

Highly Active Catalysts of Bisphosphine Oxides for Asymmetric Heck Reaction

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21 Nanyang Link, Singapore 637371

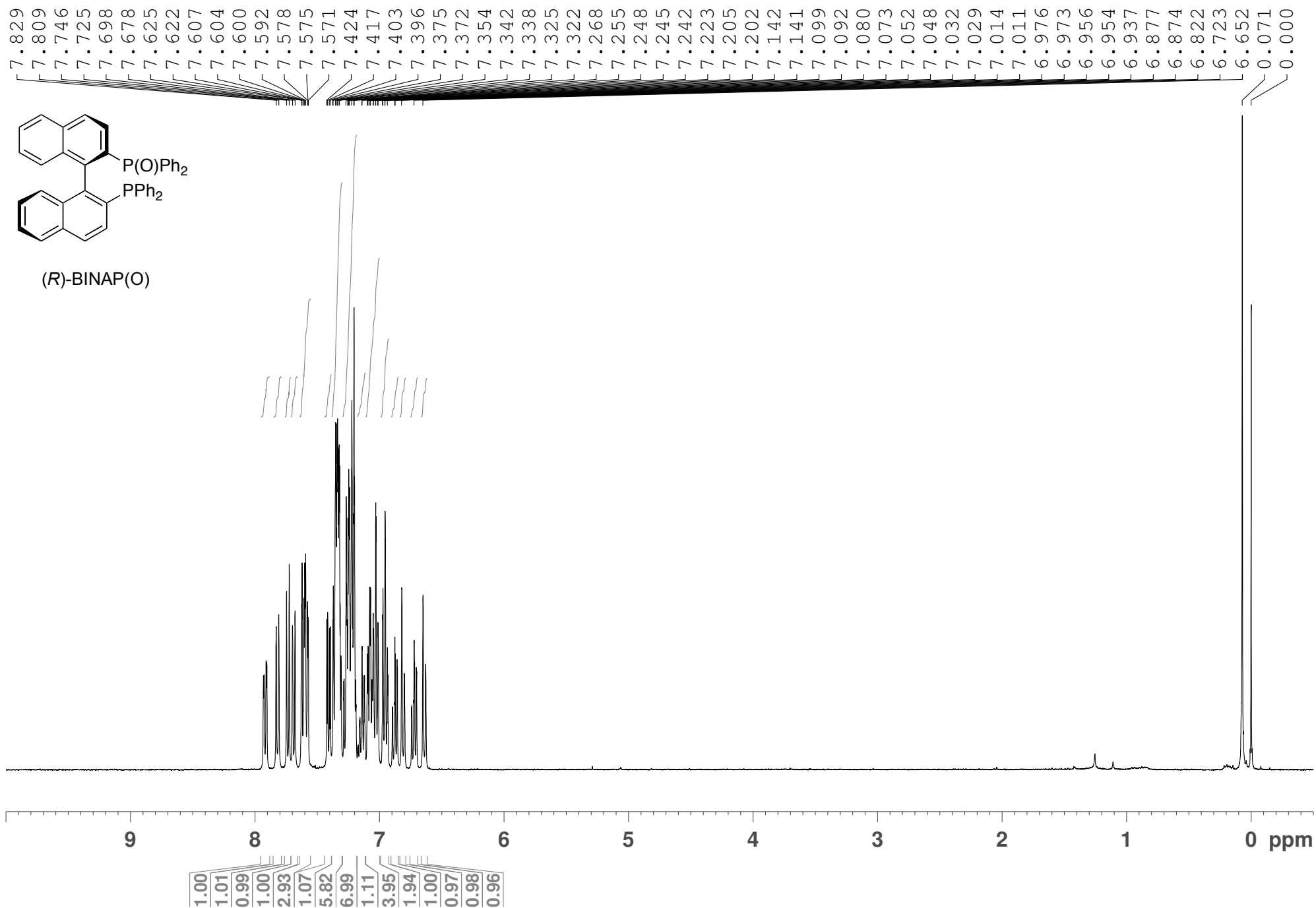
E-mail: jrzhou@ntu.edu.sg

Supporting Information: NMR Spectra

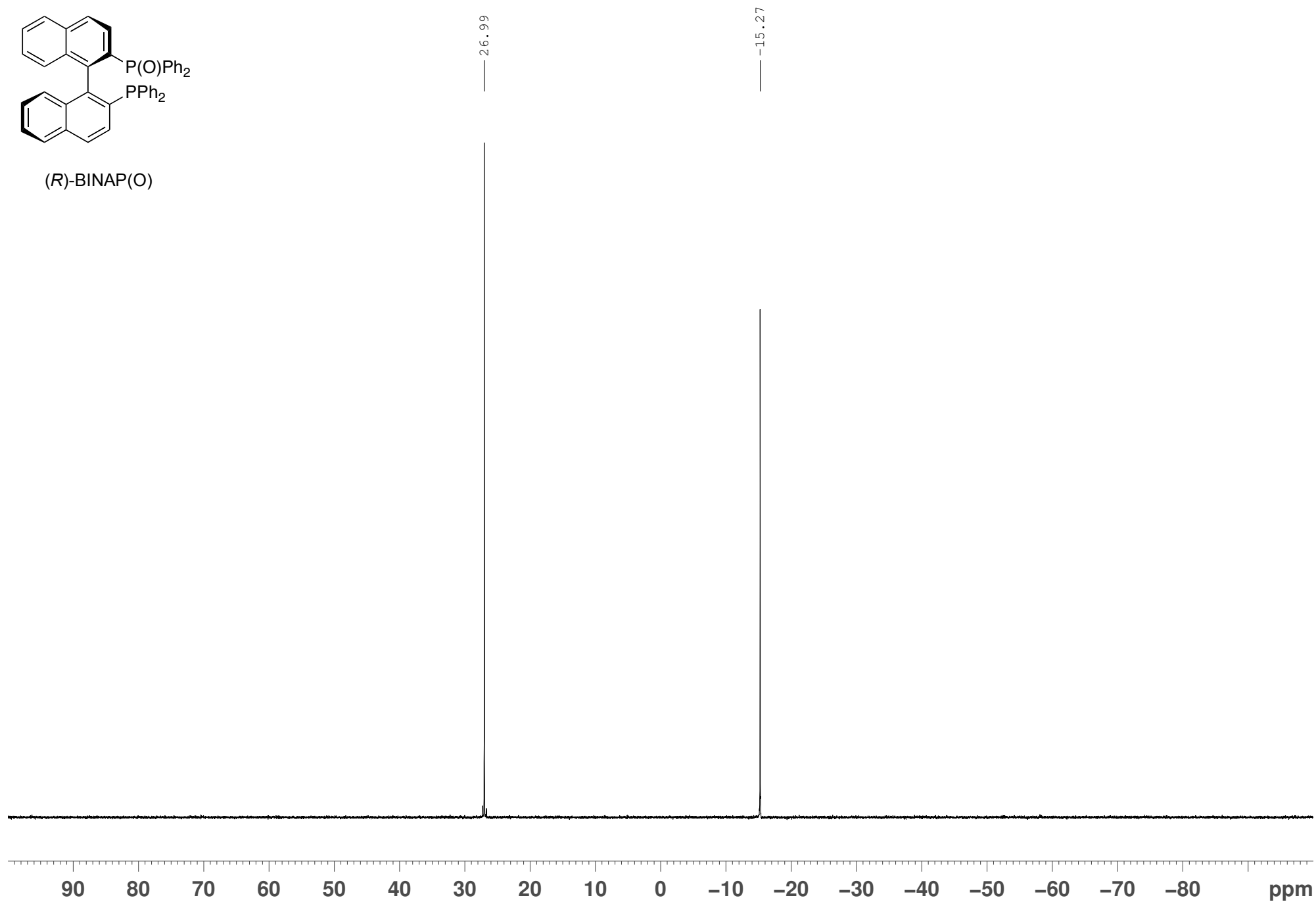
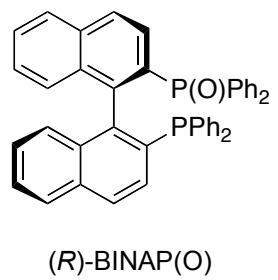
- I. Chiral bisphosphine monoxides
- II. Asymmetric Heck products
- III. Vinylaryl triflates
- IV. Mechanistic study

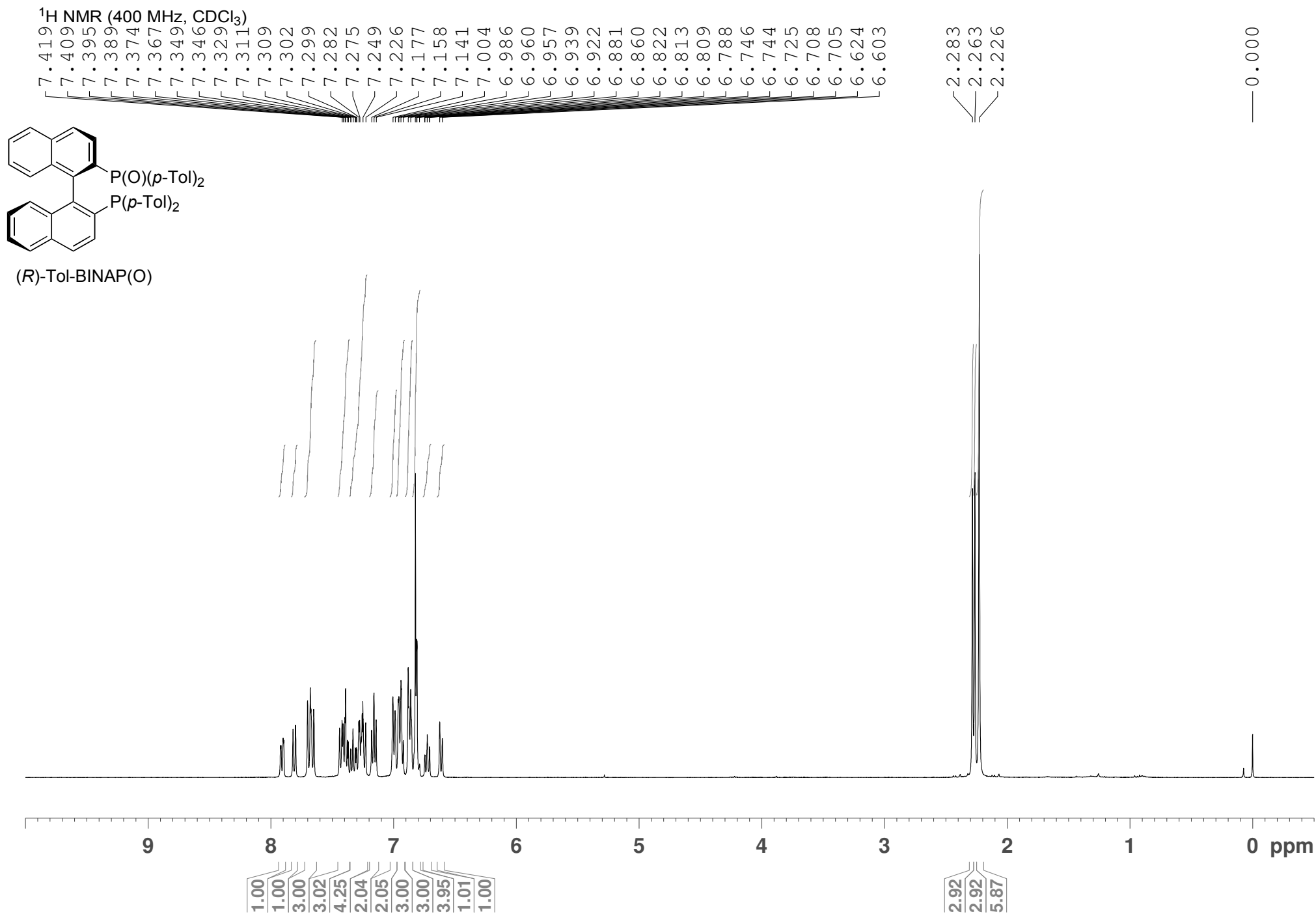
¹H NMR (400 MHz, CDCl₃)

S2

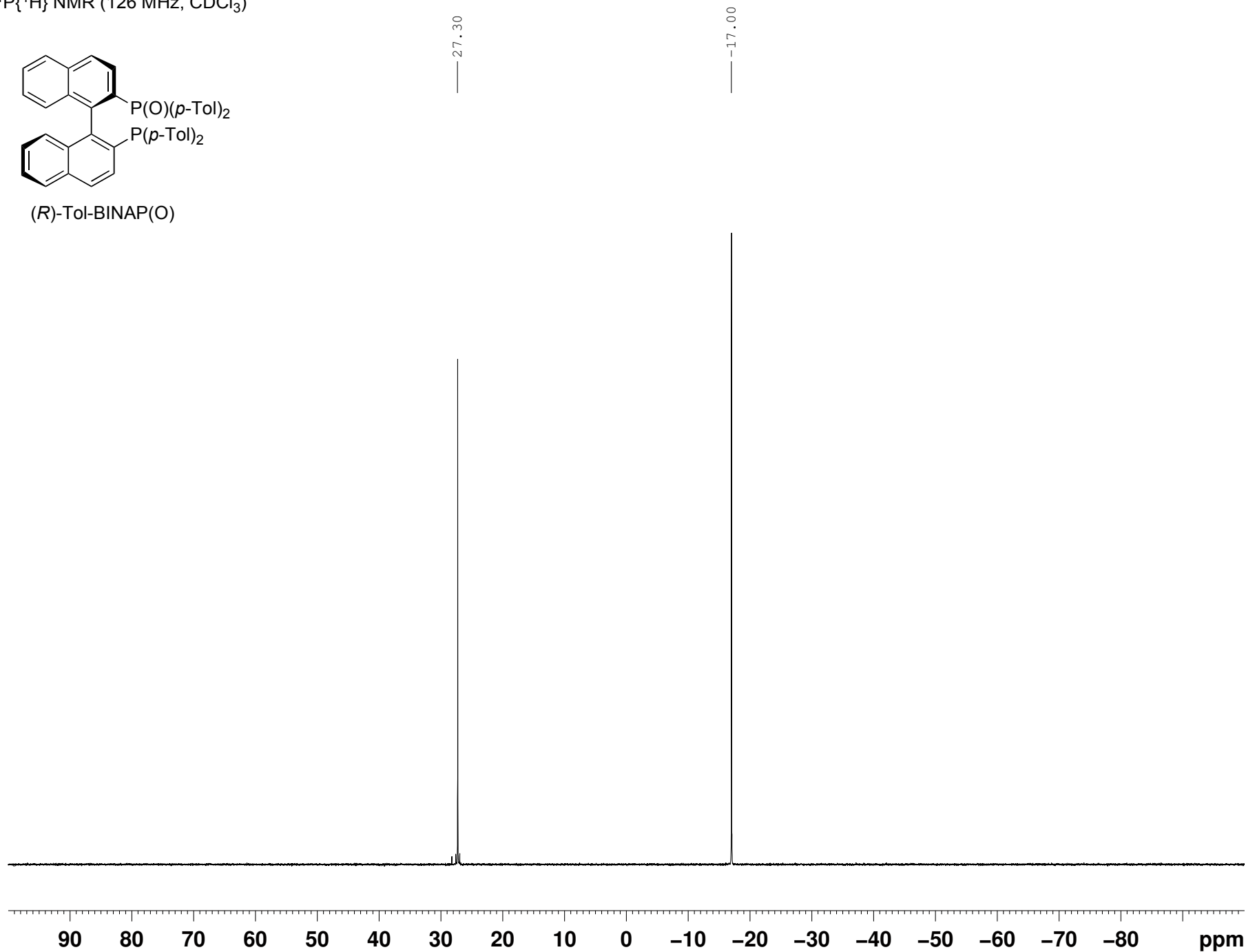
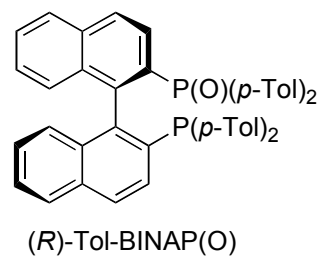


$^{31}\text{P}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

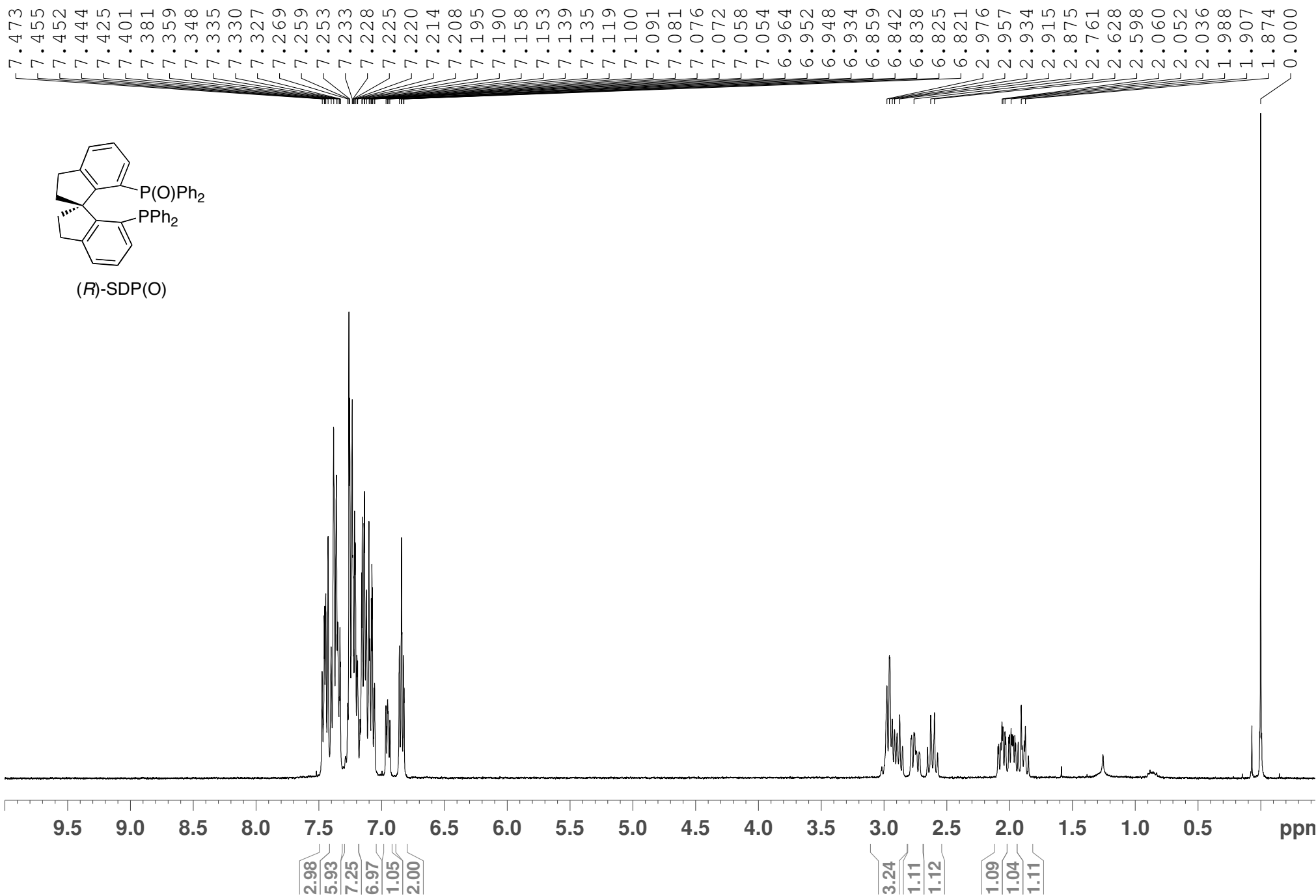




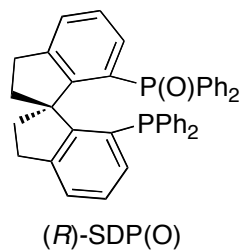
$^{31}\text{P}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)



¹H NMR (400 MHz, CDCl₃)



$^{31}\text{P}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

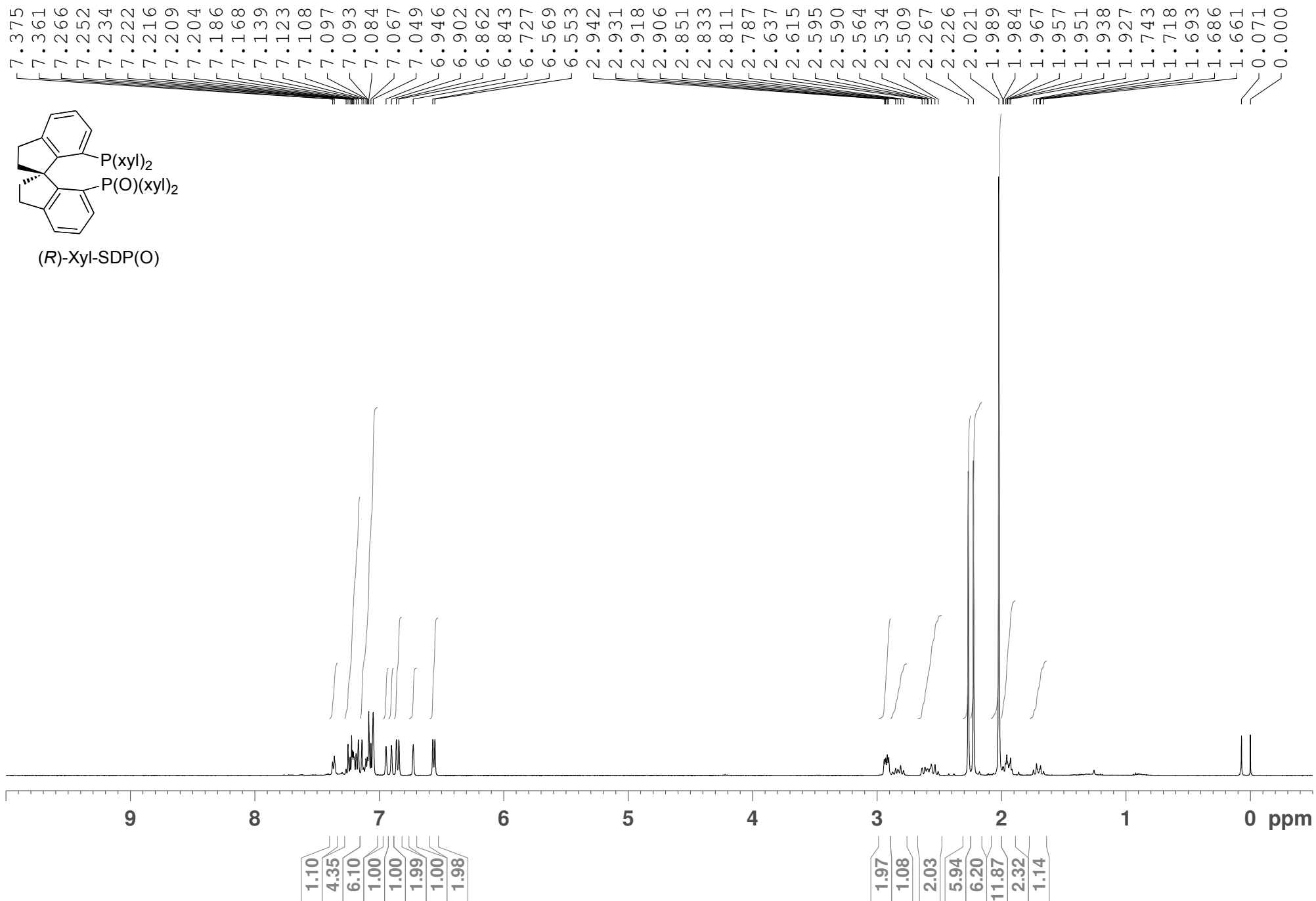


29.42

-18.33



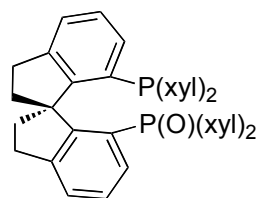
¹H NMR (400 MHz, CDCl₃)



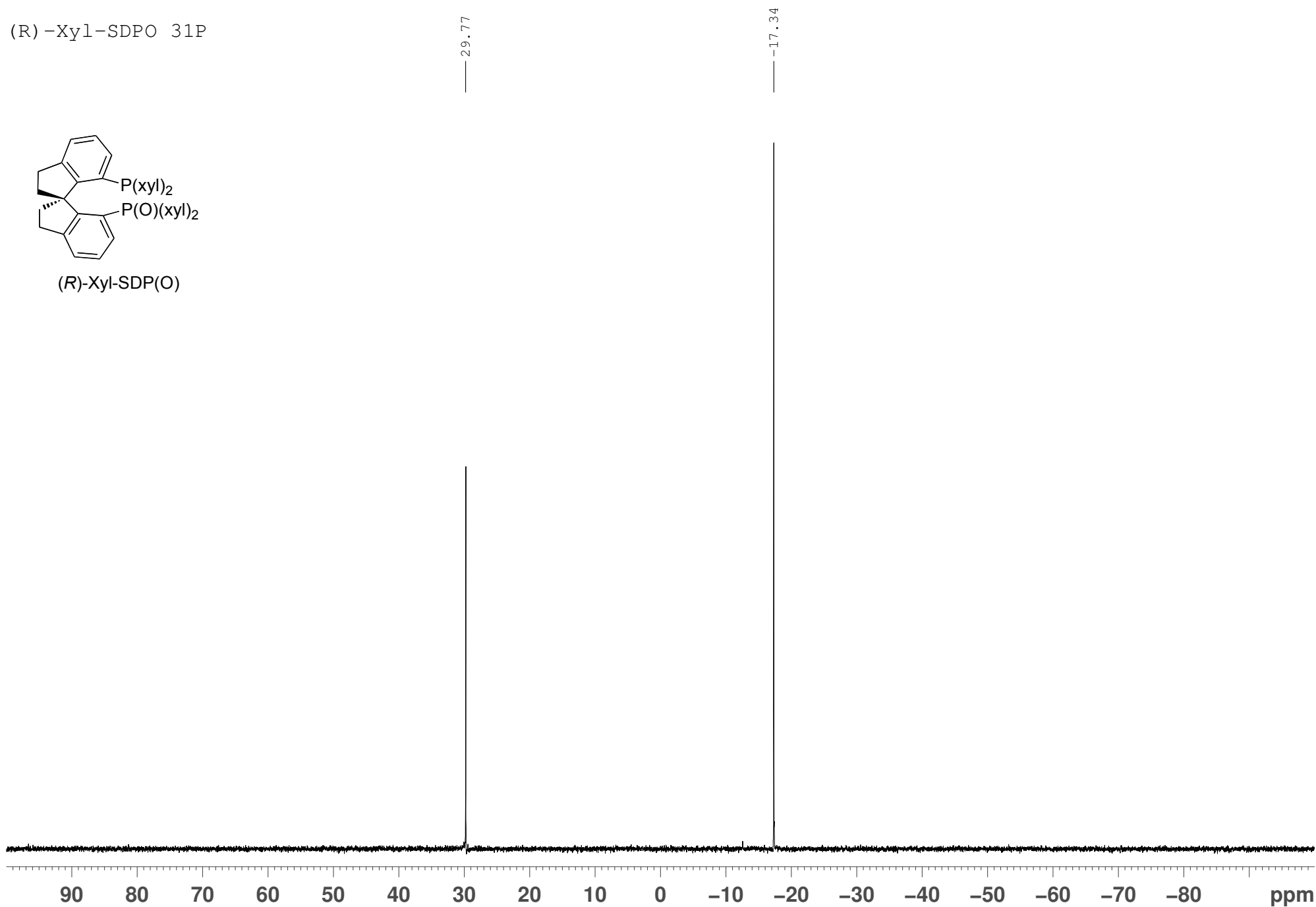
(R)-Xyl-SDPO 31P

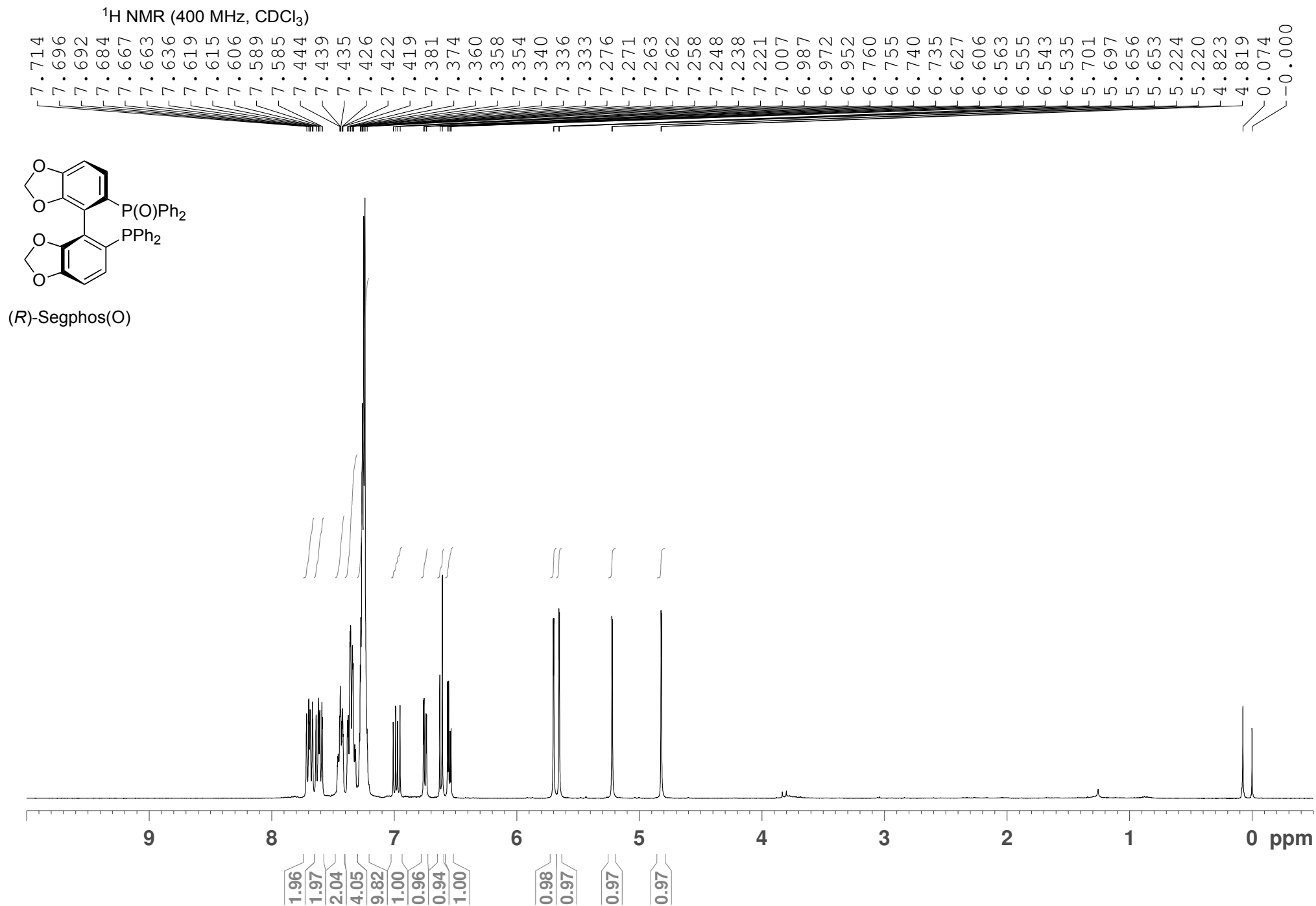
— 29.77

— -17.34

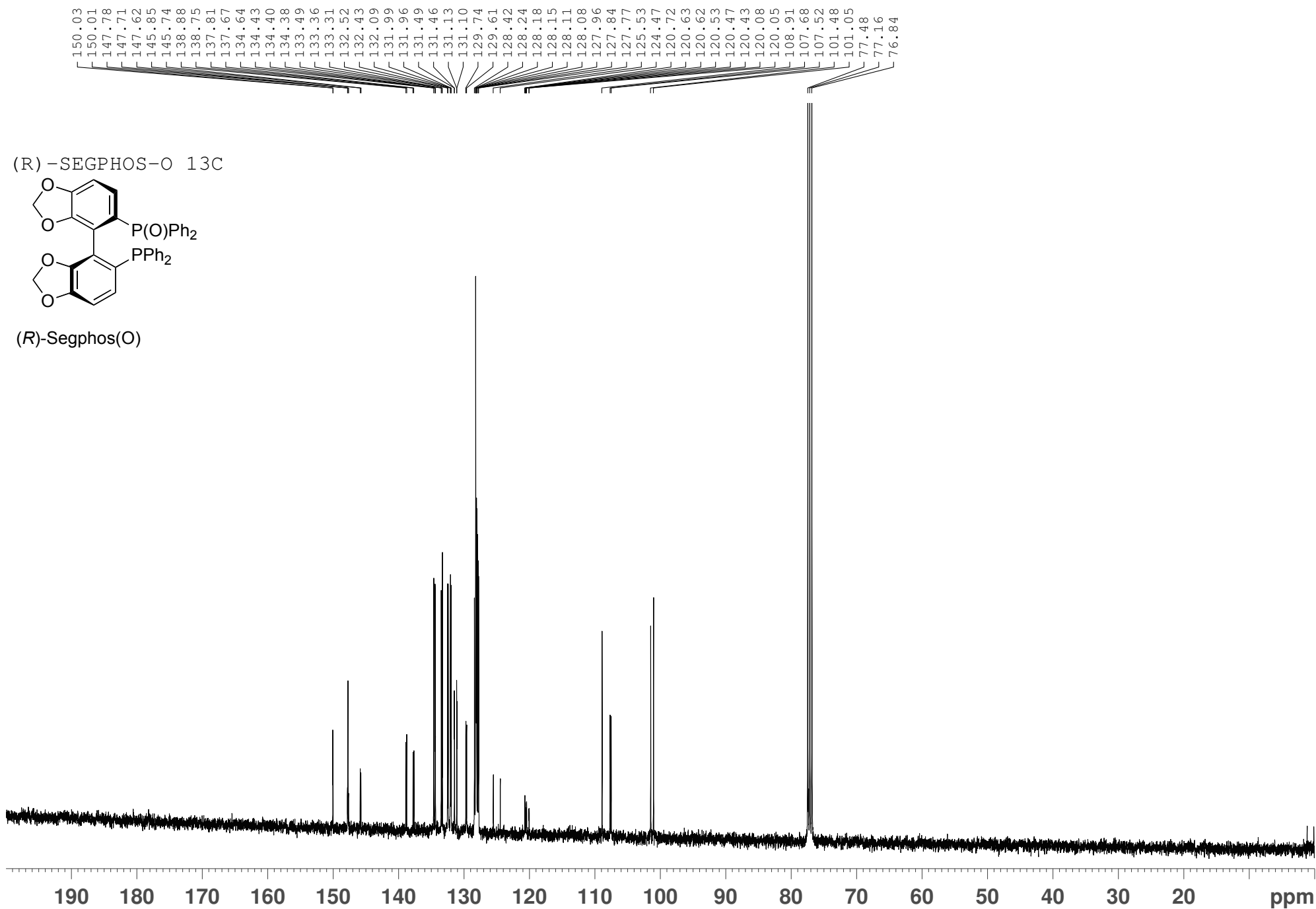


(R)-Xyl-SDP(O)



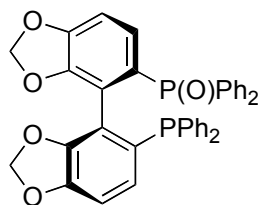


¹³C NMR (100 MHz, CDCl₃)

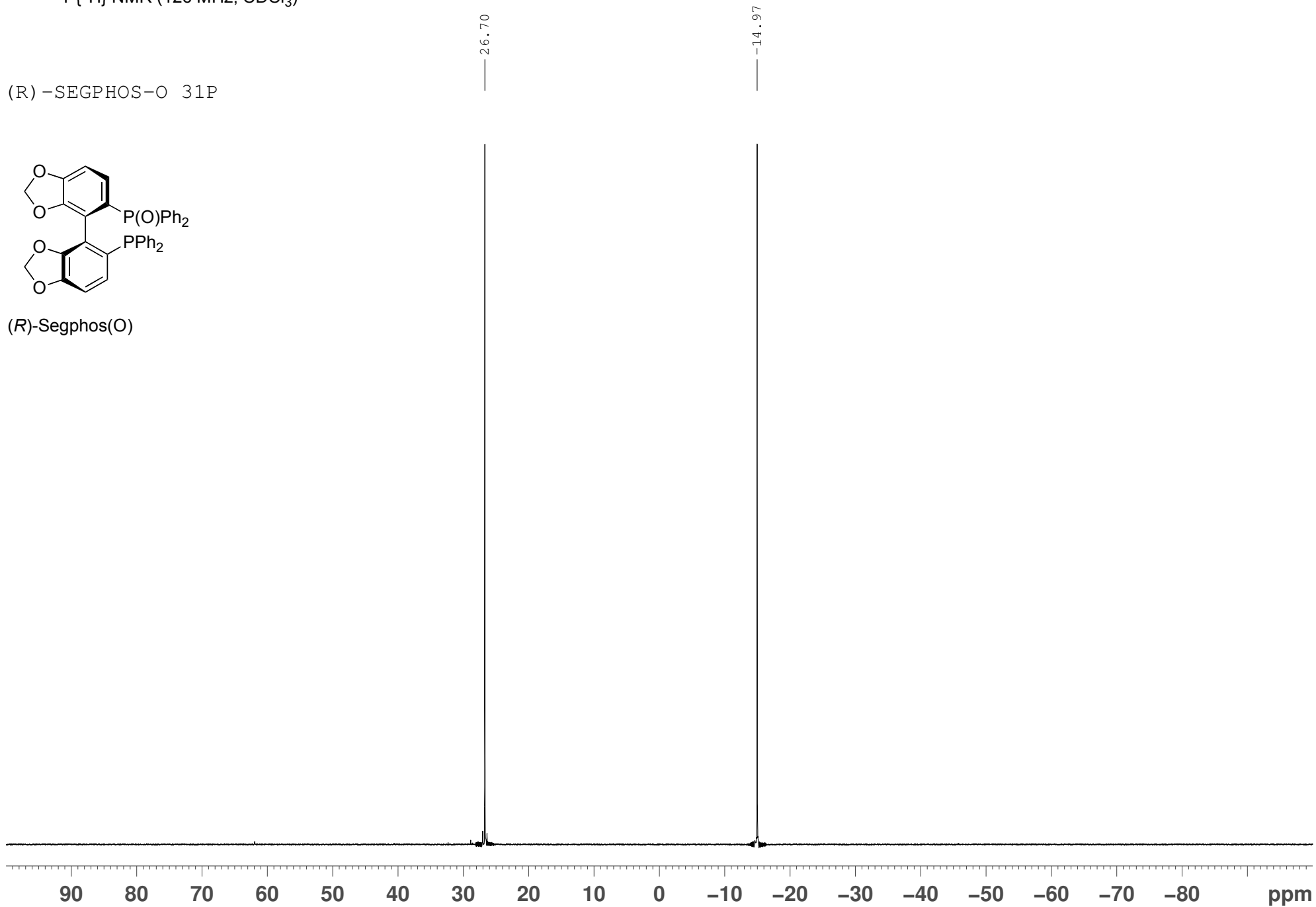


$^{31}\text{P}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

(R)-SEGPHOS-O 31P

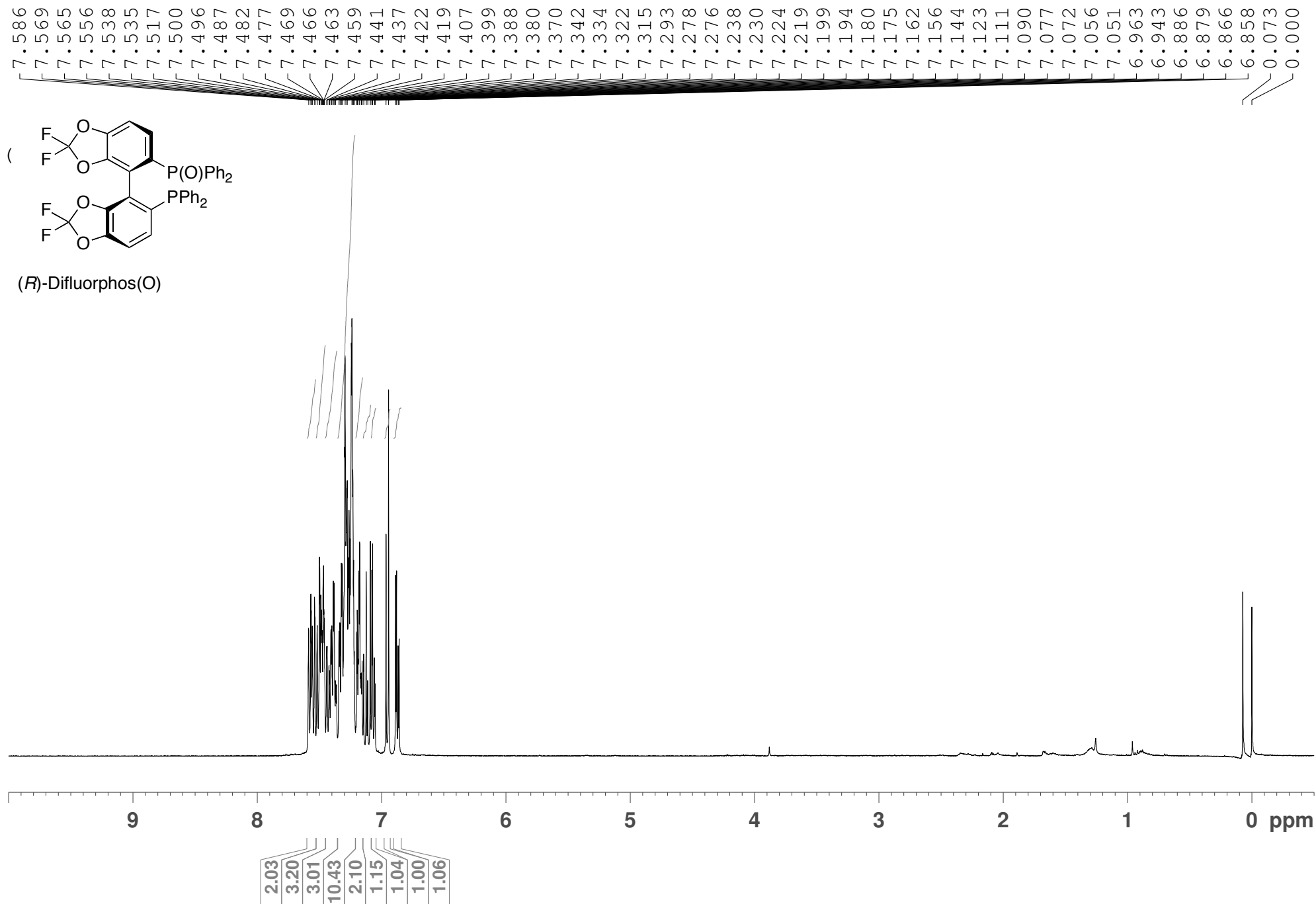


(R)-Segphos(O)

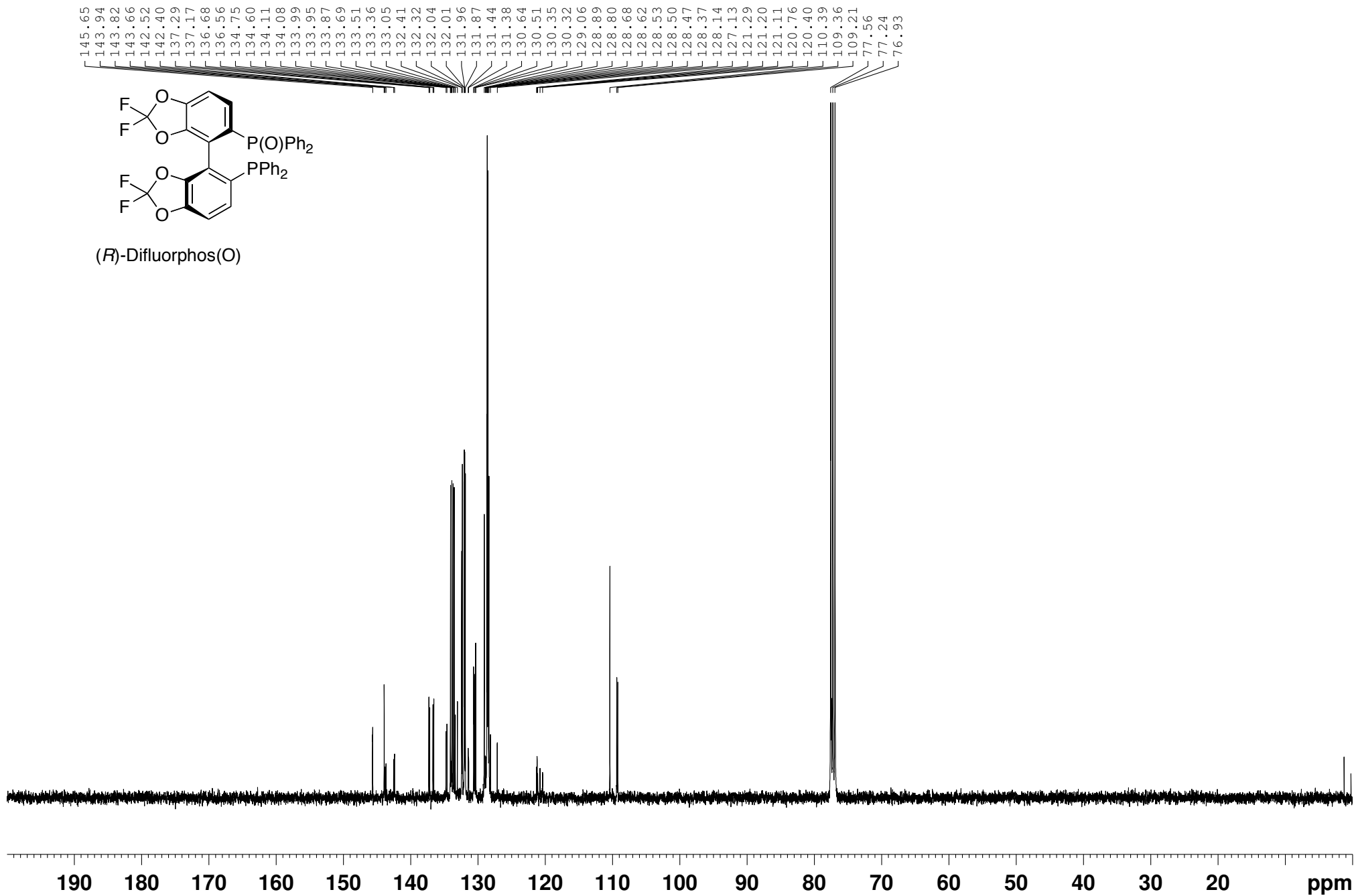


^1H NMR (400 MHz, CDCl_3)

S13

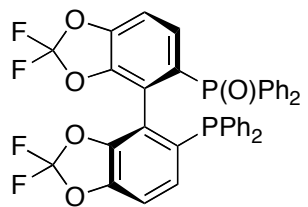


^{13}C NMR (100 MHz, CDCl_3)



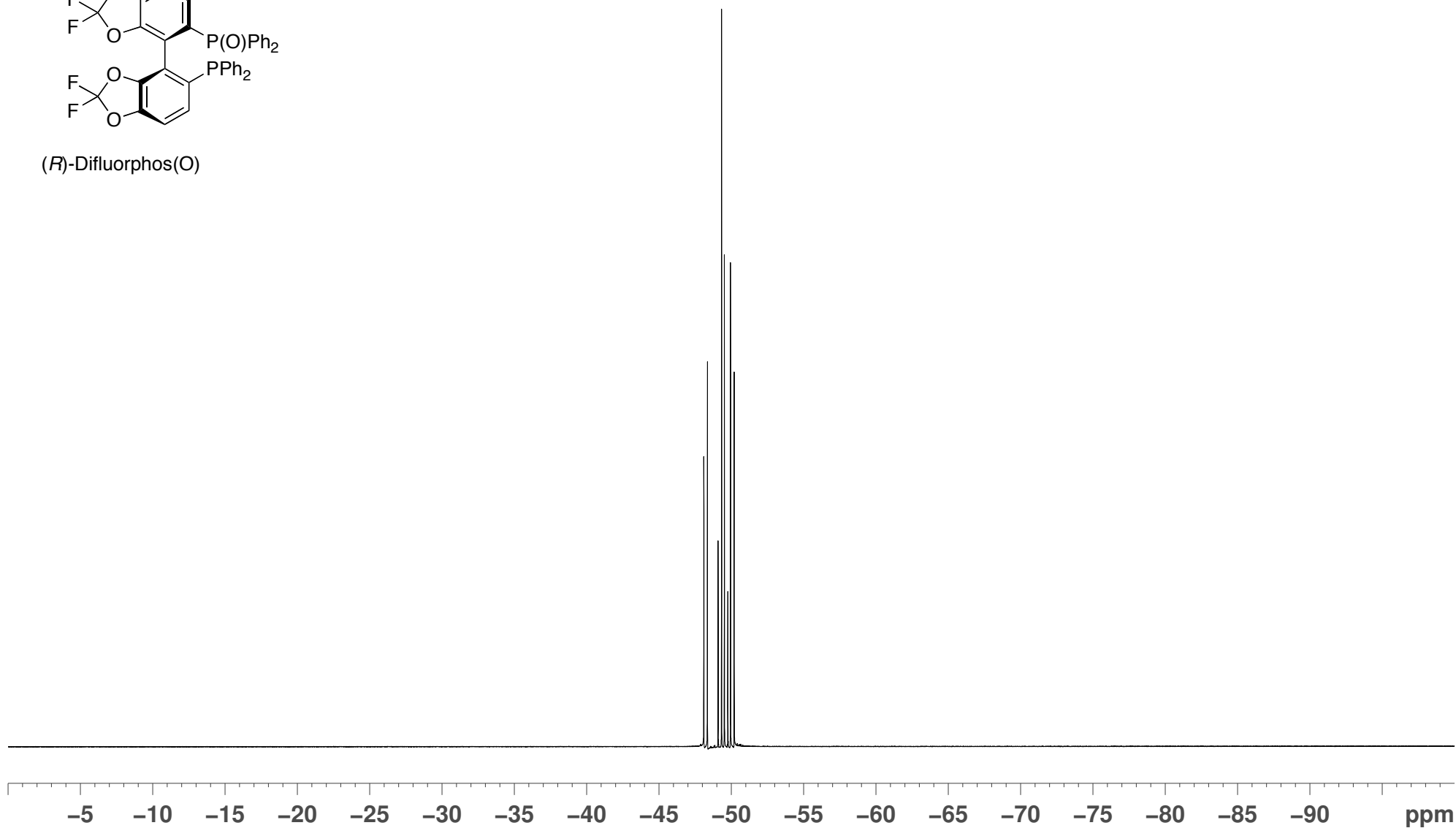
$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3)

(R)-DIFLUOROPHOS-O 19F

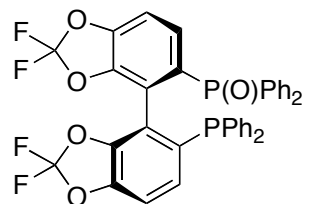


(R)-Difluorophos(O)

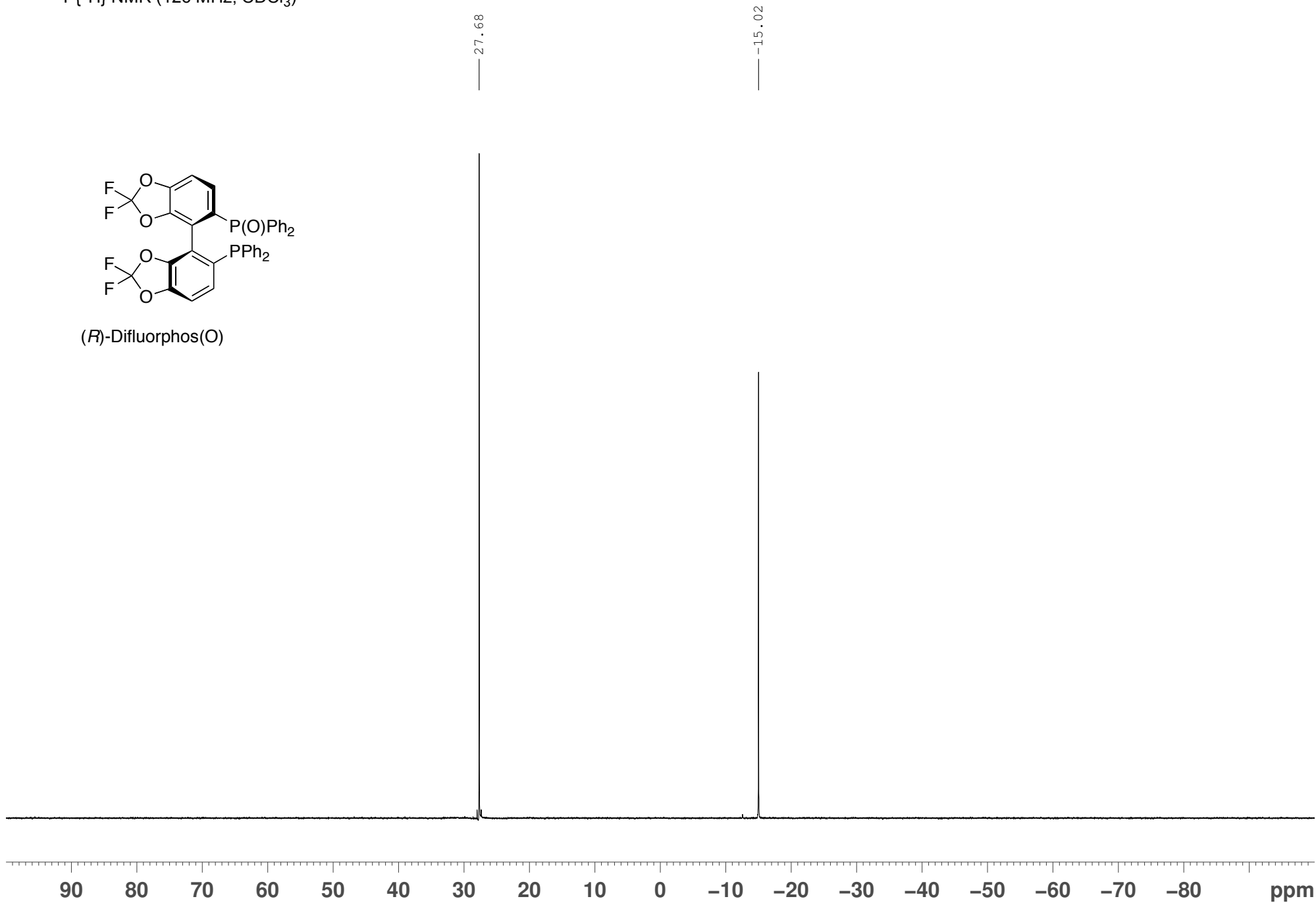
-48.10
-48.35
-49.09
-49.32
-49.52
-49.76
-49.94
-50.19



$^{31}\text{P}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)



(*R*)-Difluorophos(O)



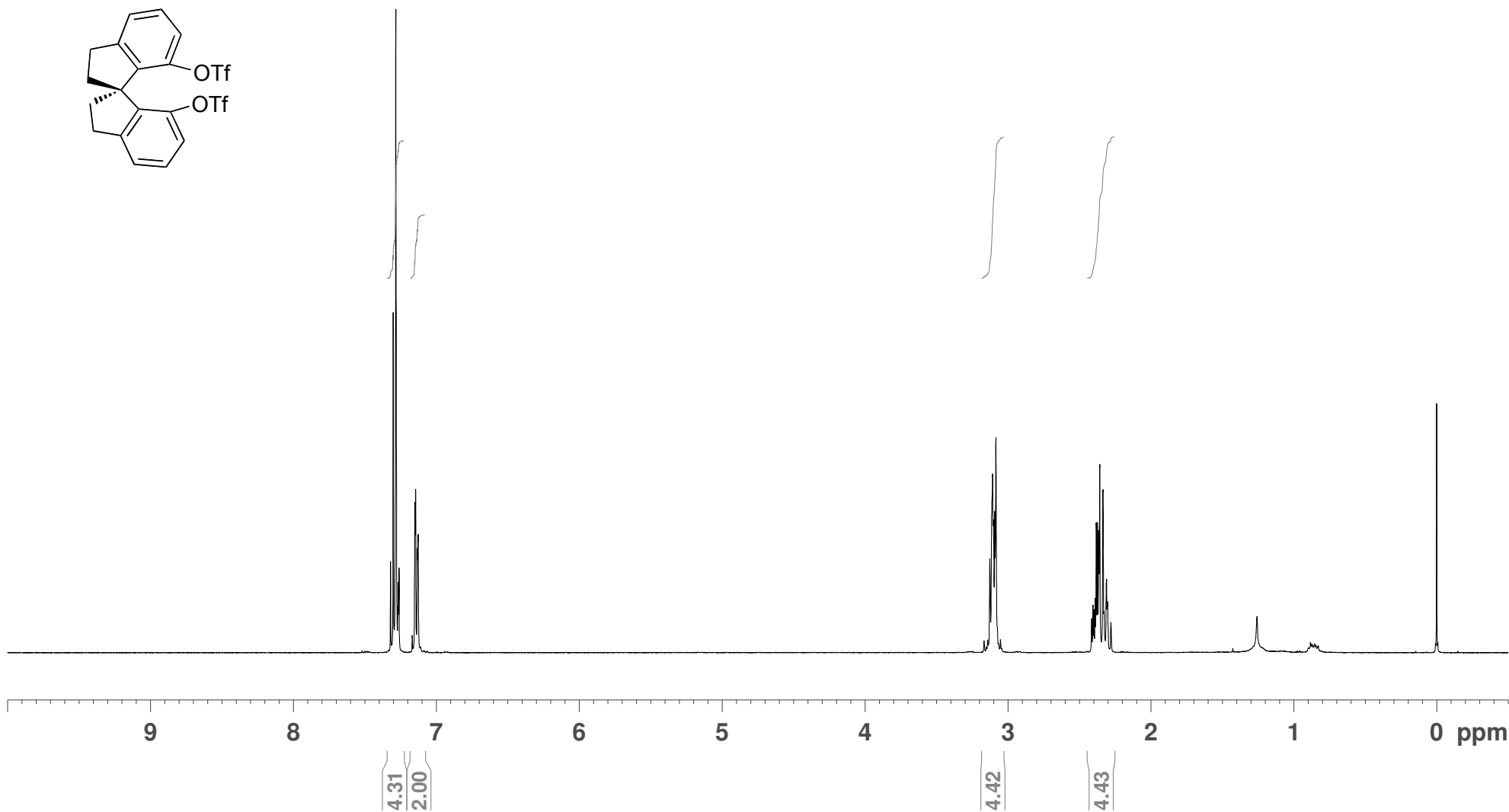
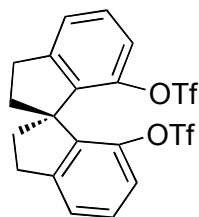
^1H NMR (400 MHz, CDCl_3)

7.319
7.300
7.282
7.279
7.265
7.259
7.166
7.150
7.145
7.132
7.127

3.168
3.126
3.110
3.107
3.101
3.092
3.084
3.053
2.414
2.382
2.374
2.365
2.357
2.335
2.310
2.280

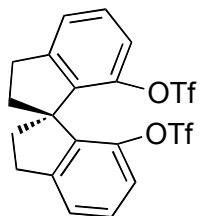
— 0.000

(R)-SPINOL-OTf

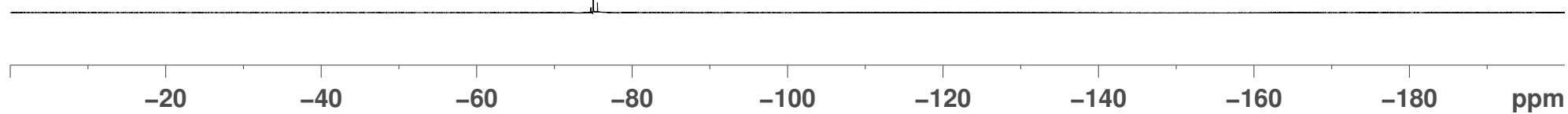


$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3)

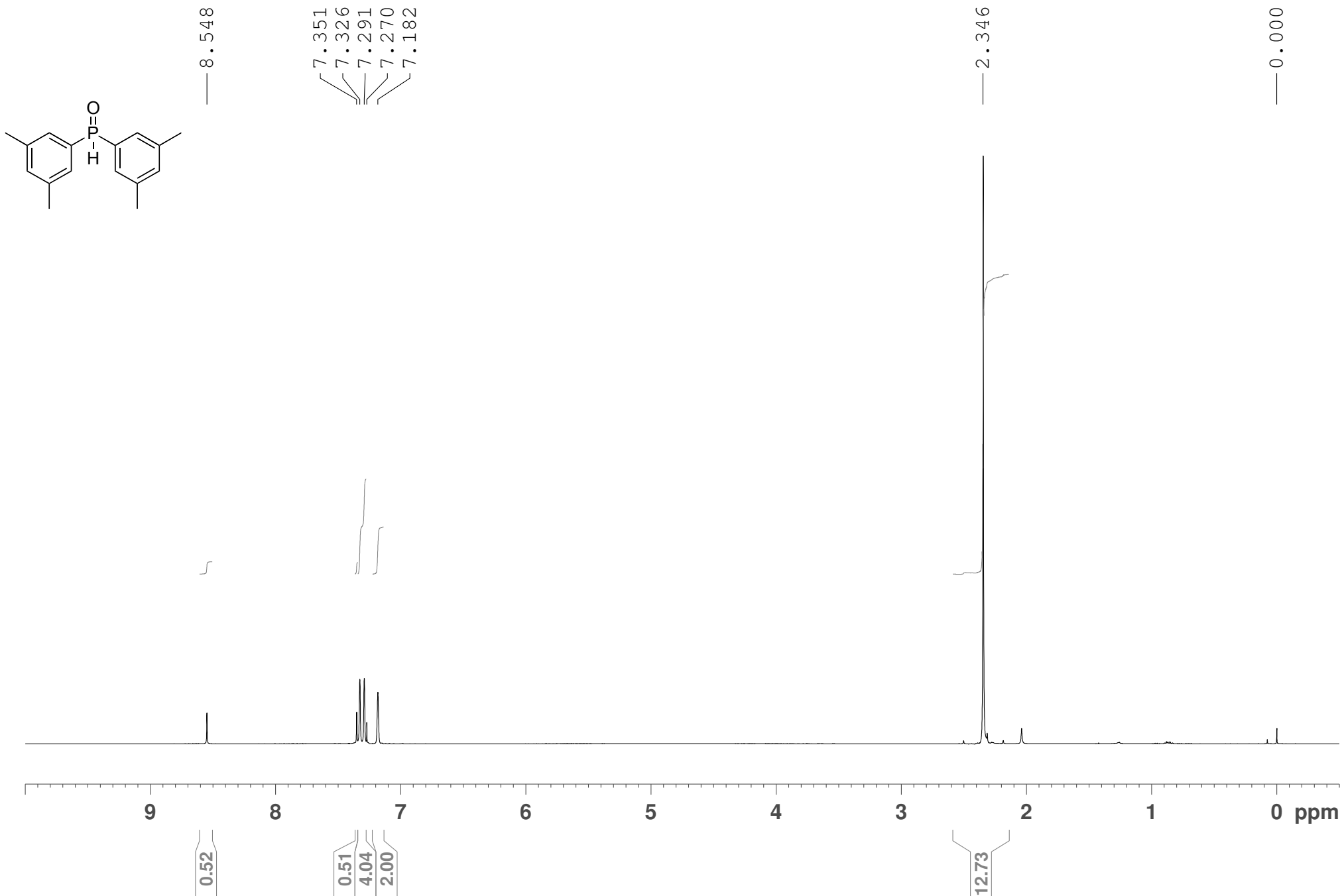
(R)-SPINOL-OTf 19F



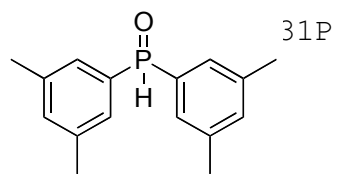
—75.00



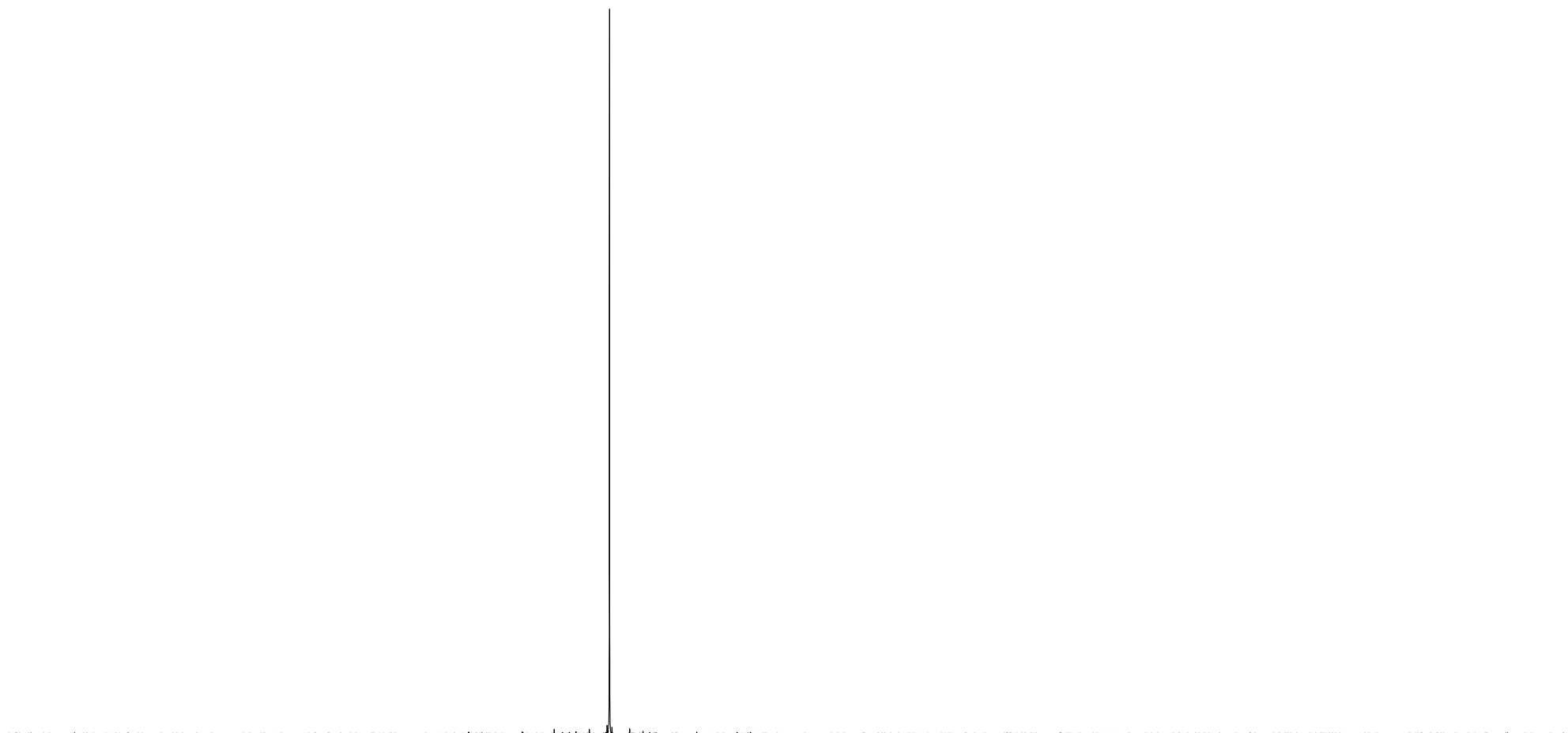
^1H NMR (400 MHz, CDCl_3)



$^{31}\text{P}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

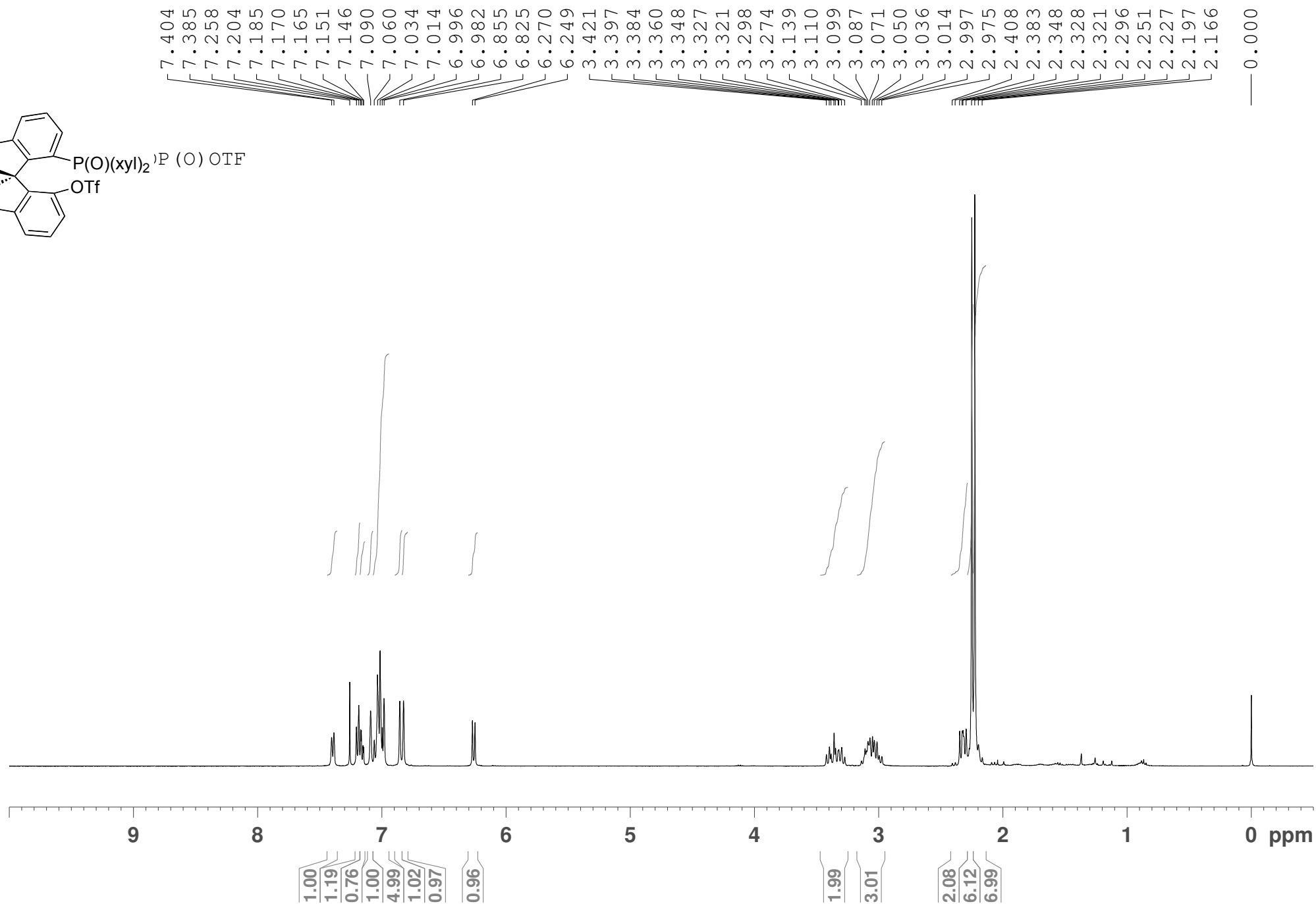
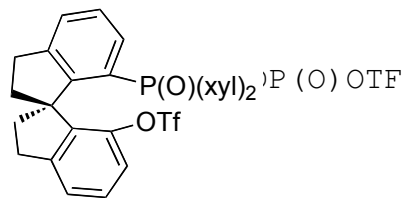


— 23.00

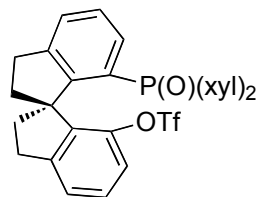


90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm

¹H NMR (400 MHz, CDCl₃)

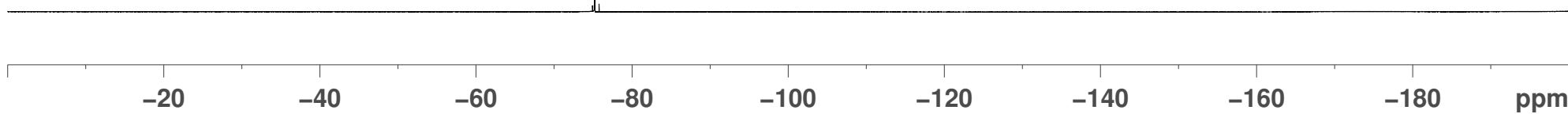


$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3)



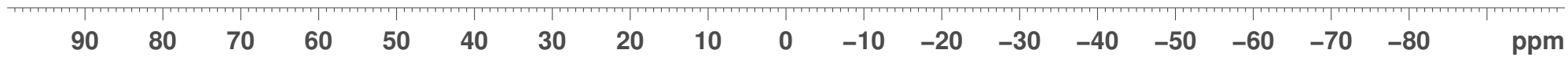
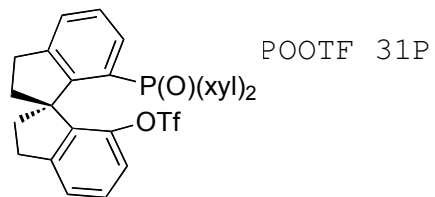
POOTF 19F

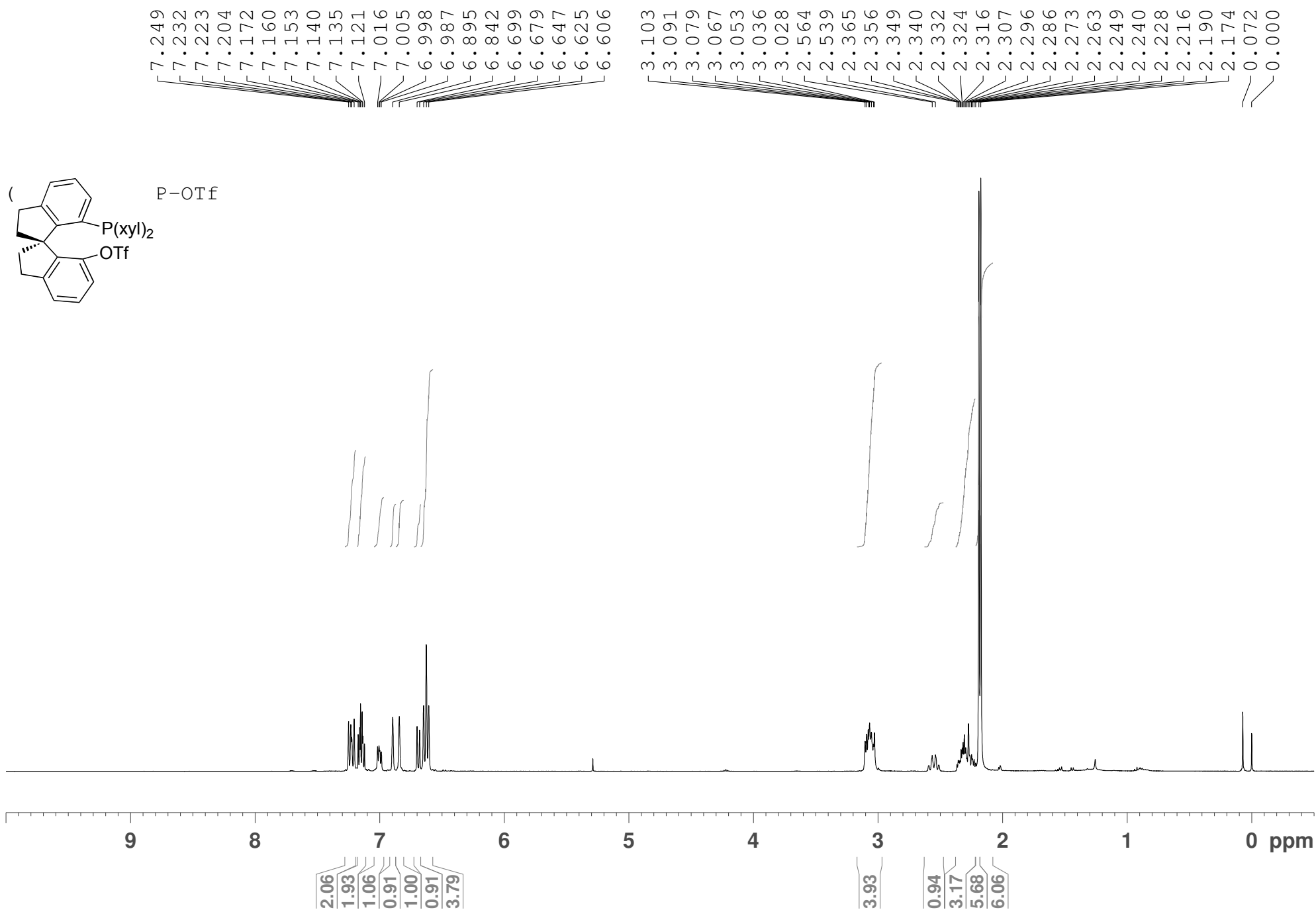
-75.23



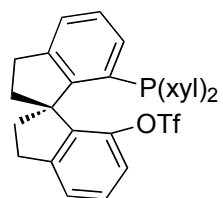
$^{31}\text{P}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

30.31



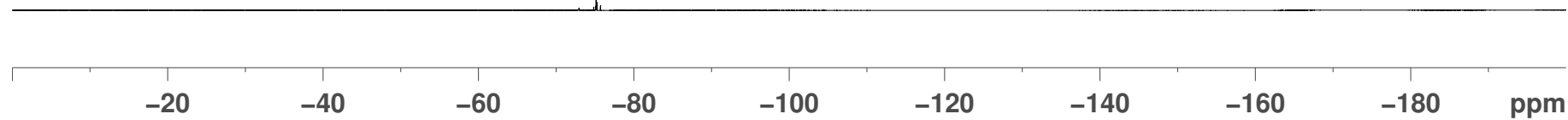


$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3)

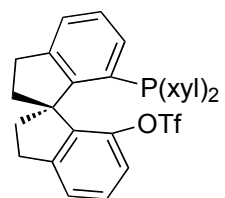


DP-OTF 19F

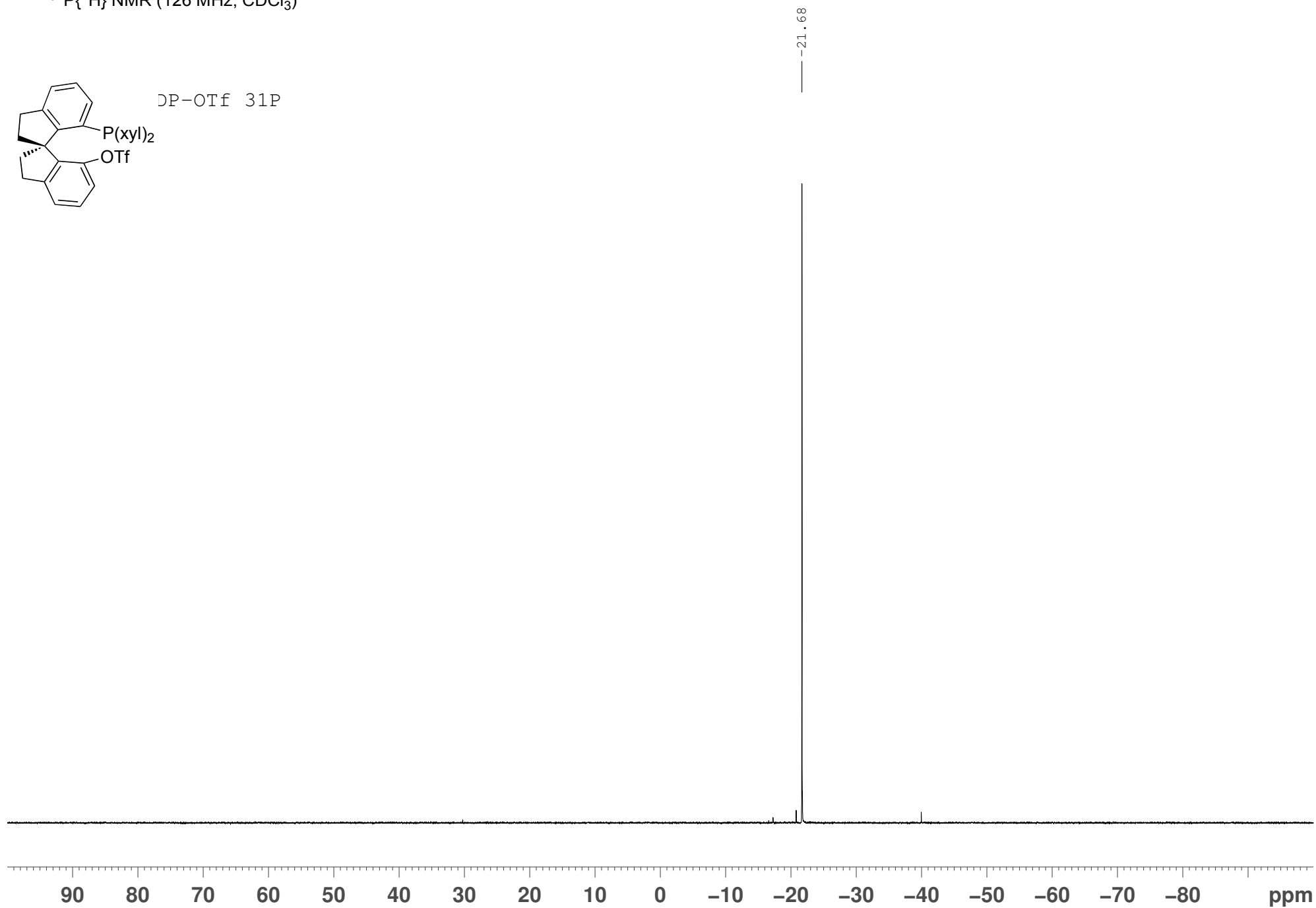
-75.13



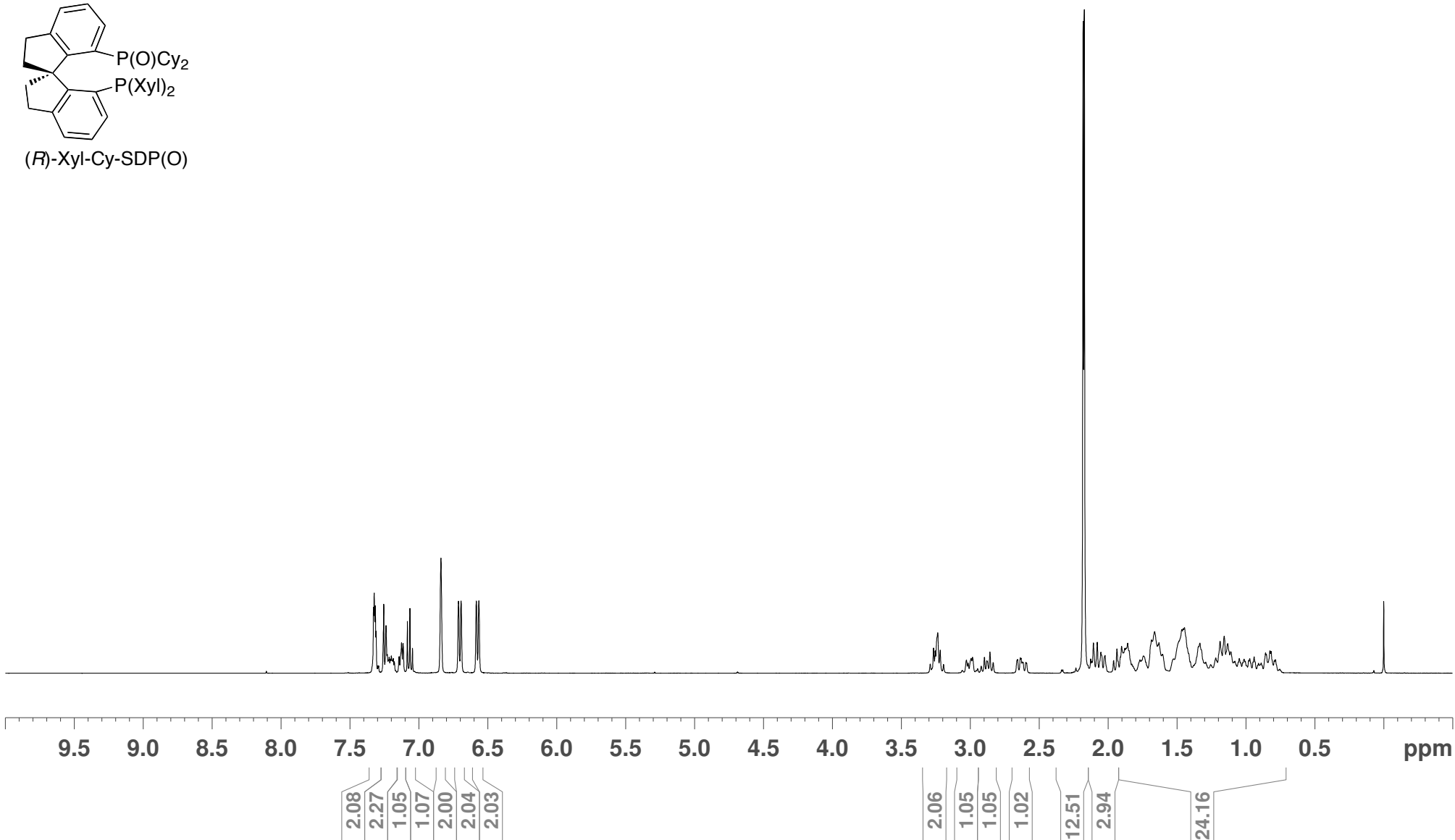
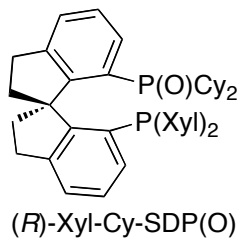
$^{31}\text{P}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)



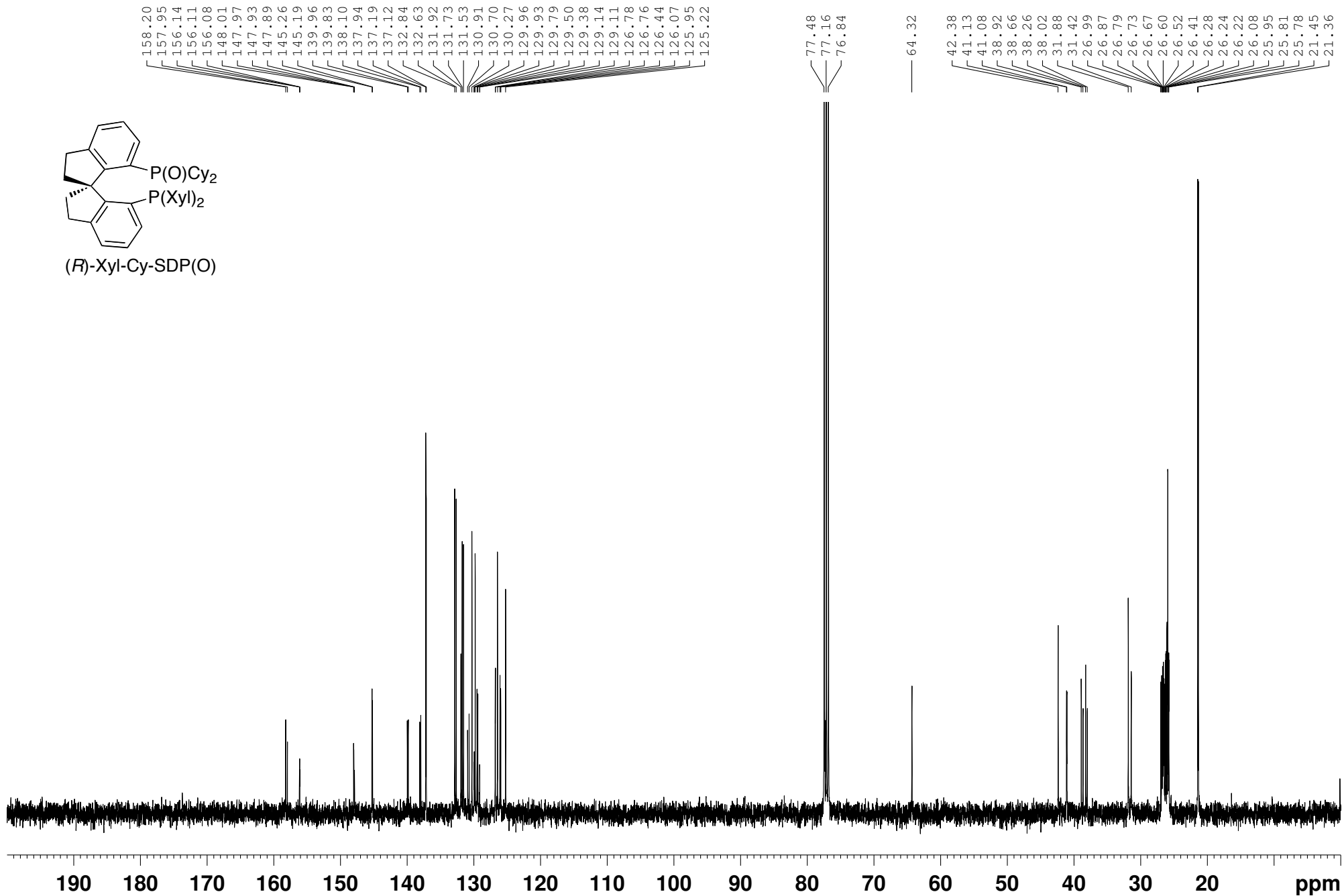
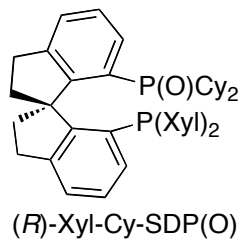
DP-OTf 31P



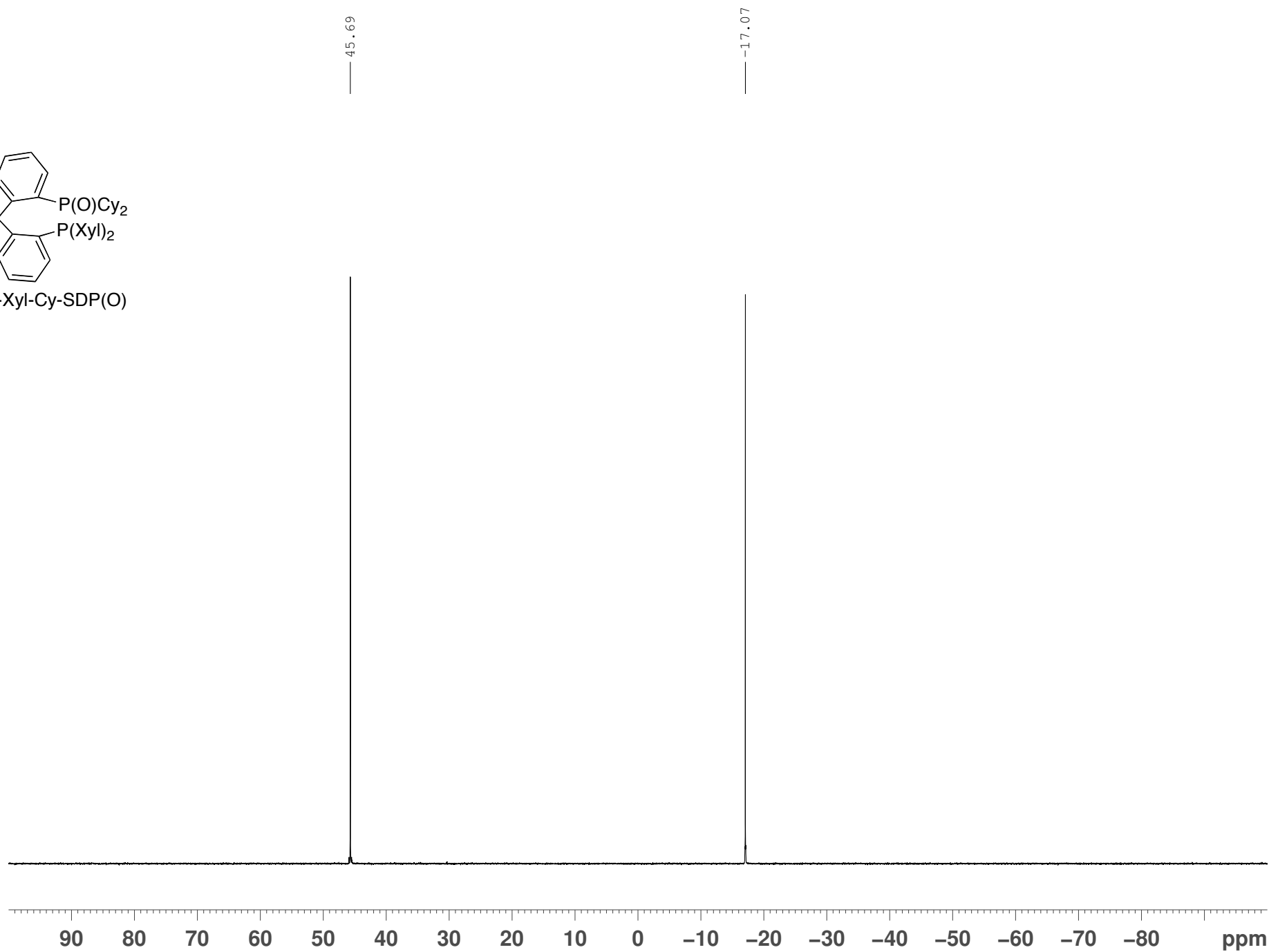
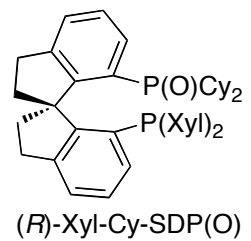
7.329
7.324
7.316
7.310
7.255
7.238
7.229
7.215
7.199
7.143
7.125
7.114
7.083
7.065
7.046
6.840
6.712
6.693
6.583
6.565
3.266
3.254
3.236
3.218
2.983
2.897
2.857
2.636
2.181
2.172
2.106
2.078
2.052
2.022
1.935
1.911
1.902
1.879
1.869
1.857
1.847
1.743
1.685
1.663
1.631
1.605
1.465
1.455
1.446
1.334
1.187
1.158
1.132
1.109
0.940
0.857
0.826
0.818
0.000



^{13}C NMR (100 MHz, CDCl_3)



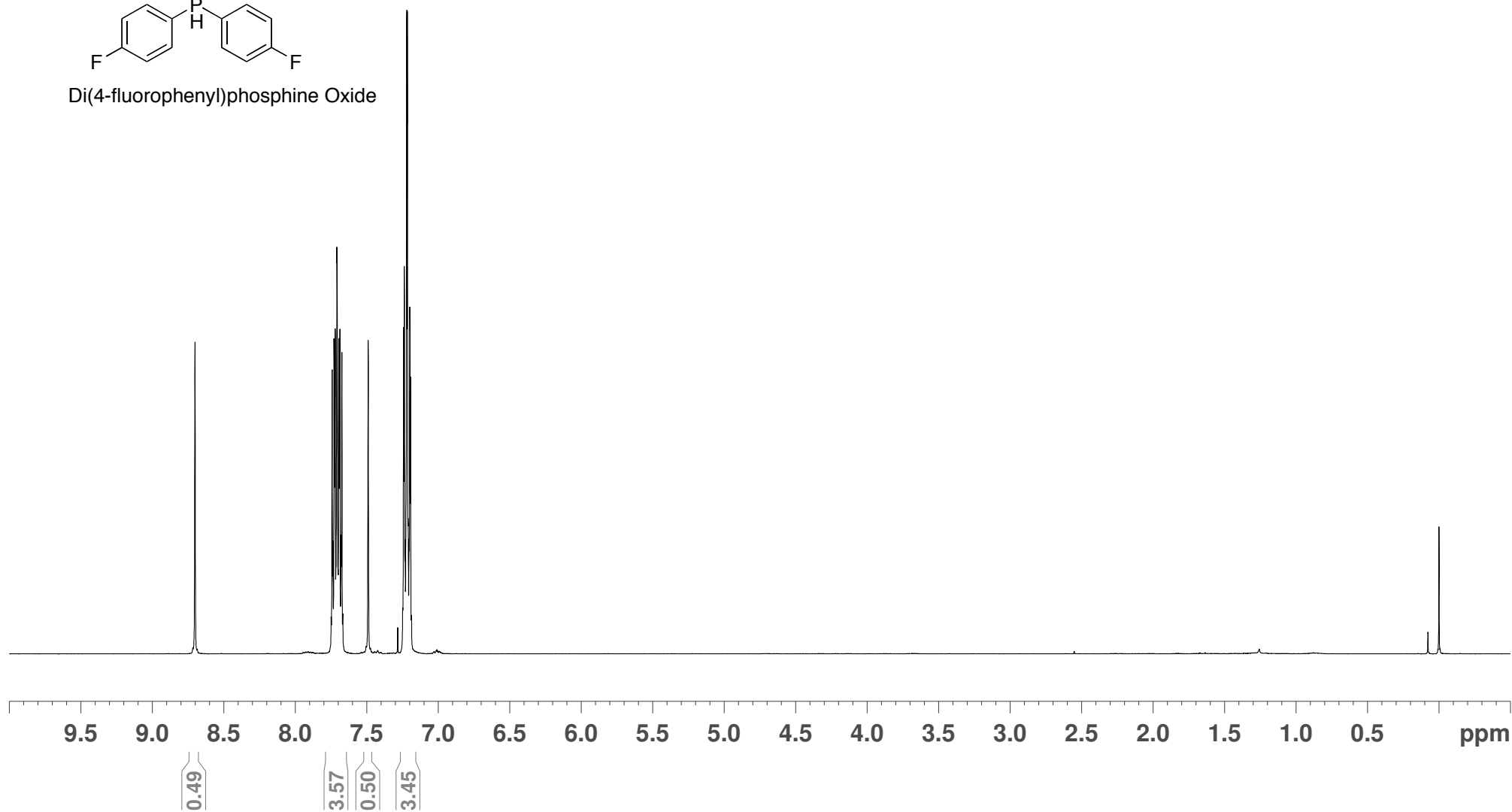
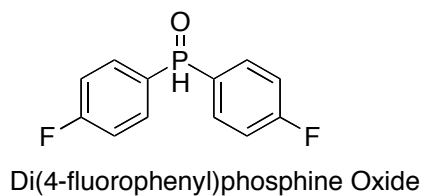
$^{31}\text{P}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)



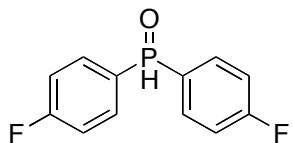
¹H NMR (400 MHz, CDCl₃)

8.700
7.741
7.736
7.727
7.725
7.719
7.708
7.706
7.699
7.694
7.686
7.678
7.673
7.489
7.282
7.247
7.241
7.236
7.231
7.219
7.214
7.209
7.202
7.197
7.192
7.186

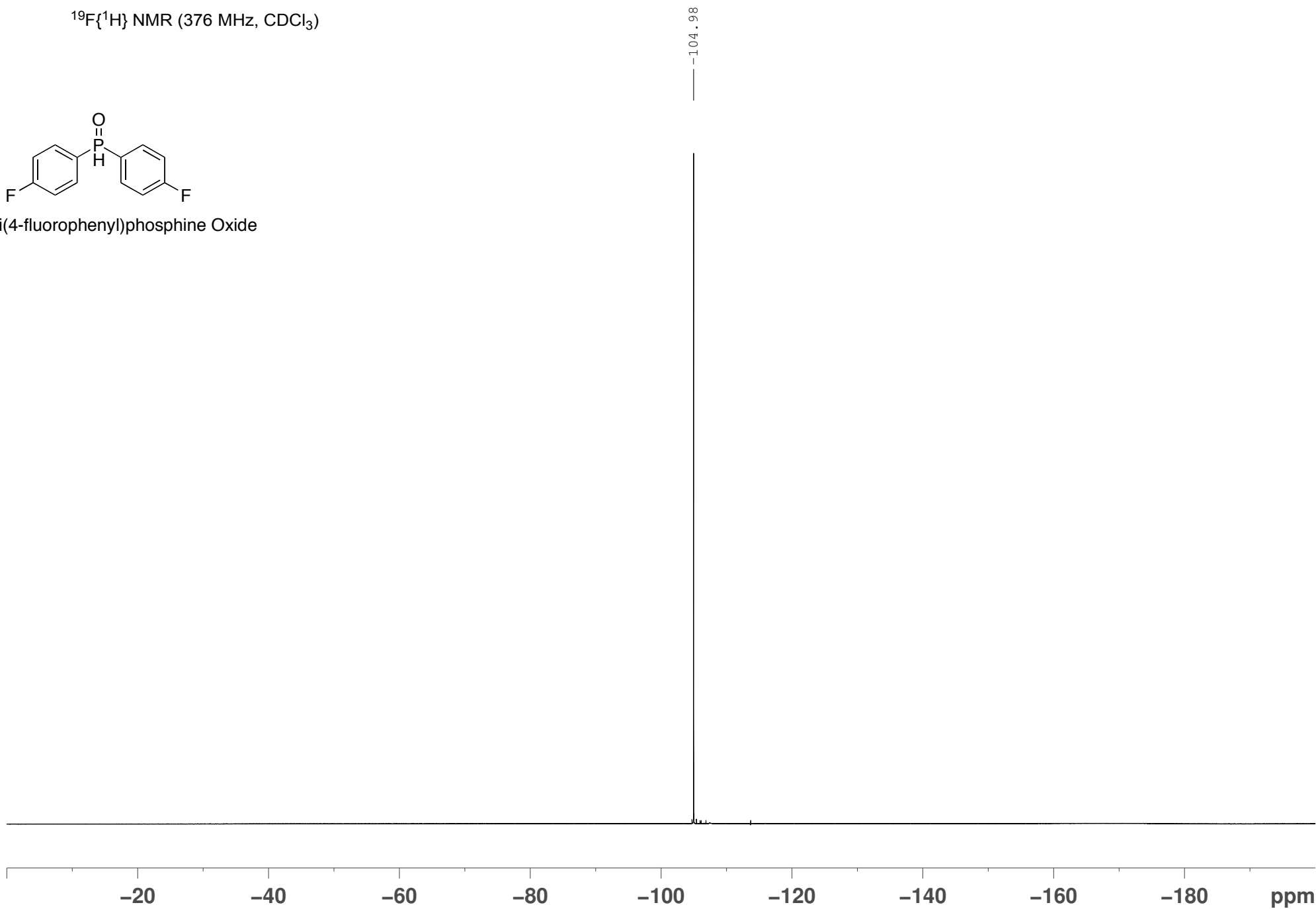
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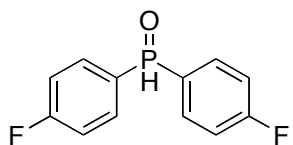
$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3)



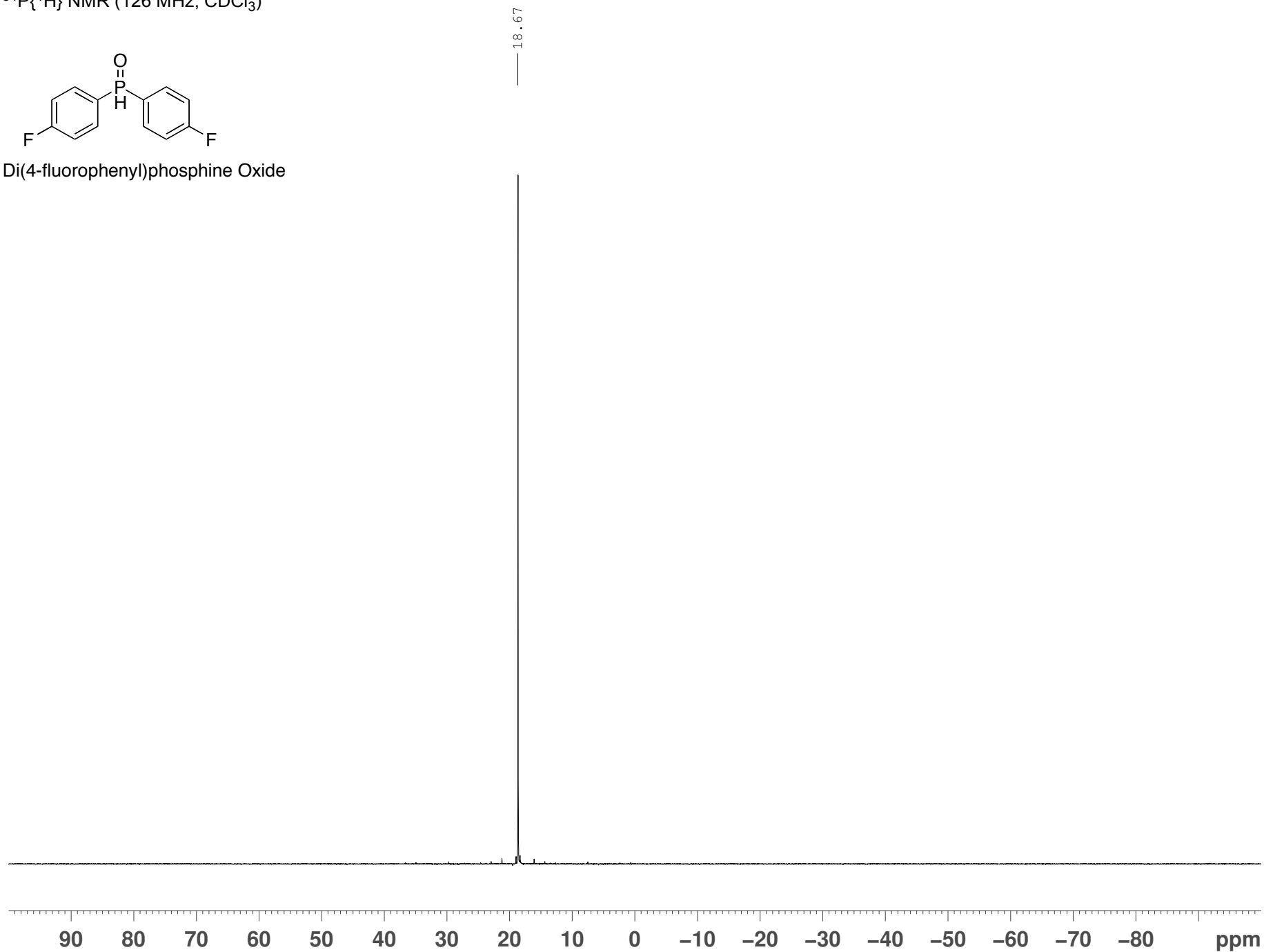
Di(4-fluorophenyl)phosphine Oxide

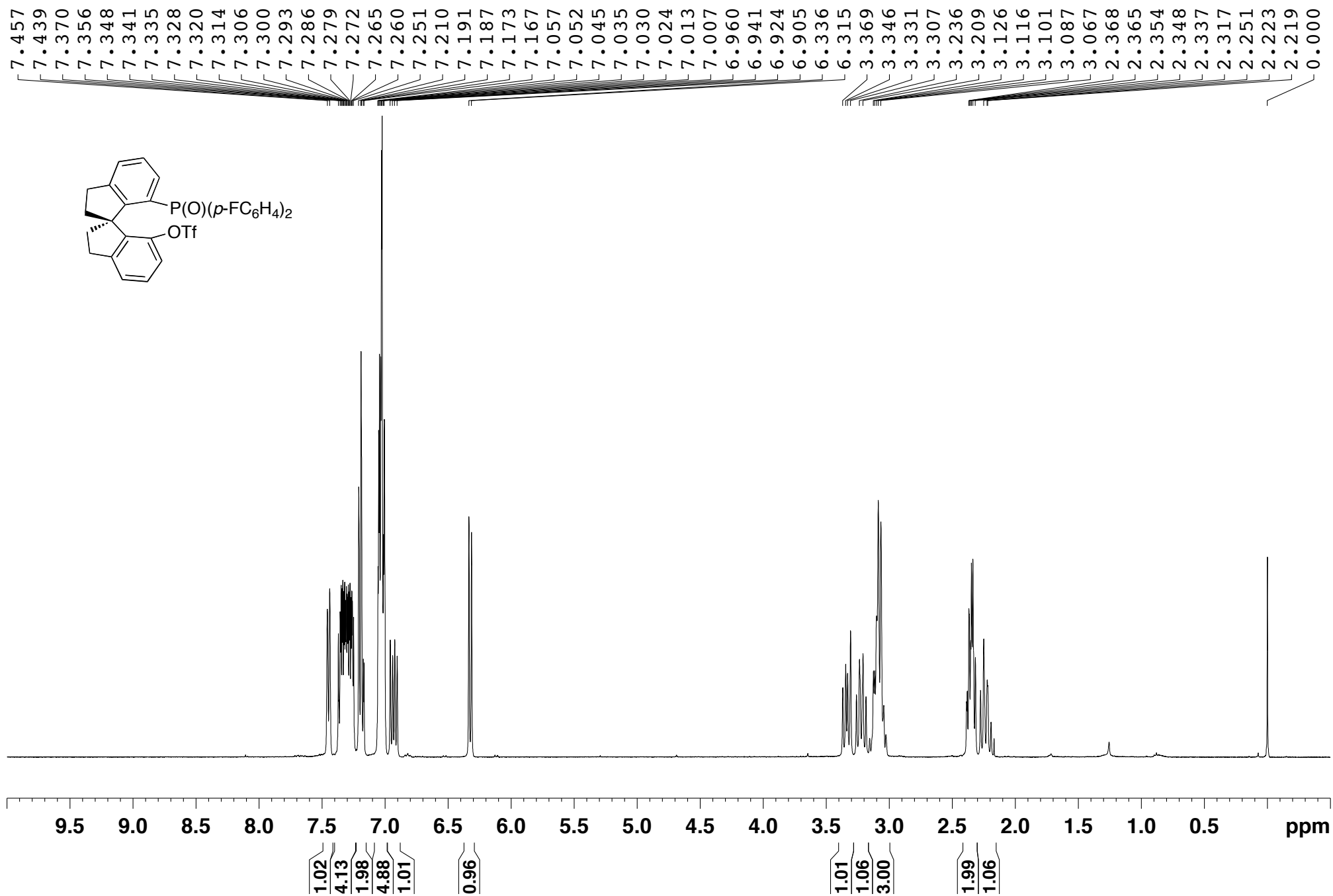


$^{31}\text{P}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)



Di(4-fluorophenyl)phosphine Oxide





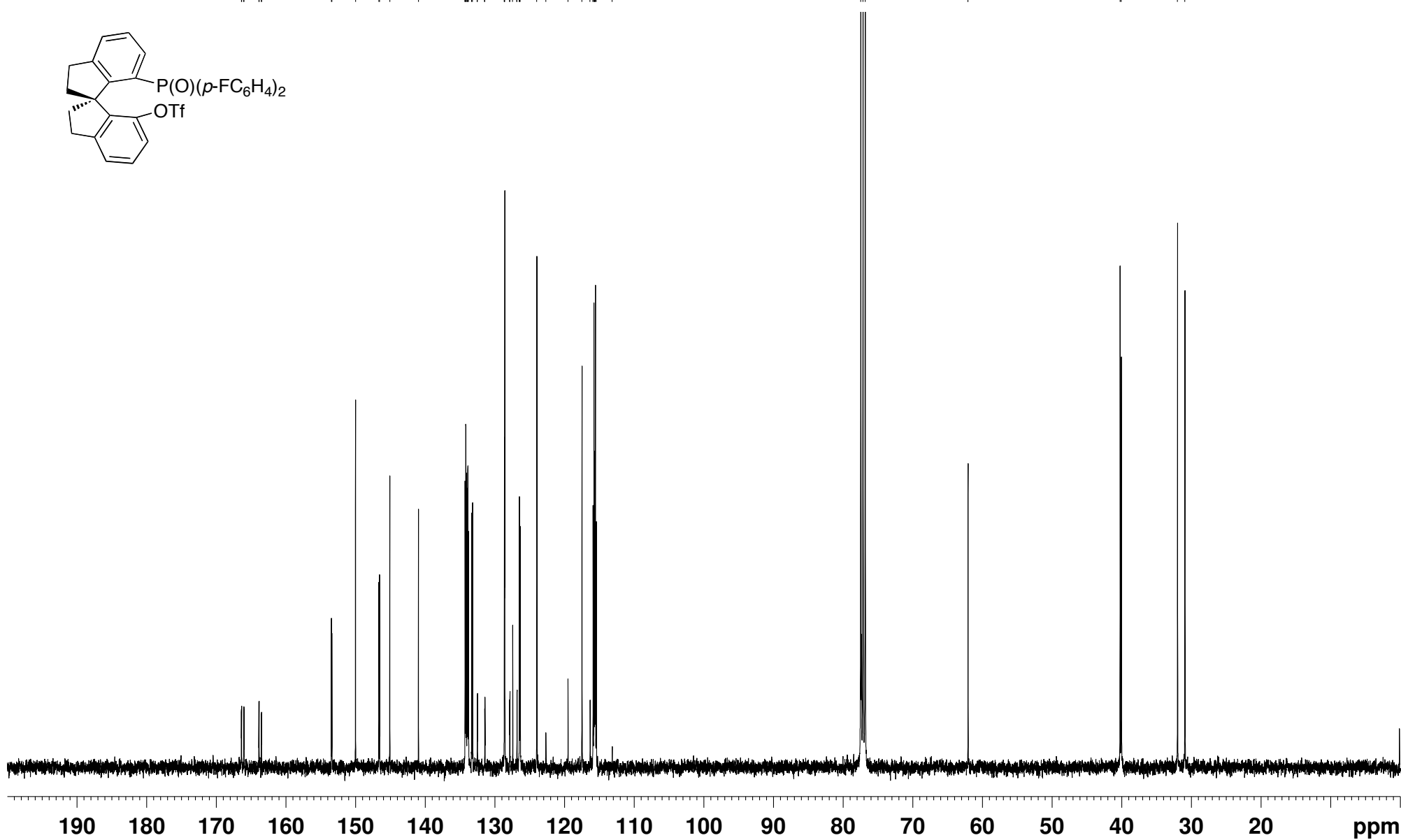
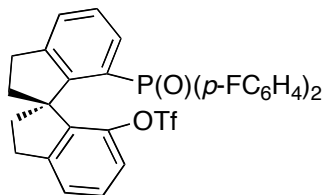
^{13}C NMR (100 MHz, CDCl_3)

166.39
166.36
166.05
166.02
163.87
163.84
163.53
163.50
153.46
153.39
150.00
146.65
146.55
145.08
140.96
134.30
134.22
134.19
134.11
134.00
133.92
133.89
133.81
133.35
133.21
132.54
132.51
131.47
131.44
128.66
128.63
128.59
127.90
127.86
127.45
126.85
126.82
126.51
126.44
126.38
123.99
122.69
119.51
117.51
116.34
115.92
115.79
115.71
115.66
115.58
115.45
113.16
77.48
77.16
76.84

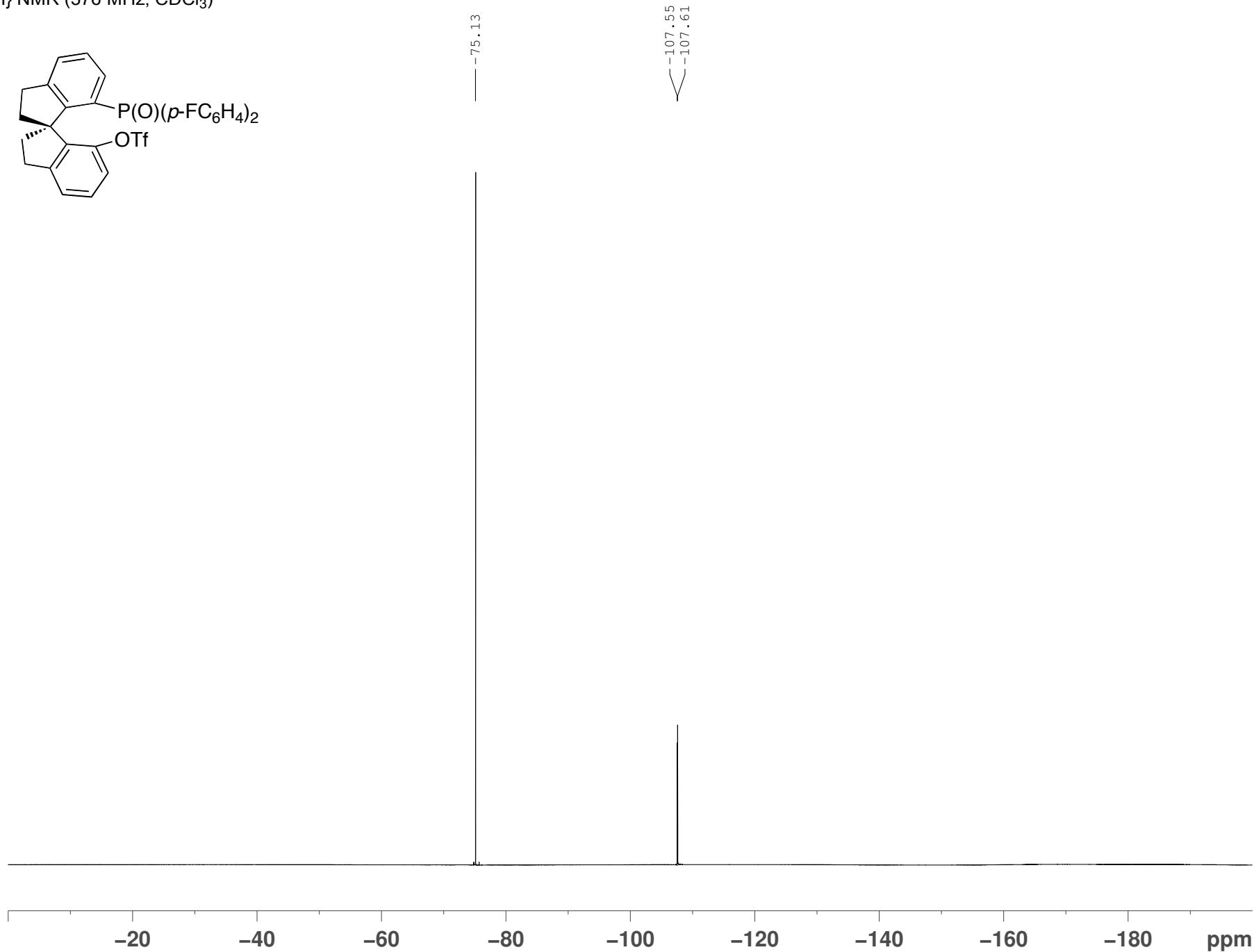
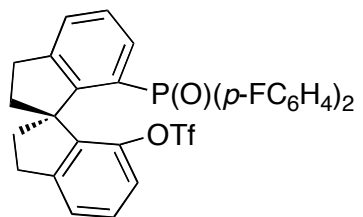
62.09
62.07

40.24
40.06

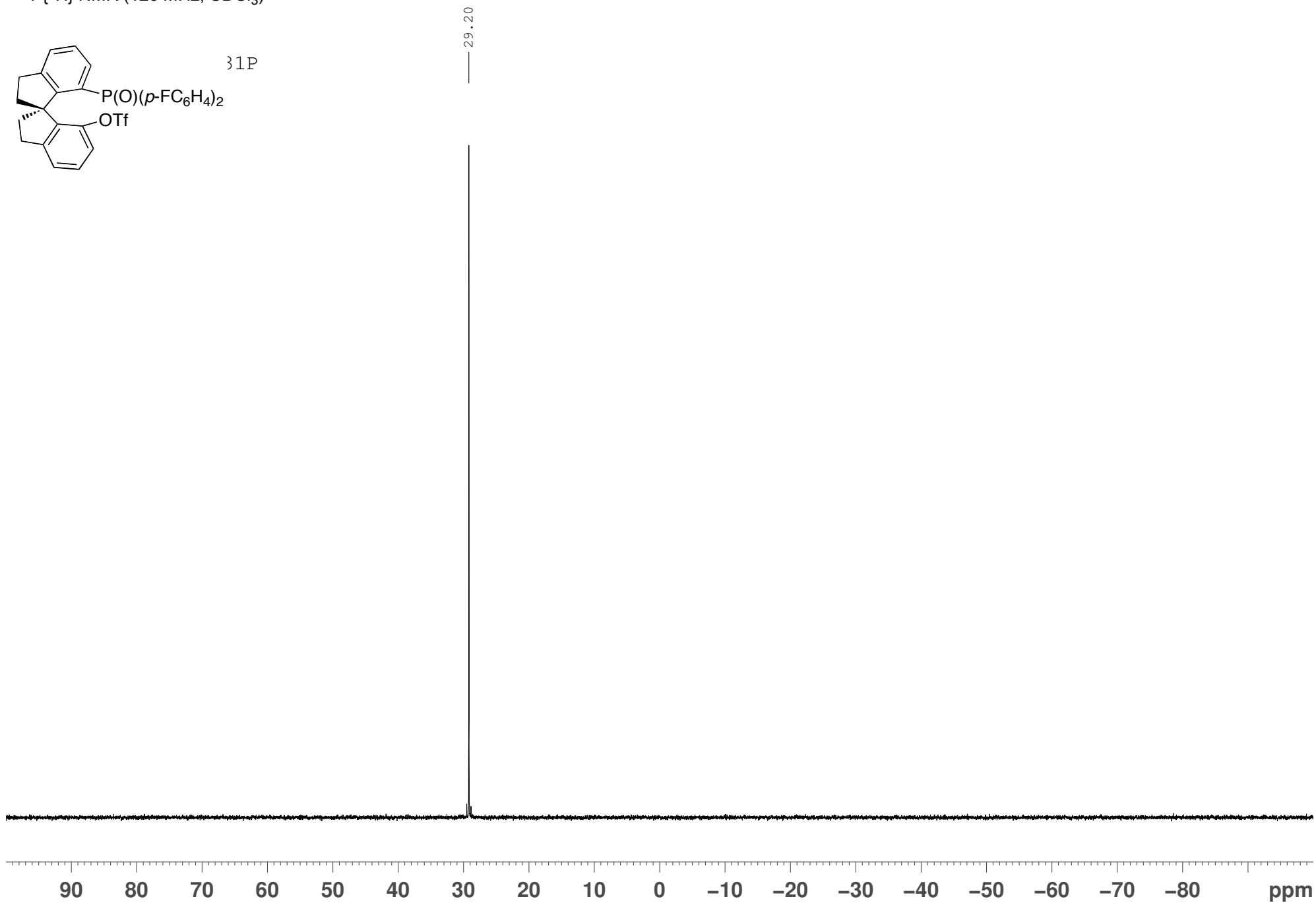
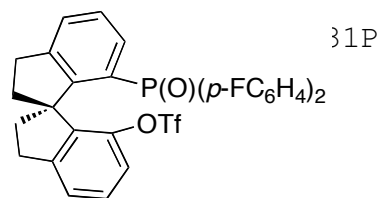
31.99
30.93

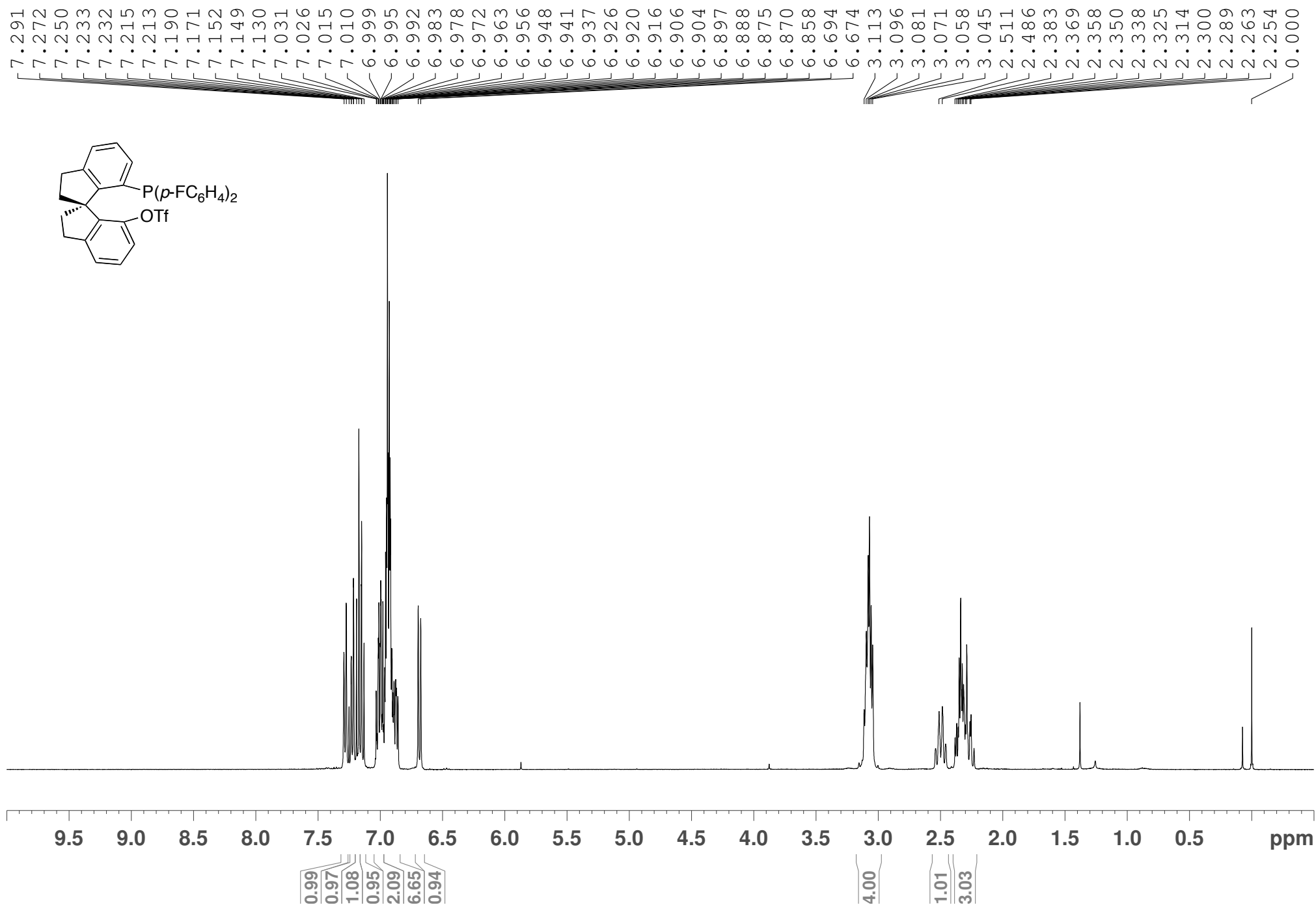


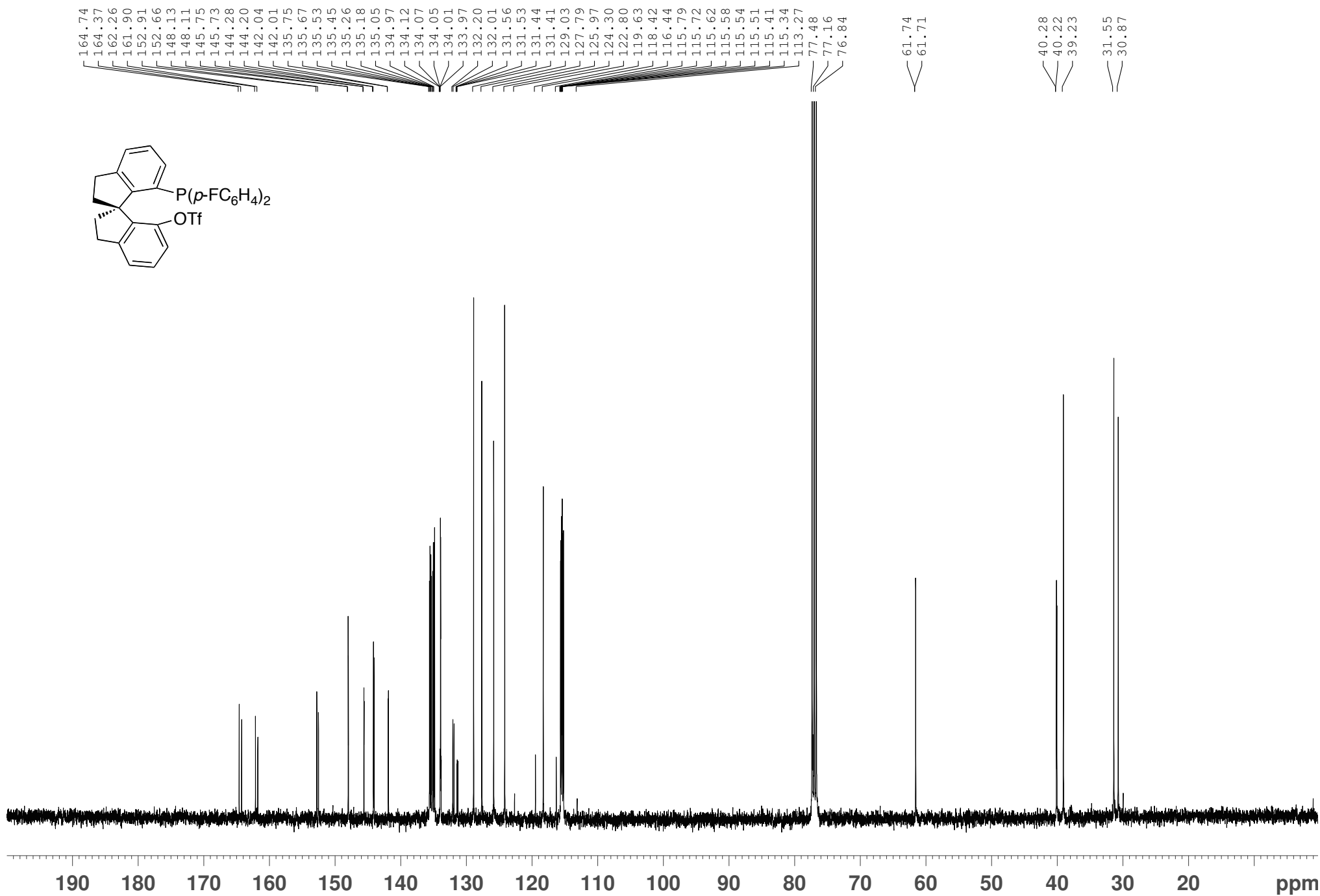
$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3)



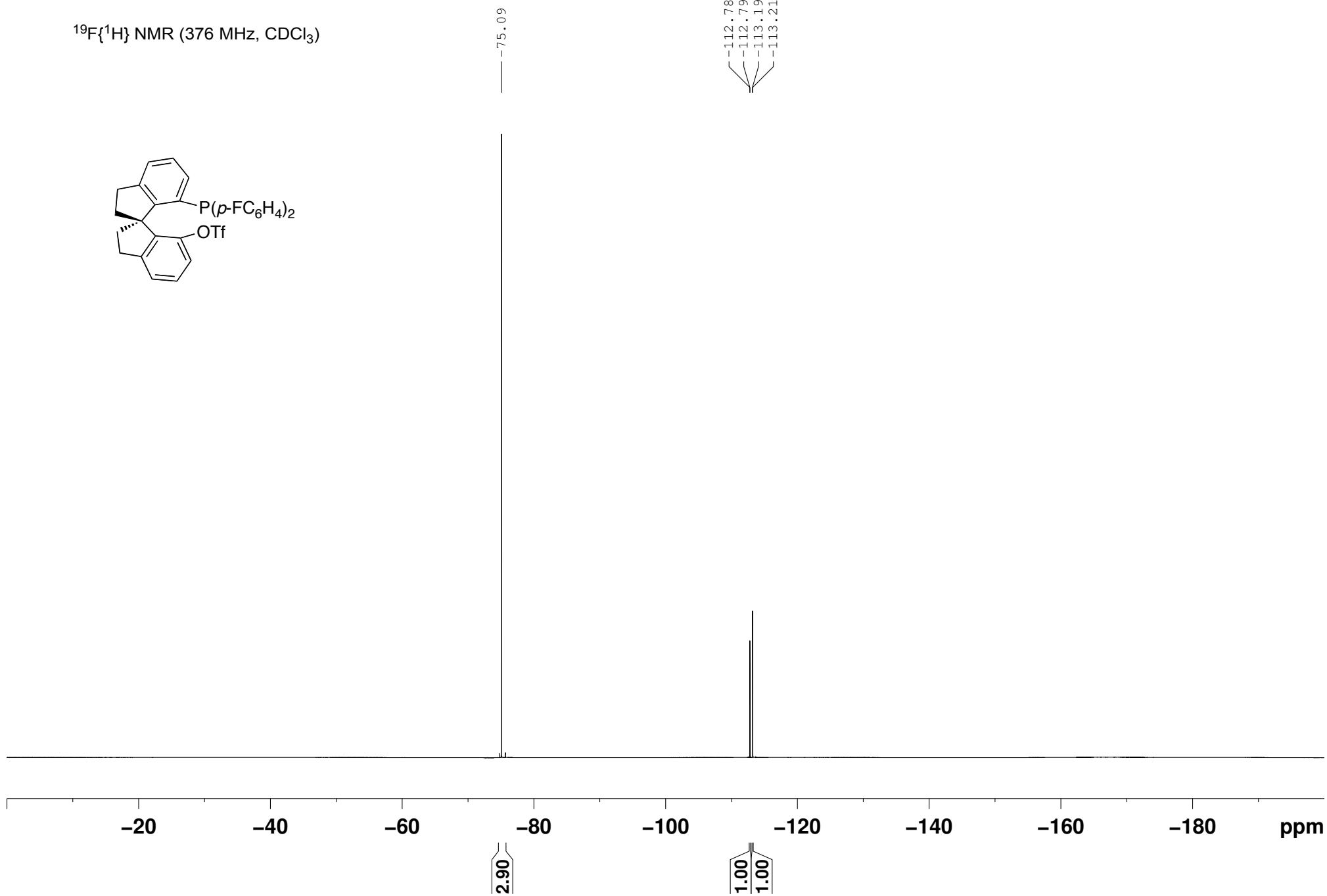
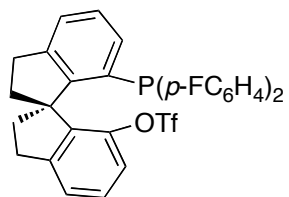
$^{31}\text{P}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)



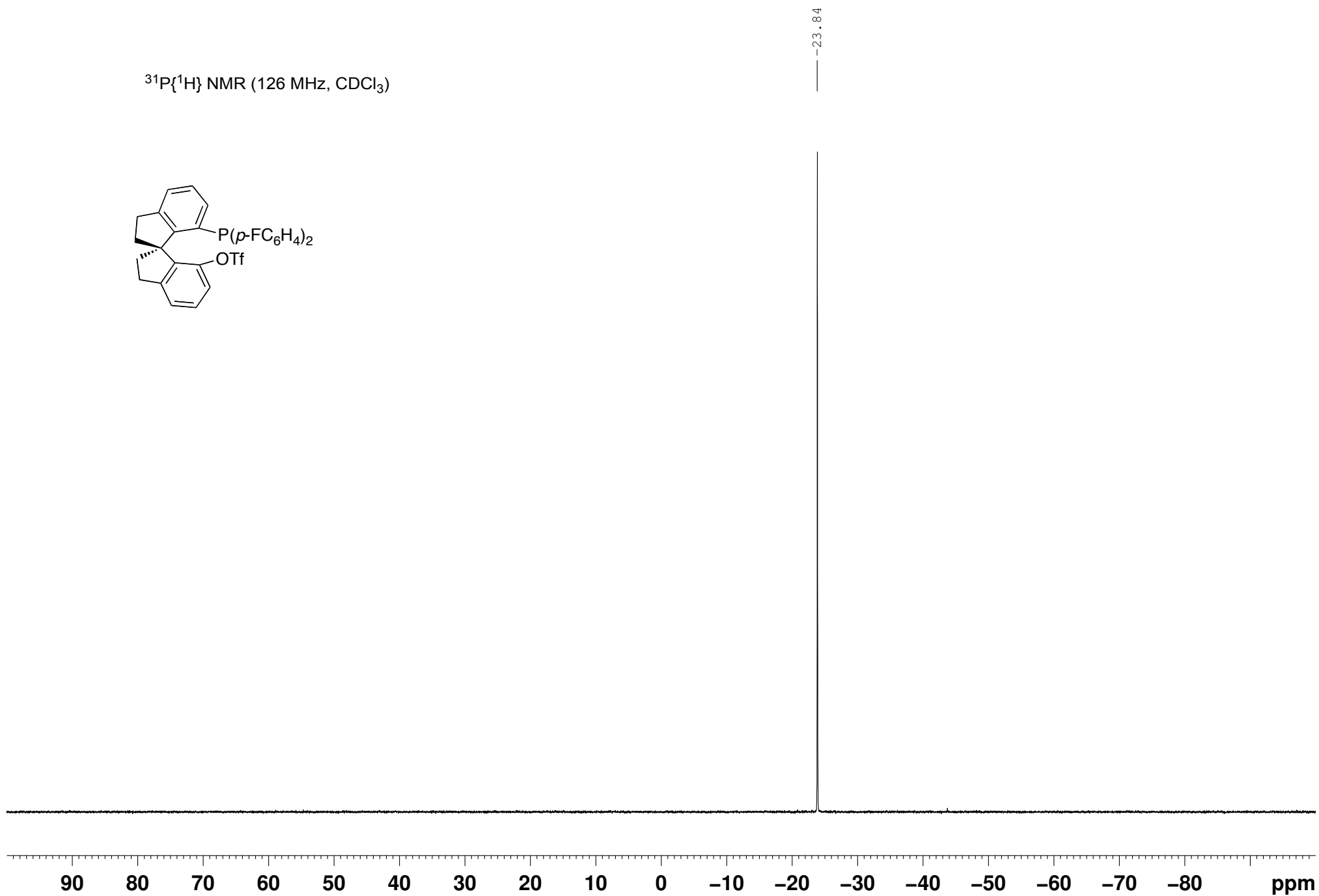
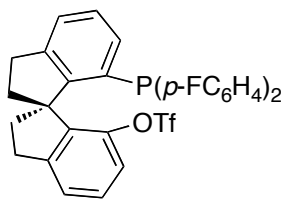




$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3)

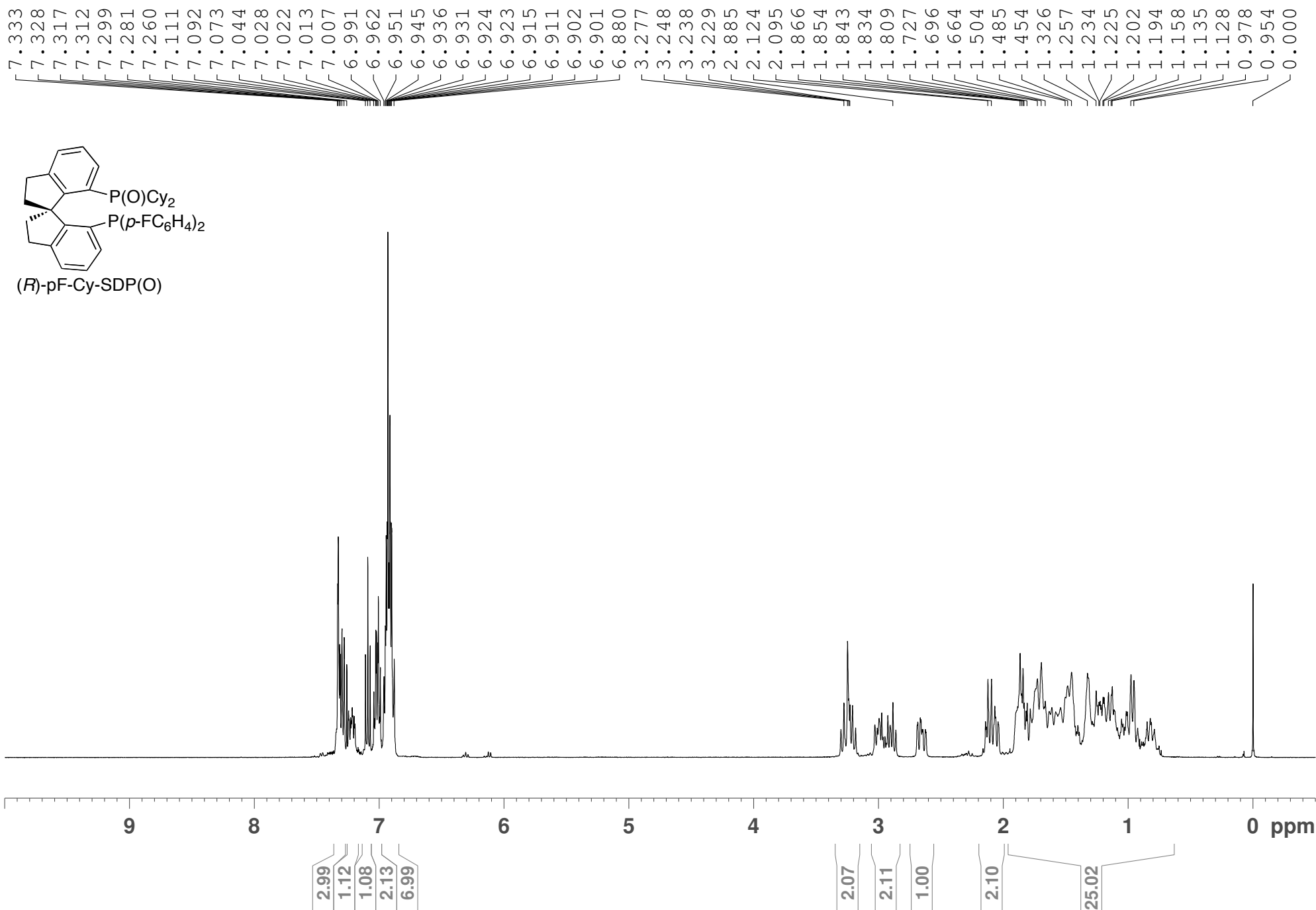


$^{31}\text{P}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

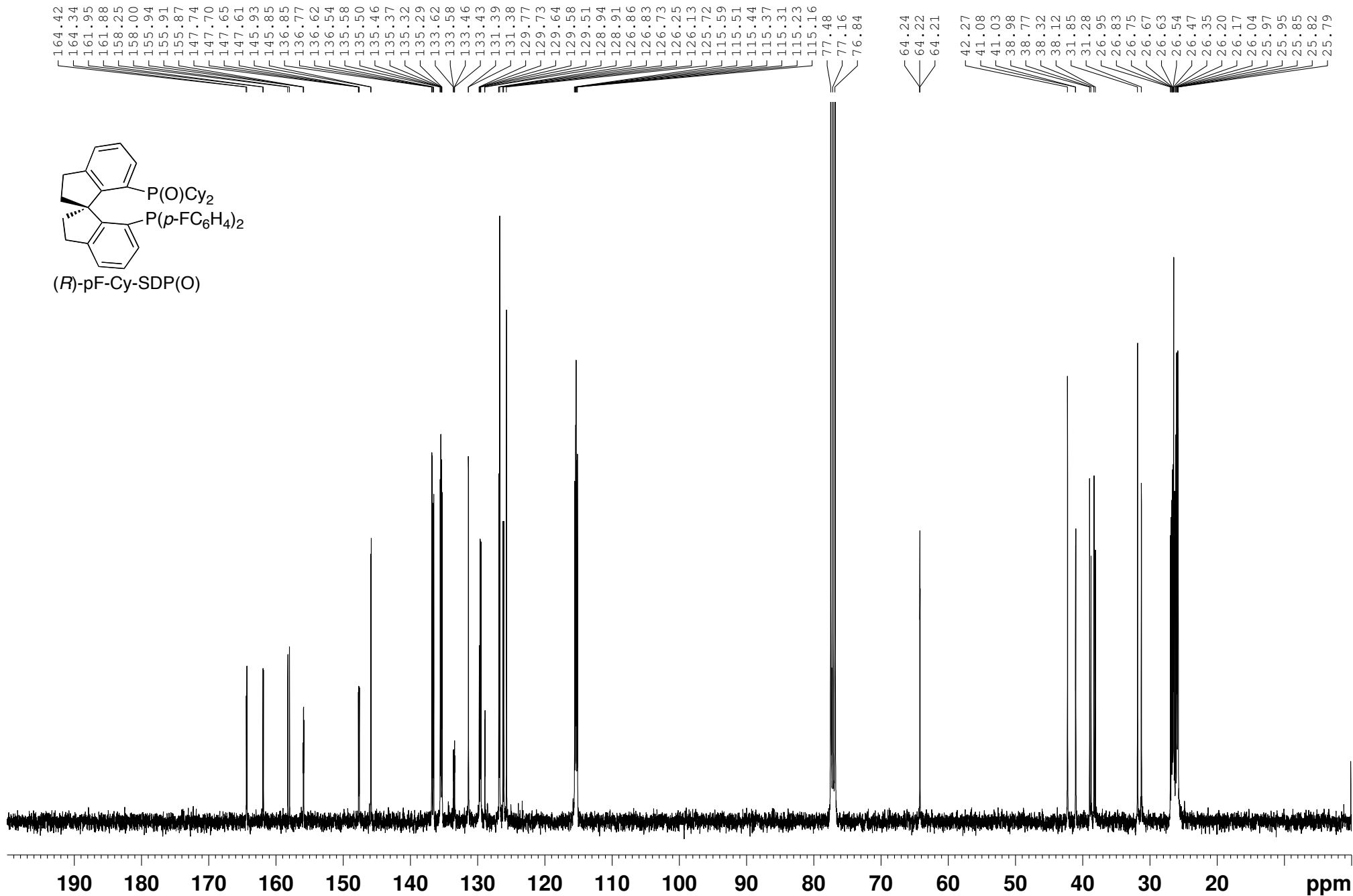


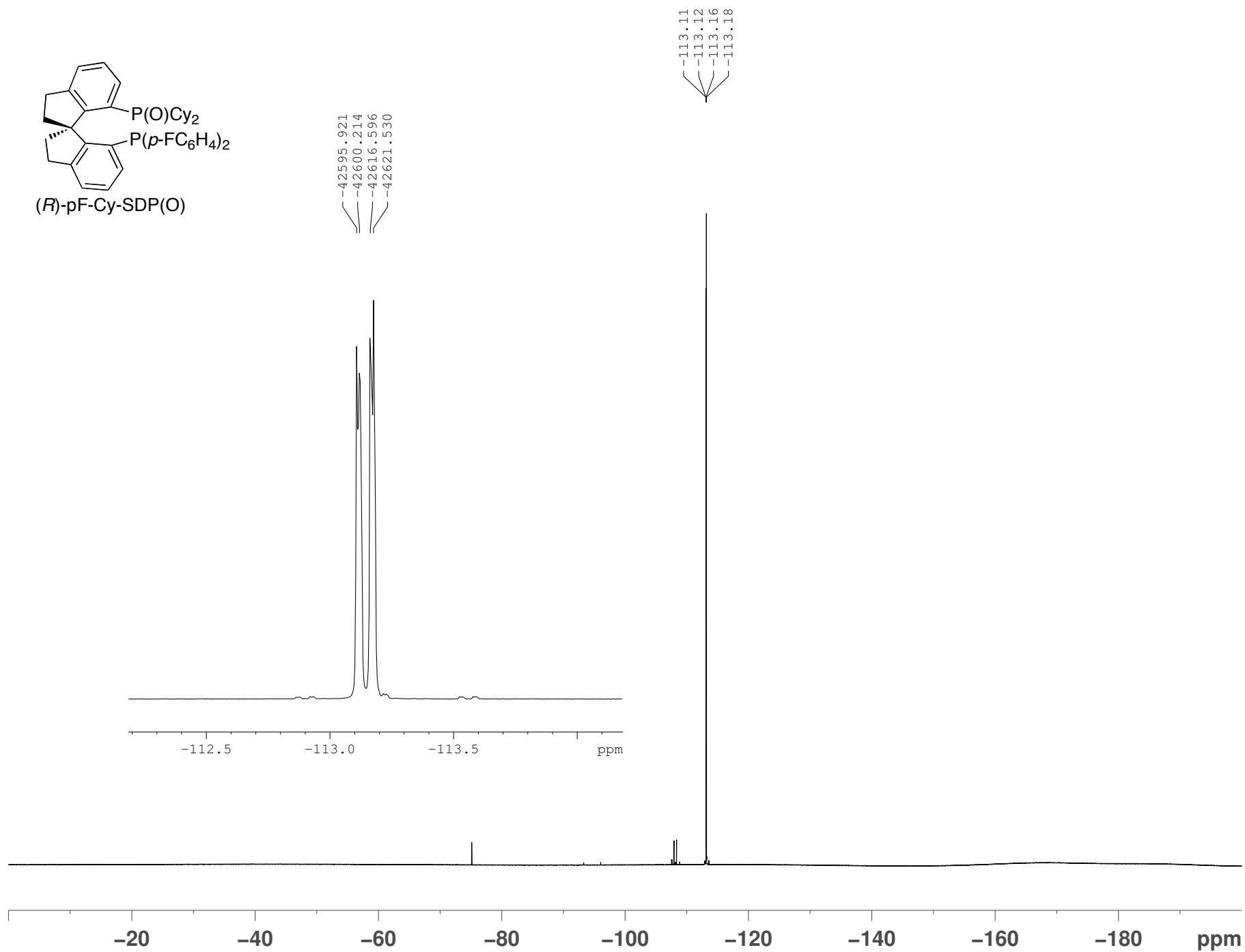
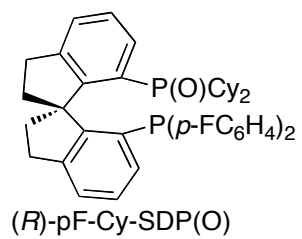
¹H NMR (400 MHz, CDCl₃)

S41

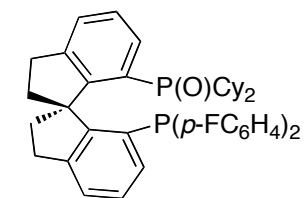


^{13}C NMR (100 MHz, CDCl_3)

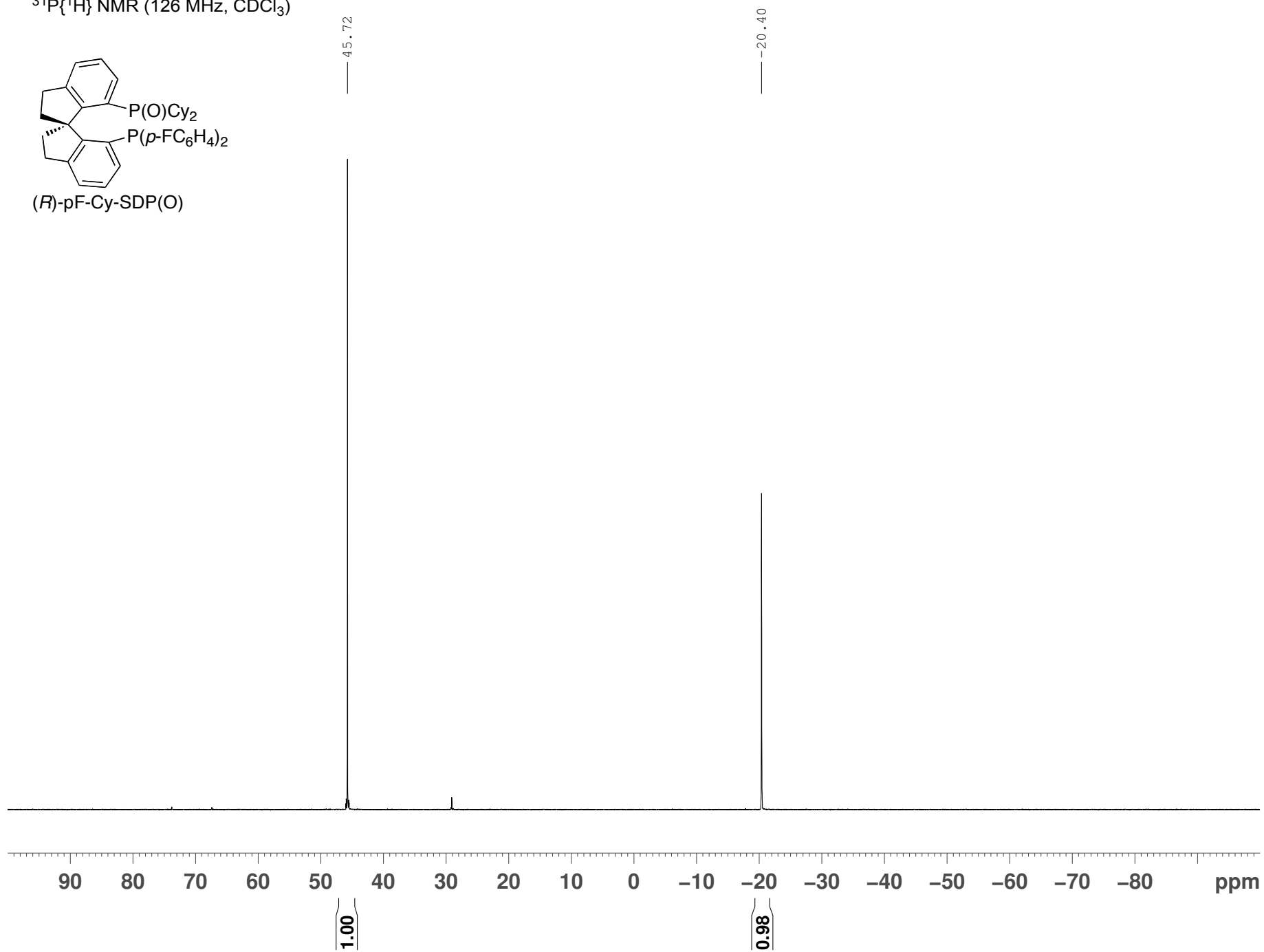




$^{31}\text{P}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

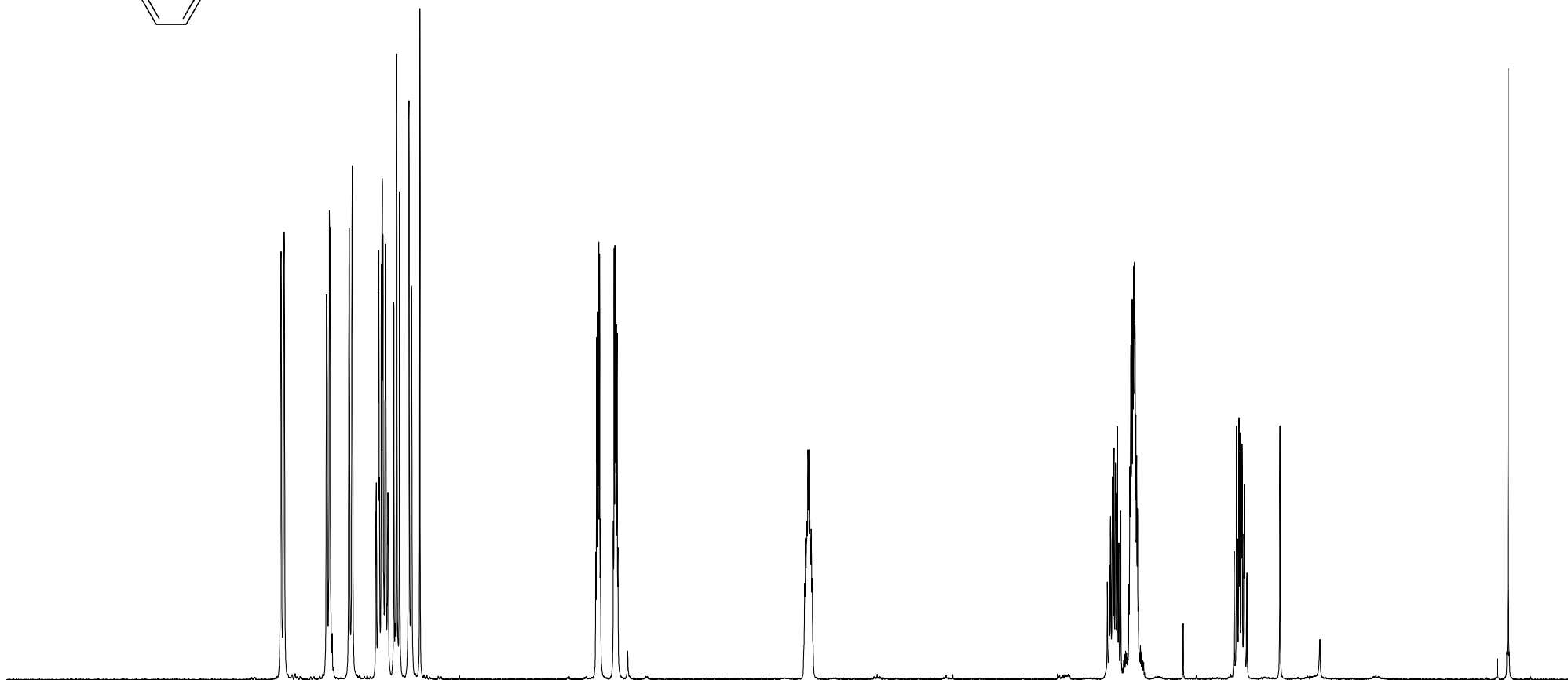
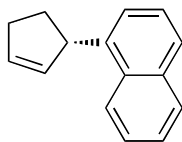


(*R*)-pF-Cy-SDP(O)



¹H NMR (400 MHz, CDCl₃)

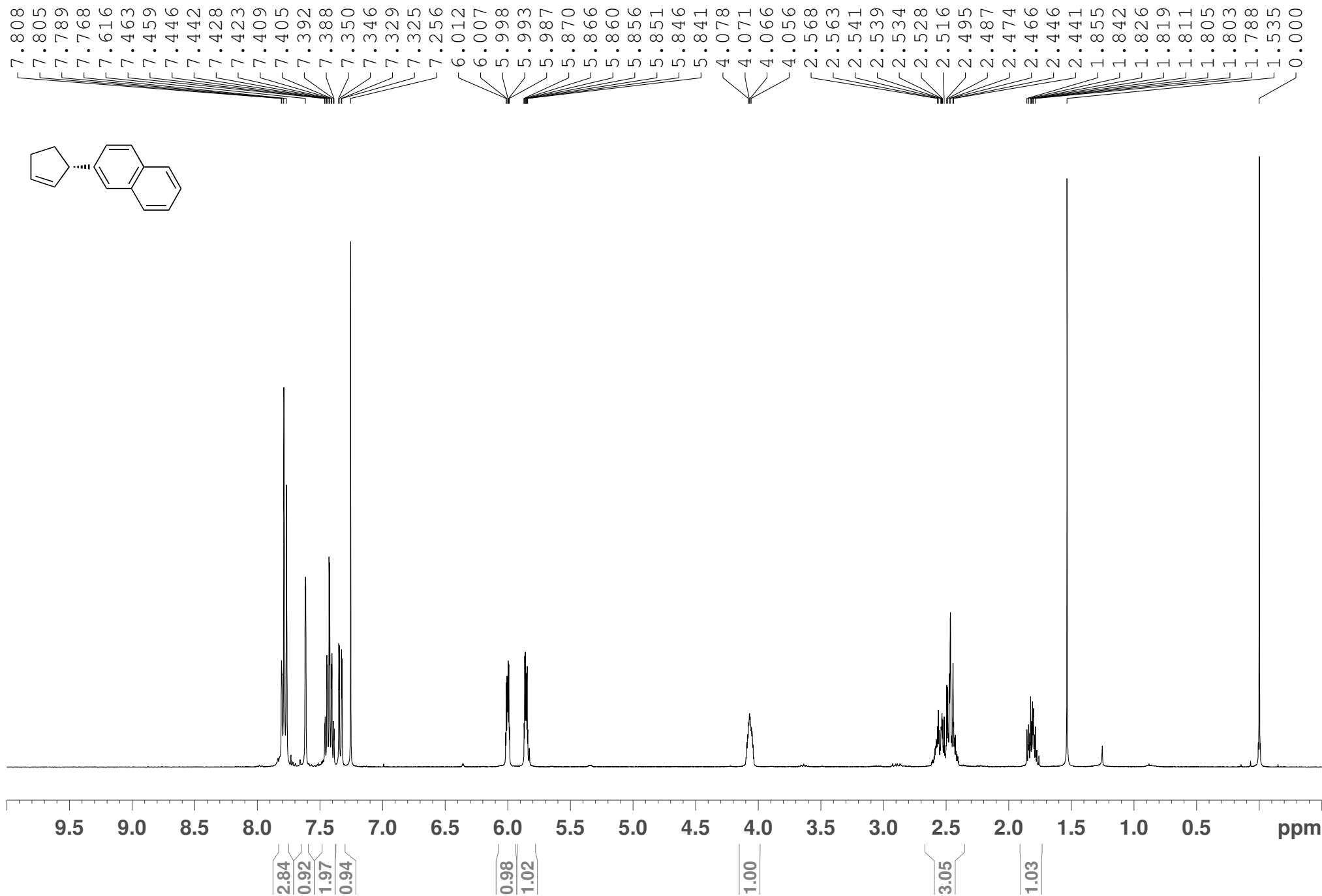
8.171
8.151
7.869
7.849
7.846
7.718
7.697
7.537
7.524
7.520
7.516
7.503
7.497
7.493
7.476
7.474
7.460
7.421
7.402
7.382
7.321
7.319
7.303
7.302
7.247
6.071
6.066
6.057
6.051
5.955
5.949
5.944
5.940
5.935
4.663
4.657
2.635
2.625
2.615
2.612
2.603
2.519
2.512
2.506
2.500
2.495
2.490
2.485
2.479
2.474
2.469
1.809
1.793
1.787
1.777
1.772
1.756
1.520
0.000



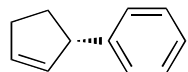
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

1.00
1.07
1.00
2.08
1.01
0.99
0.97
0.97
1.03
1.07
2.05
1.05

¹H NMR (400 MHz, CDCl₃)

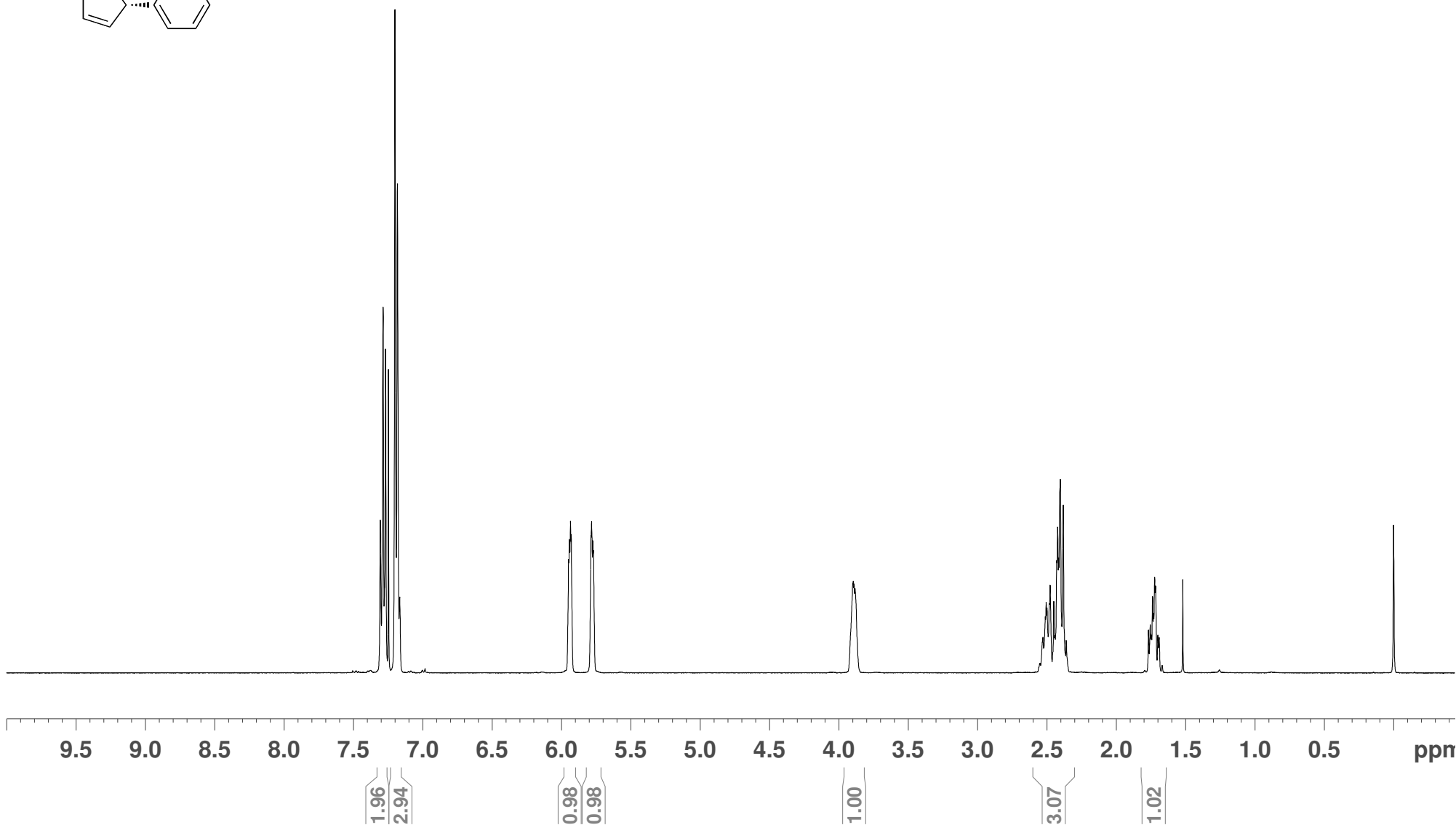


¹H NMR (400 MHz, CDCl₃)



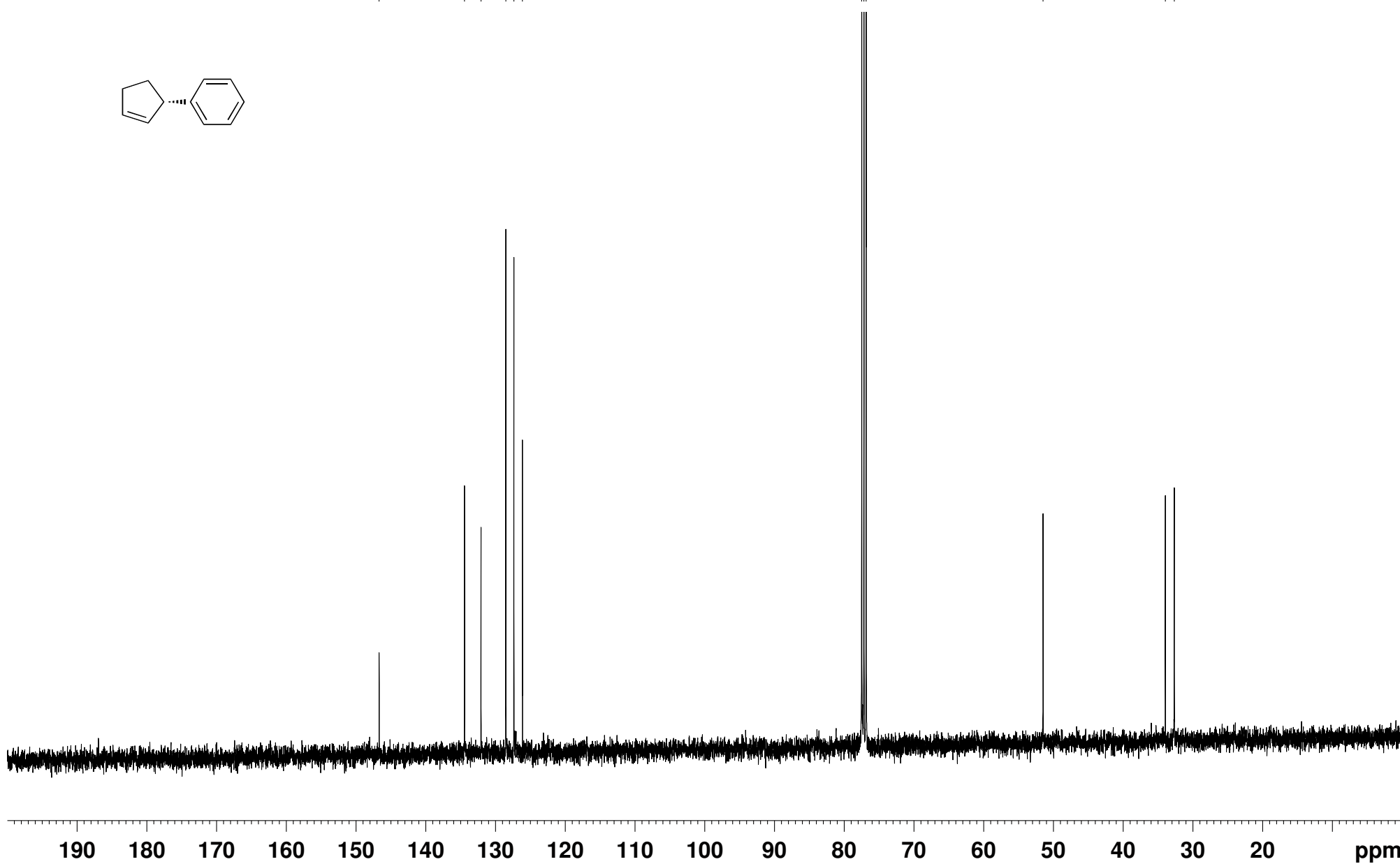
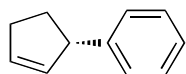
7.306
7.286
7.269
7.247
7.201
7.183
7.166
5.949
5.943
5.935
5.930
5.787
5.783
5.774
5.769

3.896
3.890
3.883
2.529
2.511
2.505
2.499
2.482
2.476
2.450
2.442
2.429
2.422
2.415
2.403
2.382
2.360
1.767
1.754
1.747
1.738
1.731
1.723
1.716
1.700
1.690
1.520
0.000



^{13}C NMR (100 MHz, CDCl_3)

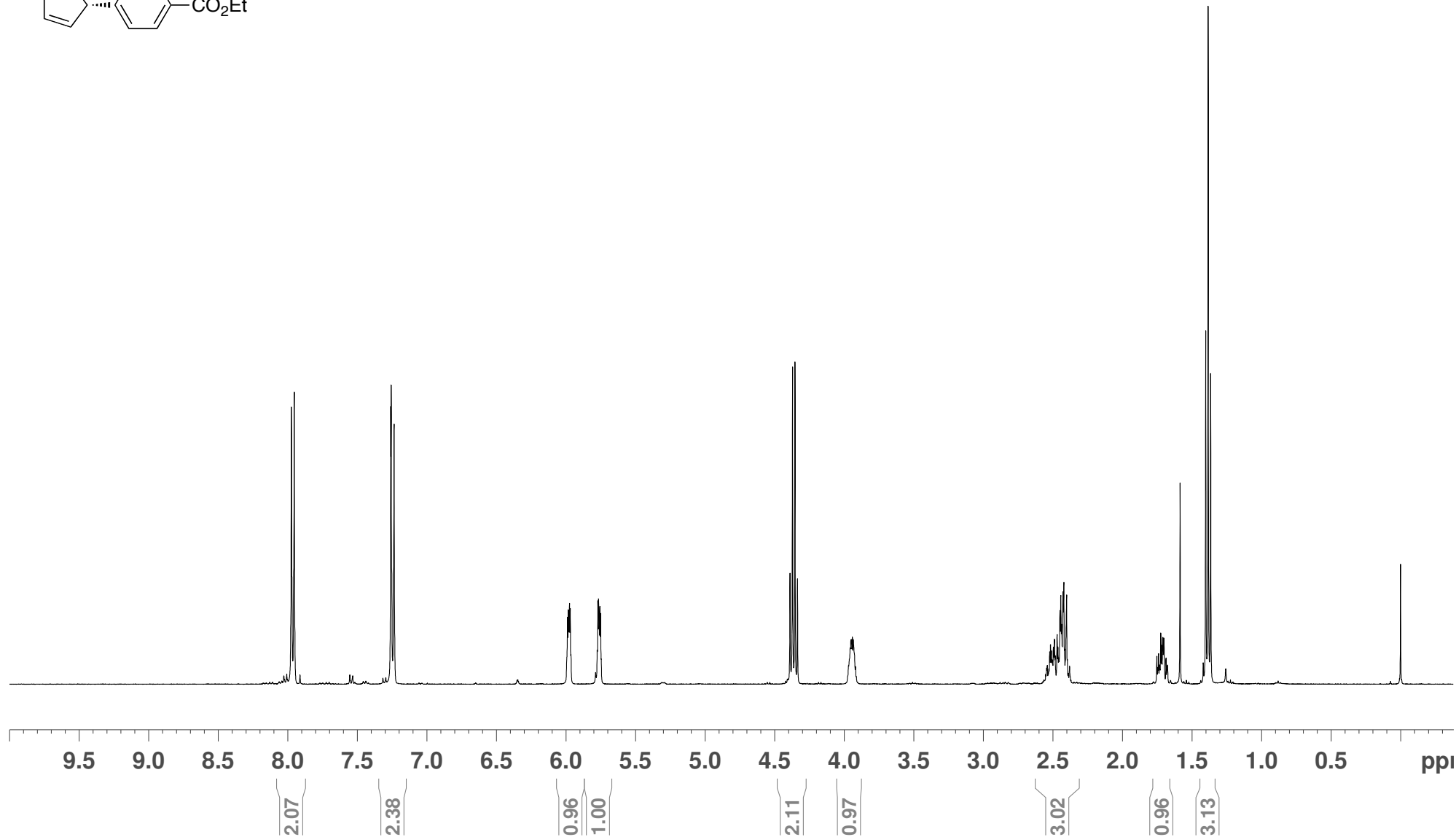
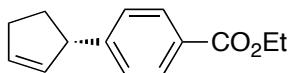
146.68
134.43
132.07
128.52
127.36
126.12
77.48
77.16
76.84
51.47
33.94
32.65

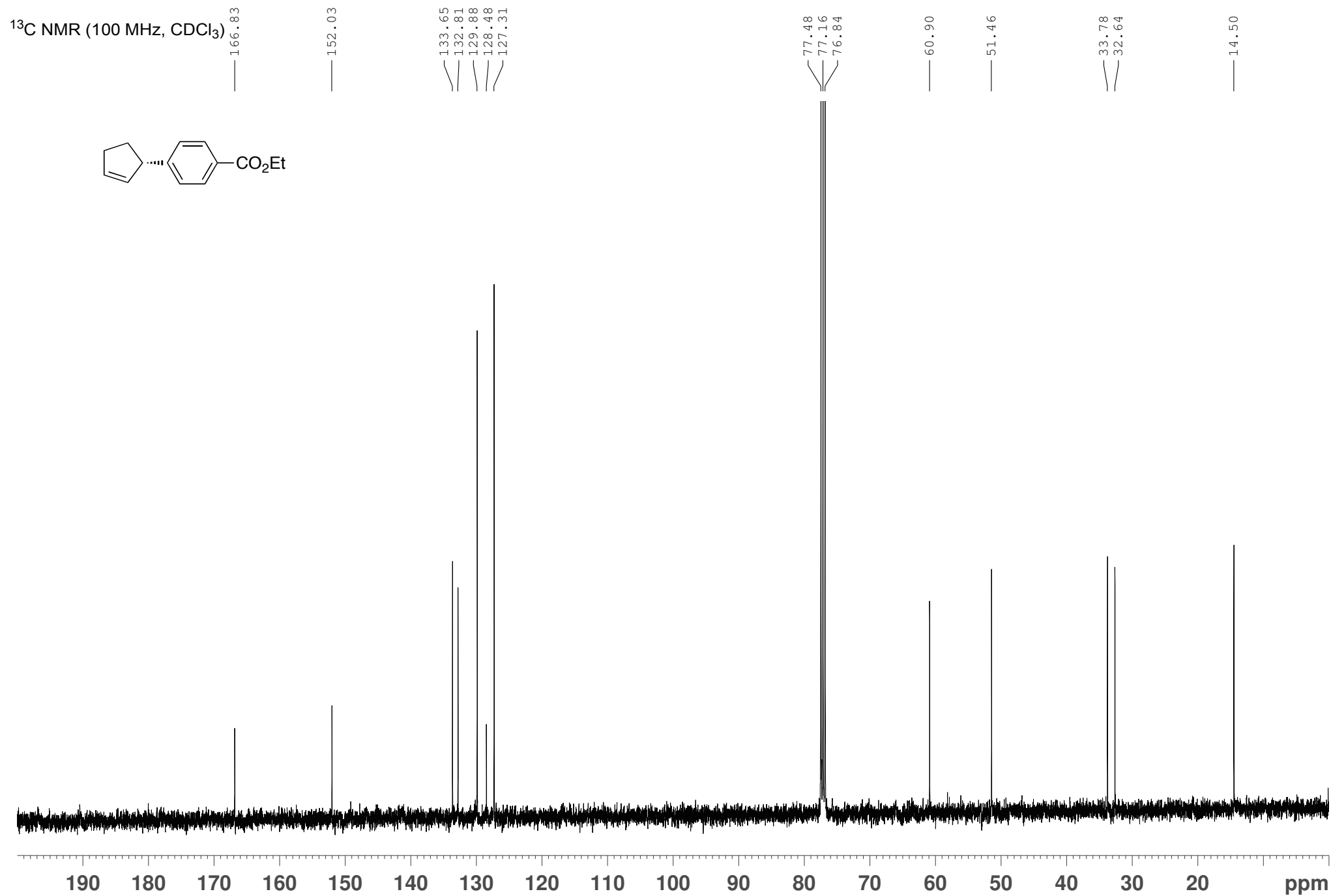


¹H NMR (400 MHz, CDCl₃)

S49

7.973
7.952
7.260
7.257
7.236
5.989
5.984
5.975
5.970
5.965
5.776
5.771
5.766
5.762
5.757
5.752
5.747
4.389
4.372
4.354
4.336
3.957
3.952
3.947
3.941
3.935
2.540
2.522
2.516
2.510
2.505
2.501
2.496
2.489
2.483
2.469
2.464
2.457
2.449
2.443
2.436
2.427
2.421
2.416
2.401
2.396
1.752
1.740
1.732
1.724
1.717
1.709
1.701
1.686
1.675
1.401
1.383
1.365
0.000

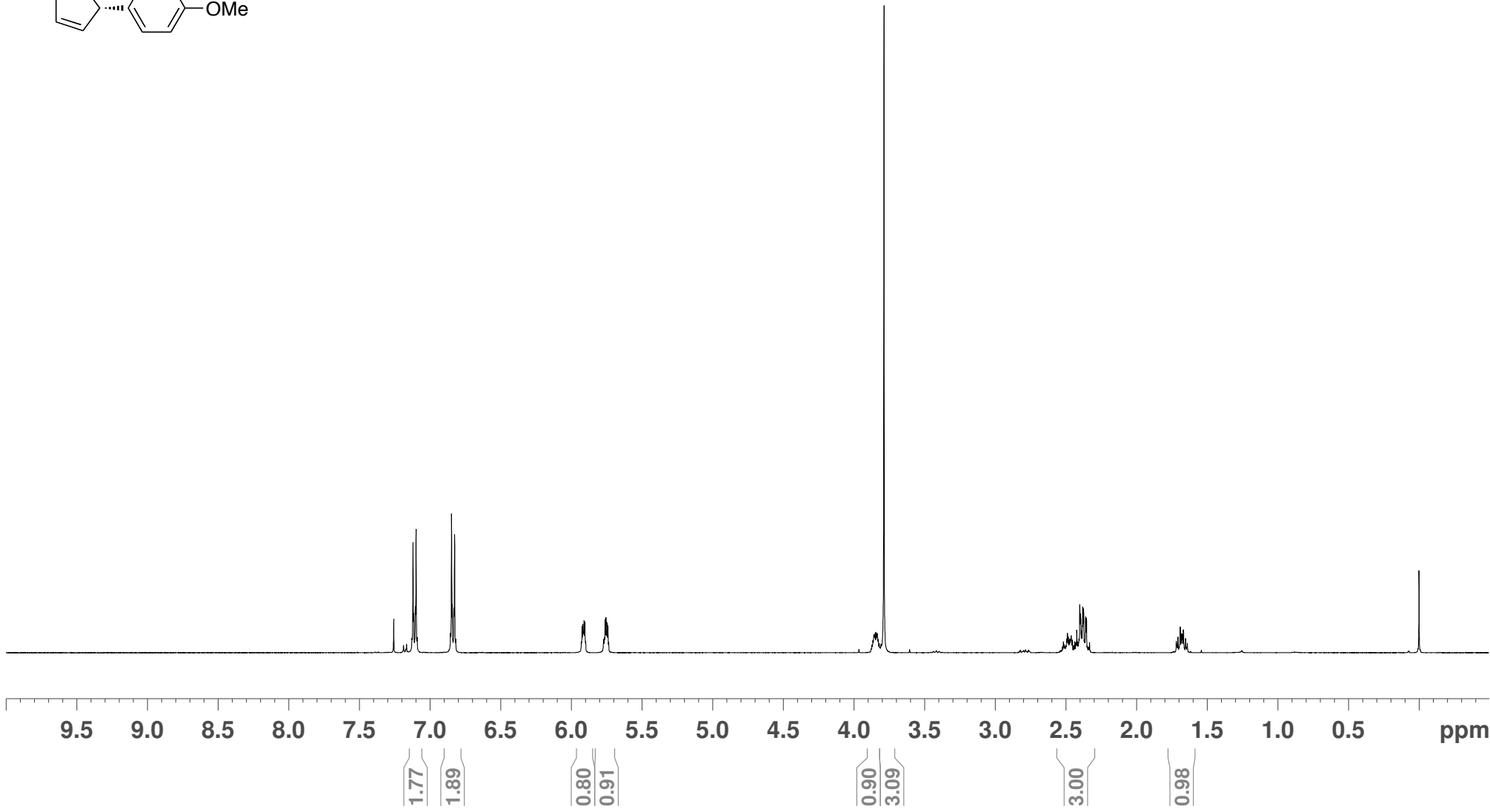
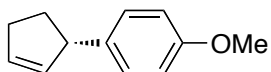




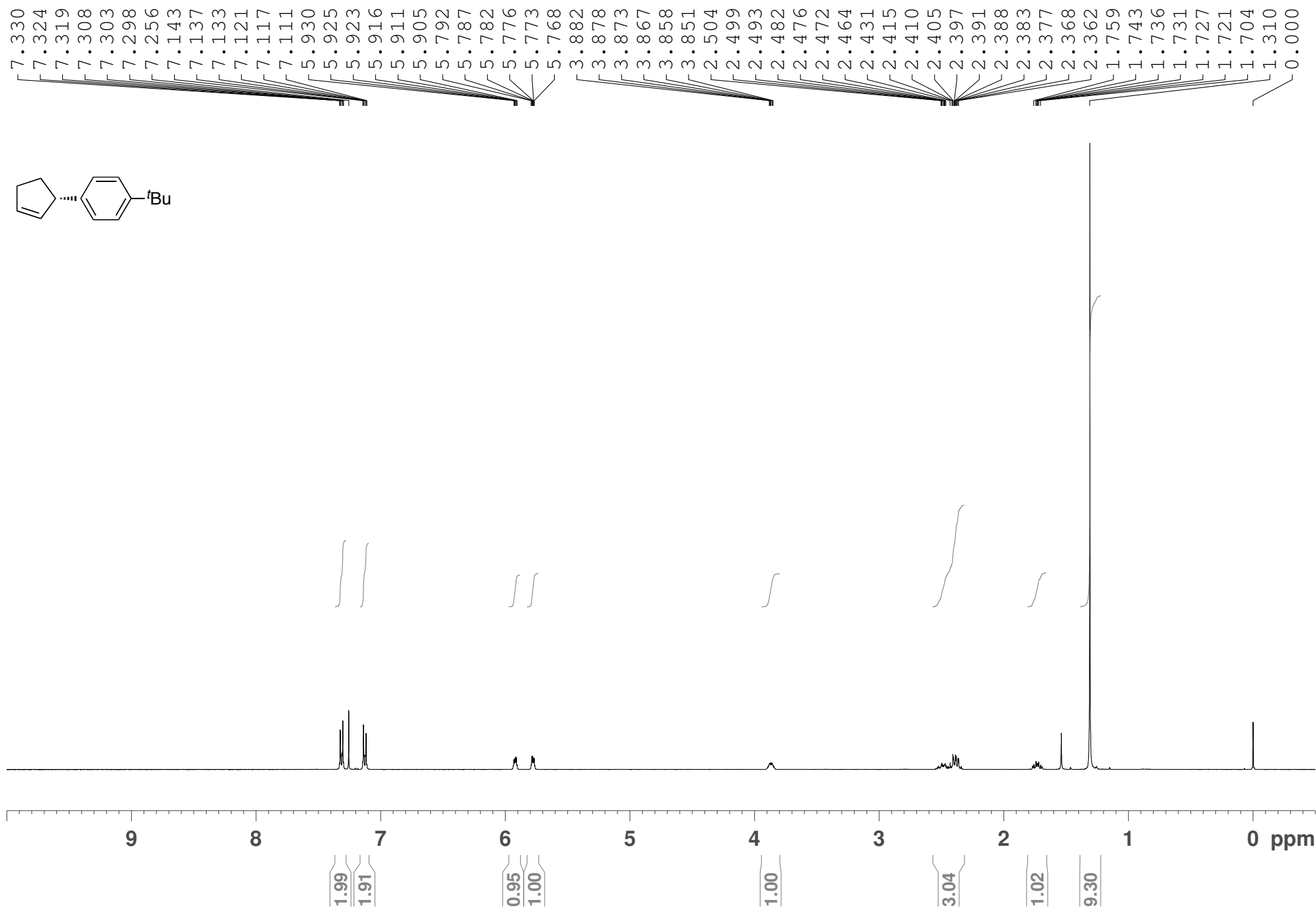
¹H NMR (400 MHz, CDCl₃)

S51

7.126
7.119
7.114
7.103
7.097
7.090
6.854
6.846
6.841
6.830
6.825
6.817
5.924
5.918
5.910
5.904
5.771
5.766
5.761
5.755
5.751
5.750
5.747
5.741
3.859
3.855
3.849
3.843
3.837
3.835
3.828
3.787
2.494
2.489
2.483
2.472
2.467
2.462
2.454
2.422
2.407
2.401
2.397
2.389
2.383
2.380
2.374
2.369
2.360
2.354
1.706
1.690
1.683
1.678
1.675
1.668
1.667
1.652
0.000

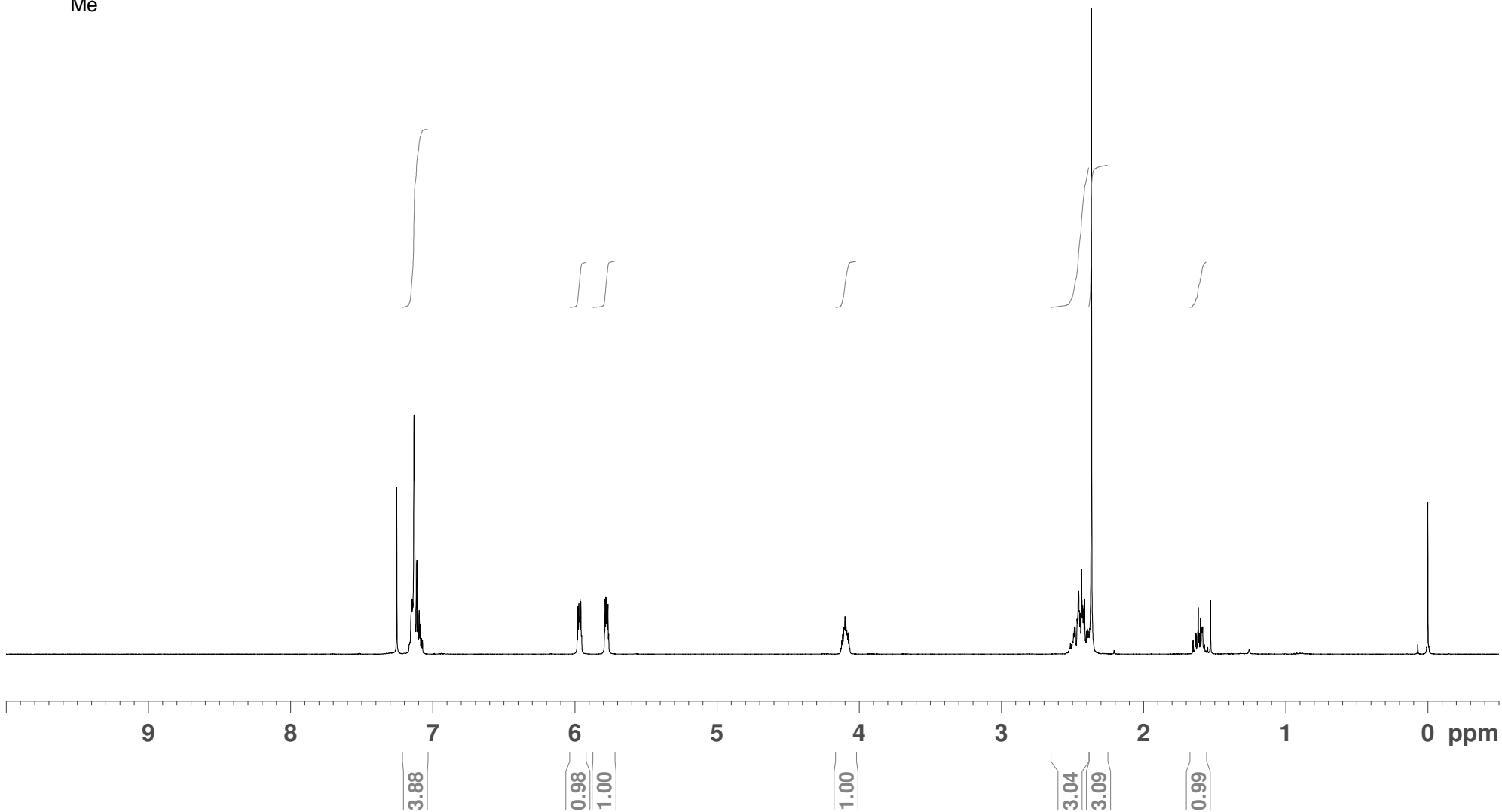
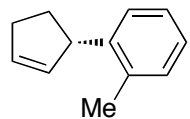


¹H NMR (400 MHz, CDCl₃)

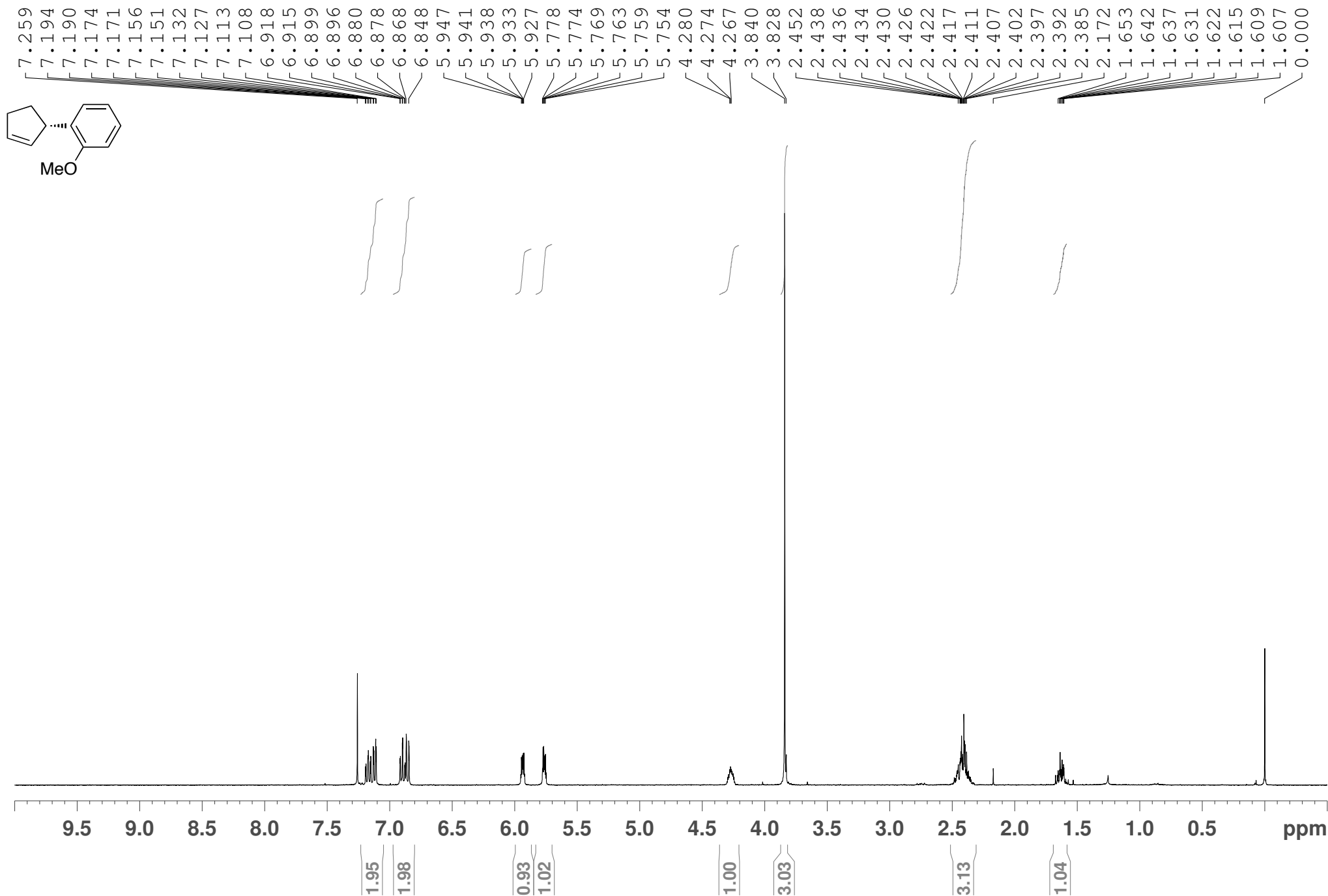


¹H NMR (400 MHz, CDCl₃)

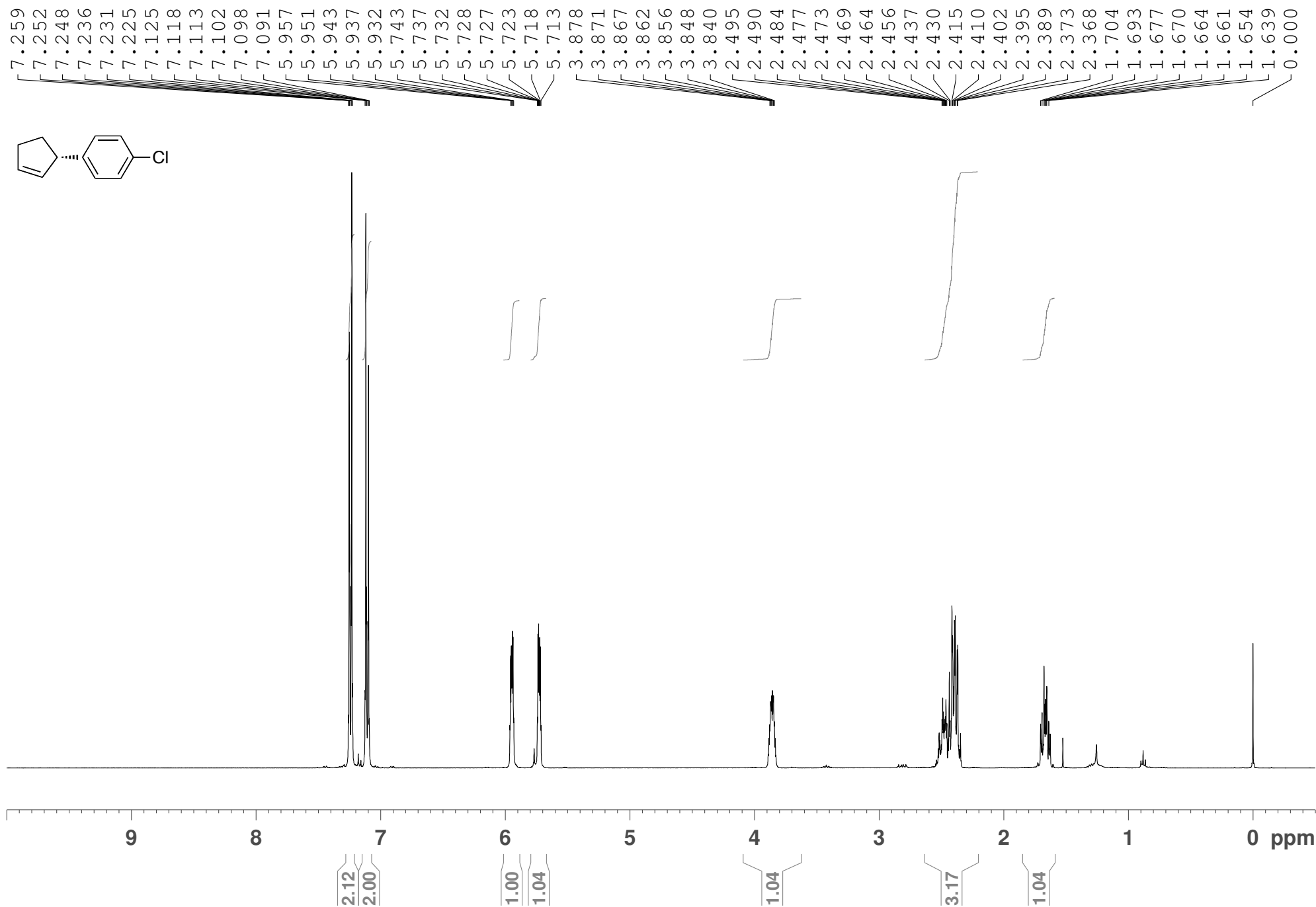
7.253
7.147
7.142
7.131
7.127
7.112
7.104
7.095
7.088
7.079
5.983
5.978
5.972
5.970
5.964
5.958
5.953
5.791
5.786
5.781
5.777
5.772
5.767
5.762
4.116
4.106
4.100
4.093
4.087
4.078
4.072
2.491
2.486
2.481
2.467
2.465
2.455
2.452
2.445
2.436
2.427
2.422
2.414
2.401
2.395
2.389
2.385
2.378
2.366
1.631
1.615
1.608
1.599
1.591
1.588
1.584
1.529
0.000



¹H NMR (400 MHz, CDCl₃)



¹H NMR (400 MHz, CDCl₃)



^{13}C NMR (100 MHz, CDCl_3)

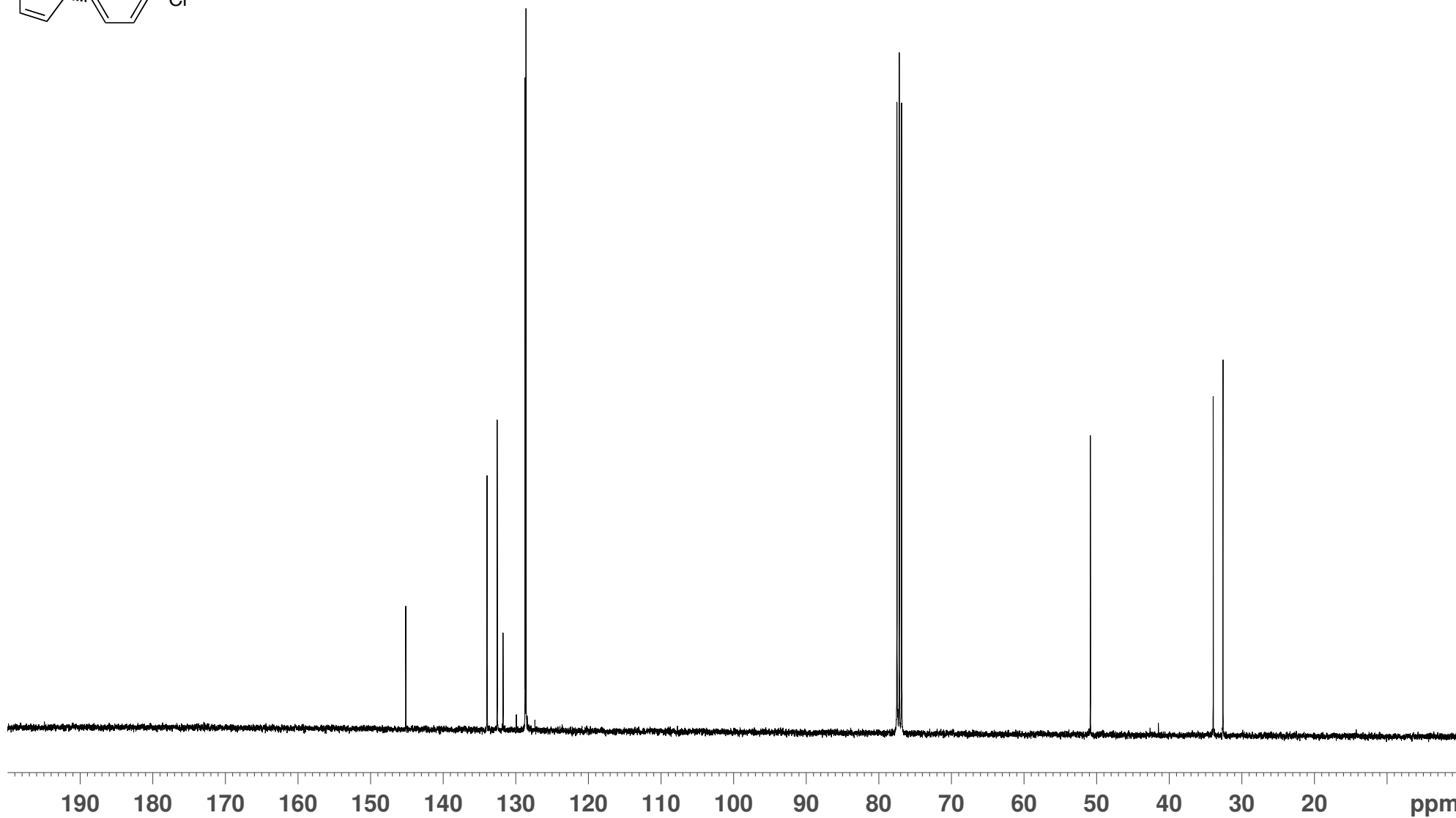
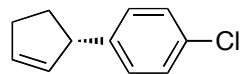
145.14

133.95
132.55
131.74
128.70
128.58

77.48
77.16
76.84

50.84

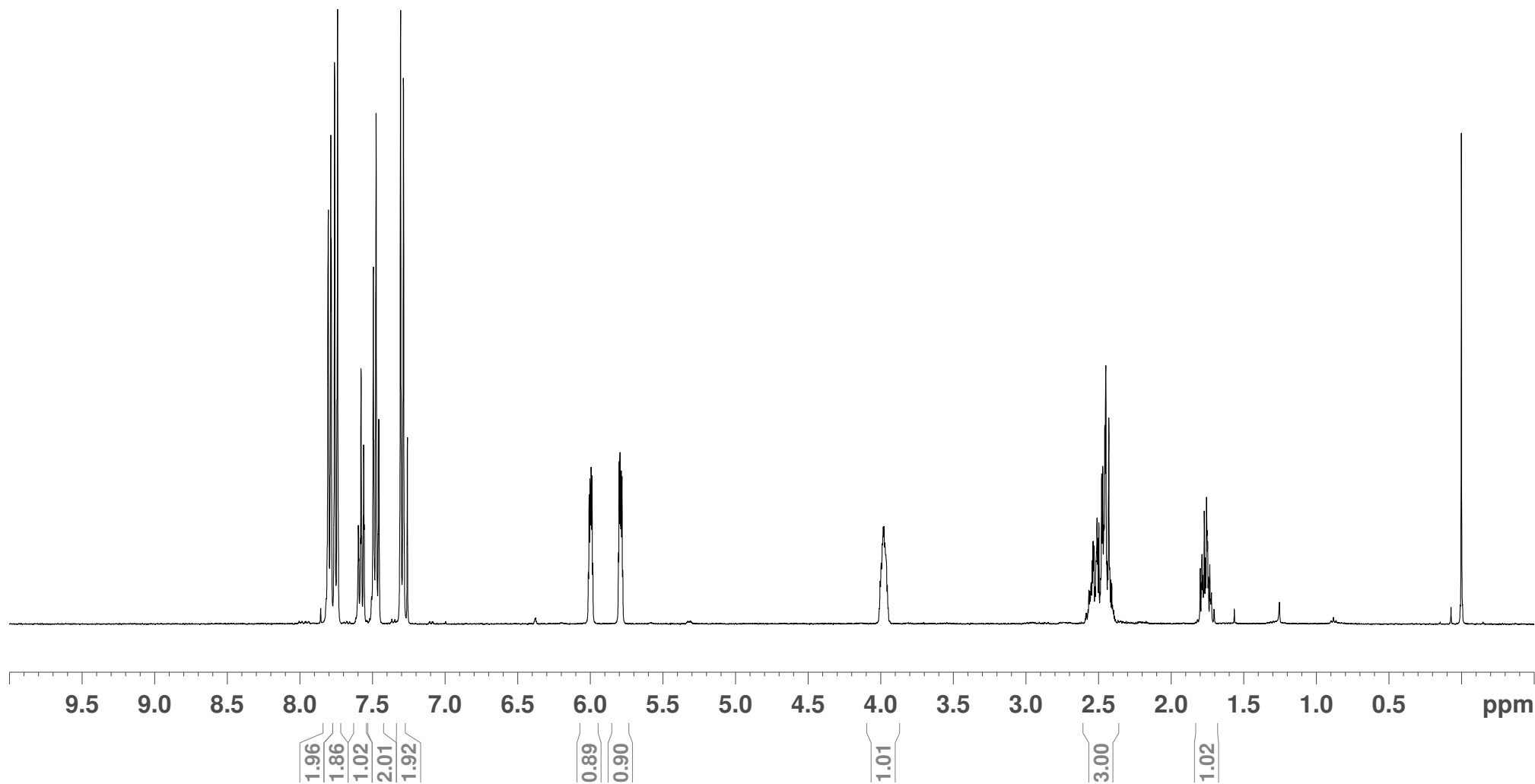
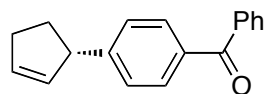
33.91
32.57

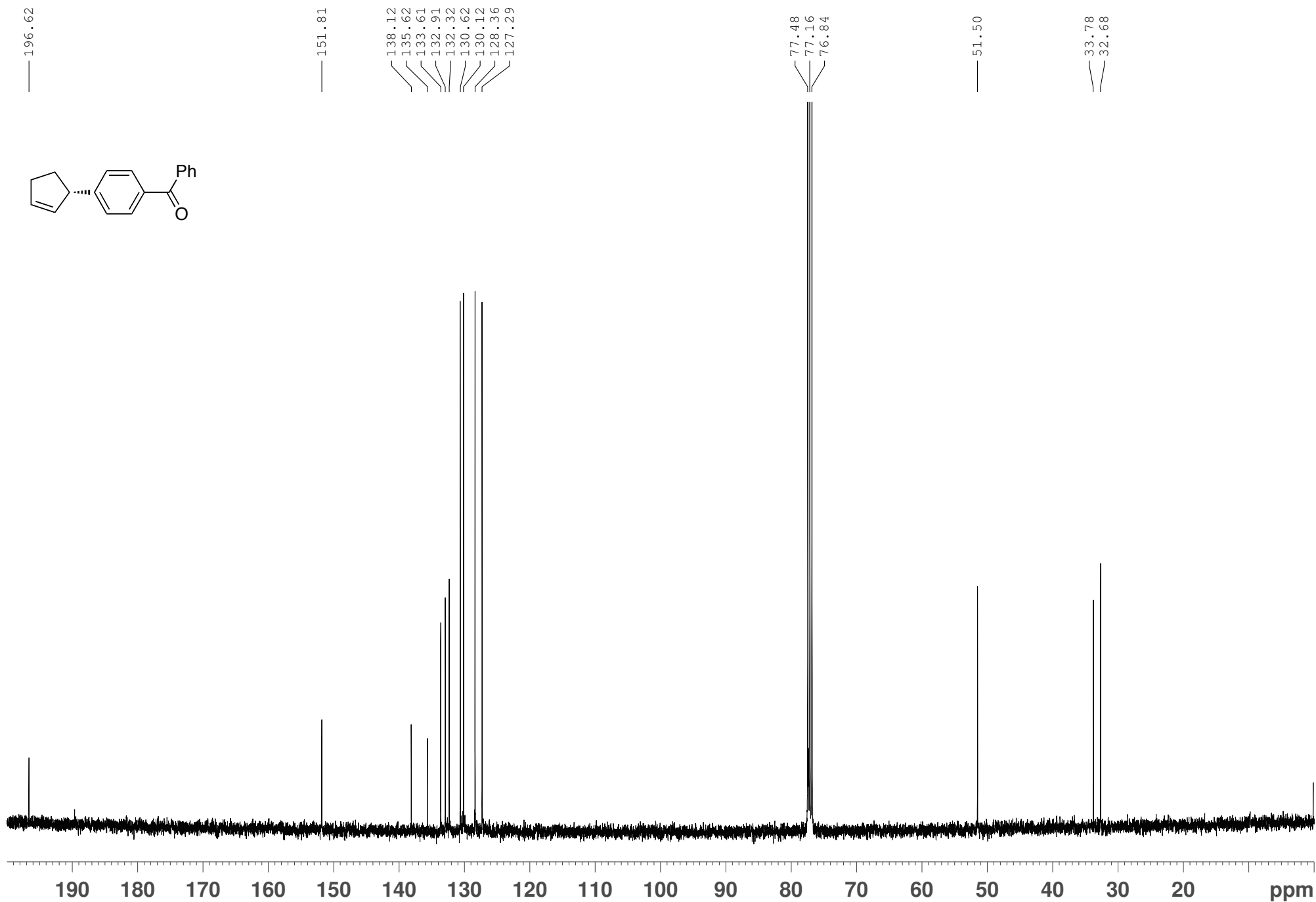


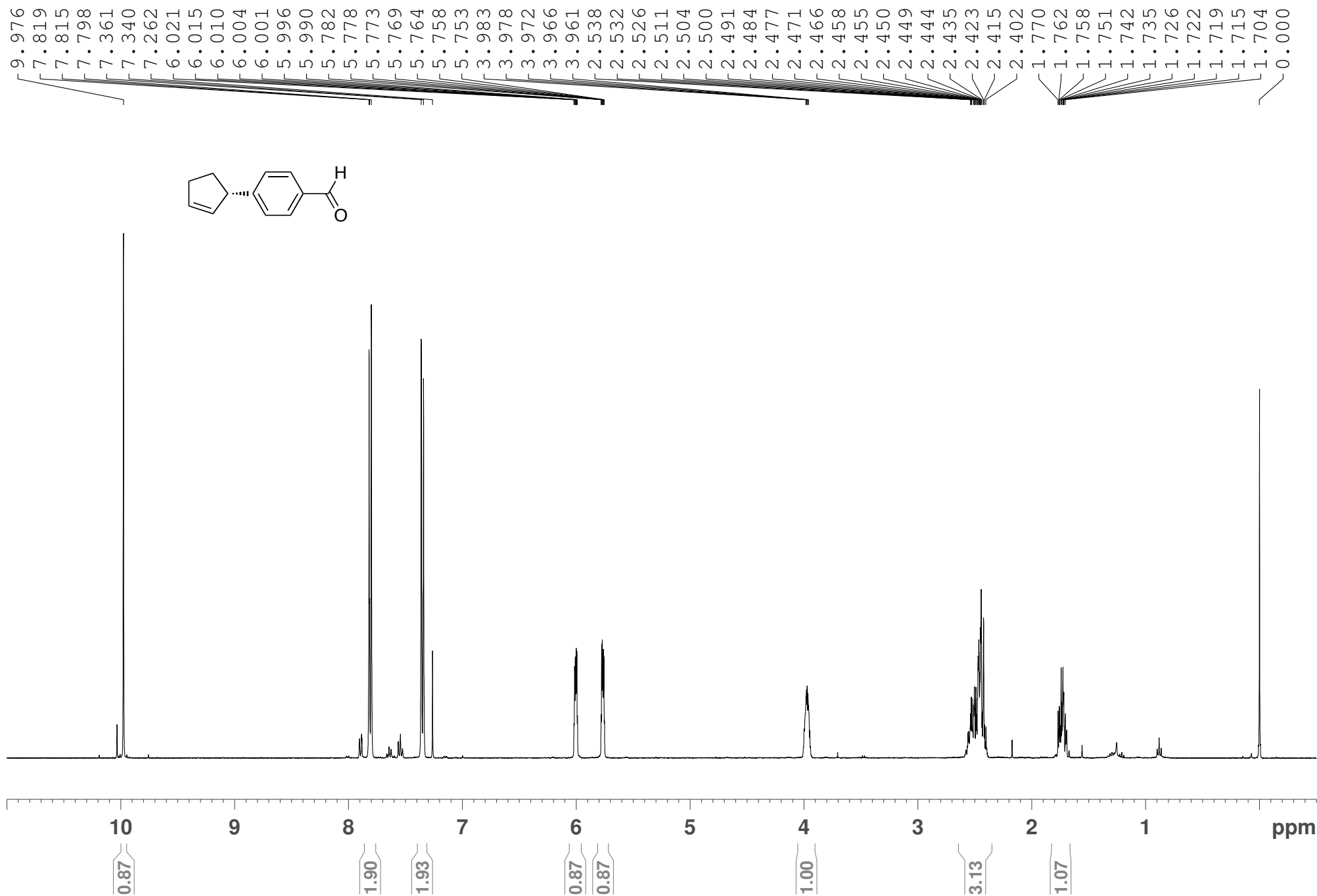
¹H NMR (400 MHz, CDCl₃)

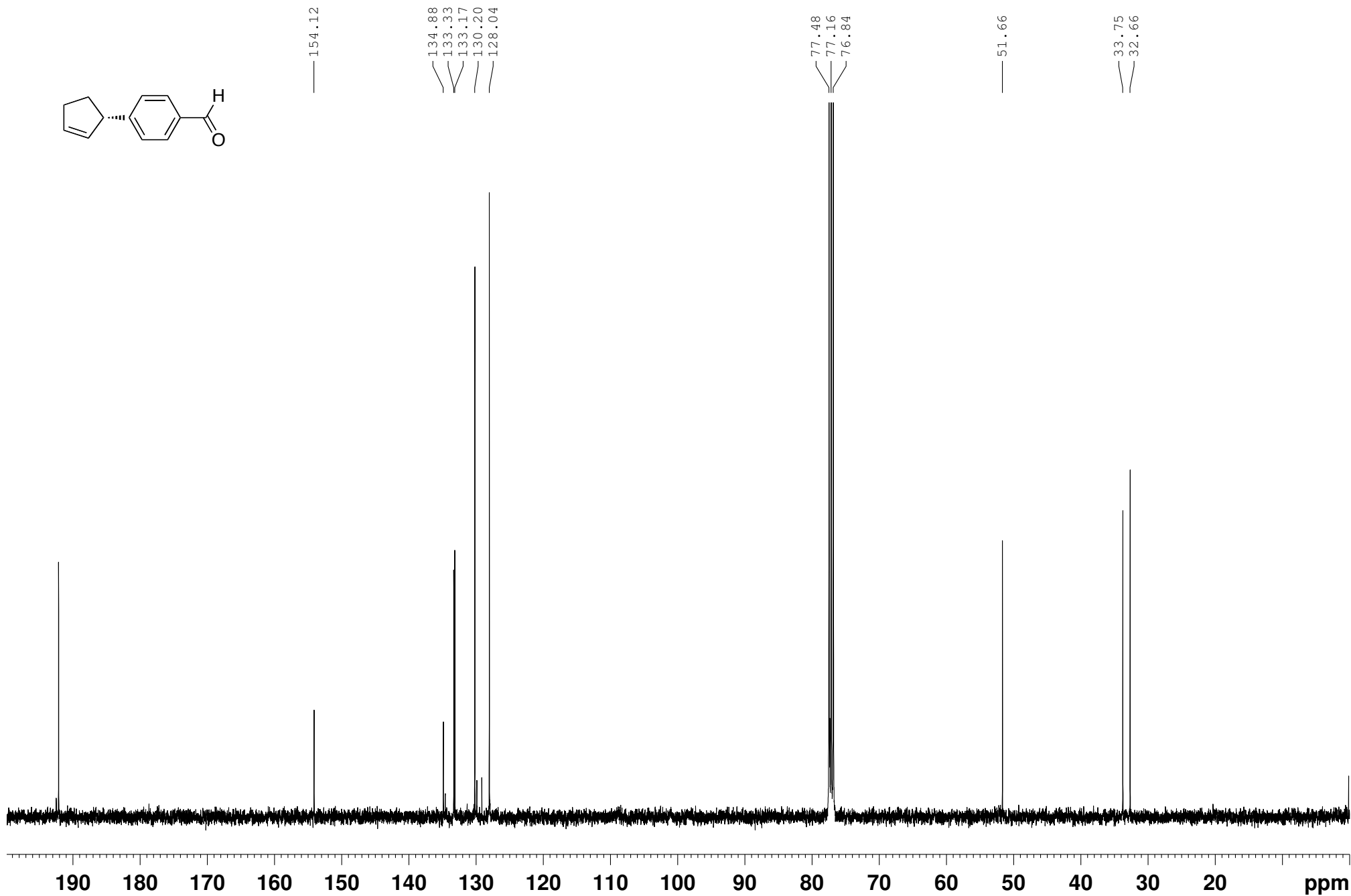
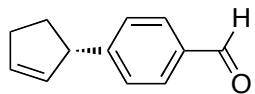
S57

7.805
7.792
7.787
7.784
7.761
7.757
7.740
7.597
7.594
7.584
7.579
7.574
7.563
7.560
7.557
7.494
7.475
7.457
7.307
7.286
7.260
6.008
6.002
5.994
5.988
5.805
5.801
5.795
5.791
5.787
5.782
3.996
3.988
3.982
3.976
3.971
2.543
2.537
2.531
2.517
2.514
2.509
2.504
2.497
2.477
2.470
2.464
2.461
2.456
2.449
2.443
2.428
1.787
1.771
1.764
1.755
1.751
1.748
0.000



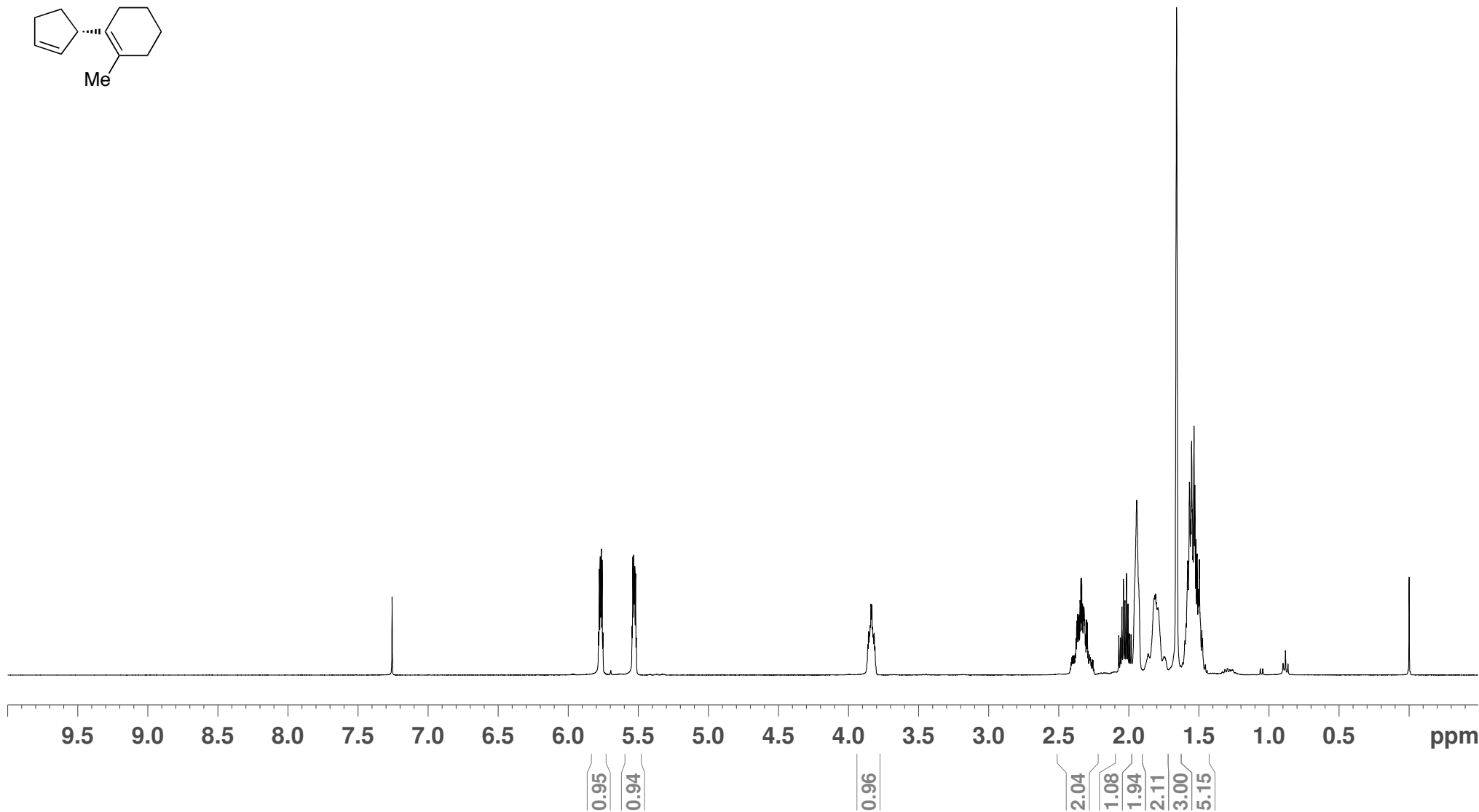
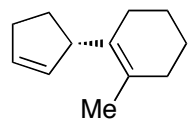




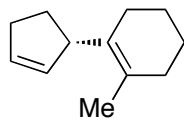


¹H NMR (400 MHz, CDCl₃)

7.258
5.779
5.773
5.765
5.759
5.545
5.540
5.534
5.531
5.526
5.520
3.846
3.840
3.835
3.829
2.372
2.366
2.360
2.355
2.349
2.342
2.337
2.331
2.325
2.320
2.315
2.303
2.297
2.050
2.039
2.028
2.017
2.006
1.960
1.944
1.930
1.821
1.814
1.809
1.804
1.799
1.792
1.659
1.592
1.580
1.567
1.559
1.552
1.547
1.543
1.535
1.529
1.521
1.514
1.512
1.506
1.502
1.497
0.000



^{13}C NMR (100 MHz, CDCl_3)

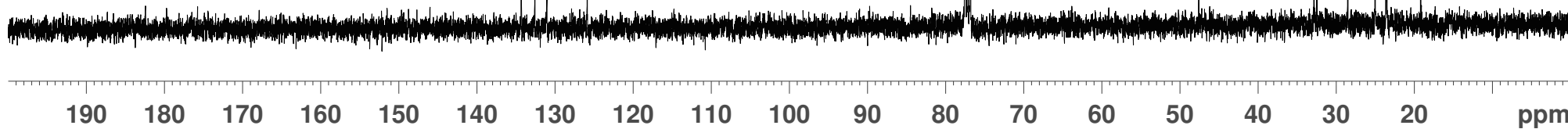


134.32
132.60
131.05
125.89

77.48
77.16
76.84

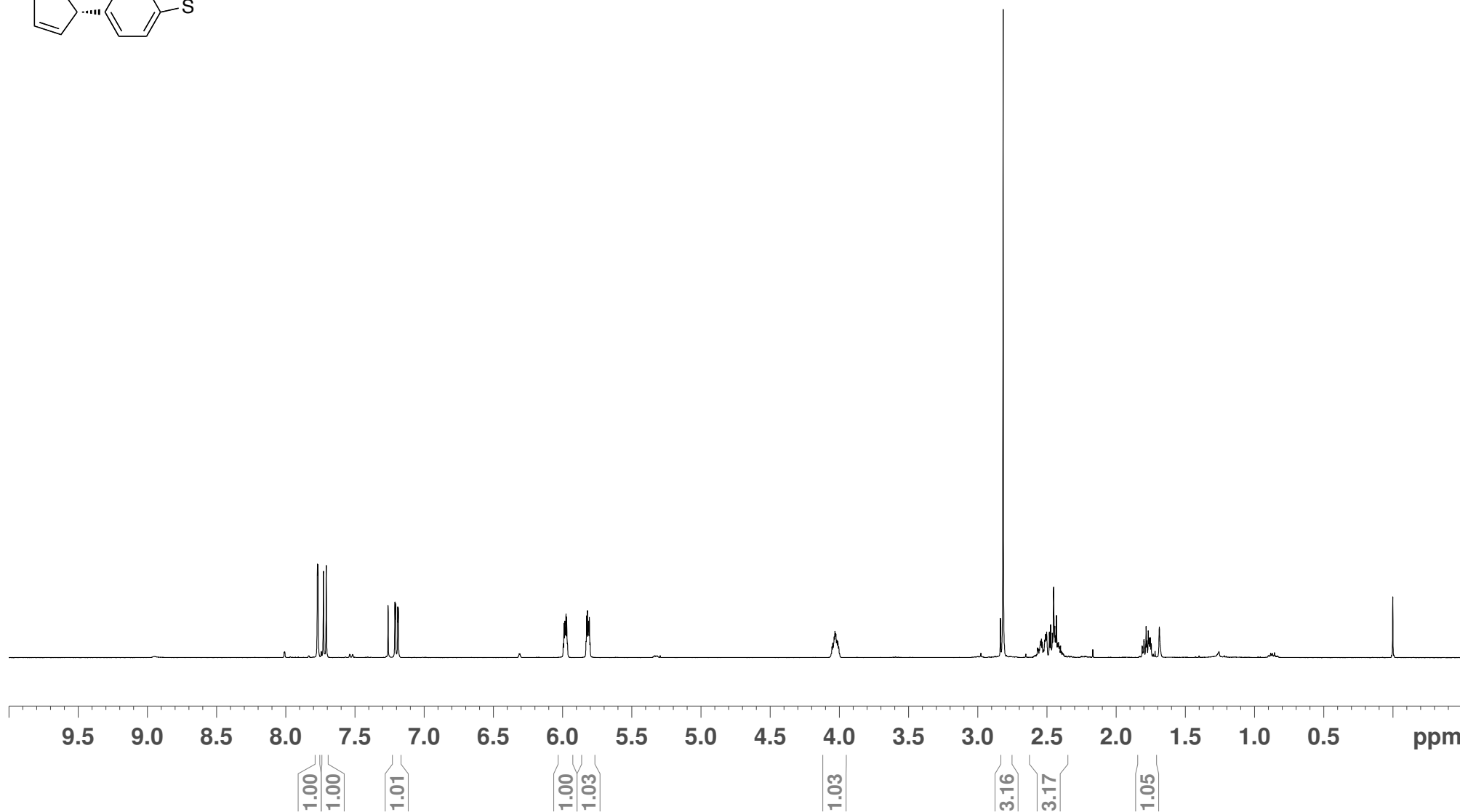
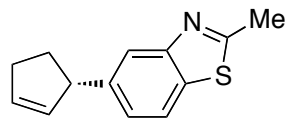
47.59

32.84
32.47
28.52
25.02
23.65
23.51
19.18

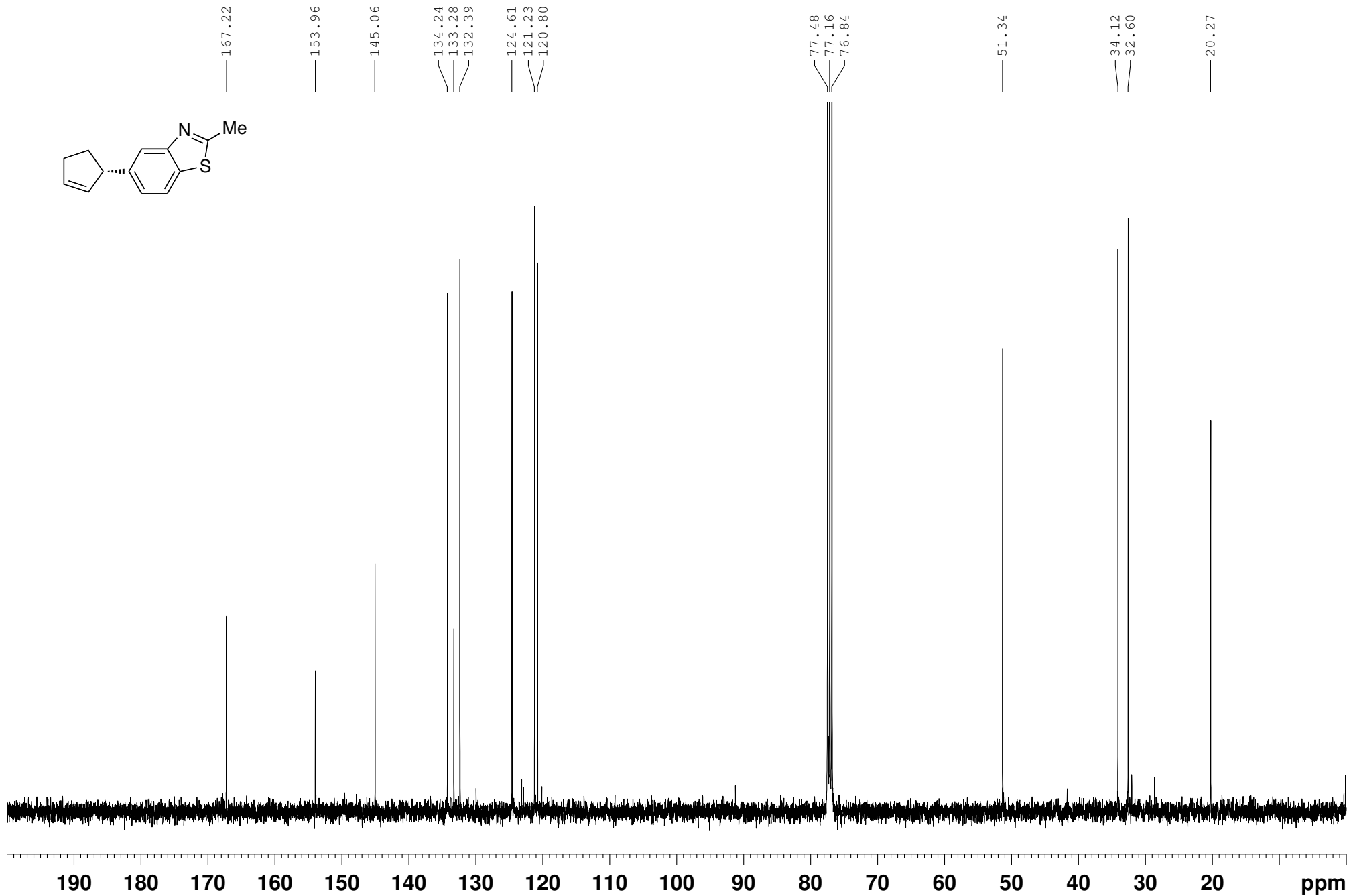


¹H NMR (400 MHz, CDCl₃)

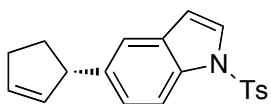
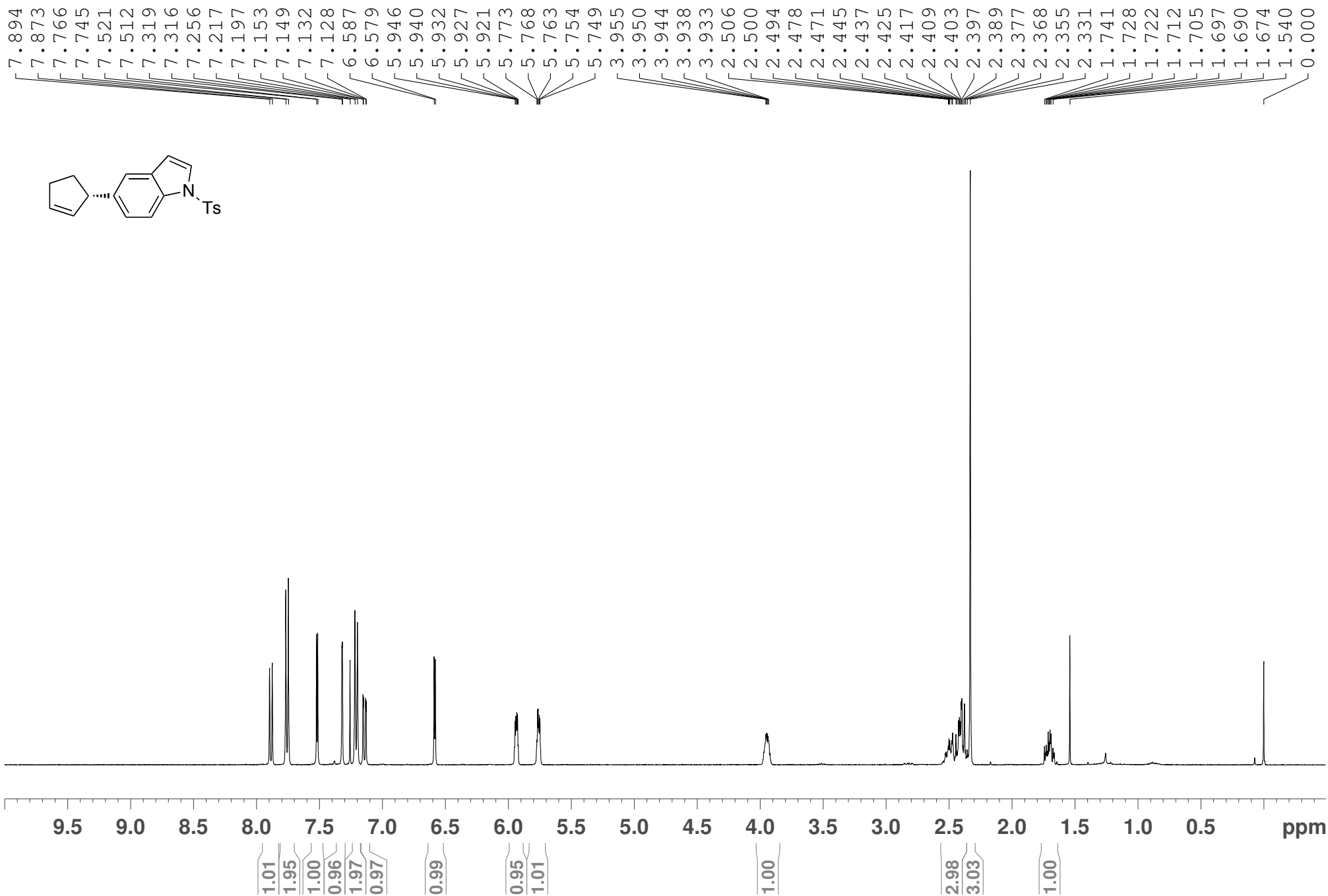
7.771
7.767
7.728
7.707
7.260
7.211
7.207
7.190
7.186
5.994
5.989
5.983
5.980
5.975
5.969
5.964
5.830
5.825
5.820
5.814
5.811
5.806
5.801
4.047
4.037
4.031
4.025
4.018
4.010
2.816
2.549
2.545
2.539
2.533
2.515
2.510
2.506
2.501
2.481
2.472
2.460
2.451
2.442
2.437
2.430
2.422
2.416
2.401
1.811
1.798
1.796
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1.776
1.767
1.760
1.752
1.745
1.687
0.000



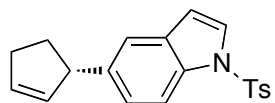
^{13}C NMR (100 MHz, CDCl_3)



¹H NMR (400 MHz, CDCl₃)



^{13}C NMR (100 MHz, CDCl_3)



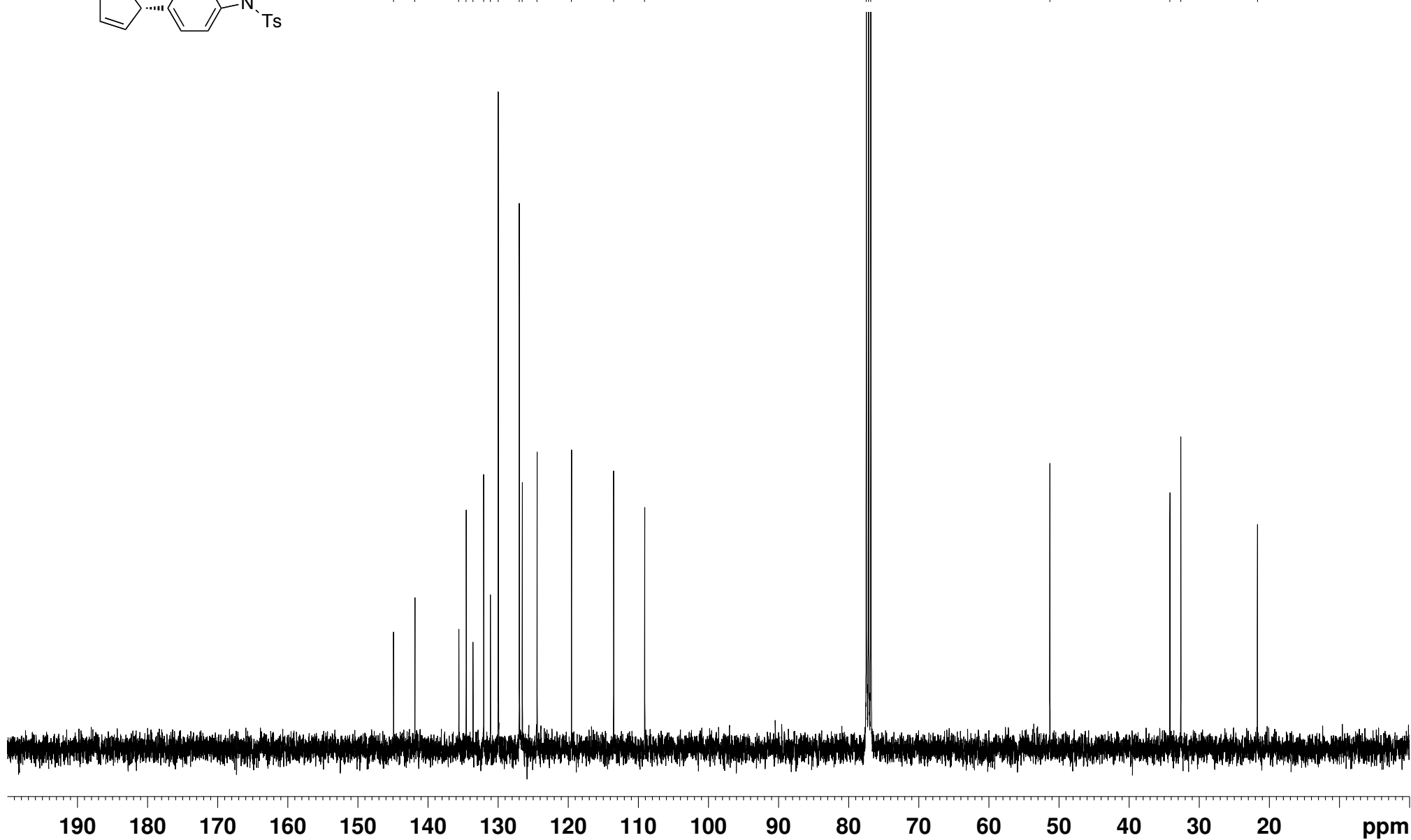
144.93
141.88
135.61
134.56
133.59
132.06
131.11
129.98
126.98
126.56
124.45
119.54
113.53
109.10

77.48
77.16
76.84

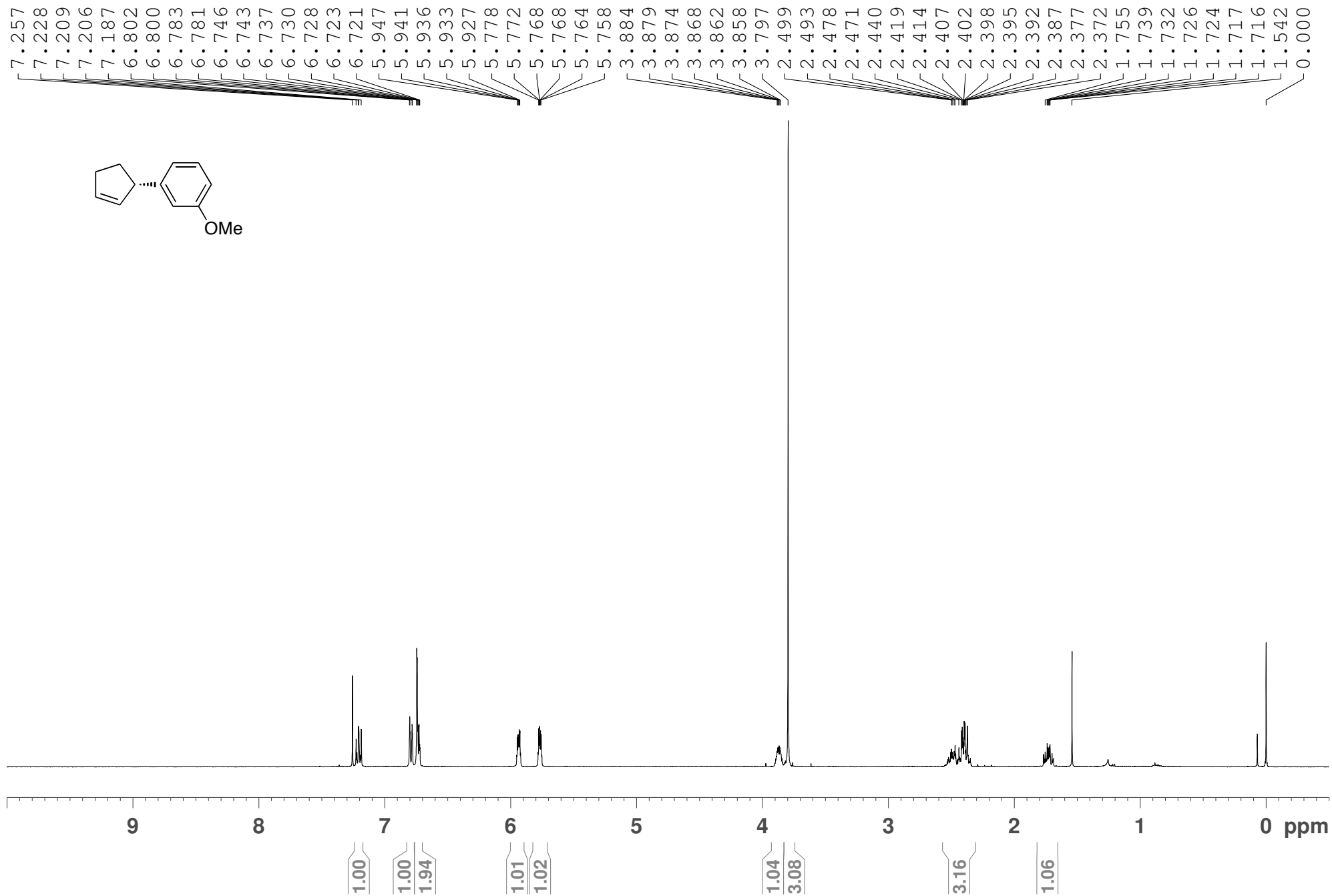
51.30

34.17
32.62

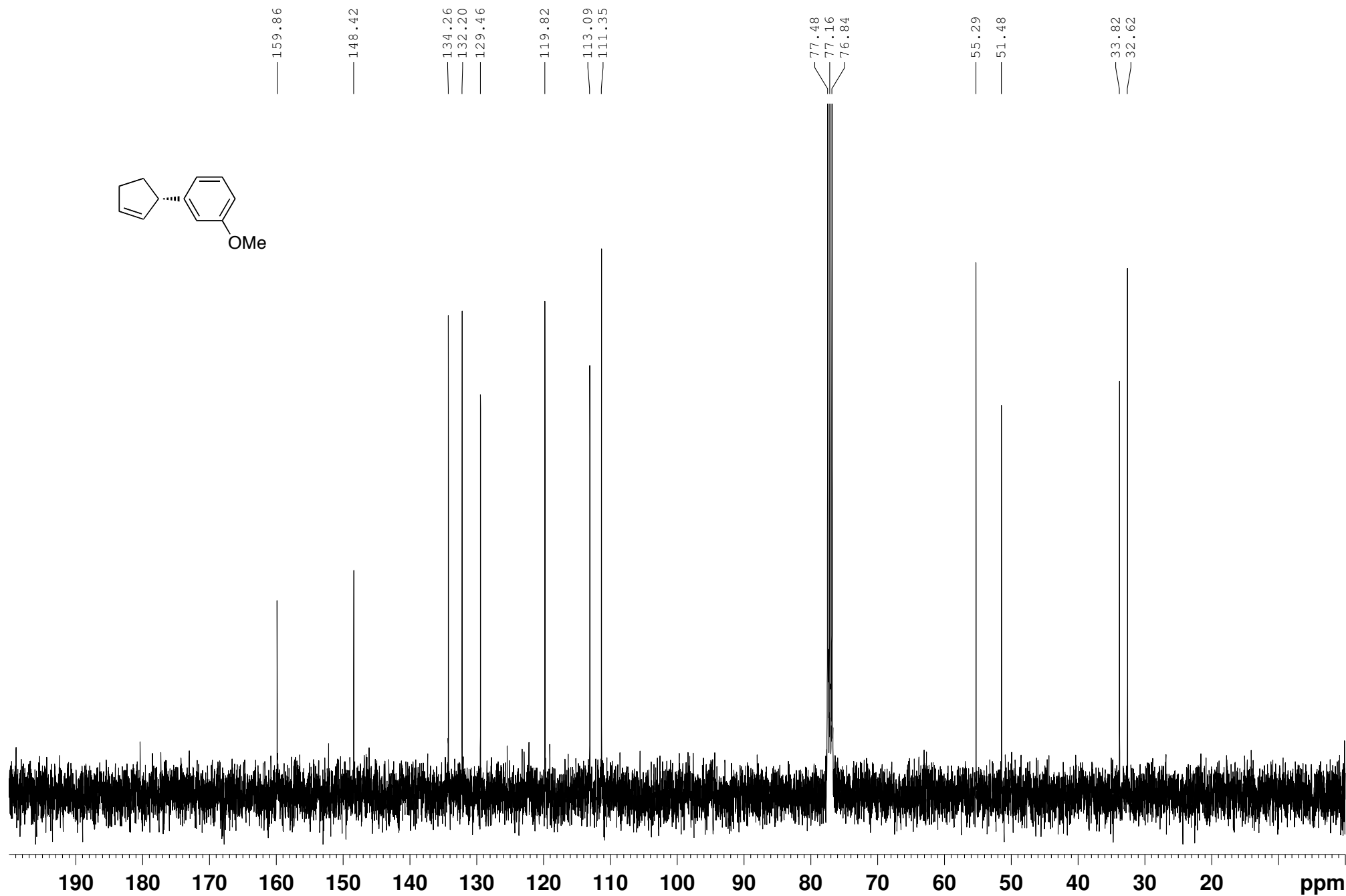
21.69



¹H NMR (400 MHz, CDCl₃)

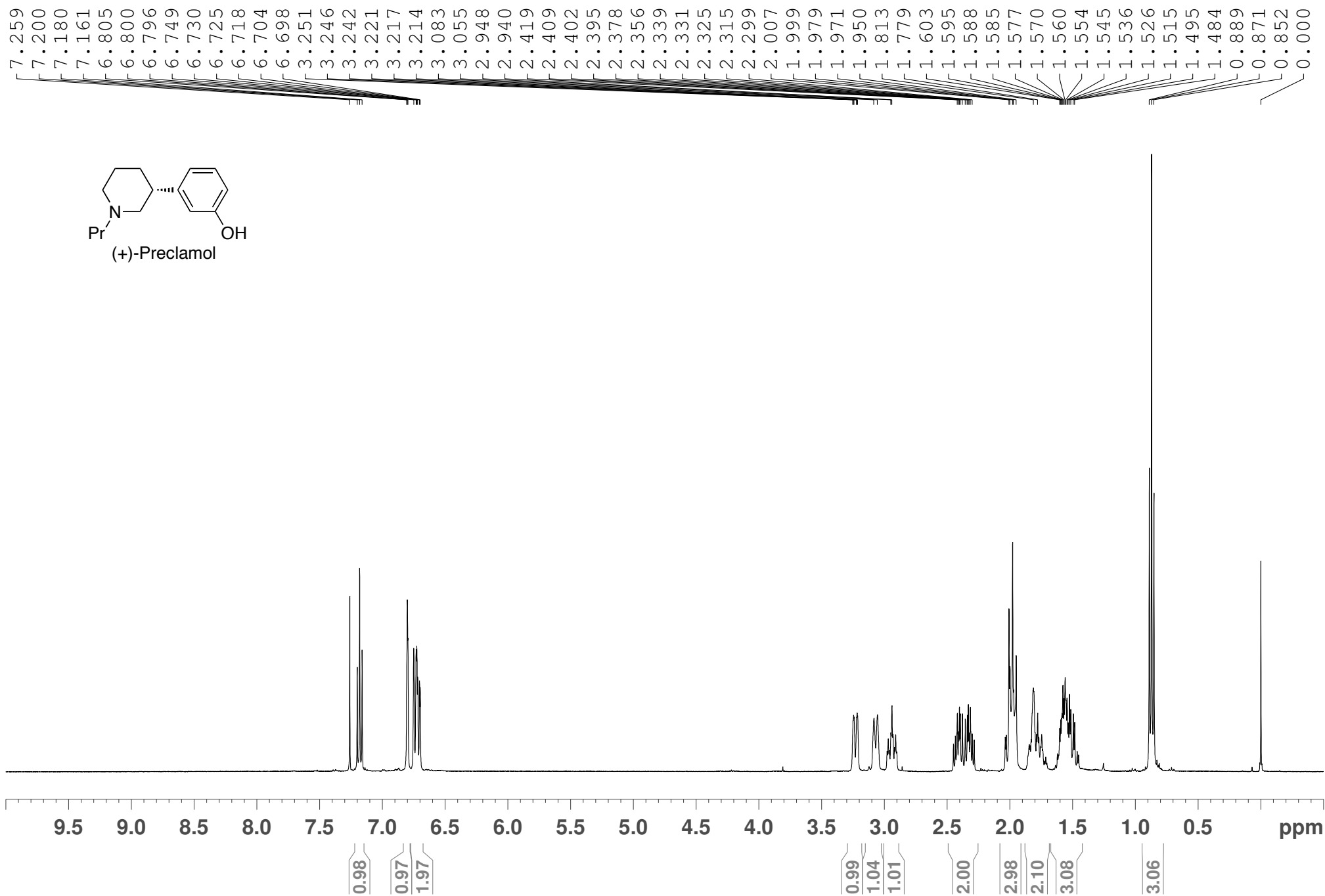


^{13}C NMR (100 MHz, CDCl_3)

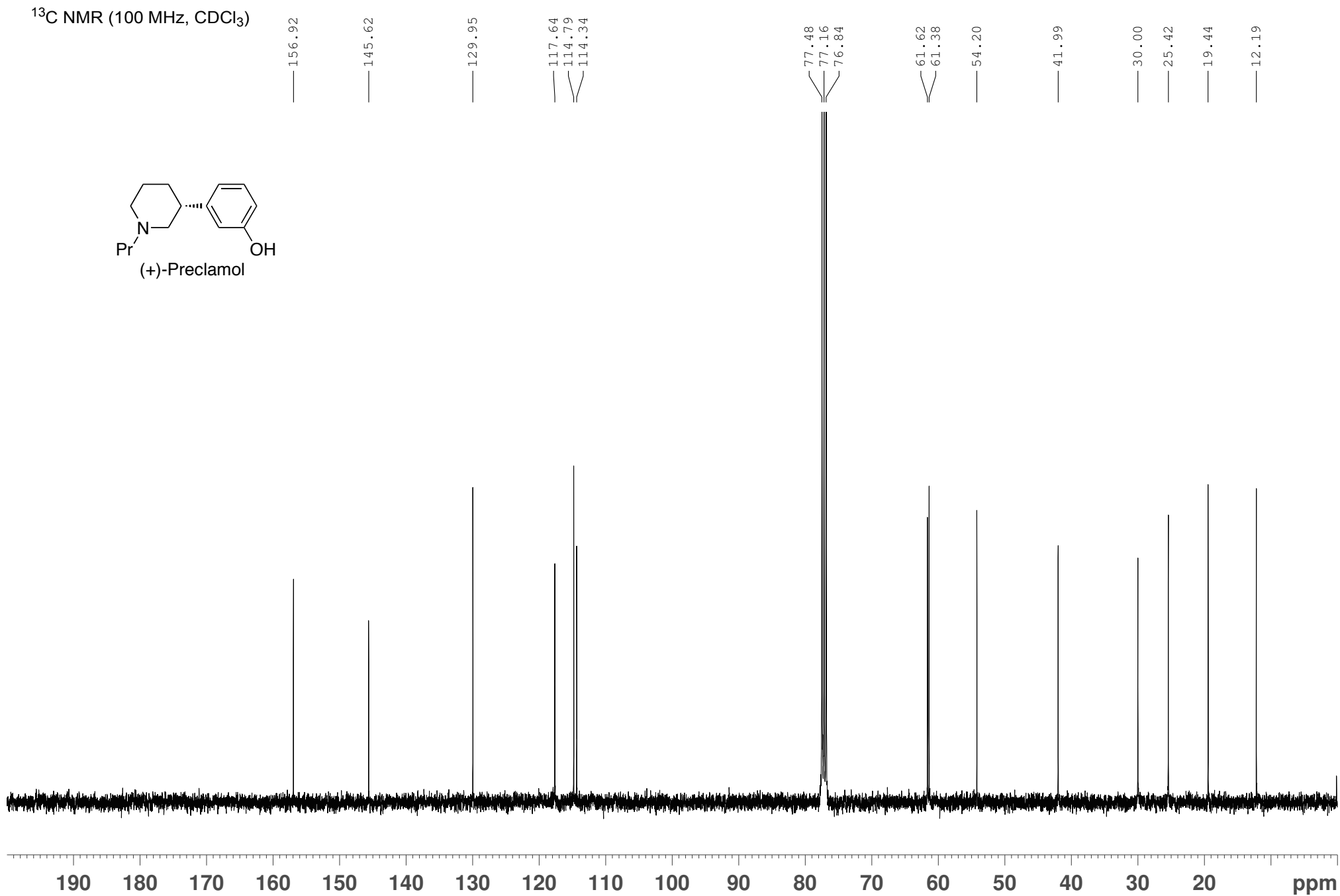
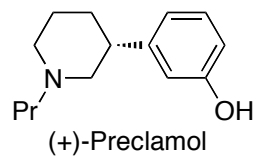


¹H NMR (400 MHz, CDCl₃)

S69



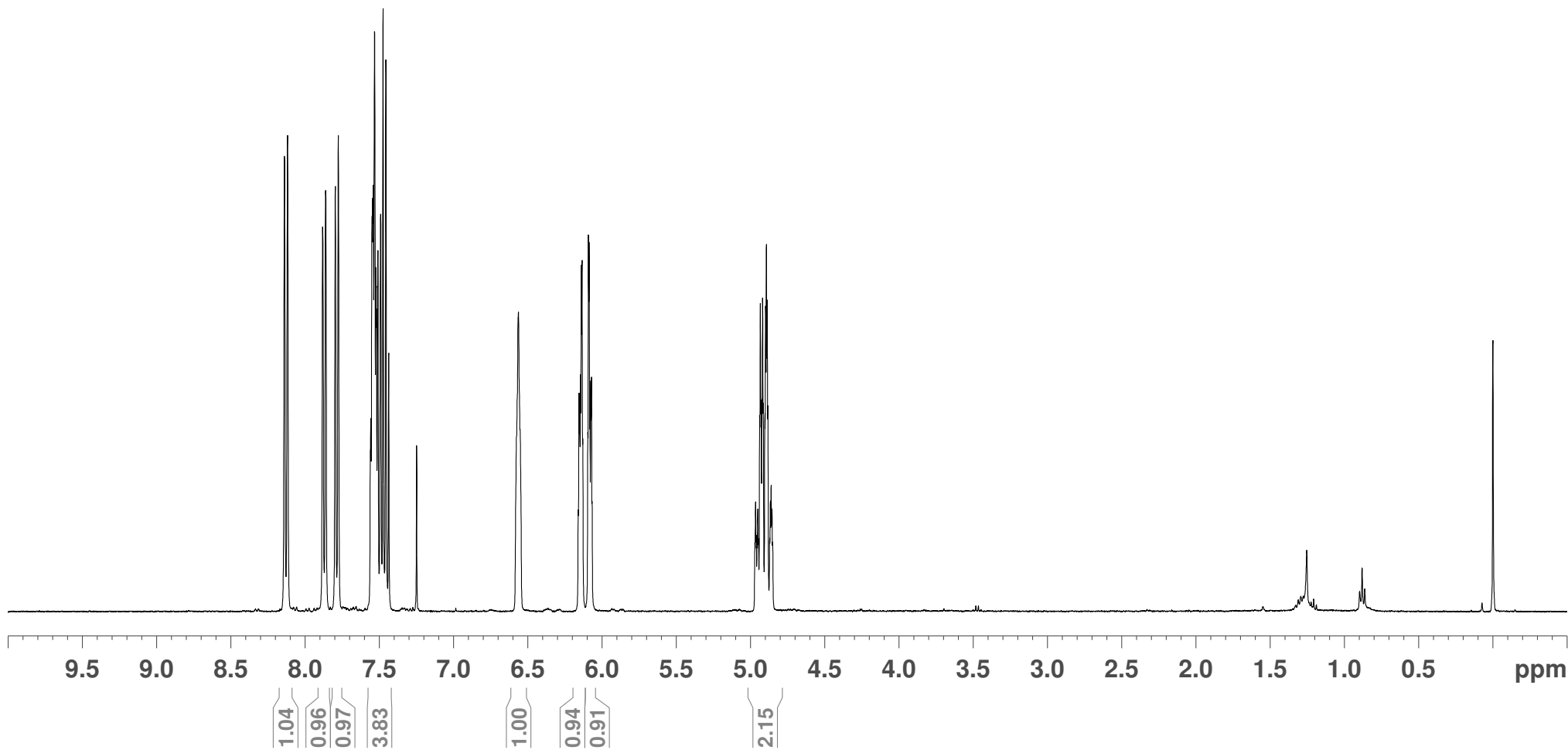
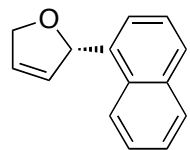
^{13}C NMR (100 MHz, CDCl_3)



¹H NMR (400 MHz, CDCl₃)

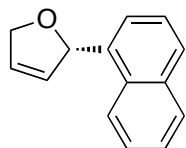
S71

8.138
8.118
7.881
7.861
7.796
7.776
7.560
7.557
7.548
7.544
7.540
7.531
7.523
7.519
7.511
7.509
7.490
7.474
7.455
7.436
7.248
6.583
6.578
6.564
6.553
6.547
6.161
6.156
6.151
6.146
6.141
6.136
6.131
6.096
6.092
6.088
6.083
6.077
6.072
6.068
6.067
4.962
4.952
4.939
4.934
4.930
4.924
4.919
4.915
4.904
4.899
4.894
4.888
4.884
4.871
4.867
4.861
4.856
0.000



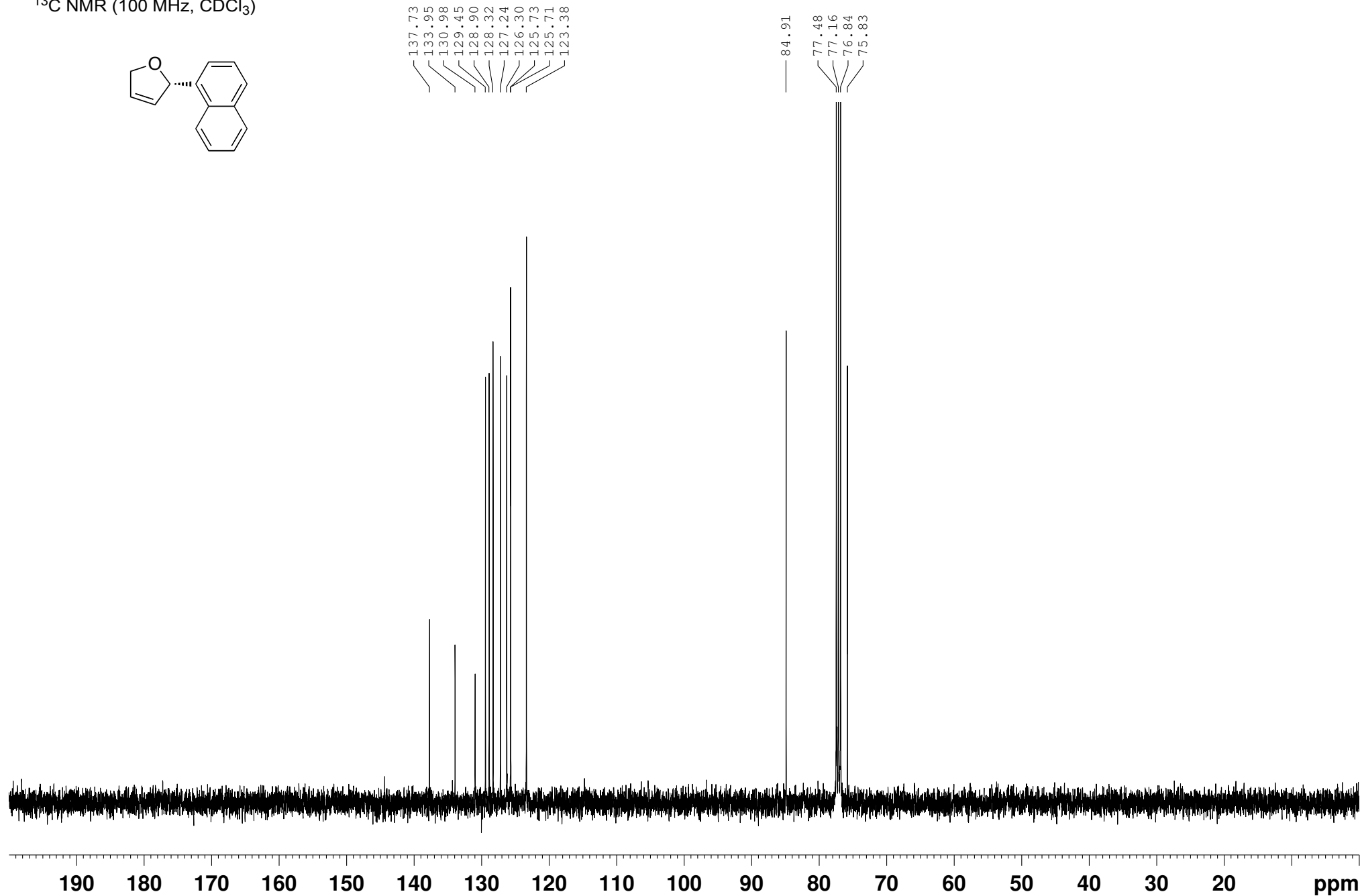
hj5031(17) rxn 1. in CDCl₃ 1-naph dihydrofuran 13C

¹³C NMR (100 MHz, CDCl₃)



137.73
133.95
130.98
129.45
128.90
128.32
127.24
126.30
125.73
125.71
123.38

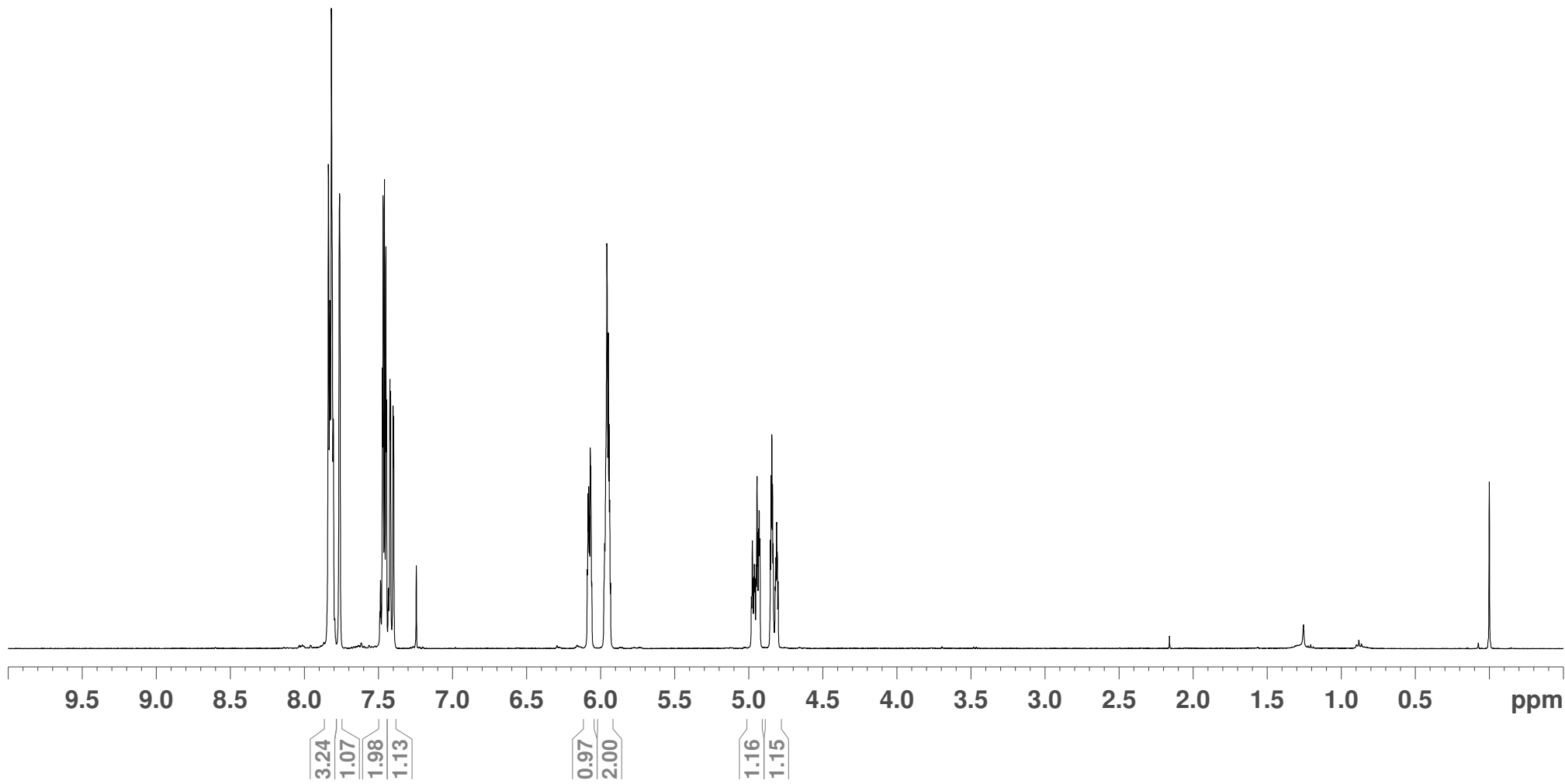
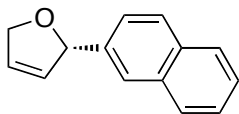
84.91
77.48
77.16
76.84
75.83

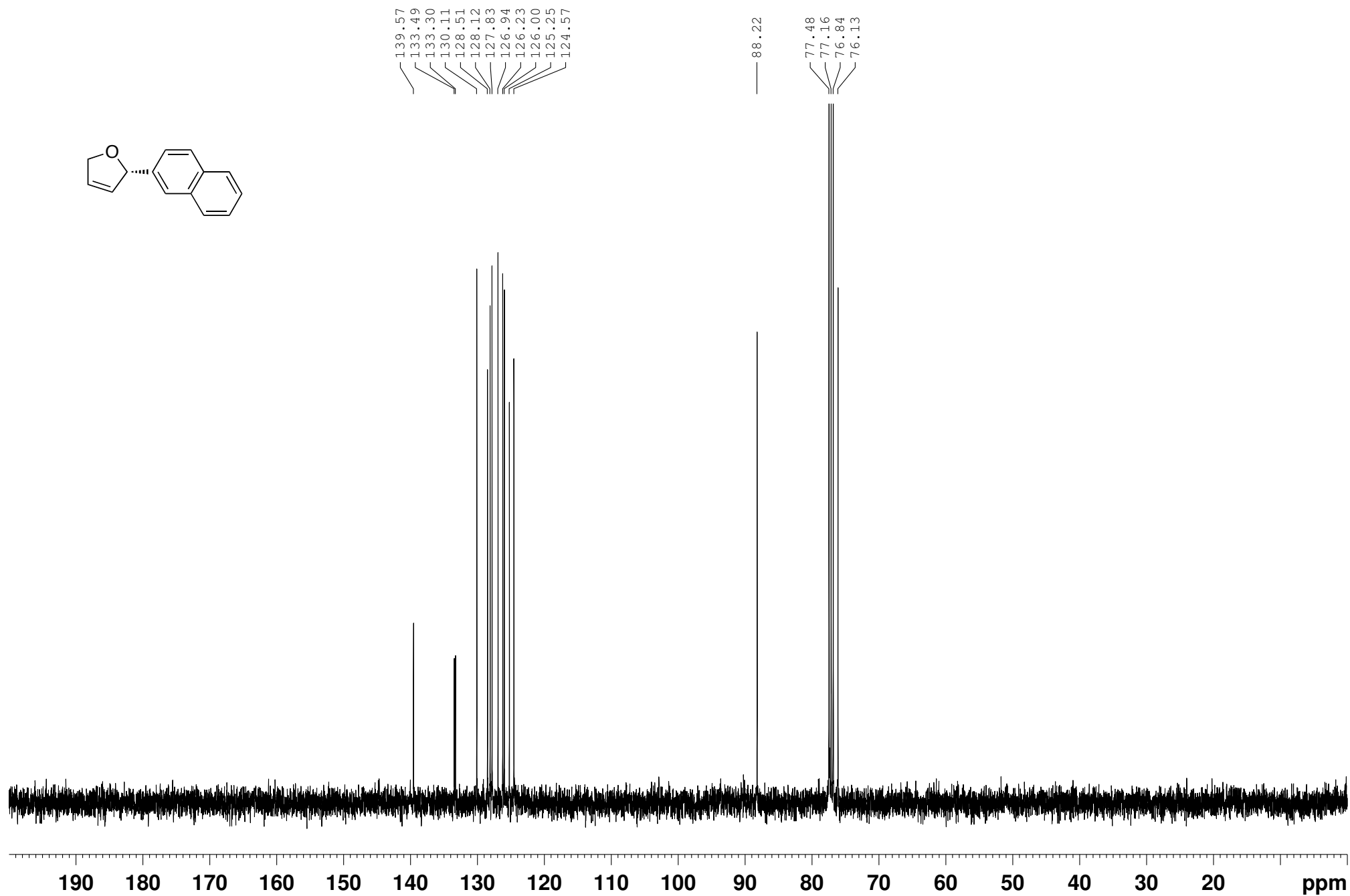
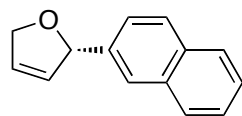


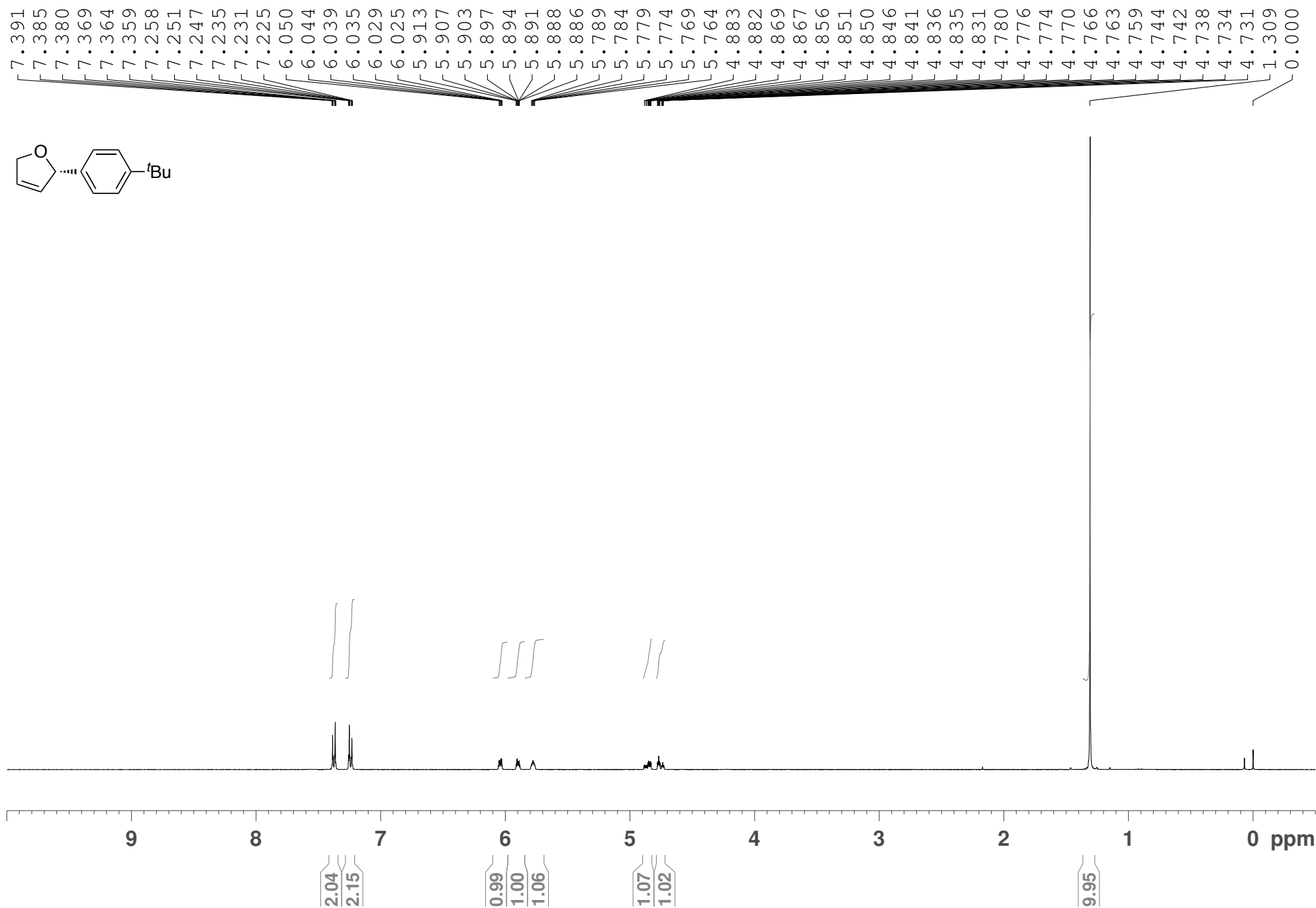
¹H NMR (400 MHz, CDCl₃)

7.491
7.487
7.474
7.469
7.460
7.451
7.446
7.434
7.423
7.419
7.402
7.398
7.245
6.090
6.085
6.081
6.076
6.071
6.067
6.061
5.973
5.958
5.949
5.944
5.940
5.934
4.983
4.976
4.972
4.966
4.963
4.958
4.951
4.945
4.940
4.934
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4.928
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4.840
4.835
4.822
4.817
4.812
4.808
4.802

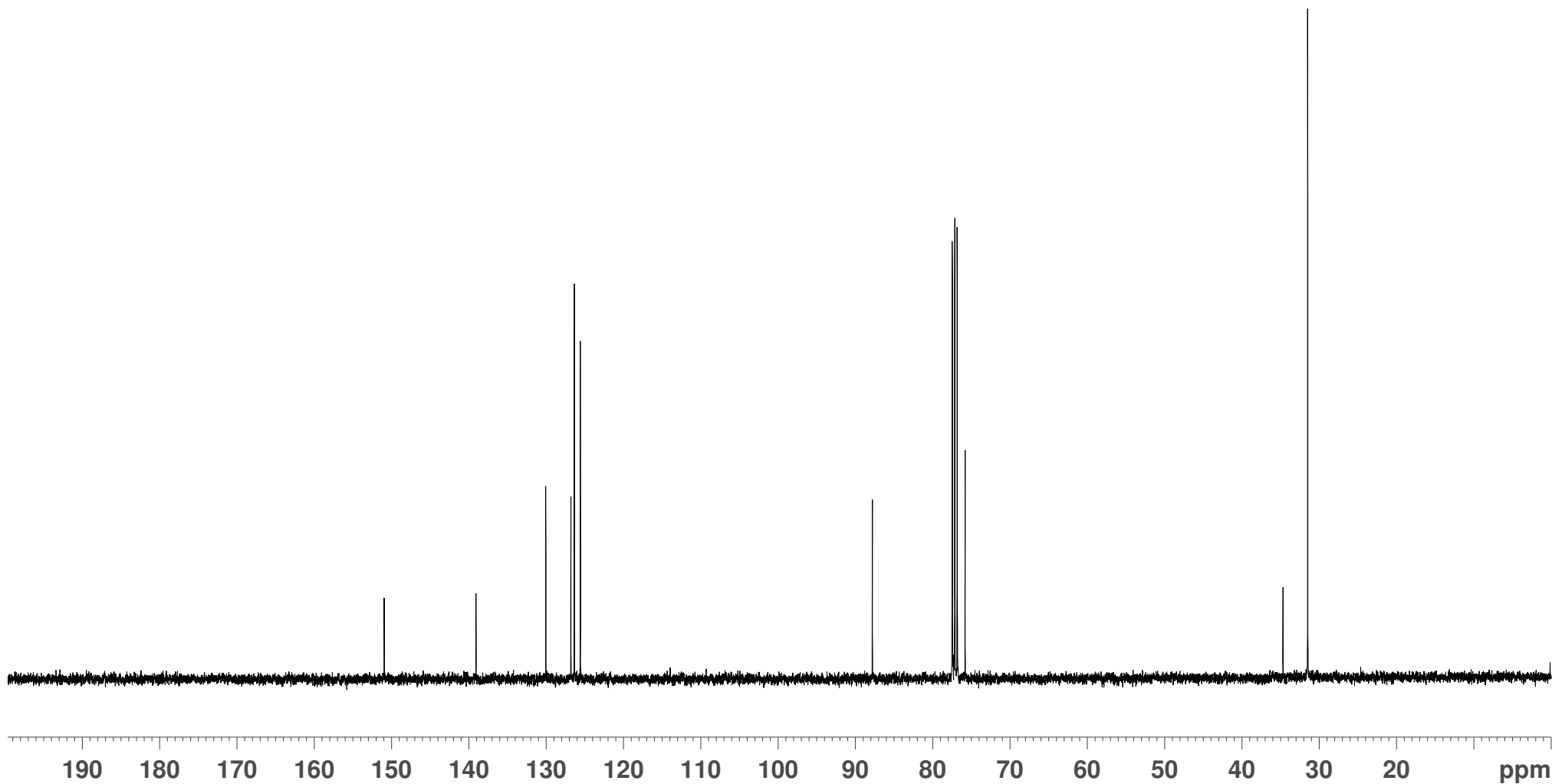
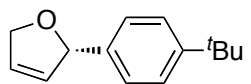
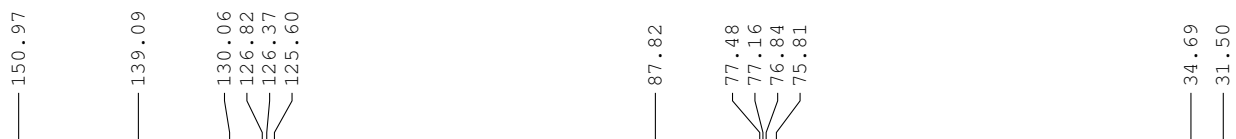
— 0.000





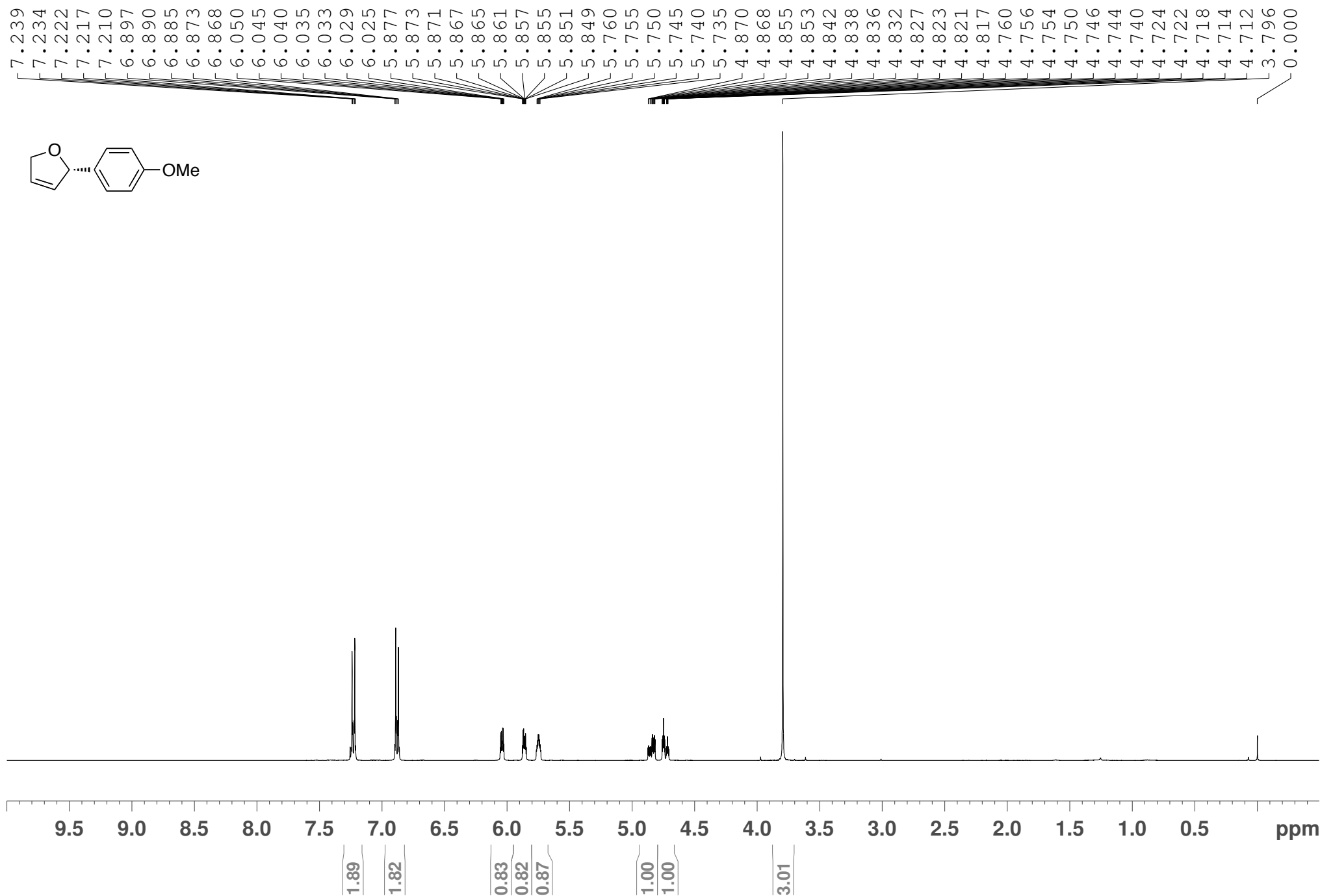


^{13}C NMR (100 MHz, CDCl_3)

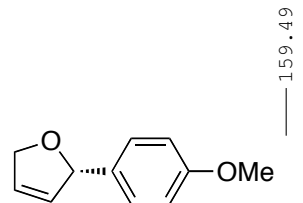


¹H NMR (400 MHz, CDCl₃)

S77



^{13}C NMR (100 MHz, CDCl_3)



159.49

134.25

130.12

128.01

126.83

114.02

87.66

77.48

77.16

76.84

75.67

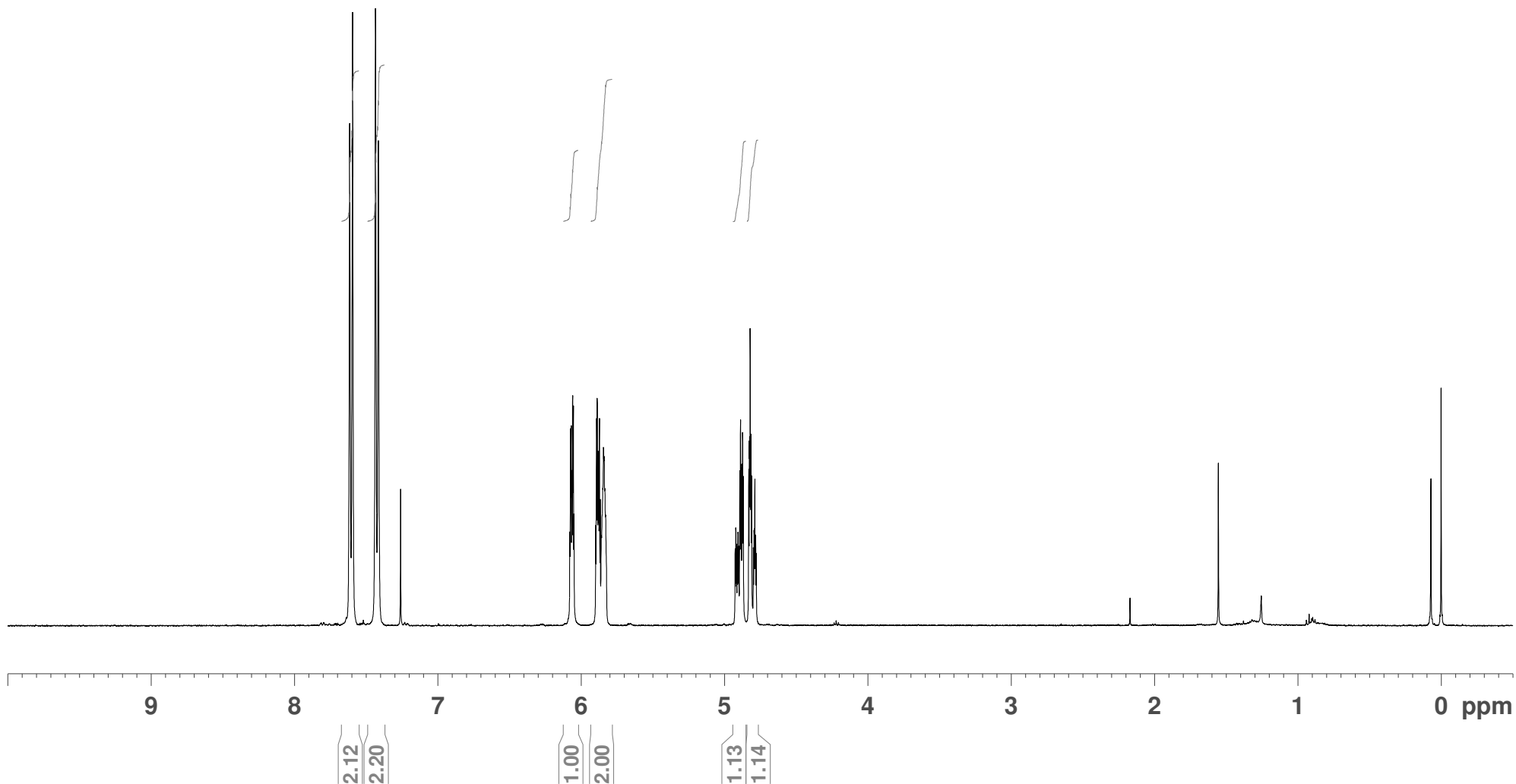
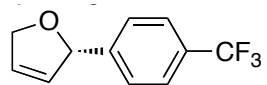
55.43



190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

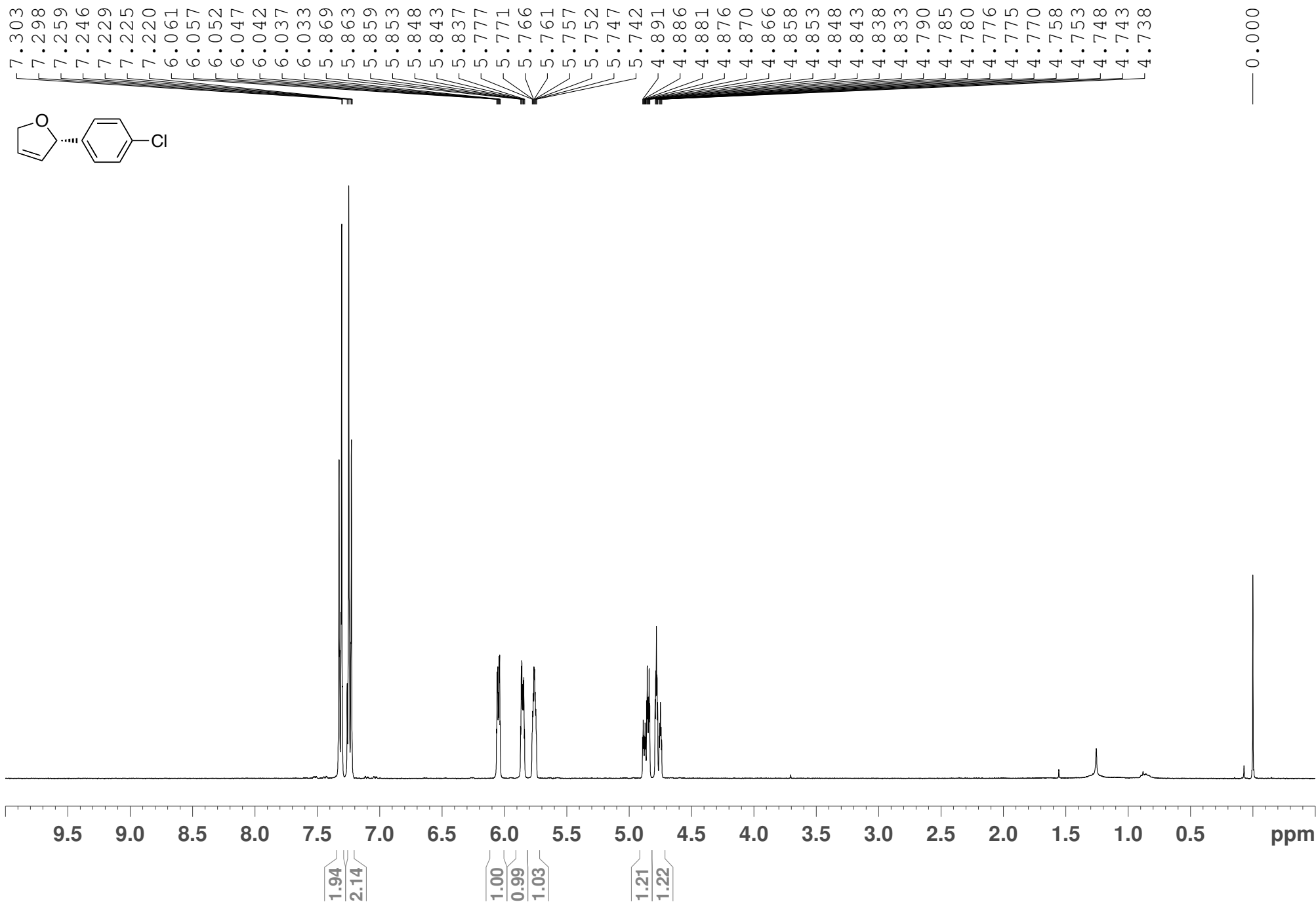
¹H NMR (400 MHz, CDCl₃)

7.433
7.413
7.259
6.079
6.075
6.069
6.064
6.059
6.054
6.050
5.898
5.892
5.888
5.882
5.877
5.872
5.867
5.859
5.849
5.844
5.840
5.835
5.830
4.925
4.921
4.920
4.915
4.910
4.906
4.905
4.900
4.893
4.888
4.883
4.878
4.874
4.868
4.831
4.826
4.824
4.820
4.816
4.814
4.810
4.798
4.794
4.792
4.788
4.784
4.782
4.778
2.171
1.554
1.255
0.071
0.000

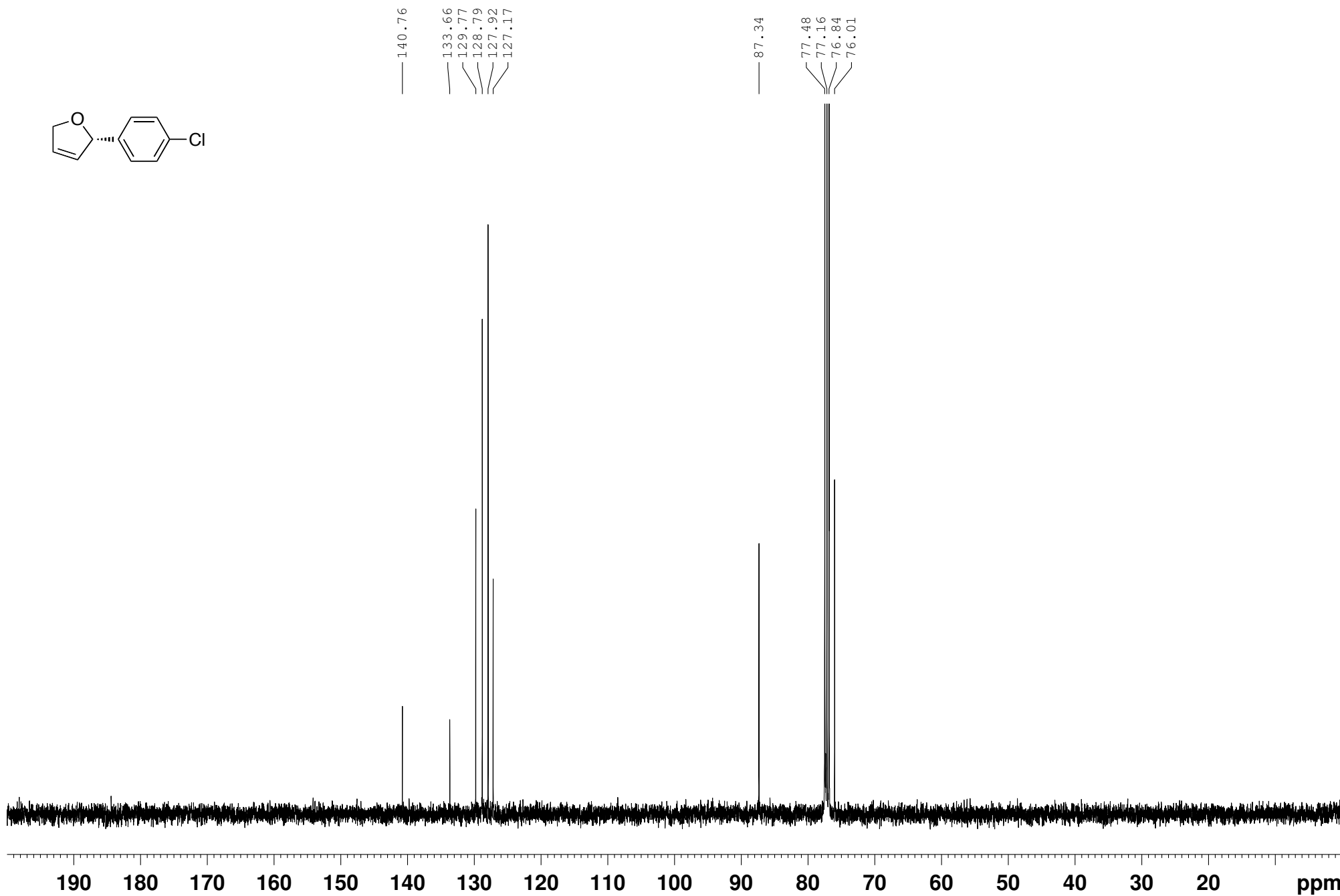
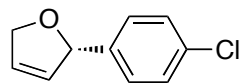


¹H NMR (400 MHz, CDCl₃)

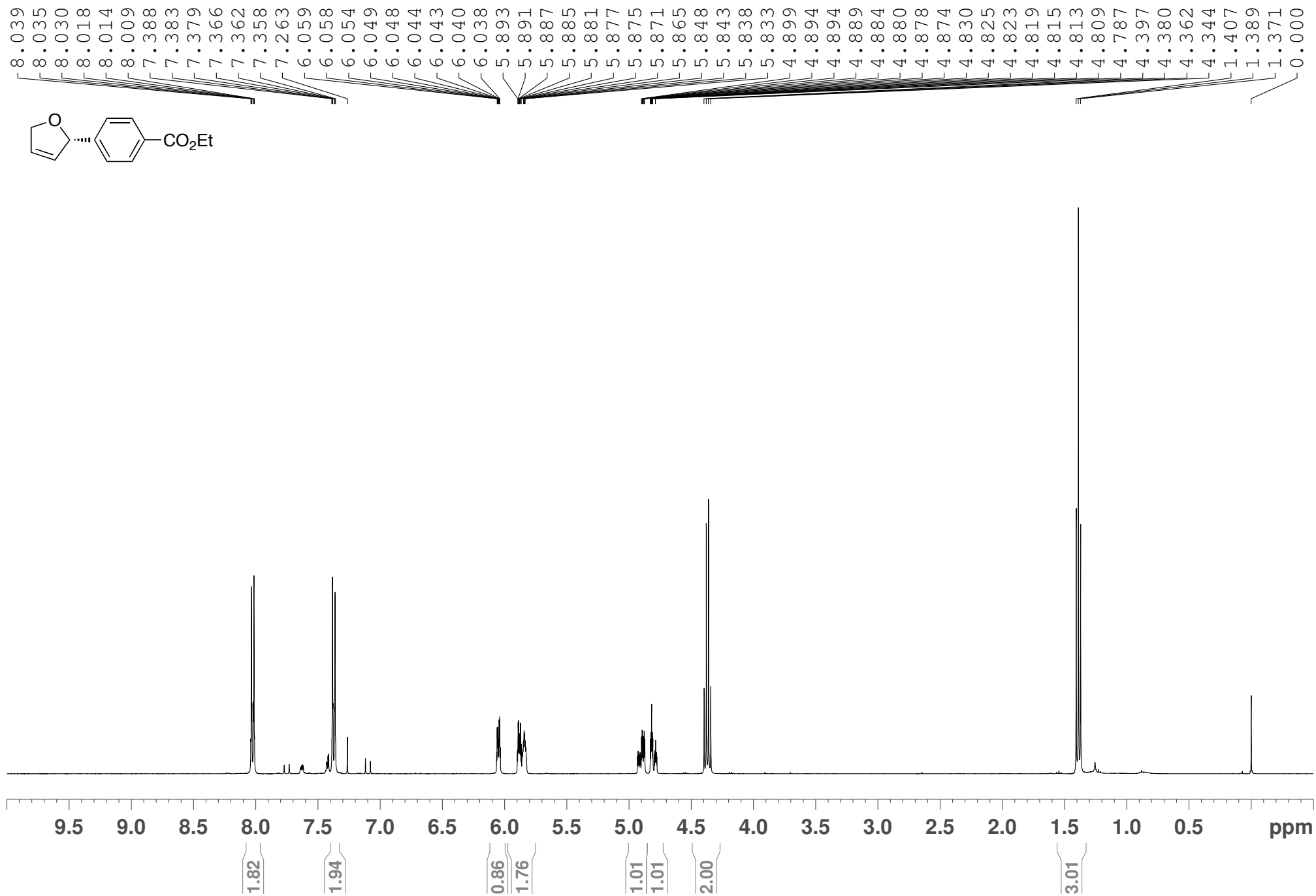
S80



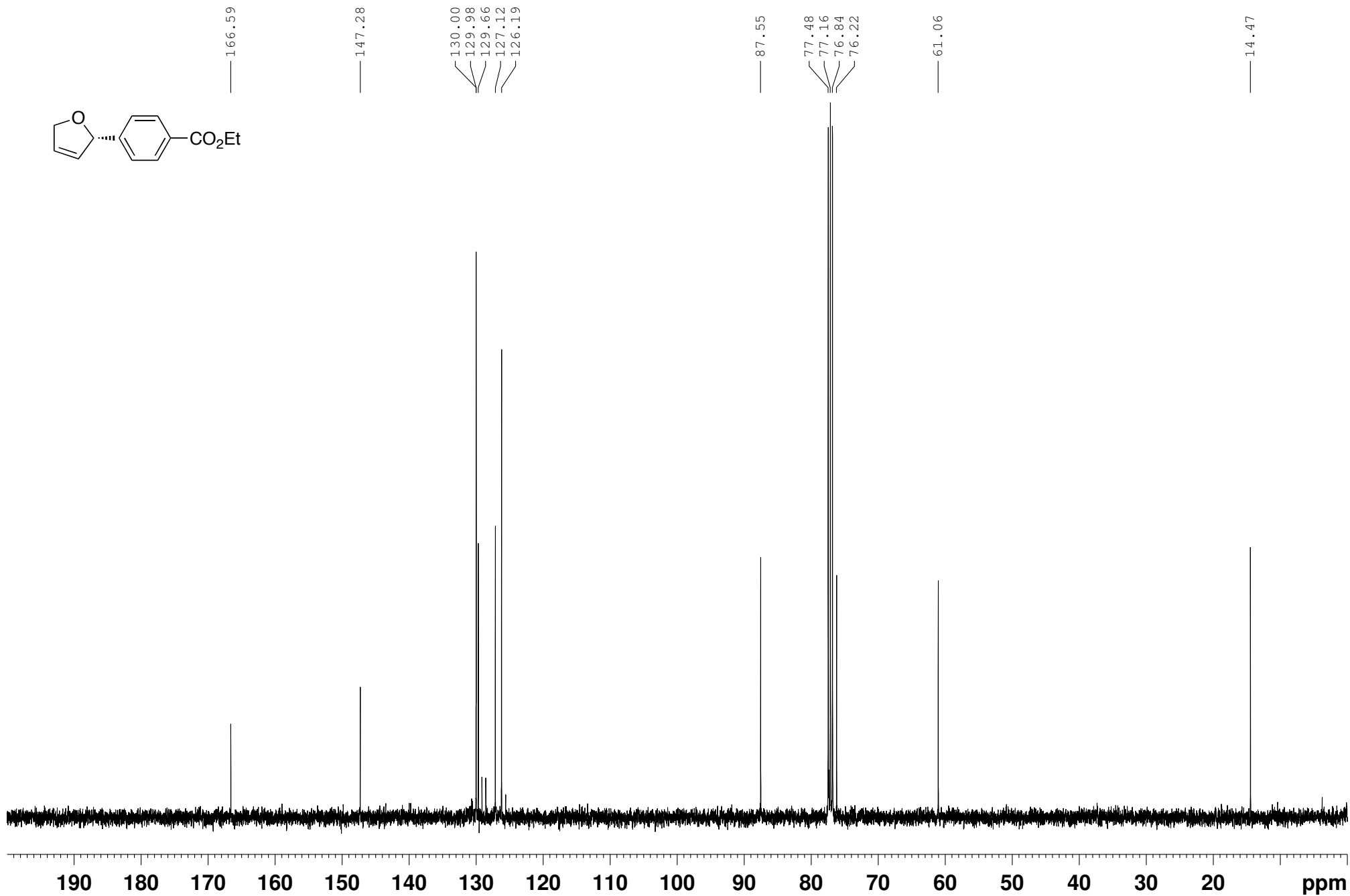
^{13}C NMR (100 MHz, CDCl_3)



¹H NMR (400 MHz, CDCl₃)

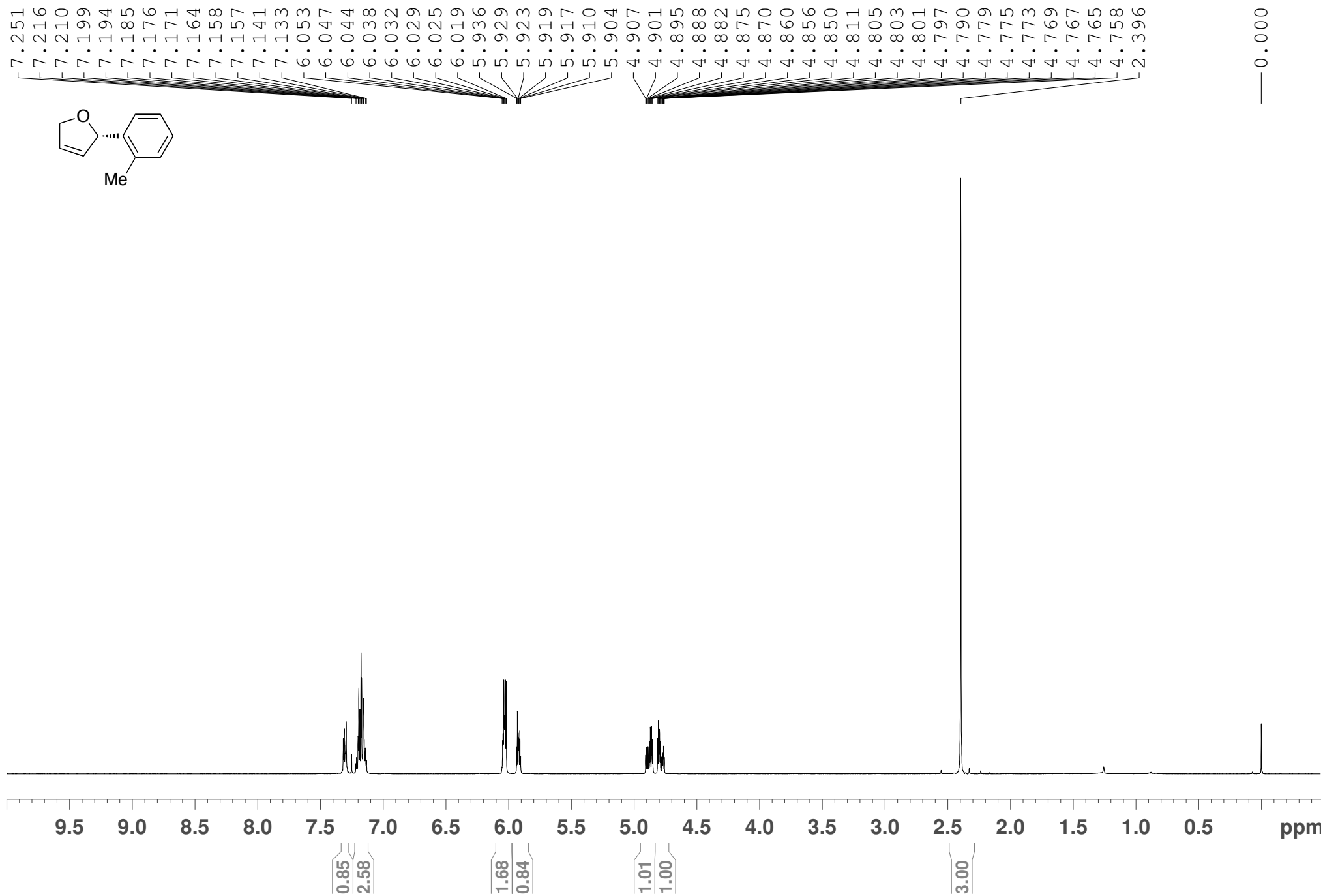


^{13}C NMR (100 MHz, CDCl_3)

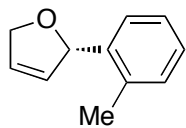


¹H NMR (400 MHz, CDCl₃)

S84



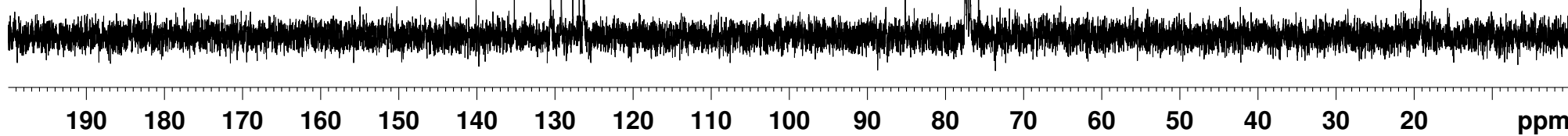
^{13}C NMR (100 MHz, CDCl_3)



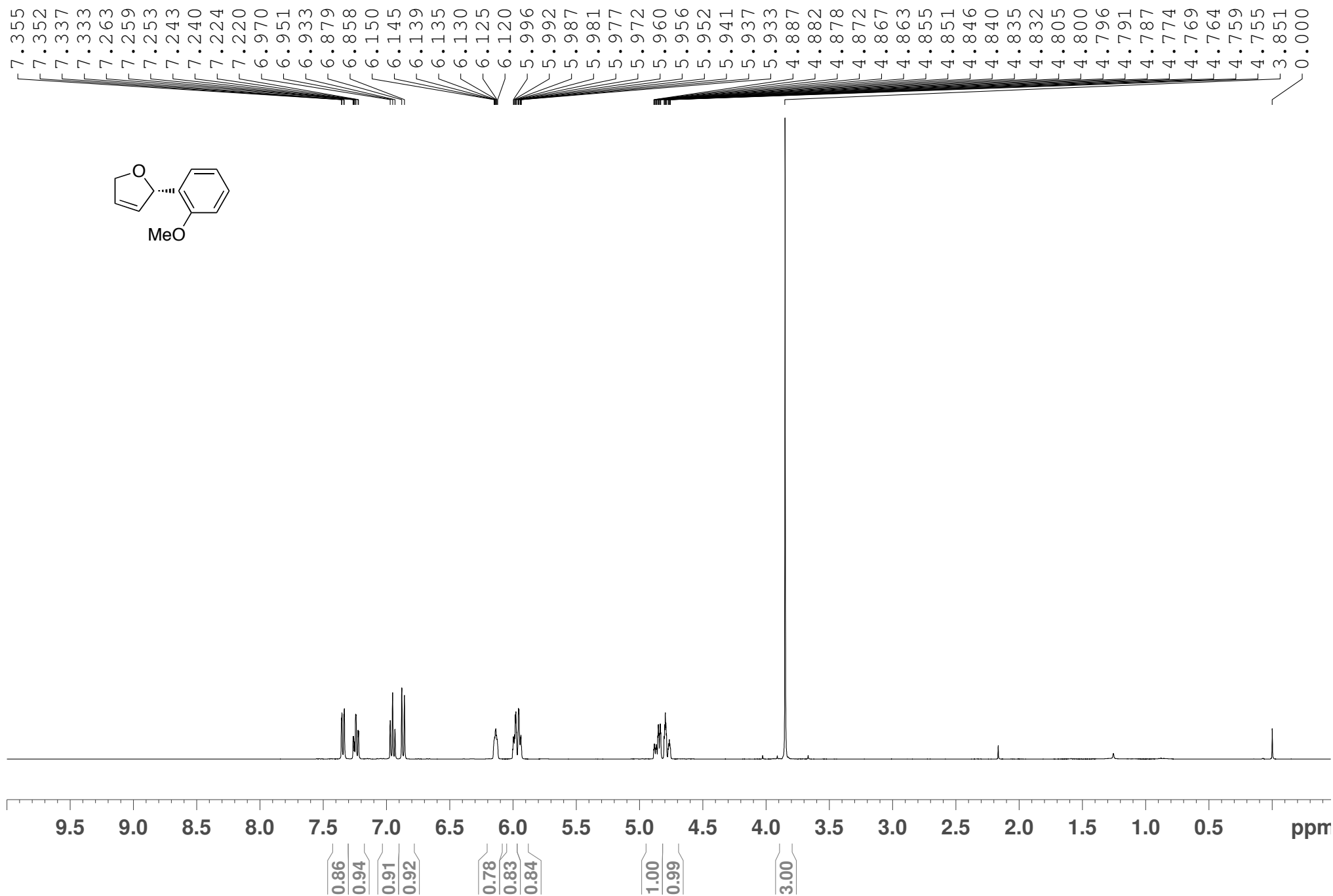
140.08
135.20
130.56
129.18
127.71
126.89
126.36
126.28

85.15
77.48
77.36
77.16
76.84
75.76

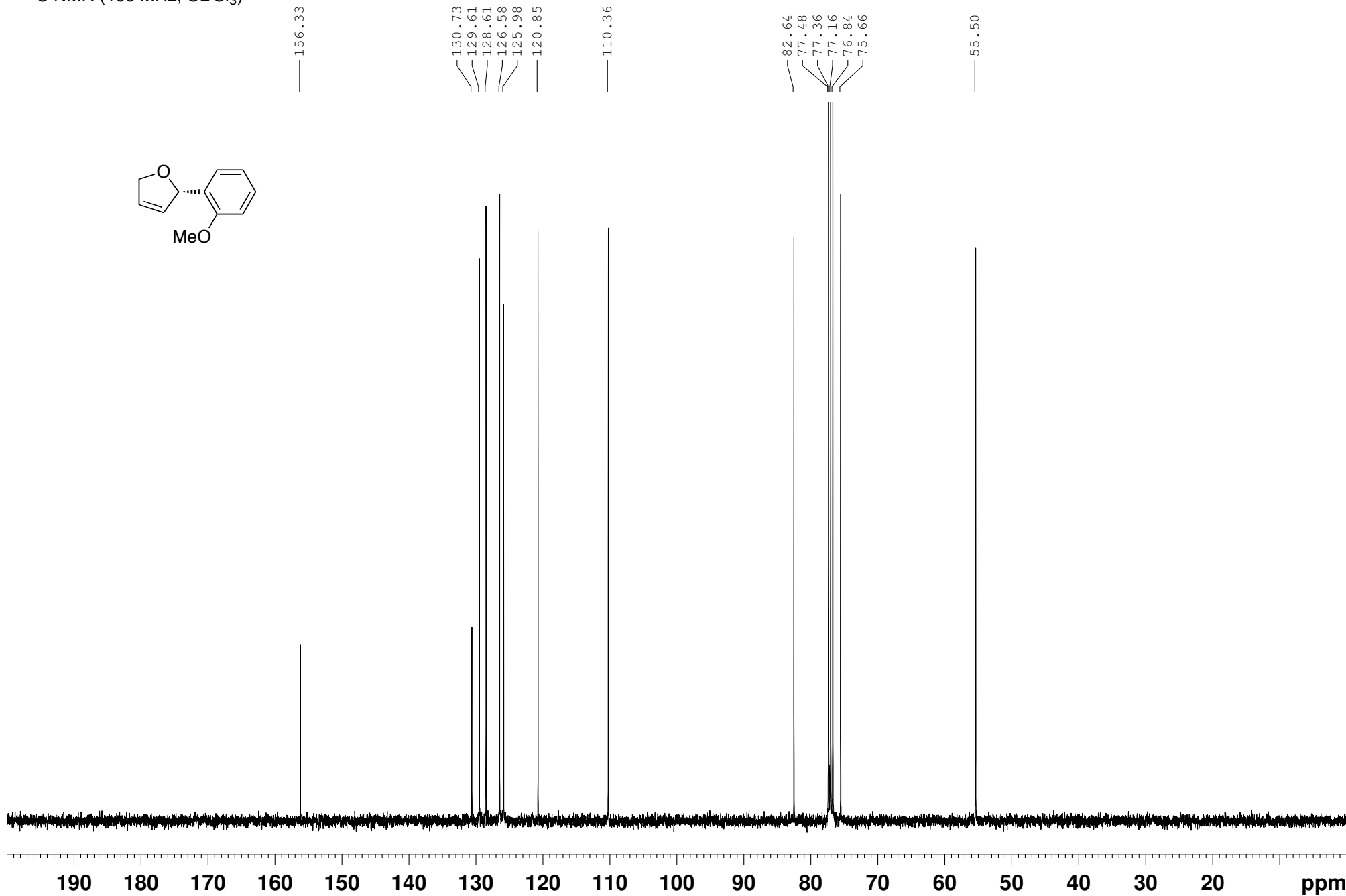
19.12



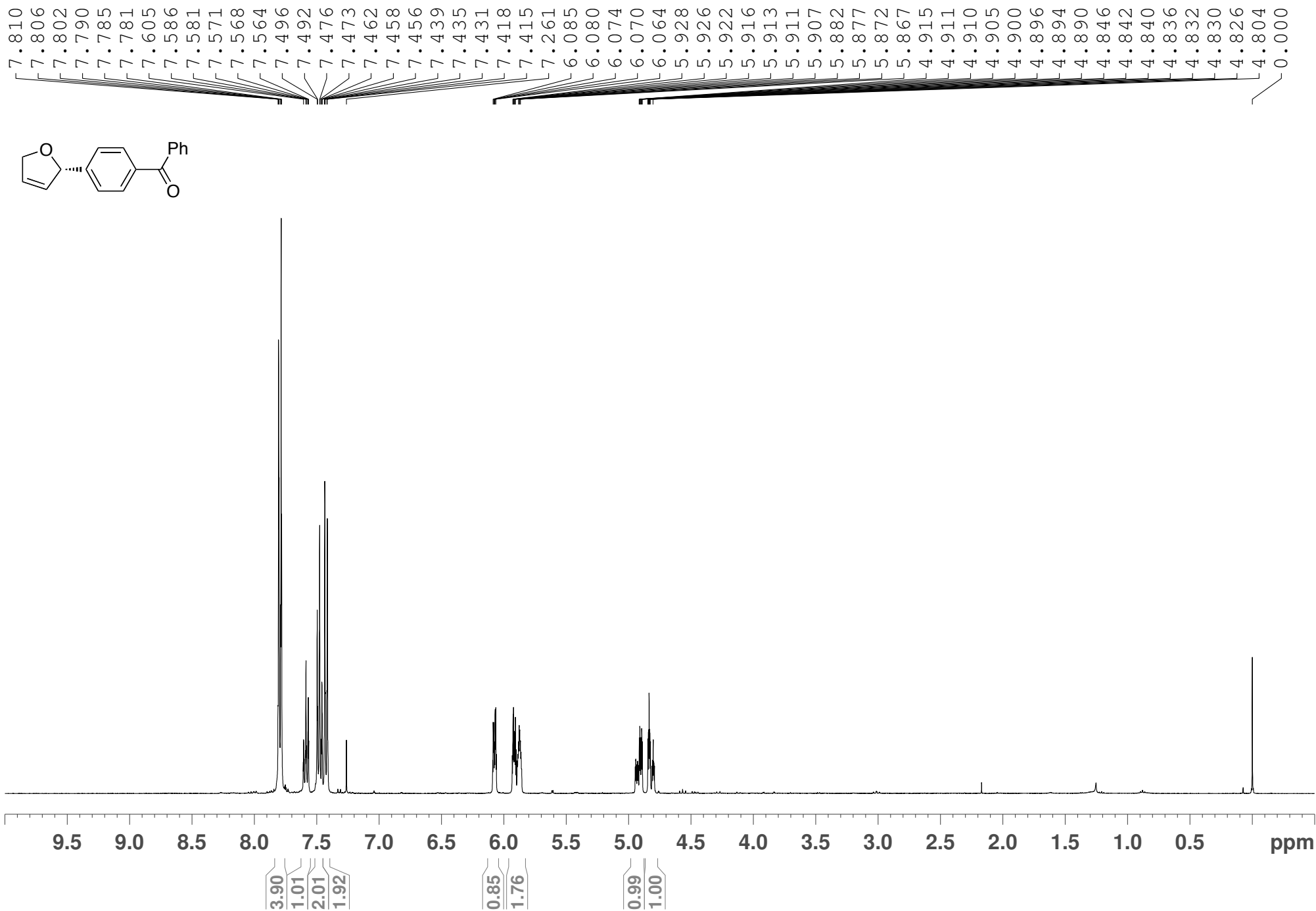
¹H NMR (400 MHz, CDCl₃)



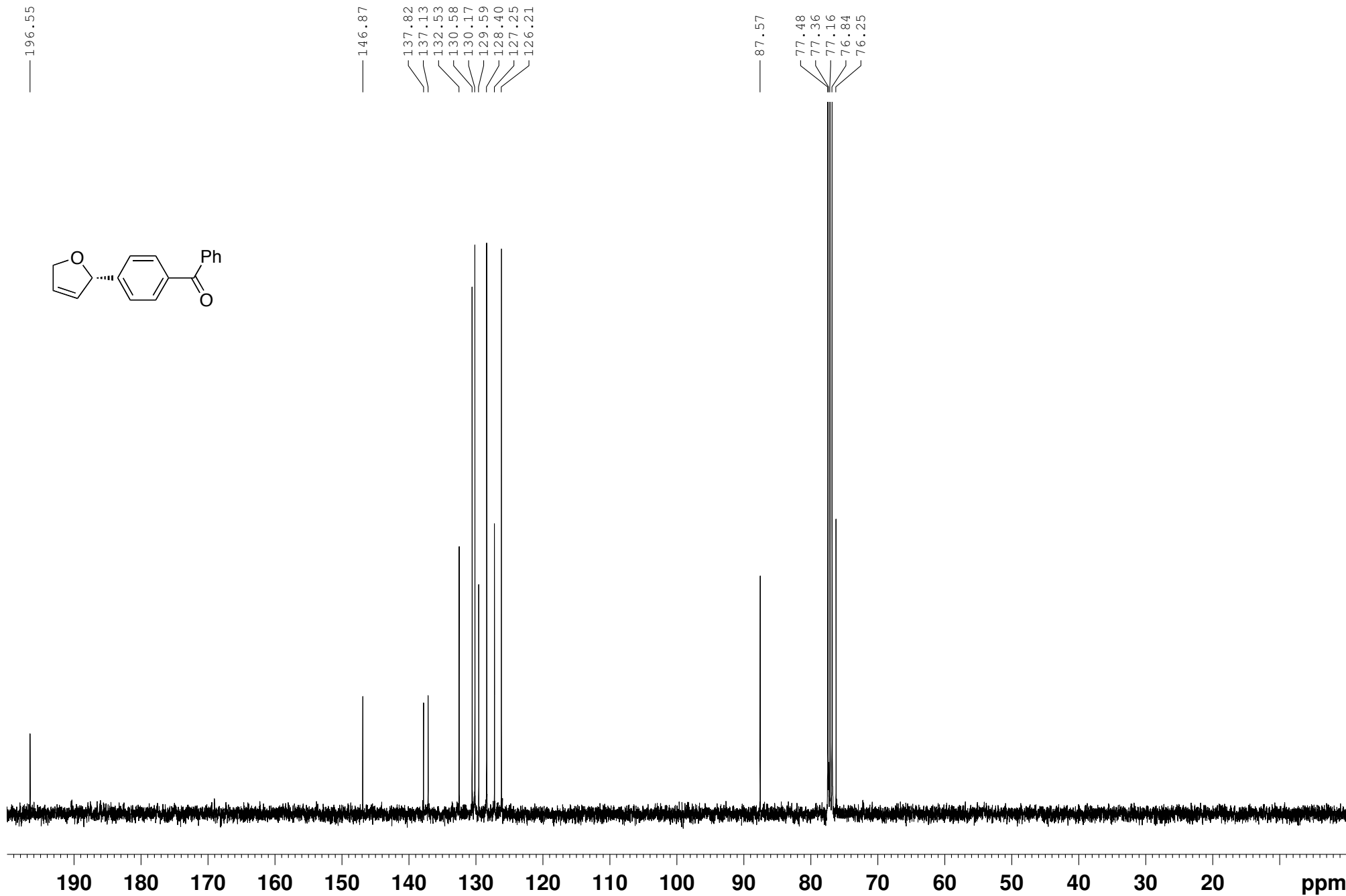
^{13}C NMR (100 MHz, CDCl_3)



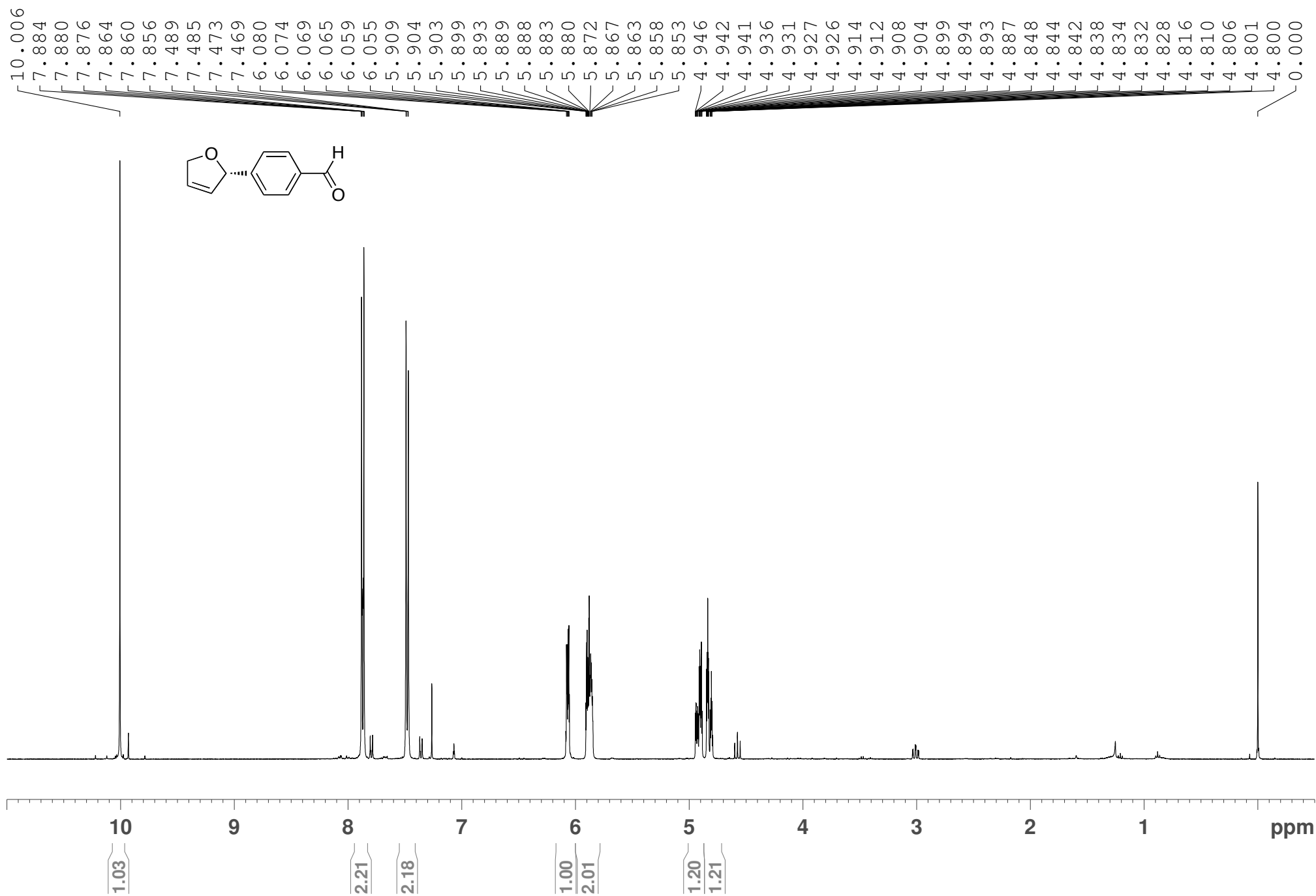
¹H NMR (400 MHz, CDCl₃)

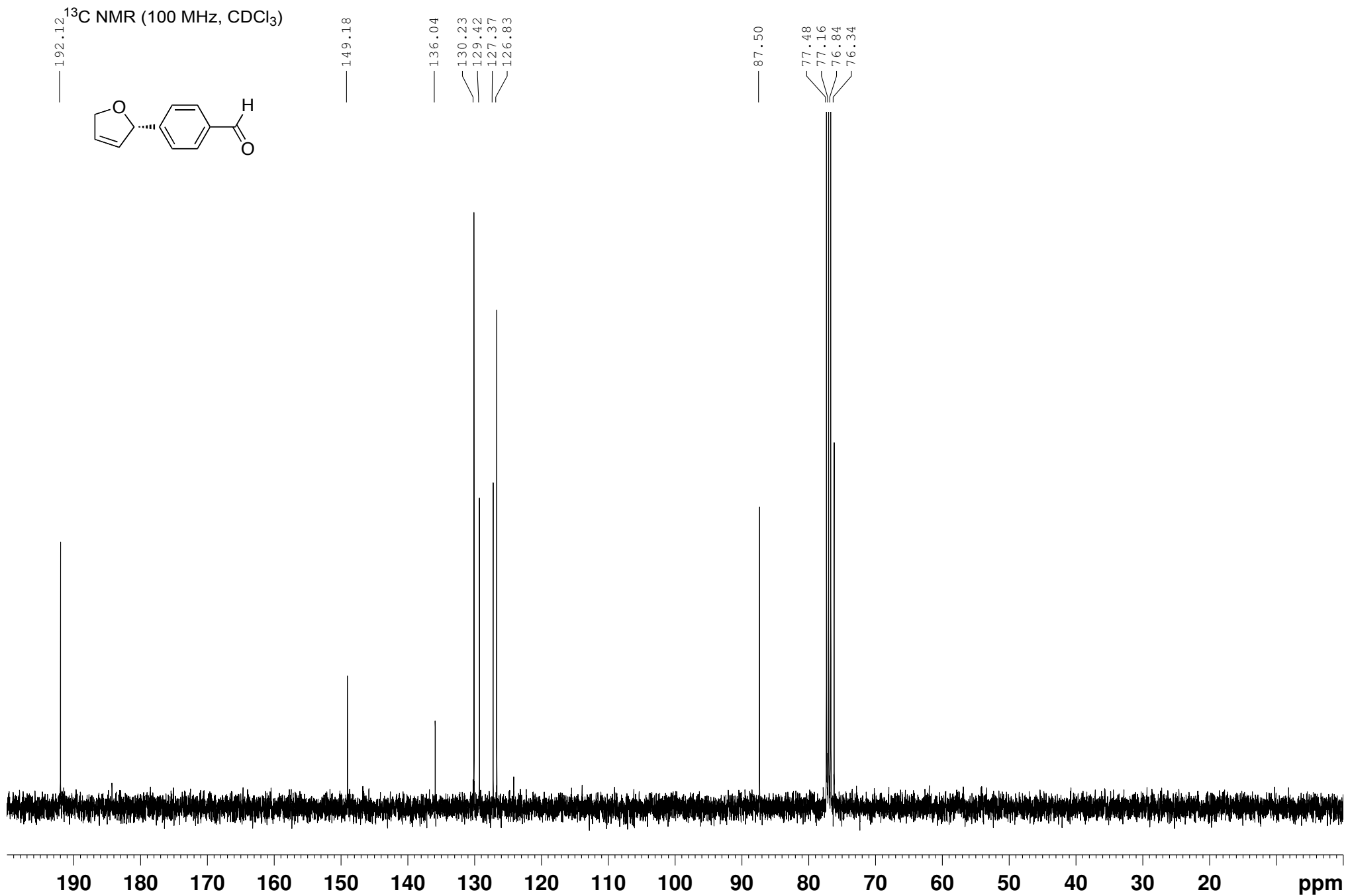


^{13}C NMR (100 MHz, CDCl_3)

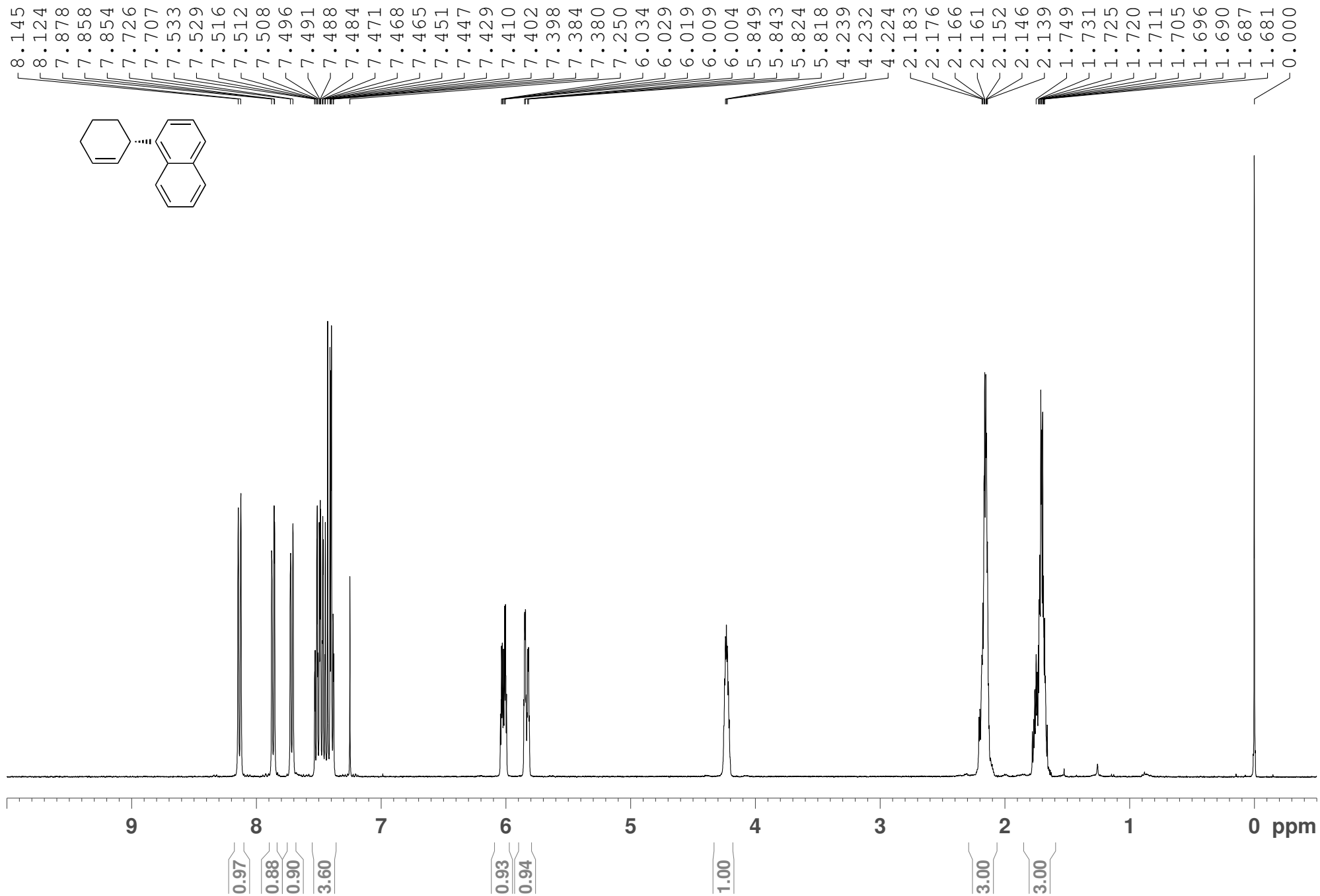


¹H NMR (400 MHz, CDCl₃)

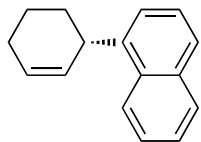




¹H NMR (400 MHz, CDCl₃)



^{13}C NMR (100 MHz, CDCl_3)



142.08
134.18
131.56
130.37
129.09
128.94
126.77
125.88
125.59
125.44
125.23
123.57

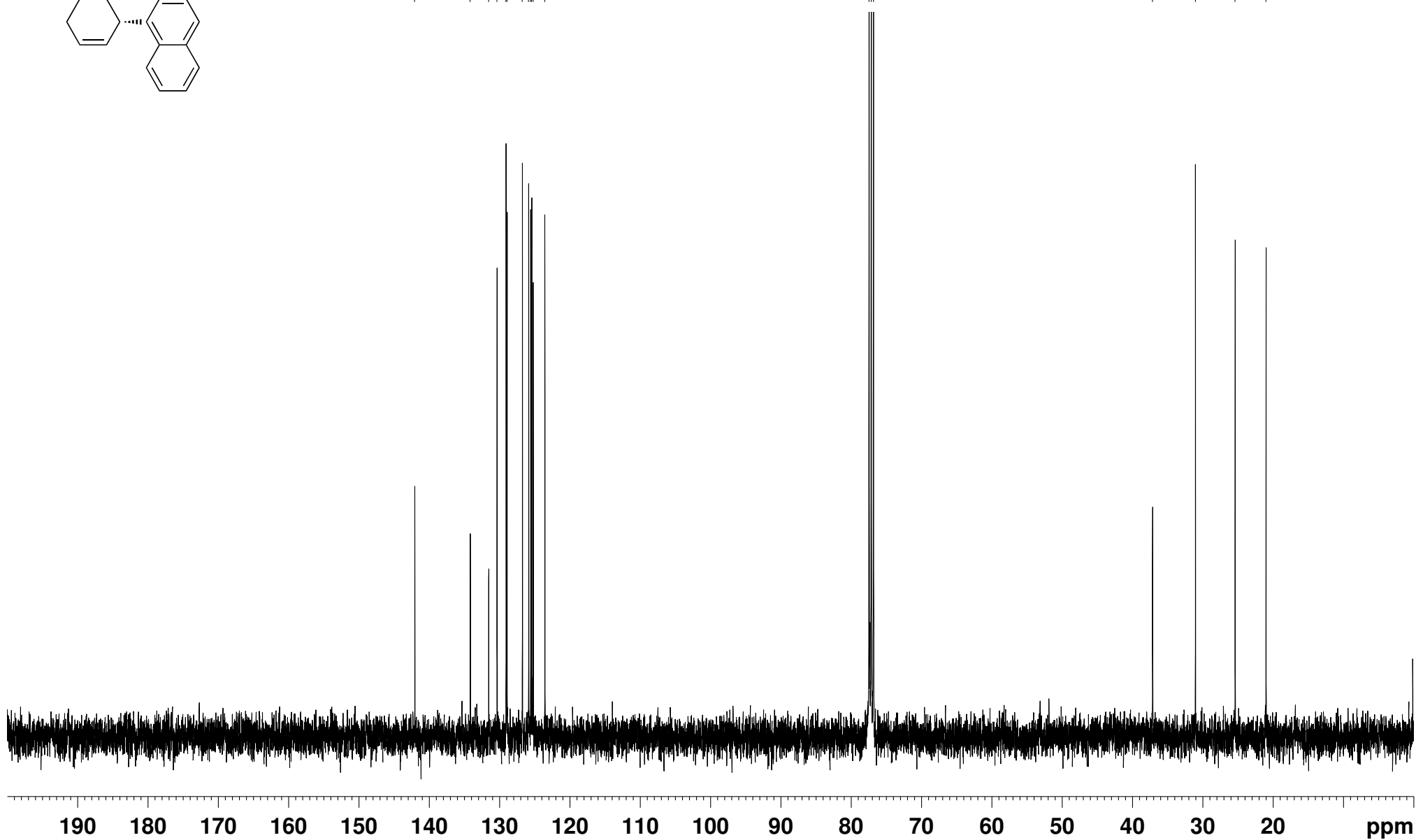
77.48
77.16
76.84

37.15

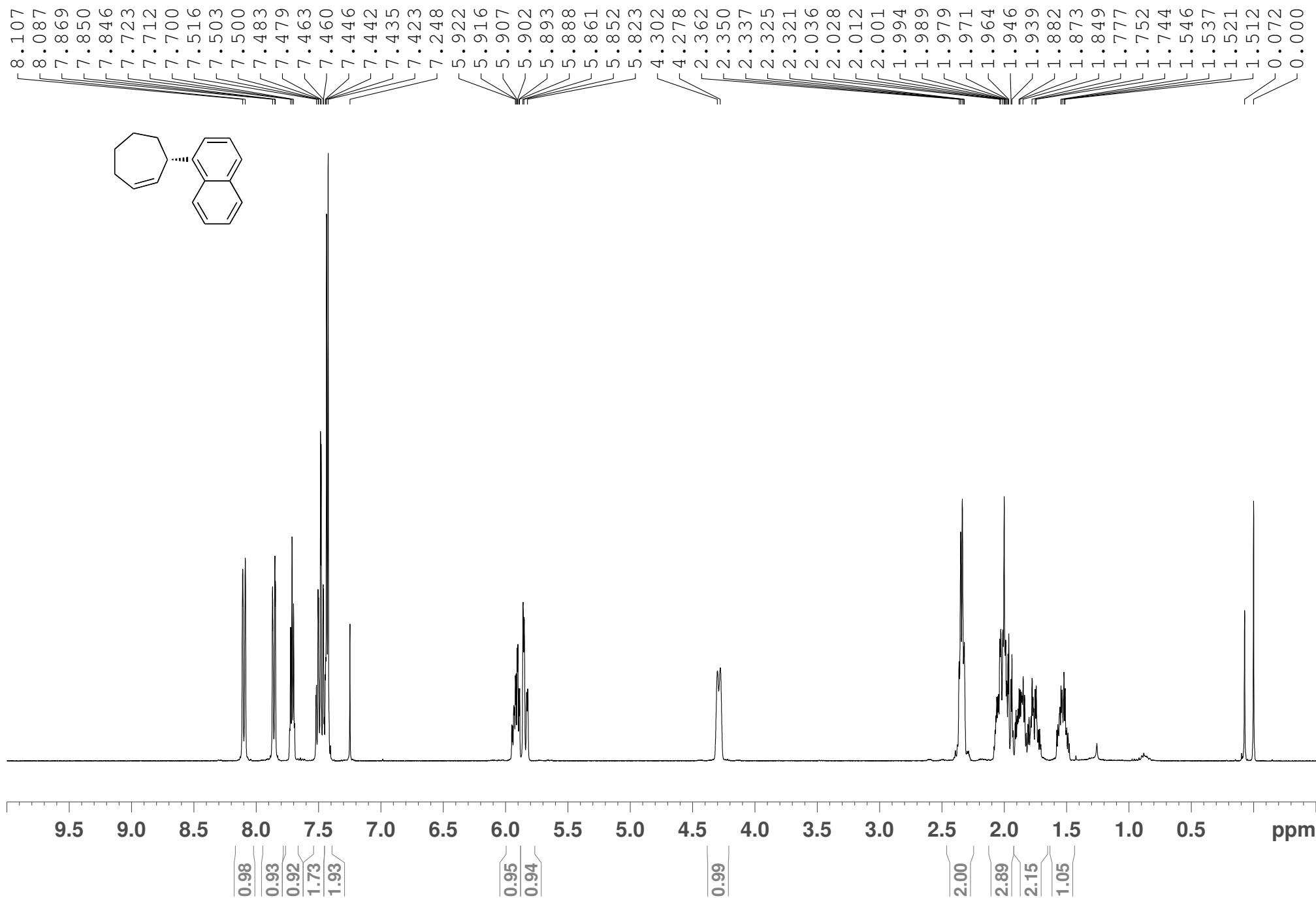
31.06

25.41

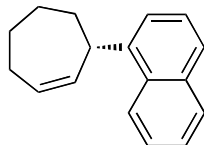
21.01



¹H NMR (400 MHz, CDCl₃)



^{13}C NMR (100 MHz, CDCl_3)

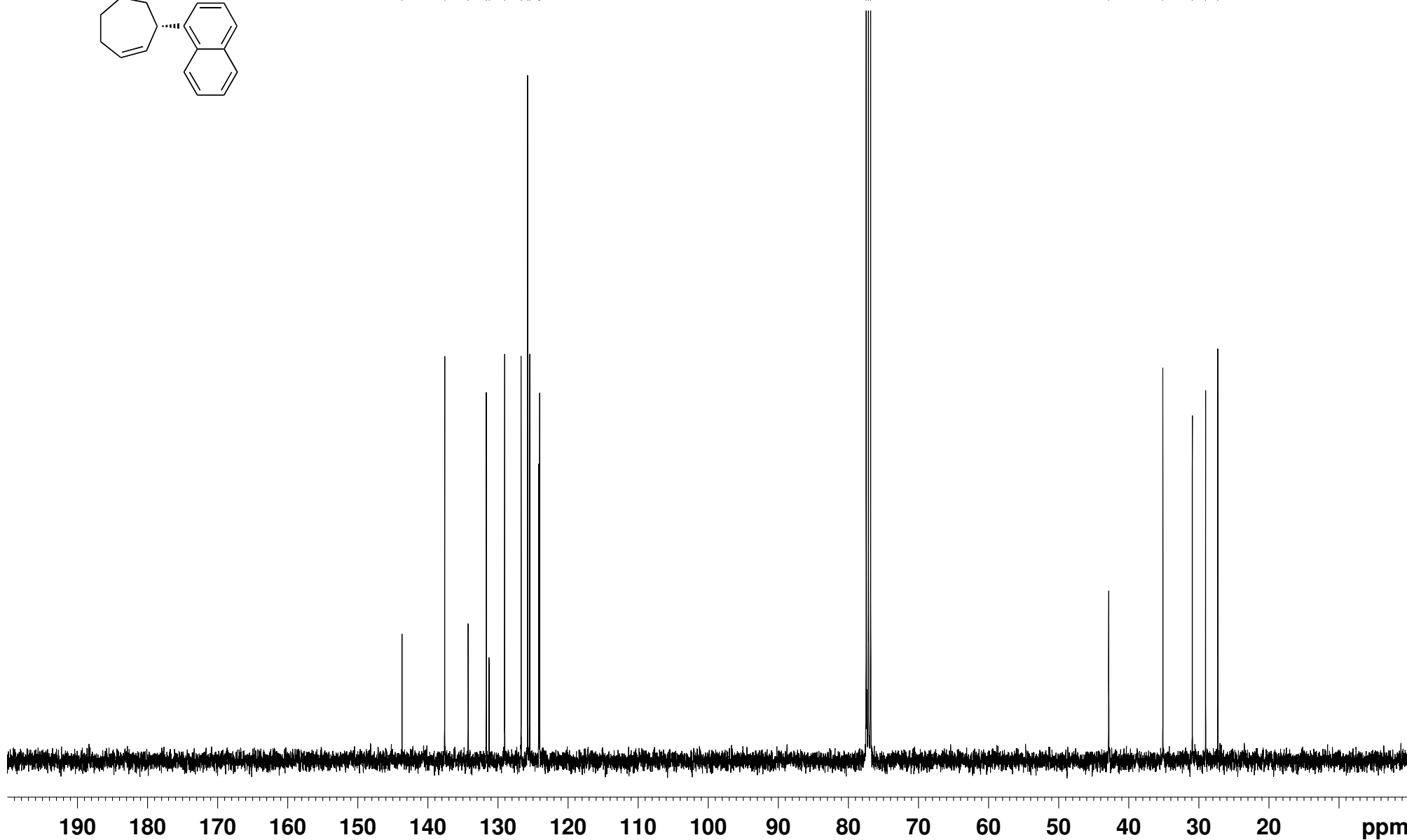


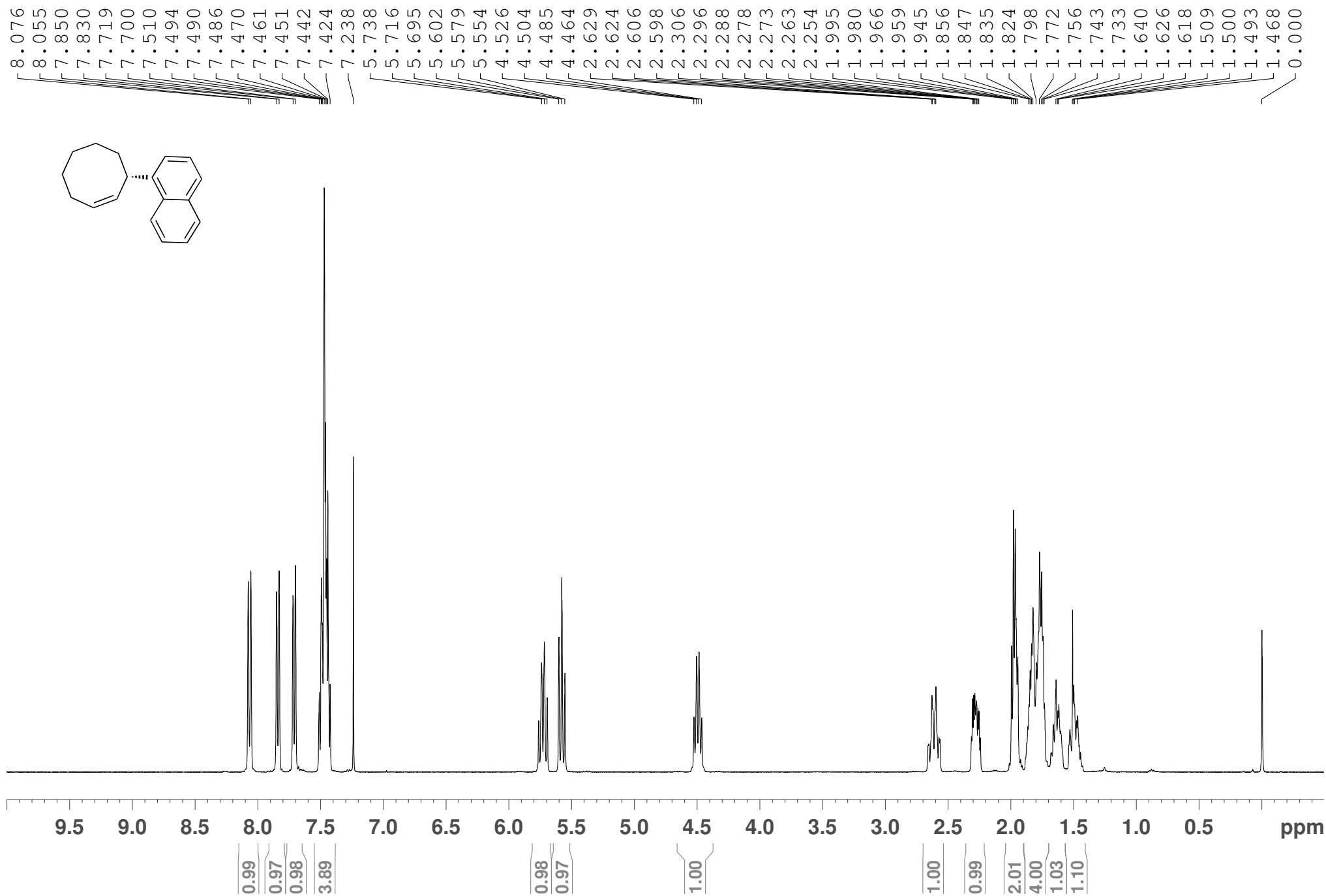
143.68
137.59
134.25
131.65
131.26
129.04
126.68
125.75
125.46
124.17
124.05

77.48
77.16
76.84

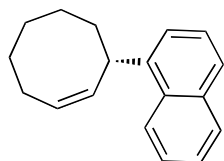
42.88

35.14
30.95
29.05
27.31





^{13}C NMR (100 MHz, CDCl_3)

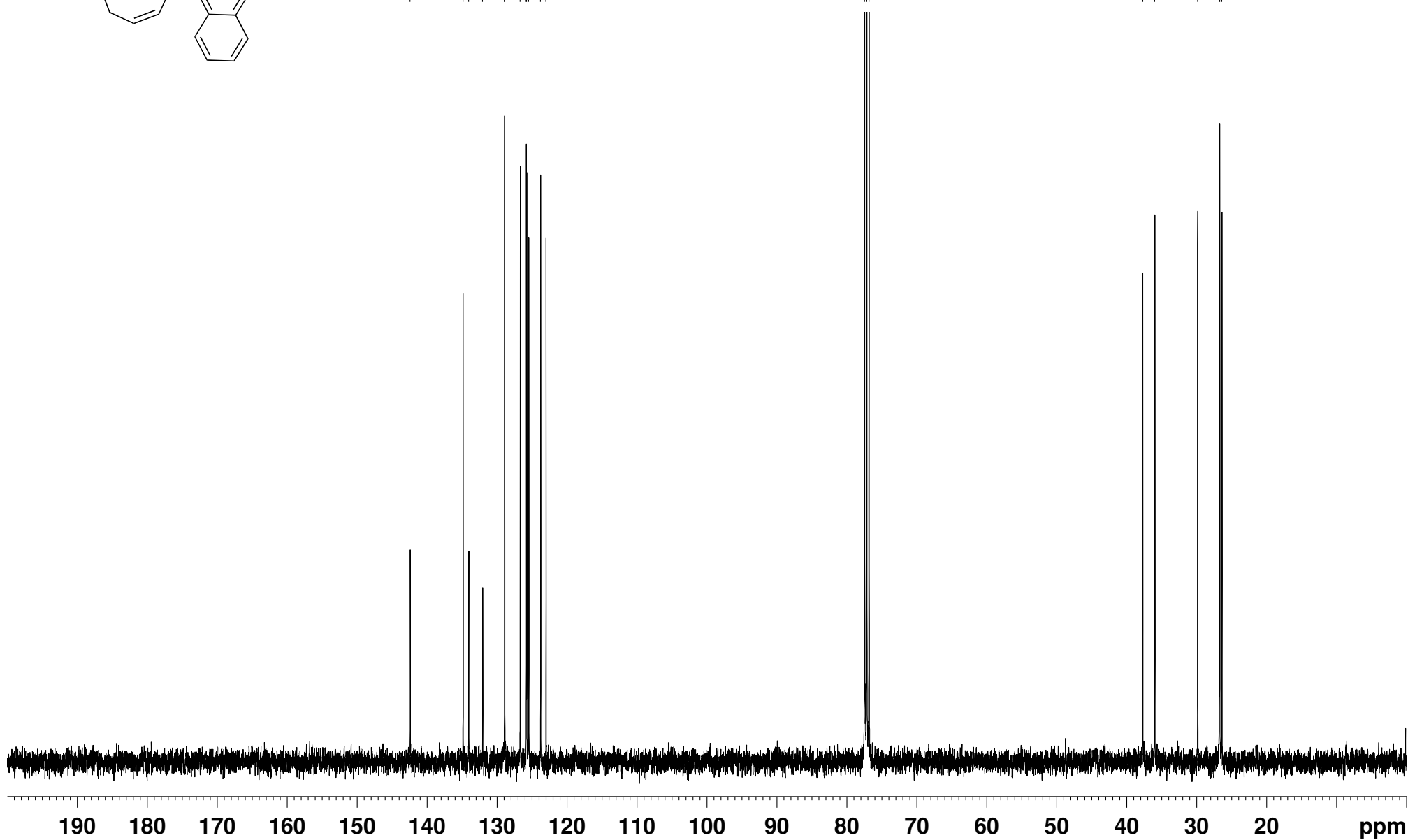


142.42
134.87
134.06
132.07
128.95
128.93
126.71
125.83
125.77
125.48
123.78
123.02

77.48
77.16
76.84

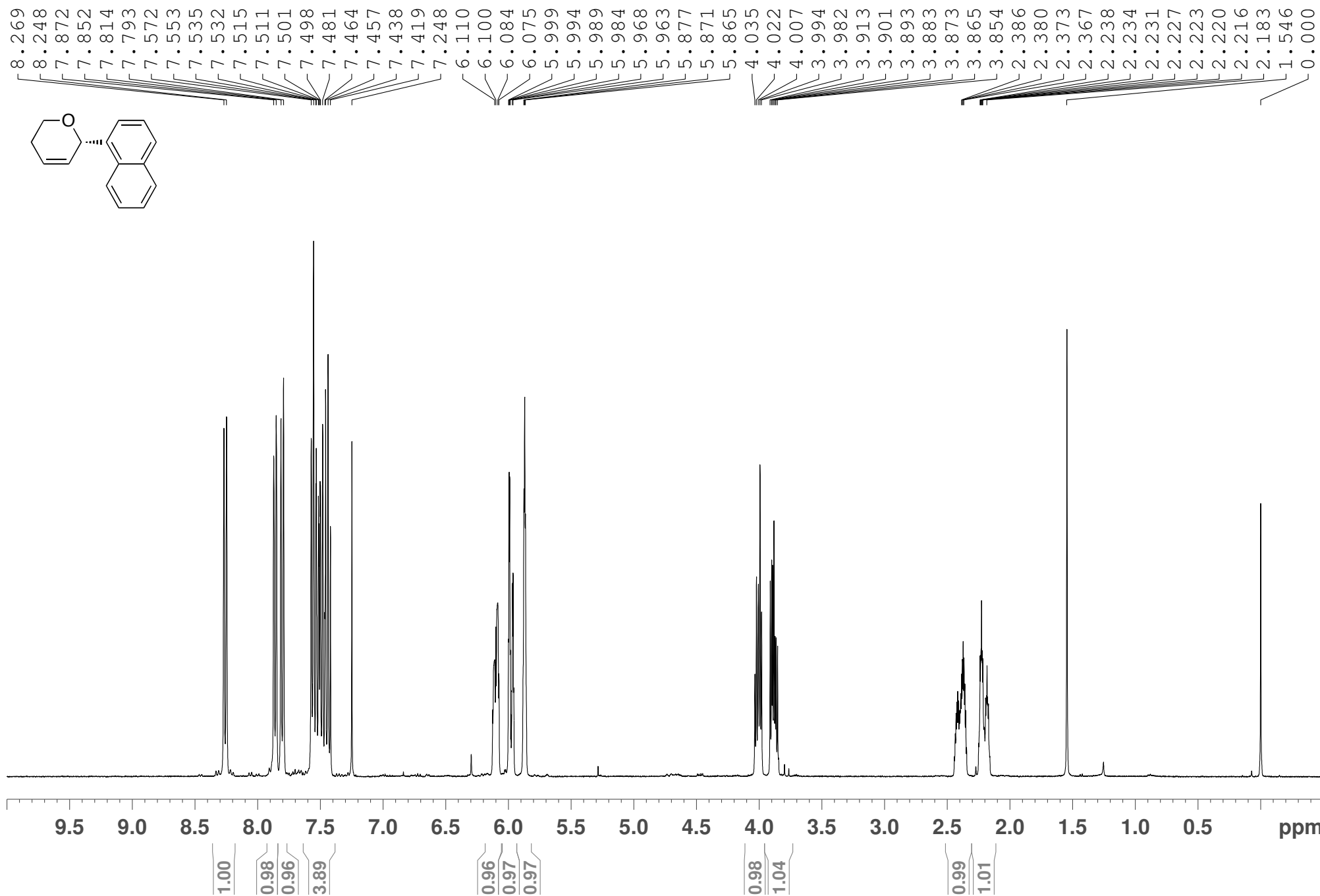
37.71
35.98

29.86
26.77
26.70
26.39



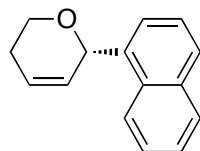
¹H NMR (400 MHz, CDCl₃)

S98



^{13}C NMR (100 MHz, CDCl_3)

hj6243(64) hj6235-1pc.(tlc) in CDCl_3 13C-1H

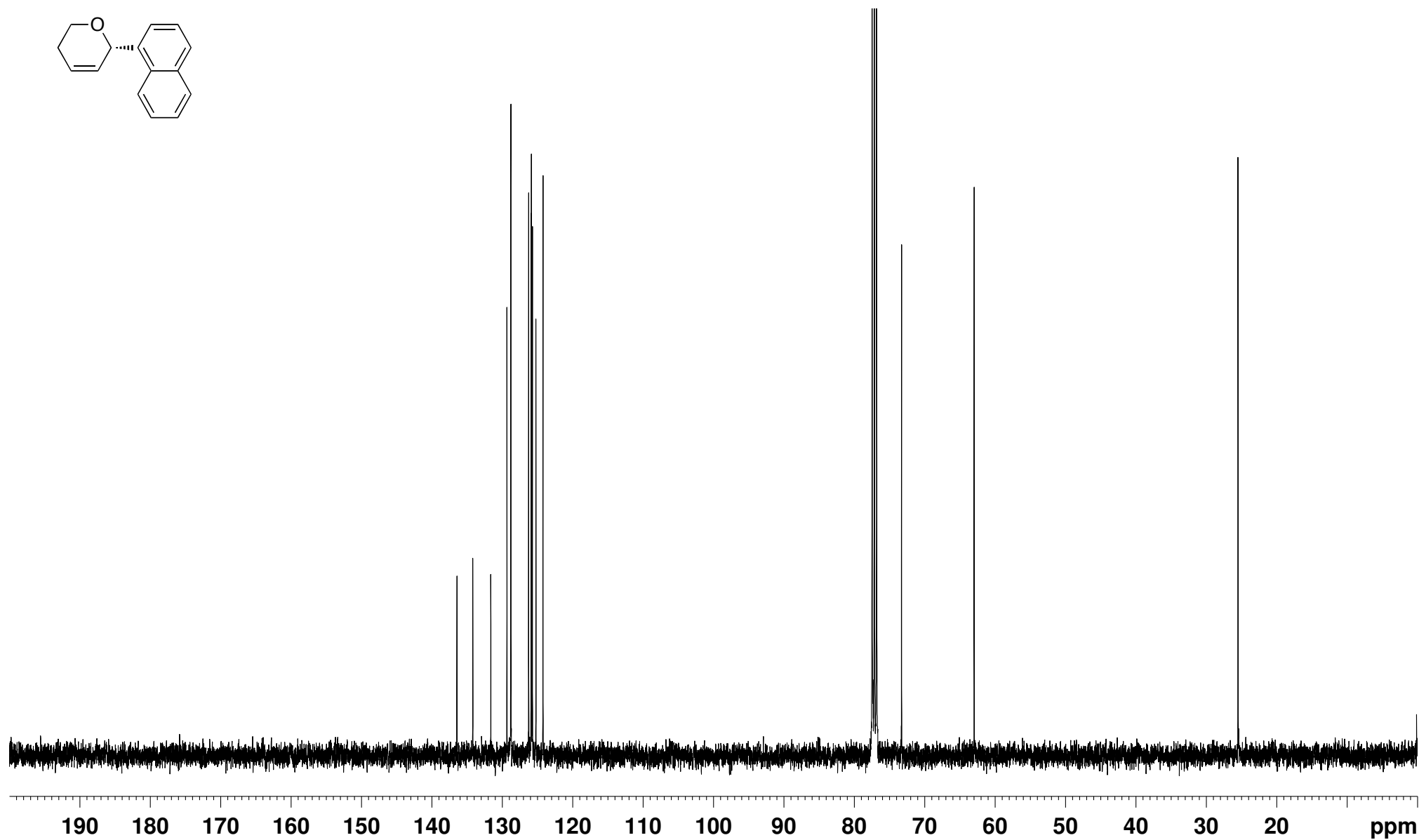


136.45
134.21
131.64
129.36
128.81
128.79
126.27
125.92
125.89
125.73
125.23
124.23

77.48
77.16
76.84
73.30

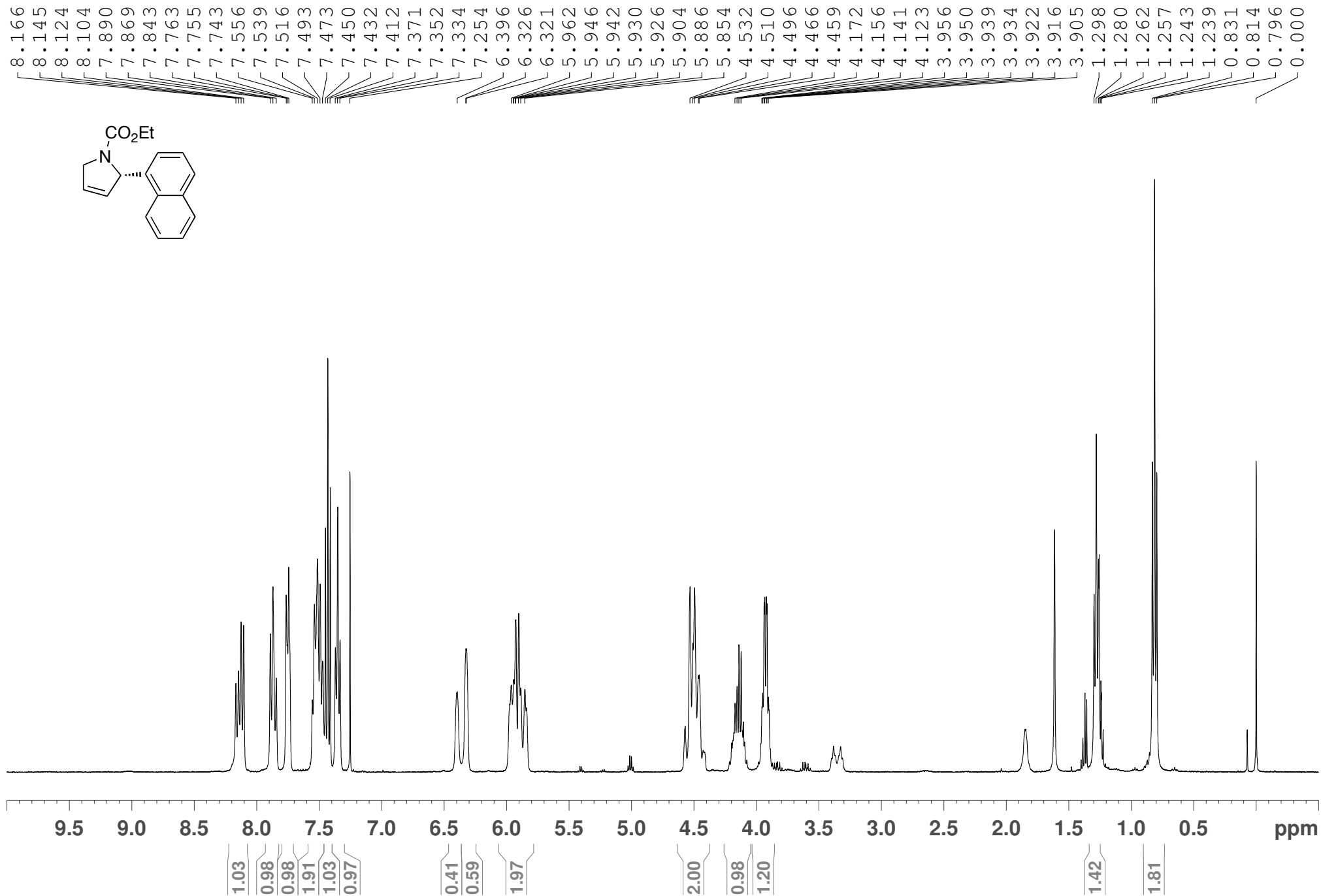
62.99

25.50

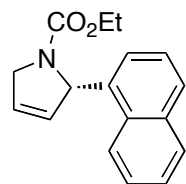


¹H NMR (400 MHz, CDCl₃)

S100



^{13}C NMR (100 MHz, CDCl_3)

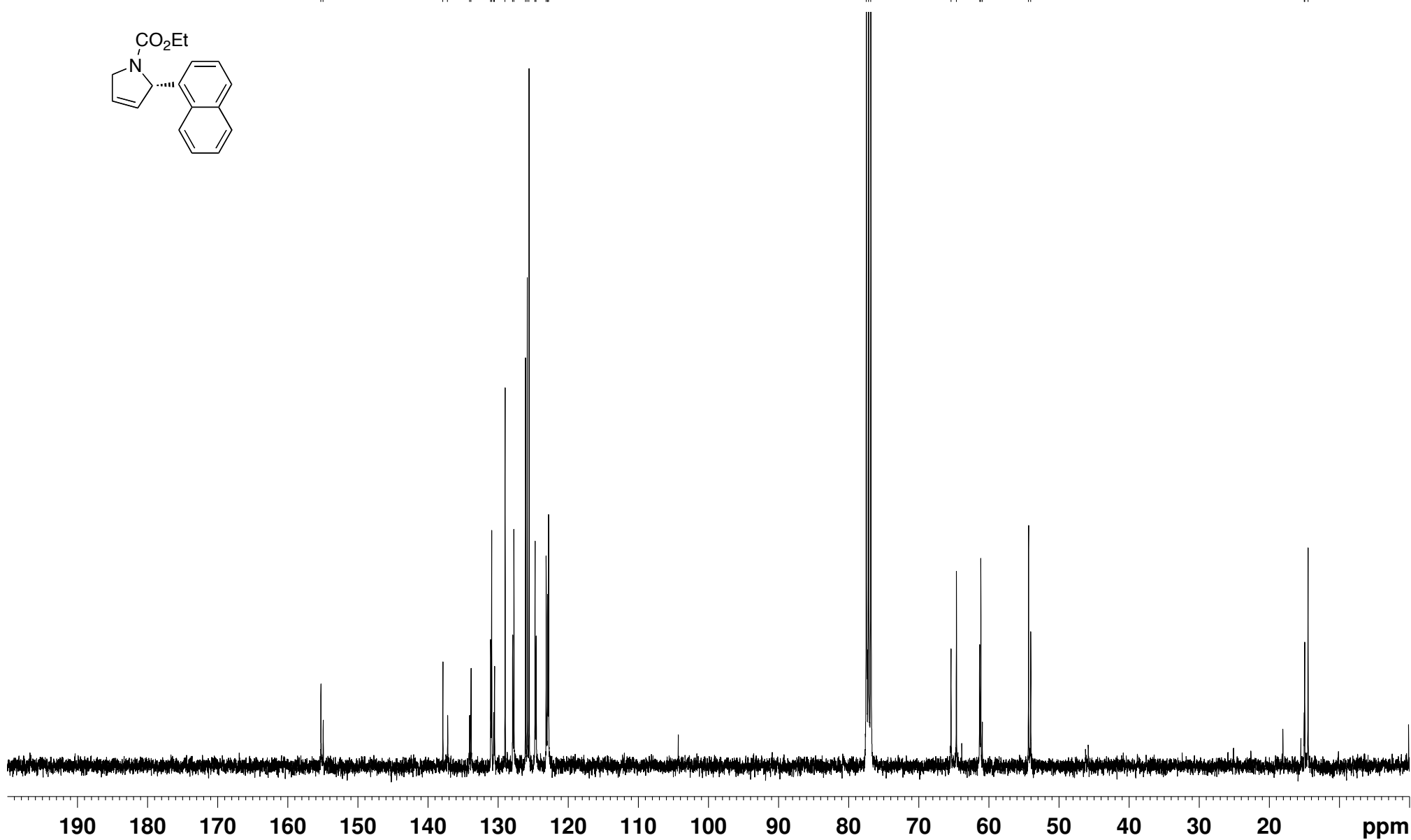


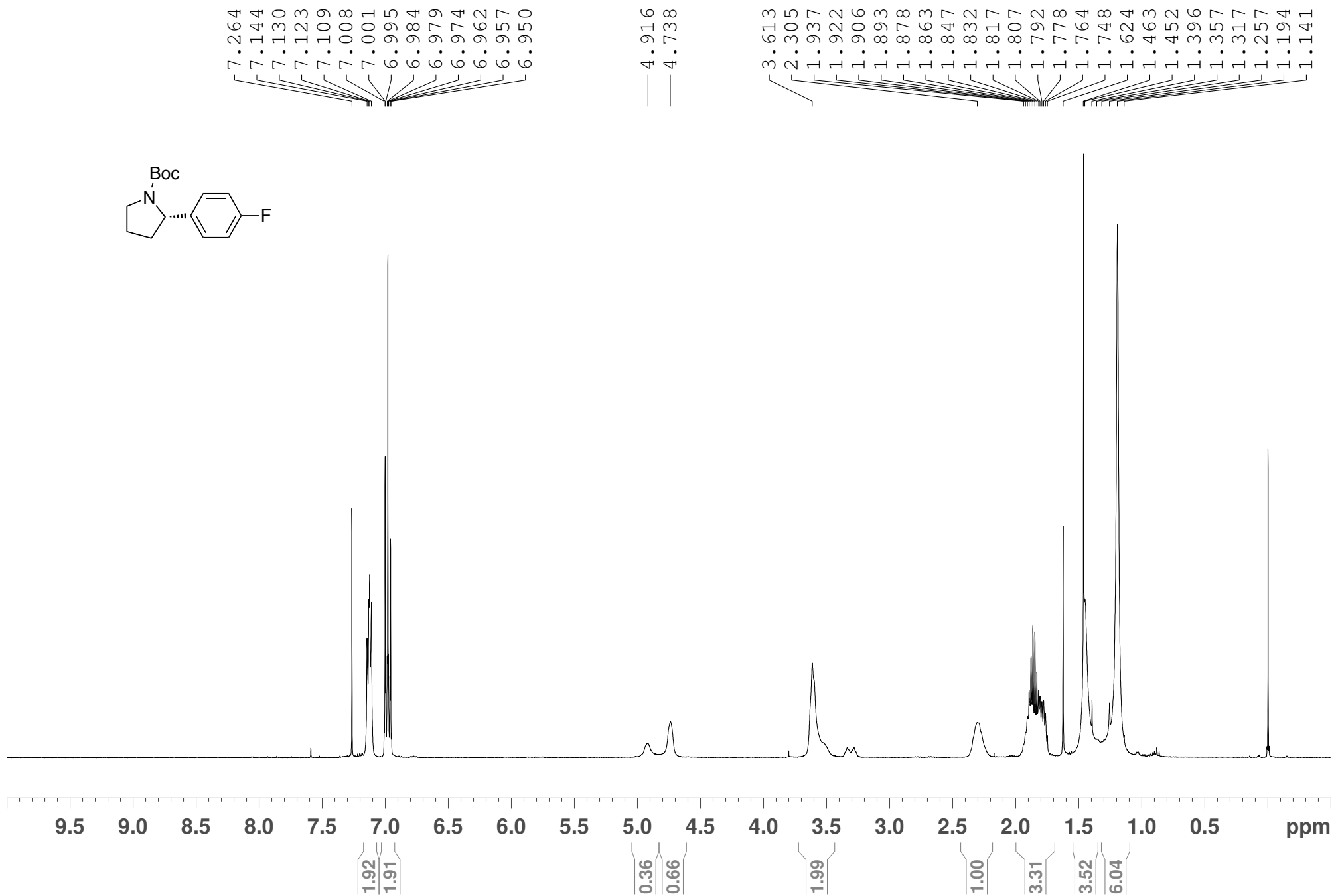
155.29
154.96
137.89
137.21
134.07
133.87
131.07
130.93
130.64
130.52
129.02
127.93
127.75
126.10
125.85
125.59
124.74
124.59
123.16
122.96
122.92
122.81

77.48
77.16
76.84

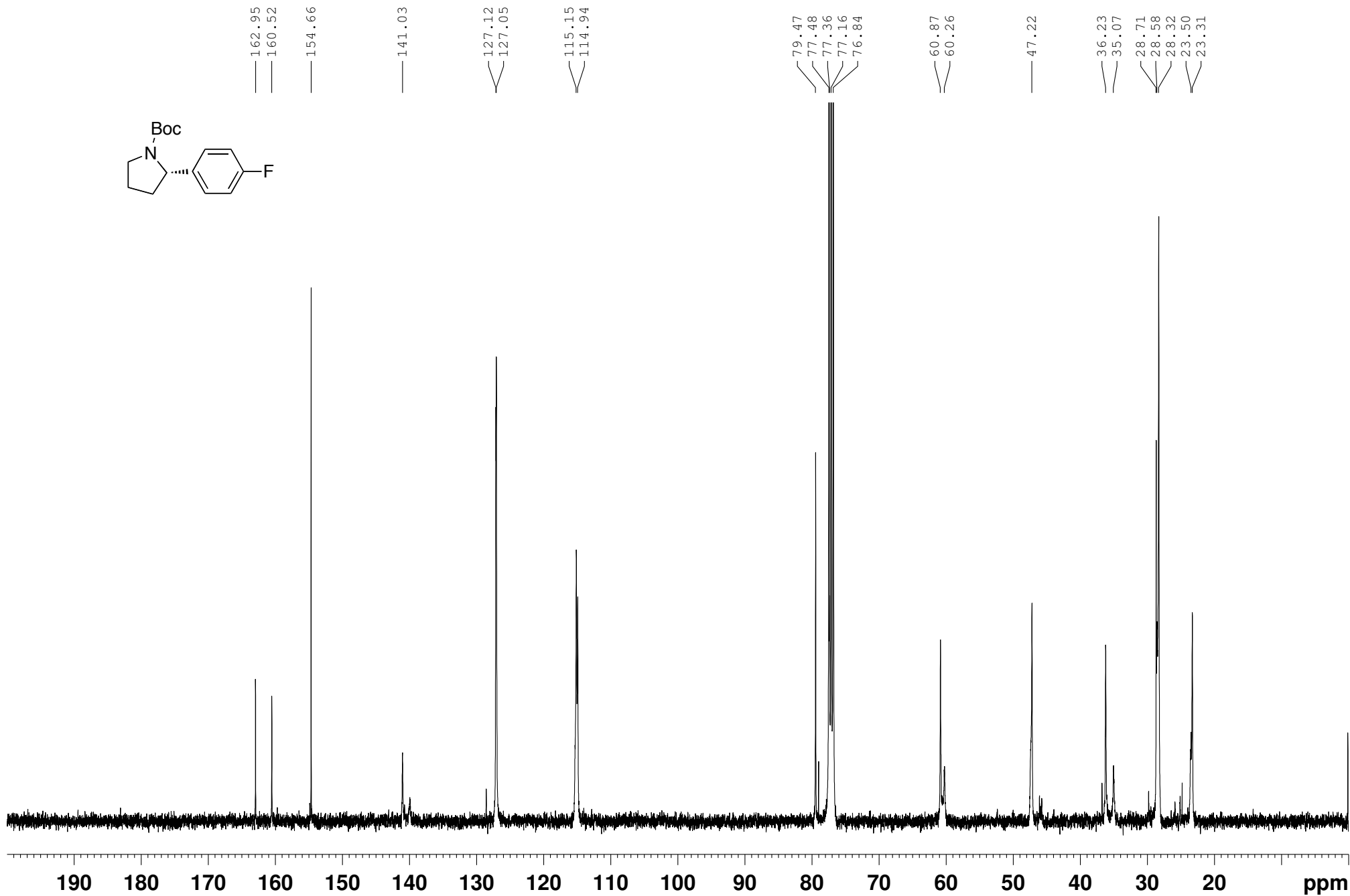
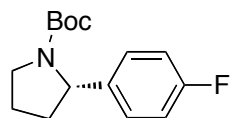
65.41
64.64
61.32
61.15
60.94
54.35
54.04

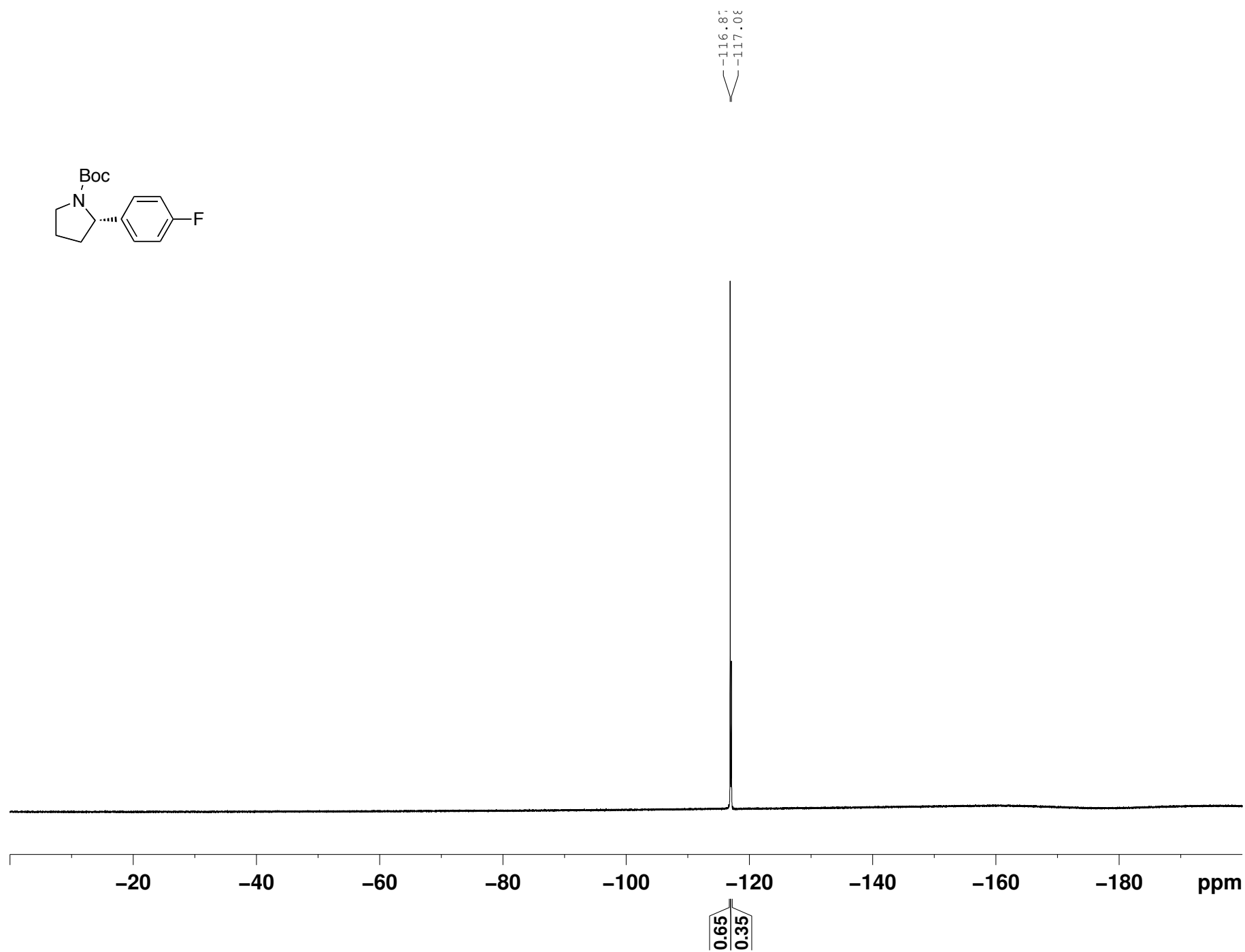
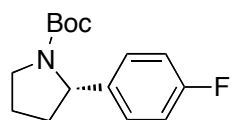
15.02
14.95
14.47





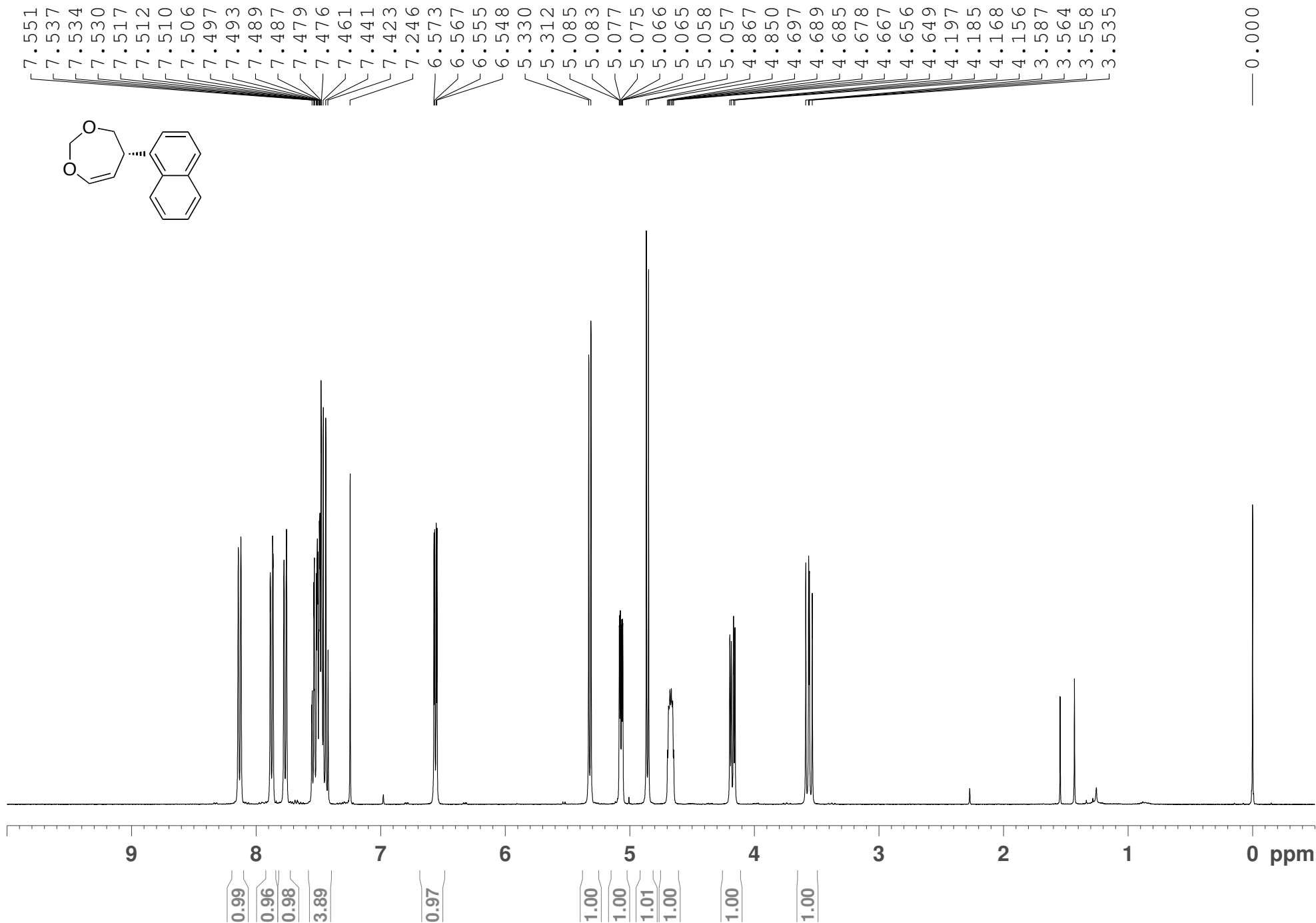
^{13}C NMR (100 MHz, CDCl_3)



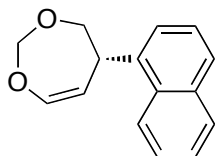


¹H NMR (400 MHz, CDCl₃)

S105



^{13}C NMR (100 MHz, CDCl_3)



— 146.42

— 136.57

— 134.18

— 131.27

— 129.25

— 127.83

— 126.37

— 125.78

— 123.09

— 113.02

— 98.37

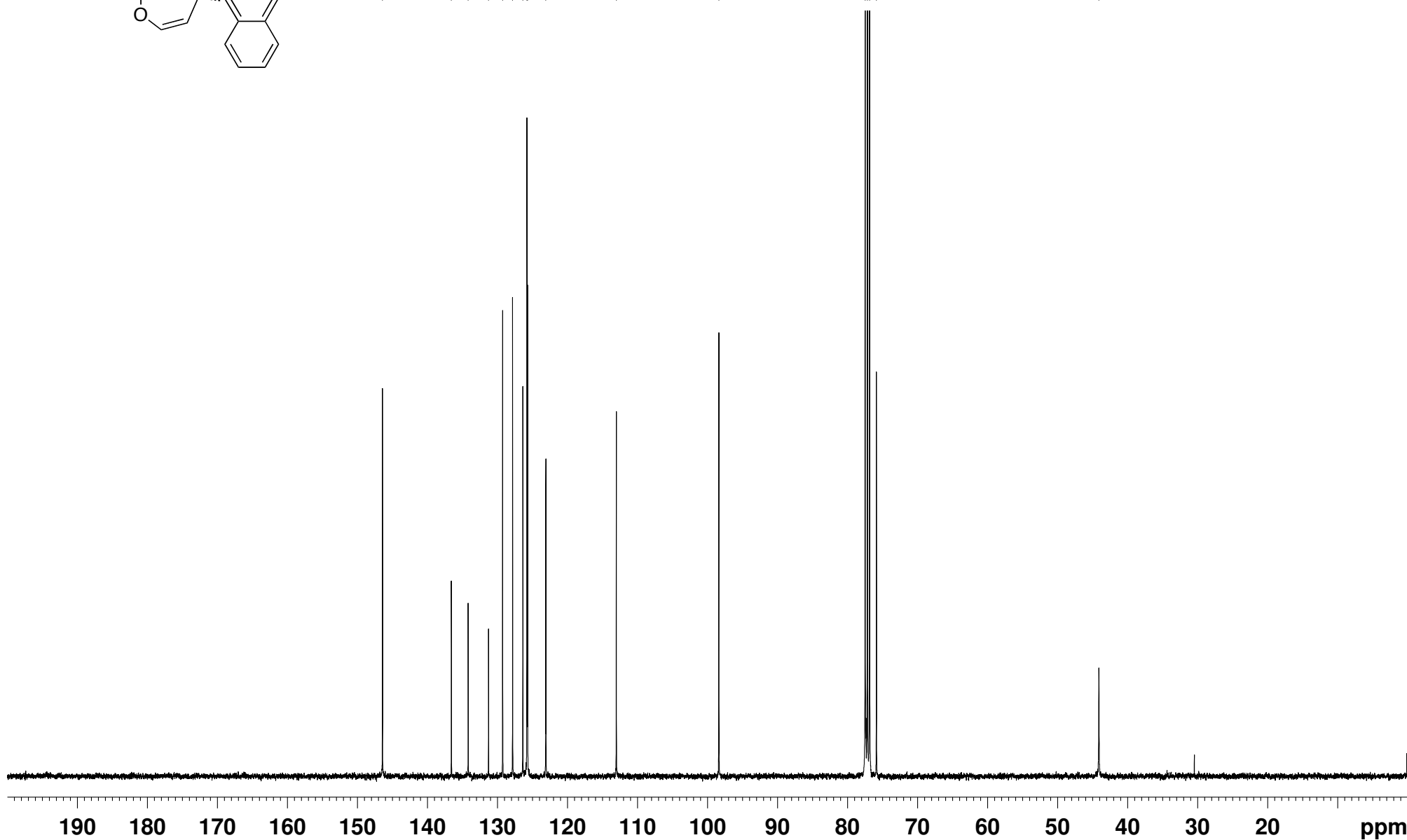
77.48

77.16

76.84

75.87

— 44.10



¹H NMR (400 MHz, CD₂Cl₂)

S107

