Supporting Information for

Magnesium-promoted Additions of Difluoroenolates to Unactivated Imines

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I. X-ray Experimental

Diffraction data were collected at low temperature (90K) with MoKα (λ=0.71073 Å) for **30** and **31** or CuKα radiation (λ=1.54184 Å) for **32** on a Bruker Kappa Apex-II DUO diffractometer. Refinement was by full-matrix least squares using SHELXL2014/7. H atoms were visible in difference maps, but were placed in idealized positions in the refinements except for those on N, for which positions were refined. Approximately 50:50 disorder of the naphthyl group was present in **31**. The crystal of **31** was a twin, and the crystal of **32** was also a twin with two independent molecules present in the asymmetric unit. Crystal data: for **30**: $C_{25}H_{19}F_2NO$, monoclinic $P2_1/c$, a=5.7571(4), b=18.4857(13), c=17.5890(13) Å, β=94.410(4)°, Z=4, μ(MoKα)=0.10 mm^{-1}, θ_{max}=30.6°, 5689 independent data, 265 variables, R=0.057, CCDC 1816639; for **31**: $C_{26}H_{21}F_2NO_2$, triclinic P-1, a=5.6561(3), b=9.7402(4), c=19.2384(9) Å, α=102.673(3), β=96.750(3), γ=97.299(3)°, Z=2, μ(MoKα)=0.10 mm^{-1}, θ_{max}=28.4°, 14427 independent data, 352 variables, R=0.051, CCDC 1816640; for **32**: $C_{27}H_{22}F_3NO$, triclinic P-1, a=10.1332(6), b=10.5209(5), c=20.5621(10) Å, α=77.223(3), β=81.352(4), γ=89.909(3)°, Z=4, μ(CuKα)=0.84 mm^{-1}, θ_{max}=68.3°, 7629 independent data, 587 variables, R=0.116, CCDC 1816641.

II. X-ray Crystallographic Data

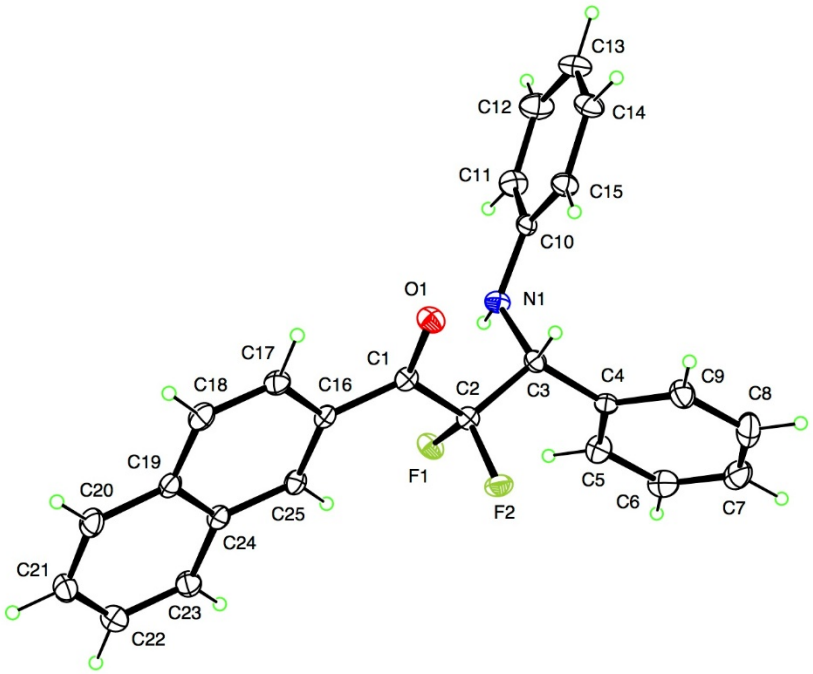


Figure S1. ORTEP Diagram of **30** with 50% ellipsoids.

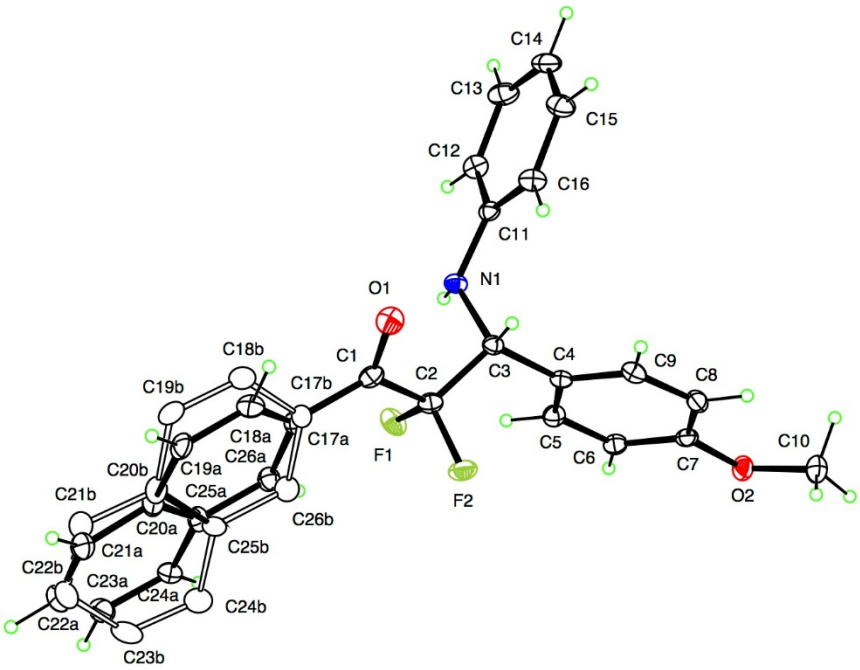


Figure S2. ORTEP Diagram of **31**. with 50% ellipsoids, showing disorder of naphthyl group.

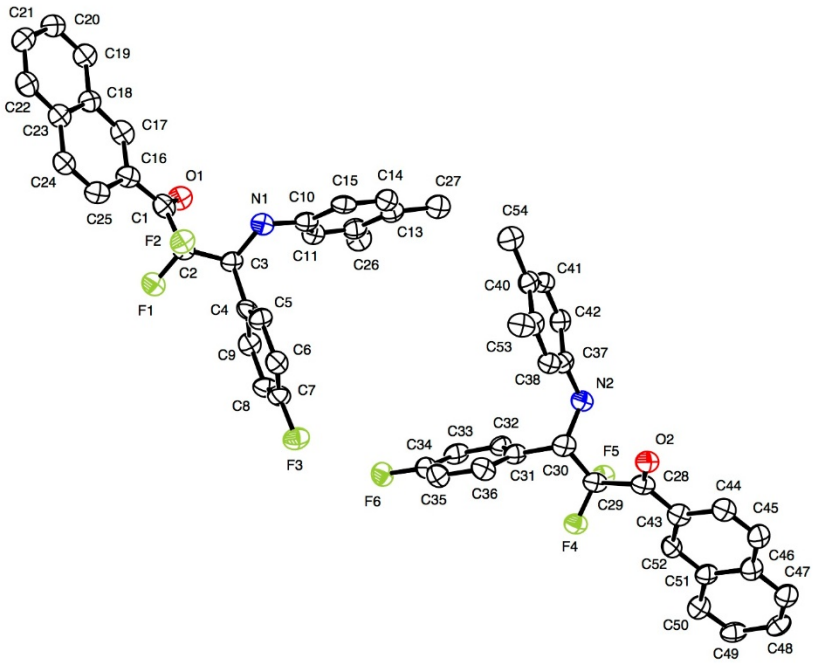
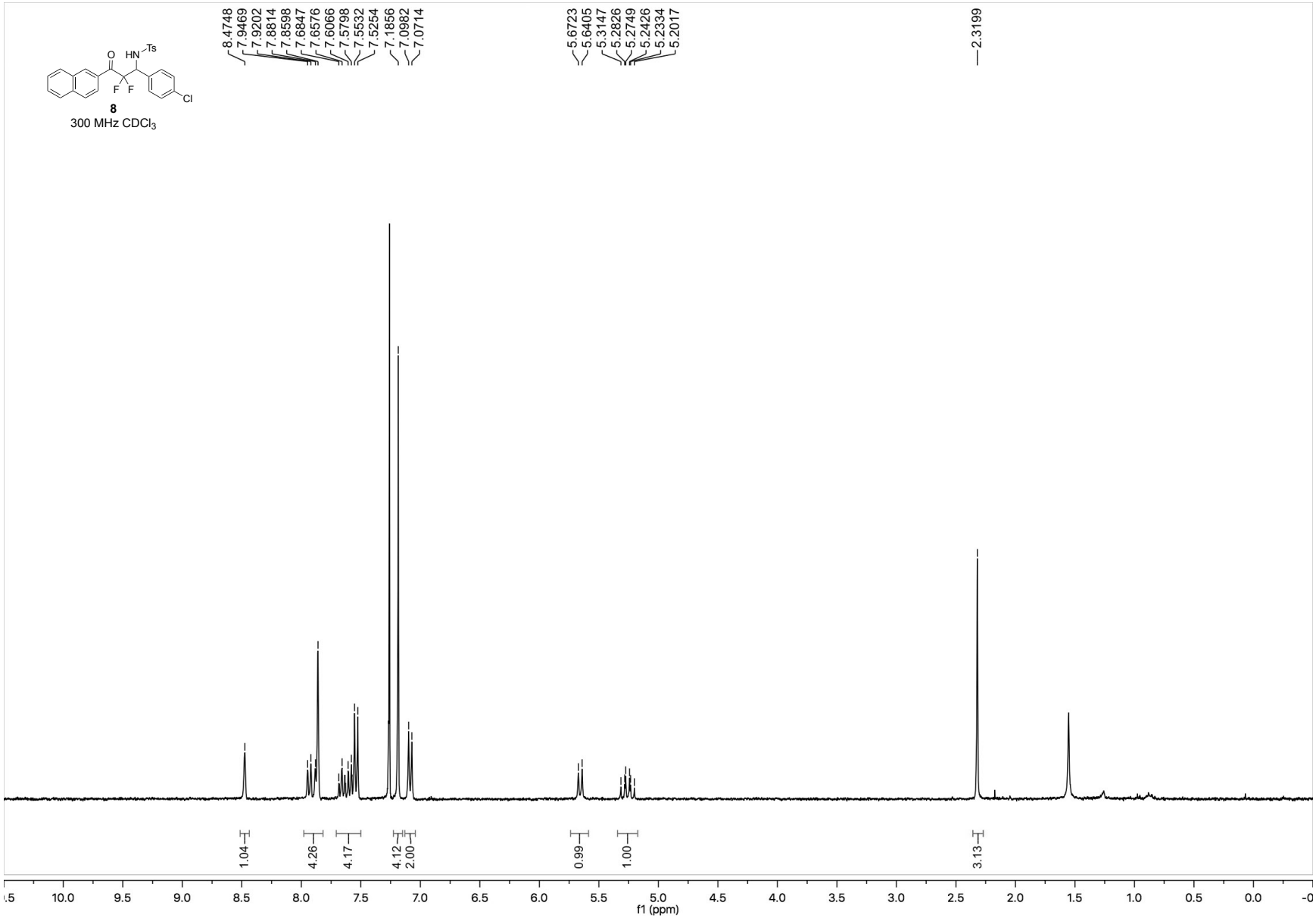


Figure S3. ORTEP Diagram of **32** with 50% ellipsoids. H atoms are not shown.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5.2749
5.2426
5.2334
5.2017
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HN
Ts
F
F
Cl
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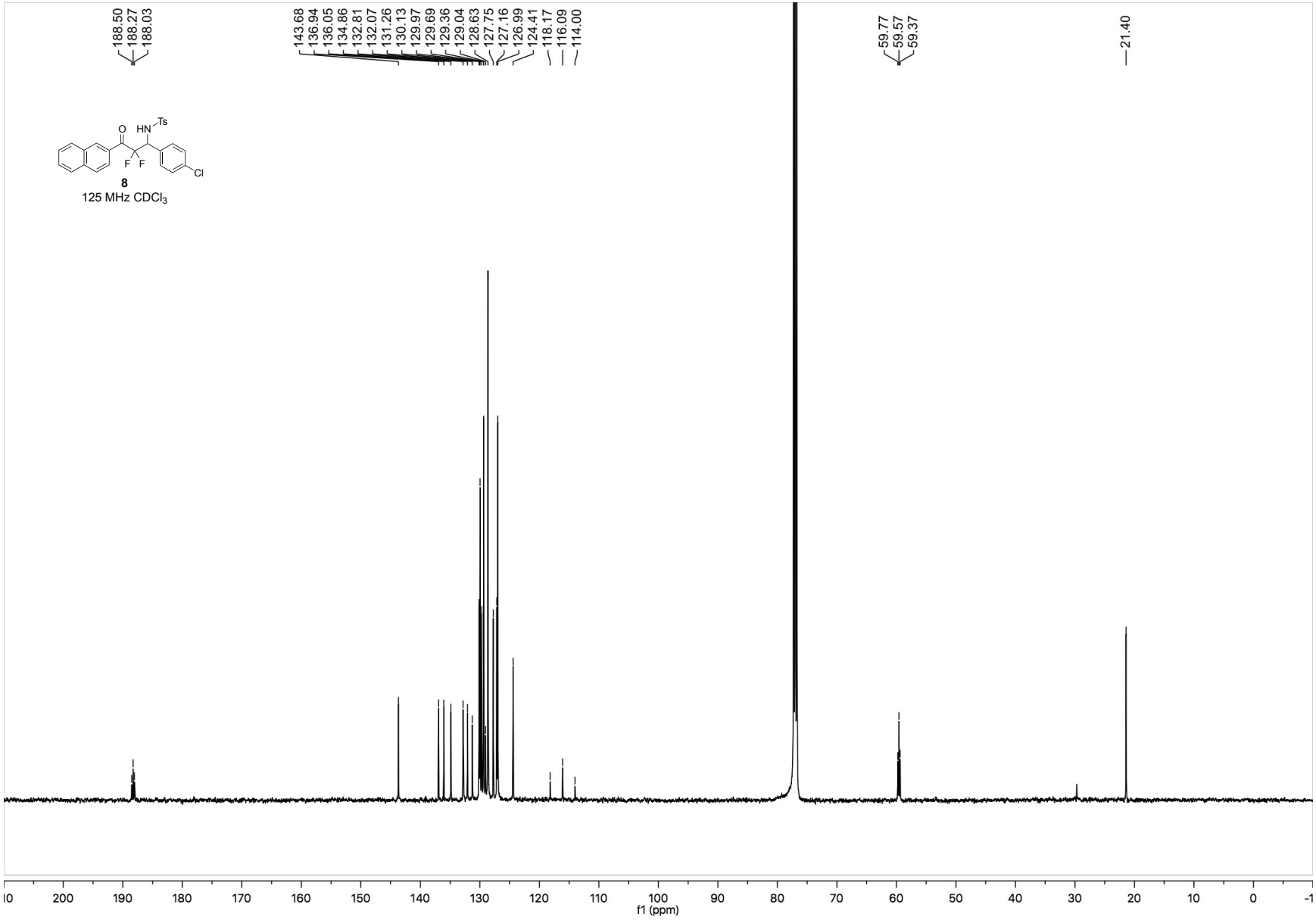
f1 (ppm)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Cl
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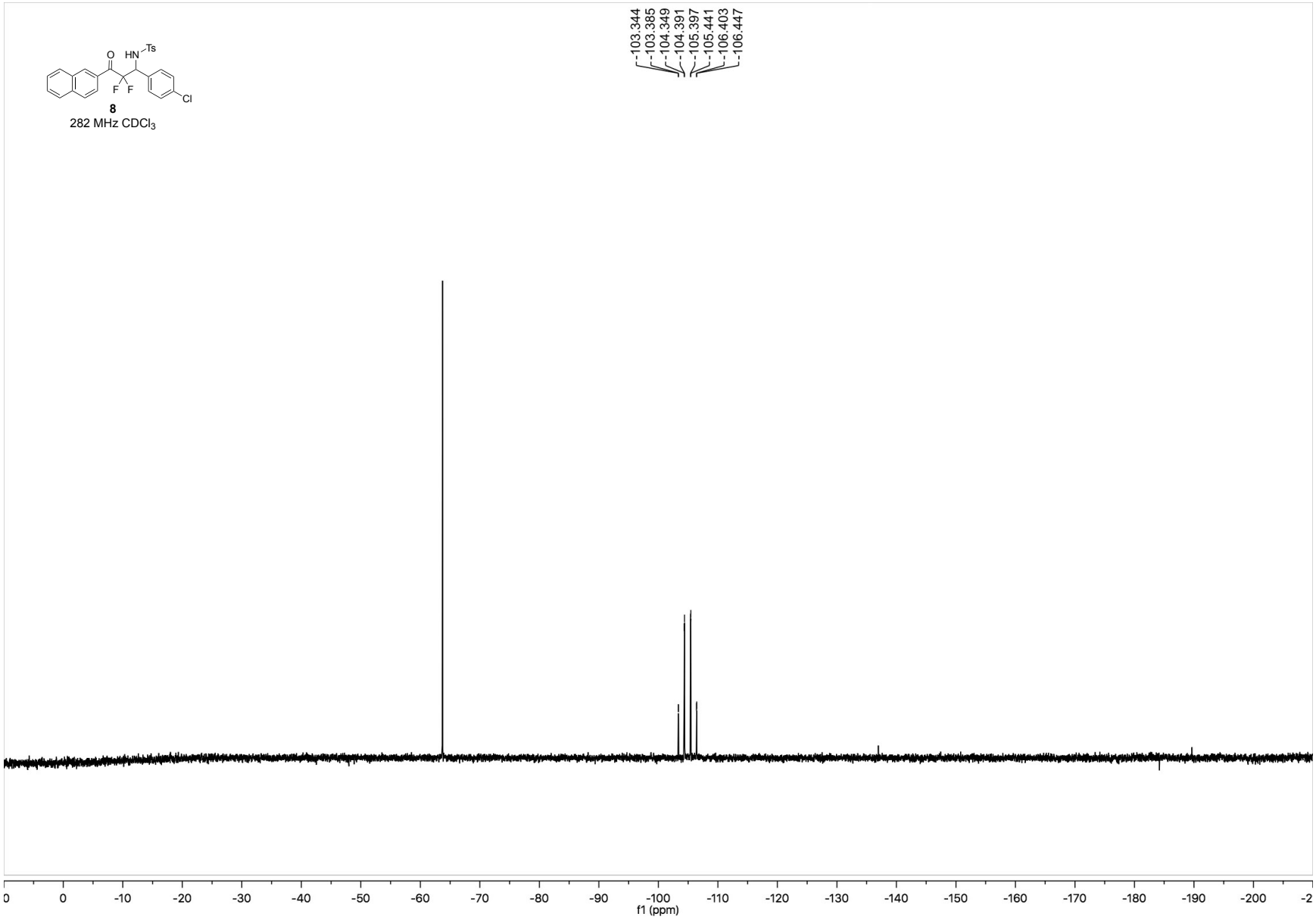
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F
Cl
8
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-30
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-60
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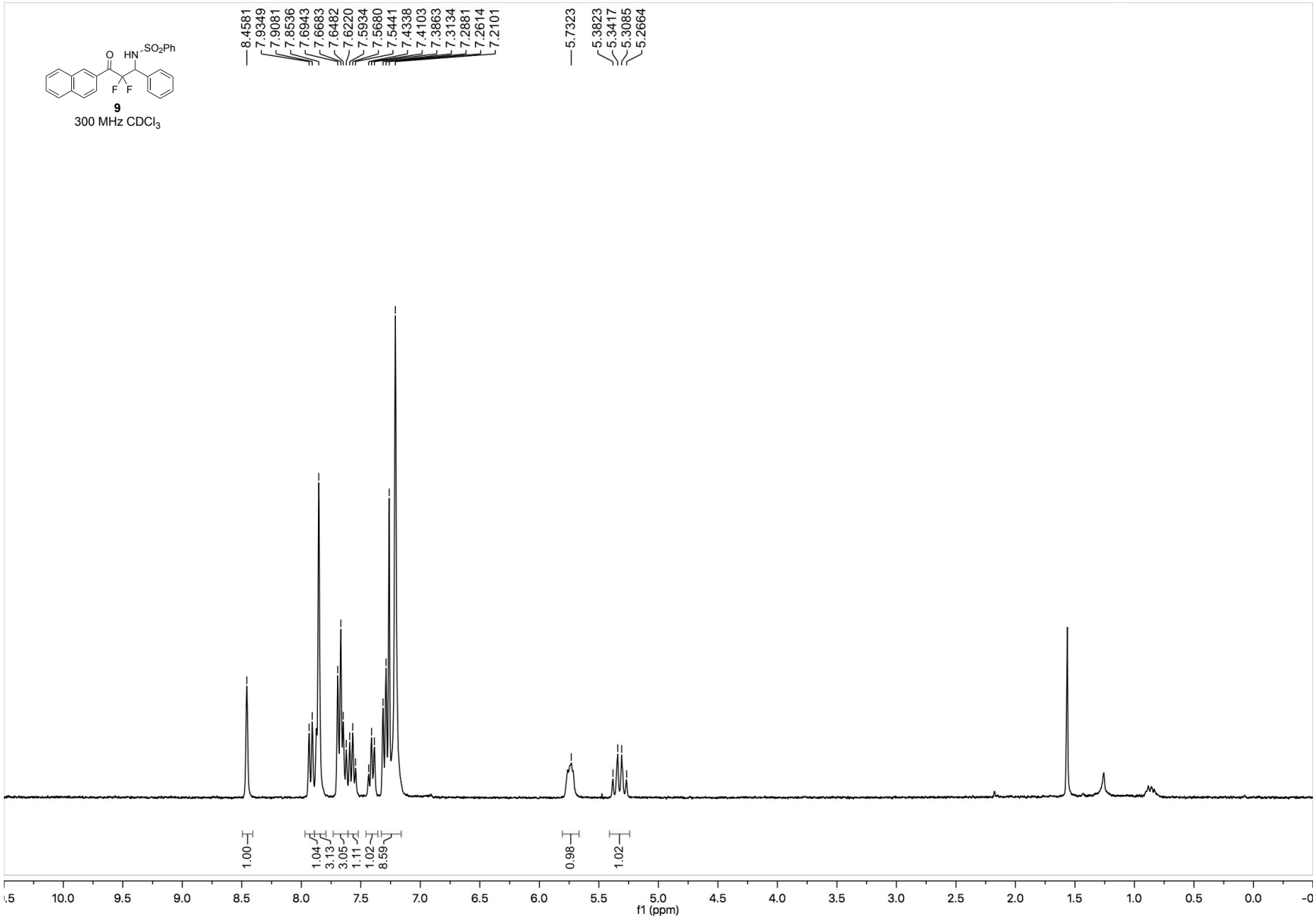
f1 (ppm)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SO2Ph
F F
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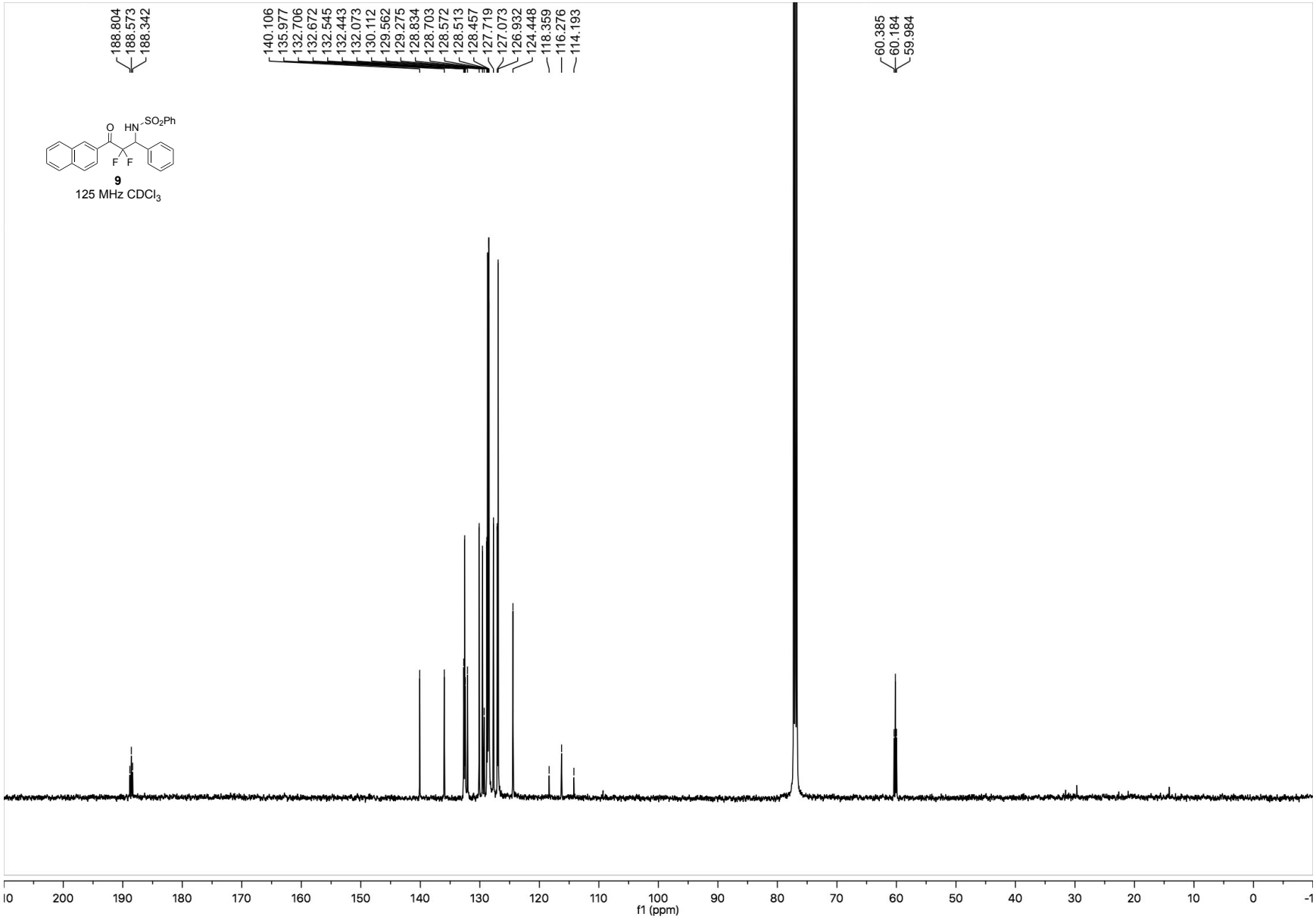
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F F
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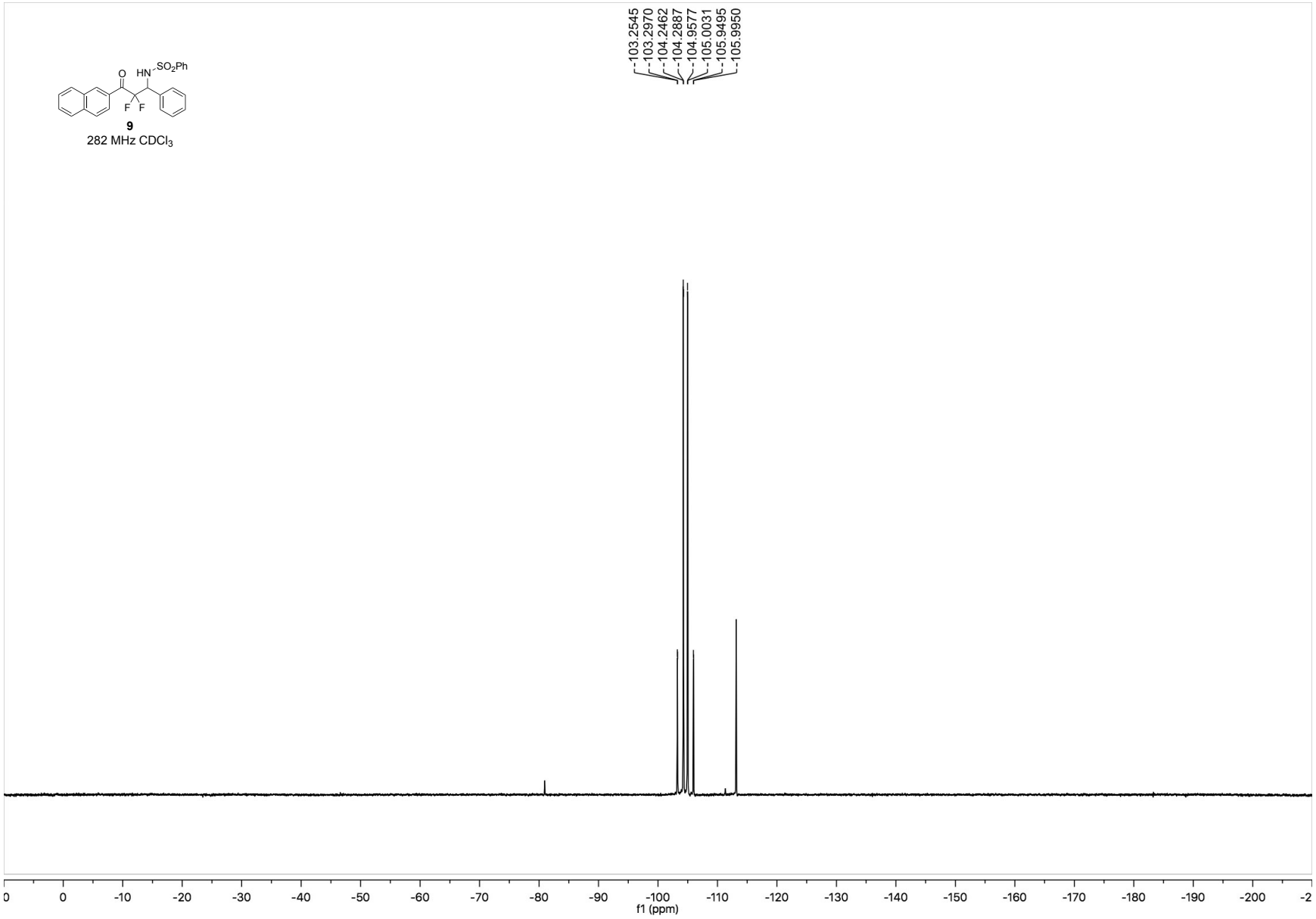
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F F
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0
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-60
-70
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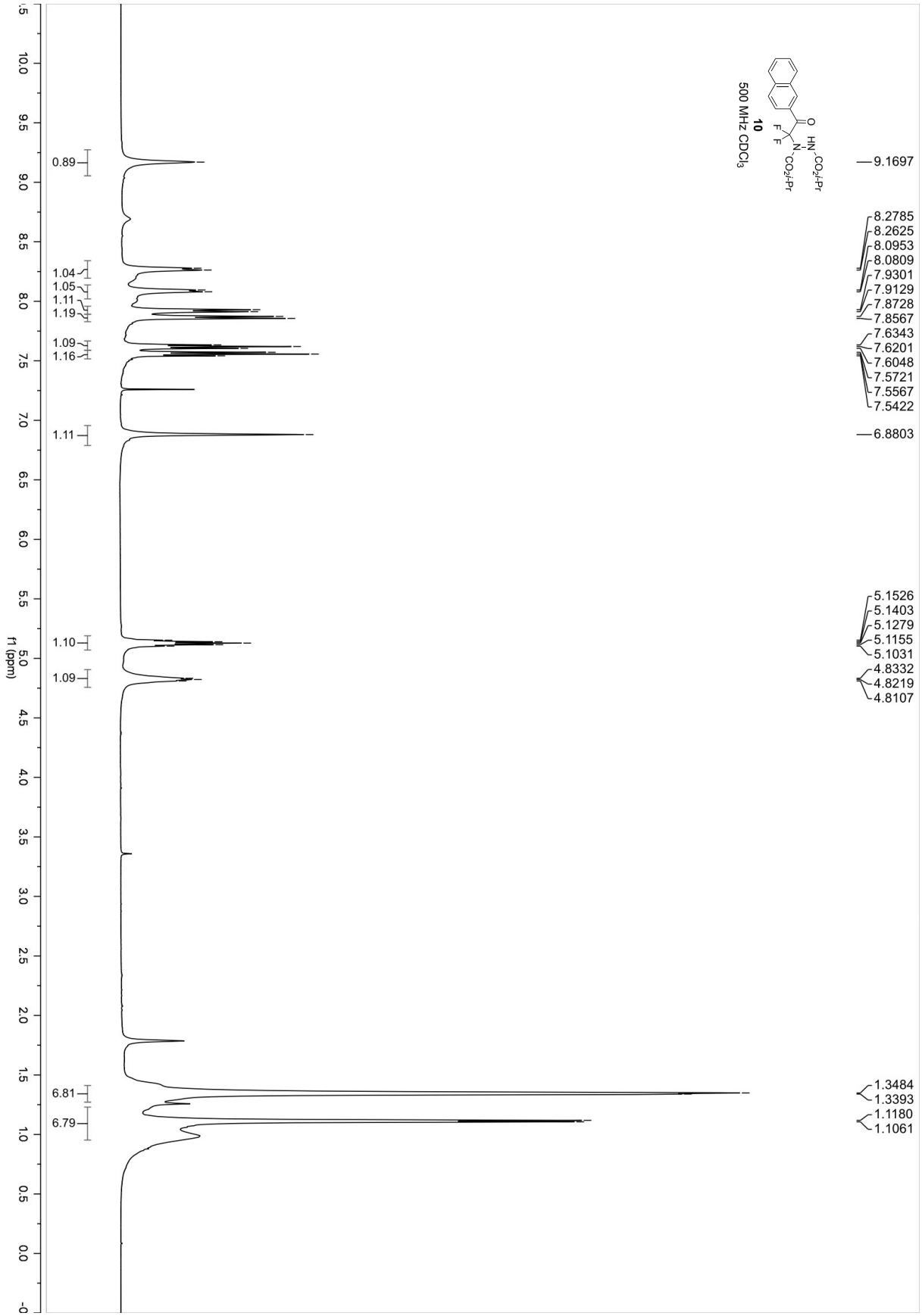
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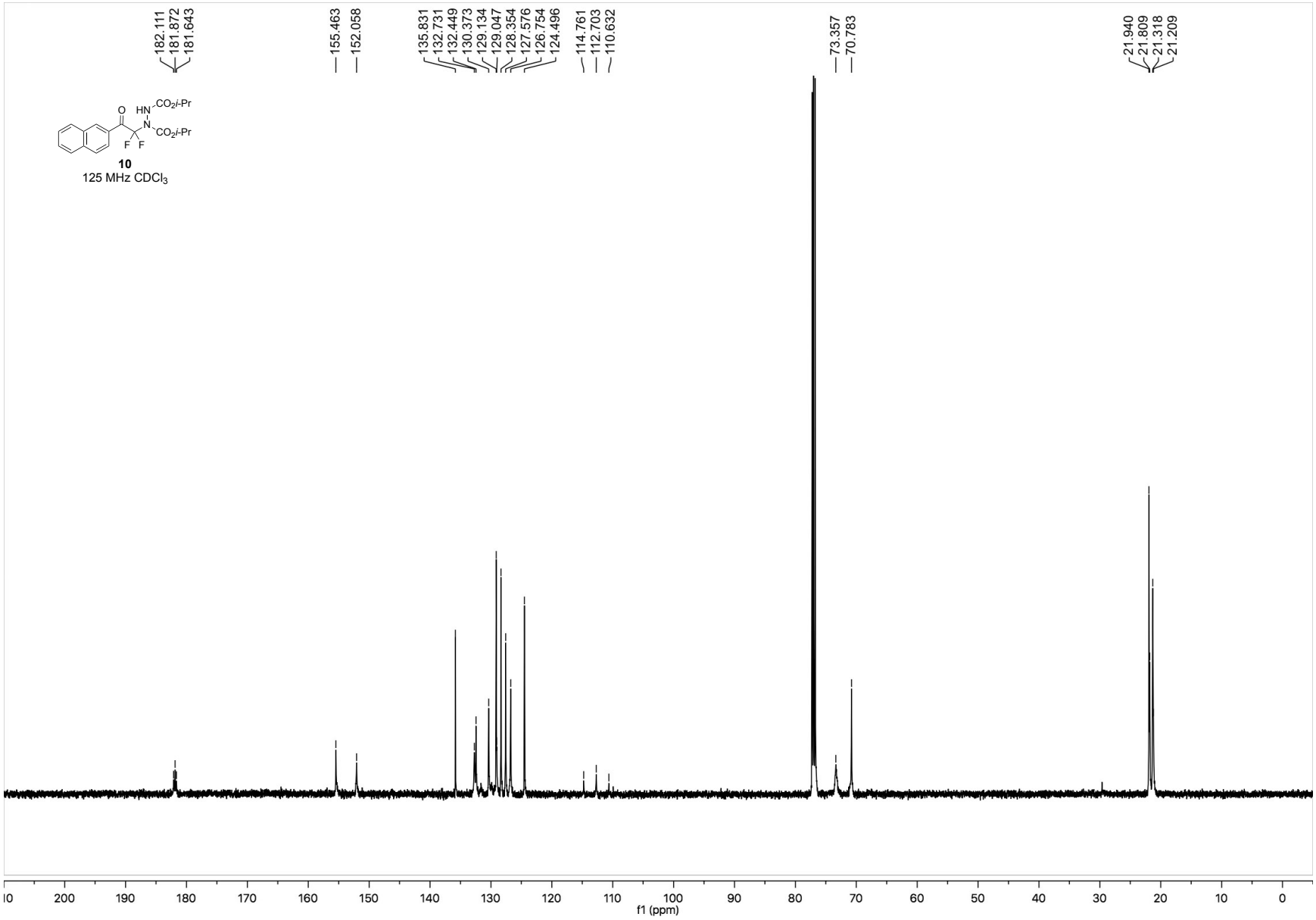
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126.754
124.496
114.761
112.703
110.632
73.357
70.783
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N
CO2i-Pr
F F
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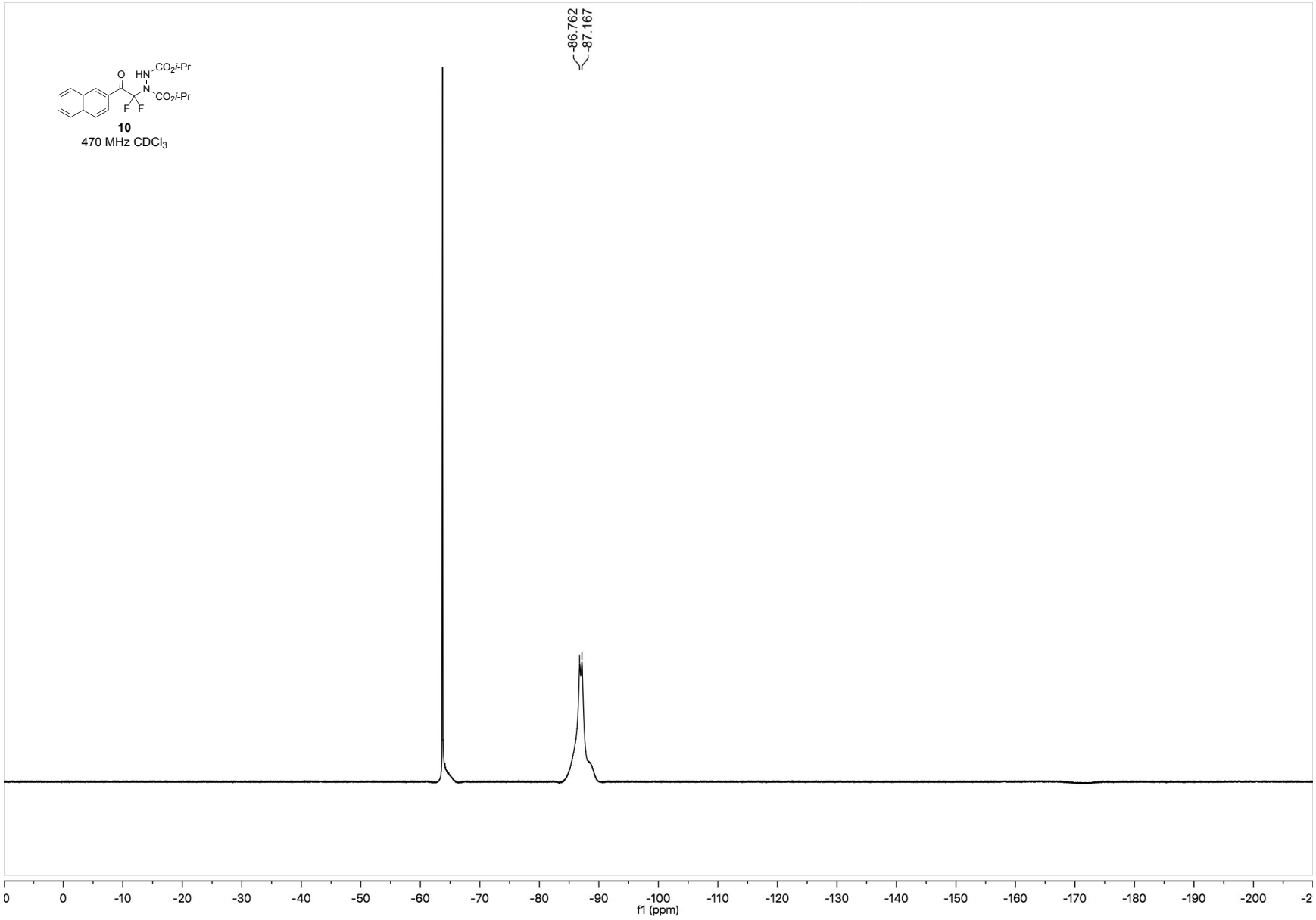
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-50
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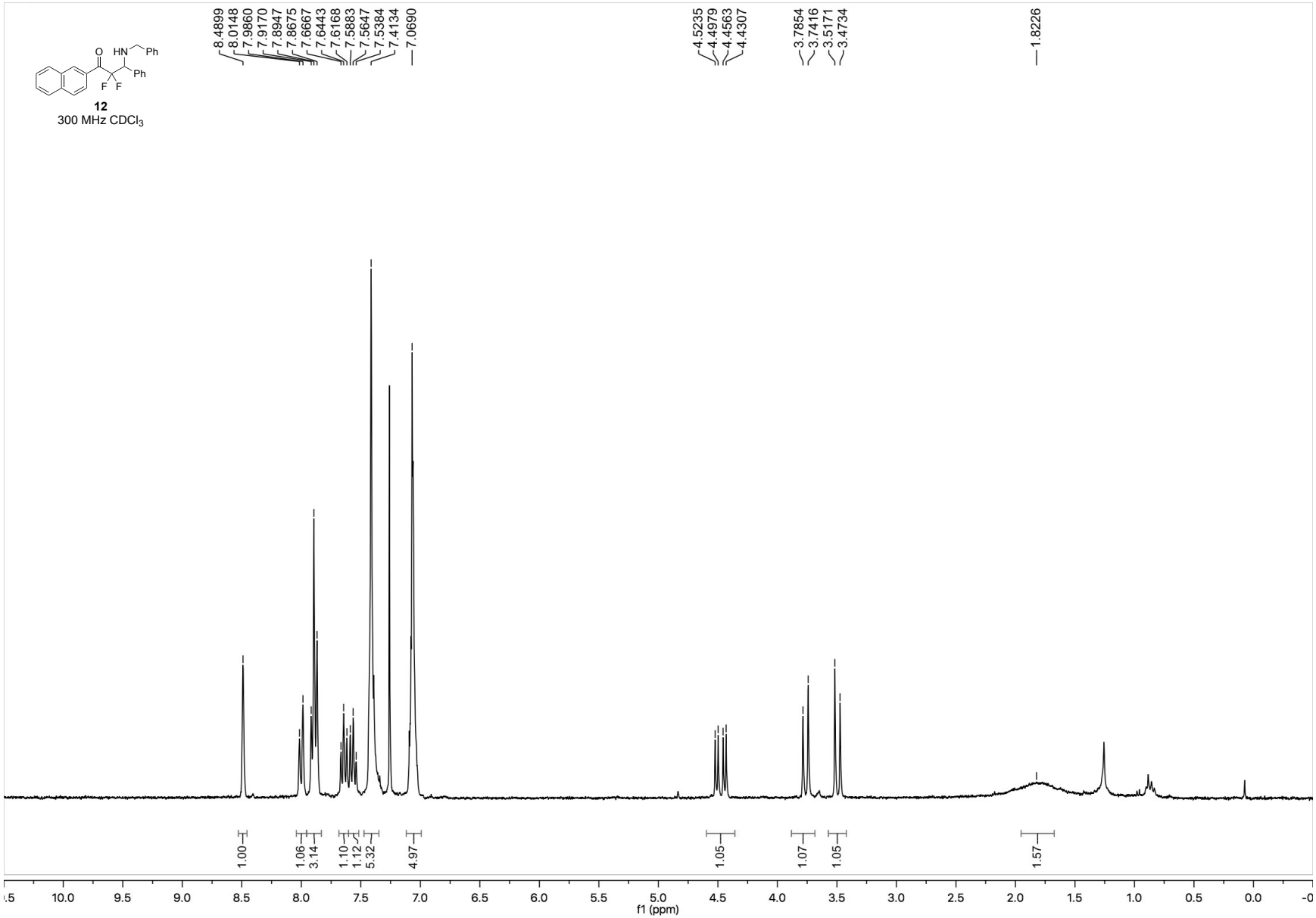
f1 (ppm)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3.5171
3.4734
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HN
Ph
Ph
F F
12
300 MHz CDCl3
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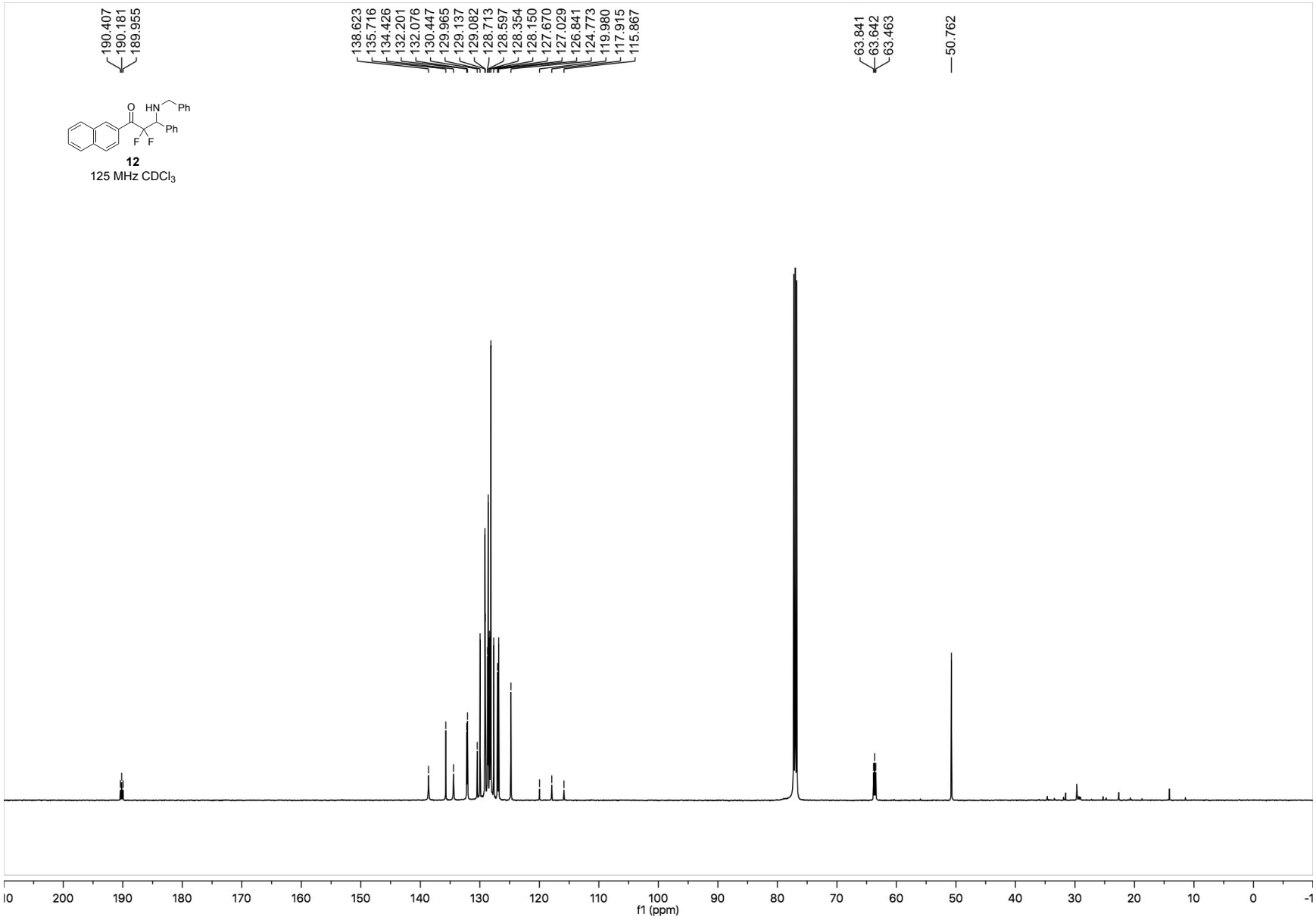
f1 (ppm)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Ph
F
F
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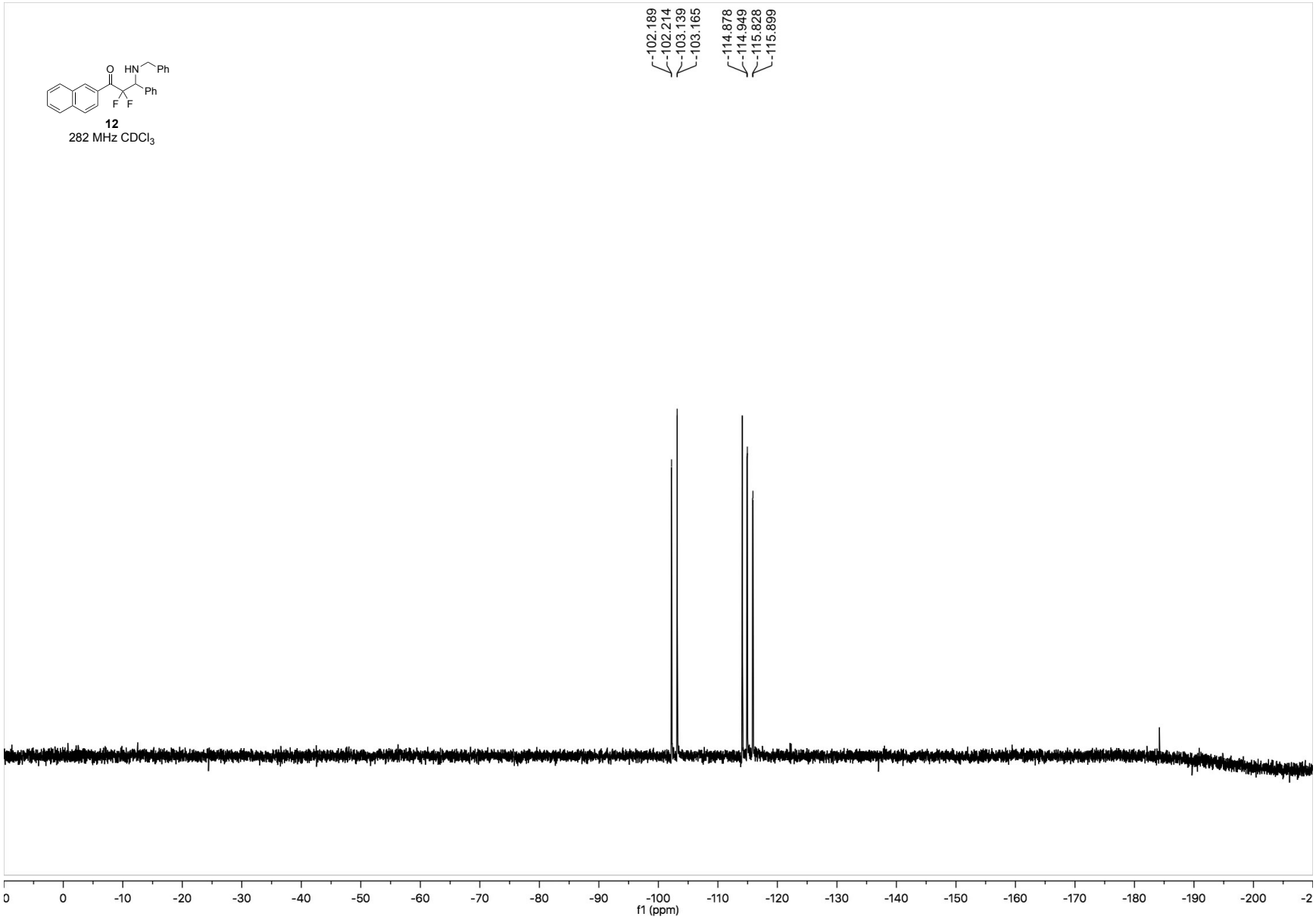
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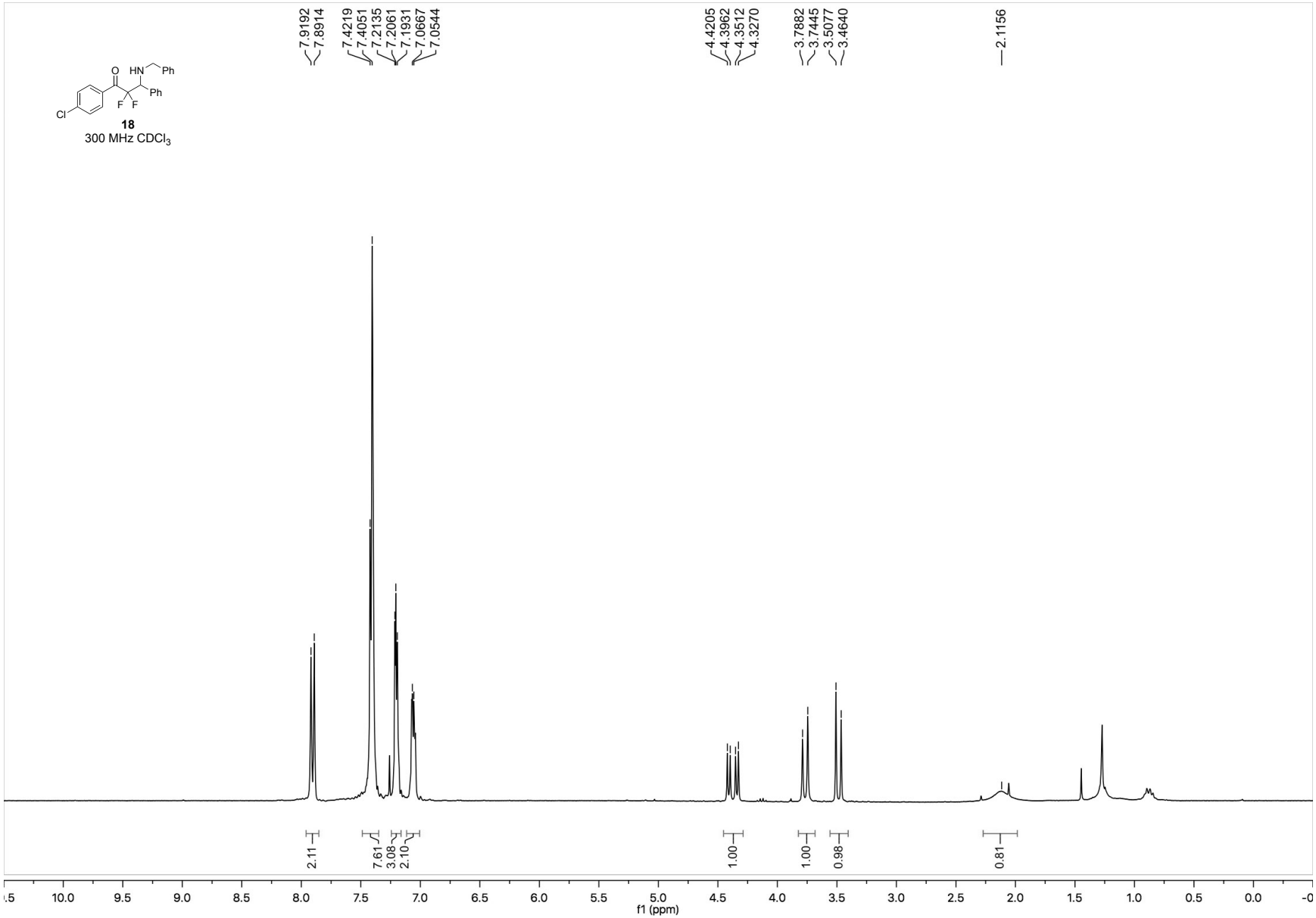
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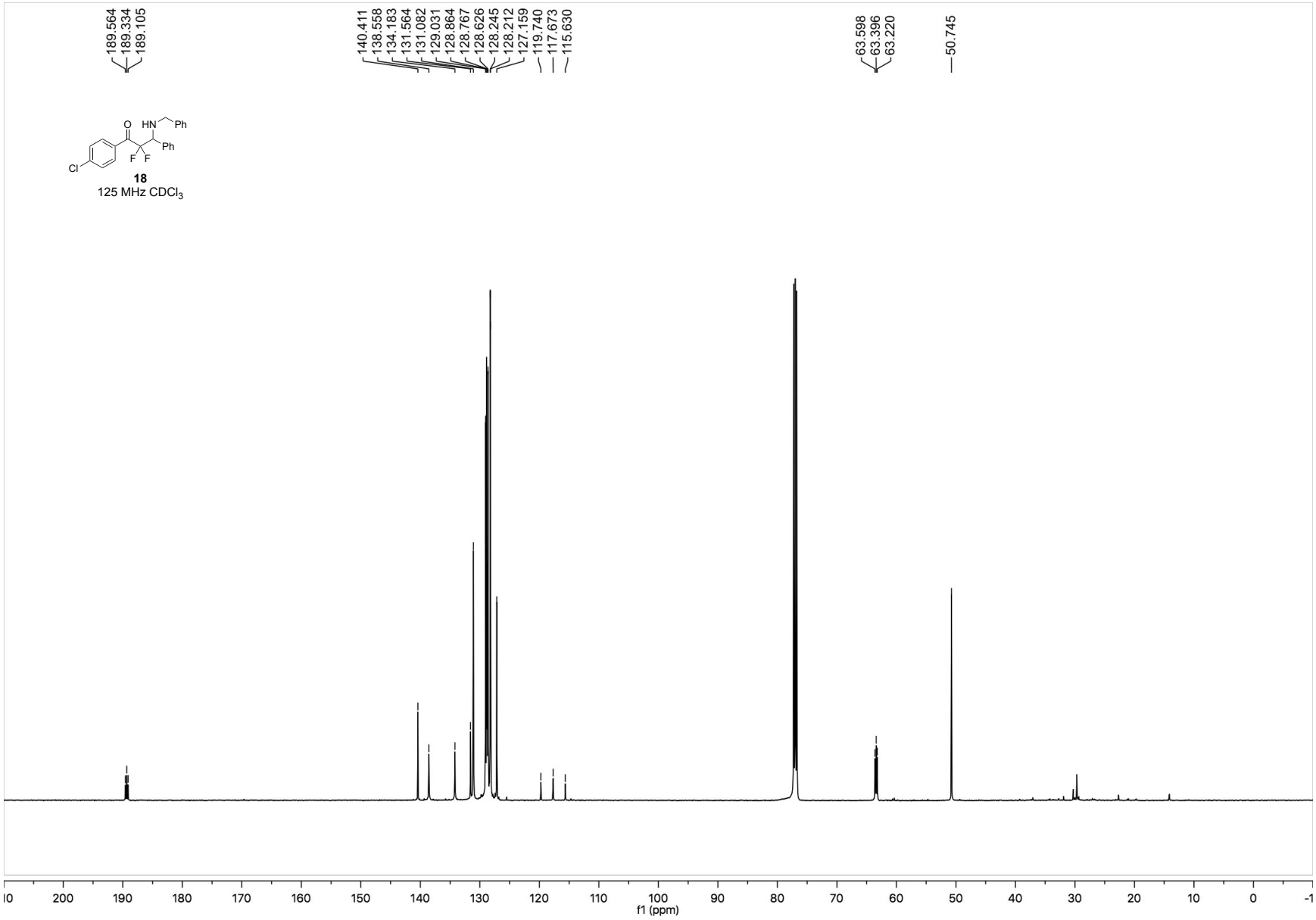
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Cl
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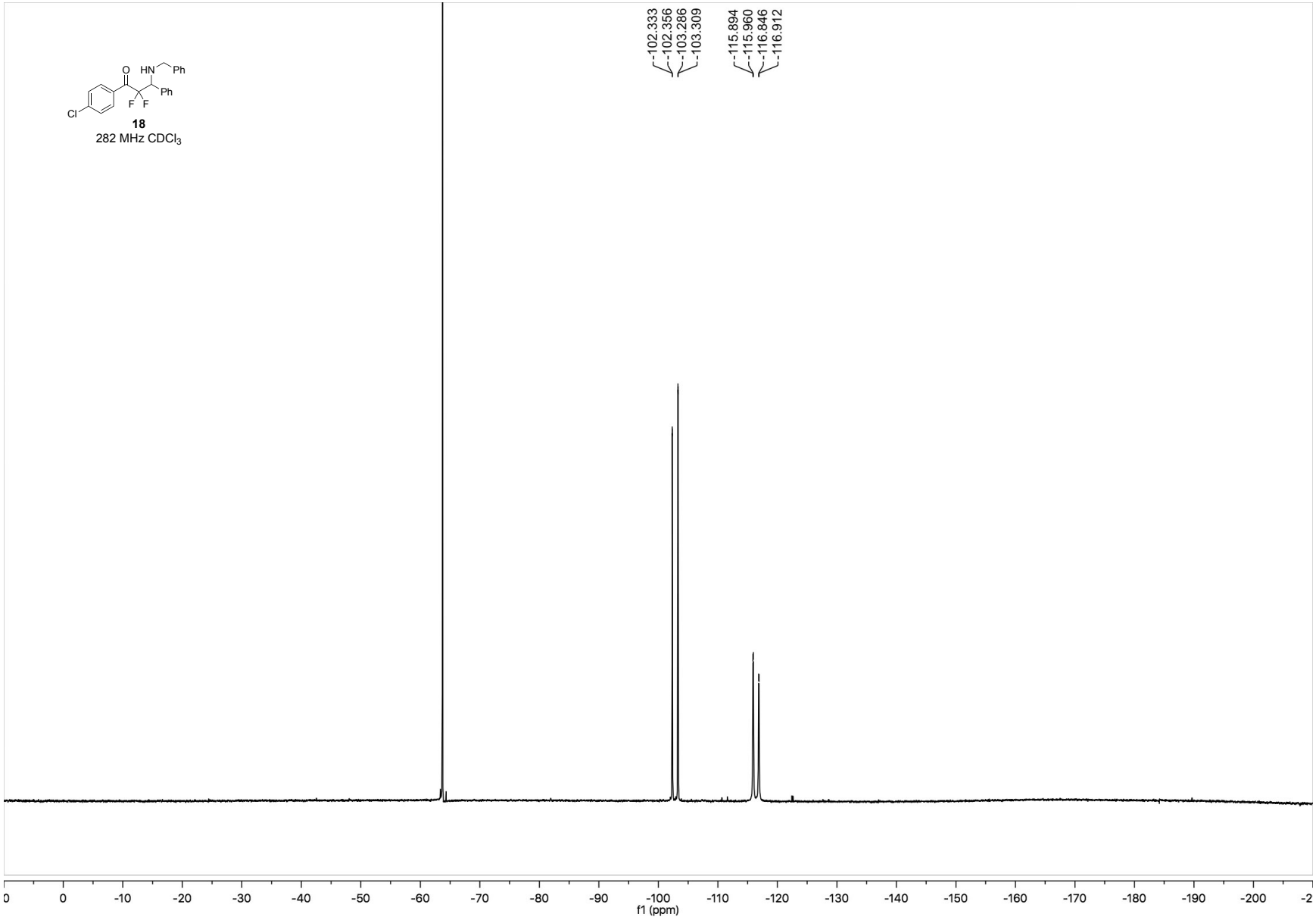
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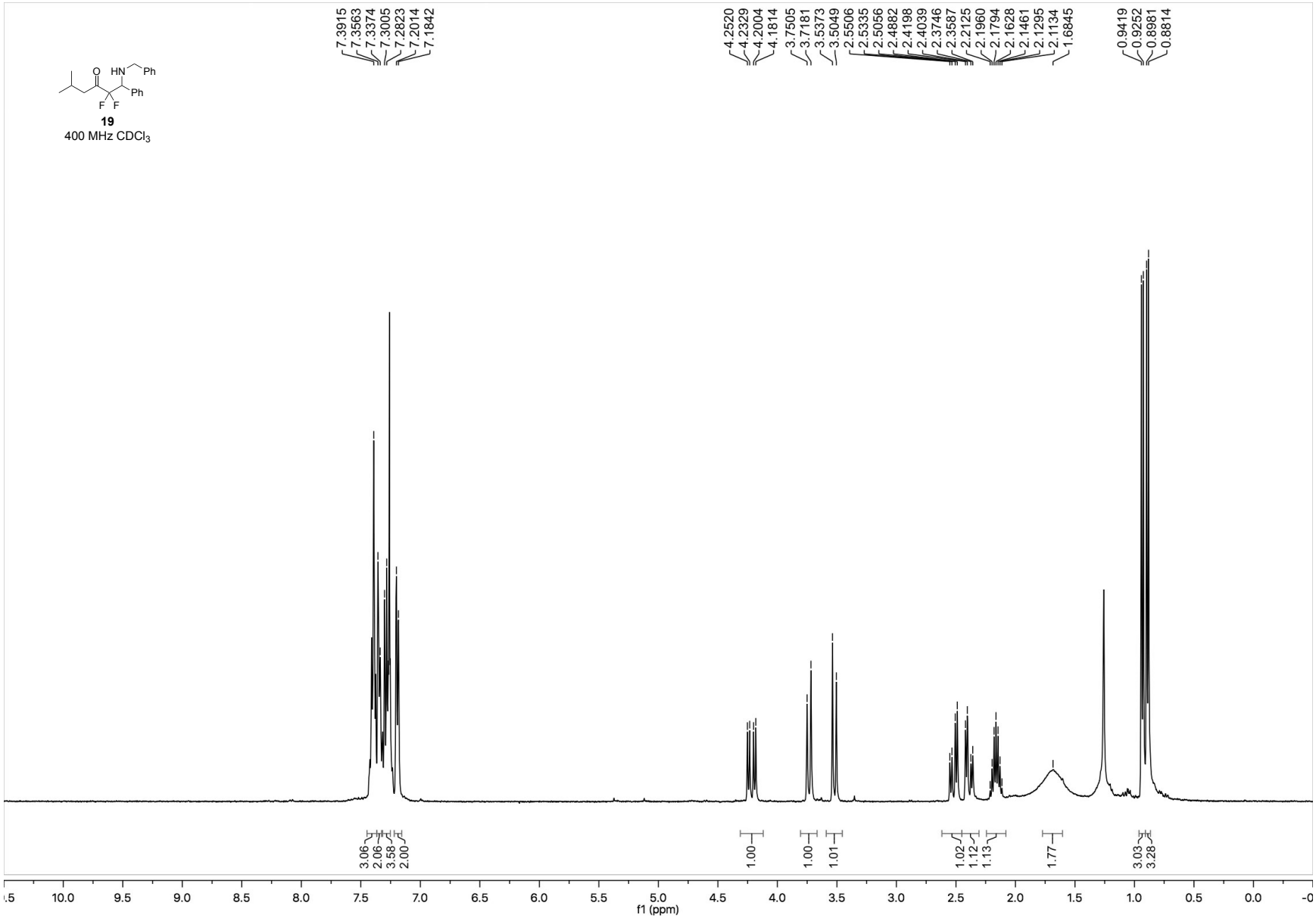
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Ph
Ph
F F
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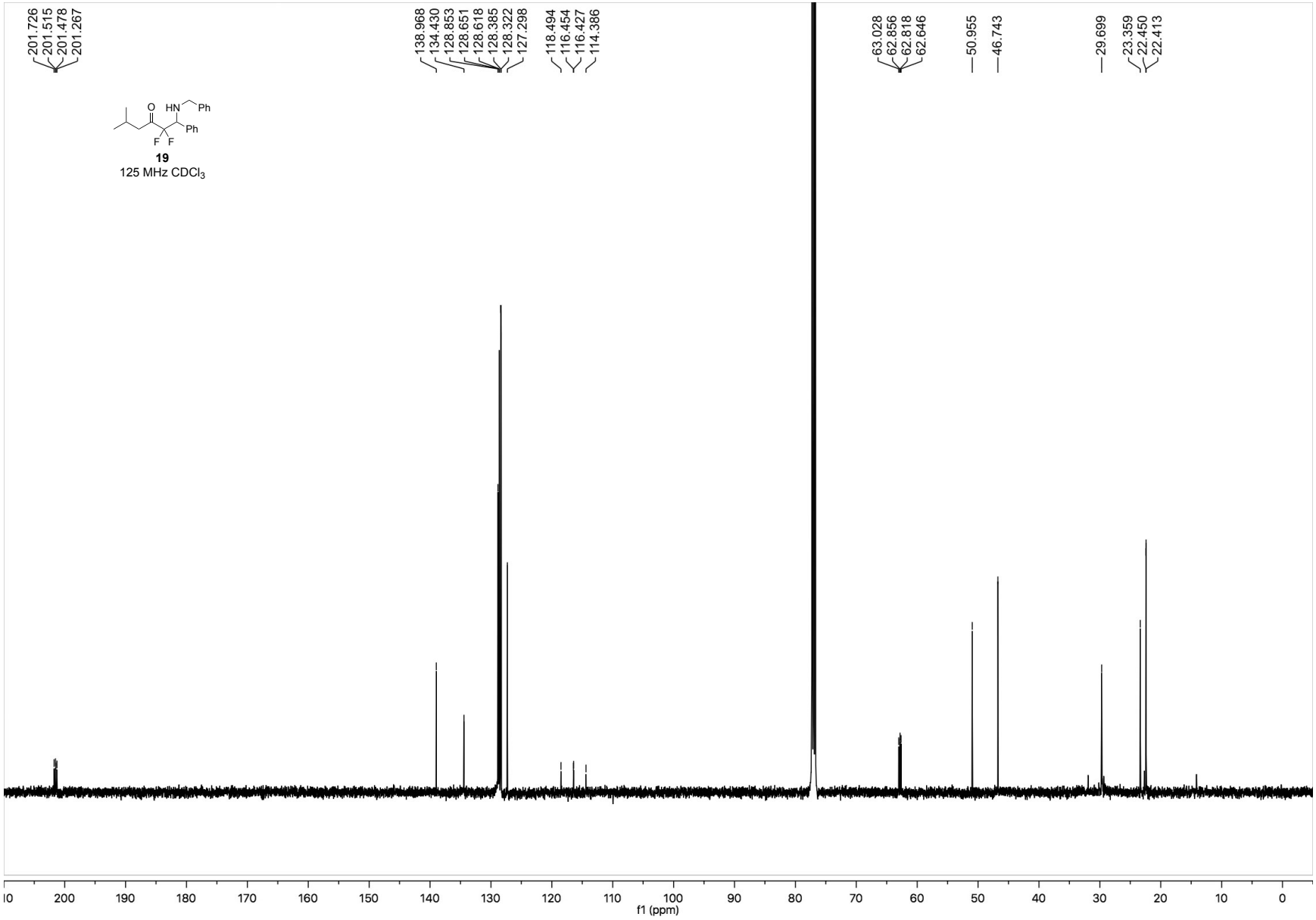
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116.427
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Ph
F F
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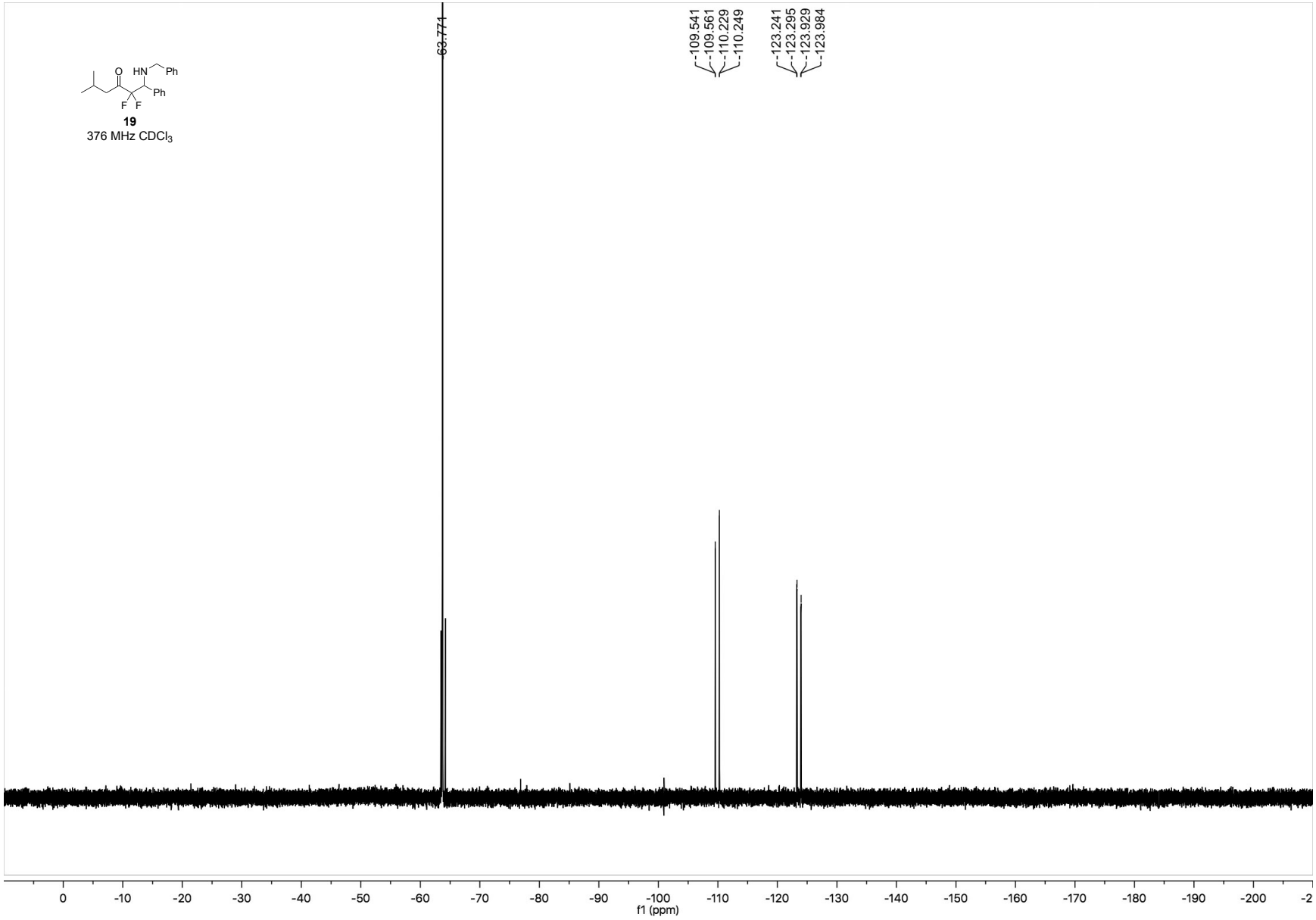
125 MHz CDCl3
f1 (ppm)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Ph
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F F
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-60
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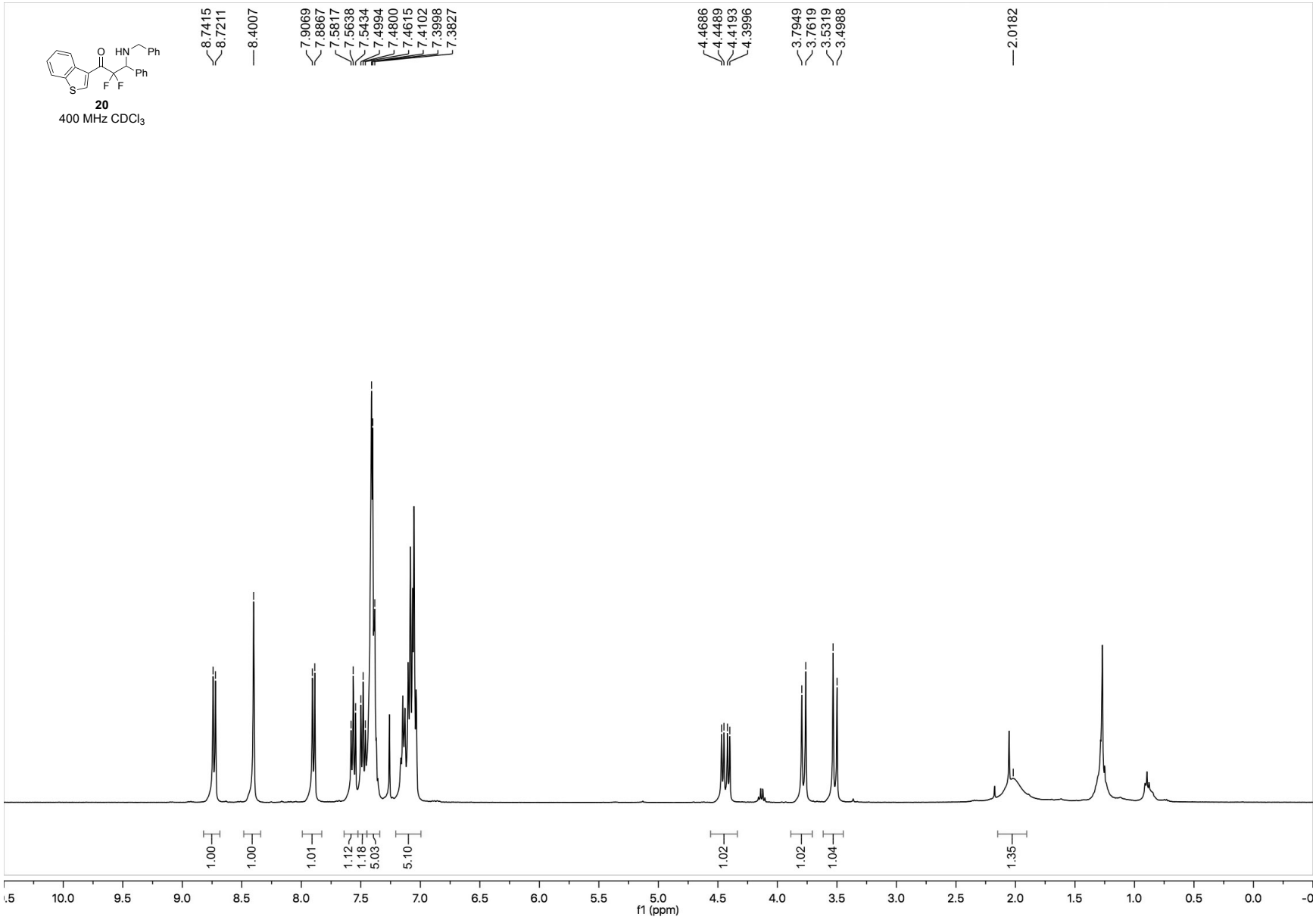
-200
f1 (ppm)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4.4489
4.4193
4.3996
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3.7619
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Ph
Ph
F F
S
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400 MHz CDCl3
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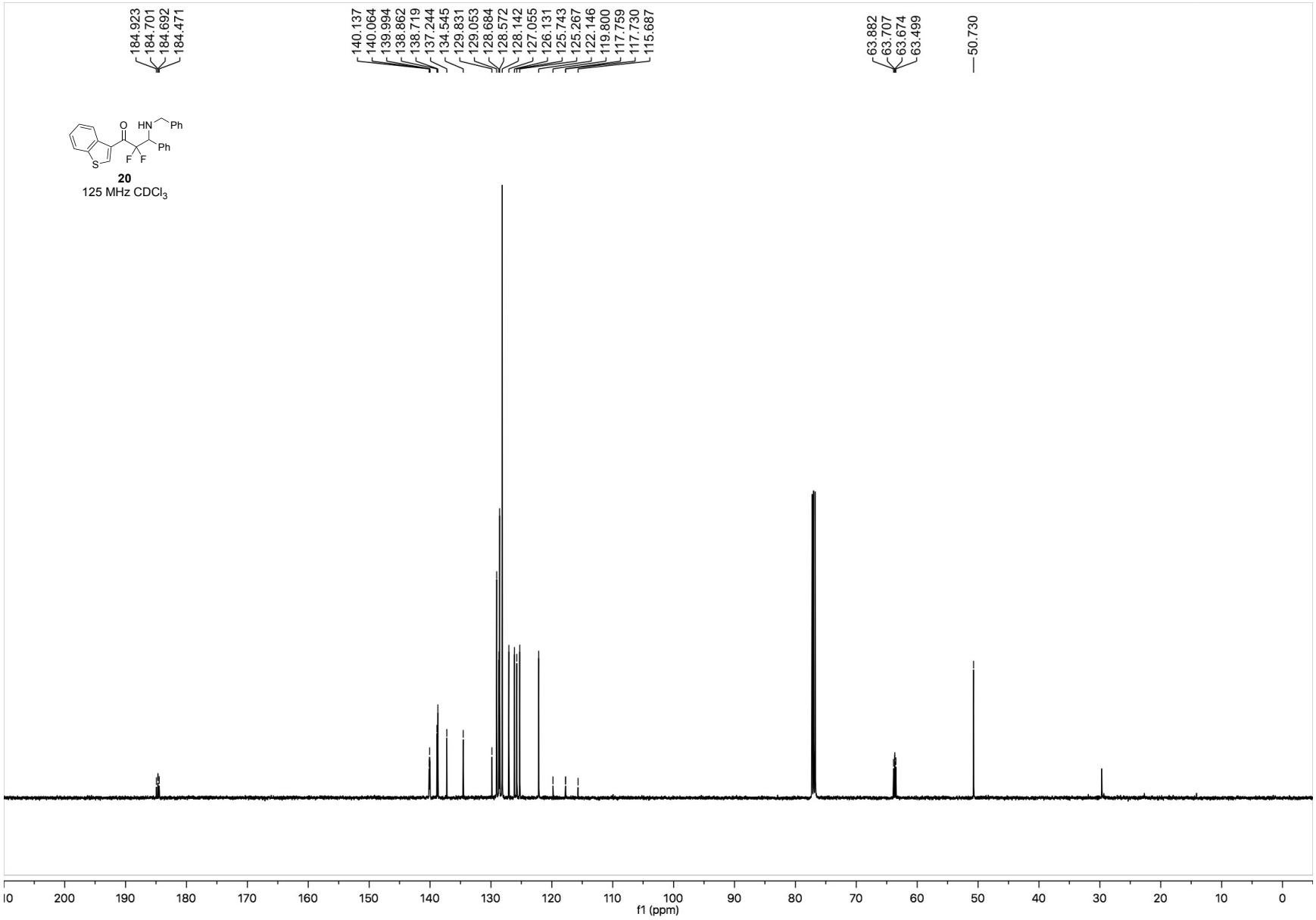
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128.572
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Ph
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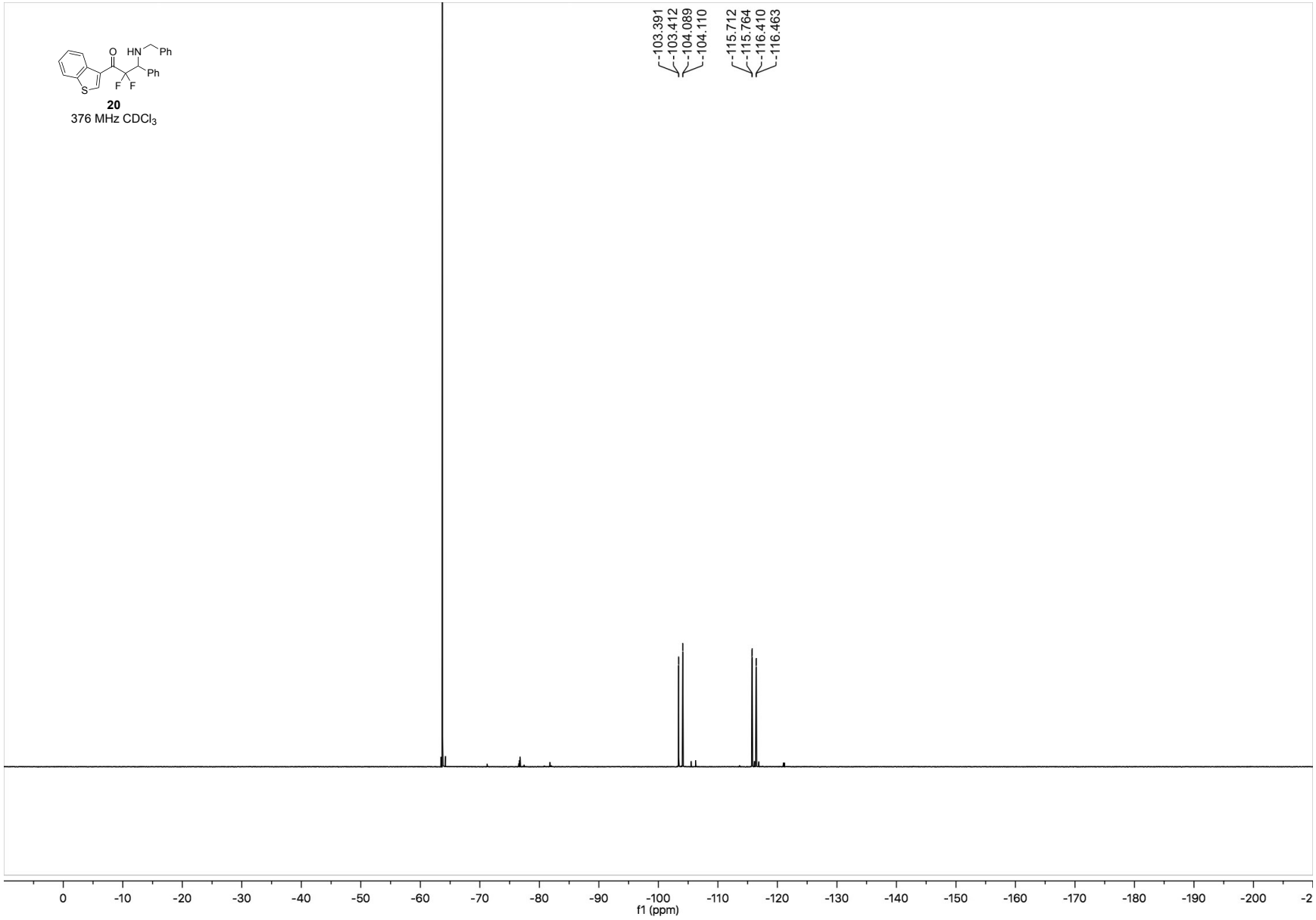
F
F
S
20
125 MHz CDCl3
f1 (ppm)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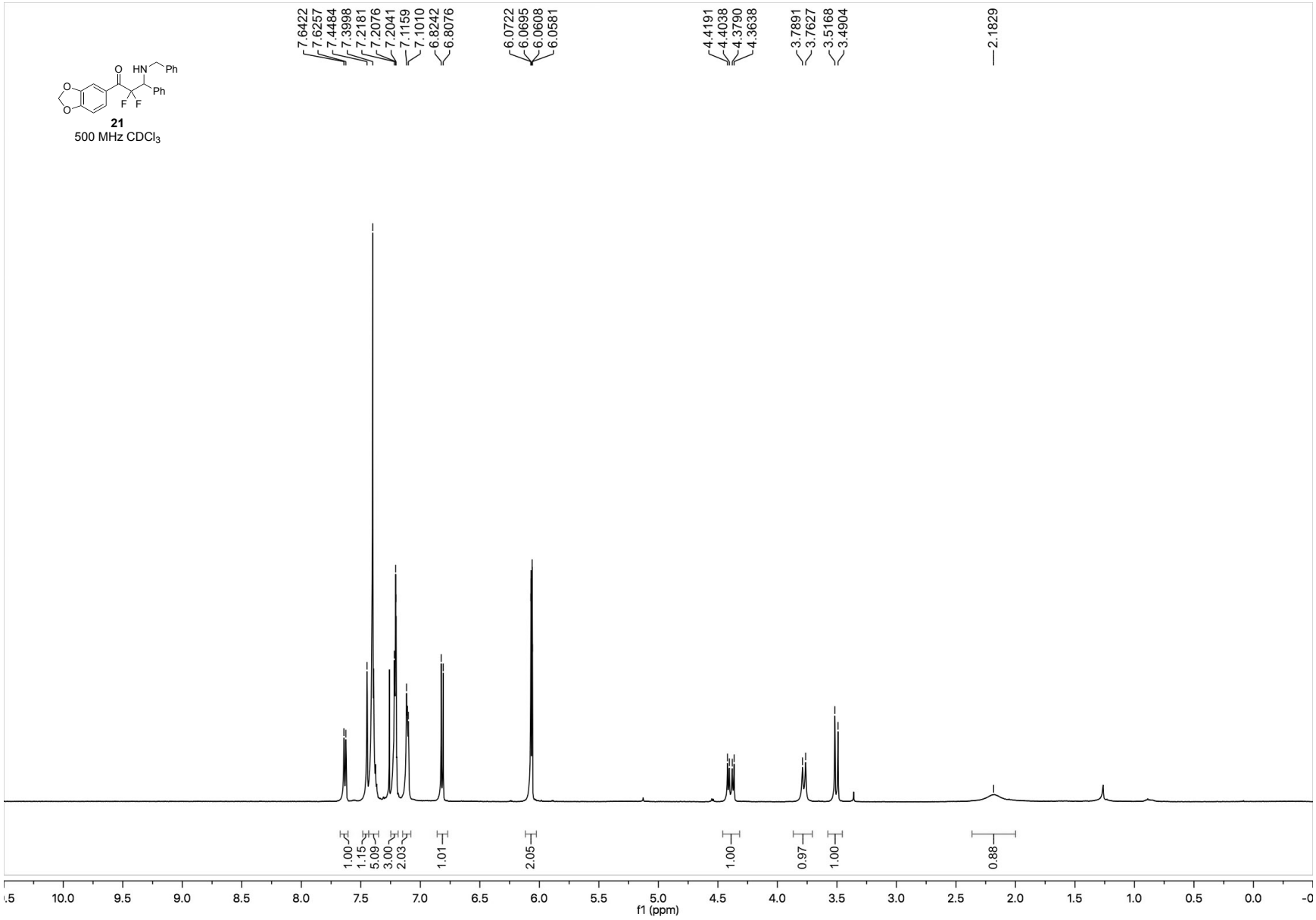
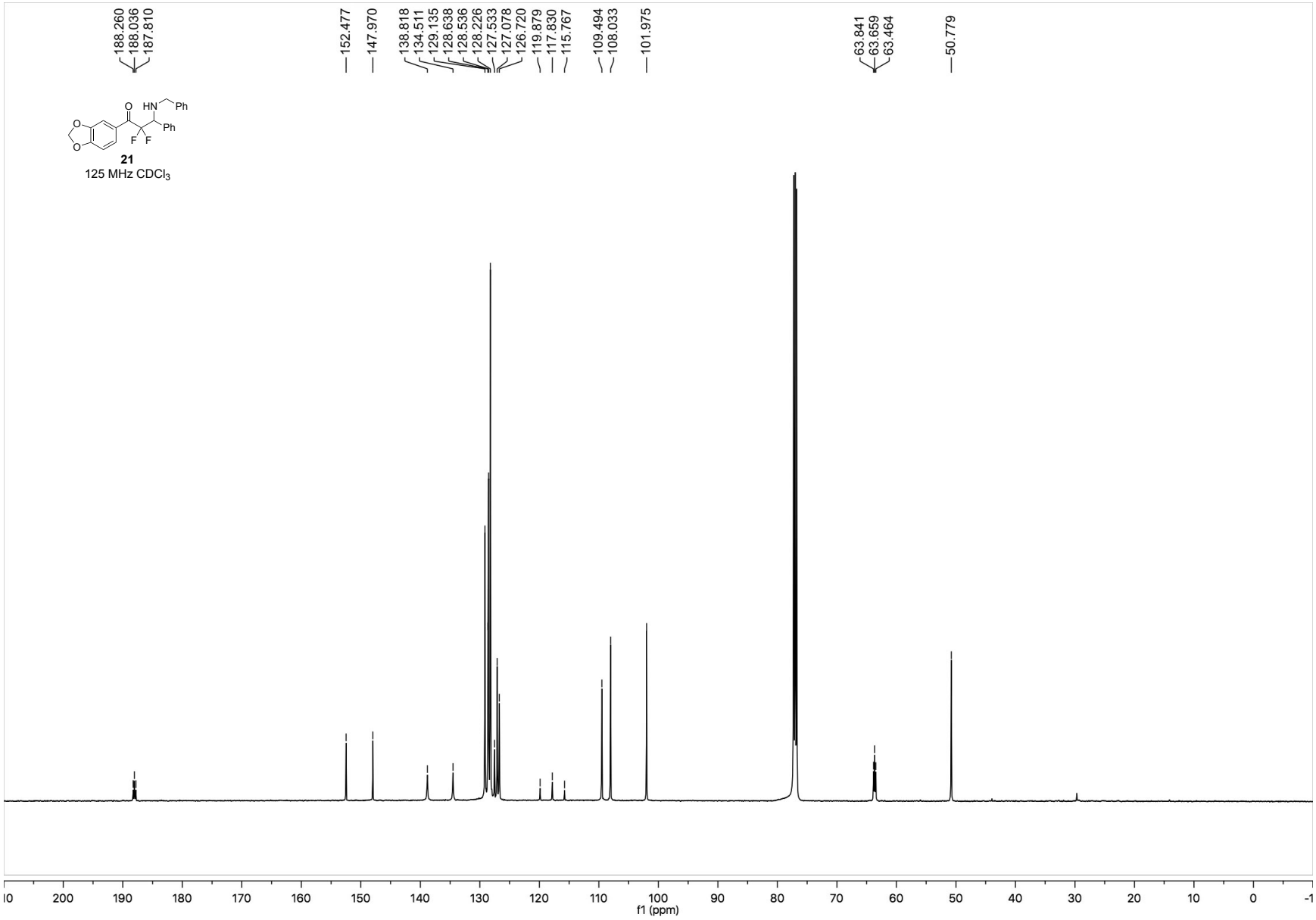
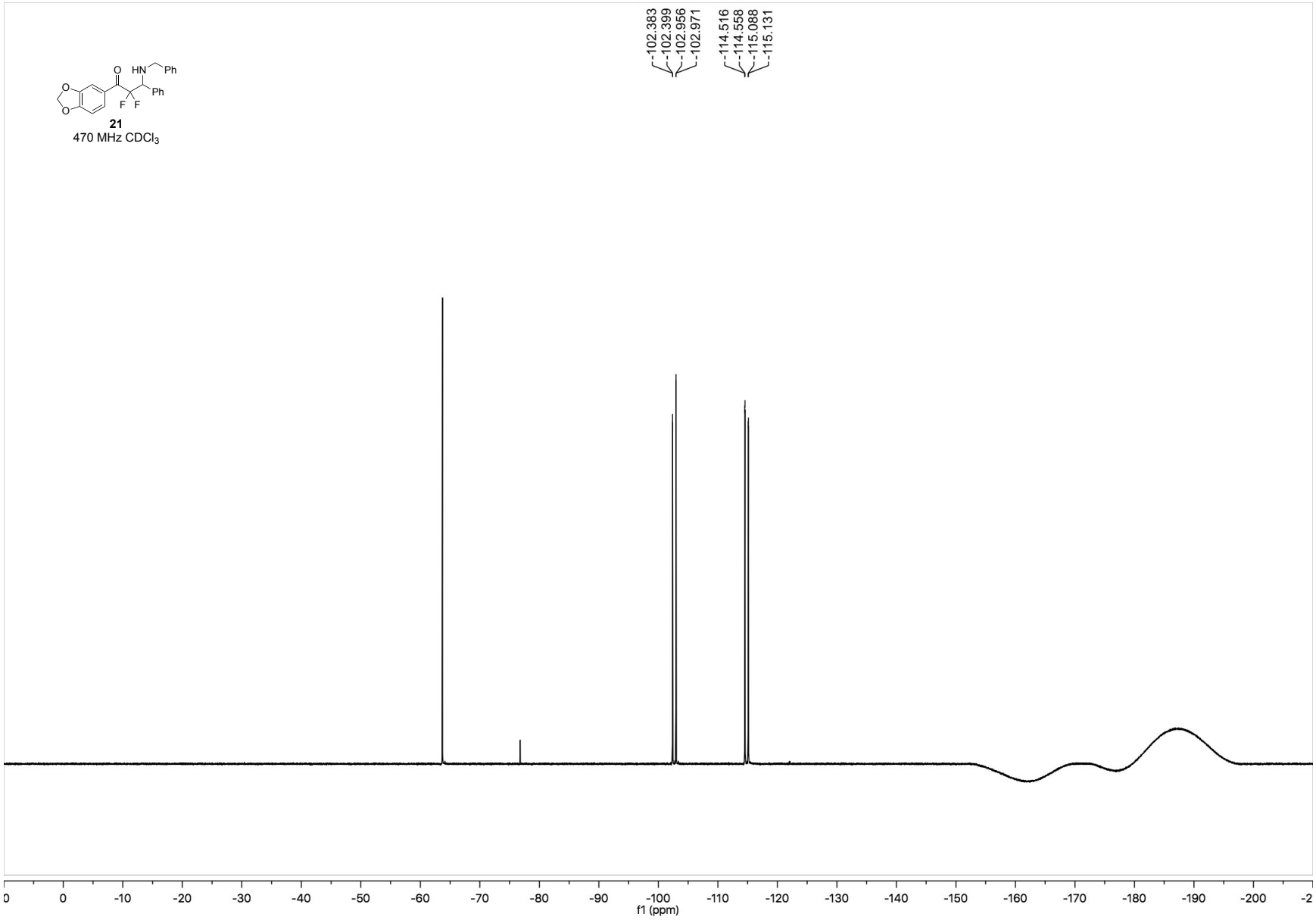
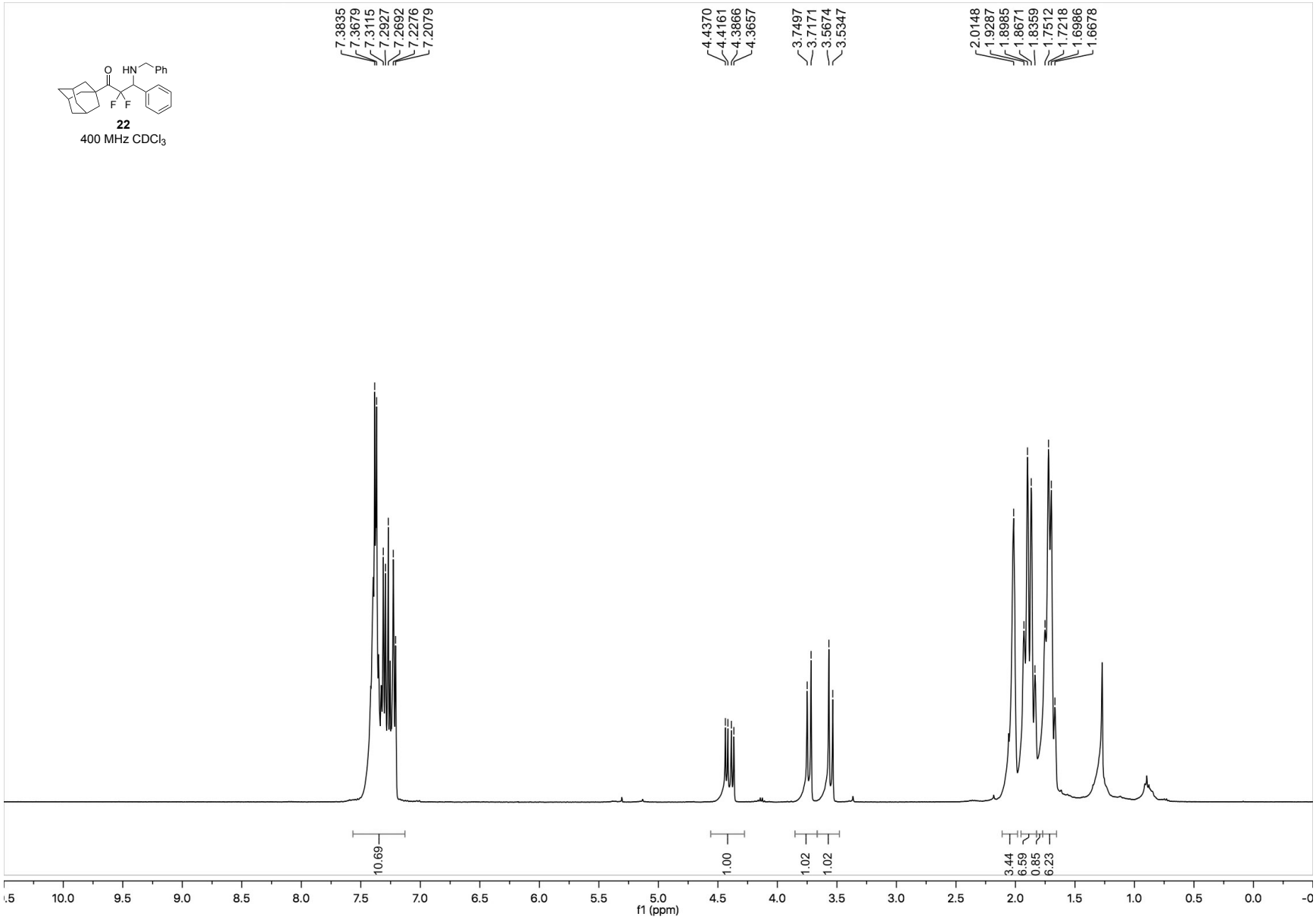
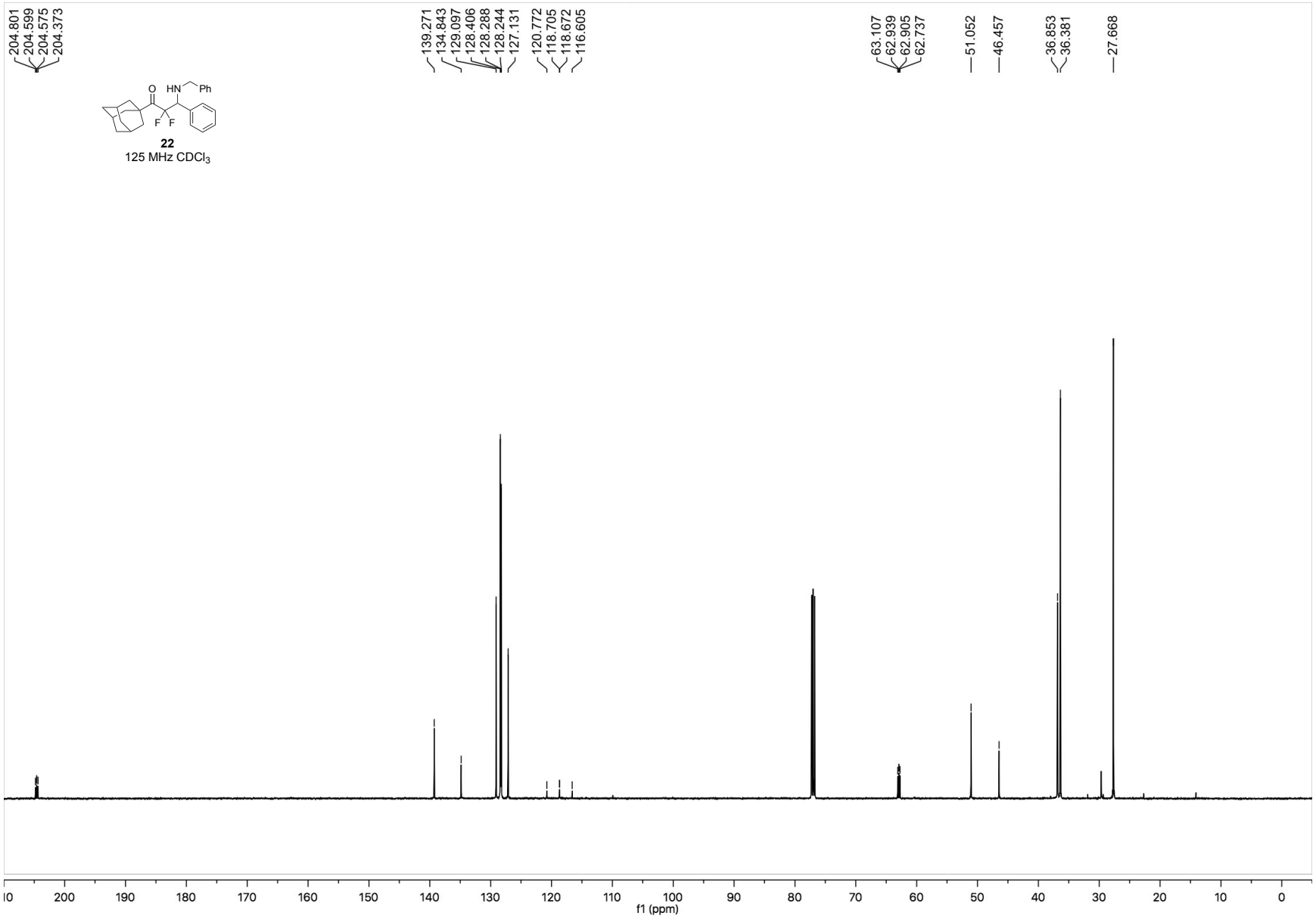
376 MHz CDCl3
f1 (ppm)

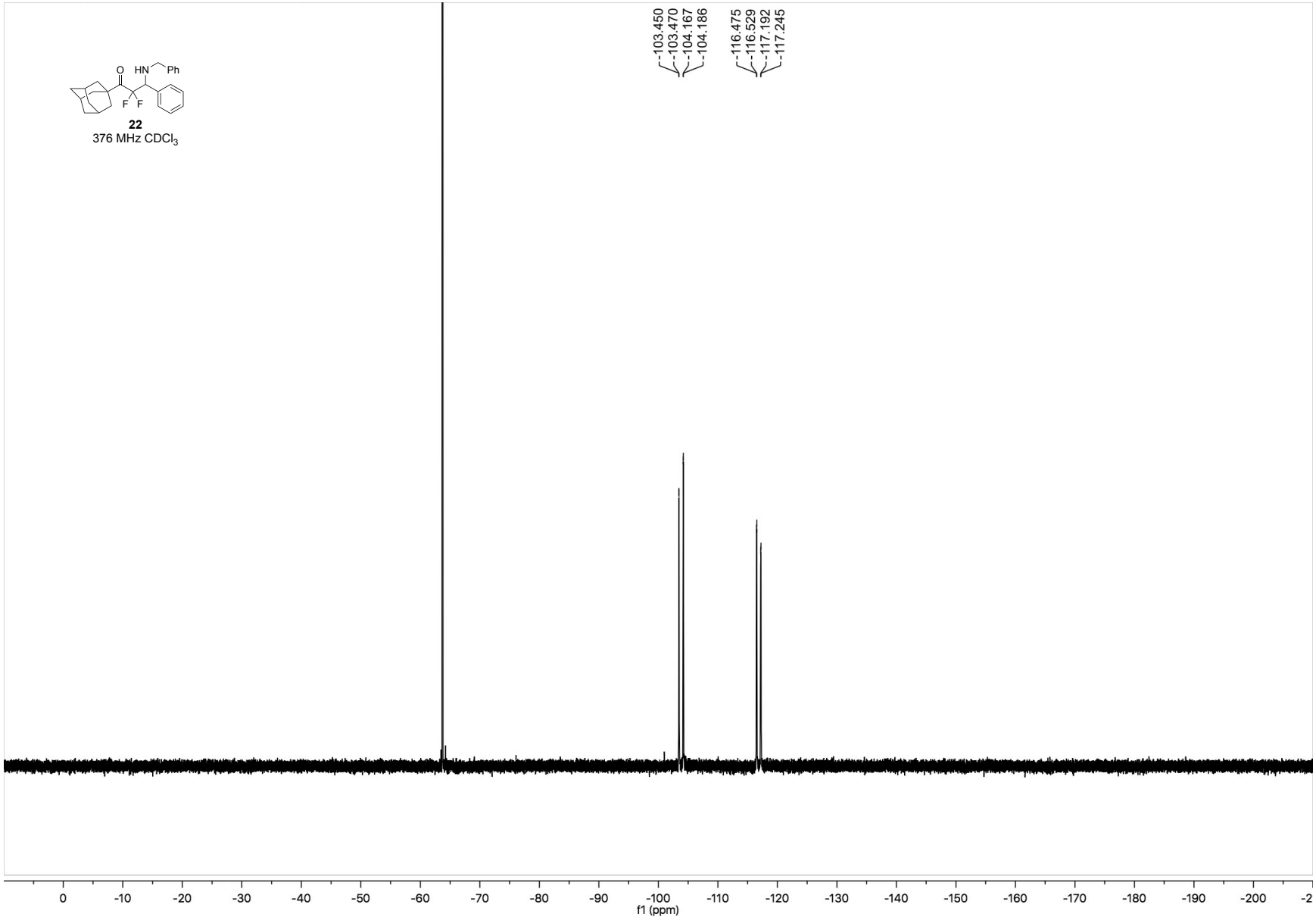

7.6422
7.6257
7.4484
7.3998
7.2181
7.2076
7.2041
7.1159
7.1010
6.8242
6.8076
6.0722
6.0695
6.0608
6.0581
4.4191
4.4038
4.3790
4.3638
3.7891
3.7627
3.5168
3.4904
2.1829
O
HN
Ph
Ph
F F
O
O
21
500 MHz CDCl3
1.00
1.15
5.09
3.00
2.03
1.01
2.05
1.00
0.97
1.00
0.88
f1 (ppm)

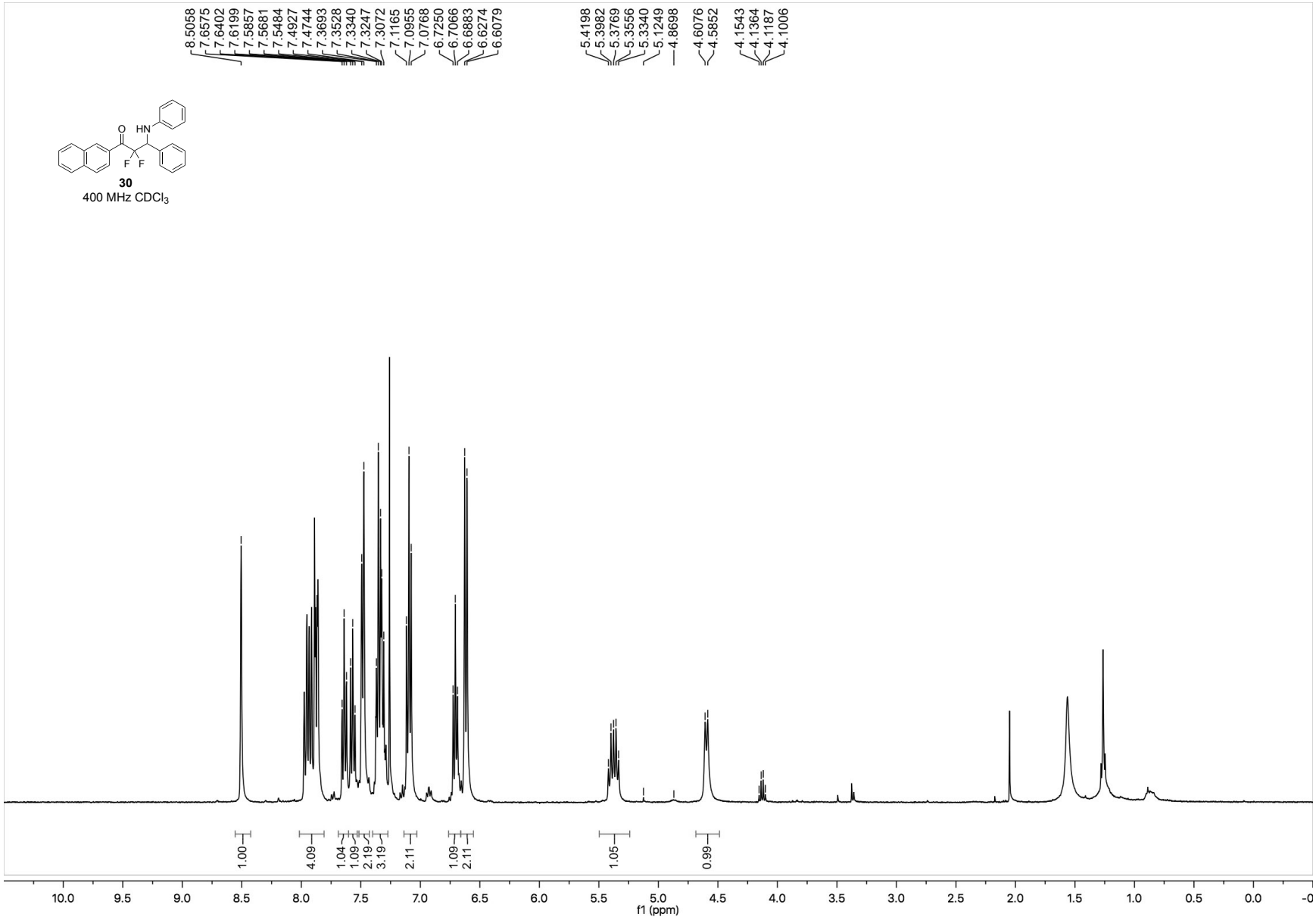

188.260
188.036
187.810
152.477
147.970
138.818
134.511
129.135
128.638
128.536
128.226
127.533
127.078
126.720
119.879
117.830
115.767
109.494
108.033
101.975
63.841
63.659
63.464
50.779
O
HN
Ph
Ph
O
O
F
F
21
125 MHz CDCl3
f1 (ppm)

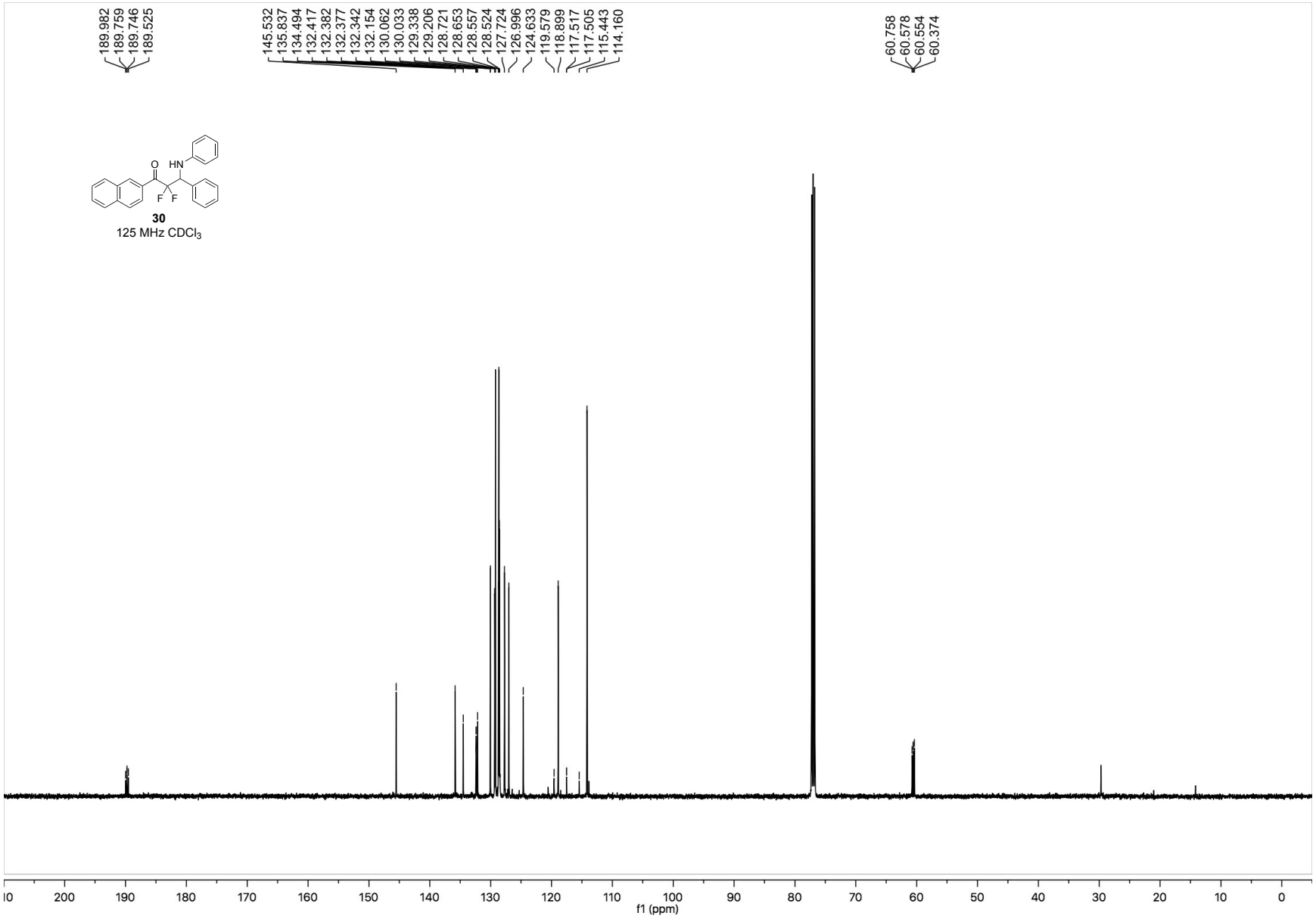

-102.383
-102.399
-102.956
-102.971
-114.516
-114.558
-115.088
-115.131
O
HN
Ph
Ph
F F
O
O
21
470 MHz CDCl3
0
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-2
f1 (ppm)

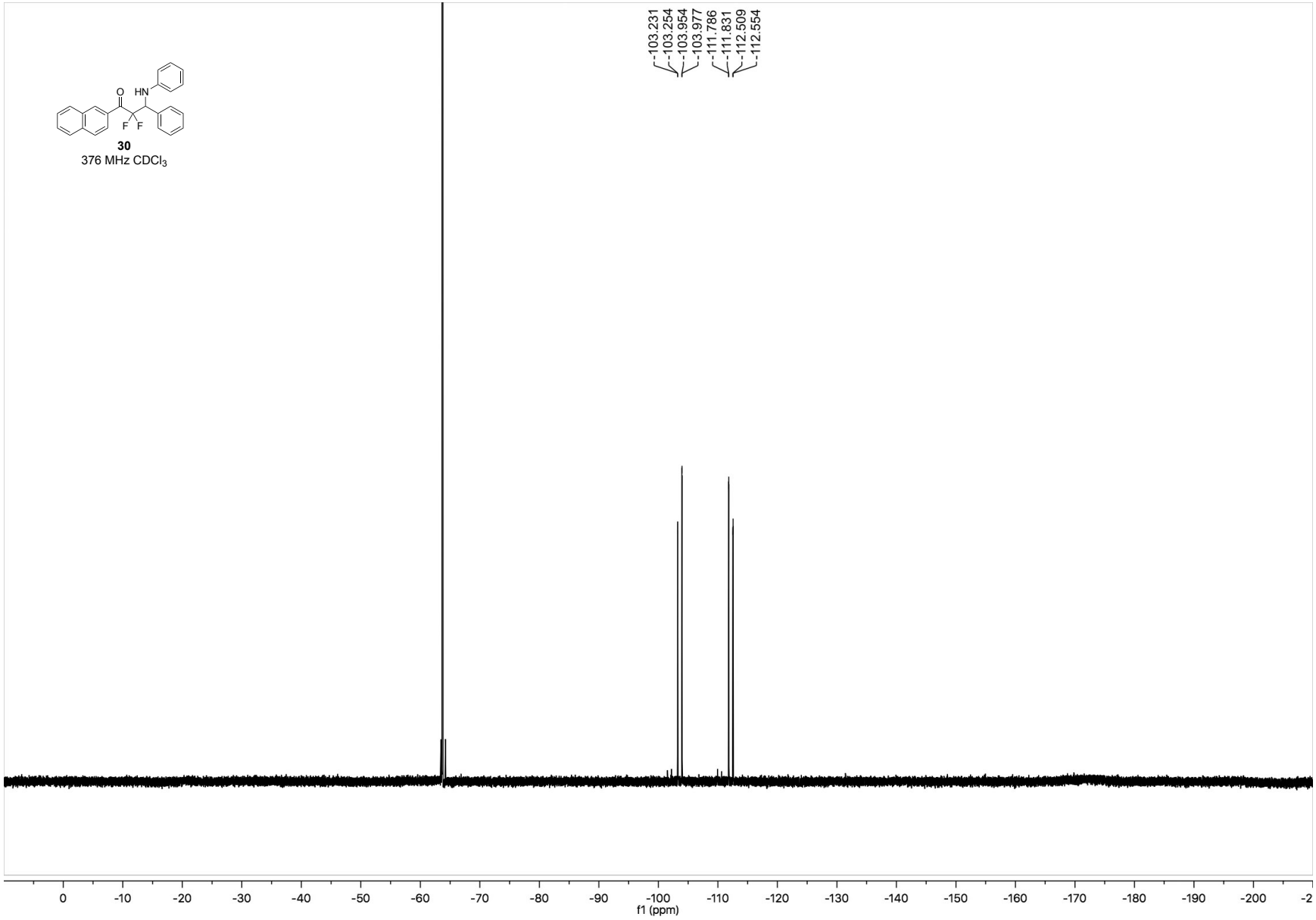

7.3835
7.3679
7.3115
7.2927
7.2692
7.2276
7.2079
4.4370
4.4161
4.3866
4.3657
3.7497
3.7171
3.5674
3.5347
2.0148
1.9287
1.8985
1.8671
1.8359
1.7512
1.7218
1.6986
1.6678
O
HN
Ph
F F
22
400 MHz CDCl3
10.69
1.00
1.02
1.02
3.44
6.59
0.85
6.23
f1 (ppm)

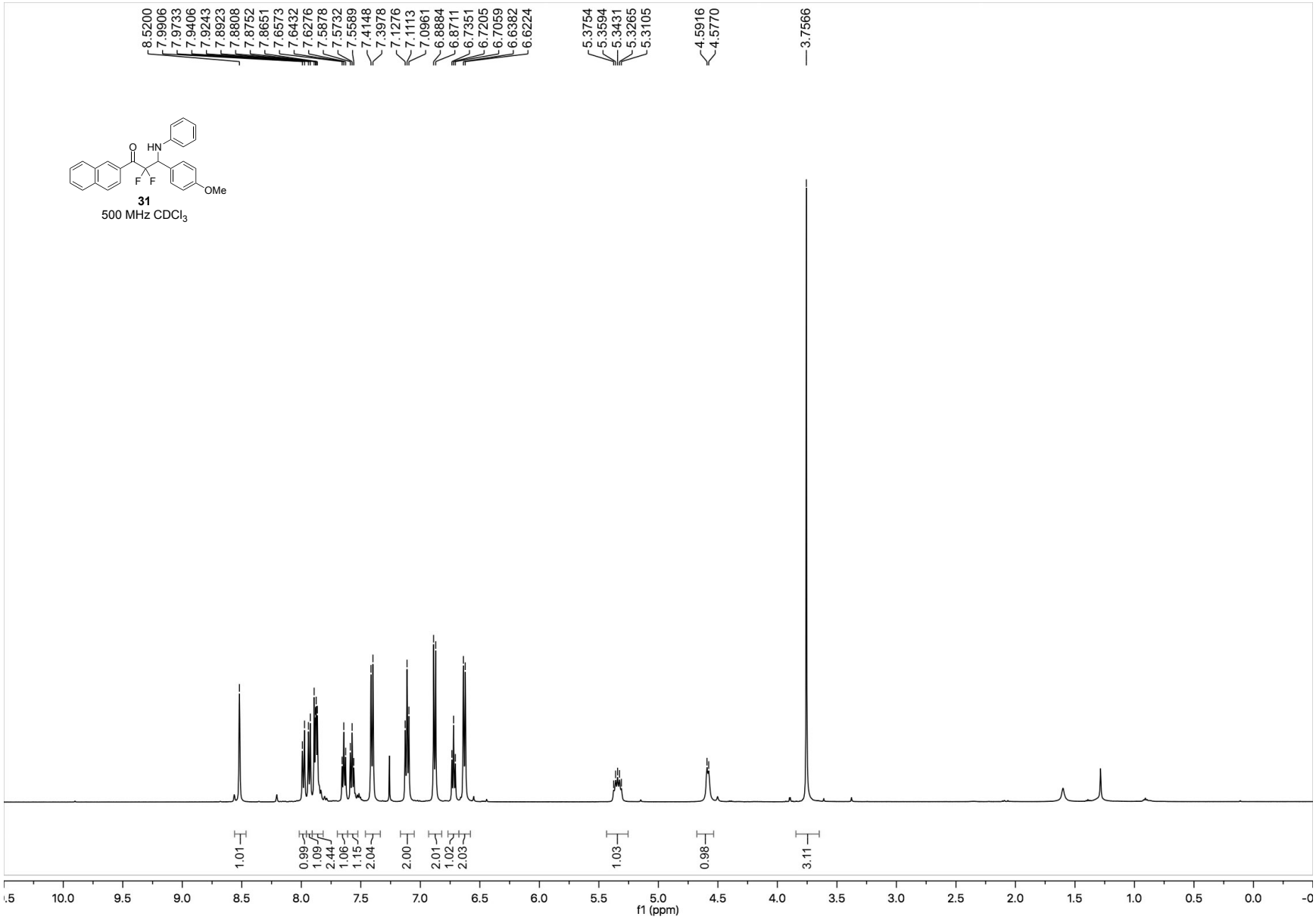

204.801
204.599
204.575
204.373
139.271
134.843
129.097
128.406
128.288
128.244
127.131
120.772
118.705
118.672
116.605
63.107
62.939
62.905
62.737
51.052
46.457
36.853
36.381
27.668
O
HN
Ph
F F
22
125 MHz CDCl3
f1 (ppm)

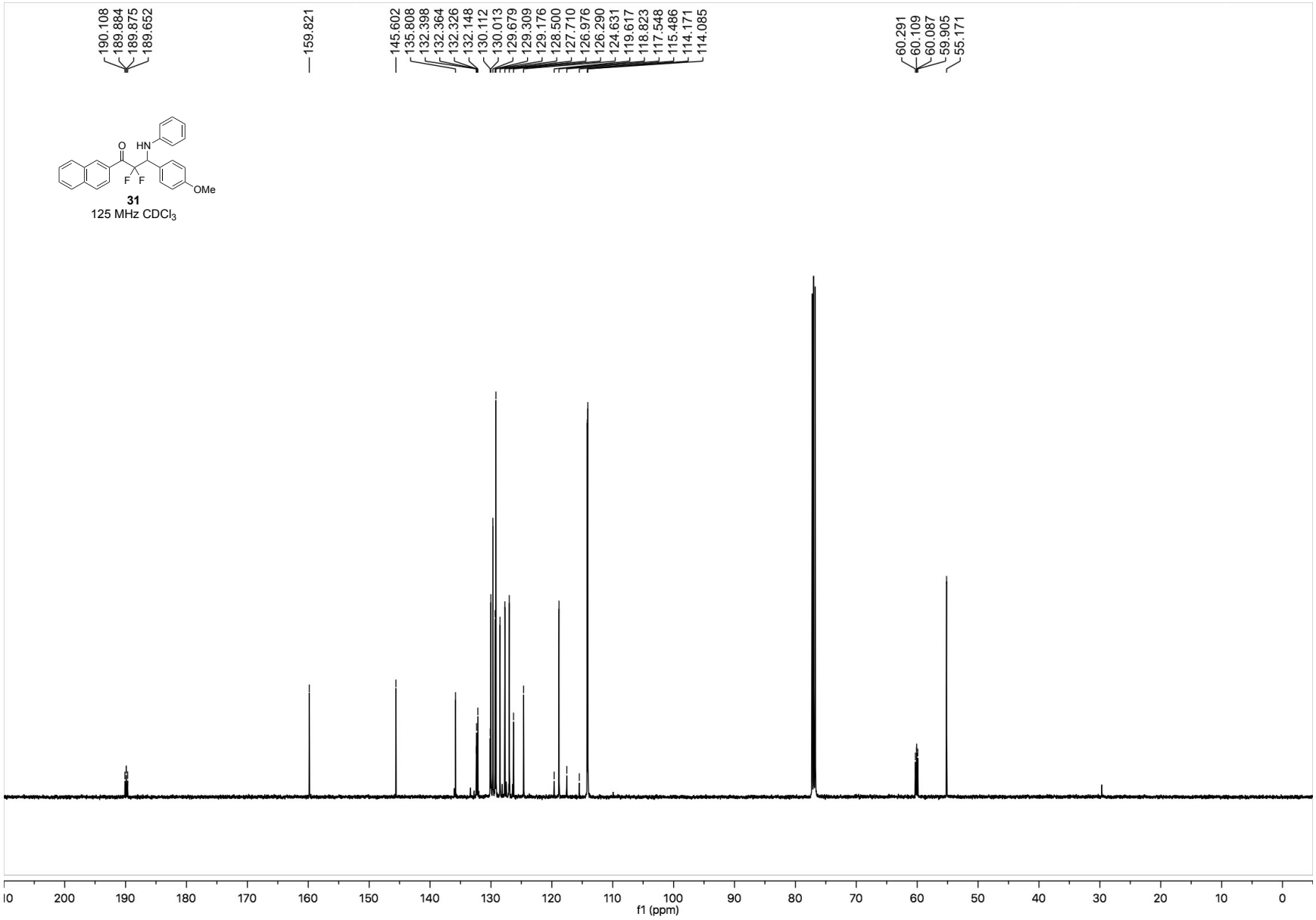

O
HN
Ph
F F
22
376 MHz CDCl3
-103.450
-103.470
-104.167
-104.186
-116.475
-116.529
-117.192
-117.245
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-2
f1 (ppm)

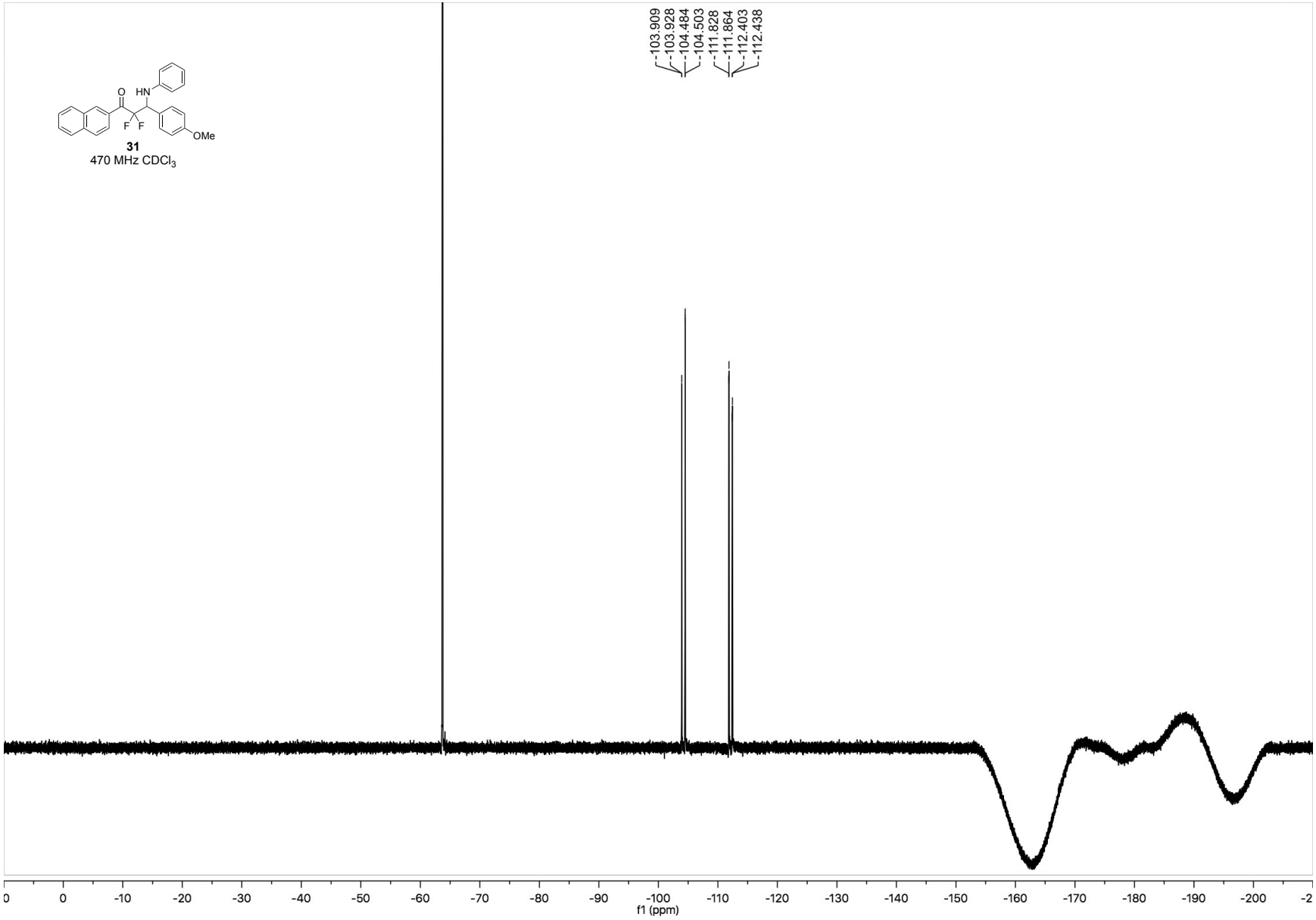

8.5058
7.6575
7.6402
7.6199
7.5857
7.5681
7.5484
7.4927
7.4744
7.3693
7.3528
7.3340
7.3247
7.3072
7.1165
7.0955
7.0768
6.7250
6.7066
6.6883
6.6274
6.6079
5.4198
5.3982
5.3769
5.3556
5.3340
5.1249
4.8698
4.6076
4.5852
4.1543
4.1364
4.1187
4.1006
O
HN
F F
30
400 MHz CDCl3
1.00
4.09
1.04
1.09
2.19
3.19
2.11
1.09
2.11
1.05
0.99
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)

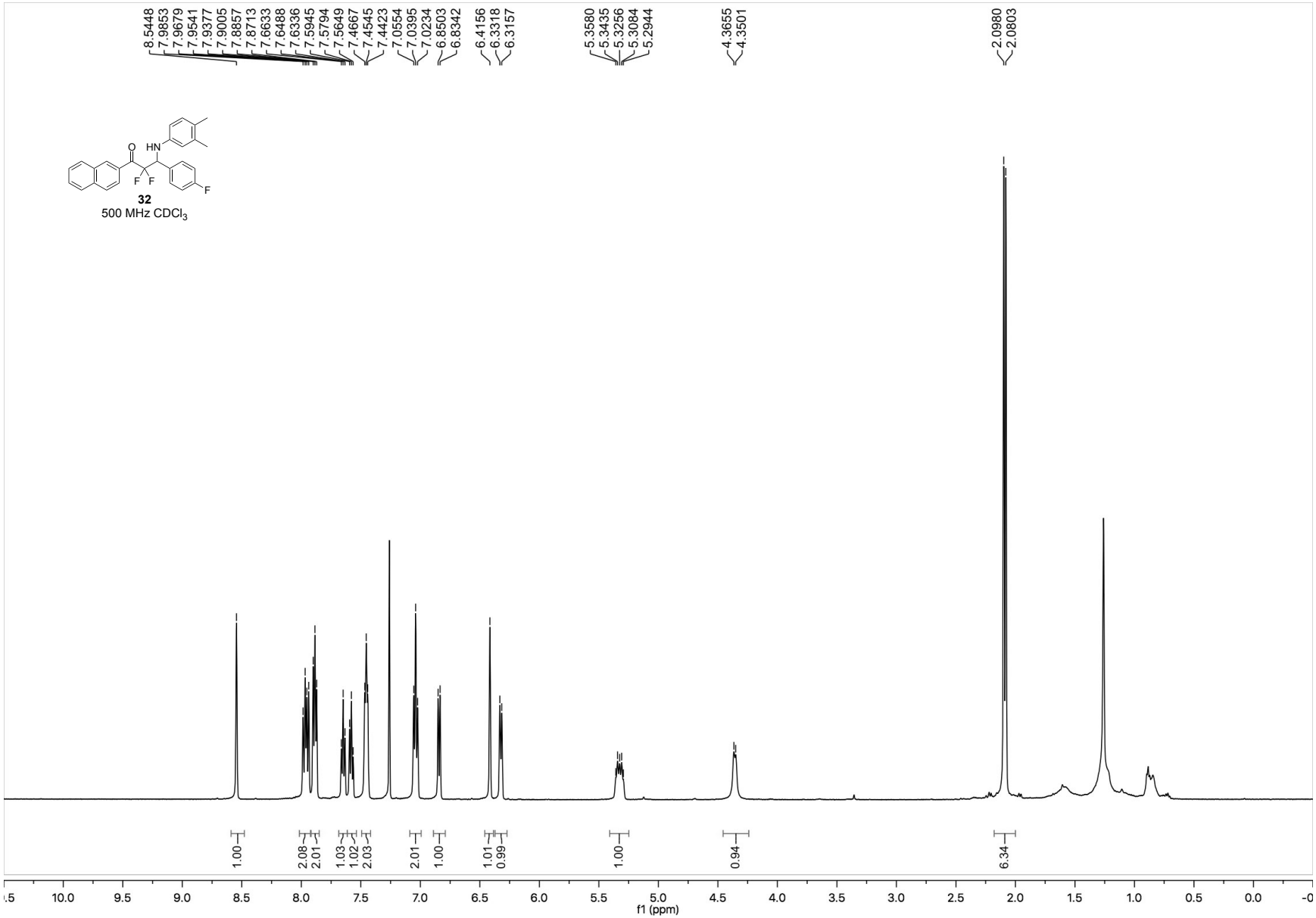

189.982
189.759
189.746
189.525
145.532
135.837
134.494
132.417
132.382
132.377
132.342
132.154
130.062
130.033
129.338
129.206
128.721
128.653
128.557
128.524
127.724
126.996
124.633
119.579
118.899
117.517
117.505
115.443
114.160
60.758
60.578
60.554
60.374
O
HN
F F
30
125 MHz CDCl3
f1 (ppm)

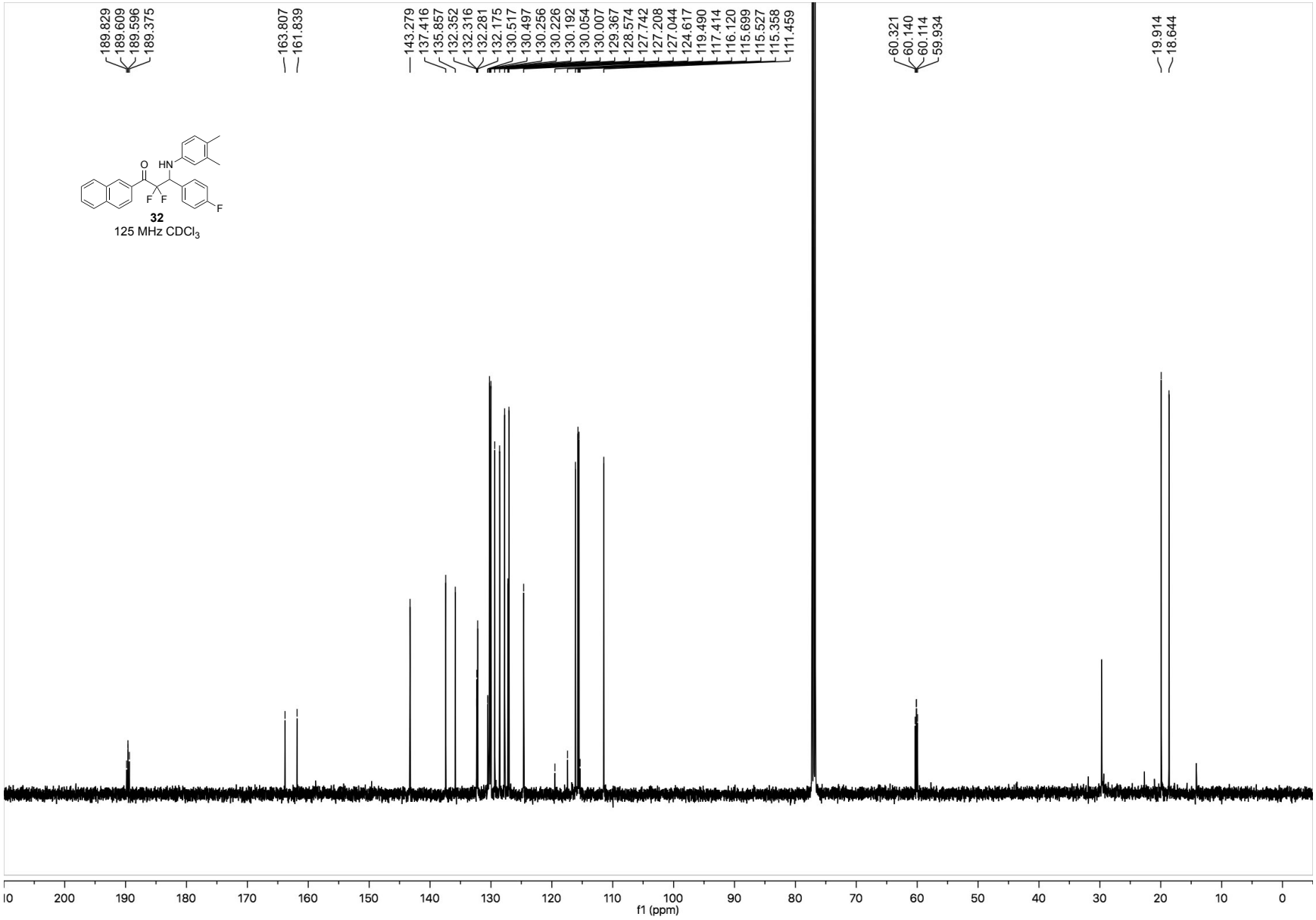

-103.231
-103.254
-103.954
-103.977
-111.786
-111.831
-112.509
-112.554
O
HN
F F
30
376 MHz CDCl3
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

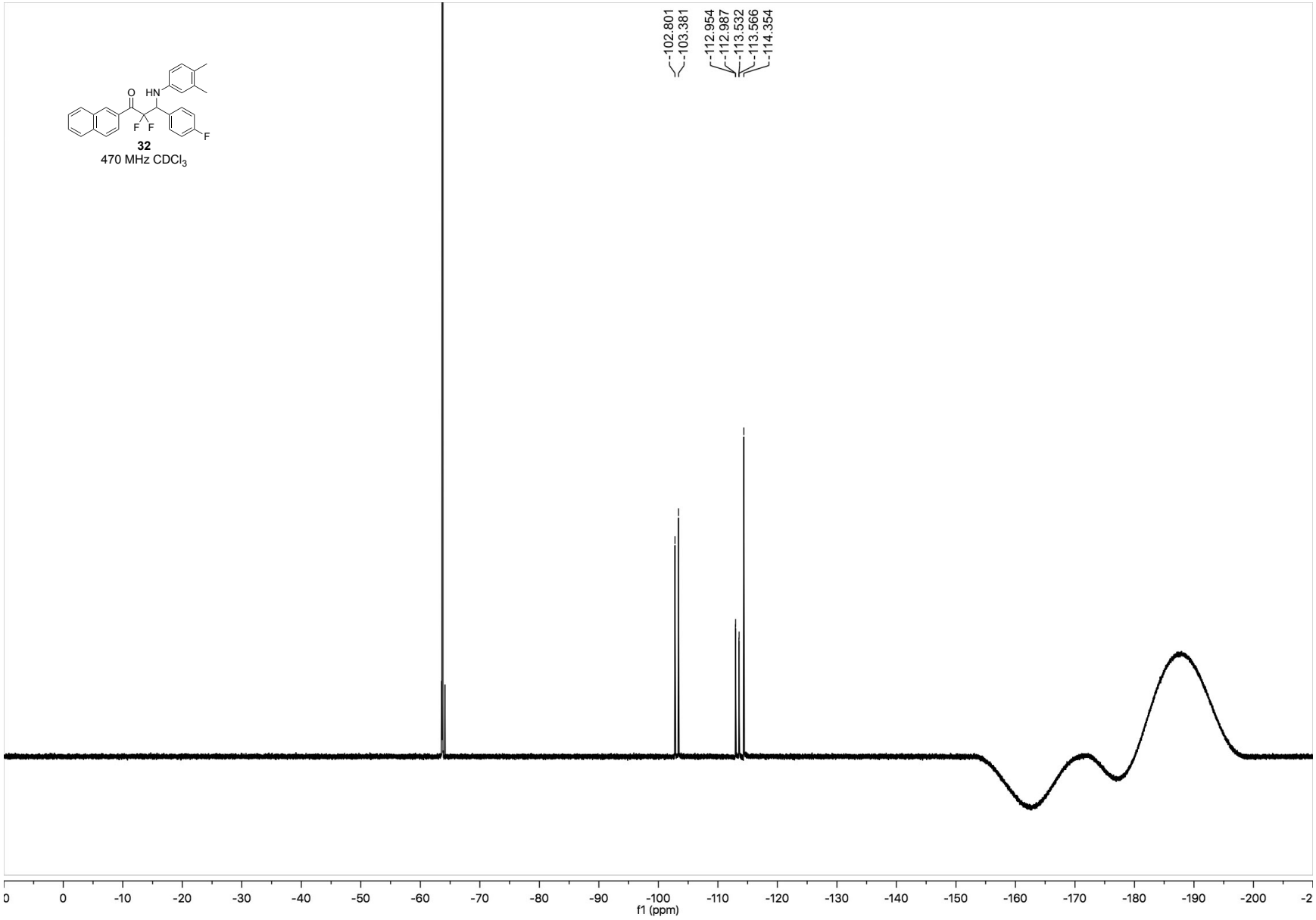

8.5200
7.9906
7.9733
7.9406
7.9243
7.8923
7.8808
7.8752
7.8651
7.6573
7.6432
7.6276
7.5878
7.5732
7.5589
7.4148
7.3978
7.1276
7.1113
7.0961
6.8884
6.8711
6.7351
6.7205
6.7059
6.6382
6.6224
5.3754
5.3594
5.3431
5.3265
5.3105
4.5916
4.5770
3.7566
O
HN
F F
OMe
31
500 MHz CDCl3
1.01
0.99
1.09
2.44
1.06
1.15
2.04
2.00
2.01
1.02
2.03
1.03
0.98
3.11
f1 (ppm)

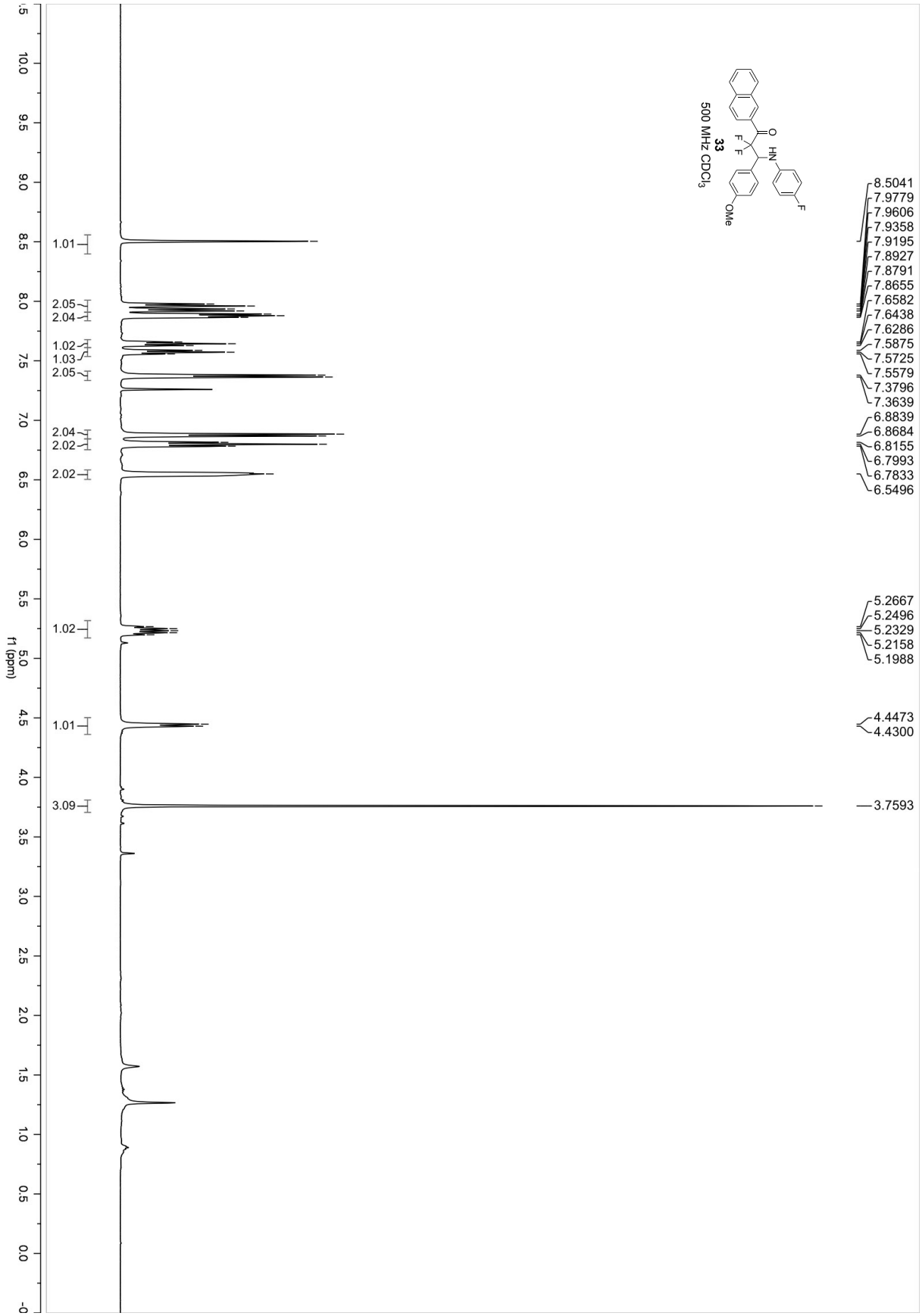

190.108
189.884
189.875
189.652
159.821
145.602
135.808
132.398
132.364
132.326
132.148
130.112
130.013
129.679
129.309
129.176
128.500
127.710
126.976
126.290
124.631
119.617
118.823
117.548
115.486
114.171
114.085
60.291
60.109
60.087
59.905
55.171
O
HN
F F
OMe
31
125 MHz CDCl3
f1 (ppm)

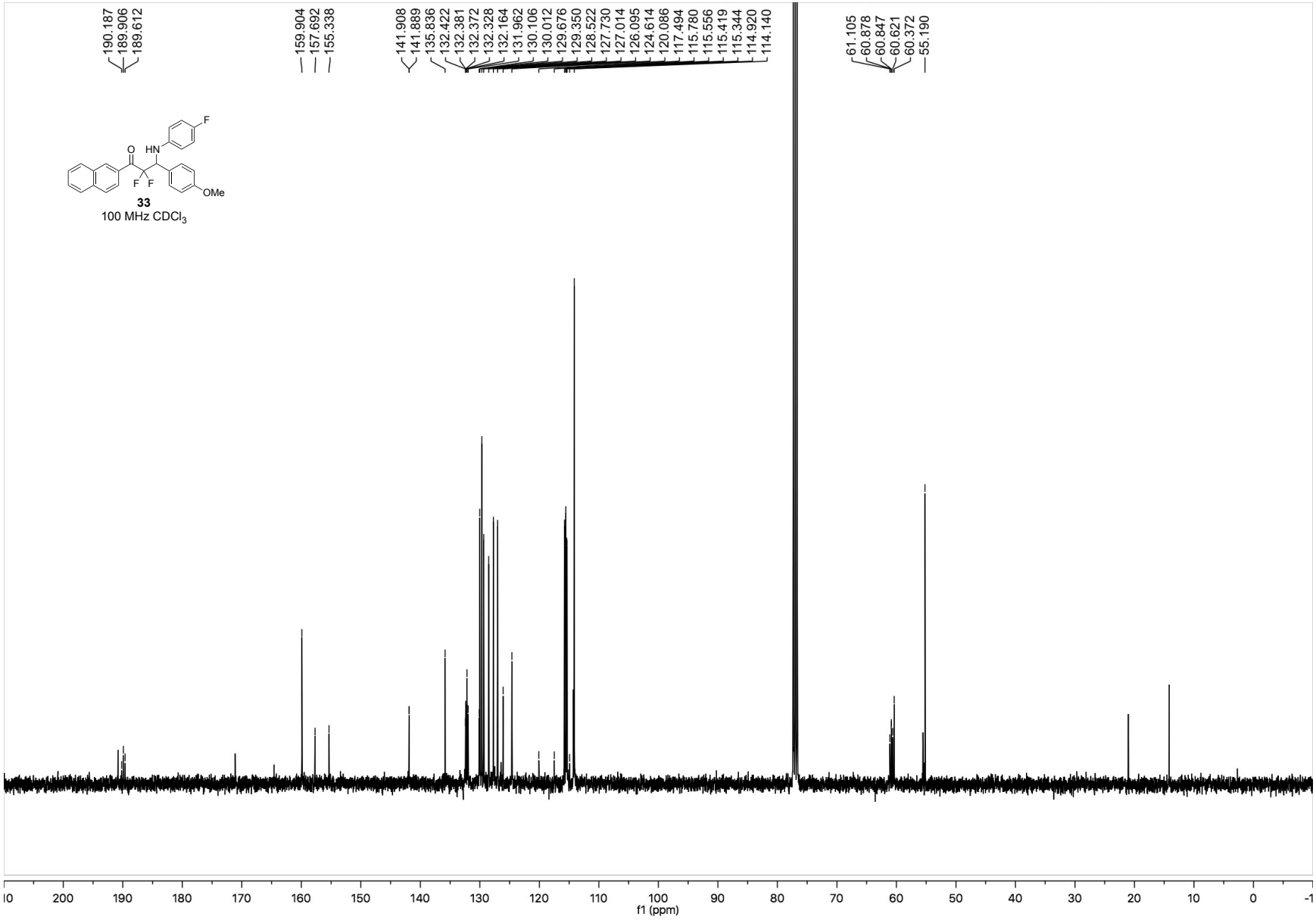

-103.909
-103.928
-104.484
-104.503
-111.828
-111.864
-112.403
-112.438
O
HN
F F
OMe
31
470 MHz CDCl3
0
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-2
f1 (ppm)

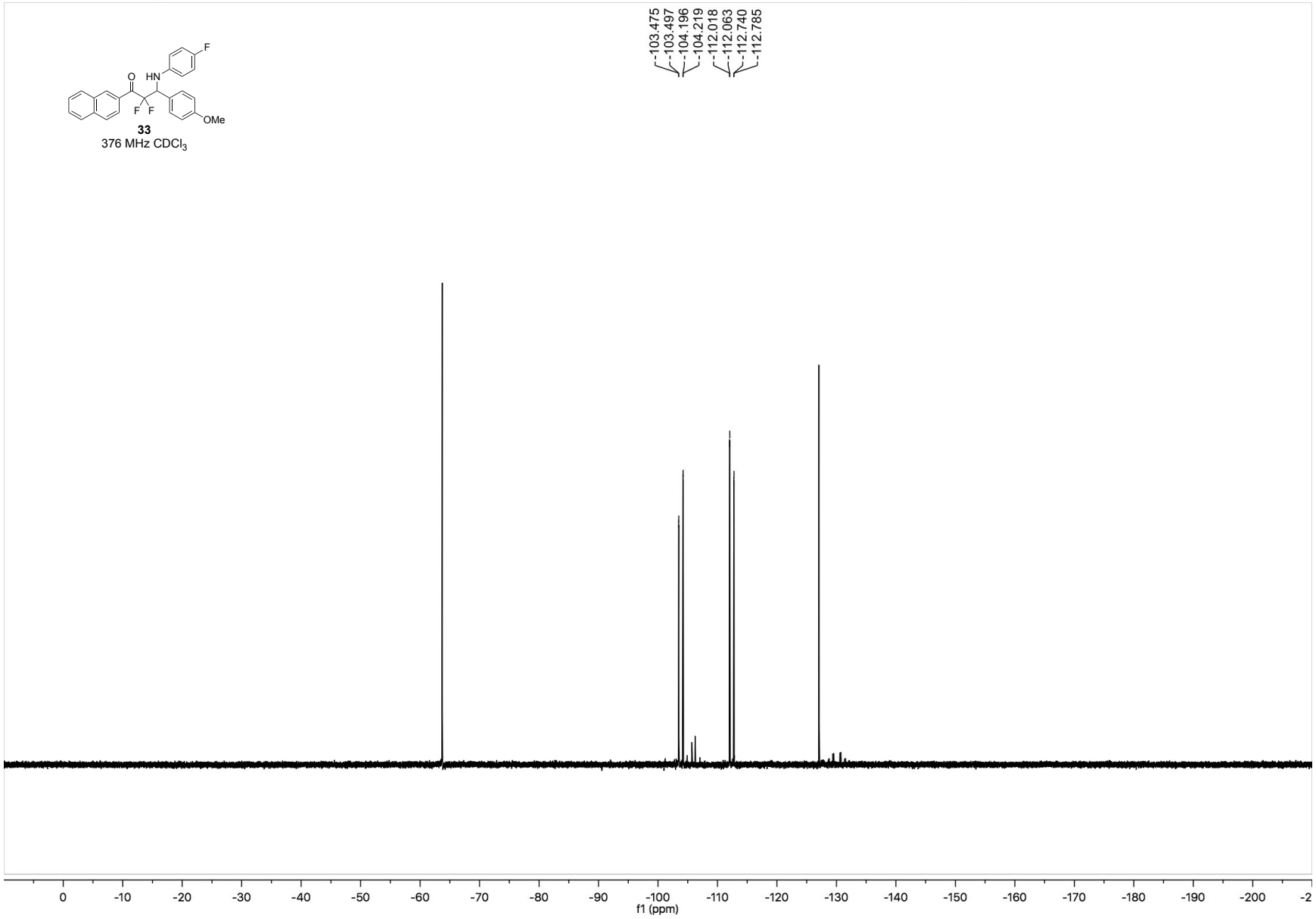

8.5448
7.9853
7.9679
7.9541
7.9377
7.9005
7.8857
7.8713
7.6633
7.6488
7.6336
7.5945
7.5794
7.5649
7.4667
7.4545
7.4423
7.0554
7.0395
7.0234
6.8503
6.8342
6.4156
6.3318
6.3157
5.3580
5.3435
5.3256
5.3084
5.2944
4.3655
4.3501
2.0980
2.0803
O
HN
F F
F
32
500 MHz CDCl3
1.00
2.08
2.01
1.03
1.02
2.03
2.01
1.00
1.01
0.99
1.00
0.94
6.34
f1 (ppm)

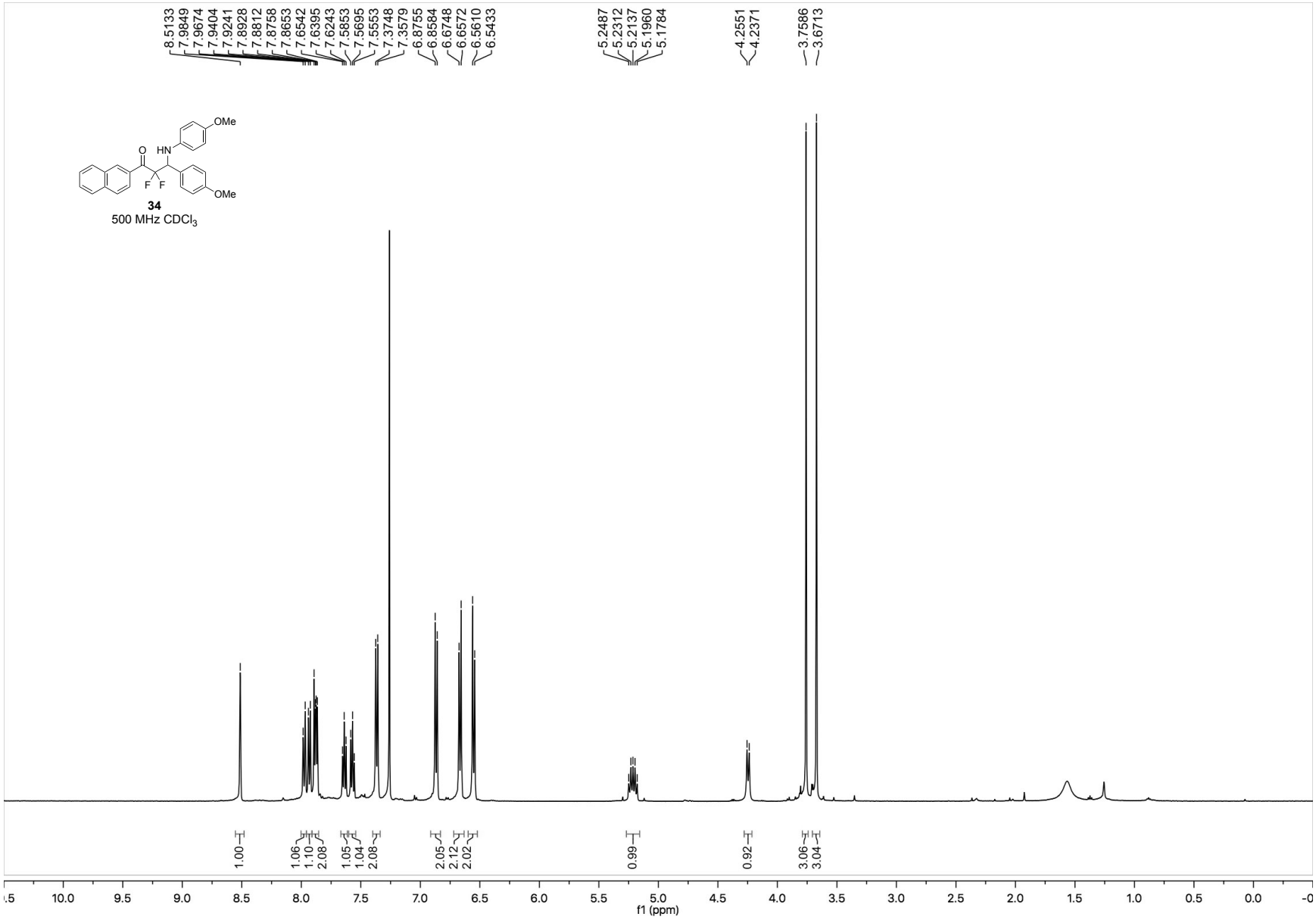

189.829
189.609
189.596
189.375
163.807
161.839
143.279
137.416
135.857
132.352
132.316
132.281
132.175
130.517
130.497
130.256
130.226
130.192
130.054
130.007
129.367
128.574
127.742
127.208
127.044
124.617
119.490
117.414
116.120
115.699
115.527
115.358
111.459
60.321
60.140
60.114
59.934
19.914
18.644
O
HN
F F
F
32
125 MHz CDCl3
f1 (ppm)

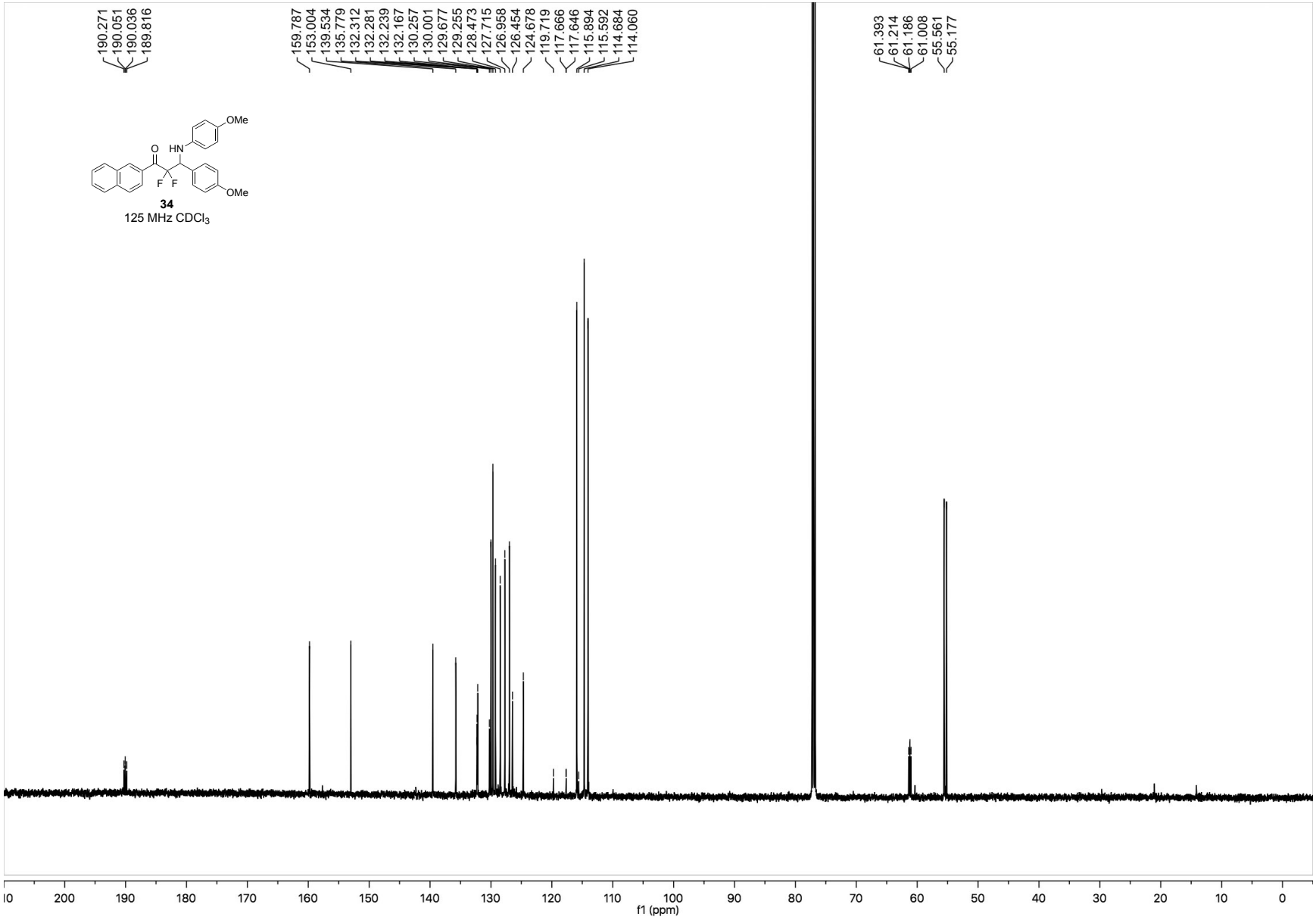

-102.801
-103.381
-112.954
-112.987
-113.532
-113.566
-114.354
O
HN
F
F
F
32
470 MHz CDCl3
0
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-2
f1 (ppm)

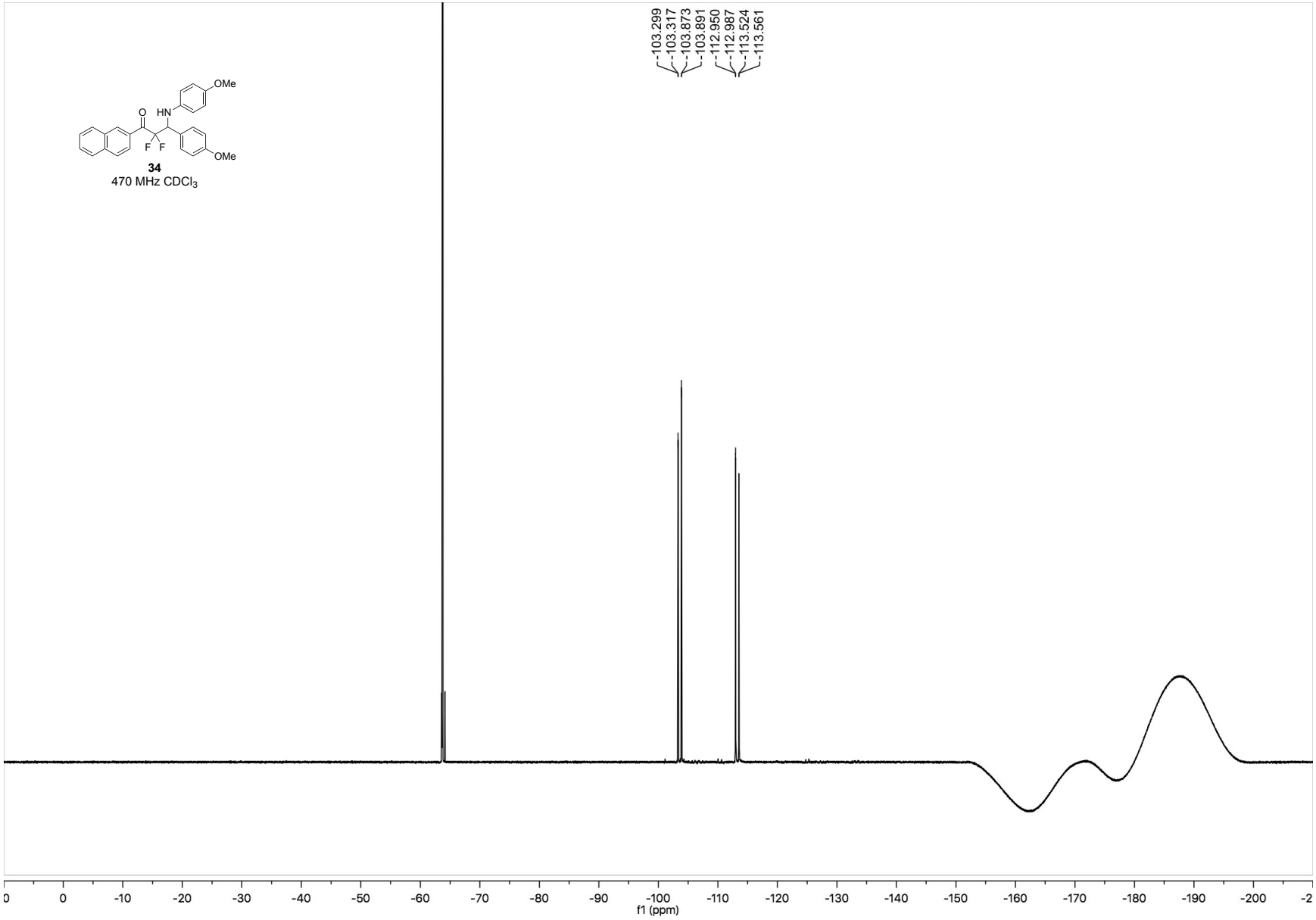

33
500 MHz CDCl3
F
F
O
HN
OMe
F
8.5041
7.9779
7.9606
7.9358
7.9195
7.8927
7.8791
7.8655
7.6582
7.6438
7.6286
7.5875
7.5725
7.5579
7.3796
7.3639
6.8839
6.8684
6.8155
6.7993
6.7833
6.5496
5.2667
5.2496
5.2329
5.2158
5.1988
4.4473
4.4300
3.7593
1.01
2.05
2.04
1.02
1.03
2.05
2.04
2.02
2.02
1.02
1.01
3.09
f1 (ppm)

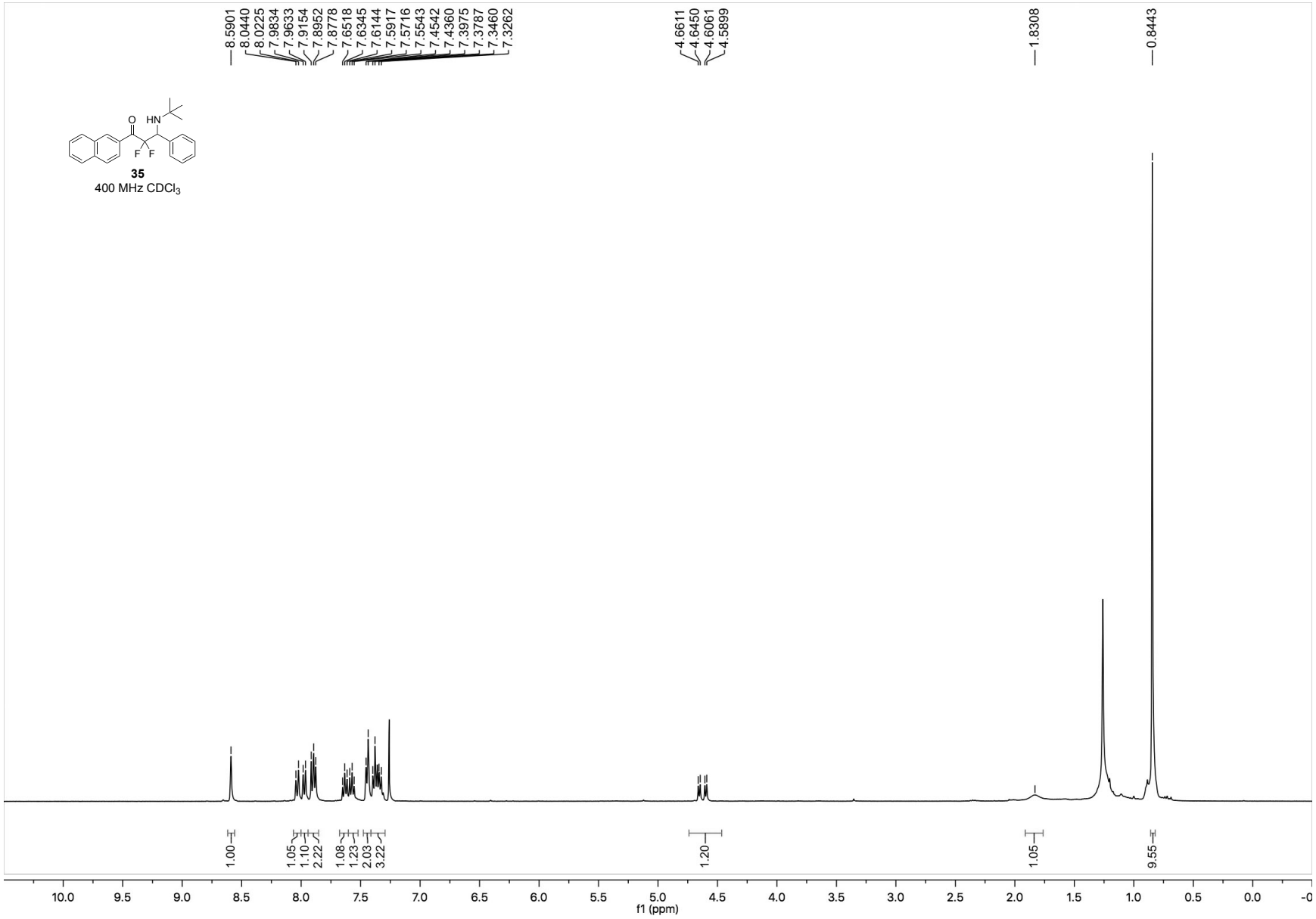

190.187
189.906
189.612
159.904
157.692
155.338
141.908
141.889
135.836
132.422
132.381
132.372
132.328
132.164
131.962
130.106
130.012
129.676
129.350
128.522
127.730
127.014
126.095
124.614
120.086
117.494
115.780
115.556
115.419
115.344
114.920
114.140
61.105
60.878
60.847
60.621
60.372
55.190
F
O
HN
F F
OMe
33
100 MHz CDCl3
f1 (ppm)

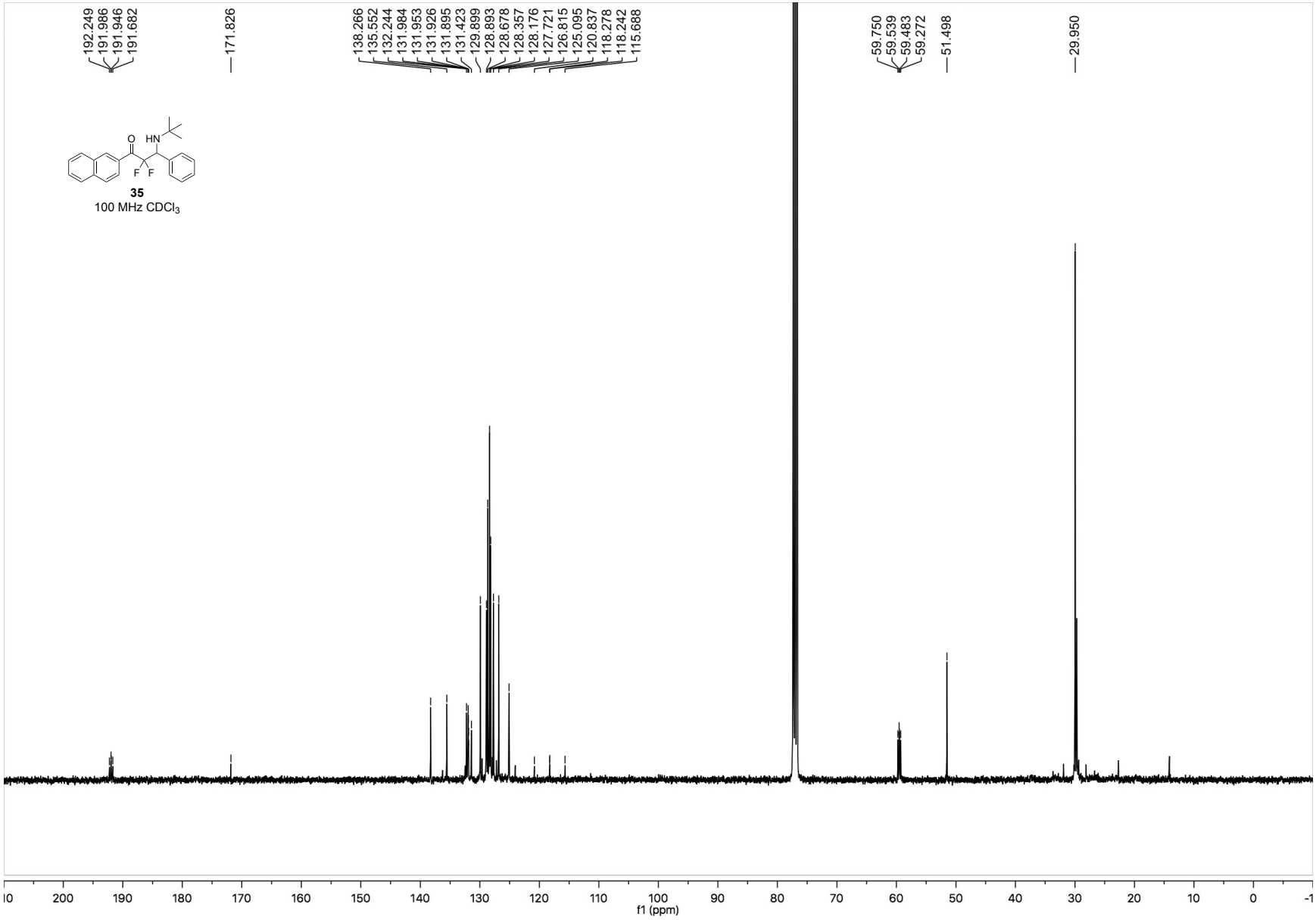

-103.475
-103.497
-104.196
-104.219
-112.018
-112.063
-112.740
-112.785
F
O
HN
F
F
OMe
33
376 MHz CDCl3
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-2
f1 (ppm)

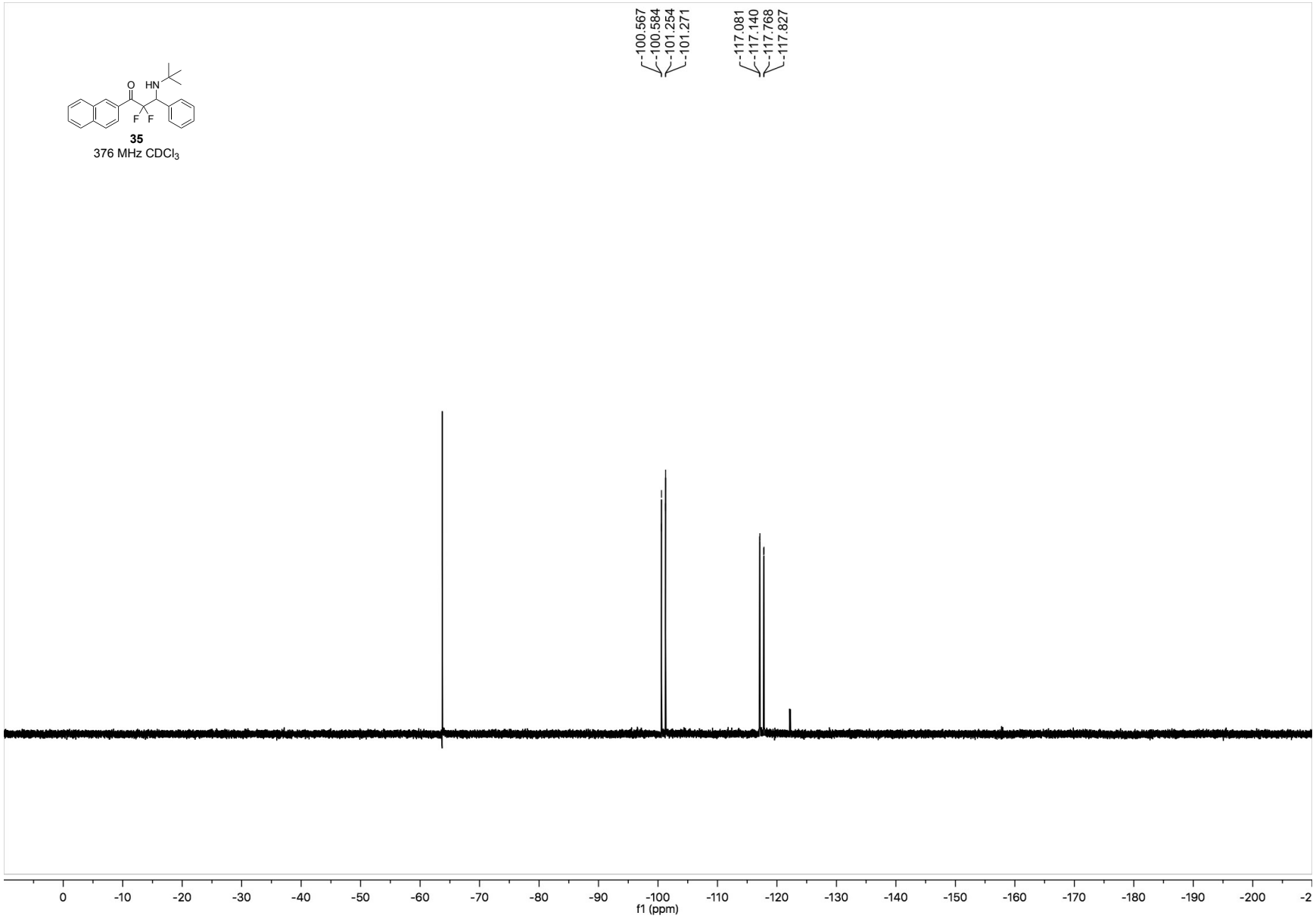

8.5133
7.9849
7.9674
7.9404
7.9241
7.8928
7.8812
7.8758
7.8653
7.6542
7.6395
7.6243
7.5853
7.5695
7.5553
7.3748
7.3579
6.8755
6.8584
6.6748
6.6572
6.5610
6.5433
5.2487
5.2312
5.2137
5.1960
5.1784
4.2551
4.2371
3.7586
3.6713
OMe
HN
O
F F
OMe
34
500 MHz CDCl3
1.00
1.06
1.10
2.08
1.05
1.04
2.08
2.05
2.12
2.02
0.99
0.92
3.06
3.04
f1 (ppm)

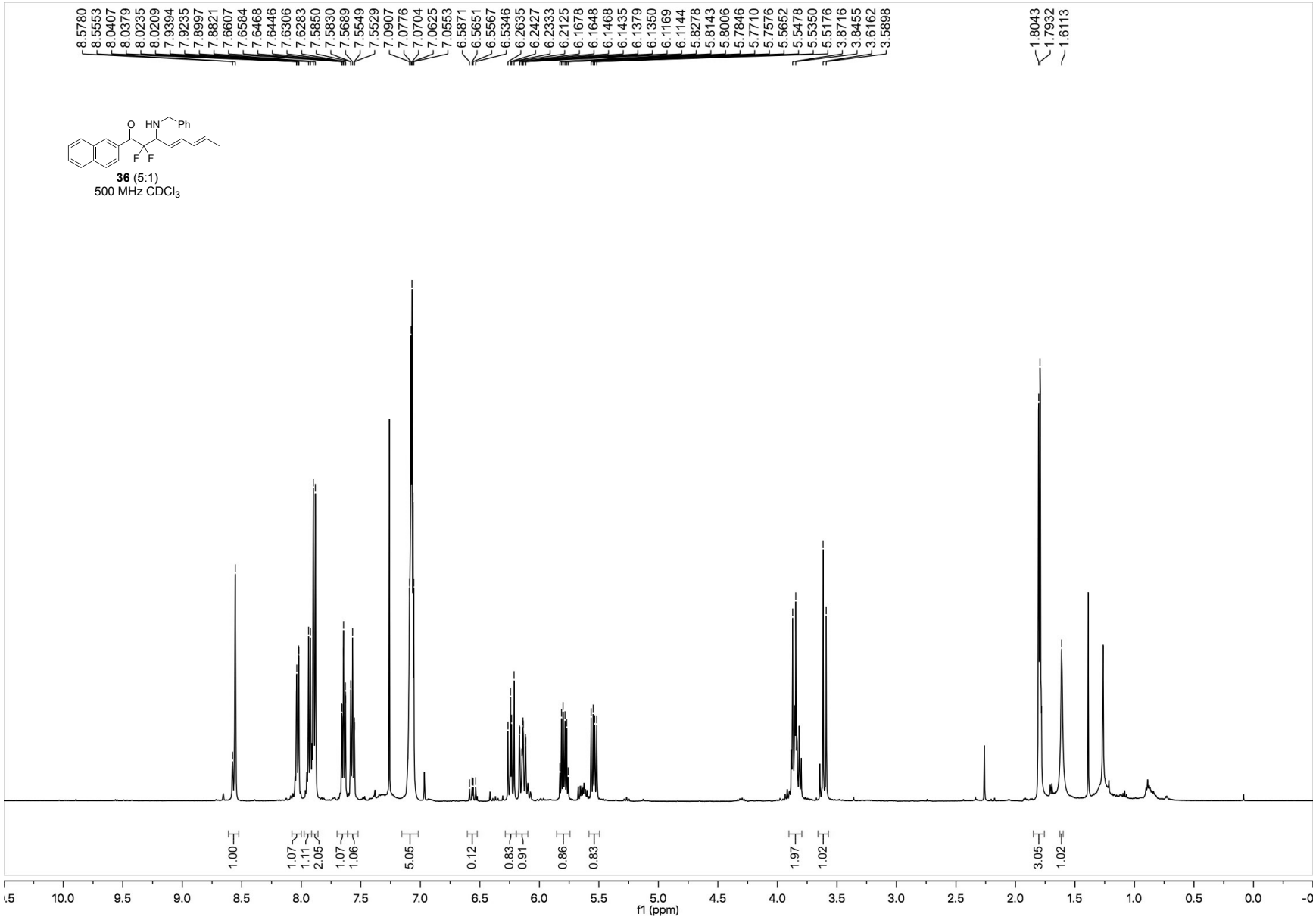

190.271
190.051
190.036
189.816
159.787
153.004
139.534
135.779
132.312
132.281
132.239
132.167
130.257
130.001
129.677
129.255
128.473
127.715
126.958
126.454
124.678
119.719
117.666
117.646
115.894
115.592
114.684
114.060
61.393
61.214
61.186
61.008
55.561
55.177
OMe
O
HN
F F
OMe
34
125 MHz CDCl3
f1 (ppm)

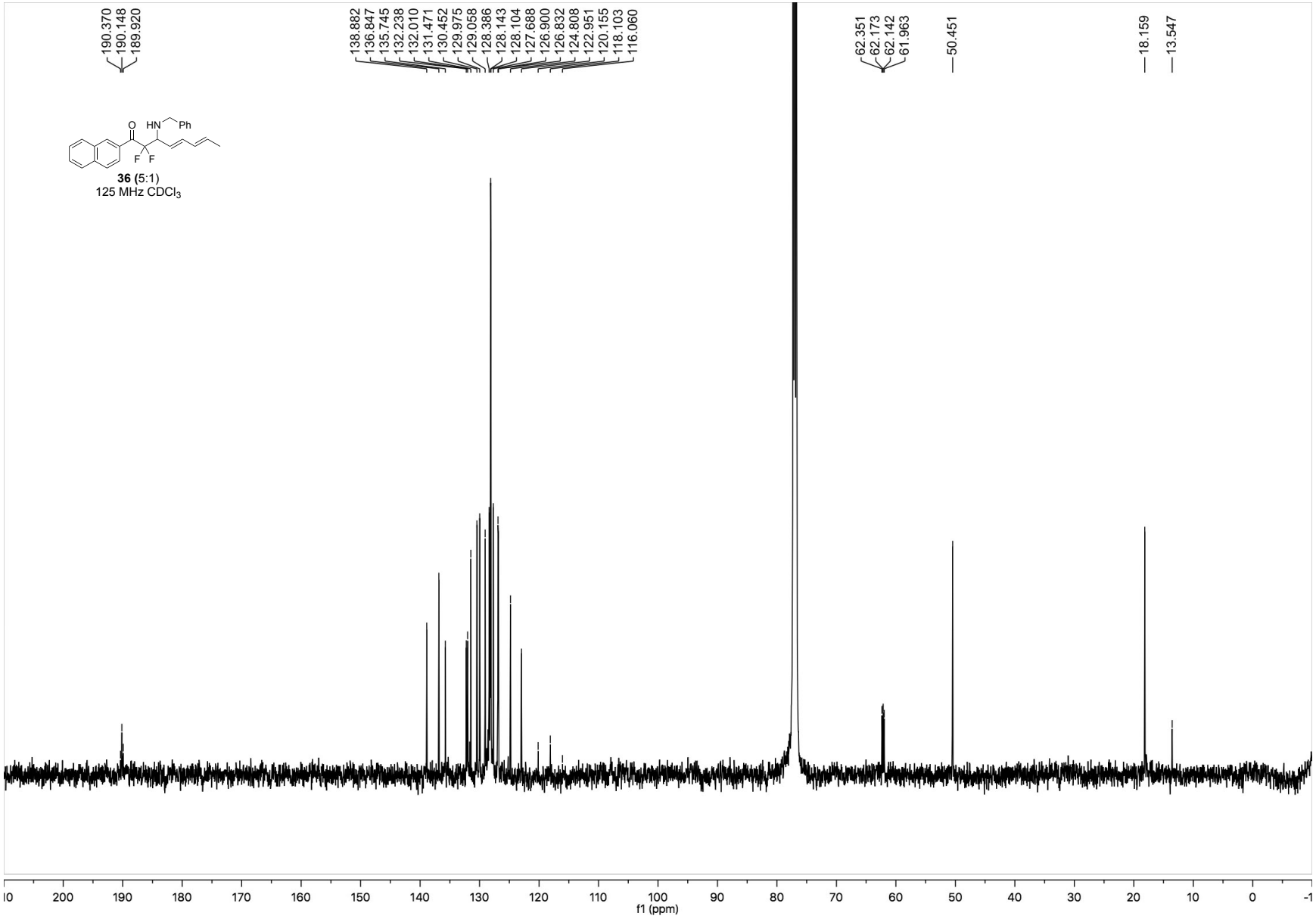

-103.299
-103.317
-103.873
-103.891
-112.950
-112.987
-113.524
-113.561
OMe
O
HN
F F
OMe
34
470 MHz CDCl3
0
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-2
f1 (ppm)

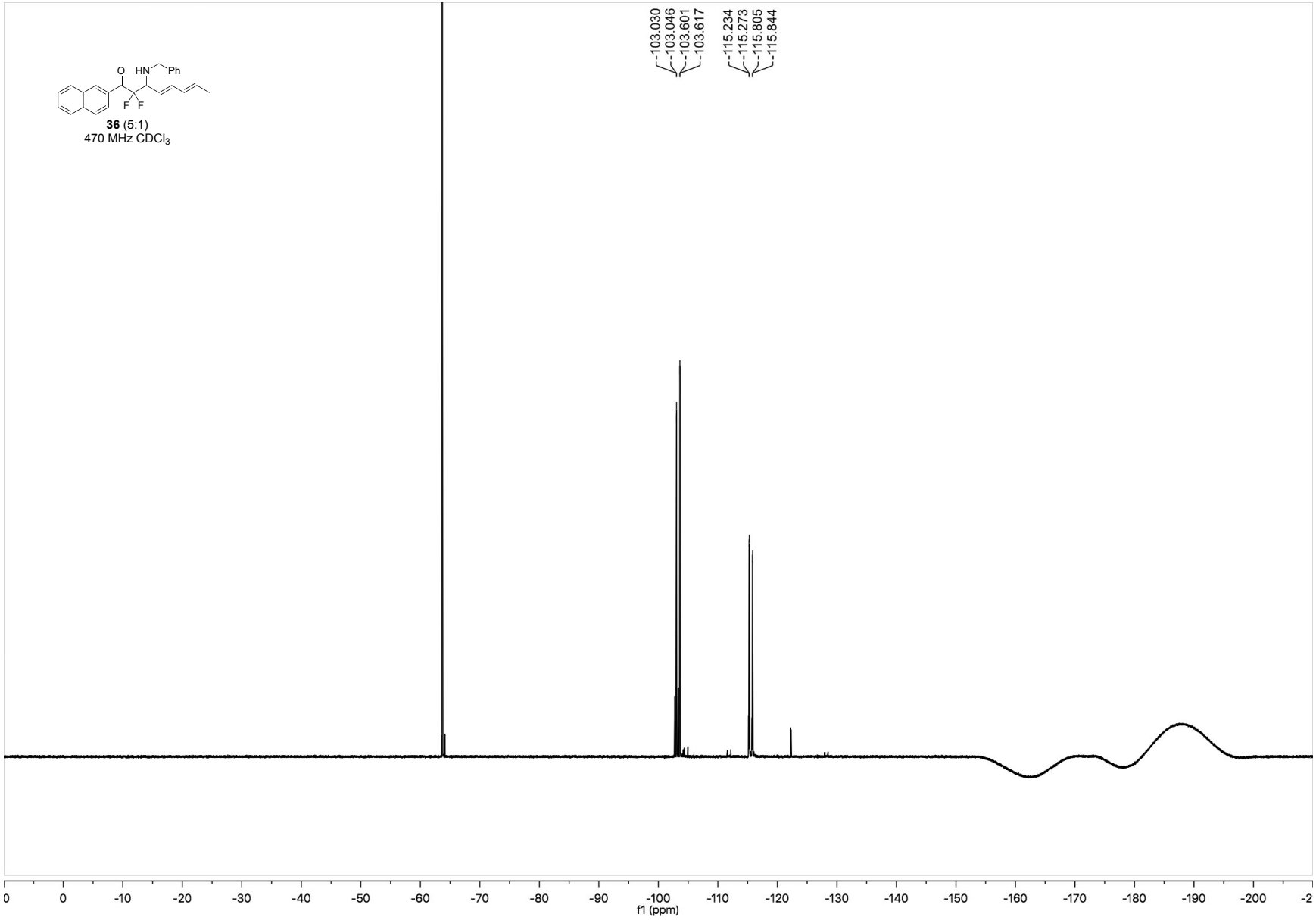

8.5901
8.0440
8.0225
7.9834
7.9633
7.9154
7.8952
7.8778
7.6518
7.6345
7.6144
7.5917
7.5716
7.5543
7.4542
7.4360
7.3975
7.3787
7.3460
7.3262
4.6611
4.6450
4.6061
4.5899
1.8308
0.8443
O
HN
F F
35
400 MHz CDCl3
1.00
1.05
1.10
2.22
1.08
1.23
2.03
3.22
1.20
1.05
9.55
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

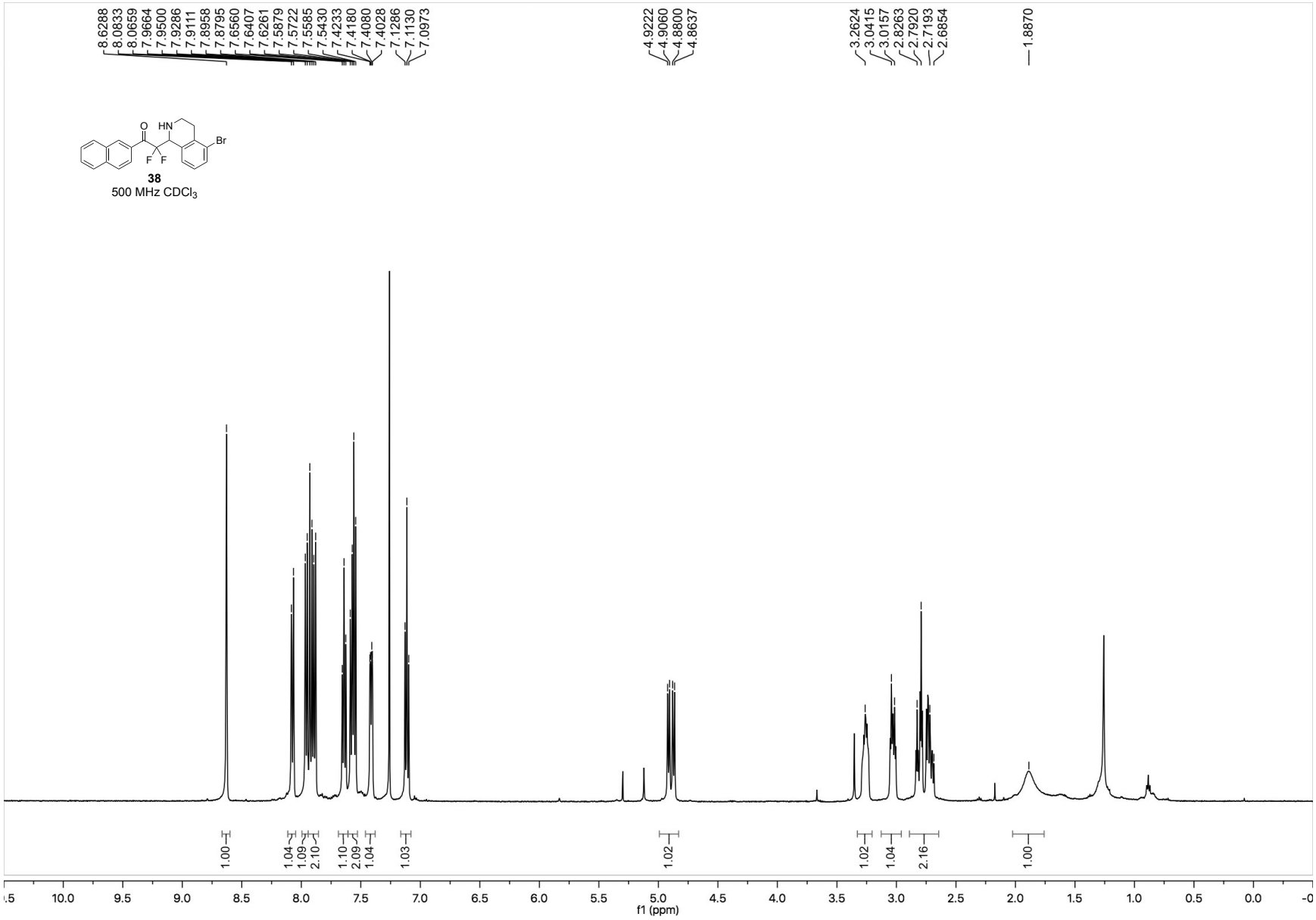

192.249
191.986
191.946
191.682
171.826
138.266
135.552
132.244
131.984
131.953
131.926
131.895
131.423
129.899
128.893
128.678
128.357
128.176
127.721
126.815
125.095
120.837
118.278
118.242
115.688
59.750
59.539
59.483
59.272
51.498
29.950
O
HN
F F
35
100 MHz CDCl3
f1 (ppm)

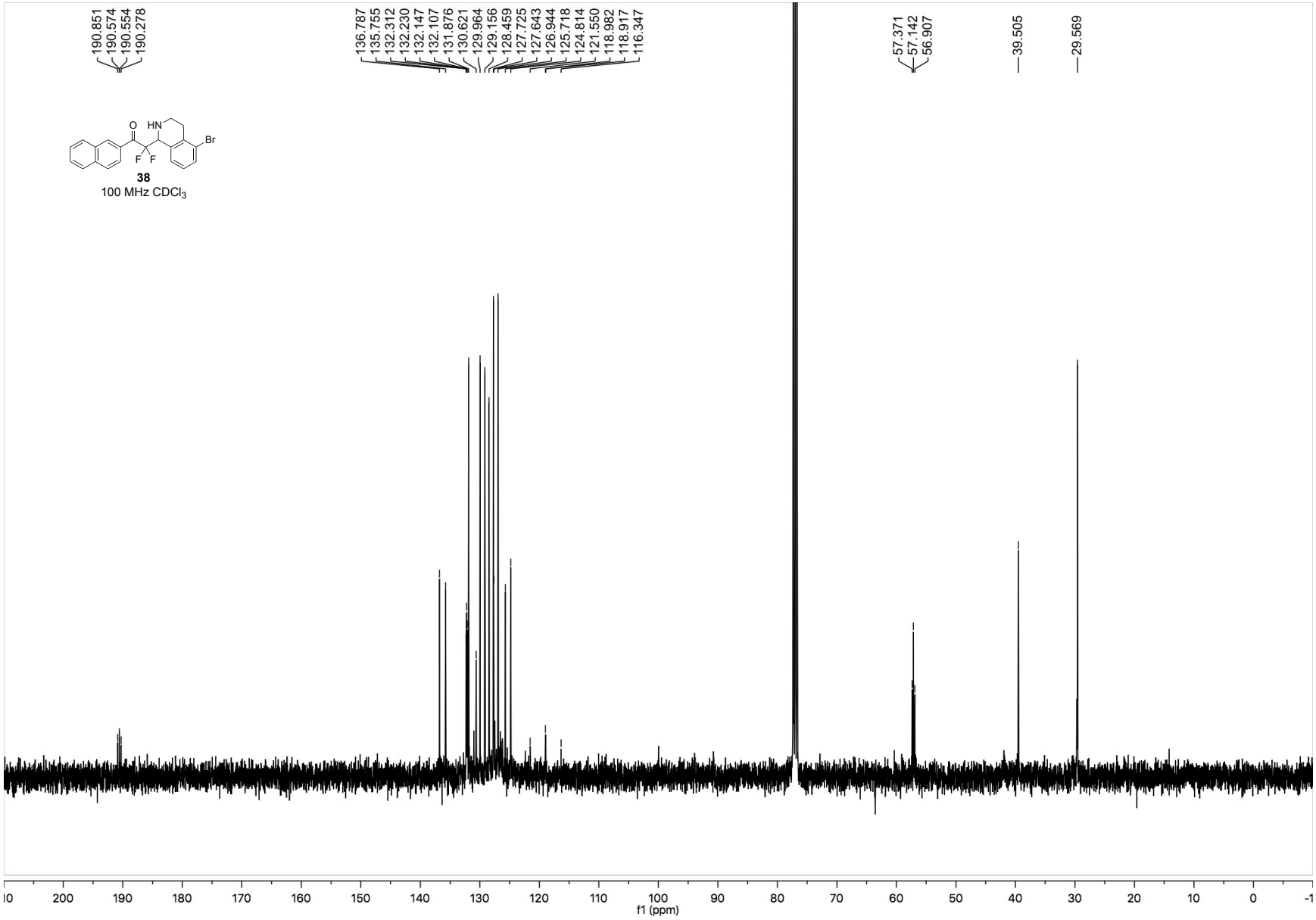

-100.567
-100.584
-101.254
-101.271
-117.081
-117.140
-117.768
-117.827
O
HN
F F
35
376 MHz CDCl3
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-2
f1 (ppm)

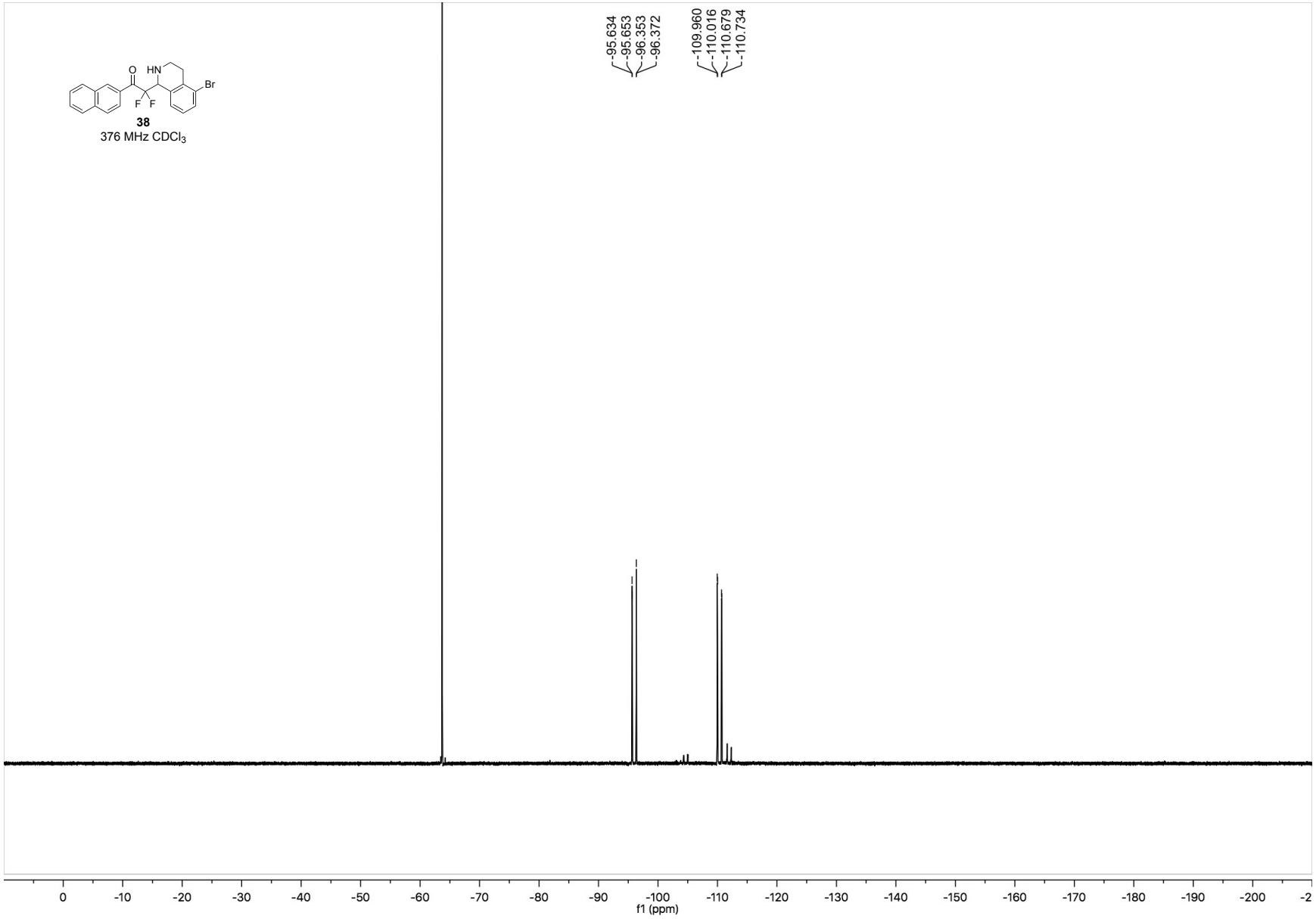

8.5780
8.5553
8.0407
8.0379
8.0235
8.0209
7.9394
7.9235
7.8997
7.8821
7.6607
7.6584
7.6468
7.6446
7.6306
7.6283
7.5850
7.5830
7.5689
7.5549
7.5529
7.0907
7.0776
7.0704
7.0625
7.0553
6.5871
6.5651
6.5567
6.5346
6.2635
6.2427
6.2333
6.2125
6.1678
6.1648
6.1468
6.1435
6.1379
6.1350
6.1169
6.1144
5.8278
5.8143
5.8006
5.7846
5.7710
5.7576
5.5652
5.5478
5.5350
5.5176
3.8716
3.8455
3.6162
3.5898
1.8043
1.7932
1.6113
O
HN
Ph
F F
36 (5:1)
500 MHz CDCl3
1.00
1.07
1.11
2.05
1.07
1.06
5.05
0.12
0.83
0.91
0.86
0.83
1.97
1.02
3.05
1.02
f1 (ppm)

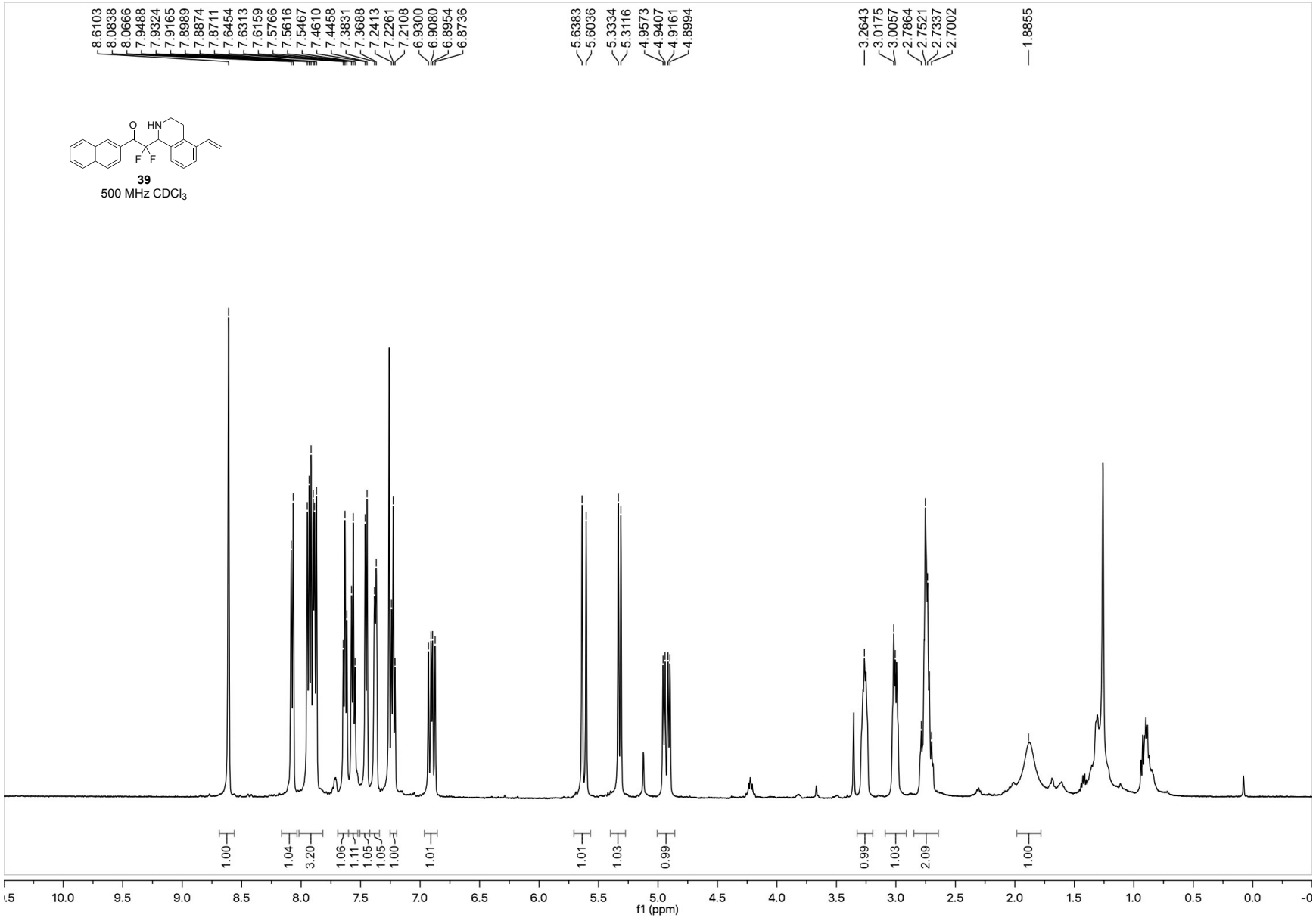

190.370
190.148
189.920
138.882
136.847
135.745
132.238
132.010
131.471
130.452
129.975
129.058
128.386
128.143
128.104
127.688
126.900
126.832
124.808
122.951
120.155
118.103
116.060
62.351
62.173
62.142
61.963
50.451
18.159
13.547
O
HN
Ph
F F
36 (5:1)
125 MHz CDCl3
f1 (ppm)

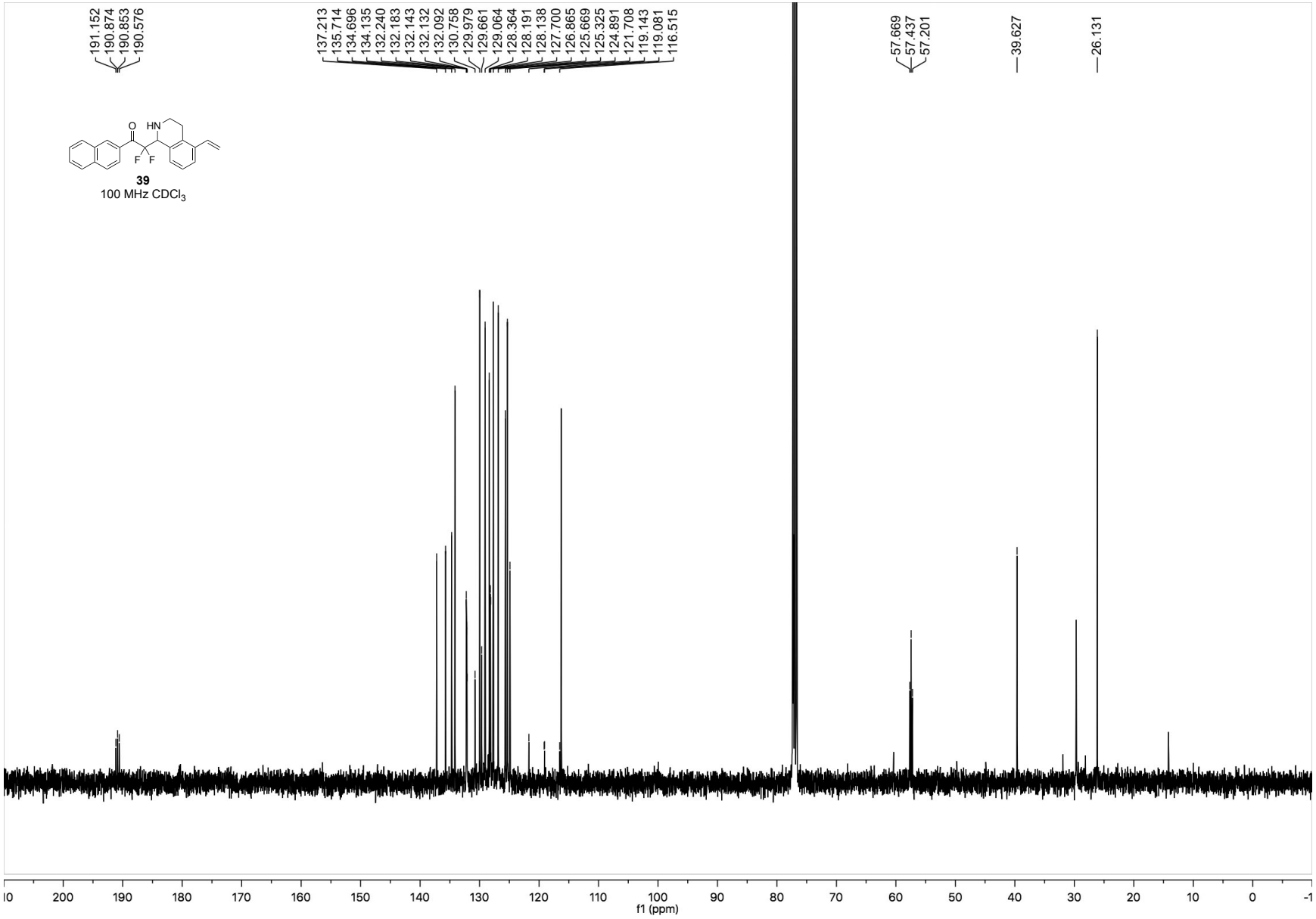

-103.030
-103.046
-103.601
-103.617
-115.234
-115.273
-115.805
-115.844
O
HN
Ph
F F
36 (5:1)
470 MHz CDCl3
f1 (ppm)

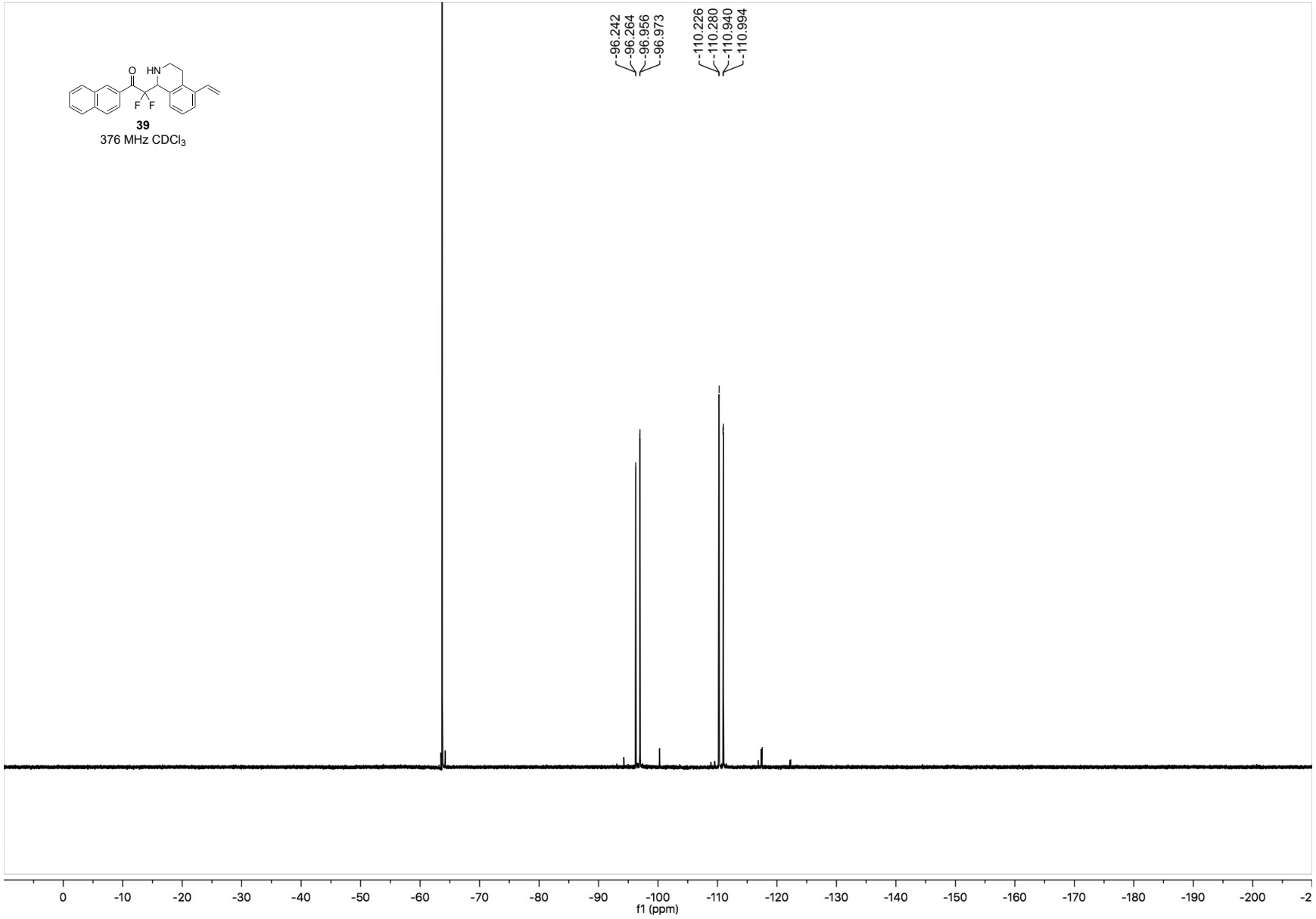

8.6288
8.0833
8.0659
7.9664
7.9500
7.9286
7.9111
7.8958
7.8795
7.6560
7.6407
7.6261
7.5879
7.5722
7.5585
7.5430
7.4233
7.4180
7.4080
7.4028
7.1286
7.1130
7.0973
4.9222
4.9060
4.8800
4.8637
3.2624
3.0415
3.0157
2.8263
2.7920
2.7193
2.6854
1.8870
O
HN
Br
F F
38
500 MHz CDCl3
1.00
1.04
1.09
2.10
1.10
2.09
1.04
1.03
1.02
1.02
1.04
2.16
1.00
f1 (ppm)

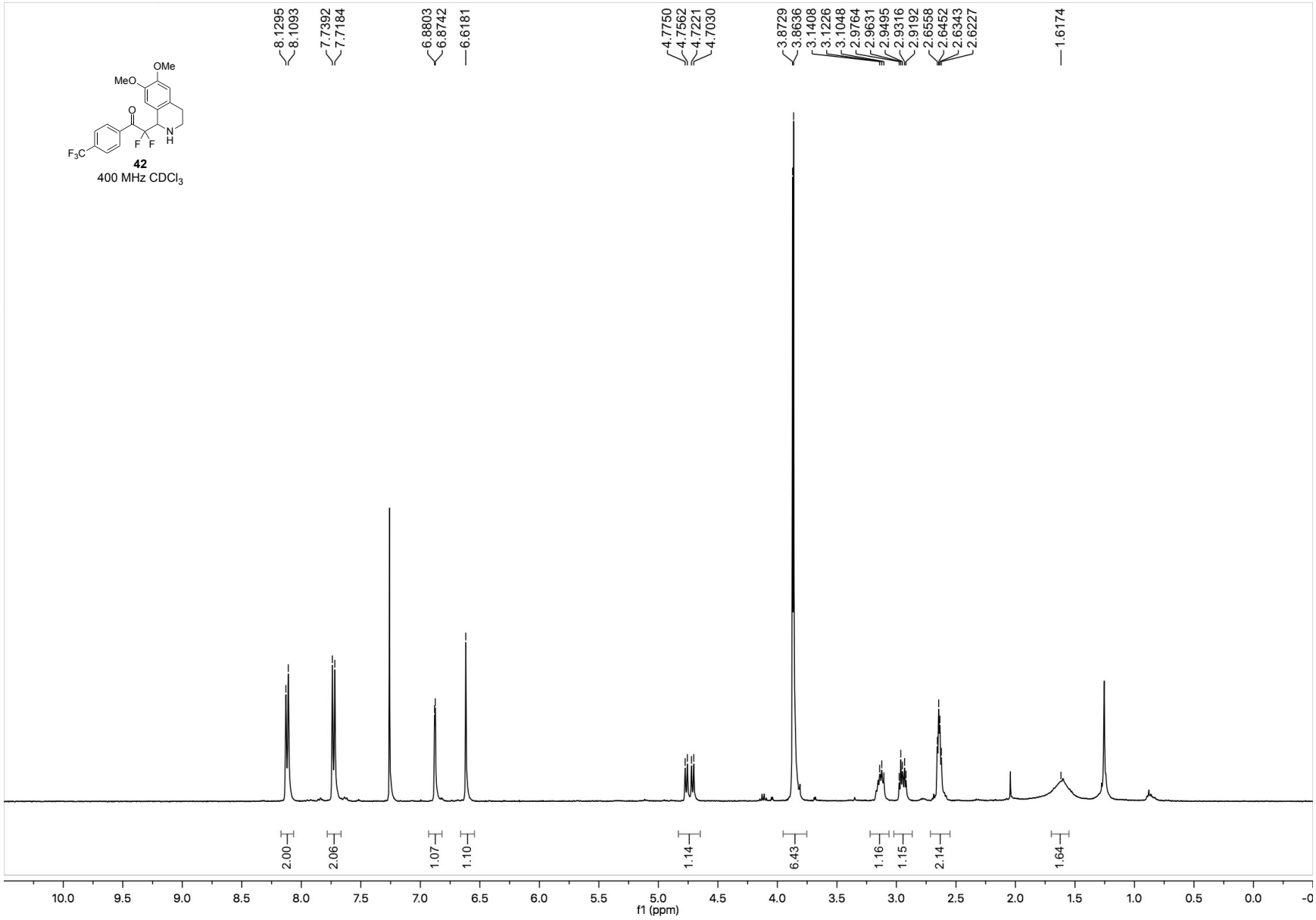

190.851
190.574
190.554
190.278
136.787
135.755
132.312
132.230
132.147
132.107
131.876
130.621
129.964
129.156
128.459
127.725
127.643
126.944
125.718
124.814
121.550
118.982
118.917
116.347
57.371
57.142
56.907
39.505
29.569
O
HN
Br
F F
38
100 MHz CDCl3
f1 (ppm)

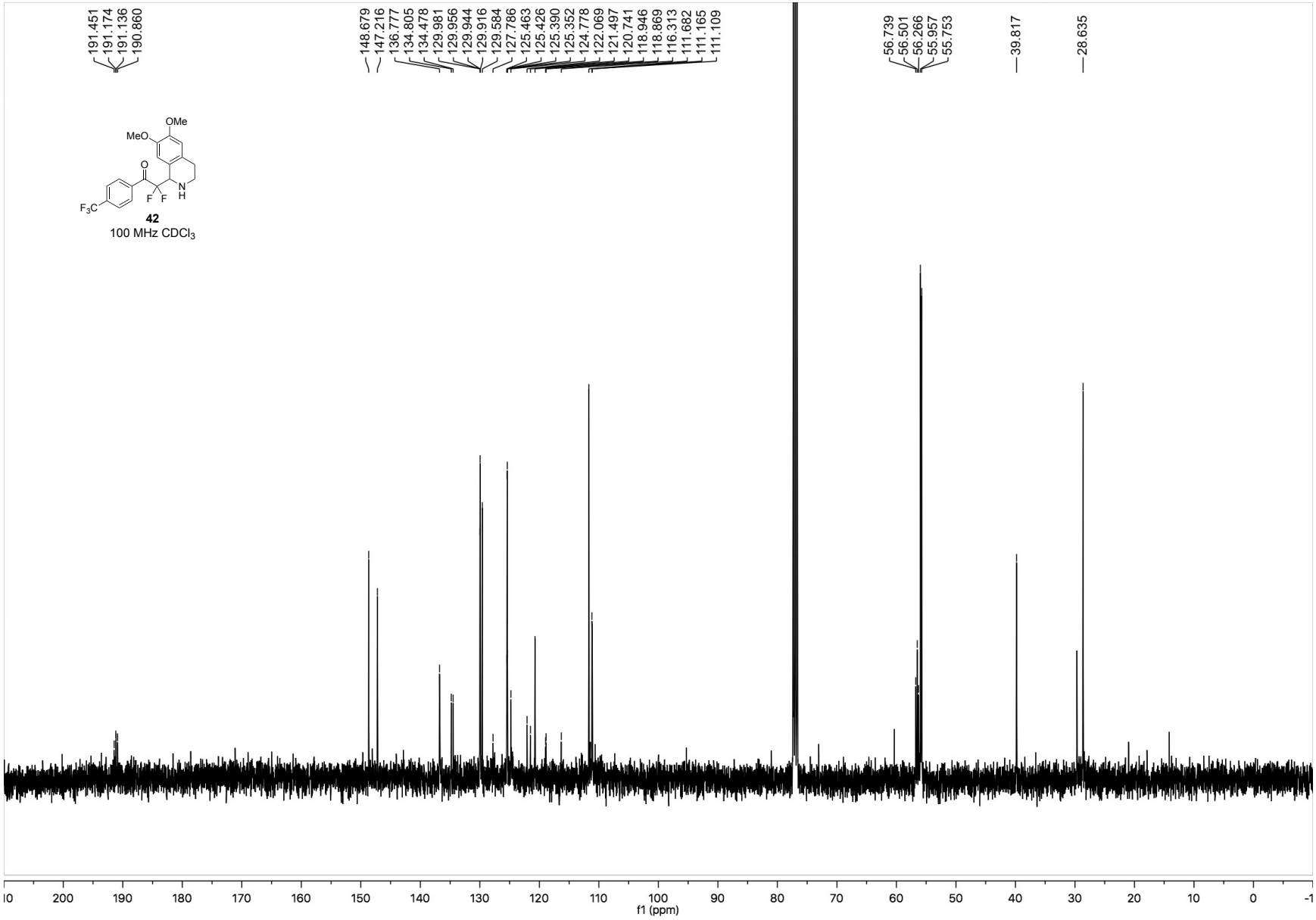

-95.634
-95.653
-96.353
-96.372
-109.960
-110.016
-110.679
-110.734
O
HN
Br
F F
38
376 MHz CDCl3
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

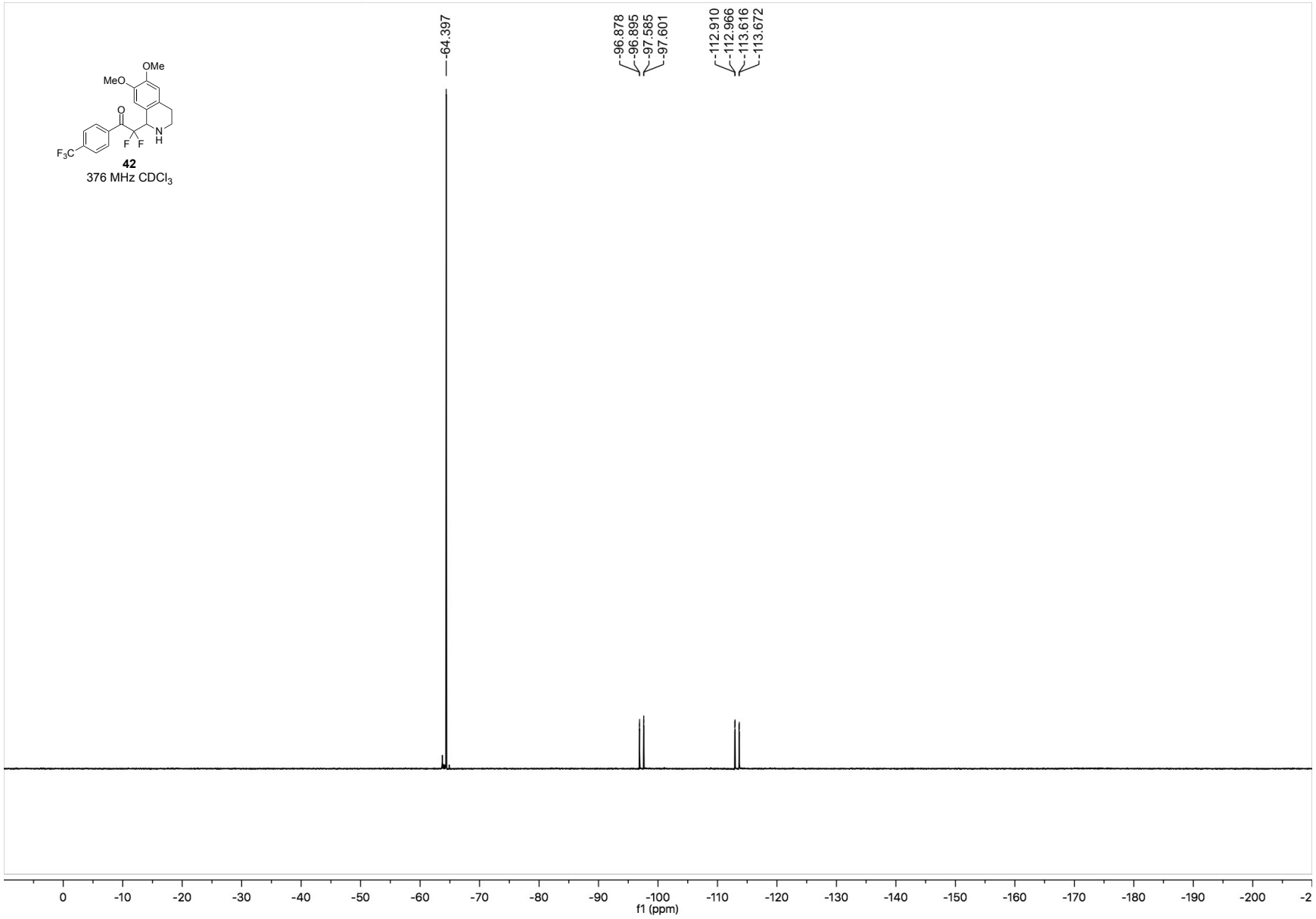

8.6103
8.0838
8.0666
7.9488
7.9324
7.9165
7.8989
7.8874
7.8711
7.6454
7.6313
7.6159
7.5766
7.5616
7.5467
7.4610
7.4458
7.3831
7.3688
7.2413
7.2261
7.2108
6.9300
6.9080
6.8954
6.8736
5.6383
5.6036
5.3334
5.3116
4.9573
4.9407
4.9161
4.8994
3.2643
3.0175
3.0057
2.7864
2.7521
2.7337
2.7002
1.8855
O
HN
F F
39
500 MHz CDCl3
1.00
1.04
3.20
1.06
1.11
1.05
1.05
1.00
1.01
1.01
1.03
0.99
0.99
1.03
2.09
1.00
f1 (ppm)

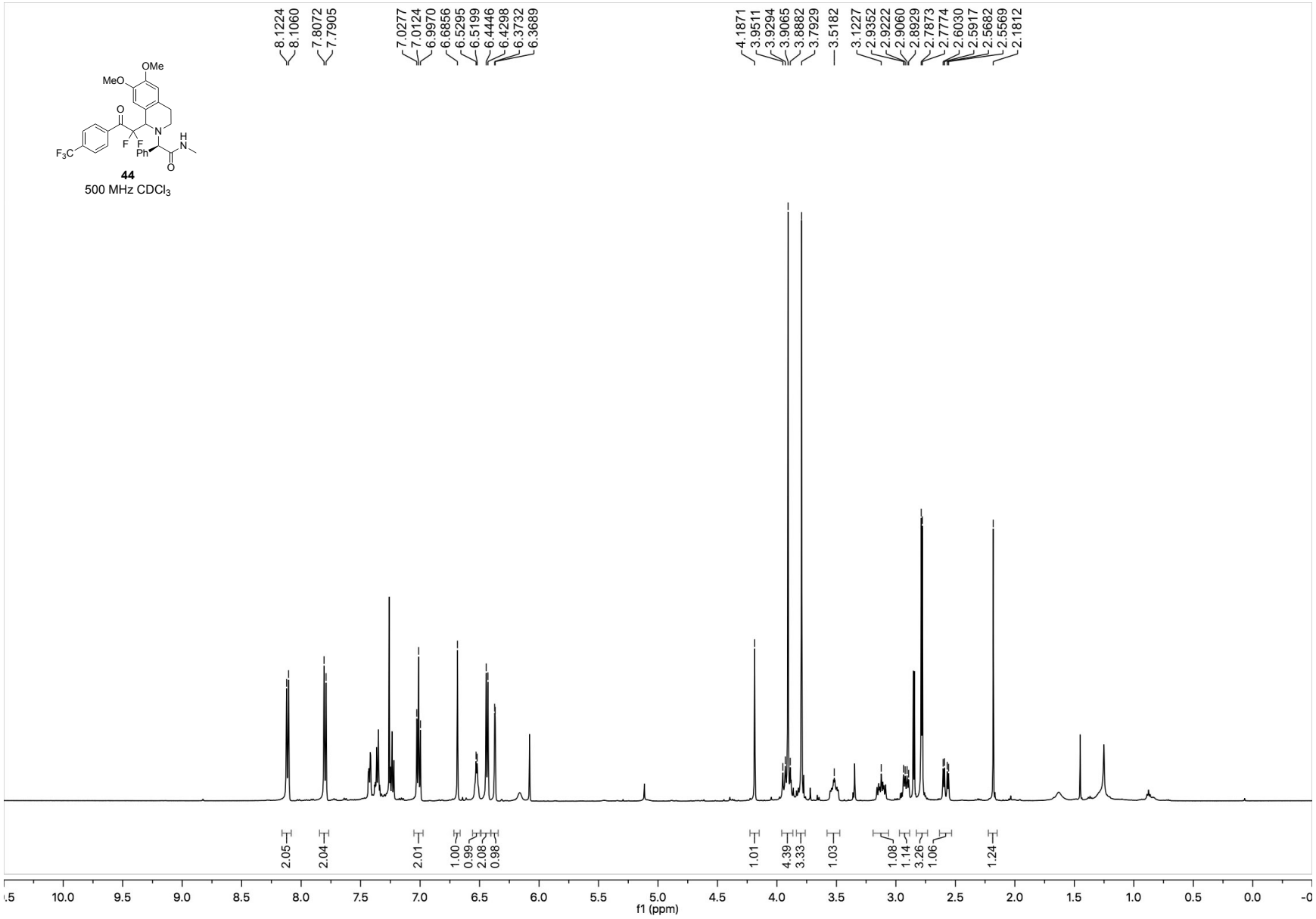

191.152
190.874
190.853
190.576
137.213
135.714
134.696
134.135
132.240
132.183
132.143
132.132
132.092
130.758
129.979
129.661
129.064
128.364
128.191
128.138
127.700
126.865
125.669
125.325
124.891
121.708
119.143
119.081
116.515
57.669
57.437
57.201
39.627
26.131
O
HN
F F
39
100 MHz CDCl3
f1 (ppm)

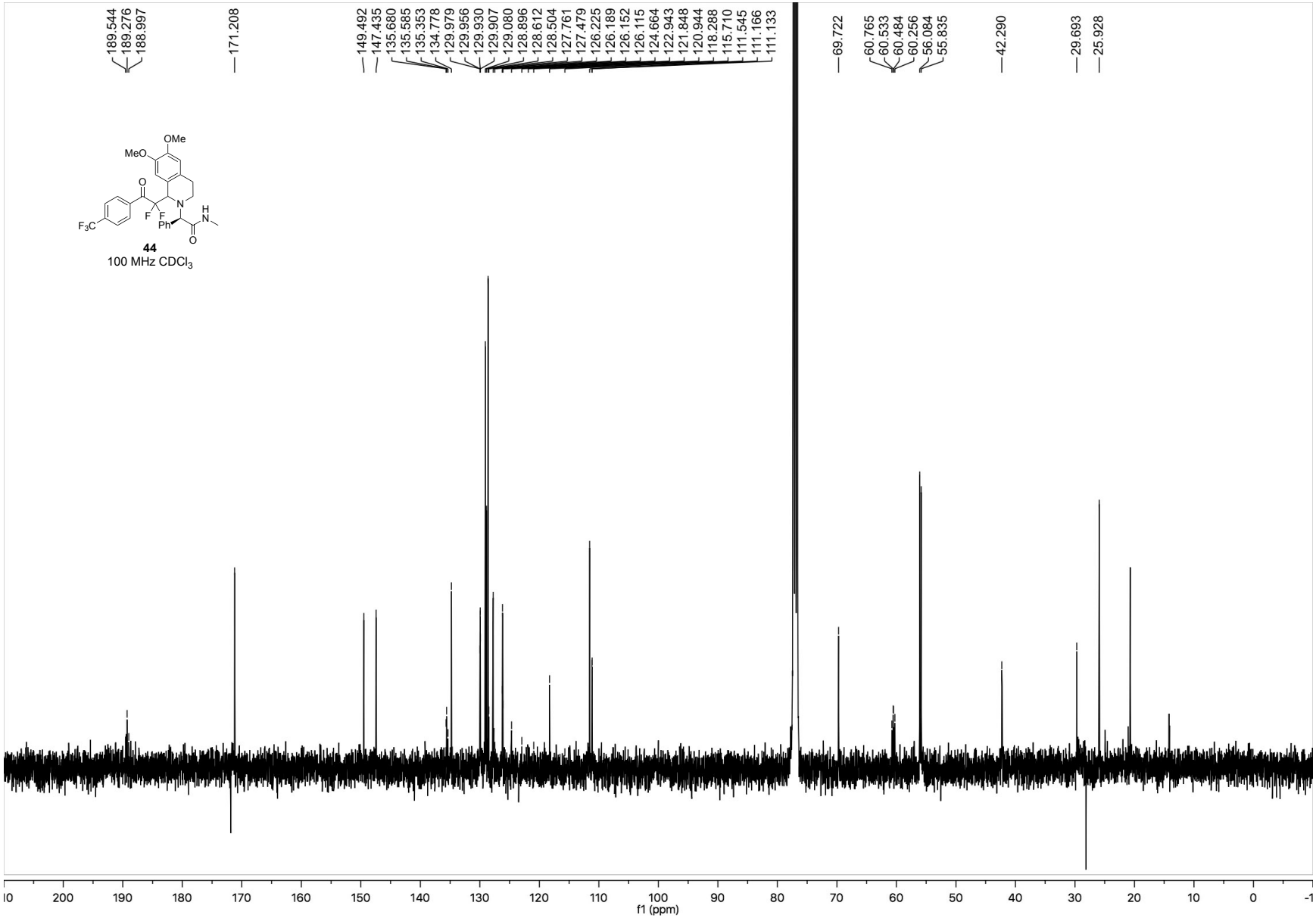

-96.242
-96.264
-96.956
-96.973
-110.226
-110.280
-110.940
-110.994
O
HN
F F
39
376 MHz CDCl3
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

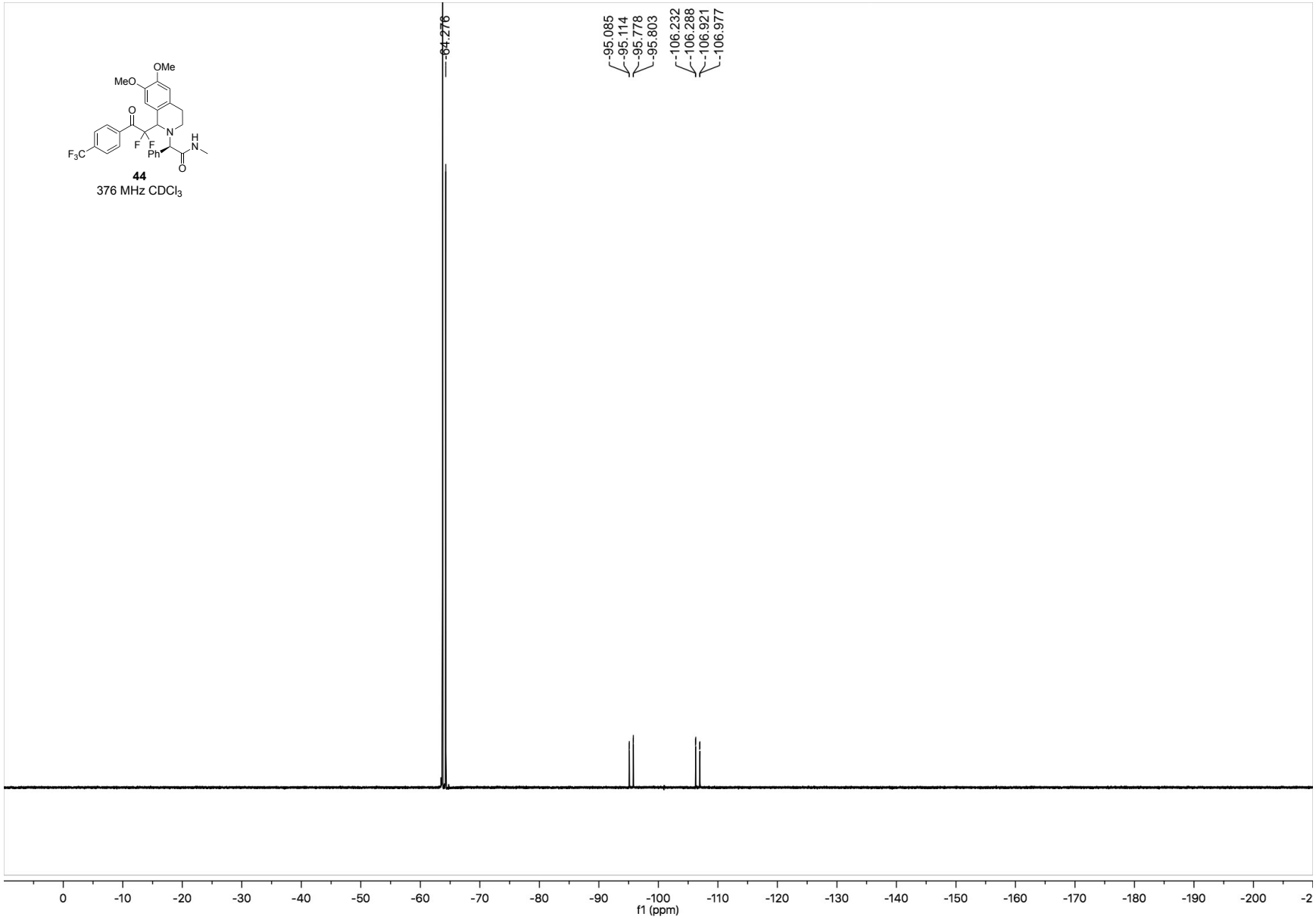

8.1295
8.1093
7.7392
7.7184
6.8803
6.8742
6.6181
4.7750
4.7562
4.7221
4.7030
3.8729
3.8636
3.1408
3.1226
3.1048
2.9764
2.9631
2.9495
2.9316
2.9192
2.6558
2.6452
2.6343
2.6227
1.6174
OMe
MeO
O
F F
N
H
F3C
42
400 MHz CDCl3
2.00
2.06
1.07
1.10
1.14
6.43
1.16
1.15
2.14
1.64
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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)


191.451
191.174
191.136
190.860
148.679
147.216
136.777
134.805
134.478
129.981
129.956
129.944
129.916
129.584
127.786
125.463
125.426
125.390
125.352
124.778
122.069
121.497
120.741
118.946
118.869
116.313
111.682
111.165
111.109
56.739
56.501
56.266
55.957
55.753
39.817
28.635
OMe
MeO
O
N
H
F F
F3C
42
100 MHz CDCl3
f1 (ppm)


-64.397
-96.878
-96.895
-97.585
-97.601
-112.910
-112.966
-113.616
-113.672
OMe
MeO
O
F F
N
H
F3C
42
376 MHz CDCl3
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)


8.1224
8.1060
7.8072
7.7905
7.0277
7.0124
6.9970
6.6856
6.5295
6.5199
6.4446
6.4298
6.3732
6.3689
4.1871
3.9511
3.9294
3.9065
3.8882
3.7929
3.5182
3.1227
2.9352
2.9222
2.9060
2.8929
2.7873
2.7774
2.6030
2.5917
2.5682
2.5569
2.1812
OMe
MeO
O
F
F
N
H
N
Ph
O
F3C
44
500 MHz CDCl3
2.05
2.04
2.01
1.00
0.99
2.08
0.98
1.01
4.39
3.33
1.03
1.08
1.14
3.26
1.06
1.24
f1 (ppm)


189.544
189.276
188.997
171.208
149.492
147.435
135.680
135.585
135.353
134.778
129.979
129.956
129.930
129.907
129.080
128.896
128.612
128.504
127.761
127.479
126.225
126.189
126.152
126.115
124.664
122.943
121.848
120.944
118.288
115.710
111.545
111.166
111.133
69.722
60.765
60.533
60.484
60.256
56.084
55.835
42.290
29.693
25.928
OMe
MeO
O
F
F
N
H
N
F3C
Ph
O
44
100 MHz CDCl3
f1 (ppm)


OMe
MeO
O
F
F
N
H
N
F3C
Ph
O
44
376 MHz CDCl3
-64.276
-95.085
-95.114
-95.778
-95.803
-106.232
-106.288
-106.921
-106.977
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)