Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Intramolecular Aminocyanation of Alkenes Promoted by Hypervalent Iodine

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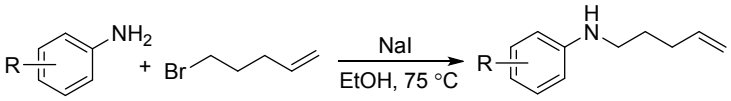
1. General Methods

^{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) 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

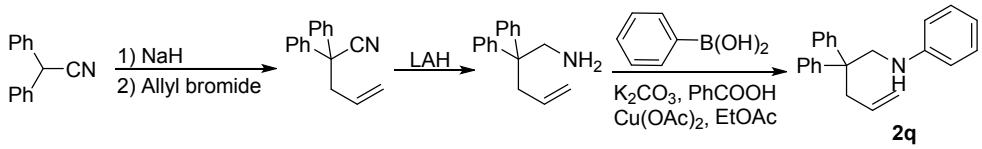
2.1 General procedure for synthesis of 2a-p



2

Compound **2a-p** were synthesized according to the reported method:[1] To a solution of aniline (5 mmol) and 5-bromo-1-pentene (1 mmol for **2a-d**, **2f, 2o, 2p** and 3 mmol for **2e**, **2g-n**) in ethanol (25 mL) was added NaI (0.1 mmol,). The mixture was stirred overnight at 75 °C and the solvent was removed *in vacuo*. The resulting oily residue was chromatographed to give **2a-p**.

2.2 Procedure for synthesis of 2q



2q

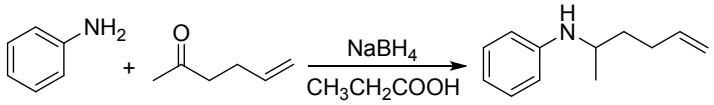
Compound **2q** were synthesized according to the reported method:[1,2] To a solution of diphenylacetonitrile (4.83 g, 25 mmol) in DMF (10 mL) was added slowly a suspension of NaH (0.66 g, 28 mmol) in DMF (25 mL), and the resulting mixture was stirred at room temperature for 1 h. The resulting bright yellow suspension was cooled to 0 °C, treated with allyl bromide (3.33 g, 28 mmol), warmed to room temperature and stirred at room temperature for 12 hours. The resulting solution was poured into ice/water (100 mL) and was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layer was washed with water (2 x 25 mL), dried with anhydrous $MgSO_4$, and concentrated to give 2,2-diphenyl-4-pentenenitrile which was used in the subsequent step without further purification.

To a suspension of LAH (1.52 g, 40 mmol) in ether (130 mL) was added 2,2-diphenyl-4-

pentenenitrile (2.33 g, 10 mmol) at 0 °C. The mixture was slowly warmed to room temperature and stirred overnight. The resulting suspension was cooled to 0 °C and quenched by slow addition of 6 M NaOH (50 mL). The resulting mixture was extracted with ether (4 x 100 mL) and the combined ether extracts were dried ($MgSO_4$) and concentrated. The crude oil was purified by column chromatography to give 2,2-diphenyl-4-penten-1-amine as a pale yellow.

To a premixed ethyl acetate solution of $Cu(OAc)_2$ (0.18 g, 1 mmol), benzoic acid (0.31 g, 2.5 mmol), and K_2CO_3 (0.69 g, 5 mmol) was added 2,2-diphenyl-4-penten-1-amine (1.19 g, 5 mmol) and phenylboronic acid (1.83 g, 15 mmol) at room temperature. The resulting mixture was allowed to run at 80 °C until the starting material is consumed completely. The solvent was removed using a rotary evaporator to produce a residue that was purified by column chromatography on silica gel to yield the final desired product **2q** as white solid.

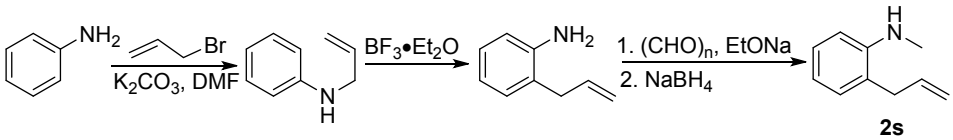
2.3 Procedure for synthesis of 2r



2r

Compound **2r** were synthesized according to the reported method:[3]To an ice cooled, stirred mixture of aniline (1.2 mL，14 mmol), hex-5-en-2-one (4 mL，34 mmol) and propionic acid (0.35 mL，5 mmol) was added sodium borohydride (380 mg，10 mmol) portionwise at such a rate as to keep the temperature less than 5°C. The reaction mixture was allowed to warm up to room temperature and stirred for 4 h. The reaction mixture was then poured into an ice water mixture, and extracted with ethyl acetate. The organic phase was washed with water, 2% hydrochloric acid and water. The dried organic phase was evaporated to purified by column chromatography on silica gel to yield **2r** as yellow oil.

2.4 Procedure for synthesis of 2s



2s

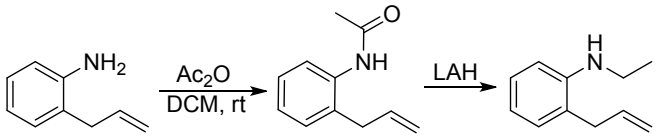
Compound **2s** were synthesized according to the reported method:[4,5] Allyl bromide (1.40 mL, 16.24 mmol) was added dropwise to a solution of aniline (16.24 mmol) and K_2CO_3 (5.39 g, 38.97 mmol) in DMF (37 mL). The solution was stirred at room temperature for overnight. The reaction mixture was then filtered, washed with water (3 x 20 mL) and extracted with Et_2O (3 x 15 mL). The combined organic extracts were washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography to afford the *N*-allyl aniline as yellowish oil.

Next, *N*-allyl aniline (2 g, 15 mmol) was dissolved in *p*-xylene (15 mL) at 0 °C under nitrogen atmosphere. $BF_3 \cdot Et_2O$ (2.1 mL, 16.5 mmol) was added and the solution was heated at 150 °C for

24 h. After dilution with ether (30 mL), the mixture was washed with a saturated $NaHCO_3$ solution (3 x 50 mL) and the aqueous phase was further extracted with ether (3 x 40 mL). The combined organic layers were washed with brine (2 x 40 mL), dried over anhydrous Na_2SO_4, then concentrated *in vacuo*. The reaction residue was purified by silica gel chromatography to afford *o*-allylanline .

To a 50 mL oven-dried flask with a magnetic stirring bar, *o*-allylanline (2.08 g, 10.0 mmol) and paraformaldehyde (0.5 g, 15.0 mmol) was dissolved in CH_3OH (20.0 mL), and EtONa (3.43 g, 50 mmol) was added slowly over 5 min. After stirring at 80 °C for 6 h, $NaBH_4$ (0.42 g, 11.0 mmol) was added slowly at rt. The mixture was refluxed for 5 h, and then the residue was quenched with saturated ammonium chloride solution (50 mL). The aqueous phase was extracted with ethyl acetate (3 x 25 mL). The combined organic phase was dried with anhydrous Na_2SO_4, the crude product was purified by column chromatography to obtain **2s** as yellow oil.

2.5 Procedure for synthesis of 2t

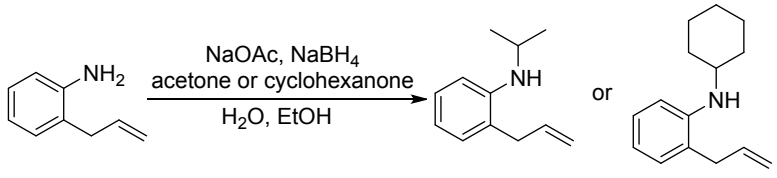


2t

Compound **2t** were synthesized according to the reported method:[6] *o*-allylanline (2.08 g, 10 mmol) was added to a round-bottom flask via syringe and fitted with a rubber septum. The flask was purged with argon and dry DCM (30 mL) was added. Acetic anhydride (1.13 mL, 12 mmol,) was added and the reaction was stirred at room temperature and monitored by TLC. Upon completion the reaction mixture was washed with a saturated solution of sodium carbonate, the organic layers dried with anhydrous $MgSO_4$ and the solvent removed under reduced pressure. The product was obtained in quantitative yield.

A round bottomed flask was charged with aryl amide (1.40 g, 8 mmol) in THF (25 mL), flushed with argon and cooled to 0 °C. LAH (0.79 g, 21 mmol) was added slowly to the flask. The reaction was let warm to room temperature and react overnight. The reaction was quenched by cooling to 0 °C and adding $Na_2SO_4 \cdot 10H_2O$ until LAH was consumed completely. The solution was let stir for 0.5 hour then filtered through a frit, the solid was washed with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The crude extracts were purified by column chromatography to obtain **2t** as light yellow oil.

2.6 Procedure for synthesis of 2u and 2w

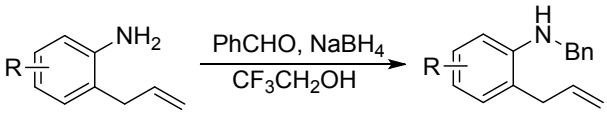


2u **2w**

Compound **2u** and **2w** were synthesized according to the reported method:[7] To a water and

ethanol (1:1) solution (25 mL) of *o*-allylanline (2.08 g, 10 mmol), sodium acetate trihydrate (4.3 g, 32 mmol), acetic acid (10 mL), and acetone or cyclohexanone (45 mmol), at 0 °C was added sodium borohydride (1.89 g, 50 mmol) slowly; the reaction mixture was stirred at rt for 30 min before basified with 10% aqueous solution of NaOH. The organic layer was extracted with diethyl ether, concentrated and eluted through a silica gel column give compound **2u** and **2w** as light yellow oil.

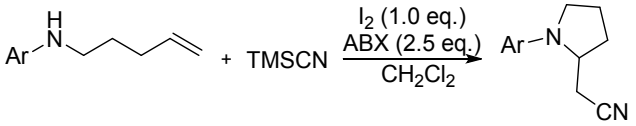
2.7 Procedure for synthesis of 2v and 2x-z



2v, **2x-z**

Compound **2v** and **2x-z** were synthesized according to the reported method:[8] A solution of benzaldehyde (0.3 mL, 3 mmol) and TFE (6 mL) was magnetically stirred at 35-40 °C. After 5 min, the respective *o*-allylanline (3 mmol) was added and the mixture vigorously stirred. After stirring for 15 min, $NaBH_4$ (0.14 g, 3.6 mmol) was added and the progress of the reaction conversion was followed by TLC. After completion of the reaction, the mixture was filtered and the residue was washed with TFE (6 mL). The solvent was distilled off (to recover for the next run) and the crude product was further purified by silica gel column chromatography to give compound **2v** and **2x-z**.

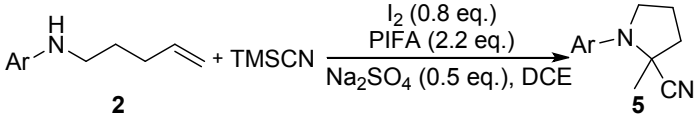
2.8 General procedure for synthesis of 3



2 **3**

To a stirred mixture of alkenylamine **2** (0.5 mmol) and dichloromethane (5 mL) in a seal tube was successively added TMSCN (0.32 mL, 2.5 mmol) and iodine (127 mg, 0.5 mmol) at room temperature. After three minutes, ABX (383 mg, 1.25 mmol) was added and the resulting mixture was stirred at 35 °C for 5 h. Subsequently, into the mixture was poured saturated aqueous $NaHCO_3$ (3 mL) and $Na_2S_2O_3$ (3 mL), then extracted with dichloromethane. The organic layer was washed with brine, dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The residue was chromatographed on a silica gel column to give cyanated pyrrolidine **3.**

2.9 General procedure for synthesis of 5

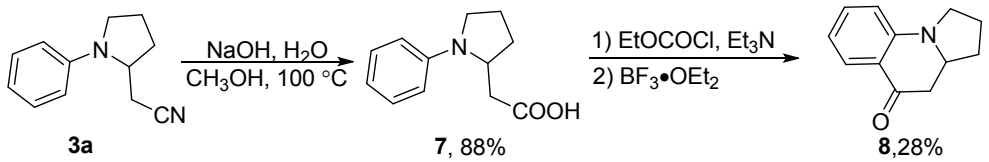


2 **5**

To a stirred mixture of alkenylamine **2** (0.5 mmol) and dichloroethane (5 mL) in a seal tube was successively added TMSCN (0.19 mL, 1.5 mmol), Na_2SO_4 (36 mg, 0.25 mmol) and iodine (102 mg, 0.4 mmol) at room temperature. After cooling to 0°C and addition of PIFA (473 mg, 1.1

mmol), the resulting mixture was stirred for 0.5 h. Subsequently, into the mixture was poured saturated aqueous $NaHCO_3$ (3 mL) and $Na_2S_2O_3$ (3 mL), then extracted with dichloromethane. The organic layer was washed with brine, dried over magnesium sulfate and concentrated *in vacuo*.. The residue was chromatographed on a silica gel column to give 2-cyano pyrrolidine **5**.

2.10 Procedure for synthesis of 8

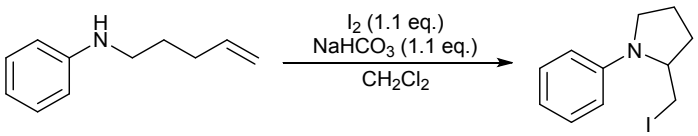


3a **7**, 88% **8**,28%

Compound **8** was synthesized according to the reported method:[9,10] **3a** (744 mg, 4 mmol) was added to a mixture of aqueous sodium hydroxide (25%, 20 mL) and methanol (50 mL). The solution was stirred under reflux for 6 h, cooled to 0 °C, and then washed twice with CH_2Cl_2. The aqueous layer was acidified to pH 5 with 2 N aqueous hydrochloric acid. Ethyl acetate and brine were then added. The organic layer was separated, dried over anhydrous $MgSO_4$, and evaporated to give the crude product which was further purified by silica gel column chromatography to give the desired acid **7** as colourless oil.

Triethylamine (0.70 mL, 5 mmol) was added to a solution of compound **7** (205 mg, 1 mmol) in dry THF (2 mL).The solution was cooled to 0 °C, and ethyl chloroformate (0.2 mL, 2 mmol) was added dropwise. The reaction mixture was stirred at 0 °C for 40 min. The solvent was removed, and the crude solid was dissolved in dry ether. Triethylamine hydrochloride was removed by filtration. The filtrate was then evaporated to give the crude anhydride which was used in the subsequent step without further purification. The obtained anhydride was dissolved in dry CH_2Cl_2 (2 mL) and added dropwise (20 min) at 40 °C to a solution of $BF_3{\cdot}OEt_2$ (0.63 mL, 5 mmol) in dry CH_2Cl_2 (10 mL). The solution was stirred under reflux for 3 h and then cooled. Water was added, and after decantation and separation, the aqueous layer was extracted twice with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and evaporated. The crude residue was purified by chromatography on silica gel to yield compound **8** as yellow solid.

2.11 Procedure for synthesis of 9



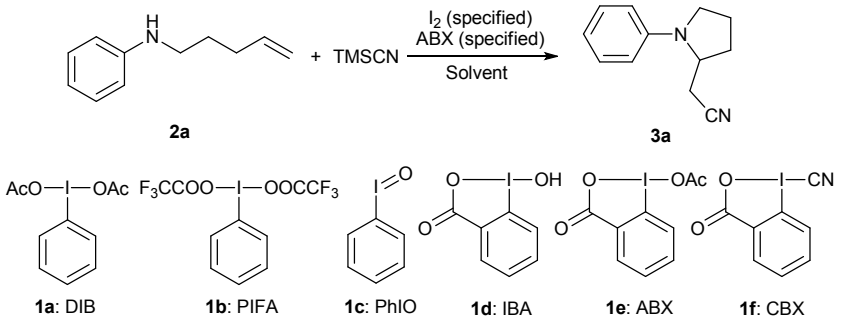
2a **9**

Compound **9** was synthesized according to the reported method:[11] To a solution of the substrate (1 mmol) in anhydrous CH_2Cl_2 (10 mL) ware added solid $NaHCO_3$ (1.1 mmol) and I_2 (1.1 mmol) at 0 °C. After stirring for 0.5 h, the reaction mixture was extracted with ethyl acetate, washed with aqueous $NaHCO_3$, saturated NaCl solution, dried over $MgSO_4$, filtrated and concentrated. The

crude residue was purified by chromatography on silica gel to give compound **9** as yellow oil in 65% yield.

3. Optimization of reaction conditions

Table 1S. **Evaluation of oxidants, solvents and reaction time for the synthesis of 3**[a]



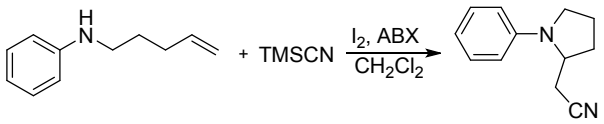
Entry	Oxidant	Solvent	Reaction time (h)	Yield (%)[b]
1[c]	PhIO	DCE	4	0
2	PhIO	DCE	4	28
3	DIB	DCE	4	0
4	PIFA	DCE	4	0
5	IBA	DCE	4	25
6	ABX	DCE	4	35
7	CBX	DCE	4	39
8[d]	CBX	DCE	4	7
9	TBHP	DCE	4	0
10	DDQ	DCE	4	0
11	NIS	DCE	4	0
12	ABX	CH_3CN	4	31
13	ABX	DCM	4	42
14	ABX	$CHCl_3$	4	33
15	ABX	acetone	4	19
16	ABX	THF	4	0
17	ABX	toluene	4	0
18	ABX	dioxane	4	0
19	ABX	DMF	4	0
20	ABX	DMSO	4	0
21	ABX	EtOAc	4	0
22	ABX	CH_3OH	4	0
23	ABX	Et_2O	4	0
24	ABX	DCM	5	48
25	ABX	DCM	6	47
26	ABX	DCM	7	45
27	ABX	DCM	8	45

[a] Reaction conditions: **2a** (0.5 mmol), oxidant (0.75 mmol), TMSCN (1.5 mmol), I_2 (0.5 mmol), solvent (4 mL), 10 °C. [b] Isolated yields. [c] In the absent of I_2. [d] In the absent of TMSCN.

Different oxidants, solvents and reaction time were screened, the highest yield was obtained when

using ABX as oxidant and DCM as solvent. The best reaction time was 5 h.

Table 2S. **Optimization of reaction conditions for the synthesis of 3**[a]



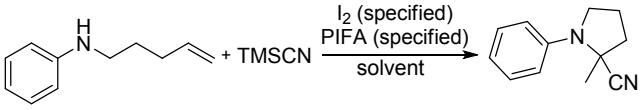
2a **3a**

Entry	I_2 (eq.)	ABX (eq.)	TMSCN (eq.)	Temperature (°C)	CH_2Cl_2 (mL)	Additive[b]	Yield (%)[c]
1	0.5	1.5	3	10	4	-	43
2	1	1.5	3	10	4	-	48
3	1.5	1.5	3	10	4	-	21
4	0.2	1.5	3	10	4	-	16
5	1	2	3	10	4	-	47
6	1	2.5	3	10	4	-	53
7	1	3	3	10	4	-	53
8	1	3.5	3	10	4	-	52
9	1	2.5	2	10	4	-	28
10	1	2.5	4	10	4	-	67
11	1	2.5	5	10	4	-	72
12	1	2.5	5	10	3	-	70
13	1	2.5	5	10	5	-	74
14[d]	1	2.5	5	10	5	-	78
15	1	2.5	5	0	5	-	36
16	1	2.5	5	35	5	-	80
17	1	2.5	5	55	5	-	71
18	1	2.5	5	35	5	HOAc	76
10	1	2.5	5	35	5	Et_3N	0
20[e]	1	2.5	5	35	5	4Å M. S.	75
21	1	2.5	5	35	5	$MgSO_4$	77
22	1	2.5	5	35	5	$FeCl_2$	54
23	1	2.5	5	35	5	$Cu(OAc)_2$	20
24[f]	1	2.5	-	35	5	-	0
25[g]	1	2.5	-	35	5	-	0
26[h]	1	2.5	-	35	5	-	0

[a] Reaction conditions: **2a** (specified), oxidant (specified), TMSCN (specified), I_2 (specified), solvent (5 mL), 10 °C, 5h. [b] 20 mol%. [c] Isolated yields. [d] Under the protection of argon in dry DCM. [e] 0.2 wt% 4 Å M. S. was added. [f] CuCN instead of TMSCN. [g] $K_3[Fe(CN)_6]$ instead of TMSCN. [e] EtOOCCN instead of TMSCN. M. S. = molecular sieve.

Different amounts of I_2, ABX, TMSCN, DCM, and reaction temperature were evaluated (Table 2S), 1 equiv of I_2, 2.5 equiv of ABX, 5 equiv of TMSCN, 5 mL of DCM and 35 °C were observed to be optimal for this reaction. Different additives and cyanide sources were also screened, but they are not beneficial to the reaction.

Table 3S. **Optimization of reaction conditions for the synthesis of 5**[a]



2a **5a**

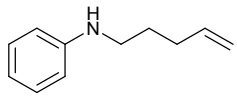
Entry	Solvent	Additive[b]	Temperature (°C)	Time (h)	I_2 (eq.)	PIFA (eq.)	TMSCN (eq.)	Yield (%)[c]
1	CH_3CN	-	rt	1	1	1.5	3	17
2	DCM	-	rt	1	1	1.5	3	20
3	$CHCl_3$	-	rt	1	1	1.5	3	19
4	acetone	-	rt	1	1	1.5	3	trace
5	THF	-	rt	1	1	1.5	3	trace
6	toluene	-	rt	1	1	1.5	3	21
7	dioxane	-	rt	1	1	1.5	3	15
8	DMF	-	rt	1	1	1.5	3	12
9	EtOAc	-	rt	1	1	1.5	3	20
10	CH_3OH	-	rt	1	1	1.5	3	0
11	cyclohexane	-	rt	1	1	1.5	3	16
12	DCE	-	rt	1	1	1.5	3	23
13[d]	DCE	3Å M. S.	rt	1	1	1.5	3	14
14[e]	DCE	4Å M. S.	rt	1	1	1.5	3	21
15[f]	DCE	5Å M. S.	rt	1	1	1.5	3	14
16	DCE	NaI	rt	1	1	1.5	3	16
17	DCE	Na_2SO_3	rt	1	1	1.5	3	27
18	DCE	NaOAc	rt	1	1	1.5	3	9
19	DCE	$FeCl_2$	rt	1	1	1.5	3	7
20	DCE	$FeCl_3$	rt	1	1	1.5	3	0
21	DCE	$Cu(OAc)_2$	rt	1	1	1.5	3	0
22	DCE	CuI	rt	1	1	1.5	3	0
23	DCE	HOAc	rt	1	1	1.5	3	18
24	DCE	Et_3N	rt	1	1	1.5	3	0
25	DCE	TFA	rt	1	1	1.5	3	15
26	DCE	Na_2SO_4	rt	1	1	1.5	3	27
27	DCE	Na_2SO_4	40	1	1	1.5	3	18
28	DCE	Na_2SO_4	0	1	1	1.5	3	29
29	DCE	Na_2SO_4	-15	1	1	1.5	3	15
30	DCE	Na_2SO_4	0	1.5	1	1.5	3	28
31	DCE	Na_2SO_4	0	2.5	1	1.5	3	25
32	DCE	Na_2SO_4	0	0.5	1	1.5	3	28
33	DCE	Na_2SO_4	0	0.5	1	1.2	3	15
34	DCE	Na_2SO_4	0	0.5	1	2	3	31
35	DCE	Na_2SO_4	0	0.5	1	2.2	3	32
36	DCE	Na_2SO_4	0	0.5	1	2.5	3	28
37	DCE	Na_2SO_4	0	0.5	0.5	2.2	3	26
38	DCE	Na_2SO_4	0	0.5	0.8	2.2	3	34
39	DCE	Na_2SO_4	0	0.5	1.3	2.2	3	25
40	DCE	Na_2SO_4	0	0.5	0.8	2.2	2	30
41	DCE	Na_2SO_4	0	0.5	0.8	2.2	2.5	32

42	DCE	Na_2SO_4	0	0.5	0.8	2.2	3.5	34
43	DCE	Na_2SO_4	0	0.5	0.8	2.2	4	28

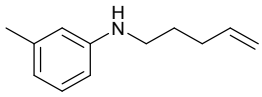
[a] Reaction conditions: **2a** (0.5 mmol), PIFA (specified), TMSCN (specified), I_2 (specified), solvent (5 mL). [b] 20 mol%. [c] Isolated yields. [d] 0.2 wt% of 3 Å M. S. [e] 0.2 wt% of 4 Å M. S. [f] 0.2 wt% of 5 Å M. S. M. S. = molecular sieve.

Different solvents, additives, reaction temperature, reaction time and amounts of I_2, PIFA, TMSCN were evaluated (Table 3S). DCE, Na_2SO_4 and 0 °C were the most favorable ones, and 0.8 equiv of I_2, 2.2 equiv of PIFA, 3 equiv of TMSCN were observed to be optimal for this reaction.

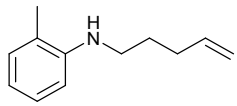
4. ^{1}H- and ^{13}C-NMR analytical data



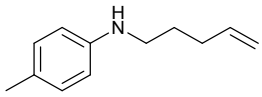
***N*-(pent-4-en-1-yl)aniline (2a):** Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19-7.15 (m, 2H), 6.68 (tt, *J* = 7.0, 1.0 Hz, 1H), 6.59 (dd, *J* = 8.5, 1.0 Hz, 2H), 5.88-5.80 (m, 1H), 5.08-5.03 (m, 1H), 5.01-4.98 (m, 1H), 3.60 (br s, 1H), 3.12 (t, *J* = 7.0 Hz, 2H), 2.19-2.14 (m, 2H), 1.74-1.68 (m, 2H).



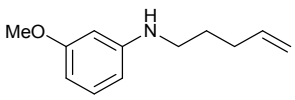
3-Methyl-*N*-(pent-4-en-1-yl)aniline (2b): Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (td, *J* = 7.5, 0.5 Hz, 1H), 6.51 (d, *J* = 7.0 Hz, 1H), 6.42-6.41 (m, 2H), 5.88-5.80 (m, 1H), 5.08-4.98 (m, 2H), 3.56 (br s, 1H), 3.12 (t, *J* = 7.0 Hz, 2H), 2.27 (s, 3H), 2.18-2.14 (m, 2H), 1.74-1.68 (m, 2H).



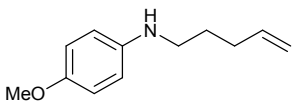
2-Methyl-*N*-(pent-4-en-1-yl)aniline (2c): Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (td, *J* = 7.5, 1.0 Hz, 1H), 7.04 (d, *J* = 7.0 Hz, 1H), 6.66-6.60 (m, 2H), 5.90-5.82 (m, 1H), 5.09-4.99 (m, 2H), 3.47 (br s, 1H), 3.18 (t, *J* = 7.0 Hz, 2H), 2.22-2.17 (m, 2H), 2.13 (s, 3H), 1.80-1.74 (m, 2H).



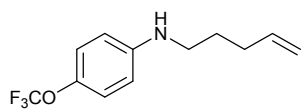
4-Methyl-*N*-(pent-4-en-1-yl)aniline (2d): Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (d, *J* = 8.0 Hz, 2H), 6.53 (d, *J* = 8.5 Hz, 2H), 5.88-5.79 (m, 1H), 5.07-4.97 (m, 2H), 3.48 (br s, 1H), 3.11 (t, *J* = 7.0 Hz, 2H), 2.23 (s, 3H), 2.18-2.14 (m, 2H), 1.73-1.68 (m, 2H).



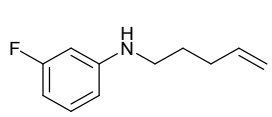
3-Methoxy-*N*-(pent-4-en-1-yl)aniline (2e): Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (t, *J* = 8.0 Hz, 1H), 6.27-6.21 (m, 2H), 6.15 (t, *J* = 2.5 Hz, 1H), 5.88-5.79 (m, 1H), 5.08-4.98 (m, 2H), 3.77 (s, 3H), 3.65 (br s, 1H), 3.12 (t, *J* = 7.0 Hz, 2H), 2.19-2.14 (m, 2H), 1.74-1.68 (m, 2H).



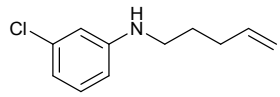
4-Methoxy-*N*-(pent-4-en-1-yl)aniline (2f): Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.78 (d, *J* = 8.5 Hz, 2H), 6.53 (d, *J* = 9.0 Hz, 2H), 5.88-5.80 (m, 1H), 5.07-4.98 (m, 2H), 3.74 (s, 3H), 3.35 (br s, 1H), 3.09 (t, *J* = 7.0 Hz, 2H), 2.19-2.14 (m, 2H), 1.73-1.67 (m, 2H).



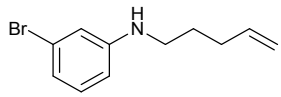
***N*-(pent-4-en-1-yl)-4-(trifluoromethoxy)aniline (2g):** Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (d, *J* = 7.5 Hz, 2H), 6.43 (d, *J* = 7.0 Hz, 2H), 5.82-5.66 (m, 1H), 4.99-4.91 (m, 2H), 3.59 (br s, 1H), 3.01 (m, 2H), 2.08-2.07 (m, 2H), 1.61 (m, 2H).



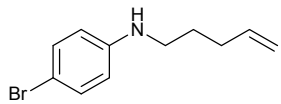
3-Fluoro-*N*-(pent-4-en-1-yl)aniline (2h): Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10-7.05 (m, 1H), 6.38-6.33 (m, 2H), 6.27 (dt, *J* = 12.0, 2.5 Hz, 1H), 5.87-5.79 (m, 1H), 5.08-4.99 (m, 2H), 3.75 (br s, 1H), 3.11 (t, *J* = 7.0 Hz, 2H), 2.19-2.14 (m, 2H), 1.74-1.68 (m, 2H).



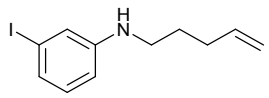
3-Chloro-*N*-(pent-4-en-1-yl)aniline (2i): Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (t, *J* = 8.0 Hz, 1H), 6.65-6.63 (m, 1H), 6.56 (t, *J* = 2.0 Hz, 1H), 6.45 (dd, *J* = 8.0, 2.0 Hz, 1H), 5.87-5.79 (m, 1H), 5.08-5.00 (m, 2H), 3.71 (br s, 1H), 3.13-3.09 (m, 2H), 2.19-2.14 (m, 2H), 1.74-1.68 (m, 2H).



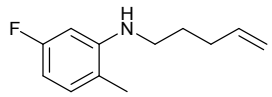
3-Bromo-*N*-(pent-4-en-1-yl)aniline (2j): Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 (t, *J* = 8.0 Hz, 1H), 6.80-6.78 (m, 1H), 6.72 (t, *J* = 2.5 Hz, 1H), 6.50-6.48 (m, 1H), 5.87-5.79 (m, 1H), 5.08-5.00 (m, 2H), 3.69 (br s, 1H), 3.10 (m, 2H), 2.18-2.14 (m, 2H), 1.74-1.68 (m, 2H).



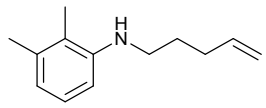
4-Bromo-*N*-(pent-4-en-1-yl)aniline (2k): Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.5 Hz, 2H), 6.47 (d, *J* = 9.0 Hz, 2H), 5.87-5.79 (m, 1H), 5.07-4.99 (m, 2H), 3.65 (br s, 1H), 3.09 (t, *J* = 7.0 Hz, 2H), 2.18-2.14 (m, 2H), 1.73-1.67 (m, 2H).



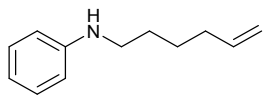
3-Iodo-*N*-(pent-4-en-1-yl)aniline (2l): Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00-6.98 (m, 1H), 6.93 (t, *J* = 2.0 Hz, 1H), 6.86 (t, *J* = 8.0 Hz, 1H), 6.54-6.52 (m, 1H), 5.87-5.79 (m, 1H), 5.08-5.00 (m, 2H), 3.65 (br s, 1H), 3.09 (t, *J* = 7.0 Hz, 2H), 2.18-2.14 (m, 2H), 1.73-1.67 (m, 2H).



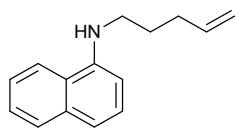
5-Fluoro-2-methyl-*N*-(pent-4-en-1-yl)aniline (2m): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (t, *J* = 7.2 Hz, 1H), 6.32-6.28 (m, 2H), 5.90-5.80 (m, 1H), 5.10-5.00 (m, 2H), 3.57 (br s, 1H), 3.14 (m, 2H), 2.22-2.17 (m, 2H), 2.06 (s, 3H), 1.80-1.73 (m, 2H).



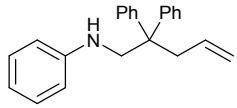
2,3-Dimethyl-*N*-(pent-4-en-1-yl)aniline (2n): Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 (t, *J* = 8.0 Hz, 1H), 6.57 (d, *J* = 7.0 Hz, 1H), 6.50 (d, *J* = 8.0 Hz, 1H), 5.89-5.81 (m, 1H), 5.08-4.98 (m, 2H), 3.46 (br s, 1H), 3.15 (t, *J* = 7.0 Hz, 2H), 2.27 (s, 3H), 2.19-2.17 (m, 2H), 2.02 (s, 3H), 1.77–1.74 (m, 2H).



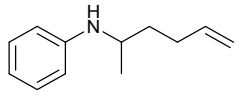
***N*-(hex-5-en-1-yl)aniline (2o):** Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.5 Hz, 2H), 6.69 (t, *J* = 7.0 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 2H), 5.84-5.79 (m, 1H), 5.04-4.96 (m, 2H), 3.12 (t, *J* = 7.0 Hz, 2H), 2.11-2.10 (m, 2H), 1.66-1.63 (m, 2H), 1.52-1.49 (m, 2H).



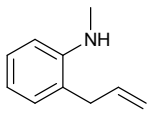
***N*-(pent-4-en-1-yl)naphthalen-1-amine (2p):** Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79-7.77 (m, 2H), 7.46-7.40 (m, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 6.60 (d, *J* = 7.5 Hz, 1H), 5.94-5.86 (m, 1H), 5.12-5.02 (m, 2H), 4.34 (br s, 1H), 3.30 (t, *J* = 7.0 Hz, 2H), 2.29-2.24 (m, 2H), 1.91-1.85 (m, 2H).



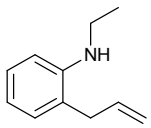
***N*-(2,2-diphenylpent-4-en-1-yl)aniline (2q):** White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.28 (m, 4H), 7.24-7.22 (m, 6H), 7.14-7.11 (m, 2H), 6.68-6.65 (m, 1H), 6.55-6.53 (m, 2H), 5.42-5.35 (m, 1H), 5.02-4.95 (m, 2H), 3.73 (s, 2H), 3.21 (s, 1H), 3.00 (d, *J* = 6.4 Hz, 2H).



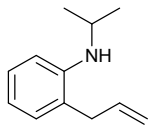
***N*-(hex-5-en-2-yl)aniline (2r):** Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17-7.14 (m, 2H), 6.67-6.64 (m, 1H), 6.57 (dd, *J* = 8.5, 1.0 Hz, 2H), 5.86-5.80 (m, 1H), 5.05-4.96 (m, 2H), 3.51-3.47 (m, 1H), 3.40 (br s, 1H), 2.18-2.14 (m, 2H), 1.68-1.63 (m, 1H), 1.57-1.51 (m, 1H), 1.18 (d, *J* = 6.5 Hz, 3H).



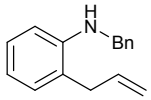
2-Allyl-*N*-methylaniline (2s): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.71 (t, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 5.99-5.89 (m, 1H), 5.13-5.07 (m, 2H), 3.76 (br s, 1H), 3.28 (d, *J* = 6.0 Hz, 2H), 2.85 (s, 3H).



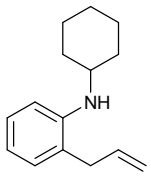
2-Allyl-*N*-ethylaniline (2t): Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.69 (t, *J* = 7.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 5.98-5.90 (m, 1H), 5.13-5.09 (m, 2H), 3.61 (br s, 1H), 3.28 (d, *J* = 6.5 Hz, 2H), 3.16 (q, *J* = 7.0 Hz, 2H), 1.26 (t, *J* = 7.0 Hz, 3H).



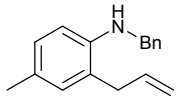
2-Allyl-*N*-isopropylaniline (2u): Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (td, *J* = 8.0, 1.0 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.67-6.64 (m, 2H), 5.97-5.89 (m, 1H), 5.13-5.08 (m, 2H), 3.65-3.64 (m, 1H), 3.55 (br s, 1H), 3.26 (d, *J* = 6.0 Hz, 2H), 1.20 (d, *J* = 6.0 Hz, 6H).



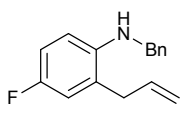
2-Allyl-*N*-benzylaniline (2v): Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.32 (m, 4H), 7.28-7.27 (m, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.71 (t, *J* = 7.0 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.00-5.92 (m, 1H), 5.13-5.06 (m, 2H), 4.35 (d, *J* = 5.5 Hz, 2H), 4.12 (br s, 1H), 3.32 (d, *J* = 6.0 Hz, 2H).



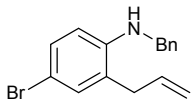
2-Allyl-*N*-cyclohexylaniline (2w): Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (td, *J* = 8.5, 1.5 Hz, 1H), 7.03 (d, *J* = 7.0 Hz, 1H), 6.66-6.62 (m, 2H), 5.97-5.89 (m, 1H), 5.13-5.09 (m, 2H), 3.65 (br s, 1H), 3.27 (d, *J* = 6.0 Hz, 2H), 2.05-2.01 (m, 2H), 1.76-1.72 (m, 2H), 1.65-1.61 (m, 1H), 1.43-1.34 (m, 2H), 1.29-1.14 (m, 4H).



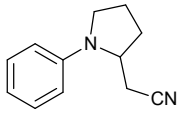
2-Allyl-*N*-benzyl-4-methylaniline (2x): Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.26 (m, 5H), 6.93 (d, *J* = 8.5 Hz, 1H), 6.90 (s, 1H), 6.54 (d, *J* = 8.5 Hz, 1H), 6.00-5.92 (m, 1H), 5.12-5.06 (m, 2H), 4.33 (s, 2H), 3.99 (br s, 1H), 3.30 (d, *J* = 6.0 Hz, 2H), 2.24 (s, 3H).



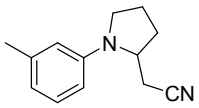
2-Allyl-*N*-benzyl-4-fluoroaniline (2y): Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.27 (m, 5H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.52 (d, *J* = 4.5 Hz, 1H), 5.94-5.90 (m, 1H), 5.15-5.06 (m, 2H), 4.29 (s, 2H), 3.91 (br s, 1H), 3.27 (m, 2H).



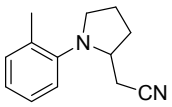
2-Allyl-*N*-benzyl-4-bromoaniline (2z): Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.15 (m, 5H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.45-6.44 (m, 1H), 5.92-5.86 (m, 1H), 5.14-5.05 (m, 2H), 4.28 (s, 2H), 4.10 (br s, 1H), 3.24 (m, 2H).



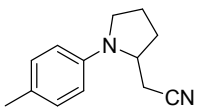
2-(1-Phenylpyrrolidin-2-yl)acetonitrile (3a): Yellow solid; 80% yield, 75 mg; mp 36-38 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.24 (m, 2H), 6.75 (t, *J* = 7.0 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 2H), 4.11-4.07 (m, 1H), 3.55-3.51 (m, 1H), 3.25-3.20 (m, 1H), 2.71 (dd, *J* = 17.0, 3.0 Hz, 1H), 2.43 (dd, *J* = 17.0, 8.5 Hz, 1H), 2.24-2.06 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1, 129.7, 118.3, 117.1, 112.3, 55.3, 48.7, 31.0, 23.1, 21.6. HRMS (ESI) calcd for $C_{12}H_{14}N_2$ $[M+H]^+$ 187.1230, found 187.1224.



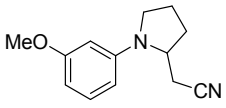
2-(1-(m-Tolyl)pyrrolidin-2-yl)acetonitrile (3b): Yellow solid; 64% yield, 64 mg; mp 36-38 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16-7.13 (m, 1H), 6.58 (d, *J* = 7.5 Hz, 1H), 6.40-6.39 (m, 2H), 4.10-4.07 (m, 1H), 3.54-3.50 (m, 1H), 3.24-3.19 (m, 1H), 2.72 (dd, *J* = 16.5, 3.0 Hz, 1H), 2.42 (dd, *J* = 16.5, 8.5 Hz, 1H), 2.33 (s, 3H), 2.22-2.06 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.2, 139.5, 129.6, 118.4, 118.1, 113.0, 109.5, 55.3, 48.7, 31.0, 23.1, 22.0, 21.6. HRMS (ESI) calcd for $C_{13}H_{16}N_2$ $[M+H]^+$ 201.1386, found 201.1390.



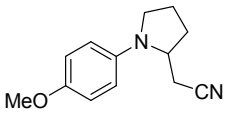
2-(1-(o-Tolyl)pyrrolidin-2-yl)acetonitrile (3c): Colourless oil; 80% yield, 80 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18-7.13 (m, 2H), 7.00-6.96 (m, 2H), 3.93-3.88 (m, 1H), 3.62-3.57 (m, 1H), 2.85-2.80 (m, 1H), 2.46 (dd, *J* = 17.0, 3.5 Hz, 1H), 2.35 (dd, *J* = 17.0, 7.0 Hz, 1H), 2.33-2.30 (m, 4H), 2.07-2.01 (m, 1H), 1.96-1.87 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 133.8, 131.8, 126.7, 123.3, 119.1, 118.3, 56.2, 53.9, 31.3, 23.9, 22.4, 19.2. HRMS (ESI) calcd for $C_{13}H_{16}N_2$ $[M+H]^+$ 201.1386, found 201.1383.



2-(1-(p-Tolyl)pyrrolidin-2-yl)acetonitrile (3d): Yellow solid; 67% yield, 67 mg; mp 51-53 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.5 Hz, 2H), 6.50 (d, *J* = 8.5 Hz, 2H), 4.07-4.03 (m, 1H), 3.53-3.49 (m, 1H), 3.21-3.16 (m, 1H), 2.70 (dd, *J* = 17.0, 3.0 Hz, 1H), 2.41 (dd, *J* = 17.0, 8.5 Hz, 1H), 2.26 (s, 3H), 2.23-2.03 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 130.2, 126.3, 118.5, 112.3, 55.5, 48.9, 31.1, 23.2, 21.7, 20.4. HRMS (ESI) calcd for $C_{13}H_{16}N_2$ $[M+H]^+$ 201.1386, found 201.1378.

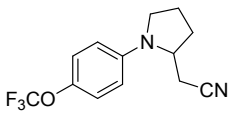


2-(1-(3-Methoxyphenyl)pyrrolidin-2-yl)acetonitrile (3e): Yellow oil; 46% yield, 50 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (t, *J* = 8.5 Hz, 1H), 6.32 (dd, *J* = 8.0, 2.5 Hz, 1H), 6.20 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.12 (t, *J* = 2.5 Hz, 1H), 4.09-4.05 (m, 1H), 3.80 (s, 3H), 3.53-3.49 (m, 1H), 3.25-3.20 (m, 1H) 2.71 (dd, *J* = 17.0, 3.0 Hz, 1H), 2.44 (dd, *J* = 17.0, 8.5 Hz, 1H), 2.23-2.13 (m, 2H), 2.12-2.04 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.2, 147.5, 130.5, 118.3, 105.5, 101.9, 99.1, 55.40, 55.36, 48.8, 31.0, 23.1, 21.6. HRMS (ESI) calcd for $C_{13}H_{16}N_2O$ $[M+H]^+$ 217.1336, found 217.1334.

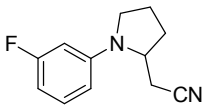


2-(1-(4-Methoxyphenyl)pyrrolidin-2-yl)acetonitrile (3f): Brown solid; 57% yield, 62 mg; mp 43-45 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 (d, *J* = 9.0

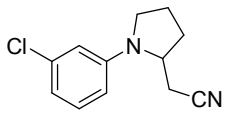
Hz, 2H), 6.54 (d, *J* = 9.0 Hz, 2H), 4.03-4.00 (m, 1H), 3.76 (s, 3H), 3.52-3.49 (m, 1H), 3.19-3.14 (m, 1H), 2.68 (dd, *J* = 17.0, 3.0 Hz, 1H), 2.41 (dd, *J* = 17.0, 8.5 Hz, 1H), 2.24-2.12 (m, 2H), 2.09-2.05 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.8, 140.8, 118.5, 115.4, 113.3, 56.1, 55.8, 49.4, 31.2, 23.3, 21.8. HRMS (ESI) calcd for $C_{13}H_{16}N_2O$ $[M+H]^+$ 217.1336, found 217.1340.



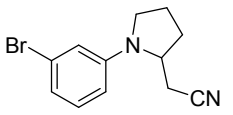
2-(1-(4-(Trifluoromethoxy)phenyl)pyrrolidin-2-yl)acetonitrile (3g): Yellow oil; 66% yield, 89 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, *J* = 9.0 Hz, 2H), 6.53 (d, *J* = 9.0 Hz, 2H), 4.08-4.05 (m, 1H), 3.55-3.51 (m, 1H), 3.24-3.19 (m, 1H), 2.68 (dd, *J* = 16.5, 3.0 Hz, 1H), 2.46 (dd, *J* = 17.0, 8.5 Hz, 1H), 2.26-2.08 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 140.4, 122.9, 120.8 (q, *J* = 250 Hz), 118.1, 112.5, 55.5, 49.1, 31.2, 23.2, 21.6. HRMS (ESI) calcd for $C_{13}H_{13}N_2OF_3$ $[M+H]^+$ 271.1053, found 271.1065.



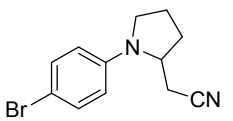
2-(1-(3-Fluorophenyl)pyrrolidin-2-yl)acetonitrile (3h): Light yellow solid; 46% yield, 47 mg; mp 34-36 °C;. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (td, *J* = 8.5, 7.0 Hz, 1H), 6.44 (td, *J* = 8.5, 2.0 Hz, 1H), 6.33 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.26 (dt, *J* = 12.5, 2.0 Hz, 1H), 4.08-4.04 (m, 1H), 3.53-3.49 (m, 1H), 3.25-3.21 (m, 1H) 2.69 (dd, *J* = 17.0, 3.0 Hz, 1H), 2.46 (dd, *J* = 17.0, 8.5 Hz, 1H), 2.24-2.16 (m, 2H), 2.15-2.08 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4 (d, *J* = 241.3 Hz), 147.8 (d, *J* = 11.3 Hz), 130.8 (d, *J* = 11.3 Hz), 118.1, 108.0 (d, *J* = 1.3 Hz), 103.7 (d, *J* = 22.5 Hz), 99.5 (d, *J* = 26.3 Hz), 55.5, 48.9, 31.1, 23.1, 21.5. HRMS (ESI) calcd for $C_{12}H_{13}N_2F$ $[M+H]^+$ 205.1136, found 205.1127.



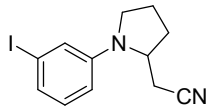
2-(1-(3-Chlorophenyl)pyrrolidin-2-yl)acetonitrile (3i): Yellow soild; 56% yield, 62 mg; mp 61-62 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (t, *J* = 8.0 Hz, 1H), 6.71 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.54 (t, *J* = 2.5 Hz, 1H), 6.45 (dd, *J* = 8.0, 2.0 Hz, 1H), 4.08-4.04 (m, 1H), 3.53-3.50 (m, 1H), 3.24-3.19 (m, 1H), 2.68 (dd, *J* = 17.0, 3.5 Hz, 1H), 2.46 (dd, *J* = 17.0, 8.5 Hz, 1H), 2.27-2.14 (m, 2H), 2.10-2.06 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.2, 135.6, 130.6, 118.0, 117.1, 112.3, 110.5, 55.3, 48.8, 31.0, 23.1, 21.5. HRMS (ESI) calcd for $C_{12}H_{13}N_2Cl$ $[M+H]^+$ 221.0840, found 221.0844.



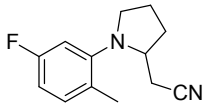
2-(1-(3-Bromophenyl)pyrrolidin-2-yl)acetonitrile (3j): Yellow soild; 52% yield, 69 mg; mp 60-62 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (t, *J* = 8.0 Hz, 1H), 6.86 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.70 (t, *J* = 2.0 Hz, 1H), 6.49 (dd, *J* = 8.5, 2.5 Hz, 1H), 4.08-4.05 (m, 1H), 3.53-3.49 (m, 1H), 3.24-3.19 (m, 1H), 2.68 (dd, *J* = 17.0, 3.5 Hz, 1H), 2.46 (dd, *J* = 17.0, 8.5 Hz, 1H), 2.27-2.16 (m, 2H), 2.14-2.07 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.3, 130.9, 123.9, 120.0, 118.1, 115.1, 110.9, 55.3, 48.8, 31.0, 23.1, 21.5. HRMS (ESI) calcd for $C_{12}H_{13}N_2Br$ $[M+H]^+$ 265.0335, found 265.0323.



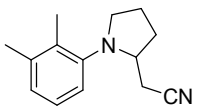
2-(1-(4-Bromophenyl)pyrrolidin-2-yl)acetonitrile (3k): Yellow solid; 64% yield, 85 mg; mp 60-62 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 9.0 Hz, 2H), 6.45 (d, *J* = 9.0 Hz, 2H), 4.06-4.03 (m, 1H), 3.52-3.48 (m, 1H), 3.21-3.18 (m, 1H), 2.67 (dd, *J* = 17.0, 3.0 Hz, 1H), 2.44 (dd, *J* = 17.0, 8.5 Hz, 1H), 2.23-2.08 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 132.4, 118.1, 113.9, 109.1, 55.4, 48.9, 31.1, 23.2, 21.5. HRMS (ESI) calcd for $C_{12}H_{13}N_2Br$ $[M+H]^+$ 265.0335, found 265.0348.



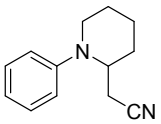
2-(1-(3-Iodophenyl)pyrrolidin-2-yl)acetonitrile (3l): Light yellow oil; 63% yield, 98 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.0 Hz, 1H), 6.95 (t, *J* = 8.5 Hz, 1H), 6.90 (t, *J* = 2.5 Hz, 1H), 6.53 (dd, *J* = 8.0, 2.0 Hz, 1H), 4.07-4.03 (m, 1H), 3.52-3.48 (m, 1H), 3.22-3.17 (m, 1H), 2.67 (dd, *J* = 17.0, 3.5 Hz, 1H), 2.45 (dd, *J* = 17.0, 8.5 Hz, 1H), 2.26-2.15 (m, 2H), 2.13-2.06 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.2, 131.0, 126.1, 121.1, 118.0, 111.6, 95.9, 55.2, 48.8, 31.0, 23.1, 21.5. HRMS (ESI) calcd for $C_{12}H_{13}N_2I$ $[M+H]^+$ 313.0196, found 313.0202.



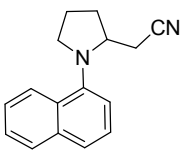
2-(1-(5-Fluoro-2-methylphenyl)pyrrolidin-2-yl)acetonitrile (3m): Yellow oil; 70% yield, 76 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (t, *J* = 7.6 Hz, 1H), 6.68-6.63 (m, 2H), 3.89-3.87 (m, 1H), 3.66-3.60 (m, 1H), 2.89-2.83 (m, 1H), 2.50-2.30 (m, 3H), 2.24 (s, 3H), 2.08-1.88 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.9 (d, *J* = 242.5 Hz), 148.1 (d, *J* = 7.5 Hz), 132.6 (d, *J* = 8.8 Hz), 128.3 (d, *J* = 5.0 Hz), 118.0, 109.3 (d, *J* = 20.0 Hz), 105.7 (d, *J* = 22.5 Hz), 56.0, 53.7, 31.3, 24.0, 22.3, 18.9. HRMS (ESI) calcd for $C_{13}H_{15}N_2F$ $[M+H]^+$ 219.1292, found 219.1302.



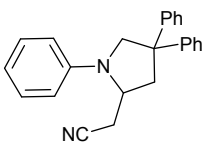
2-(1-(2,3-Dimethylphenyl)pyrrolidin-2-yl)acetonitrile (3n): Light yellow oil; 77% yield, 82 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 2H), 3.82-3.79 (m, 1H), 3.54-3.49 (m, 1H), 2.77-2.72 (m, 1H), 2.46-2.28 (m, 6H), 2.22 (s, 3H), 2.05-2.02 (m, 1H), 1.95-1.89 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 138.6, 133.5, 126.0, 125.6, 118.4, 117.5, 56.8, 54.5, 31.1, 23.6, 22.5, 20.9, 14.6. HRMS (ESI) calcd for $C_{14}H_{18}N_2$ $[M+H]^+$ 215.1543, found 215.1542.



2-(1-Phenylpiperidin-2-yl)acetonitrile (3o): Yellow oil; 34% yield, 34 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.5 Hz, 2H), 6.75-6.70 (m, 3H), 4.08 (dd, *J* = 15.5, 5.0 Hz, 1H), 3.74-3.69 (m, 1H), 3.51 (dd, *J* = 15.0, 9.5 Hz, 1H), 3.31-3.26 (m, 1H), 3.09-3.03 (m, 1H), 2.01-1.93 (m, 1H), 1.89-1.74 (m, 4H), 1.57-1.51 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.4, 129.9, 121.8, 117.3, 111.7, 51.4, 50.3, 30.9, 29.8, 27.4, 24.6. HRMS (ESI) calcd for $C_{13}H_{16}N_2$ $[M+H]^+$ 201.1386, found 201.1381.

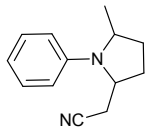


2-(1-(Naphthalen-1-yl)pyrrolidin-2-yl)acetonitrile (3p): Yellow oil; 70% yield, 83 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25-8.23 (m, 1H), 7.83-7.81 (m, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.50-7.46 (m, 2H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 7.0 Hz, 1H), 4.07-4.03 (m, 1H), 3.87-3.83 (m, 1H), 3.01-2.96 (m, 1H), 2,50 (dd, *J* = 16.5, 3.5 Hz, 1H), 2.44-2.39 (m, 2H), 2.17-2.13 (m, 1H), 2.08-1.95 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.3, 135.1, 130.7, 128.3, 126.3, 125.9, 125.6, 124.4, 124.1, 118.4, 115.4, 56.9, 55.9, 31.3, 23.9, 22.4. HRMS (ESI) calcd for $C_{16}H_{16}N_2$ $[M+H]^+$ 237.1386, found 237.1377.

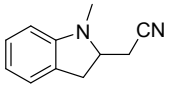


2-(1,4,4-Triphenylpyrrolidin-2-yl)acetonitrile (3q): White solid ; 34% yield, 58 mg; mp 60-62 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.29 (m, 6H), 7.25-7.20 (m, 3H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.11-7.09 (m, 2H), 6.83 (t, *J* = 7.0 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 2H), 4.24 (d, *J* = 10.0 Hz, 1H), 4.01-3.96

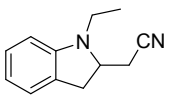
(m, 2H), 3.00 (dd, *J* = 12.5, 7.5 Hz, 1H), 2.84 (dd, *J* = 12.5, 6.5 Hz, 1H), 2.73 (dd, *J* = 17.0, 3.0 Hz, 1H), 2.26 (dd, *J* = 17.0, 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.04, 145.98, 145.6, 129.8, 128.9, 128.7, 127.1, 127.0, 126.7, 118.04, 118.00, 113.2, 60.1, 54.5, 53.0, 43.8, 21.7. HRMS (ESI) calcd for $C_{24}H_{22}N_2$ $[M+H]^+$ 339.1856, found 339.1846.



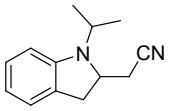
2-(5-Methyl-1-phenylpyrrolidin-2-yl)acetonitrile (3r): Yellow solid; mixture of two diastereoisomers (dr = 10:1); 79% yield, 79 mg; mp 63-65 °C. Major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26-7.22 (m, 2H), 6.70 (t, *J* = 7.0 Hz, 1H), 6.58 (d, *J* = 8.5 Hz, 2H), 4.19 (td, *J* = 9.0, 2.5 Hz, 1H), 4.13-4.08 (m, 1H), 2.72 (dd, *J* = 17.0, 3.0 Hz, 1H), 2.41-2.25 (m, 3H), 2.03 (dd, *J* = 12.5, 6.5 Hz, 1H), 1.75 (dd, *J* = 11.5, 6.5 Hz, 1H), 1.11 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 129.7, 118.5, 116.8, 114.0, 54.5, 53.4, 30.1, 28.4, 20.2, 18.2. HRMS (ESI) calcd for $C_{13}H_{16}N_2$ $[M+H]^+$ 201.1386, found 201.1393.



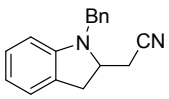
2-(1-Methylindolin-2-yl)acetonitrile (3s): Light yellow oil; 42% yield, 36 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.07 (m, 2H), 6.72 (t, *J* = 7.2 Hz, 1H), 6.49 (d, *J* = 7.6 Hz, 1H), 3.69-3.67 (m, 1H), 3.28 (dd, *J* = 15.6, 8.8 Hz, 1H), 2.89 (dd, *J* = 15.6, 9.2 Hz, 1H), 2.79 (s, 3H), 2.73-2.61 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4, 128.1, 127.4, 124.5, 119.0, 117.6, 107.9, 63.1, 35.3, 34.5, 22.1. HRMS (ESI) calcd for $C_{11}H_{12}N_2$ $[M+H]^+$ 173.1073, found 173.1078.



2-(1-Ethylindolin-2-yl)acetonitrile (3t): Light yellow oil; 42% yield, 39 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10-7.06 (m, 2H), 6.68 (t, *J* = 7.0 Hz, 1H), 6.46 (d, *J* = 7.5 Hz, 1H), 3.96-3.93 (m, 1H), 3.36-3.28 (m, 2H), 3.20-3.14 (m, 1H), 2.88 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.69 (dd, *J* = 16.5, 4.0 Hz, 1H), 2.60 (dd, *J* = 16.5, 7.0 Hz, 1H), 1.15 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.8, 128.0, 127.4, 124.6, 118.4, 117.7, 107.5, 59.3, 40.8, 35.3, 22.7, 11.6. HRMS (ESI) calcd for $C_{12}H_{14}N_2$ $[M+H]^+$ 187.1230, found 187.1232.

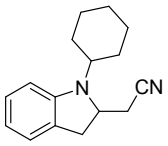


2-(1-Isopropylindolin-2-yl)acetonitrile (3u): Yellow oil; 38% yield, 38 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09-7.06 (m, 2H), 6.69 (t, *J* = 7.0 Hz, 1H), 6.56 (d, *J* = 7.5 Hz, 1H), 4.04-3.99 (m, 1H), 3.73-3.68 (m, 1H), 3.38 (dd, *J* = 16.0, 9.5 Hz, 1H), 2.86 (dd, *J* = 16.0, 5.0 Hz, 1H), 2.61 (dd, *J* = 16.5, 4.5 Hz, 1H), 2.54 (dd, *J* = 16.5, 7.5 Hz, 1H), 1.28 (d, *J* = 7.0 Hz, 3H), 1.22 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.0, 127.93, 127.89, 124.9, 118.7, 118.0, 109.6, 56.1, 49.2, 35.9, 25.6, 20.7, 19.5. HRMS (ESI) calcd for $C_{13}H_{16}N_2$ $[M+H]^+$ 201.1386, found 201.1391.

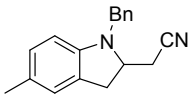


2-(1-Benzylindolin-2-yl)acetonitrile (3v): Light yellow oil; 66% yield, 82 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.32 (m, 4H), 7.29-7.25 (m, 1H), 7.10 (d, *J* = 7.0 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.73 (t, *J* = 7.5 Hz, 1H), 6.44 (d, *J* = 8.0 Hz, 1H), 4.37 (d, *J* = 16.0 Hz, 1H), 4.32 (d, *J* = 16.0 Hz, 1H), 3.95-3.89 (m, 1H), 3.36 (dd, *J* = 16.0, 9.5 Hz, 1H), 2.98 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.60 (dd, *J* = 17.0, 4.0 Hz, 1H), 2.53 (dd, *J* = 16.5, 7.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.7, 138.1, 129.0, 128.1, 127.7, 127.5, 127.2, 124.7, 119.0, 117.5, 107.9, 61.0, 52.3, 35.3, 22.9. HRMS (ESI) calcd for $C_{17}H_{16}N_2$ $[M+H]^+$ 249.1386,

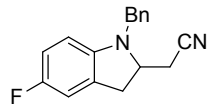
found 249.1385.



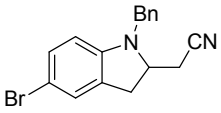
2-(1-Cyclohexylindolin-2-yl)acetonitrile (3w): Light yellow oil; 36% yield, 43 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08-7.05 (m, 2H), 6.68 (td, *J* = 7.5, 0.5 Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 4.08-4.03 (m, 1H), 3.39 (dd, *J* = 16.5, 10.0 Hz, 1H), 3.25 (tt, *J* = 11.5, 3.5 Hz, 1H), 2.86 (dd, *J* = 16.0, 4.5 Hz, 1H), 2.60 (dd, *J* = 16.5, 4.0 Hz, 1H), 2.52 (dd, *J* = 16.5, 8.0 Hz, 1H), 1.96 (d, *J* = 12.0 Hz, 1H), 1.90-1.78 (m, 3H), 1.70 (d, *J* = 13.0 Hz, 1H), 1.51-1.26 (m, 4H), 1.16 (ddt, *J* = 26.0, 13.0, 4.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.1, 127.9, 127.8, 124.9, 118.5, 118.1, 109.4, 58.1, 56.2, 35.9, 31.9, 29.9, 26.5, 26.3, 26.0, 25.9. HRMS (ESI) calcd for $C_{16}H_{20}N_2$ $[M+H]^+$ 241.1699, found 241.1706.



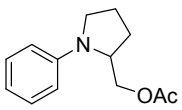
2-(1-Benzyl-5-methylindolin-2-yl)acetonitrile (3x): Light yellow solid ; 45% yield, 59 mg; mp 80-82 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.26 (m, 5H), 6.94 (s, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.34 (d, *J* = 8.0 Hz, 1H), 4.32 (d, *J* = 16.0 Hz, 1H), 4.28 (d, *J* = 16.0 Hz, 1H), 3.89-3.85 (m, 1H), 3.32 (dd, *J* = 16.0, 9.0 Hz, 1H), 2.94 (dd, *J* = 15.5, 8.0 Hz, 1H), 2.59 (dd, *J* = 17.0, 4.0 Hz, 1H), 2.52 (dd, *J* = 16.5, 7.0 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.6, 138.3, 128.9, 128.4, 128.2, 127.62, 127.57, 127.5, 125.6, 117.6, 107.9, 61.4, 52.9, 35.3, 22.9, 20.9. HRMS (ESI) calcd for $C_{18}H_{18}N_2$ $[M+H]^+$ 263.1543, found 263.1538.



2-(1-Benzyl-5-fluoroindolin-2-yl)acetonitrile (3y): Light yellow solid; 54% yield, 72 mg; mp 78-80 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.33 (m, 4H), 7.31-7.28 (m, 1H), 6.85-6.82 (m, 1H), 6.73 (td, *J* = 9.0, 2.5 Hz, 1H), 6.31 (dd, *J* = 8.5, 4.0 Hz, 1H), 4.32 (d, *J* = 16.0 Hz, 1H), 4.26 (d, *J* = 15.5 Hz, 1H), 3.93-3.88 (m, 1H), 3.33 (dd, *J* = 16.0, 9.0 Hz, 1H), 2.96 (dd, *J* = 16.5, 8.5 Hz, 1H), 2.61 (dd, *J* = 16.5, 4.0 Hz, 1H), 2.55 (dd, *J* = 16.5, 6.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.1 (d, *J* = 235 Hz), 148.0, 137.8, 129.0, 128.8 (d, *J* = 8.8 Hz), 127.8, 127.5, 117.4, 113.9 (d, *J* = 22.5 Hz), 112.3 (d, *J* = 23.8 Hz), 108.2 (d, *J* = 8.8 Hz), 61.6, 53.1, 35.2 (d, *J* = 1.25 Hz), 22.9. HRMS (ESI) calcd for $C_{17}H_{15}N_2F$ $[M+H]^+$ 267.1292, found 267.1298.

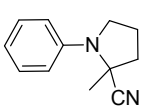


2-(1-Benzyl-5-bromoindolin-2-yl)acetonitrile (3z): White solid; 28% yield, 46 mg; mp 82-84 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.28 (m, 5H), 7.19 (s, 1H), 7.14 (d, *J* = 8.5 Hz, 1H), 6.29 (d, *J* = 8.5 Hz, 1H), 4.37 (d, *J* = 16.0 Hz, 1H), 4.28 (d, *J* = 16.0 Hz, 1H), 3.97-3.91 (m, 1H), 3.34 (dd, *J* = 16.5, 9.5 Hz, 1H), 2.97 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.60 (dd, *J* = 17.0, 4.0 Hz, 1H), 2.54 (dd, *J* = 17.0, 7.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.7, 137.4, 130.7, 129.5, 129.1, 127.9, 127.7, 127.5, 117.2, 110.5, 109.1, 60.9, 51.9, 34.9, 22.8. HRMS (ESI) calcd for $C_{17}H_{15}N_2Br$ $[M+H]^+$ 327.0492, found 327.0493.

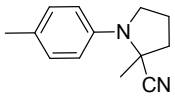


(1-Phenylpyrrolidin-2-yl)methyl acetate (4): Yellow oil; 23% yield, 25 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.5 Hz, 2H), 6.71-6.70 (m, 3H), 4.30 (dd, *J* = 11.0, 3.0 Hz, 1H), 4.00-3.92 (m, 1H), 3.81 (t, *J* = 10.0 Hz, 1H), 3.46 (t, *J* = 7.5 Hz, 1H), 3.16-3.11 (m, 1H), 2.07-1.97 (m, 7H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2,

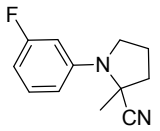
147.5, 129.5, 116.5, 112.2, 64.3, 57.2, 48.7, 28.8, 23.4, 21.1. HRMS (ESI) calcd for $C_{13}H_{17}N_2O$ $[M+H]^+$ 220.1332, found 220.1339.



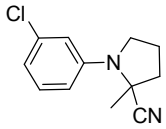
2-Methyl-1-phenylpyrrolidine-2-carbonitrile (5a): Yellow oil; 34% yield, 32 mg. ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.84 (t, *J* = 7.5 Hz, 1H), 3.62-3.57 (m, 1H), 3.45-3.41 (m, 1H), 2.67-2.63 (m, 1H), 2.19-2.07 (m, 3H), 1.70 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 129.3, 121.9, 118.8, 115.3, 56.7, 50.6, 42.8, 24.3, 22.8. HRMS (ESI) calcd for $C_{12}H_{14}N_2$ $[M+H]^+$ 187.1230, found 187.1238.



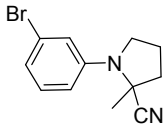
2-Methyl-1-(p-tolyl)pyrrolidine-2-carbonitrile (5b): Yellow oil; 45% yield, 45 mg. ^1H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 3.59-3.55 (m, 1H), 3.41-3.37 (m, 1H), 2.64-2.59 (m, 1H), 2.28 (s, 3H), 2.17-2.04 (m, 3H), 1.67 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.4, 129.8, 128.6, 122.0, 116.0, 57.1, 50.8, 42.6, 24.4, 22.6, 20.6. HRMS (ESI) calcd for $C_{13}H_{16}N_2$ $[M+H]^+$ 201.1386, found 201.1392.



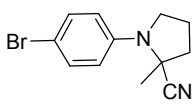
1-(3-Fluorophenyl)-2-methylpyrrolidine-2-carbonitrile (5c): Yellow oil; 23% yield, 23 mg. ^1H NMR (500 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 16.0, 8.5 Hz, 1H), 6.65 (d, *J* = 8.5 Hz, 1H), 6.56-6.51 (m, 2H), 3.59-3.54 (m, 1H), 3.44-3.40 (m, 1H), 2.69-2.66 (m, 1H), 2.21-2.07 (m, 3H), 1.71 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8 (d, *J* = 242.5 Hz), 146.20 (d, *J* = 8.8 Hz), 130.3 (d, *J* = 10.0 Hz), 121.5, 110.5 (d, *J* = 2.5 Hz), 105.2 (d, *J* = 21.3 Hz), 102.1 (d, *J* = 26.3 Hz), 56.6, 50.7, 42.8, 24.2, 22.8. HRMS (ESI) calcd for $C_{12}H_{13}N_2F$ $[M+H]^+$ 205.1136, found 205.1127.



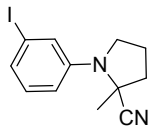
1-(3-Chlorophenyl)-2-methylpyrrolidine-2-carbonitrile (5d): Yellow oil; 28% yield, 31 mg. ^1H NMR (500 MHz, $CDCl_3$) δ 7.19 (t, *J* = 8.0 Hz, 1H), 6.81-6.78 (m, 3H), 3.59-3.54 (m, 1H), 3.44-3.40 (m, 1H), 2.69-2.64 (m, 1H), 2.19-2.08 (m, 3H), 1.71 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.7, 135.1, 130.2, 121.5, 118.6, 115.0, 113.0, 56.6, 50.7, 42.8, 24.2, 22.8. HRMS (ESI) calcd for $C_{12}H_{13}N_2Cl$ $[M+H]^+$ 221.0840, found 221.0846.



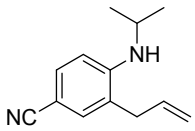
1-(3-Bromophenyl)-2-methylpyrrolidine-2-carbonitrile (5e): Yellow oil; 24% yield, 32 mg. ^1H NMR (500 MHz, $CDCl_3$) δ 7.13 (t, *J* = 8.0 Hz, 1H), 6.96-6.95 (m, 2H), 6.84 (dd, *J* = 8.0, 1.5 Hz, 1H), 3.59-3.54 (m, 1H), 3.43-3.39 (m, 1H), 2.69-2.63 (m, 1H), 2.20-2.06 (m, 3H), 1.70 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8, 130.4, 123.4, 121.5, 121.4, 117.9, 113.5, 56.6, 50.7, 42.8, 24.2, 22.8. HRMS (ESI) calcd for $C_{12}H_{13}N_2Br$ $[M+H]^+$ 265.0335, found 265.0342.



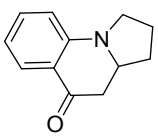
1-(4-Bromophenyl)-2-methylpyrrolidine-2-carbonitrile (5f): Yellow oil; 38% yield, 50 mg. ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 9.0 Hz, 2H), 6.76 (d, *J* = 9.0 Hz, 2H), 3.58-3.54 (m, 1H), 3.41-3.37 (m, 1H), 2.68-2.62 (m, 1H), 2.16-2.05 (m, 3H), 1.68 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 132.0, 121.5, 116.7, 111.1, 56.7, 50.7, 42.7, 24.2, 22.8. HRMS (ESI) calcd for $C_{12}H_{13}N_2Br$ $[M+H]^+$ 265.0335, found 265.0347.



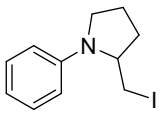
1-(3-Iodophenyl)-2-methylpyrrolidine-2-carbonitrile (5g): Yellow oil; 24% yield, 37 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17-7.14 (m, 2H), 6.99 (t, *J* = 8.5 Hz, 1H), 6.89 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.58-3.53 (m, 1H), 3.42-3.38 (m, 1H), 2.68-2.62 (m, 1H), 2.18-2.07 (m, 3H), 1.69 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.7, 130.6, 127.6, 123.8, 121.4, 114.1, 95.3, 56.5, 50.6, 42.8, 24.2, 22.8. HRMS (ESI) calcd for $C_{12}H_{13}N_2I$ $[M+H]^+$ 313.0196, found 313.0190.



3-Allyl-4-(isopropylamino)benzonitrile (6): Yellow oil; 12% yield, 12 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.5 Hz, 1H), 7.28 (s, 1H), 6.59 (d, *J* = 8.5 Hz, 1H), 5.92-5.84 (m, 1H), 5.19 (d, *J* = 10.0 Hz, 1H), 5.12 (d, *J* = 17.0 Hz, 1H), 4.09 (br s, 1H), 3.70-3.66 (m, 1H), 3.23 (d, *J* = 6.0 Hz, 2H), 1.23 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.0, 134.7, 133.7, 132.7, 123.3, 120.8, 117.6, 110.2, 98.1, 44.1, 36.2, 22.9. HRMS (ESI) calcd for $C_{13}H_{16}N_2$ $[M+H]^+$ 201.1386, found 201.1386.



2,3,3a,4-Tetrahydropyrrolo[1,2-a]quinolin-5(1H)-one (8): Yellow solid; 28% yield, 52 mg; mp 68-70 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.37 (t, *J* = 8.5 Hz, 1H), 6.67 (t, *J* = 7.0 Hz, 1H), 6.56 (d, *J* = 8.5 Hz, 1H), 3.65-3.60 (m, 1H), 3.52-3.47 (m, 1H), 3.29 (td, *J* = 9.5, 3.0 Hz, 1H), 2.77 (dd, *J* = 16.0, 3.5 Hz, 1H), 2.47 (t, *J* = 15.5 Hz, 1H), 2.27-2.16 (m, 2H), 1.99-1.93 (m, 1H), 1.80-1.68 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.1, 150.2, 135.7, 128.2, 118.5, 116.1, 113.0, 58.3, 46.3, 43.9, 33.0, 23.1. HRMS (ESI) calcd for $C_{12}H_{13}NO$ $[M+H]^+$ 188.1070, found 188.1070. All spectroscopic data are in agreement with the reported ones.[12]



2-(Iodomethyl)-1-phenylpyrrolidine (9): Yellow oil; 65% yield, 187 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (t, *J* = 8.5 Hz, 2H), 6.72 (t, *J* = 7.5 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 2H), 4.05-4.02 (m, 1H), 3.49 (t, *J* = 7.5 Hz, 1H), 3.34 (d, *J* = 9.5 Hz, 1H), 3.17 (dd, *J* = 15.5, 8.0 Hz, 1H), 2.95 (t, *J* = 10.5 Hz, 1H), 2.15-2.02 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3, 129.7, 116.7, 120.0, 60.9, 49.2, 30.6, 23.0, 9.76.

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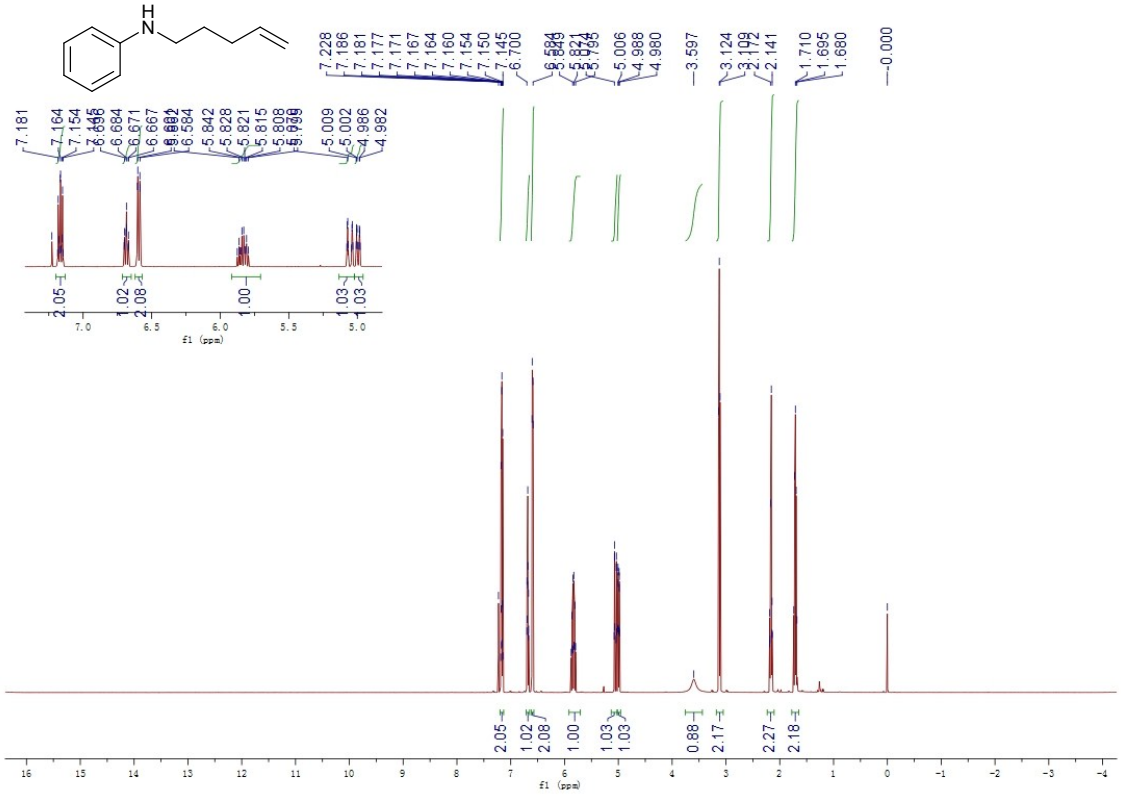
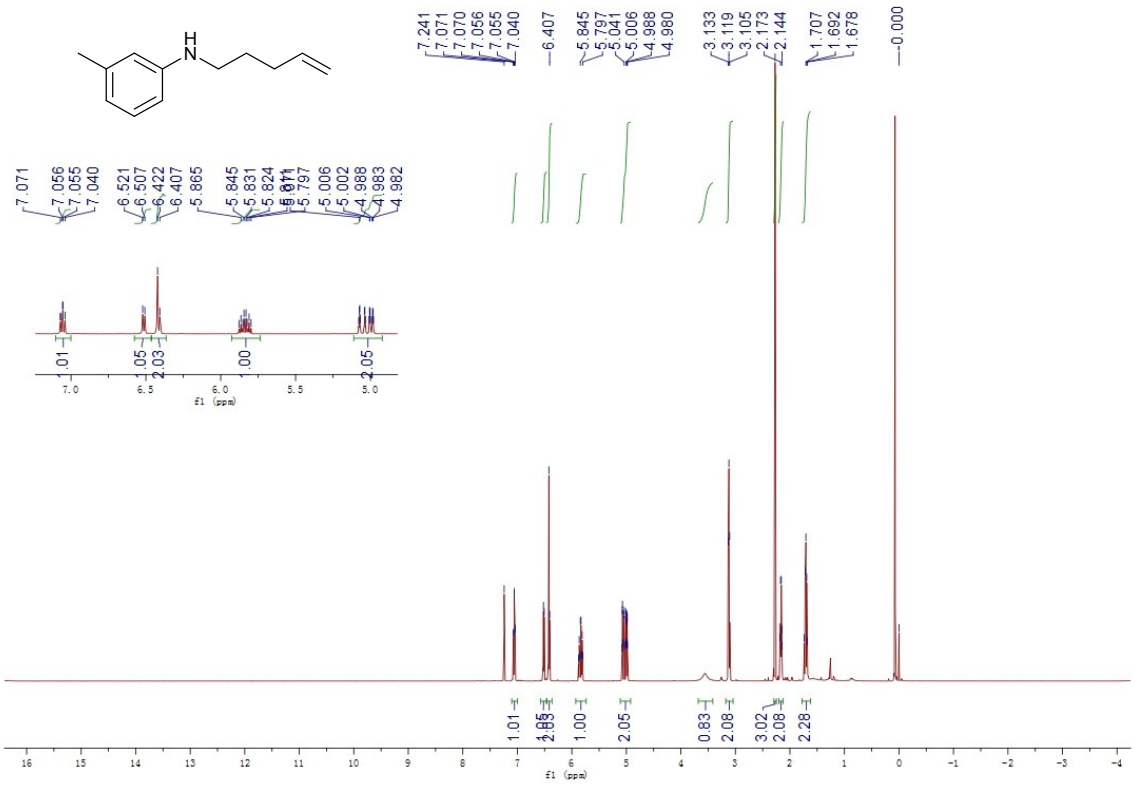
6. ^{1}H- and ^{13}C-NMR spectra

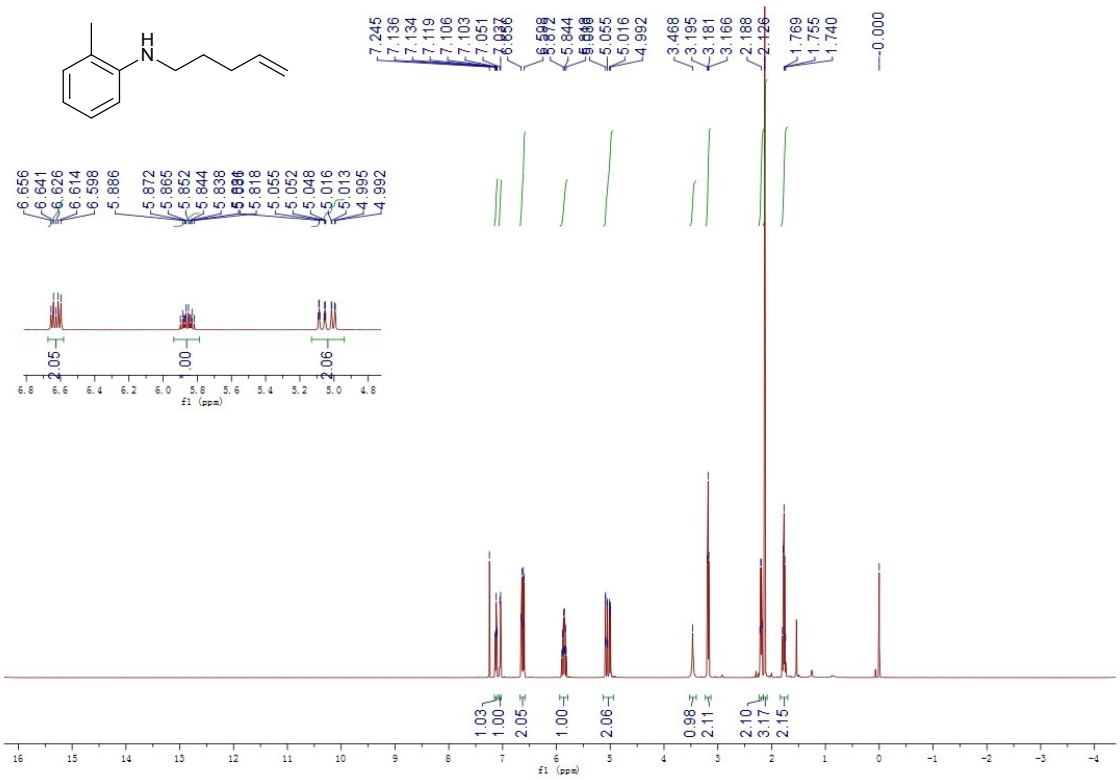
***N*-(pent-4-en-1-yl)aniline (2a)**



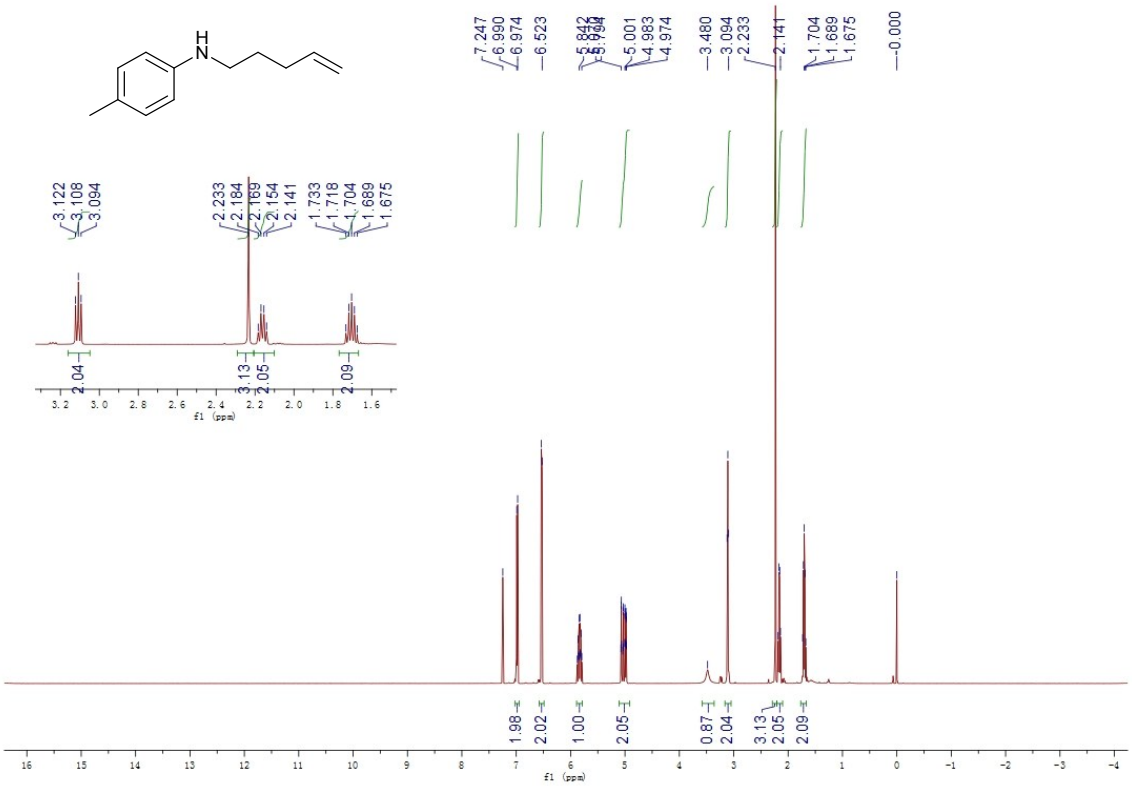
3-Methyl-*N*-(pent-4-en-1-yl)aniline (2b)



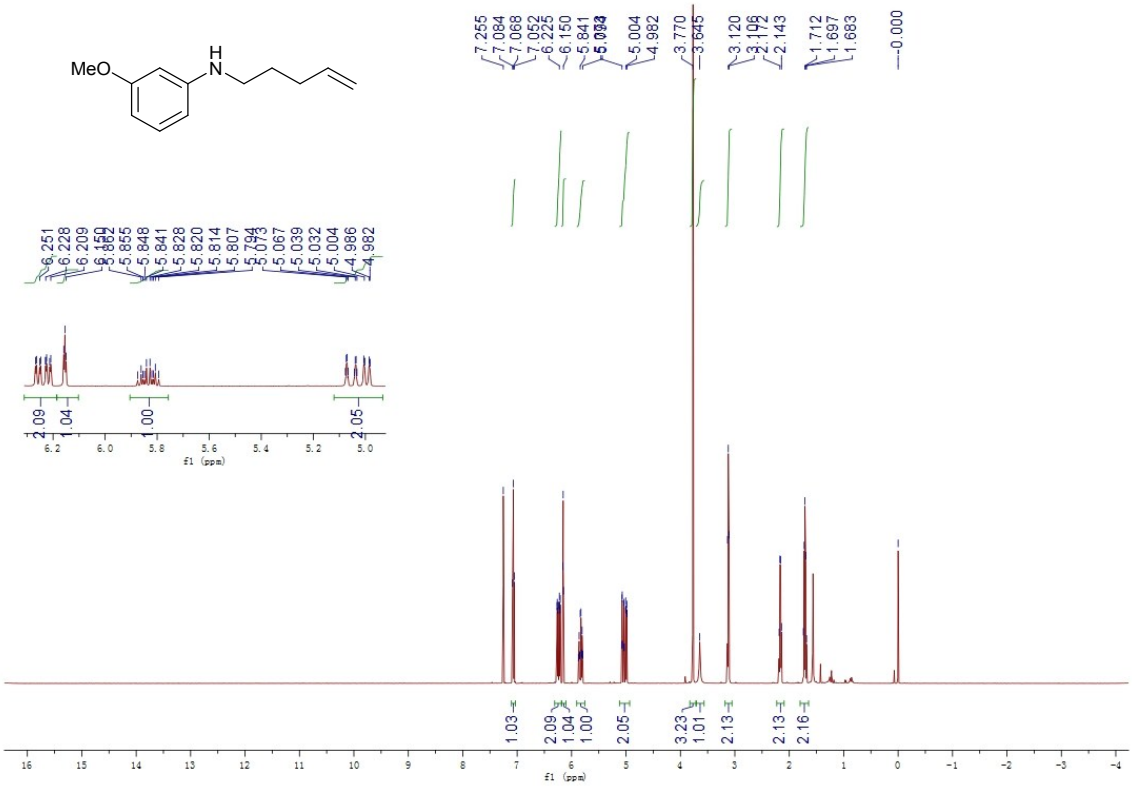
2-Methyl-*N*-(pent-4-en-1-yl)aniline (2c)



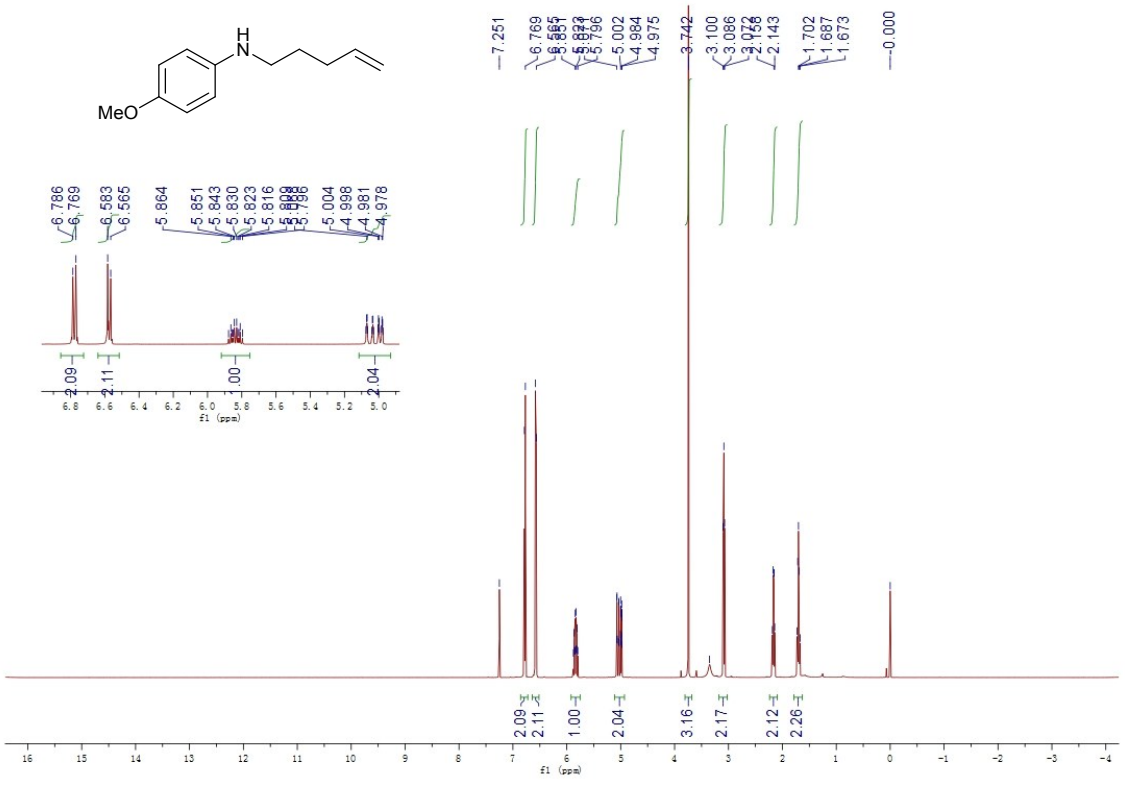
4-Methyl-*N*-(pent-4-en-1-yl)aniline (2d)



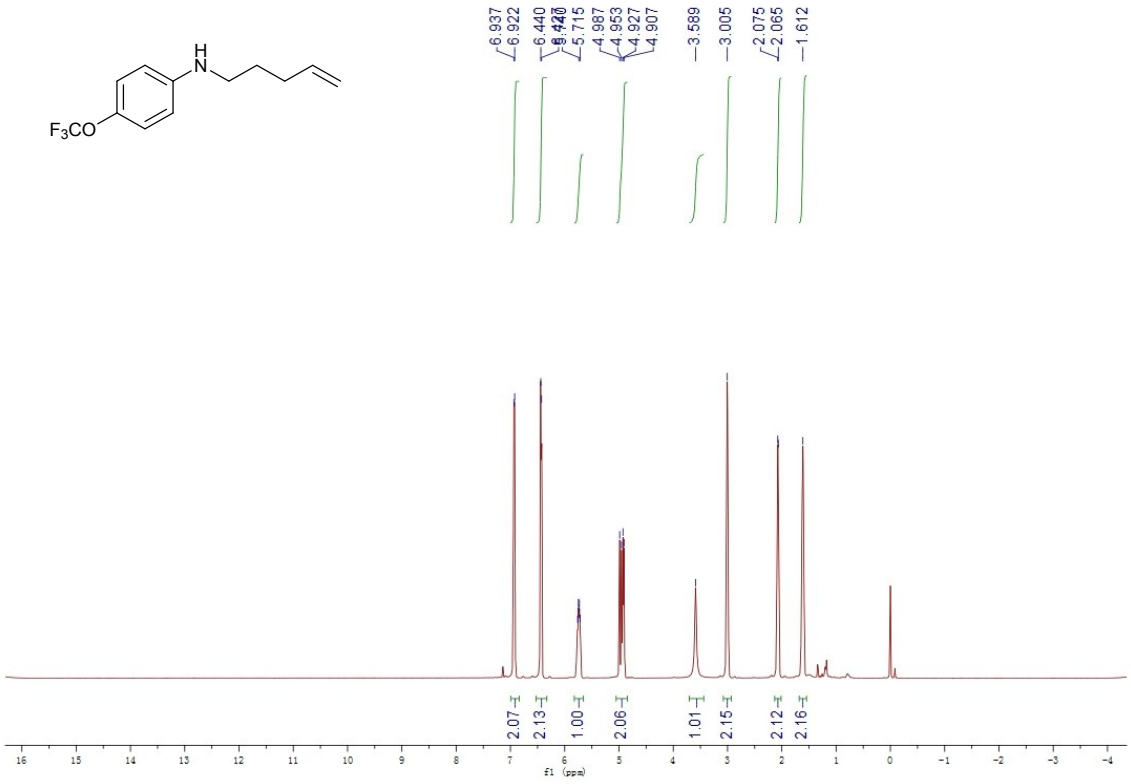
3-Methoxy-*N*-(pent-4-en-1-yl)aniline (2e)



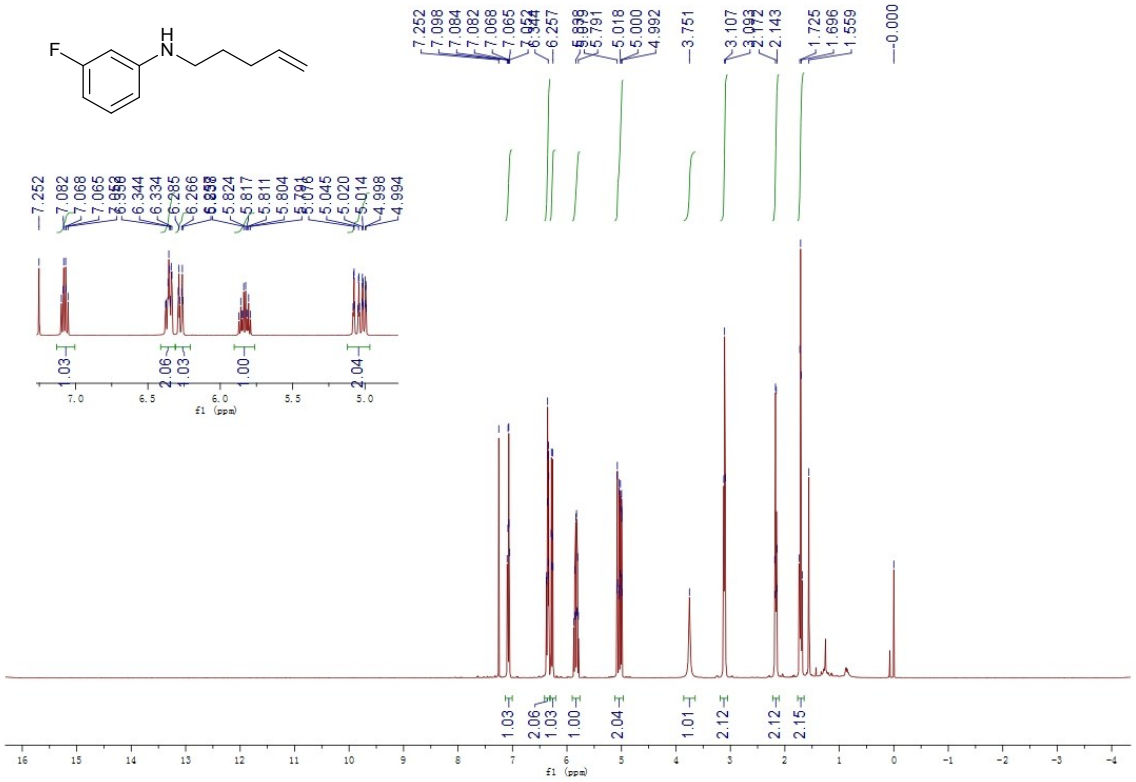
4-Methoxy-*N*-(pent-4-en-1-yl)aniline (2f)



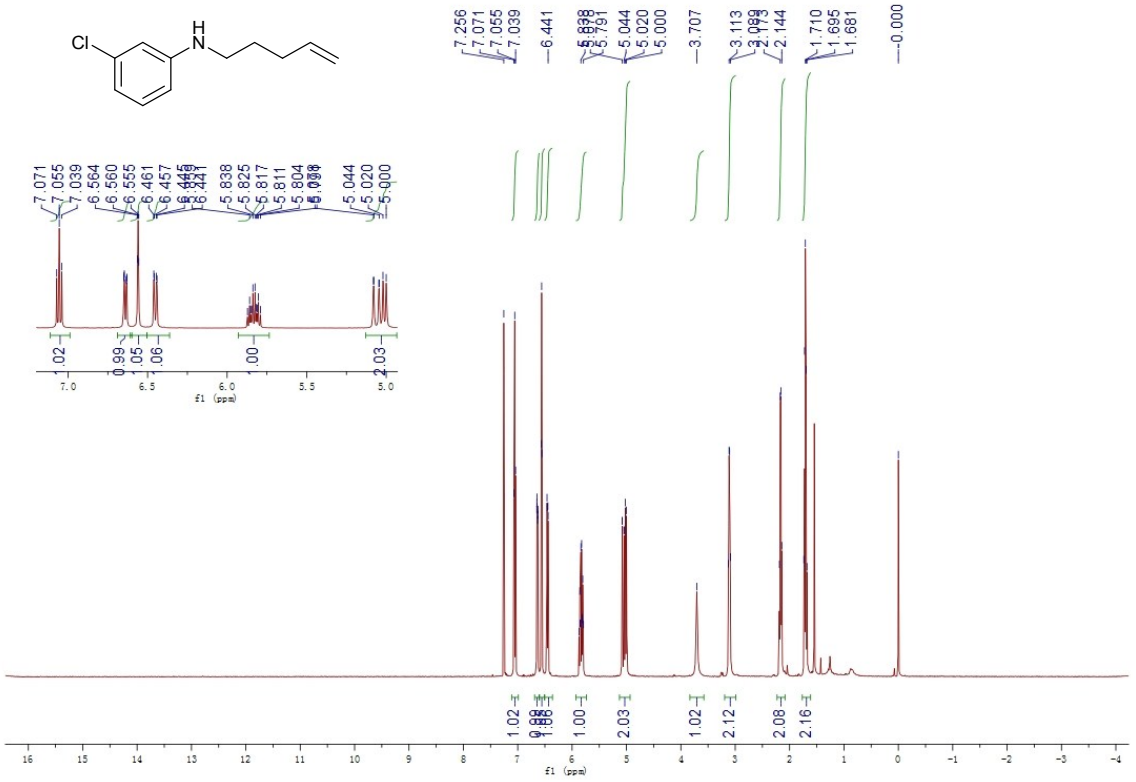
***N*-(pent-4-en-1-yl)-4-(trifluoromethoxy)aniline (2g)**



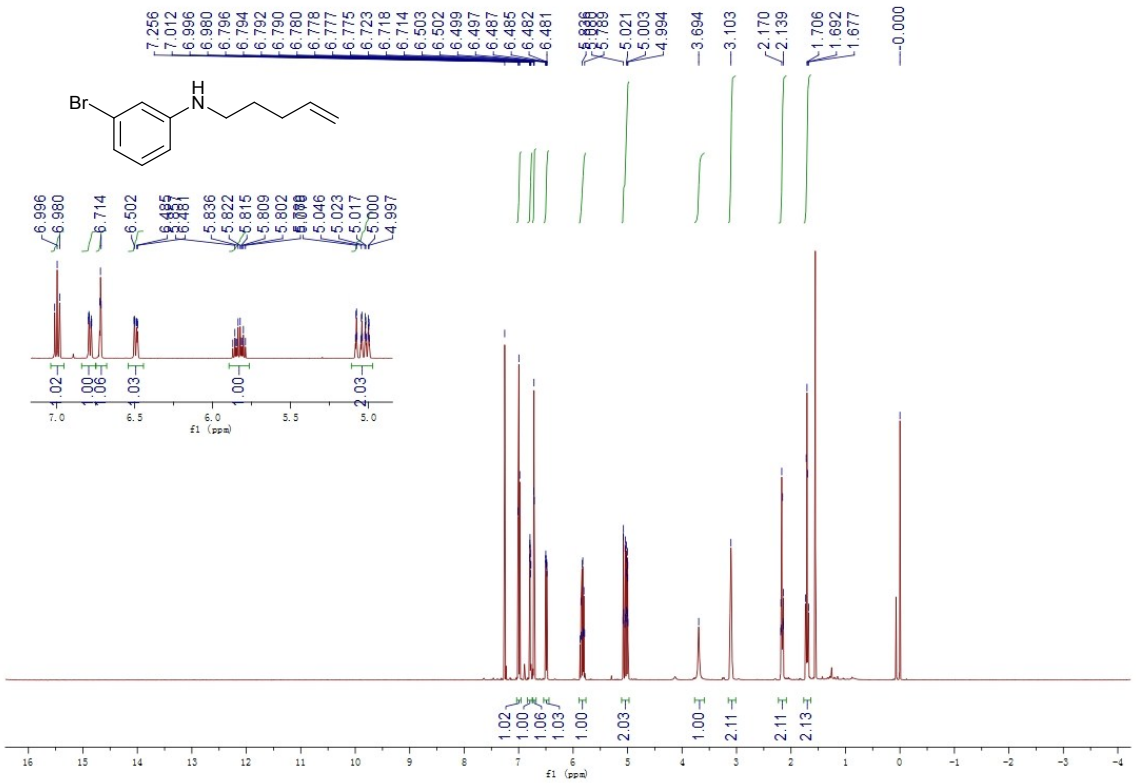
3-Fluoro-*N*-(pent-4-en-1-yl)aniline (2h)



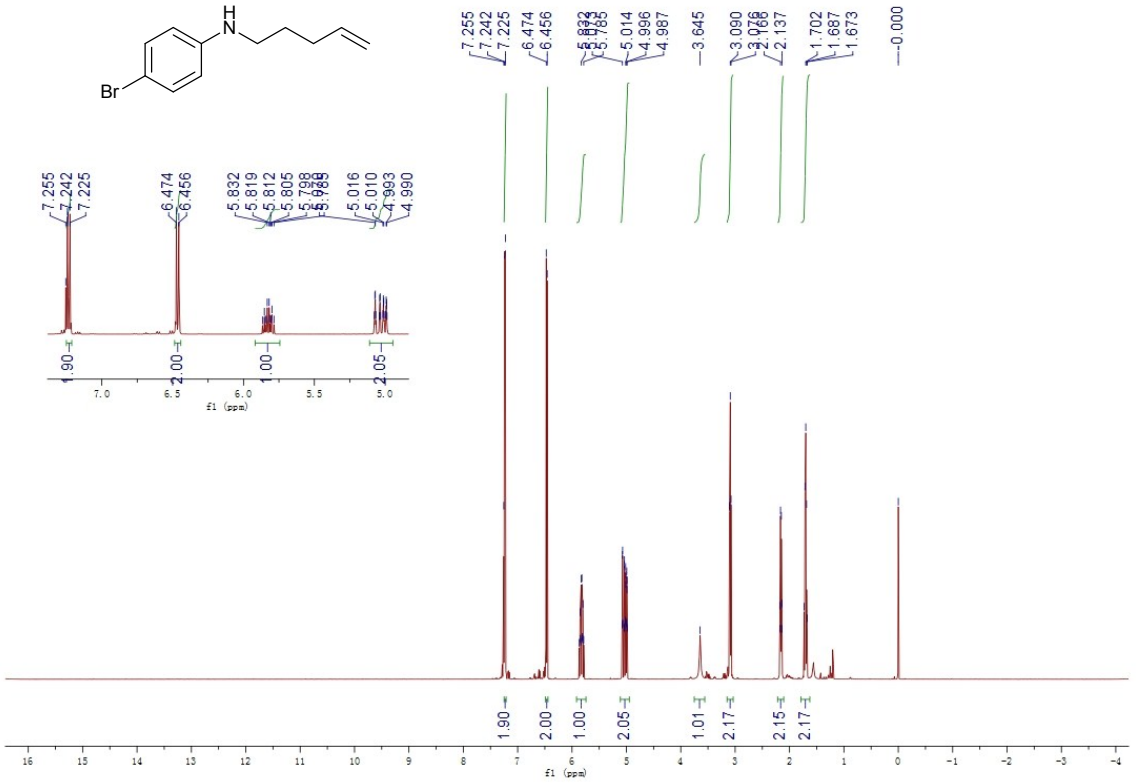
3-Chloro-*N*-(pent-4-en-1-yl)aniline (2i)



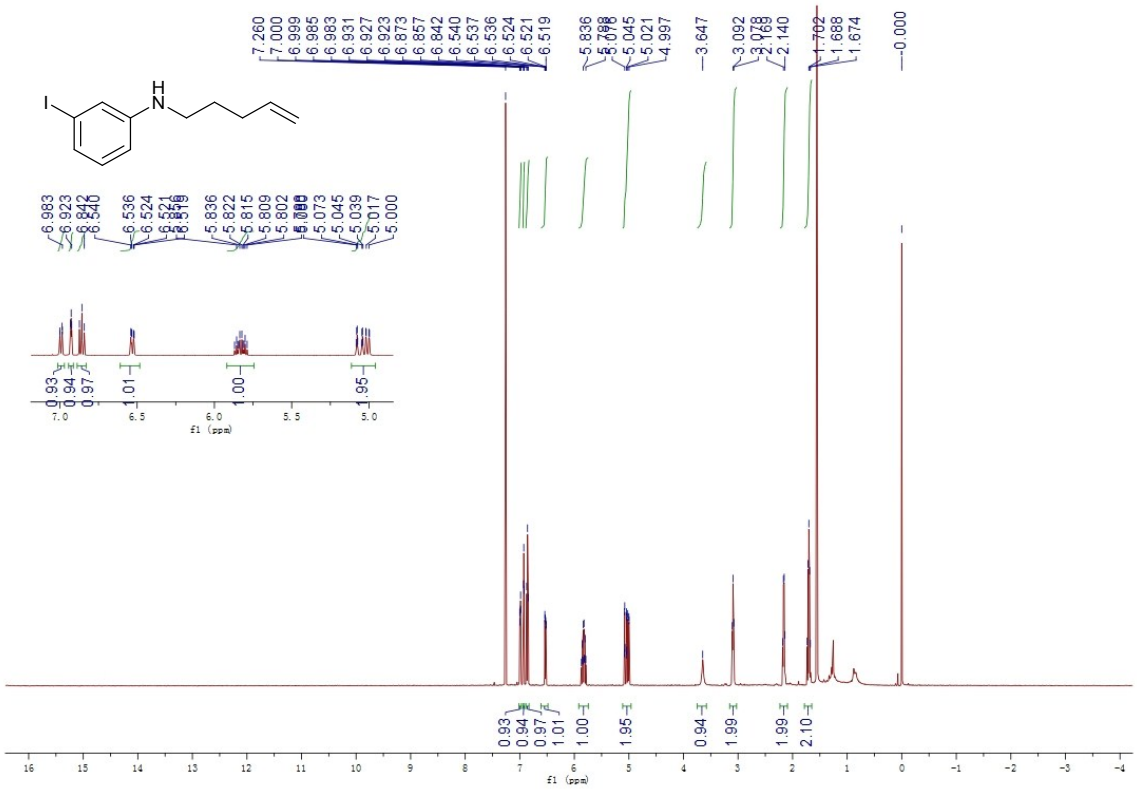
3-Bromo-*N*-(pent-4-en-1-yl)aniline (2j)



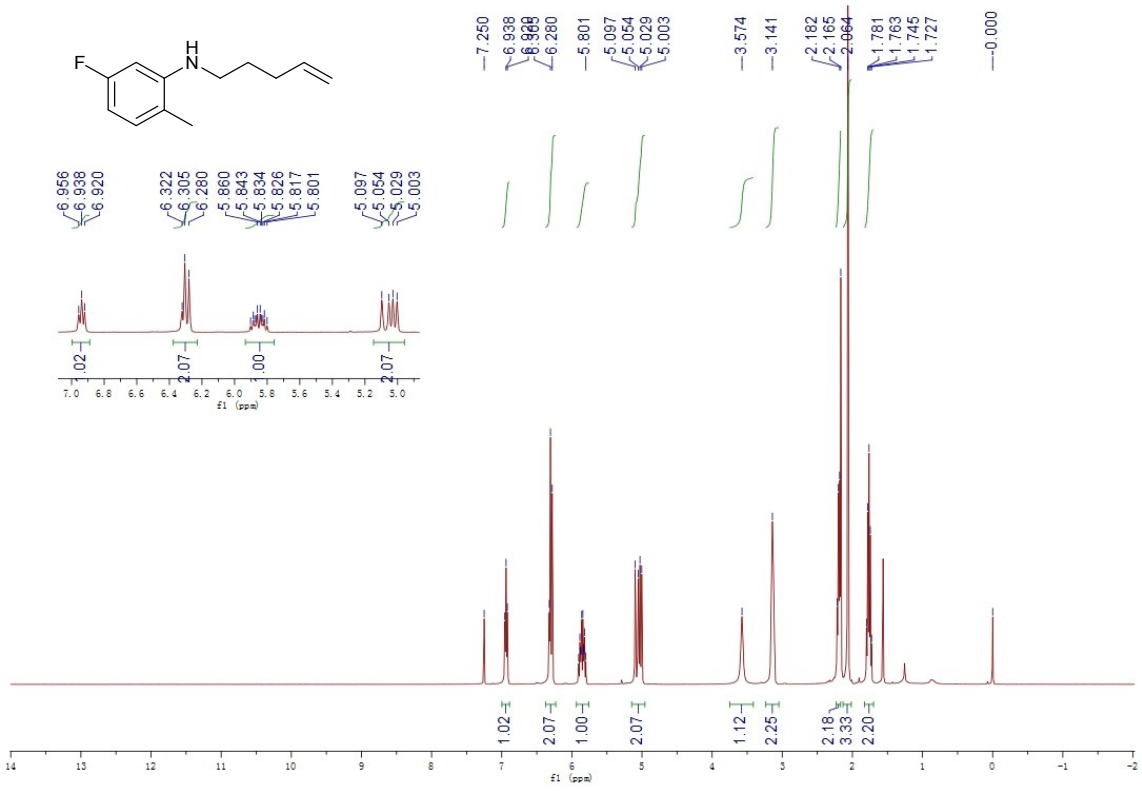
4-Bromo-*N*-(pent-4-en-1-yl)aniline (2k)



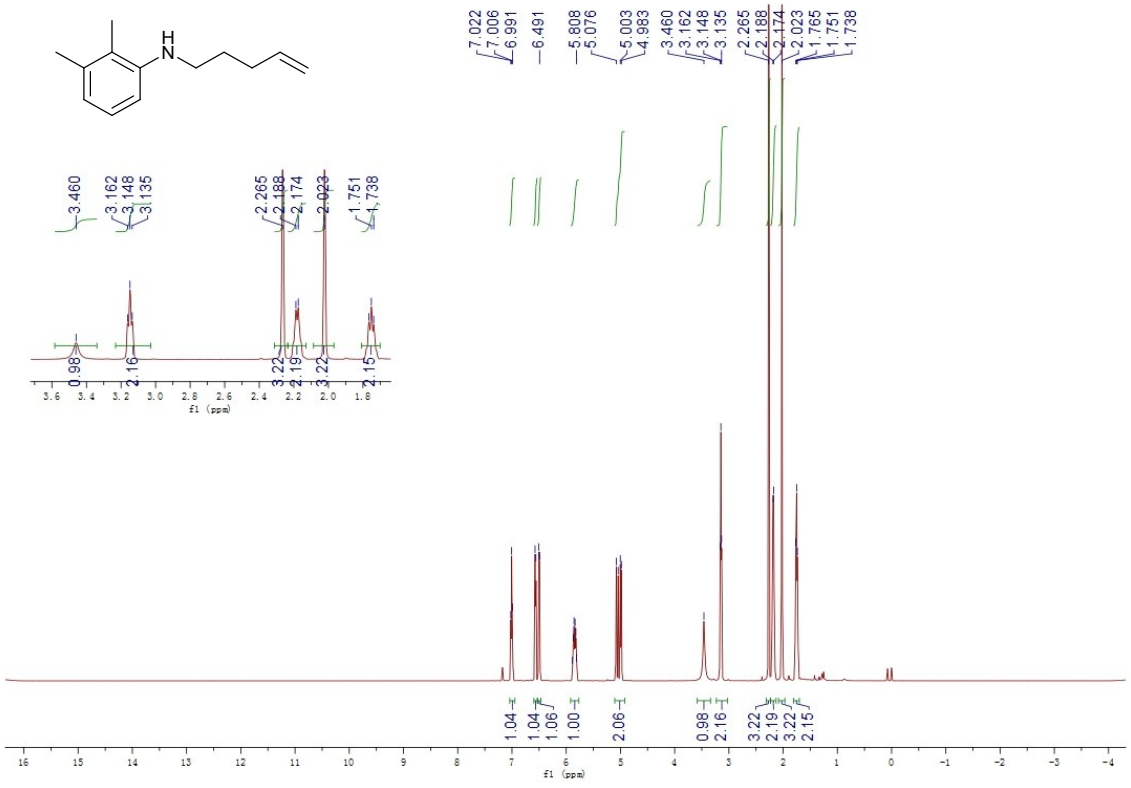
3-Iodo-*N*-(pent-4-en-1-yl)aniline (2l)



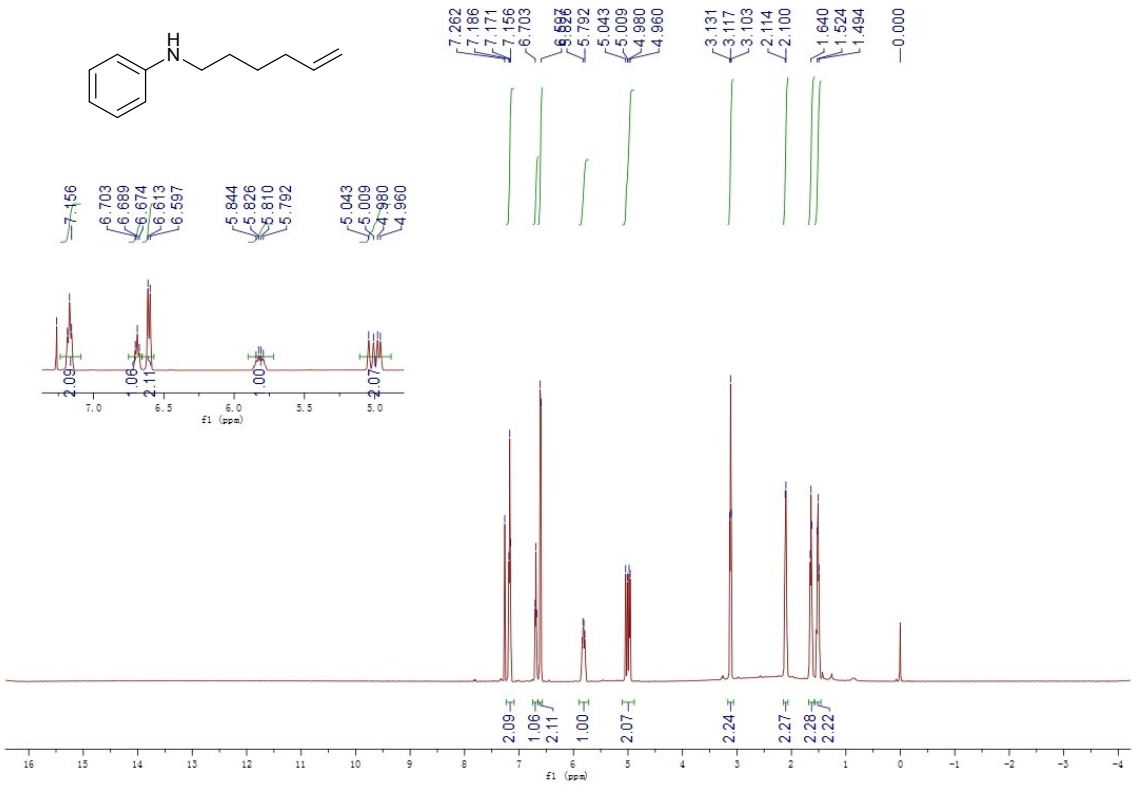
5-Fluoro-2-methyl-*N*-(pent-4-en-1-yl)aniline (2m)



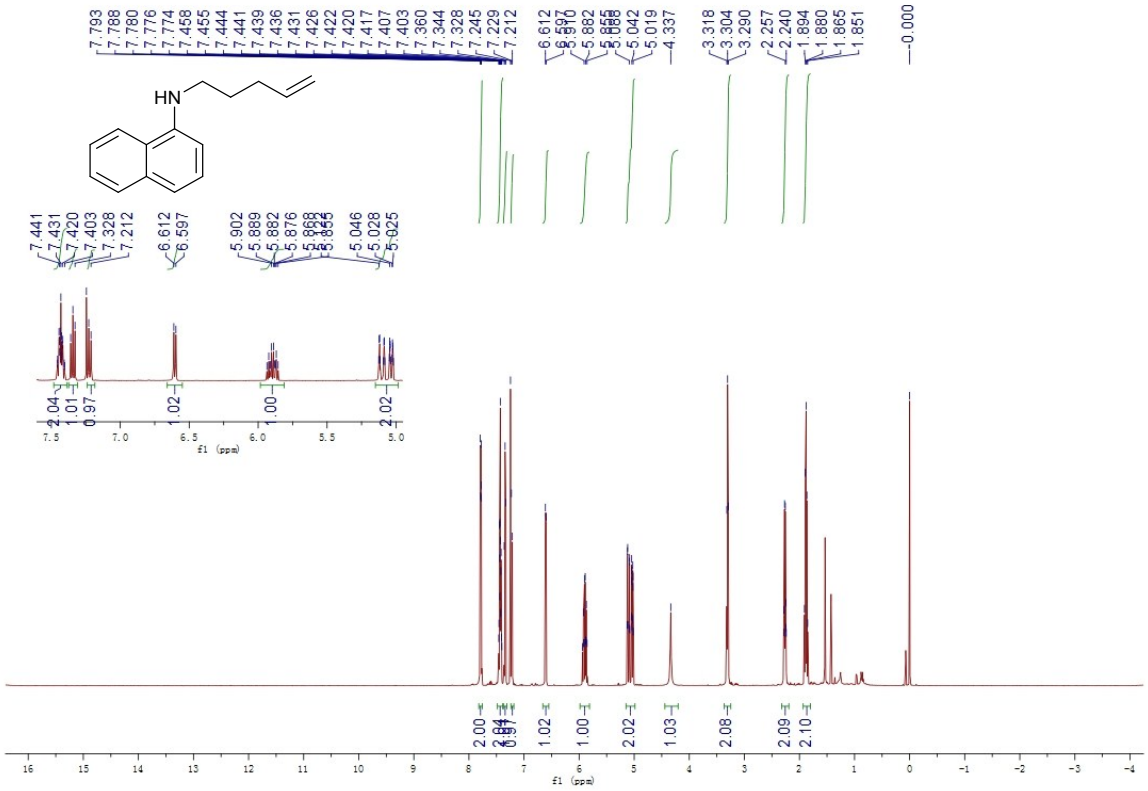
2,3-Dimethyl-*N*-(pent-4-en-1-yl)aniline (2n)



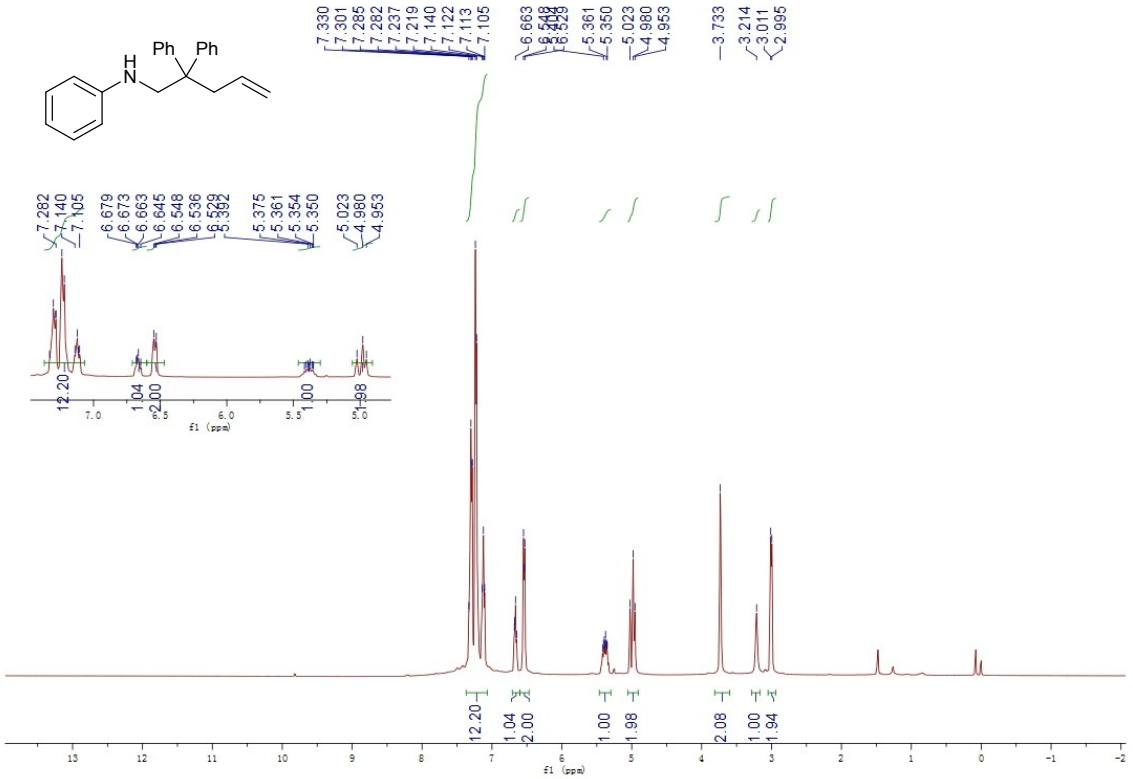
***N*-(hex-5-en-1-yl)aniline (2o)**



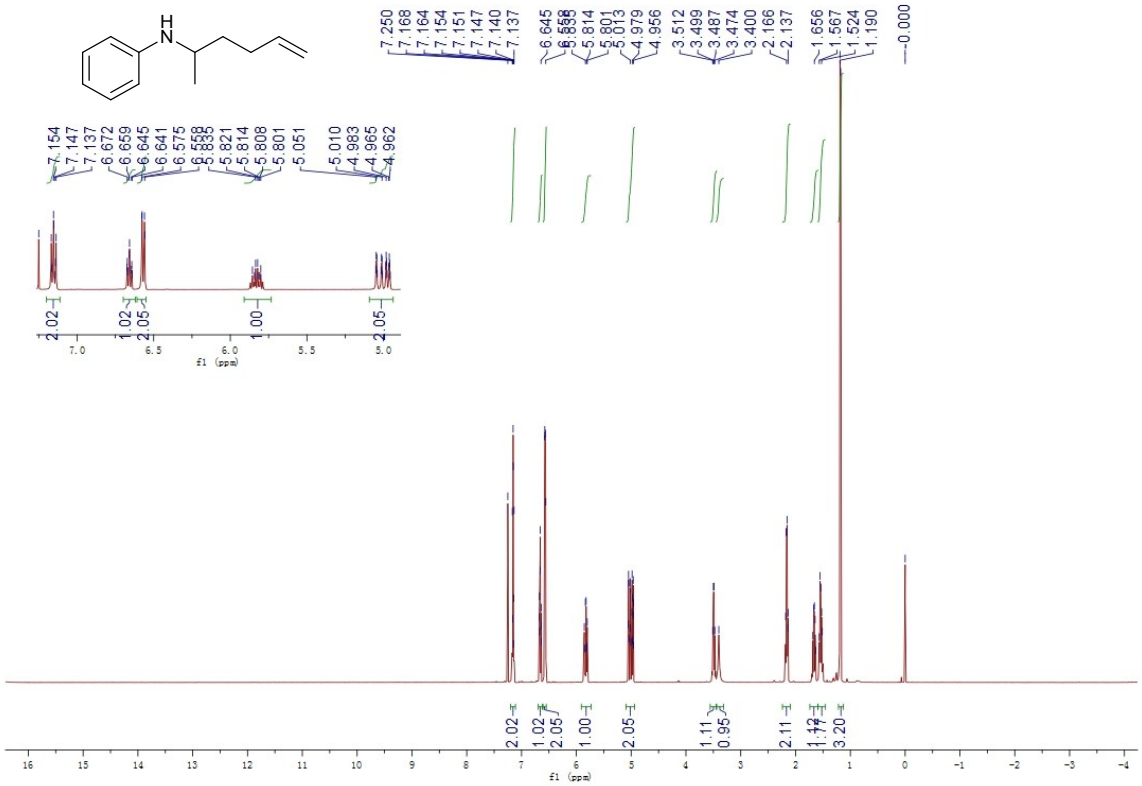
***N*-(pent-4-en-1-yl)naphthalen-1-amine (2p)**



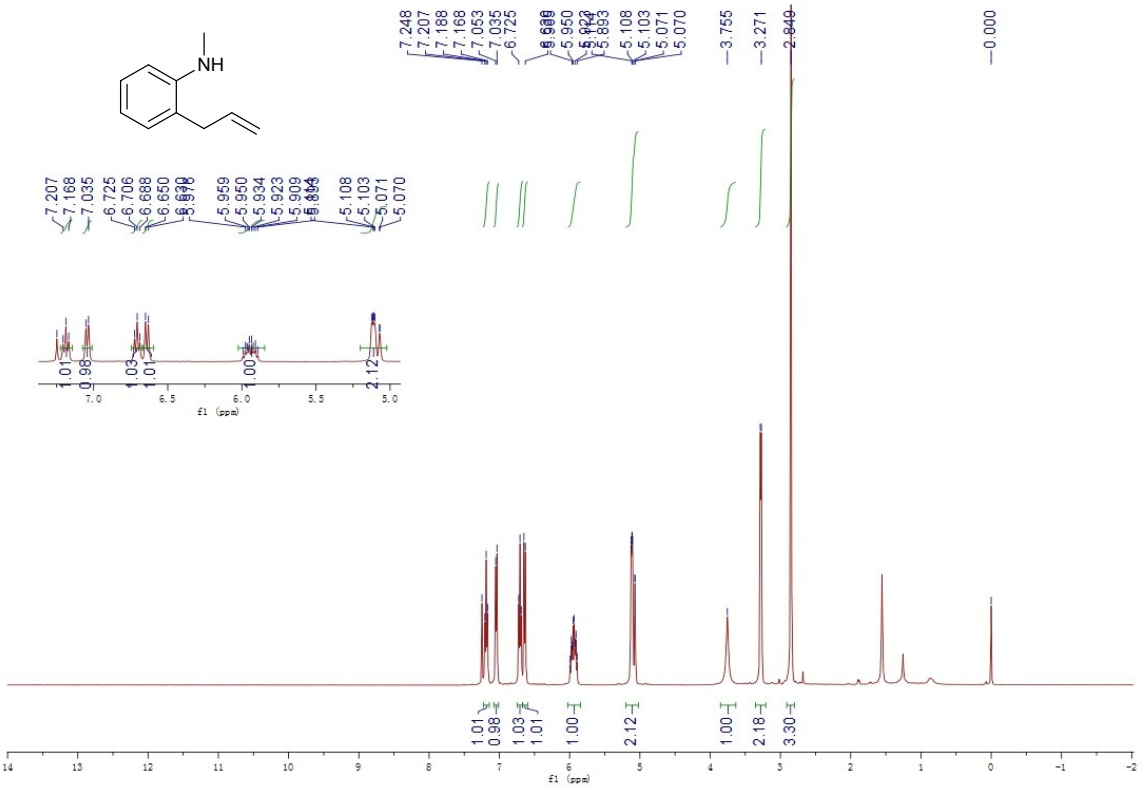
_N_-(2,2-diphenylpent-4-en-1-yl)aniline (2q)



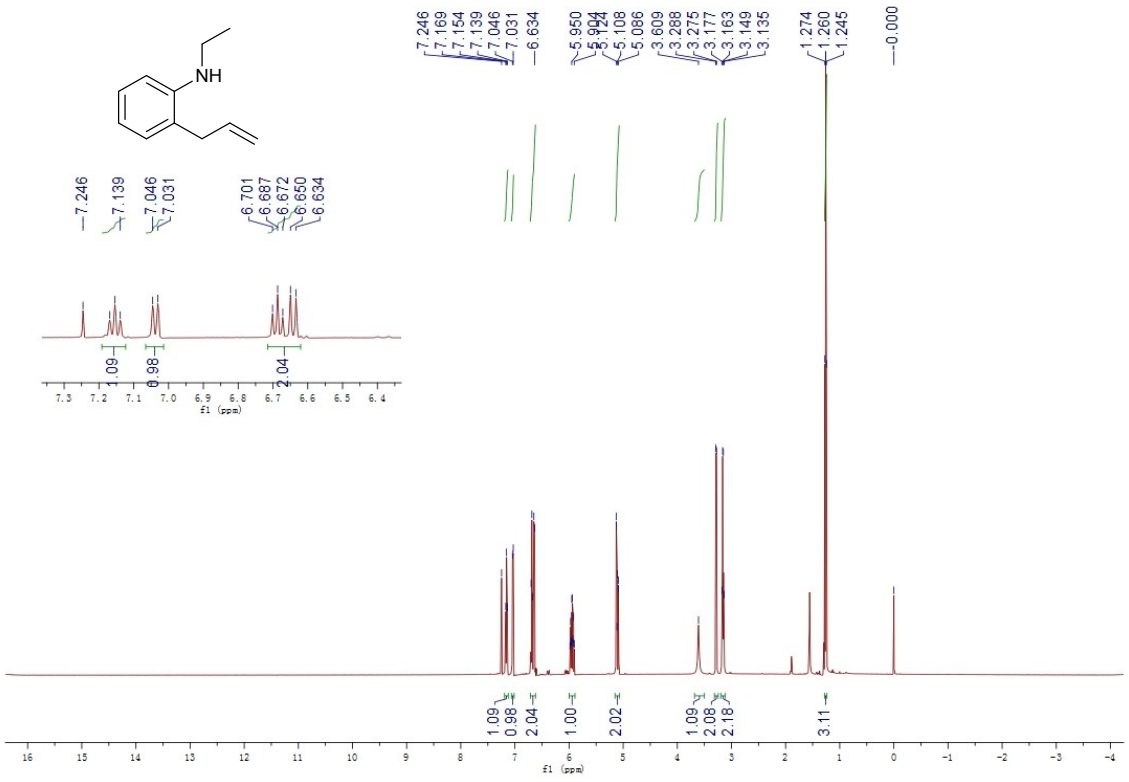
_N_-(hex-5-en-2-yl)aniline (2r)



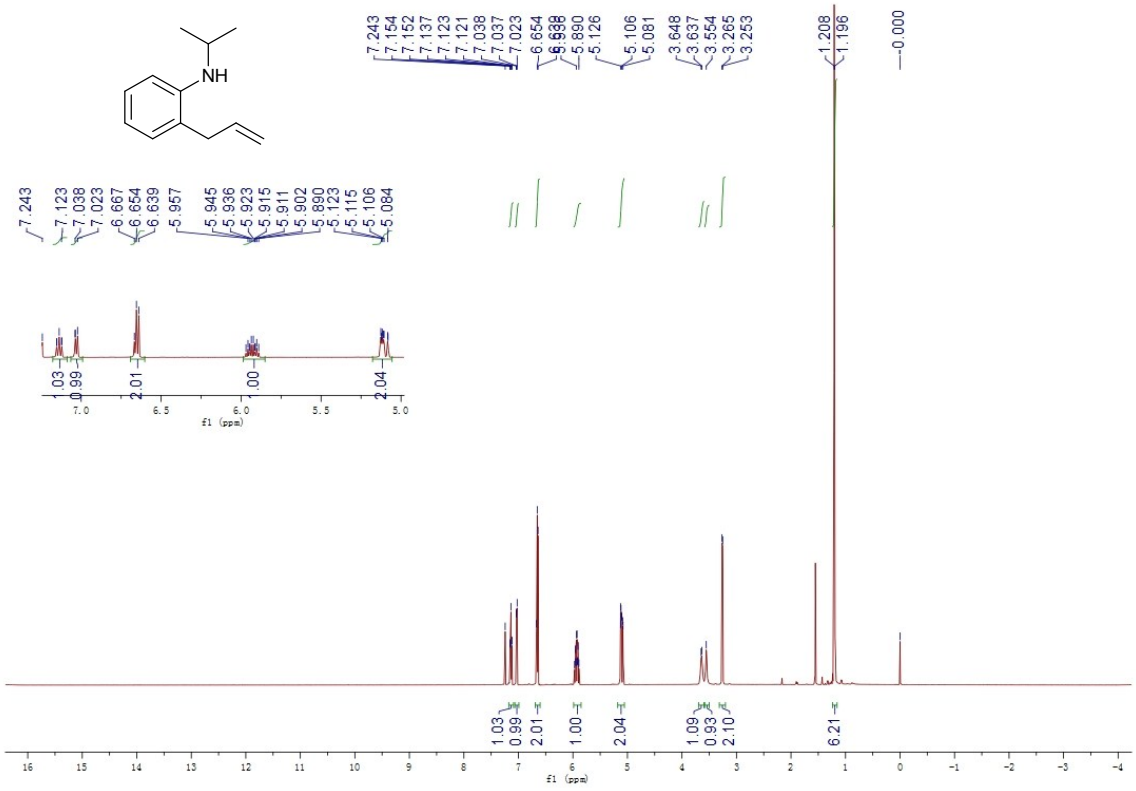
2-Allyl-*N*-methylaniline (2s)



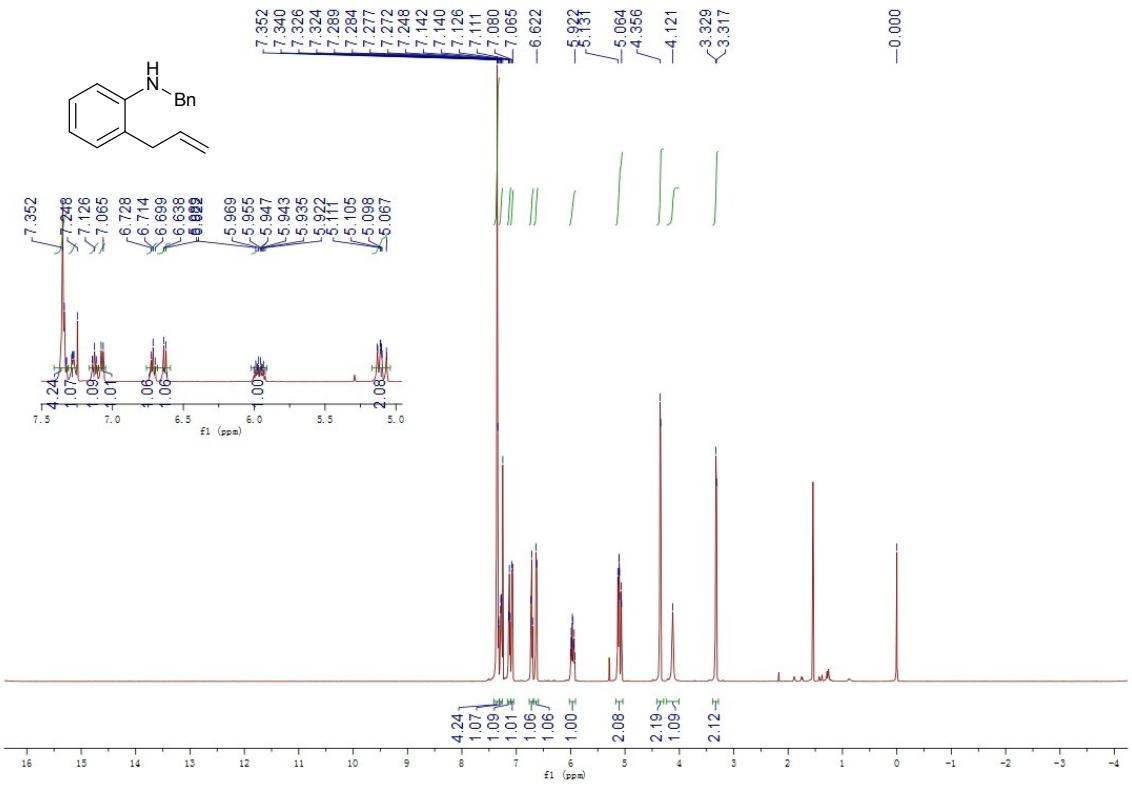
2-Allyl-*N*-ethylaniline (2t)



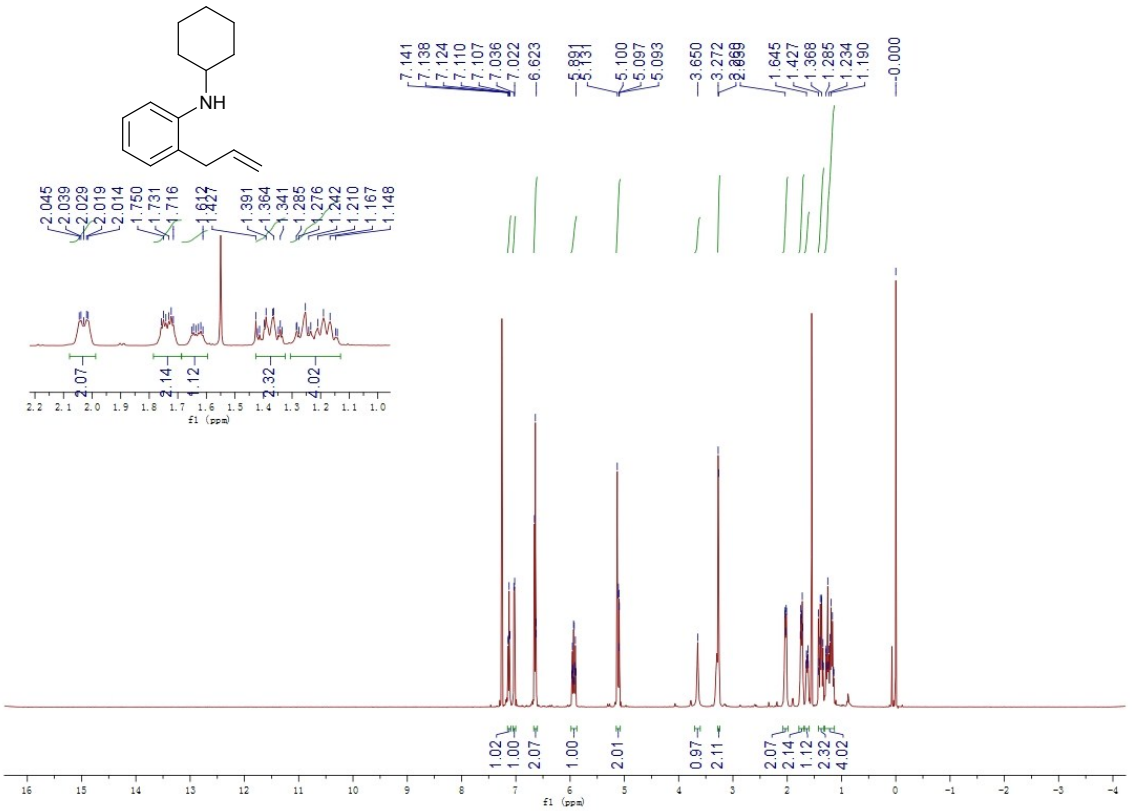
2-Allyl-*N*-isopropylaniline (2u)



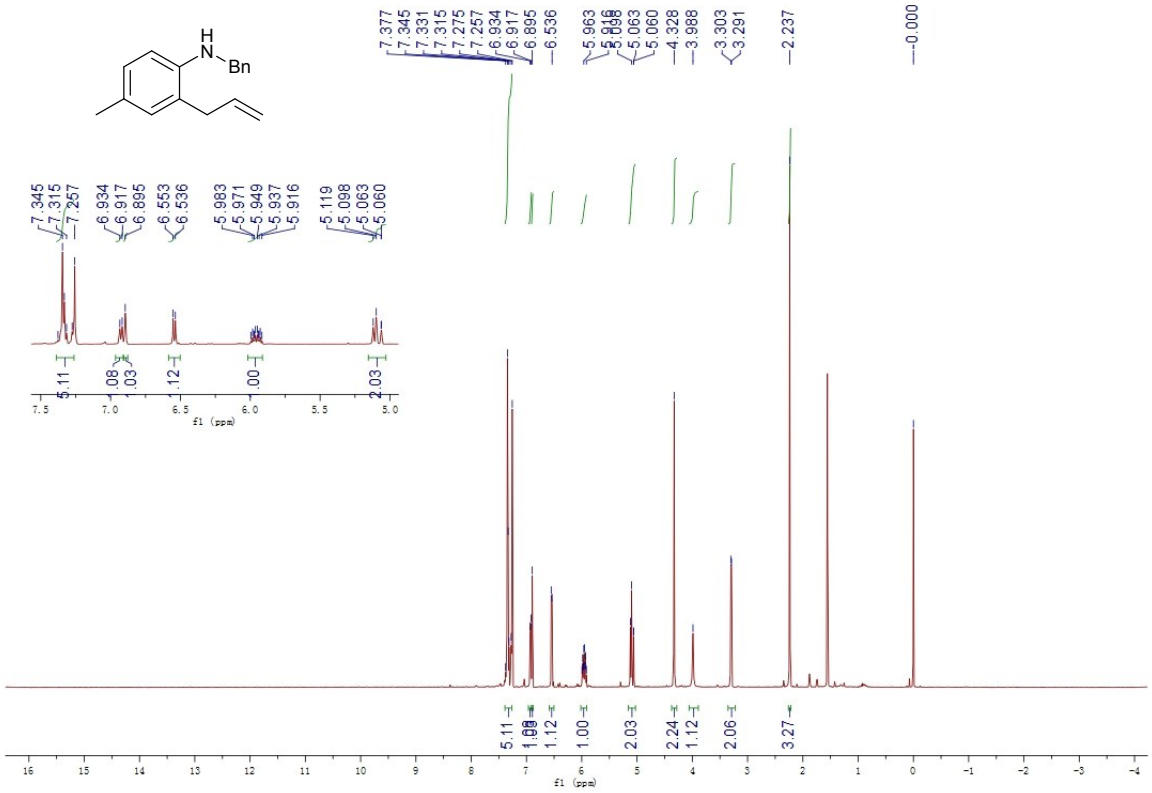
2-Allyl-*N*-benzylaniline (2v)



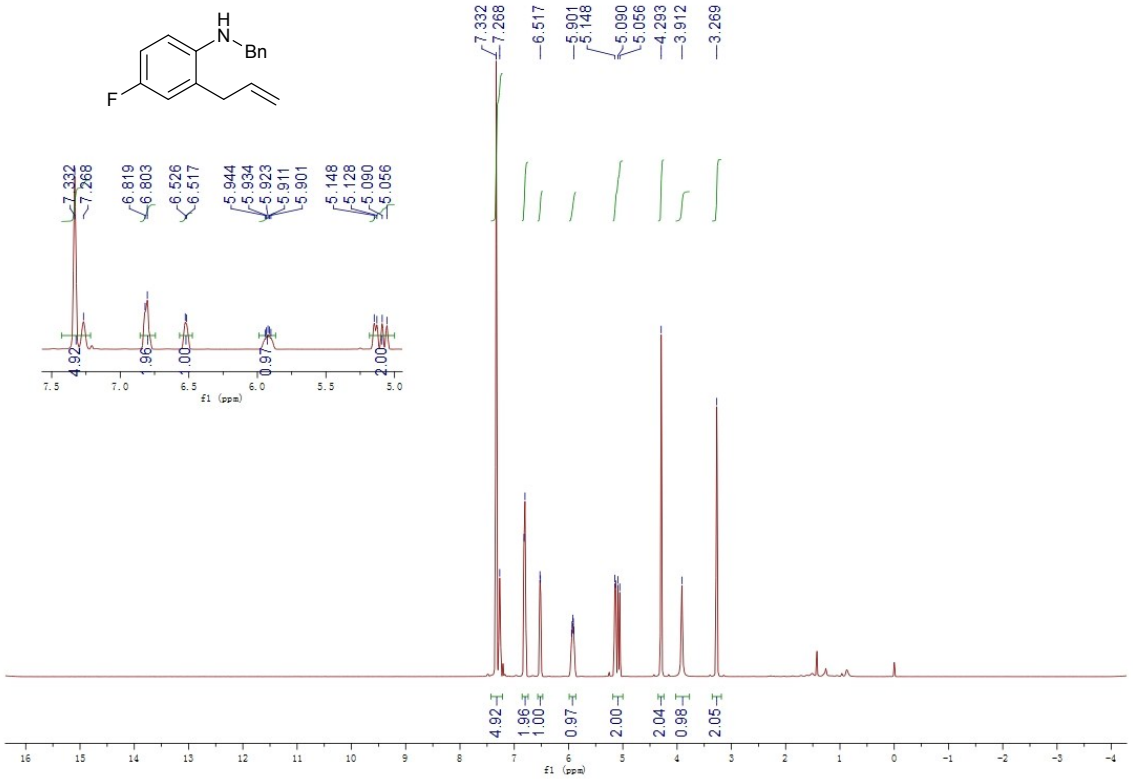
2-Allyl-*N*-cyclohexylaniline (2w)



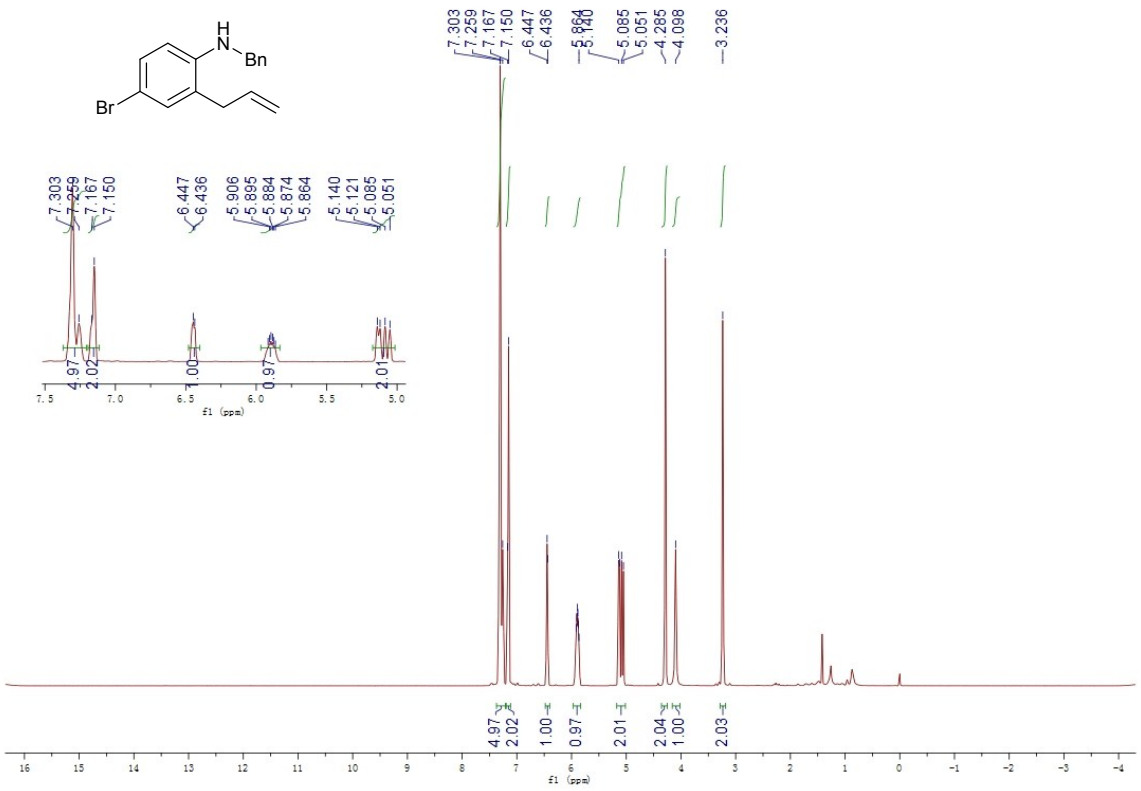
2-Allyl-*N*-benzyl-4-methylaniline (2x)



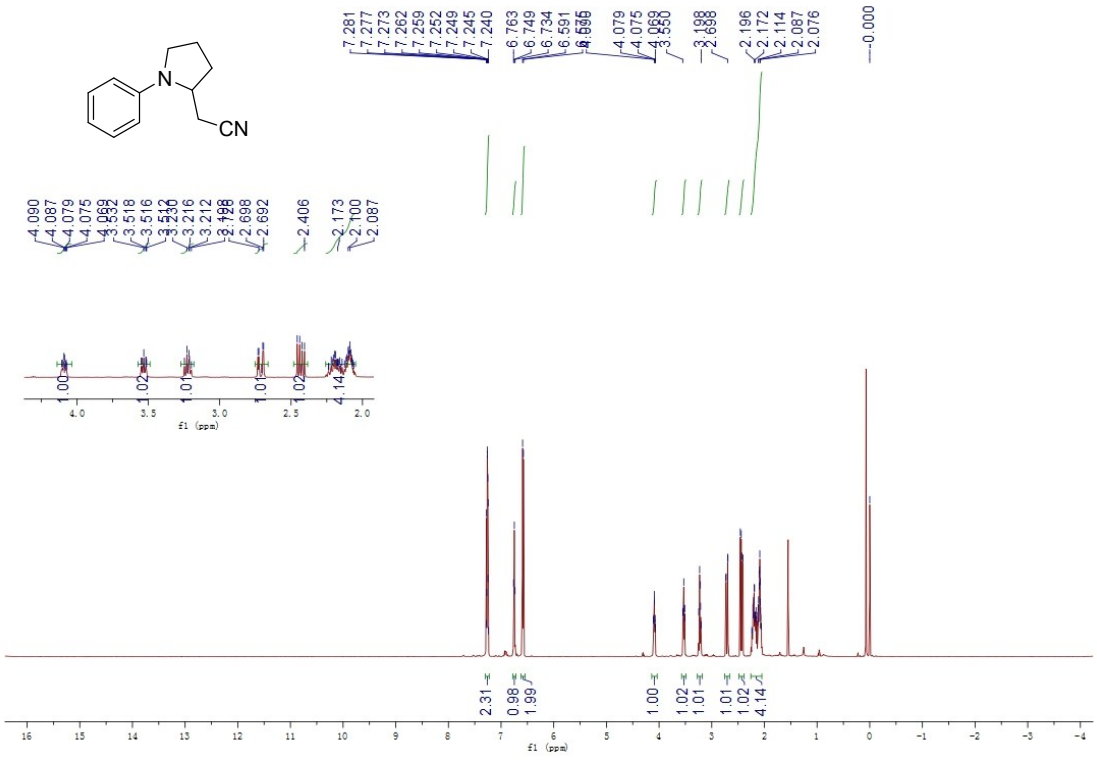
2-Allyl-*N*-benzyl-4-fluoroaniline (2y)

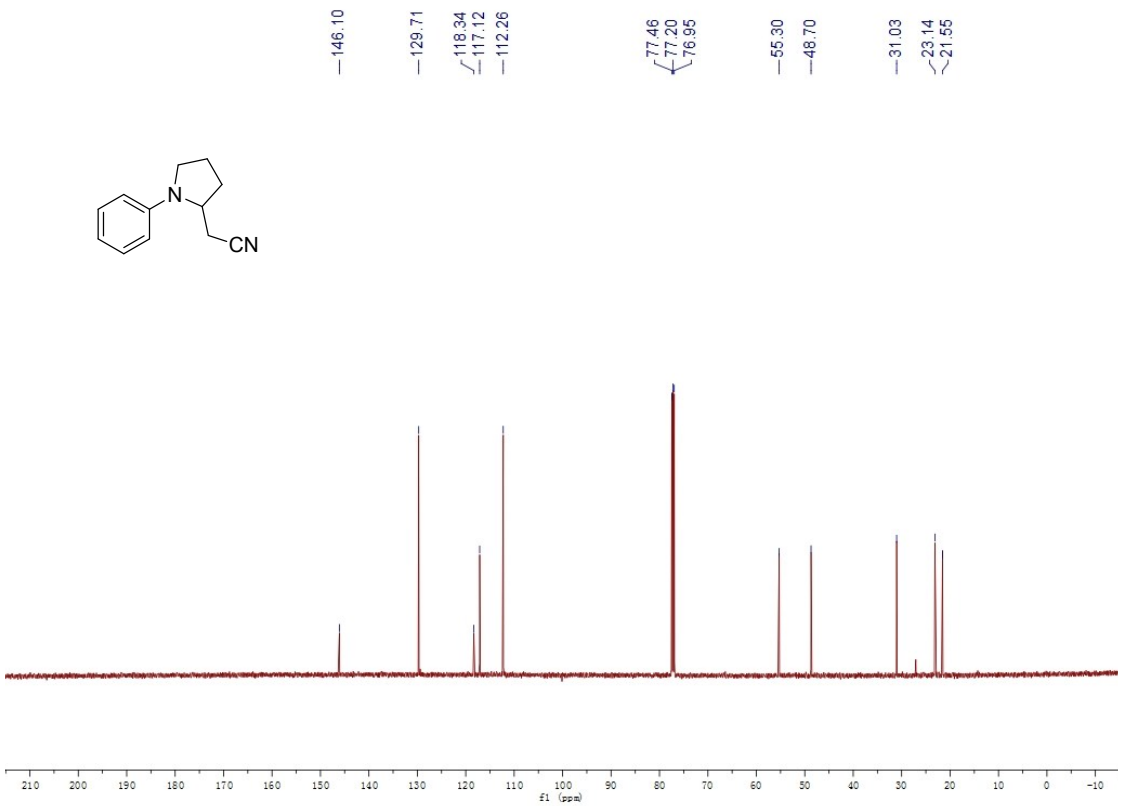


2-Allyl-*N*-benzyl-4-bromoaniline (2z)

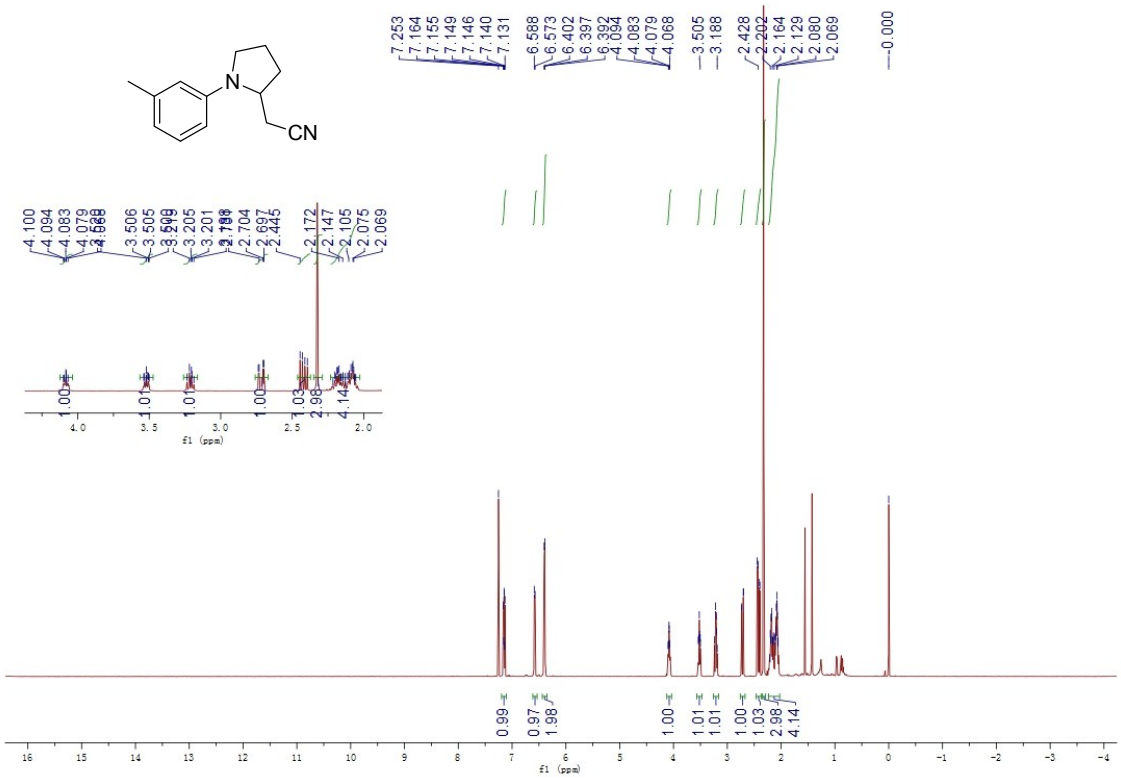


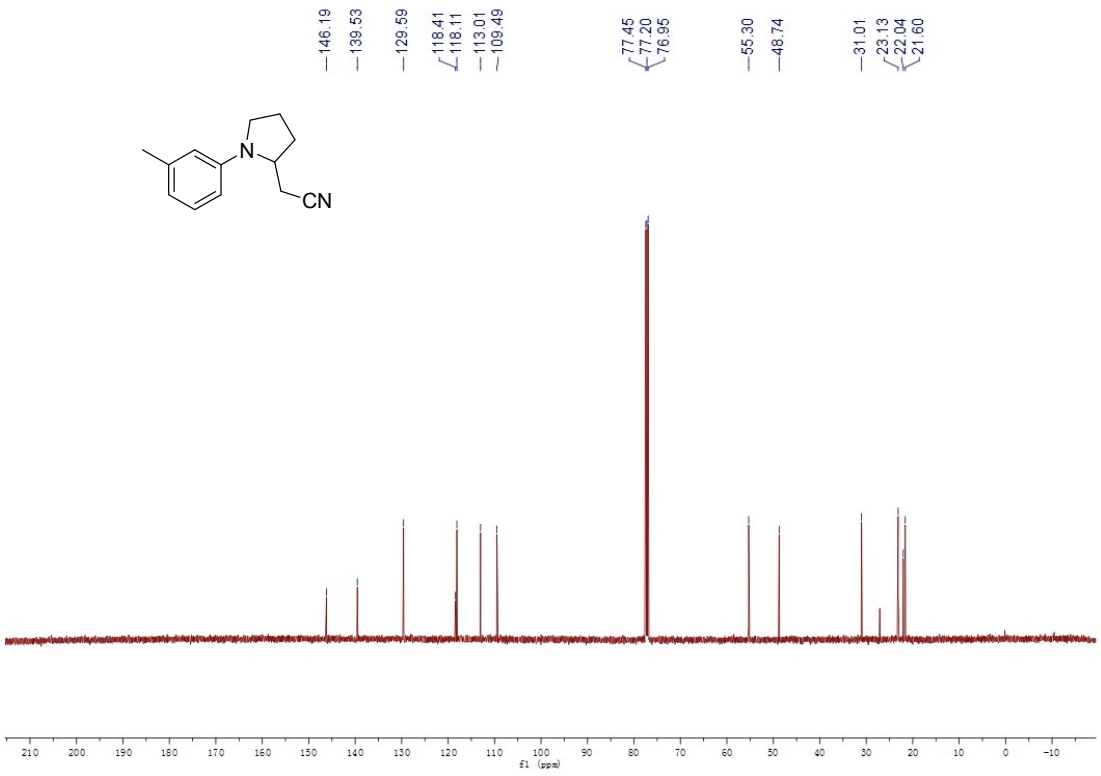
2-(1-Phenylpyrrolidin-2-yl)acetonitrile (3a)



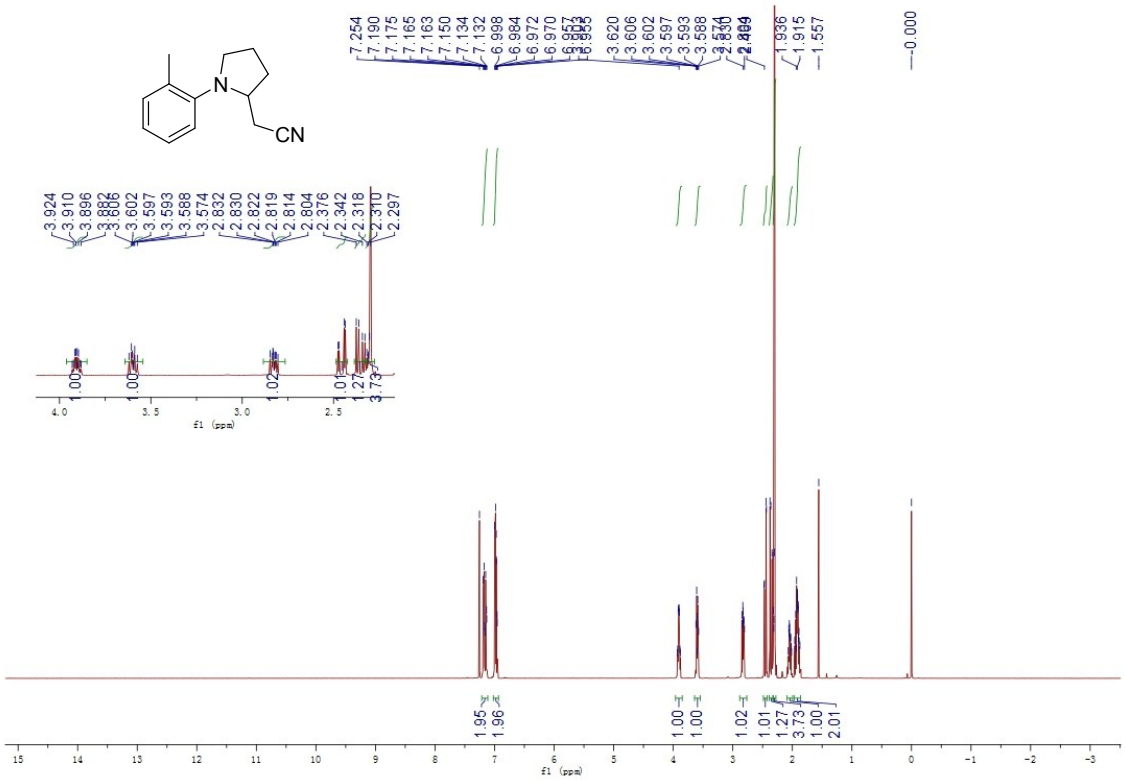


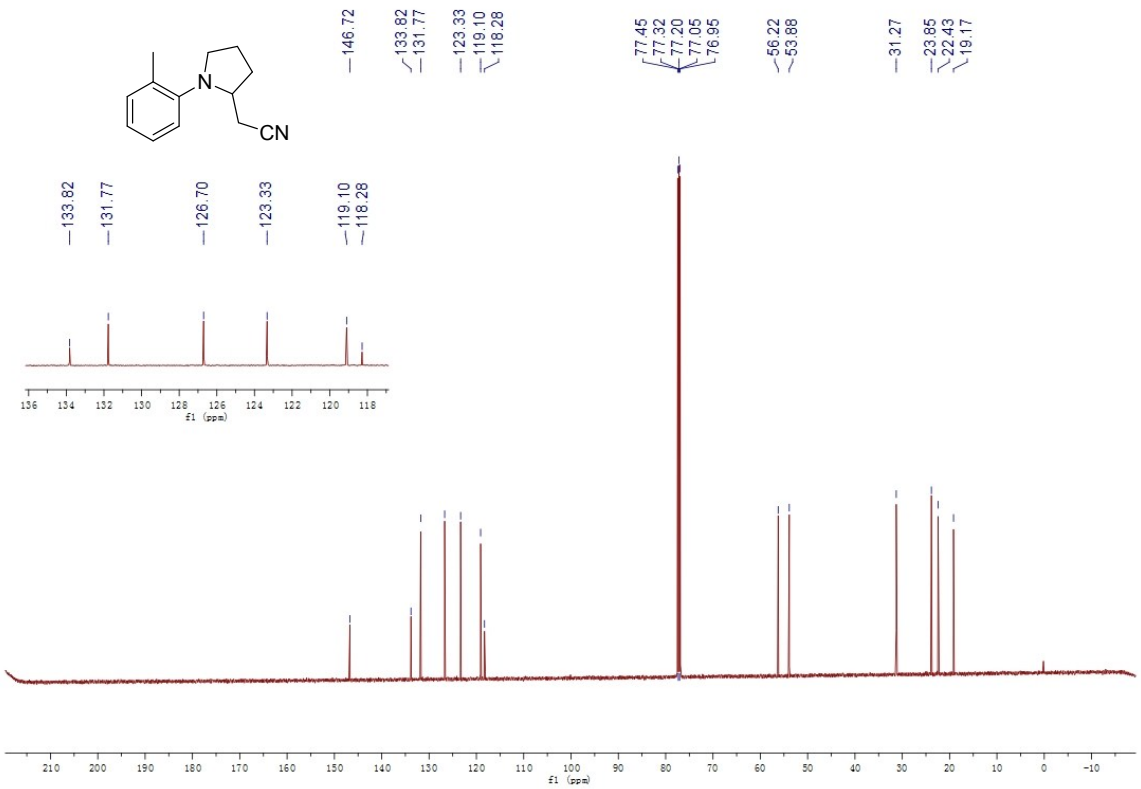
2-(1-(m-Tolyl)pyrrolidin-2-yl)acetonitrile (3b)



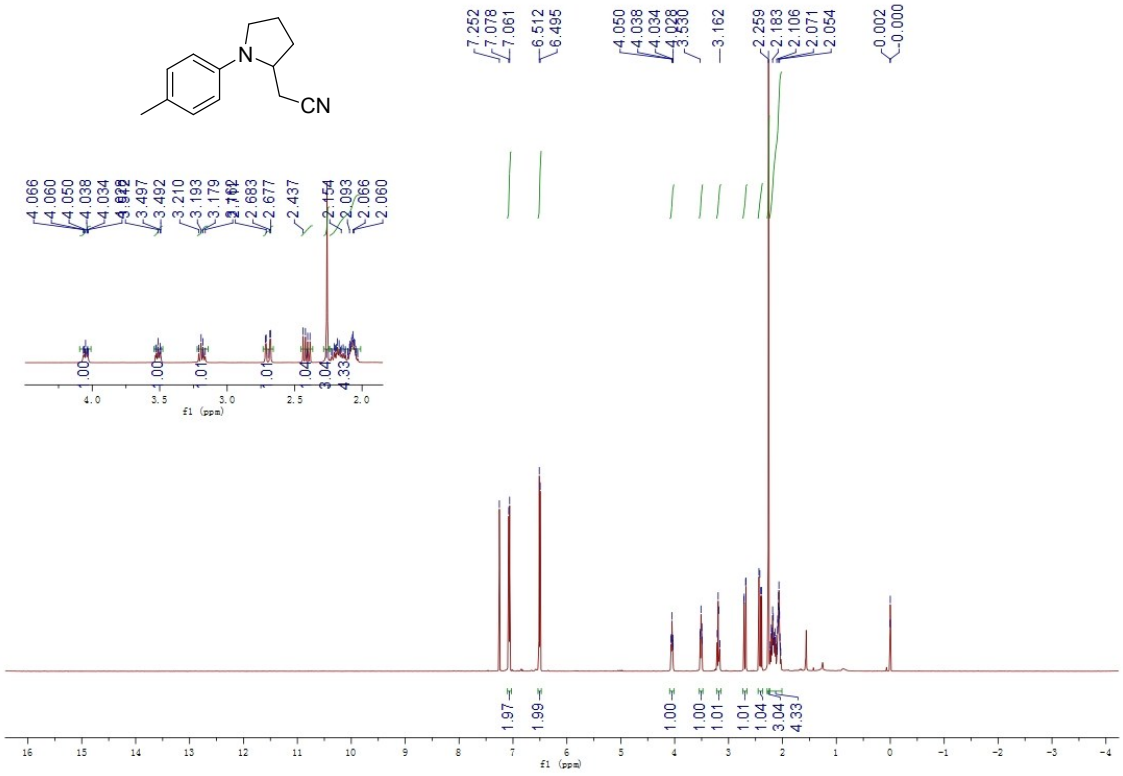


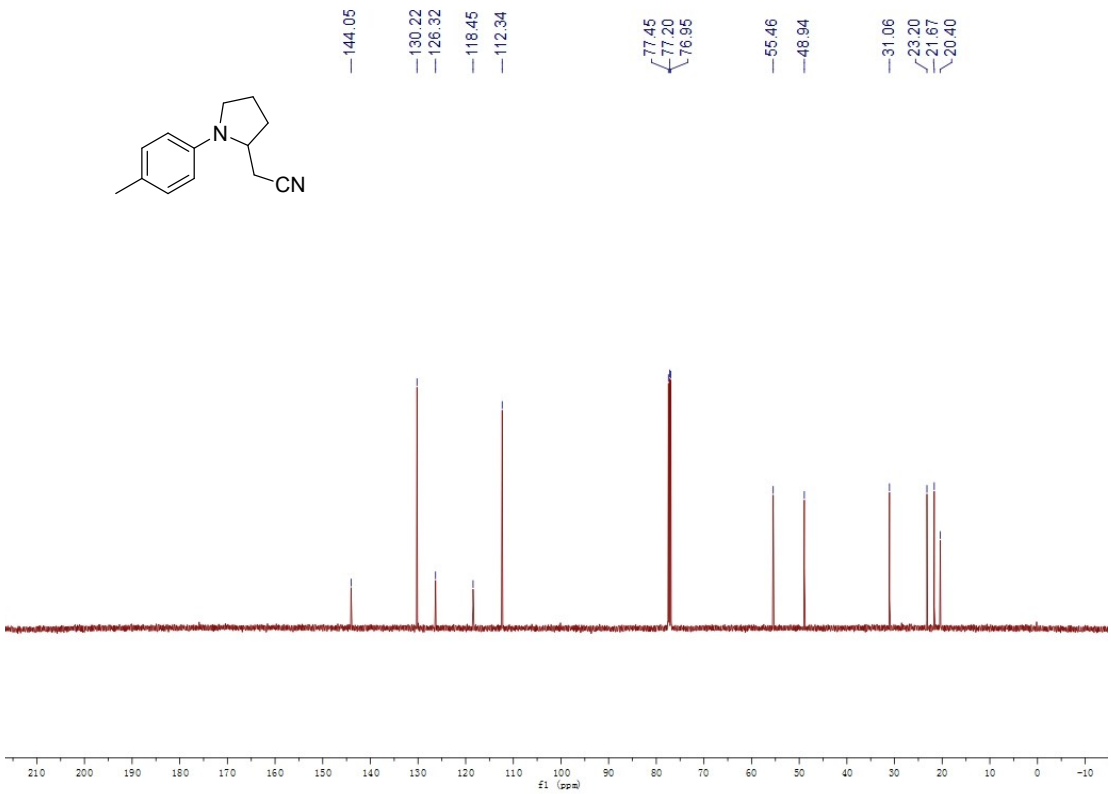
2-(1-(o-Tolyl)pyrrolidin-2-yl)acetonitrile (3c)



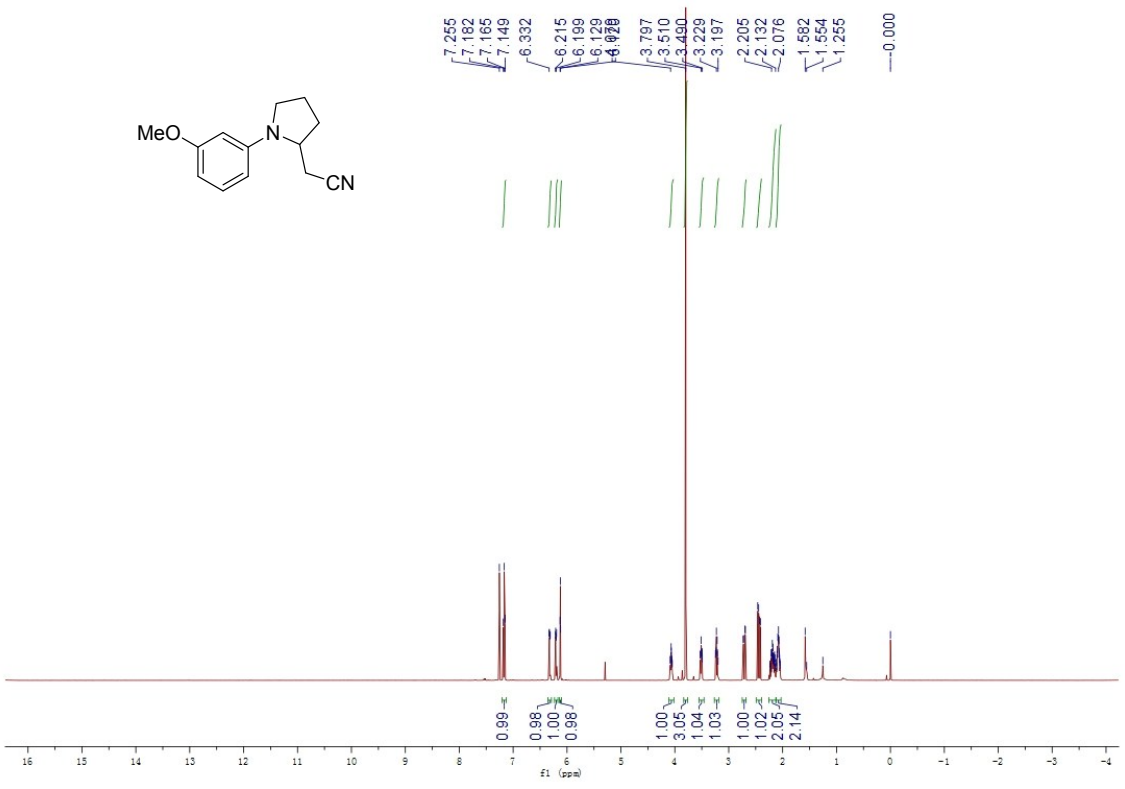


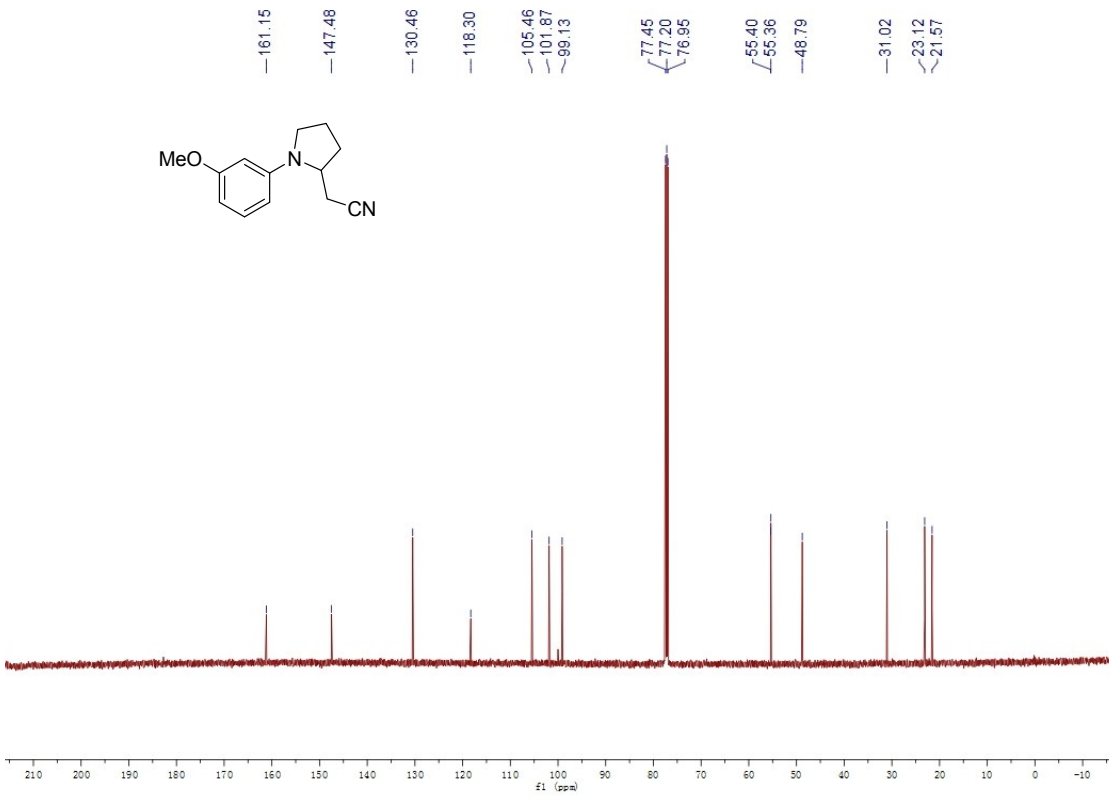
2-(1-(p-Tolyl)pyrrolidin-2-yl)acetonitrile (3d)



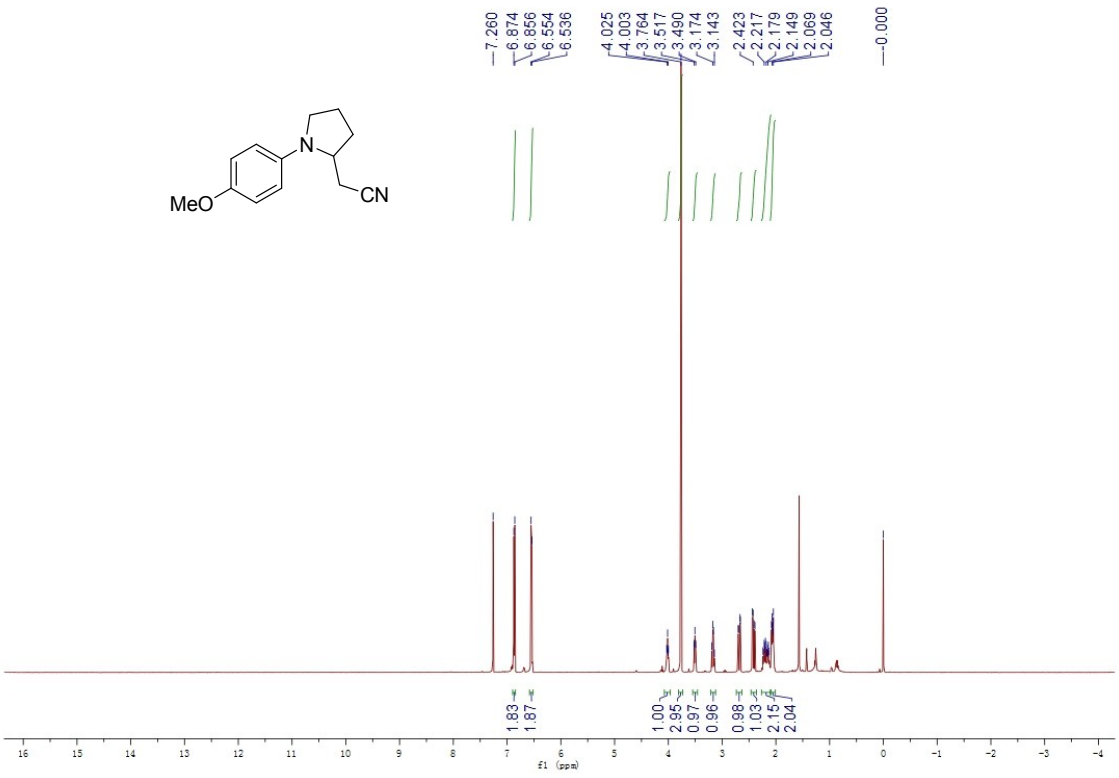


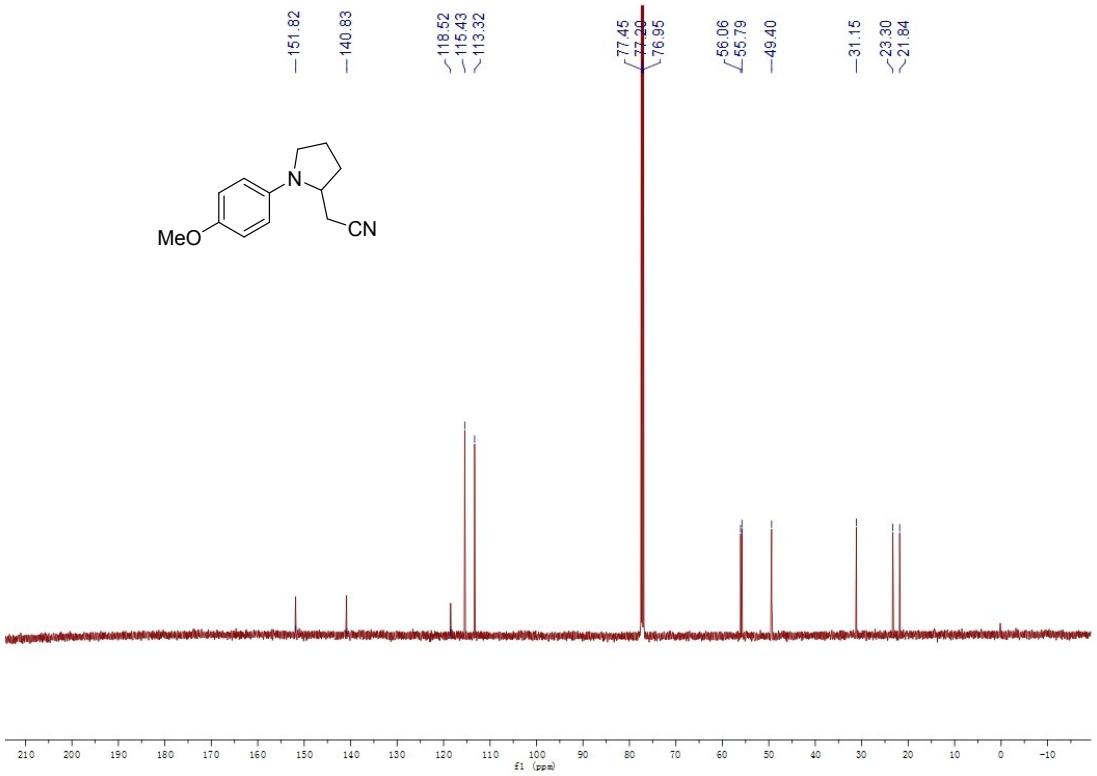
2-(1-(3-Methoxyphenyl)pyrrolidin-2-yl)acetonitrile (3e)



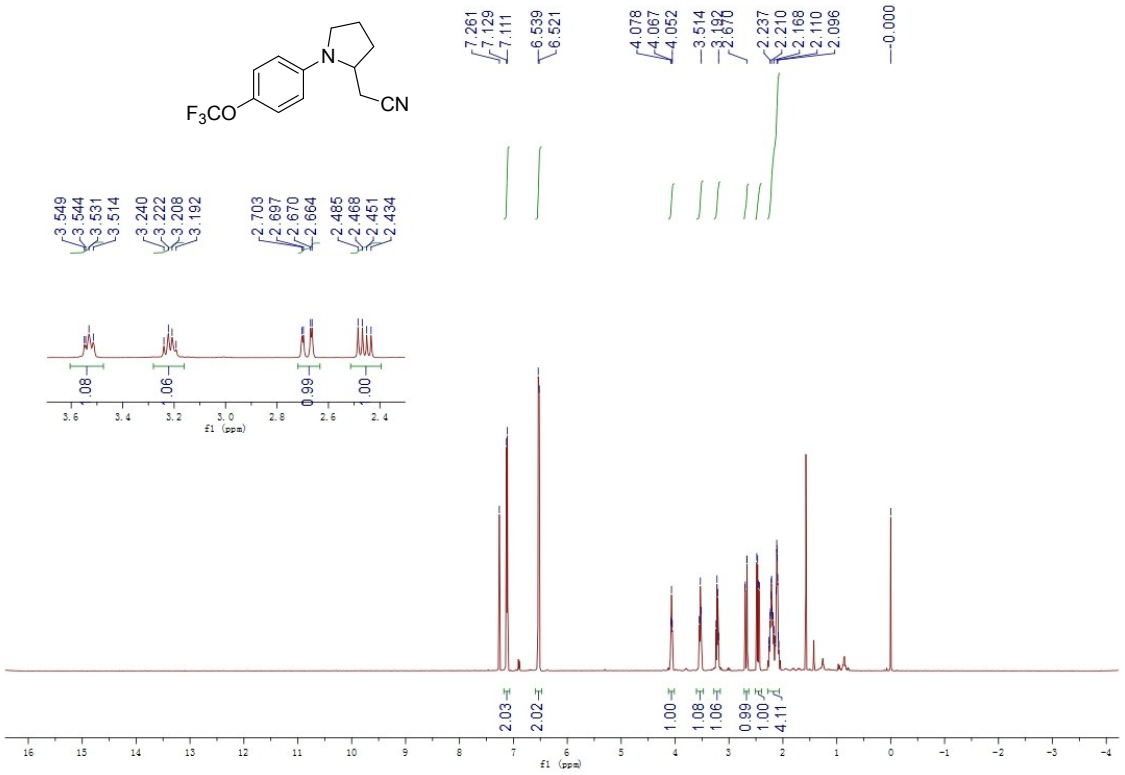


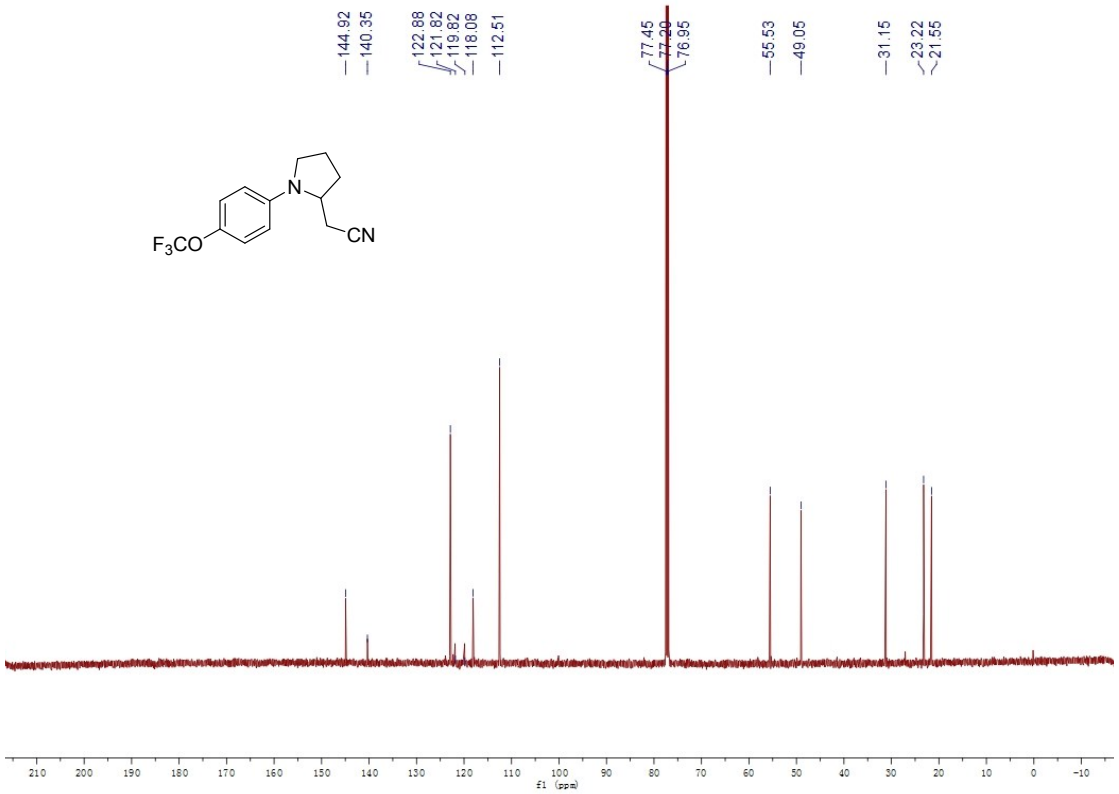
2-(1-(4-Methoxyphenyl)pyrrolidin-2-yl)acetonitrile (3f)



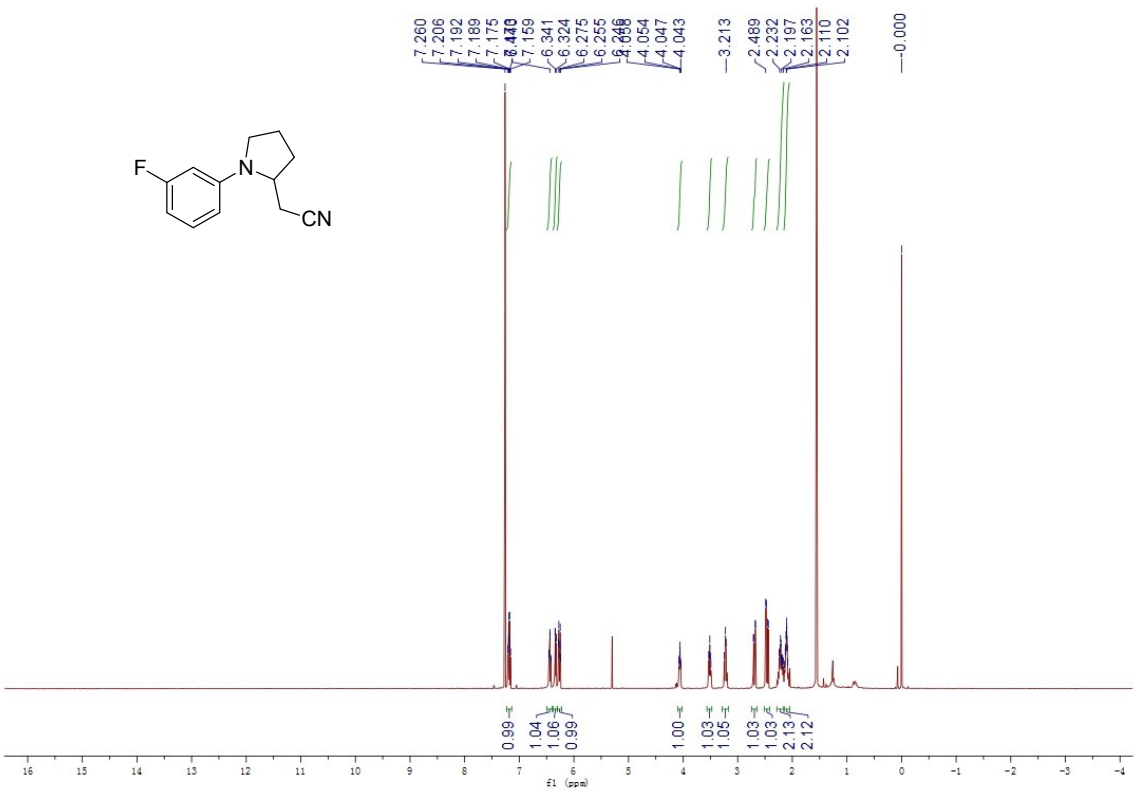


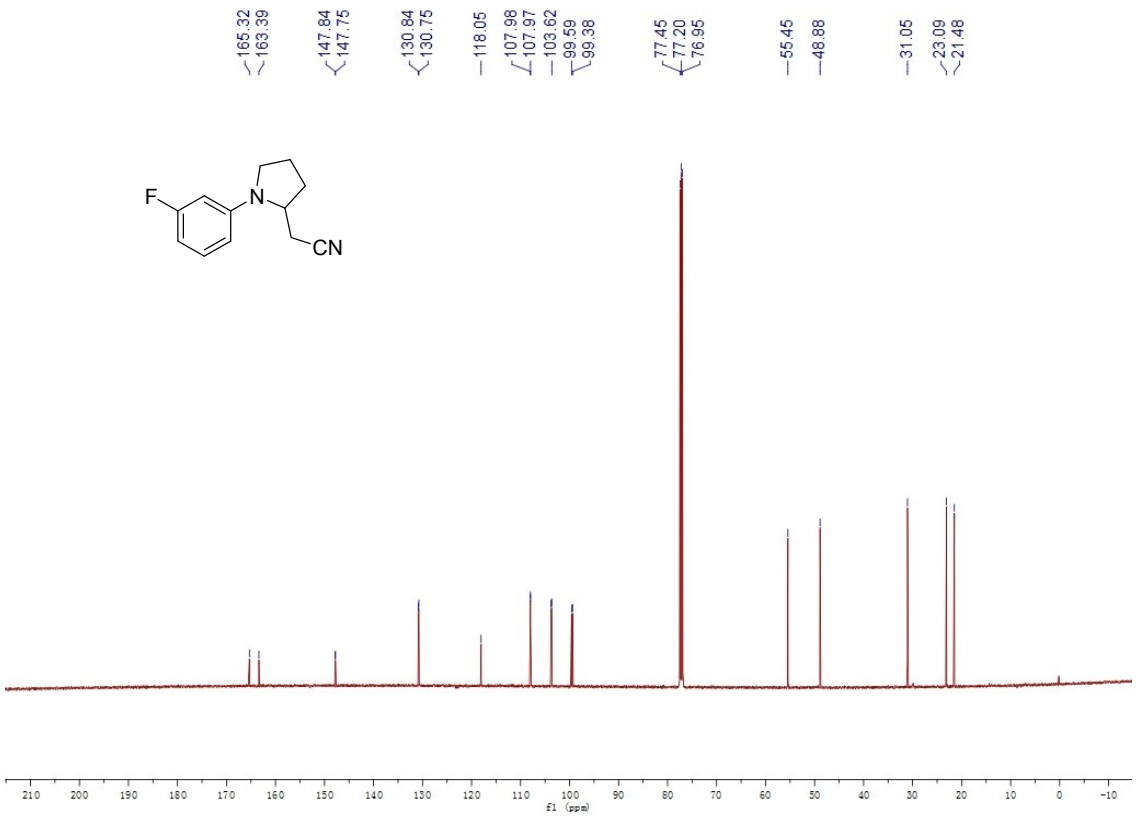
2-(1-(4-(Trifluoromethoxy)phenyl)pyrrolidin-2-yl)acetonitrile (3g)



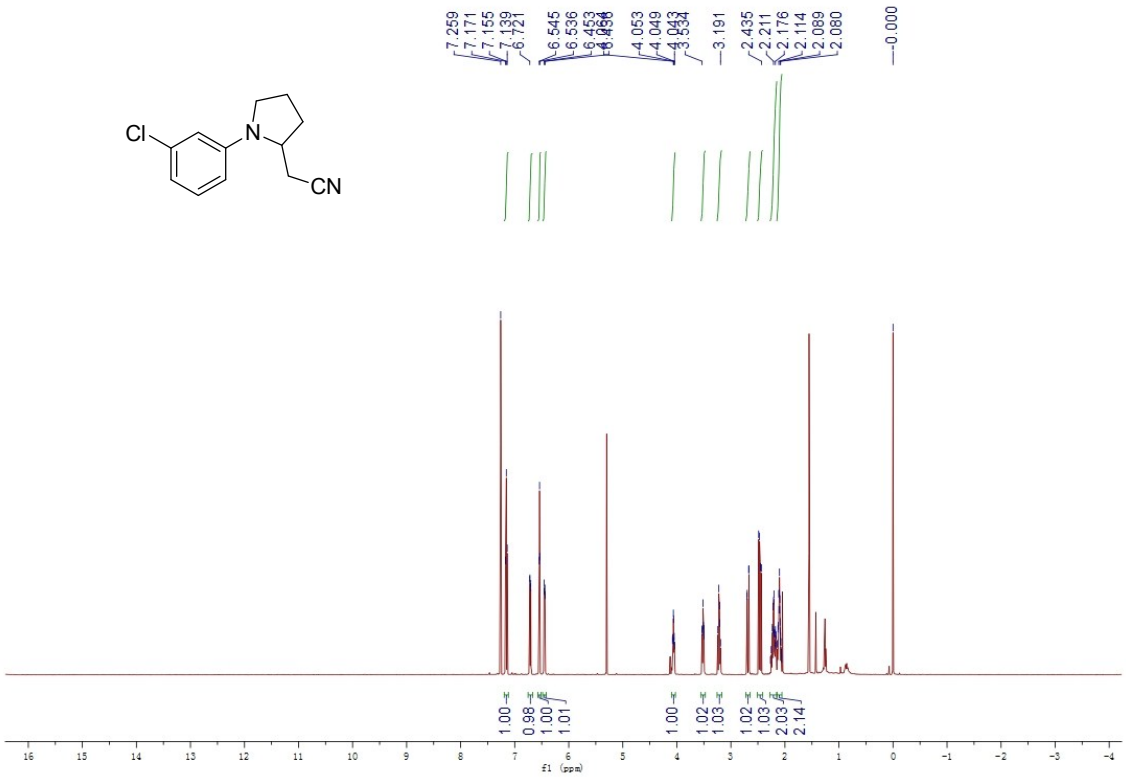


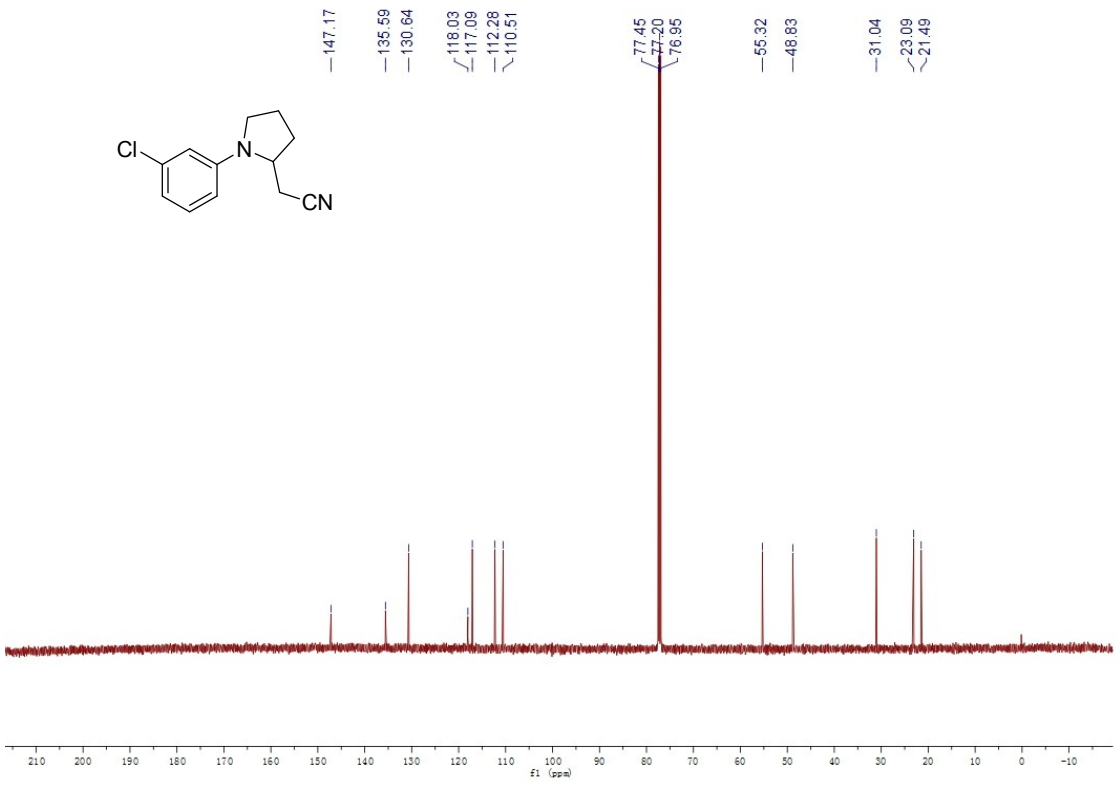
2-(1-(3-Fluorophenyl)pyrrolidin-2-yl)acetonitrile (3h)



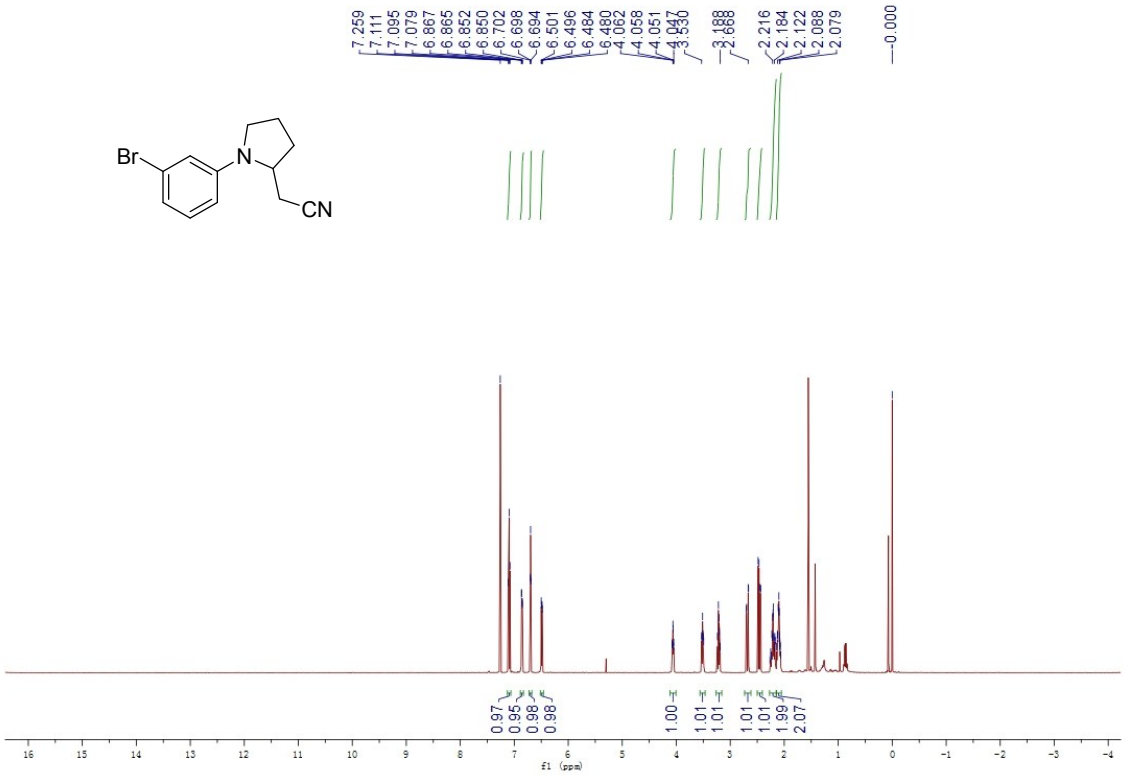


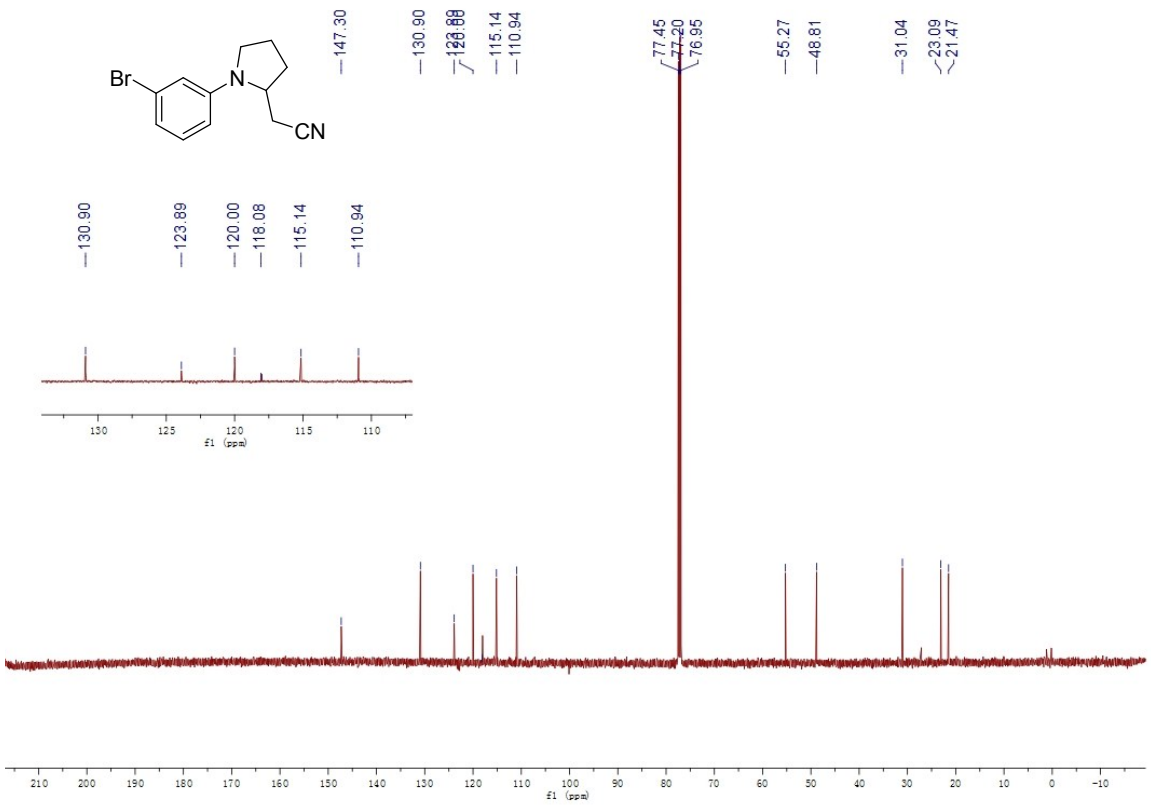
2-(1-(3-Chlorophenyl)pyrrolidin-2-yl)acetonitrile (3i)



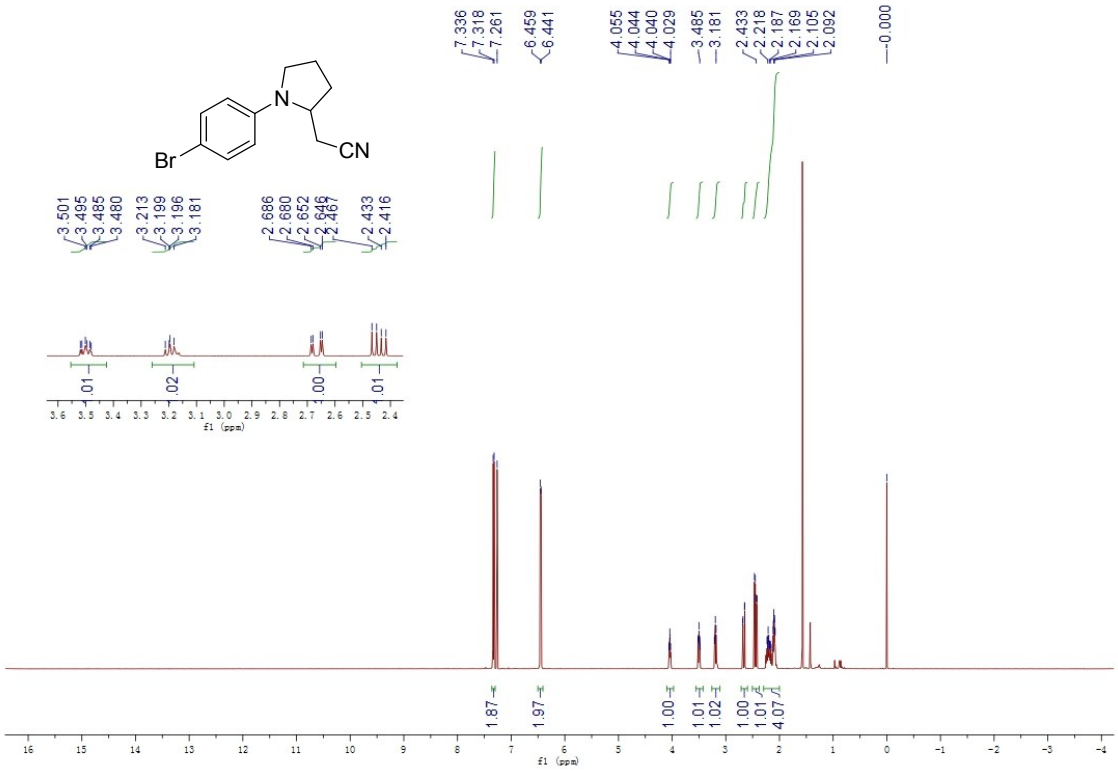


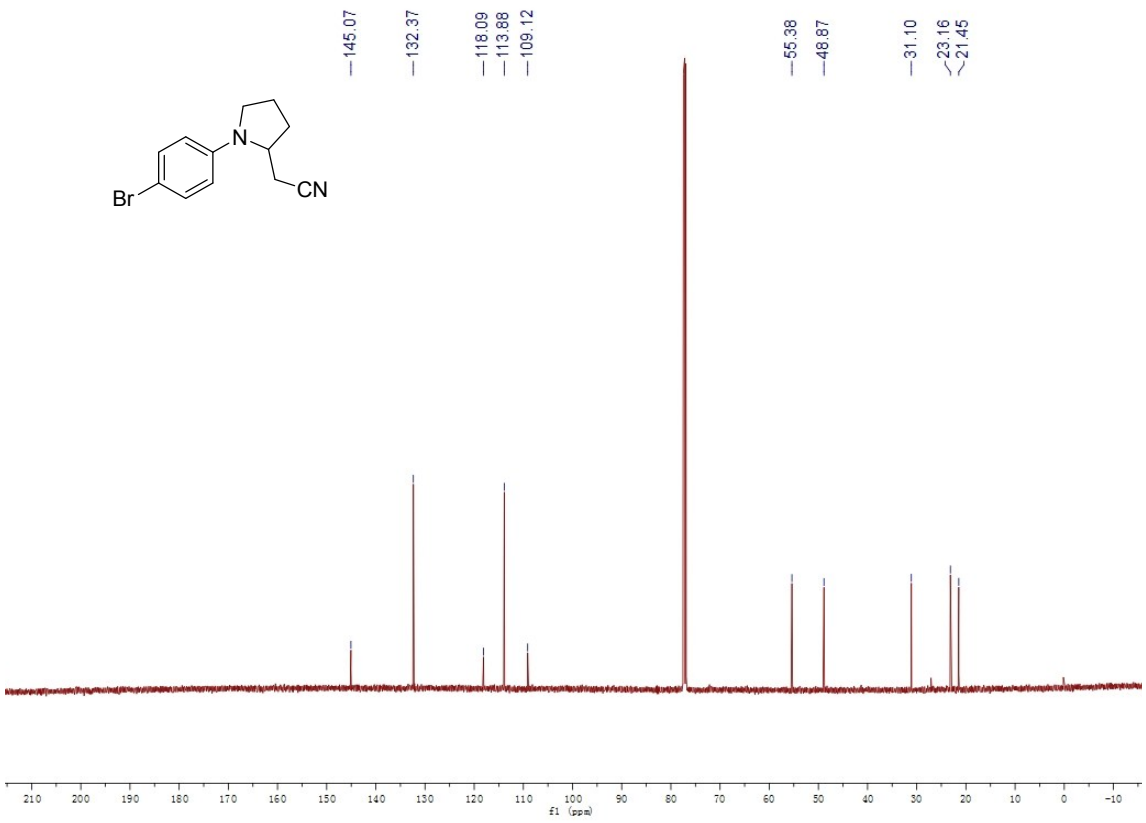
2-(1-(3-Bromophenyl)pyrrolidin-2-yl)acetonitrile (3j)



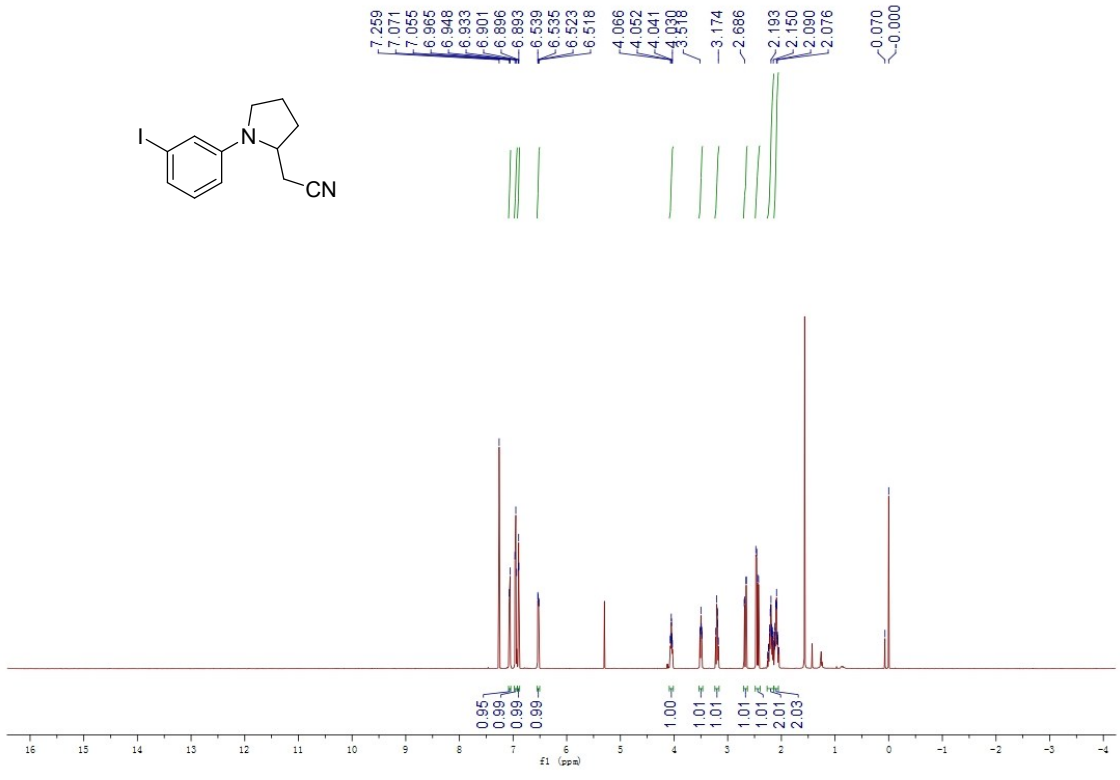


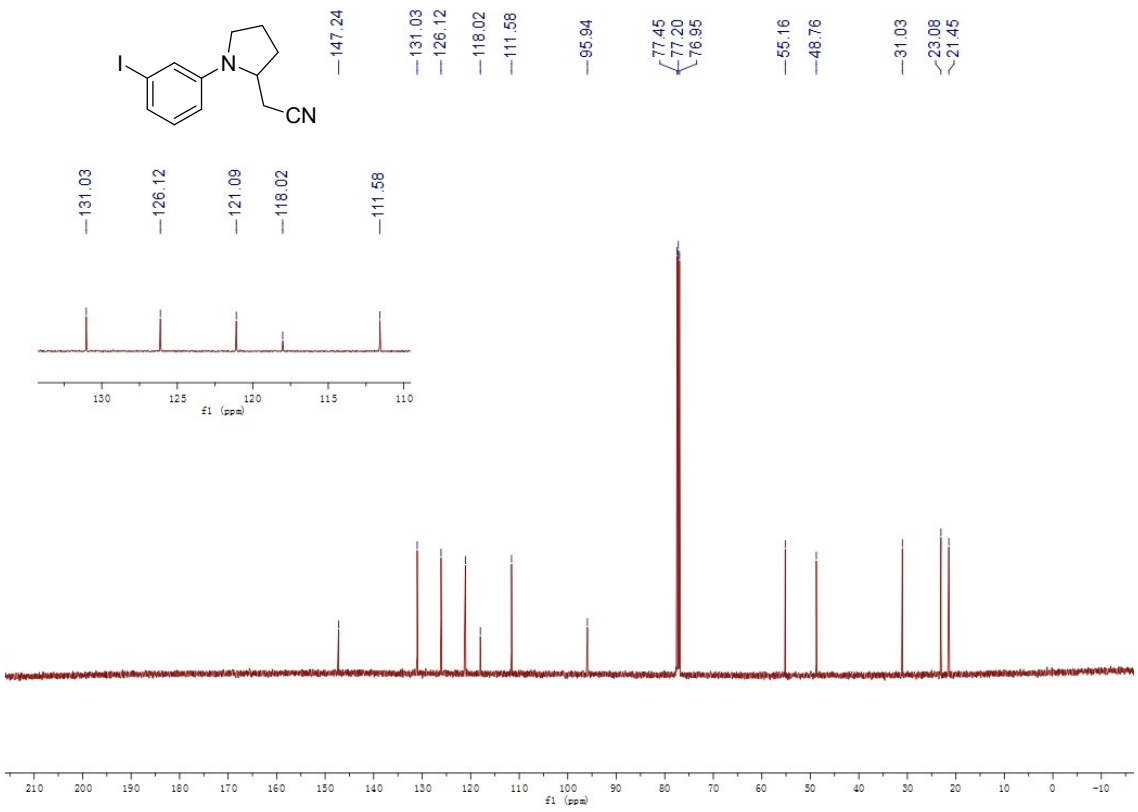
2-(1-(4-Bromophenyl)pyrrolidin-2-yl)acetonitrile (3k)



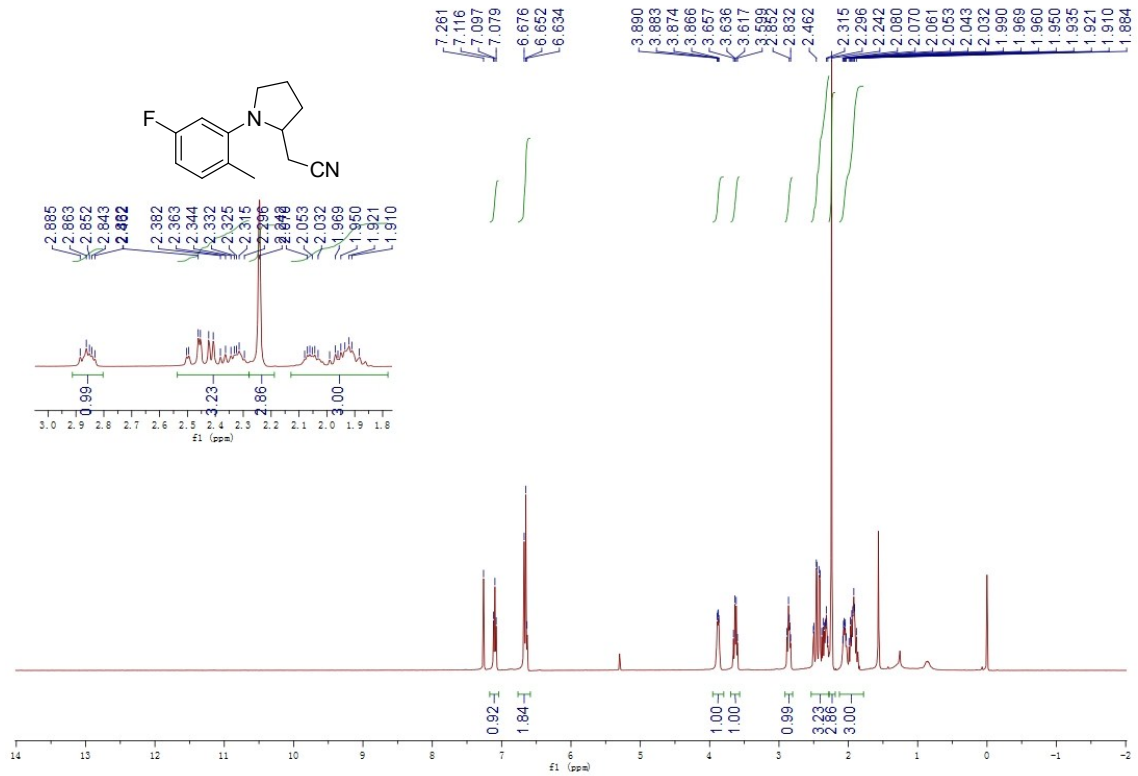


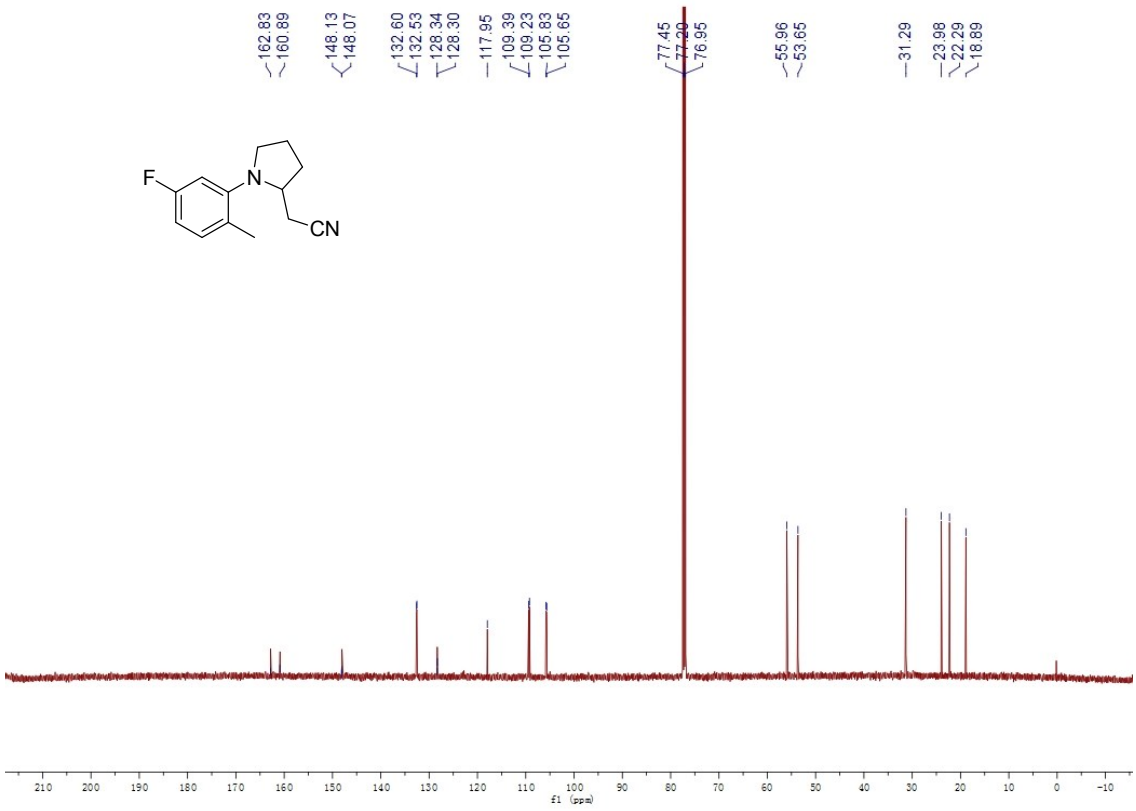
2-(1-(3-Iodophenyl)pyrrolidin-2-yl)acetonitrile (3l)



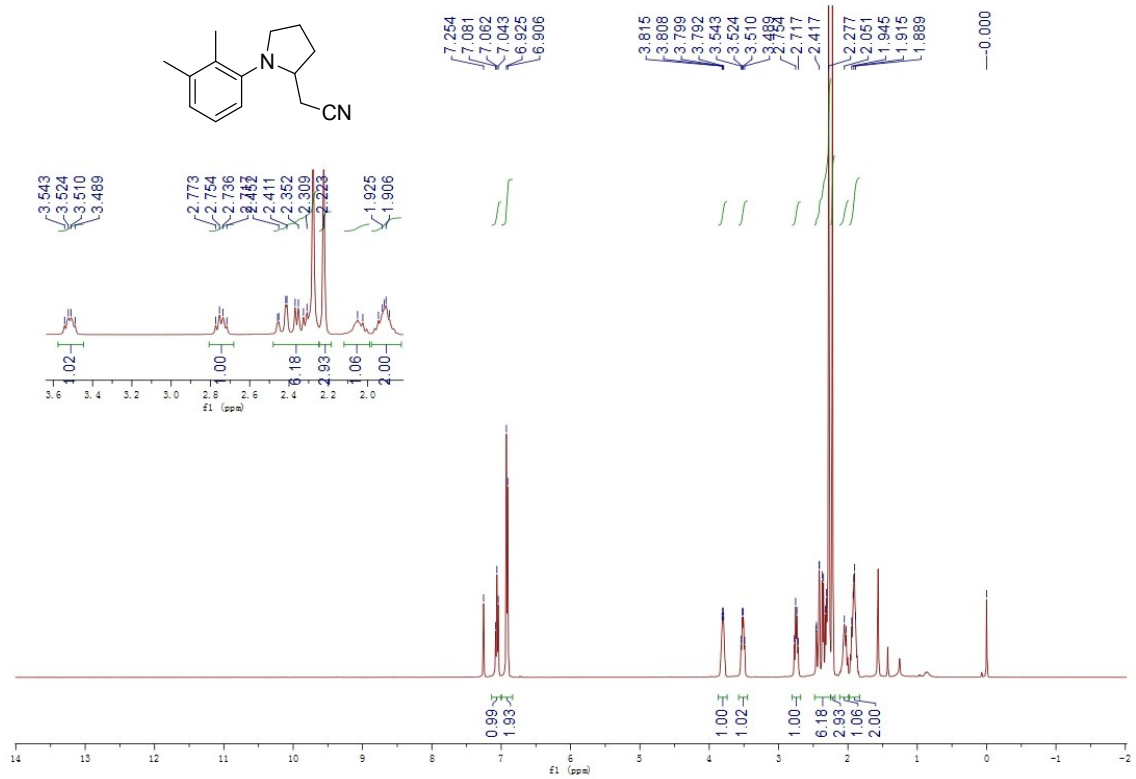


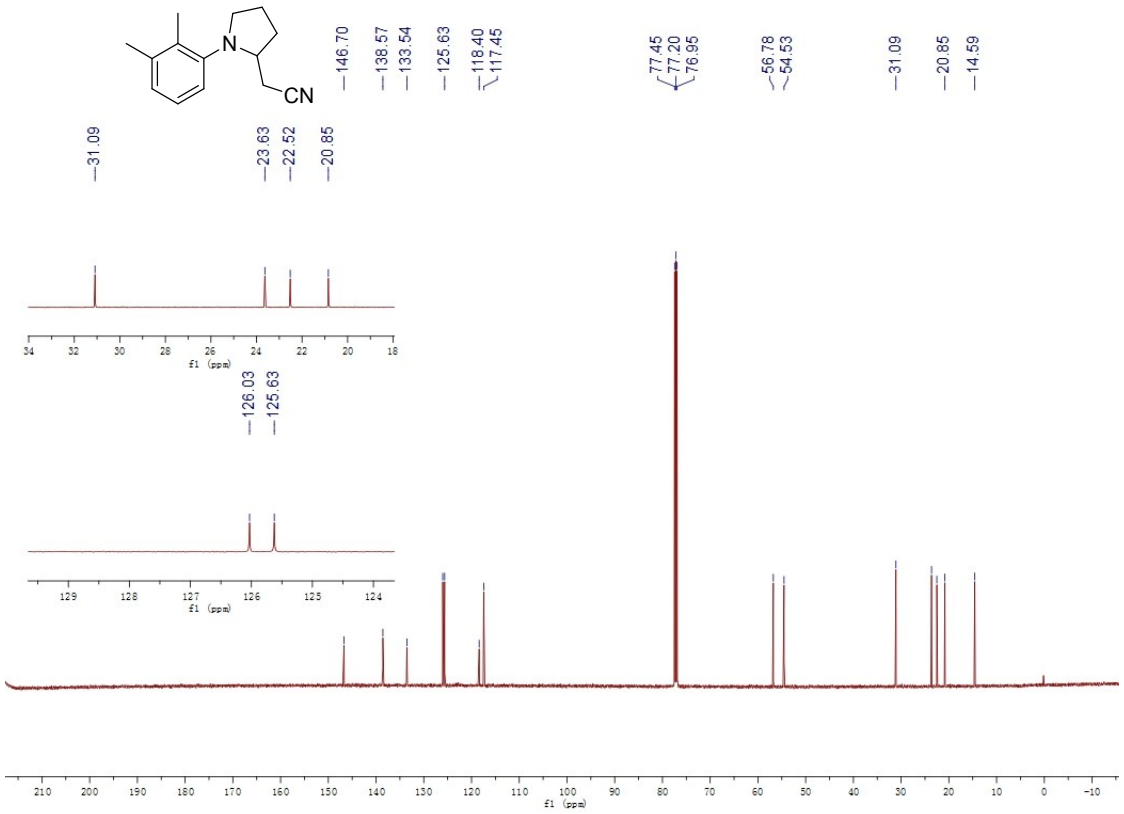
2-(1-(5-Fluoro-2-methylphenyl)pyrrolidin-2-yl)acetonitrile (3m)



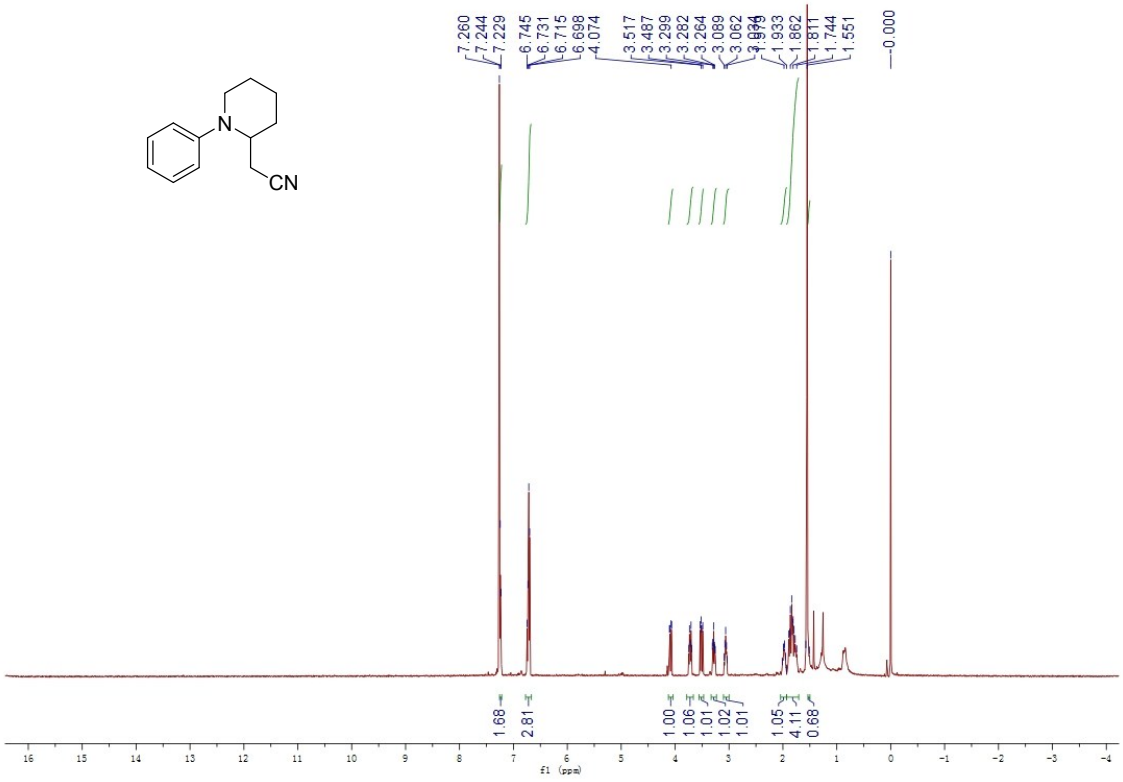


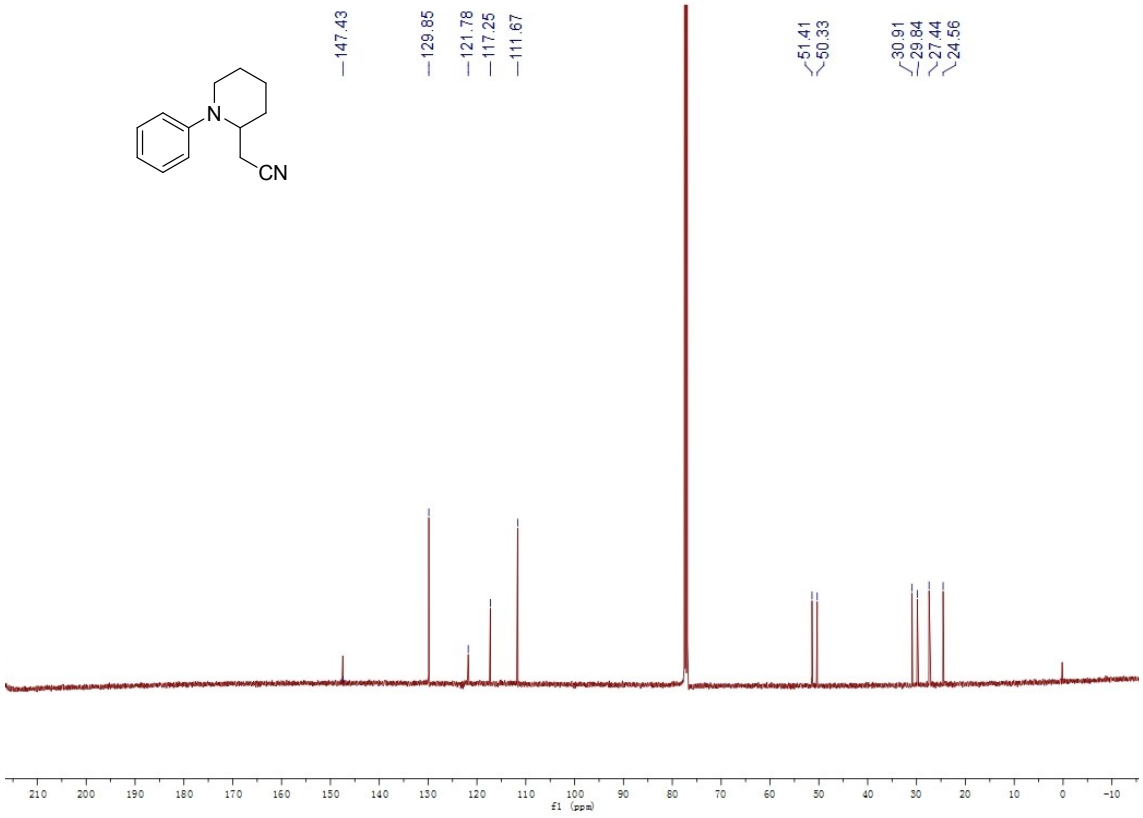
2-(1-(2,3-Dimethylphenyl)pyrrolidin-2-yl)acetonitrile (3n)



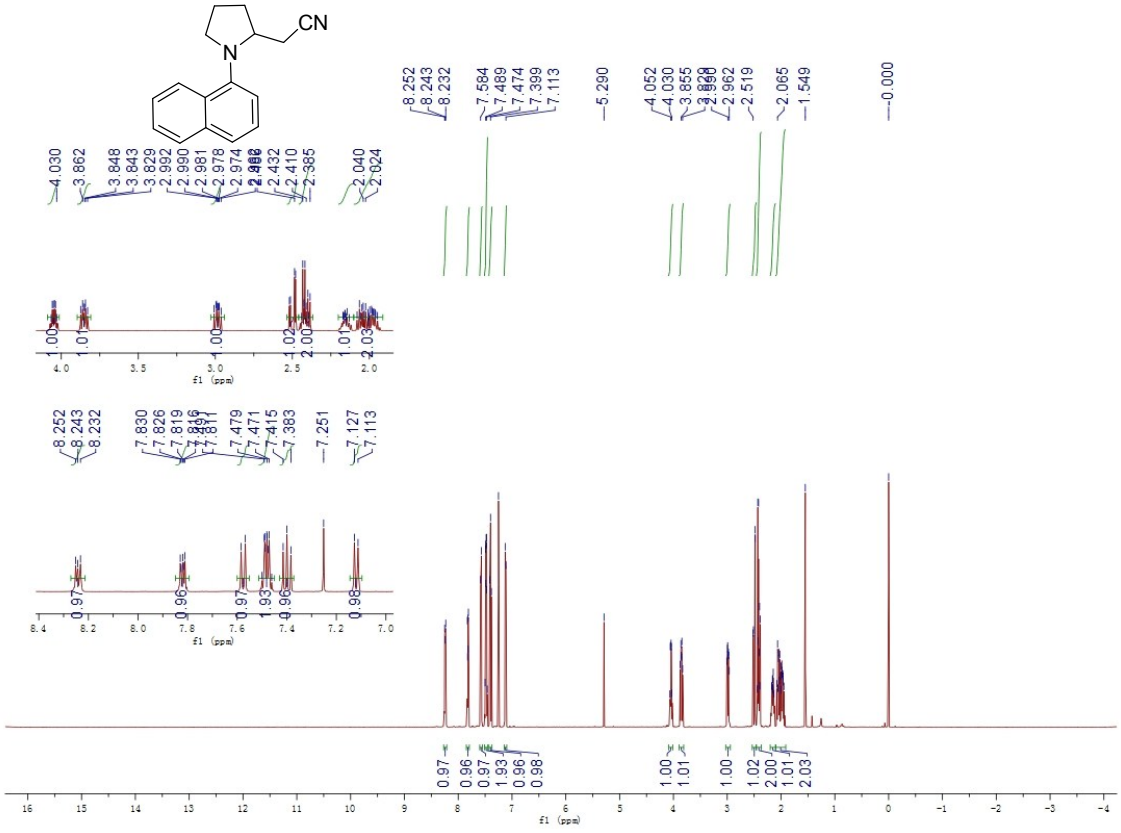


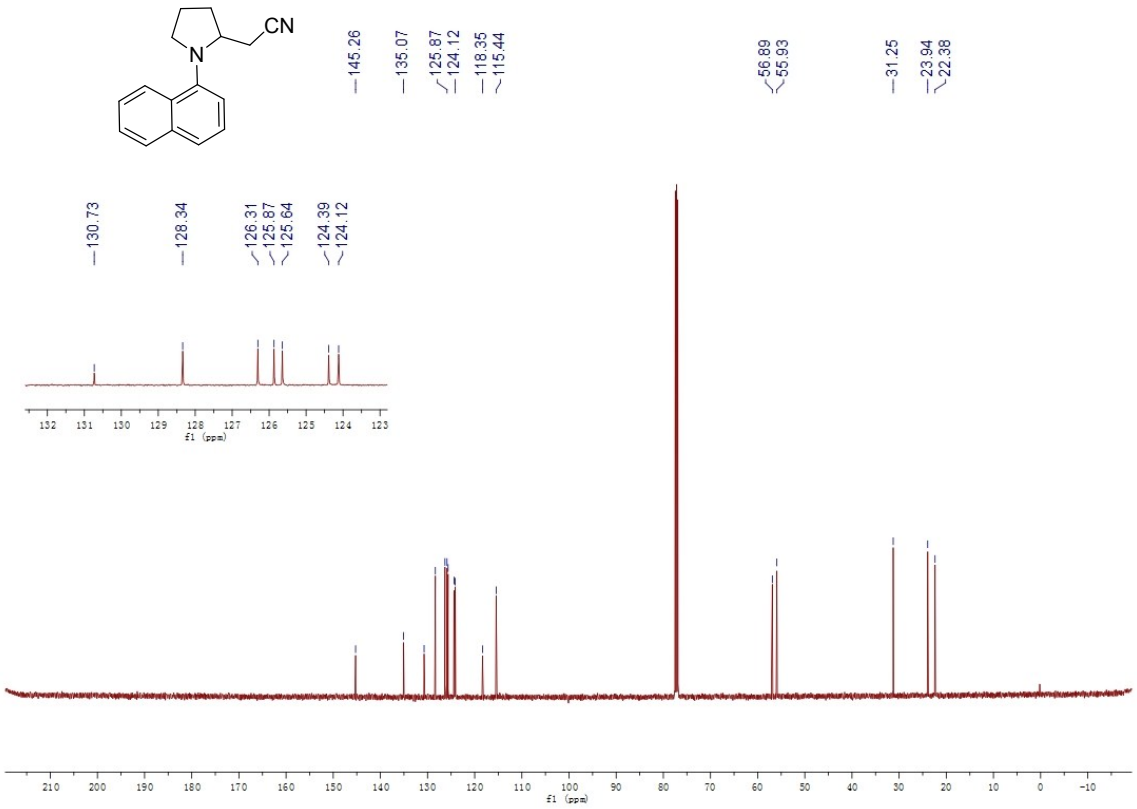
2-(1-Phenylpiperidin-2-yl)acetonitrile (3o)



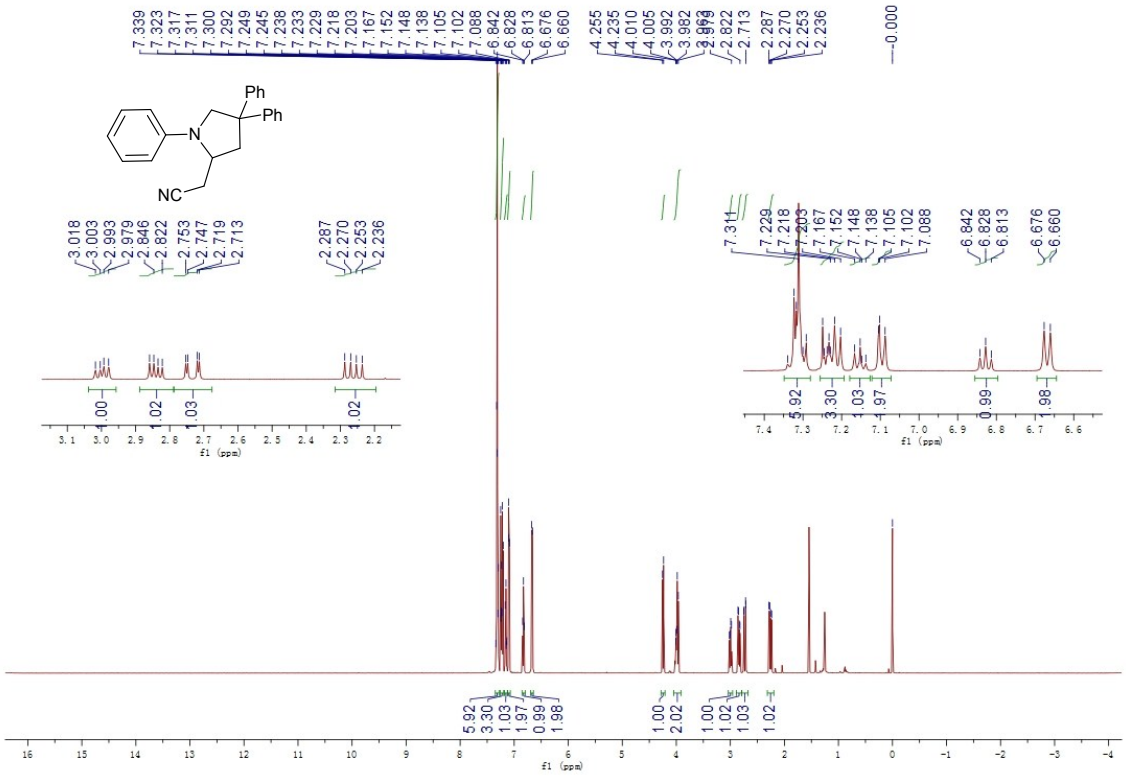


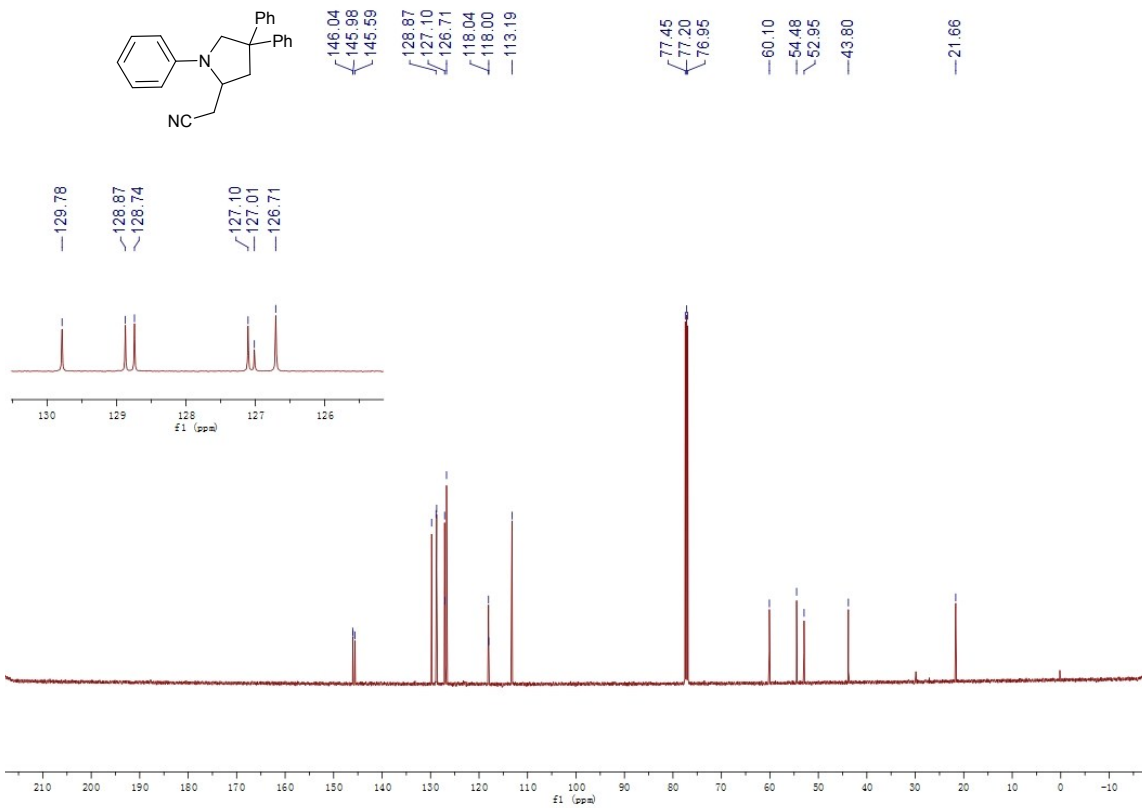
2-(1-(Naphthalen-1-yl)pyrrolidin-2-yl)acetonitrile (3p)



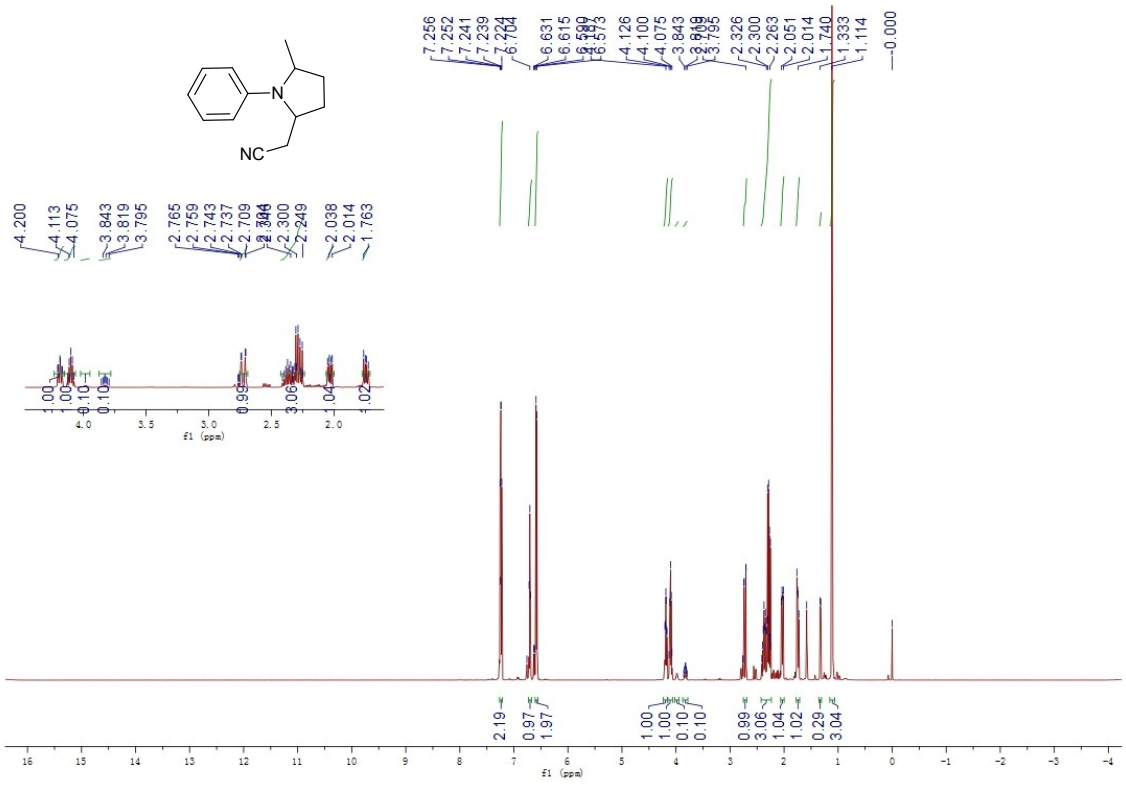


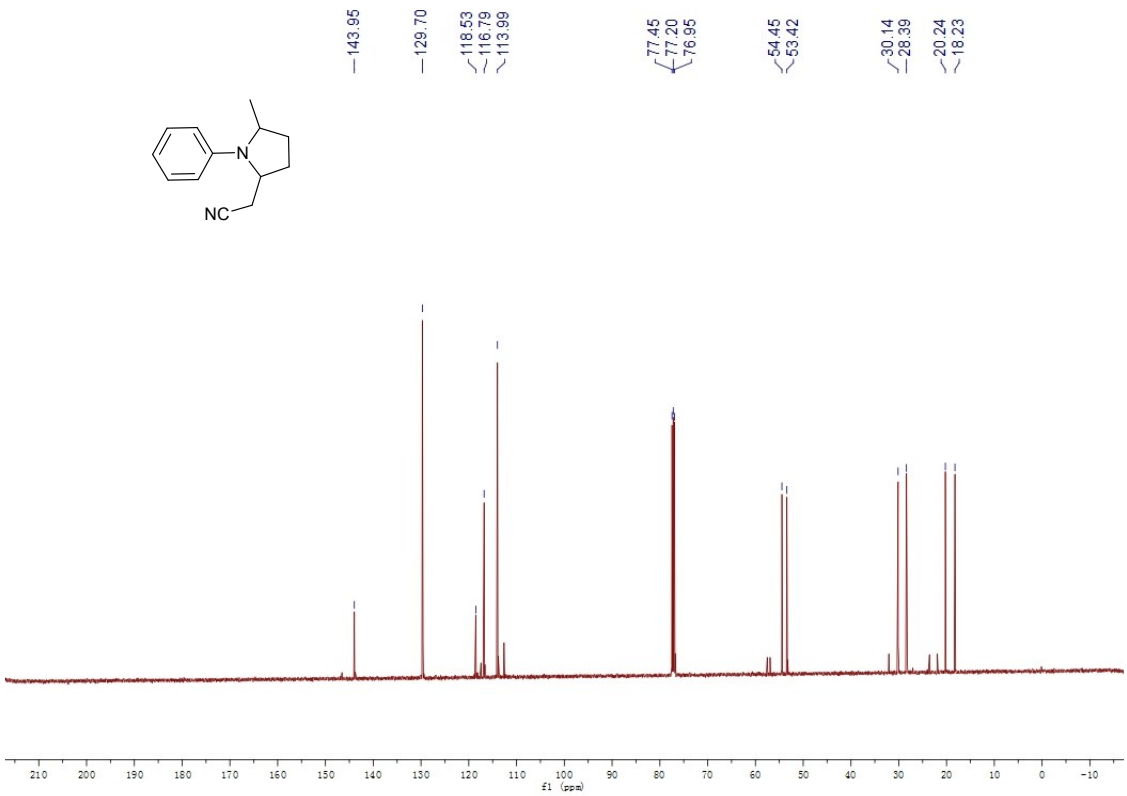
2-(1,4,4-Triphenylpyrrolidin-2-yl)acetonitrile (3q)



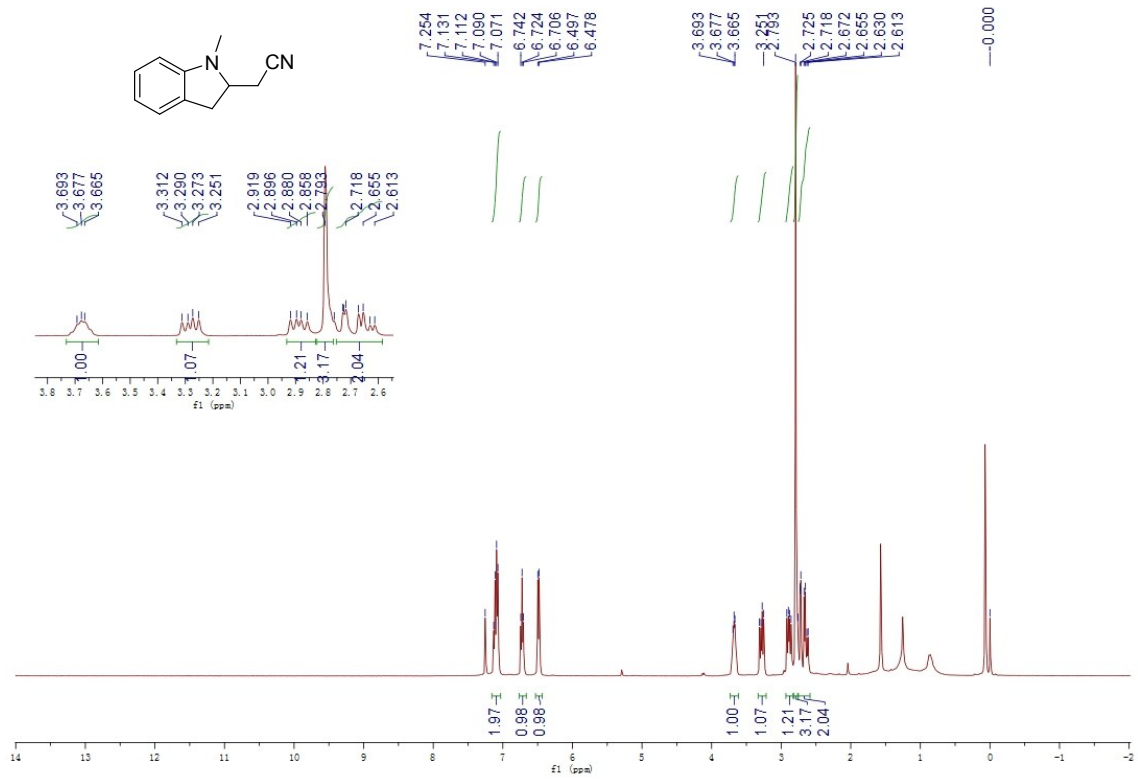


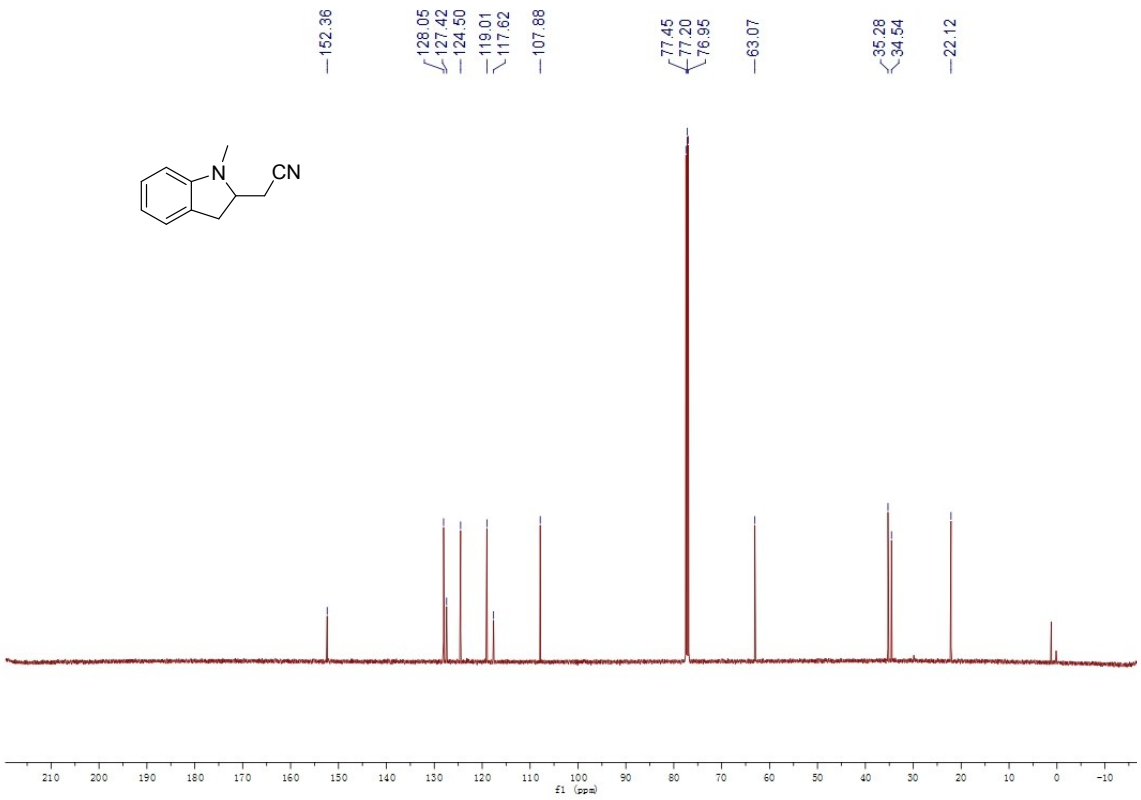
2-(5-Methyl-1-phenylpyrrolidin-2-yl)acetonitrile (3r)



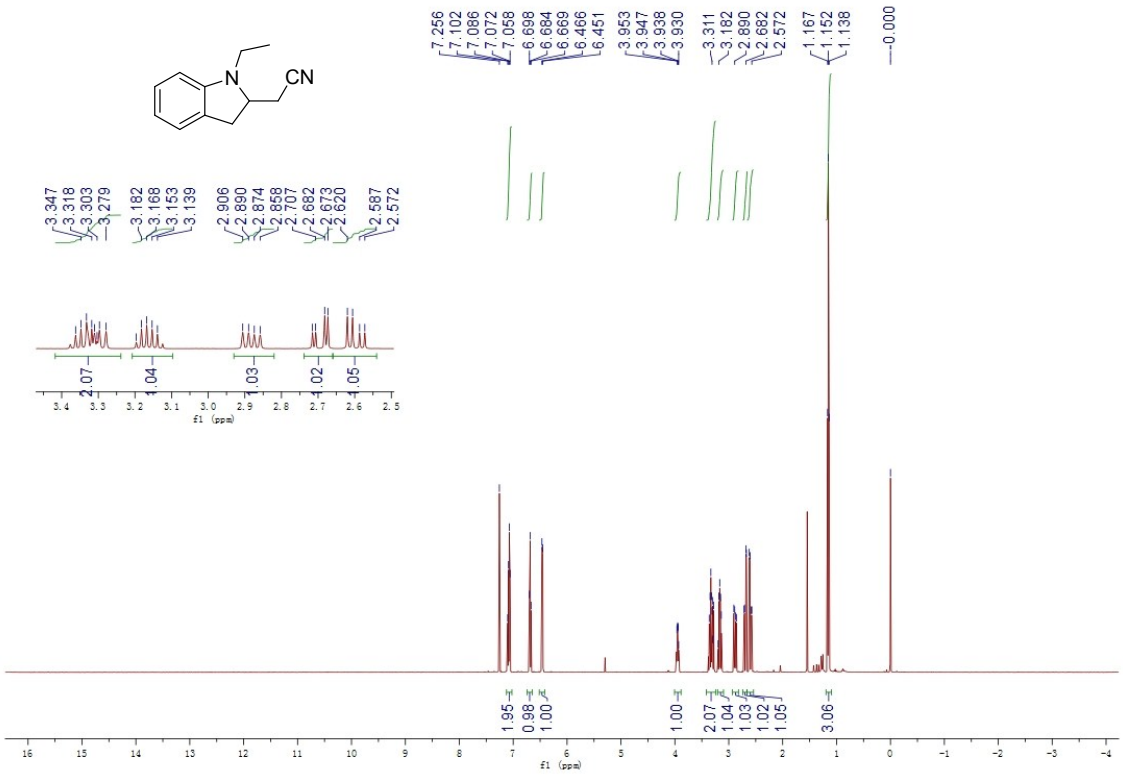


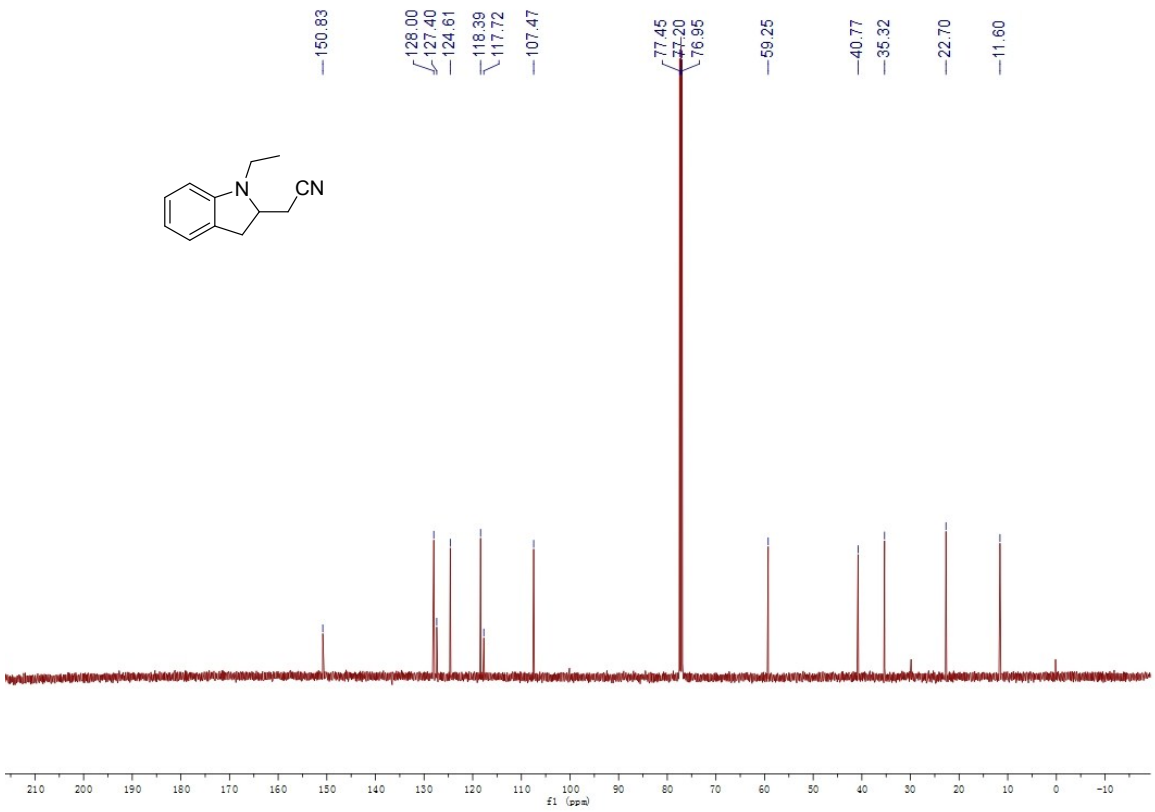
2-(1-Methylindolin-2-yl)acetonitrile (3s)



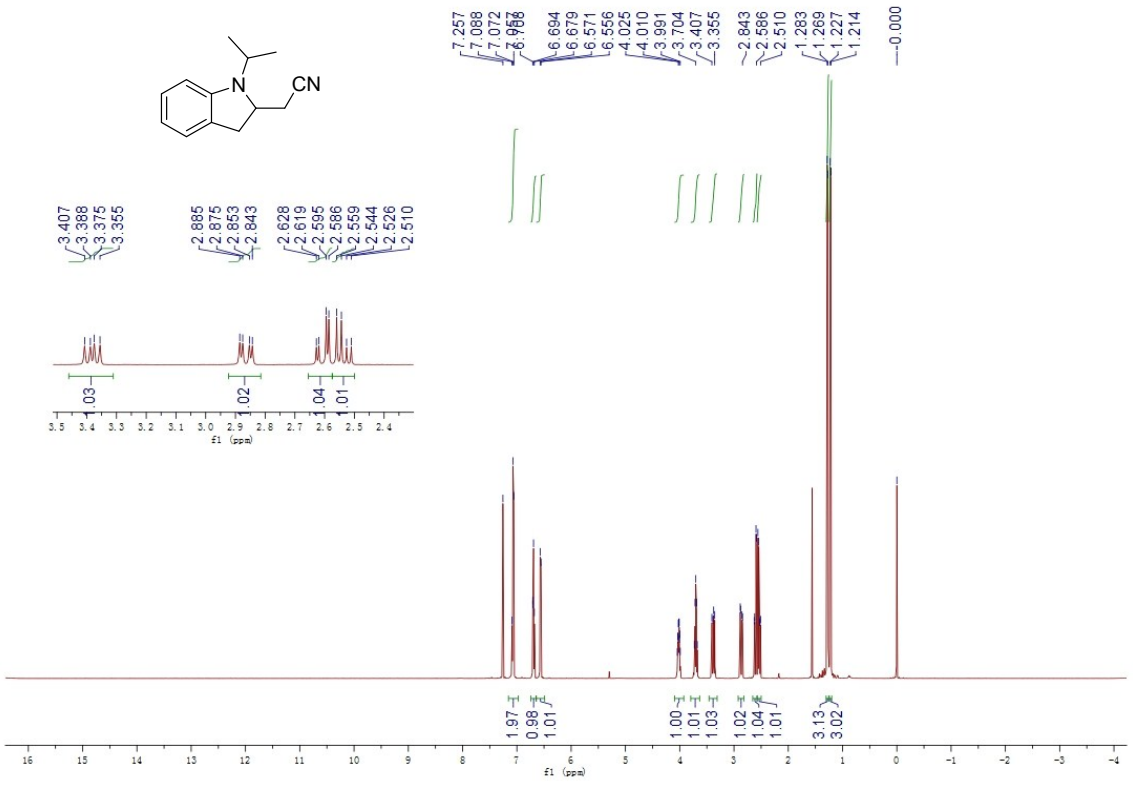


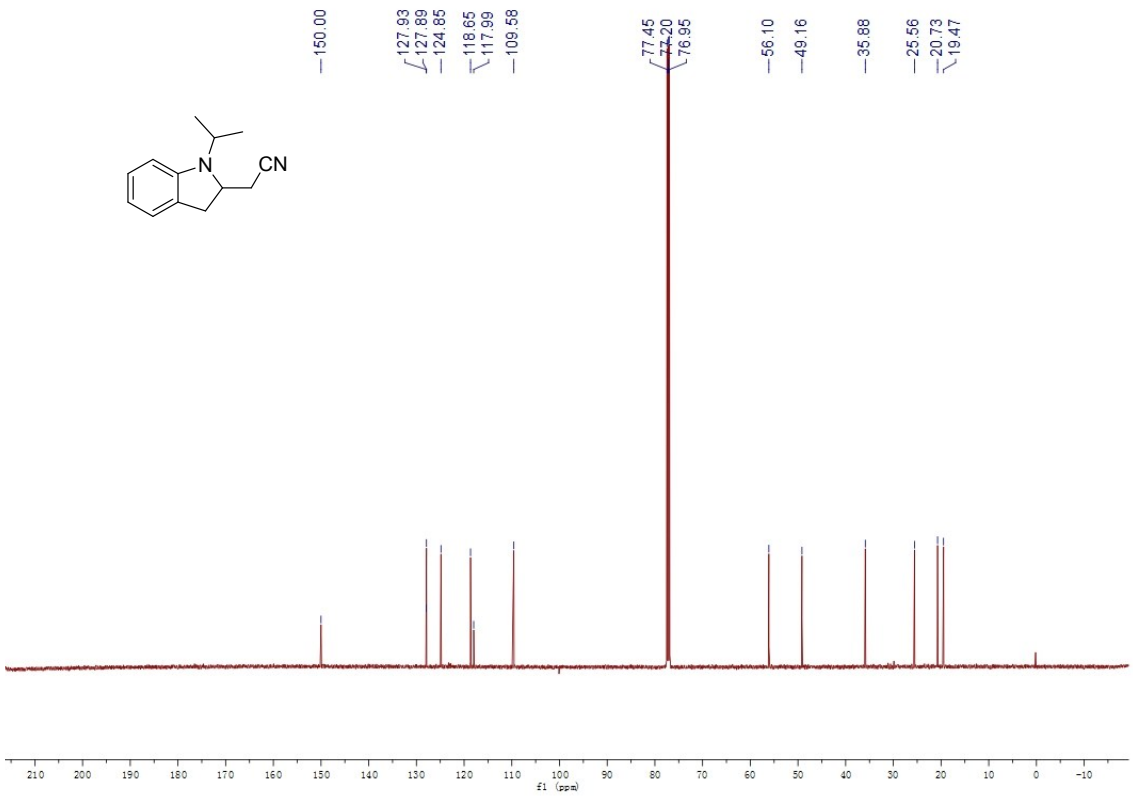
2-(1-Ethylindolin-2-yl)acetonitrile (3t)



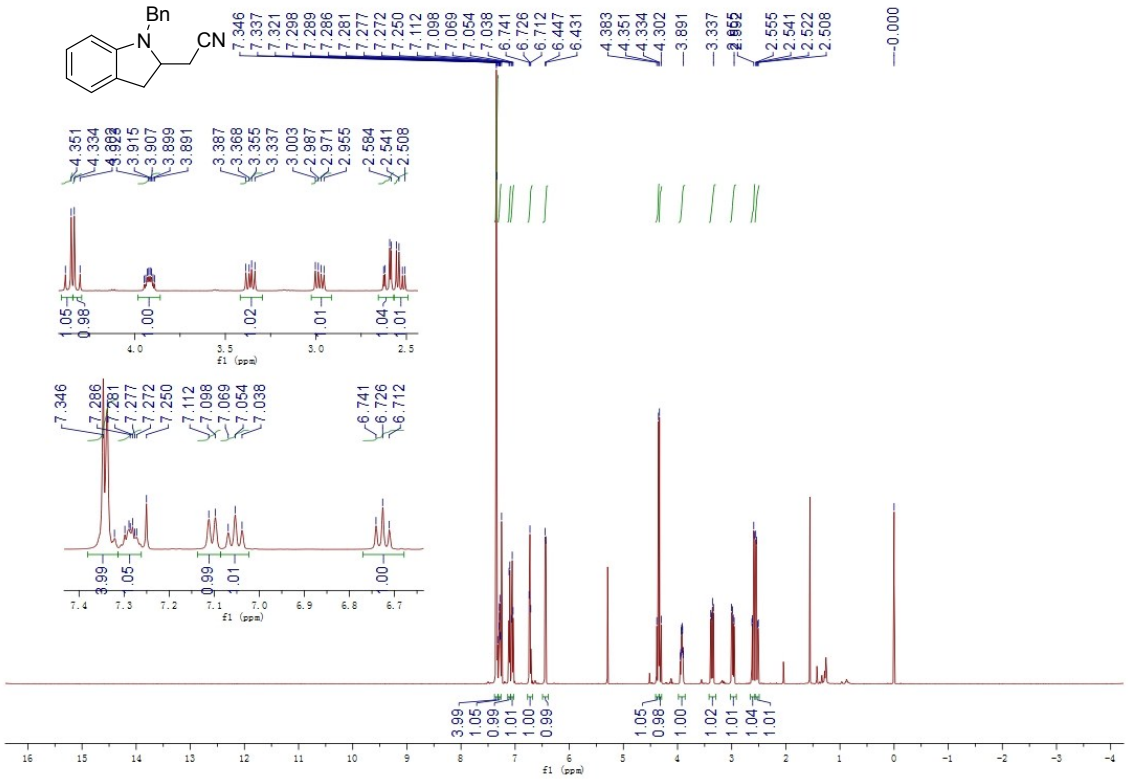


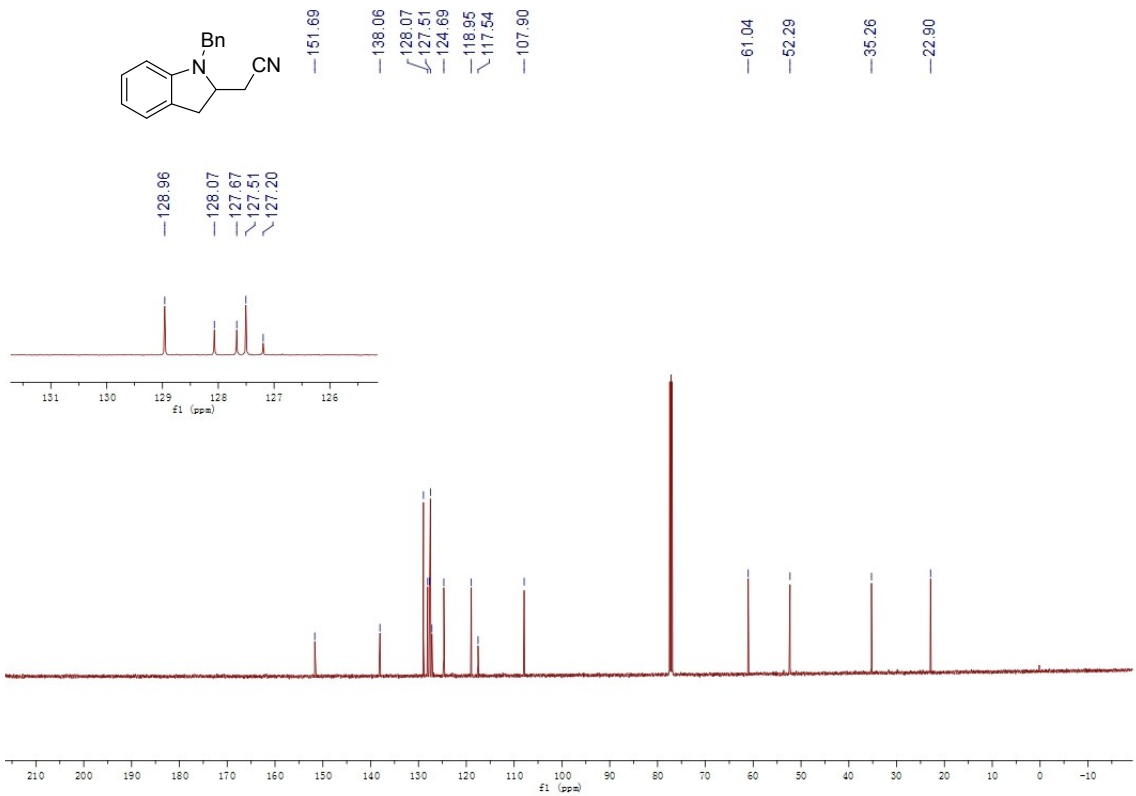
2-(1-Isopropylindolin-2-yl)acetonitrile (3u)



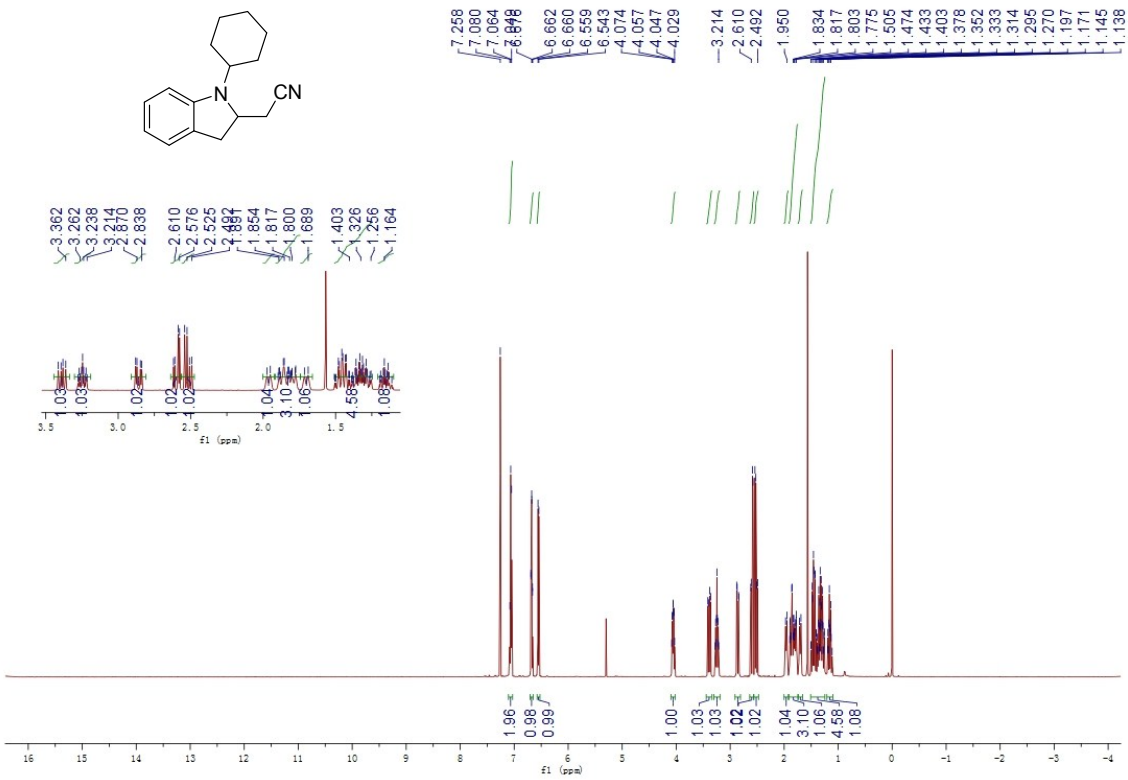


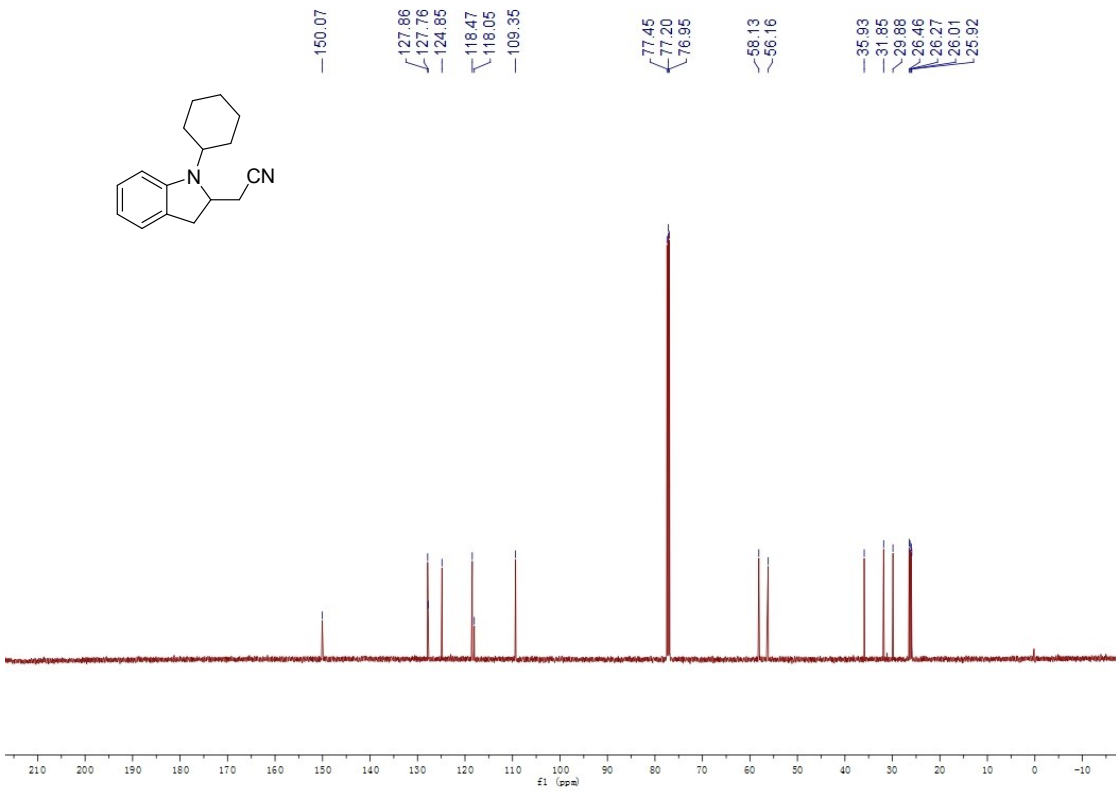
2-(1-Benzylindolin-2-yl)acetonitrile (3v)



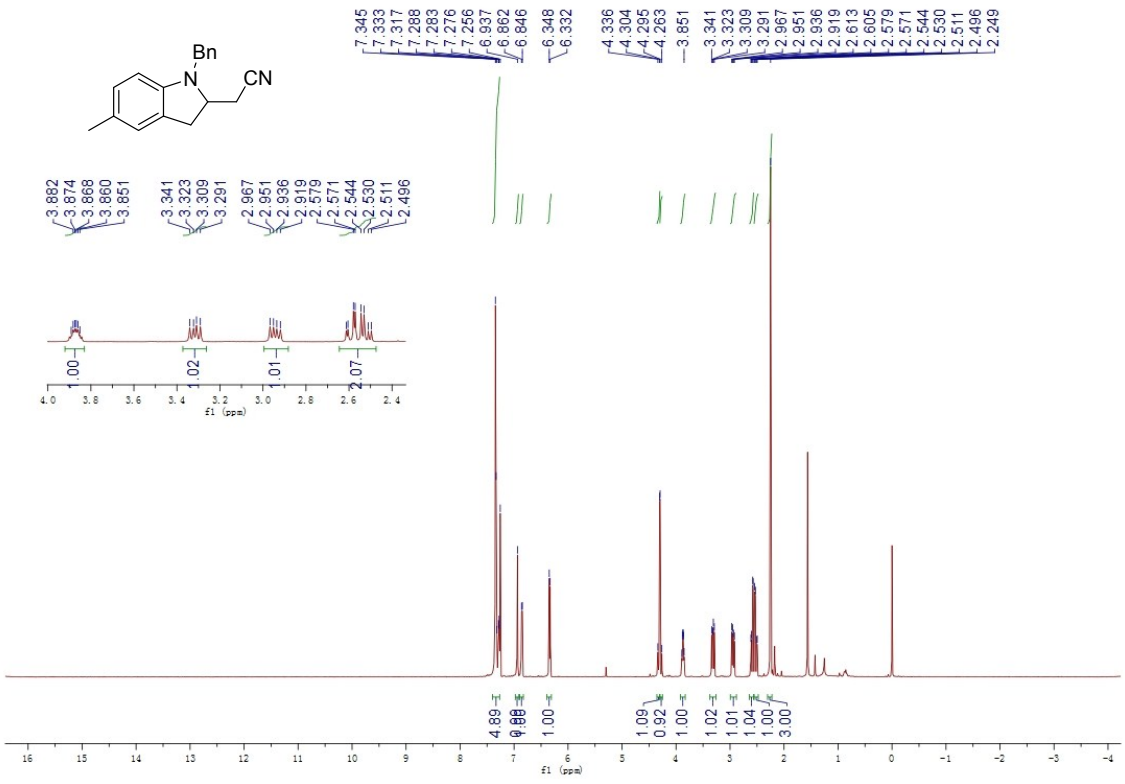


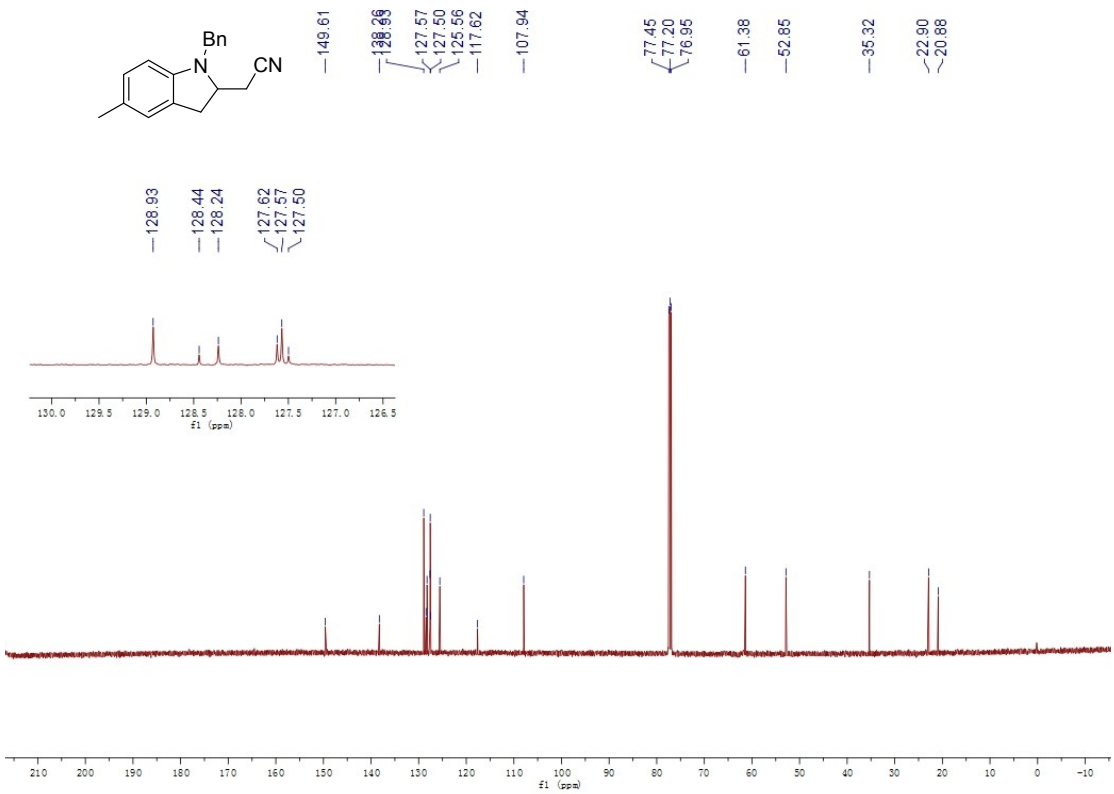
2-(1-Cyclohexylindolin-2-yl)acetonitrile (3w)



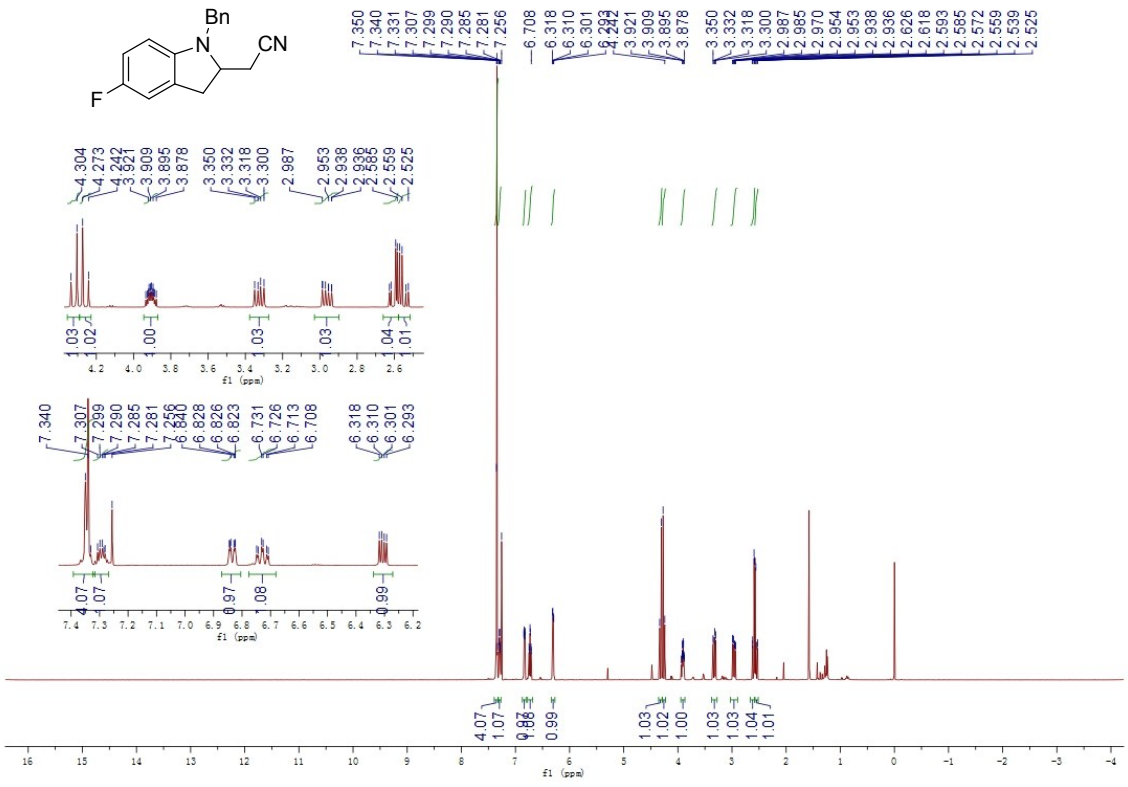


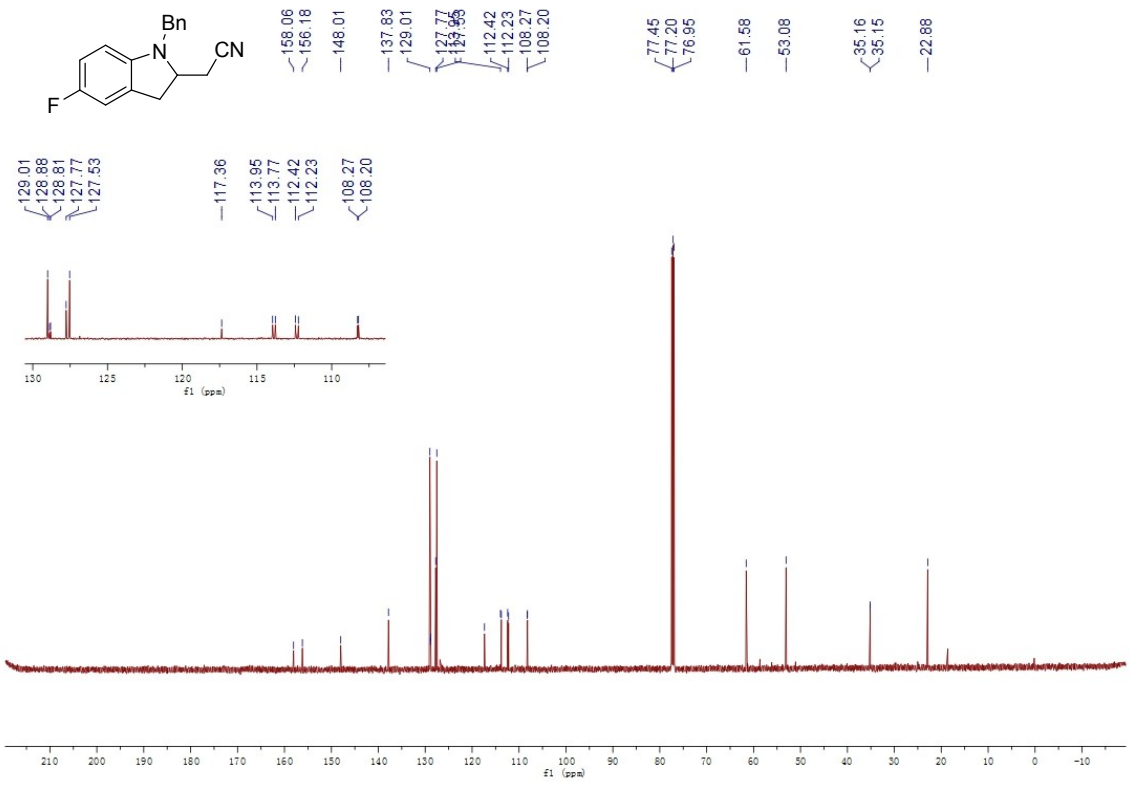
2-(1-Benzyl-5-methylindolin-2-yl)acetonitrile (3x)



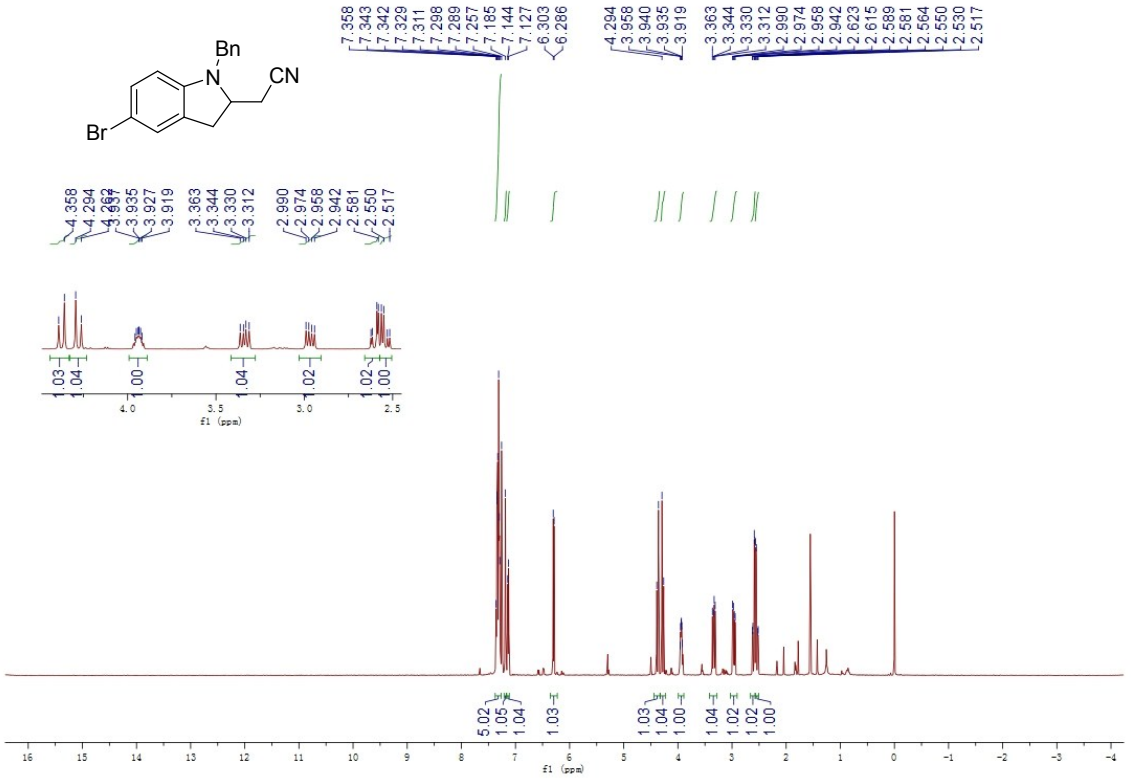


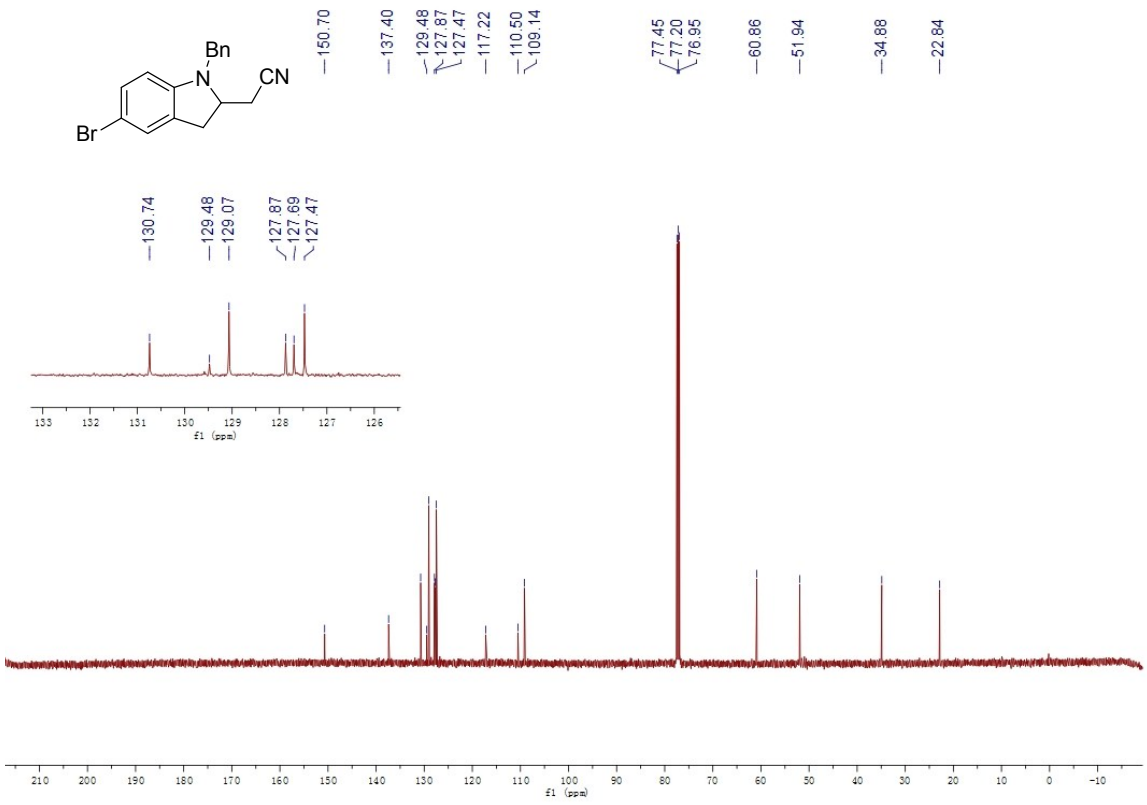
2-(1-Benzyl-5-fluoroindolin-2-yl)acetonitrile (3y)



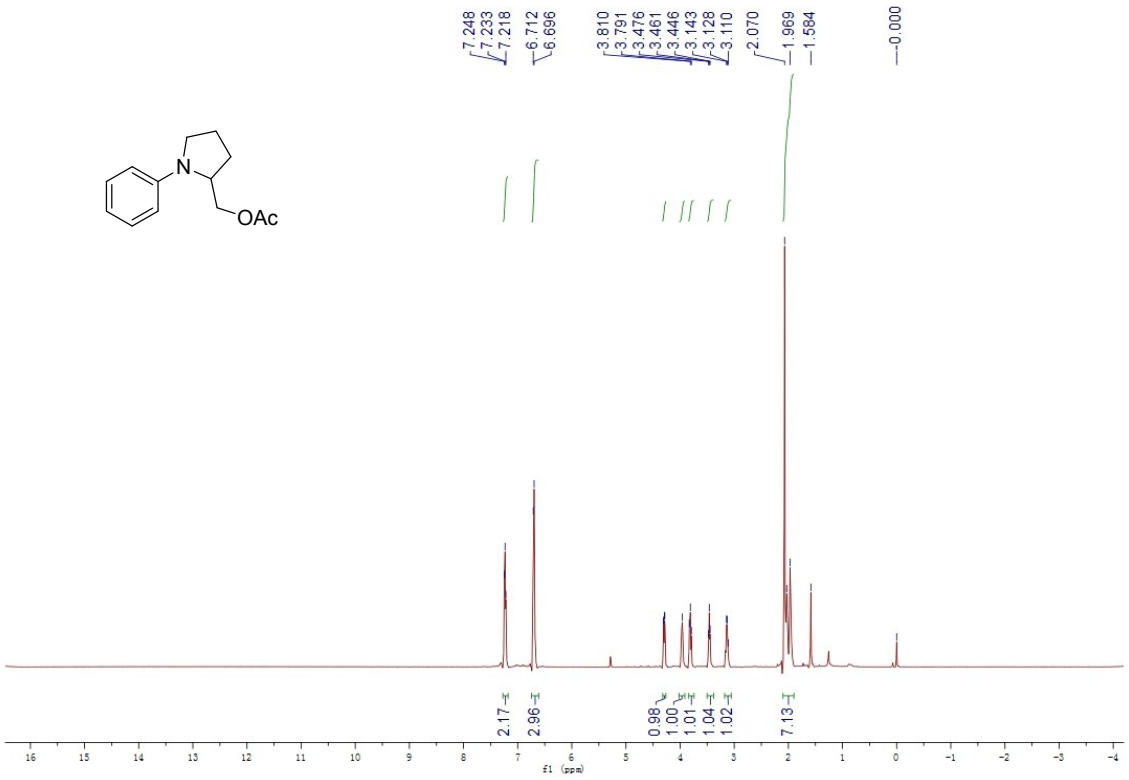


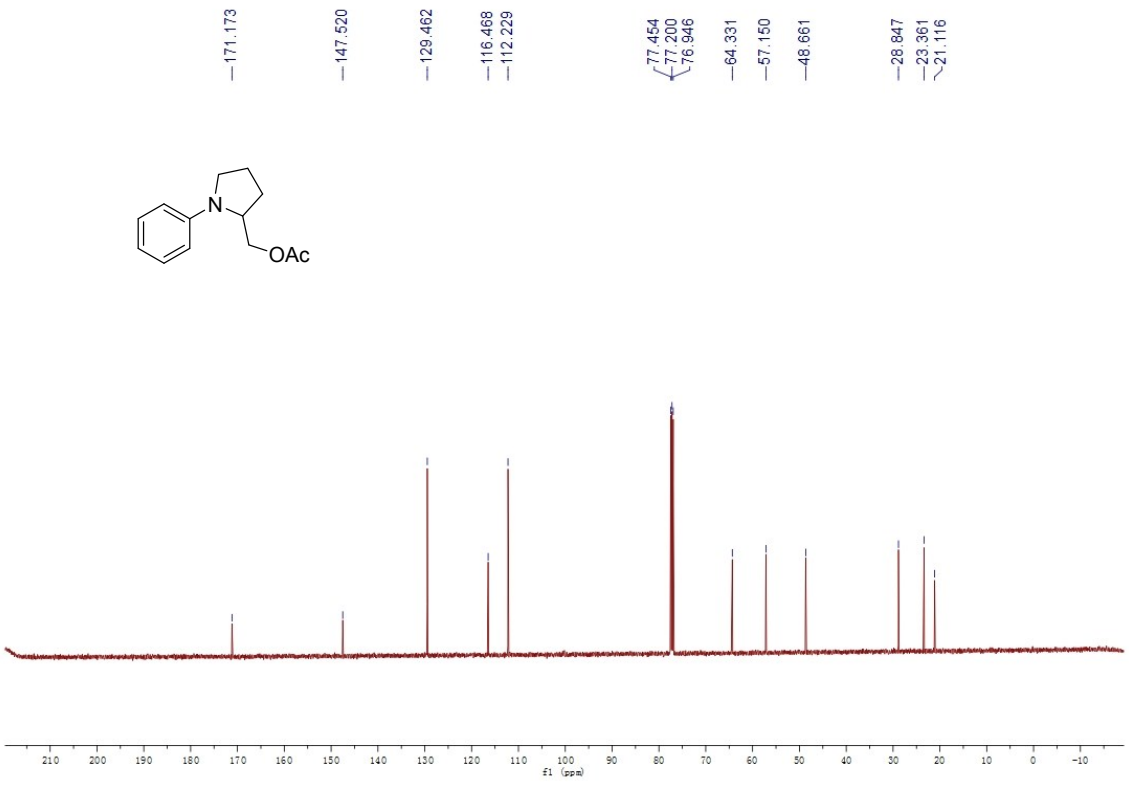
2-(1-Benzyl-5-bromoindolin-2-yl)acetonitrile (3z)



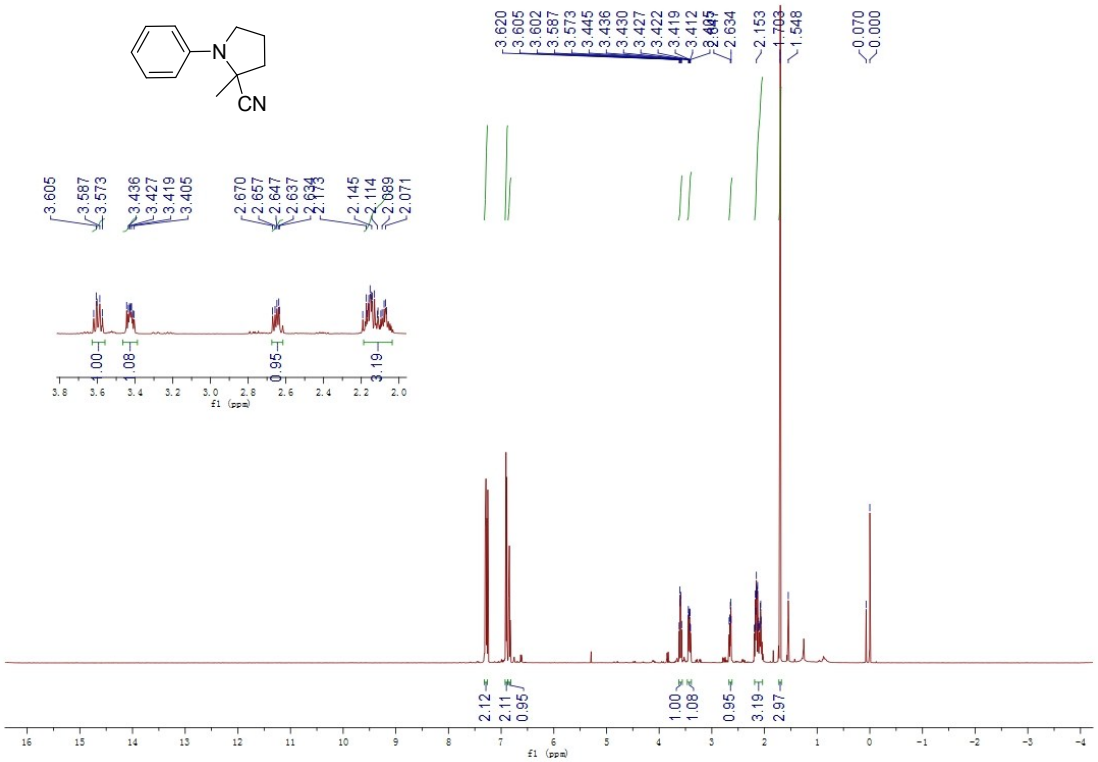


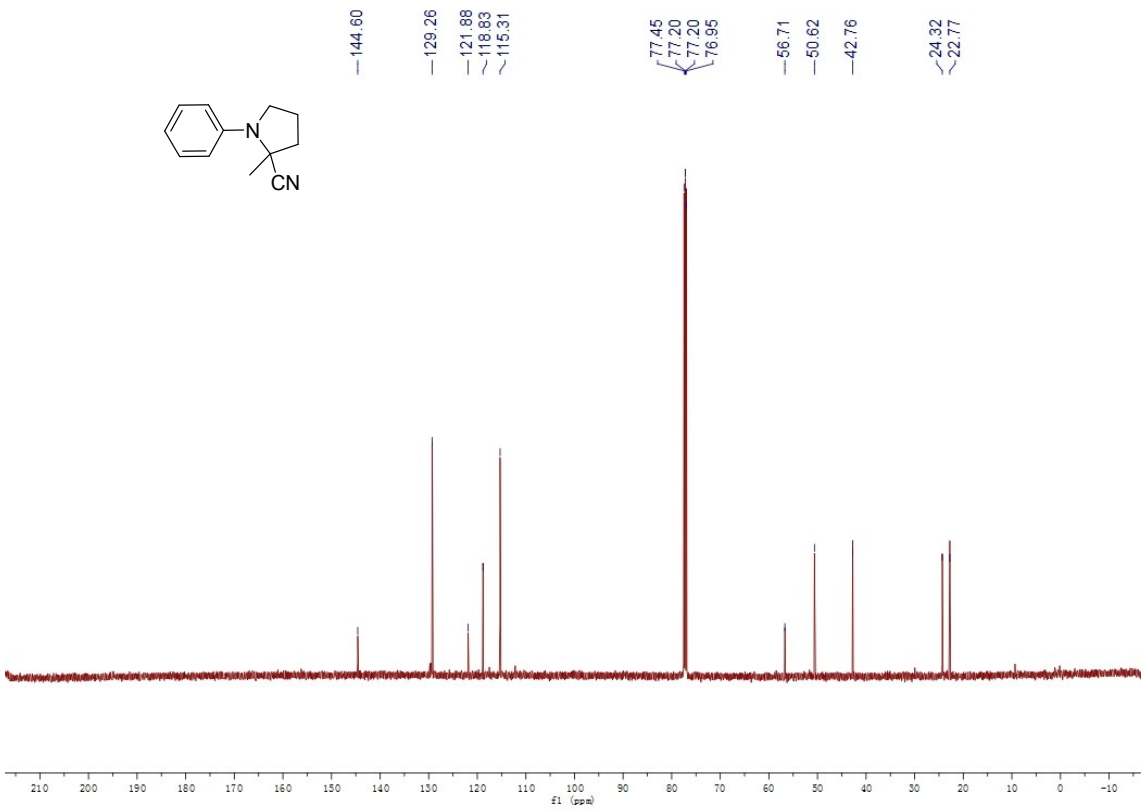
2-(1-Phenylpyrrolidin-2-yl)acetonitrile (4)



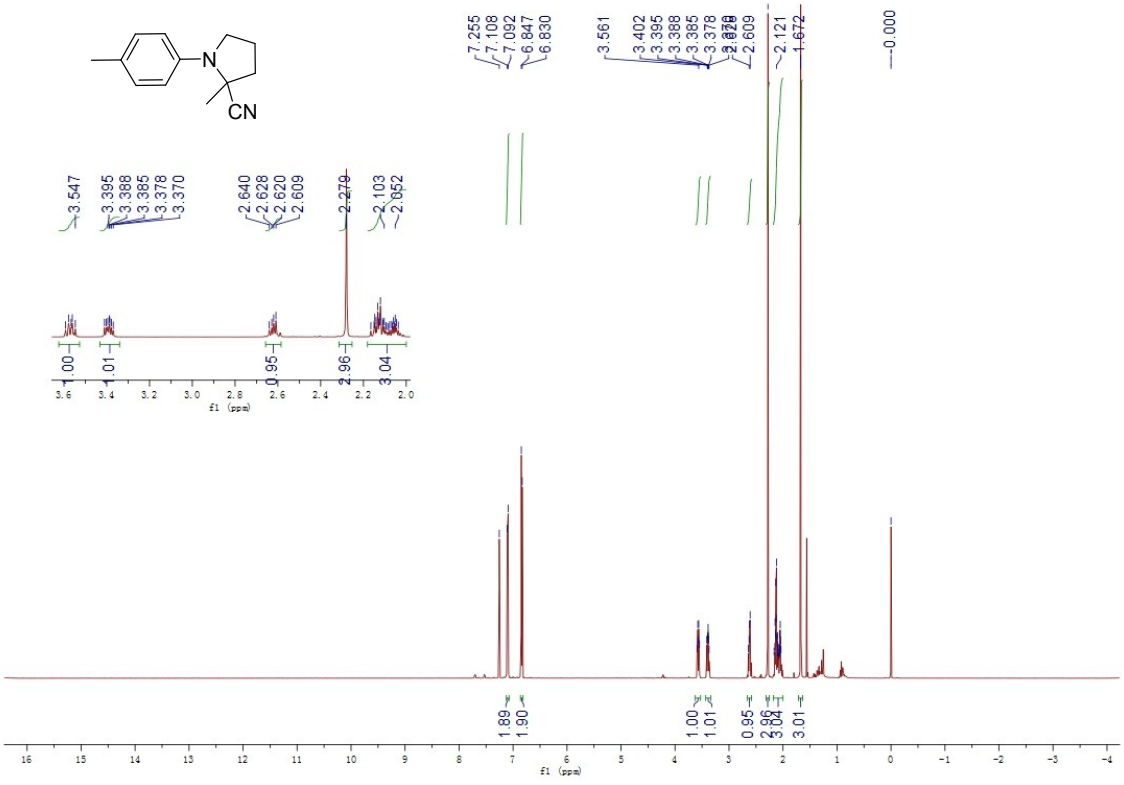


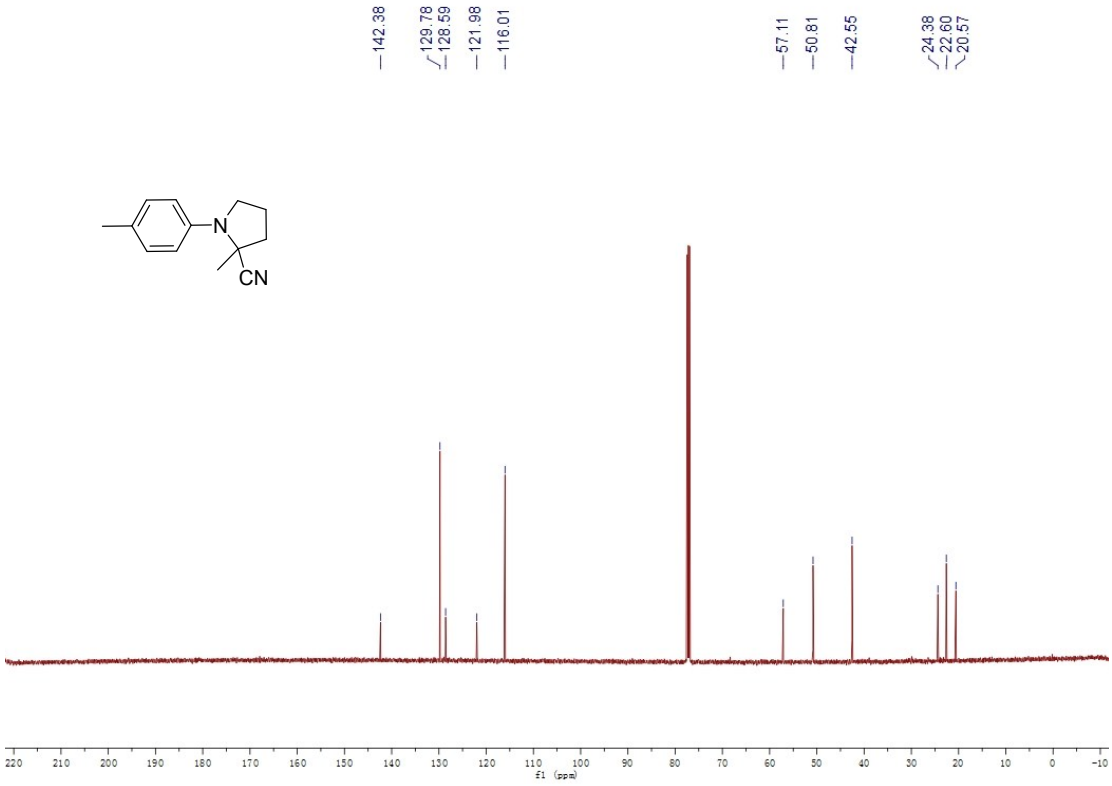
2-Methyl-1-phenylpyrrolidine-2-carbonitrile (5a)



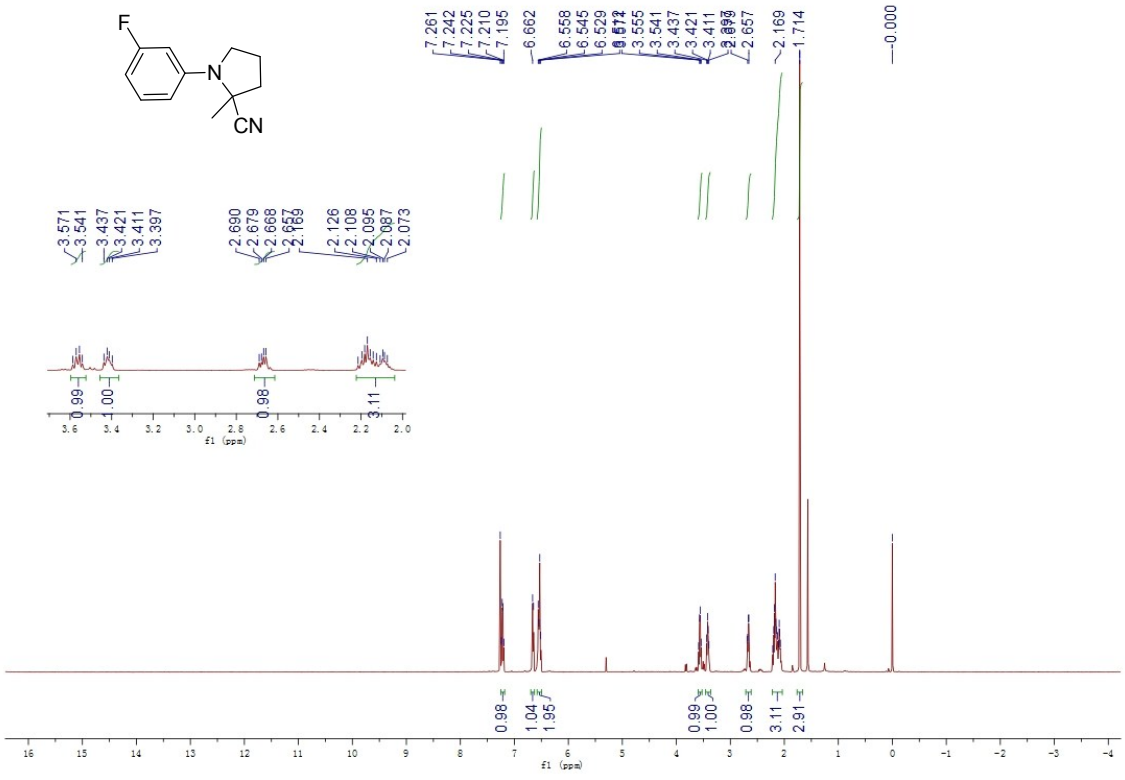


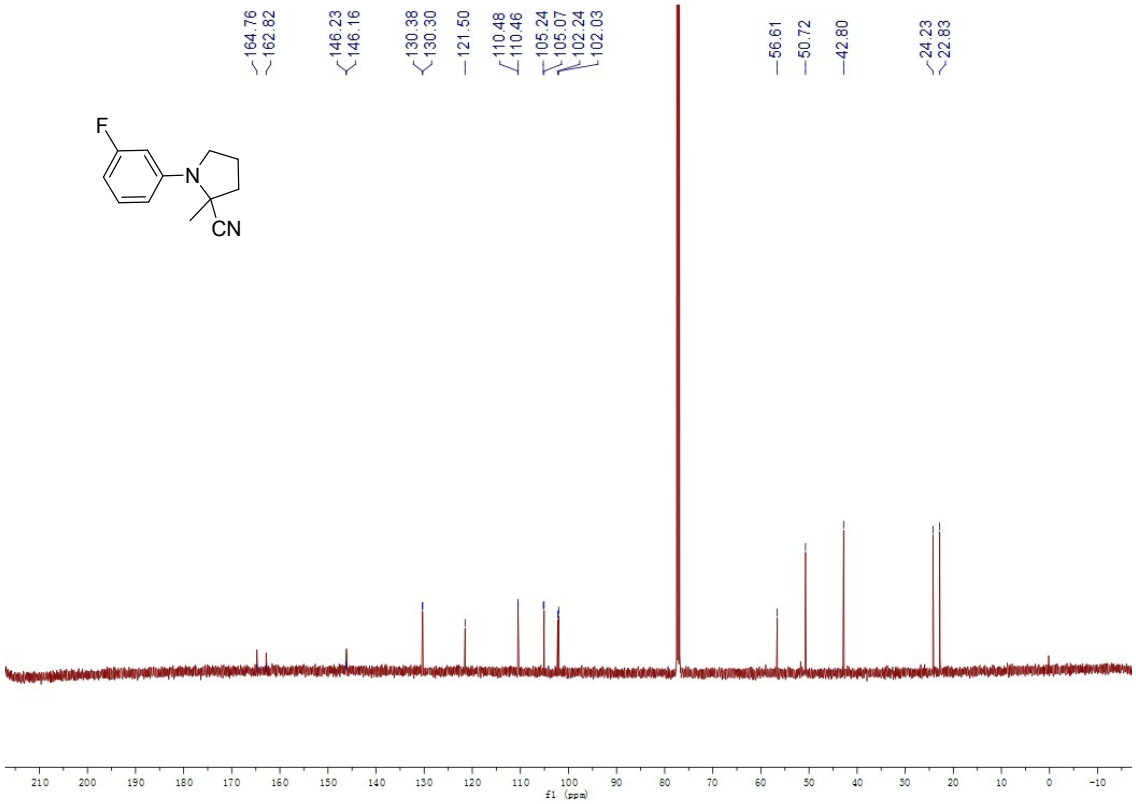
2-Methyl-1-(p-tolyl)pyrrolidine-2-carbonitrile (5b)



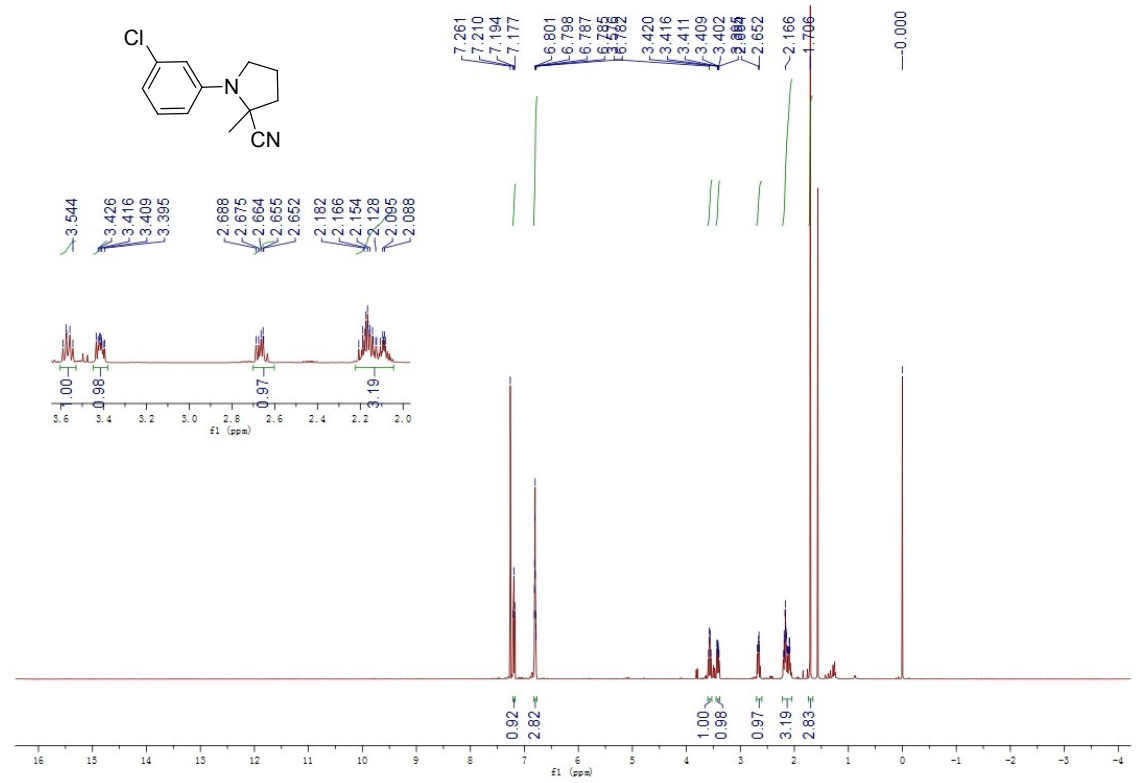


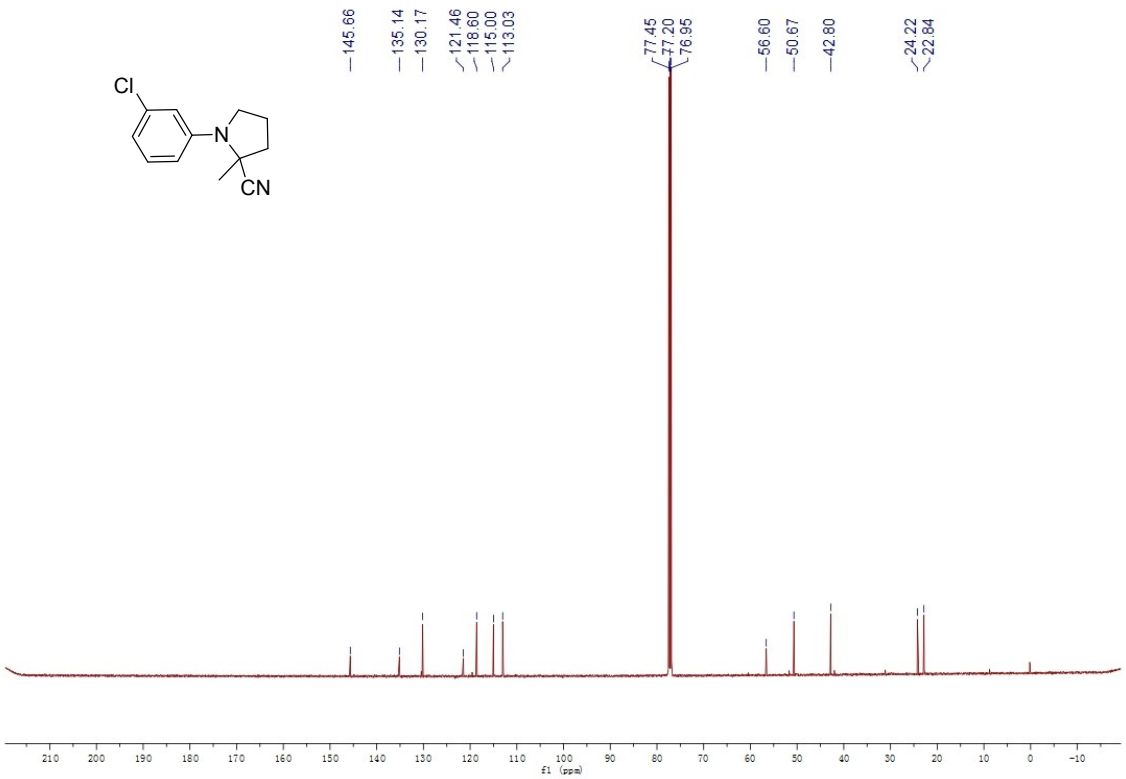
1-(3-Fluorophenyl)-2-methylpyrrolidine-2-carbonitrile (5c)



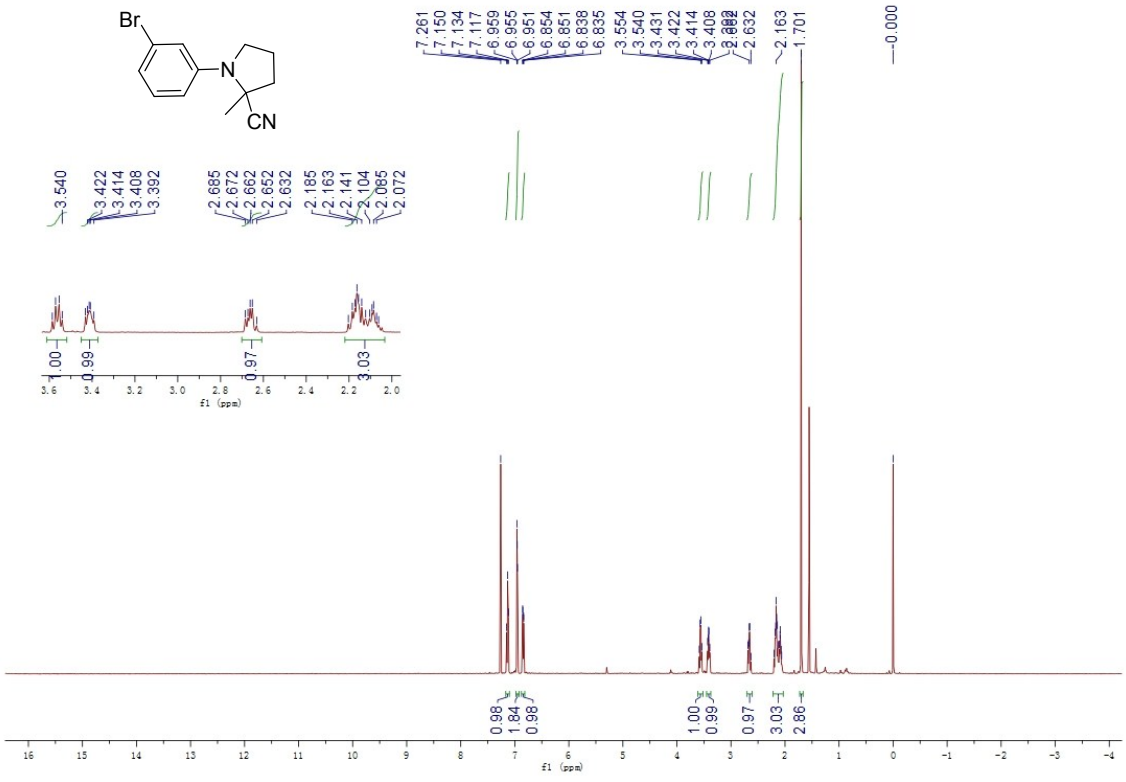


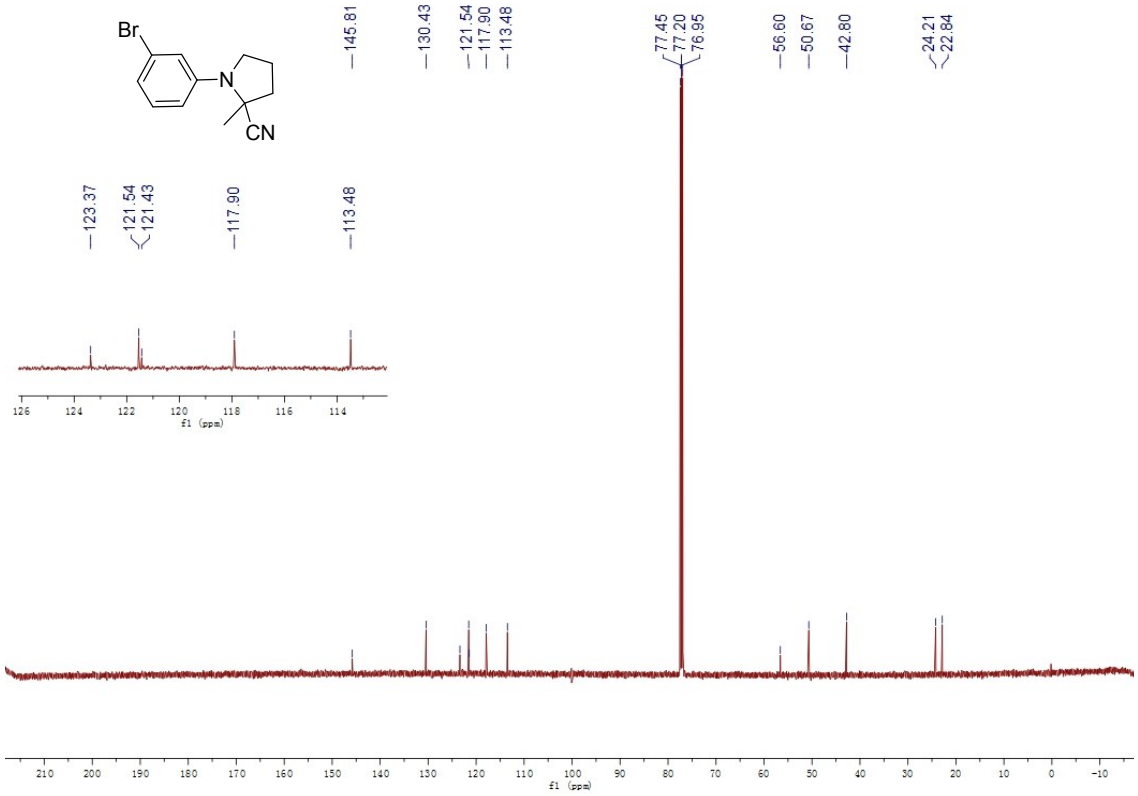
1-(3-Chlorophenyl)-2-methylpyrrolidine-2-carbonitrile (5d)



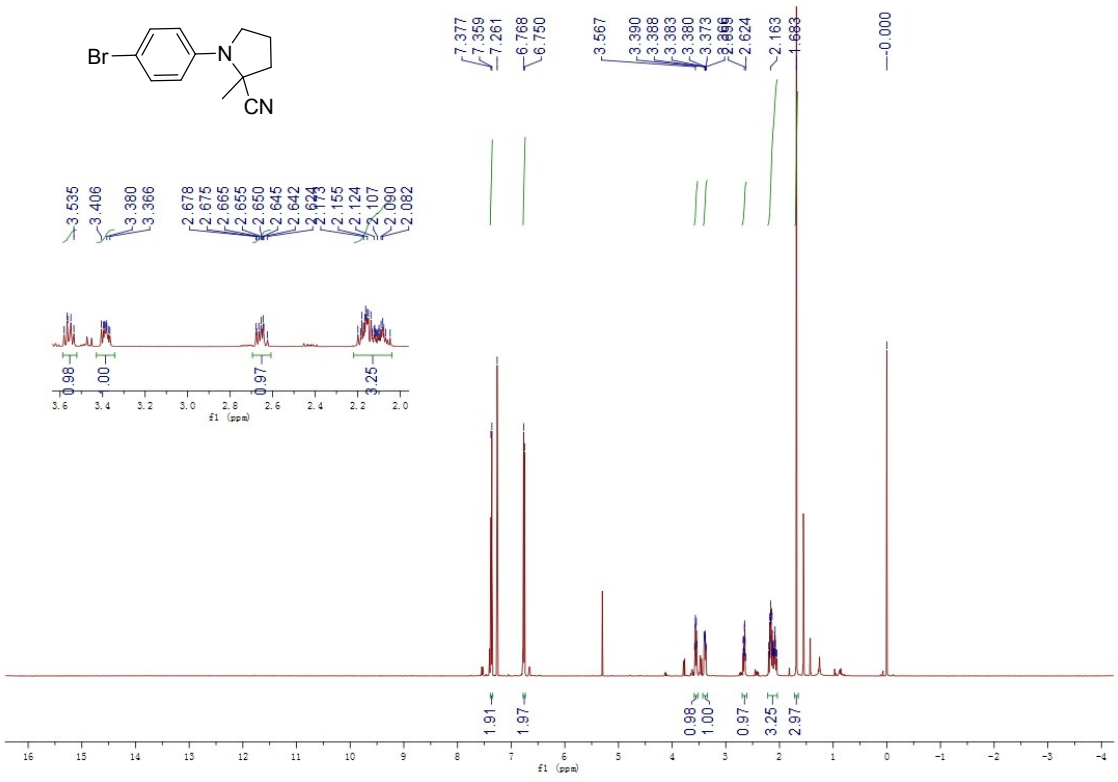


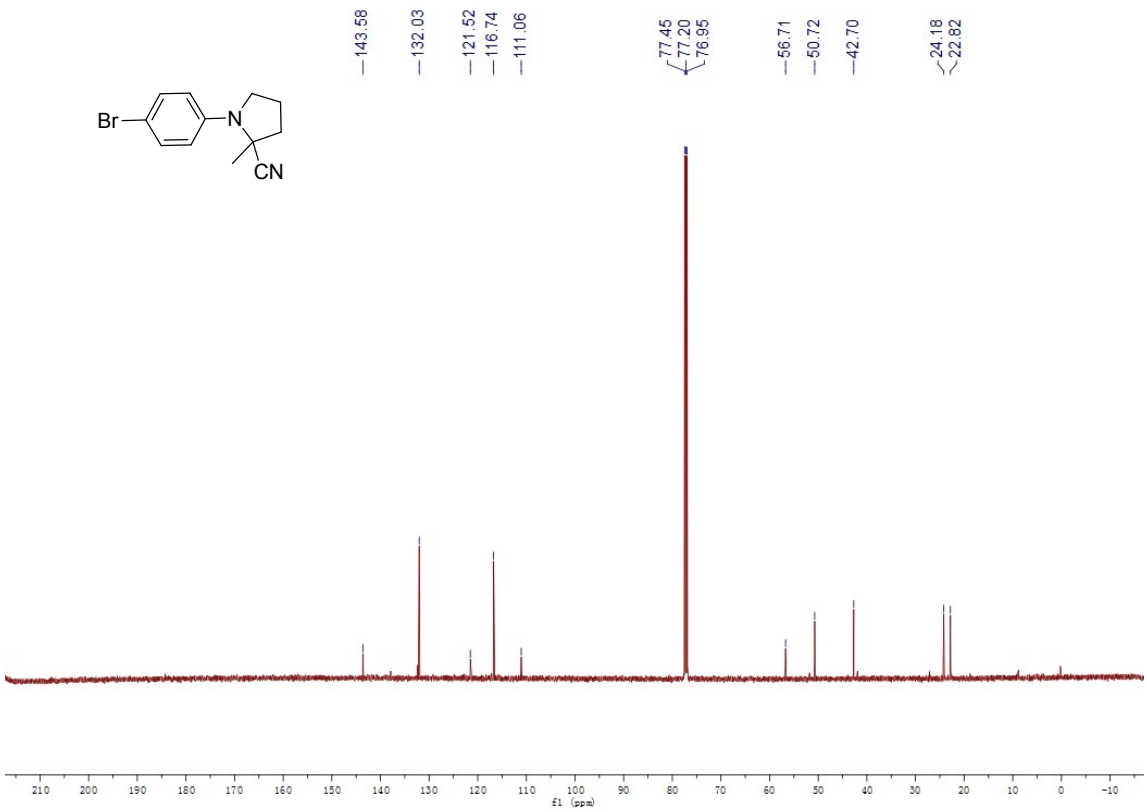
1-(3-Bromophenyl)-2-methylpyrrolidine-2-carbonitrile (5e)



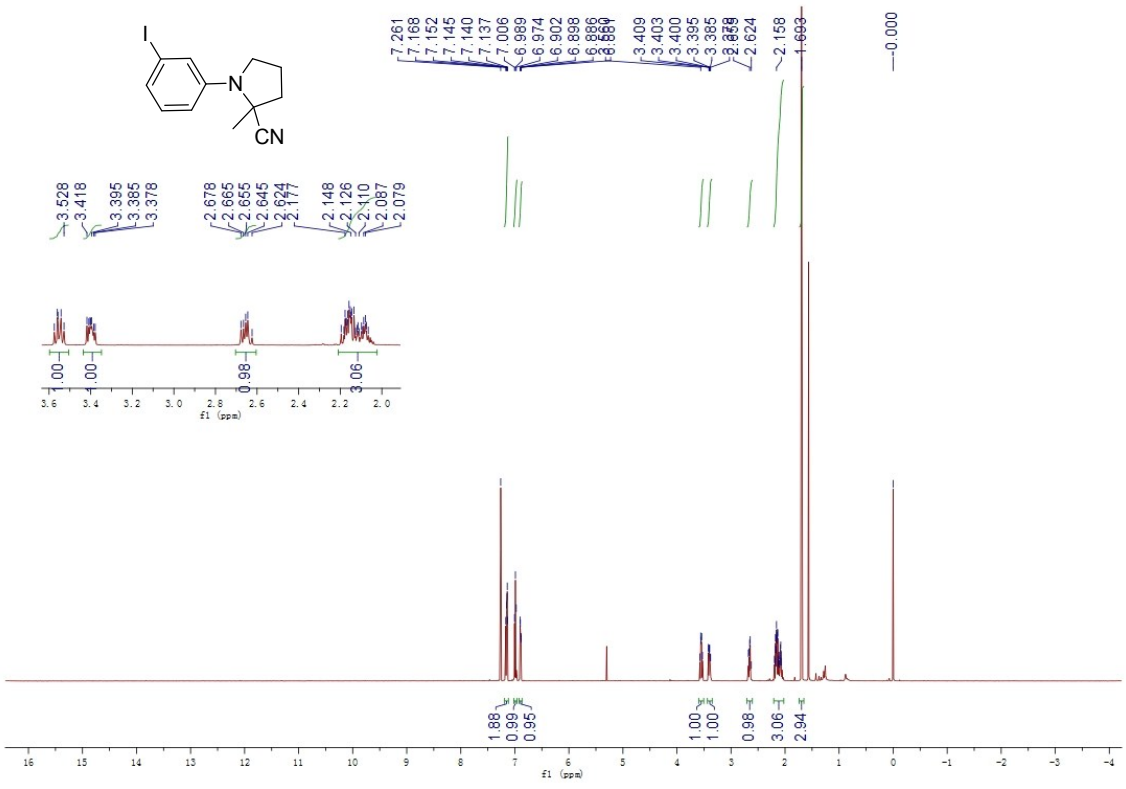


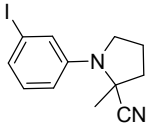
1-(4-Bromophenyl)-2-methylpyrrolidine-2-carbonitrile (5f)

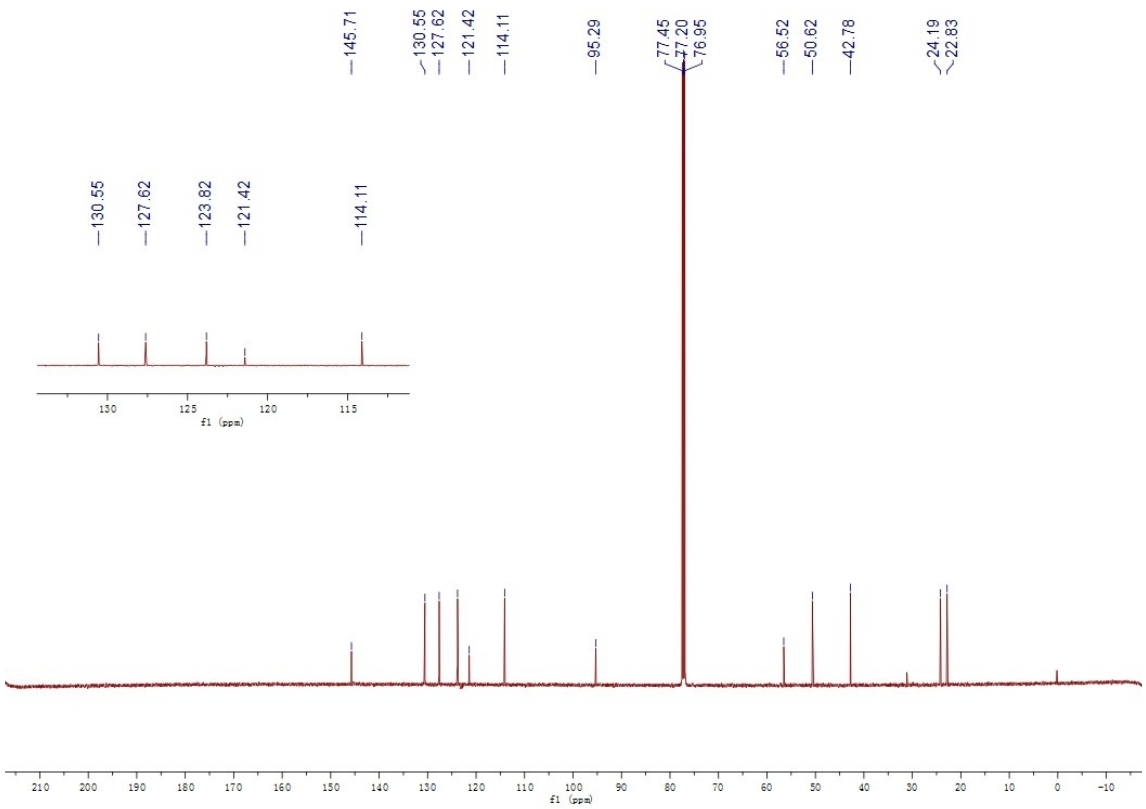




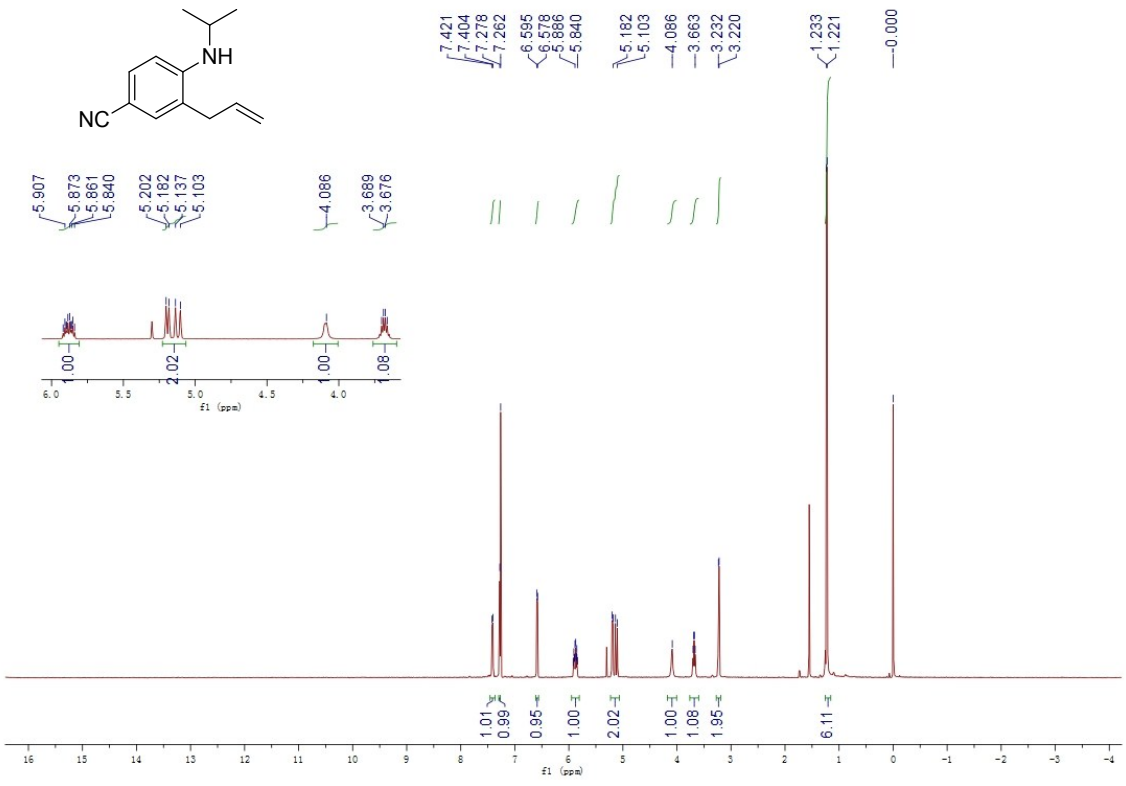
1-(3-Iodophenyl)-2-methylpyrrolidine-2-carbonitrile (5g)

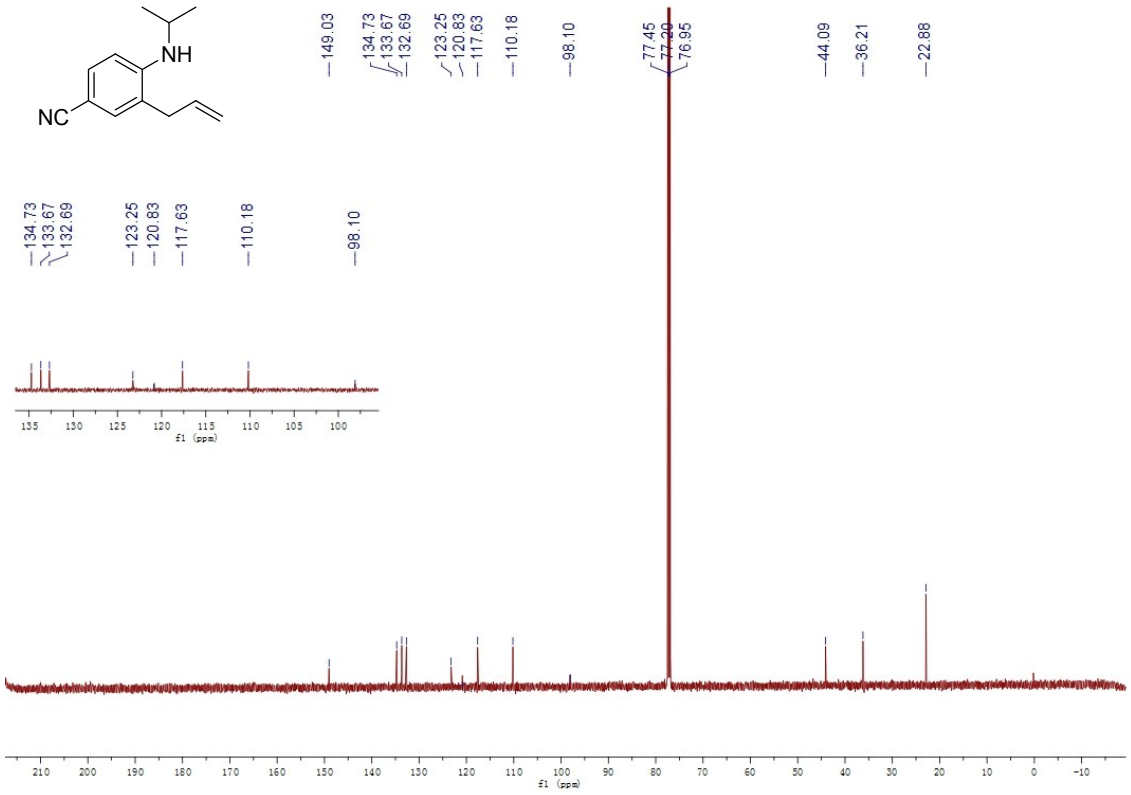




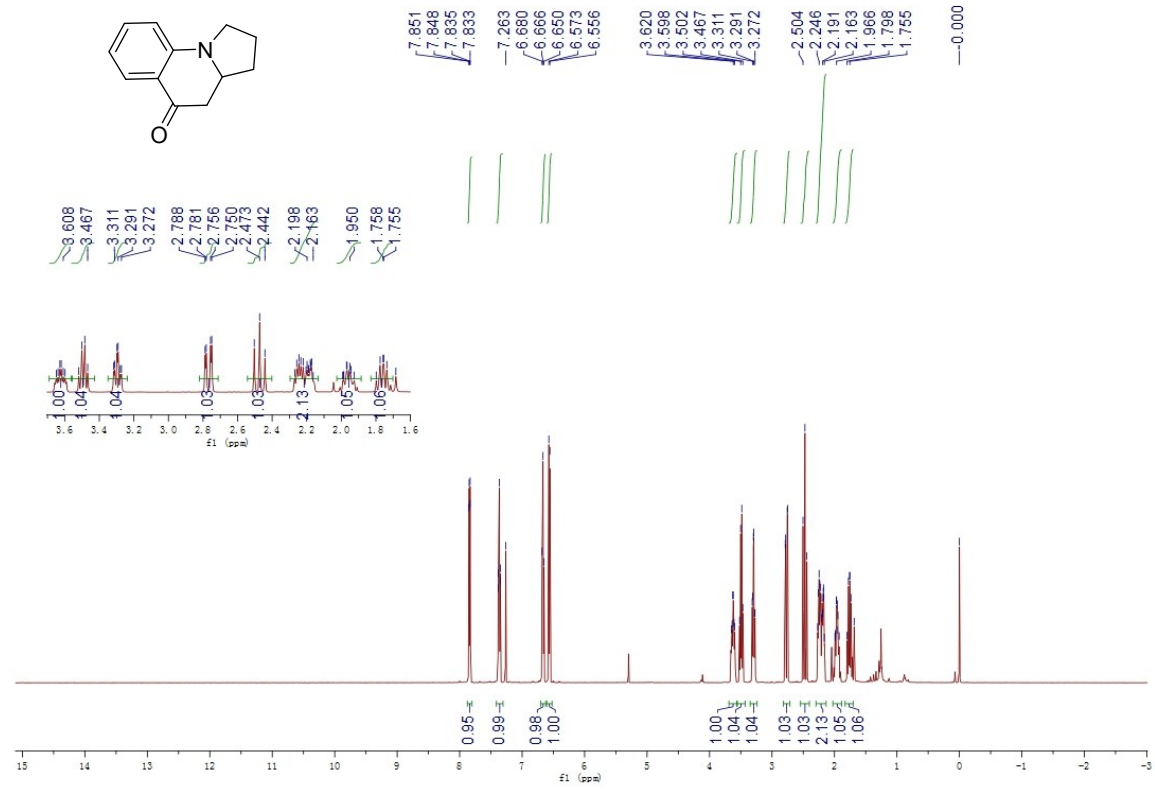


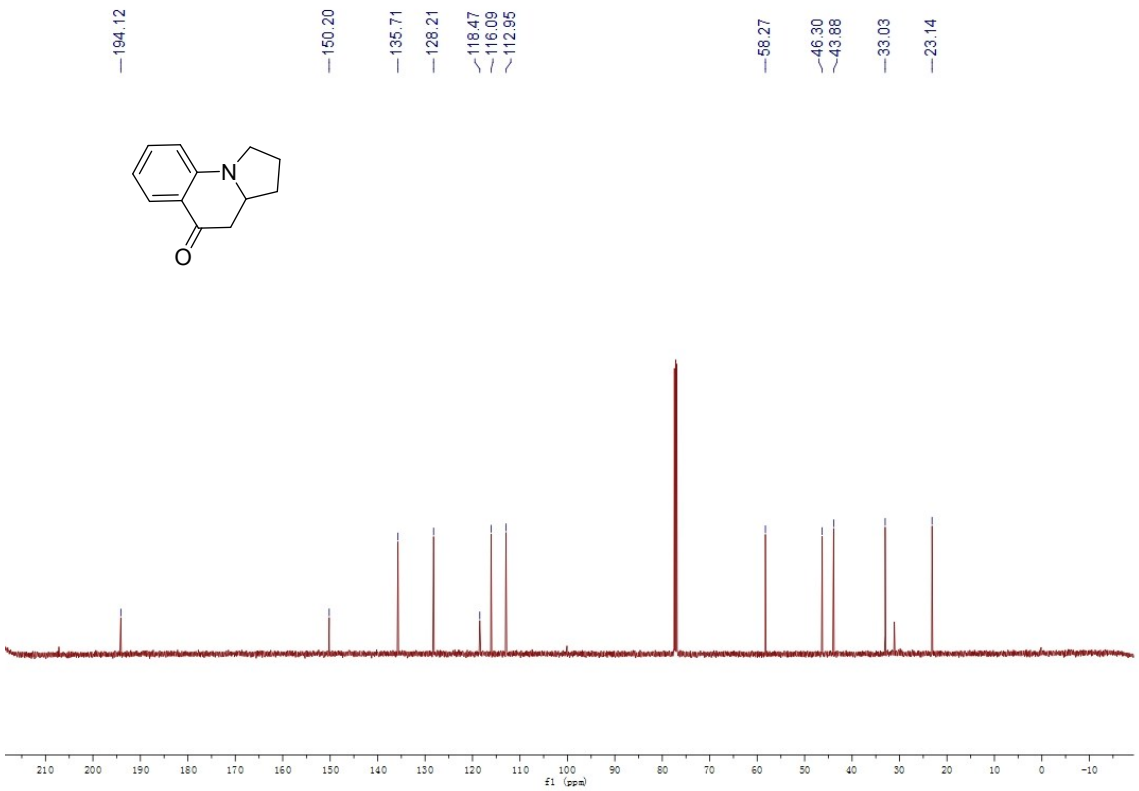
3-Allyl-4-(isopropylamino)benzonitrile (6)



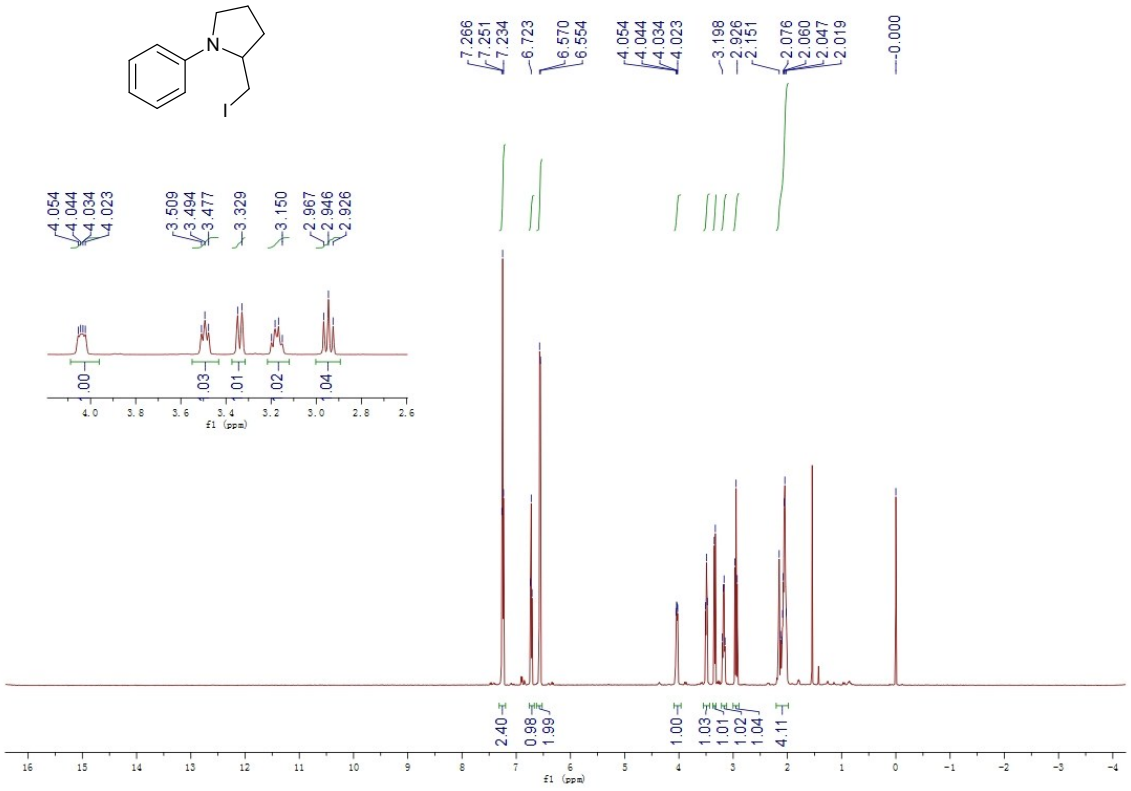


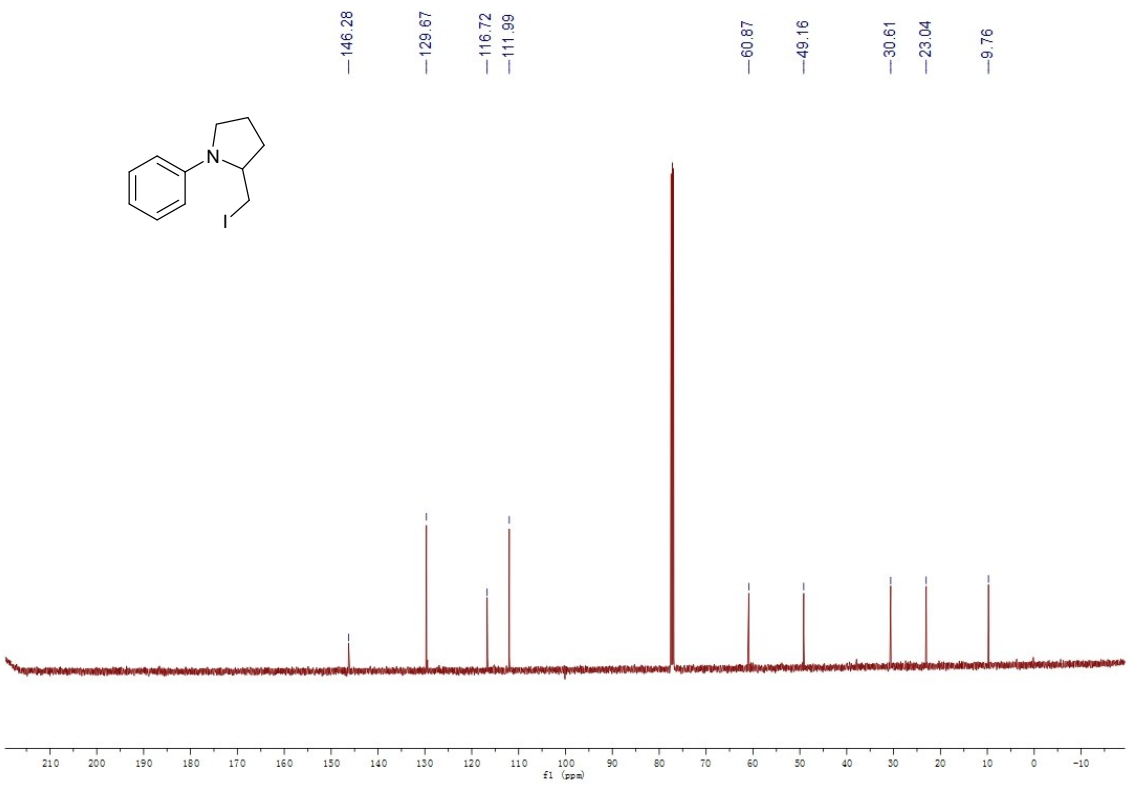
2,3,3a,4-Tetrahydropyrrolo[1,2-a]quinolin-5(1H)-one (8)





2-(Iodomethyl)-1-phenylpyrrolidine (9)




146.28
129.67
116.72
111.99
60.87
49.16
30.61
23.04
9.76
N
I
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)