Supporting Information for

Palladium(II) Oxide Impregnated on Magnetite as Catalyst for the Synthesis of 4-Arylcoumarins via a Heck-arylation/cyclization process

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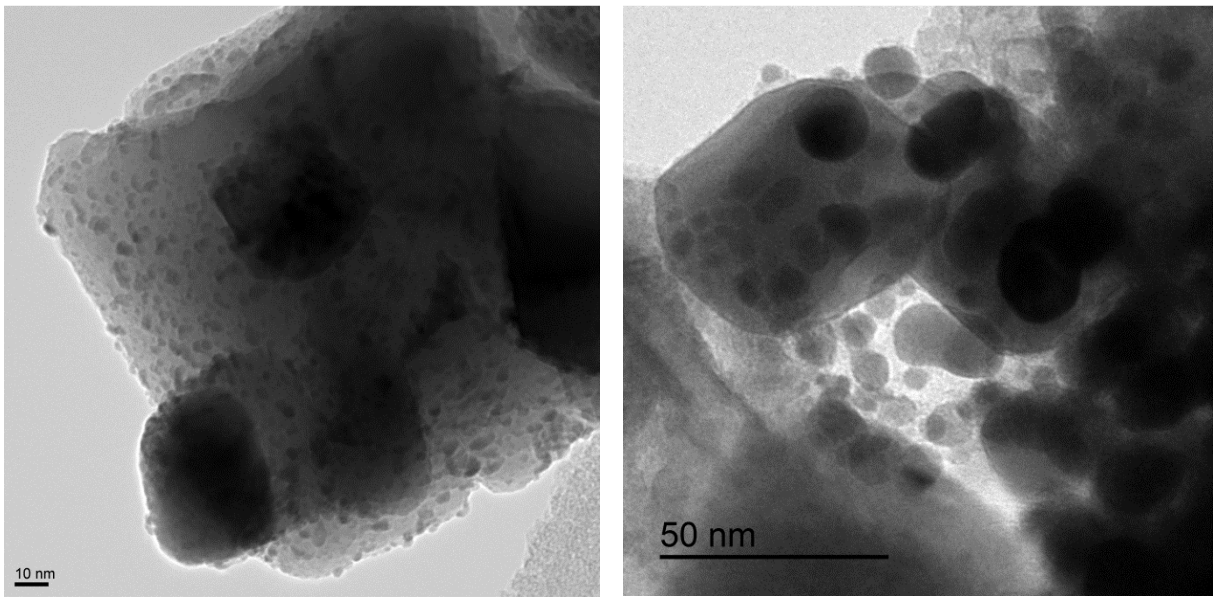
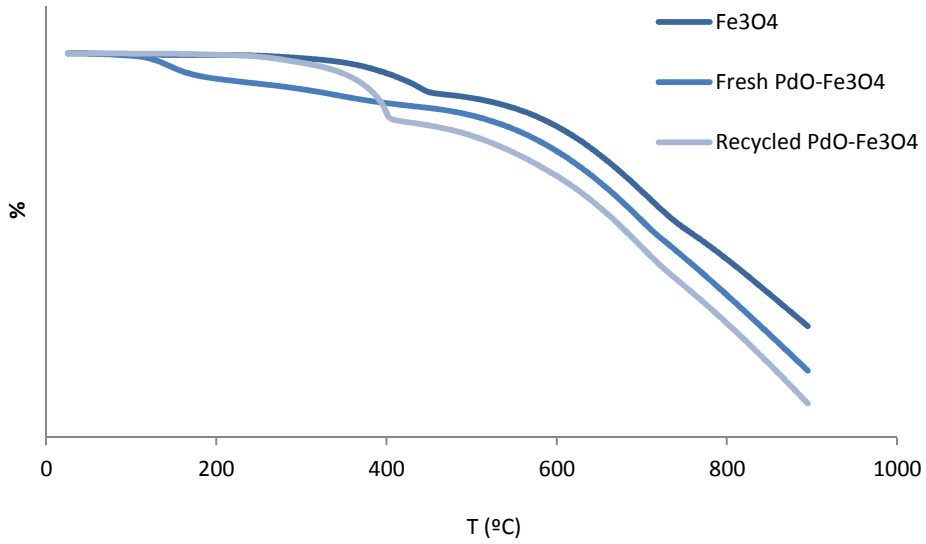
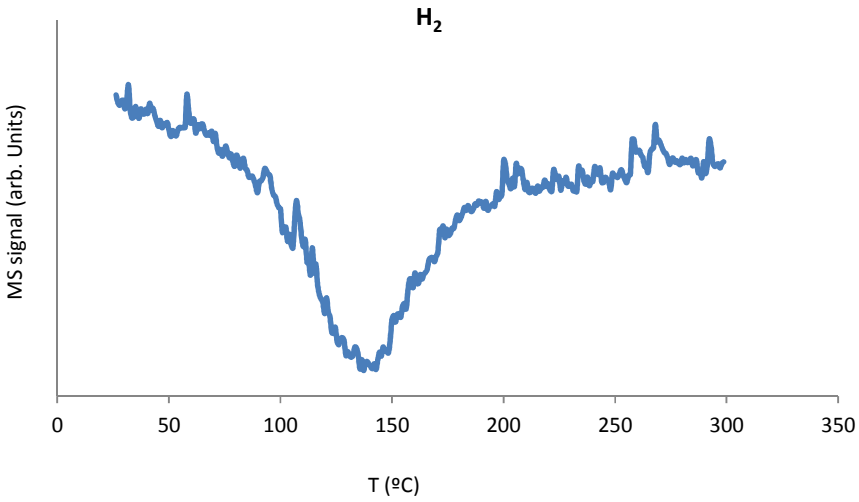
I. TEM Images

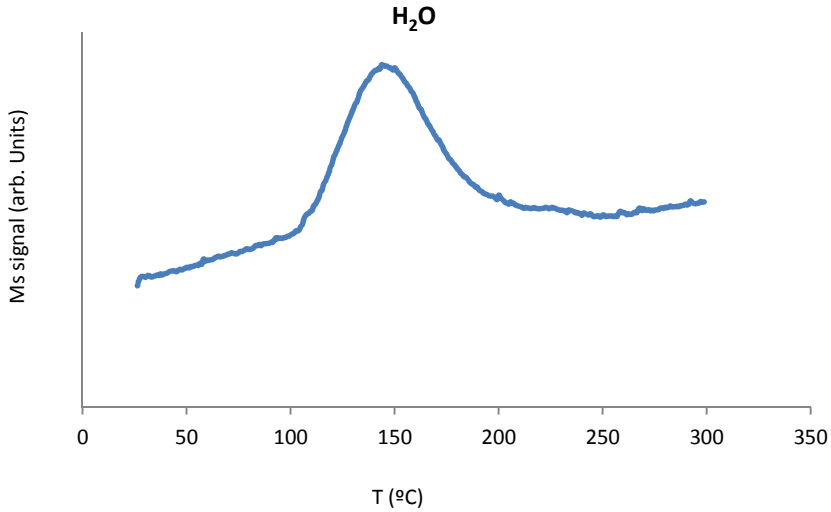


II. RTP analysis

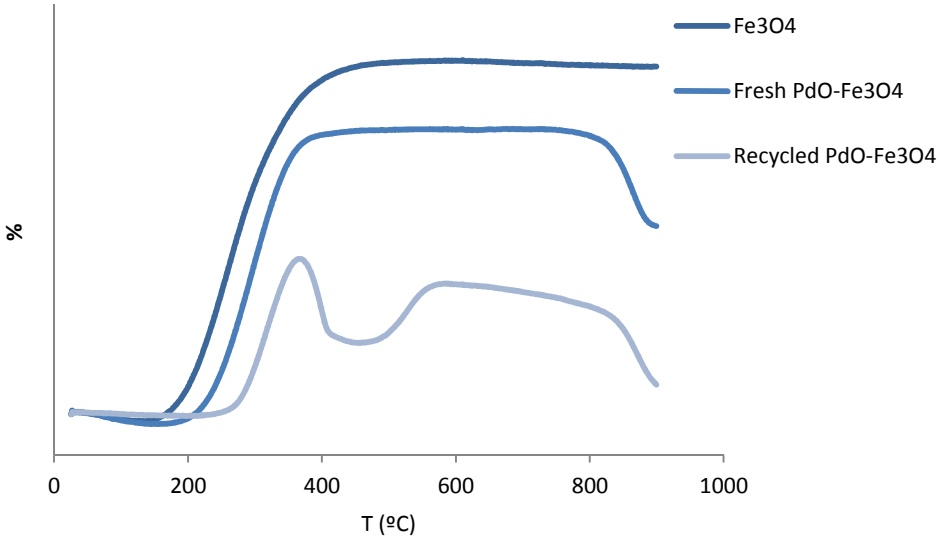


III. MS analysis on Fresh Catalyst under reductive conditions

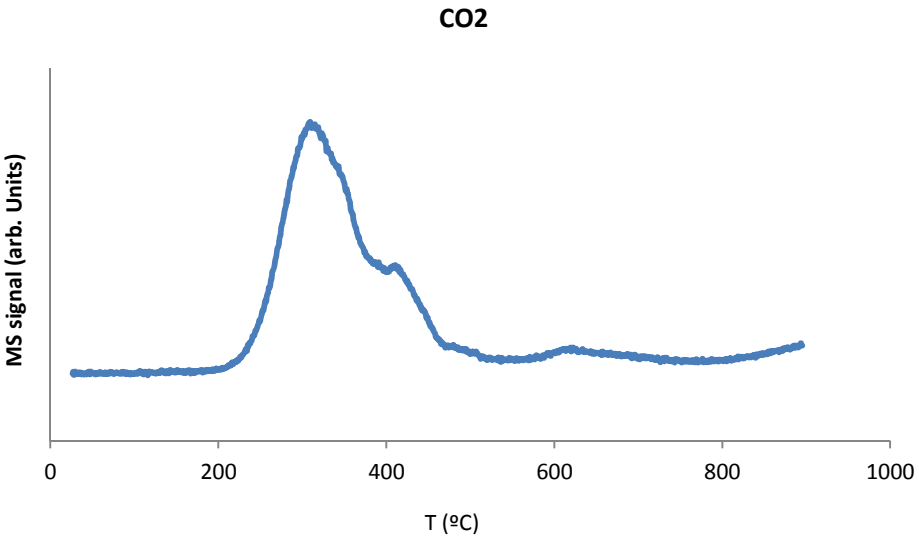


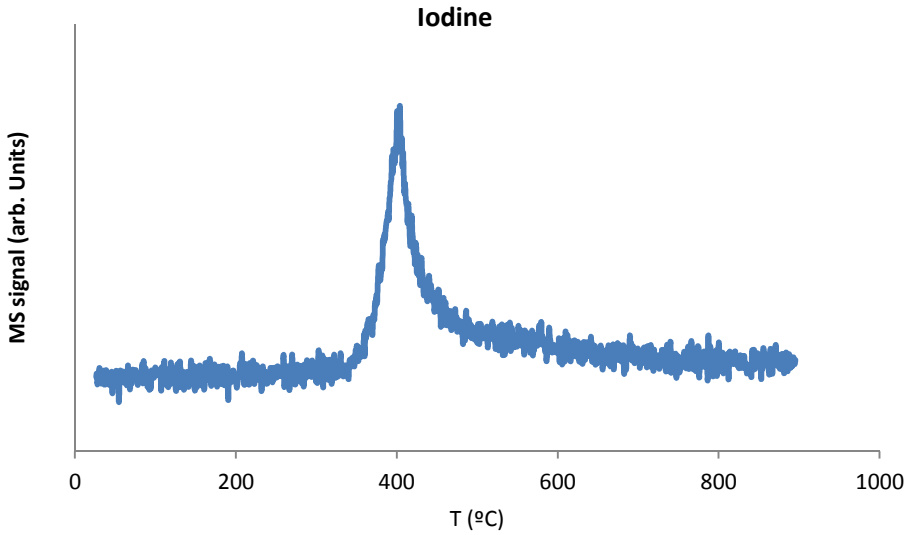


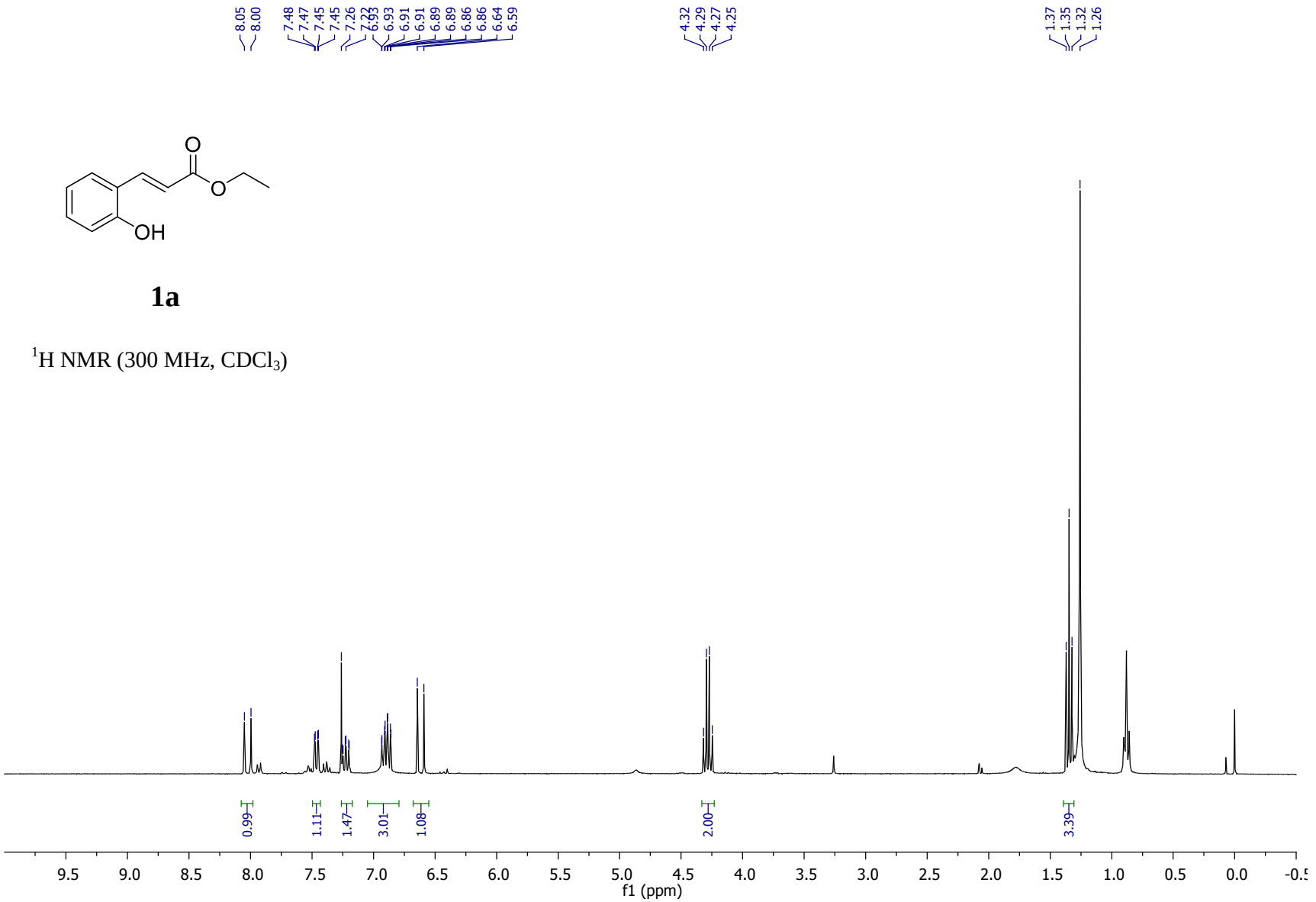
IV. OTP analysis



V. MS analysis on Recycled Catalyst under oxidative conditions

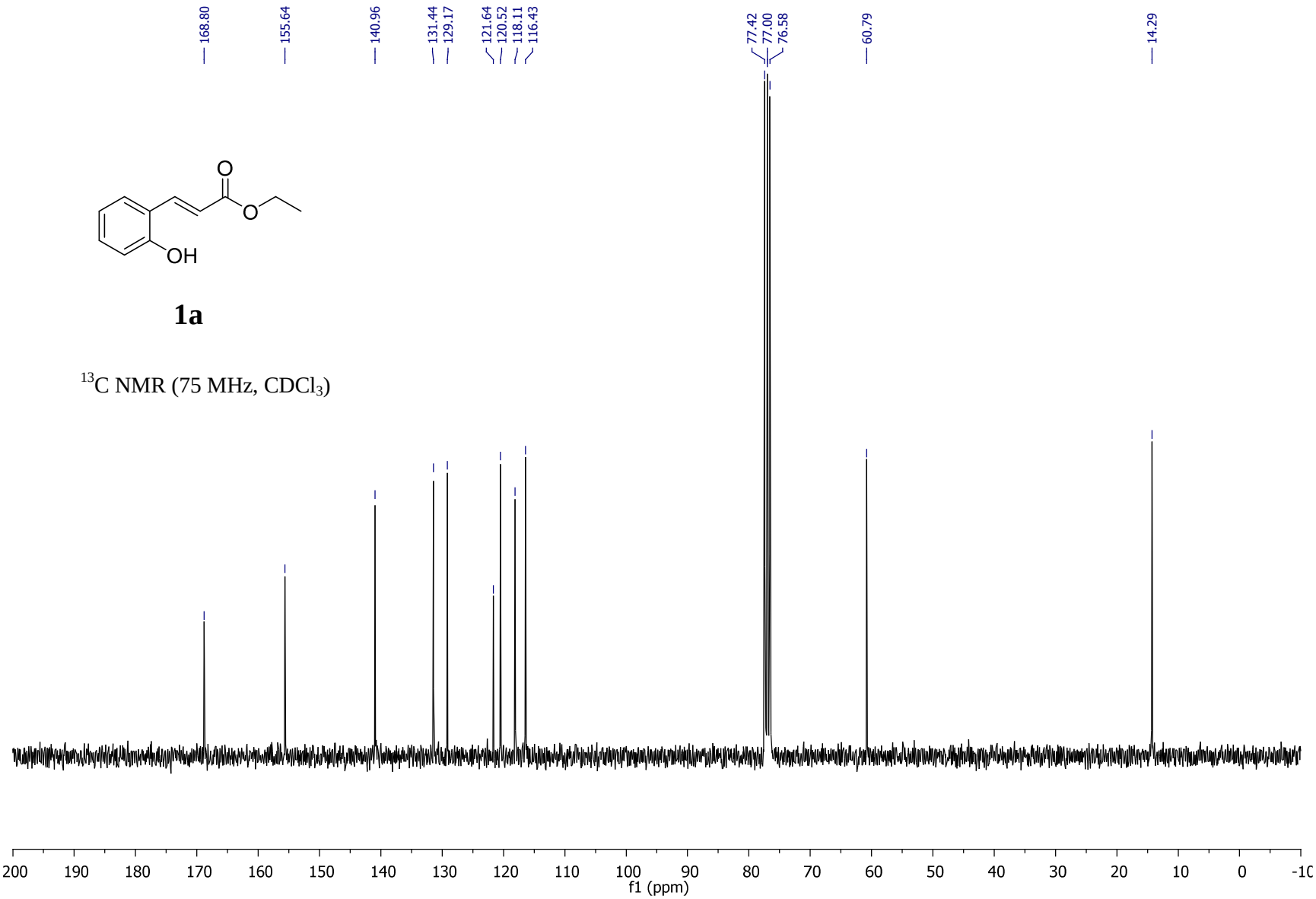



Iodine
MS signal (arb. Units)
0
200
400
600
800
1000
T (ºC)



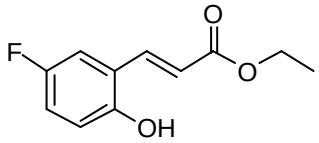
1a

^{1}H NMR (300 MHz, $CDCl_3$)



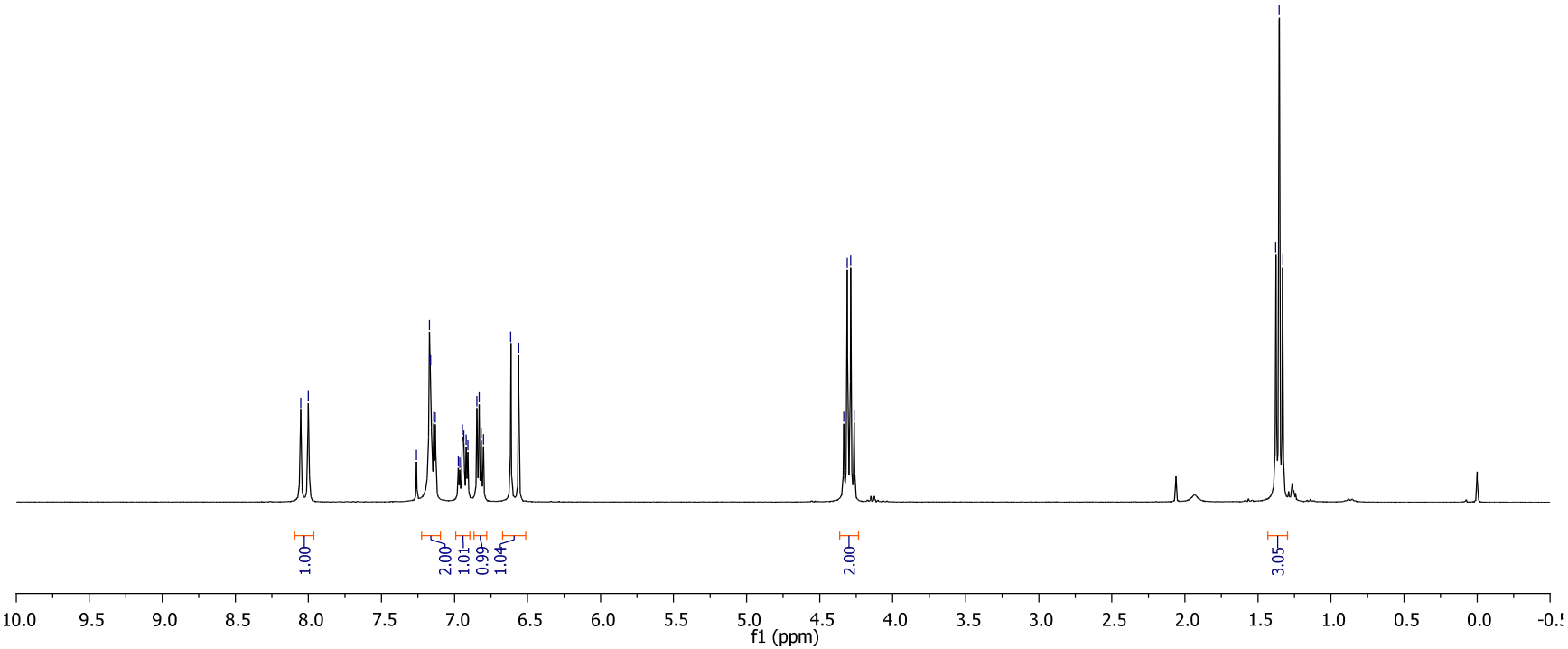
1a

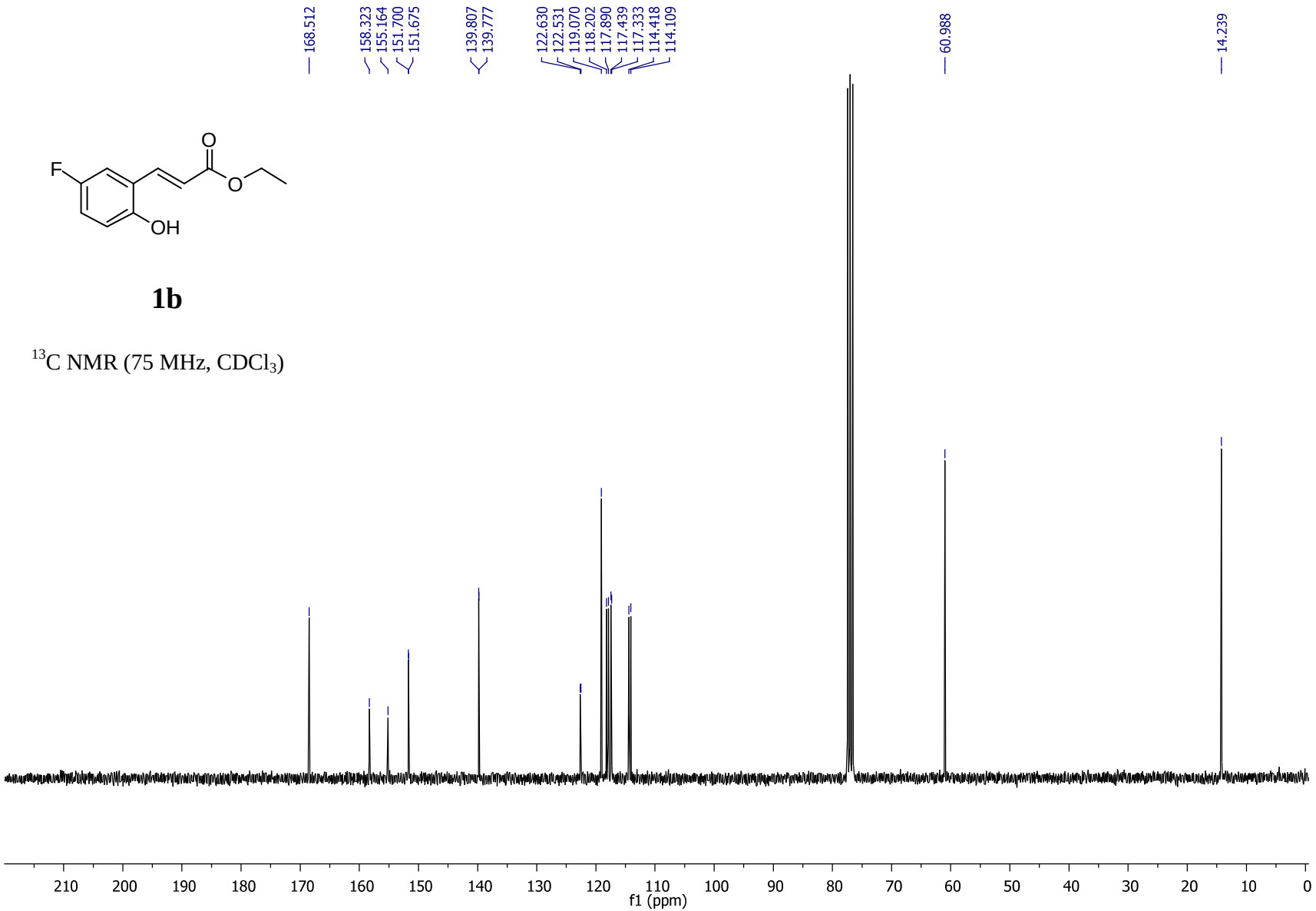
^{13}C NMR (75 MHz, $CDCl_3$)



1b

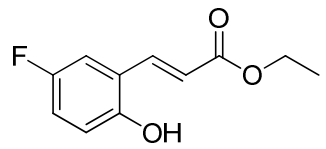
^{1}H NMR (300 MHz, $CDCl_3$)





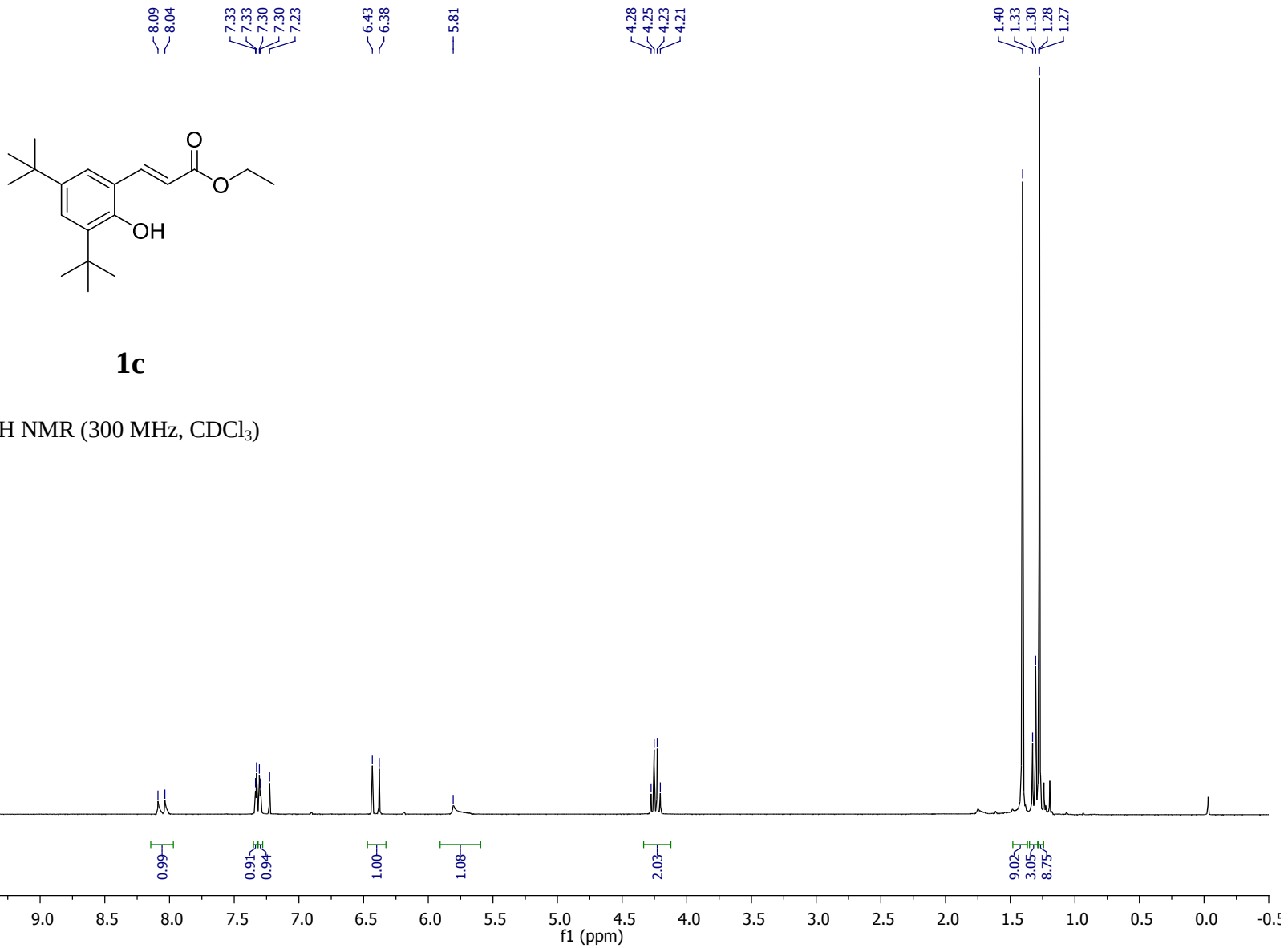
1b

^{13}C NMR (75 MHz, $CDCl_3$)



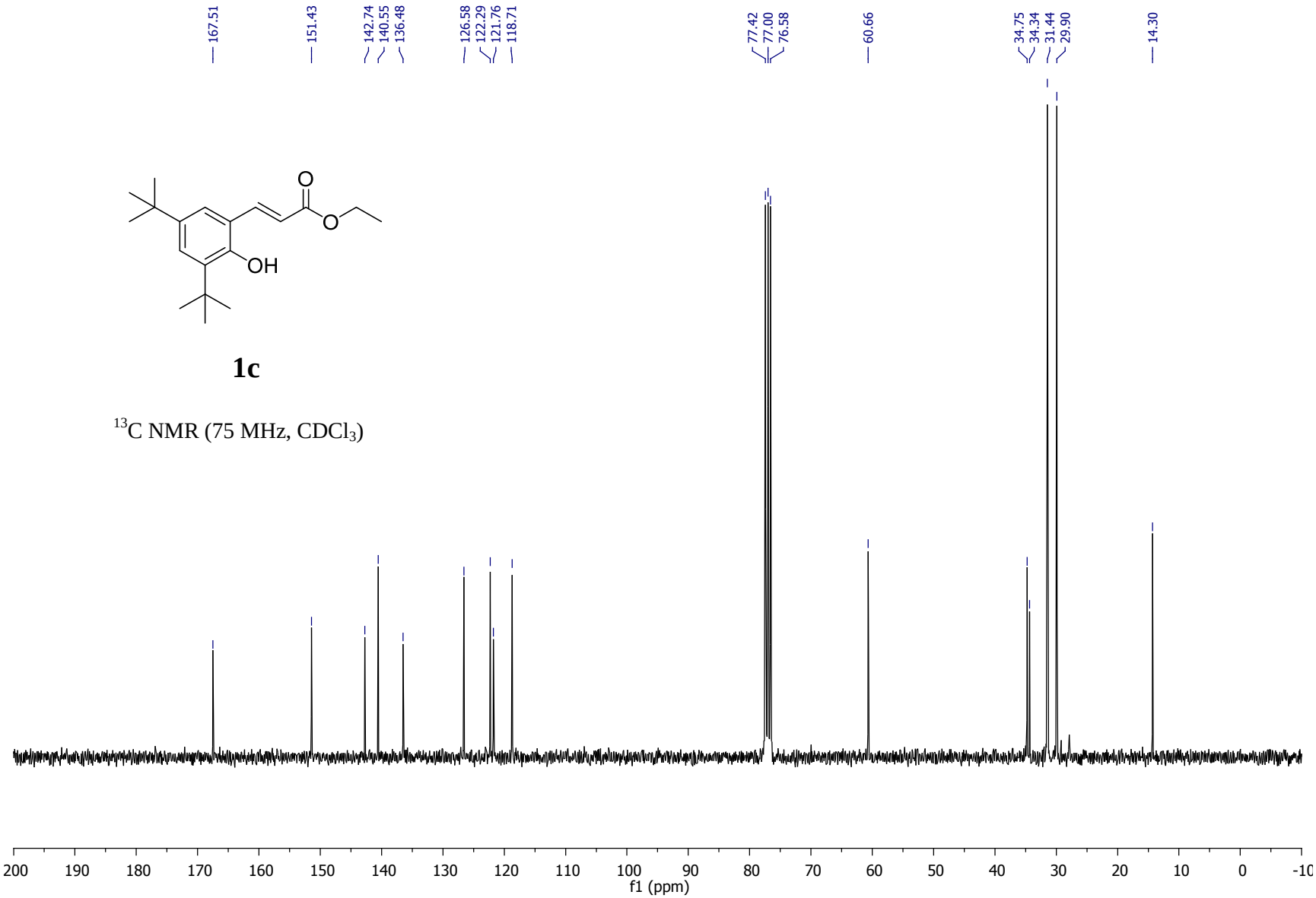
1b

^{19}F NMR (282 MHz, $CDCl_3$)



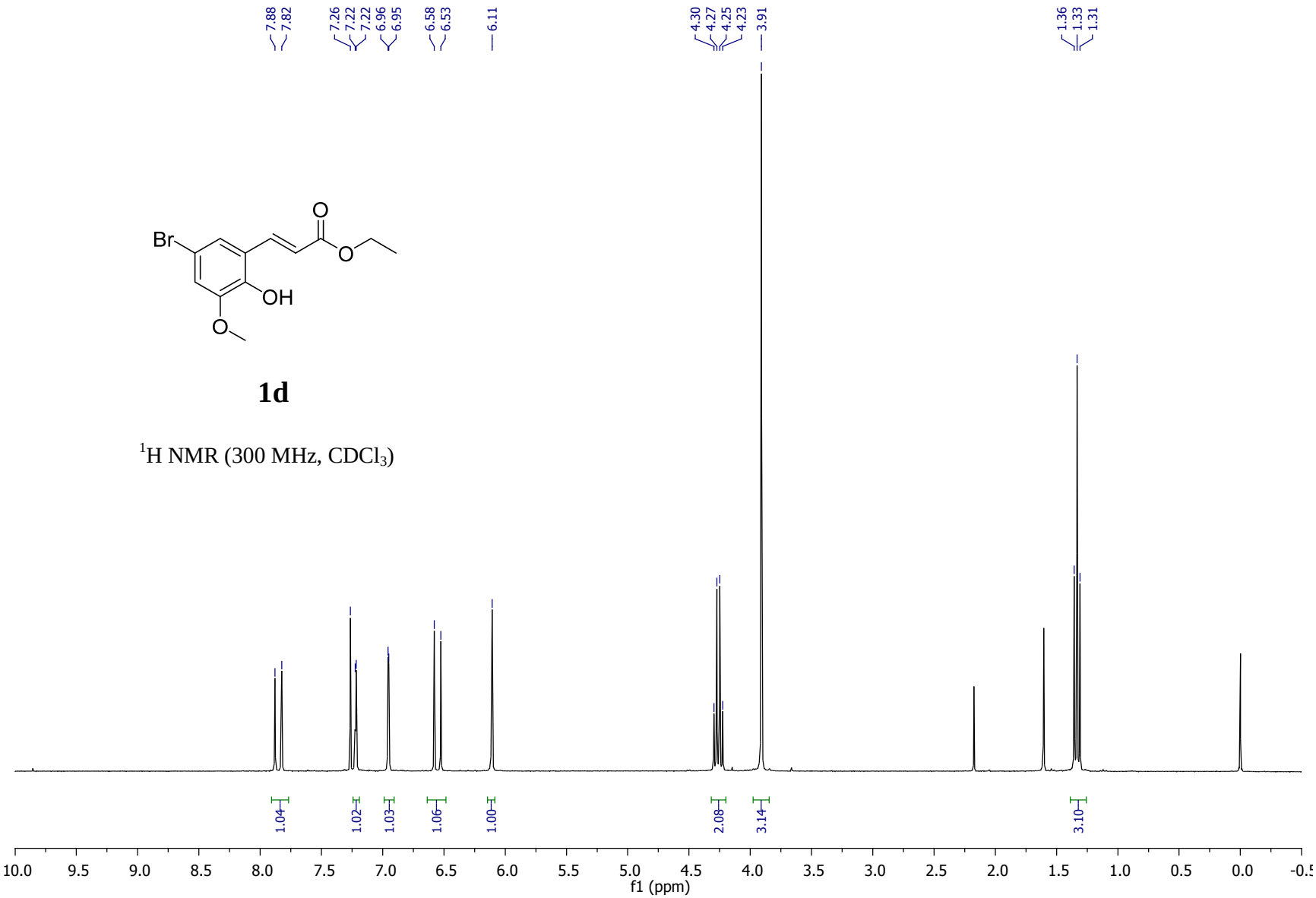
1c

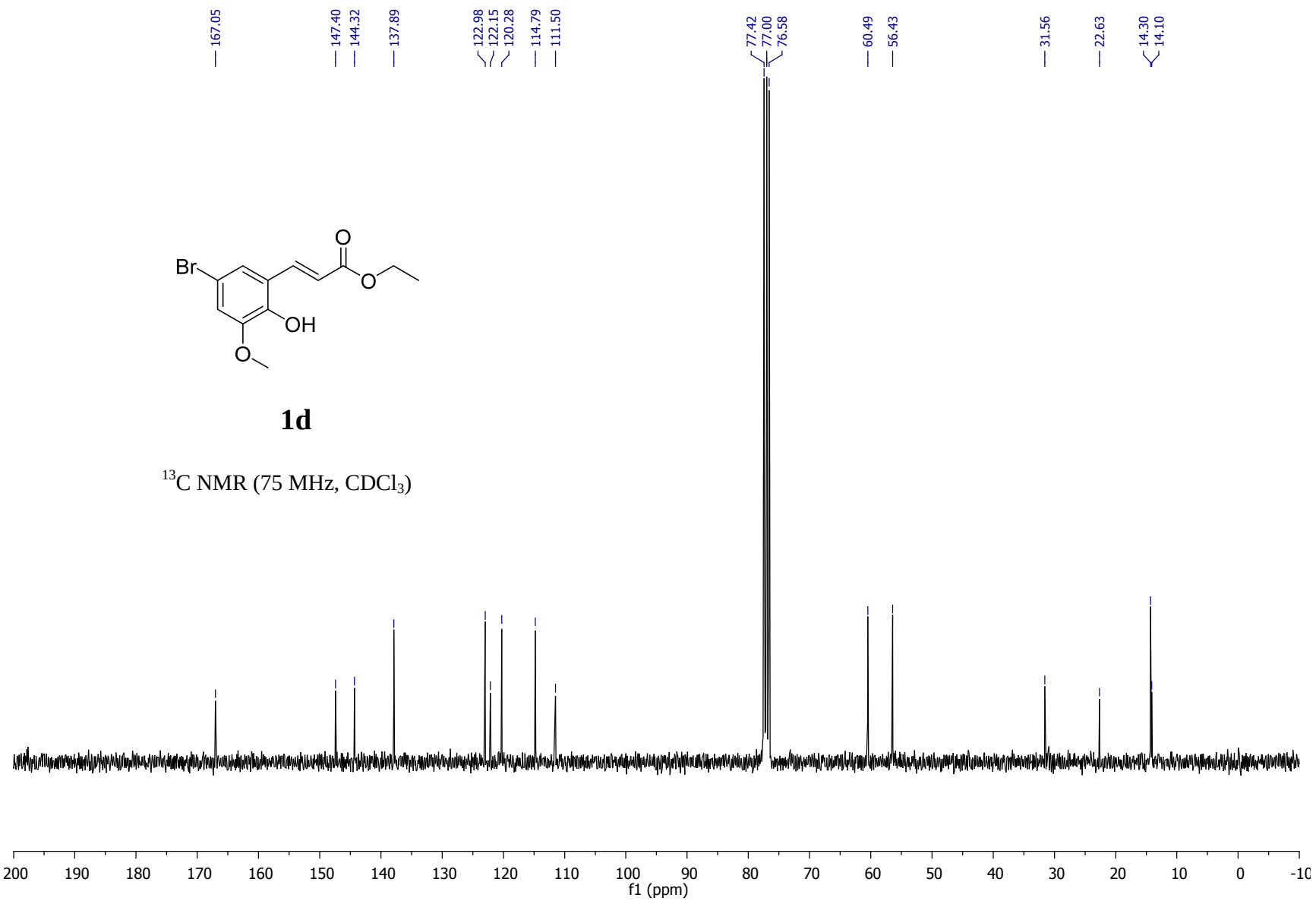
^{1}H NMR (300 MHz, $CDCl_3$)



1c

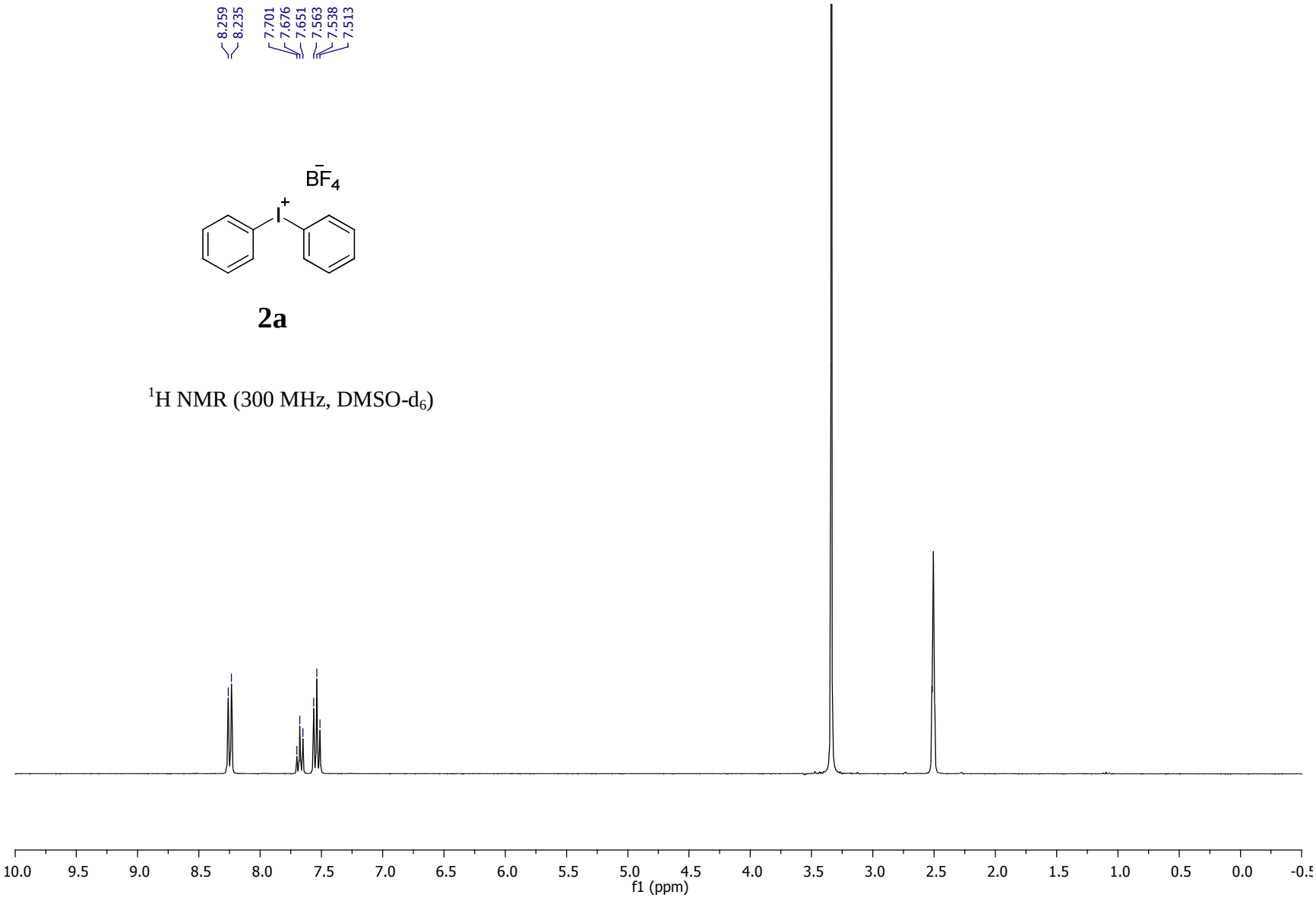
^{13}C NMR (75 MHz, $CDCl_3$)


7.88
7.82
7.26
7.22
7.22
6.96
6.95
6.58
6.53
6.11
4.30
4.27
4.25
4.23
3.91
1.36
1.33
1.31
Br
O
O
OH
O
1d
1H NMR (300 MHz, CDCl3)
1.04
1.02
1.03
1.06
1.00
2.08
3.14
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



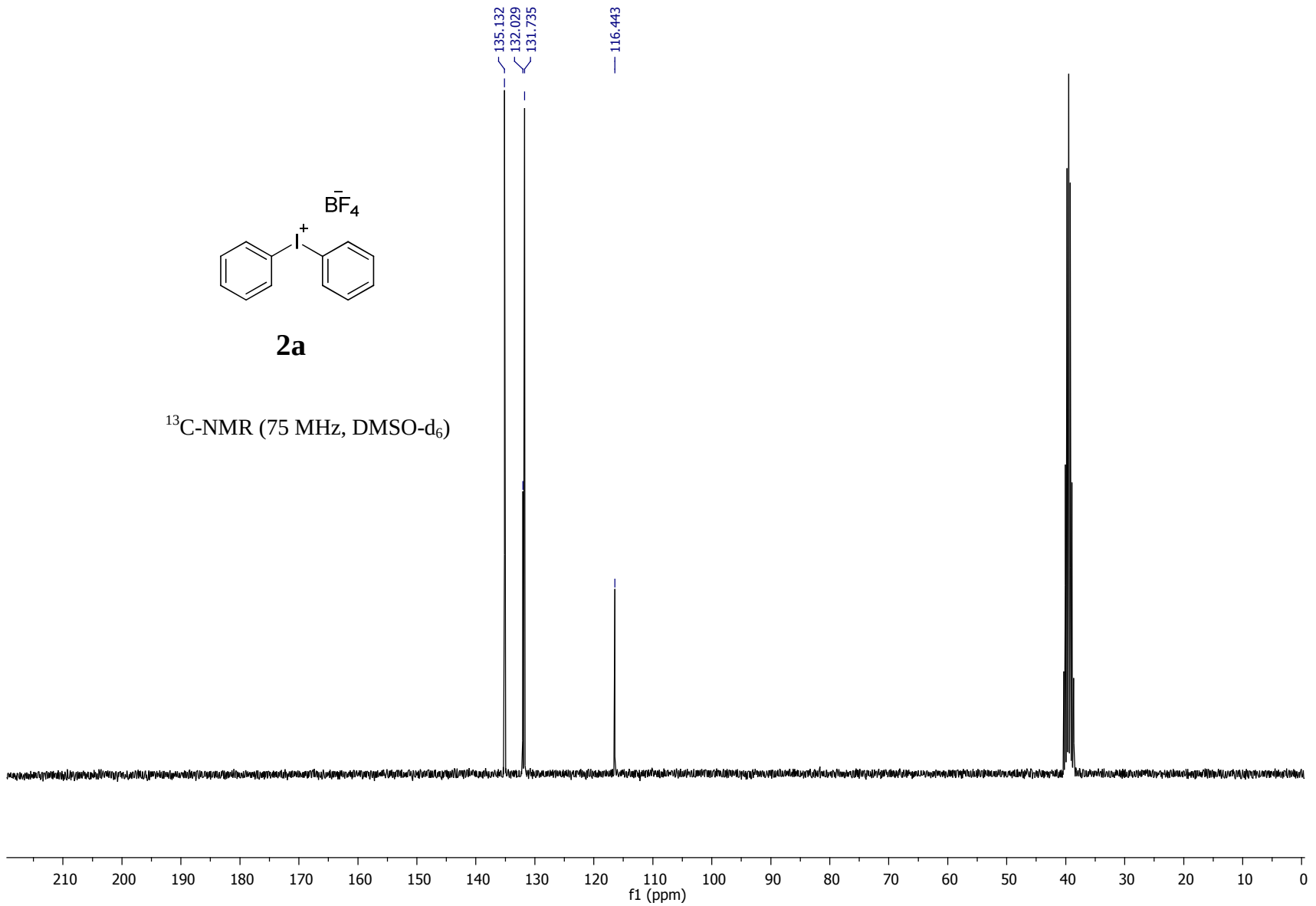
1d

^{13}C NMR (75 MHz, $CDCl_3$)



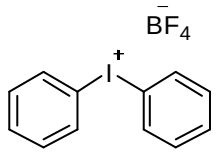
2a

^{1}H NMR (300 MHz, DMSO-d_6)



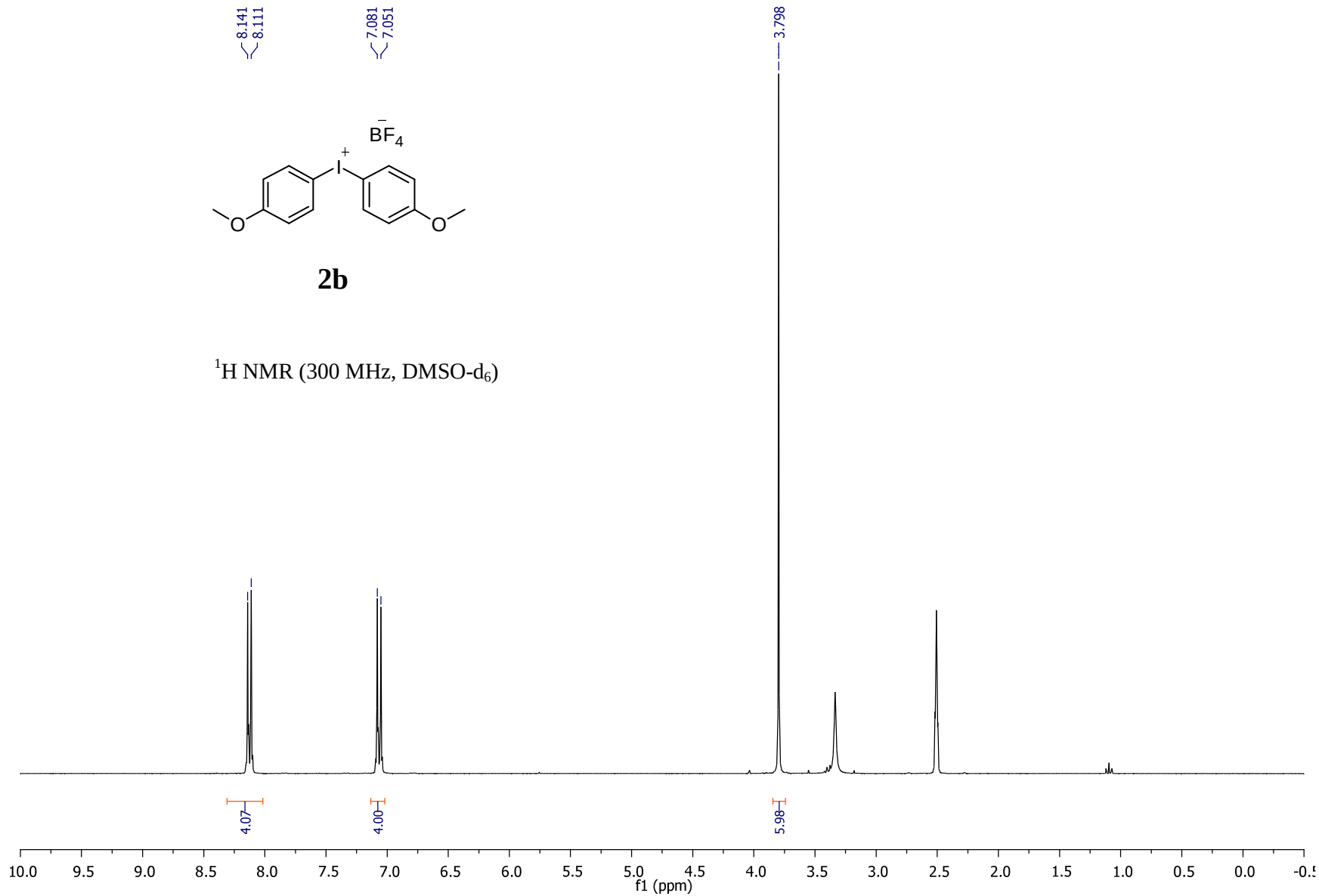
2a

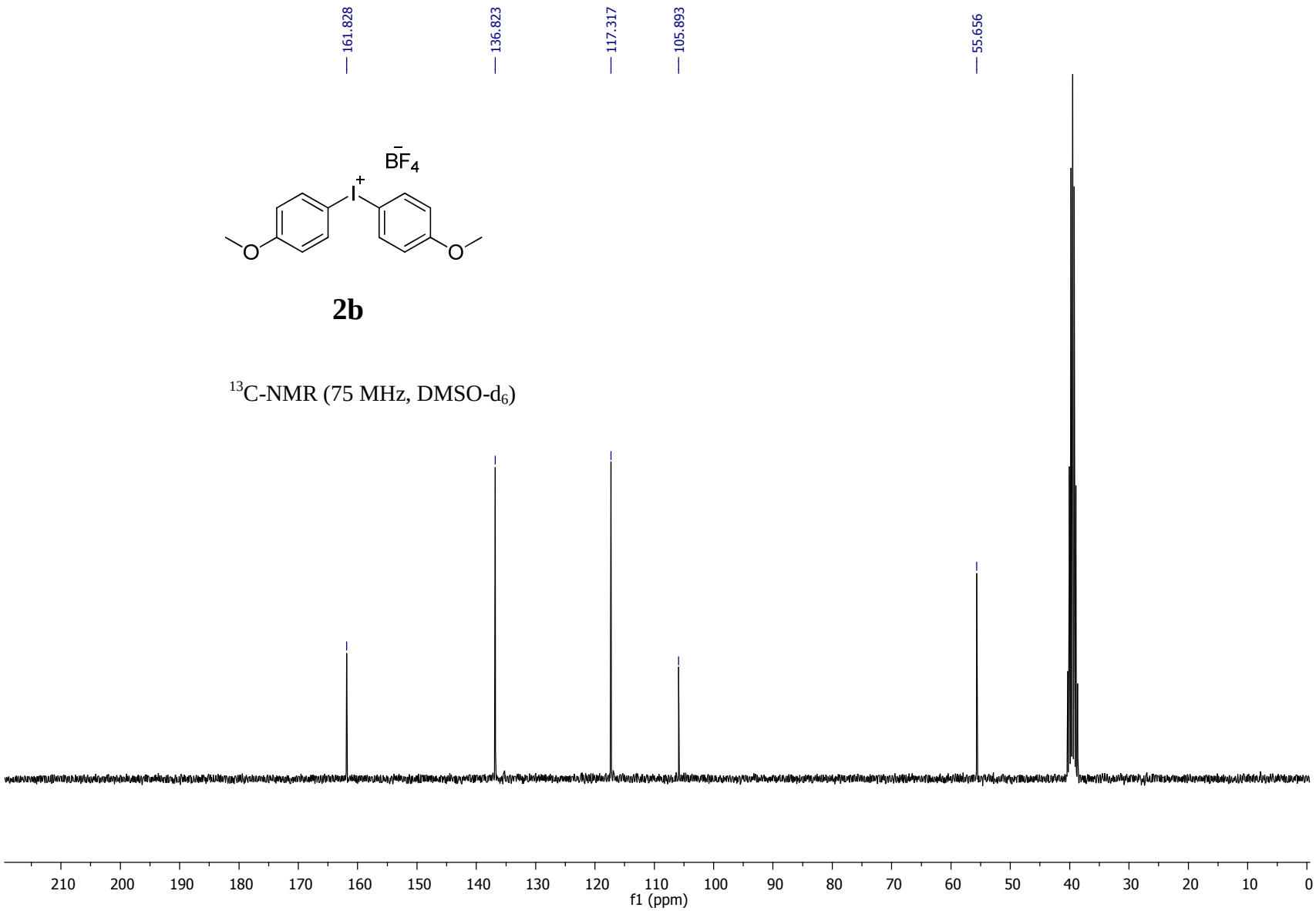
^{13}C-NMR (75 MHz, DMSO-d_6)



2a

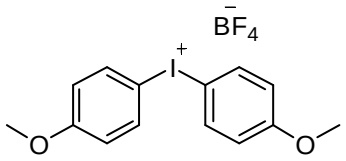
^{19}F NMR (282 MHz, DMSO-d_6)


8.141
8.111
7.081
7.051
3.798
BF4
2b
1H NMR (300 MHz, DMSO-d6)
4.07
4.00
5.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



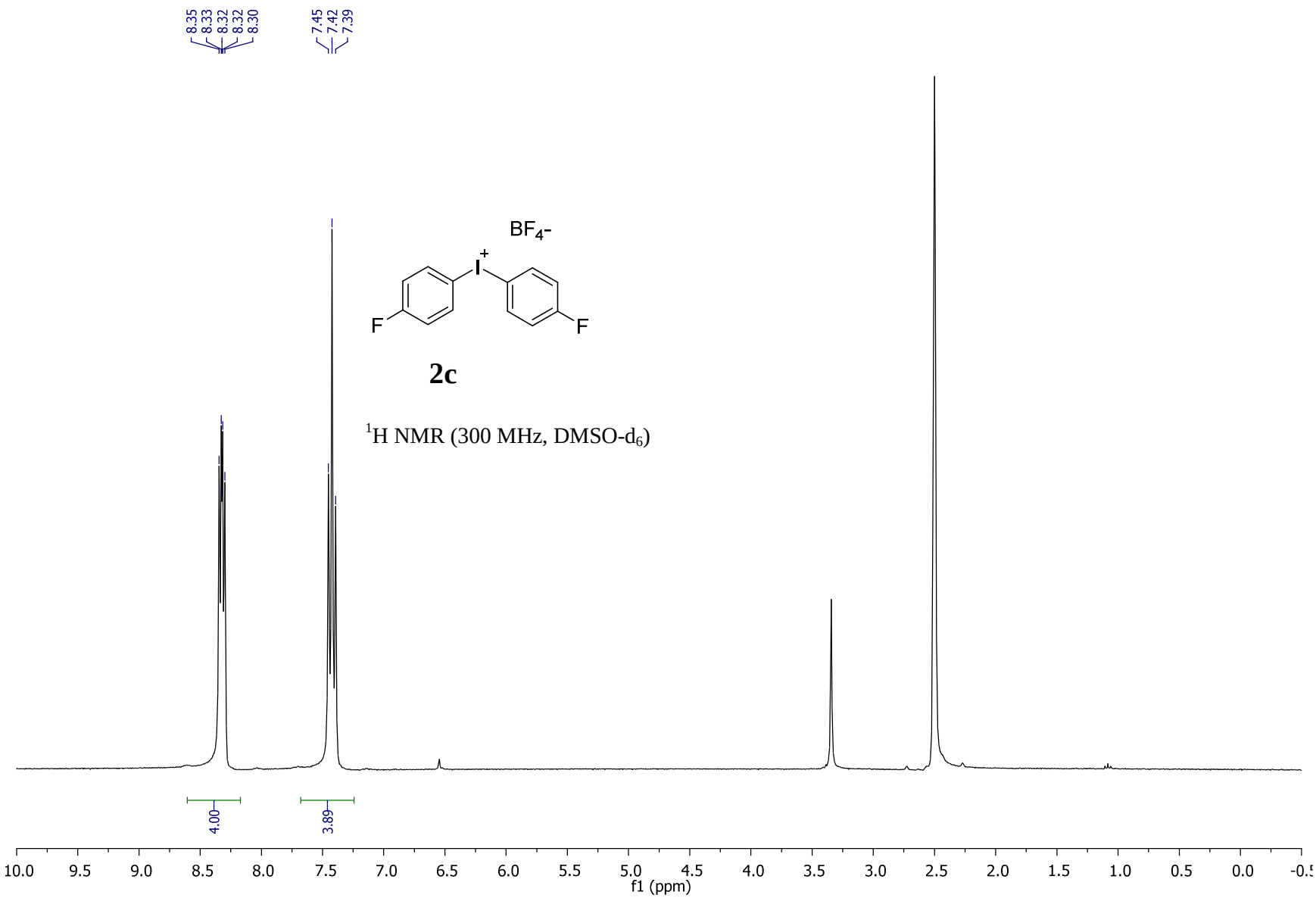
2b

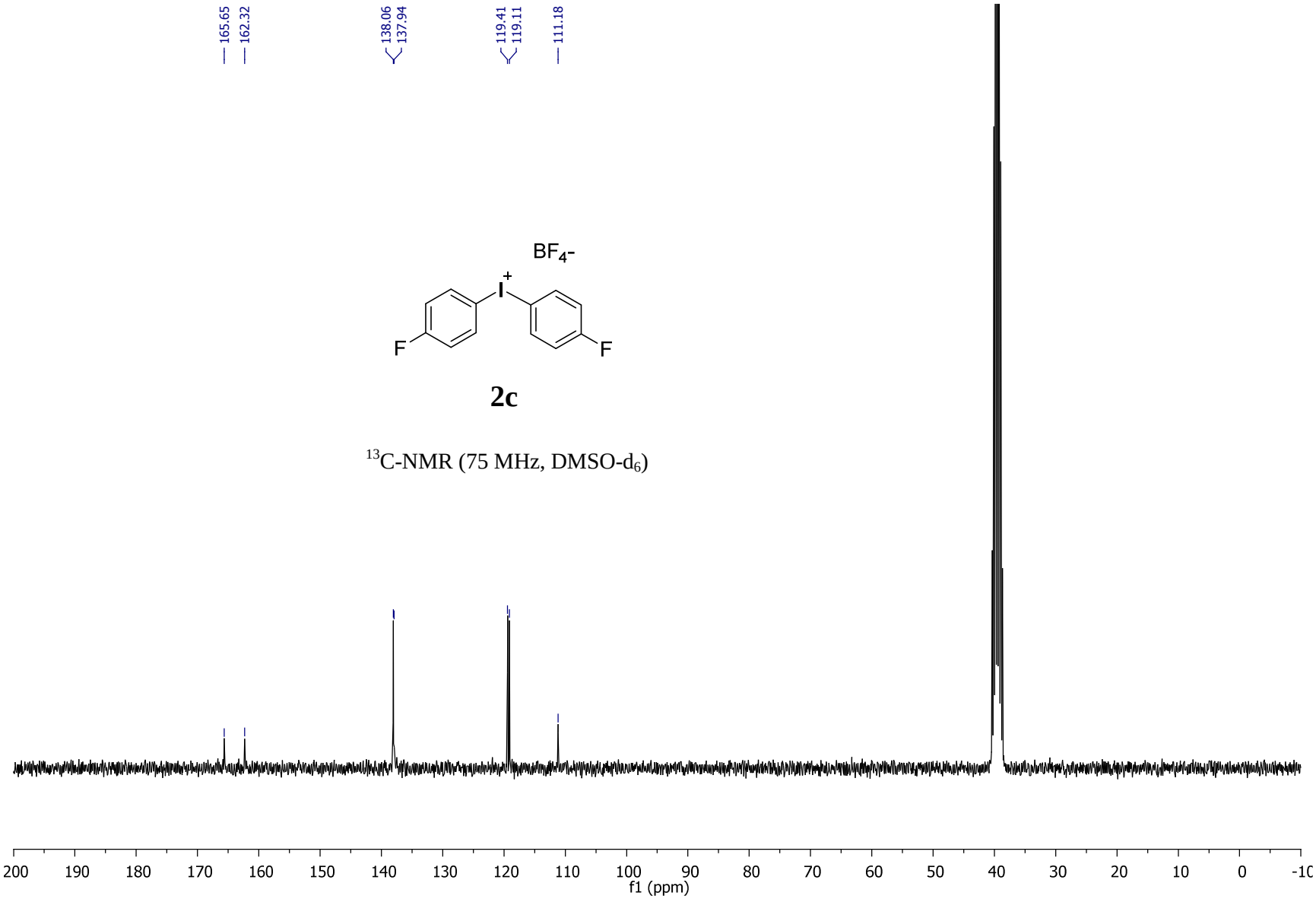
^{13}C-NMR (75 MHz, DMSO-d_6)



2b

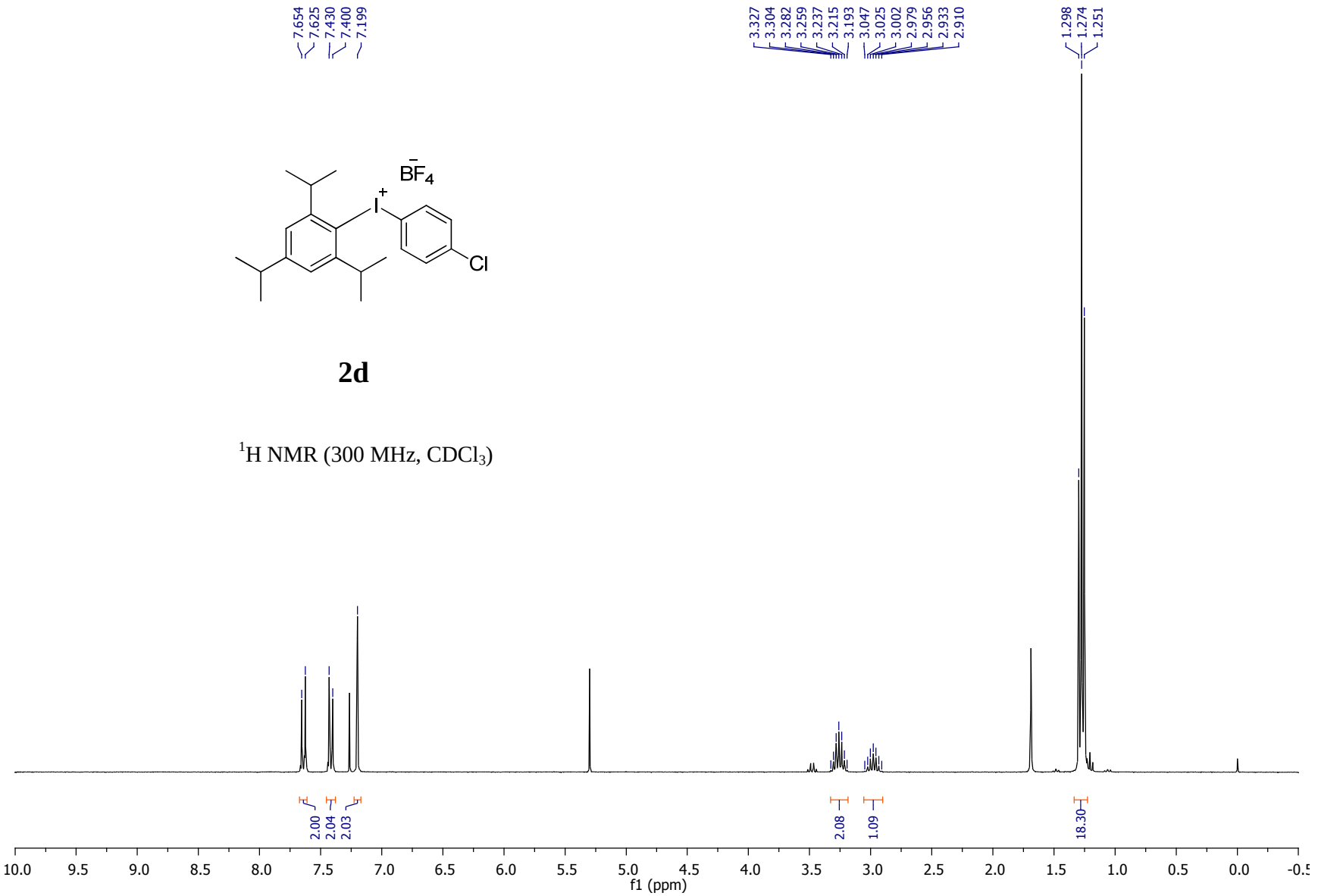
^{19}F NMR (282 MHz, DMSO-d_6)


8.35
8.33
8.32
8.32
8.30
7.45
7.42
7.39
BF4-
F
F
2c
1H NMR (300 MHz, DMSO-d6)
4.00
3.89
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



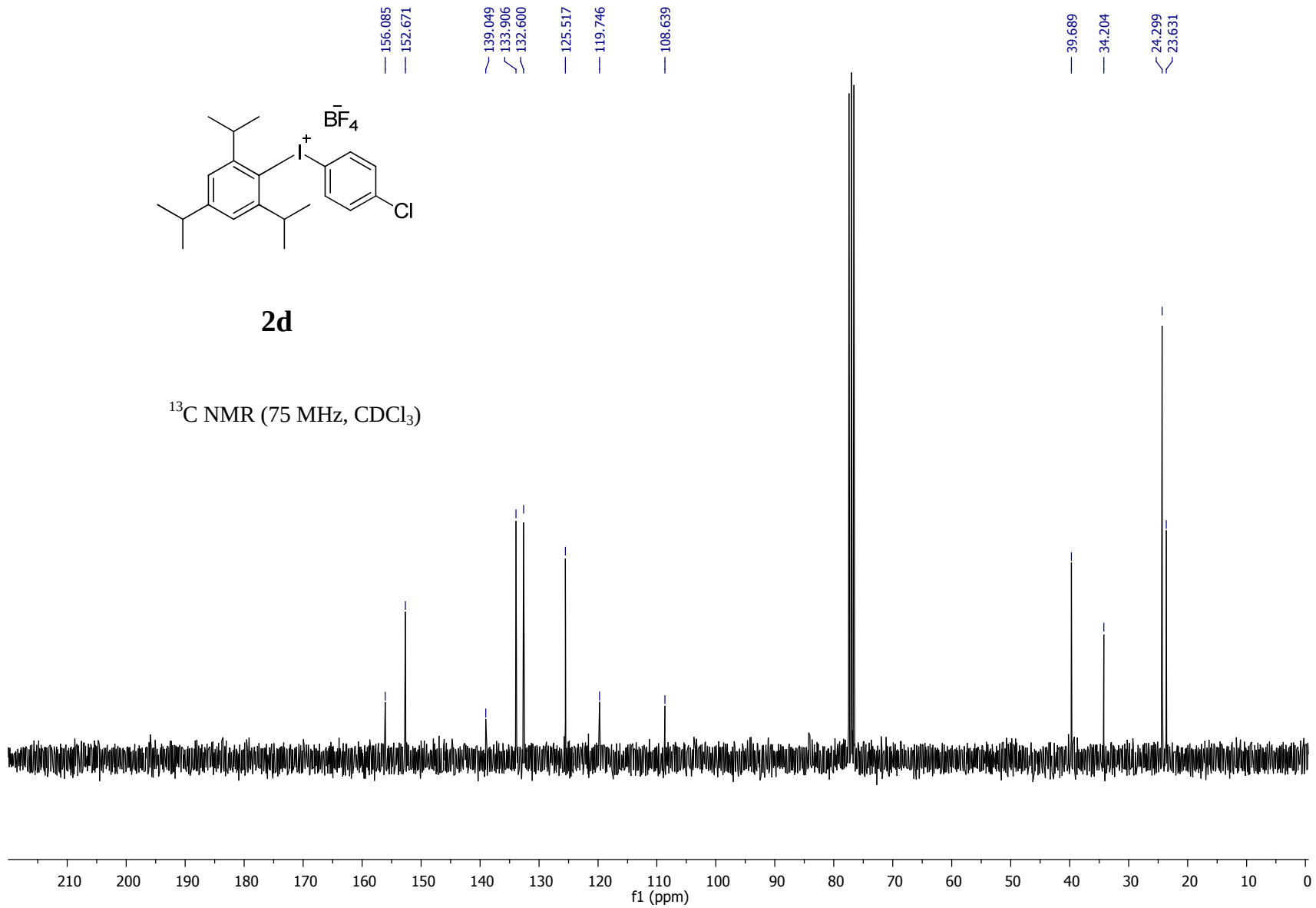
2c

^{13}C-NMR (75 MHz, DMSO-d_6)



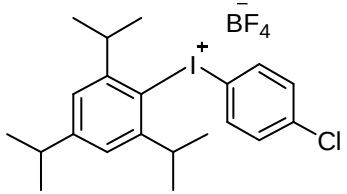
2d

^{1}H NMR (300 MHz, $CDCl_3$)



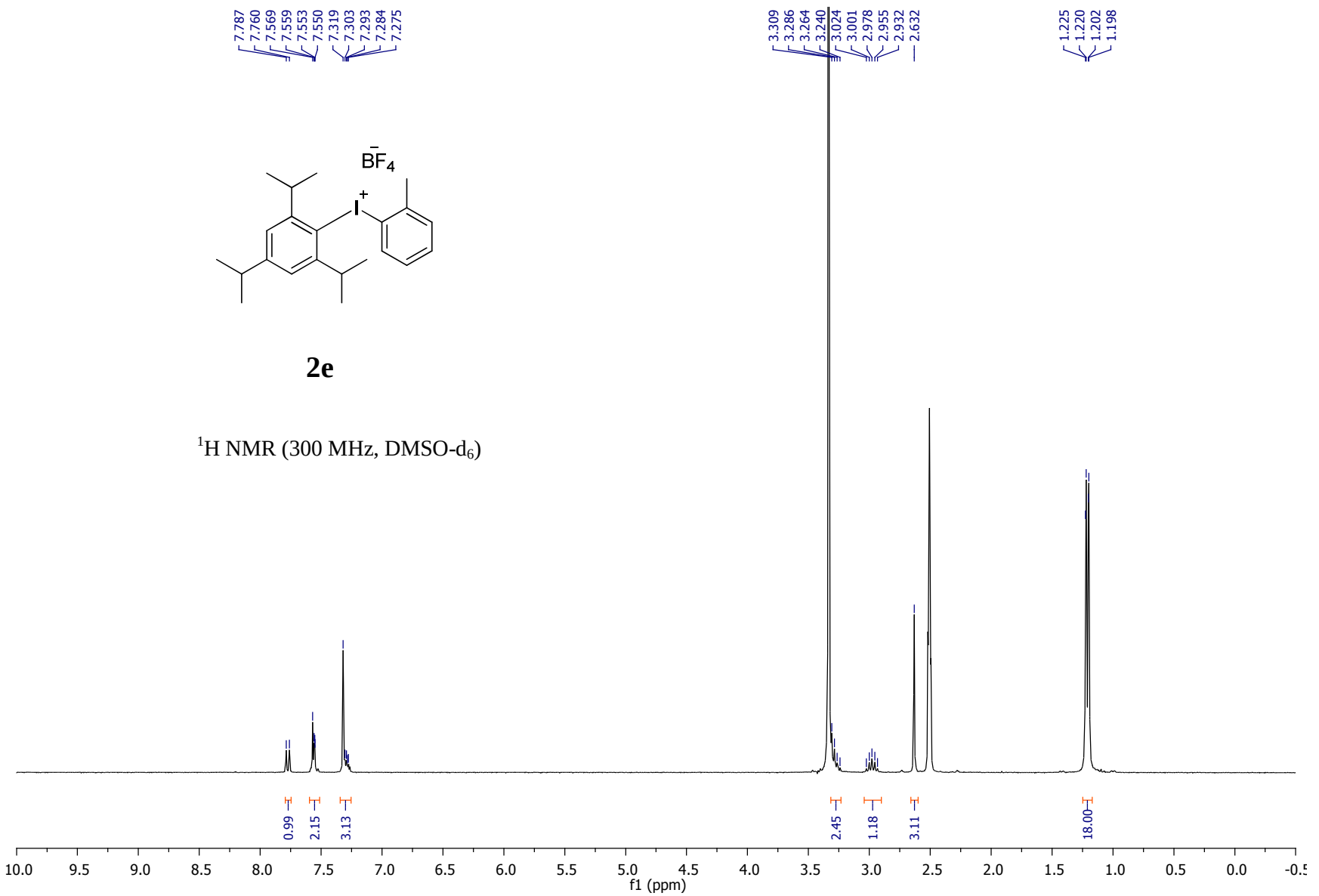
2d

^{13}C NMR (75 MHz, $CDCl_3$)



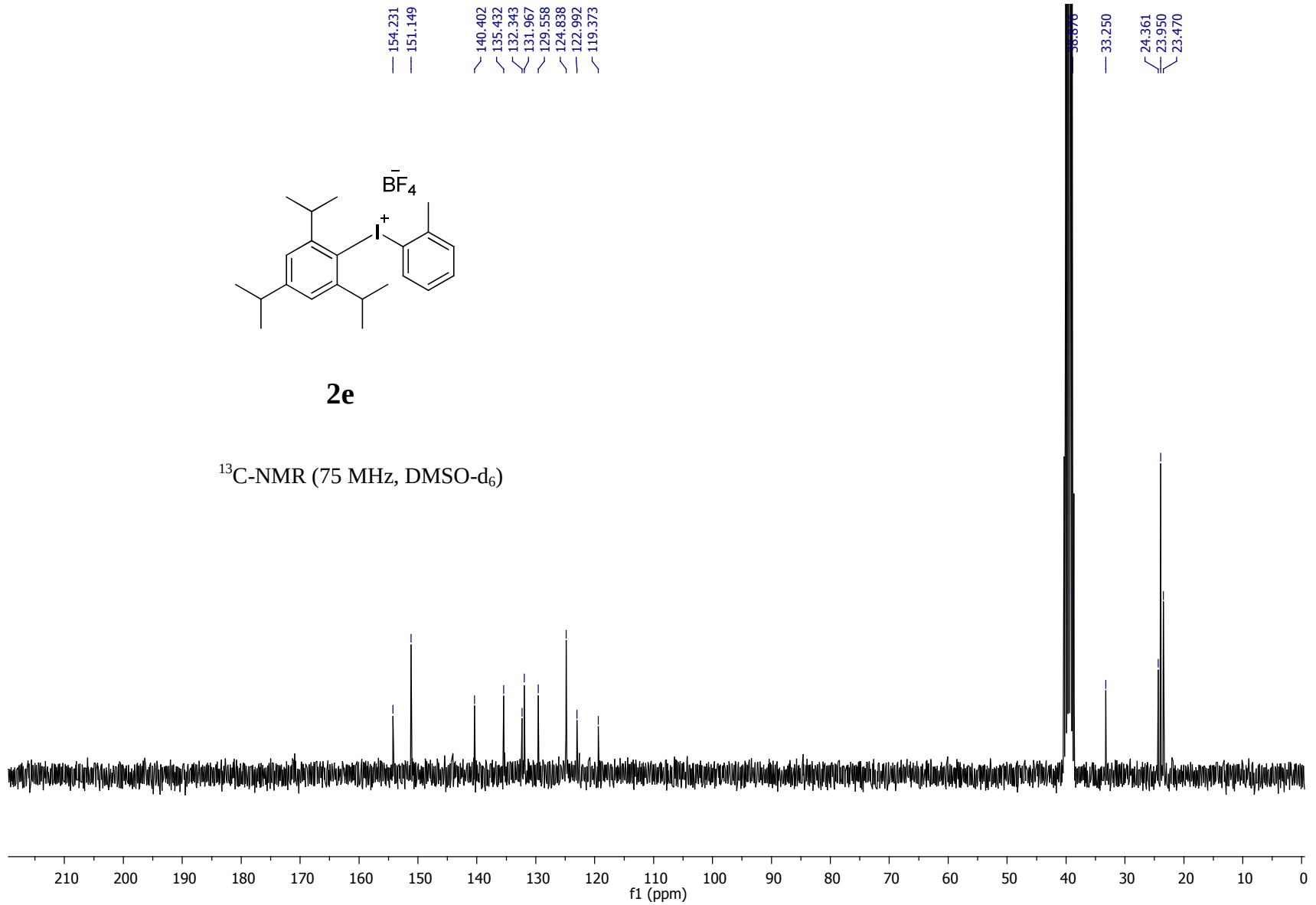
2d

^{19}F NMR (282 MHz, $CDCl_3$)



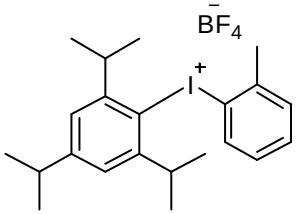
2e

^{1}H NMR (300 MHz, DMSO-d_6)



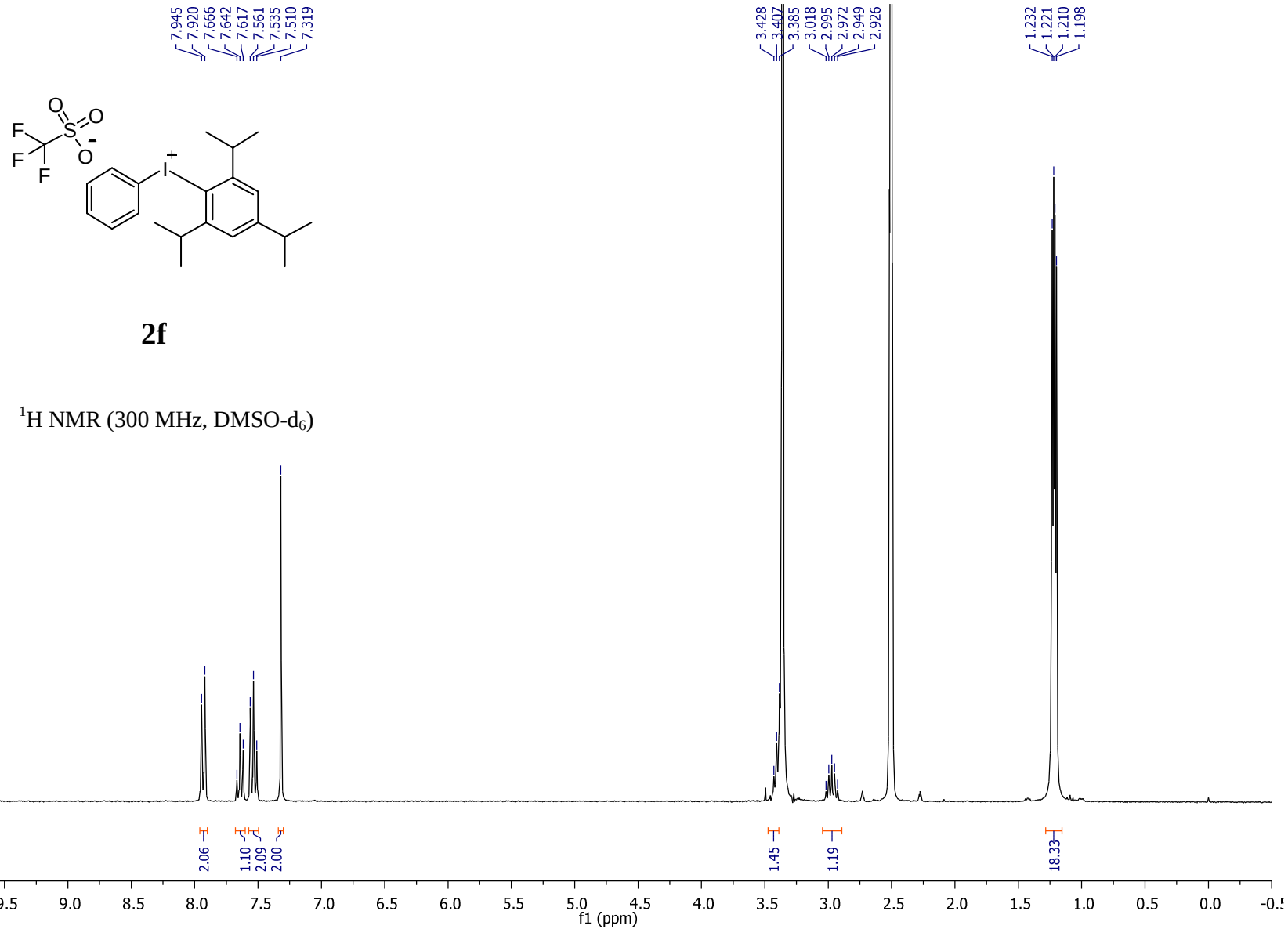
2e

^{13}C-NMR (75 MHz, DMSO-d_6)



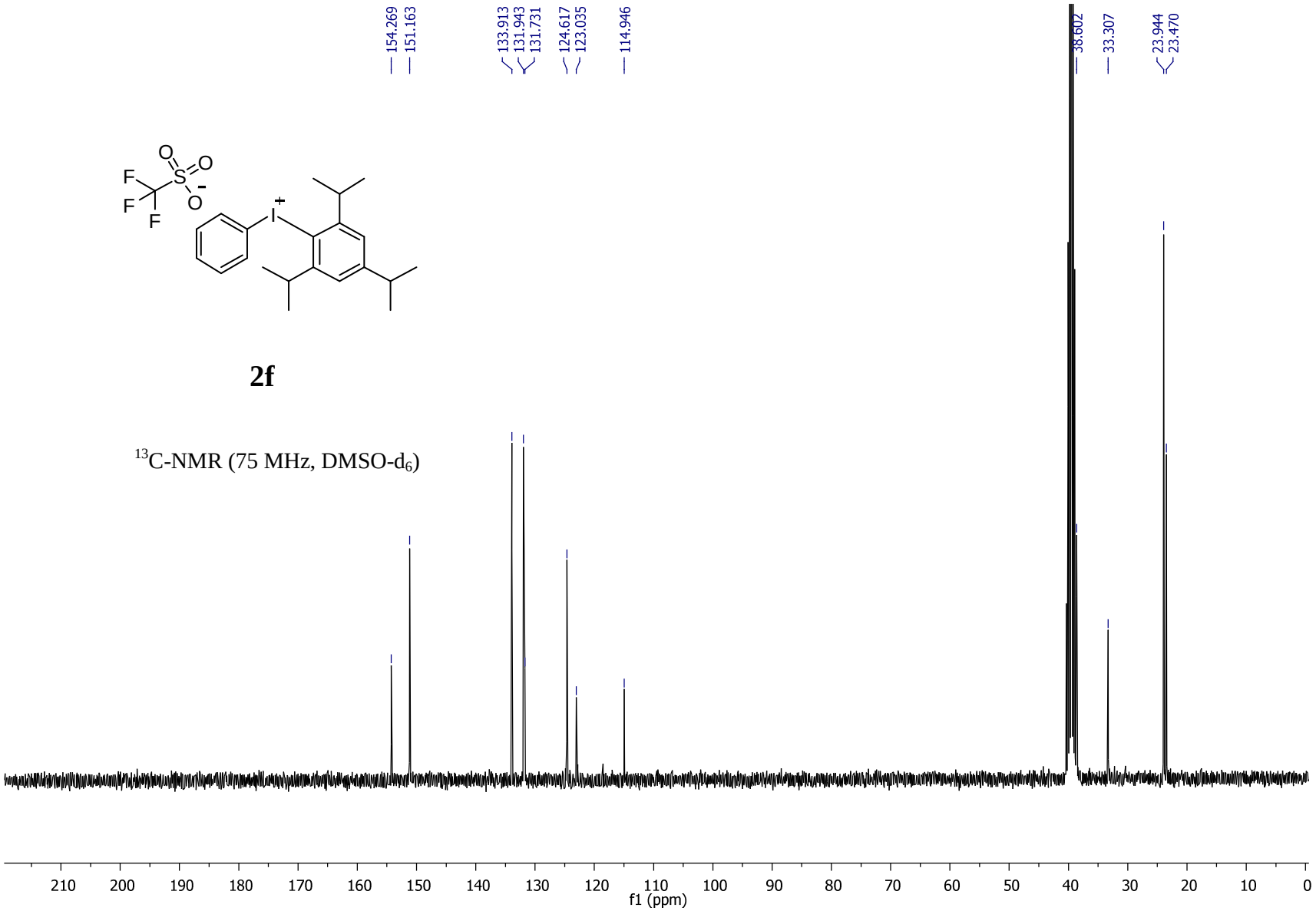
2e

^{19}F NMR (282 MHz, DMSO-d_6)



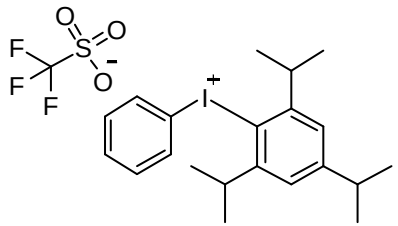
2f

^{1}H NMR (300 MHz, DMSO-d_6)



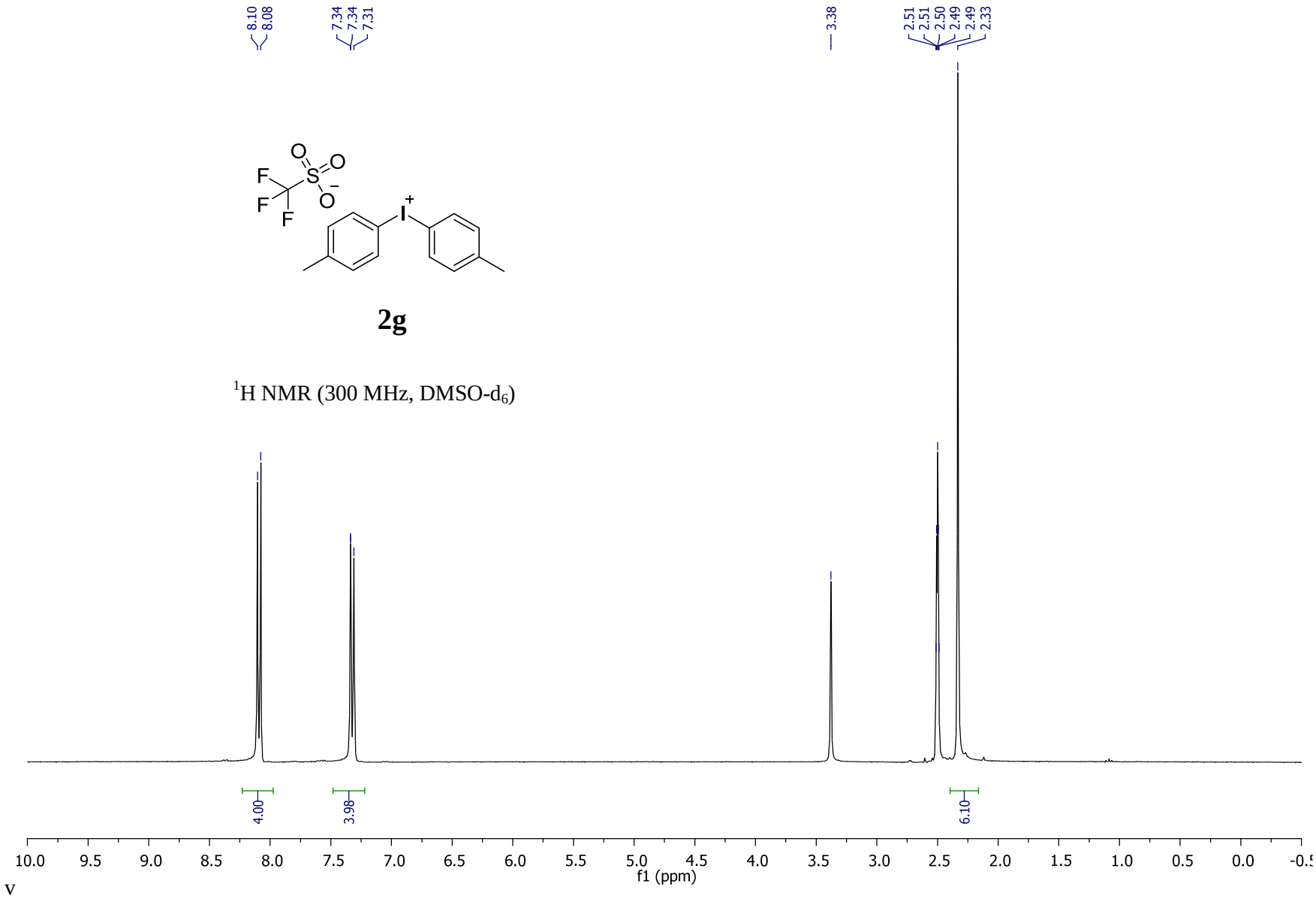
2f

^{13}C-NMR (75 MHz, DMSO-d_6)



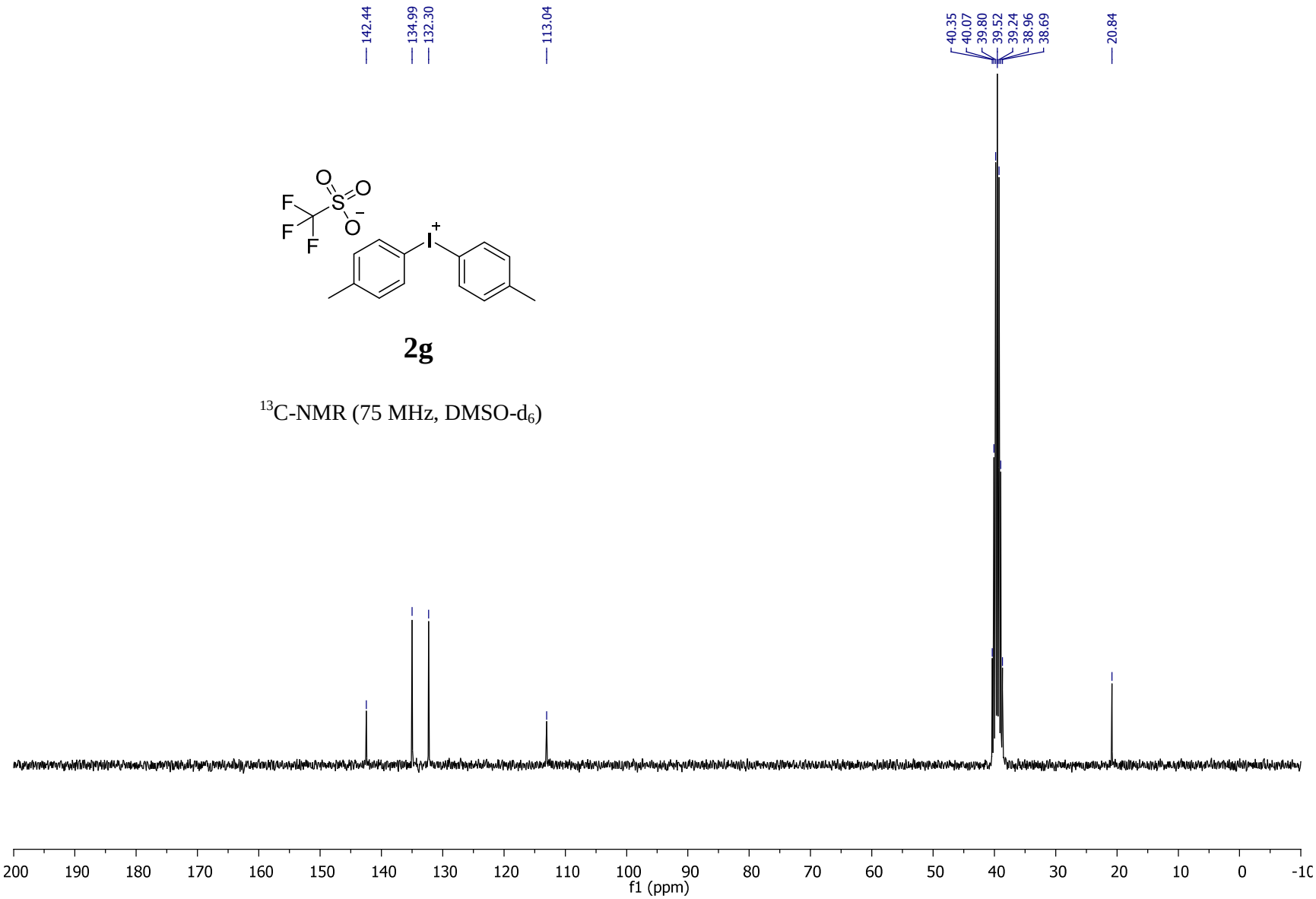
2f

^{19}F NMR (282 MHz, DMSO-d_6)



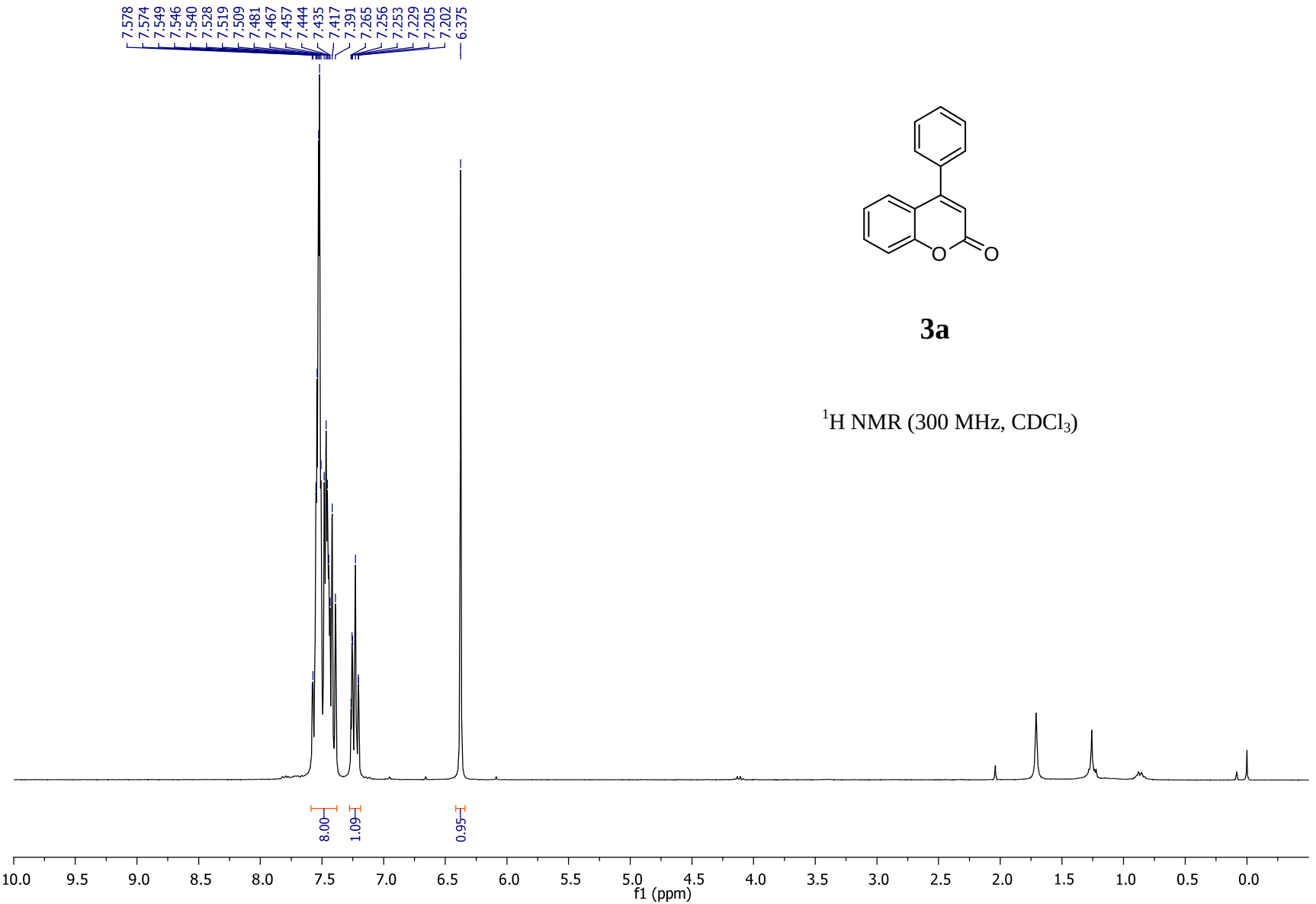
2g

^{1}H NMR (300 MHz, DMSO-d_6)



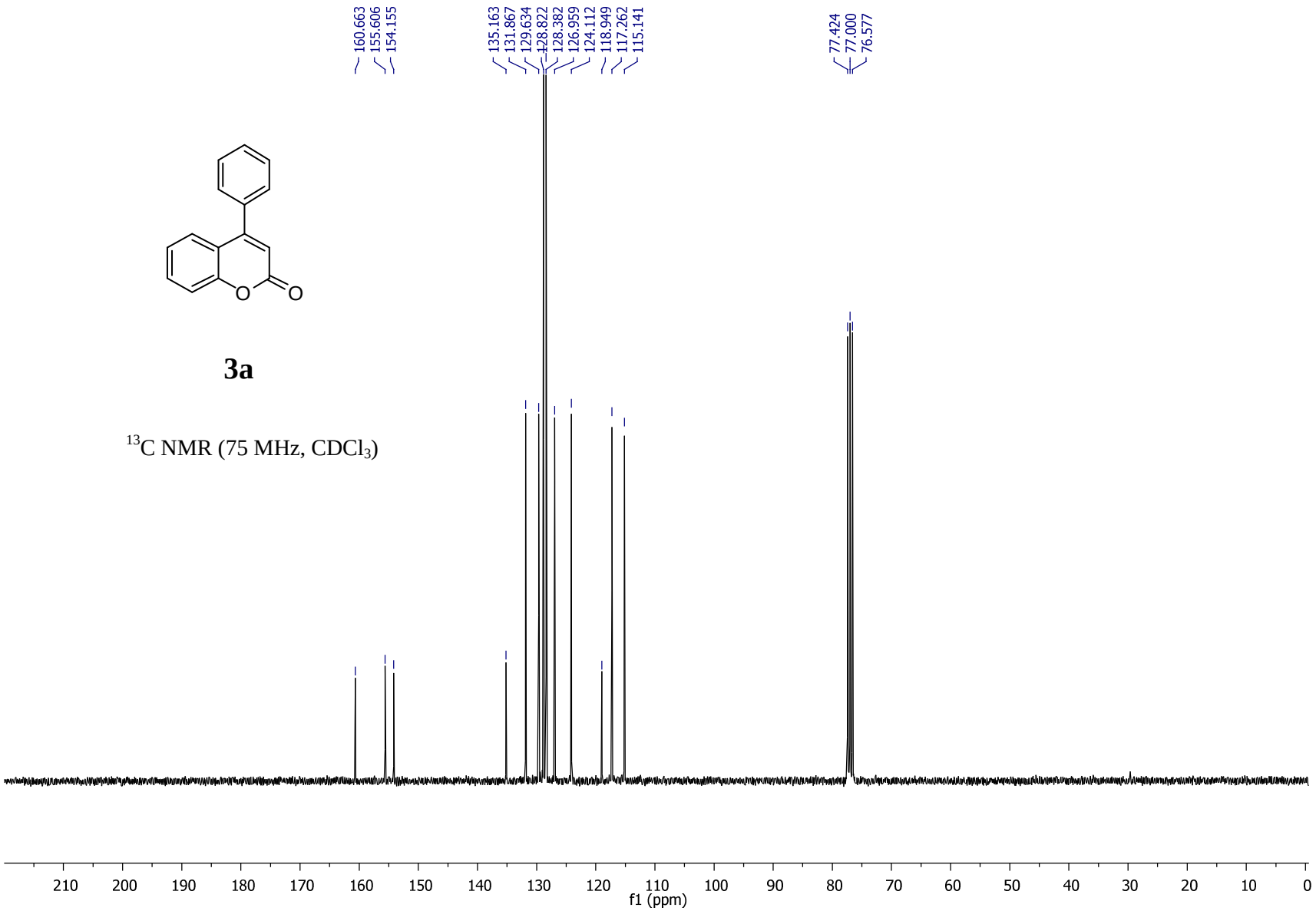
2g

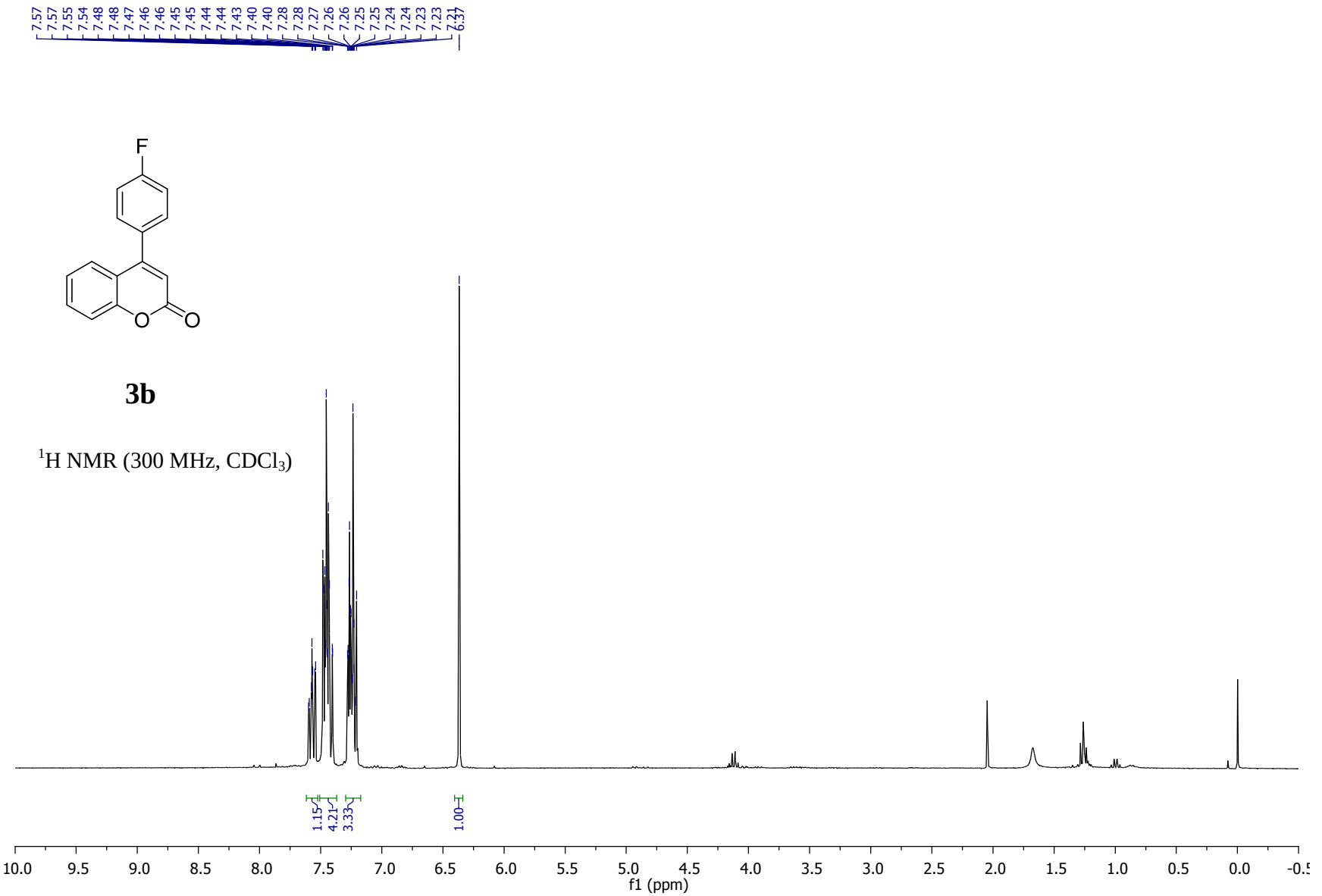
^{13}C-NMR (75 MHz, DMSO-d_6)

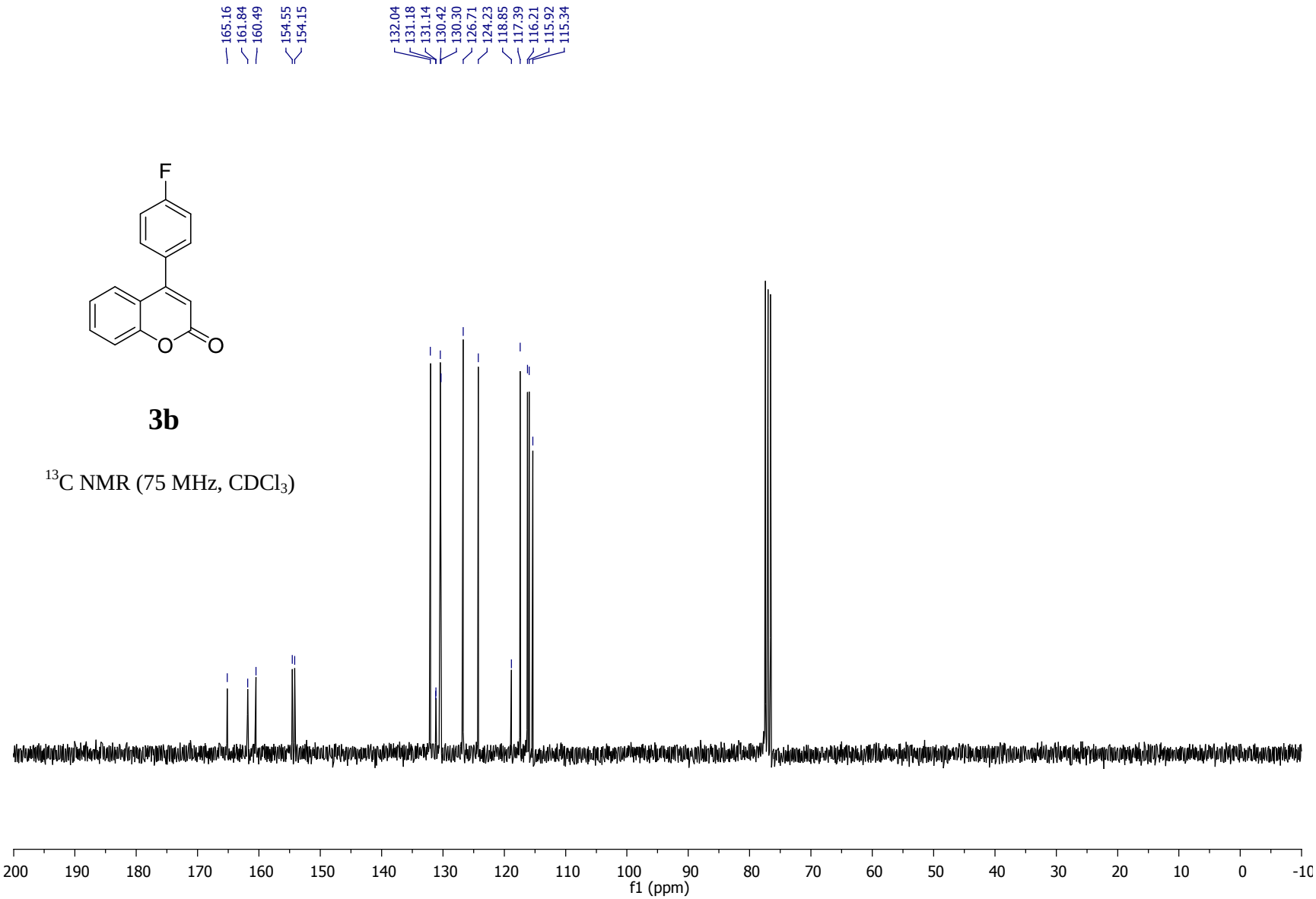


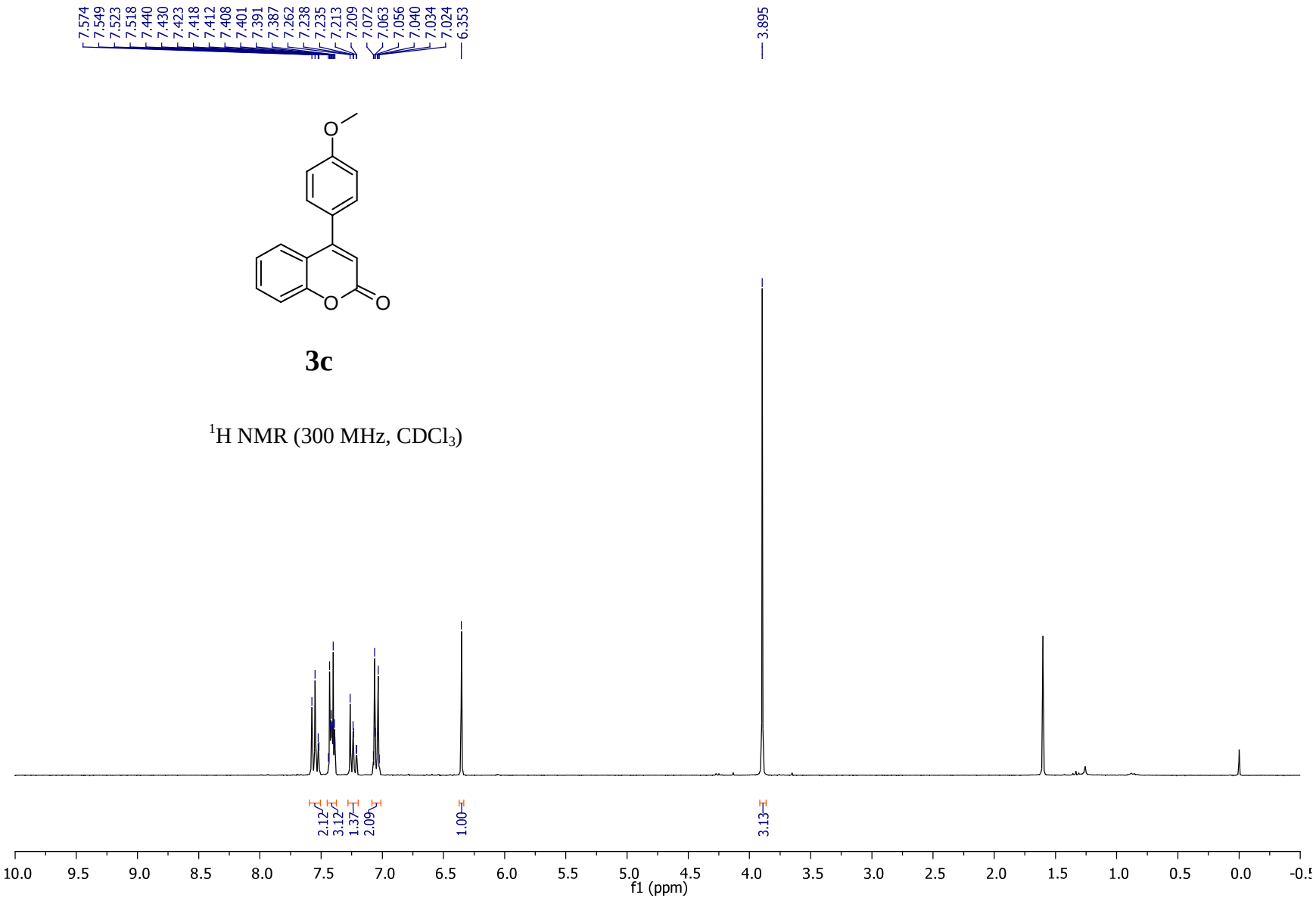
3a

^{1}H NMR (300 MHz, $CDCl_3$)


160.663
155.606
154.155
135.163
131.867
129.634
128.822
128.382
126.959
124.112
118.949
117.262
115.141
77.424
77.000
76.577
O
O
3a
13C NMR (75 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

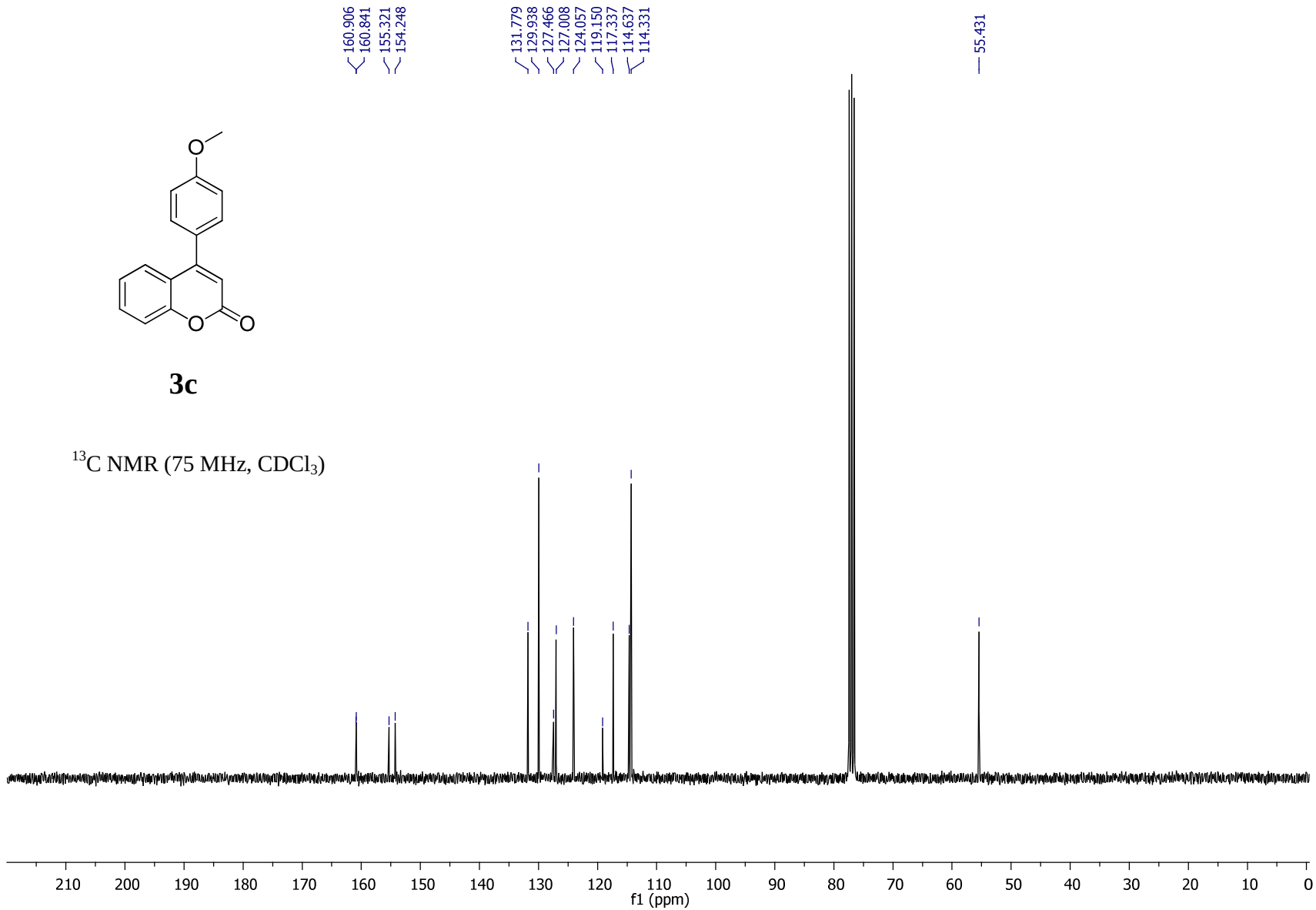

7.57
7.57
7.55
7.54
7.48
7.48
7.47
7.46
7.46
7.45
7.45
7.44
7.44
7.43
7.40
7.40
7.28
7.28
7.27
7.26
7.26
7.25
7.25
7.24
7.24
7.23
7.21
6.37
F
O
O
3b
1H NMR (300 MHz, CDCl3)
1.15
4.21
3.33
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


165.16
161.84
160.49
154.55
154.15
132.04
131.18
131.14
130.42
130.30
126.71
124.23
118.85
117.39
116.21
115.92
115.34
F
O
O
3b
13C NMR (75 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



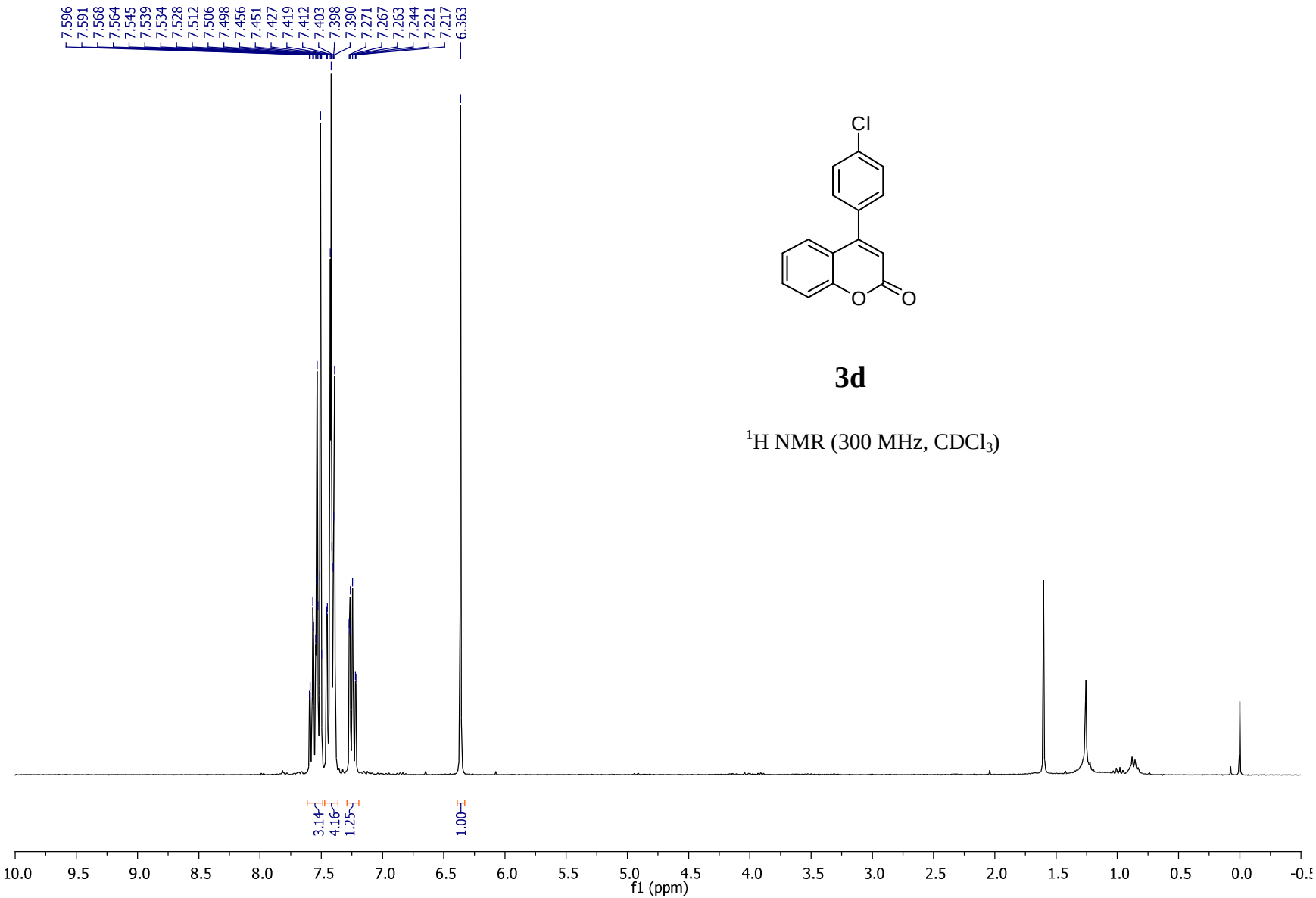
3c

^{1}H NMR (300 MHz, $CDCl_3$)



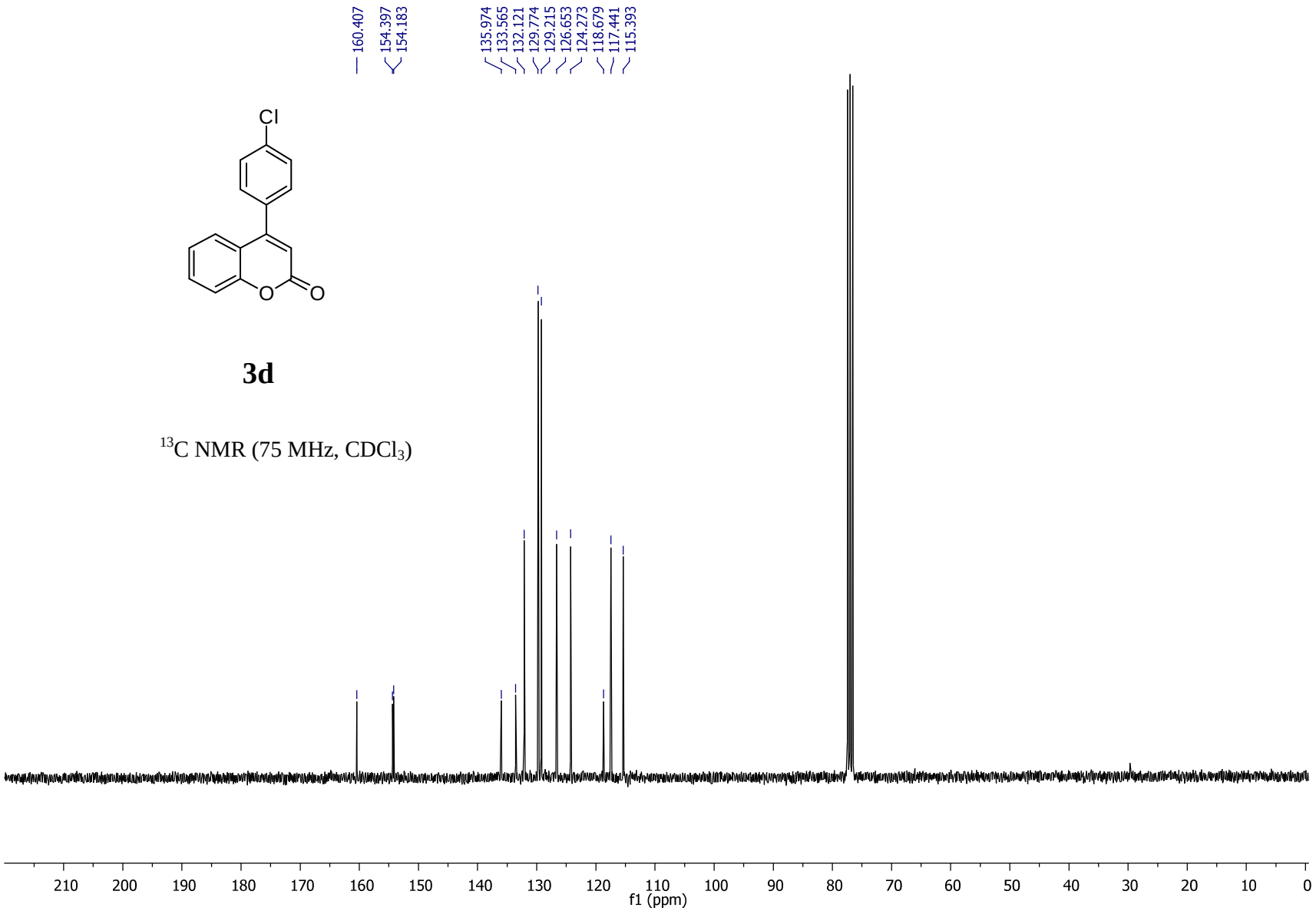
3c

^{13}C NMR (75 MHz, $CDCl_3$)



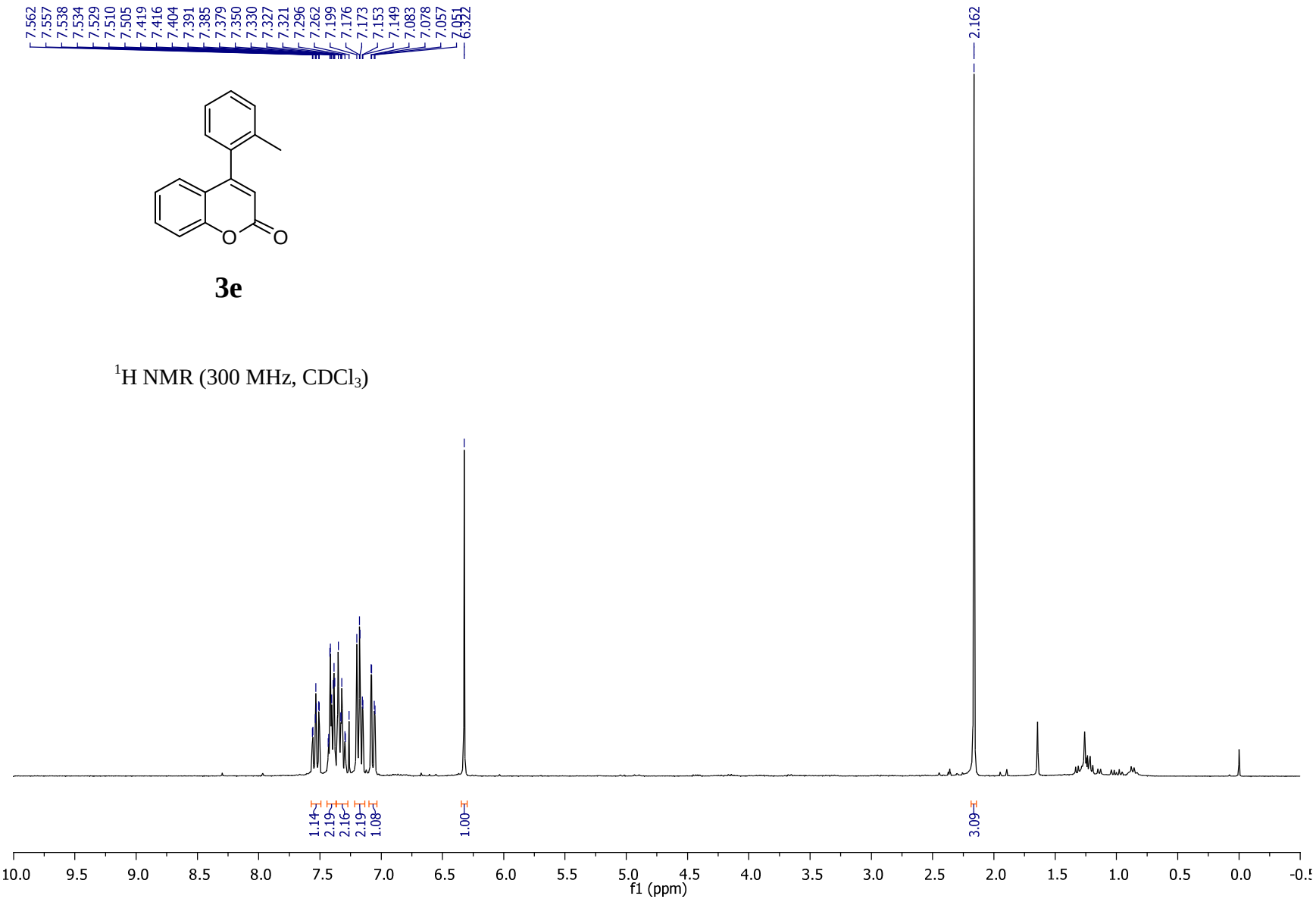
3d

^{1}H NMR (300 MHz, $CDCl_3$)



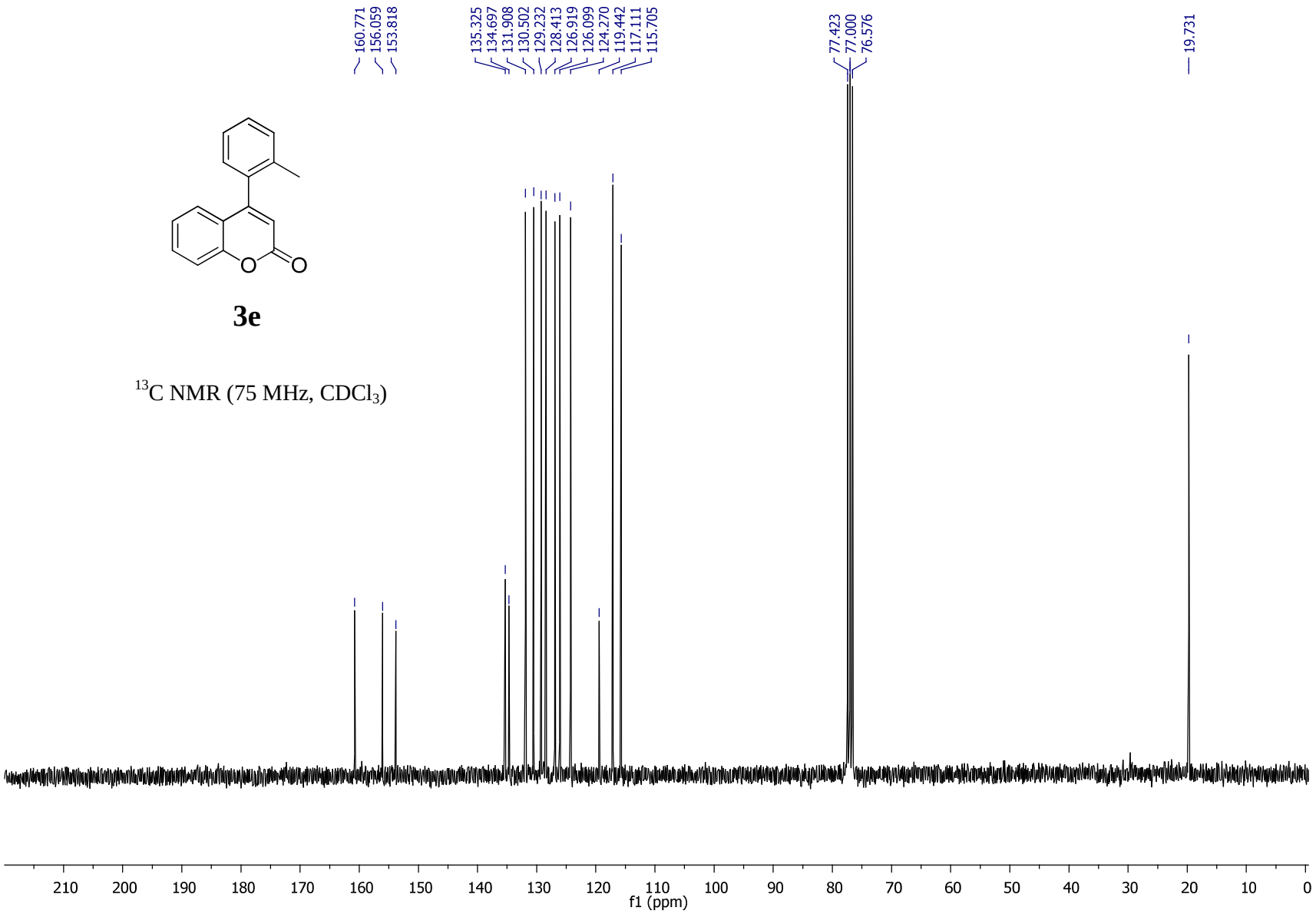
3d

^{13}C NMR (75 MHz, $CDCl_3$)



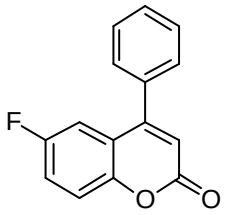
3e

^{1}H NMR (300 MHz, $CDCl_3$)



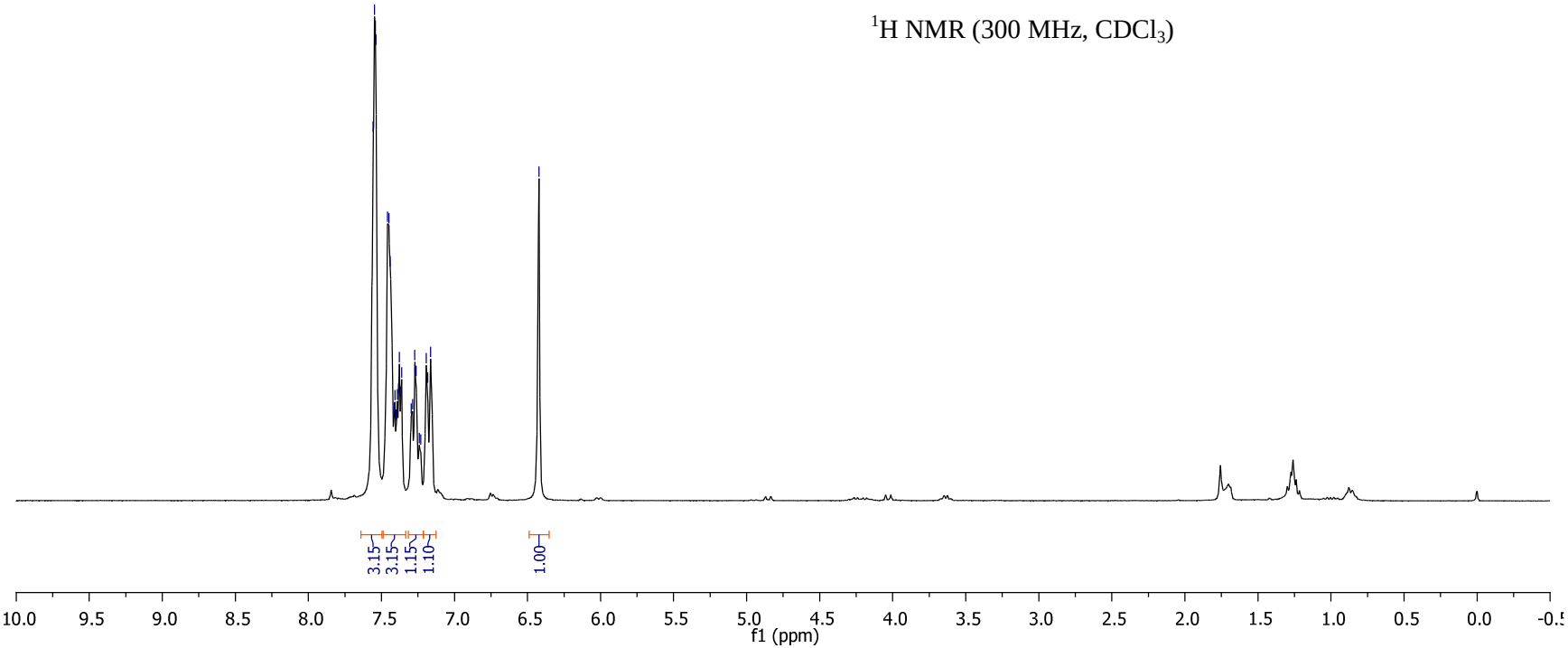
3e

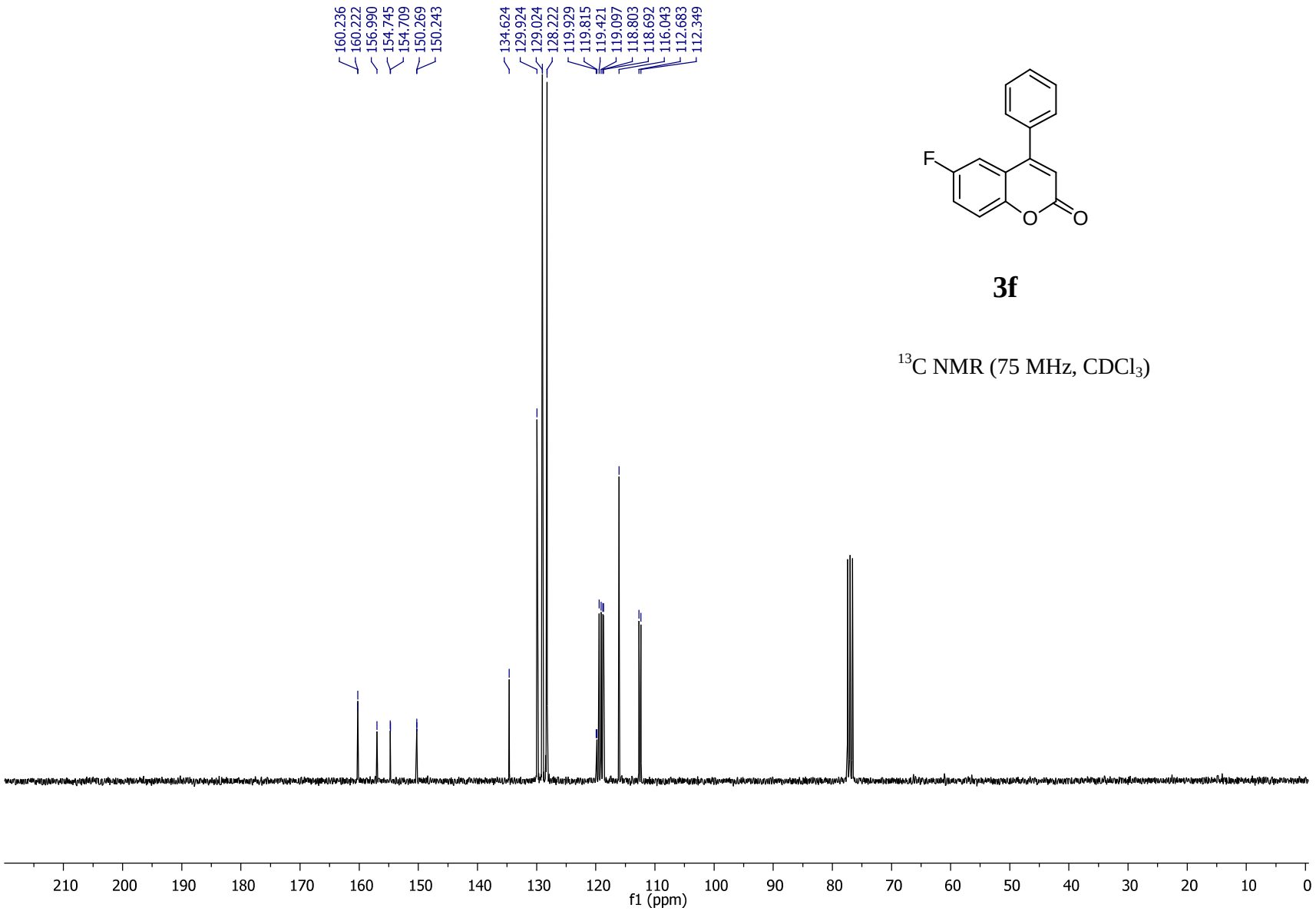
^{13}C NMR (75 MHz, $CDCl_3$)



3f

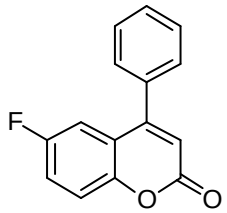
^{1}H NMR (300 MHz, $CDCl_3$)





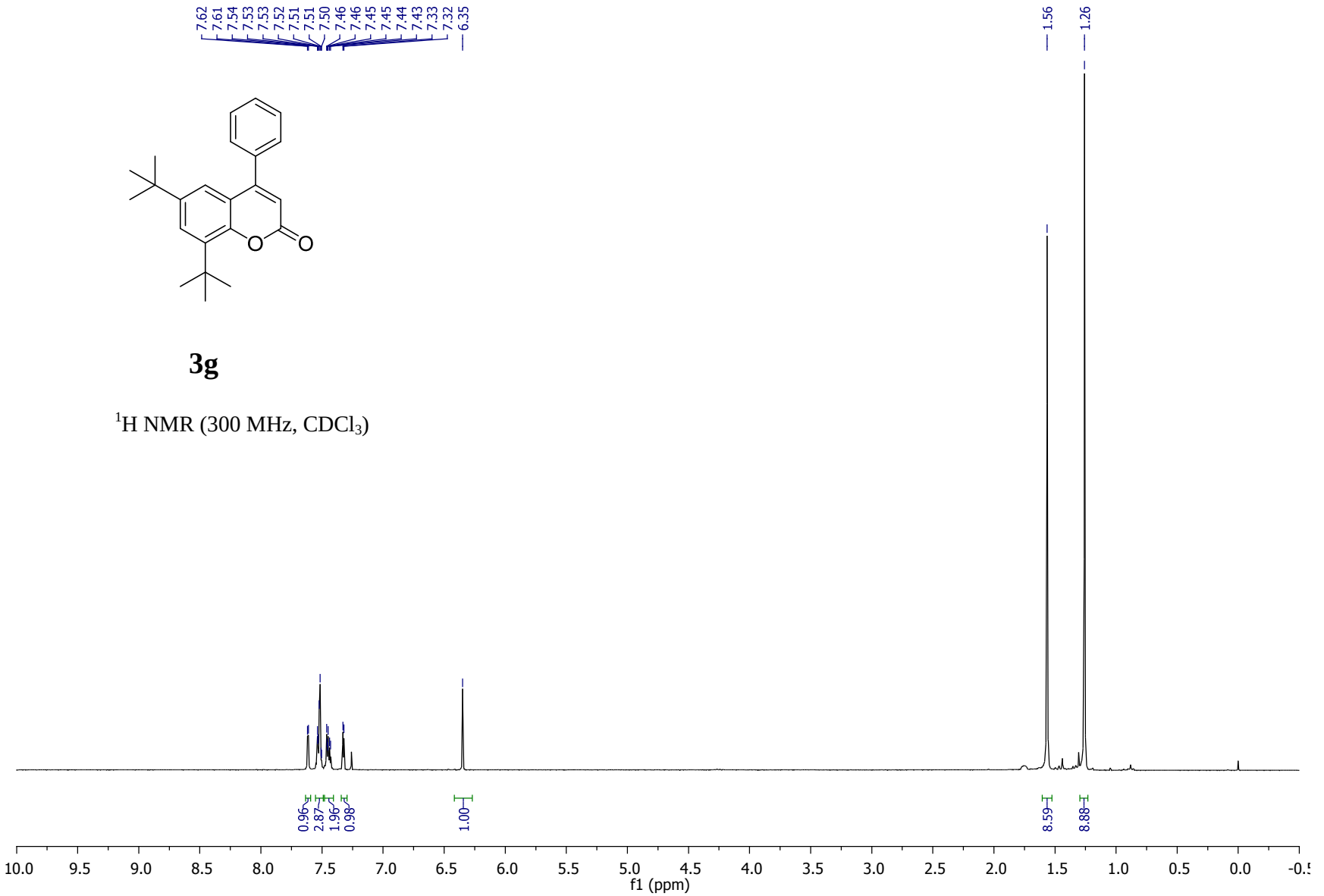
3f

^{13}C NMR (75 MHz, $CDCl_3$)



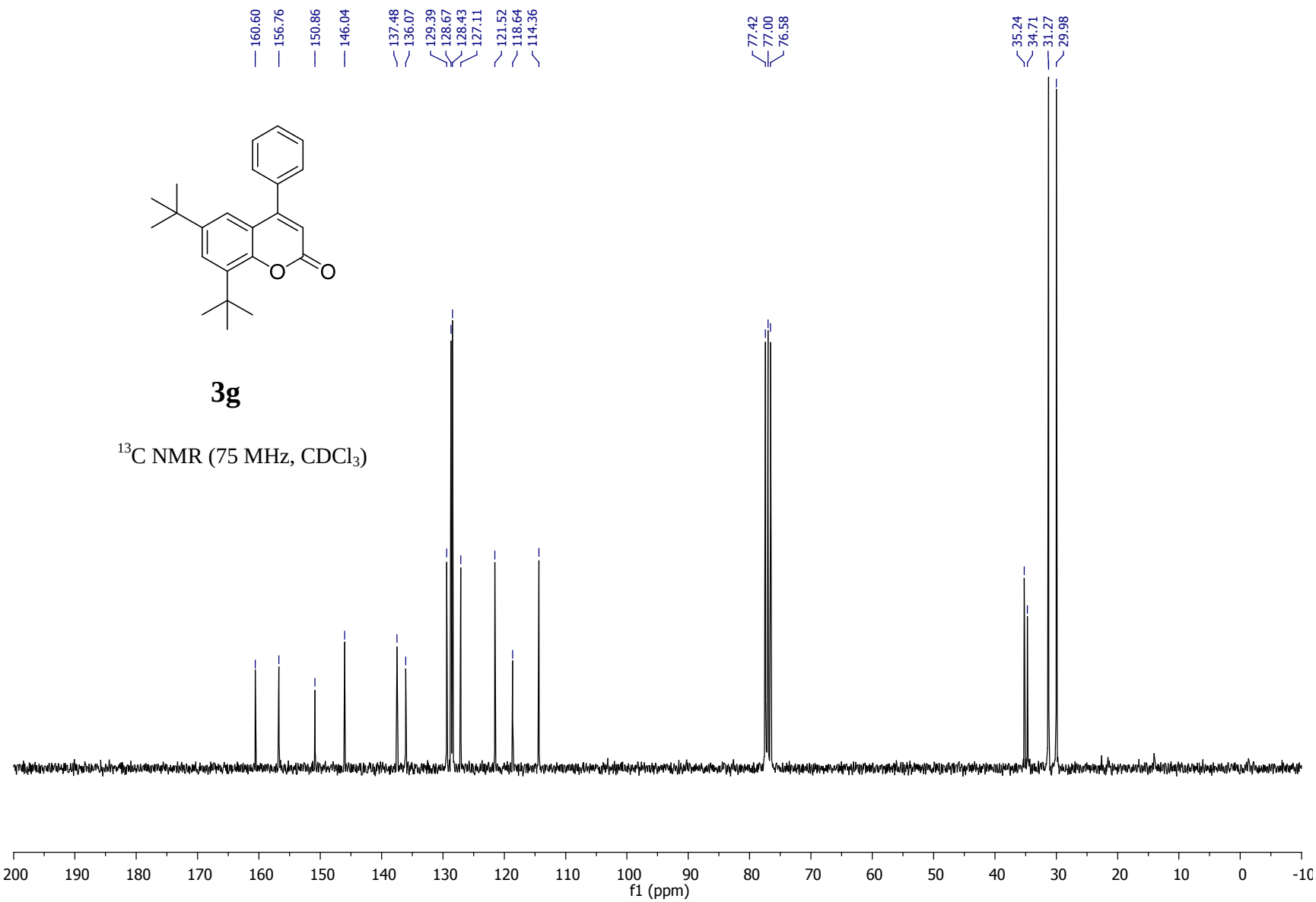
3f

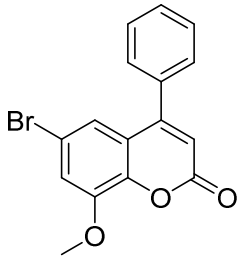
^{19}F NMR (282 MHz, $CDCl_3$)



3g

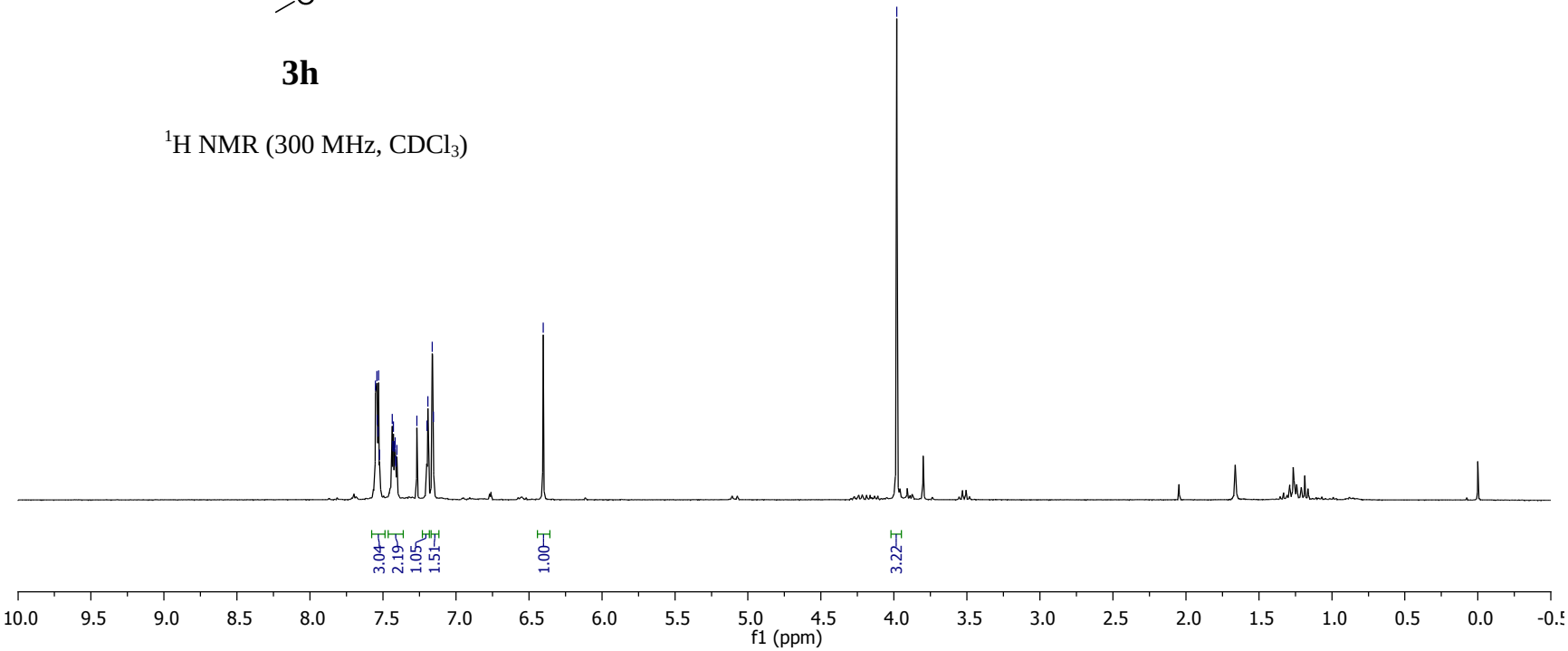
^{1}H NMR (300 MHz, $CDCl_3$)

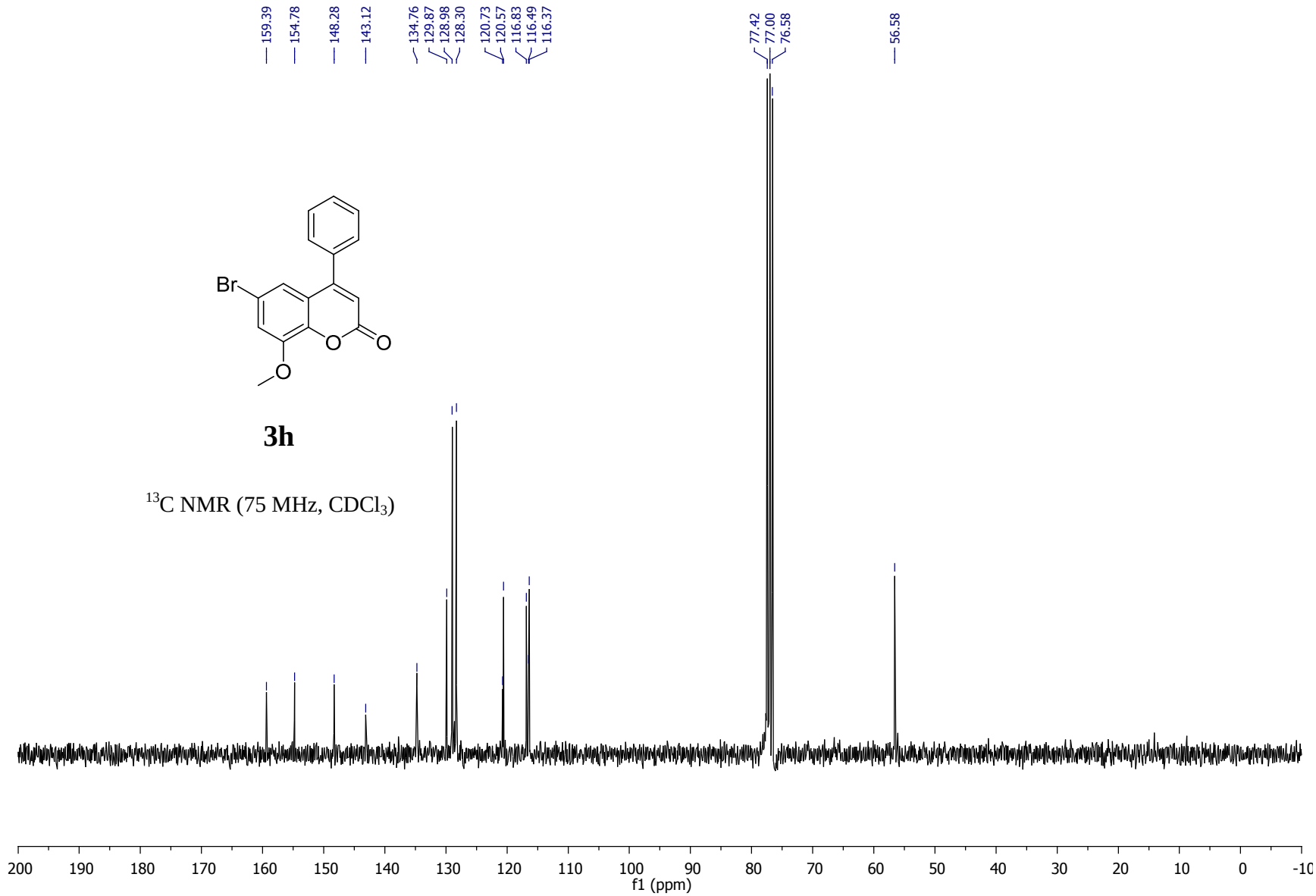

160.60
156.76
150.86
146.04
137.48
136.07
129.39
128.67
128.43
127.11
121.52
118.64
114.36
77.42
77.00
76.58
35.24
34.71
31.27
29.98
O
O
3g
13C NMR (75 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

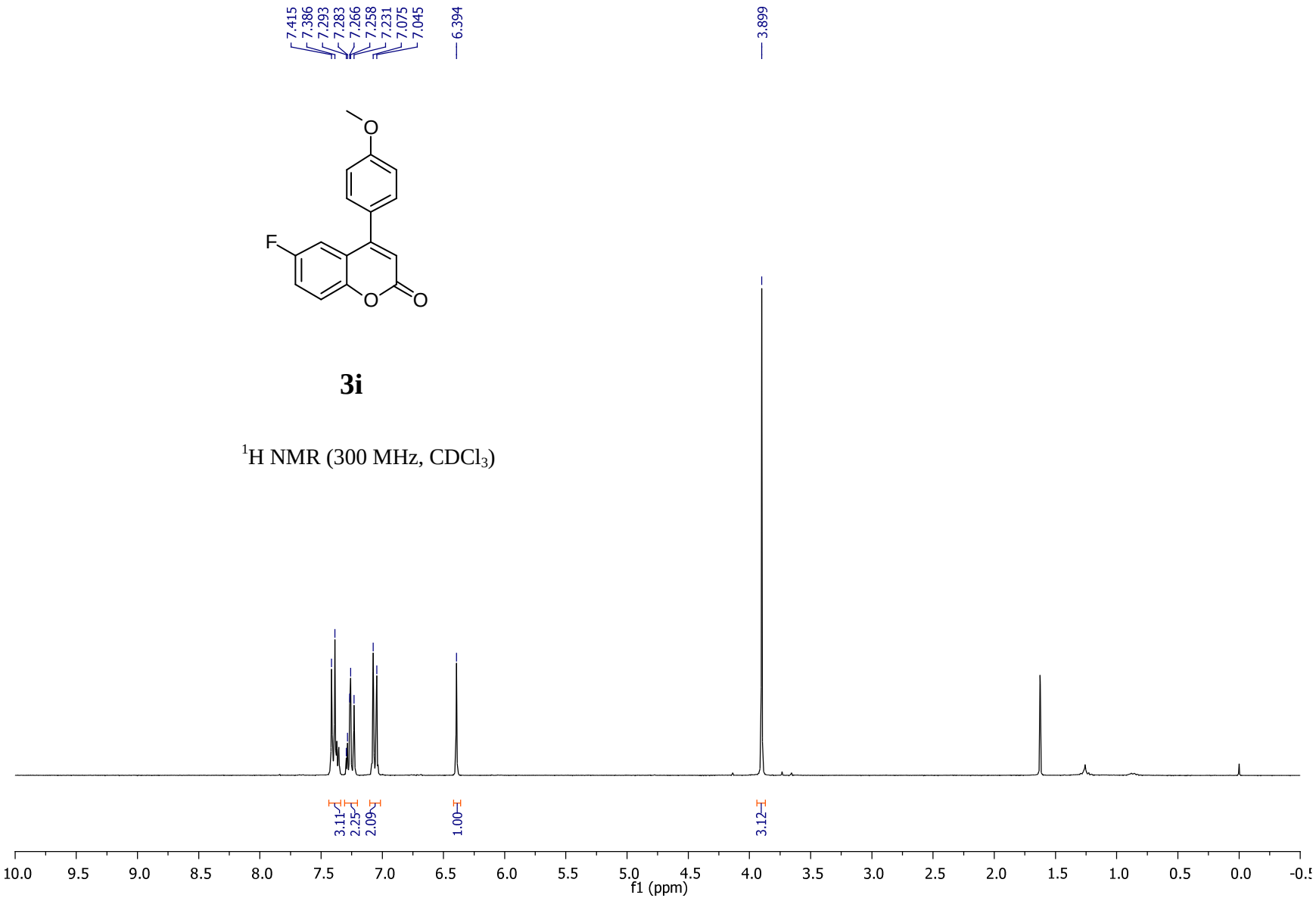


3h

^{1}H NMR (300 MHz, $CDCl_3$)

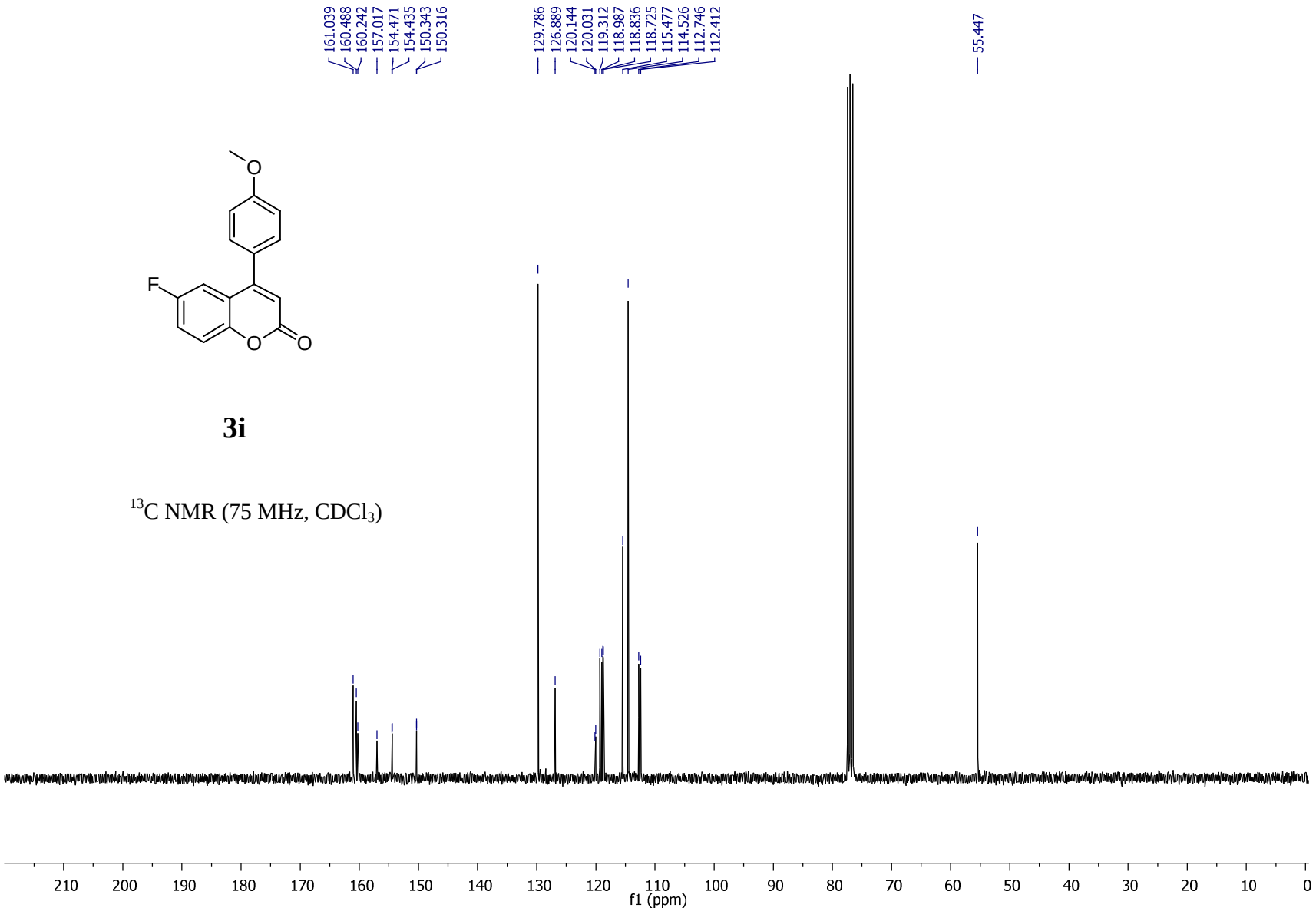



159.39
154.78
148.28
143.12
134.76
129.87
128.98
128.30
120.73
120.57
116.83
116.49
116.37
77.42
77.00
76.58
56.58
Br
O
O
O
3h
13C NMR (75 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



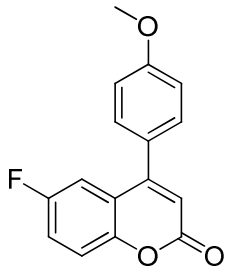
3i

^{1}H NMR (300 MHz, $CDCl_3$)



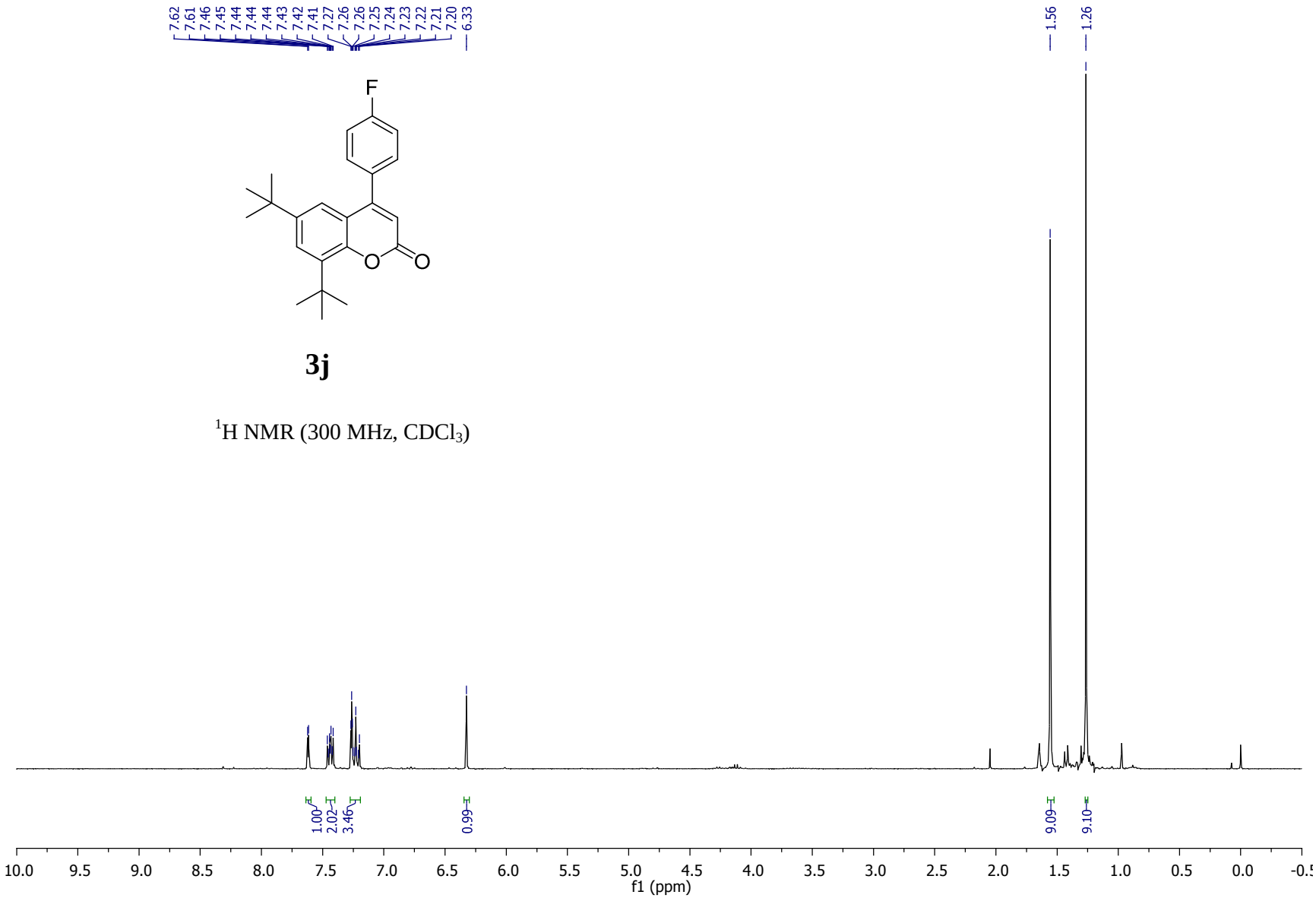
3i

^{13}C NMR (75 MHz, $CDCl_3$)



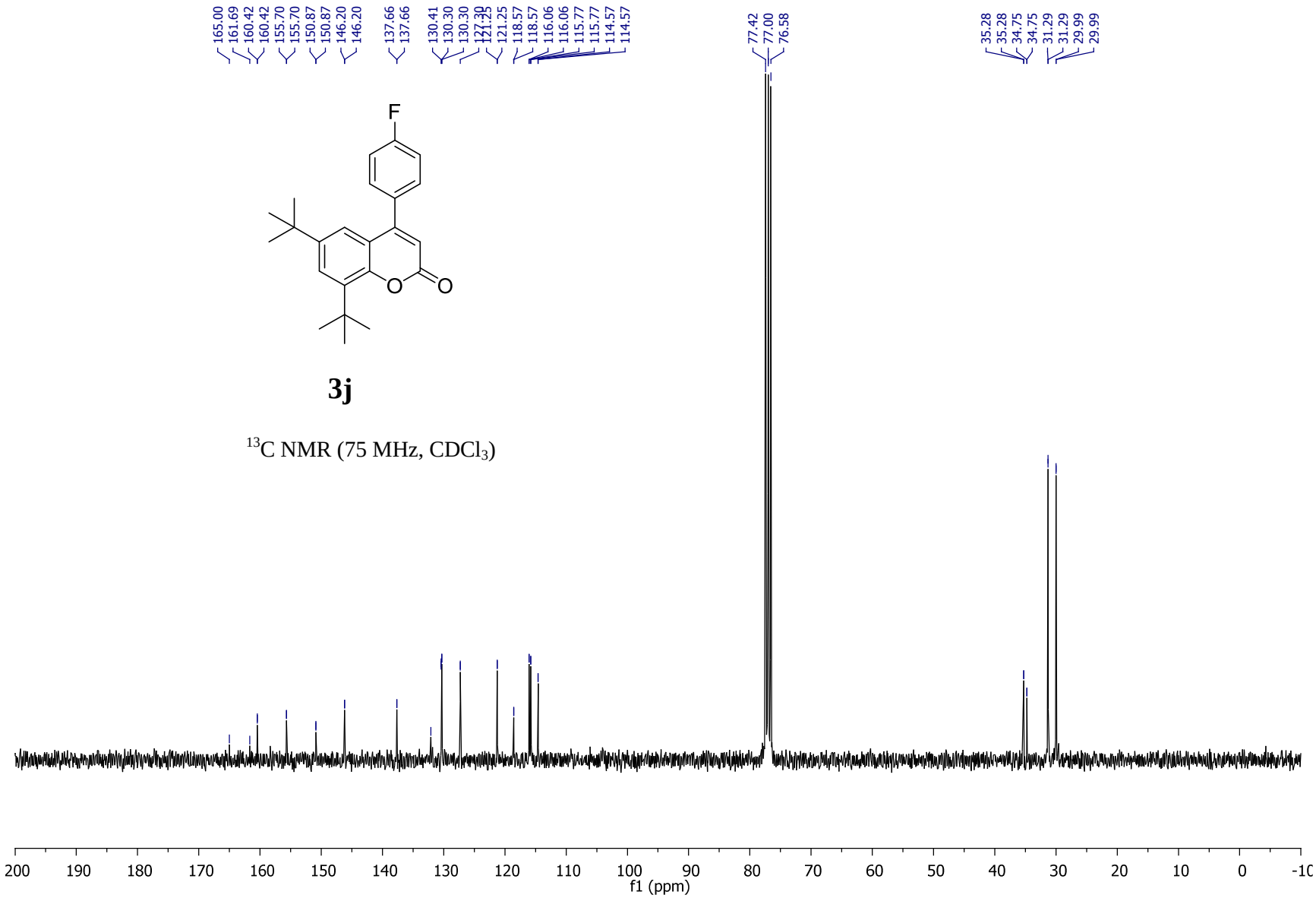
3i

^{19}F NMR (282 MHz, $CDCl_3$)



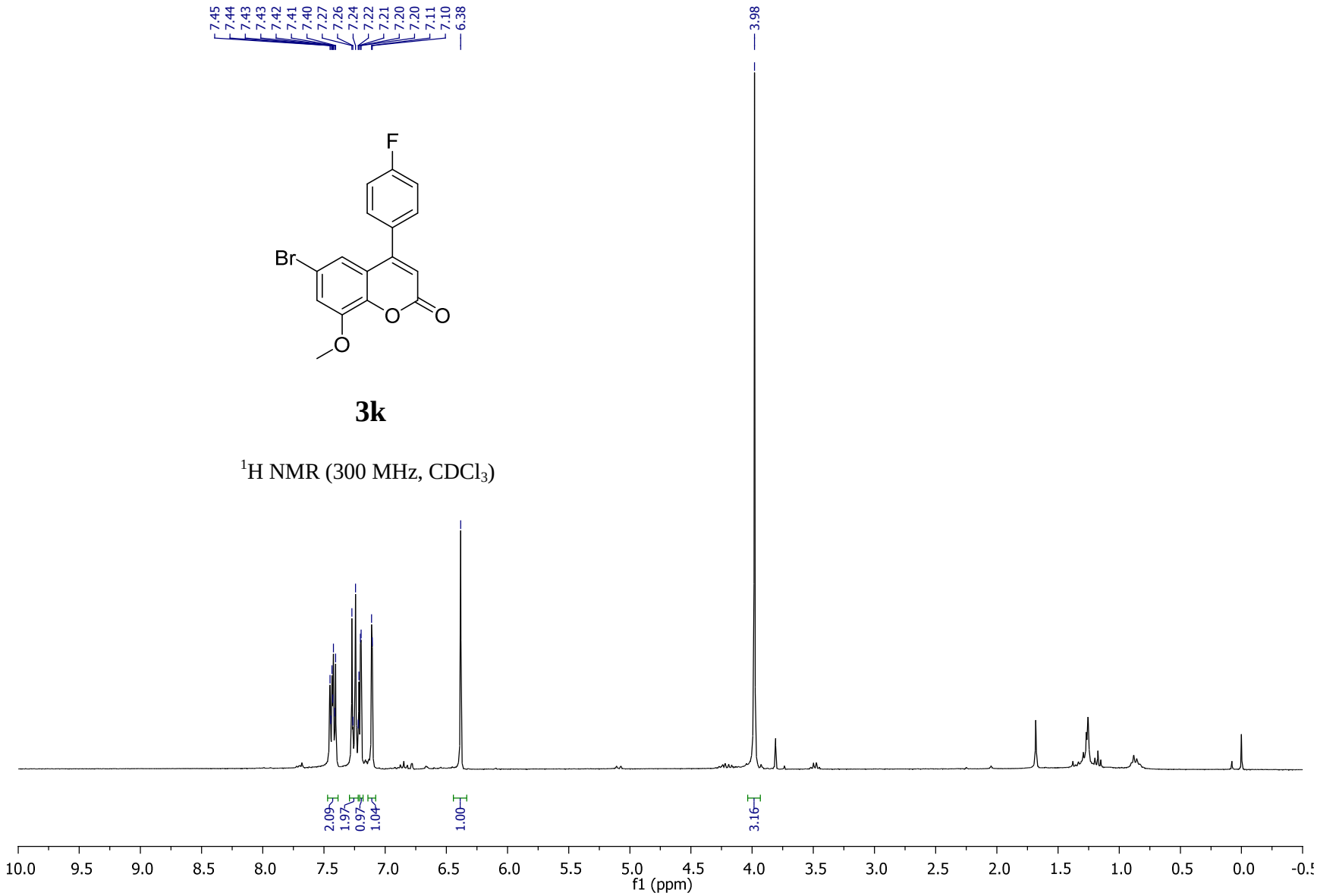
3j

^{1}H NMR (300 MHz, $CDCl_3$)



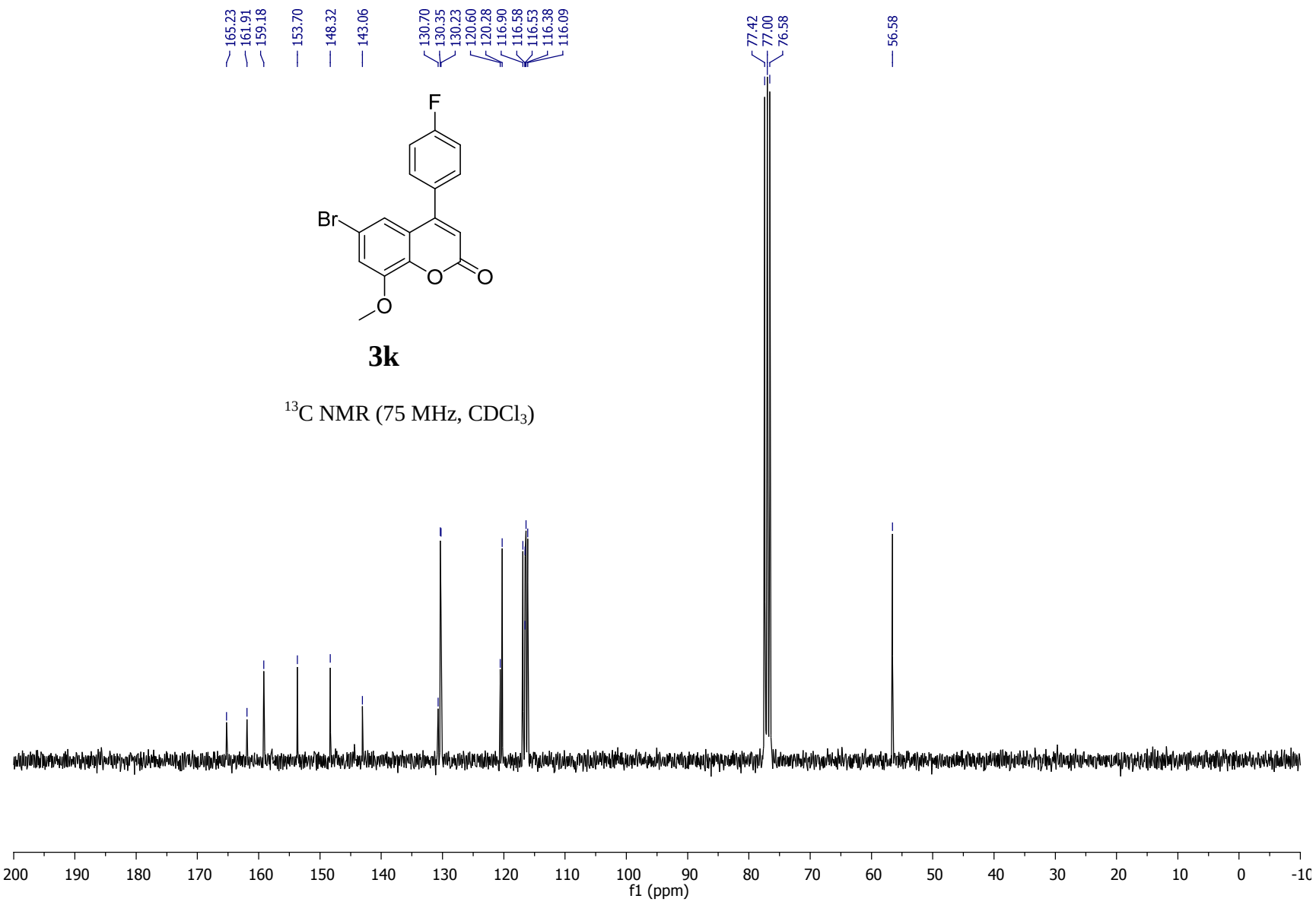
3j

^{13}C NMR (75 MHz, $CDCl_3$)



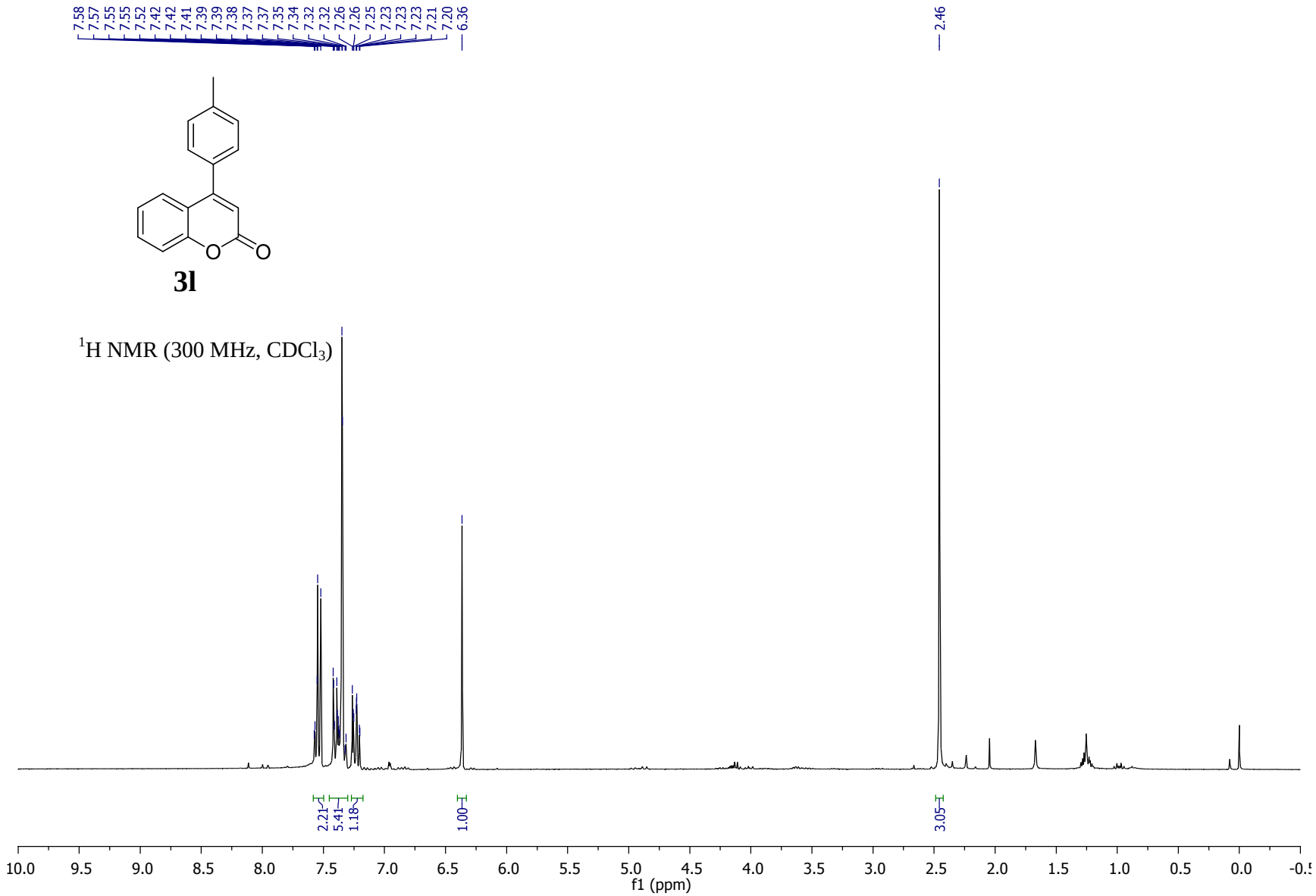
3k

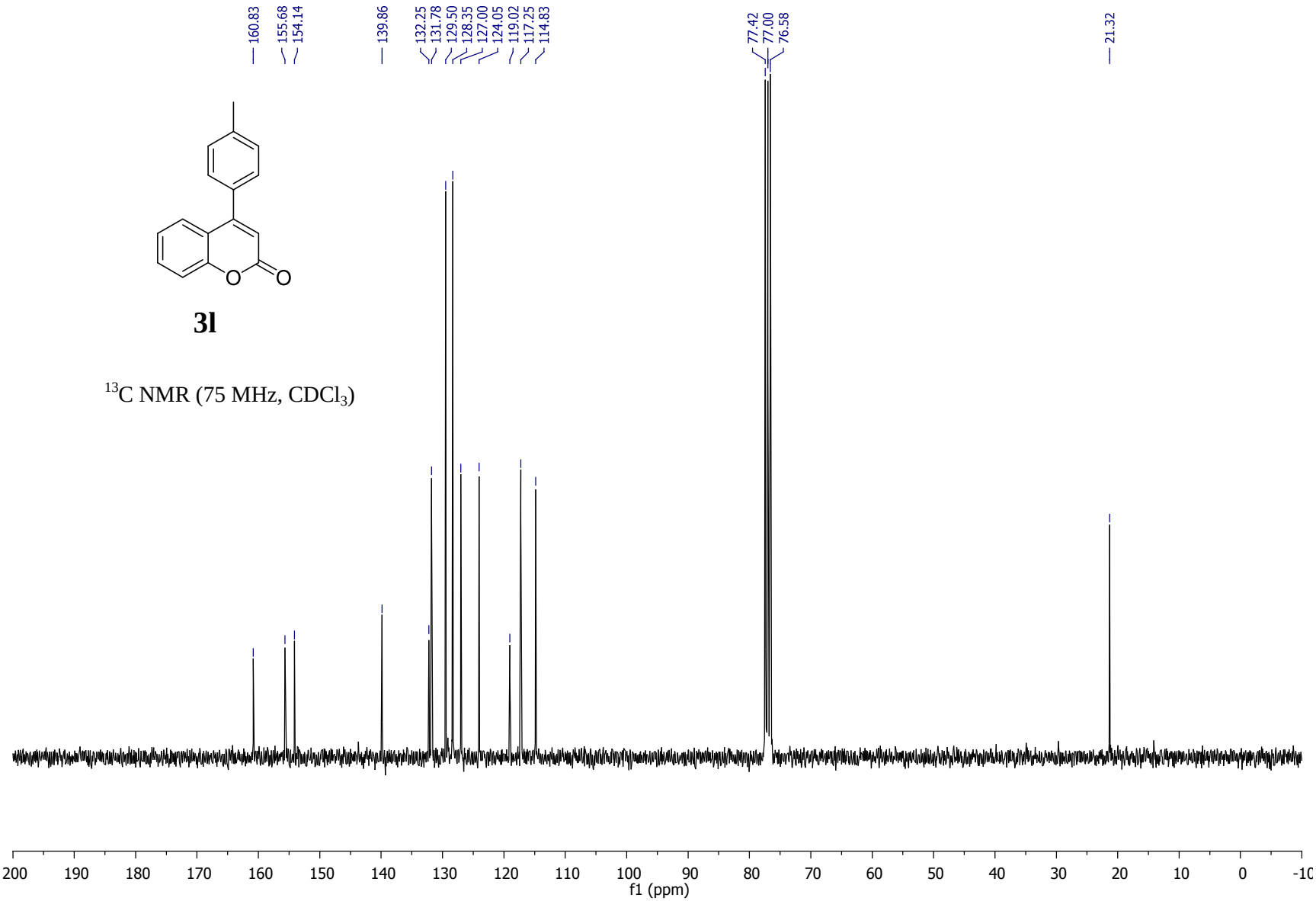
^{1}H NMR (300 MHz, $CDCl_3$)



3k

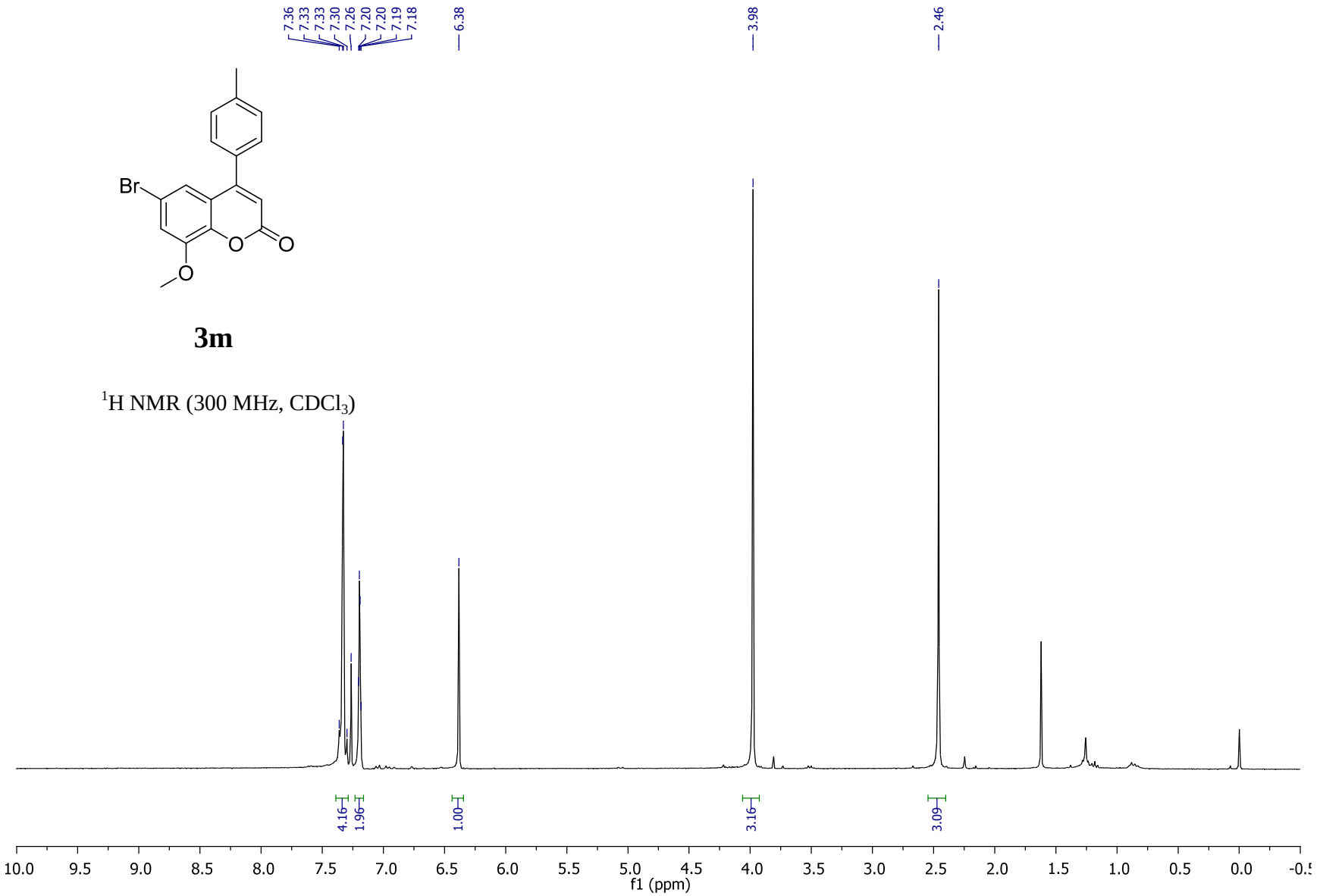
^{13}C NMR (75 MHz, $CDCl_3$)


7.58
7.57
7.55
7.55
7.52
7.42
7.42
7.41
7.39
7.39
7.38
7.37
7.37
7.35
7.34
7.32
7.32
7.26
7.26
7.25
7.23
7.23
7.23
7.21
7.20
6.36
2.46
O
O
3l
1H NMR (300 MHz, CDCl3)
2.21
5.41
1.18
1.00
3.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



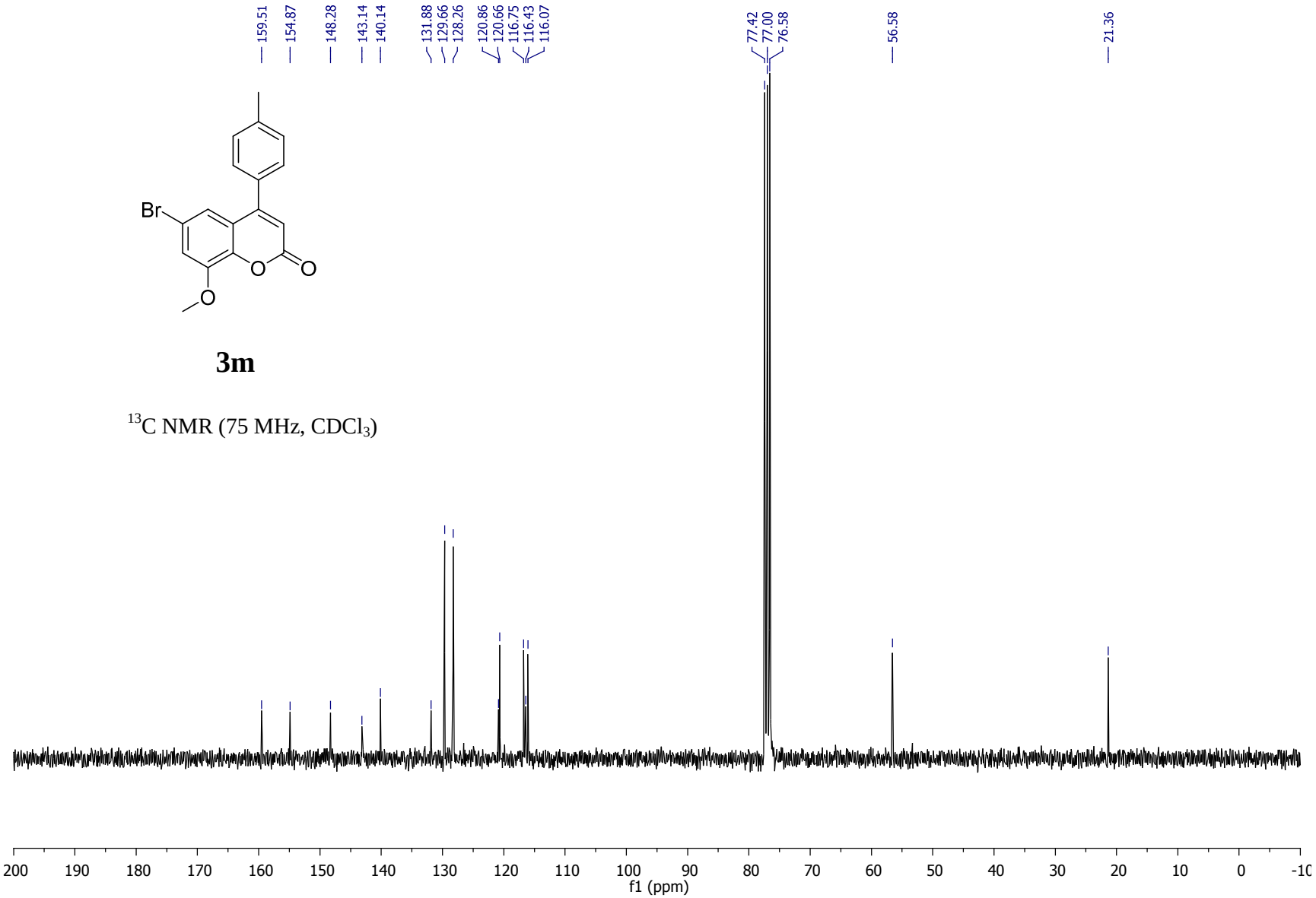
3l

^{13}C NMR (75 MHz, $CDCl_3$)



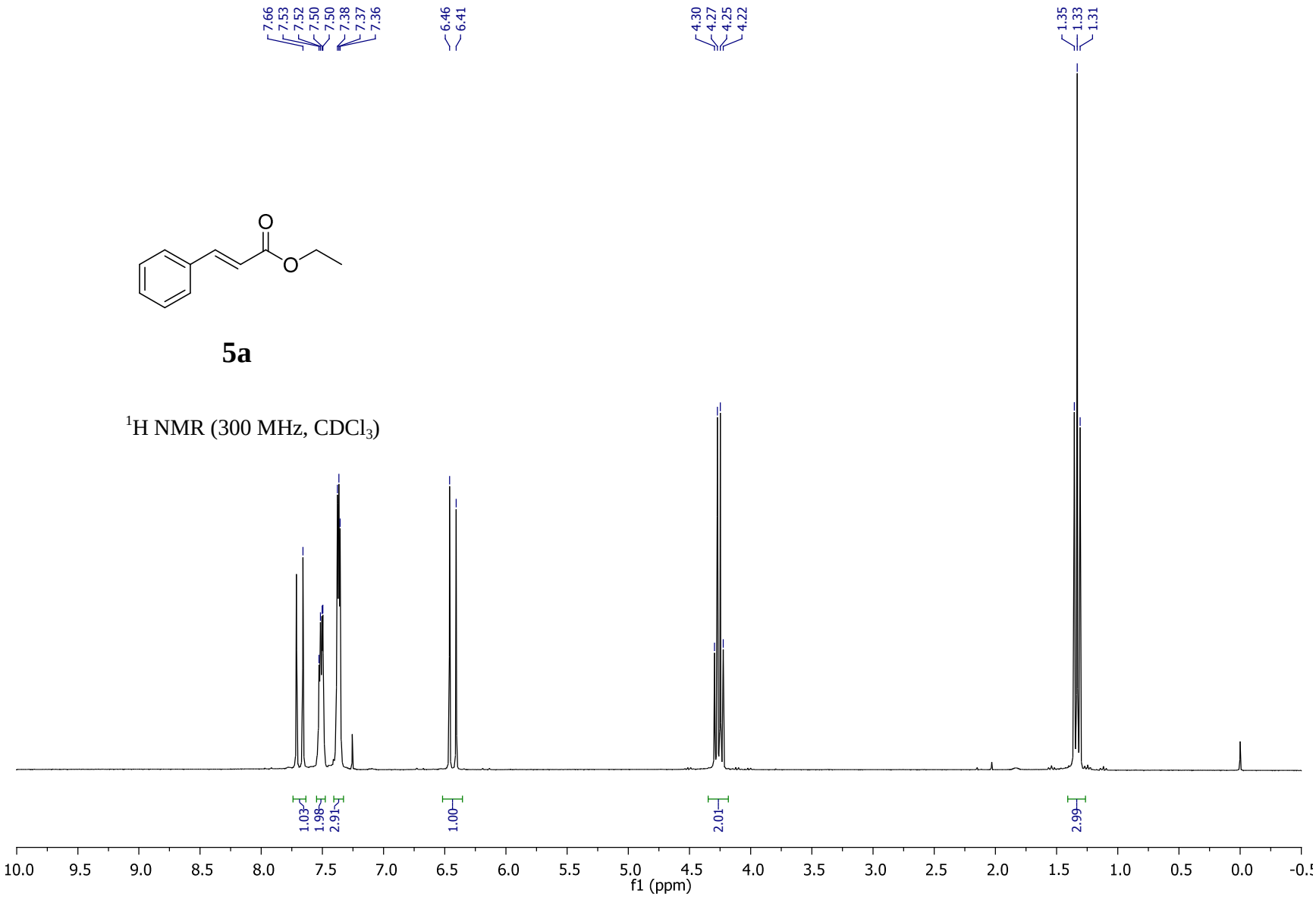
3m

^{1}H NMR (300 MHz, $CDCl_3$)



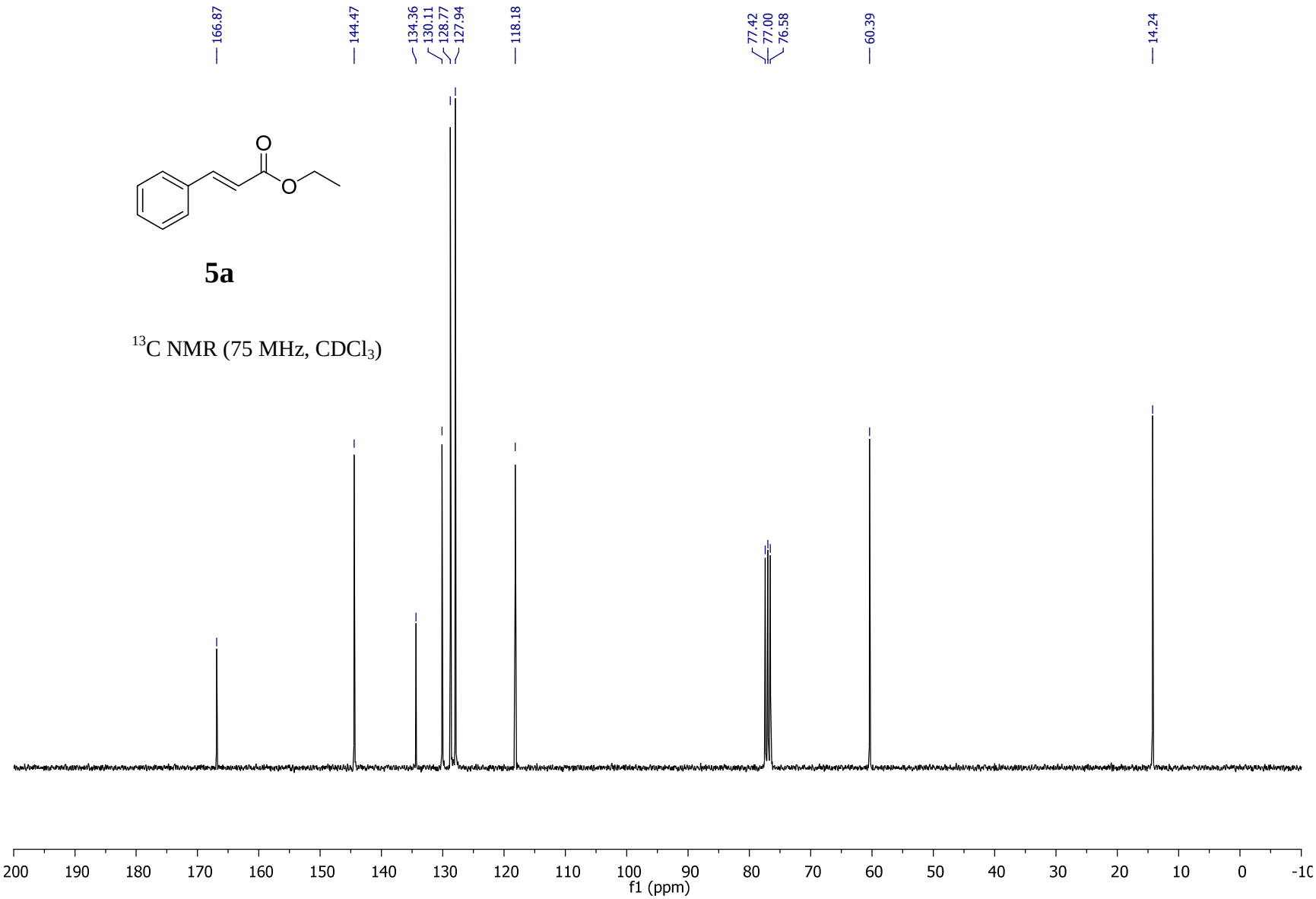
3m

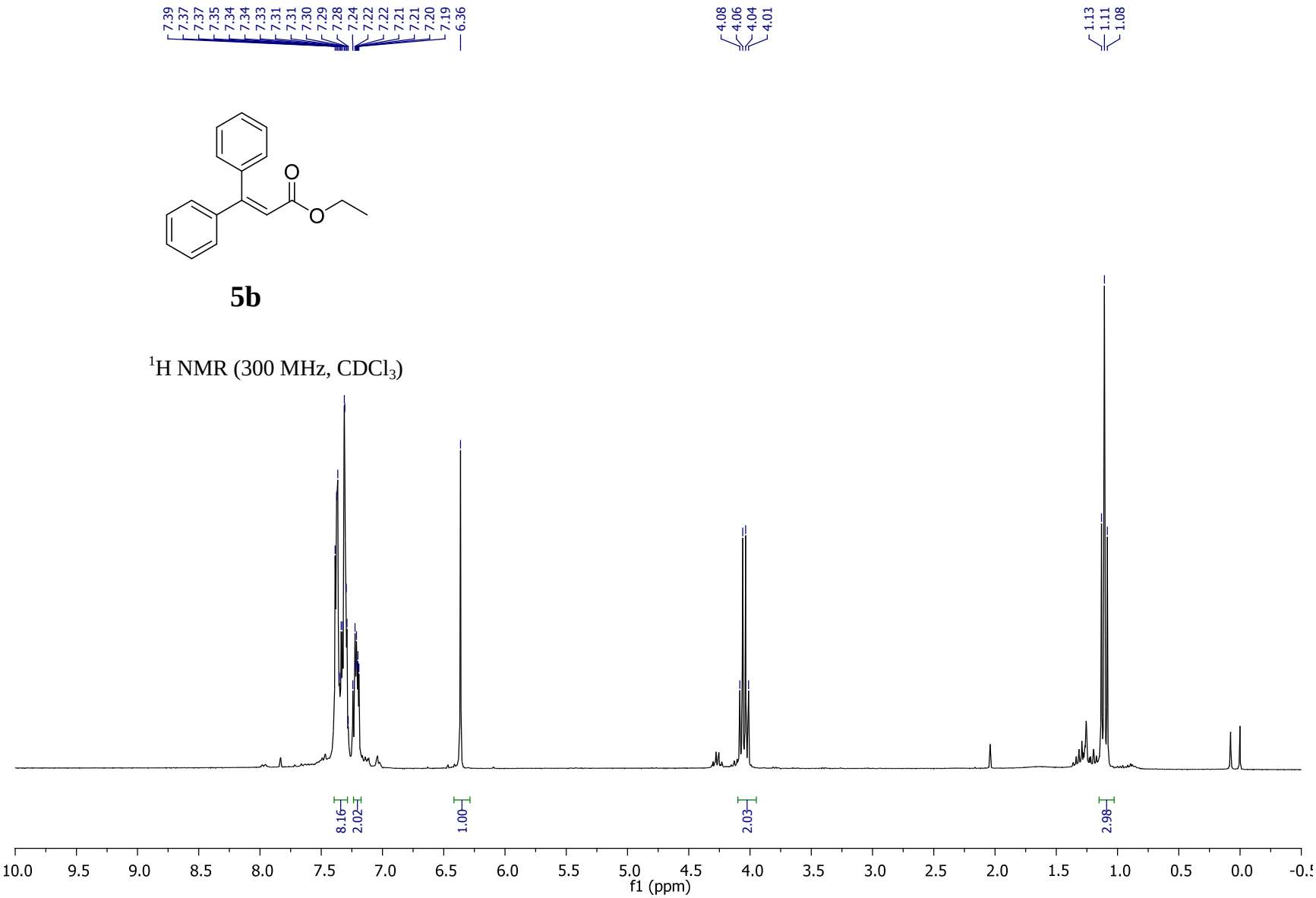
^{13}C NMR (75 MHz, $CDCl_3$)



5a

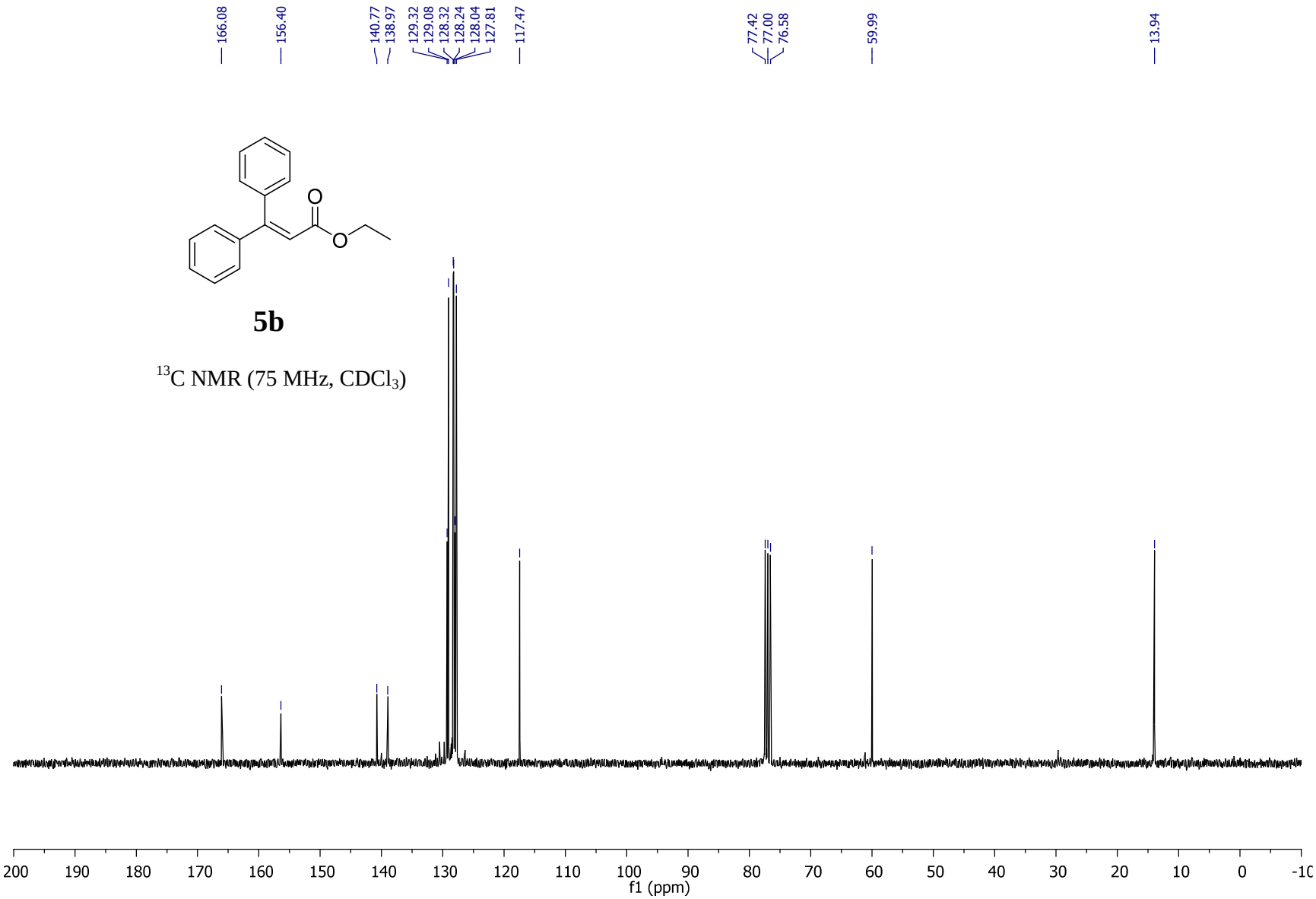
^{1}H NMR (300 MHz, $CDCl_3$)

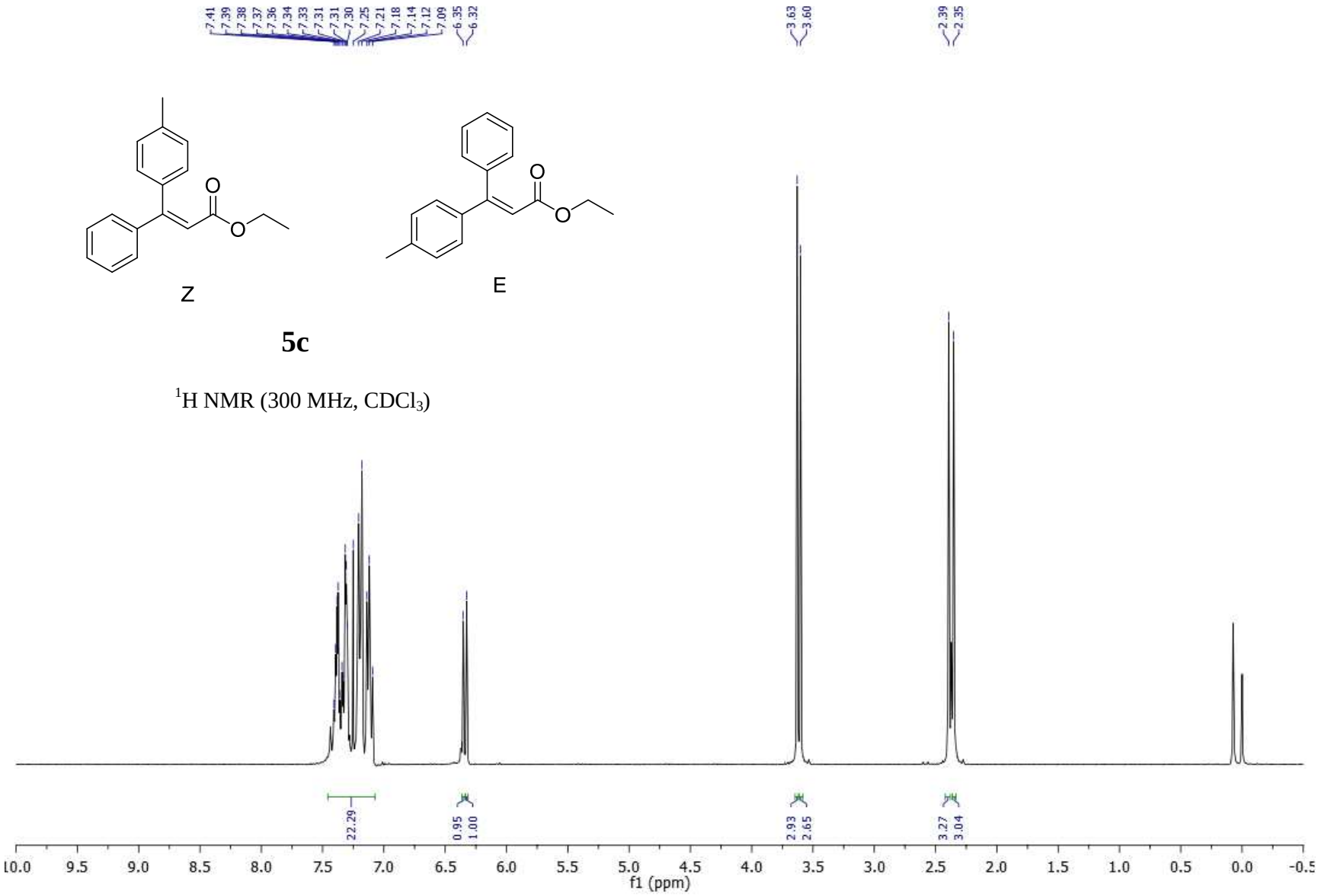

166.87
144.47
134.36
130.11
128.77
127.94
118.18
77.42
77.00
76.58
60.39
14.24
O
O
5a
13C NMR (75 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



5b

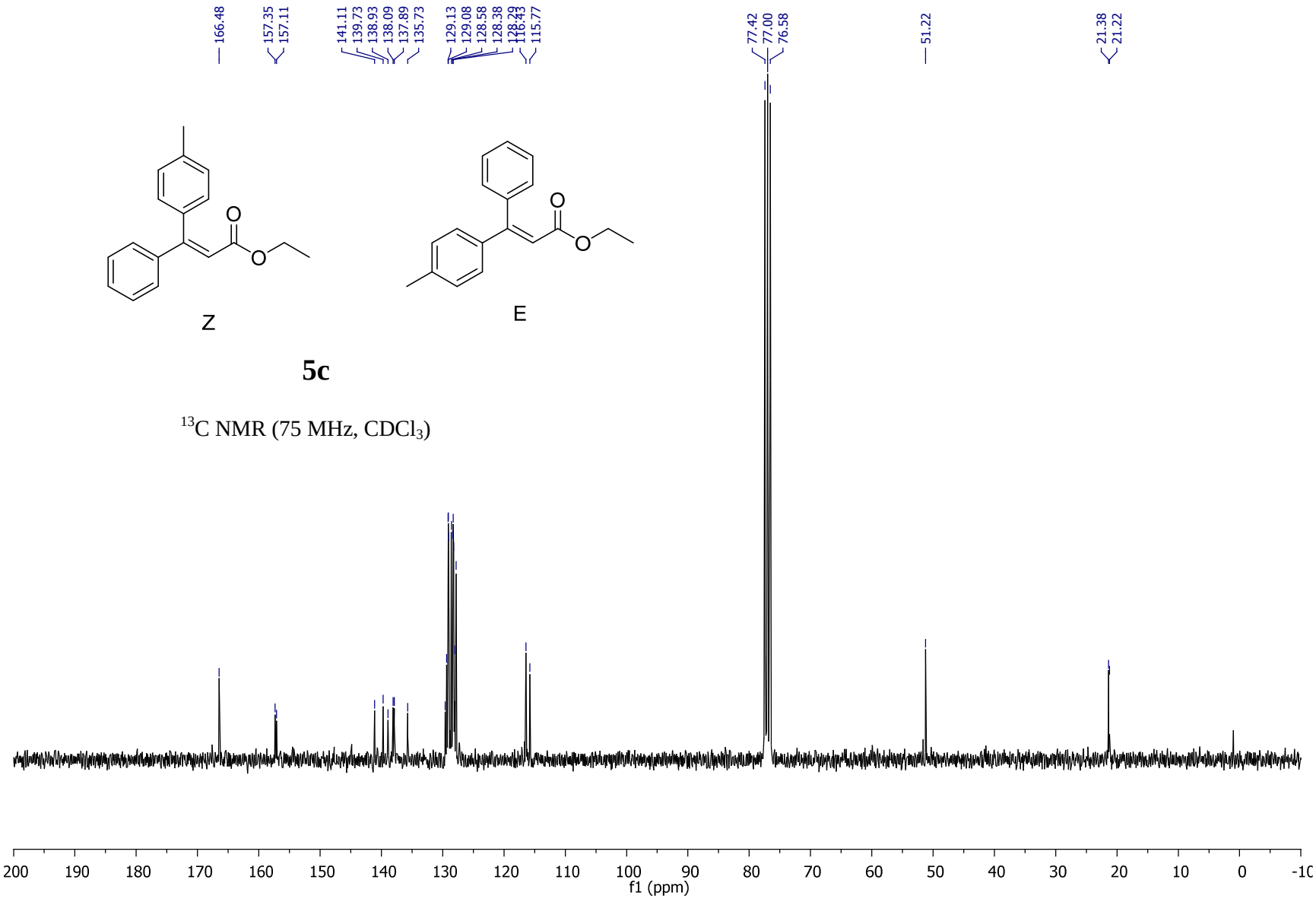
^{1}H NMR (300 MHz, $CDCl_3$)

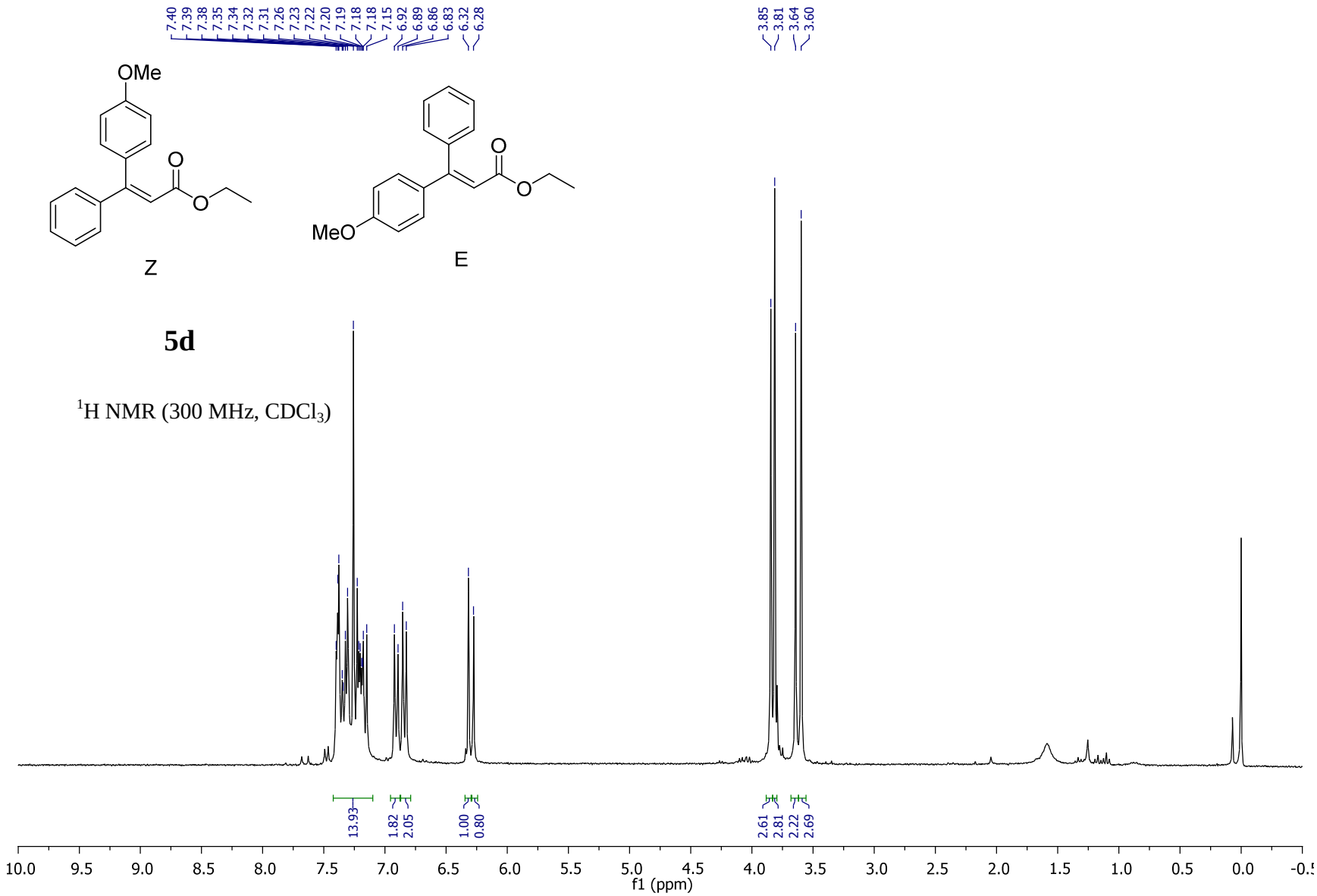

166.08
156.40
140.77
138.97
129.32
129.08
128.32
128.24
128.04
127.81
117.47
77.42
77.00
76.58
59.99
13.94
O
O
5b
13C NMR (75 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

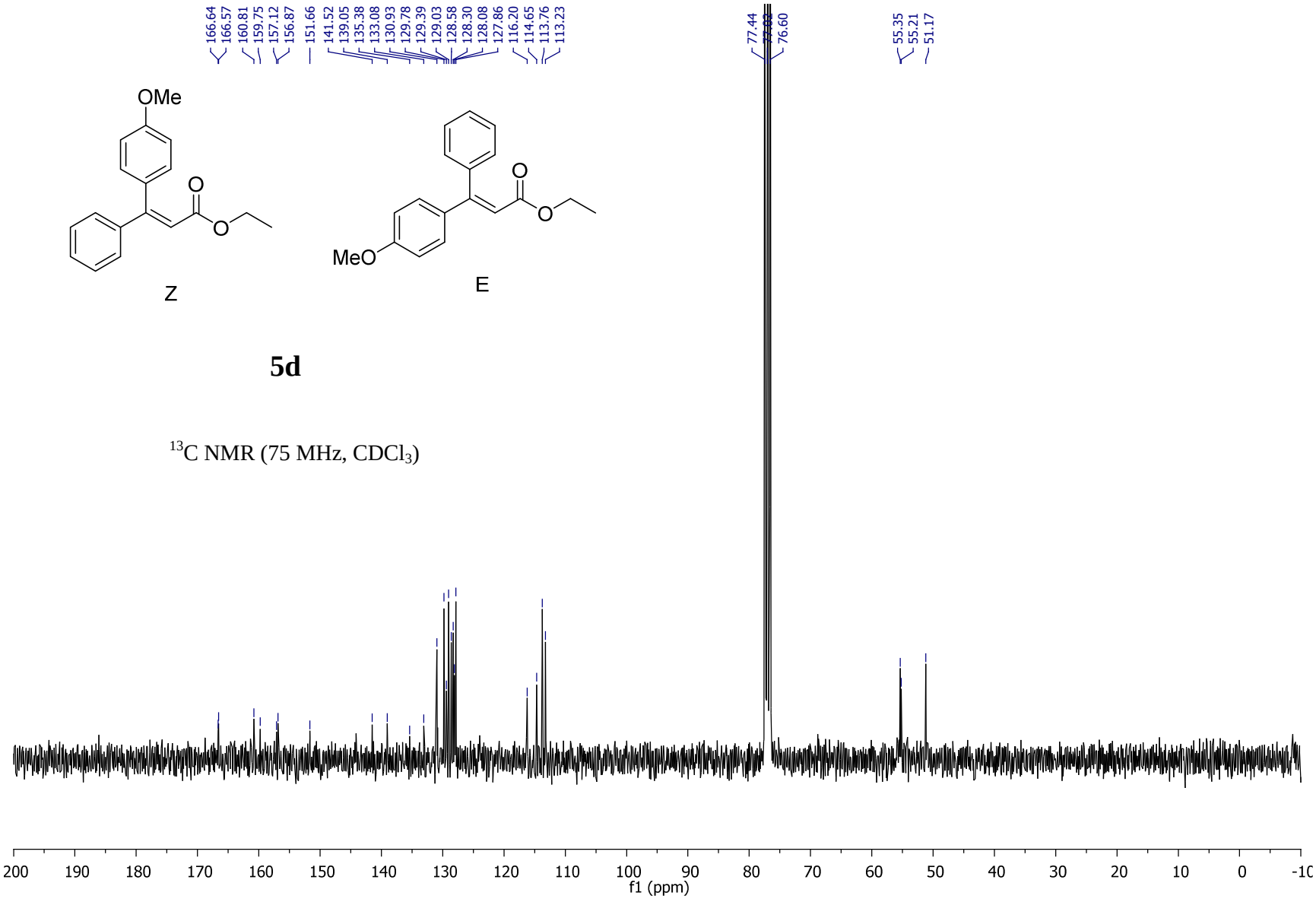


5c

^{1}H NMR (300 MHz, $CDCl_3$)


166.48
157.35
157.11
141.11
139.73
138.93
138.09
137.89
135.73
129.13
129.08
128.58
128.38
128.29
116.43
115.77
77.42
77.00
76.58
51.22
21.38
21.22
Z
E
5c
13C NMR (75 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.40
7.39
7.38
7.35
7.34
7.32
7.31
7.26
7.23
7.22
7.20
7.19
7.18
7.18
7.15
6.92
6.89
6.86
6.83
6.32
6.28
3.85
3.81
3.64
3.60
OMe
O
O
Z
MeO
O
O
E
5d
1H NMR (300 MHz, CDCl3)
13.93
1.82
2.05
1.00
0.80
2.61
2.81
2.22
2.69
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



5d

^{13}C NMR (75 MHz, $CDCl_3$)