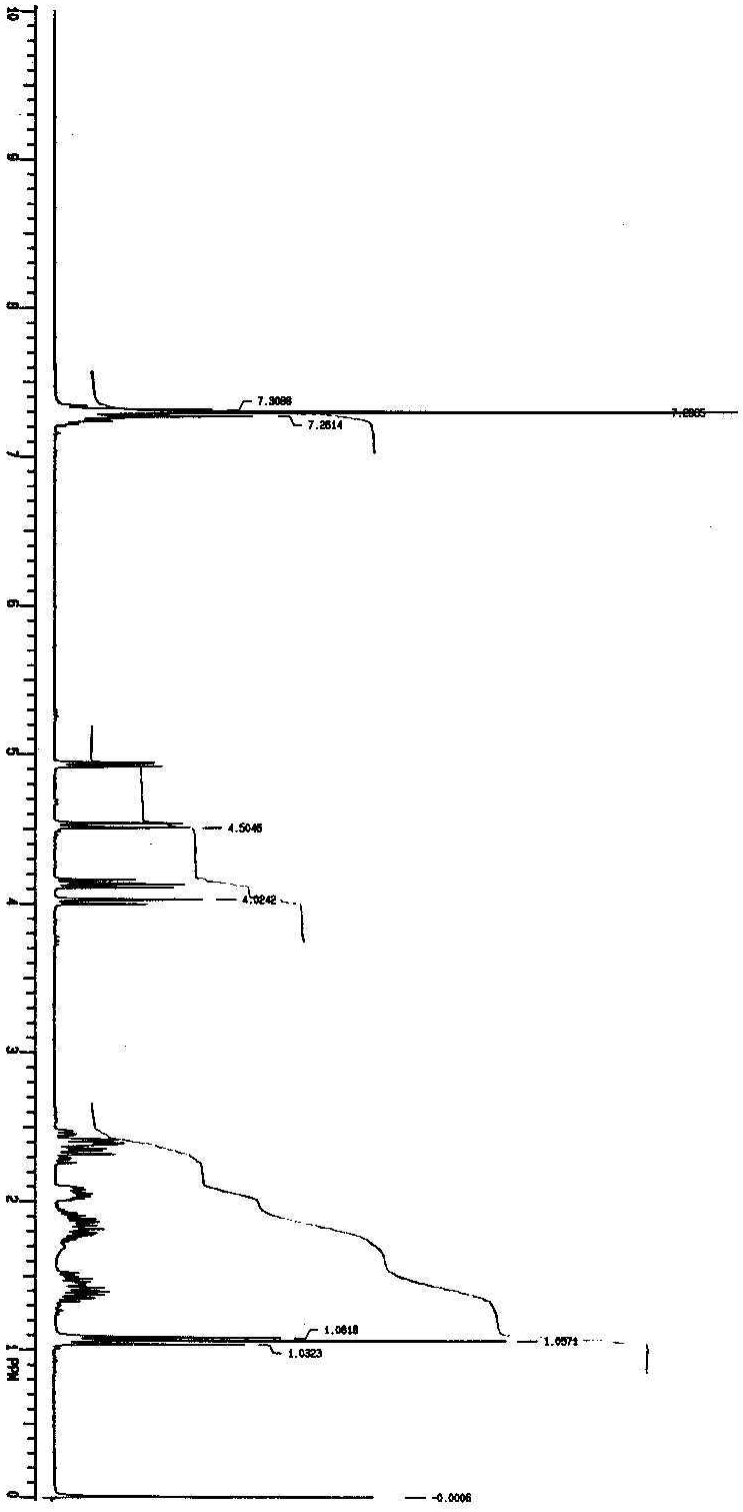
Supporting Information

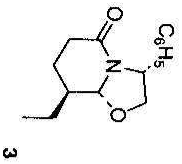
General procedure for the preparation of 6a,b and 7a,b:

Lithium bis(trimethylsilyl)amide (2.2 eq of a 1.0 M solution in THF) was slowly added at –78 °C to a 0.07 M solution of lactam **3** (4 mmol) in anhydrous THF, and the resulting mixture was stirred for 1 h. Then, methyl or benzyl chloroformate (1.0 eq) and, after 30 min of continuous stirring at –78 °C, a 0.7 M solution of PhSeCl (1.4 eq) in THF, were sequentially added. The resulting mixture was stirred for 50 min and poured into 1 N HCl. The aqueous layer was extracted with AcOEt, and the combined organic extracts were dried and concentrated. Flash chromatography (AcOEt:hexane 3:7) of the crude mixture afforded compounds **4a** (86%) or **4b** (89%) as mixtures of C-6 epimers.

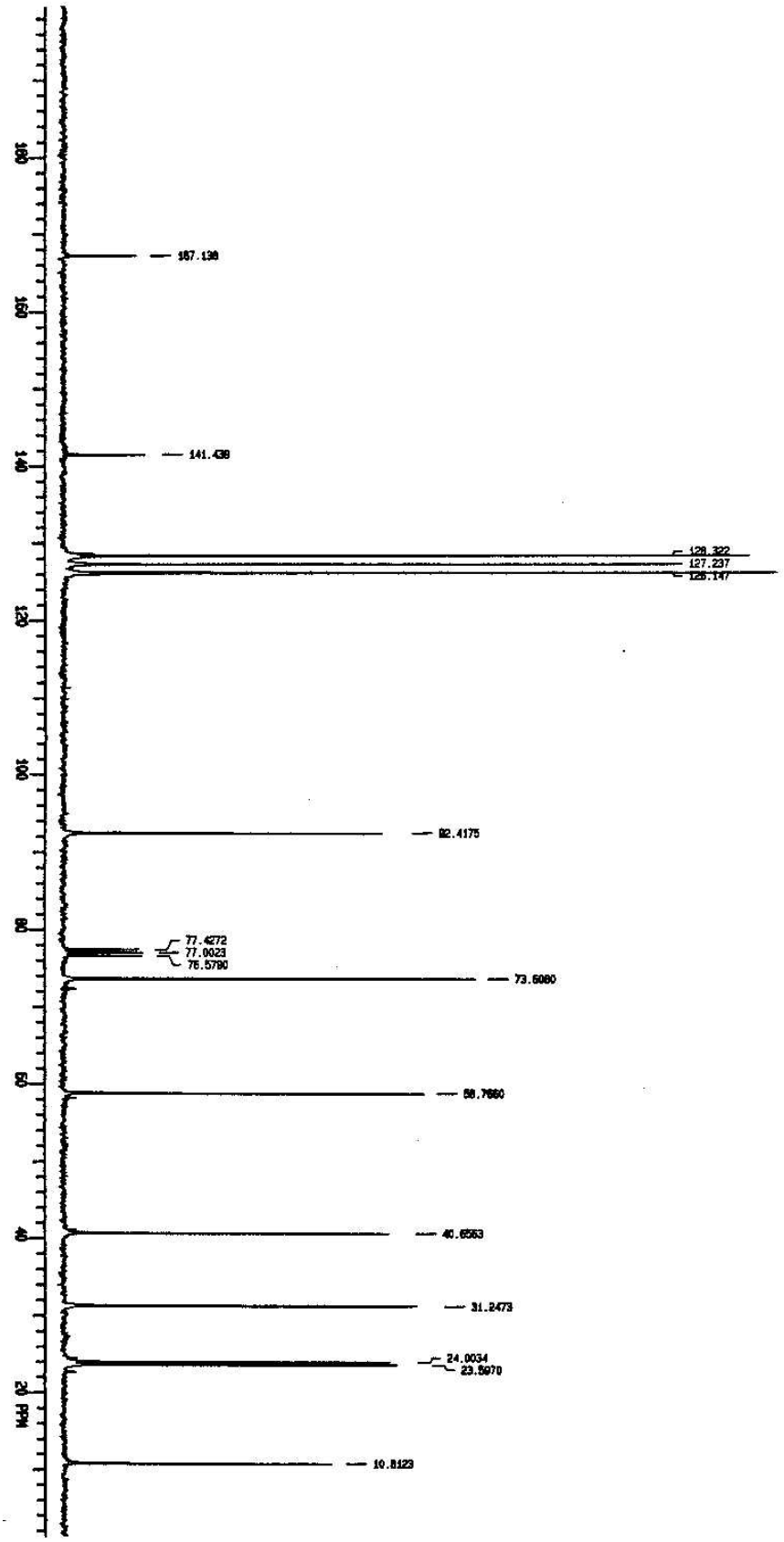
A stream of ozone gas was bubbled through a cooled (-78 °C) 0.05 M solution of selenides **4a** or **4b** in anhydrous CH_2Cl_2 until it turned pale blue. The solution was purged with O_2, and the temperature was slowly raised to 25 °C. After 30 min of stirring, the mixture was poured into brine, and the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were dried and concentrated under reduced pressure (external temperature 25 °C) to give **8a** or **8b** as oils, which were used in the next reaction without further purification.

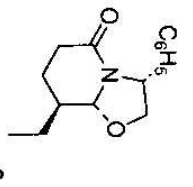
A 1.5 M solution of the above crude unsaturated lactams **8a** or **8b** (1.0 eq) in anhydrous THF was added dropwise at –78 °C to a 0.08 M solution of MeCu(CN)Li or (C_6H_5)Cu(CN)Li (5 eq) in THF, and the resulting solution was stirred for 7 h (methyl series) or 18 h (phenyl series). The mixture was allowed to reach 25 °C, poured into saturated aqueous NH_4Cl, and extracted with AcOEt. The organic layer was whased with saturated aqueous $NaHCO_3$, and the combined organic extracts were dried and concentrated. The residue was purified by flash chromatography (eluents: AcOEt:hexane gradient from 1:4 to 3:7). **6a** (38% from **4a**); **7a** (80% from **4a**); **6b** (40% from **4b**); **7b** (75% from **4b**).



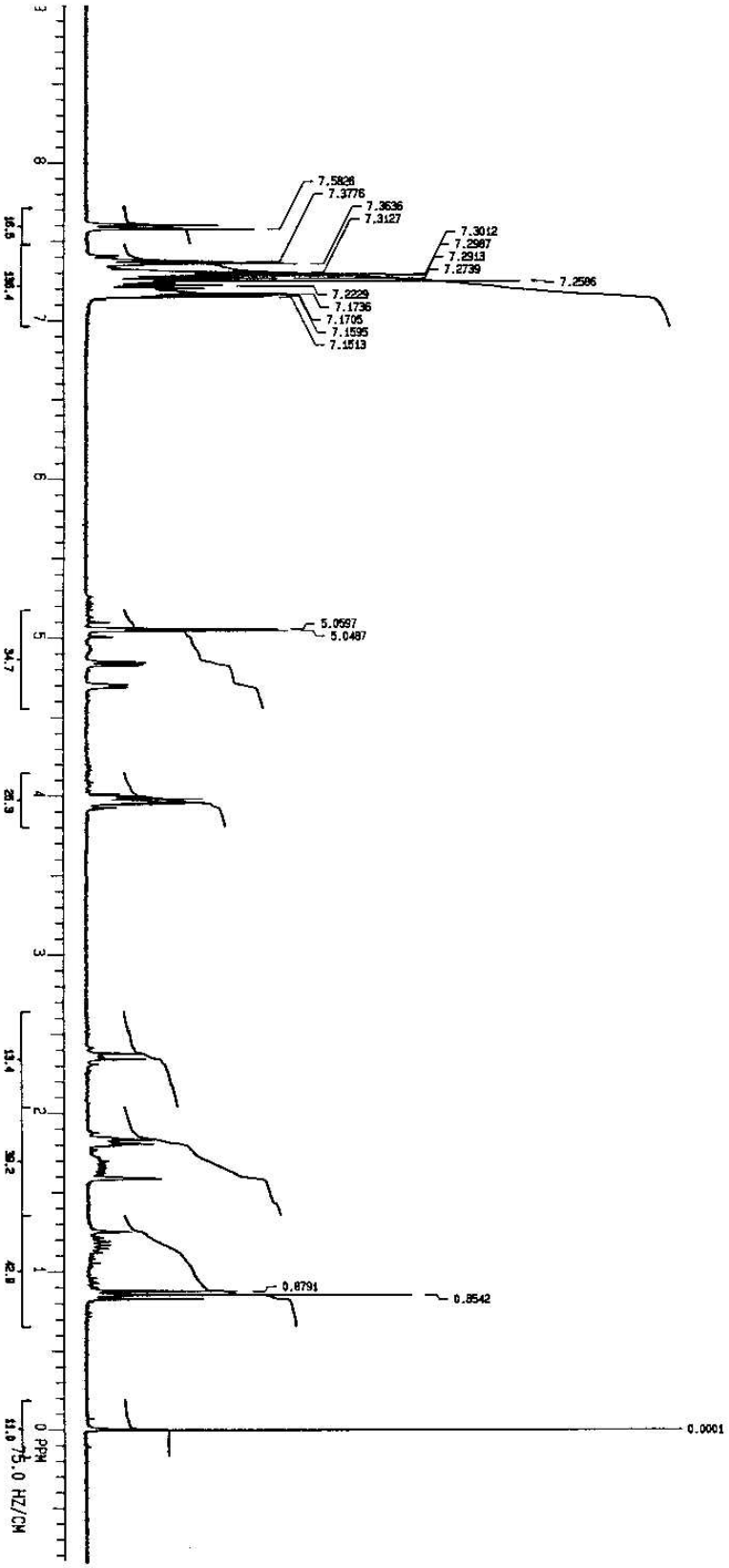


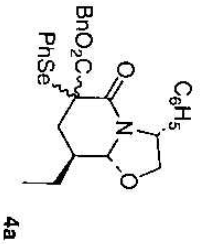
3


167.138
141.438
128.322
127.237
126.147
82.4175
77.4272
77.0023
76.5790
73.5080
58.7660
40.6563
31.2473
24.0034
23.5970
10.8123
PPM

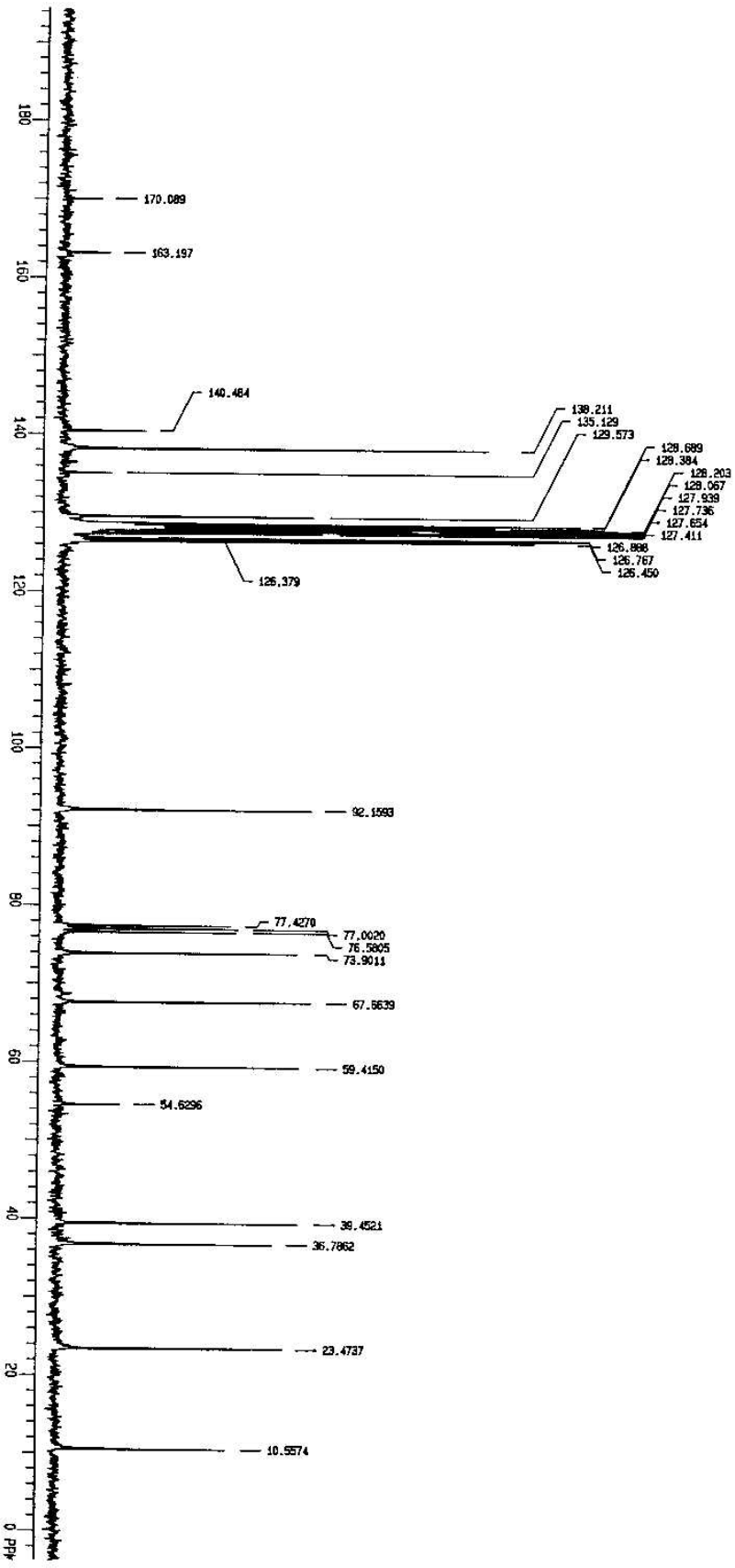

O
N
O
C_6H_5

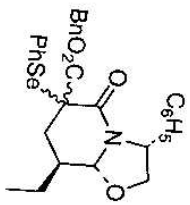
3


7.5826
7.3776
7.3636
7.3127
7.3012
7.2967
7.2913
7.2739
7.2506
7.2229
7.1736
7.1705
7.1595
7.1513
5.0597
5.0487
0.8791
0.8542
0.0001
PPM
75.0 HZ/CM

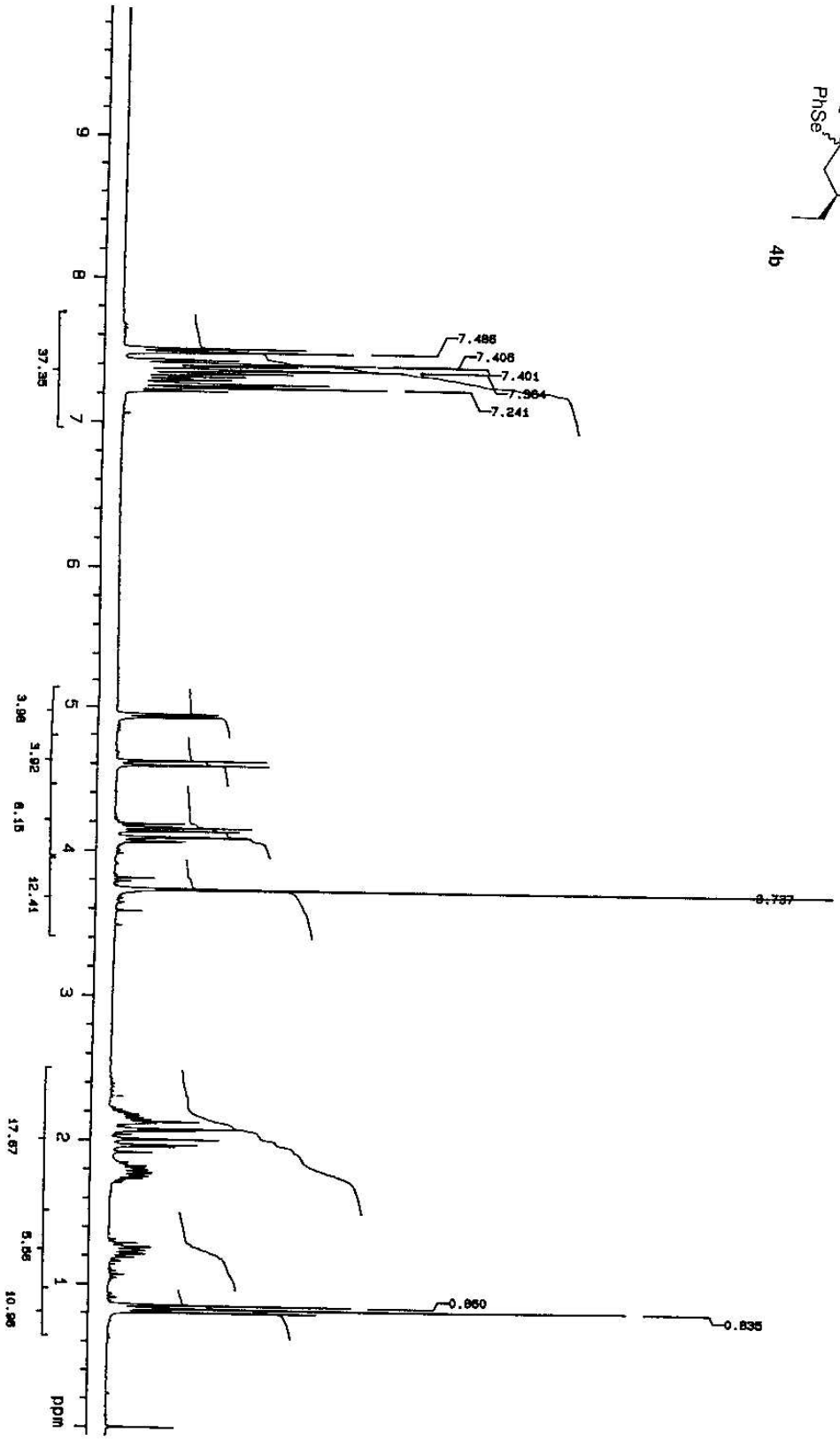

BnO2C
PhSe
O
N
O
C6H5

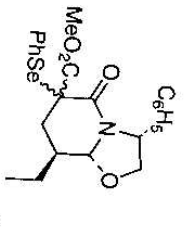
4a


170.089
163.197
140.464
138.211
135.129
129.573
128.689
128.384
128.203
128.067
127.939
127.736
127.654
127.411
126.888
126.767
126.450
126.379
92.1593
77.4270
77.0020
76.5805
73.9011
67.5639
59.4150
54.6296
39.4521
36.7862
23.4737
10.5574
PPM

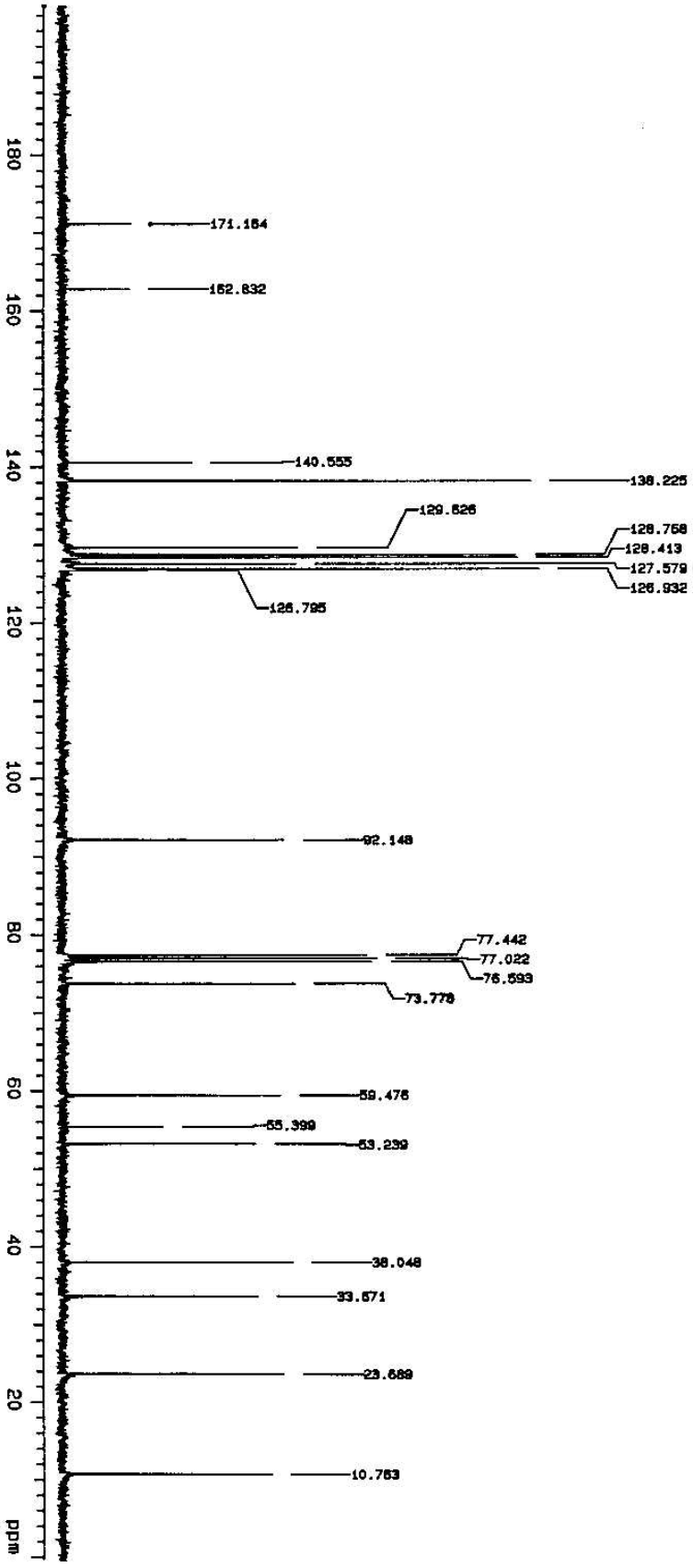

BnO2C
PhSe
O
N
O
C6H5

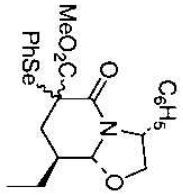
4a


7.486
7.406
7.401
7.364
7.241
0.737
0.660
0.635
37.35
3.98
3.92
6.15
12.41
17.67
5.55
10.26
ppm

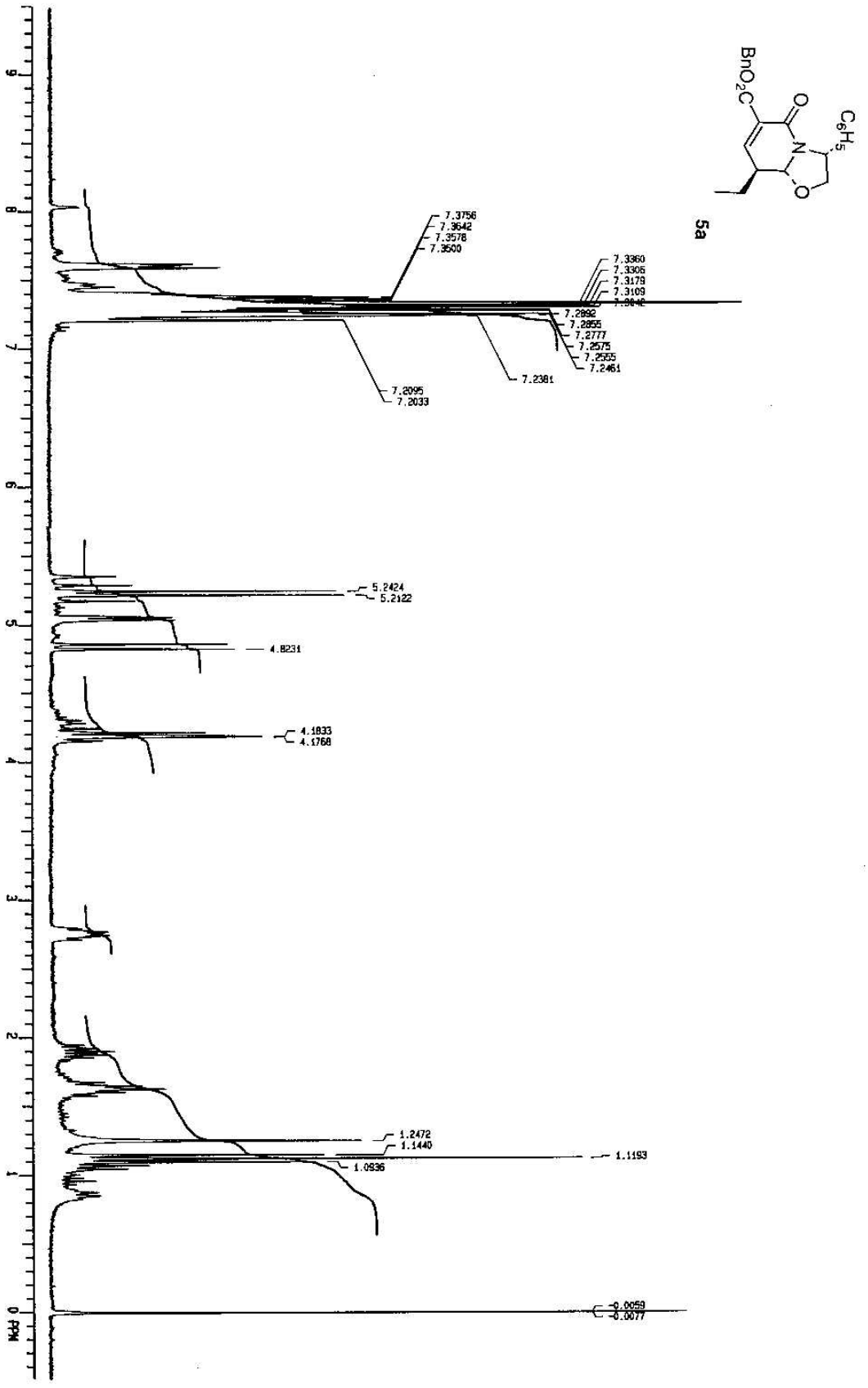

MeO2C
PhSe
O
N
O
C6H5

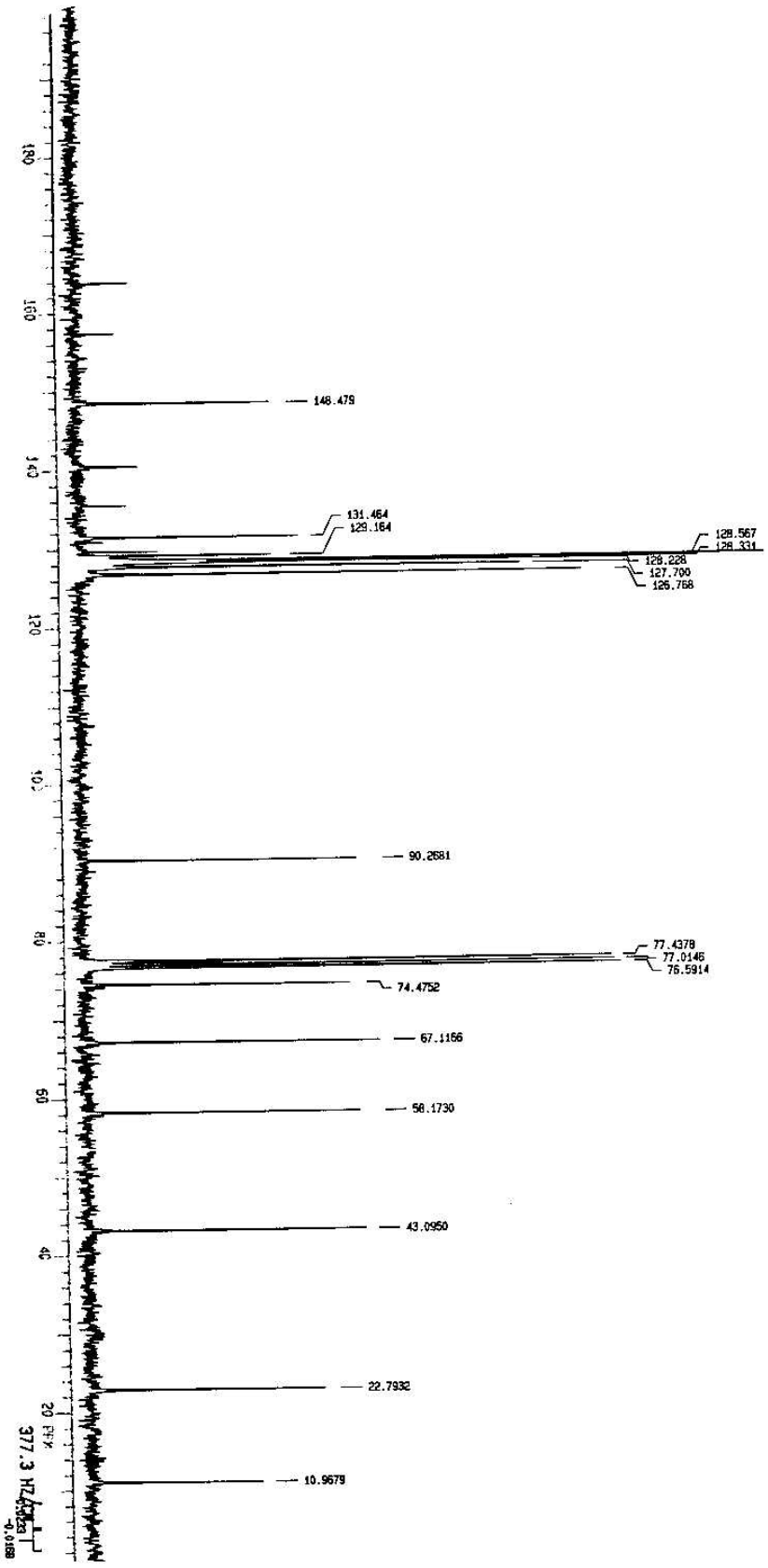
4b

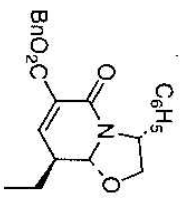

171.164
162.832
140.555
138.225
129.626
128.758
128.413
127.579
126.932
126.795
92.148
77.442
77.022
76.593
73.778
59.476
55.399
53.239
38.048
33.671
23.689
10.763
ppm


MeO2C
PhSe
O
N
O
C6H5

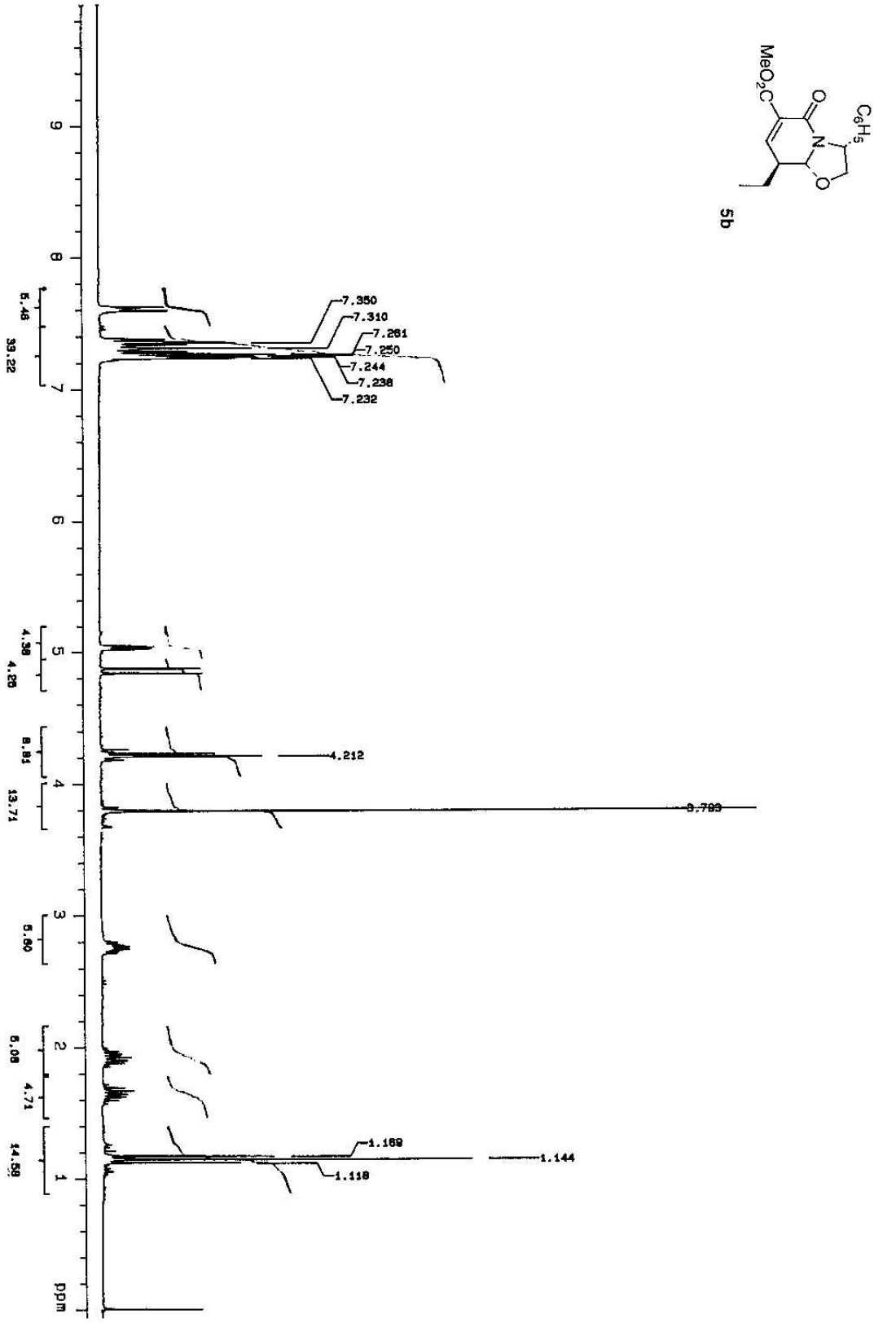
4b

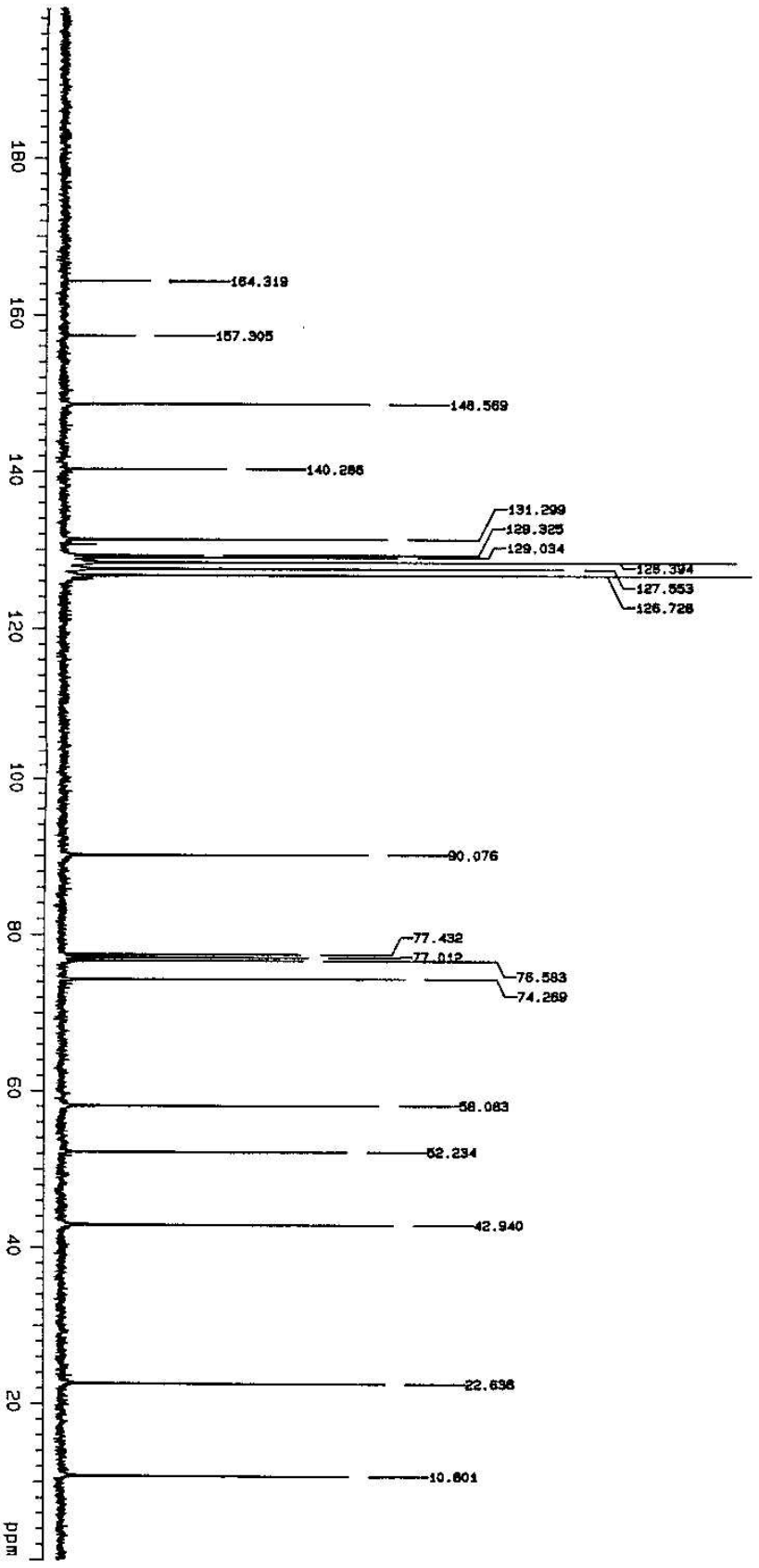

BnO2C
O
N
O
C6H5
5a
7.3756
7.3642
7.3578
7.3500
7.3360
7.3305
7.3179
7.3109
7.2892
7.2855
7.2777
7.2575
7.2555
7.2461
7.2381
7.2095
7.2033
5.2424
5.2122
4.8231
4.1833
4.1768
1.2472
1.1440
1.1193
1.0936
0.0059
0.0077
PPM

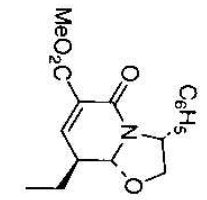

148.479
131.464
129.164
128.567
128.331
128.228
127.700
126.768
90.2681
77.4378
77.0146
76.5914
74.4752
67.1166
58.1730
43.0950
22.7932
10.9679
377.3 MZ


BnO2C
O
N
O
C6H5

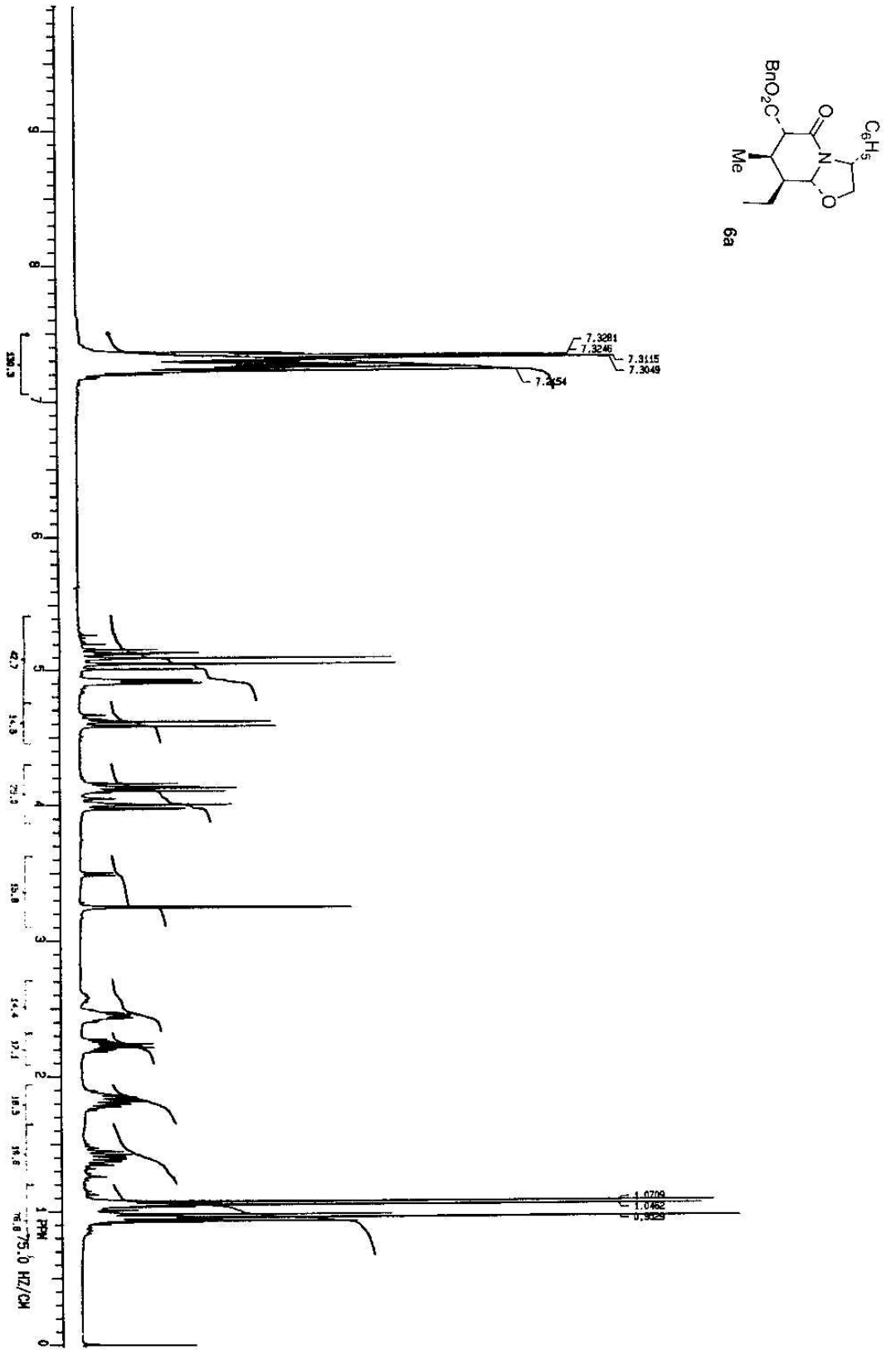
5a

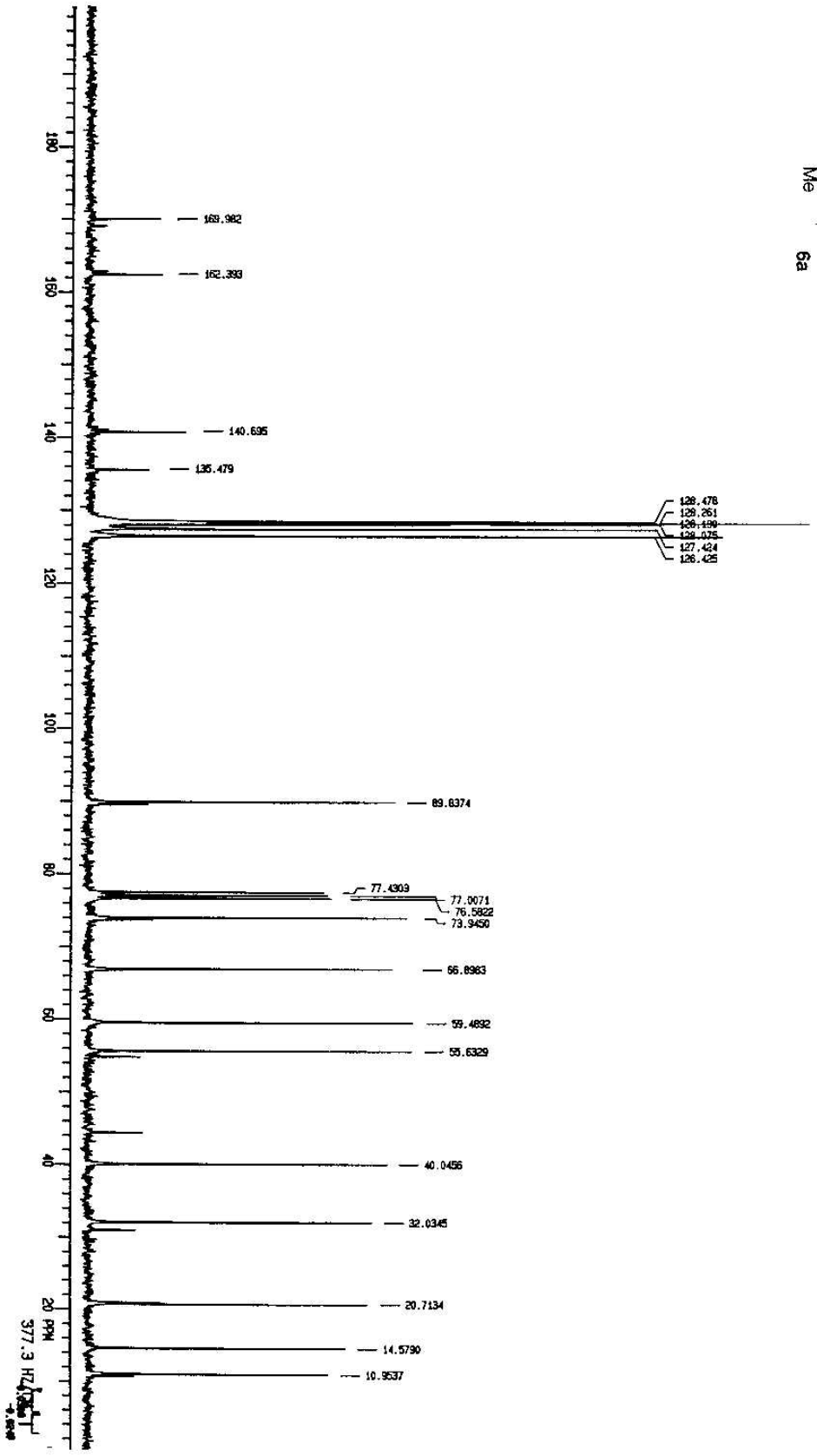

MeO2C
C6H5
O
N
O
5b
7.350
7.310
7.261
7.250
7.244
7.238
7.232
4.212
3.793
1.169
1.144
1.118
5.46
33.22
4.38
4.25
8.84
13.71
5.80
5.08
4.71
14.59
ppm

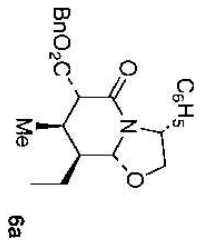

164.319
157.305
148.569
140.286
131.299
129.325
129.034
128.394
127.553
126.728
90.076
77.432
77.012
76.583
74.269
58.083
52.234
42.940
22.636
10.801
ppm
180
160
140
120
100
80
60
40
20


MeO2C
O
N
O
C6H5

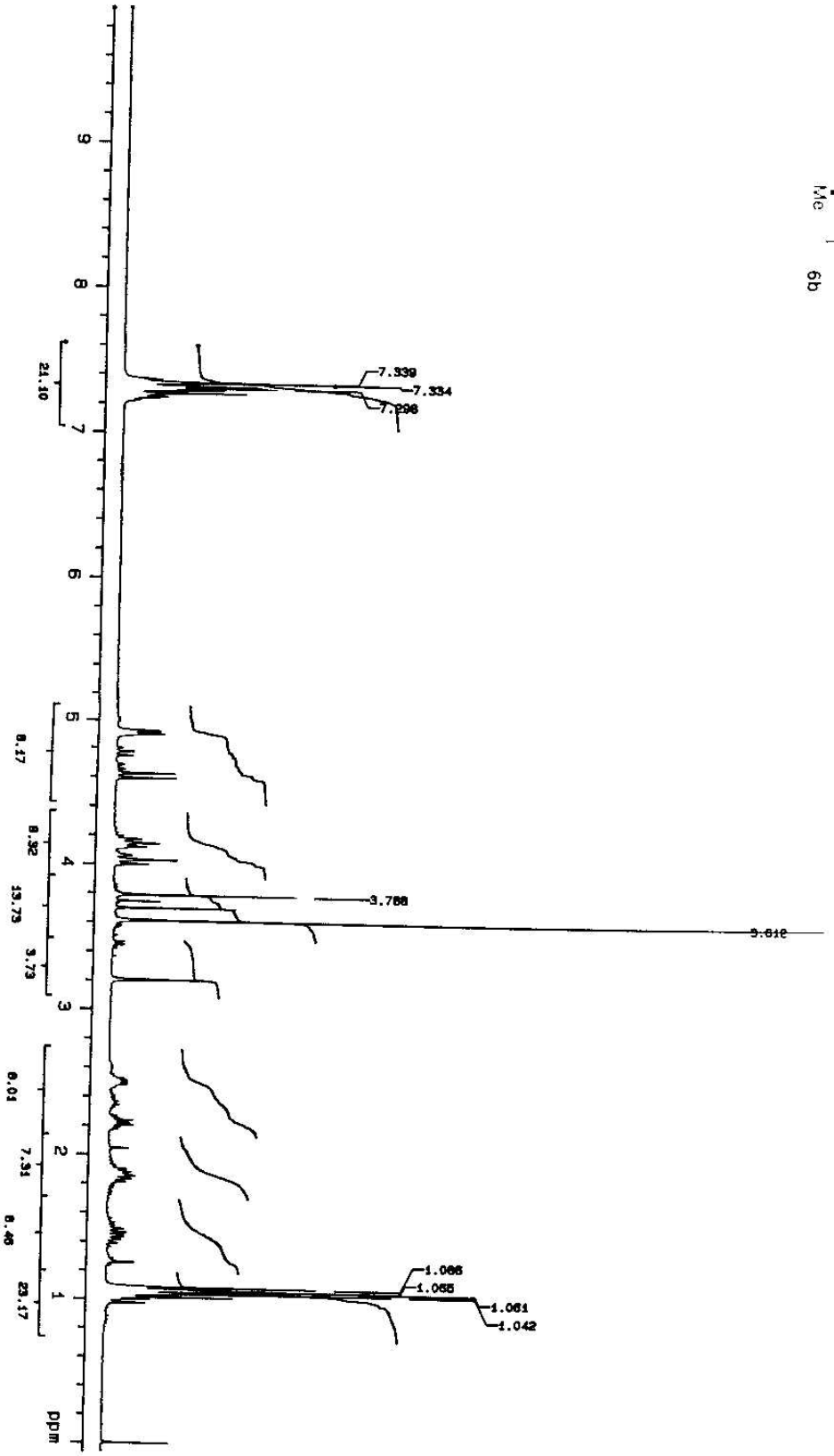
5b


BnO2C
Me
C6H5
O
N
O
6a
7.3281
7.3246
7.3115
7.3049
7.2954
1.0709
1.0462
0.9929
PPM
75.0 HZ/CM

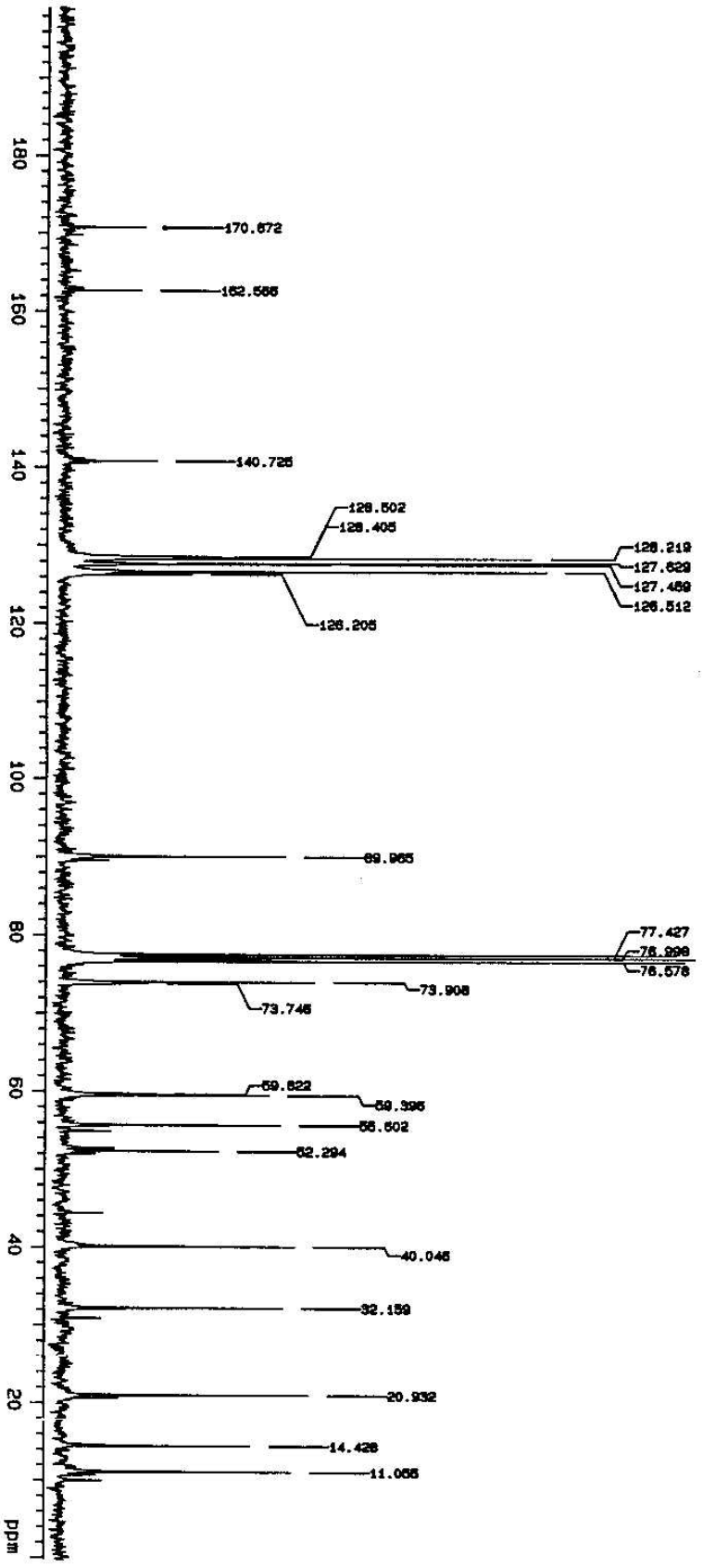

169.982
162.393
140.695
135.479
128.476
128.261
128.190
128.075
127.424
126.425
89.8374
77.4309
77.0071
76.5822
73.9450
66.8983
59.4892
55.6329
40.0456
32.0345
20.7134
14.5790
10.9537
180
160
140
120
100
80
60
40
20
PPM
377.3 HZ

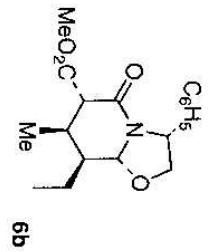

BnO2C
O
N
O
C6H5
Me

6a

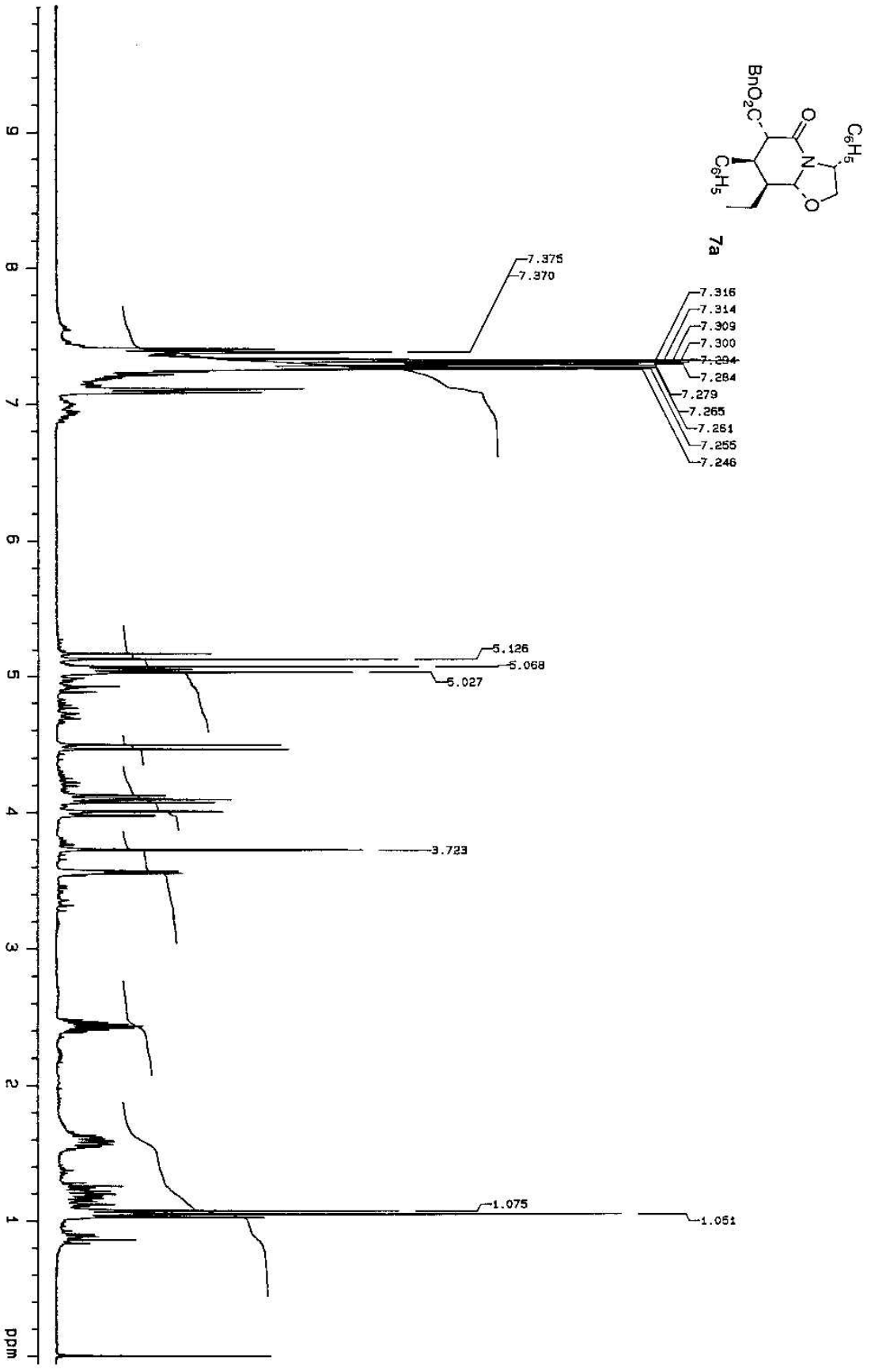

7.339
7.334
7.298
3.766
3.612
1.066
1.055
1.061
1.042
21.10
8.47
8.32
13.73
3.73
6.01
7.31
8.46
23.17
ppm

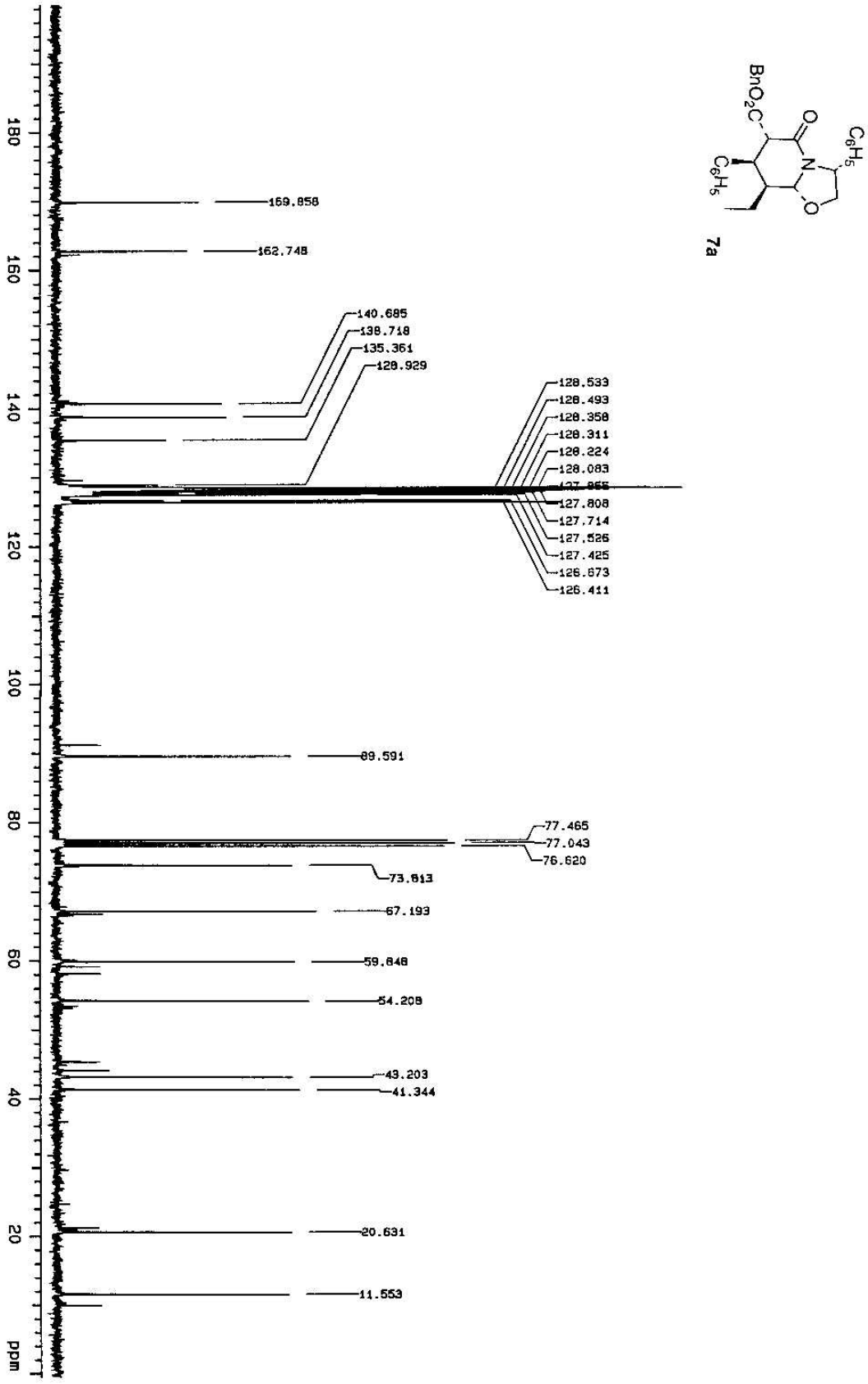
6b

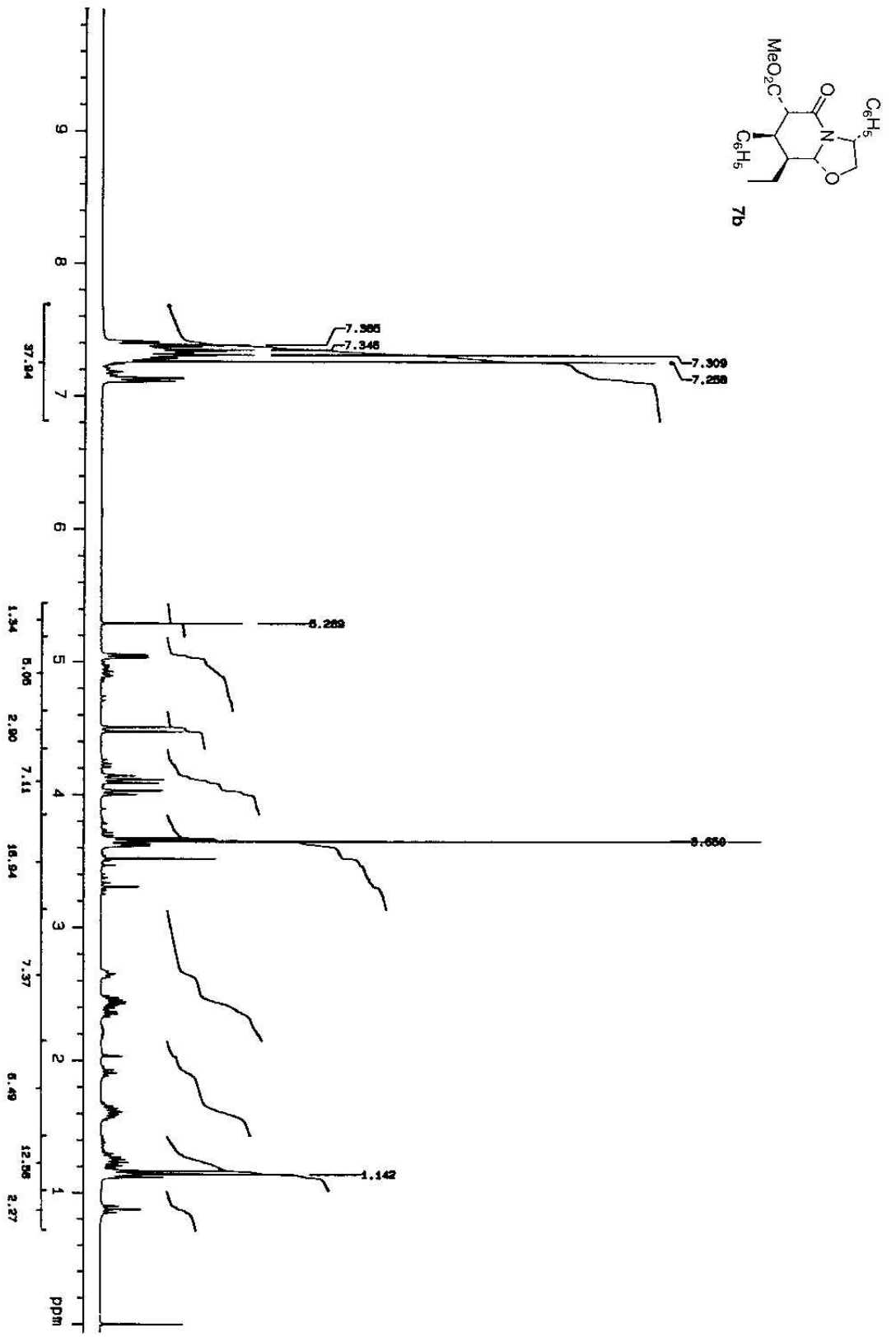

180
160
140
120
100
80
60
40
20
ppm
170.672
162.566
140.726
128.502
128.405
128.219
127.629
127.469
126.512
126.205
89.965
77.427
76.998
76.576
73.908
73.746
59.822
59.396
56.502
52.294
40.046
32.159
20.932
14.428
11.055

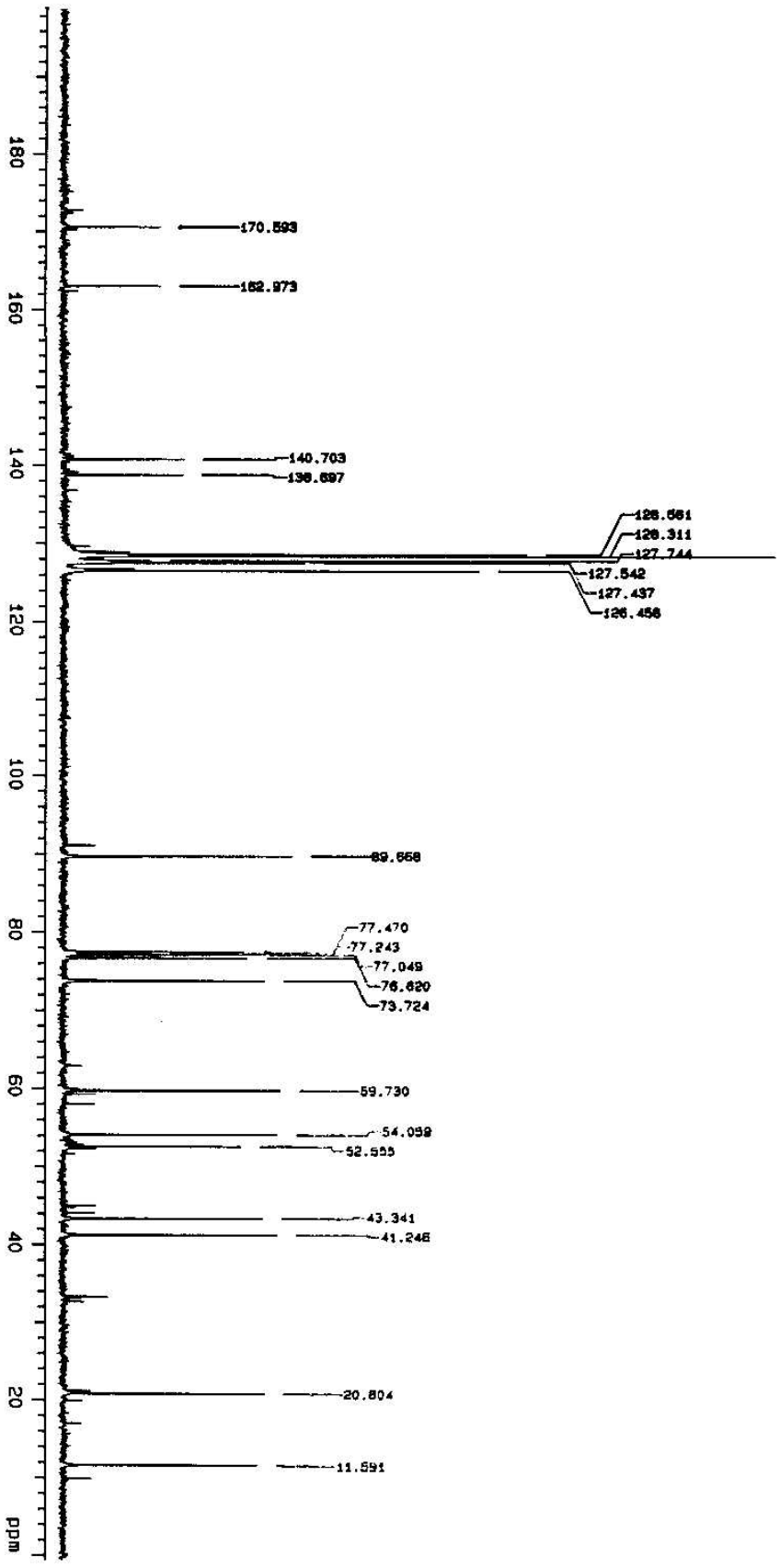

MeO2C
O
C6H5
Me
N
O

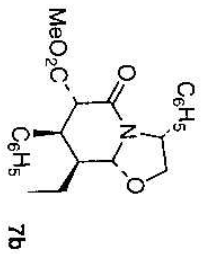
6b


7.375
7.370
7.316
7.314
7.309
7.300
7.294
7.284
7.279
7.265
7.251
7.255
7.246
5.126
5.068
5.027
3.723
1.075
1.051
ppm
7a

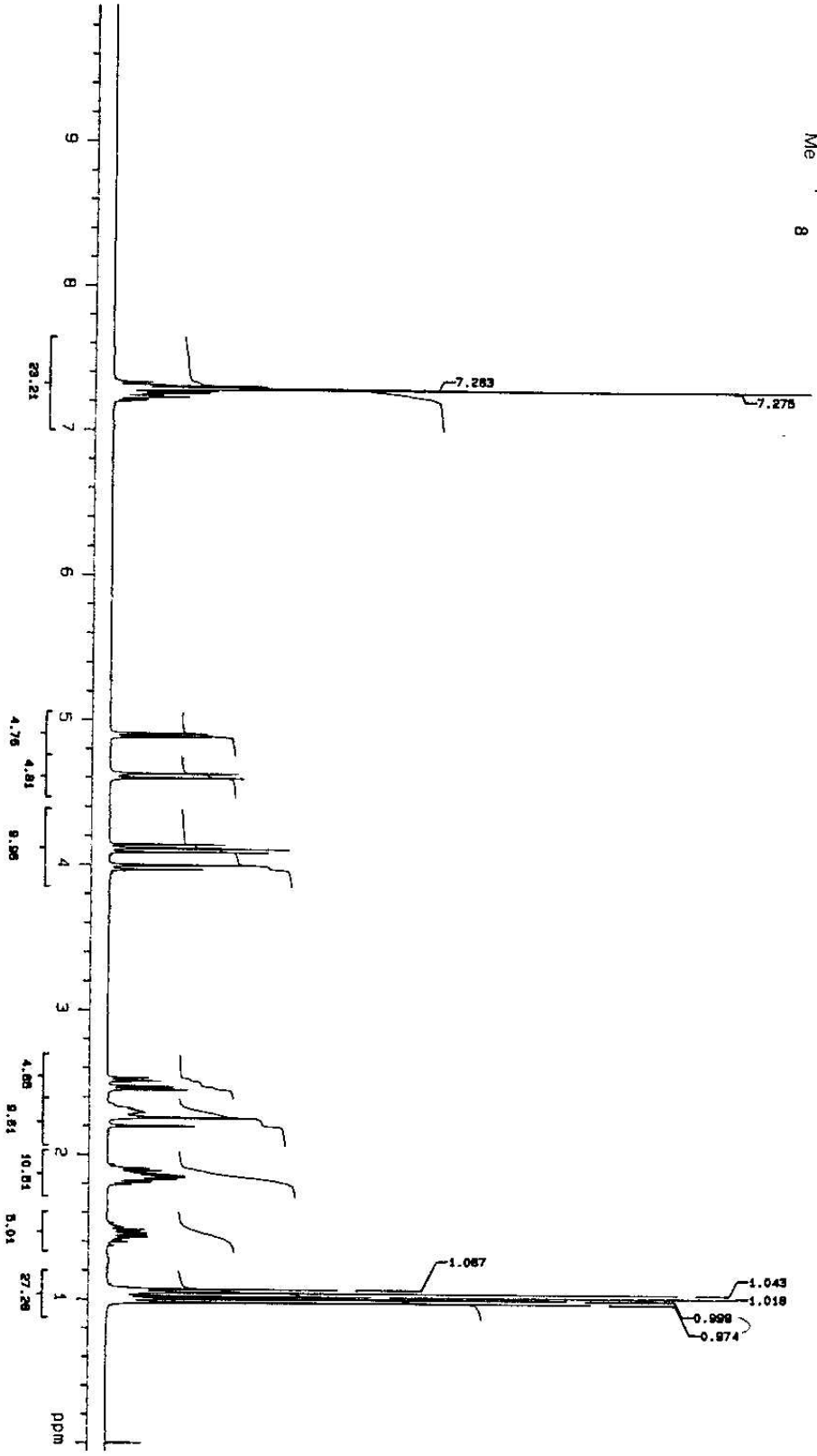

169.858
162.748
140.685
138.718
135.361
128.929
128.533
128.493
128.358
128.311
128.224
128.083
127.808
127.714
127.526
127.425
126.873
126.411
89.591
77.465
77.043
76.620
73.813
67.193
59.848
54.208
43.203
41.344
20.631
11.553
ppm
BnO2C
C6H5
C6H5
O
N
O
7a

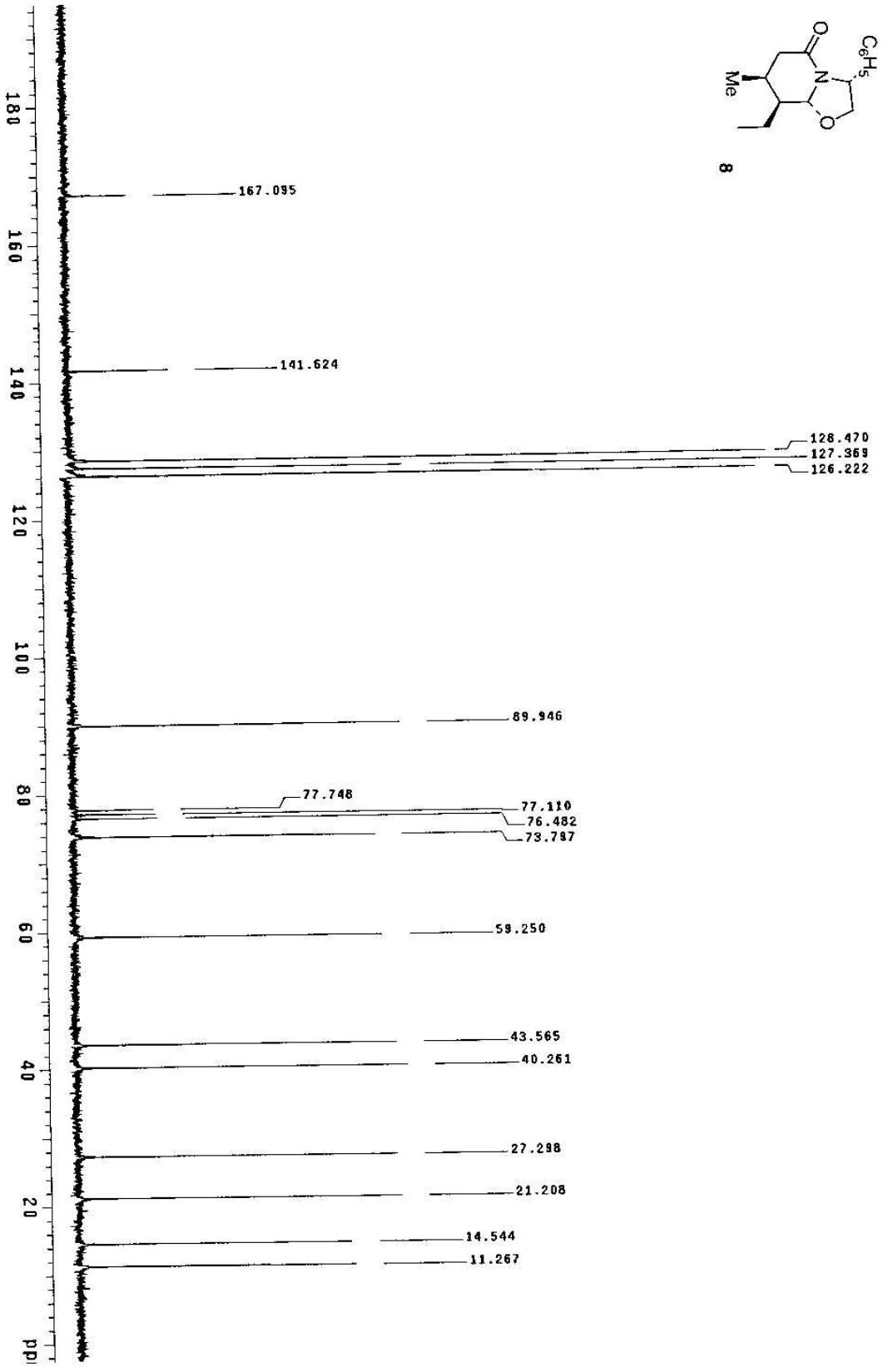

MeO2C
C6H5
C6H5
7b
7.386
7.346
7.309
7.258
5.269
3.659
1.142
ppm

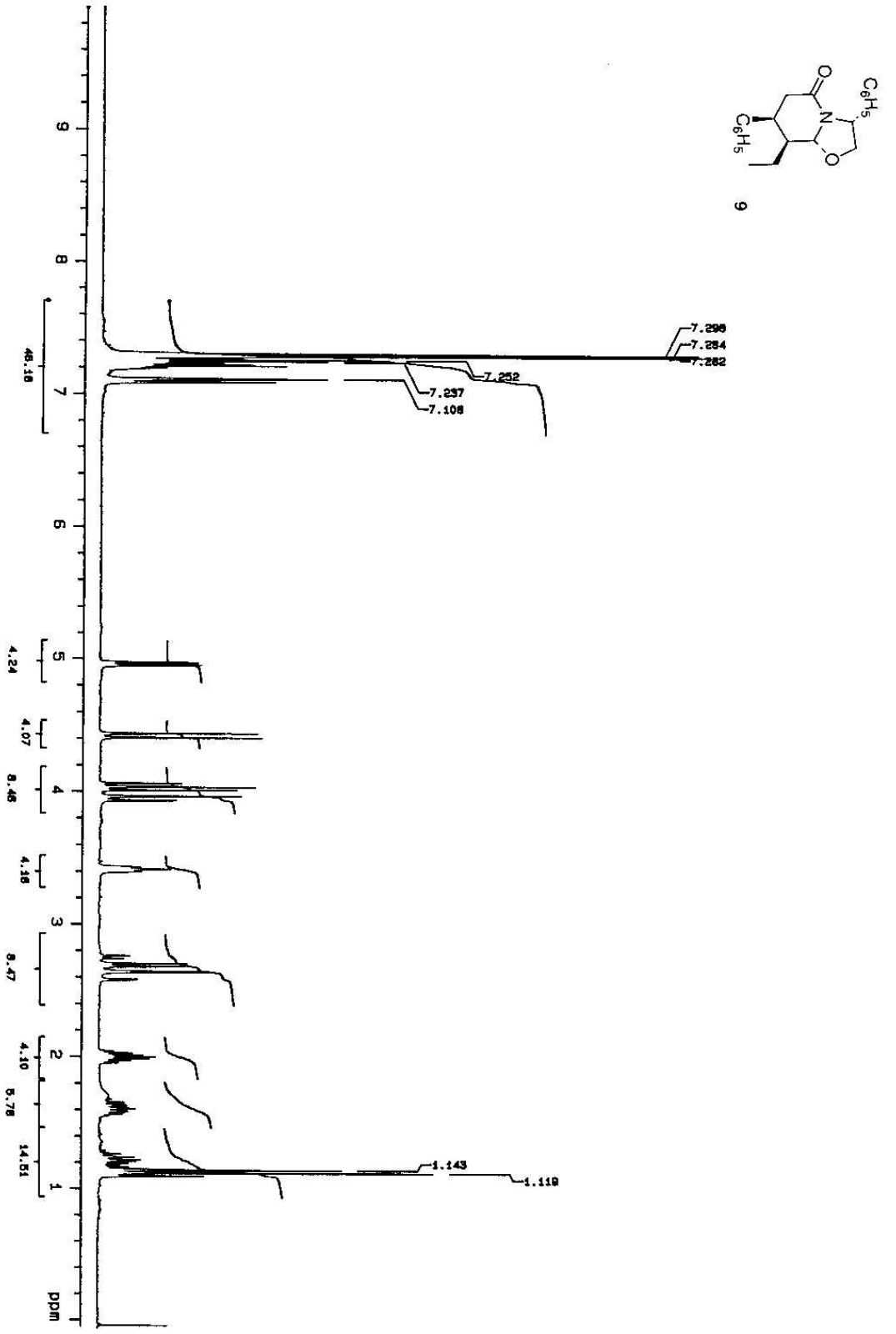

170.593
162.973
140.703
136.697
128.561
128.311
127.744
127.542
127.437
126.456
89.668
77.470
77.243
77.049
76.620
73.724
59.730
54.059
52.555
43.341
41.248
20.804
11.591
ppm


MeO2C
C6H5
C6H5
O
N
O

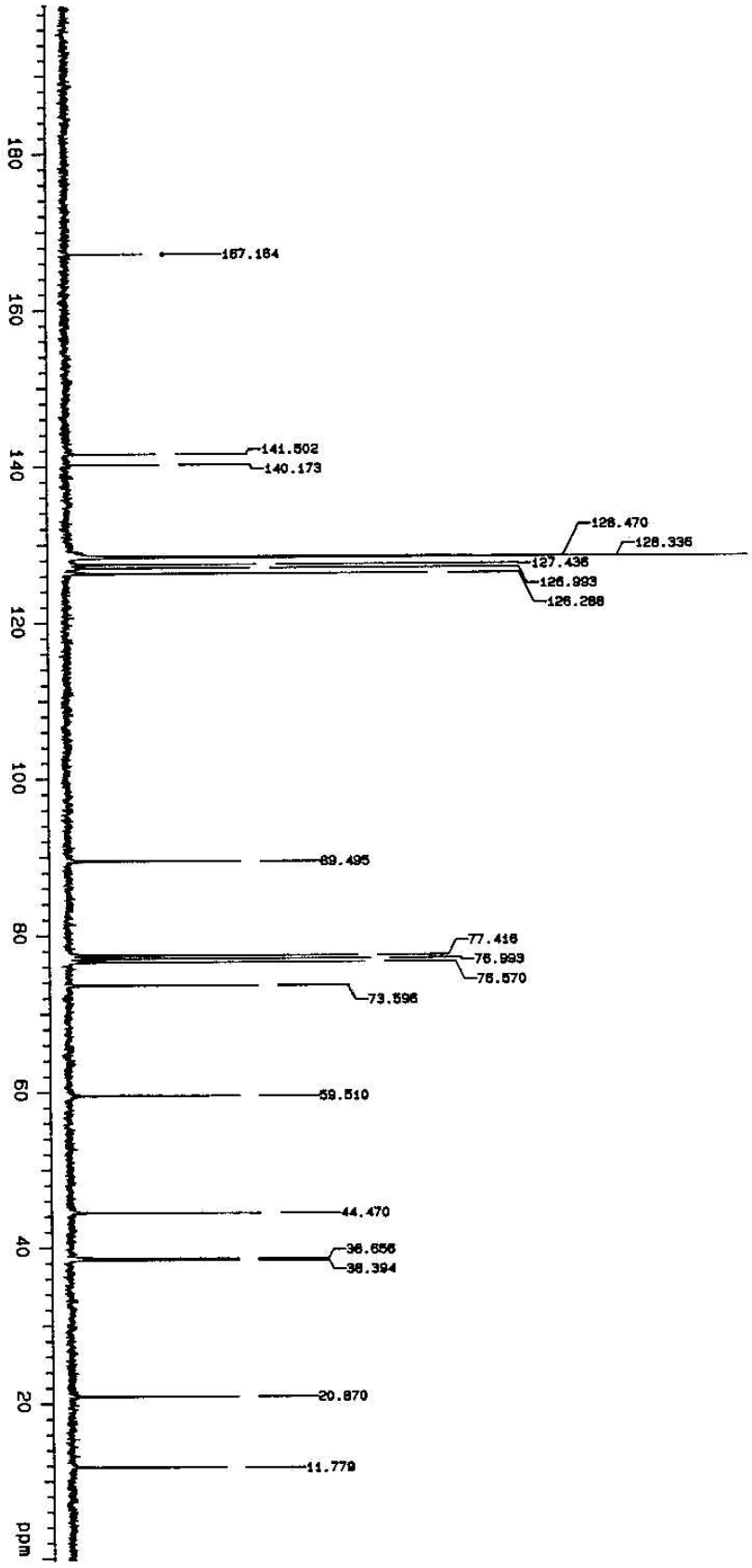
7b

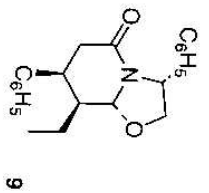

7.283
7.275
1.067
1.043
1.018
0.999
0.974
23.21
4.76
4.81
9.96
4.88
9.81
10.81
5.01
27.29
ppm
Me
C_6H_5
8


167.095
141.624
128.470
127.369
126.222
89.946
77.748
77.110
76.482
73.787
59.250
43.565
40.261
27.298
21.208
14.544
11.267
Me
C_6H_5
O
N
O
8
180
160
140
120
100
80
60
40
20
ppm

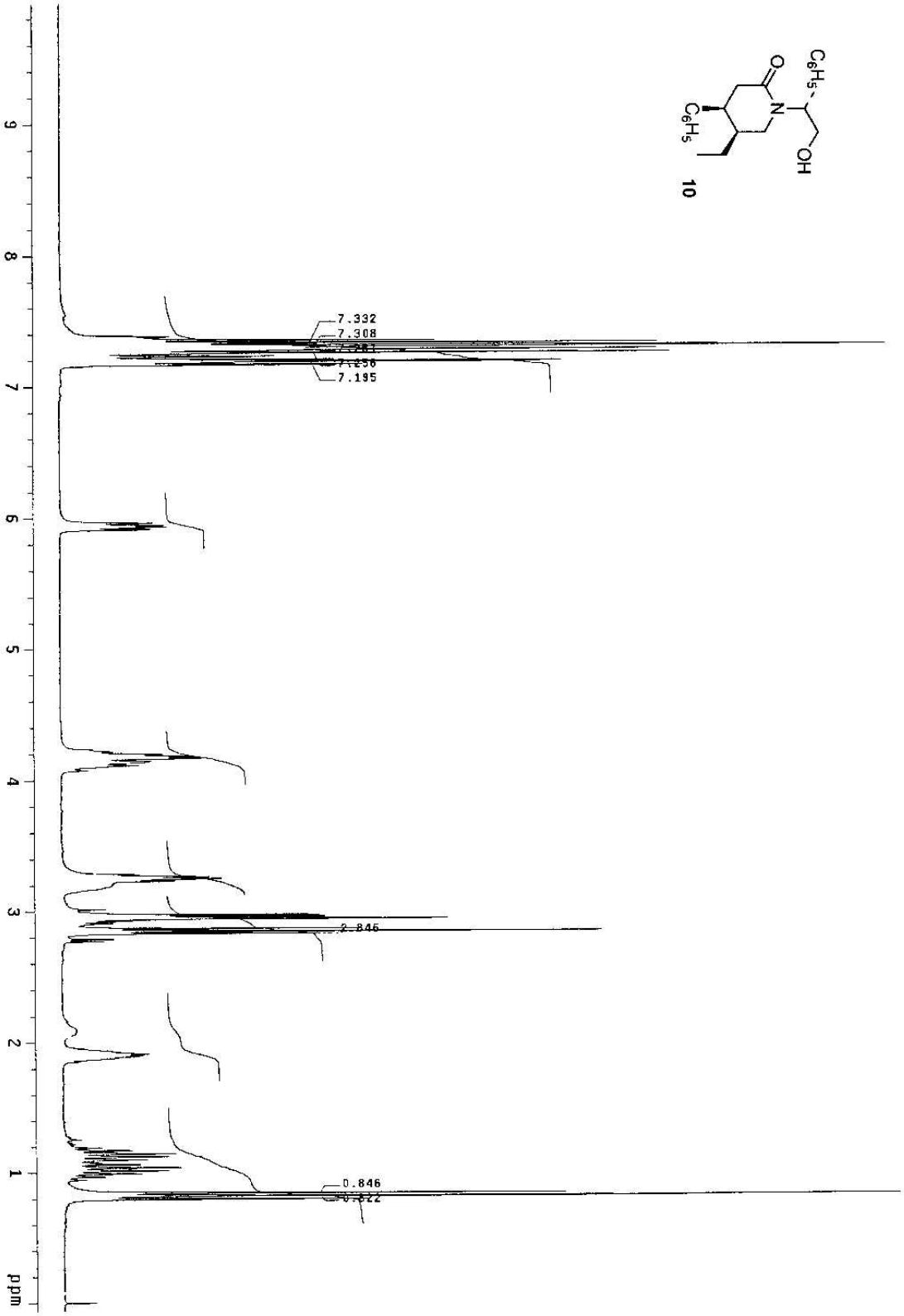

7.298
7.284
7.282
7.252
7.237
7.108
1.143
1.119
46.18
4.24
4.07
8.46
4.16
8.47
4.10
5.78
14.51
ppm
C6H5
C6H5
O
N
O

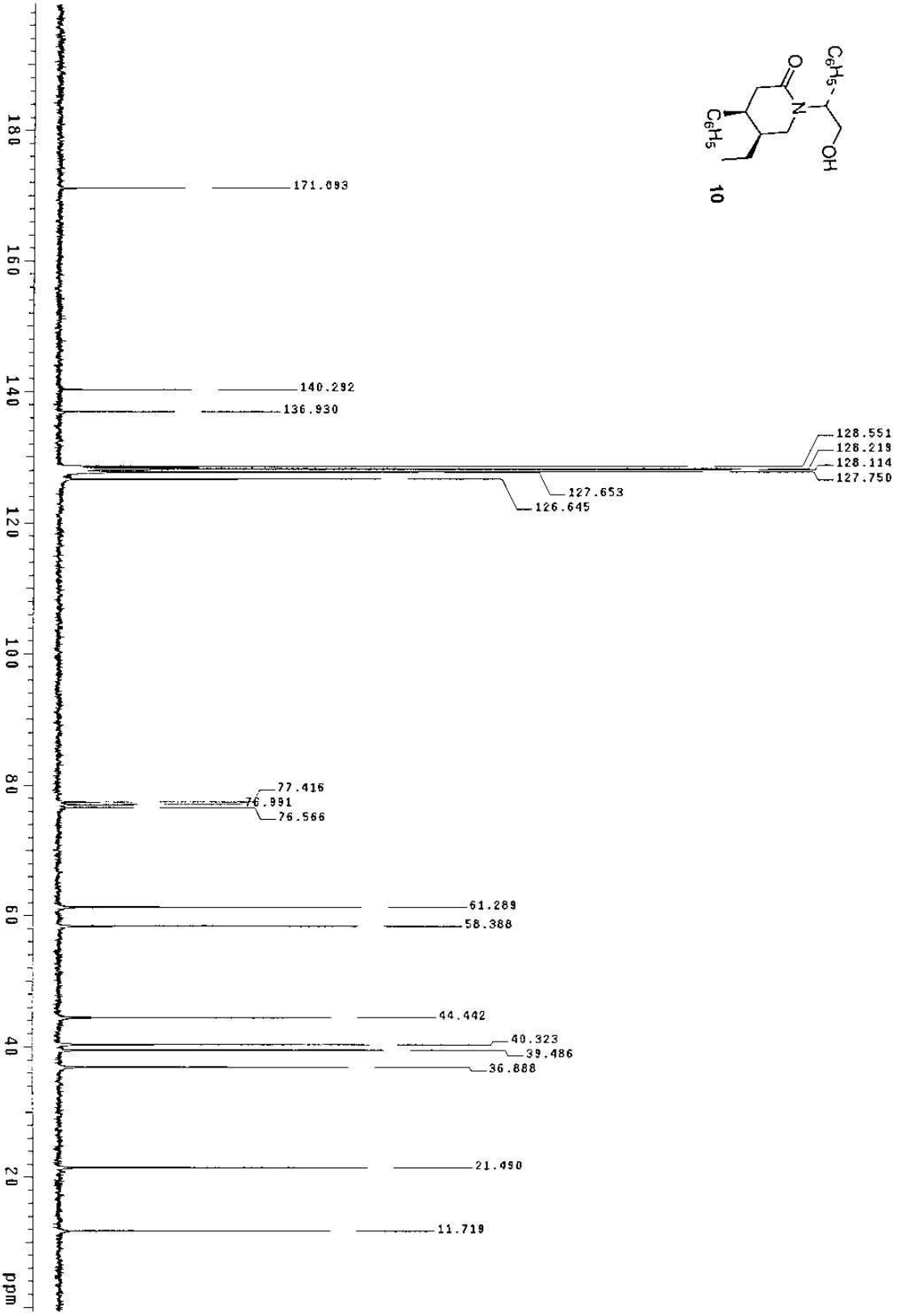
9

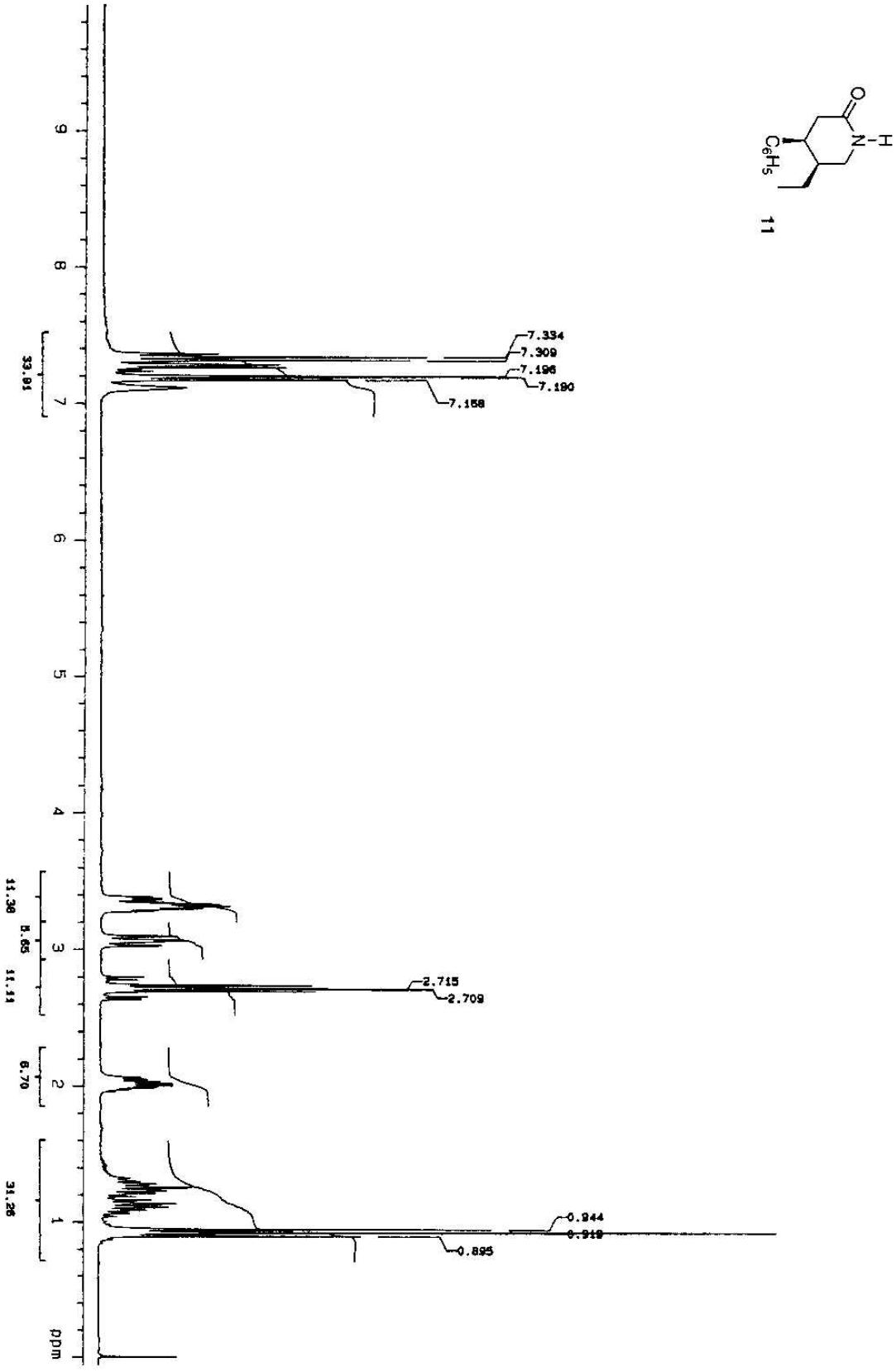

167.164
141.502
140.173
128.470
128.336
127.436
126.993
126.288
89.495
77.416
76.993
76.570
73.596
59.510
44.470
36.656
36.394
20.870
11.779
ppm


O
N
O
C_6H_5
C_6H_5

9

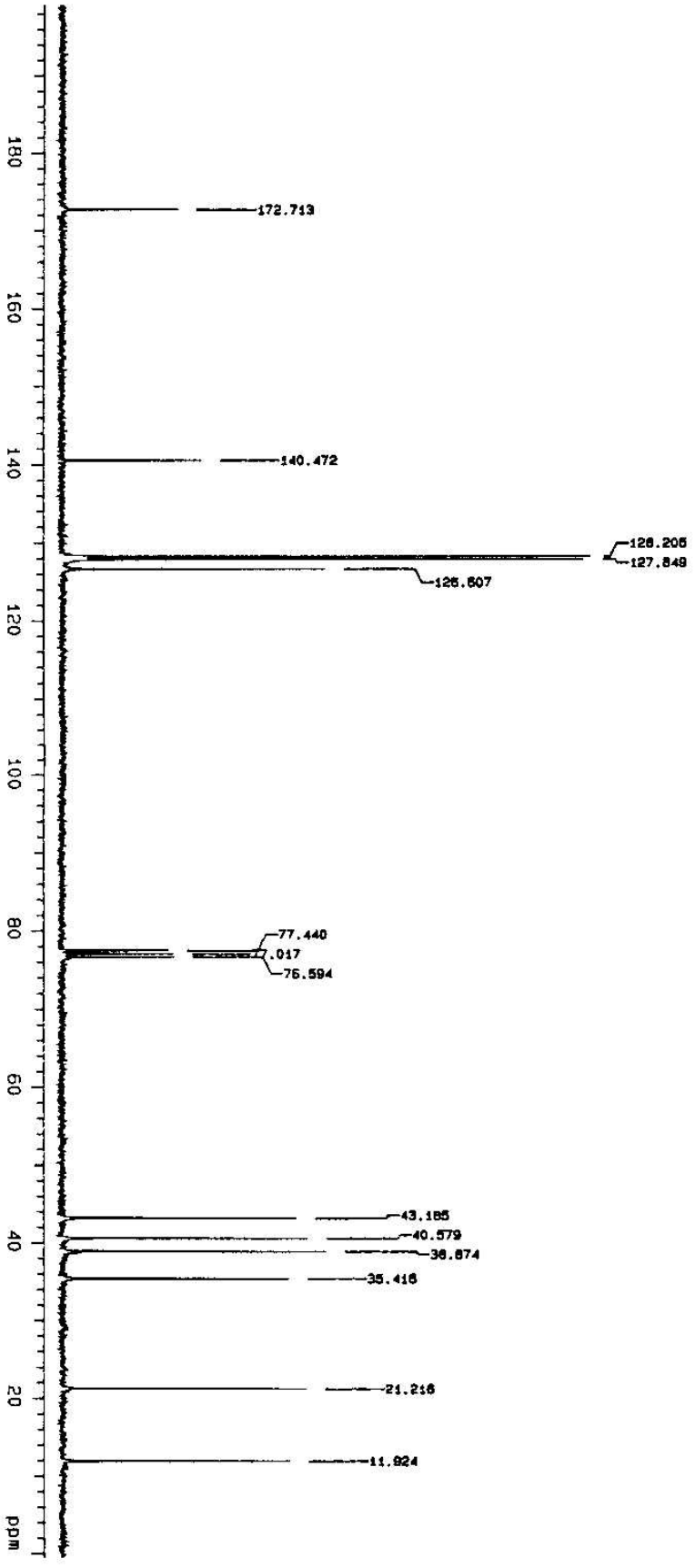

7.332
7.308
7.256
7.195
2.846
0.846
0.822
ppm
10

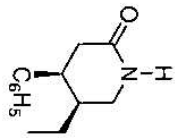

171.093
140.292
136.930
128.551
128.219
128.114
127.750
127.653
126.645
77.416
76.991
76.566
61.289
58.388
44.442
40.323
39.486
36.888
21.490
11.719
ppm
10


7.334
7.309
7.196
7.190
7.158
2.715
2.709
0.944
0.918
0.895
33.91
11.36
5.65
11.11
6.70
31.28
ppm

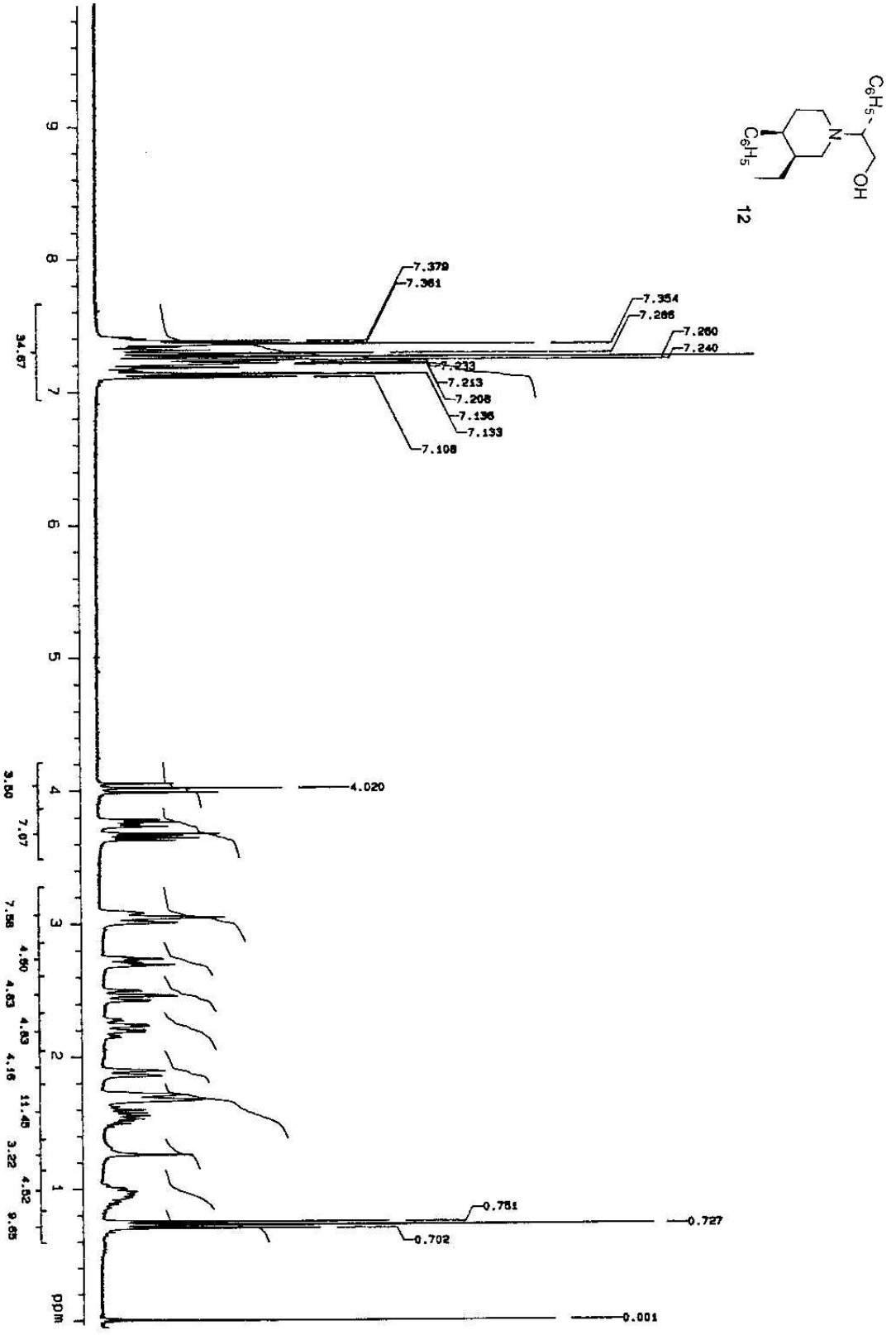
O
N
H
C6H5

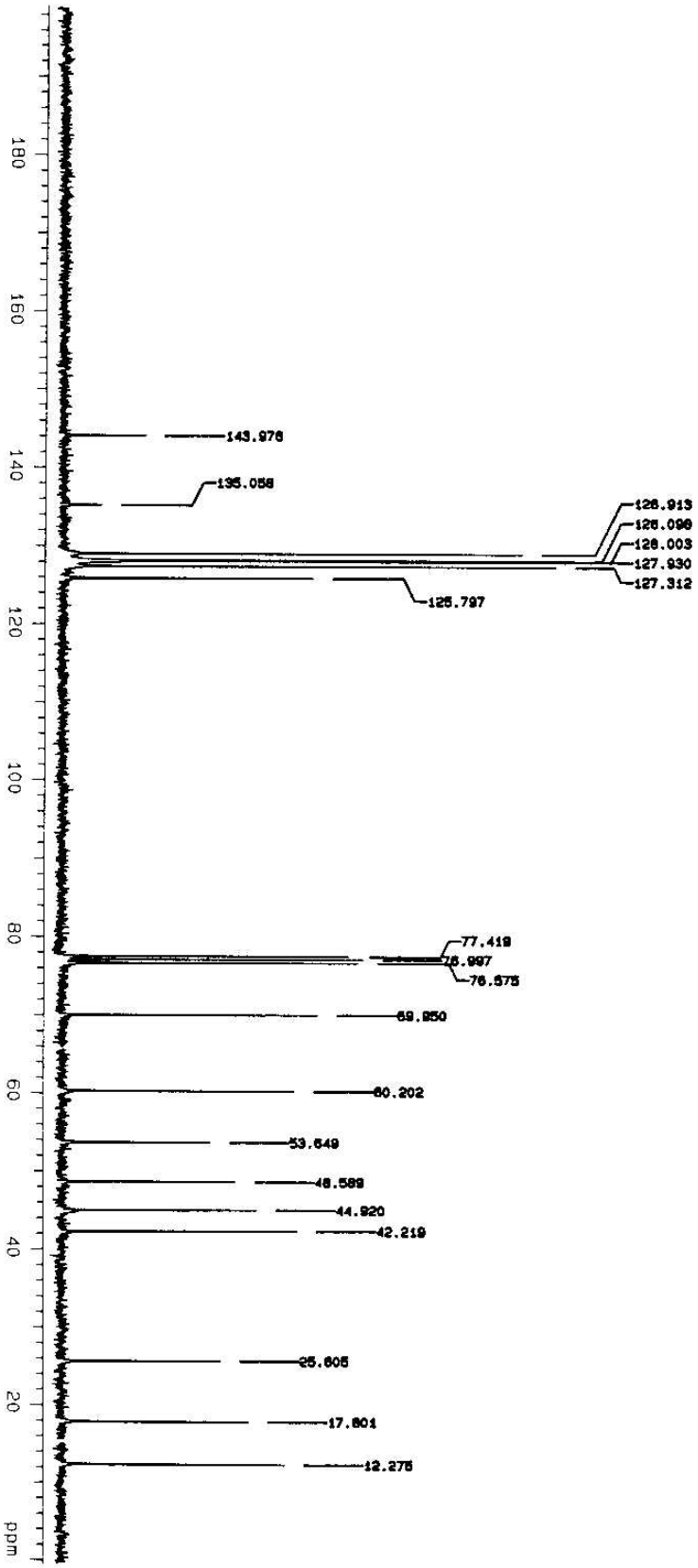
11

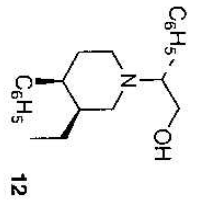

172.713
140.472
128.205
127.849
126.607
77.440
.017
76.594
43.185
40.579
38.674
35.416
21.216
11.924
ppm
180
160
140
120
100
80
60
40
20


O
N
H
C6H5

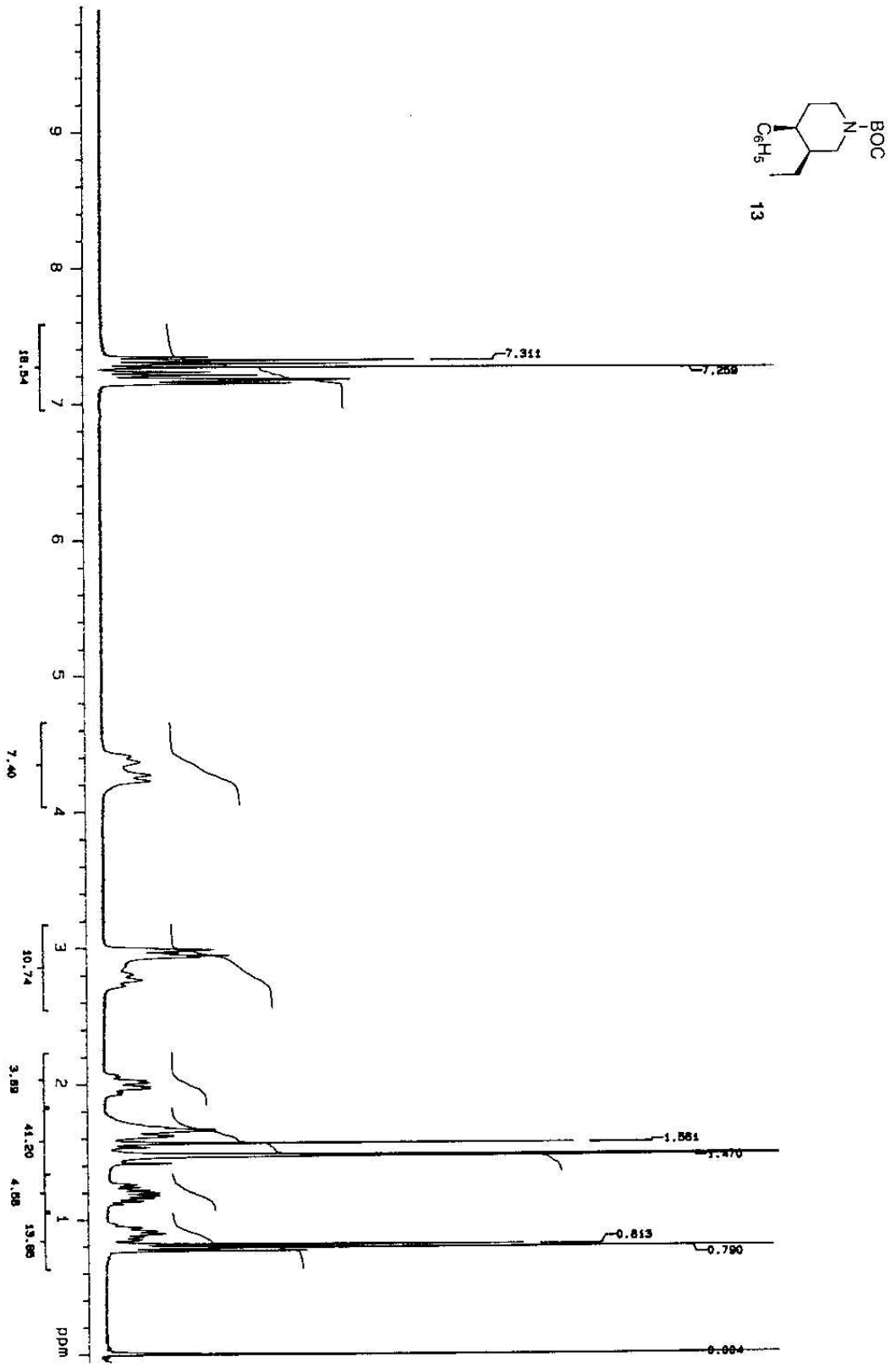
11

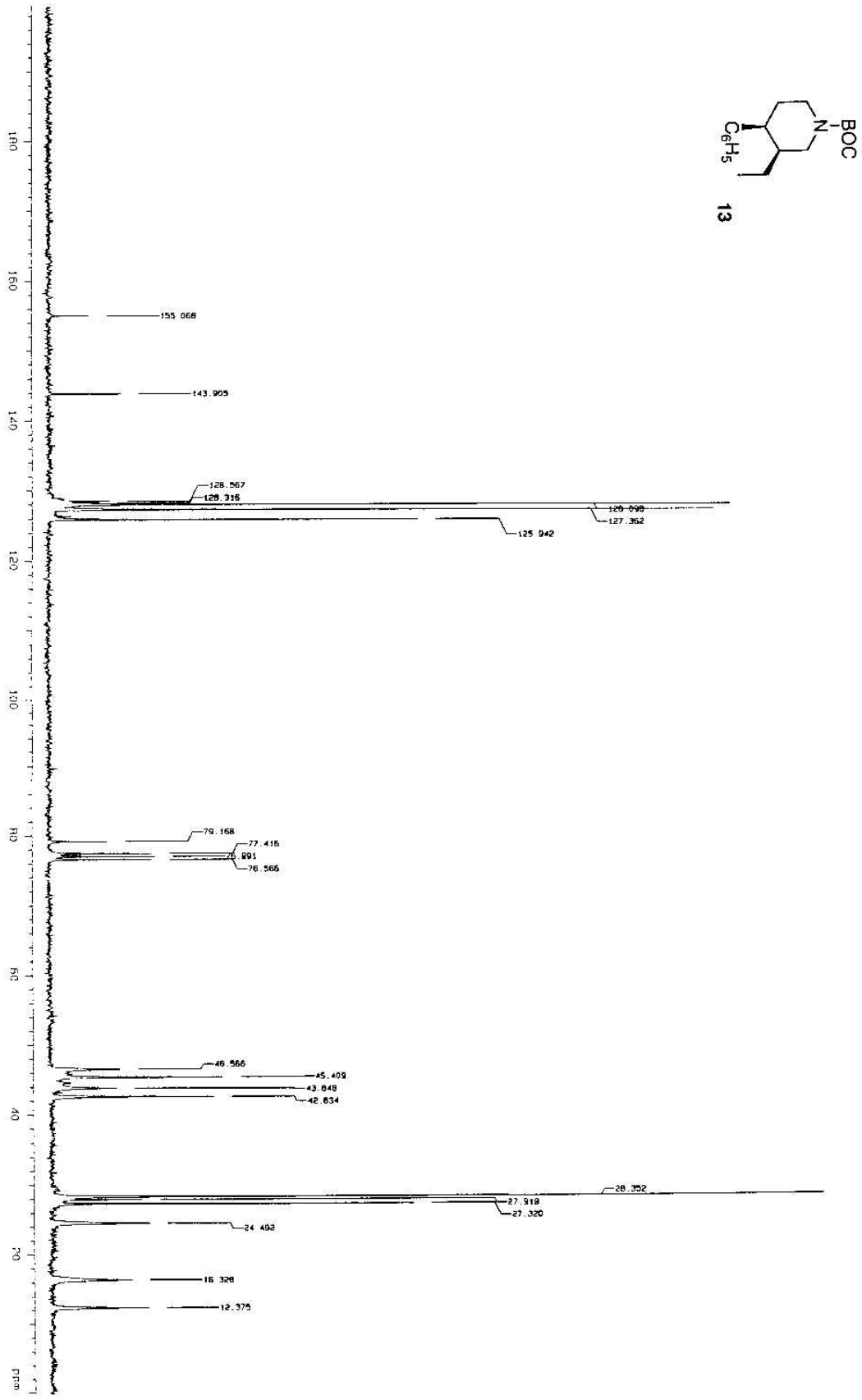

7.379
7.361
7.354
7.266
7.260
7.240
7.233
7.213
7.208
7.136
7.133
7.108
4.020
0.751
0.727
0.702
0.001
34.67
3.50
7.07
7.58
4.50
4.63
4.83
4.16
11.45
3.22
4.52
9.65
ppm
12

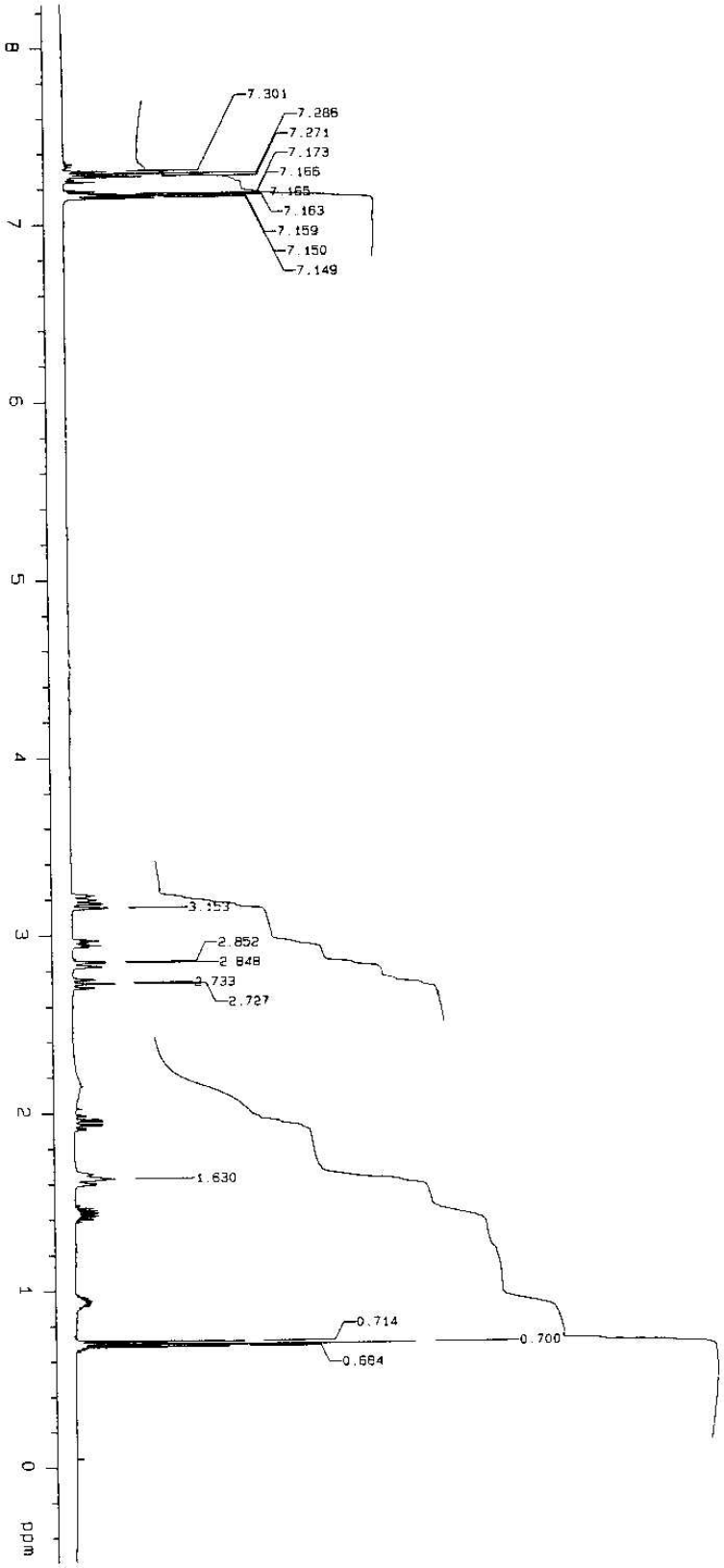

180
160
140
120
100
80
60
40
20
ppm
143.976
135.058
128.913
128.096
128.003
127.930
127.312
125.797
77.419
76.997
76.575
69.950
60.202
53.649
48.589
44.920
42.219
25.605
17.801
12.276

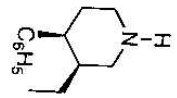

C6H5
N
C6H5
OH

12

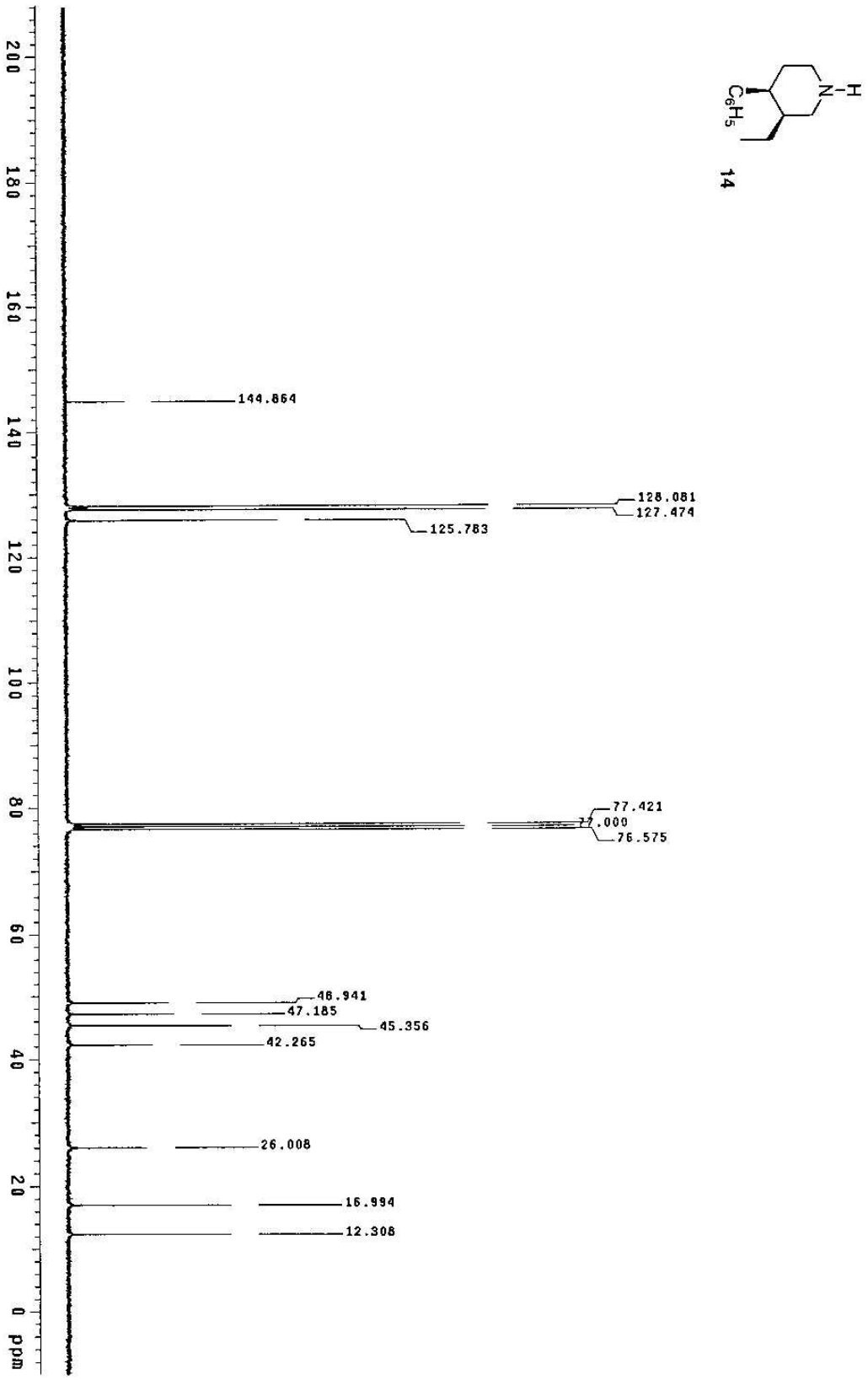

BOC
N
C6H5
13
7.311
7.259
1.561
1.470
0.813
0.790
0.004
18.54
7.40
10.74
3.89
41.20
4.58
13.98
ppm


BOC
N
C6H5
13
155.068
143.905
128.567
128.316
126.098
127.362
125.942
79.168
77.416
75.991
76.566
46.566
45.409
43.848
42.634
28.352
27.919
27.320
24.492
16.328
12.375
ppm

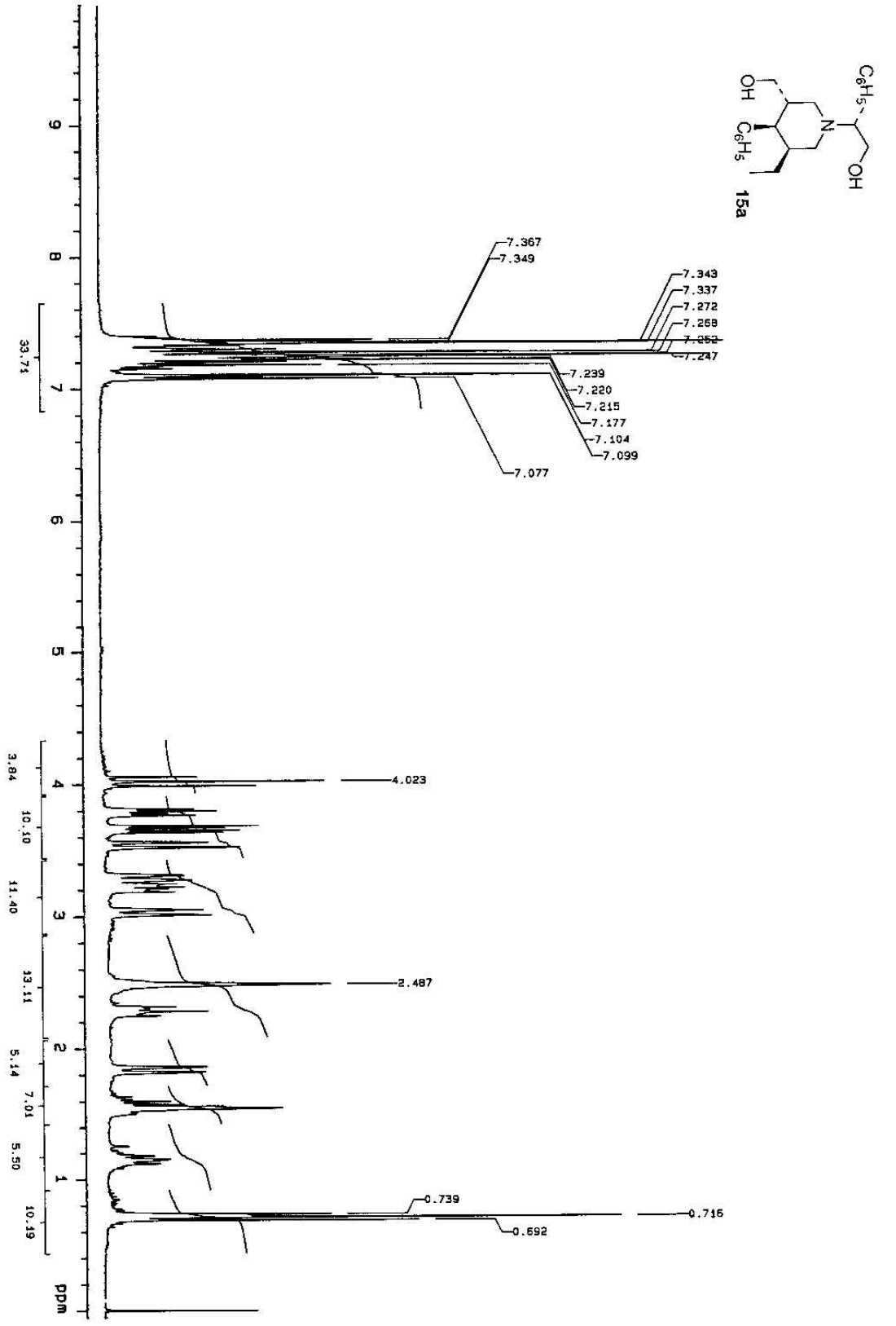

7.301
7.286
7.271
7.173
7.166
7.165
7.163
7.159
7.150
7.149
3.153
2.852
2.848
2.733
2.727
1.630
0.714
0.700
0.684
ppm

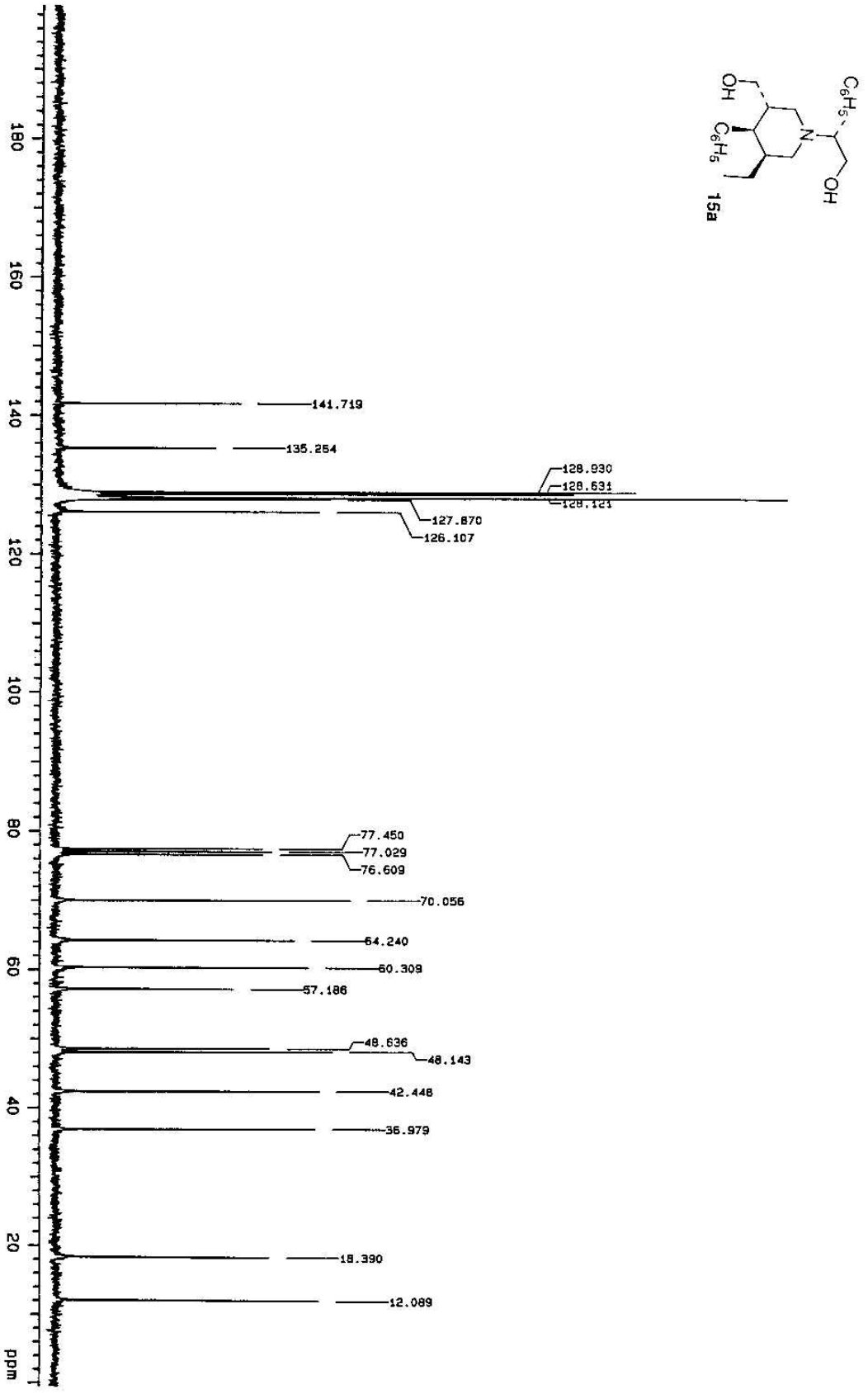

H
N
C6H5

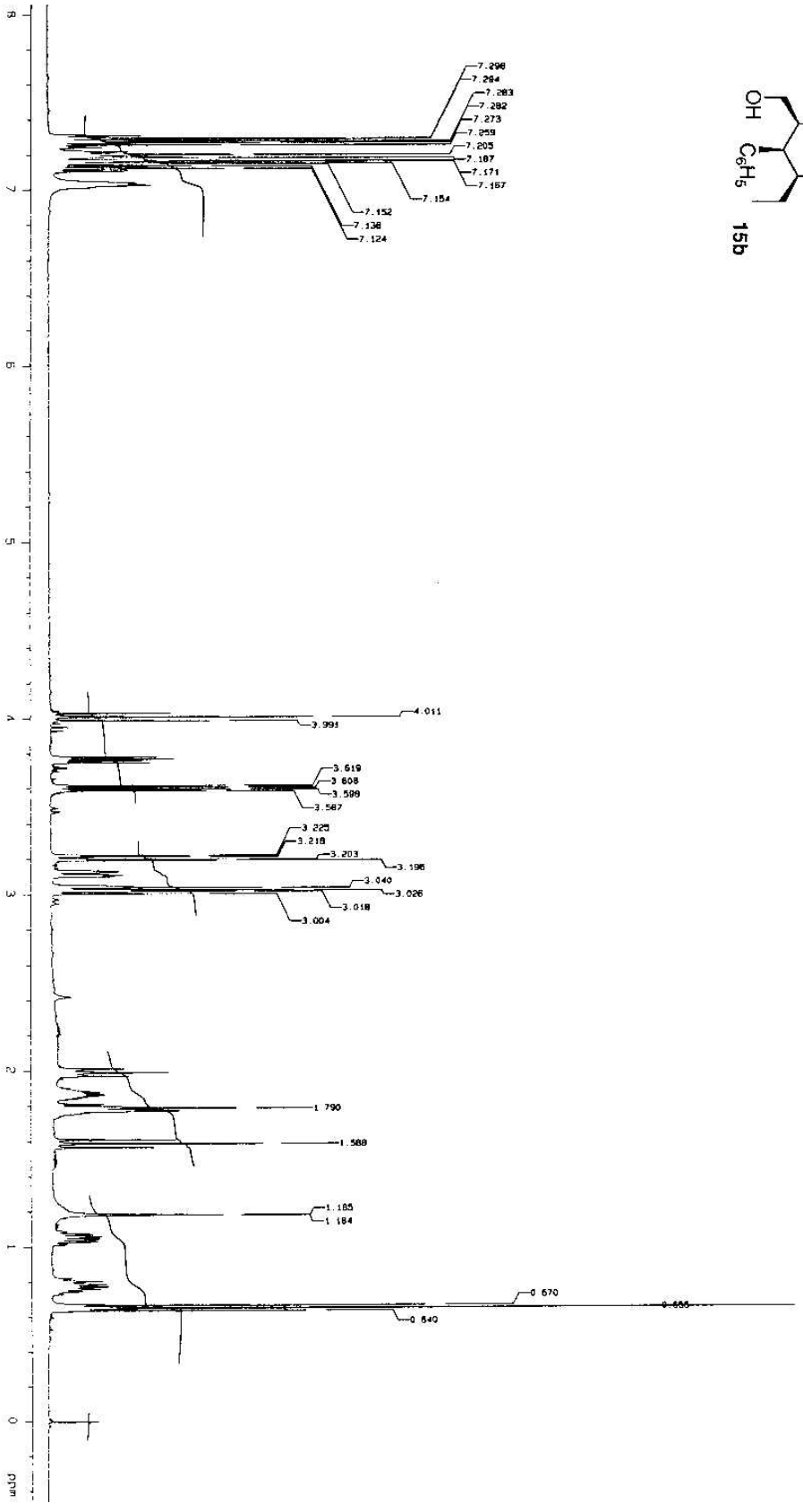
14

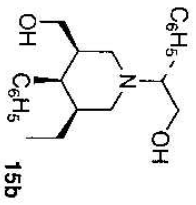

144.864
128.081
127.474
125.783
77.421
77.000
76.575
46.941
47.185
45.356
42.265
26.008
16.994
12.308
200
180
160
140
120
100
80
60
40
20
0 ppm
C6H5
N-H

14

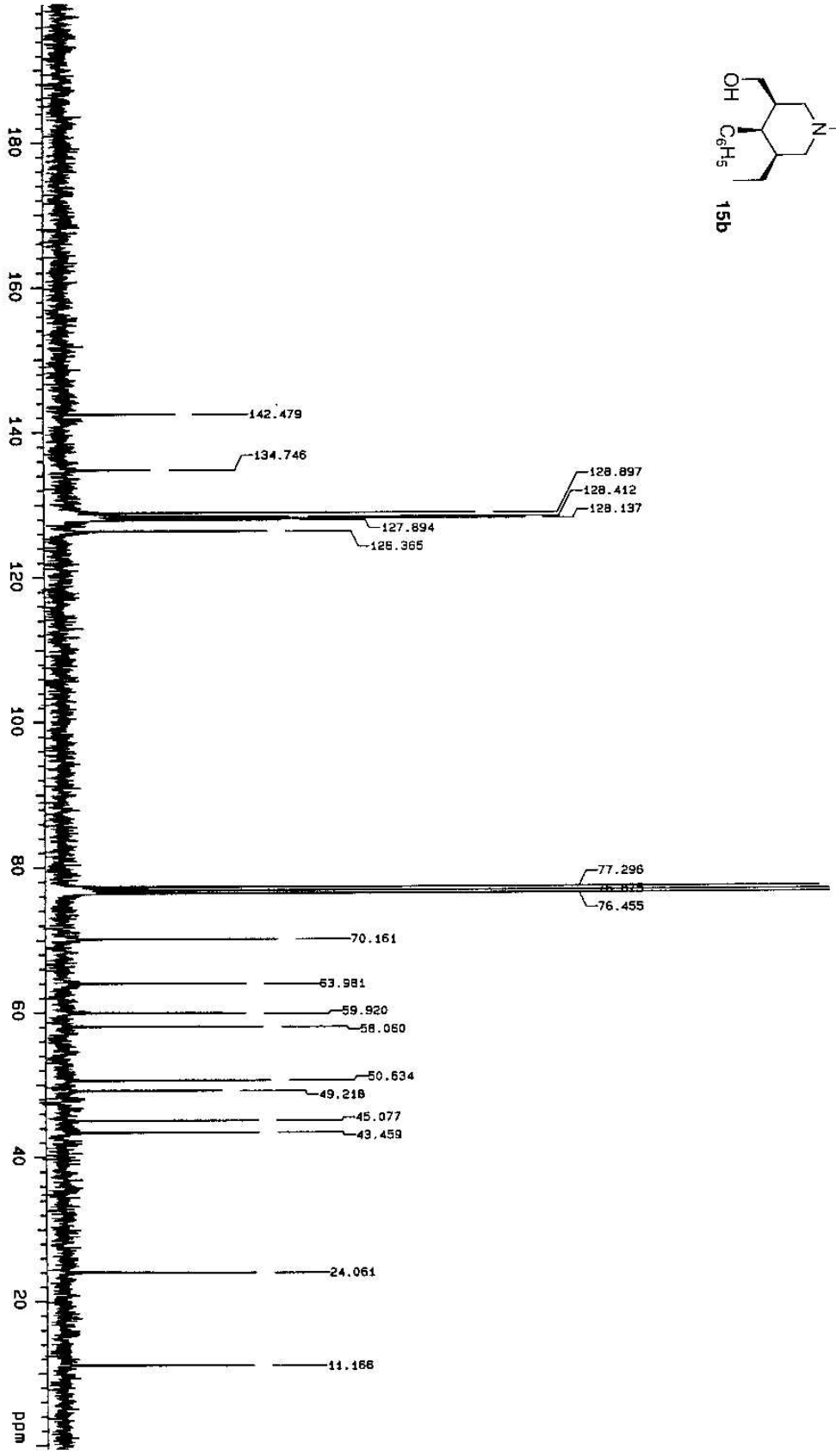

OH
C_6H_5
C_6H_5
N
C_6H_5
OH
15a
7.367
7.349
7.343
7.337
7.272
7.268
7.252
7.247
7.239
7.220
7.215
7.177
7.104
7.099
7.077
4.023
2.487
0.739
0.716
0.692
33.71
3.84
10.10
11.40
13.11
5.14
7.01
5.50
10.19
ppm

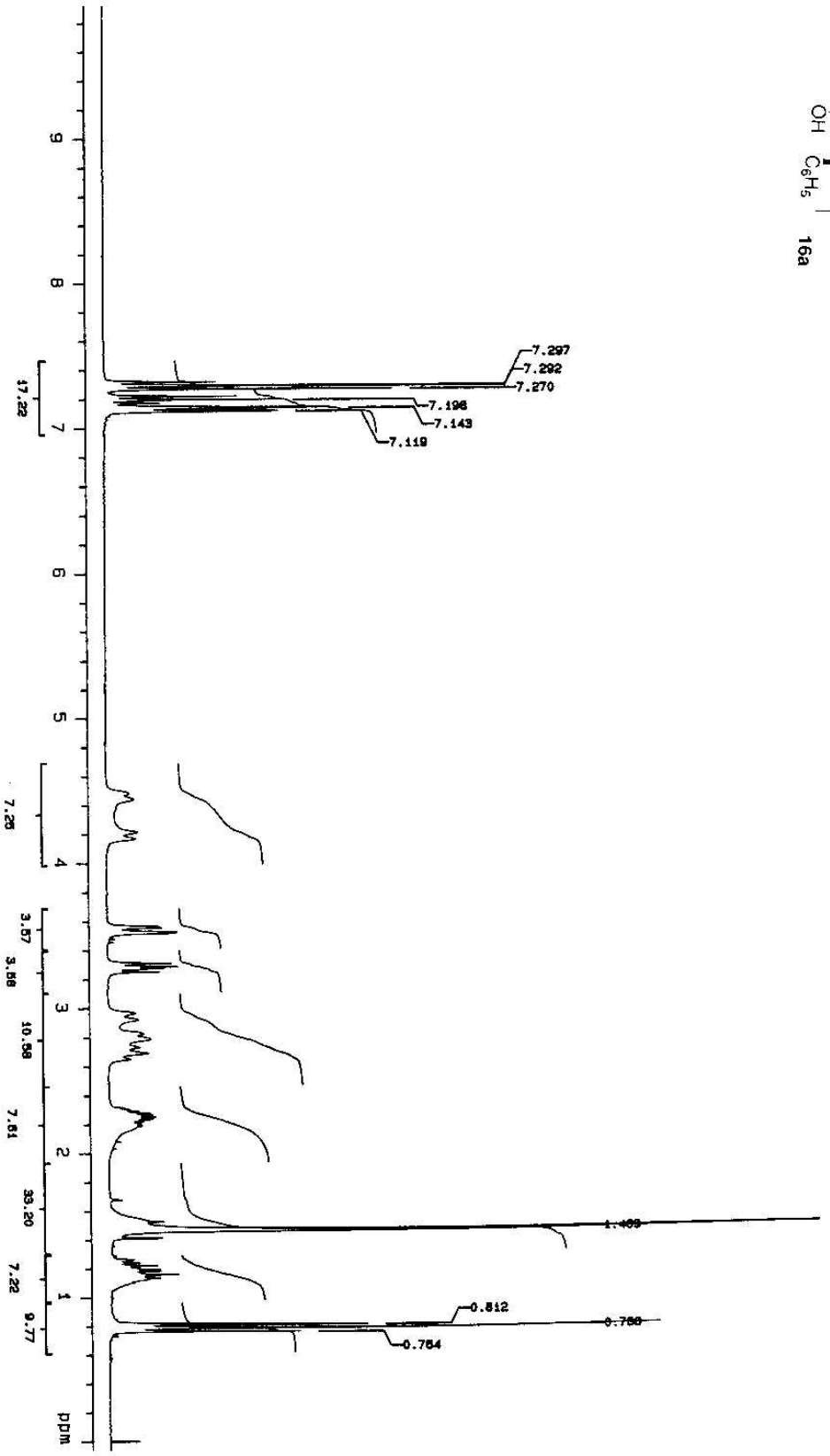

141.719
135.254
128.930
128.631
128.121
127.870
126.107
77.450
77.029
76.609
70.056
64.240
60.309
57.186
48.636
48.143
42.448
36.979
18.390
12.089
ppm
OH
C_6H_5
C_6H_5
N
OH
15a

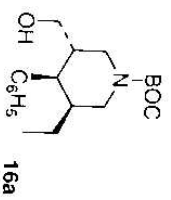

7.298
7.284
7.283
7.282
7.273
7.259
7.205
7.187
7.171
7.157
7.154
7.152
7.138
7.124
4.011
3.991
3.619
3.608
3.598
3.587
3.225
3.218
3.203
3.196
3.040
3.026
3.018
3.004
1.790
1.588
1.185
1.184
0.670
0.640
ppm


OH
C6H5
N
C6H5
OH

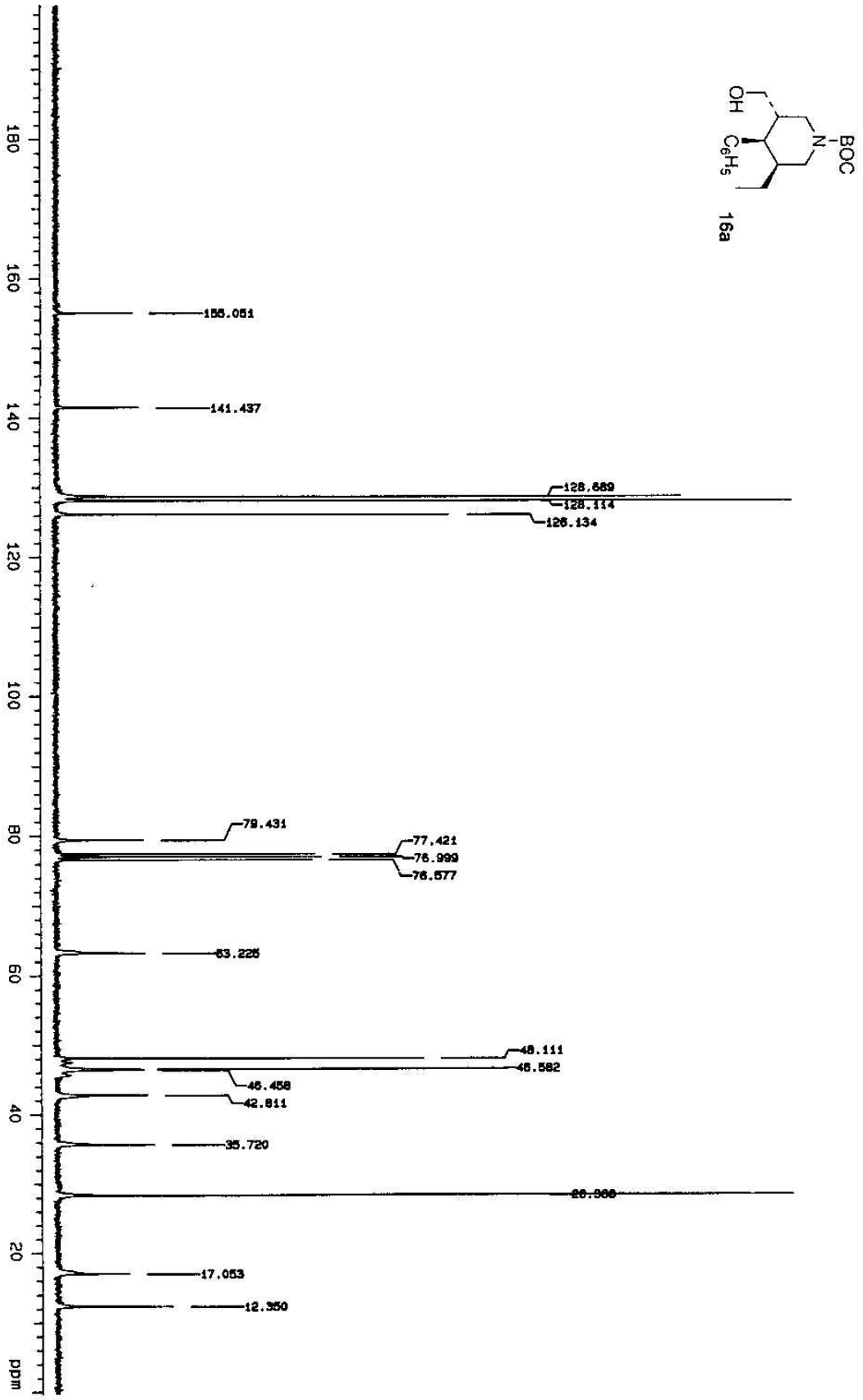
15b

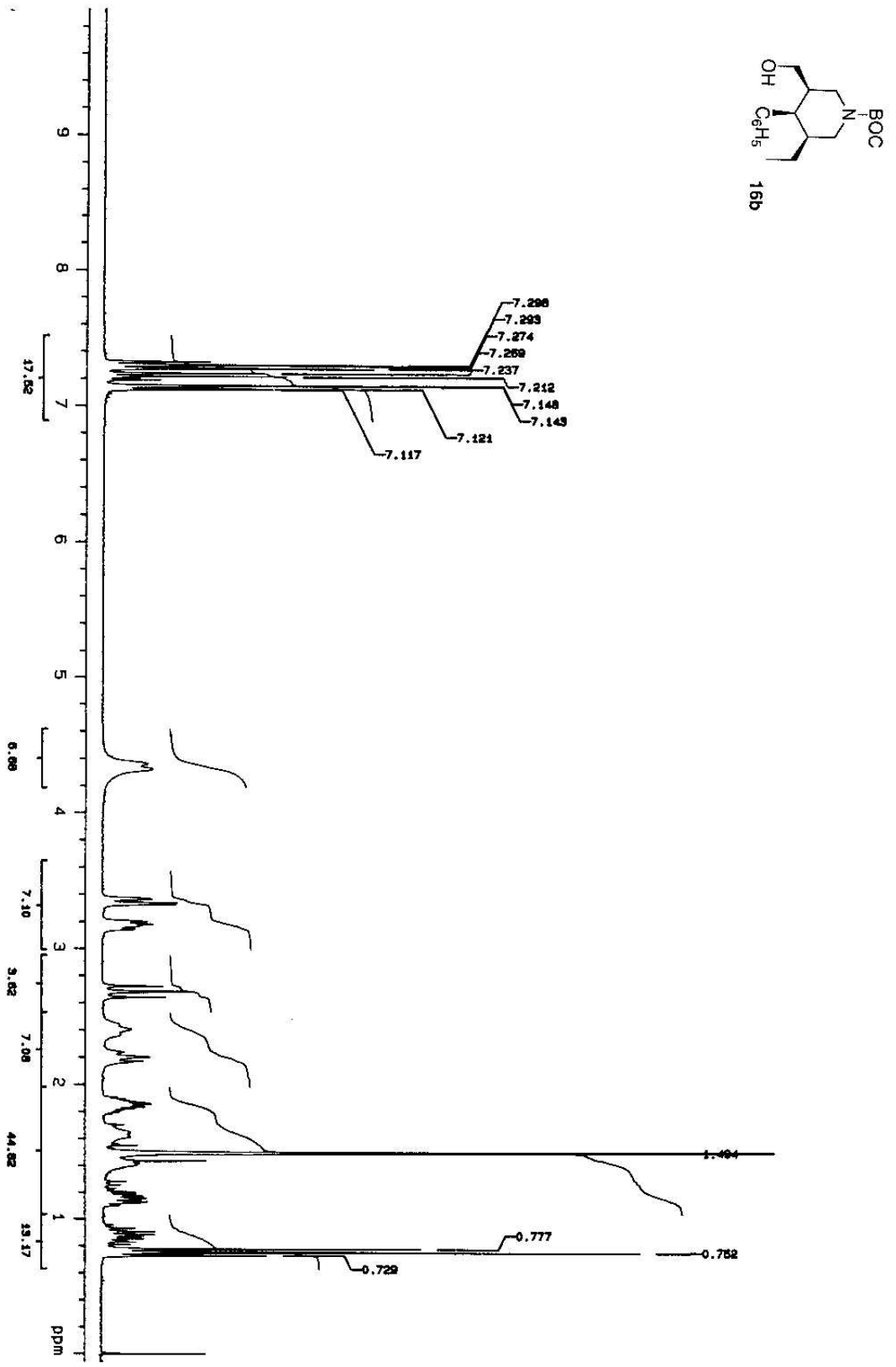

OH
C_6H_5
C_6H_5
N
OH
15b
142.479
134.746
128.897
128.412
128.137
127.894
126.365
77.296
76.455
70.161
63.981
59.920
58.060
50.634
49.218
45.077
43.459
24.061
11.166
180
160
140
120
100
80
60
40
20
ppm

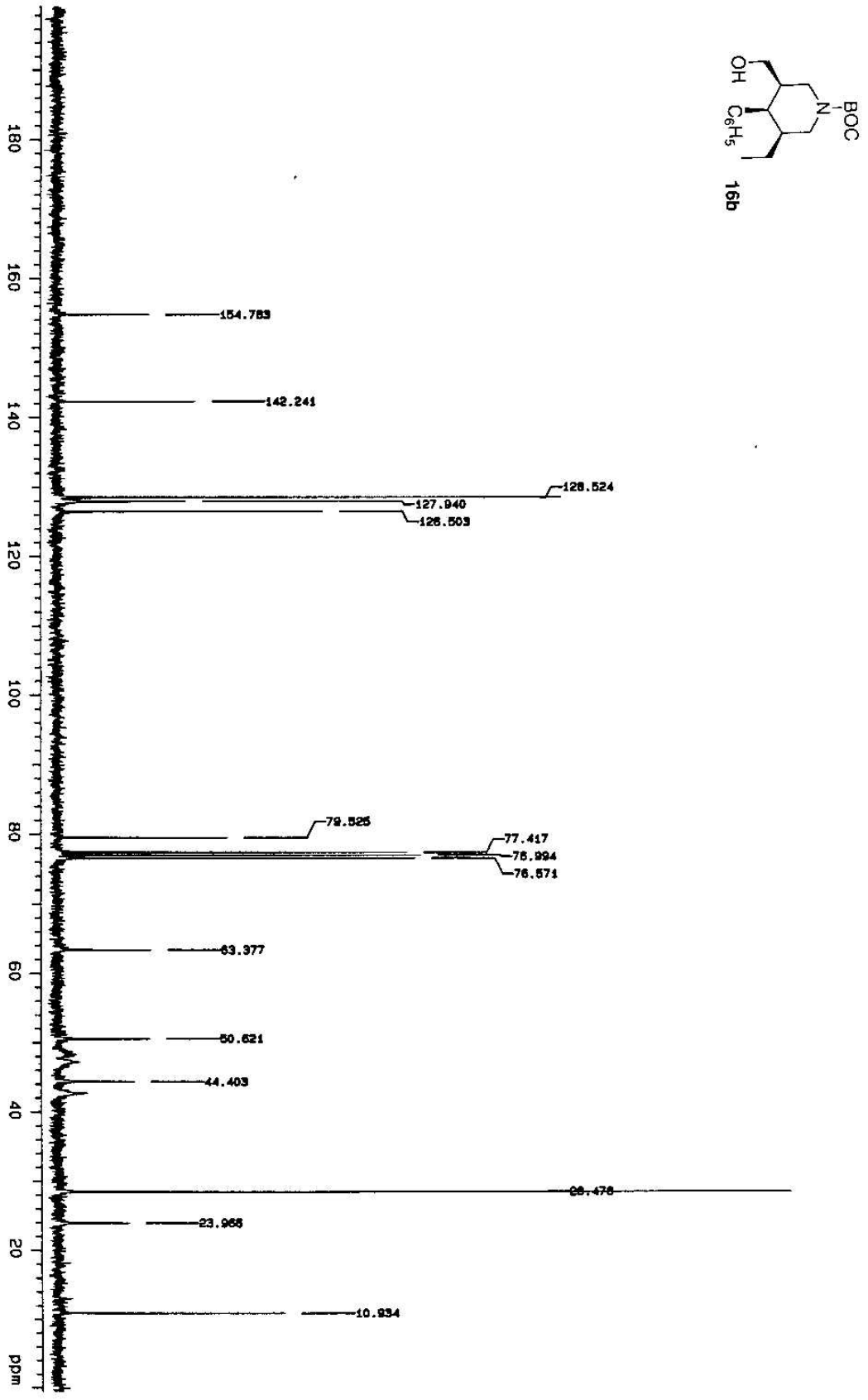

7.297
7.292
7.270
7.196
7.143
7.119
0.812
0.784
1.409
17.22
7.25
3.57
3.56
10.58
7.61
33.20
7.22
9.77
ppm

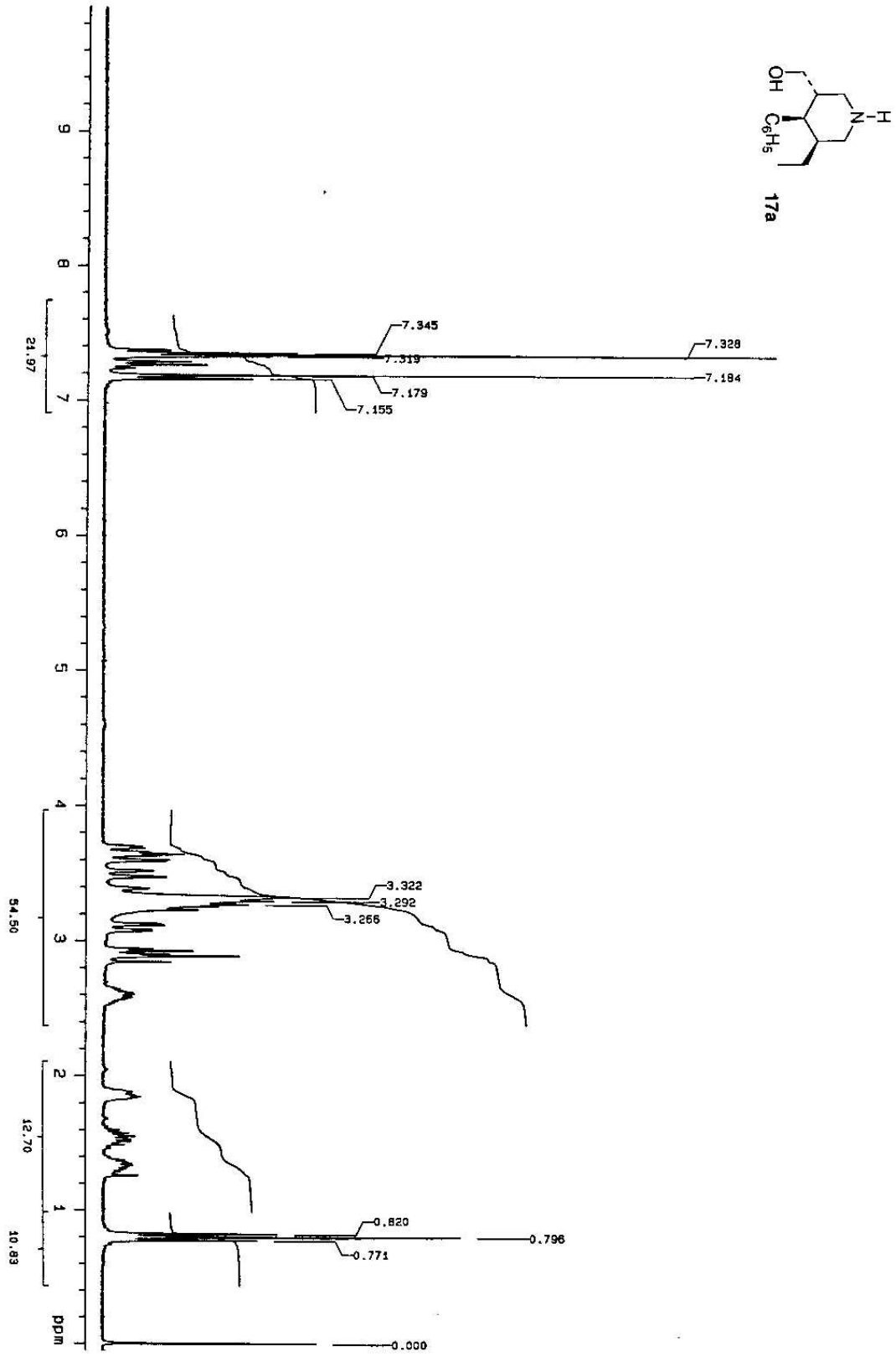

OH
C6H5
N
BOC

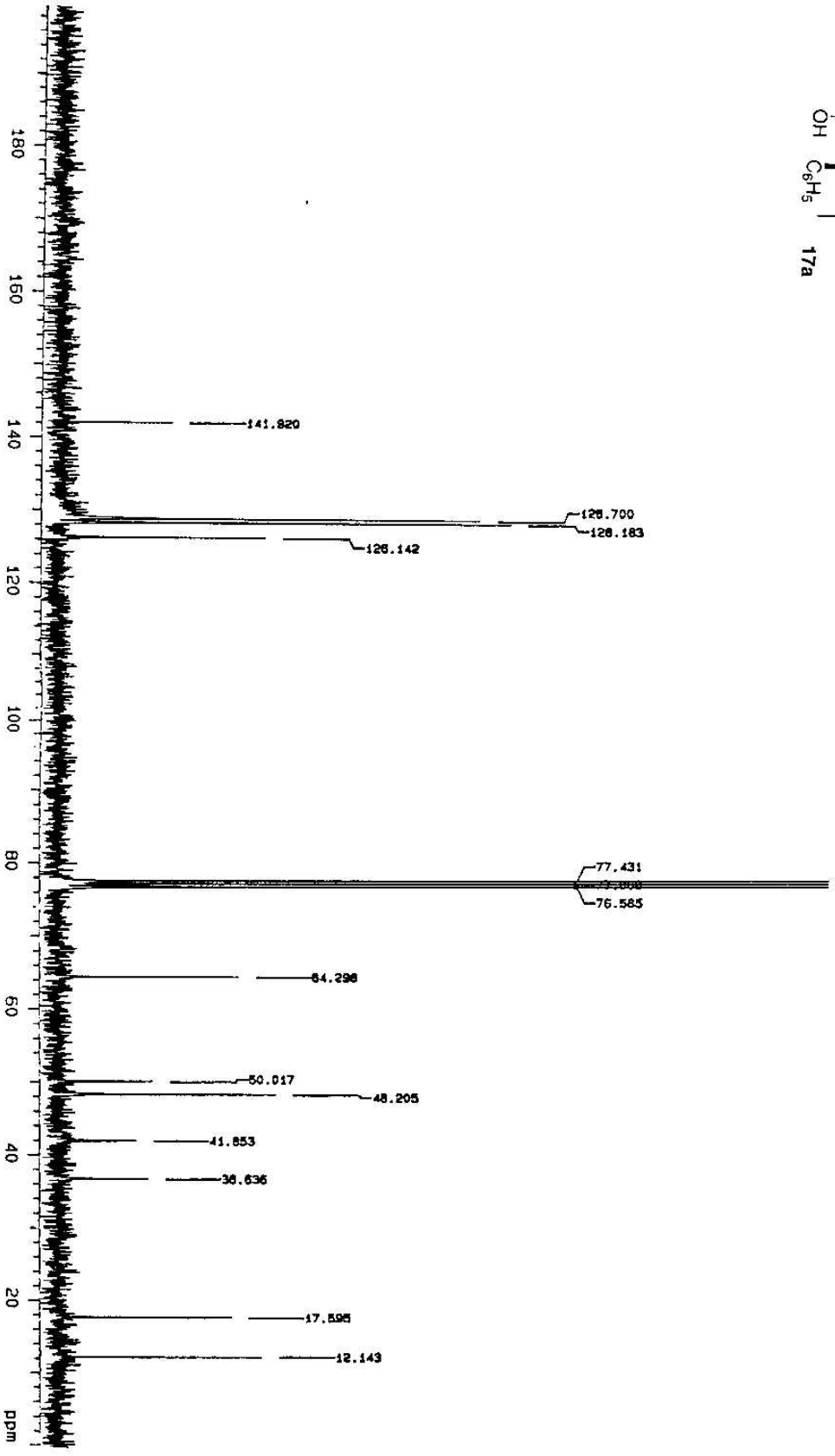
16a

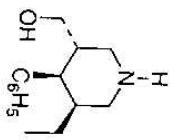

OH
C6H5
N
BOC
16a
155.051
141.437
128.689
128.114
126.134
79.431
77.421
76.999
76.577
63.226
48.111
46.582
46.458
42.811
35.720
28.366
17.053
12.350
ppm


OH
C_6H_5
N
BOC
16b
7.296
7.293
7.274
7.269
7.237
7.212
7.148
7.143
7.121
7.117
1.494
0.777
0.752
0.729
ppm


OH
C6H5
N
BOC
16b
154.783
142.241
128.524
127.940
126.503
79.525
77.417
76.994
76.571
63.377
50.621
44.403
28.476
23.968
10.934
ppm


OH
C6H5
N-H
17a
7.345
7.328
7.319
7.184
7.179
7.155
3.322
3.292
3.266
0.820
0.796
0.771
0.000
21.97
54.50
12.70
10.83
ppm


141.820
128.700
128.183
126.142
77.431
76.585
64.298
50.017
48.205
41.853
36.636
17.595
12.143
ppm


OH
C6H5
N
H

17a

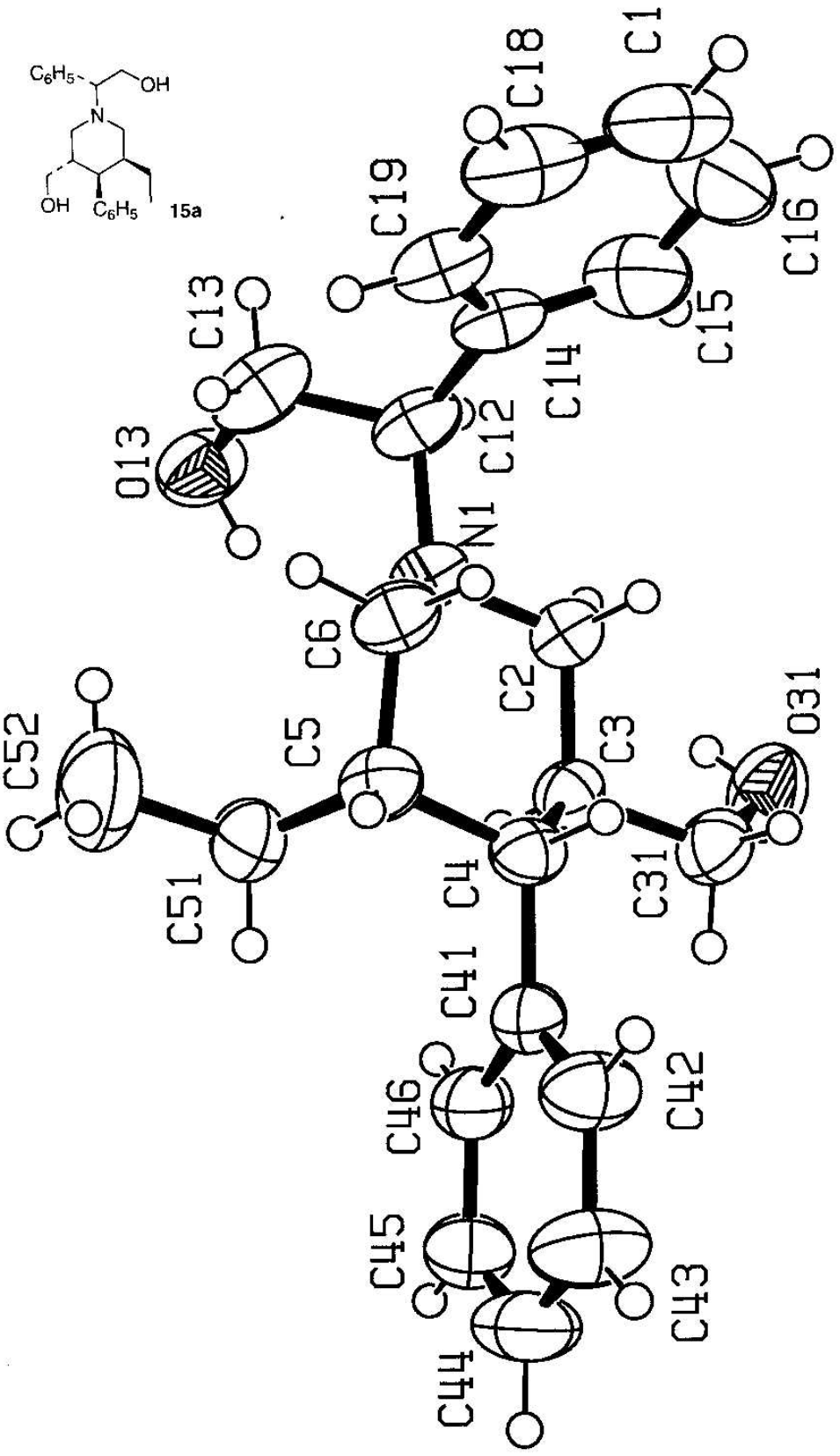

C6H5
OH
N
OH
C6H5
15a
C18
C1
C19
C16
C13
C15
C14
O13
C12
N1
C6
C2
C52
C5
C3
O31
C51
C4
C31
C41
C42
C46
C45
C43
C44

Table 1. Crystal data and structure refinement for 1.

Identification code	jb152
Empirical formula	C22 H29 N O2
Formula weight	339.46
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C2
Unit cell dimensions	a = 16.570 (4)A b = 10.150 (4)A beta = 96.62 (2)deg. c = 11.597 (2)A
Volume	1937.4 A^3
Z, Calculated density	4, 1.164 Mg/m^3
Absorption coefficient	0.073 mm^-1
F(000)	736
Crystal size	0.7 x 0.5 x 0.18 mm
Theta range for data collection	2.36 to 28.42 deg.
Limiting indices	0<=h<=22, -13<=k<=0, -15<=l<=15
Reflections collected / unique	2659 / 2159 [R(int) = 0.0204]
Completeness to theta = 28.42	83.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2159 / 1 / 250
Goodness-of-fit on F^2	0.958
Final R indices [I>2sigma(I)]	R1 = 0.0470, wR2 = 0.1096
R indices (all data)	R1 = 0.0968, wR2 = 0.1220
Extinction coefficient	0.0047(11)
Largest diff. peak and hole	0.133 and -0.147 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 1.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	-2106(1)	-7939(3)	-3136(2)	49(1)
O(13)	-3051(3)	-9067(6)	-4949(4)	71(1)
O(13A)	-4112(3)	-8932(8)	-4561(4)	101(2)
O(31)	-902(4)	-4148(5)	-3057(5)	80(2)
O(31A)	-489(4)	-4375(8)	-3518(7)	66(2)
C(2)	-1758(2)	-6648(3)	-2826(3)	48(1)
C(3)	-855(2)	-6596(3)	-2962(3)	45(1)
C(31)	-499(2)	-5260(3)	-2577(3)	58(1)
C(4)	-405(2)	-7699(4)	-2248(2)	45(1)
C(41)	510(2)	-7734(3)	-2299(3)	48(1)
C(42)	1028(2)	-7943(4)	-1304(3)	65(1)
C(43)	1862(2)	-8017(5)	-1318(4)	84(1)
C(44)	2188(2)	-7880(5)	-2345(4)	80(1)
C(45)	1685(2)	-7660(4)	-3341(3)	69(1)
C(46)	862(2)	-7572(4)	-3319(3)	58(1)
C(5)	-811(2)	-9057(3)	-2522(3)	51(1)
C(51)	-670(2)	-9625(4)	-3694(3)	63(1)
C(52)	-970(3)	-11019(5)	-3913(5)	115(2)
C(6)	-1710(2)	-8940(4)	-2361(3)	54(1)
C(12)	-3006(2)	-7934(4)	-3217(3)	57(1)
C(13)	-3319(2)	-9071(5)	-3996(3)	80(1)
C(14)	-3356(2)	-7898(4)	-2068(3)	59(1)
C(15)	-3573(3)	-6697(5)	-1602(4)	85(1)
C(16)	-3877(3)	-6645(6)	-539(5)	97(2)
C(17)	-3975(2)	-7769(7)	68(4)	92(1)
C(18)	-3773(2)	-8957(7)	-376(4)	87(1)
C(19)	-3467(2)	-9026(4)	-1427(3)	66(1)

Table 3. Bond lengths [A] and angles [deg] for 1.

N(1)-C(2)	1.460(4)
N(1)-C(6)	1.461(4)
N(1)-C(12)	1.484(3)
C(2)-C(3)	1.524(4)
C(3)-C(31)	1.525(4)
C(3)-C(4)	1.534(4)
C(31)-O(31)	1.394(6)
C(31)-O(31A)	1.415(8)
C(4)-C(41)	1.524(4)
C(4)-C(5)	1.550(5)
C(41)-C(42)	1.372(4)
C(41)-C(46)	1.388(4)
C(42)-C(43)	1.386(4)
C(43)-C(44)	1.371(5)
C(44)-C(45)	1.362(5)
C(45)-C(46)	1.370(4)
C(5)-C(51)	1.519(5)
C(5)-C(6)	1.527(4)
C(51)-C(52)	1.511(6)
C(12)-C(14)	1.515(4)
C(12)-C(13)	1.520(5)
C(13)-O(13)	1.237(5)
C(13)-O(13A)	1.406(6)
C(14)-C(19)	1.388(5)
C(14)-C(15)	1.397(6)
C(15)-C(16)	1.385(6)
C(16)-C(17)	1.360(7)
C(17)-C(18)	1.369(7)
C(18)-C(19)	1.375(6)

C(2)-N(1)-C(6)	109.7(2)
C(2)-N(1)-C(12)	112.2(3)
C(6)-N(1)-C(12)	114.8(2)
N(1)-C(2)-C(3)	111.7(2)
C(2)-C(3)-C(31)	110.6(3)
C(2)-C(3)-C(4)	109.9(2)
C(31)-C(3)-C(4)	110.1(3)
O(31)-C(31)-O(31A)	39.2(3)
O(31)-C(31)-C(3)	116.9(3)
O(31A)-C(31)-C(3)	112.2(4)
C(41)-C(4)-C(3)	114.8(3)
C(41)-C(4)-C(5)	112.4(3)
C(3)-C(4)-C(5)	111.5(2)
C(42)-C(41)-C(46)	116.8(3)
C(42)-C(41)-C(4)	120.0(3)
C(46)-C(41)-C(4)	123.3(3)
C(41)-C(42)-C(43)	121.8(3)
C(44)-C(43)-C(42)	119.9(3)
C(45)-C(44)-C(43)	119.3(3)
C(44)-C(45)-C(46)	120.5(3)
C(45)-C(46)-C(41)	121.7(3)
C(51)-C(5)-C(6)	113.1(3)
C(51)-C(5)-C(4)	114.4(2)
C(6)-C(5)-C(4)	108.2(3)
C(52)-C(51)-C(5)	115.1(3)
N(1)-C(6)-C(5)	110.7(3)
N(1)-C(12)-C(14)	115.4(2)

N(1)-C(12)-C(13)	107.9(3)
C(14)-C(12)-C(13)	113.7(3)
O(13)-C(13)-O(13A)	89.8(4)
O(13)-C(13)-C(12)	113.2(4)
O(13A)-C(13)-C(12)	115.9(5)
C(19)-C(14)-C(15)	117.2(3)
C(19)-C(14)-C(12)	122.6(4)
C(15)-C(14)-C(12)	120.2(4)
C(16)-C(15)-C(14)	120.9(4)
C(17)-C(16)-C(15)	120.4(5)
C(16)-C(17)-C(18)	119.7(4)
C(17)-C(18)-C(19)	120.7(5)
C(18)-C(19)-C(14)	121.2(5)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 1. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
N(1)	42(1)	53(2)	51(2)	7(2)	1(1)	-9(1)
O(13)	64(3)	97(4)	52(3)	-5(3)	11(2)	-22(3)
O(13A)	53(3)	176(7)	72(3)	12(4)	-6(2)	-45(4)
O(31)	90(4)	49(3)	95(4)	-2(3)	-9(3)	-1(3)
O(31A)	52(4)	55(5)	89(5)	16(4)	4(4)	-11(3)
C(2)	44(2)	49(2)	50(2)	1(2)	2(1)	-4(2)
C(3)	44(2)	50(2)	41(2)	0(2)	6(1)	-8(2)
C(31)	57(2)	55(2)	61(2)	-2(2)	10(2)	-12(2)
C(4)	41(2)	58(2)	38(2)	1(2)	8(1)	-2(2)
C(41)	45(2)	51(2)	49(2)	-3(2)	9(1)	-4(2)
C(42)	50(2)	90(3)	54(2)	8(2)	1(1)	3(2)
C(43)	47(2)	118(4)	85(3)	16(3)	-1(2)	3(2)
C(44)	44(2)	88(3)	110(3)	7(3)	19(2)	3(2)
C(45)	55(2)	78(3)	78(2)	-5(2)	26(2)	-9(2)
C(46)	49(2)	69(3)	56(2)	-5(2)	9(1)	-4(2)
C(5)	50(2)	47(2)	58(2)	11(2)	7(1)	-2(2)
C(51)	66(2)	49(2)	75(2)	-6(2)	16(2)	-7(2)
C(52)	143(5)	68(3)	140(4)	-29(3)	40(4)	-26(3)
C(6)	47(2)	56(2)	57(2)	12(2)	5(1)	-9(2)
C(12)	39(2)	63(2)	65(2)	12(2)	-8(1)	-9(2)
C(13)	64(2)	92(3)	80(3)	7(3)	-13(2)	-24(2)
C(14)	32(1)	75(3)	68(2)	7(2)	-1(1)	-9(2)
C(15)	64(3)	90(3)	102(3)	9(3)	16(2)	3(2)
C(16)	73(3)	115(4)	108(4)	-16(4)	28(3)	17(3)
C(17)	51(2)	145(5)	81(3)	12(4)	12(2)	-8(3)
C(18)	56(2)	126(4)	79(3)	20(3)	9(2)	-18(3)
C(19)	46(2)	73(3)	78(2)	10(2)	8(2)	-16(2)