Total Synthesis of (±)-Przewalskin B

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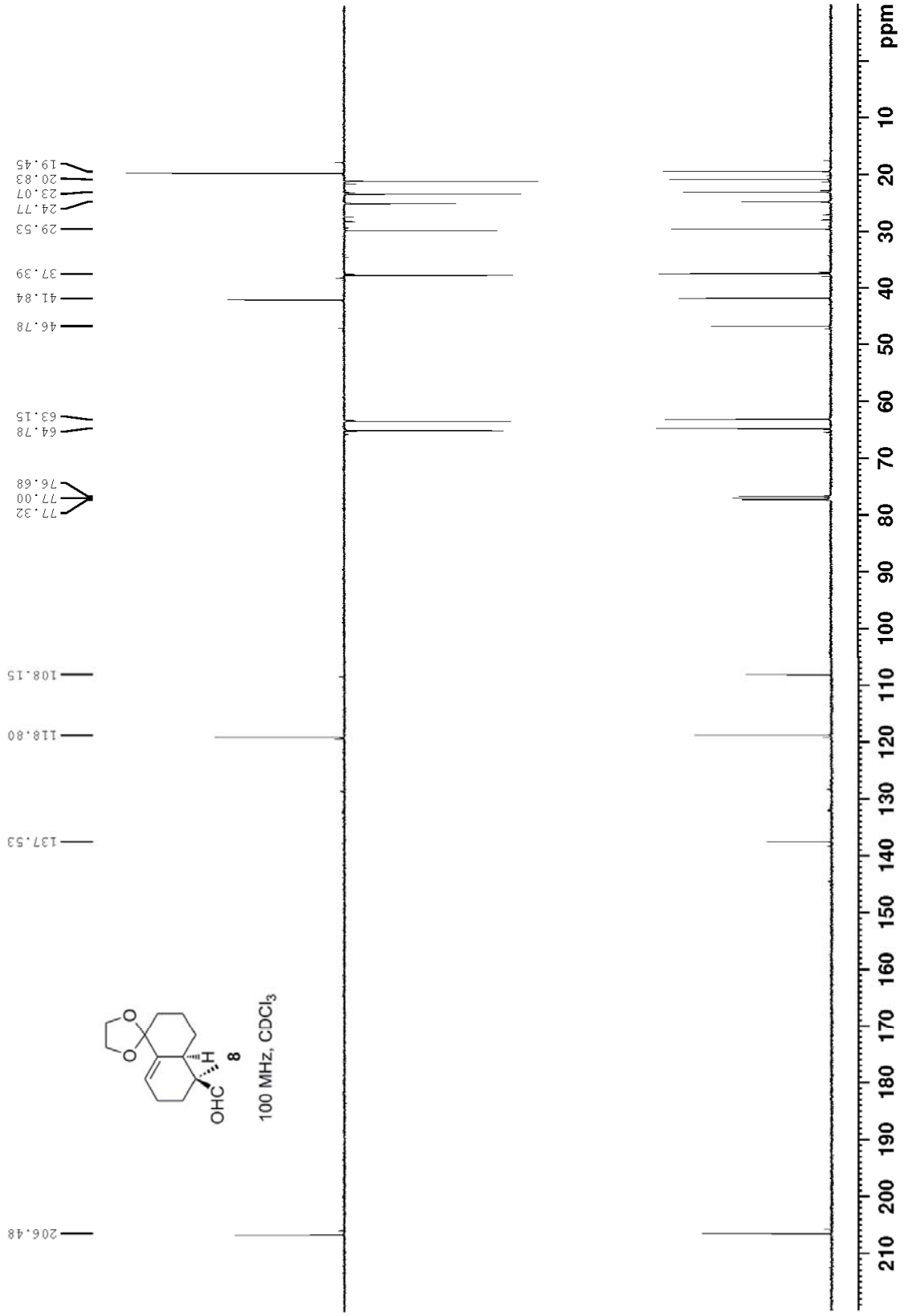
General information: Oxygen- and moisture-sensitive reactions were carried out under argon atmosphere. Solvents were purified and dried by standard methods prior to use. All commercially available reagents were used without further purification unless otherwise noted. Column chromatography was performed on silica gel (200-300 mesh). NMR spectra were recorded on a 400 MHz spectrometer (^{13}C NMR and DEPT 135 spectra of Przewalskin B were recorded on a 150 MHz spectrometer). Chemical shifts are reported as δ values relative to internal chloroform (δ 7.27 for 1H NMR and 77.0 for 13C NMR). High resolution mass spectra (HRMS) were obtained on a 4G mass spectrometer by using electrospray ionization (ESI) analyzed by quadrupole time-of-flight (QTof). NMR Spectra for all new compounds are described below.

ppm
0
1
2
3
4
5
6
7
8
9
1.00
0.06
1.00
0.08
3.48
1.09
1.06
1.14
1.30
1.20
5.95
1.17
1.21
3.13
OHC
H
8
400 MHz, CDCl3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29.53
24.77
23.07
20.83
19.45
ppm
10
20
30
40
50
60
70
80
90
100
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120
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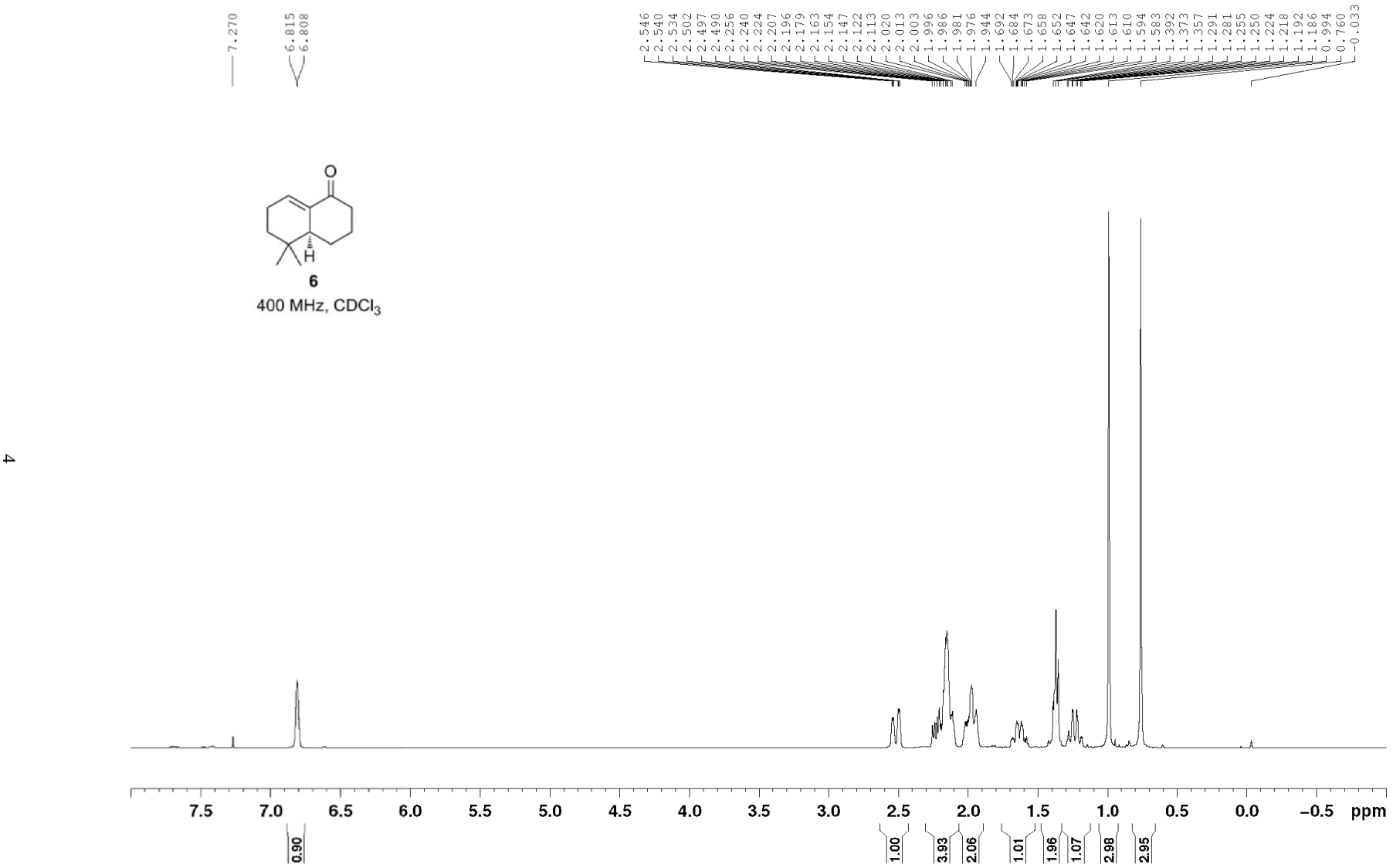
140
150
160
170
180
190
200
210
100 MHz, CDCl3
8
OHC
H
O
O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2.256
2.240
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2.207
2.196
2.179
2.163
2.154
2.147
2.122
2.113
2.020
2.013
2.003
1.996
1.986
1.981
1.976
1.944
1.692
1.684
1.673
1.658
1.652
1.647
1.642
1.620
1.613
1.610
1.594
1.583
1.392
1.373
1.357
1.291
1.281
1.255
1.250
1.224
1.218
1.192
1.186
0.994
0.760
-0.033
O
H
6
400 MHz, CDCl3
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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
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ppm
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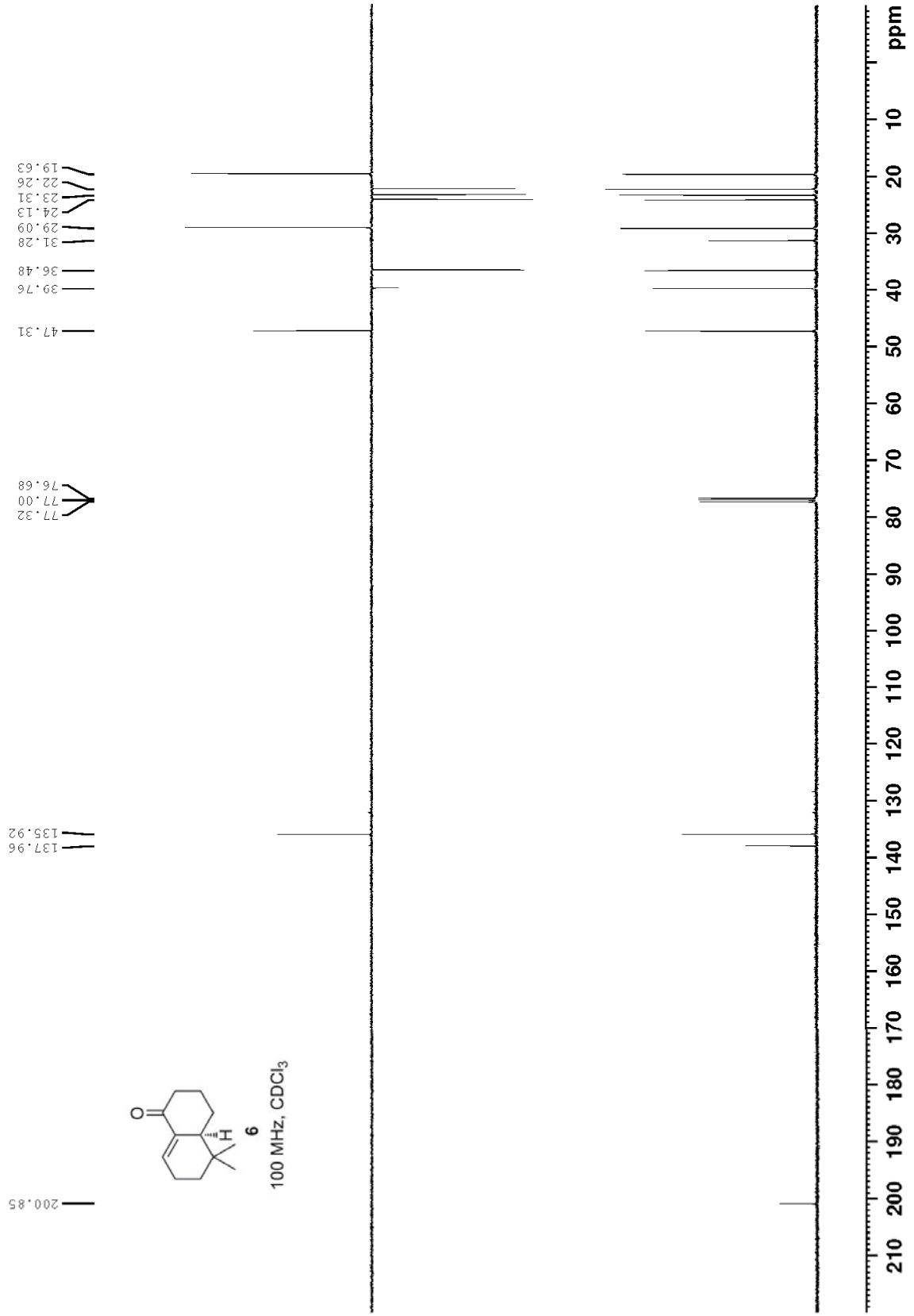
3.93
2.06
1.01
1.96
1.07
2.98
2.95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39.76
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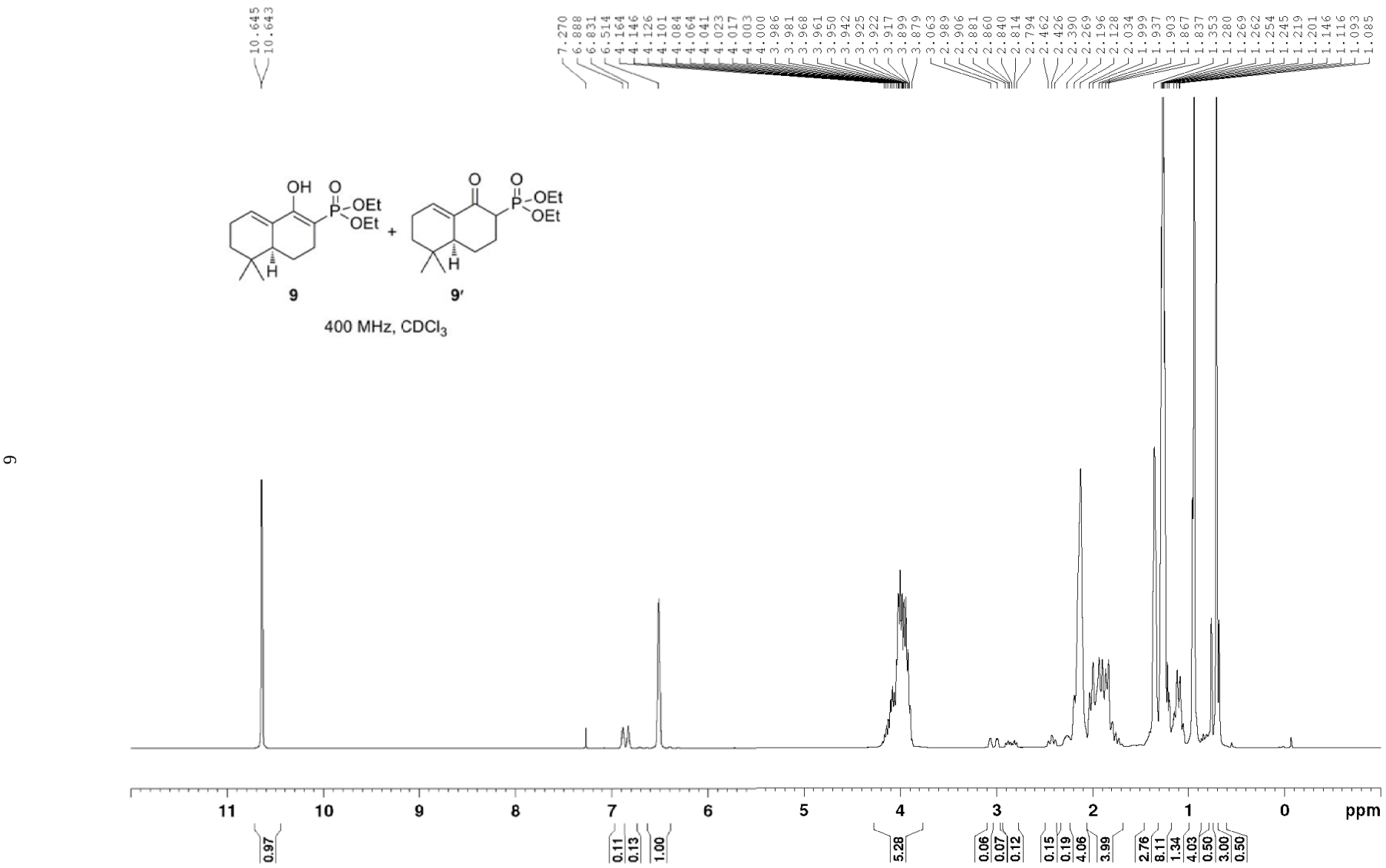
23.31
22.26
19.63
O
H
6
100 MHz, CDCl3
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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4.101
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4.064
4.041
4.023
4.017
4.003
4.000
3.986
3.981
3.968
3.961
3.950
3.942
3.925
3.922
3.917
3.899
3.879
3.063
2.989
2.906
2.881
2.860
2.840
2.814
2.794
2.462
2.426
2.390
2.269
2.196
2.128
2.034
1.999
1.937
1.903
1.867
1.837
1.353
1.280
1.269
1.262
1.254
1.245
1.219
1.201
1.146
1.116
1.093
1.085
OH
O
P
OEt
OEt
H
9
O
O
P
OEt
OEt
H
9′
400 MHz, CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.97
0.11
0.13
1.00
5.28
0.06
0.07
0.12
0.15
0.19
4.06
3.99
2.76
8.11
1.34
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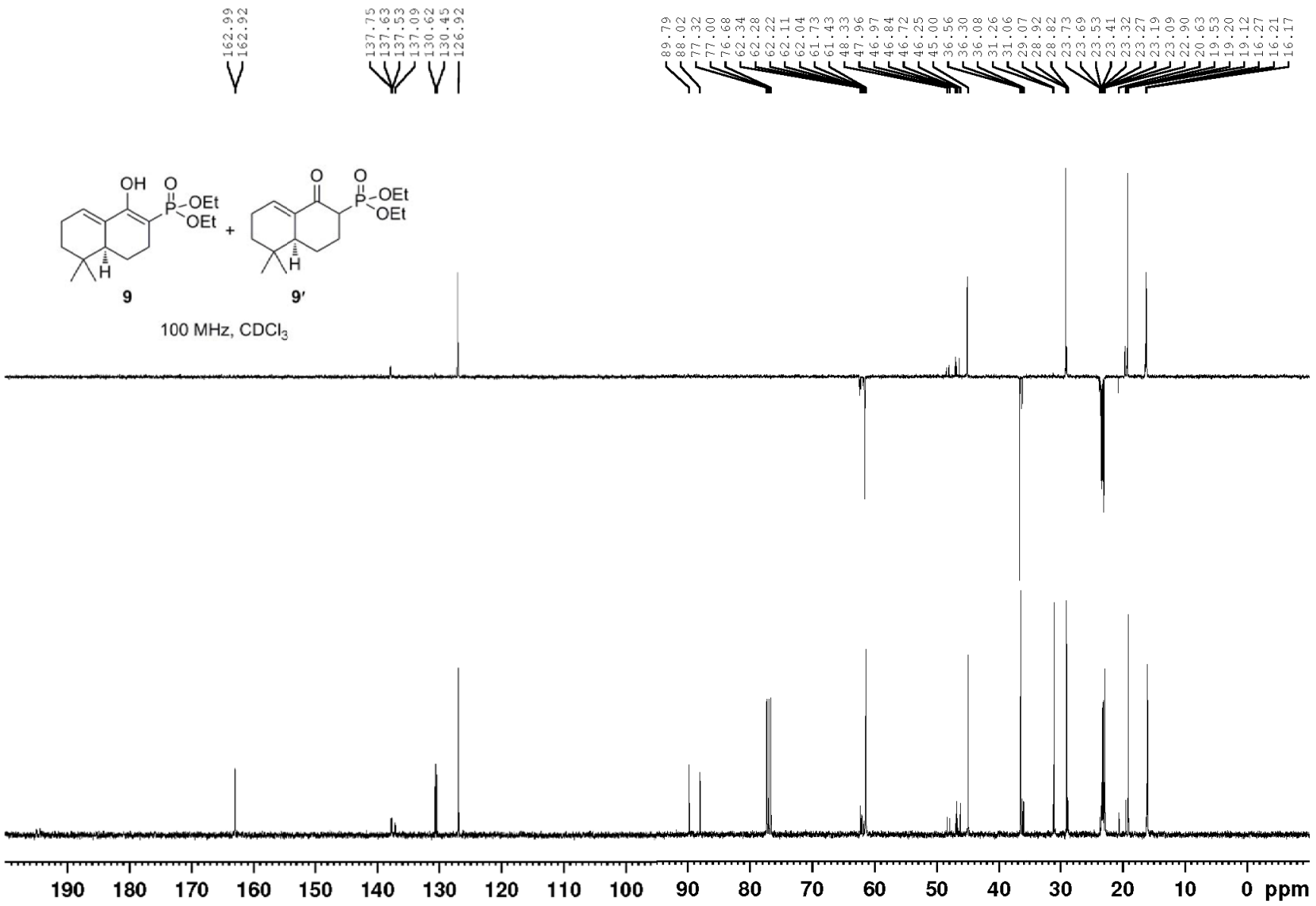
3.00
0.50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137.09
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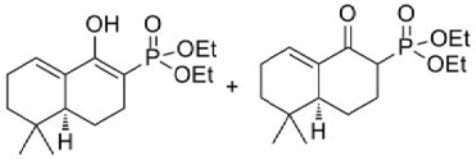
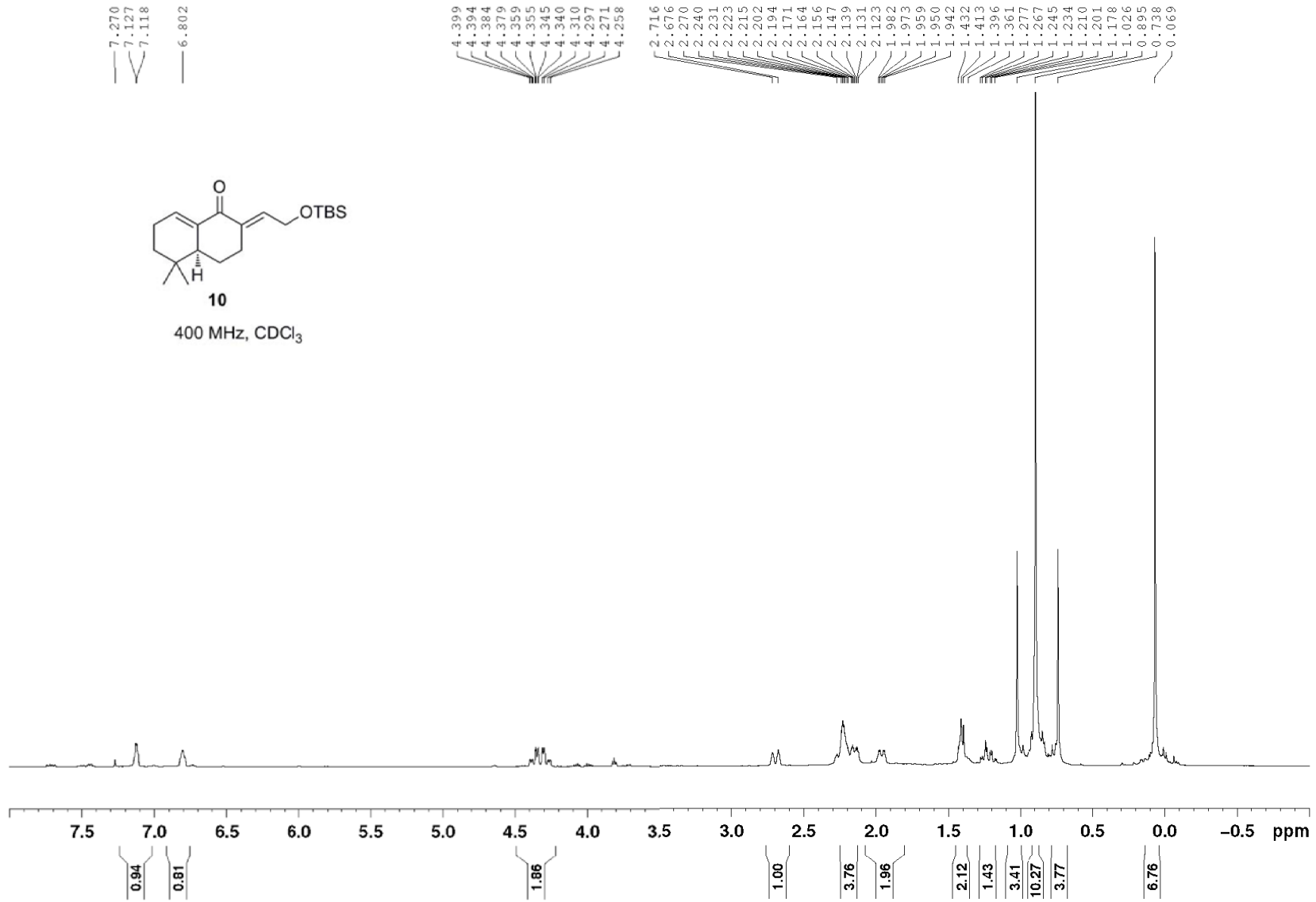
77.00
76.68
62.34
62.28
62.22
62.11
62.04
61.73
61.43
48.33
47.96
46.97
46.84
46.72
46.25
45.00
36.56
36.30
36.08
31.26
31.06
29.07
28.92
28.82
23.73
23.69
23.53
23.41
23.32
23.27
23.19
23.09
22.90
20.63
19.53
19.20
19.12
16.27
16.21
16.17
OH
O
P
OEt
OEt
H
9
O
O
P
OEt
OEt
H
9′
100 MHz, CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm



9 **9′**

400 MHz, $CDCl_3$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4.355
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4.310
4.297
4.271
4.258
2.716
2.676
2.270
2.240
2.231
2.223
2.215
2.202
2.194
2.171
2.164
2.156
2.147
2.139
2.131
2.123
1.982
1.973
1.959
1.950
1.942
1.432
1.413
1.396
1.361
1.277
1.267
1.245
1.234
1.210
1.201
1.178
1.026
0.895
0.738
0.069
O
OTBS
H
10
400 MHz, CDCl3
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
0.94
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1.00
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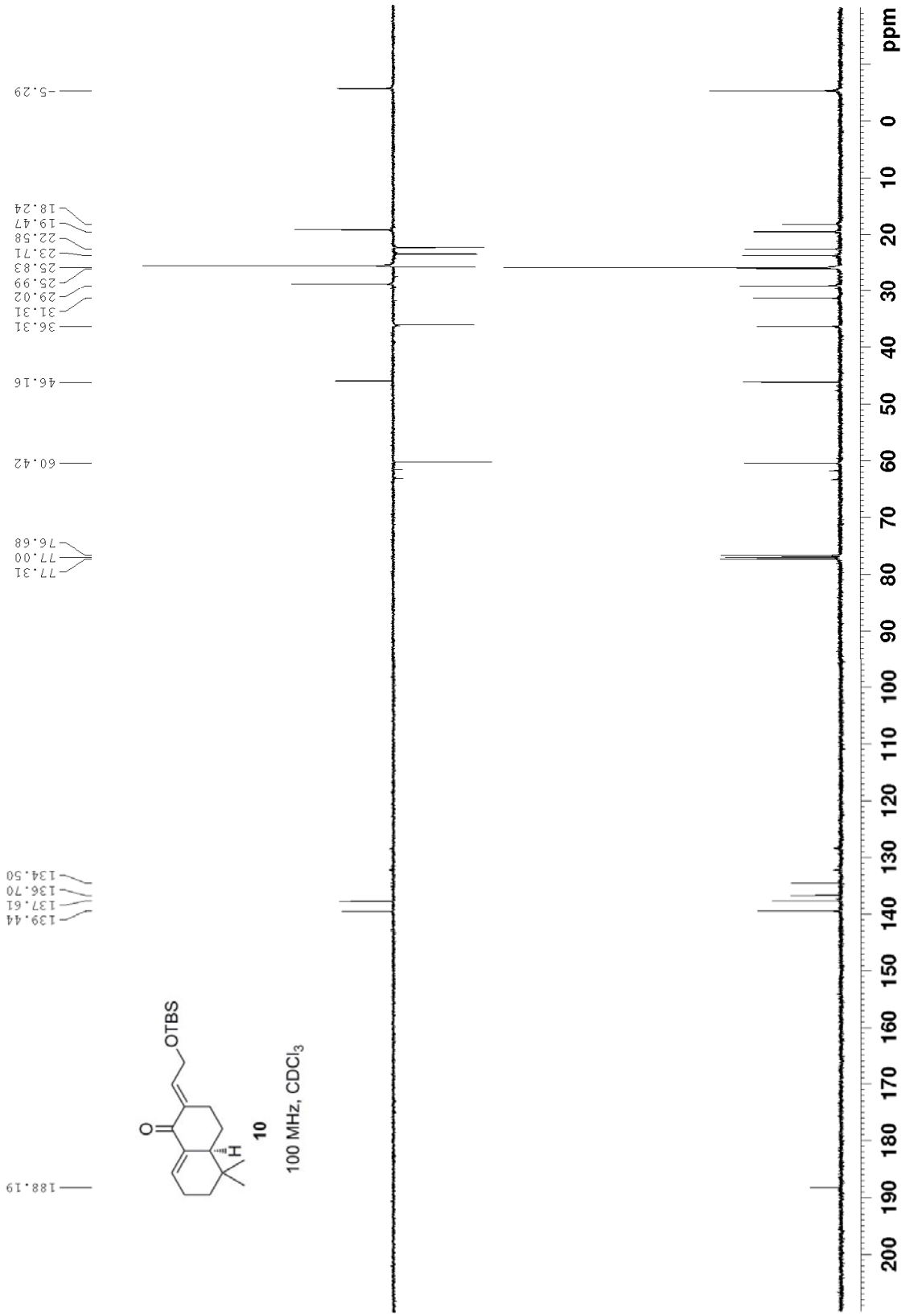
1.43
3.41
10.27
3.77
6.76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77.00
76.68
60.42
46.16
36.31
31.31
29.02
25.99
25.83
23.71
22.58
19.47
18.24
-5.29
OTBS
O
H
10
100 MHz, CDCl3
ppm
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10
20
30
40
50
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80
90
100
110
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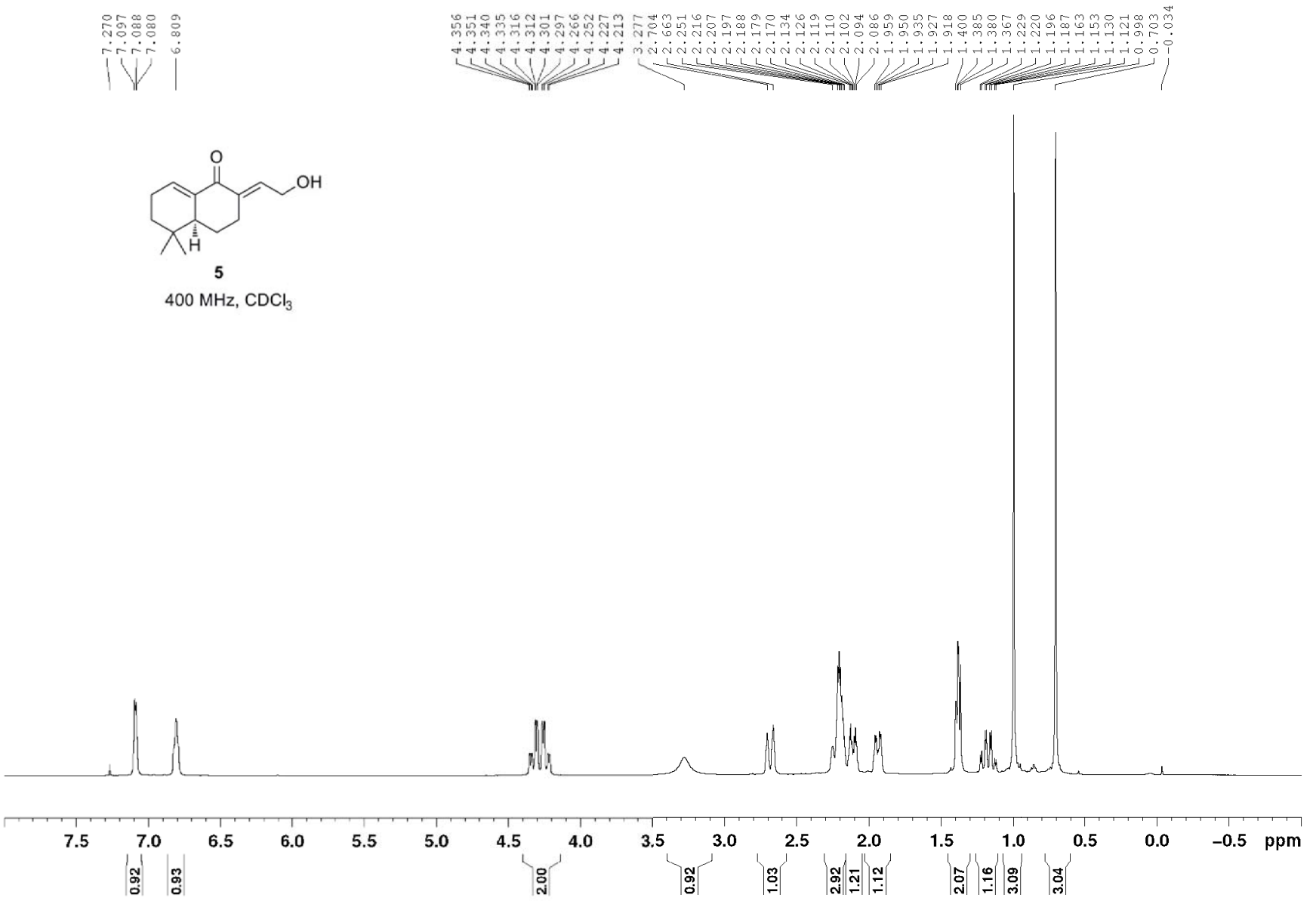
140
150
160
170
180
190
200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4.301
4.297
4.266
4.252
4.227
4.213
3.277
2.704
2.663
2.251
2.216
2.207
2.197
2.188
2.179
2.170
2.134
2.126
2.119
2.110
2.102
2.094
2.086
1.959
1.950
1.935
1.927
1.918
1.400
1.385
1.380
1.367
1.229
1.220
1.196
1.187
1.163
1.153
1.130
1.121
0.998
0.703
-0.034
O
OH
H
5
400 MHz, CDCl3
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
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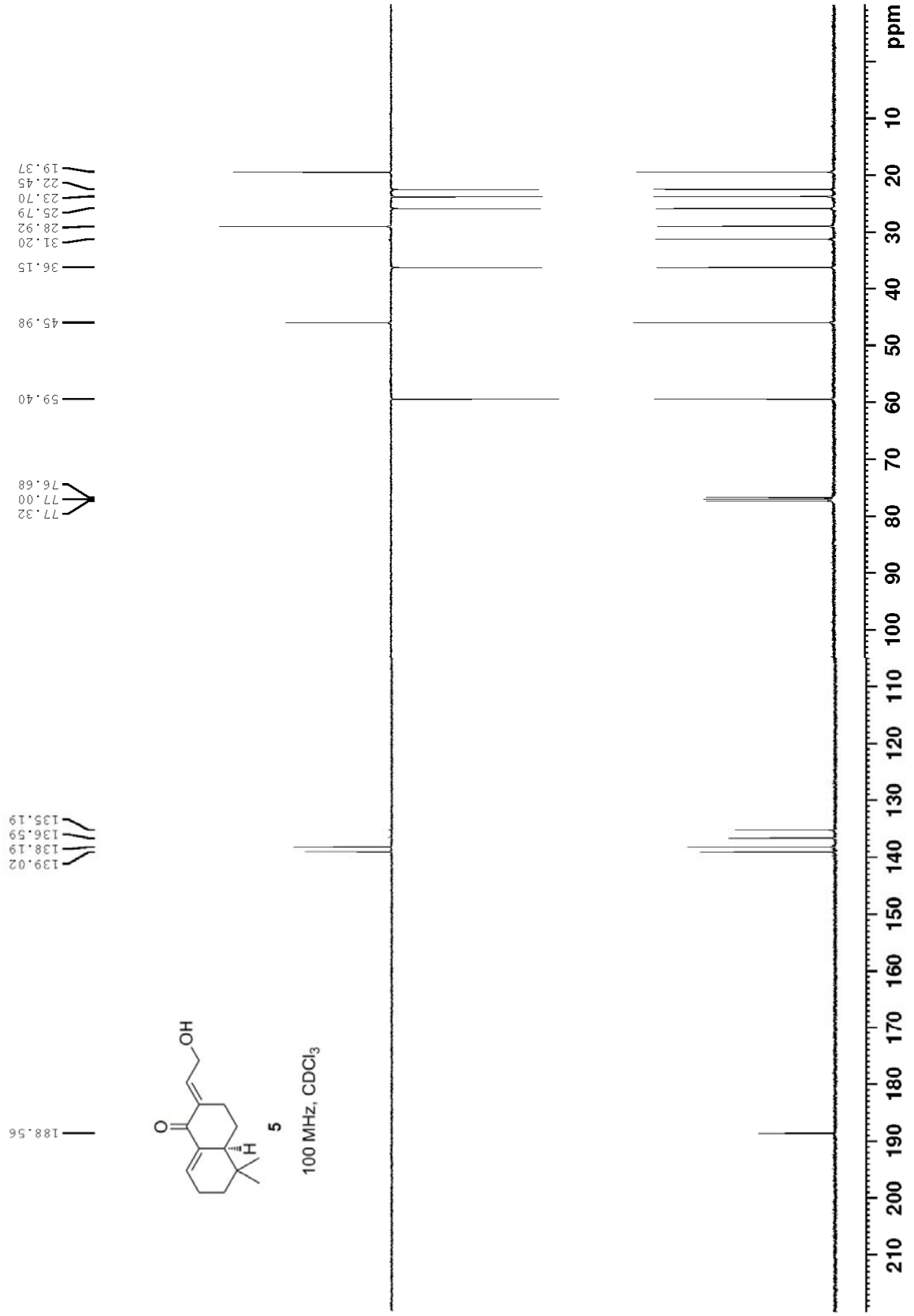
1.21
1.12
2.07
1.16
3.09
3.04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135.19
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76.68
59.40
45.98
36.15
31.20
28.92
25.79
23.70
22.45
19.37
O
OH
H
5
100 MHz, CDCl3
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

CO2Me
O
H
11b
+
CO2Me
O
H
11a
2 : 1
400 MHz, CDCl3
ppm
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
1.55
3.17
4.84
5.07
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0.59
1.11
1.08
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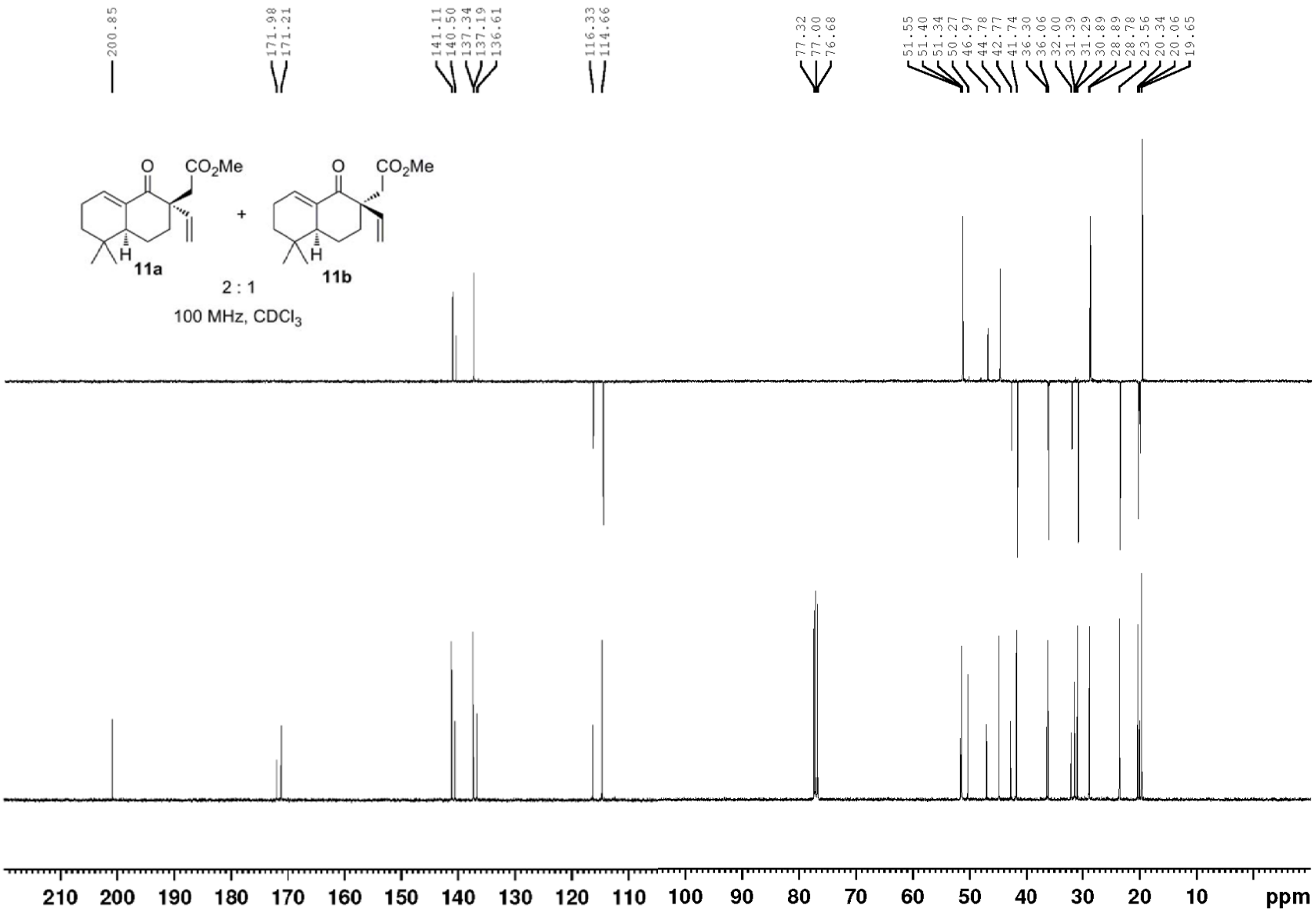
4.79
3.16
0.46
1.00
1.46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137.34
137.19
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114.66
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76.68
51.55
51.40
51.34
50.27
46.97
44.78
42.77
41.74
36.30
36.06
32.00
31.39
31.29
30.89
28.89
28.78
23.56
20.34
20.06
19.65
O
CO2Me
H
11a
+
O
CO2Me
H
11b
2 : 1
100 MHz, CDCl3
210
200
190
180
170
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150
140
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100
90
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70
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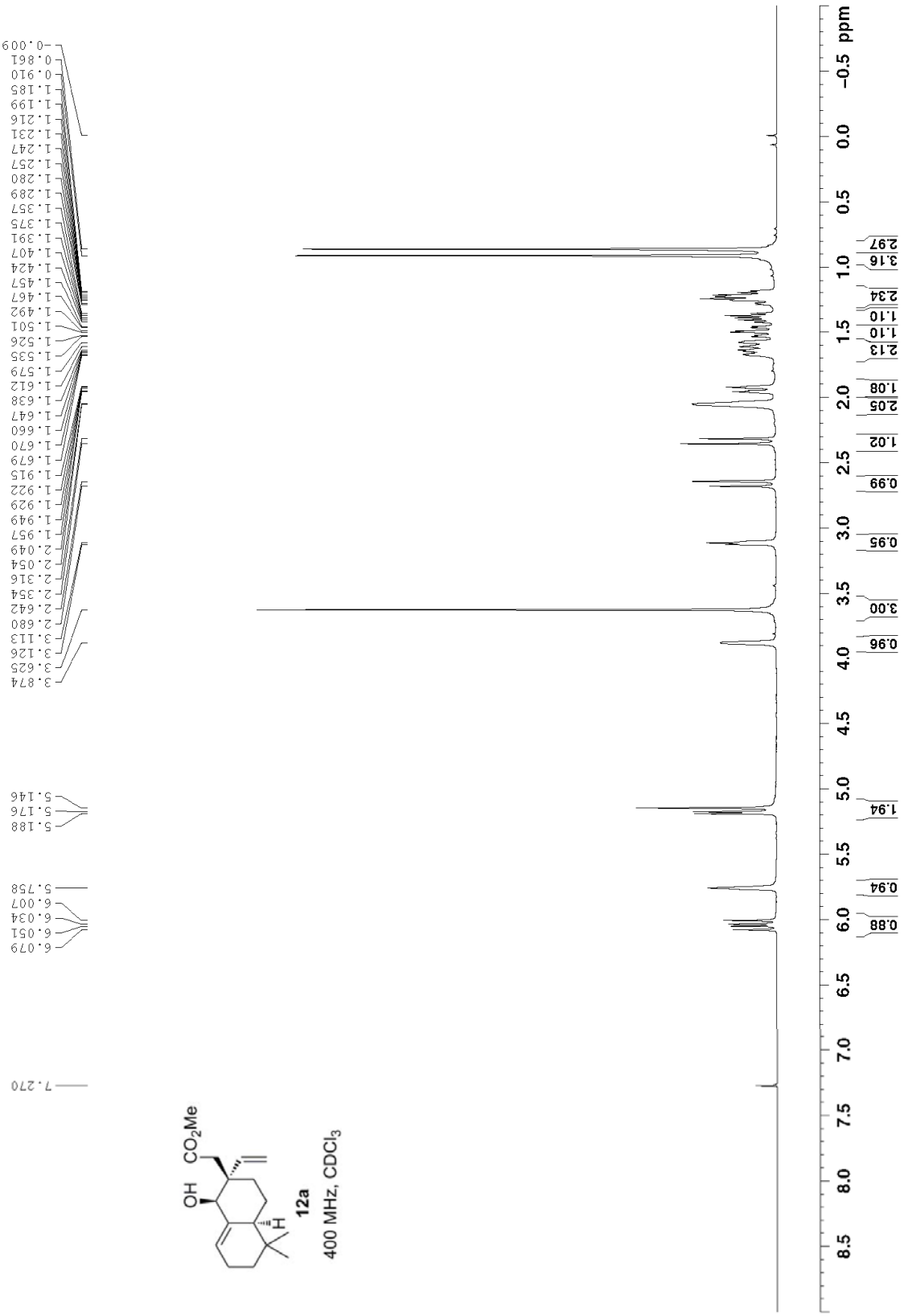
50
40
30
20
10
ppm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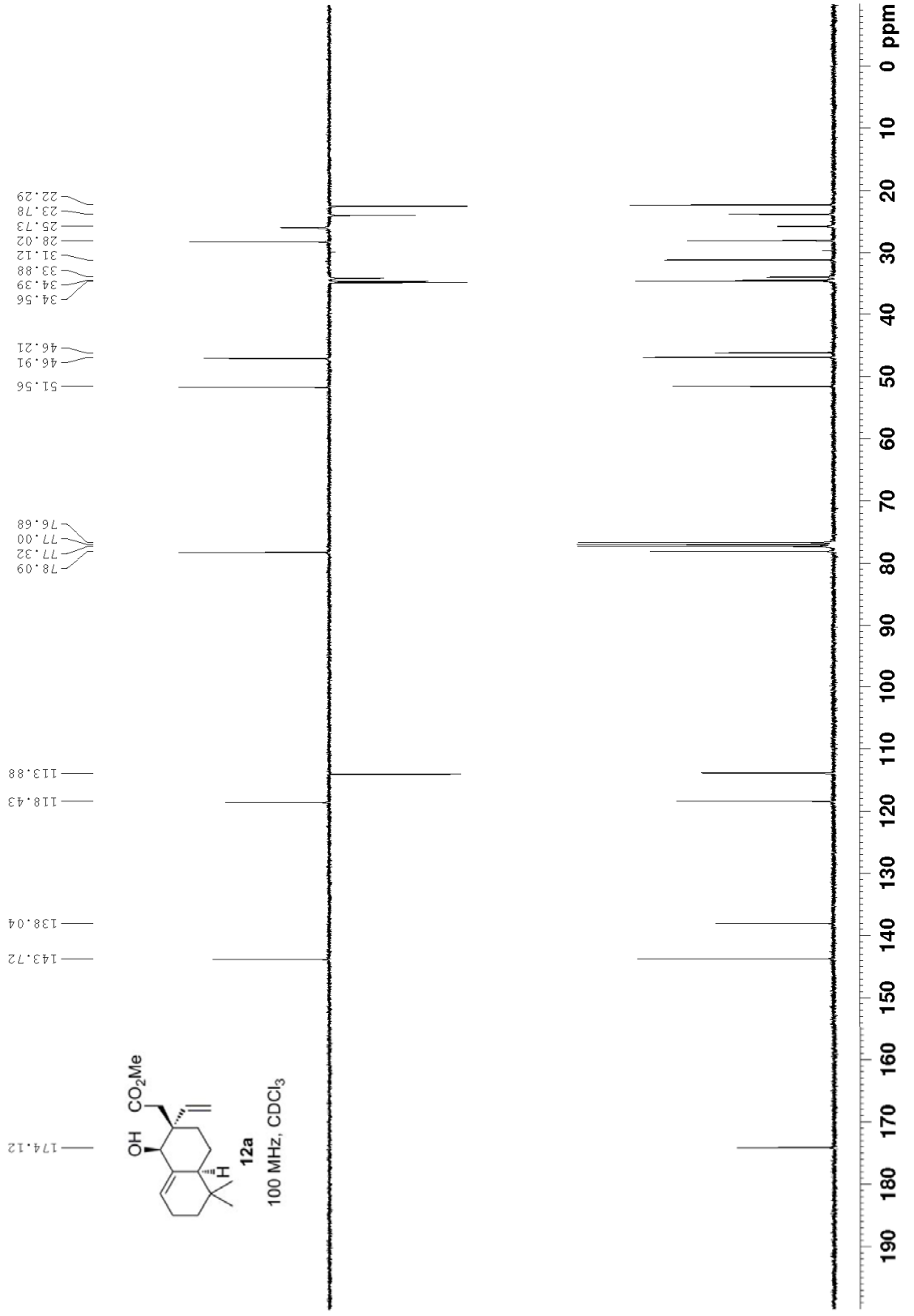
CO2Me
H
12a
400 MHz, CDCl3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77.00
77.32
78.09
113.88
118.43
138.04
143.72
174.12
OH
CO2Me
H
12a
100 MHz, CDCl3
0 ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190

7.270
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5.865
5.838
5.744
5.161
5.141
5.115
4.614
2.552
2.510
2.187
2.145
2.012
2.007
1.864
1.855
1.847
1.828
1.820
1.811
1.795
1.786
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1.745
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1.672
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1.641
1.616
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1.263
1.241
1.232
1.221
1.209
1.201
1.188
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0.874
−0.026
O
O
H
3
400 MHz, CDCl3
ppm
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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
1.00
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0.94
1.00
1.09
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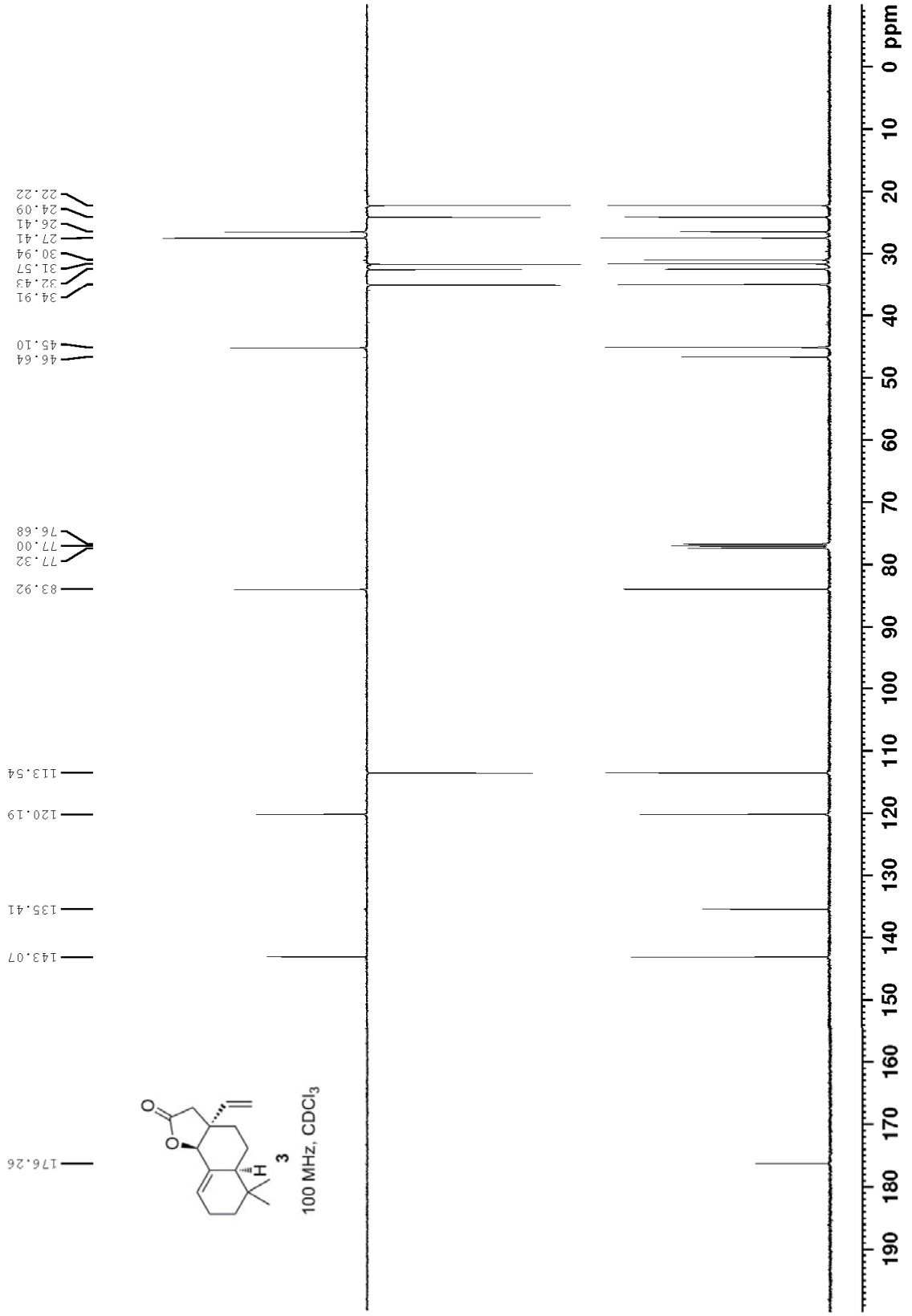
1.16
1.07
1.15
2.27
6.24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34.91
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77.32
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143.07
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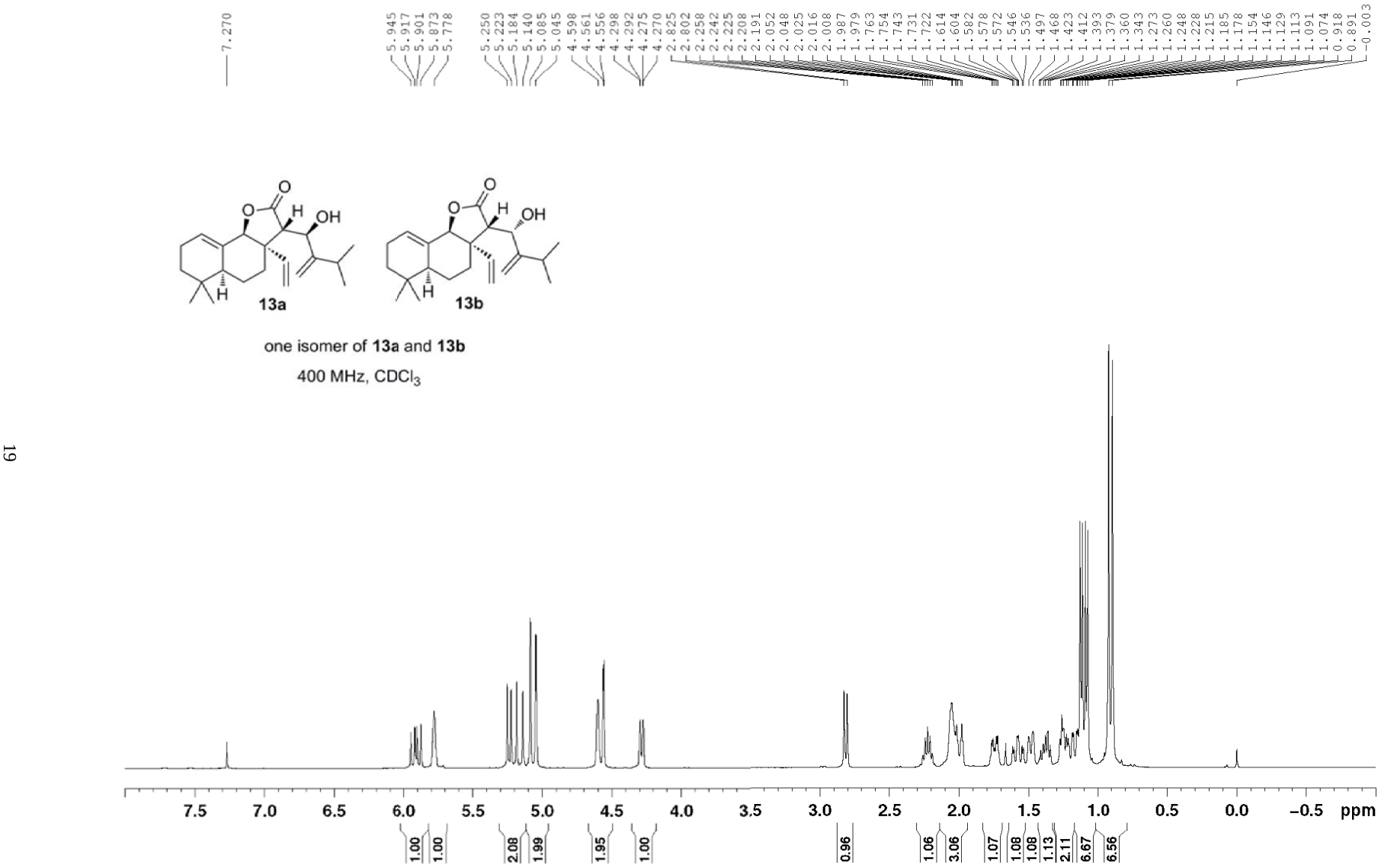
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4.598
4.561
4.556
4.298
4.292
4.275
4.270
2.825
2.802
2.258
2.242
2.225
2.208
2.191
2.052
2.048
2.025
2.016
2.008
1.987
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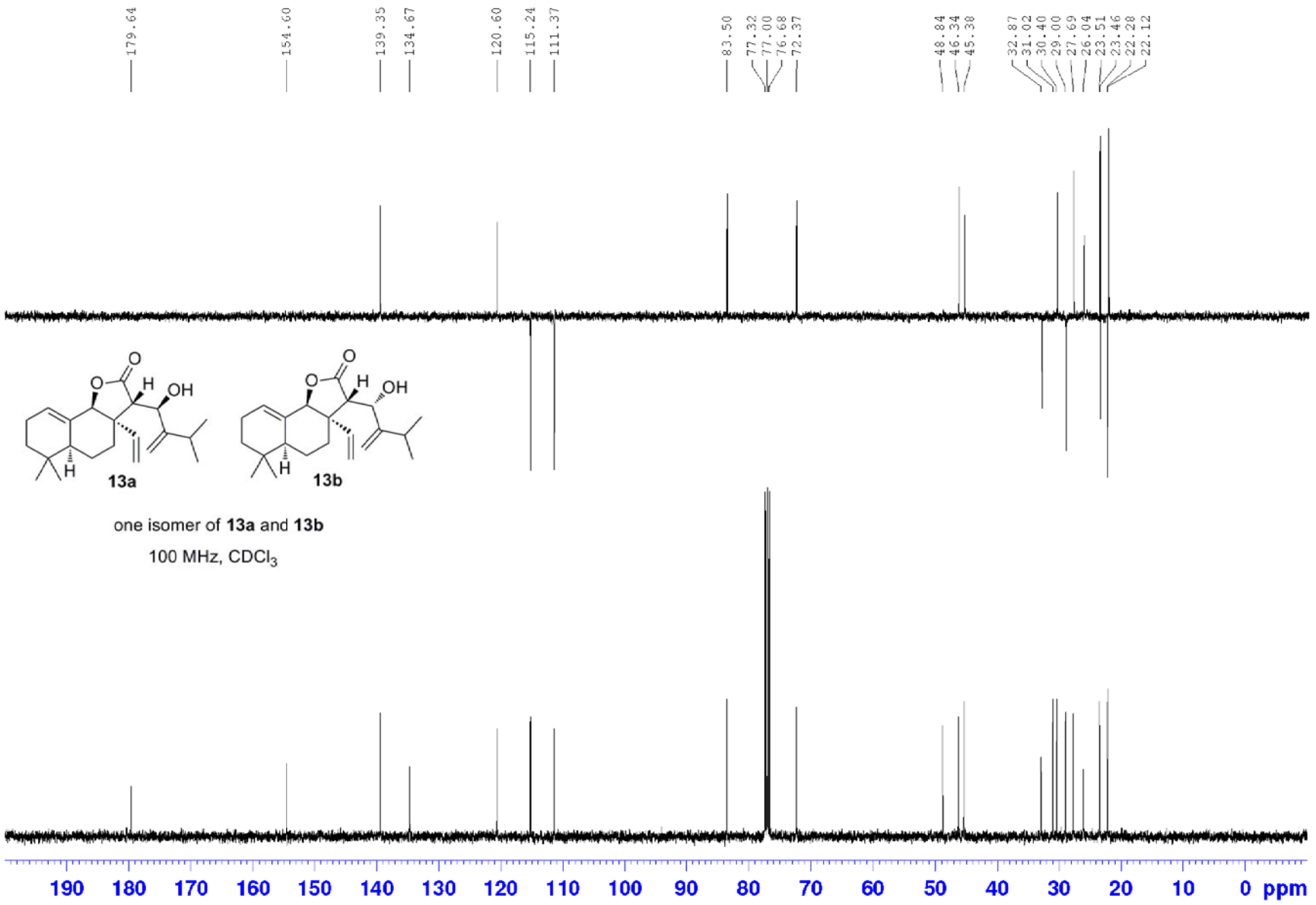
1.763
1.754
1.743
1.731
1.722
1.614
1.604
1.582
1.578
1.572
1.546
1.536
1.497
1.468
1.423
1.412
1.393
1.379
1.360
1.343
1.273
1.260
1.248
1.228
1.215
1.185
1.178
1.154
1.146
1.129
1.113
1.091
1.074
0.918
0.891
-0.003
O
O
H
OH
H
13a
O
O
H
OH
H
13b
one isomer of 13a and 13b
400 MHz, CDCl3
7.5
7.0
6.5
6.0
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
1.00
1.00
2.08
1.99
1.95
1.00
0.96
1.06
3.06
1.07
1.08
1.08
1.13
2.11
6.67
6.56


179.64
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115.24
111.37
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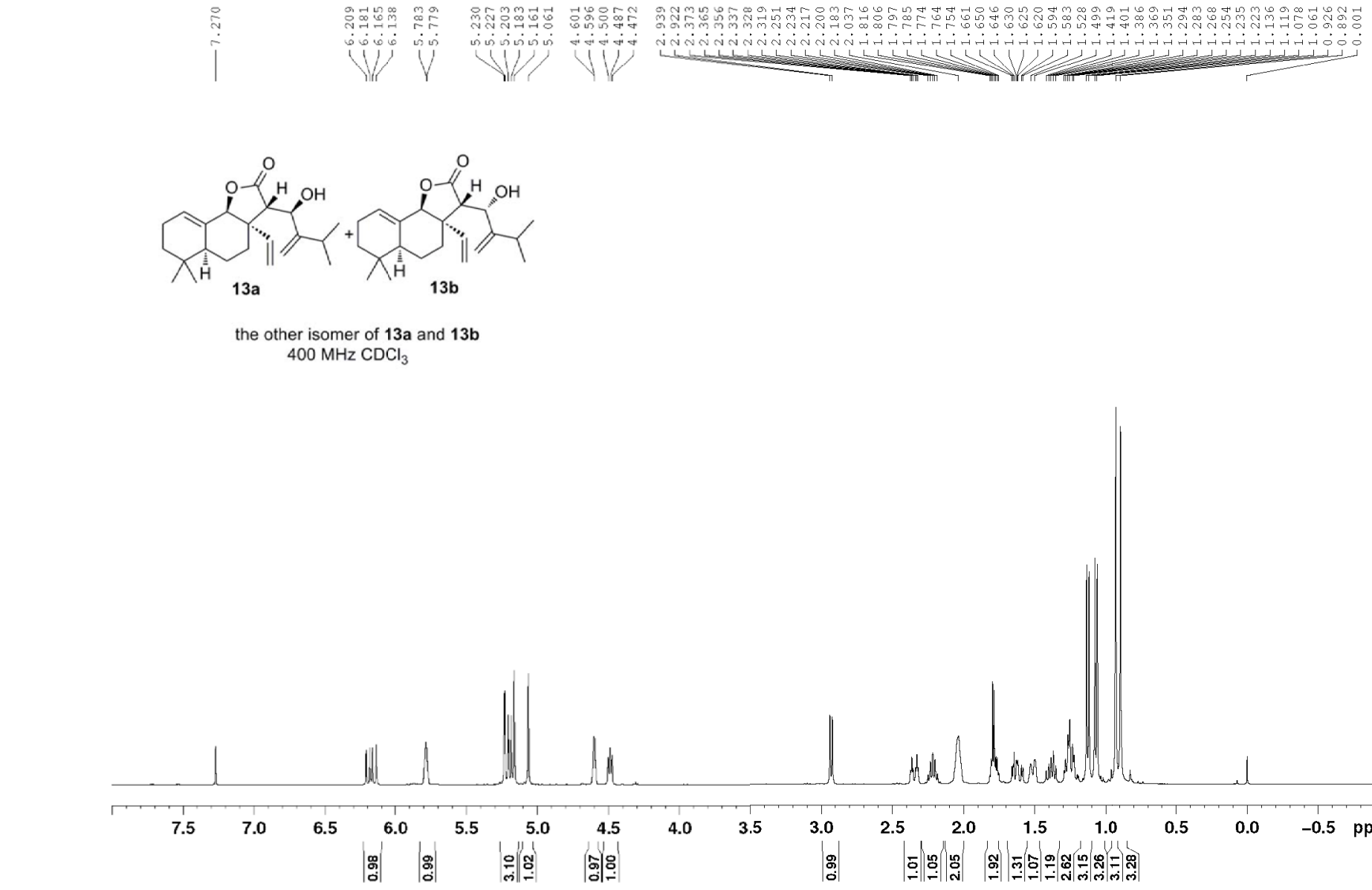
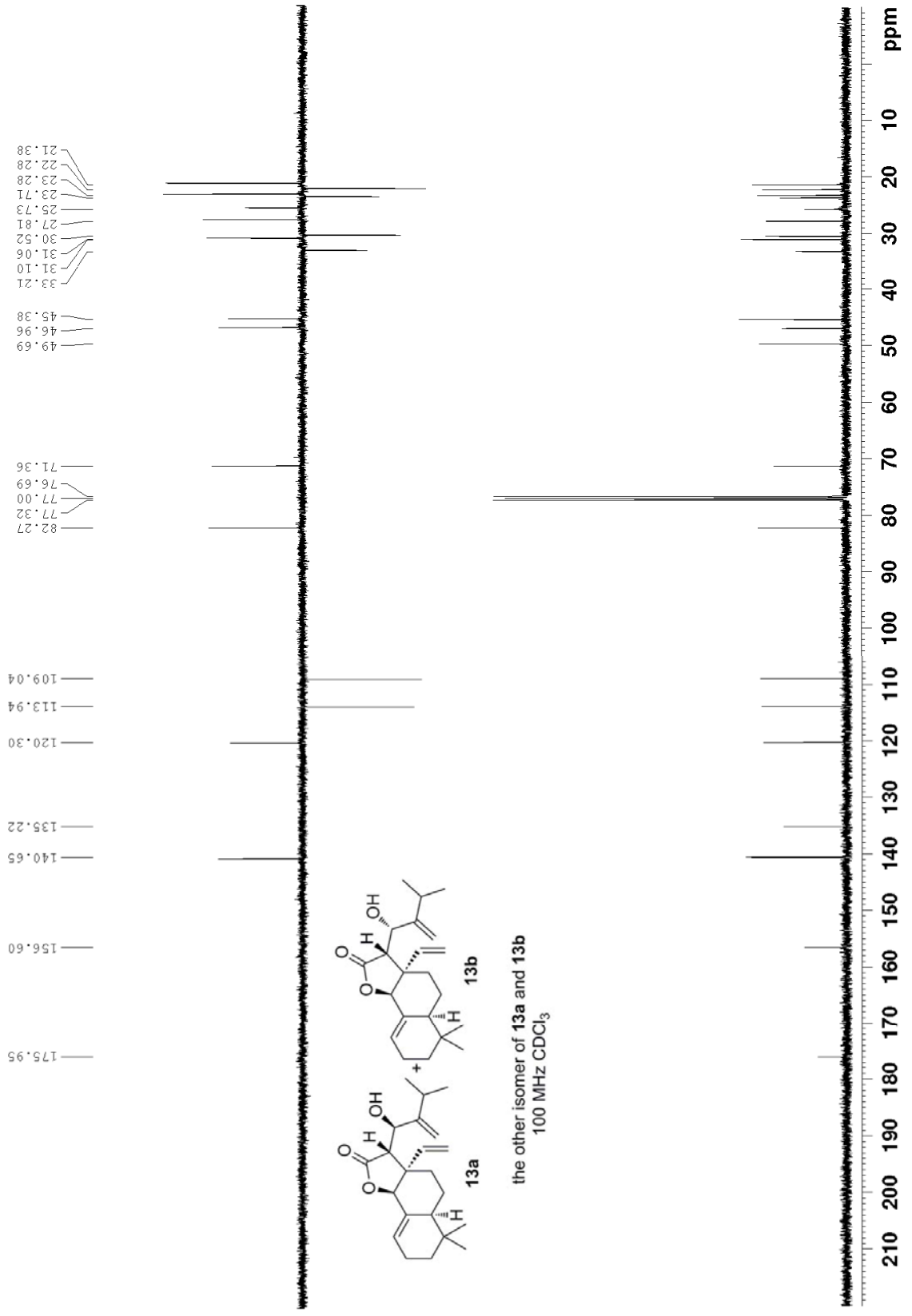
77.00
76.68
72.37
48.84
46.34
45.38
32.87
31.02
30.40
29.00
27.69
26.04
23.51
23.46
22.28
22.12
O
H
OH
H
13a
O
H
OH
H
13b
one isomer of 13a and 13b
100 MHz, CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm



13a + **13b**

the other isomer of **13a** and **13b**
400 MHz $CDCl_3$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25.73
27.81
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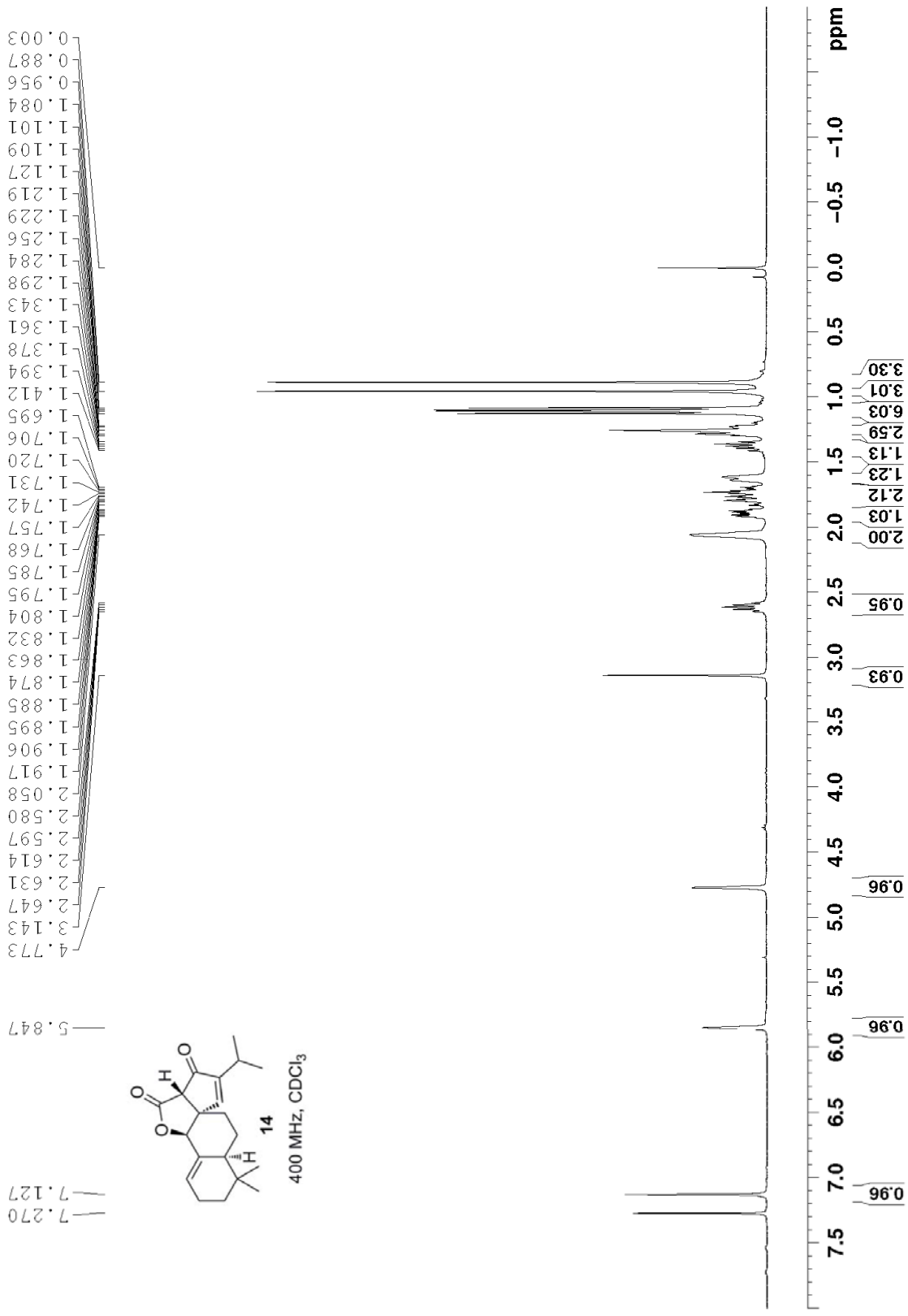
31.06
31.10
33.21
45.38
46.96
49.69
71.36
76.69
77.00
77.32
82.27
109.04
113.94
120.30
135.22
140.65
156.60
175.95
13b
13a
the other isomer of 13a and 13b
100 MHz CDCl3
ppm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400 MHz, CDCl3
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7.270
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2.580
2.058
1.917
1.906
1.895
1.885
1.874
1.863
1.832
1.804
1.795
1.785
1.768
1.757
1.742
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1.378
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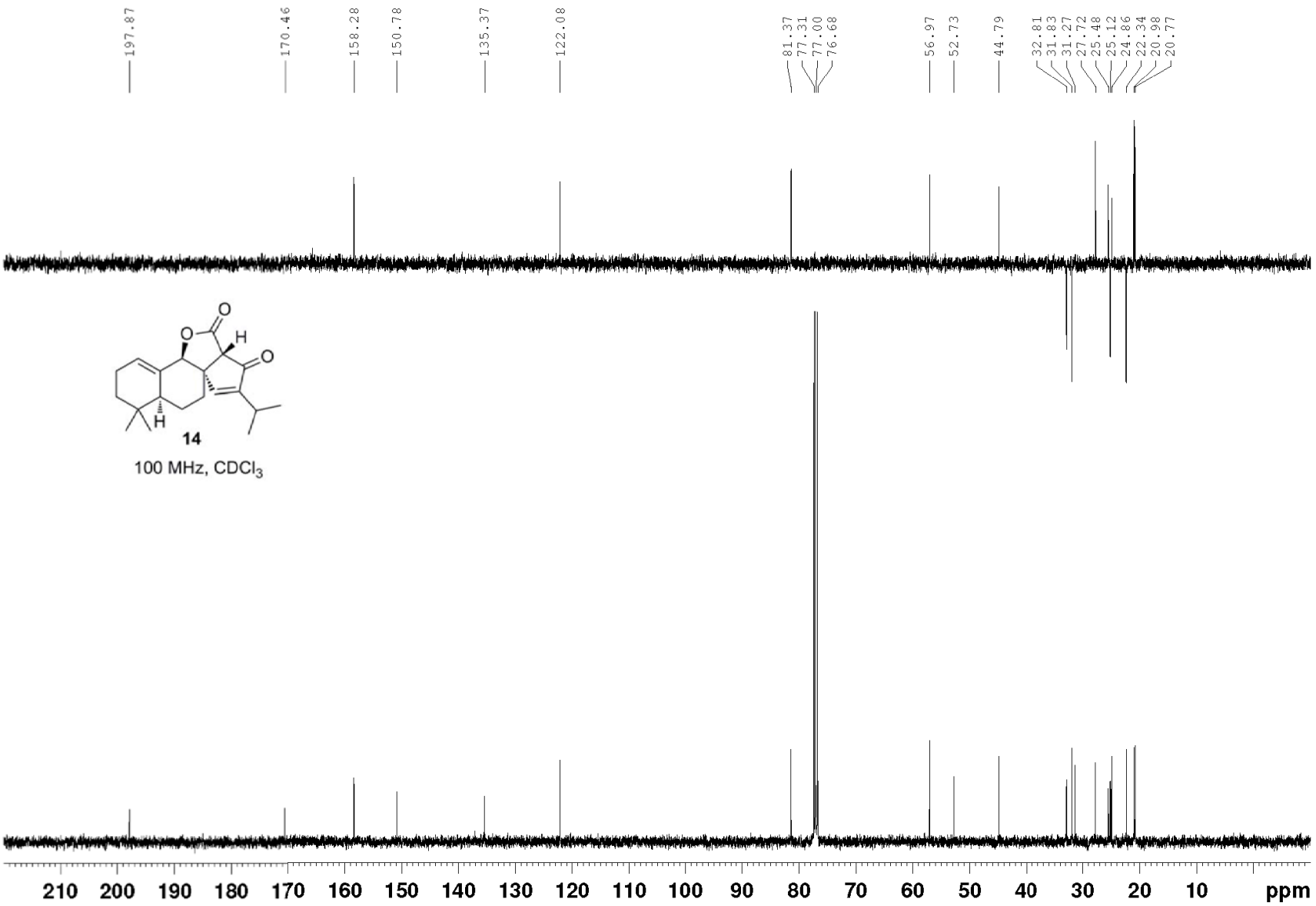
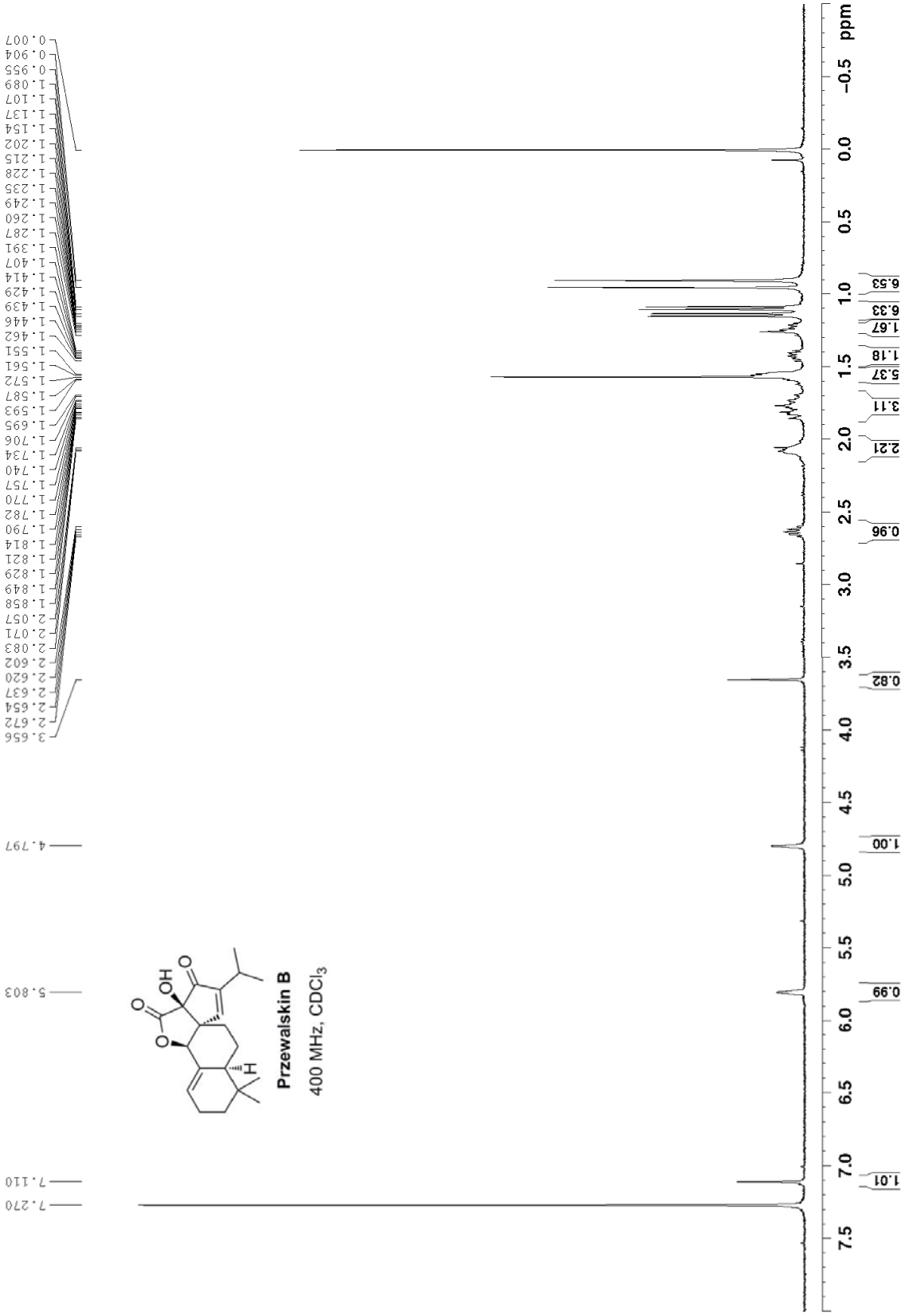
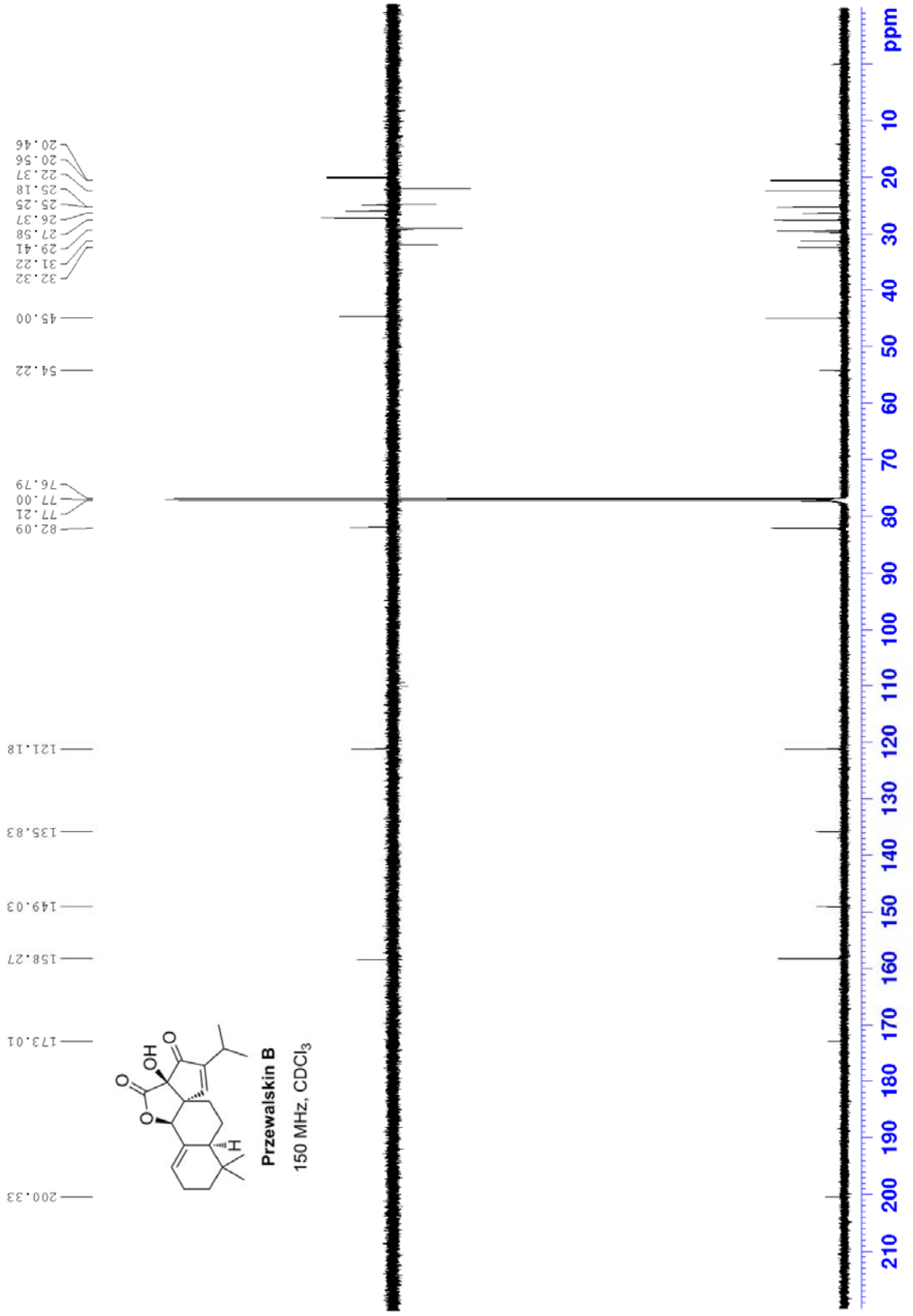
1.298
1.284
1.256
1.229
1.219
1.127
1.109
1.101
1.084
0.956
0.887
0.003
3.30
3.01
6.03
2.59
1.13
1.23
2.12
1.03
2.00
0.95
0.93
0.96
0.96
0.96


197.87
170.46
158.28
150.78
135.37
122.08
81.37
77.31
77.00
76.68
56.97
52.73
44.79
32.81
31.83
31.27
27.72
25.48
25.12
24.86
22.34
20.98
20.77
O
O
H
O
H
14
100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Przewalskin B
400 MHz, CDCl3
OH
O
O
O
H
ppm
7.270
7.110
5.803
4.797
3.656
2.672
2.654
2.637
2.620
2.602
2.083
2.071
2.057
1.858
1.849
1.829
1.821
1.814
1.790
1.782
1.770
1.757
1.740
1.734
1.706
1.695
1.593
1.587
1.572
1.561
1.551
1.462
1.446
1.439
1.429
1.414
1.407
1.391
1.287
1.260
1.249
1.235
1.228
1.215
1.202
1.154
1.137
1.107
1.089
0.955
0.904
0.007
1.01
0.99
1.00
0.82
0.96
2.21
3.11
5.37
1.18
1.67
6.33
6.53


Przewalskin B
150 MHz, CDCl3
OH
O
O
O
H
200.33
173.01
158.27
149.03
135.83
121.18
82.09
77.21
77.00
76.79
54.22
45.00
32.32
31.22
29.41
27.58
26.37
25.25
25.18
22.37
20.56
20.46
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210