Supporting Information

Synthesis of 3-Fluoroindoles via Photoredox Catalysis

Liubov I. Panferova,[†] Vladimir O. Smirnov,[†] Vitalij V. Levin,[†] Vladimir A. Kokorekin,[†,‡] Marina I. Struchkova,[†] Alexander D. Dilman[†,*]

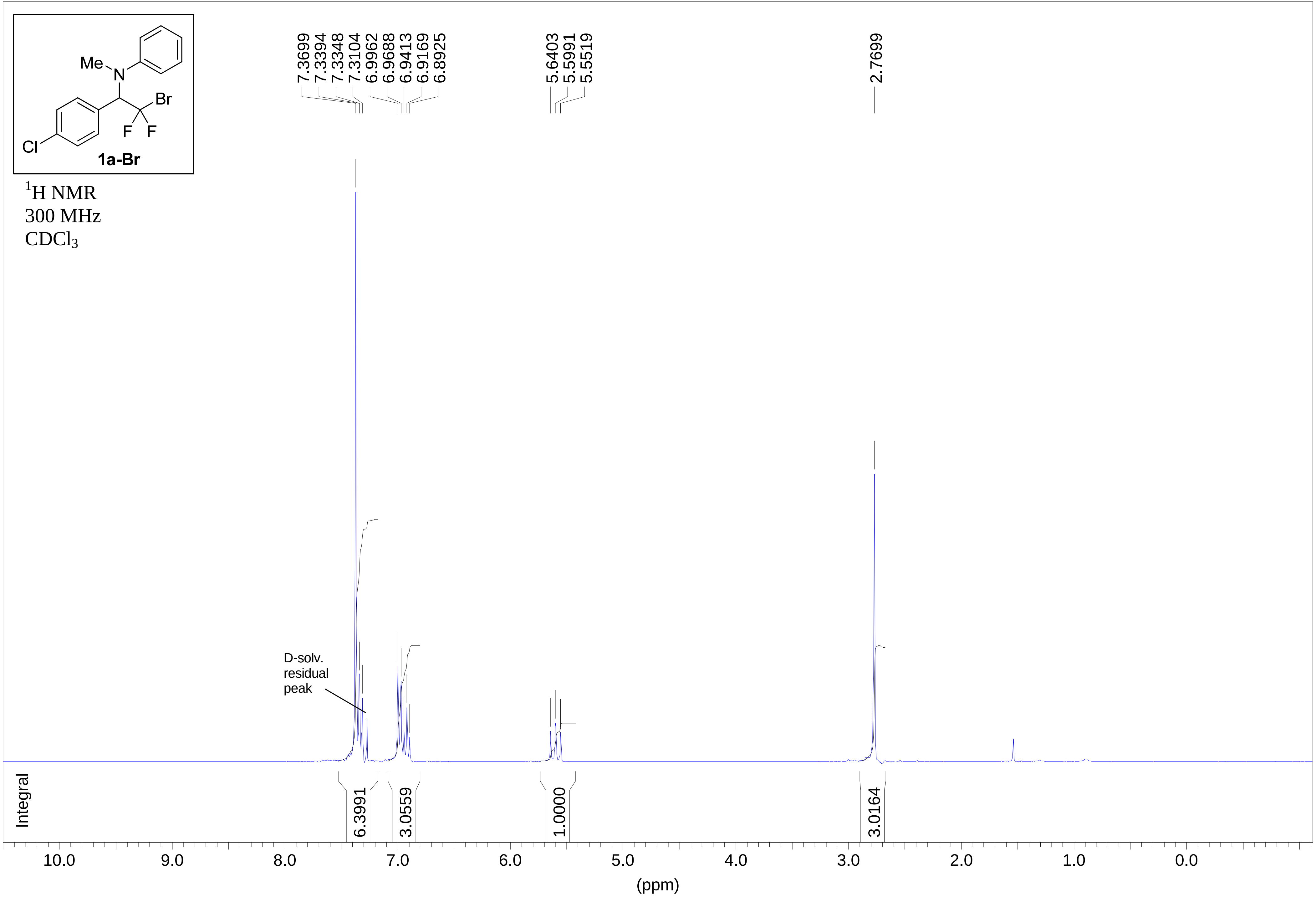
[†]*N. D. Zelinsky Institute of Organic Chemistry, 119991 Moscow, Leninsky prosp. 47, Russian Federation*

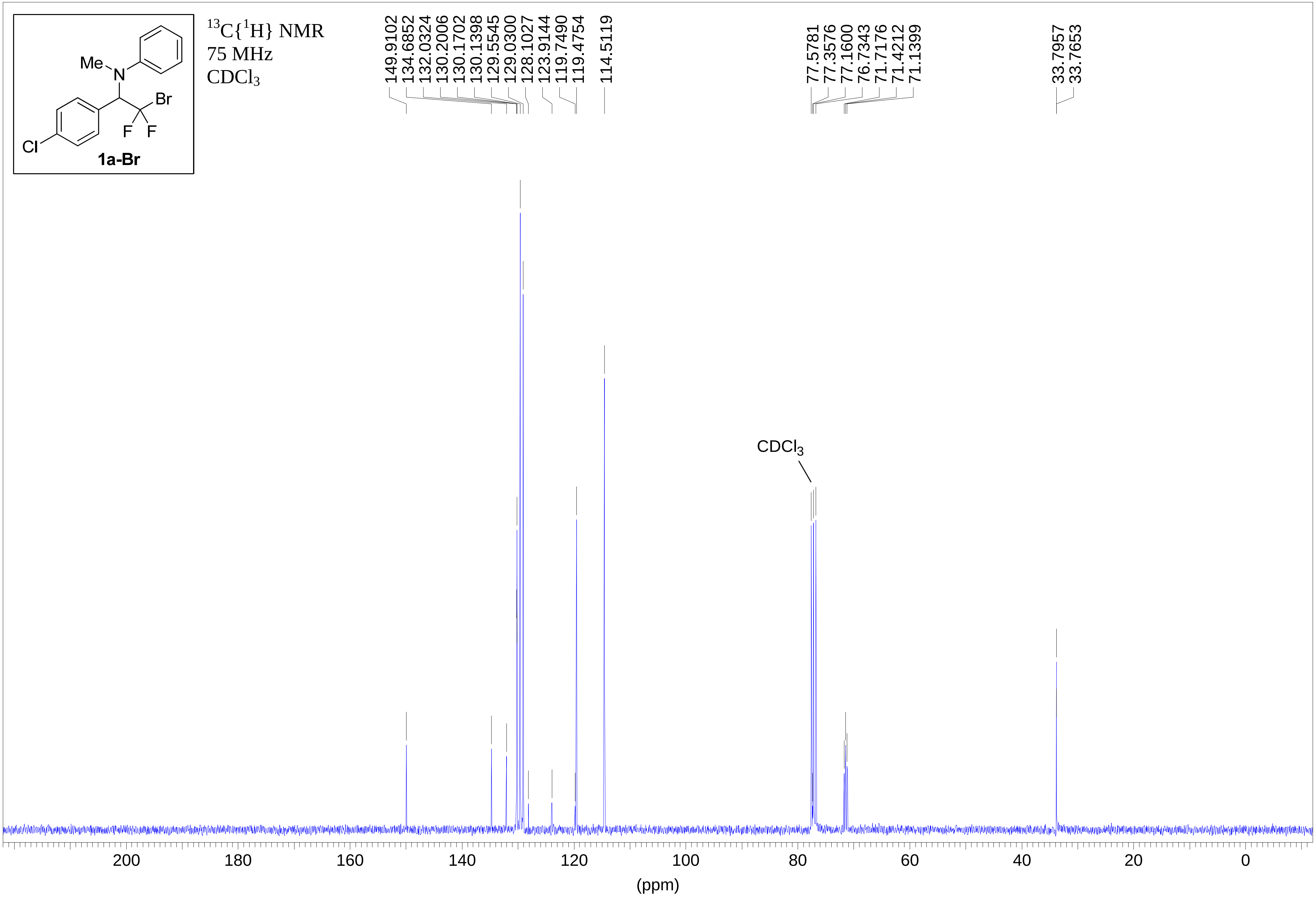
[‡]*First I. M. Sechenov Moscow State Medical University, 119991 Moscow, Trubetskaya st. 8-2, Russian Federation*

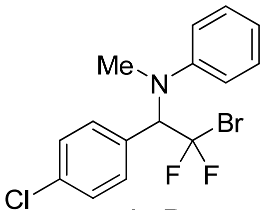
adil25@mail.ru

Content

NMR spectra

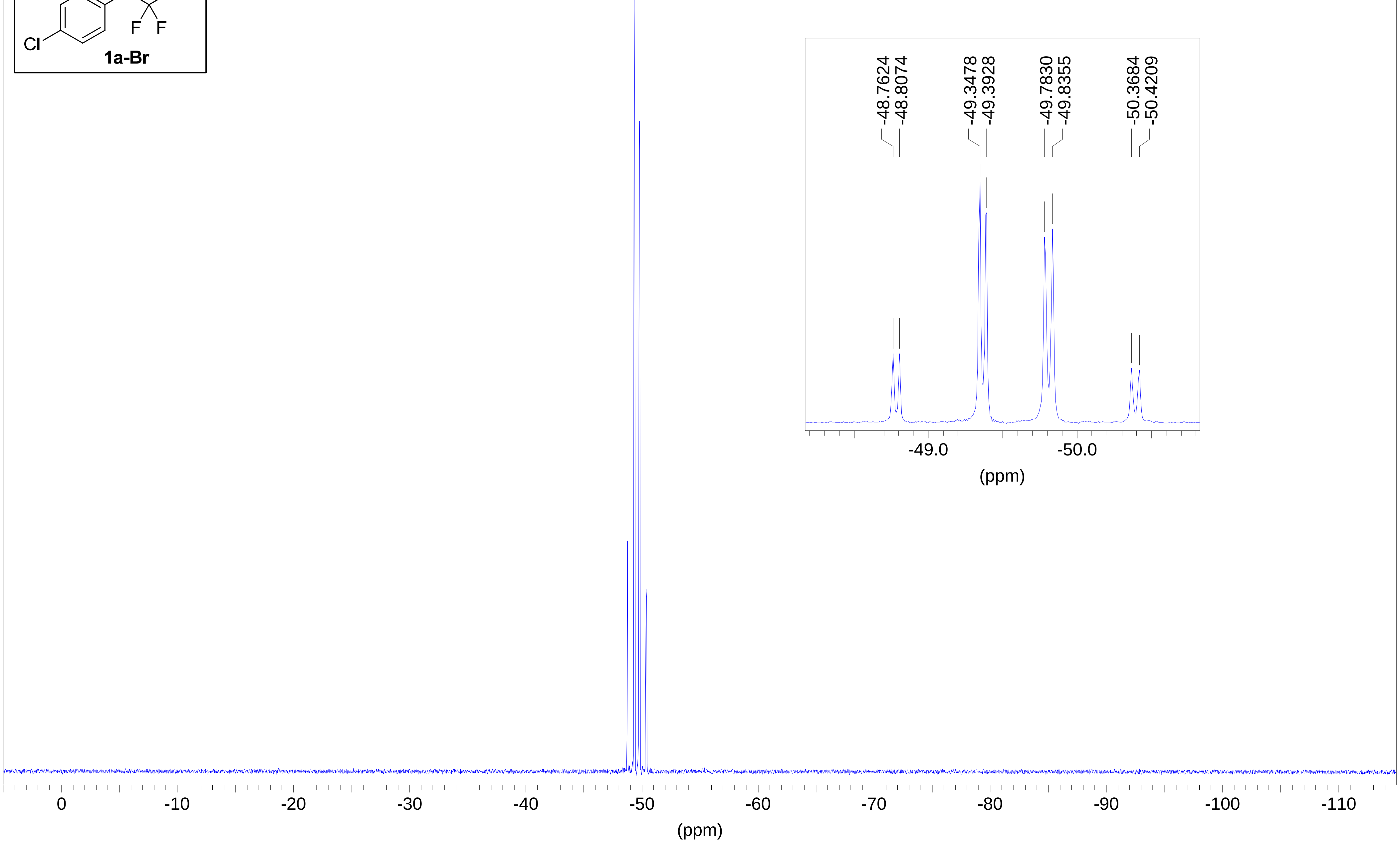

Me
N
Br
F F
Cl
1a-Br
^{1}H NMR
300 MHz
$CDCl_3$
7.3699
7.3394
7.3348
7.3104
6.9962
6.9688
6.9413
6.9169
6.8925
5.6403
5.5991
5.5519
2.7699
D-solv.
residual
peak
Integral
6.3991
3.0559
1.0000
3.0164
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

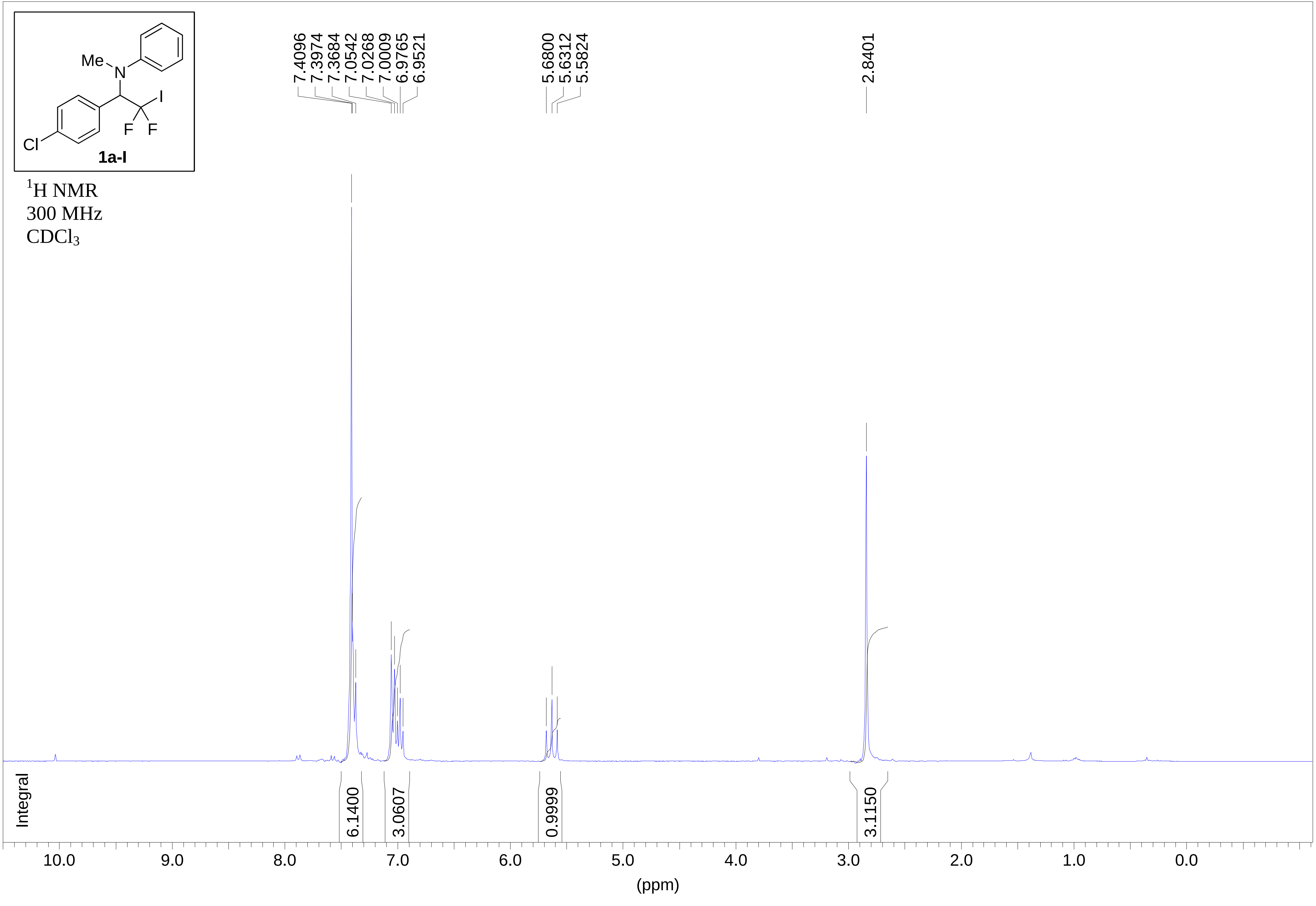

Me
N
Br
F F
Cl
1a-Br
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
149.9102
134.6852
132.0324
130.2006
130.1702
130.1398
129.5545
129.0300
128.1027
123.9144
119.7490
119.4754
114.5119
77.5781
77.3576
77.1600
76.7343
71.7176
71.4212
71.1399
33.7957
33.7653
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)

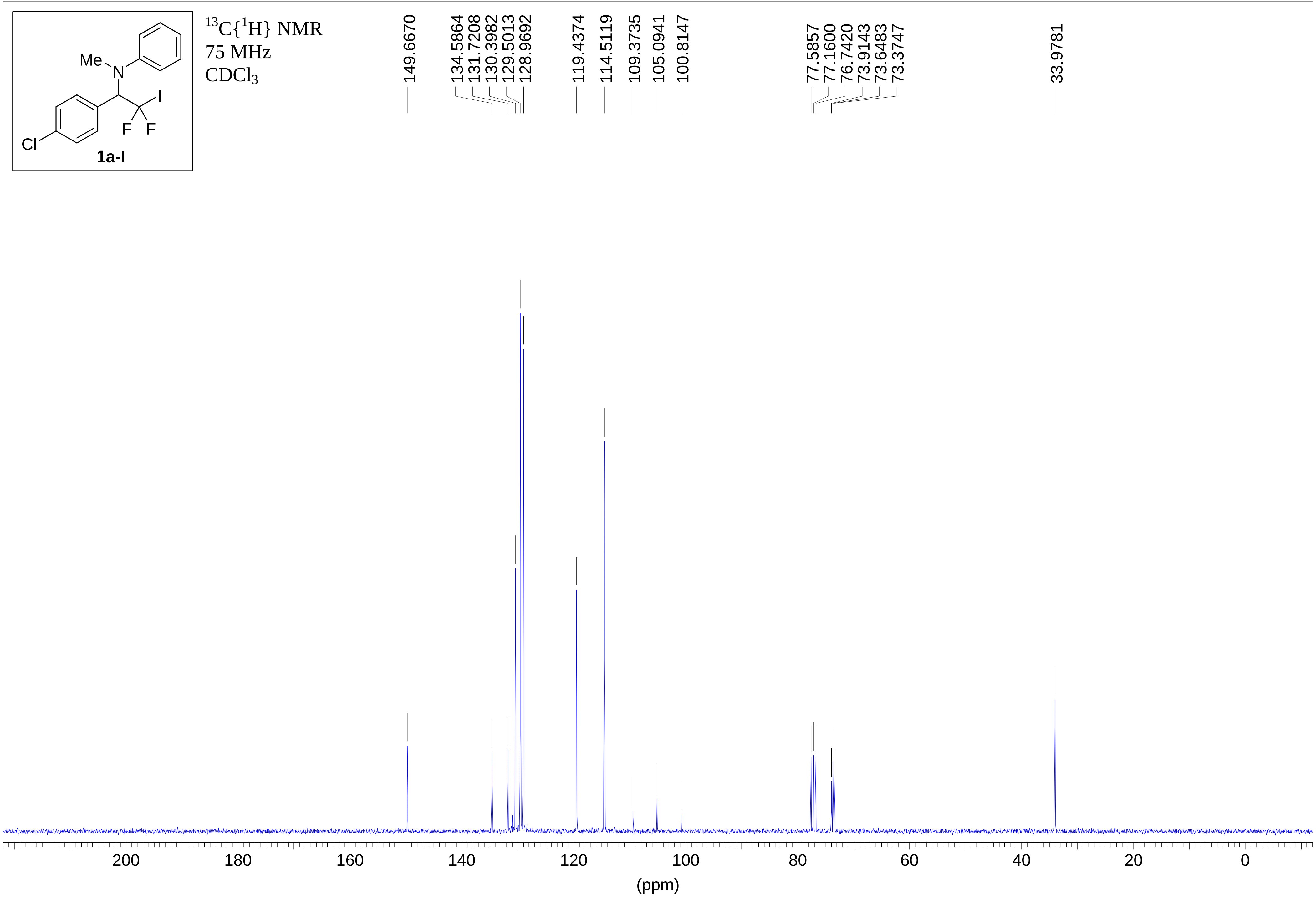


1a-Br

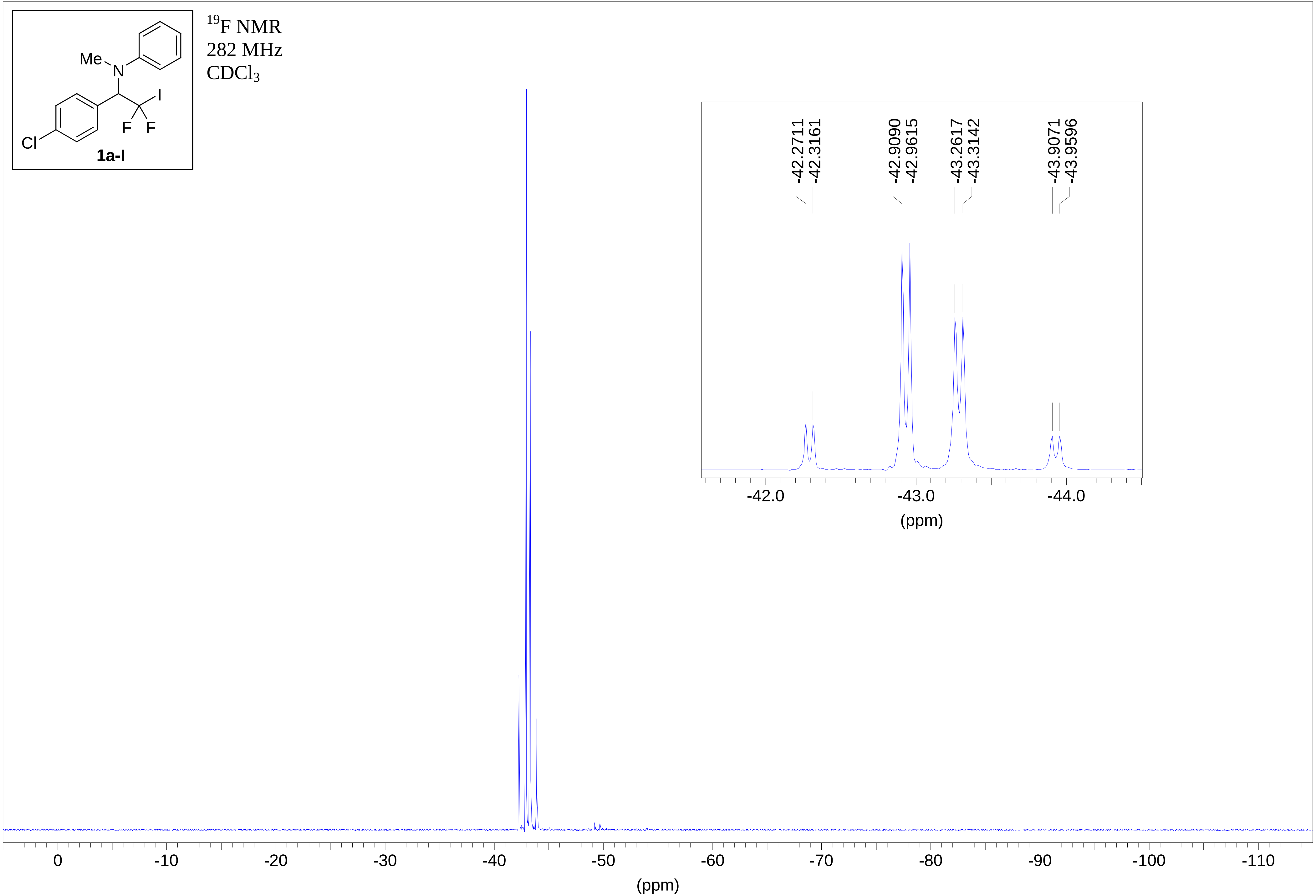
^{19}F NMR
282 MHz
$CDCl_3$

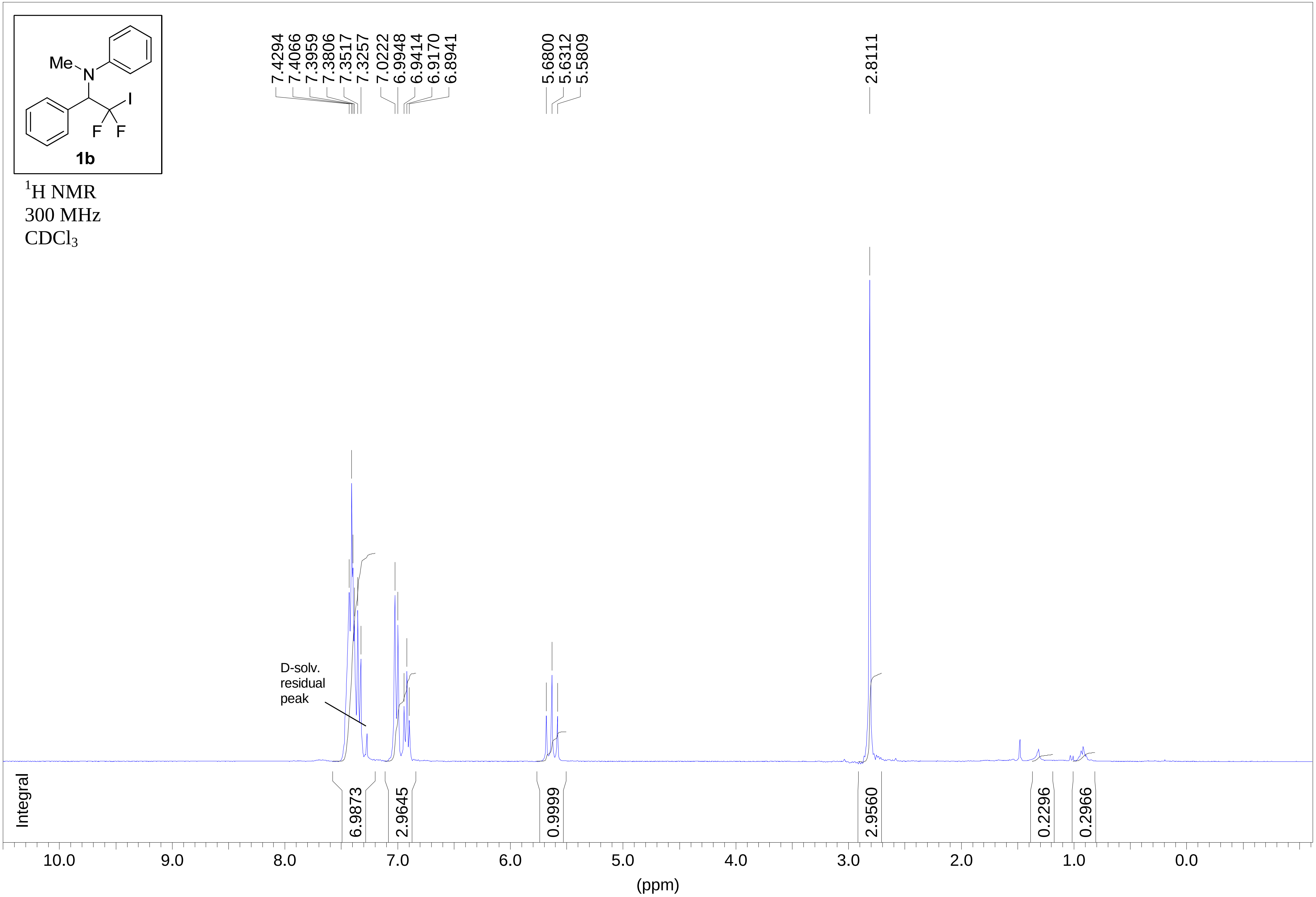


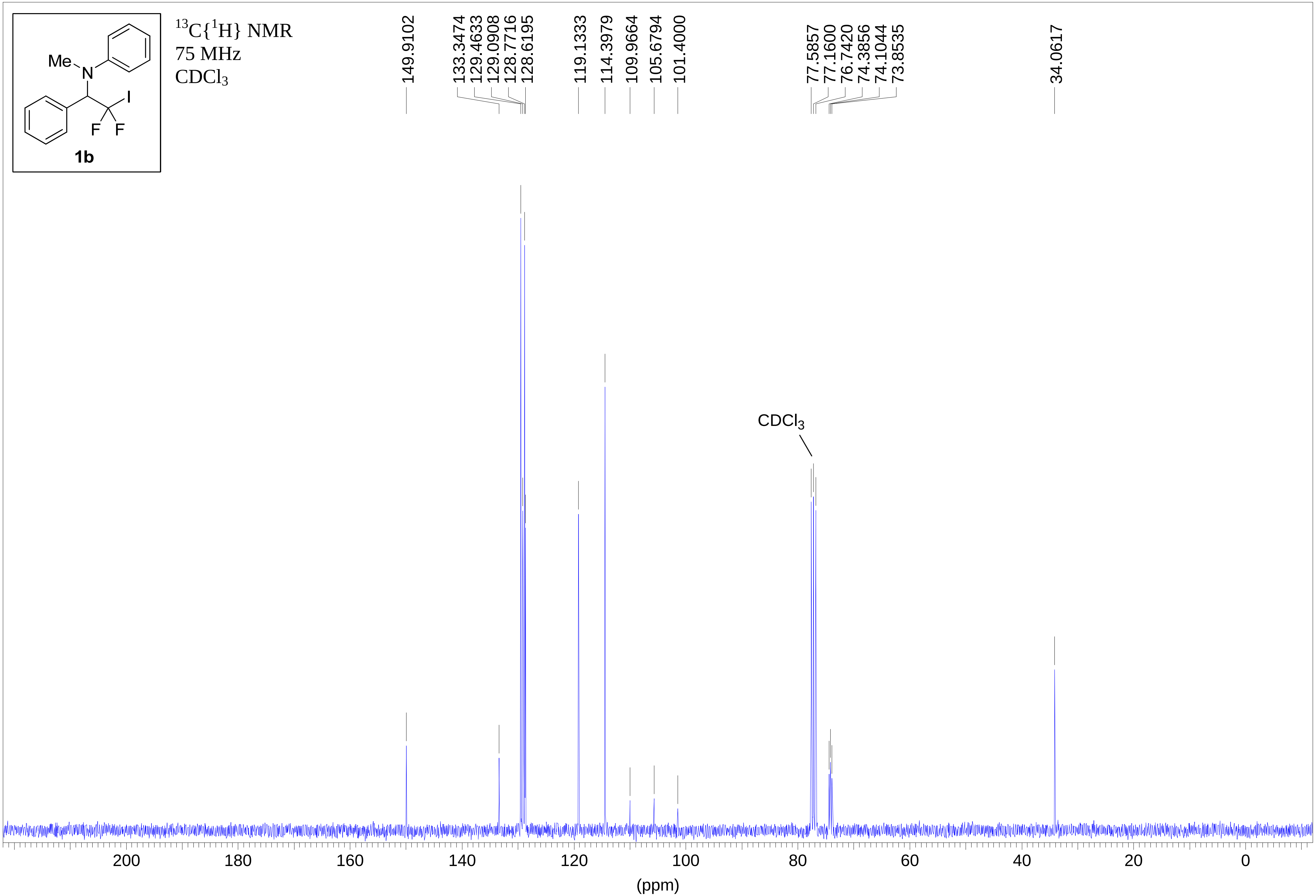

Me
N
I
F
F
Cl
1a-I
1H NMR
300 MHz
CDCl3
7.4096
7.3974
7.3684
7.0542
7.0268
7.0009
6.9765
6.9521
5.6800
5.6312
5.5824
2.8401
Integral
6.1400
3.0607
0.9999
3.1150
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)



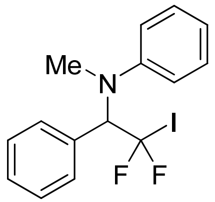
Me
N
I
F F
Cl
1a-I
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
149.6670
134.5864
131.7208
130.3982
129.5013
128.9692
119.4374
114.5119
109.3735
105.0941
100.8147
77.5857
77.1600
76.7420
73.9143
73.6483
73.3747
33.9781
200
180
160
140
120
100
80
60
40
20
0
(ppm)


Me
N
I
F F
Cl
1a-I
19F NMR
282 MHz
CDCl3
-42.2711
-42.3161
-42.9090
-42.9615
-43.2617
-43.3142
-43.9071
-43.9596
-42.0
-43.0
-44.0
(ppm)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
(ppm)


Me
N
I
F F
1b
^{1}H NMR
300 MHz
$CDCl_3$
7.4294
7.4066
7.3959
7.3806
7.3517
7.3257
7.0222
6.9948
6.9414
6.9170
6.8941
5.6800
5.6312
5.5809
2.8111
D-solv.
residual
peak
Integral
6.9873
2.9645
0.9999
2.9560
0.2296
0.2966
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

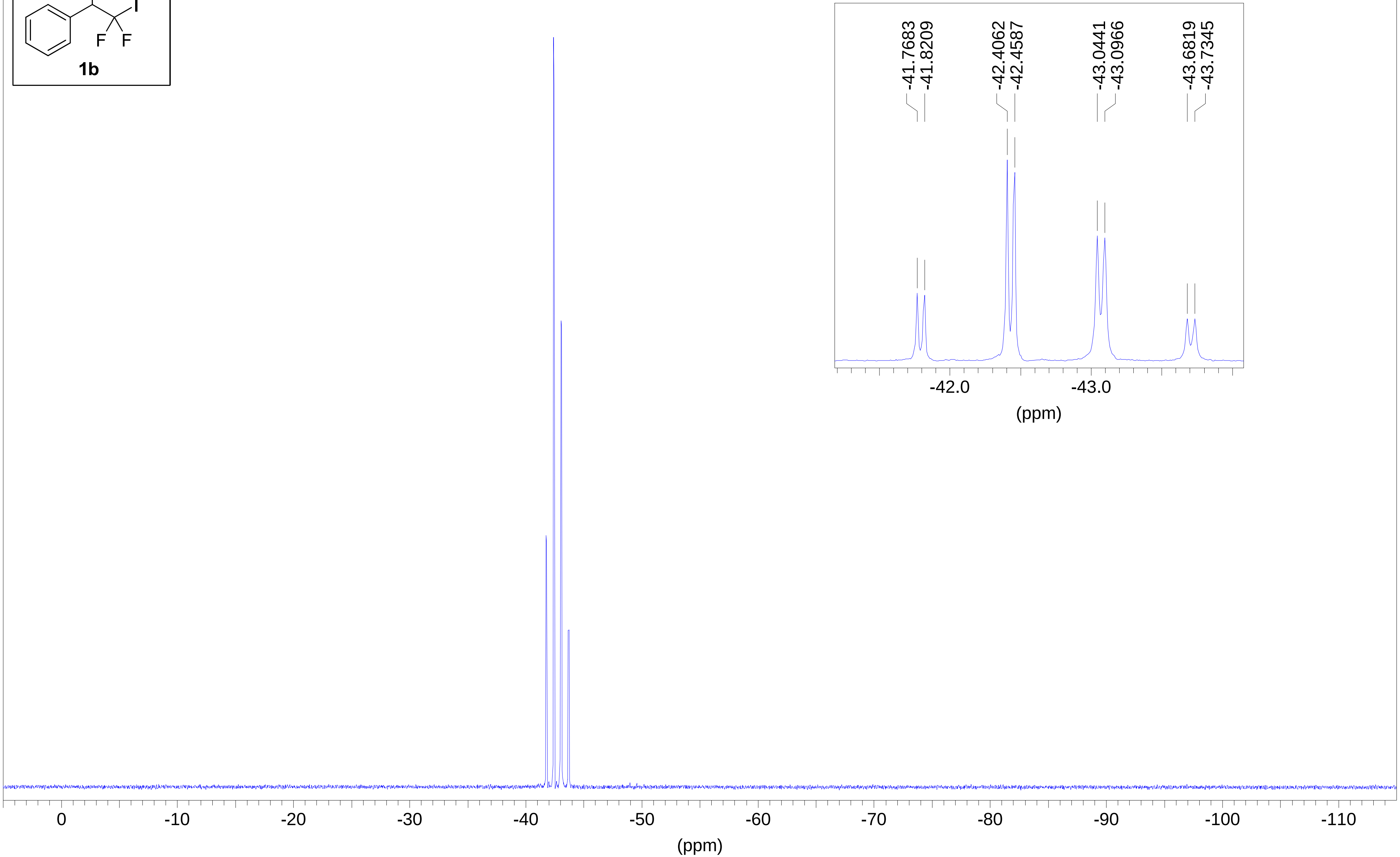


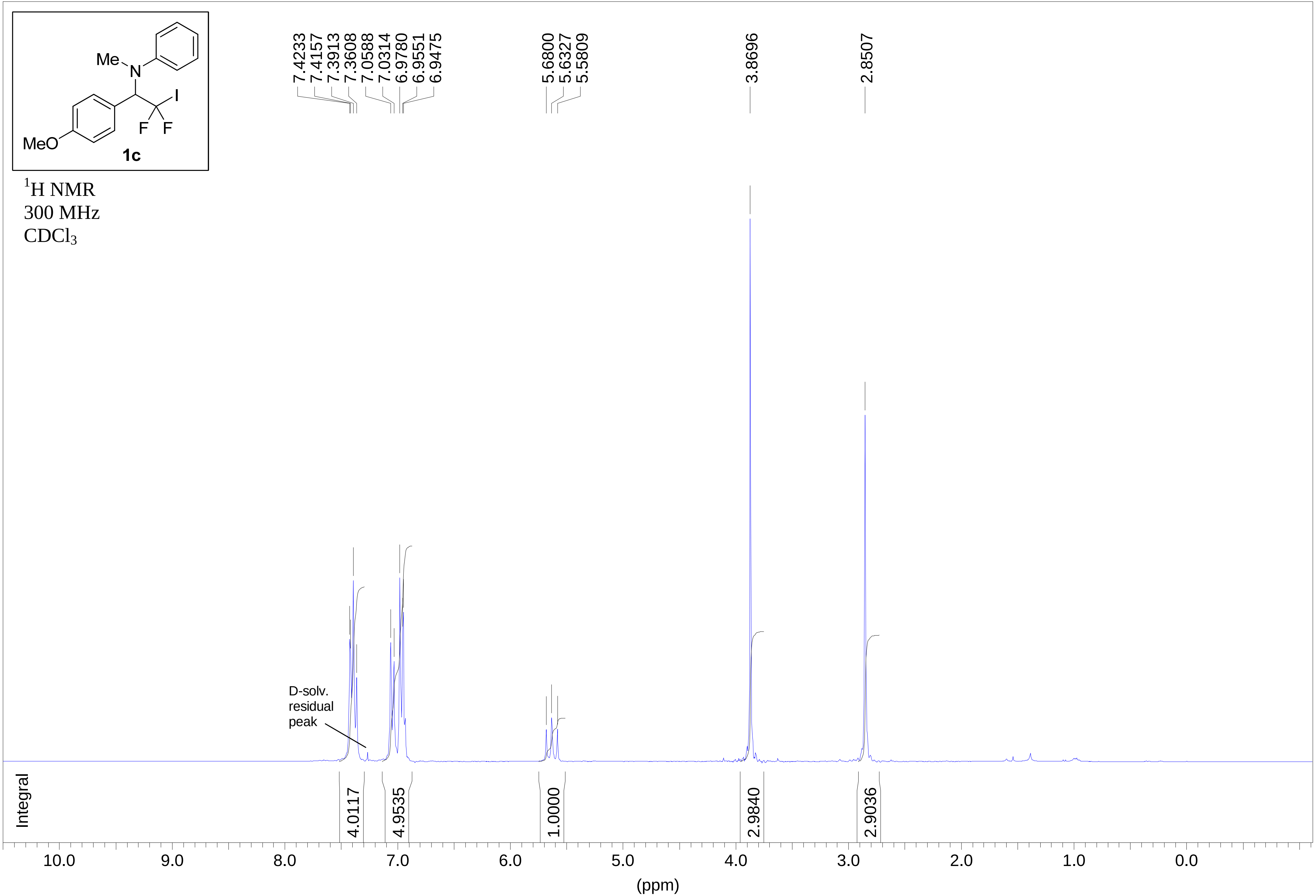
Me
N
I
F F
1b
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
149.9102
133.3474
129.4633
129.0908
128.7716
128.6195
119.1333
114.3979
109.9664
105.6794
101.4000
77.5857
77.1600
76.7420
74.3856
74.1044
73.8535
34.0617
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)



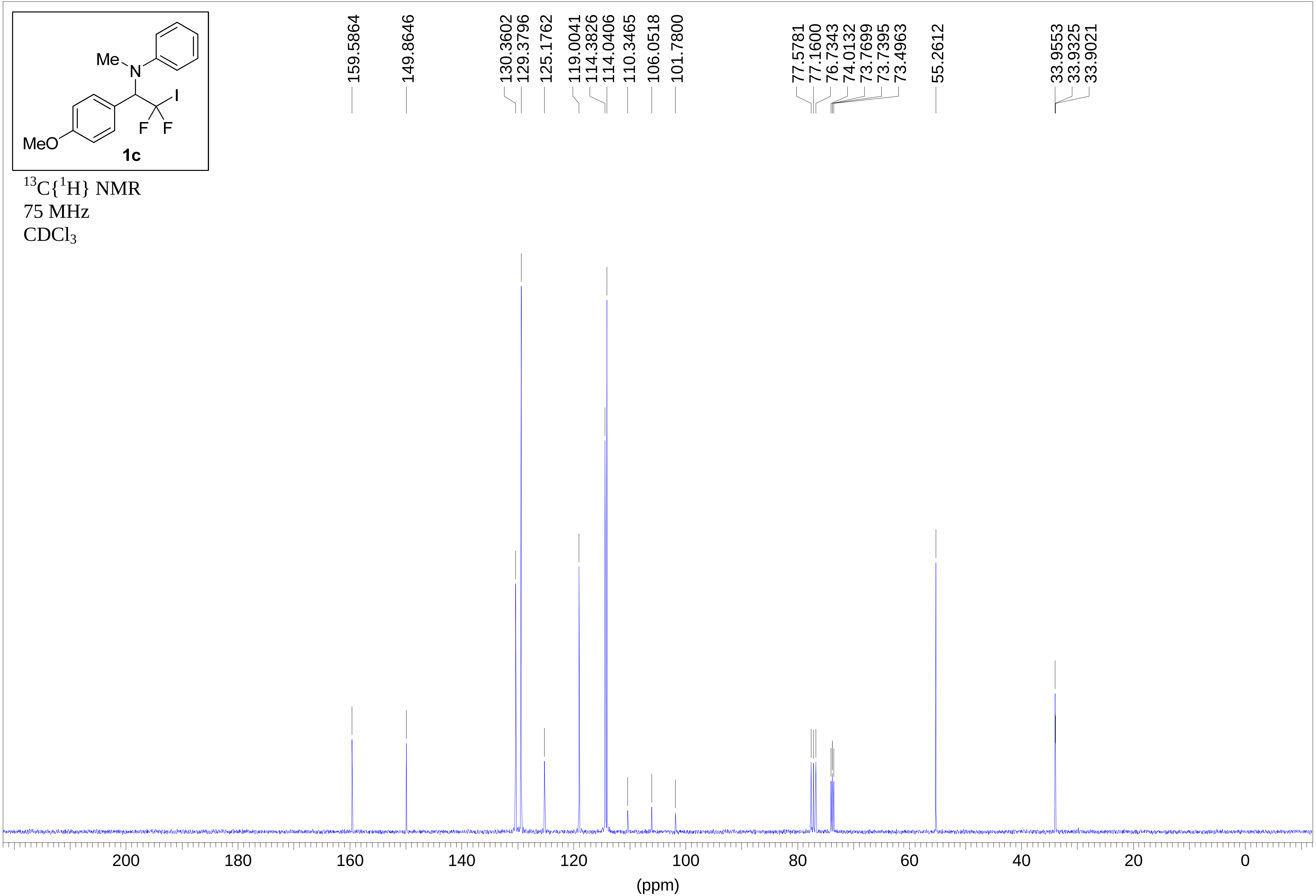
1b

^{19}F NMR
282 MHz
$CDCl_3$

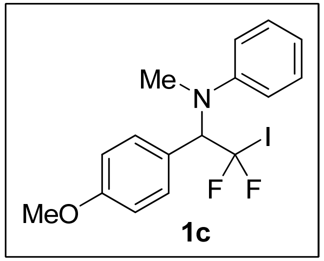




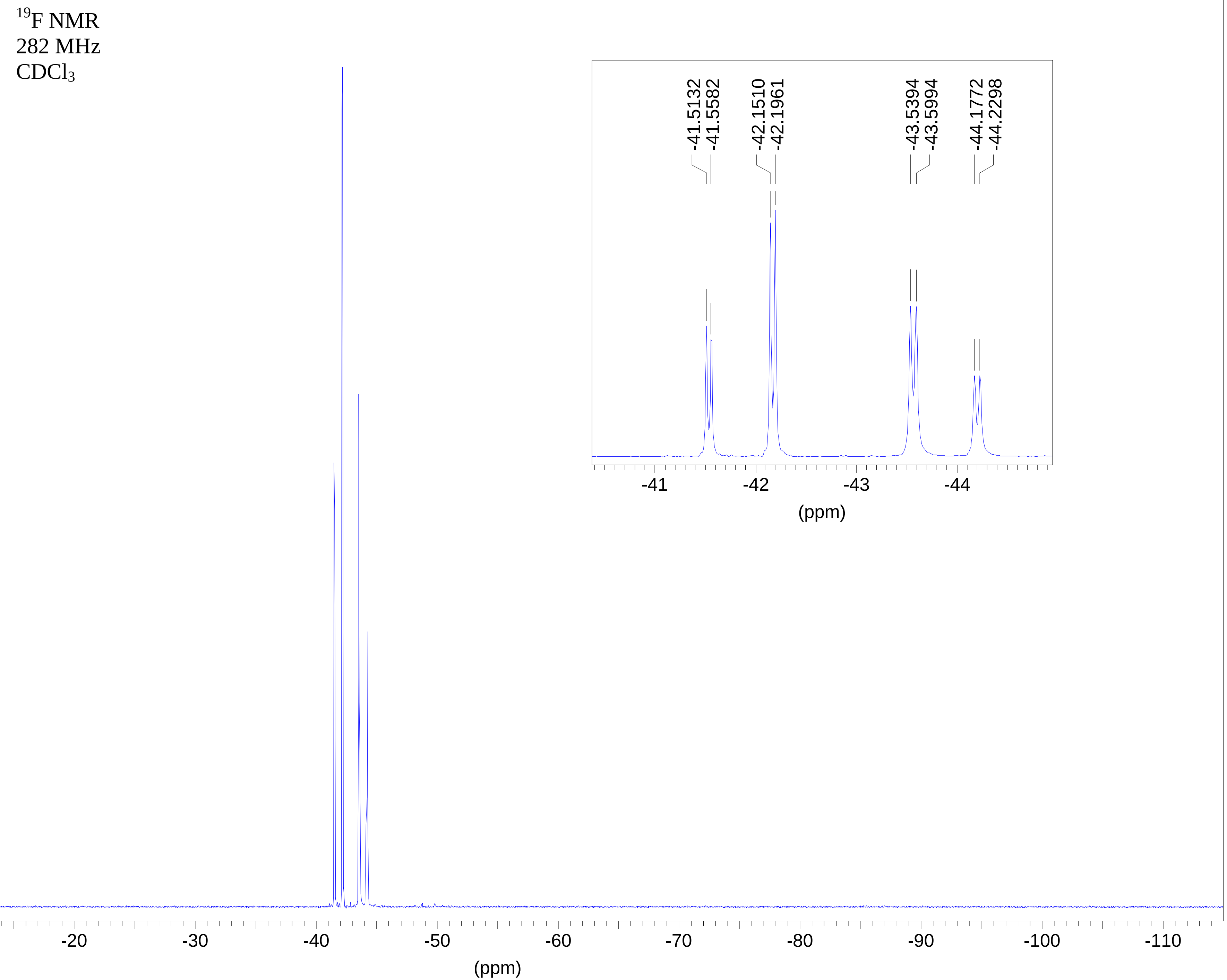
Me
N
I
F F
MeO
1c
^{1}H NMR
300 MHz
$CDCl_3$
7.4233
7.4157
7.3913
7.3608
7.0588
7.0314
6.9780
6.9551
6.9475
5.6800
5.6327
5.5809
3.8696
2.8507
D-solv.
residual
peak
Integral
4.0117
4.9535
1.0000
2.9840
2.9036
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)



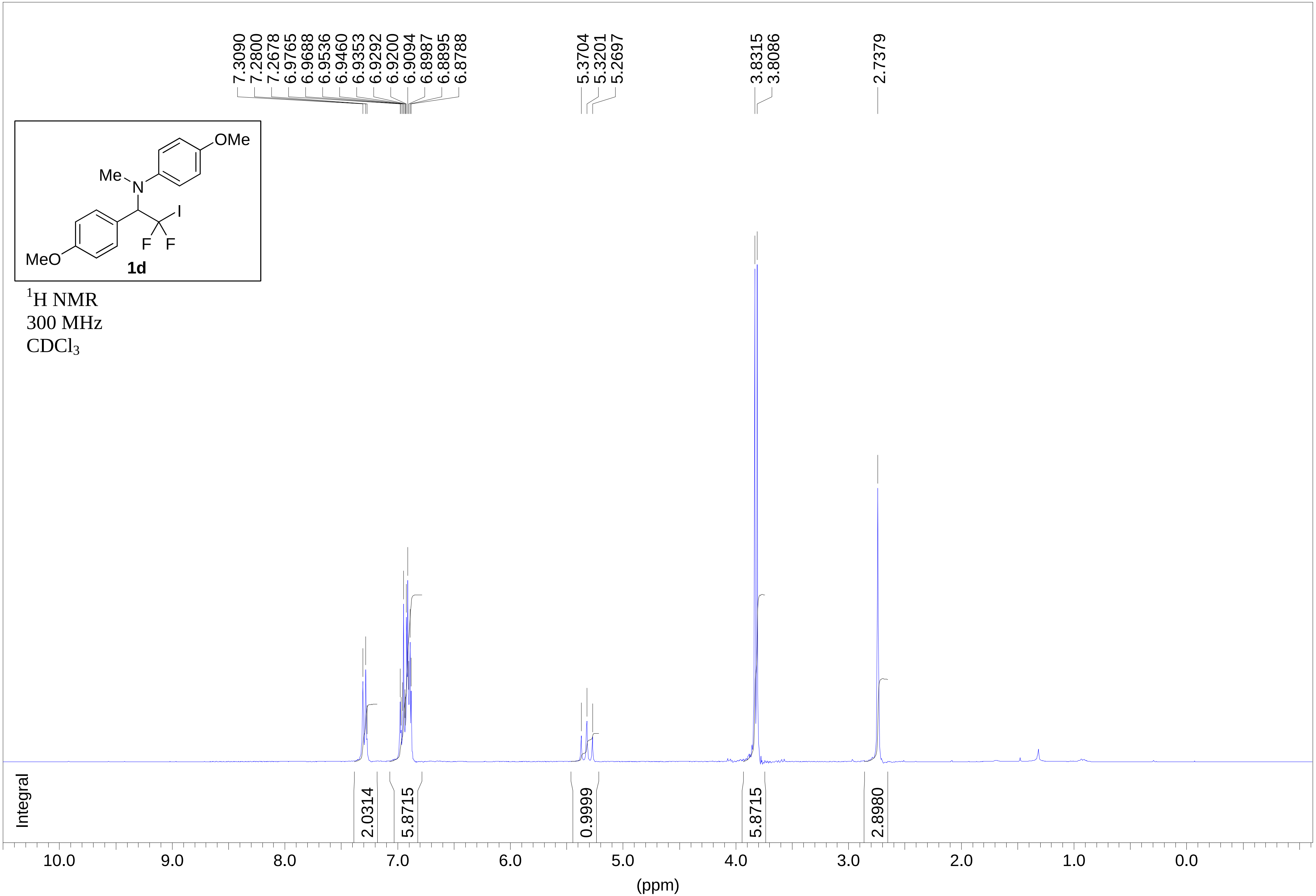
Me
N
I
F F
MeO
1c
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
159.5864
149.8646
130.3602
129.3796
125.1762
119.0041
114.3826
114.0406
110.3465
106.0518
101.7800
77.5781
77.1600
76.7343
74.0132
73.7699
73.7395
73.4963
55.2612
33.9553
33.9325
33.9021
200
180
160
140
120
100
80
60
40
20
0
(ppm)

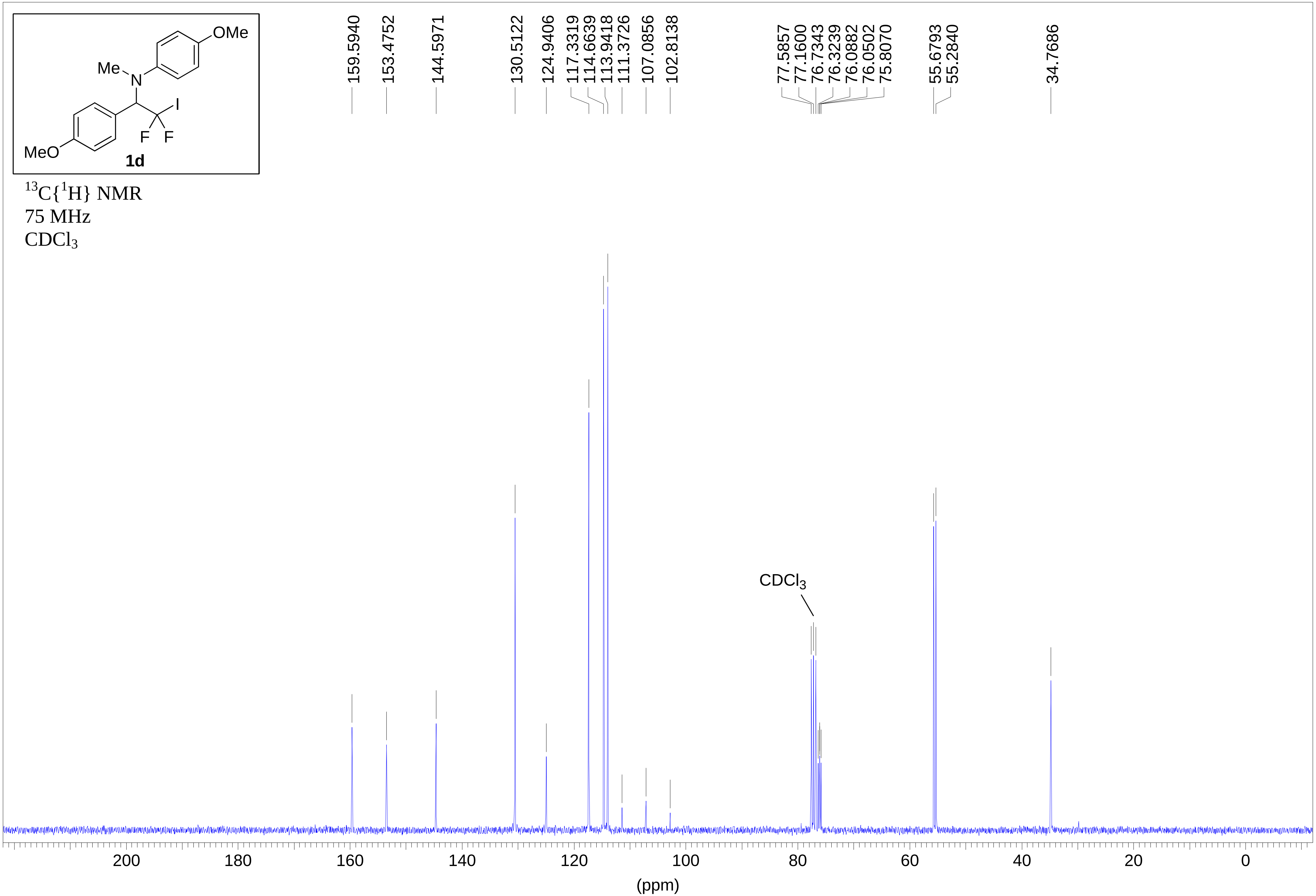


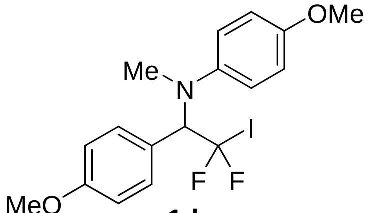
Me
N
I
F F
MeO
1c



^{19}F NMR
282 MHz
$CDCl_3$
-41.5132
-41.5582
-42.1510
-42.1961
-43.5394
-43.5994
-44.1772
-44.2298
-41
-42
-43
-44
(ppm)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
(ppm)

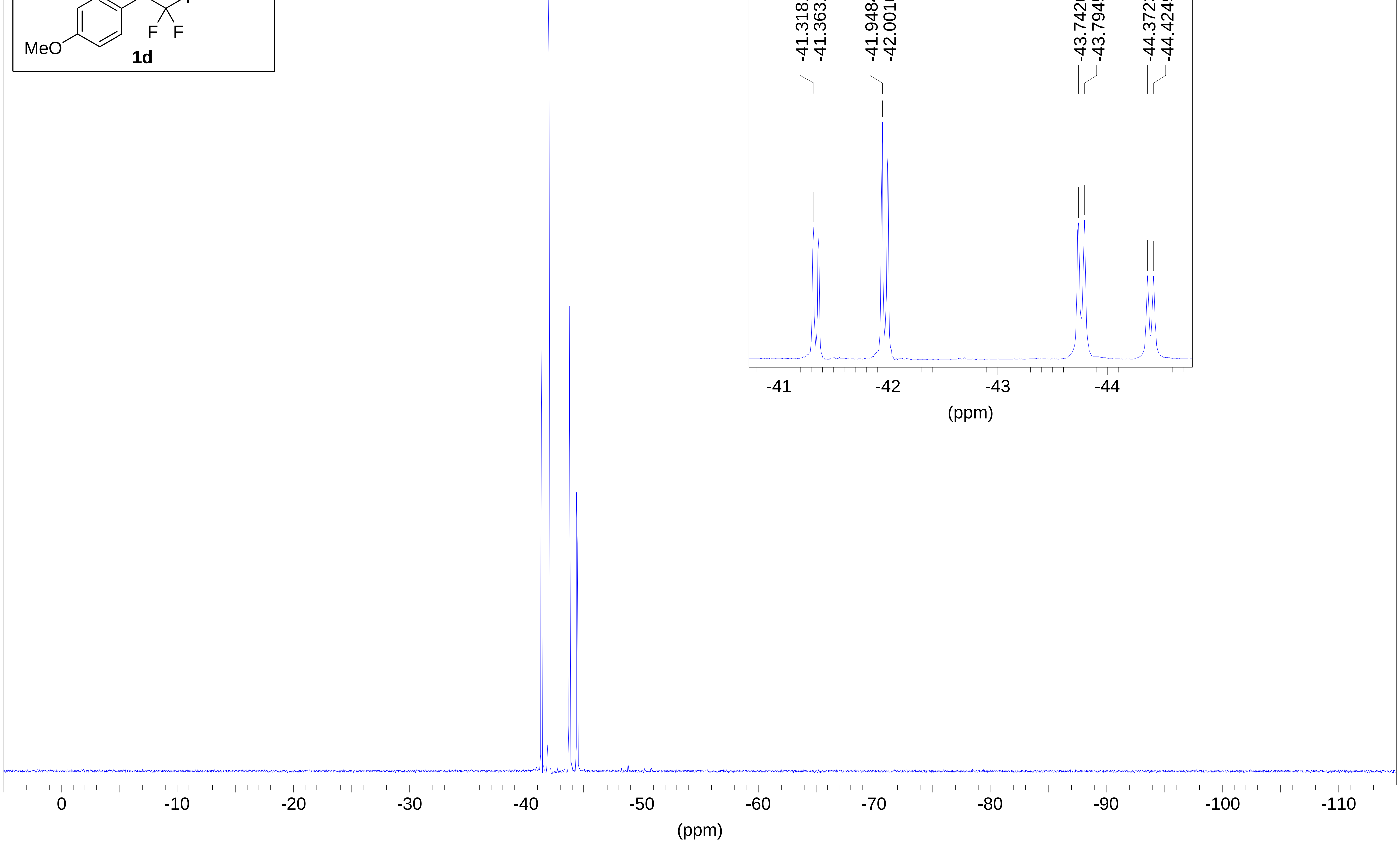

7.3090
7.2800
7.2678
6.9765
6.9688
6.9536
6.9460
6.9353
6.9292
6.9200
6.9094
6.8987
6.8895
6.8788
5.3704
5.3201
5.2697
3.8315
3.8086
2.7379
OMe
Me
N
I
F
F
MeO
1d
1H NMR
300 MHz
CDCl3
Integral
2.0314
5.8715
0.9999
5.8715
2.8980
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

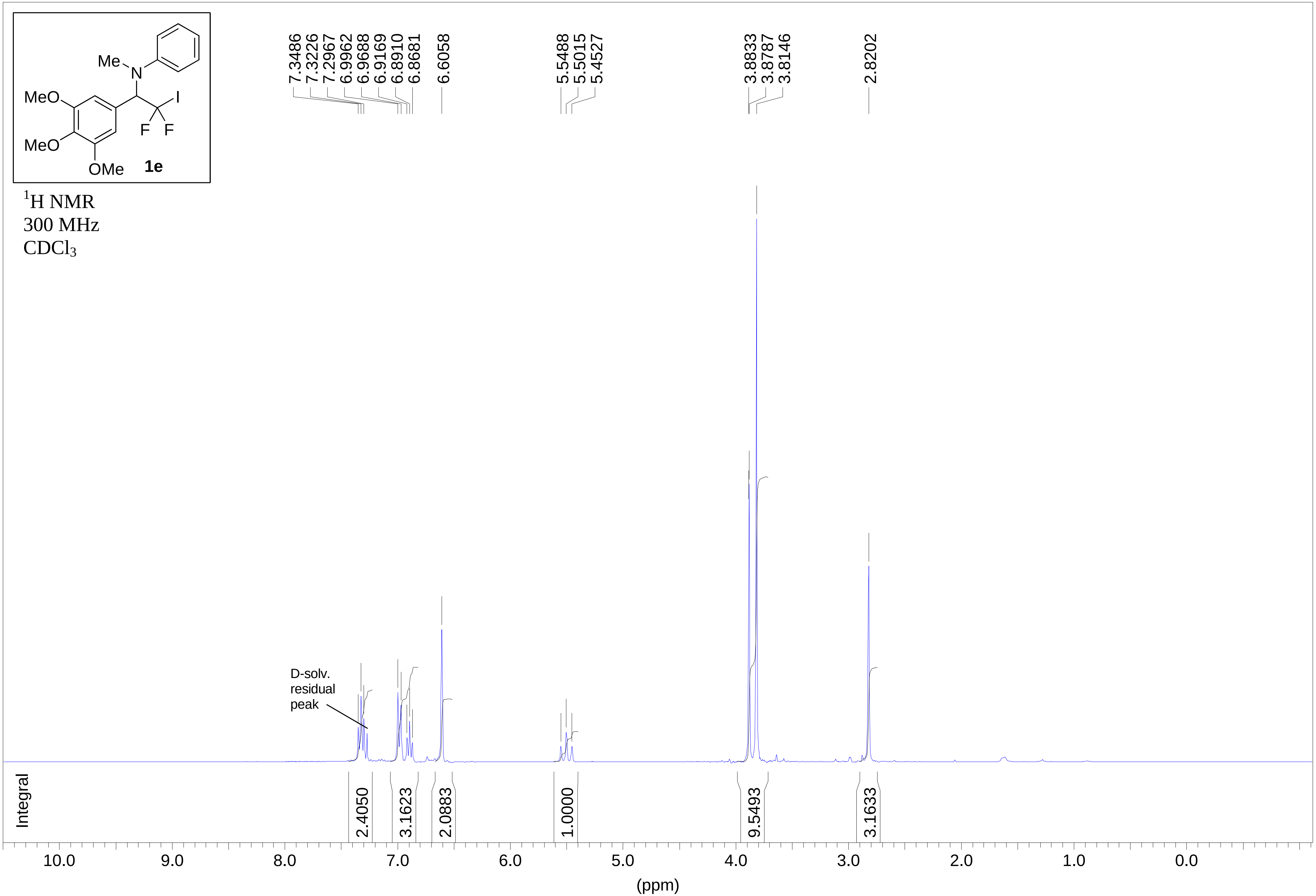

OMe
Me
N
I
F F
MeO
1d
$^{13}C\{^1H\}$ NMR
75 MHz
$CDCl_3$
159.5940
153.4752
144.5971
130.5122
124.9406
117.3319
114.6639
113.9418
111.3726
107.0856
102.8138
77.5857
77.1600
76.7343
76.3239
76.0882
76.0502
75.8070
55.6793
55.2840
34.7686
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)



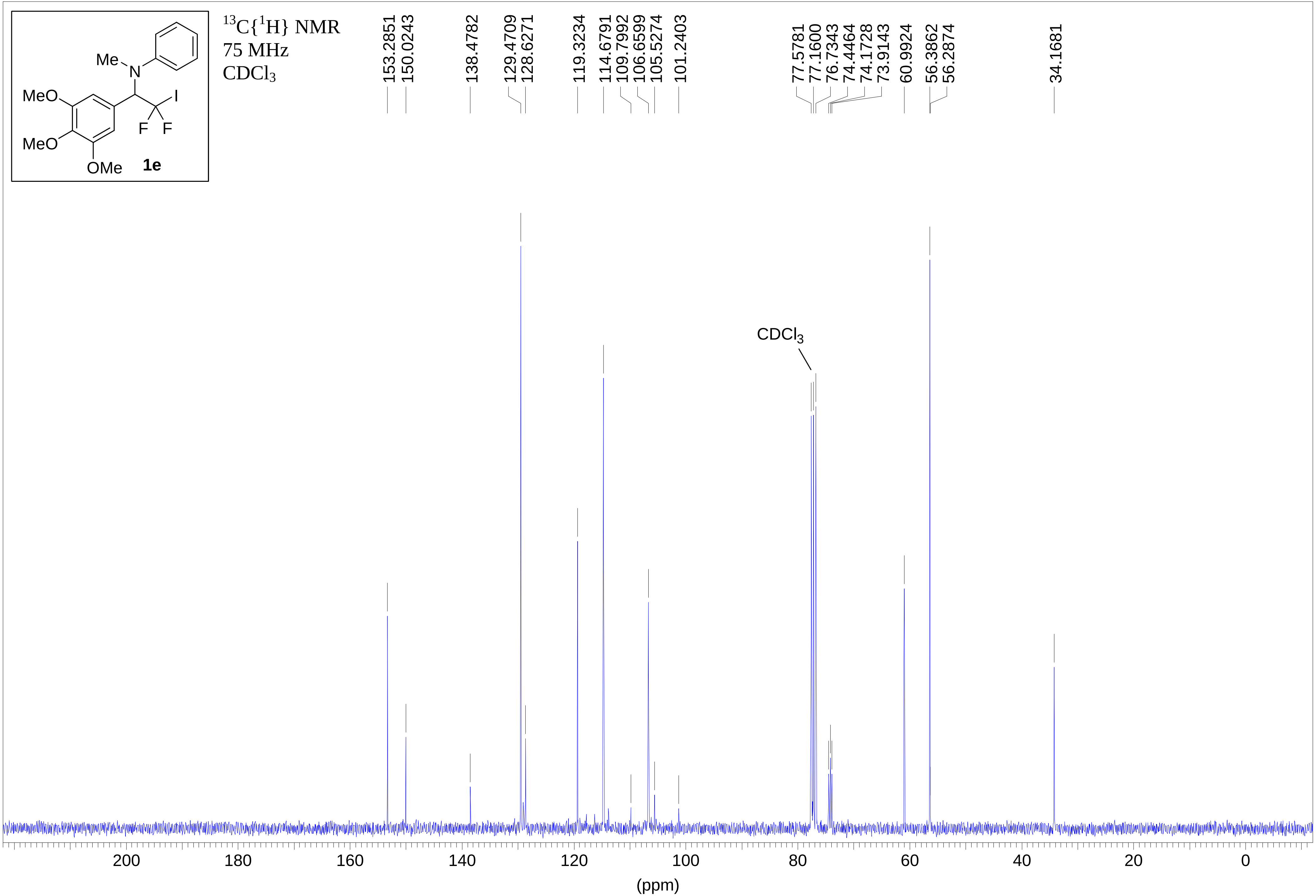
1d

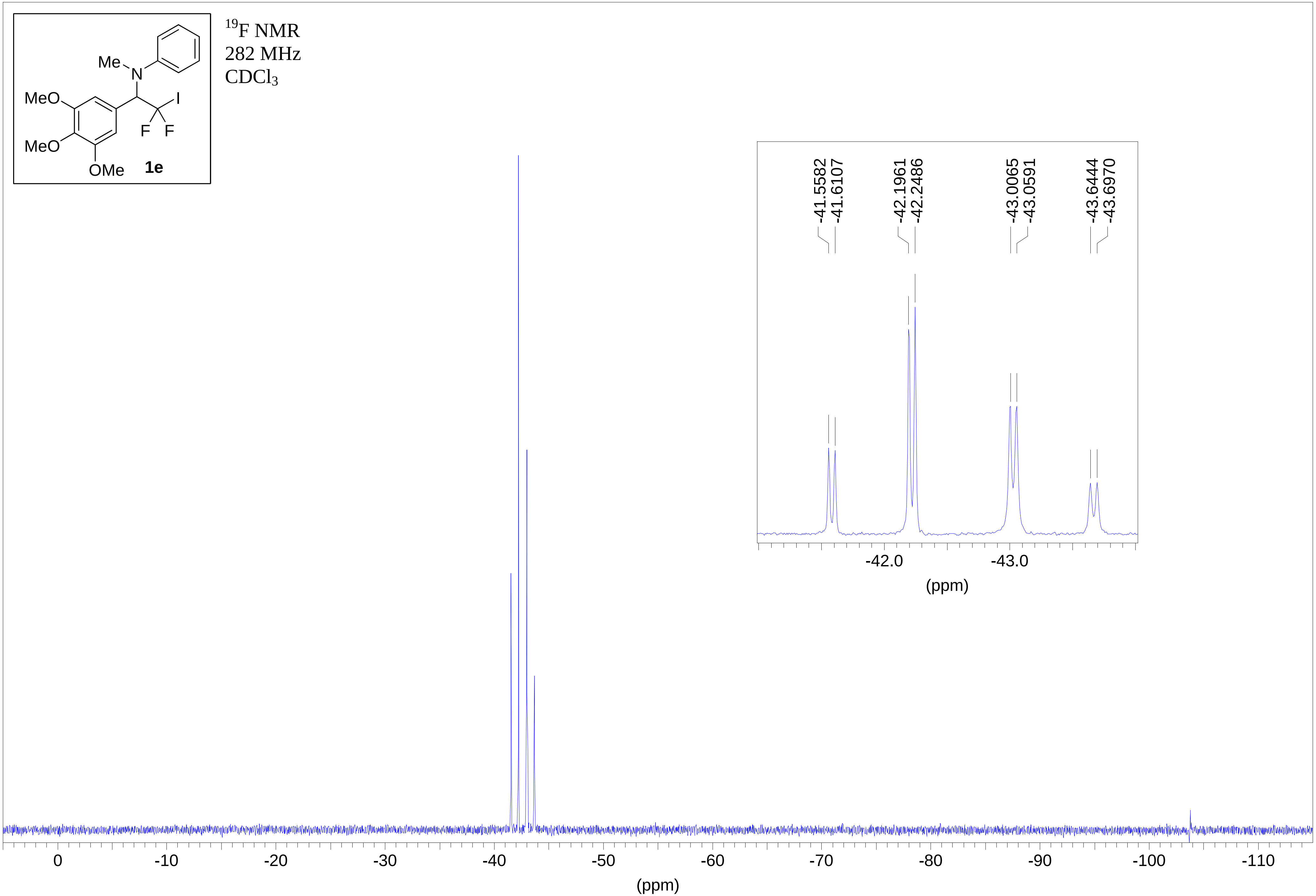
^{19}F NMR
282 MHz
$CDCl_3$



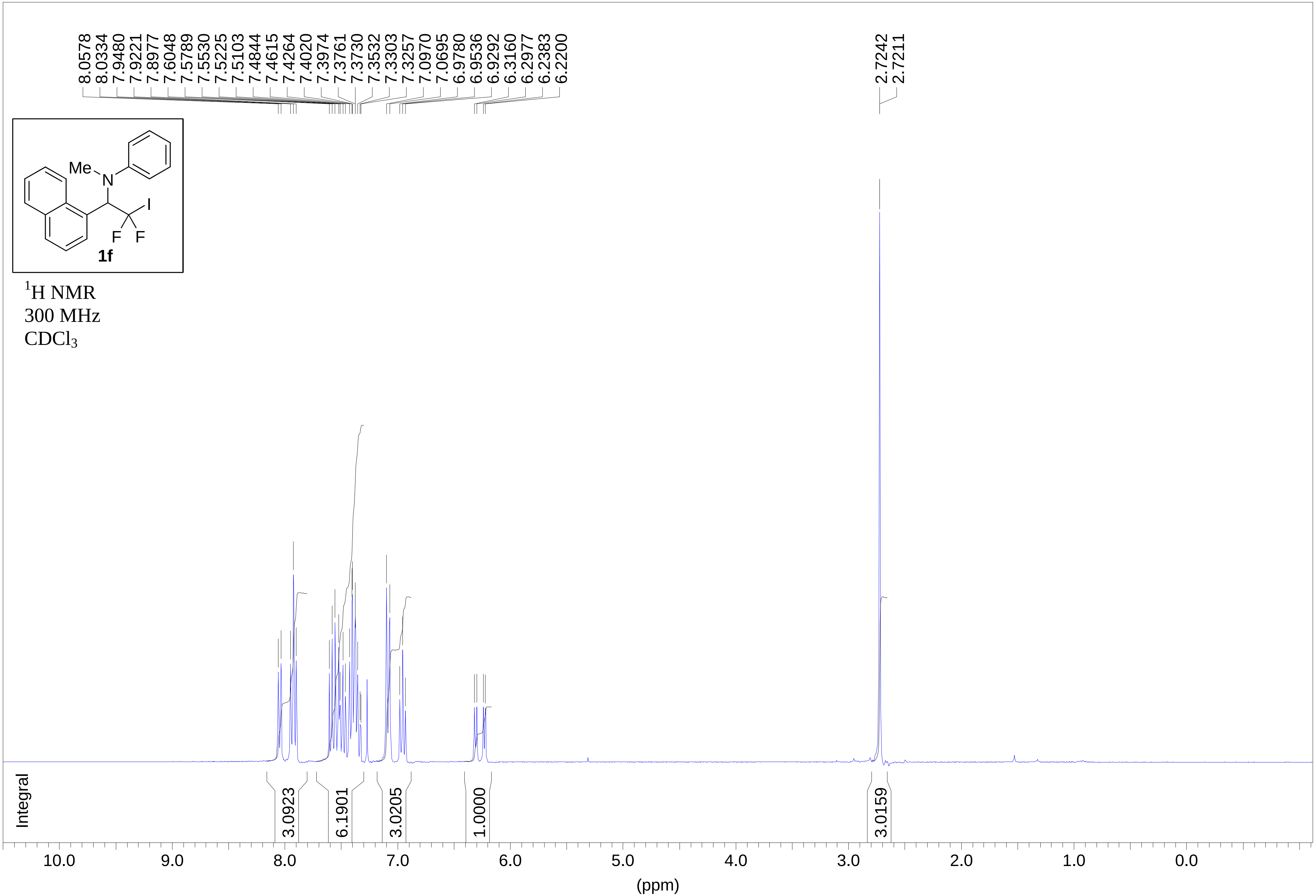


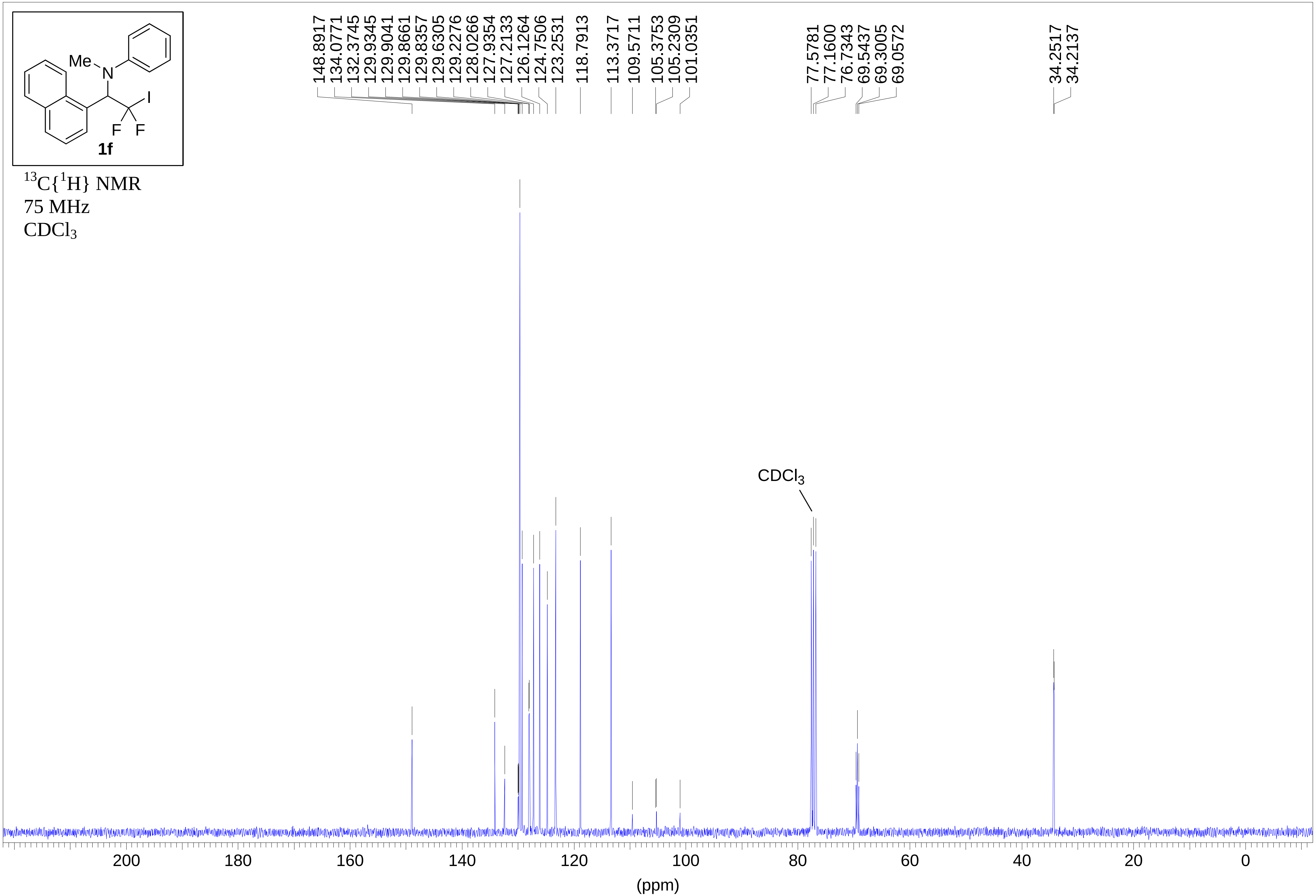
Me
N
MeO
I
F F
MeO
OMe
1e
^{1}H NMR
300 MHz
$CDCl_3$
7.3486
7.3226
7.2967
6.9962
6.9688
6.9169
6.8910
6.8681
6.6058
5.5488
5.5015
5.4527
3.8833
3.8787
3.8146
2.8202
D-solv. residual peak
Integral
2.4050
3.1623
2.0883
1.0000
9.5493
3.1633
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


Me
N
MeO
MeO
OMe
I
F
F
1e
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
153.2851
150.0243
138.4782
129.4709
128.6271
119.3234
114.6791
109.7992
106.6599
105.5274
101.2403
77.5781
77.1600
76.7343
74.4464
74.1728
73.9143
60.9924
56.3862
56.2874
34.1681
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)

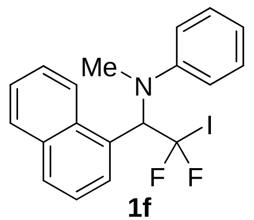


Me
N
MeO
I
F F
MeO
OMe
1e
^{19}F NMR
282 MHz
$CDCl_3$
-41.5582
-41.6107
-42.1961
-42.2486
-43.0065
-43.0591
-43.6444
-43.6970
-42.0
-43.0
(ppm)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
(ppm)


8.0578
8.0334
7.9480
7.9221
7.8977
7.6048
7.5789
7.5530
7.5225
7.5103
7.4844
7.4615
7.4264
7.4020
7.3974
7.3761
7.3730
7.3532
7.3303
7.3257
7.0970
7.0695
6.9780
6.9536
6.9292
6.3160
6.2977
6.2383
6.2200
2.7242
2.7211
Me
N
I
F
F
1f
^{1}H NMR
300 MHz
$CDCl_3$
Integral
3.0923
6.1901
3.0205
1.0000
3.0159
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

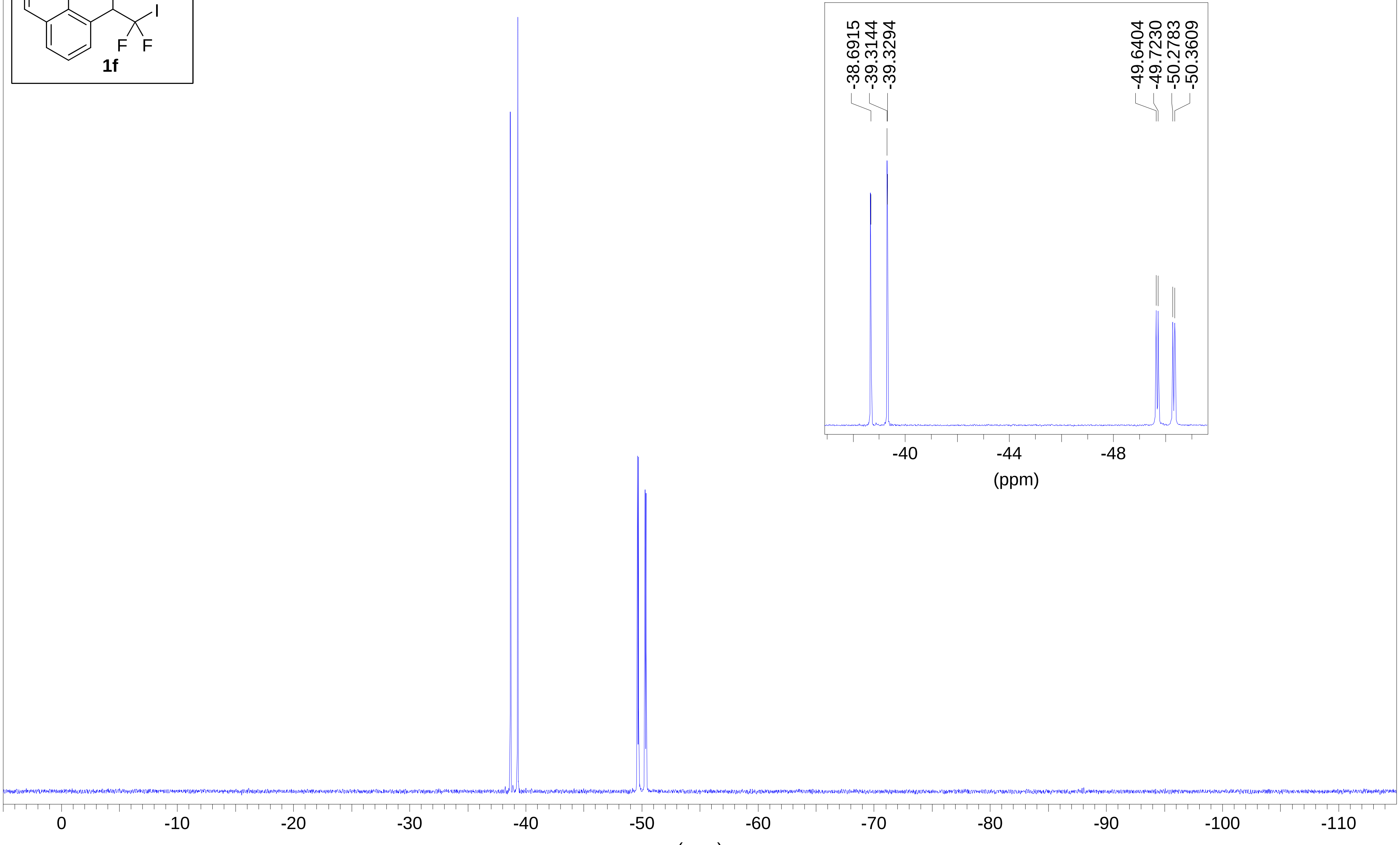


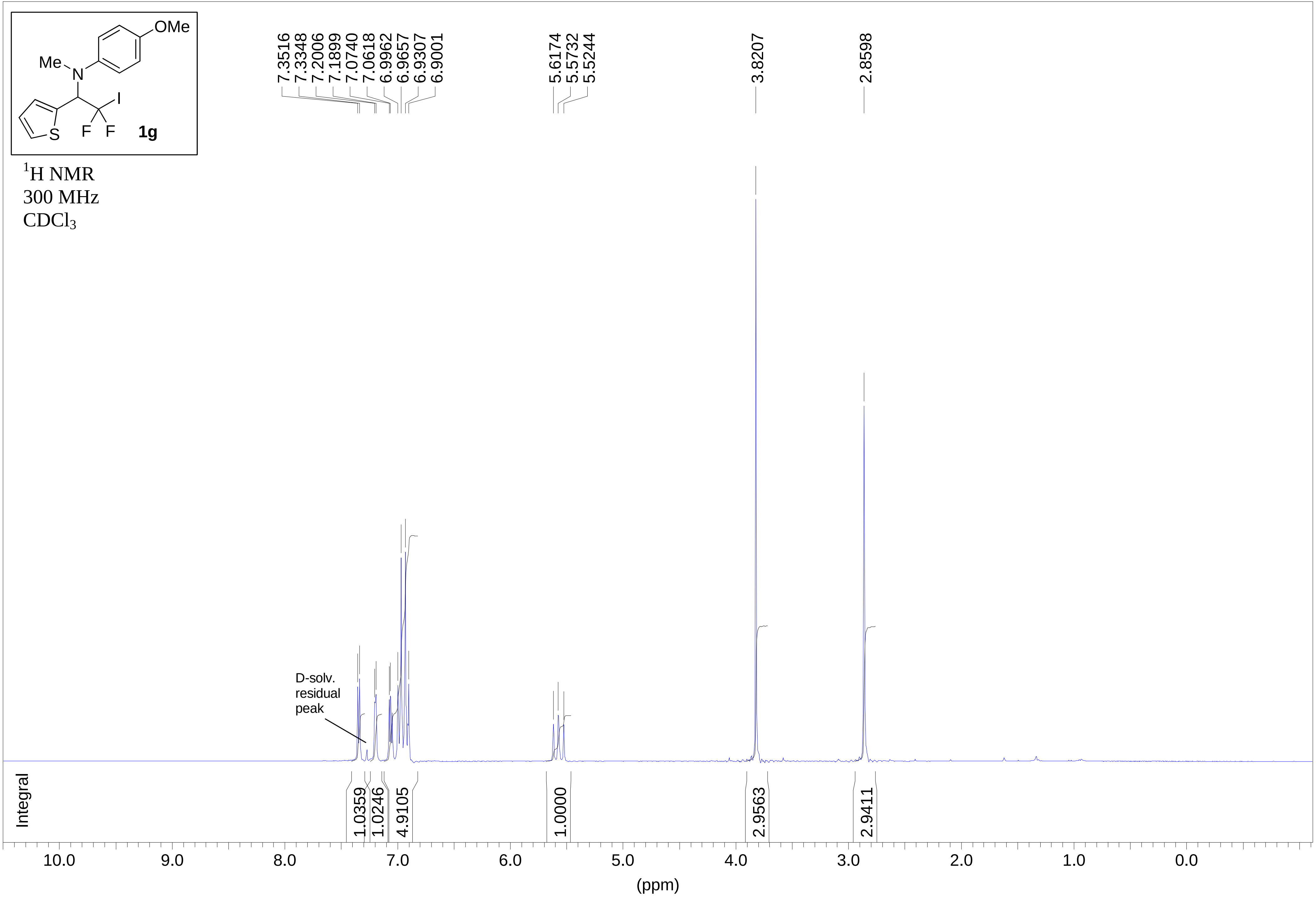
$^{13}C\{^1H\}$ NMR
75 MHz
$CDCl_3$



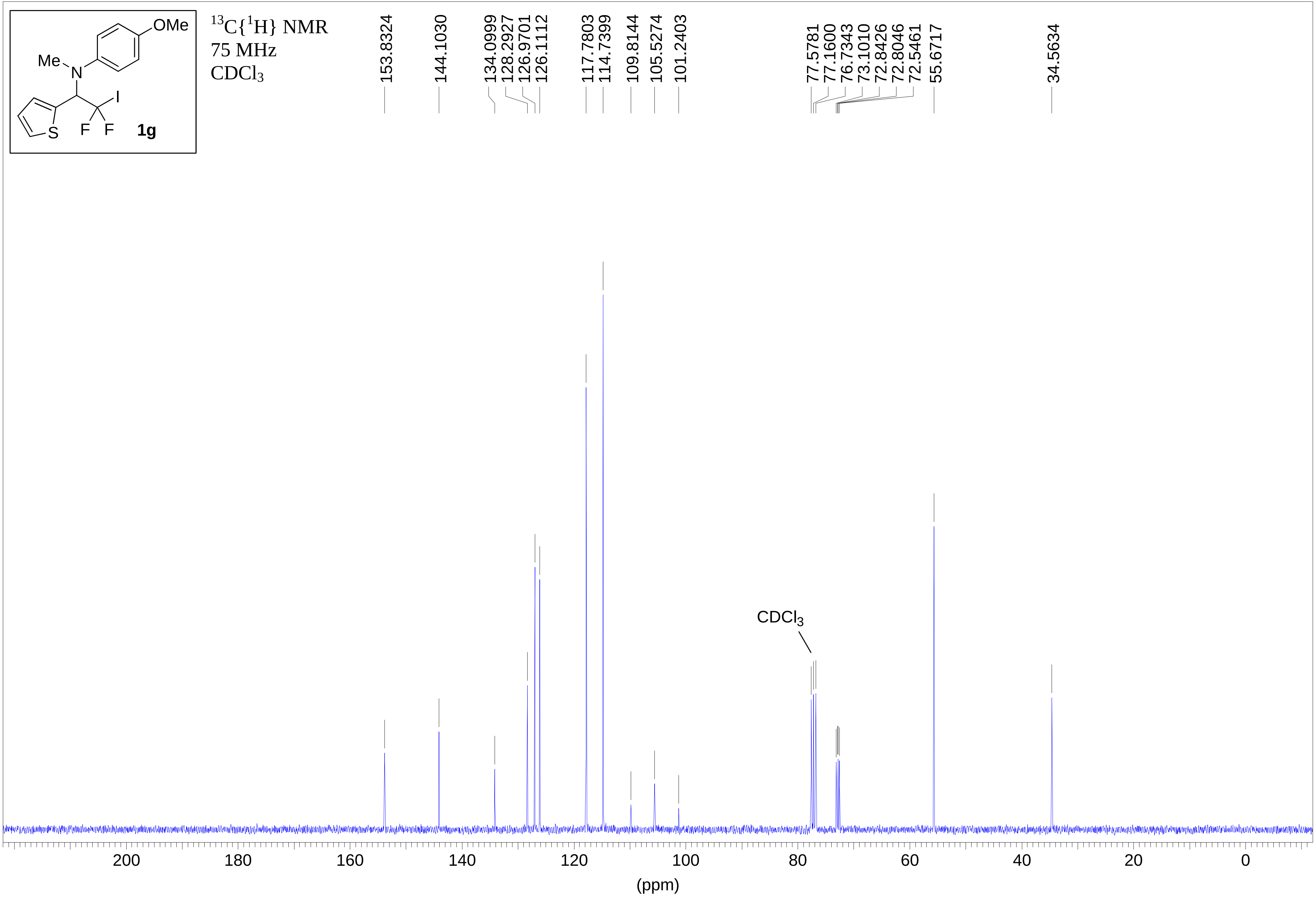
1f

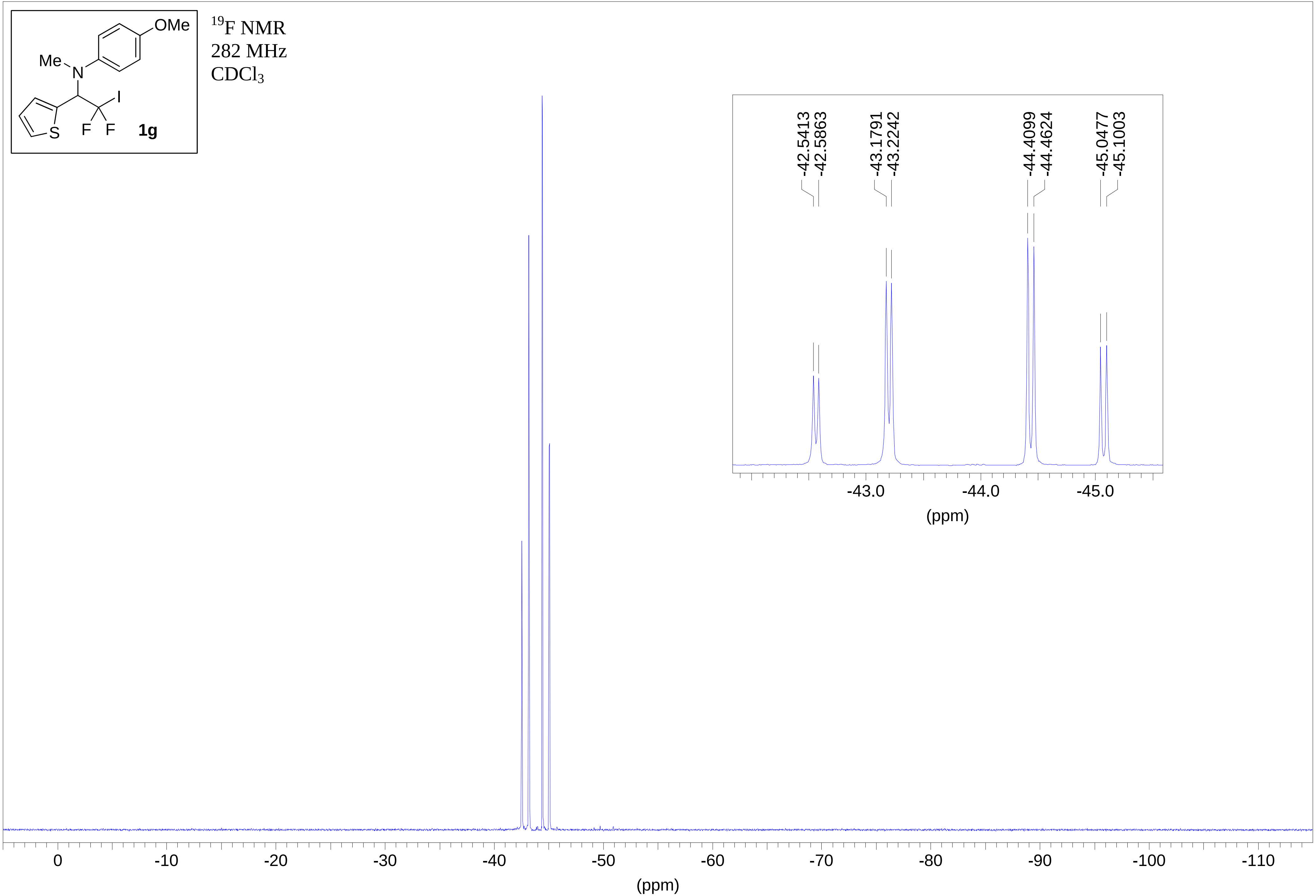
^{19}F NMR
282 MHz
$CDCl_3$

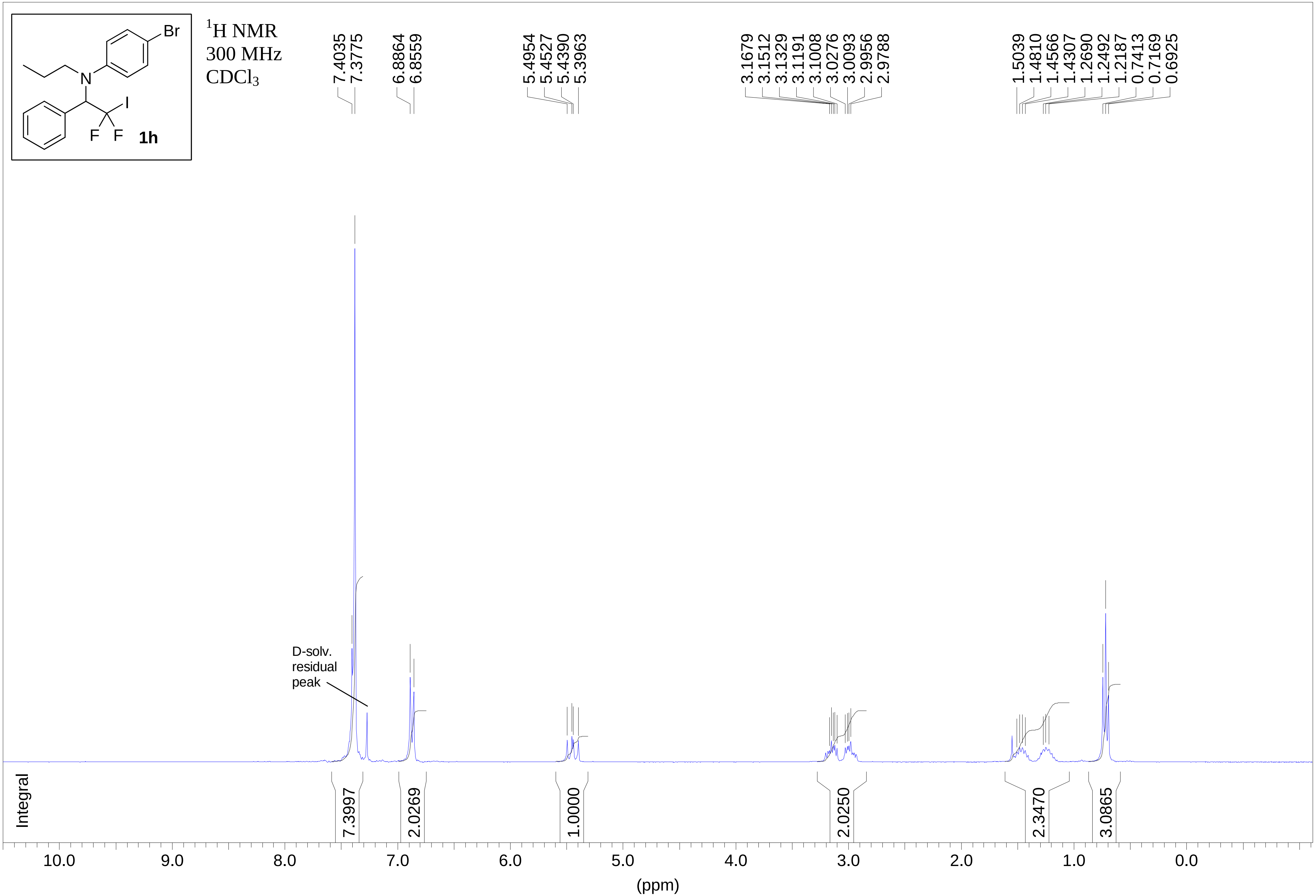




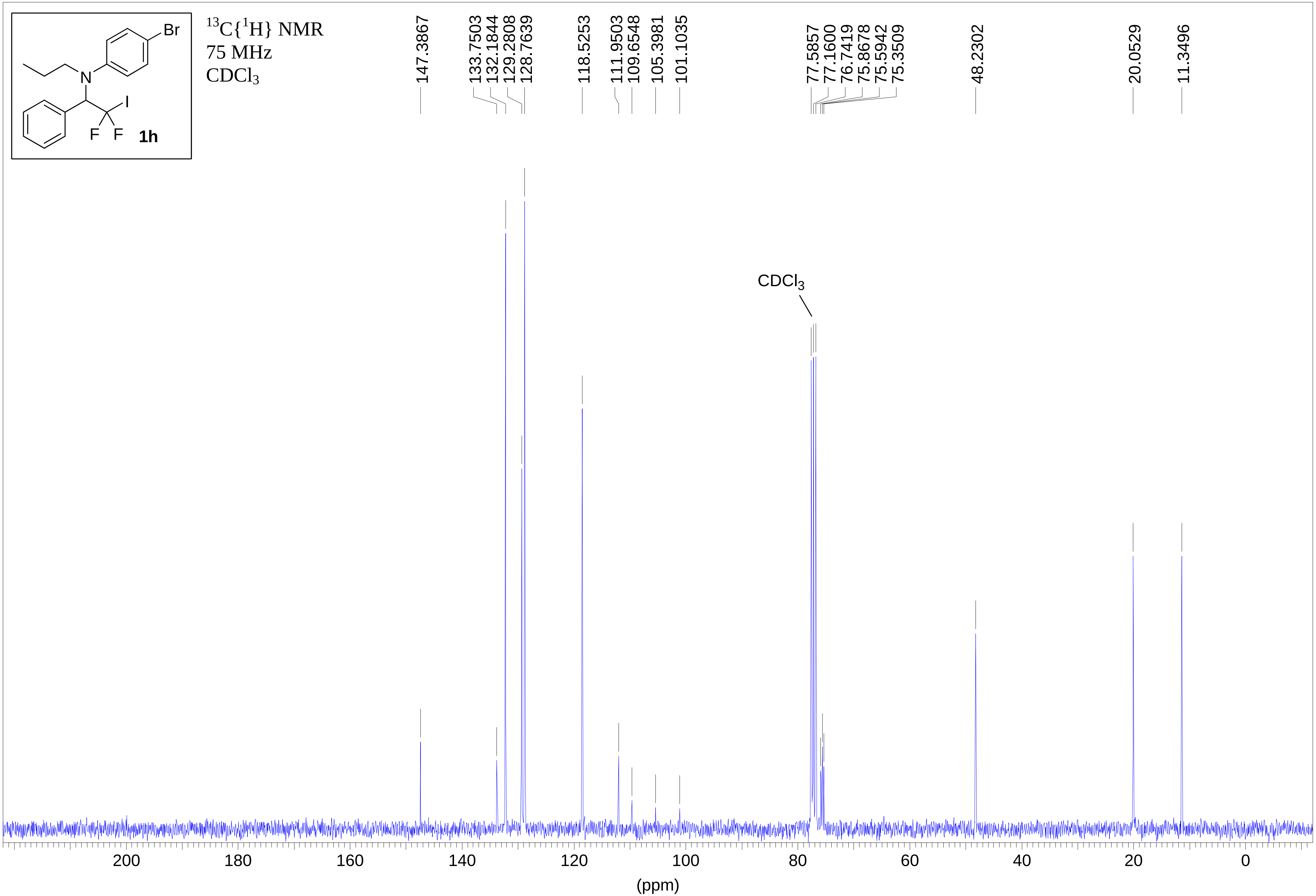
OMe
Me
N
I
S
F
F
1g
¹H NMR
300 MHz
CDCl₃
7.3516
7.3348
7.2006
7.1899
7.0740
7.0618
6.9962
6.9657
6.9307
6.9001
5.6174
5.5732
5.5244
3.8207
2.8598
D-solv. residual peak
Integral
1.0359
1.0246
4.9105
1.0000
2.9563
2.9411
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

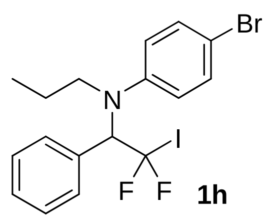

OMe
Me
N
I
S
F F
1g
13C{1H} NMR
75 MHz
CDCl3
153.8324
144.1030
134.0999
128.2927
126.9701
126.1112
117.7803
114.7399
109.8144
105.5274
101.2403
77.5781
77.1600
76.7343
73.1010
72.8426
72.8046
72.5461
55.6717
34.5634
CDCl3
200
180
160
140
120
100
80
60
40
20
0
(ppm)


OMe
Me
N
I
S
F
F
1g
19F NMR
282 MHz
CDCl3
-42.5413
-42.5863
-43.1791
-43.2242
-44.4099
-44.4624
-45.0477
-45.1003
-43.0
-44.0
-45.0
(ppm)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
(ppm)



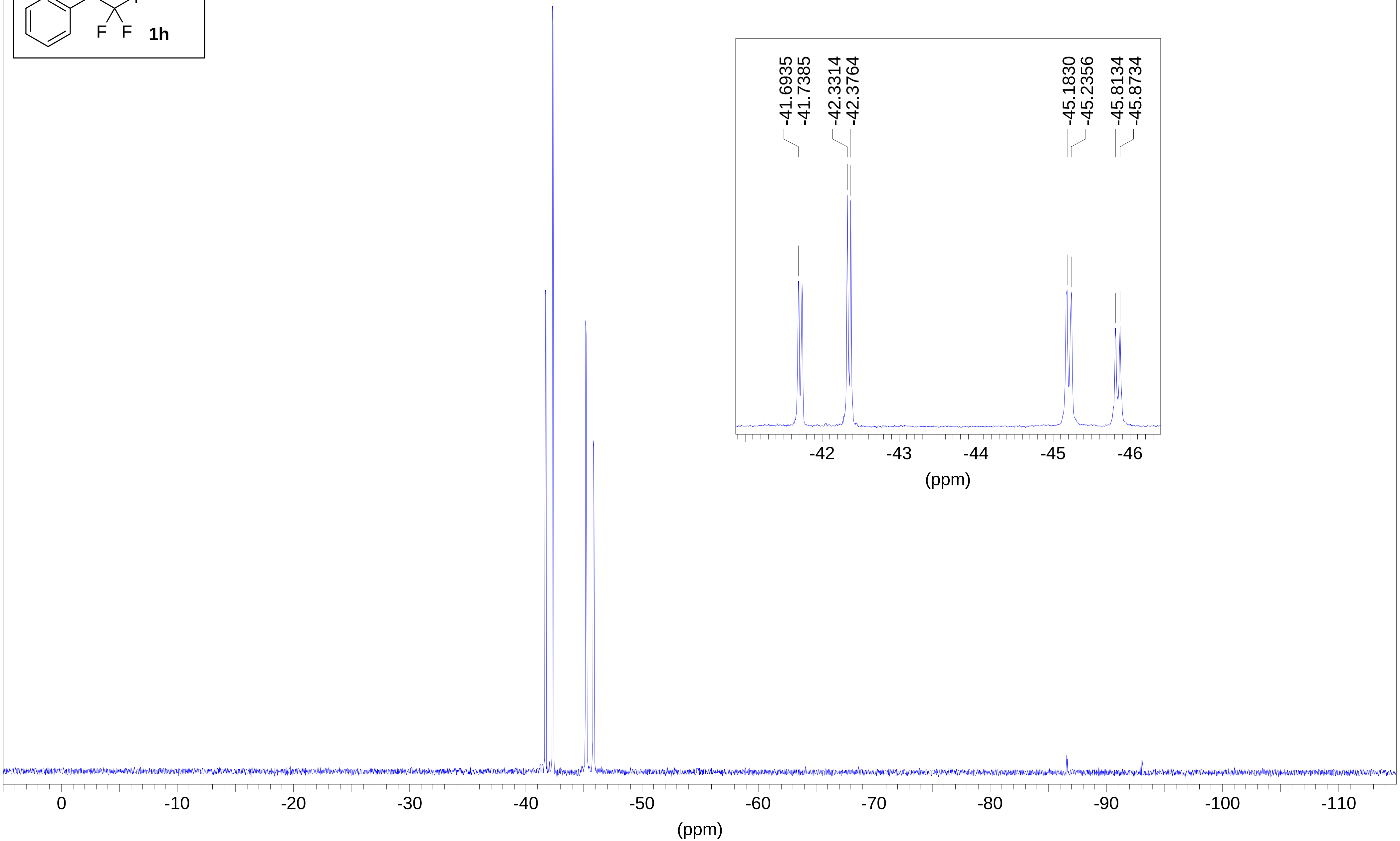
Br
N
I
F F
1h
1H NMR
300 MHz
CDCl3
7.4035
7.3775
6.8864
6.8559
5.4954
5.4527
5.4390
5.3963
3.1679
3.1512
3.1329
3.1191
3.1008
3.0276
3.0093
2.9956
2.9788
1.5039
1.4810
1.4566
1.4307
1.2690
1.2492
1.2187
0.7413
0.7169
0.6925
D-solv.
residual
peak
Integral
7.3997
2.0269
1.0000
2.0250
2.3470
3.0865
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

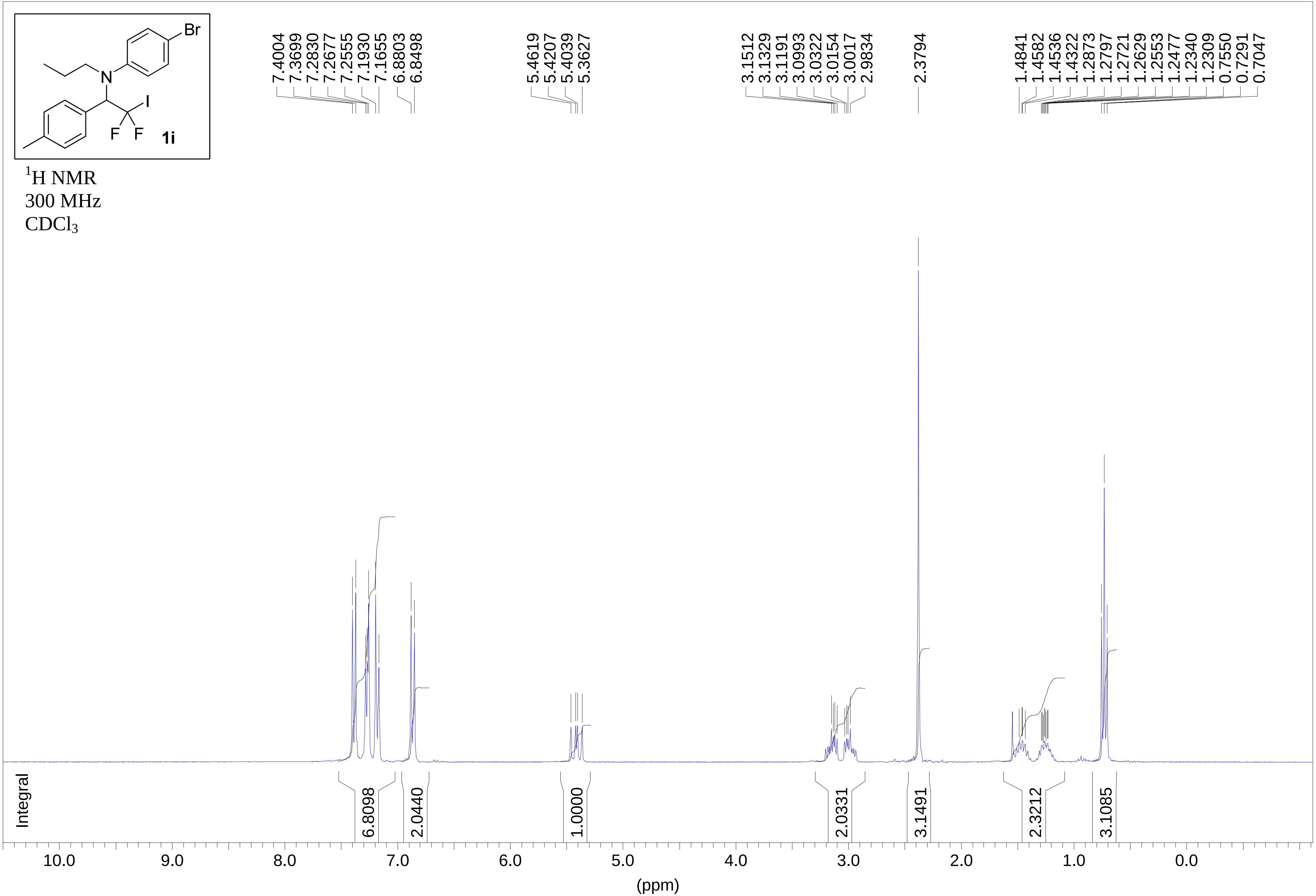

Br
N
I
F F
1h
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
147.3867
133.7503
132.1844
129.2808
128.7639
118.5253
111.9503
109.6548
105.3981
101.1035
77.5857
77.1600
76.7419
75.8678
75.5942
75.3509
48.2302
20.0529
11.3496
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)



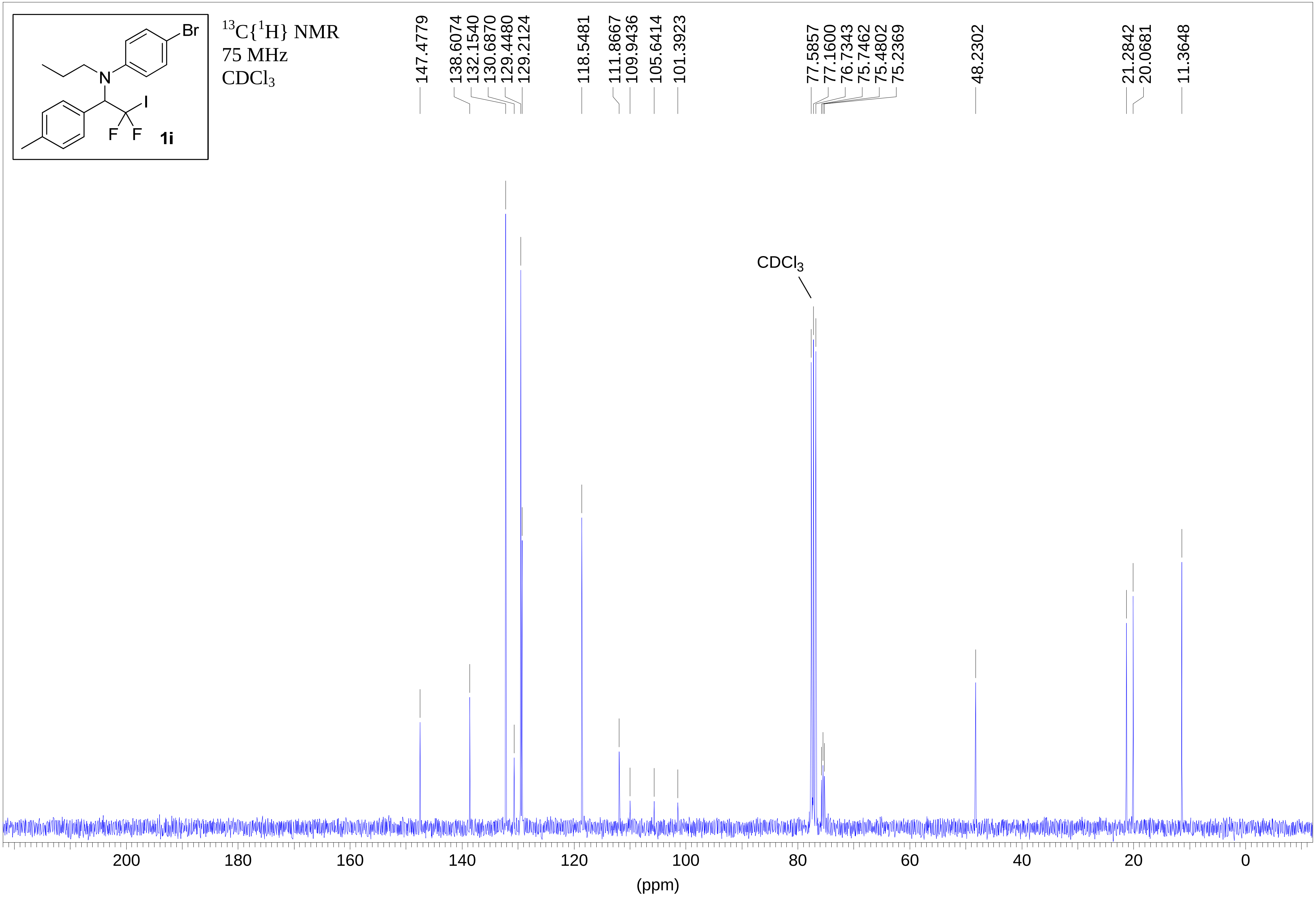
1h

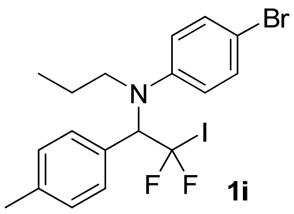
^{19}F NMR
282 MHz
$CDCl_3$





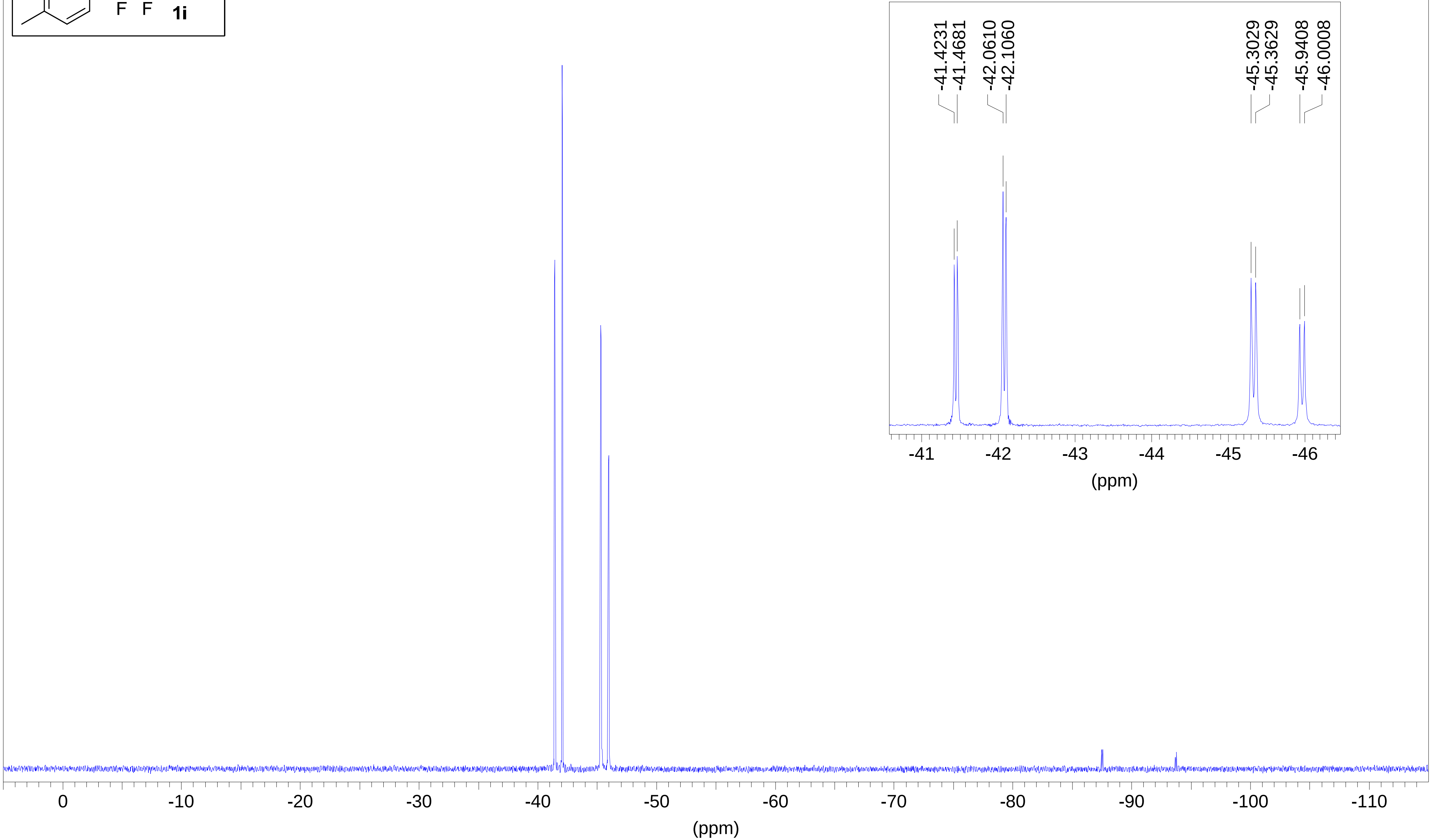
Br
N
I
F F
1i
[1]H NMR
300 MHz
$CDCl_3$
7.4004
7.3699
7.2830
7.2677
7.2555
7.1930
7.1655
6.8803
6.8498
5.4619
5.4207
5.4039
5.3627
3.1512
3.1329
3.1191
3.0993
3.0322
3.0154
3.0017
2.9834
2.3794
1.4841
1.4582
1.4536
1.4322
1.2873
1.2797
1.2721
1.2629
1.2553
1.2477
1.2340
1.2309
0.7550
0.7291
0.7047
Integral
6.8098
2.0440
1.0000
2.0331
3.1491
2.3212
3.1085
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

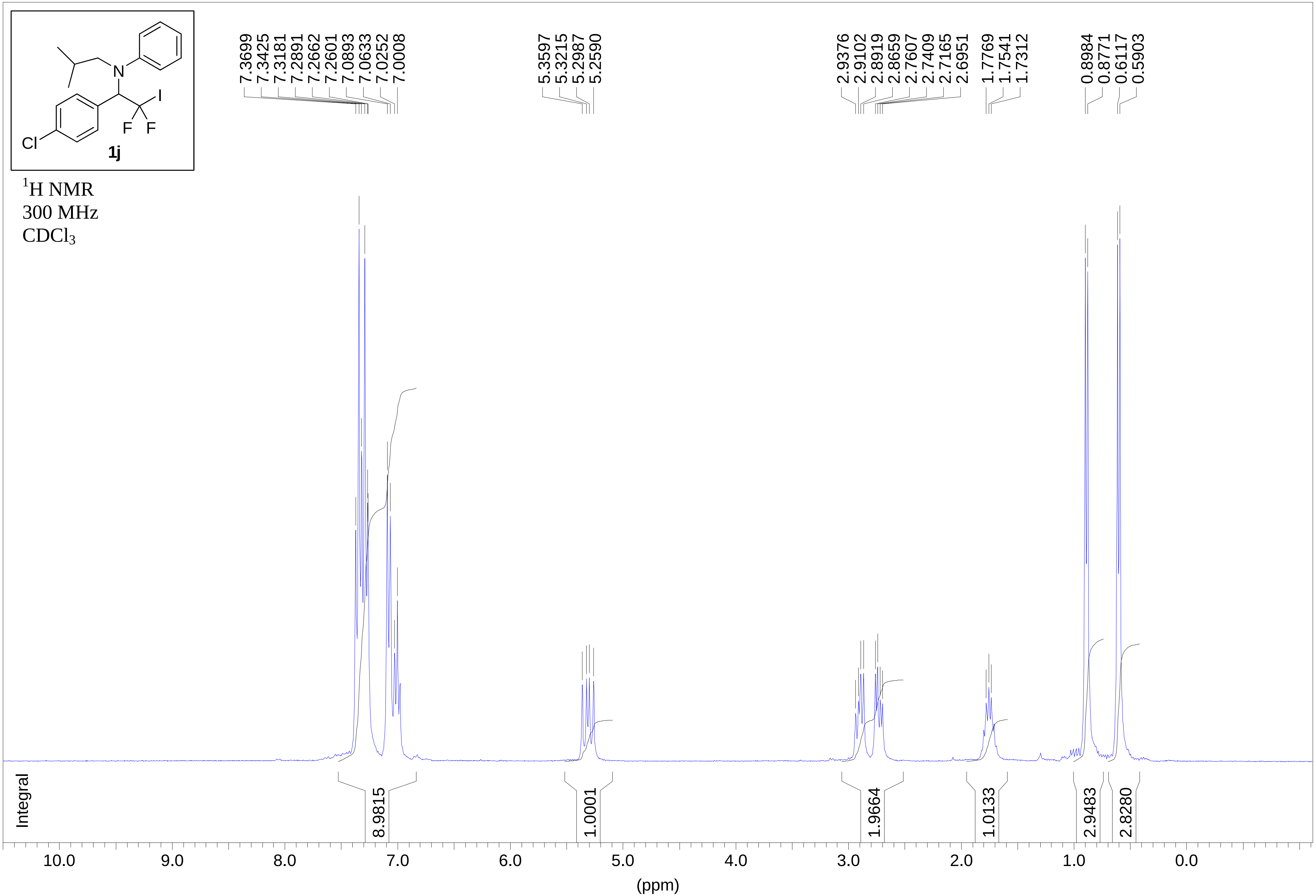

Br
N
I
F
F
1i
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
147.4779
138.6074
132.1540
130.6870
129.4480
129.2124
118.5481
111.8667
109.9436
105.6414
101.3923
77.5857
77.1600
76.7343
75.7462
75.4802
75.2369
48.2302
21.2842
20.0681
11.3648
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)



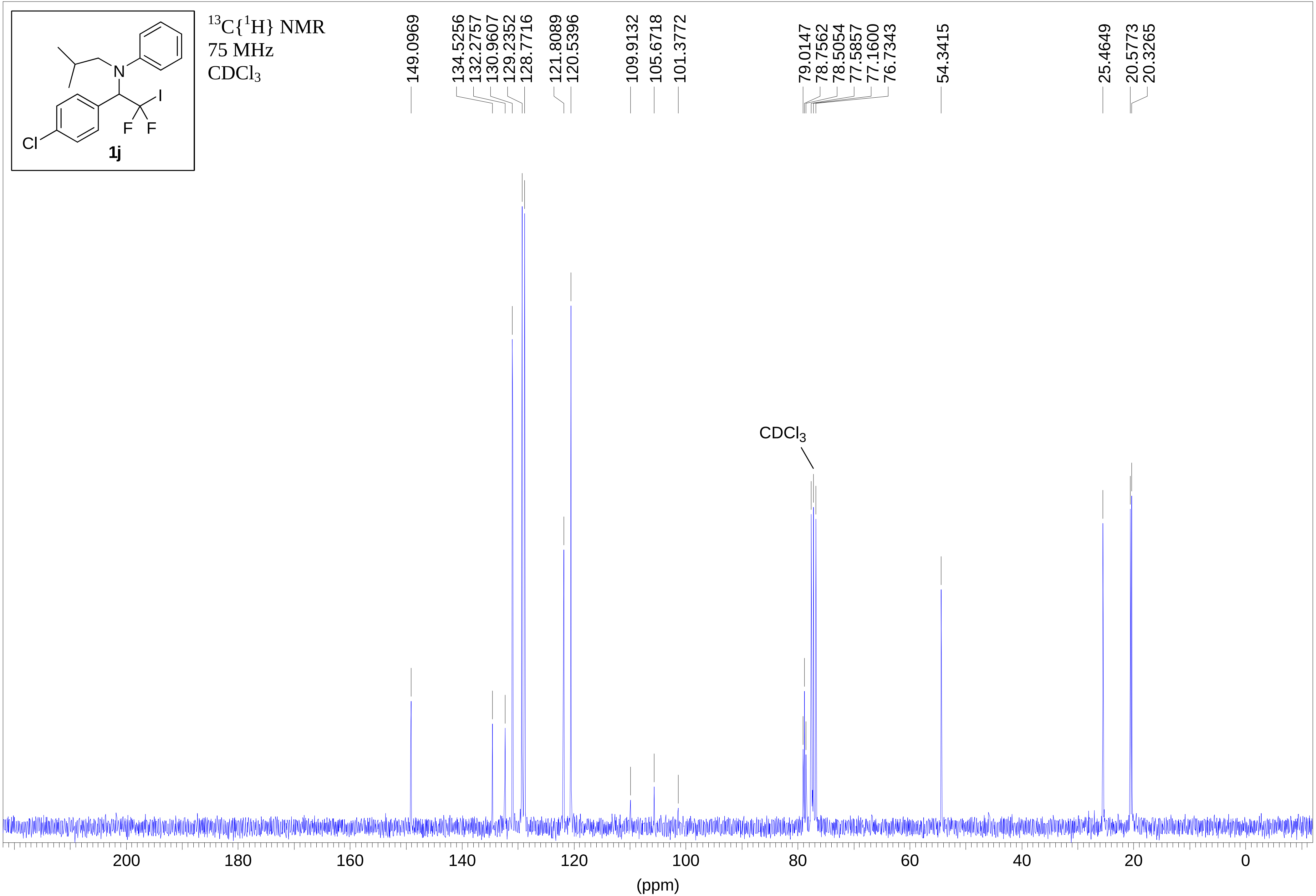
1i

^{19}F NMR
282 MHz
$CDCl_3$

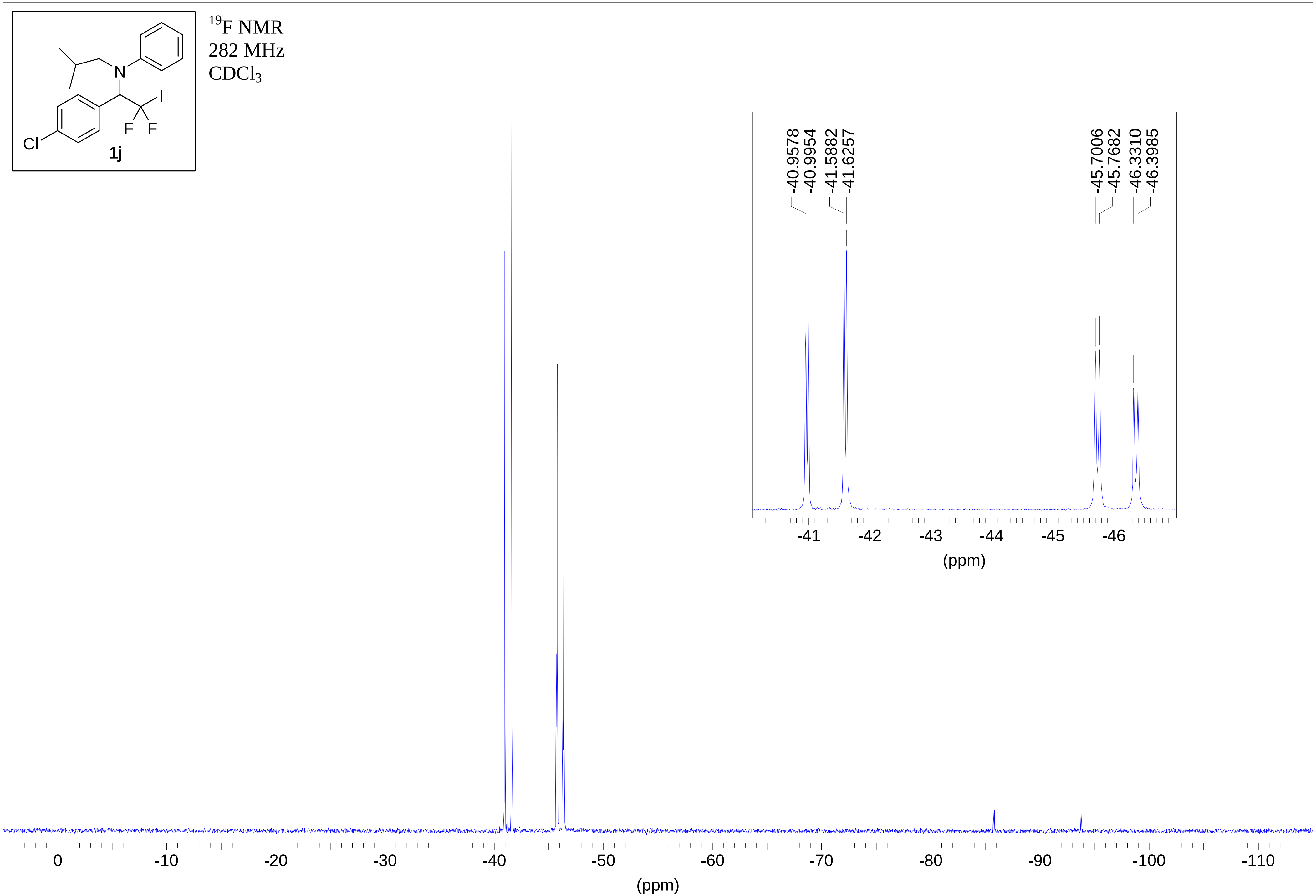




1j
¹H NMR
300 MHz
CDCl3
7.3699
7.3425
7.3181
7.2891
7.2662
7.2601
7.0893
7.0633
7.0252
7.0008
5.3597
5.3215
5.2987
5.2590
2.9376
2.9102
2.8919
2.8659
2.7607
2.7409
2.7165
2.6951
1.7769
1.7541
1.7312
0.8984
0.8771
0.6117
0.5903
Integral
8.9815
1.0001
1.9664
1.0133
2.9483
2.8280
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)



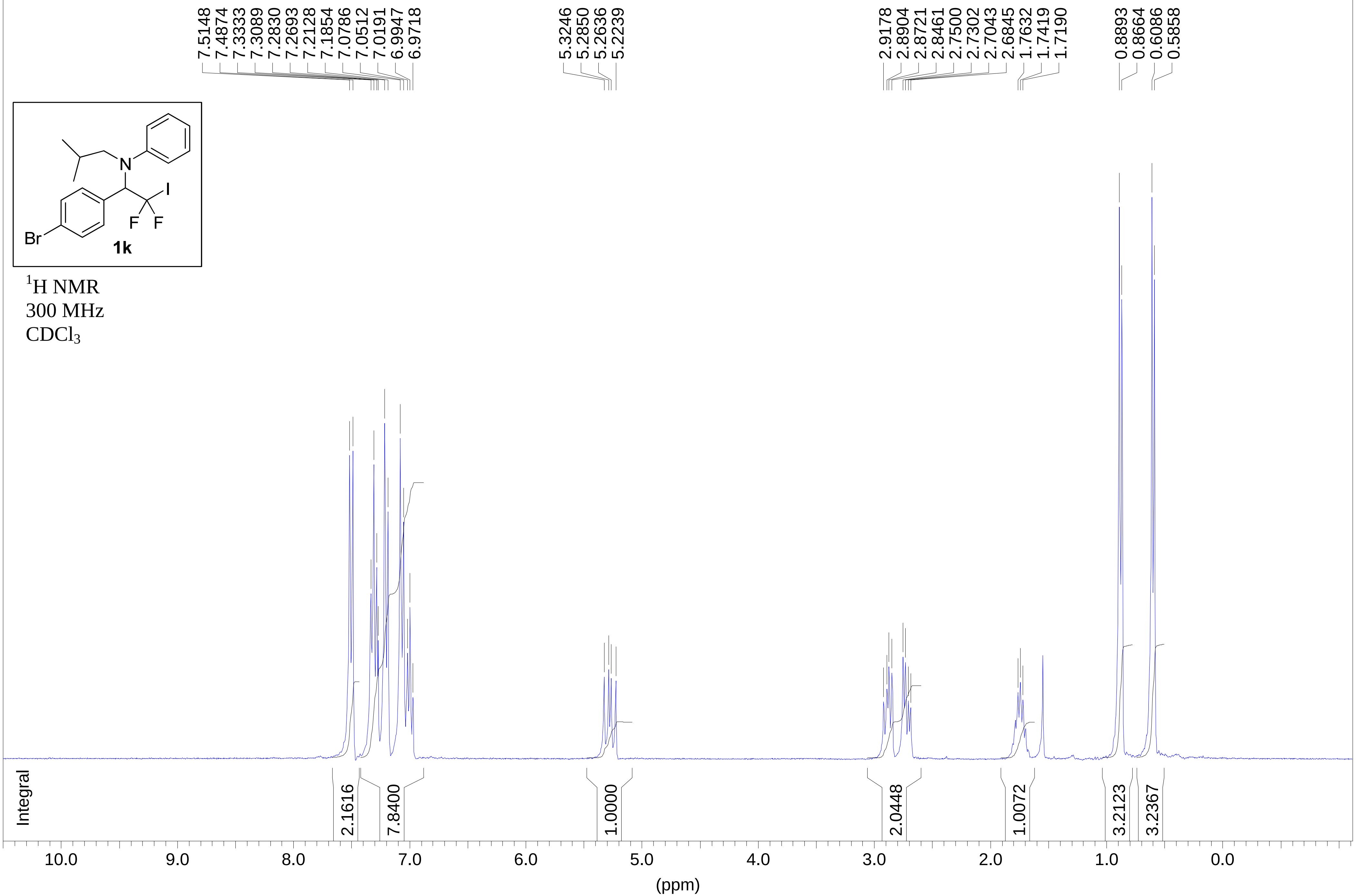
Cl
N
I
F F
1j
$^{13}C\{^1H\}$ NMR
75 MHz
$CDCl_3$
149.0969
134.5256
132.2757
130.9607
129.2352
128.7716
121.8089
120.5396
109.9132
105.6718
101.3772
79.0147
78.7562
78.5054
77.5857
77.1600
76.7343
54.3415
25.4649
20.5773
20.3265
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)

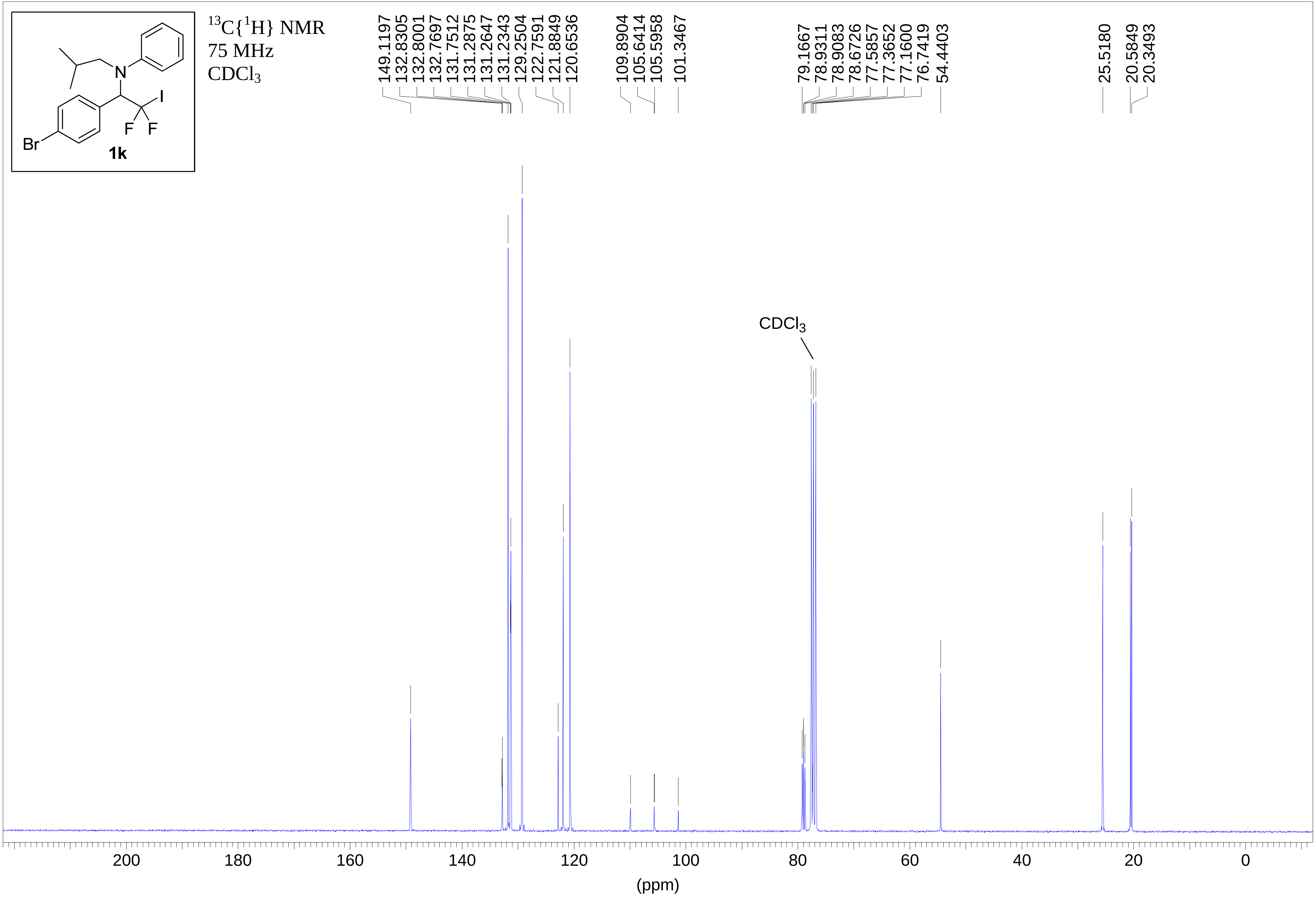


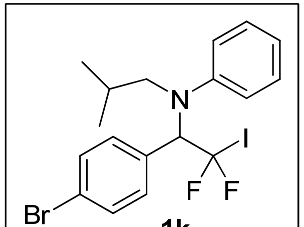
Cl
N
I
F F
1j
19F NMR
282 MHz
CDCl3
-40.9578
-40.9954
-41.5882
-41.6257
-45.7006
-45.7682
-46.3310
-46.3985
-41
-42
-43
-44
-45
-46
(ppm)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
(ppm)

1k

[1]H NMR
300 MHz
$CDCl_3$

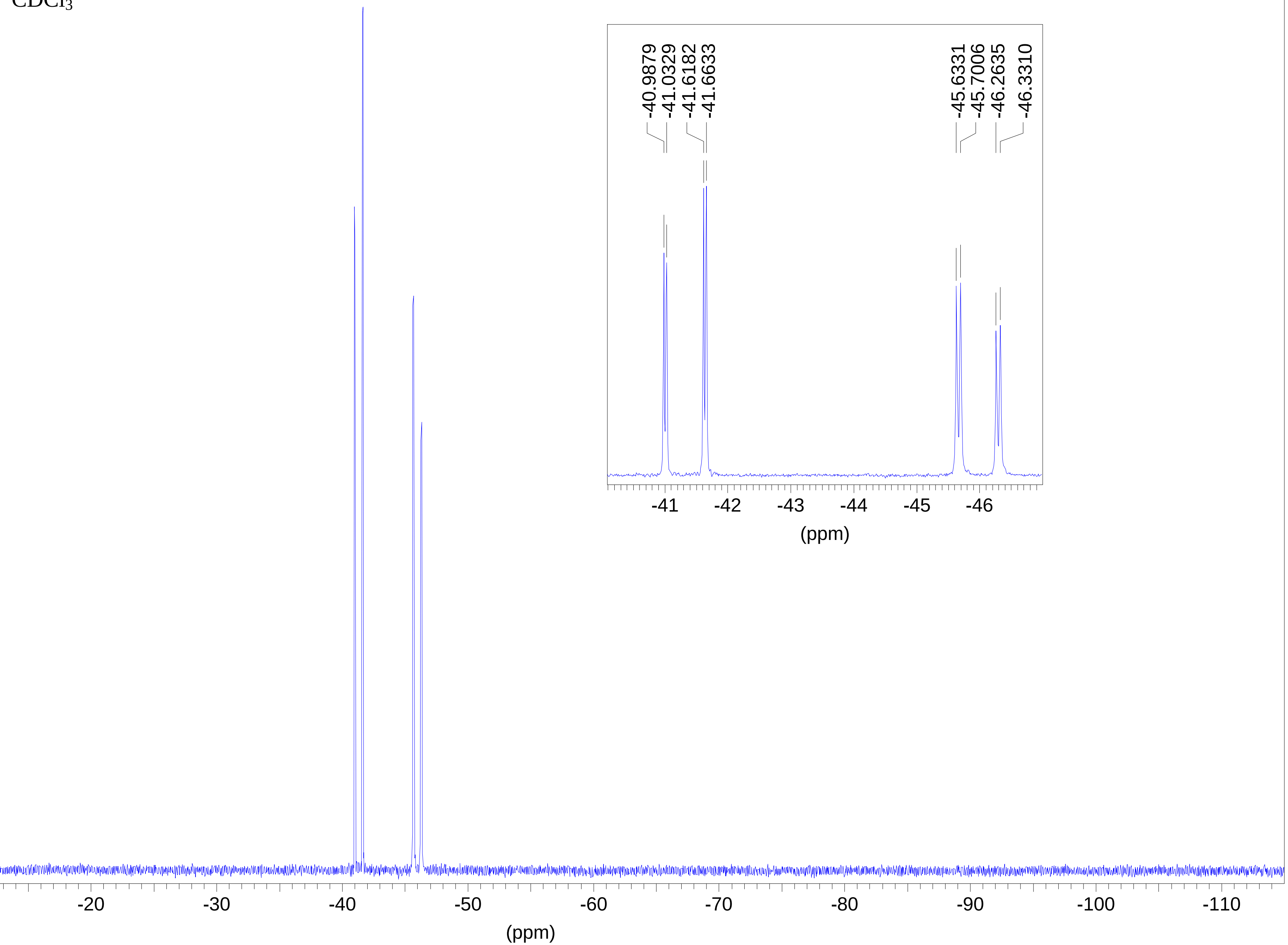


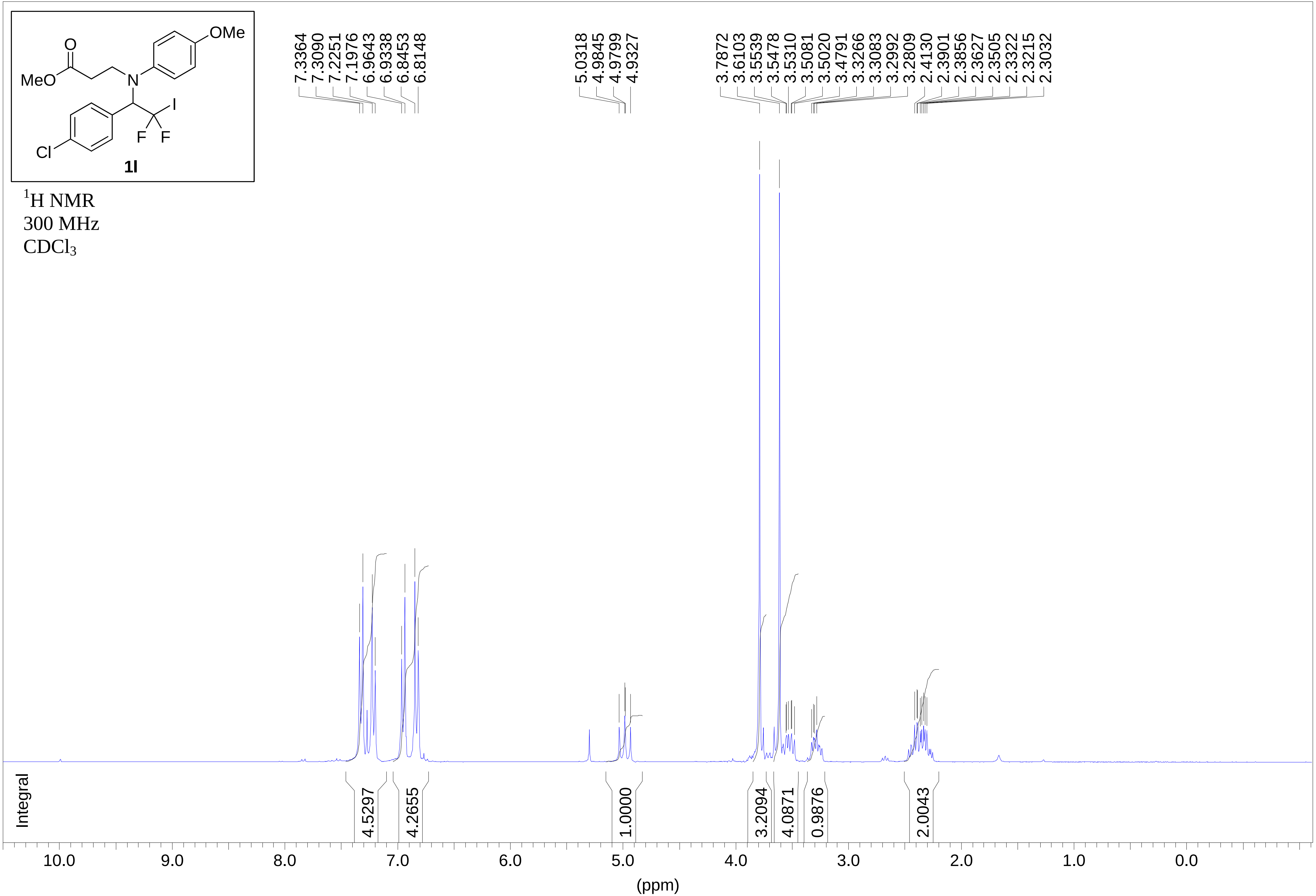

1k
$^{13}C\{^1H\}$ NMR
75 MHz
$CDCl_3$
149.1197
132.8305
132.8001
132.7697
131.7512
131.2875
131.2647
131.2343
129.2504
122.7591
121.8849
120.6536
109.8904
105.6414
105.5958
101.3467
79.1667
78.9311
78.9083
78.6726
77.5857
77.3652
77.1600
76.7419
54.4403
25.5180
20.5849
20.3493
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)



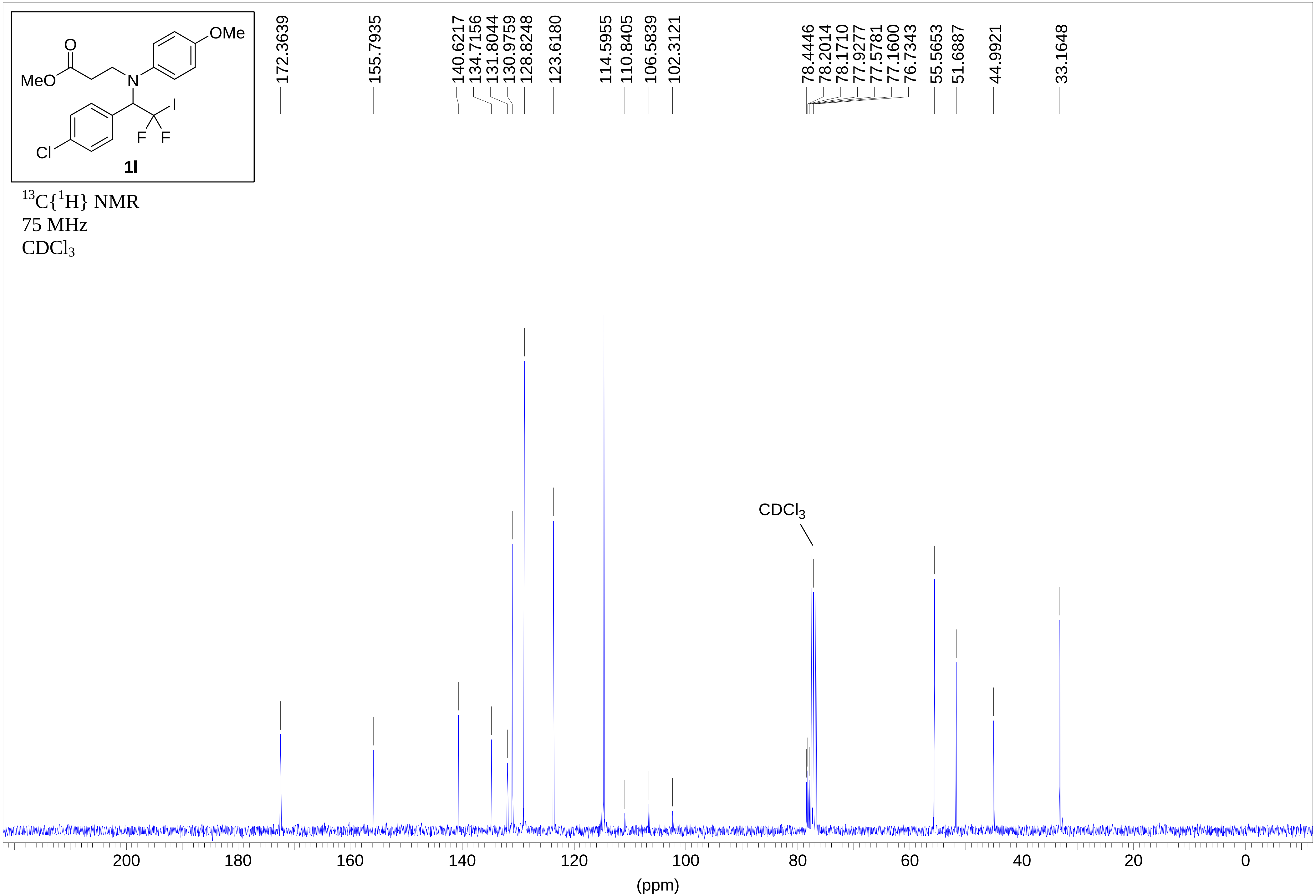
1k

^{19}F NMR
282 MHz
$CDCl_3$

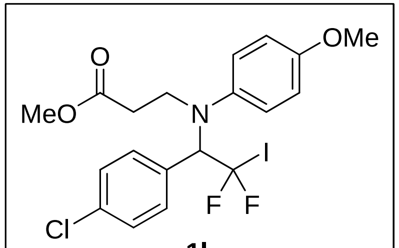




OMe
O
MeO
N
I
F F
Cl
1l
¹H NMR
300 MHz
CDCl3
7.3364
7.3090
7.2251
7.1976
6.9643
6.9338
6.8453
6.8148
5.0318
4.9845
4.9799
4.9327
3.7872
3.6103
3.5539
3.5478
3.5310
3.5081
3.5020
3.4791
3.3266
3.3083
3.2992
3.2809
2.4130
2.3901
2.3856
2.3627
2.3505
2.3322
2.3215
2.3032
Integral
4.5297
4.2655
1.0000
3.2094
4.0871
0.9876
2.0043
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

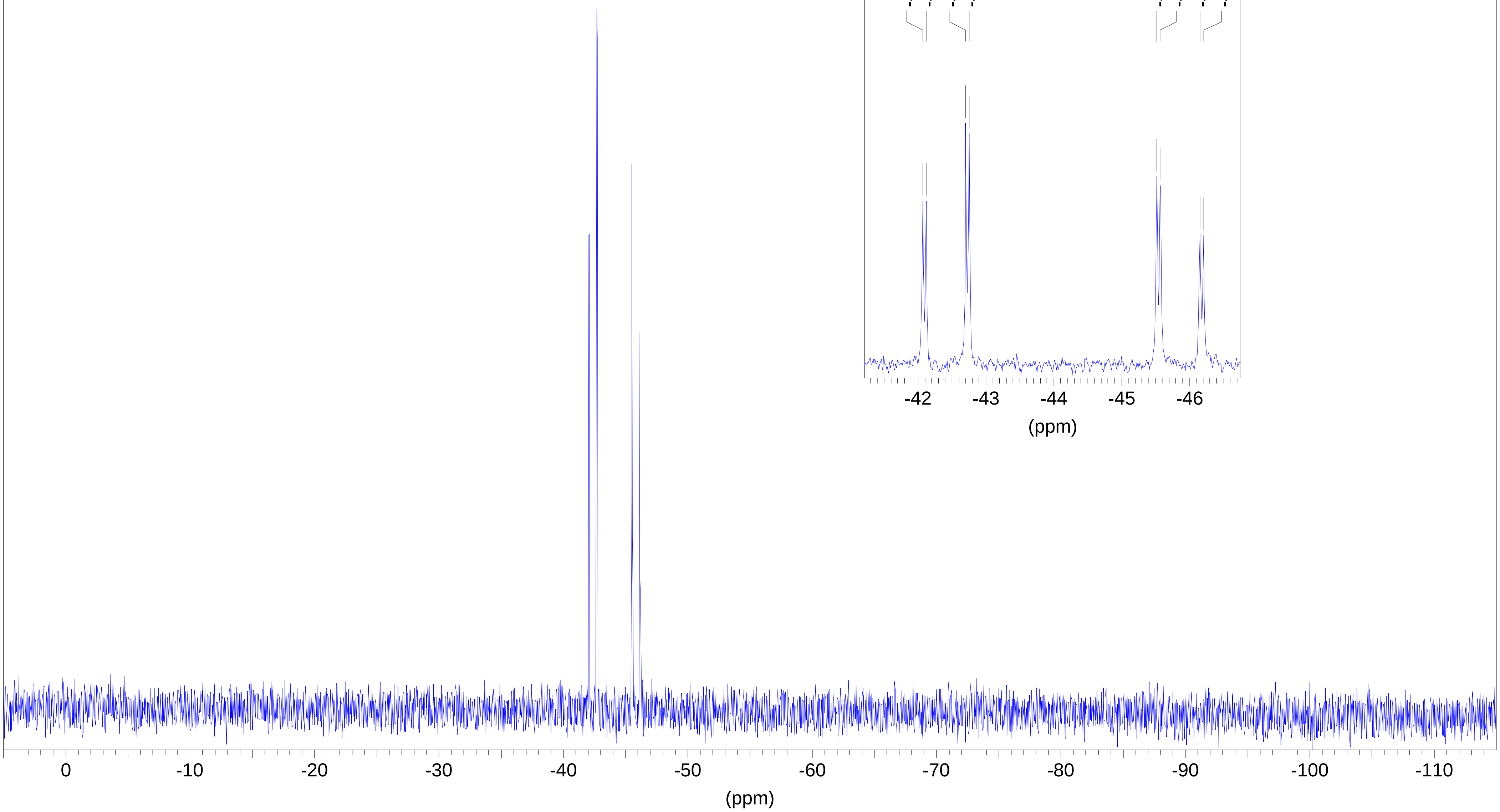


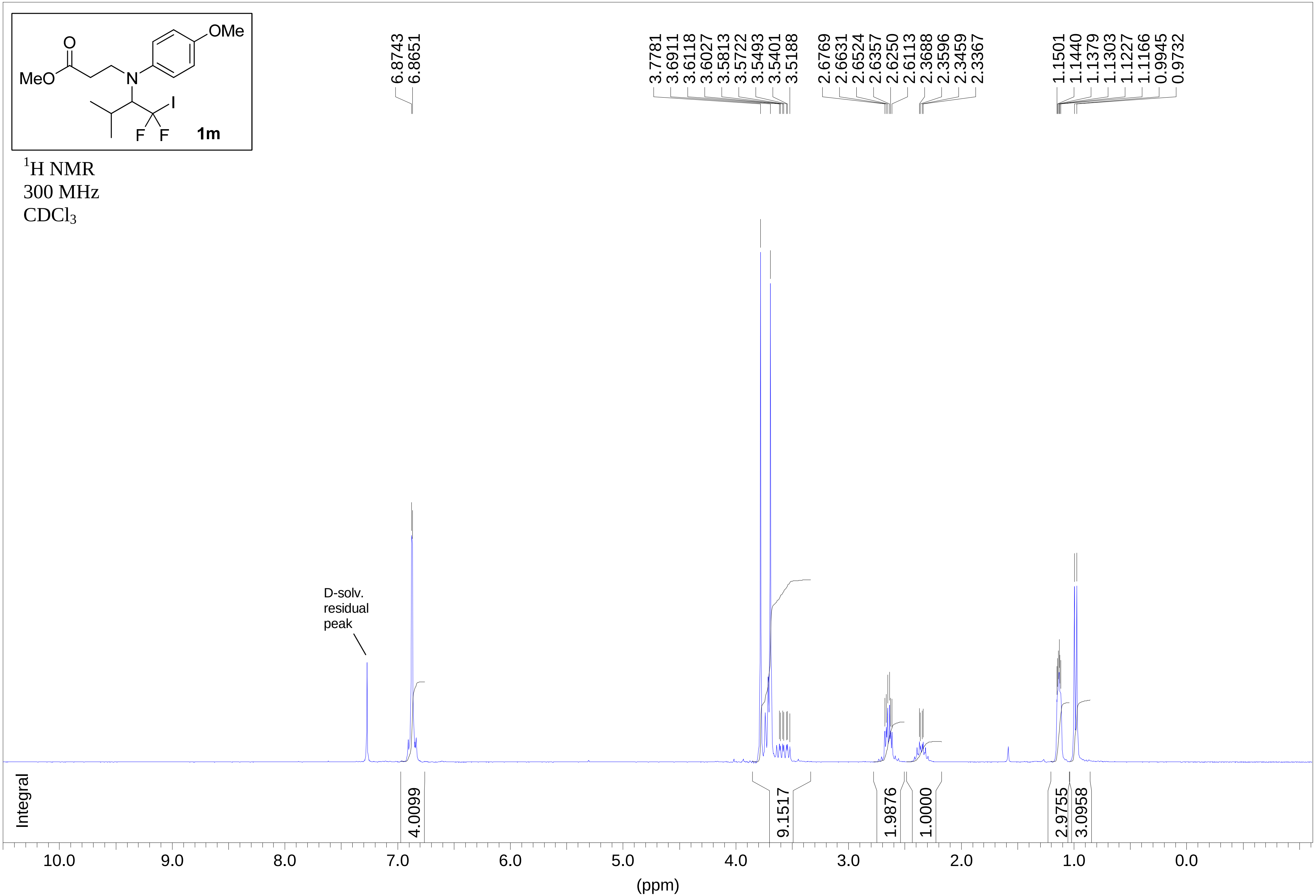
OMe
O
MeO
N
I
F
F
Cl
1l
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
172.3639
155.7935
140.6217
134.7156
131.8044
130.9759
128.8248
123.6180
114.5955
110.8405
106.5839
102.3121
78.4446
78.2014
78.1710
77.9277
77.5781
77.1600
76.7343
55.5653
51.6887
44.9921
33.1648
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)

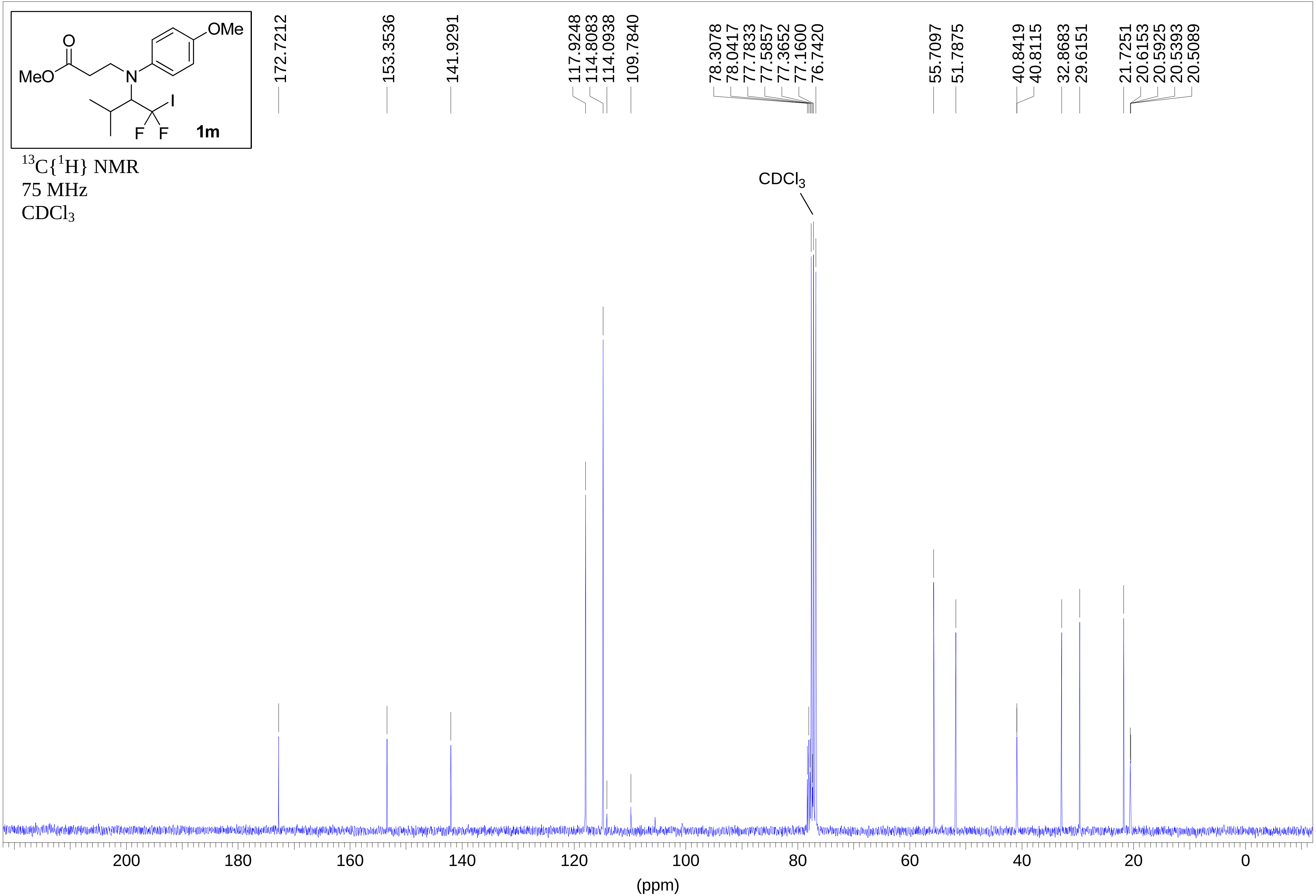


1l

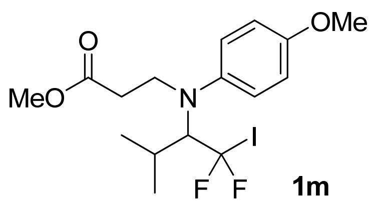
^{19}F NMR
282 MHz
$CDCl_3$



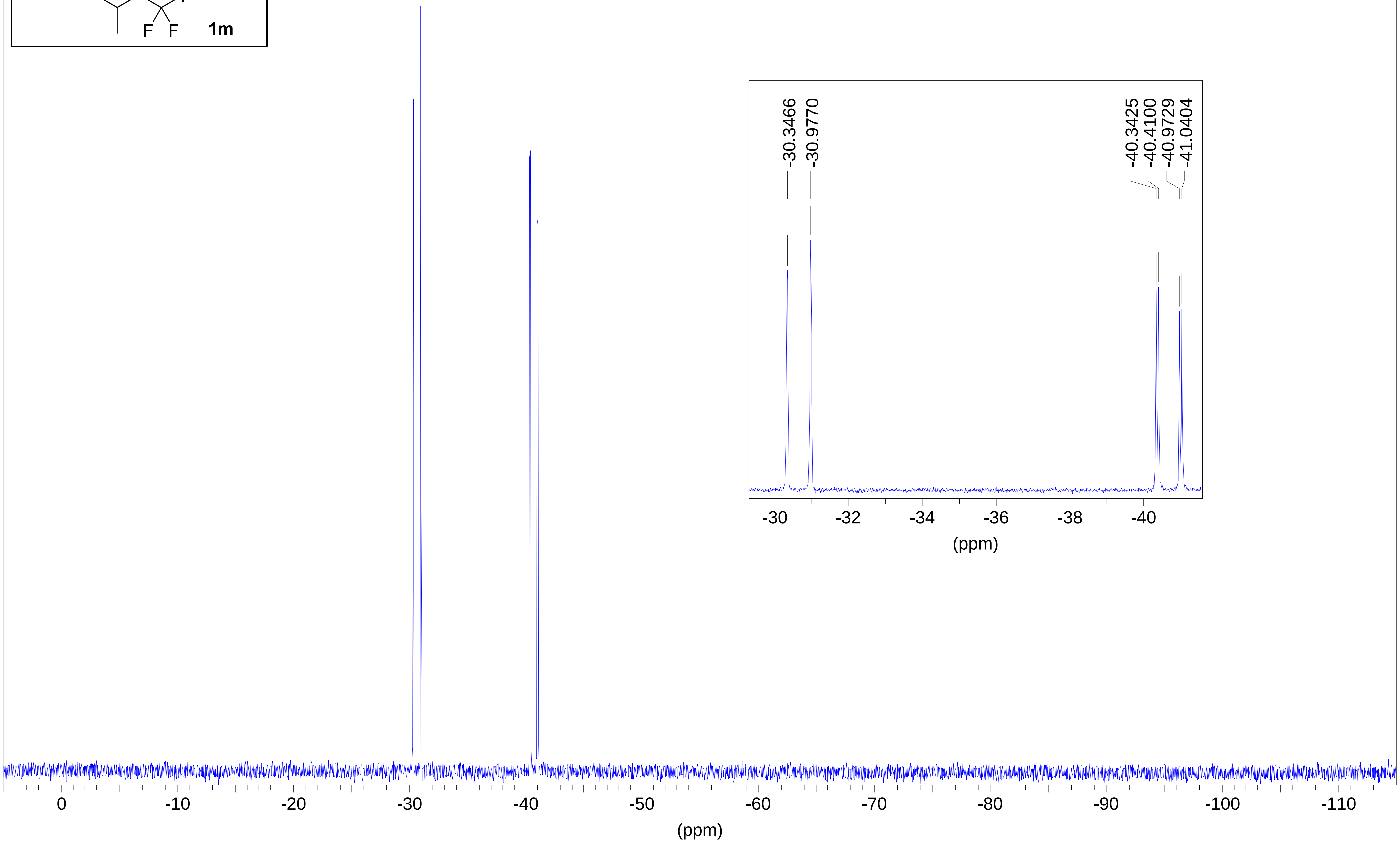

MeO
O
N
OMe
I
F
F
1m
[1]H NMR
300 MHz
$CDCl_3$
6.8743
6.8651
3.7781
3.6911
3.6118
3.6027
3.5813
3.5722
3.5493
3.5401
3.5188
2.6769
2.6631
2.6524
2.6357
2.6250
2.6113
2.3688
2.3596
2.3459
2.3367
1.1501
1.1440
1.1379
1.1303
1.1227
1.1166
0.9945
0.9732
D-solv.
residual
peak
Integral
4.0099
9.1517
1.9876
1.0000
2.9755
3.0958
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)



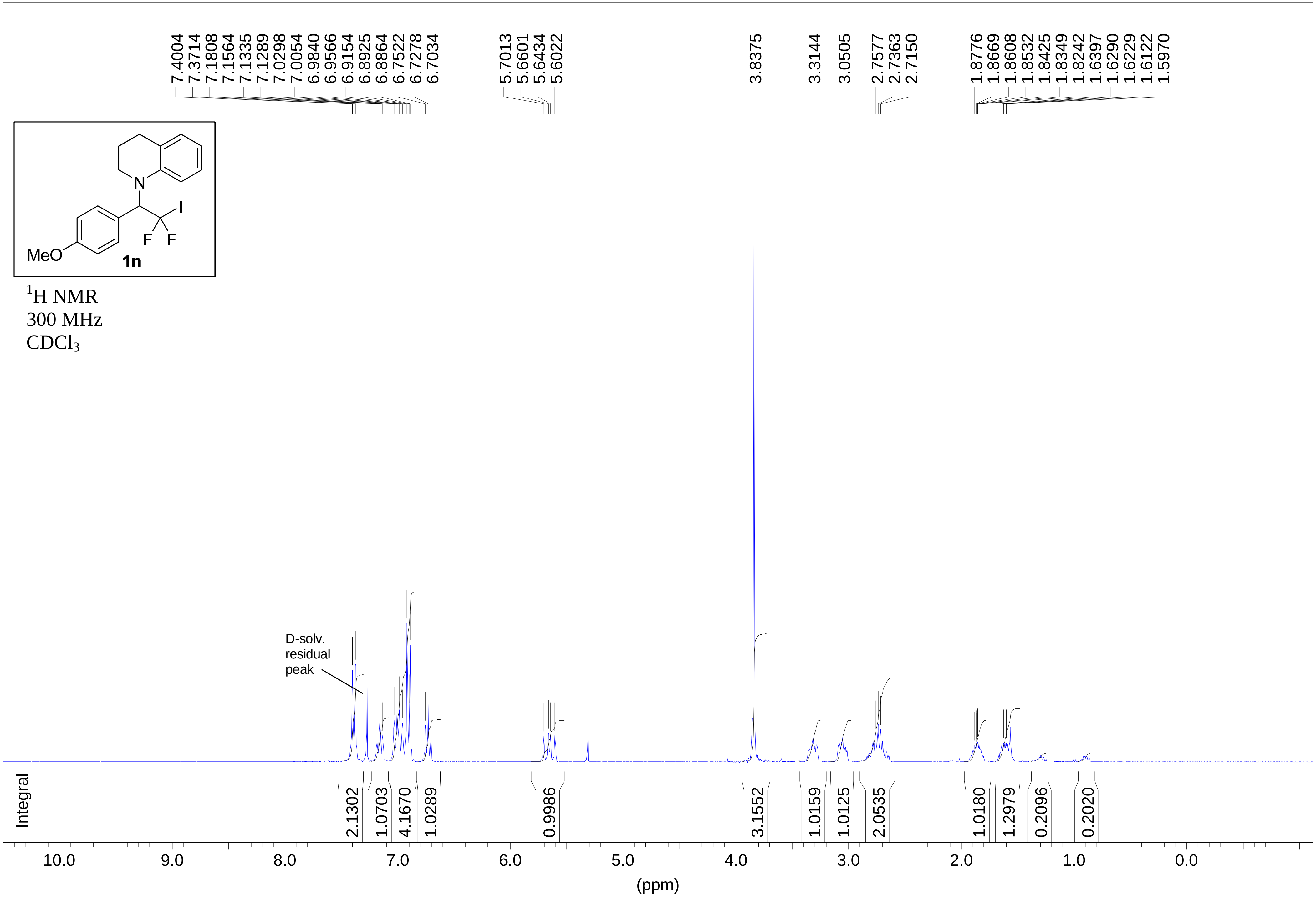
O
MeO
N
OMe
I
F F
1m
$^{13}C\{^1H\}$ NMR
75 MHz
$CDCl_3$
172.7212
153.3536
141.9291
117.9248
114.8083
114.0938
109.7840
78.3078
78.0417
77.7833
77.5857
77.3652
77.1600
76.7420
55.7097
51.7875
40.8419
40.8115
32.8683
29.6151
21.7251
20.6153
20.5925
20.5393
20.5089
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)



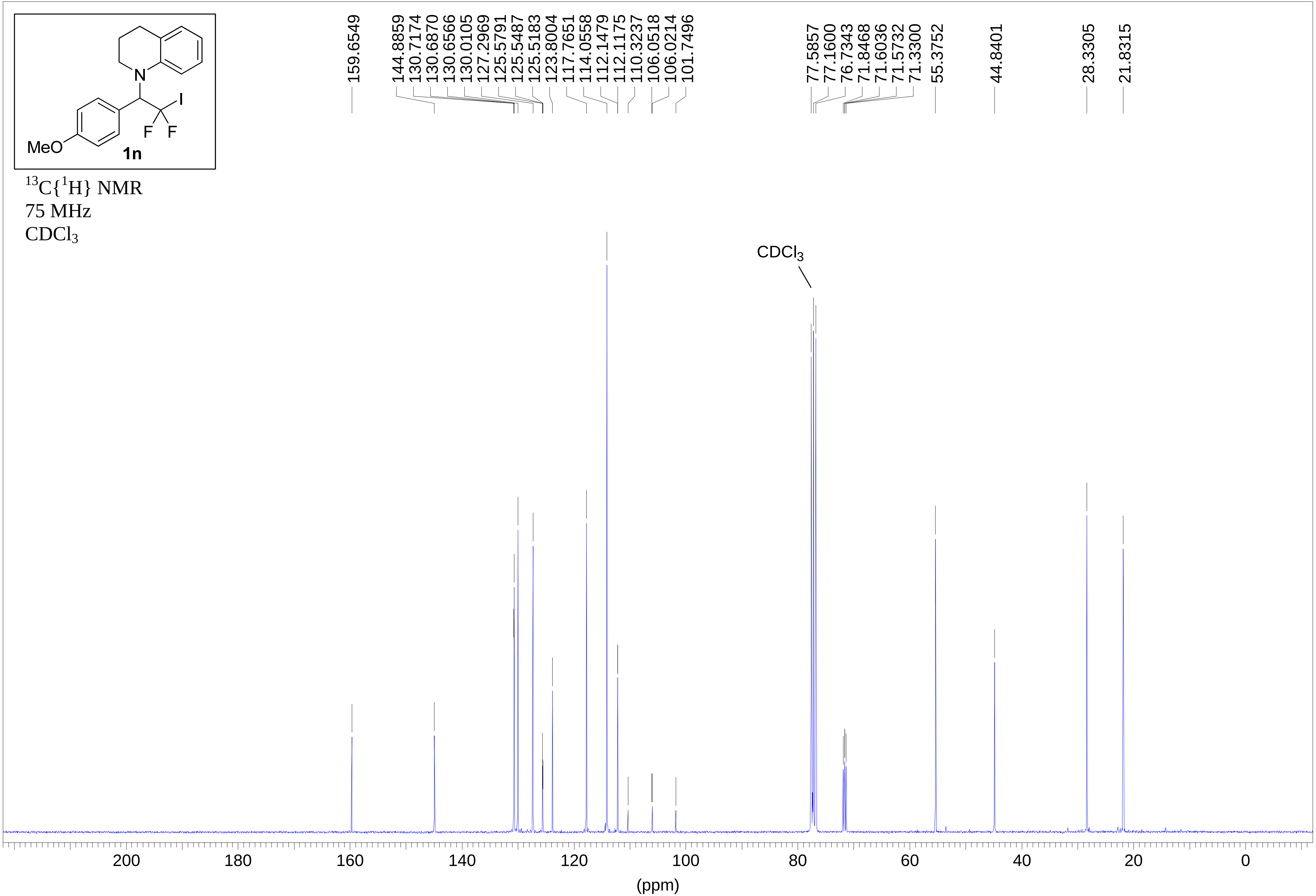
1m

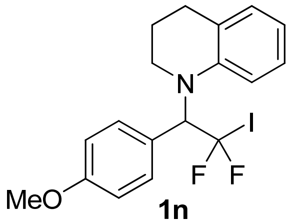


19F NMR
282 MHz
CDCl3
-30.3466
-30.9770
-40.3425
-40.4100
-40.9729
-41.0404
-30
-32
-34
-36
-38
-40
(ppm)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
(ppm)

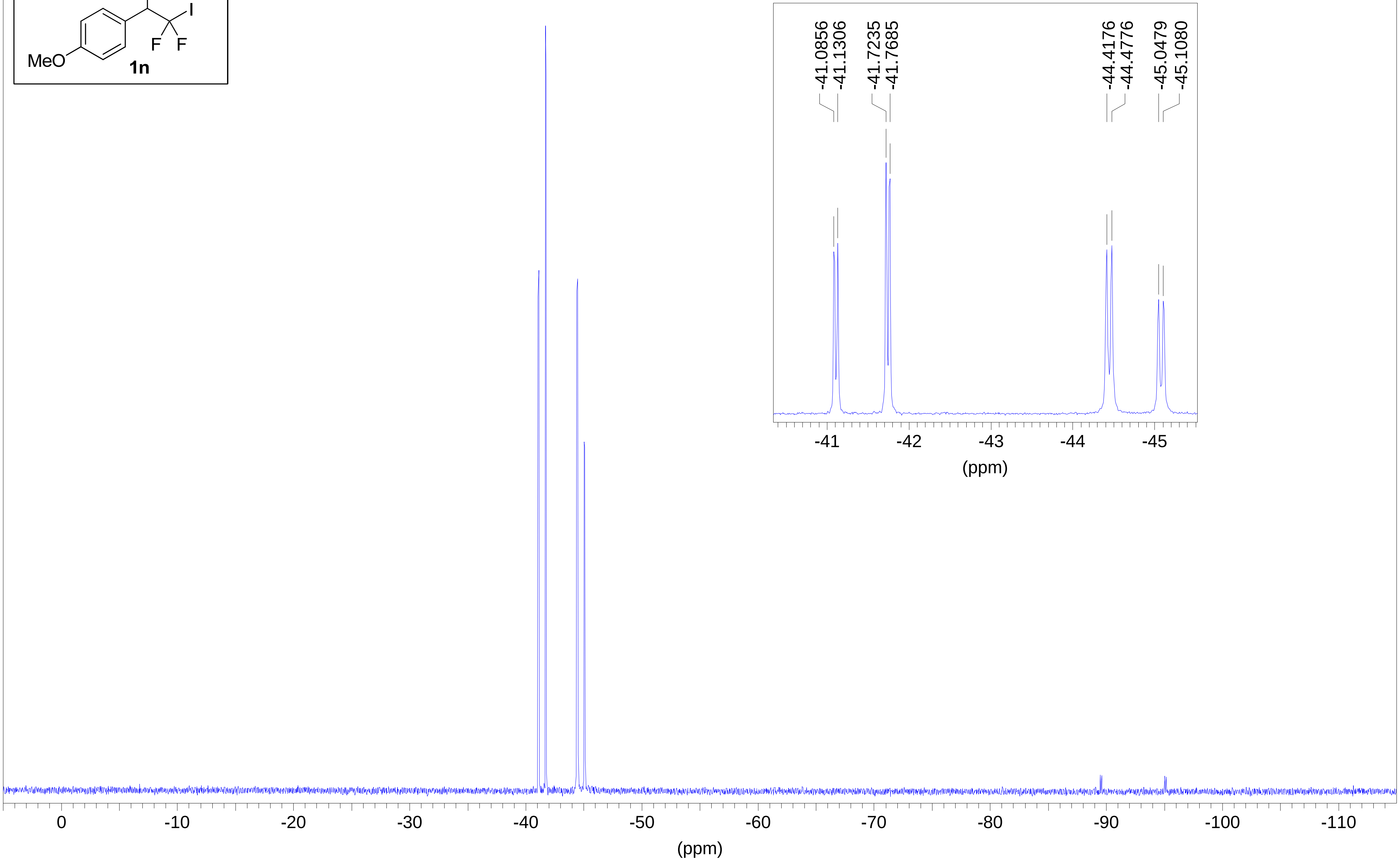


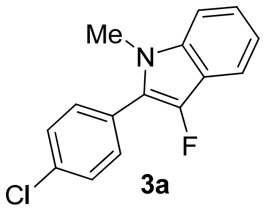
7.4004
7.3714
7.1808
7.1564
7.1335
7.1289
7.0298
7.0054
6.9840
6.9566
6.9154
6.8925
6.8864
6.7522
6.7278
6.7034
5.7013
5.6601
5.6434
5.6022
3.8375
3.3144
3.0505
2.7577
2.7363
2.7150
1.8776
1.8669
1.8608
1.8532
1.8425
1.8349
1.8242
1.6397
1.6290
1.6229
1.6122
1.5970
N
I
F
F
MeO
1n
[1]H NMR
300 MHz
$CDCl_3$
D-solv.
residual
peak
Integral
2.1302
1.0703
4.1670
1.0289
0.9986
3.1552
1.0159
1.0125
2.0535
1.0180
1.2979
0.2096
0.2020
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


N
I
F
F
MeO
1n
$^{13}C\{^1H\}$ NMR
75 MHz
$CDCl_3$
159.6549
144.8859
130.7174
130.6870
130.6566
130.0105
127.2969
125.5791
125.5487
125.5183
123.8004
117.7651
114.0558
112.1479
112.1175
110.3237
106.0518
106.0214
101.7496
77.5857
77.1600
76.7343
71.8468
71.6036
71.5732
71.3300
55.3752
44.8401
28.3305
21.8315
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)


MeO
N
I
F
F

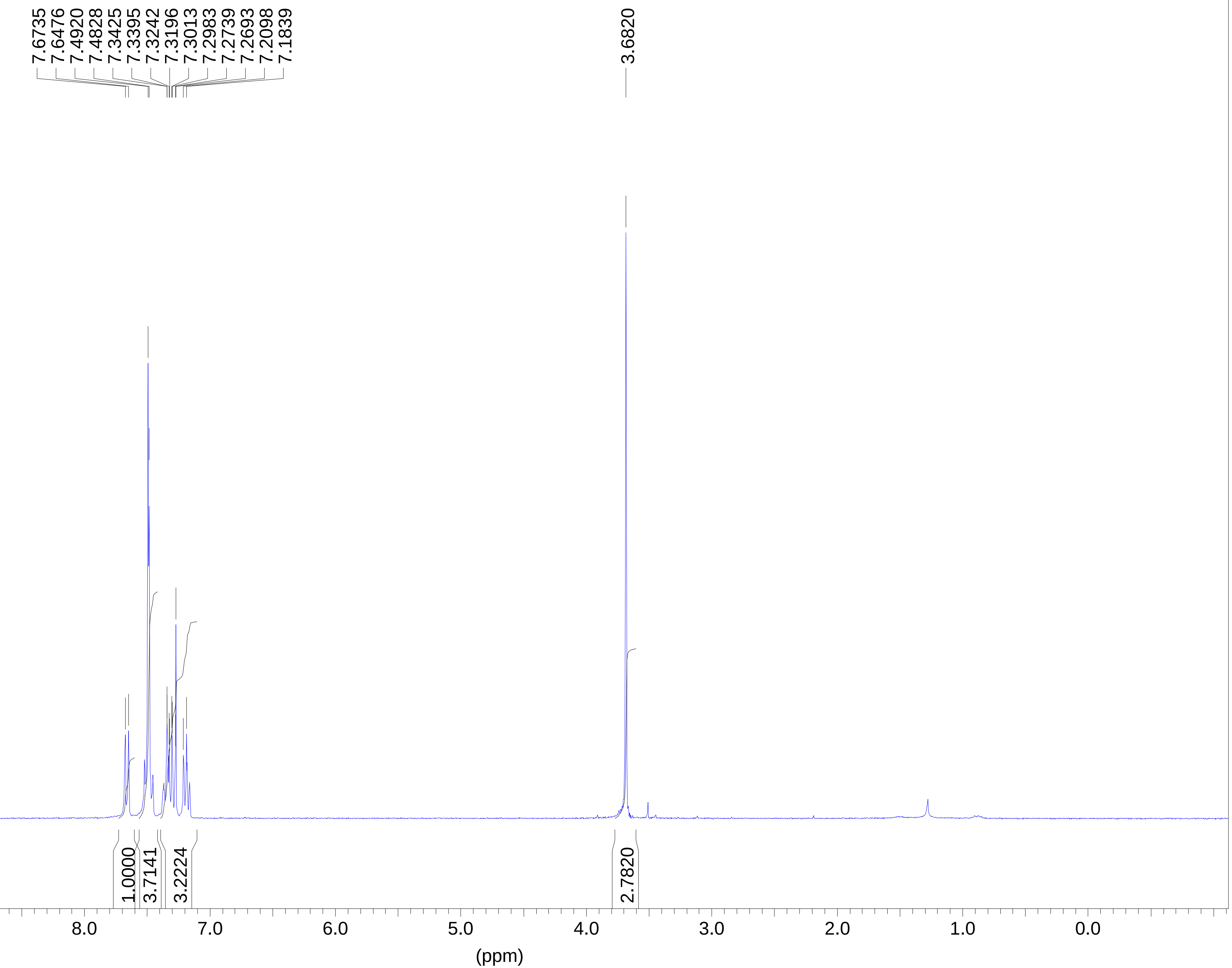
1n

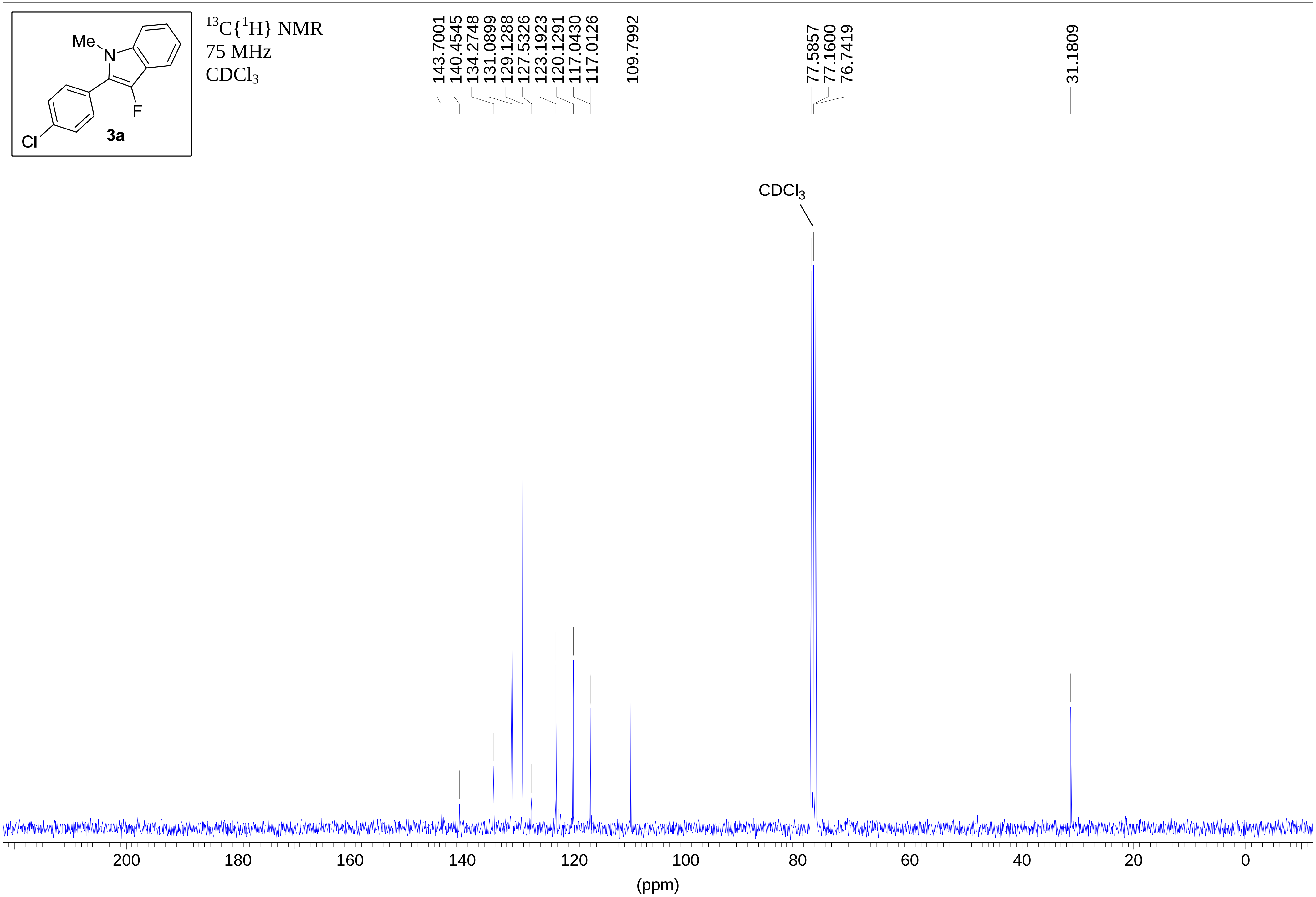

^{19}F NMR
282 MHz
$CDCl_3$
-41.0856
-41.1306
-41.7235
-41.7685
-44.4176
-44.4776
-45.0479
-45.1080
-41
-42
-43
-44
-45
(ppm)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
(ppm)

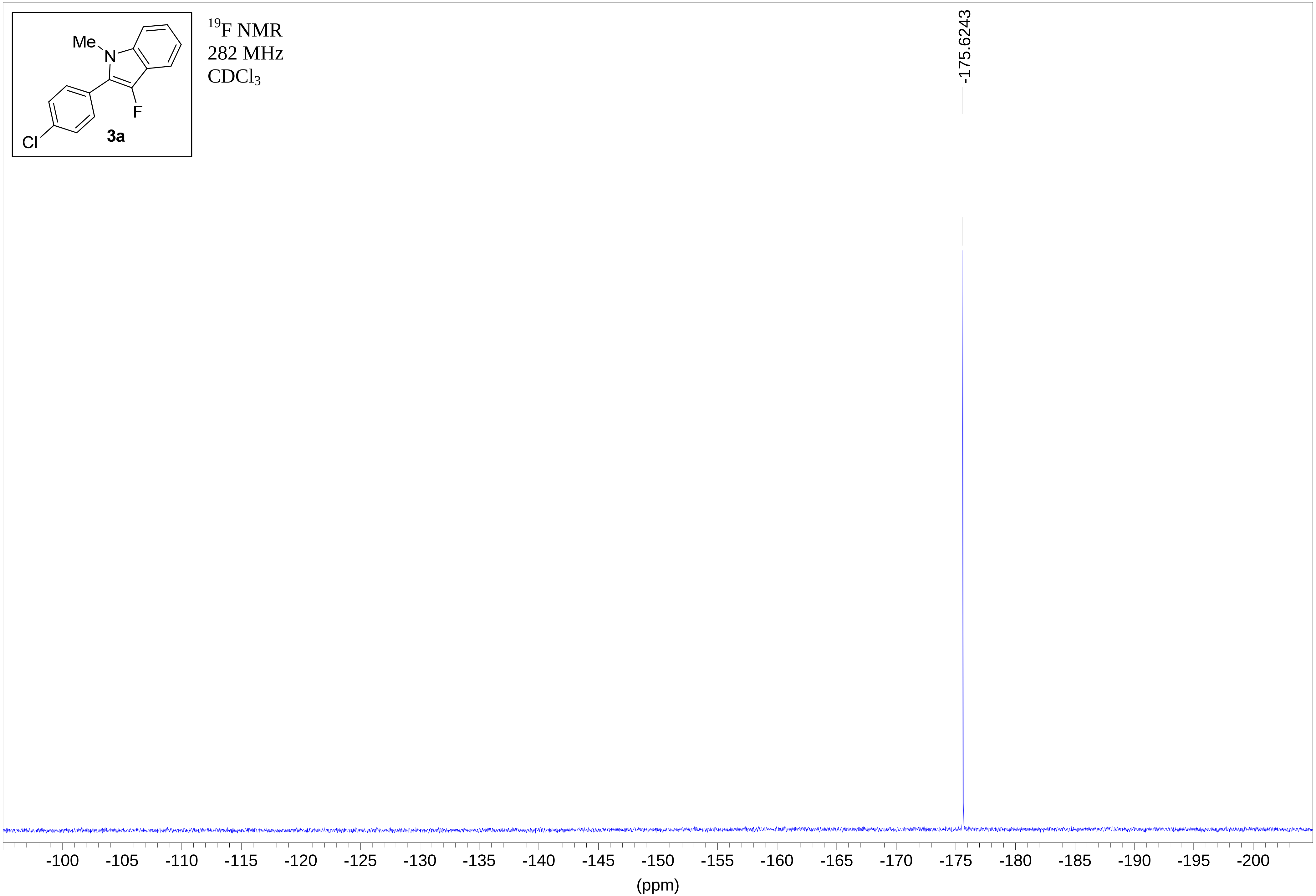


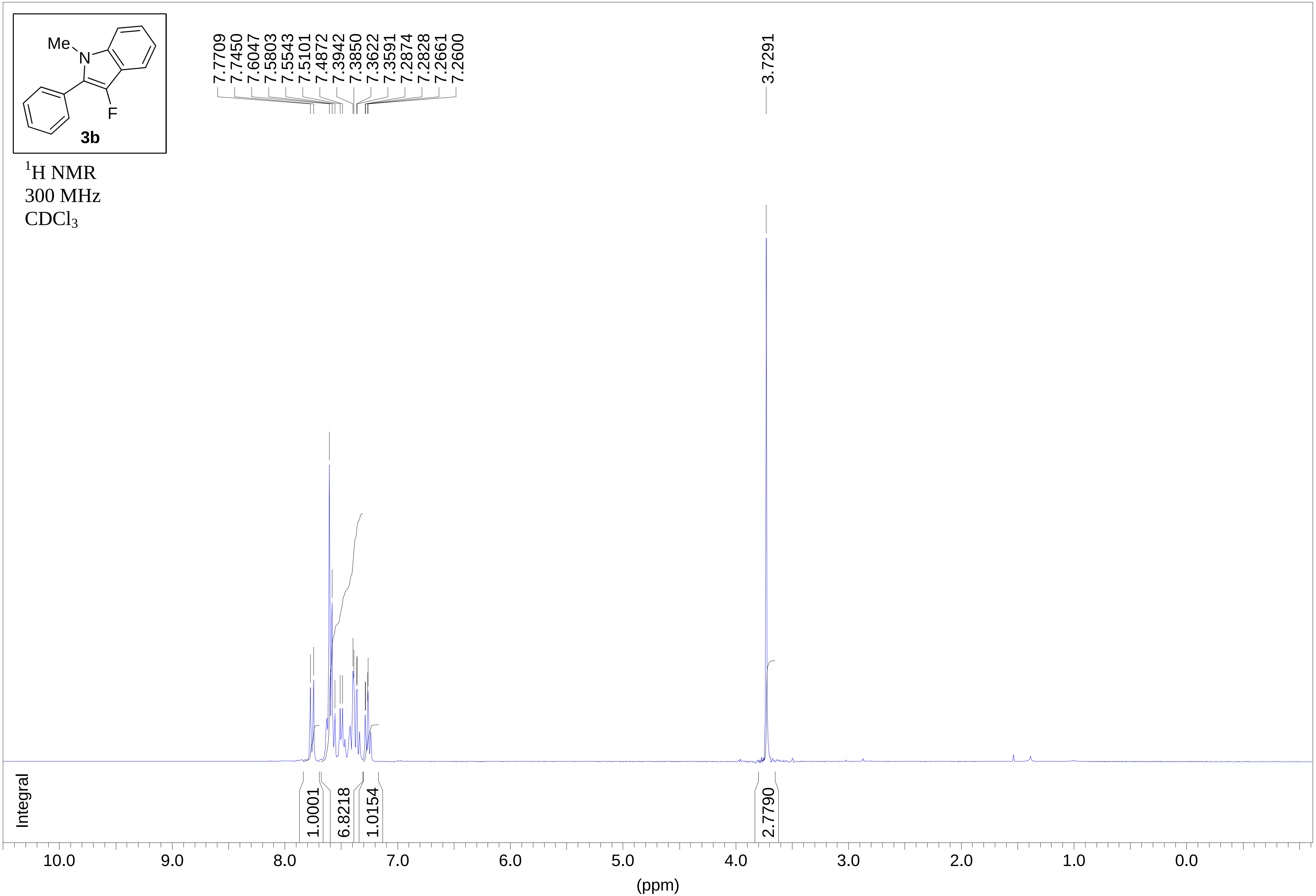
3a

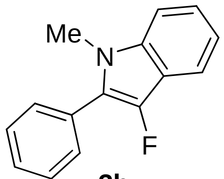
^{1}H NMR
300 MHz
$CDCl_3$



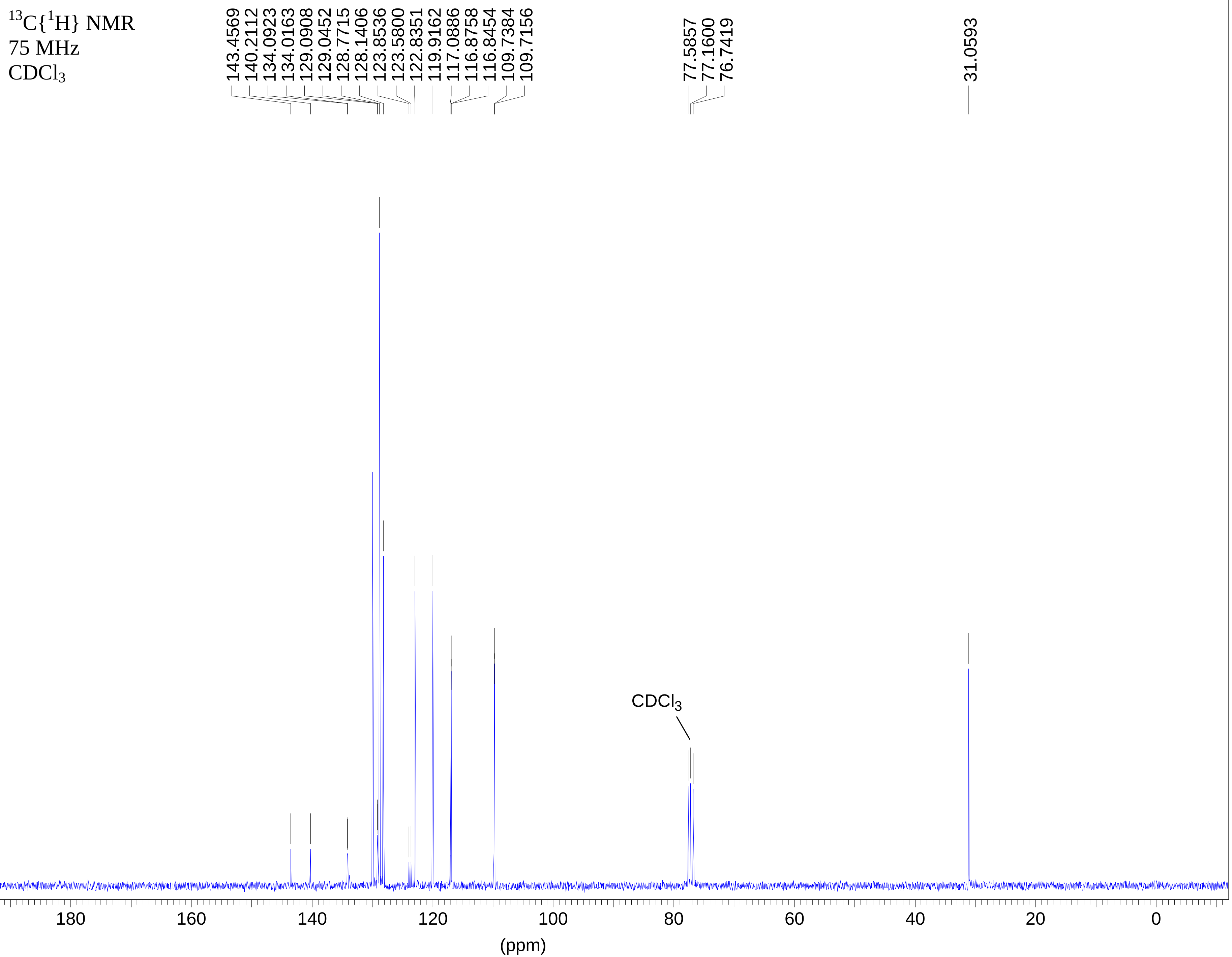

Me
N
F
Cl
3a
$^{13}C\{^1H\}$ NMR
75 MHz
$CDCl_3$
143.7001
140.4545
134.2748
131.0899
129.1288
127.5326
123.1923
120.1291
117.0430
117.0126
109.7992
77.5857
77.1600
76.7419
31.1809
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)

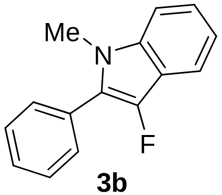

Me
N
F
Cl
3a
^{19}F NMR
282 MHz
$CDCl_3$
-175.6243
-100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 -200
(ppm)


Me
N
F
3b
^{1}H NMR
300 MHz
$CDCl_3$
7.7709
7.7450
7.6047
7.5803
7.5543
7.5101
7.4872
7.3942
7.3850
7.3622
7.3591
7.2874
7.2828
7.2661
7.2600
3.7291
Integral
1.0001
6.8218
1.0154
2.7790
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


Me
N
F

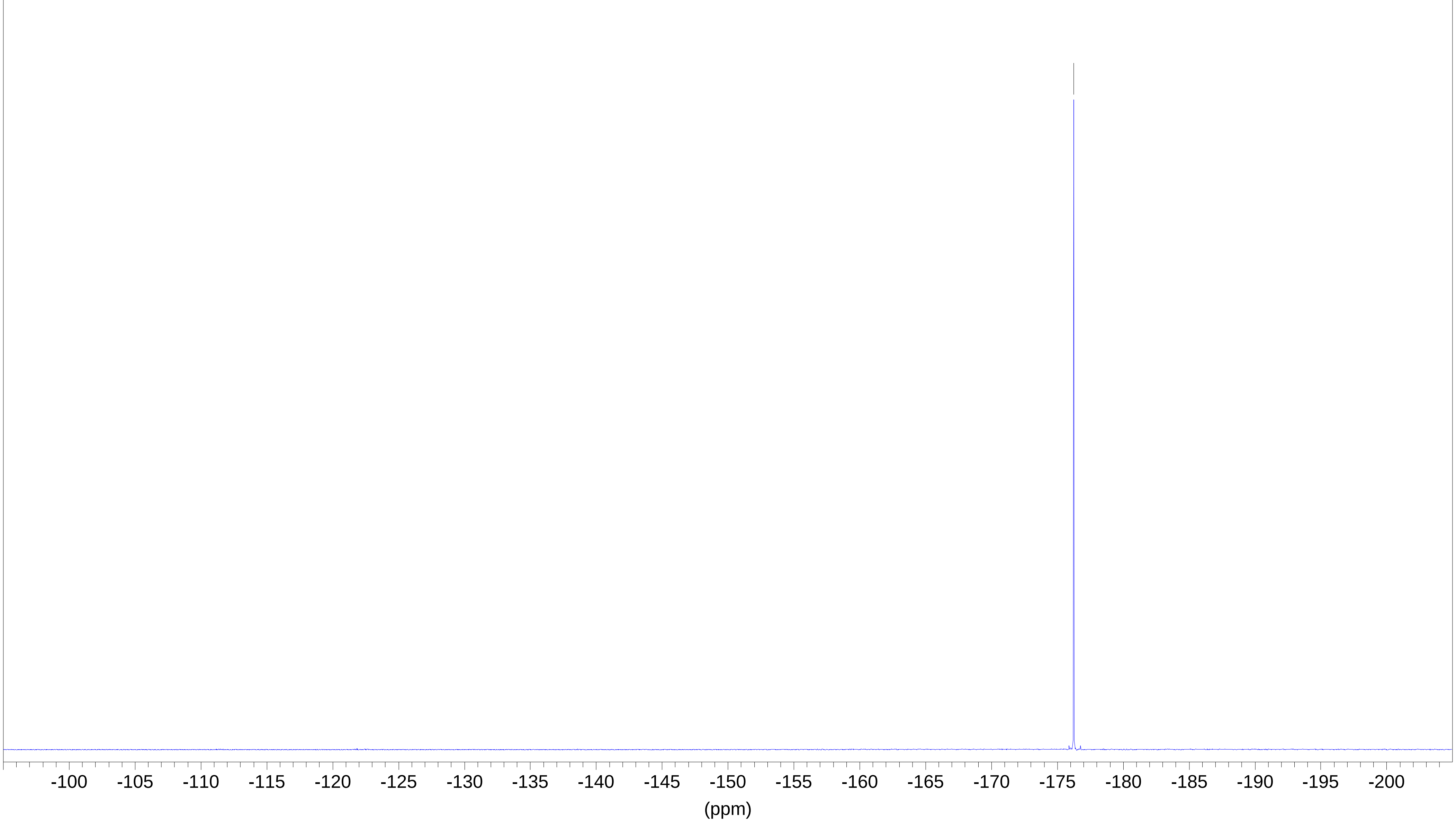
3b

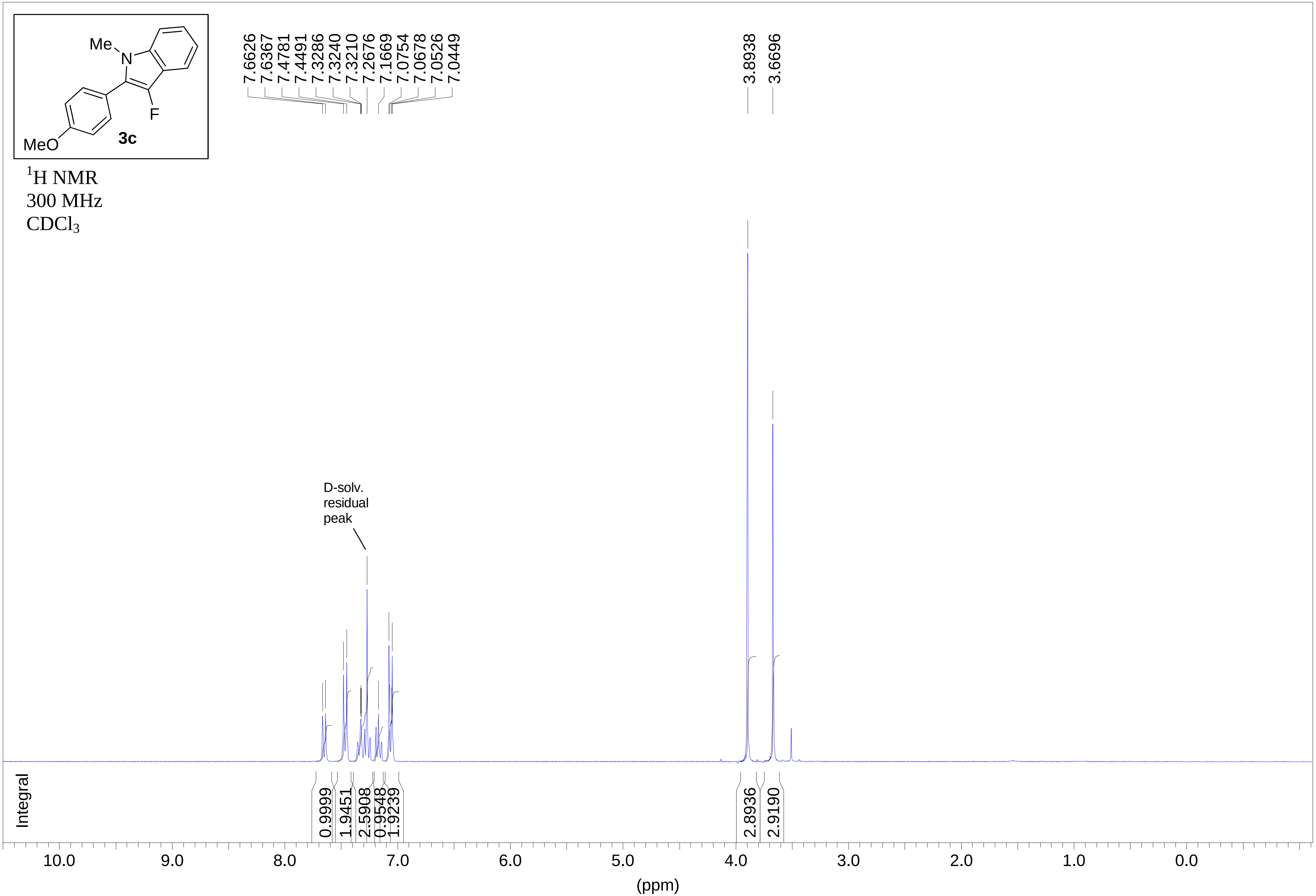

$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
143.4569
140.2112
134.0923
134.0163
129.0908
129.0452
128.7715
128.1406
123.8536
123.5800
122.8351
119.9162
117.0886
116.8758
116.8454
109.7384
109.7156
77.5857
77.1600
76.7419
31.0593
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)

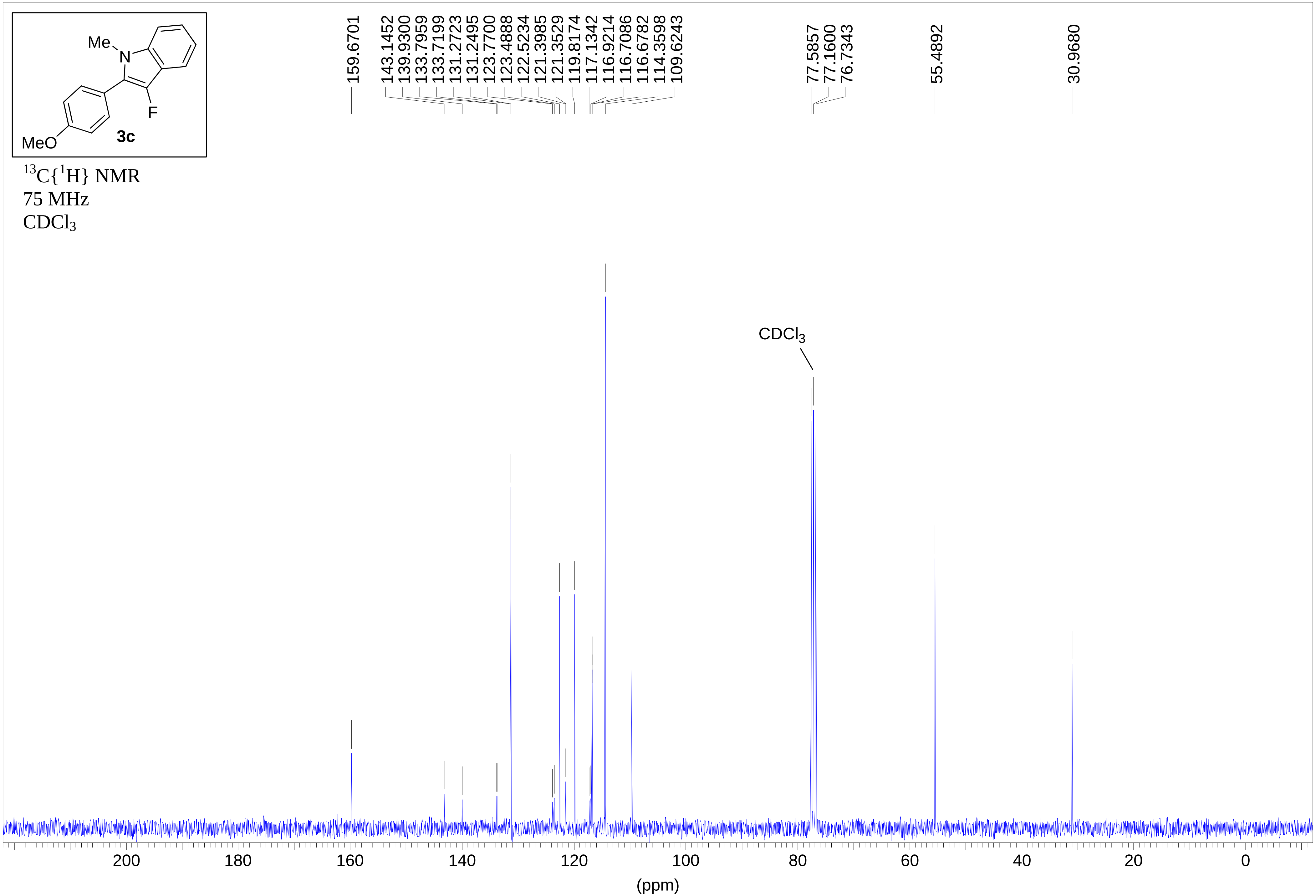


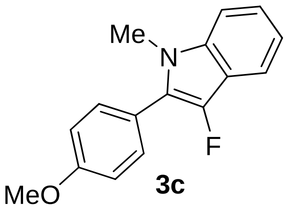
3b

^{19}F NMR
282 MHz
$CDCl_3$



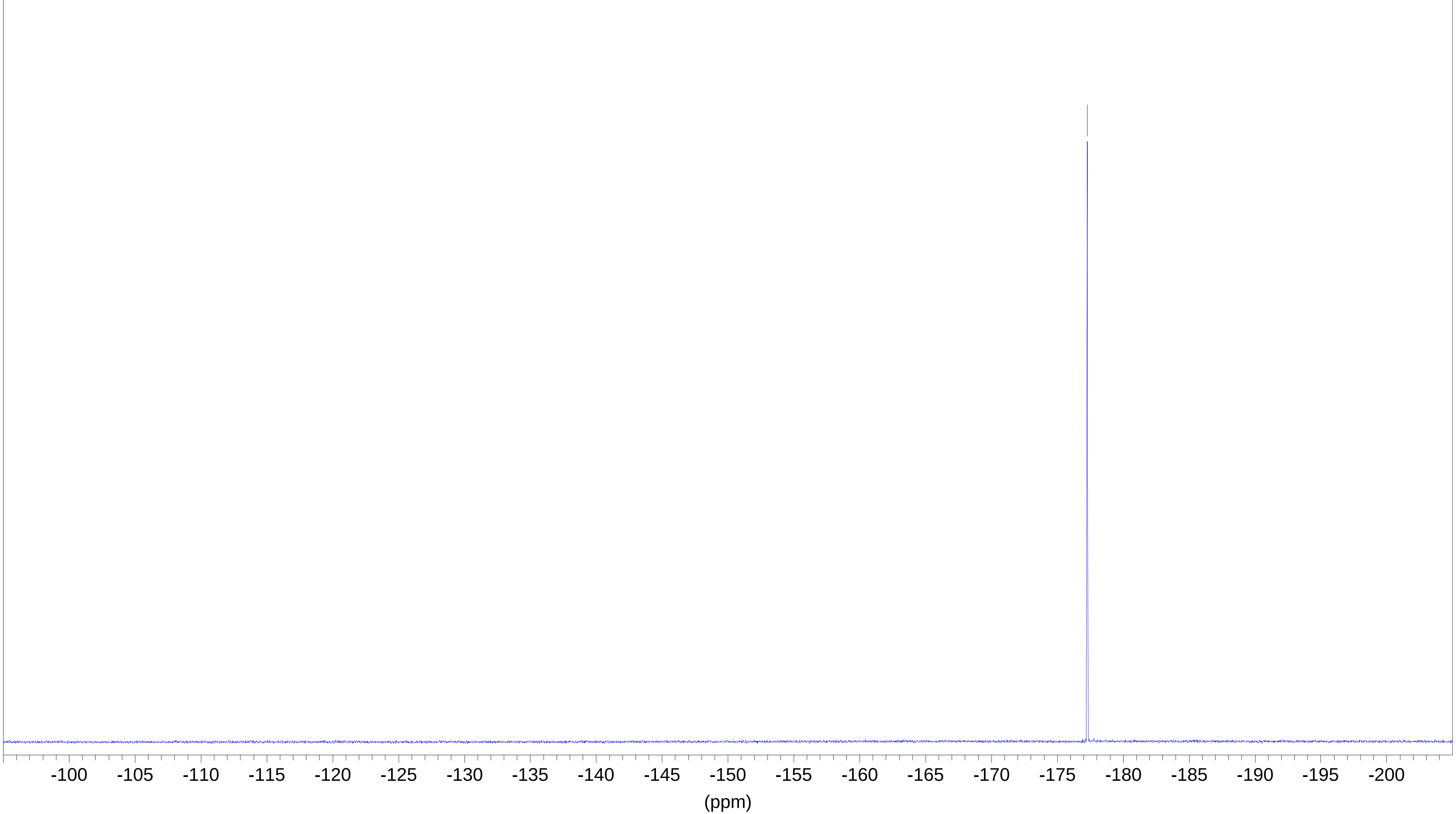

Me
N
F
MeO
3c
¹H NMR
300 MHz
CDCl3
7.6626
7.6367
7.4781
7.4491
7.3286
7.3240
7.3210
7.2676
7.1669
7.0754
7.0678
7.0526
7.0449
3.8938
3.6696
D-solv.
residual
peak
Integral
0.9999
1.9451
2.5908
0.9548
1.9239
2.8936
2.9190
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

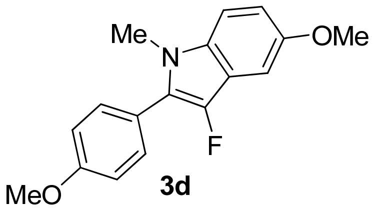

Me
N
F
MeO
3c
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
159.6701
143.1452
139.9300
133.7959
133.7199
131.2723
131.2495
123.7700
123.4888
122.5234
121.3985
121.3529
119.8174
117.1342
116.9214
116.7086
116.6782
114.3598
109.6243
77.5857
77.1600
76.7343
55.4892
30.9680
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)



3c

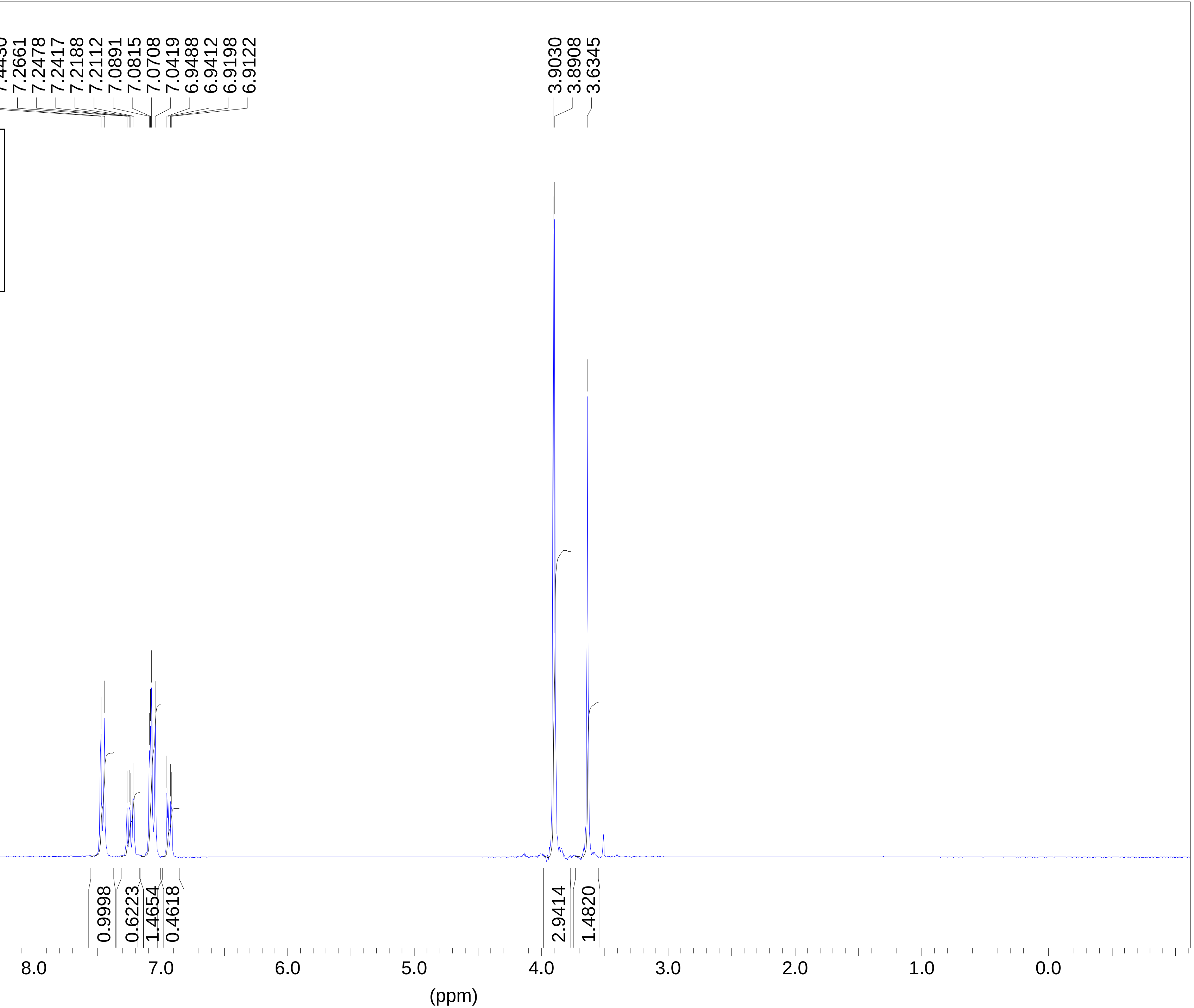
^{19}F NMR
282 MHz
$CDCl_3$

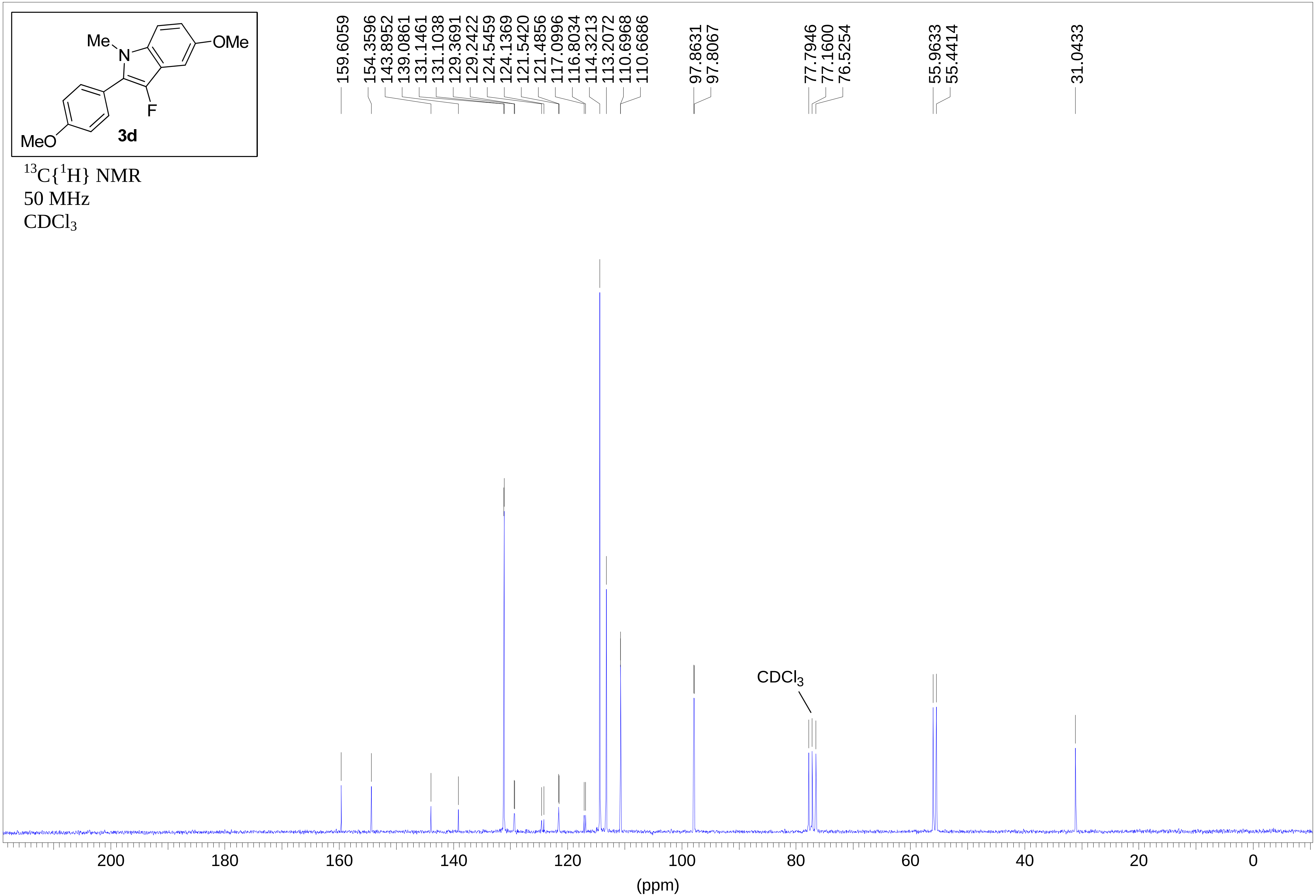


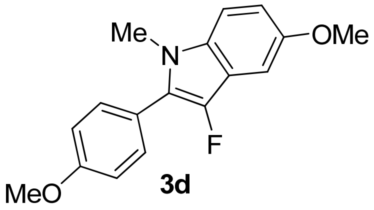


3d

^{1}H NMR
300 MHz
$CDCl_3$

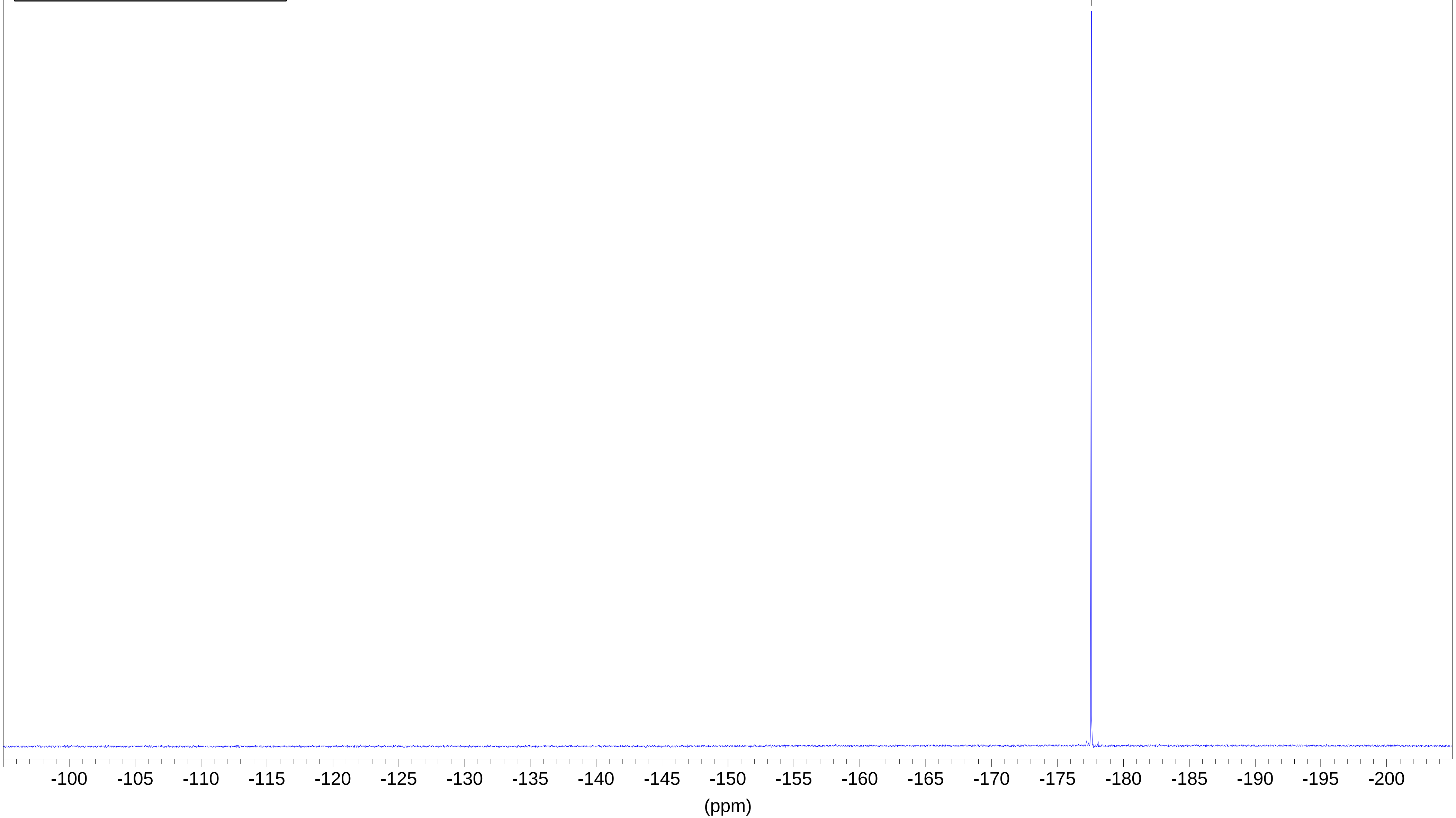


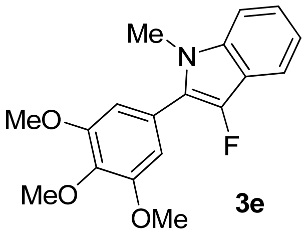

159.6059
154.3596
143.8952
139.0861
131.1461
131.1038
129.3691
129.2422
124.5459
124.1369
121.5420
121.4856
117.0996
116.8034
114.3213
113.2072
110.6968
110.6686
97.8631
97.8067
77.7946
77.1600
76.5254
55.9633
55.4414
31.0433
Me
N
OMe
F
MeO
3d
$^{13}C\{^{1}H\}$ NMR
50 MHz
$CDCl_3$
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)



3d

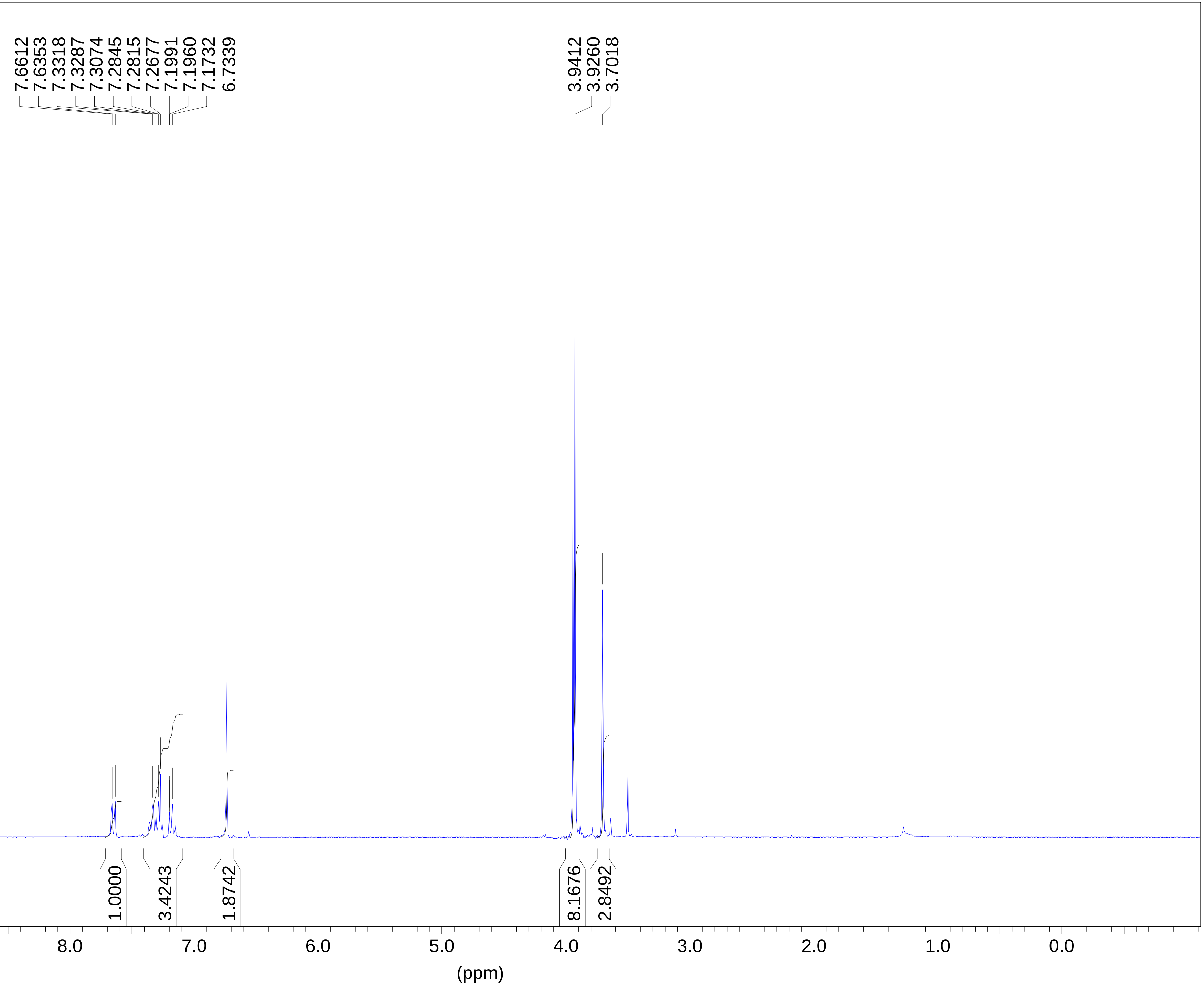
^{19}F NMR
282 MHz
$CDCl_3$

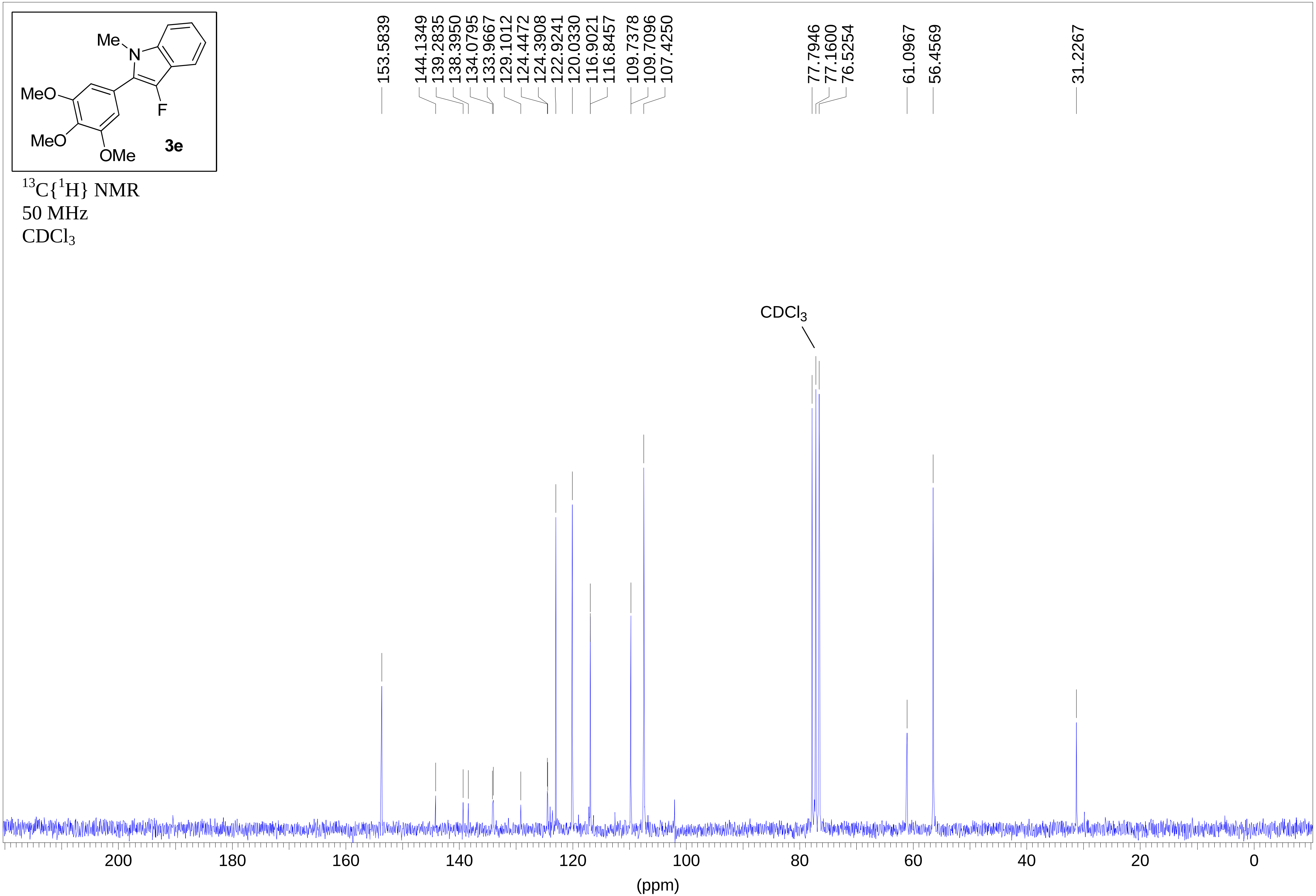


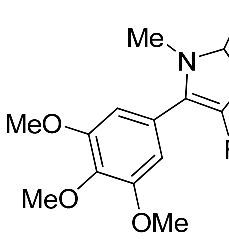


3e

^{1}H NMR
300 MHz
$CDCl_3$

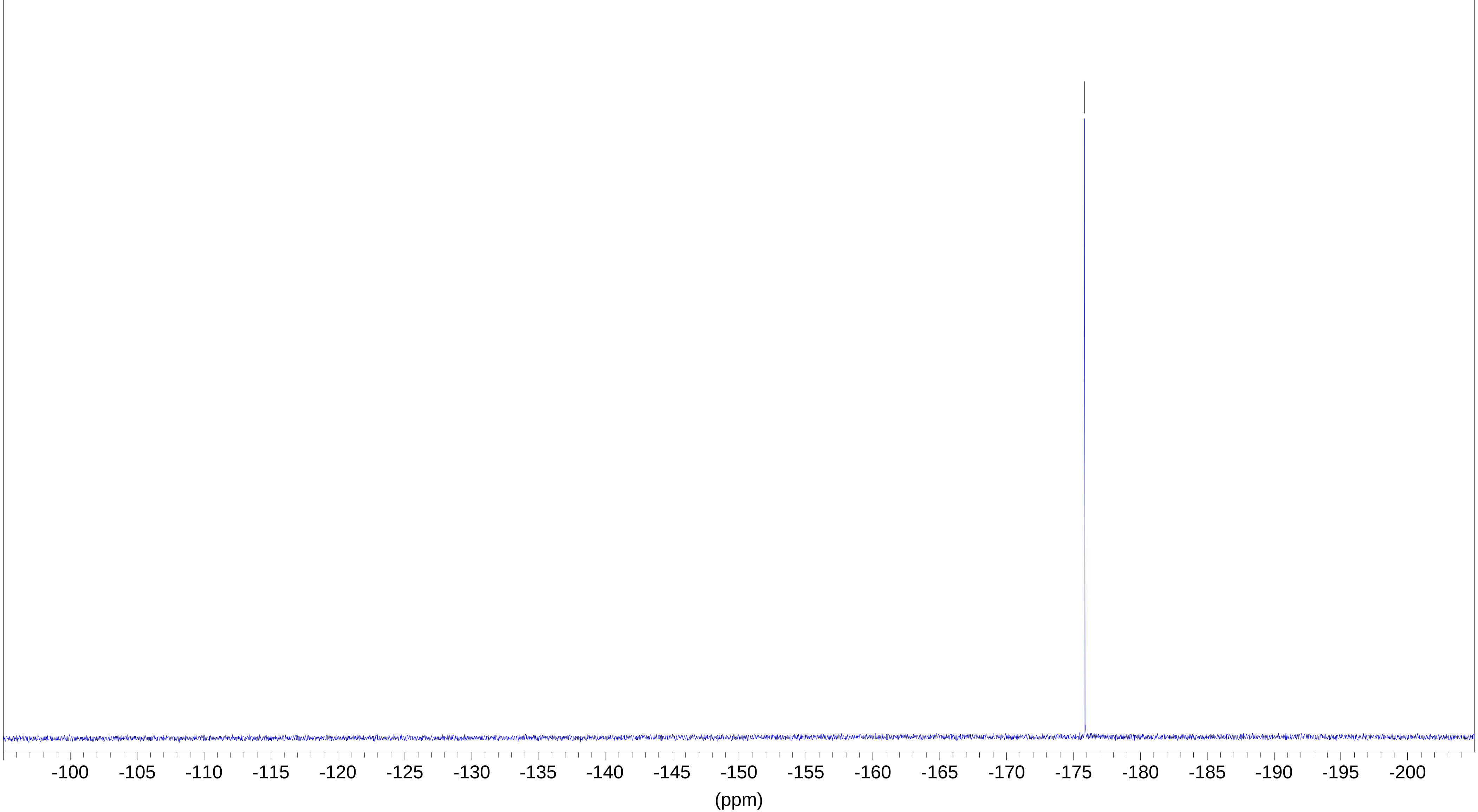


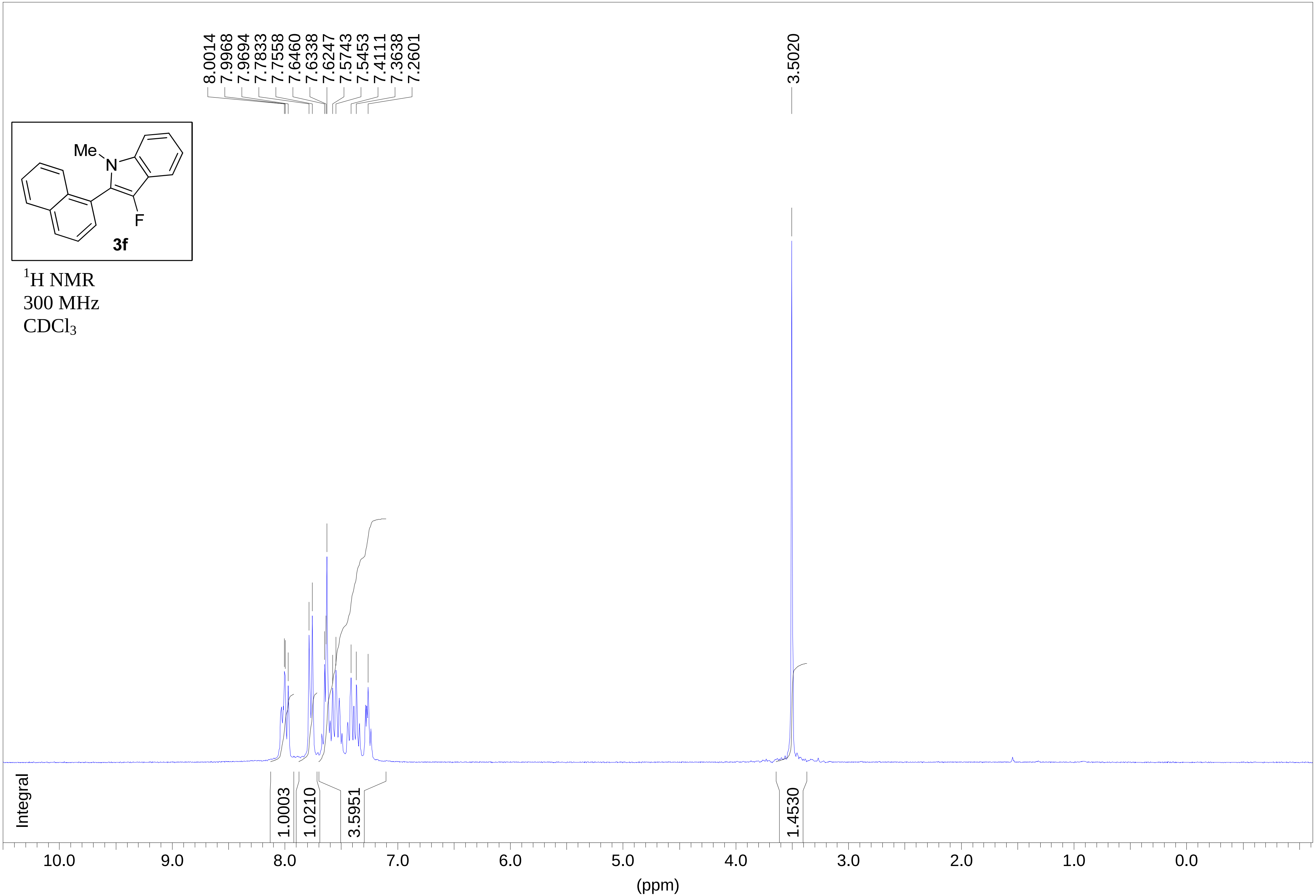

Me
N
MeO
F
MeO
OMe
3e
$^{13}C\{^1H\}$ NMR
50 MHz
$CDCl_3$
153.5839
144.1349
139.2835
138.3950
134.0795
133.9667
129.1012
124.4472
124.3908
122.9241
120.0330
116.9021
116.8457
109.7378
109.7096
107.4250
77.7946
77.1600
76.5254
61.0967
56.4569
31.2267
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)



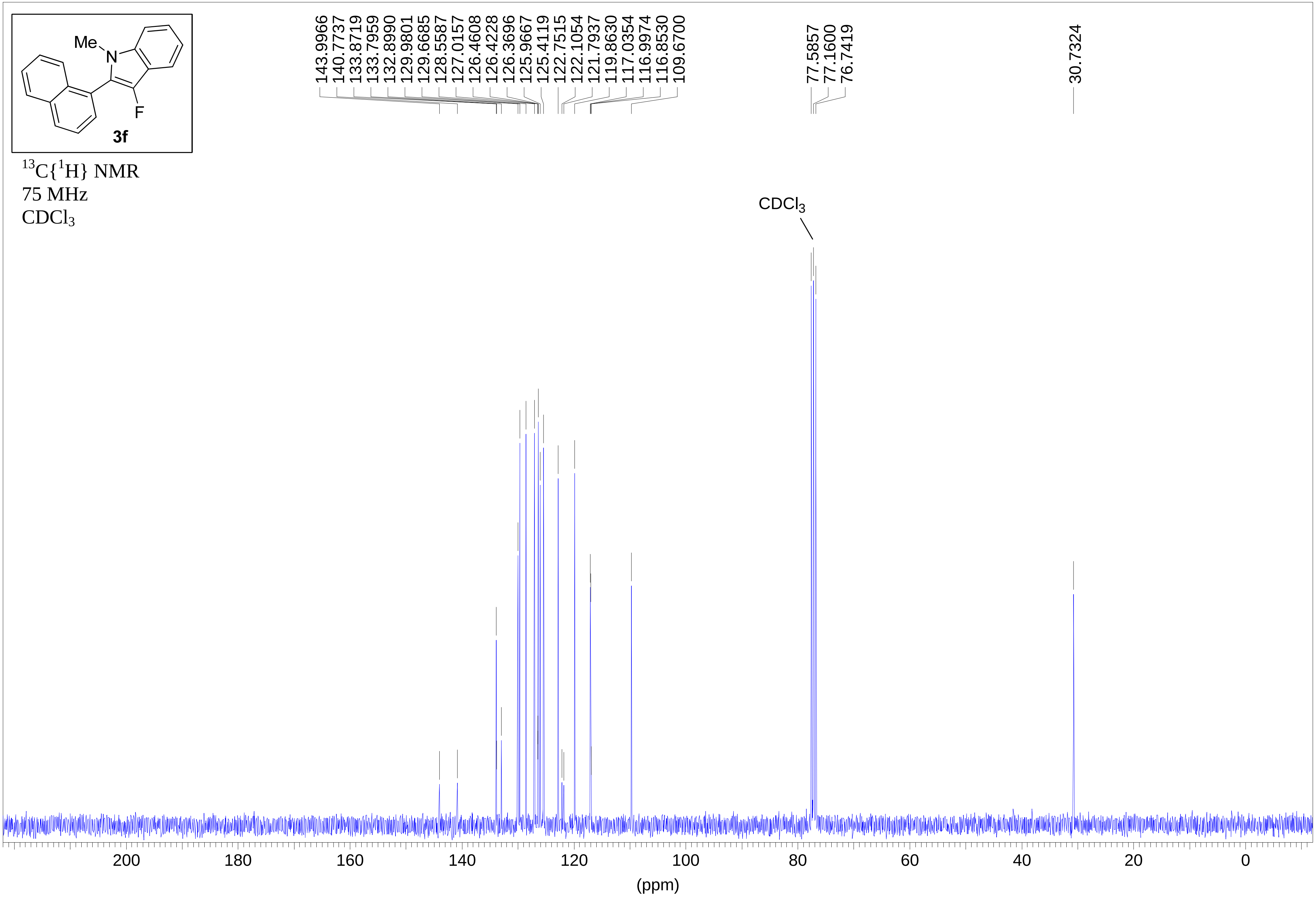
3e

^{19}F NMR
282 MHz
$CDCl_3$

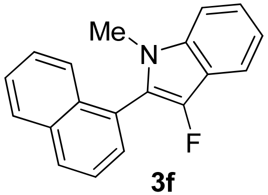




8.0014
7.9968
7.9694
7.7833
7.7558
7.6460
7.6338
7.6247
7.5743
7.5453
7.4111
7.3638
7.2601
3.5020
Me
N
F
3f
1H NMR
300 MHz
CDCl3
Integral
1.0003
1.0210
3.5951
1.4530
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

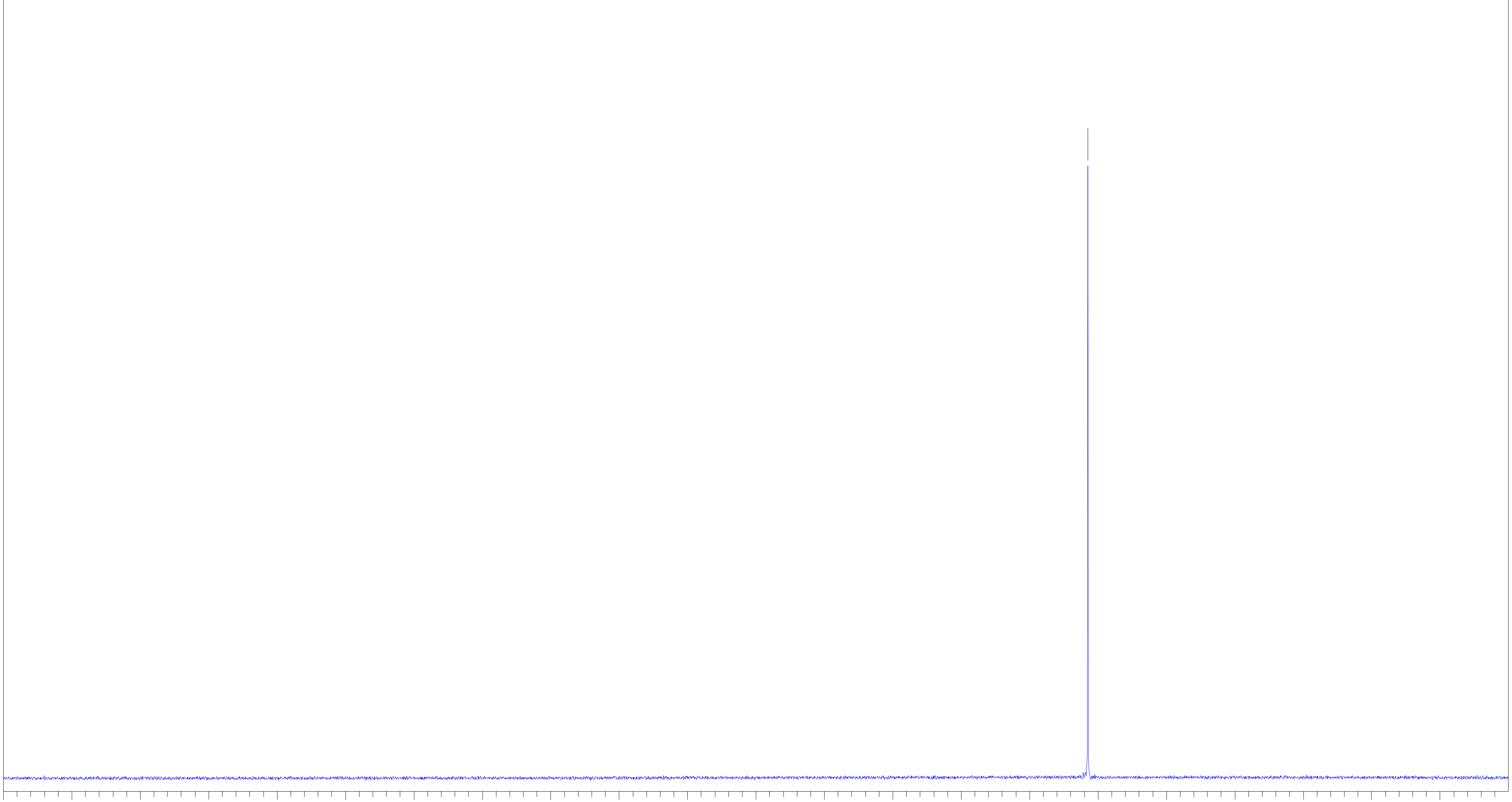


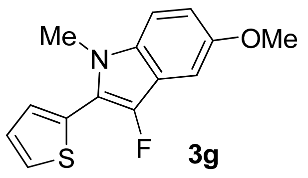
Me
N
F
3f
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
143.9966
140.7737
133.8719
133.7959
132.8990
129.9801
129.6685
128.5587
127.0157
126.4608
126.4228
126.3696
125.9667
125.4119
122.7515
122.1054
121.7937
119.8630
117.0354
116.9974
116.8530
109.6700
77.5857
77.1600
76.7419
30.7324
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)



3f

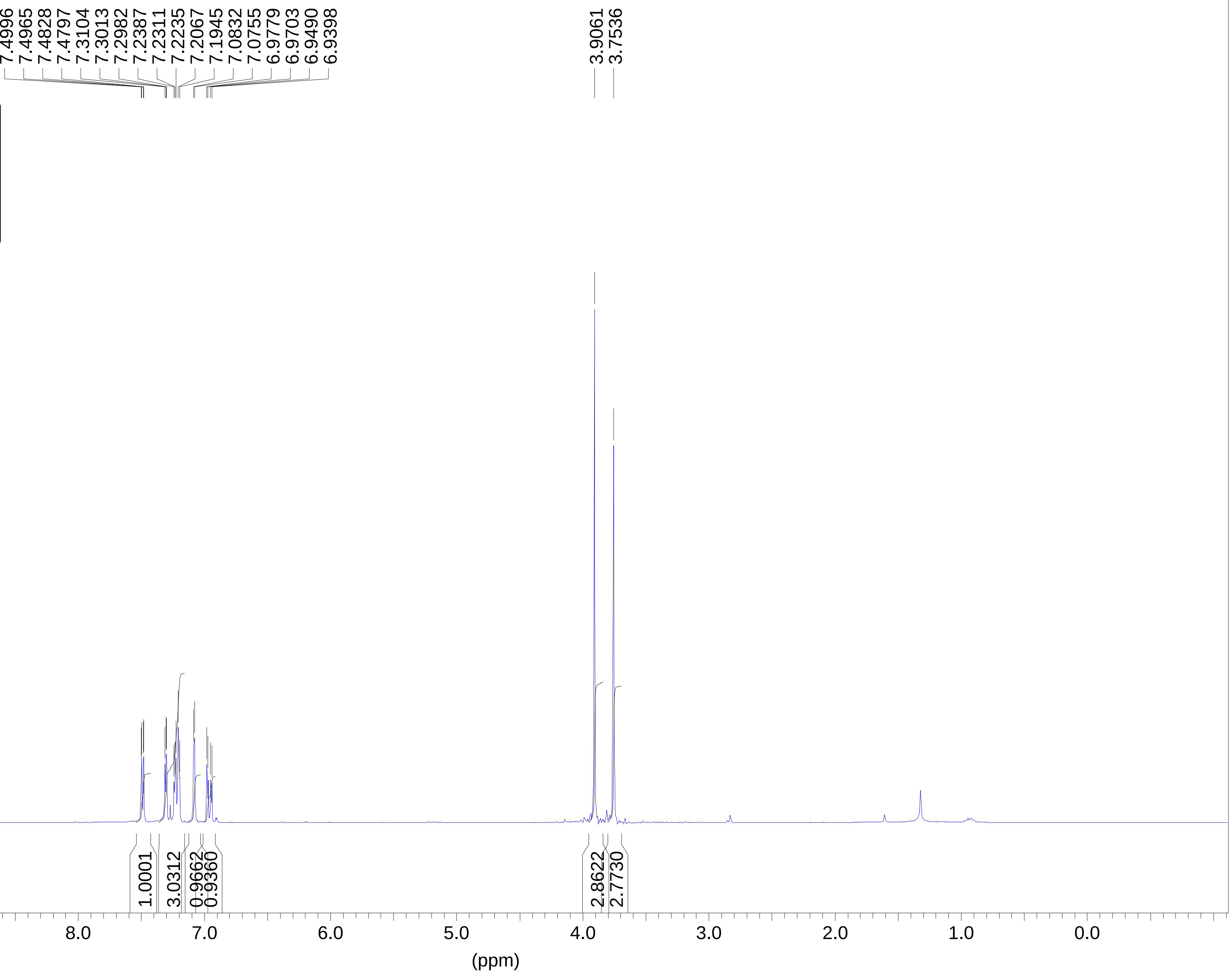
^{19}F NMR
282 MHz
$CDCl_3$

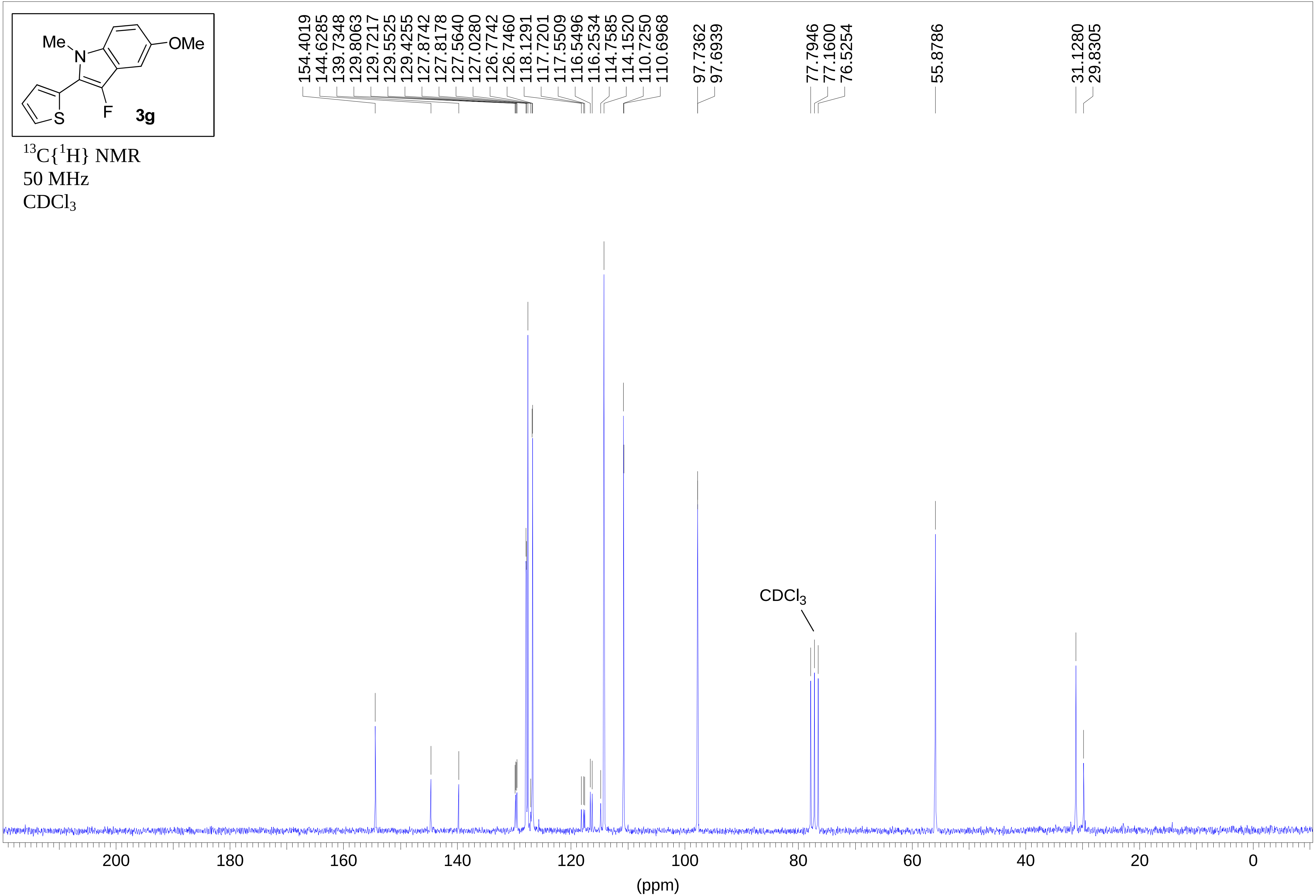


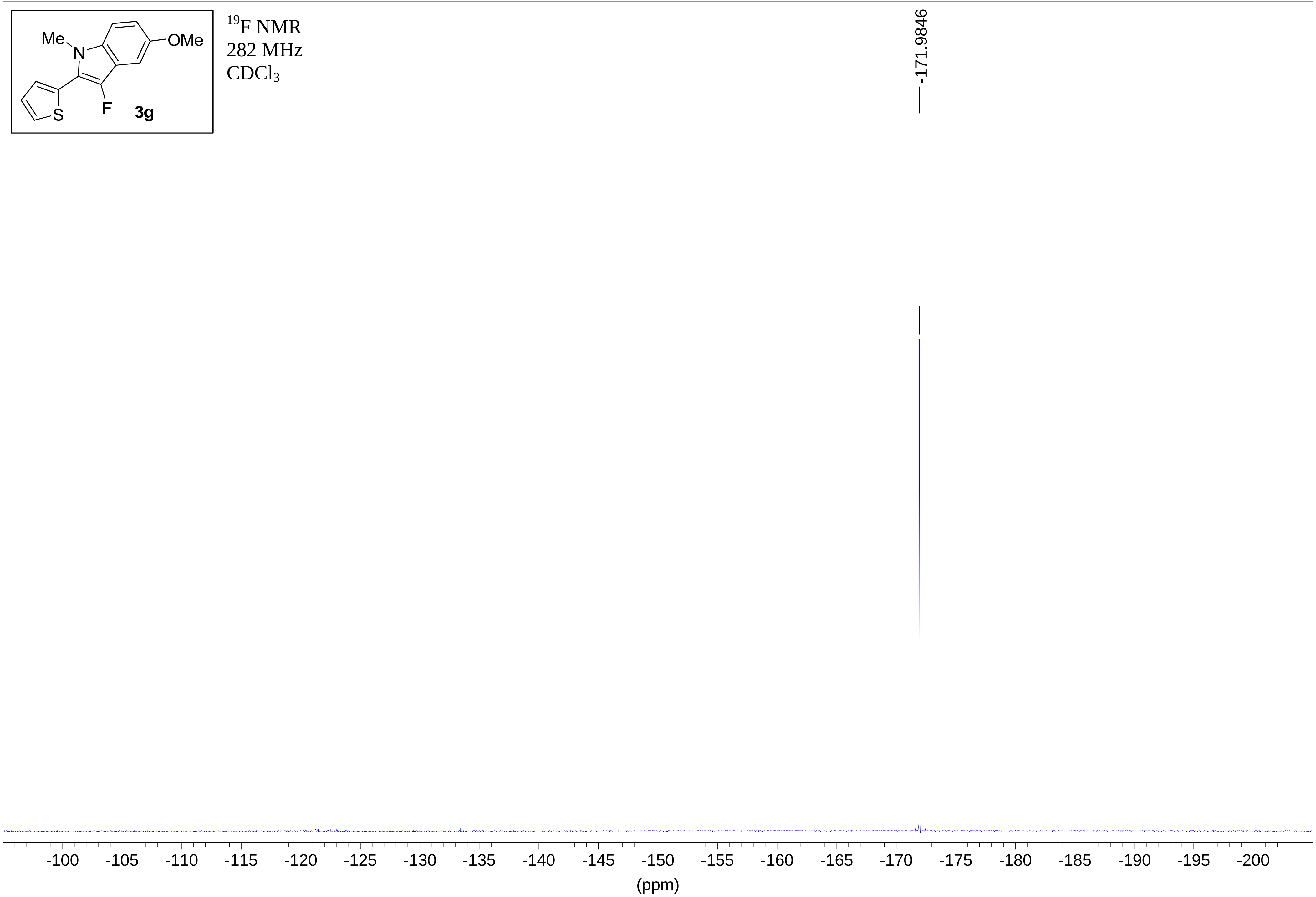


3g

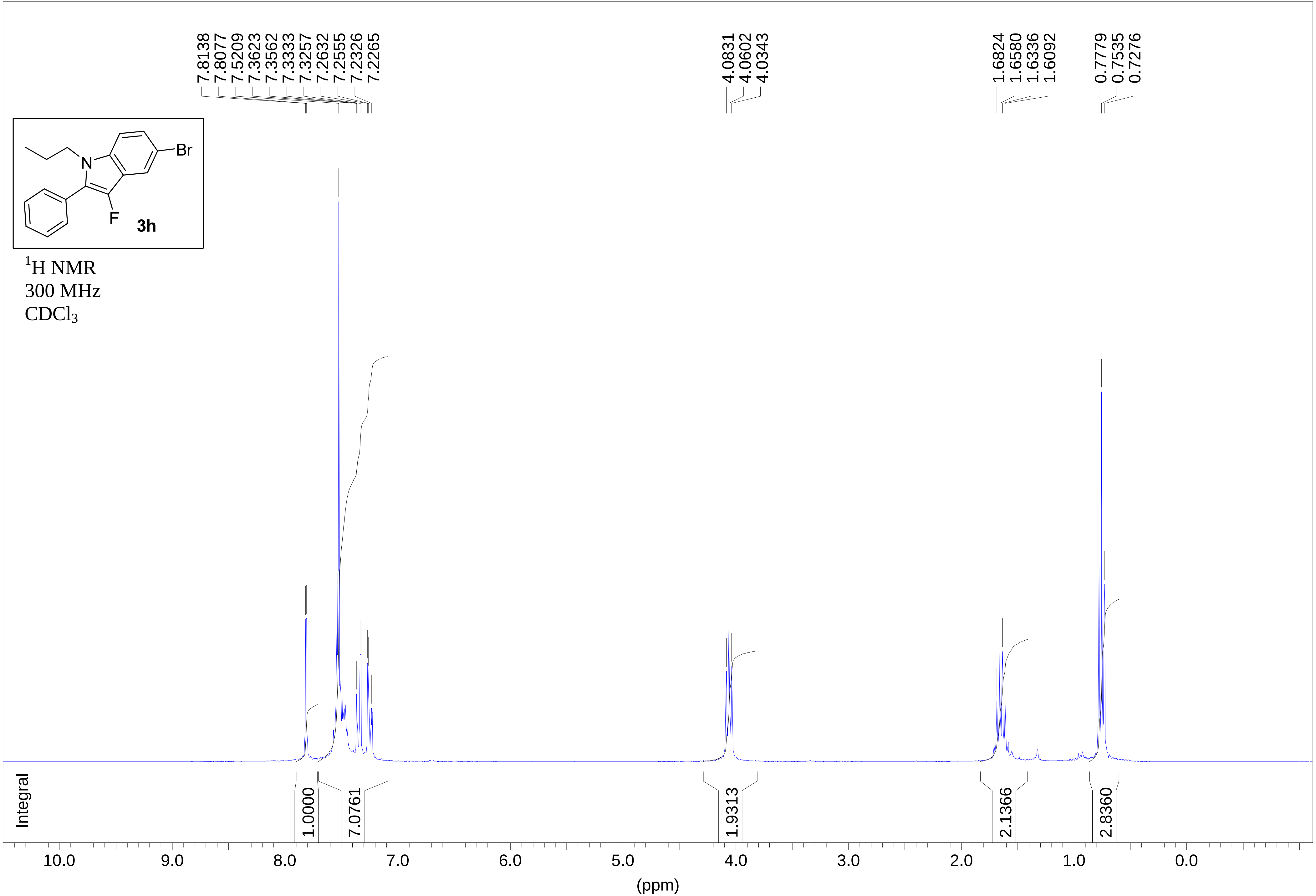
^{1}H NMR
300 MHz
$CDCl_3$

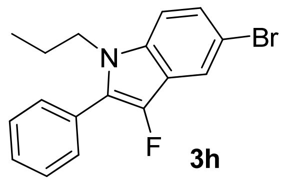



Me
N
OMe
S
F
3g
$^{13}C\{^{1}H\}$ NMR
50 MHz
$CDCl_3$
154.4019
144.6285
139.7348
129.8063
129.7217
129.5525
129.4255
127.8742
127.8178
127.5640
127.0280
126.7742
126.7460
118.1291
117.7201
117.5509
116.5496
116.2534
114.7585
114.1520
110.7250
110.6968
97.7362
97.6939
77.7946
77.1600
76.5254
55.8786
31.1280
29.8305
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)



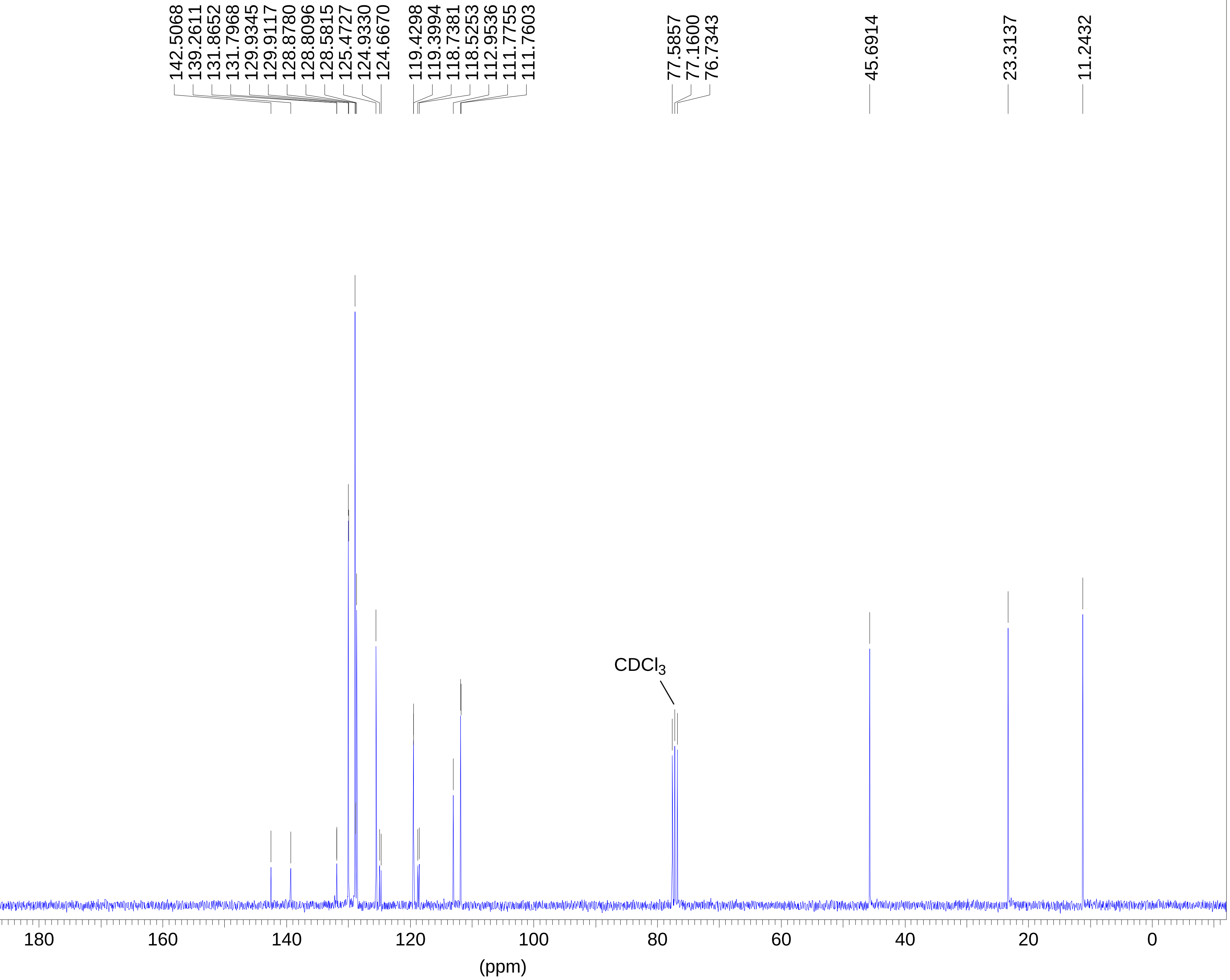
3g
19F NMR
282 MHz
CDCl3
-171.9846
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
-185
-190
-195
-200
(ppm)

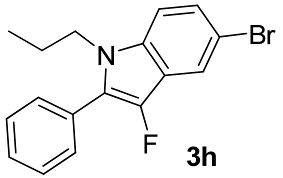

7.8138
7.8077
7.5209
7.3623
7.3562
7.3333
7.3257
7.2632
7.2555
7.2326
7.2265
4.0831
4.0602
4.0343
1.6824
1.6580
1.6336
1.6092
0.7779
0.7535
0.7276
Br
N
F
3h
1H NMR
300 MHz
CDCl3
Integral
1.0000
7.0761
1.9313
2.1366
2.8360
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)



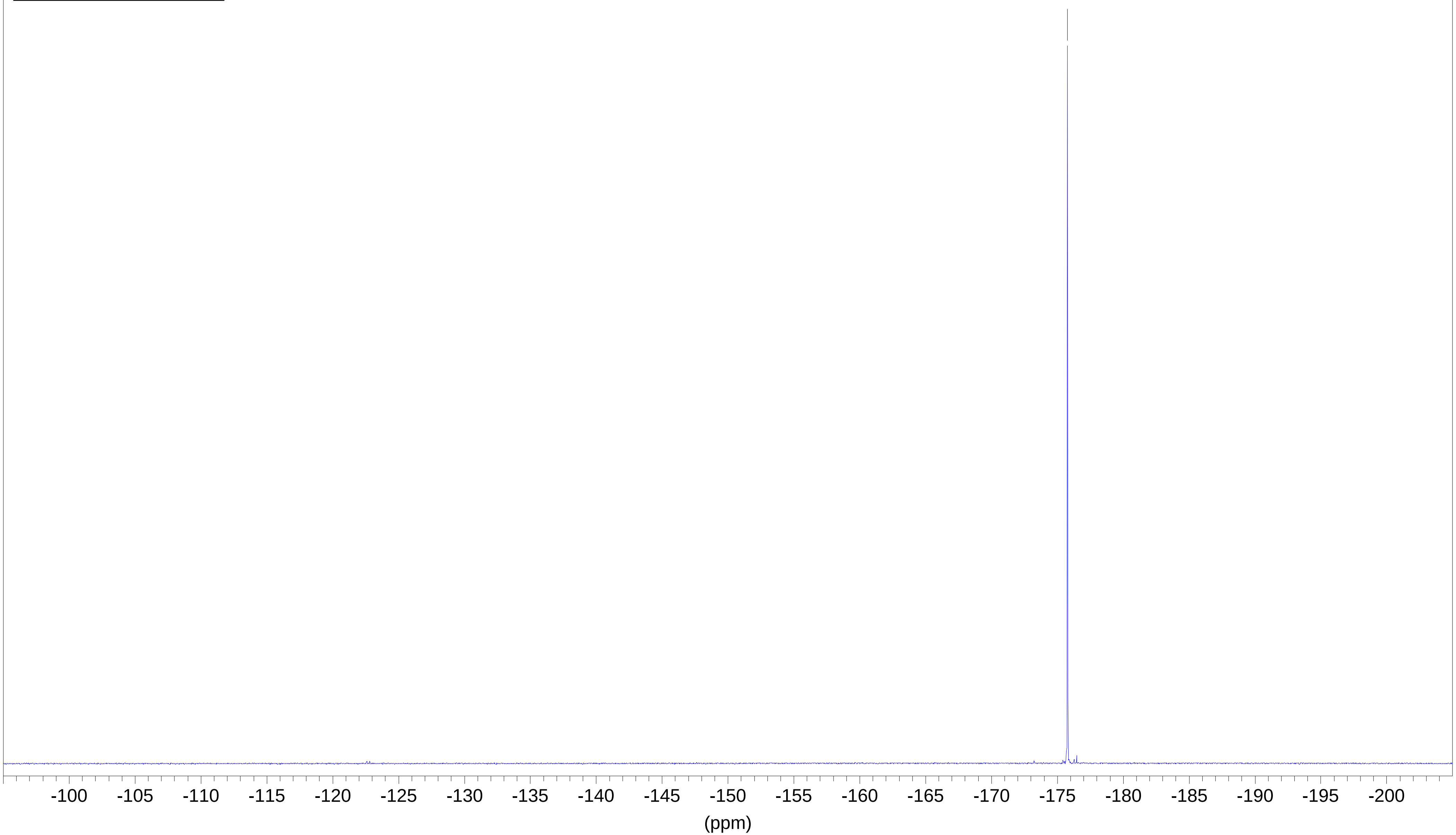
3h

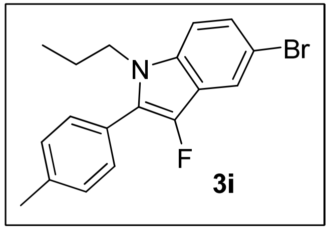
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$




3h

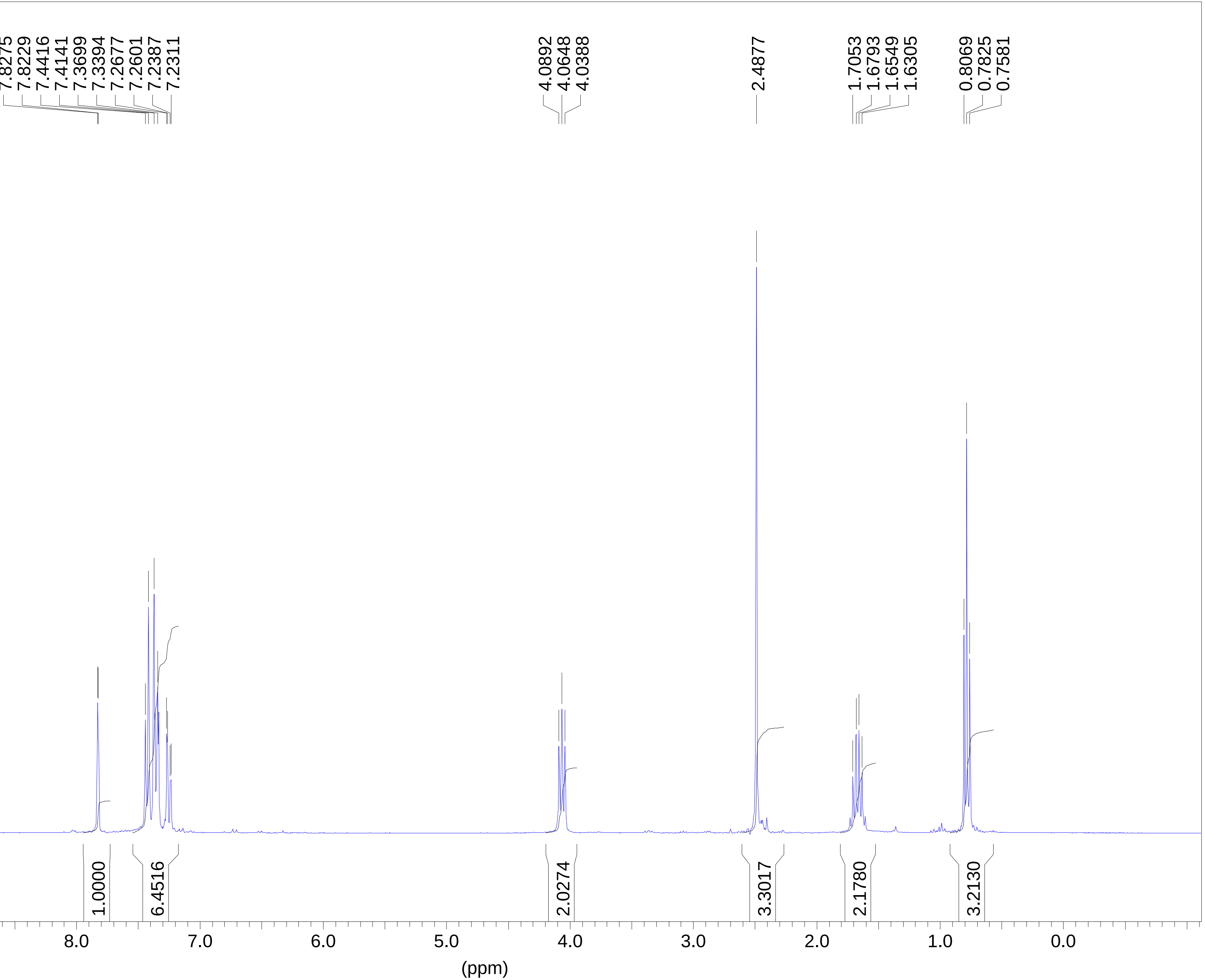
^{19}F NMR
282 MHz
$CDCl_3$

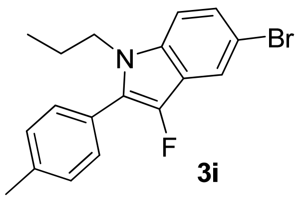




3i

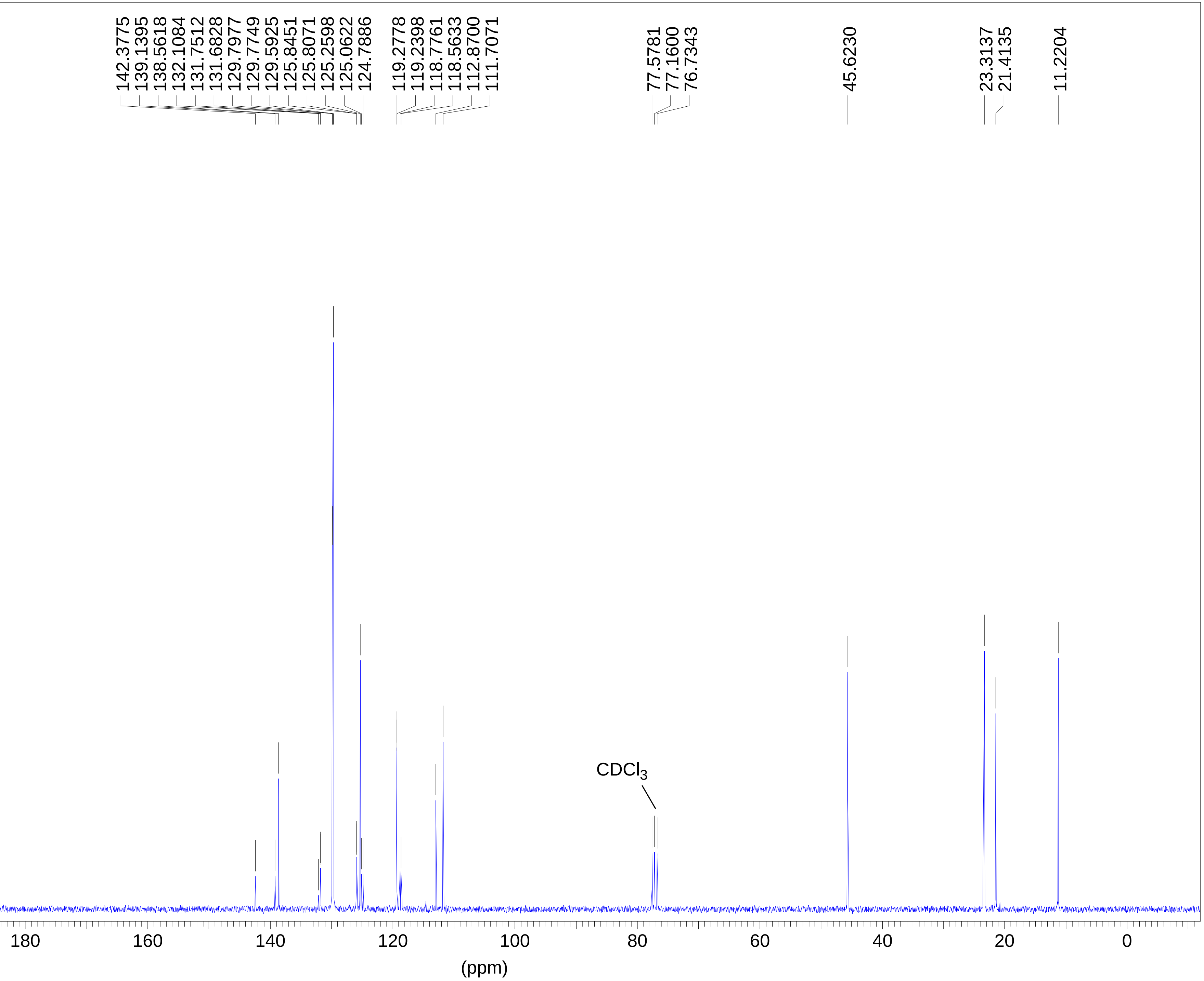
[1]H NMR
300 MHz
$CDCl_3$

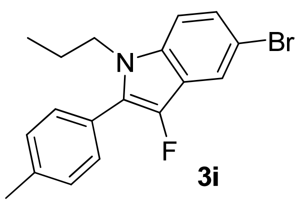




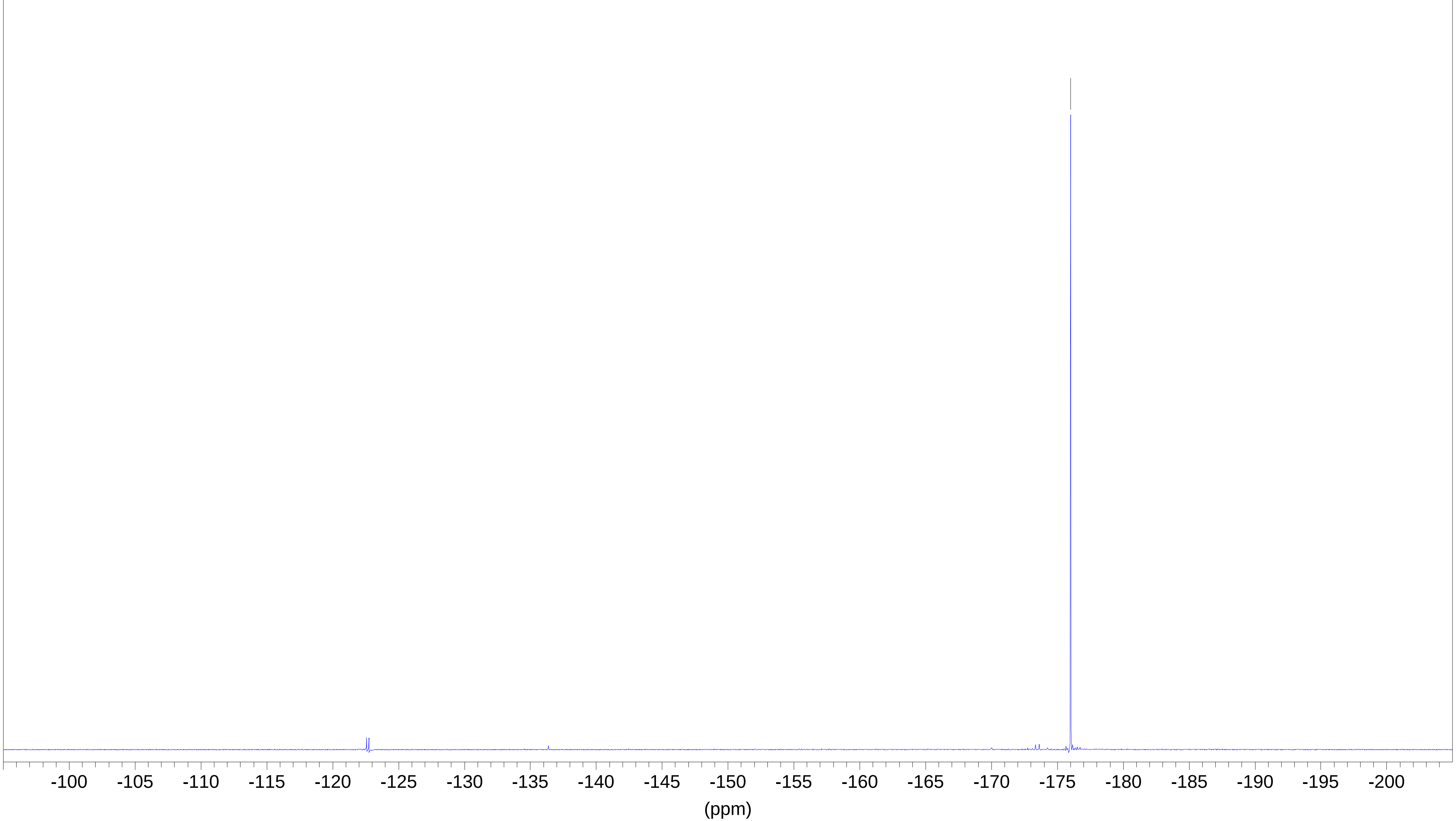
3i

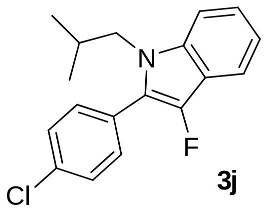
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$





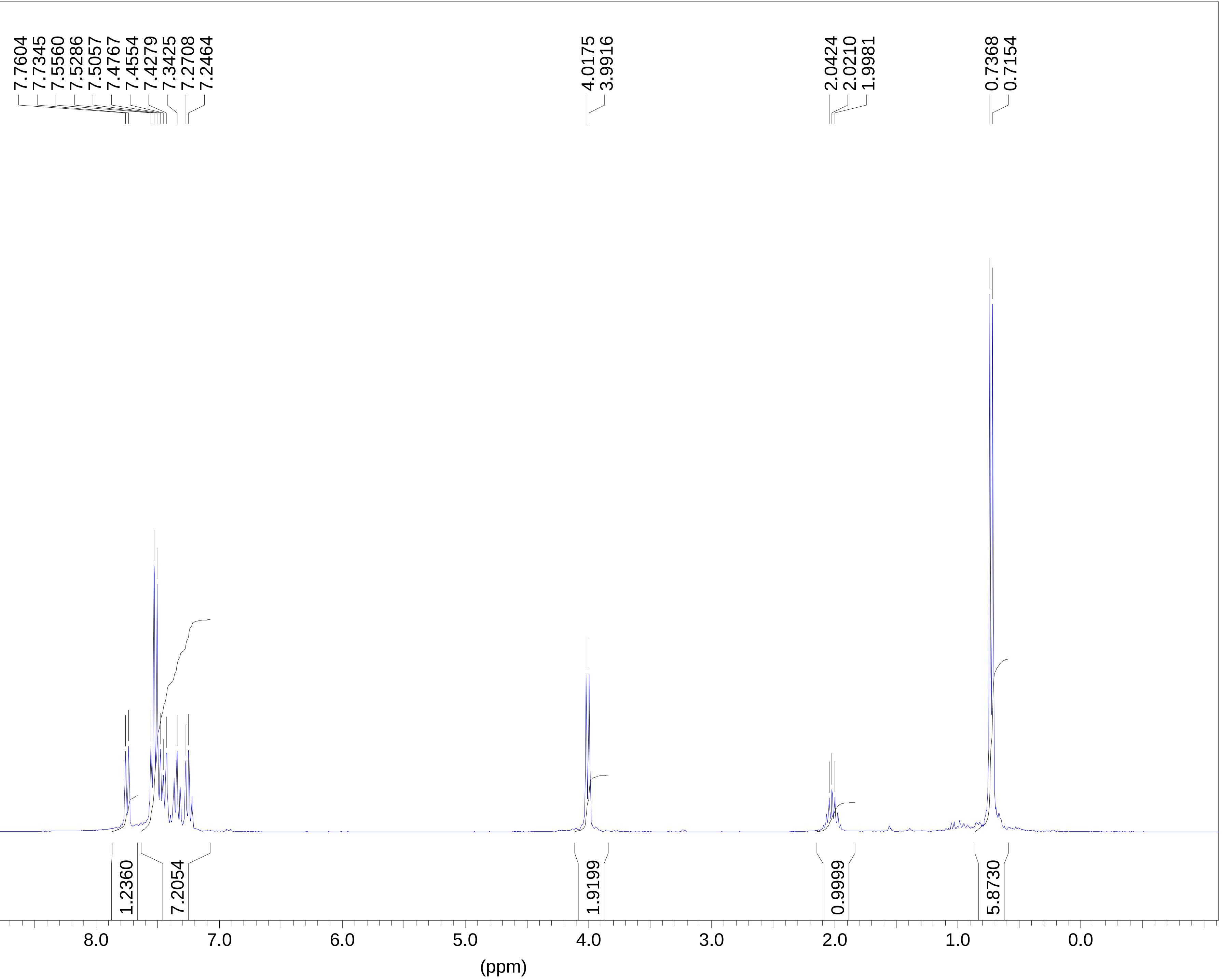
3i

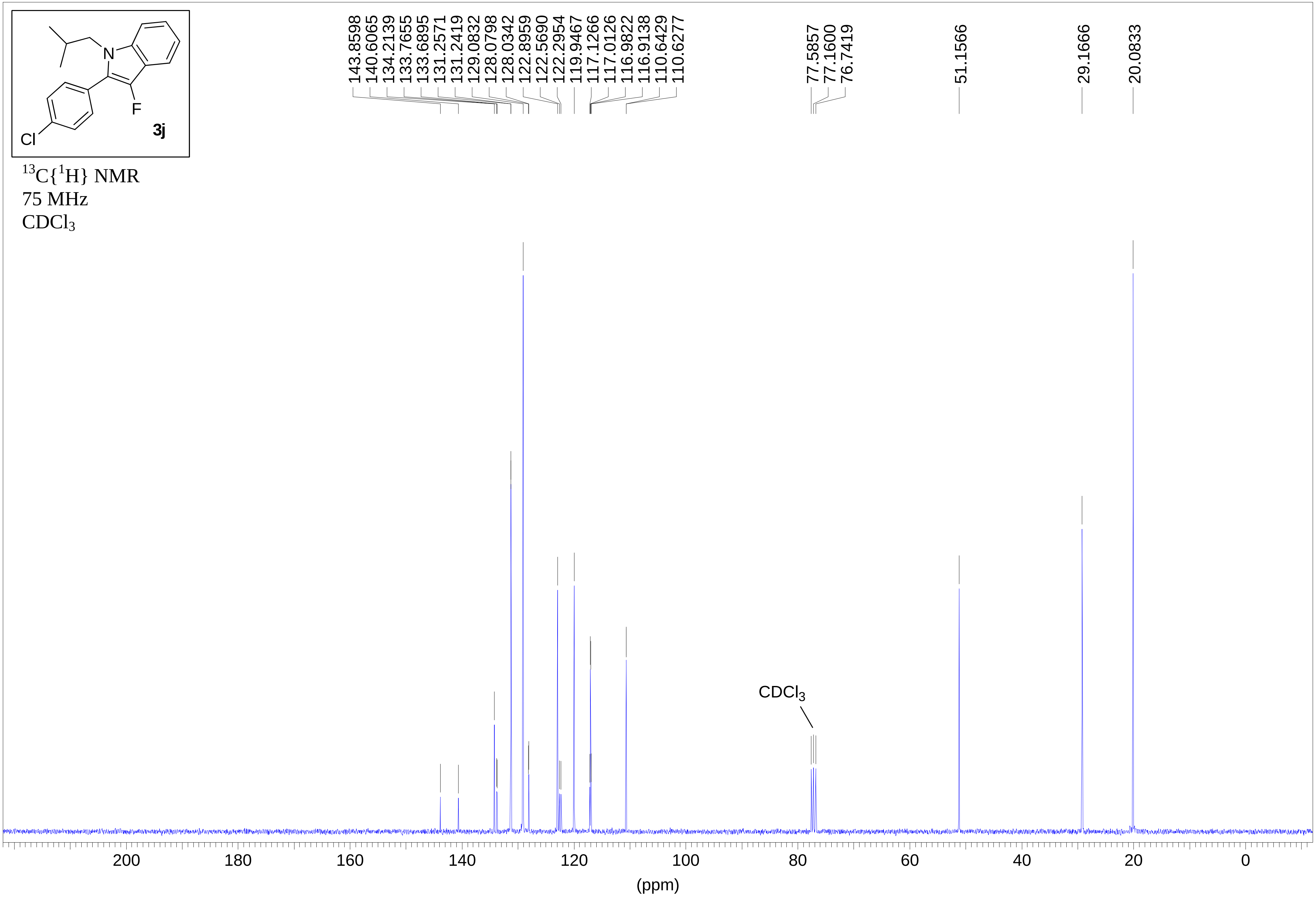

^{19}F NMR
282 MHz
$CDCl_3$
-176.0295
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
-185
-190
-195
-200
(ppm)

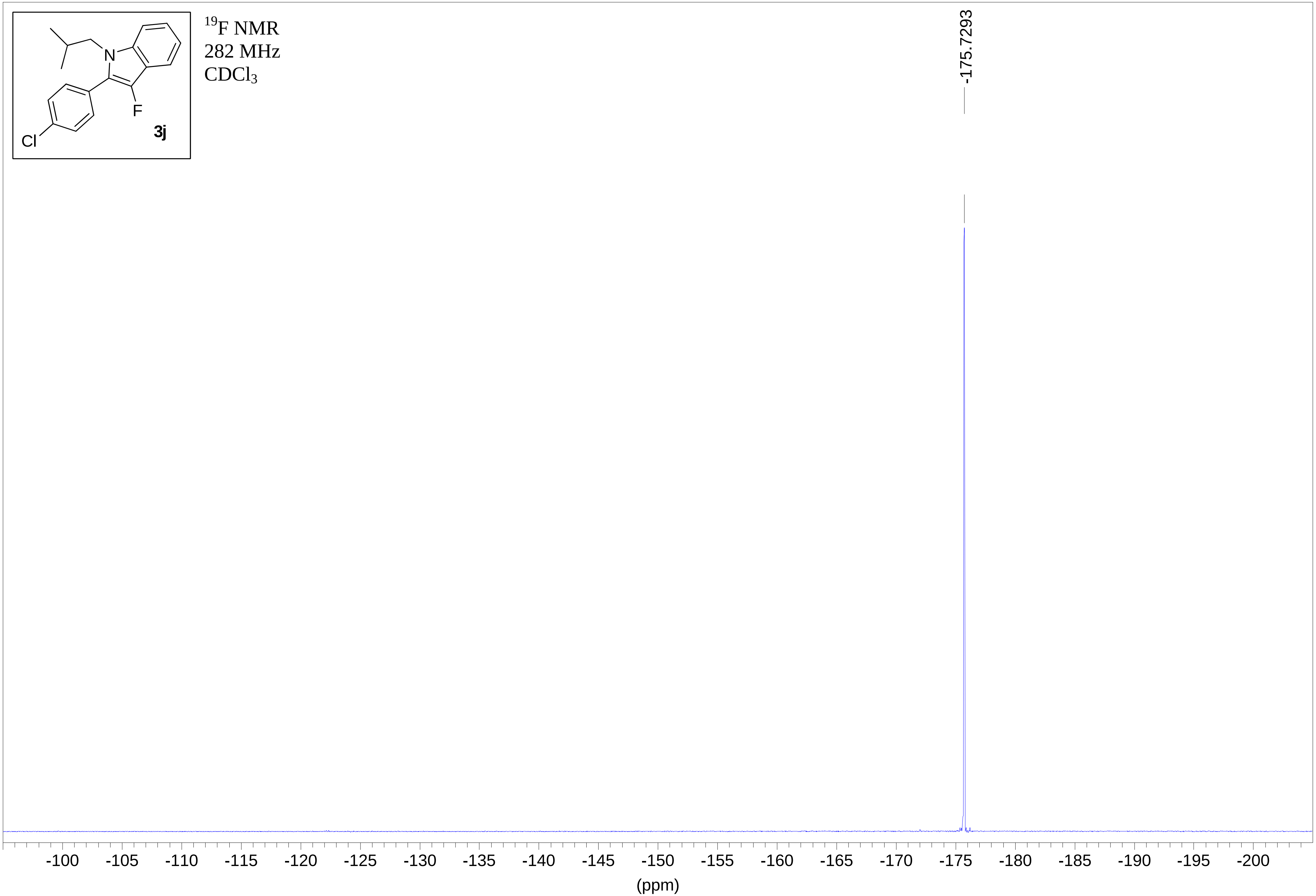


3j

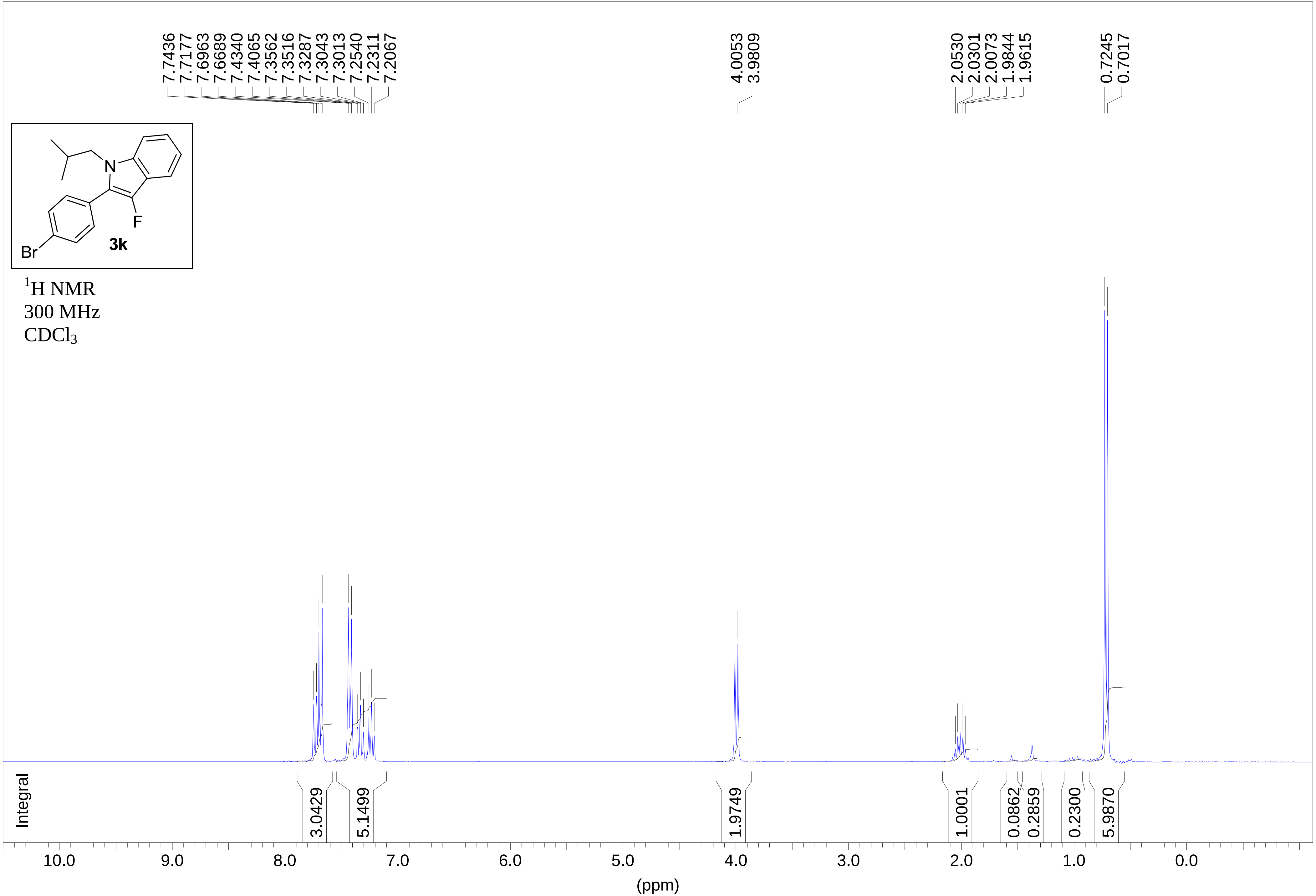
^{1}H NMR
300 MHz
$CDCl_3$

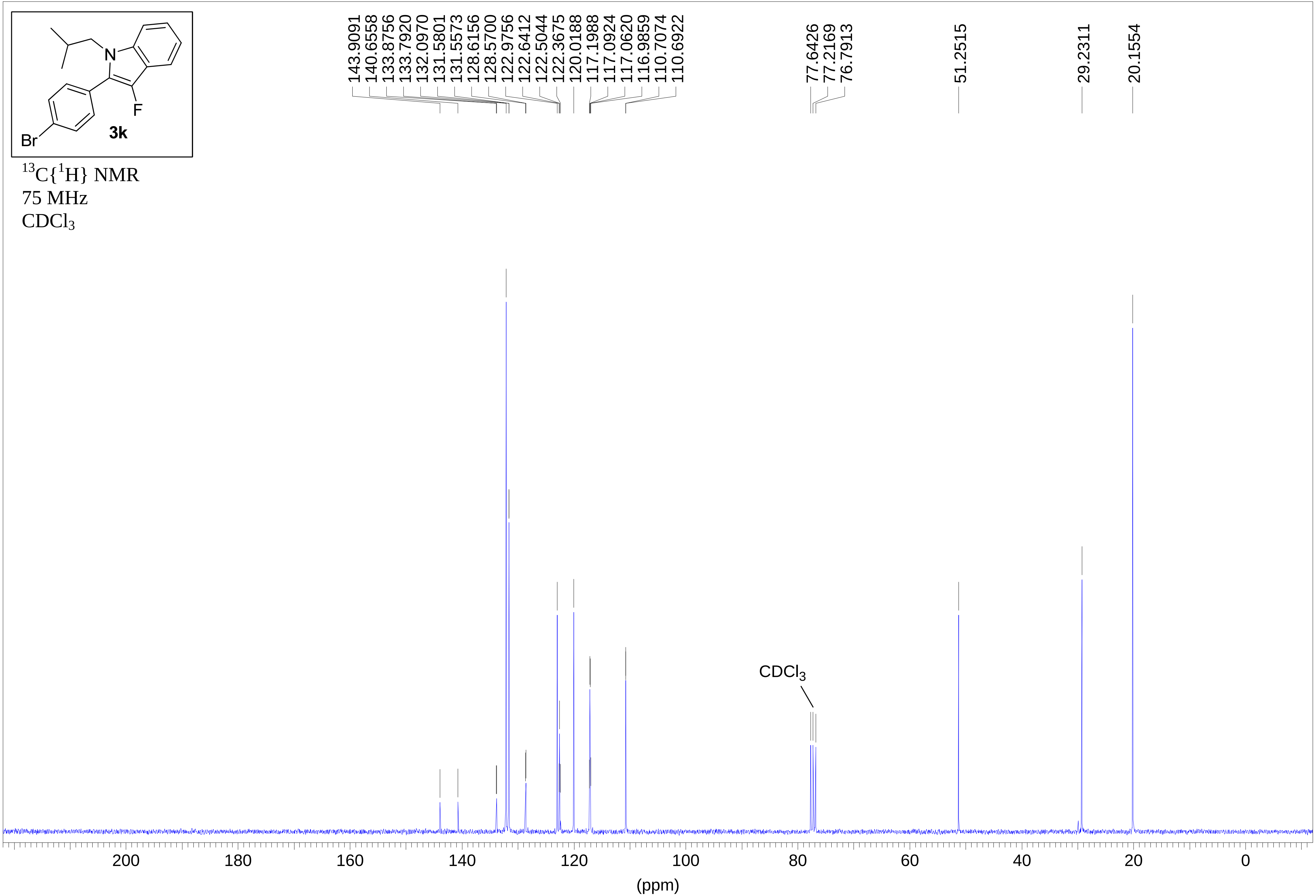



143.8598
140.6065
134.2139
133.7655
133.6895
131.2571
131.2419
129.0832
128.0798
128.0342
122.8959
122.5690
122.2954
119.9467
117.1266
117.0126
116.9822
116.9138
110.6429
110.6277
77.5857
77.1600
76.7419
51.1566
29.1666
20.0833
N
F
Cl
3j
$^{13}C\{^1H\}$ NMR
75 MHz
$CDCl_3$
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)

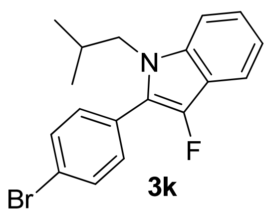


^{19}F NMR
282 MHz
$CDCl_3$
N
F
Cl
3j
-175.7293
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
-185
-190
-195
-200
(ppm)


7.7436
7.7177
7.6963
7.6689
7.4340
7.4065
7.3562
7.3516
7.3287
7.3043
7.3013
7.2540
7.2311
7.2067
4.0053
3.9809
2.0530
2.0301
2.0073
1.9844
1.9615
0.7245
0.7017
N
F
Br
3k
^{1}H NMR
300 MHz
$CDCl_3$
Integral
3.0429
5.1499
1.9749
1.0001
0.0862
0.2859
0.2300
5.9870
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

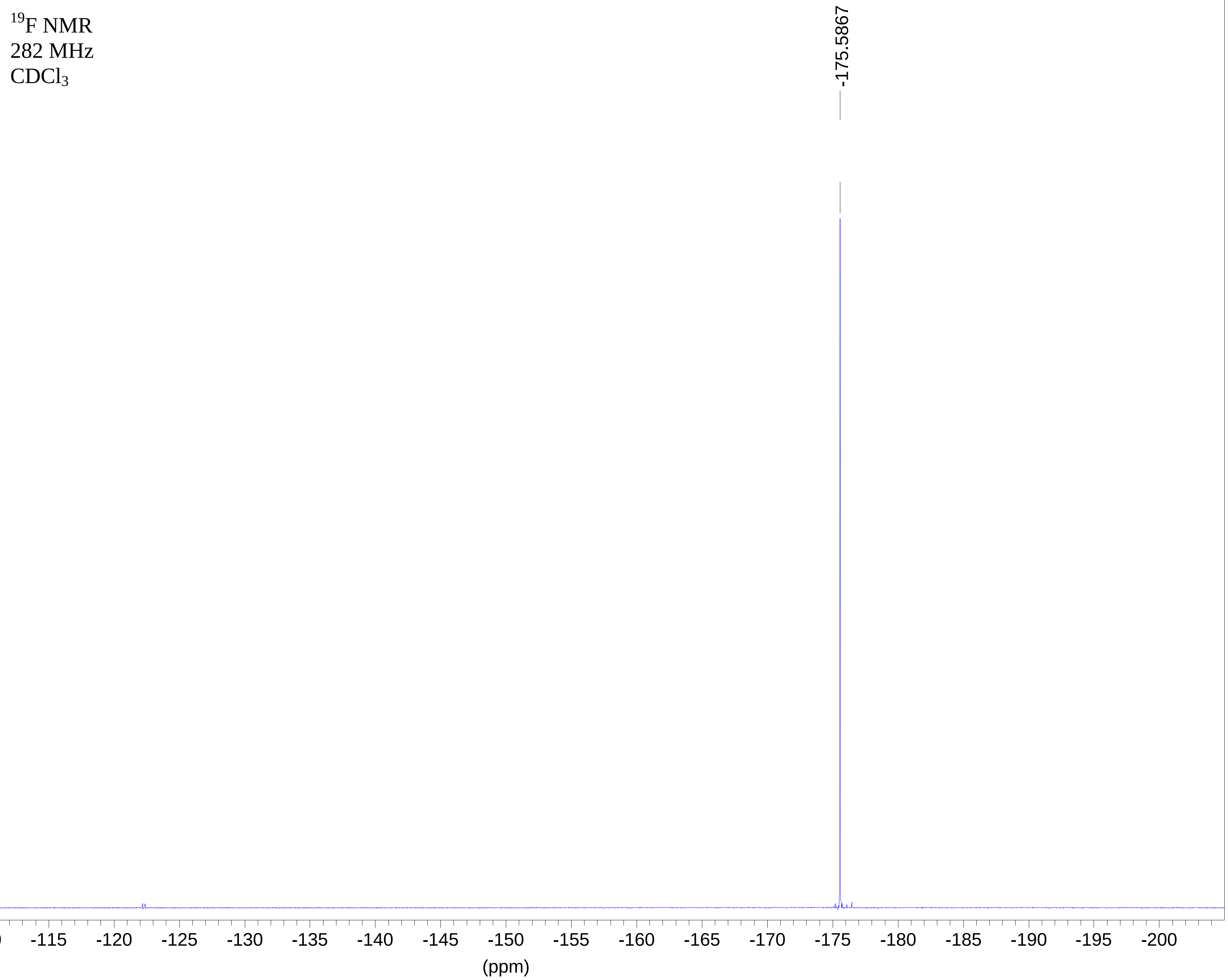


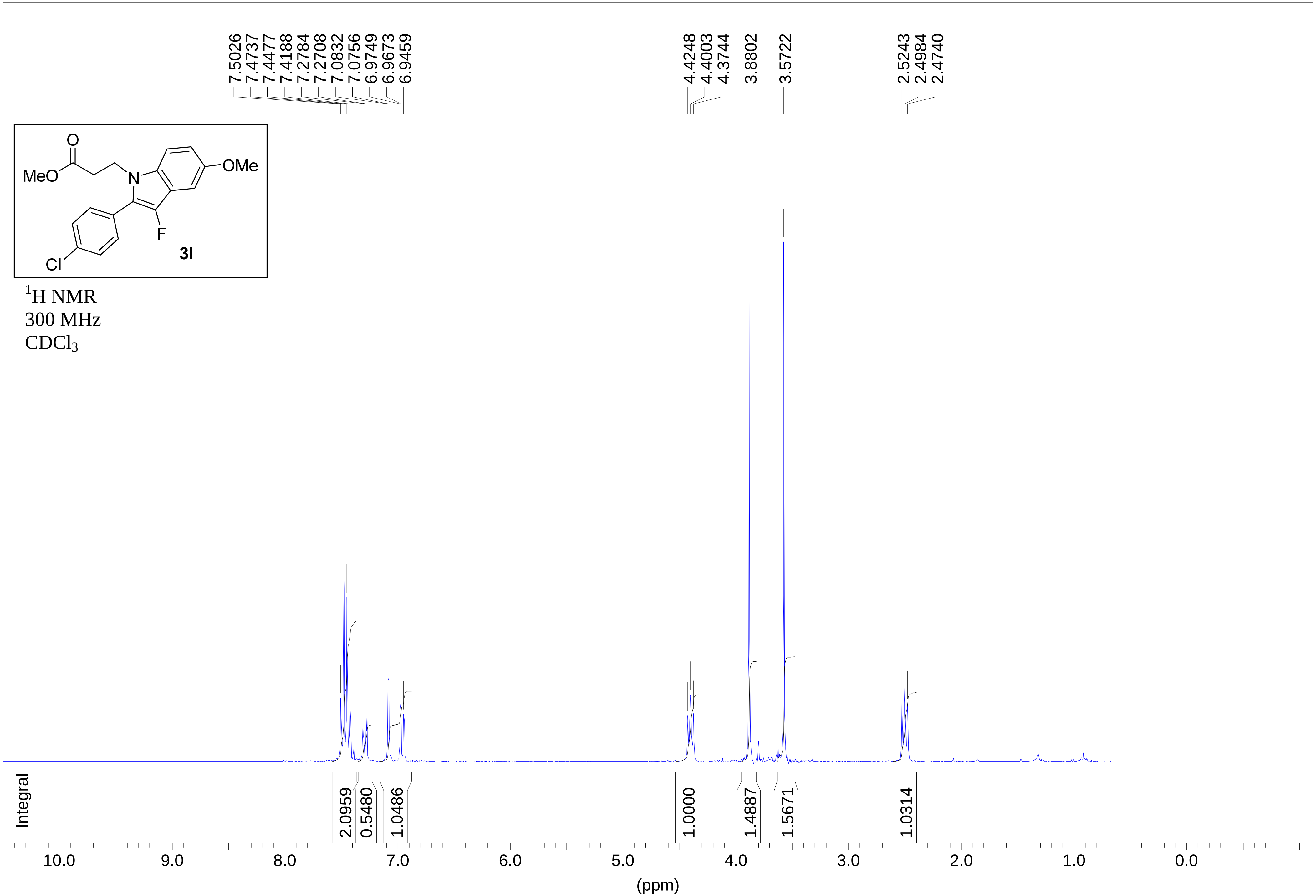
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$



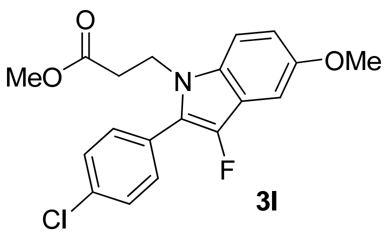
3k

^{19}F NMR
282 MHz
$CDCl_3$



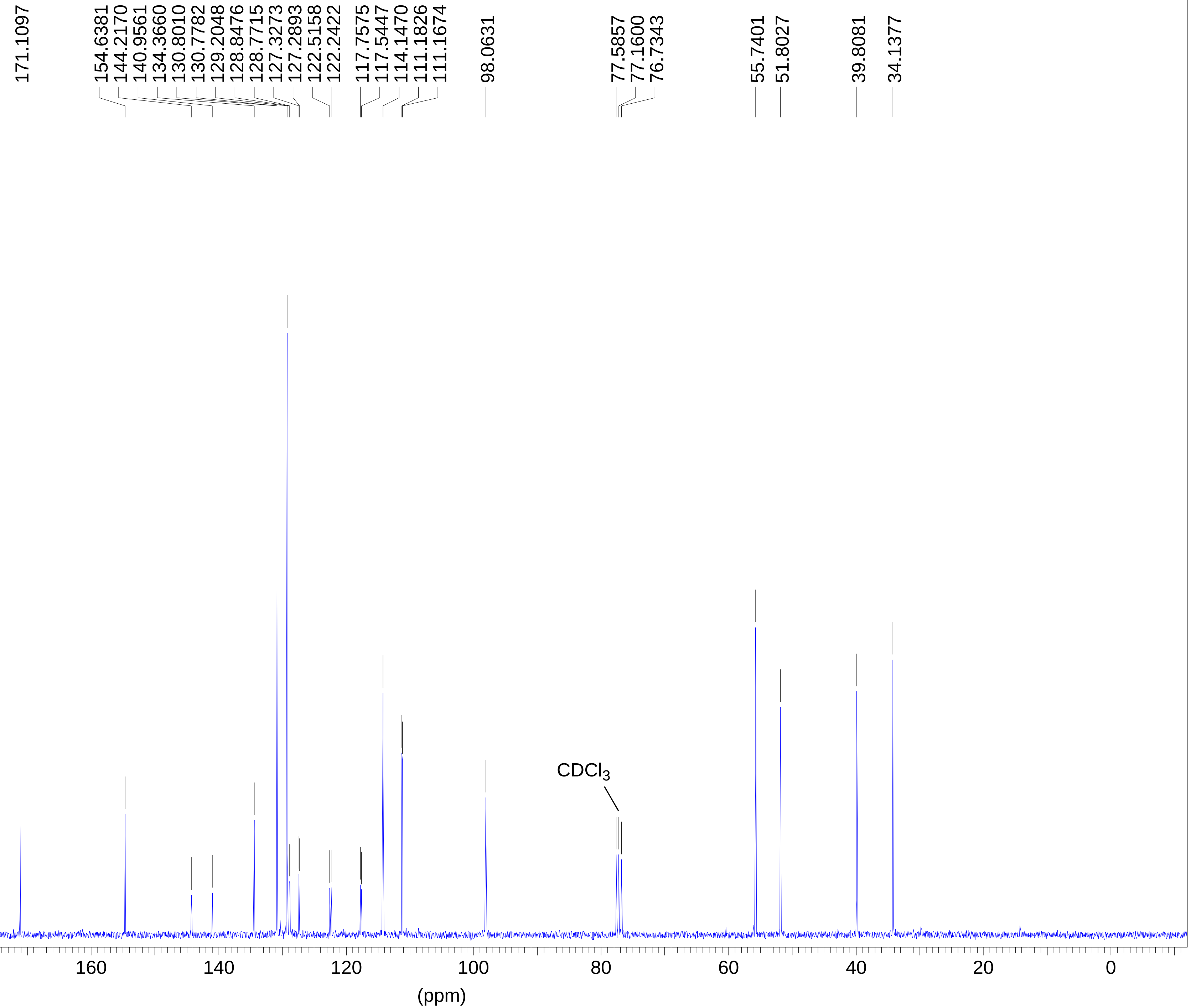


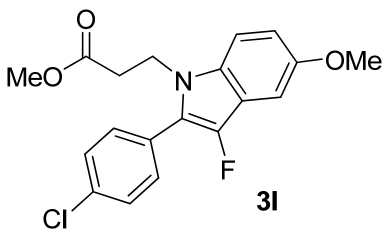
7.5026
7.4737
7.4477
7.4188
7.2784
7.2708
7.0832
7.0756
6.9749
6.9673
6.9459
4.4248
4.4003
4.3744
3.8802
3.5722
2.5243
2.4984
2.4740
O
MeO
N
OMe
F
Cl
3l
^{1}H NMR
300 MHz
$CDCl_3$
Integral
2.0959
0.5480
1.0486
1.0000
1.4887
1.5671
1.0314
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)



3l

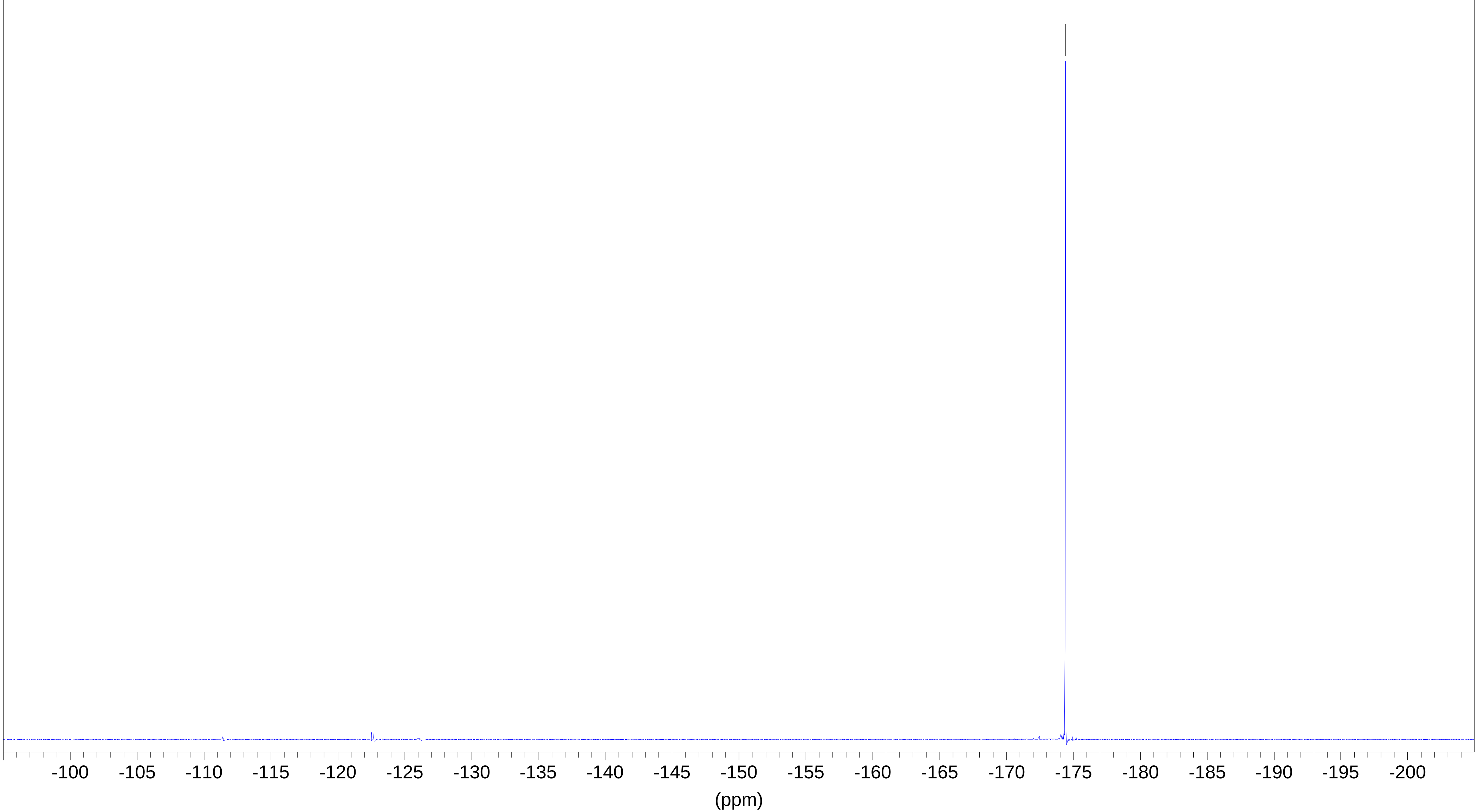
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$

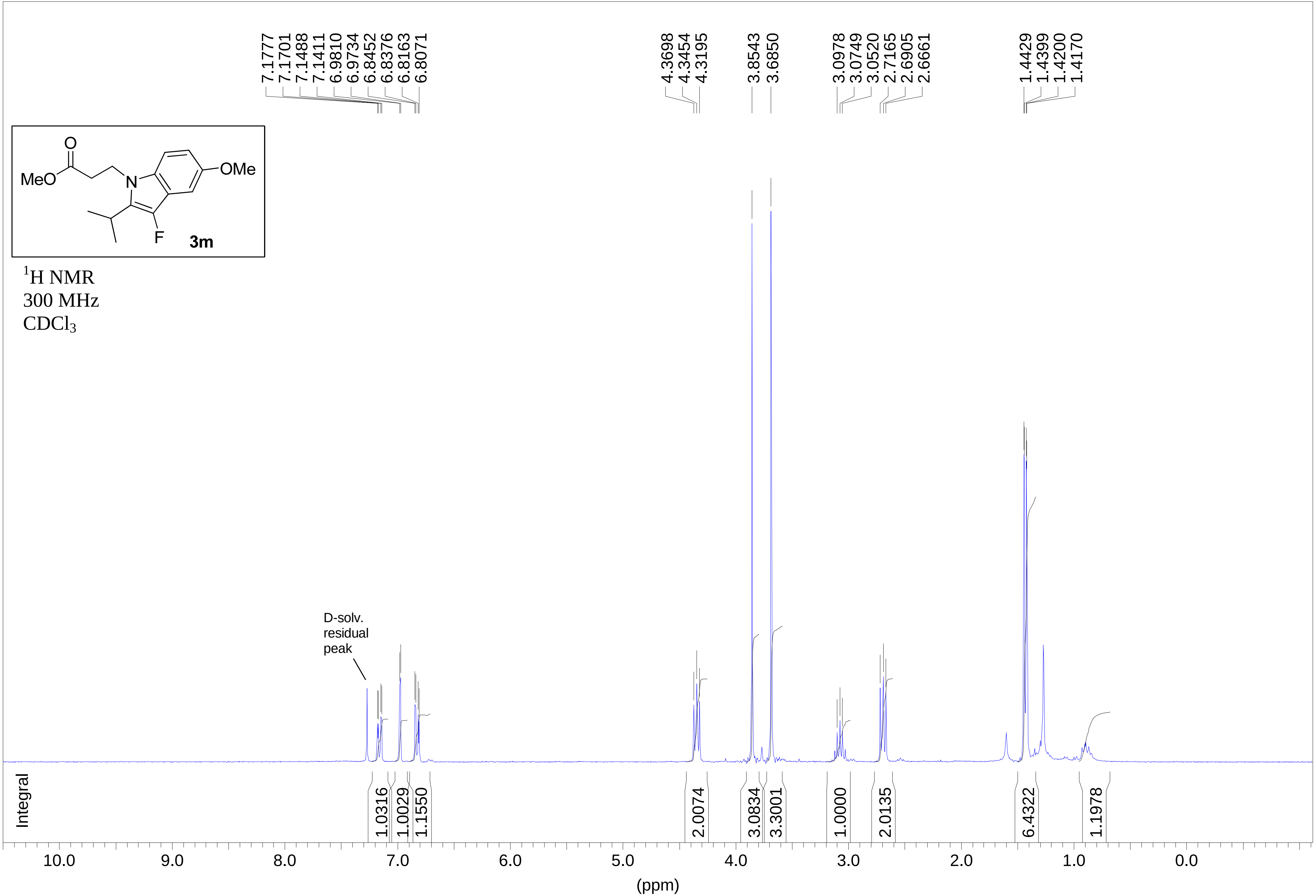




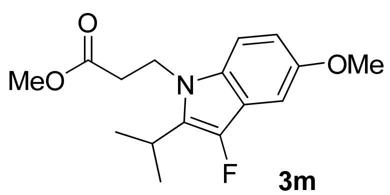
3l

^{19}F NMR
282 MHz
$CDCl_3$



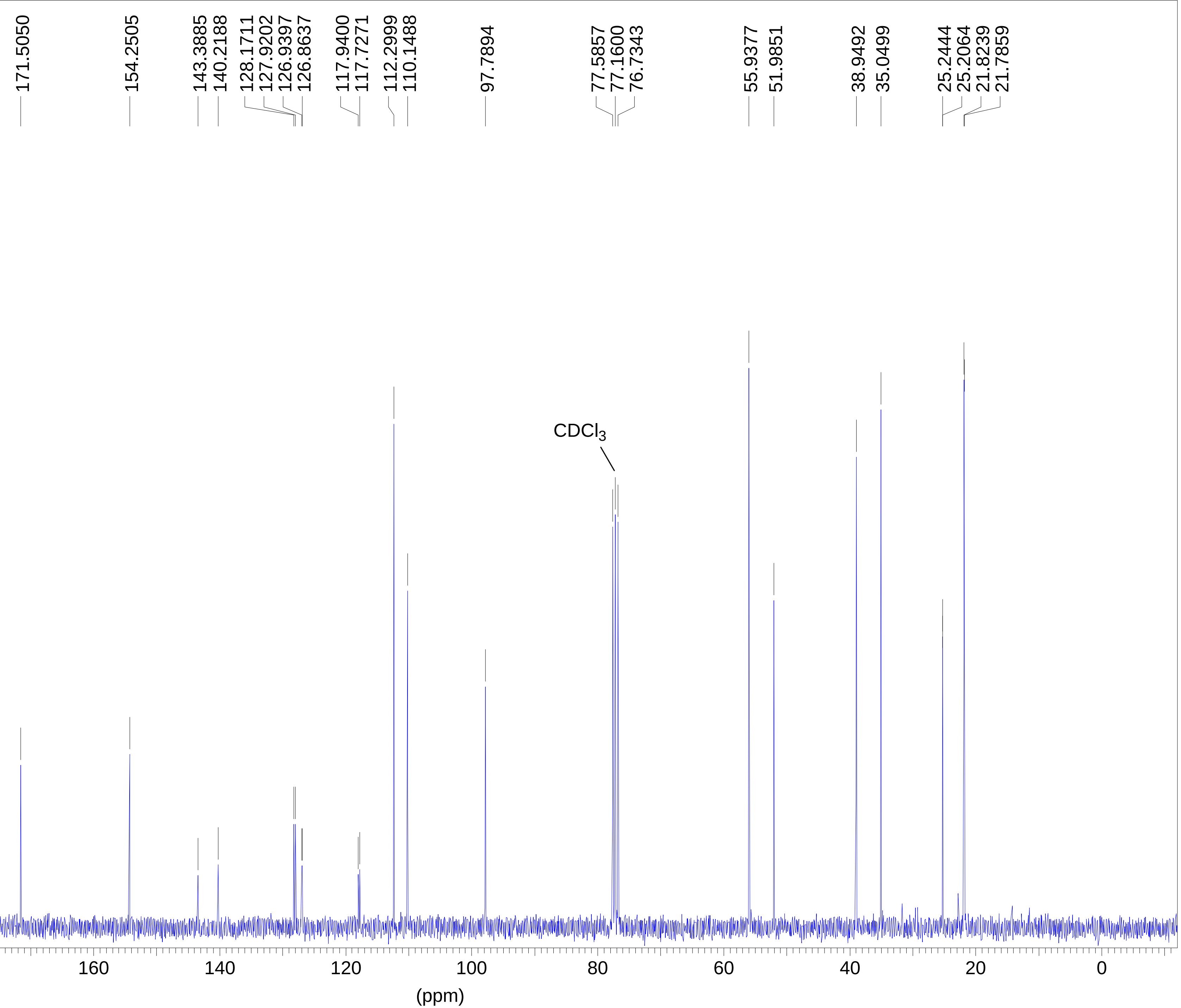


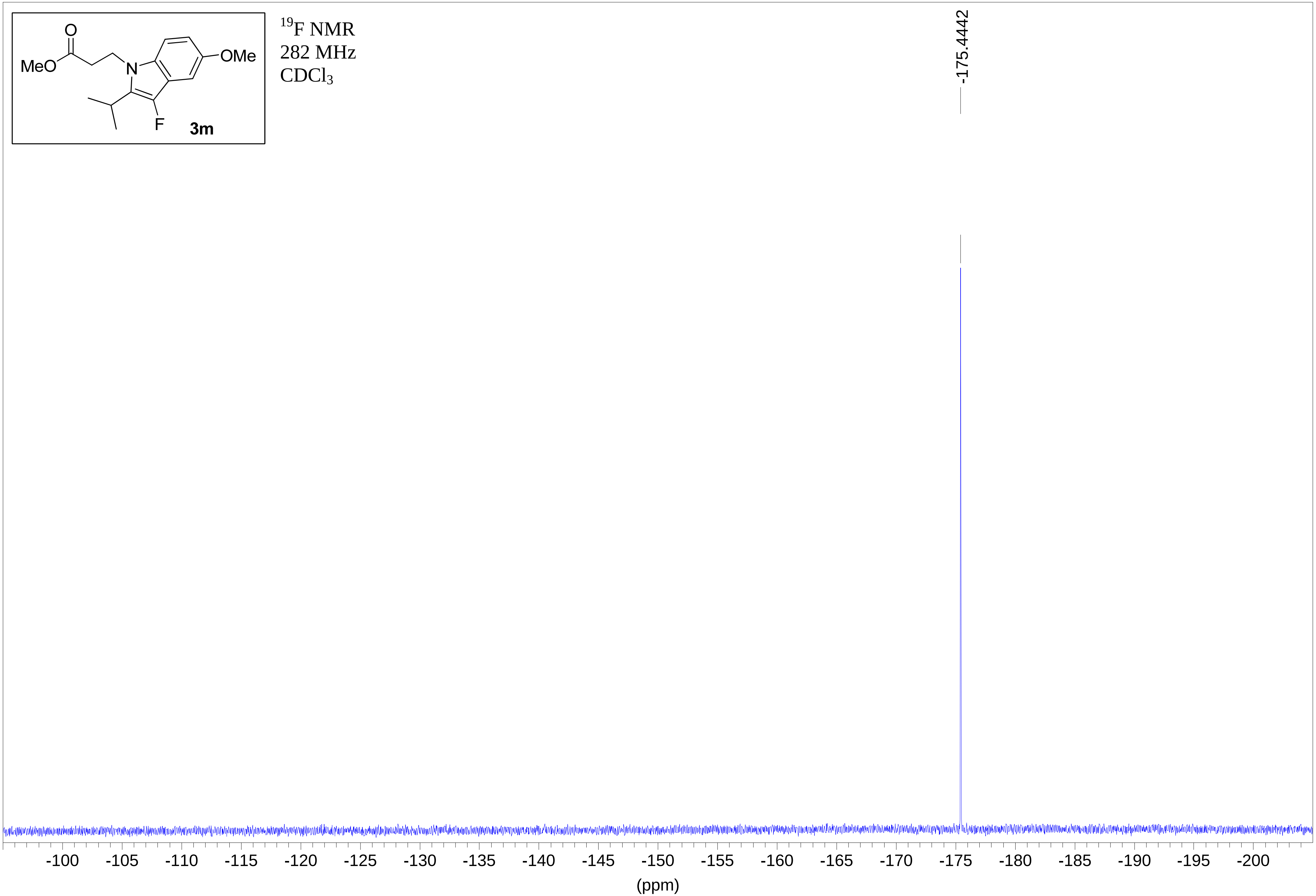
^{1}H NMR
300 MHz
$CDCl_3$

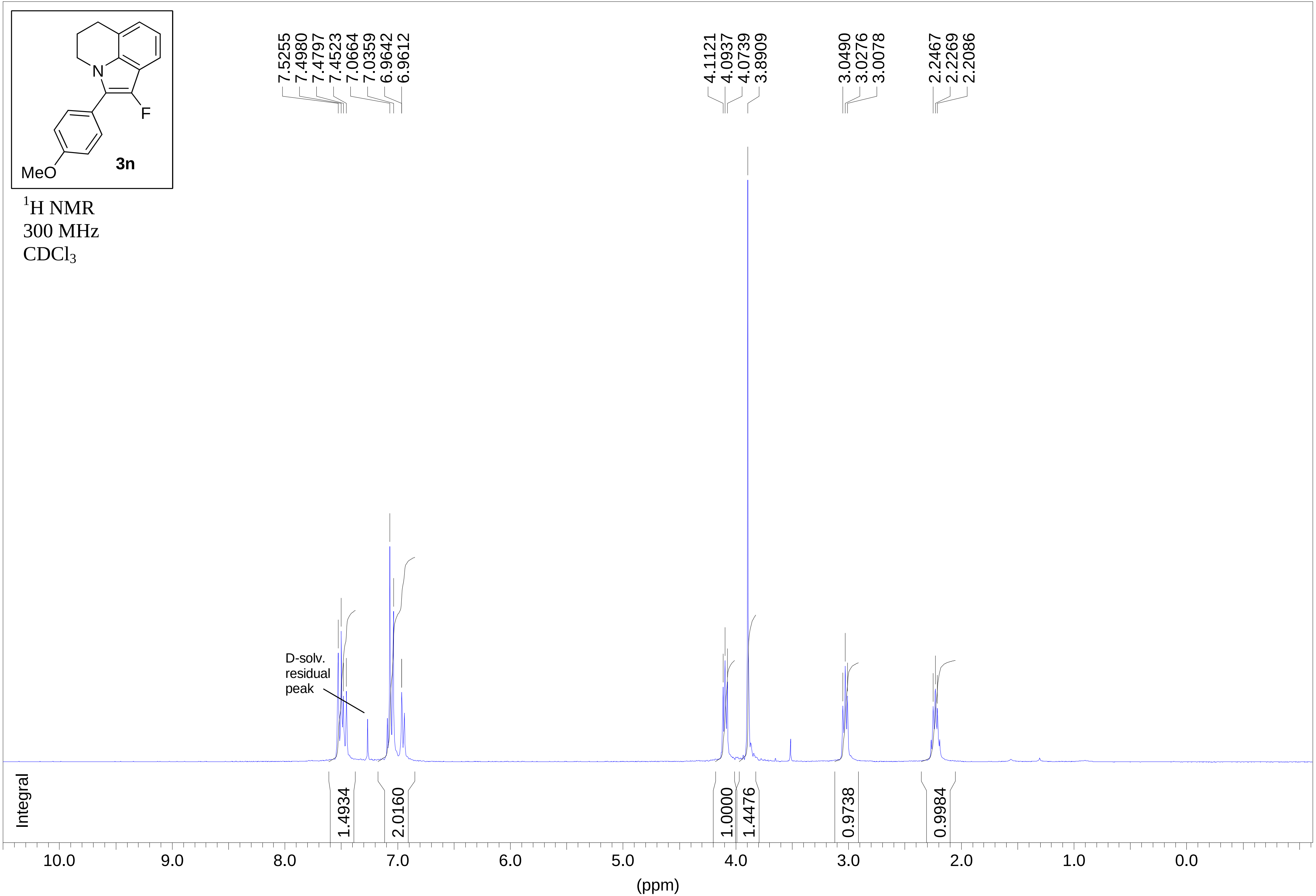


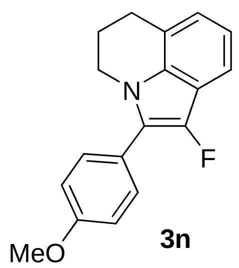
3m

$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$



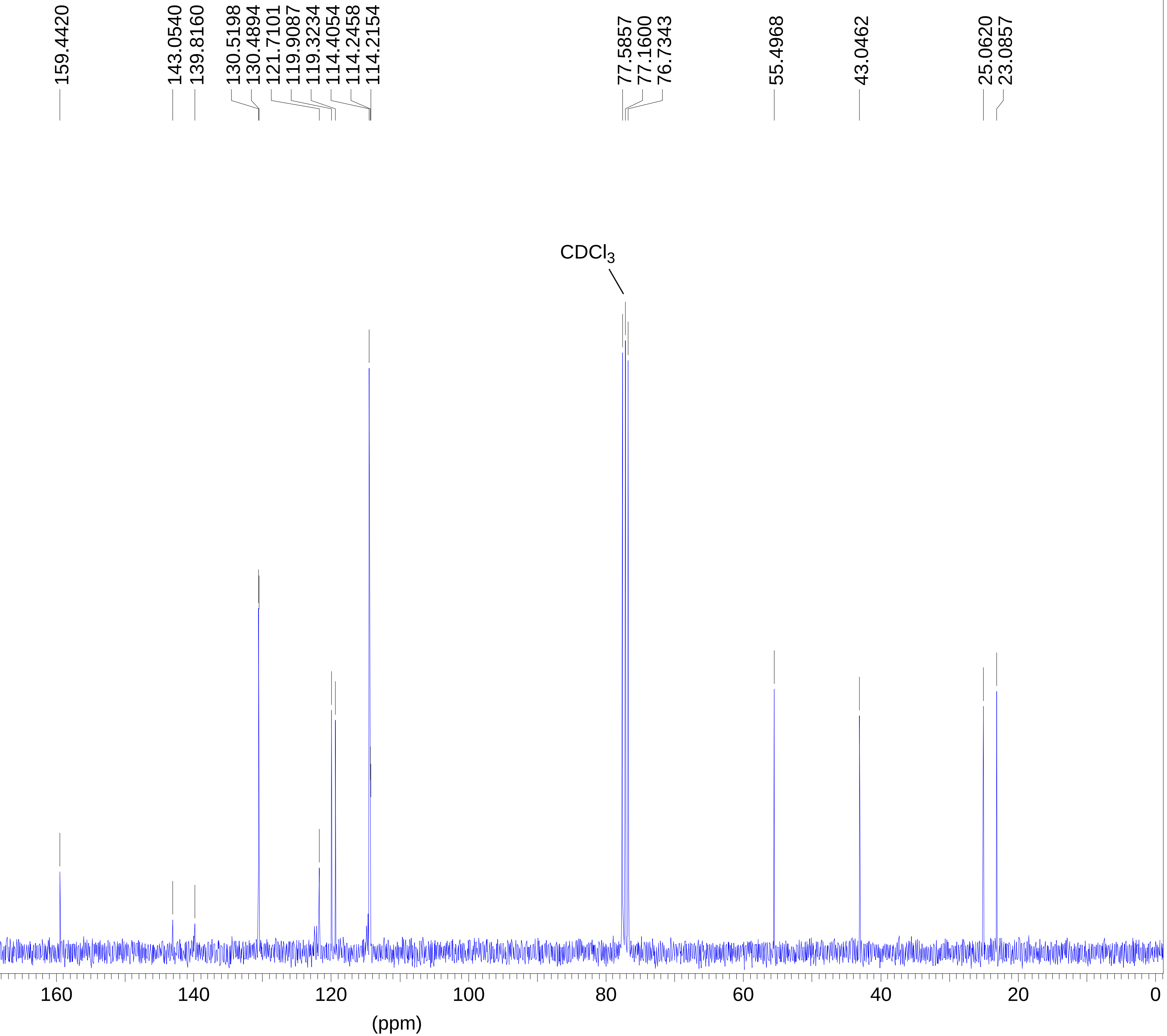

O
MeO
N
OMe
F
3m
^{19}F NMR
282 MHz
$CDCl_3$
-175.4442
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
-185
-190
-195
-200
(ppm)

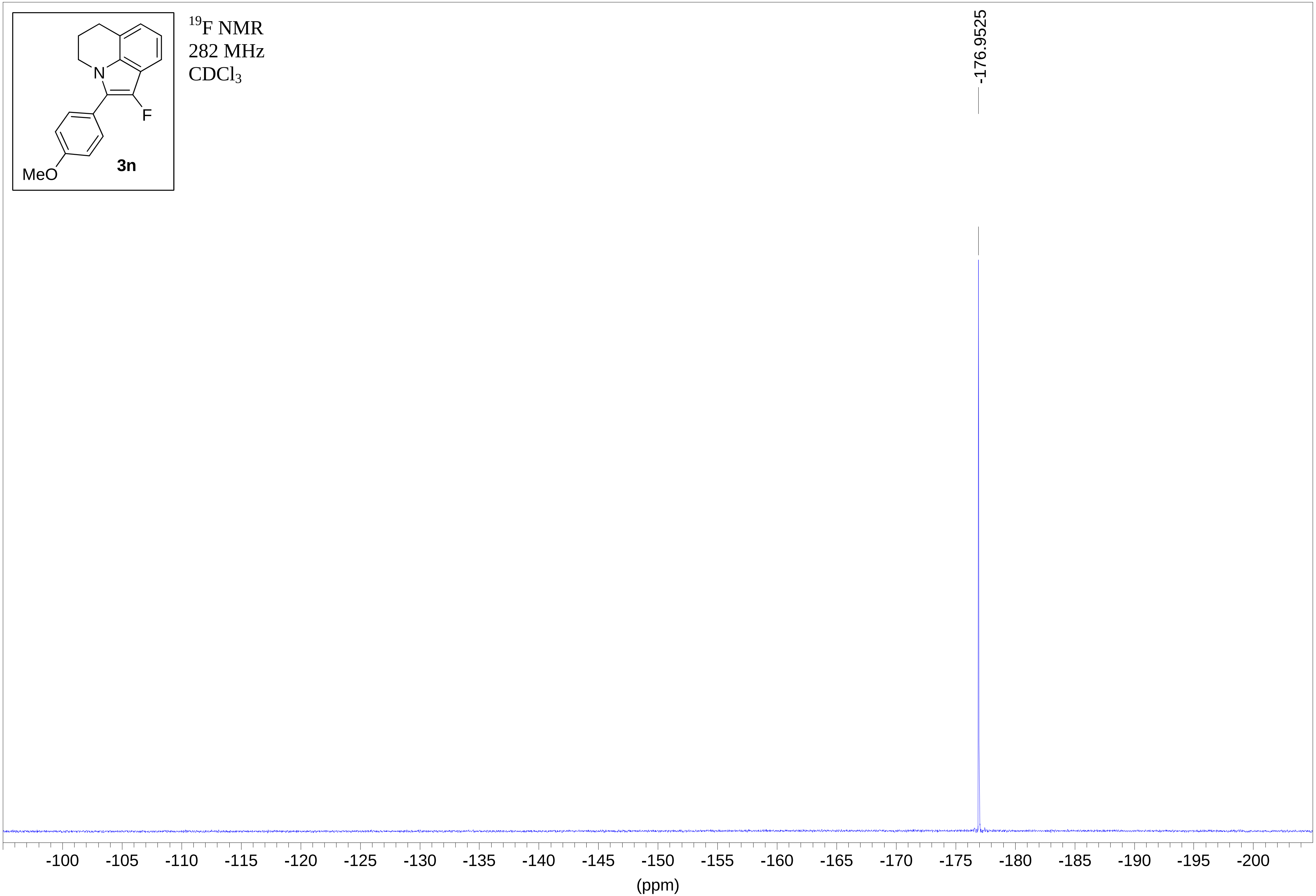

F
MeO
3n
^{1}H NMR
300 MHz
$CDCl_3$
7.5255
7.4980
7.4797
7.4523
7.0664
7.0359
6.9642
6.9612
4.1121
4.0937
4.0739
3.8909
3.0490
3.0276
3.0078
2.2467
2.2269
2.2086
D-solv.
residual
peak
Integral
1.4934
2.0160
1.0000
1.4476
0.9738
0.9984
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)



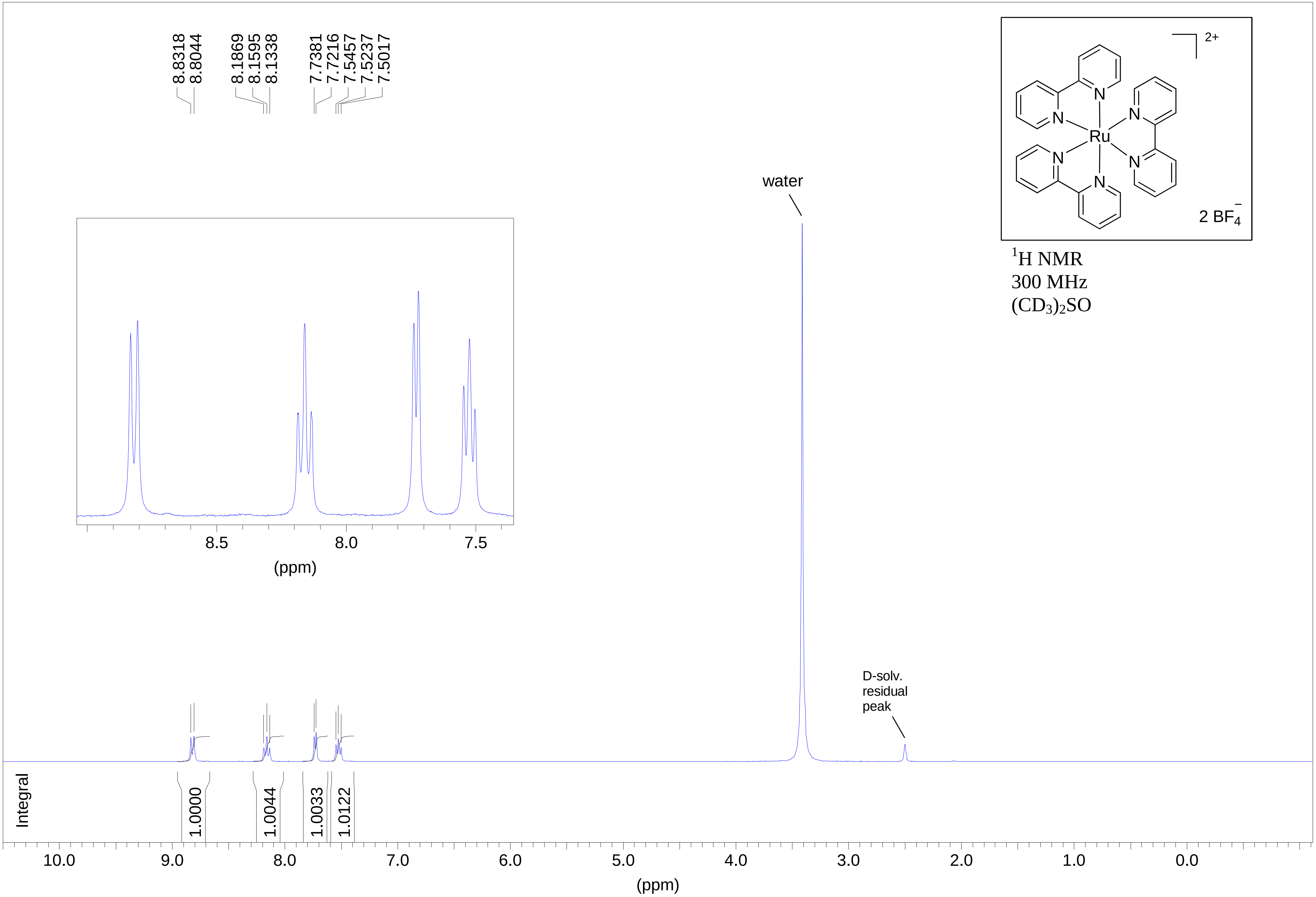
3n

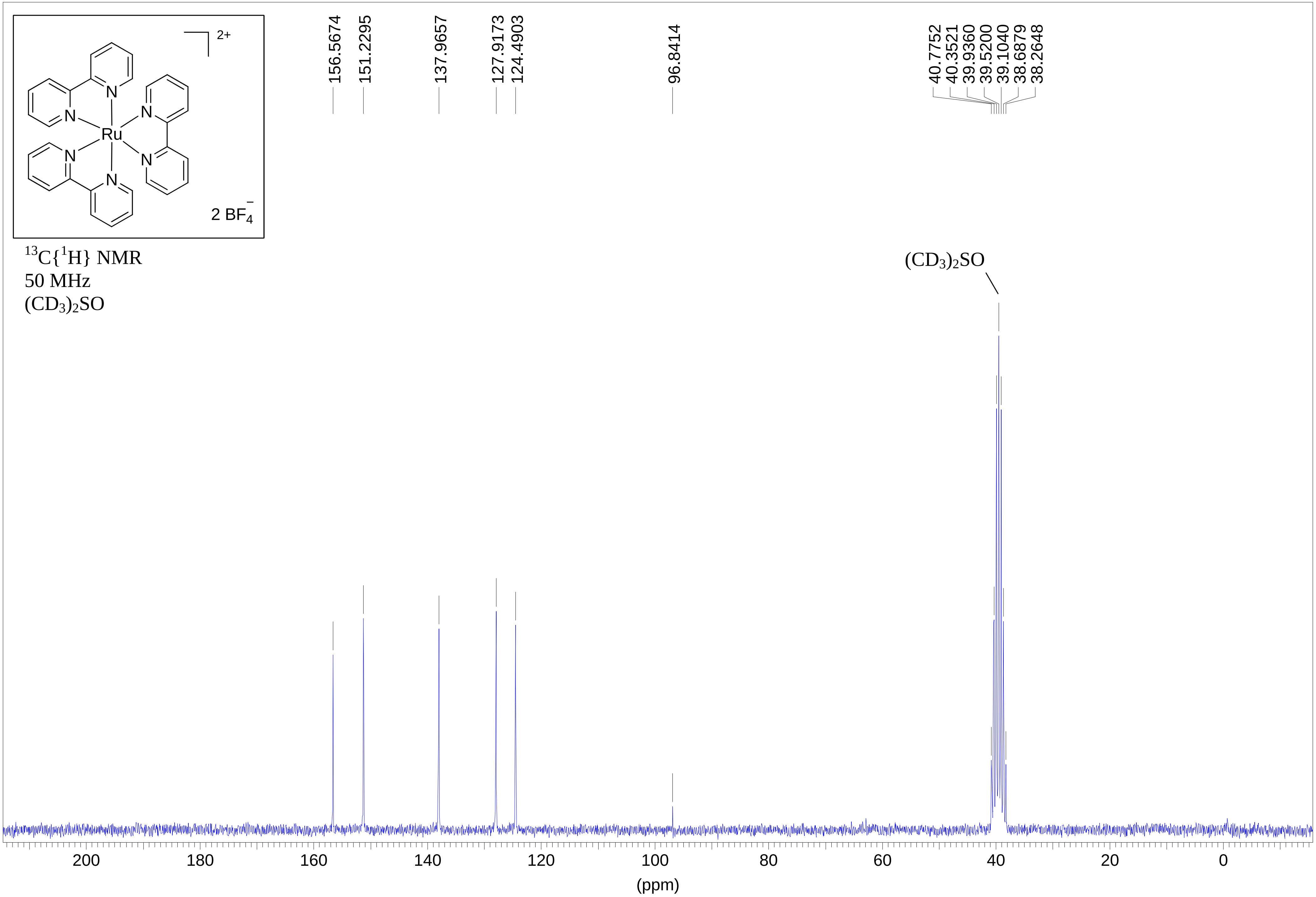
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$





^{19}F NMR
282 MHz
$CDCl_3$
F
N
MeO
3n
-176.9525
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
-185
-190
-195
-200
(ppm)


8.8318
8.8044
8.1869
8.1595
8.1338
7.7381
7.7216
7.5457
7.5237
7.5017
2+
Ru
N
2 BF4−
1H NMR
300 MHz
(CD3)2SO
water
D-solv.
residual
peak
8.5
8.0
7.5
(ppm)
Integral
1.0000
1.0044
1.0033
1.0122
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


2+
Ru
N
2 BF4−
13C{1H} NMR
50 MHz
(CD3)2SO
156.5674
151.2295
137.9657
127.9173
124.4903
96.8414
40.7752
40.3521
39.9360
39.5200
39.1040
38.6879
38.2648
(CD3)2SO
200
180
160
140
120
100
80
60
40
20
0
(ppm)

Cyclic voltammetry (CV) curves. Experiments were performed with the concentration of studied compounds of 1 mM in MeCN containing Et_4NClO_4 (0.1 M); Pt electrode; scan rate 0.1 $V \cdot s^{-1}$; temperature 25 °C.

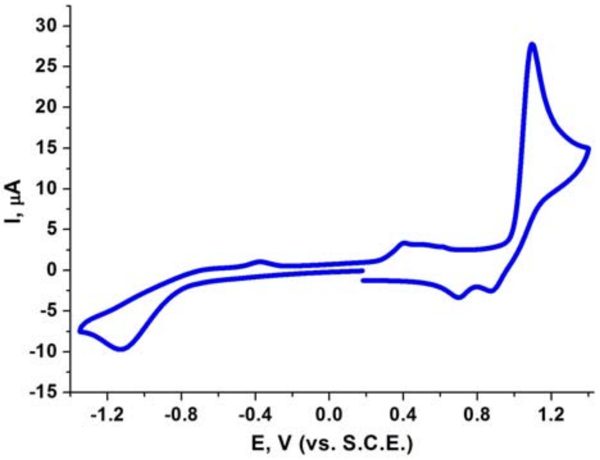


Figure S1. Compound **1a-I** (initial cathodic scan).

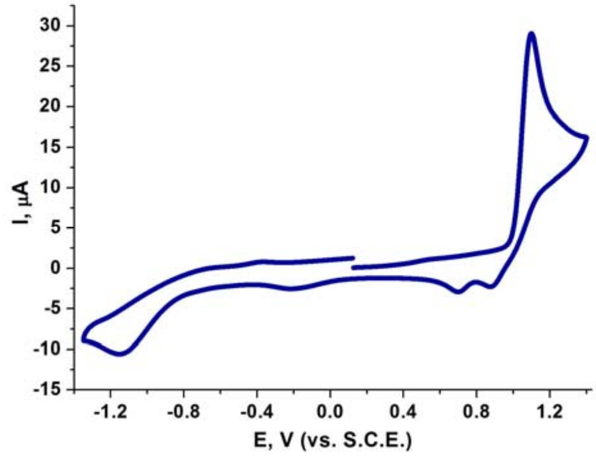


Figure S2. Compound **1a-I** (initial anodic scan).

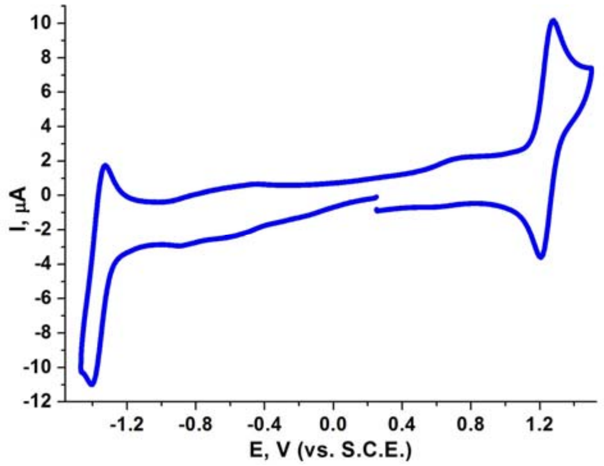


Figure S3. $Ru(bpy)_3(BF_4)_2$ (initial cathodic scan).

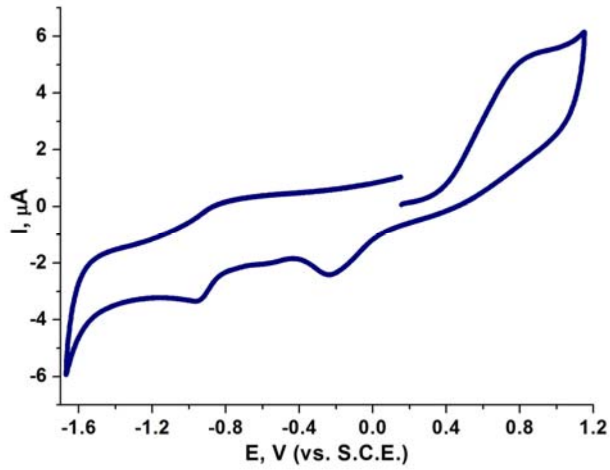


Figure S4. PPh_3 (initial anodic scan).

Table S1. Redox potentials.

Redox couple	E, V (vs. S.C.E.)[a]
1a-I$^{\bullet+}$/**1a-I**	+1.10
1a-I/**1a-I**$^{\bullet-}$	–1.15
Ru(III)/Ru(II)	+1.28 (+1.29)[1]
Ru(II)/Ru(I)	–1.33 (–1.33)[1]
Ru(II)*/Ru(I)	(+0.84)[1]
Ru(II)*/Ru(III)	(–0.83)[1]
$PPh_3^{\bullet+}$/PPh_3	+0.77 (+0.95)[2]

[a] Potentials measured in this work. Literature data are given in parentheses.

Table S2. Calculated electromotive forces (EMF).

Redox process	EMF, V
Ru(II)* + **1a-I** → Ru(I) + **1a-I**$^{\bullet+}$	–0.26
Ru(II)* + **1a-I** → Ru(III) + **1a-I**$^{\bullet-}$	–0.32
Ru(II)* + PPh_3 → Ru(I) + $PPh_3^{\bullet+}$	+0.07
Ru(I) + **1a-I** → Ru(II) + **1a-I**$^{\bullet-}$	+0.18

1. Teplý, F. *Collect. Czech. Chem. Commun.* **2011**, *76*, 859–917.
2. Kargin, Y. M.; Nikitin, E. V.; Parakin, O. V.; Romanov, G. V.; Pudovik, A. N. *Phosphorus, Sulfur Relat. Elem.* **1980**, *8*, 55–58.