N-Heterocyclic Carbene Catalyzed [8+3] Annulation of Tropone and Enals *via* Homoenolate

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Contents

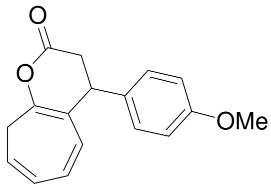
(1) General remarks: All reactions were carried out in oven-dried glassware. Progress of the reaction was monitored by Thin Layer Chromatography while purification was effected by column chromatography, using silica gel (60-120 mesh). Melting points were recorded on a Buchi melting point apparatus and are uncorrected. NMR spectra were recorded at 300 (^{1}H) and 75 (^{13}C) MHz respectively on a Brucker Advance DPX-300 MHz. Chemical shifts are reported in δ (ppm) relative to TMS (^{1}H) or $CDCl_3$ (^{13}C) as internal standards. IR spectra were recorded on Bomem MB series FT-IR spectrometer, absorbencies are reported in cm^{-1}

(2) General experimental procedures:

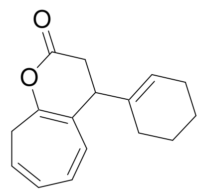
Typical procedure for the synthesis of bicylic δ-lactone derivative (**4**):- KO^{t}Bu (12 mg, 10 mol%) was added to a suspension of the 1,3-dimesityl imidazolium chloride **3** (25 mg, 7 mol%) in 5 ml dry THF under argon atmosphere. This was followed by the addition of enals **2** (0.74 mmol) and tropone **1** (46 mg, 0.43 mmol) and the resulting solution was stirred for 12h at room temperature (30°C). Initial yellow colour of the reaction mixture gradually changed into dark brown on completion of the reaction. The reaction mixture was then passed through a short pad of Celite®. After the removal of the solvent, the residue was subjected to chromatography on a silica gel (60-120 mesh) column using 95:5 hexane-ethyl acetate solvent mixture as eluent to afford **4**.

(3) Characterization data

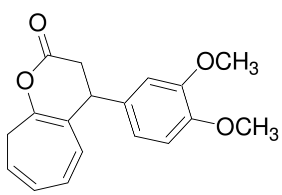
Compound 4b:

	White solid Mp. 92-93°C. **IR** (KBr) ν_{max}: 3012, 2836, 2095, 1773, 1649, 1606, 1512, 1249, 1177, 1125, 1027, 876, 759 cm^{-1}. **^{1}H NMR**: δ 6.94 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.42-6.36 (m, 1H), 6.21-6.16 (m, 2H), 5.60-5.52 (m, 1H), 3.79-3.78 (m, 1H), 3.76 (s, 3H), 3.02-2.92 (m, 1H), 2.81-2.64 (m, 3H), **^{13}CNMR:** δ 167.5, 158.8, 139.7, 132.6, 129.0, 128.7, 128.0, 127.6 , 121.1, 114.3,113.7, 96.1, 55.1, 40.2, 37.1, 30.5 . **HRMS** for $C_{17}H_{16}O_3$: calcd. (M^+): 268.11, found: 268.21.

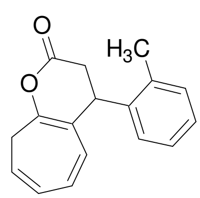
Compound 4c:

	Viscous liquid. **IR** (neat) ν_{max}: 3021, 2929, 2851, 1772, 1682, 1542, 1421, 1338, 1216, 1338, 1216, 1138, 963, 876, 764 cm^{-1}. **^{1}H NMR**: δ 6.43-6.38 (m, 1H), 6.25-6.13 (m, 2H), 5.52-5.36 (m, 1H), 5.36 (s, 1H), 3.05-3.03 (m, 1H), 2.69-2.63 (m, 4H), 1.96 (s, 2H), 1.85-1.85 (m, 2H), 1.61-1.52 (m, 4H), **^{13}CNMR:** δ 168.3, 139.5, 136.0, 129.3, 128.4, 127.5, 125.3, 124. 3, 120.9, 112.9, 96.1, 42.9, 33.8, 30.5, 29.7, 25.5. **HRMS** for $C_{16}H_{18}O_2$: calcd. (M^+): 242.13, found: 242.12.

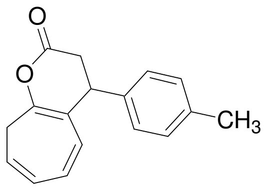
Compound 4d:

	Viscous liquid. **IR** (neat) ν_{max}: 3002, 2929, 2832, 1771, 1650, 1514, 1464, 1344, 1258, 1141, 1026, 878, 763 cm^{-1}. **^{1}H NMR**: δ 6.84-6.72 (m, 2H), 6.56 (dd, *J* = 2.01 Hz, *J* = 8.22 Hz, 1H), 6.48-6.47 (m, 1H), 6.44-6.38 (m, 1H), 6.22-6.17 (m, 2H), 5.61-5.53 (m, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.08-2.94 (m, 1H), 2.85-2.72 (m, 2H), 2.67-2.55 (m, 1H) **^{13}CNMR:** δ 167.7, 149.5, 148.5, 139.9, 133.3, 129.3, 128.9, 127. 8, 119.9, 117.2, 113.7, 111.8, 110.8, 96.3, 56.0, 40.8, 37.3, 30.7 . **HRMS** for $C_{18}H_{18}O_4$: calcd. (M^+): 298.12, found: 298.01.

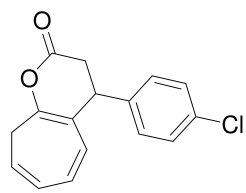
Compound 4e:

	Viscous liquid. **IR** (neat) ν_{max}: 3021, 2946, 2862, 1772, 1686, 1548, 1436, 1342, 1219, 1143, 1026, 946, 865, 746 cm^{-1}. **^{1}H NMR**: δ 7.25-7.06 (m, 4H), 6.80-6.78 (m, 1H), 6.41-6.35 (m, 1H), 6.22-6.17 (m, 1H), 5.59 (q, *J* = 6.93 Hz, 1H), 4.09-4.05 (m, 1H), 2.96-2.87 (m, 2H), 2.73-2.65 (m, 2H), 2.44 (s, 3H), **^{13}CNMR:** δ 176.3, 156.2, 140.6, 137.0, 136.0, 133.8, 131.0, 128. 6, 127.5, 124.6, 119.6, 117.0, 96.1, 38.4, 36.5, 35.9, 19.6 . **HRMS** for $C_{17}H_{16}O_2$: calcd. (M^+): 252.12, found: 253.07.

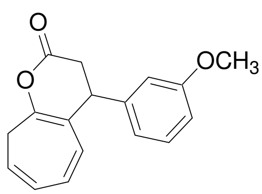
Compound 4f:

	Viscous liquid. **IR** (neat) ν_{max}: 3047, 2931, 2862, 1773, 1678, 1554, 1448, 1336, 1214, 1136, 1024, 946, 862, 745 cm^{-1}. ^{1}**H NMR**: δ 7.07 (d, *J* = 7.88 Hz, 3H), 6.91 (d, *J* = 8.04 Hz, 2H), 6.43-6.35 (m, 1H), 6.20-6.15 (m, 2H), 5.58-5.51 (m, 1H), 3.79-3.75 (m, 1H), 2.98-2.91 (m, 1H), 2.80-2.68 (m, 2H), 2.29 (s, 3H) ^{13}**CNMR:** δ 167.5, 139.7, 137.6, 136.9, 129.6, 129.0, 128.6, 127.6, 126.8, 121.1, 113.5, 96.1, 40.6, 37.0, 30.5, 21.0 . **HRMS** for $C_{17}H_{16}O_2$: calcd. (M^+): 252.12, found: 253.07.

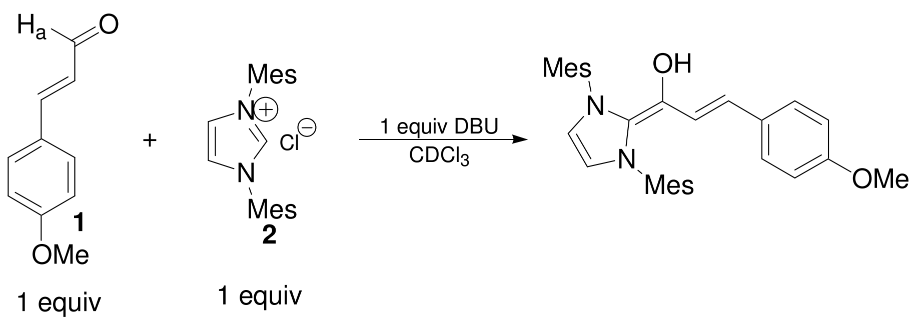
Compound 4g:

	Viscous liquid. **IR** (neat) ν_{max}: 3065, 2924, 2854, 1772, 1651, 1552, 1491, 1335, 1268, 1222, 1197, 1092, 968, 888, 737 cm^{-1}. ^{1}**H NMR**: δ 7.32-7.07 (m, 4H), 6.34-6.26 (m, 1H), 6.05-6.02 (m, 2H), 5.92-5.90 (m, 1H), 4.84-4.80 (m, 1H), 3.27 (dd, *J* = 4.32 Hz, *J* = 13.77 Hz, 1H) 3.14-3.07(m, 1H), 2.96-2.87(m, 2H) ^{13}**CNMR:** δ 167.8, 140.5, 136.1, 132.4, 129.9, 128.8, 125.9, 122.2, 113.1, 101.8, 96.1, 48.4, 41.4, 38.1, 35.9, 29.7, 28.2 . **HRMS** for $C_{16}H_{13}ClO_2$: calcd. (M^+): 272.06, found: 270.92.

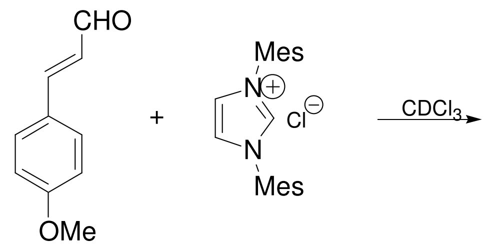
Compound 4h:

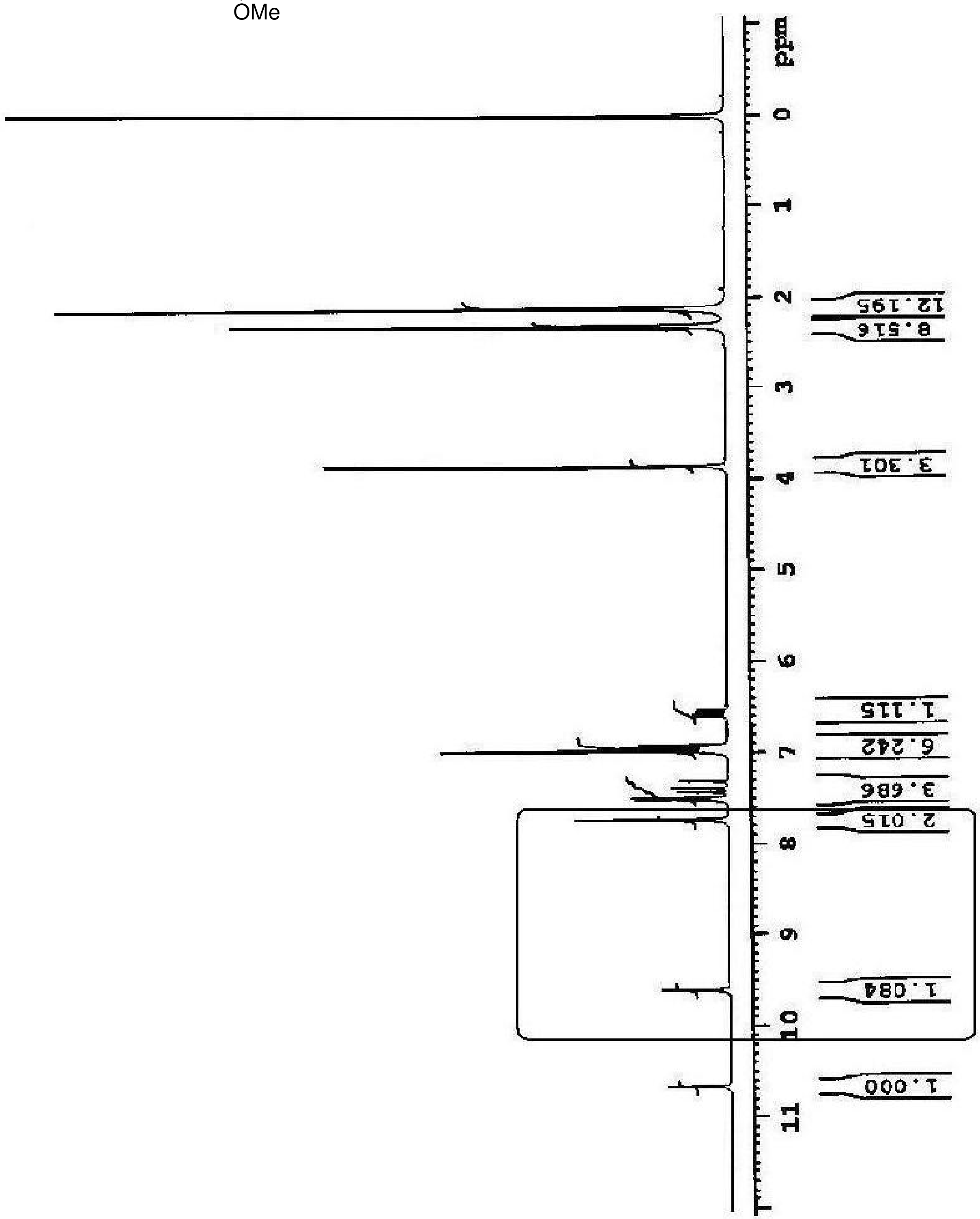
	Viscous liquid. **IR** (neat) ν_{max}: 3016, 2939, 2836, 1773, 1649, 1600, 1491, 1344, 1263, 1121, 1047, 878, 784 cm^{-1}. ^{1}**H NMR**: δ 7.25-7.16 (m, 2H), 6.74 (dd, *J* = 2.31 Hz, *J* = 8.01 Hz 2H), 6.67-6.61 (m, 1H), 6.43-6.37 (m, 1H), 6.21-6.17 (m, 2H), 5.60-5.52 (m, 1H), 3.74 (s, 3H), 2.96-2.93 (m, 1H), 2.82-2.81 (m, 1H), 2.77-2.75 (m, 1H), 2.70-2.67 (m, 1H) ^{13}**CNMR:** δ 160.0, 142.3, 139.9, 130.0, 129.0, 128.8, 127.7, 121.2, 119.8, 118.5, 113.2, 112.8, 96.1, 55.0, 41.0, 36.9, 30.6 . **HRMS** for $C_{17}H_{16}O_3$: calcd. (M^+): 268.11, found: 267.97.

NMR Studies on Homoenol Formation



A solution of the enal **1** (1.0 equiv.) and IMes-Cl **2** (1 equiv.) in $CDCl_3$ was taken in an NMR tube and the ^1H NMR spectrum was measured (see page S5). After the addition of 1 equiv. of DBU to the mixture, the NMR measurements were repeated at regular intervals of time (15 min), to monitor the formation of homoenol intermediate. A progressive decrease in the intensity of the signal at δ 9.61 corresponding H_a was indicative of the consumption of enal and the formation of homoenol. (Page S6).


CHO
OMe
+
Mes
N
Cl
N
Mes
CDCl3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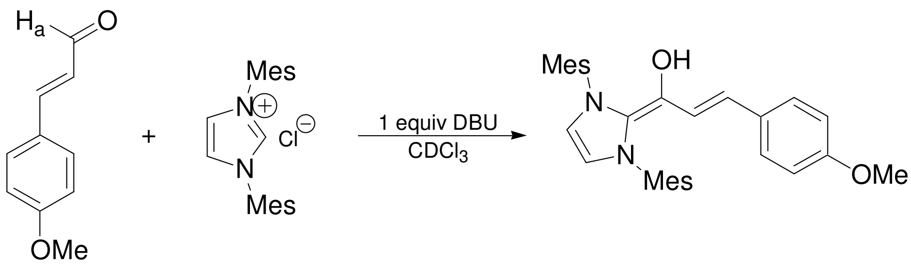
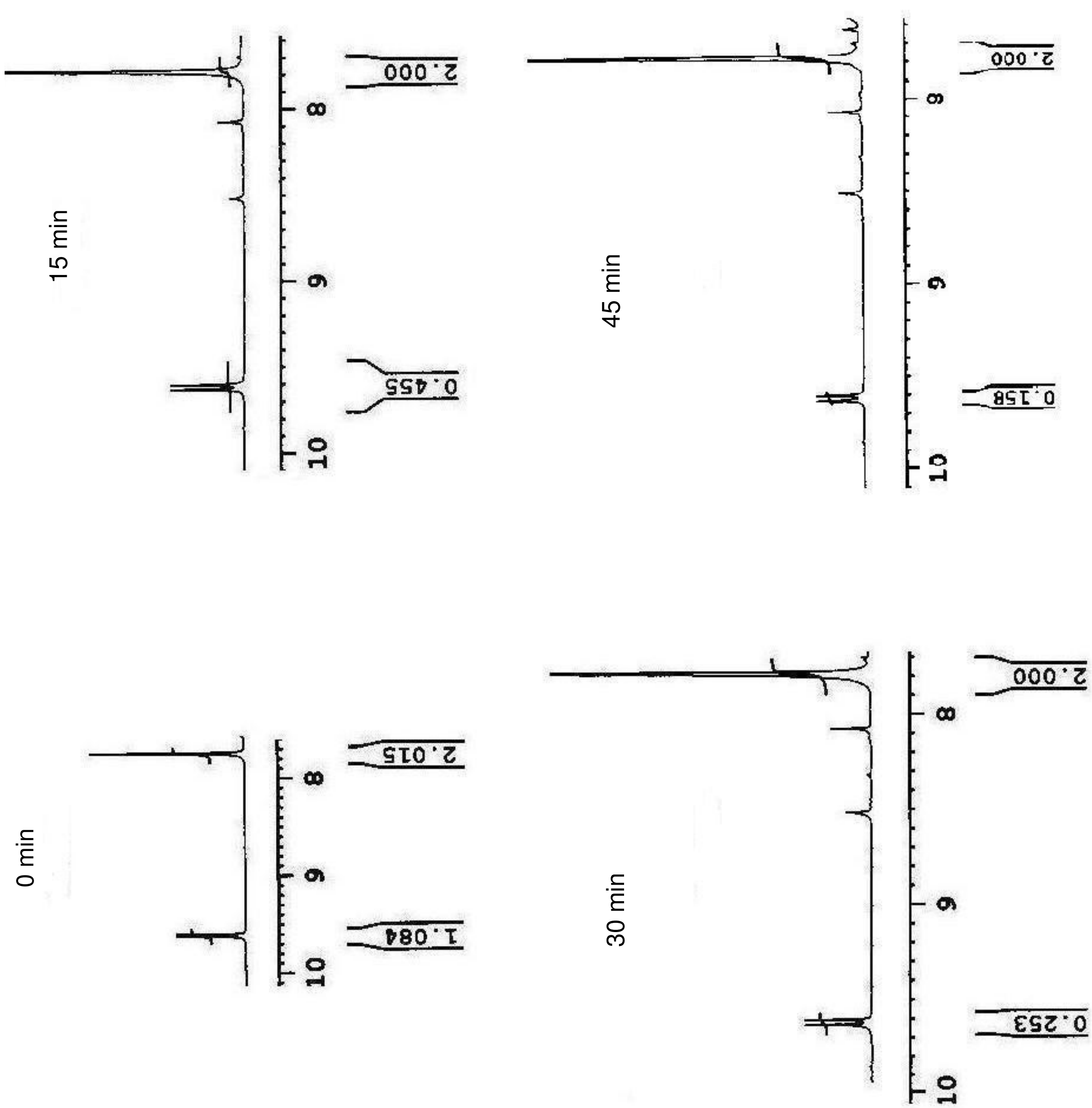
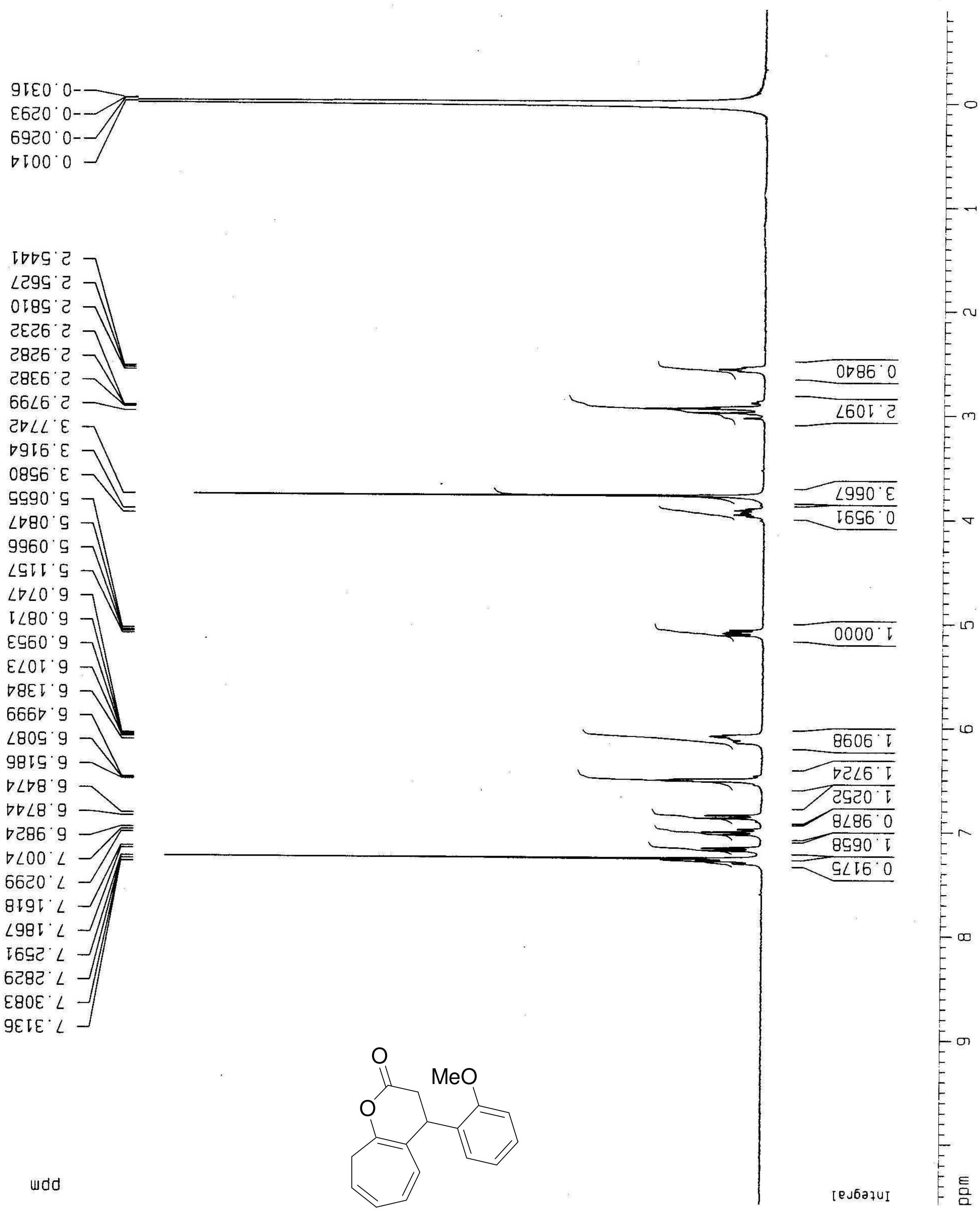
3.301
1.115
6.242
3.686
2.015
1.084
1.000


1 equiv DBU
CDCl3

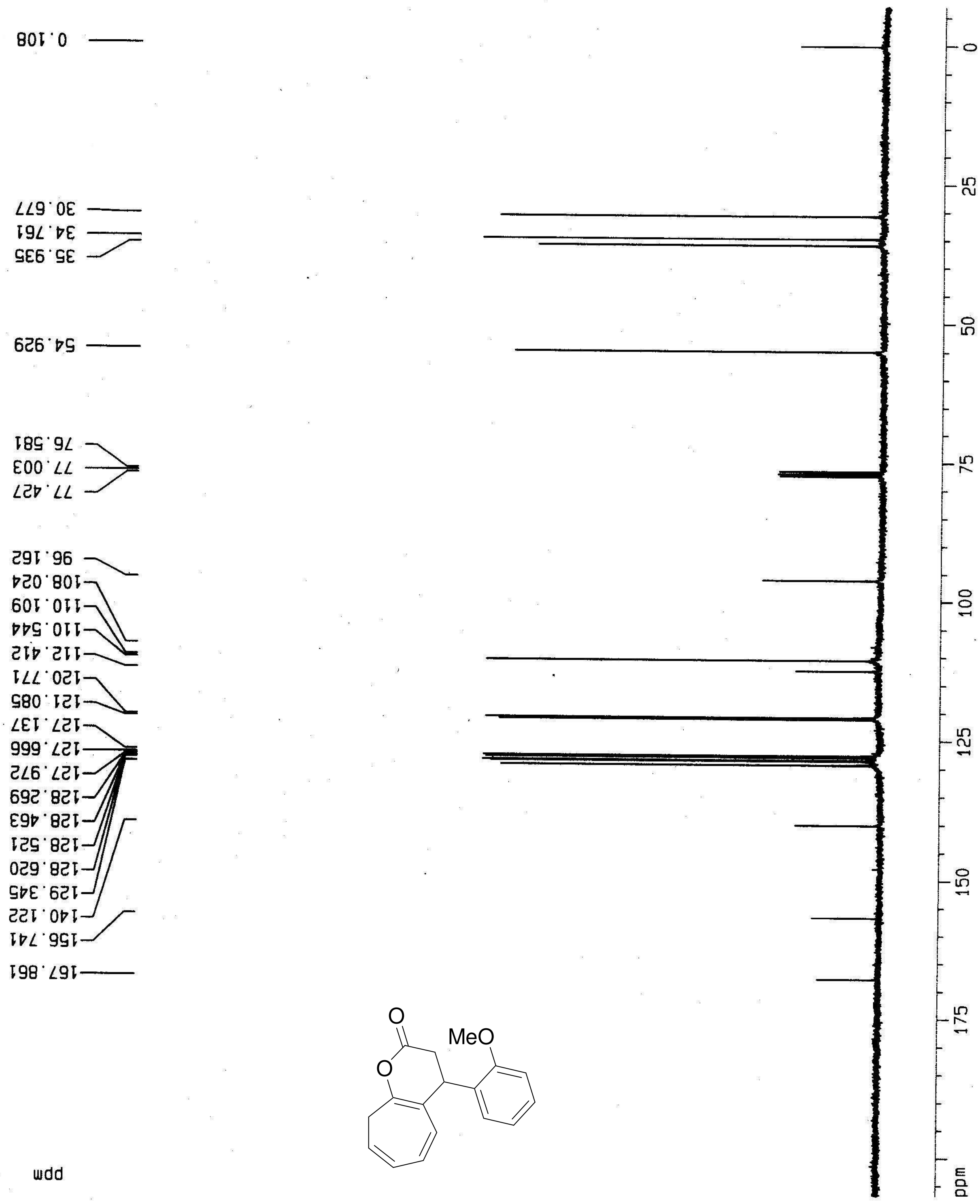

0 min
15 min
30 min
45 min
2.015
1.084
2.000
0.455
0.253
0.158

Compound 4a



-0.0316
-0.0293
-0.0269
0.0014
2.5441
2.5627
2.5810
2.9232
2.9282
2.9382
2.9799
3.7742
3.9164
3.9580
5.0655
5.0847
5.0966
5.1157
6.0747
6.0871
6.0953
6.1073
6.1384
6.4999
6.5087
6.5186
6.8474
6.8744
6.9824
7.0074
7.0299
7.1618
7.1867
7.2591
7.2829
7.3083
7.3136
ppm
0.9840
2.1097
3.0667
0.9591
1.0000
1.9098
1.9724
1.0252
0.9878
1.0658
0.9175
Integral
ppm
O
O
MeO

Compound 4a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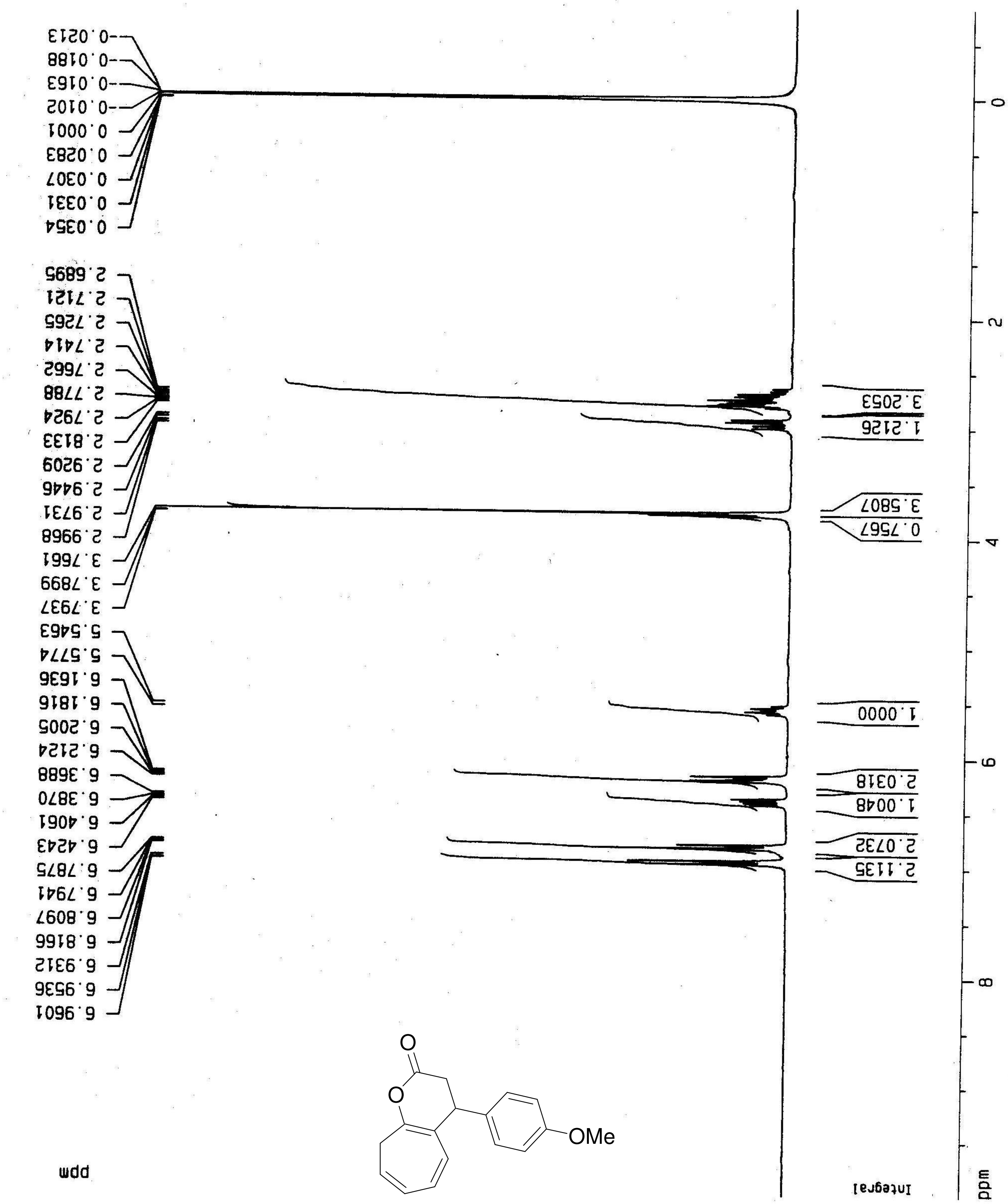
30.677
34.761
35.935
54.929
76.581
77.003
77.427
96.162
108.024
110.109
110.544
112.412
120.771
121.085
127.137
127.666
127.972
128.269
128.463
128.521
128.620
129.345
140.122
156.741
167.861
ppm
0
25
50
75
100
125
150
175
ppm
O
O
MeO

Compound 4b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-0.0188
-0.0163
-0.0102
0.0001
0.0283
0.0307
0.0331
0.0354
2.6895
2.7121
2.7265
2.7414
2.7662
2.7788
2.7924
2.8133
2.9209
2.9446
2.9731
2.9968
3.7661
3.7899
3.7937
5.5463
5.5774
6.1636
6.1816
6.2005
6.2124
6.3688
6.3870
6.4061
6.4243
6.7875
6.7941
6.8097
6.8166
6.9312
6.9536
6.9601
ppm
3.2053
1.2126
3.5807
0.7567
1.0000
2.0318
1.0048
2.0732
2.1135
Integral
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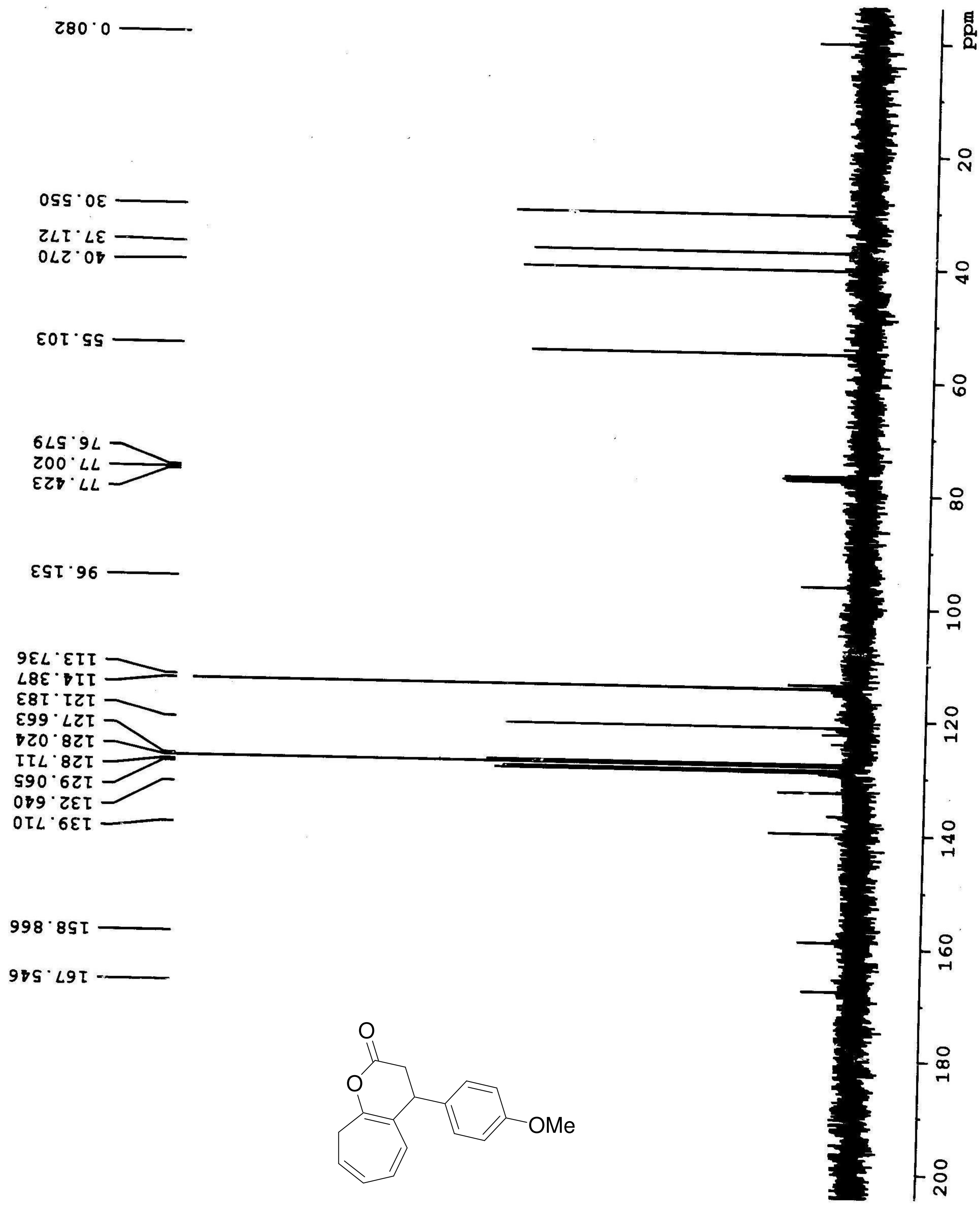
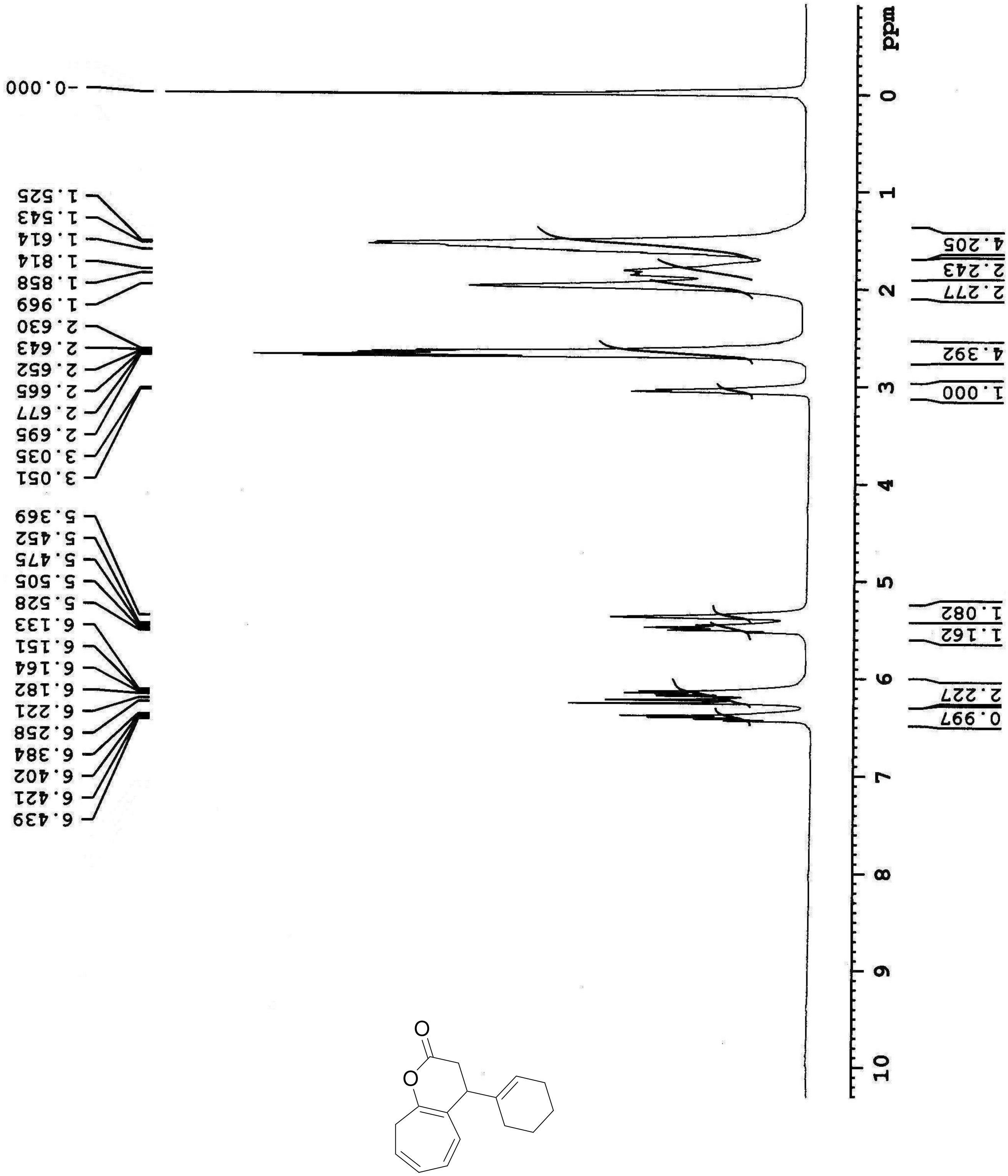
2
4
6
8
ppm
O
O
OMe

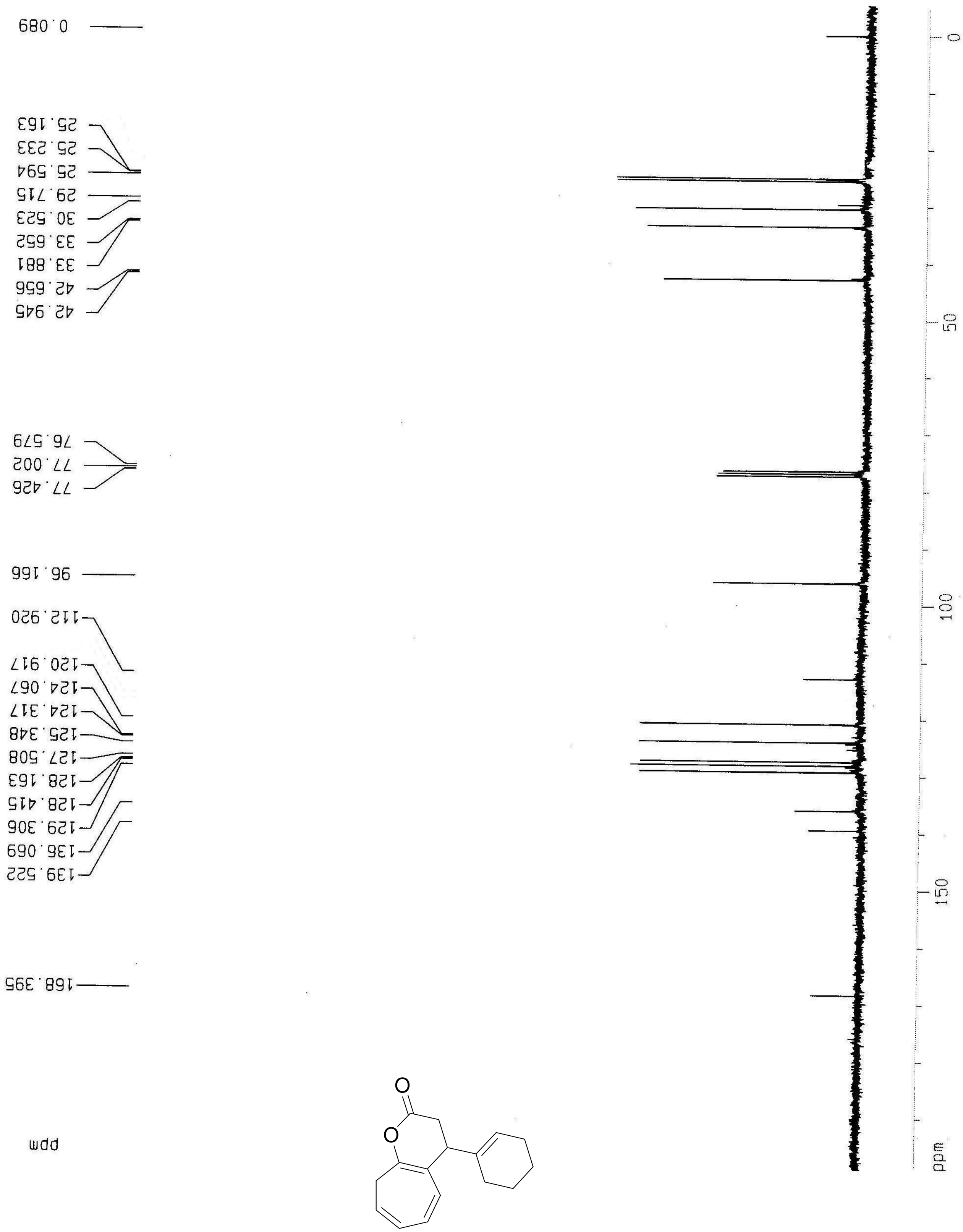
Compound 4b


0.082
30.550
37.172
40.270
55.103
76.579
77.002
77.423
96.153
113.736
114.387
121.183
127.663
128.024
128.711
129.065
132.640
139.710
158.866
167.546
ppm
20
40
60
80
100
120
140
160
180
200
O
O
OMe

Compound 4c



Compound 4c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25.233
25.594
29.715
30.523
33.652
33.881
42.656
42.945
76.579
77.002
77.426
96.166
112.920
120.917
124.067
124.317
125.348
127.508
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129.306
136.069
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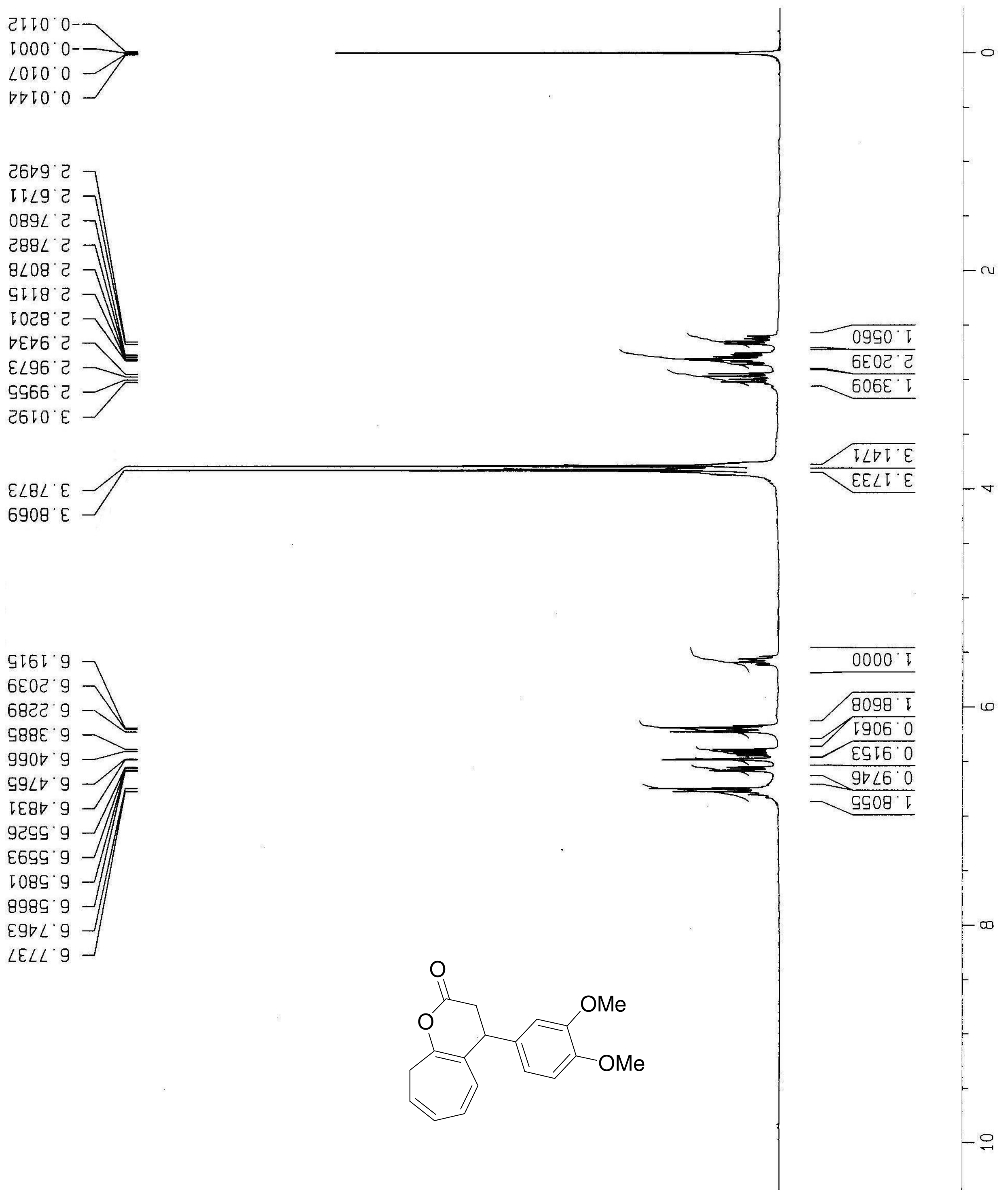
ppm
0
50
100
150
ppm
O
O

Compound 4d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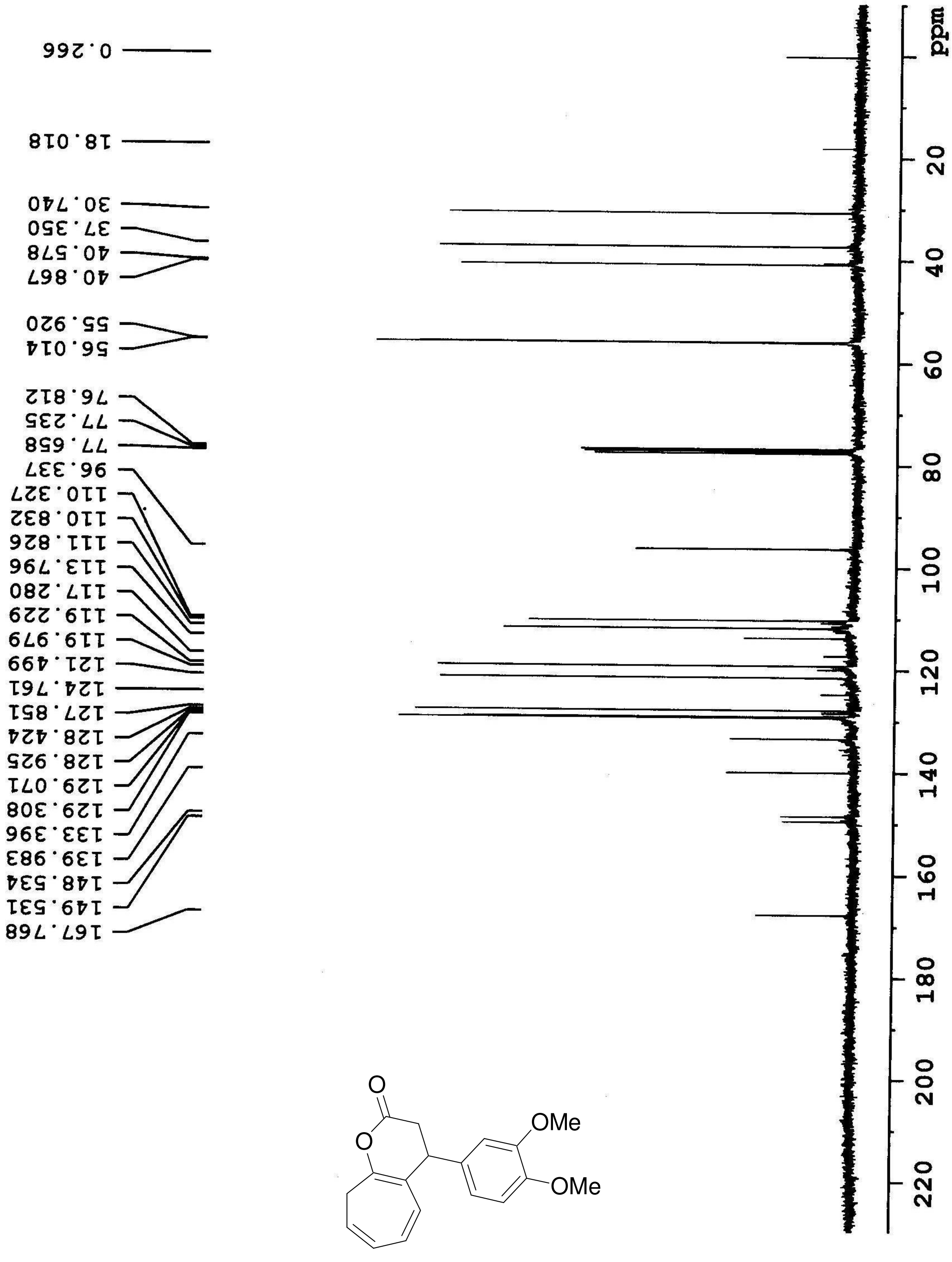
-0.0001
0.0107
0.0144
2.6492
2.6711
2.7680
2.7882
2.8078
2.8115
2.8201
2.9434
2.9673
2.9955
3.0192
3.7873
3.8069
6.1915
6.2039
6.2289
6.3885
6.4066
6.4765
6.4831
6.5526
6.5593
6.5801
6.5868
6.7463
6.7737
1.0560
2.2039
1.3909
3.1471
3.1733
1.0000
1.8608
0.9061
0.9153
0.9746
1.8055
0
2
4
6
8
10
O
O
OMe
OMe

Compound 4d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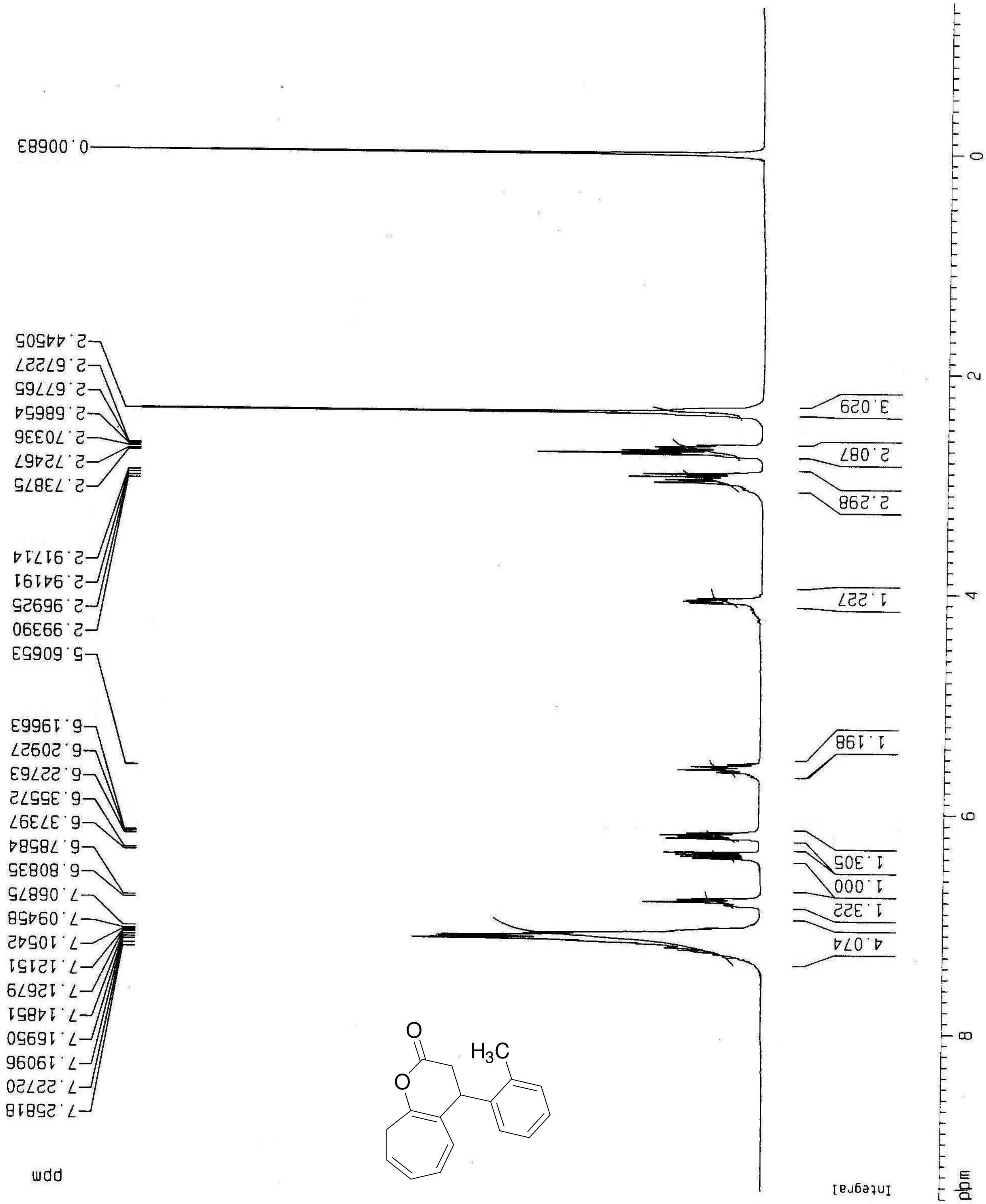
18.018
30.740
37.350
40.578
40.867
55.920
56.014
76.812
77.235
77.658
96.337
110.327
110.832
111.826
113.796
117.280
119.229
119.979
121.499
124.761
127.851
128.424
128.925
129.071
129.308
133.396
139.983
148.534
149.531
167.768
ppm
OMe
OMe
O

Compound 4e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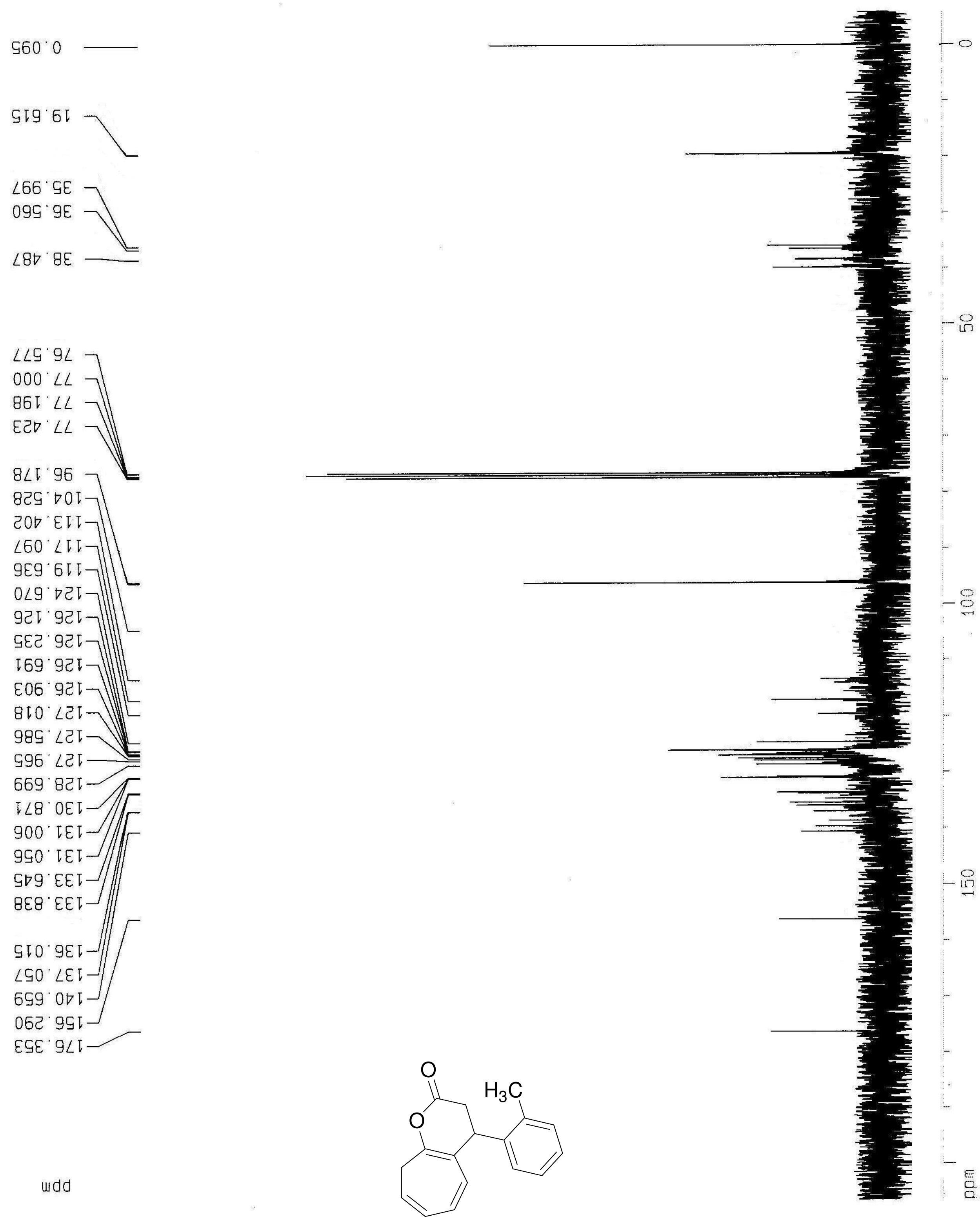
2.67765
2.68654
2.70336
2.72467
2.73875
2.91714
2.94191
2.96925
2.99390
5.60653
6.19663
6.20927
6.22763
6.35572
6.37397
6.78584
6.80835
7.06875
7.09458
7.10542
7.12151
7.12679
7.14851
7.16950
7.19096
7.22720
7.25818
ppm
3.029
2.087
2.298
1.227
1.198
1.305
1.000
1.322
4.074
Integral
0
2
4
6
8
ppm
O
O
H_3C

Compound 4e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19.615
35.997
36.560
38.487
76.577
77.000
77.198
77.423
96.178
104.528
113.402
117.097
119.636
124.670
126.126
126.235
126.691
126.903
127.018
127.586
127.965
128.699
130.871
131.006
131.056
133.645
133.838
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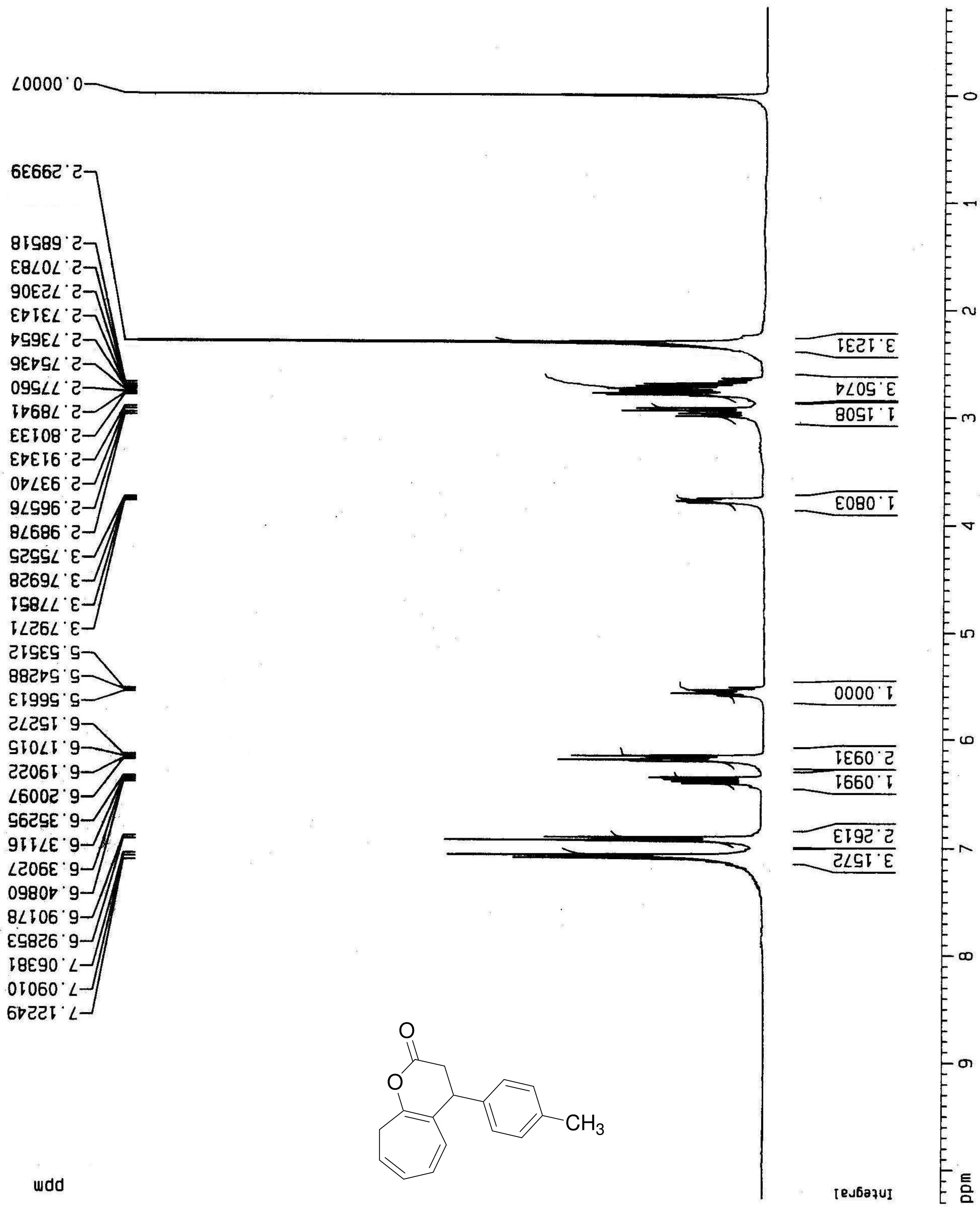
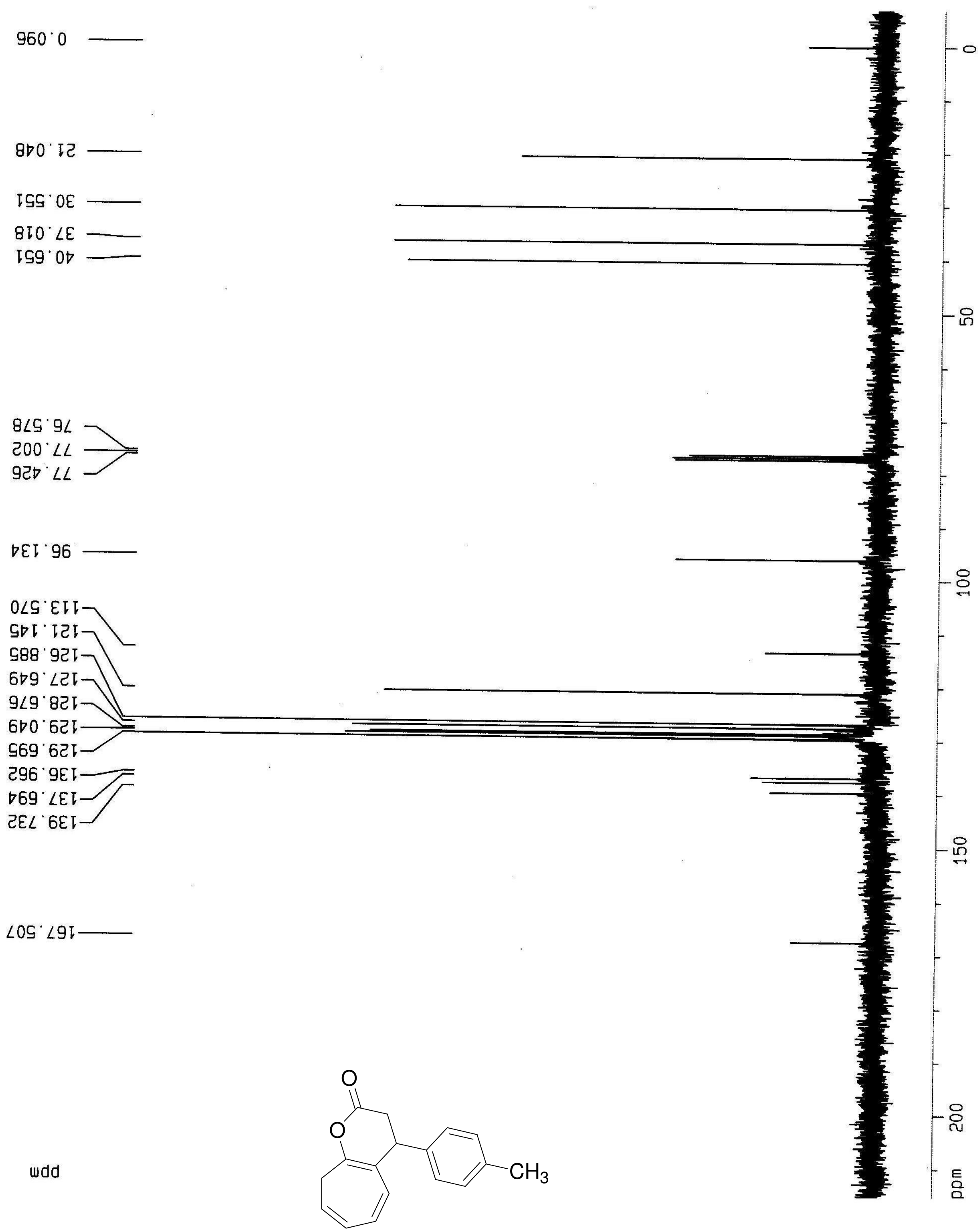
0
50
100
150
ppm
O
O
H3C

Compound 4f



Compound 4f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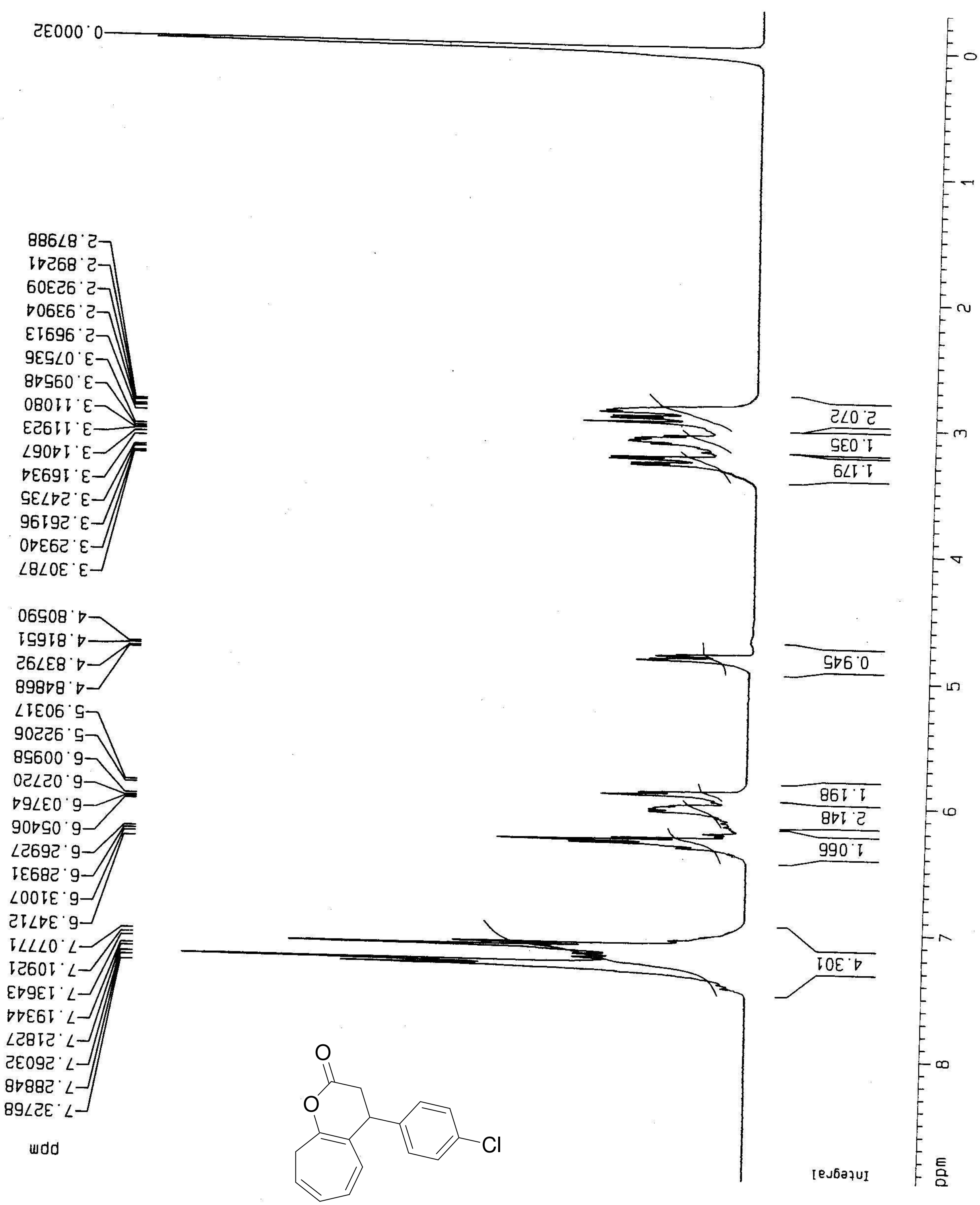
37.018
40.651
76.578
77.002
77.426
96.134
113.570
121.145
126.885
127.649
128.676
129.049
129.695
136.962
137.694
139.732
167.507
ppm
0
50
100
150
200
ppm
O
O
CH3

Compound 4g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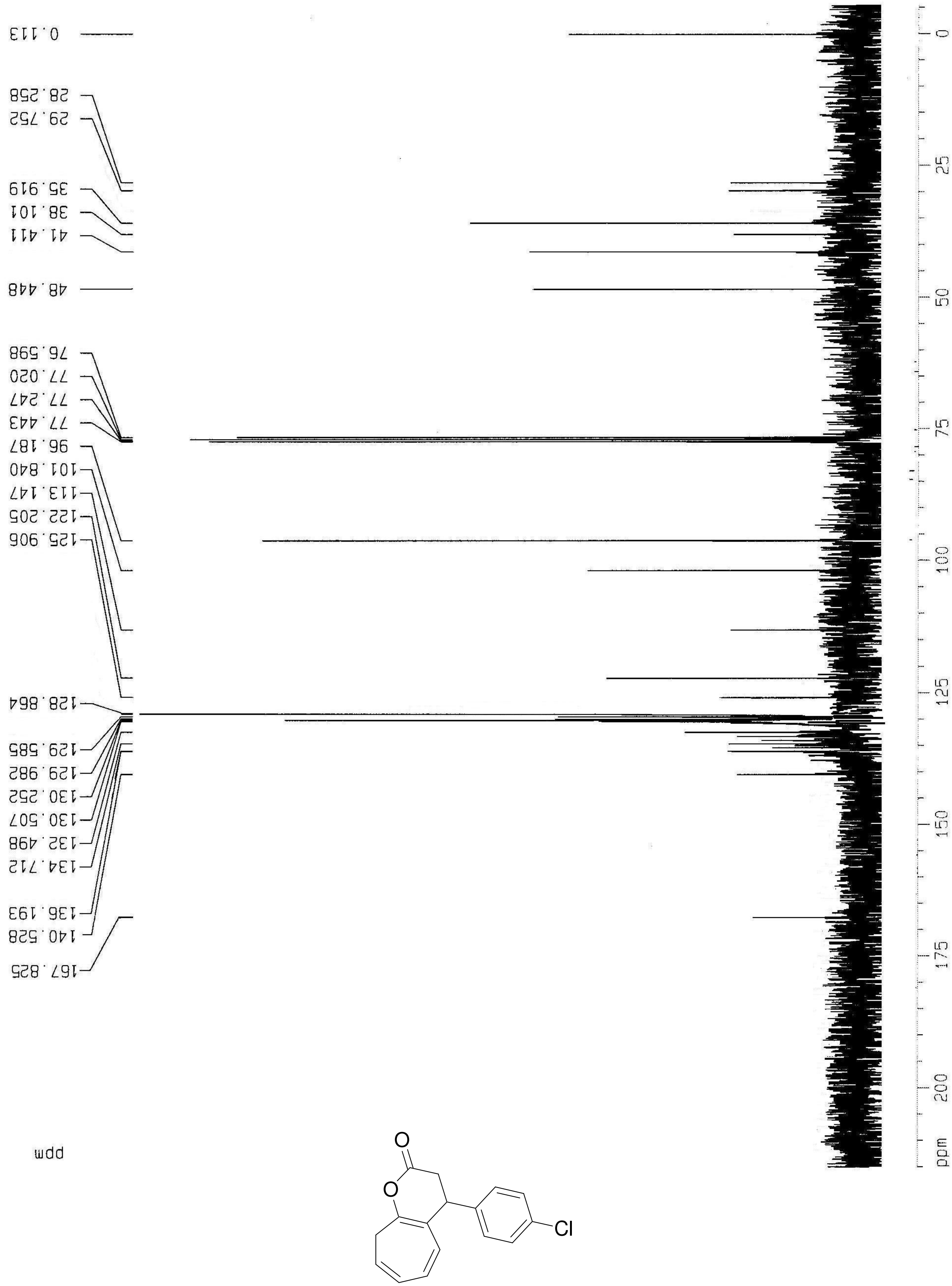
2.92309
2.93904
2.96913
3.07536
3.09548
3.11080
3.11923
3.14067
3.16934
3.24735
3.26196
3.29340
3.30787
4.80590
4.81651
4.83792
4.84868
5.90317
5.92206
6.00958
6.02720
6.03764
6.05406
6.26927
6.28931
6.31007
6.34712
7.07771
7.10921
7.13643
7.19344
7.21827
7.26032
7.28848
7.32768
ppm
2.072
1.035
1.179
0.945
1.198
2.148
1.066
4.301
Integral
ppm
O
O
Cl

Compound 4g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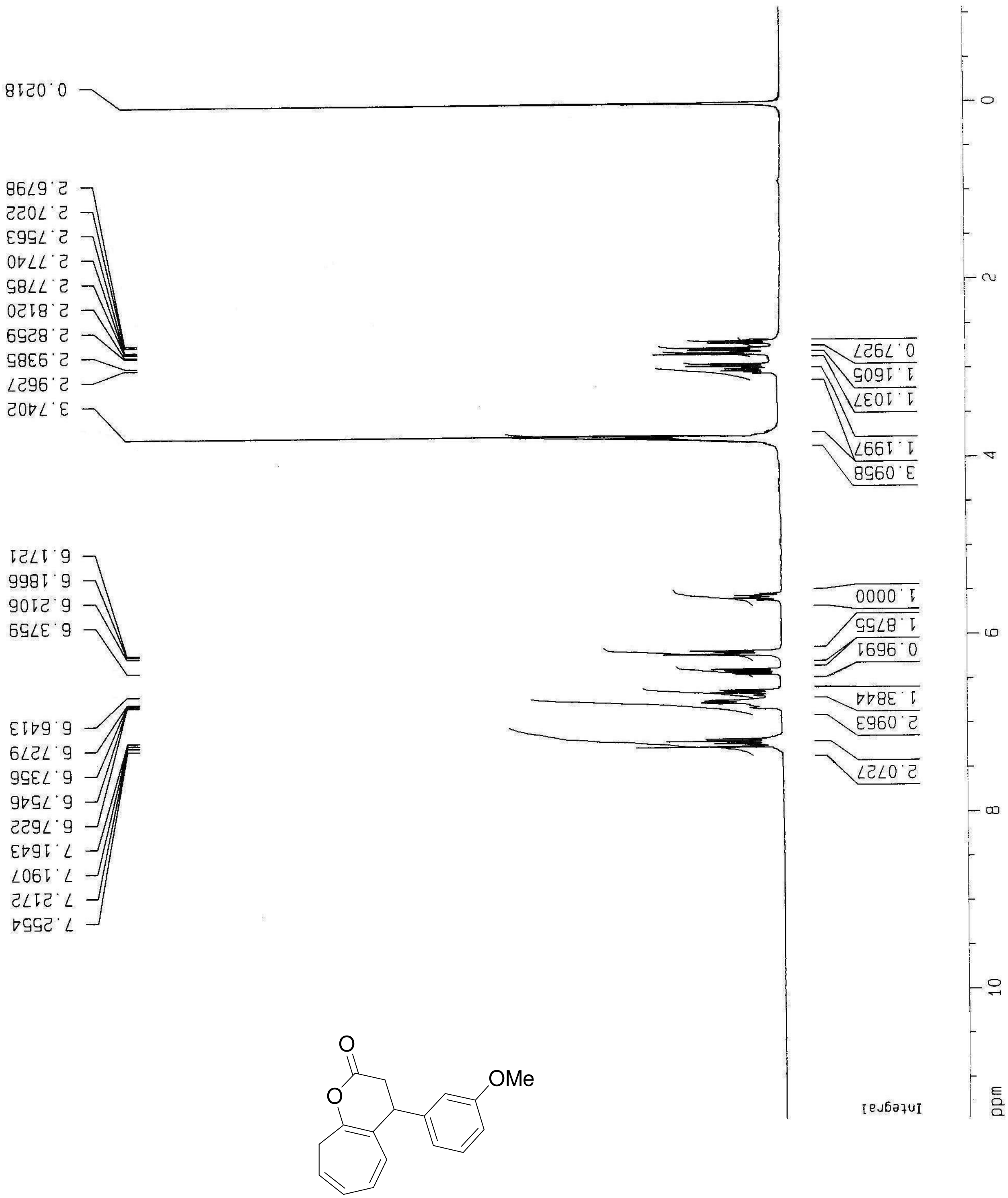
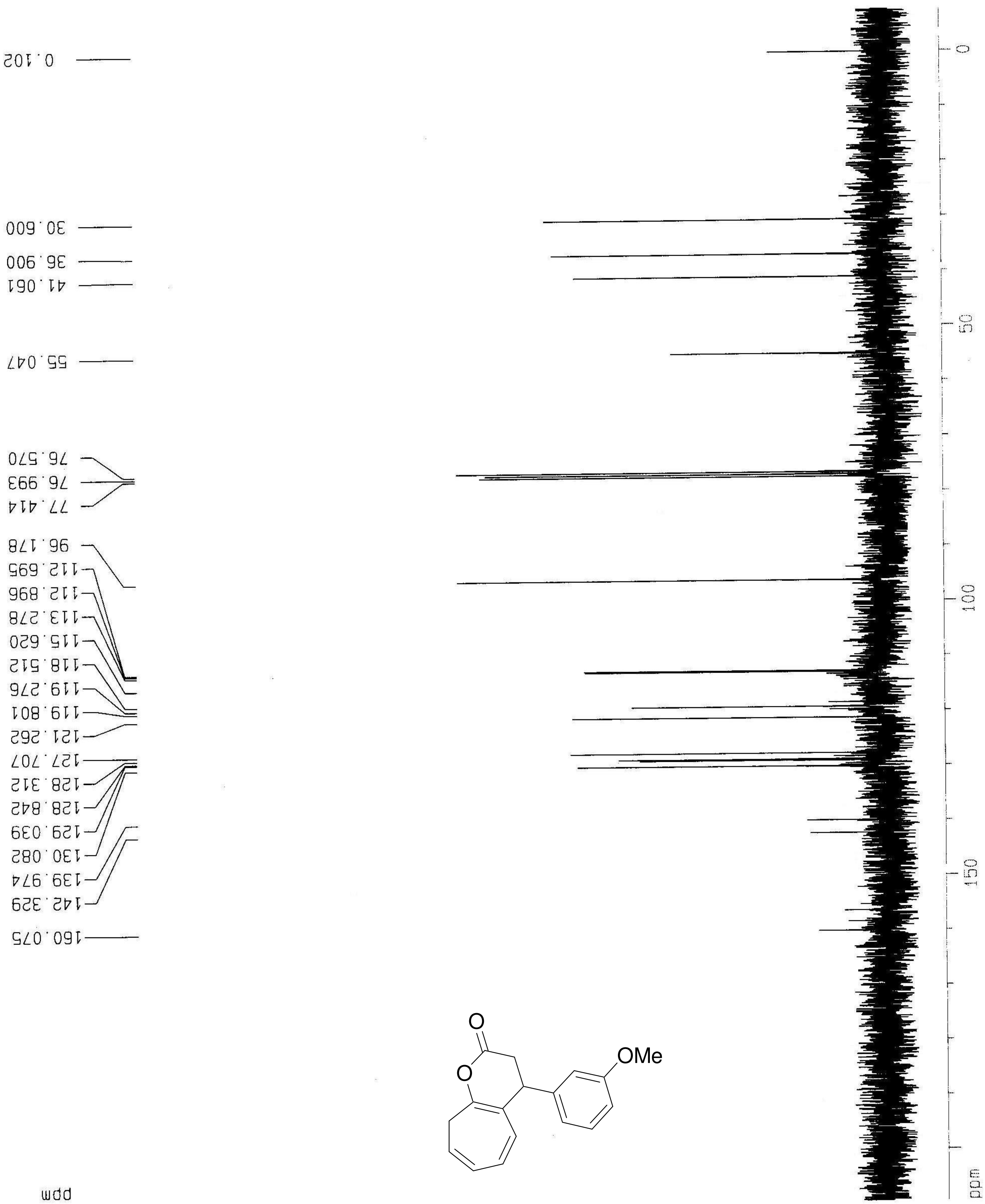
28.258
29.752
35.919
38.101
41.411
48.448
76.598
77.020
77.247
77.443
96.187
101.840
113.147
122.205
125.906
128.864
129.585
129.982
130.252
130.507
132.498
134.712
136.193
140.528
167.825
ppm
0
25
50
75
100
125
150
175
200
ppm
O
O
Cl

Compound 4h



Compound 4h


0.102
30.600
36.900
41.061
55.047
76.570
76.993
77.414
96.178
112.695
112.896
113.278
115.620
118.512
119.276
119.801
121.262
127.707
128.312
128.842
129.039
130.082
139.974
142.329
160.075
ppm
O
O
OMe
0
50
100
150
ppm