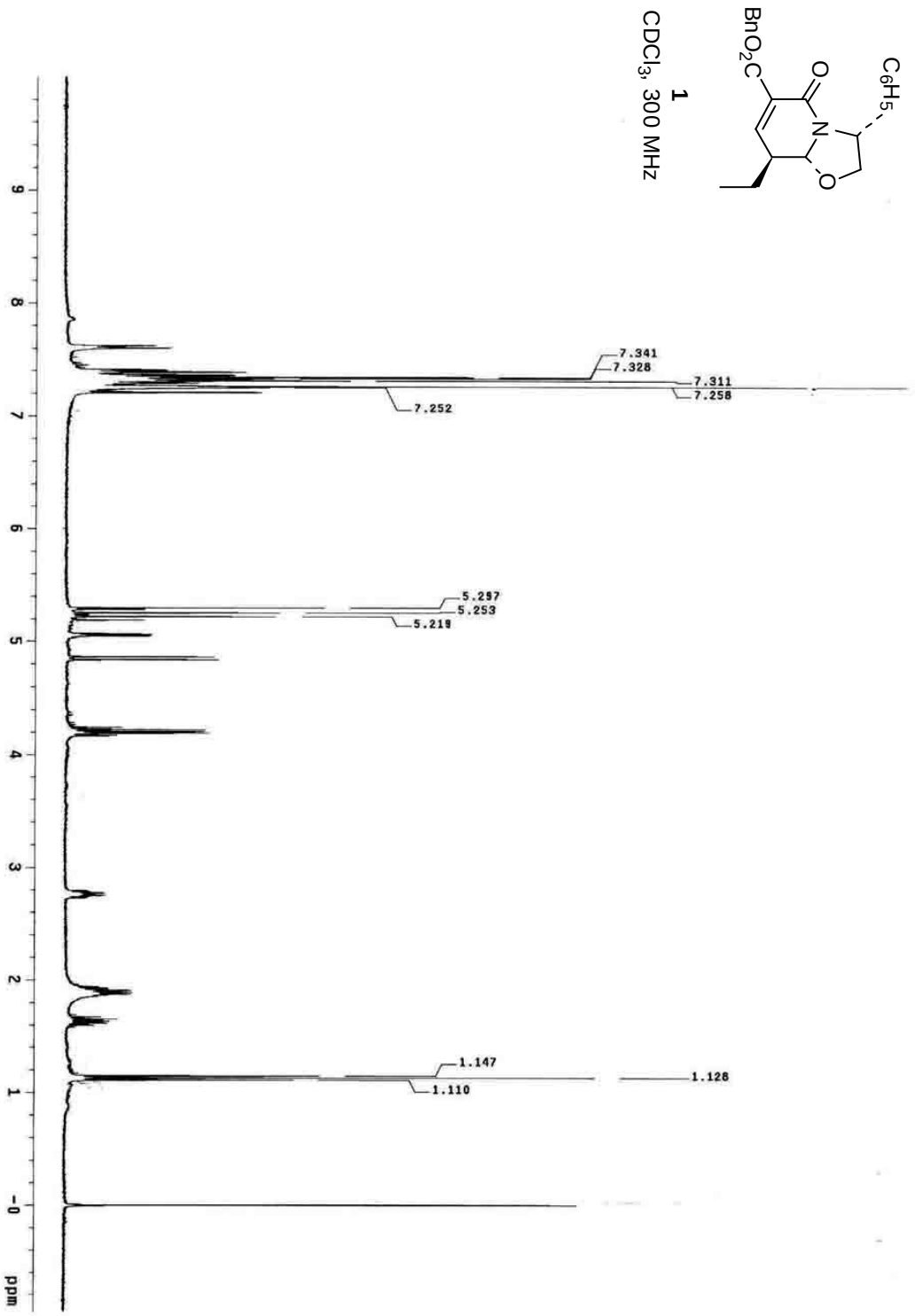
Supporting information

A Synthetic Approach to Ervatamine-Silicine Alkaloids.

Enantioselective Total Synthesis of (−)-16-Episilicine

Mercedes Amat,[†] *Núria Llor,*[†] *Begoña Checa,*[†] *Elies Molins,*[‡] *and Joan Bosch**[†]

- ^{1}H NMR and ^{13}C NMR spectra for all compounds: pages S2-S67.
- X-ray crystallographic data for compounds **16a**, **16b** and **21**: pages S68-S94.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BnO2C
C6H5
O
N
O
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7.252
5.257
5.253
5.219
1.147
1.128
1.110
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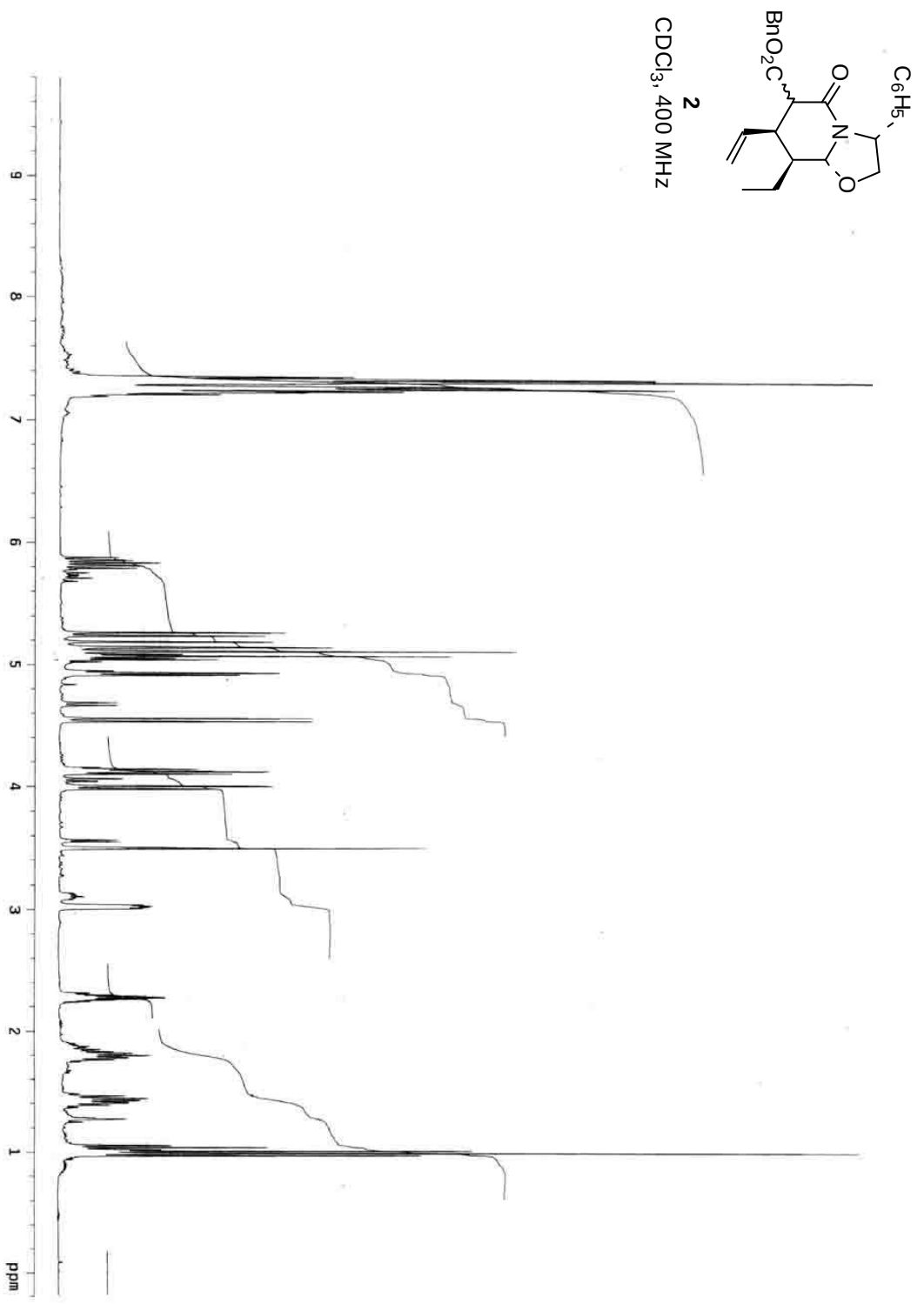
BnO2C
C6H5
O
N
O
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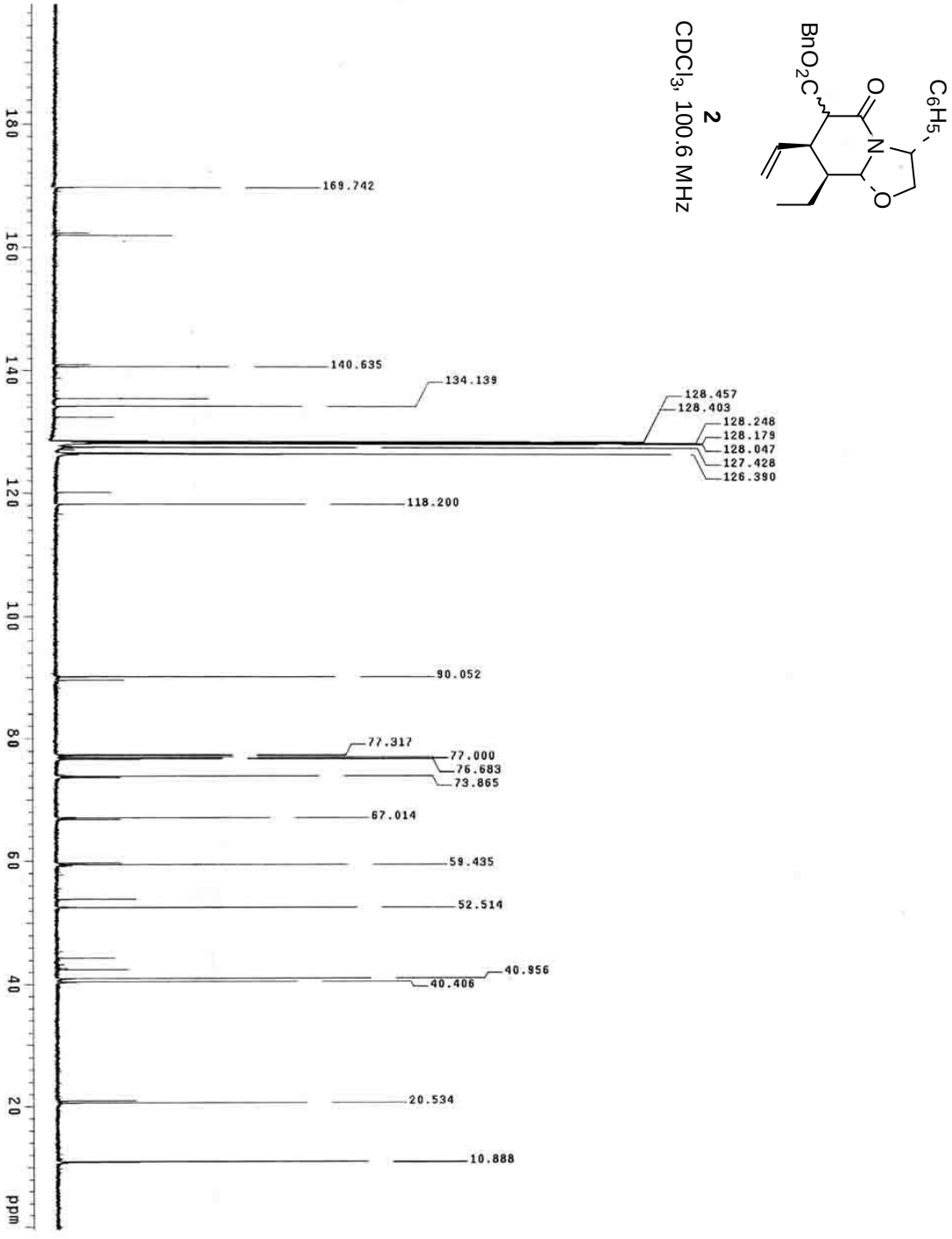
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BnO2C
O
N
O
C6H5
169.742
140.635
134.139
128.457
128.403
128.248
128.179
128.047
127.428
126.390
118.200
90.052
77.317
77.000
76.683
73.865
67.014
59.435
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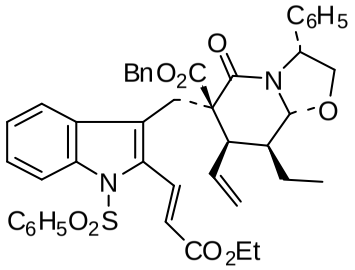
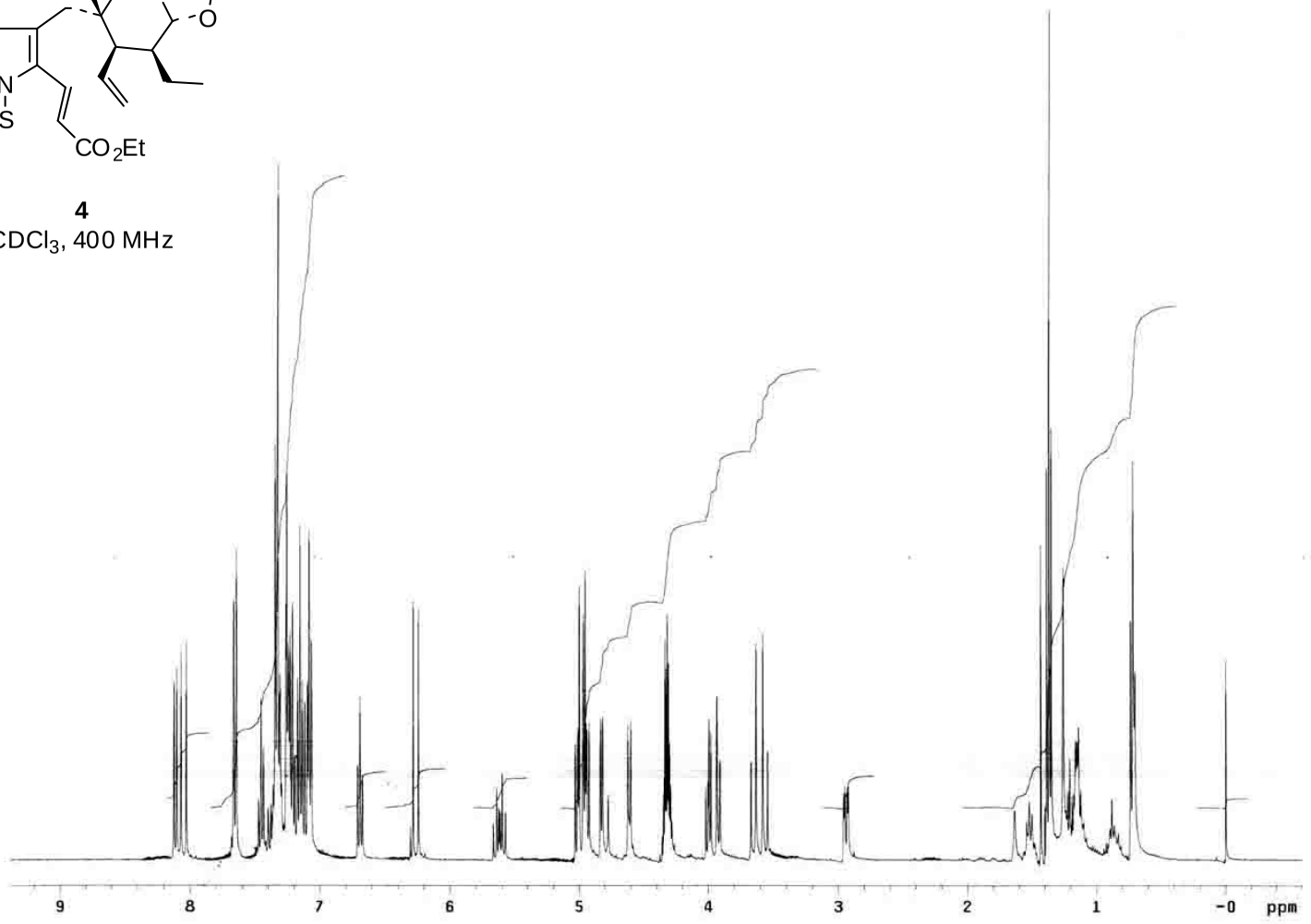
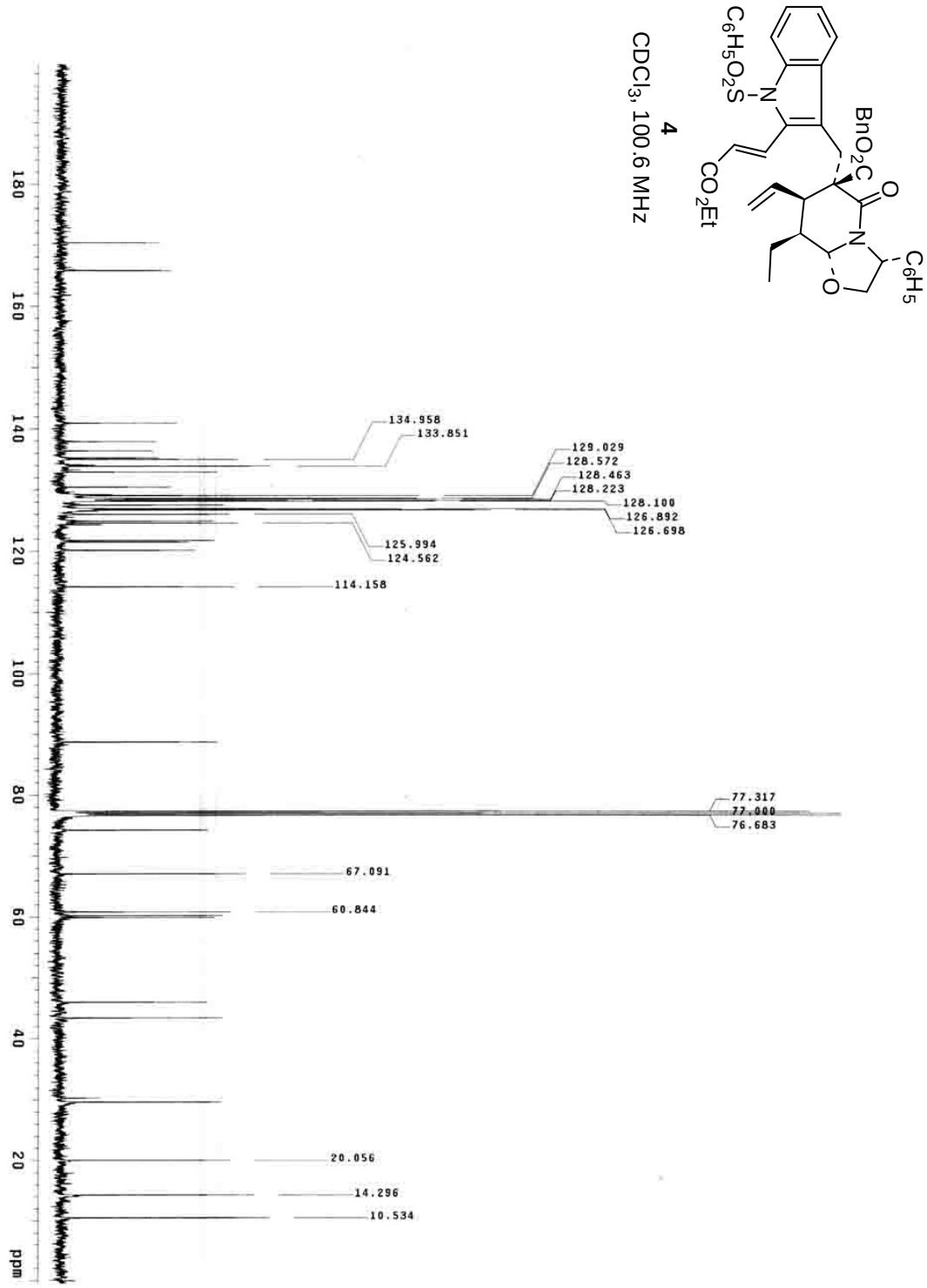
40.956
40.406
20.534
10.888
180
160
140
120
100
80
60
40
20
ppm

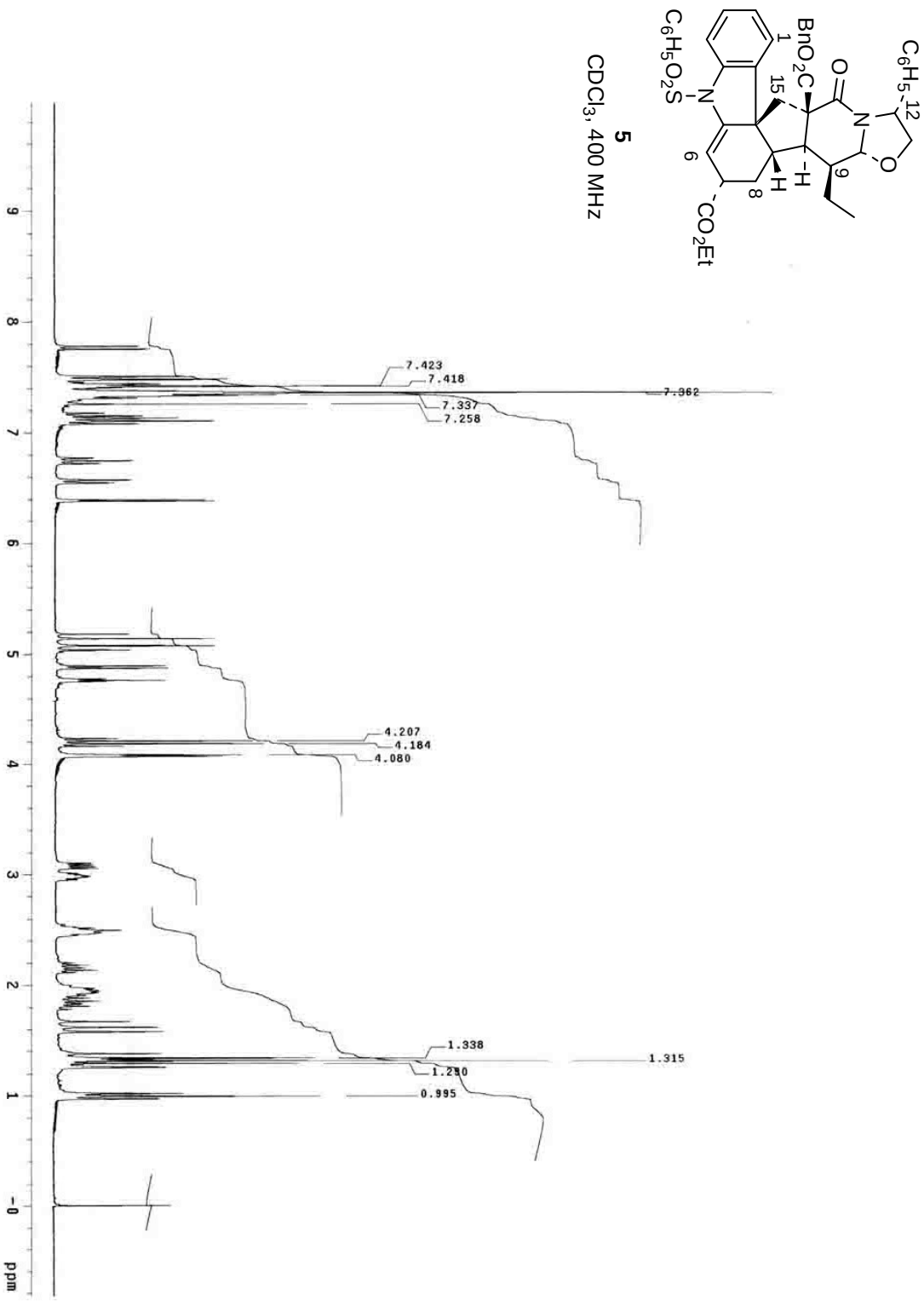


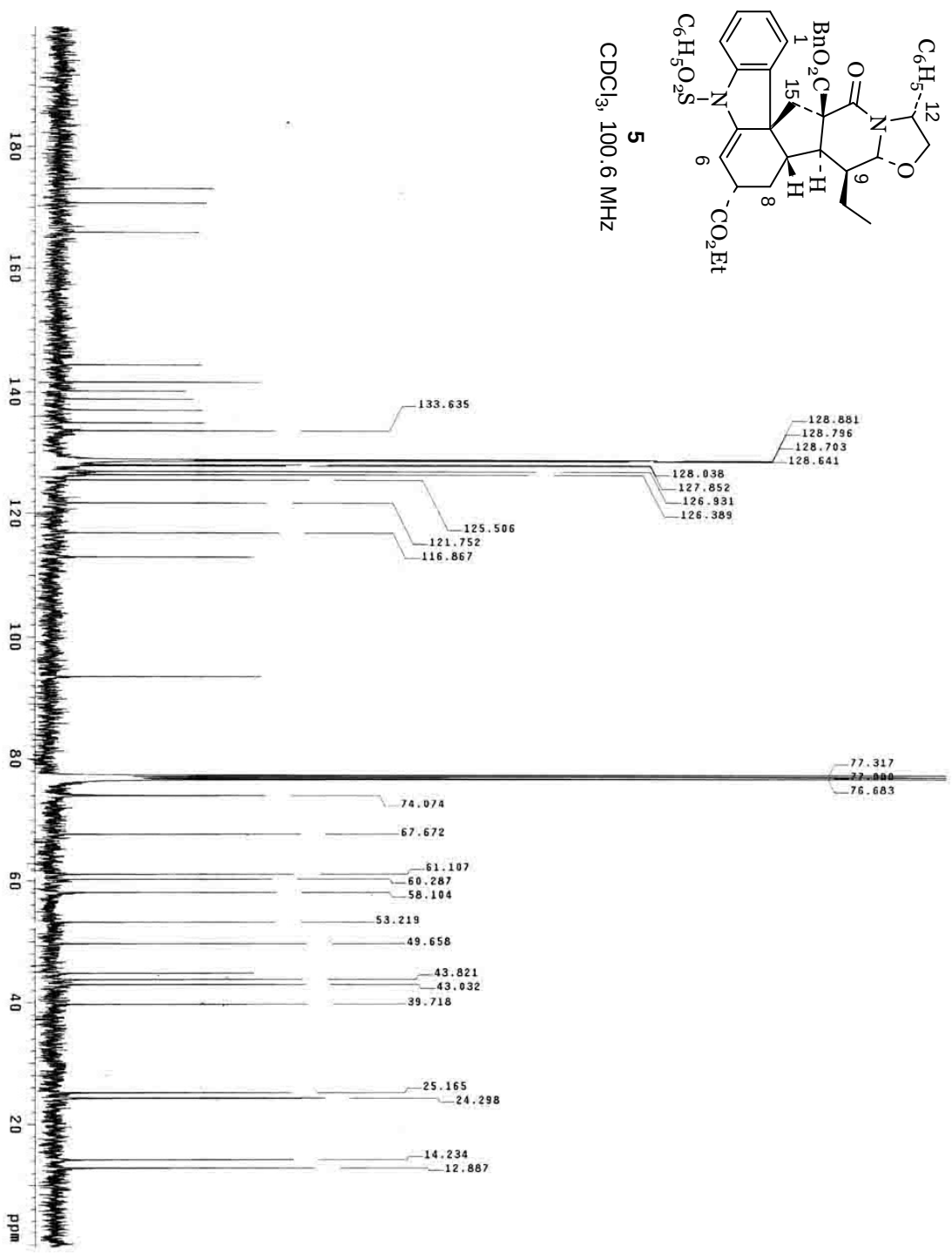
4

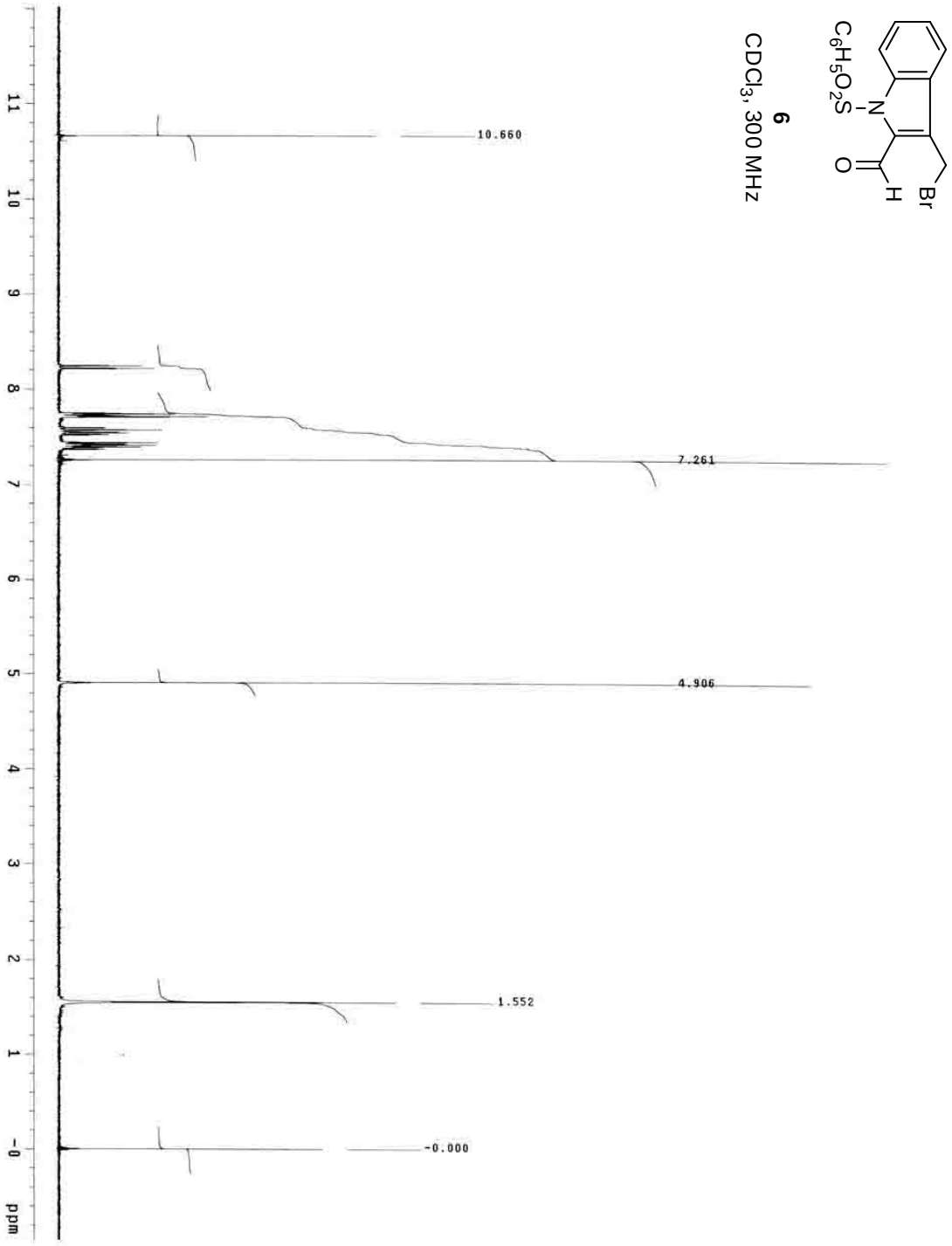
$CDCl_3$, 400 MHz

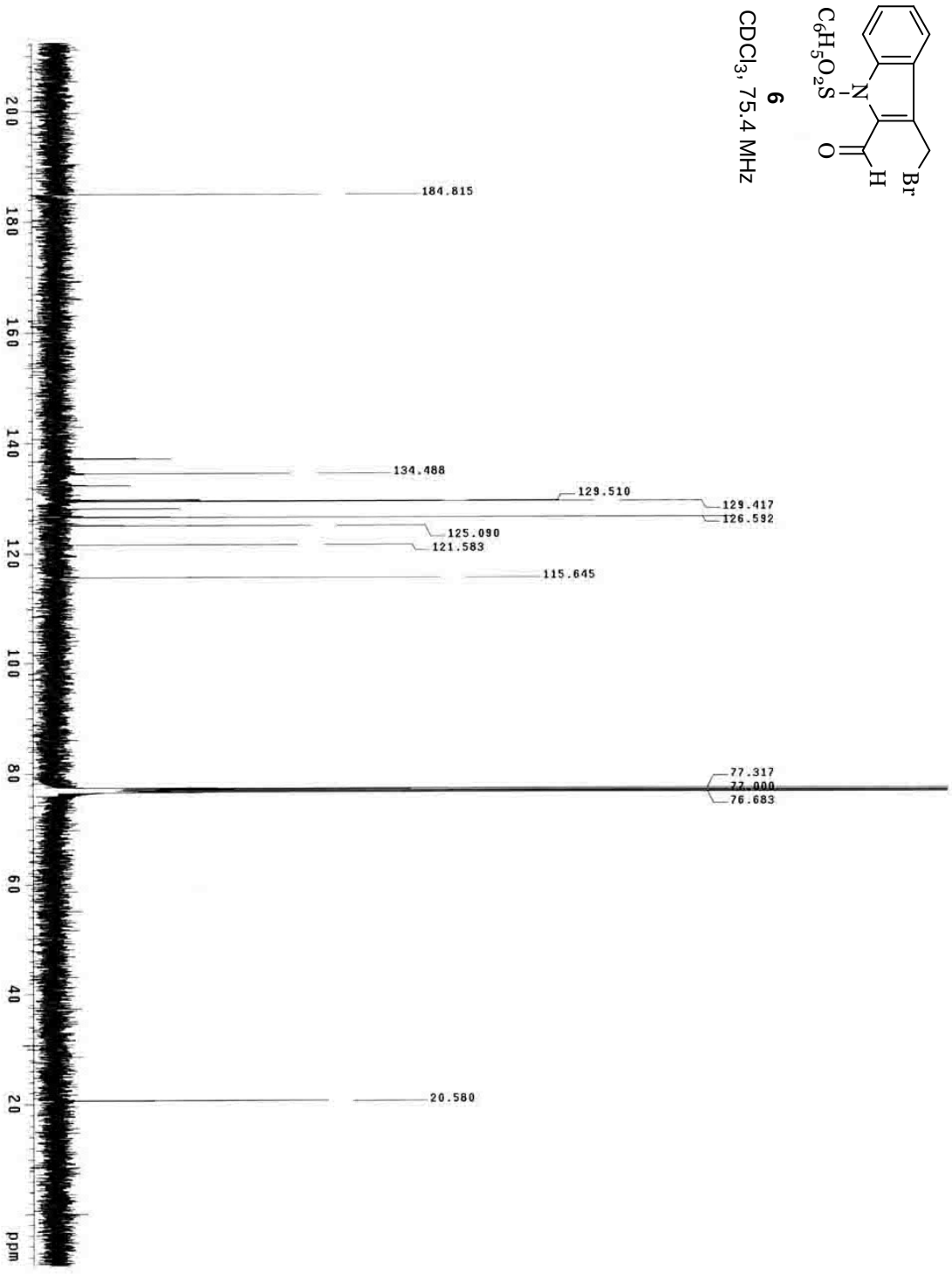


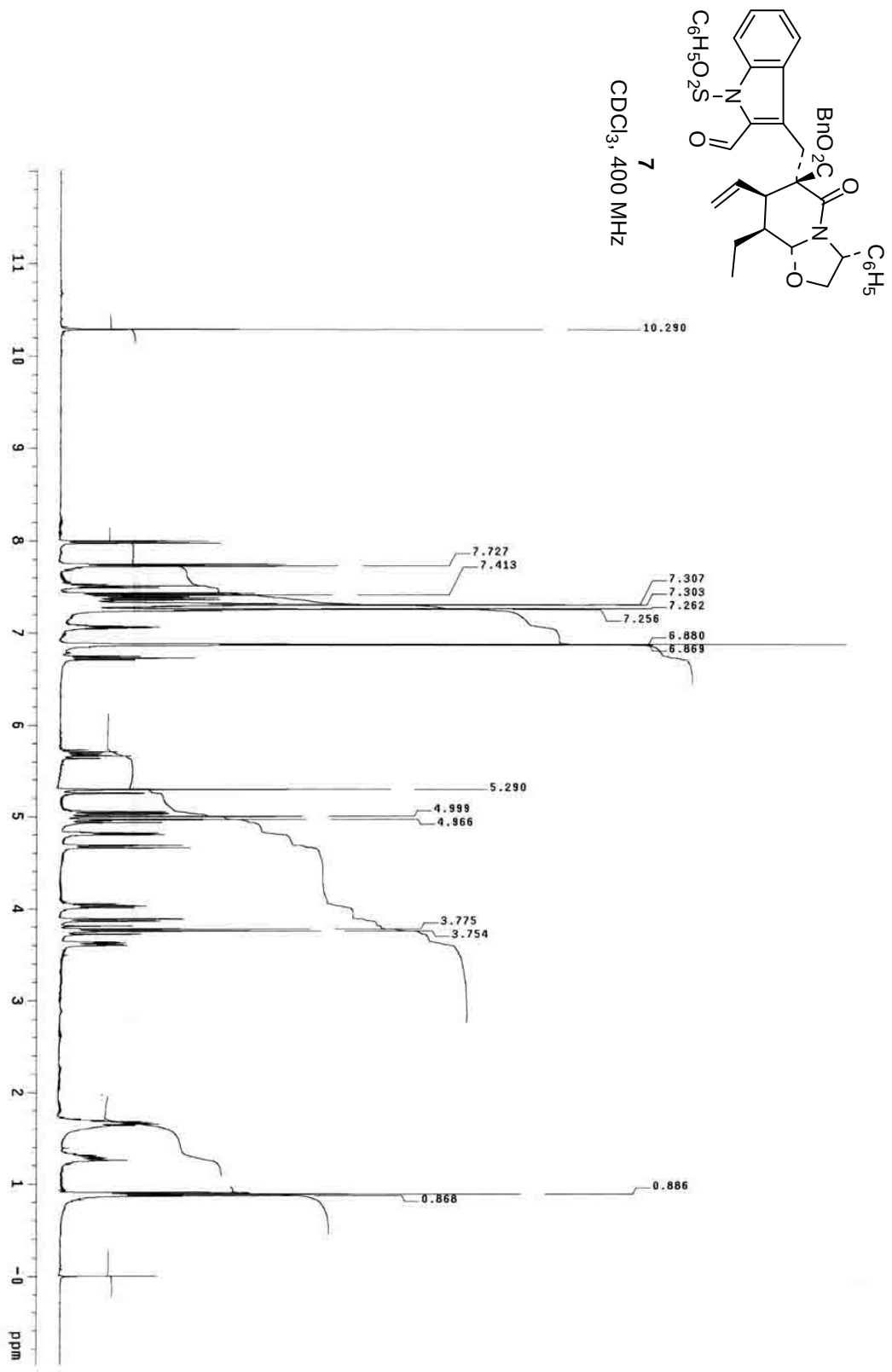

4
CDCl3, 100.6 MHz
C6H5O2S
N
BnO2C
O
CO2Et
N
O
C6H5
180
160
140
120
100
80
60
40
20
ppm
134.958
133.851
129.029
128.572
128.463
128.223
128.100
126.892
126.698
125.994
124.562
114.158
77.317
77.000
76.683
67.091
60.844
20.056
14.296
10.534

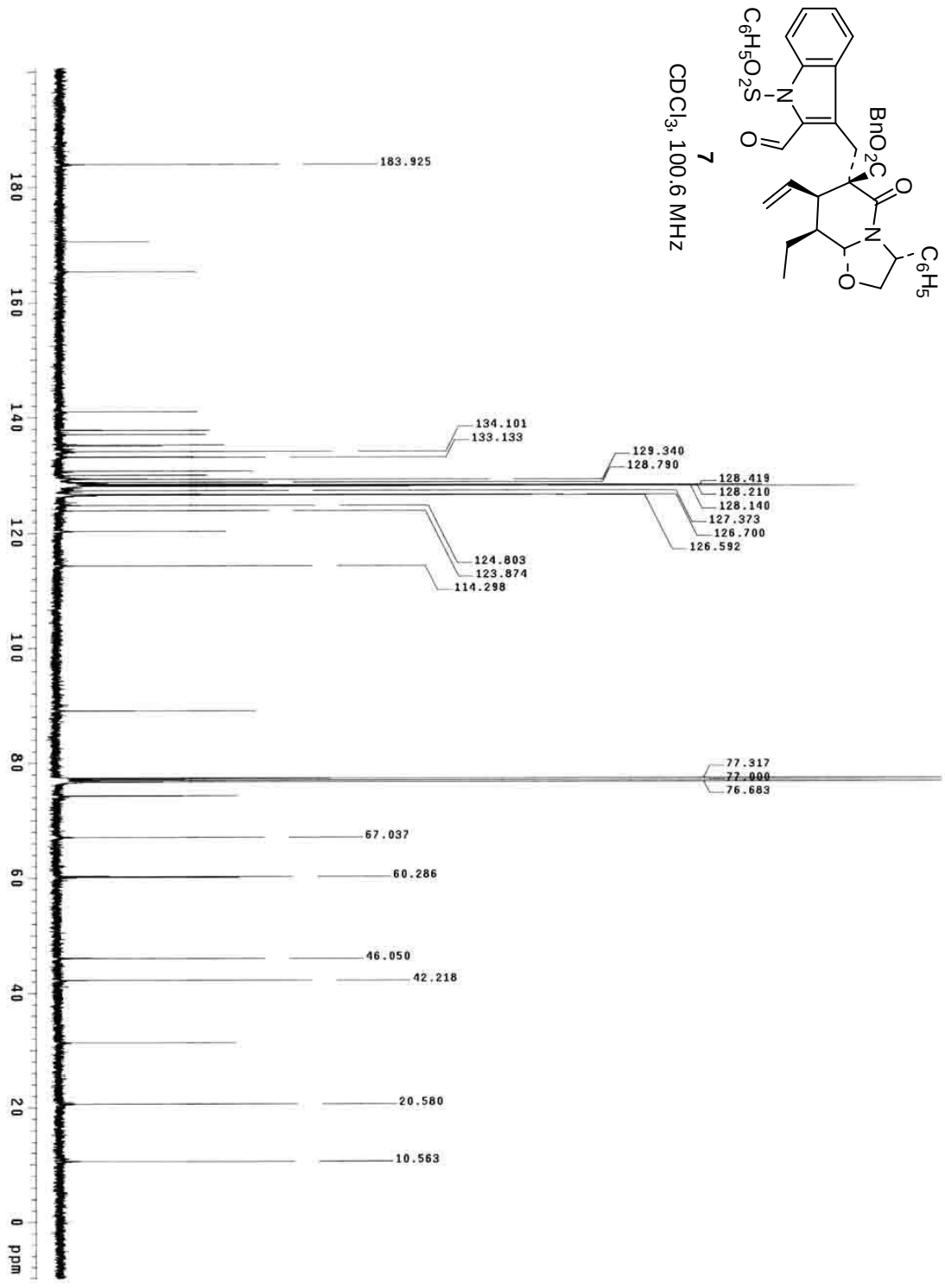

5
CDCl3, 400 MHz
C6H5O2S
BnO2C
C6H5
CO2Et
7.423
7.418
7.362
7.337
7.258
4.207
4.184
4.080
1.338
1.315
1.280
0.995
ppm

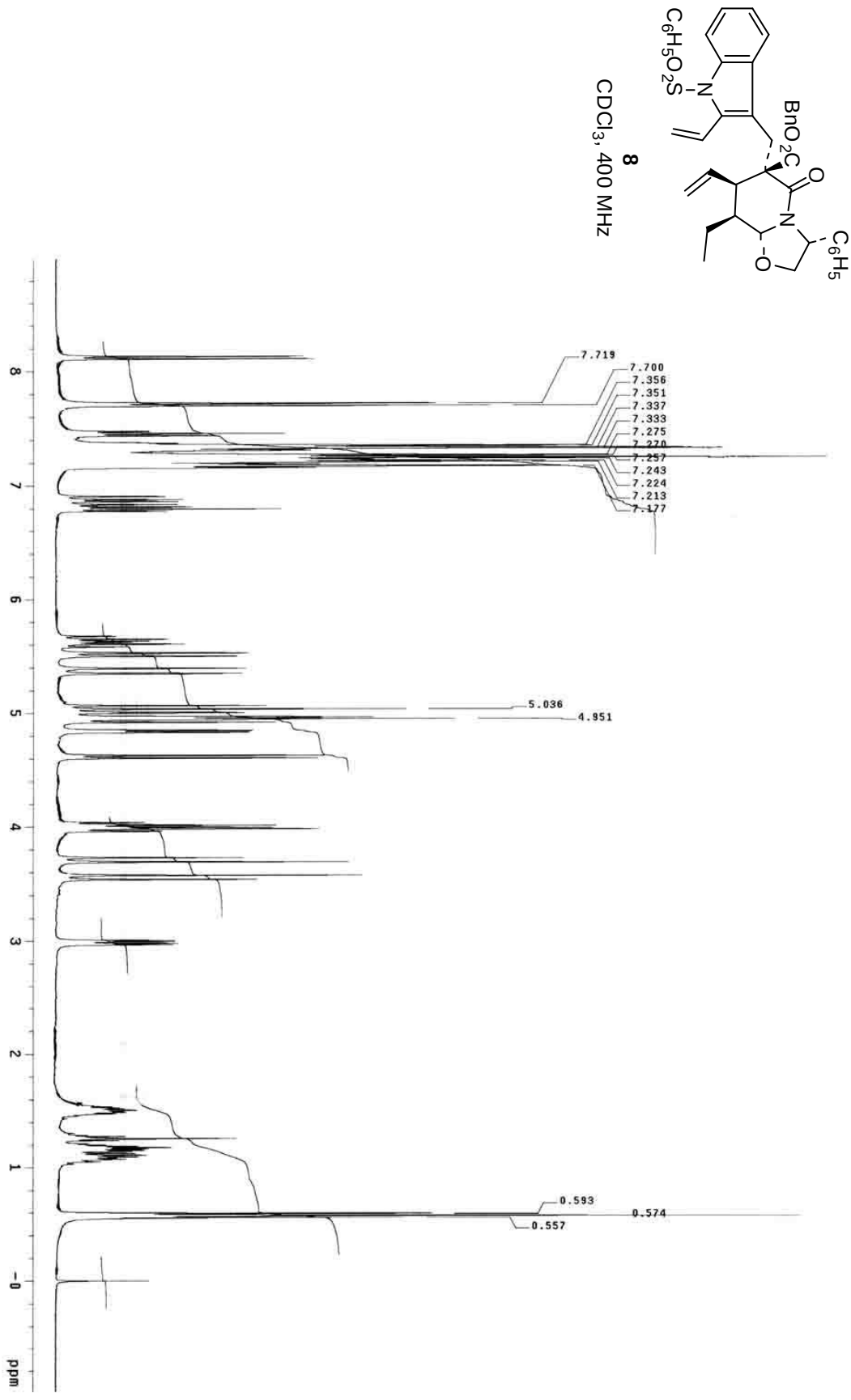

5
CDCl3, 100.6 MHz
C6H5O2S
BnO2C
C6H5
CO2Et
133.635
128.881
128.796
128.703
128.641
128.038
127.852
126.931
126.389
125.506
121.752
116.867
77.317
76.683
74.074
67.672
61.107
60.287
58.104
53.219
49.658
43.821
43.032
39.718
25.165
24.298
14.234
12.887
ppm

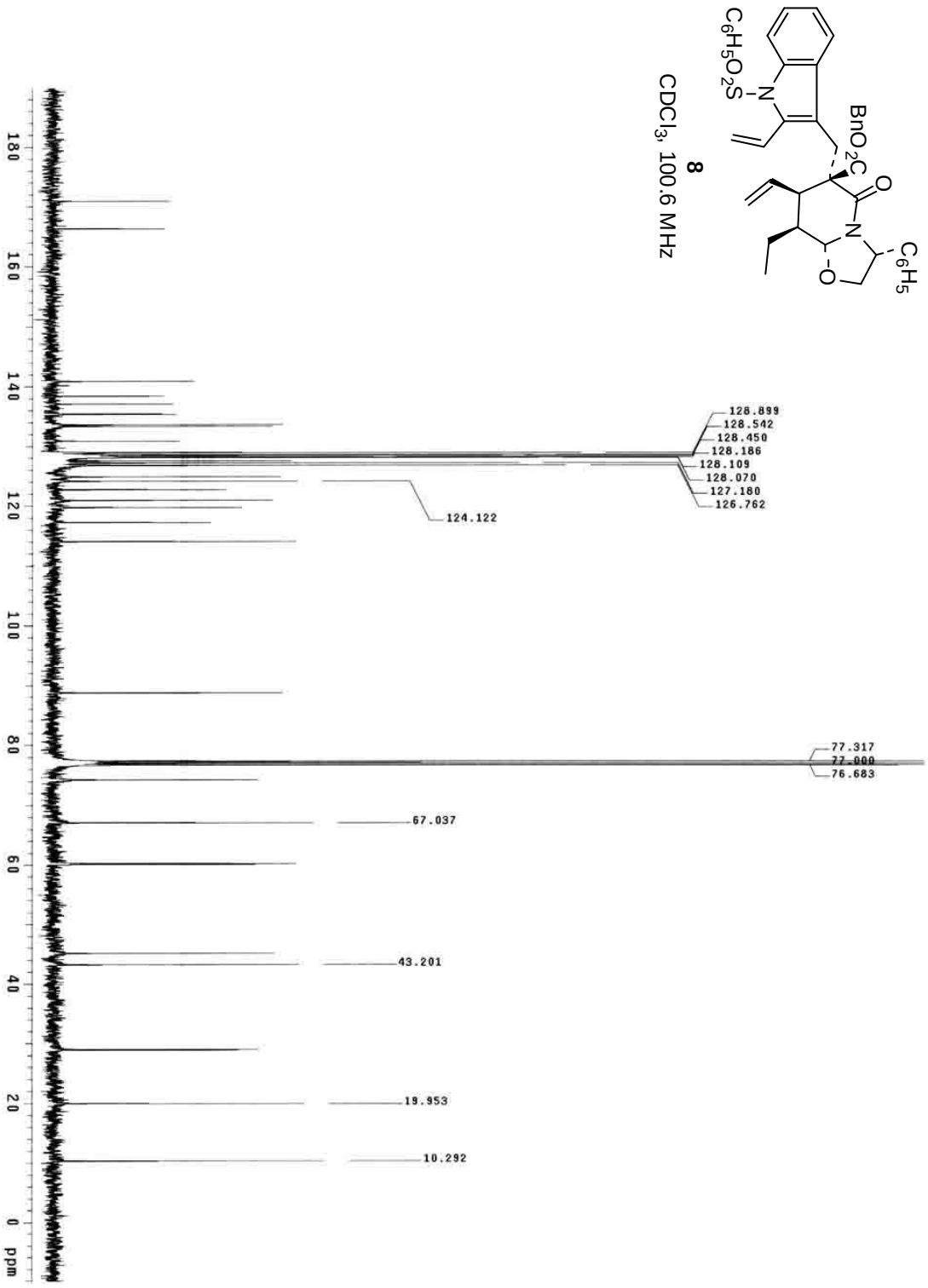

C6H5O2S
N
O
H
Br
6
CDCl3, 300 MHz
10.660
7.261
4.906
1.552
-0.000
11
10
9
8
7
6
5
4
3
2
1
-0
ppm

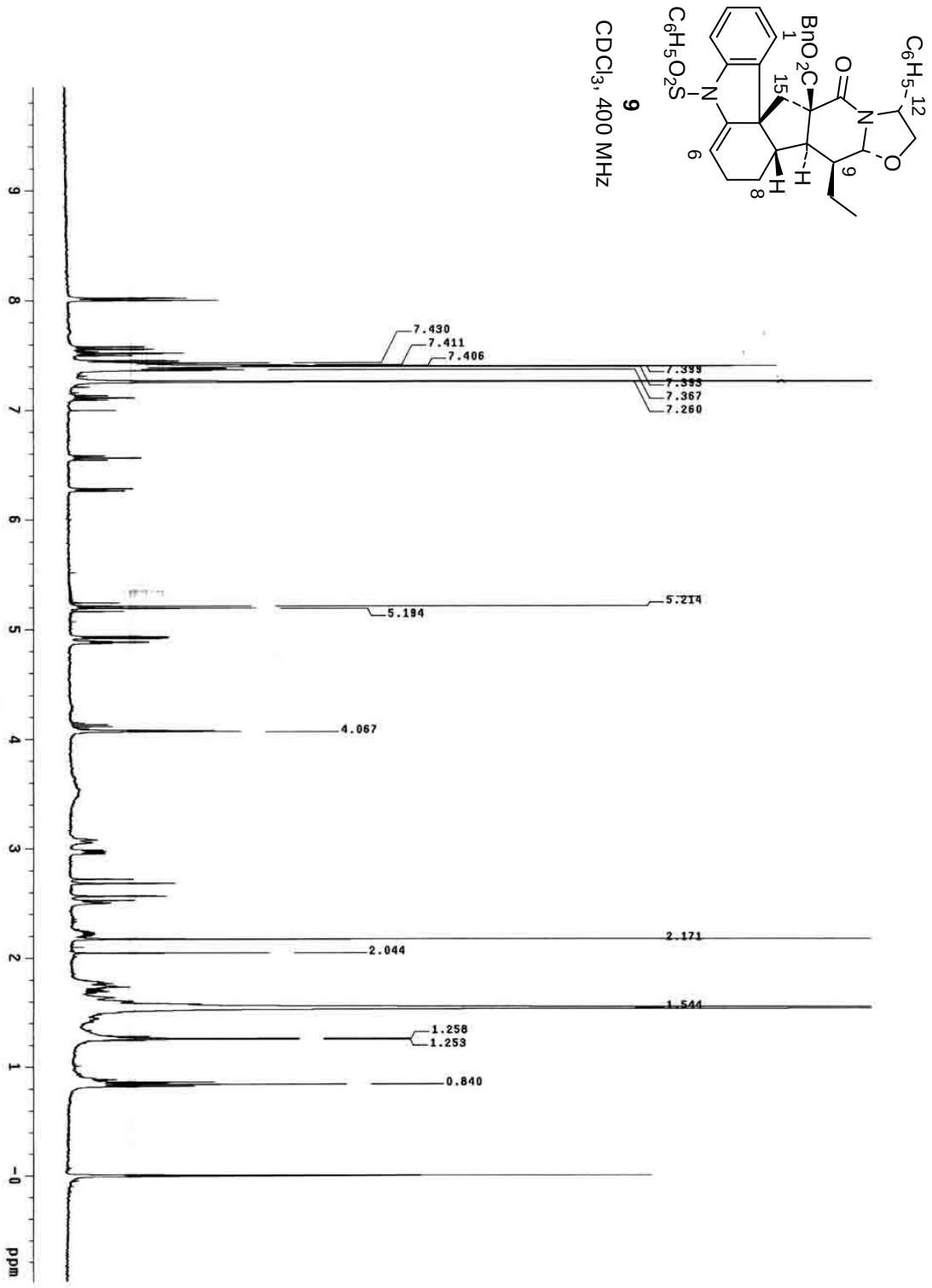

6
CDCl3, 75.4 MHz
C6H5O2S
N
O
H
Br
184.815
134.488
129.510
129.417
126.592
125.090
121.583
115.645
77.317
77.000
76.683
20.580
ppm

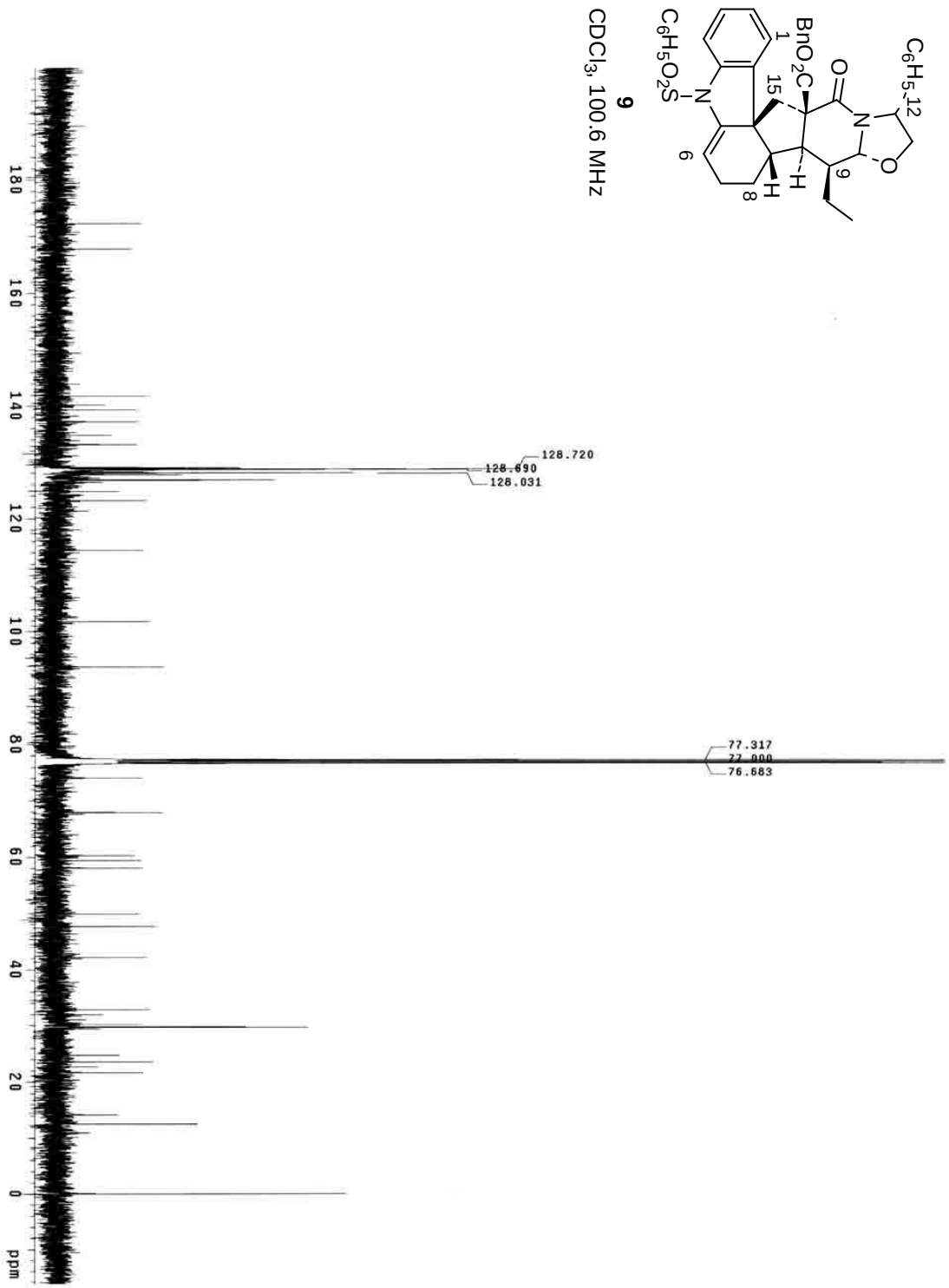

7
CDCl3, 400 MHz
C6H5O2S
N
O
BnO2C
O
N
O
C6H5
10.290
7.727
7.413
7.307
7.303
7.262
7.256
6.880
6.869
5.290
4.999
4.966
3.775
3.754
0.886
0.868
11
10
9
8
7
6
5
4
3
2
1
-0
ppm

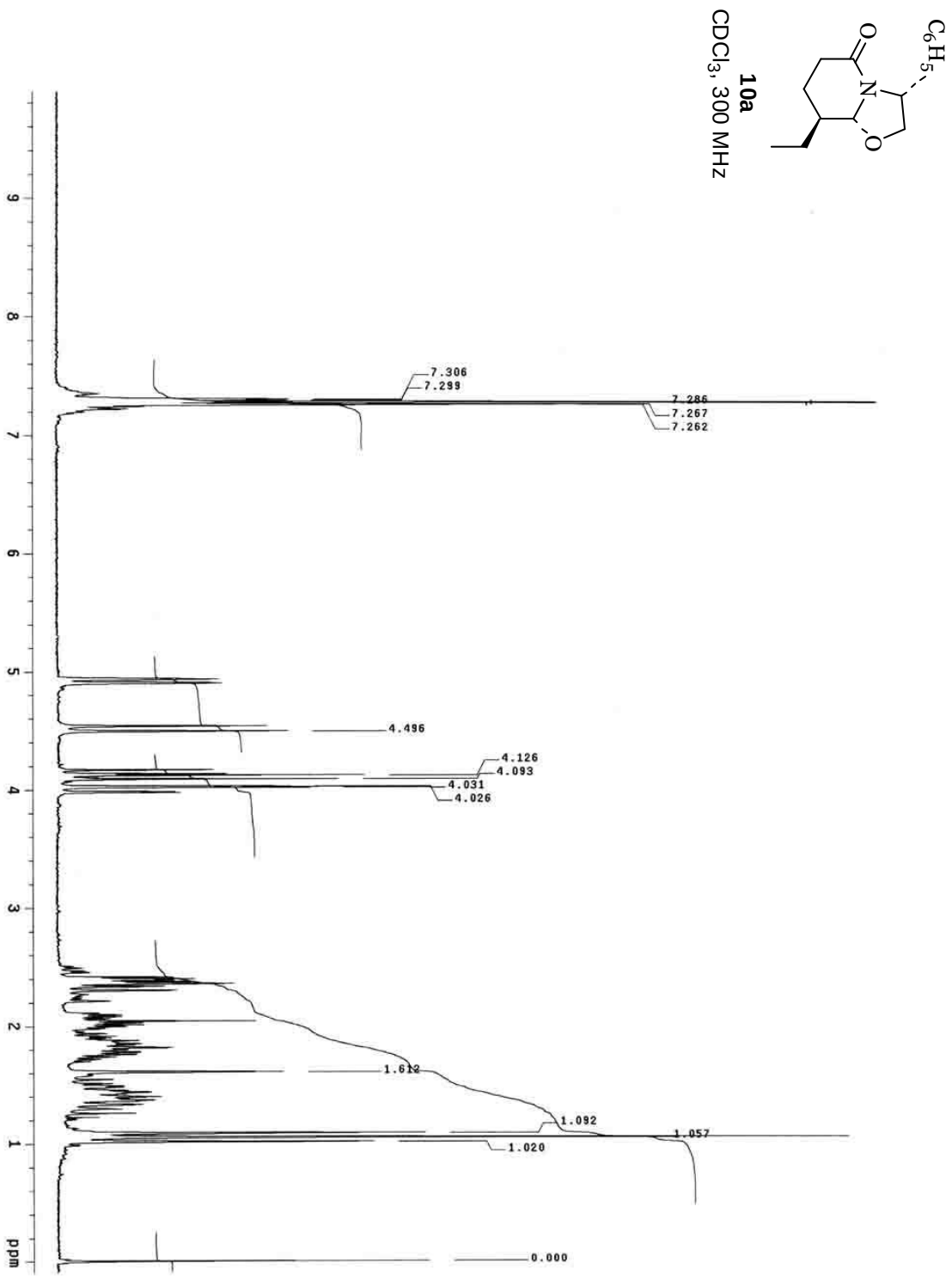

7
CDCl3, 100.6 MHz
C6H5O2S
N
O
BnO2C
O
N
O
C6H5
183.925
134.101
133.133
129.340
128.790
128.419
128.210
128.140
127.373
126.700
126.592
124.803
123.874
114.298
77.317
77.000
76.683
67.037
60.286
46.050
42.218
20.580
10.563
180
160
140
120
100
80
60
40
20
0
ppm

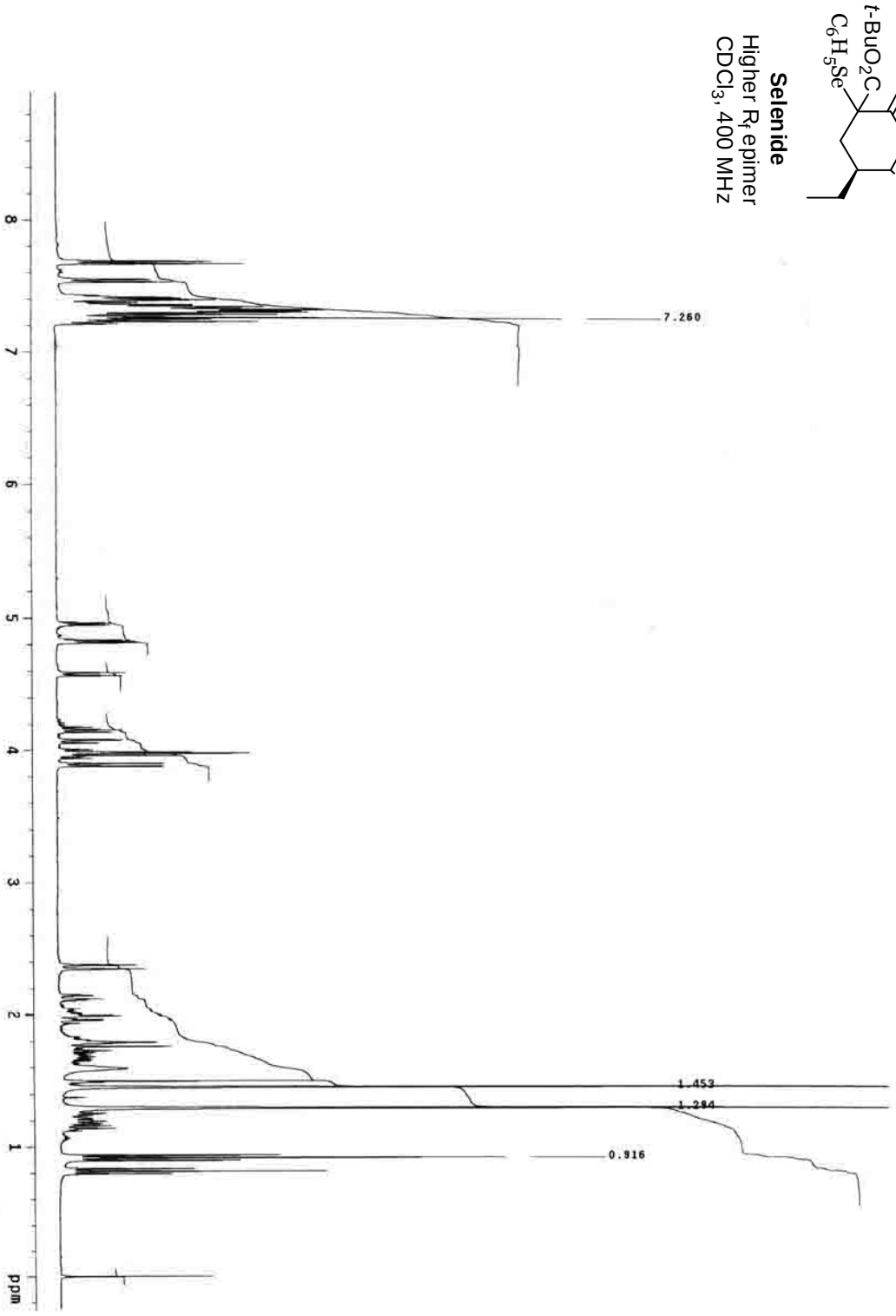

C6H5O2S
N
BnO2C
O
N
O
C6H5
8
CDCl3, 400 MHz
7.719
7.700
7.356
7.351
7.337
7.333
7.275
7.270
7.257
7.243
7.224
7.213
7.177
5.036
4.951
0.593
0.574
0.557
ppm

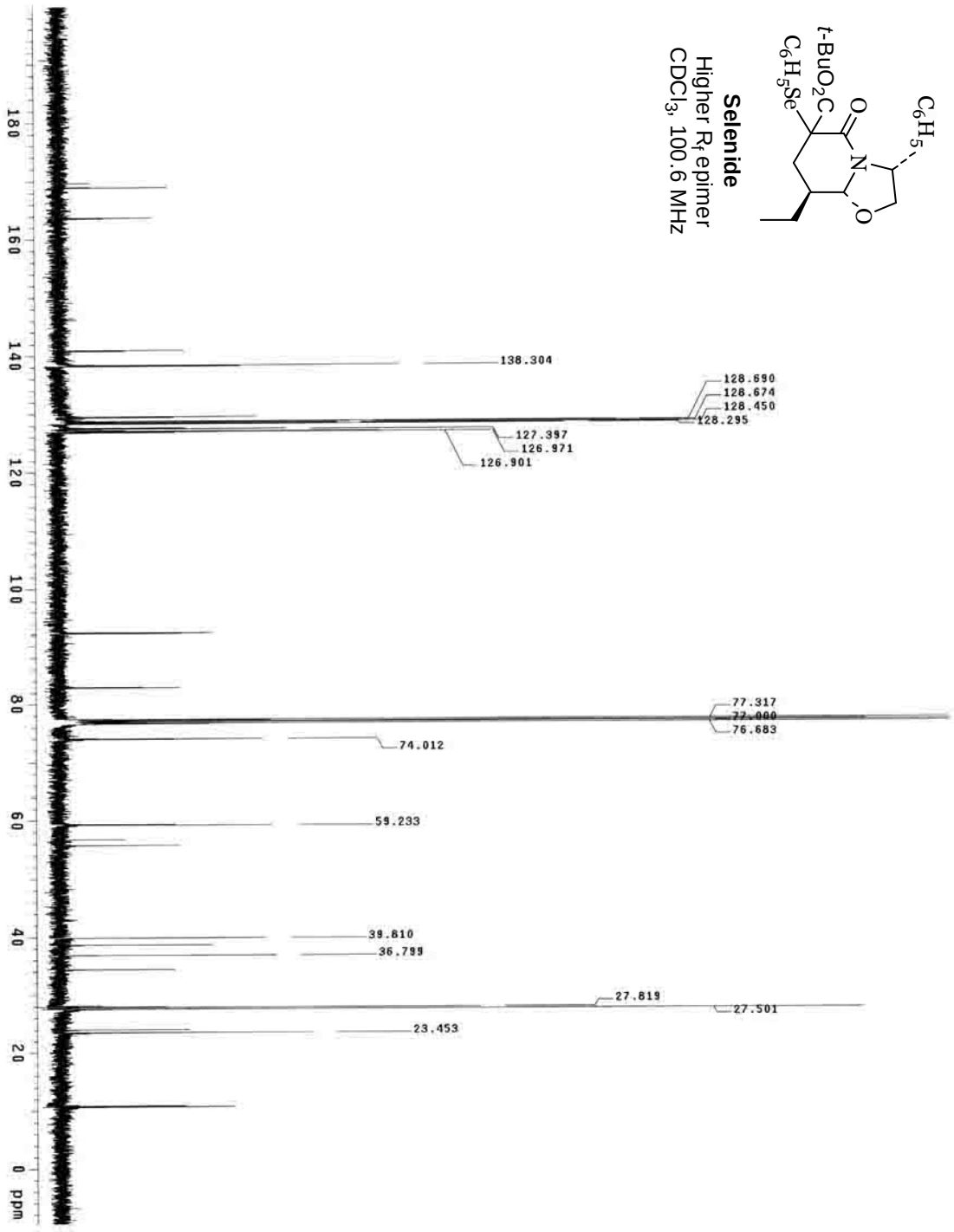

8
CDCl3, 100.6 MHz
C6H5O2S
N
BnO2C
O
N
O
C6H5
128.899
128.542
128.450
128.186
128.109
128.070
127.180
126.762
124.122
77.317
77.000
76.683
67.037
43.201
19.953
10.292
180
160
140
120
100
80
60
40
20
0
ppm

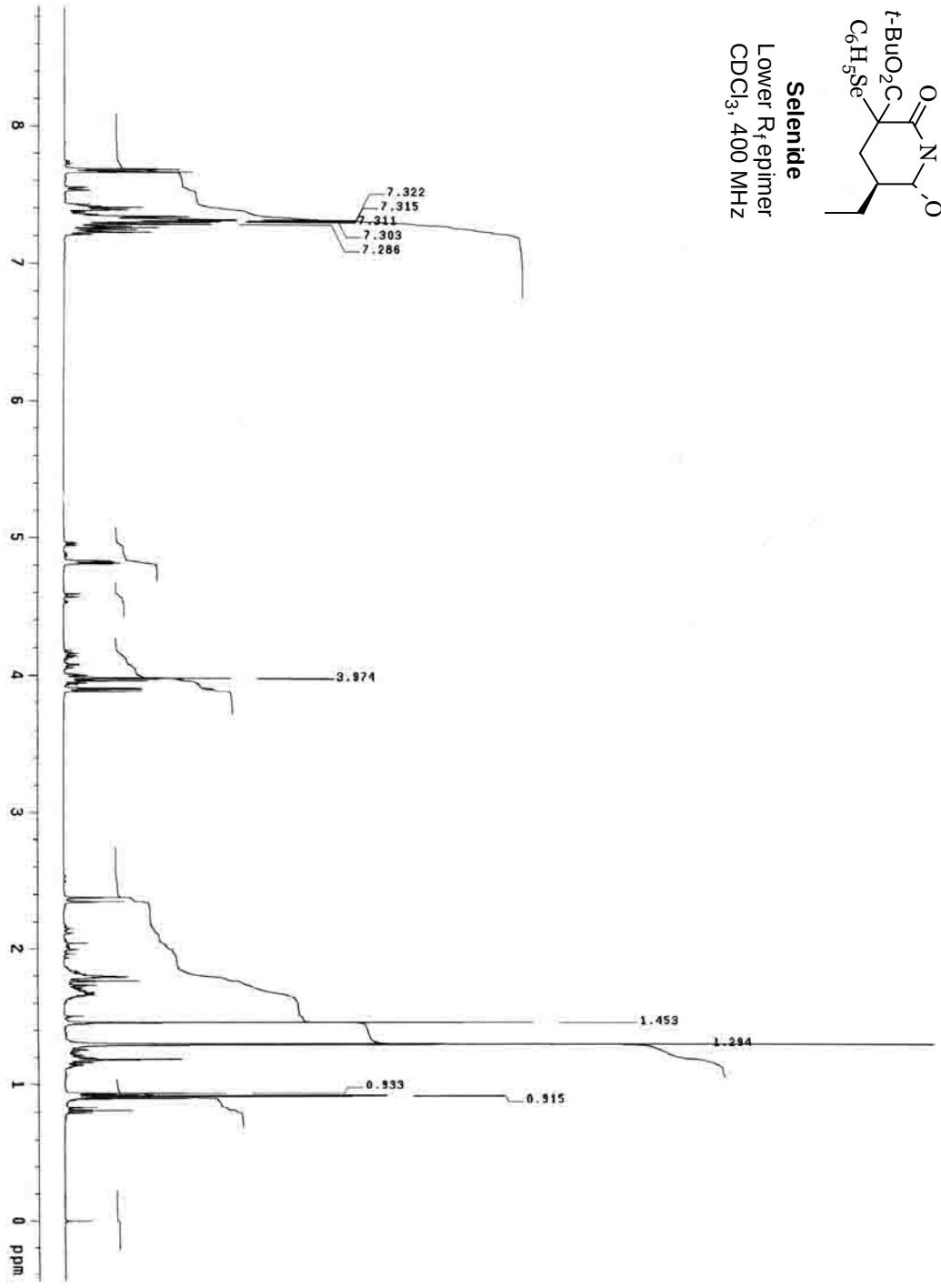

9
CDCl3, 400 MHz
C6H5O2S
BnO2C
C6H5
7.430
7.411
7.406
7.399
7.383
7.367
7.260
5.214
5.194
4.067
2.171
2.044
1.544
1.258
1.253
0.840
ppm

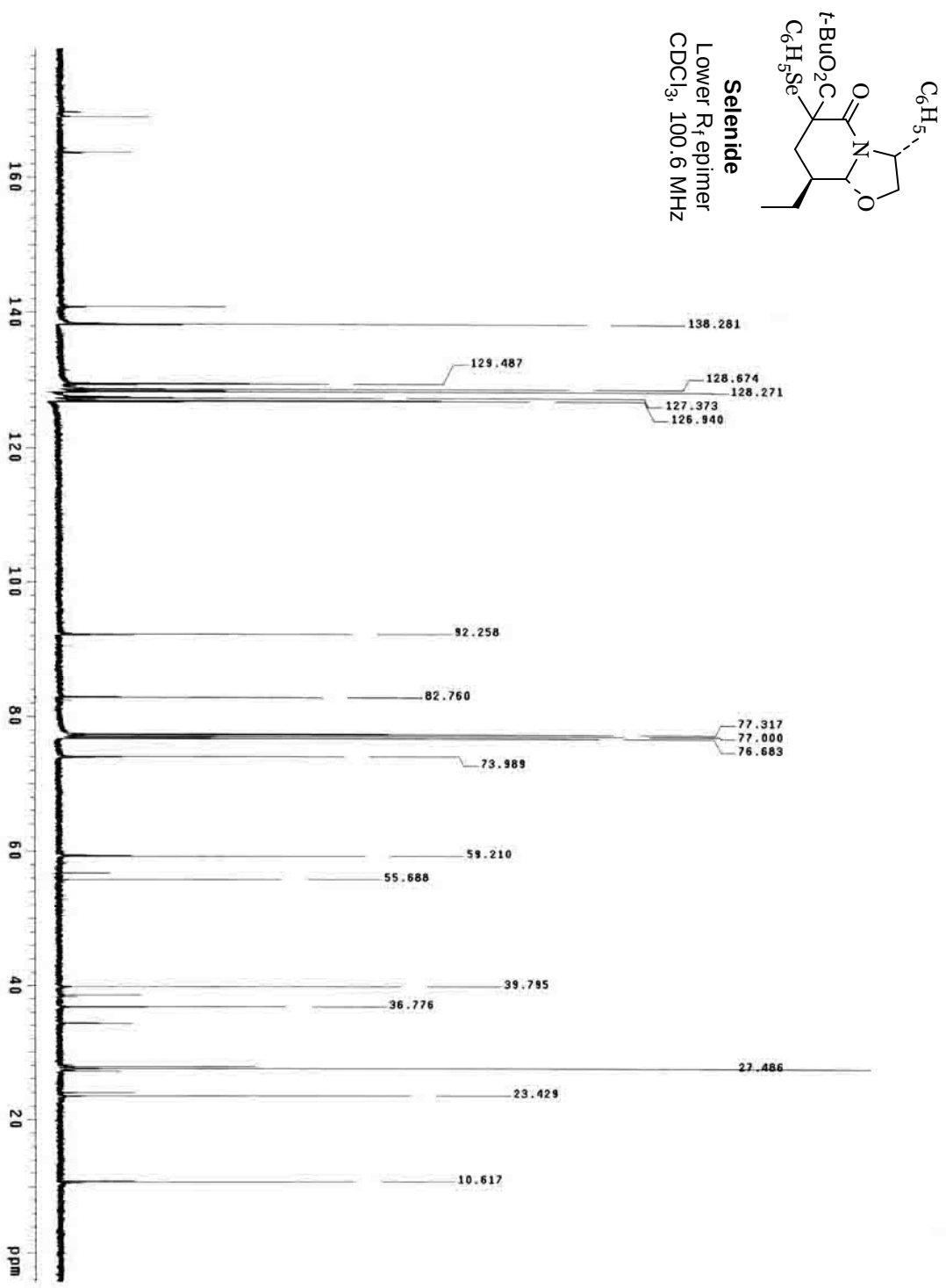

9
CDCl3, 100.6 MHz
C6H5O2S
BnO2C
C6H5
128.720
128.690
128.031
77.317
77.000
76.683
ppm


10a
CDCl3, 300 MHz
C6H5
O
N
O
7.306
7.299
7.286
7.267
7.262
4.496
4.126
4.093
4.031
4.026
1.612
1.092
1.057
1.020
0.000
ppm


C6H5
t-BuO2C
C6H5Se
O
N
O
Selenide
Higher Rf epimer
CDCl3, 400 MHz
7.260
1.453
1.284
0.916
ppm


Selenide
Higher R_f epimer
$CDCl_3$, 100.6 MHz
C_6H_5
t-BuO_2C
C_6H_5Se
O
N
O
138.304
128.690
128.674
128.450
128.295
127.397
126.971
126.901
77.317
77.000
76.683
74.012
59.233
39.810
36.799
27.819
27.501
23.453
180
160
140
120
100
80
60
40
20
0
ppm


7.322
7.315
7.311
7.303
7.286
3.874
1.453
1.294
0.933
0.915
8
7
6
5
4
3
2
1
0 ppm
Selenide
Lower R_f epimer
$CDCl_3$, 400 MHz
C_6H_5
t-BuO_2C
C_6H_5Se
O
N
O


Seleride
Lower R_f epimer
$CDCl_3$, 100.6 MHz
C_6H_5Se
t-BuO_2C
O
N
O
C_6H_5
138.281
129.487
128.674
128.271
127.373
126.940
92.258
82.760
77.317
77.000
76.683
73.989
59.210
55.688
39.795
36.776
27.486
23.429
10.617
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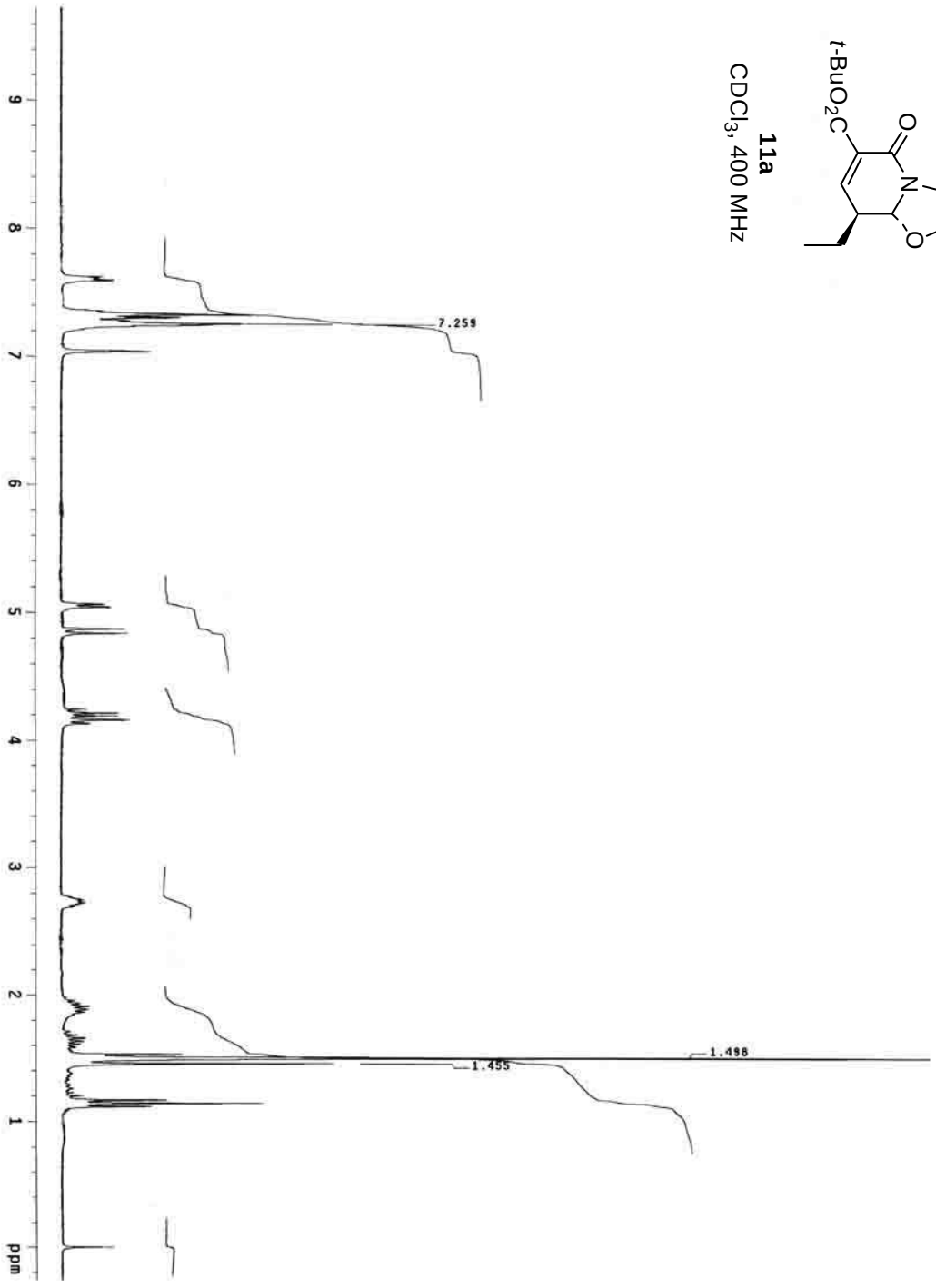
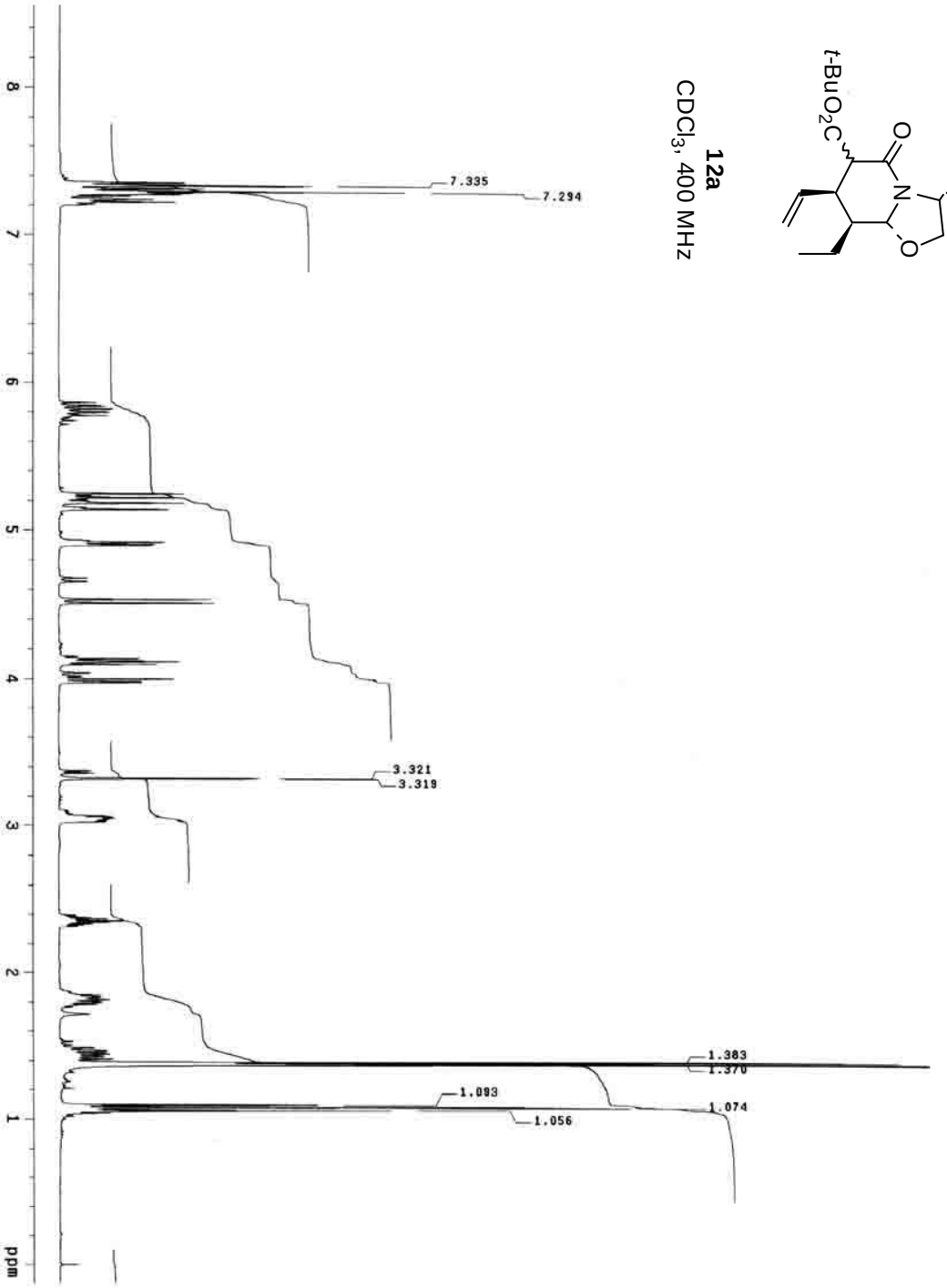
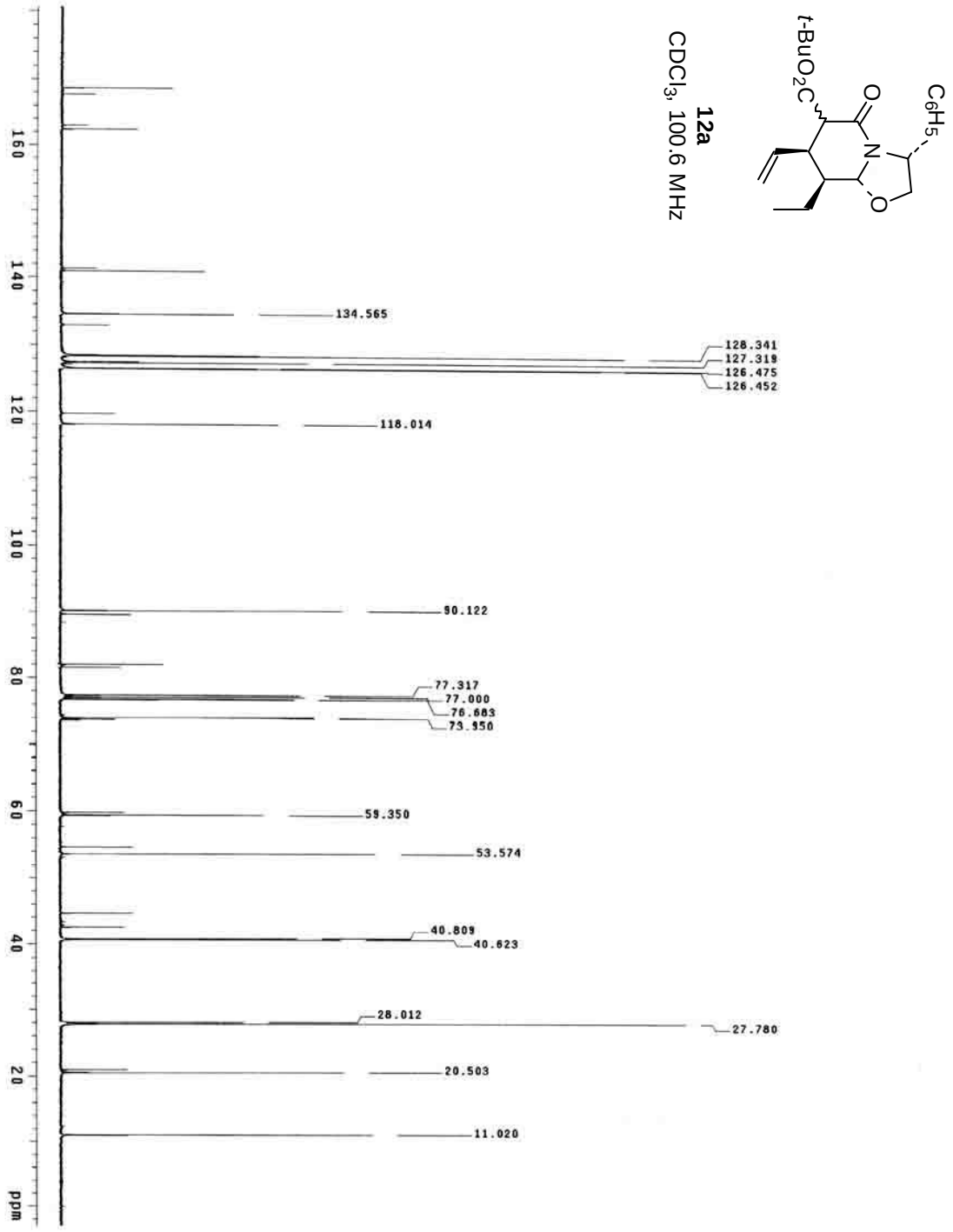
140
120
100
80
60
40
20
ppm


t-BuO2C
C6H5
O
N
O
11a
CDCl3, 400 MHz
7.259
1.498
1.455
ppm


12a
CDCl3, 400 MHz
t-BuO2C
C6H5
7.335
7.294
3.321
3.319
1.383
1.370
1.093
1.074
1.056
ppm


12a
CDCl3, 100.6 MHz
t-BuO2C
C6H5
O
N
O
160
140
120
100
80
60
40
20
ppm
134.565
128.341
127.319
126.475
126.452
118.014
90.122
77.317
77.000
76.683
73.950
59.350
53.574
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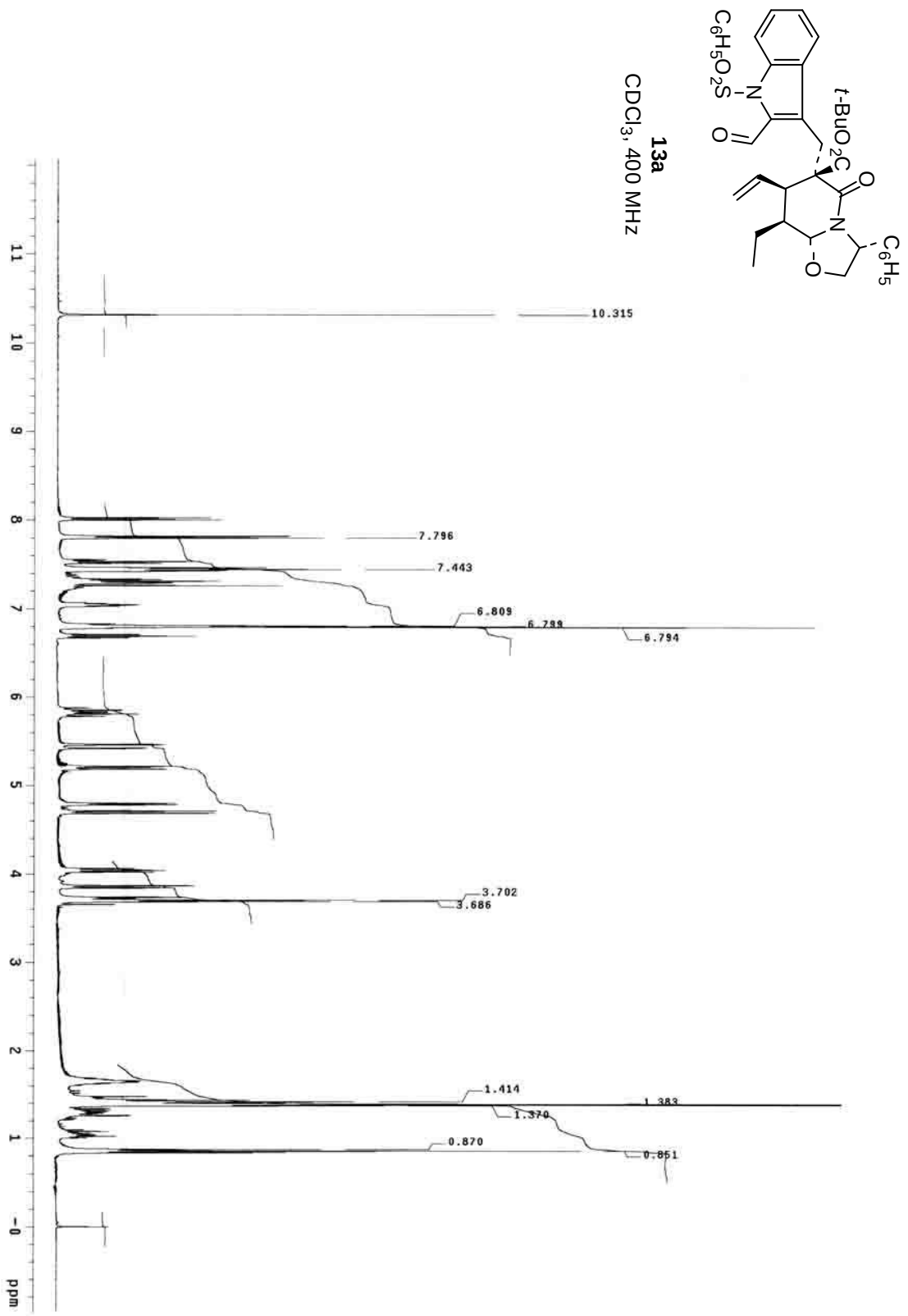
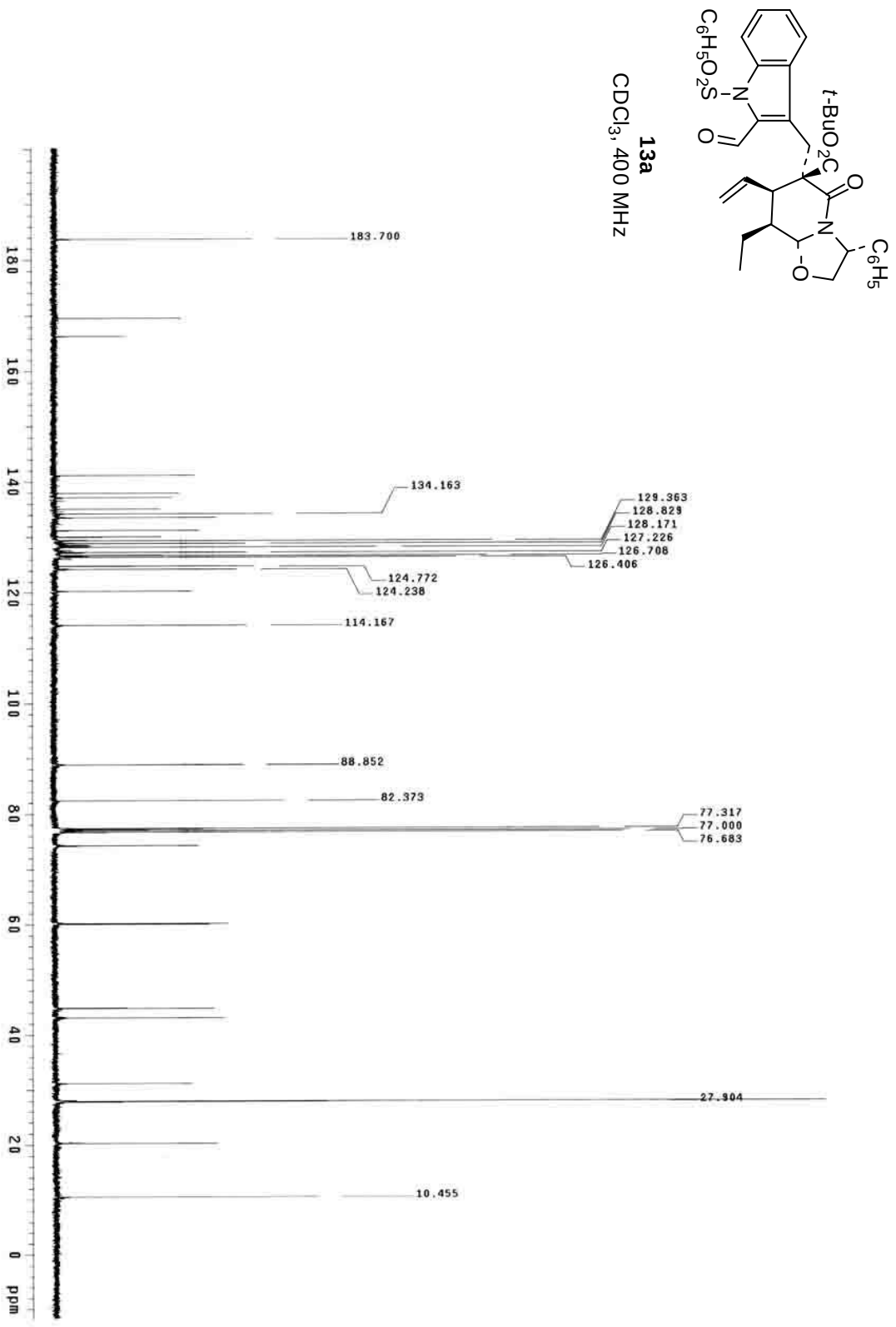
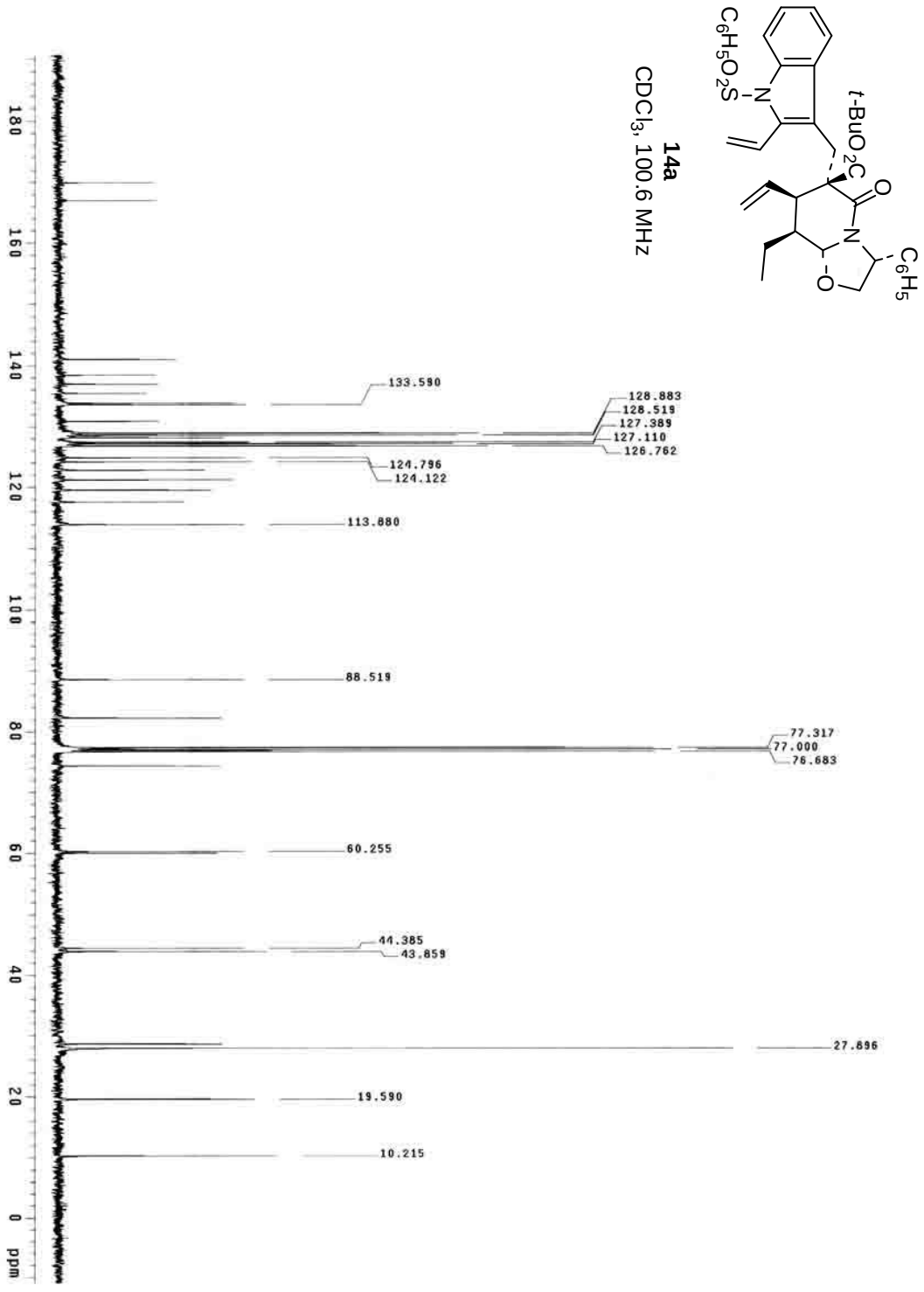
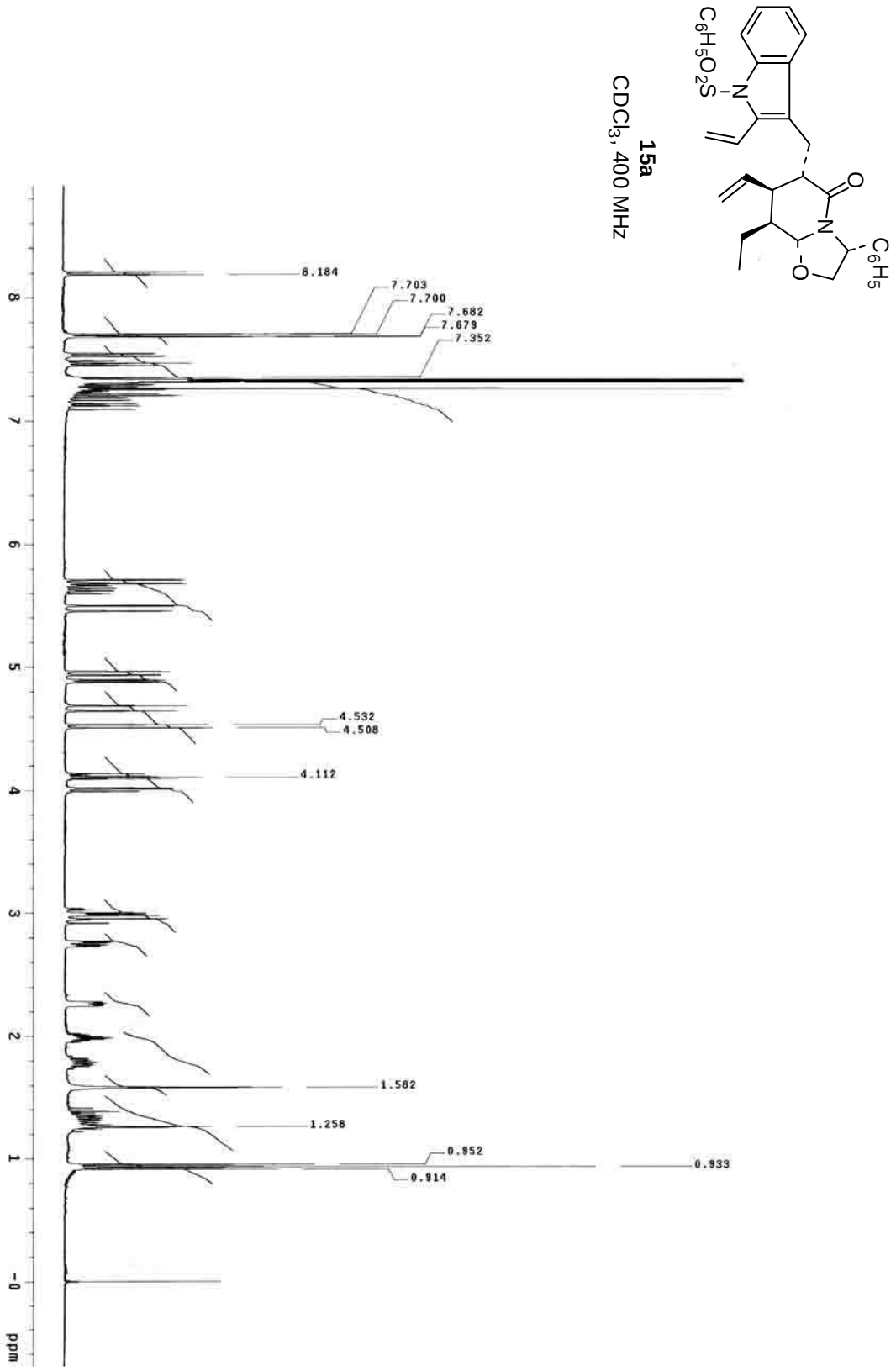
40.623
28.012
27.780
20.503
11.020

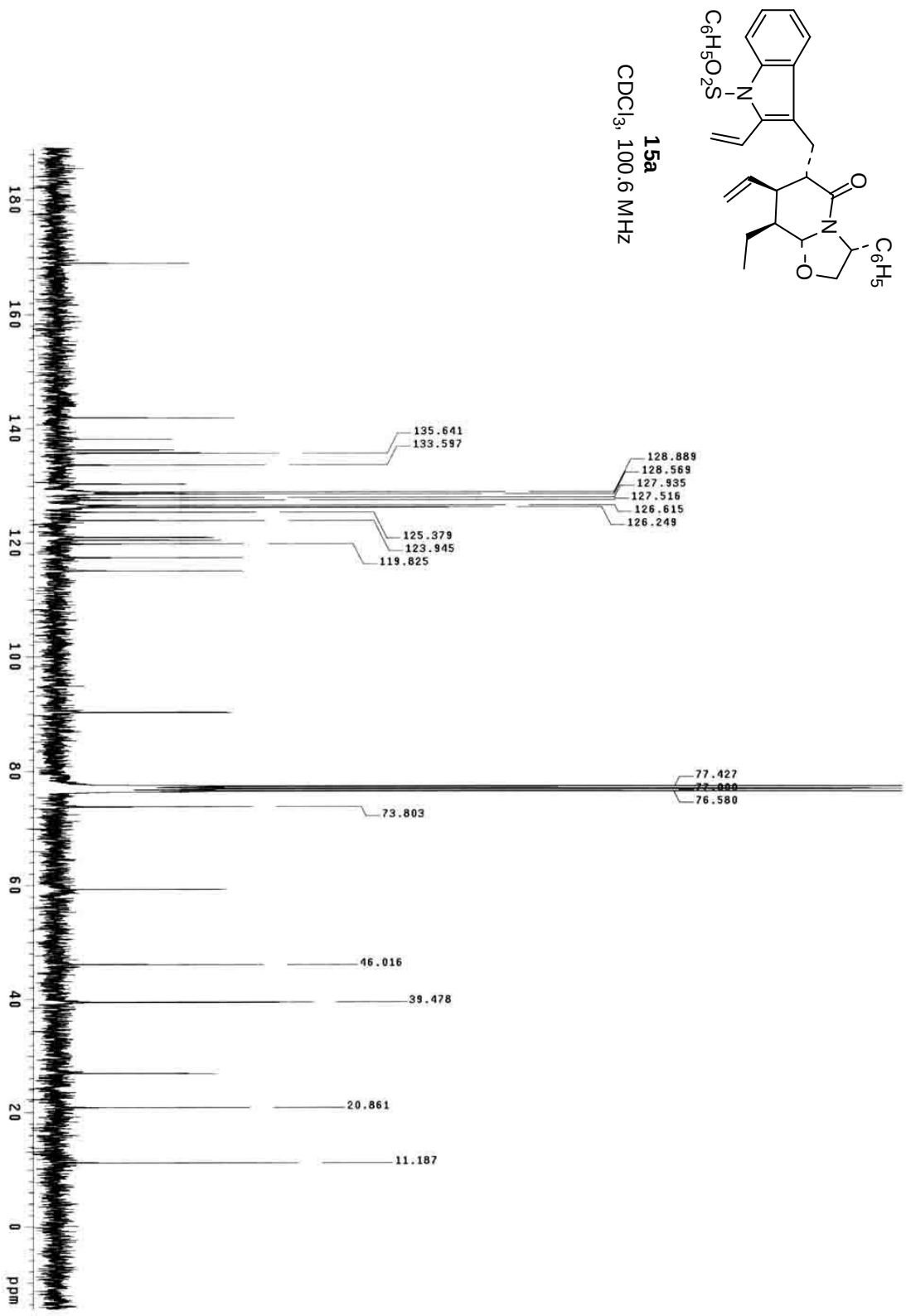

13a
CDCl3, 400 MHz
10.315
7.796
7.443
6.809
6.799
6.794
3.702
3.686
1.414
1.383
1.370
0.870
0.851
ppm


13a
CDCl3, 400 MHz
C6H5O2S
N
O
t-BuO2C
O
N
O
C6H5
183.700
134.163
129.363
128.829
128.171
127.226
126.708
126.406
124.772
124.238
114.167
88.852
82.373
77.317
77.000
76.683
27.904
10.455
180
160
140
120
100
80
60
40
20
0
ppm


14a
CDCl3, 400 MHz
C6H5O2S
N
t-BuO2C
O
N
O
C6H5
8.111
7.734
7.731
7.713
7.709
7.354
7.334
7.260
7.236
7.191
7.143
7.140
7.123
5.120
3.622
3.535
1.409
1.255
0.587
0.569
0.550
ppm


14a
CDCl3, 100.6 MHz
C6H5O2S
N
t-BuO2C
O
N
O
C6H5
133.580
128.883
128.519
127.389
127.110
126.762
124.796
124.122
113.880
88.519
77.317
77.000
76.683
60.255
44.385
43.859
27.696
19.590
10.215
180
160
140
120
100
80
60
40
20
0
ppm


15a
CDCl3, 400 MHz
C6H5O2S
N
O
N
O
C6H5
8.184
7.703
7.700
7.682
7.679
7.352
4.532
4.508
4.112
1.582
1.258
0.952
0.914
0.933
ppm


15a
CDCl3, 100.6 MHz
C6H5O2S
N
O
N
O
C6H5
135.641
133.597
128.889
128.569
127.935
127.516
126.615
126.249
125.379
123.945
119.825
77.427
77.088
76.580
73.803
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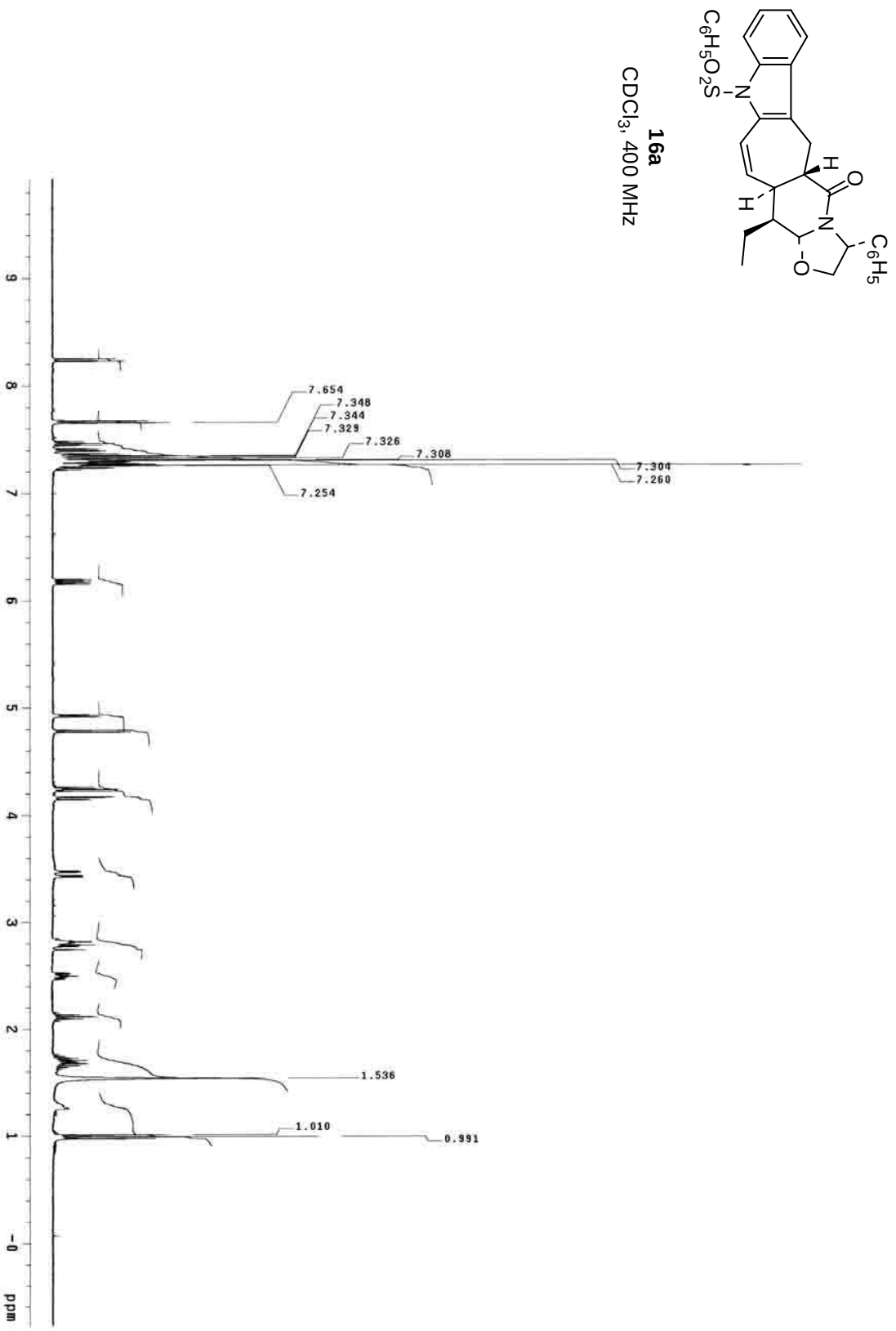
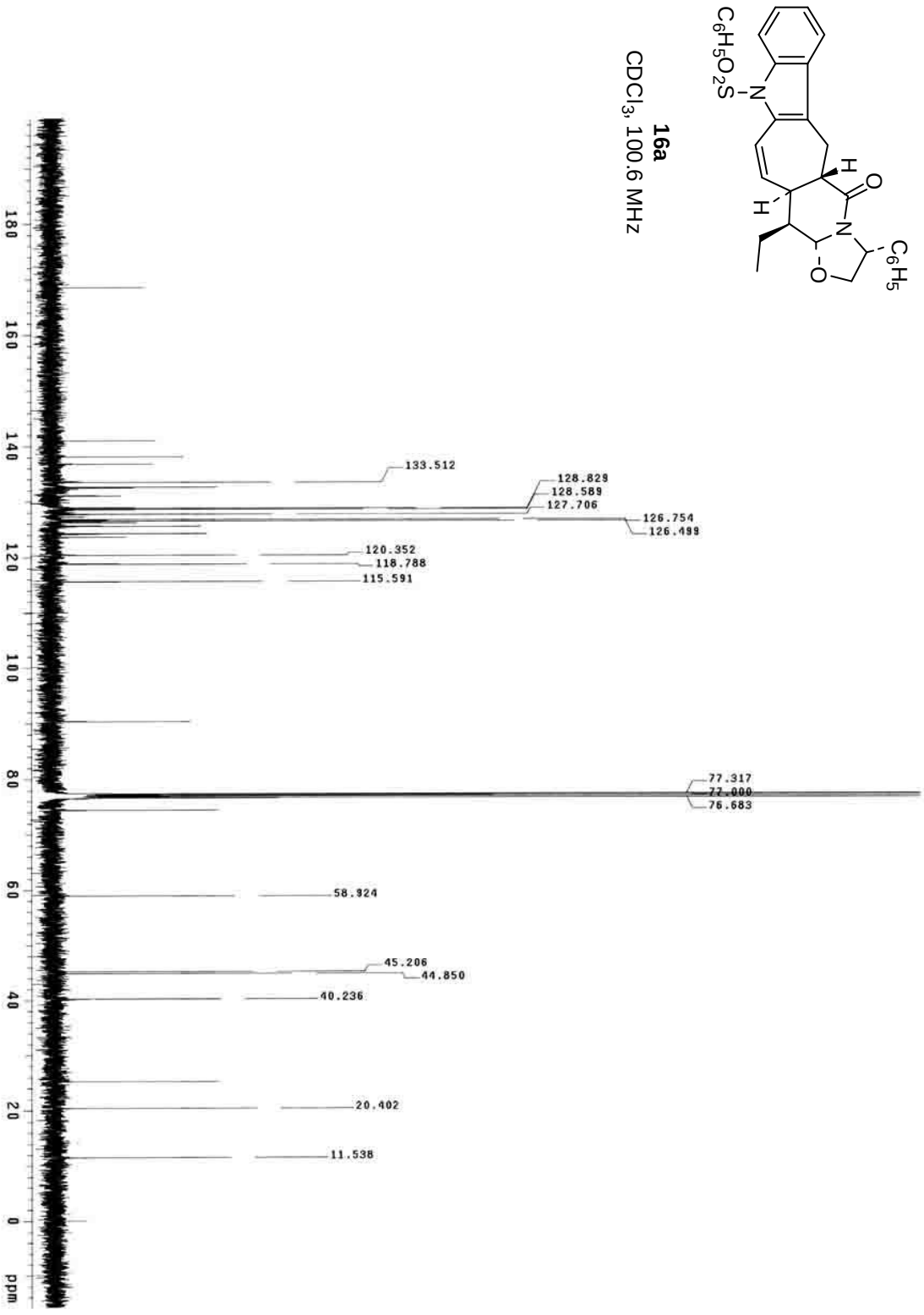
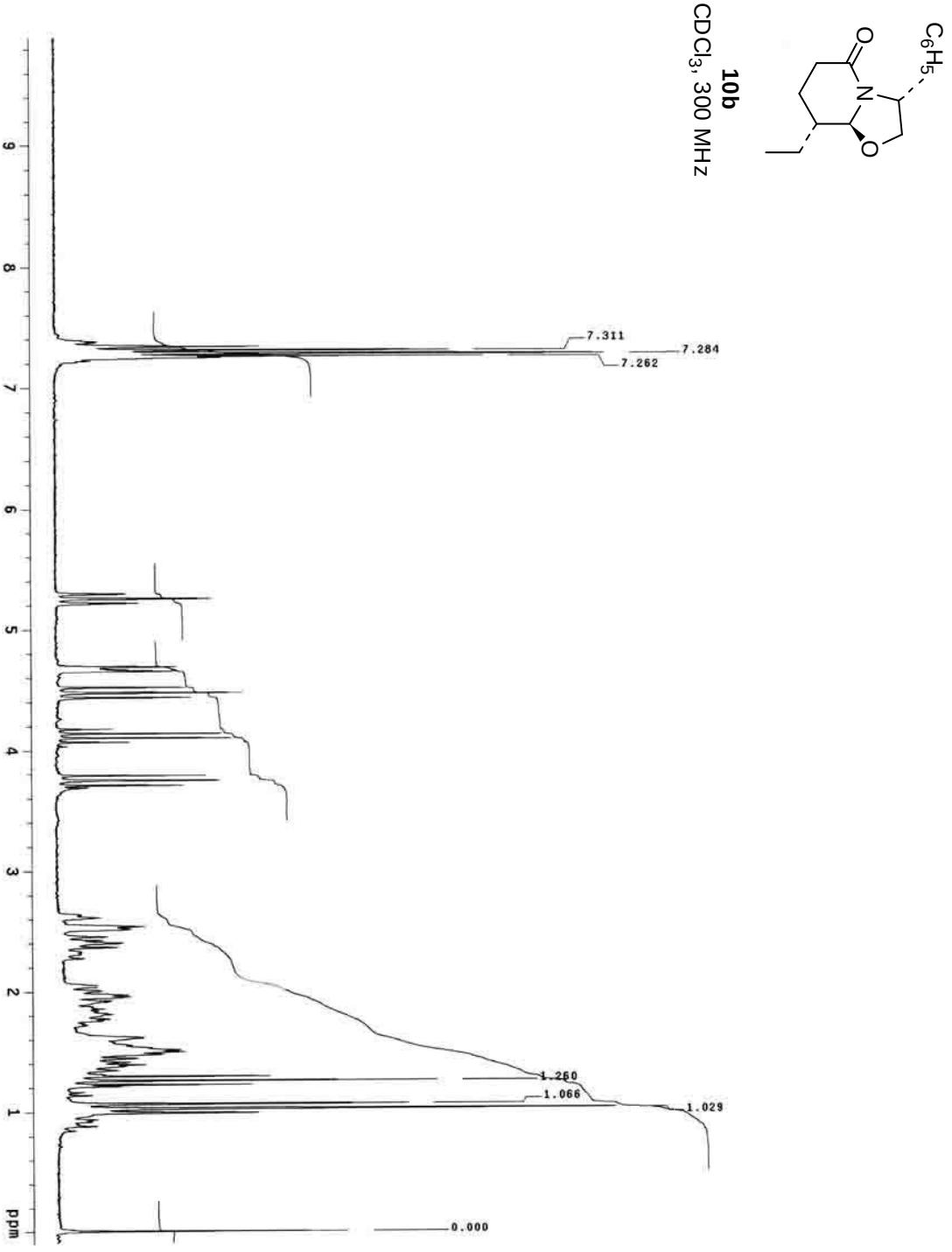
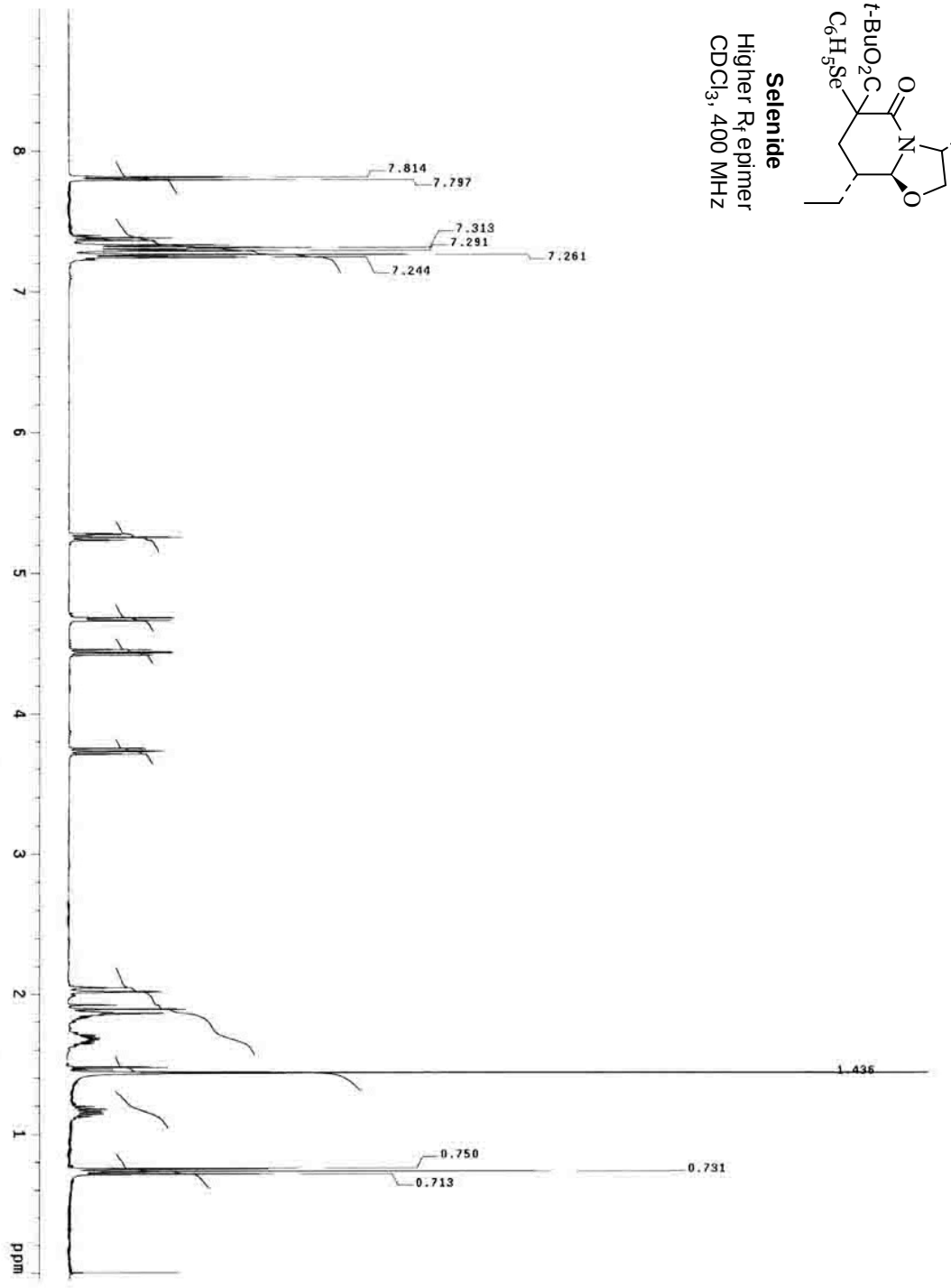
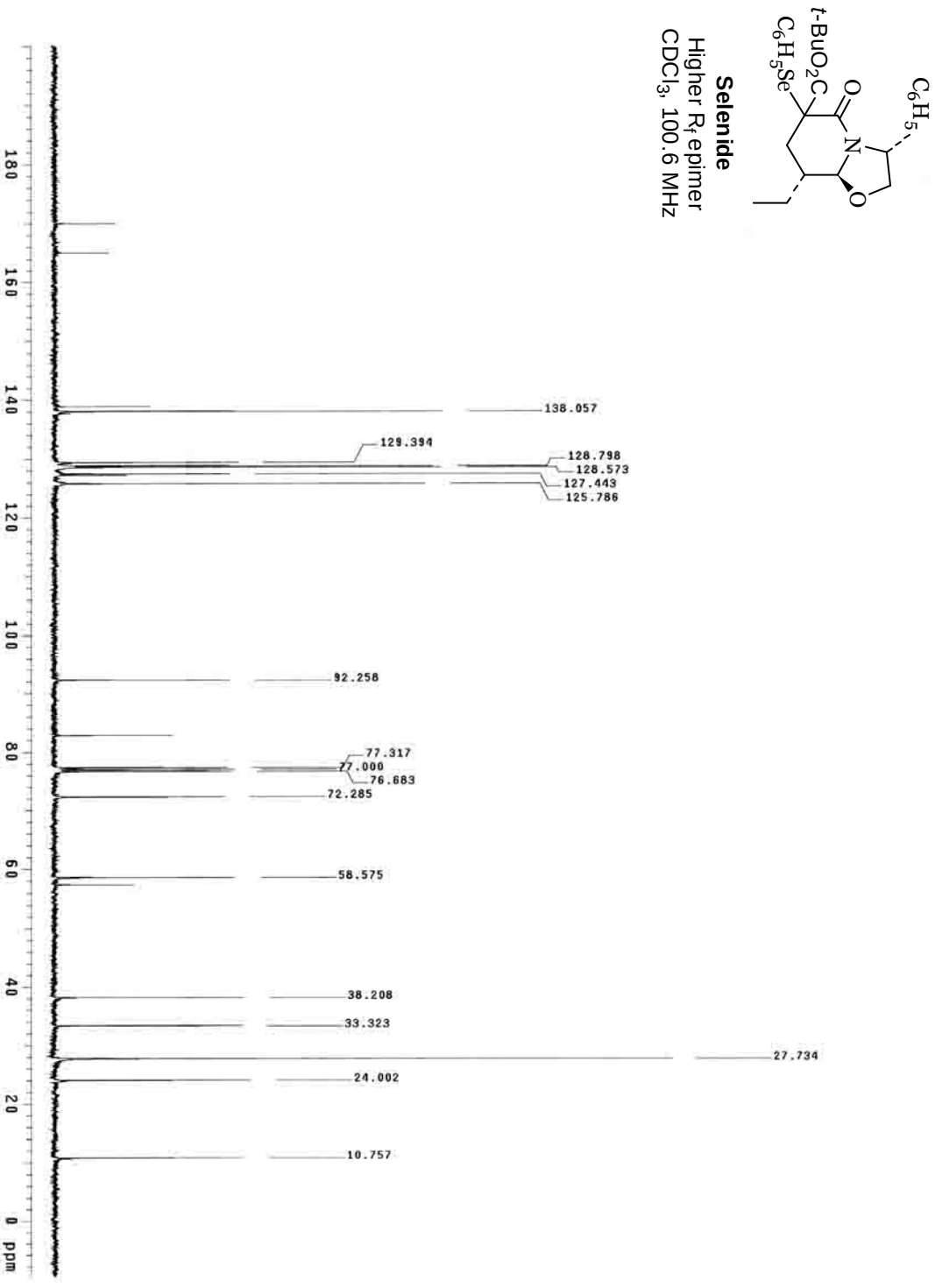
39.478
20.861
11.187
180
160
140
120
100
80
60
40
20
0
ppm

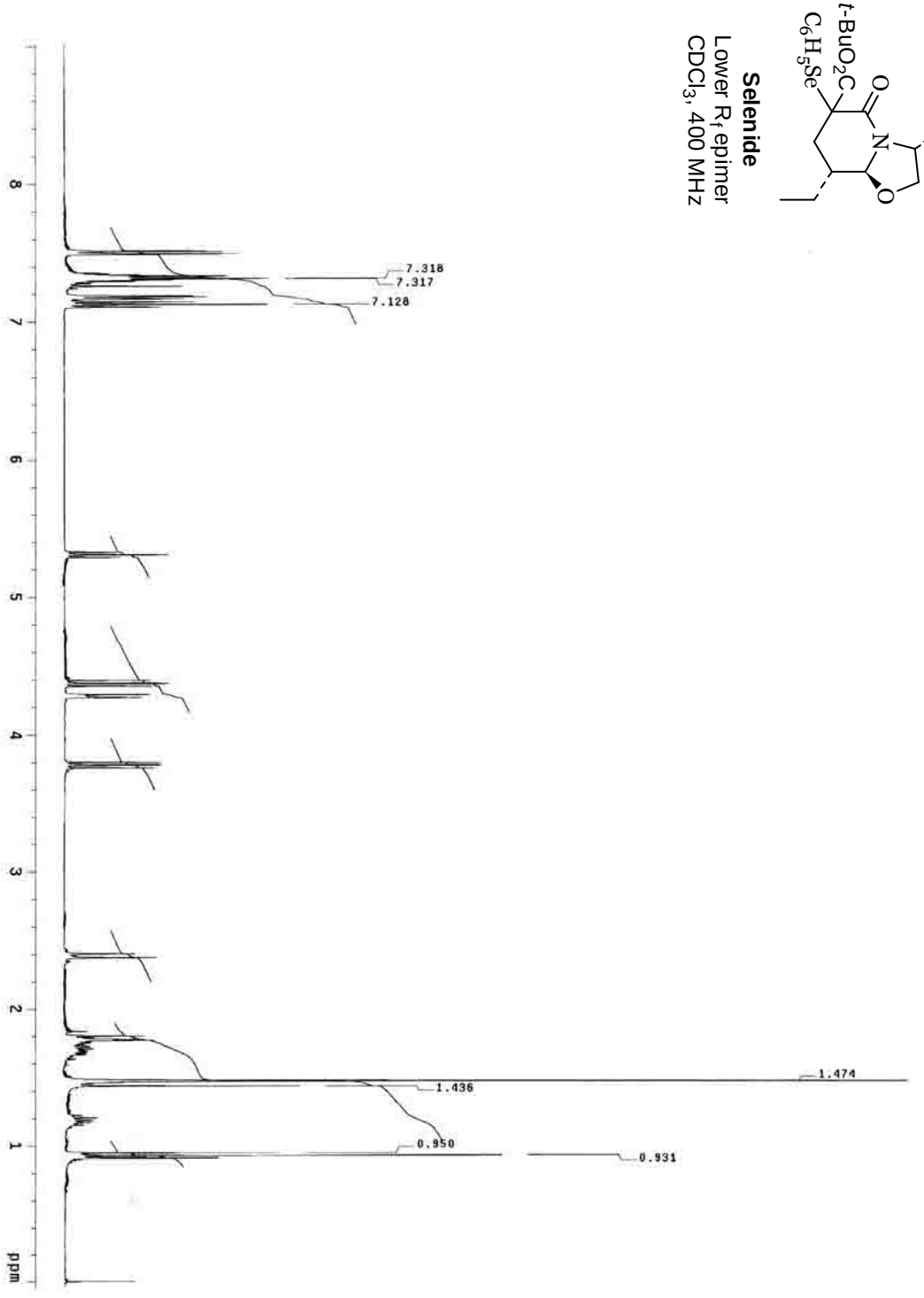

16a
CDCl3, 400 MHz
C6H5O2S
N
H
H
O
N
O
C6H5
9
8
7
6
5
4
3
2
1
0
ppm
7.654
7.348
7.344
7.329
7.326
7.308
7.304
7.260
7.254
1.536
1.010
0.991

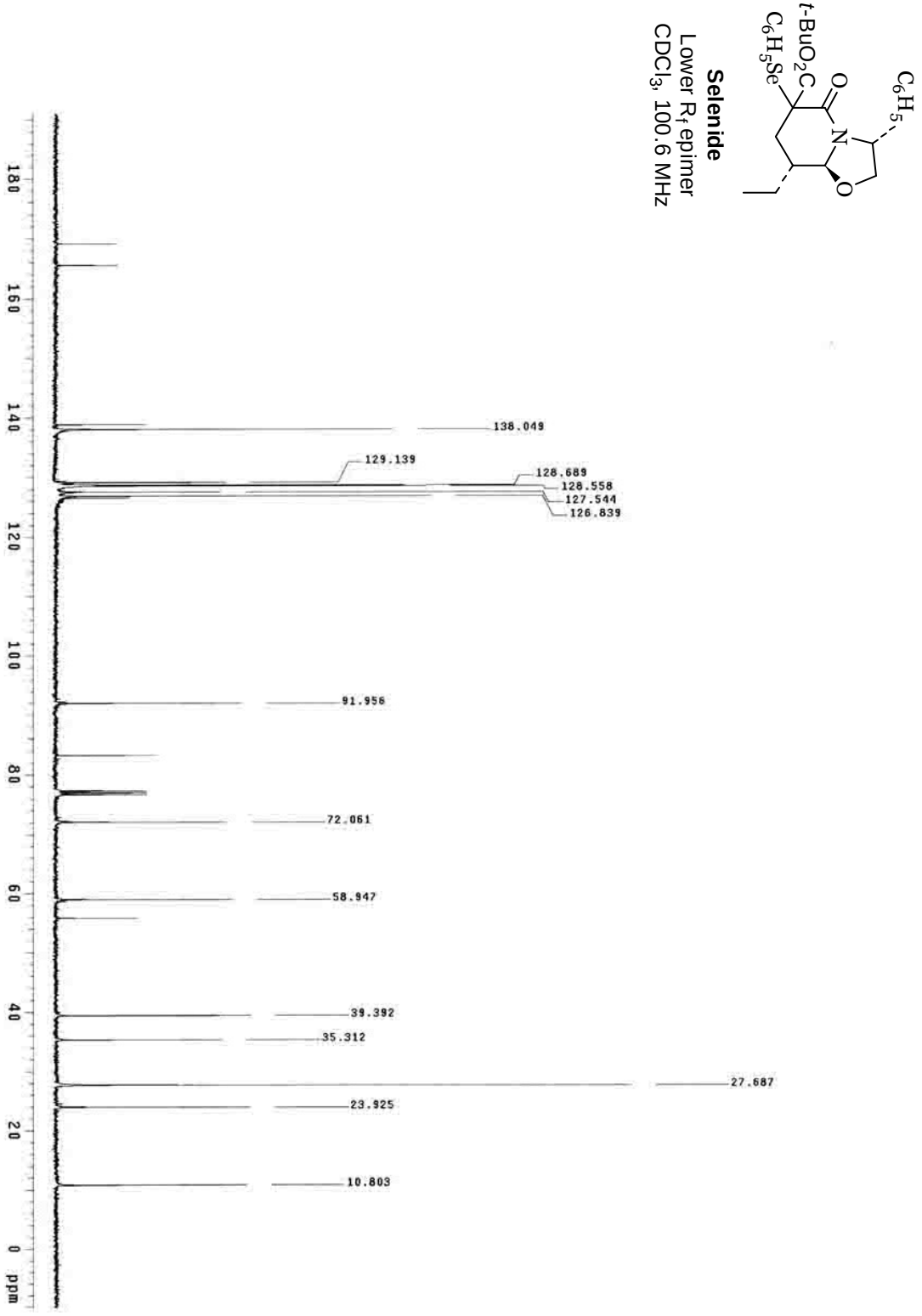

16a
CDCl3, 100.6 MHz
C6H5O2S
N
H
H
O
N
O
C6H5
133.512
128.829
128.589
127.706
126.754
126.499
120.352
118.788
115.591
77.317
77.000
76.683
58.924
45.206
44.850
40.236
20.402
11.538
180
160
140
120
100
80
60
40
20
0
ppm

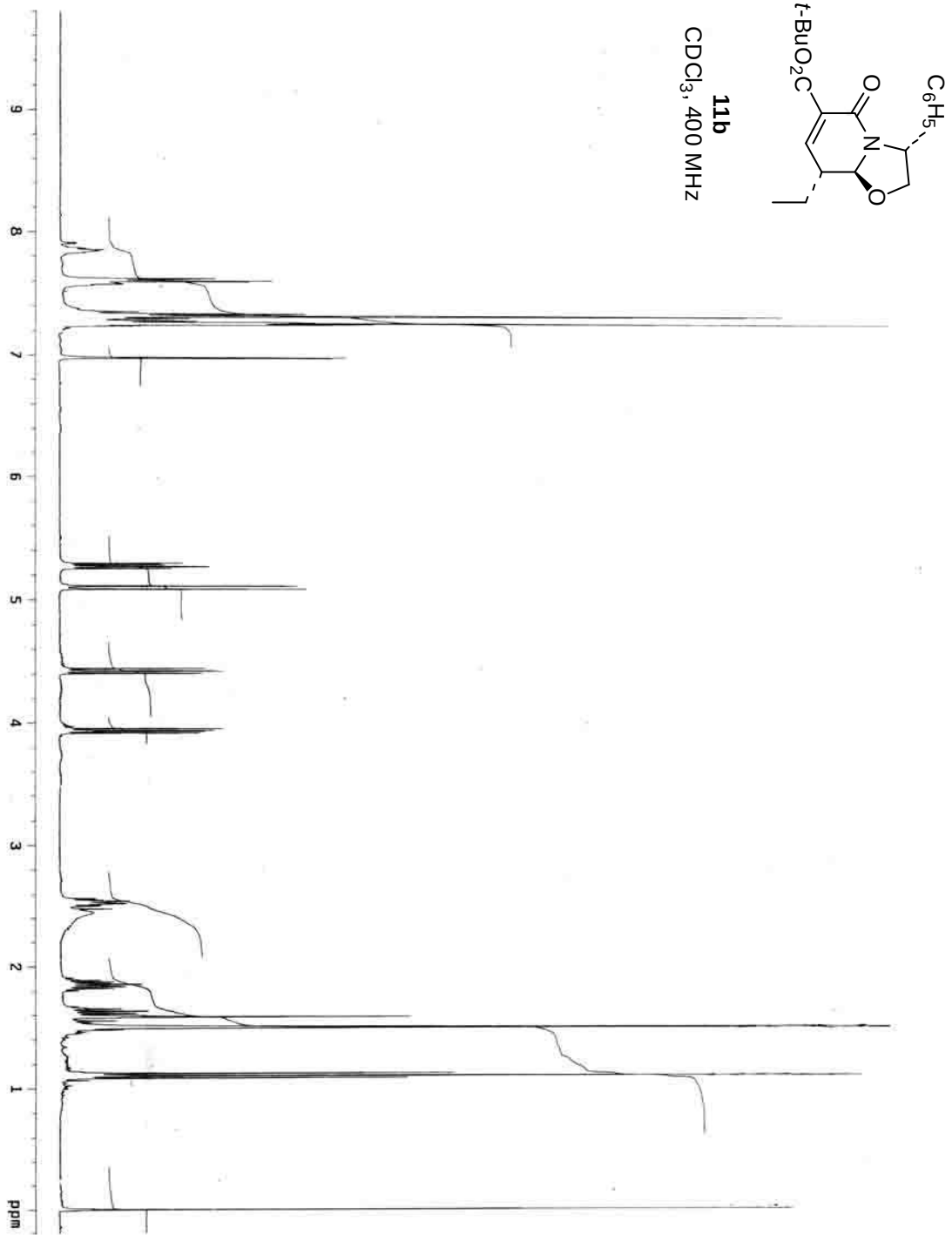

C6H5
O
N
O
10b
CDCl3, 300 MHz
7.311
7.284
7.262
1.260
1.066
1.029
0.000
ppm
9
8
7
6
5
4
3
2
1

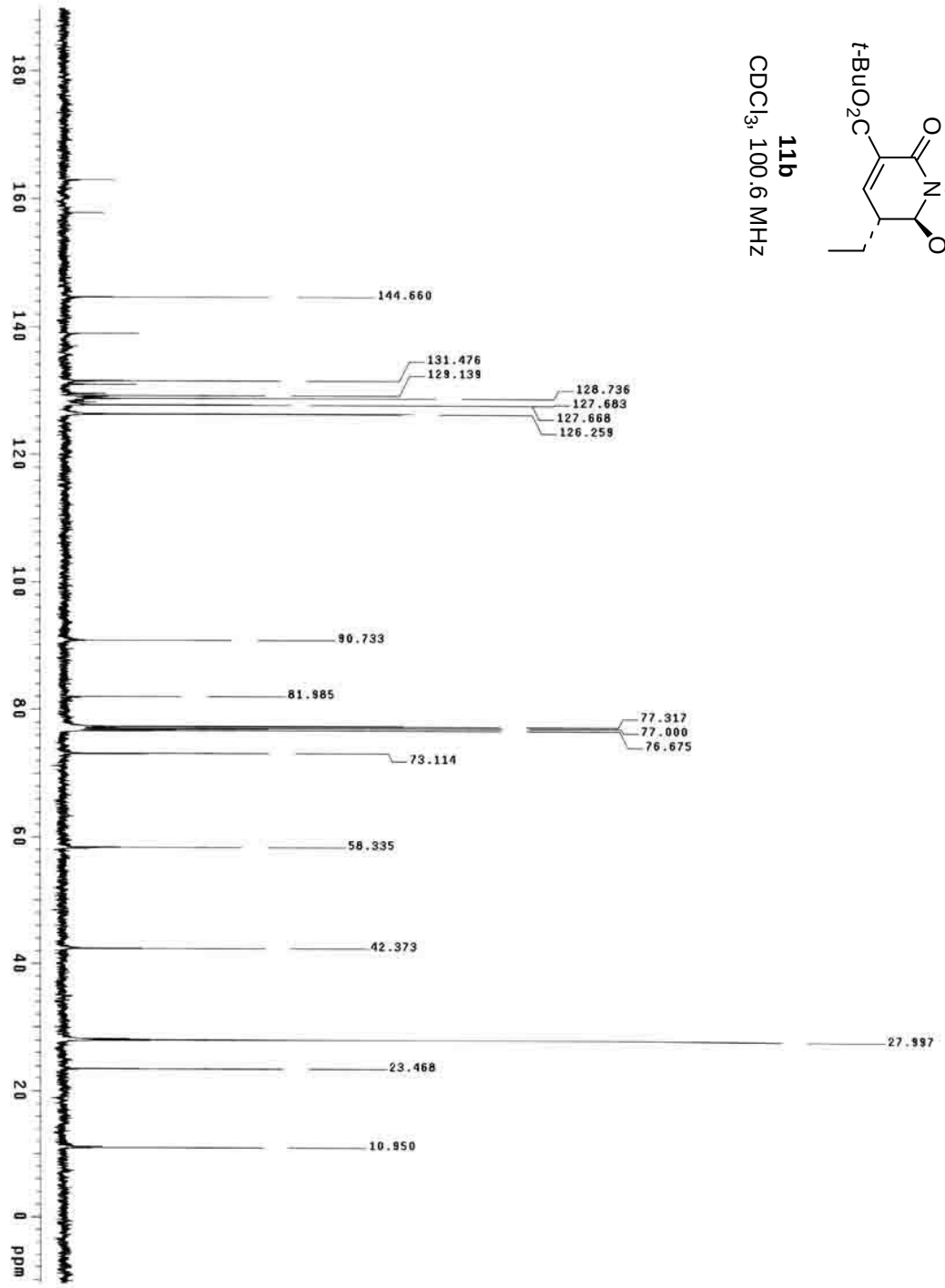

Seleniide
Higher R_f epimer
$CDCl_3$, 400 MHz
C_6H_5
t-BuO_2C
C_6H_5Se
O
N
O
7.814
7.797
7.313
7.291
7.261
7.244
1.435
0.750
0.791
0.713
8
7
6
5
4
3
2
1
ppm

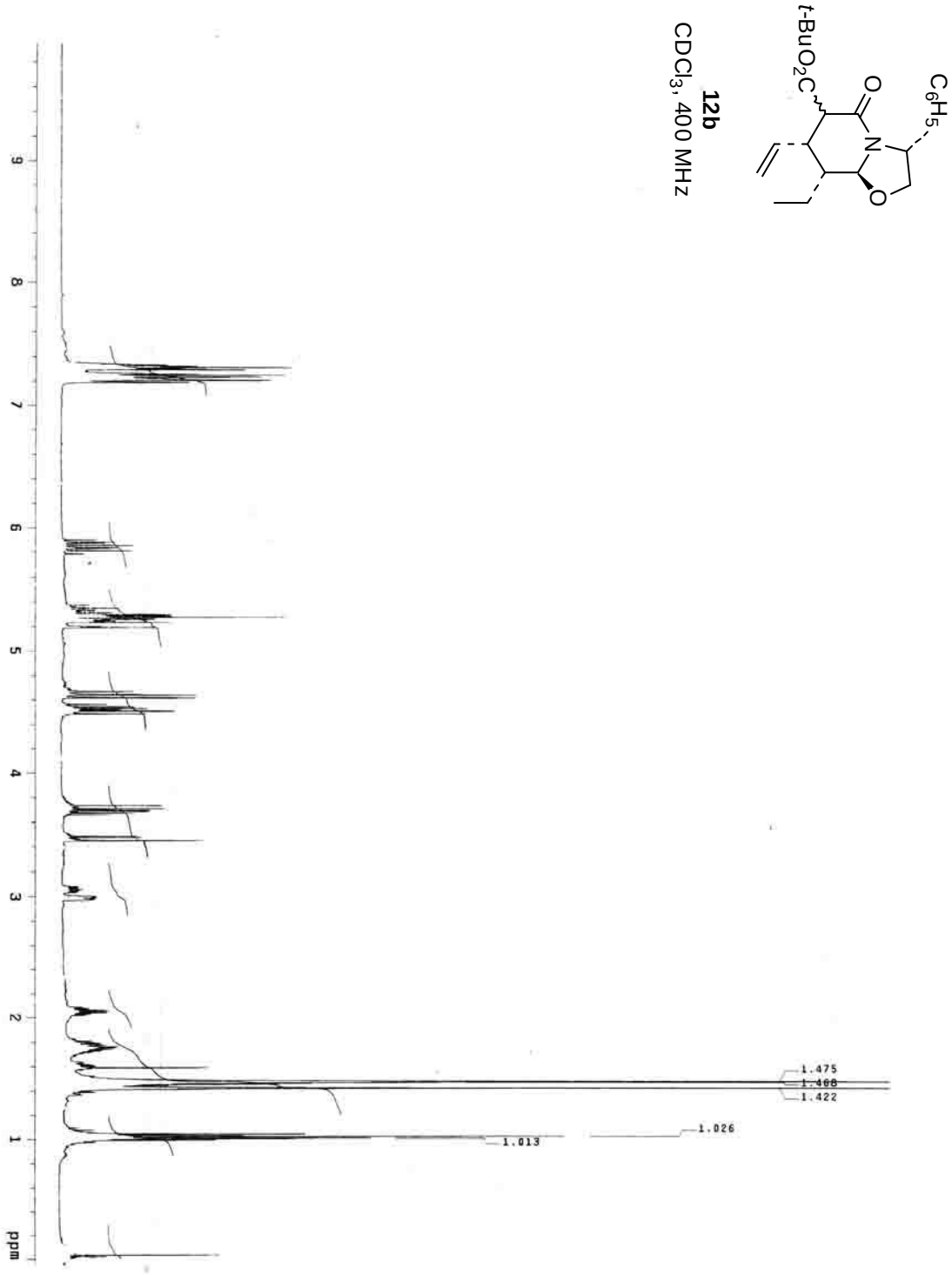

Seleride
Higher R_f epimer
$CDCl_3$, 100.6 MHz
C_6H_5
t-BuO_2C
C_6H_5Se
O
N
O
138.057
129.394
128.798
128.573
127.443
125.786
92.258
77.317
77.000
76.683
72.285
58.575
38.208
33.323
27.734
24.002
10.757
180
160
140
120
100
80
60
40
20
0 ppm

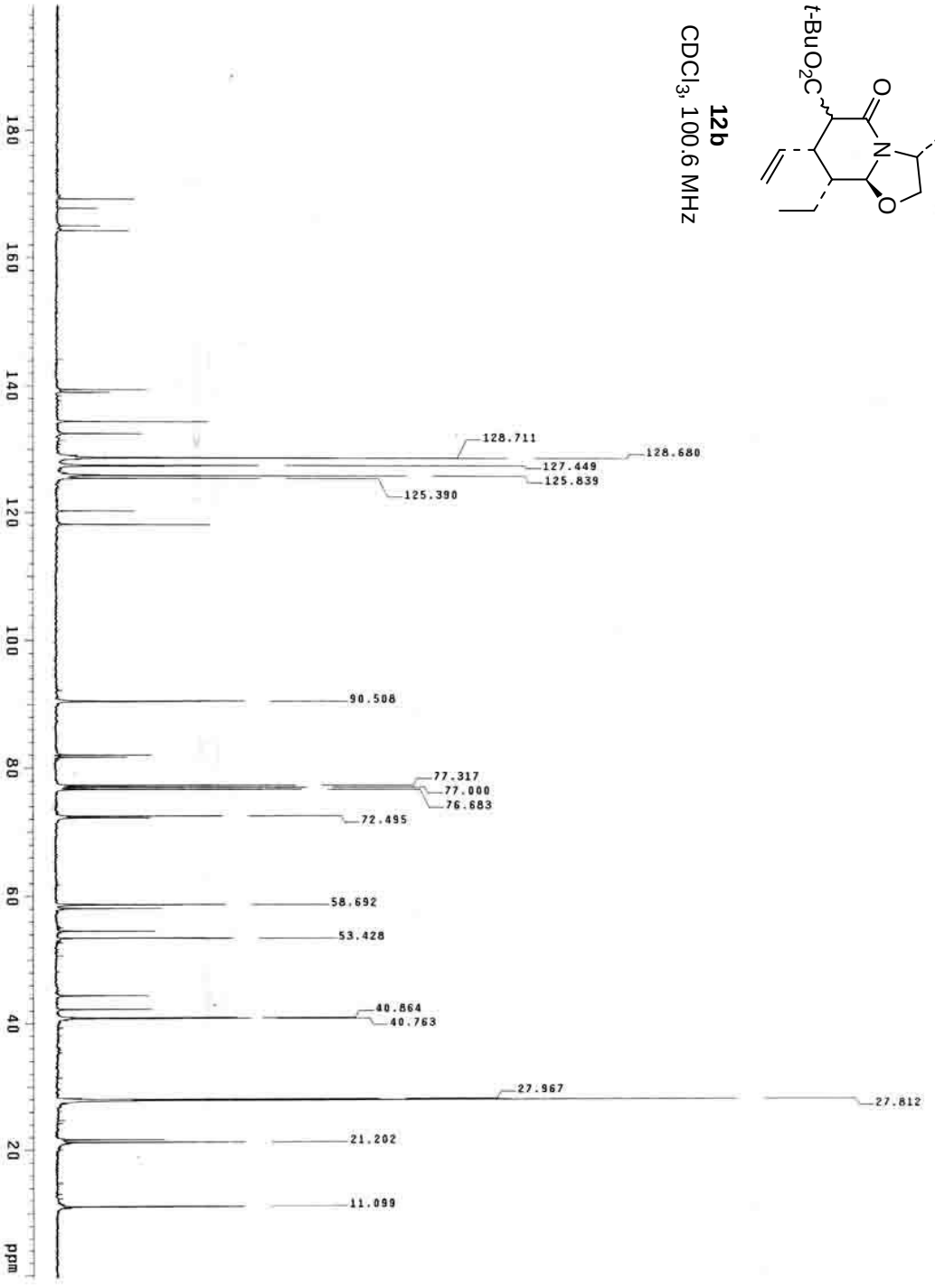

Selenide
Lower R_f epimer
$CDCl_3$, 400 MHz
C_6H_5
t-BuO_2C
C_6H_5Se
O
N
O
7.318
7.317
7.128
1.474
1.436
0.950
0.931
ppm

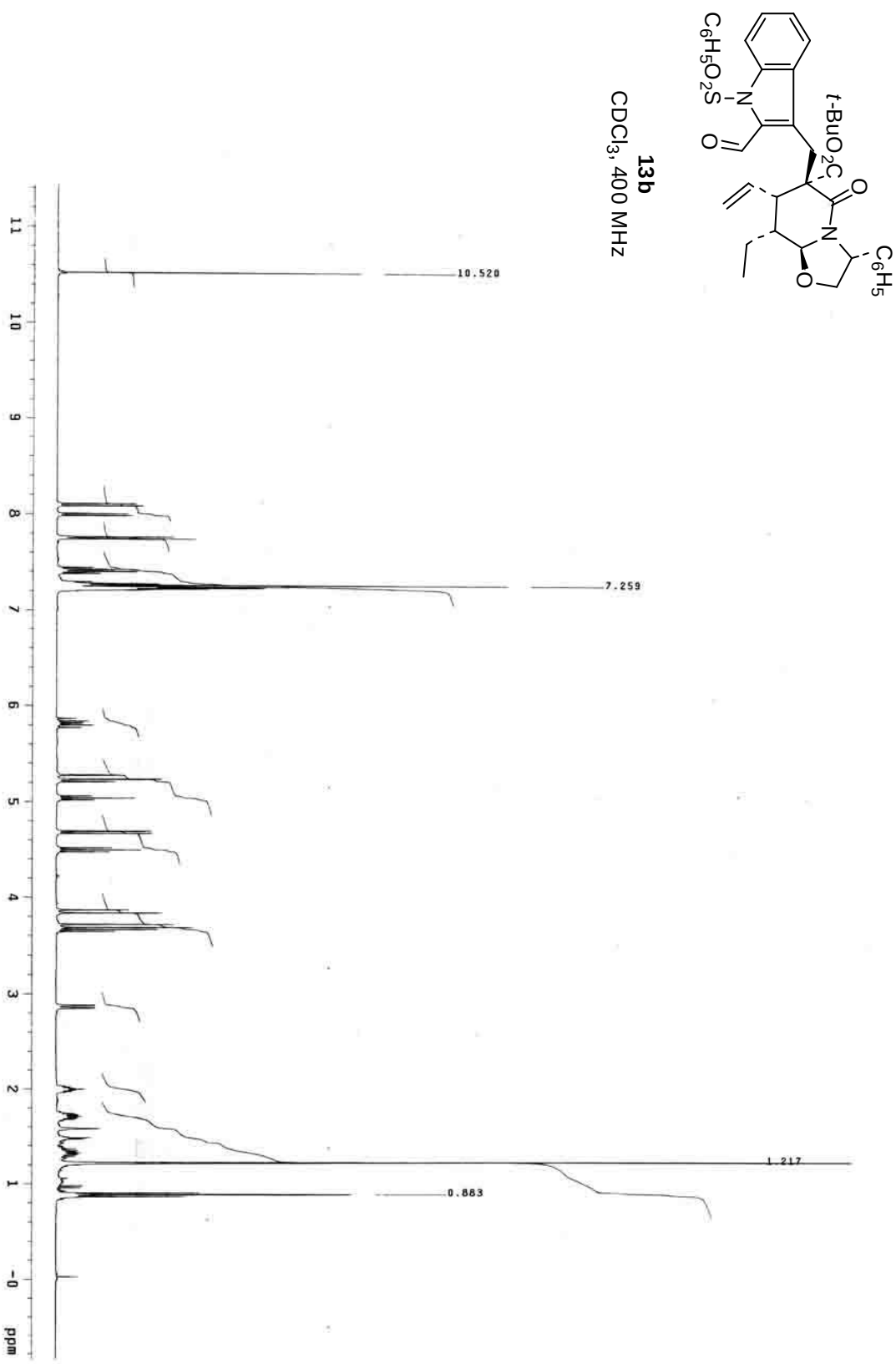

Selenide
Lower R_f epimer
$CDCl_3$, 100.6 MHz
C_6H_5
t-BuO_2C
C_6H_5Se
O
N
O
138.049
129.139
128.689
128.558
127.544
126.839
91.956
72.061
58.947
39.392
35.312
27.687
23.925
10.803
180
160
140
120
100
80
60
40
20
0
ppm

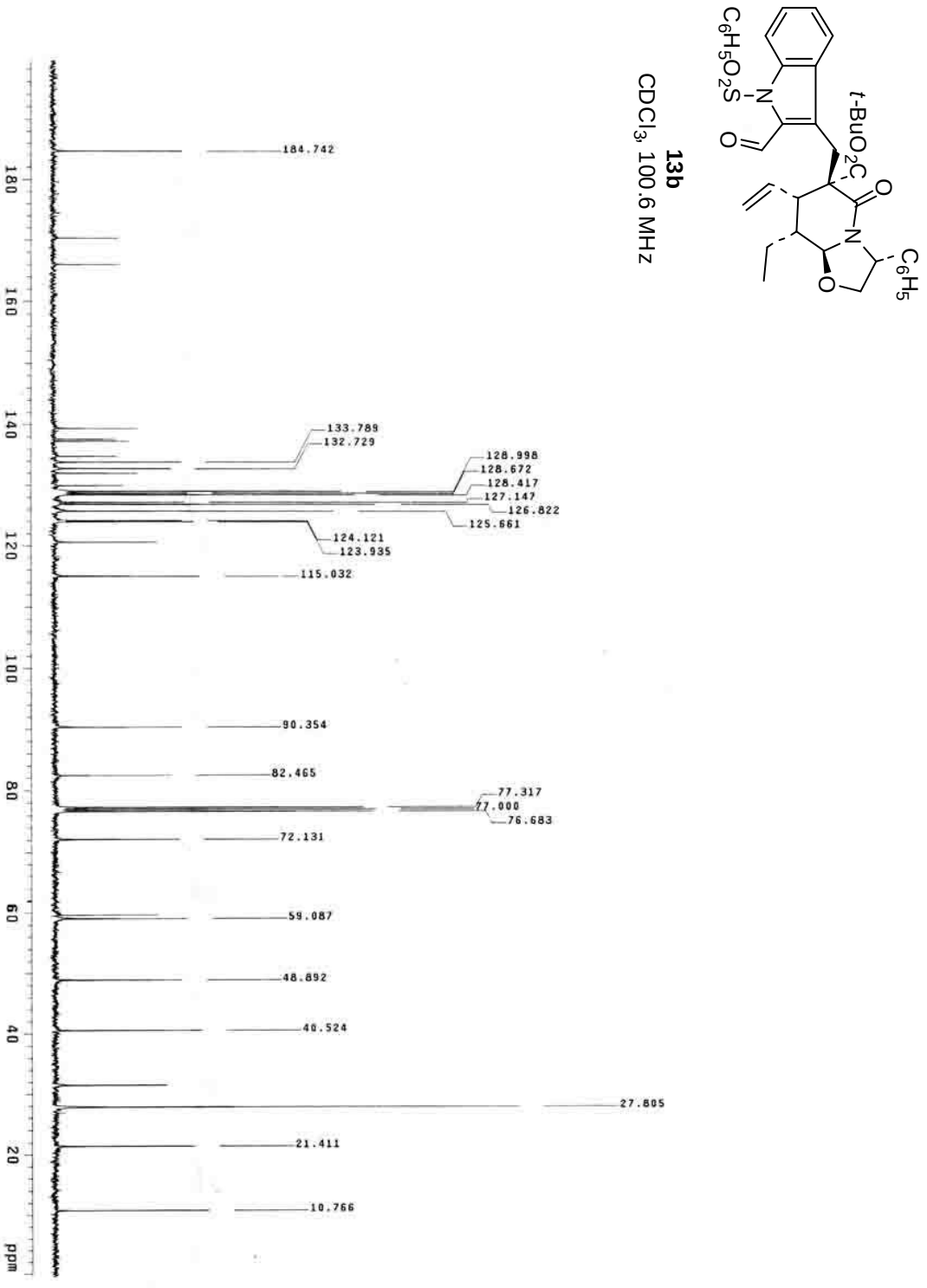

C6H5
t-BuO2C
O
N
O
11b
CDCl3, 400 MHz
9
8
7
6
5
4
3
2
1
ppm

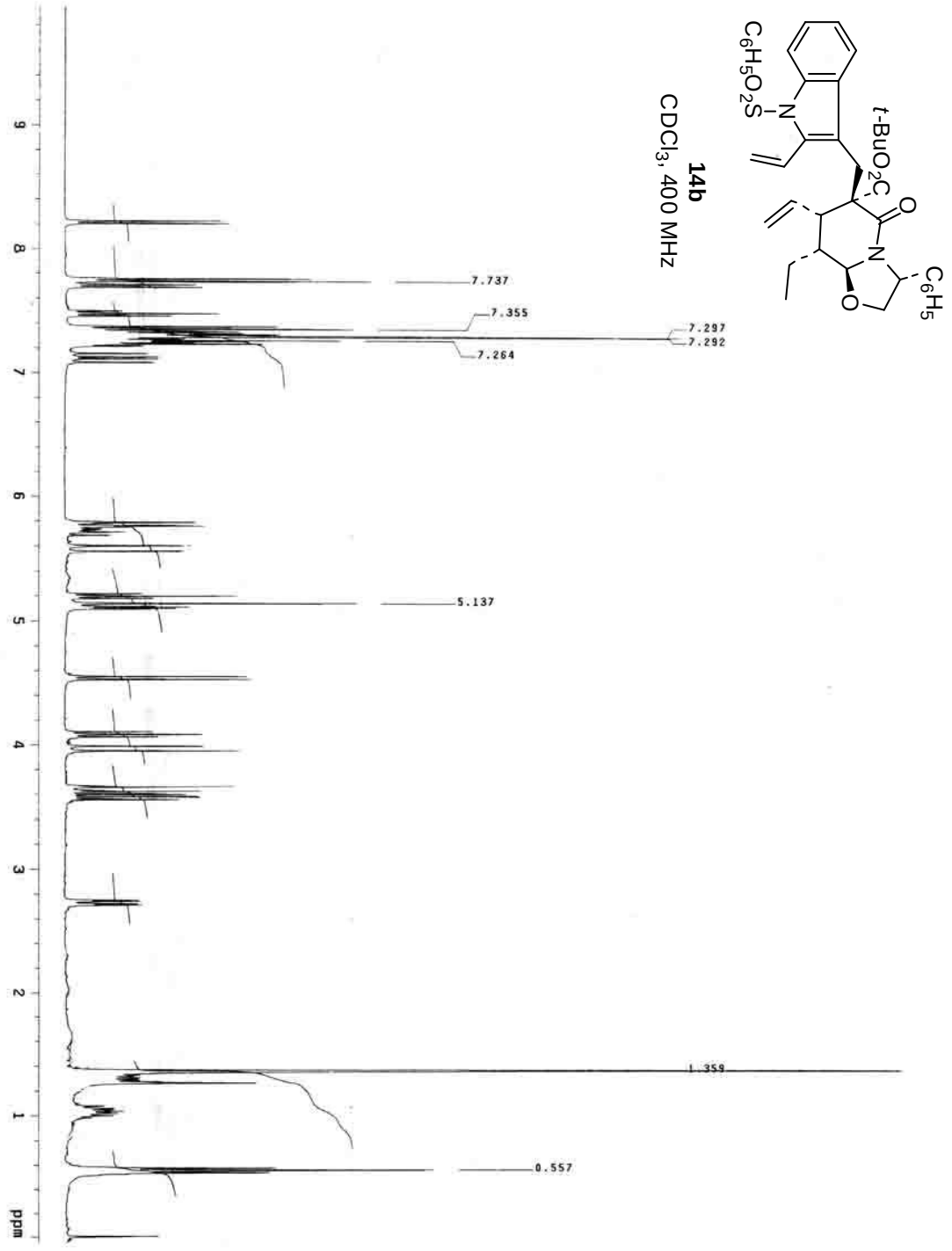

11b
CDCl3, 100.6 MHz
t-BuO2C
C6H5
O
N
O
144.660
131.476
129.139
128.736
127.683
127.668
126.259
90.733
81.985
77.317
77.000
76.675
73.114
58.335
42.373
27.997
23.468
10.950
180
160
140
120
100
80
60
40
20
0
ppm

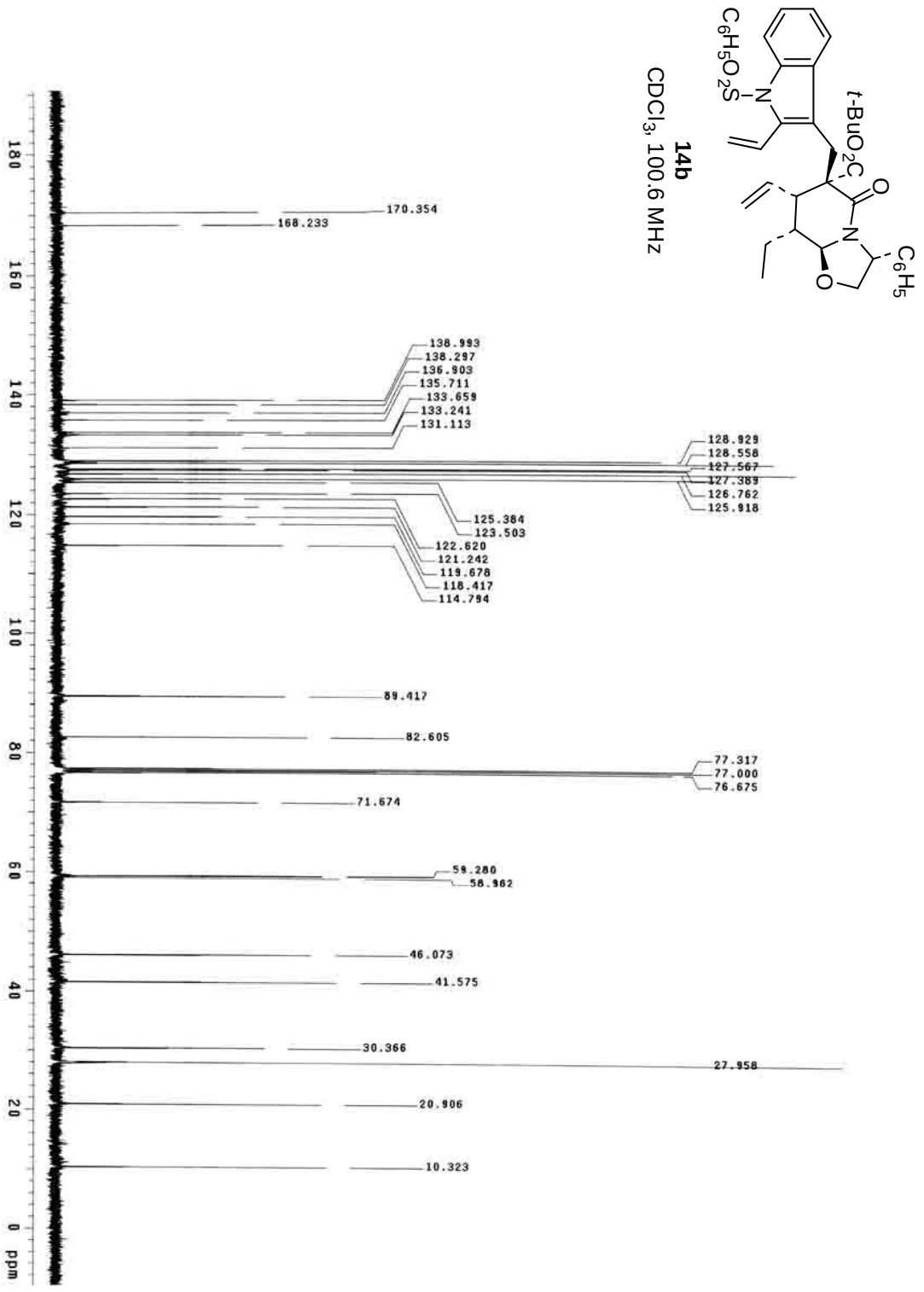

12b
CDCl3, 400 MHz
t-BuO2C
C6H5
O
N
O
ppm
1
2
3
4
5
6
7
8
9
1.475
1.468
1.422
1.026
1.013

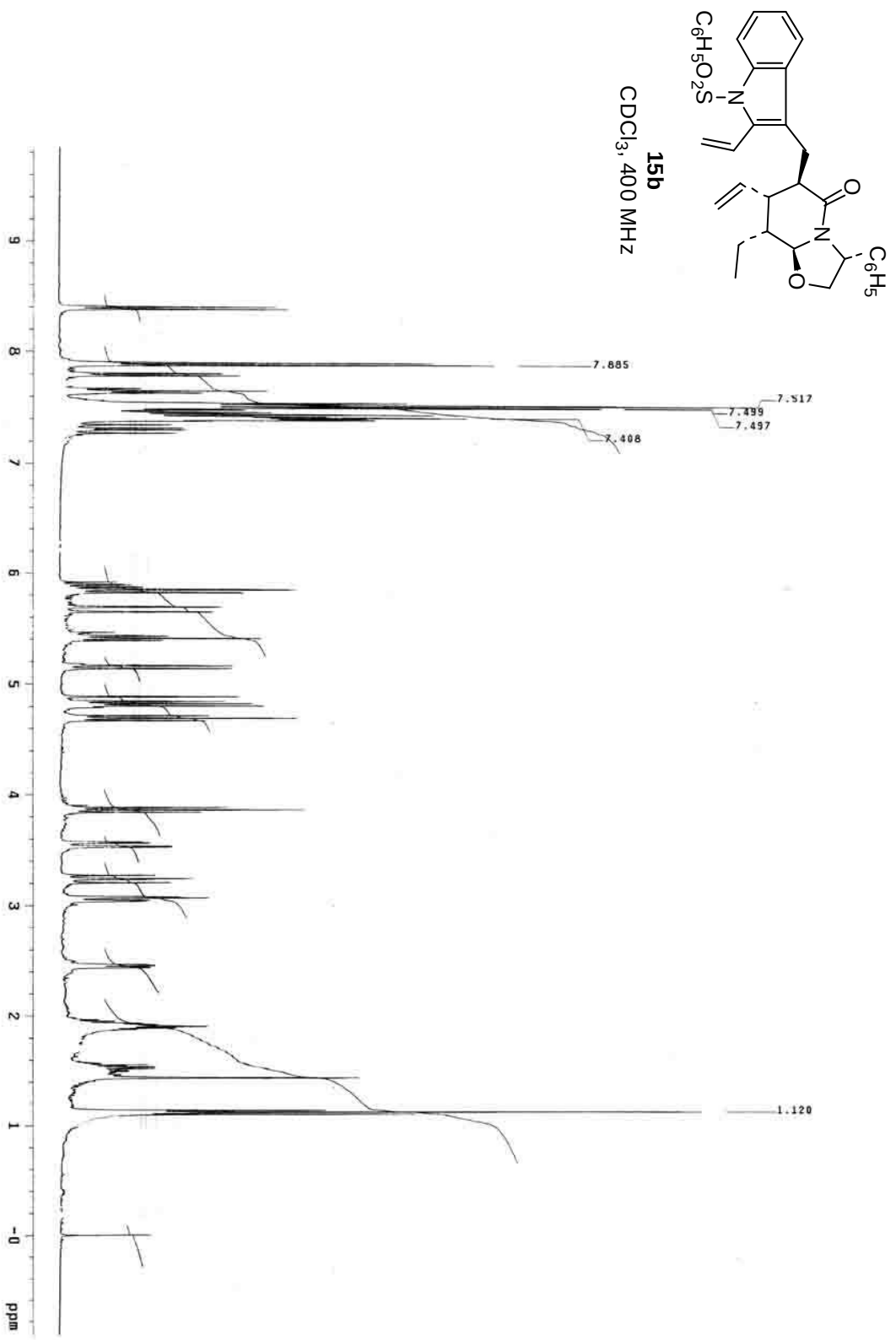

12b
CDCl3, 100.6 MHz
t-BuO2C
O
N
O
C6H5
180
160
140
120
100
80
60
40
20
ppm
128.711
128.680
127.449
125.839
125.390
90.508
77.317
77.000
76.683
72.495
58.692
53.428
40.864
40.763
27.967
27.812
21.202
11.099

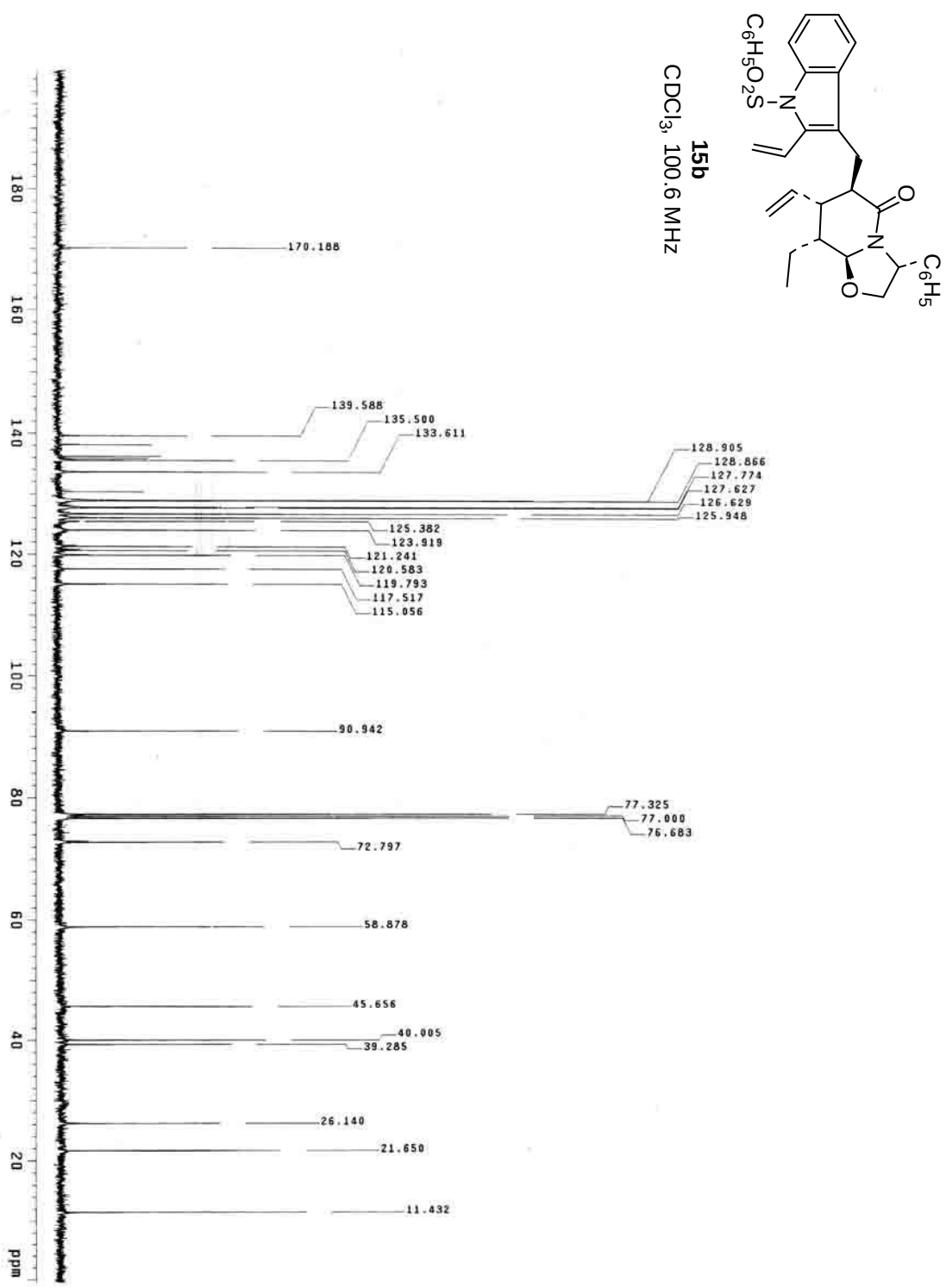

13b
CDCl3, 400 MHz
C6H5O2S
N
O
t-BuO2C
O
N
O
C6H5
10.520
7.259
1.217
0.883
ppm

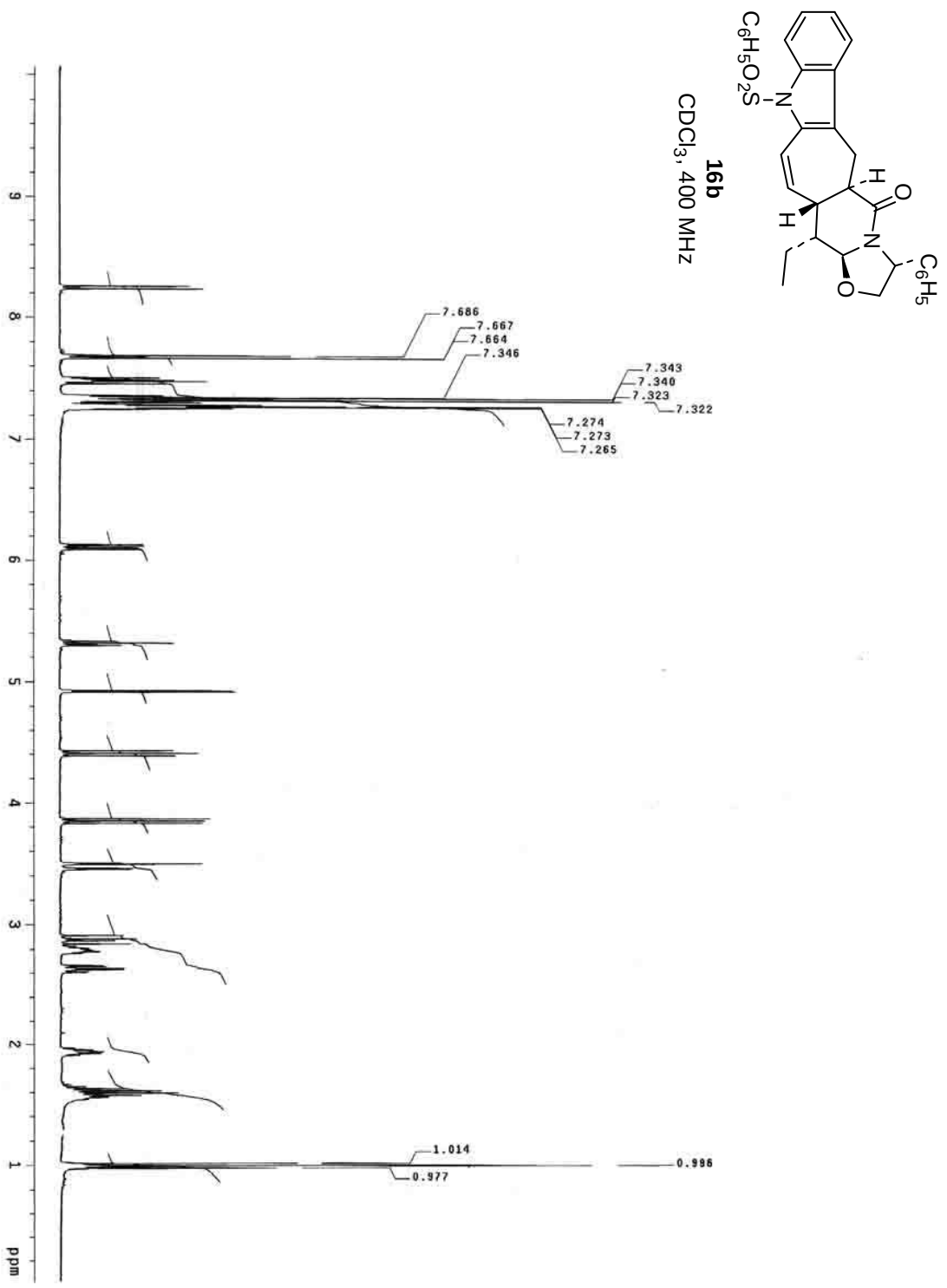

13b
CDCl3, 100.6 MHz
C6H5O2S
N
O
t-BuO2C
O
N
O
C6H5
184.742
133.789
132.729
128.998
128.672
128.417
127.147
126.822
125.661
124.121
123.935
115.032
90.354
82.465
77.317
77.000
76.683
72.131
59.087
48.892
40.524
27.805
21.411
10.766
ppm

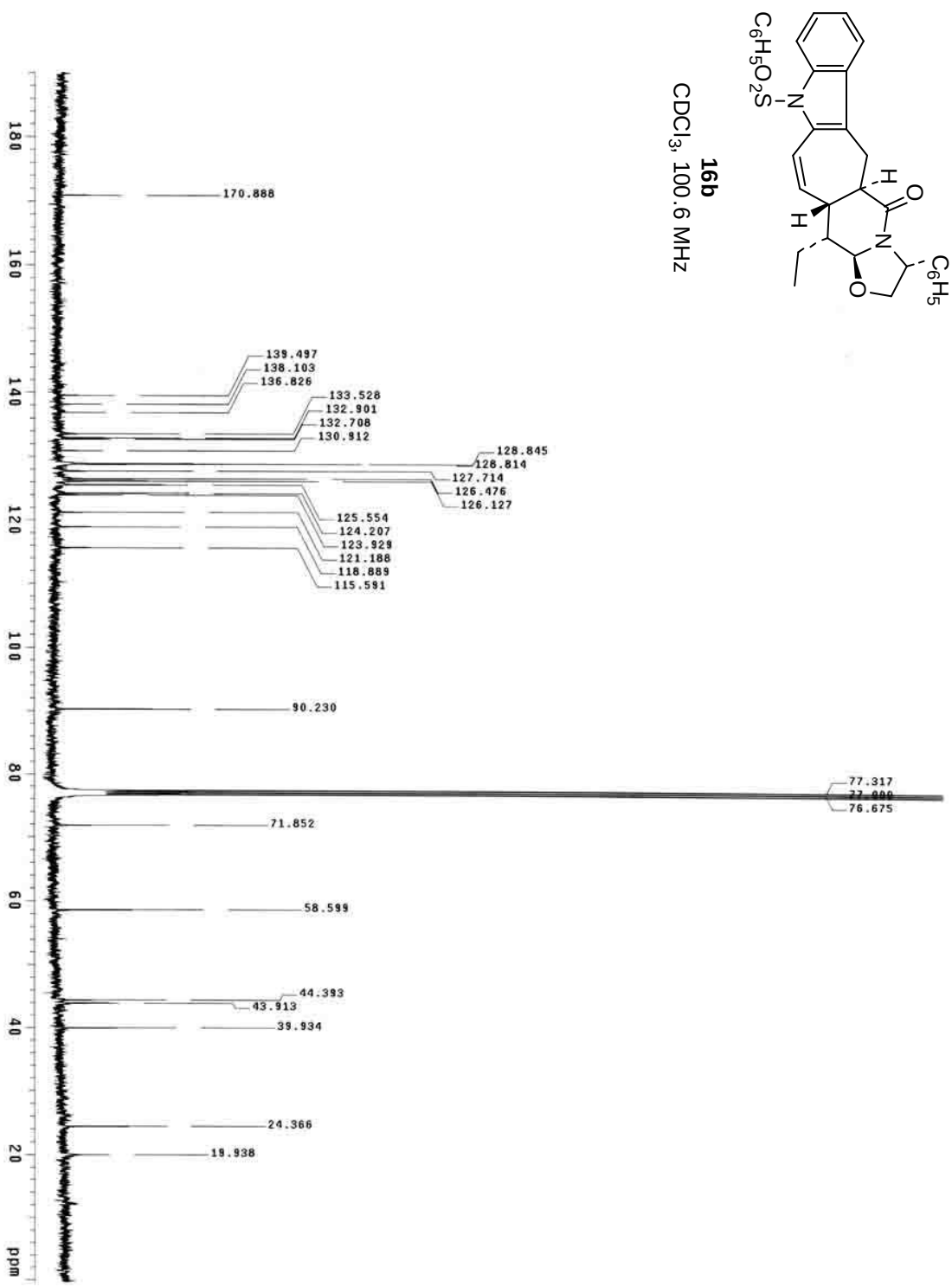

14b
CDCl3, 400 MHz
C6H5O2S
t-BuO2C
C6H5
7.737
7.355
7.297
7.292
7.264
5.137
1.359
0.557
ppm

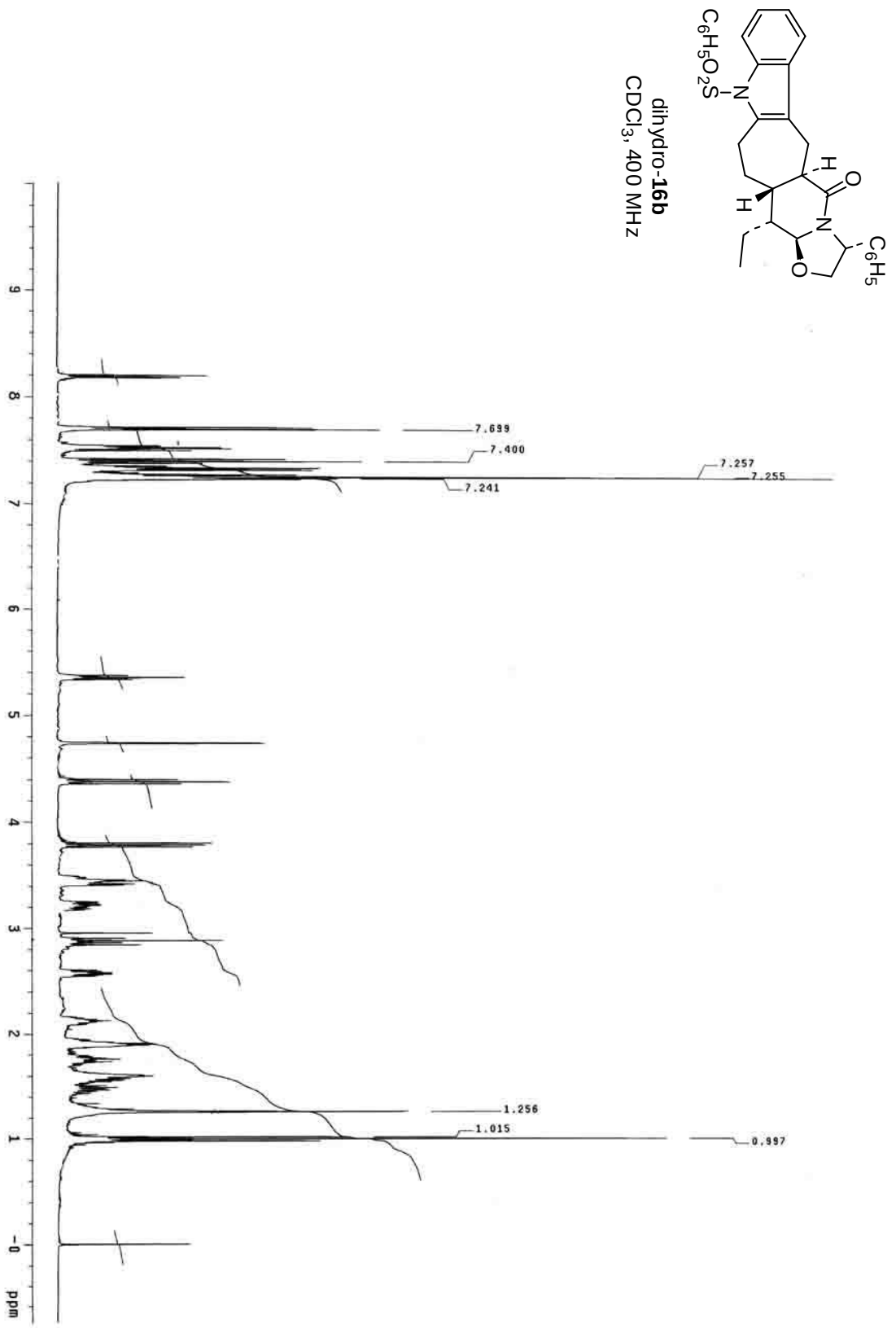

14b
CDCl3, 100.6 MHz
C6H5O2S
N
t-BuO2C
O
N
O
C6H5
170.354
168.233
138.993
138.297
136.903
135.711
133.659
133.241
131.113
128.929
128.558
127.567
127.389
126.762
125.918
125.384
123.503
122.620
121.242
119.678
118.417
114.794
89.417
82.605
77.317
77.000
76.675
71.674
59.280
58.962
46.073
41.575
30.366
27.958
20.906
10.323
180
160
140
120
100
80
60
40
20
0 ppm

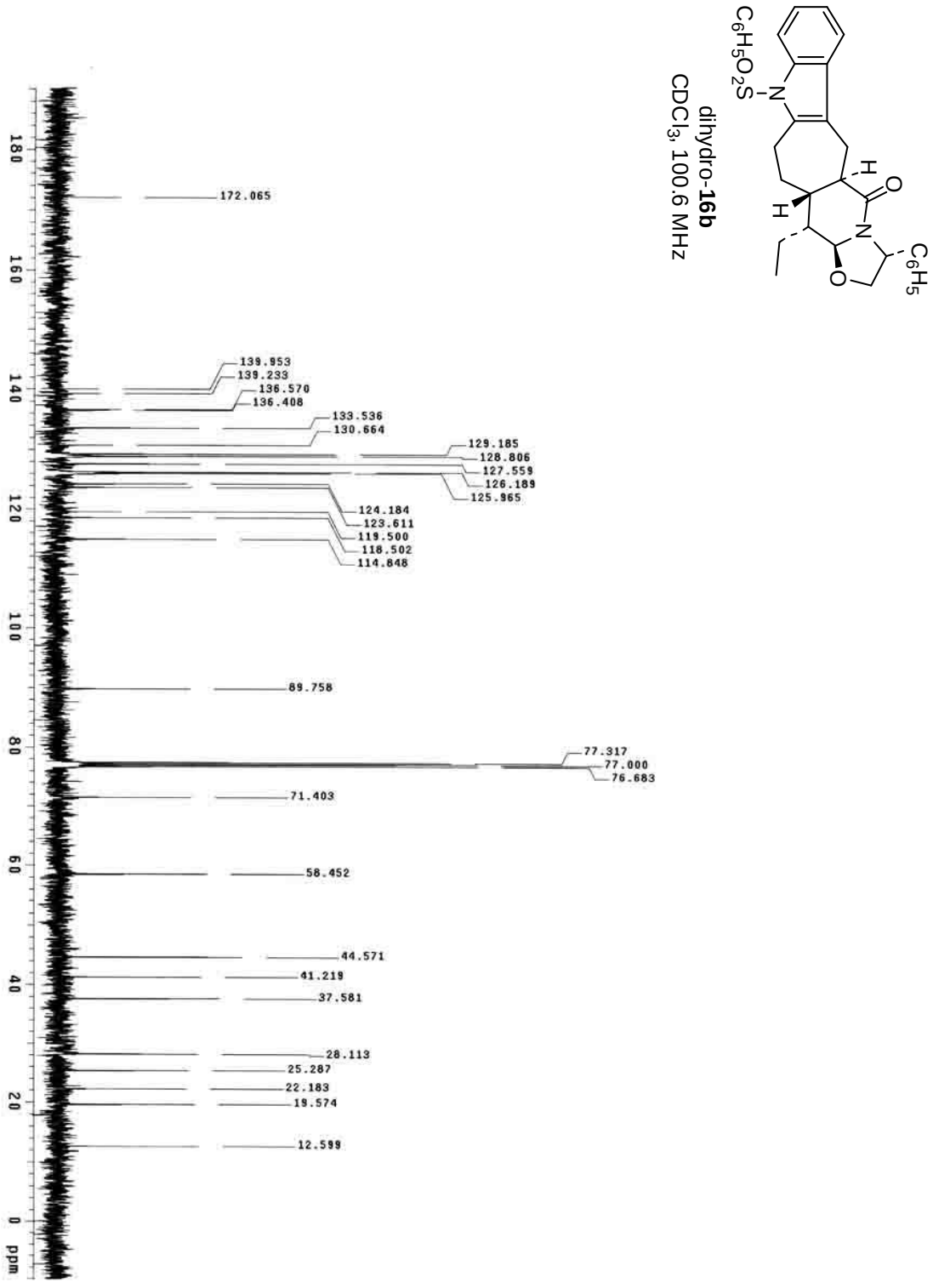

15b
CDCl3, 400 MHz
C6H5O2S
N
O
N
O
C6H5
7.885
7.517
7.499
7.497
7.408
1.120
9
8
7
6
5
4
3
2
1
-0
ppm

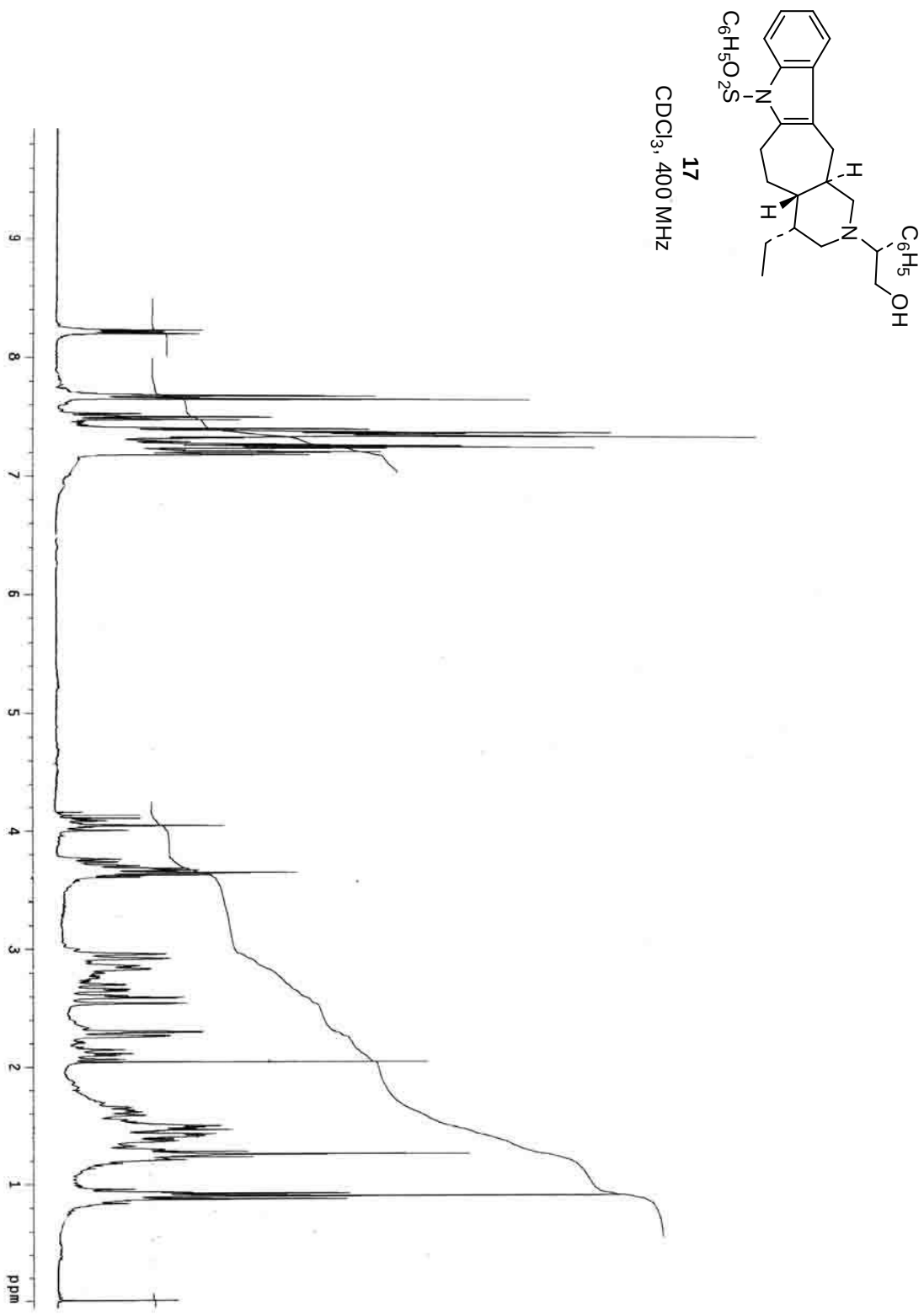

15b
CDCl3, 100.6 MHz
C6H5O2S
N
O
N
O
C6H5
170.188
139.588
135.500
133.611
128.905
128.866
127.774
127.627
126.629
125.948
125.382
123.919
121.241
120.583
119.793
117.517
115.056
90.942
77.325
77.000
76.683
72.797
58.878
45.656
40.005
39.285
26.140
21.650
11.432
ppm

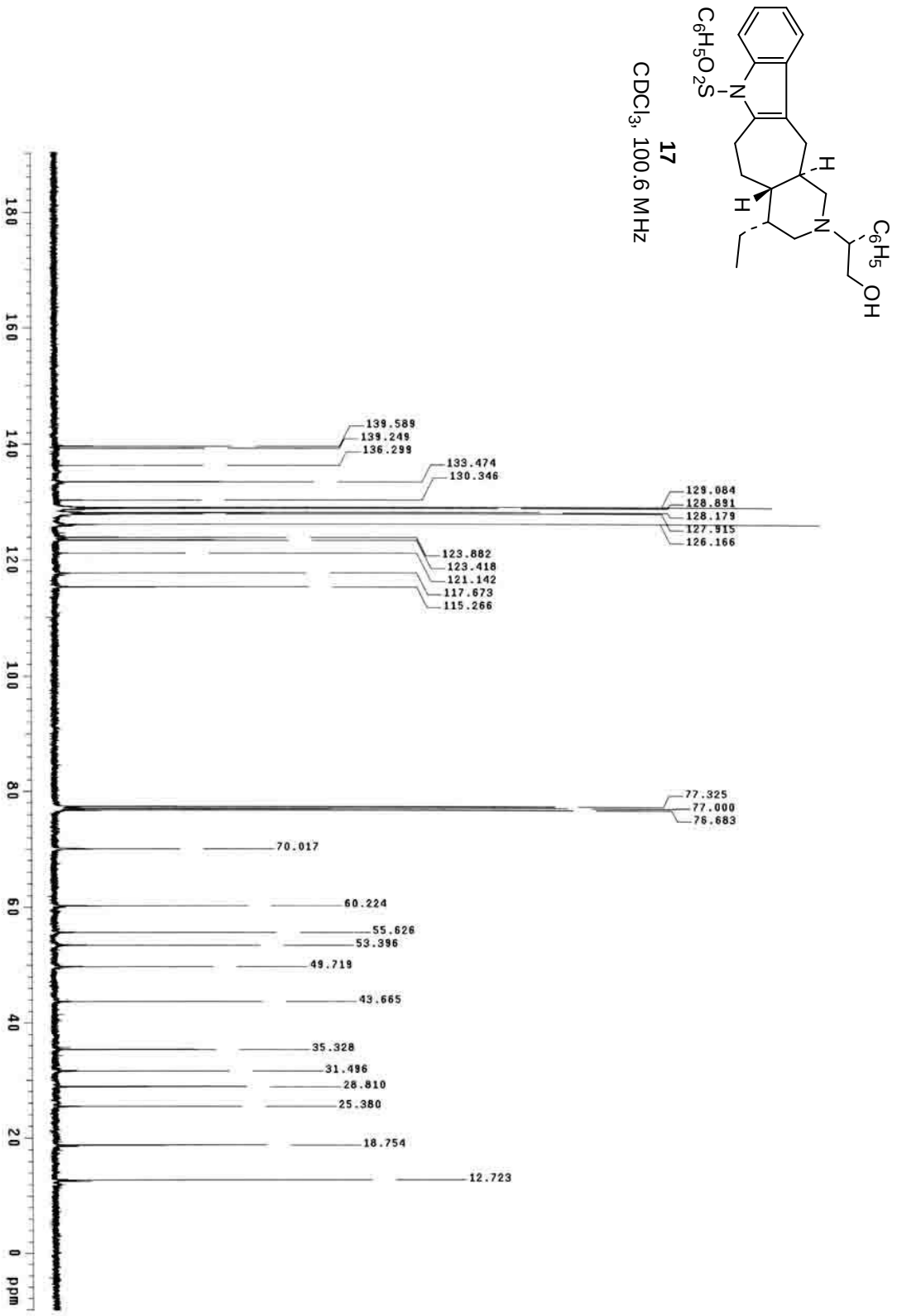

16b
CDCl3, 400 MHz
C6H5O2S
N
H
O
H
N
O
C6H5
7.686
7.667
7.664
7.346
7.343
7.340
7.323
7.322
7.274
7.273
7.265
1.014
0.977
0.986
ppm

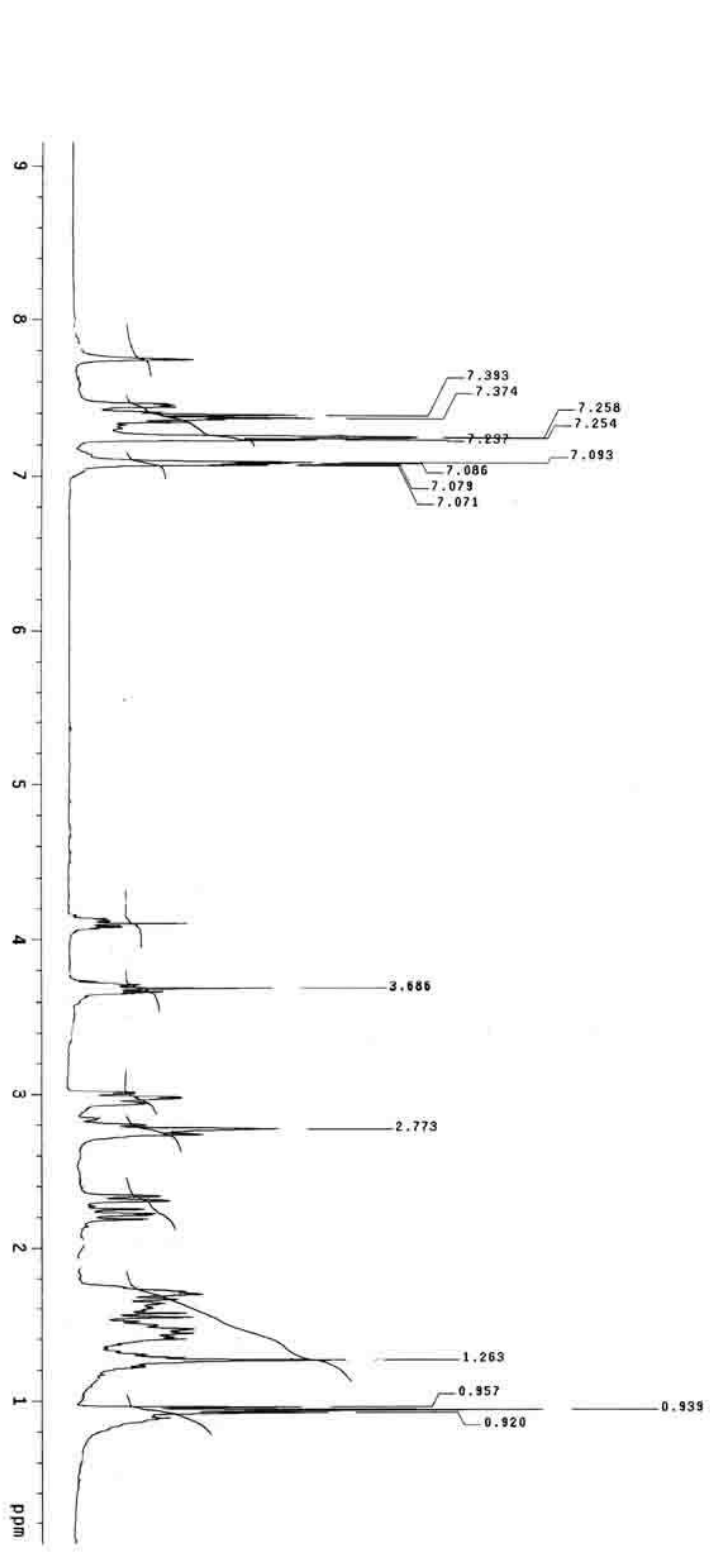

16b
CDCl3, 100.6 MHz
C6H5O2S
C6H5
170.888
139.497
138.103
136.826
133.528
132.901
132.708
130.912
128.845
128.814
127.714
126.476
126.127
125.554
124.207
123.929
121.188
118.889
115.591
90.230
77.317
76.675
71.852
58.599
44.393
43.913
39.934
24.366
19.938
ppm


dihydro-16b
CDCl3, 400 MHz
C6H5O2S
N
H
O
H
N
O
C6H5
7.699
7.400
7.257
7.255
7.241
1.256
1.015
0.997
ppm

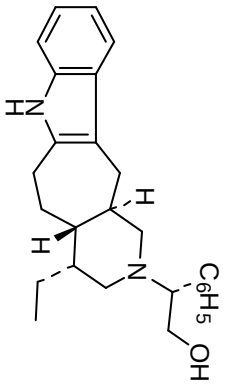

dihydro-16b
CDCl3, 100.6 MHz
C6H5O2S
C6H5
H
H
O
O
N
N
172.065
139.953
139.233
136.570
136.408
133.536
130.664
129.185
128.806
127.559
126.189
125.965
124.184
123.611
119.500
118.502
114.848
89.758
77.317
77.000
76.683
71.403
58.452
44.571
41.219
37.581
28.113
25.287
22.183
19.574
12.599
ppm

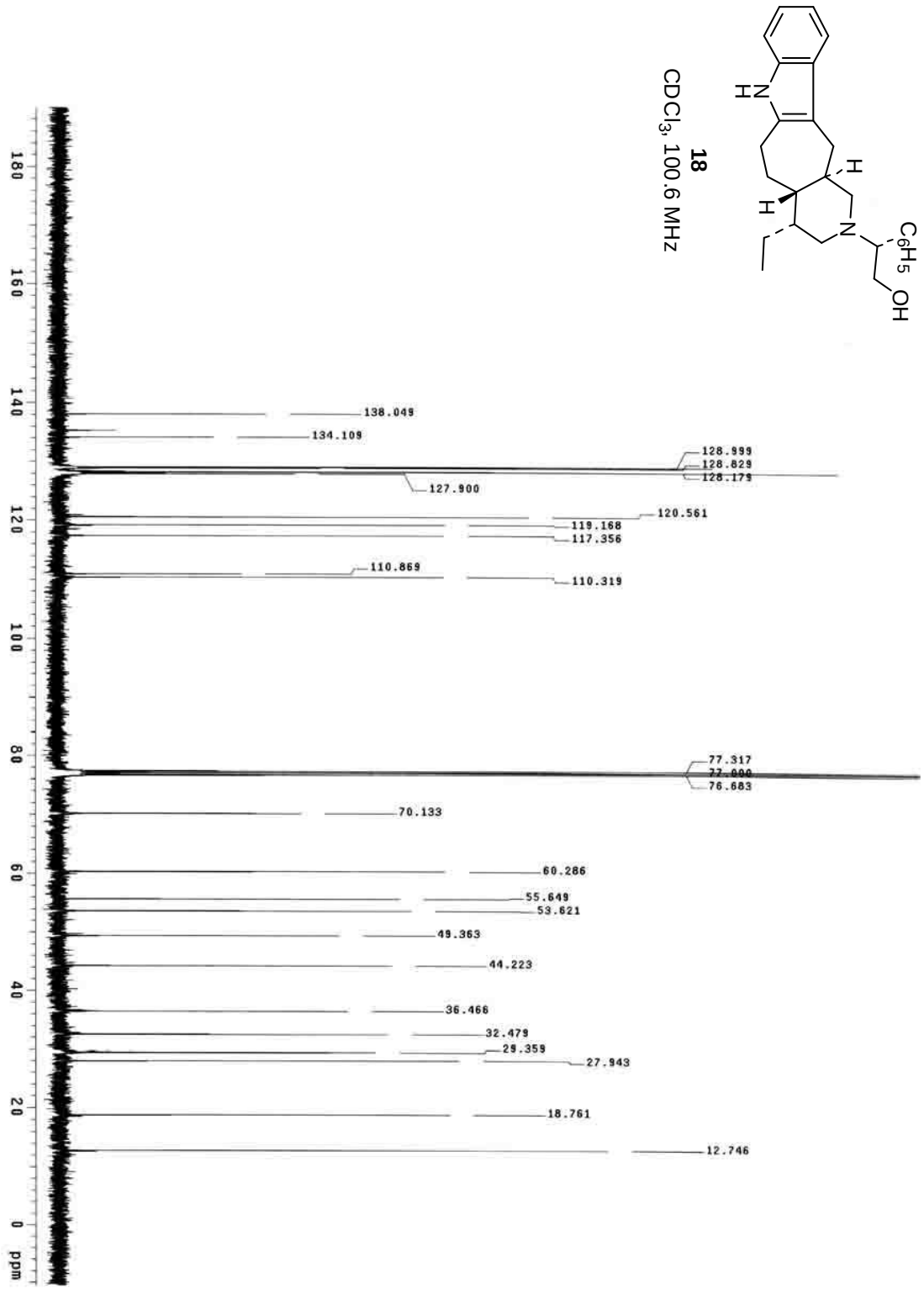

17
CDCl3, 400 MHz
C6H5O2S
N
H
H
N
C6H5
OH
9
8
7
6
5
4
3
2
1
ppm

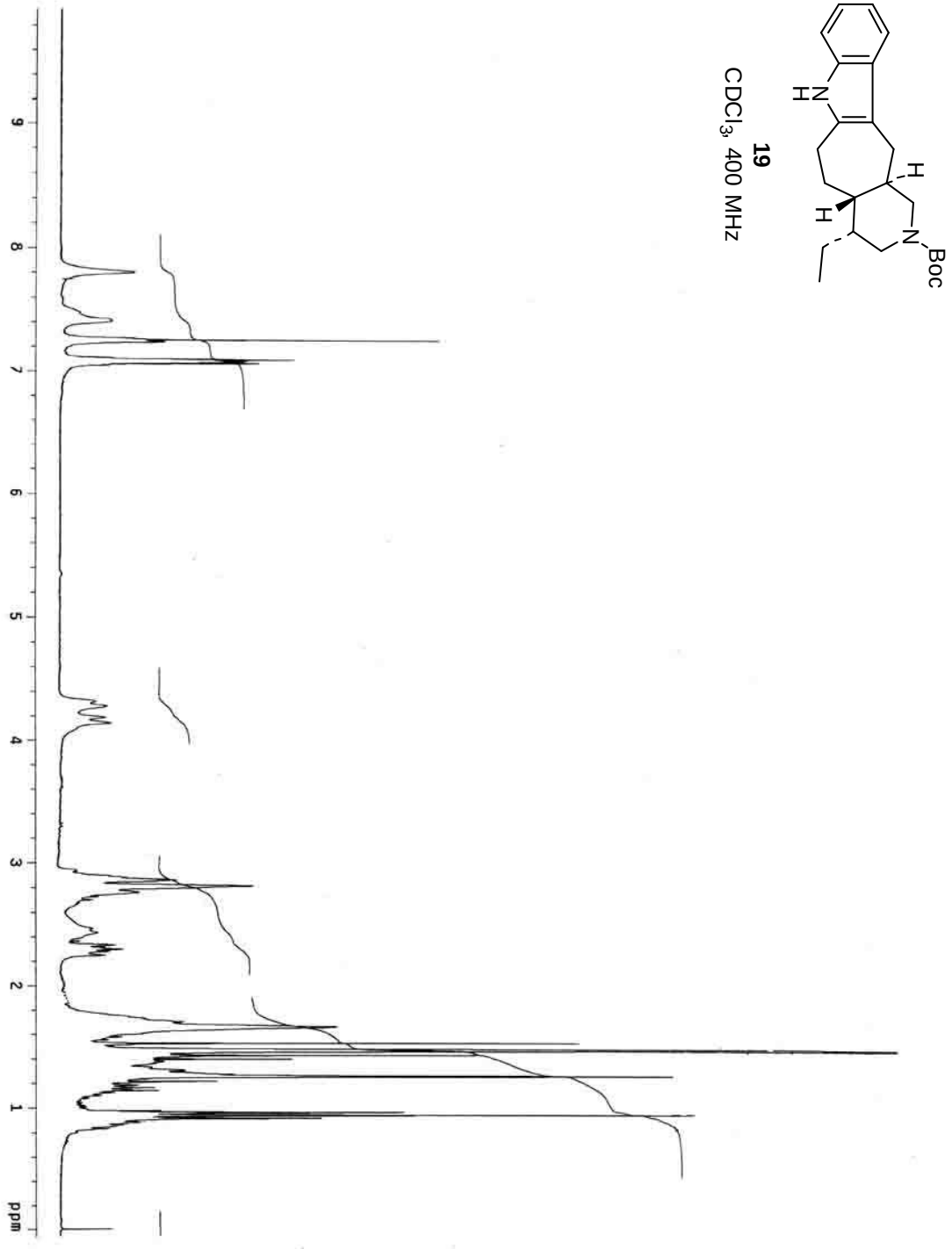

17
CDCl3, 100.6 MHz
C6H5O2S
N
H
H
N
C6H5
OH
180
160
140
120
100
80
60
40
20
0 ppm
139.589
139.249
136.299
133.474
130.346
129.084
128.891
128.179
127.915
126.166
123.882
123.418
121.142
117.673
115.266
77.325
77.000
76.683
70.017
60.224
55.626
53.396
49.719
43.665
35.328
31.496
28.810
25.380
18.754
12.723

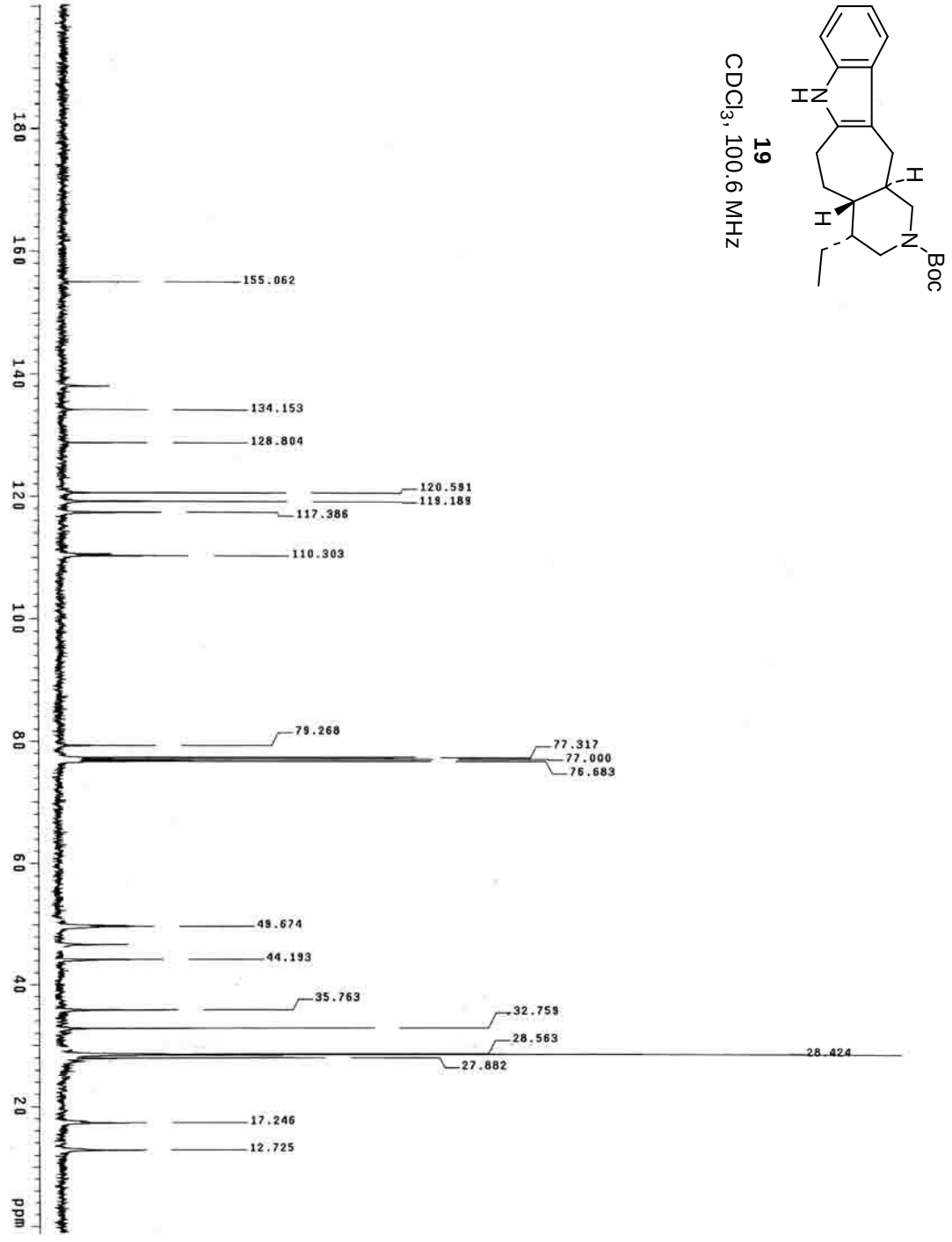


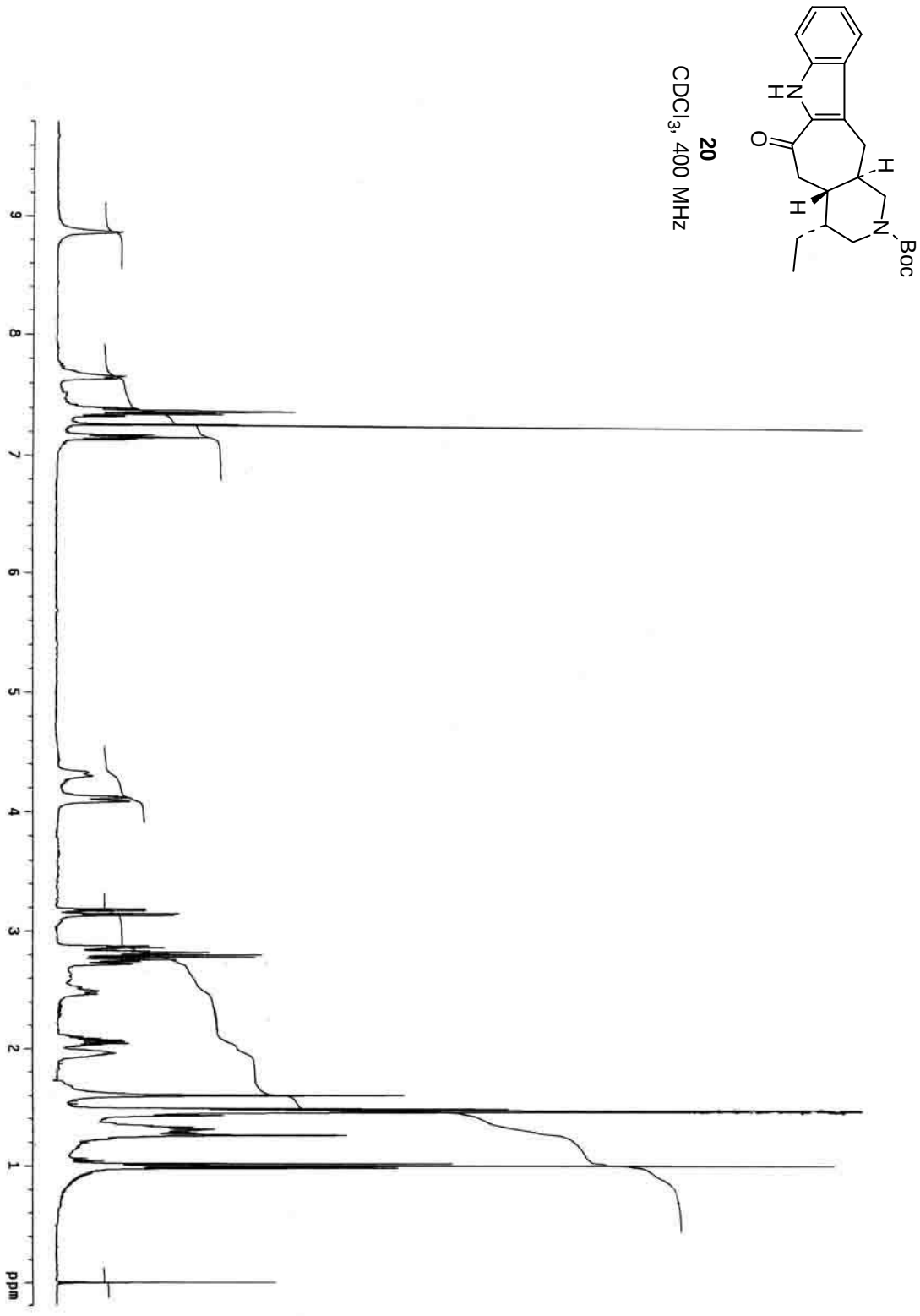
18
$CDCl_3$, 400 MHz

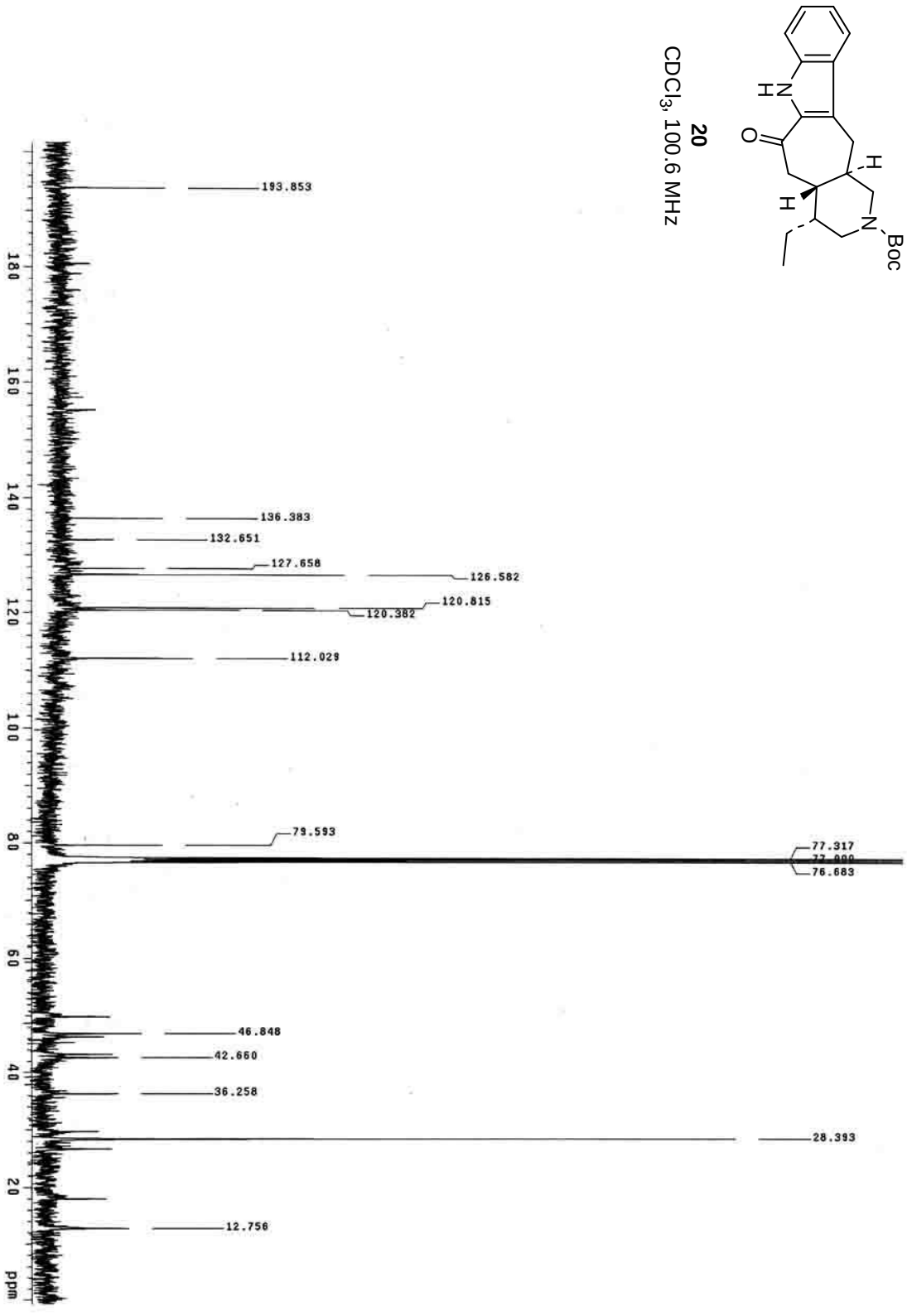


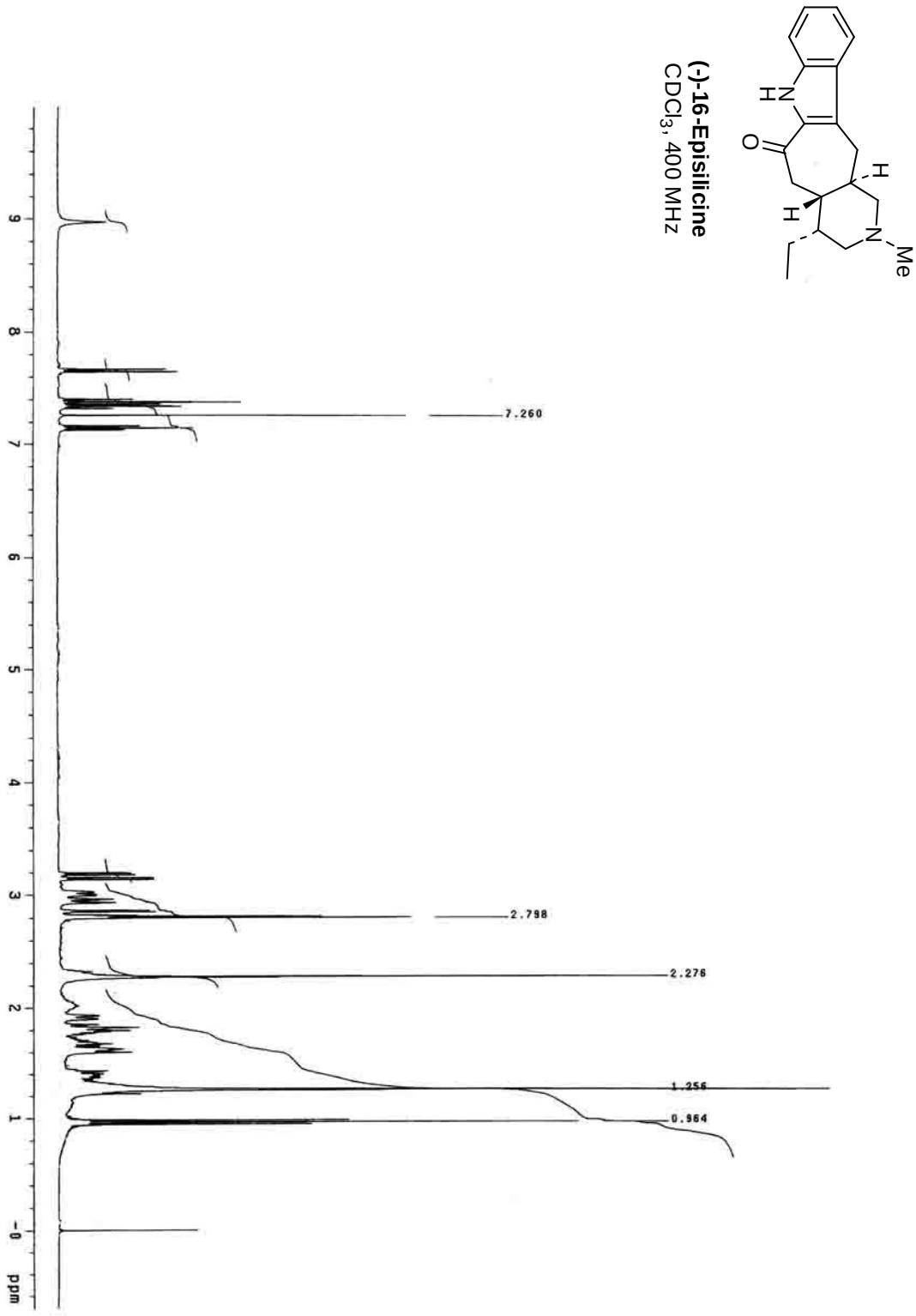

18
CDCl3, 100.6 MHz
C6H5
OH
138.049
134.109
128.999
128.829
128.179
127.900
120.561
119.168
117.356
110.869
110.319
77.317
77.000
76.683
70.133
60.286
55.649
53.621
49.363
44.223
36.466
32.479
29.359
27.943
18.761
12.746
ppm

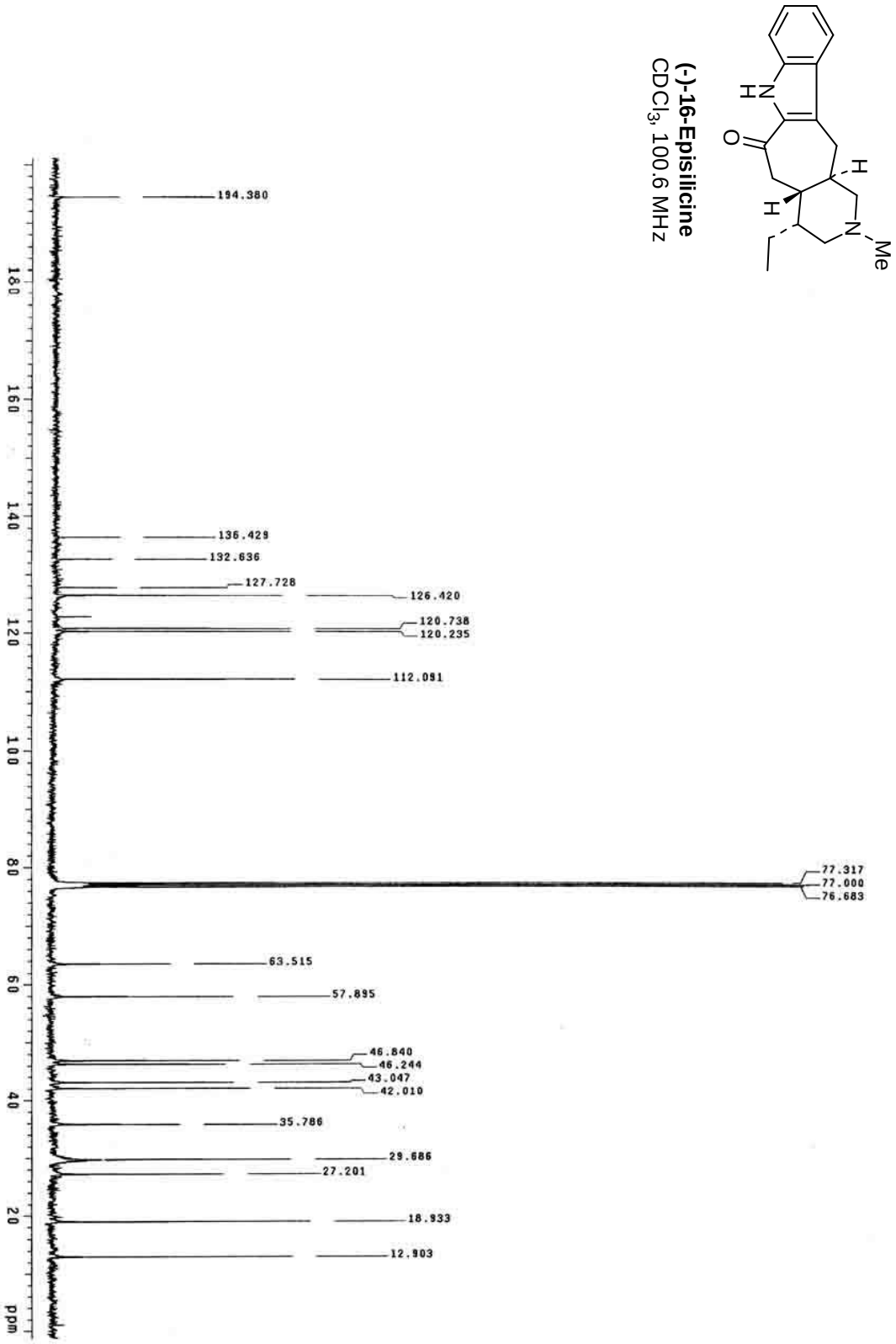

19
CDCl3, 400 MHz
N
H
H
H
N
Boc
ppm
9
8
7
6
5
4
3
2
1

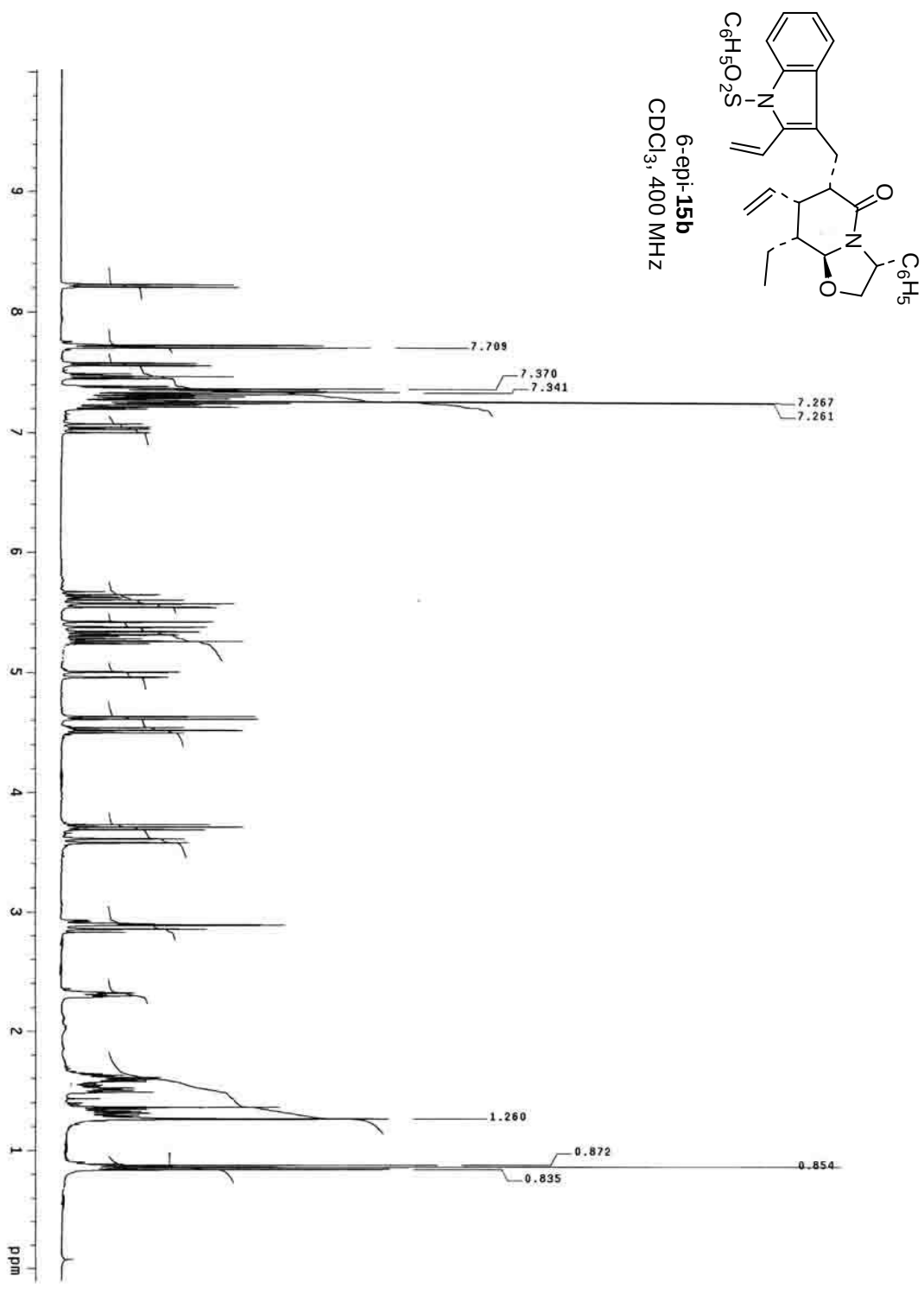

19
CDCl3, 100.6 MHz
H
N
H
H
N
Boc
180
160
140
120
100
80
60
40
20
ppm
155.062
134.153
128.804
120.591
119.189
117.386
110.303
79.268
77.317
77.000
76.683
49.674
44.193
35.763
32.759
28.563
28.424
27.882
17.246
12.725

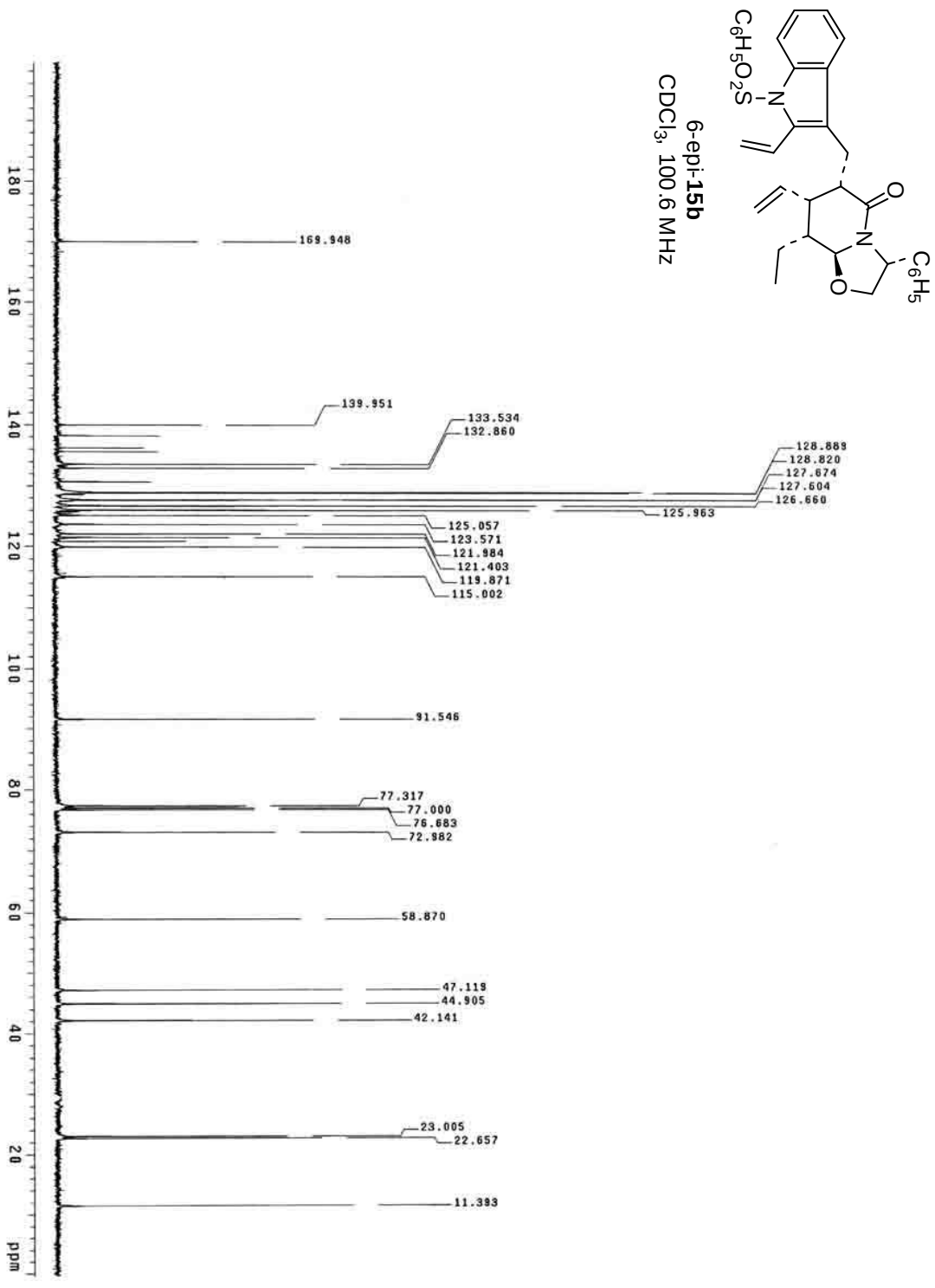

20
CDCl3, 400 MHz
H
N
O
H
H
N
Boc
9
8
7
6
5
4
3
2
1
ppm


20
CDCl3, 100.6 MHz
193.853
136.383
132.651
127.658
126.582
120.815
120.382
112.029
79.593
77.317
77.000
76.683
46.848
42.660
36.258
28.393
12.756
ppm
Boc


(-)-16-Episilicine
CDCl3, 400 MHz
N
H
O
H
H
N
Me
7.260
2.798
2.276
1.256
0.964
ppm


(-)-16-Episilicine
CDCl3, 100.6 MHz
194.380
136.429
132.636
127.728
126.420
120.738
120.235
112.091
77.317
77.000
76.683
63.515
57.895
46.840
46.244
43.047
42.010
35.786
29.686
27.201
18.933
12.903
ppm


6-epi-15b
CDCl3, 400 MHz
C6H5O2S
N
O
N
O
C6H5
7.709
7.370
7.341
7.267
7.261
1.260
0.872
0.854
0.835
ppm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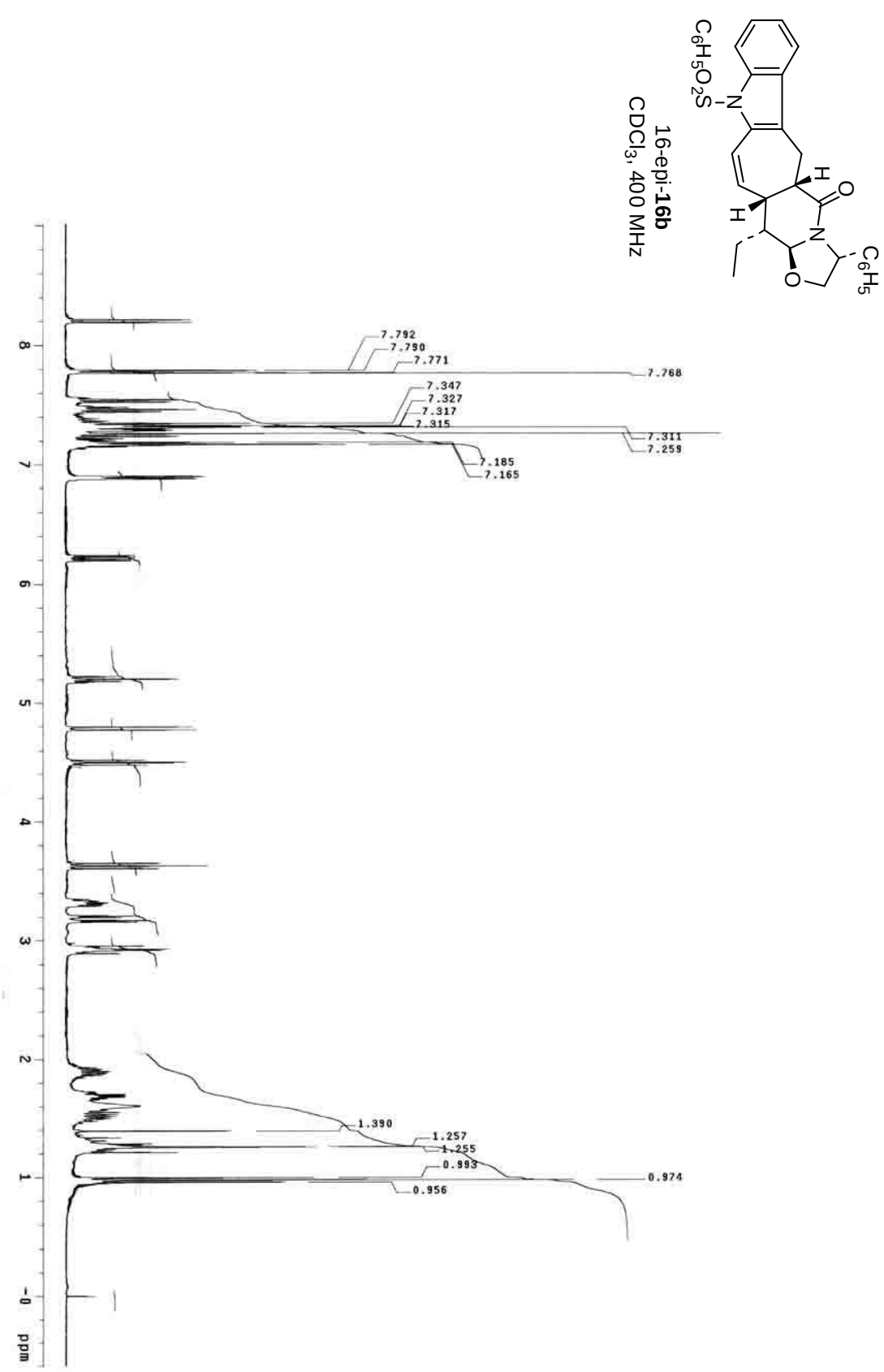
C6H5O2S
N
O
N
O
C6H5
169.948
139.951
133.534
132.860
128.889
128.820
127.674
127.604
126.660
125.963
125.057
123.571
121.984
121.403
119.871
115.002
91.546
77.317
77.000
76.683
72.982
58.870
47.118
44.905
42.141
23.005
22.657
11.393
180
160
140
120
100
80
60
40
20
ppm


16-epi-16b
CDCl3, 400 MHz
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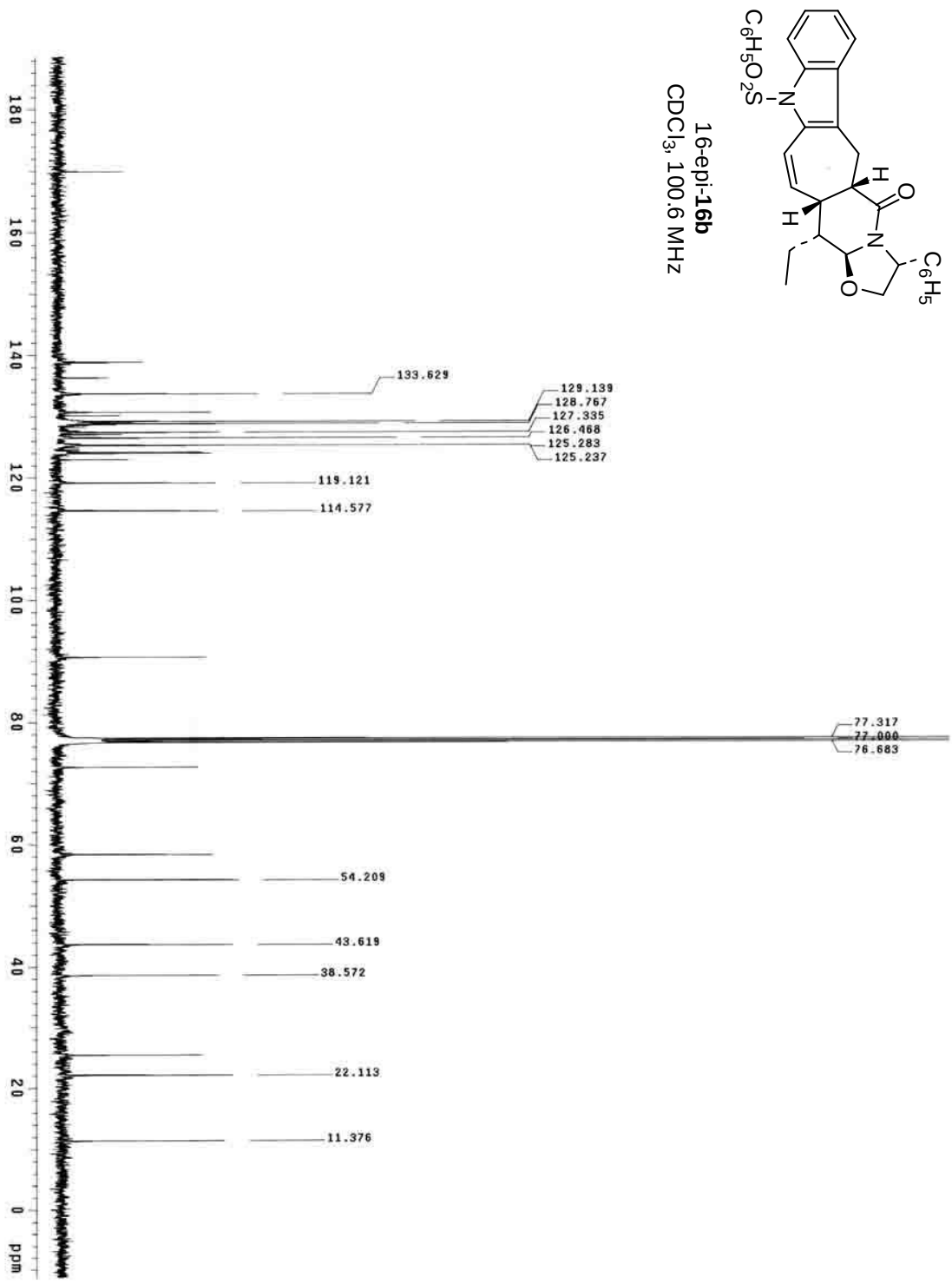
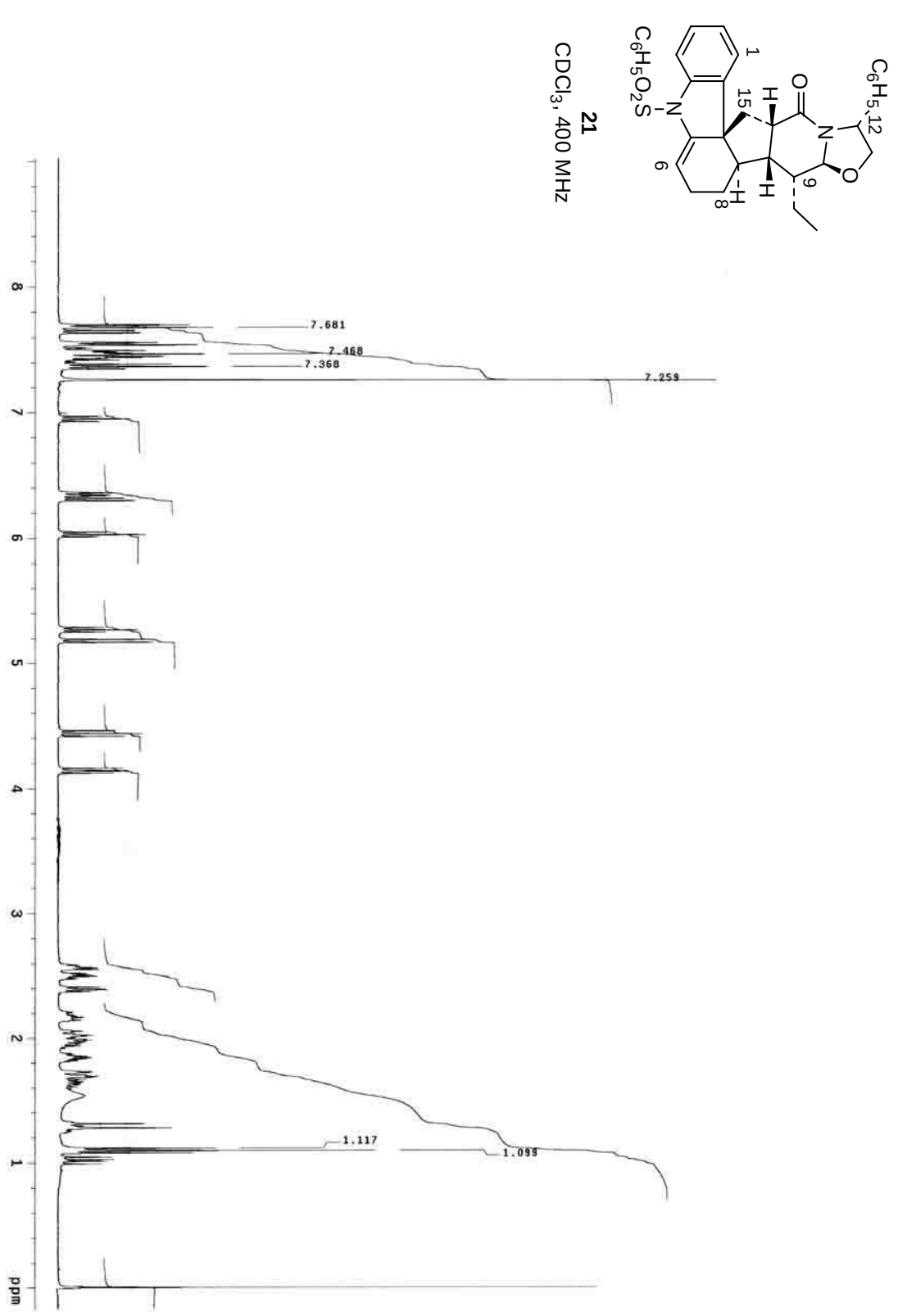
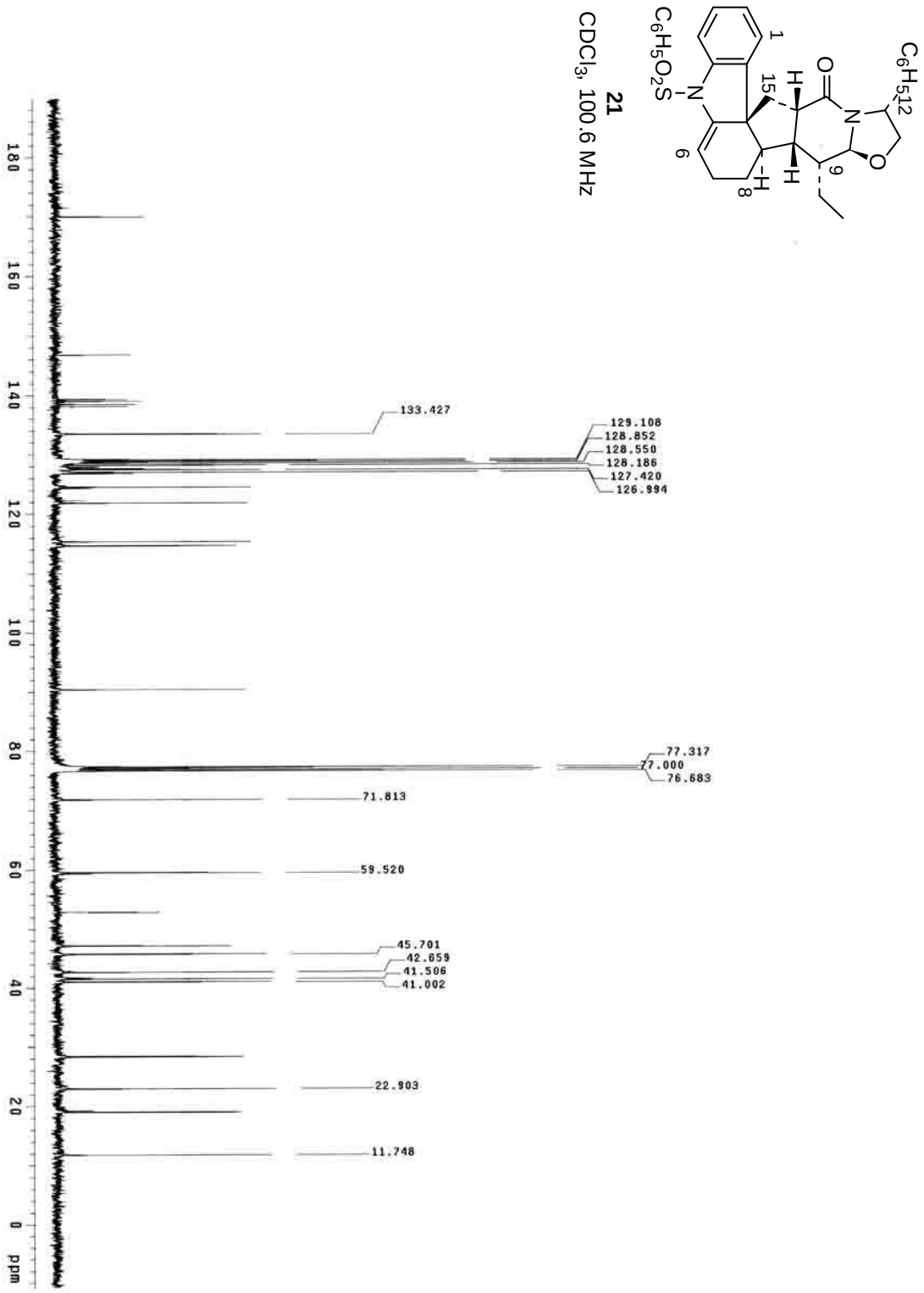
N
H
O
H
N
O
C6H5
7.792
7.790
7.771
7.768
7.347
7.327
7.317
7.315
7.311
7.259
7.185
7.165
1.390
1.257
1.255
0.993
0.974
0.956
8
7
6
5
4
3
2
1
-0
ppm


16-epi-16b
CDCl3, 100.6 MHz
C6H5O2S
N
H
O
H
N
O
C6H5
180
160
140
120
100
80
60
40
20
0
ppm
133.629
129.139
128.767
127.335
126.468
125.283
125.237
119.121
114.577
77.317
77.000
76.683
54.209
43.619
38.572
22.113
11.376


21
CDCl3, 400 MHz
C6H5O2S
C6H5,12
7.681
7.468
7.368
7.259
1.117
1.099
ppm


21
CDCl3, 100.6 MHz
C6H5O2S
C6H5
133.427
129.108
128.852
128.550
128.186
127.420
126.994
77.317
77.000
76.683
71.813
59.520
45.701
42.659
41.506
41.002
22.903
11.748
ppm

X- ray crystal structure of **16a**

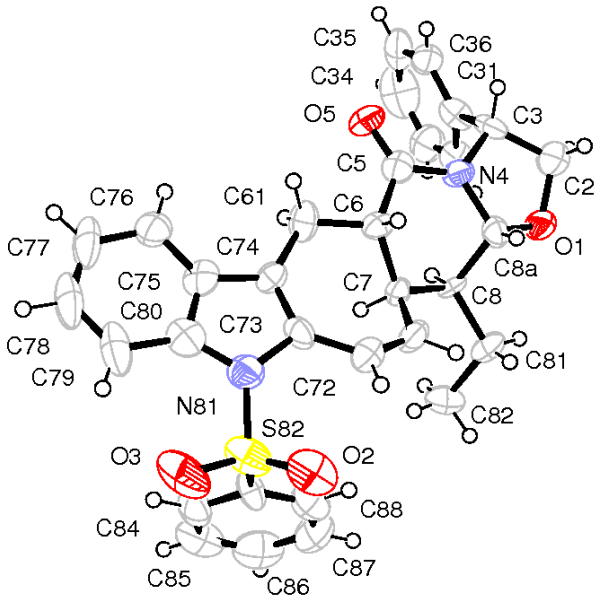


Table 1. Crystal data and structure refinement for **16a**.

Identification code	**16a**	
Empirical formula	C32 H30 N2 O4 S	
Formula weight	538.64	
Temperature	292(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 9.822(2) Å	α= 90°.
	b = 15.050(2) Å	β= 90°.
	c = 18.015(3) Å	γ = 90°.
Volume	2663.0(8) $Å^3$	
Z	4	
Density (calculated)	1.343 Mg/m^3	
Absorption coefficient	0.163 mm^{-1}	
F(000)	1136	
Crystal size	0.38 x 0.33 x 0.25 mm^3	
Theta range for data collection	2.26 to 22.75°.	
Index ranges	0<=h<=10, 0<=k<=16, 0<=l<=19	
Reflections collected	2032	
Independent reflections	2032	
Completeness to theta = 22.75°	98.3 %	
Max. and min. transmission	0.9603 and 0.9405	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2032 / 0 / 353
Goodness-of-fit on F^2	0.864
Final R indices [I>2sigma(I)]	R1 = 0.0489, wR2 = 0.1040
R indices (all data)	R1 = 0.1868, wR2 = 0.1305
Absolute structure parameter	-0.1(3)
Largest diff. peak and hole	0.236 and -0.236 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **16a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(82)	1796(4)	3316(2)	8438(2)	65(1)
O(1)	-2456(6)	8409(4)	9468(3)	53(2)
O(2)	386(8)	3165(4)	8267(4)	76(2)
O(3)	2825(8)	2718(4)	8163(4)	90(3)
O(5)	1361(7)	8585(4)	8119(3)	53(2)
N(4)	-683(8)	8389(5)	8642(3)	42(2)
N(81)	2218(9)	4323(5)	8105(4)	54(2)
C(2)	-2474(10)	9244(7)	9071(6)	65(3)
C(3)	-1069(10)	9332(5)	8736(5)	46(3)
C(5)	505(11)	8093(7)	8352(5)	46(3)
C(6)	562(8)	7074(5)	8323(5)	37(2)
C(7)	-1(8)	6577(5)	9003(4)	36(2)
C(8)	-934(8)	7167(5)	9510(4)	34(2)
C(8A)	-1679(9)	7818(6)	9010(5)	41(2)
C(31)	-77(10)	9847(6)	9217(5)	44(2)
C(32)	-61(10)	9723(6)	9971(6)	48(3)
C(33)	820(12)	10216(7)	10418(6)	69(3)
C(34)	1677(15)	10831(9)	10119(9)	96(5)
C(35)	1673(11)	10942(6)	9362(9)	77(4)
C(36)	796(10)	10461(6)	8910(6)	54(3)
C(61)	2031(9)	6806(6)	8150(5)	56(3)
C(71)	-670(10)	5738(6)	8731(5)	50(3)
C(72)	11(10)	5100(7)	8386(5)	49(3)
C(73)	1446(10)	5132(6)	8224(5)	45(3)

C(74)	2322(10)	5831(6)	8136(4)	40(3)
C(75)	3635(11)	5484(8)	7932(5)	51(3)
C(76)	4835(11)	5960(7)	7739(5)	59(3)
C(77)	5962(12)	5429(10)	7544(5)	80(4)
C(78)	5907(13)	4516(10)	7552(6)	83(4)
C(79)	4737(13)	4054(9)	7722(5)	77(4)
C(80)	3543(13)	4552(8)	7931(5)	57(3)
C(81)	-1876(9)	6665(6)	10034(4)	50(3)
C(82)	-1098(9)	6061(6)	10586(5)	69(3)
C(83)	1960(11)	3394(6)	9410(5)	49(3)
C(84)	3155(11)	3157(6)	9746(7)	64(3)
C(85)	3212(14)	3152(7)	10521(8)	78(4)
C(86)	2084(16)	3369(8)	10918(7)	84(4)
C(87)	882(13)	3611(7)	10586(7)	74(3)
C(88)	847(12)	3618(6)	9818(6)	61(3)

Table 3. Bond lengths [Å] and angles [°] for **16a**.

S(82)-O(2)	1.437(7)
S(82)-O(3)	1.441(7)
S(82)-N(81)	1.682(8)
S(82)-C(83)	1.763(9)
O(1)-C(8A)	1.434(9)
O(1)-C(2)	1.446(10)
O(5)-C(5)	1.196(9)
N(4)-C(5)	1.354(10)
N(4)-C(8A)	1.461(10)
N(4)-C(3)	1.479(10)
N(81)-C(80)	1.382(12)
N(81)-C(73)	1.450(10)
C(2)-C(3)	1.512(12)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(31)	1.516(11)
C(3)-H(3)	0.9800
C(5)-C(6)	1.535(12)
C(6)-C(61)	1.530(10)
C(6)-C(7)	1.539(10)
C(6)-H(6)	0.9800

C(7)-C(71)	1.507(11)
C(7)-C(8)	1.570(10)
C(7)-H(7)	0.9800
C(8)-C(8A)	1.518(10)
C(8)-C(81)	1.522(9)
C(8)-H(8)	0.9800
C(8A)-H(8A)	0.9800
C(31)-C(32)	1.373(11)
C(31)-C(36)	1.376(11)
C(32)-C(33)	1.395(12)
C(32)-H(32)	0.9300
C(33)-C(34)	1.362(14)
C(33)-H(33)	0.9300
C(34)-C(35)	1.374(14)
C(34)-H(34)	0.9300
C(35)-C(36)	1.390(12)
C(35)-H(35)	0.9300
C(36)-H(36)	0.9300
C(61)-C(74)	1.496(12)
C(61)-H(61A)	0.9700
C(61)-H(61B)	0.9700
C(71)-C(72)	1.325(11)
C(71)-H(71)	0.9300
C(72)-C(73)	1.440(12)
C(72)-H(72)	0.9300
C(73)-C(74)	1.369(12)
C(74)-C(75)	1.438(12)
C(75)-C(80)	1.405(13)
C(75)-C(76)	1.423(13)
C(76)-C(77)	1.410(13)
C(76)-H(76)	0.9300
C(77)-C(78)	1.375(14)
C(77)-H(77)	0.9300
C(78)-C(79)	1.378(14)
C(78)-H(78)	0.9300
C(79)-C(80)	1.442(14)
C(79)-H(79)	0.9300
C(81)-C(82)	1.549(11)

C(81)-H(81A)	0.9700
C(81)-H(81B)	0.9700
C(82)-H(82A)	0.9600
C(82)-H(82B)	0.9600
C(82)-H(82C)	0.9600
C(83)-C(88)	1.359(12)
C(83)-C(84)	1.367(11)
C(84)-C(85)	1.399(13)
C(84)-H(84)	0.9300
C(85)-C(86)	1.358(15)
C(85)-H(85)	0.9300
C(86)-C(87)	1.372(13)
C(86)-H(86)	0.9300
C(87)-C(88)	1.385(13)
C(87)-H(87)	0.9300
C(88)-H(88)	0.9300
O(2)-S(82)-O(3)	120.2(5)
O(2)-S(82)-N(81)	107.7(5)
O(3)-S(82)-N(81)	105.5(4)
O(2)-S(82)-C(83)	108.1(5)
O(3)-S(82)-C(83)	108.6(5)
N(81)-S(82)-C(83)	105.8(4)
C(8A)-O(1)-C(2)	105.1(7)
C(5)-N(4)-C(8A)	124.0(8)
C(5)-N(4)-C(3)	125.4(8)
C(8A)-N(4)-C(3)	110.0(7)
C(80)-N(81)-C(73)	108.5(8)
C(80)-N(81)-S(82)	122.5(8)
C(73)-N(81)-S(82)	125.1(7)
O(1)-C(2)-C(3)	105.3(7)
O(1)-C(2)-H(2A)	110.7
C(3)-C(2)-H(2A)	110.7
O(1)-C(2)-H(2B)	110.7
C(3)-C(2)-H(2B)	110.7
H(2A)-C(2)-H(2B)	108.8
N(4)-C(3)-C(2)	101.2(8)
N(4)-C(3)-C(31)	113.0(7)
C(2)-C(3)-C(31)	113.8(8)

N(4)-C(3)-H(3)	109.5
C(2)-C(3)-H(3)	109.5
C(31)-C(3)-H(3)	109.5
O(5)-C(5)-N(4)	122.5(9)
O(5)-C(5)-C(6)	125.5(9)
N(4)-C(5)-C(6)	111.9(9)
C(61)-C(6)-C(5)	107.7(8)
C(61)-C(6)-C(7)	111.9(7)
C(5)-C(6)-C(7)	116.5(7)
C(61)-C(6)-H(6)	106.7
C(5)-C(6)-H(6)	106.7
C(7)-C(6)-H(6)	106.7
C(71)-C(7)-C(6)	107.8(7)
C(71)-C(7)-C(8)	114.1(7)
C(6)-C(7)-C(8)	113.5(6)
C(71)-C(7)-H(7)	107.0
C(6)-C(7)-H(7)	107.0
C(8)-C(7)-H(7)	107.0
C(8A)-C(8)-C(81)	113.3(7)
C(8A)-C(8)-C(7)	107.5(7)
C(81)-C(8)-C(7)	115.7(6)
C(8A)-C(8)-H(8)	106.6
C(81)-C(8)-H(8)	106.6
C(7)-C(8)-H(8)	106.6
O(1)-C(8A)-N(4)	104.6(7)
O(1)-C(8A)-C(8)	108.3(7)
N(4)-C(8A)-C(8)	109.0(7)
O(1)-C(8A)-H(8A)	111.5
N(4)-C(8A)-H(8A)	111.5
C(8)-C(8A)-H(8A)	111.5
C(32)-C(31)-C(36)	118.8(9)
C(32)-C(31)-C(3)	120.3(10)
C(36)-C(31)-C(3)	120.9(9)
C(31)-C(32)-C(33)	120.4(10)
C(31)-C(32)-H(32)	119.8
C(33)-C(32)-H(32)	119.8
C(34)-C(33)-C(32)	121.1(11)
C(34)-C(33)-H(33)	119.5

C(32)-C(33)-H(33)	119.5
C(33)-C(34)-C(35)	118.3(13)
C(33)-C(34)-H(34)	120.9
C(35)-C(34)-H(34)	120.9
C(34)-C(35)-C(36)	121.4(12)
C(34)-C(35)-H(35)	119.3
C(36)-C(35)-H(35)	119.3
C(31)-C(36)-C(35)	120.0(10)
C(31)-C(36)-H(36)	120.0
C(35)-C(36)-H(36)	120.0
C(74)-C(61)-C(6)	116.3(8)
C(74)-C(61)-H(61A)	108.2
C(6)-C(61)-H(61A)	108.2
C(74)-C(61)-H(61B)	108.2
C(6)-C(61)-H(61B)	108.2
H(61A)-C(61)-H(61B)	107.4
C(72)-C(71)-C(7)	122.7(8)
C(72)-C(71)-H(71)	118.7
C(7)-C(71)-H(71)	118.7
C(71)-C(72)-C(73)	124.4(10)
C(71)-C(72)-H(72)	117.8
C(73)-C(72)-H(72)	117.8
C(74)-C(73)-C(72)	131.6(9)
C(74)-C(73)-N(81)	107.4(8)
C(72)-C(73)-N(81)	120.9(10)
C(73)-C(74)-C(75)	108.3(8)
C(73)-C(74)-C(61)	129.2(9)
C(75)-C(74)-C(61)	122.2(9)
C(80)-C(75)-C(76)	123.8(11)
C(80)-C(75)-C(74)	107.8(10)
C(76)-C(75)-C(74)	128.4(10)
C(77)-C(76)-C(75)	115.2(9)
C(77)-C(76)-H(76)	122.4
C(75)-C(76)-H(76)	122.4
C(78)-C(77)-C(76)	122.2(13)
C(78)-C(77)-H(77)	118.9
C(76)-C(77)-H(77)	118.9
C(77)-C(78)-C(79)	122.6(13)

C(77)-C(78)-H(78)	118.7
C(79)-C(78)-H(78)	118.7
C(78)-C(79)-C(80)	118.3(12)
C(78)-C(79)-H(79)	120.8
C(80)-C(79)-H(79)	120.8
N(81)-C(80)-C(75)	108.0(10)
N(81)-C(80)-C(79)	134.1(12)
C(75)-C(80)-C(79)	117.8(12)
C(8)-C(81)-C(82)	112.9(7)
C(8)-C(81)-H(81A)	109.0
C(82)-C(81)-H(81A)	109.0
C(8)-C(81)-H(81B)	109.0
C(82)-C(81)-H(81B)	109.0
H(81A)-C(81)-H(81B)	107.8
C(81)-C(82)-H(82A)	109.5
C(81)-C(82)-H(82B)	109.5
H(82A)-C(82)-H(82B)	109.5
C(81)-C(82)-H(82C)	109.5
H(82A)-C(82)-H(82C)	109.5
H(82B)-C(82)-H(82C)	109.5
C(88)-C(83)-C(84)	121.0(9)
C(88)-C(83)-S(82)	118.7(8)
C(84)-C(83)-S(82)	120.0(9)
C(83)-C(84)-C(85)	118.5(11)
C(83)-C(84)-H(84)	120.7
C(85)-C(84)-H(84)	120.7
C(86)-C(85)-C(84)	119.4(12)
C(86)-C(85)-H(85)	120.3
C(84)-C(85)-H(85)	120.3
C(85)-C(86)-C(87)	122.5(12)
C(85)-C(86)-H(86)	118.8
C(87)-C(86)-H(86)	118.8
C(86)-C(87)-C(88)	117.3(12)
C(86)-C(87)-H(87)	121.4
C(88)-C(87)-H(87)	121.4
C(83)-C(88)-C(87)	121.2(10)
C(83)-C(88)-H(88)	119.4
C(87)-C(88)-H(88)	119.4

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **16a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(82)	98(3)	48(2)	49(2)	-11(2)	-7(2)	13(2)
O(1)	50(4)	46(4)	64(4)	7(4)	22(4)	4(4)
O(2)	97(6)	62(4)	68(6)	-14(4)	-36(5)	-3(5)
O(3)	147(8)	57(4)	66(6)	-19(4)	12(5)	46(5)
O(5)	51(4)	49(4)	58(5)	5(3)	10(4)	-15(4)
N(4)	45(5)	35(5)	45(5)	2(4)	10(4)	-3(5)
N(81)	62(7)	53(6)	48(6)	5(5)	11(5)	6(5)
C(2)	56(7)	65(8)	74(8)	11(7)	19(7)	8(7)
C(3)	66(7)	31(6)	40(6)	12(5)	2(6)	16(6)
C(5)	48(7)	55(8)	34(6)	0(6)	0(5)	-1(6)
C(6)	43(6)	46(6)	24(6)	5(5)	-1(5)	-5(5)
C(7)	26(5)	41(5)	40(6)	4(5)	-2(5)	-5(5)
C(8)	32(6)	36(5)	33(5)	9(4)	12(5)	-12(5)
C(8A)	36(6)	43(5)	43(6)	-1(5)	3(6)	9(6)
C(31)	62(7)	32(6)	39(7)	-14(5)	-13(6)	6(6)
C(32)	54(7)	42(6)	48(7)	-8(5)	-7(6)	-5(6)
C(33)	67(8)	73(8)	68(8)	-8(8)	7(8)	1(7)
C(34)	96(11)	99(12)	91(11)	-55(10)	-13(11)	24(11)
C(35)	41(7)	30(6)	162(14)	-18(8)	2(10)	-1(6)
C(36)	51(7)	40(6)	72(7)	4(6)	8(7)	0(6)
C(61)	46(7)	66(7)	55(7)	-15(6)	15(5)	10(7)
C(71)	39(6)	43(6)	67(7)	-2(6)	18(6)	-9(6)
C(72)	45(7)	58(7)	43(6)	0(6)	2(6)	-6(6)
C(73)	53(7)	40(6)	42(7)	-1(5)	8(6)	19(6)
C(74)	40(7)	44(6)	35(6)	-3(5)	7(5)	-5(6)
C(75)	60(9)	71(9)	22(6)	-2(6)	11(5)	2(8)
C(76)	55(8)	70(8)	51(8)	15(6)	-4(6)	-1(8)
C(77)	46(9)	140(12)	53(7)	-1(9)	16(7)	31(10)
C(78)	56(10)	133(13)	58(8)	-12(9)	9(8)	46(11)
C(79)	56(9)	122(11)	53(9)	-4(8)	-6(7)	43(9)
C(80)	70(10)	65(9)	34(7)	-3(6)	-1(6)	8(8)
C(81)	49(6)	57(6)	45(5)	2(6)	20(5)	-12(6)

C(82)	78(8)	64(7)	64(7)	31(6)	4(7)	3(7)
C(83)	47(6)	47(6)	51(6)	-15(6)	-4(6)	20(6)
C(84)	58(8)	43(6)	90(10)	-11(6)	2(7)	13(6)
C(85)	87(11)	52(7)	95(11)	2(7)	-63(9)	-20(8)
C(86)	108(12)	70(9)	74(10)	1(8)	-26(10)	-27(10)
C(87)	71(9)	87(9)	64(9)	3(7)	23(9)	-8(8)
C(88)	70(9)	51(7)	61(9)	-6(6)	-10(8)	5(6)

X- ray crystal structure of **16b**

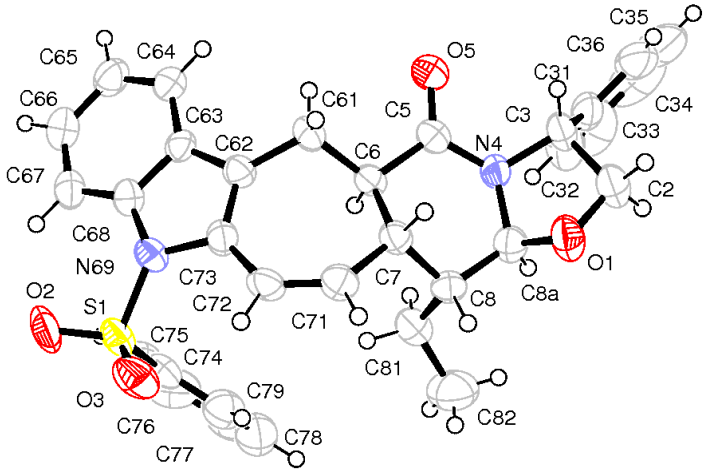


Table 1. Crystal data and structure refinement for **16b**.

Identification code	**16b**	
Empirical formula	C32 H30 N2 O4 S	
Formula weight	538.64	
Temperature	565(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21 21 21	
Unit cell dimensions	a = 9.004(5) Å	α= 90°.
	b = 14.264(3) Å	β= 90°.
	c = 20.840(6) Å	γ = 90°.
Volume	2676.5(18) $Å^3$	
Z	4	
Density (calculated)	1.337 Mg/m^3	
Absorption coefficient	0.163 mm^{-1}	
F(000)	1136	
Crystal size	0.47 x 0.23 x 0.21 mm^3	
Theta range for data collection	1.73 to 24.94°.	
Index ranges	0<=h<=10, 0<=k<=16, 0<=l<=14	
Reflections collected	2022	
Independent reflections	2022	
Max. and min. transmission	0.9667 and 0.9275	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2022 / 0 / 353	

Goodness-of-fit on F^2	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0411, wR2 = 0.0739
R indices (all data)	R1 = 0.0740, wR2 = 0.0832
Absolute structure parameter	-0.22(15)
Largest diff. peak and hole	0.147 and -0.164 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **16b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	2864(2)	947(1)	8883(1)	52(1)
O(1)	5027(4)	6802(2)	8553(2)	61(1)
O(2)	3006(4)	-43(2)	8857(2)	70(1)
O(3)	1497(4)	1380(2)	8708(2)	65(1)
O(5)	8297(4)	4910(2)	7880(2)	68(1)
N(4)	6937(4)	5781(2)	8568(2)	43(1)
N(69)	4164(4)	1384(3)	8394(2)	43(1)
C(2)	6317(5)	7367(3)	8469(3)	58(2)
C(3)	7612(5)	6664(3)	8346(3)	49(2)
C(5)	7211(6)	4974(3)	8228(3)	44(1)
C(6)	6112(4)	4179(3)	8309(3)	39(1)
C(7)	4540(5)	4610(3)	8325(3)	41(1)
C(8)	4416(5)	5232(3)	8927(3)	43(1)
C(8A)	5561(5)	6007(3)	8901(3)	46(1)
C(31)	8997(6)	6953(4)	8682(3)	54(2)
C(32)	9361(7)	6611(4)	9281(4)	84(2)
C(33)	10616(8)	6920(6)	9610(4)	116(3)
C(34)	11503(10)	7568(8)	9318(6)	141(6)
C(35)	11167(9)	7932(7)	8743(5)	125(4)
C(36)	9908(6)	7618(4)	8417(3)	81(2)
C(61)	6324(5)	3429(3)	7806(2)	44(1)
C(62)	5719(5)	2502(3)	8022(2)	40(1)
C(63)	6514(5)	1625(3)	8045(2)	40(1)
C(64)	7979(6)	1372(3)	7879(3)	52(2)
C(65)	8431(6)	478(4)	7983(3)	58(2)
C(66)	7489(6)	-178(3)	8256(3)	57(2)

C(67)	6048(6)	47(3)	8417(3)	53(2)
C(68)	5572(5)	946(3)	8302(3)	45(1)
C(71)	3237(5)	3965(3)	8283(2)	46(1)
C(72)	3130(5)	3026(3)	8265(2)	47(1)
C(73)	4324(5)	2354(3)	8236(3)	43(1)
C(74)	3382(6)	1328(4)	9642(3)	50(2)
C(75)	4327(6)	789(4)	10011(4)	72(2)
C(76)	4686(7)	1079(6)	10621(4)	87(2)
C(77)	4149(8)	1904(6)	10848(4)	83(2)
C(78)	3216(8)	2440(4)	10486(4)	80(2)
C(79)	2808(7)	2152(4)	9874(4)	65(2)
C(81)	4540(6)	4686(4)	9560(3)	61(2)
C(82)	3881(7)	5183(4)	10130(3)	90(2)

Table 3. Bond lengths [Å] and angles [°] for **16b**.

S(1)-O(2)	1.420(3)
S(1)-O(3)	1.424(3)
S(1)-N(69)	1.673(4)
S(1)-C(74)	1.736(5)
O(1)-C(2)	1.425(5)
O(1)-C(8A)	1.428(5)
O(5)-C(5)	1.220(5)
N(4)-C(5)	1.375(6)
N(4)-C(8A)	1.457(6)
N(4)-C(3)	1.473(5)
N(69)-C(68)	1.426(5)
N(69)-C(73)	1.429(5)
C(2)-C(3)	1.558(6)
C(3)-C(31)	1.489(7)
C(5)-C(6)	1.514(6)
C(6)-C(61)	1.509(6)
C(6)-C(7)	1.543(6)
C(7)-C(71)	1.494(6)
C(7)-C(8)	1.541(6)
C(8)-C(8A)	1.512(6)
C(8)-C(81)	1.534(6)
C(31)-C(36)	1.370(7)

C(31)-C(32)	1.380(8)
C(32)-C(33)	1.392(8)
C(33)-C(34)	1.364(11)
C(34)-C(35)	1.340(12)
C(35)-C(36)	1.396(10)
C(61)-C(62)	1.499(6)
C(62)-C(73)	1.349(6)
C(62)-C(63)	1.441(6)
C(63)-C(68)	1.394(6)
C(63)-C(64)	1.410(6)
C(64)-C(65)	1.357(6)
C(65)-C(66)	1.386(6)
C(66)-C(67)	1.378(7)
C(67)-C(68)	1.374(6)
C(71)-C(72)	1.344(6)
C(72)-C(73)	1.442(6)
C(74)-C(79)	1.372(7)
C(74)-C(75)	1.381(7)
C(75)-C(76)	1.374(8)
C(76)-C(77)	1.356(9)
C(77)-C(78)	1.363(8)
C(78)-C(79)	1.389(8)
C(81)-C(82)	1.506(7)
O(2)-S(1)-O(3)	120.0(2)
O(2)-S(1)-N(69)	106.5(2)
O(3)-S(1)-N(69)	106.7(2)
O(2)-S(1)-C(74)	108.8(3)
O(3)-S(1)-C(74)	109.3(3)
N(69)-S(1)-C(74)	104.5(2)
C(2)-O(1)-C(8A)	103.8(3)
C(5)-N(4)-C(8A)	125.7(4)
C(5)-N(4)-C(3)	118.7(4)
C(8A)-N(4)-C(3)	108.1(4)
C(68)-N(69)-C(73)	107.6(4)
C(68)-N(69)-S(1)	122.7(3)
C(73)-N(69)-S(1)	124.9(3)
O(1)-C(2)-C(3)	105.4(4)
N(4)-C(3)-C(31)	115.7(4)

N(4)-C(3)-C(2)	101.0(3)
C(31)-C(3)-C(2)	111.9(4)
O(5)-C(5)-N(4)	120.8(4)
O(5)-C(5)-C(6)	122.3(5)
N(4)-C(5)-C(6)	116.9(4)
C(61)-C(6)-C(5)	111.8(4)
C(61)-C(6)-C(7)	114.4(4)
C(5)-C(6)-C(7)	107.7(4)
C(71)-C(7)-C(8)	110.3(4)
C(71)-C(7)-C(6)	118.3(4)
C(8)-C(7)-C(6)	108.3(4)
C(8A)-C(8)-C(81)	110.6(4)
C(8A)-C(8)-C(7)	110.0(4)
C(81)-C(8)-C(7)	113.7(4)
O(1)-C(8A)-N(4)	102.8(4)
O(1)-C(8A)-C(8)	111.7(4)
N(4)-C(8A)-C(8)	115.8(4)
C(36)-C(31)-C(32)	117.8(6)
C(36)-C(31)-C(3)	120.2(6)
C(32)-C(31)-C(3)	121.8(5)
C(31)-C(32)-C(33)	121.7(7)
C(34)-C(33)-C(32)	118.1(9)
C(35)-C(34)-C(33)	121.9(10)
C(34)-C(35)-C(36)	119.6(10)
C(31)-C(36)-C(35)	120.8(8)
C(62)-C(61)-C(6)	111.8(4)
C(73)-C(62)-C(63)	108.4(4)
C(73)-C(62)-C(61)	125.1(4)
C(63)-C(62)-C(61)	126.5(4)
C(68)-C(63)-C(64)	119.1(4)
C(68)-C(63)-C(62)	108.3(4)
C(64)-C(63)-C(62)	132.6(5)
C(65)-C(64)-C(63)	118.8(5)
C(64)-C(65)-C(66)	121.1(5)
C(67)-C(66)-C(65)	121.3(5)
C(68)-C(67)-C(66)	118.0(5)
C(67)-C(68)-C(63)	121.7(5)
C(67)-C(68)-N(69)	131.5(5)

C(63)-C(68)-N(69)	106.8(4)
C(72)-C(71)-C(7)	132.2(4)
C(71)-C(72)-C(73)	127.7(4)
C(62)-C(73)-N(69)	108.8(4)
C(62)-C(73)-C(72)	127.1(4)
N(69)-C(73)-C(72)	124.0(4)
C(79)-C(74)-C(75)	120.8(6)
C(79)-C(74)-S(1)	119.2(5)
C(75)-C(74)-S(1)	120.0(5)
C(76)-C(75)-C(74)	119.5(7)
C(77)-C(76)-C(75)	120.0(7)
C(76)-C(77)-C(78)	120.9(7)
C(77)-C(78)-C(79)	120.3(7)
C(74)-C(79)-C(78)	118.5(6)
C(82)-C(81)-C(8)	114.3(4)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **16b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	43(1)	49(1)	65(1)	2(1)	0(1)	-17(1)
O(1)	51(2)	40(2)	93(3)	9(2)	-7(2)	-2(2)
O(2)	69(2)	40(2)	100(3)	0(2)	0(2)	-26(2)
O(3)	36(2)	74(2)	84(3)	14(2)	-5(2)	-11(2)
O(5)	56(2)	56(2)	93(3)	-11(2)	28(2)	-14(2)
N(4)	40(2)	35(2)	52(3)	-2(2)	4(2)	-3(2)
N(69)	36(2)	43(2)	49(3)	3(2)	0(2)	-8(2)
C(2)	53(3)	42(3)	79(5)	14(3)	-5(4)	-5(3)
C(3)	52(3)	34(3)	61(4)	8(3)	1(3)	-7(2)
C(5)	40(3)	45(3)	47(4)	2(3)	-2(3)	-4(3)
C(6)	35(3)	39(3)	42(4)	6(3)	1(2)	-2(2)
C(7)	36(3)	40(3)	47(4)	6(3)	1(3)	0(2)
C(8)	33(3)	48(3)	48(4)	-1(3)	4(3)	3(2)
C(8A)	47(3)	43(3)	47(4)	4(3)	-1(3)	1(3)
C(31)	48(4)	43(3)	71(6)	-7(3)	4(3)	-4(3)
C(32)	63(4)	71(4)	117(7)	-10(5)	-28(4)	-14(4)

C(33)	70(5)	128(7)	149(8)	-37(6)	-48(6)	-3(5)
C(34)	43(5)	161(11)	217(15)	-107(11)	-16(8)	-1(6)
C(35)	63(6)	115(7)	199(13)	-88(8)	49(7)	-41(5)
C(36)	64(4)	74(4)	105(6)	-30(4)	32(4)	-15(4)
C(61)	42(3)	41(3)	50(4)	0(3)	3(3)	-9(2)
C(62)	39(3)	45(3)	37(4)	-2(3)	-1(3)	-6(3)
C(63)	40(3)	42(3)	40(4)	-12(3)	1(3)	-4(3)
C(64)	54(4)	48(3)	55(4)	-13(3)	10(3)	-6(3)
C(65)	47(3)	55(3)	72(5)	-18(3)	6(3)	5(3)
C(66)	65(4)	42(3)	65(5)	-6(3)	-11(3)	1(3)
C(67)	59(4)	40(3)	59(5)	-6(3)	-3(3)	-6(3)
C(68)	45(3)	38(3)	51(4)	-3(3)	-3(3)	-3(3)
C(71)	37(3)	53(3)	49(4)	-3(3)	-2(3)	0(3)
C(72)	30(3)	53(3)	58(4)	5(3)	6(3)	-5(2)
C(73)	43(3)	37(3)	50(4)	-1(3)	-2(3)	-3(3)
C(74)	44(3)	54(3)	51(5)	5(3)	3(3)	-19(3)
C(75)	58(4)	86(5)	72(6)	13(4)	0(4)	5(4)
C(76)	61(4)	135(7)	67(7)	10(5)	-6(4)	-3(5)
C(77)	71(5)	114(6)	64(6)	-14(5)	14(4)	-41(5)
C(78)	95(6)	72(4)	74(8)	-1(5)	21(5)	-9(4)
C(79)	71(4)	69(4)	55(6)	4(4)	7(4)	-1(4)
C(81)	69(4)	58(4)	56(5)	0(4)	11(4)	-13(3)
C(82)	95(5)	113(5)	61(5)	-8(4)	21(4)	-6(5)

X- ray crystal structure of **21**

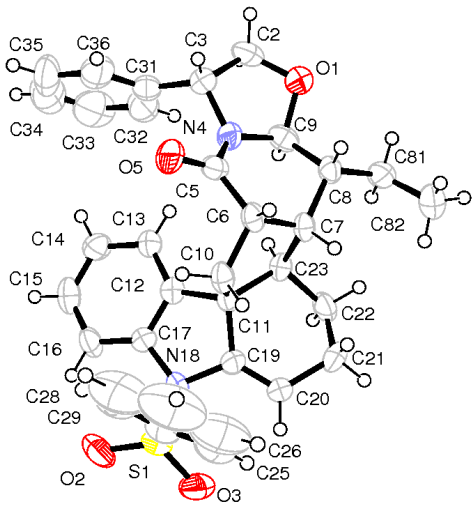


Table 1. Crystal data and structure refinement for **21**.

Identification code	**21**	
Empirical formula	C35 H38 N2 O5 S	
Formula weight	598.73	
Temperature	294(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 9.2040(18) Å	α= 90°.
	b = 14.1890(18) Å	β= 94.66(2)°.
	c = 11.795(3) Å	γ = 90°.
Volume	1535.3(5) $Å^3$	
Z	2	
Density (calculated)	1.295 Mg/m^3	
Absorption coefficient	0.151 mm^{-1}	
F(000)	636	
Crystal size	0.46 x 0.21 x 0.03 mm^3	
Theta range for data collection	1.73 to 24.97°.	
Index ranges	-10<=h<=10, 0<=k<=16, 0<=l<=14	
Reflections collected	2793	
Independent reflections	2793	
Completeness to theta = 24.97°	99.9 %	
Max. and min. transmission	0.9955 and 0.9337	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2793 / 3 / 390	

Goodness-of-fit on F^2	0.939
Final R indices [I>2sigma(I)]	R1 = 0.0587, wR2 = 0.1245
R indices (all data)	R1 = 0.1251, wR2 = 0.1446
Absolute structure parameter	0.0(2)
Largest diff. peak and hole	0.231 and -0.217 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **21**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	2374(2)	8481(2)	10440(2)	65(1)
O(1)	-2844(5)	12425(4)	5294(5)	69(2)
O(2)	3829(6)	8765(4)	10813(5)	89(2)
O(3)	1507(6)	8023(4)	11234(5)	80(2)
O(5)	1093(5)	10758(4)	5433(4)	67(2)
N(4)	-741(6)	11705(4)	5898(5)	53(2)
N(18)	1515(6)	9447(4)	10026(5)	57(2)
C(2)	-1709(8)	13074(7)	5084(7)	75(3)
C(3)	-307(8)	12484(6)	5171(7)	66(2)
C(5)	-61(8)	10858(6)	5881(6)	54(2)
C(6)	-765(7)	10024(5)	6424(6)	51(2)
C(7)	-2174(7)	10246(5)	7005(6)	48(2)
C(8)	-3086(7)	10958(5)	6286(6)	50(2)
C(9)	-2240(7)	11866(6)	6212(6)	53(2)
C(10)	198(7)	9535(5)	7386(6)	51(2)
C(11)	-85(7)	10064(5)	8501(6)	49(2)
C(12)	1182(7)	10717(5)	8822(6)	47(2)
C(13)	1533(7)	11588(5)	8397(6)	55(2)
C(14)	2849(8)	11992(6)	8769(7)	60(2)
C(15)	3795(9)	11555(6)	9558(7)	67(2)
C(16)	3461(8)	10696(6)	10004(7)	63(2)
C(17)	2135(7)	10290(5)	9628(6)	54(2)
C(19)	27(8)	9416(5)	9510(6)	57(2)
C(20)	-1041(8)	8940(6)	9876(7)	68(2)
C(21)	-2594(8)	9120(6)	9325(8)	75(3)
C(22)	-2733(7)	10171(6)	9090(7)	64(2)

C(23)	-1635(6)	10508(5)	8234(5)	43(2)
C(24)	2386(11)	7779(6)	9237(7)	72(2)
C(25)	1268(12)	7124(8)	9026(10)	94(3)
C(26)	1304(19)	6564(9)	8068(13)	133(5)
C(27)	2370(20)	6659(11)	7357(13)	144(6)
C(28)	3507(16)	7301(12)	7577(11)	126(5)
C(29)	3480(11)	7878(8)	8504(9)	96(3)
C(31)	1015(9)	13013(6)	5663(8)	69(2)
C(32)	987(9)	13594(7)	6606(9)	83(3)
C(33)	2239(16)	14092(8)	7021(10)	113(4)
C(34)	3467(15)	14019(10)	6470(16)	133(6)
C(35)	3540(12)	13470(10)	5548(14)	117(5)
C(36)	2303(10)	12953(7)	5128(9)	92(3)
C(81)	-4588(7)	11172(6)	6710(7)	65(2)
C(82)	-5588(8)	10297(7)	6693(8)	84(3)
O(1M)	1786(18)	10533(18)	3204(8)	335(11)
C(1M)	3289(16)	10711(17)	3466(19)	271(13)

Table 3. Bond lengths [Å] and angles [°] for **21**.

S(1)-O(2)	1.433(6)
S(1)-O(3)	1.435(5)
S(1)-N(18)	1.637(6)
S(1)-C(24)	1.735(9)
O(1)-C(9)	1.419(8)
O(1)-C(2)	1.430(9)
O(5)-C(5)	1.232(7)
N(4)-C(5)	1.356(9)
N(4)-C(9)	1.474(8)
N(4)-C(3)	1.475(9)
N(18)-C(17)	1.422(9)
N(18)-C(19)	1.453(9)
C(2)-C(3)	1.534(10)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(31)	1.505(11)
C(3)-H(3)	0.9800

C(5)-C(6)	1.515(10)
C(6)-C(10)	1.546(9)
C(6)-C(7)	1.548(9)
C(6)-H(6)	0.9800
C(7)-C(8)	1.526(9)
C(7)-C(23)	1.540(9)
C(7)-H(7)	0.9800
C(8)-C(9)	1.511(10)
C(8)-C(81)	1.537(8)
C(8)-H(8)	0.9800
C(9)-H(9)	0.9800
C(10)-C(11)	1.554(9)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(11)-C(19)	1.501(9)
C(11)-C(12)	1.514(9)
C(11)-C(23)	1.569(9)
C(12)-C(17)	1.380(9)
C(12)-C(13)	1.382(10)
C(13)-C(14)	1.379(9)
C(13)-H(13)	0.9300
C(14)-C(15)	1.371(10)
C(14)-H(14)	0.9300
C(15)-C(16)	1.372(11)
C(15)-H(15)	0.9300
C(16)-C(17)	1.389(10)
C(16)-H(16)	0.9300
C(19)-C(20)	1.295(9)
C(20)-C(21)	1.542(9)
C(20)-H(20)	0.9300
C(21)-C(22)	1.520(12)
C(21)-H(21A)	0.9700
C(21)-H(21B)	0.9700
C(22)-C(23)	1.561(9)
C(22)-H(22A)	0.9700
C(22)-H(22B)	0.9700
C(23)-H(23)	0.9800
C(24)-C(29)	1.386(12)

C(24)-C(25)	1.394(13)
C(25)-C(26)	1.384(15)
C(25)-H(25)	0.9300
C(26)-C(27)	1.348(18)
C(26)-H(26)	0.9300
C(27)-C(28)	1.396(18)
C(27)-H(27)	0.9300
C(28)-C(29)	1.368(15)
C(28)-H(28)	0.9300
C(29)-H(29)	0.9300
C(31)-C(32)	1.386(12)
C(31)-C(36)	1.390(11)
C(32)-C(33)	1.406(13)
C(32)-H(32)	0.9300
C(33)-C(34)	1.353(16)
C(33)-H(33)	0.9300
C(34)-C(35)	1.343(17)
C(34)-H(34)	0.9300
C(35)-C(36)	1.411(15)
C(35)-H(35)	0.9300
C(36)-H(36)	0.9300
C(81)-C(82)	1.545(11)
C(81)-H(81A)	0.9700
C(81)-H(81B)	0.9700
C(82)-H(82A)	0.9600
C(82)-H(82B)	0.9600
C(82)-H(82C)	0.9600
O(1M)-C(1M)	1.416(5)
O(1M)-H(1M)	0.8200
C(1M)-H(1M1)	0.9600
C(1M)-H(1M2)	0.9600
C(1M)-H(1M3)	0.9600

O(2)-S(1)-O(3)	118.8(4)
O(2)-S(1)-N(18)	105.8(3)
O(3)-S(1)-N(18)	107.0(3)
O(2)-S(1)-C(24)	110.2(4)
O(3)-S(1)-C(24)	108.4(4)

N(18)-S(1)-C(24)	105.8(4)
C(9)-O(1)-C(2)	104.2(5)
C(5)-N(4)-C(9)	125.7(6)
C(5)-N(4)-C(3)	120.6(6)
C(9)-N(4)-C(3)	109.4(6)
C(17)-N(18)-C(19)	106.1(6)
C(17)-N(18)-S(1)	127.3(5)
C(19)-N(18)-S(1)	121.0(5)
O(1)-C(2)-C(3)	105.0(7)
O(1)-C(2)-H(2A)	110.7
C(3)-C(2)-H(2A)	110.7
O(1)-C(2)-H(2B)	110.7
C(3)-C(2)-H(2B)	110.7
H(2A)-C(2)-H(2B)	108.8
N(4)-C(3)-C(31)	113.4(6)
N(4)-C(3)-C(2)	100.5(6)
C(31)-C(3)-C(2)	113.8(7)
N(4)-C(3)-H(3)	109.6
C(31)-C(3)-H(3)	109.6
C(2)-C(3)-H(3)	109.6
O(5)-C(5)-N(4)	121.5(7)
O(5)-C(5)-C(6)	120.3(7)
N(4)-C(5)-C(6)	118.1(6)
C(5)-C(6)-C(10)	114.9(6)
C(5)-C(6)-C(7)	115.5(6)
C(10)-C(6)-C(7)	102.6(5)
C(5)-C(6)-H(6)	107.8
C(10)-C(6)-H(6)	107.8
C(7)-C(6)-H(6)	107.8
C(8)-C(7)-C(23)	118.9(6)
C(8)-C(7)-C(6)	109.4(6)
C(23)-C(7)-C(6)	104.4(5)
C(8)-C(7)-H(7)	107.9
C(23)-C(7)-H(7)	107.9
C(6)-C(7)-H(7)	107.9
C(9)-C(8)-C(7)	109.5(5)
C(9)-C(8)-C(81)	109.4(6)
C(7)-C(8)-C(81)	114.7(6)

C(9)-C(8)-H(8)	107.7
C(7)-C(8)-H(8)	107.7
C(81)-C(8)-H(8)	107.7
O(1)-C(9)-N(4)	102.2(5)
O(1)-C(9)-C(8)	110.4(6)
N(4)-C(9)-C(8)	112.3(6)
O(1)-C(9)-H(9)	110.5
N(4)-C(9)-H(9)	110.5
C(8)-C(9)-H(9)	110.5
C(6)-C(10)-C(11)	106.2(5)
C(6)-C(10)-H(10A)	110.5
C(11)-C(10)-H(10A)	110.5
C(6)-C(10)-H(10B)	110.5
C(11)-C(10)-H(10B)	110.5
H(10A)-C(10)-H(10B)	108.7
C(19)-C(11)-C(12)	100.1(5)
C(19)-C(11)-C(10)	111.7(6)
C(12)-C(11)-C(10)	109.2(5)
C(19)-C(11)-C(23)	114.1(5)
C(12)-C(11)-C(23)	118.3(6)
C(10)-C(11)-C(23)	103.7(5)
C(17)-C(12)-C(13)	119.2(7)
C(17)-C(12)-C(11)	109.7(6)
C(13)-C(12)-C(11)	130.9(7)
C(14)-C(13)-C(12)	118.8(7)
C(14)-C(13)-H(13)	120.6
C(12)-C(13)-H(13)	120.6
C(15)-C(14)-C(13)	121.4(8)
C(15)-C(14)-H(14)	119.3
C(13)-C(14)-H(14)	119.3
C(14)-C(15)-C(16)	120.8(8)
C(14)-C(15)-H(15)	119.6
C(16)-C(15)-H(15)	119.6
C(15)-C(16)-C(17)	117.6(8)
C(15)-C(16)-H(16)	121.2
C(17)-C(16)-H(16)	121.2
C(12)-C(17)-C(16)	122.1(7)
C(12)-C(17)-N(18)	110.3(6)

C(16)-C(17)-N(18)	127.5(7)
C(20)-C(19)-N(18)	126.3(7)
C(20)-C(19)-C(11)	125.3(7)
N(18)-C(19)-C(11)	108.4(6)
C(19)-C(20)-C(21)	118.4(7)
C(19)-C(20)-H(20)	120.8
C(21)-C(20)-H(20)	120.8
C(22)-C(21)-C(20)	107.5(6)
C(22)-C(21)-H(21A)	110.2
C(20)-C(21)-H(21A)	110.2
C(22)-C(21)-H(21B)	110.2
C(20)-C(21)-H(21B)	110.2
H(21A)-C(21)-H(21B)	108.5
C(21)-C(22)-C(23)	111.7(6)
C(21)-C(22)-H(22A)	109.3
C(23)-C(22)-H(22A)	109.3
C(21)-C(22)-H(22B)	109.3
C(23)-C(22)-H(22B)	109.3
H(22A)-C(22)-H(22B)	107.9
C(7)-C(23)-C(22)	111.1(6)
C(7)-C(23)-C(11)	108.1(5)
C(22)-C(23)-C(11)	111.9(6)
C(7)-C(23)-H(23)	108.6
C(22)-C(23)-H(23)	108.6
C(11)-C(23)-H(23)	108.6
C(29)-C(24)-C(25)	121.3(10)
C(29)-C(24)-S(1)	120.4(9)
C(25)-C(24)-S(1)	118.4(8)
C(26)-C(25)-C(24)	117.5(11)
C(26)-C(25)-H(25)	121.3
C(24)-C(25)-H(25)	121.3
C(27)-C(26)-C(25)	121.2(16)
C(27)-C(26)-H(26)	119.4
C(25)-C(26)-H(26)	119.4
C(26)-C(27)-C(28)	121.5(16)
C(26)-C(27)-H(27)	119.2
C(28)-C(27)-H(27)	119.2
C(29)-C(28)-C(27)	118.5(14)

C(29)-C(28)-H(28)	120.8
C(27)-C(28)-H(28)	120.8
C(28)-C(29)-C(24)	119.9(12)
C(28)-C(29)-H(29)	120.0
C(24)-C(29)-H(29)	120.0
C(32)-C(31)-C(36)	118.2(9)
C(32)-C(31)-C(3)	122.6(8)
C(36)-C(31)-C(3)	119.1(9)
C(31)-C(32)-C(33)	120.7(10)
C(31)-C(32)-H(32)	119.7
C(33)-C(32)-H(32)	119.7
C(34)-C(33)-C(32)	119.2(13)
C(34)-C(33)-H(33)	120.4
C(32)-C(33)-H(33)	120.4
C(35)-C(34)-C(33)	122.1(14)
C(35)-C(34)-H(34)	118.9
C(33)-C(34)-H(34)	118.9
C(34)-C(35)-C(36)	119.6(12)
C(34)-C(35)-H(35)	120.2
C(36)-C(35)-H(35)	120.2
C(31)-C(36)-C(35)	120.2(11)
C(31)-C(36)-H(36)	119.9
C(35)-C(36)-H(36)	119.9
C(8)-C(81)-C(82)	112.8(7)
C(8)-C(81)-H(81A)	109.0
C(82)-C(81)-H(81A)	109.0
C(8)-C(81)-H(81B)	109.0
C(82)-C(81)-H(81B)	109.0
H(81A)-C(81)-H(81B)	107.8
C(81)-C(82)-H(82A)	109.5
C(81)-C(82)-H(82B)	109.5
H(82A)-C(82)-H(82B)	109.5
C(81)-C(82)-H(82C)	109.5
H(82A)-C(82)-H(82C)	109.5
H(82B)-C(82)-H(82C)	109.5
C(1M)-O(1M)-H(1M)	109.5
O(1M)-C(1M)-H(1M1)	109.5
O(1M)-C(1M)-H(1M2)	109.5

H(1M1)-C(1M)-H(1M2)	109.5
O(1M)-C(1M)-H(1M3)	109.5
H(1M1)-C(1M)-H(1M3)	109.5
H(1M2)-C(1M)-H(1M3)	109.5

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **21**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	64(1)	65(1)	66(1)	22(1)	-7(1)	8(1)
O(1)	55(3)	74(4)	77(4)	15(3)	1(3)	1(3)
O(2)	62(3)	91(5)	107(5)	22(4)	-28(3)	9(3)
O(3)	88(4)	81(4)	72(4)	33(4)	12(3)	5(3)
O(5)	47(3)	82(4)	73(4)	0(3)	15(3)	4(3)
N(4)	47(3)	55(4)	57(4)	5(3)	7(3)	5(3)
N(18)	39(3)	60(4)	70(4)	20(4)	-5(3)	1(3)
C(2)	59(5)	87(7)	78(6)	35(5)	-5(4)	8(5)
C(3)	61(5)	69(6)	65(5)	21(5)	-4(4)	-11(5)
C(5)	54(4)	61(5)	45(4)	5(4)	-1(4)	4(4)
C(6)	48(4)	41(4)	62(5)	-11(4)	1(4)	-4(4)
C(7)	36(4)	48(4)	60(5)	-7(4)	0(3)	-6(3)
C(8)	41(4)	56(5)	54(4)	0(4)	4(3)	2(4)
C(9)	55(4)	52(5)	49(4)	0(4)	-9(4)	13(4)
C(10)	39(4)	47(5)	65(5)	-7(4)	1(3)	-2(3)
C(11)	44(4)	50(5)	51(4)	1(4)	-2(3)	-4(4)
C(12)	48(4)	43(5)	50(4)	-4(4)	5(3)	-2(4)
C(13)	52(4)	58(6)	53(4)	-1(4)	4(3)	2(4)
C(14)	57(5)	53(5)	69(5)	5(4)	0(4)	-12(4)
C(15)	50(4)	75(7)	74(5)	-14(5)	-1(4)	-15(5)
C(16)	47(4)	72(6)	67(5)	-2(5)	-7(4)	0(4)
C(17)	52(4)	51(5)	59(5)	0(4)	0(4)	-3(4)
C(19)	51(4)	48(5)	71(5)	18(4)	-1(4)	-3(4)
C(20)	51(5)	68(6)	85(6)	31(5)	-5(4)	-5(4)
C(21)	51(5)	79(6)	94(7)	33(5)	5(4)	-9(5)
C(22)	45(4)	86(6)	62(5)	12(5)	1(4)	5(4)

C(23)	37(3)	39(4)	53(4)	-8(3)	1(3)	-3(3)
C(24)	84(6)	60(6)	70(6)	12(5)	-2(5)	11(5)
C(25)	109(8)	78(8)	92(8)	5(6)	-5(6)	15(7)
C(26)	199(15)	88(10)	106(11)	0(9)	-16(10)	30(10)
C(27)	222(19)	111(12)	90(10)	-9(9)	-34(11)	56(13)
C(28)	148(12)	154(14)	76(8)	2(9)	11(8)	46(10)
C(29)	101(8)	96(8)	90(8)	17(7)	2(6)	36(6)
C(31)	64(5)	50(5)	92(7)	31(5)	-3(5)	1(5)
C(32)	74(6)	67(6)	104(7)	20(6)	-18(5)	-18(6)
C(33)	151(11)	70(7)	114(10)	10(7)	-20(9)	-23(9)
C(34)	90(9)	91(11)	211(18)	60(11)	-19(11)	-22(9)
C(35)	69(7)	81(9)	205(15)	55(10)	22(8)	6(8)
C(36)	71(6)	75(7)	130(9)	43(7)	10(6)	3(6)
C(81)	53(4)	71(6)	72(5)	21(5)	5(4)	11(4)
C(82)	49(5)	109(8)	92(6)	14(6)	-1(4)	-14(5)
O(1M)	305(19)	490(30)	207(13)	-23(19)	21(14)	20(20)
C(1M)	132(13)	300(30)	390(30)	40(30)	132(18)	43(18)

Table 5. Hydrogen bonds for **21** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1M)-H(1M)...O(5)	0.82	2.02	2.773(9)	151.6