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Supporting Information

Iron-Catalyzed Sequential Reaction toward α-Aminonitriles from Secondary Amines, Primary Alcohols and Trimethylsilyl Cyanide

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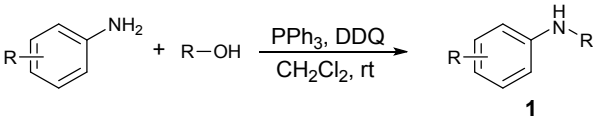
1. General Methods

^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ solution on a Bruker Avance 500 spectrometer at 20~25 °C. ^{1}H NMR spectra were reported in parts per million using tetramethylsilane TMS (δ = 0.00 ppm) as an internal standard. The data of ^{1}H NMR are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet), coupling constants (*J*, Hz), and integration. ^{13}C NMR spectra were reported in parts per million using solvent $CDCl_3$ (δ = 77.2 ppm) or DMSO (δ = 39.5 ppm) as an internal standard, The data of ^{13}C NMR are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet), and coupling constants (*J*, Hz). High resolution mass spectra (HRMS) were obtained with a Q-TOF MS spectrometer. Reactions were monitored by TLC and column chromatography was performed using silica gel. Commercially available reagents were used without further purification unless otherwise specified.

2. Experimental Procedures

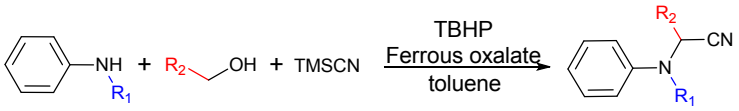
2.1 General procedure for synthesis of 1e, 1f, 1m, 1n and 1o-s



1

Compound **1** were synthesized according to the reported method:[1] To a flask containing a stirred mixture of Ph_3P (0.314 g, 1.2 mmol) and DDQ (0.272 g, 1.2 mmol) in dichloromethane (5 mL) was added aniline (1.2 mmol) at room temperature. Alcohol (1.0 mmol) was then added to the reaction mixture. TLC monitoring showed the completion of the reaction. The solvent was evaporated and the residue was chromatographed on a silica gel colum to give secondary amine.

2.2 General procedure for synthesis of 2

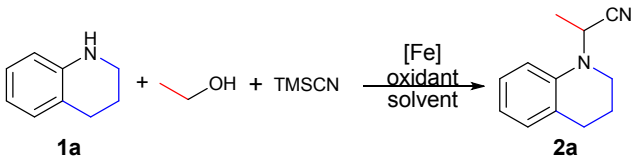


1 **2**

Alcohol (3.75 mmol), TMSCN (0.272 mL, 2 mmol) and ferrous oxalate (0.007 g, 0.05 mmol) were successively added to the stirred solution of secondary amine **1** (0.5 mmol) in a seal tube at room temperature. After addition of TBHP (0.3 mL, 2 mmol, ≥65% in *tert*-butanol), the mixture was stirred at room temperature for 4 h or rosed to 90 °C for overnight. Subsequently, the mixture was poured into aqueous $NaHCO_3$ and $Na_2S_2O_3$ solution, and extracted with ethyl acetate. The organic layer was washed with brine, dried over magnesium sulfate and concentrated in vacuo. The residue was chromatographed on a silica gel colum to give α-aminonitrile **2**.

3. Optimization of reaction conditions and control experiment

Table 1S. Evaluation of oxidants, catalysts and solvents[a]



1a **2a**

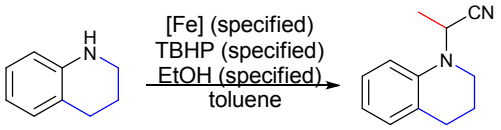
Entry	Catalyst	Oxidant	Solvent	Time (h)	Yield (%)[b]
3	CuI	TBHP	DCE	10	0
5	$Cu(OAc)_2$	TBHP	DCE	10	0
1	$FeCl_2·6H_2O$	TBHP	DCE	10	17
2	$FeCl_3$	TBHP	DCE	10	trace
6	$FeCl_2$	TBHP	DCE	10	27
7	$Fe(COO)_2•2H_2O$	TBHP	DCE	10	46
8	$Fe(COO)_2$	TBHP	DCE	10	49
9	$FeSO_4•5H_2O$	TBHP	DCE	10	41
10	$Fe(OAc)_2$	TBHP	DCE	10	0
11	$Fe(acac)_2$	TBHP	DCE	10	0
12	FeS	TBHP	DCE	10	0
13	$NiCl_2•6H_2O$	TBHP	DCE	10	0
14	$CoCl_2•6H_2O$	TBHP	DCE	10	0
15	$Fe(COO)_2$	TBHP	DCE	5	52
16	$Fe(COO)_2$	TBHP	DCE	4	60
17	$Fe(COO)_2$	TBHP	DCE	3	47
18	$Fe(COO)_2$	DIB	DCE	4	0
19	$Fe(COO)_2$	Oxone	DCE	4	0
20	$Fe(COO)_2$	mCPBA	DCE	4	0
21	$Fe(COO)_2$	DDQ	DCE	4	0
22	$Fe(COO)_2$	NIS	DCE	4	0
23	$Fe(COO)_2$	F-TEDA	DCE	4	0
24	$Fe(COO)_2$	H_2O_2	DCE	4	38
25	$Fe(COO)_2$	TBHP	DCM	4	59
26	$Fe(COO)_2$	TBHP	$CHCl_3$	4	56
27	**$Fe(COO)_2$**	**TBHP**	**Toluene**	**4**	**63**
28	$Fe(COO)_2$	TBHP	THF	4	0
29	$Fe(COO)_2$	TBHP	CH_3CN	4	0
30	$Fe(COO)_2$	TBHP	Et_2O	4	0
31	$Fe(COO)_2$	TBHP	DMF	4	0
32	$Fe(COO)_2$	TBHP	1,4-dioxane	4	0
33	$Fe(COO)_2$	TBHP	ethyl acetate	4	0
34	$Fe(COO)_2$	TBHP	DMSO	4	0
35	$Fe(COO)_2$	TBHP	acetone	4	0
36	$Fe(COO)_2$	TBHP	CH_3NO_2	4	0
37	$Fe(COO)_2$	TBHP	hexane	4	30

[a] Reaction conditions: 1,2,3,4-tetrahydroquinoline (0.5 mmol), EtOH (2.5 mmol), oxidant (1.5 mmol), catalyst (0.15 mmol), solvent (4 mL), rt. [b] Yield determined by ^1H NMR using mesitylene as internal

standard.

Different catalysts, oxidants, solvents and reaction time were screened, the highest yield was obtained when using $Fe(COO)_2$ as catalyst, TBHP as oxidant and toluene as solvent. The best reaction time was 4 h.

Table 2S. Optimization of Reaction Conditions[a]



1a **2a**

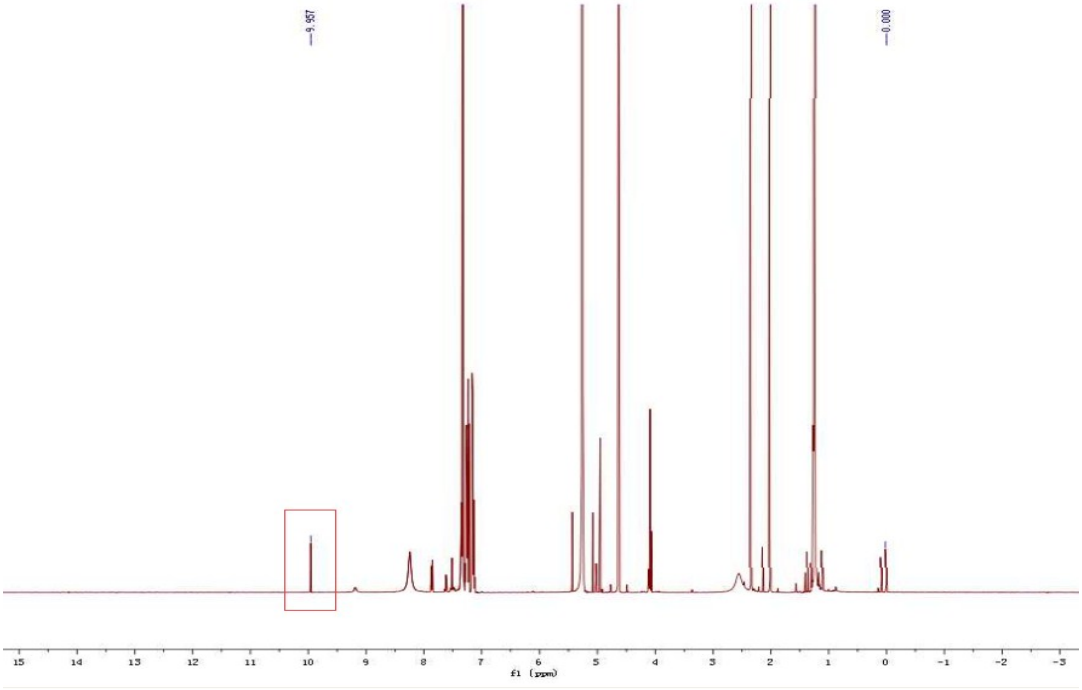
Entry	TBHP (eq)	EtOH (eq)	TMSCN (eq)	[Fe] (eq)	Yield (%)[b]
1	2	5	3	0.3	47
2	4	5	3	0.3	64
3	5	5	3	0.3	62
4	6	5	3	0.3	56
5	3.5	5	3	0.3	56
6	4.5	5	3	0.3	58
7	4	3	3	0.3	55
8	4	6	3	0.3	68
9	4	7	3	0.3	71
10	4	7.5	3	0.3	73
11	4	8	3	0.3	73
12	4	8.5	3	0.3	68
13	4	9	3	0.3	67
14	4	11	3	0.3	70
15	4	7.5	2	0.3	71
16	4	7.5	4	0.3	76
17	4	7.5	5	0.3	70
18	4	7.5	6	0.3	66
19	4	7.5	3.5	0.3	73
20	4	7.5	4.5	0.3	72
21	4	7.5	4	0.2	74
22	4	7.5	4	0.4	72
23	**4**	7.5	**4**	**0.1**	**76**
24	4	7.5	4	0.05	70
25	4	7.5	4	0.02	53
26	4	7.5	4	0.1	0[c]
27	4	7.5	4	0.1	0[d]
28	4	7.5	4	0.1	Complex[e]

[a] Reaction conditions: 1,2,3,4-tetrahydroquinoline (0.5 mmol), oxidant (specified), EtOH (specified), TMSCN (specified), catalyst (specified), solvent (4 mL), 4 h, rt. [b] Yield determined by ^{1}H NMR using mesitylene as internal standard. [c] 0.2 eq K_2CO_3 was added. [d] 0.2 wt% 4 Å M. S. was added. [e] 0.2 eq DBU was added. M. S. = molecular sieve.

Different amounts of TBHP, EtOH, TMSCN and iron salt were evaluated (Table 2S) and the highest yield was obtained when using 4 equivalents of TBHP, 7.5 equivalents of EtOH, 4

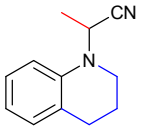
equivalents of TMSCN and 0.1 equivalent of iron salt.

Figure 1S. ^{1}H NMR spectroscopic analysis of the intermediate aldehyde.

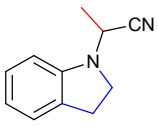


TBHP (0.3 mL, 2 mmol, ≥65% in *tert*-butanol) was added to the stirred mixture of benzyl alcohol (0.52 mL, 0.5 mmol) and ferrous oxalate (0.007 g, 0.05 mmol) in 4 mL toluene and rosed to 90 °C for 5 h. Subsequently, the mixture was poured into aqueous $NaHCO_3$ and $Na_2S_2O_3$ solution, and extracted with ethyl acetate. The organic layer was washed with brine, dried over magnesium sulfate and concentrated in vacuo. The residue was analyzed by ^{1}H NMR and the chemical shift of aldehyde group of benzaldehyde was the same as reported data.

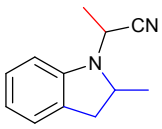
4. ^{1}H- and ^{13}C-NMR analytical data



2-(3,4-dihydroquinolin-1(2H)-yl)propanenitrile (2a): Yellow oil; 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (td, *J* = 8.0, 1.5 Hz, 1H), 7.03 (d, *J* = 7.0 Hz, 1H), 6.75 (td, *J* = 7.5, 0.5 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 4.83 (q, *J* = 7.0 Hz, 1H), 3.35-3.31 (m, 1H), 3.26-3.21 (m, 1H), 2.82-2.71 (m, 2H), 2.03-1.98 (m, 2H), 1.62 (d, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 129.8, 127.4, 125.6, 119.1, 119.0, 112.1, 45.7, 43.9, 27.9, 22.3, 17.3. HRMS (ESI) calcd for $C_{12}H_{14}N_2$ $[M+H]^+$ 187.1230, found 187.1221.

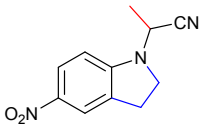


2-(indolin-1-yl)propanenitrile (2b): White solid; 69% yield; mp 78-79 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15-7.12 (m, 2H), 6.82 (td, *J* = 8.0, 0.5 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 4.56 (q, *J* = 7.5 Hz, 1H), 3.57 (td, *J* = 8.5, 3.5 Hz, 1H), 3.23 (dt, *J* = 11, 8.5 Hz, 1H), 3.05-2.99 (m, 2H), 1.63 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3, 130.7, 127.6, 125.1, 120.6, 118.1, 108.6, 49.1, 45.0, 28.3, 17.8. HRMS (ESI) calcd for $C_{11}H_{12}N_2$ $[M+H]^+$ 173.1073, found 173.1081.

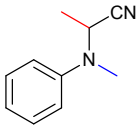


2-(2-methylindolin-1-yl)propanenitrile (2c): Yellow oil; mixture of two diastereoisomers (dr = 2:1); 94% yield. Major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13-7.08 (m, 2H), 6.78 (t, *J* = 7.5 Hz, 1H), 6.62 (d, *J* = 7.5 Hz, 1H), 4.37 (q, *J* = 7.5 Hz, 1H), 3.87-3.81 (m, 1H), 3.16 (dd, *J* = 15.5, 8.5 Hz, 1H),. 2.64 (dd, *J* = 15.5, 7.5 Hz, 1H). Two isomers: ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.1, 148.3, 129.7,

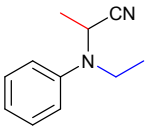
129.4, 127.62, 127.56, 125.01, 124.97, 120.3, 119.8, 119.2, 119.0, 109.7, 108.4, 58.9, 58.8, 45.4, 42.7, 37.8, 37.3, 22.2, 19.2, 18.1, 18.0. HRMS (ESI) calcd for $C_{12}H_{14}N_2$ $[M+H]^+$ 187.1230 , found 187.1236.



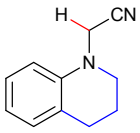
2-(5-nitroindolin-1-yl)propanenitrile (2d): Yellow solid; 76% yield; mp 109-112 °C.. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.37 (d, *J* = 2.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 4.63 (q, *J* = 7.0 Hz, 1H), 7.34-3.70 (m, 1H), 3.42 (dt, *J* = 11.0, 9.0 Hz, 1H), 3.19-3.06 (m, 2H), 1.68 (d, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.4, 148.6, 138.3, 125.0, 117.4, 116.5, 102.9, 49.3, 44.6, 28.3, 17.6. HRMS (ESI) calcd for $C_{11}H_{11}N_3O_2$ $[M+H]^+$ 218.0924, found 218.0930.



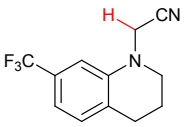
2-(methyl(phenyl)amino)propanenitrile (2e):[2] Yellow oil; 60% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 8.0 Hz, 2H), 6.96-6.93 (m, 3H), 4.62 (q, *J* = 7.5 Hz, 1H), 2.90 (s, 3H), 1.59 (d, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.1, 129.5, 121.3, 118.6, 117.2, 49.2, 34.5, 18.1. HRMS (ESI) calcd for $C_{10}H_{12}N_2$ $[M+H]^+$ 161.1073, found 161.1068.



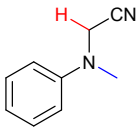
2-(ethyl(phenyl)amino)propanenitrile (2f):[3] Yellow oil; 42% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (td, *J* = 7.0, 2.0 Hz, 2H), 7.00-6.97 (m, 3H), 4.47 (q, *J* = 7.0 Hz, 1H), 3.38-3.32 (m, 2H), 1.56 (d, *J* = 7.0 Hz, 3H), 1.18 (t, *J* = 7.0 Hz, 3H),. ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.0, 129.5, 121.9, 119.6, 119.2, 48.4, 43.8, 18.7, 14.0. HRMS (ESI) calcd for $C_{11}H_{14}N_2$ $[M+H]^+$ 175.1230, found 175.1234.



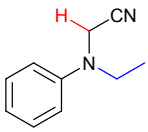
2-(3,4-dihydroquinolin-1(2H)-yl)acetonitrile (2g): Yellow solid; 45% yield; mp 59-62 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (td, *J* = 8.0, 1.0 Hz, 1H), 7.03 (d, *J* = 7.0 Hz, 1H), 6.78 (t, *J* = 7.0 Hz, 1H), 6.67 (d, *J* = 8.5 Hz, 1H), 4.16 (s, 2H), 3.29 (t, *J* = 6.0 Hz, 2H), 2.79 (t, *J* = 6.5 Hz, 2H), 2.07-2.02 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 129.8, 127.5, 124.8, 119.4, 116.0, 112.0, 50.2, 40.4, 27.5, 22.4. HRMS (ESI) calcd for $C_{11}H_{12}N_2$ $[M+H]^+$ 173.1073, found 173.1082.



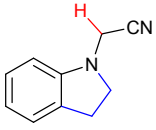
2-(7-(trifluoromethyl)-3,4-dihydroquinolin-1(2H)-yl)acetonitrile (2h): Yellow oil; 30% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.83 (s, 1H), 4.20 (s, 2H), 3.35 (t, *J* = 6.0 Hz, 2H), 2.83 (t, *J* = 6.5 Hz, 2H), 2.08-2.03 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 130.0, 129.9 (q, *J* = 32.5 Hz), 128.5, 124.4 (q, *J* = 270 Hz), 115.9 (q, *J* = 3.8 Hz), 115.4, 108.3 (q, *J* = 3.8 Hz), 50.0, 40.2, 27.5, 21.9. HRMS (ESI) calcd for $C_{12}H_{11}N_2F_3$ $[M+H]^+$ 241.0947, found 241.0935.



***N*-methyl-*N*-phenylaminoacetonitrile (2i):[2]** Yellow oil; 44% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.5 Hz, 2H), 6.93 (t, *J* = 7.0 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 2H), 4.18 (s, 2H), 3.01 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 129.6, 120.4, 115.7, 115.1, 42.5, 39.4. HRMS (ESI) calcd for $C_9H_{10}N_2$ $[M+H]^+$ 147.0917, found 147.0915.

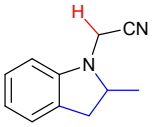


***N*-ethyl-*N*-phenylaminoacetonitrile (2j):[3]** Yellow oil; 51% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (td, *J* = 7.5, 1.0 Hz, 2H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 2H), 4.14 (s, 2H), 3.44 (q, *J* = 7.0 Hz, 2H), 1.25 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.0, 129.7, 120.0, 116.5, 115.1, 46.5, 39.7, 12.4. HRMS (ESI) calcd for $C_{10}H_{12}N_2$ $[M+H]^+$ 161.1073, found 161.1066.

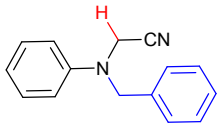


2-(indolin-1-yl)acetonitrile (2k): Yellow oil; 44% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16-7.13 (m, 2H), 6.83 (t, *J* = 7.0 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H),

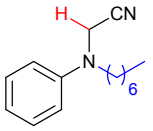
4.07 (s, 2H), 3.43 (t, J = 8.0 Hz, 2H), 3.03 (t, J = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.4, 130.6, 127.7, 125.1, 120.5, 115.1, 108.3, 53.7, 37.7, 28.7. HRMS (ESI) calcd for $C_{10}H_{10}N_2$ $[M+H]^+$ 159.0917, found 159.0921.



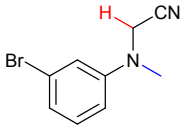
2-(2-methylindolin-1-yl)acetonitrile (2l): Yellow oil; 39% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (t, J = 7.5 Hz, 1H), 7.11 (d, J = 7.5 Hz, 1H), 6.82 (td, J = 7.5, 0.5 Hz, 1H), 6.55 (d, J = 8.0 Hz, 1H), 4.20 (d, J = 18.0 Hz, 1H), 3.96 (d, J = 18.0 Hz, 1H), 3.70-3.65 (m, 1H), 3.17 (dd, J = 15.0, 8.0 Hz, 1H), 2.67 (dd, J = 15.5, 10.5 Hz, 1H), 1.38 (d, J = 6.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.6, 129.6, 127.7, 124.8, 120.6, 115.2, 108.3, 60.7, 37.3, 35.2, 18.5. HRMS (ESI) calcd for $C_{11}H_{12}N_2$ $[M+H]^+$ 173.1073 , found 173.1078.



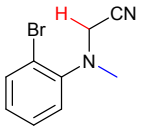
***N*-benzyl-*N*-phenylaminoacetonitrile (2m)**:[4] Yellow oil; 26% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.31 (m, 7H), 6.98-6.94 (m, 3H), 4.52 (s, 2H), 4.07 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.1, 137.0, 129.7, 129.1, 128.0, 127.8, 120.9, 116.0, 115.8, 55.9, 39.7. HRMS (ESI) calcd for $C_{15}H_{14}N_2$ $[M+H]^+$ 223.1230, found 223.1235.



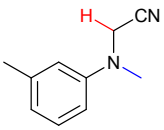
***N*-heptyl-*N*-phenylaminoacetonitrile (2n)**: Yellow oil; 21% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (td, J = 7.5, 1.0 Hz, 2H), 6.89 (t, J = 7.5 Hz, 1H), 6.85 (d, J = 8.0 Hz, 2H), 4.14 (s, 2H), 3.33 (t, J = 8.0 Hz, 2H), 1.66-1.63 (m, 2H), 1.35-1.28 (m, 8H), 0.89 (t, J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.4, 129.7, 119.9, 116.5, 114.9, 52.3, 40.2, 32.0, 29.2, 27.4, 27.2, 22.8, 14.2. HRMS (ESI) calcd for $C_{15}H_{22}N_2$ $[M+H]^+$ 231.1856, found 231.1849.



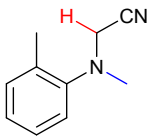
***N*-(3-bromophenyl)-*N*-methylaminoacetonitrile (2o)**:[5] Yellow oil; 49% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (t, J = 8.0 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H), 6.98 (t, J = 2.0 Hz, 1H), 6.76 (dd, J = 8.4, 2.4 Hz, 1H), 4.16 (s, 2H), 3.01 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.1, 130.9, 123.7, 123.1, 117.8, 115.3, 113.3, 42.1, 39.4. HRMS (ESI) calcd for $C_9H_9BrN_2$ $[M+H]^+$ 225.0022, found 225.0016.



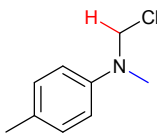
***N*-(2-bromophenyl)-*N*-methylaminoacetonitrile (2p)**:[6] Yellow solid; 30% yield; mp 37-39 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, J = 8.0, 1.0 Hz, 1H), 7.34 (td, J = 8.5, 1.5 Hz, 1H), 7.28 (dd, J = 8.0, 1.5 Hz, 1H), 7.03 (td, J = 7.5, 1.5 Hz, 1H), 4.09 (s, 2H), 2.94 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6, 134.2, 128.8, 126.5, 123.0, 119.9, 115.3, 45.0, 40.8. HRMS (ESI) calcd for $C_9H_9BrN_2$ $[M+H]^+$ 225.0022, found 225.0017.



***N*-Methyl-*N*-(3-methylphenyl)aminoacetonitrile (2q)**:[6] Yellow oil; 39% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21-7.18 (m, 1H), 6.74 (d, J = 7.5 Hz, 1H), 6.68-6.67 (m, 2H), 4.15 (s, 2H), 2.99 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3, 137.7, 127.8, 119.6, 114.2, 114.0, 110.6, 40.8, 37.7, 20.2. HRMS (ESI) calcd for $C_{10}H_{12}N_2$ $[M+H]^+$ 161.1073, found 161.1075.

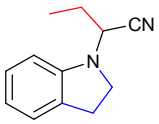


***N*-Methyl-*N*-(2-methylphenyl)aminoacetonitrile (2r)**:[6] Yellow oil; 60% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23-7.19 (m, 3H), 7.09-7.05 (m, 1H), 3.85 (s, 2H), 2.86 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.7, 133.0, 131.5, 127.1, 125.2, 120.9, 115.8, 45.2, 41.2, 17.9. HRMS (ESI) calcd for $C_{10}H_{12}N_2$ $[M+H]^+$ 161.1073, found 161.1079.

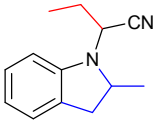


***N*-Methyl-*N*-(4-methylphenyl)aminoacetonitrile (2s)**:[6] Yellow oil; 36% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (d, J = 8.5 Hz, 2H), 6.80 (d, J = 8.5 Hz, 2H),

4.14 (s, 2H), 2.97 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.9, 130.2, 130.1, 115.7, 115.6, 43.1, 39.7, 20.6. HRMS (ESI) calcd for $C_{10}H_{12}N_2$ $[M+H]^+$ 161.1073, found 161.1070.

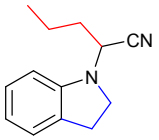


2-(indolin-1-yl)butanenitrile (2t): Yellow solid; 38% yield; mp 85-87 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14-7.11 (m, 2H), 6.80 (td, *J* = 7.5, 0.5 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 4.30 (t, *J* = 8.0 Hz, 1H), 3.53 (td, *J* = 9.0, 3.5 Hz, 1H), 3.24 (tt, *J* = 11.0, 8.5 Hz, 1H), 3.05-2.99 (m, 2H), 2.00-1.93 (m, 2H), 1.16 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.6, 130.5, 127.6, 125.1, 120.4, 117.6, 108.4, 51.8, 49.2, 28.4, 25.4, 10.8. HRMS (ESI) calcd for $C_{12}H_{14}N_2$ $[M+H]^+$ 187.1230, found 187.1233.

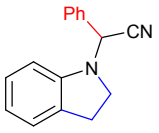


2-(2-methylindolin-1-yl)butanenitrile (2u): Major isomer: Yellow oil; 41% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12-7.09 (m, 2H), 6.77 (td, *J* = 7.0, 0.5 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 4.05 (t, *J* = 8.0 Hz, 1H), 3.83-3.78 (m, 1H), 3.16 (dd, *J* = 15.5, 8.5 Hz, 1H), 2.65 (dd, *J* = 15.5, 8.0 Hz, 1H), 2.15-2.03 (m, 2H), 1.35 (d, *J* = 6.0 Hz, 3H), 1.14 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.6, 129.3, 127.5, 124.9, 119.7, 118.4, 108.5, 59.5, 49.9, 37.3, 25.5, 19.3, 11.2. HRMS (ESI) calcd for $C_{13}H_{16}N_2$ $[M+H]^+$ 201.1386, found 201.1380.

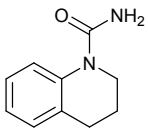
Minor isomer: Yellow oil; 21% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12-7.08 (m, 2H), 6.78 (td, *J* = 7.5, 1.0 Hz, 1H), 6.61 (d, *J* = 7.5 Hz, 1H), 4.20 (dd, *J* = 9.0, 7.5 Hz, 1H), 3.92-3.86 (m, 1H), 3.32 (dd, *J* = 16.0, 9.0 Hz, 1H), 2.63 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.06-1.93 (m, 2H), 1.36 (d, *J* = 6.0 Hz, 3H), 1.15 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.5, 129.6, 127.6, 125.0, 120.1, 118.1, 109.2, 59.4, 52.8, 37.8, 26.2, 22.1, 11.0. HRMS (ESI) calcd for $C_{13}H_{16}N_2$ $[M+H]^+$ 201.1386, found 201.1378.



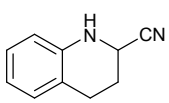
2-(indolin-1-yl)pentanenitrile (2v): Yellow solid; 18% yield; mp 89-91 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14-7.11 (m, 2H), 6.80 (td, *J* = 7.5, 1.0 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 4.40 (t, *J* = 8.0 Hz, 1H), 3.53 (td, *J* = 8.5, 3.0 Hz, 1H), 3.24 (tt, *J* = 11.0, 8.5 Hz, 1H), 3.05-2.99 (m, 2H), 1.94-1.89 (m, 2H), 1.62-1.57 (m, 2H), 1.02 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.6, 130.5, 127.6, 125.1, 120.4, 117.7, 108.4, 49.8, 49.3, 33.7, 28.4, 19.4, 13.5. HRMS (ESI) calcd for $C_{13}H_{16}N_2$ $[M+H]^+$ 201.1386, found 201.1384.



2-(indolin-1-yl)-2-phenylacetonitrile (2w): White solid; 18% yield; mp 94-96 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.0 Hz, 2H), 7.47-7.42 (m, 3H), 7.17-7.13 (m, 2H), 6.85 (t, *J* = 7.5 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 5.76 (s, 1H), 3.30-3.19 (m, 2H), 3.05-2.92 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3, 132.8, 130.9, 129.32, 129.25, 127.62, 127.60, 125.3, 120.8, 116.0, 108.8, 54.5, 50.5, 28.3. HRMS (ESI) calcd for $C_{16}H_{14}N_2$ $[M+H]^+$ 235.1230, found 235.1234.

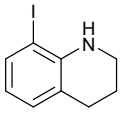


3,4-dihydroquinoline-1(2H)-carboxamide (3): Brown solid; 30% yield; mp 145-147 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 1H), 7.20-7.16 (m, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 5.04 (br s, 2H), 3.76 (t, *J* = 6.5 Hz, 2H), 2.76 (t, *J* = 6.5 Hz, 2H), 1.98-1.92 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.5, 139.5, 132.7, 129.5, 126.8, 124.7, 123.3, 43.6, 27.2, 24.1. HRMS (ESI) calcd for $C_{10}H_{12}N_2O$ $[M+H]^+$ 177.1023, found 177.1018.



1,2,3,4-tetrahydroquinoline-2-carbonitrile (4):[7] Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05-7.01 (m, 2H), 6.76 (td, *J* = 7.5, 1.0 Hz, 1H), 6.55 (d, *J* = 7.5 Hz, 1H), 4.44-4.42 (m, 1H), 4.14 (s, 1H), 3.09 (ddd, *J* = 17.0, 11.5, 6.0 Hz, 1H), 2.82 (dt, *J* = 17.0, 4.5 Hz, 1H), 2.27-2.17 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.9, 129.7,

127.5, 120.3, 120.1, 119.6, 115.3, 42.9, 25.4, 23.7. HRMS (ESI) calcd for $C_{10}H_{12}N_2$ $[M+H]^+$ 159.0917, found 159.0913.



8-iodo-1,2,3,4-tetrahydroquinoline (5): Yellow oil; 81% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22-7.21 (m, 2H), 7.19 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.23 (d, *J* = 8.5 Hz, 1H), 3.27 (t, *J* = 5.5 Hz, 2H), 2.70 (t, *J* = 6.5 Hz, 2H), 1.91-1.87 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.5, 137.9, 135.4, 124.2 116.2, 77.3, 41.9, 26.9, 21.8. HRMS (ESI) calcd for $C_9H_{10}IN$ $[M+H]^+$ 259.9931, found 259.9919.

5. References

(1) N. Iranpoor, H. Firouzabadi, N. Nowrouzi and D. Khalili, *Tetrahedron*, 2009, **65**, 3893.

(2) S. Murahashi, T. Nakae, H. Terai and N. Komiya, *J. Am. Chem. Soc.*, 2008, **130**, 11005.

(3) Y. Zhang, H. Peng, M. Zhang, Y. Cheng and C. Zhu, *Chem. Commun*., 2011, 2354.

(4) K. T. V. Rao, B. Haribabu, P. S. S. Prasad and N. Lingaiah, *ChemCatChem*, 2012, **4**, 1173.

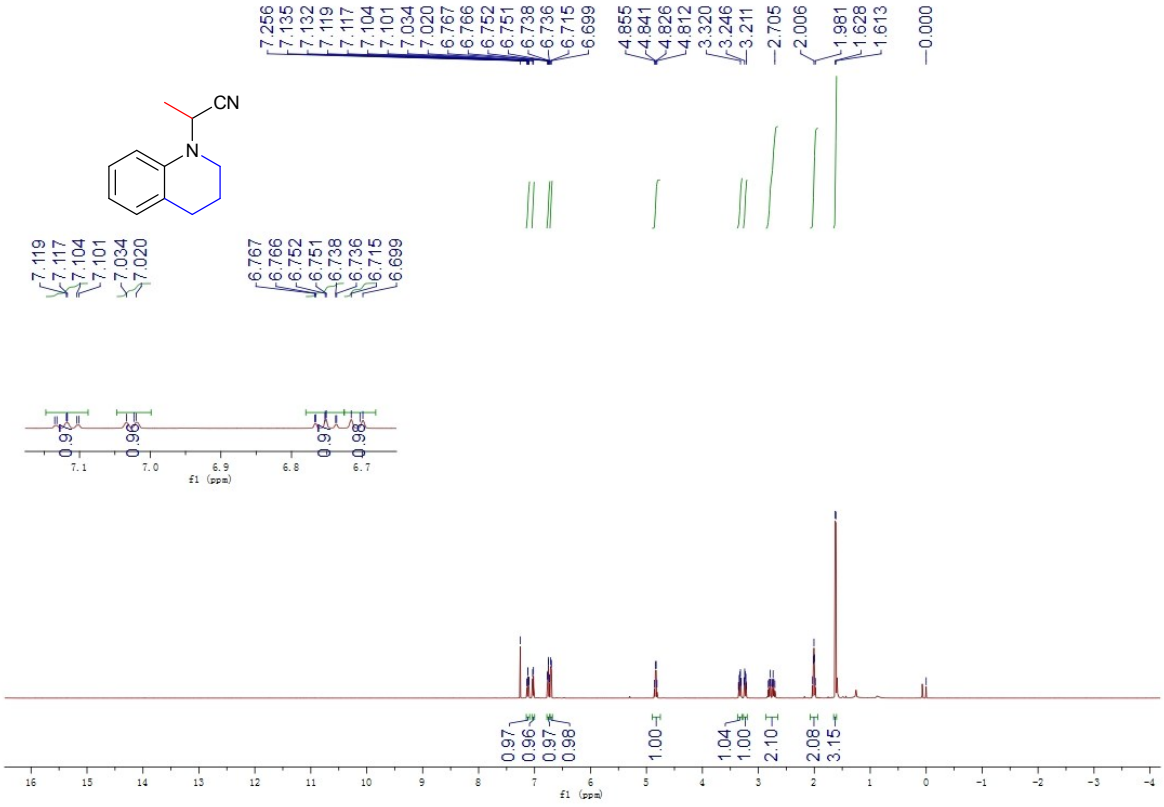
(5) C. Zhang, C. Liu, Y. Shao, X. Bao and X. Wan, *Chem. Eur. J.*, 2013, **19**, 17917.

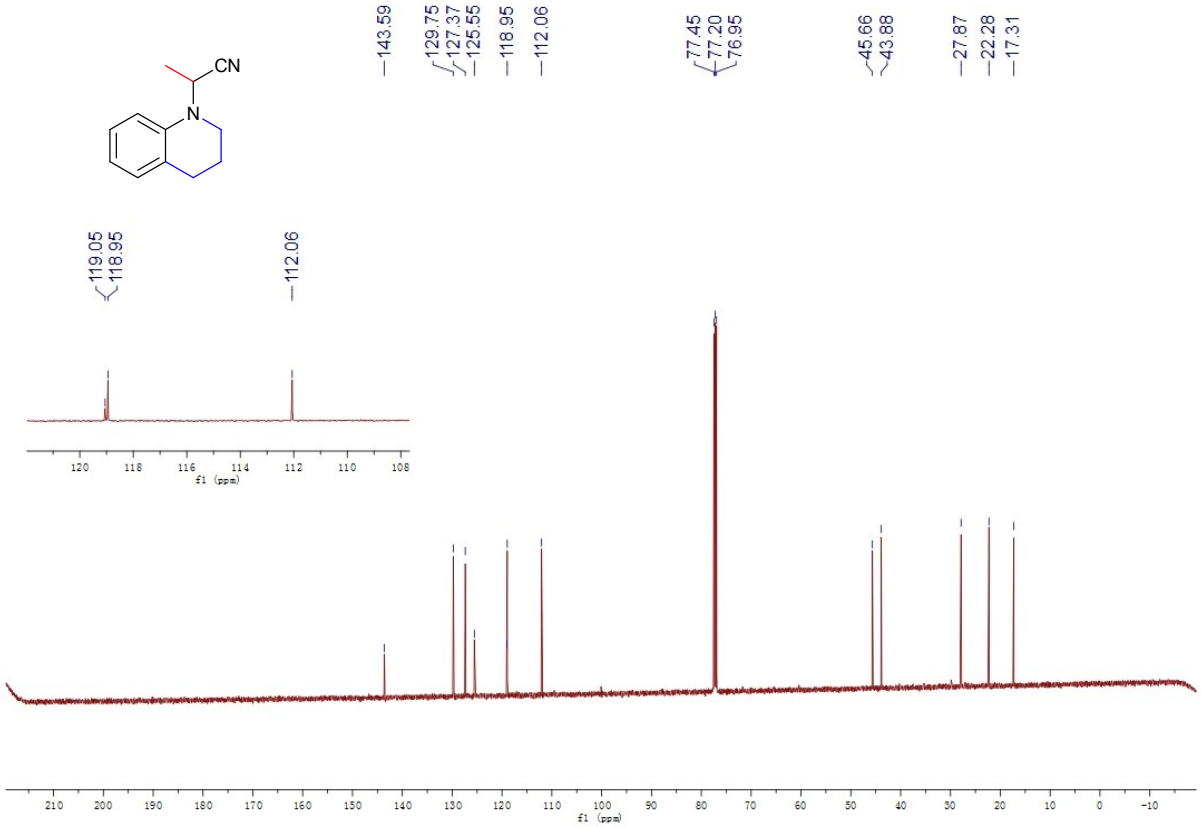
(6) W. Han and A. R. Ofial, *Chem. Commun*., 2009, 5024.

(7) G. Spadoni, A. Bedini, S. Lucarini, M. Mari, D.-H. Caignard, J. A. Boutin, P. Delagrange, V. Lucini, F. Scaglione and A. Lodola, *J. Med. Chem*., 2015, **58**, 7512.

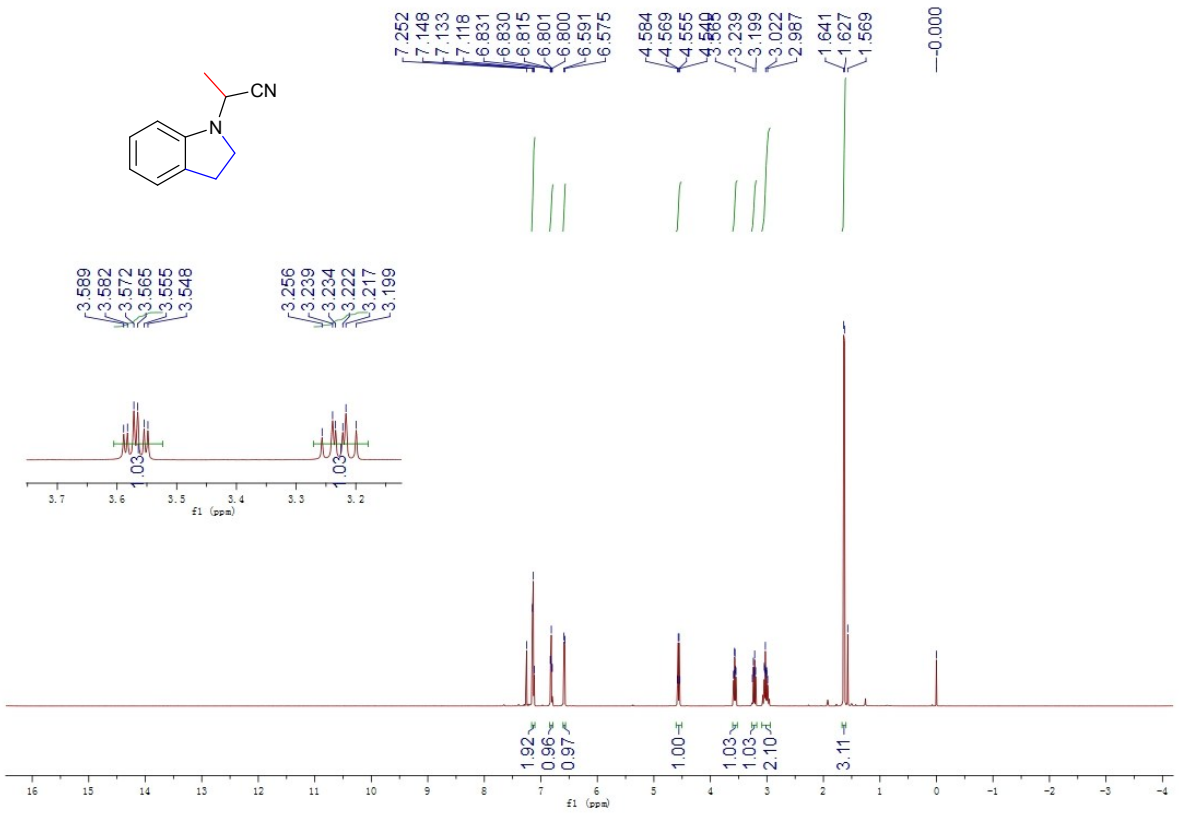
6. ^{1}H- and ^{13}C-NMR spectra

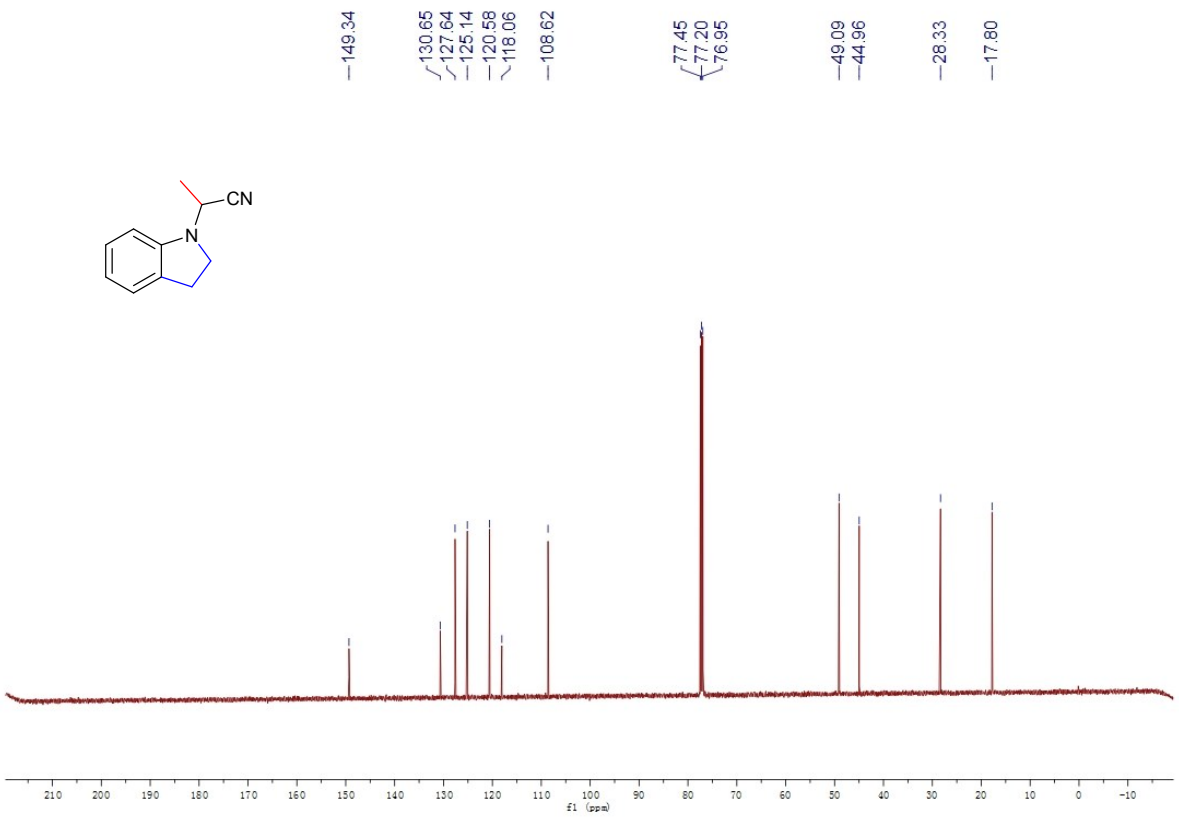
2-(3,4-dihydroquinolin-1(2H)-yl)propanenitrile (2a)



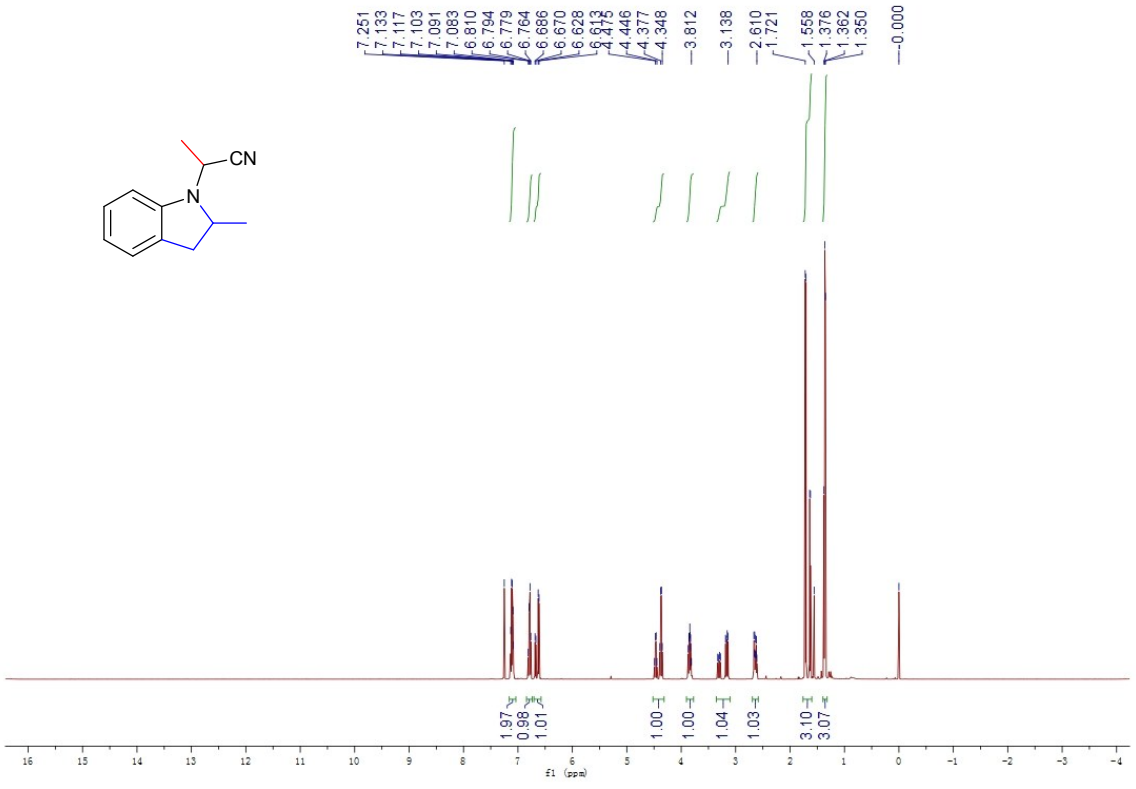


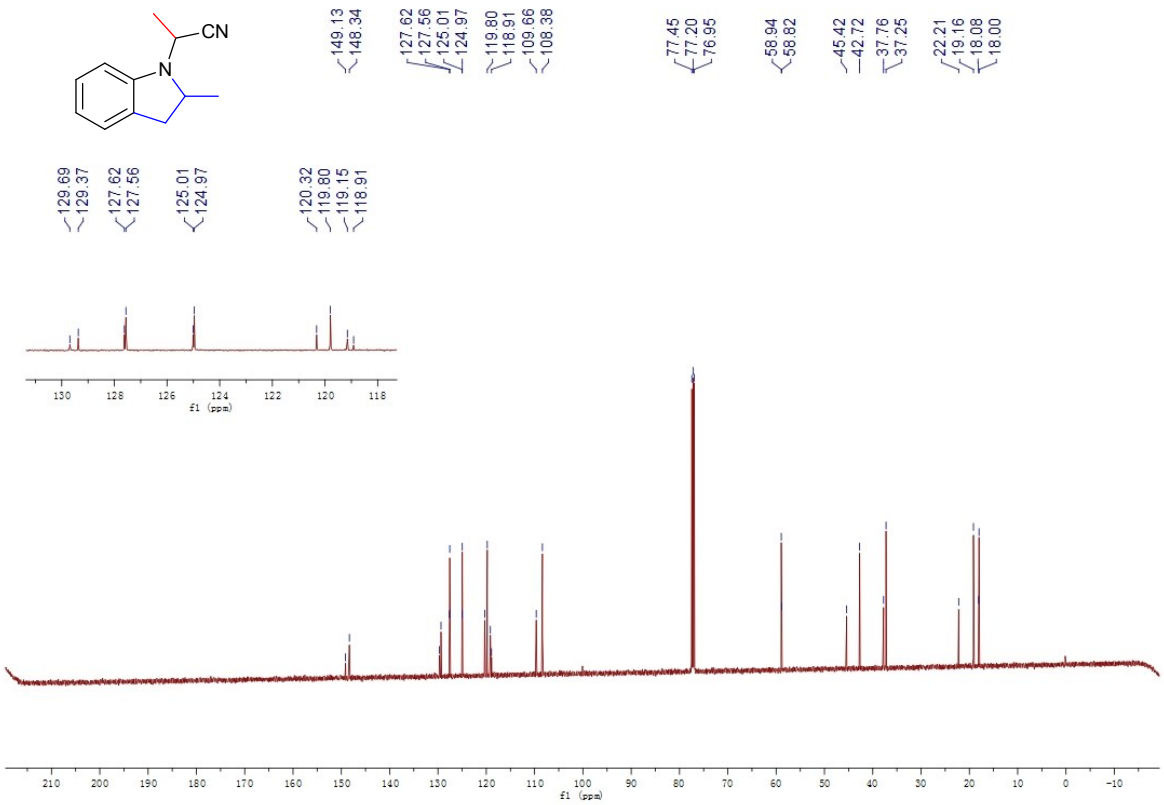
2-(indolin-1-yl)propanenitrile (2d)



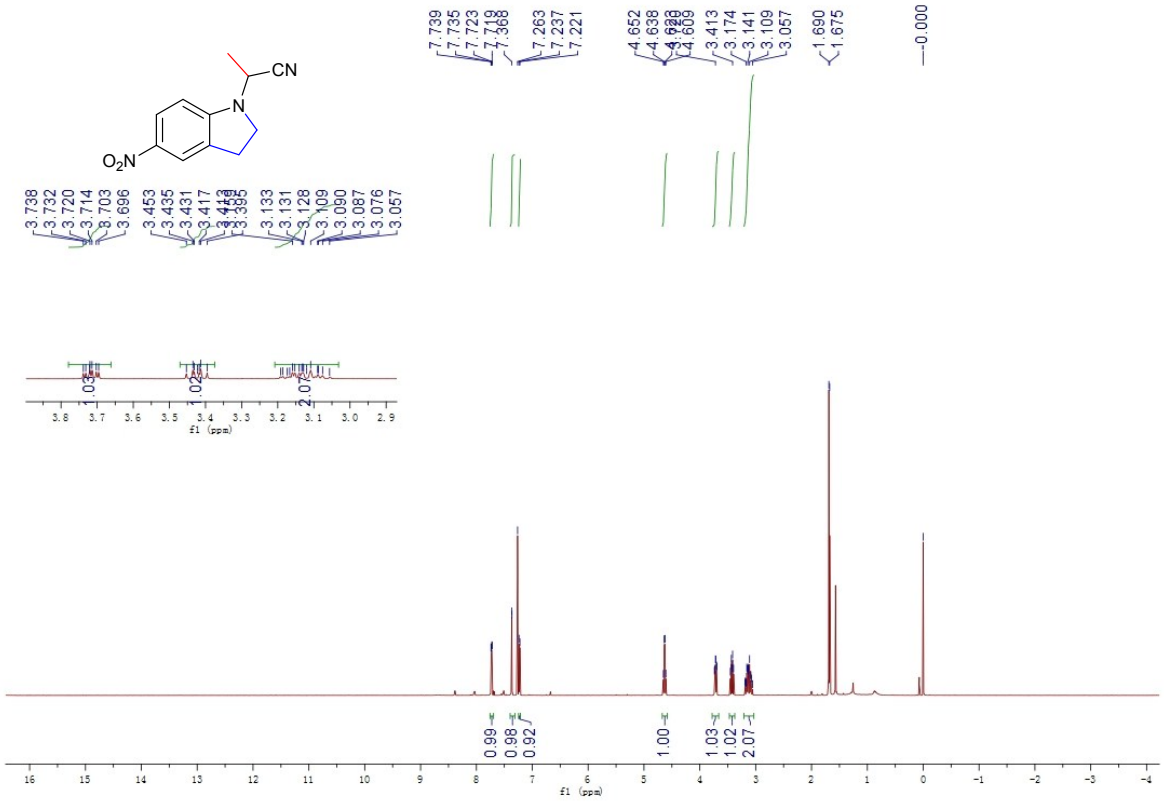


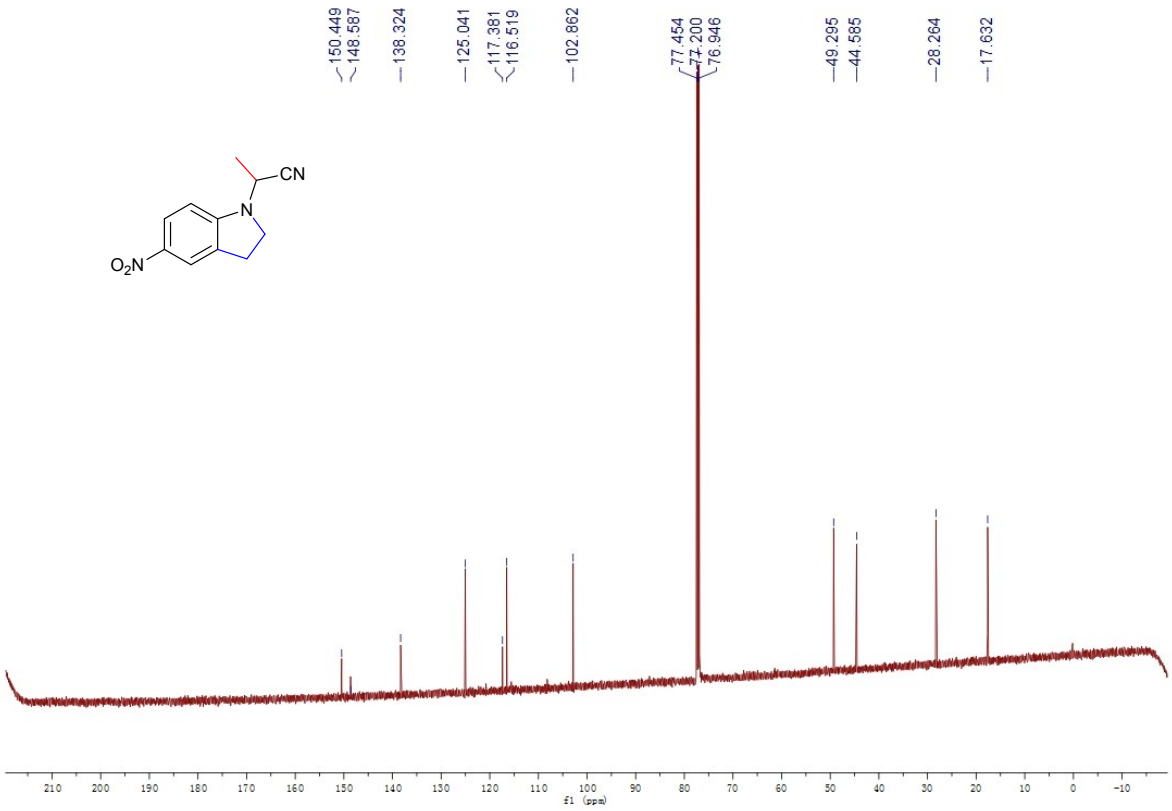
2-(2-methylindolin-1-yl)propanenitrile (2c) mixture of two diastereoisomers (dr = 2:1)



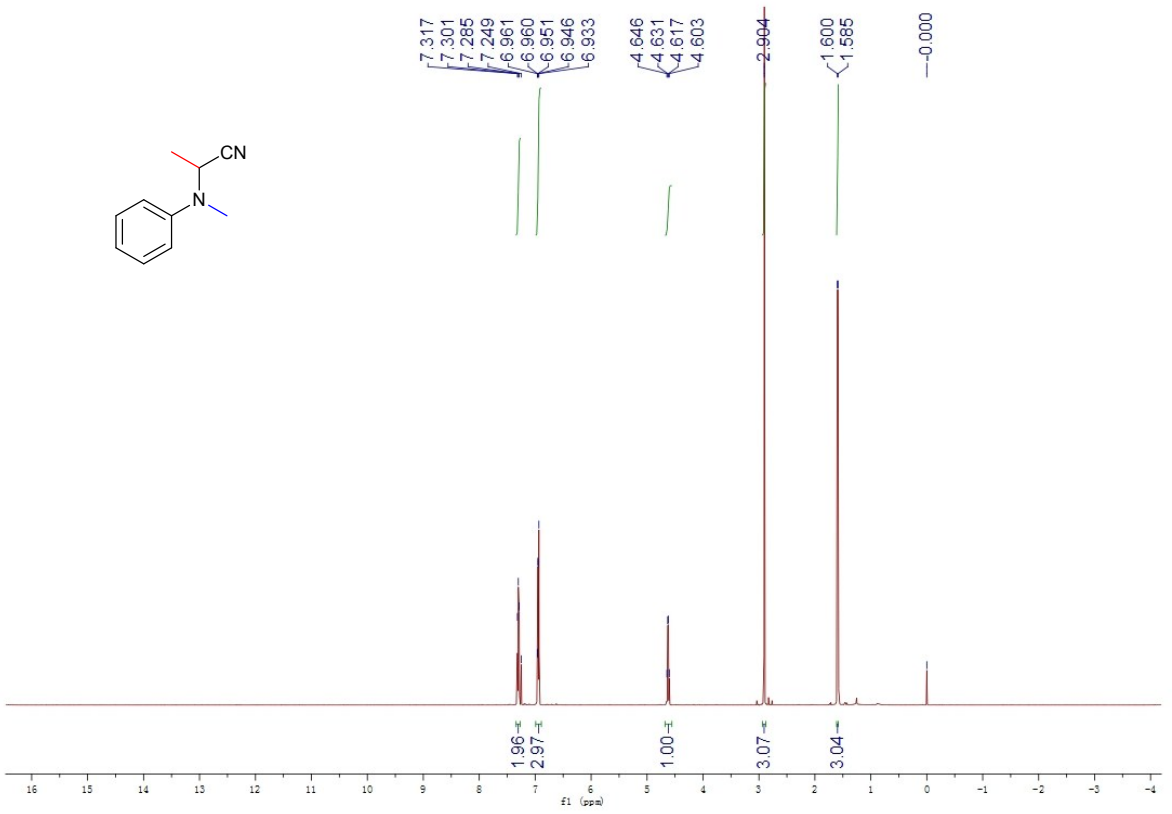


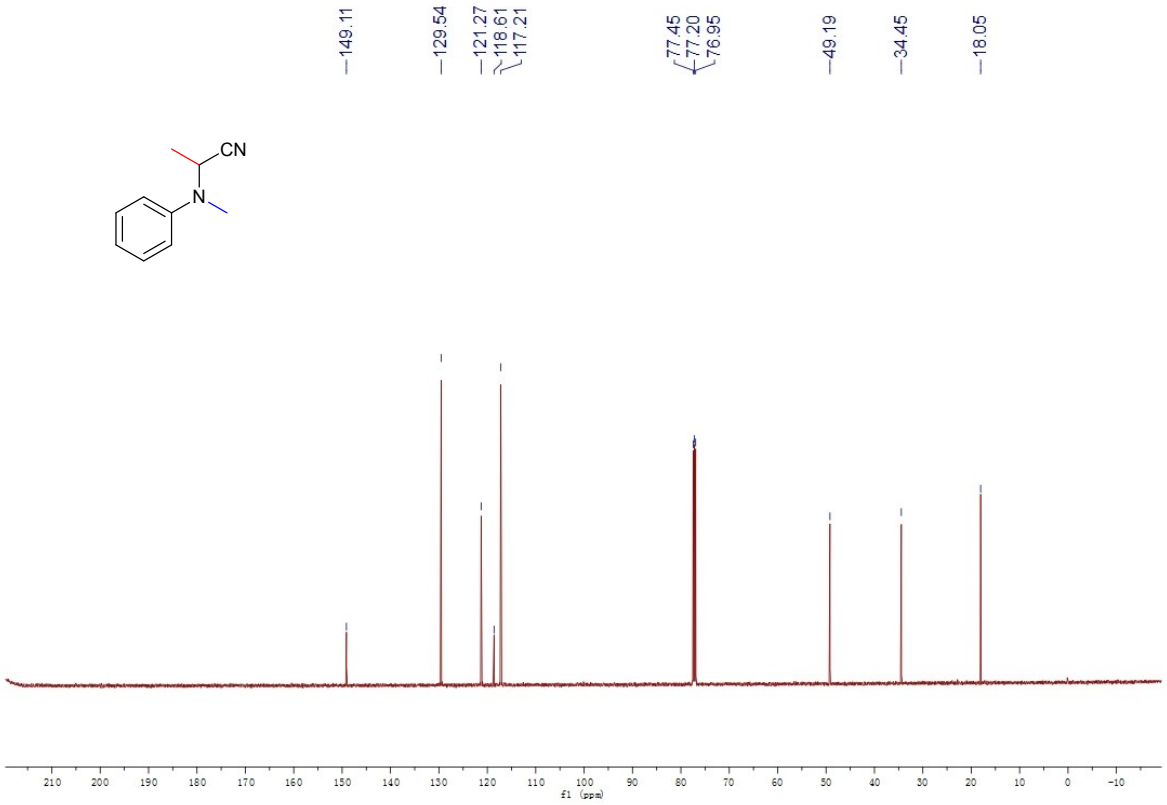
2-(5-nitroindolin-1-yl)propanenitrile (2d)



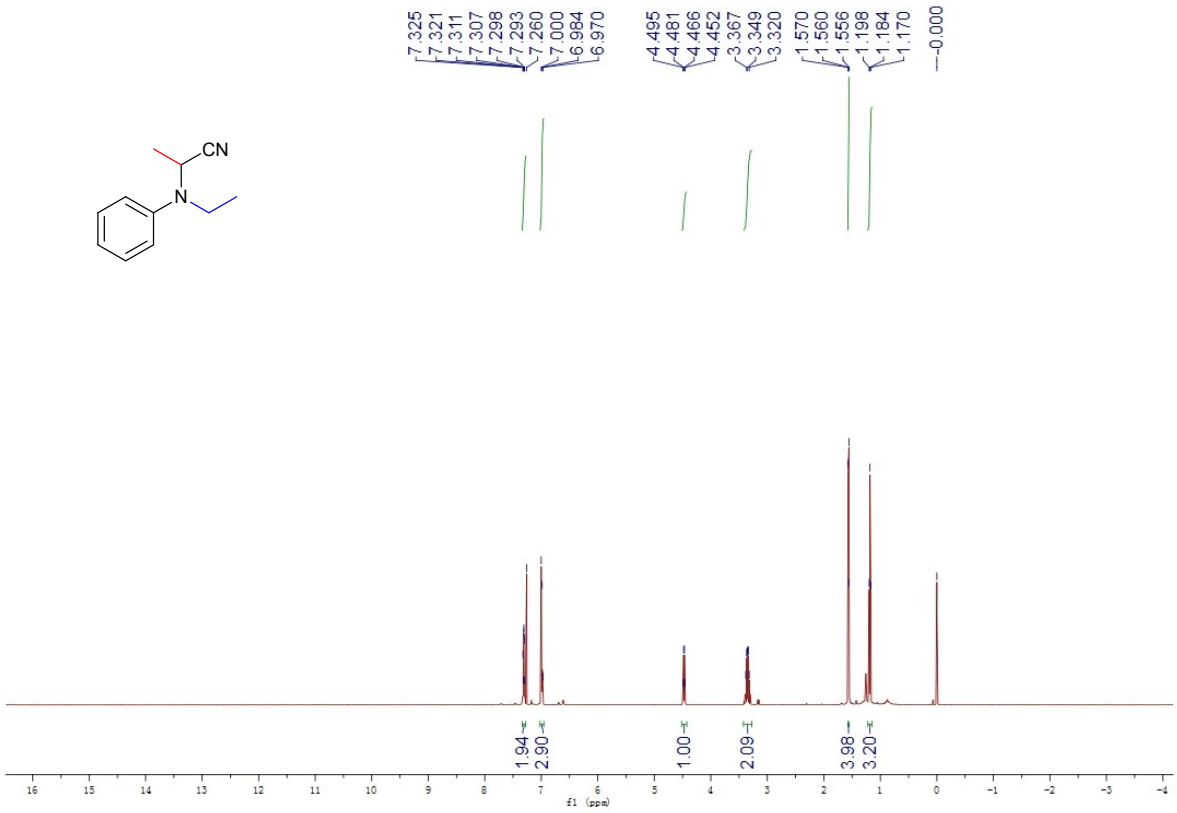


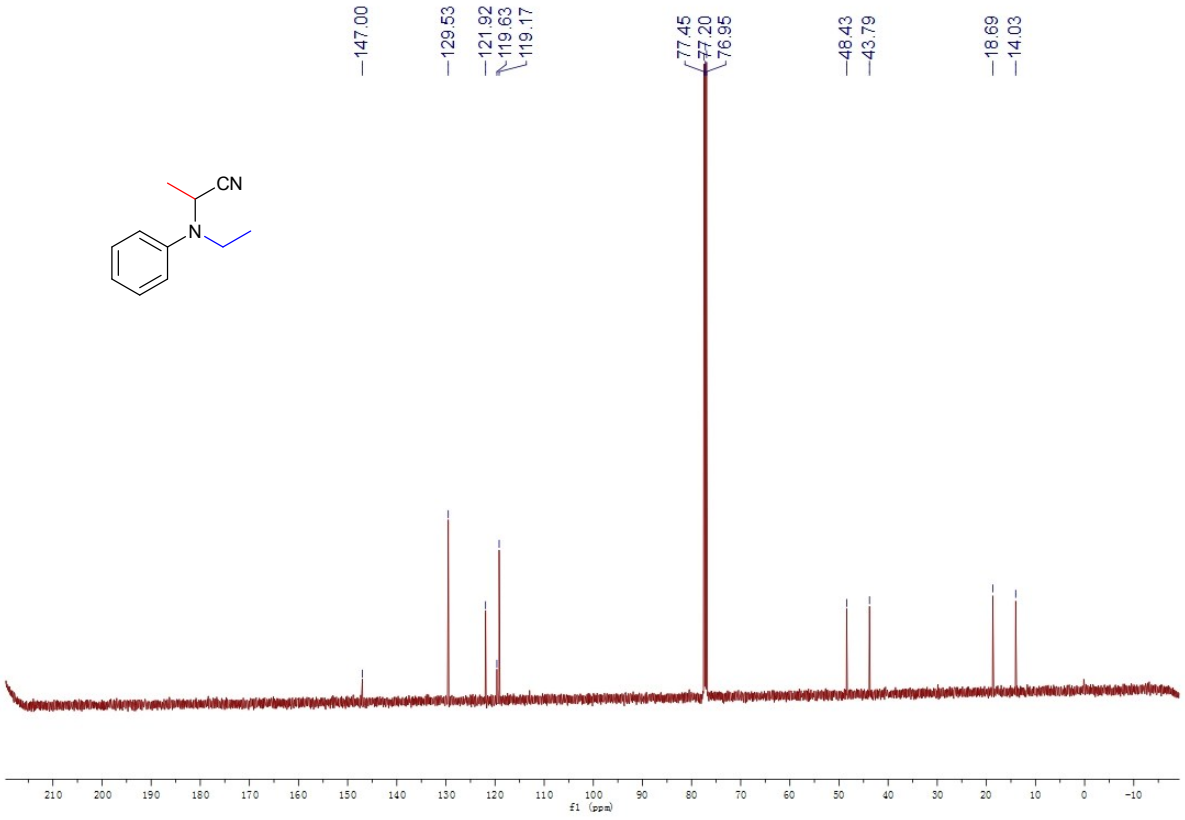
2-(methyl(phenyl)amino)propanenitrile (2e)



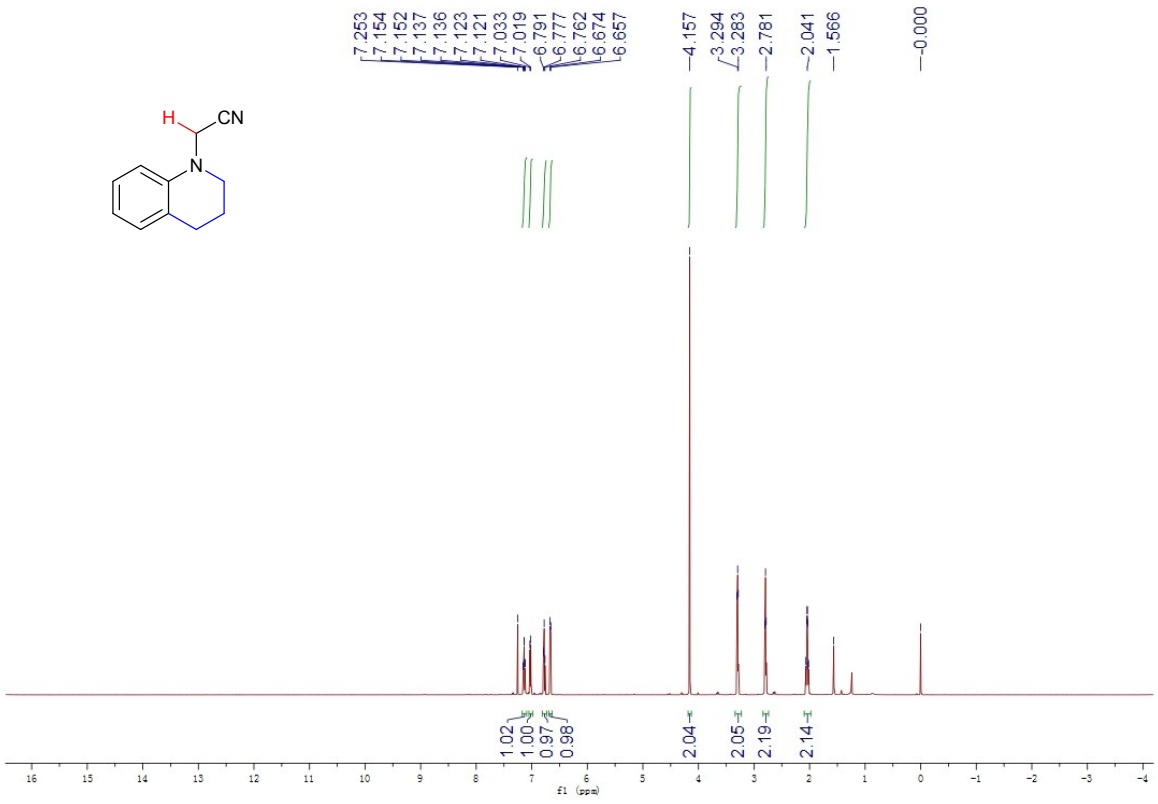


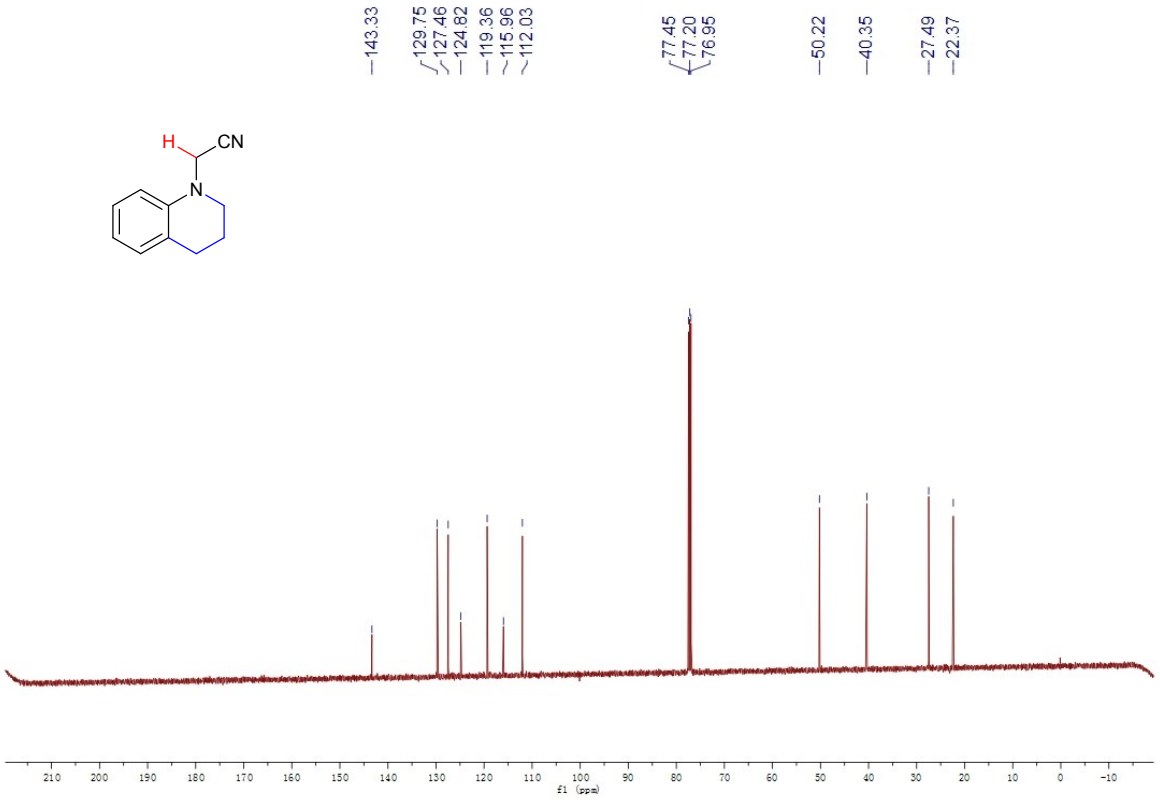
2-(ethyl(phenyl)amino)propanenitrile (2f)



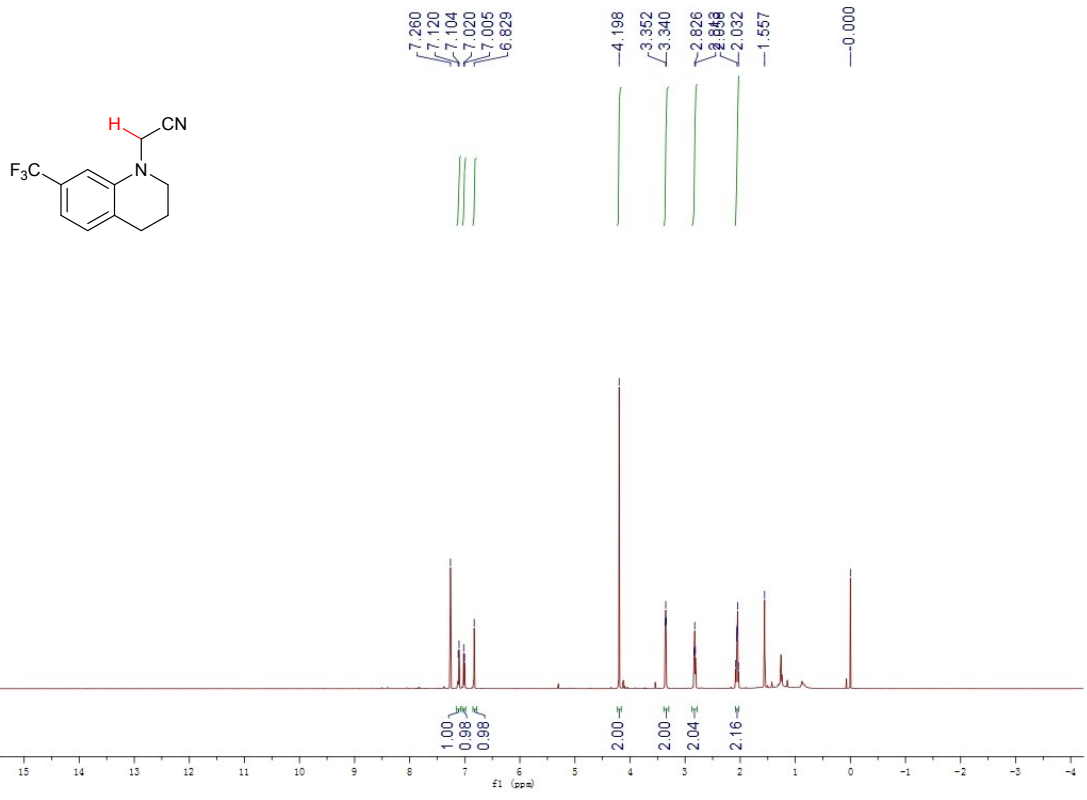


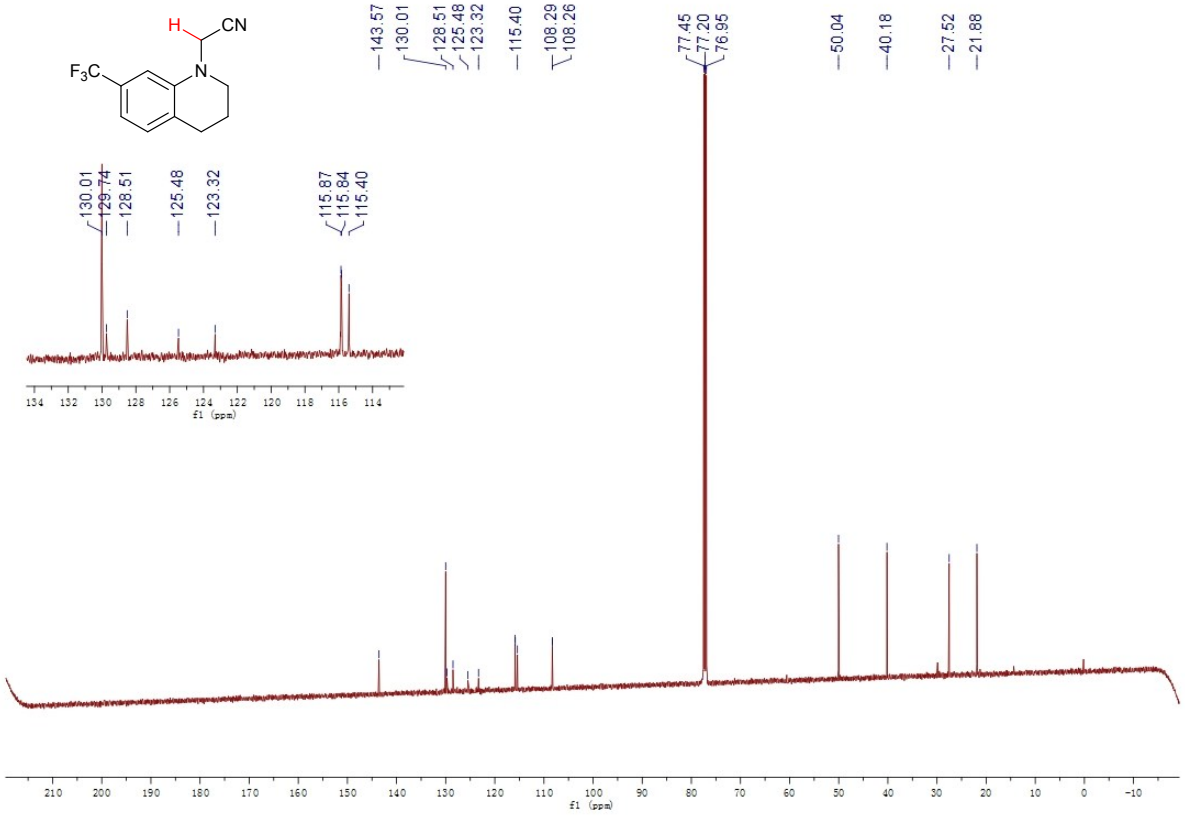
2-(3,4-dihydroquinolin-1(2H)-yl)acetonitrile (2g)



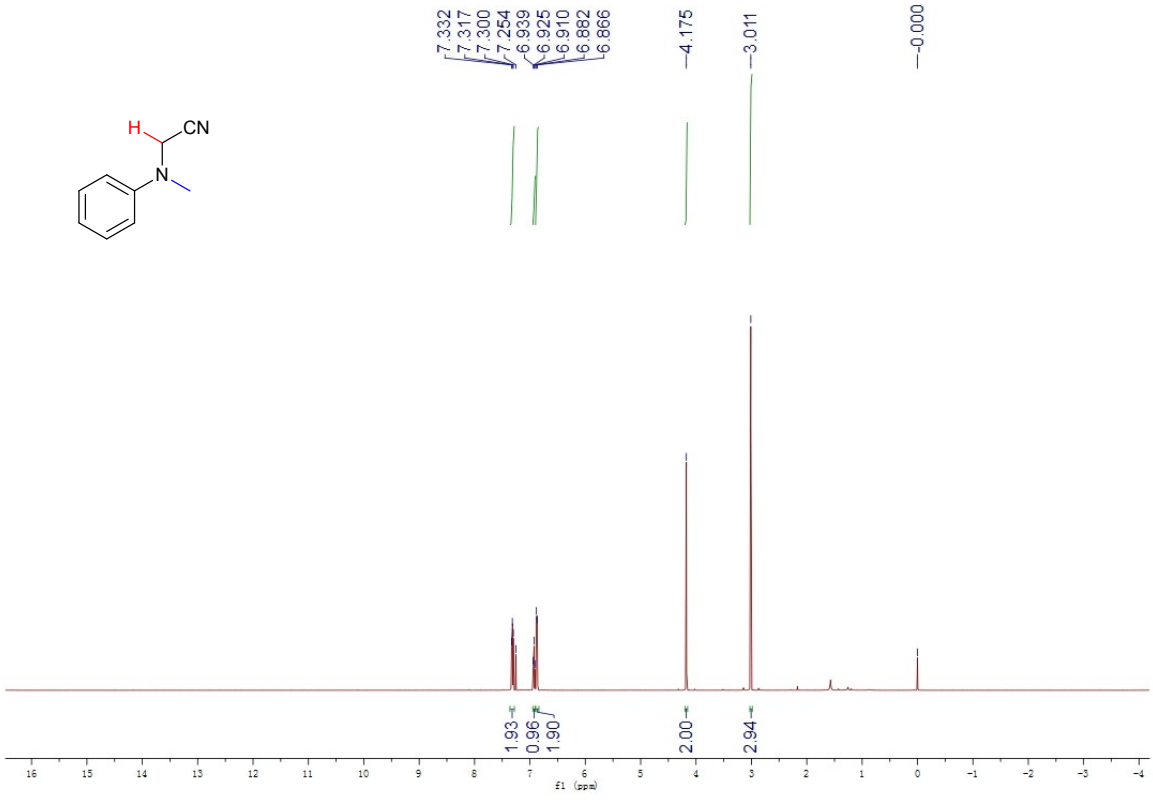


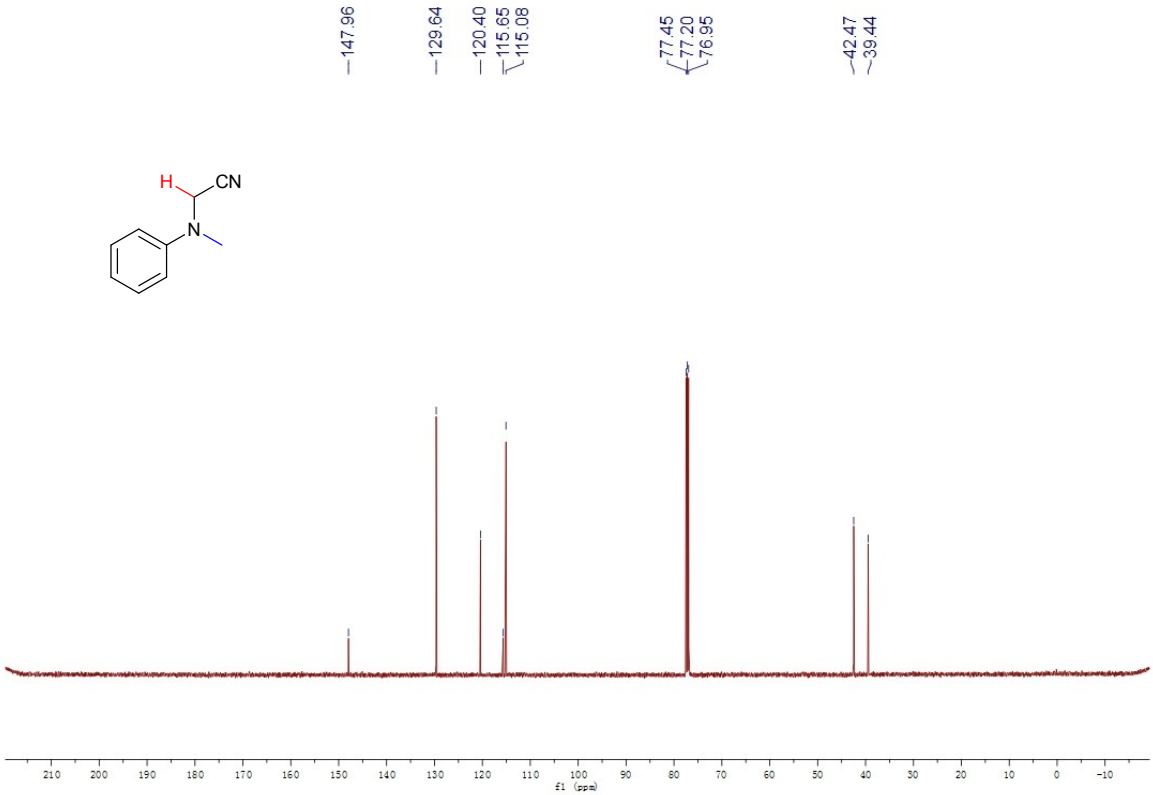
2-(7-(trifluoromethyl)-3,4-dihydroquinolin-1(2H)-yl)acetonitrile (2h)



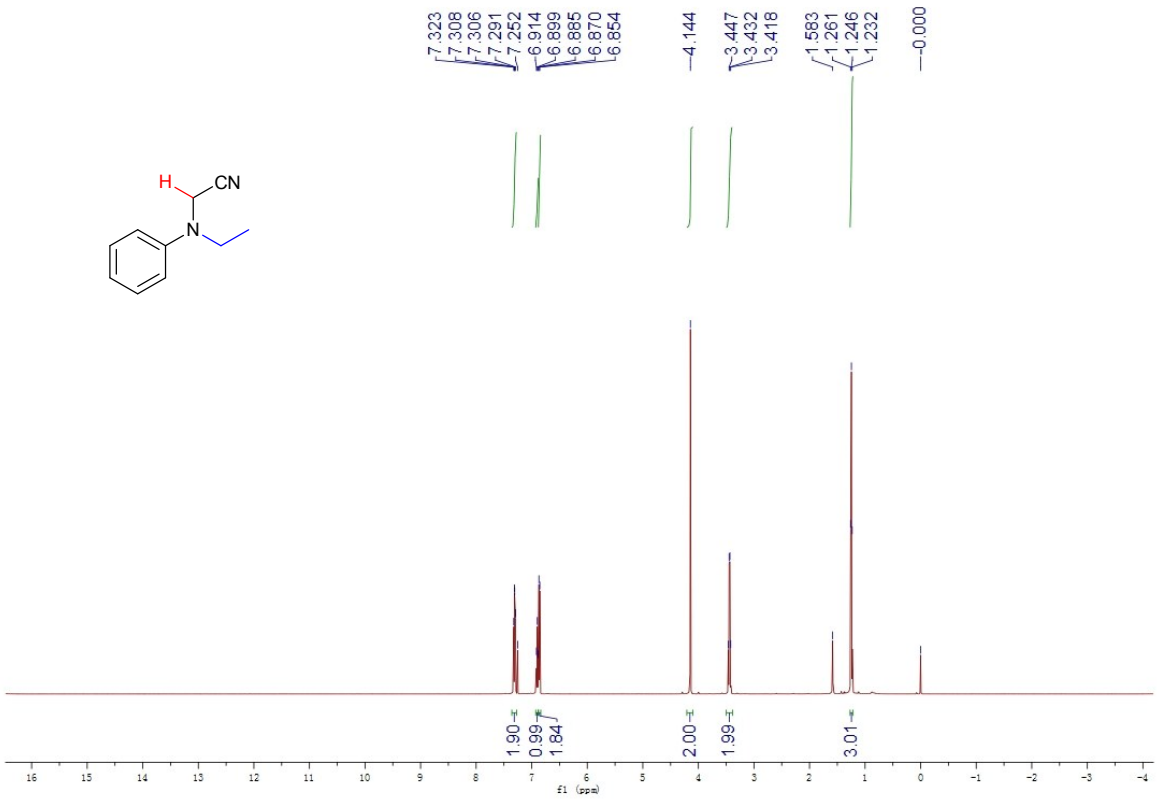


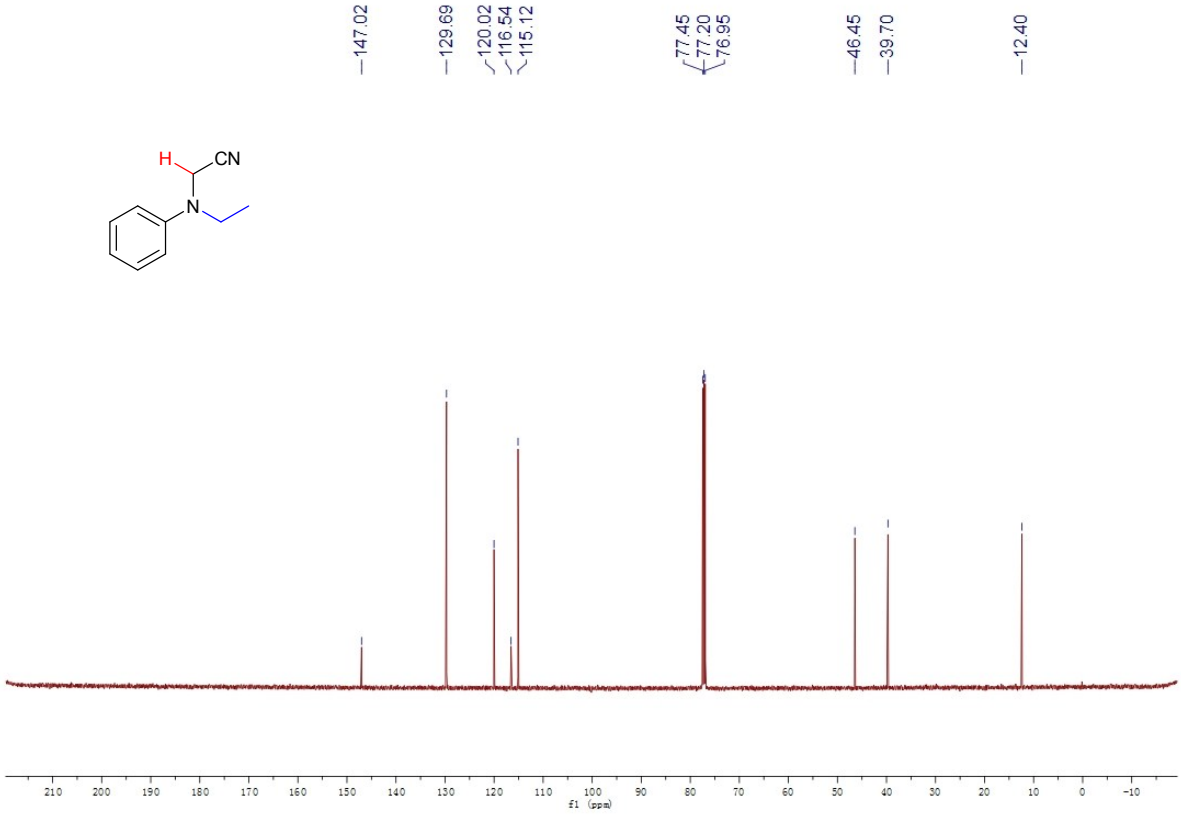
***N*-methyl-*N*-phenylaminoacetonitrile (2i)**



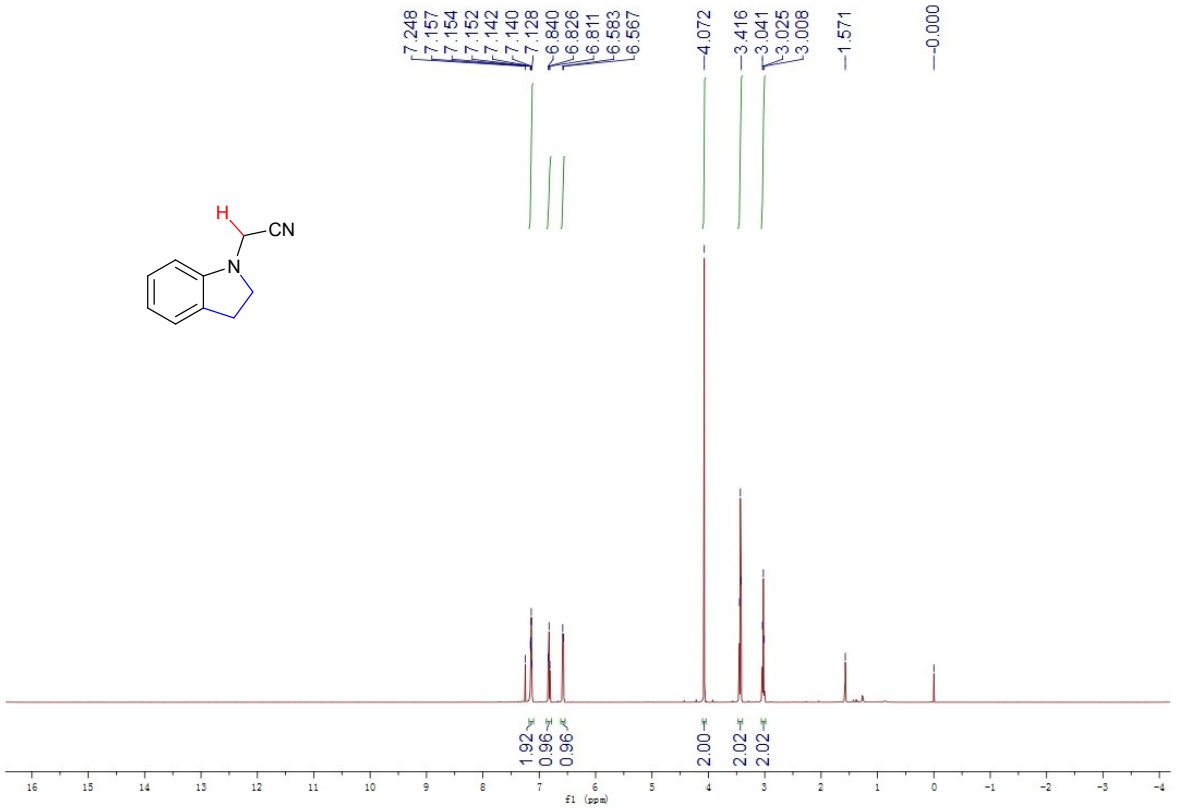


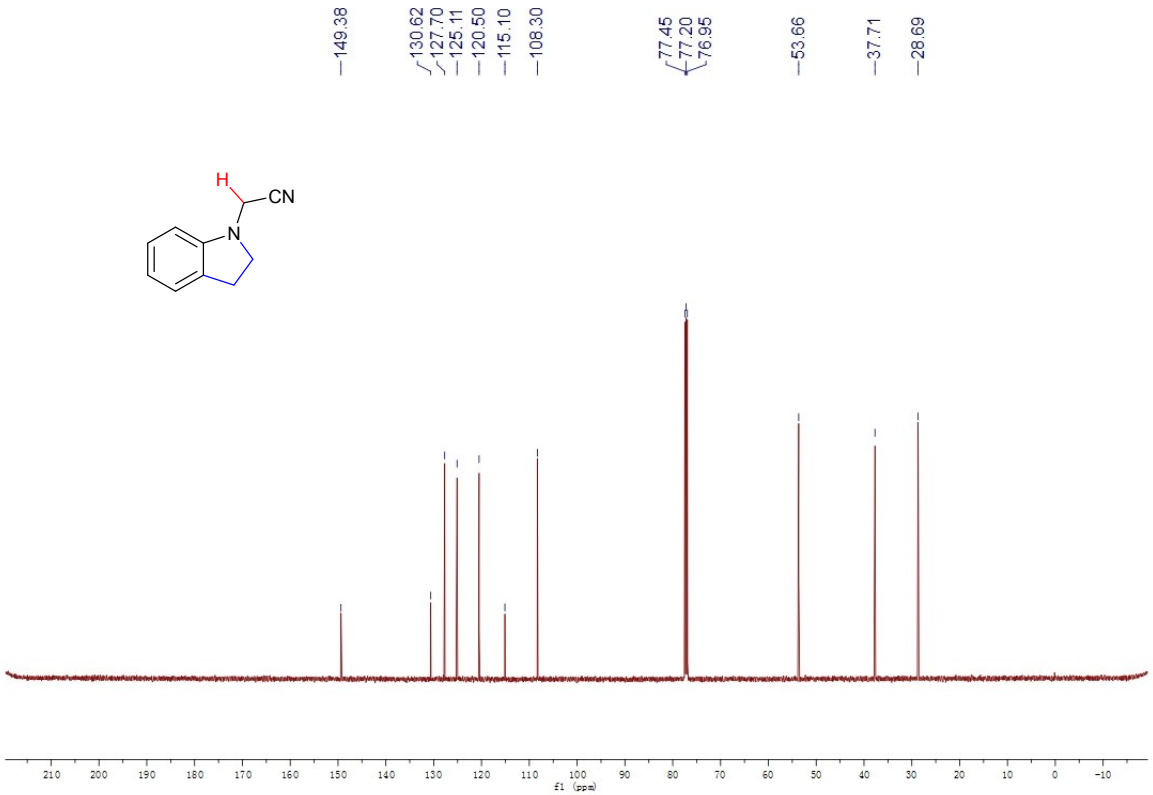
***N*-ethyl-*N*-phenylaminoacetonitrile (2j)**



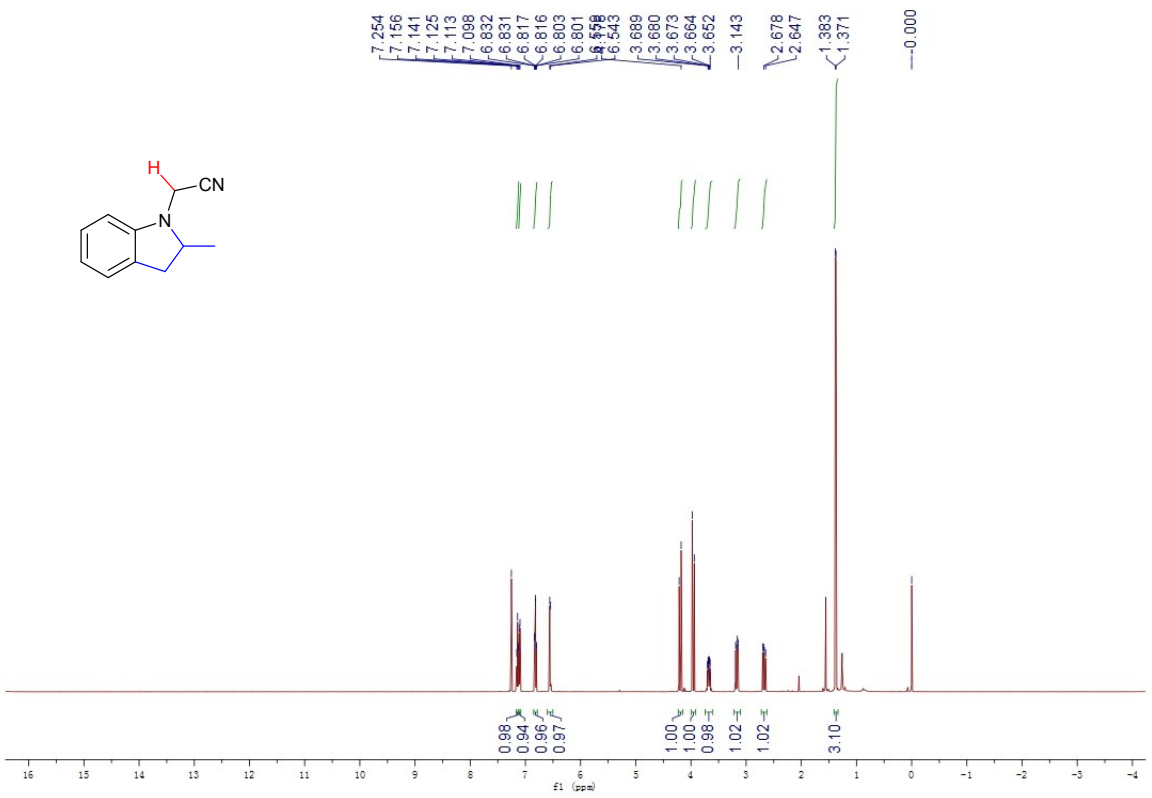


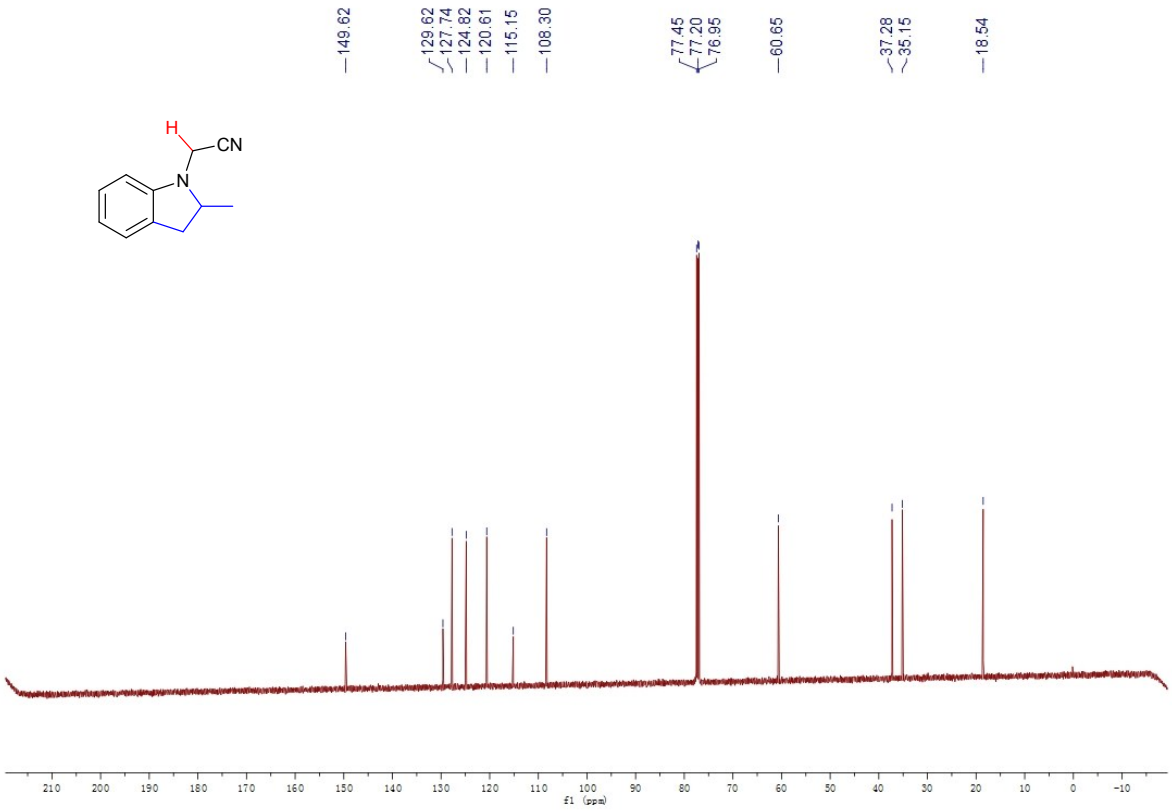
2-(indolin-1-yl)acetonitrile (2k)



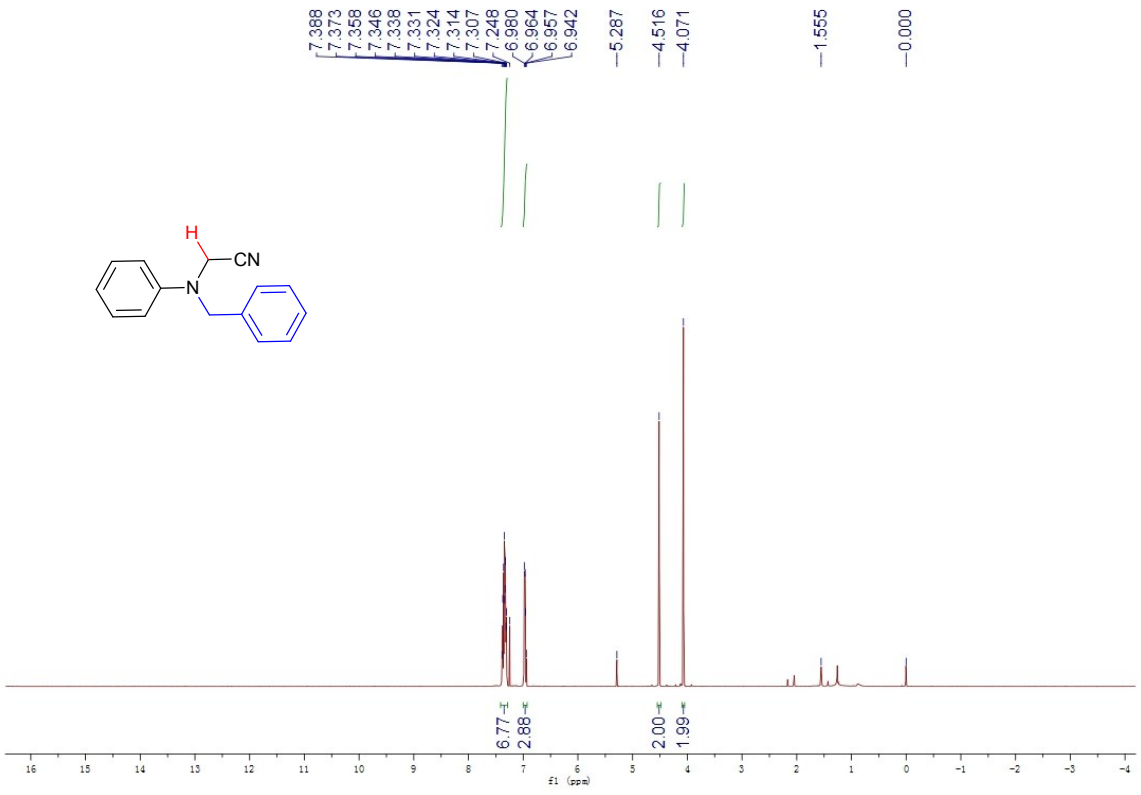


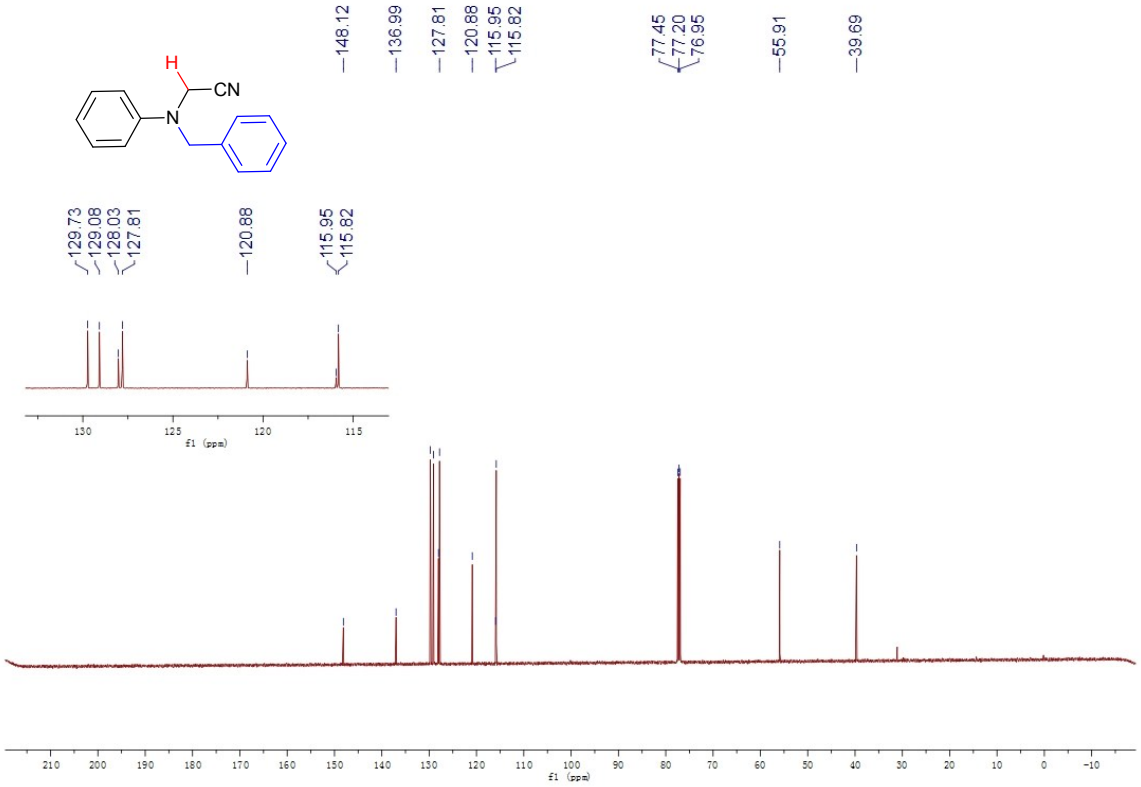
2-(2-methylindolin-1-yl)acetonitrile (2l)



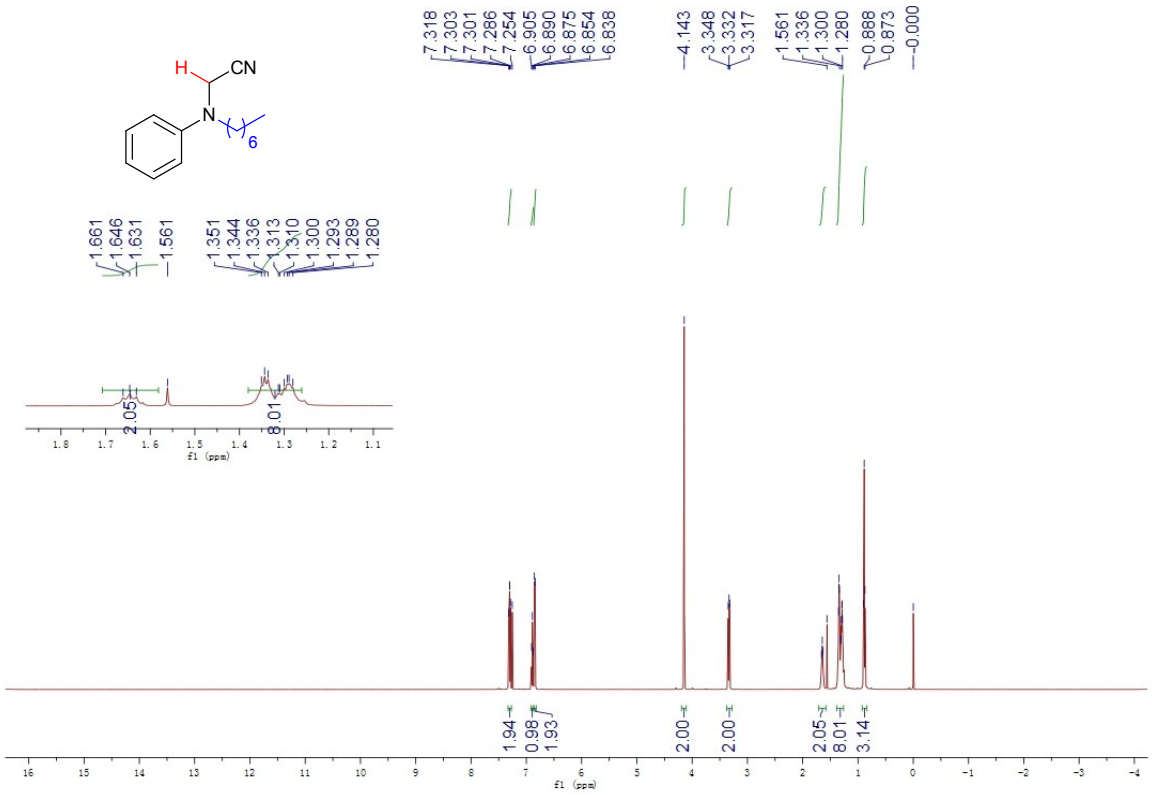


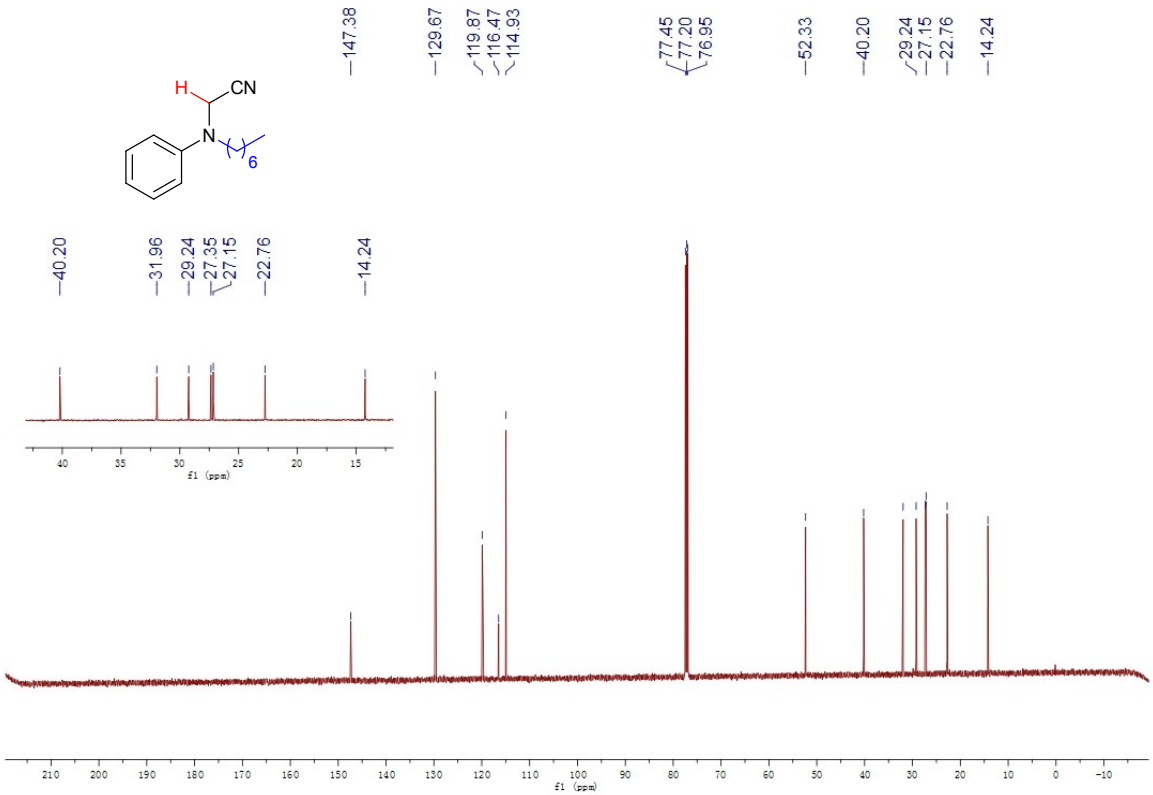
***N*-benzyl-*N*-phenylaminoacetonitrile (2m)**



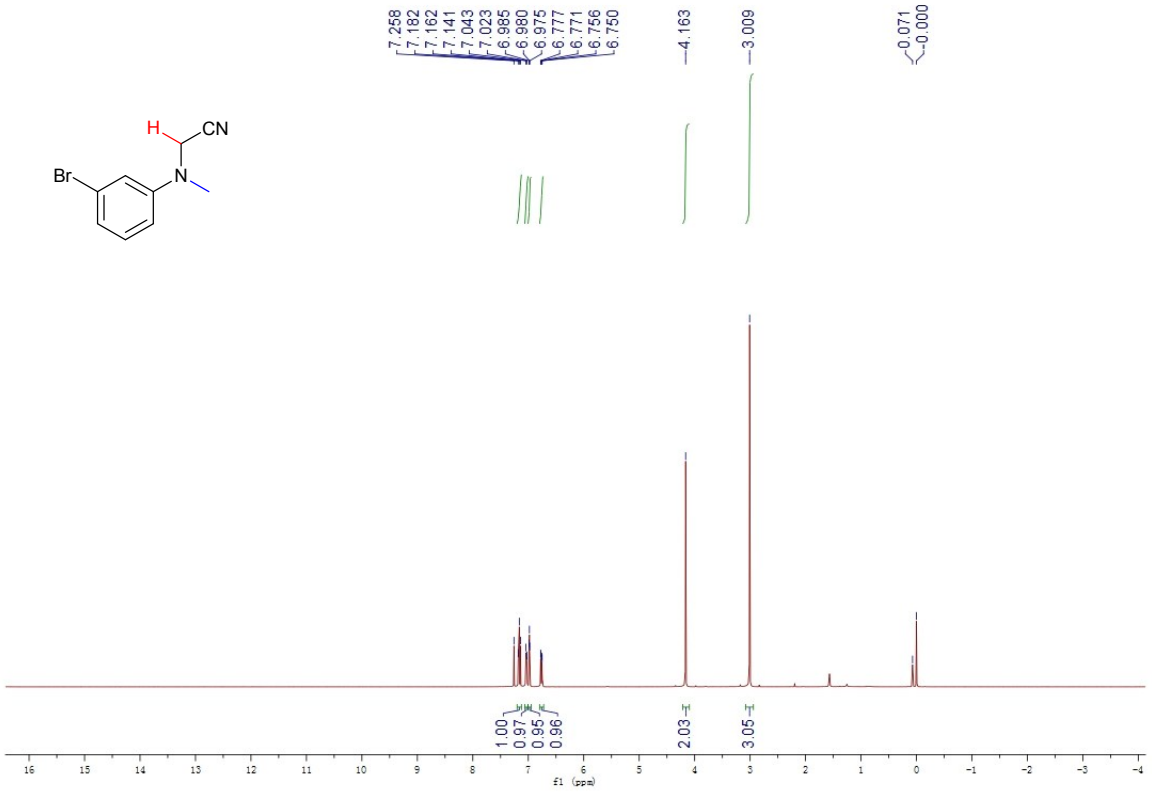


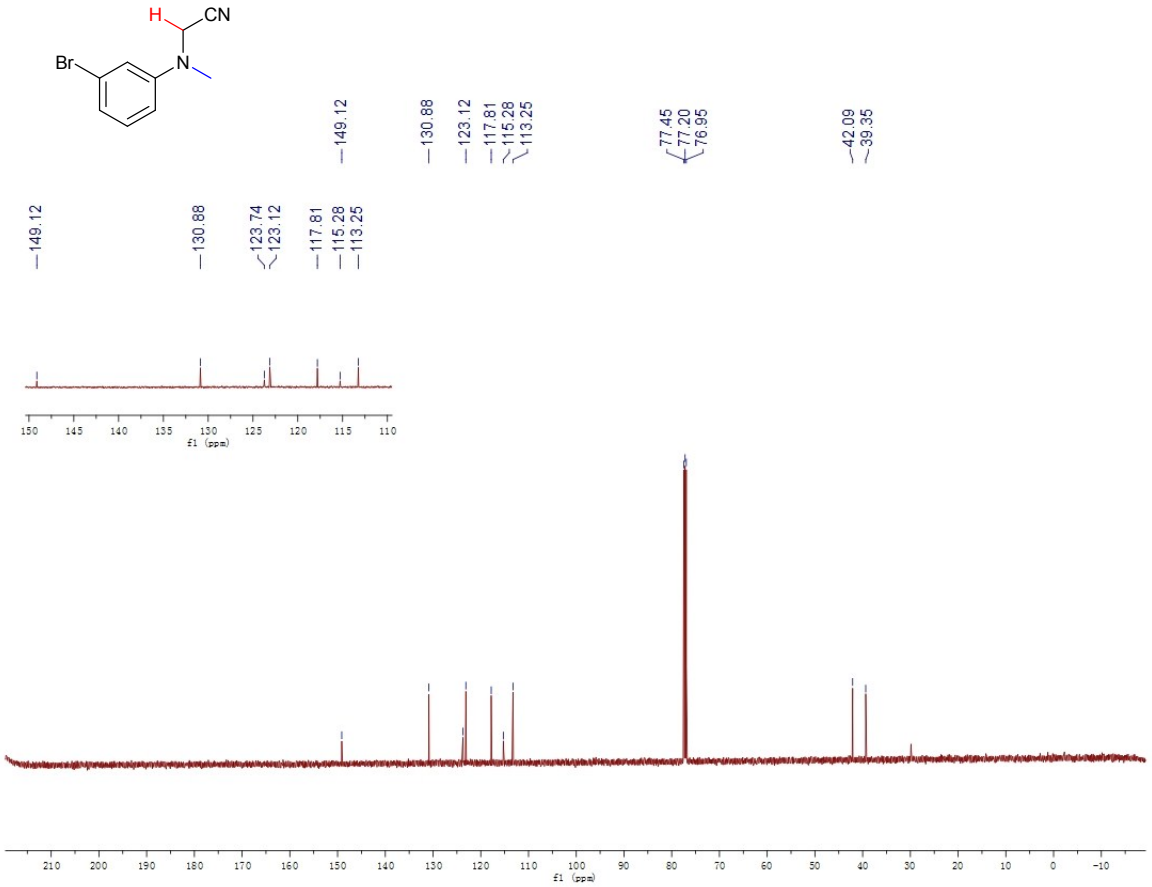
***N*-heptyl-*N*-phenylaminoacetonitrile (2n)**



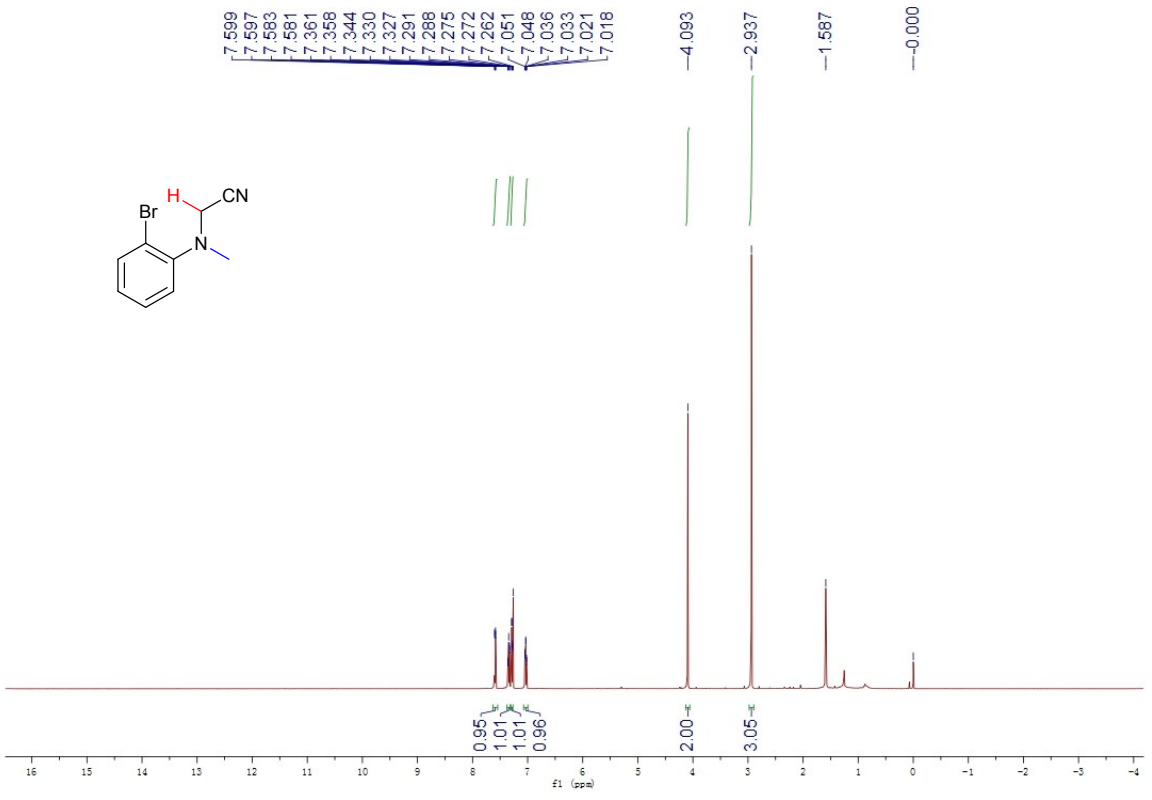


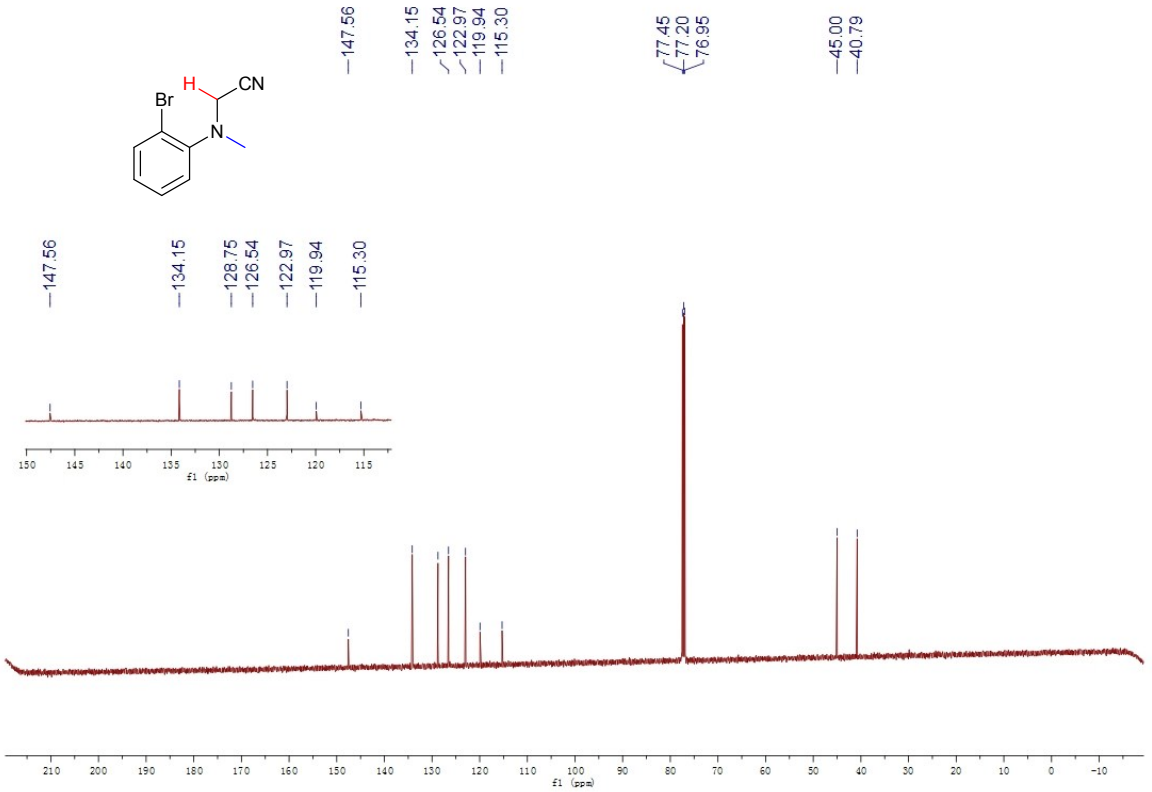
***N*-(3-bromophenyl)-*N*-methylaminoacetonitrile (2o)**



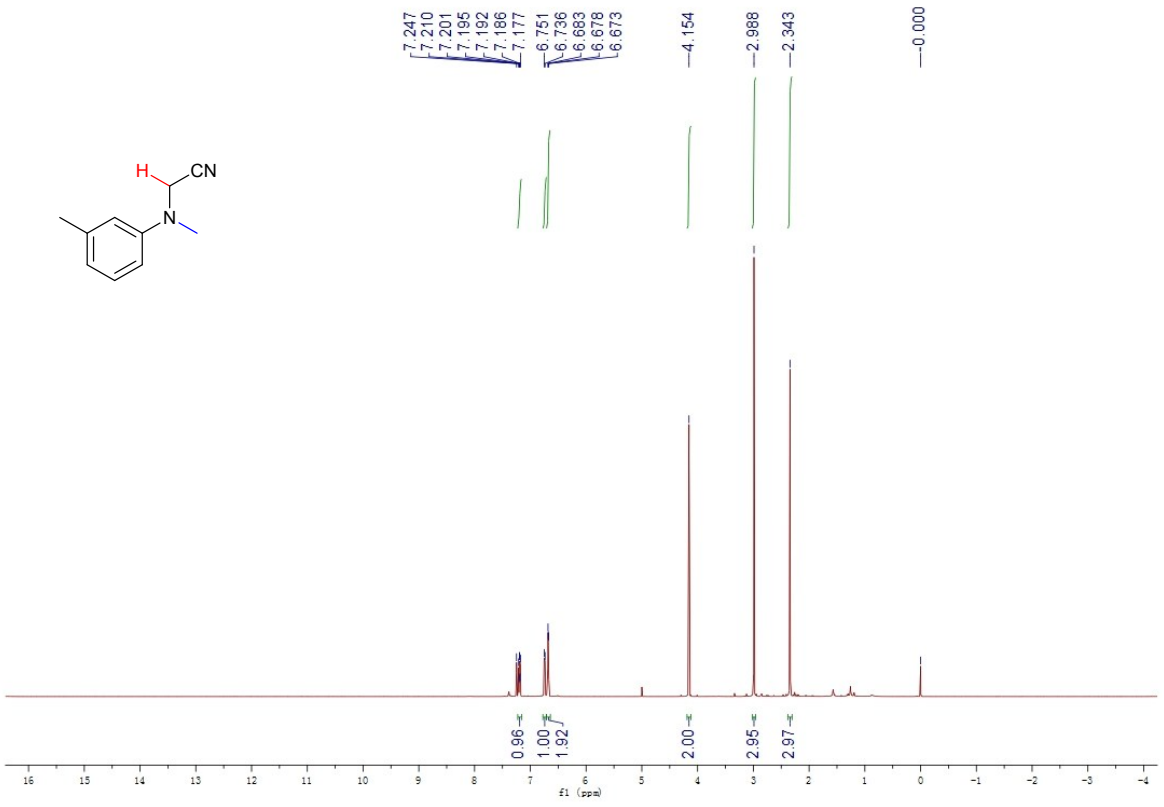


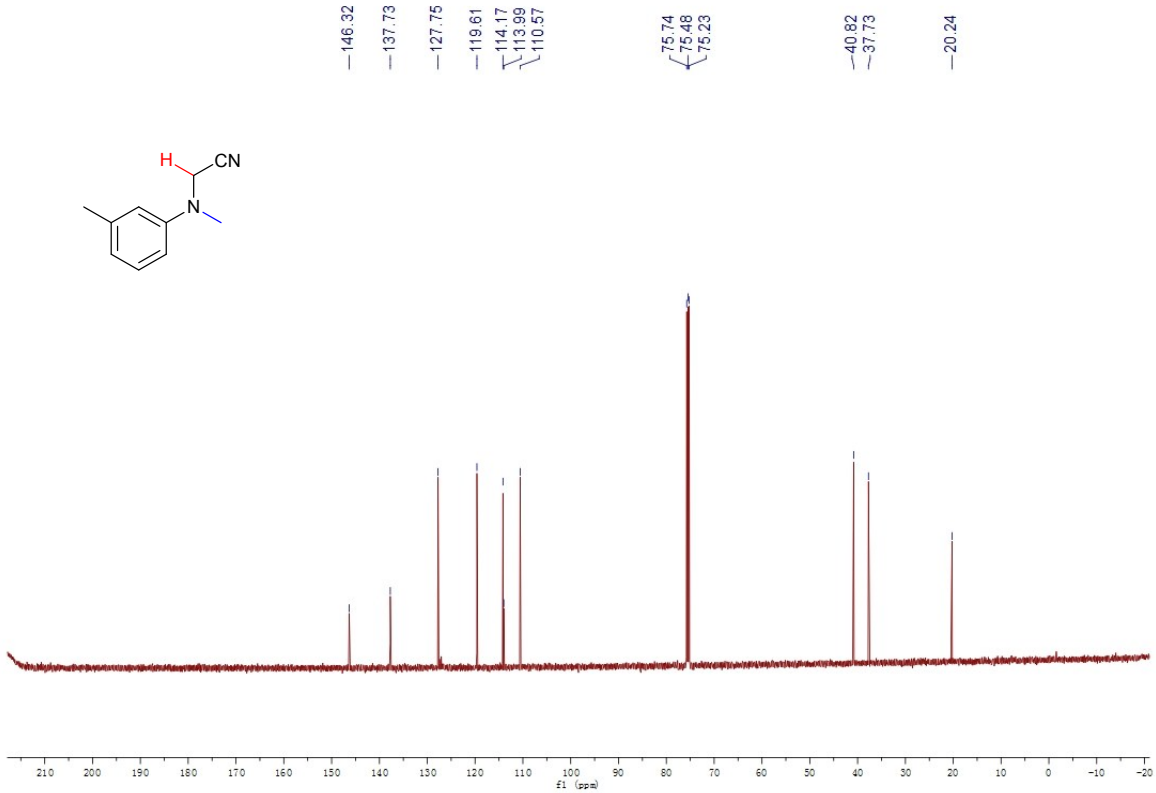
***N*-(2-bromophenyl)-*N*-methylaminoacetonitrile (2p)**



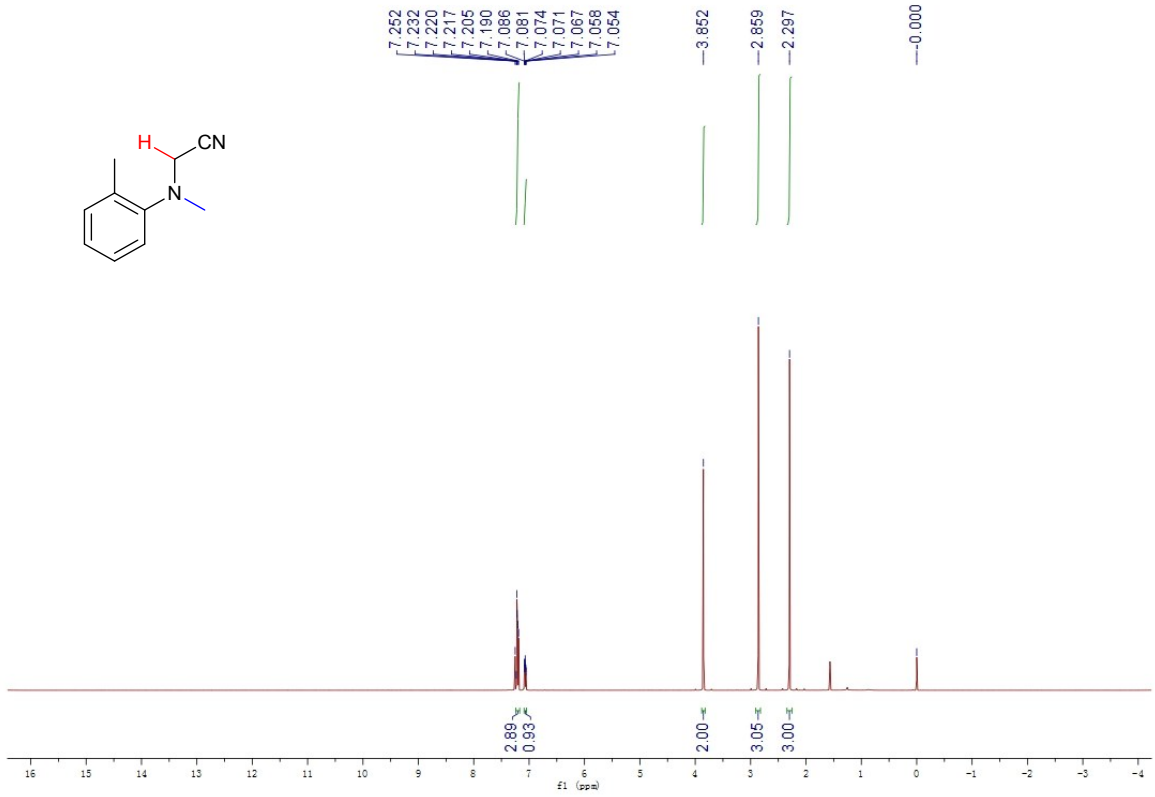


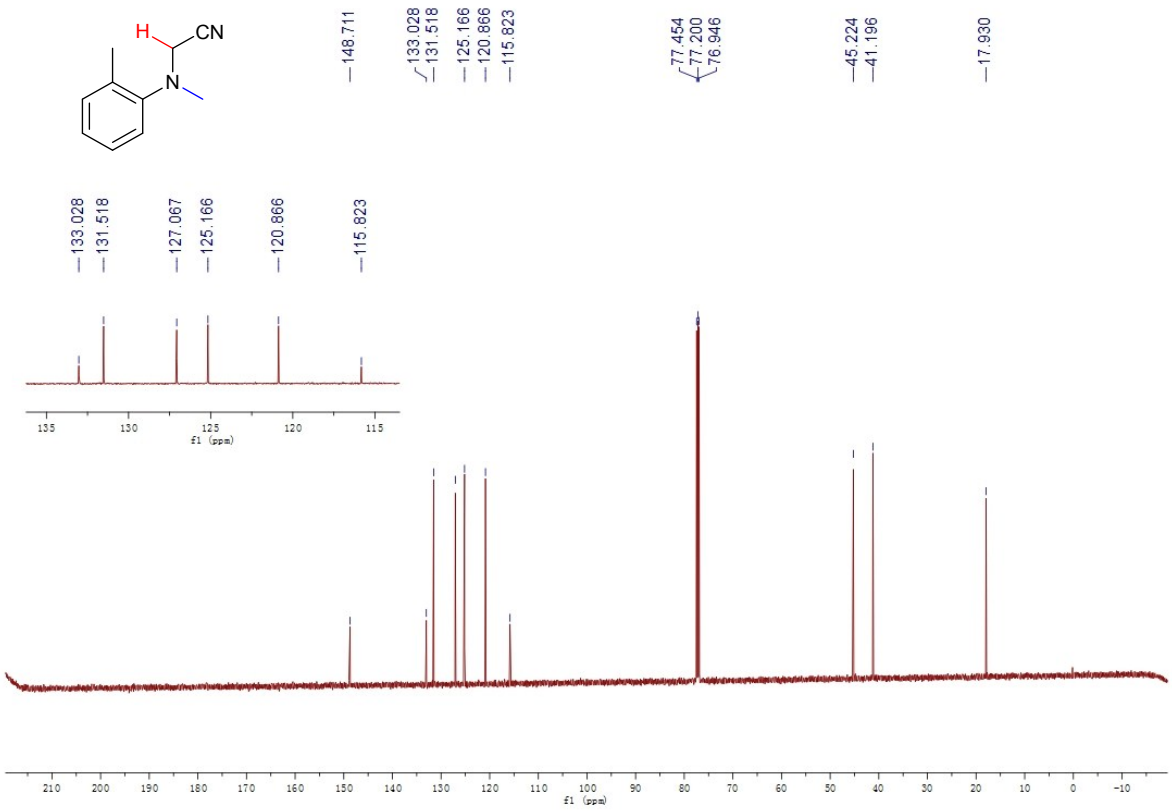
_N_-Methyl-_N_-(3-methylphenyl)aminoacetonitrile (2q)



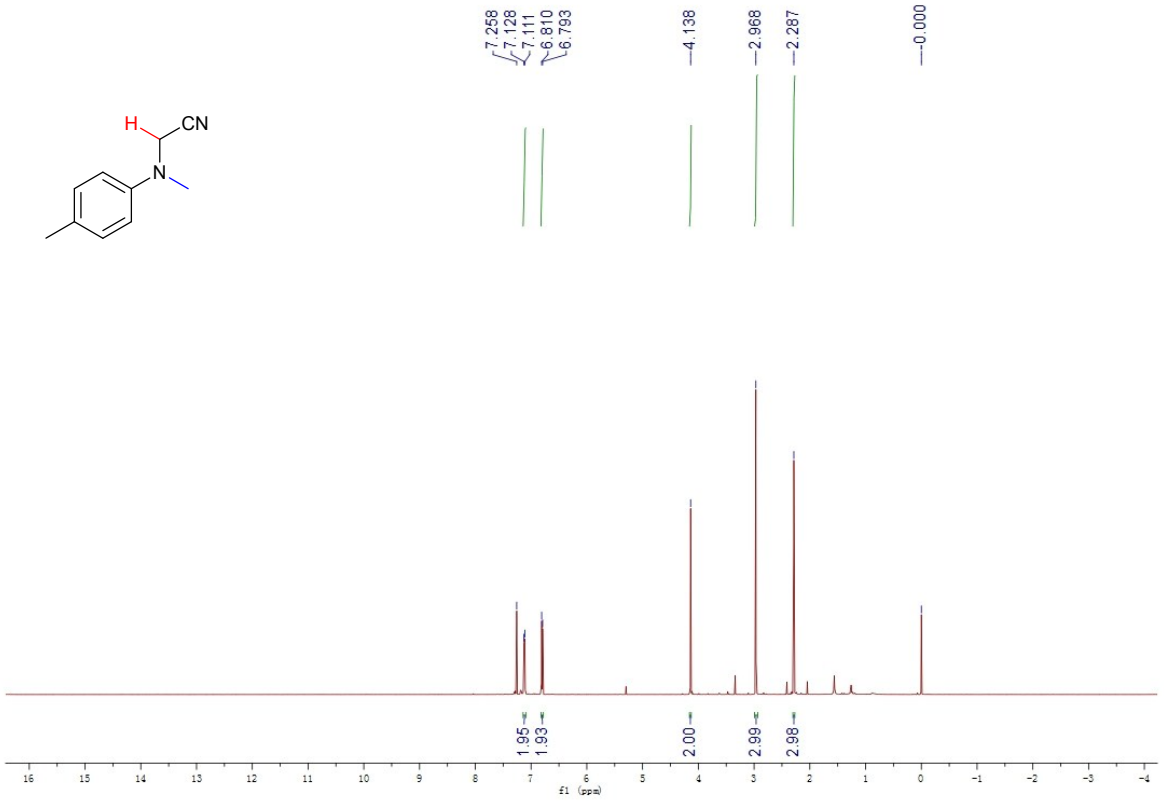


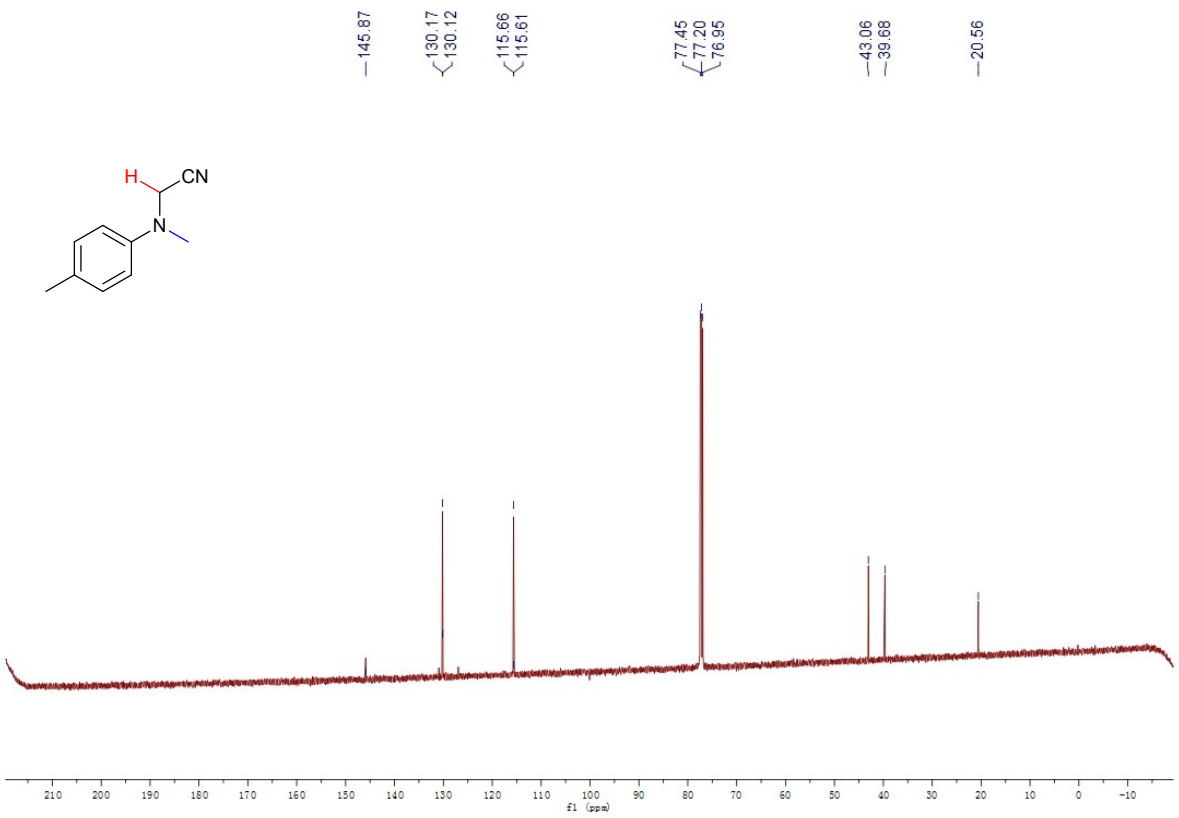
***N*-Methyl-*N*-(2-methylphenyl)aminoacetonitrile (2r)**



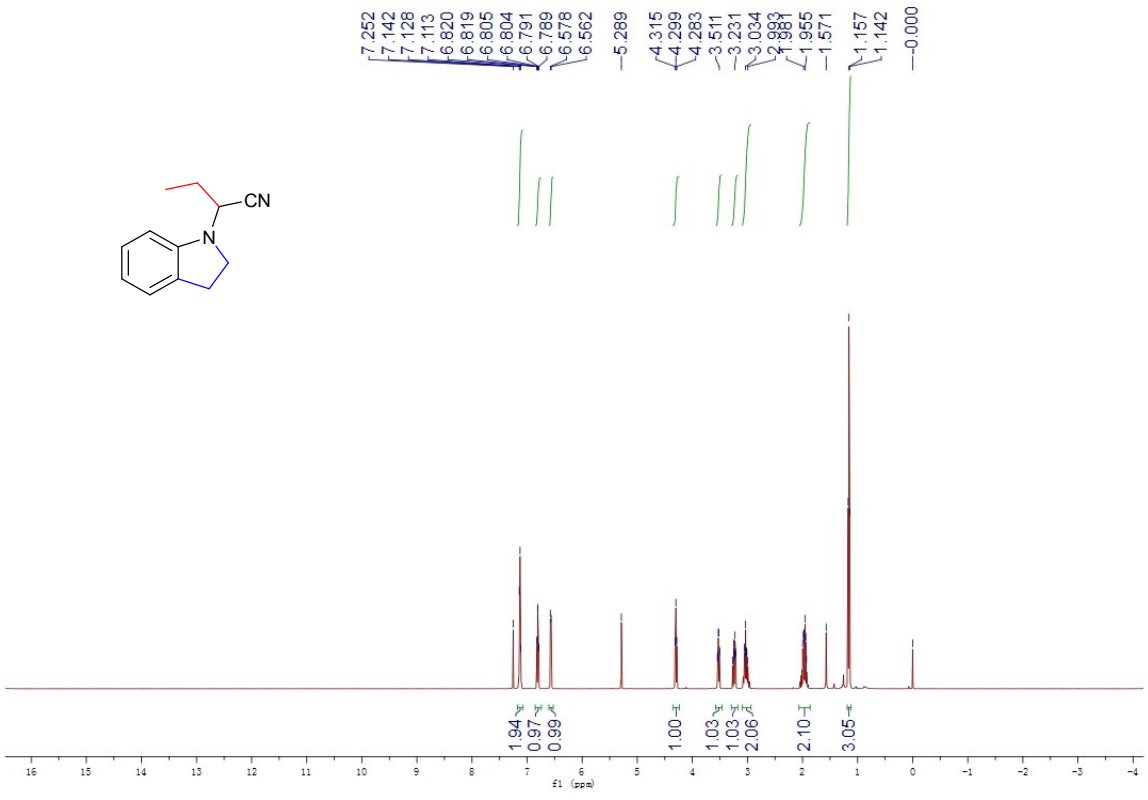


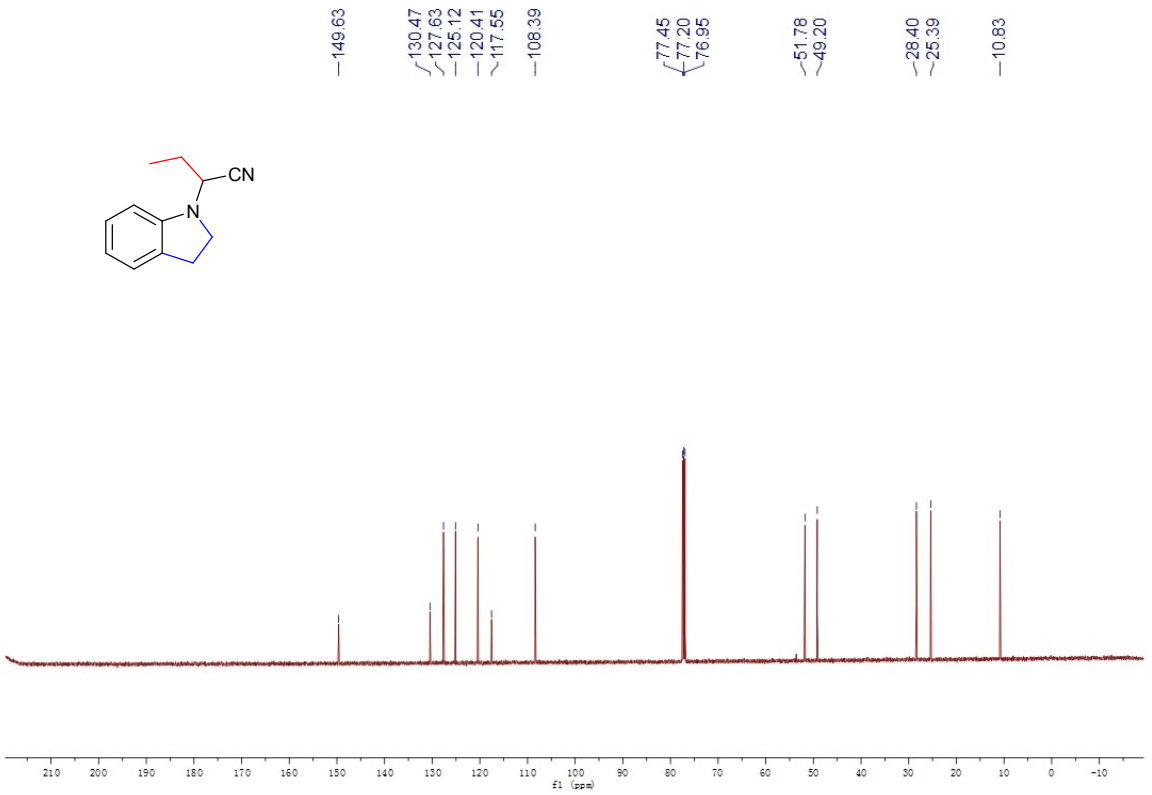
***N*-Methyl-*N*-(4-methylphenyl)aminoacetonitrile (2s)**



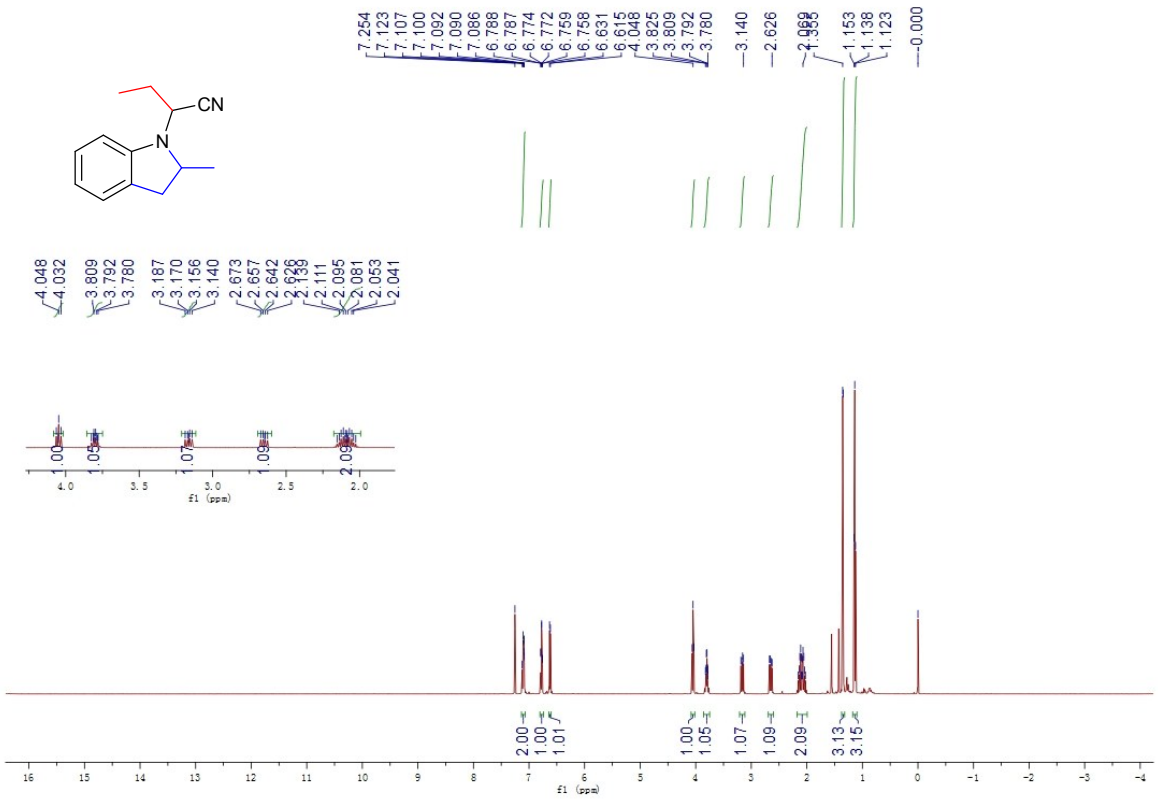


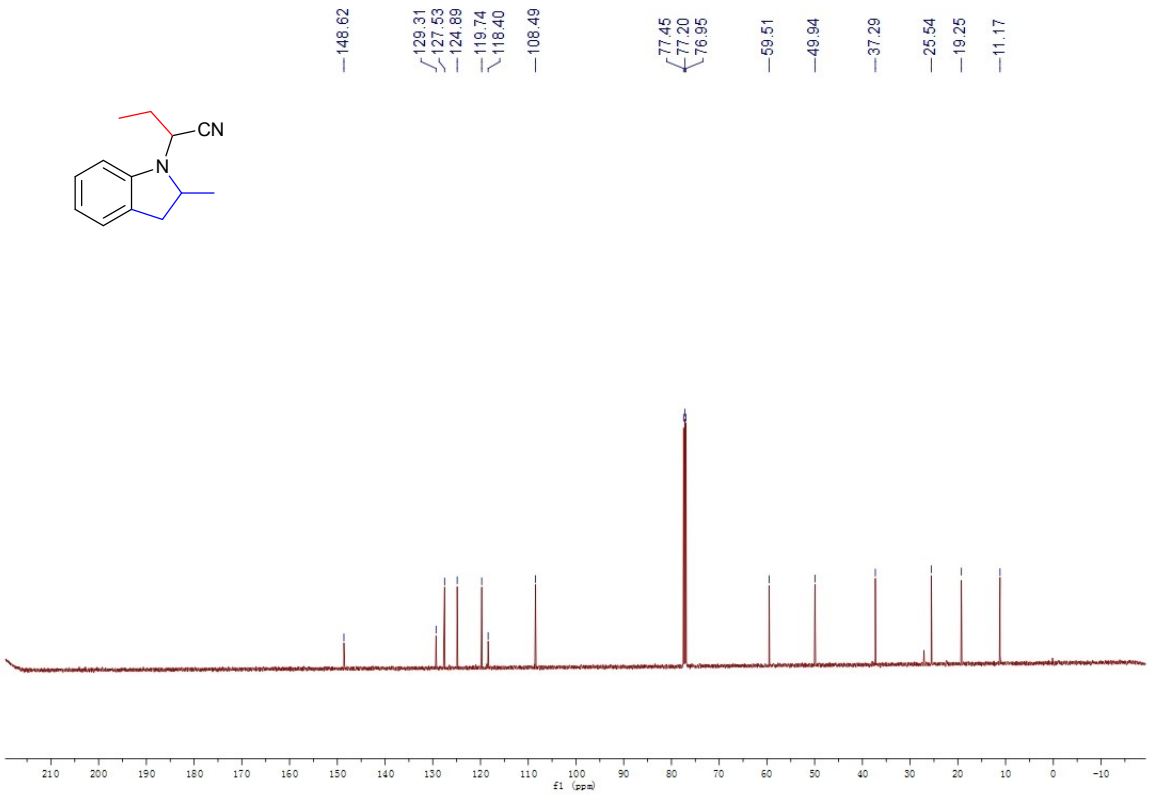
2-(indolin-1-yl)butanenitrile (2t)



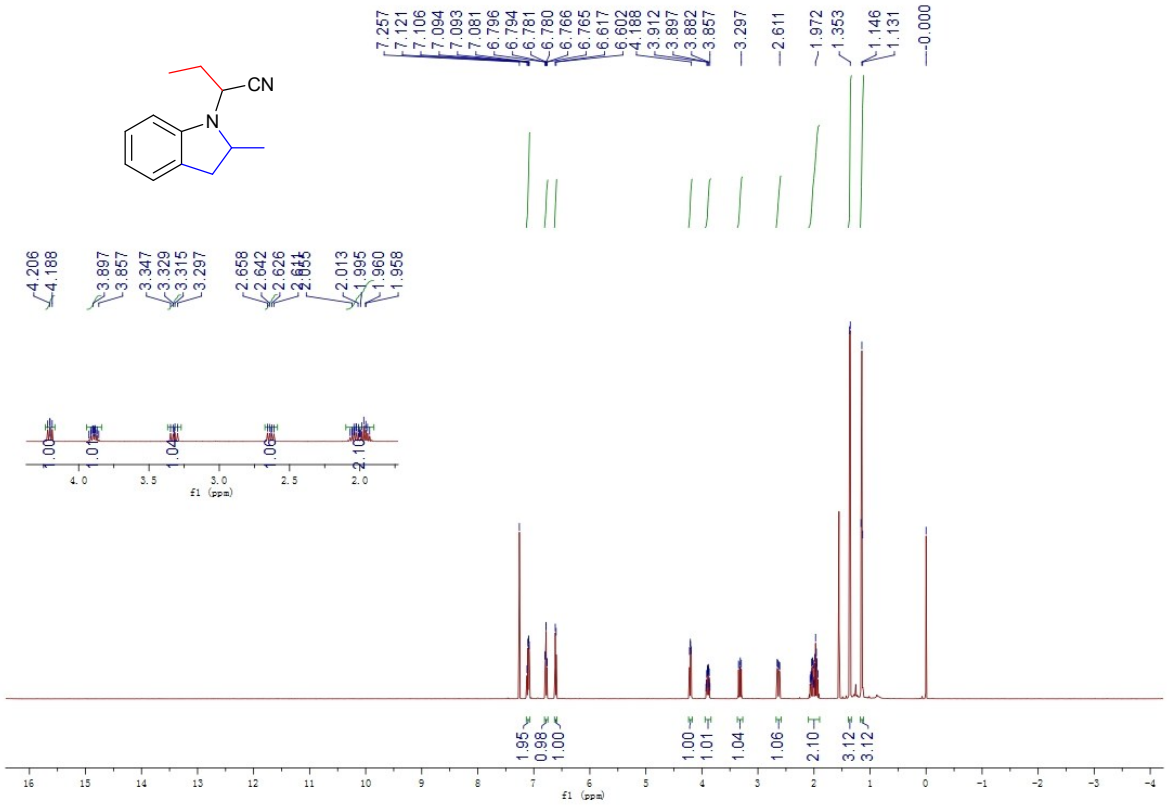


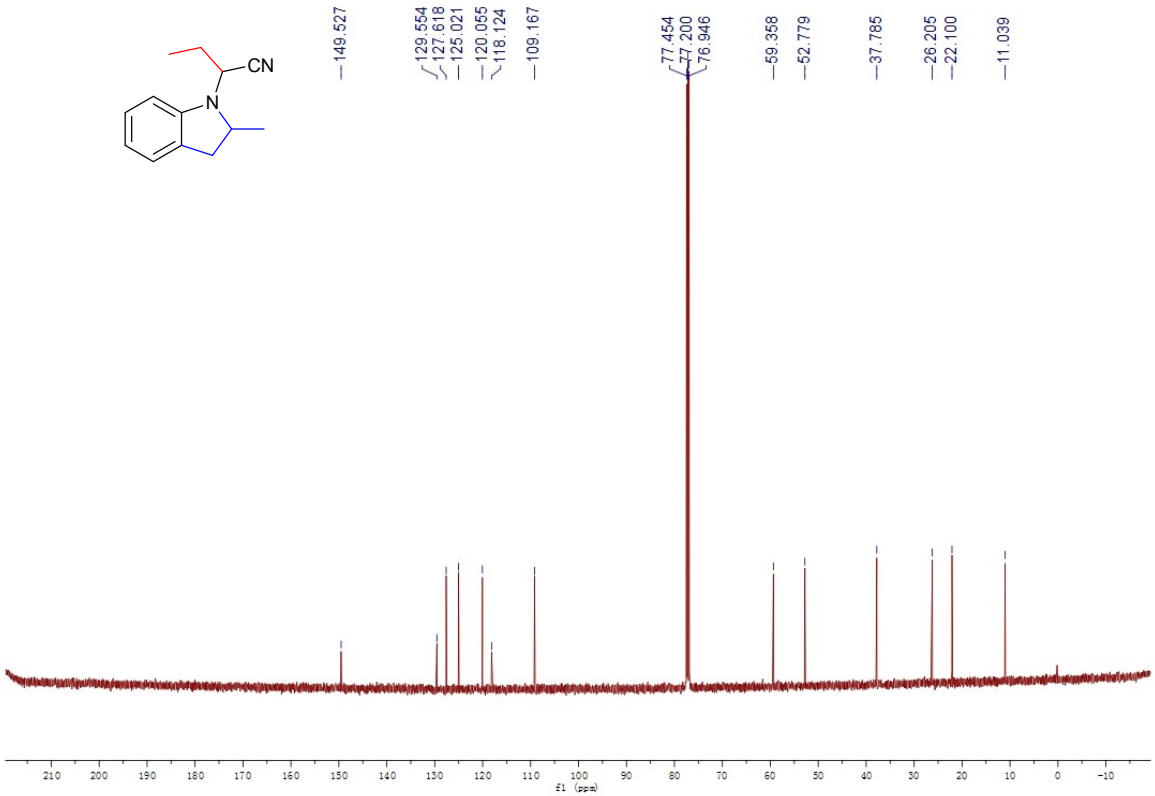
2-(2-methylindolin-1-yl)butanenitrile (2u) (Major isomer)



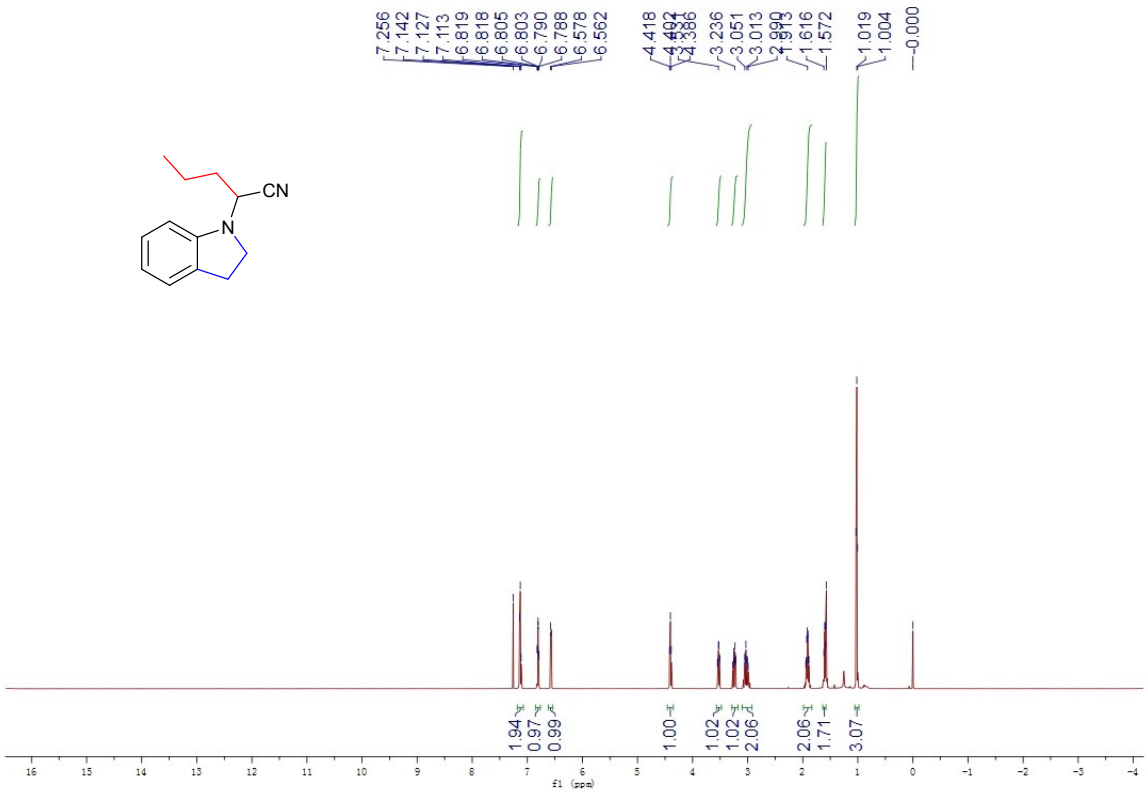


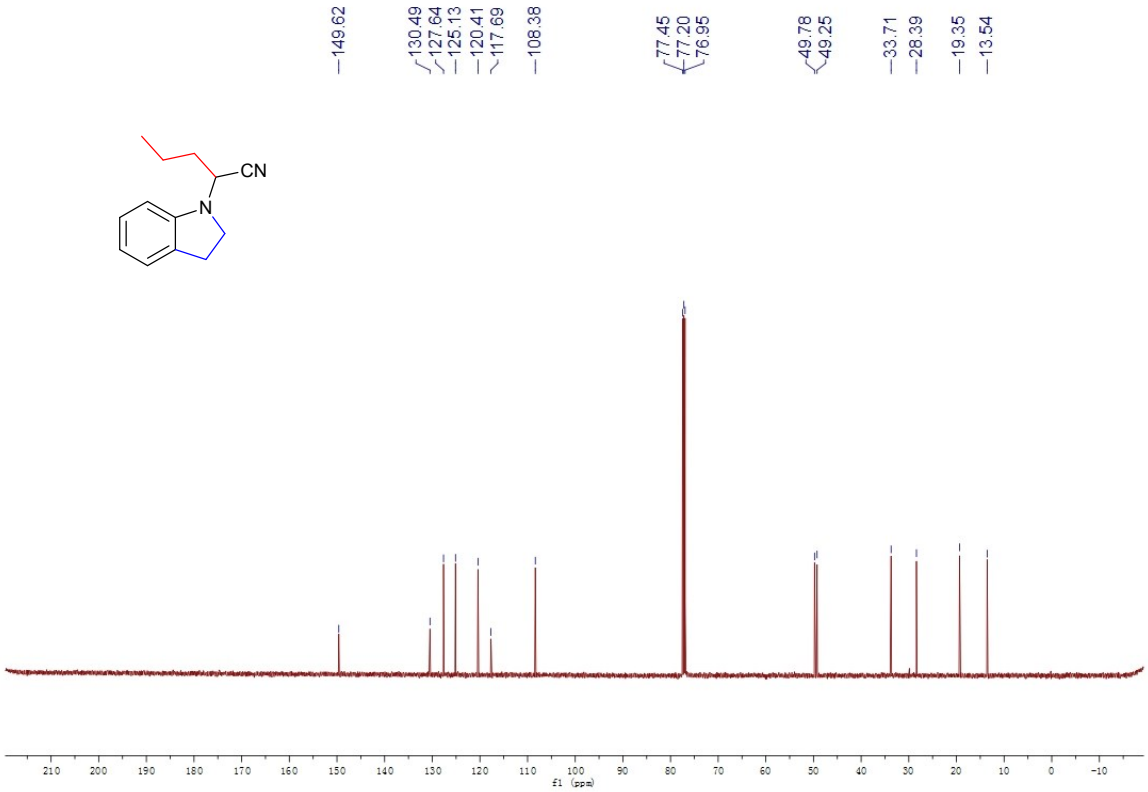
2-(2-methylindolin-1-yl)butanenitrile (2u) (Minor isomer)



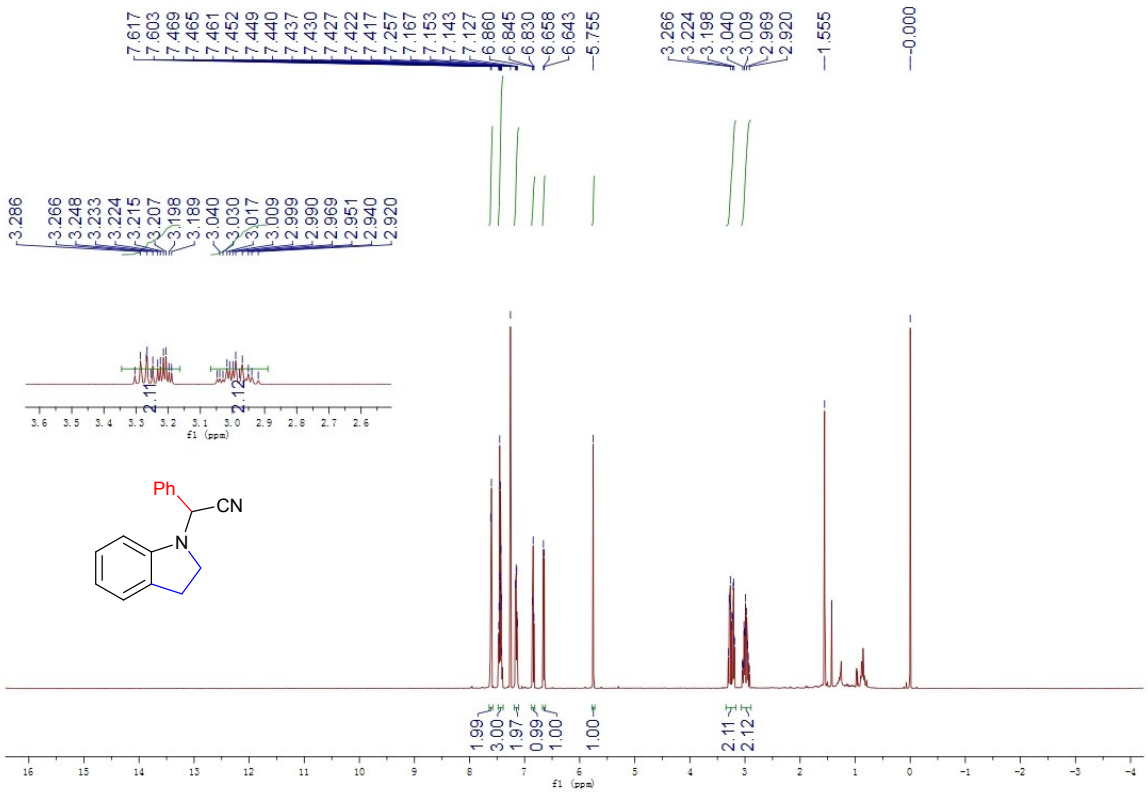


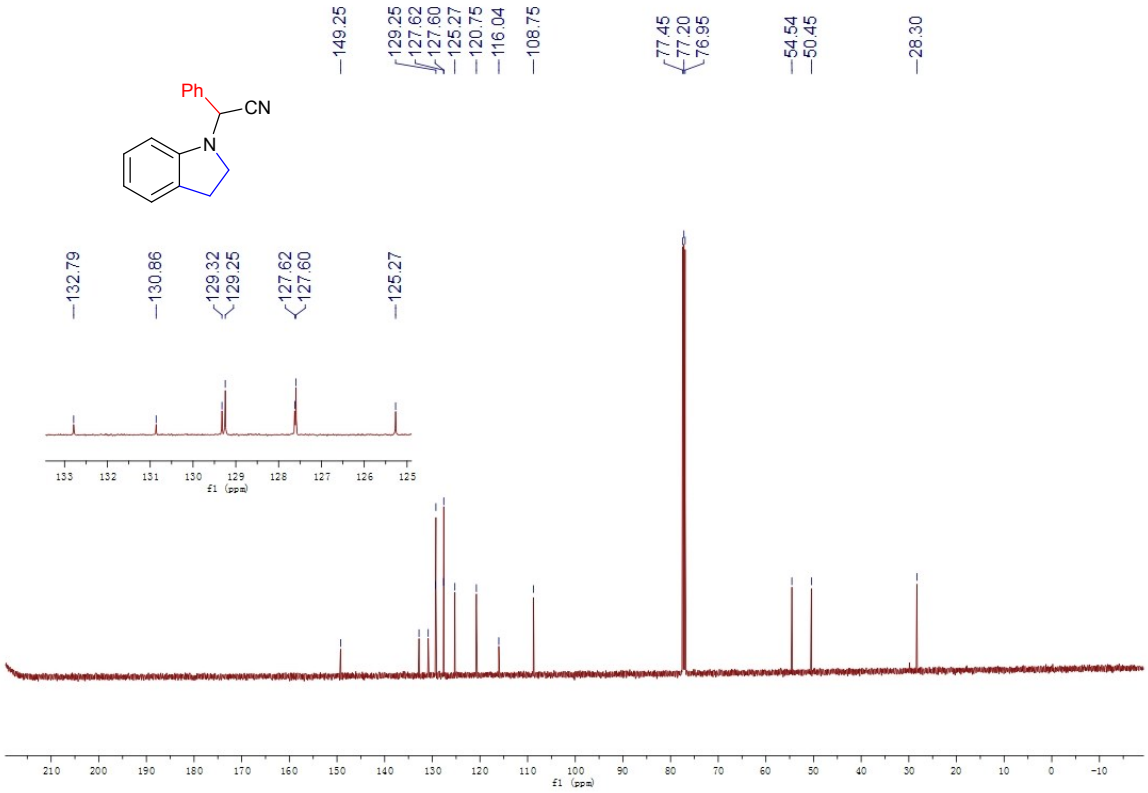
2-(indolin-1-yl)pentanenitrile (2v)



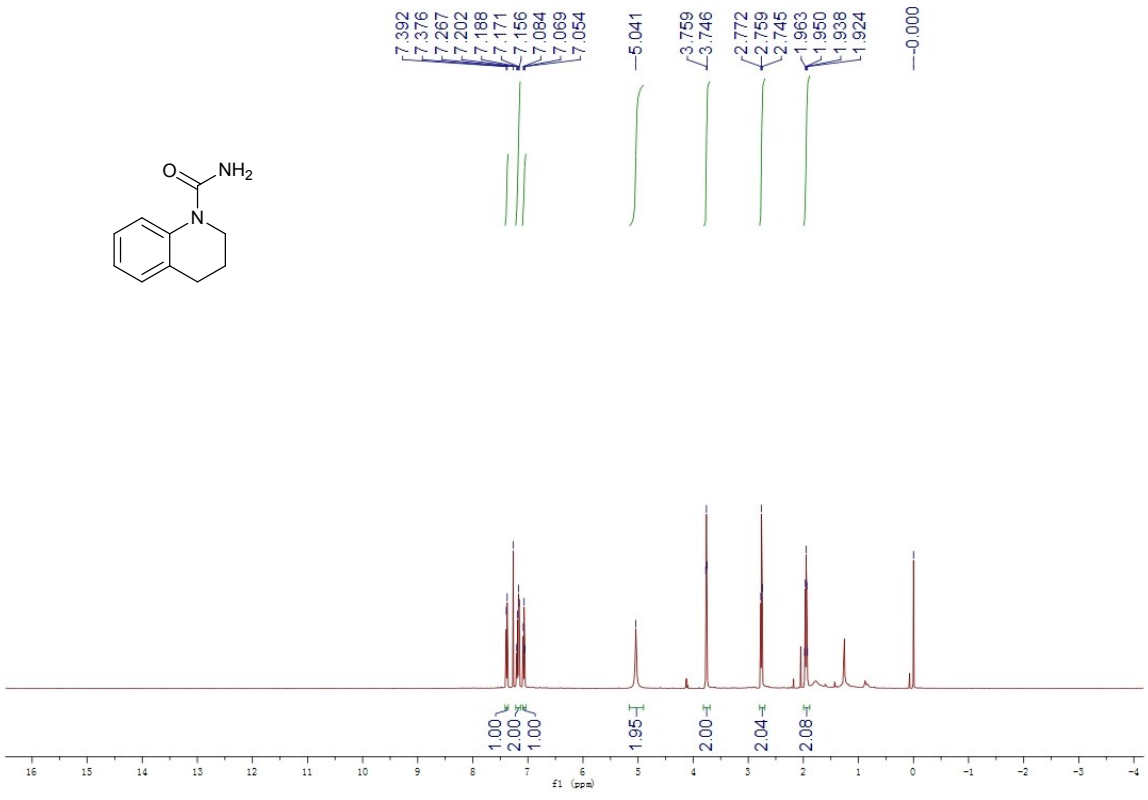


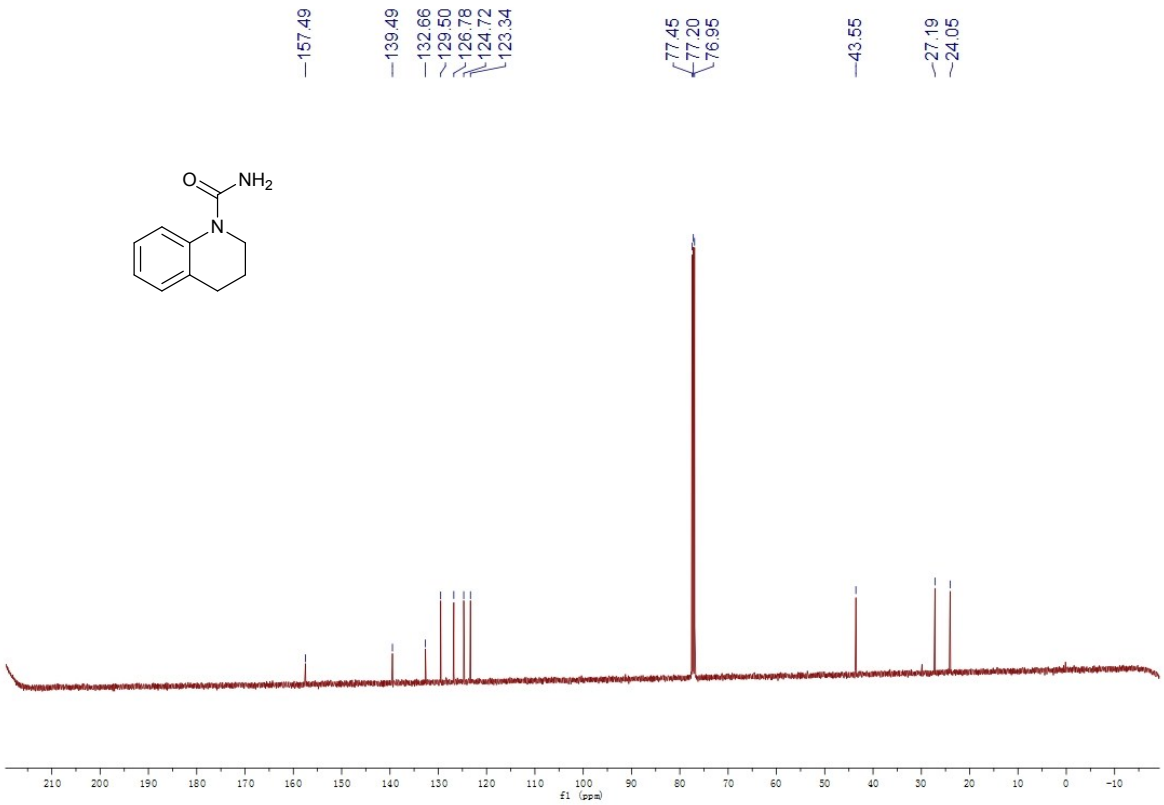
2-(indolin-1-yl)-2-phenylacetonitrile (2w)



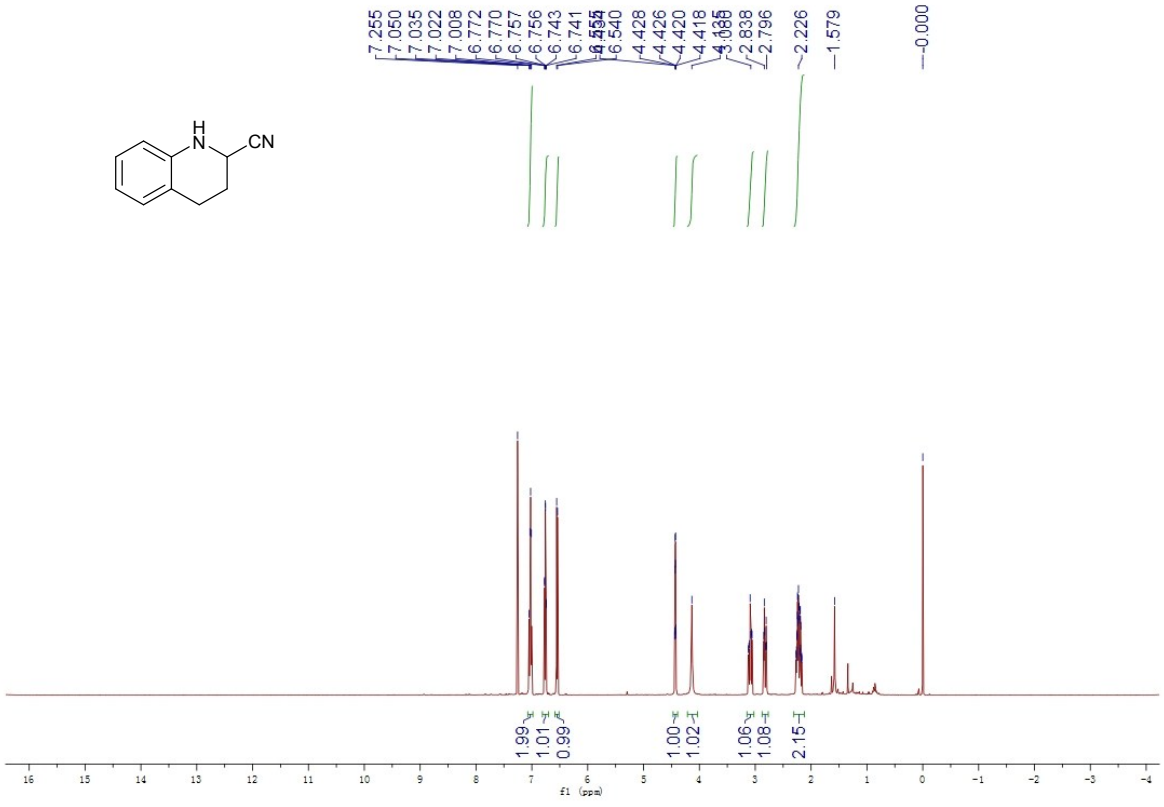


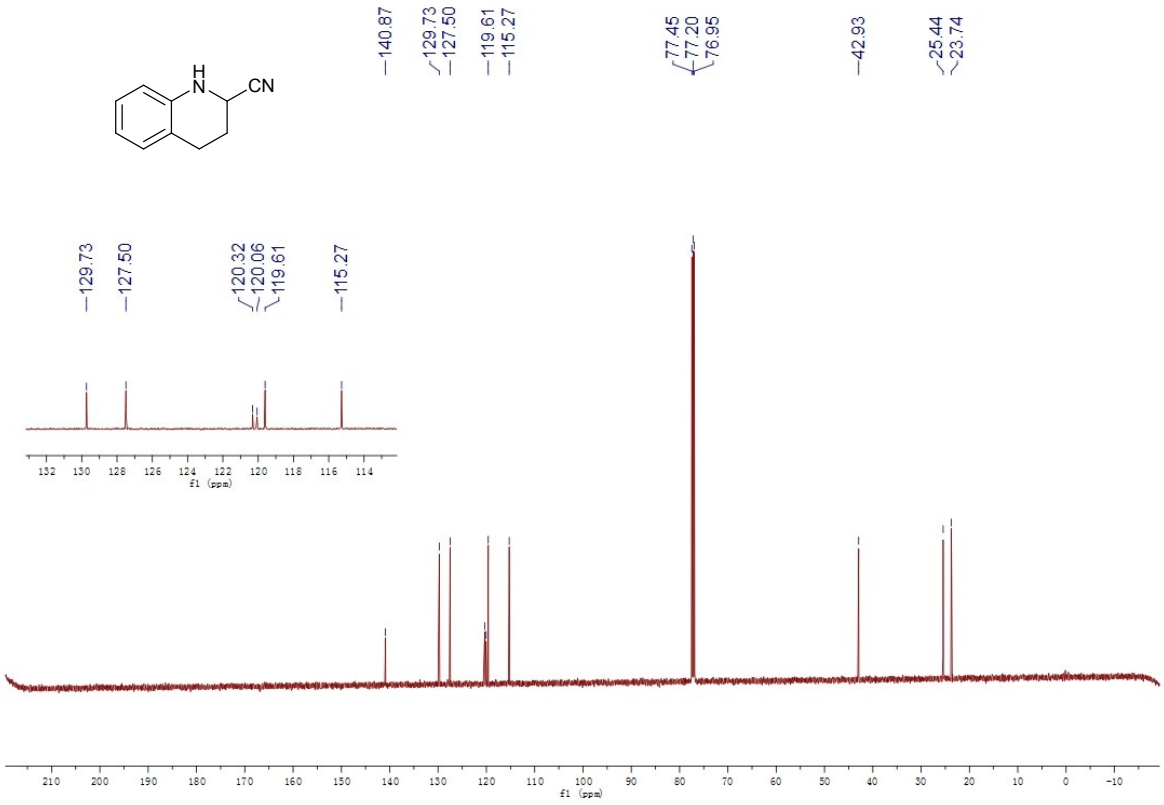
3,4-dihydroquinoline-1(2H)-carboxamide (3)



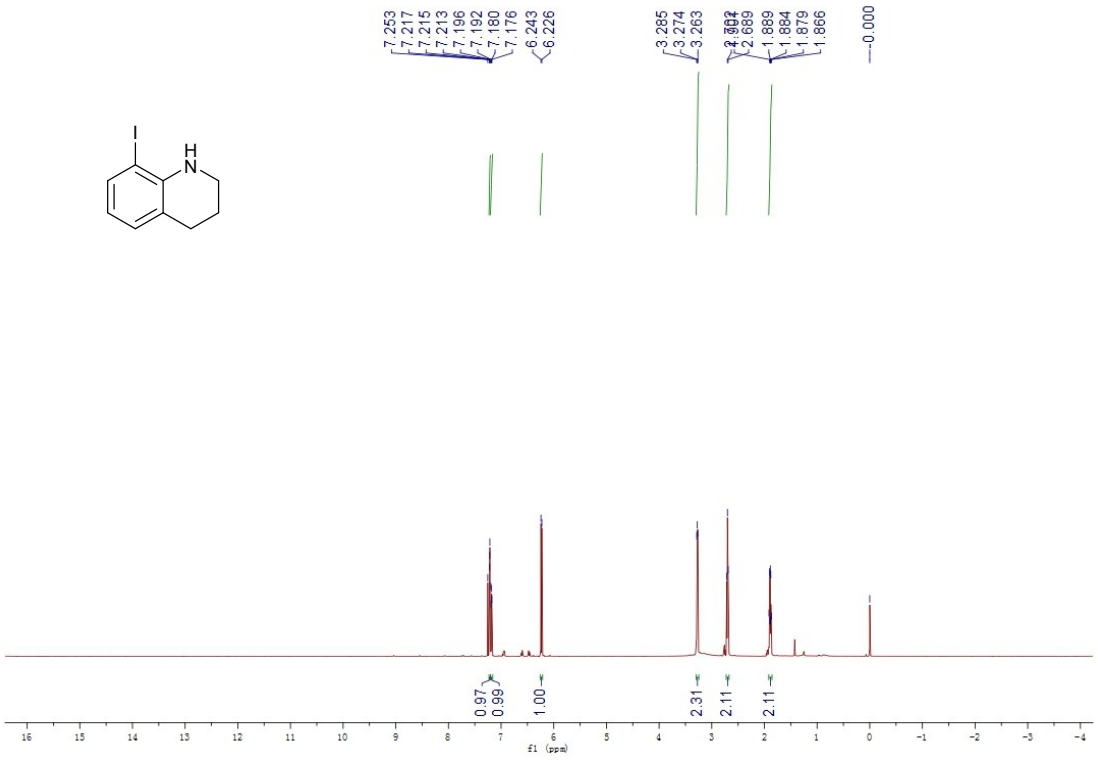


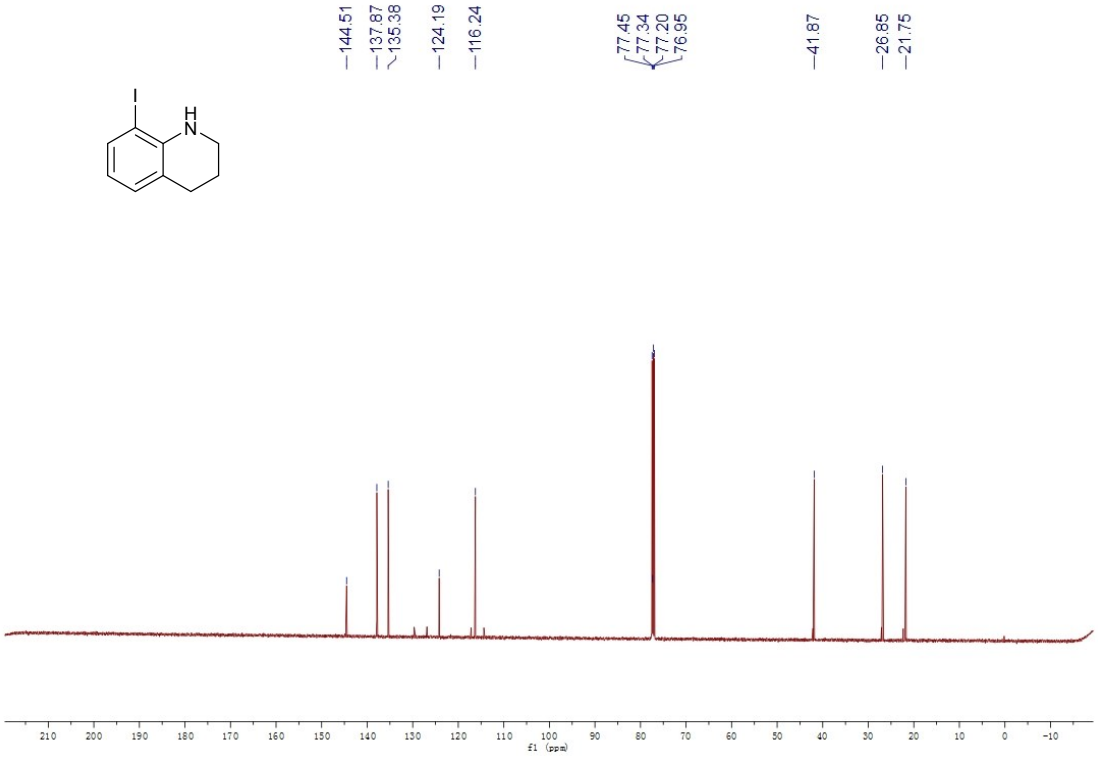
1,2,3,4-tetrahydroquinoline-2-carbonitrile (4)





8-iodo-1,2,3,4-tetrahydroquinoline (5)

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26.85
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I
H
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)