Supporting Information for

Copper-mediated oxidative [3+2]-annulation of nitroalkenes and pyridinium ylides: a general access to functionalized indolizines. Efficient synthesis of 1-fluoroindolizines

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[c] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov str. 28, Moscow, 119991, Russia.*

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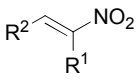
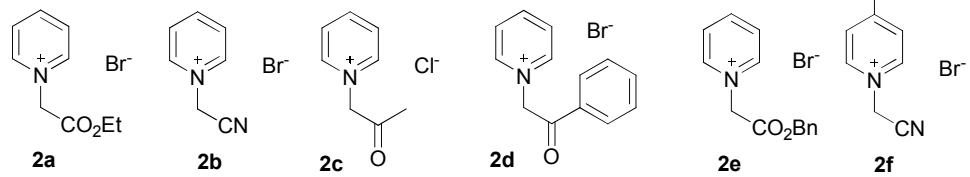
List of starting compounds:

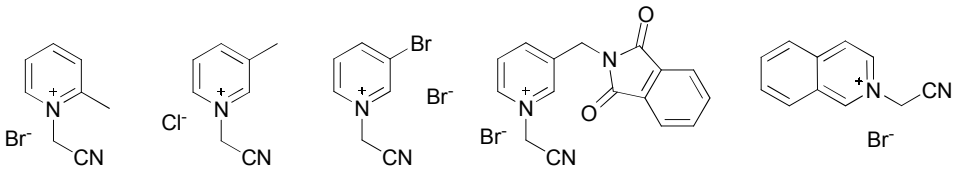


1

1a, R^1 = F, R^2 = 4-Cl-C_6H_4-
1b, R^1 = F, R^2 = 2-Br-C_6H_4-
1c, R^1 = F, R^2 = 4-F-C_6H_4-
1d, R^1 = F, R^2 = 4-Br-C_6H_4-
1e, R^1 = F, R^2 = 4-Me-C_6H_4-
1f, R^1 = F, R^2 = 4-CN-C_6H_4-
1g, R^1 = F, R^2 = 4-CO_2Me-C_6H_4-
1h, R^1 = F, R^2 = 4-NO_2-C_6H_4-
1i, R^1 = F, R^2 = 4-OMe-C_6H_4-
1j, R^1 = Me, R^2 = 4-Cl-C_6H_4-
1k, R^1 = H, R^2 = 4-Cl-C_6H_4-
1l, R^1 = Me, R^2 = H
1m, R^1 = Et, R^2 = H
1n, R^1 = iPr, R^2 = Me
1o, R^1 = Cl, R^2 = 4-OMe-C_6H_4-
1p, R^1 = CO_2Et, R^2 = 4-Cl-C_6H_4-

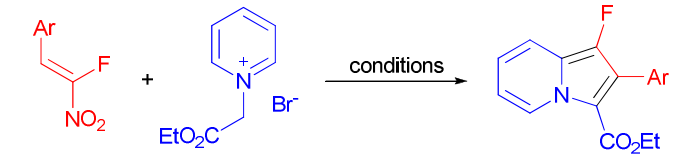


2a **2b** **2c** **2d** **2e** **2f**



2g **2h** **2i** **2j** **2k**

Extended Table 1. Optimization of the reaction conditions.



1a **2a** **3a**

Ar = 4-Cl-C_6H_4-

Entry	Oxidant (equiv.)	Base (equiv.)	Solvent	Yield **3a**[a], %
1	-	Et_3N (1.5)	CH_2Cl_2	trace
2	$Cu(OAc)_2·H_2O$ (1.5)	Et_3N (1.5)	CH_2Cl_2	23
3	$Cu(OAc)_2·H_2O$ (1.5)	DBU (1.5)	CH_2Cl_2	33
4	$Cu(OAc)_2·H_2O$ (1.5)	DIPEA (1.5)	CH_2Cl_2	26
5	$Cu(OAc)_2·H_2O$ (1.5)	Py (1.5)	CH_2Cl_2	24(50)[b]
6	$Cu(OAc)_2·H_2O$ (1.5)	Py (5)	CH_2Cl_2	48
7	$Cu(OAc)_2·H_2O$ (1.5)	Py (5)	MeCN	38
8	$Cu(OAc)_2·H_2O$ (1.5)	Py (5)	DMF	17
9	$Cu(OAc)_2·H_2O$ (1.5)	Py (5)	DCE	52
10	$Cu(OAc)_2·H_2O$ (1.5)	K_2CO_3 (2.5)	DMSO	15
11[d]	$Cu(OAc)_2·H_2O$ (1.5)	Py (5)	DCE	61
12[d]	$Cu(OAc)_2·H_2O$ (1.5)	DMAP (5)	DCE	24
13[d]	$Cu(OAc)_2·H_2O$ (1.5)	2,6-lutidine (5)	DCE	63
14[d]	$Cu(OAc)_2·H_2O$ (1.0)	2,6-lutidine (5)	DCE	45
15[d]	$Cu(OAc)_2·H_2O$ (2.0)	2,6-lutidine (6)	DCE	56
16[d]	$Cu(NO_3)_2·3H_2O$ (1.5)	2,6-lutidine (5)	DCE	53
17[d]	$Cu(OTf)_2$ (1.5)	2,6-lutidine (5)	DCE	57
18[d]	$CuCl_2$ (1.5)	2,6-lutidine (5)	DCE	n.r.[c]
19[d]	$FeCl_3$ (1.5)	2,6-lutidine (5)	DCE	0
20[d]	MnO_2 (1.5)	2,6-lutidine (5)	DCE	0
21[d]	$(NH_4)_2Ce(NO_3)_6$ (1.5)	2,6-lutidine (5)	DCE	trace
22[d]	DDQ (1.5)	2,6-lutidine (5)	DCE	0
23[e]	Ag_2CO_3 (2)	-	THF	45
24[d]	$Cu(OAc)_2·H_2O$ (1.5), TEMPO (1)	2,6-lutidine (5)	DCE	20
25[d]	$Cu(OAc)_2·H_2O$ (1.5), BHT (2)	2,6-lutidine (5)	DCE	34
26[d,f]	**$Cu(OAc)_2·H_2O$ (1.5)**	**2,6-lutidine (5)**	**DCE**	**69**
27[d,g]	**$Cu(OAc)_2·H_2O$ (1.5)**	**2,6-lutidine (5)**	**DCE**	**77**
28[d,h]	$Cu(OAc)_2·H_2O$ (1.5)	2,6-lutidine (5)	DCE	40

Typical experiment: **1a** (0.1 mmol, 1.0 equiv.), **2a** (1.2 equiv.), oxidant , base, solvent (0.1 M), MS4Å (50 mg), r. t., 2-10 h (TLC monitoring)

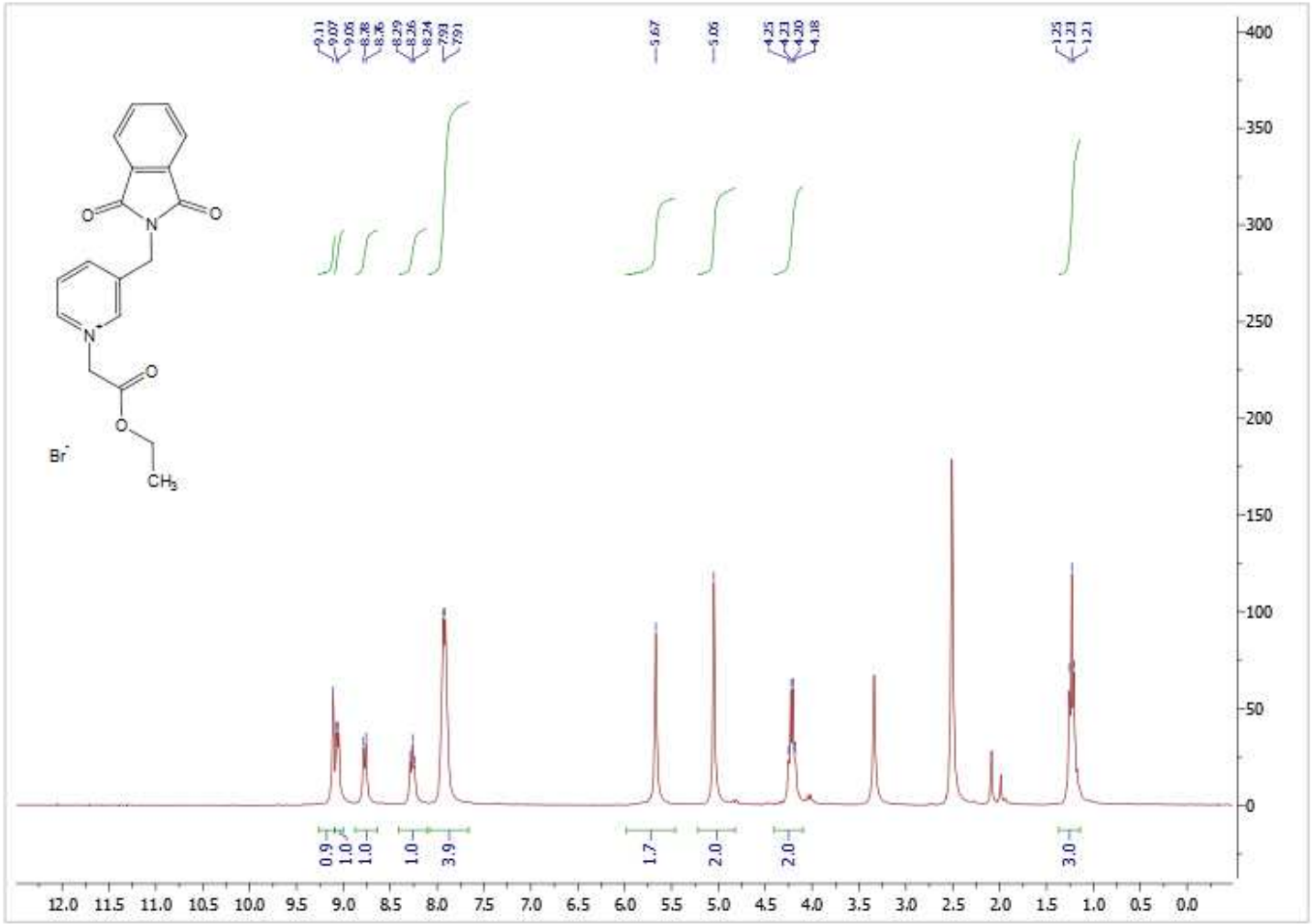
[a] Yields were determined by ^{19}F NMR with $PhCF_3$ as internal standard; [b] Yield of recovered **1a** in brackets; [c] n. r. = no reaction (**1a** was recovered); [d] The reagents were mixed at 0°C, then stirred at r. t.; [e] 65 °C. Optimal conditions from ref.[6a]. [f] 1.5 equiv. of **2a**; [g] 2.0 equiv. of **2a**. [h] Without molecular sieves.

TEMPO = 2,2,6,6-tetramethylpiperidinne 1-oxyl; BHT = 2,6-di-*tert*-butyl-4-methylphenol.

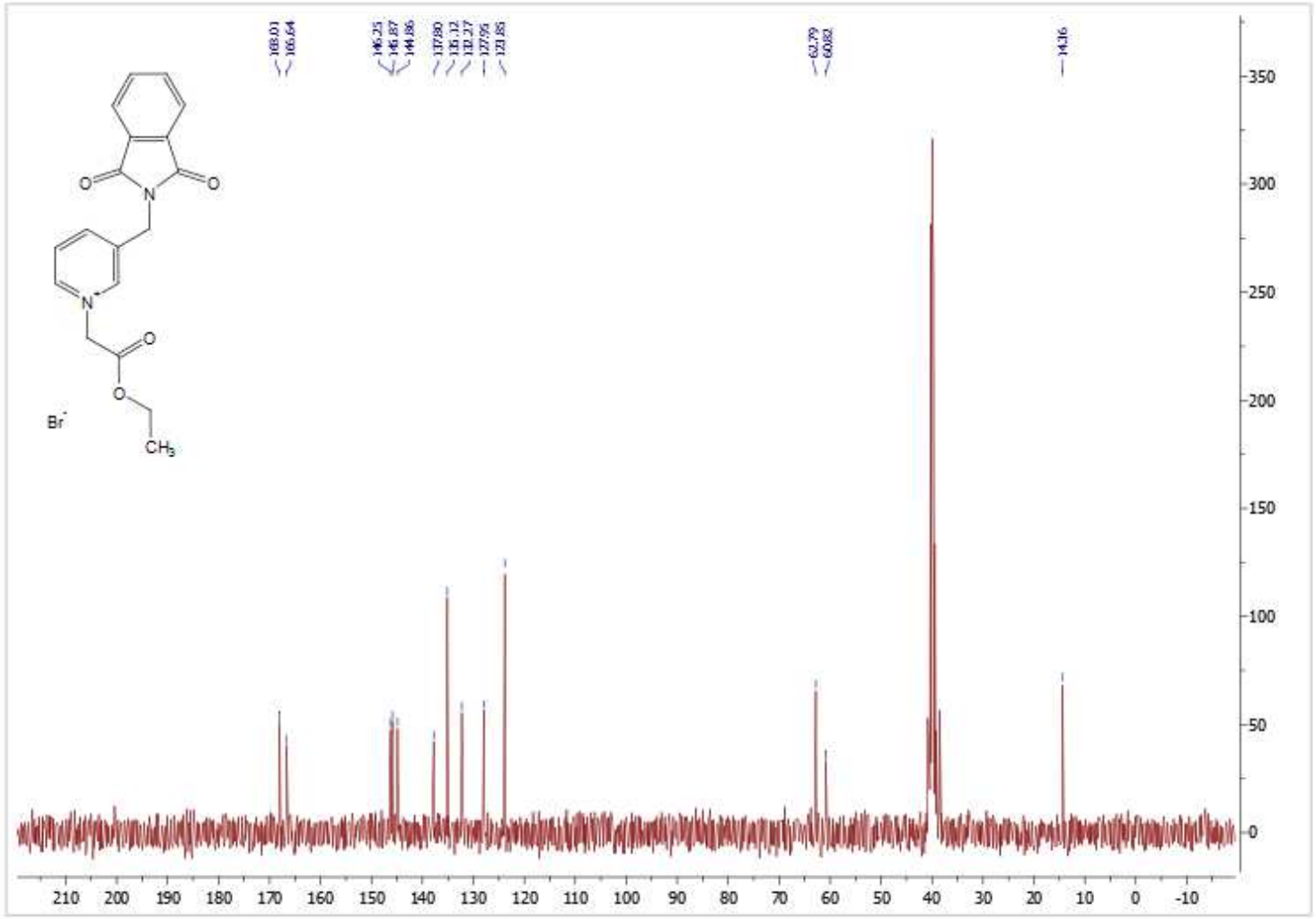
Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra

1-(ethyloxycarbonylmethyl)-3-(phthalimidomethyl)pyridinium bromide 2j

^{1}H NMR



^{13}C NMR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145.87
144.86
137.80
135.12
132.27
127.96
123.83
62.79
60.82
14.16
O
N
O
N+
O
O
Br-
CH3
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300
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150
100
50
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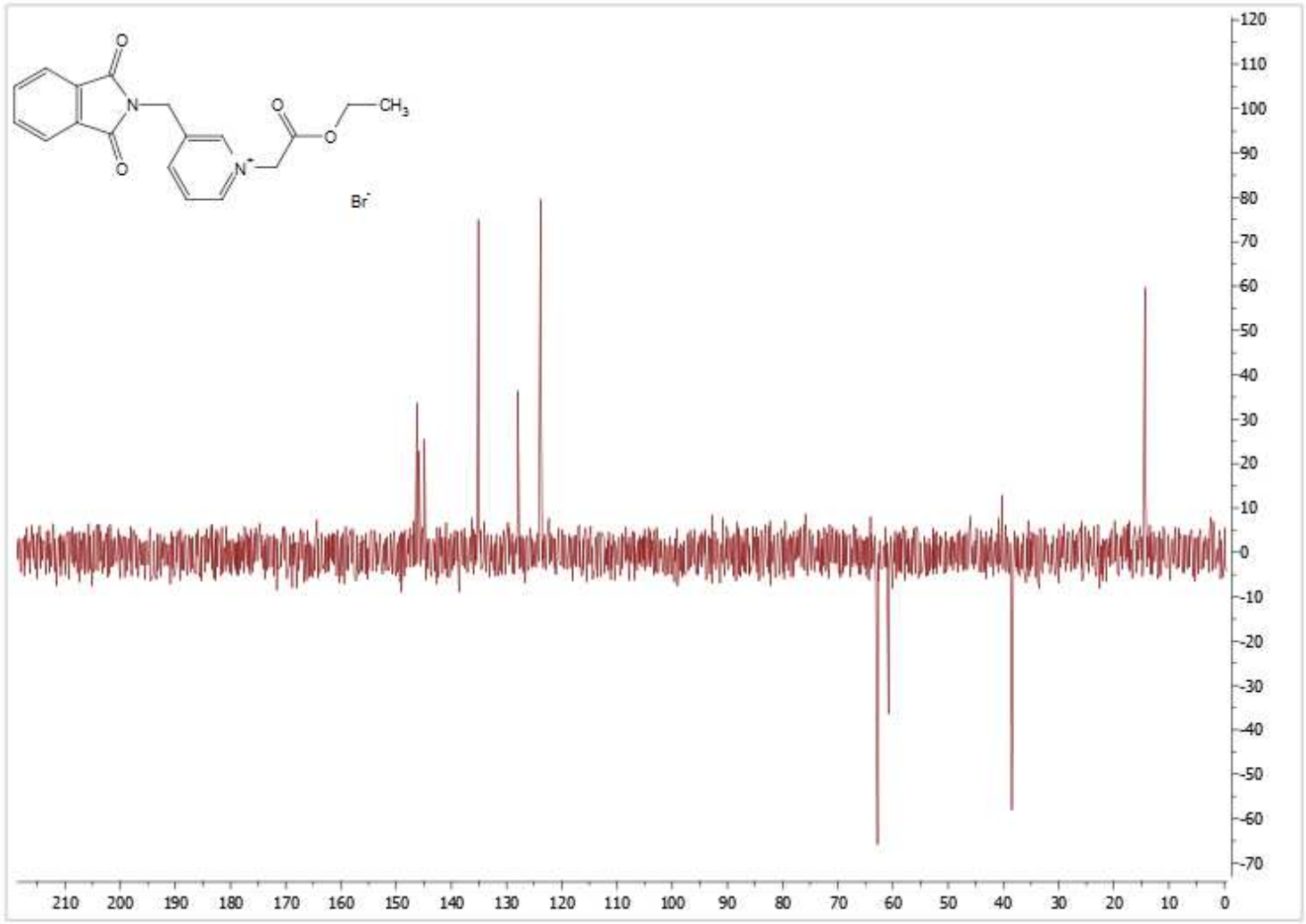
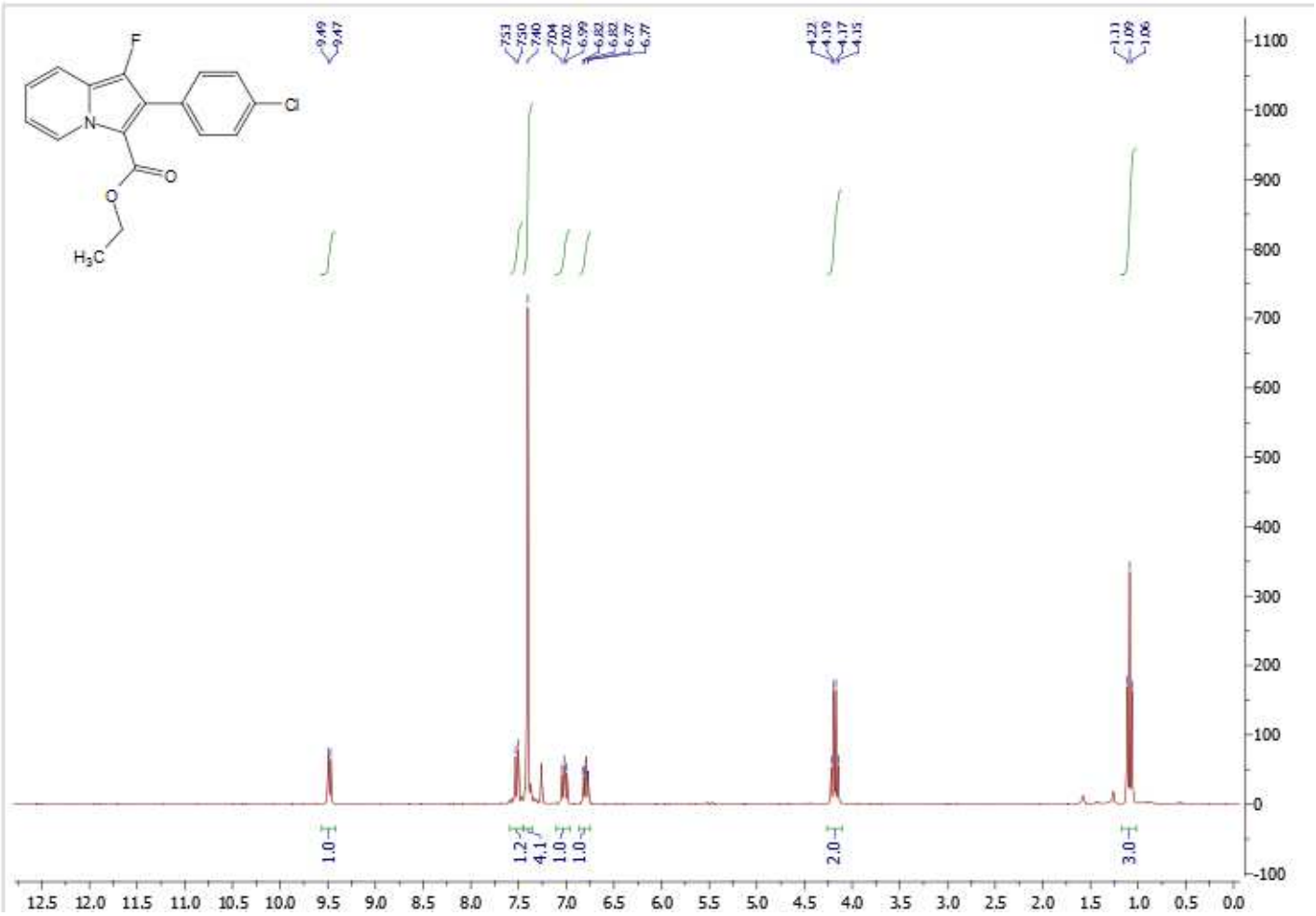
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

^{13}C DEPT-135 NMR

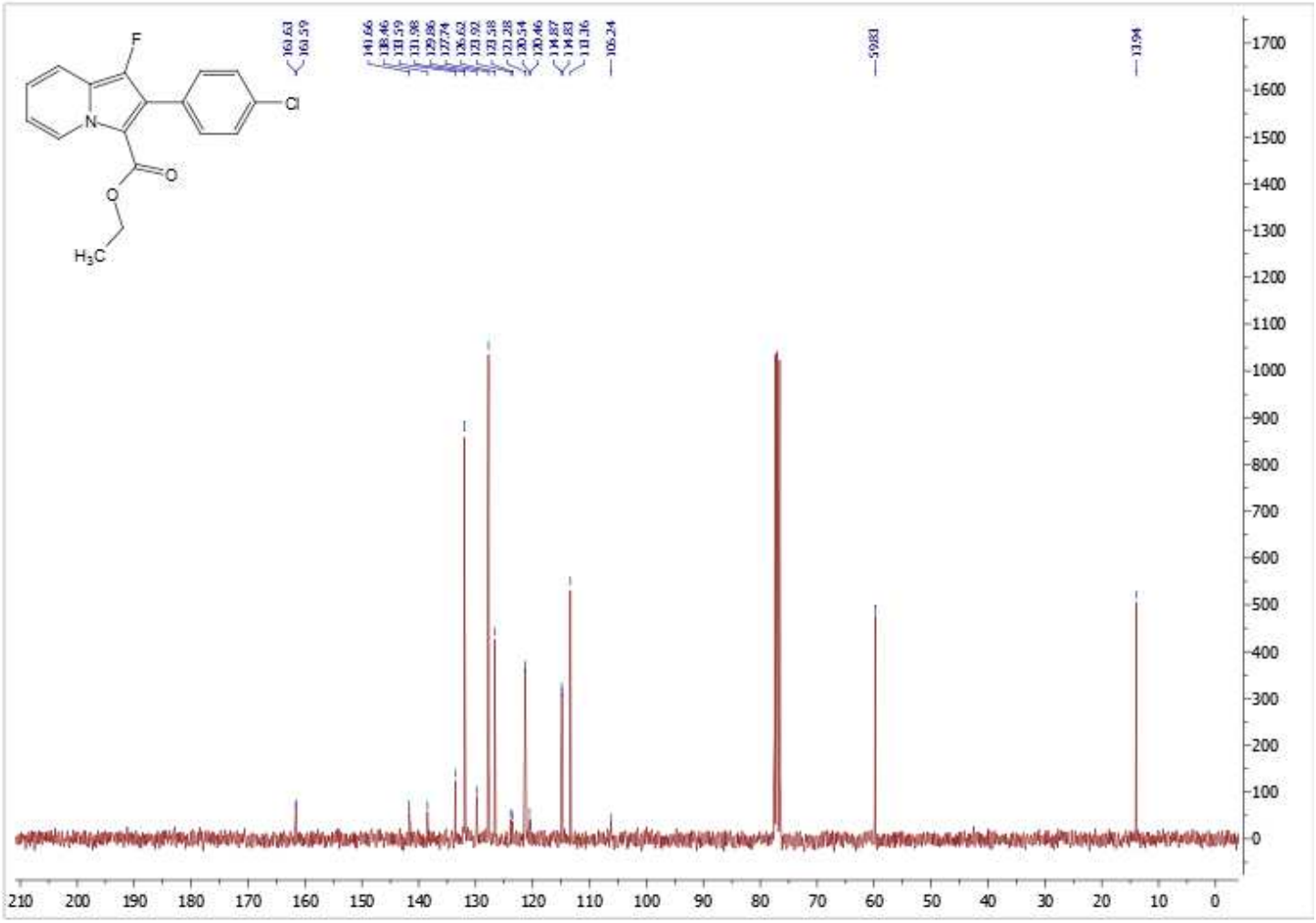


1-fluoro-2-(4-chlorophenyl)-3-(ethyloxycarbonyl)-indolizine 3a

^{1}H NMR



^{13}C NMR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123.92
123.58
123.28
120.54
120.46
114.87
114.83
113.36
105.24
59.83
13.94
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
210
200
190
180
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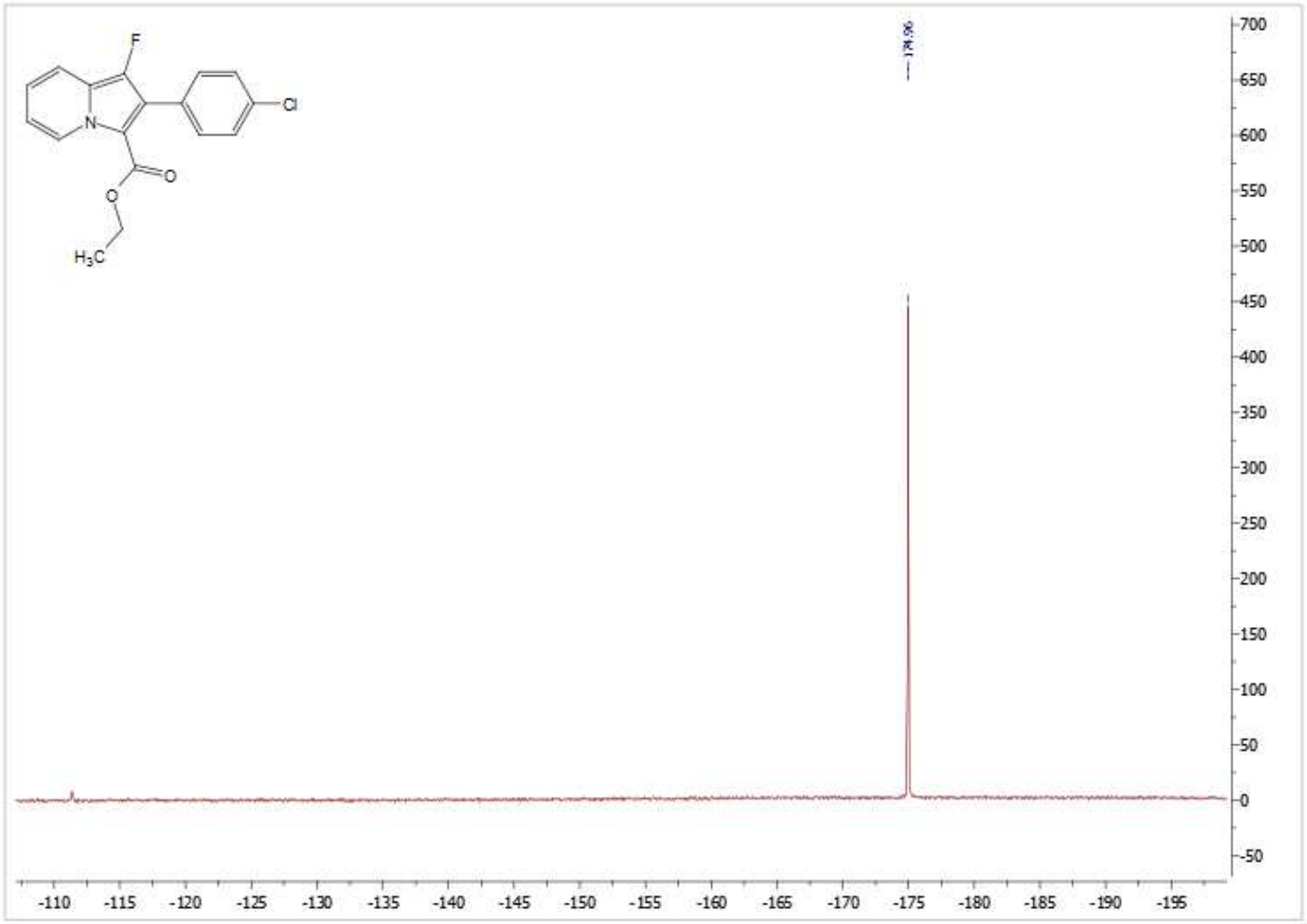
50
40
30
20
10
0

^{19}F NMR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100
50
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-50
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-120
-125
-130
-135
-140
-145
-150
-155
-160
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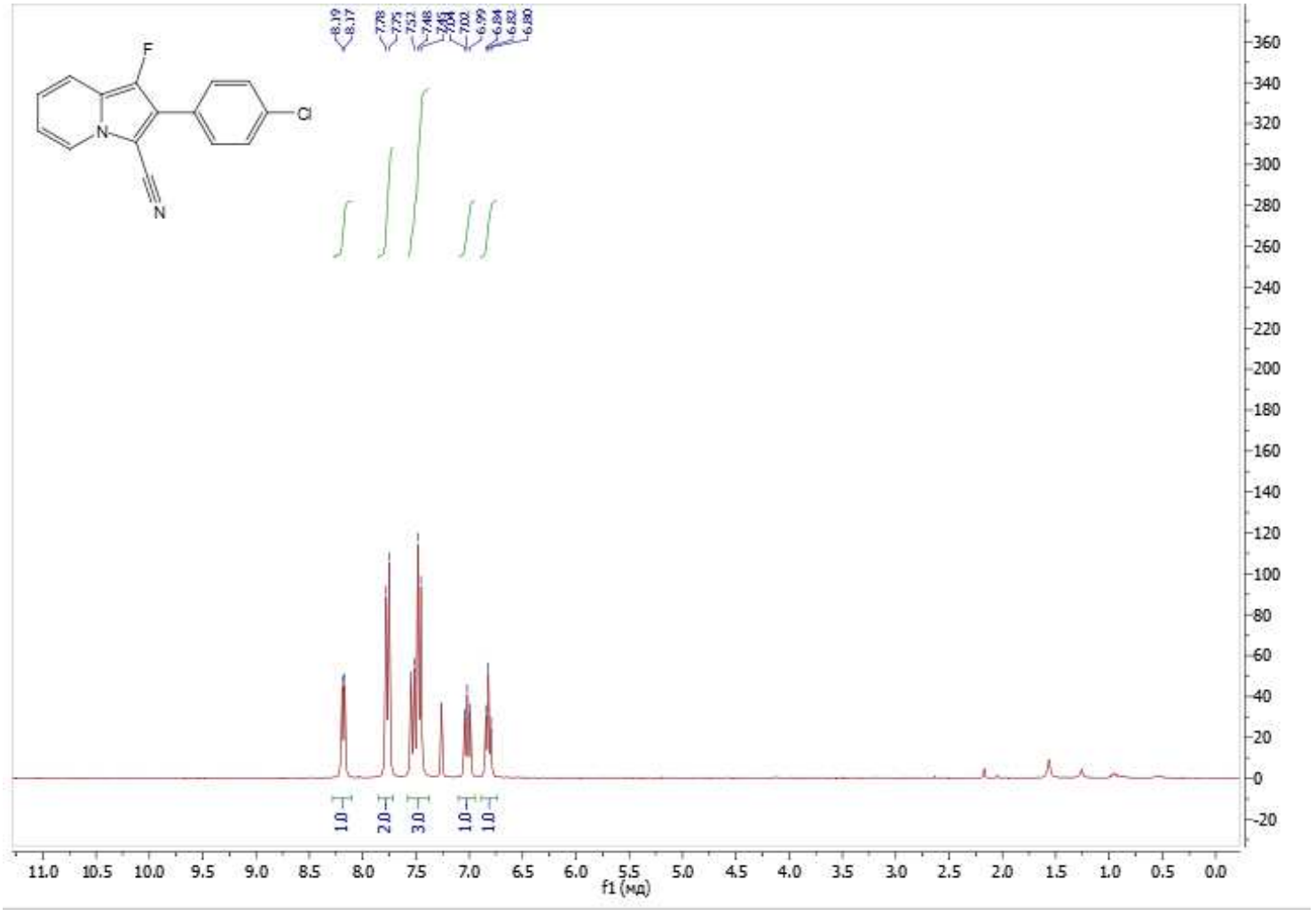
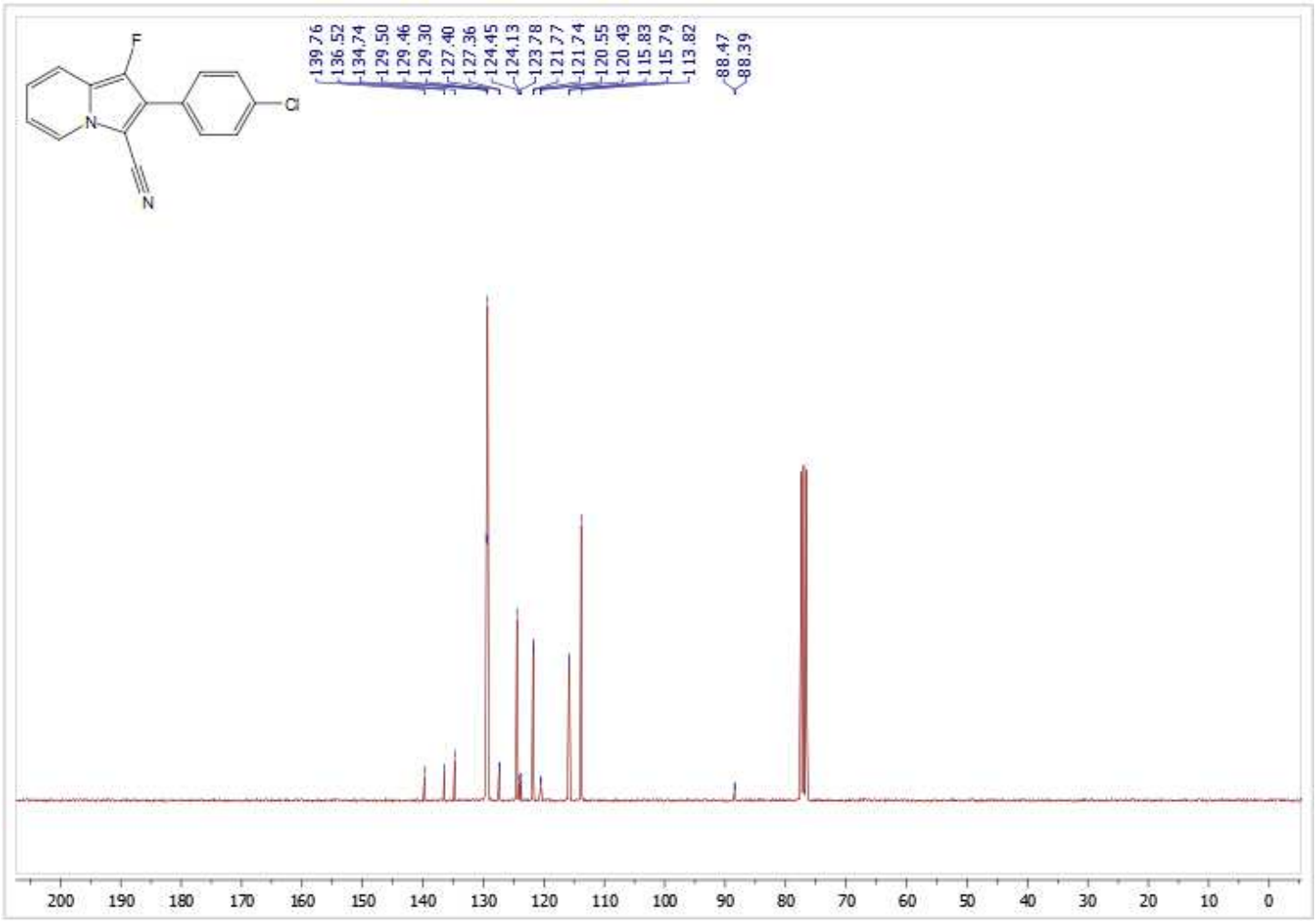
-190
-195

1-fluoro-2-(4-chlorophenyl)-indolizine-3-carbonitrile 3b

^{1}H NMR



^{13}C NMR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115.83
115.79
113.82
88.47
88.39
200
190
180
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90
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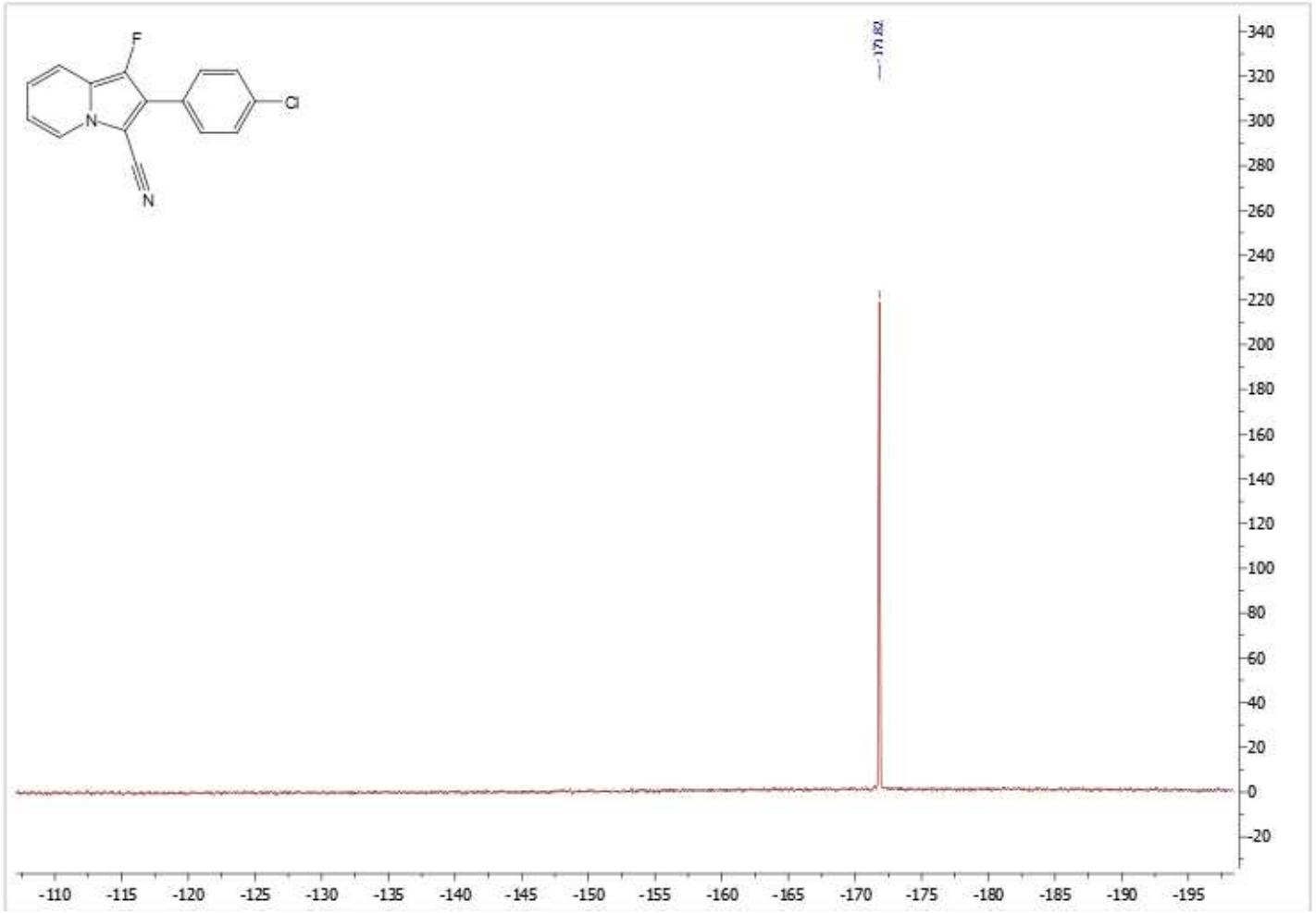
70
60
50
40
30
20
10
0

^{19}F NMR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-150
-155
-160
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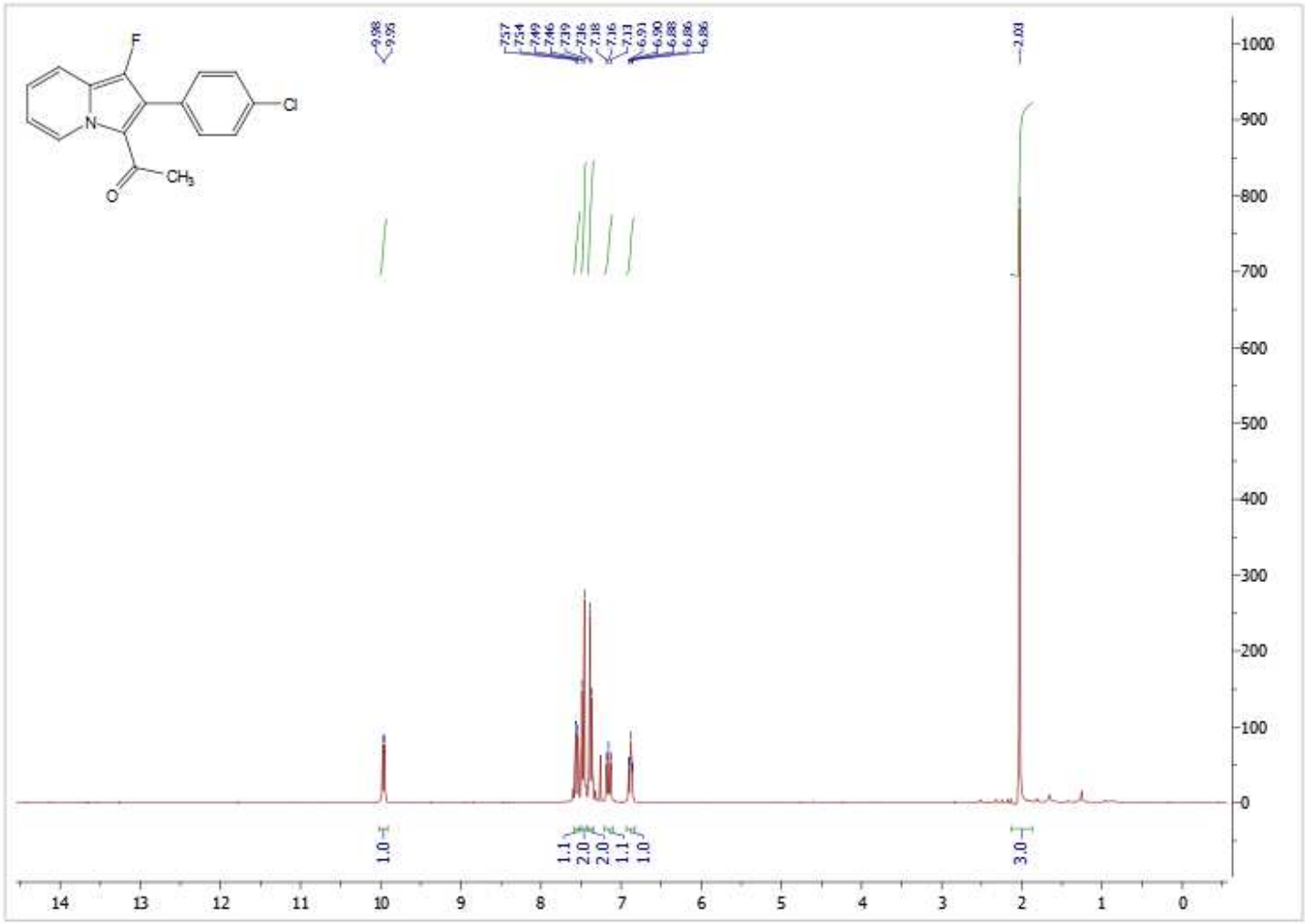
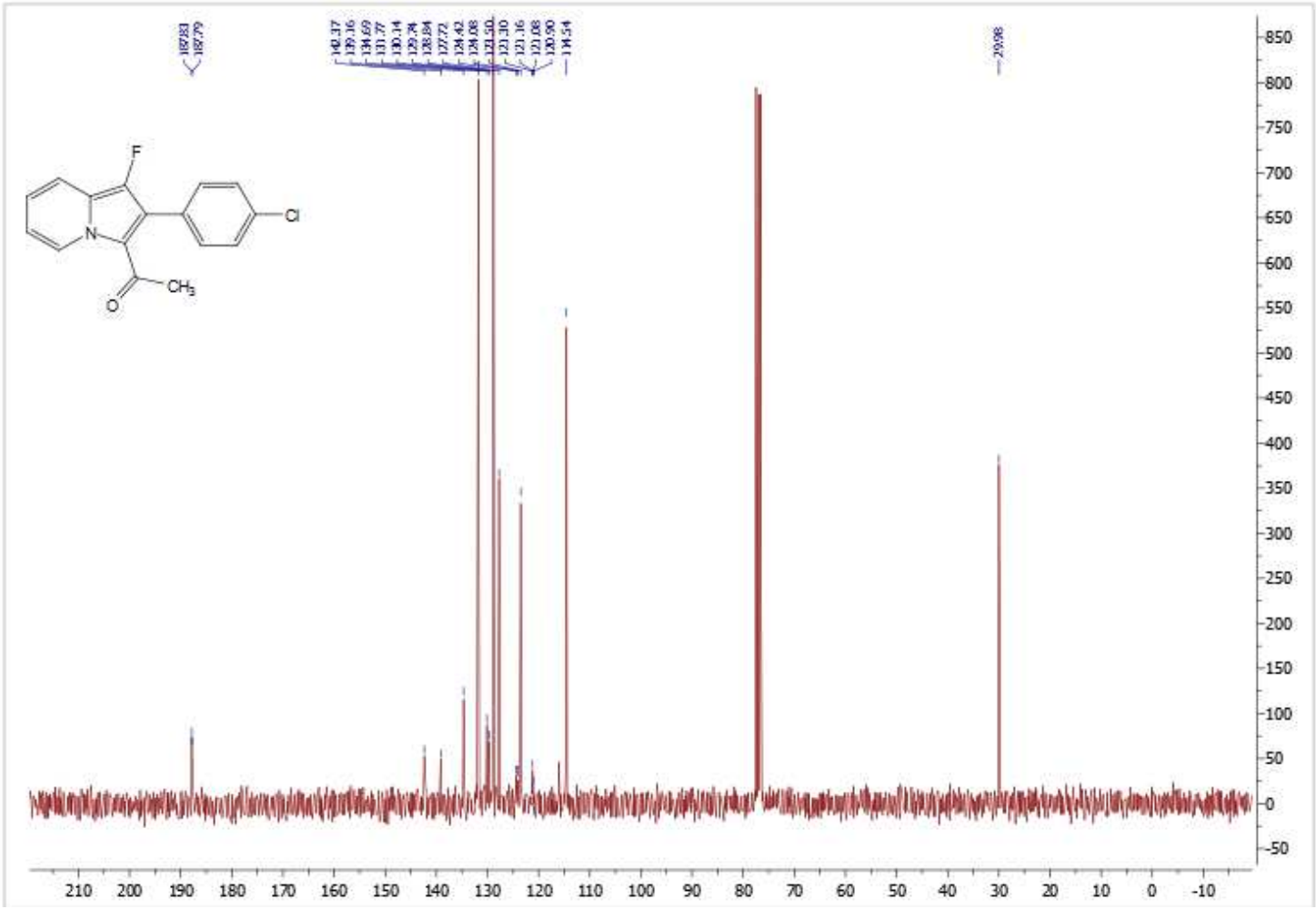
1-fluoro-2-(4-chlorophenyl)-3-(methylcarbonyl)-indolizine 3c

^{1}H NMR



^{13}C NMR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123.30
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121.08
120.90
114.54
29.98
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700
650
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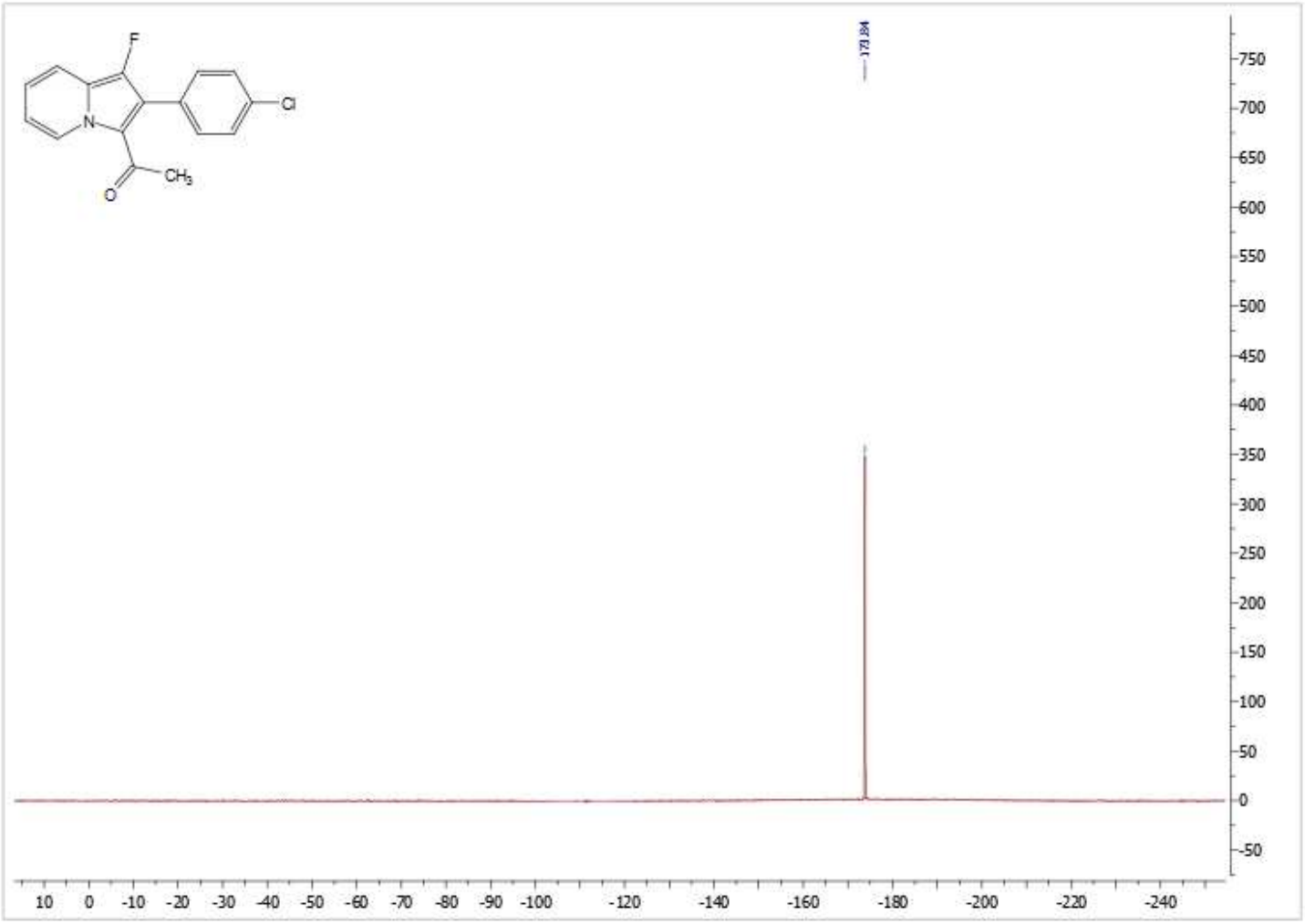
^{19}F NMR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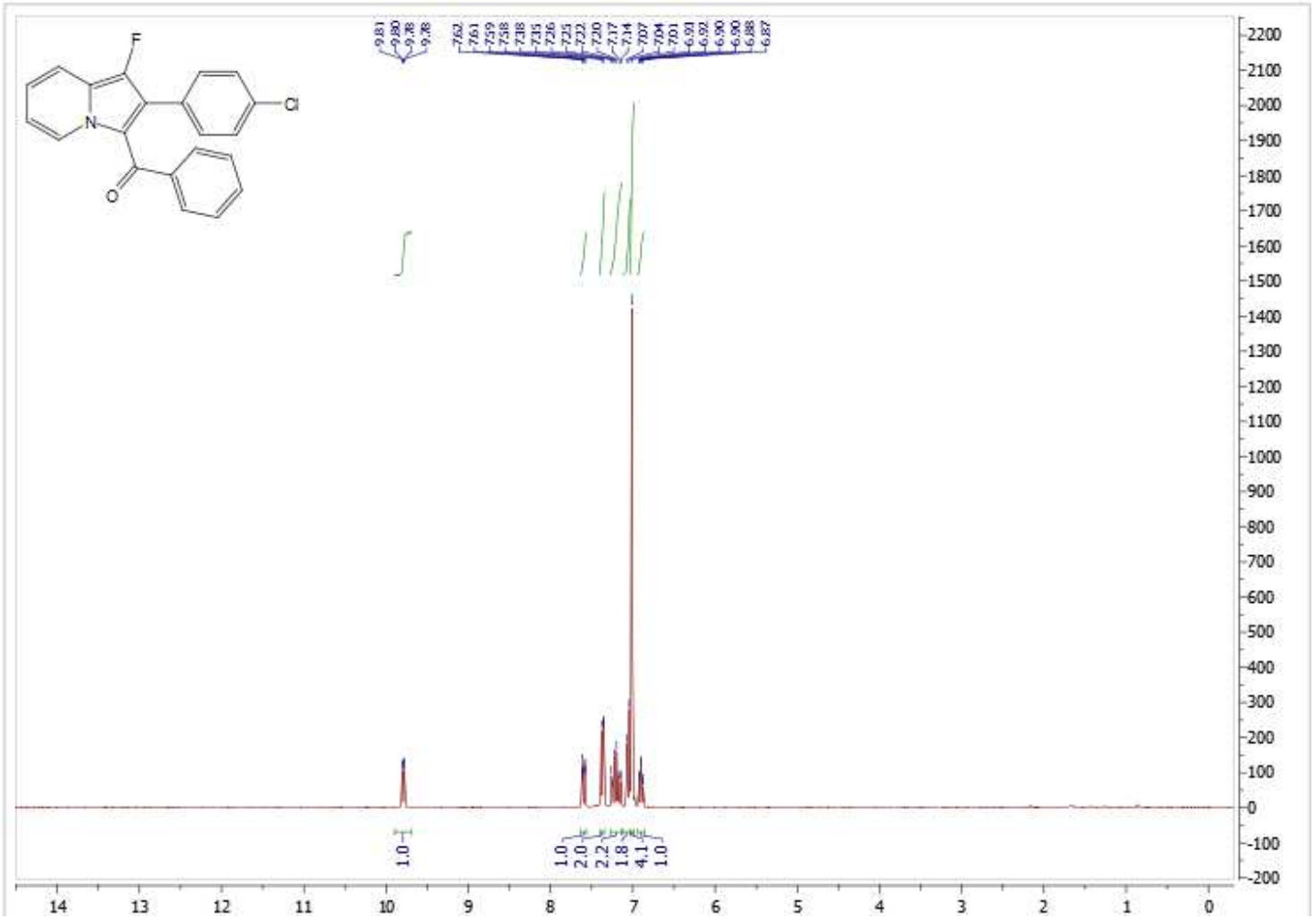
1-fluoro-2-(4-chlorophenyl)-3-(phenylcarbonyl)-indolizine 3d

^{1}H NMR



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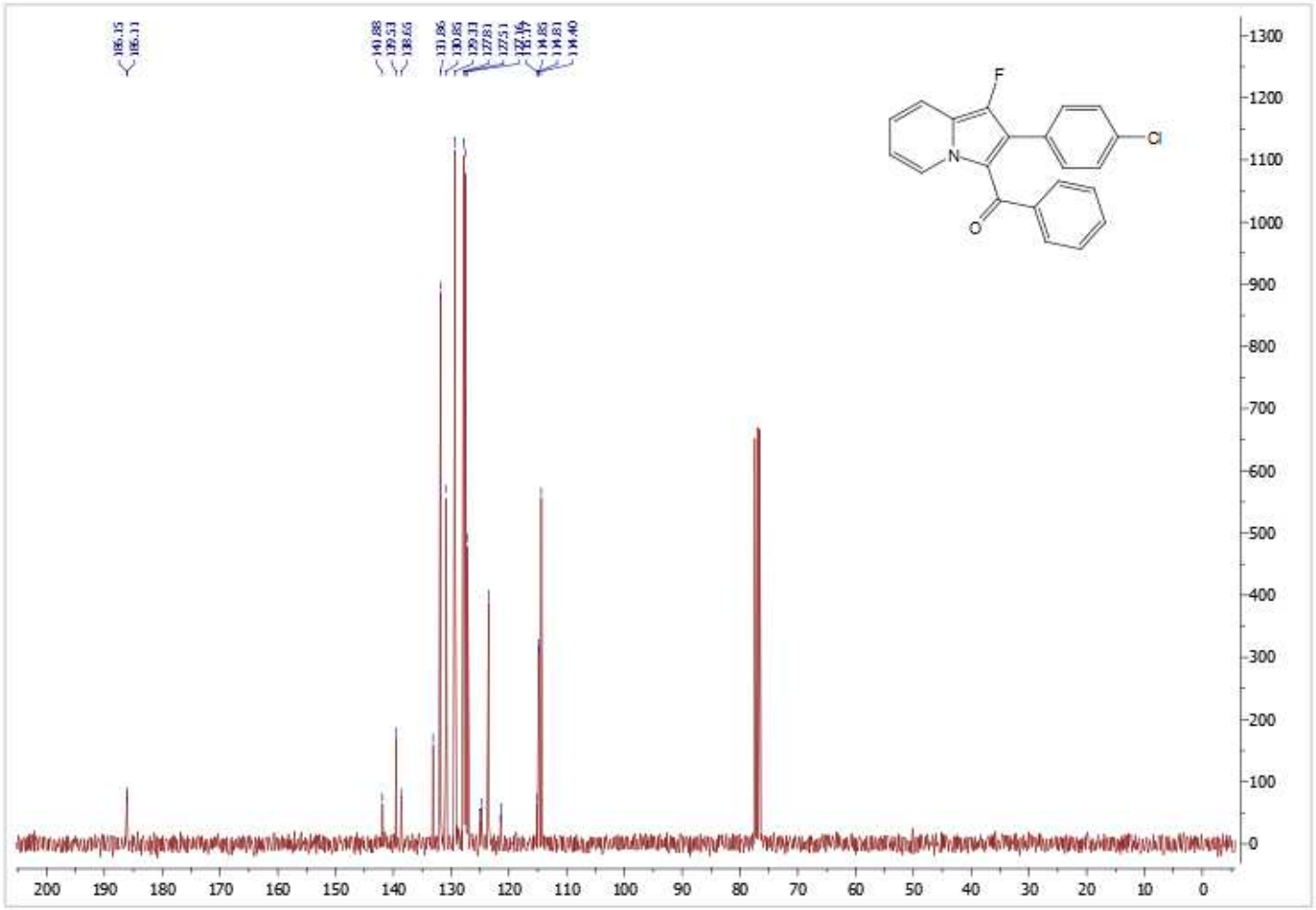
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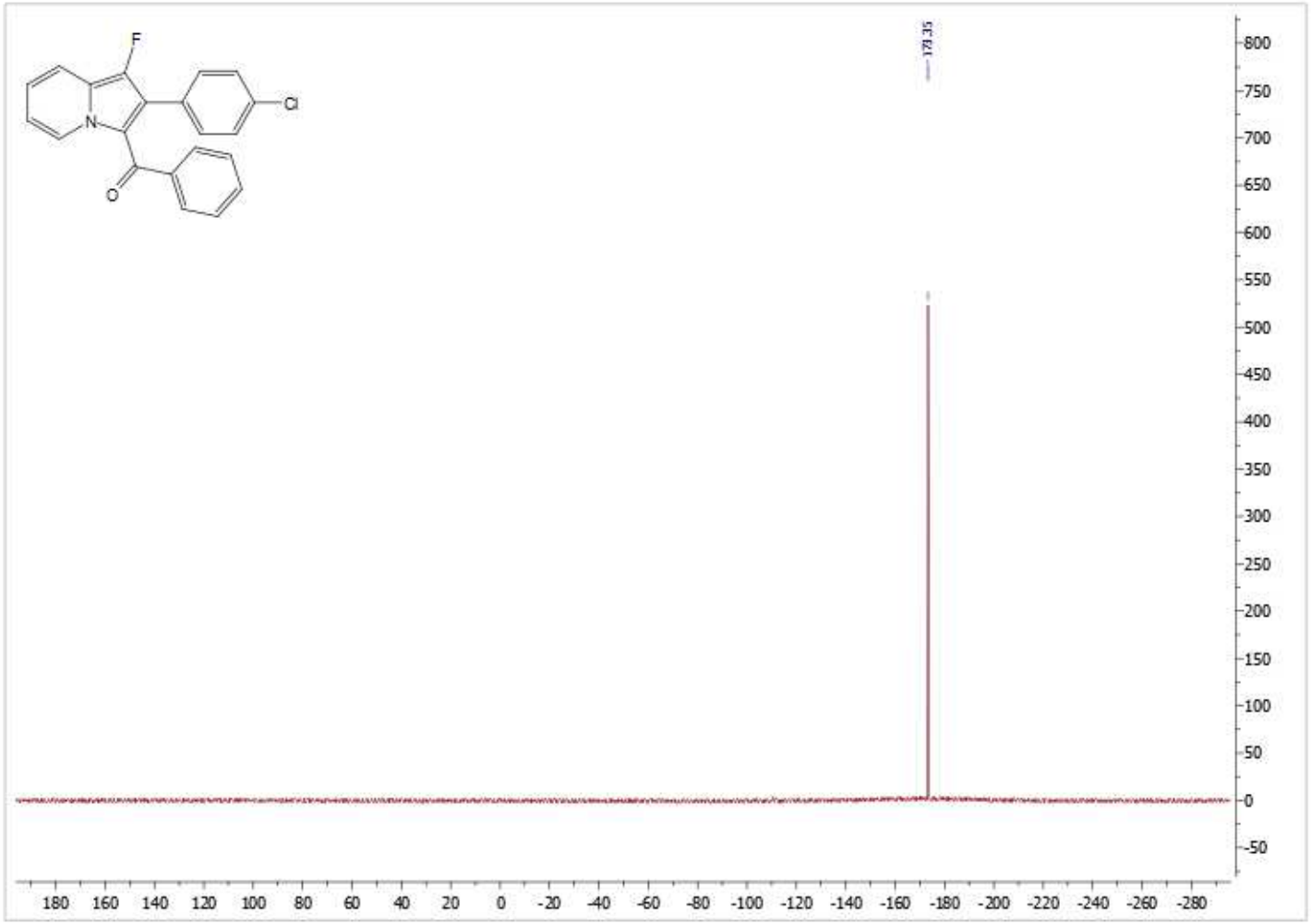
^{19}F NMR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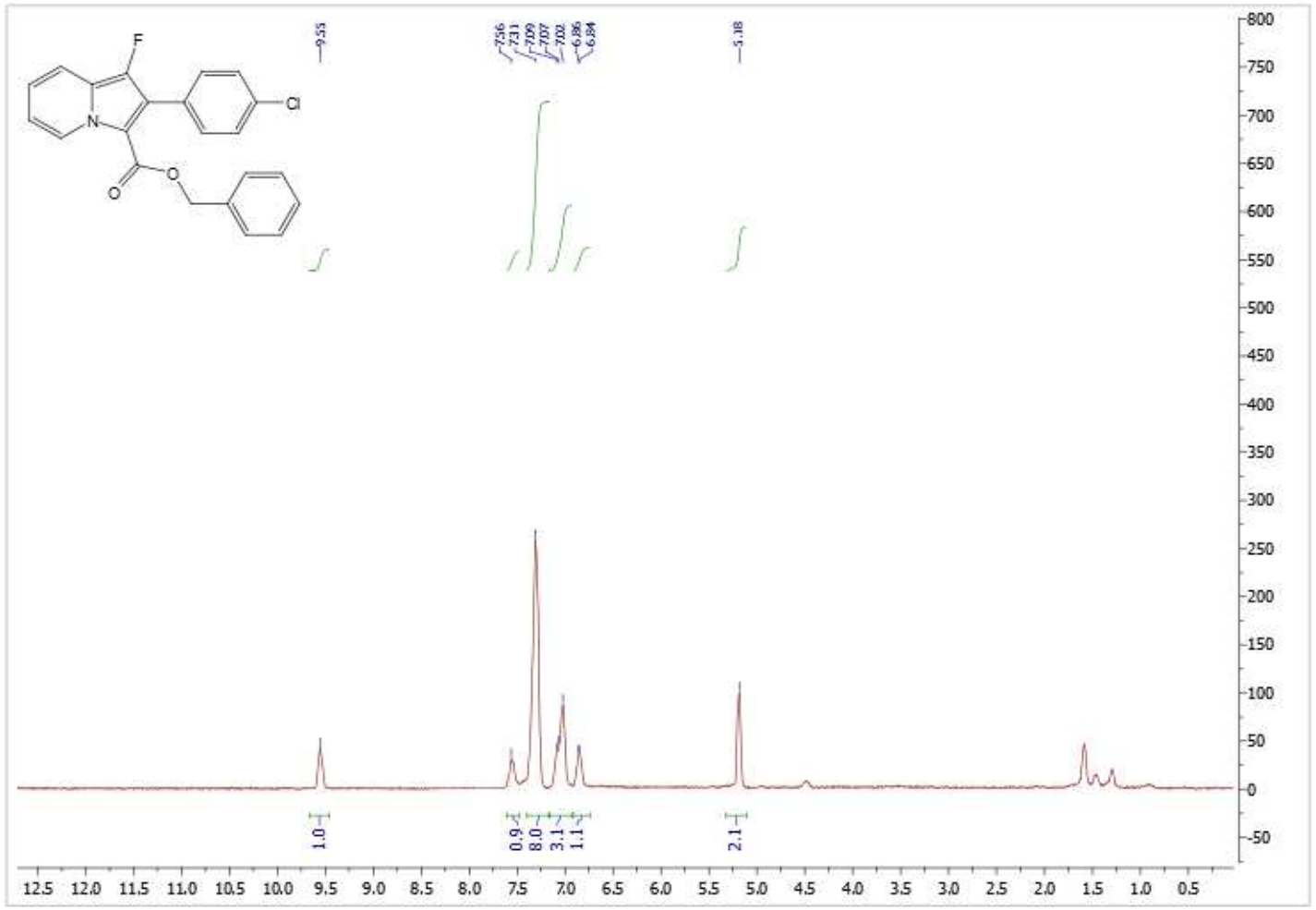
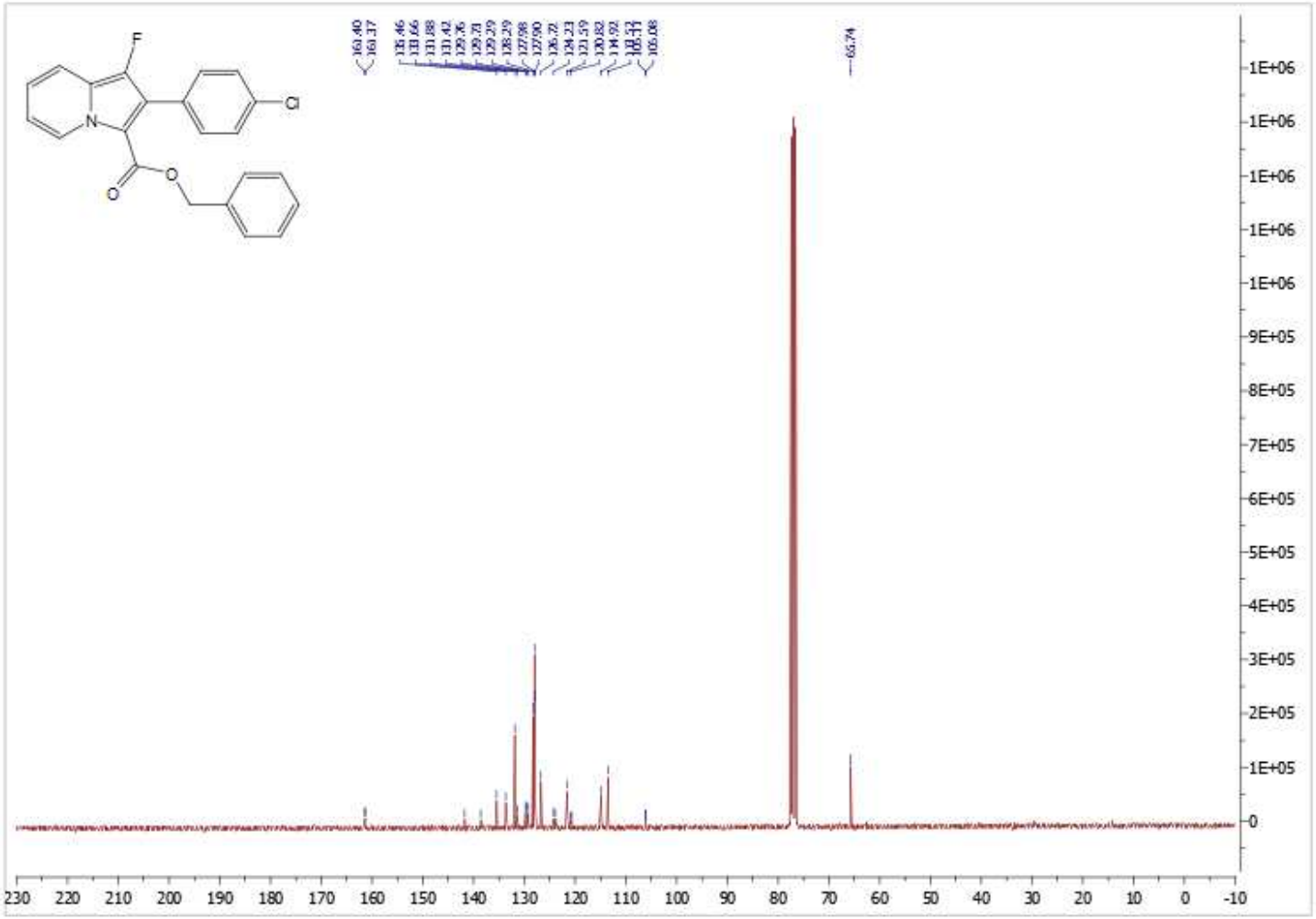
100
50
0
-50
180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280

1-fluoro-2-(4-chlorophenyl)-3-(benzyloxycarbonyl)-indolizine 3e

^{1}H NMR



^{13}C NMR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128.29
127.98
127.90
126.72
124.23
121.59
120.82
114.92
105.08
65.74
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1E+06
1E+06
1E+06
1E+06
9E+05
8E+05
7E+05
6E+05
5E+05
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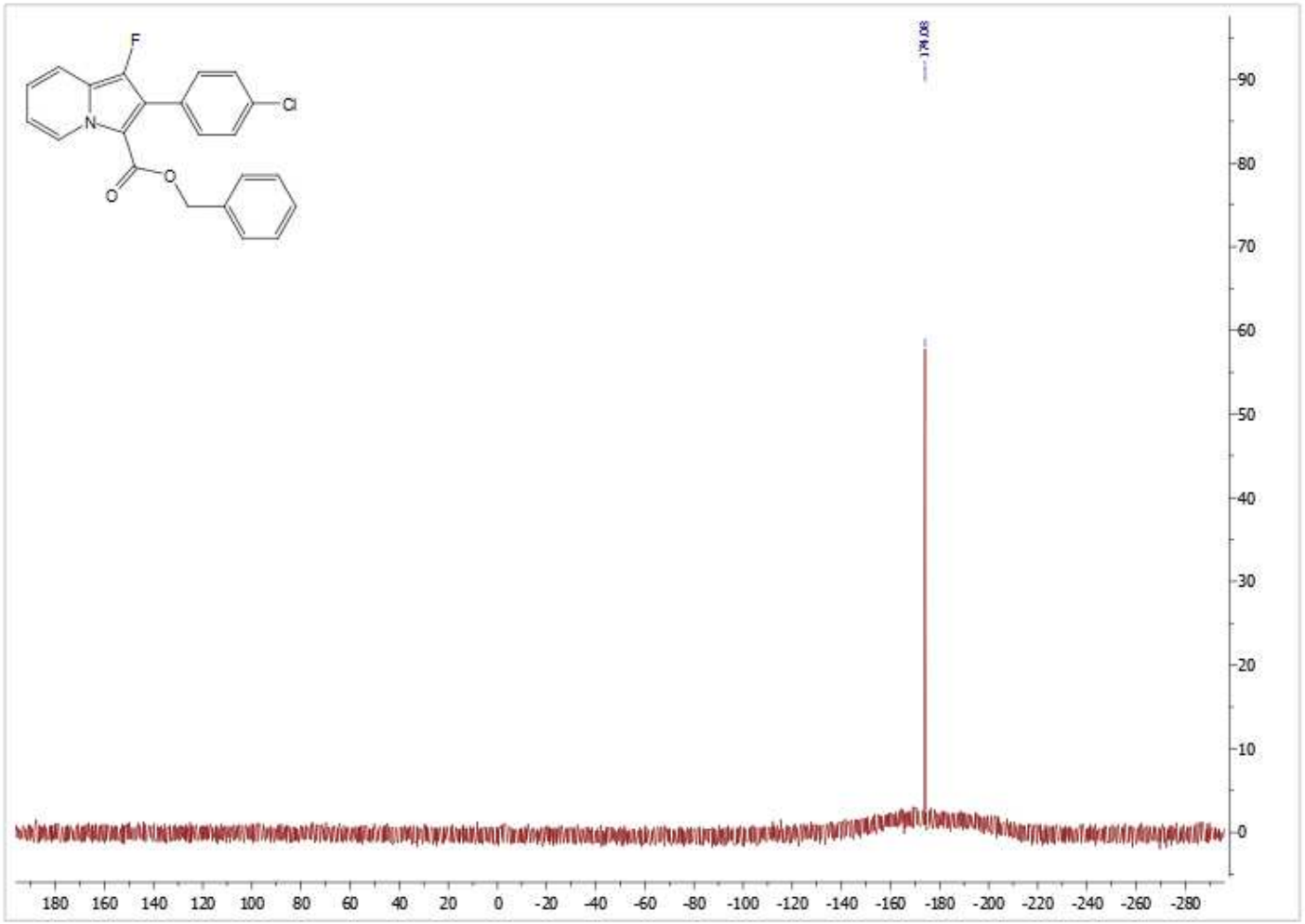
^{19}F NMR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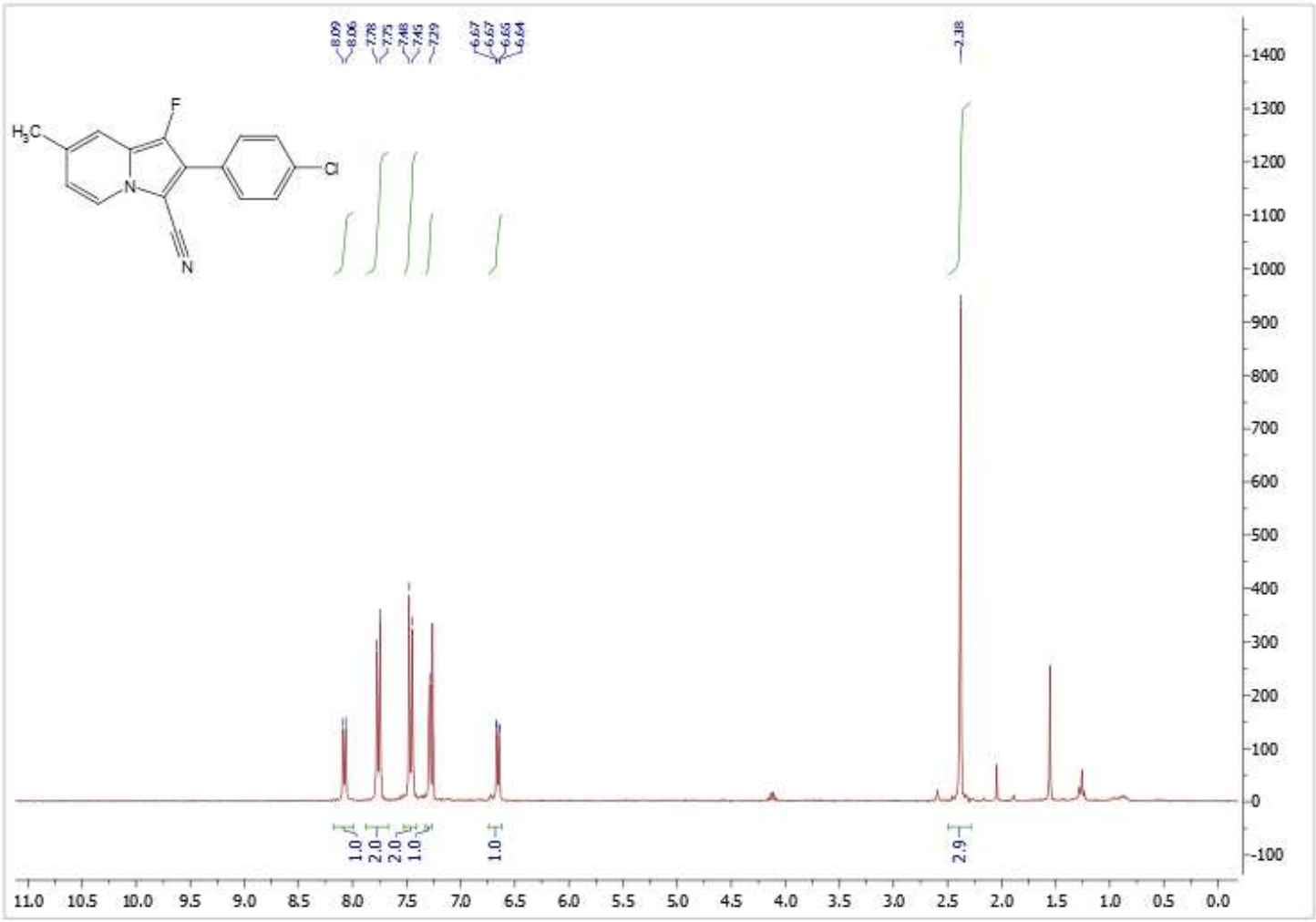
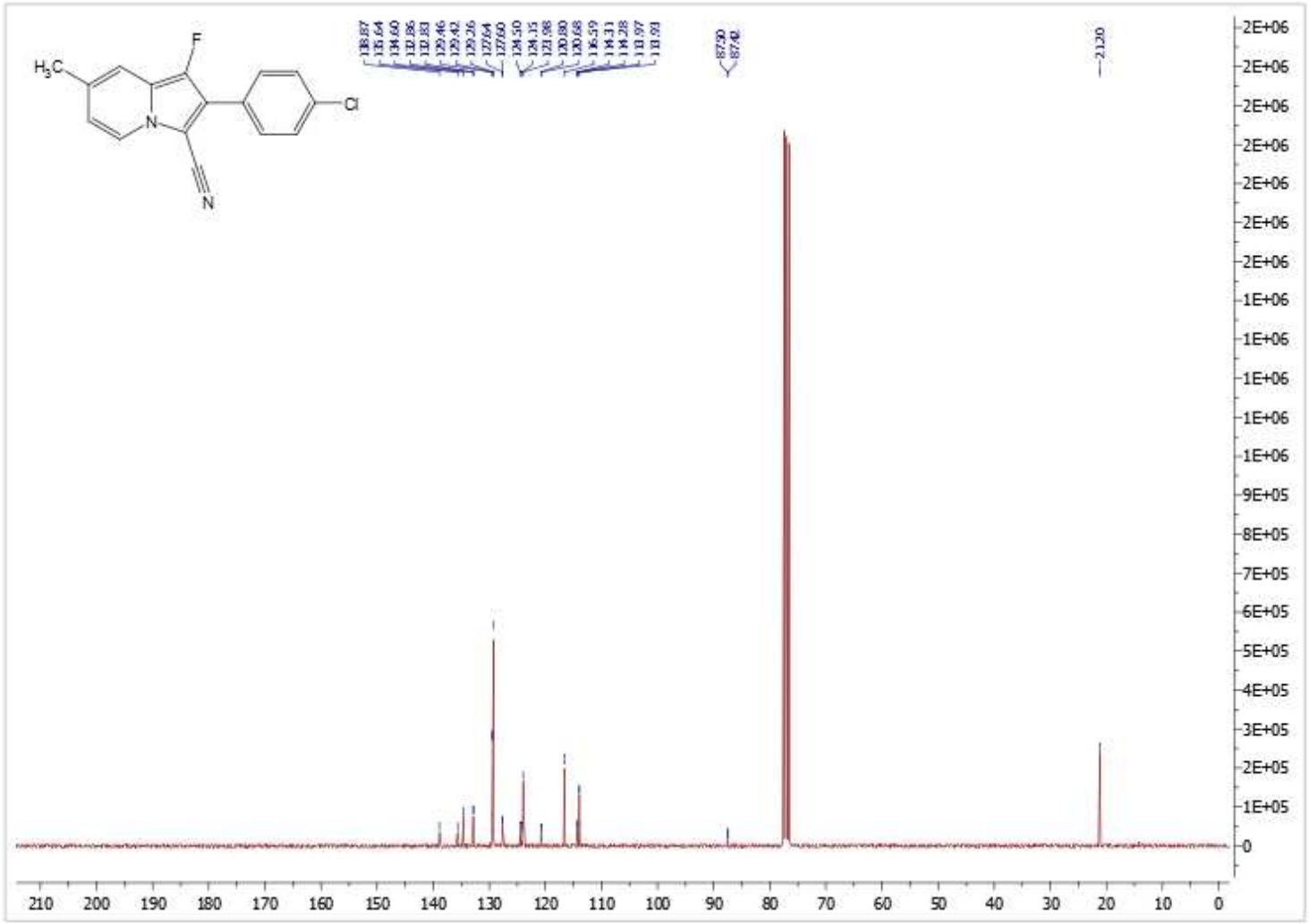
70
60
50
40
30
20
10
0
180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280

1-fluoro-2-(4-chlorophenyl)-7-methyl-indolizine-3-carbonitrile 3f

^{1}H NMR



^{13}C NMR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127.60
124.50
124.35
121.98
120.80
120.68
116.59
114.31
114.28
113.97
113.91
87.20
87.42
21.20
2E+06
1E+06
9E+05
8E+05
7E+05
6E+05
5E+05
4E+05
3E+05
2E+05
1E+05
0
210
200
190
180
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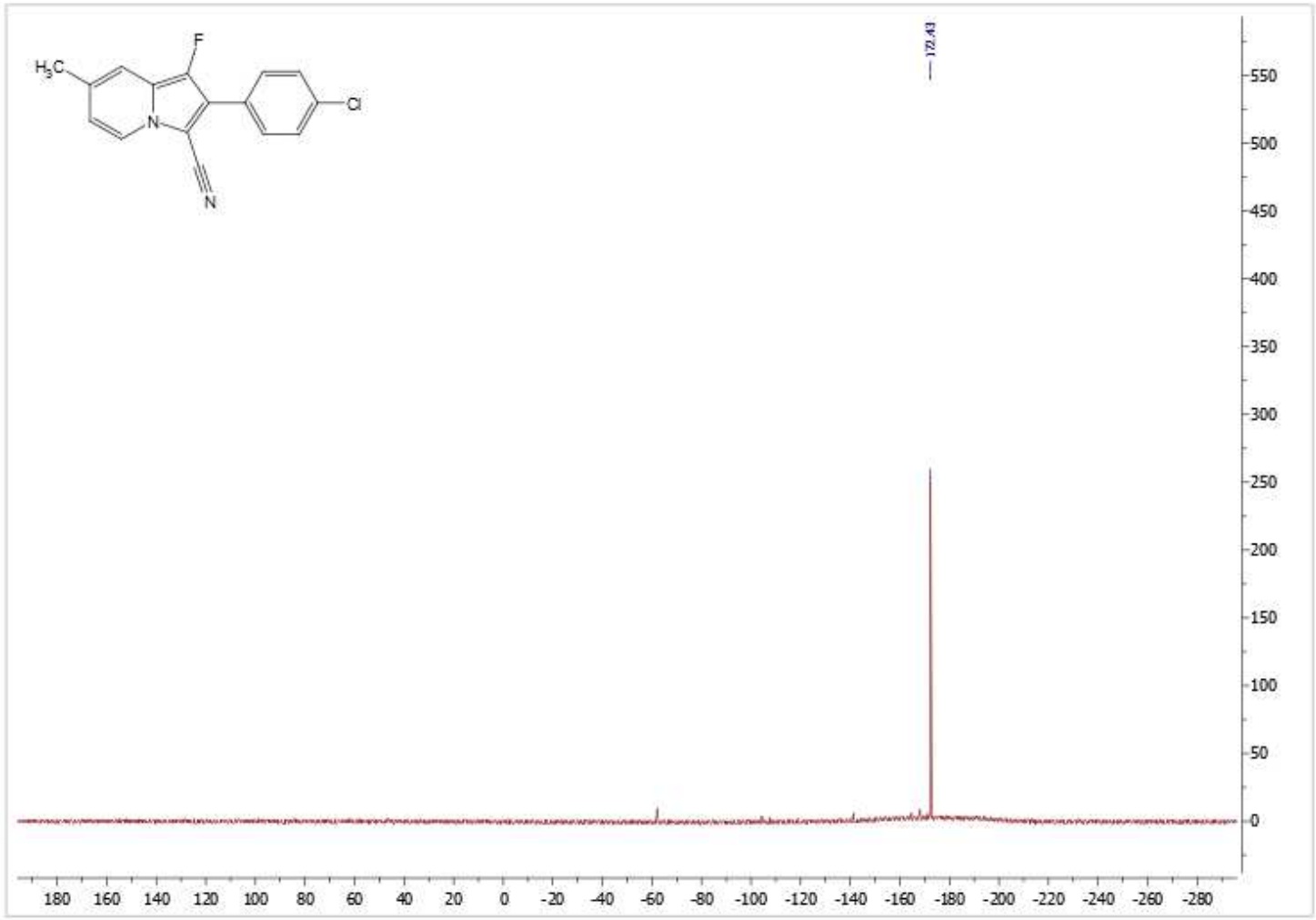
10
0

^{19}F NMR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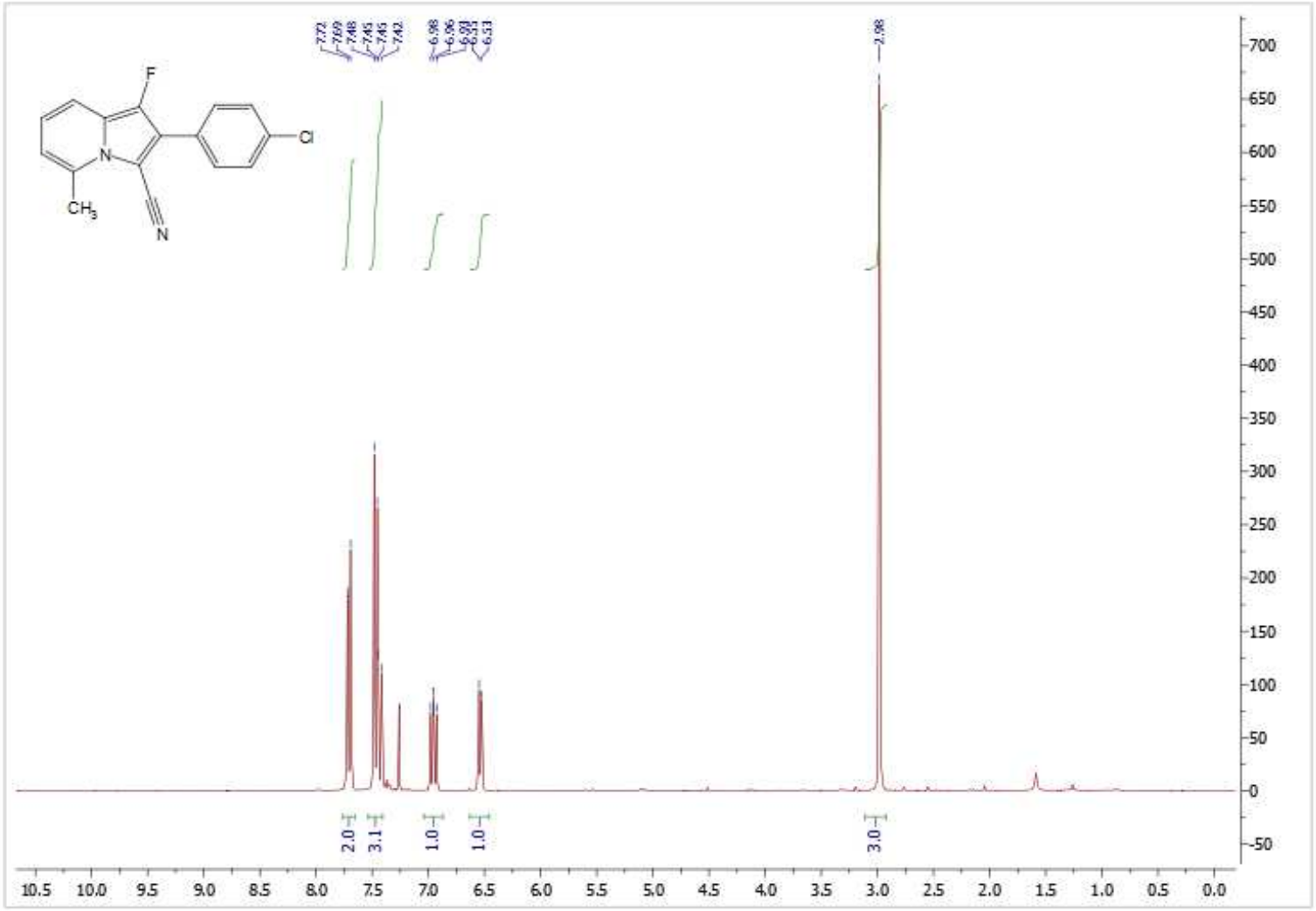
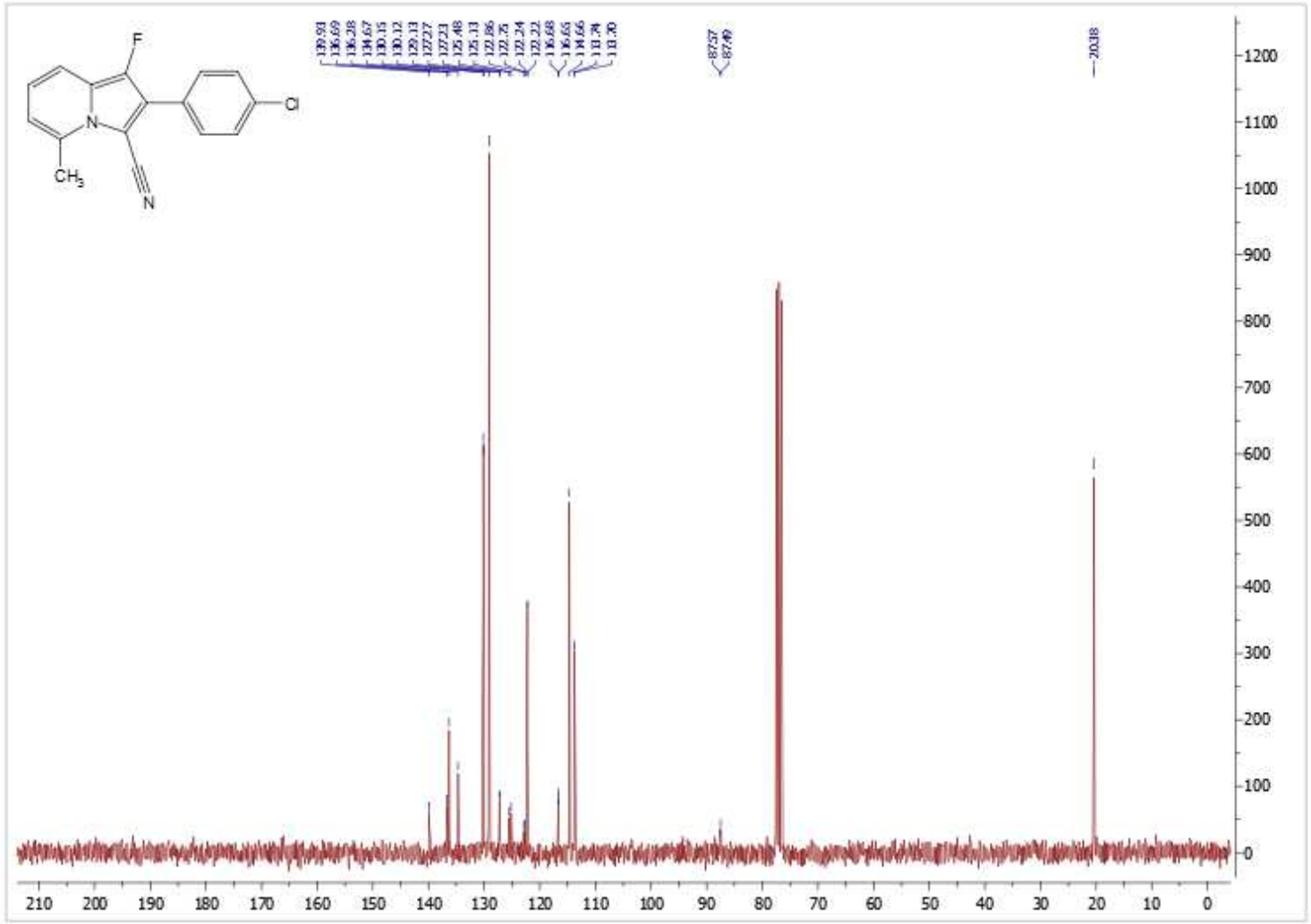
180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280

1-fluoro-2-(4-chlorophenyl)-5-methyl-indolizine-3-carbonitrile 3g

^{1}H NMR



^{13}C NMR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122.22
116.68
116.65
114.66
113.74
113.70
87.57
87.49
20.38
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
210
200
190
180
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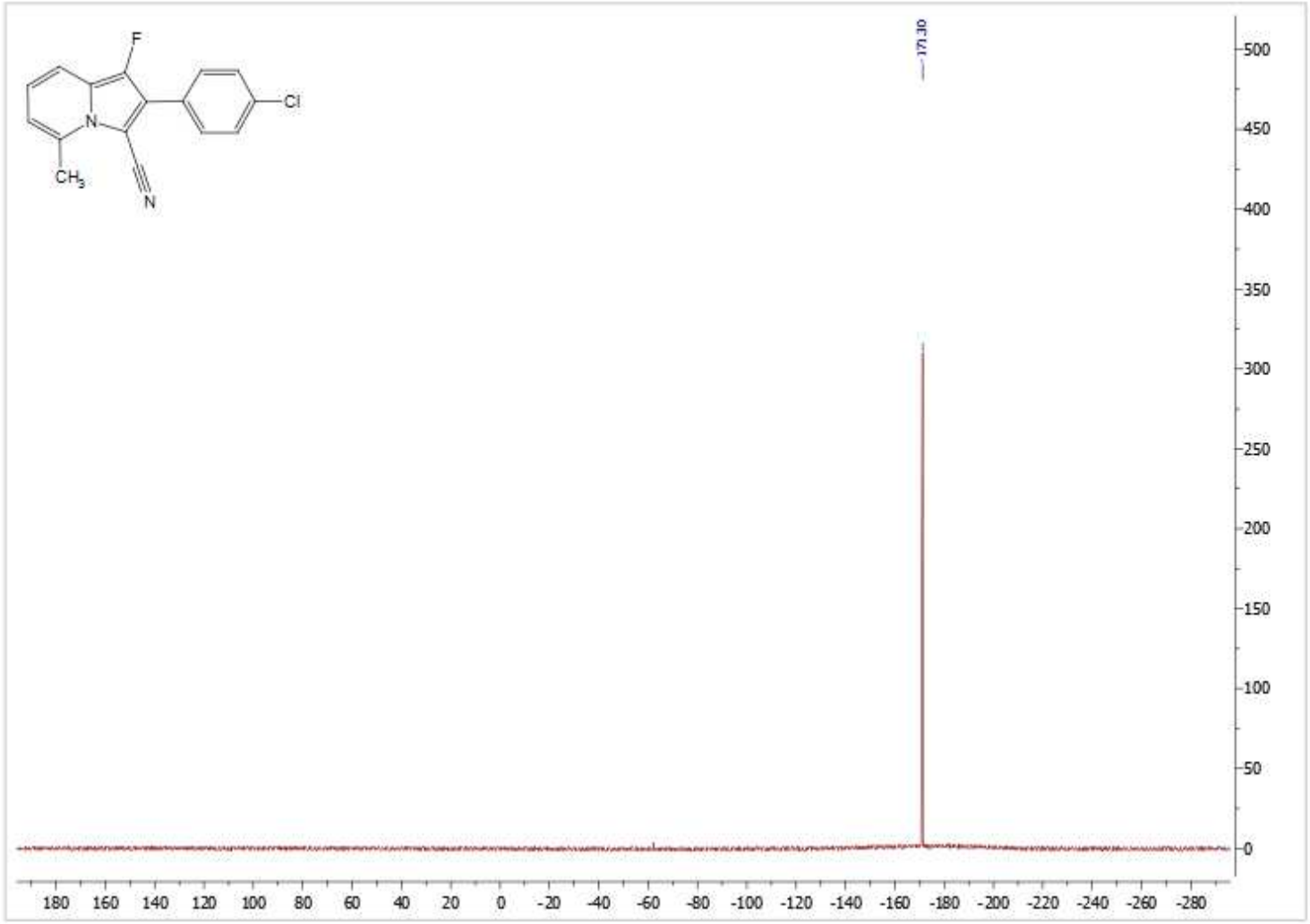
50
40
30
20
10
0

^{19}F NMR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Cl
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N
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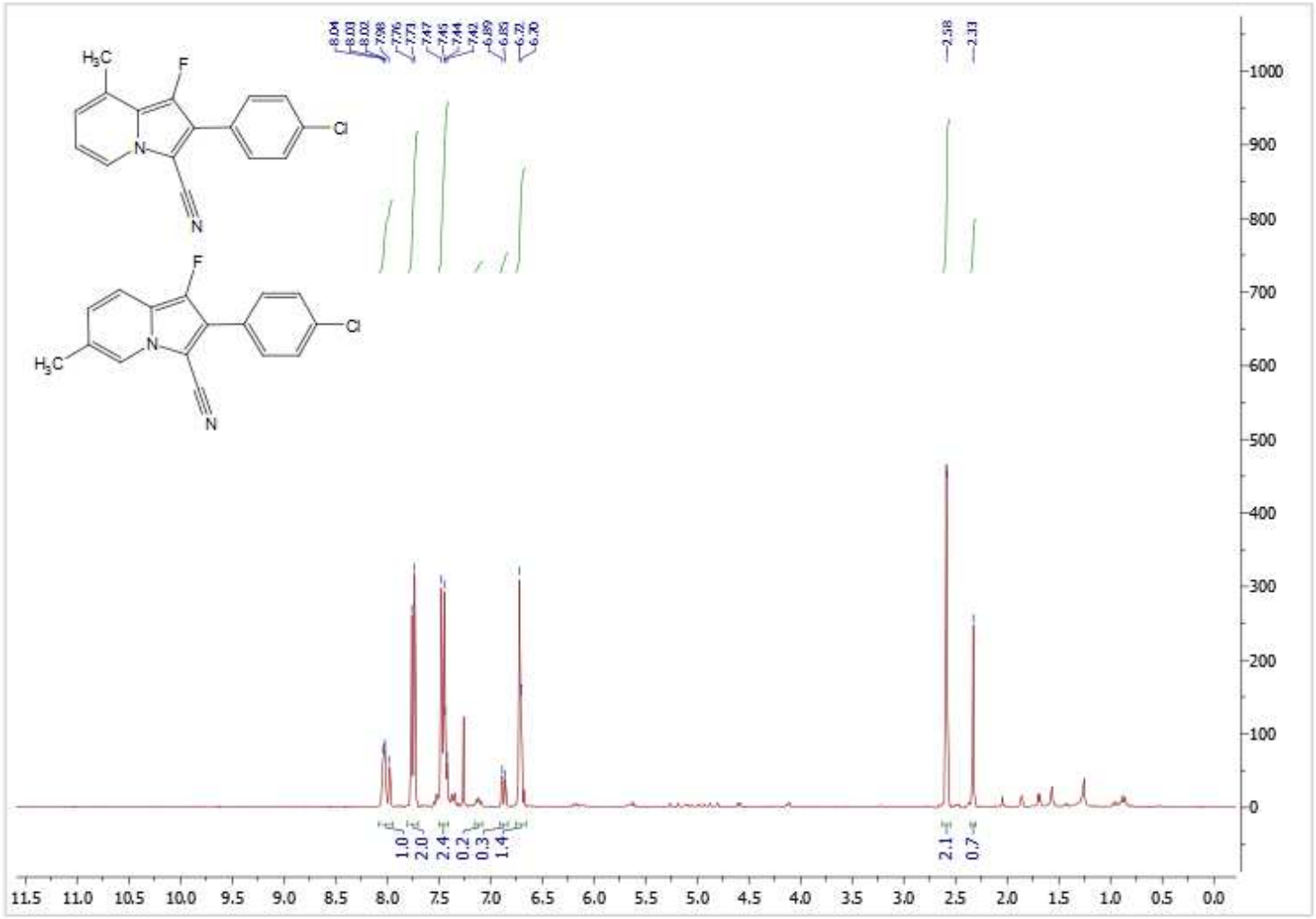
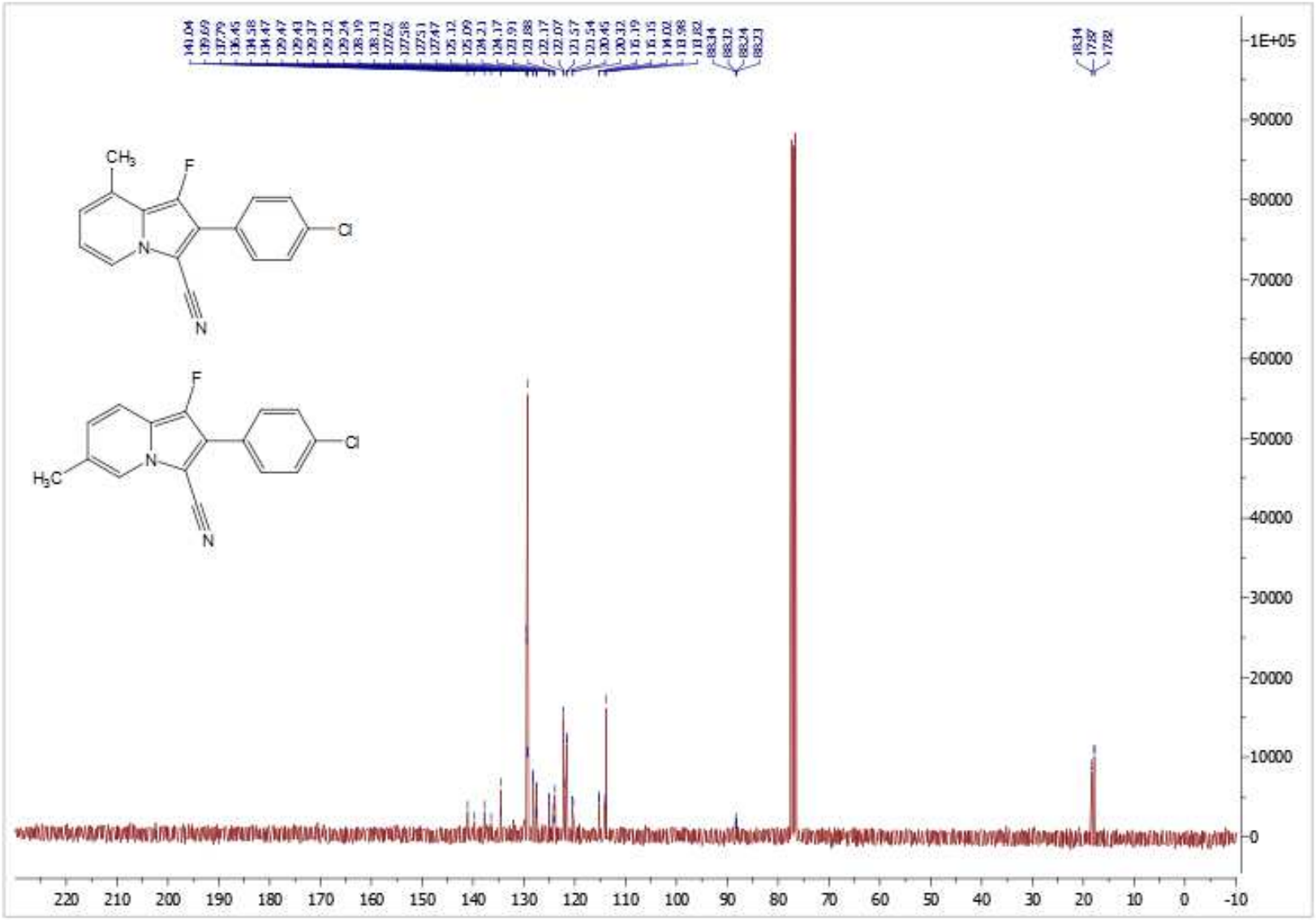
500
450
400
350
300
250
200
150
100
50
0
180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280

1-fluoro-2-(4-chlorophenyl)-8-methyl-indolizine-3-carbonitrile and 1-fluoro-2-(4-chlorophenyl)-6-methyl-indolizine-3-carbonitrile 3h

^{1}H NMR



^{13}C NMR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Cl
N
F
Cl
H3C
N
1E+05
90000
80000
70000
60000
50000
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30000
20000
10000
0
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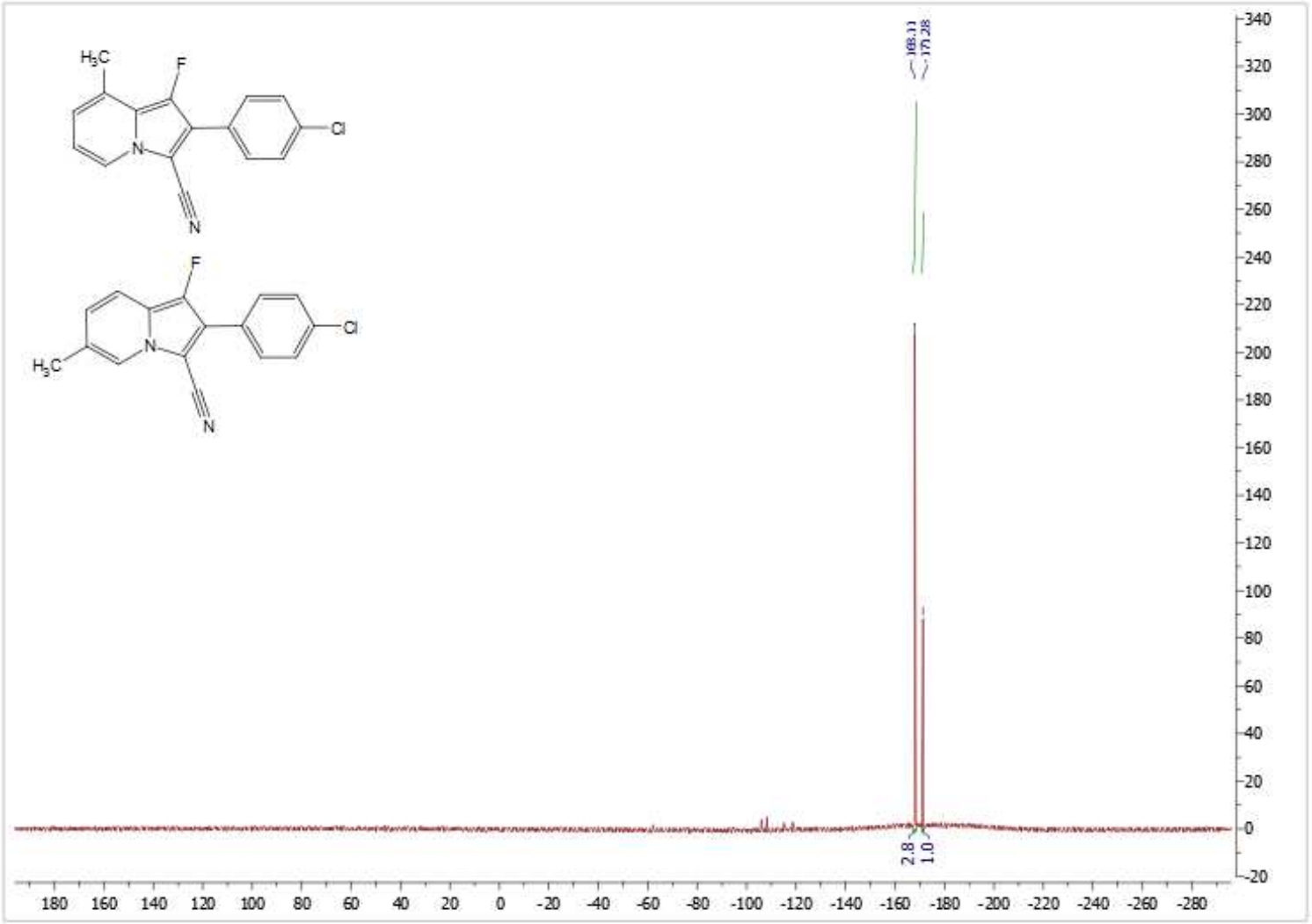
^{19}F NMR


H3C
F
Cl
N
N
F
Cl
H3C
N
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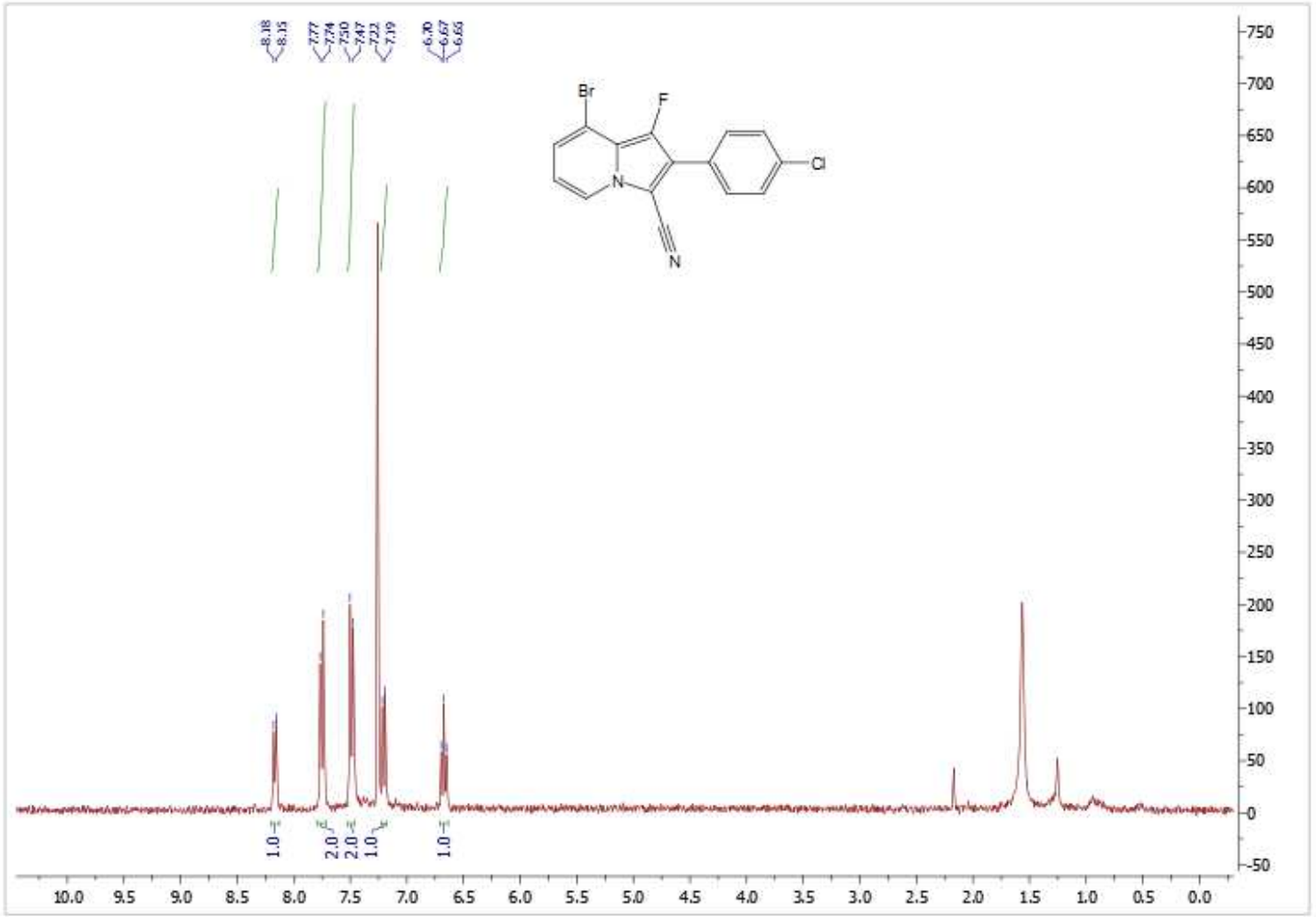
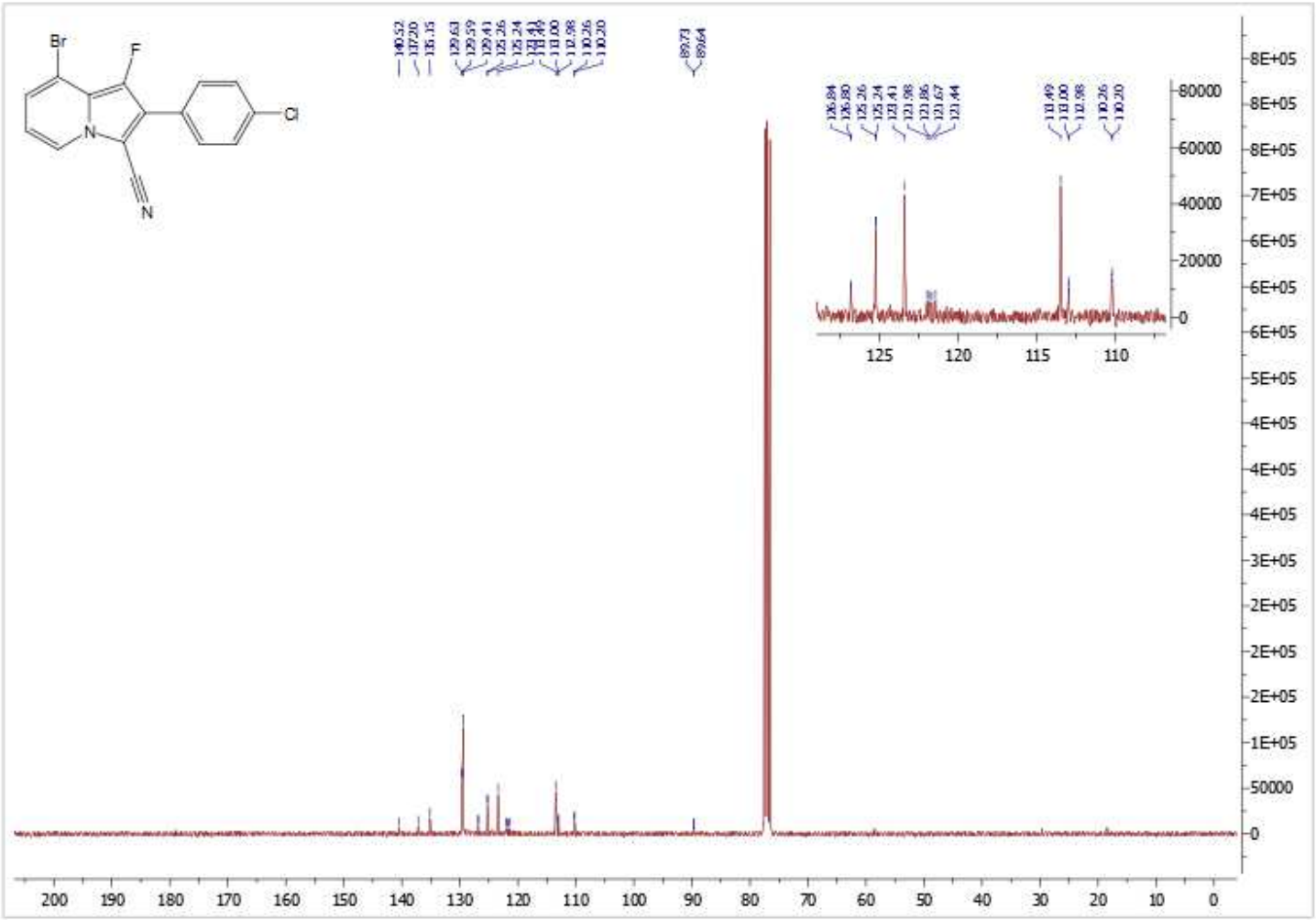
-175.28
2.8
1.0
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280

1-fluoro-2-(4-chlorophenyl)-8-bromo-indolizine-3-carbonitrile 3i

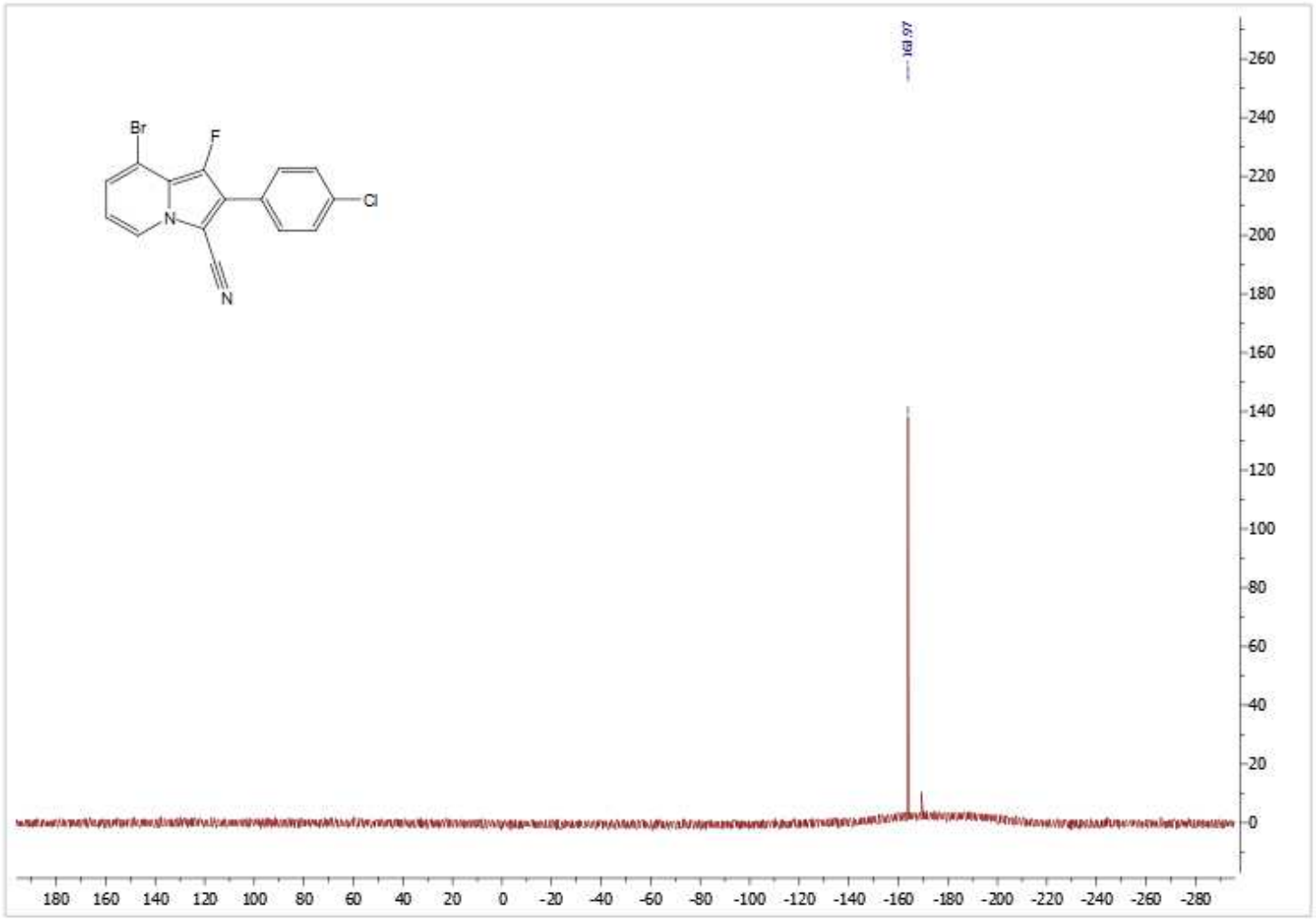
^{1}H NMR



^{13}C NMR


Br
F
Cl
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
125
120
115
110

^{19}F NMR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Cl
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N
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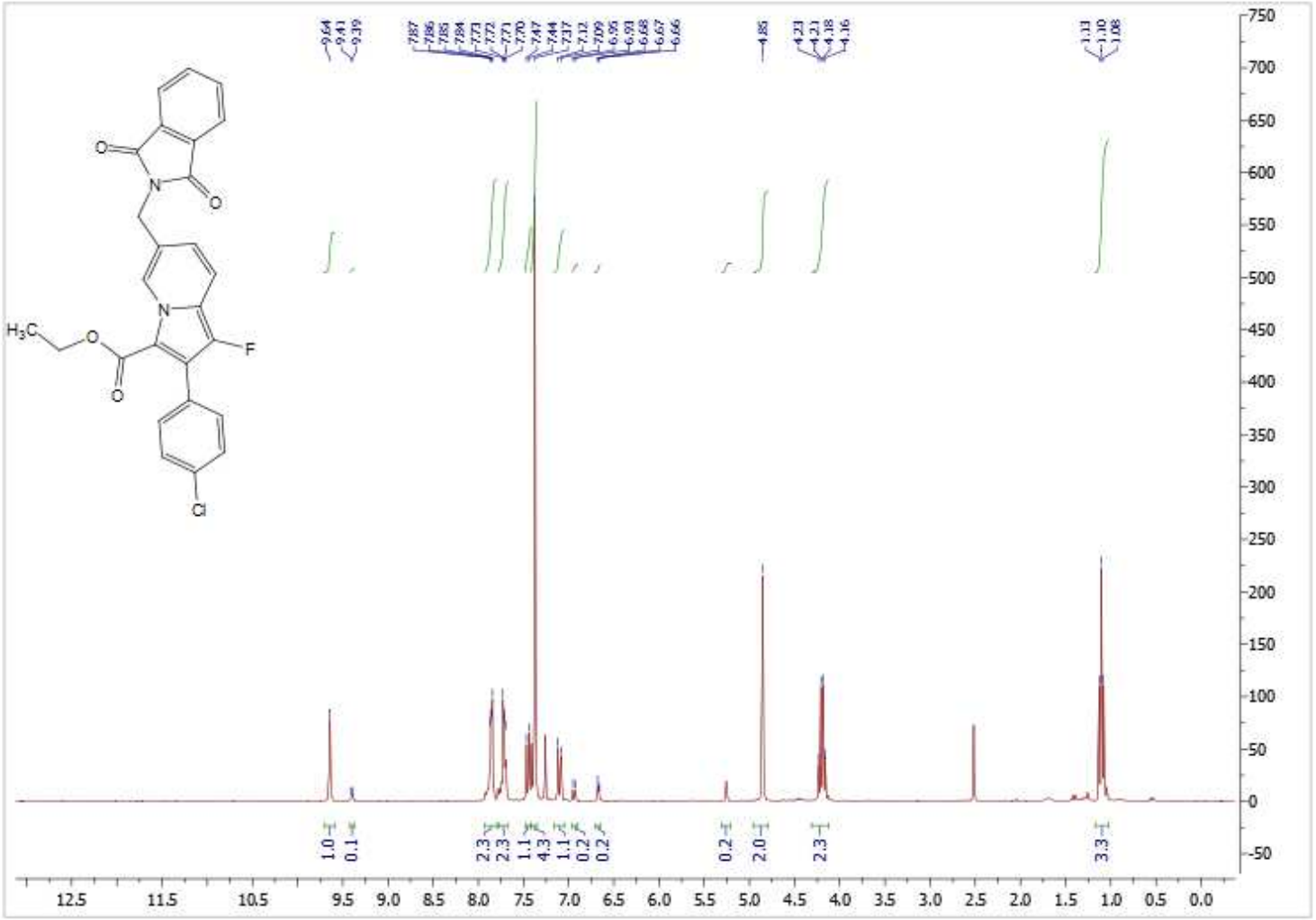
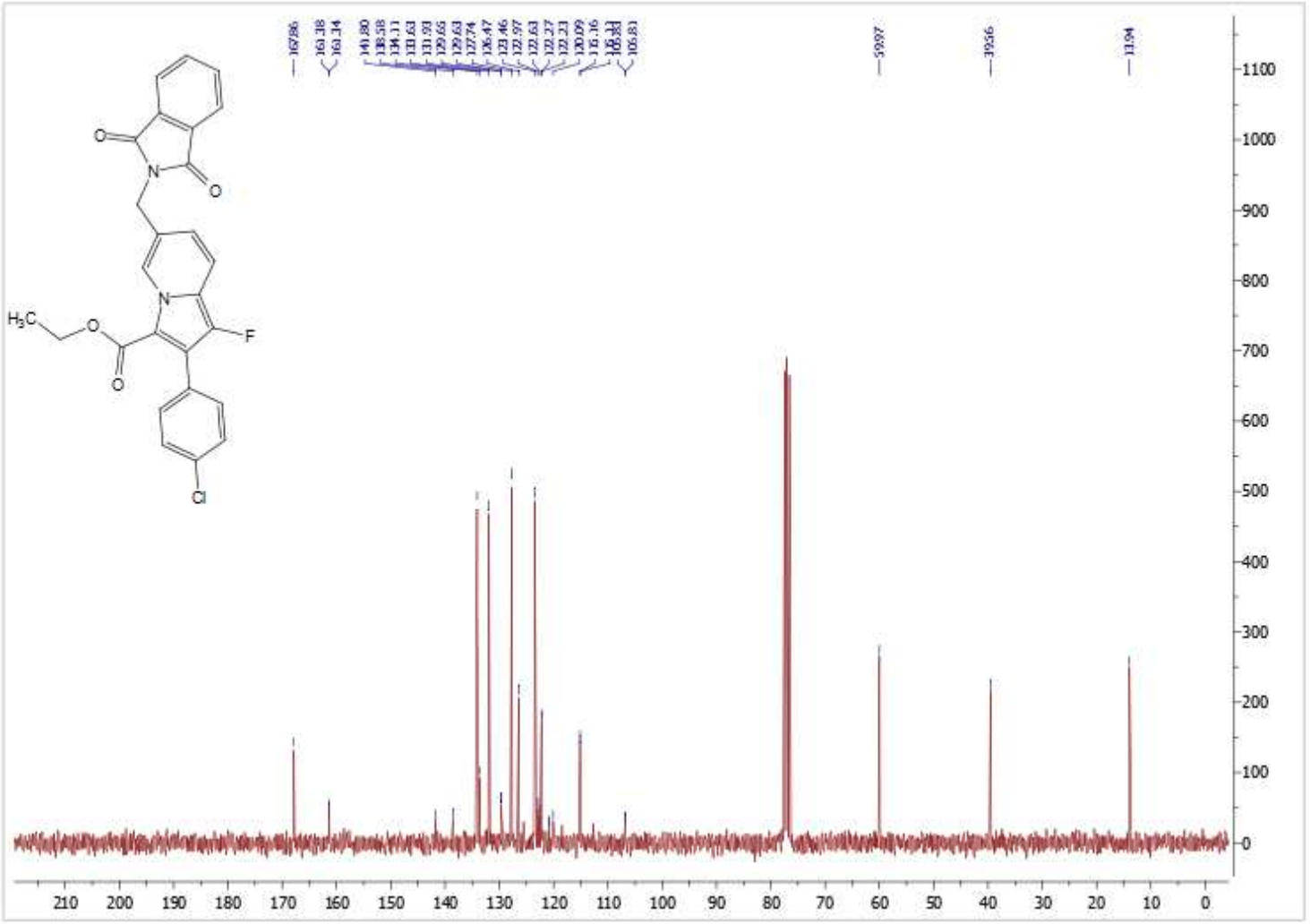
260
240
220
200
180
160
140
120
100
80
60
40
20
0
180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280

1-fluoro-2-(4-chlorophenyl)- 3-(ethyloxycarbonyl)-6-(phthalimidomethyl)-indolizine 3j

^{1}H NMR



^{13}C NMR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141.80
138.58
134.11
133.63
131.93
129.65
129.63
127.74
126.47
123.46
122.97
122.63
122.27
122.23
120.09
116.16
116.11
105.83
59.97
39.56
13.94
O
N
O
O
N
H3C
O
F
O
Cl
1100
1000
900
800
700
600
500
400
300
200
100
0
210
200
190
180
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90
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30
20
10
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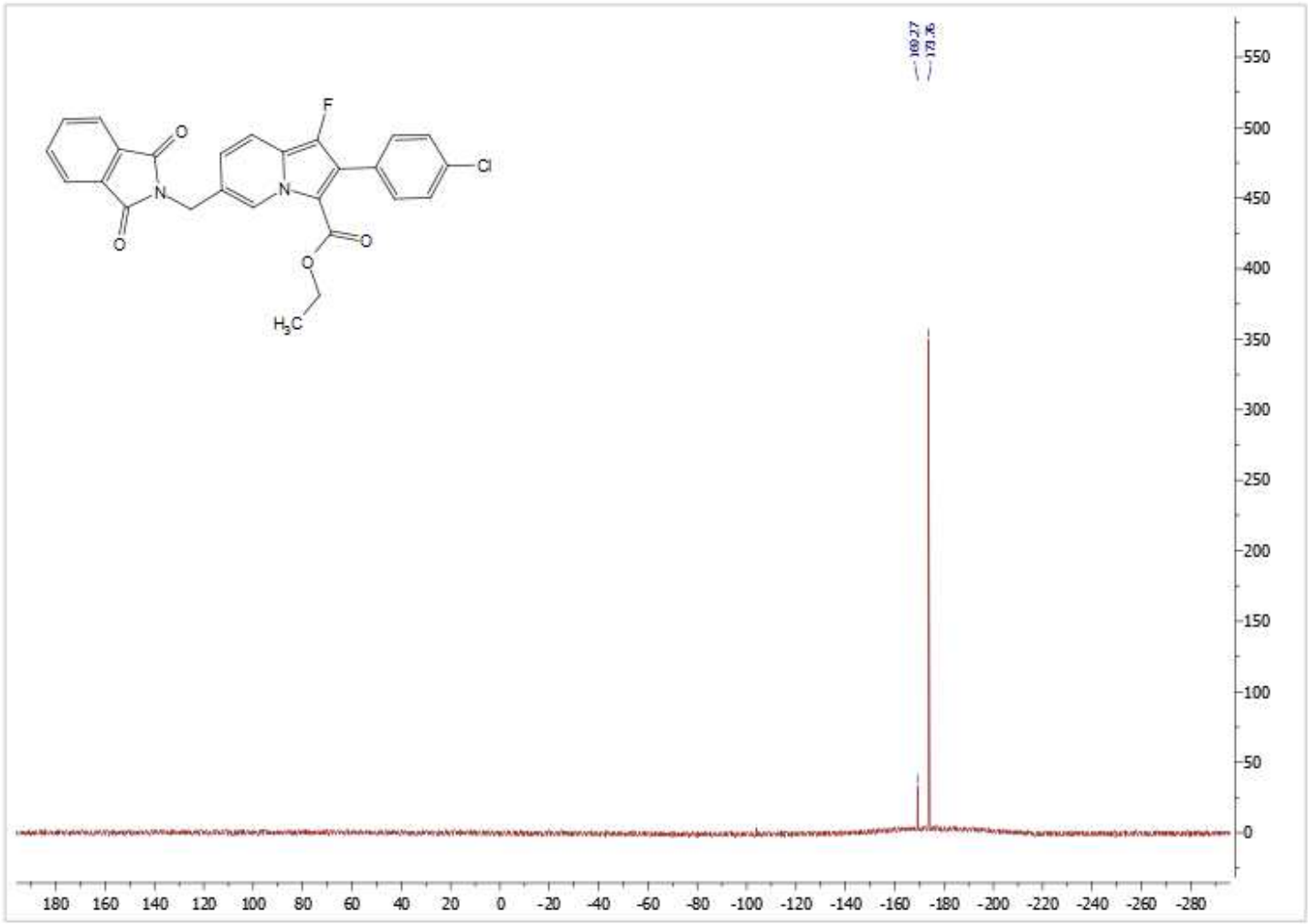
^{19}F NMR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-173.86
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N
O
Cl
N
O
O
O
H3C
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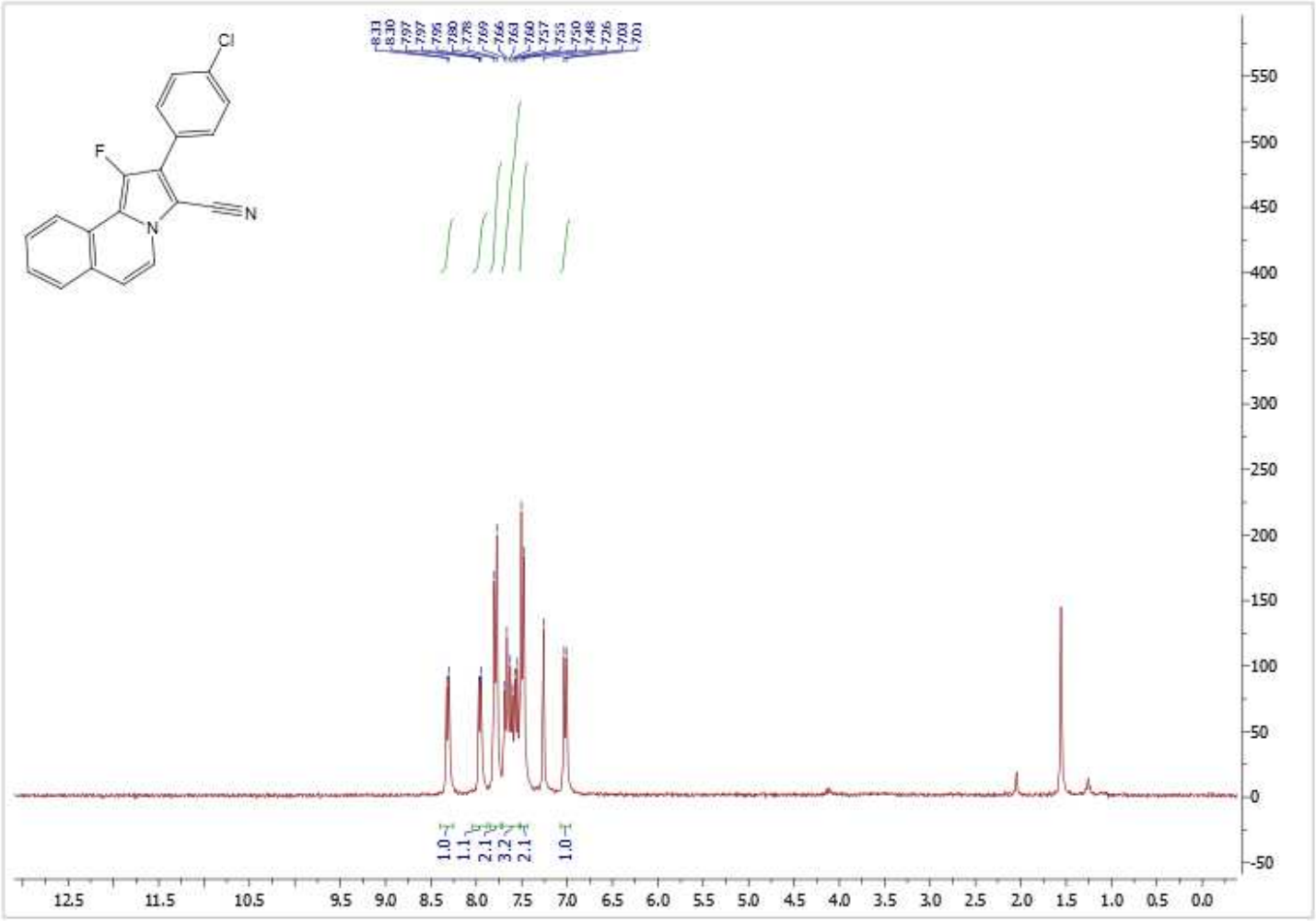
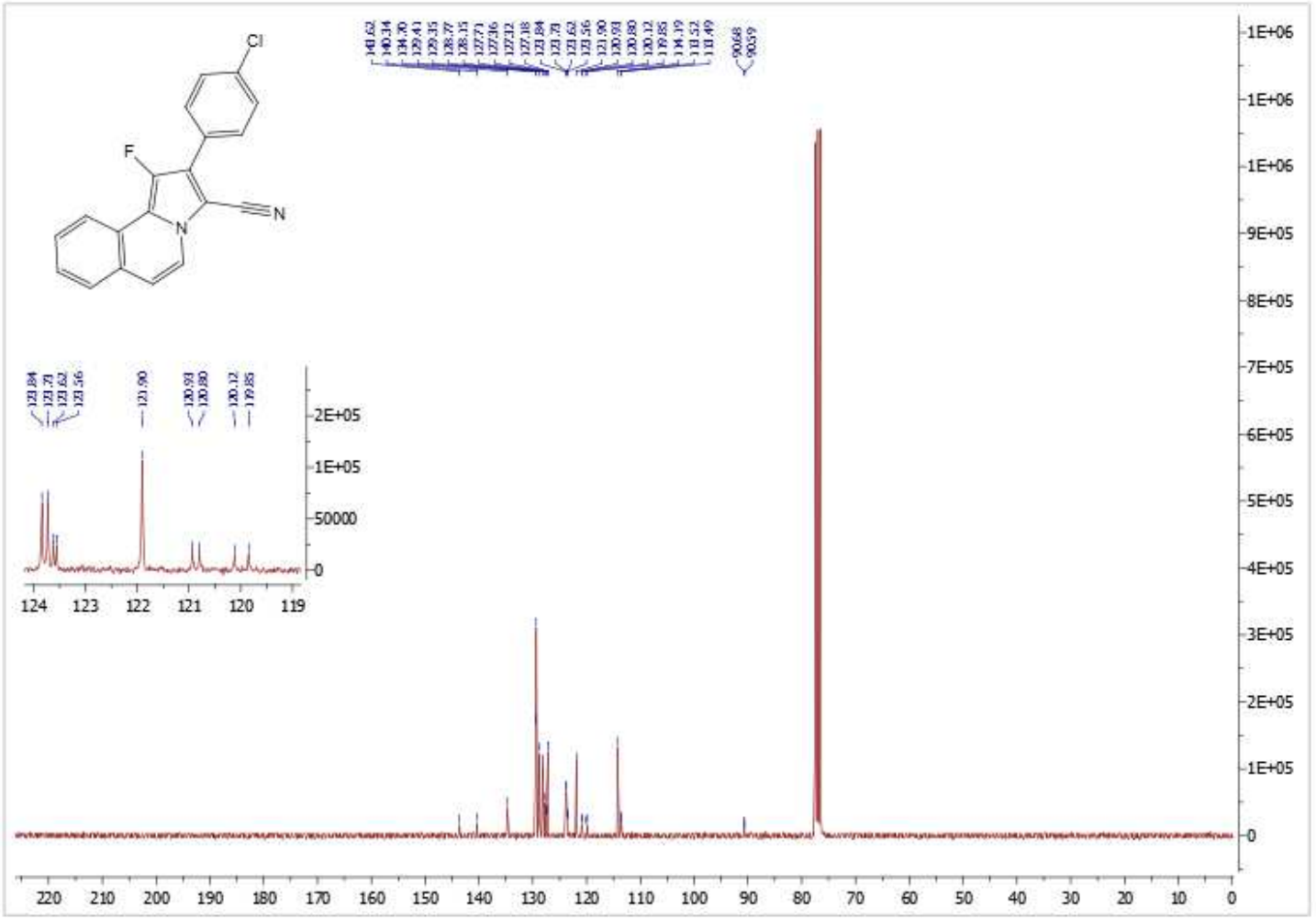
500
450
400
350
300
250
200
150
100
50
0
180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280

2-(4-chlorophenyl)-1-fluoropyrrolo[2,1-*a*]isoquinoline-3-carbonitrile 3k

^{1}H NMR



^{13}C NMR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140.14
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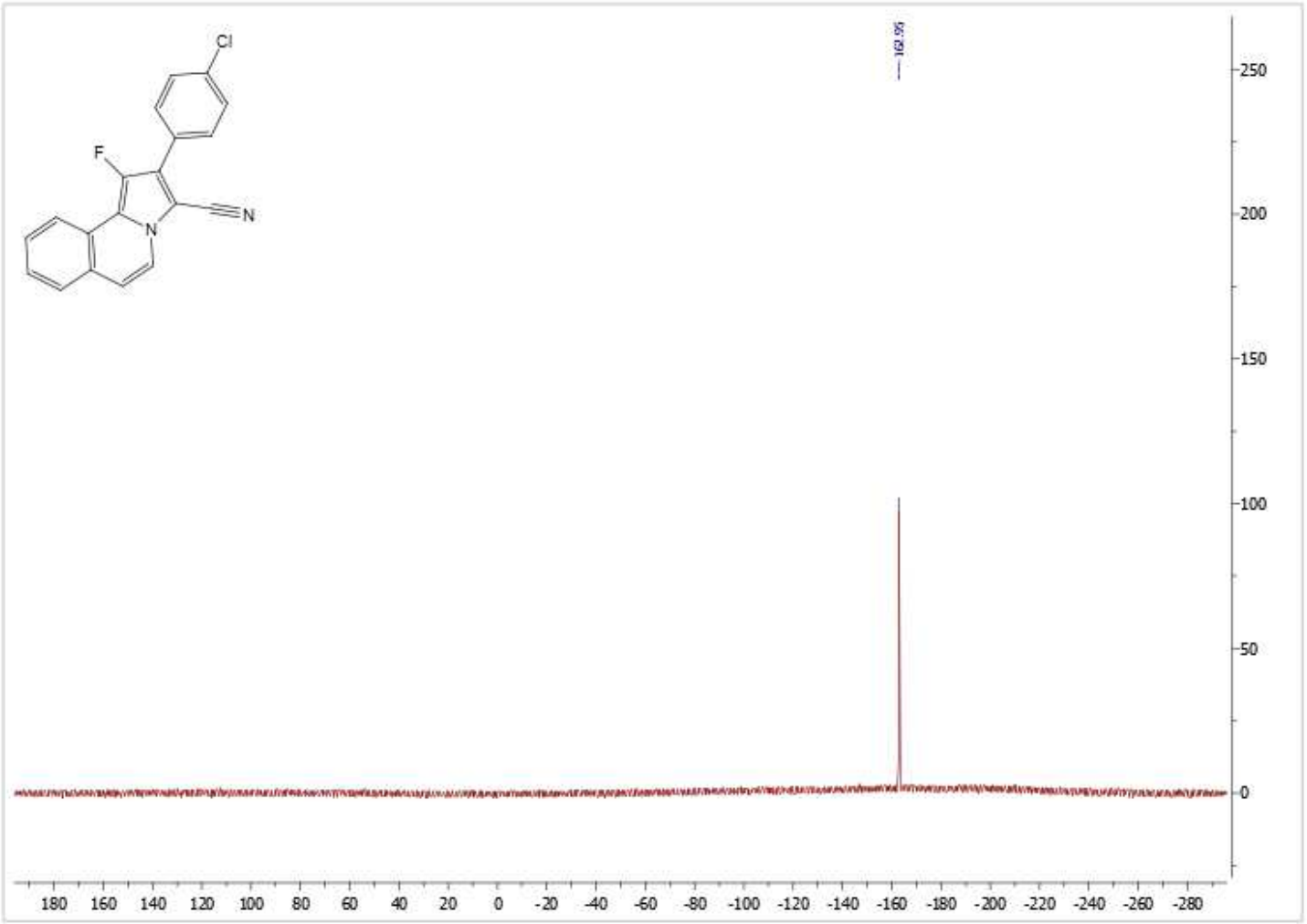
129.41
129.35
128.77
128.15
127.71
127.36
127.12
127.18
123.84
123.71
123.62
123.56
121.90
120.93
120.80
120.12
119.85
114.19
111.52
111.49
90.68
90.59
123.84
123.71
123.62
123.56
121.90
120.93
120.80
120.12
119.85
2E+05
1E+05
50000
0
124
123
122
121
120
119
1E+06
1E+06
1E+06
9E+05
8E+05
7E+05
6E+05
5E+05
4E+05
3E+05
2E+05
1E+05
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{19}F NMR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N
N
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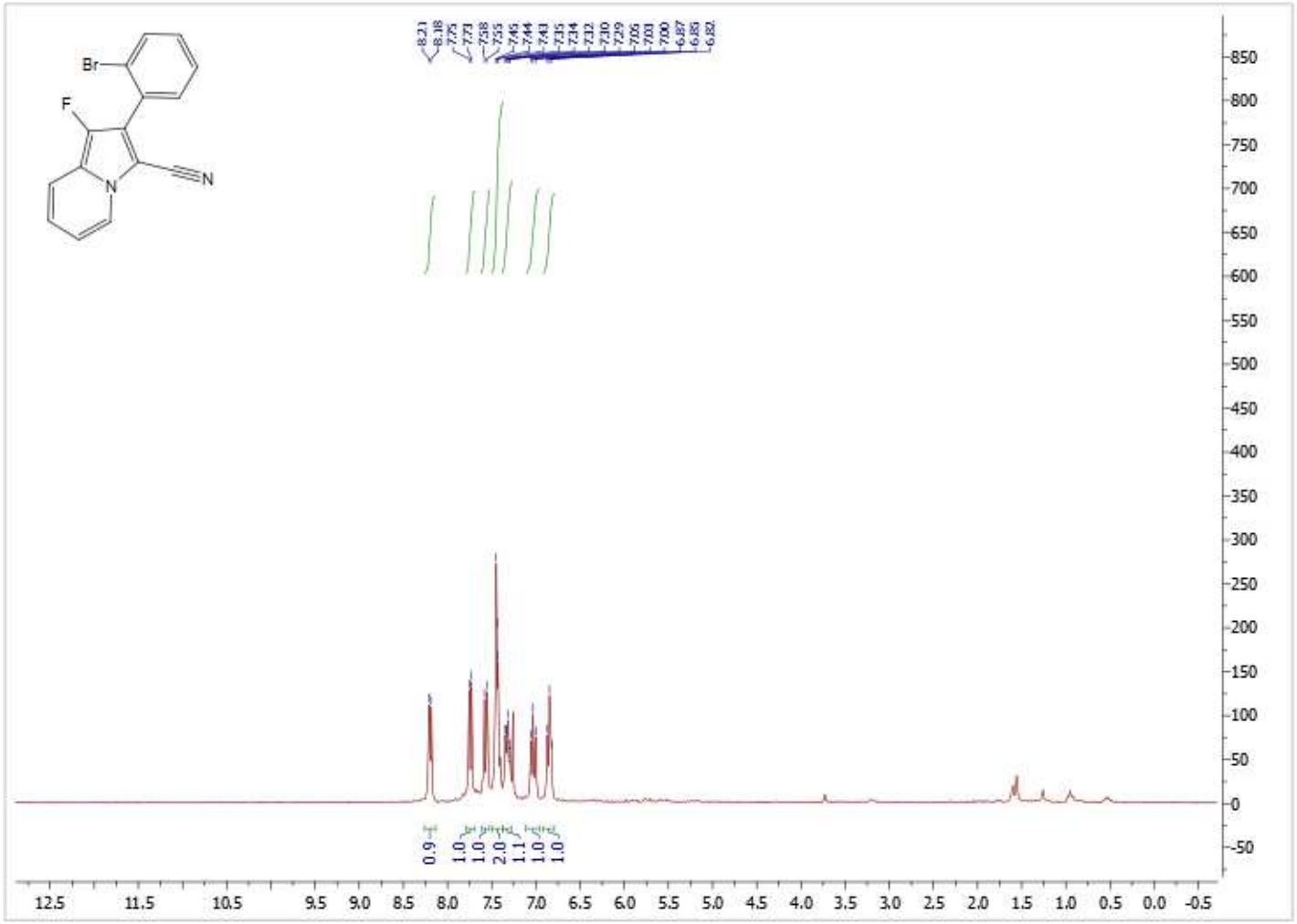
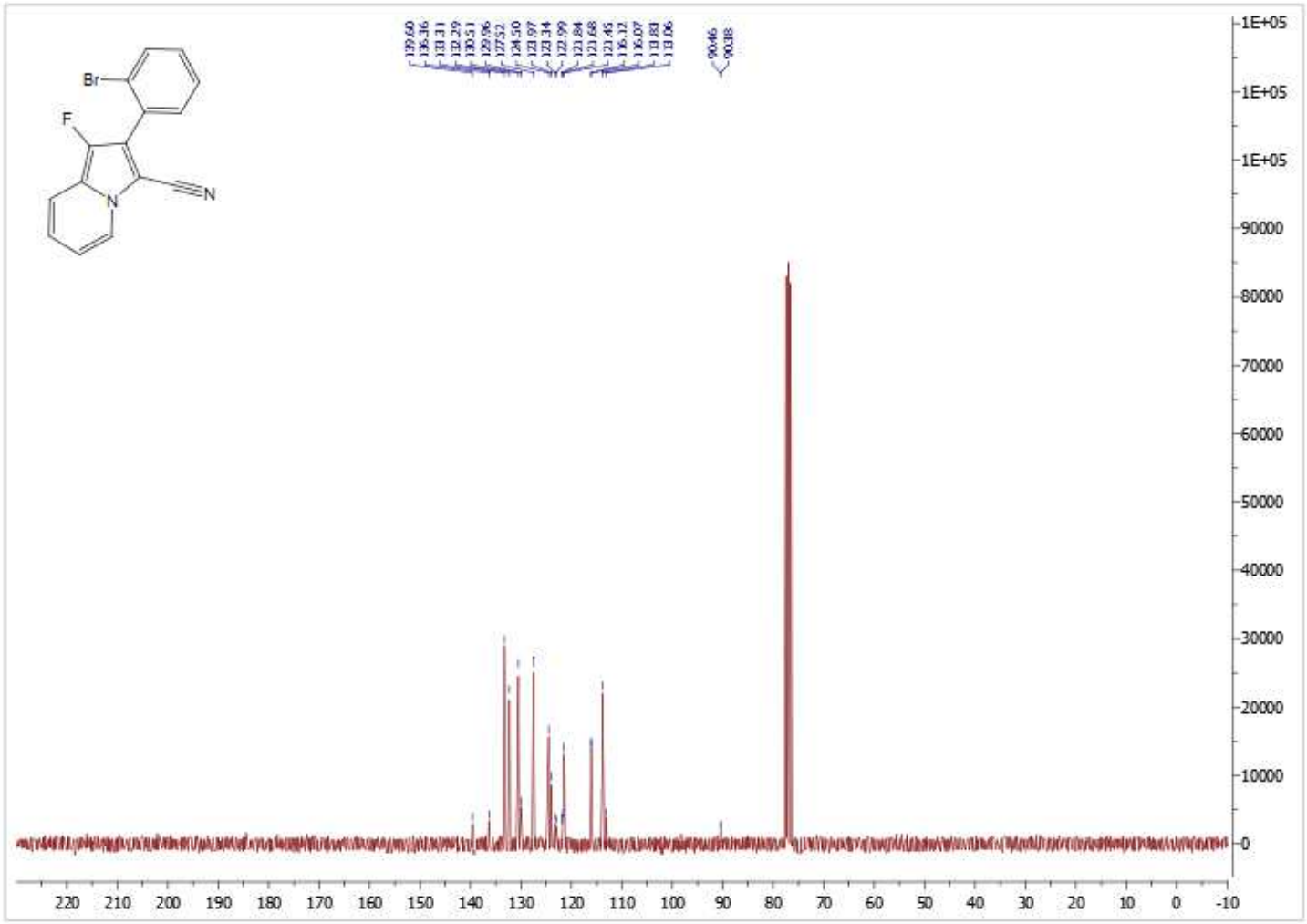
250
200
150
100
50
0
180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280

1-fluoro-2-(2-bromophenyl)-indolizine-3-carbonitrile 3l

^{1}H NMR



^{13}C NMR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N
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129.96
127.52
124.50
123.97
123.34
122.99
121.84
121.68
121.45
116.12
116.07
113.83
113.06
90.46
90.18
1E+05
1E+05
1E+05
90000
80000
70000
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20000
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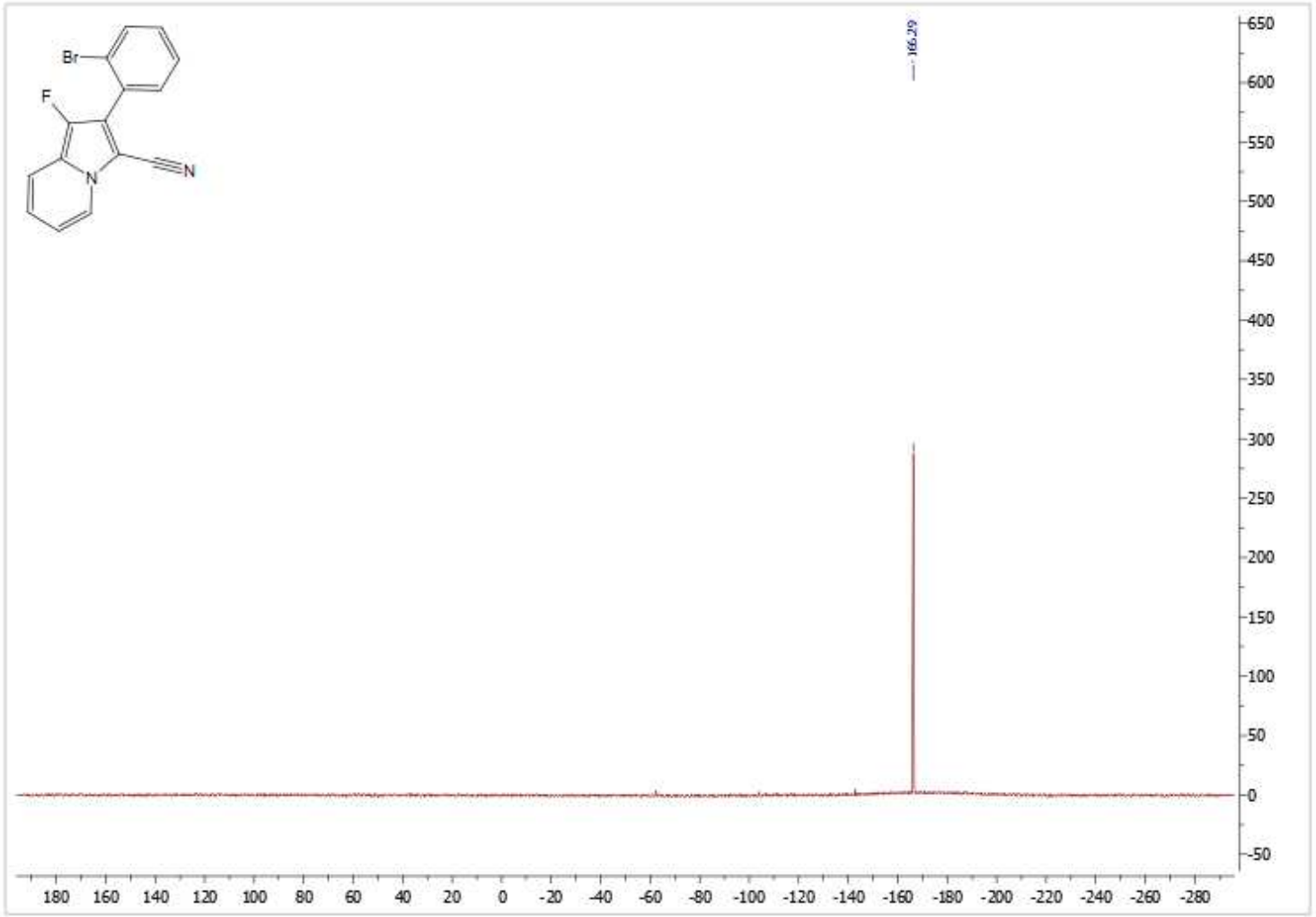
^{19}F NMR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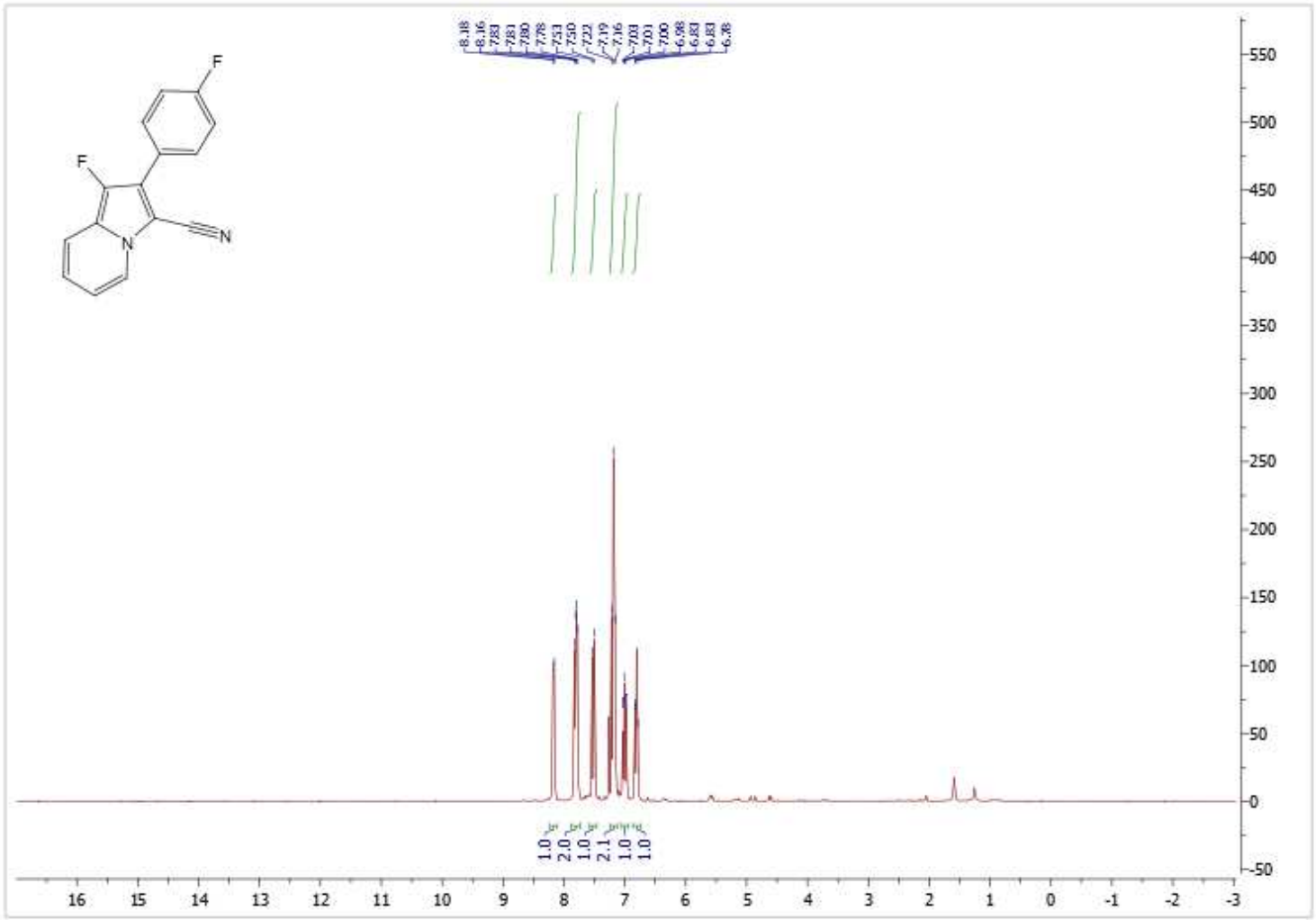
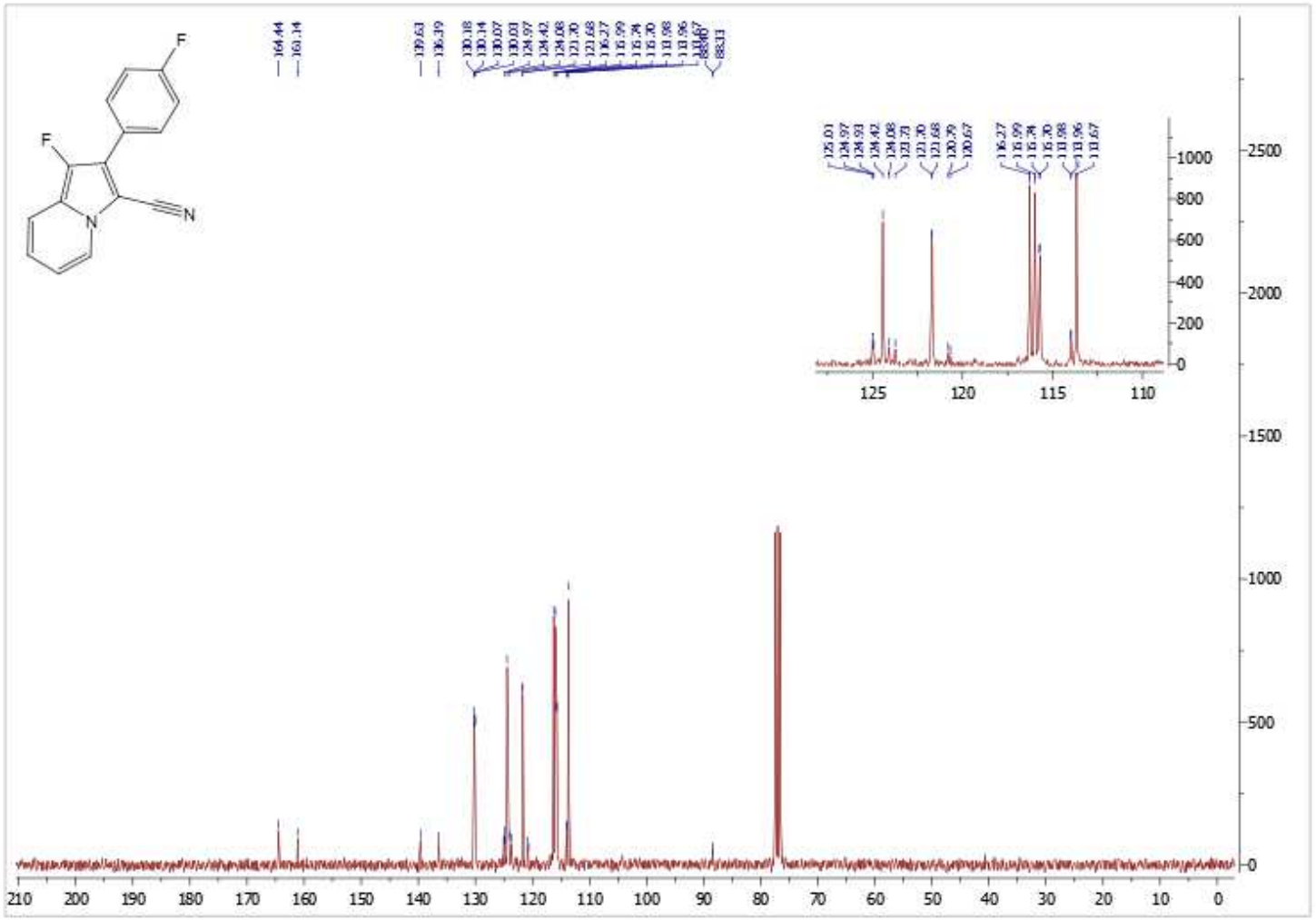
550
500
450
400
350
300
250
200
150
100
50
0
-50
180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280

1-fluoro-2-(4-fluorophenyl)-indolizine-3-carbonitrile 3m

^{1}H NMR



^{13}C NMR


F
F
N
N
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139.63
136.39
130.18
130.14
130.07
130.01
124.97
124.42
124.08
123.70
121.68
116.27
115.99
115.74
115.70
113.98
113.96
113.67
88.33
125.01
124.97
124.93
124.42
124.08
123.73
121.70
121.68
120.99
120.67
116.27
115.99
115.74
115.70
113.98
113.96
113.67
125
120
115
110
1000
800
600
400
200
0
2500
2000
1500
1000
500
0
210
200
190
180
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90
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50
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30
20
10
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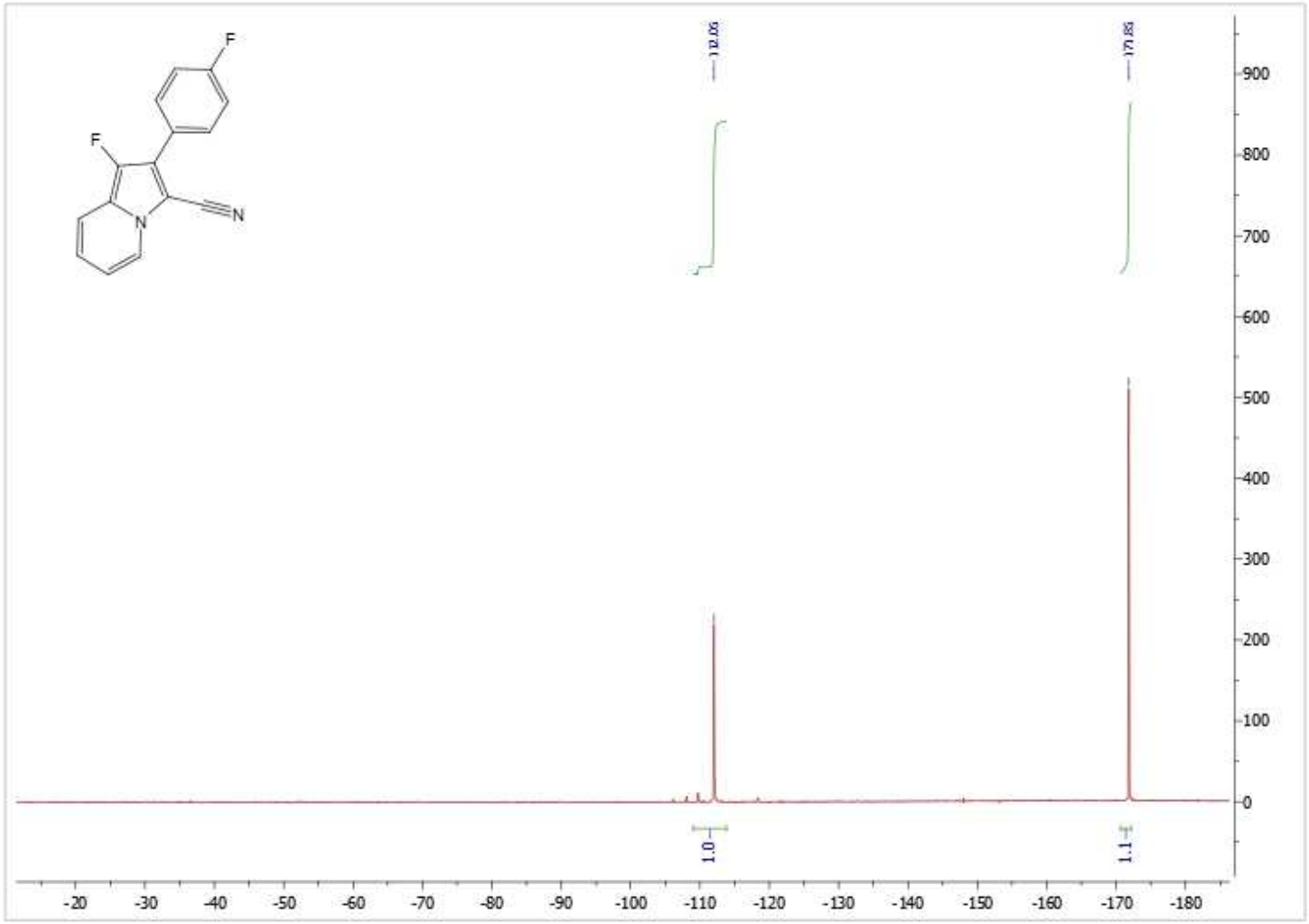
^{19}F NMR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200
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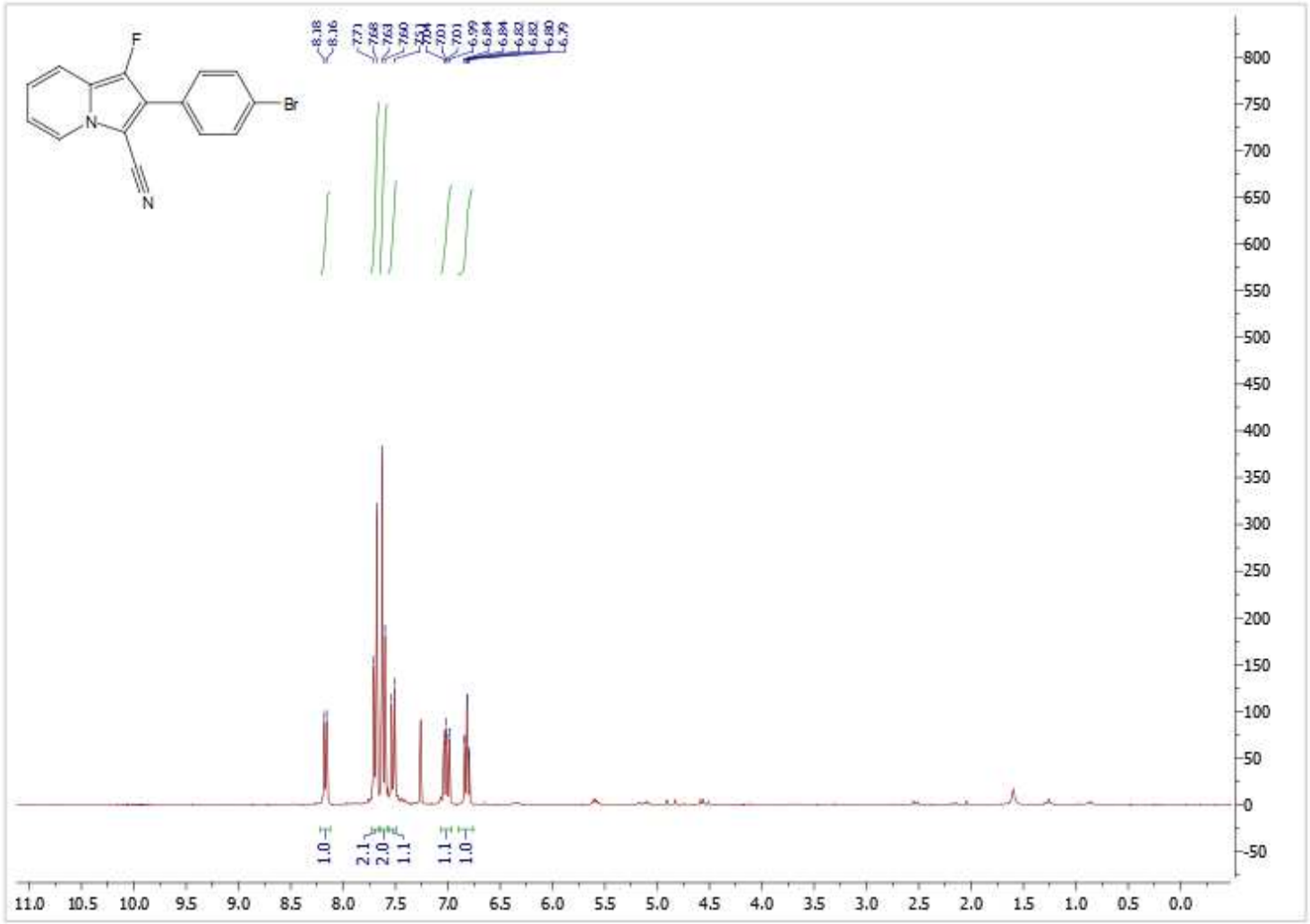
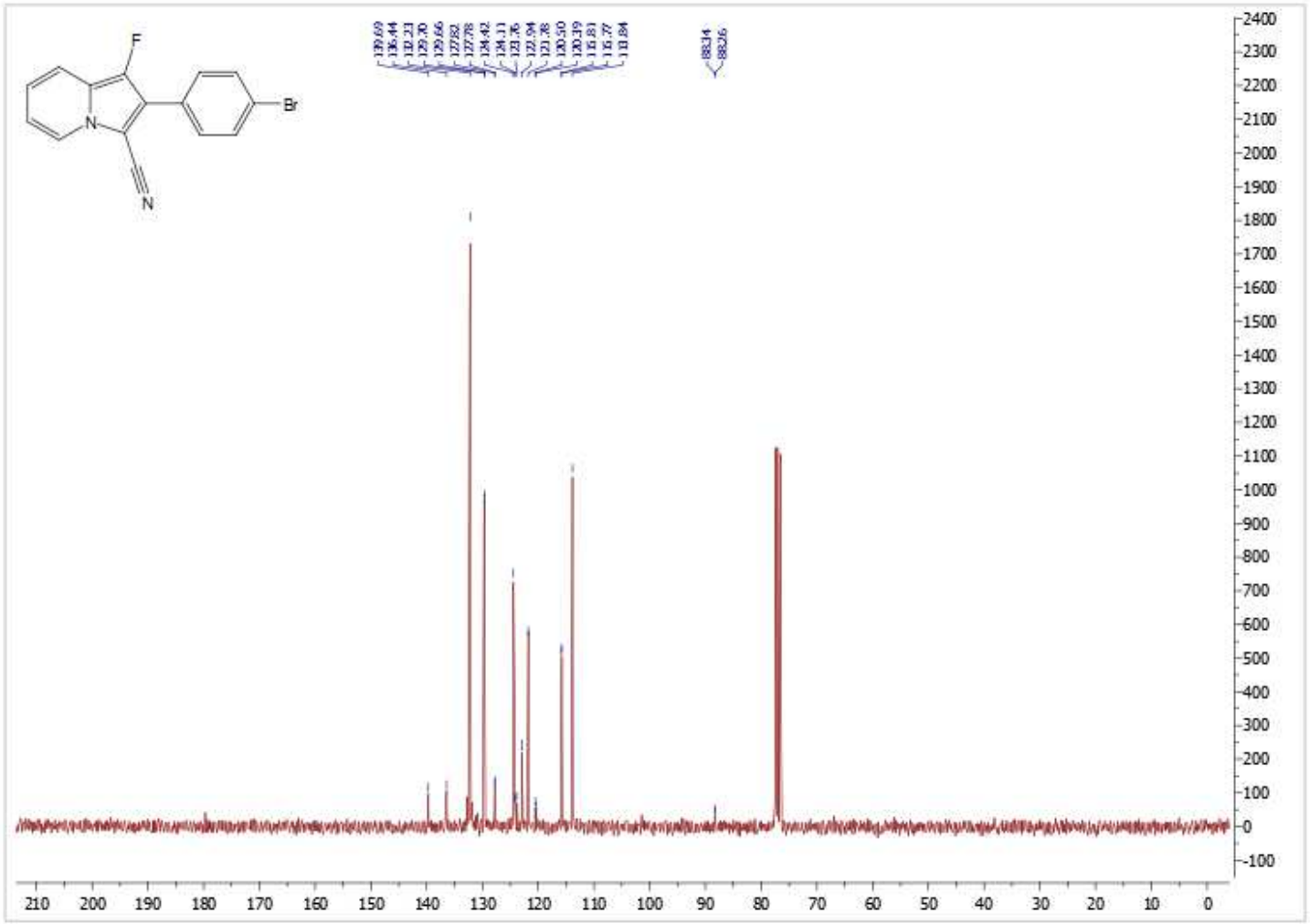
1.1
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180

1-fluoro-2-(4-bromophenyl)-indolizine-3-carbonitrile 3n

^{1}H NMR



^{13}C NMR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132.23
129.30
129.66
127.82
127.78
124.42
124.11
123.36
122.94
121.78
120.50
120.39
116.81
116.77
110.84
88.34
88.26
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
200
190
180
170
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130
120
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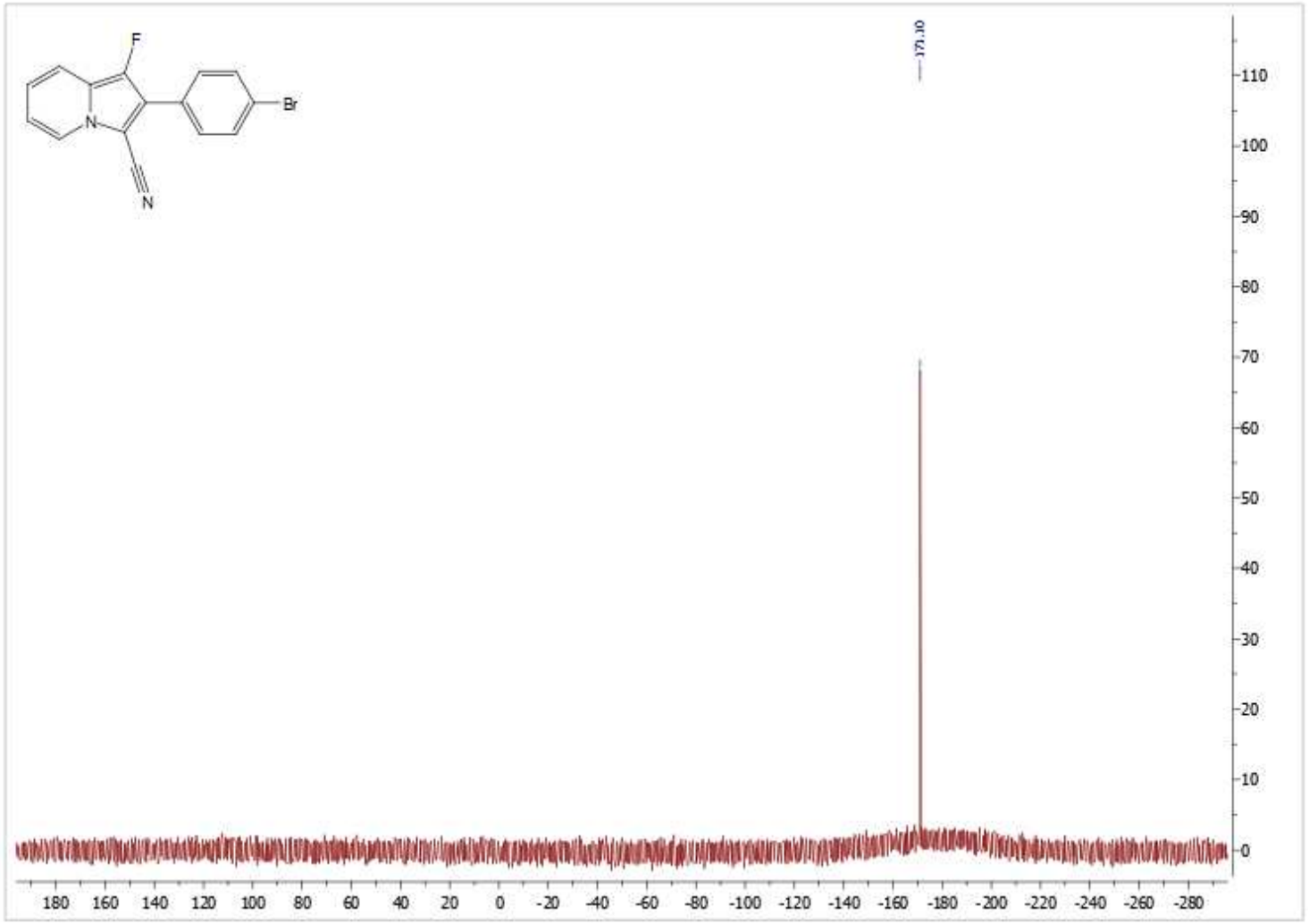
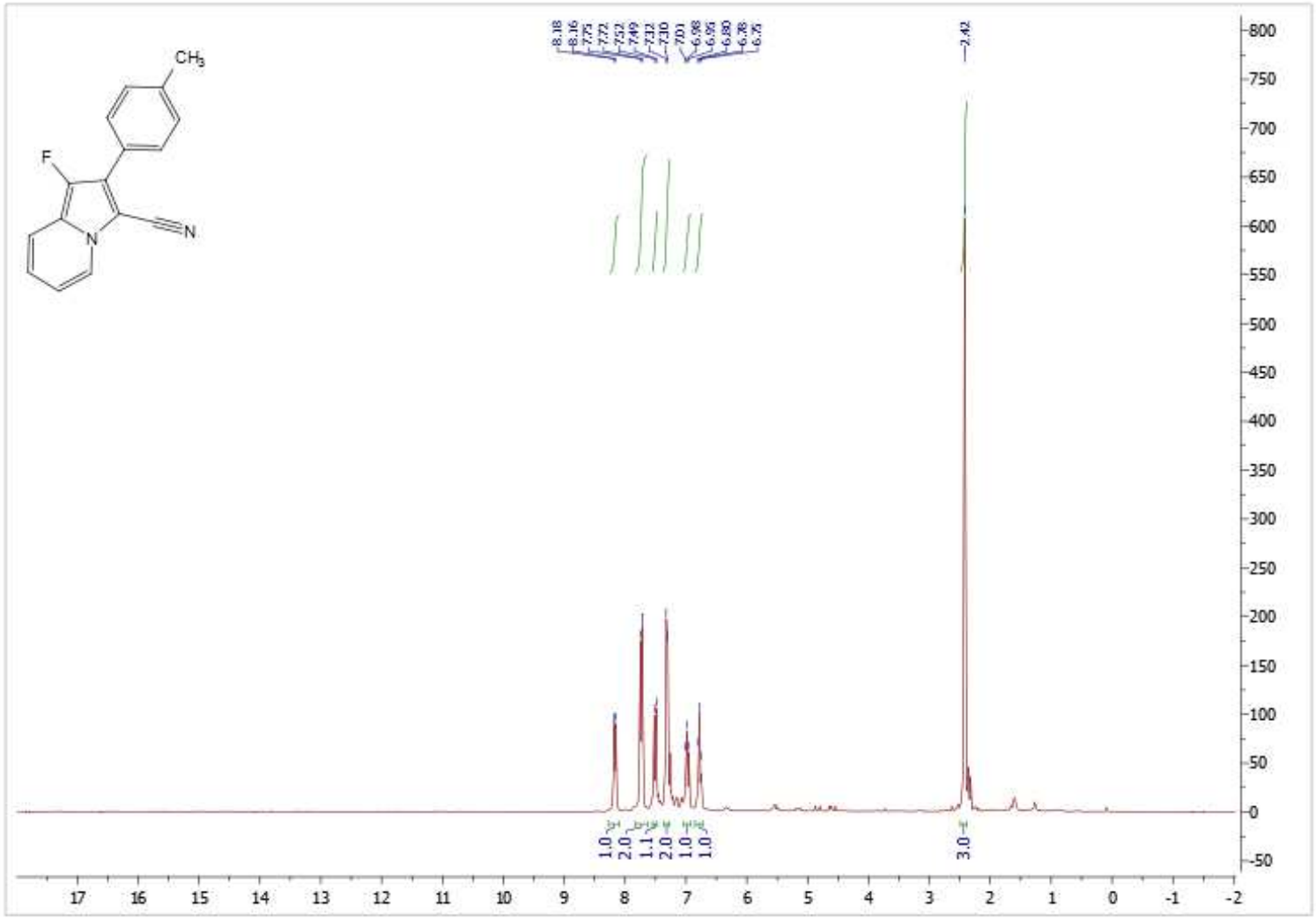
90
80
70
60
50
40
30
20
10
0

^{19}F NMR

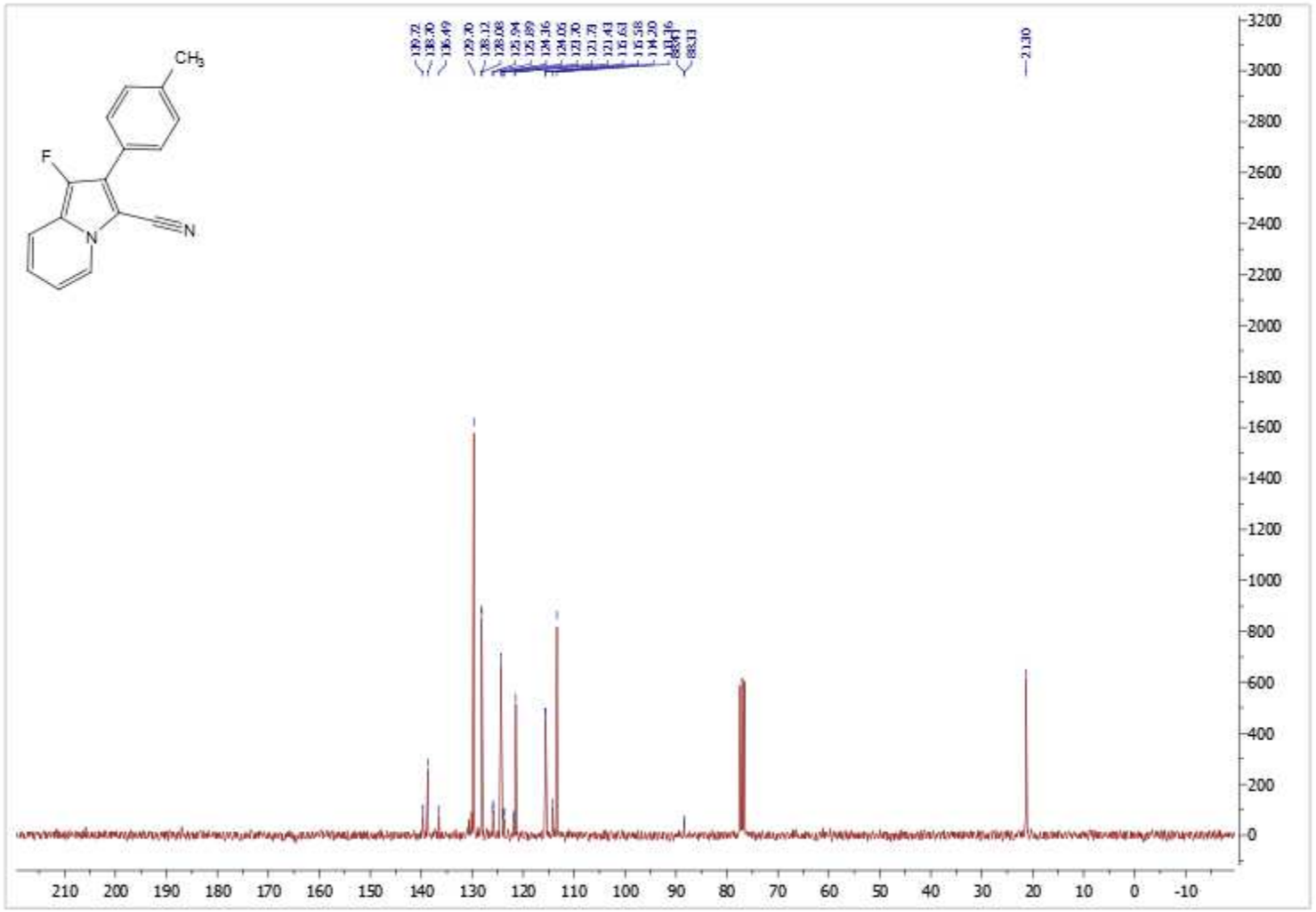

F
Br
N
N
-171.10
110
100
90
80
70
60
50
40
30
20
10
0
180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280

1-fluoro-2-(4-methylphenyl)-indolizine-3-carbonitrile 3o

^{1}H NMR



^{13}C NMR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123.89
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121.73
121.43
116.58
114.20
88.33
21.30
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
210
200
190
180
170
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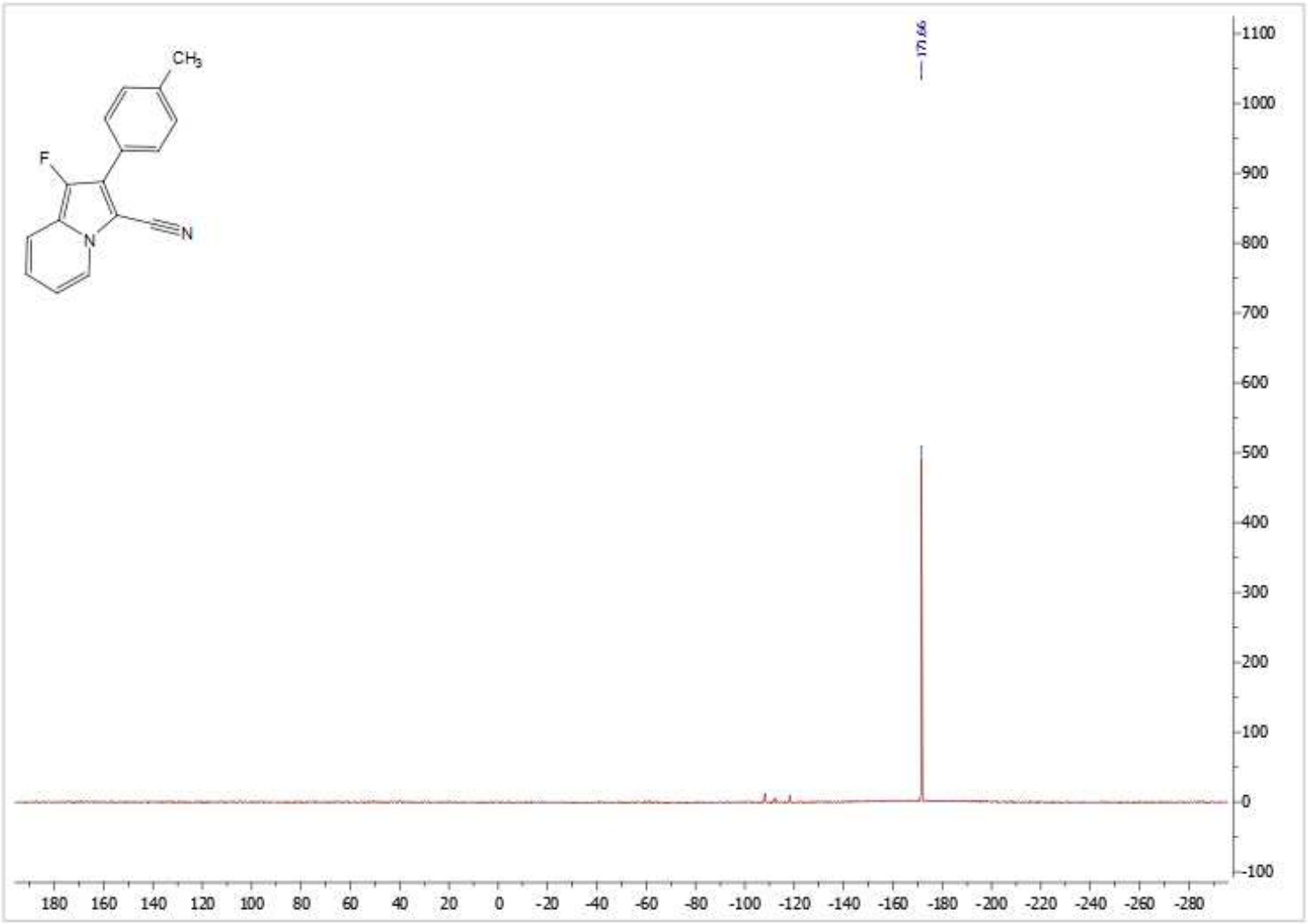
-10

^{19}F NMR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800
700
600
500
400
300
200
100
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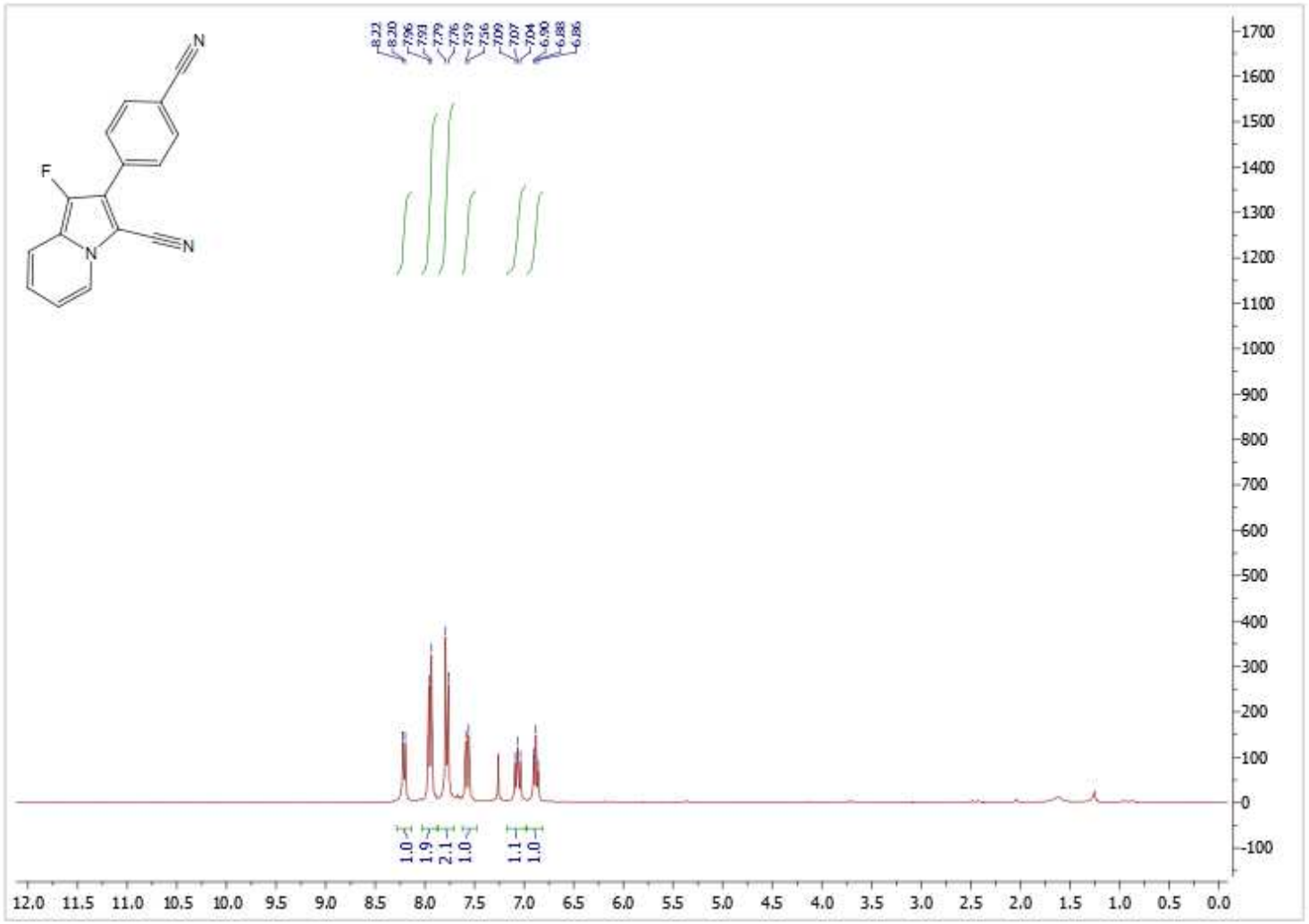
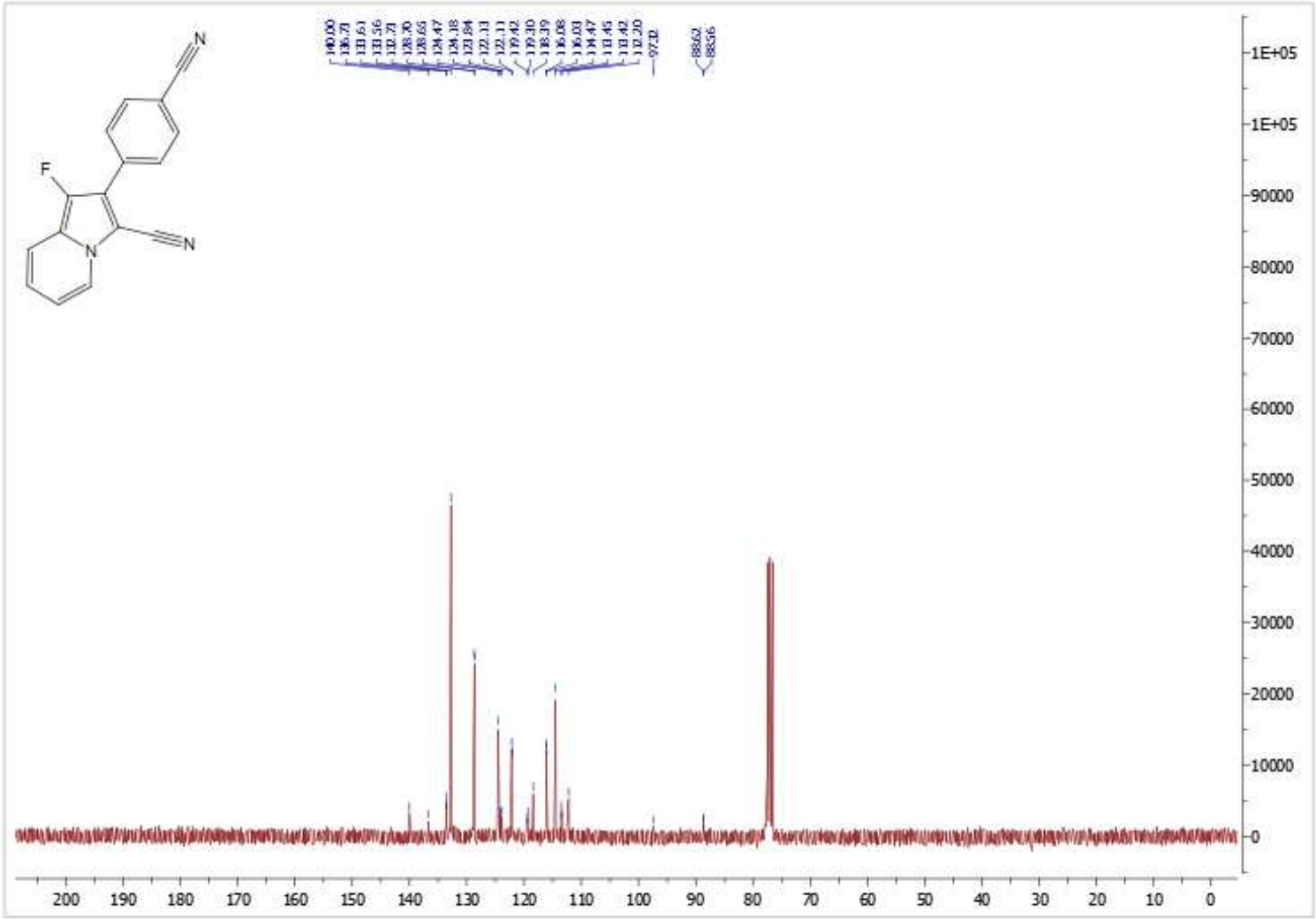
-100
180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280

1-fluoro-2-(4-cyanophenyl)-indolizine-3-carbonitrile 3p

^{1}H NMR



^{13}C NMR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F
N
N
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131.56
131.21
128.70
128.65
124.47
124.18
123.84
122.13
122.11
119.42
119.30
118.39
116.08
116.03
114.47
113.45
113.42
112.20
97.20
88.62
88.56
1E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
200
190
180
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10
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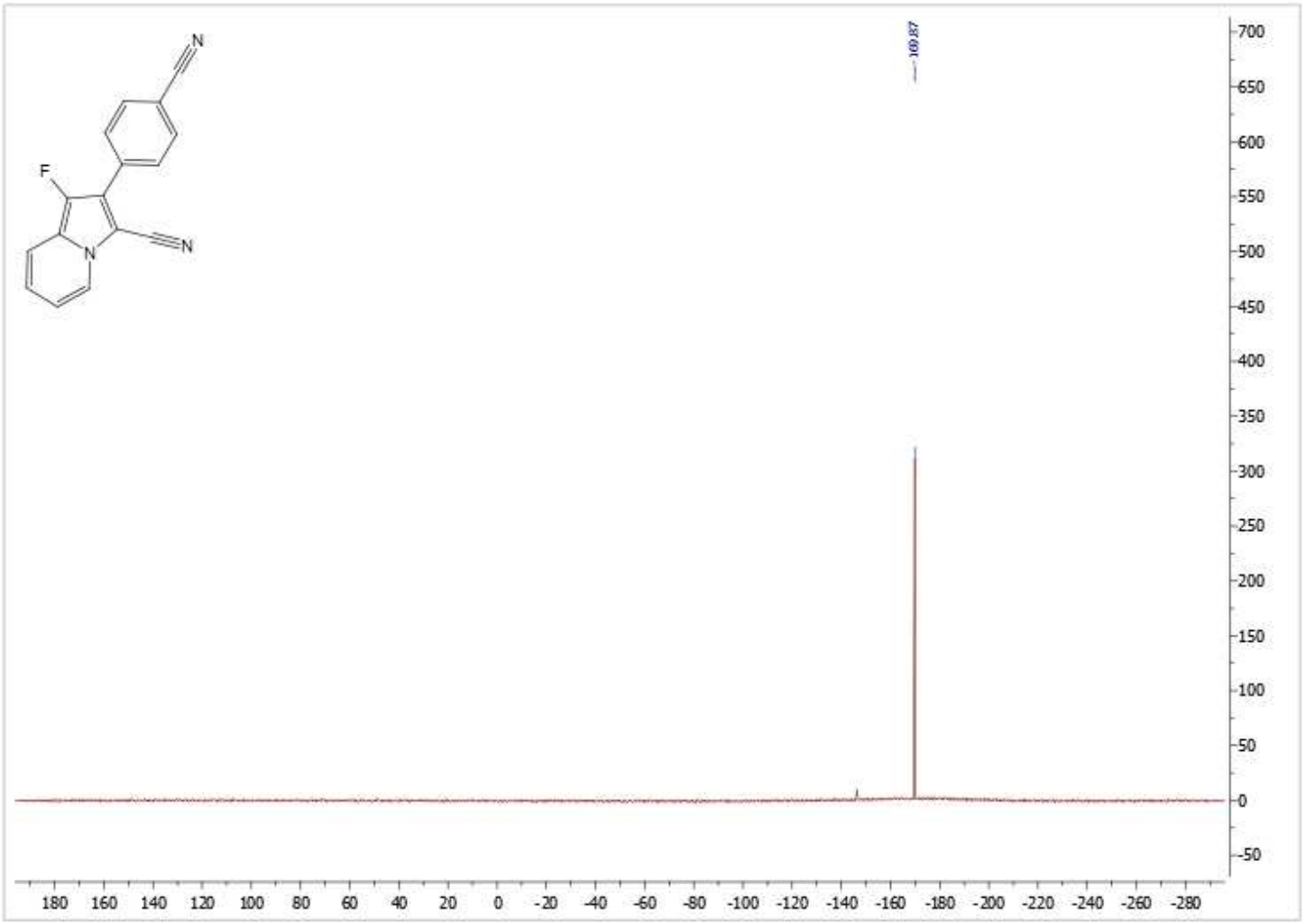
^{19}F NMR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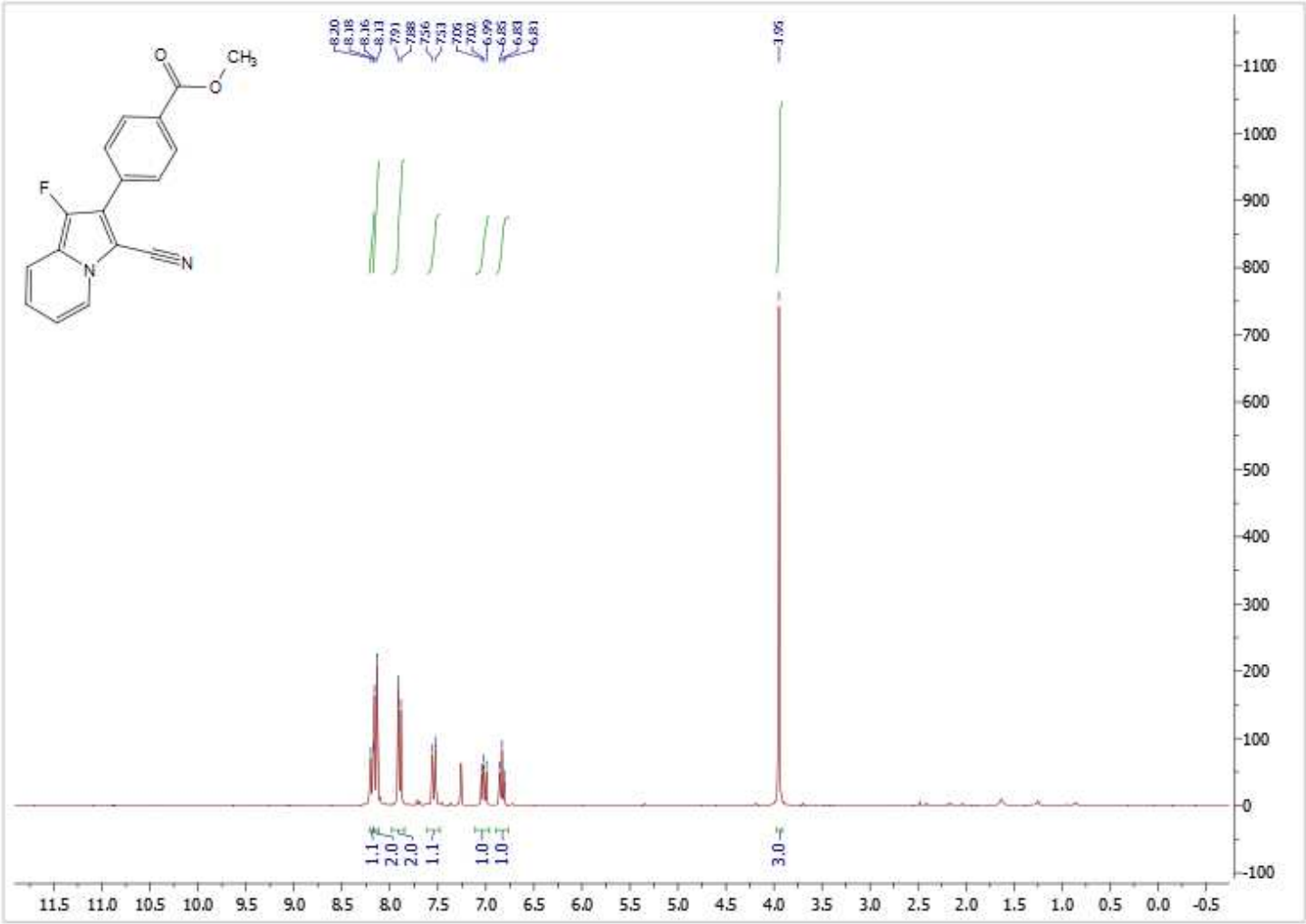
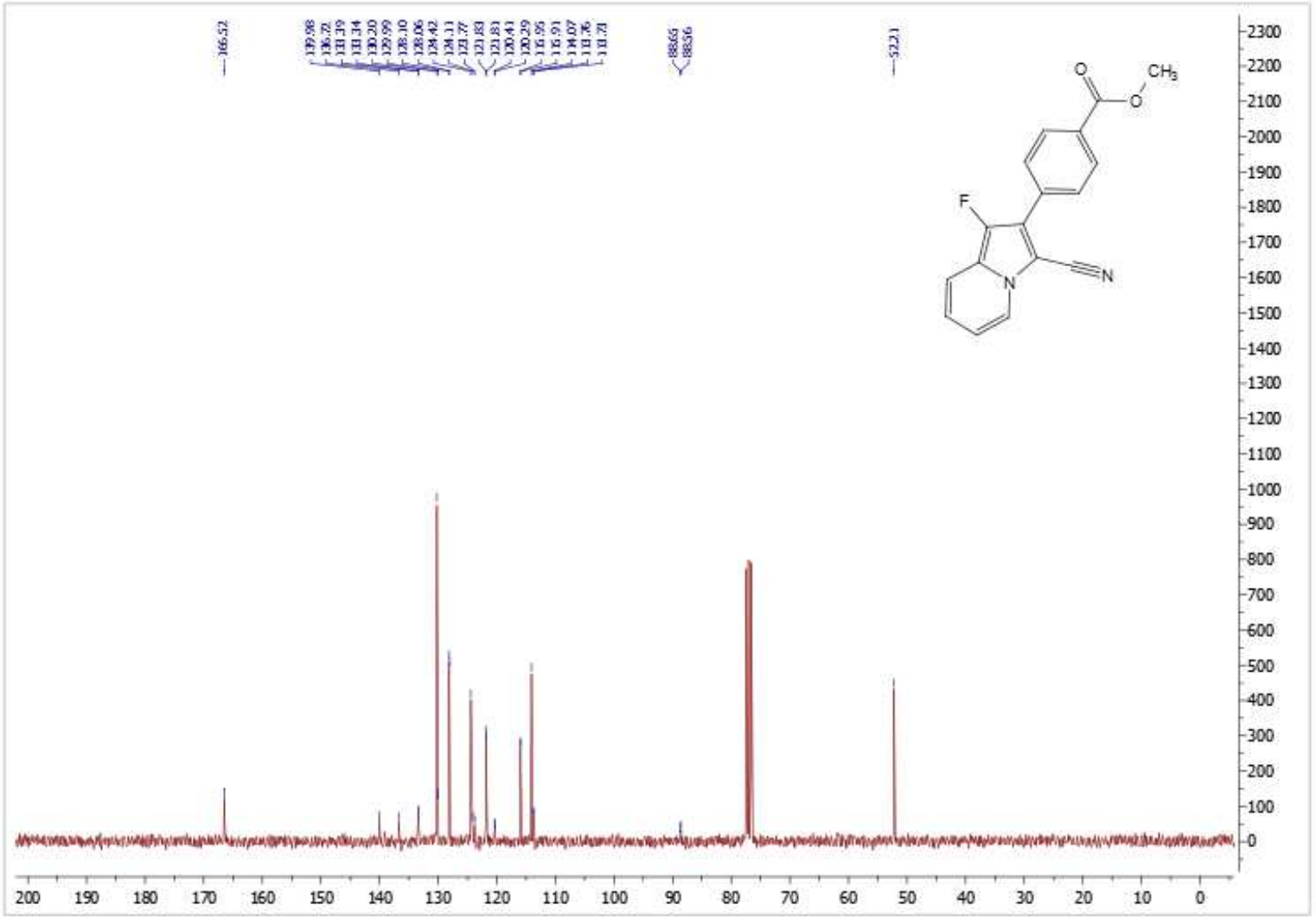
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280

1-fluoro-2-(4-(methyloxycarbonyl)phenyl)-indolizine-3-carbonitrile 3q

^{1}H NMR



^{13}C NMR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130.20
129.99
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124.42
124.11
123.77
121.83
121.83
120.41
120.29
116.95
115.91
114.07
113.76
113.71
88.65
88.56
52.21
O
O
CH3
F
N
N
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
200
190
180
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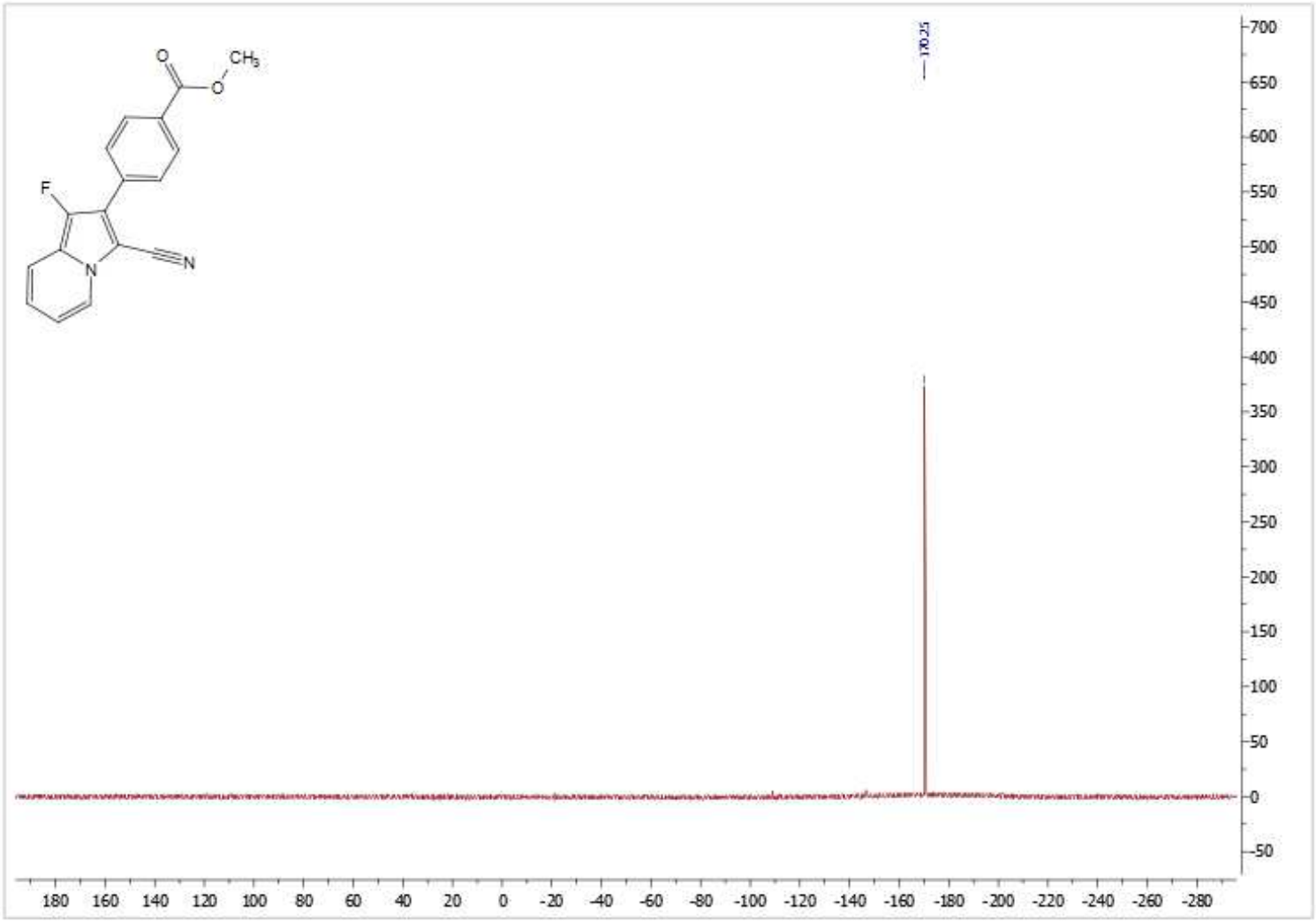
0

^{19}F NMR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O
CH3
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N
N
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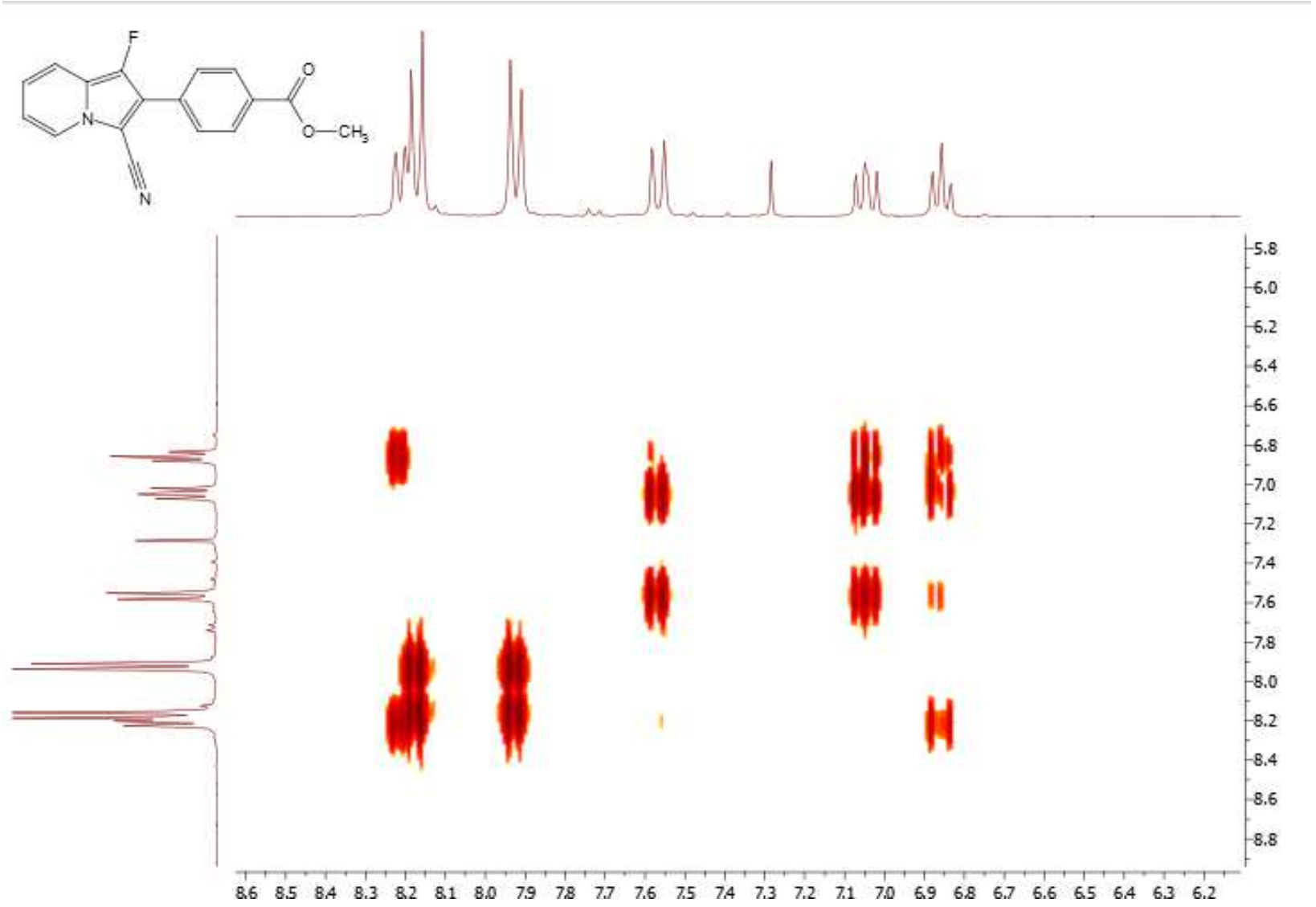
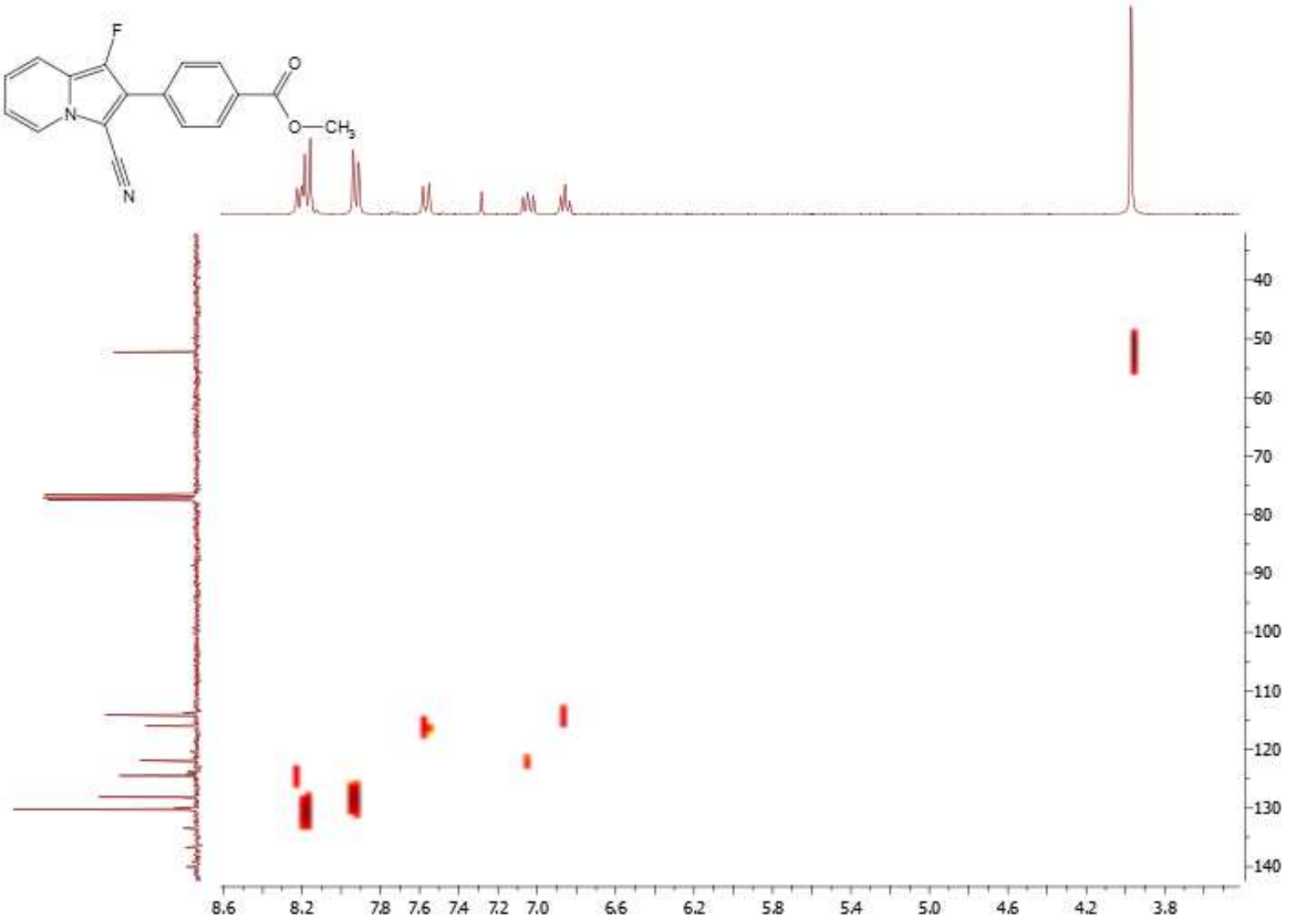
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280

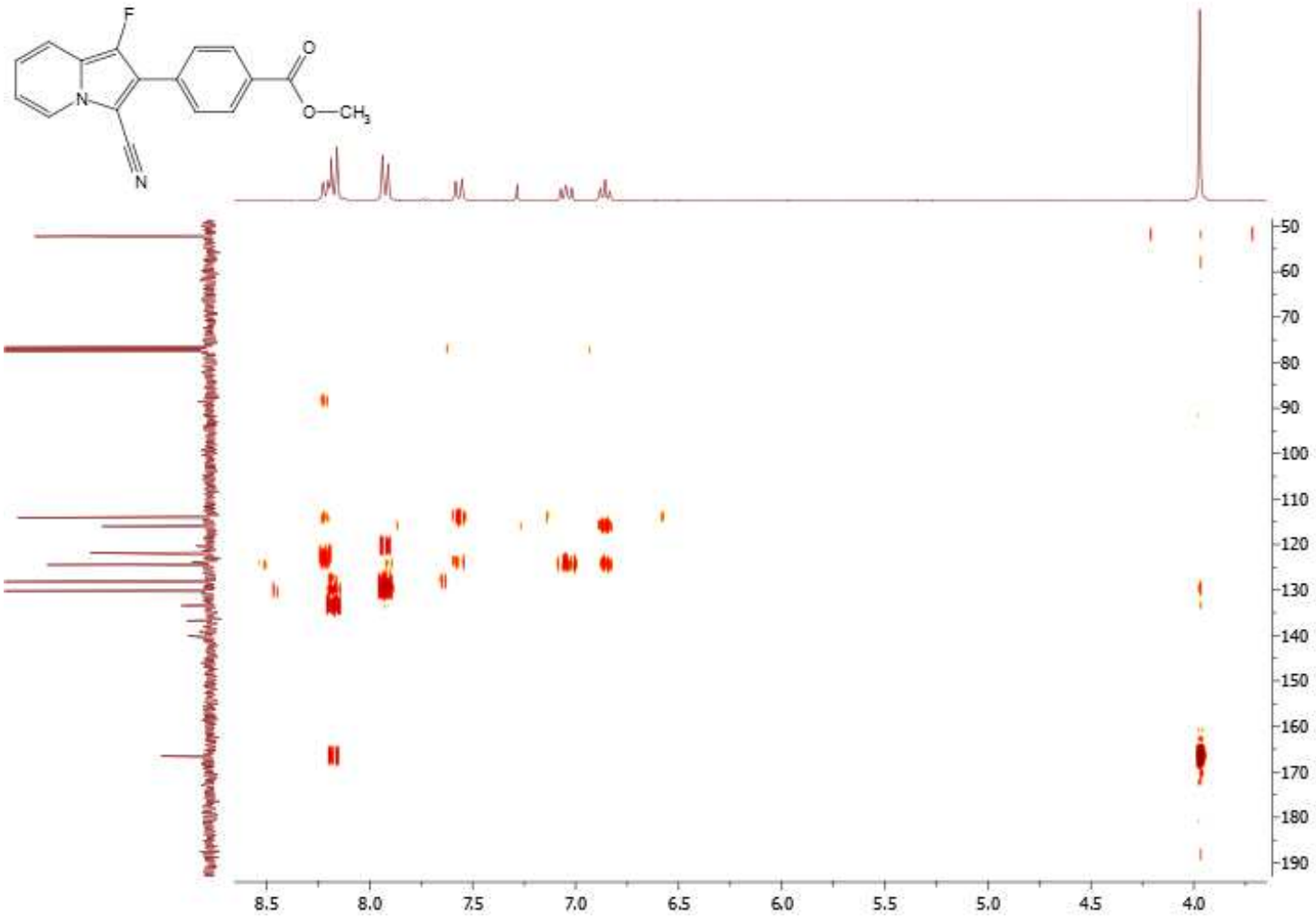
^{1}H-^{1}H COSY


F
O
O—CH3
N
N
5.8
6.0
6.2
6.4
6.6
6.8
7.0
7.2
7.4
7.6
7.8
8.0
8.2
8.4
8.6
8.8
8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2

^{1}H-^{13}C HSQC

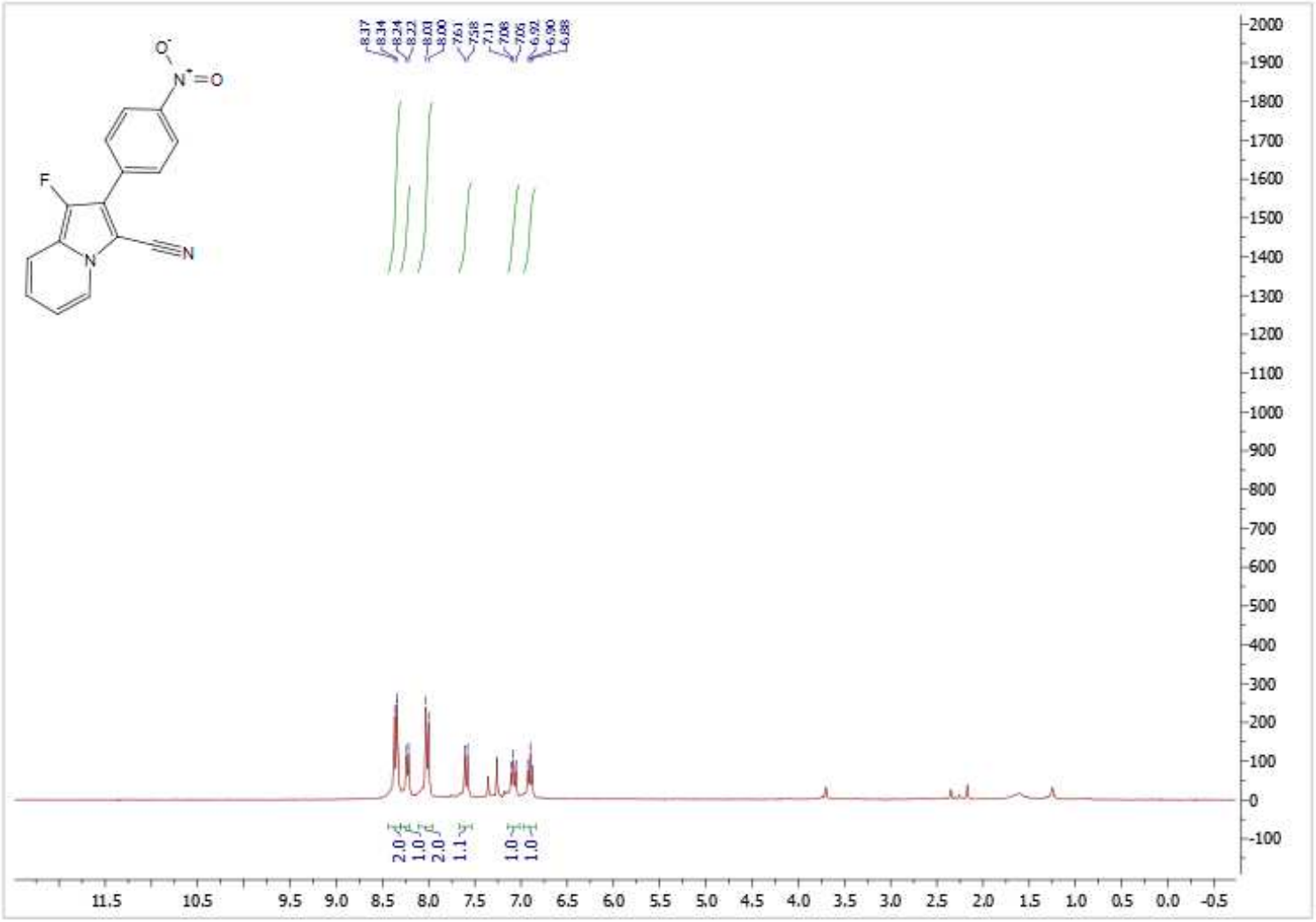

F
O
O
CH3
N
N
40
50
60
70
80
90
100
110
120
130
140
8.6
8.2
7.8
7.6
7.4
7.2
7.0
6.6
6.2
5.8
5.4
5.0
4.6
4.2
3.8

^{1}H-^{13}C HMBC

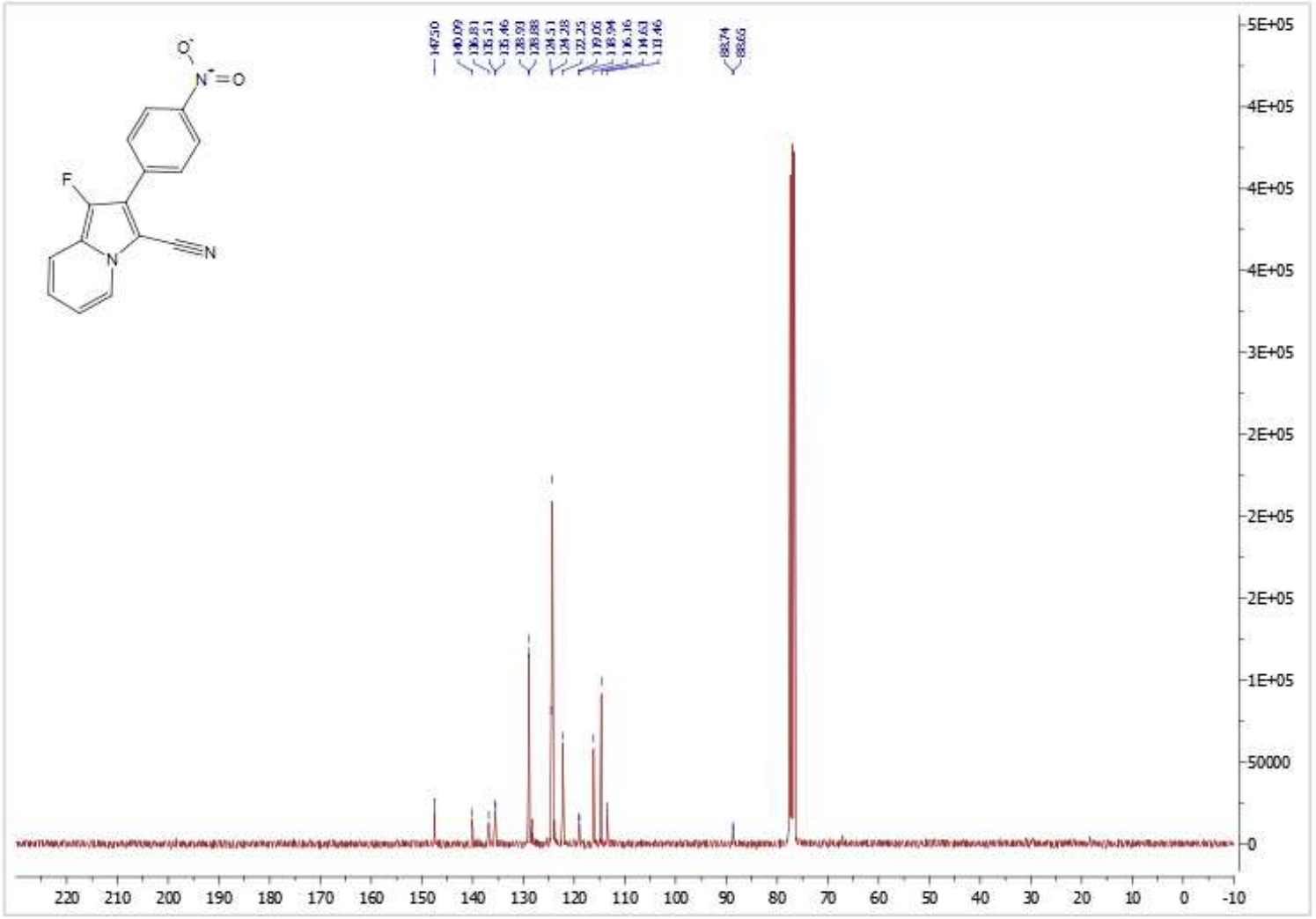

F
O
N
O—CH3
N
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0

1-fluoro-2-(4-nitrophenyl)-indolizine-3-carbonitrile 3r

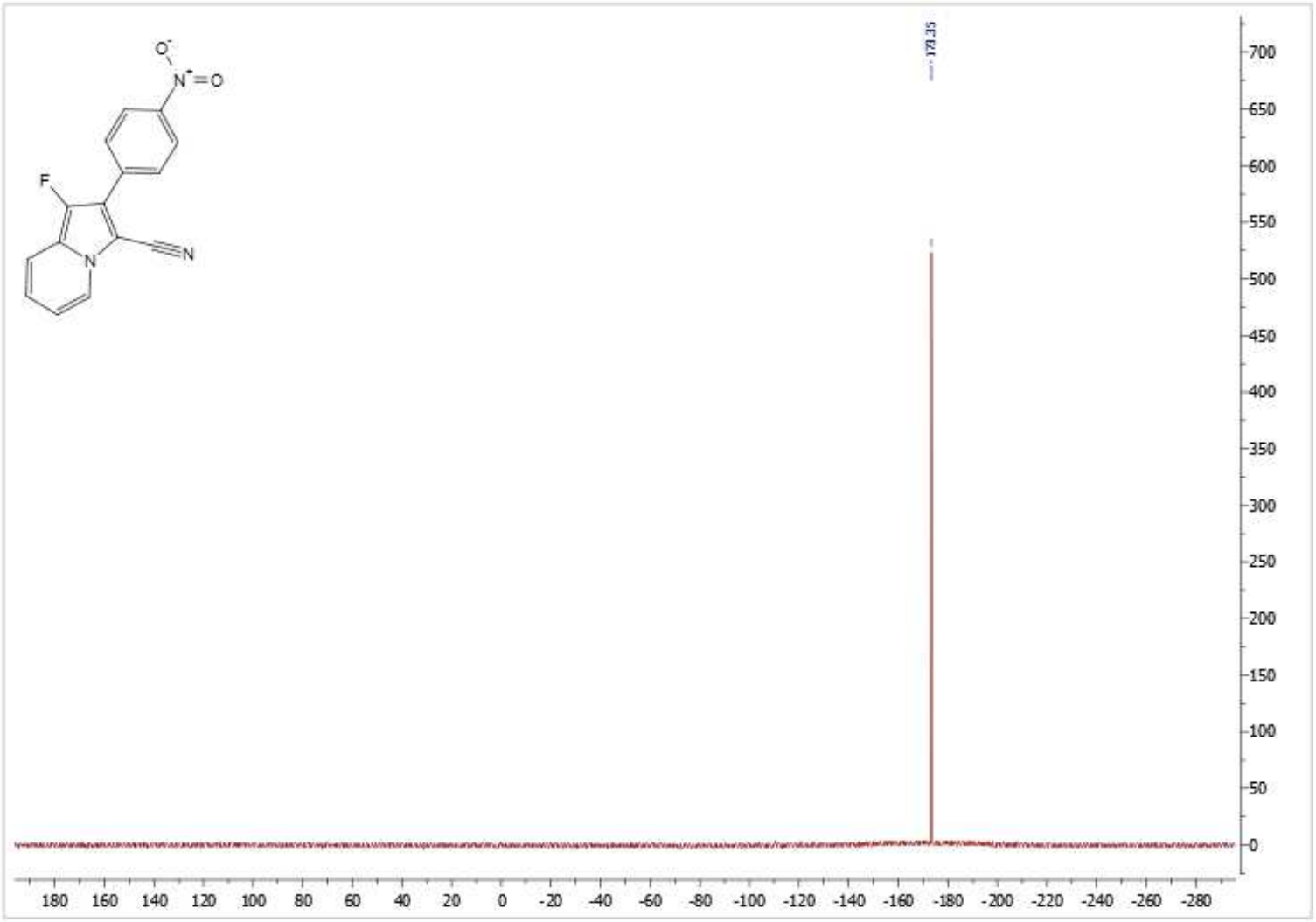
^{1}H NMR



^{13}C NMR

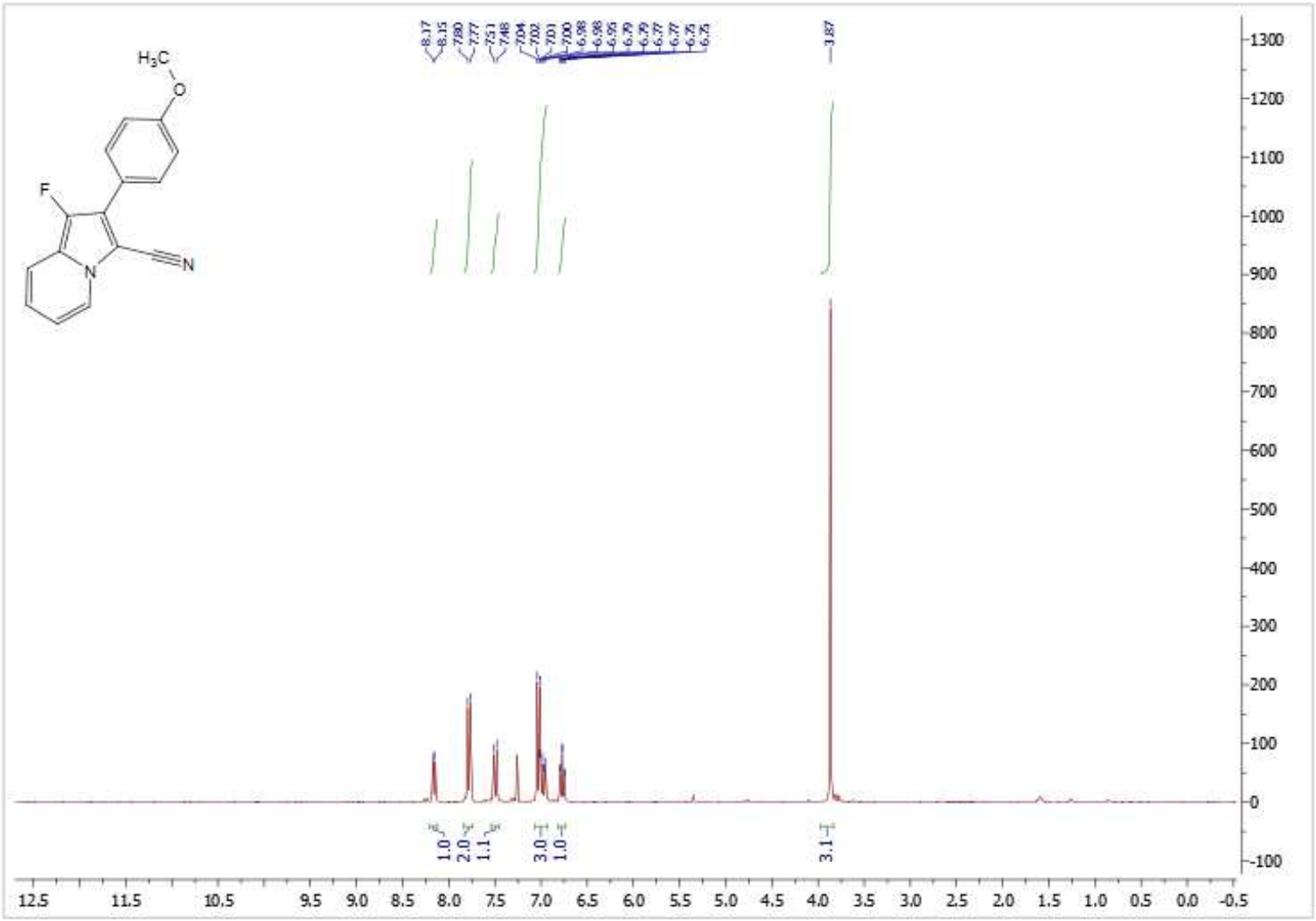

147.50
140.09
136.81
135.51
133.46
128.93
128.88
124.51
124.28
122.25
119.06
116.94
116.16
114.63
113.46
88.74
88.65
5E+05
4E+05
4E+05
4E+05
3E+05
2E+05
2E+05
2E+05
1E+05
50000
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

^{19}F NMR

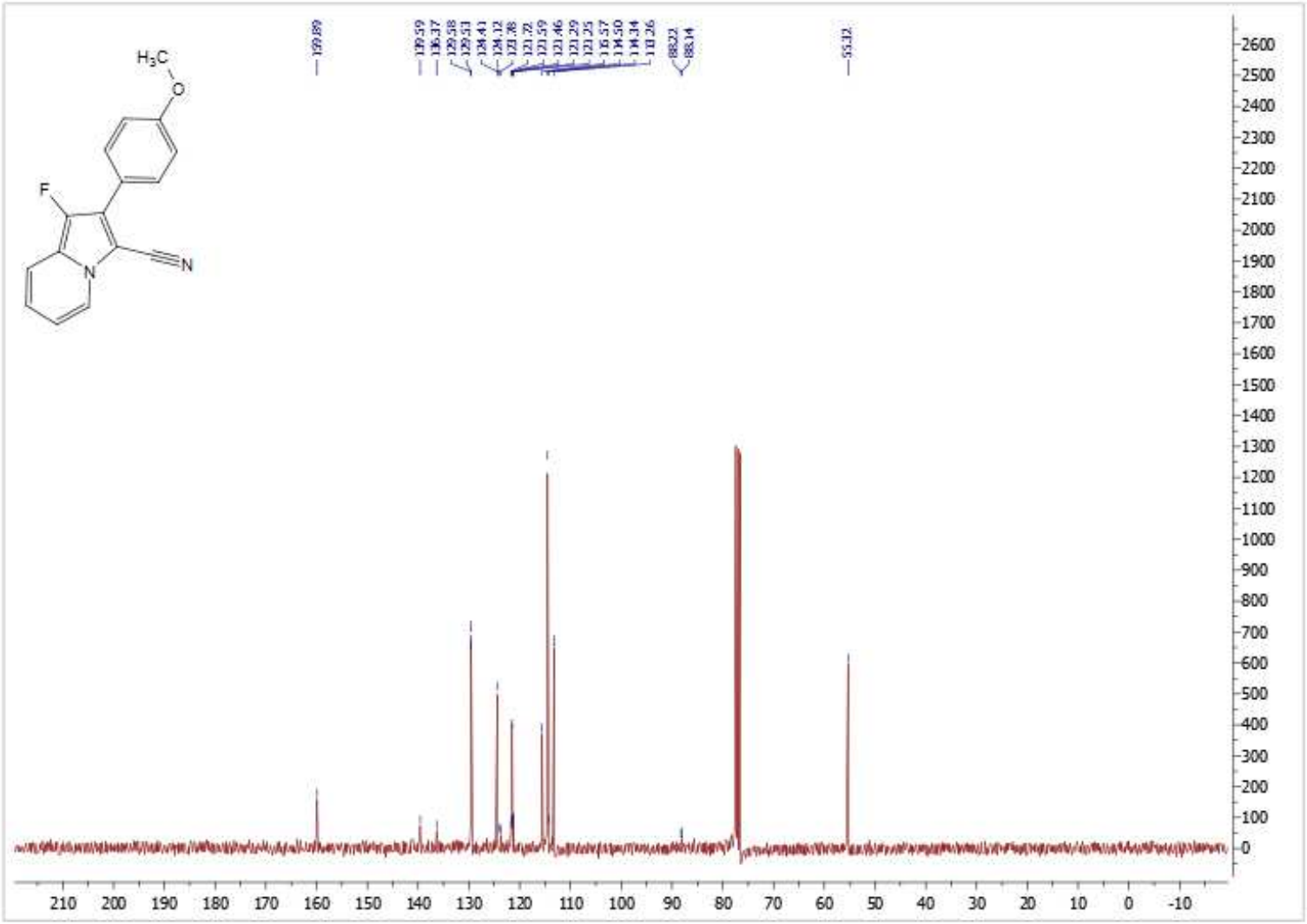

-178.35
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280

1-fluoro-2-(4-methoxyphenyl)-indolizine-3-carbonitrile 3s

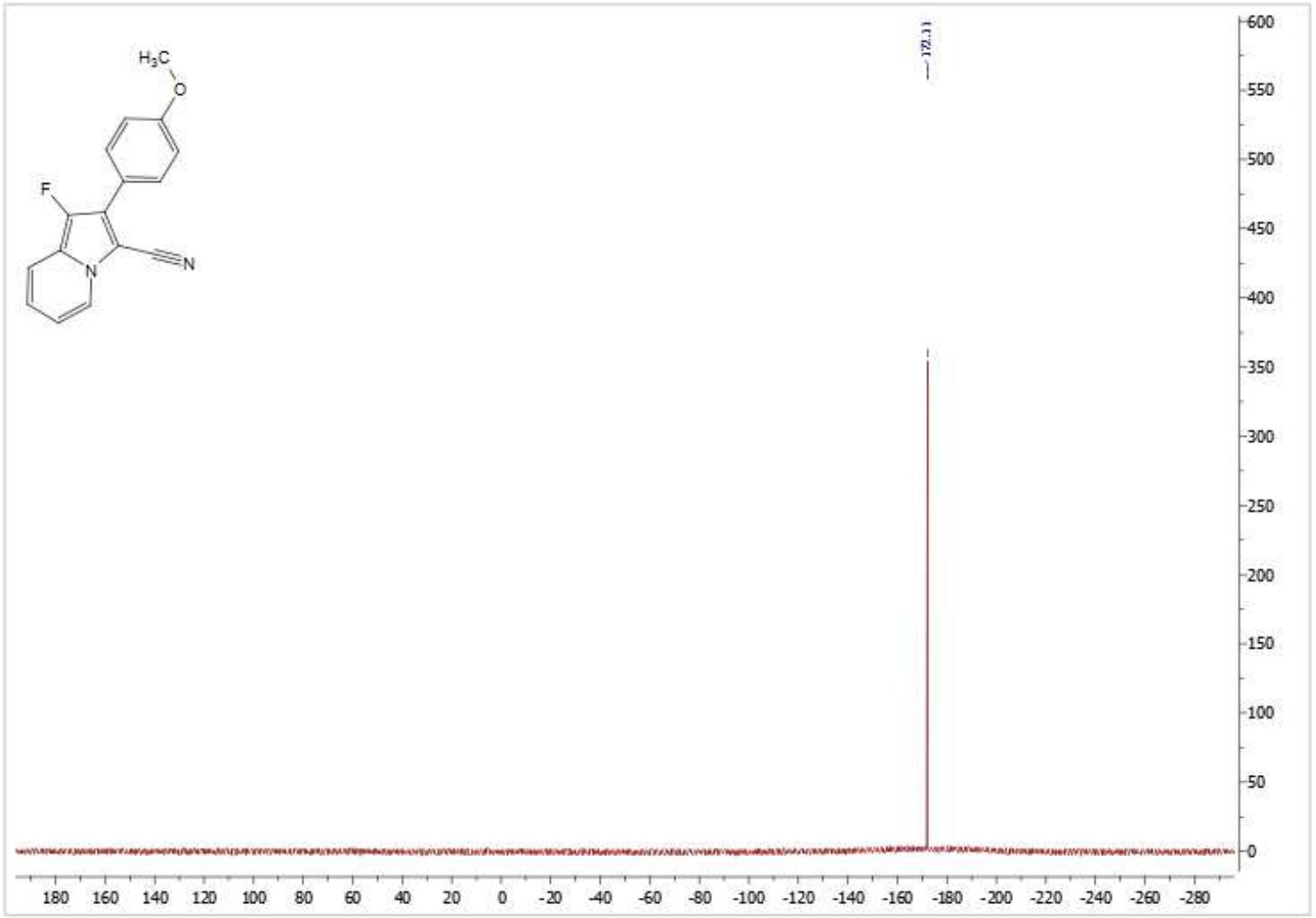
^{1}H NMR



^{13}C NMR

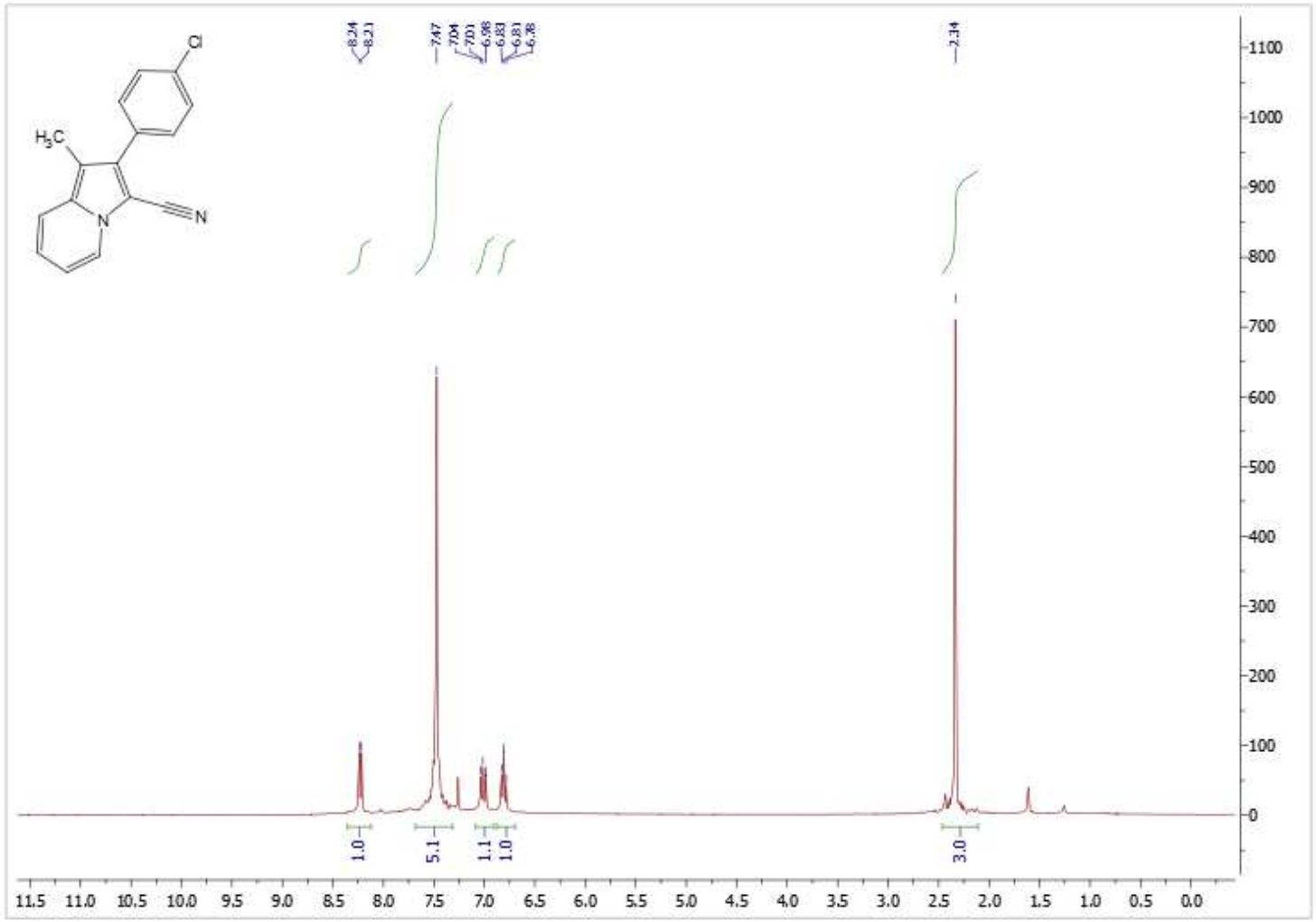

H3C
O
F
N
N
159.89
139.59
136.37
129.58
129.53
124.41
124.12
123.88
123.72
123.59
121.46
121.29
121.25
116.57
114.50
114.34
113.26
88.22
88.14
55.32
2600
2500
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

^{19}F NMR


H3C
O
F
N
N
600
550
500
450
400
350
300
250
200
150
100
50
0
180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280

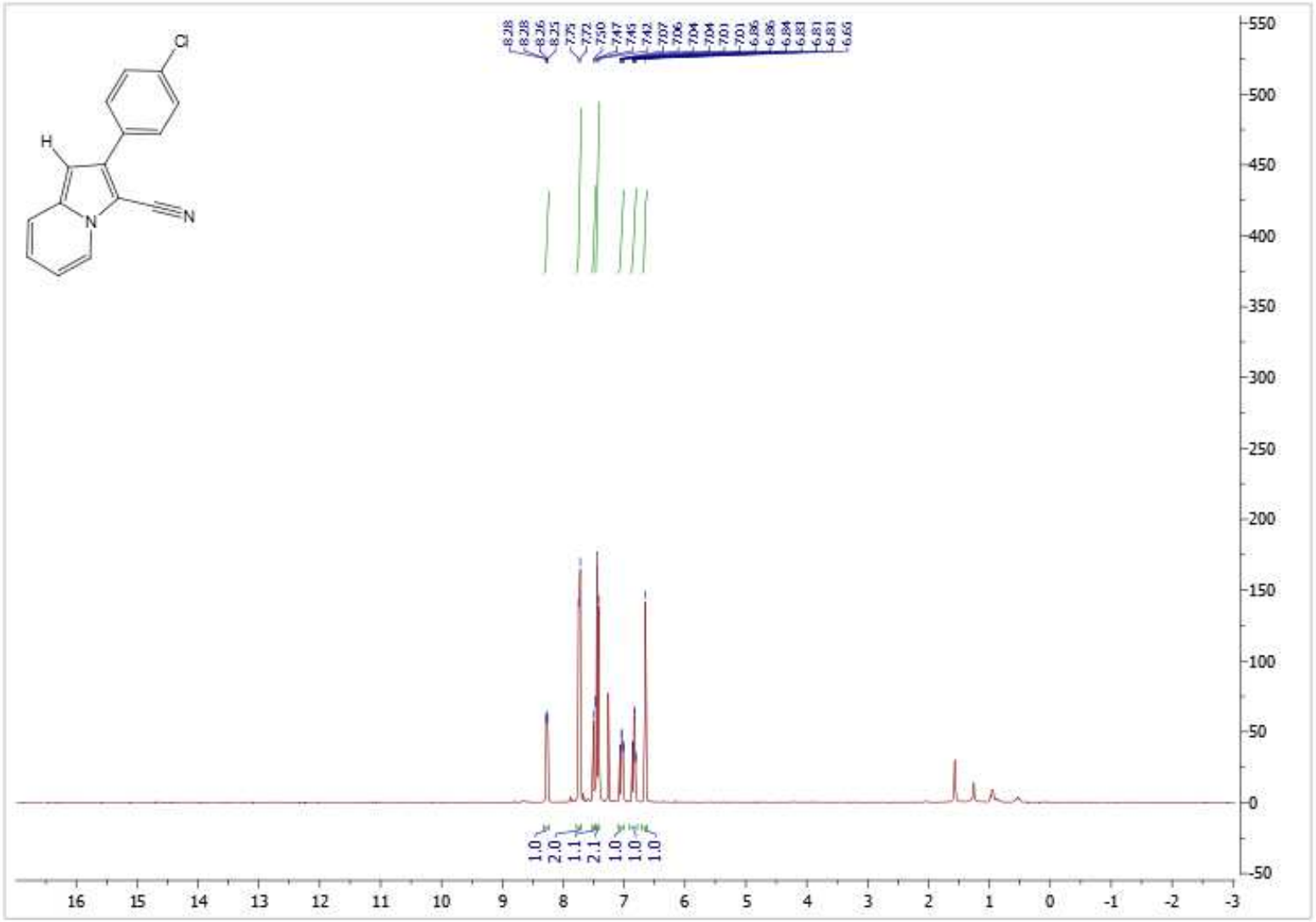
1-methyl-2-(4-chlorophenyl)-indolizine-3-carbonitrile 4

^{1}H NMR

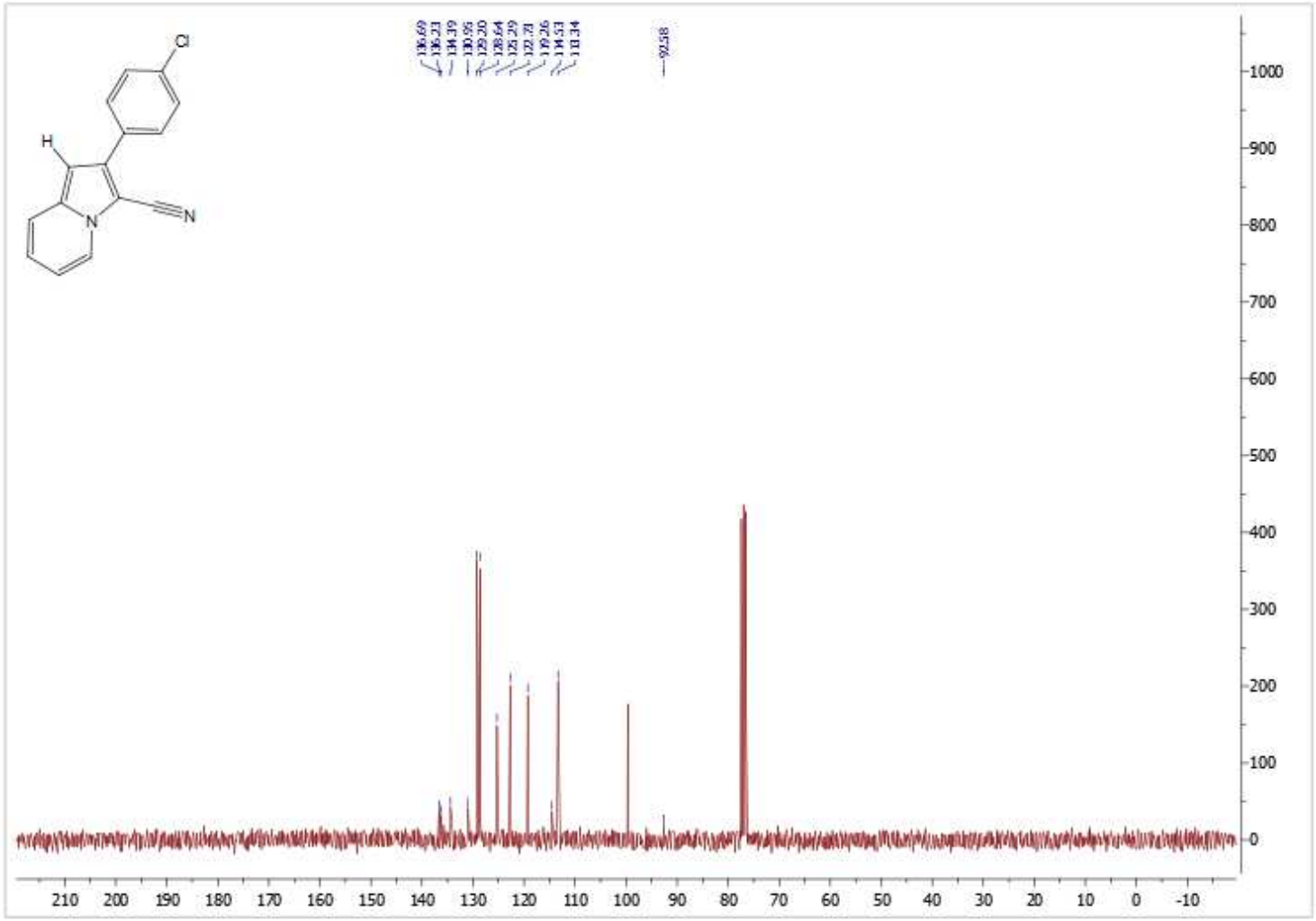


2-(4-chlorophenyl)-indolizine-3-carbonitrile 5

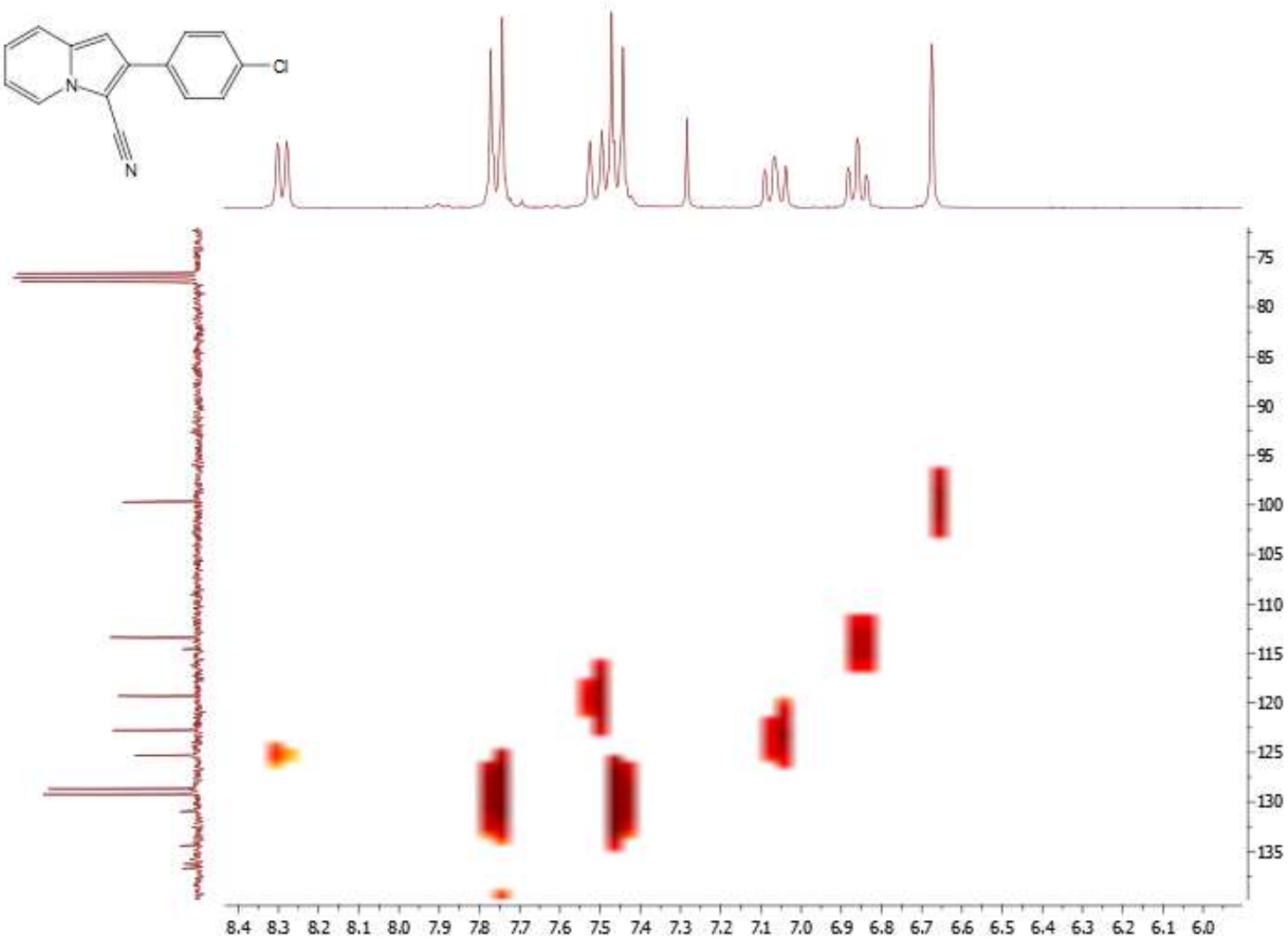
^{1}H NMR



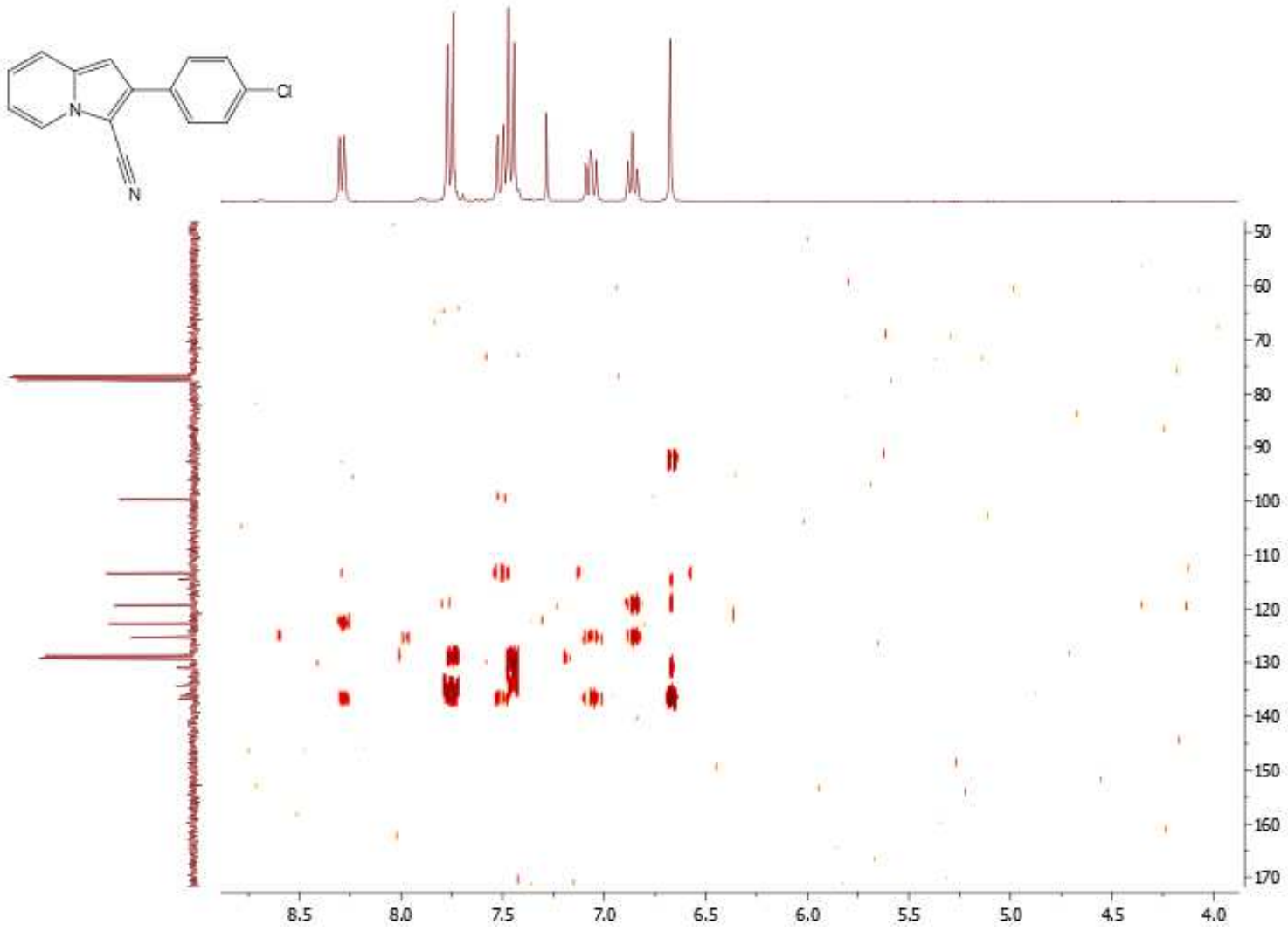
^{13}C NMR


Cl
H
N
N
136.69
136.23
134.39
130.95
129.20
128.64
125.29
122.73
119.26
114.53
111.34
92.58
1000
900
800
700
600
500
400
300
200
100
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

^{1}H-^{13}C HSQC

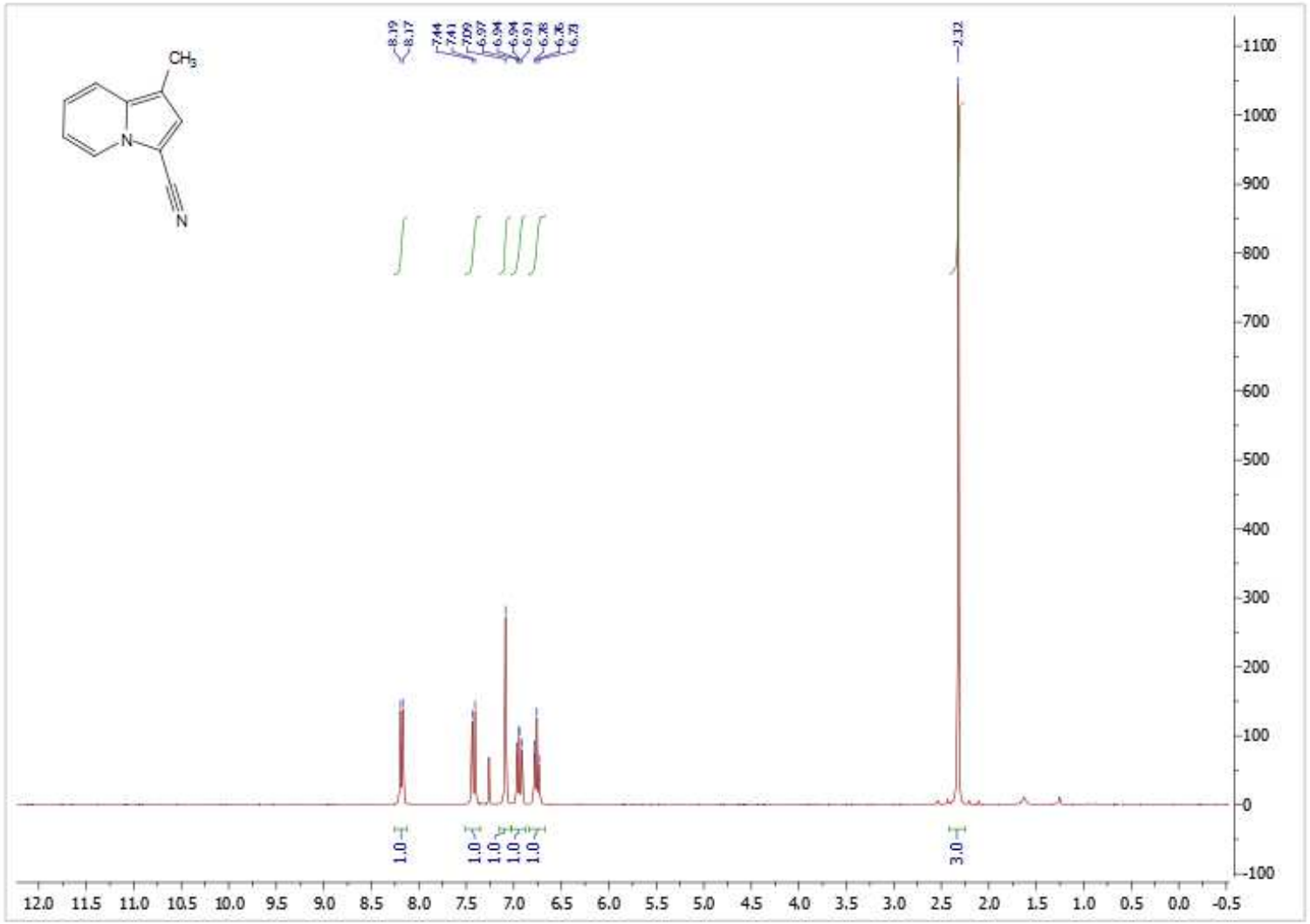

Cl
N
N
75
80
85
90
95
100
105
110
115
120
125
130
135
8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0

^{1}H-^{13}C HMBC

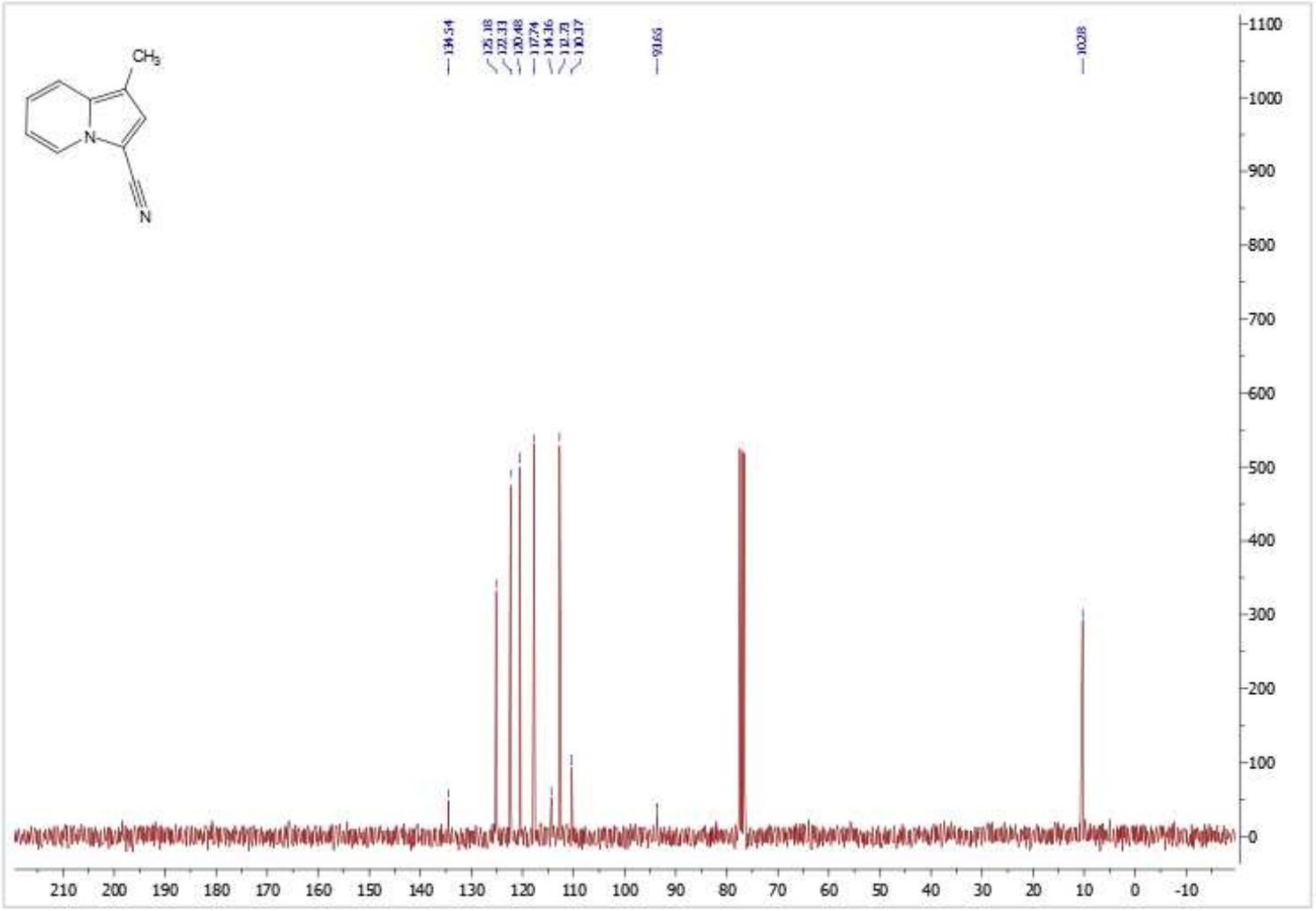

Cl
N
N
50
60
70
80
90
100
110
120
130
140
150
160
170
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0

1-methyl-indolizine-3-carbonitrile 6a

^{1}H NMR

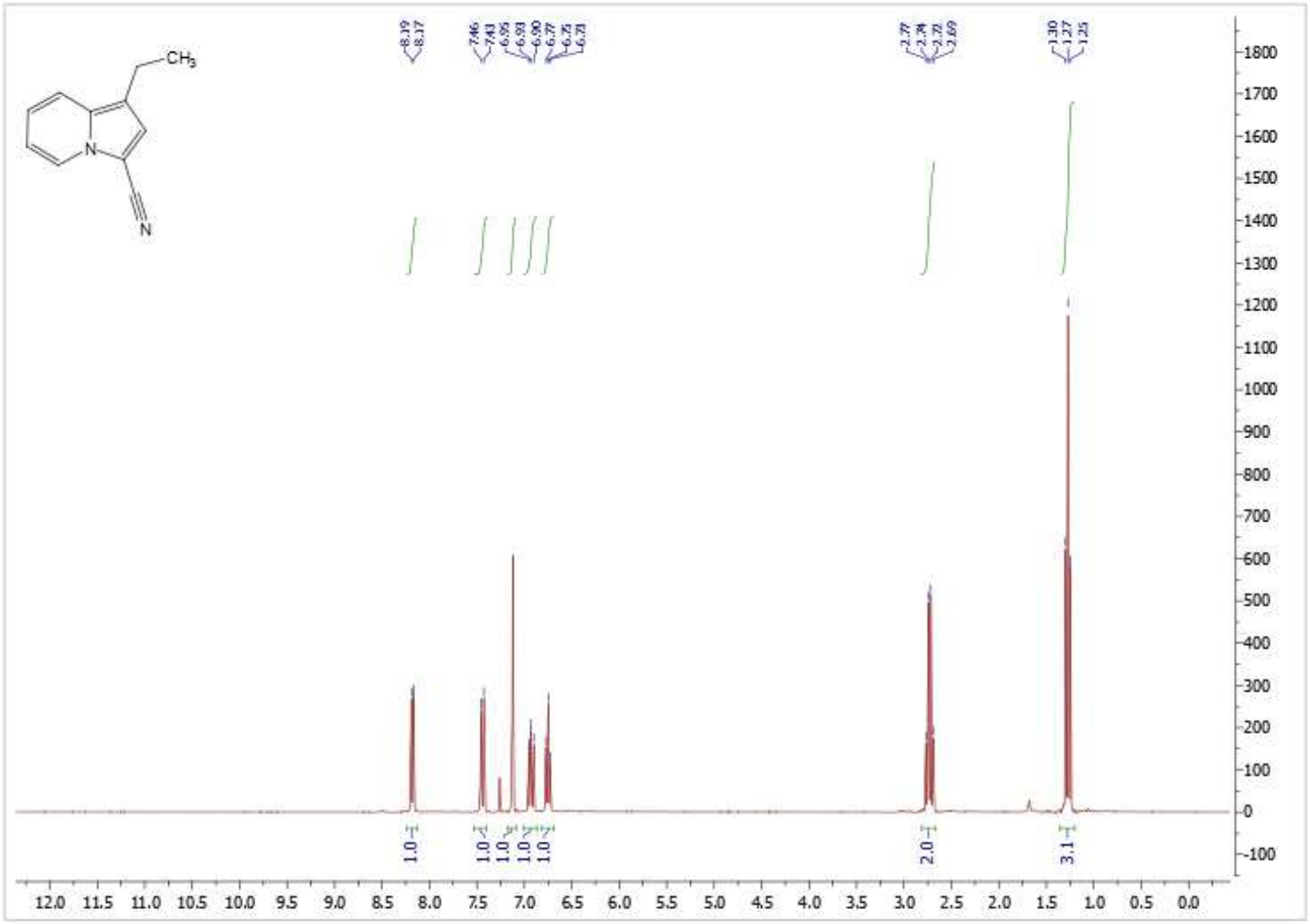


^{13}C NMR

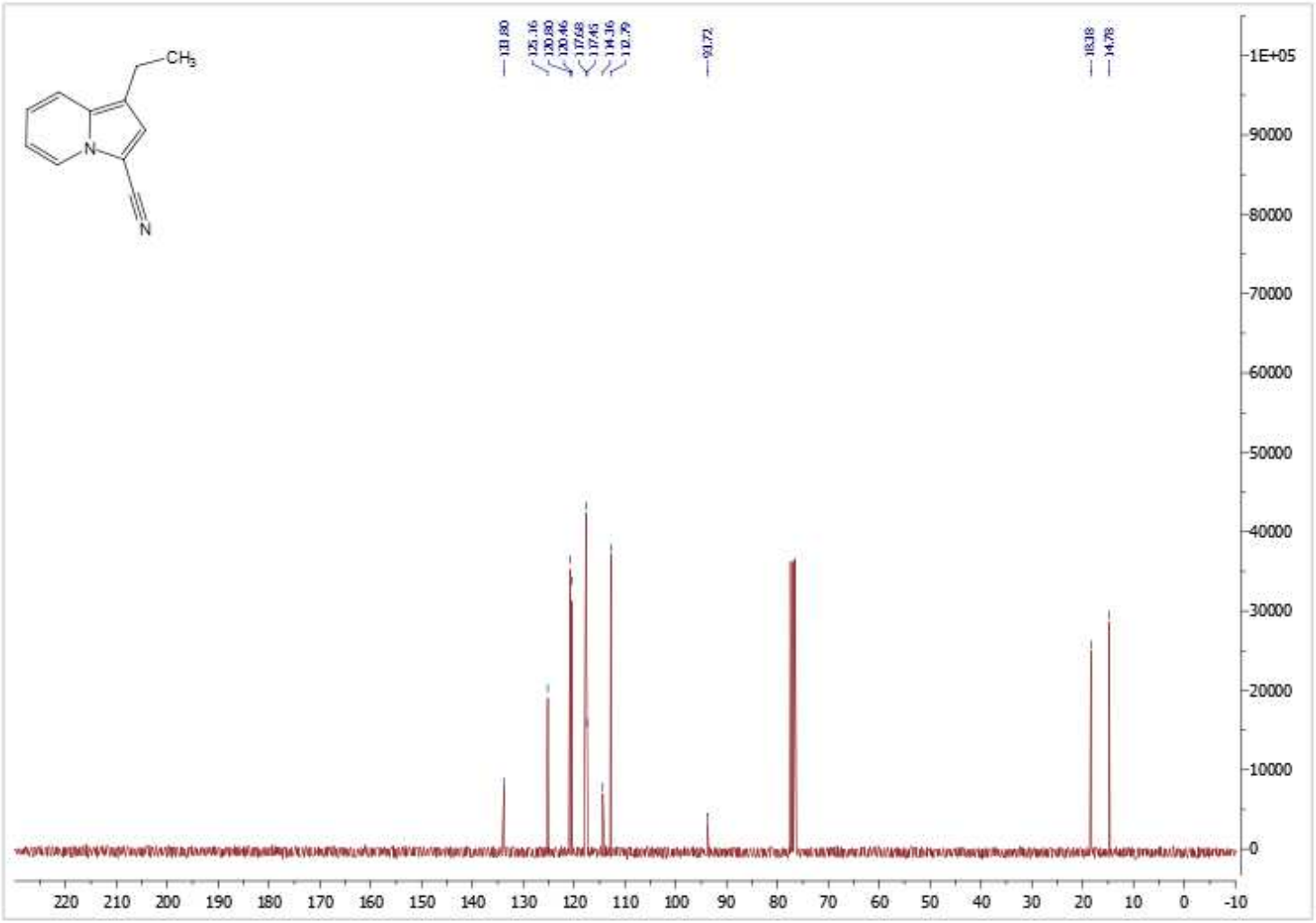

CH3
N
N
134.54
125.18
122.33
120.48
117.74
114.36
112.73
110.17
93.65
10.28
1100
1000
900
800
700
600
500
400
300
200
100
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

1-ethyl-indolizine-3-carbonitrile 6b

^{1}H NMR

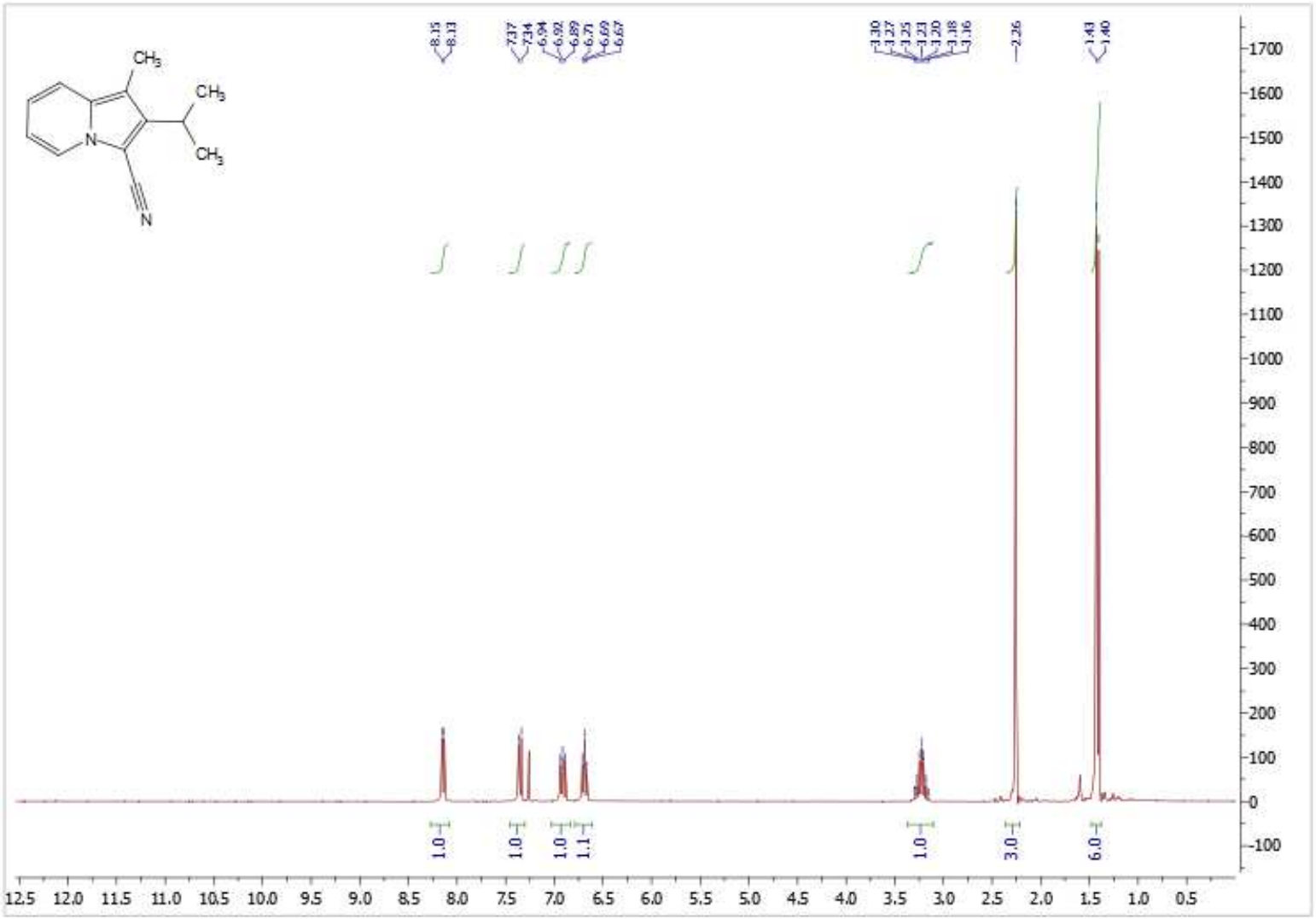


^{13}C NMR

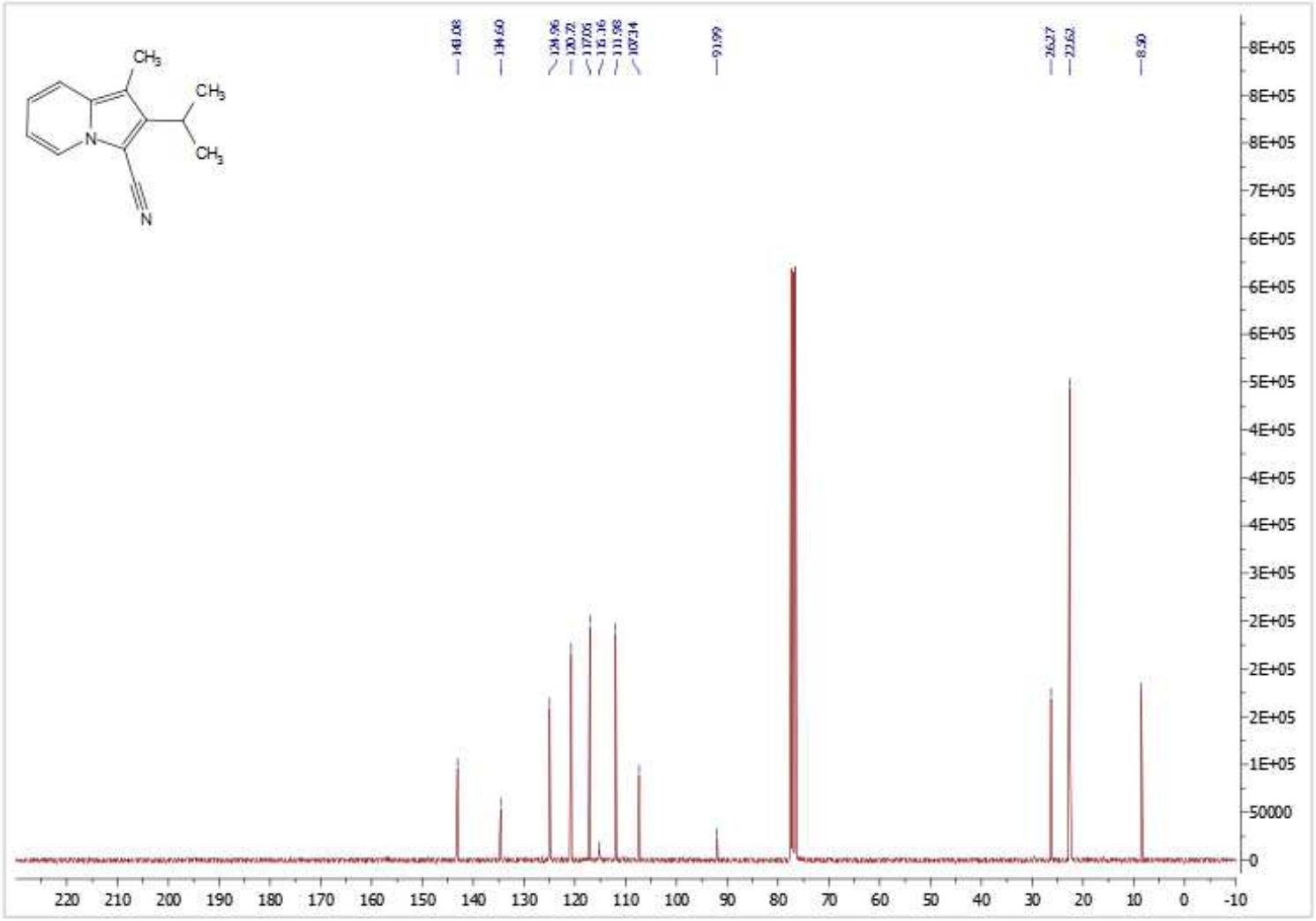

CH3
N
N
133.80
125.16
120.80
120.46
117.68
117.45
114.36
112.79
93.72
18.38
14.78
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

1-methyl-2-isopropyl-indolizine-3-carbonitrile 7

^{1}H NMR

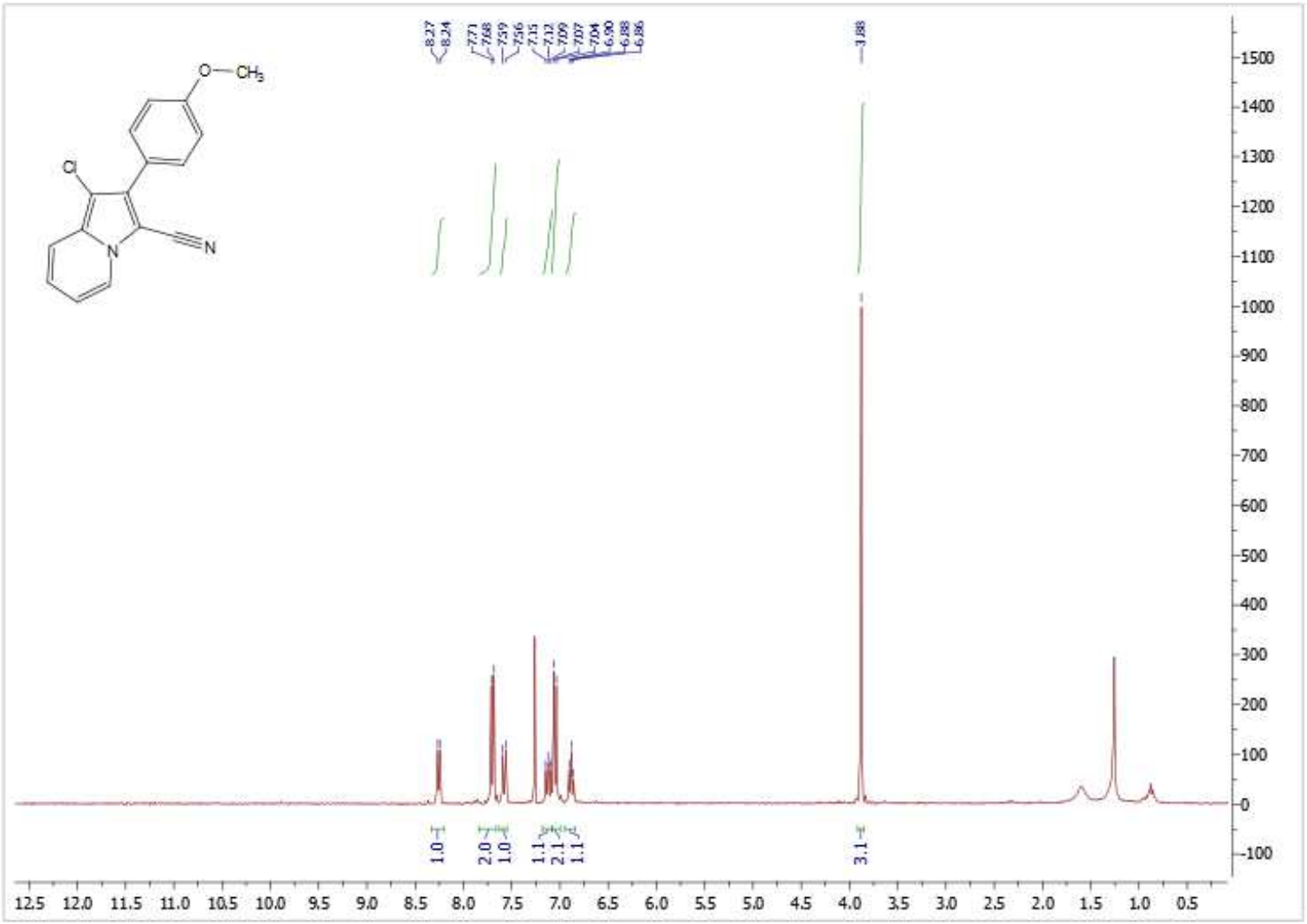


^{13}C NMR

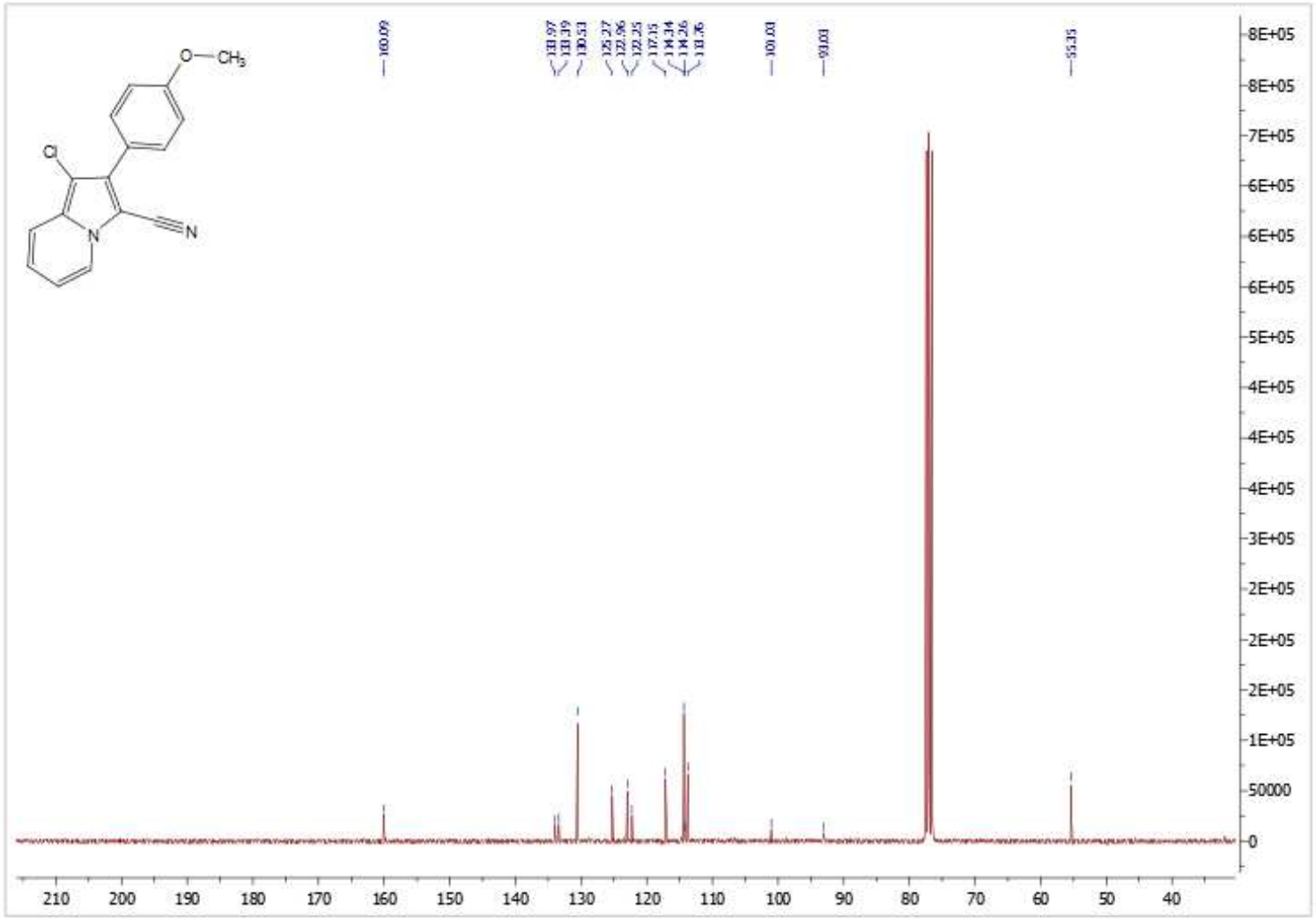

CH3
CH3
CH3
N
N
141.08
134.60
120.96
120.72
117.05
115.16
111.98
107.34
91.99
26.27
22.62
8.50
8E+05
8E+05
8E+05
7E+05
6E+05
6E+05
6E+05
5E+05
4E+05
4E+05
4E+05
3E+05
2E+05
2E+05
2E+05
1E+05
50000
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

1-chloro-2-(4-methoxyphenyl)-indolizine-3-carbonitrile 8

^{1}H NMR

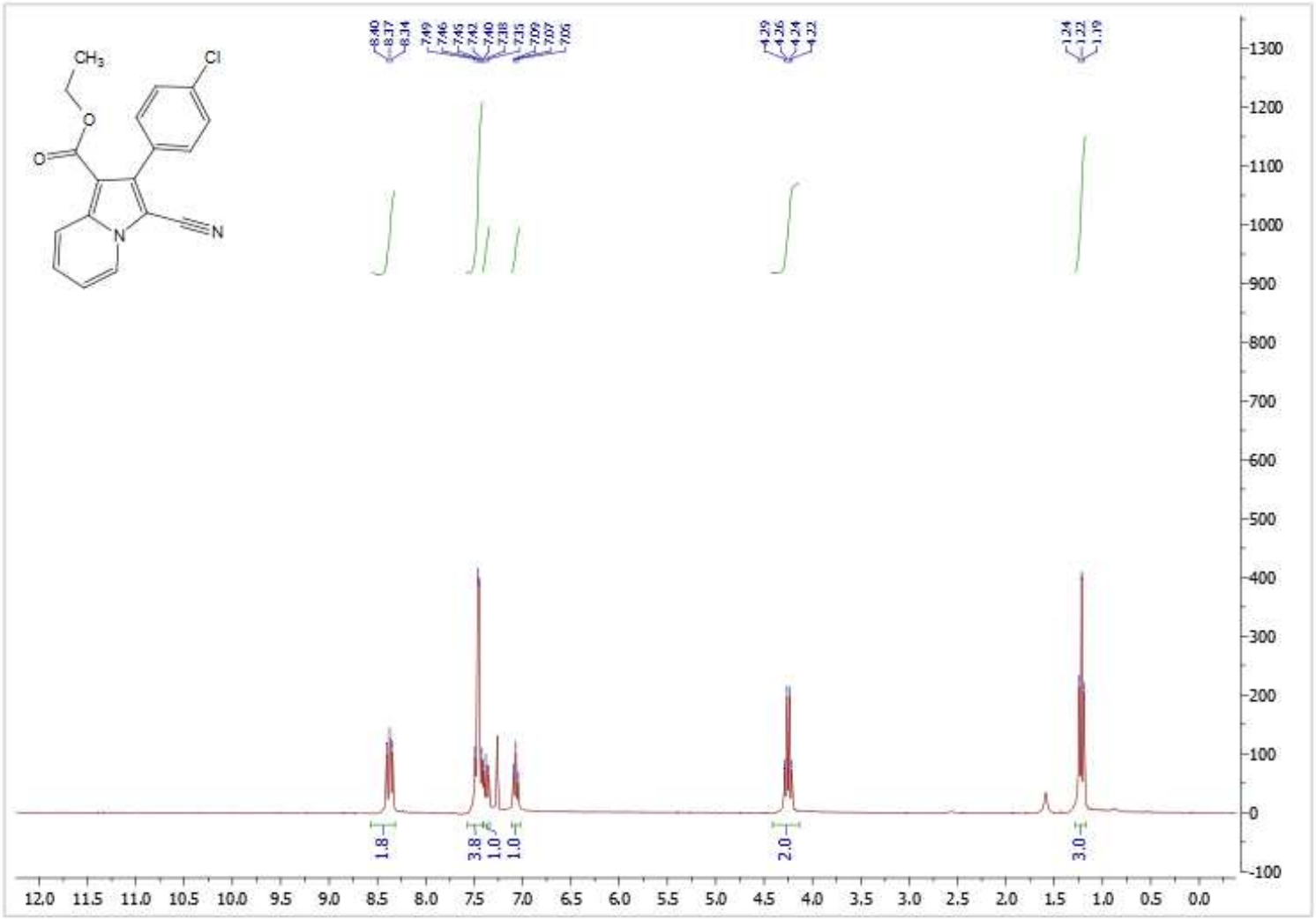


^{13}C NMR

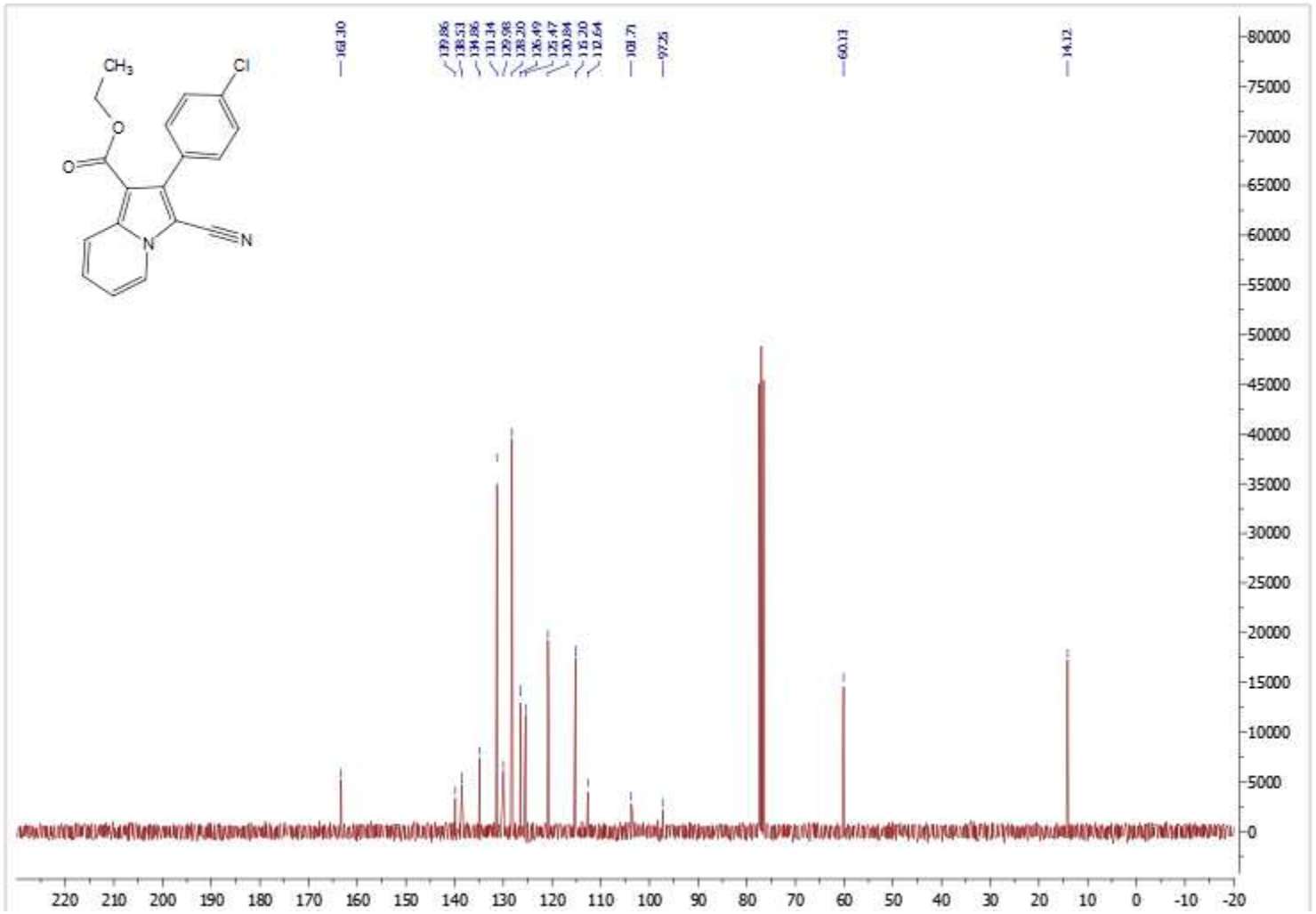

160.09
133.97
133.39
130.53
125.27
122.96
122.25
117.15
114.34
114.26
113.76
101.03
93.03
55.35
O
CH3
Cl
N
N
8E+05
8E+05
7E+05
6E+05
6E+05
6E+05
5E+05
4E+05
4E+05
4E+05
3E+05
2E+05
2E+05
2E+05
1E+05
50000
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40

1-(ethyloxycarbonyl)-2-(4-chlorophenyl)-indolizine-3-carbonitrile 9

^{1}H NMR

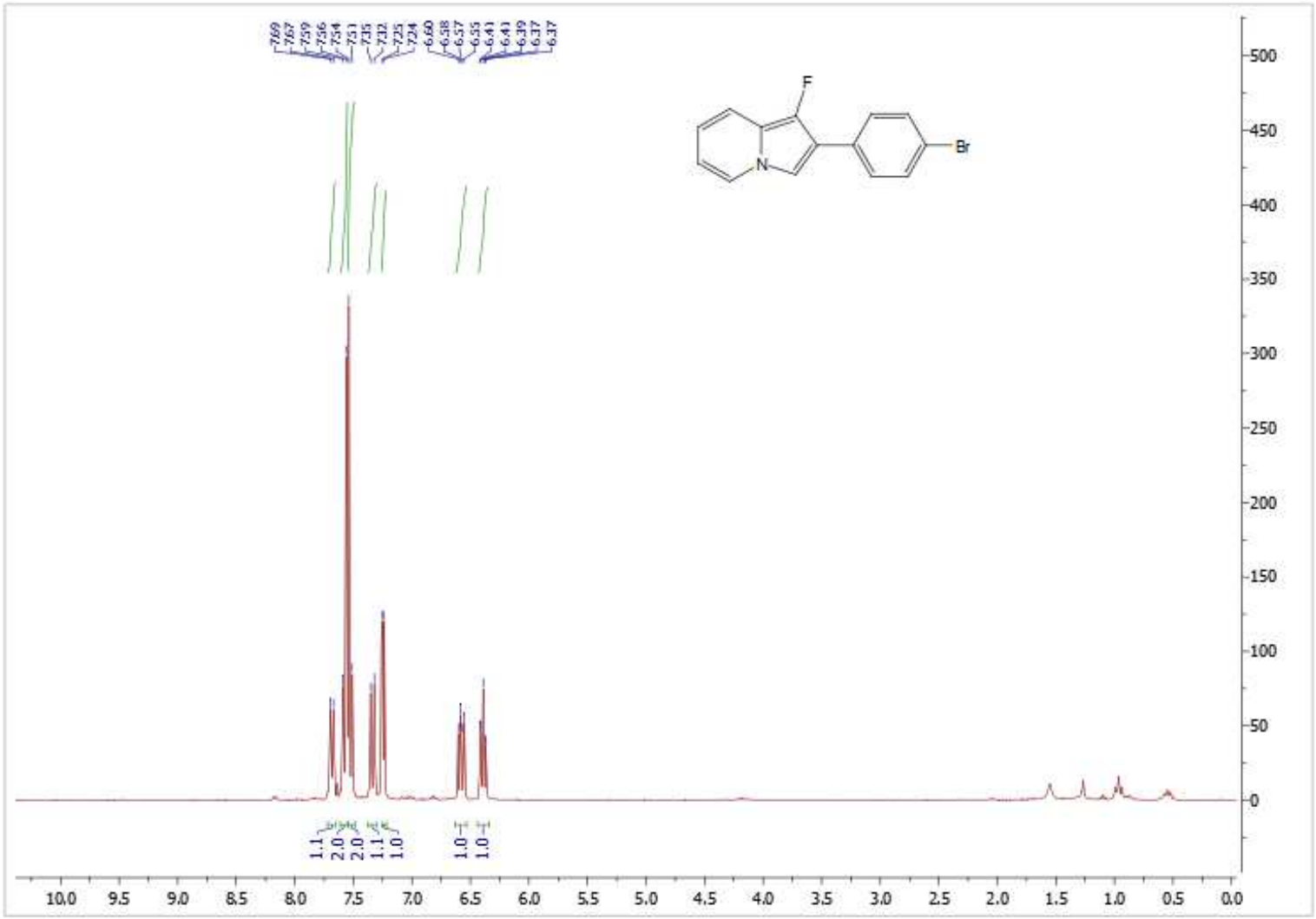


^{13}C NMR

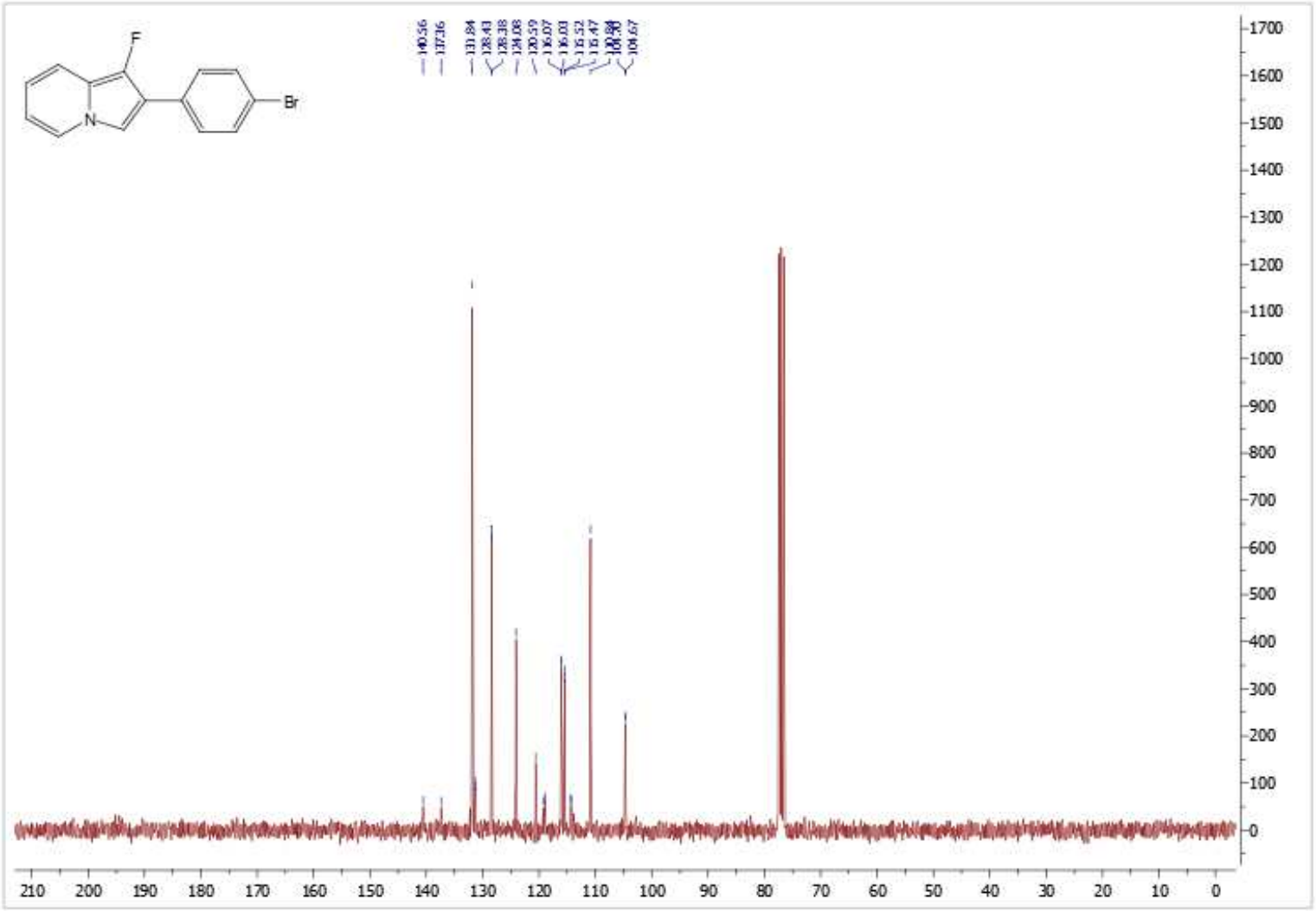

CH3
Cl
O
O
N
N
161.30
139.86
138.53
134.86
131.34
129.98
128.20
126.49
125.47
120.84
116.20
112.64
101.71
97.25
60.13
14.12
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

1-fluoro-2-(4-bromophenyl)-indolizine 10n

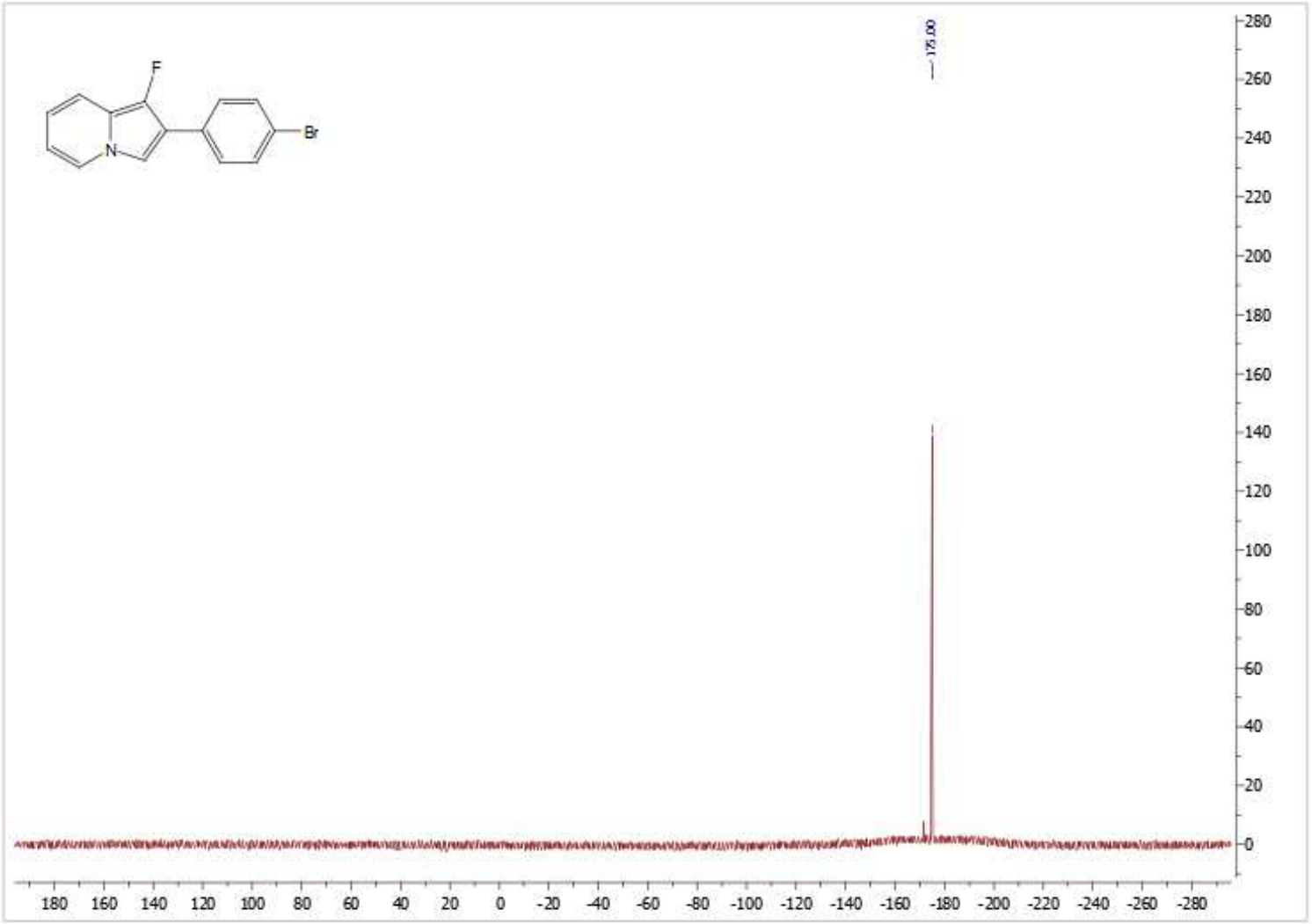
^{1}H NMR



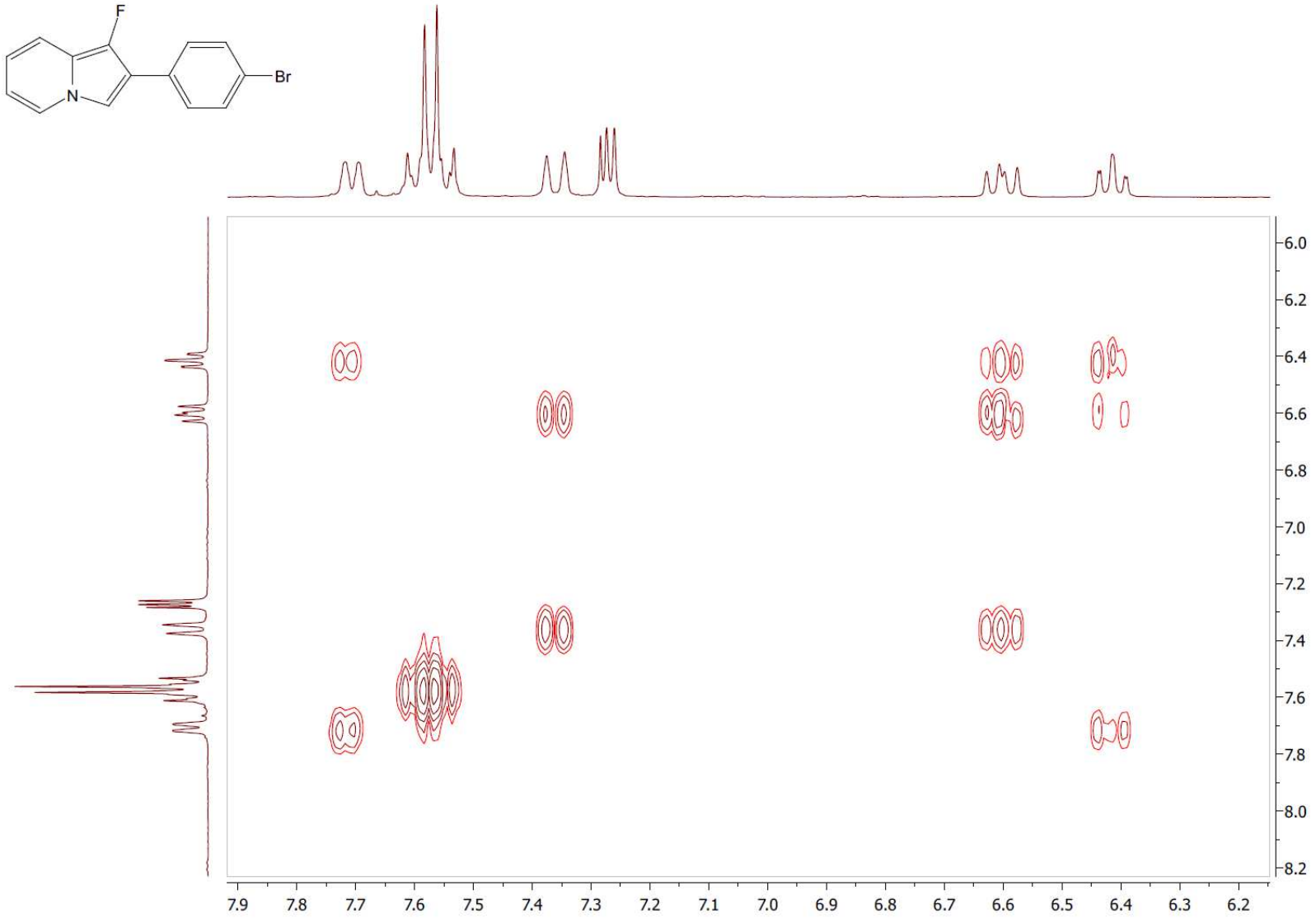
^{13}C NMR


F
N
Br
140.56
137.36
131.84
128.43
128.38
124.08
120.59
106.07
106.03
105.52
105.47
104.67
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

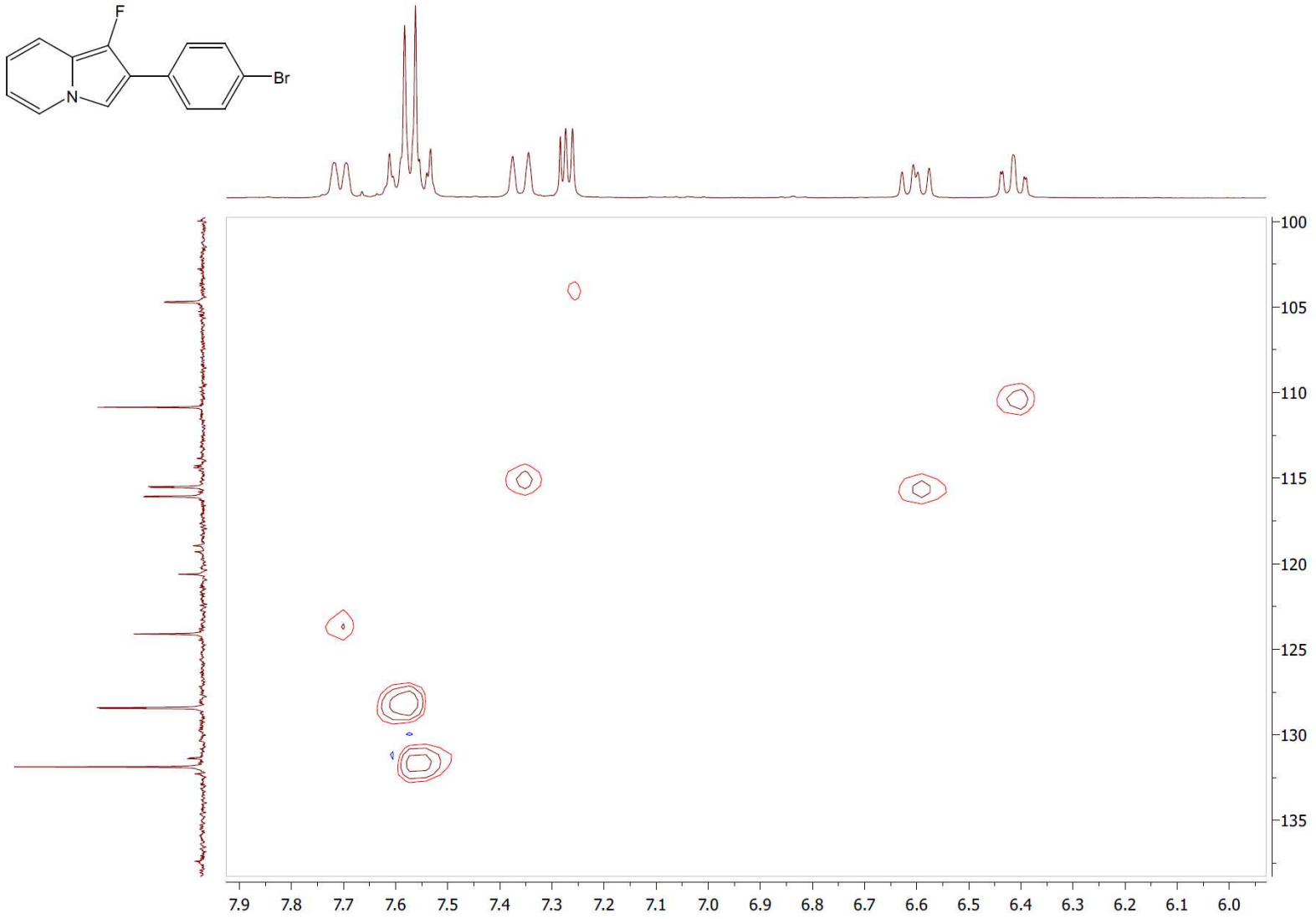
^{19}F NMR


F
N
Br
-175.00
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280

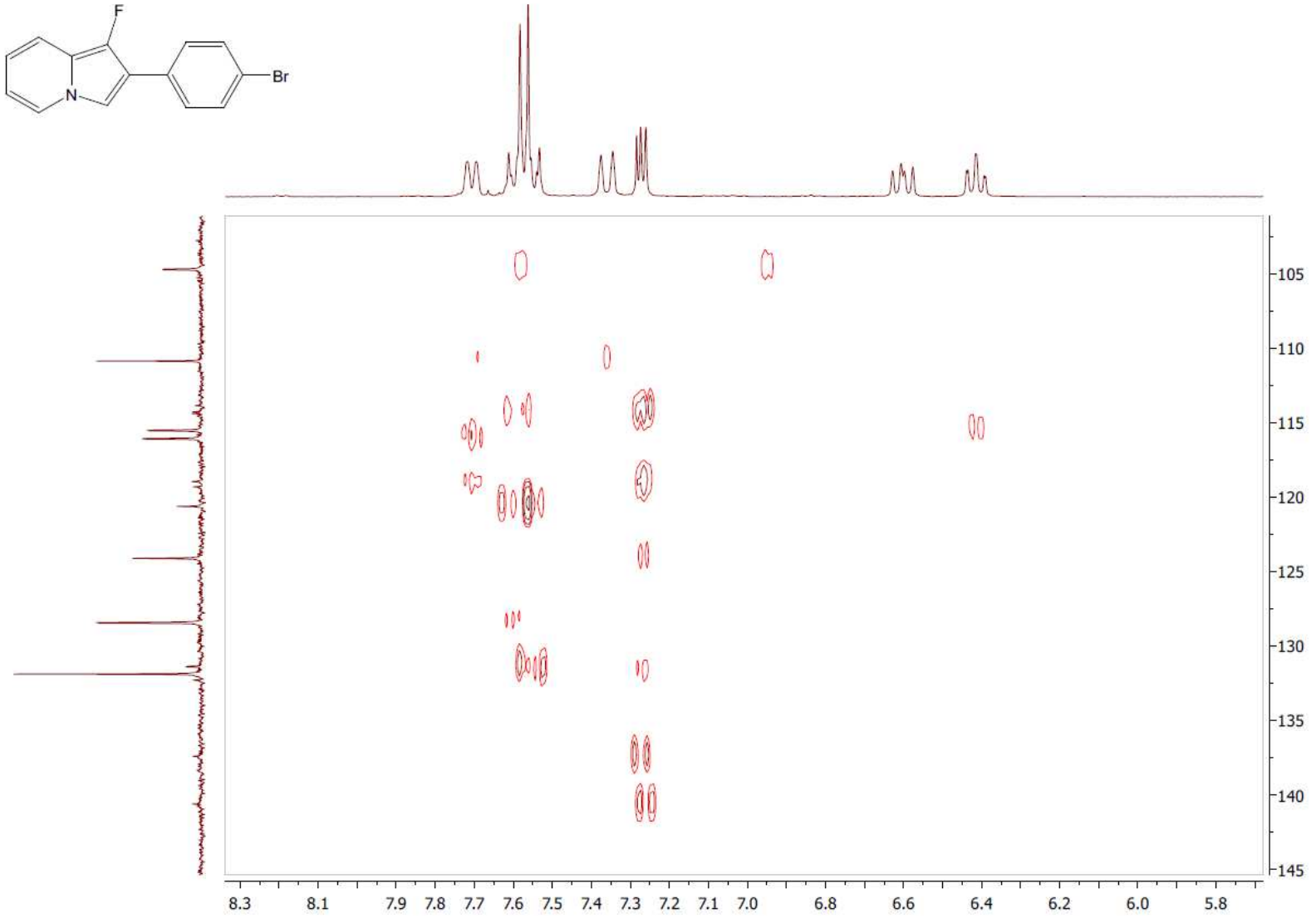
^{1}H-^{1}H COSY


F
Br
N
6.0
6.2
6.4
6.6
6.8
7.0
7.2
7.4
7.6
7.8
8.0
8.2
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2

^{1}H-^{13}C HSQC

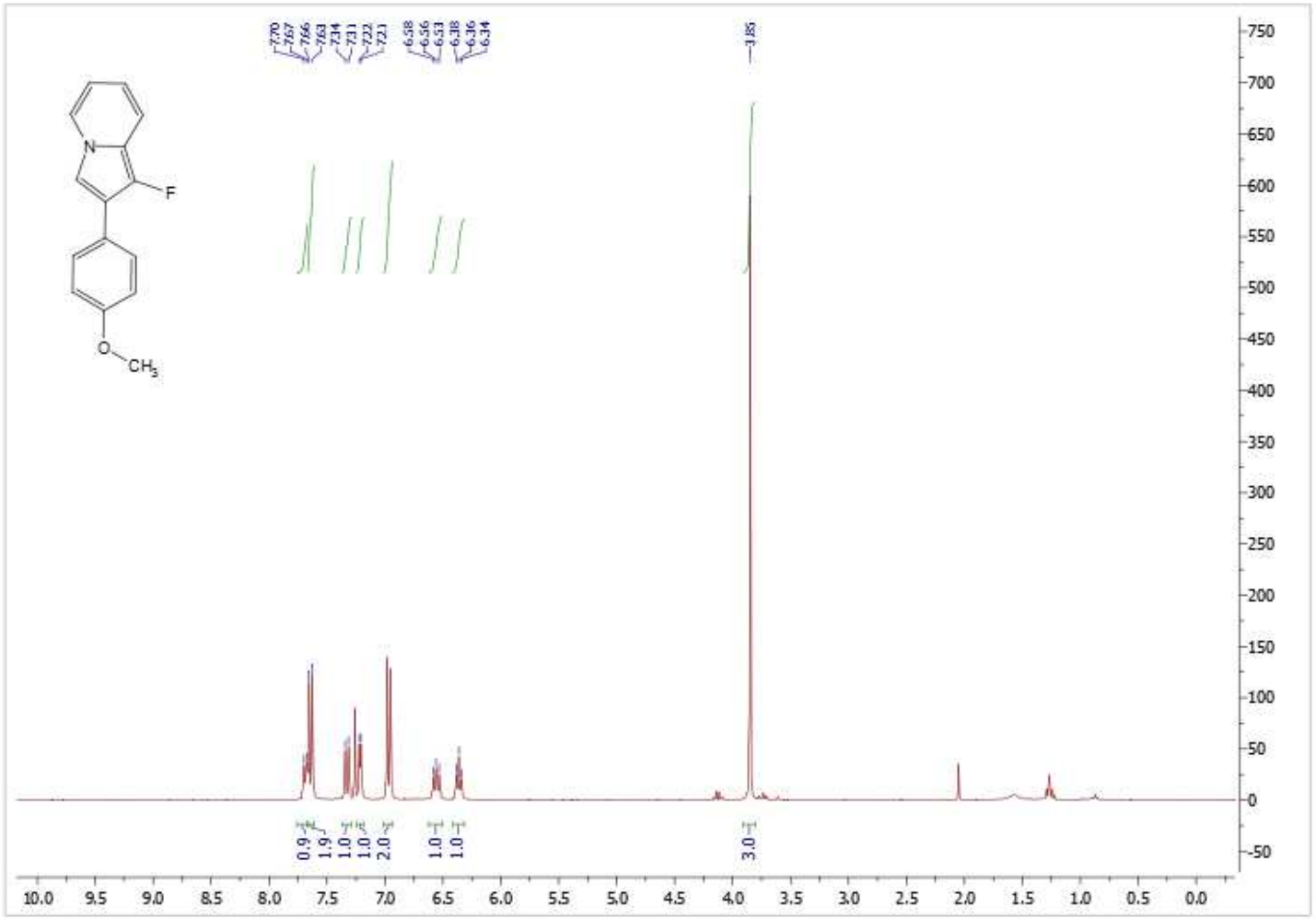

F
N
Br
100
105
110
115
120
125
130
135
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
6.0

^{1}H-^{13}C HMBC

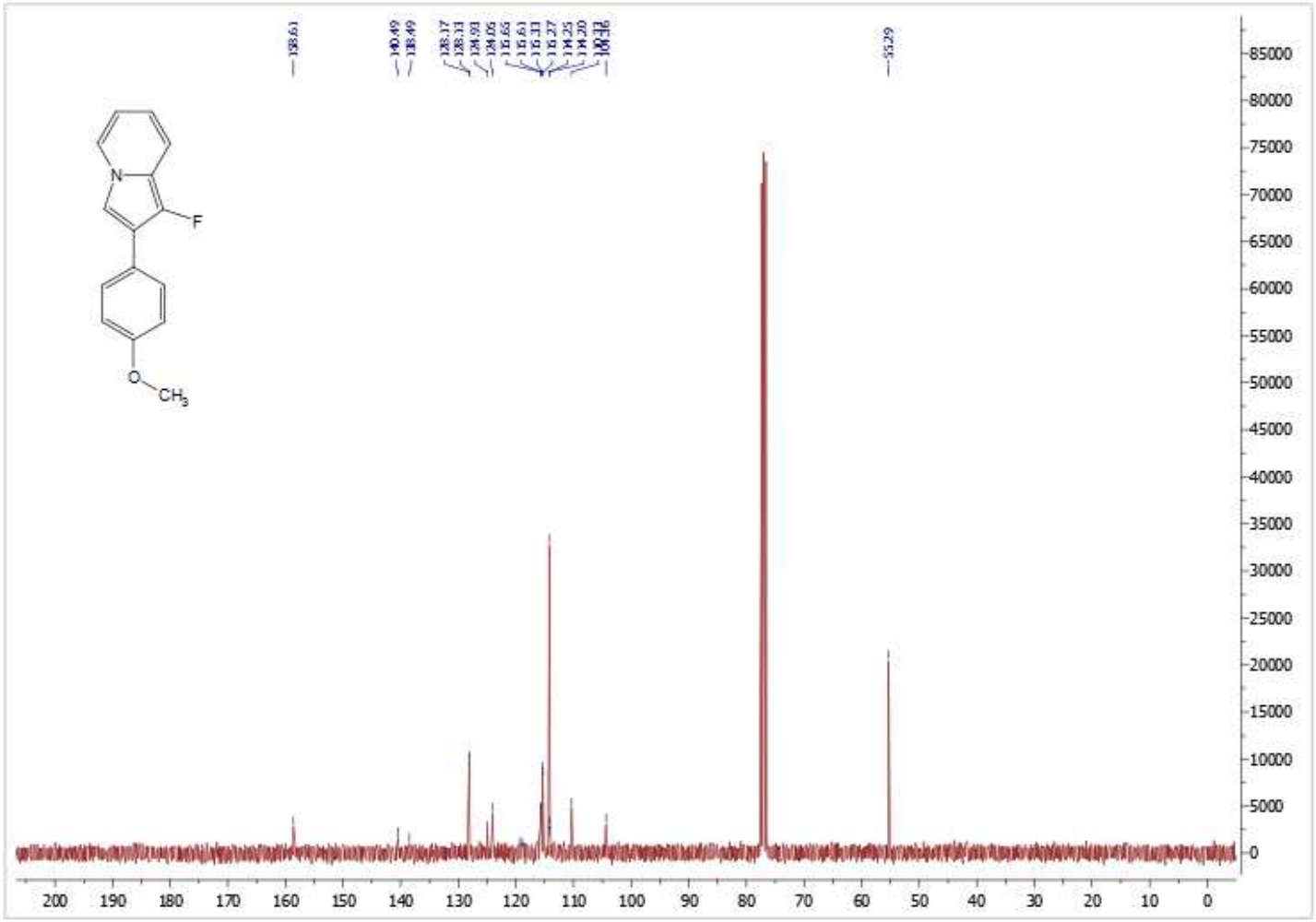

F
N
Br
105
110
115
120
125
130
135
140
145
8.3
8.1
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.8
6.6
6.4
6.2
6.0
5.8

1-fluoro-2-(4-methoxyphenyl)-indolizine 10s

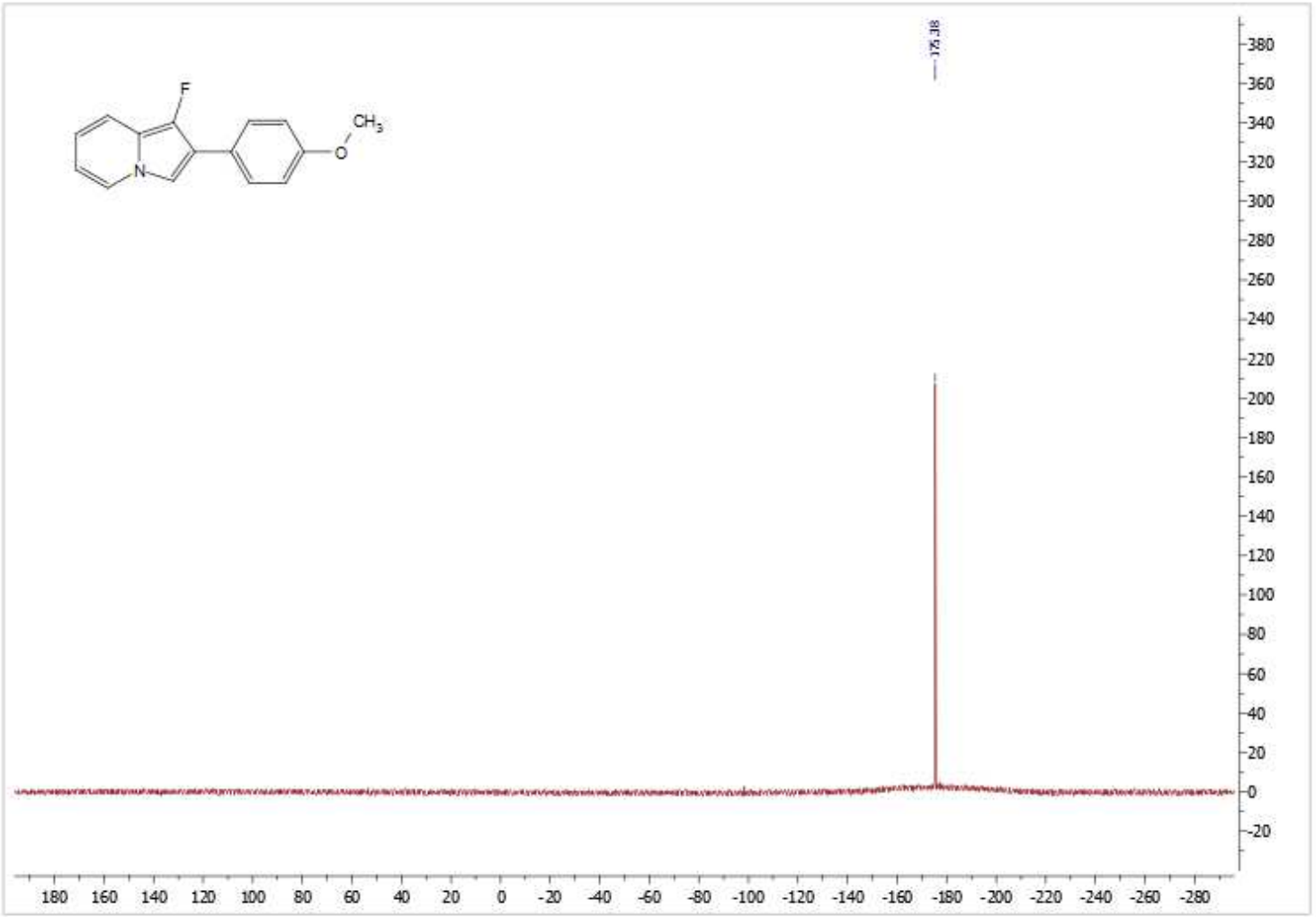
^{1}H NMR



^{13}C NMR

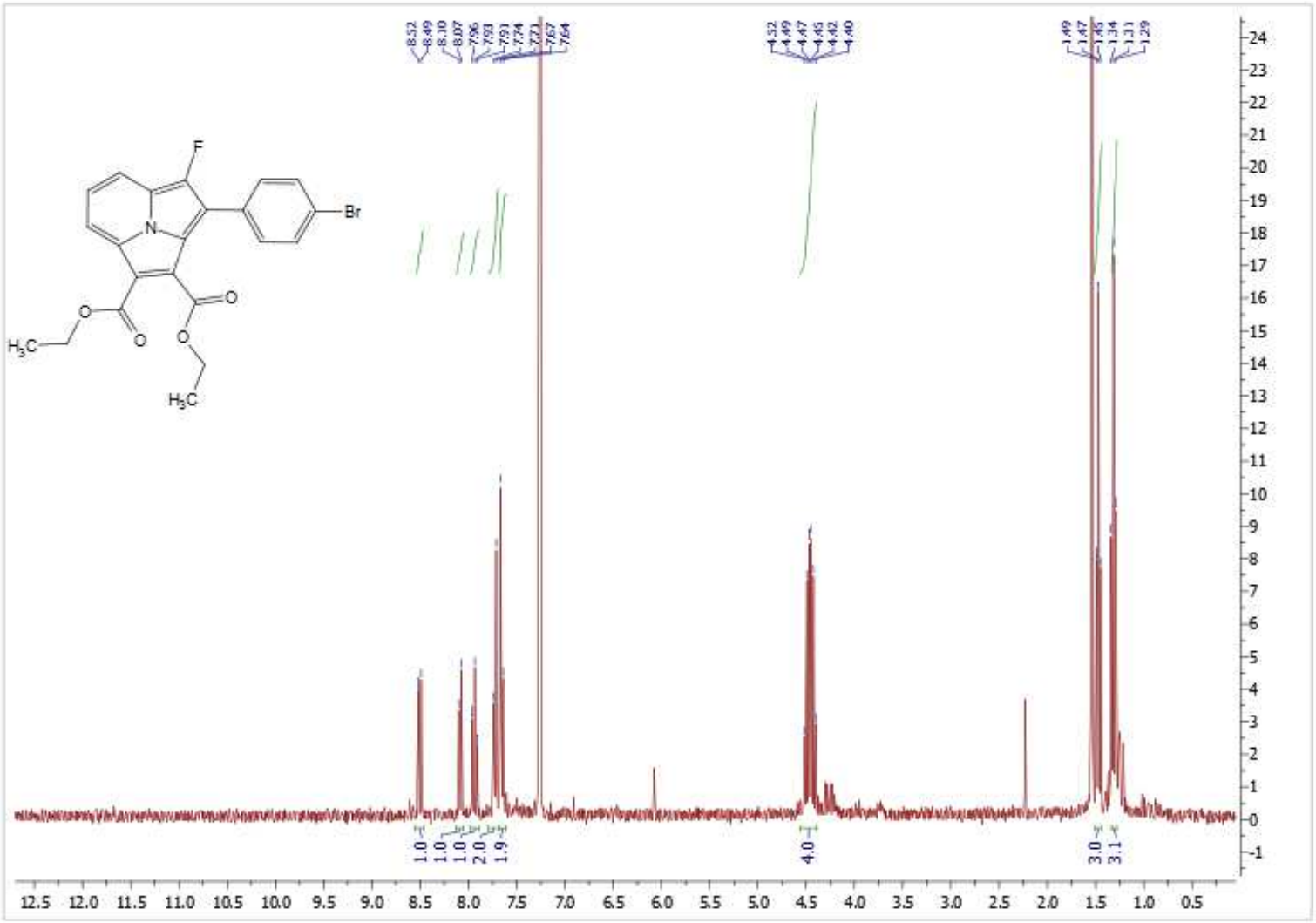

N
F
O
CH3
158.61
140.49
138.49
128.17
128.13
124.93
124.05
116.65
116.61
116.33
116.27
114.25
114.20
55.29
85000
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{19}F NMR

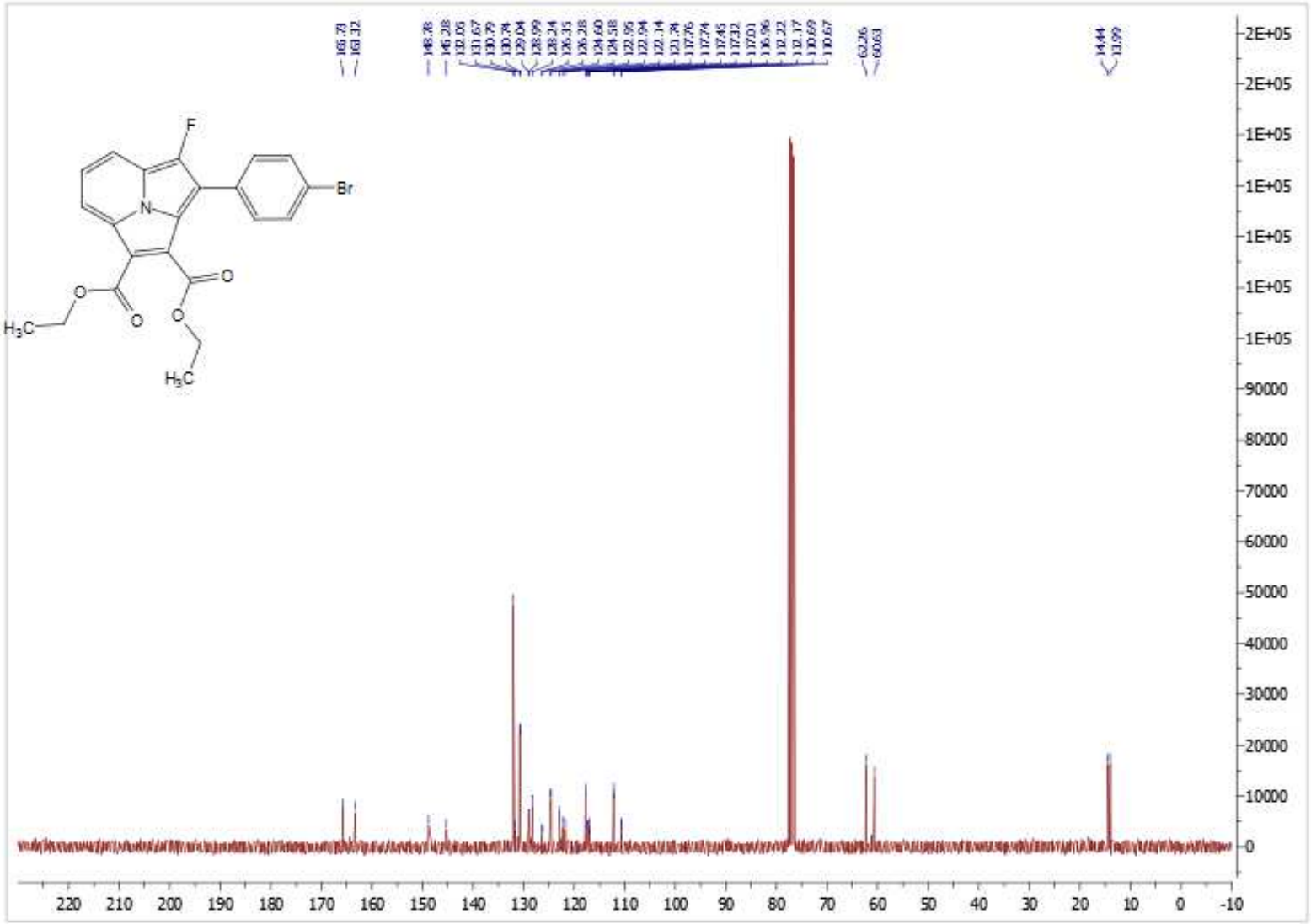

F
CH3
O
N
-175.18
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280

Diethyl 3-(4-chlorophenyl)-4-fluoro-pyrrolo[2,1,5-cd]indolizine-1,2-dicarboxylate 11n

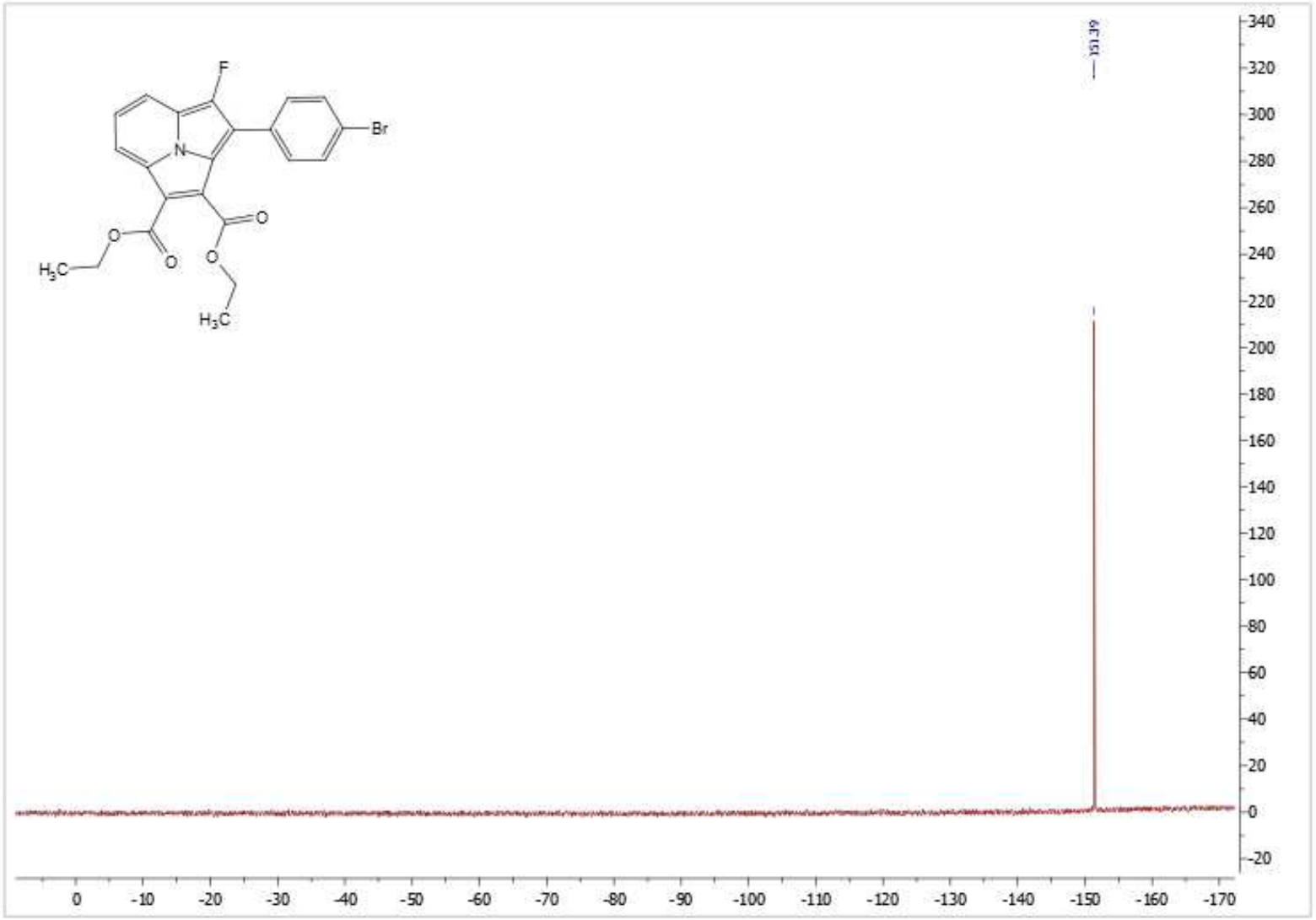
^{1}H NMR



^{13}C NMR

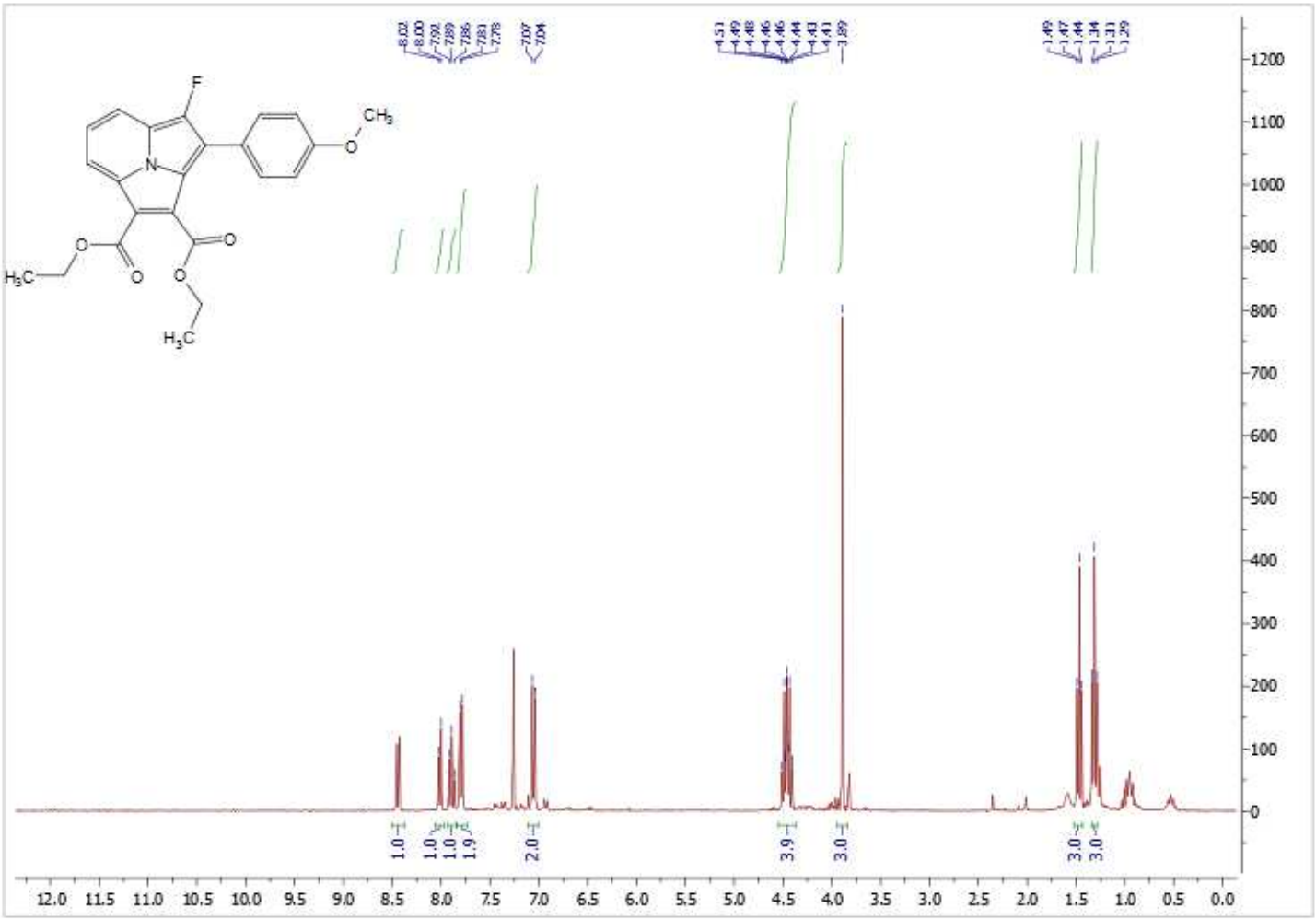

F
Br
N
O
O
O
O
H3C
H3C
166.73
163.32
146.78
146.28
132.05
131.67
130.79
130.74
129.04
128.99
128.24
126.15
126.28
124.60
124.58
122.95
122.94
122.14
121.78
117.76
117.74
117.45
117.32
117.01
116.96
112.22
112.17
110.69
110.67
62.26
60.63
14.44
13.99
2E+05
2E+05
1E+05
1E+05
1E+05
1E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

^{19}F NMR

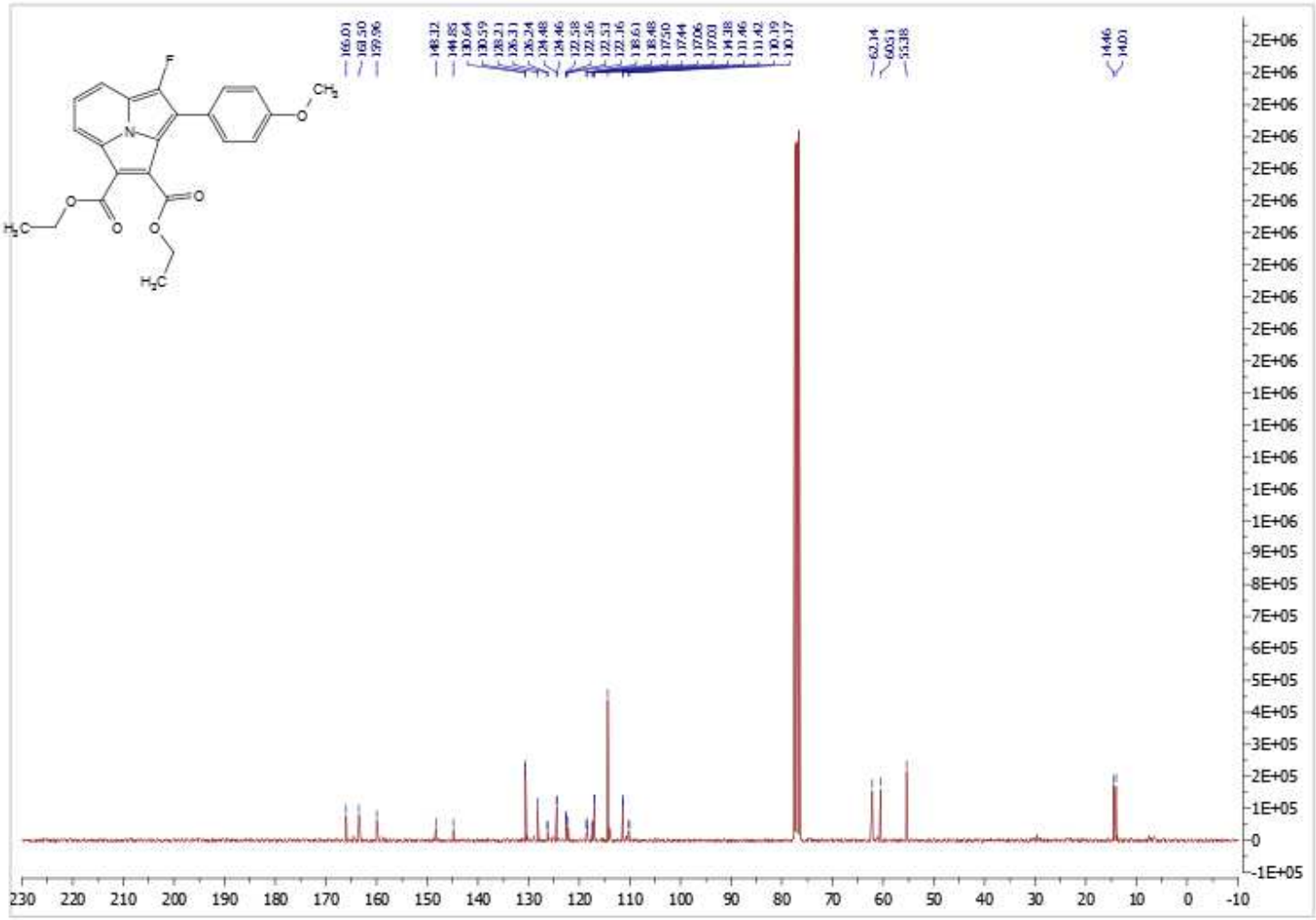

F
Br
N
O
O
O
O
H3C
H3C
-151.39
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170

Diethyl 3-(4-methoxyphenyl)-4-fluoro-pyrrolo[2,1,5-cd]indolizine-1,2-dicarboxylate 11s

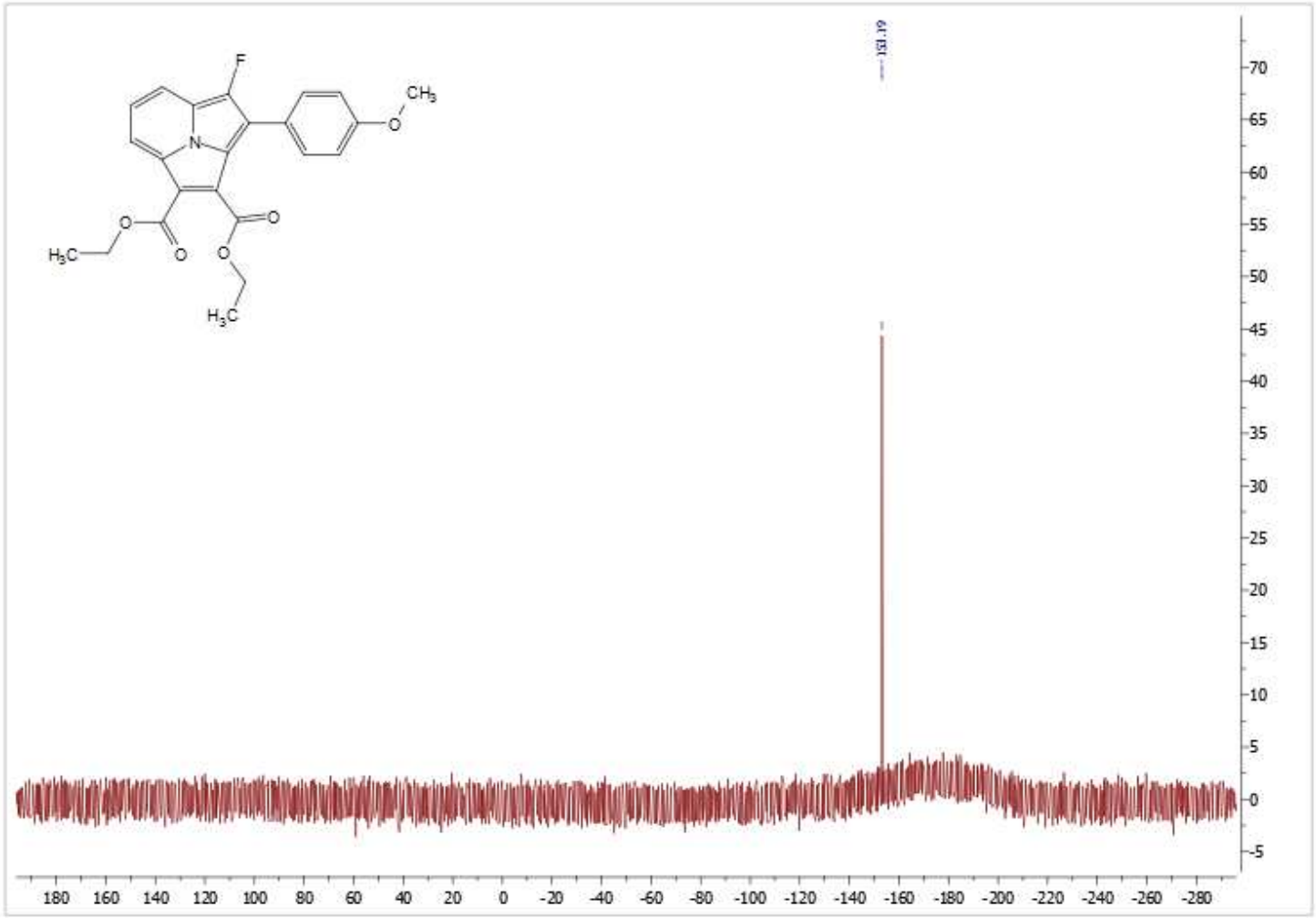
^{1}H NMR



^{13}C NMR


F
N
O
CH3
O
O
O
O
O
H3C
H2C
166.01
161.50
159.96
148.32
144.83
130.64
130.59
128.21
126.31
126.24
124.48
124.46
122.58
122.56
122.53
122.16
118.61
118.48
117.50
117.44
117.06
117.03
114.38
111.46
111.42
110.19
110.17
62.14
60.51
55.38
14.46
14.01
2E+06
1E+06
9E+05
8E+05
7E+05
6E+05
5E+05
4E+05
3E+05
2E+05
1E+05
0
-1E+05
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

^{19}F NMR


F
CH3
O
N
O
O
O
O
H3C
O
H3C
-151.19
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280