Electronic Supplementary Material (ESI) for

Supporting Information for

Ruthenium/HI-catalyzed direct hydromethylation of indoles and quinolines in DME

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1. General information

All manipulations involving organophosphines and their ruthenium complexes were carried out under a nitrogen atmosphere using standard Schlenk techniques. All solvents were dried and distilled under nitrogen prior to use. ^{1}H, ^{13}C NMR spectra were recorded on a Bruker AVIII – 500 NMR spectrometer. GC analyses were performed using an Agilent 6820 system (FID) and HP-5 column: with the injector temperature of 300 °C and detector temperature of 300 °C，column temperature 40 ºC, withdraw time 2 min, then 20 ºC/min to 230 ºC keeping for 5 min., then 20 ºC/min to 300 ºC, withdraw time for 5min., using mesitylene as the internal standard. GC–MS was carried out on DSQII, column: HP-5MS, procedures: Injector Temp:300 ºC; Detector Temp:300 ºC; column temperature 40 ºC, withdraw time 2 min, then 20 ºC/ min to 230 ºC keeping for 5 min, then 20 ºC/min to 300 ºC withdraw time for 5 min. Indoles and quinolines are purchased from Innochem Science & Technology Co., LTD and used without further purification. Hydrogen gas (99.99%) was purchased from Shijiazhuang Xisanjiao. All solvents were dried and distilled under nitrogen prior to use. Complex **Ru1** was synthesized and characterized according to the procedure reported by ourselves.[1,2]

Table S1 CAS numbers for substrates

Substrate	CAS number	Product	CAS number
indole	120-72-9	1-methylindoline	824-21-5
		indoleline	496-15-1
		1-methylindole	603-76-9
6-methylindole	3420-02-8	1,6-dimethylindoline	1384080-58-3
		1,6-dimethyl-1H-indole	5621-15-8
5-methylindole	614-96-0	1,5-dimethylindoline	1503436-23-4
		1,5-dimethyl-1H-indole	27816-53-1
4-methylindole	16096-32-5	1,4-dimethylindoline	1856504-77-2
		1,4-dimethylindole	27816-52-0

6-methoxyindole	3189-13-7	6-methoxy-1-methyl-indoline 6-methoxy-1-methyl-1H-indole	7556-48-1 1968-17-8
5-methoxyindole	1006-94-6	5-methoxy-1-methyl-indoline 5-methoxy-N-methylindole	74492-43-6 2521-13-3
4-methoxyindole	4837-90-5	4-methoxy-1-methyl-indoline 4-methoxy-1-methyl-1H-indole 4-methoxy-1H-indole	7569-83-7 7556-35-6 4837-90-5
6-fluoroindole	399-51-9	6-fluoro-1-methylindoline 6-fluoro-1-methyl-1H-indole 6-fluoro-1H-indole	1849248-48-1 441715-92-0 399-51-9
5-fluoroindole	399-52-0	5-fluoro-1-methylindoline 1,5-dimethyl-1H-indole	388078-34-0 27816-53-1
4-fluoroindole	387-42-9	4-fluoro-1-methylindoline 4-fluoro-1-methyl-1H-indole	1851835-07-8 441715-34-0
6-chloroindole	17422-33-2	6-chloro-1-methylindoline 6-chloro-1-methyl-1H-indole	99846-63-6 155868-51-2
4-chloroindole	25235-85-2	4-chloro-1-methylindoline 4-chloro-1-methyl-1H-indole	99848-88-1 77801-91-3
quinoline	91-22-5	N-methyl-1,2,3,4-tetrahydroquinoline	491-34-9
8-methylquinoline	611-32-5	1,8-dimethyl-1,2,3,4-tetrahydroquinoline 8-methyl-1,2,3,4-tetrahydroquinoline	84573-84-2 52601-70-4
7-methylquinoline	612-60-2	1,7-dimethyl-1,2,3,4-tetrahydroquinoline	91245-78-2
6-methylquinoline	91-62-3	1,6-dimethyl-1,2,3,4-tetrahydroquinoline	104524-39-2

5-methylquinoline	7661-55-4	1,5-dimethyl-1,2,3,4-tetrahydroquinoline 5-methyl-1,2,3,4-tetrahydroquinoline	1864825-92-2 58960-02-4
6-methyoxyquinoline	5263-87-6	1-methyl-6-methoxy-1,2,3,4-tetrahydroquinoline 6-methoxy-1,2,3,4-tetrahydroquinoline	74492-61-8 120-15-0
5-methyoxyquinoline	6931-19-7	1-methyl-5-methoxy-1,2,3,4-tetrahydroquinoline	1880957-62-9
8-fluoroquinoline	394-68-3	8-fluoro-1-methyl-1,2,3,4-tetrahydroquinolin 8-fluoro-1,2,3,4-tetrahydroquinoline	1862849-43-1 75414-02-7
6-fluoroquinoline	396-30-5	6-fluoro-1-methyl-1,2,3,4-tetrahydroquinolin	388078-35-1

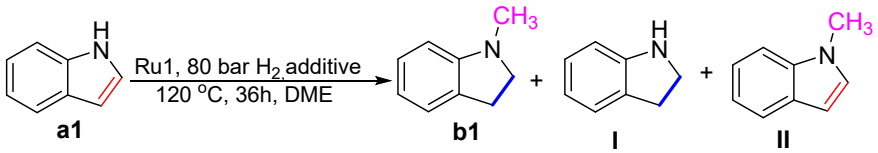
2. Experimental section

2.1 General procedure of hydromethylation

Under an atmosphere of nitrogen, a stainless steel 100 mL autoclave, equipped with a magnetic stir bar, was charged with **Ru1** (0.001 ~ 0.005 mmol) and the solvents to be used (2.5 ~ 10 mL). A solution of the substrates (0.5 mmol) in the solvent was added *via* a syringe. The autoclave was purged by three cycles of pressurization, venting with N_2 (1 ~ 5 bar), and then pressurized with the desired pressure (40 ~ 80 bar). The autoclave was heated to the desired temperature (80 ~ 140 °C) and the contents stirred. After the pre-determined reaction time, the autoclave was cooled to room temperature and the pressure slowly released. The reaction mixture was filtered through a plug of silica gel and then analyzed by GC and GC-MS. The mixture was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 80:1-20:1) to afford the hydromethylation products and detected by NMR.

2.2 Optimizing reaction conditions

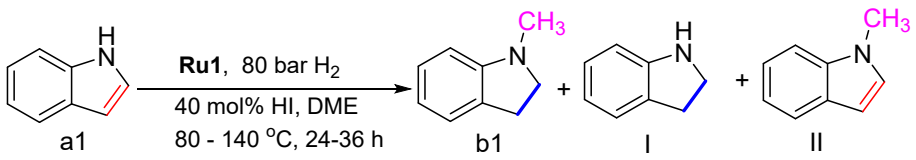
Table S2 The dosage of hydroiodic acid for hydromethylation of indole (**a1**) to 1-methylindoline (**b1**)[a]



Entry	HI (X mmol)	Conv. (%)	Yield of **b1** (%)	Yield of **I** (%)	Yield of **II** (%)
1	0.50	96.9	81.4	0	15.5
2	0.75	65.8	56.6	0	9.2
3	0.25	96.8	78.0	0	18.8
4	0.20	97.0	76.1	0	20.9
5	0.15	83.5	71.5	0	12.0
6	0.10	79.2	68.0	0	11.2
7	0.05	65.9	55.1	5.0	5.8

Conditions: Indole (0.5 mmol), **Ru1** (10 mol%), DME (10 mL), P (H_2) = 80 bar, Temp. = 120 °C, Time = 36 h. All yields are determined by GC using mesitylene as the internal standard.

Table S3 Temperature screening[a]

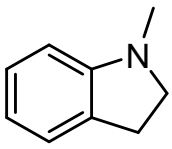
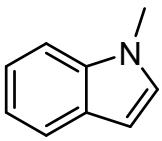
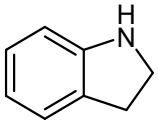
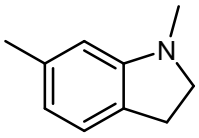


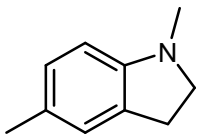
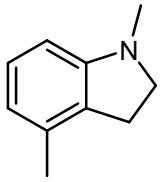
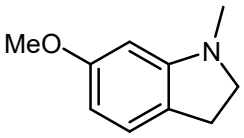
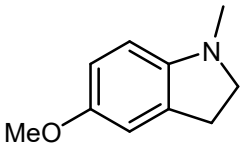
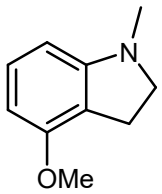
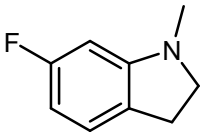
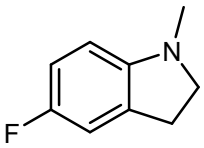
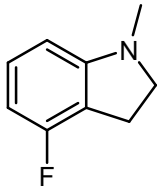
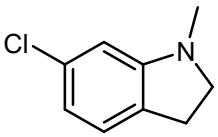
Entry	Tem. (°C)	Conv. (%)	Yield of **b1** (%)	Yield of **I** (%)	Yield of **II** (%)
1	80	39.3	36.4	0	2.9
2	100	58.7	54.3	0	4.4
3	120	97.0	76.1	0	20.9
4	140	96.4	73.6	3.0	19.8

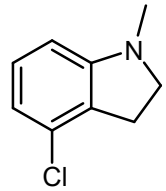
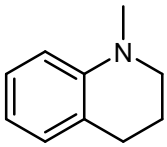
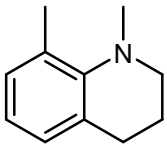
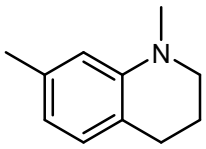
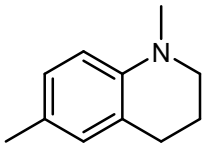
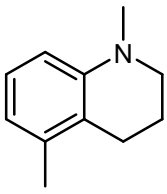
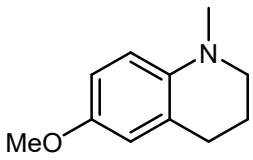
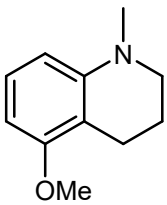
Conditions: Indole (0.5 mmol), **Ru1** (1 mol%), DME (10 mL), P (H_2) = 80 bar, Temp. = 120 °C, Time = 36 h. All yields are determined by GC using mesitylene as the internal standard.

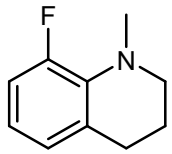
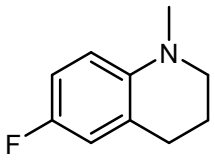
3. ^{1}H NMR, ^{13}C NMR and MS for the organic products

Table S4 ^{1}H NMR, ^{13}C NMR and MS for the organic products

Entry	Substrate	NMR and MS	Reference
1		^{1}H NMR (500 MHz, DMSO-d_6) δ 7.06 – 6.97 (m, 2H), 6.59 (t, 1H), 6.49 (d, 1H), 3.22 (t, 2H), 2.85 (t, 2H), 2.68 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 153.8, 130.2, 127.5, 124.4, 117.7, 107.4, 56.0, 36.3, 28.6. MS: *m/z* $[M]^+$, 133.06	3
2		^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.68 (m, 1H), 7.42 (d, 1H), 7.39 – 7.28 (m, 1H), 7.26 – 7.16 (m, 1H), 7.13 (d, 1H), 6.59 (d, 1H), 3.86 (d, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.8, 128.9, 128.6, 121.6, 121.0, 119.4, 109.3, 101.0, 32.9. MS: *m/z* $[M]^+$, 131.04	4
3		^{1}H NMR (400 MHz, $CDCl_3$): δ7.19 (d, 1H), 7.08 (t, 1H), 6.82 - 6.67 (m, 2H), 3.61 (t, 2H), 3.09 (t, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ151.5, 129.5, 127.3, 124.7, 118.9, 109.7, 47.4, 29.9. MS: *m/z* $[M]^+$, 119.03	3
4		^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, 1H), 6.54 (d, 1H), 6.37 (s, 1H), 3.32 (t, 2H), 2.93 (t, 2H), 2.78 (s, 3H), 2.34 (s, 3H). MS: *m/z* $[M]^+$, 147.13	3

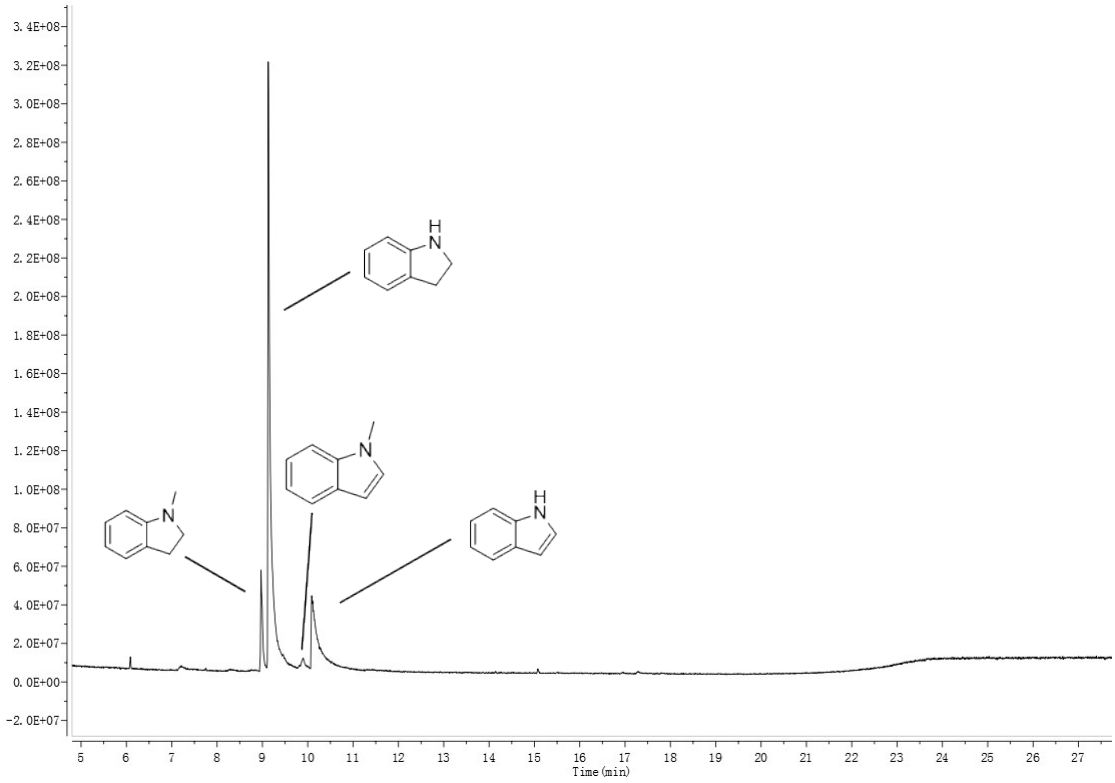
5		^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 – 6.89 (m, 2H), 6.45 (d, 1H), 3.28 (t, 2H), 2.96 – 2.91 (m, 2H), 2.76 (s, 3H), 2.28 (s, 3H). MS: *m/z* $[M]^+$, 147.12	3
6		^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (t, 1H), 6.56 (d, 1H), 6.39 (d, 1H), 3.35 (t, 2H), 2.91 (t, 2H), 2.79 (s, 3H), 2.26 (s, 3H). MS: *m/z* $[M]^+$, 147.13	3
7		^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, 1H), 6.23 (d, 1H), 6.12 (d, 1H), 3.82 (s, 3H), 3.35 (t, 2H), 2.92 (t, 2H), 2.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 154.8, 124.3, 122.7, 101.63, 94.9, 55.7, 55.5, 36.1, 28.0 MS: *m/z* $[M]^+$, 161.10	
8		^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (t, 1H), 6.69 (d, 1H), 6.47 (d, 1H), 3.78 (s, 3H), 3.27 (t, 2H), 2.97 – 2.91 (m, 2H), 2.75 (s, 3H). MS: *m/z* $[M]^+$, 163.12	5
9		^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (t, 1H), 6.34 (d, 1H), 6.24 (d, 1H), 3.86 (s, 3H), 3.35 (t, 2H), 2.95 (t, 2H), 2.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 155.2, 128.8, 102.8, 101.3, 99.2, 56.4, 55.3, 36.5, 25.7. MS: *m/z* $[M]^+$, 163.13	
10		^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 – 6.94 (m, 1H), 6.34 (d, 1H), 6.19 (d, 1H), 3.39 (t, 2H), 2.94 (t, 2H), 2.78 (s, 3H), 1.61 (s, 3H). MS: *m/z* $[M]^+$, 151.08	6
11		^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 – 6.74 (m, 2H), 6.40 (d, 1H), 3.31 (t, 2H), 2.98 – 2.92 (m, 2H), 2.76 (s, 3H). MS: *m/z* $[M]^+$, 151.11	3
12		^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (t, 1H), 6.40 (t, 1H), 6.28 (d, 1H), 3.40 (t, 2H), 3.02 (t, 2H), 2.79 (d, 3H). MS: *m/z* $[M]^+$, 151.10	7
13		^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 – 6.94 (m, 1H), 6.34 (d, 1H), 6.19 (d, 1H), 3.39 (t, 2H), 2.93 (t, 2H), 2.77 (s, 3H). MS: *m/z* $[M]^+$, 167.06	3

14		^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (t, 1H), 6.66 (d, 1H), 6.36 (d, 1H), 3.45 – 3.35 (m, 2H), 3.03 (t, 2H), 2.79 (s, 3H). MS: *m/z* $[M]^+$, 167.07	7
15		^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.06 (m, 1H), 7.02 – 6.95 (m, 1H), 6.64 (t, 2H), 3.29 – 3.21 (m, 2H), 2.92 (s, 3H), 2.80 (t, 2H), 2.07 – 1.97 (m, 2H) ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 128.9, 127.1, 122.9, 116.2, 111.0, 51.3, 39.2, 27.8, 22.5. MS: *m/z* $[M]^+$, 147.12	3
16		^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (d, 1H), 6.86 – 6.80 (m, 1H), 6.58 (d, 1H), 3.24 – 3.16 (m, 2H), 2.89 (s, 3H), 2.78 (t, 2H), 2.25 (s, 3H), 2.08 – 1.95 (m, 2H). MS: *m/z* $[M]^+$, 161.07	8
17		^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (d, 1H), 6.50 (d, 2H), 3.29 – 3.22 (m, 2H), 2.94 (d, 3H), 2.79 (t, 2H), 2.34 (s, 3H), 2.03 (q, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 136.6, 128.8, 120.0, 117.1, 111.9, 51.5, 39.2, 27.5, 22.7, 21.7. MS: *m/z* $[M]^+$, 161.09	3
18		^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (d, 1H), 6.84 (d, 1H), 6.58 (d, 1H), 3.24 – 3.17 (m, 2H), 2.90 (s, 3H), 2.79 (t, 2H), 2.26 (s, 3H), 2.08 – 1.97 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 129.7, 127.5, 125.6, 123.2, 111.5, 51.6, 39.5, 27.8, 22.7, 20.3. MS: *m/z* $[M]^+$, 161.10	3
19		^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (t, 1H), 6.62 (t, 2H), 3.36 – 3.16 (m, 2H), 2.97 (d, 3H), 2.75 (t, 2H), 2.29 (s, 3H), 2.12 (m,2H). MS: *m/z* $[M]^+$, 161.10	7
20		^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 (d, 1H), 6.66 – 6.59 (m, 2H), 3.78 (d, 3H), 3.20 – 3.13 (m, 2H), 2.88 (d, 3H), 2.81 (t, 2H) ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 141.7, 124.7, 115.1, 112.6, 112.3, 55.8, 51.7, 40.0, 28.0, 22.7. MS: *m/z* $[M]^+$, 177.09	3
21		^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (t, 1H), 6.37 (d, 1H), 6.32 (d, 1H), 3.84 (s, 3H), 3.24 – 3.17 (m, 2H), 2.93 (s, 3H), 2.72 (t, 2H), 2.06 – 1.96 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 148.0, 126.8, 110.9, 104.9, 99.2, 55.4, 51.1, 39.9, 22.0, 21.1. MS: *m/z* $[M]^+$, 177.08	

22		^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 – 6.50 (m, 3H), 3.21 – 3.12 (m, 2H), 3.06 – 2.92 (m, 3H), 2.78 (t, 2H), 1.98 – 1.87 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 136.1, 129.3, 124.7, 119.0, 114.0, 52.8, 42.7, 28.1, 20.2. MS: *m/z* $[M]^+$, 165.06	
23		^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (m, 1H), 6.74 (m, 1H), 6.55 (m, 1H), 3.20 (t, 2H), 2.89 (s, 3H), 2.79 (t, 2H), 2.12 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 143.4, 124.6, 115.5, 115.2, 113.1, 51.4, 39.7, 27.5, 22.5. MS: *m/z* $[M]^+$, 165.05	3

All the GC-MS spectra and data of the products were shown as follow:

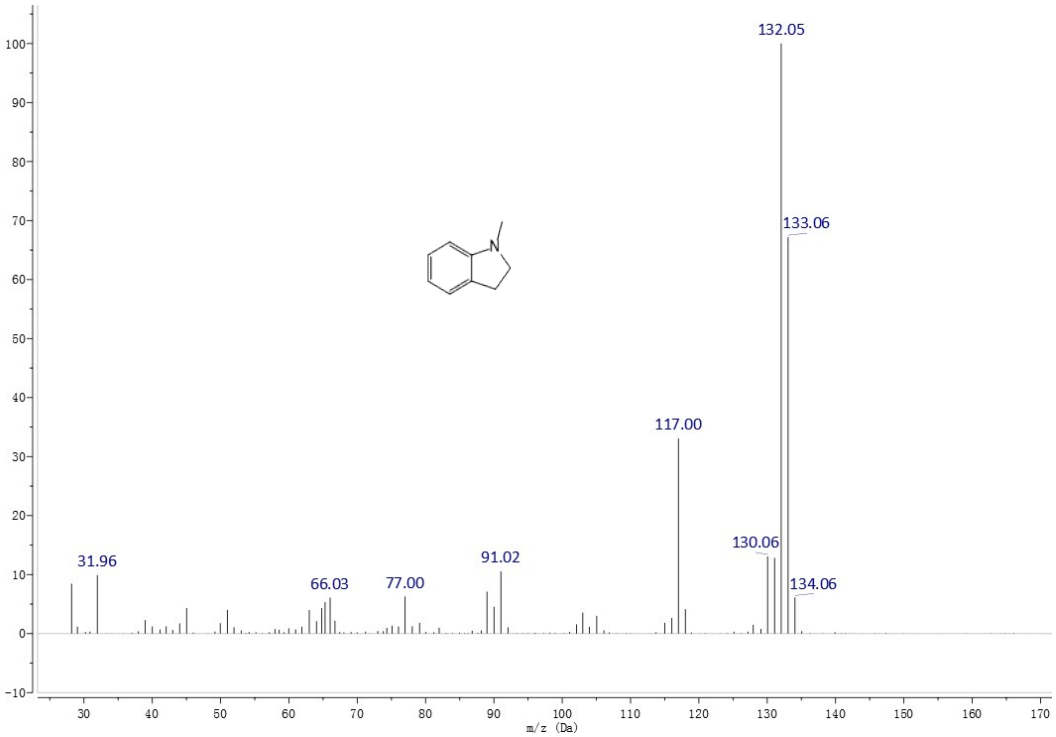
(1). GC-MS spectrum for substrate: indole

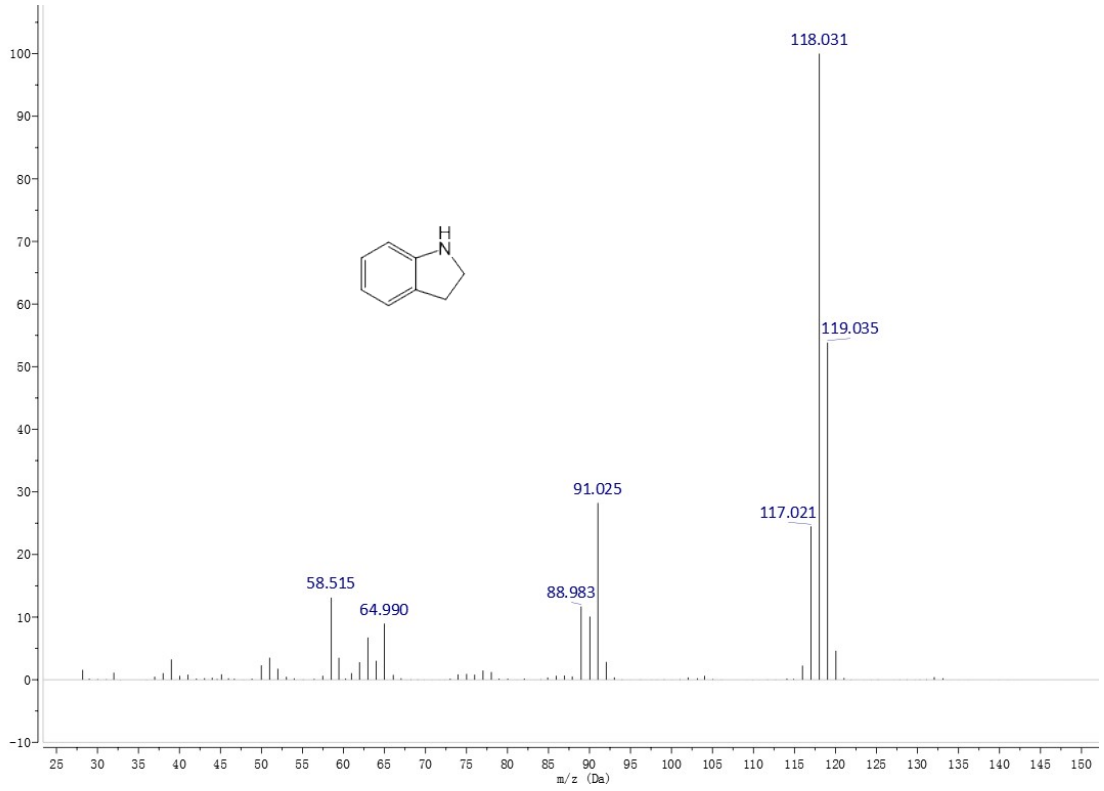


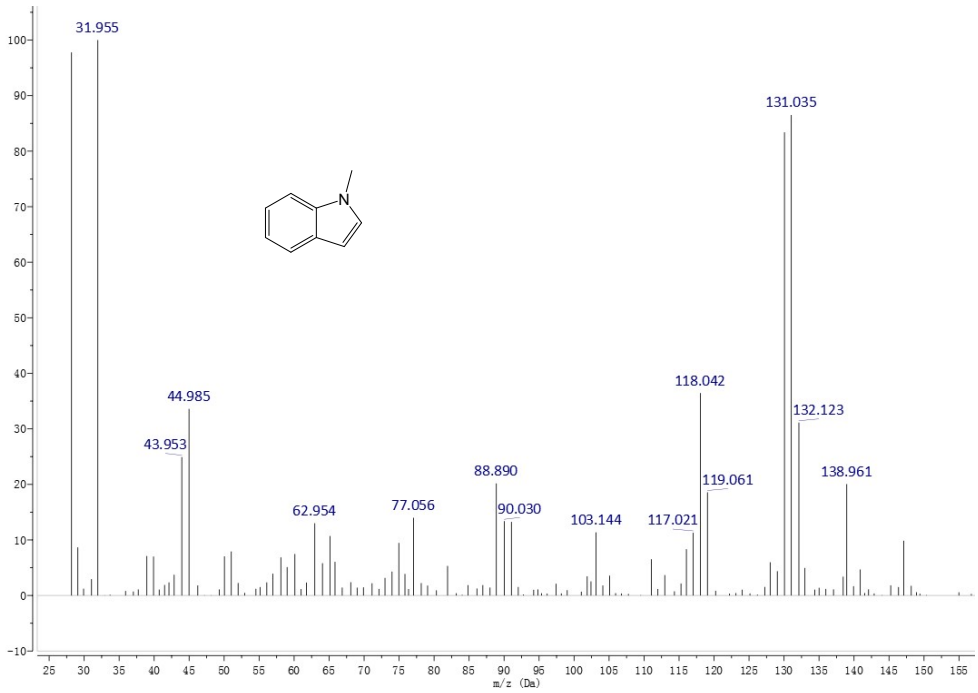
RT: 8.43 - 11.17

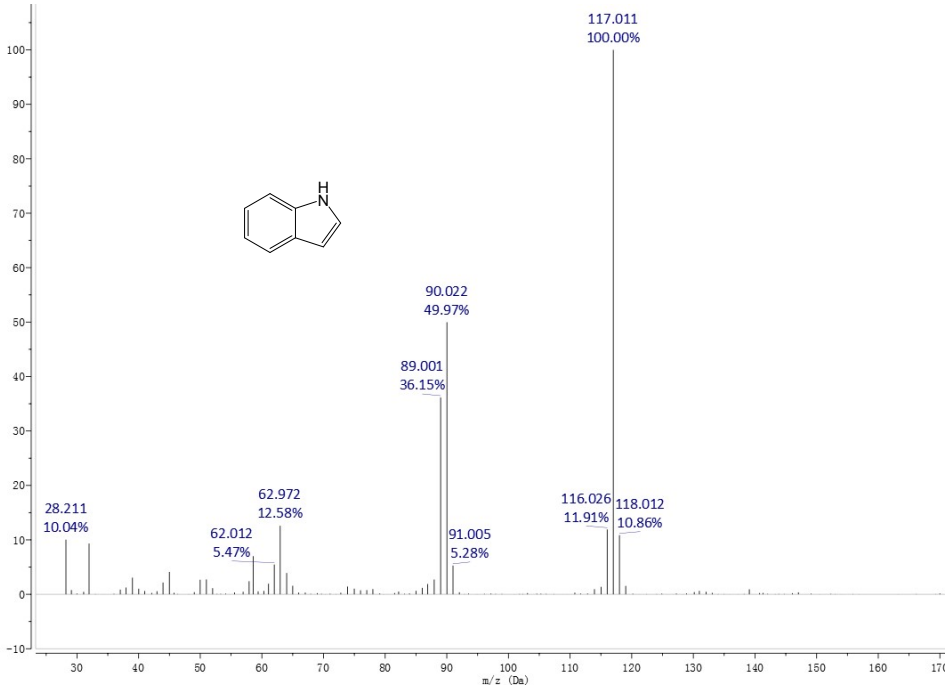
Number of detected peaks: 3

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
8.97	8.94	9.04	139792991.574	8.48	53575126.858	13.05
9.13	9.10	9.48	1214240586.970	73.69	317906620.907	77.44
10.09	10.06	10.36	293782520.736	17.83	39019590.300	9.51

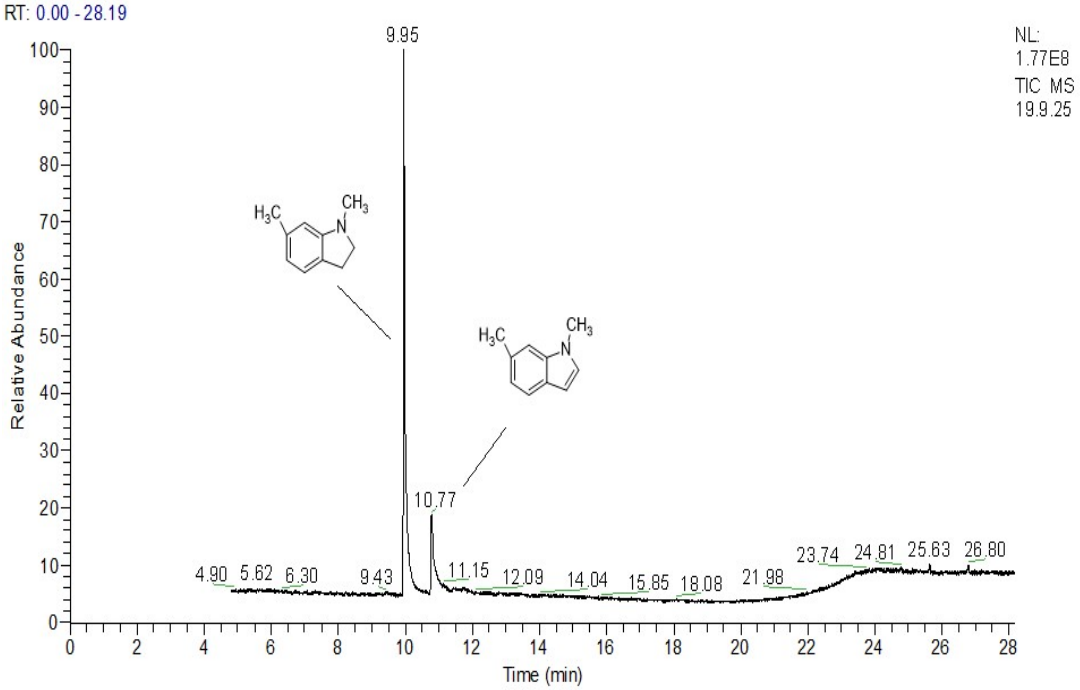

132.05
133.06
117.00
130.06
134.06
91.02
31.96
66.03
77.00
m/z (Da)


118.031
119.035
91.025
117.021
58.515
64.990
88.983
m/z (Da)


31.955
131.035
44.985
43.953
118.042
132.123
88.890
119.061
138.961
62.954
77.056
90.030
103.144
117.021
m/z (Da)

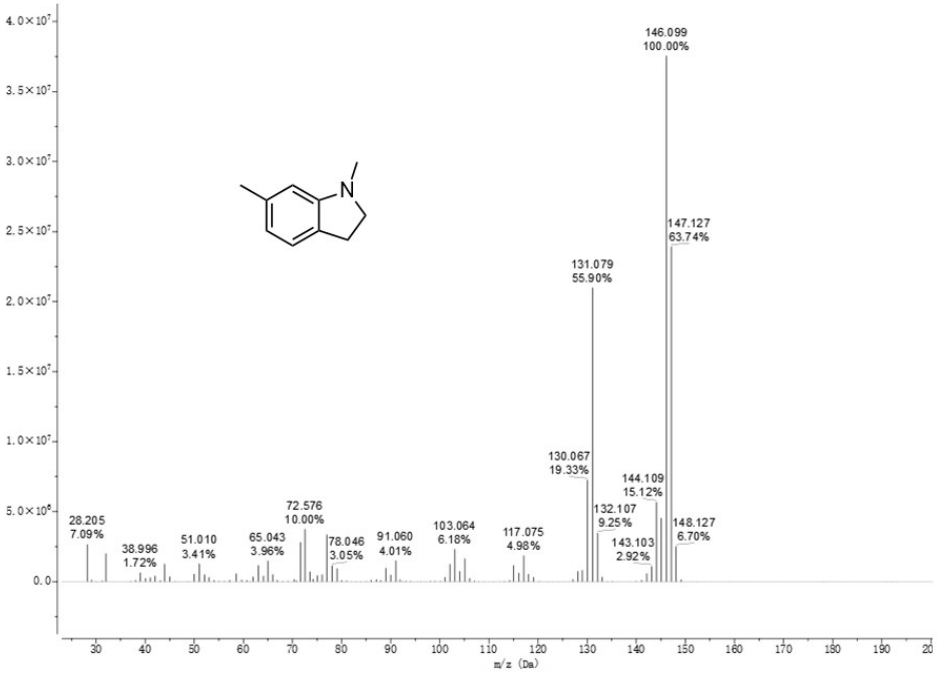

117.011
100.00%
90.022
49.97%
89.001
36.15%
28.211
10.04%
62.972
12.58%
62.012
5.47%
91.005
5.28%
116.026
11.91%
118.012
10.86%
m/z (Da)

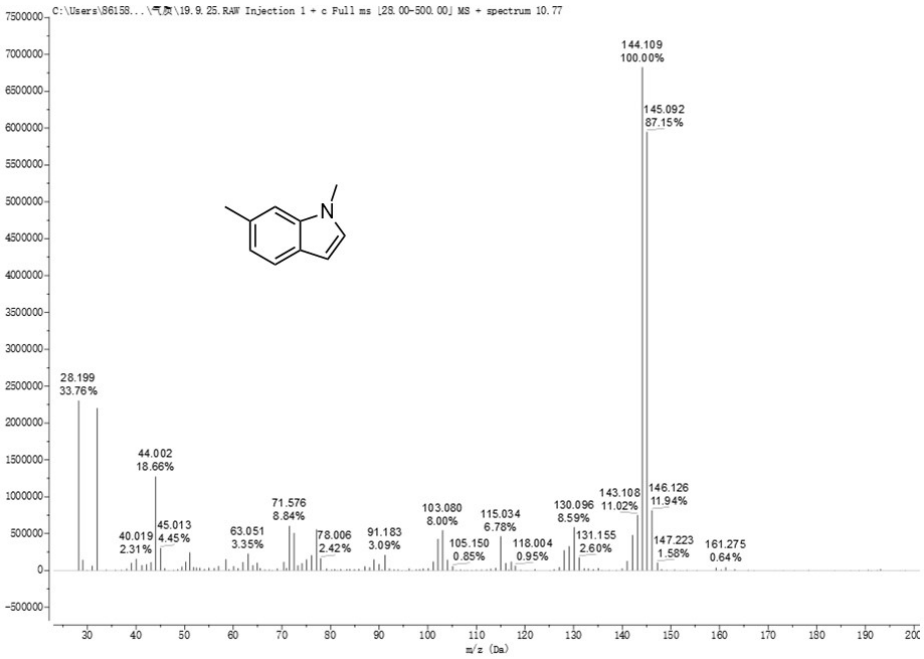
(2). GC-MS spectrum for substrate: 6-methylindole



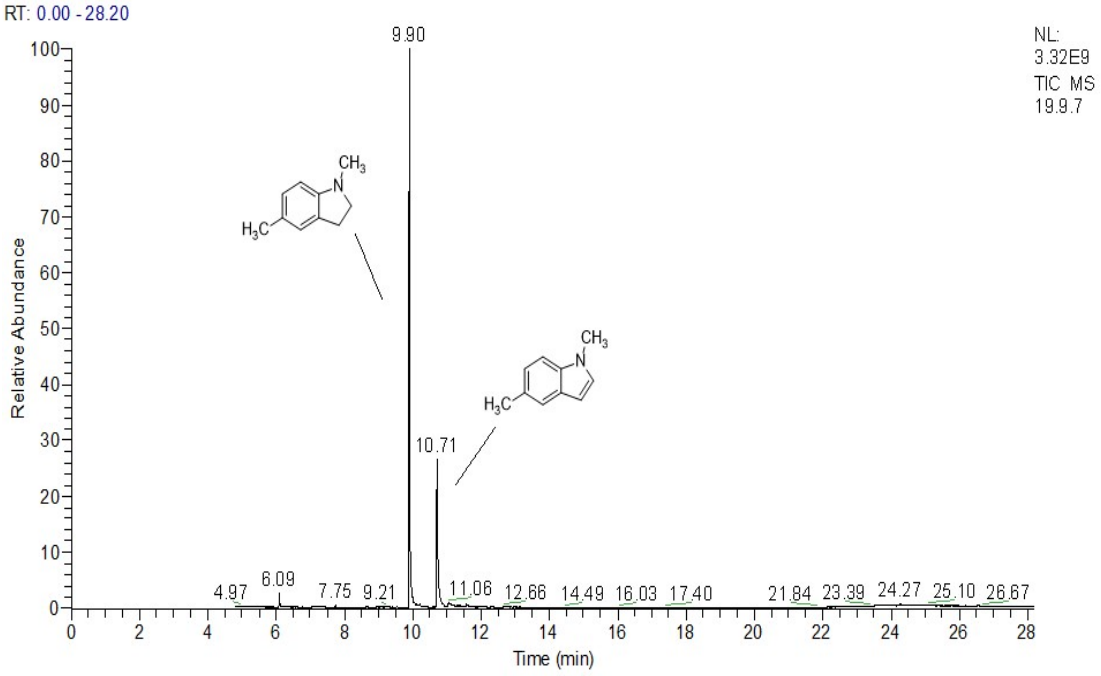
Number of detected peaks: 2

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
9.95	9.92	10.19	615118854.586	78.55	171518896.037	87.46
10.77	10.74	11.01	167985117.661	21.45	24583518.453	12.54





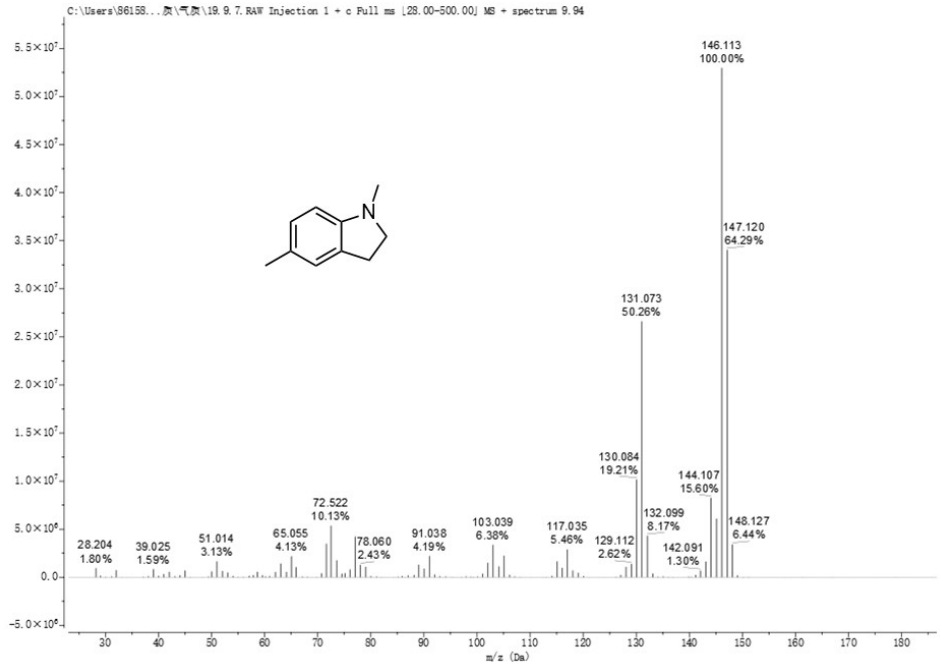
(3). GC-MS spectrum for substrate: 5-methylindole

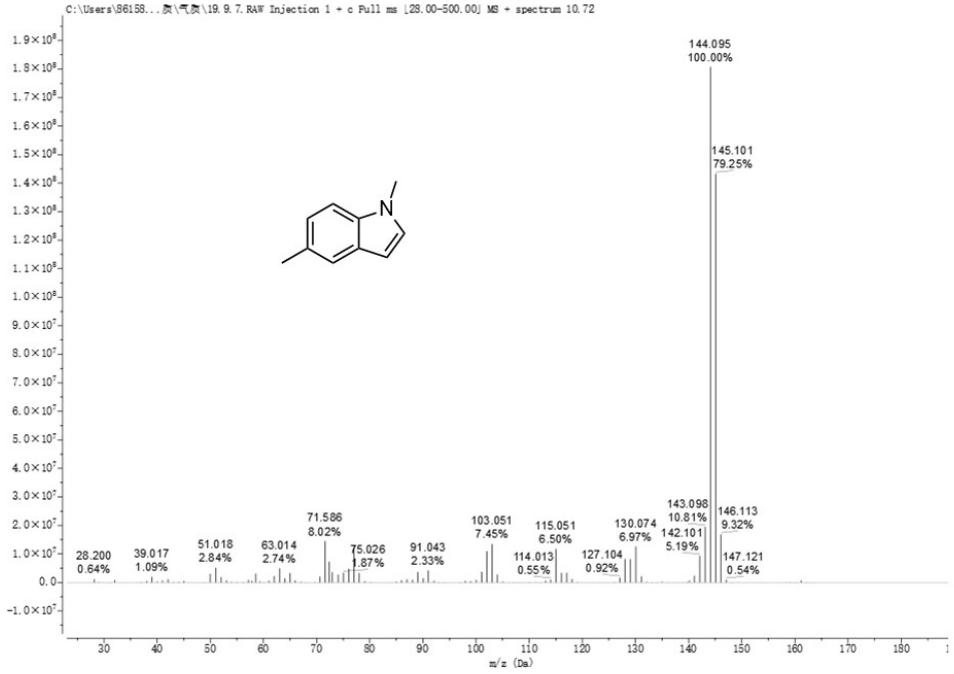


RT: 6.06 - 13.68

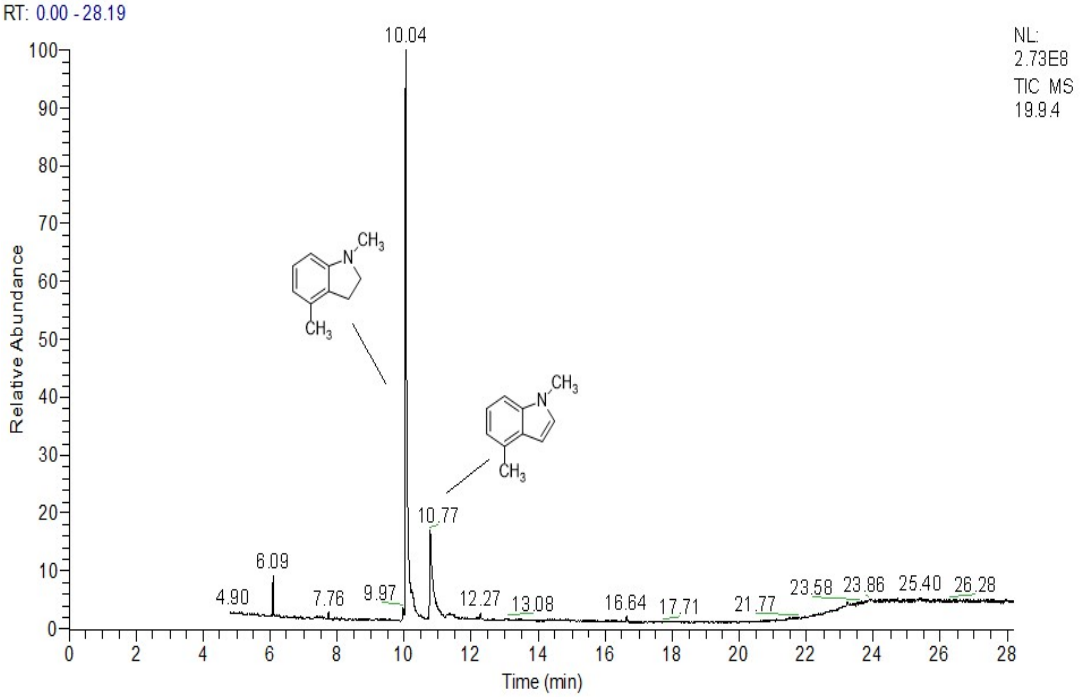
Number of detected peaks: 3

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
9.90	9.87	10.16	5195022	147.384	3320317	814.582
78.54						
10.71	10.68	10.94	1973687	093.621	884460	539.255
20.92						
11.06	11.02	11.24	168195	978.234	22602	286.381
0.53						


C:\Users\86158...质\气质\19.9.7.RAW Injection 1 + c Pull ms [28.00-500.00] MS + spectrum 9.94
146.113
100.00%
147.120
64.29%
131.073
50.26%
130.084
19.21%
144.107
15.60%
132.099
8.17%
148.127
6.44%
72.522
10.13%
28.204
1.80%
39.025
1.59%
51.014
3.13%
65.055
4.13%
78.060
2.43%
91.038
4.19%
103.039
6.38%
117.035
5.46%
129.112
2.62%
142.091
1.30%
m/z (Da)


C:\Users\86158...质\气质\19.9.7.RAW Injection 1 + c Pull ms [28.00-500.00] MS + spectrum 10.72
144.095
100.00%
145.101
79.25%
143.098
10.81%
146.113
9.32%
142.101
5.19%
147.121
0.54%
71.586
8.02%
28.200
0.64%
39.017
1.09%
51.018
2.84%
63.014
2.74%
75.026
1.87%
91.043
2.33%
103.051
7.45%
114.013
0.55%
115.051
6.50%
127.104
0.92%
130.074
6.97%
m/z (Da)

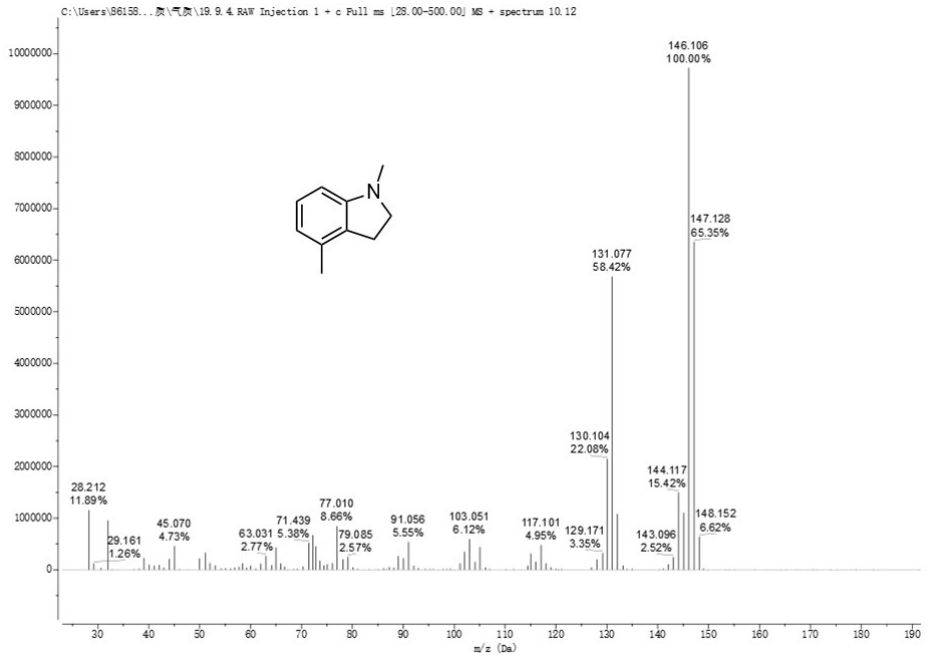
(4). GC-MS spectrum for substrate: 4-methylindole

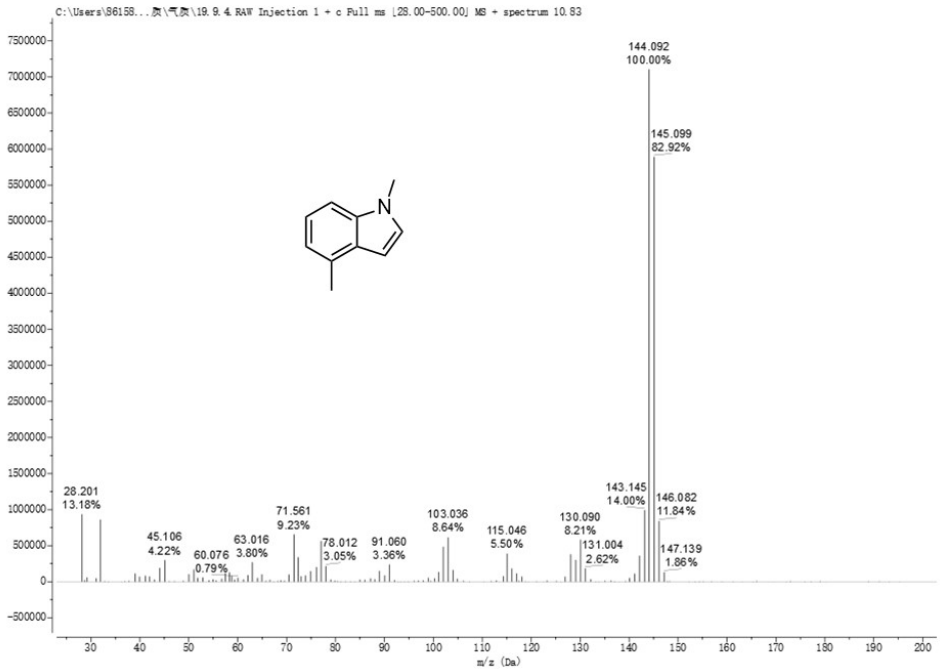


RT: 9.84 - 12.54

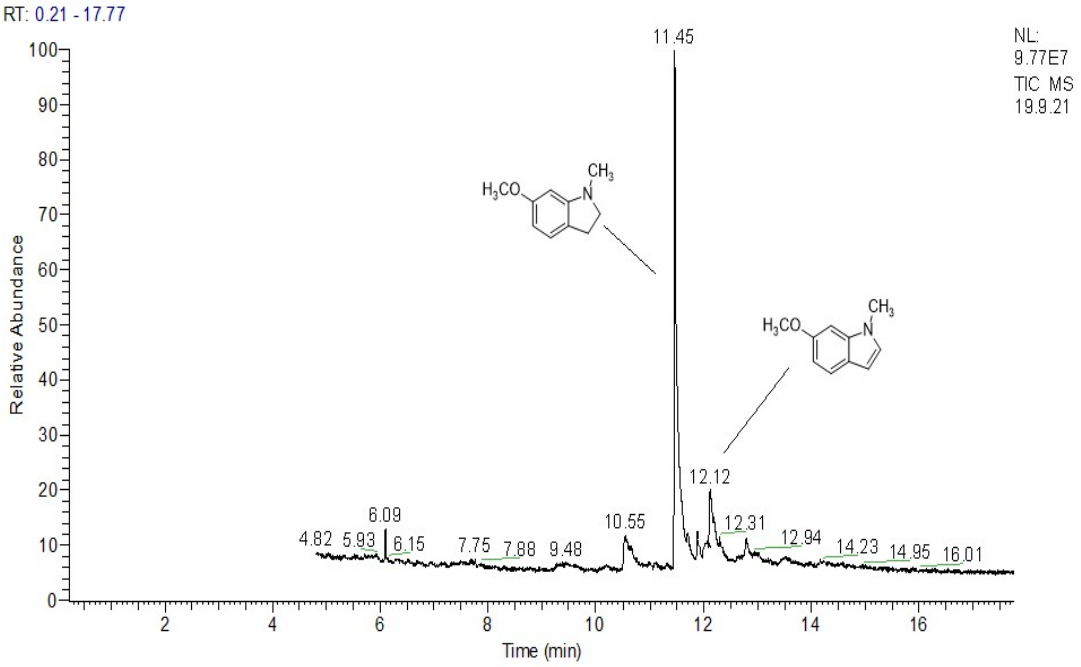
Number of detected peaks: 3

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
10.04	10.01	10.35	827762868.216	74.79	266667968.272	85.76
10.77	10.74	11.11	271504415.203	24.53	42694610.385	13.73
11.35	11.28	11.45	7558625.043	0.68	1582249.781	0.51





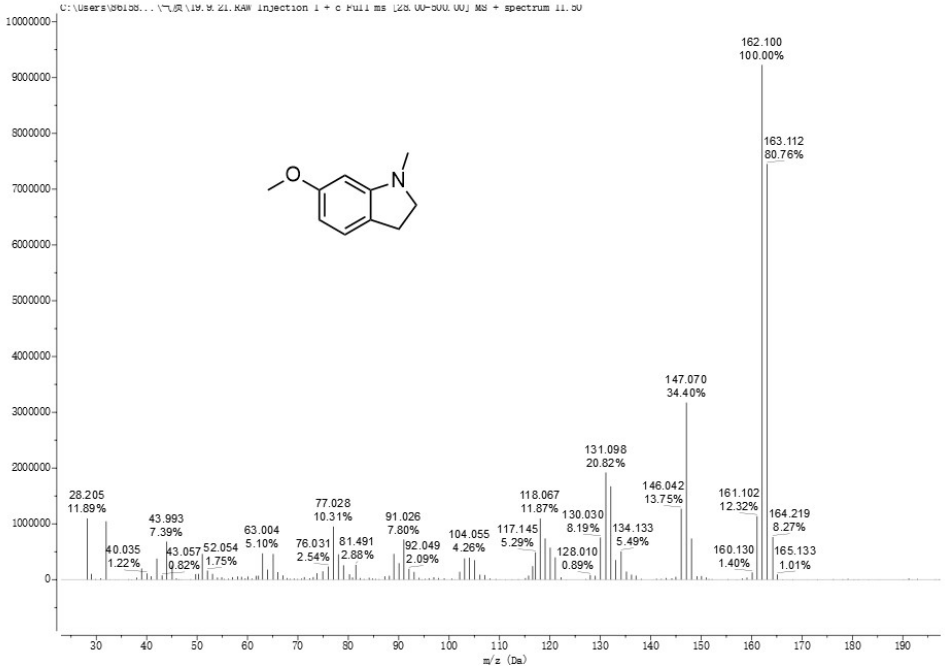
(5). GC-MS spectrum for substrate: 6-methoxy-1H-indole

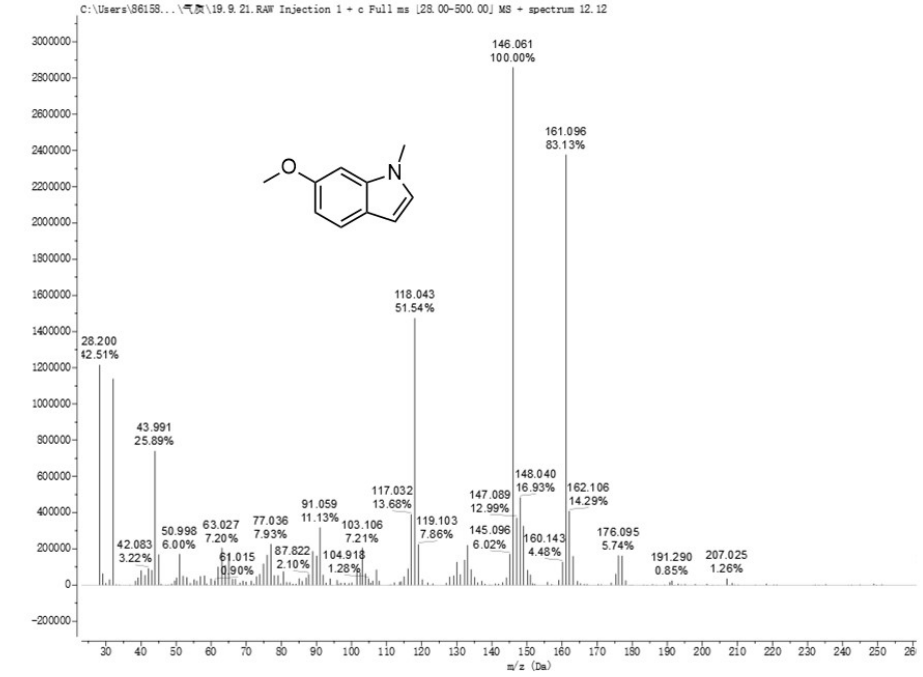


RT: 10.97 - 13.56

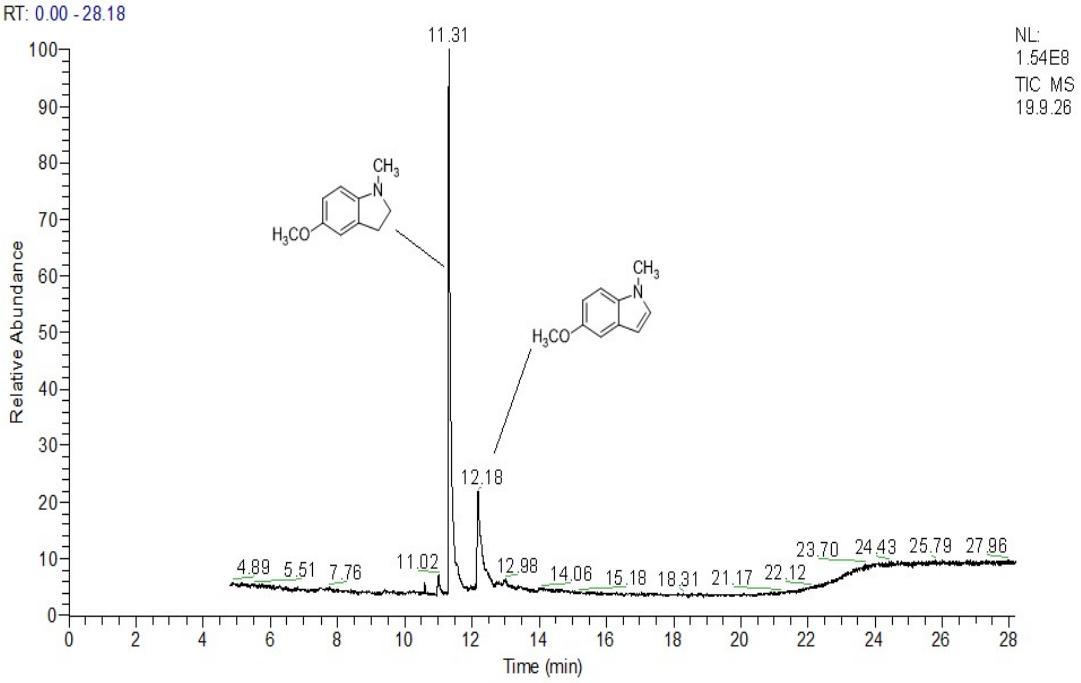
Number of detected peaks: 2

Apex RT	Start RT	End RT	Area%Area	Height	%Height
11.45	11.43	11.69	377534738.449	87.00	91727238.713 89.12
12.12	12.09	12.24	56396734.334	13.00	11203060.375 10.88


C:\Users\86158...\气质\19.9.21.RAW Injection 1 + c Full ms [28.00-500.00] MS + spectrum 11.50
162.100
100.00%
163.112
80.76%
147.070
34.40%
131.098
20.82%
146.042
13.75%
161.102
12.32%
164.219
8.27%
165.133
1.01%
160.130
1.40%
134.133
5.49%
130.030
8.19%
128.010
0.89%
118.067
11.87%
117.145
5.29%
104.055
4.26%
92.049
2.09%
91.026
7.80%
81.491
2.88%
77.028
10.31%
76.031
2.54%
63.004
5.10%
52.054
1.75%
43.057
0.82%
43.993
7.39%
40.035
1.22%
28.205
11.89%
m/z (Da)


C:\Users\86158...\气质\19.9.21.RAW Injection 1 + c Full ms [28.00-500.00] MS + spectrum 12.12
146.061
100.00%
161.096
83.13%
118.043
51.54%
28.200
42.51%
43.991
25.89%
148.040
16.93%
162.106
14.29%
117.032
13.68%
147.089
12.99%
119.103
7.86%
145.096
6.02%
160.143
4.48%
176.095
5.74%
191.290
0.85%
207.025
1.26%
91.059
11.13%
103.106
7.21%
77.036
7.93%
63.027
7.20%
50.998
6.00%
42.083
3.22%
87.822
2.10%
104.918
1.28%
61.015
0.90%
m/z (Da)

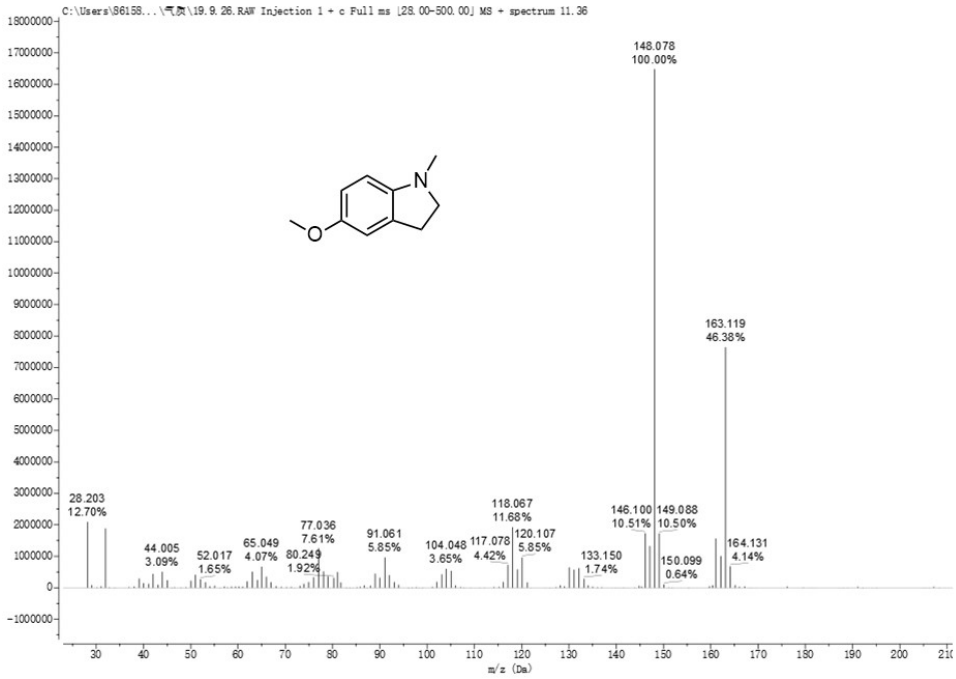
(6). GC-MS spectrum for substrate: 5-methoxy-1H-indole

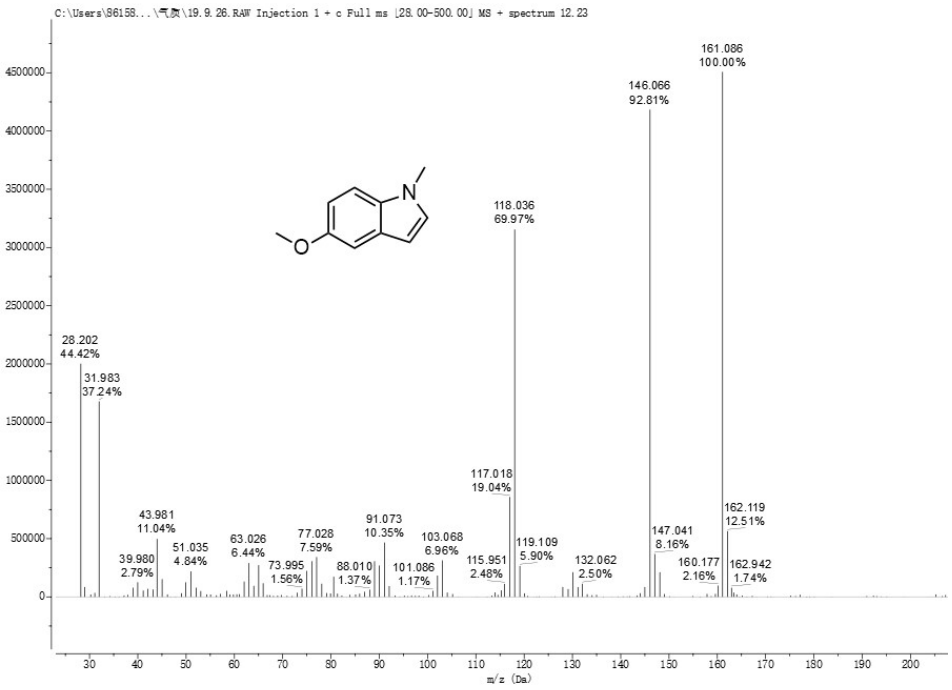


RT: 9.81 - 15.11

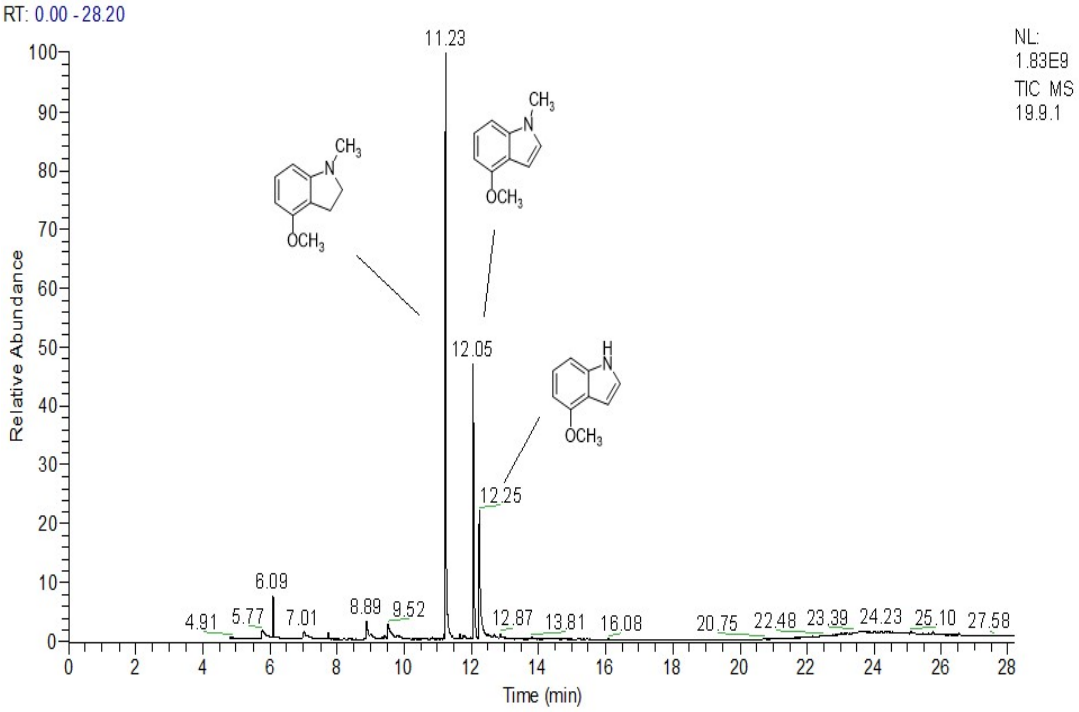
Number of detected peaks: 2

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
11.31	11.29	11.74	684074550.953	74.01	149505959.704	84.18
12.18	12.16	12.58	240194161.457	25.99	28101364.632	15.82





(7). GC-MS spectrum for substrate: 4-methoxy-1H-indole

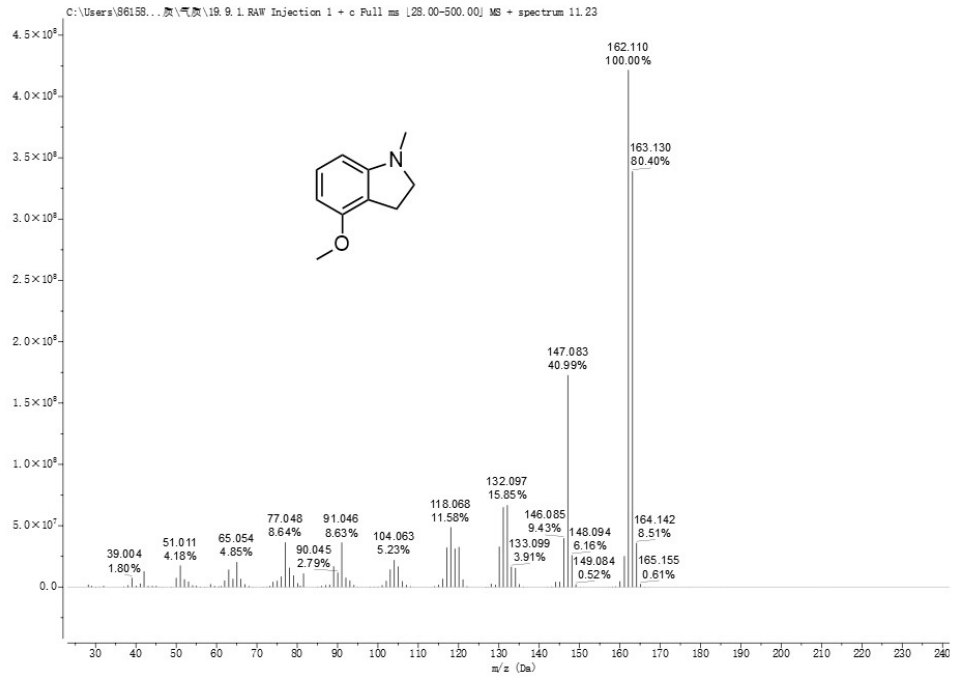


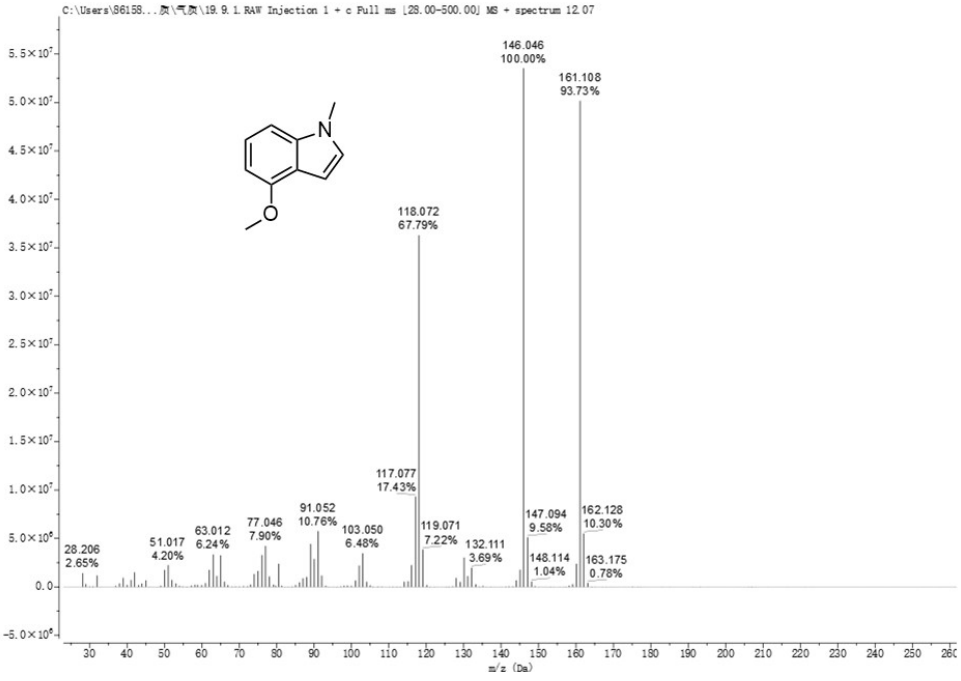
RT: 10.37 - 14.00

Number of detected peaks: 4

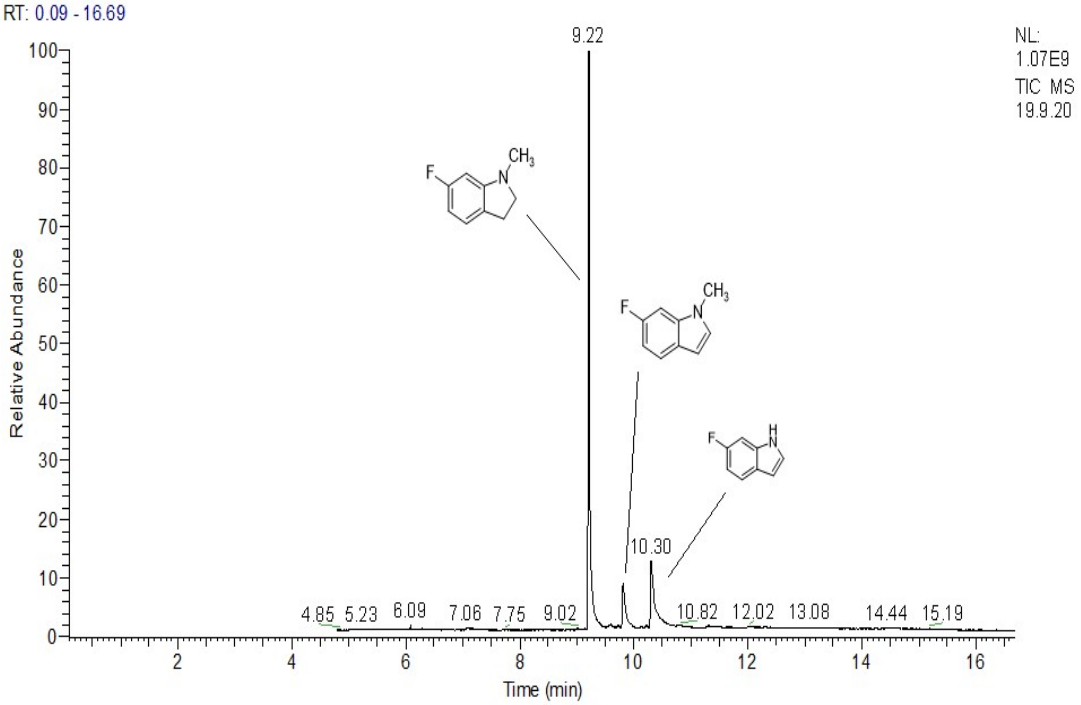
Apex RT	Start RT	End RT	Area	%Area	Height	%Height
11.23	11.20	11.53	2941429174.550	52.63	1824214091.880	59.04

11.82	11.74	11.87	50885801.751	0.91	9480786.580	0.31
12.05	12.02	12.21	1504997305.836	26.93	856099687.587	27.71
12.25	12.24	12.47	1092068605.082	19.54	400056718.147	12.95





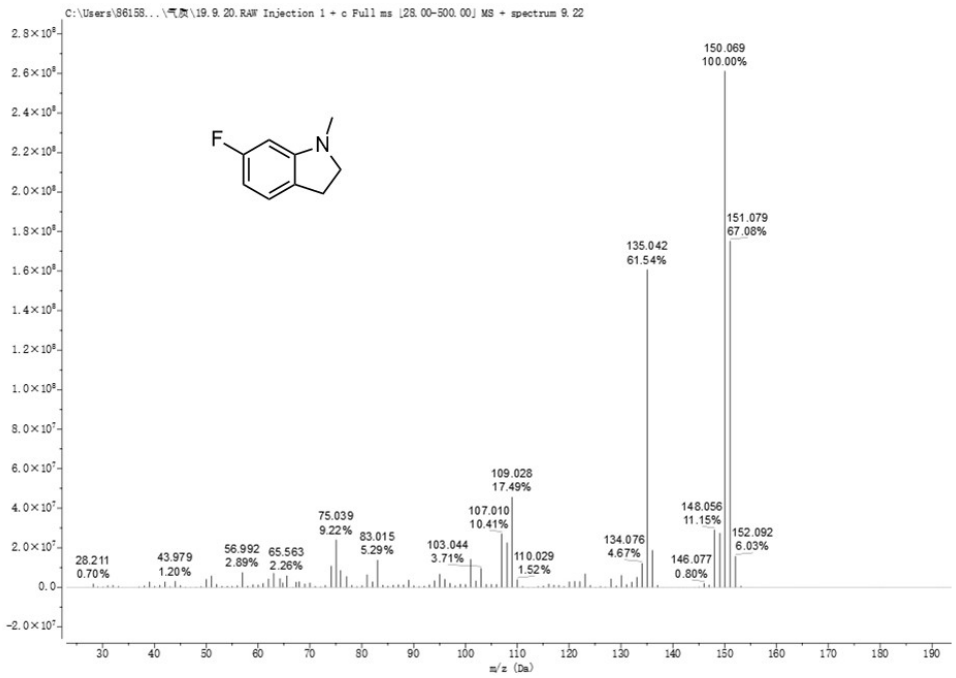
(8). GC-MS spectrum for substrate: 6-fluoroindole

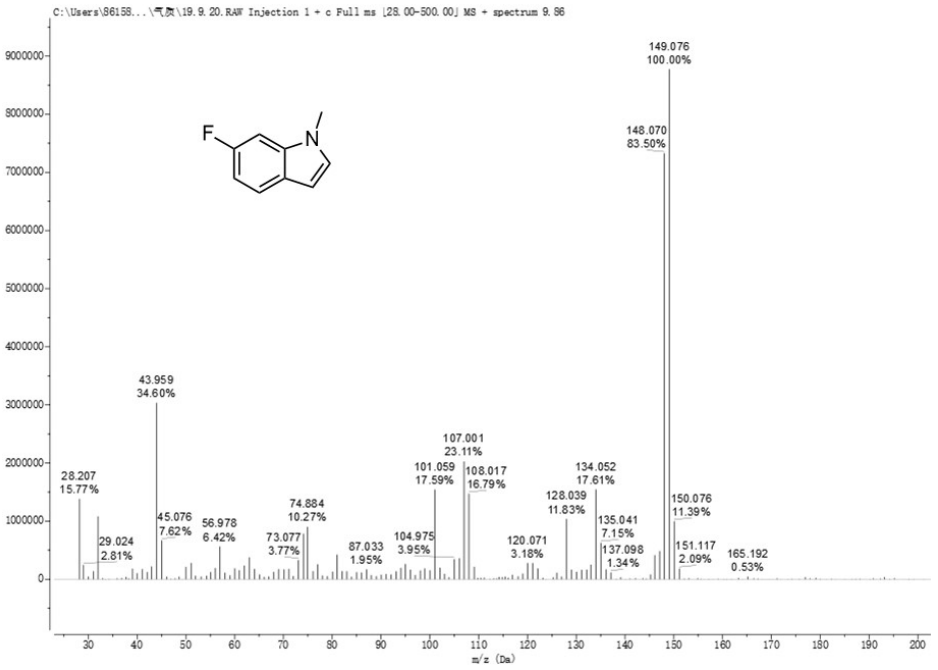


RT: 8.76 - 11.88

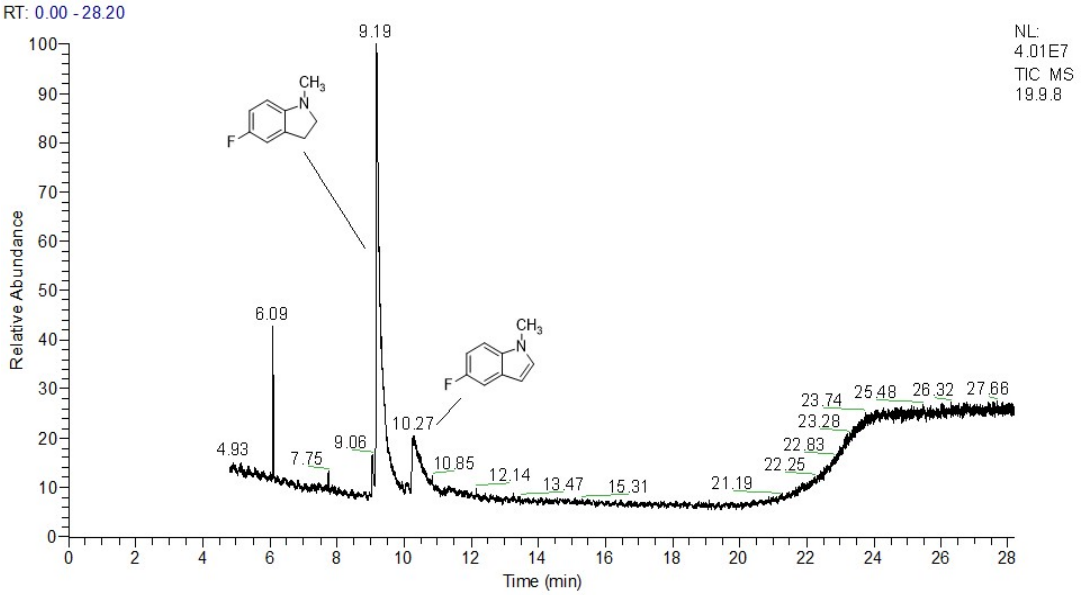
Number of detected peaks: 3

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
9.22	9.19	9.48	1945334308.656	68.08	1063441748.747	83.66
9.82	9.78	9.96	259090976.968	9.07	81552111.990	6.42
10.30	10.27	10.58	652944669.076	22.85	126194824.077	9.93





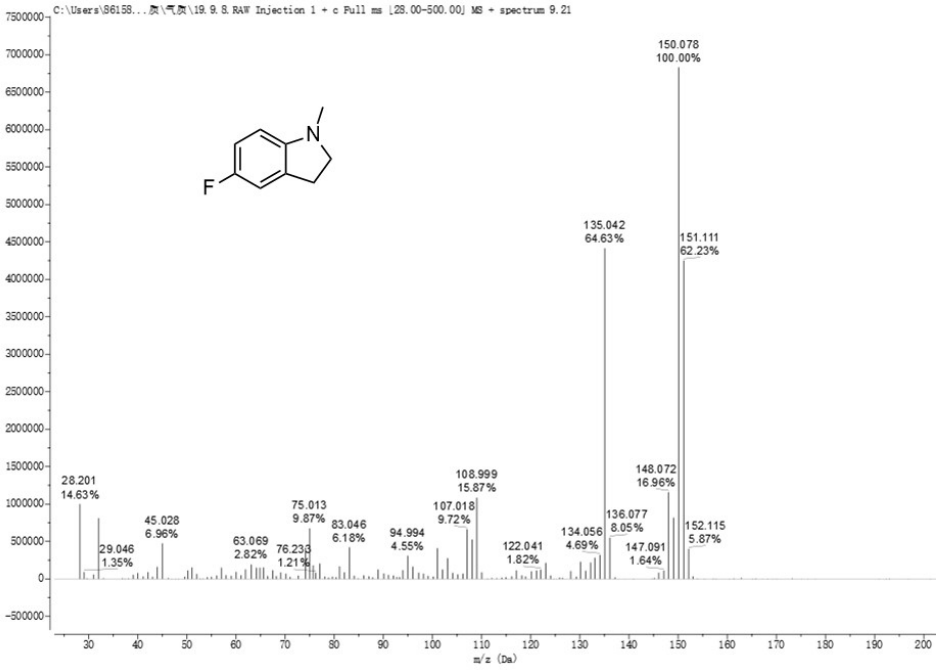
(9). GC-MS spectrum for substrate: 5-fluoroindole

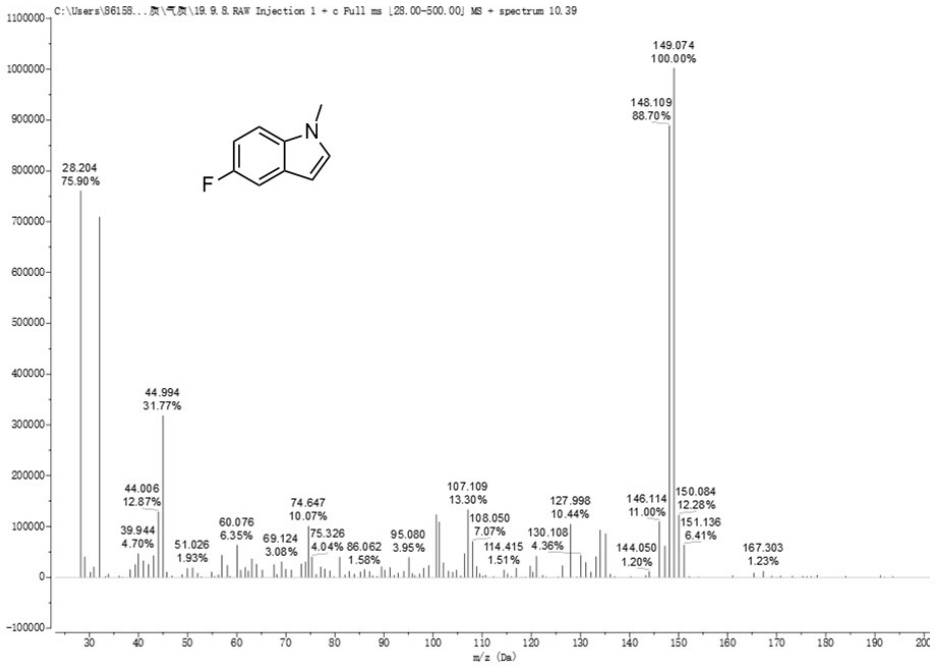


RT: 0.00 - 28.20

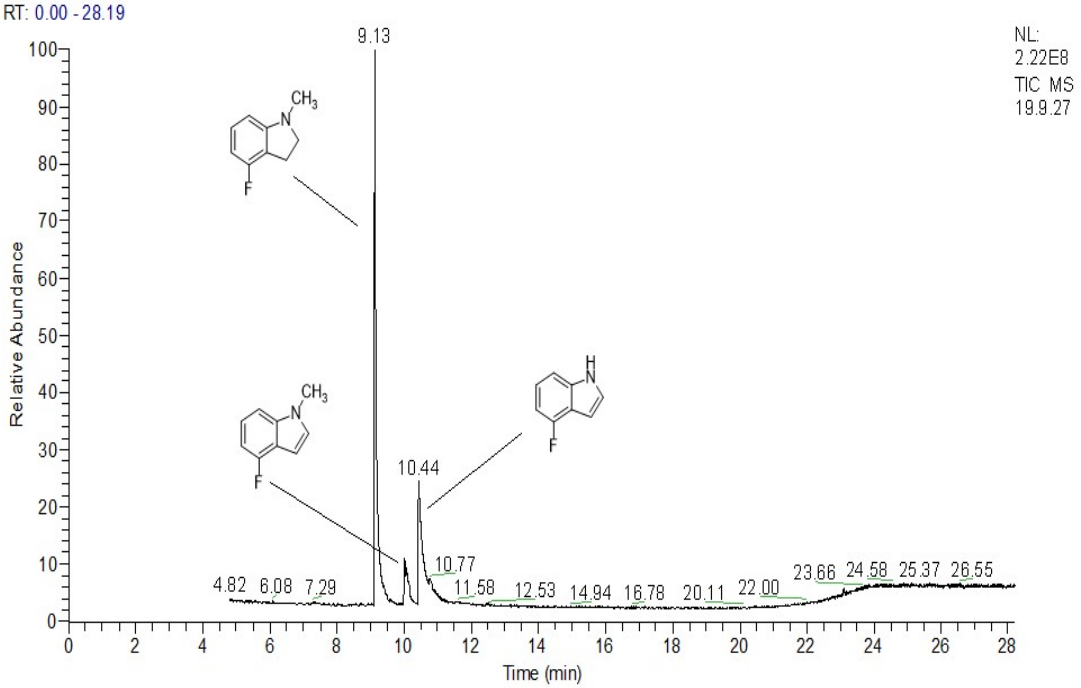
Number of detected peaks: 2

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
9.19	9.08	9.90	378567507.299	76.14	37214218.615	87.72
10.27	10.21	11.09	118661706.663	23.86	5209109.789	12.28


C:\Users\86158...质\气质\19.9.8.RAW Injection 1 + c Full ms [28.00-500.00] MS + spectrum 9.21
150.078
100.00%
135.042
64.63%
151.111
62.23%
148.072
16.96%
108.999
15.87%
28.201
14.63%
75.013
9.87%
107.018
9.72%
136.077
8.05%
45.028
6.96%
83.046
6.18%
134.056
4.69%
152.115
5.87%
94.994
4.55%
29.046
1.35%
63.069
2.82%
76.233
1.21%
122.041
1.82%
147.091
1.64%
F
N
m/z (Da)


C:\Users\86158...质\气质\19.9.8.RAW Injection 1 + c Full ms [28.00-500.00] MS + spectrum 10.39
149.074
100.00%
148.109
88.70%
28.204
75.90%
44.994
31.77%
44.006
12.87%
107.109
13.30%
74.647
10.07%
146.114
11.00%
150.084
12.28%
108.050
7.07%
127.998
10.44%
60.076
6.35%
75.326
4.04%
151.136
6.41%
39.944
4.70%
69.124
3.08%
86.062
1.58%
95.080
3.95%
130.108
4.36%
114.415
1.51%
144.050
1.20%
167.303
1.23%
51.026
1.93%
F
N
m/z (Da)

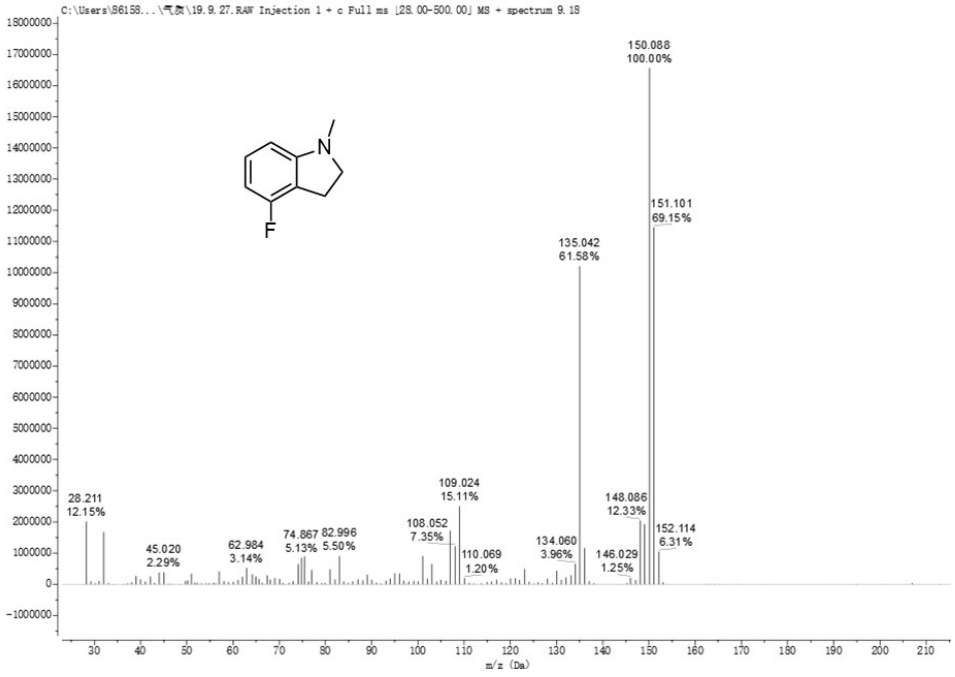
(10). GC-MS spectrum forsubstrate: 4-fluoroindole

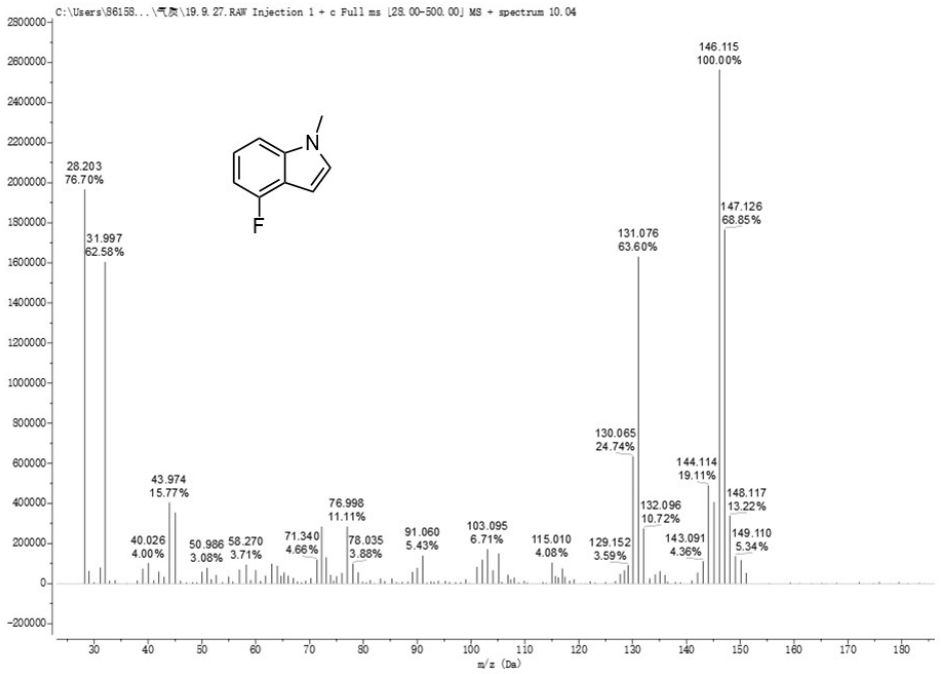


RT: 8.85 - 11.80

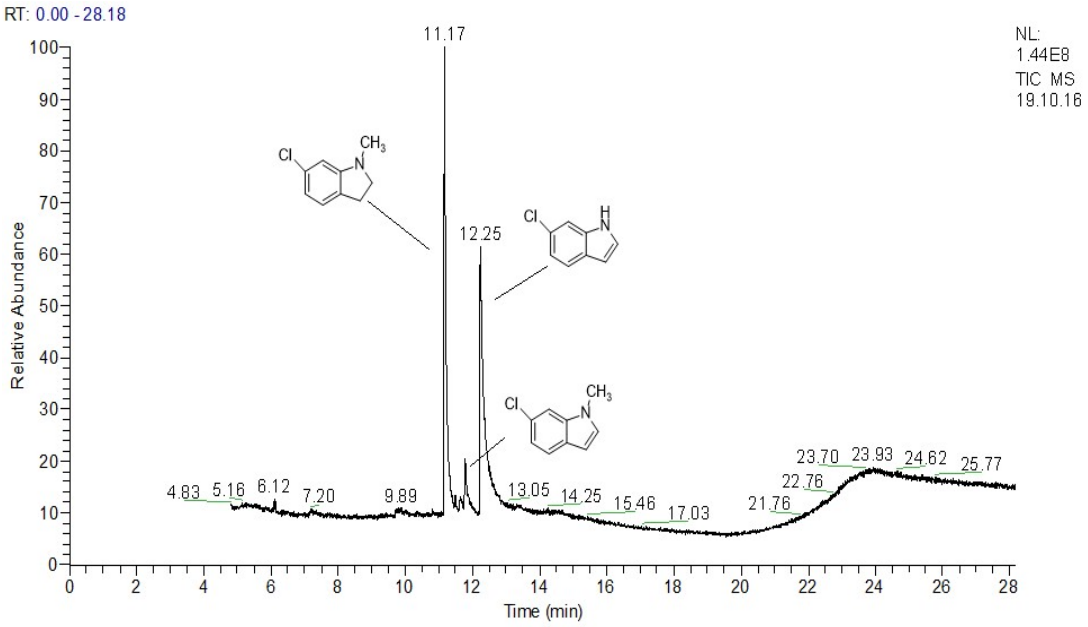
Number of detected peaks: 3

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
9.13	9.10	9.52	857198738.440	60.98	217314781.528	75.91
10.01	9.97	10.26	156369447.318	11.12	19802625.197	6.92
10.44	10.41	10.73	392138964.416	27.90	49163916.872	17.17





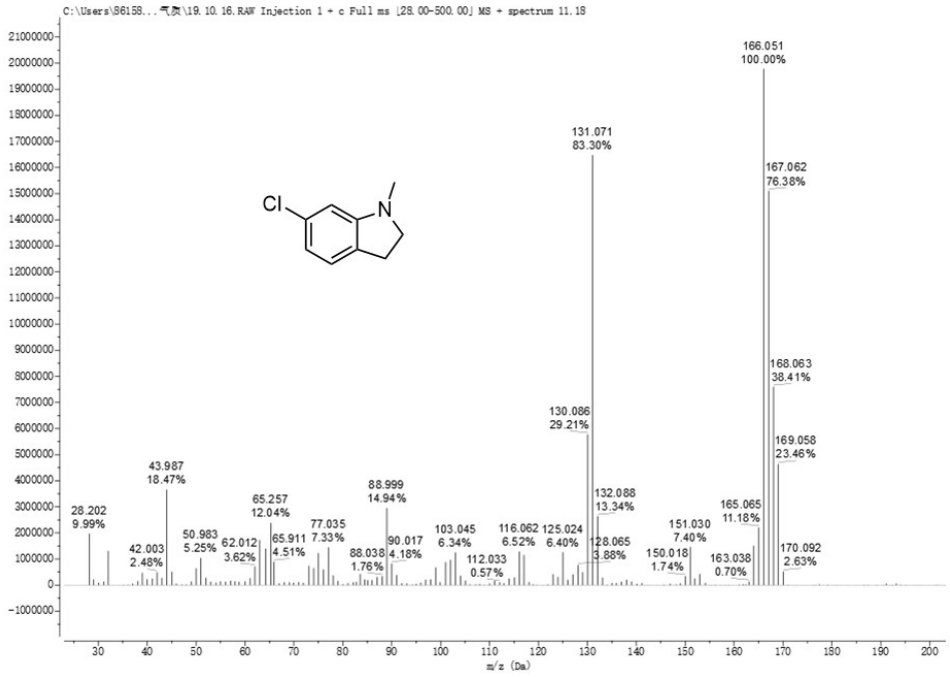
(11). GC-MS spectrum forsubstrate: 6-chloroindole

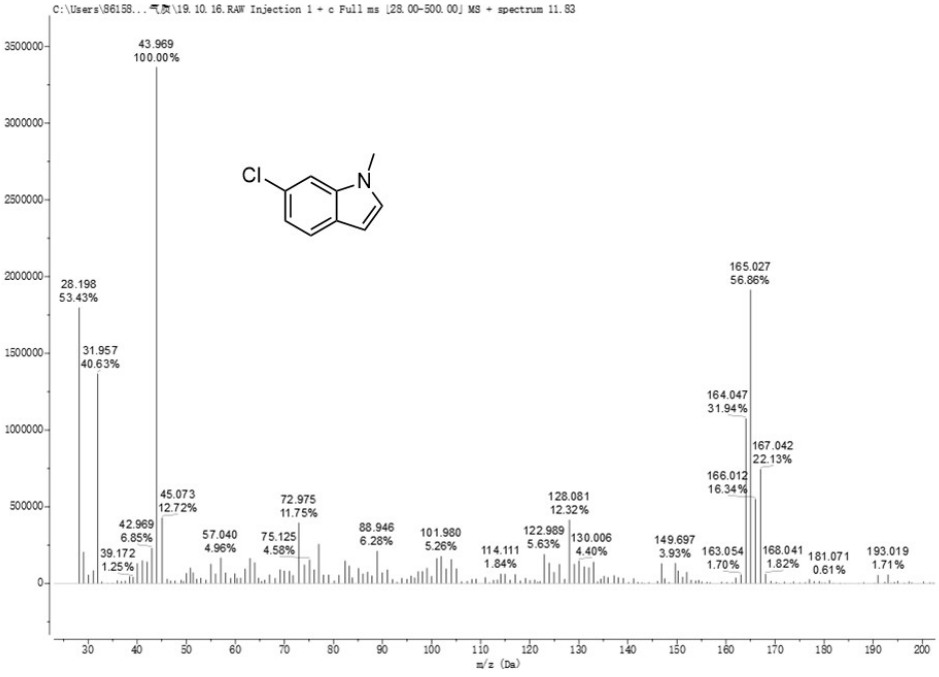


RT: 9.10 - 14.78

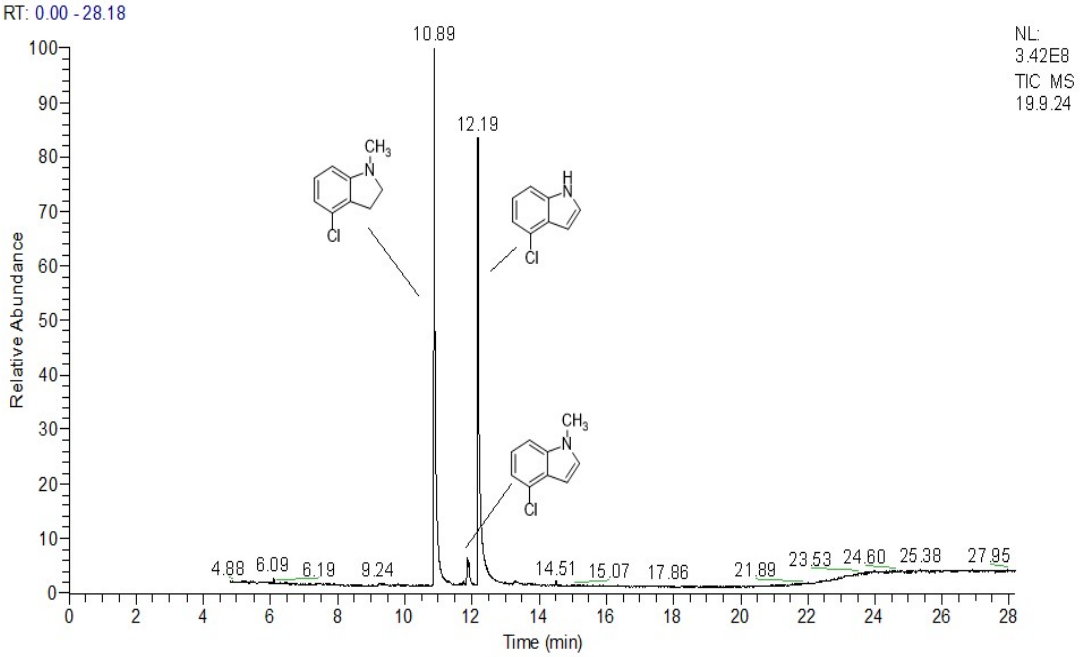
Number of detected peaks: 3

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
11.17	11.13	11.46	483013681.373	41.20	129469952.900	58.69
11.78	11.74	11.94	61972590.099	5.29	14741384.664	6.68
12.25	12.19	12.77	627516143.558	53.52	76389930.968	34.63


C:\Users\86158...\19.10.16.RAW Injection 1 + c Full ms [28.00-500.00] MS + spectrum 11.18
166.051
100.00%
131.071
83.30%
167.062
76.38%
168.063
38.41%
130.086
29.21%
169.058
23.46%
43.987
18.47%
88.999
14.94%
132.088
13.34%
65.257
12.04%
165.065
11.18%
28.202
9.99%
77.035
7.33%
151.030
7.40%
50.983
5.25%
62.012
3.62%
65.911
4.51%
103.045
6.34%
116.062
6.52%
125.024
6.40%
128.065
3.88%
170.092
2.63%
42.003
2.48%
90.017
4.18%
88.038
1.76%
112.033
0.57%
150.018
1.74%
163.038
0.70%
m/z (Da)


C:\Users\86158...\19.10.16.RAW Injection 1 + c Full ms [28.00-500.00] MS + spectrum 11.83
43.969
100.00%
165.027
56.86%
28.198
53.43%
31.957
40.63%
164.047
31.94%
167.042
22.13%
166.012
16.34%
45.073
12.72%
72.975
11.75%
128.081
12.32%
42.969
6.85%
88.946
6.28%
57.040
4.96%
75.125
4.58%
101.980
5.26%
122.989
5.63%
130.006
4.40%
149.697
3.93%
39.172
1.25%
114.111
1.84%
163.054
1.70%
168.041
1.82%
181.071
0.61%
193.019
1.71%
m/z (Da)

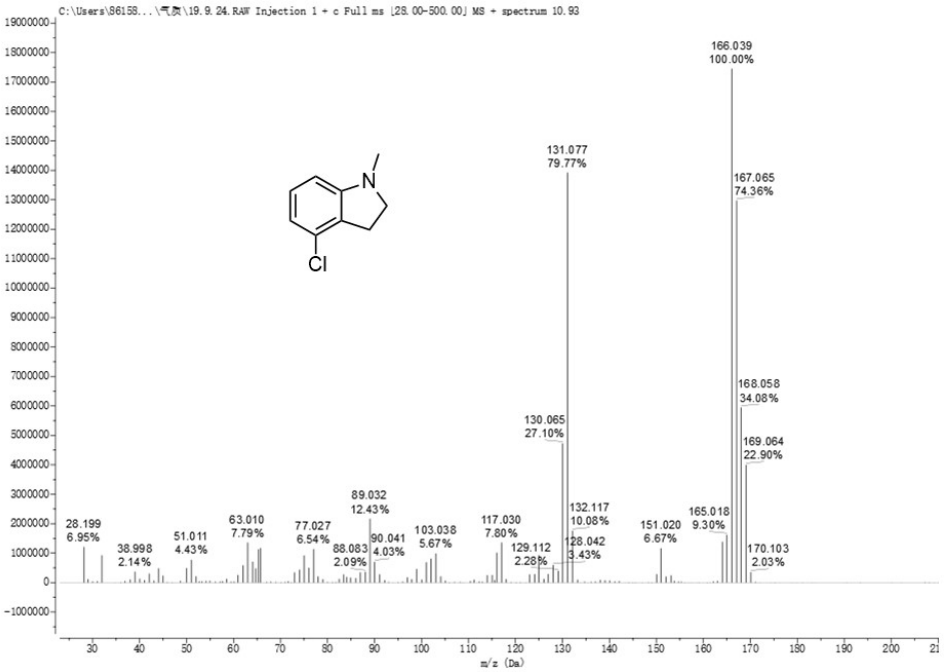
(12). GC-MS spectrum for substrate: 4-chloroindole

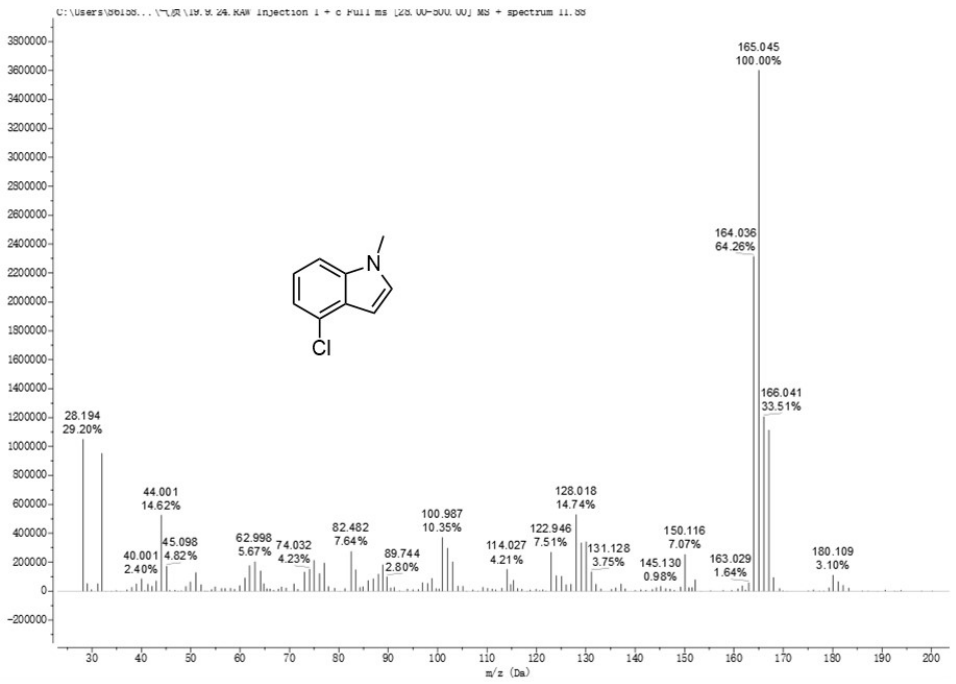


RT: 9.95 - 17.89

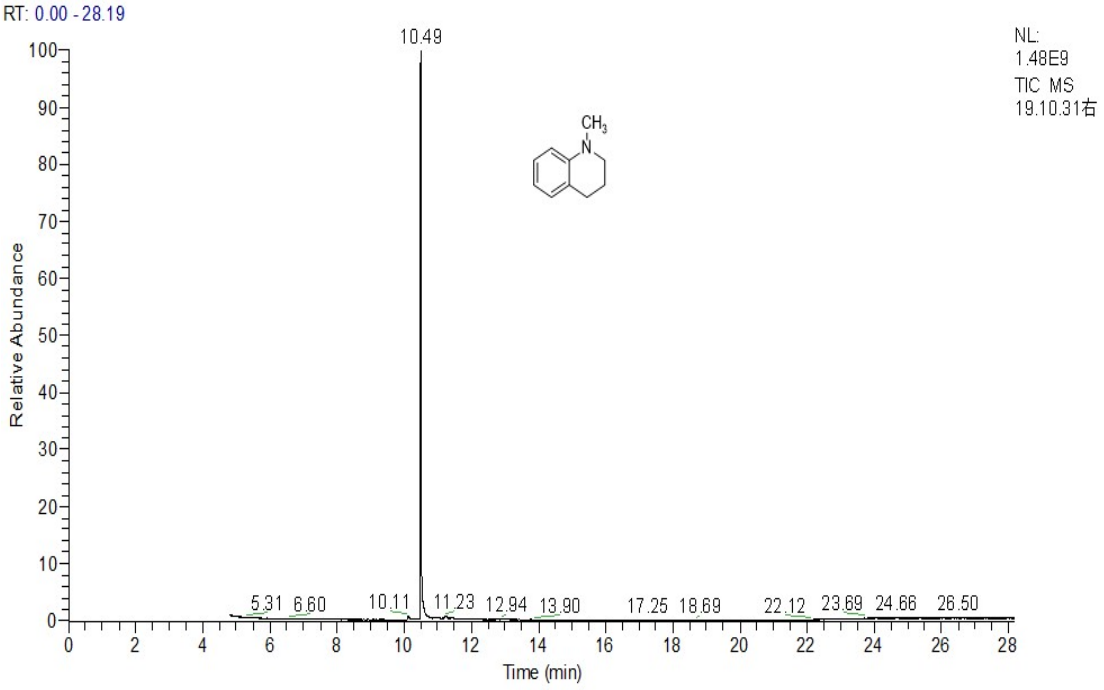
Number of detected peaks: 3

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
10.89	10.87	11.45	1075763021.516	48.38	337921127.393	53.04
11.86	11.81	12.04	91808904.408	4.13	17724087.128	2.78
12.19	12.16	12.58	1056035523.616	47.49	281494268.521	44.18





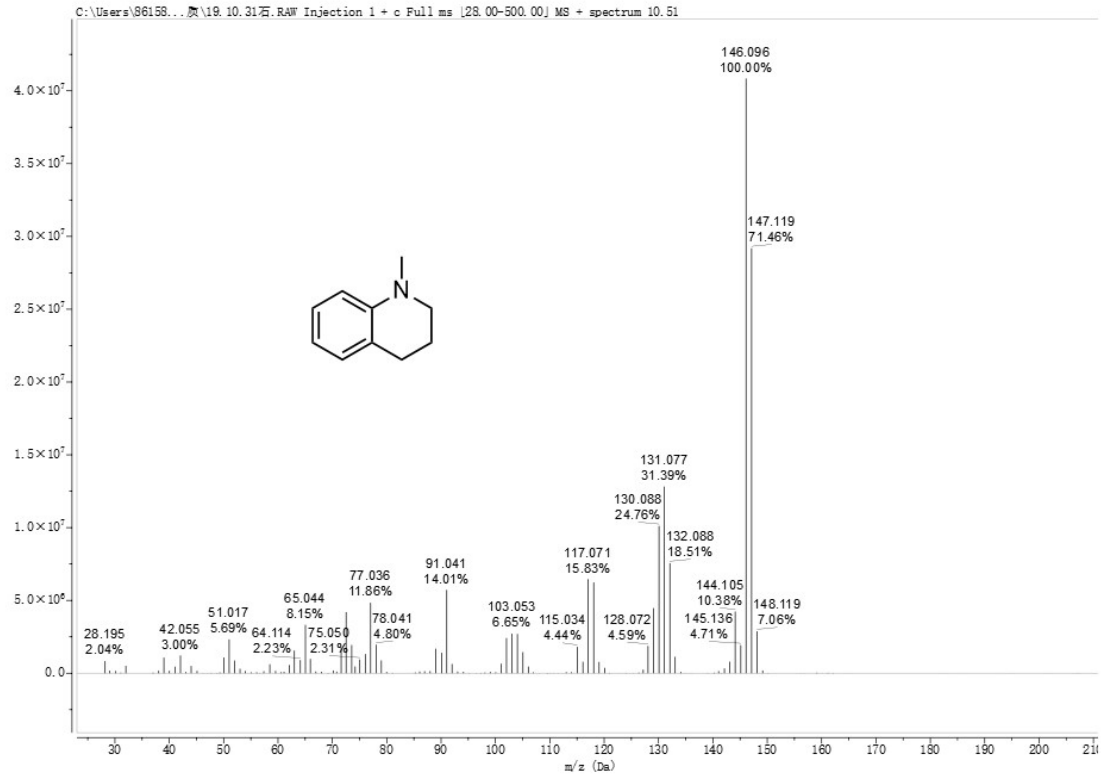
(13). GC-MS spectrum for substrate: quinoline



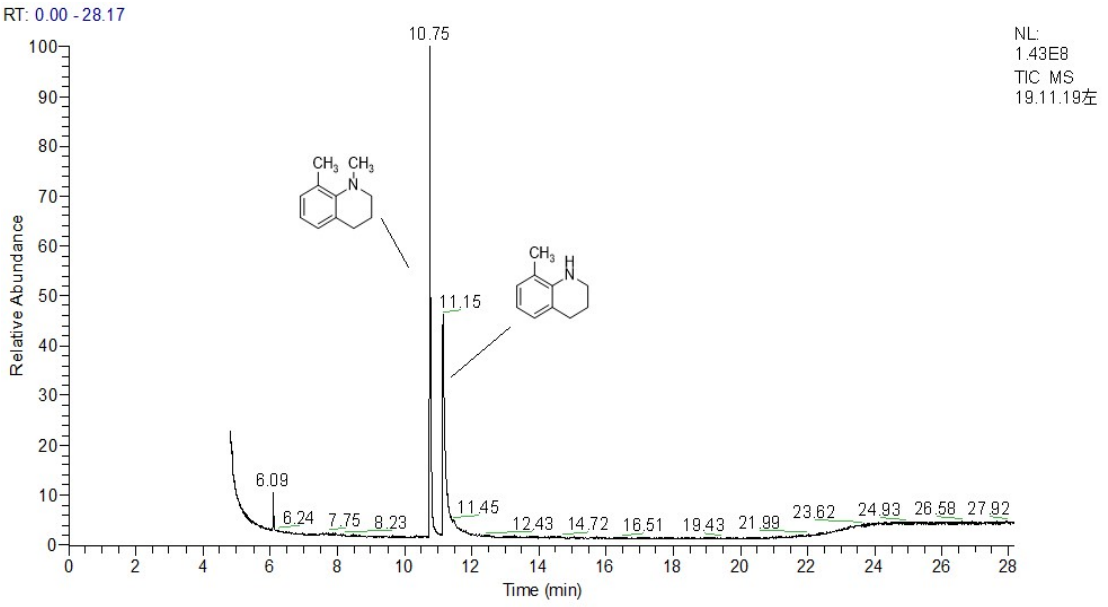
RT: 9.16 - 14.02

Number of detected peaks: 1

Apex RT	Start RT	End RT	Area%Area	Height	%Height
10.49	10.45	10.64	2288795699.069	100.00	1479789668.000	100.00



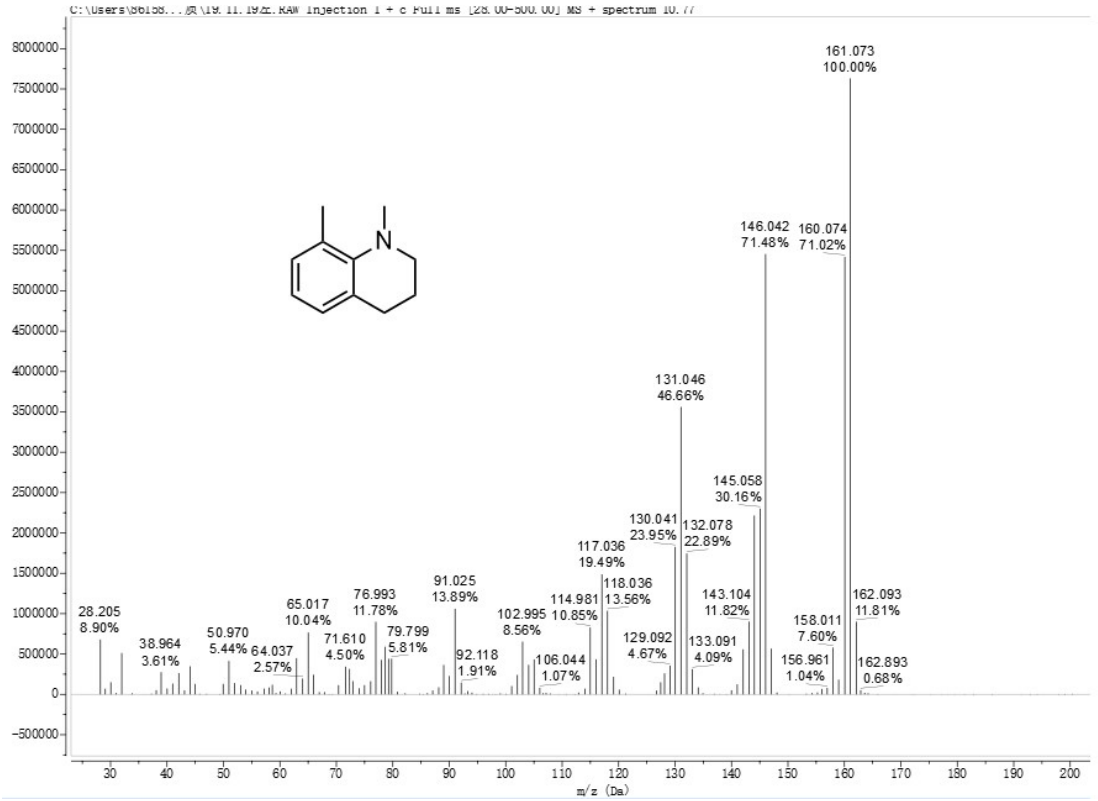
(14). GC-MS spectrum for substrate: 8-methylquinoline

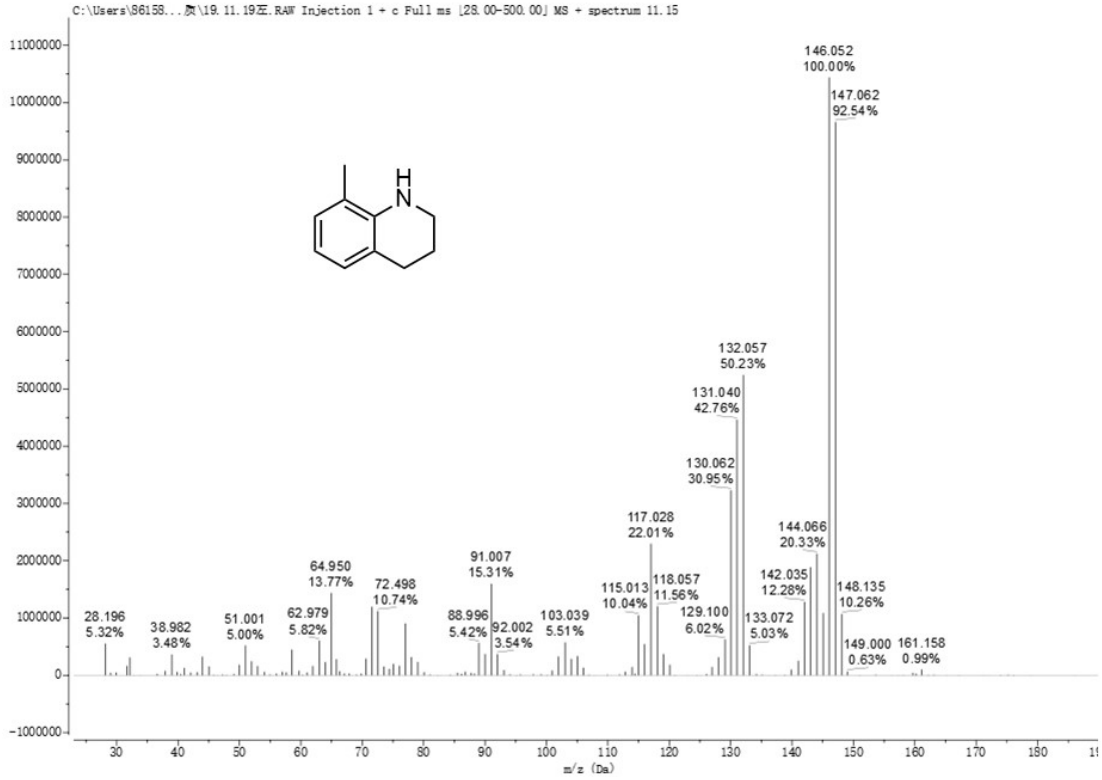


RT: 9.16 - 14.29

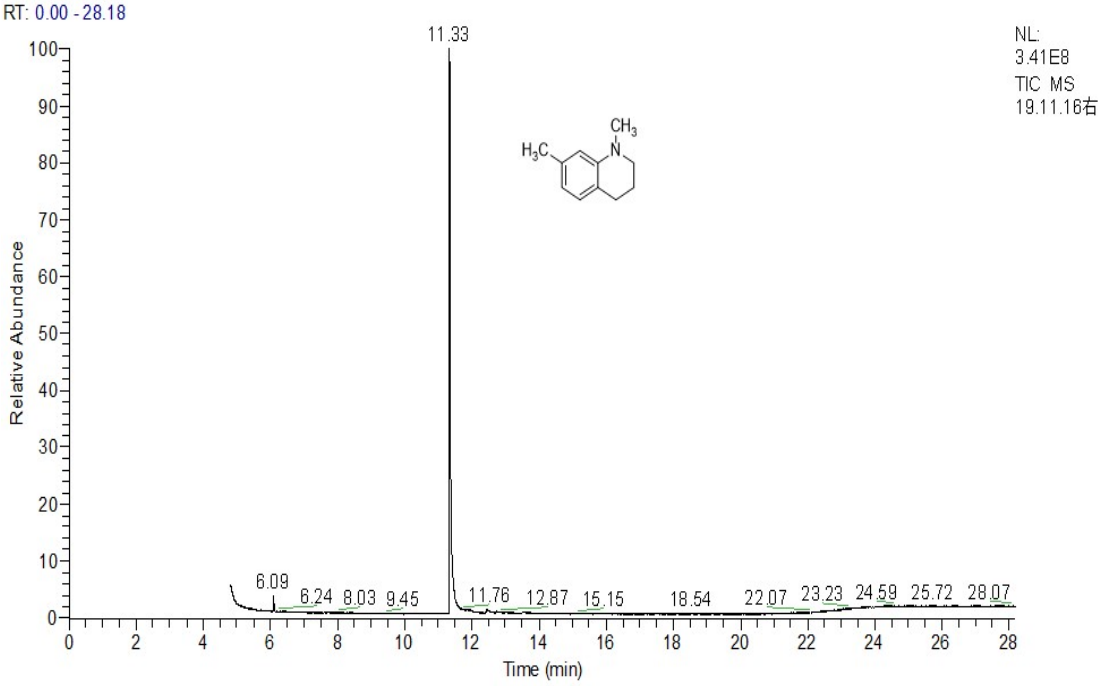
Number of detected peaks: 2

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
10.75	10.72	10.94	335596677.281	45.42	141619240.733	68.21
11.15	11.12	11.65	403251059.347	54.58	66000258.247	31.79


161.073
100.00%
146.042
71.48%
160.074
71.02%
131.046
46.66%
145.058
30.16%
130.041
23.95%
132.078
22.89%
117.036
19.49%
91.025
13.89%
118.036
13.56%
76.993
11.78%
65.017
10.04%
28.205
8.90%
114.981
10.85%
143.104
11.82%
162.093
11.81%
102.995
8.56%
158.011
7.60%
50.970
5.44%
38.964
3.61%
64.037
2.57%
71.610
4.50%
79.799
5.81%
92.118
1.91%
106.044
1.07%
129.092
4.67%
133.091
4.09%
156.961
1.04%
162.893
0.68%
m/z (Da)


146.052
100.00%
147.062
92.54%
132.057
50.23%
131.040
42.76%
130.062
30.95%
117.028
22.01%
144.066
20.33%
91.007
15.31%
64.950
13.77%
72.498
10.74%
142.035
12.28%
148.135
10.26%
118.057
11.56%
115.013
10.04%
129.100
6.02%
28.196
5.32%
38.982
3.48%
51.001
5.00%
62.979
5.82%
88.996
5.42%
92.002
3.54%
103.039
5.51%
133.072
5.03%
149.000
0.63%
161.158
0.99%
m/z (Da)

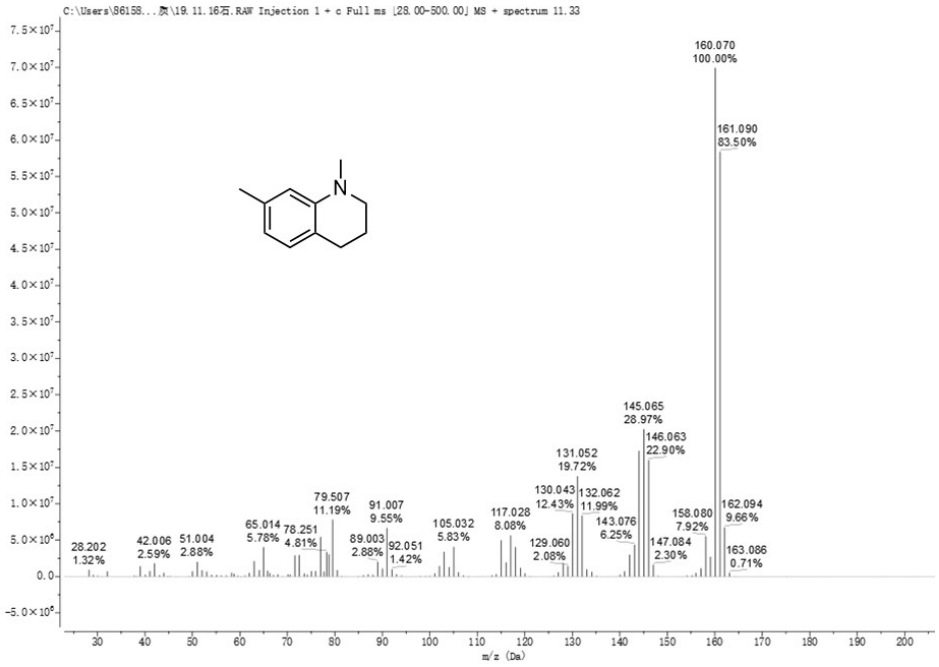
(15). GC-MS spectrum for substrate: 7-methylquinoline



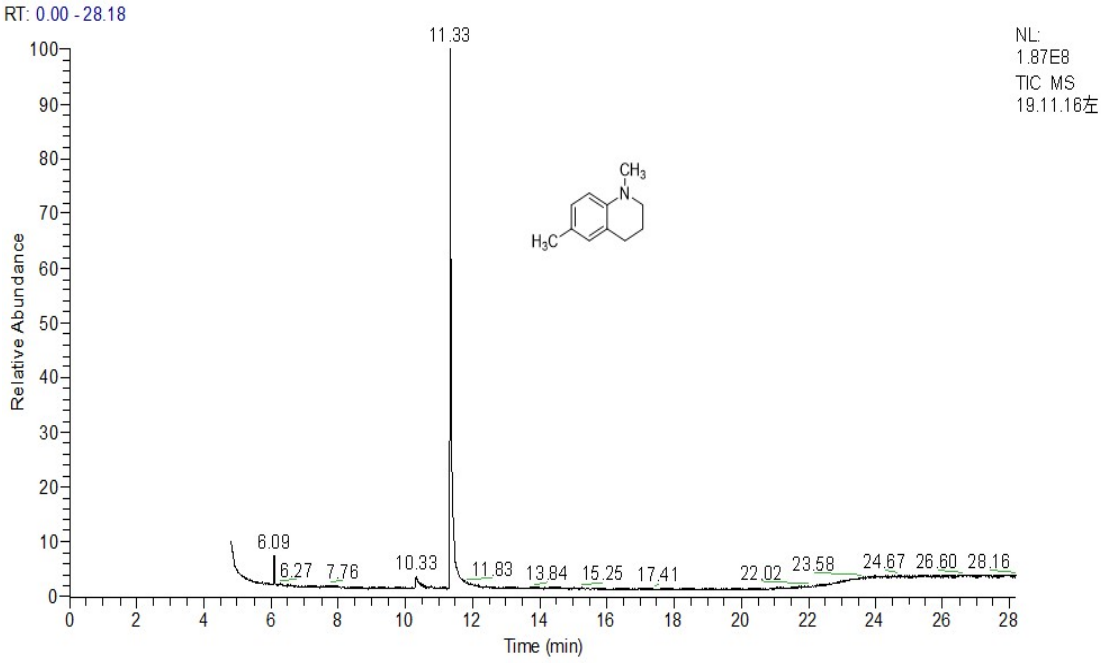
RT: 9.95 - 13.65

Number of detected peaks: 1

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
11.33	11.29	11.66	856889489.247	100.00	341153616.857	100.00



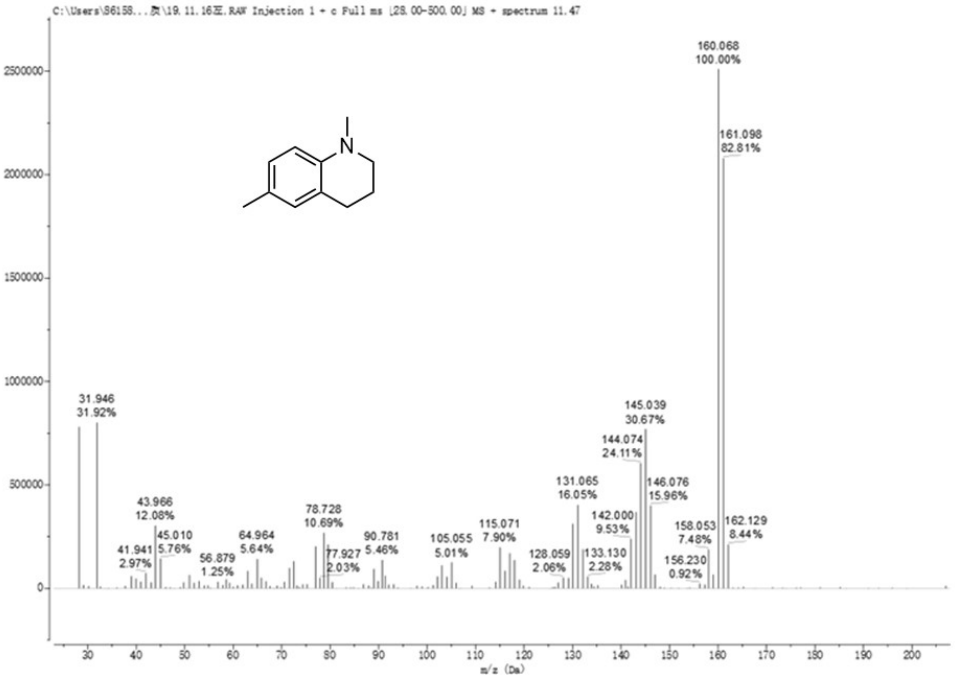
(16). GC-MS spectrum for substrate: 6-methylquinoline



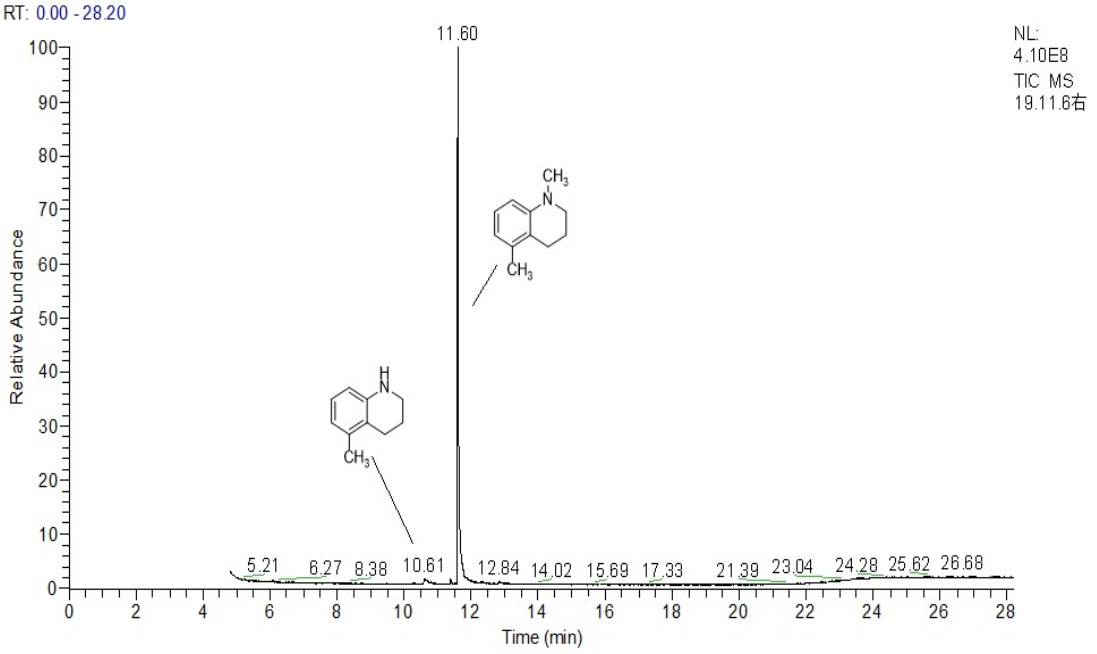
RT: 8.44 - 14.69

Number of detected peaks: 1

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
11.33	11.31	11.74	588875935.300	100.00	184578043.670	100.00



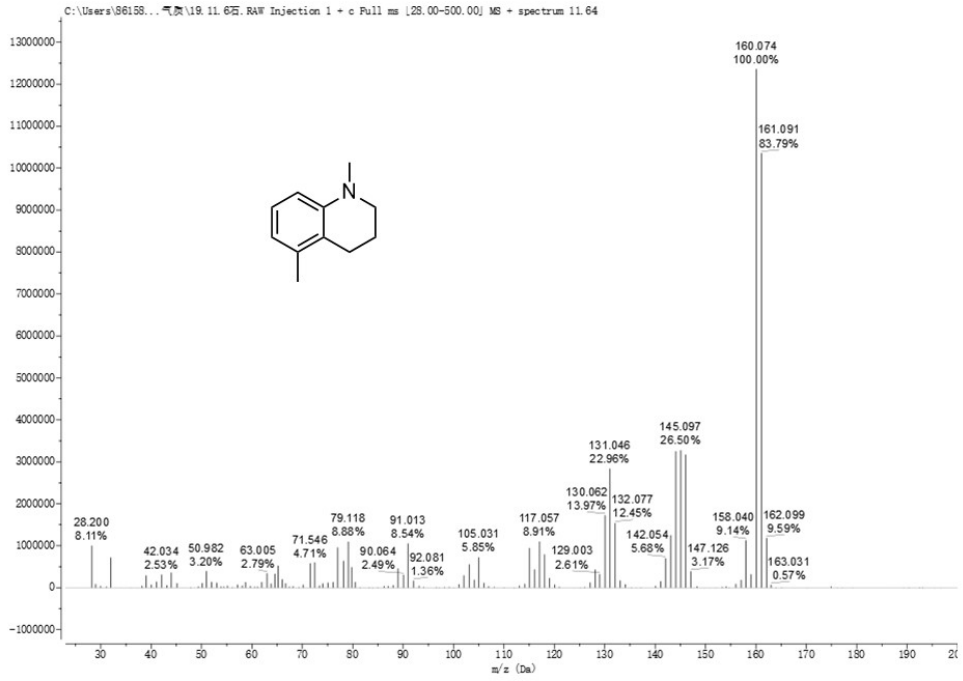
(17). GC-MS spectrum for substrate: 5-methylquinoline

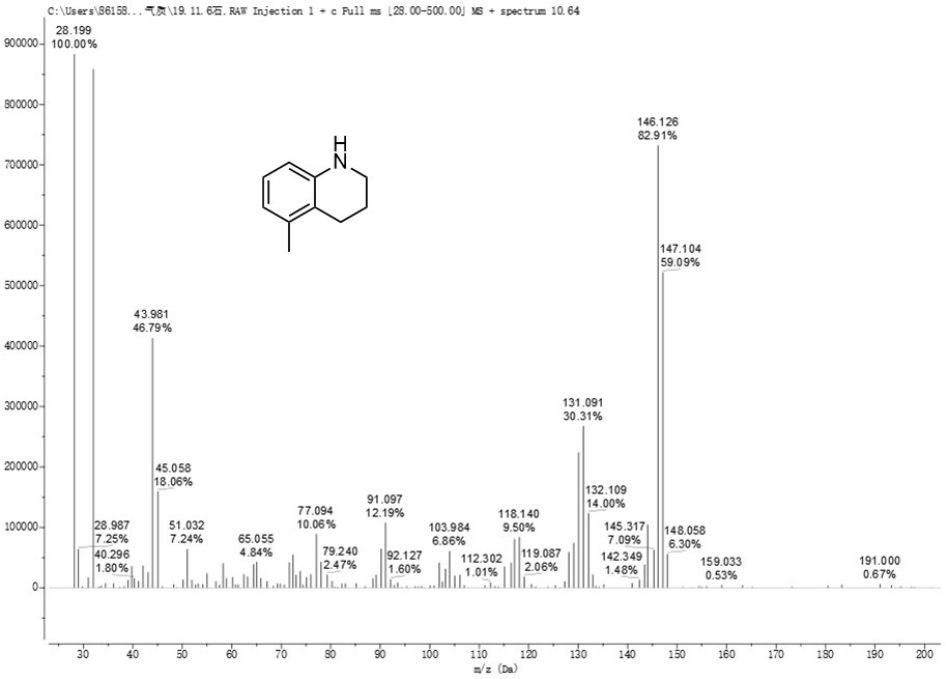


RT: 10.44 - 12.29

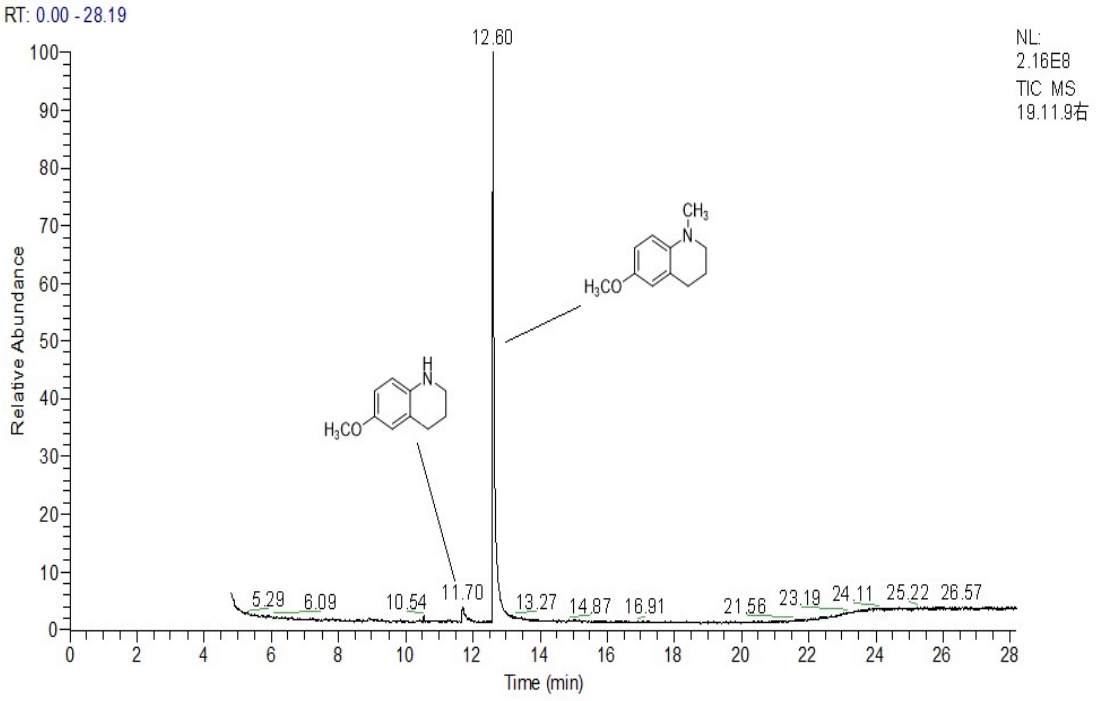
Number of detected peaks: 2

Apex RT	Start RT	End RT	Area%Area	Height	%Height
10.61	10.58	10.74	26827636.170	2.90	5359287.199	1.30
11.60	11.57	11.92	898771453.218	97.10	407492529.627	98.70





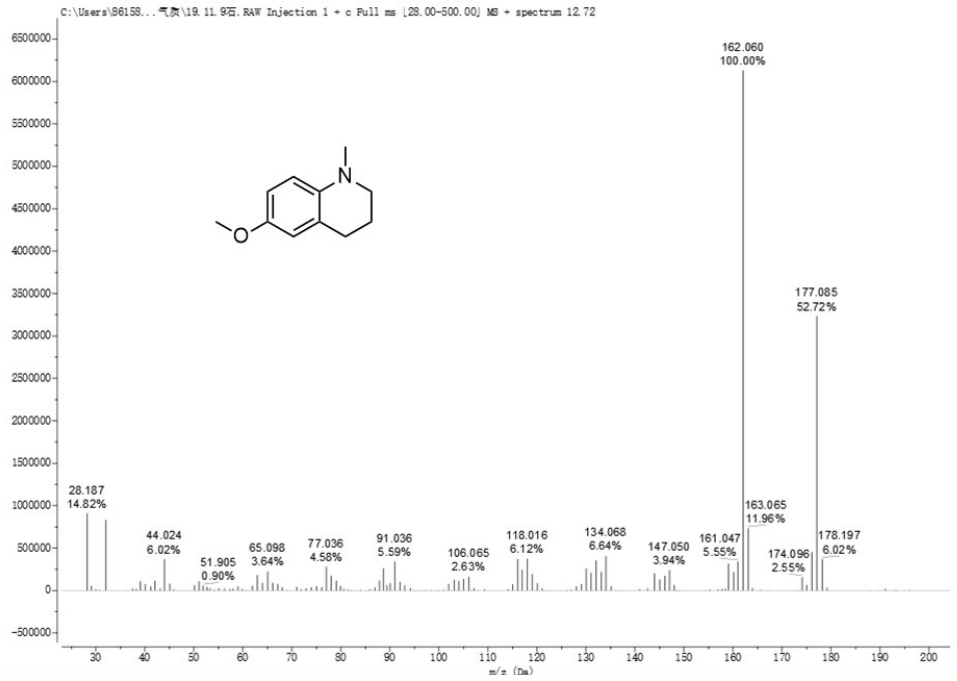
(18). GC-MS spectrum for substrate: 6-methoxyquinoline

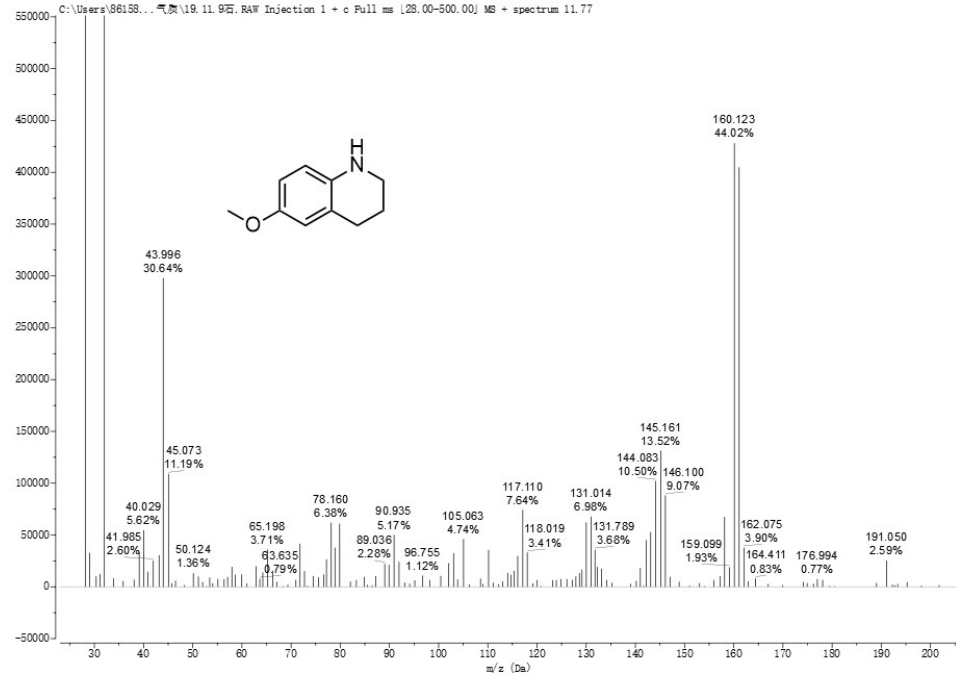


RT: 8.83 - 15.25

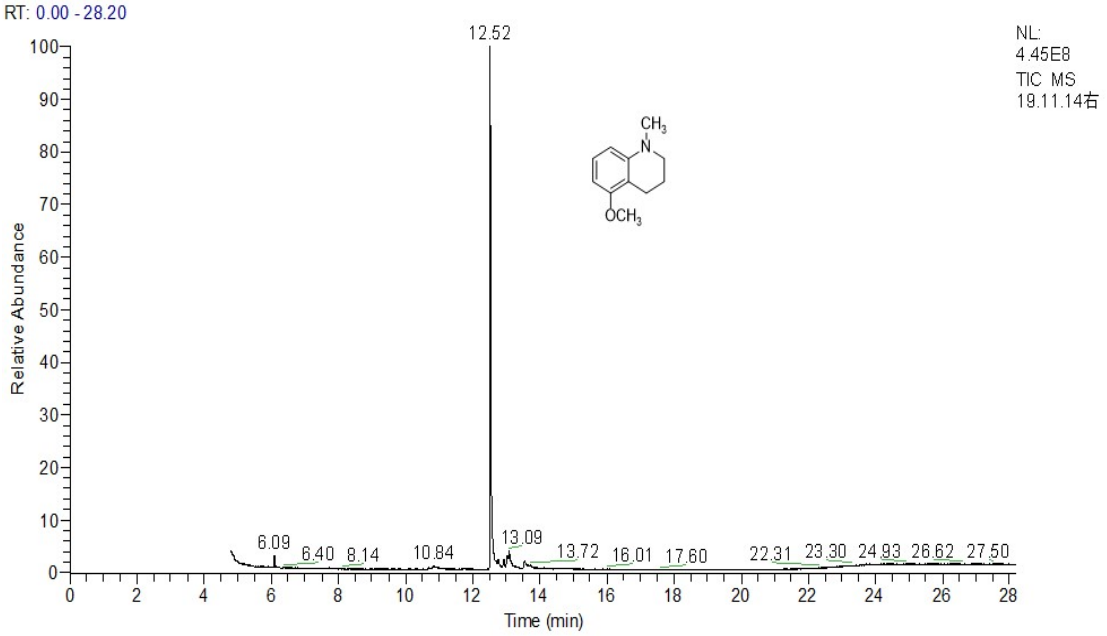
Number of detected peaks: 2

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
11.70	11.67	11.85	41830734.869	4.98	7926326.542	3.54
12.60	12.57	13.12	797333200.033	95.02	216047635.372	96.46


C:\Users\86158...气质\19.11.9石.RAW Injection 1 + c Full ms [28.00-500.00] MS + spectrum 12.72
162.060
100.00%
177.085
52.72%
28.187
14.82%
163.065
11.96%
44.024
6.02%
178.197
6.02%
51.905
0.90%
65.098
3.64%
77.036
4.58%
91.036
5.59%
106.065
2.63%
118.016
6.12%
134.068
6.64%
147.050
3.94%
161.047
5.55%
174.096
2.55%
m/z (Da)


C:\Users\86158...气质\19.11.9石.RAW Injection 1 + c Full ms [28.00-500.00] MS + spectrum 11.77
160.123
44.02%
43.996
30.64%
145.161
13.52%
144.083
10.50%
45.073
11.19%
146.100
9.07%
117.110
7.64%
131.014
6.98%
78.160
6.38%
40.029
5.62%
90.935
5.17%
105.063
4.74%
65.198
3.71%
162.075
3.90%
41.985
2.60%
89.036
2.28%
118.019
3.41%
131.789
3.68%
159.099
1.93%
191.050
2.59%
50.124
1.36%
96.755
1.12%
164.411
0.83%
176.994
0.77%
63.635
0.79%
m/z (Da)

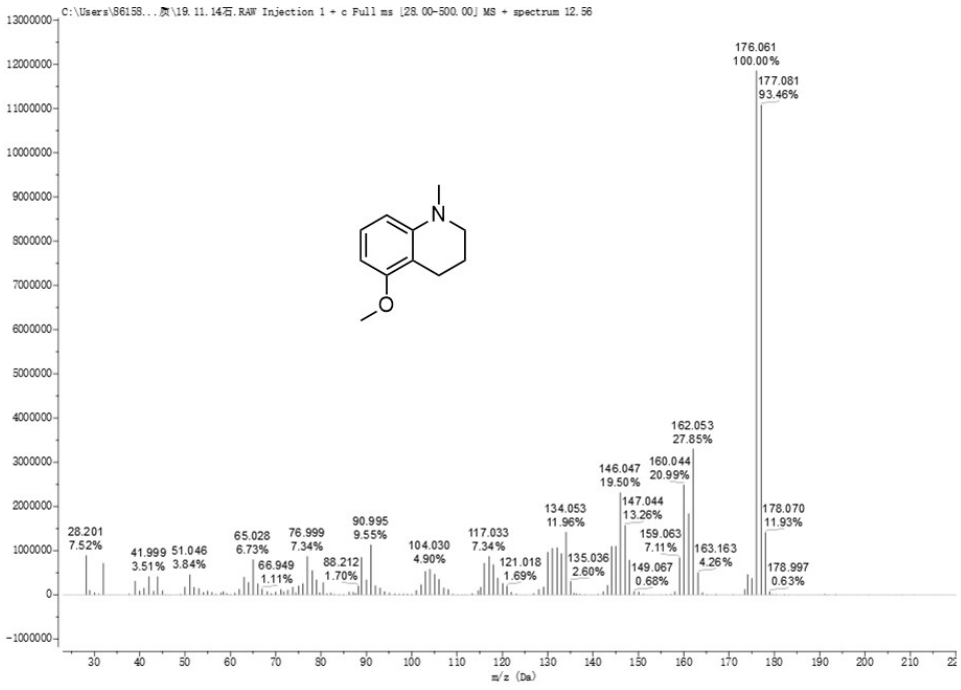
(19). GC-MS spectrum for substrate: 5-methoxyquinoline



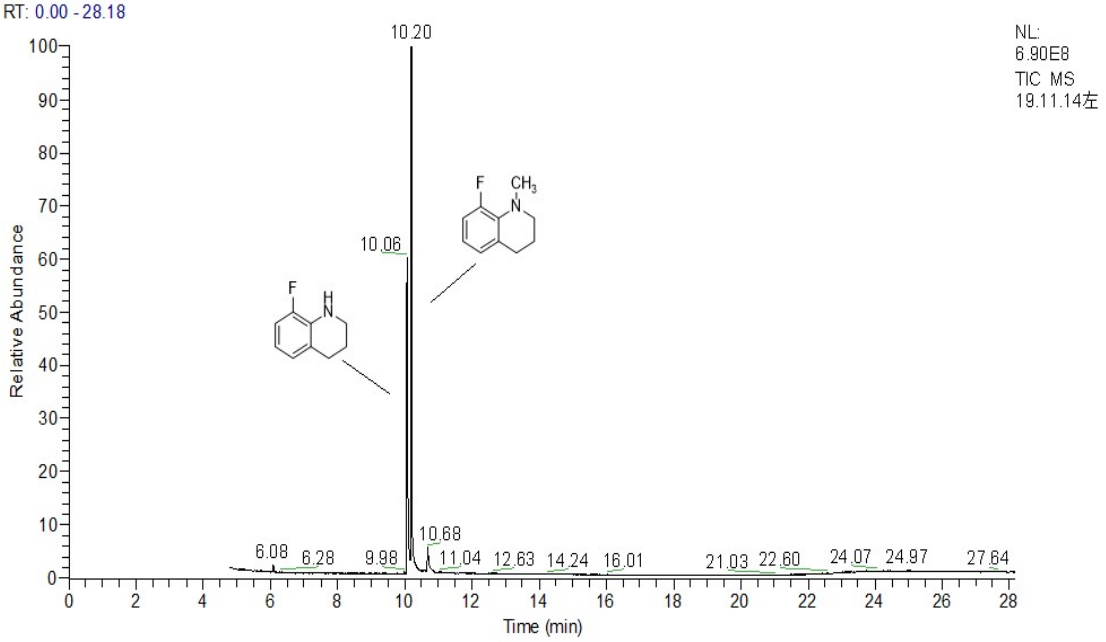
RT: 11.20 - 16.60

Number of detected peaks: 1

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
12.52	12.49	12.69	842698490.551	100.00	443040267.037	100.00



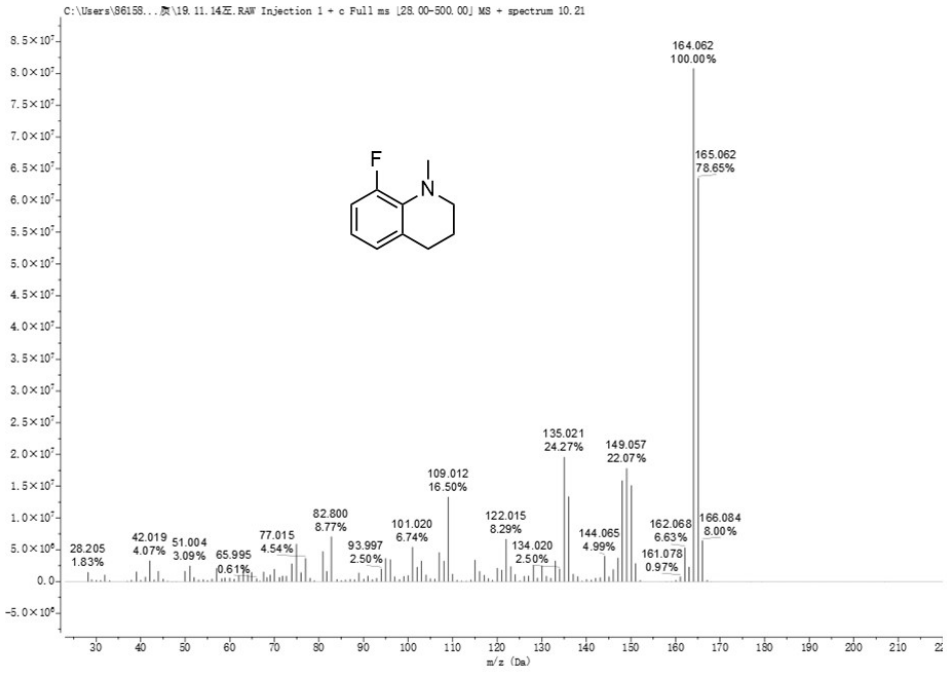
(20). GC-MS spectrum for substrate: 8-fluoroquinoline

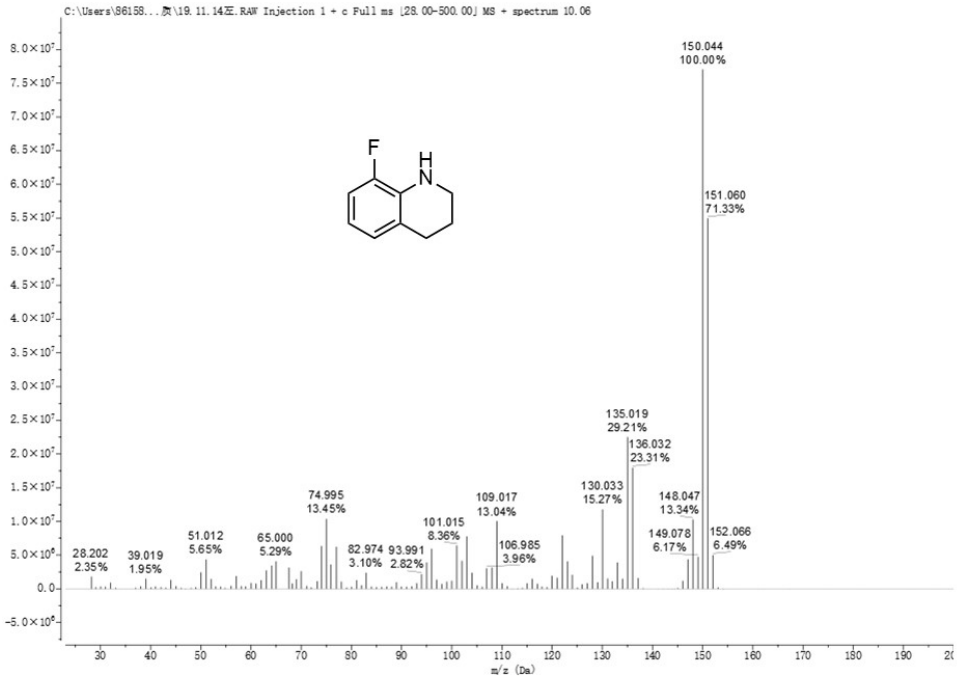


RT: 9.73 - 11.28

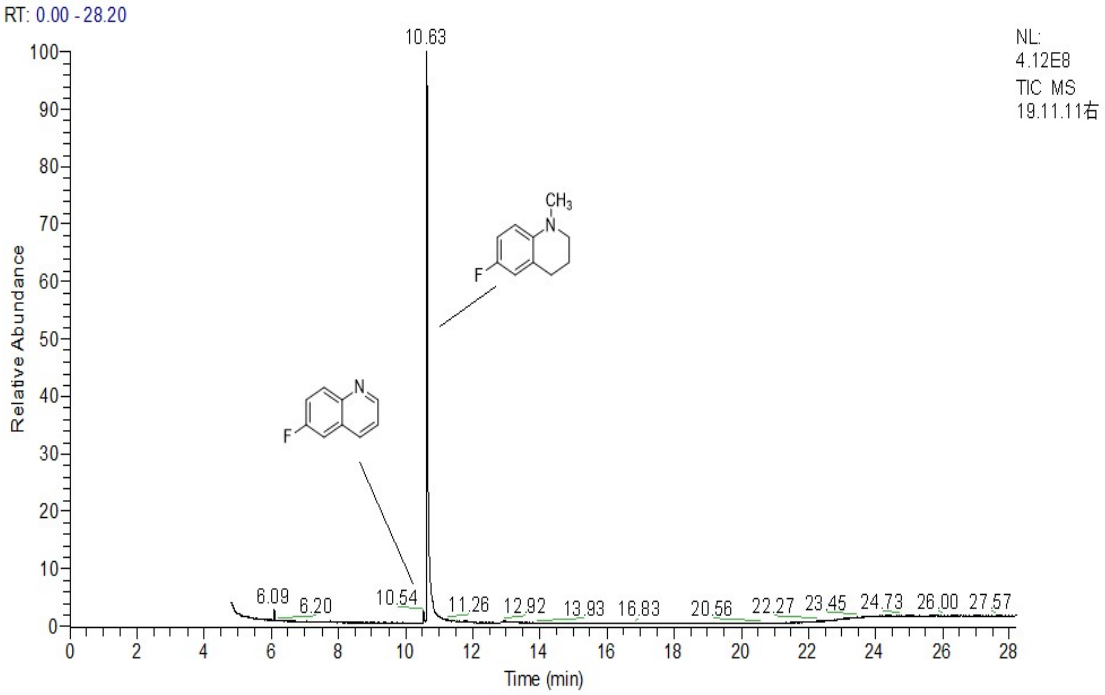
Number of detected peaks: 2

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
10.06	10.03	10.16	733392634.781	38.42	411121976.842	37.50
10.20	10.17	10.41	1175347995.005	61.58	685241265.698	62.50





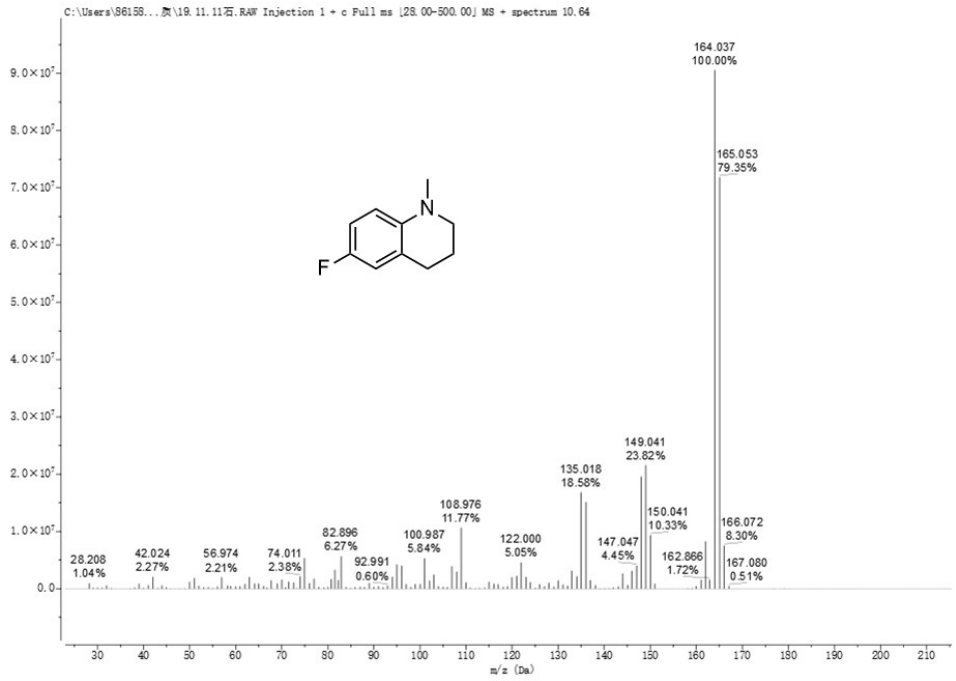
(21). GC-MS spectrum for substrate: 6-fluoroquinoline



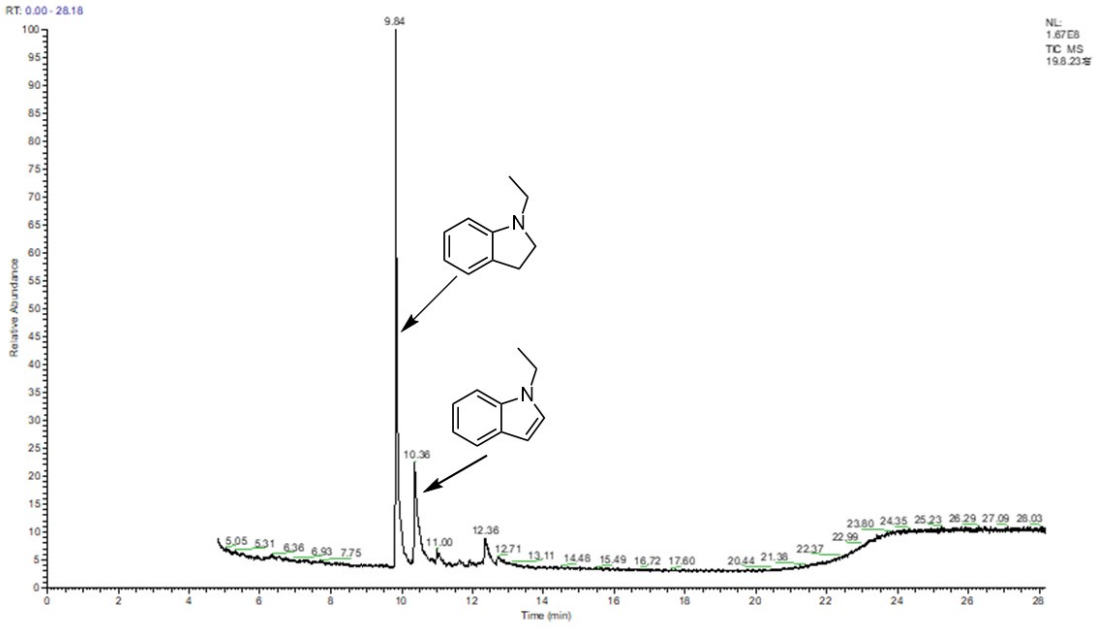
RT: 8.95 - 15.44

Number of detected peaks: 2

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
10.54	10.51	10.59	24446000.720	2.16	10054728.511	2.39
10.63	10.62	11.14	1107132951.556	97.84	410433857.654	97.61



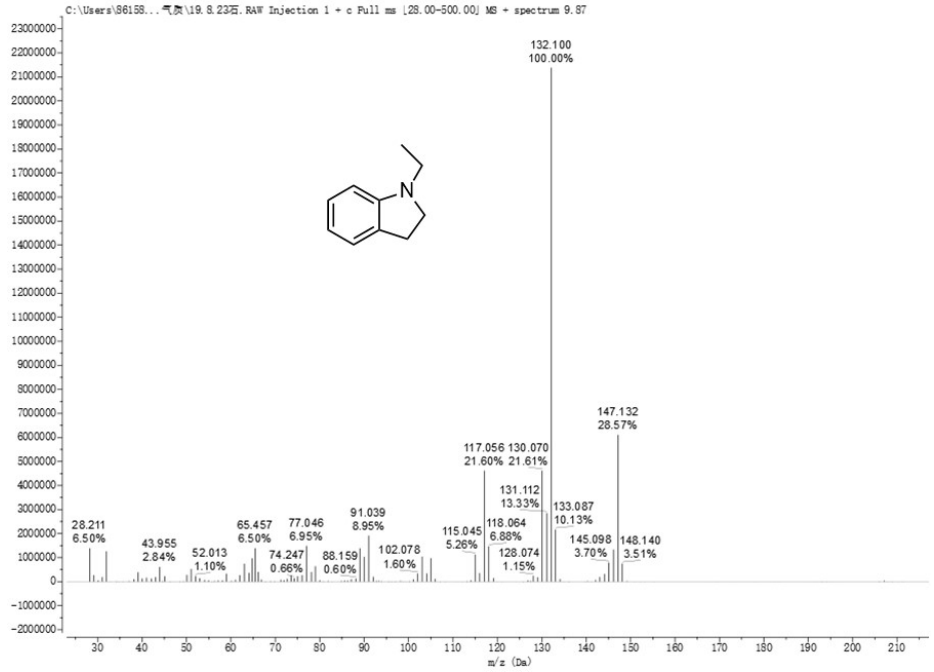
(22). GC-MS spectrum for Scheme 4

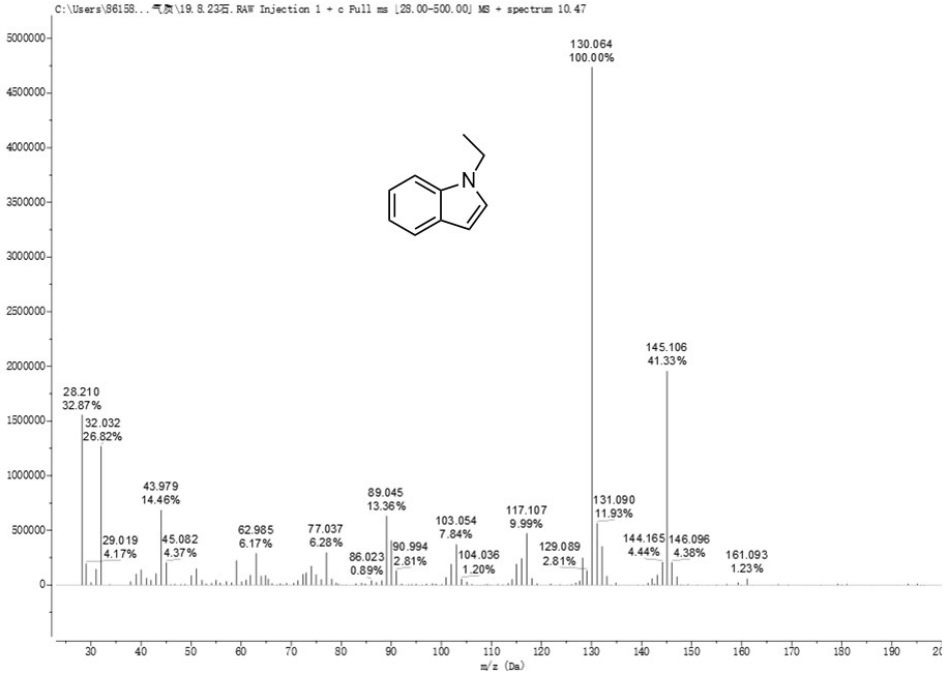


RT: 7.32 - 14.33

Number of detected peaks: 2

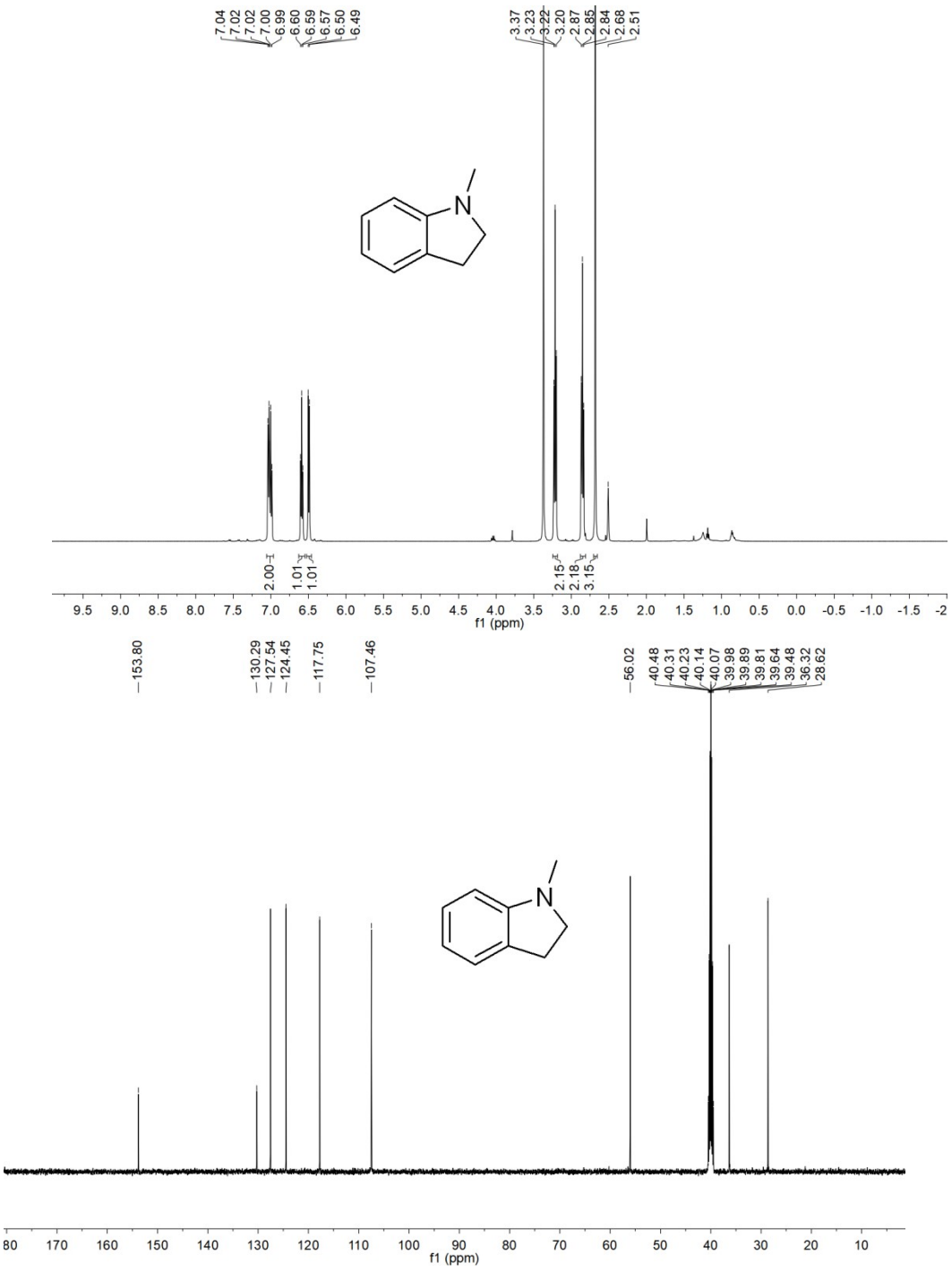
Apex RT	Start RT	End RT	Area	%Area	Height	%Height
9.84	9.79	10.26	565441844.181	71.00	160353423.235	84.40
10.36	10.34	10.78	230925790.529	29.00	29648065.246	15.60


C:\Users\86158...气质\19.8.23日.RAW Injection 1 + c Full ms [28.00-500.00] MS + spectrum 9.87
132.100
100.00%
147.132
28.57%
117.056
21.60%
130.070
21.61%
131.112
13.33%
133.087
10.13%
91.039
8.95%
65.457
6.50%
77.046
6.95%
28.211
6.50%
118.064
6.88%
115.045
5.26%
145.098
3.70%
148.140
3.51%
43.955
2.84%
52.013
1.10%
74.247
0.66%
88.159
0.60%
102.078
1.60%
128.074
1.15%
m/z (Da)

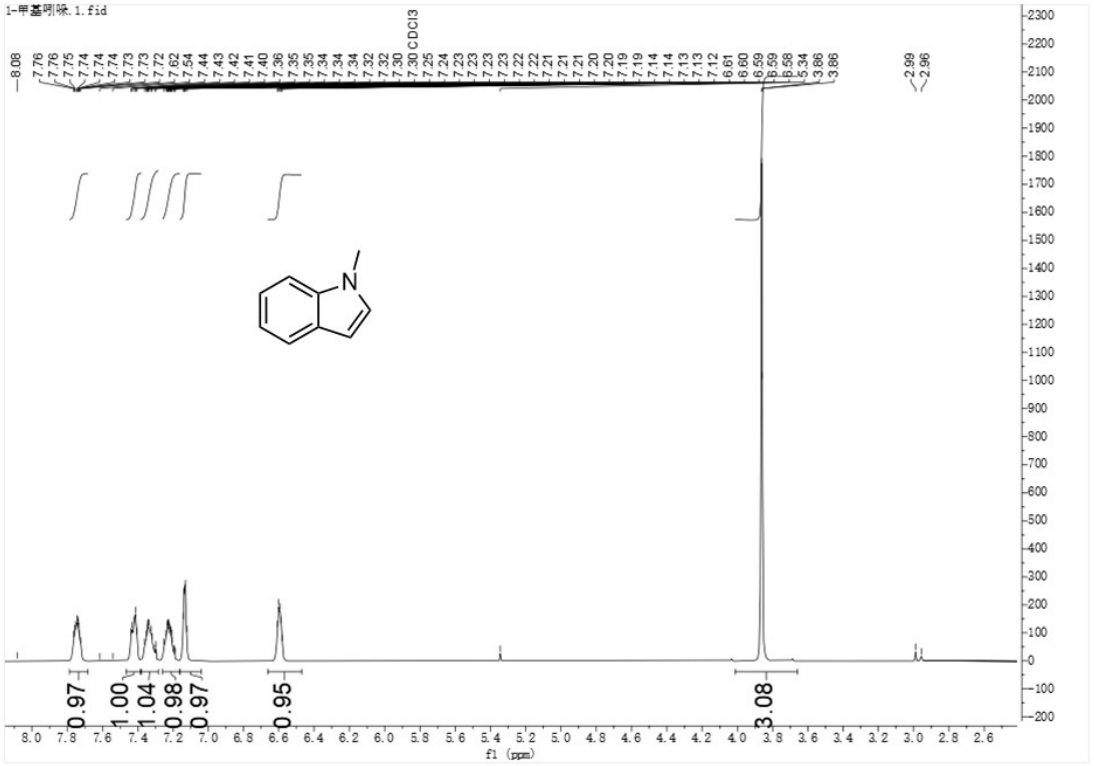

C:\Users\86158...气质\19.8.23日.RAW Injection 1 + c Full ms [28.00-500.00] MS + spectrum 10.47
130.064
100.00%
145.106
41.33%
28.210
32.87%
32.032
26.82%
43.979
14.46%
89.045
13.36%
131.090
11.93%
117.107
9.99%
103.054
7.84%
62.985
6.17%
77.037
6.28%
29.019
4.17%
45.082
4.37%
90.994
2.81%
104.036
1.20%
129.089
2.81%
144.165
4.44%
146.096
4.38%
161.093
1.23%
86.023
0.89%
m/z (Da)

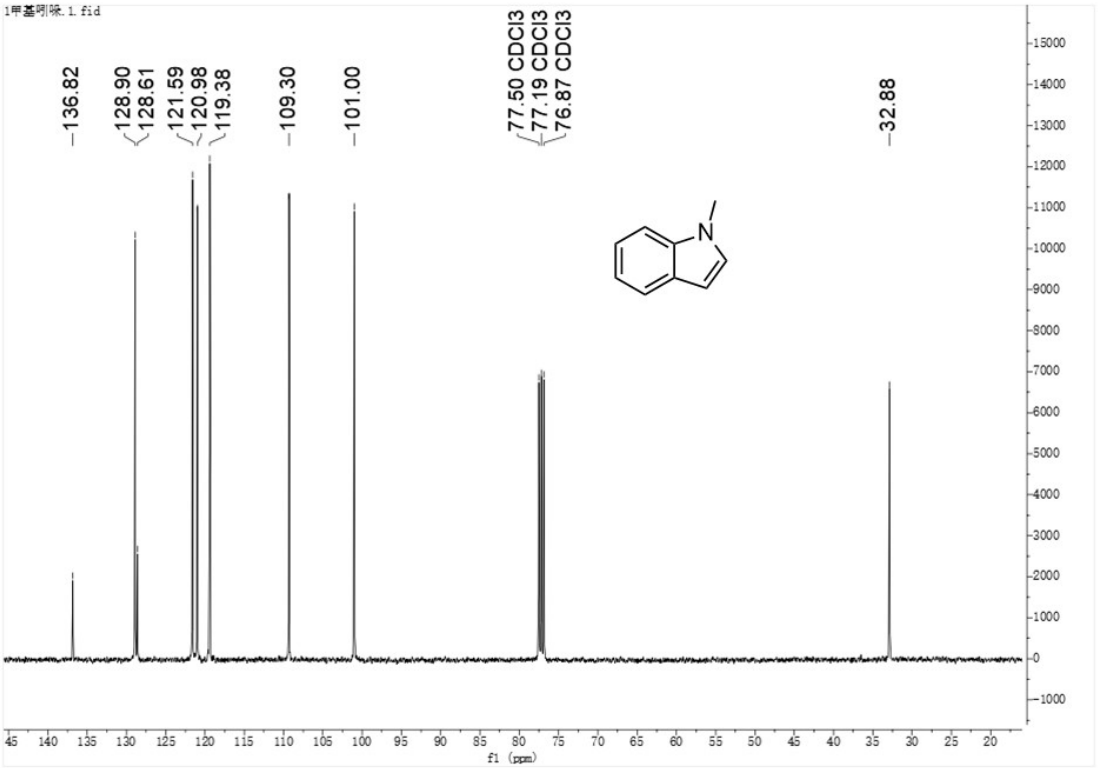
All the ^{1}H NMR and ^{13}C NMR spectra and data of the products were shown as follow:

(23) ^{1}H NMR and ^{13}C NMR spectrum for N-methylindoline

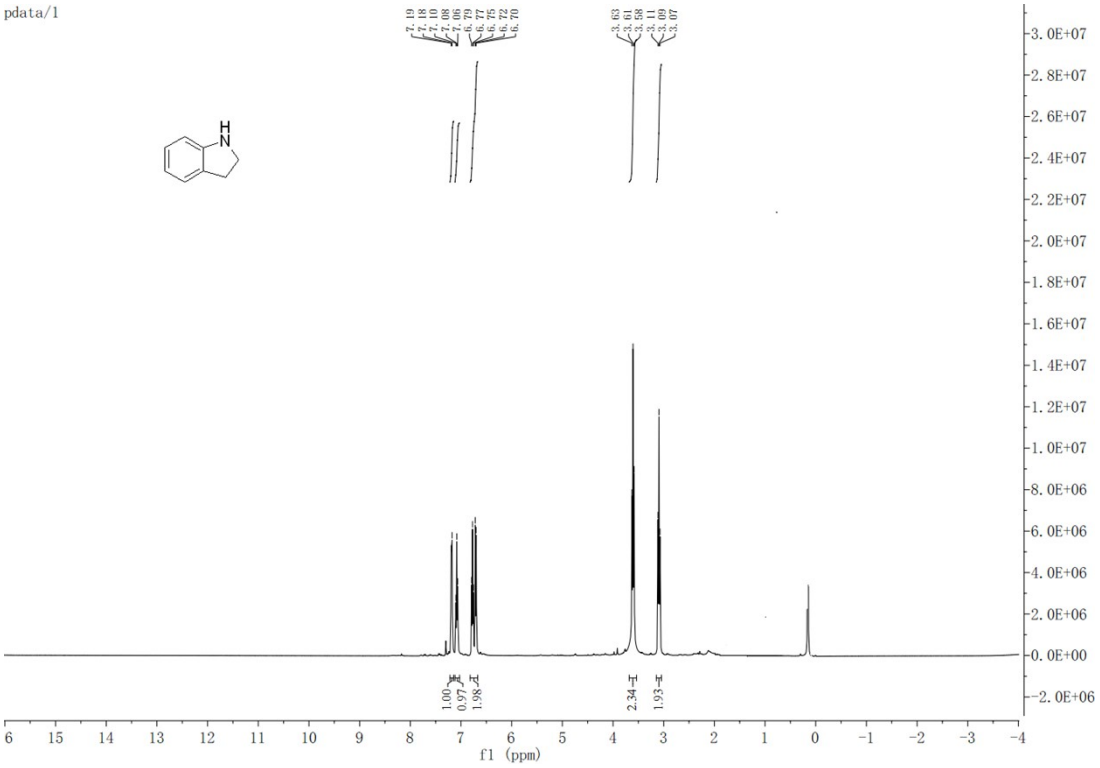


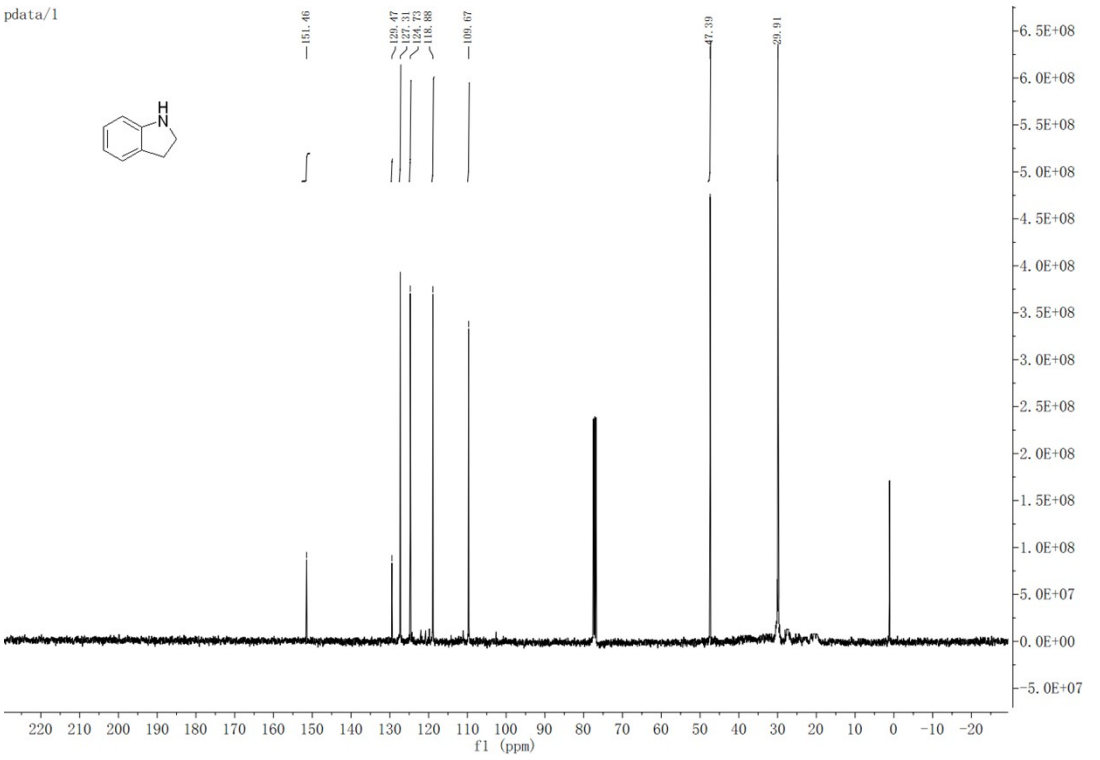
(24) ^{1}H NMR and ^{13}C NMR spectrum for N-methylindole



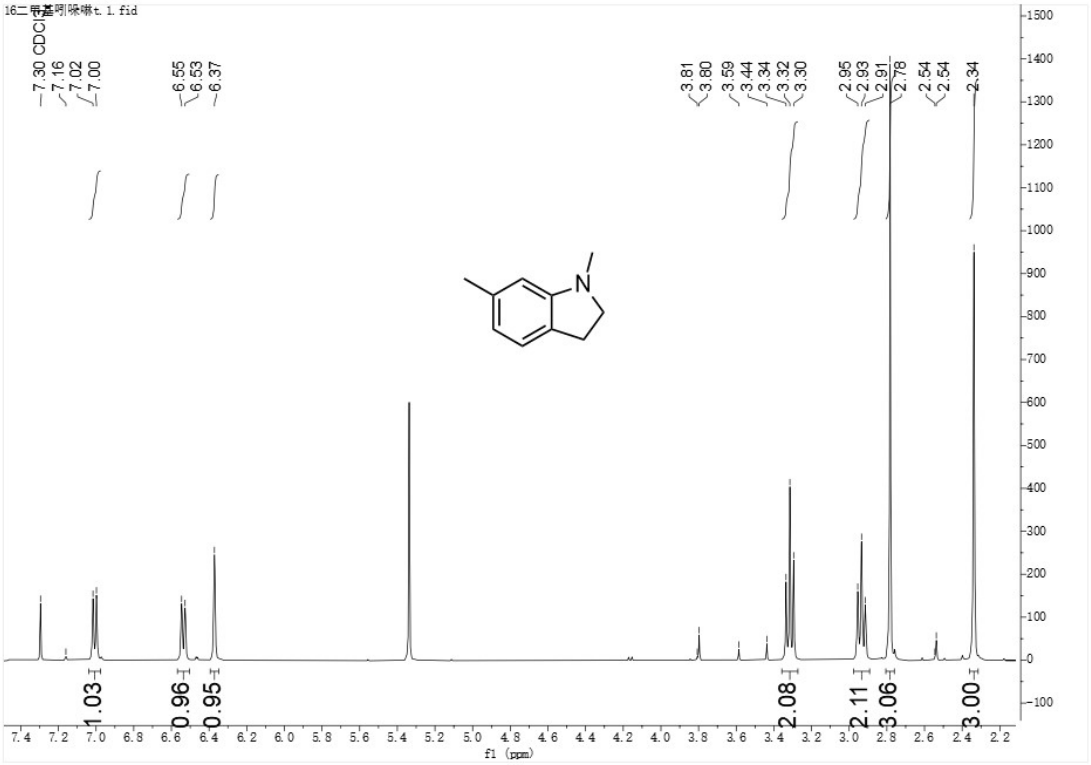


(25) ^{1}H NMR and ^{13}C NMR spectrum for indoline

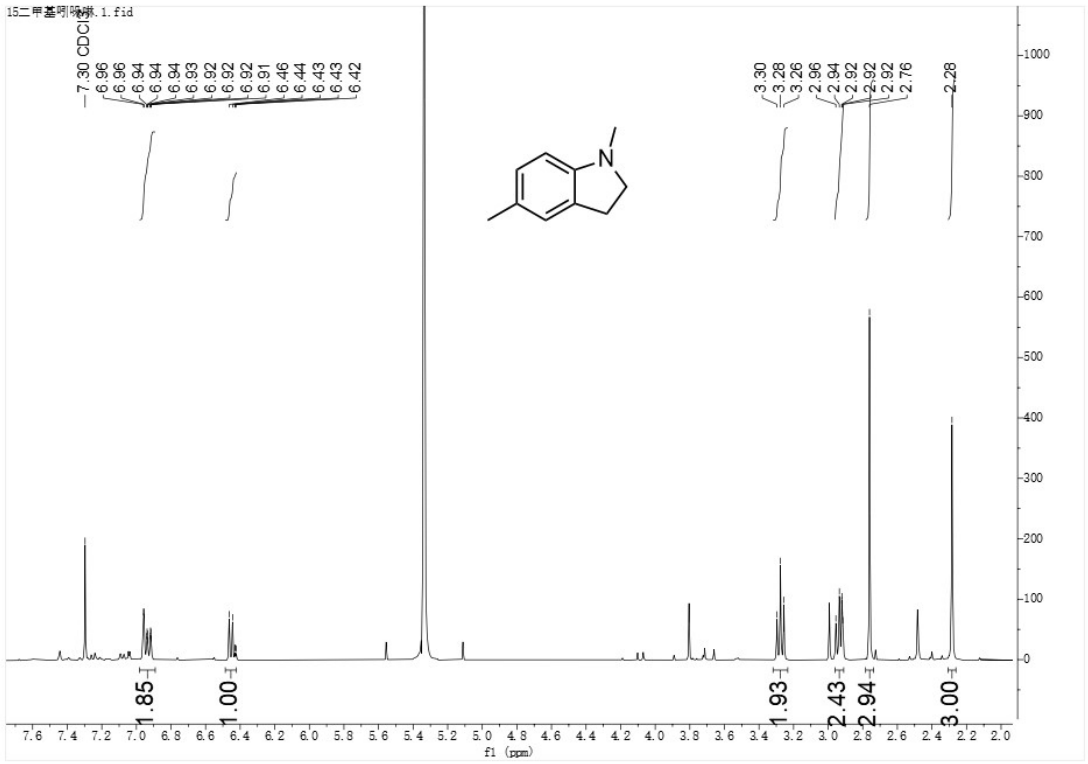




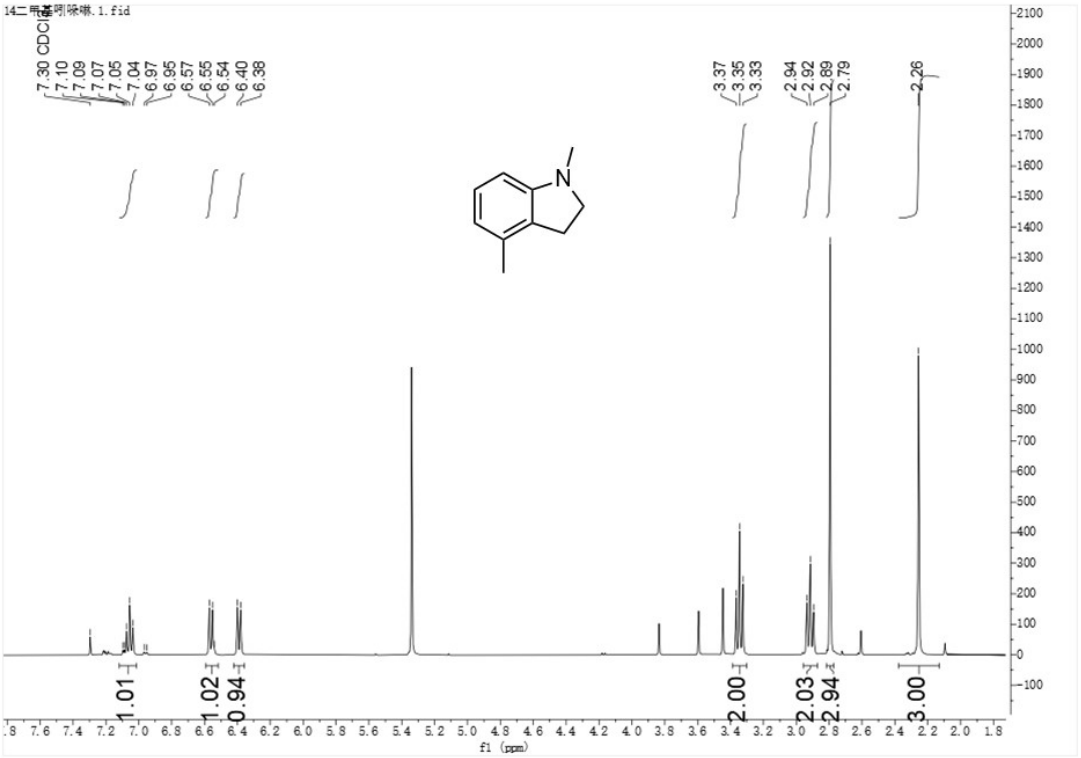
(26) ^{1}H NMR spectrum for 1,6-dimethylindoline



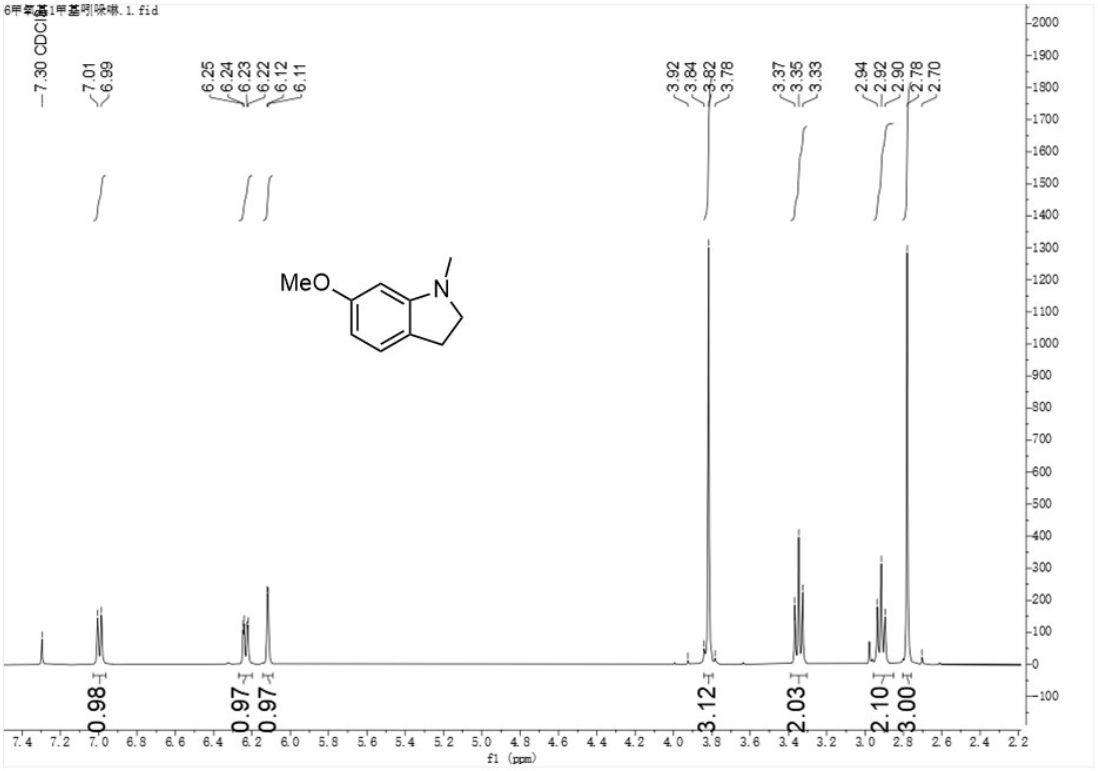
(27) ^{1}H NMR spectrum for 1,5-dimethylindoline

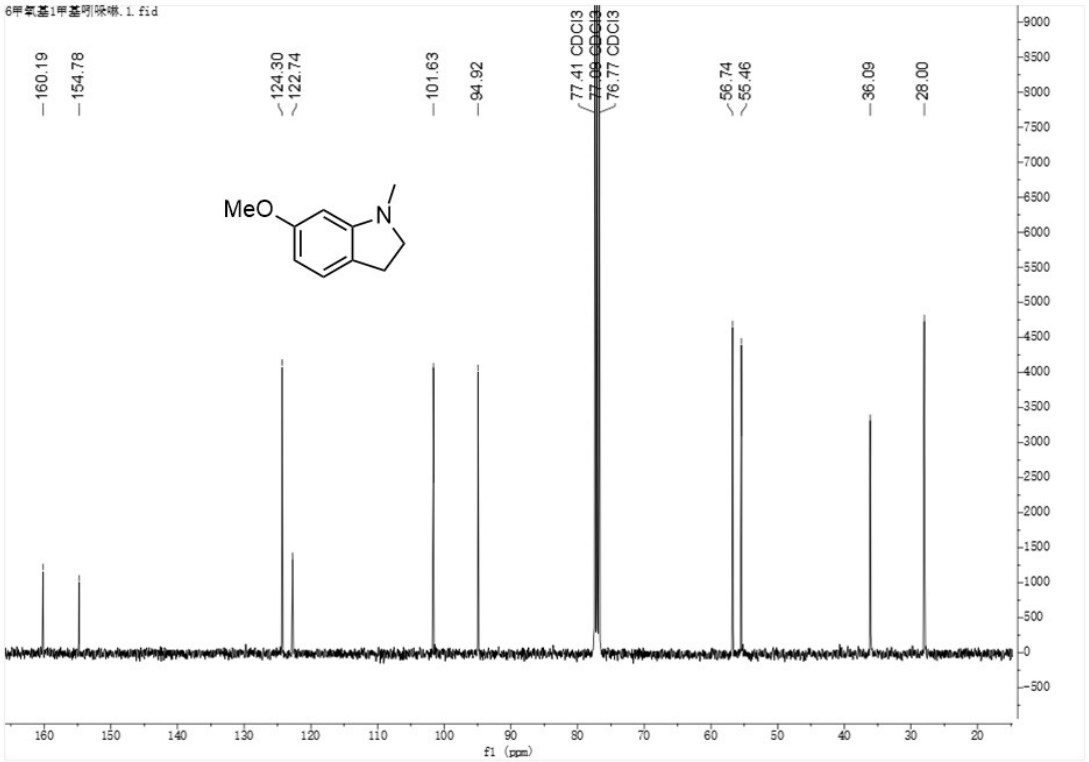


(28) ^{1}H NMR spectrum for 1,4-dimethylindoline

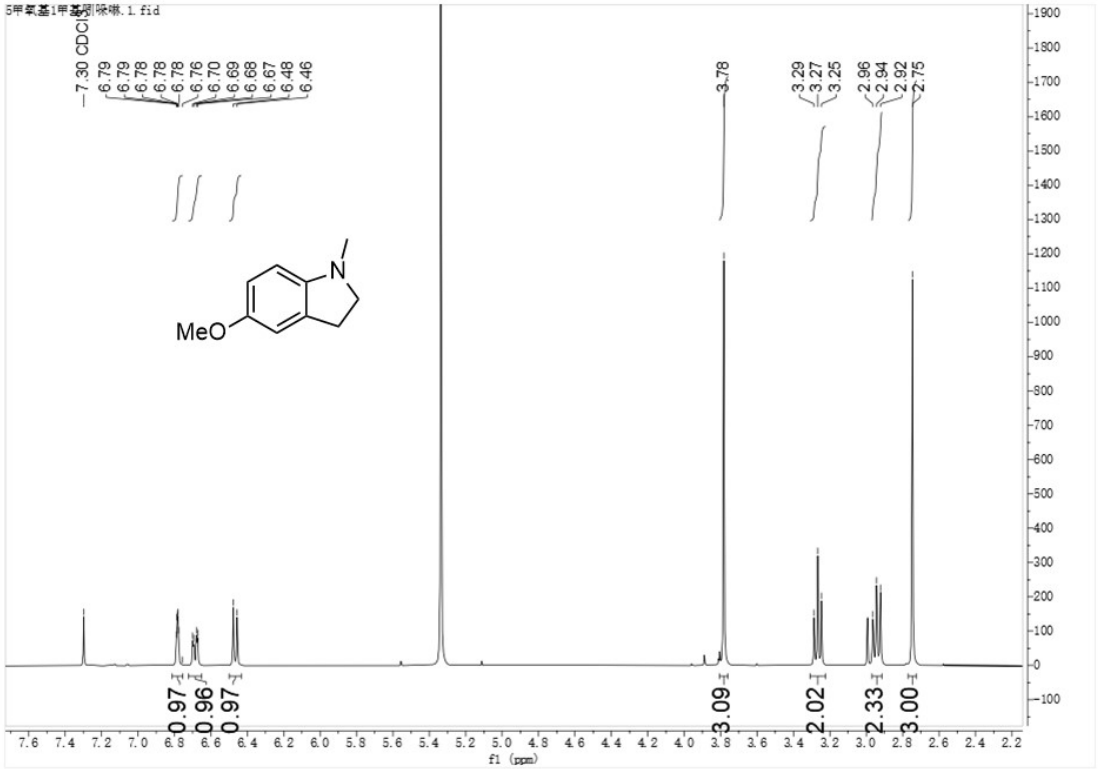


(29) ^{1}H NMR spectrum for 1-Methyl-6-methoxy-indolin

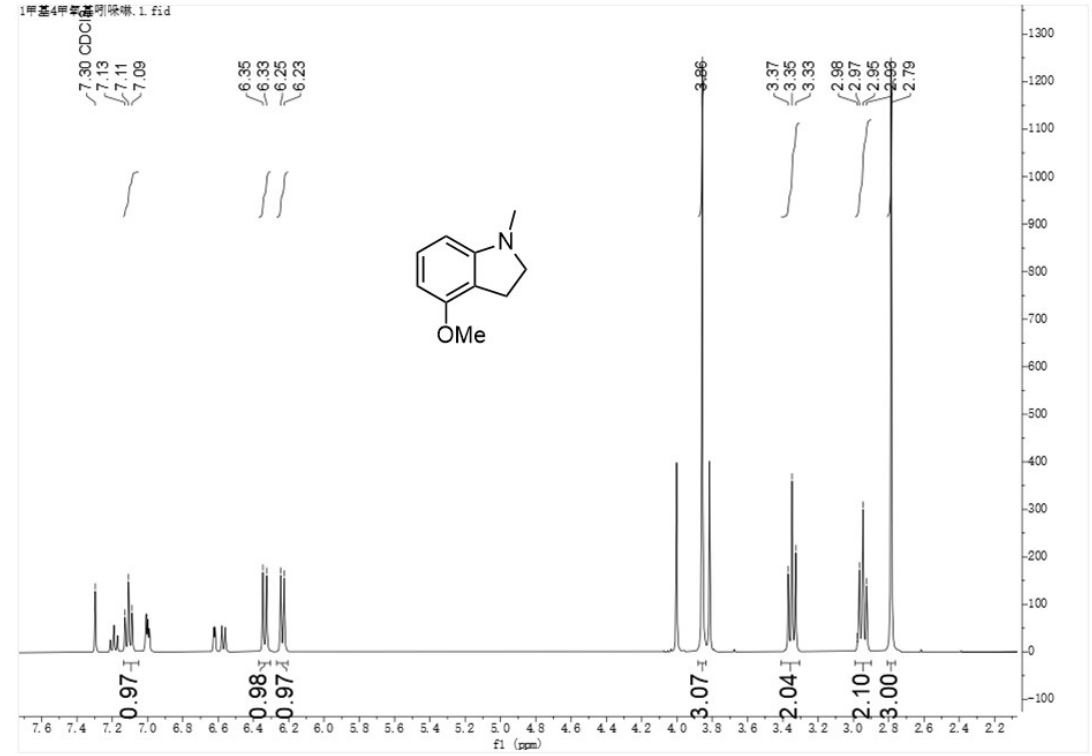


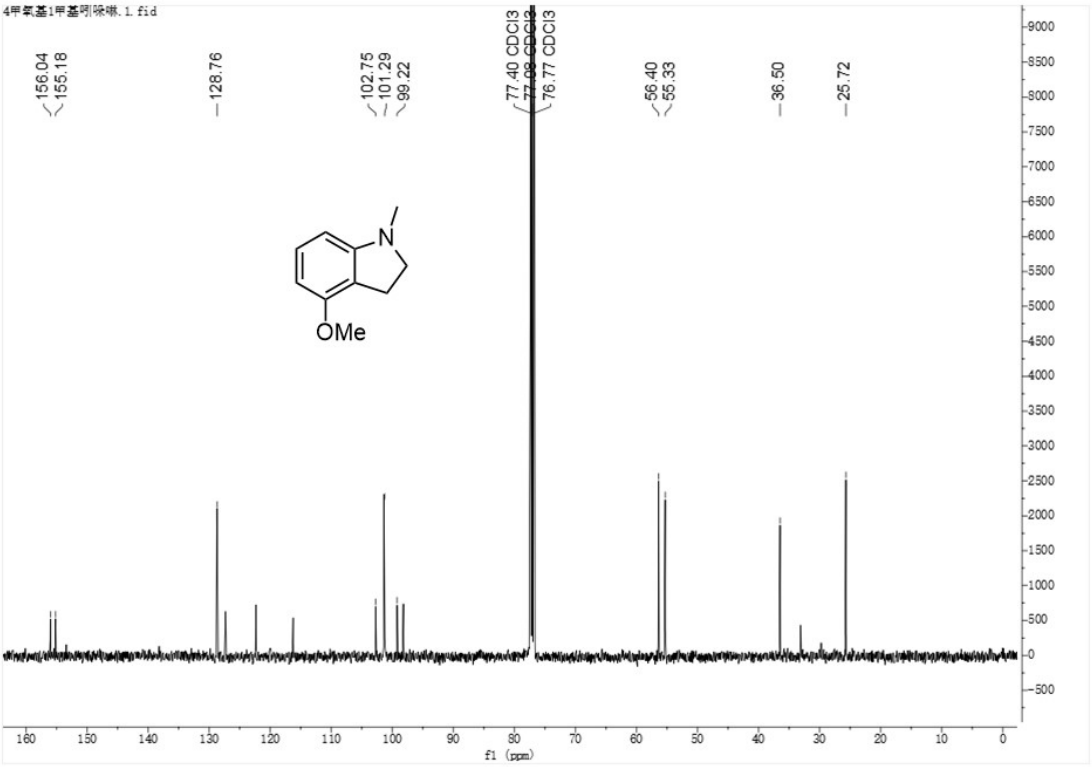


(30) ^{1}H NMR spectrum for 1-Methyl-5-methoxy-indolin

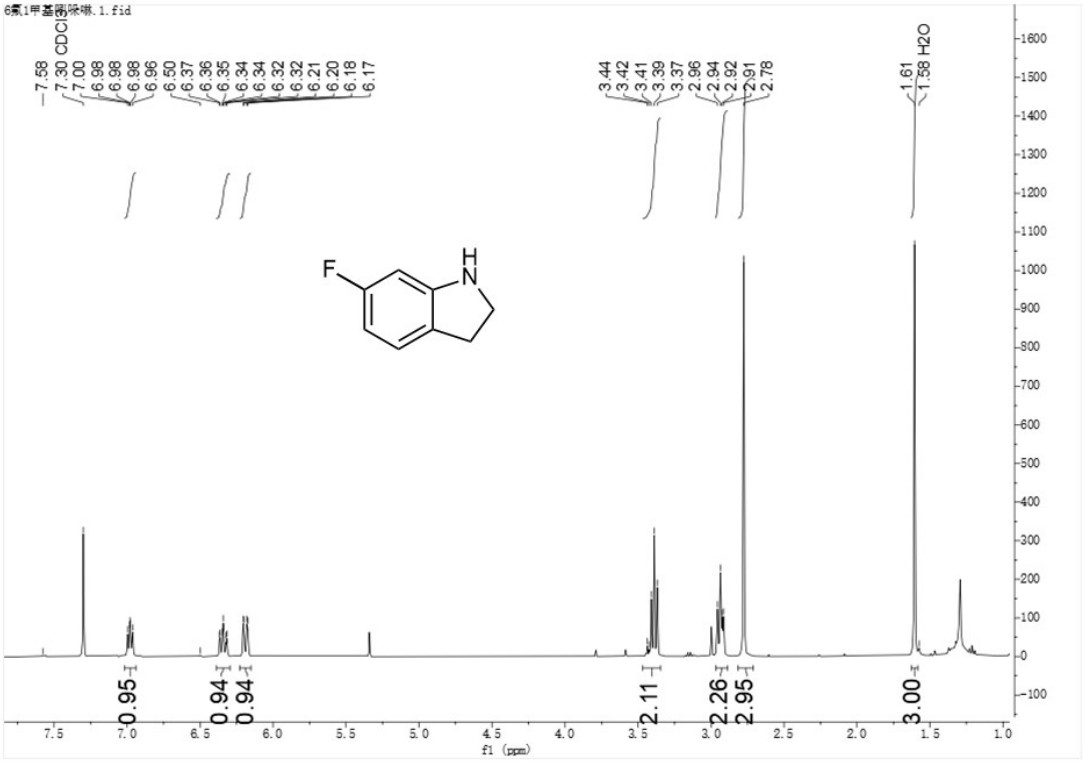


(31) ^{1}H NMR and ^{13}C NMR spectrum for 1-Methyl-4-methoxy-indolin

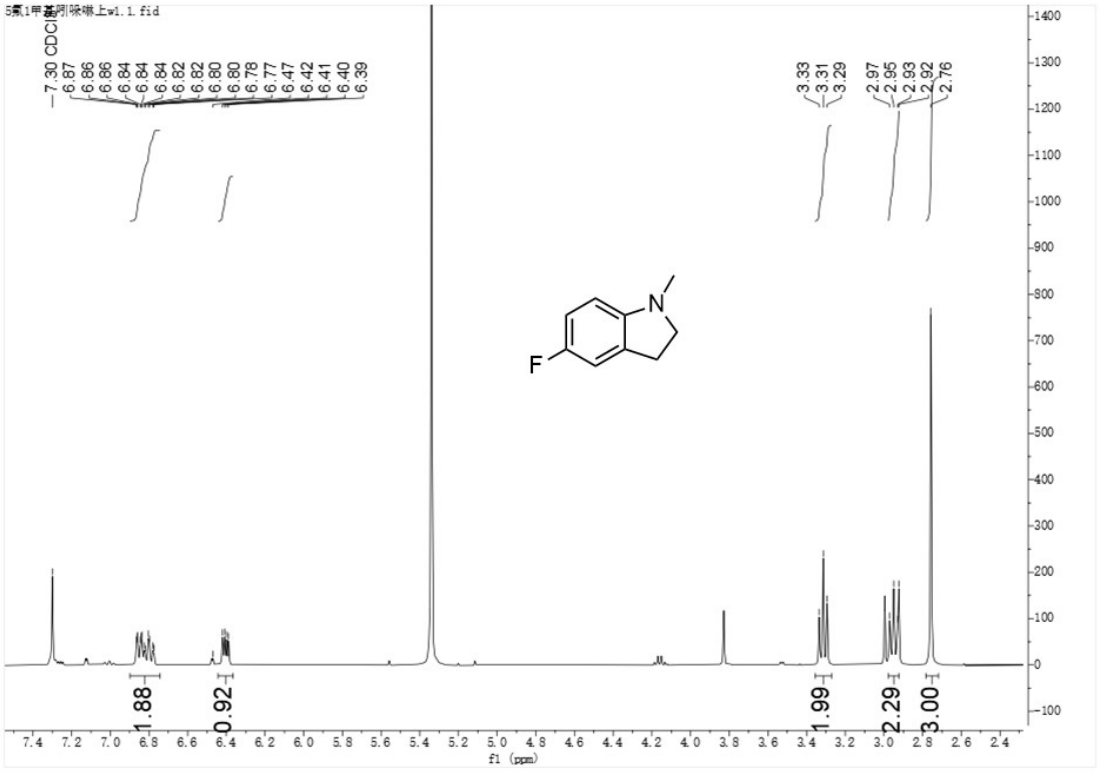




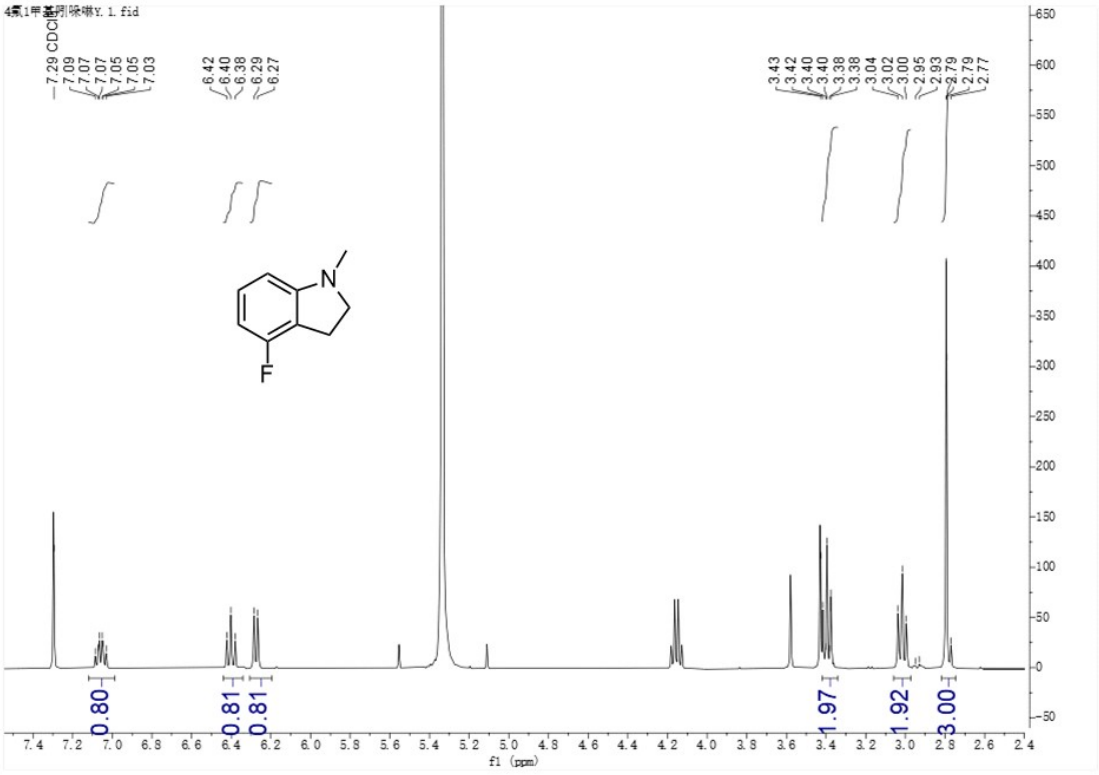
(32) ^{1}H NMR spectrum for 6-fluoro-1-methylindoline



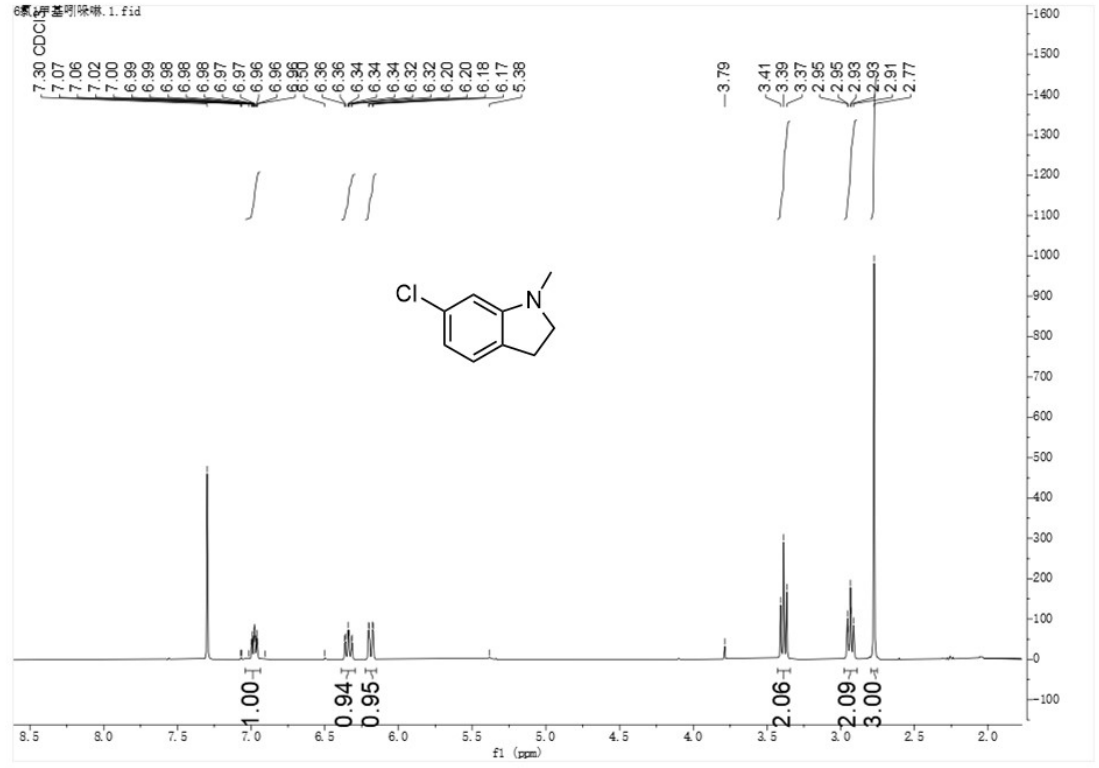
(33) ^{1}H NMR spectrum for 5-fluoro-1-methylindoline



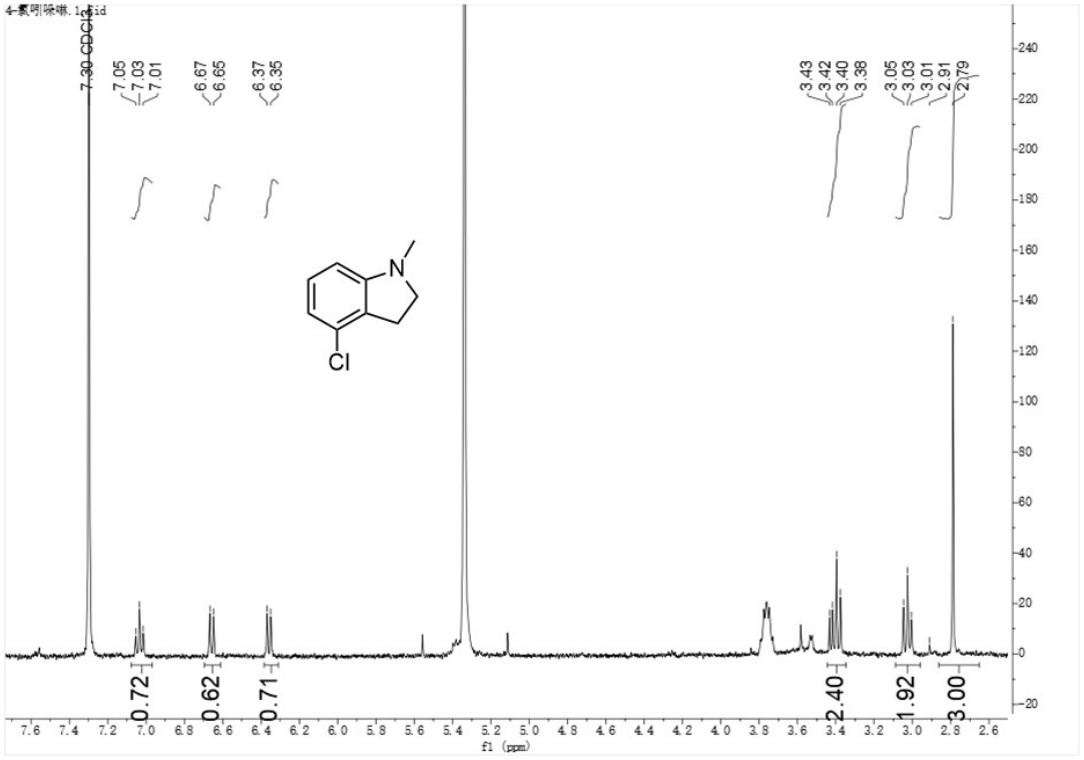
(34) ^{1}H NMR spectrum for 4-fluoro-1-methylindoline



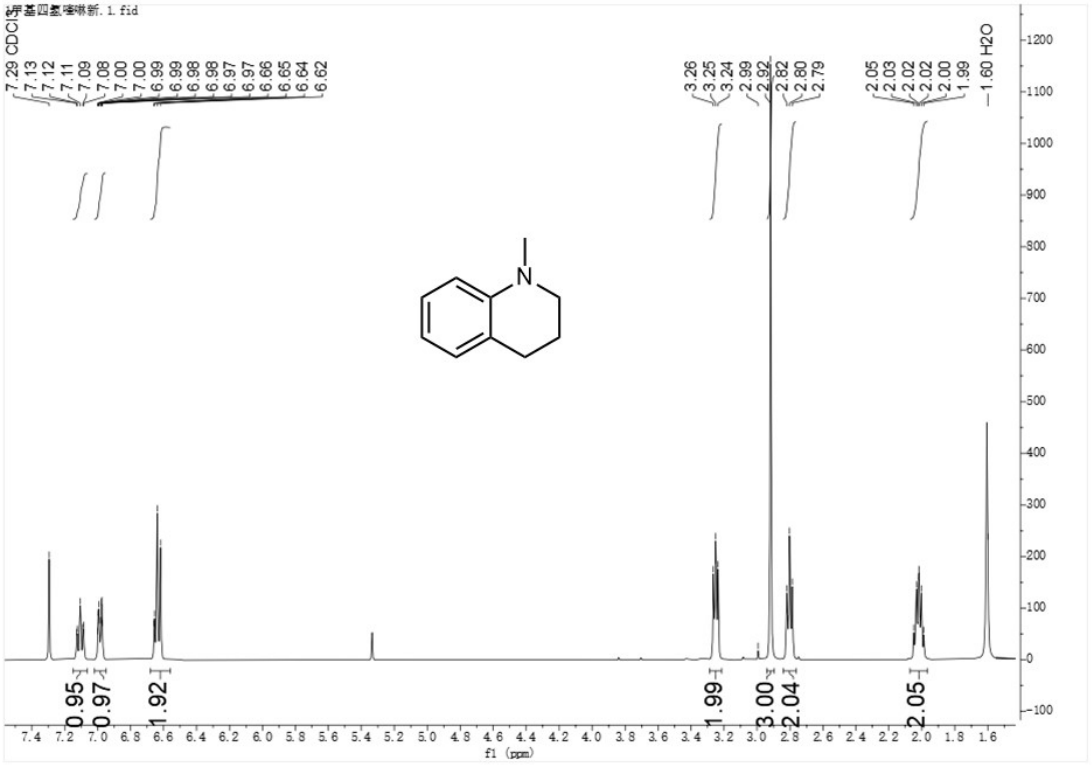
(35) ^{1}H NMR spectrum for 6-chloro-1-methylindoline

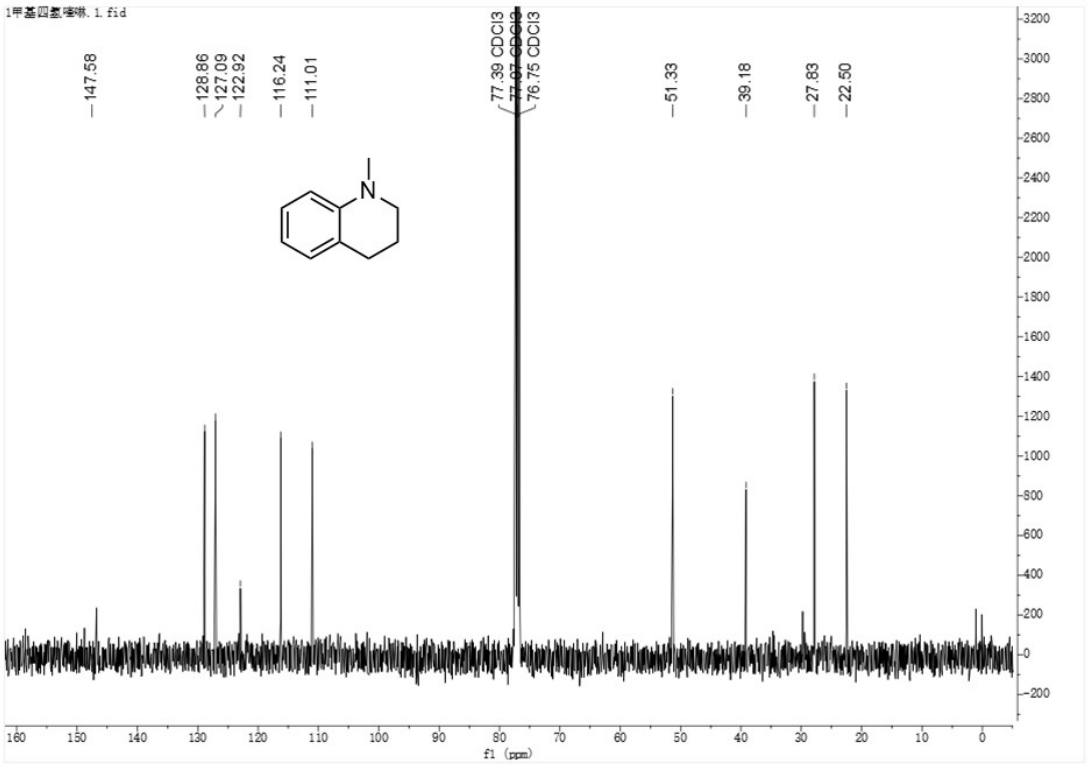


(36) ^{1}H NMR spectrum for 4-chloro-1-methylindoline

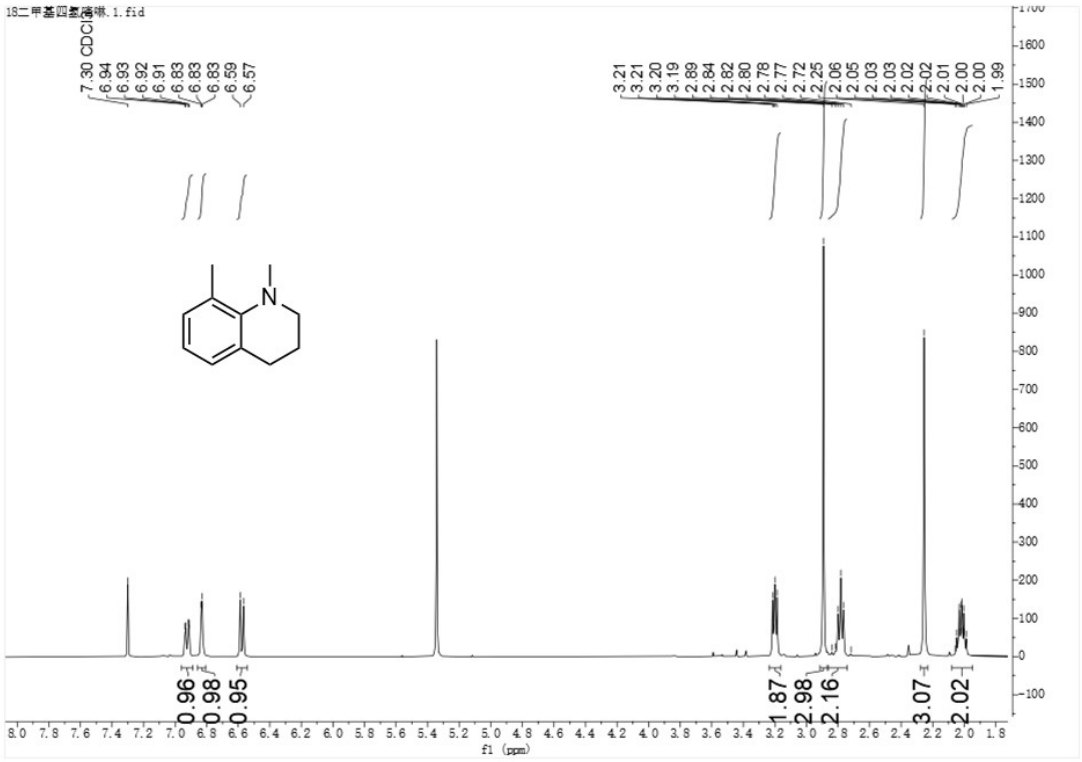


(37) ^{1}H NMR and ^{13}C NMR spectrum for N-methyl-1,2,3,4-tetrahydroquinoline

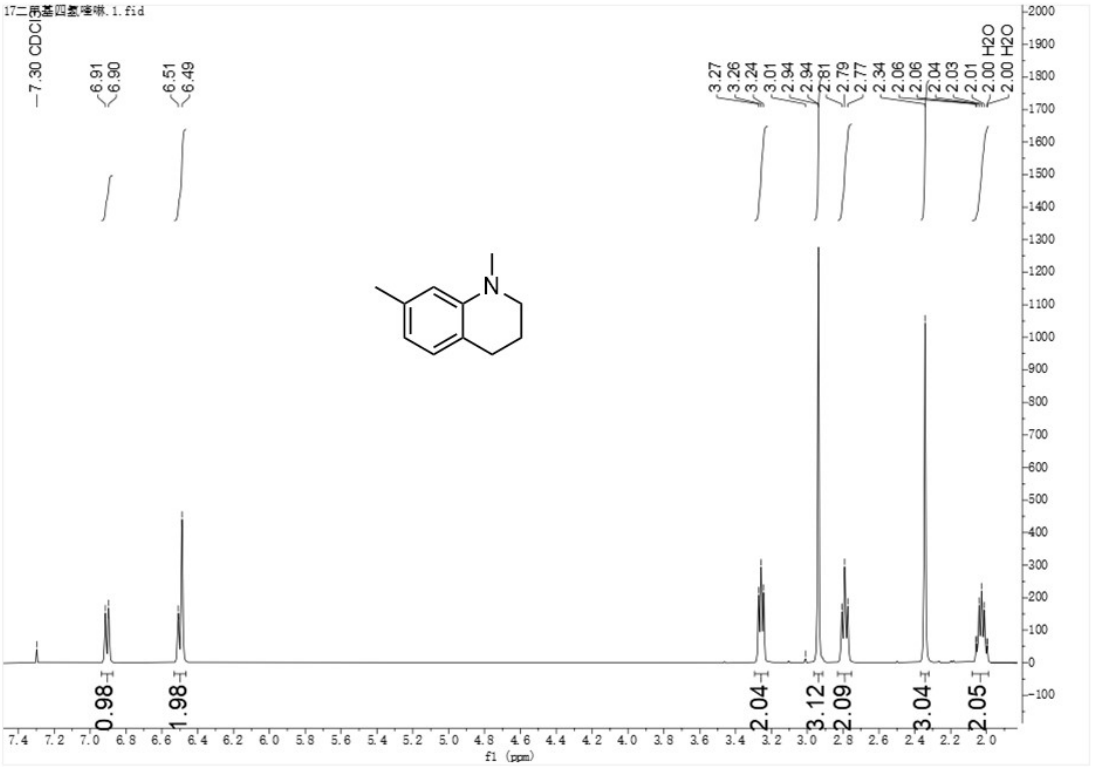


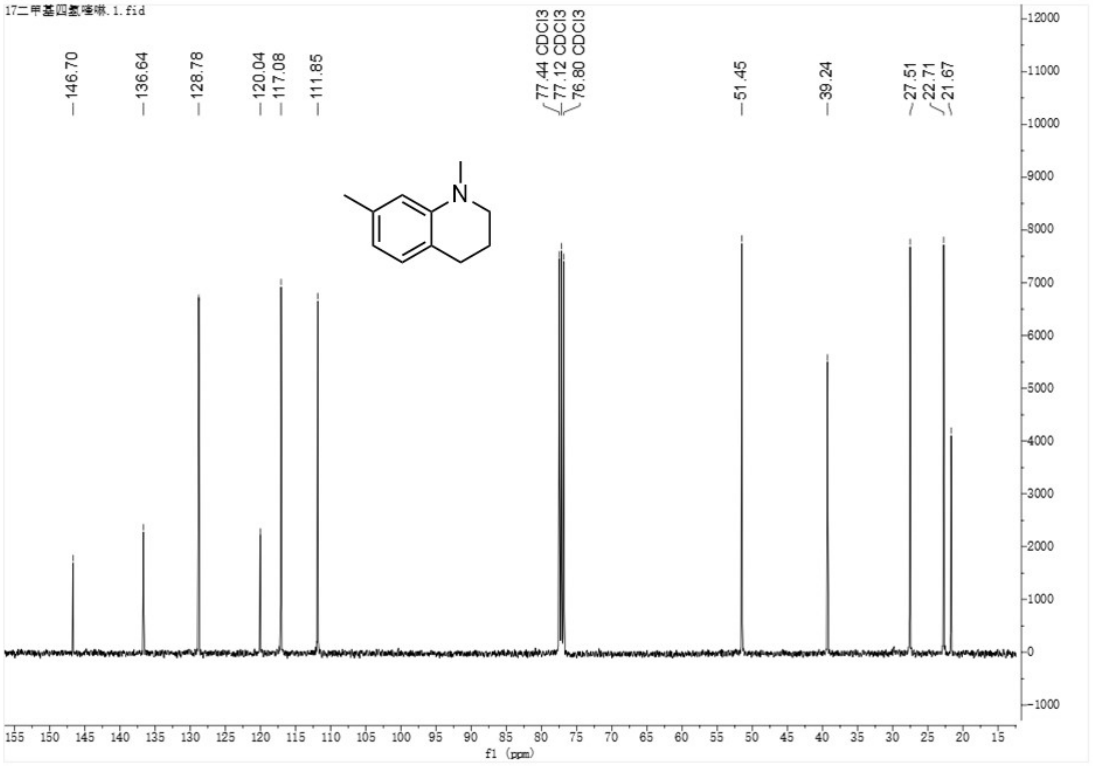


(38) ^{1}H NMR spectrum for 1,8-dimethyl-1,2,3,4-tetrahydroquinoline

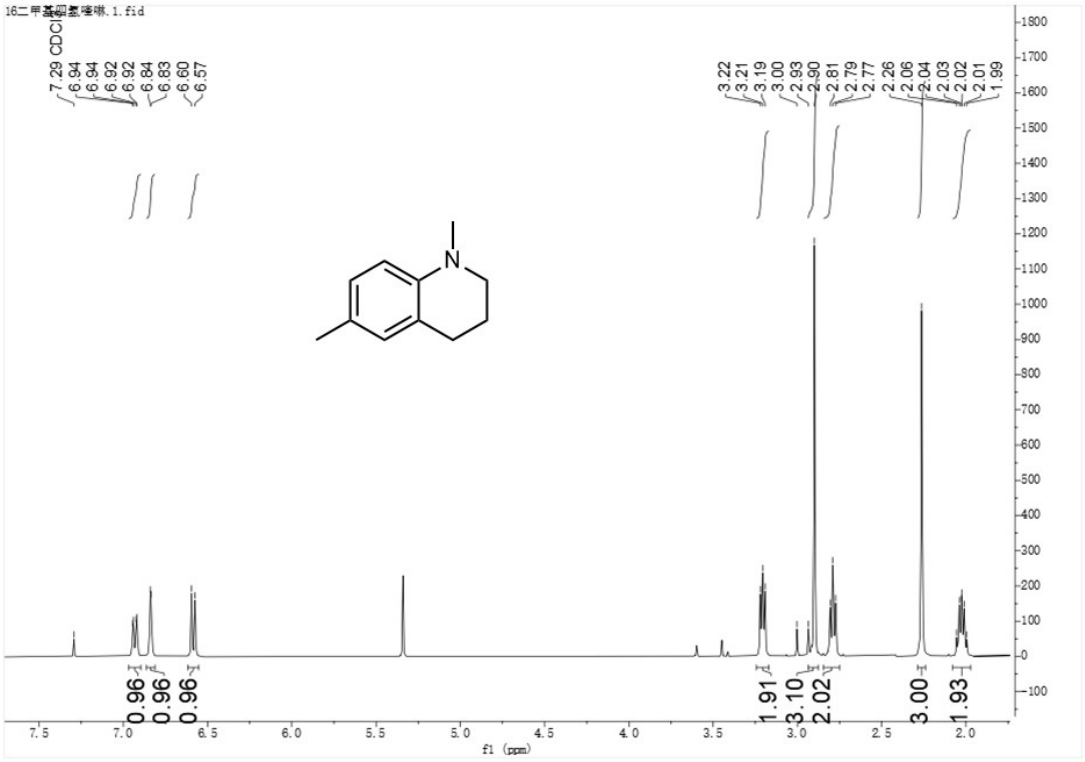


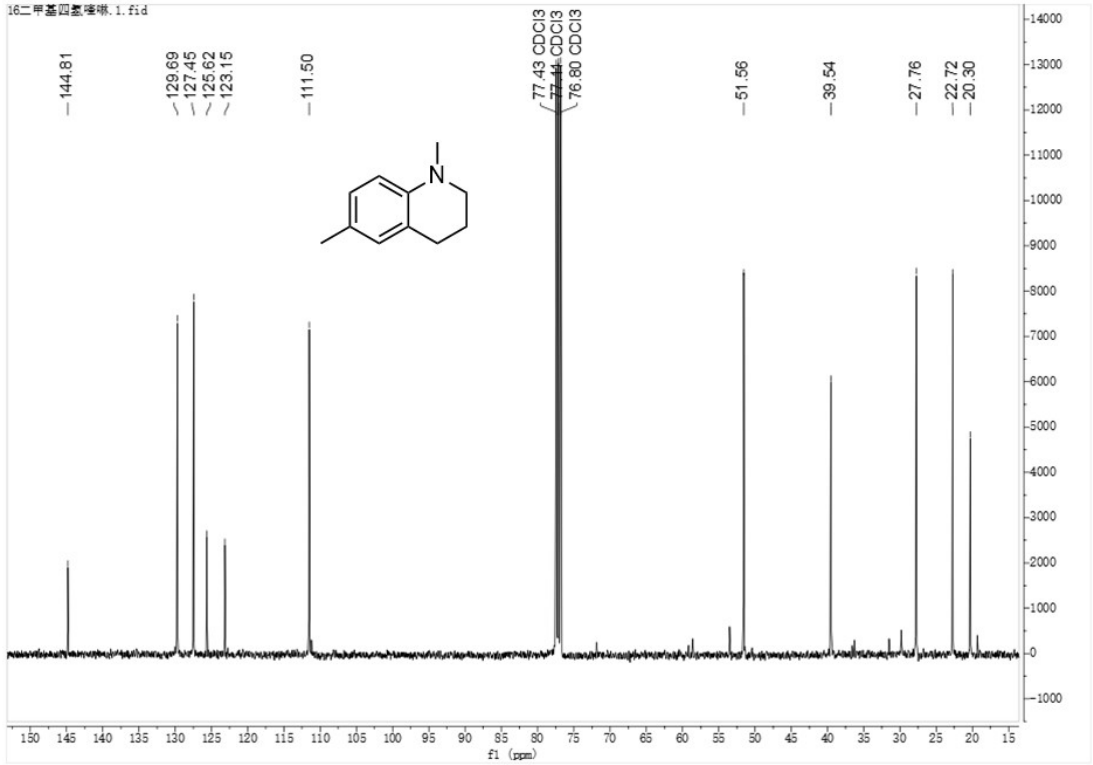
(39) ^{1}H NMR and ^{13}C NMR spectrum for 1,7-dimethyl-1,2,3,4-tetrahydroquinoline



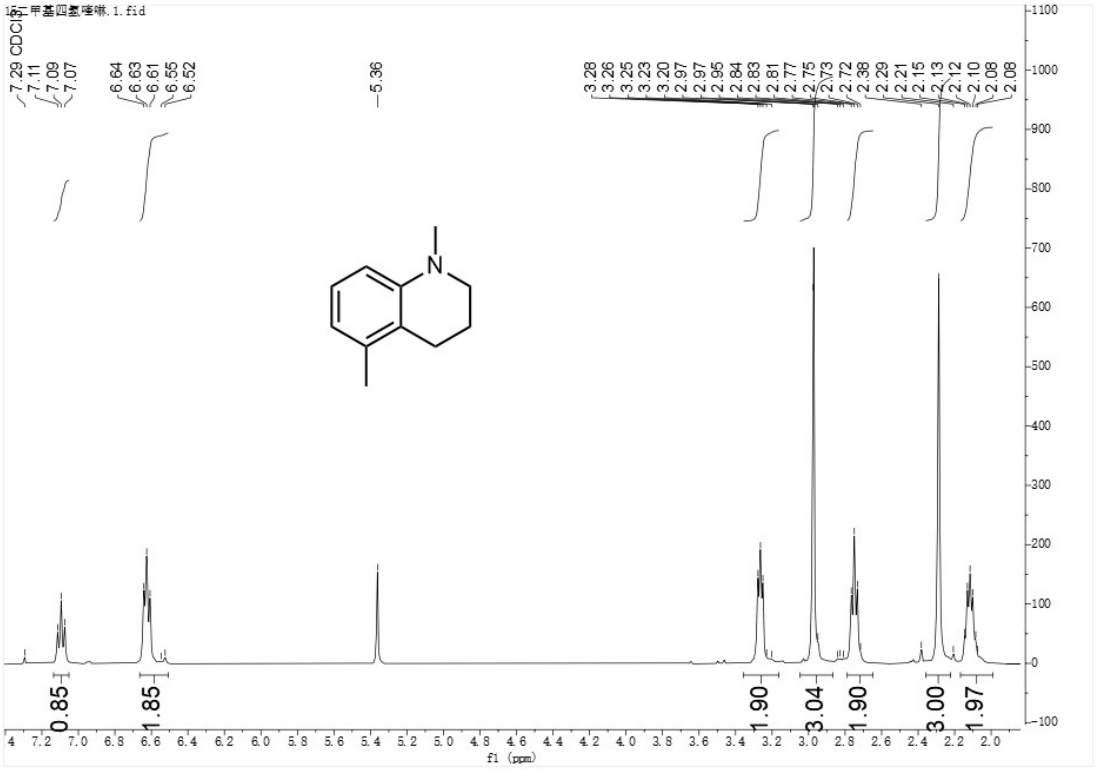


(40) ^{1}H NMR and ^{13}C NMR spectrum for 1,6-dimethyl-1,2,3,4-tetrahydroquinoline

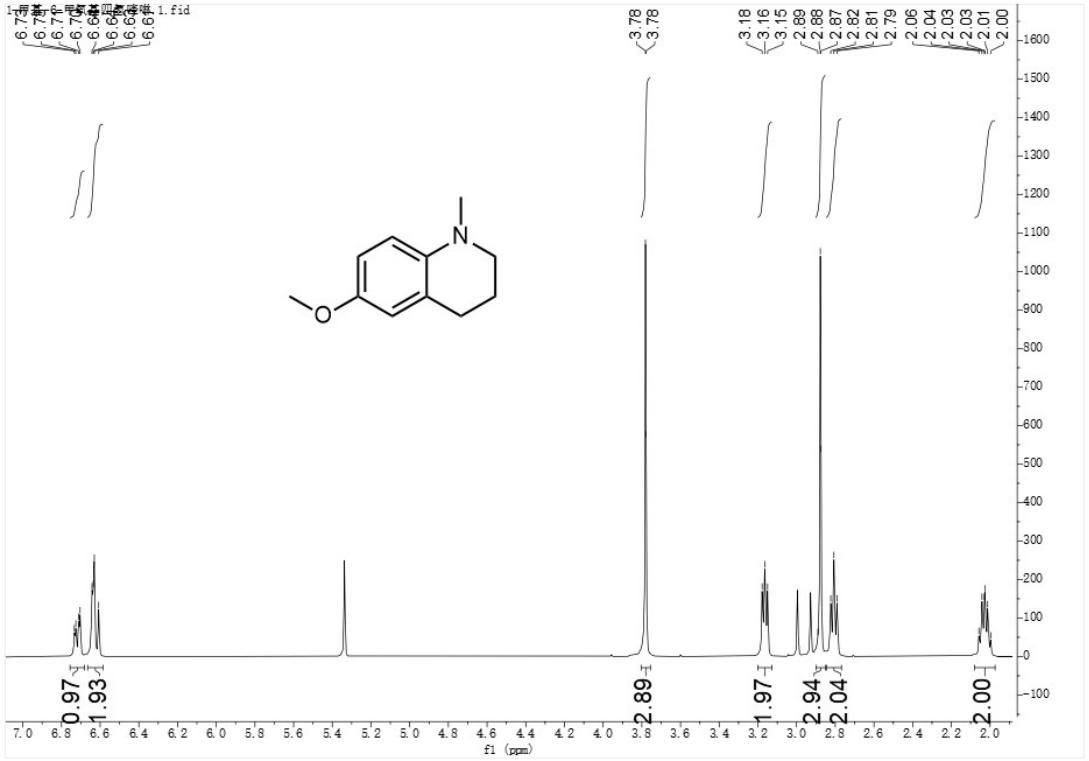


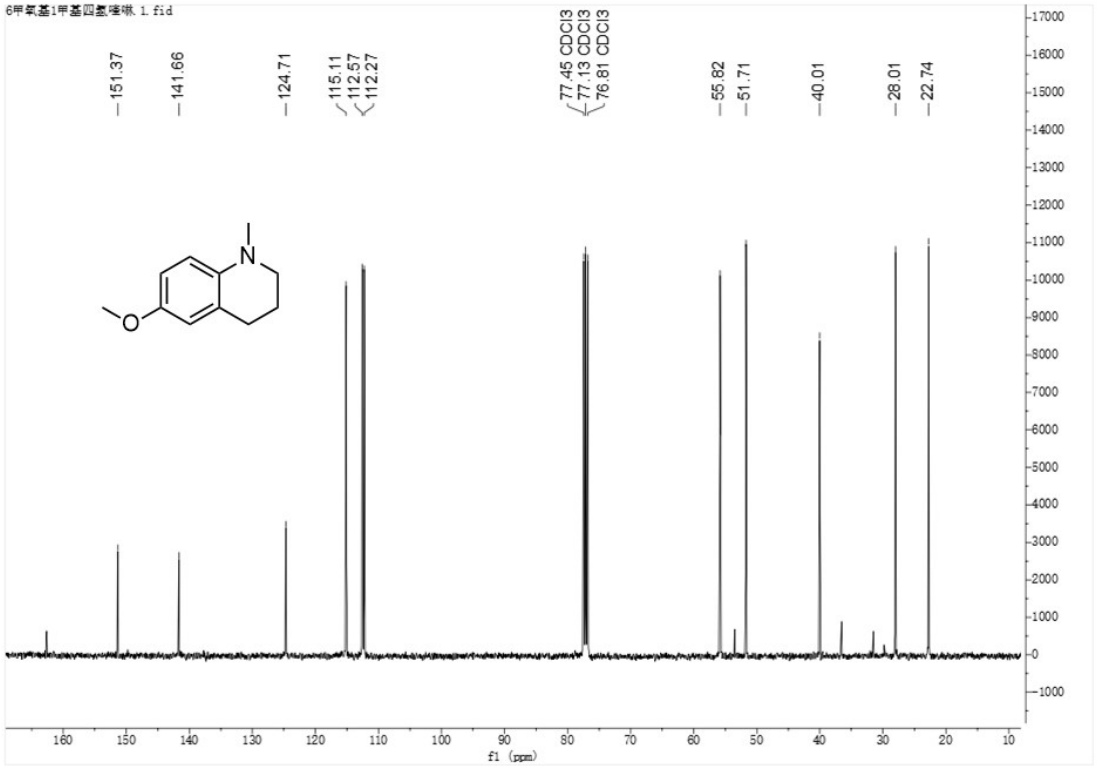


(41) ^{1}H NMR spectrum for 1,5-dimethyl-1,2,3,4-tetrahydroquinoline

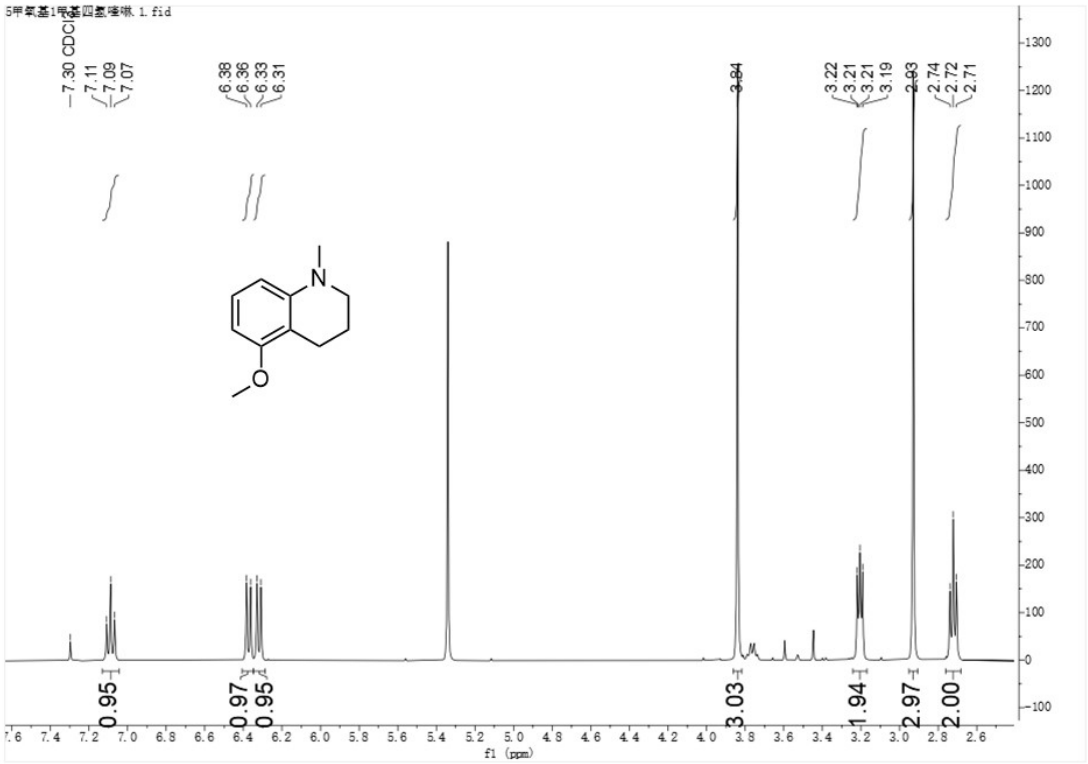


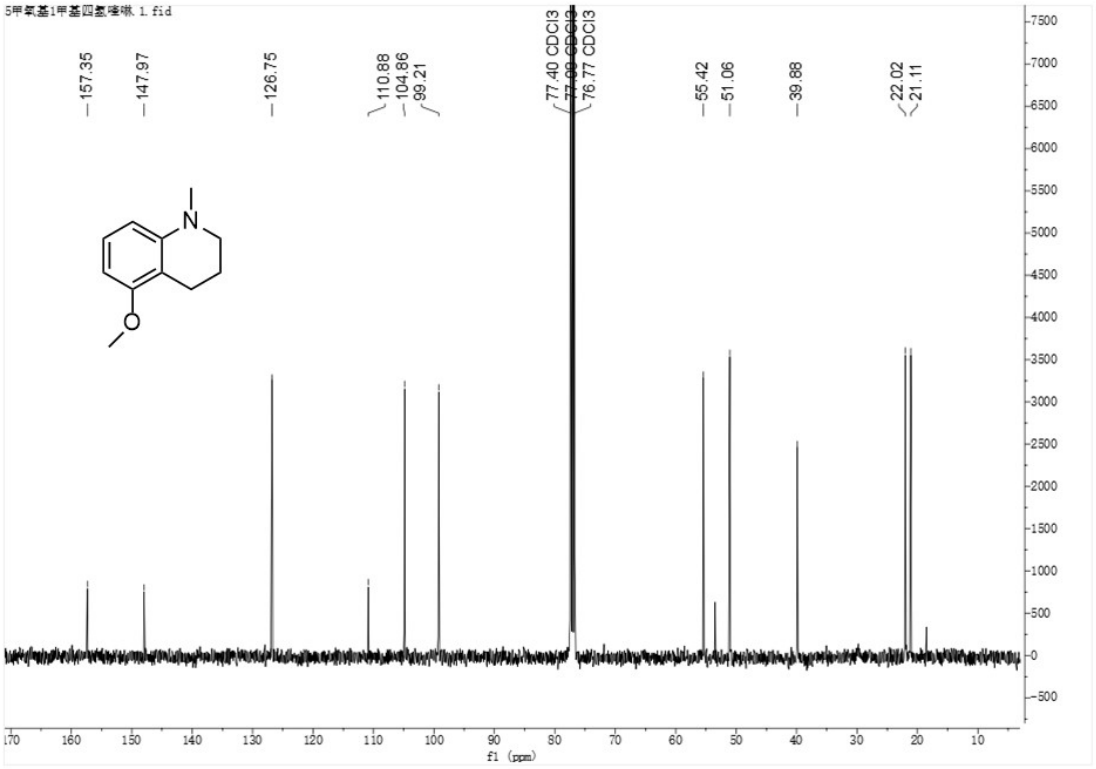
(42) ^{1}H NMR and ^{13}C NMR spectrum for 6-methoxy-1-methyl-1,2,3,4-tetrahydro quinoline



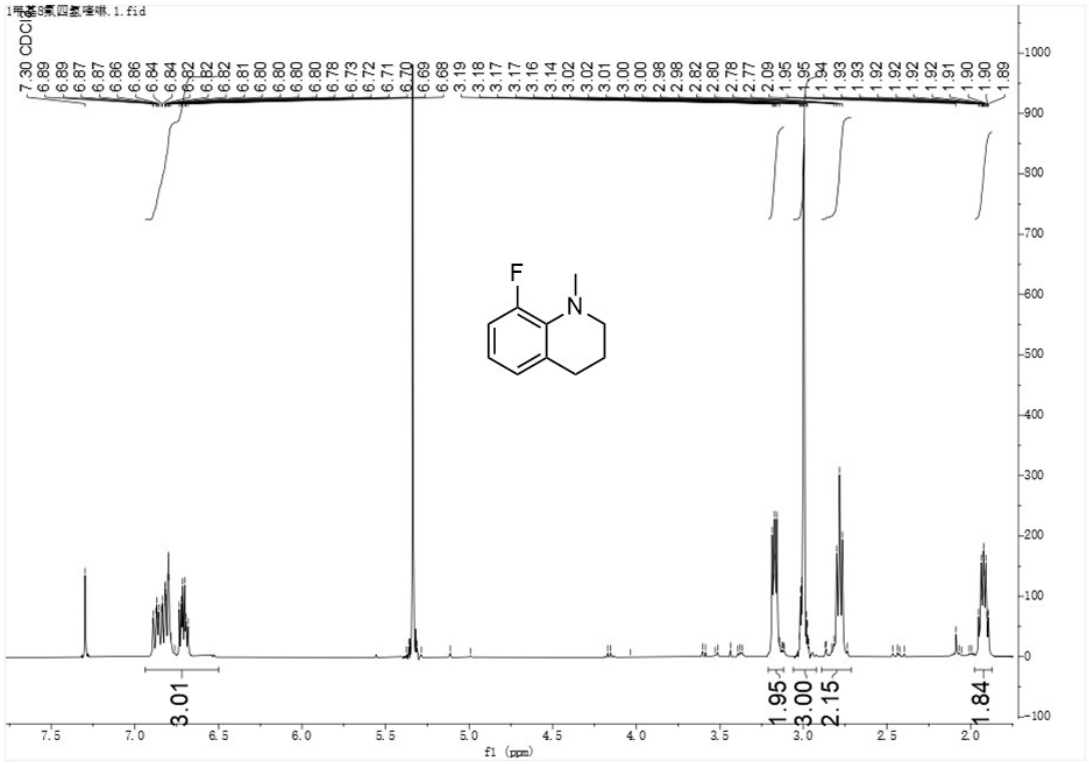


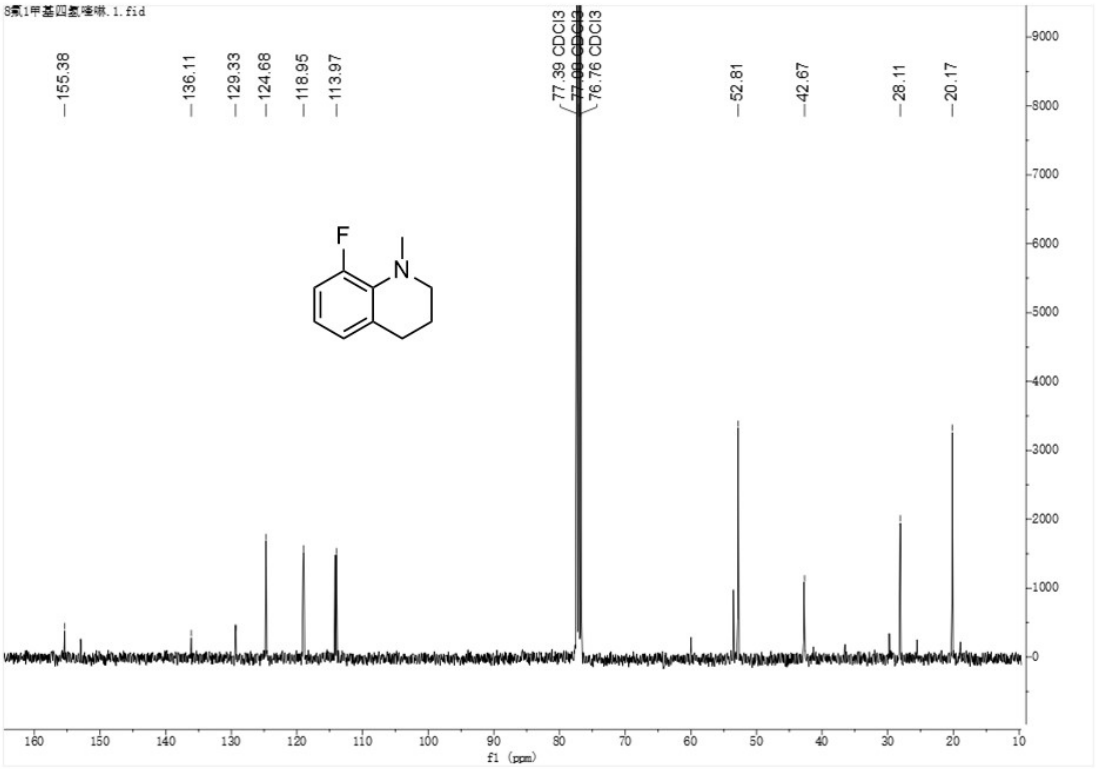
(43) ^{1}H NMR and ^{13}C NMR spectrum for 5-methoxy-1-methyl-1,2,3,4-tetrahydro quinoline



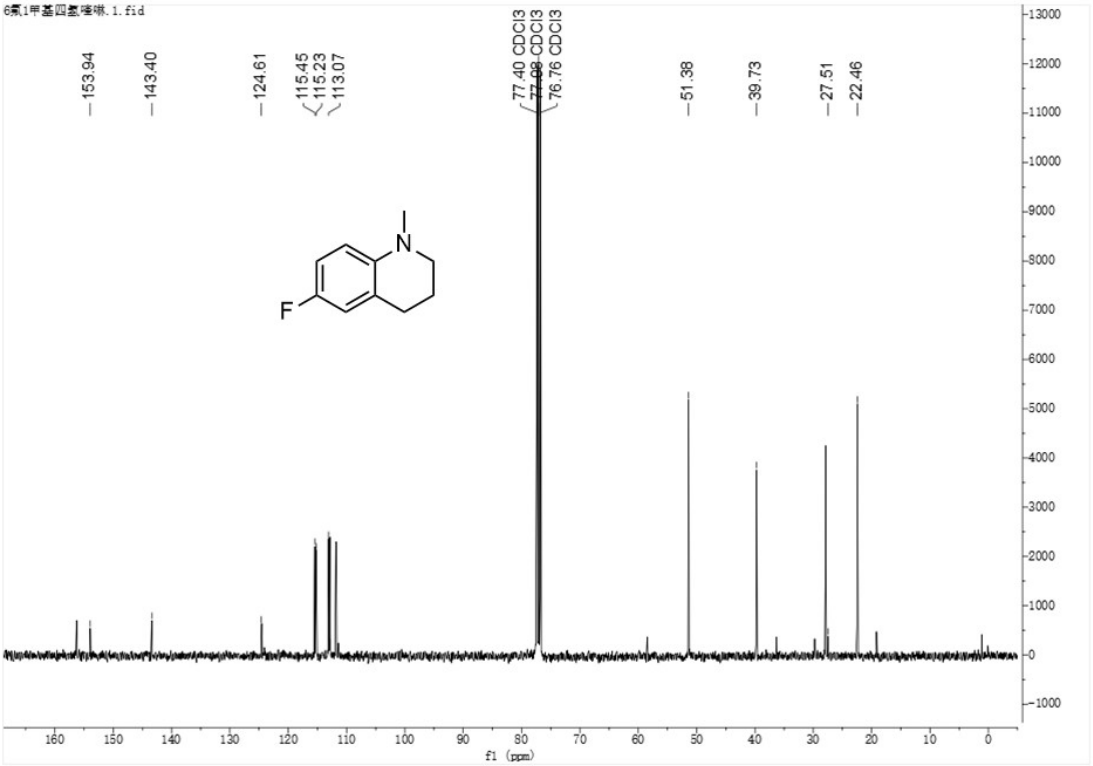


(44) ^{1}H NMR and ^{13}C NMR spectrum for 8-fluoro-1-methyl-1,2,3,4-tetrahydro quinoline





(45) ^{1}H NMR and ^{13}C NMR spectrum for 6-fluoro-1-methyl-1,2,3,4-tetrahydro quinoline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153.94
143.40
124.61
115.45
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113.07
77.40 CDCl3
77.08 CDCl3
76.76 CDCl3
51.38
39.73
27.51
22.46
F
N
f1 (ppm)

4. References

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