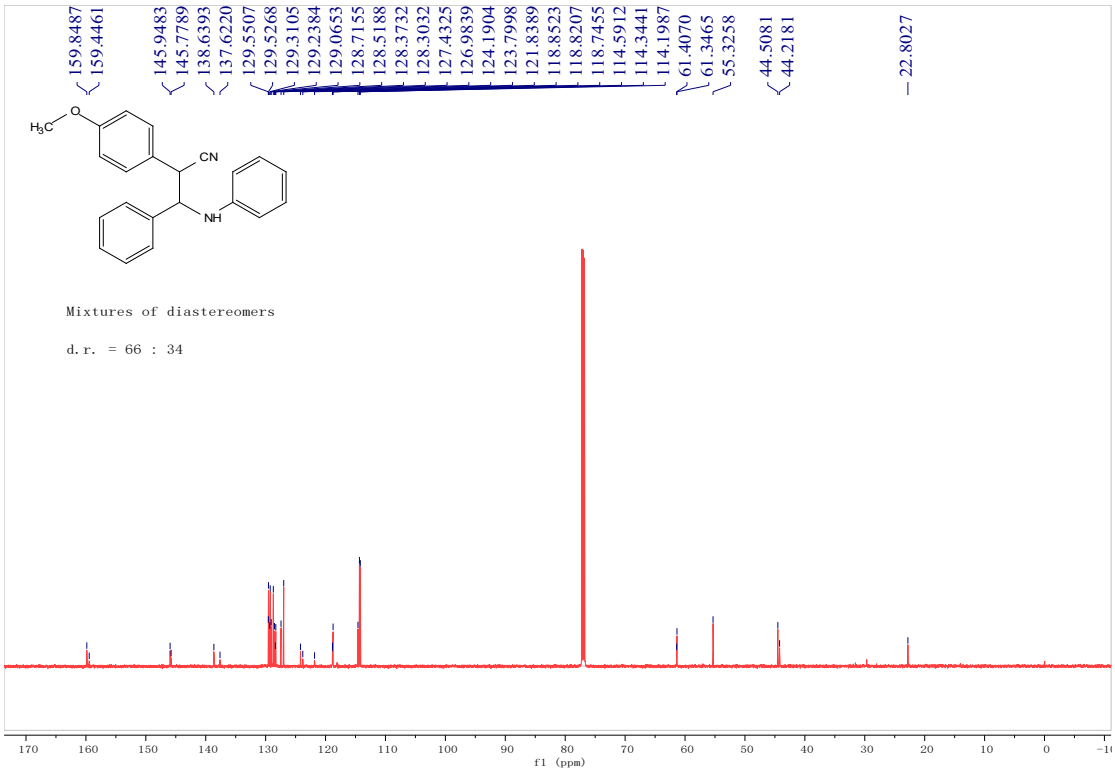
^{13}C-NMR Spectrum ($CDCl_3$) of **34**



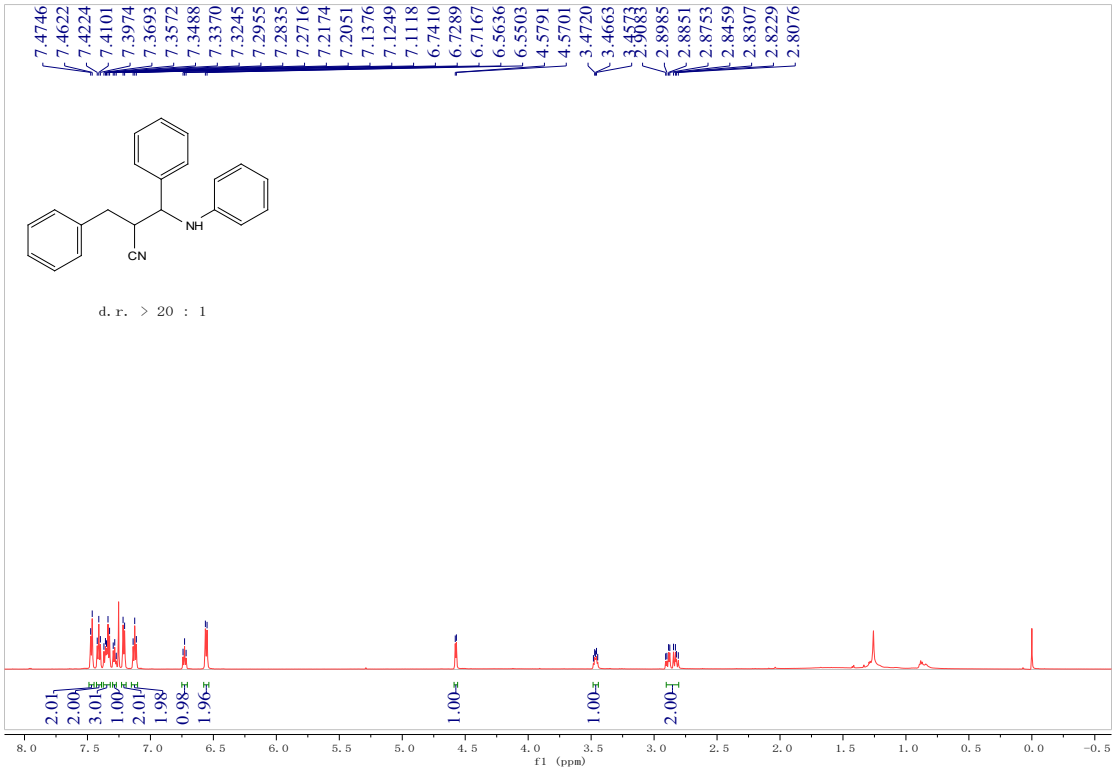
^{1}H-NMR Spectrum ($CDCl_3$) of **35**



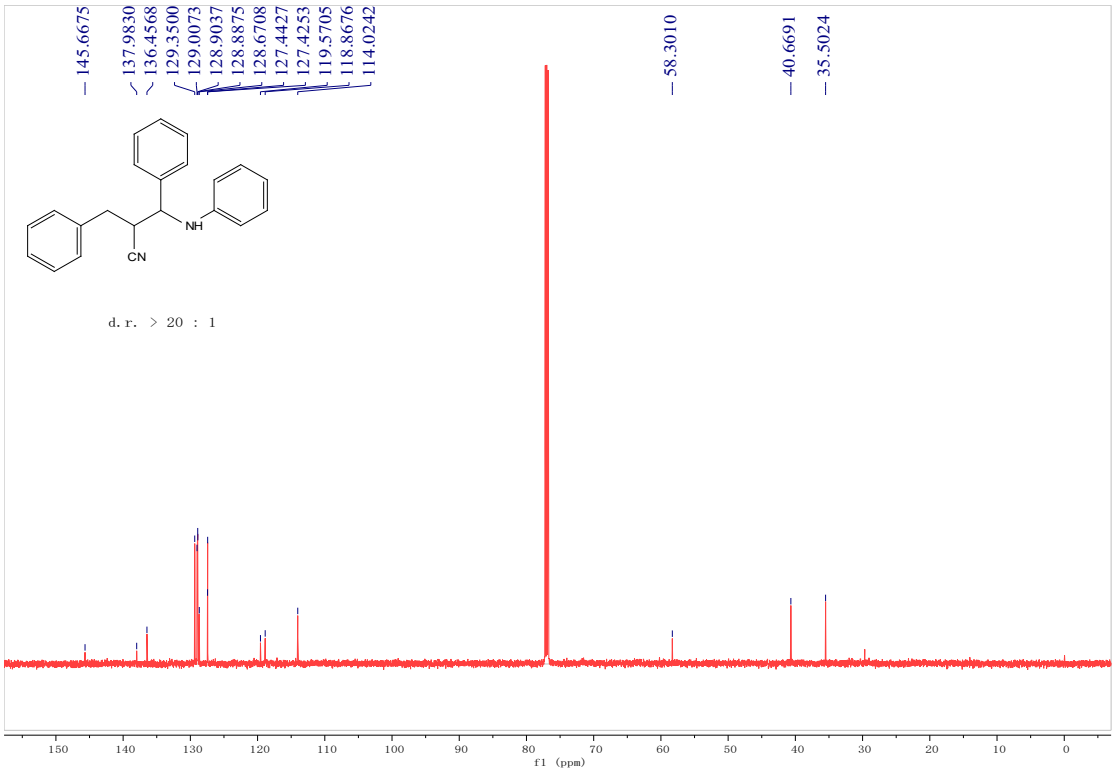
^{13}C-NMR Spectrum ($CDCl_3$) of **35**



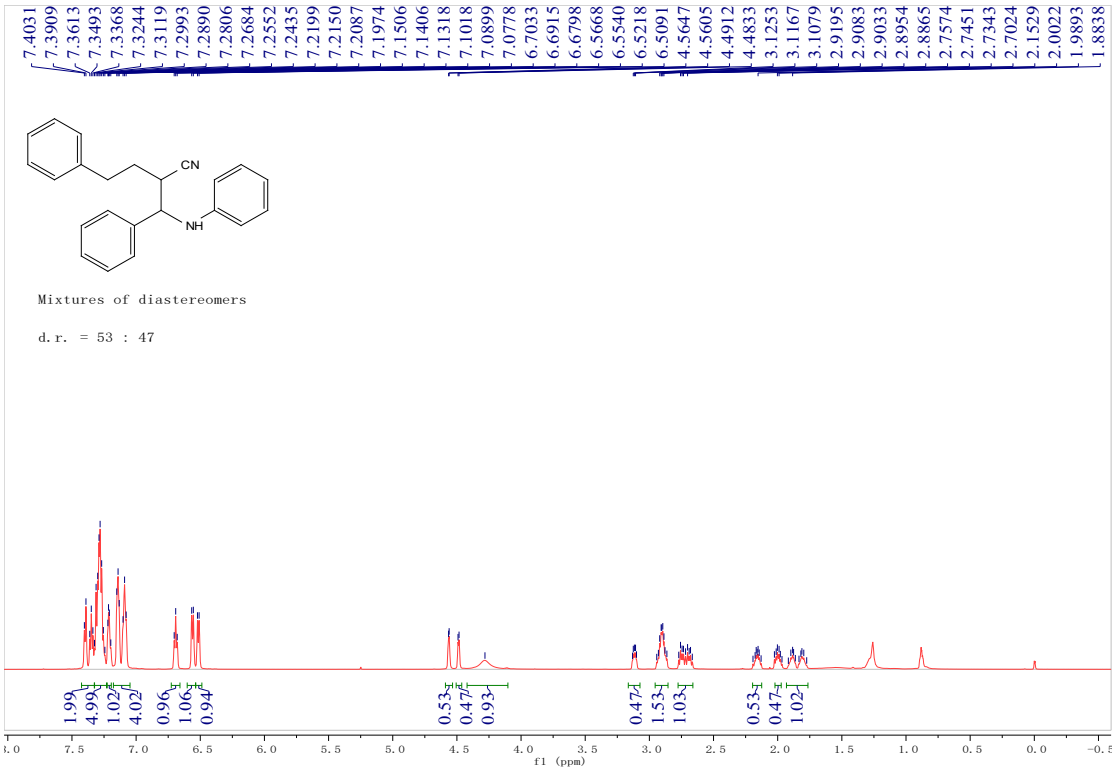
^{1}H-NMR Spectrum ($CDCl_3$) of **36**



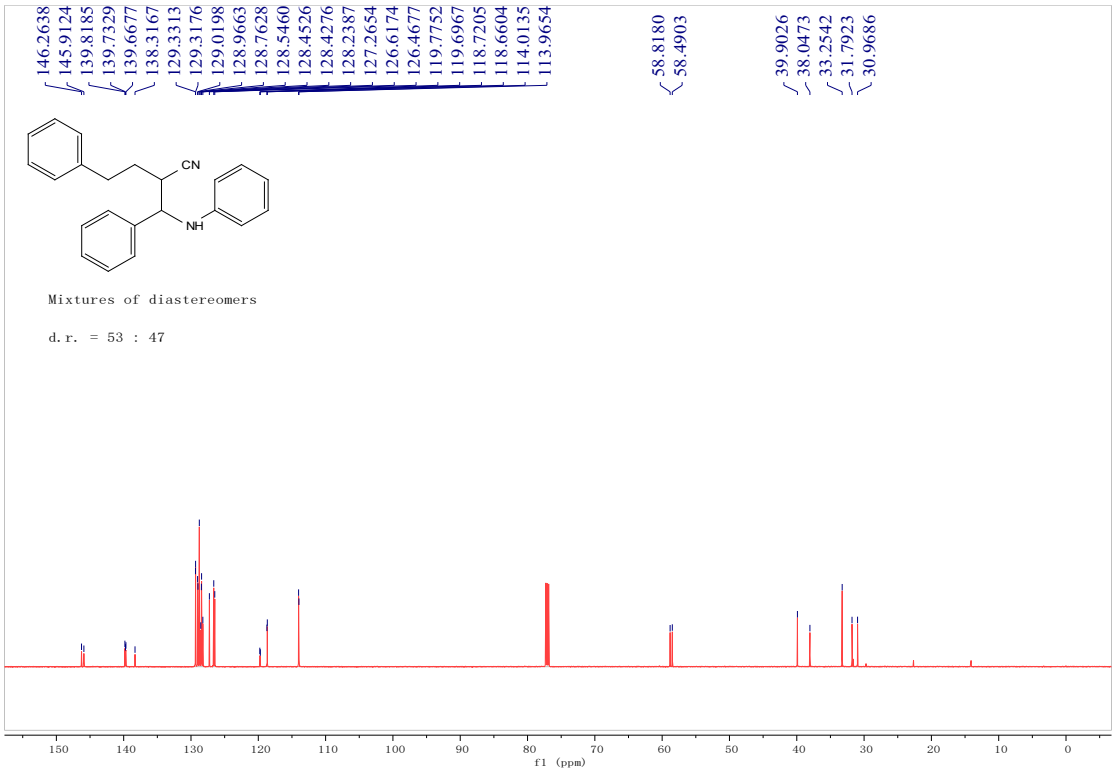
^{13}C-NMR Spectrum ($CDCl_3$) of **36**



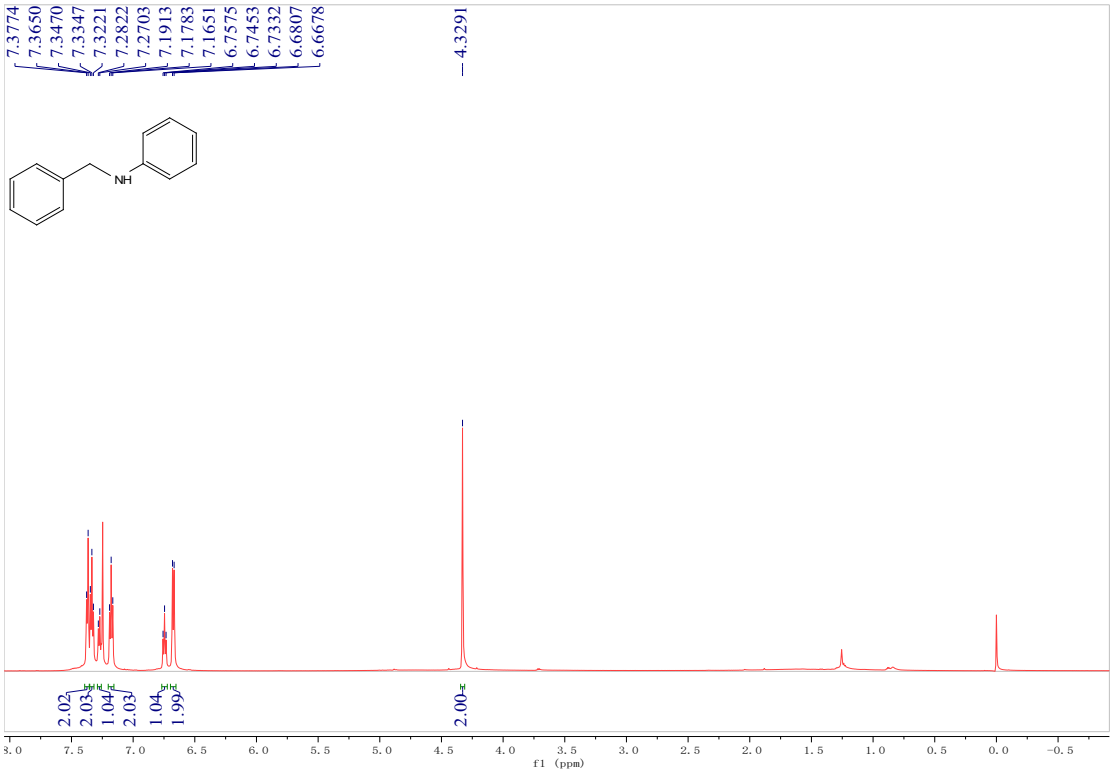
^{1}H-NMR Spectrum ($CDCl_3$) of **37**



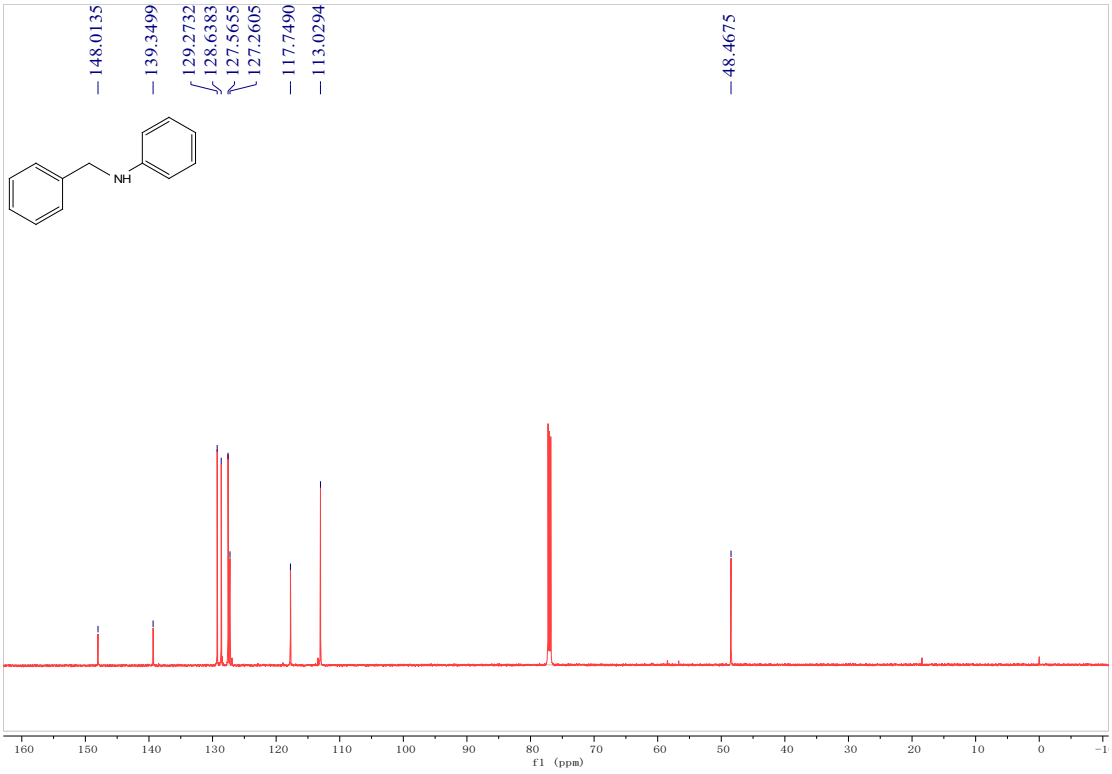
^{13}C-NMR Spectrum ($CDCl_3$) of **37**



^{1}H-NMR Spectrum ($CDCl_3$) of **1b**



^{13}C-NMR Spectrum ($CDCl_3$) of **1b**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NH
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90
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70
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30
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10
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f1 (ppm)