Supporting Information

Copper-promoted cyanoalkylation/ring-expansion of vinylcyclopropanes with *α*-C–H bonds in alkylnitriles toward 3,4-dihydronaphthalenes

Zan Chen,[†a] Quan Zhou,[†a] Qing-Nan Chen,[a] Pu Chen,[a] Bi-Quan Xiong,[a] Yun Liang,[b] Ke-Wen Tang,[a] Jun Xie,[*a] Yu Liu[*ab]

[a] Department of Chemistry and Chemical Engineering, Hunan Institute of Science and Technology, Yueyang 414006, China

[b] Key Laboratory of the Assembly and Application of Organic Functional Molecules of Hunan Province, Hunan Normal University, Changsha, Hunan 410081, China. [phone and fax number: +86073-0864-0122 and E-mail addresses: lyxtmj_613@163.com (Yu Liu) and 12108014@hnist.edu.cn (Jun Xie)]

[†] These authors contributed equally to this work

List of Contents

1. General Information

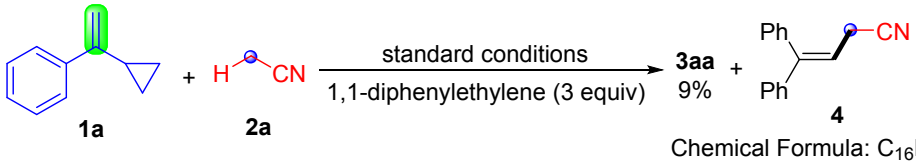
Unless otherwise stated, all commercial reagents were used as received. Cupric acetate (MACKLIN, ≥99%), Silver carbonate (BK, 99%), aldehydes (Innochem, >98%) and ketones (Innochem, >98%) were used without further treatment. All reagents and solvents were commercially available and used without any further purification unless specified. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (0.25mm, 300-400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25mm 300-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). All reactions were carried out with magnetic stirring and in dried glassware. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-400 spectrometer operating at 400 MHz, 376 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quated in Hz. The solvent peak was used as a reference value, for ^{1}H NMR: TMS = 0.00 ppm, for ^{13}C NMR: $CDCl_3$ = 77.00 ppm. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, td = triplet of doublet, q = quartet, m = multiplet, and br = broad. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

2. Experiment Section

2.1 General Procedure for the Synthesis of Vinylcyclopropanes (1):

All Vinylcyclopropane **1**[1] were synthesized according to the known methods.

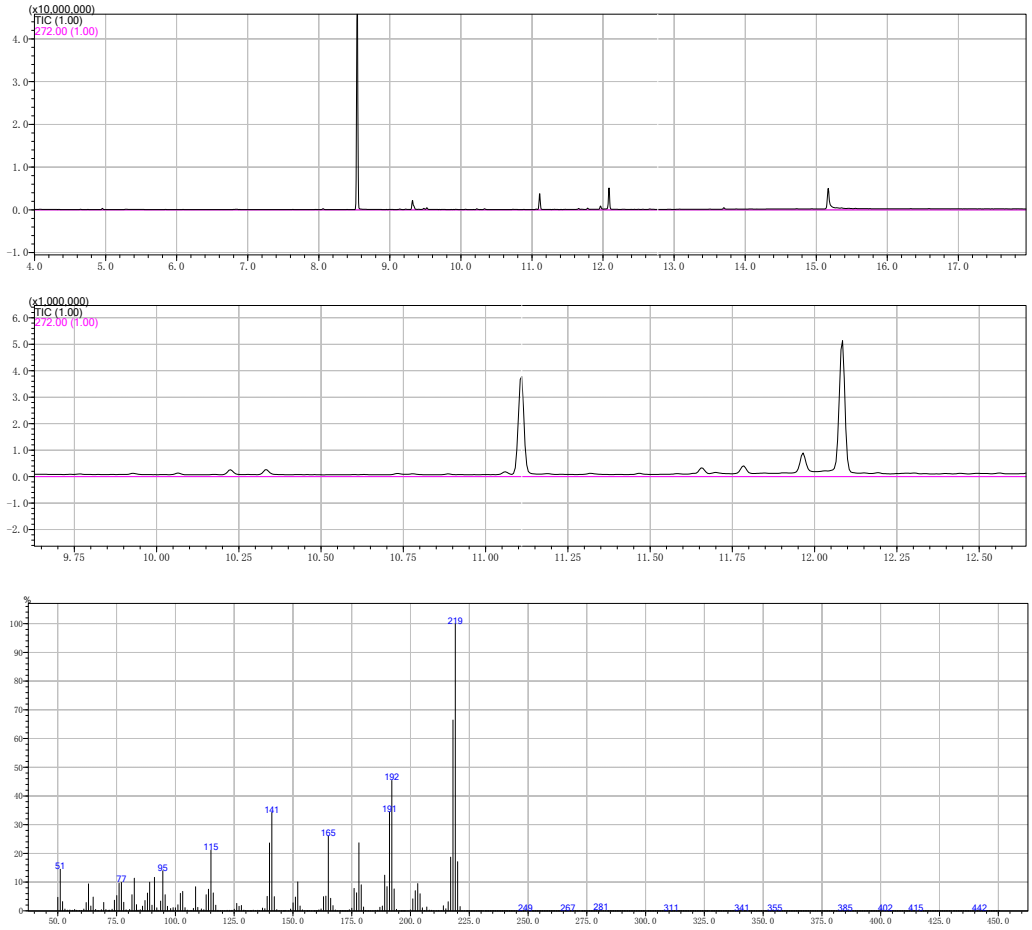
2.2 Radical Trapping Experiments.



1a **2a** **4**

Chemical Formula: $C_{16}H_{13}N$
Exact Mass: 219.1048
Molecular Weight: 219.2870
m/z: 219.1048 (100.0%), 220.1082 (17.3%), 221.1115 (1.4%)

The GC-MS analysis results of raw reaction mixture：



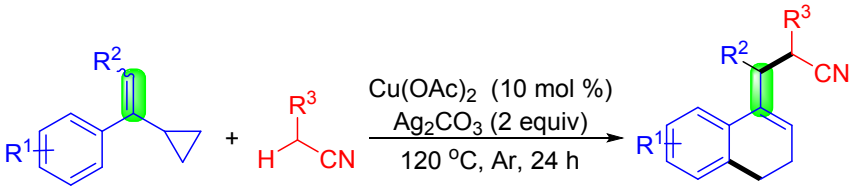
[MS Spectrum]
# of Peaks400
Raw Spectrum 11.110 (scan : 1423)
Background No
Background Spectrum
Base Peakm/z 219.05 (Inten : 482,772)
Event# 1
m/z Absolute Intensity Relative Intensity

50.00	22687	4.70	58.05	975	0.20	77.05	47592	9.86
51.05	69942	14.49	59.15	743	0.15	78.05	14444	2.99
52.05	15439	3.20	60.05	411	0.09	79.05	16750.35	
53.00	29930.62		61.05	30470.63		80.55	23590.49	
54.00	11180.23		62.05	13955	2.89	81.55	27129	5.62
55.10	13420.28		63.05	45473	9.42	82.50	54774	11.35
56.15	10090.21		64.05	80541.67		83.45	10454	2.17
57.15	22770.47		65.05	23242	4.81	84.10	12280.25	
			66.10	23800.49		85.05	18360.38	
			67.10	665	0.14	86.05	77981.62	
			68.55	18660.39		87.10	17471	3.62
			69.50	14231	2.95	88.10	29825	6.18
			70.45	21820.45		89.05	48106	9.96
			71.45	857	0.18	90.05	94411.96	
			72.05	11920.25		91.10	56239	11.65
			73.05	27140.56		92.10	50781.05	
			74.05	17745	3.68	92.70	991	0.21
			75.05	25766	5.34	93.75	16341	3.38
			76.05	46222	9.57	94.65	67443	13.97

95.65	27097	5.61	141.05	165152	34.21	185.00	593	0.12
96.65	7584	1.57	142.05	23883	4.95	186.05	886	0.18
98.00	3935	0.82	143.10	2182	0.45	187.00	6095	1.26
99.05	5257	1.09	144.10	150	0.03	188.05	8072	1.67
100.05	5002	1.04	145.10	150	0.03	189.00	59847	12.40
101.10	10098	2.09	146.00	102	0.02	190.00	40743	8.44
102.10	29324	6.07	147.00	594	0.12	191.05	165850	34.35
103.10	32668	6.77	148.00	188	0.04	192.05	219272	45.42
104.10	5242	1.09	149.00	2937	0.61	193.05	36882	7.64
105.10	1121	0.23	150.05	13335	2.76	194.05	2645	0.55
106.65	605	0.13	151.05	23097	4.78	195.15	367	0.08
107.65	4063	0.84	152.05	48566	10.06	196.10	102	0.02
108.60	40481	8.39	153.05	8145	1.69	197.10	94	0.02
109.55	5774	1.20	154.05	1591	0.33	198.00	180	0.04
111.05	3226	0.67	155.00	230	0.05	198.95	308	0.06
112.10	1828	0.38	156.00	87	0.02	199.95	1723	0.36
113.10	27033	5.60	157.00	167	0.03	201.00	20089	4.16
114.10	36295	7.52	158.00	185	0.04	202.05	33701	6.98
115.10	101881	21.10	159.00	66	0.01	203.05	45737	9.47
116.10	30108	6.24	160.00	106	0.02	204.05	28782	5.96
117.15	9584	1.99	161.05	1630	0.34	205.05	5140	1.06
118.10	894	0.19	161.95	3210	0.66	205.95	521	0.11
119.10	359	0.07	163.00	23935	4.96	206.95	6373	1.32
120.10	191	0.04	164.00	24841	5.15	208.00	1252	0.26
121.00	236	0.05	165.05	125614	26.02	208.95	1005	0.21
122.00	1006	0.21	166.05	21171	4.39	209.90	276	0.06
123.10	1031	0.21	167.05	8906	1.84	211.00	199	0.04
124.05	1020	0.21	168.05	1310	0.27	212.00	716	0.15
125.05	2696	0.56	169.00	116	0.02	213.05	480	0.10
126.10	12452	2.58	170.00	47	0.01	214.00	8465	1.75
127.10	7554	1.56	171.00	57	0.01	215.05	3555	0.74
128.10	9086	1.88	172.00	70	0.01	216.00	15254	3.16
129.10	1177	0.24	173.00	108	0.02	**217.05**	**90363**	**18.72**
129.90	137	0.03	174.00	1764	0.37	**218.05**	**320654**	**66.42**
130.90	345	0.07	175.05	4435	0.92	**219.05**	**482772**	**100.00**
131.90	111	0.02	176.00	37662	7.80	**220.05**	**82650**	**17.12**
133.10	1145	0.24	177.05	30254	6.27	**221.10**	**7199**	**1.49**
134.00	489	0.10	178.05	114315	23.68	221.90	554	0.11
135.10	969	0.20	179.05	43849	9.08	222.90	183	0.04
135.85	469	0.10	180.05	6456	1.34	223.90	108	0.02
137.05	4530	0.94	181.00	628	0.13	224.90	49	0.01
138.05	3677	0.76	182.00	130	0.03	225.90	89	0.02
139.05	24246	5.02	183.00	185	0.04	226.90	78	0.02
140.05	114076	23.63	184.00	129	0.03	227.90	57	0.01

228.90	46	0.01	236.90	36	0.01	244.90	86	0.02
229.90	52	0.01	237.90	108	0.02	245.90	58	0.01
230.90	162	0.03	238.90	55	0.01	246.90	30	0.01
231.90	81	0.02	239.90	73	0.02	247.90	58	0.01
232.90	33	0.01	240.90	29	0.01	248.90	282	0.06
233.90	73	0.02	241.90	47	0.01	249.90	106	0.02
234.90	65	0.01	242.90	60	0.01	250.90	231	0.05
235.90	103	0.02	243.90	58	0.01	251.90	68	0.01

2.3 Typical Experimental Procedure for the Synthesis of 1-cyanoethylated 3,4-dihydronaphthalenes.



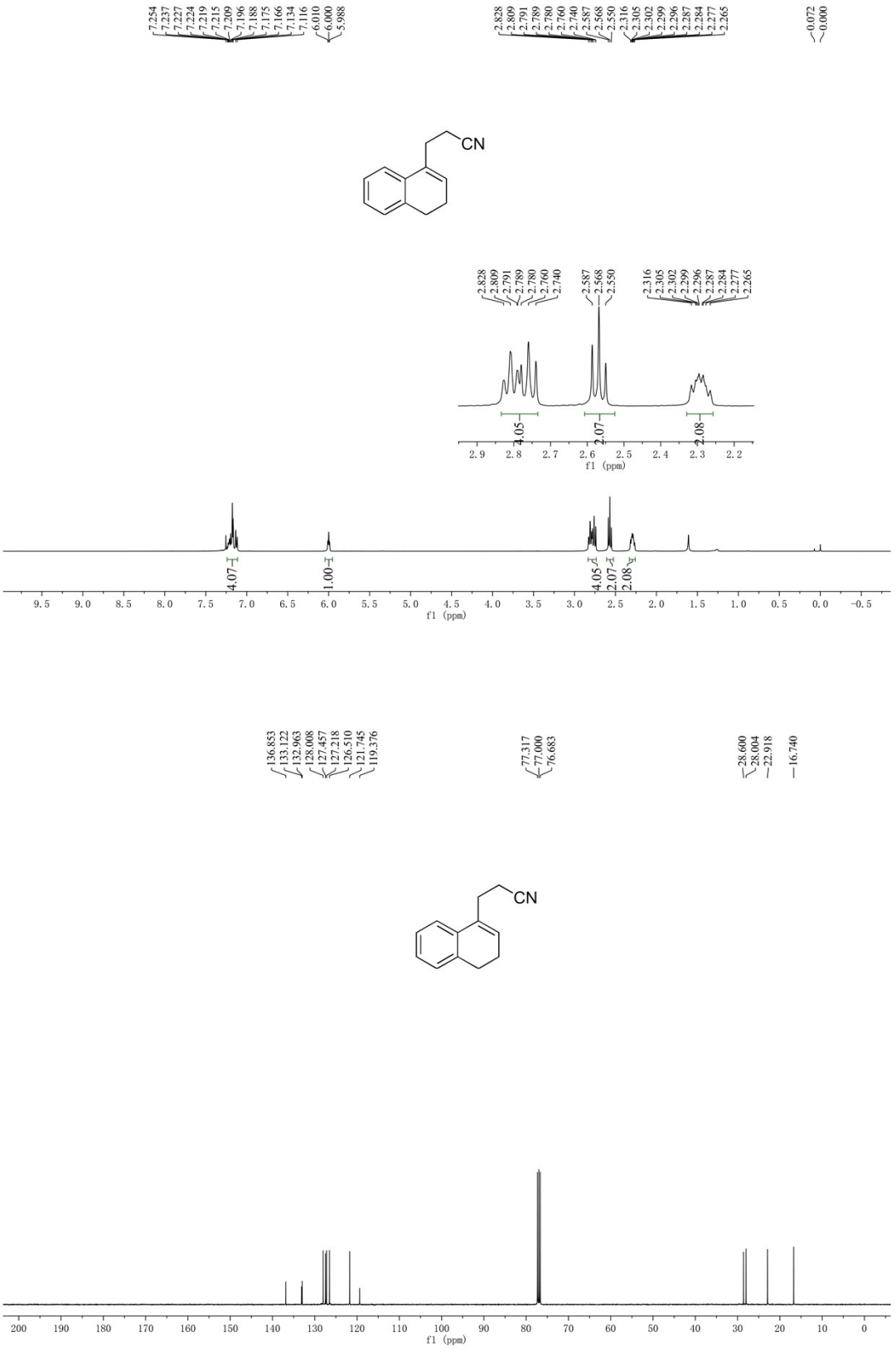
To a Schlenk tube were added VCP **1** (0.2 mmol, 0.1 M), alkyl nitriles **2a** (2 mL), $Cu(OAc)_2$ (4 mg, 10 mol %) and Ag_2CO_3 (110.3 mg, 2 equiv). Then the tube was stirred at 120 °C (oil bath temperature) in argon atmosphere for 24 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture removal of the solvent, the crude product was purified by column chromatography (petroleum ether/ethyl acetate, 20 : 1) to provide the desired products **3**. An amplified experiment conducted in the presence of VCP **1a** (1g, 6.94 mmol), $Cu(OAc)_2$ (126.1 mg, 10 mol %), Ag_2CO_3 (3.83 g, 2 equiv) and CH_3CN (50 mL) at 120 °C under argon atmosphere for 72 h could successfully afford the desired product **3aa** in 52% yield (660.8 mg).

3. References

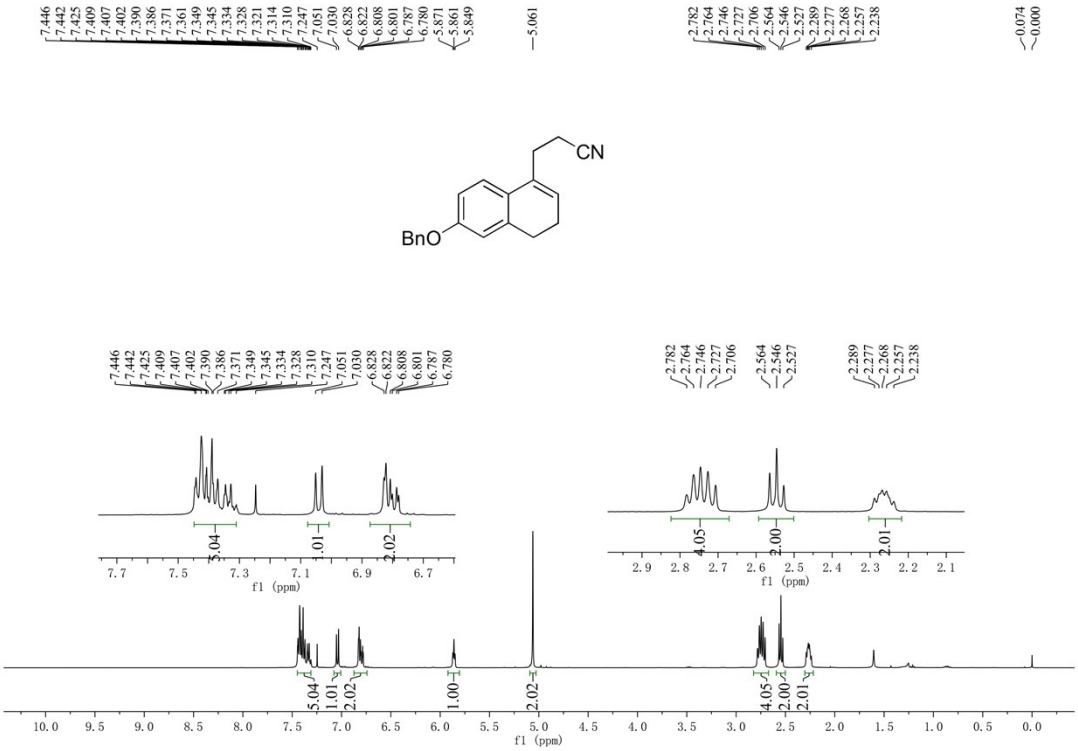
[1] Li, J.; Chen, J.-Z.; Jiao, W.; Wang, G.-Q.; Li, Y.; Cheng, X.; Li, G.-G. Difluoroalkylation/C−H Annulation Cascade Reaction Induced by Visible-Light Photoredox Catalysis. *J. Org. Chem.* **2016**, *81*, 9992−10001.

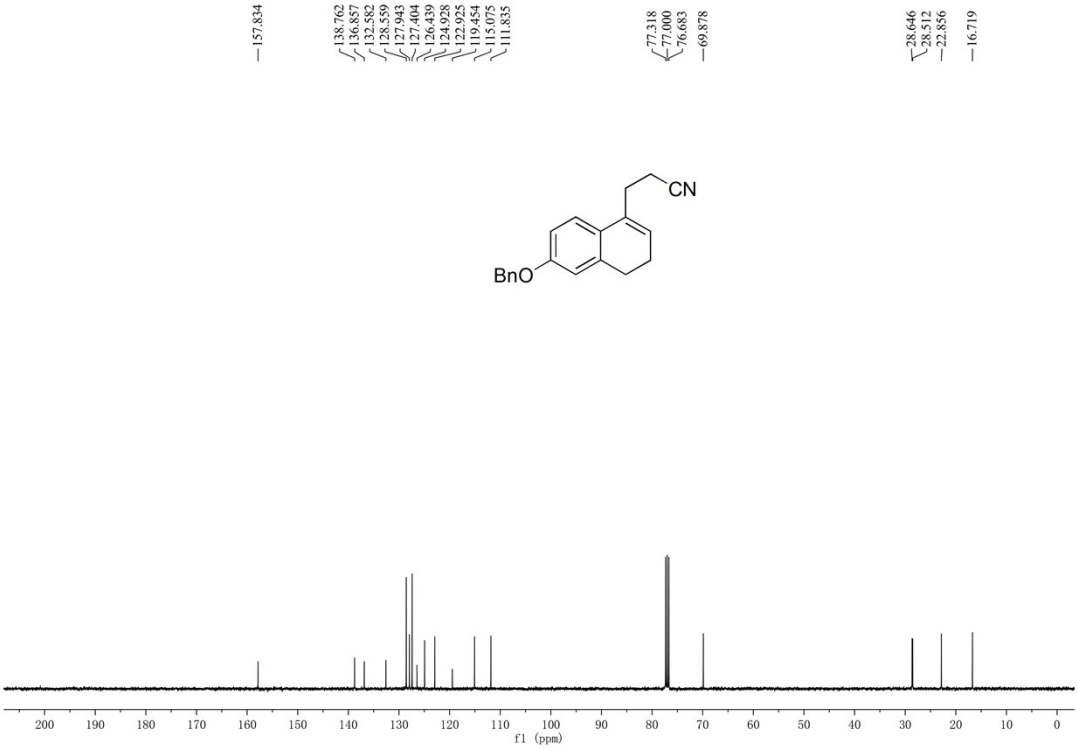
4. Spectra

3-(3,4-Dihydronaphthalen-1-yl)propanenitrile (3aa)

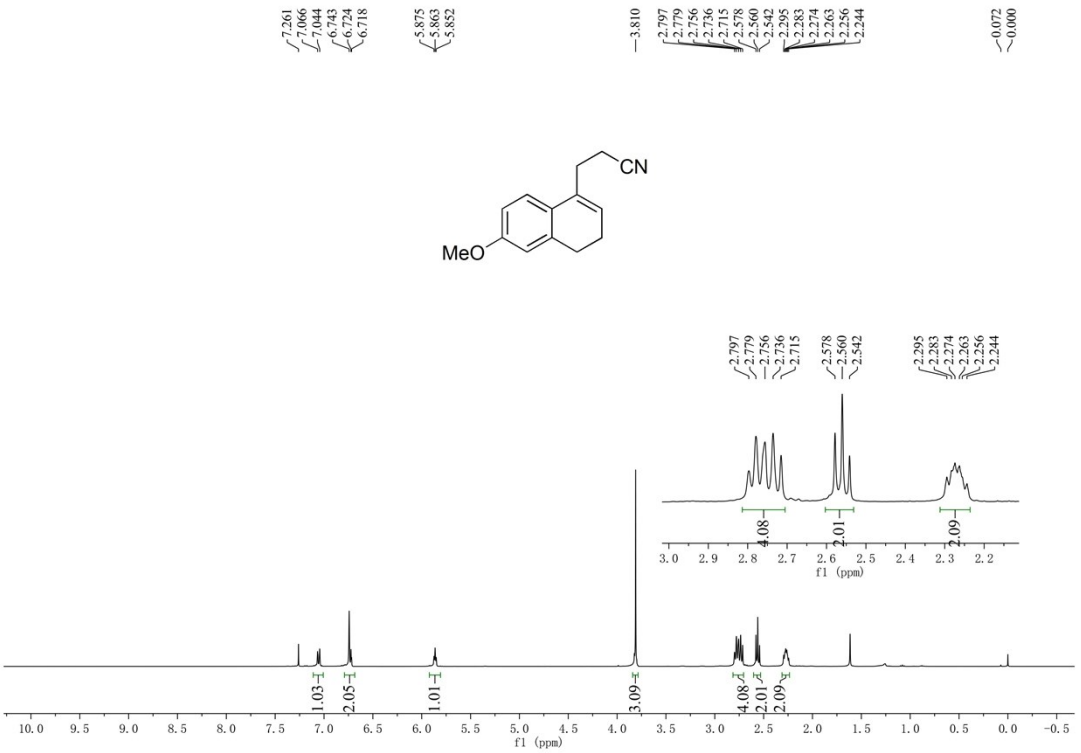


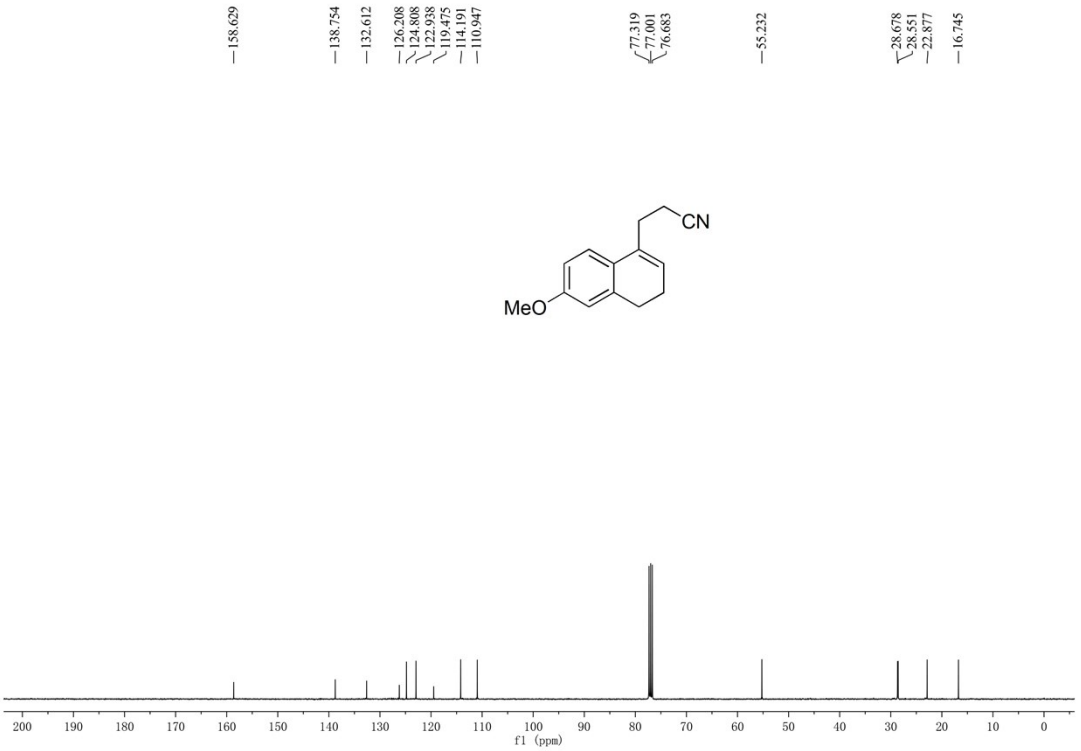
3-(6-(Benzyloxy)-3,4-dihydronaphthalen-1-yl)propanenitrile (3ba)



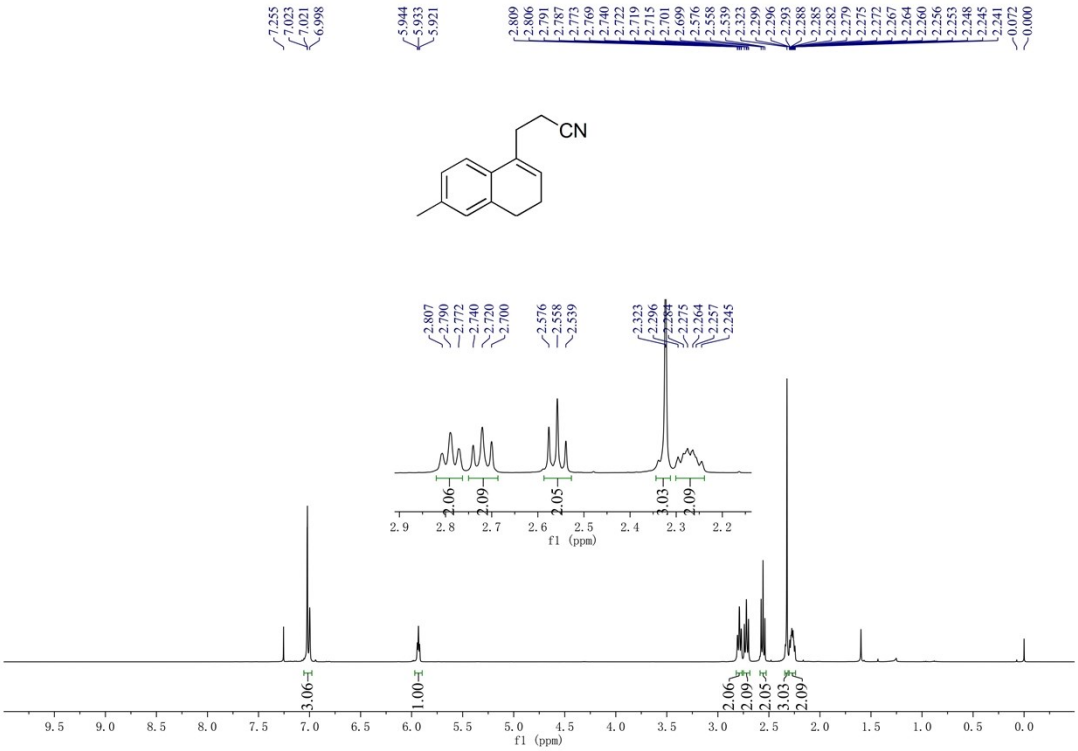


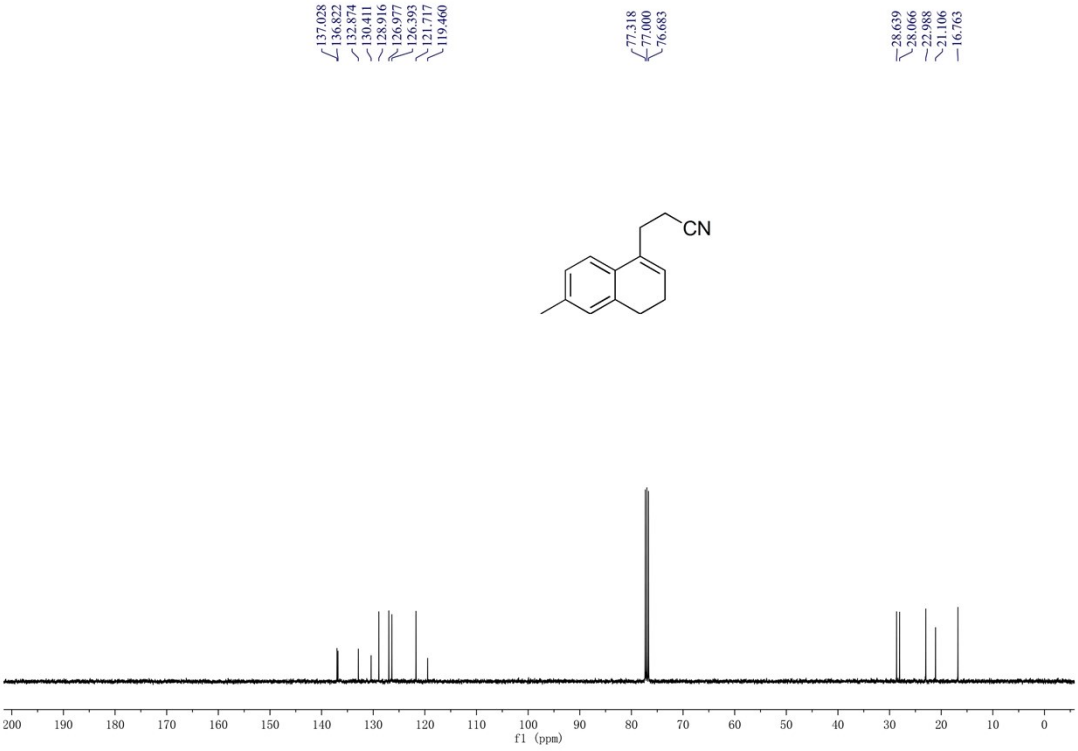
3-(6-Methoxy-3,4-dihydronaphthalen-1-yl)propanenitrile (3ca)



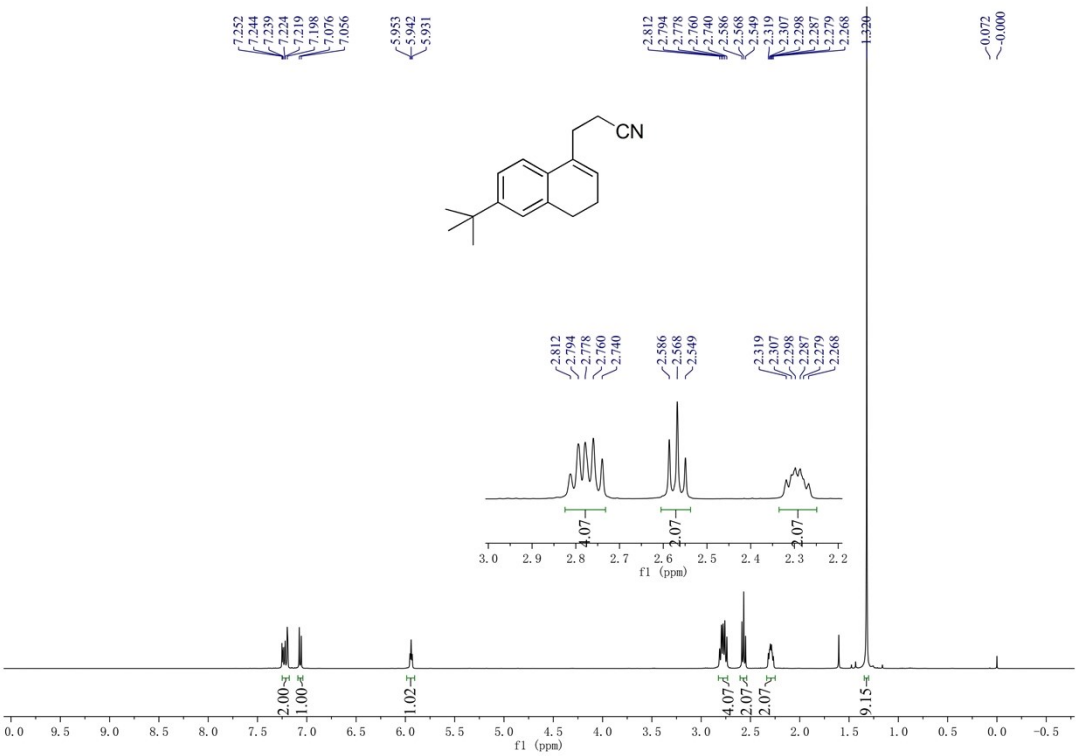


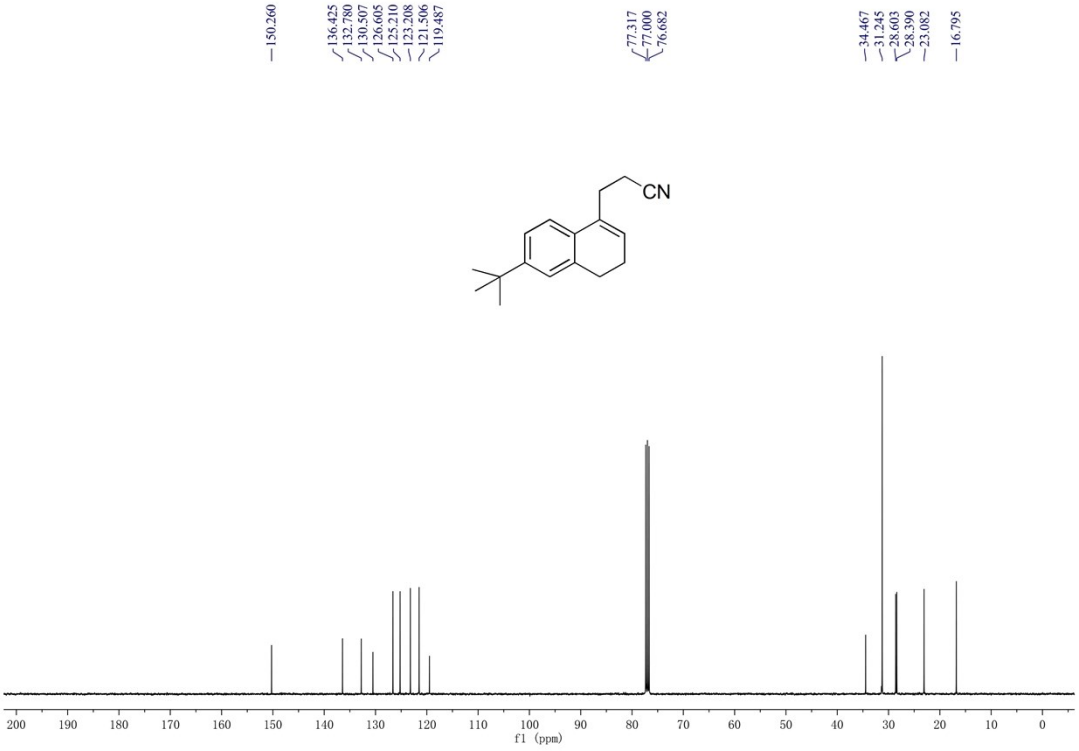
3-(6-Methyl-3,4-dihydronaphthalen-1-yl)propanenitrile (3da)



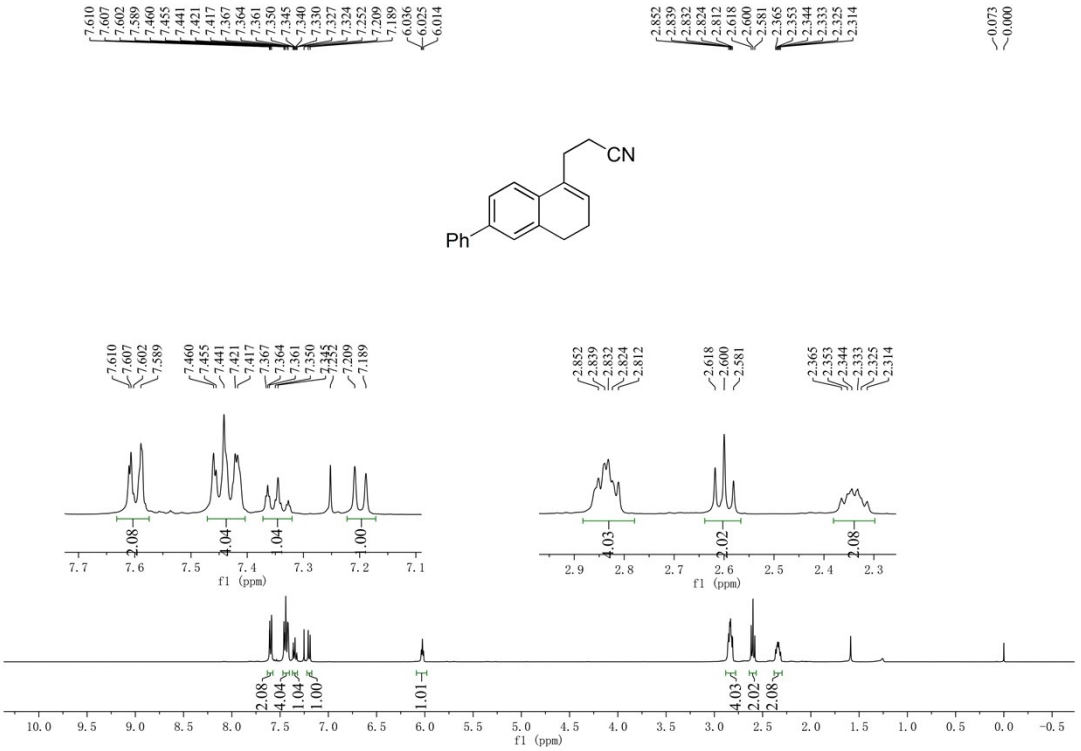


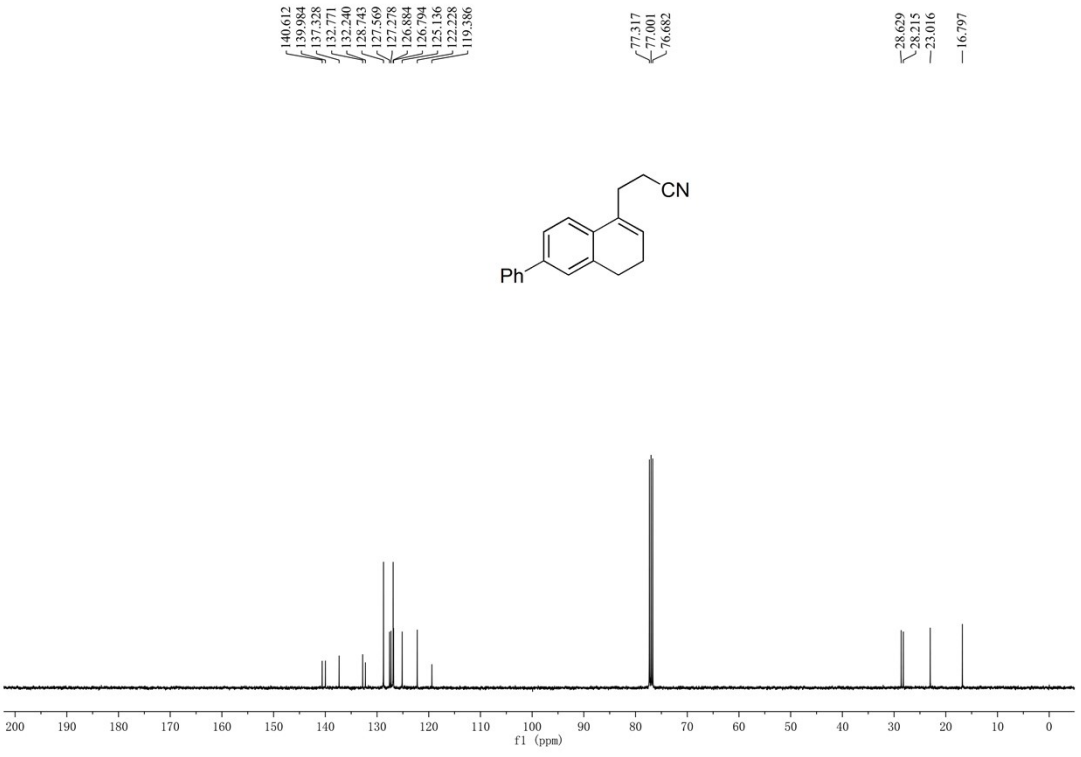
3-(6-(*tert*-Butyl)-3,4-dihydronaphthalen-1-yl)propanenitrile (3ea)



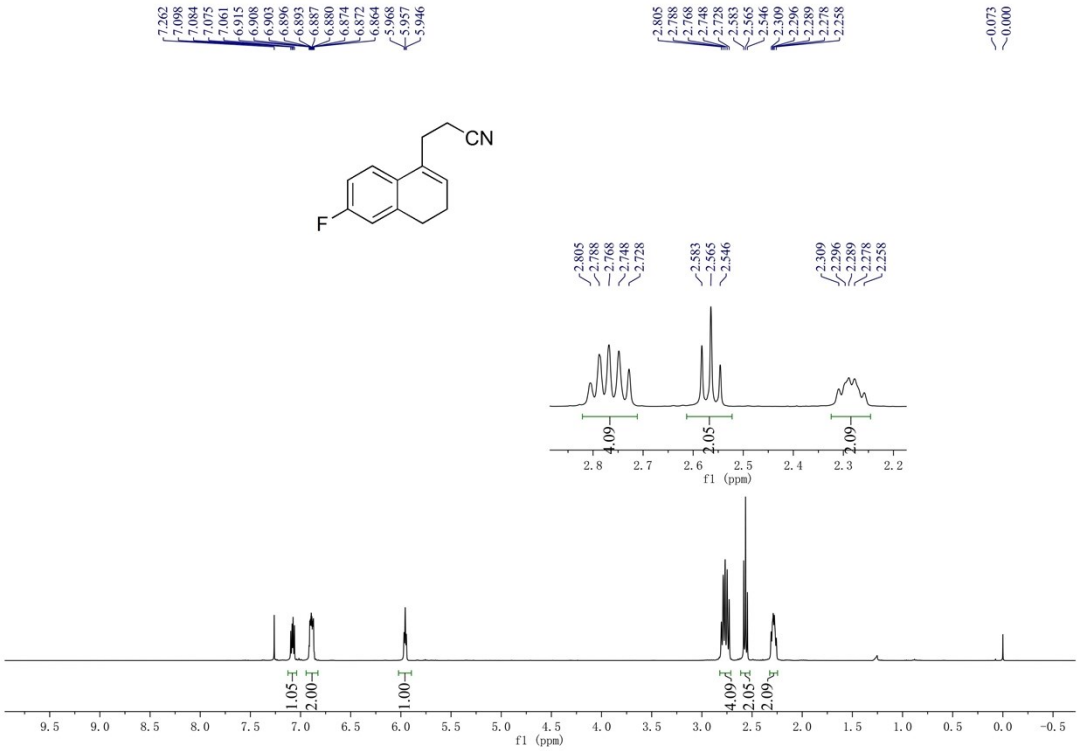


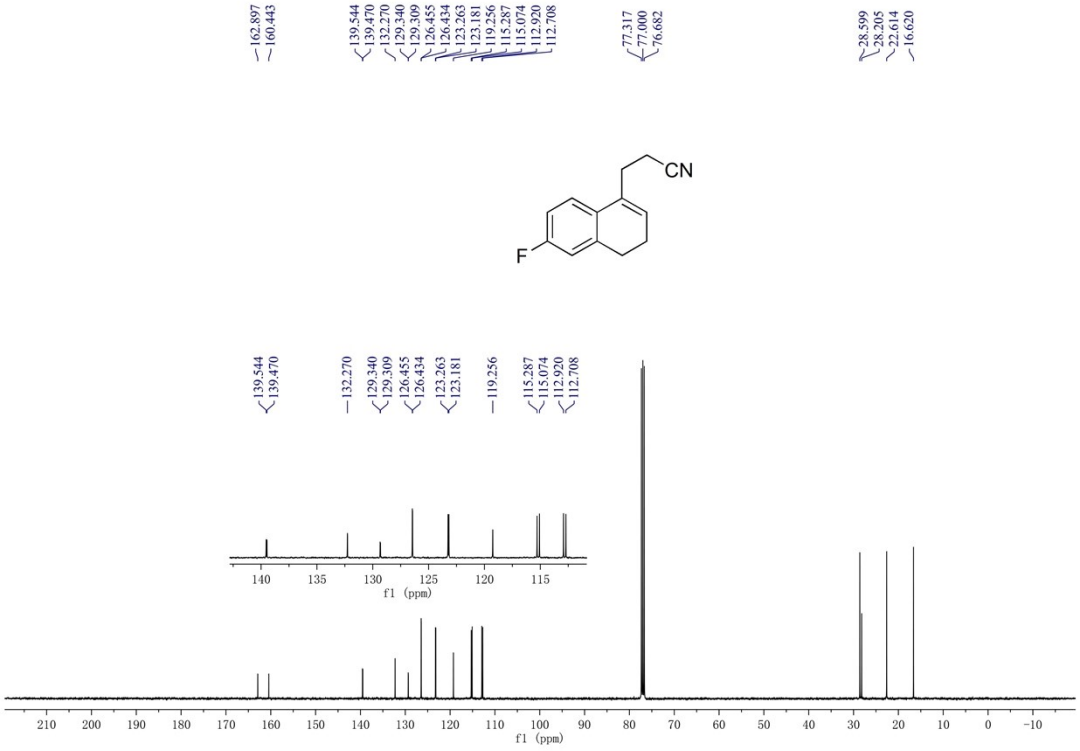
3-(6-Phenyl-3,4-dihydronaphthalen-1-yl)propanenitrile (3fa)

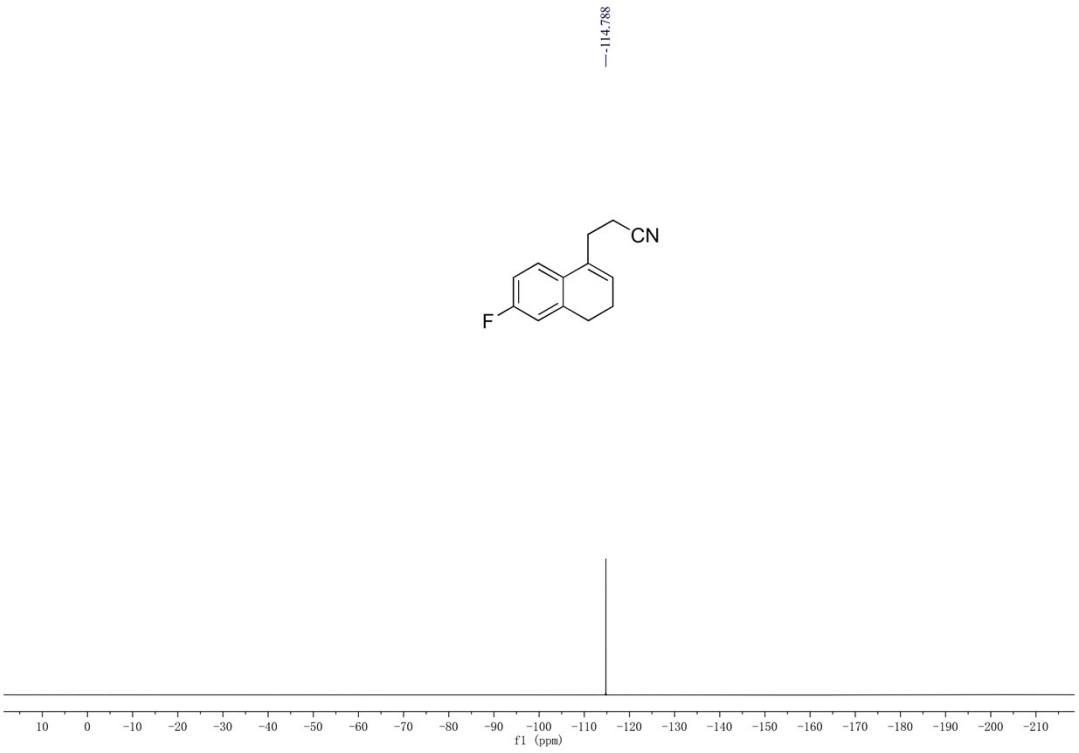




3-(6-Fluoro-3,4-dihydronaphthalen-1-yl)propanenitrile (3ga)



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CN
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-10
-20
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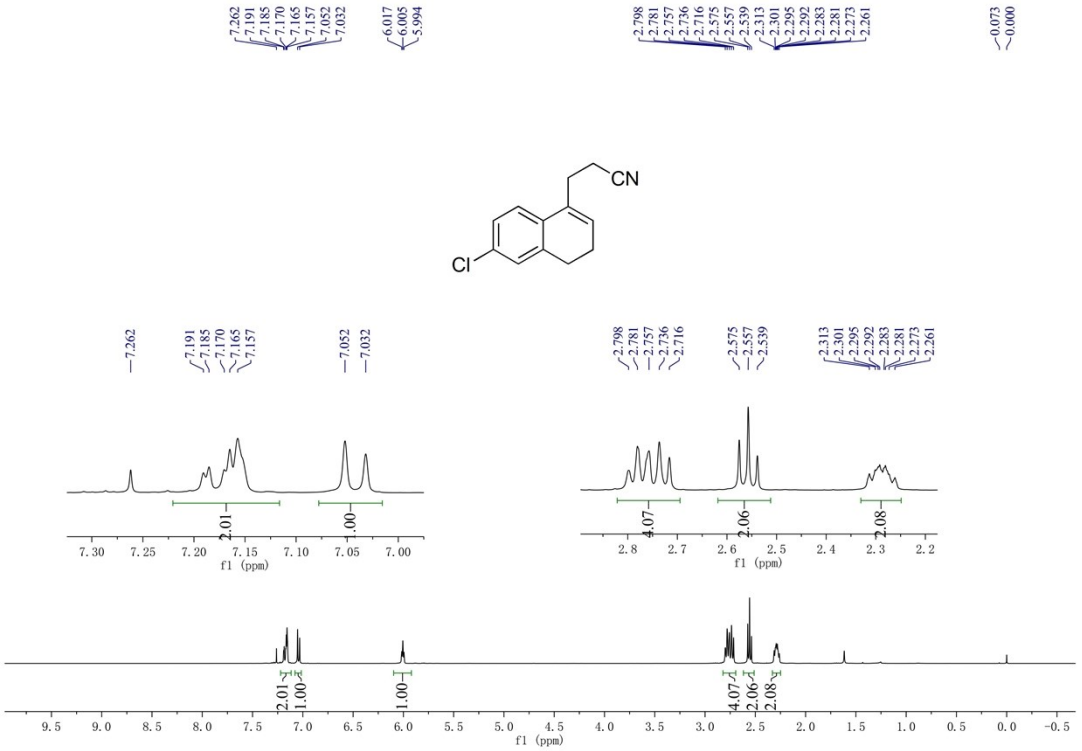
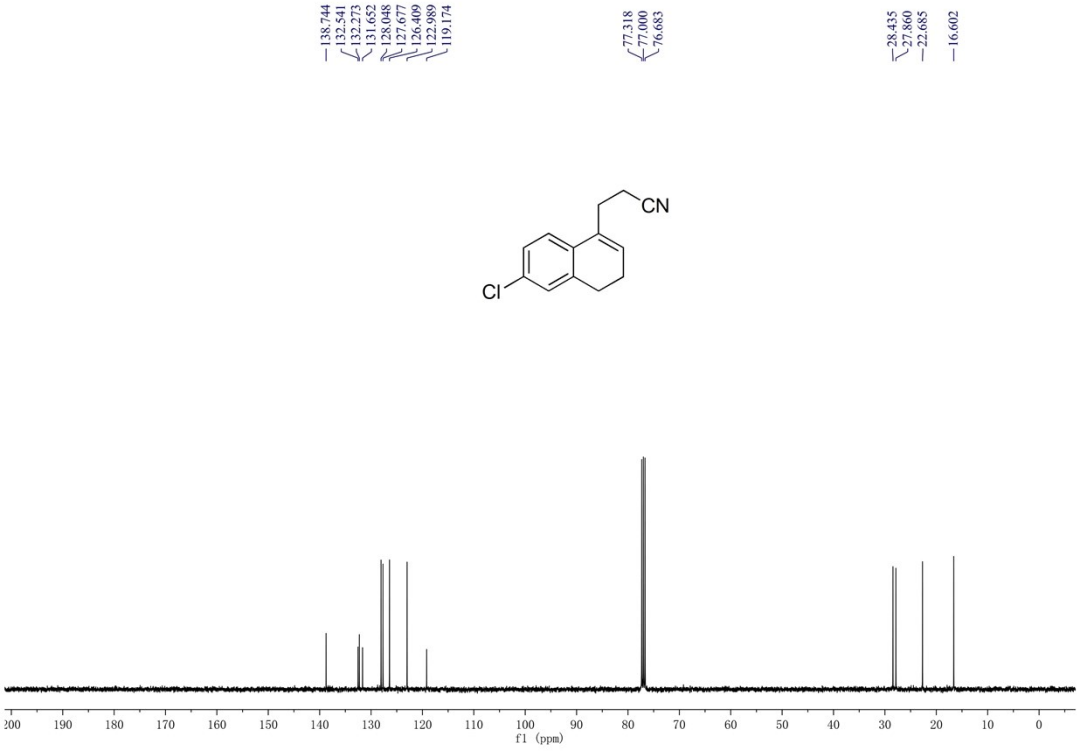
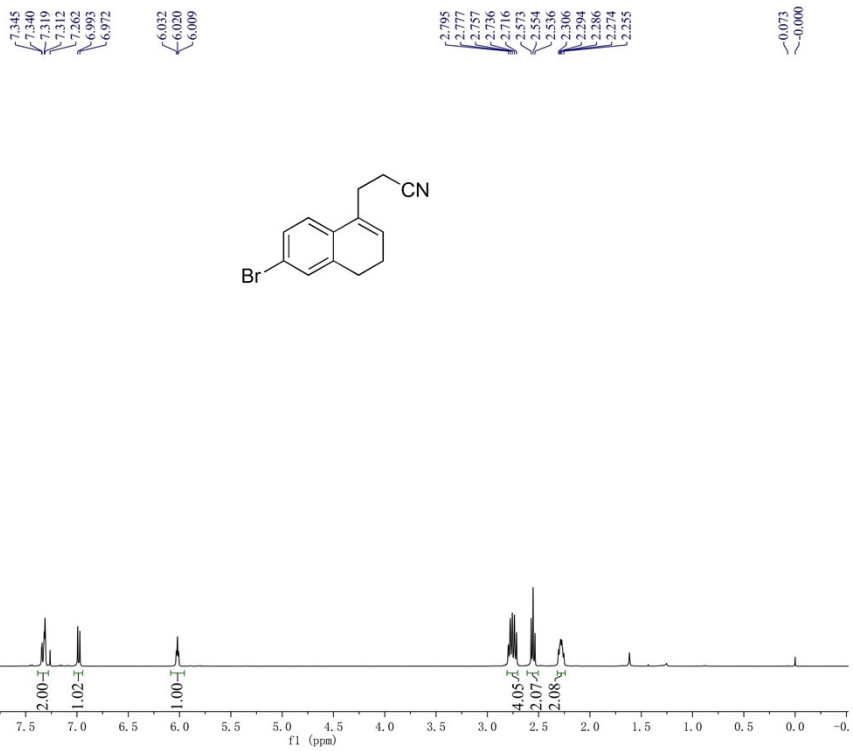
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

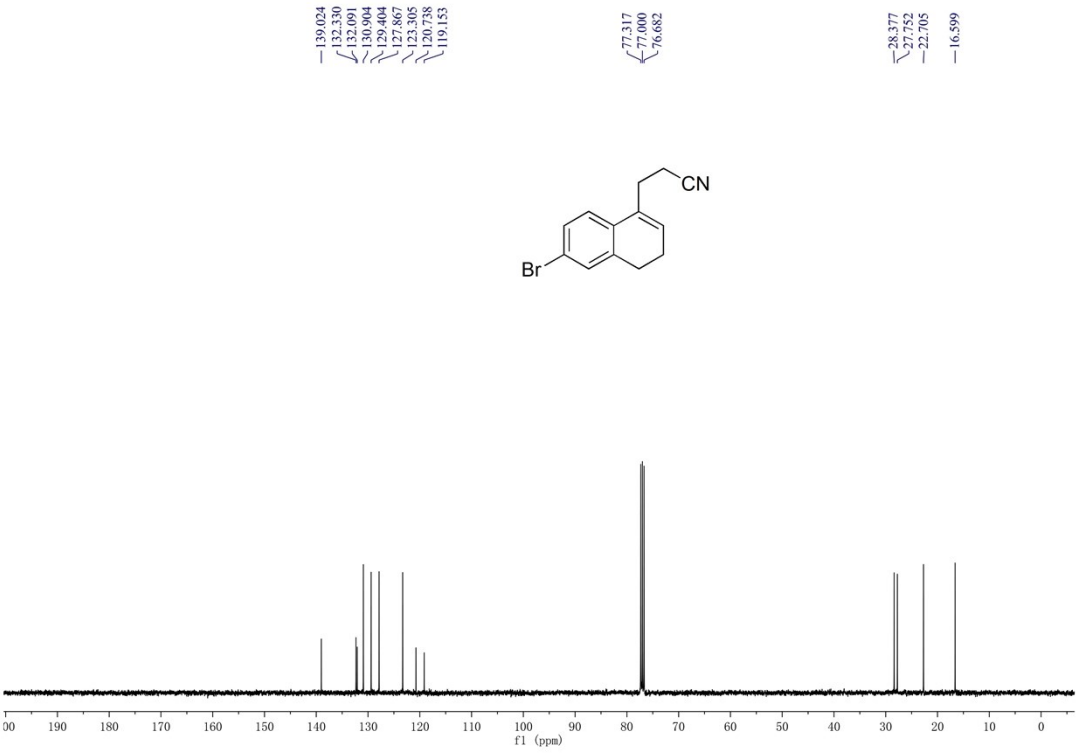
3-(6-Chloro-3,4-dihydronaphthalen-1-yl)propanenitrile (3ha)



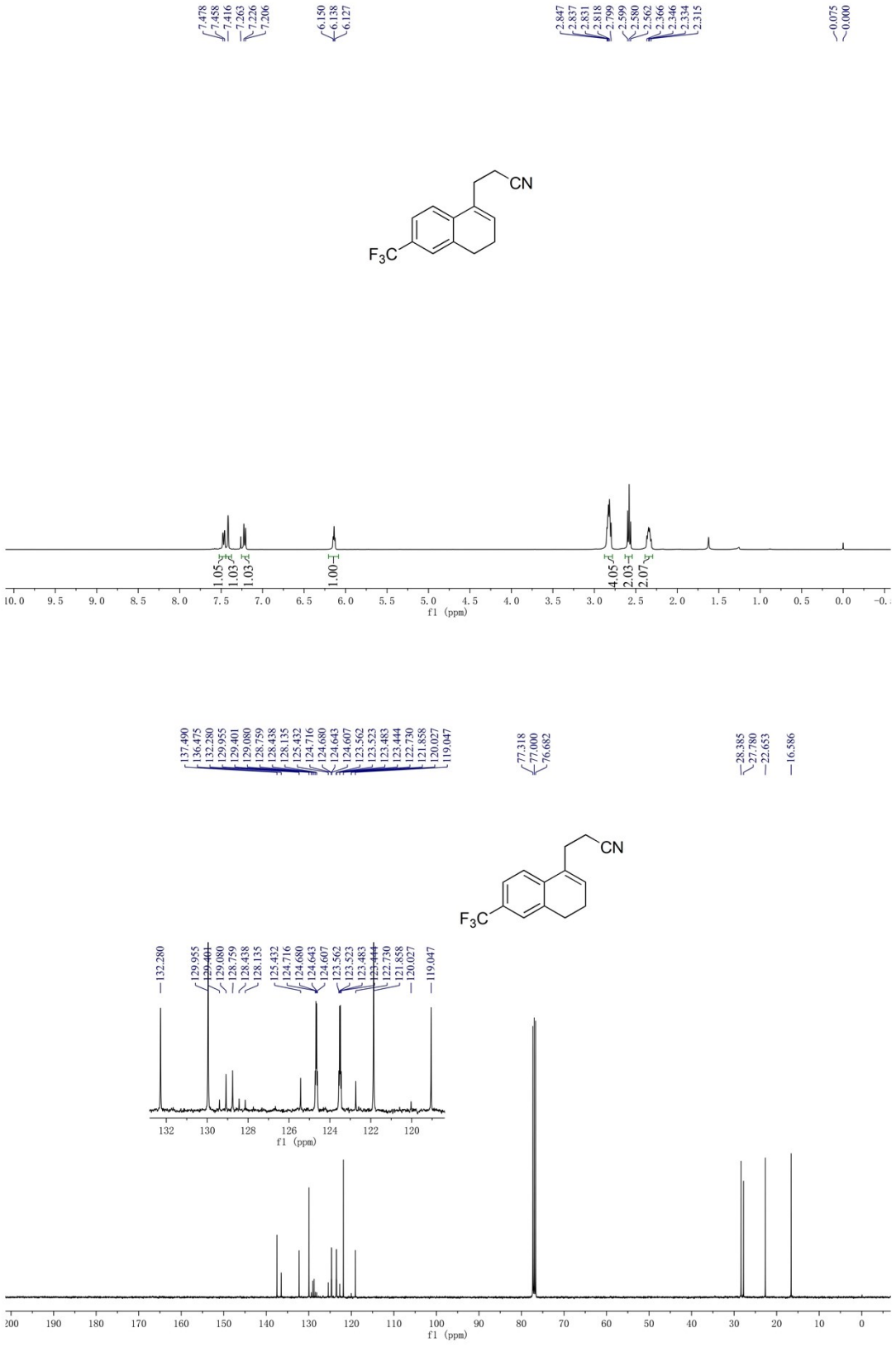


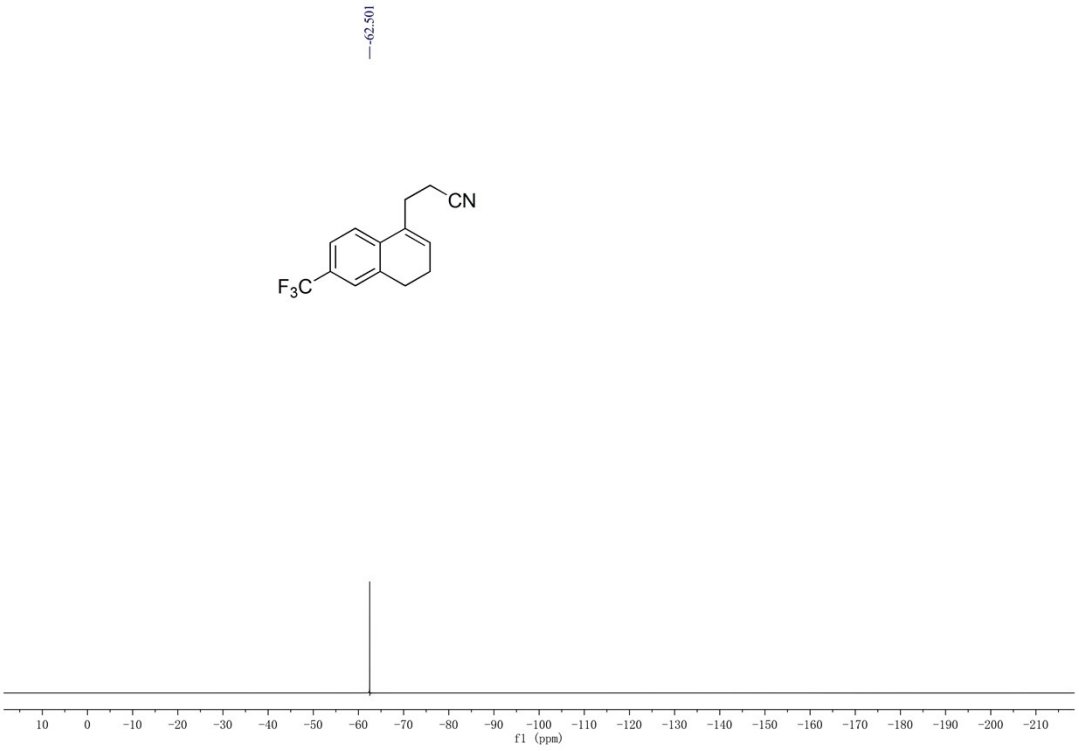
3-(6-Bromo-3,4-dihydronaphthalen-1-yl)propanenitrile (3ia)





3-(6-(Trifluoromethyl)-3,4-dihydronaphthalen-1-yl)propanenitrile (3ja)

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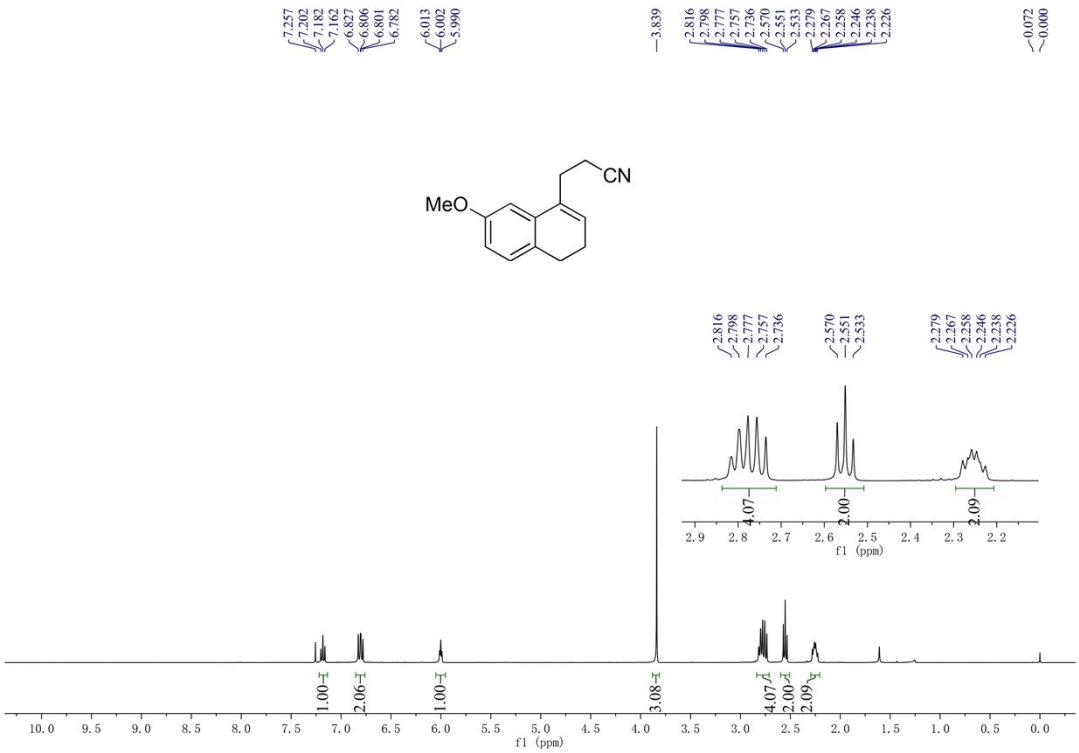
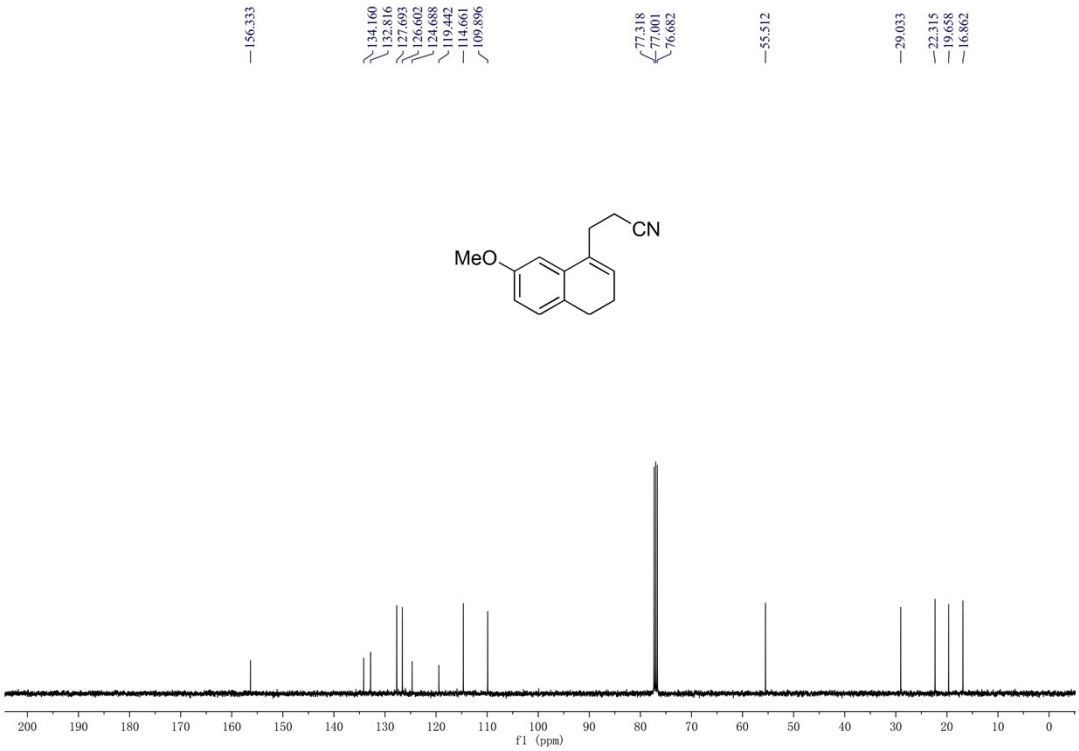
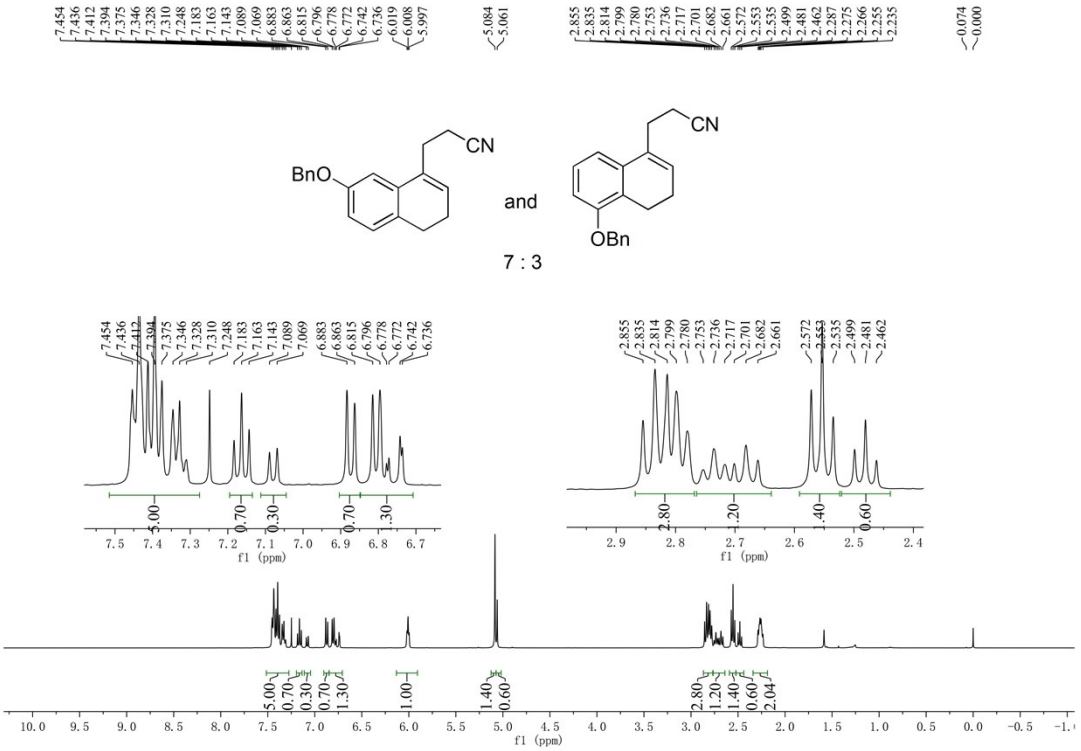
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

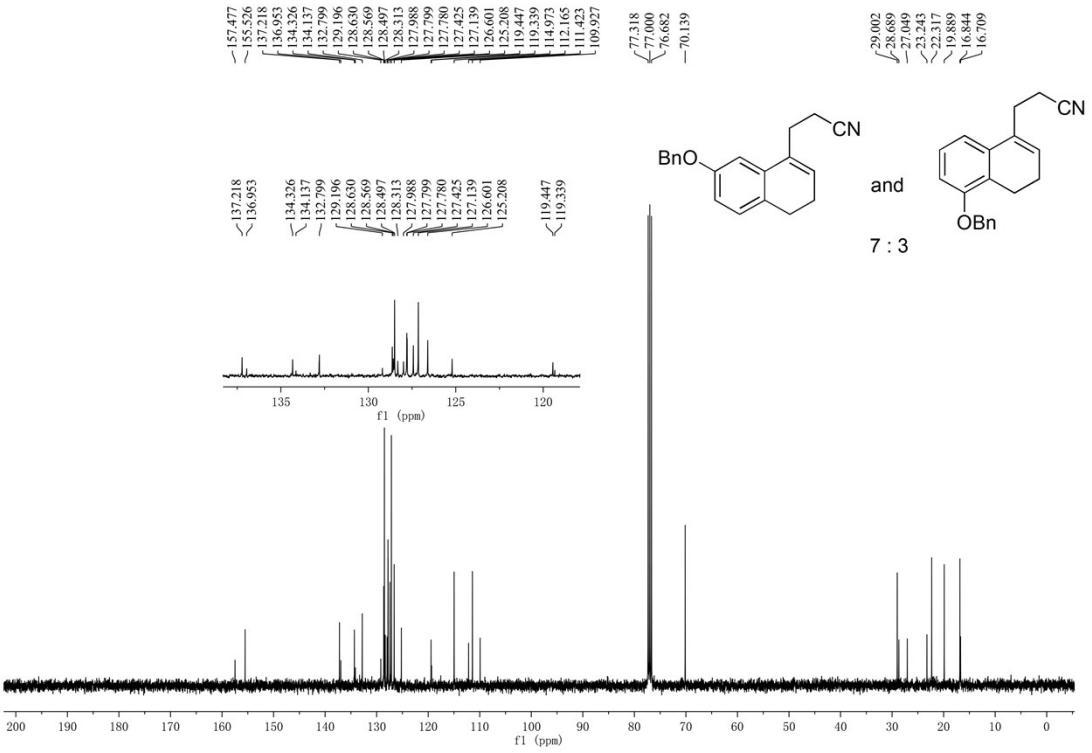
3-(7-Methoxy-3,4-dihydronaphthalen-1-yl)propanenitrile (3ka)



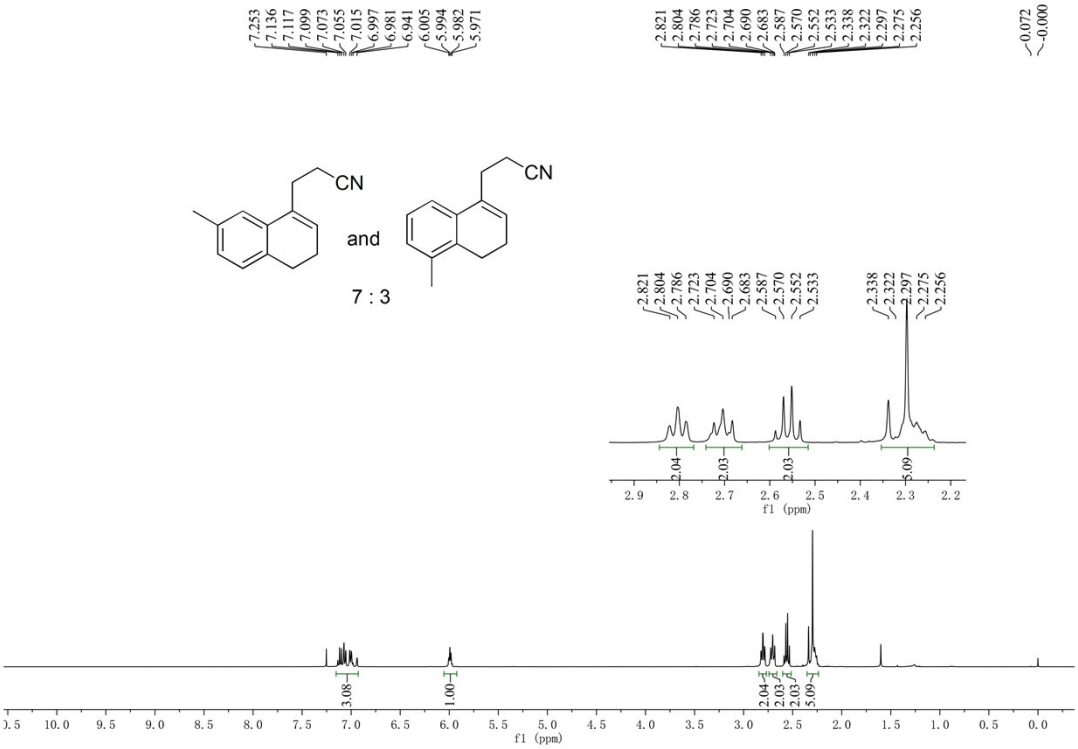


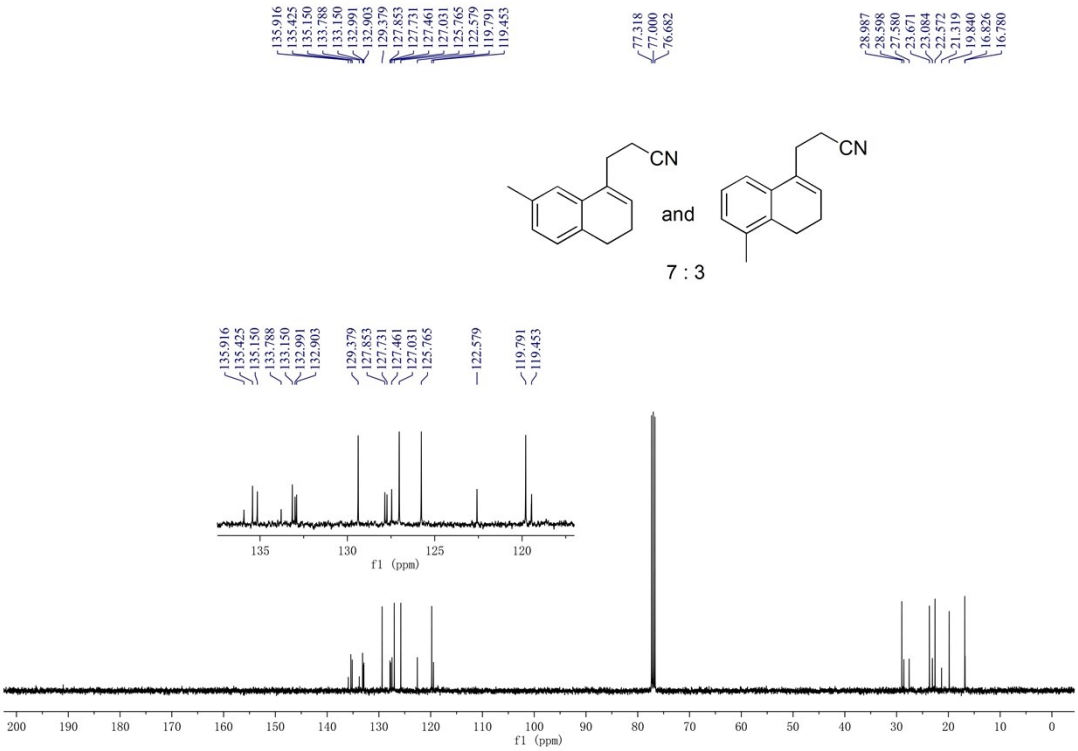
3-(7-Bbenzyloxy)-3,4-dihydronaphthalen-1-yl)propanenitrile (3la) and 3-(5-(benzyloxy)-3,4-dihydronaphthalen-1-yl)propanenitrile (3la')



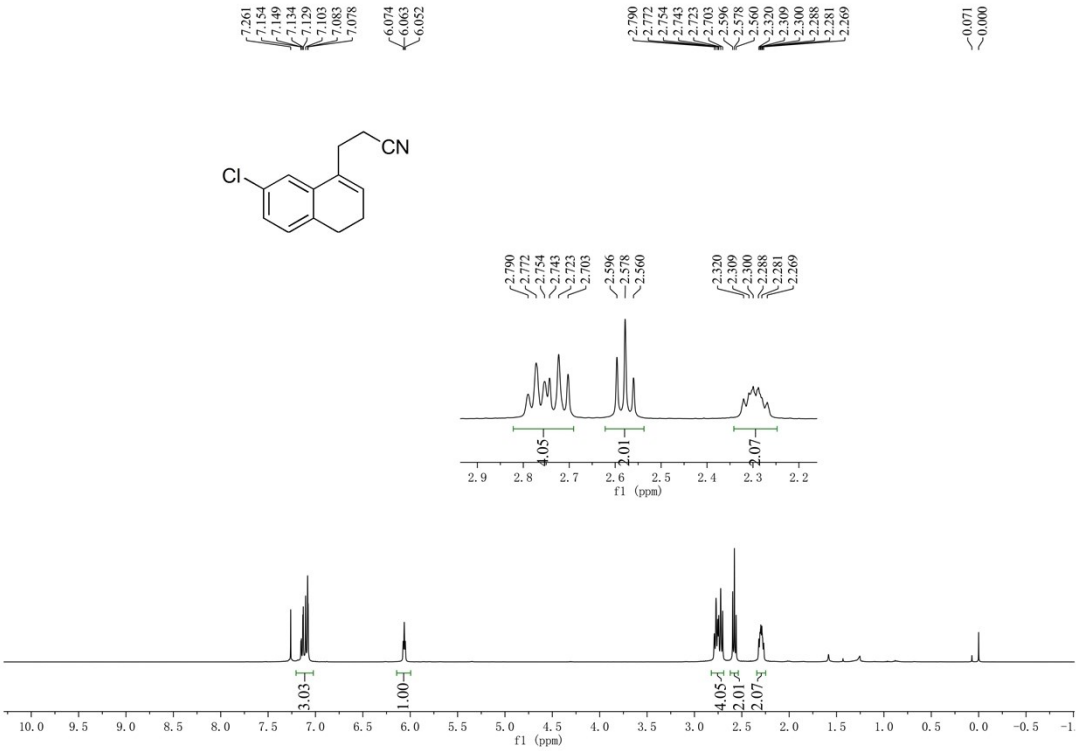


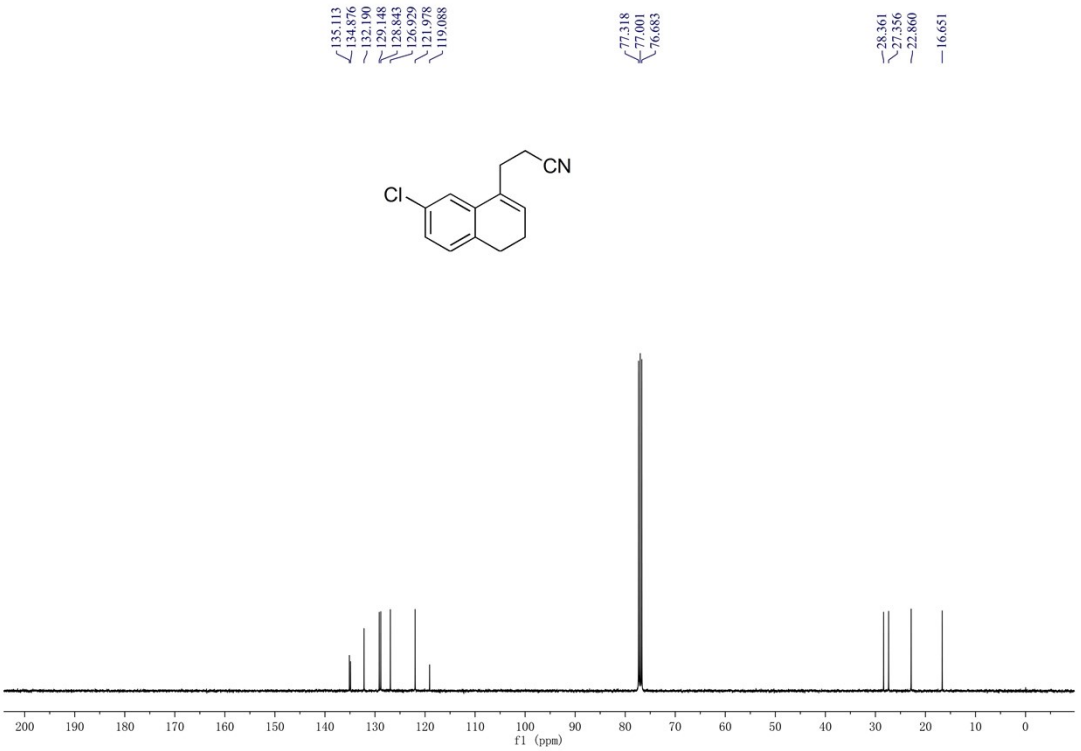
3-(7-Methyl-3,4-dihydronaphthalen-1-yl)propanenitrile (3ma) and 3-(5-methyl-3,4-dihydronaphthalen-1-yl)propanenitrile (3ma')



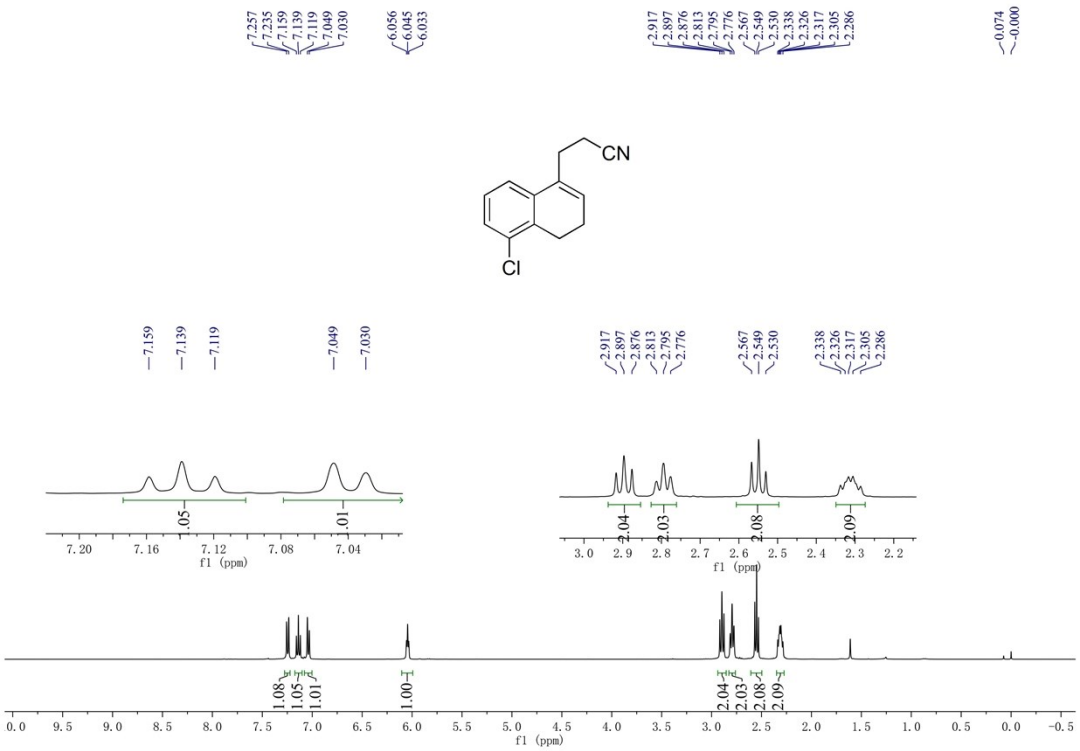


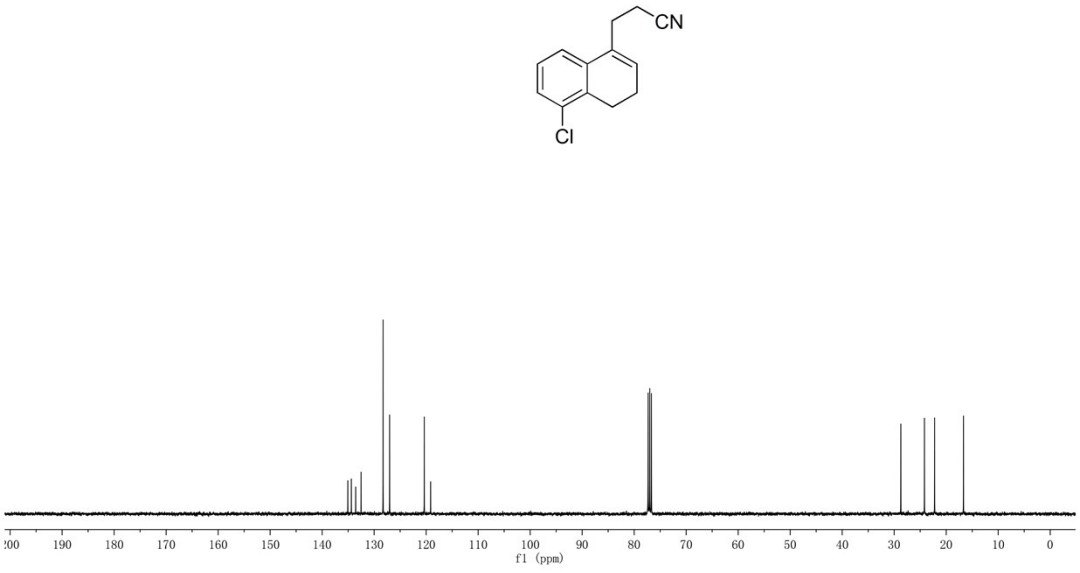
3-(7-Chloro-3,4-dihydronaphthalen-1-yl)propanenitrile (3na)



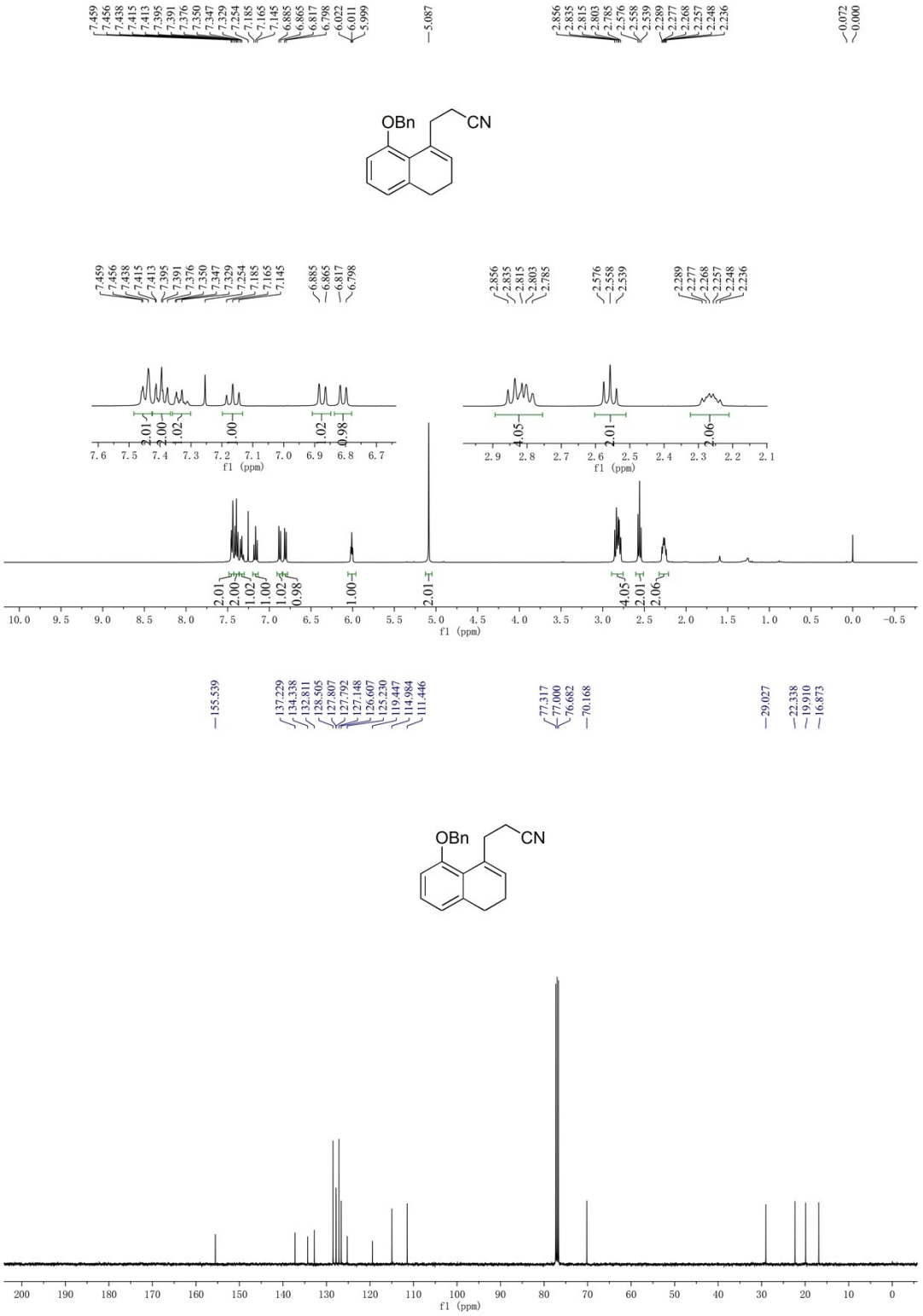


3-(5-Chloro-3,4-dihydronaphthalen-1-yl)propanenitrile (3na')

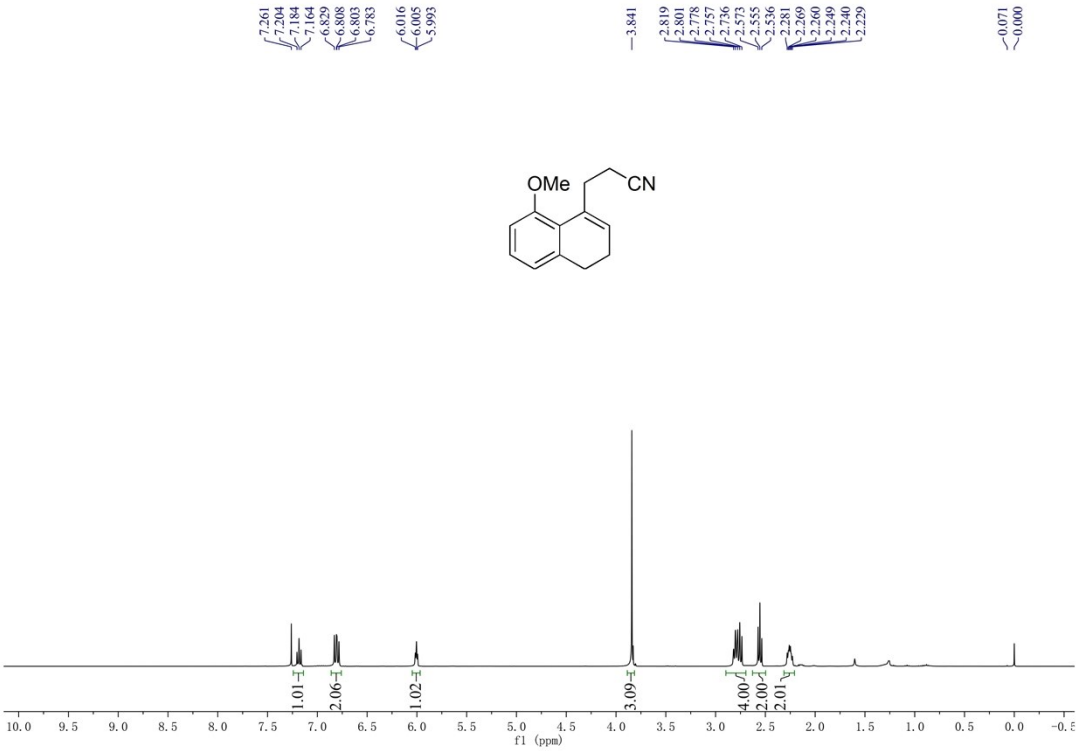


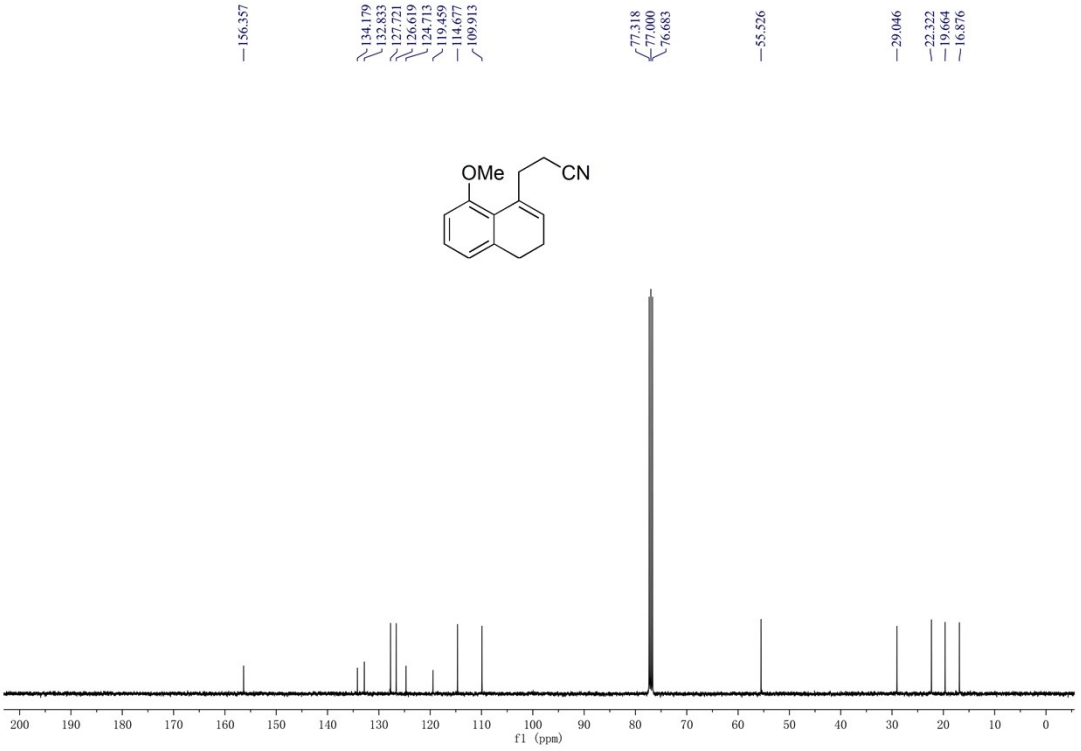


3-(8-(Benzyloxy)-3,4-dihydronaphthalen-1-yl)propanenitrile (3oa)

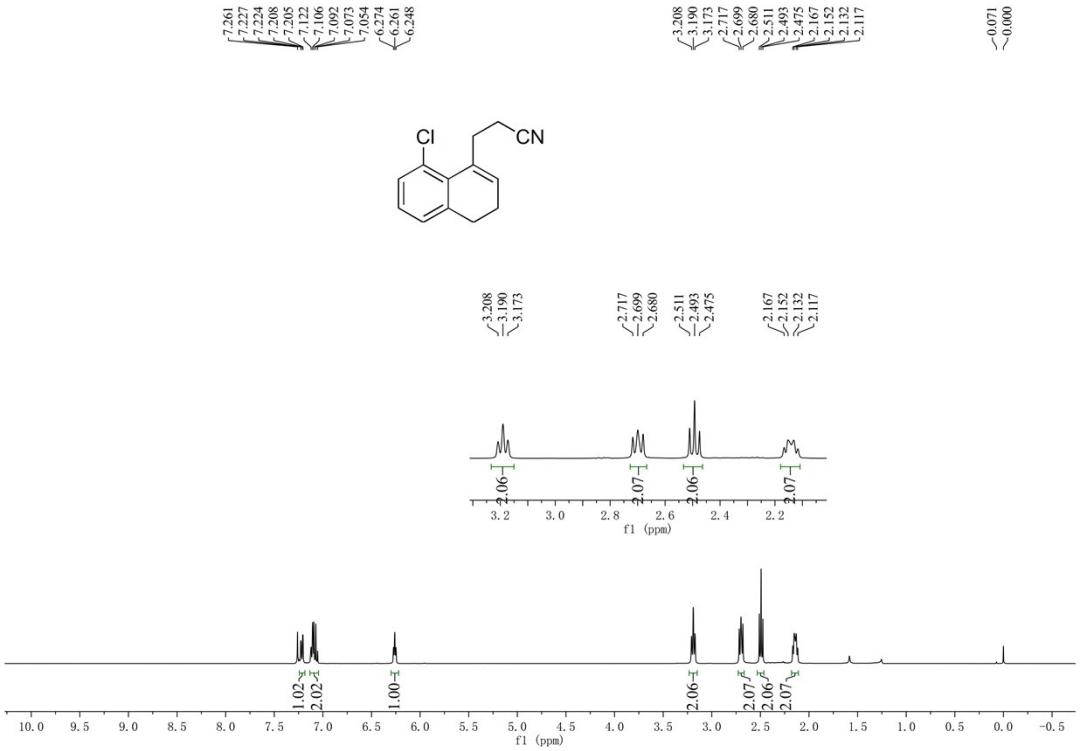


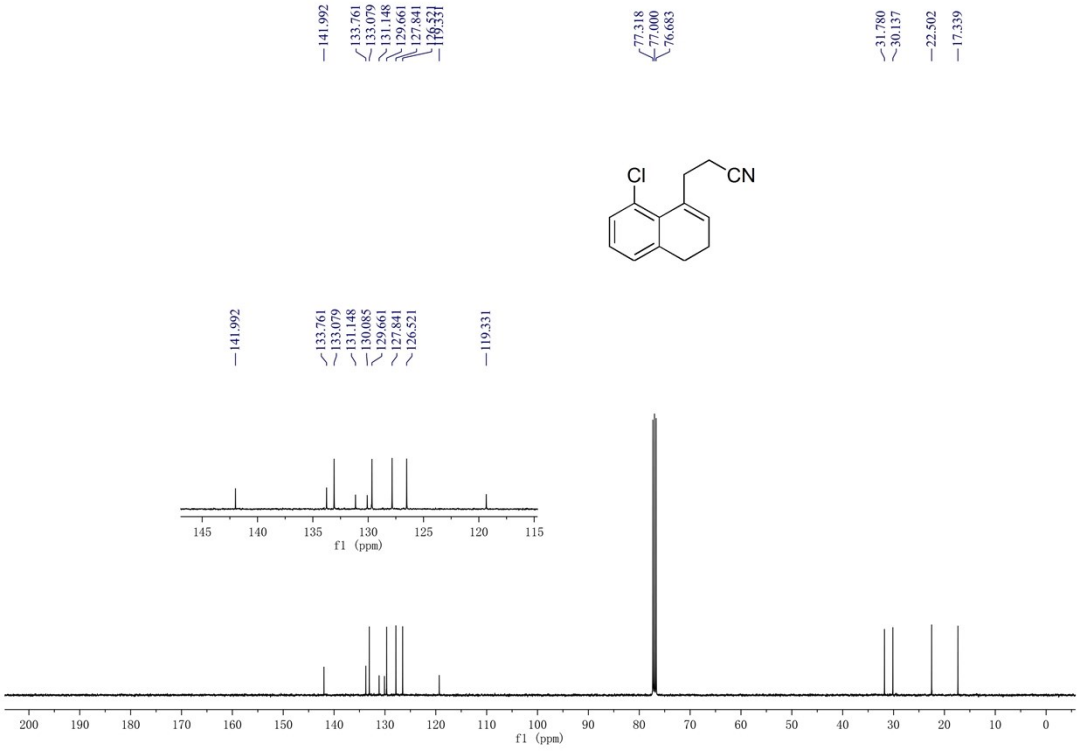
3-(8-Methoxy-3,4-dihydronaphthalen-1-yl)propanenitrile (3pa)



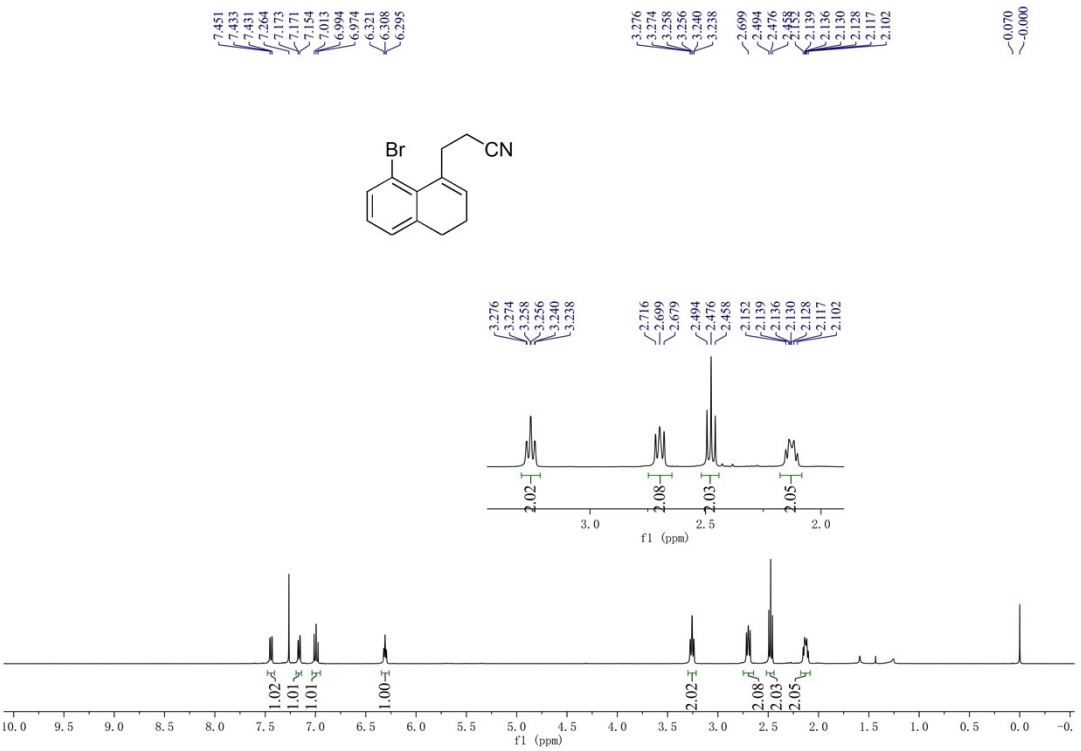


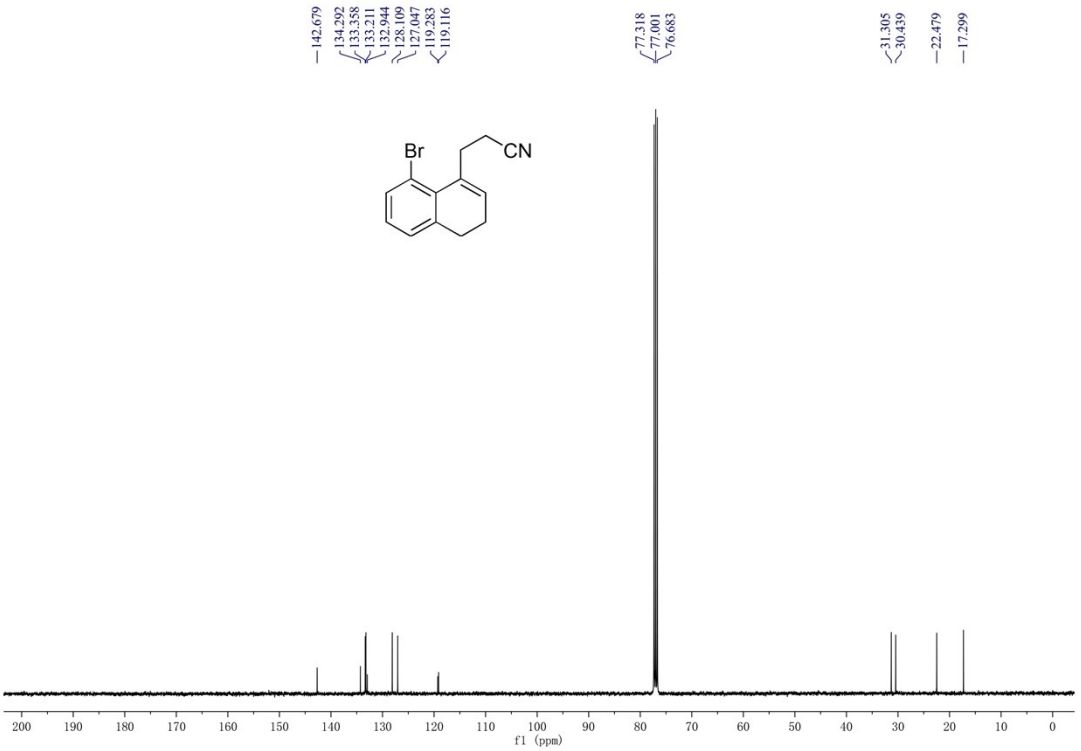
3-(8-Chloro-3,4-dihydronaphthalen-1-yl)propanenitrile (3qa)



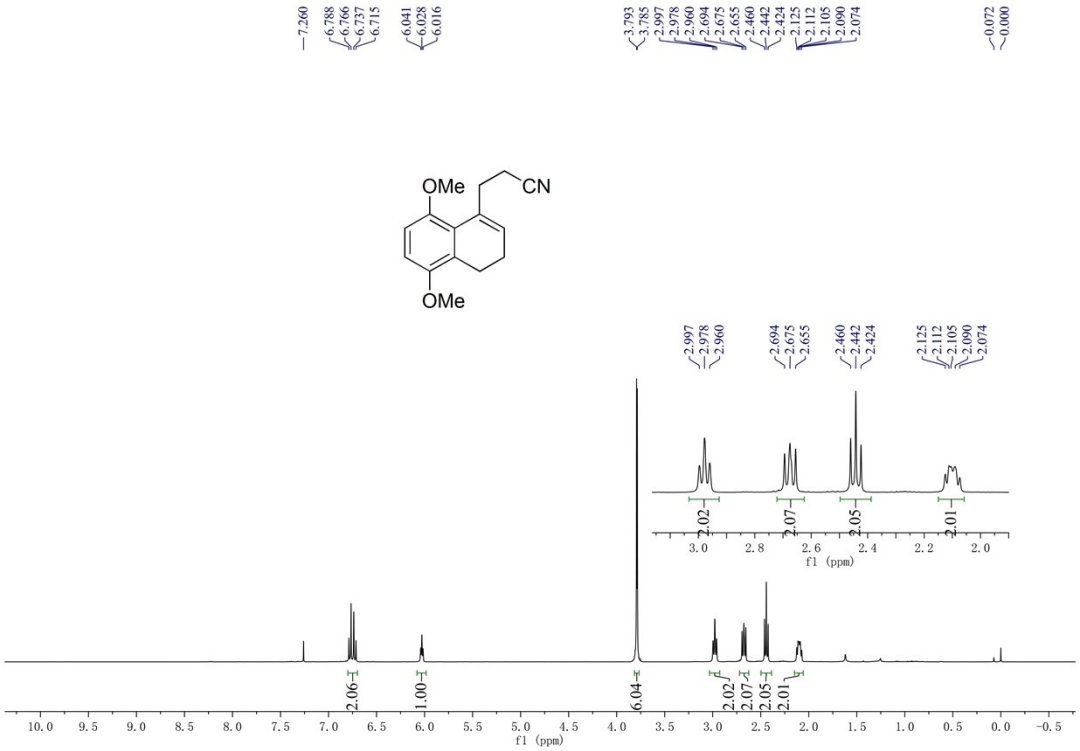


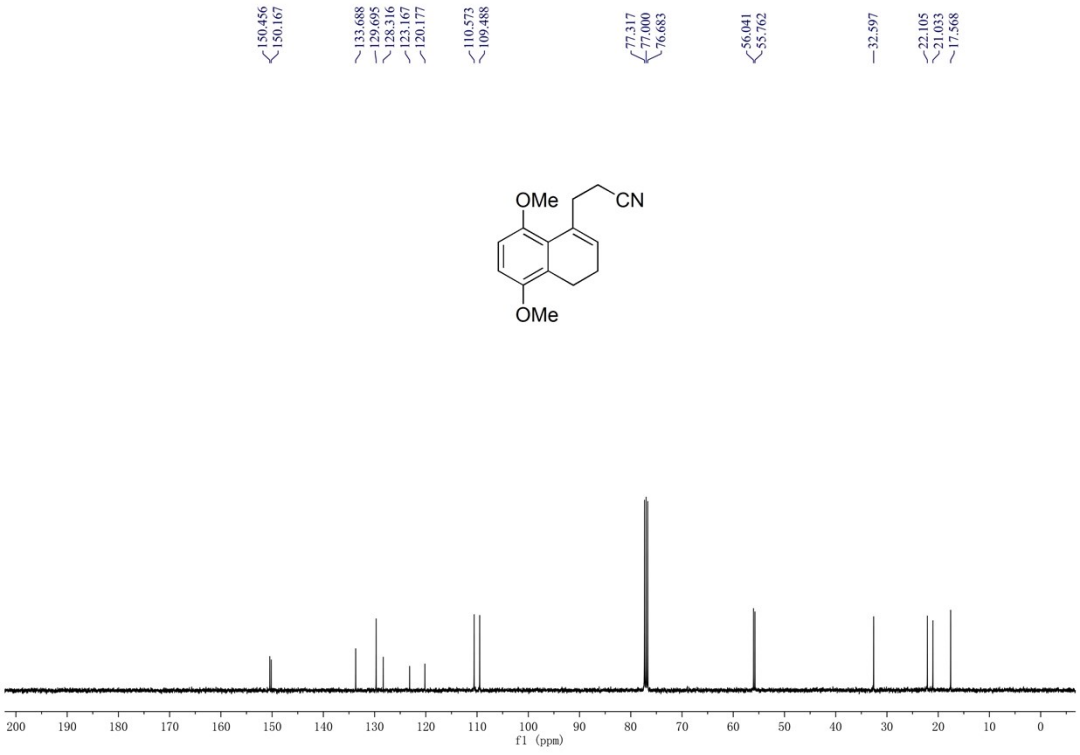
3-(8-Bromo-3,4-dihydronaphthalen-1-yl)propanenitrile (3ra)



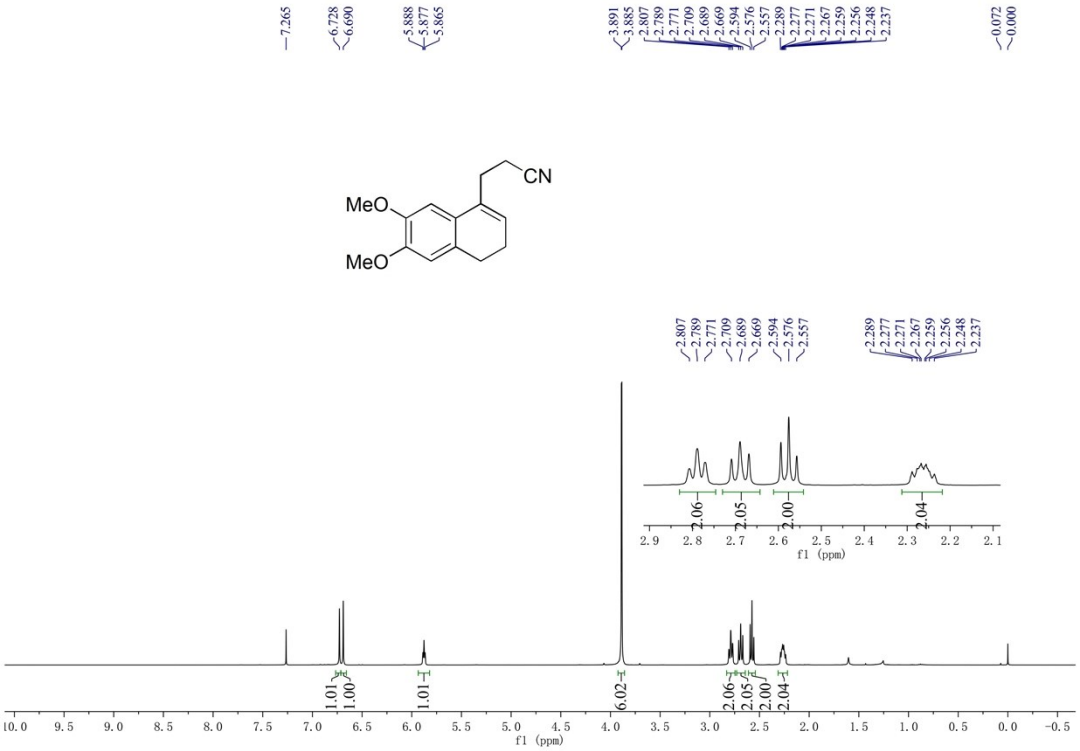


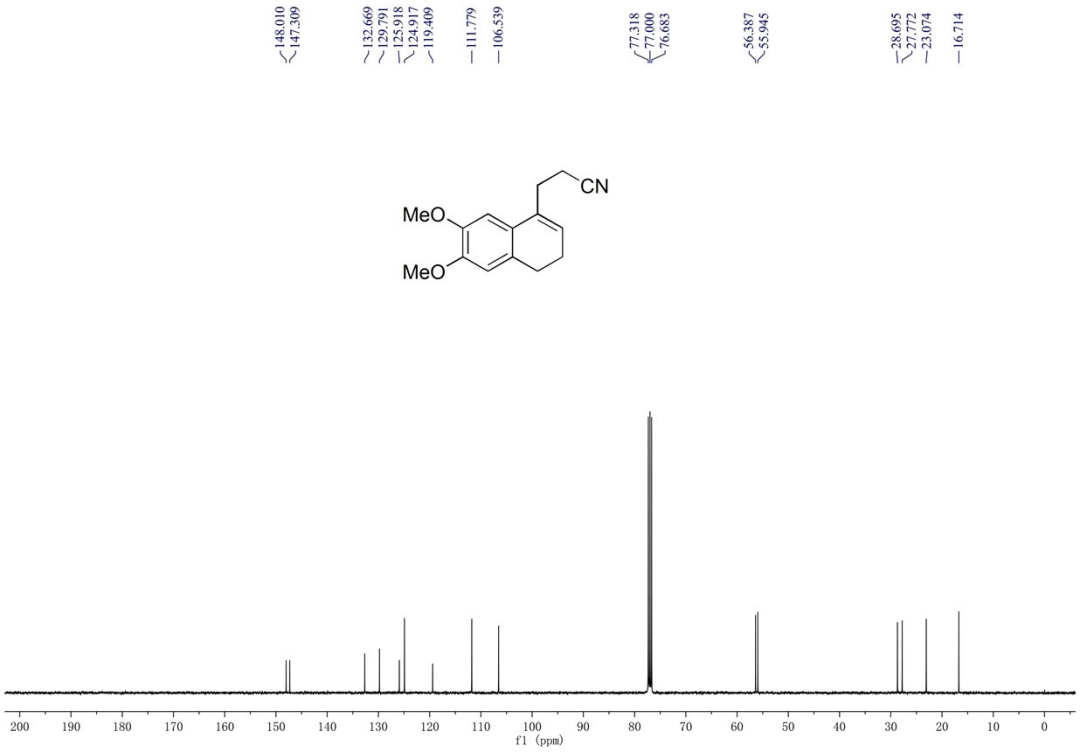
3-(5,8-Dimethoxy-3,4-dihydronaphthalen-1-yl)propanenitrile (3sa)



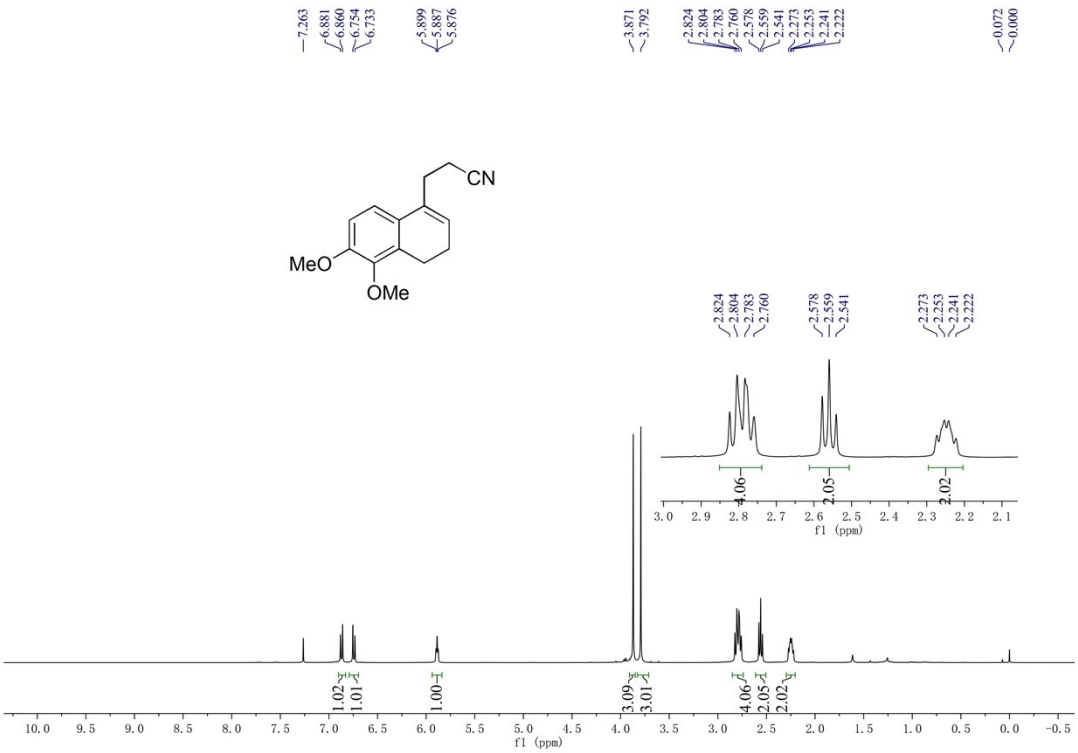


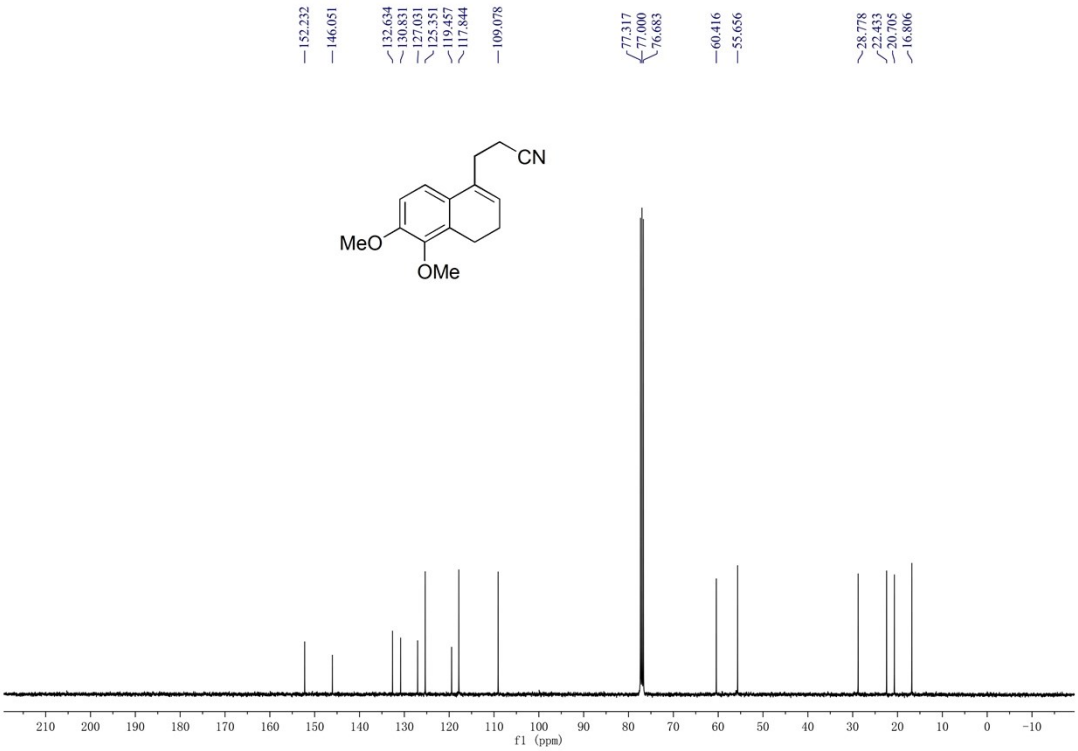
3-(5,6-Dimethoxy-3,4-dihydronaphthalen-1-yl)propanenitrile (3ta)



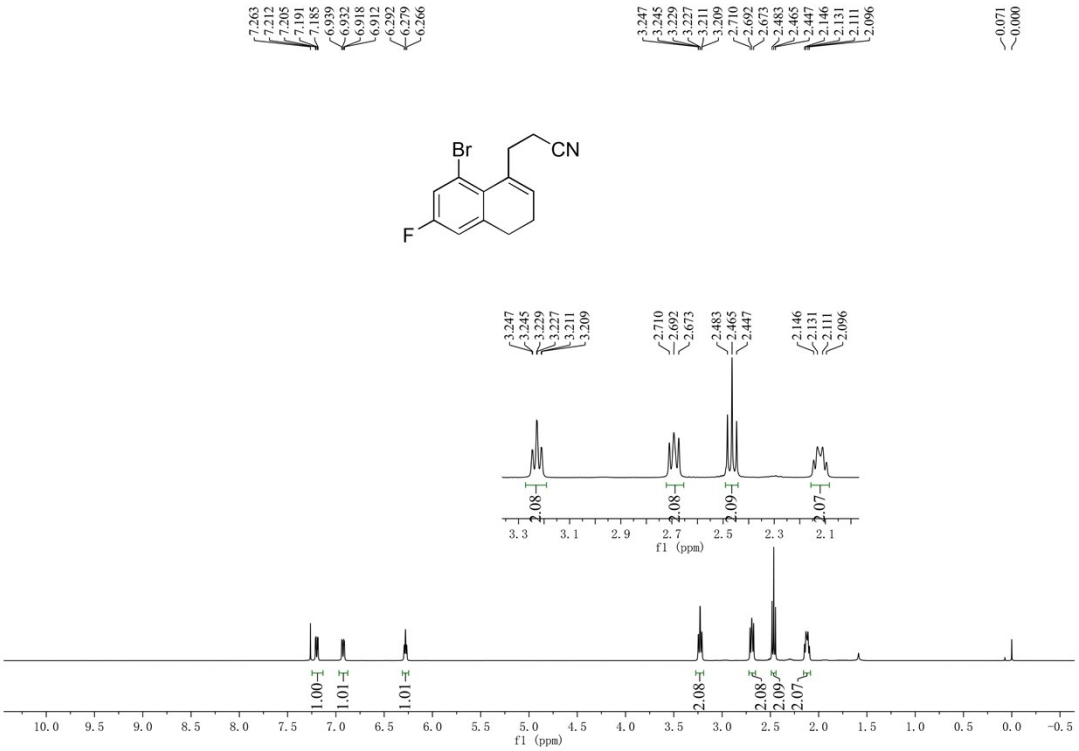


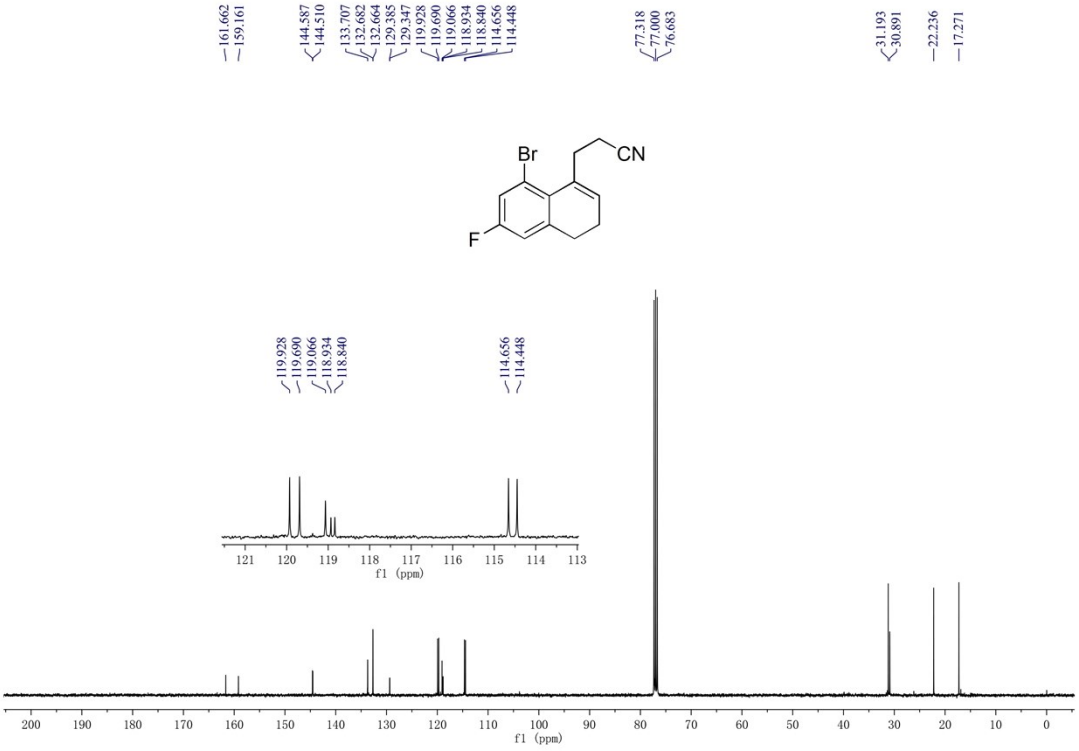
3-(6,7-Dimethoxy-3,4-dihydronaphthalen-1-yl)propanenitrile (3ta')

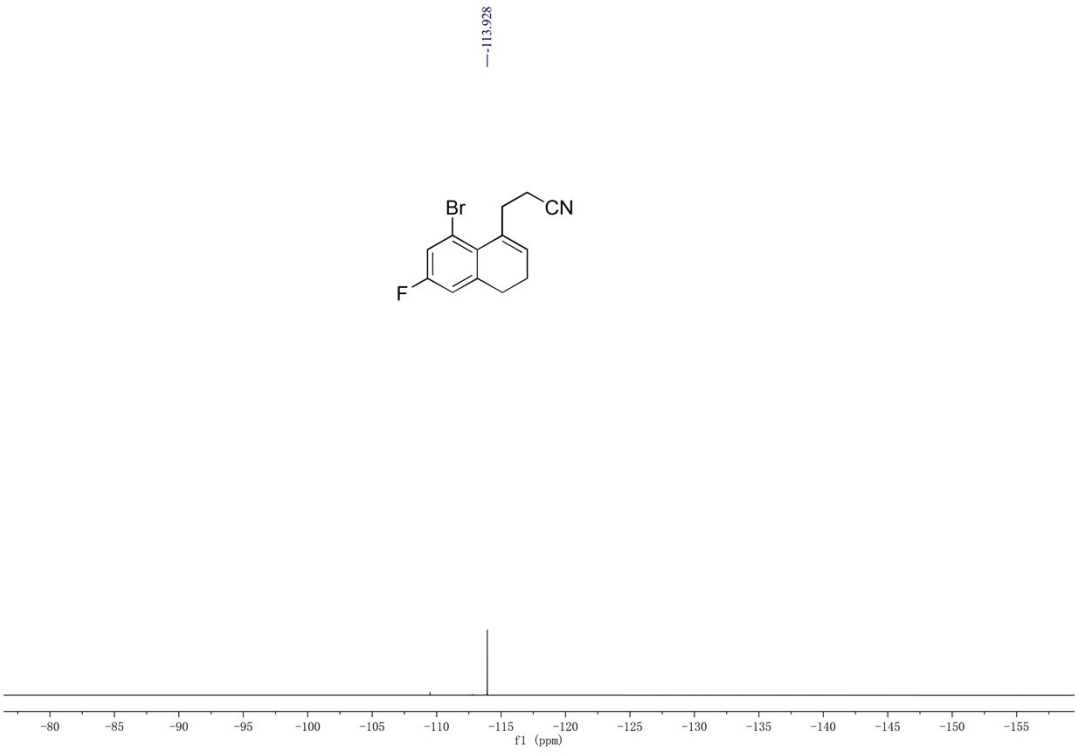




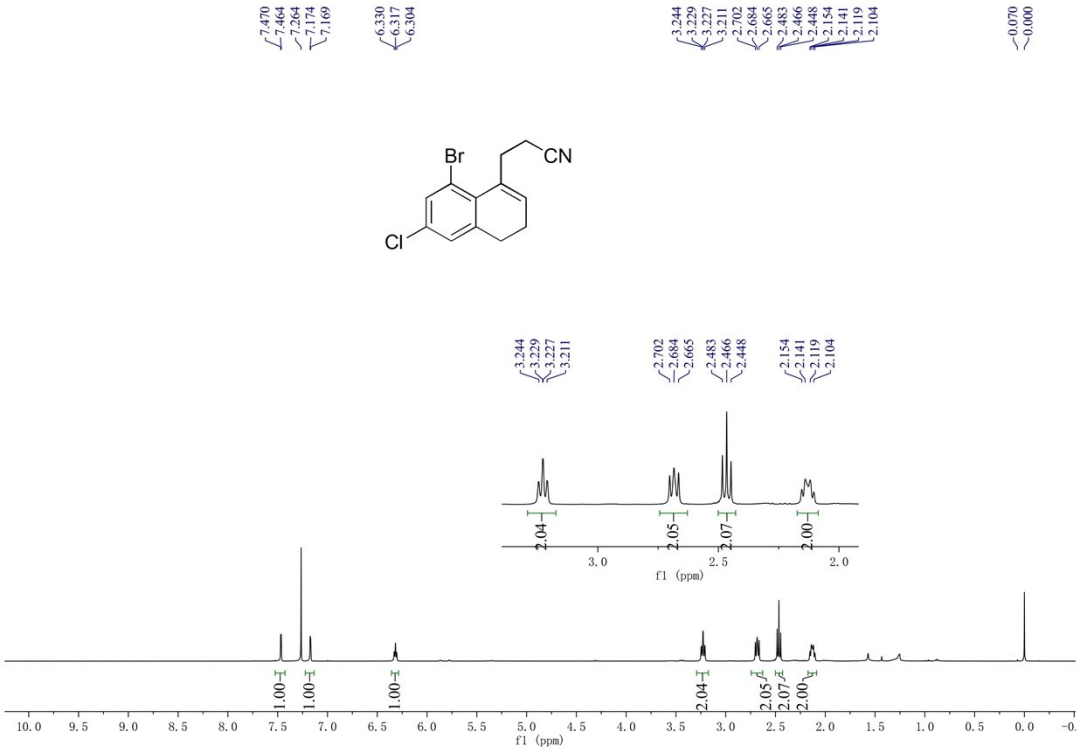
3-(8-Bromo-6-fluoro-3,4-dihydronaphthalen-1-yl)propanenitrile (3ua)

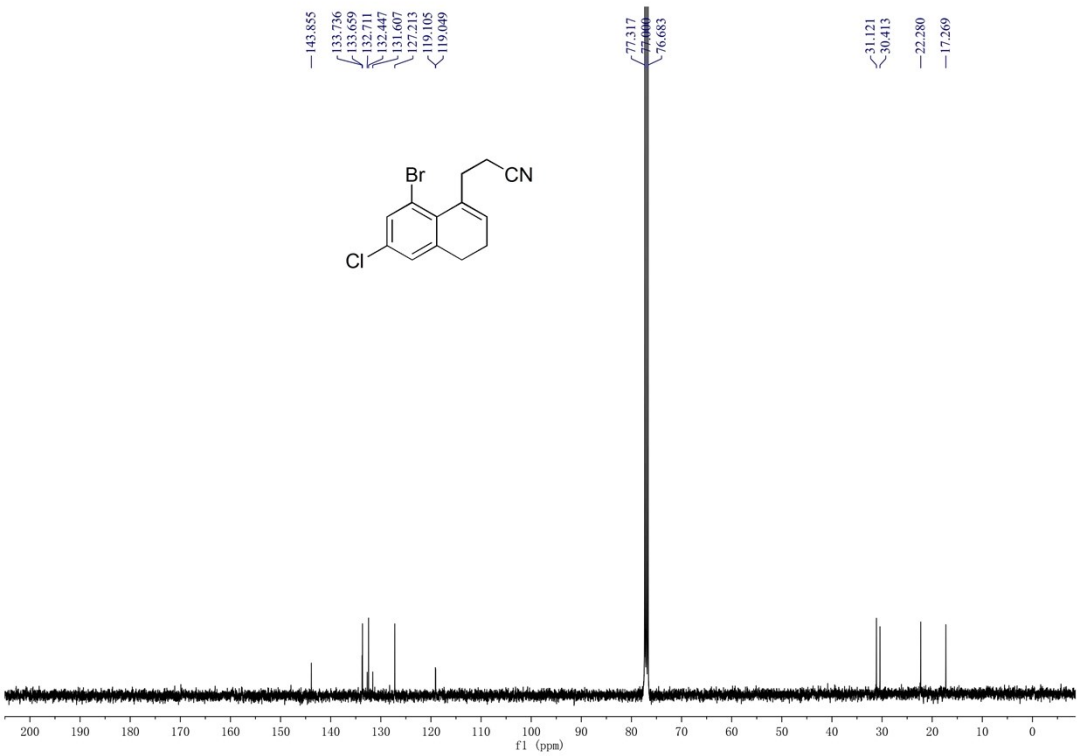




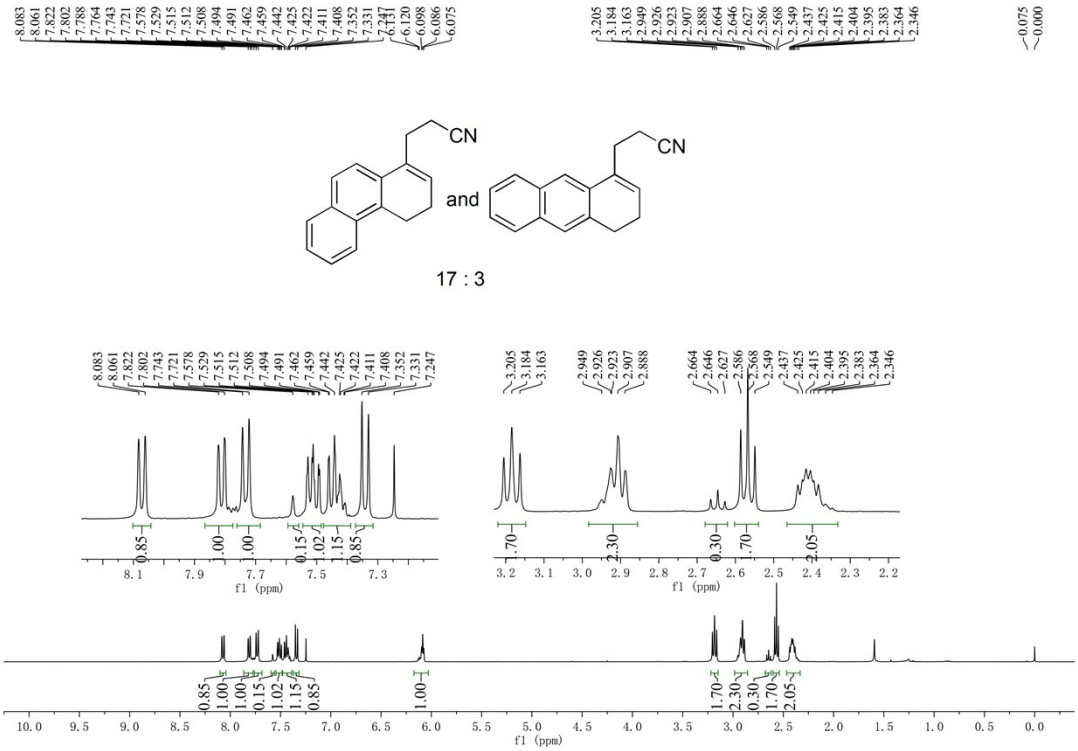

-113.928
Br
CN
F
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
f1 (ppm)

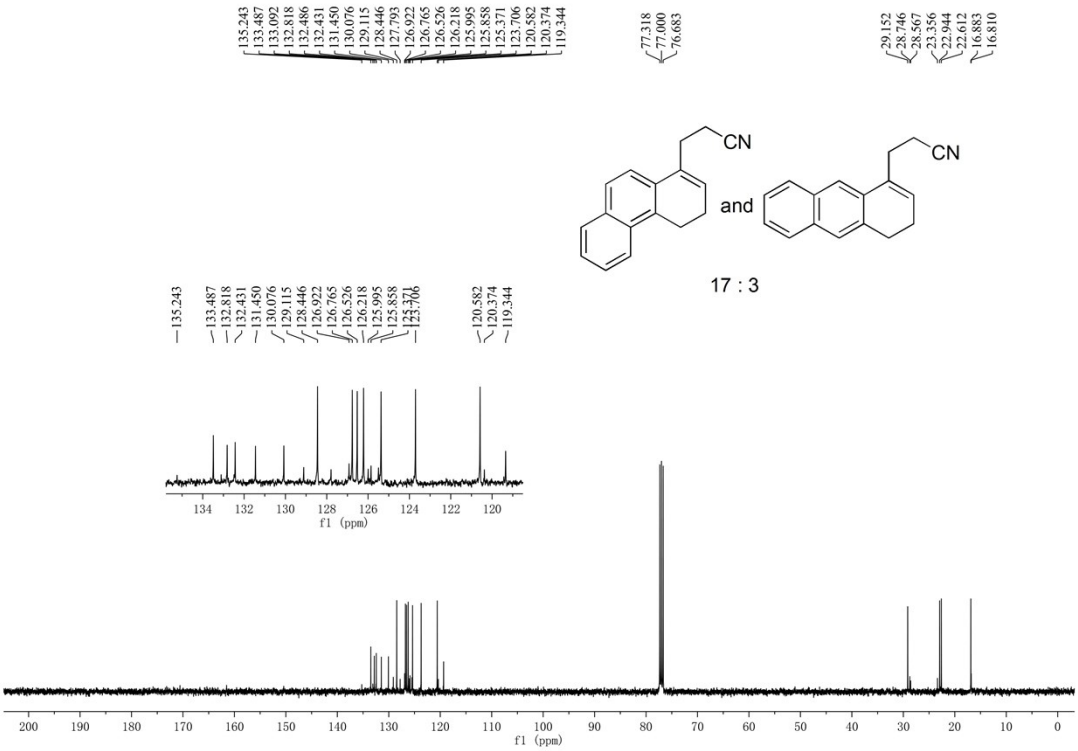
3-(8-Bromo-6-chloro-3,4-dihydronaphthalen-1-yl)propanenitrile (3va)



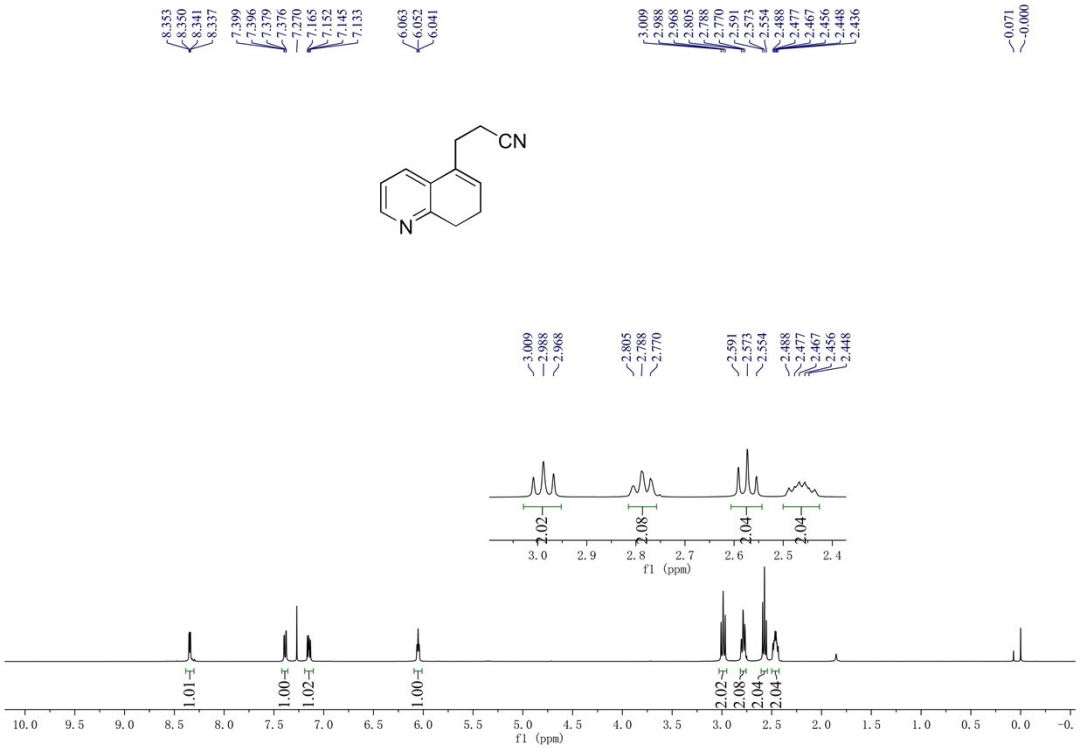


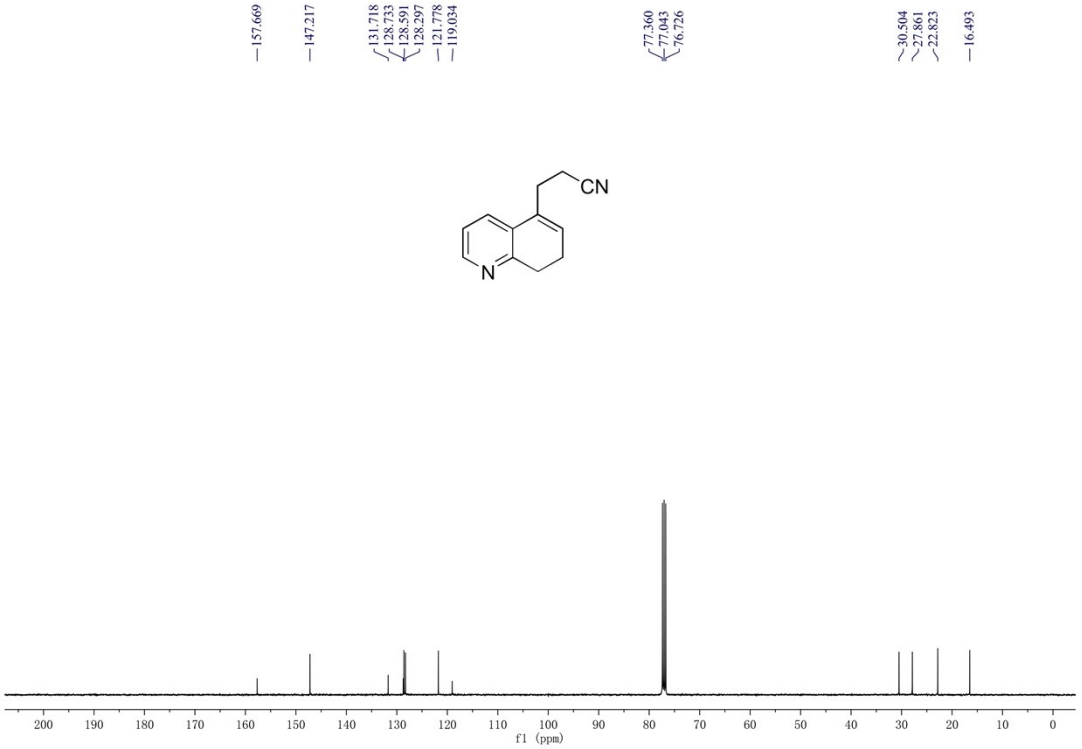
3-(3,4-dihydrophenanthren-1-yl)propanenitrile (3wa) and 3-(3,4-dihydroanthracen-1-yl)propanenitrile (3wa')



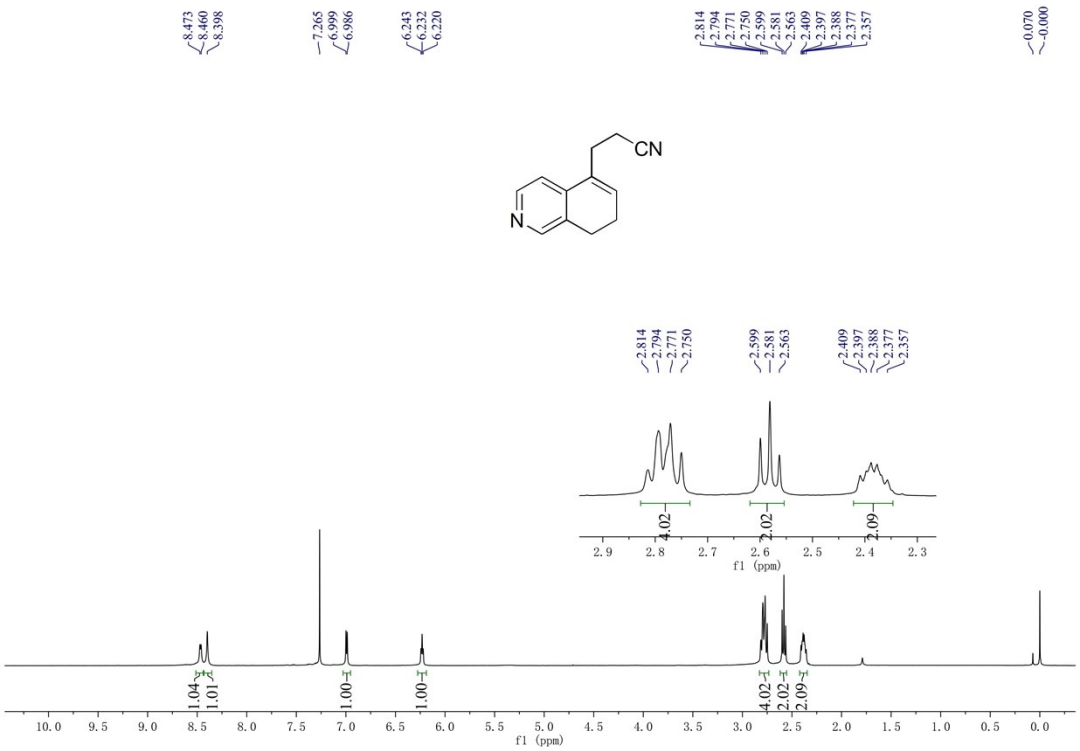


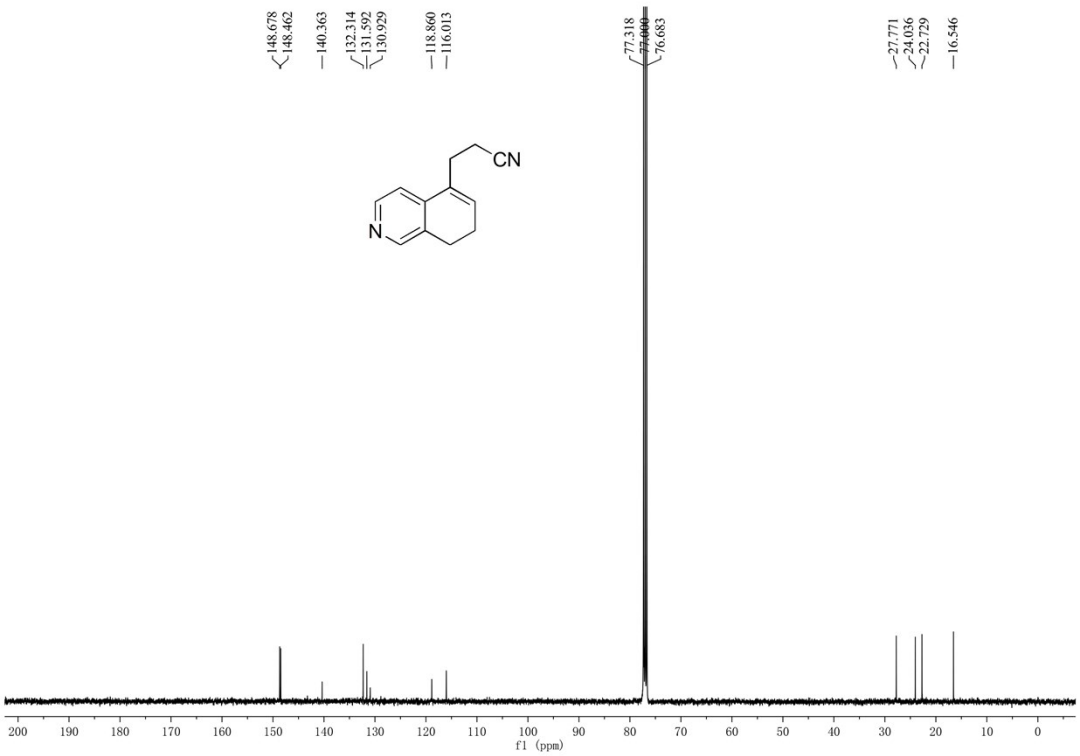
3-(5,6-Dihydroisoquinolin-8-yl)propanenitrile (3xa)



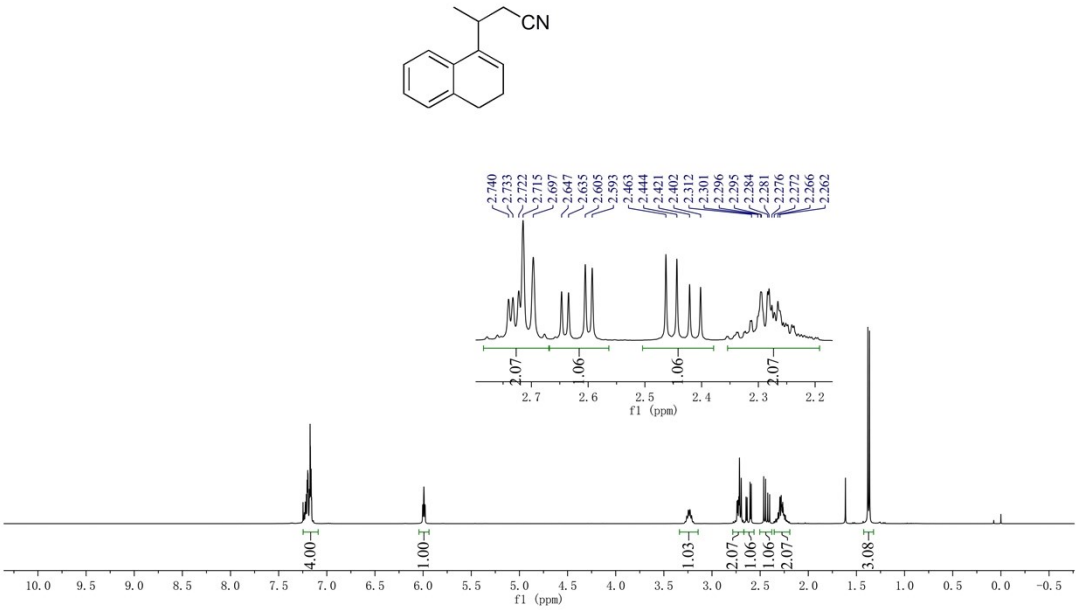


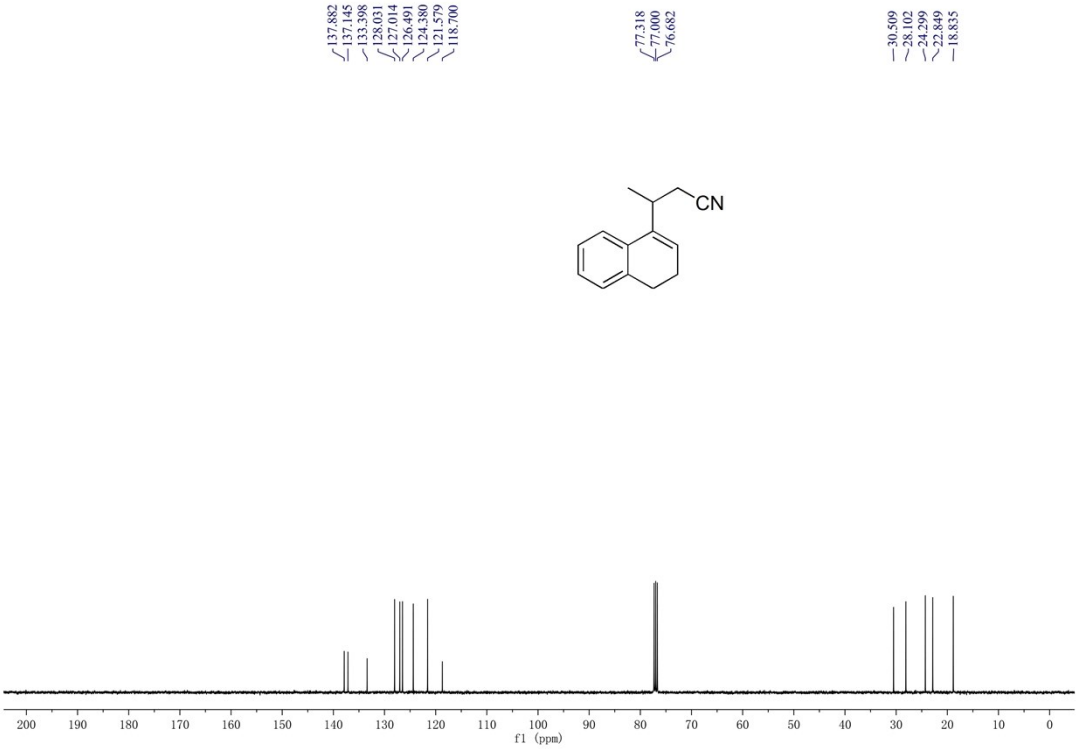
3-(7,8-Dihydroisoquinolin-5-yl)propanenitrile (3ya)



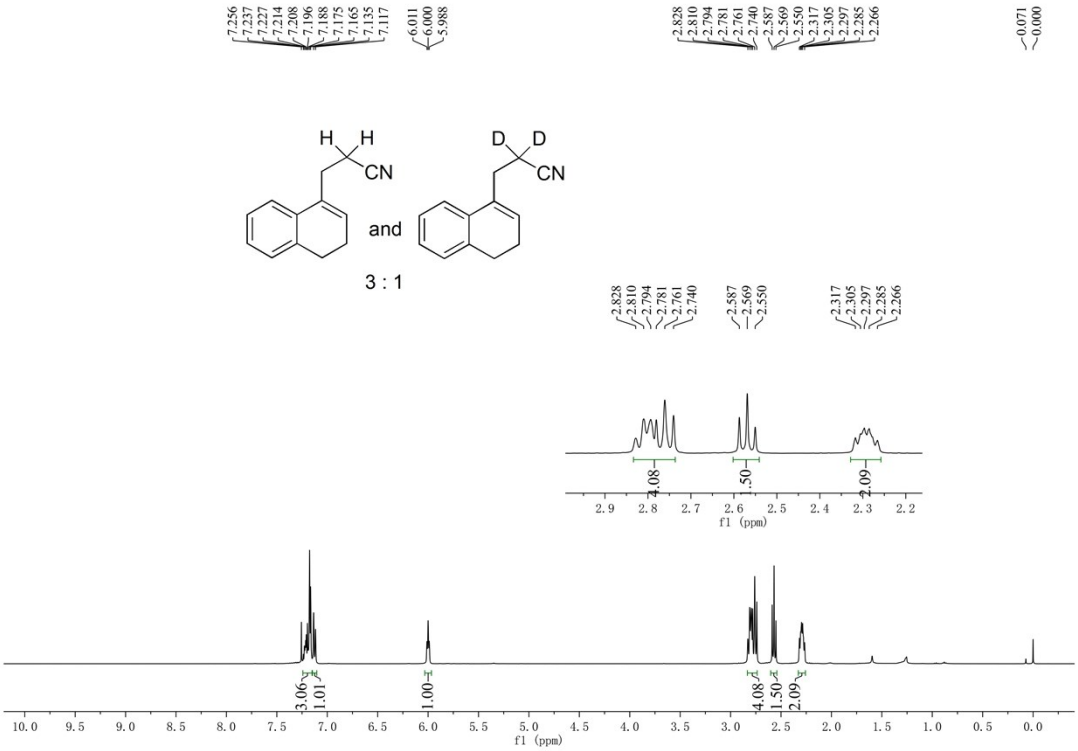


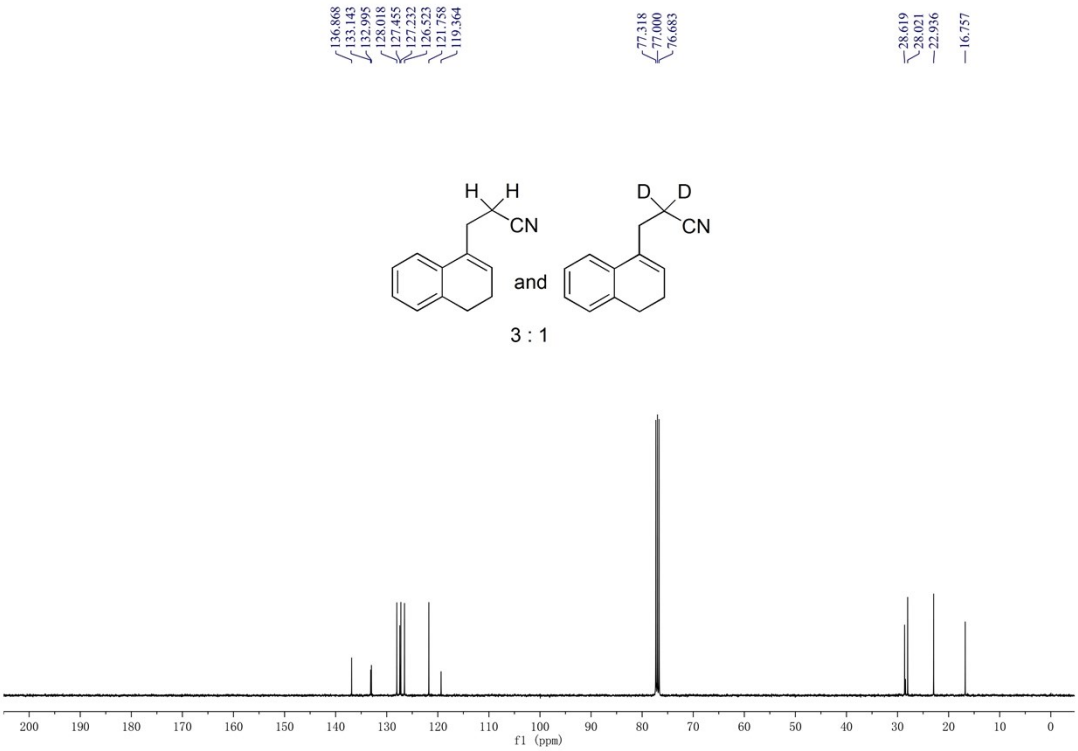
3-(3,4-Dihydronaphthalen-1-yl)butanenitrile (3aaa)



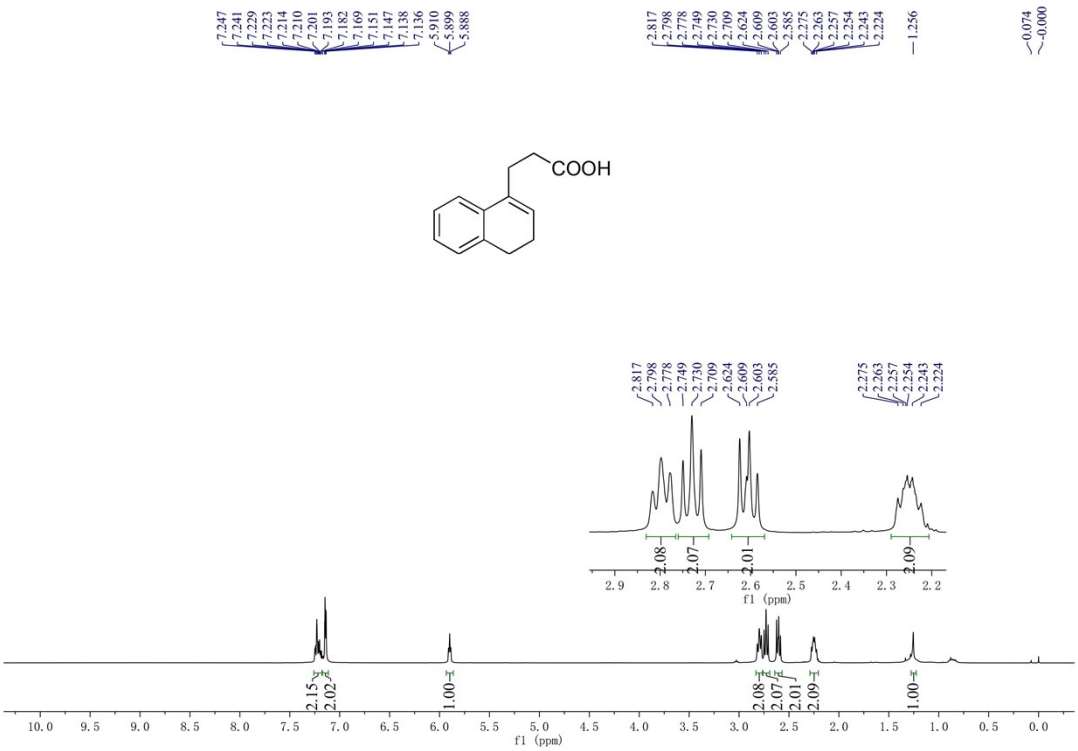


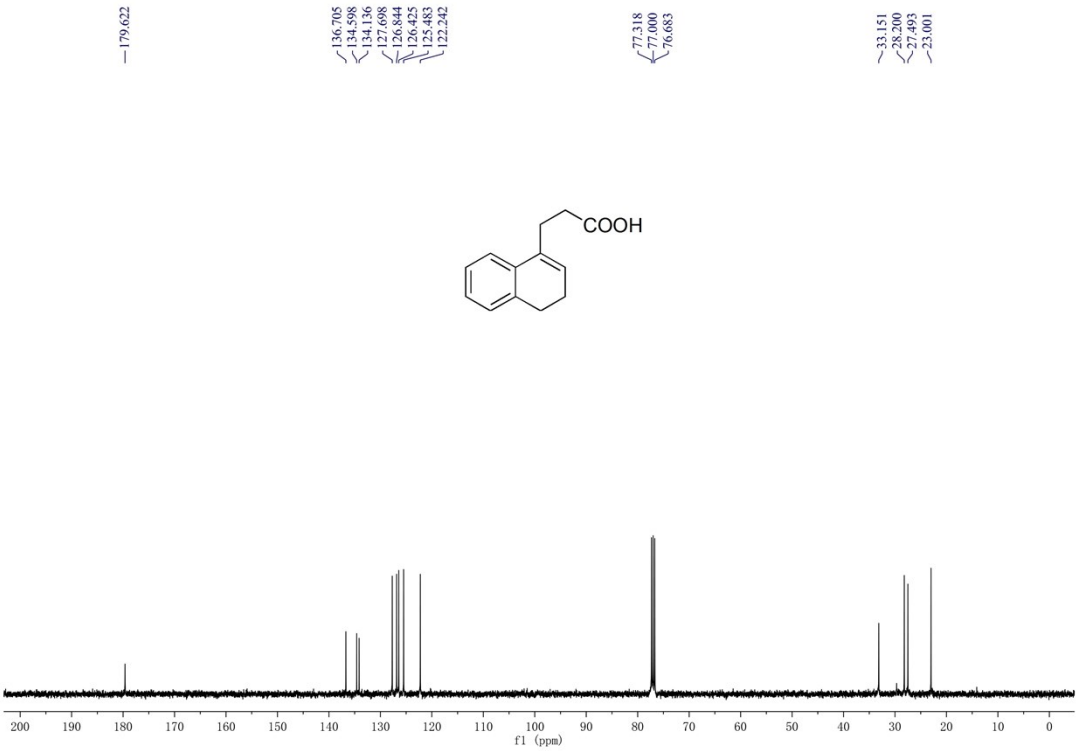
3aa+3aa-D2


7.256
7.237
7.227
7.214
7.208
7.196
7.188
7.175
7.165
7.135
7.117
6.011
6.000
5.988
2.828
2.810
2.794
2.781
2.761
2.740
2.587
2.569
2.550
2.317
2.305
2.297
2.285
2.266
0.071
0.000
H H
CN
and
D D
CN
3 : 1
4.08
1.50
2.09
f1 (ppm)
3.06
1.01
1.00
4.08
1.50
2.09
f1 (ppm)


136.868
133.143
132.995
128.018
127.455
127.232
126.523
121.758
119.364
77.318
77.000
76.683
28.619
28.021
22.936
16.757
H H
CN
and
D D
CN
3 : 1
f1 (ppm)

3-(3,4-Dihydronaphthalen-1-yl)propanoic acid (5)





3-(3,4-Dihydronaphthalen-1-yl)propanamide (6)