Supporting Information

Total Synthesis of (±)–Rocaglamide *via* Oxidation-Initiated Nazarov Cyclization

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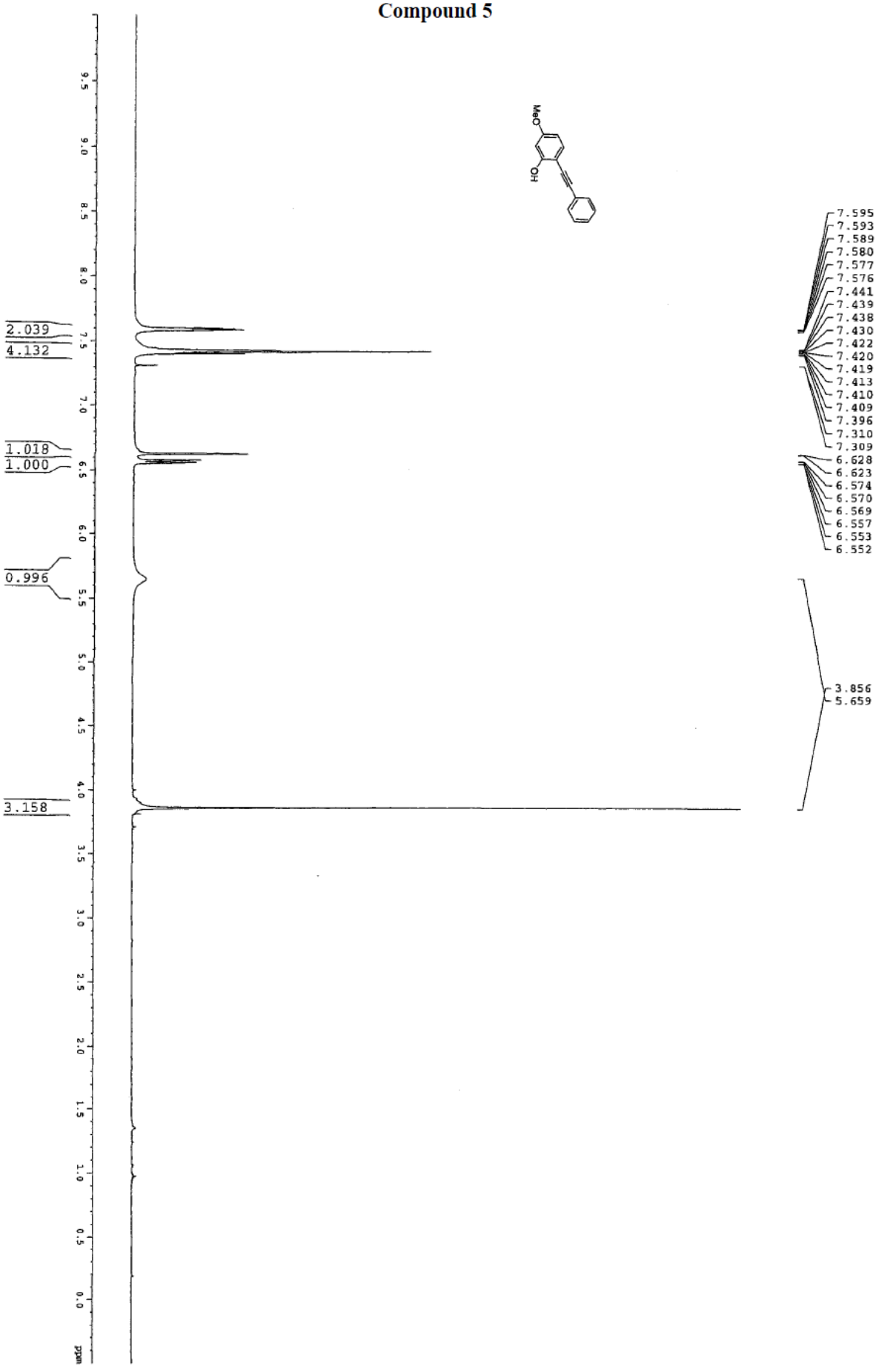
1.0. Spectral Data.

Compound 5


MeO
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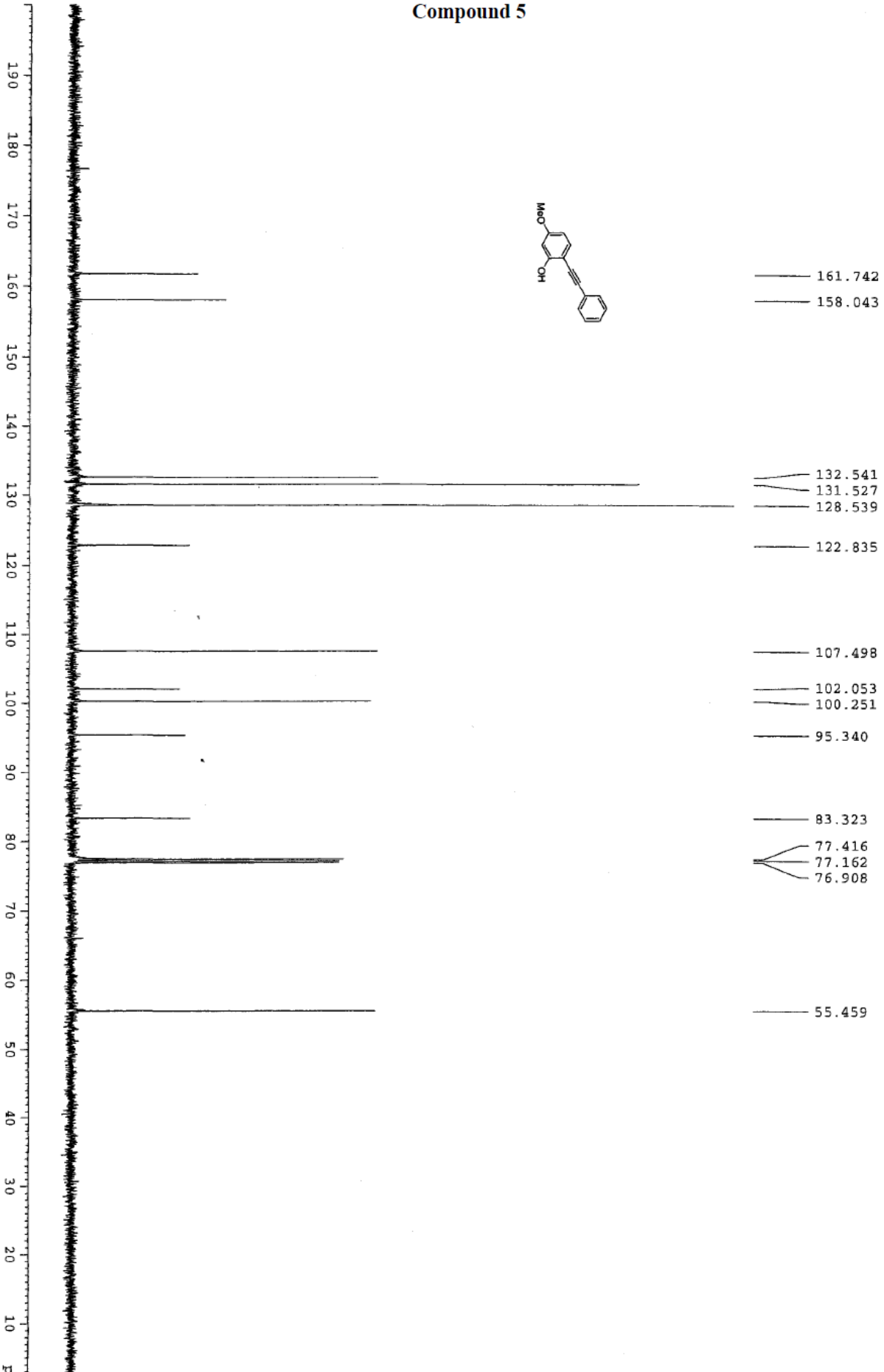
7.593
7.589
7.580
7.577
7.576
7.441
7.439
7.438
7.430
7.422
7.420
7.419
7.413
7.410
7.409
7.396
7.310
7.309
6.628
6.623
6.574
6.570
6.569
6.557
6.553
6.552
3.856
5.659
2.039
4.132
1.018
1.000
0.996
3.158
ppm

Compound 5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OH
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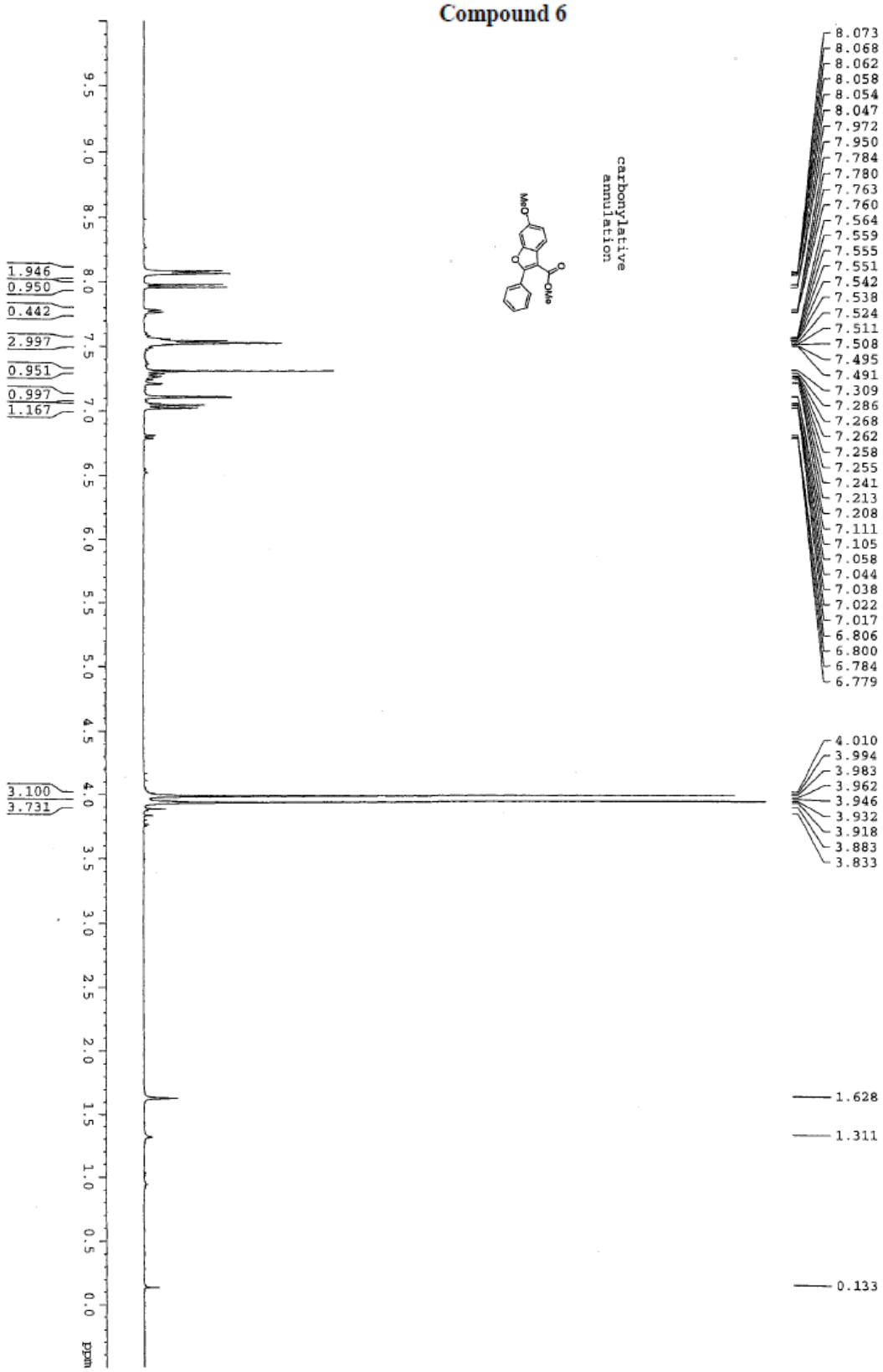
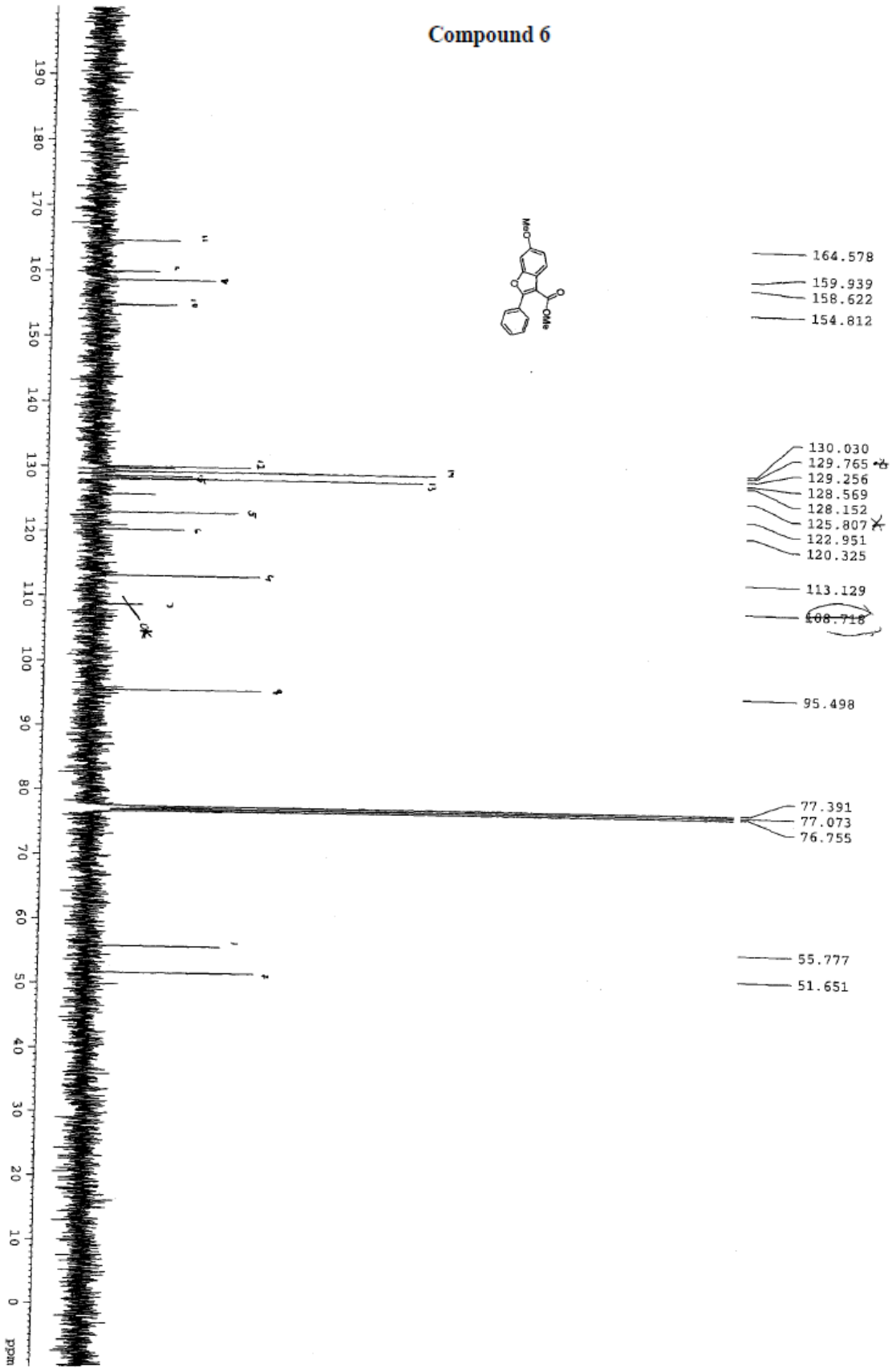
158.043
132.541
131.527
128.539
122.835
107.498
102.053
100.251
95.340
83.323
77.416
77.162
76.908
55.459

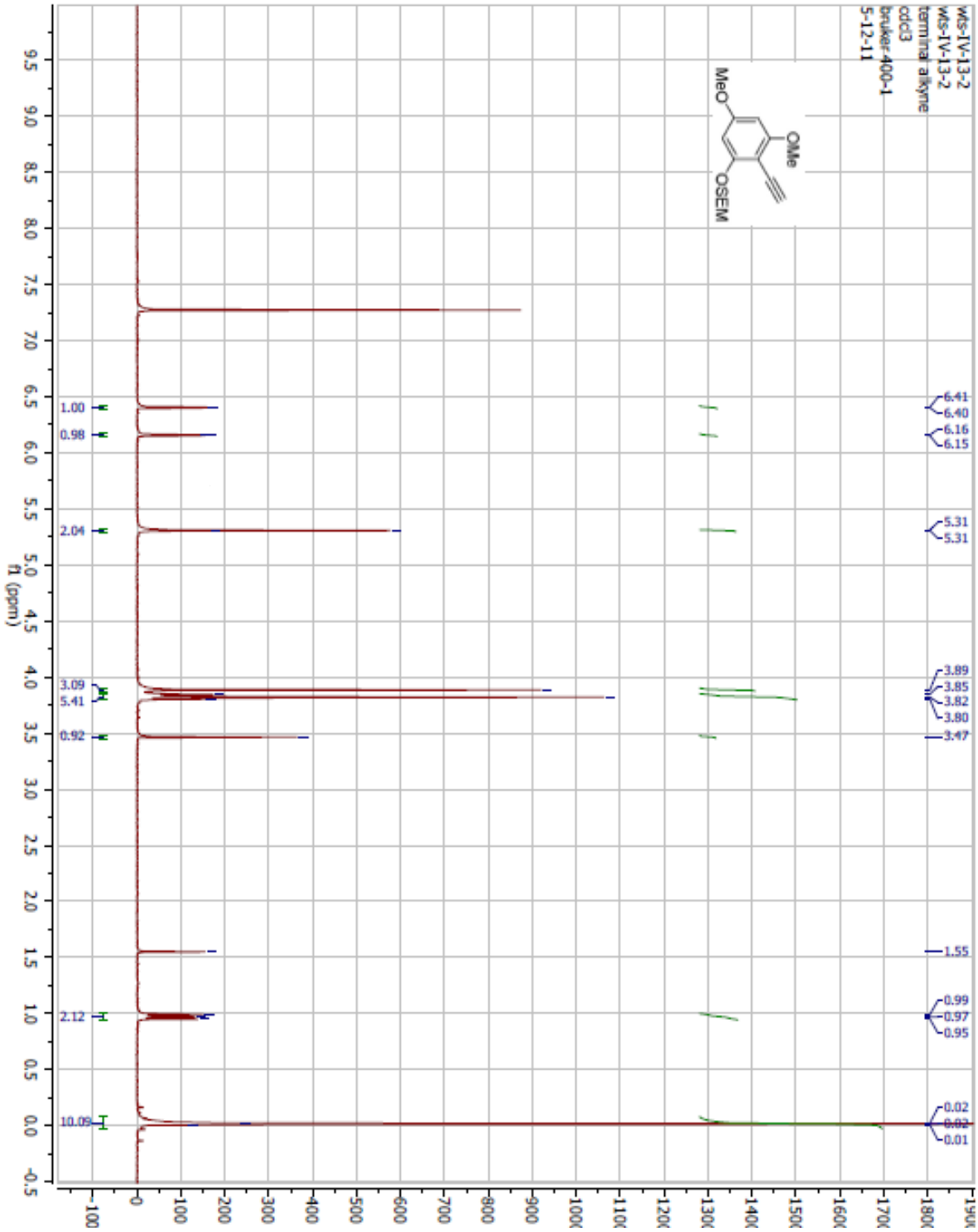
Compound 6


carbonylative
annulation
MeO
OMe
O
1.946
0.950
0.442
2.997
0.951
0.997
1.167
3.100
3.731
8.073
8.068
8.062
8.058
8.054
8.047
7.972
7.950
7.784
7.780
7.763
7.760
7.564
7.559
7.555
7.551
7.542
7.538
7.524
7.511
7.508
7.495
7.491
7.309
7.286
7.268
7.262
7.258
7.255
7.241
7.213
7.208
7.111
7.105
7.058
7.044
7.038
7.022
7.017
6.806
6.800
6.784
6.779
4.010
3.994
3.983
3.962
3.946
3.932
3.918
3.883
3.833
1.628
1.311
0.133
ppm

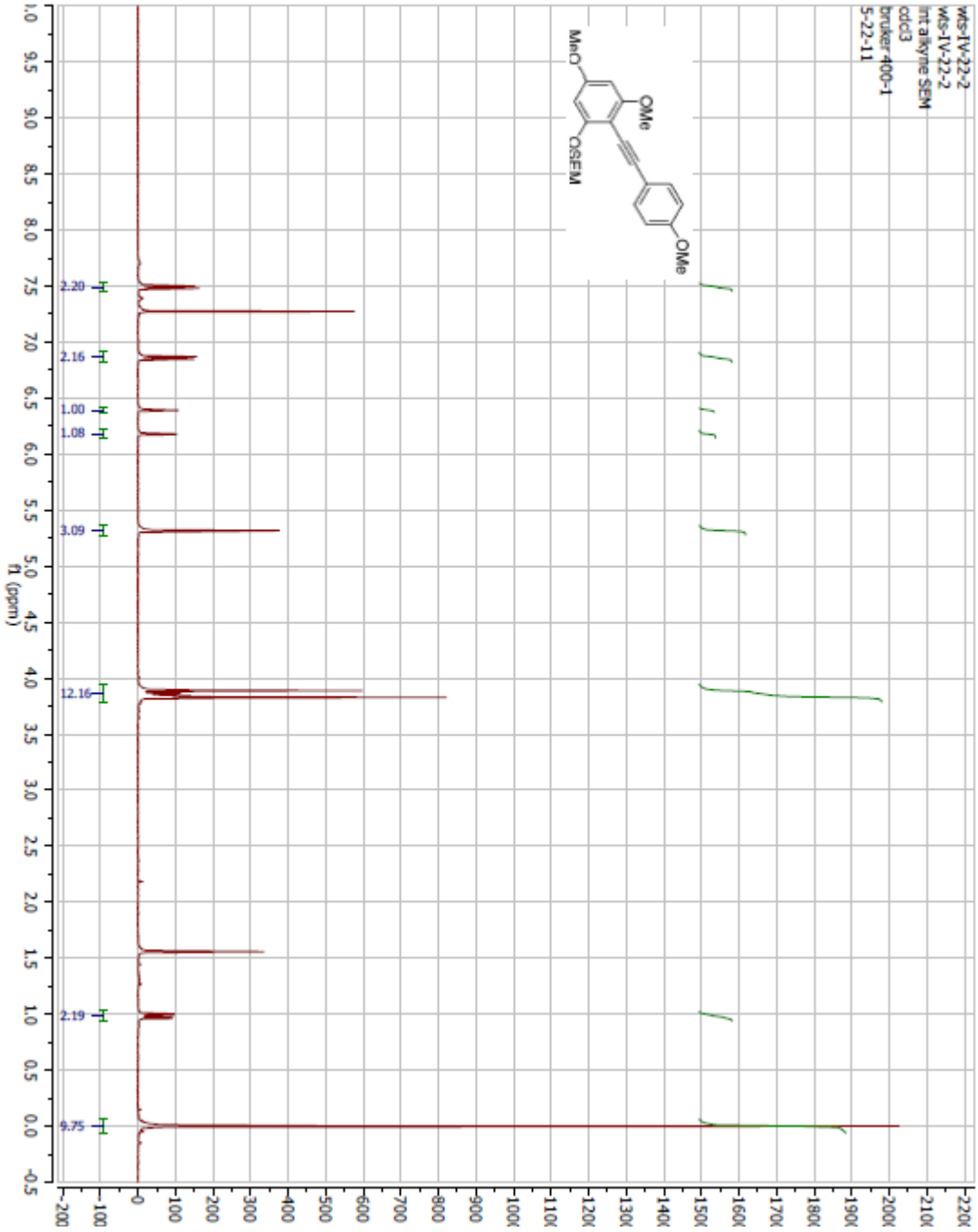
Compound 6


MeO
OMe
164.578
159.939
158.622
154.812
130.030
129.765
129.256
128.569
128.152
125.807
122.951
120.325
113.129
108.718
95.498
77.391
77.073
76.755
55.777
51.651
ppm

Compound 7a


wts-IV-13-2
wts-IV-13-2
terminal alkyne
cdcl3
bruker 400-1
5-12-11
MeO
OMe
OSEM
f1 (ppm)
1.00
0.98
2.04
3.09
5.41
0.92
2.12
10.09
6.41
6.40
6.16
6.15
5.31
5.31
3.89
3.85
3.82
3.80
3.47
1.55
0.99
0.97
0.95
0.02
0.01

Compound 8a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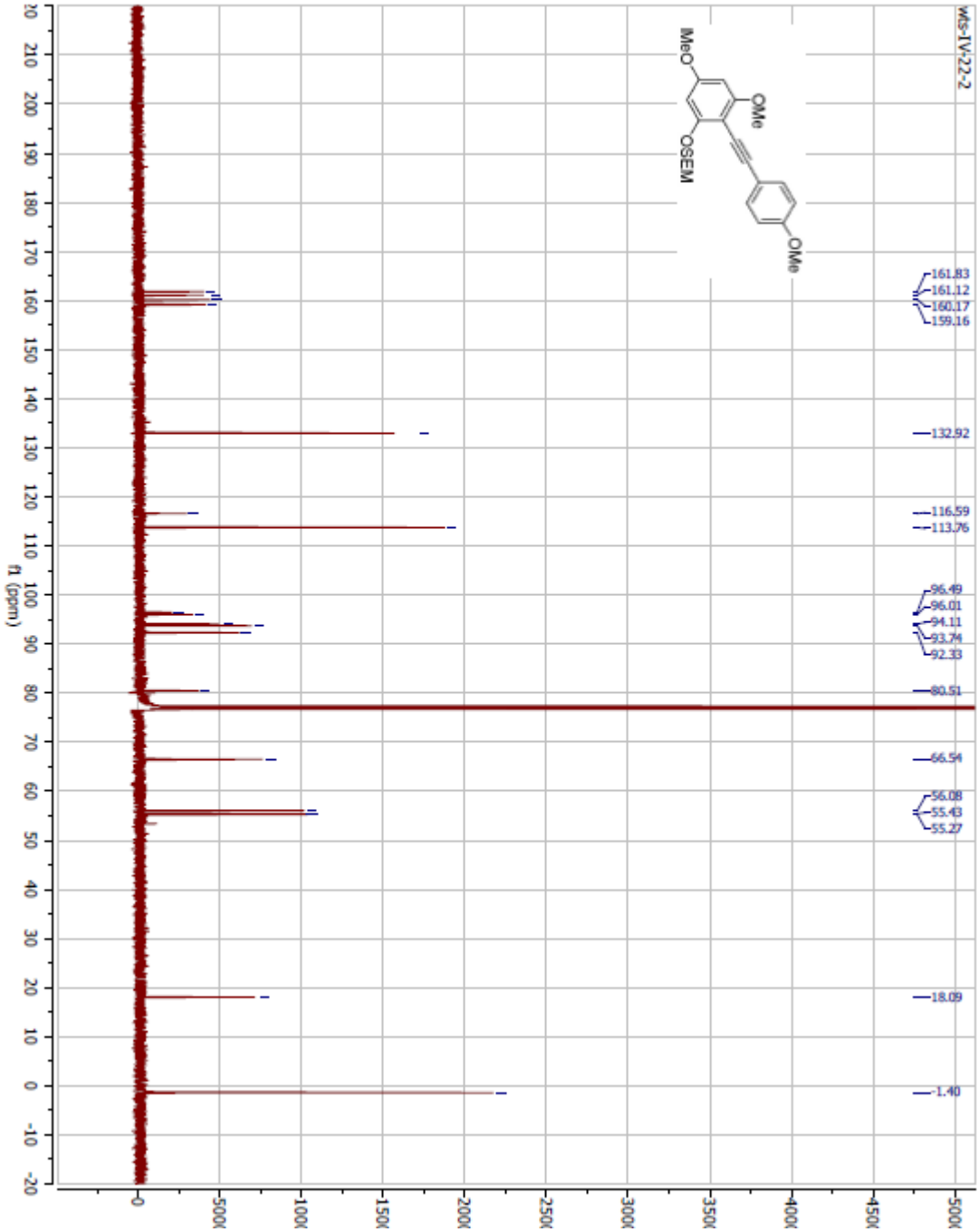
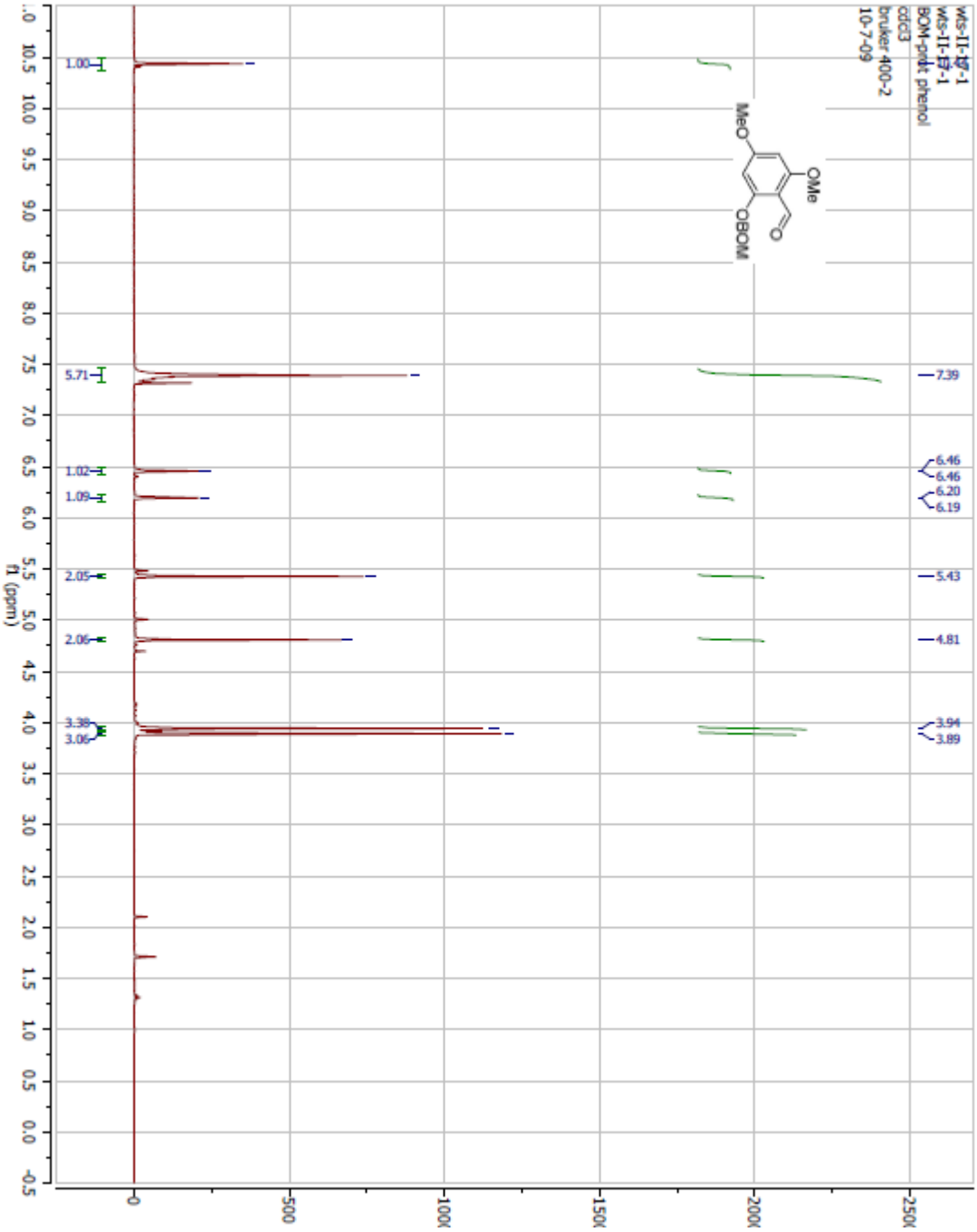
wts-IV-22-2
int alkyne SEM
cdcl3
bruker 400-1
5-22-11
MeO
OSEM
OMe
OMe
2.20
2.16
1.00
1.08
3.09
12.16
2.19
9.75
f1 (ppm)

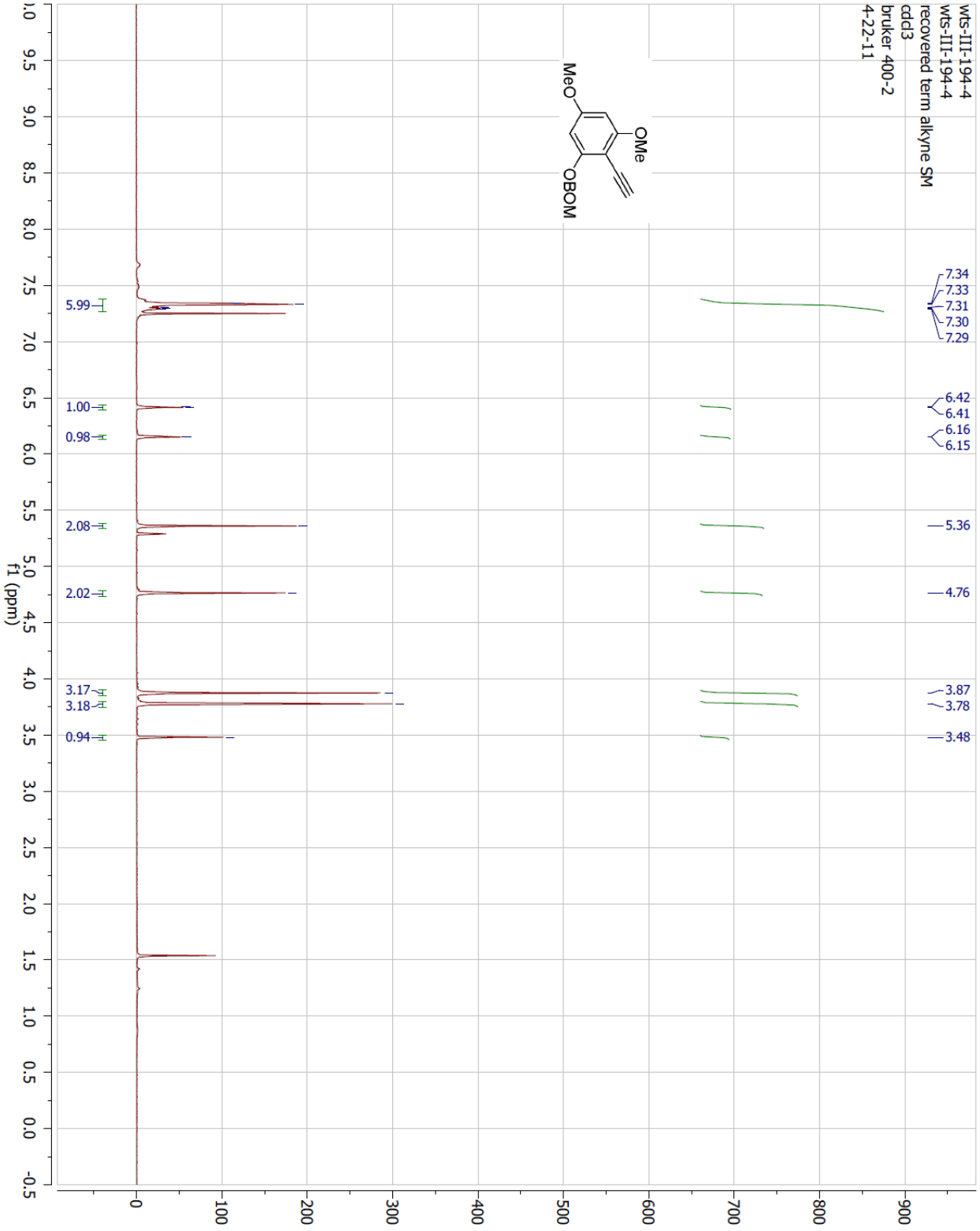
Compound 8a


wts-IV-22-2
MeO
OMe
OSEM
OMe
161.83
161.12
160.17
159.16
132.92
116.59
113.76
96.49
96.01
94.11
93.74
92.33
80.51
66.54
56.08
55.43
55.27
18.09
1.40
f1 (ppm)

2,4-dimethoxy-6-((2-(trimethylsilyl)ethoxy)methoxy)benzaldehyde (precursor to 7)



Compound 7b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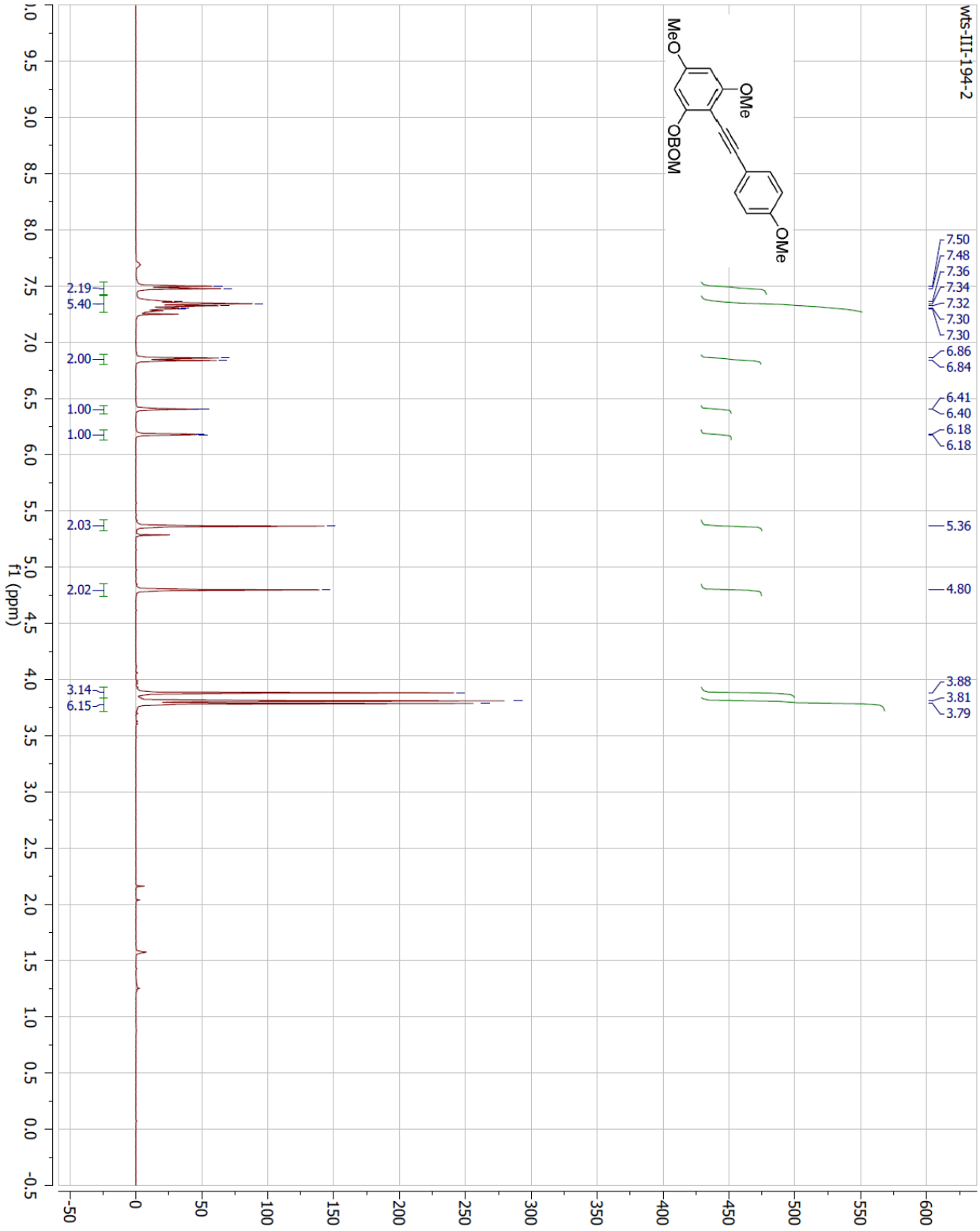
wts-III-194-4
recovered term alkyne SM
cdcl3
bruker 400-2
4-22-11
MeO
OMe
OBOM
7.34
7.33
7.31
7.30
7.29
6.42
6.41
6.16
6.15
5.36
4.76
3.87
3.78
3.48
5.99
1.00
0.98
2.08
2.02
3.17
3.18
0.94
f1 (ppm)

Compound 8b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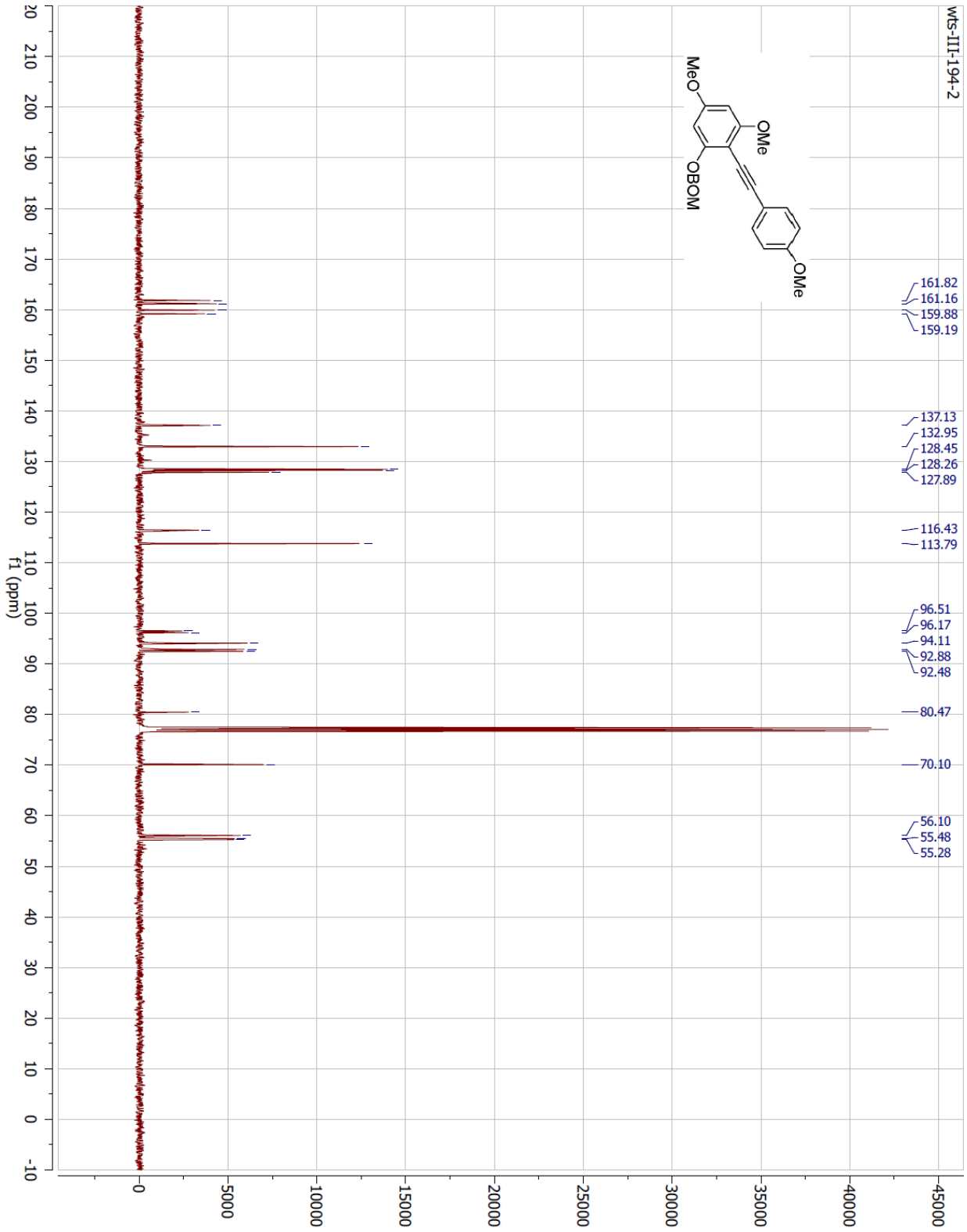
MeO
OBOM
OMe
OMe
7.50
7.48
7.36
7.34
7.32
7.30
7.30
6.86
6.84
6.41
6.40
6.18
6.18
5.36
4.80
3.88
3.81
3.79
2.19
5.40
2.00
1.00
1.00
2.03
2.02
3.14
6.15
f1 (ppm)

Compound 8b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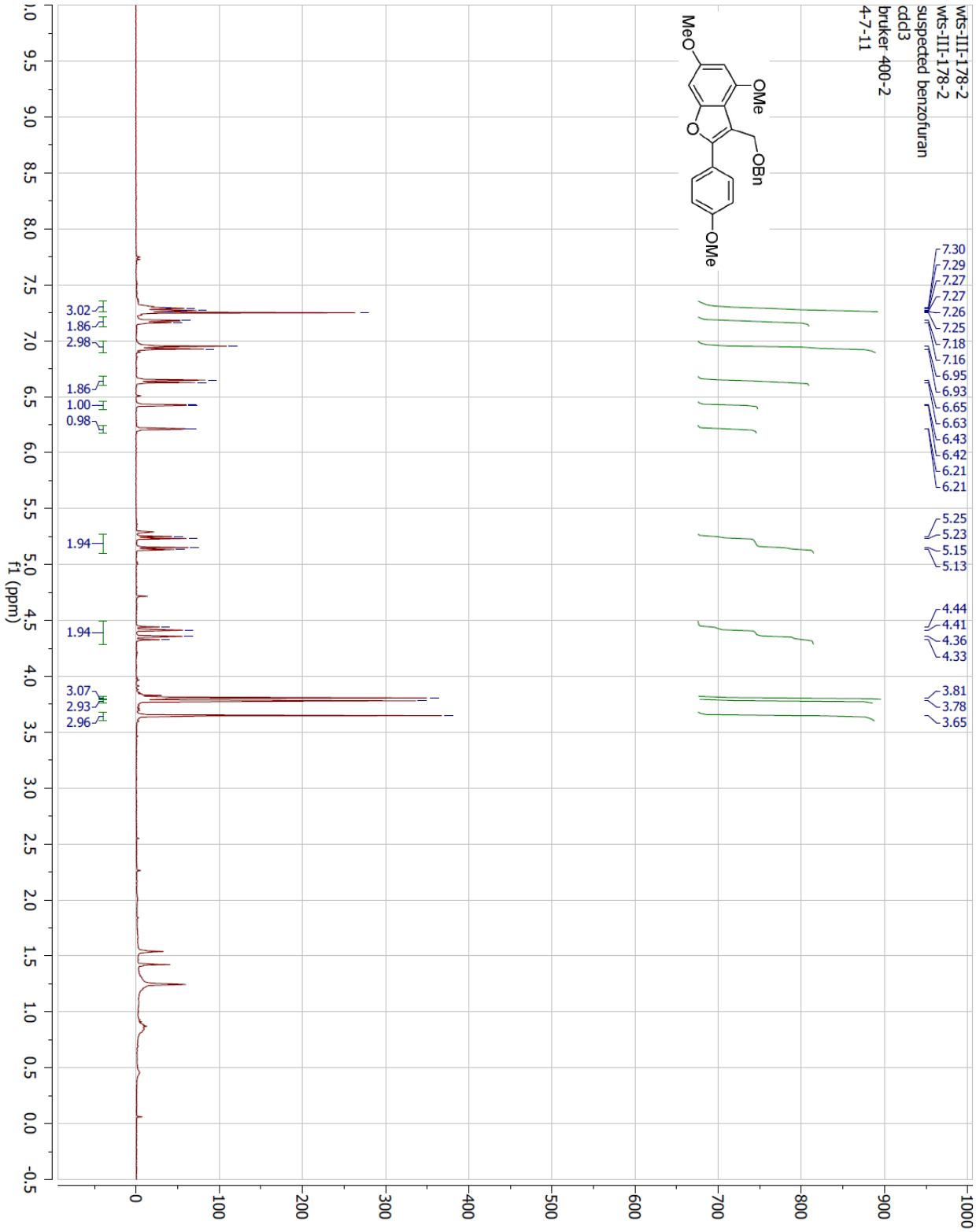
MeO
OMe
OBOM
OMe
161.82
161.16
159.88
159.19
137.13
132.95
128.45
128.26
127.89
116.43
113.79
96.51
96.17
94.11
92.88
92.48
80.47
70.10
56.10
55.48
55.28
f1 (ppm)

Compound 9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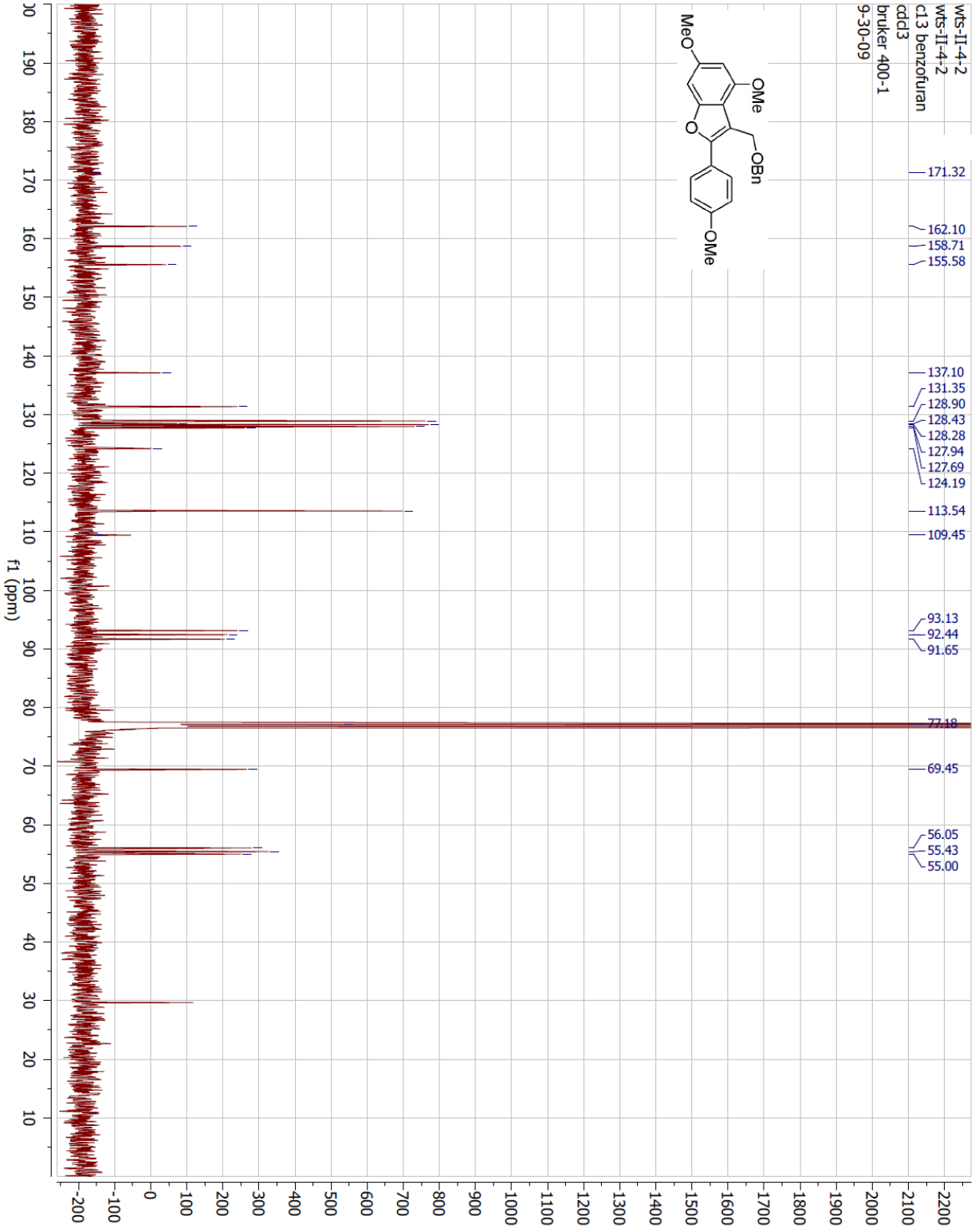
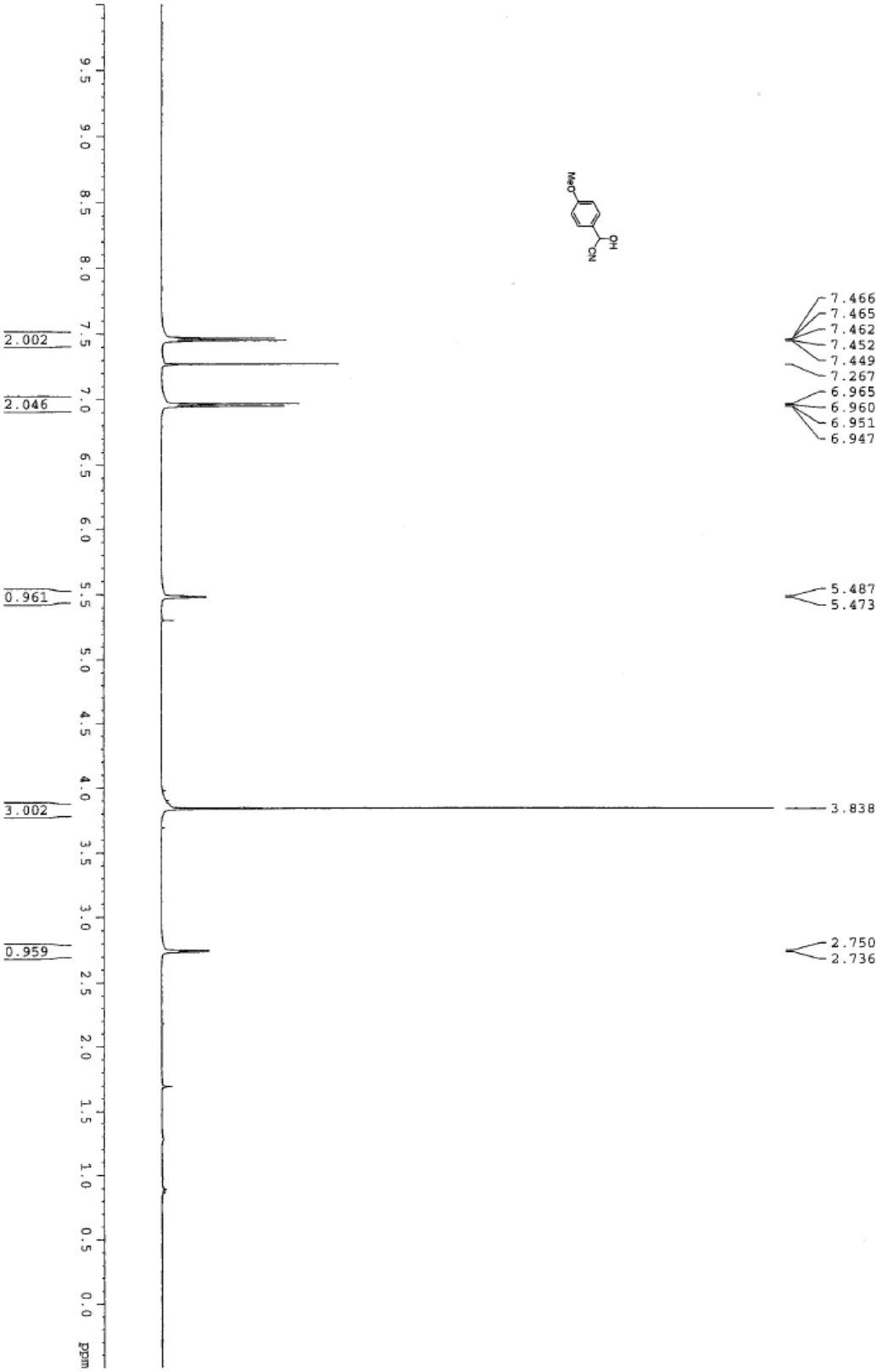
wts-III-178-2
suspected benzofuran
cdcl3
bruker 400-2
4-7-11
MeO
OMe
OBn
OMe
7.30
7.29
7.27
7.27
7.26
7.25
7.18
7.16
6.95
6.93
6.65
6.63
6.43
6.42
6.21
6.21
5.25
5.23
5.15
5.13
4.44
4.41
4.36
4.33
3.81
3.78
3.65
3.02
1.86
2.98
1.86
1.00
0.98
1.94
1.94
3.07
2.93
2.96
f1 (ppm)

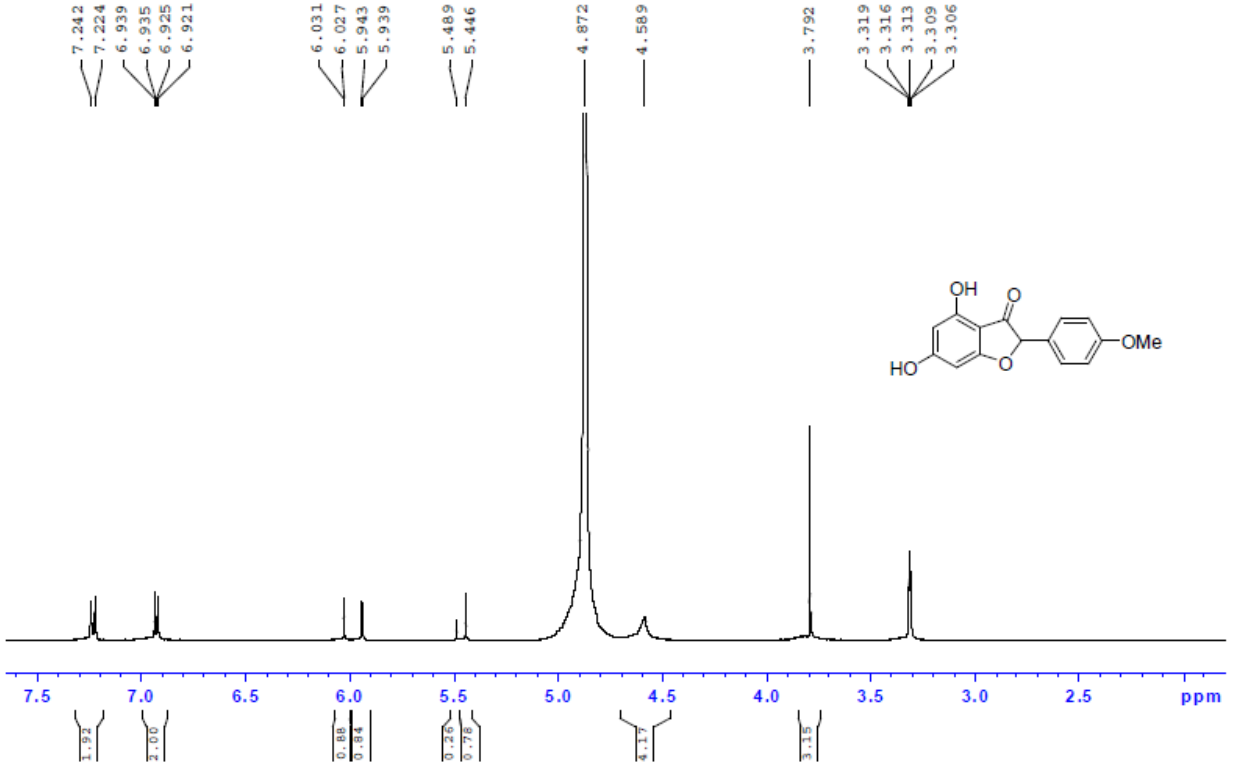
Compound 9

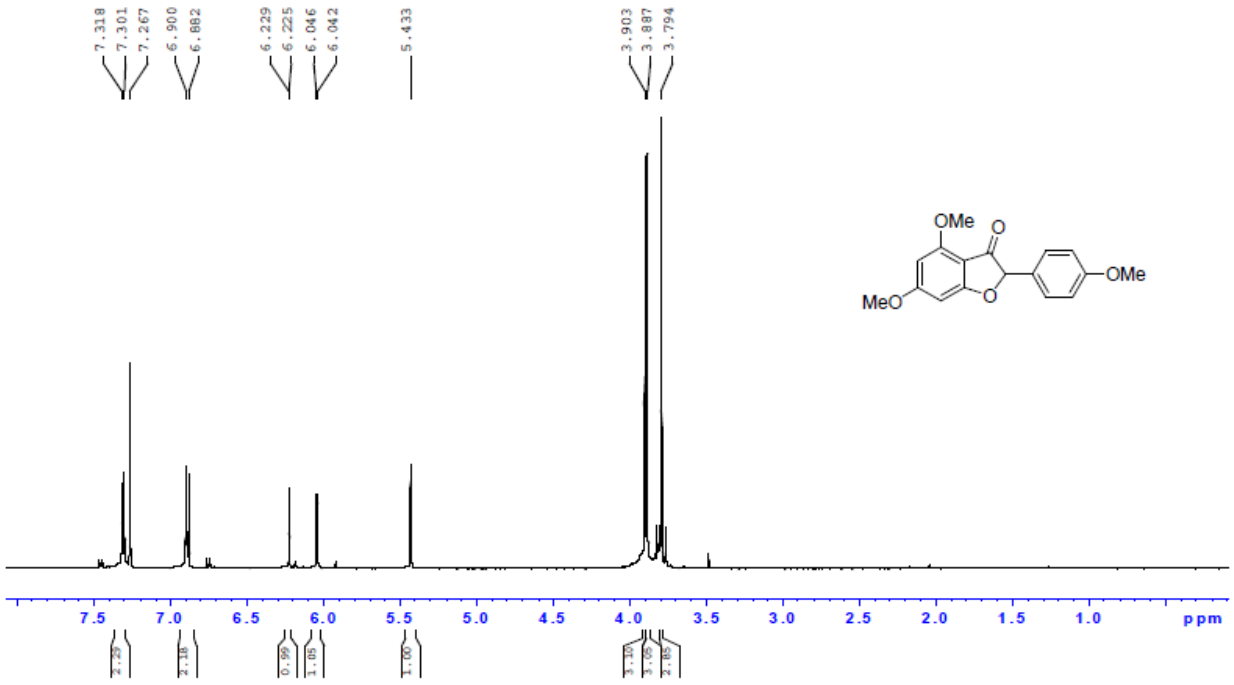

wts-II-4-2
wts-II-4-2
c13 benzofuran
cdcl3
bruker 400-1
9-30-09
MeO
OMe
OBn
OMe
171.32
162.10
158.71
155.58
137.10
131.35
128.90
128.43
128.28
127.94
127.69
124.19
113.54
109.45
93.13
92.44
91.65
77.18
69.45
56.05
55.43
55.00
f1 (ppm)

2-hydroxy-2-(4-methoxyphenyl)acetonitrile

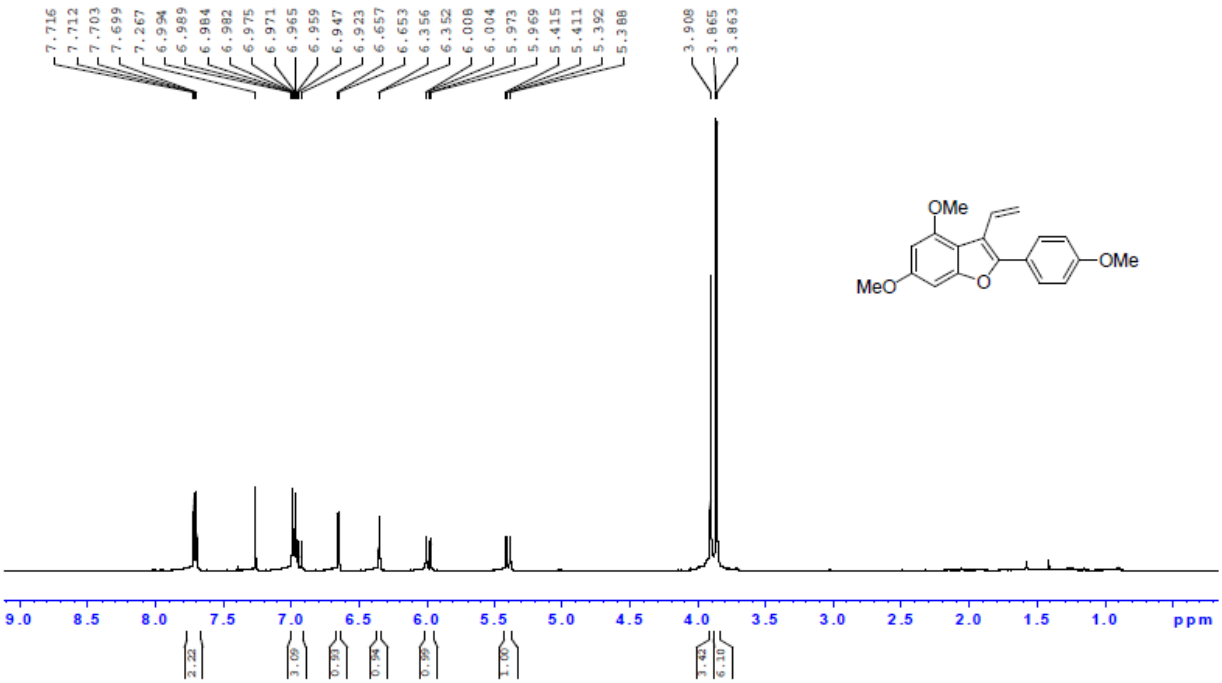


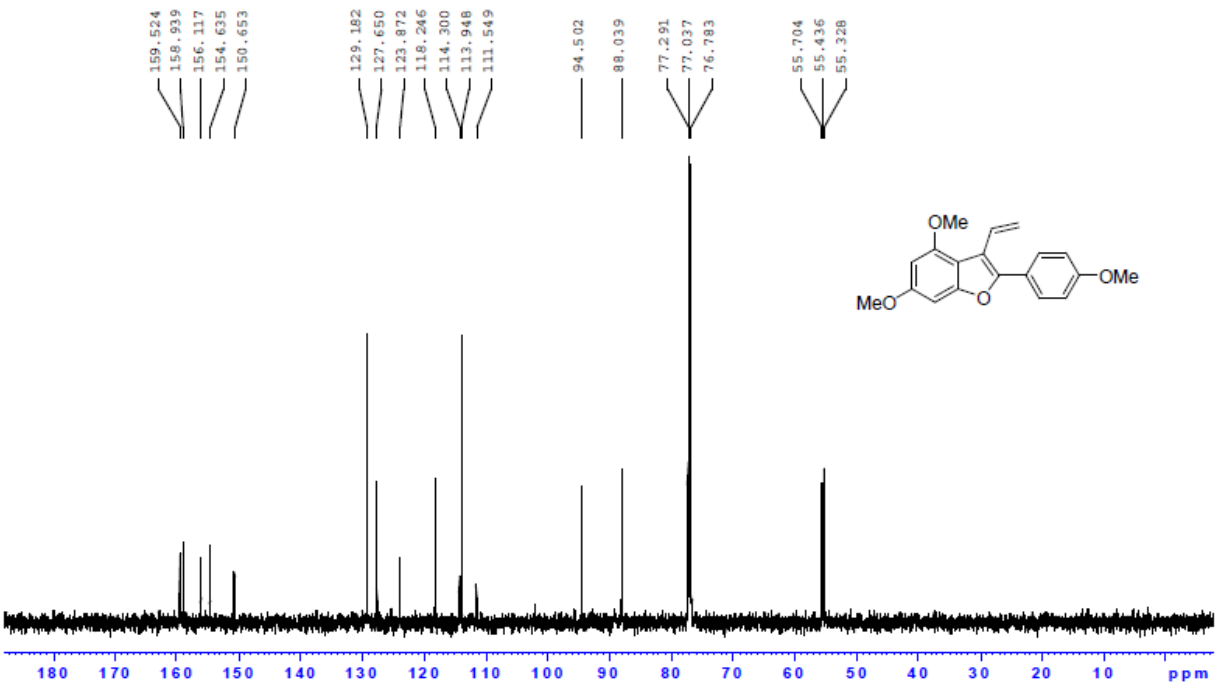
Compound 10 Precursor then Compound 10



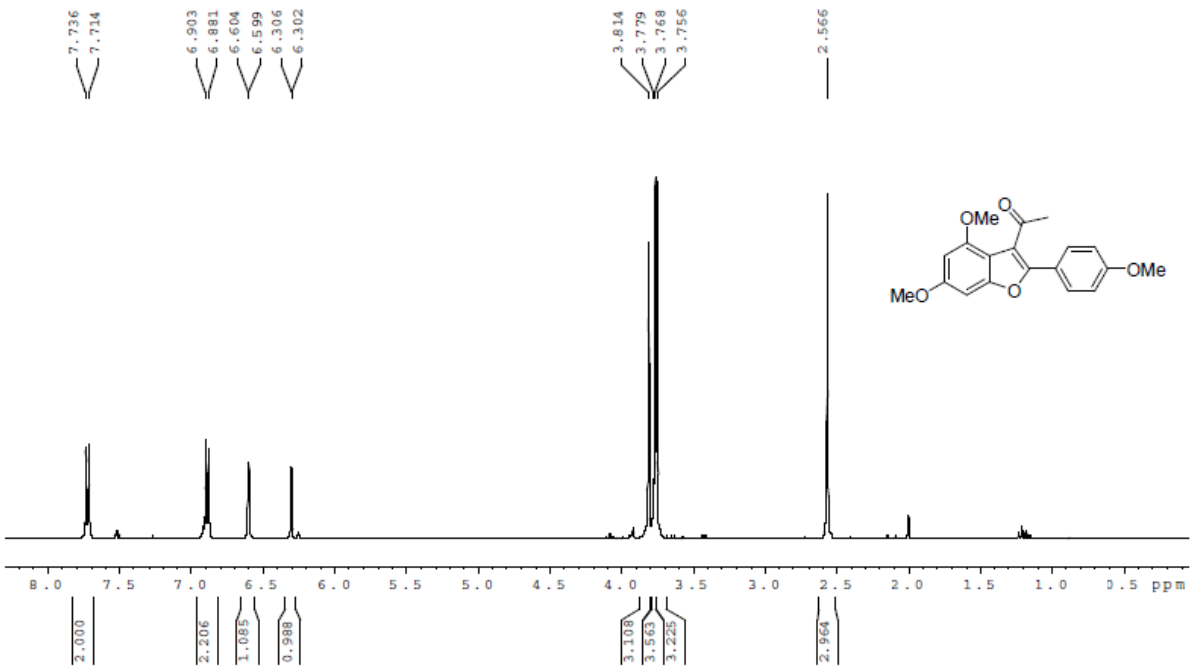


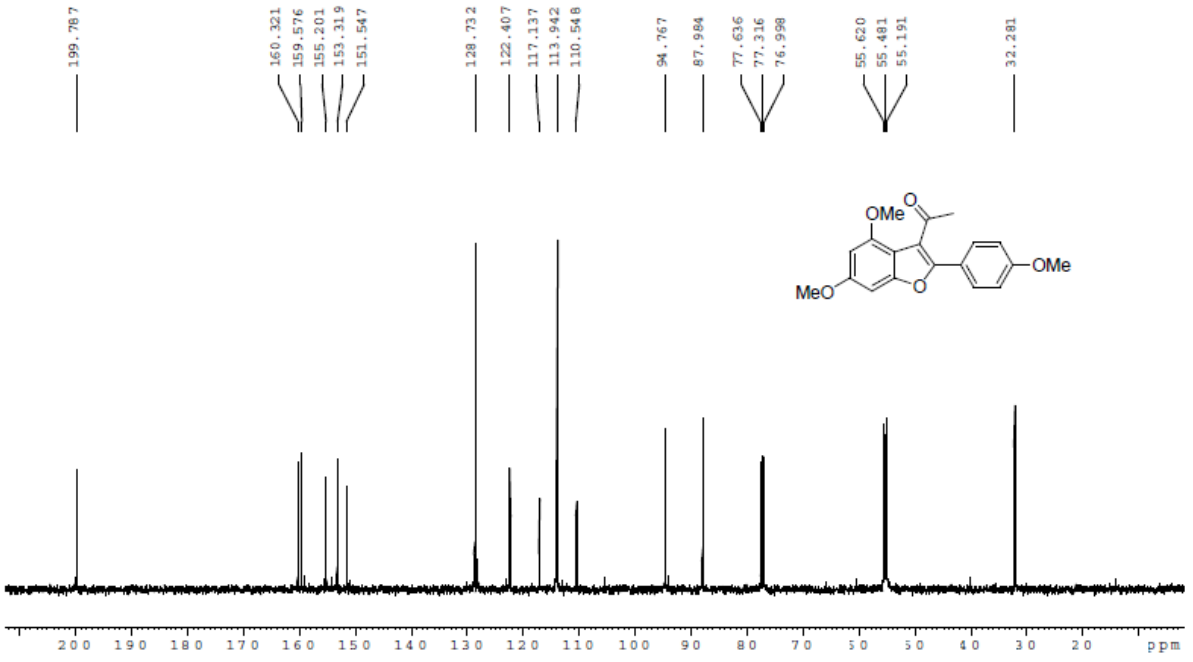
Compound 11


7.716
7.712
7.703
7.699
7.267
6.994
6.989
6.984
6.982
6.975
6.971
6.965
6.959
6.947
6.923
6.657
6.653
6.356
6.352
6.008
6.004
5.973
5.969
5.415
5.411
5.392
5.388
3.908
3.865
3.863
OMe
MeO
OMe
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 ppm
2.22
3.09
0.93
0.94
0.99
1.00
3.42
6.10

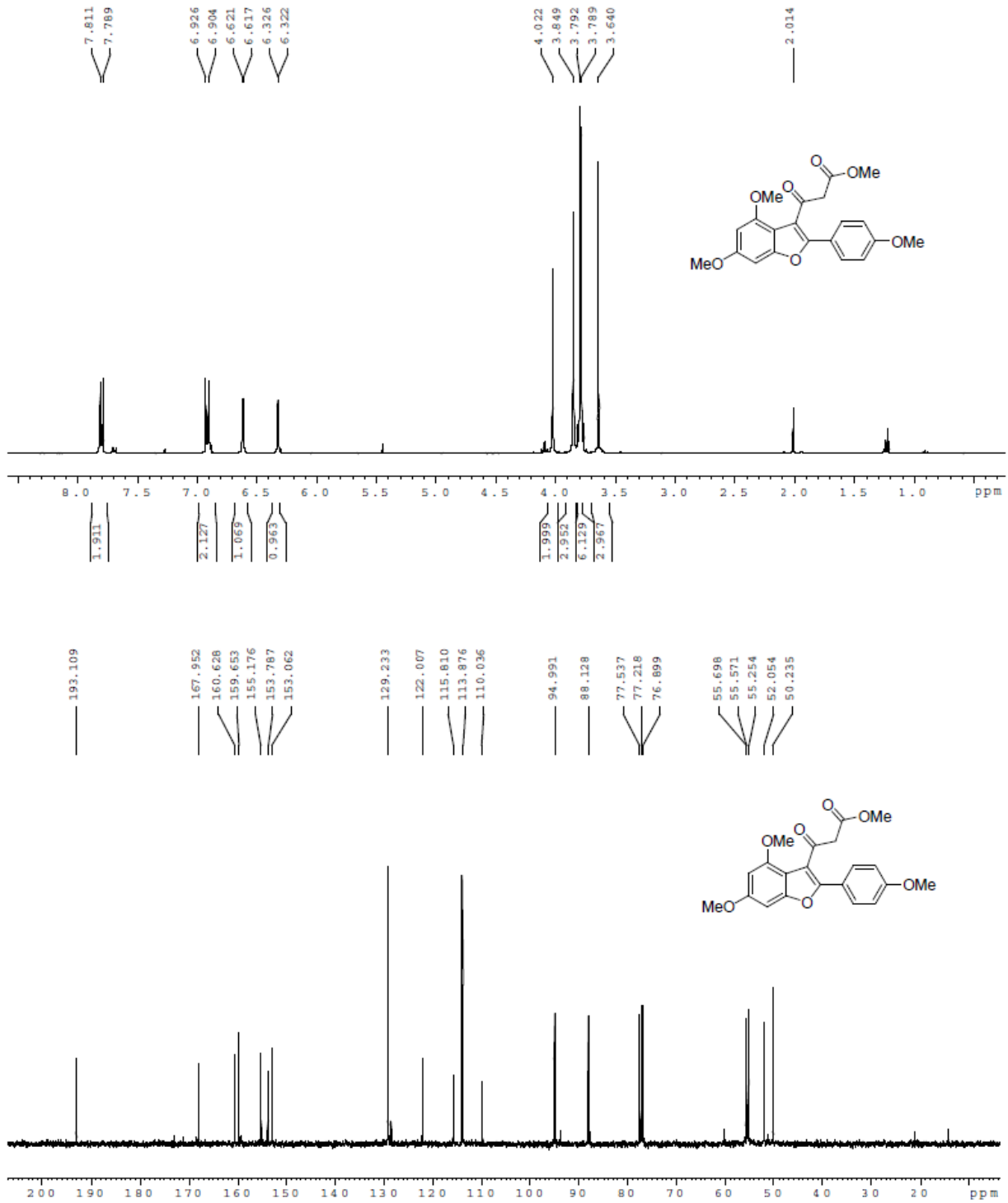

159.524
158.939
156.117
154.635
150.653
129.182
127.650
123.872
118.246
114.300
113.948
111.549
94.502
88.039
77.291
77.037
76.783
55.704
55.436
55.328
OMe
MeO
OMe
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

Compound 12

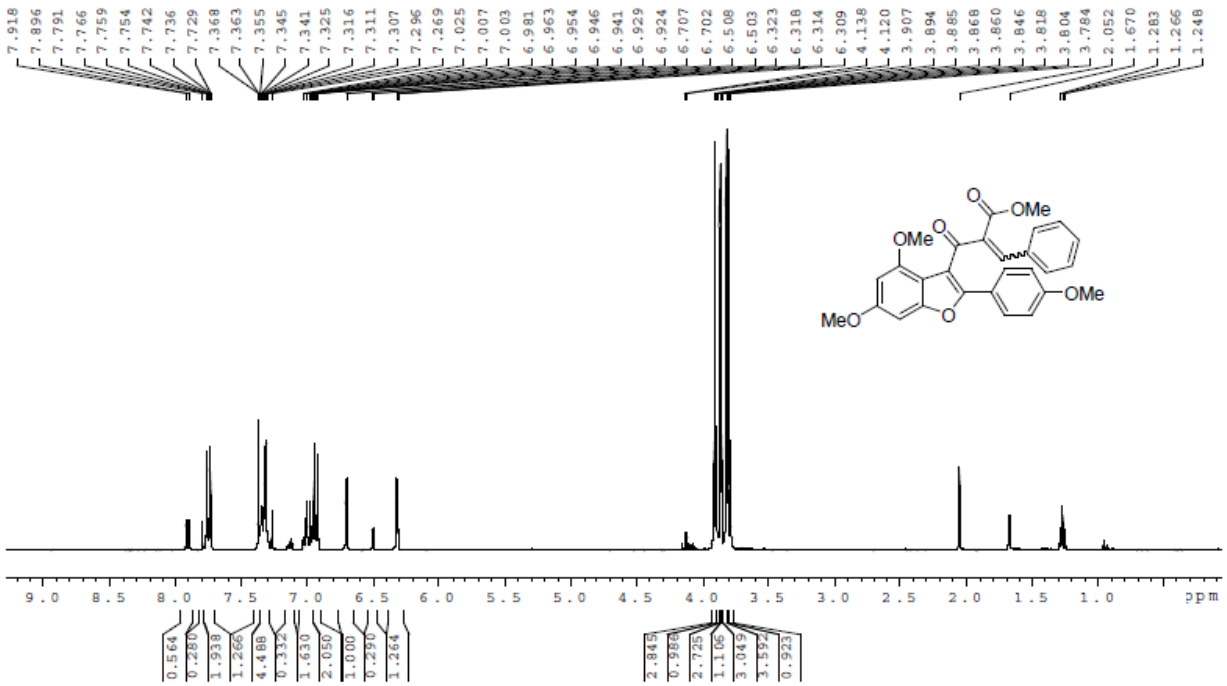

7.736
7.714
6.903
6.881
6.604
6.599
6.306
6.302
3.814
3.779
3.768
3.756
2.566
OMe
O
MeO
O
OMe
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.000
2.206
1.085
0.988
3.108
3.563
3.225
2.964

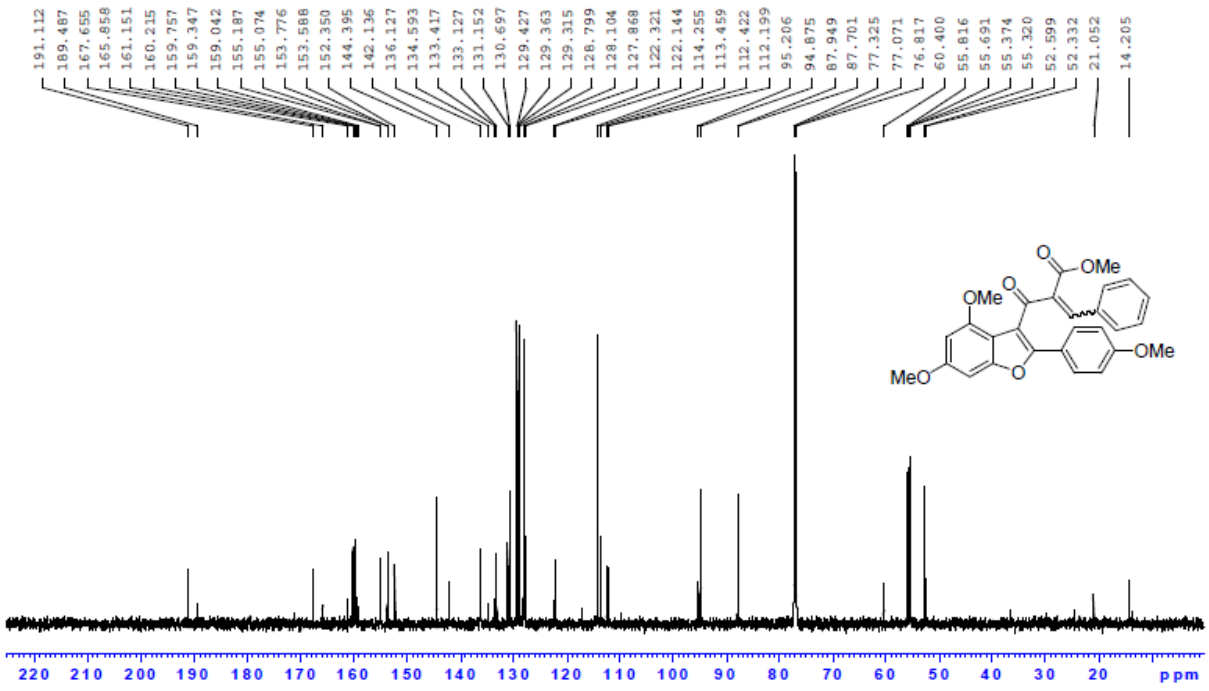

199.787
160.321
159.576
155.201
153.319
151.547
128.732
122.407
117.137
113.942
110.548
94.767
87.984
77.636
77.316
76.998
55.620
55.481
55.191
32.281
OMe
O
MeO
O
OMe
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

Compound 13

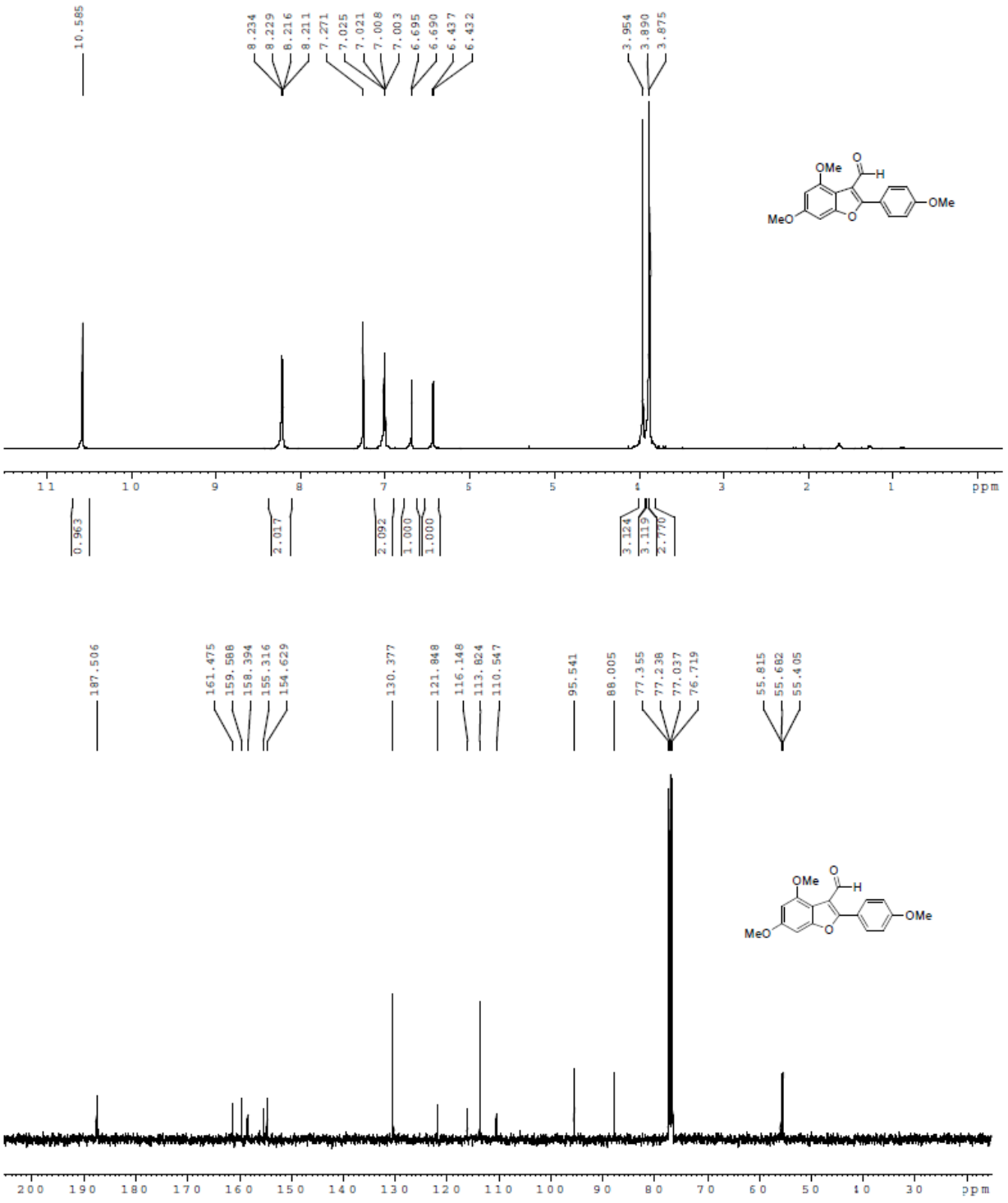

7.811
7.789
6.926
6.904
6.621
6.617
6.326
6.322
4.022
3.849
3.792
3.789
3.640
2.014
OMe
OMe
OMe
MeO
O
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.911
2.127
1.069
0.963
1.999
2.952
6.129
2.967
193.109
167.952
160.628
159.653
155.176
153.787
153.062
129.233
122.007
115.810
113.876
110.036
94.991
88.128
77.537
77.218
76.899
55.698
55.571
55.254
52.054
50.235
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

Compound 3

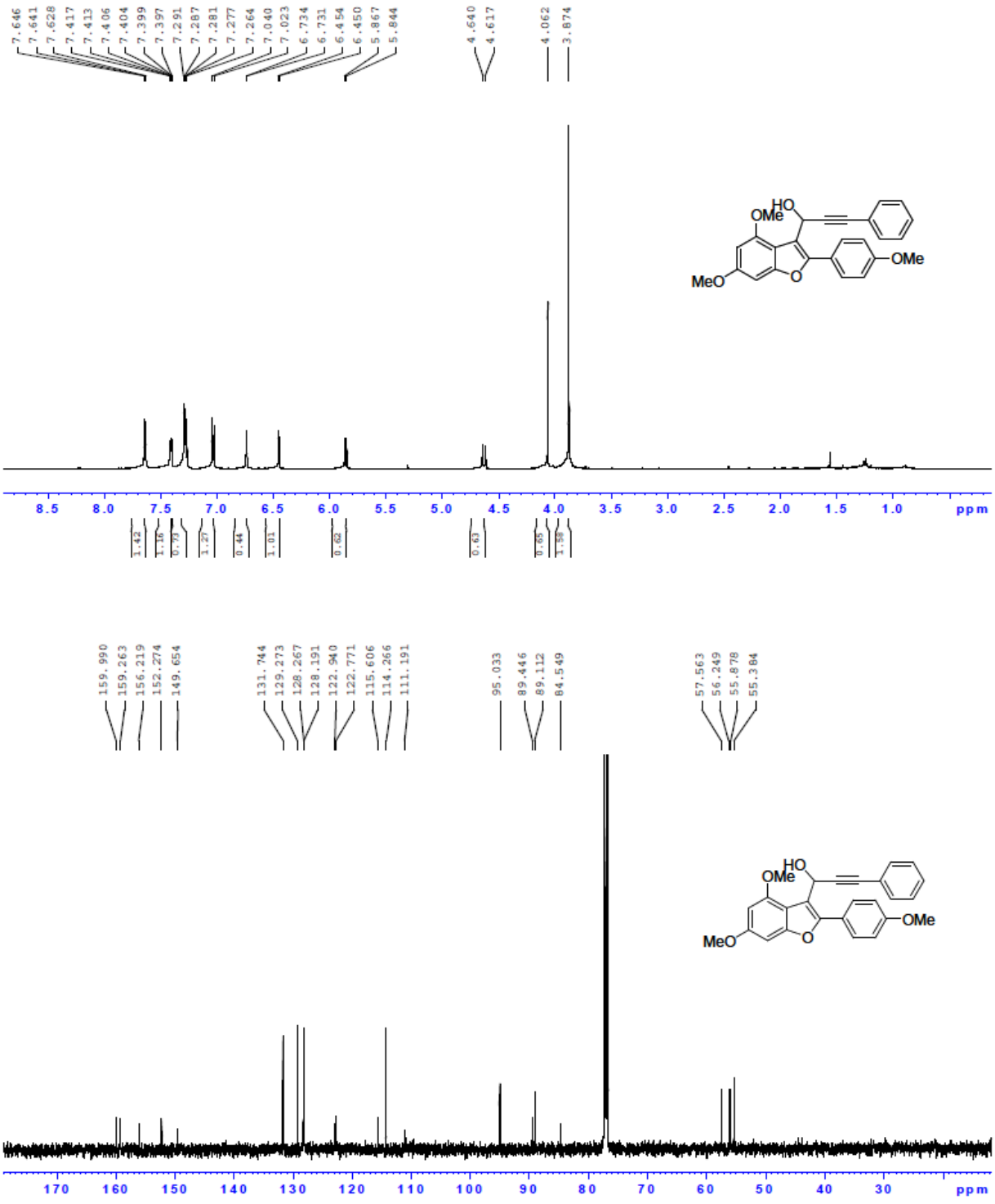

7.918
7.896
7.791
7.766
7.759
7.754
7.742
7.736
7.729
7.368
7.363
7.355
7.345
7.341
7.325
7.316
7.311
7.307
7.296
7.269
7.025
7.007
7.003
6.981
6.963
6.954
6.946
6.941
6.929
6.924
6.707
6.702
6.508
6.503
6.323
6.318
6.314
6.309
4.138
4.120
3.907
3.894
3.885
3.868
3.860
3.846
3.818
3.804
3.784
2.052
1.670
1.283
1.266
1.248
OMe
OMe
O
O
MeO
O
OMe
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 ppm
0.564
0.280
1.938
1.266
4.488
0.332
1.630
2.050
1.000
0.290
1.264
2.845
0.968
2.725
1.106
3.049
3.592
0.923


191.112
189.487
167.655
165.858
161.151
160.215
159.757
159.347
159.042
155.187
155.074
153.776
153.588
152.350
144.395
142.136
136.127
134.593
133.417
133.127
131.152
130.697
129.427
129.363
129.315
128.799
128.104
127.868
122.321
122.144
114.255
113.459
112.422
112.199
95.206
94.875
87.949
87.701
77.325
77.071
76.817
60.400
55.816
55.691
55.374
55.320
52.599
52.332
21.052
14.205
OMe
OMe
O
O
MeO
O
OMe
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

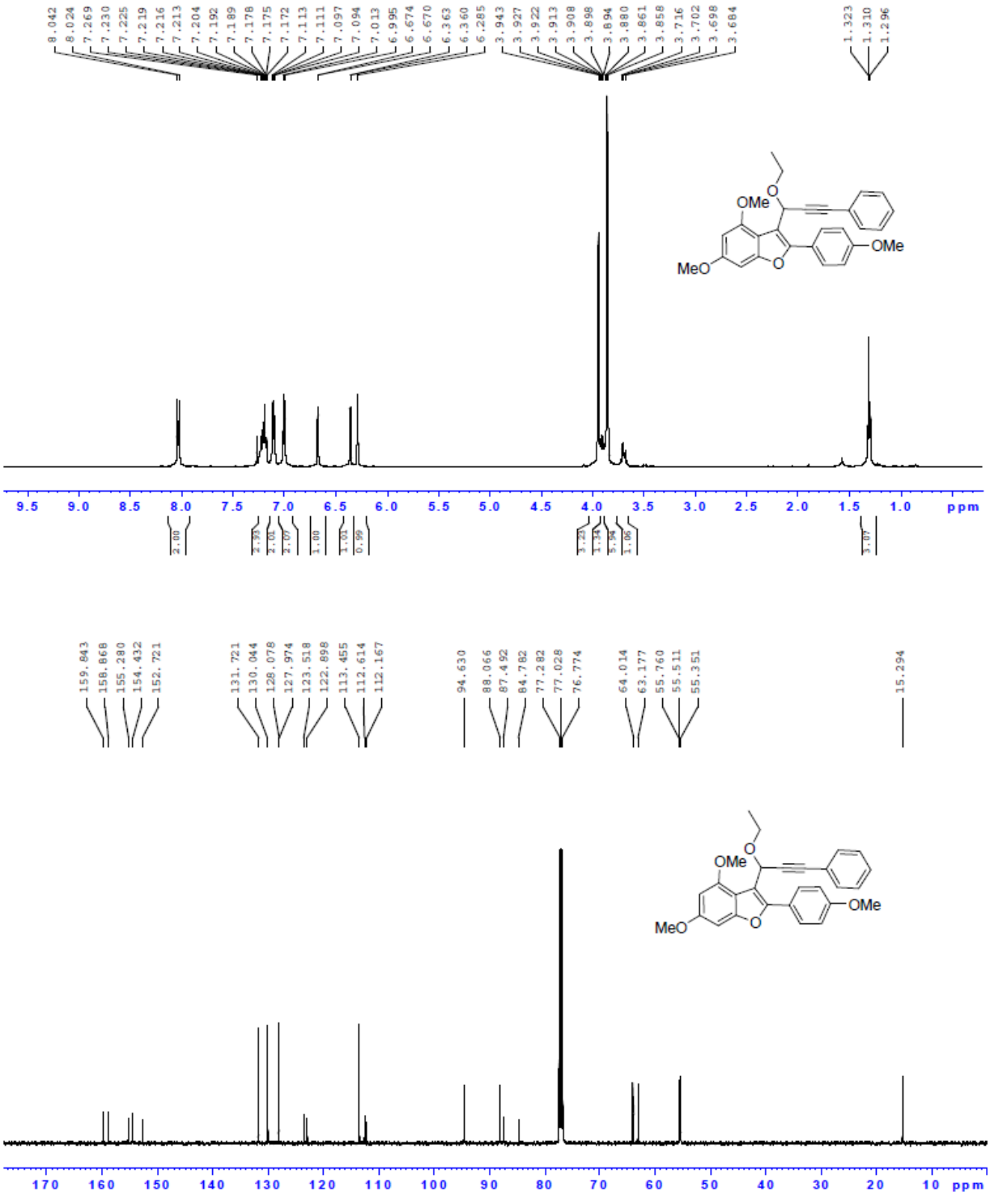
Compound 16


10.585
8.234
8.229
8.216
8.211
7.271
7.025
7.021
7.008
7.003
6.695
6.690
6.437
6.432
3.954
3.890
3.875
OMe
O
H
MeO
OMe
11
10
9
8
7
6
5
4
3
2
1
ppm
0.963
2.017
2.092
1.000
1.000
3.124
3.119
2.770
187.506
161.475
159.588
158.394
155.316
154.629
130.377
121.848
116.148
113.824
110.547
95.541
88.005
77.355
77.238
77.037
76.719
55.815
55.682
55.405
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

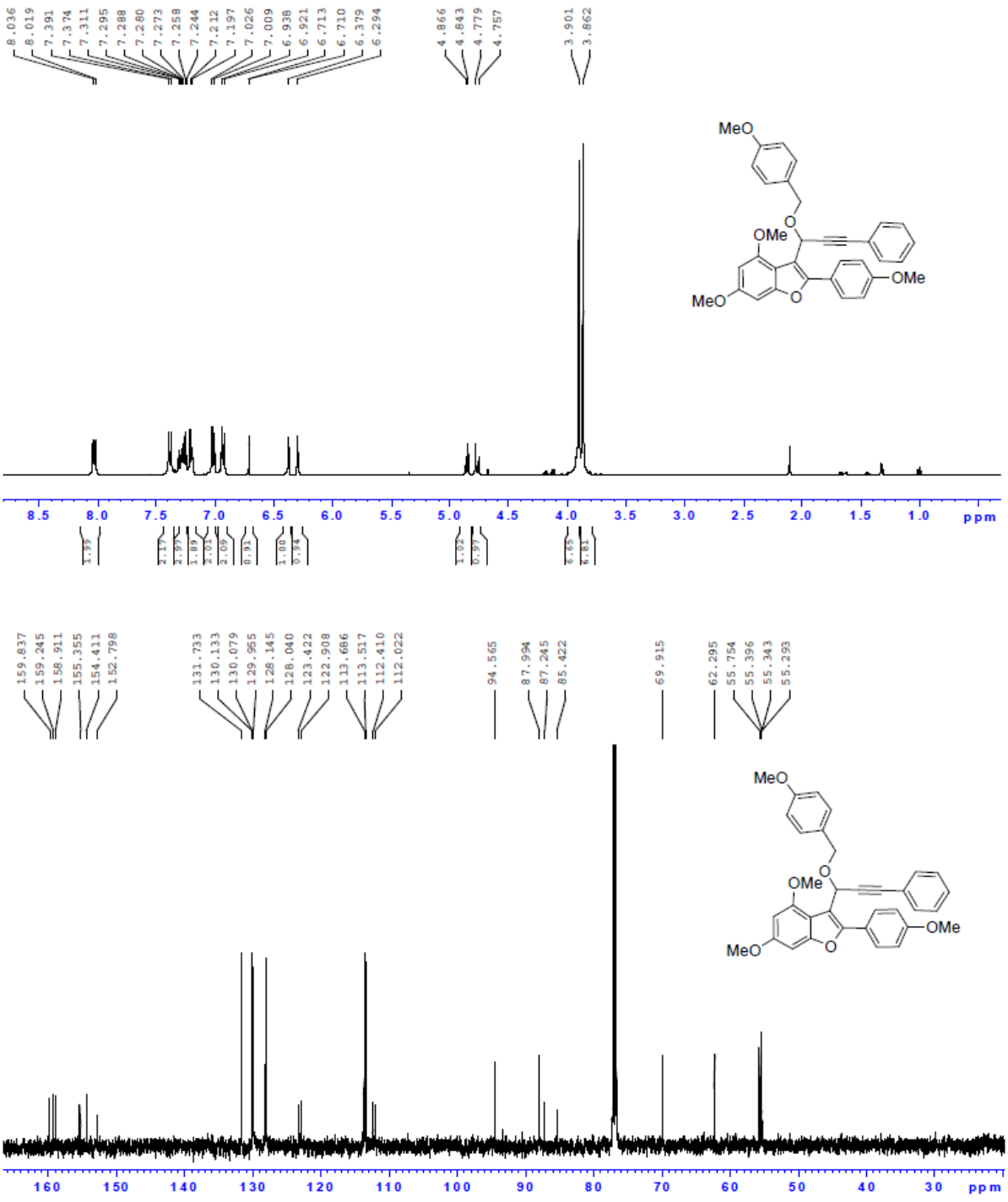
Compound 17a



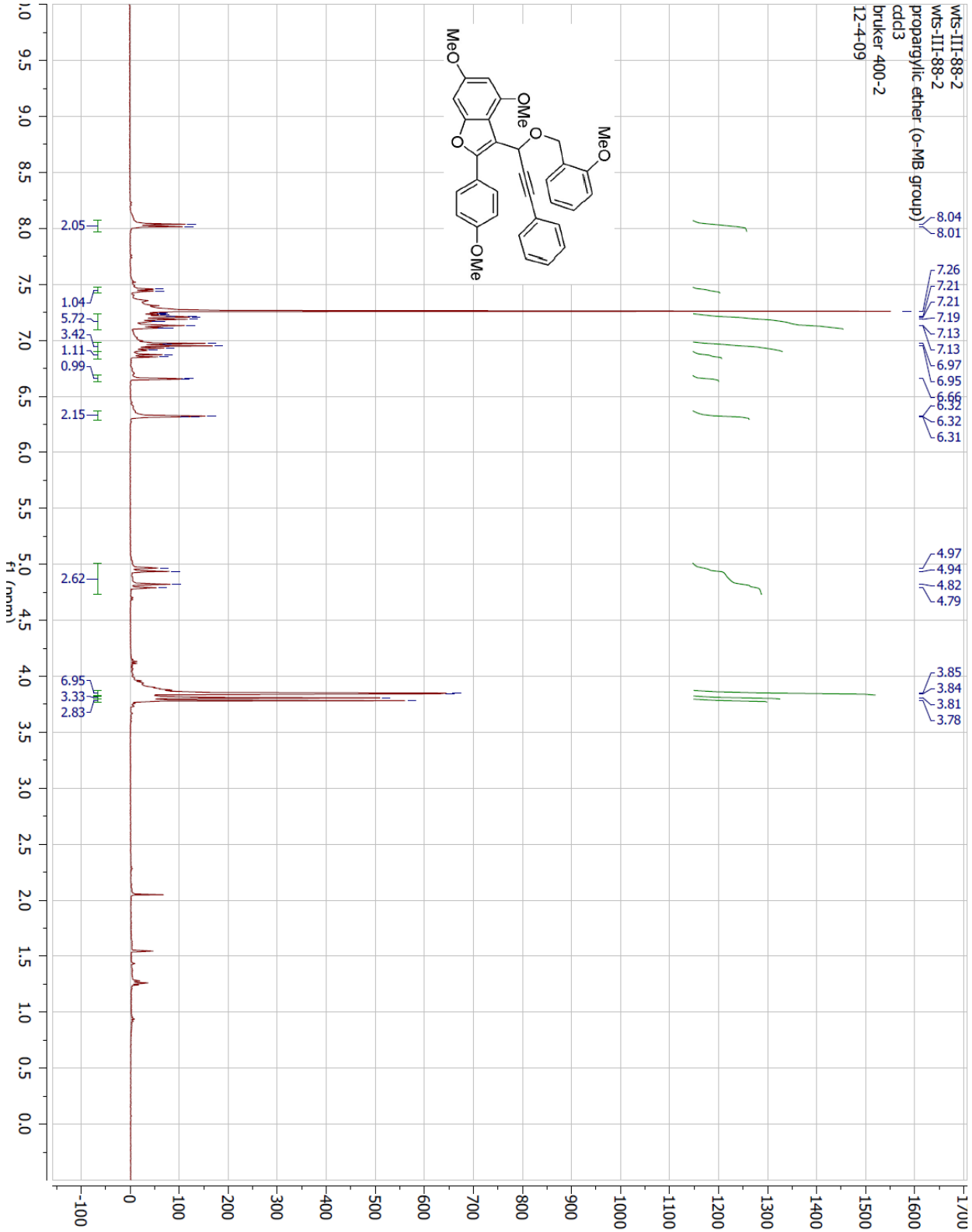
Compound 18a



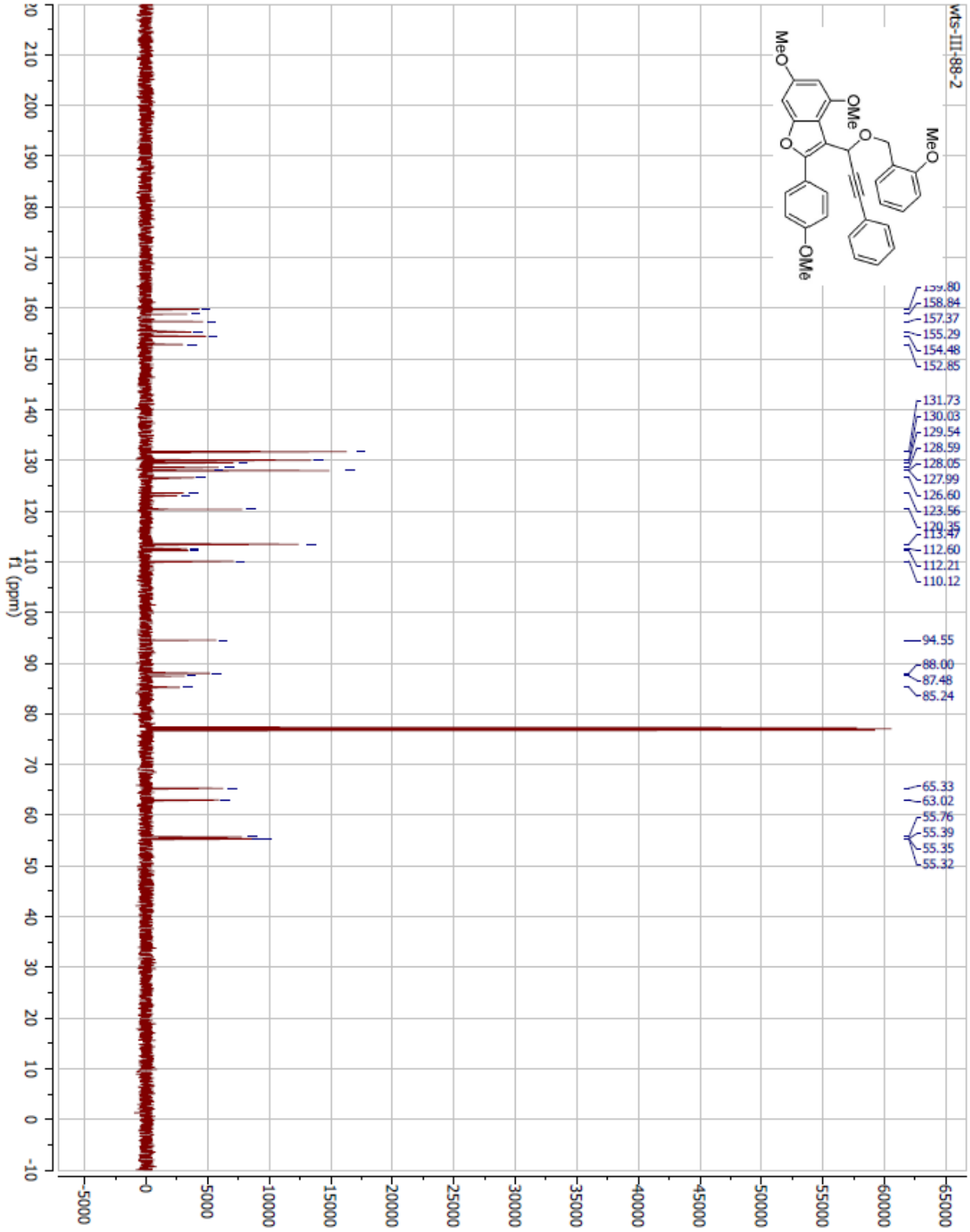
Compound 18b



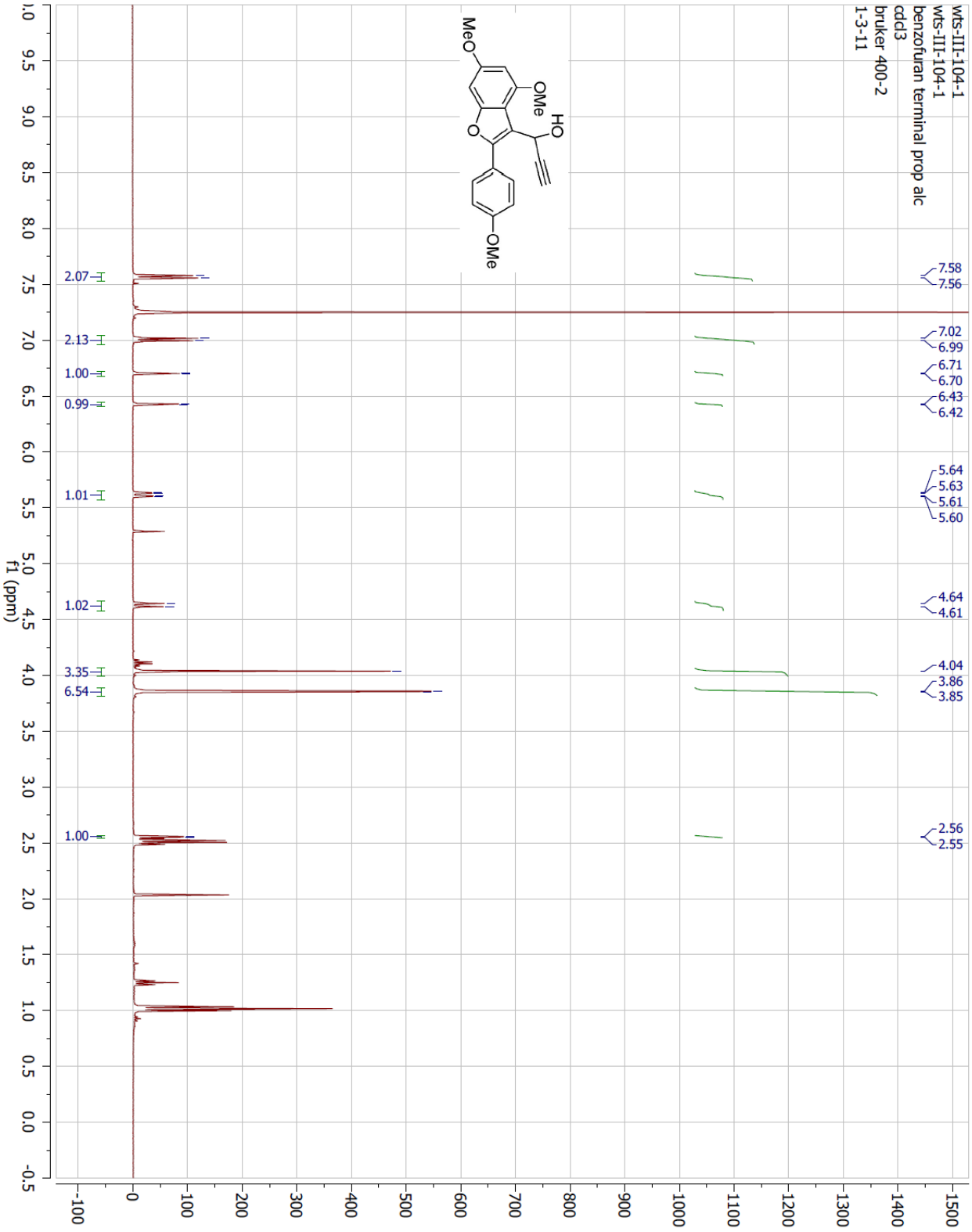
Compound 18c



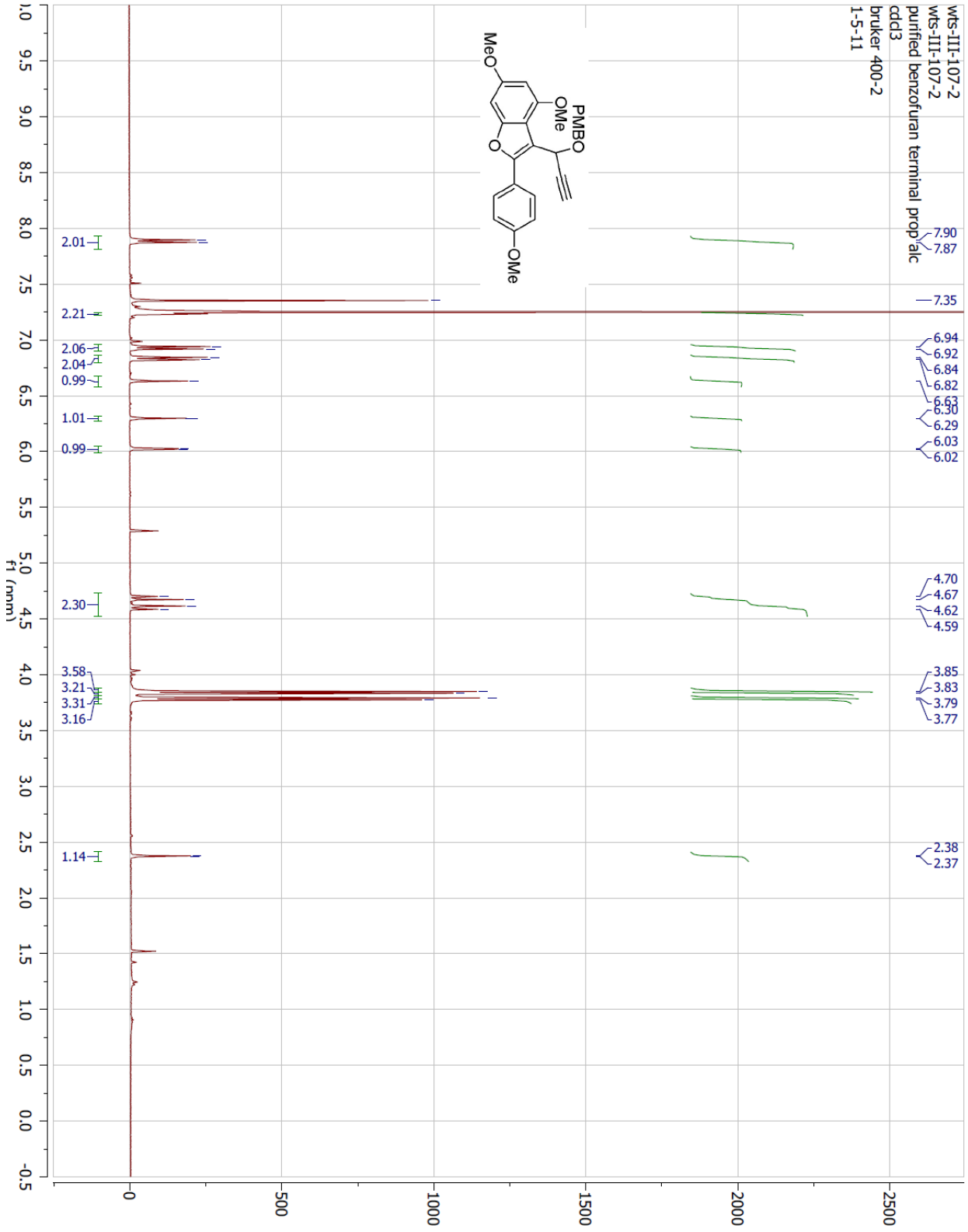
Compound 18c



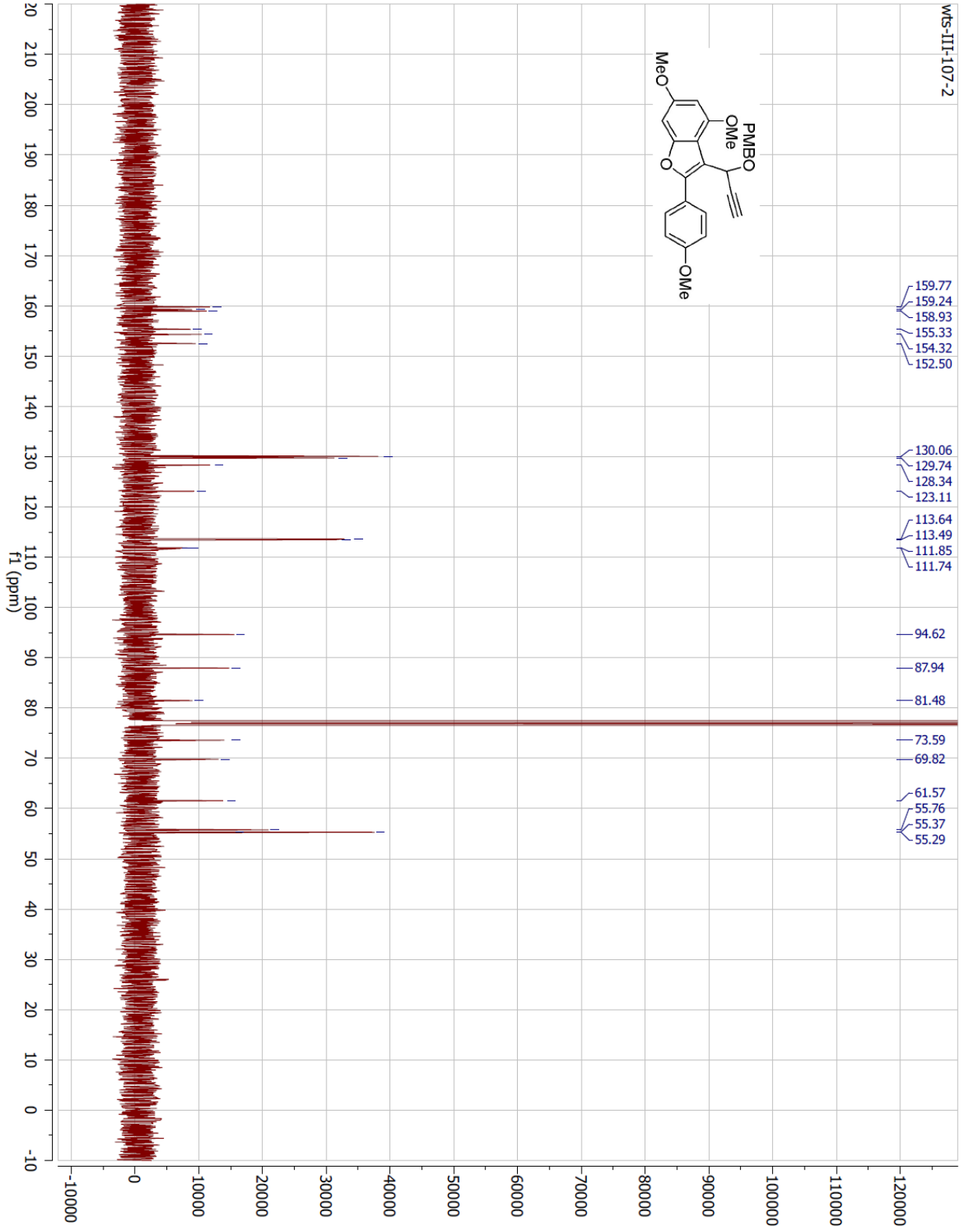
Compound 17b



Compound 18d

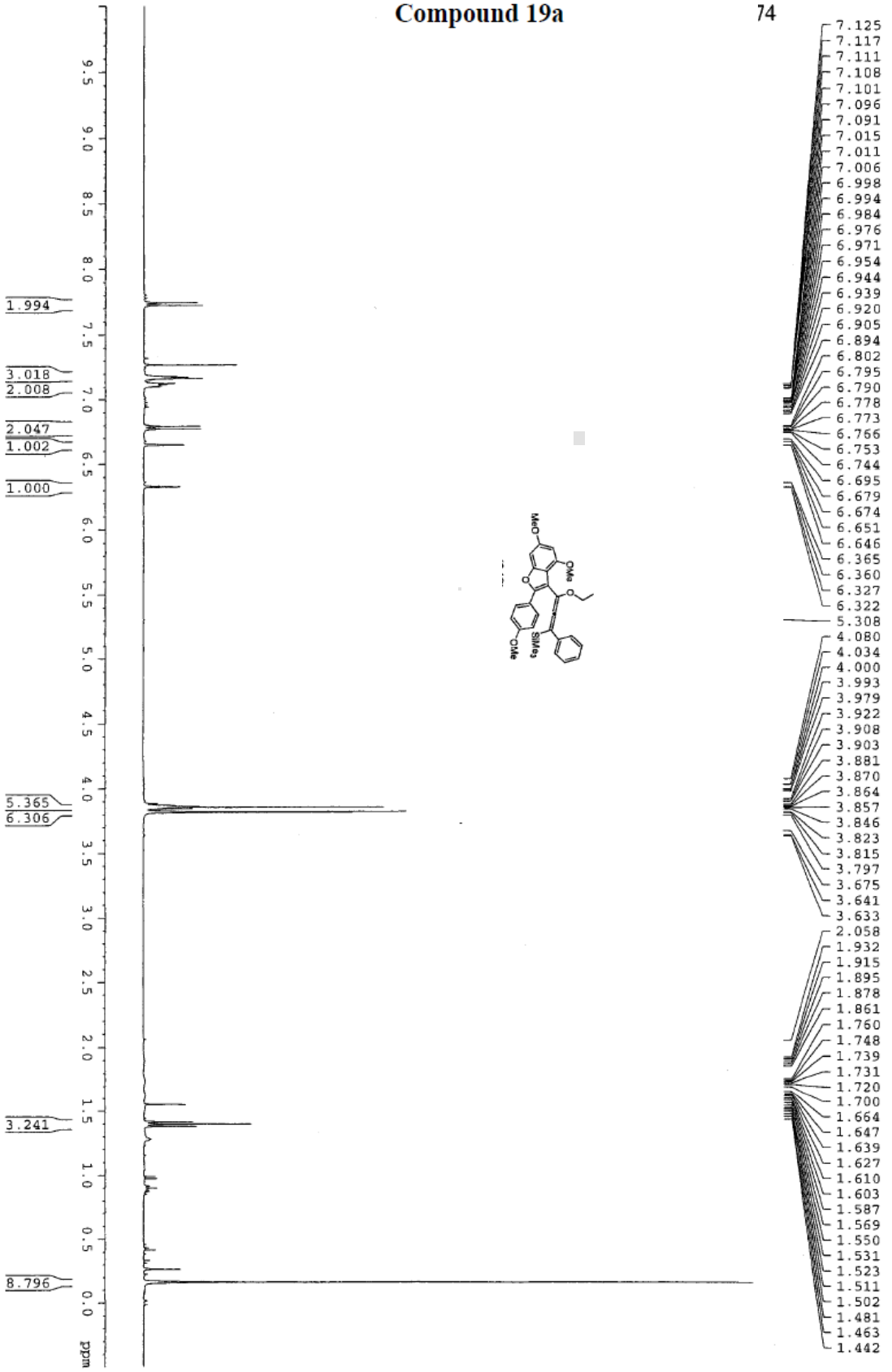


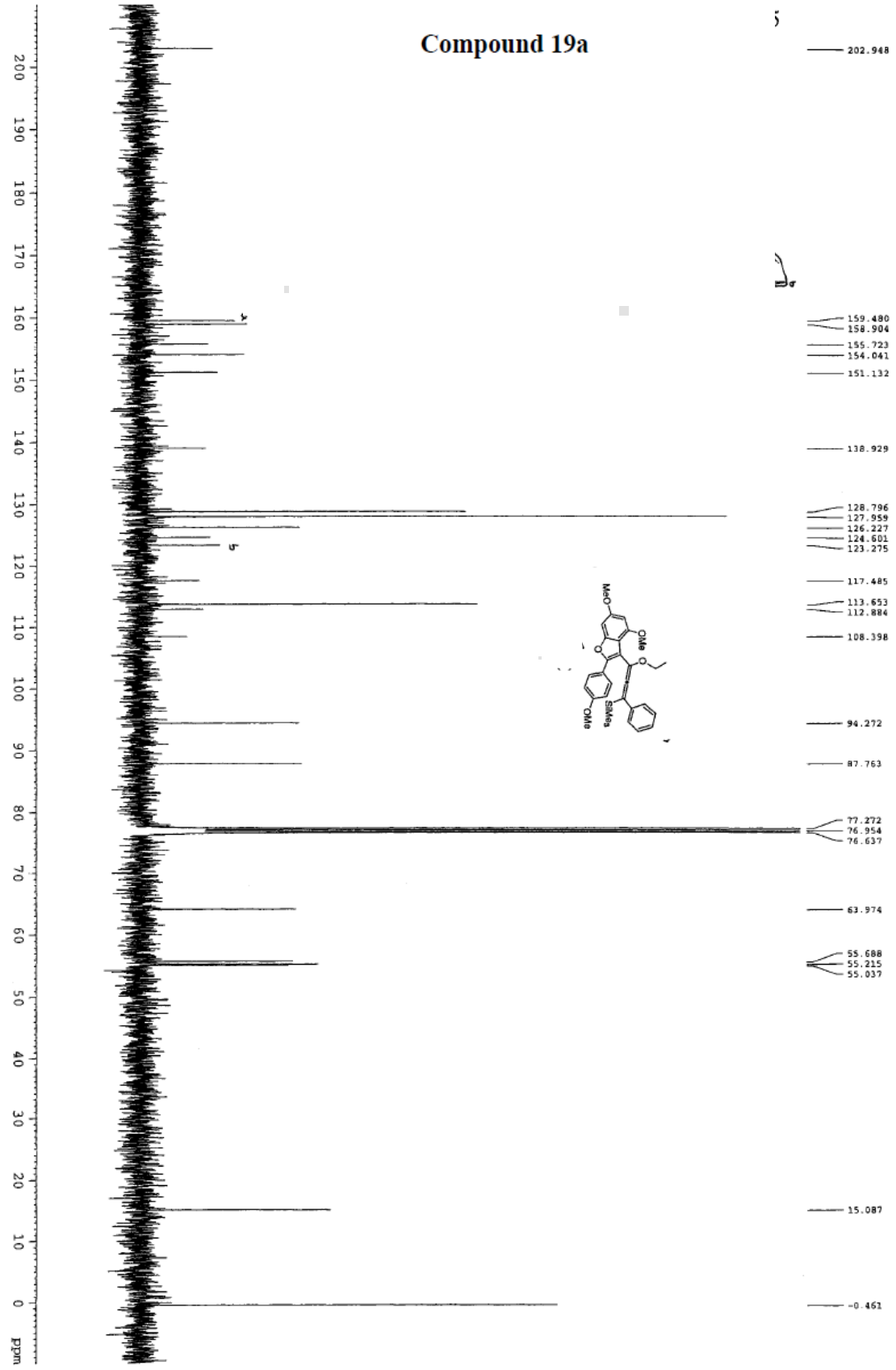
Compound 18d



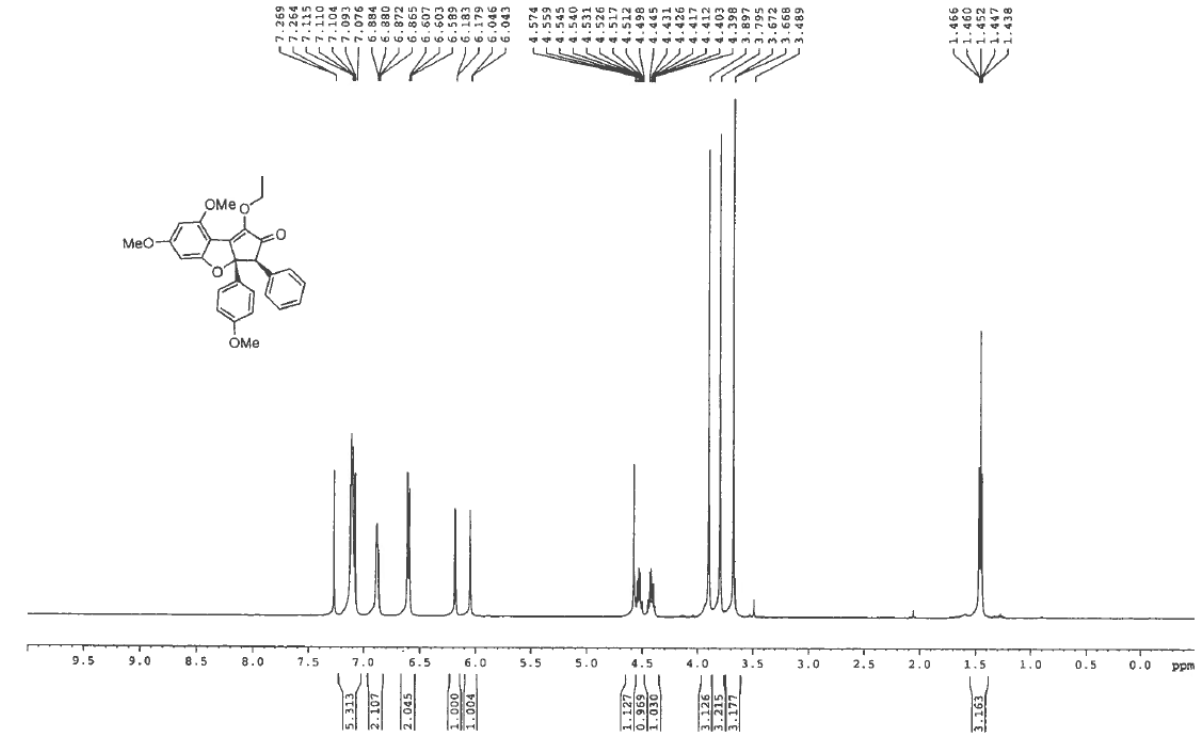
Compound 19a

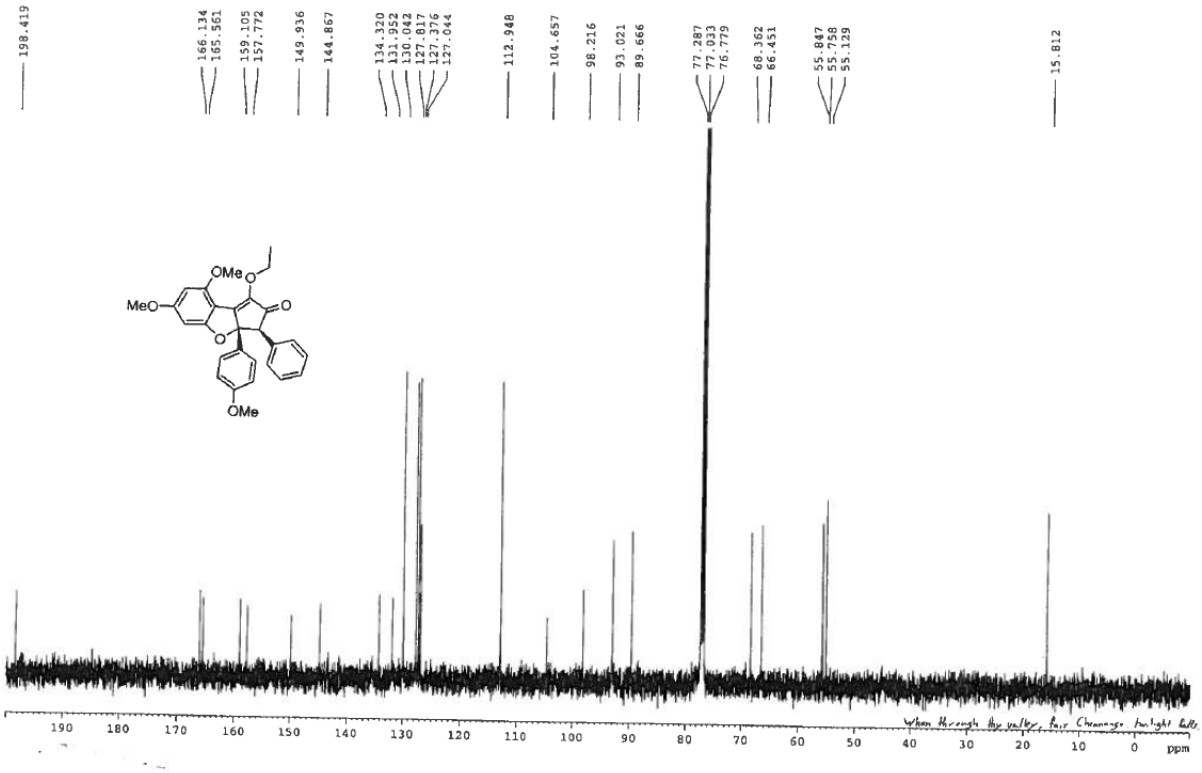
74



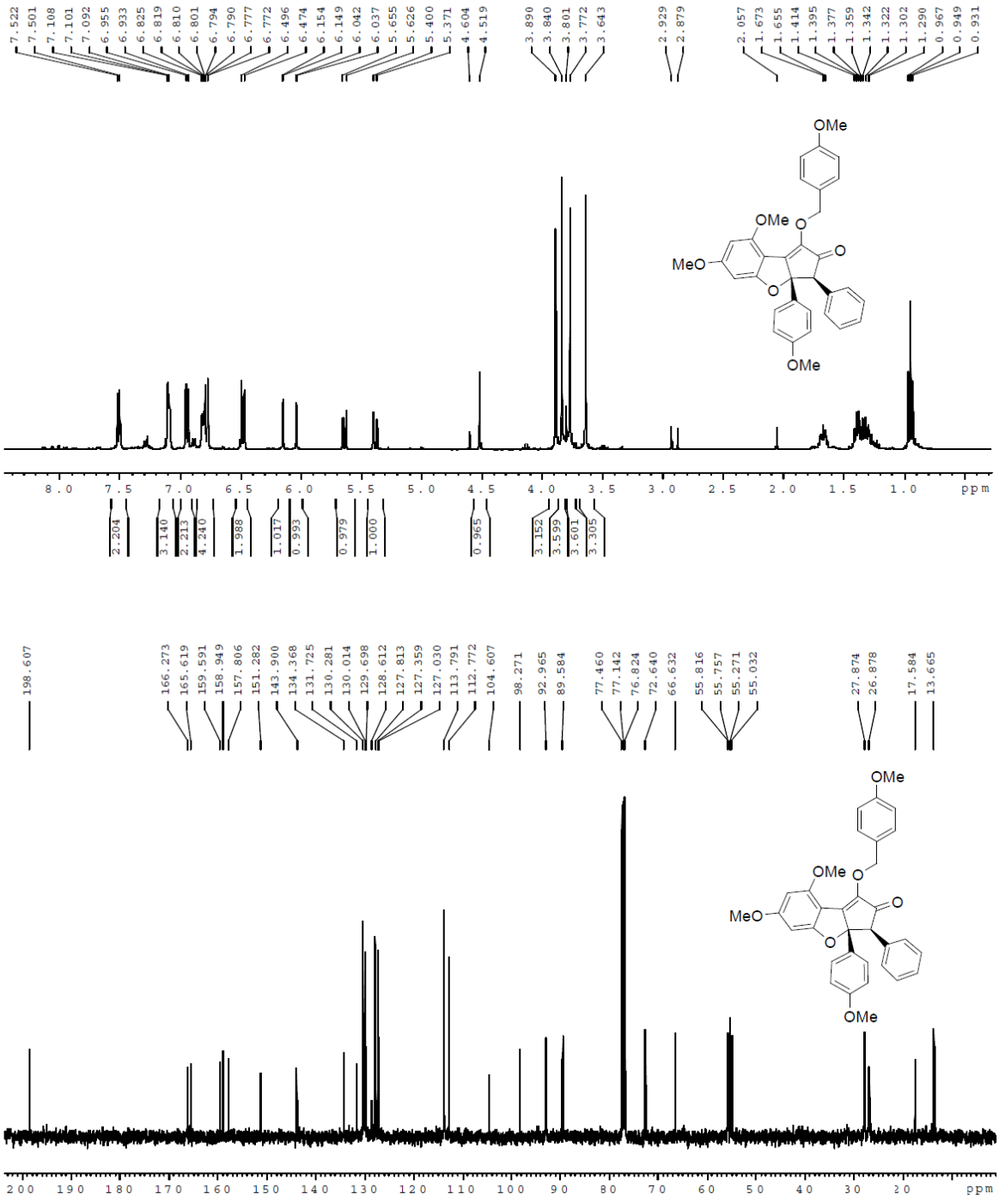

Compound 19a
202.948
159.480
158.904
155.723
154.041
151.132
138.929
128.796
127.959
126.227
124.601
123.275
117.485
113.653
112.884
108.398
94.272
87.763
77.272
76.954
76.637
63.974
55.688
55.215
55.037
15.087
-0.461
MeO
OMe
OMe
SiMe3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Compound 15a

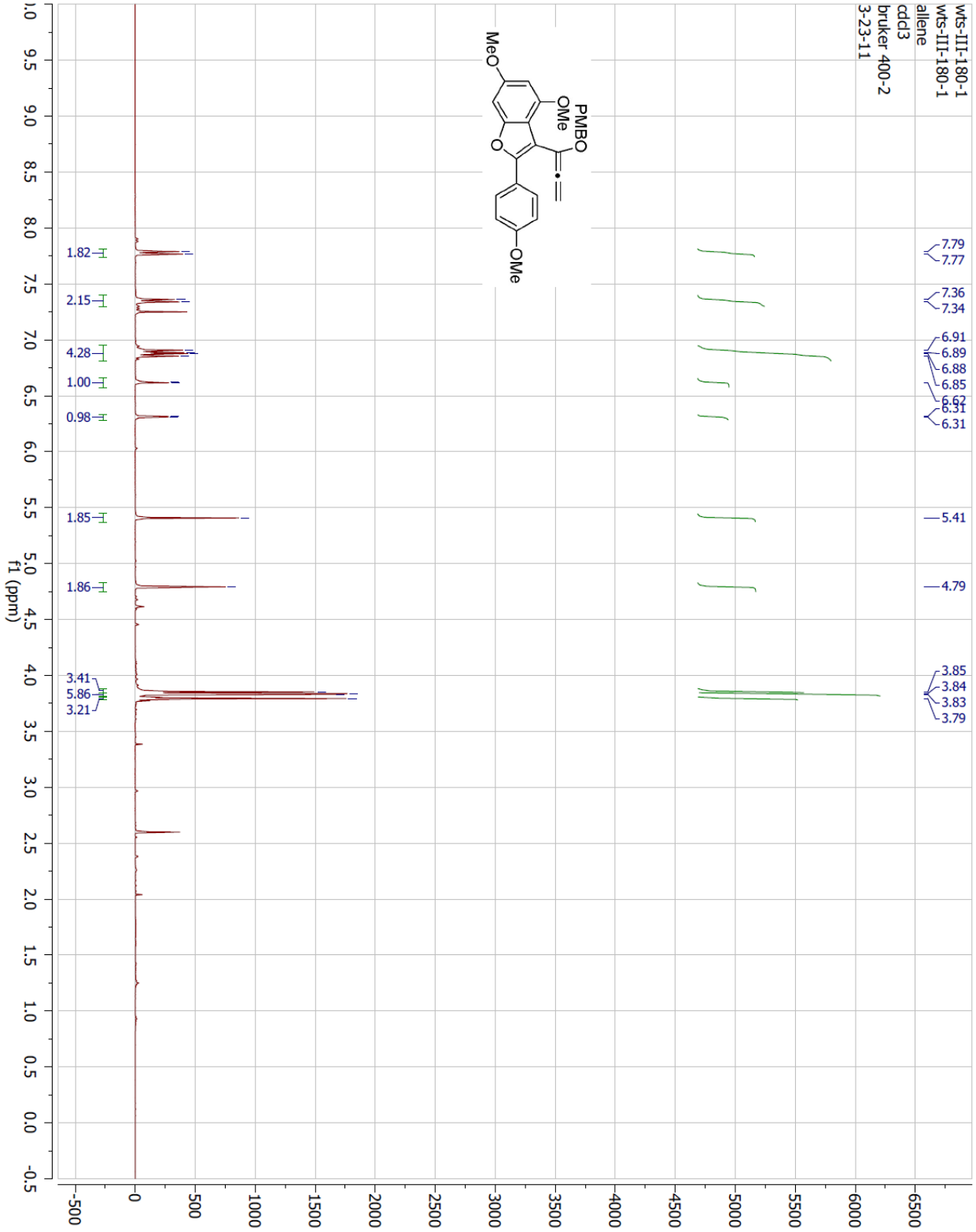




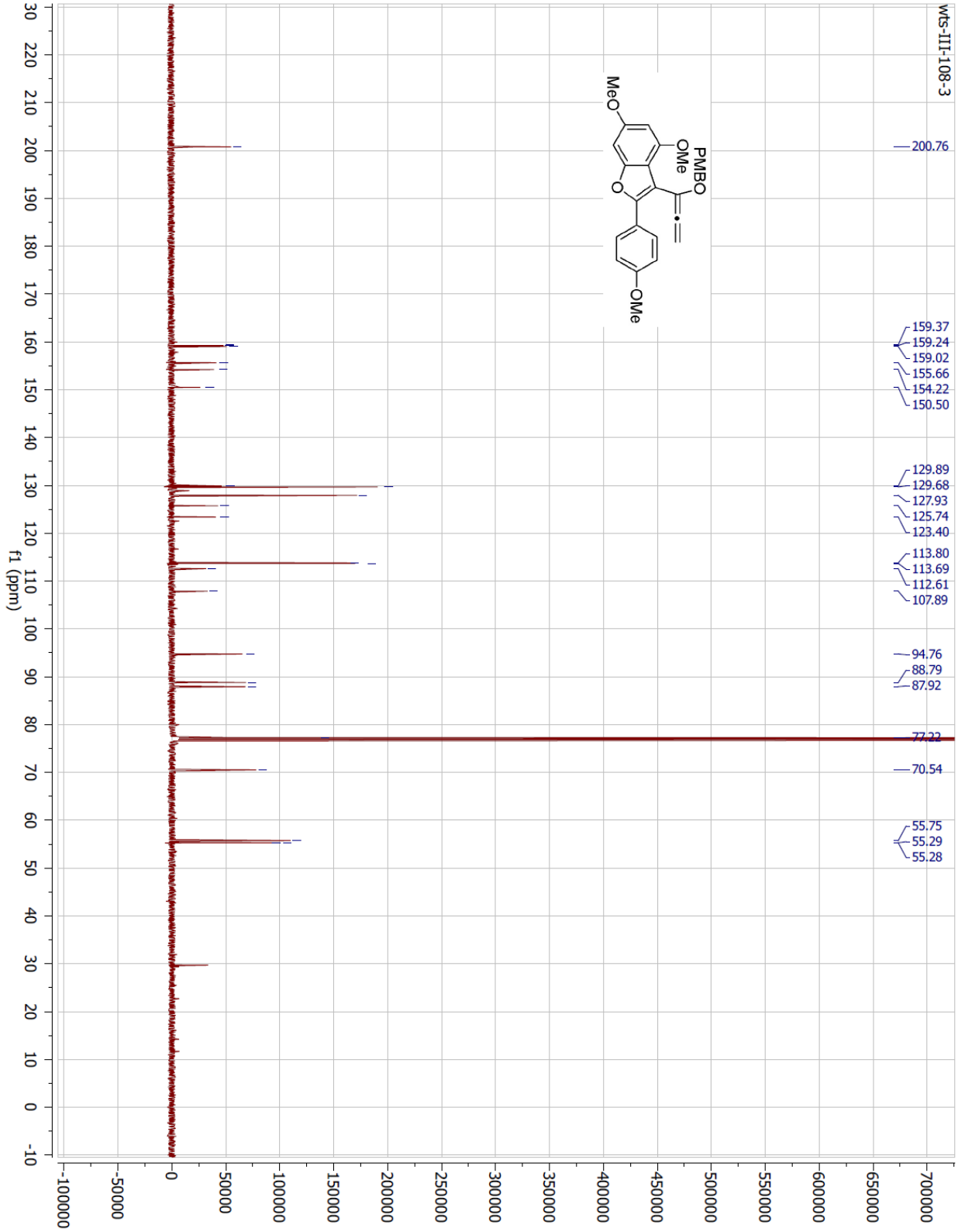
Compound 15b



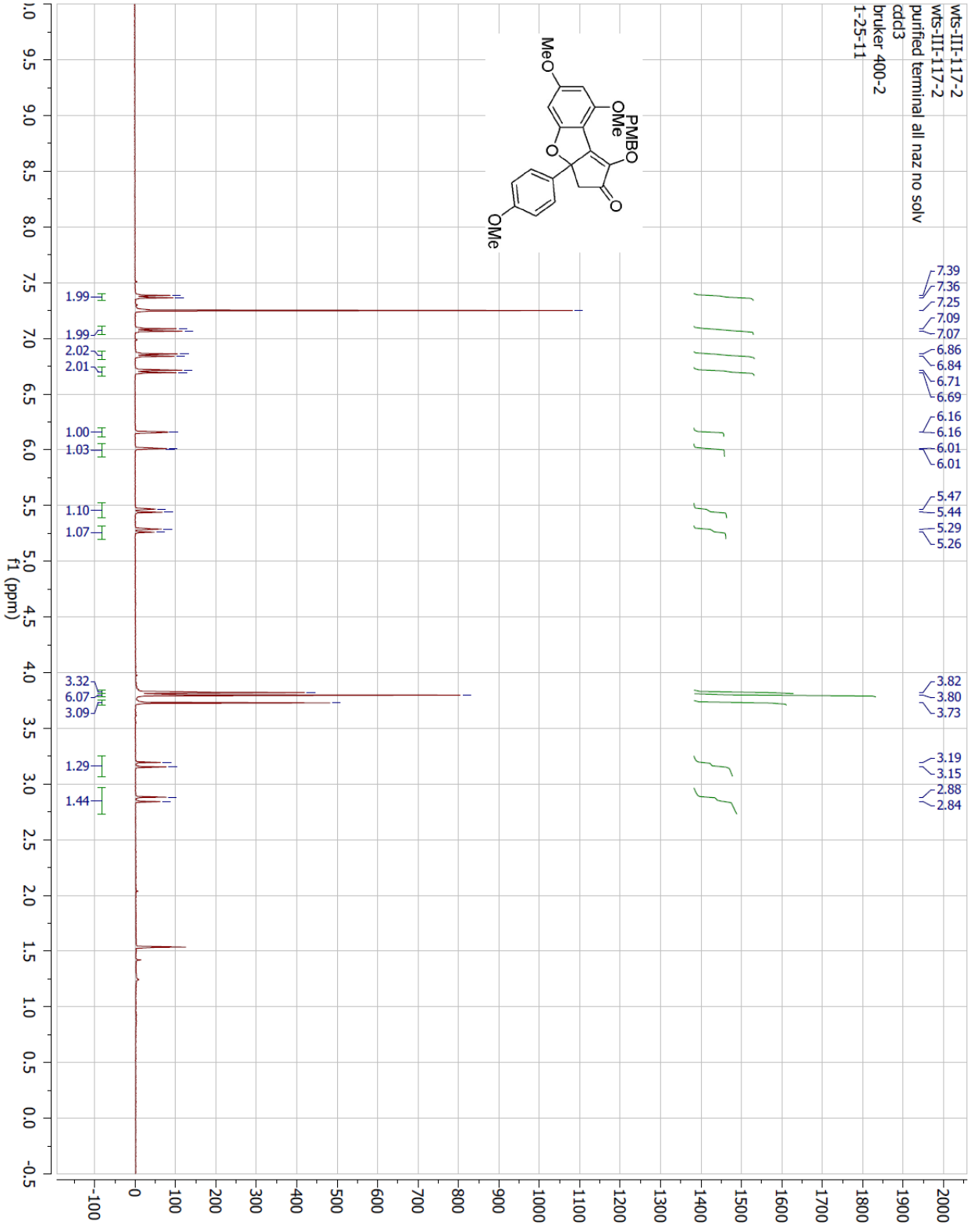
Compound 20


wts-III-180-1
wts-III-180-1
allene
cdd3
bruker 400-2
3-23-11
MeO
PMBO
OMe
OMe
1.82
2.15
4.28
1.00
0.98
1.85
1.86
3.41
5.86
3.21
7.79
7.77
7.36
7.34
6.91
6.89
6.88
6.85
6.62
6.31
6.31
5.41
4.79
3.85
3.84
3.83
3.79
f1 (ppm)

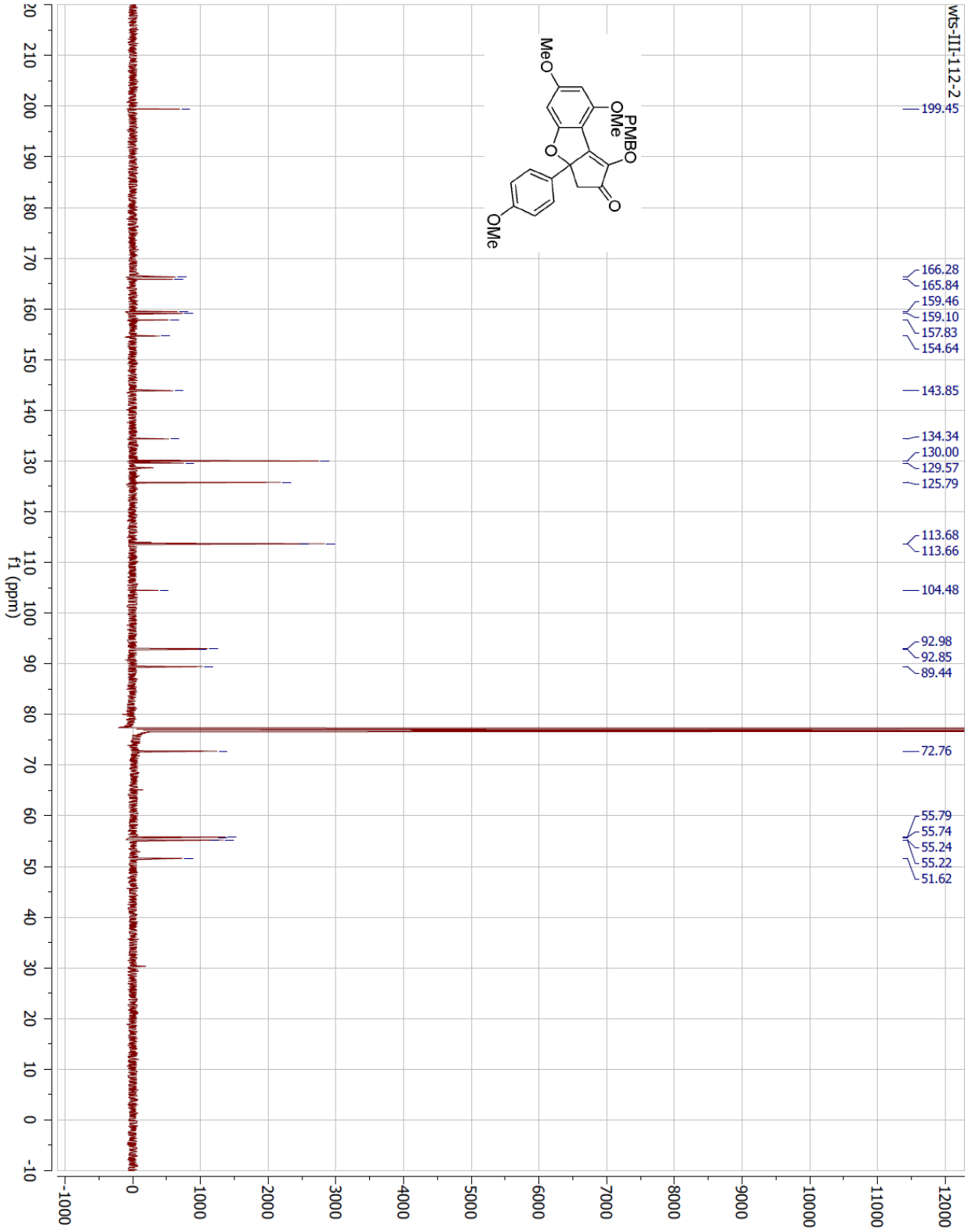
Compound 20

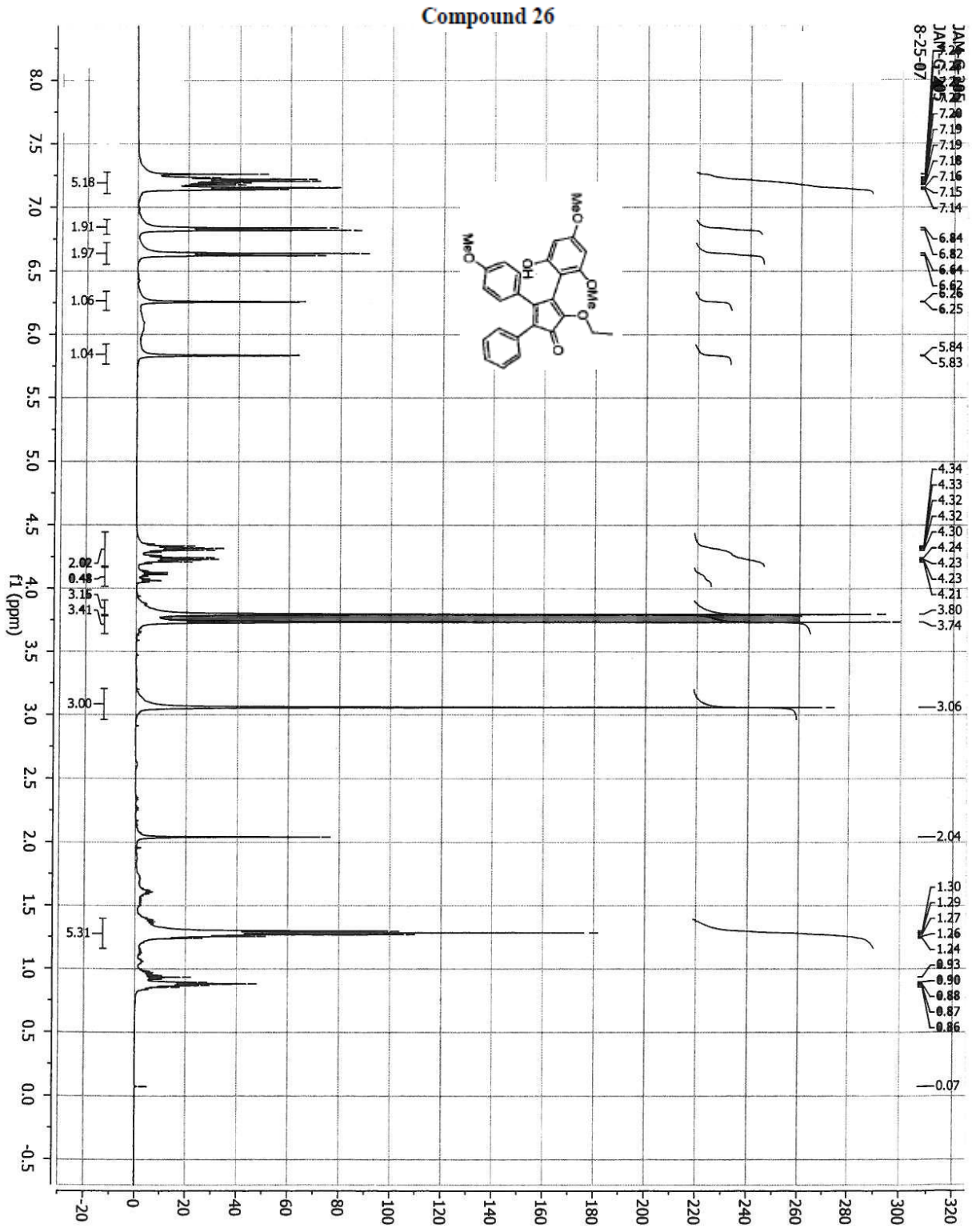

wts-III-108-3
MeO
PMBO
OMe
OMe
200.76
159.37
159.24
159.02
155.66
154.22
150.50
129.89
129.68
127.93
125.74
123.40
113.80
113.69
112.61
107.89
94.76
88.79
87.92
77.22
70.54
55.75
55.29
55.28
f1 (ppm)

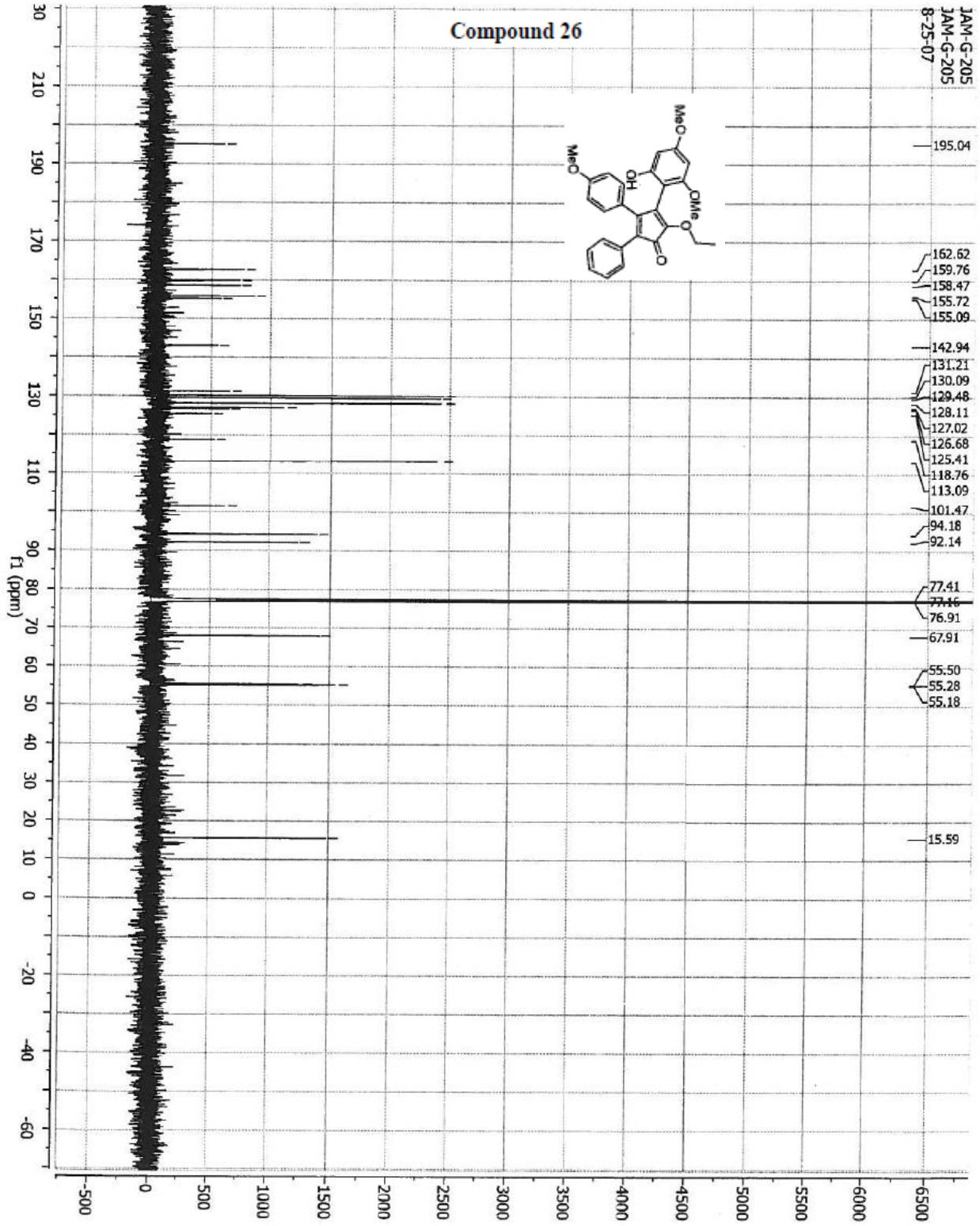
Compound 22


wts-III-117-2
wts-III-117-2
purified terminal all naz no solv
cdcl3
bruker 400-2
1-25-11
MeO
OMe
PMBO
O
O
OMe
f1 (ppm)
1.99
1.99
2.02
2.01
1.00
1.03
1.10
1.07
3.32
6.07
3.09
1.29
1.44
7.39
7.36
7.25
7.09
7.07
6.86
6.84
6.71
6.69
6.16
6.16
6.01
6.01
5.47
5.44
5.29
5.26
3.82
3.80
3.73
3.19
3.15
2.88
2.84

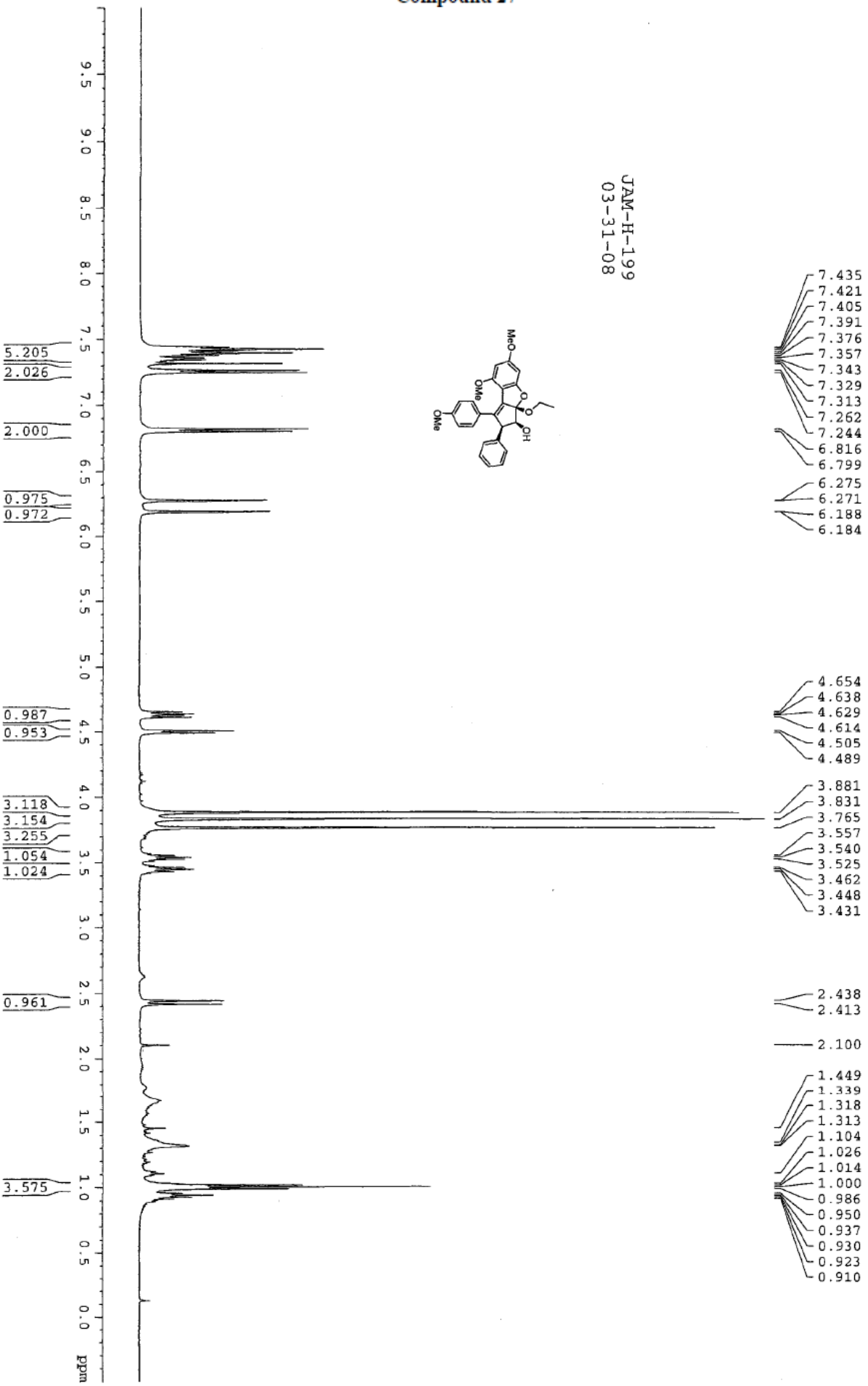
Compound 22


wts-III-112-2
MeO
PMBO
OMe
O
O
OMe
199.45
166.28
165.84
159.46
159.10
157.83
154.64
143.85
134.34
130.00
129.57
125.79
113.68
113.66
104.48
92.98
92.85
89.44
72.76
55.79
55.74
55.24
55.22
51.62
f1 (ppm)

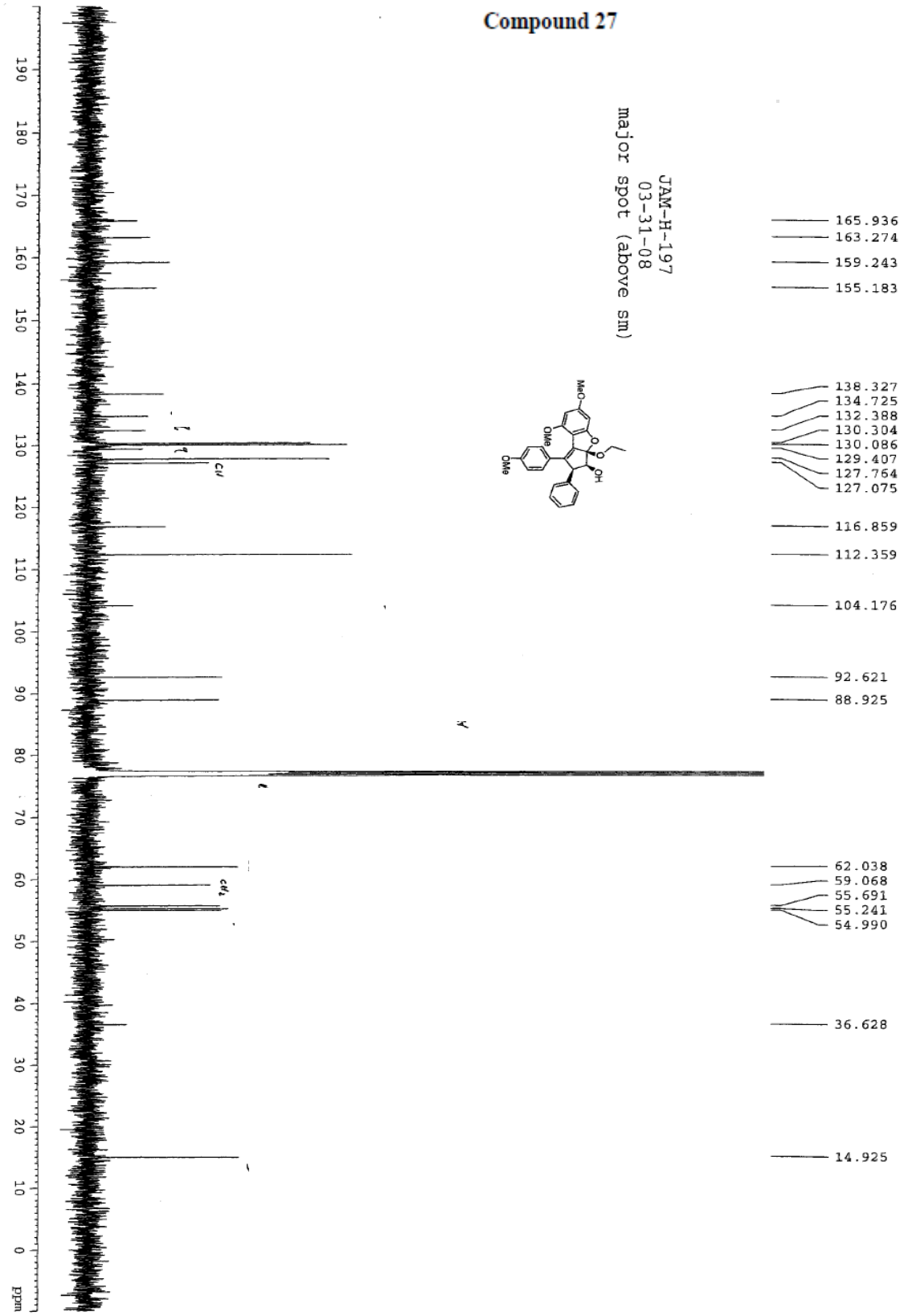

Compound 26
8-25-07
MeO
OH
OMe
O
MeO
5.18
1.91
1.97
1.06
1.04
2.02
0.48
3.15
3.41
3.00
5.31
f1 (ppm)


Compound 26
JAM-G-205
JAM-G-205
8-25-07
MeO
MeO
OH
OMe
O
O
195.04
162.62
159.76
158.47
155.72
155.09
142.94
131.21
130.09
129.48
128.11
127.02
126.68
125.41
118.76
113.09
101.47
94.18
92.14
77.41
77.16
76.91
67.91
55.50
55.28
55.18
15.59
f1 (ppm)

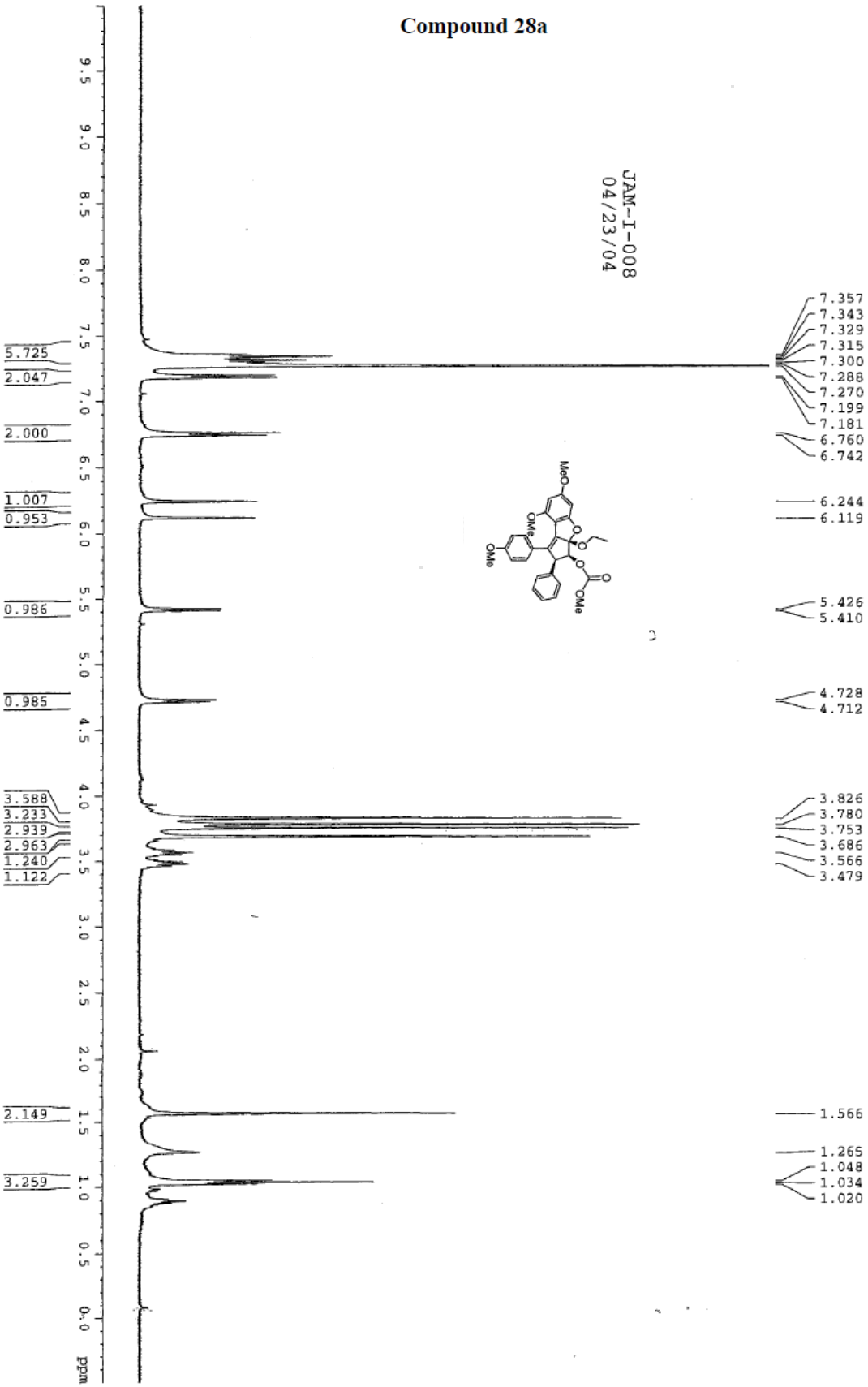
Compound 27


JAM-H-199
03-31-08
MeO
OMe
OMe
OH
7.435
7.421
7.405
7.391
7.376
7.357
7.343
7.329
7.313
7.262
7.244
6.816
6.799
6.275
6.271
6.188
6.184
4.654
4.638
4.629
4.614
4.505
4.489
3.881
3.831
3.765
3.557
3.540
3.525
3.462
3.448
3.431
2.438
2.413
2.100
1.449
1.339
1.318
1.313
1.104
1.026
1.014
1.000
0.986
0.950
0.937
0.930
0.923
0.910
5.205
2.026
2.000
0.975
0.972
0.987
0.953
3.118
3.154
3.255
1.054
1.024
0.961
3.575
ppm

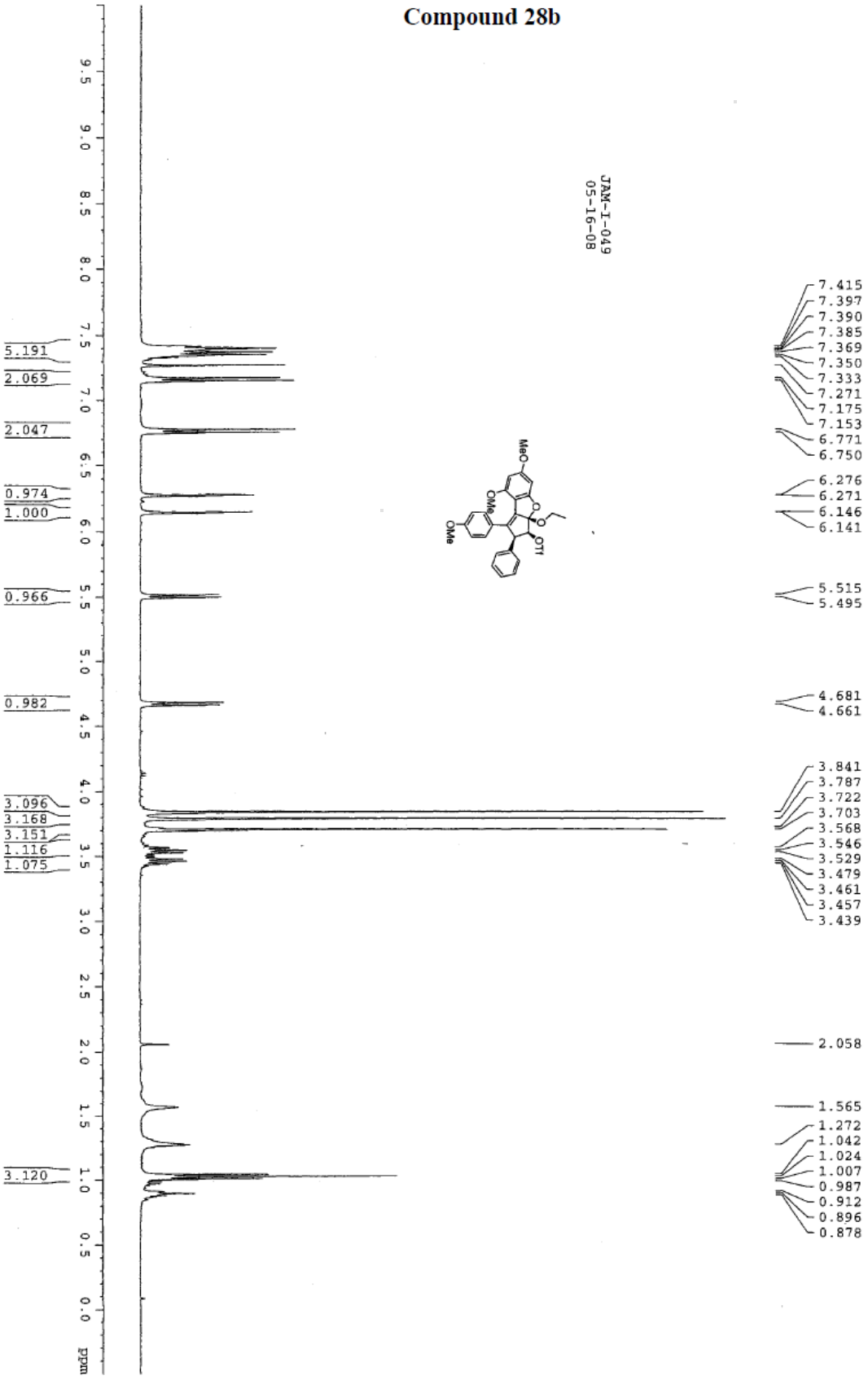
Compound 27


JAM-H-197
03-31-08
major spot (above sm)
165.936
163.274
159.243
155.183
138.327
134.725
132.388
130.304
130.086
129.407
127.764
127.075
116.859
112.359
104.176
92.621
88.925
62.038
59.068
55.691
55.241
54.990
36.628
14.925
ppm

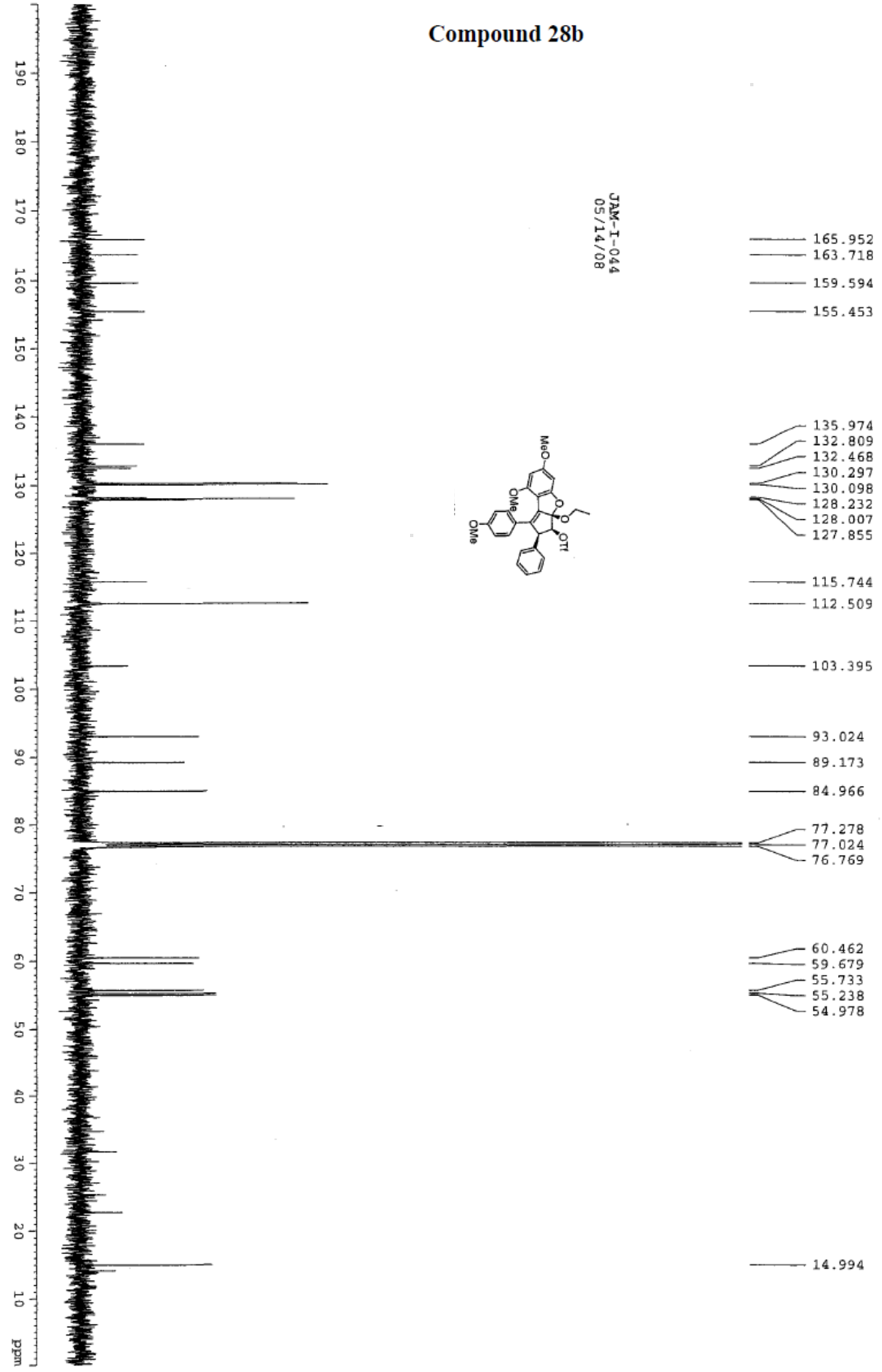
Compound 28a



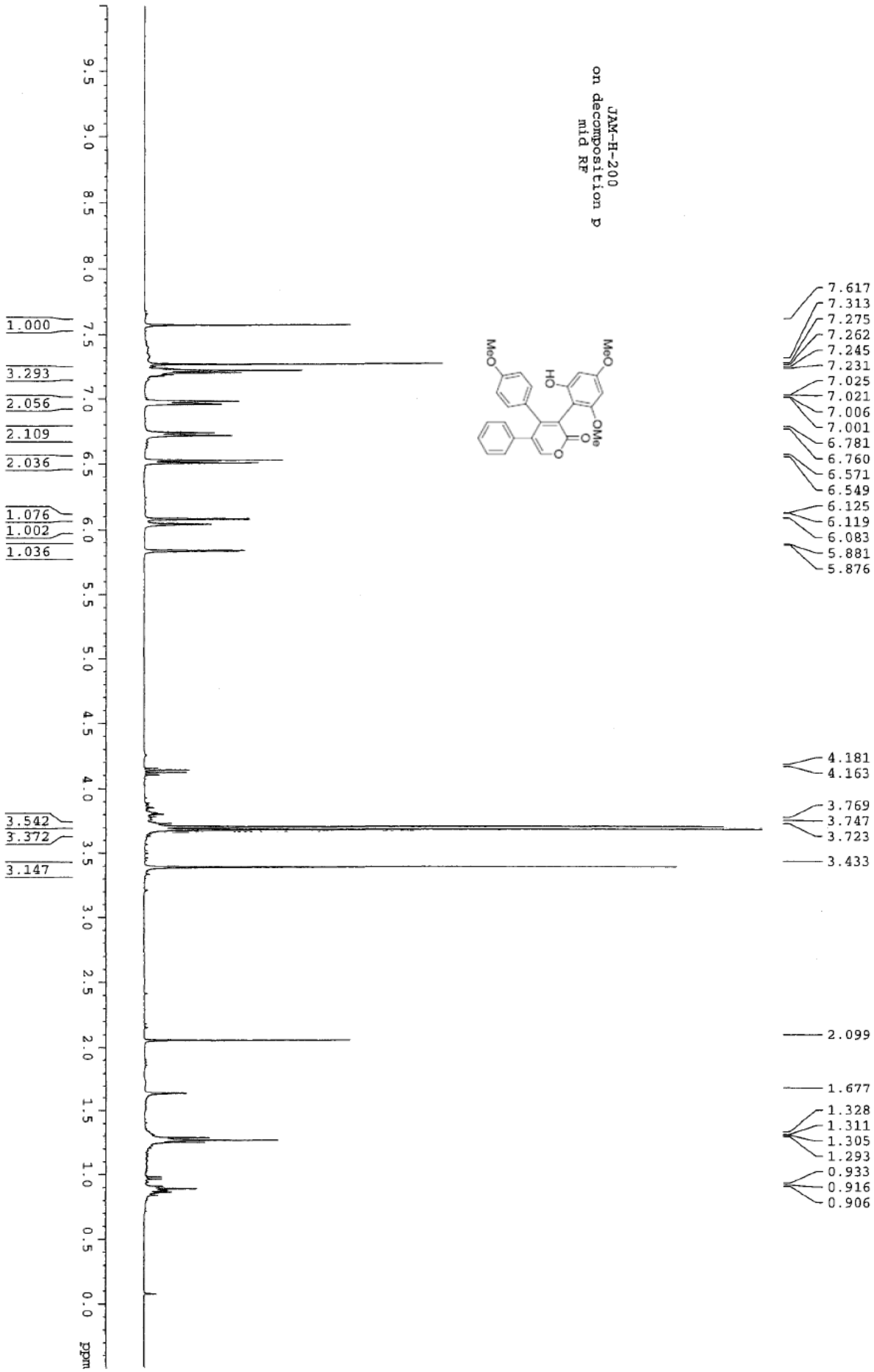
Compound 28b



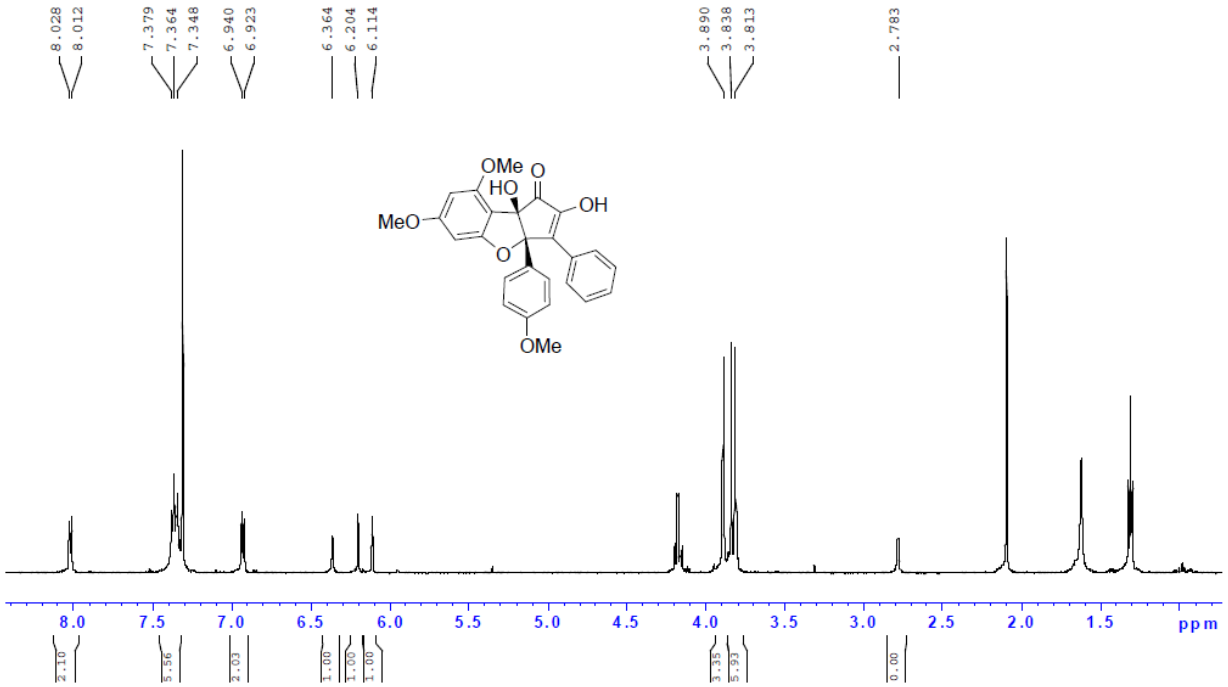
Compound 28b

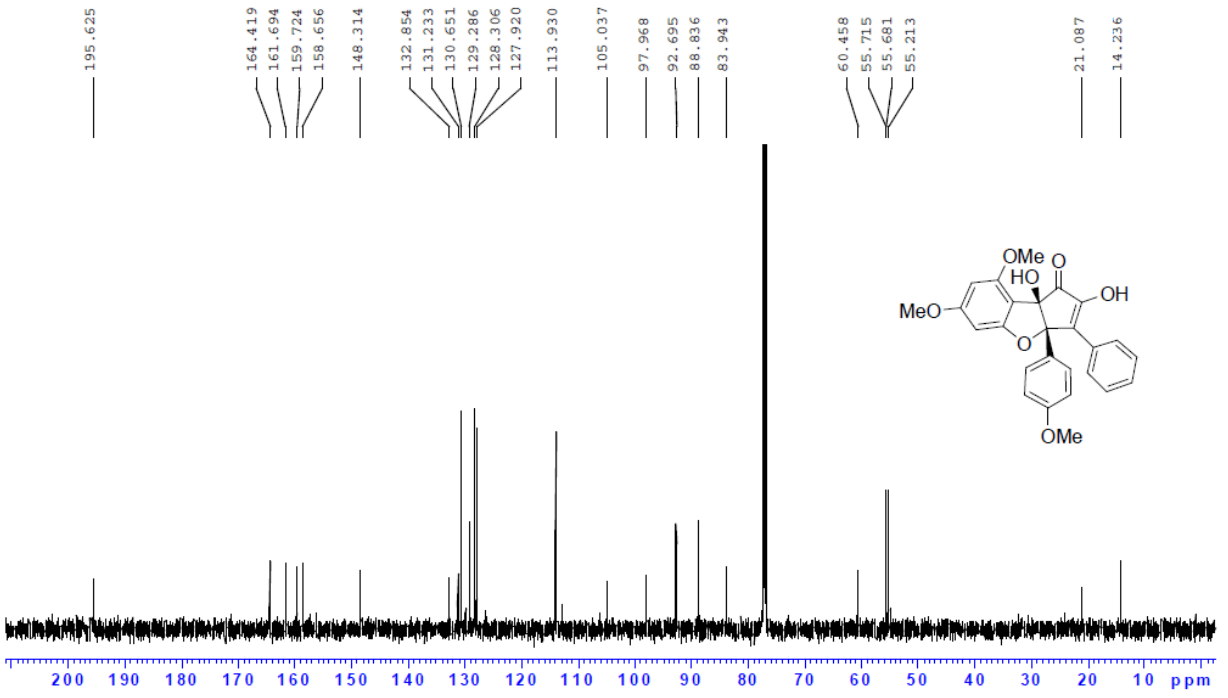


Compound 29

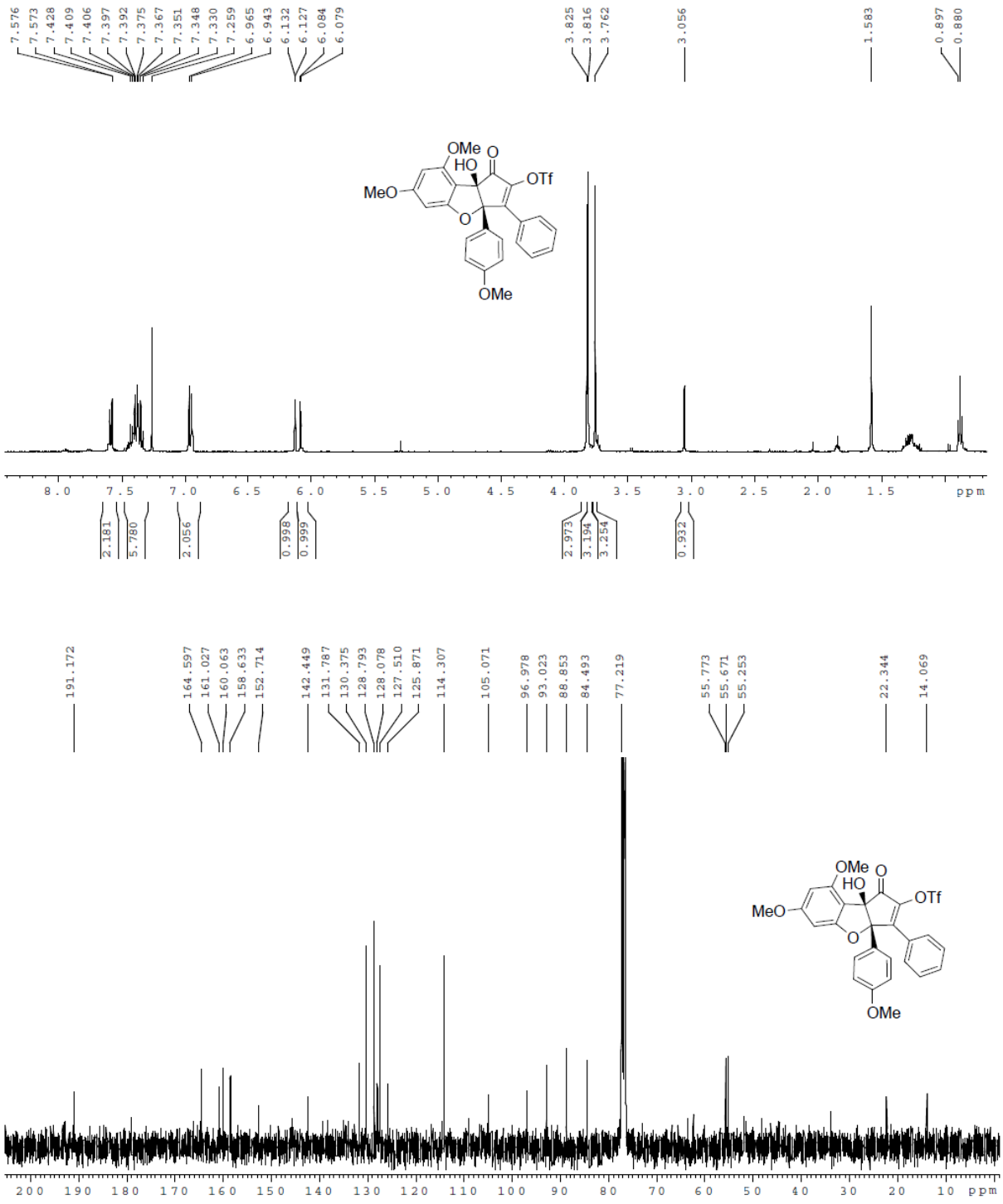

JAM-H-200
on decomposition p
mid RF
MeO
HO
MeO
OMe
O
O
1.000
3.293
2.056
2.109
2.036
1.076
1.002
1.036
3.542
3.372
3.147
7.617
7.313
7.275
7.262
7.245
7.231
7.025
7.021
7.006
7.001
6.781
6.760
6.571
6.549
6.125
6.119
6.083
5.881
5.876
4.181
4.163
3.769
3.747
3.723
3.433
2.099
1.677
1.328
1.311
1.305
1.293
0.933
0.916
0.906
ppm

Compound 37

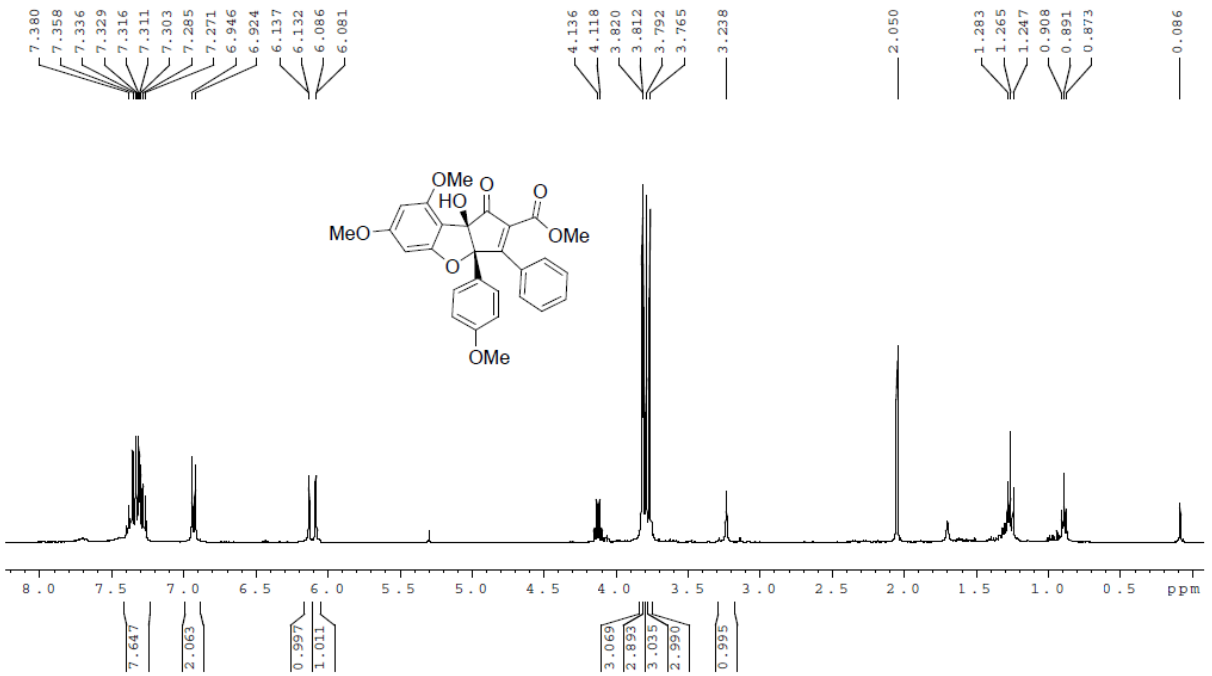

8.028
8.012
7.379
7.364
7.348
6.940
6.923
6.364
6.204
6.114
3.890
3.838
3.813
2.783
OMe
HO
O
OH
MeO
O
OMe
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
2.10
5.56
2.03
1.00
1.00
1.00
3.35
5.93
0.00

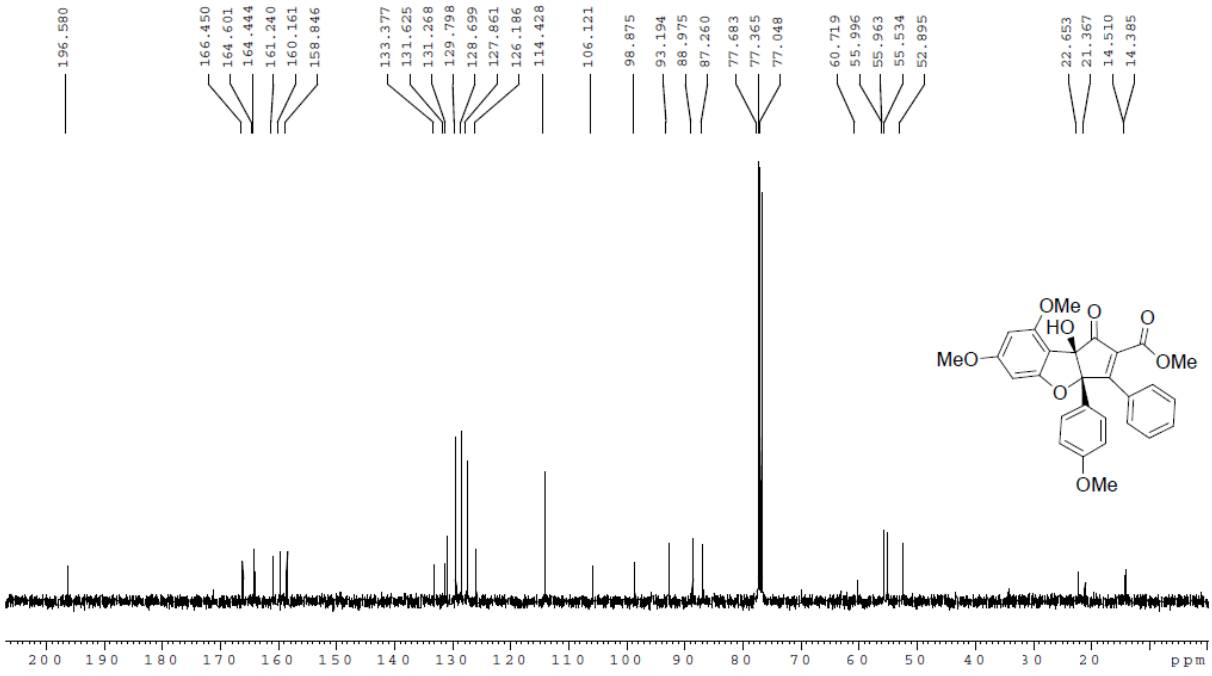

195.625
164.419
161.694
159.724
158.656
148.314
132.854
131.233
130.651
129.286
128.306
127.920
113.930
105.037
97.968
92.695
88.836
83.943
60.458
55.715
55.681
55.213
21.087
14.236
OMe
HO
O
OH
MeO
O
OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Compound 38

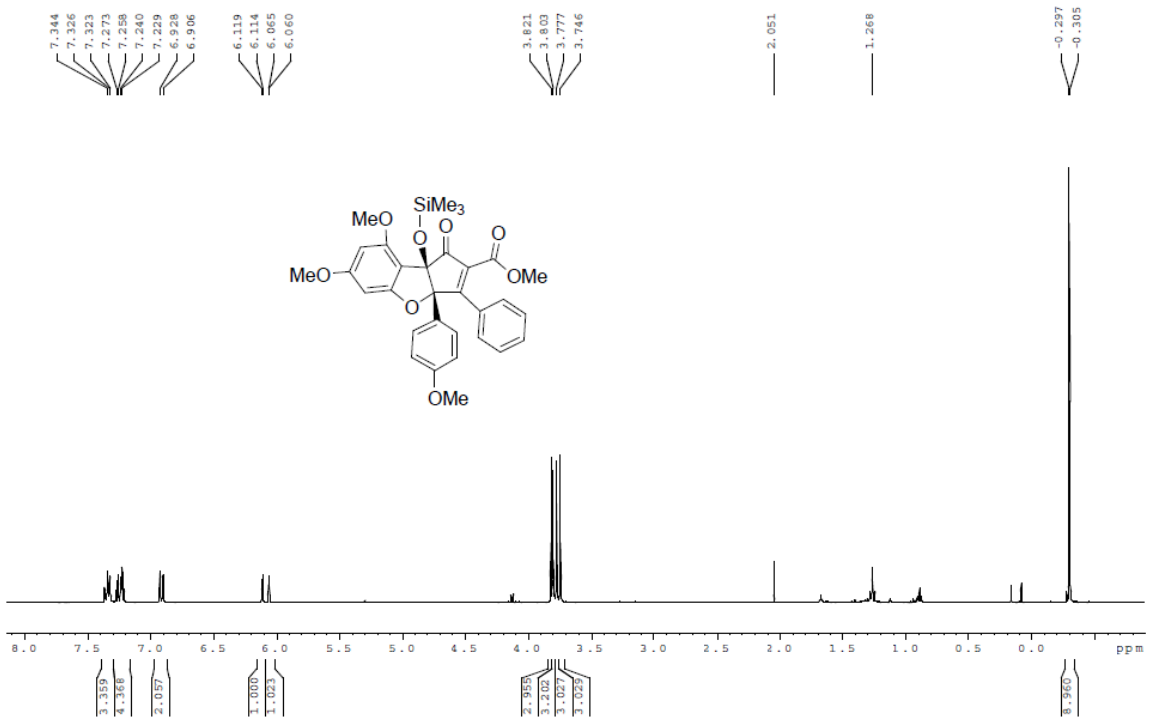

7.576
7.573
7.428
7.409
7.406
7.397
7.392
7.375
7.367
7.351
7.348
7.330
7.259
6.965
6.943
6.132
6.127
6.084
6.079
3.825
3.816
3.762
3.056
1.583
0.897
0.880
OMe
HO
O
OTf
MeO
O
OMe
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
2.181
5.780
2.056
0.998
0.999
2.973
3.194
3.254
0.932
191.172
164.597
161.027
160.063
158.633
152.714
142.449
131.787
130.375
128.793
128.078
127.510
125.871
114.307
105.071
96.978
93.023
88.853
84.493
77.219
55.773
55.671
55.253
22.344
14.069
OMe
HO
O
OTf
MeO
O
OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

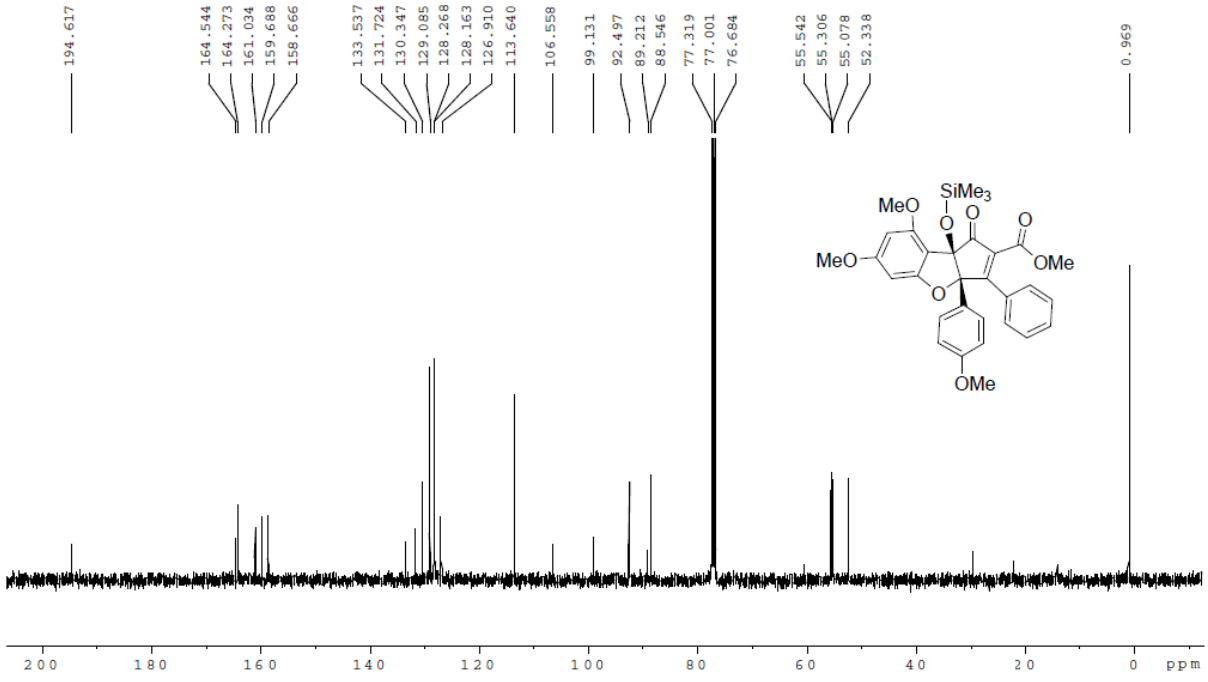
Compound 39


7.380
7.358
7.336
7.329
7.316
7.311
7.303
7.285
7.271
6.946
6.924
6.137
6.132
6.086
6.081
4.136
4.118
3.820
3.812
3.792
3.765
3.238
2.050
1.283
1.265
1.247
0.908
0.891
0.873
0.086
OMe
HO
O
O
MeO
OMe
O
OMe
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
7.647
2.063
0.997
1.011
3.069
2.893
3.035
2.990
0.995

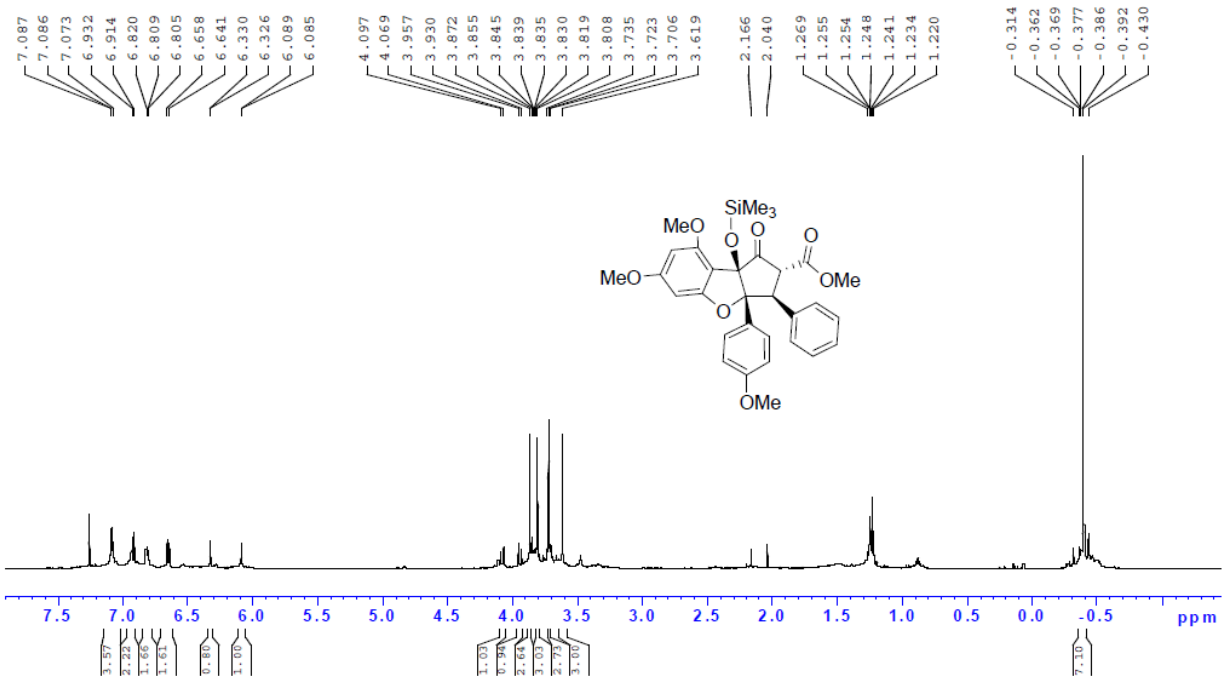

196.580
166.450
164.601
164.444
161.240
160.161
158.846
133.377
131.625
131.268
129.798
128.699
127.861
126.186
114.428
106.121
98.875
93.194
88.975
87.260
77.683
77.365
77.048
60.719
55.996
55.963
55.534
52.895
22.653
21.367
14.510
14.385
OMe
HO
O
O
MeO
OMe
O
OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

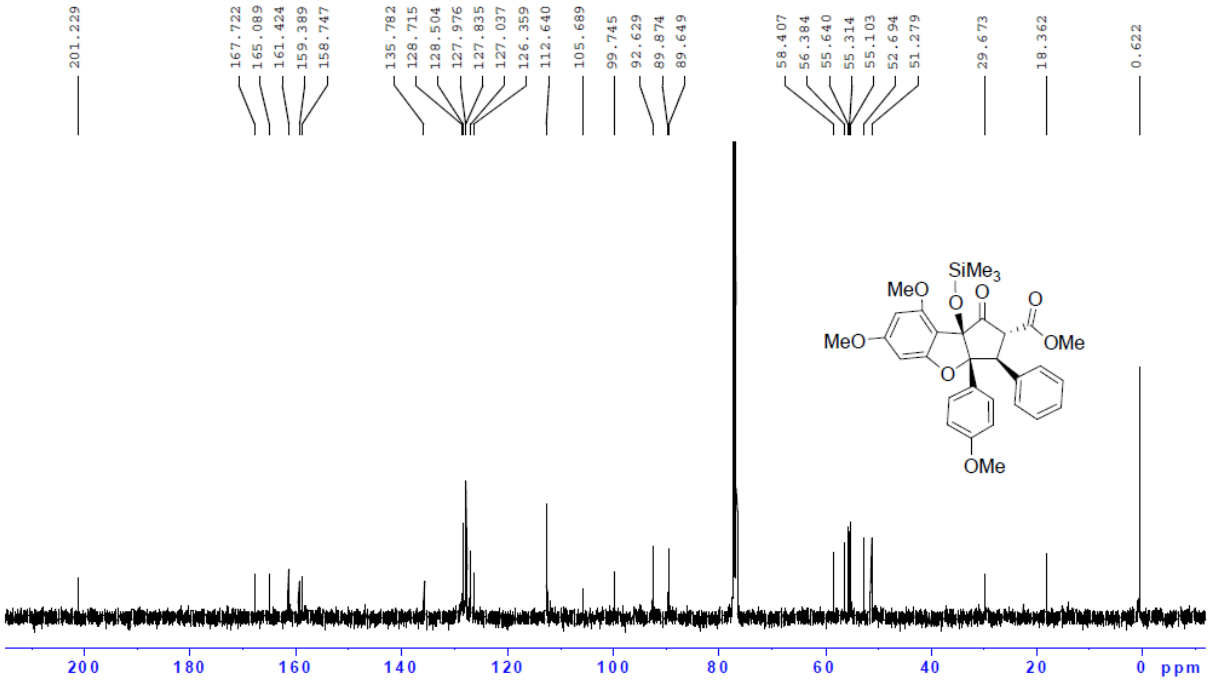
Compound 41


7.344
7.326
7.323
7.273
7.258
7.240
7.229
6.928
6.906
6.119
6.114
6.065
6.060
3.821
3.803
3.777
3.746
2.051
1.268
-0.297
-0.305
MeO
SiMe3
O
O
O
MeO
OMe
O
OMe
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
ppm
3.359
4.368
2.057
1.000
1.023
2.959
3.202
3.027
3.029
8.960

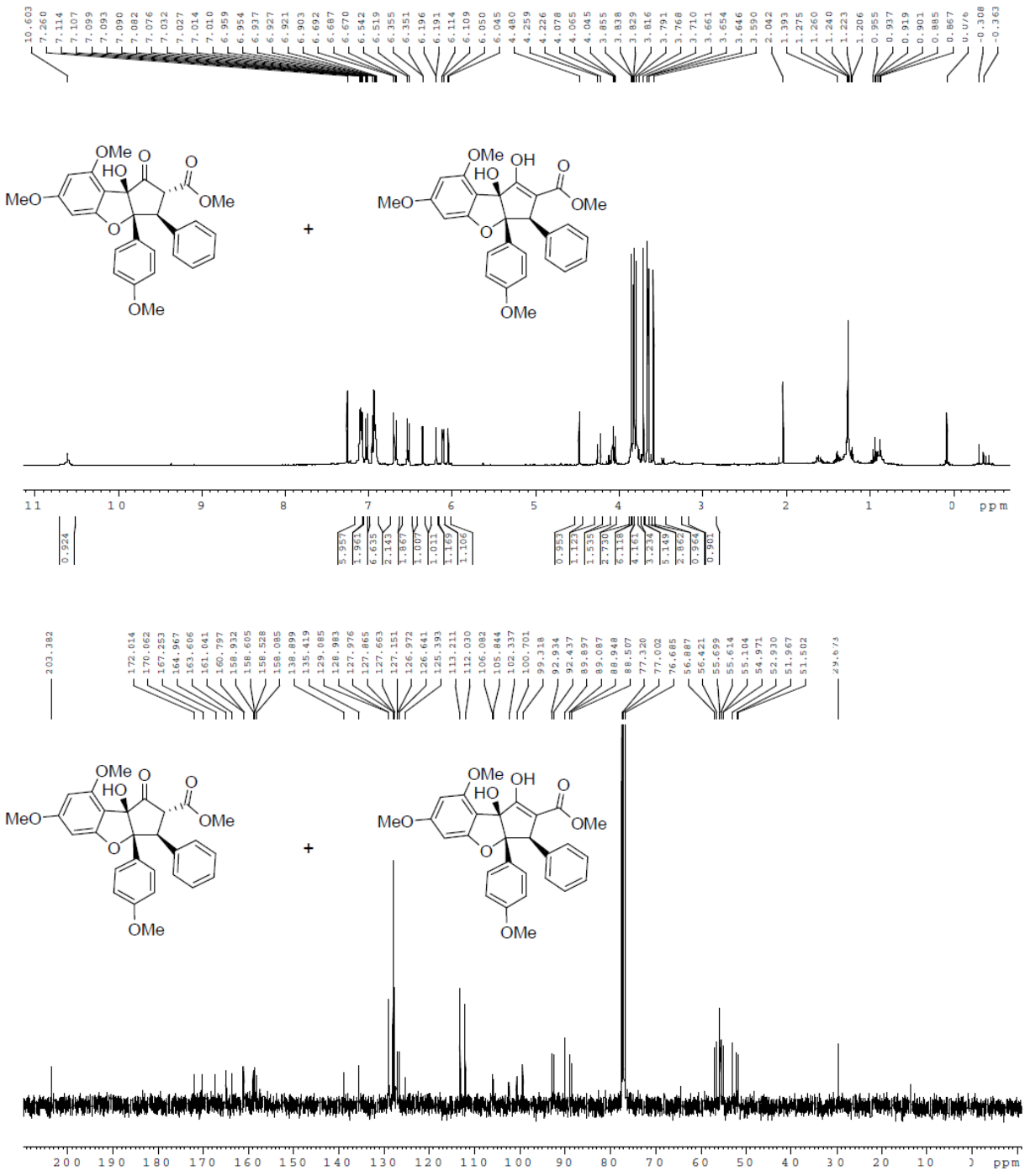

194.617
164.544
164.273
161.034
159.688
158.666
133.537
131.724
130.347
129.085
128.268
128.163
126.910
113.640
106.558
99.131
92.497
89.212
88.546
77.319
77.001
76.684
55.542
55.306
55.078
52.338
0.969
MeO
SiMe3
O
O
O
MeO
OMe
O
OMe
200
180
160
140
120
100
80
60
40
20
0
ppm

Compound 42

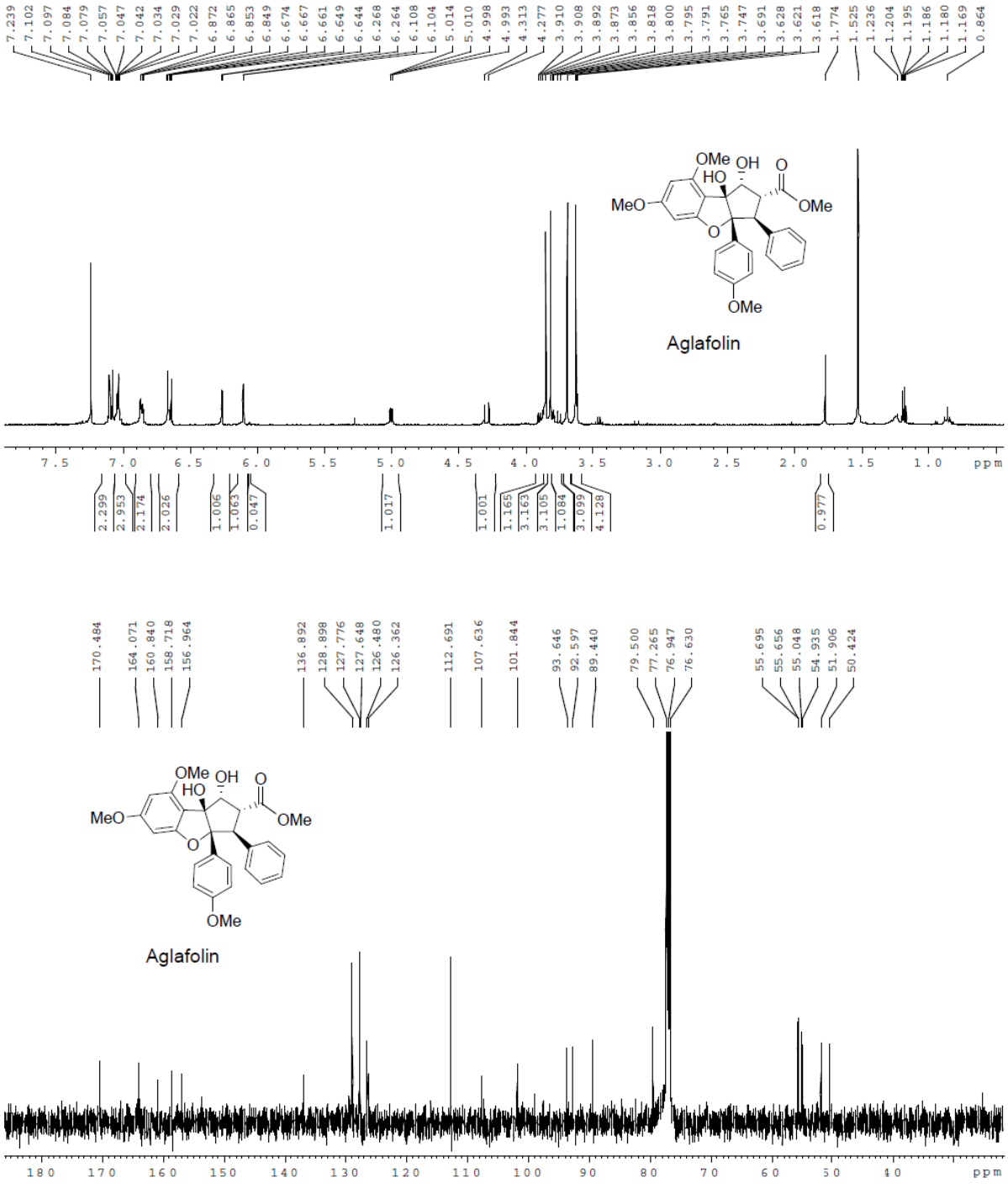

7.087
7.086
7.073
6.932
6.914
6.820
6.809
6.805
6.658
6.641
6.330
6.326
6.089
6.085
4.097
4.069
3.957
3.930
3.872
3.855
3.845
3.839
3.835
3.830
3.819
3.808
3.735
3.723
3.706
3.619
2.166
2.040
1.269
1.255
1.254
1.248
1.241
1.234
1.220
-0.314
-0.362
-0.369
-0.377
-0.386
-0.392
-0.430
SiMe3
MeO
MeO
OMe
OMe
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
-0.5
ppm


201.229
167.722
165.089
161.424
159.389
158.747
135.782
128.715
128.504
127.976
127.835
127.037
126.359
112.640
105.689
99.745
92.629
89.874
89.649
58.407
56.384
55.640
55.314
55.103
52.694
51.279
29.673
18.362
0.622
SiMe3
MeO
MeO
OMe
OMe
200
180
160
140
120
100
80
60
40
20
0
ppm

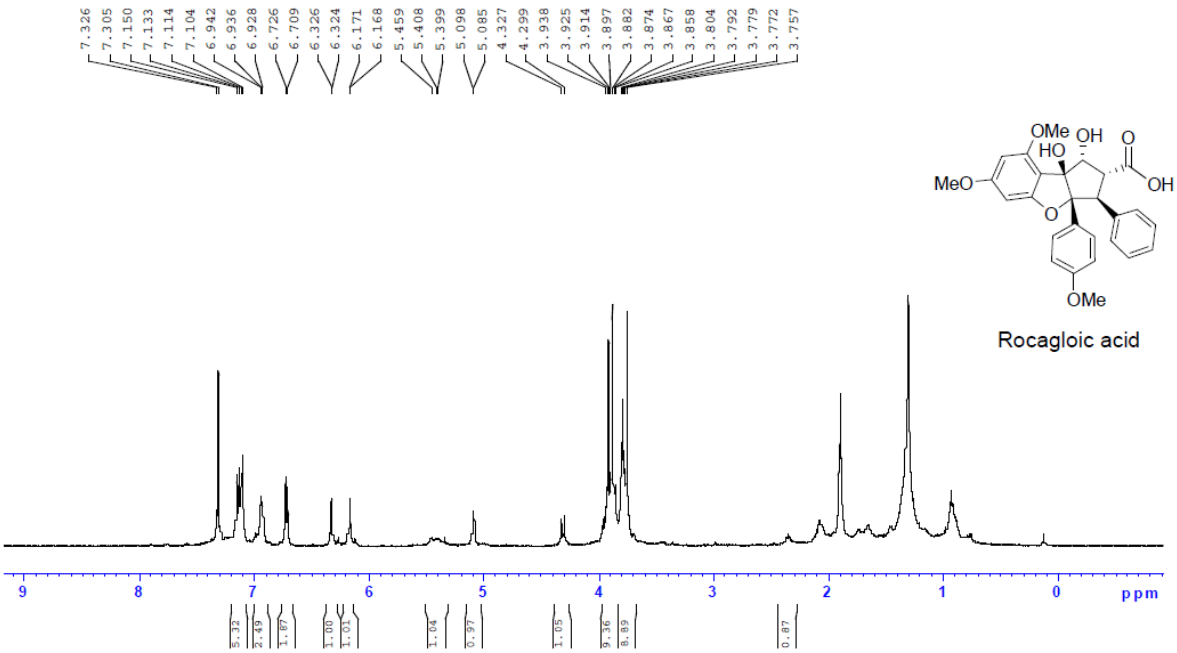
Compound 40

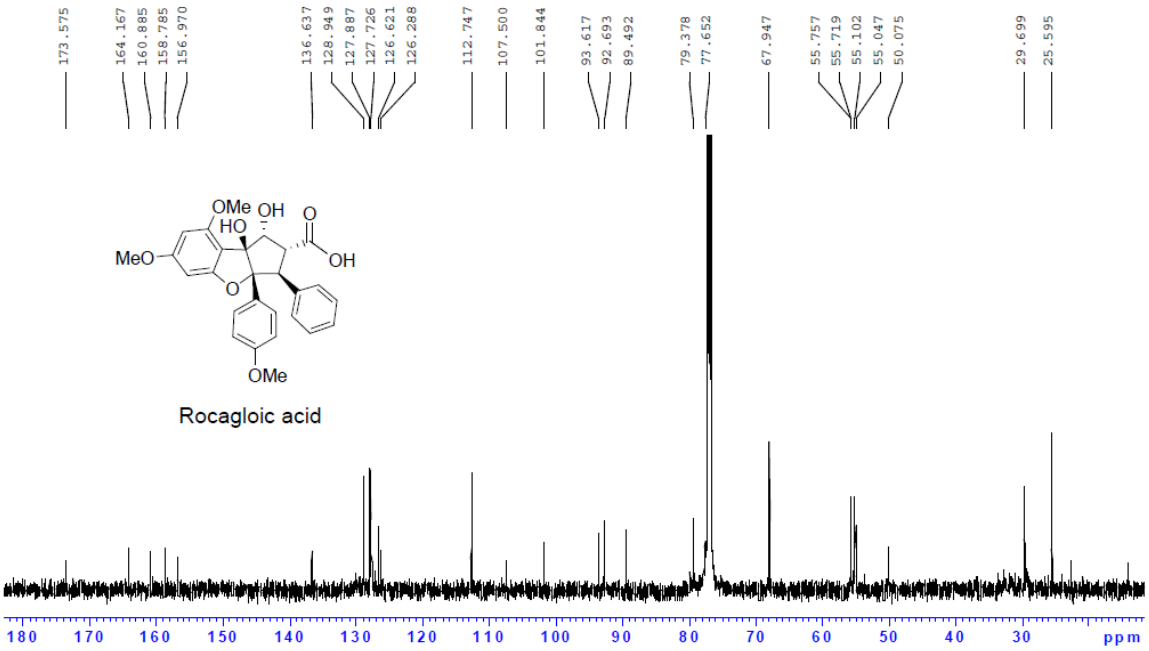

10.603
7.260
7.114
7.107
7.099
7.093
7.090
7.082
7.076
7.032
7.027
7.014
7.010
6.959
6.954
6.937
6.927
6.921
6.903
6.692
6.687
6.670
6.542
6.519
6.355
6.351
6.196
6.191
6.114
6.109
6.050
6.045
4.480
4.259
4.226
4.078
4.065
4.045
3.855
3.838
3.829
3.816
3.791
3.768
3.710
3.661
3.654
3.646
3.590
2.042
1.393
1.275
1.260
1.240
1.223
1.206
0.955
0.937
0.919
0.901
0.885
0.867
0.076
-0.308
-0.363
OMe
HO
O
O
MeO
OMe
OMe
+
OMe
OH
HO
O
MeO
OMe
OMe
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.924
5.957
1.961
6.635
2.143
1.867
1.007
1.011
1.169
1.106
0.955
1.122
1.535
2.730
6.118
4.161
3.234
5.149
2.862
0.964
0.901
203.382
172.014
170.062
167.253
164.967
163.606
161.041
160.797
158.932
158.605
158.528
158.085
138.899
135.419
129.085
128.983
127.976
127.865
127.663
127.151
126.972
126.641
125.393
113.211
112.030
106.082
105.844
102.337
100.701
99.318
92.934
92.437
89.897
89.087
88.948
88.507
77.320
77.002
76.685
56.887
56.421
55.699
55.614
55.104
54.971
52.930
51.967
51.502
29.673
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Compound 1e

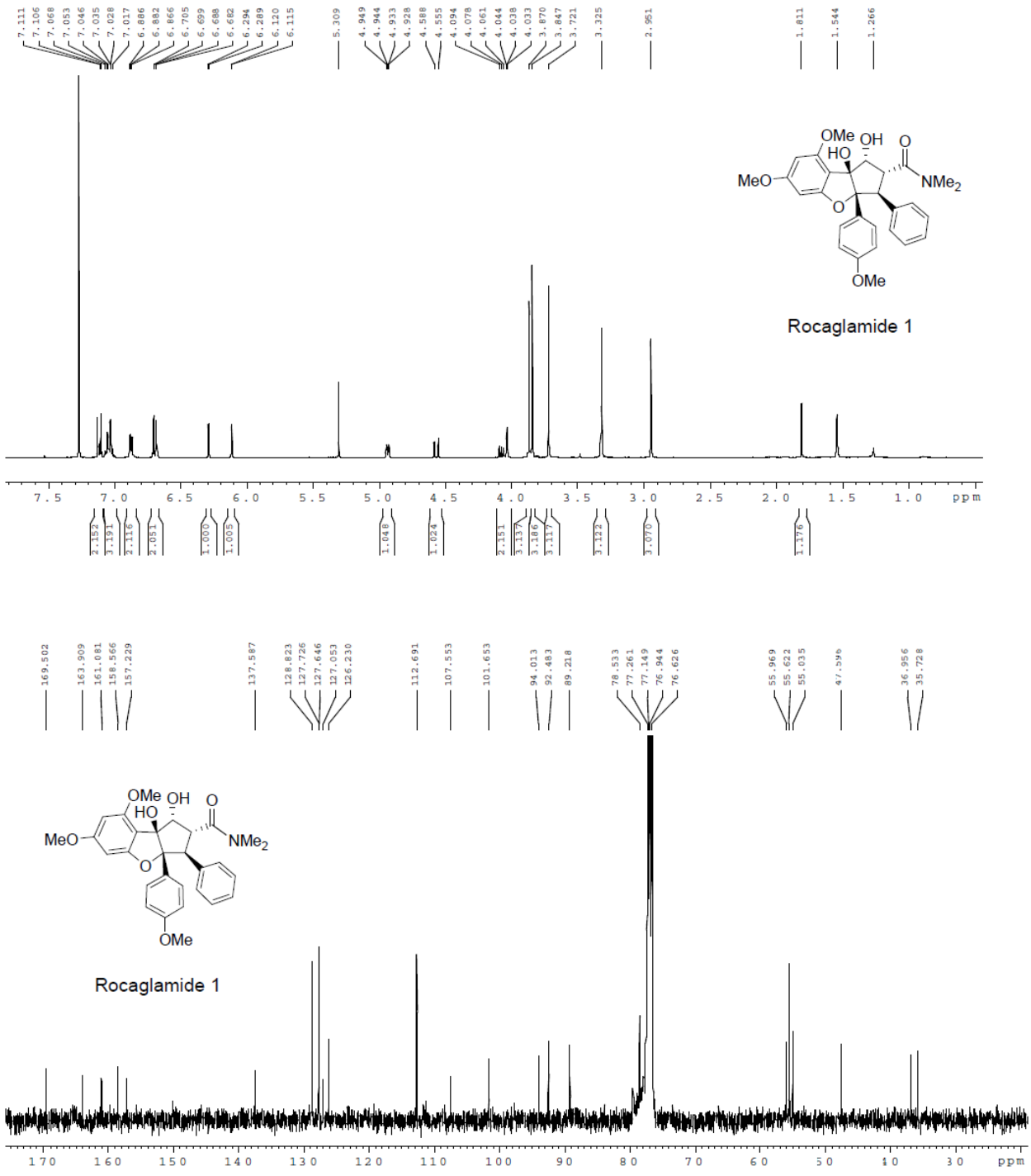

7.239 7.102 7.097 7.084 7.079 7.057 7.047 7.042 7.034 7.029 7.022 6.872 6.865 6.853 6.849 6.674 6.667 6.661 6.649 6.644 6.268 6.264 6.108 6.104 5.014 5.010 4.998 4.993 4.313 4.277 3.910 3.908 3.892 3.873 3.856 3.818 3.800 3.795 3.791 3.765 3.747 3.691 3.628 3.621 3.618 1.774 1.525 1.236 1.204 1.195 1.186 1.180 1.169 0.864
OMe OH O
HO
MeO
OMe
O
OMe
Aglafolin
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 ppm
2.299 2.953 2.174 2.026 1.006 1.063 0.047 1.017 1.001 1.165 3.163 3.105 1.084 3.099 4.128 0.977
170.484 164.071 160.840 158.718 156.964 136.892 128.898 127.776 127.648 126.480 126.362 112.691 107.636 101.844 93.646 92.597 89.440 79.500 77.265 76.947 76.630 55.695 55.656 55.048 54.935 51.906 50.424
OMe OH O
HO
MeO
OMe
O
OMe
Aglafolin
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 ppm

Compound 1d


7.326
7.305
7.150
7.133
7.114
7.104
6.942
6.936
6.928
6.726
6.709
6.326
6.324
6.171
6.168
5.459
5.408
5.399
5.098
5.085
4.327
4.299
3.938
3.925
3.914
3.897
3.882
3.874
3.867
3.858
3.804
3.792
3.779
3.772
3.757
OMe
OH
HO
O
MeO
OH
O
OMe
Rocagloic acid
9
8
7
6
5
4
3
2
1
0
ppm
5.32
2.49
1.87
1.00
1.01
1.04
0.97
1.05
9.36
8.89
0.87


173.575
164.167
160.885
158.785
156.970
136.637
128.949
127.887
127.726
126.621
126.288
112.747
107.500
101.844
93.617
92.693
89.492
79.378
77.652
67.947
55.757
55.719
55.102
55.047
50.075
29.699
25.595
OMe
OH
HO
O
MeO
OH
O
OMe
Rocagloic acid
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

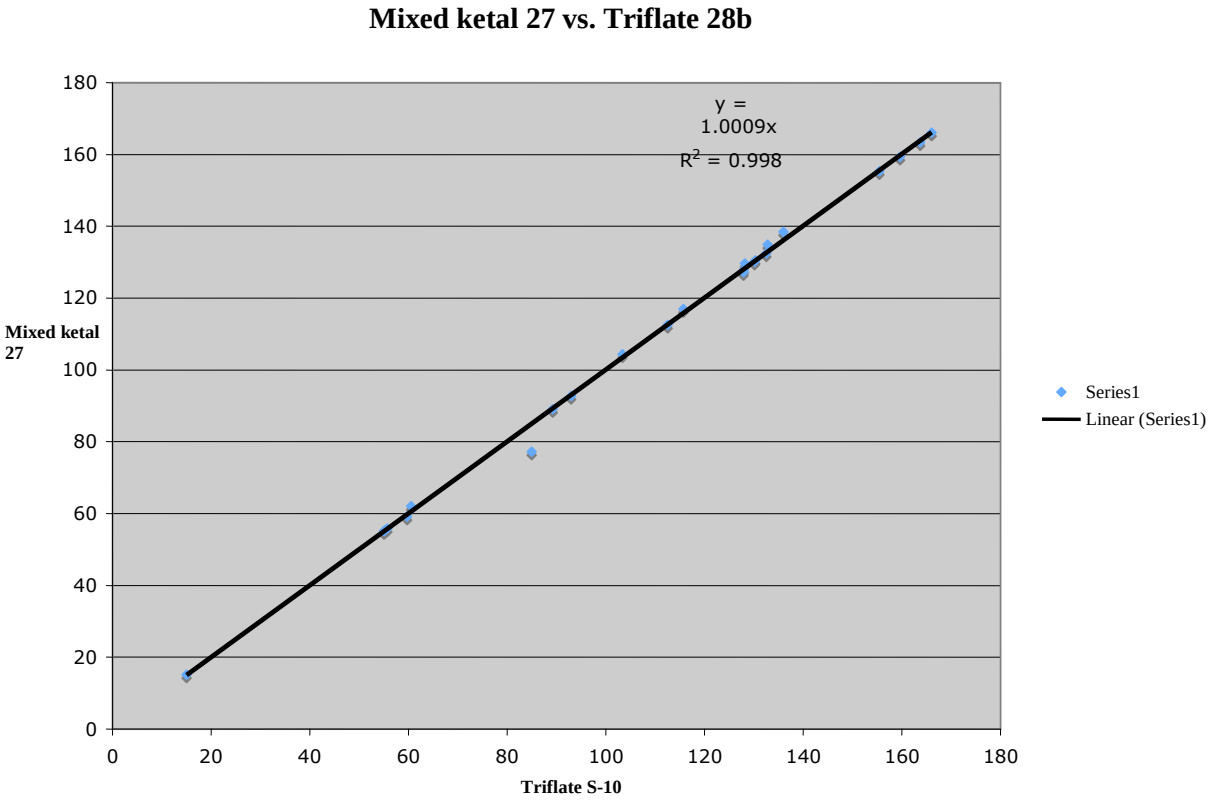
Compound 1a



2.0. Justification for Structure Assignment of Mixed Ketal 27.

The proposed structure of **27** is supported by characterization of two derivatives: carbonate **28a** (X-Ray crystal structure) and triflate **28b** (^{1}H and ^{13}C NMR data). Comparisons of ^{1}H and ^{13}C data for the mixed ketal and these derivatives reveal that the proton spectra for these compounds vary only in the loss of the doublet at 2.42 ppm (O<u>H</u>), a slight downfield shift of the benzylic proton (4.49 ppm in the free alcohol compared to 4.72 and 4.67 in the carbonate and triflate derivatives respectively) and a dramatic downfield shift of the proton *ipso* to the alcohol (4.63 ppm compared to 5.42 and 5.50 for the carbonate and triflate respectively) with concominant deconvolution of its signal from a doublet of doublets to a simple doublet in both derivatives. All other signals remain largely unperturbed among all three compounds. The ^{13}C spectra also show excellent agreement between the three structures. When directly comparing the chemical shifts of the mixed ketal to those of the triflate (Graph 1, Table 1), the average difference in peak shift was 0.03 ppm with the single largest shift being at the alcohol bearing carbon moving downfield from 77.2 ppm in the mixed ketal to 85.0 ppm in the triflate; all other shift differences all being 2.5 ppm or less. Comparison of ketone **15a** to mixed ketal **27** shows a much weaker correlation (Graph 2, Table 1). We take this as indirect evidence that the reactant in these two reactions is the mixed ketal, which has been functionalized exclusively at the secondary alcohol.

Graph 1: Comparison of ^{13}C Chemical Shifts of Mixed Ketal **27** with Triflate **28b**.



Graph 2: Comparison of ^{13}C Chemical Shifts of Ketone **15a** with Mixed Ketal **27**.

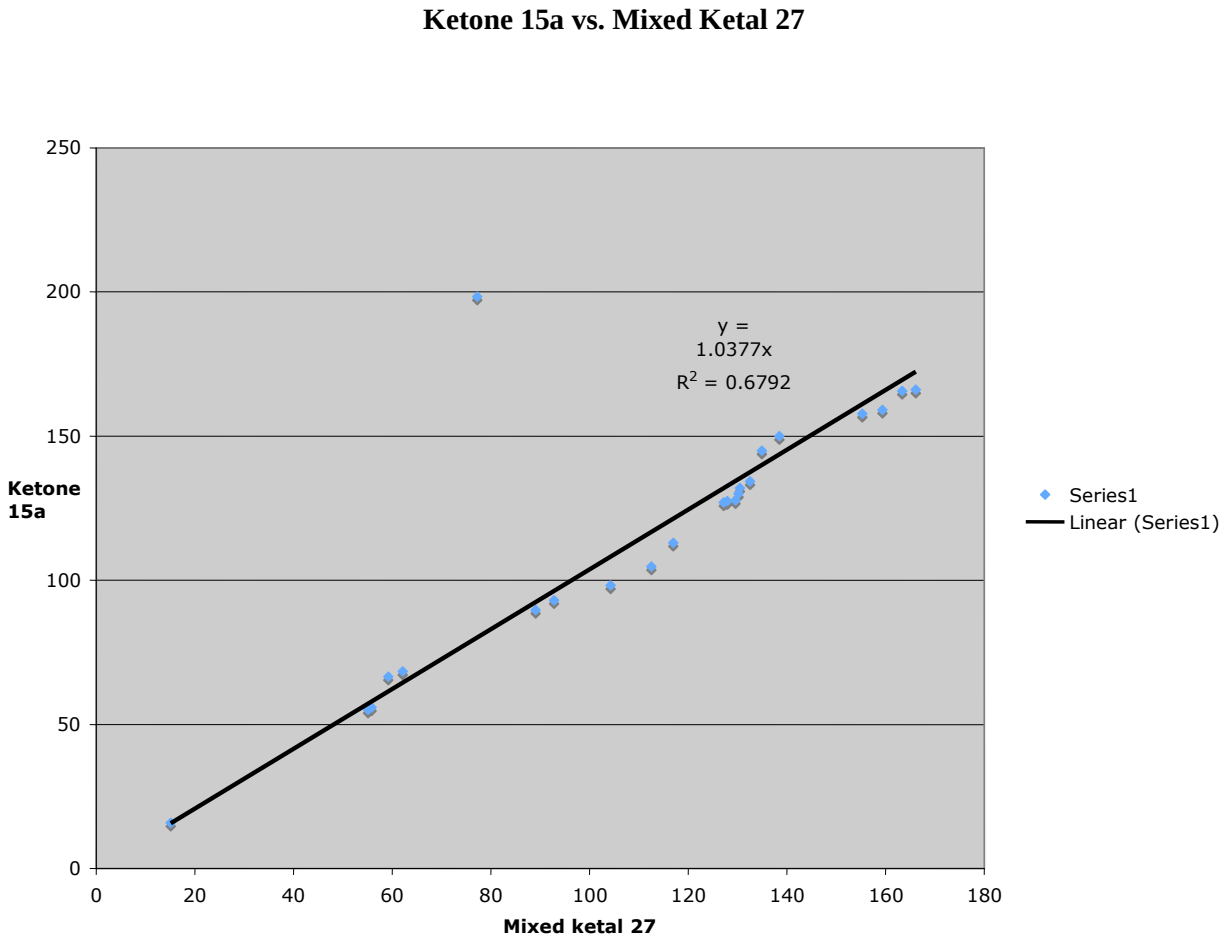


Table 1. Comparison of ^{13}C Chemical Shift Values of Triflate **S-10**, Mixed Ketal **27**, and Ketone **15a**.

Triflate **S-10**	Mixed Ketal **27**	Ketone **15a**
15	15.1	15.8
55	55.1	55.1
55.2	55.4	55.8
55.7	55.8	55.9
59.7	59.2	66.5
60.5	62.1	68.4
85	77.2	198.4
89.2	89.1	89.7
93	92.8	93
103.4	104.3	98.2
112.5	112.5	104.7
115.7	117	113
127.9	127.2	127
128	127.9	127.4
128.2	129.6	127.8
130.1	130.2	130
130.3	130.5	132
132.5	132.5	134.3
132.8	134.9	144.9
136	138.5	149.9
155.5	155.33	157.8
159.6	159.4	159.1
163.7	163.4	165.6
166	166.1	166.1