Total synthesis of varitriol, varioxirane, and enantiomer of the proposed biosynthetic precursor

Gangarajula Sudhakar,* and Jakka Raghavaiah

Division of CPC (Organic Chemistry-II), CSIR-Indian Institute of Chemical Technology, Hyderabad-500007, India

Email: *gsudhakar@iict.res.in*

Supporting Information

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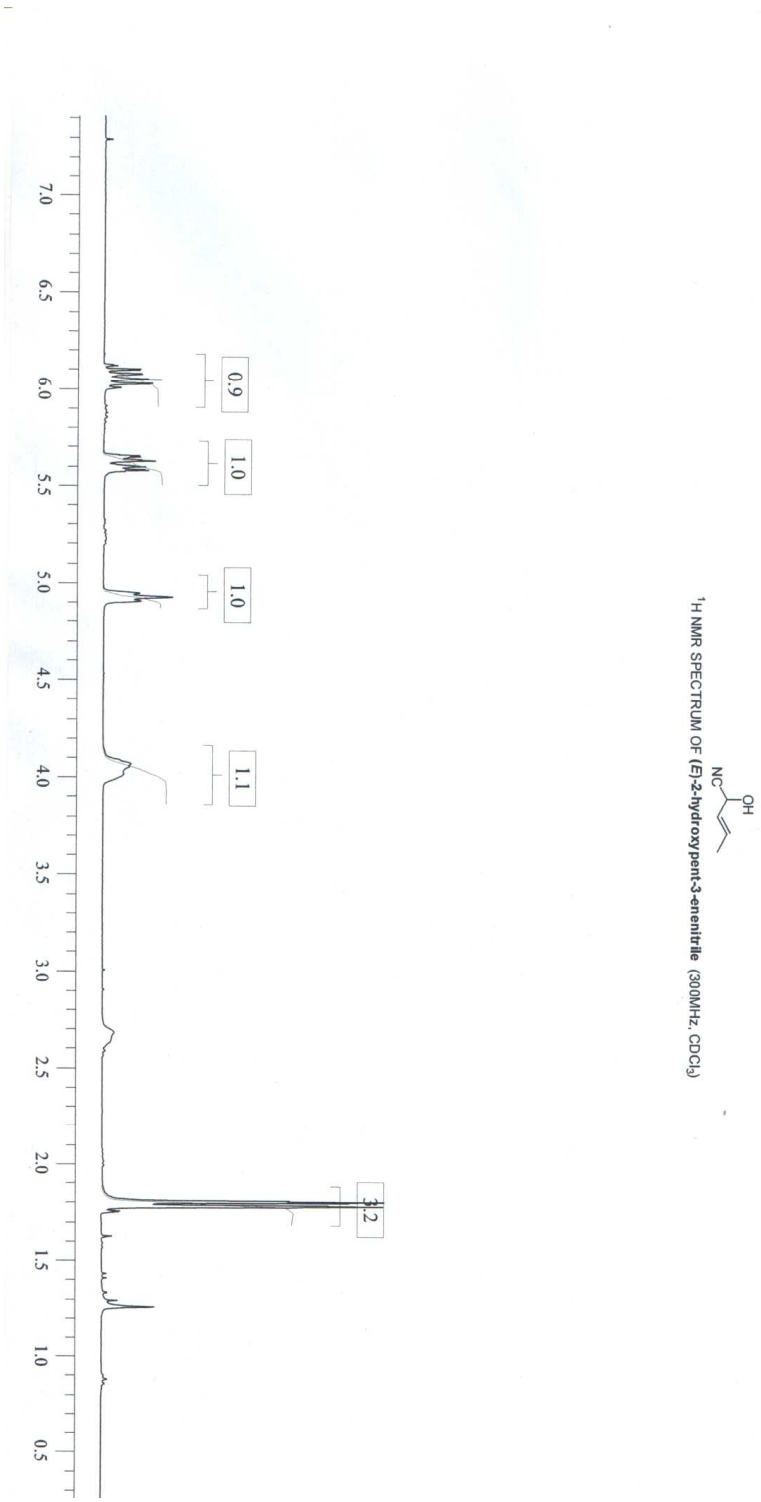
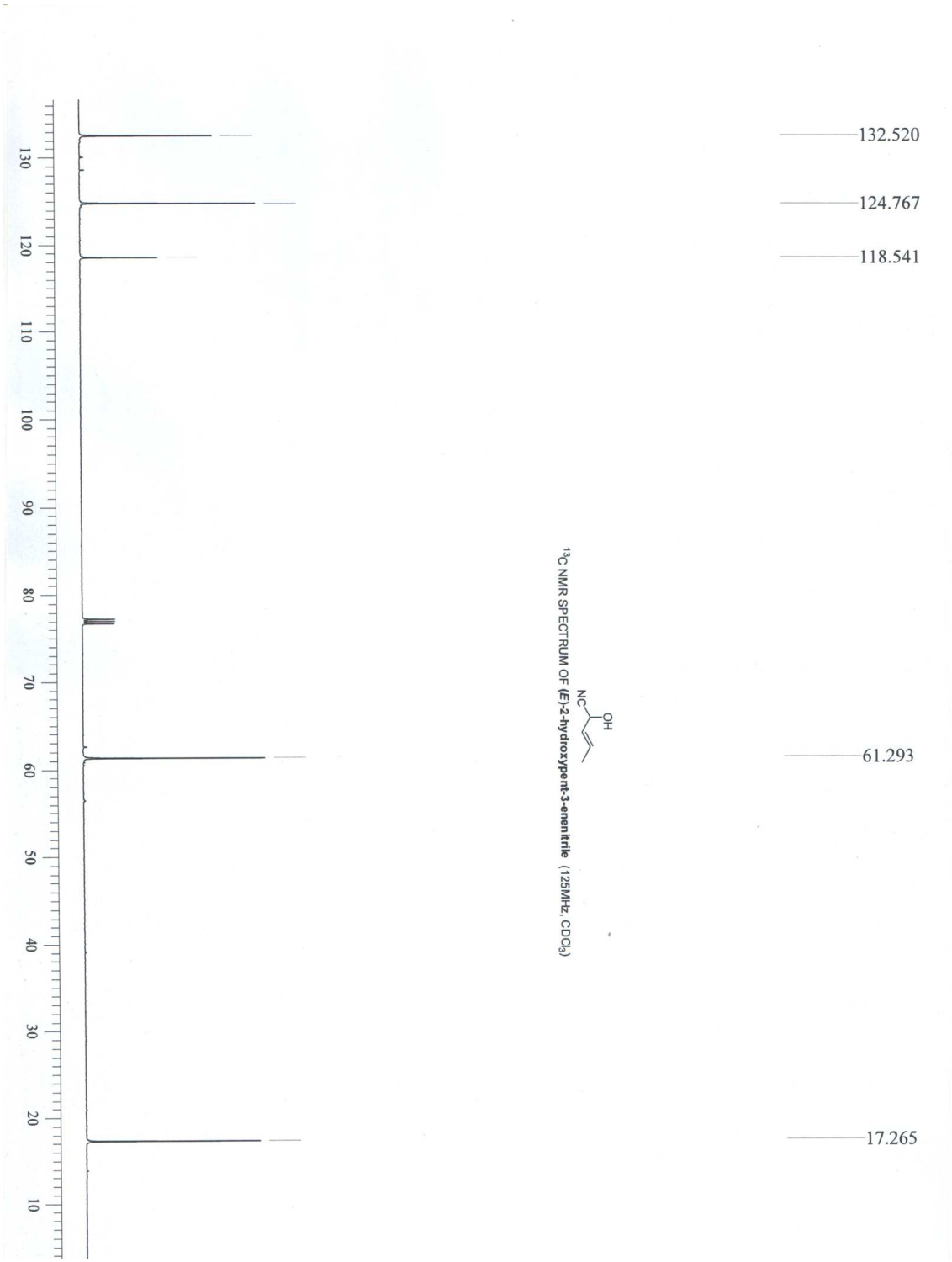
General Experimental Methods:

Anhydrous solvents were dried and distilled by standard methods prior to use. Commercially available reagents were used without further purification unless otherwise specified. All the reactions were performed under an atmosphere of nitrogen or argon in oven-dried glassware under magnetic stirring. Column chromatography was carried out using silica gel (60-120 or 100-200 or 230-400 mesh) and the column was eluted with ethyl acetate- petroleum ether or Ethyl acetate. Analytical thin layer chromatography (TLC) was performed on precoated silica gel-60 F254 (0.5 mm) glass plates. Visualization of the spots on TLC plates was achieved either by UV light or by staining the plates in methanolic anisaldehyde-sulphuric acid-acetic acid or in methanol-phosphomolybdic acid-sulphuric acid solution and charring on hot plate.

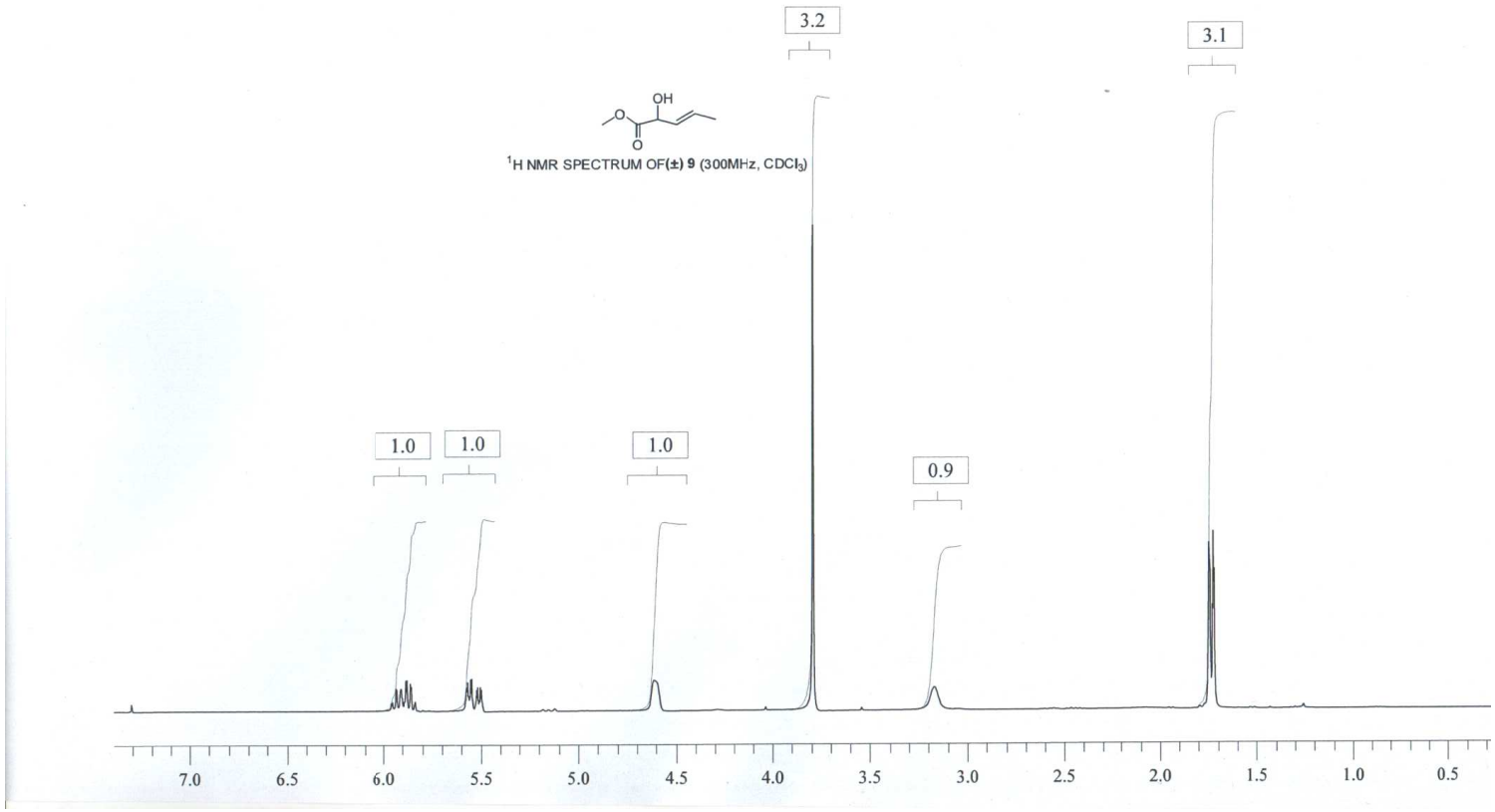
^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ solvent on 500 MHz, 400 MHz, 300 MHz and 75 MHz,100MHz, 125 MHz spectrometer, respectively at ambient temperature. Chemical shifts are reported as δ values relative to internal $CHCl_3$ δ 7.26 or TMS δ 0.0 or Acetone-d_6 δ 2.05for ^{1}H NMR and $CHCl_3$ δ 77.0 or Acetone-d_6 δ 30.83 for ^{13}C NMR. ^{1}H NMR data is recorded as follows: chemical shift [multiplicity, coupling constant(s) *J* (Hz), relative integral] where multiplicity is defined as: s = singlet; d = doublet; t = triplet; q = quartet; dd = doublet of doublet; ddd = doublet of double of doublet; dt = doublet of triplet; m = multiplet; brs = broad singlet. Optical rotation values were measured on high sensitive polarimeter using a 2 mL cell with a 10 mm path length. Mass spectrometer for ESI and are given in mass units (m/z). High resolution mass spectra (HRMS) [ESI^{+}] were obtained using either a TOF or a double focusing spectrometer.

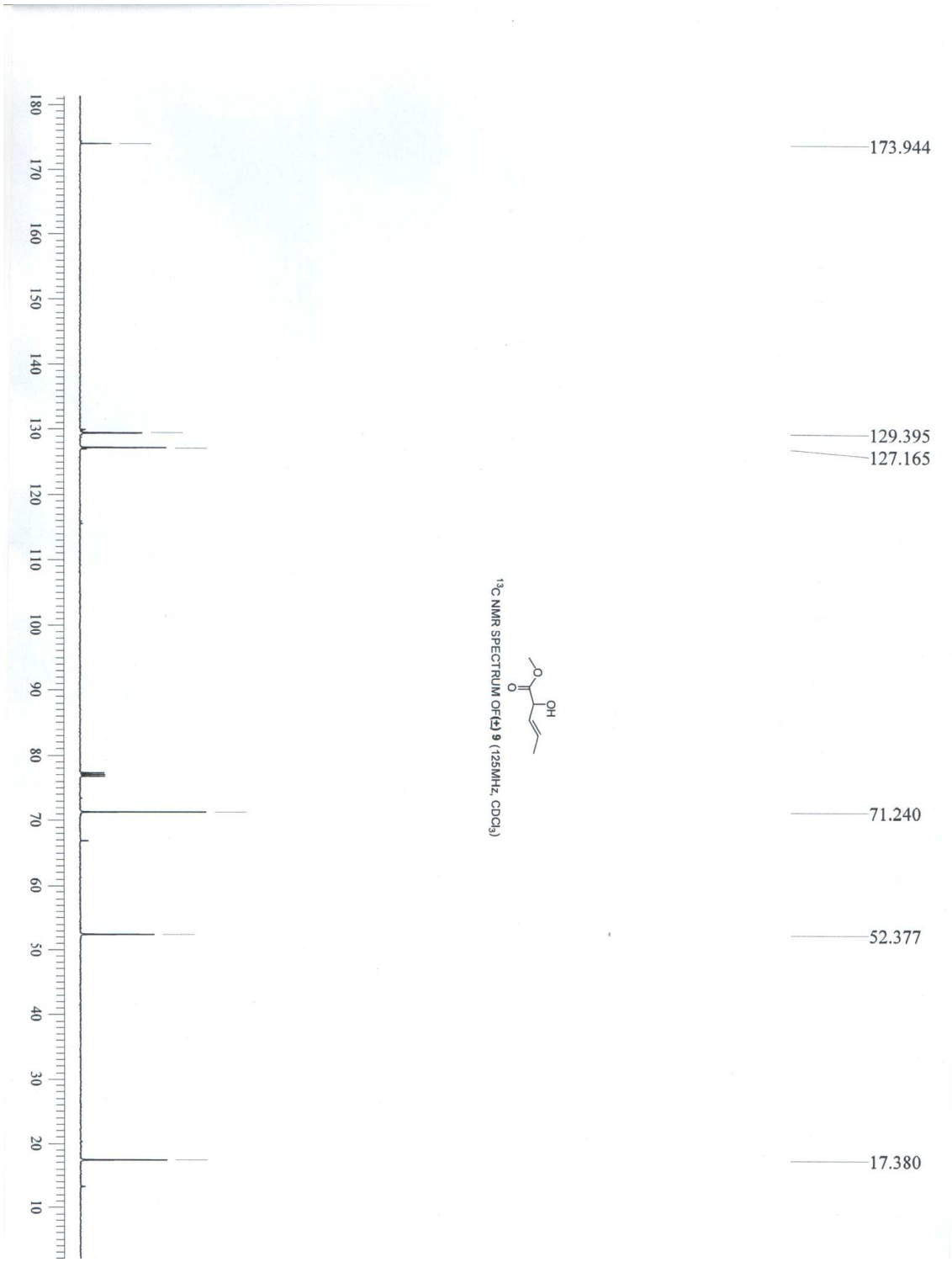
Copies of ^{1}H and ^{13}C NMR Spectra of compounds





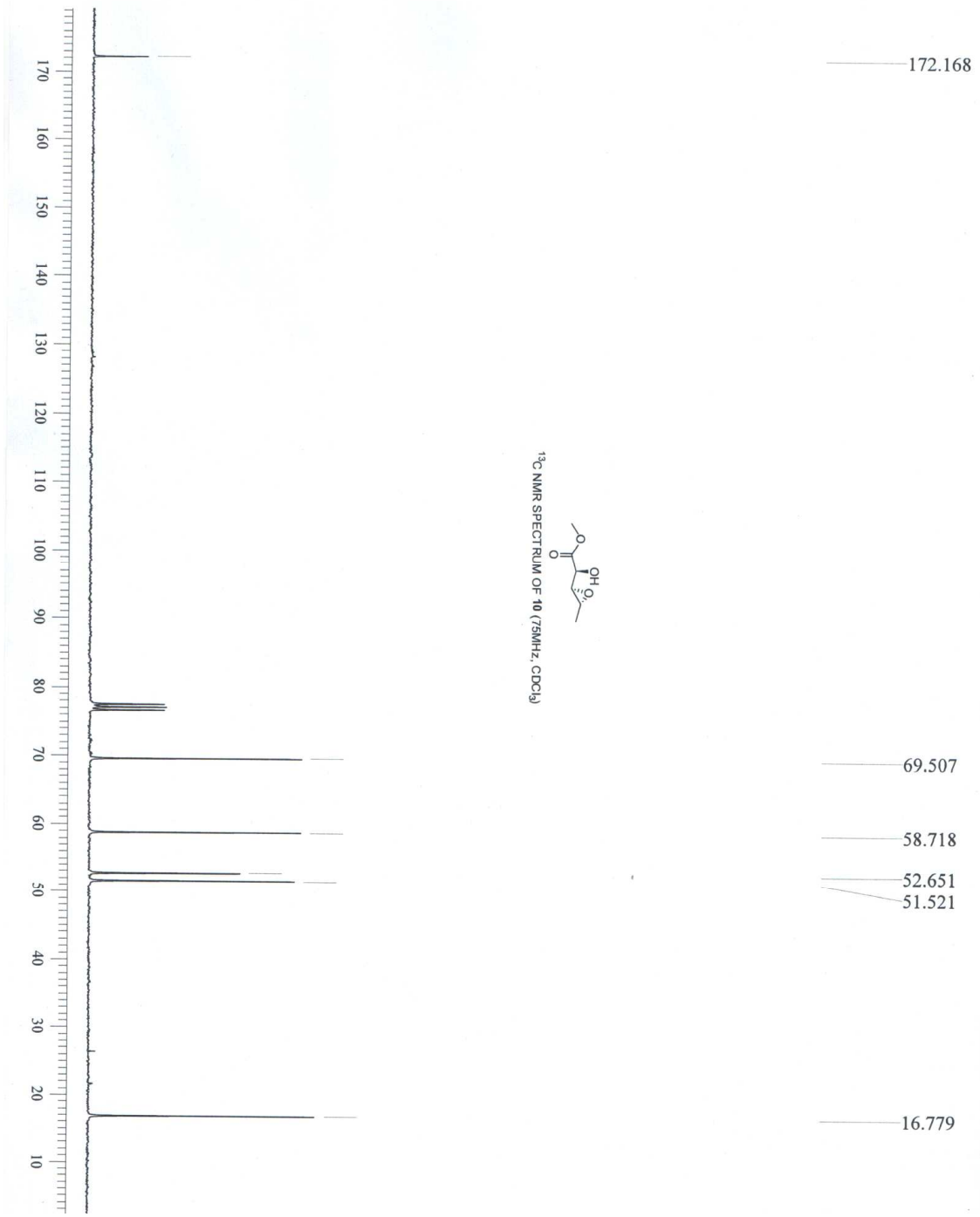
^{13}C NMR SPECTRUM OF **(*E*)-2-hydroxypent-3-enenitrile** (125MHz, $CDCl_3$)


3.2
3.1
OH
O
O
^{1}H NMR SPECTRUM OF(±) 9 (300MHz, $CDCl_3$)
1.0
1.0
1.0
0.9
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5



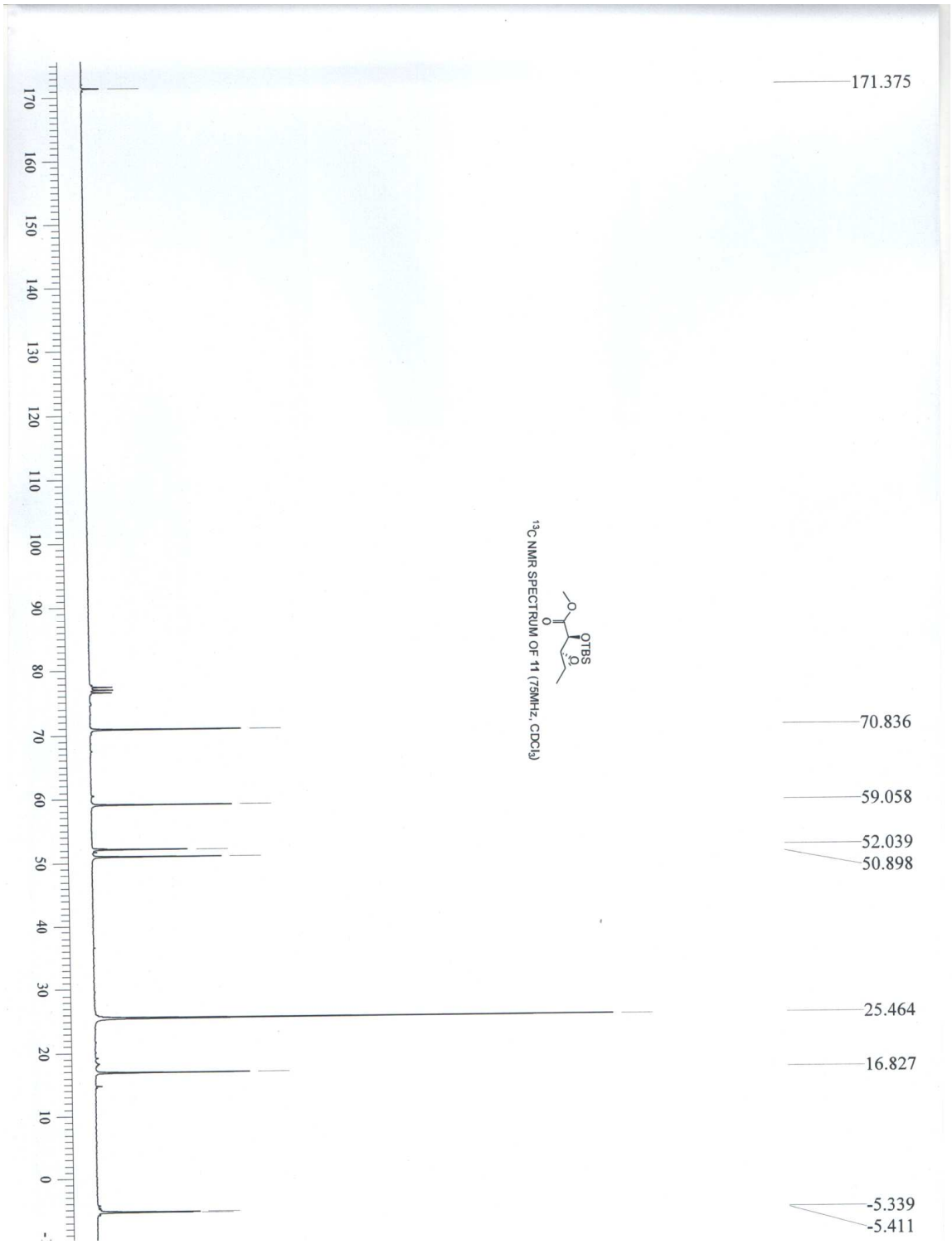
^{13}C NMR SPECTRUM OF(±) **9** (125MHz, $CDCl_3$)

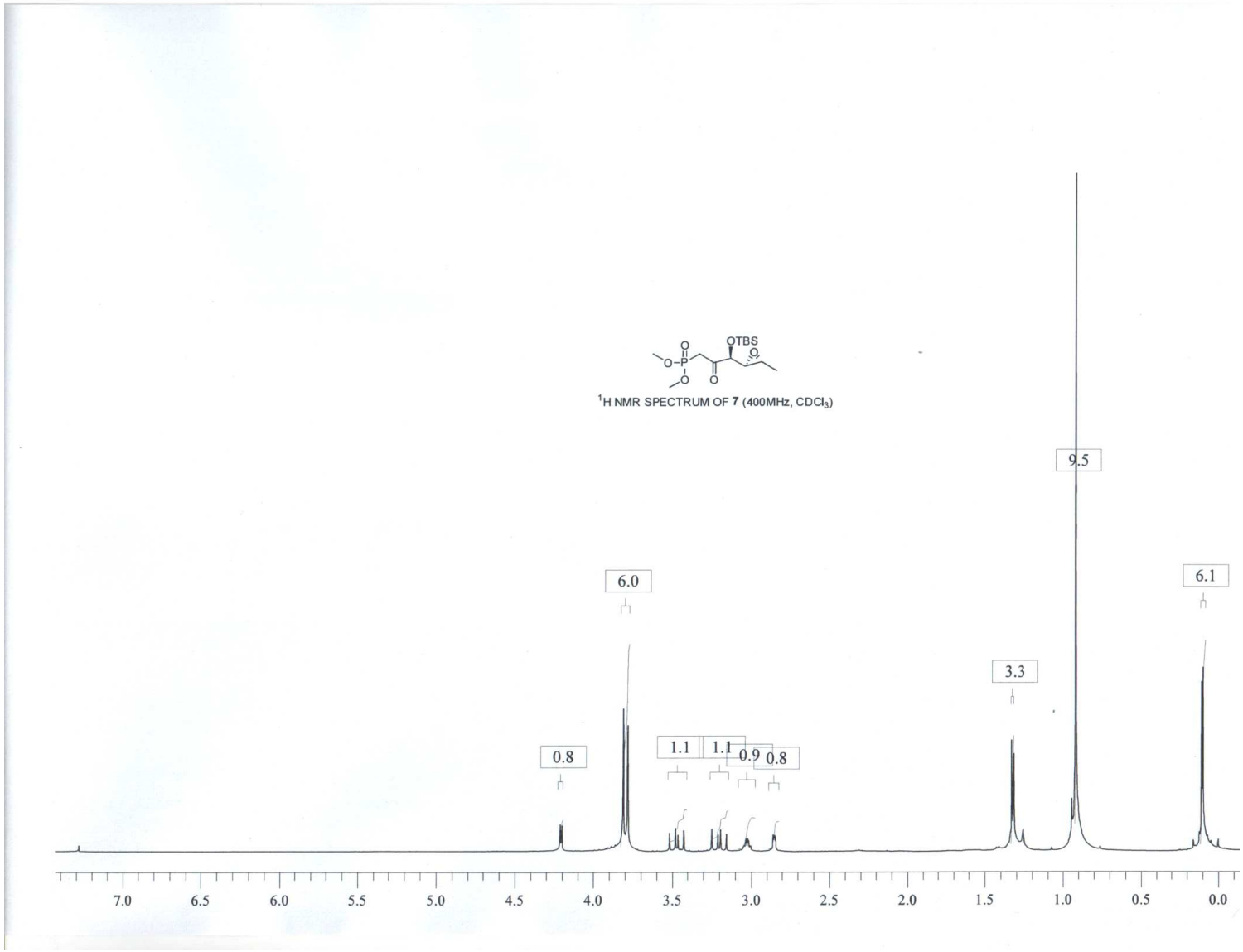
^{1}H NMR SPECTRUM OF **10** (300MHz, $CDCl_3$)

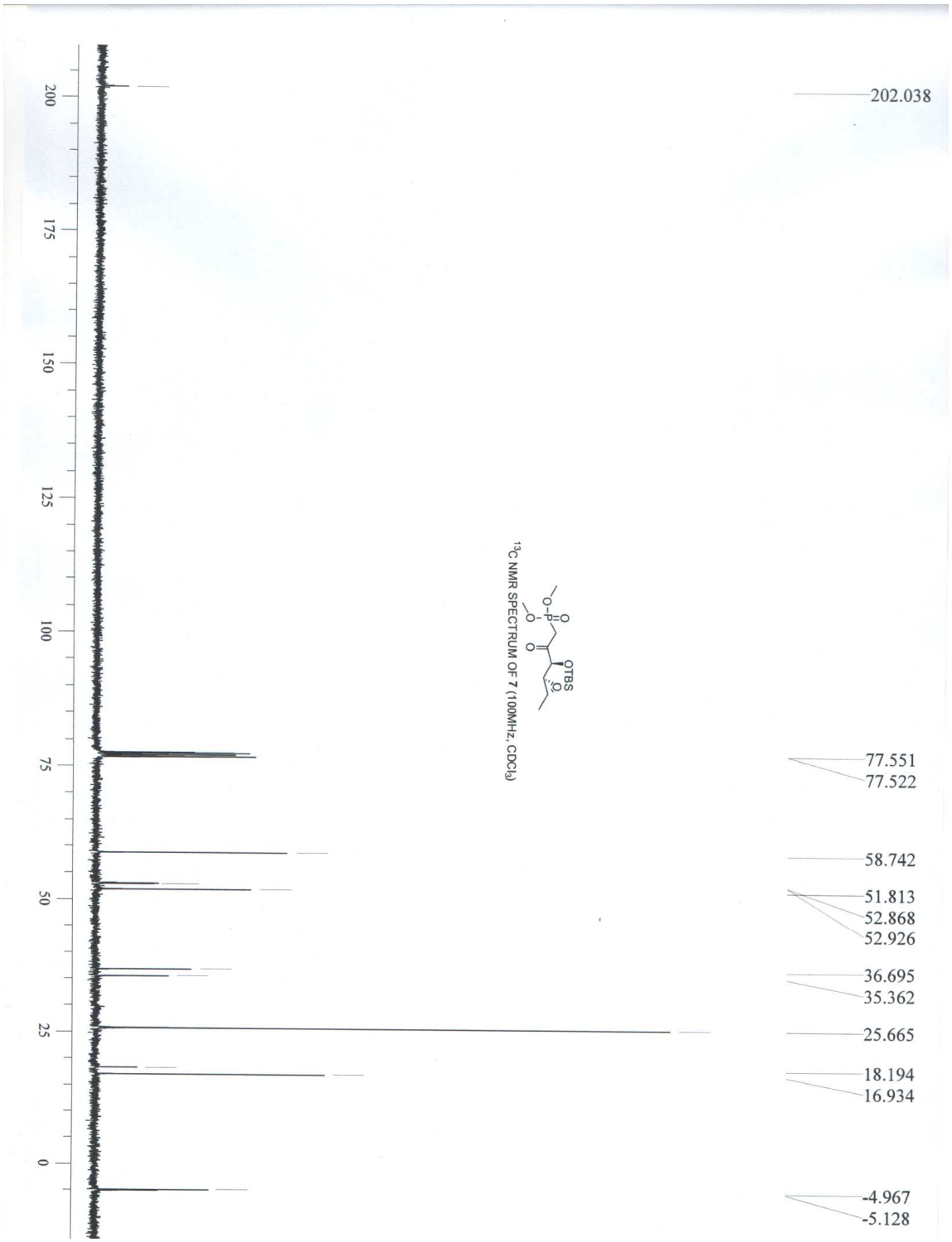


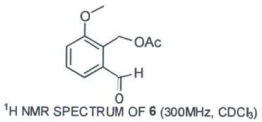
^{13}C NMR SPECTRUM OF **10** (75MHz, $CDCl_3$)

OTBS
O
O
O
^{1}H NMR SPECTRUM OF 11 (300MHz, CDCl$_3$)
1.0
3.0
0.9
1.1
3.2
9.1
6.1
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

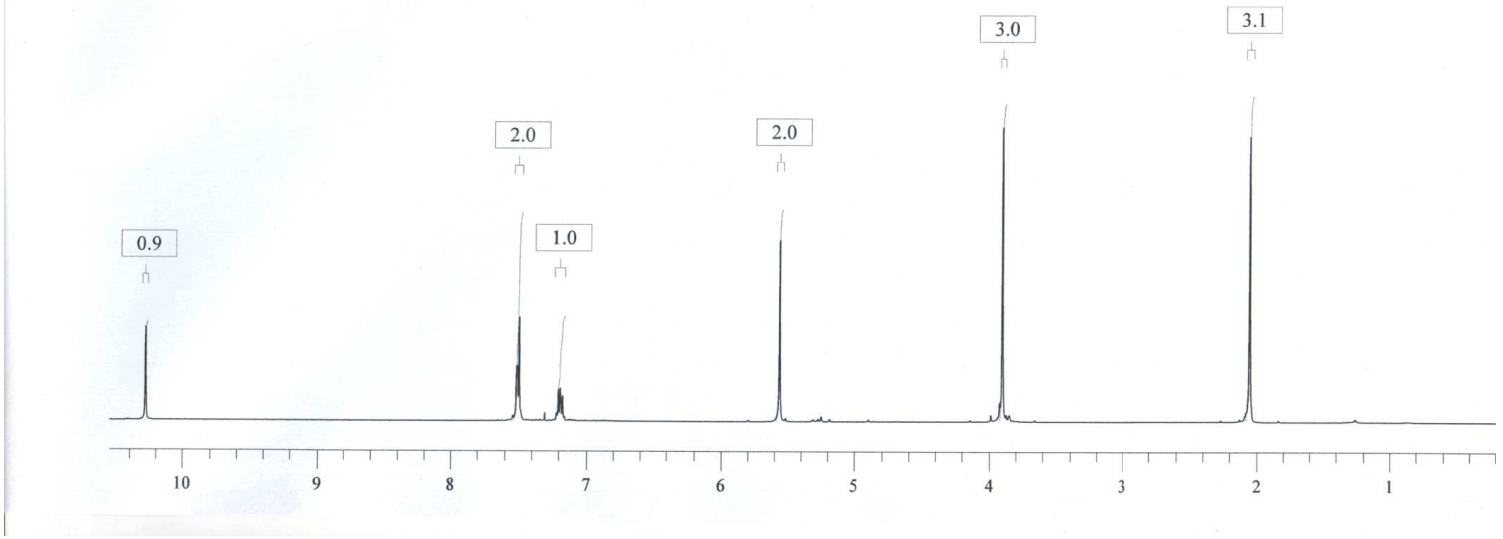

171.375
70.836
59.058
52.039
50.898
25.464
16.827
-5.339
-5.411
OTBS
^{13}C NMR SPECTRUM OF 11 (75MHz, CDCl$_3$)

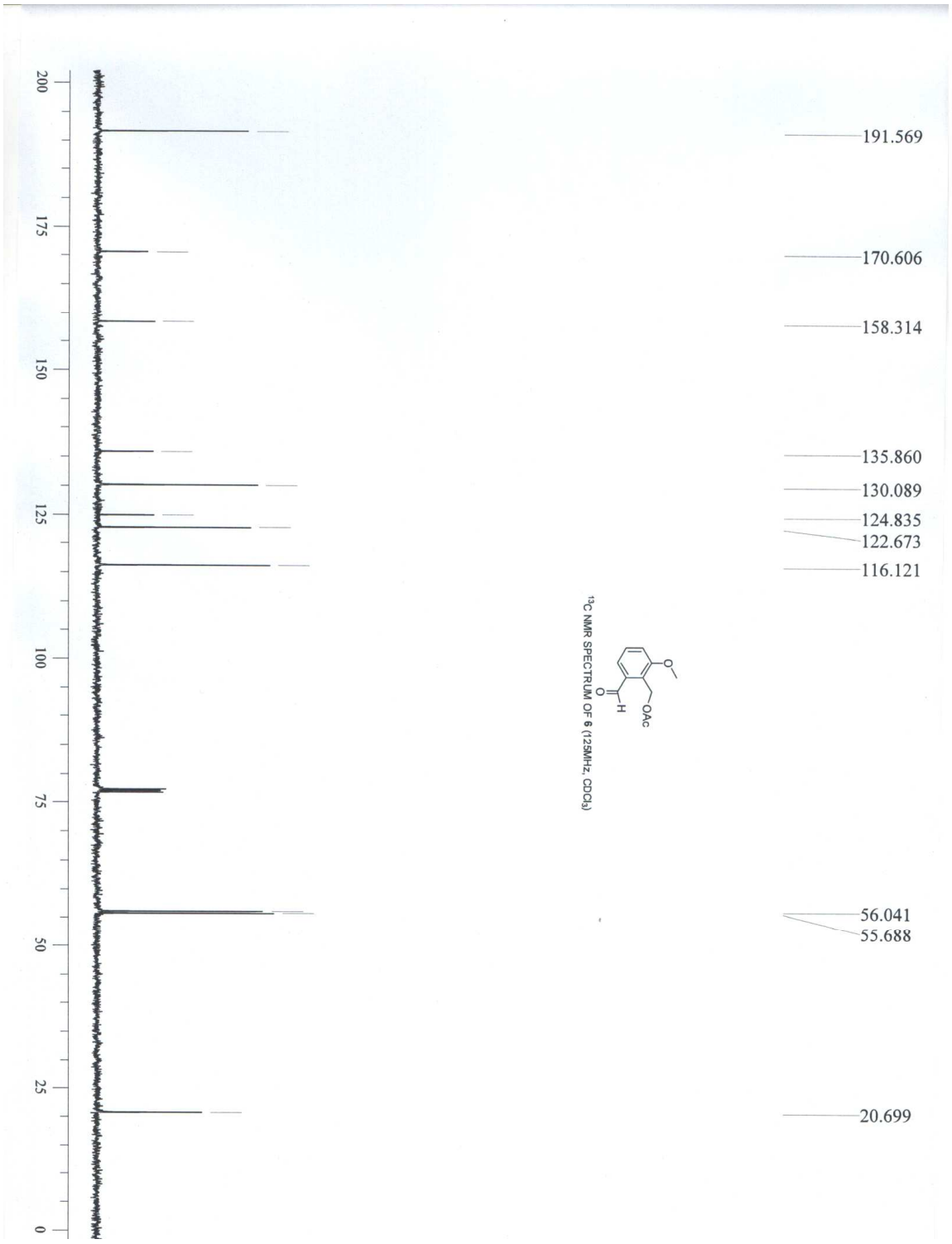

OTBS
O
O
O
O
O
O
^{1}H NMR SPECTRUM OF 7 (400MHz, CDCl$_3$)
9.5
6.0
6.1
3.3
0.8
1.1
1.1
0.9
0.8
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

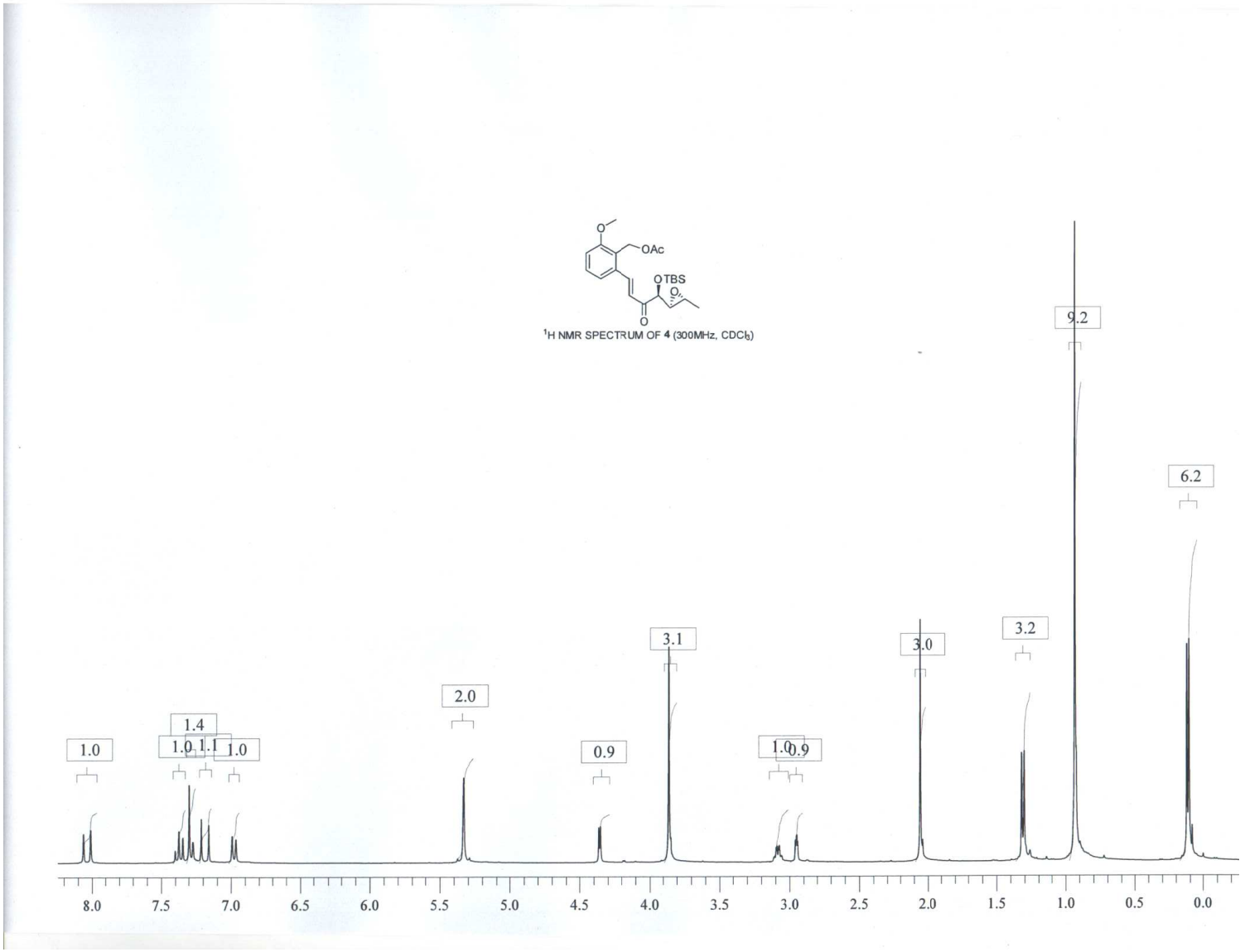

^{13}C NMR SPECTRUM OF 7 (100MHz, $CDCl_3$)
OTBS
202.038
77.551
77.522
58.742
51.813
52.868
52.926
36.695
35.362
25.665
18.194
16.934
-4.967
-5.128
200
175
150
125
100
75
50
25
0

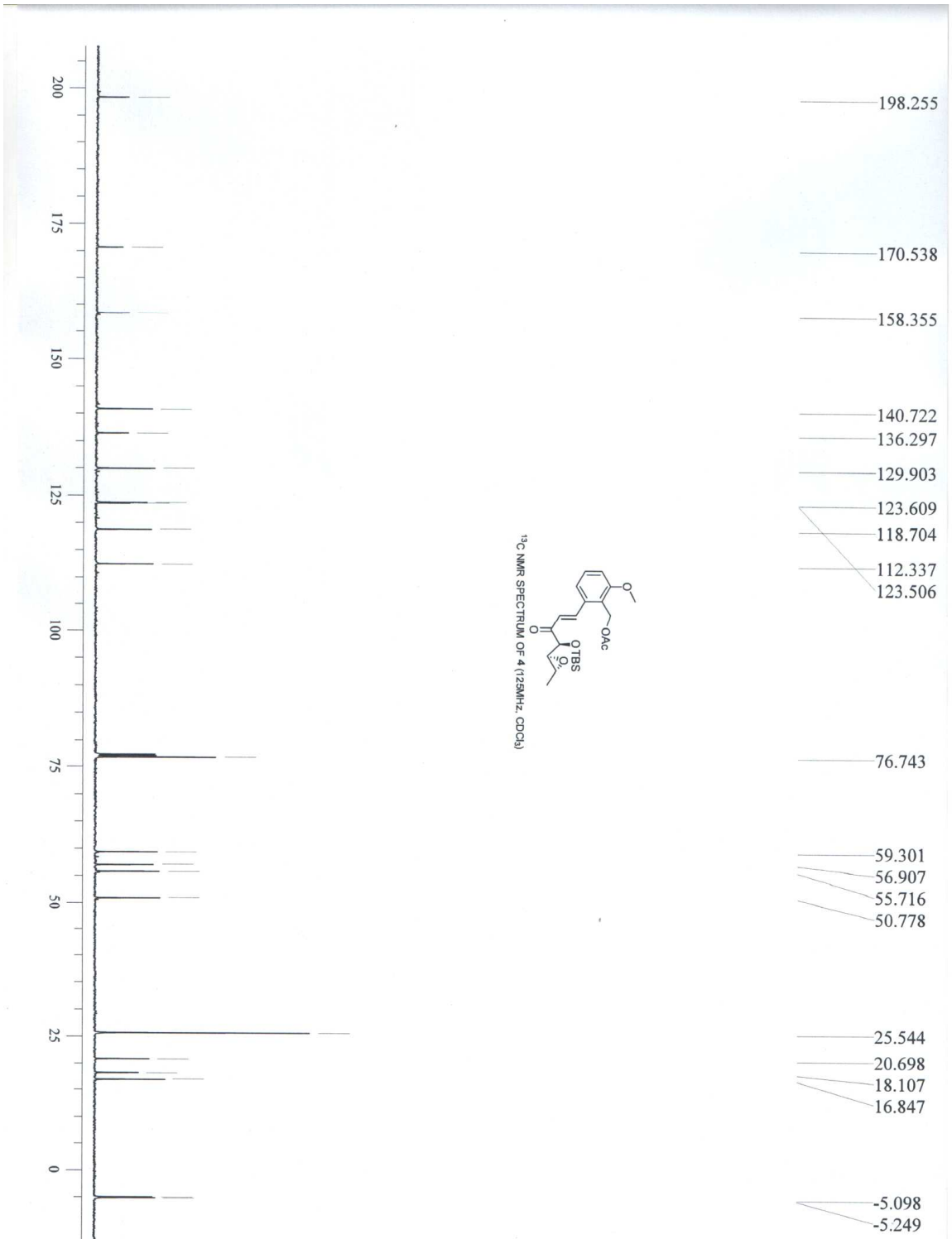


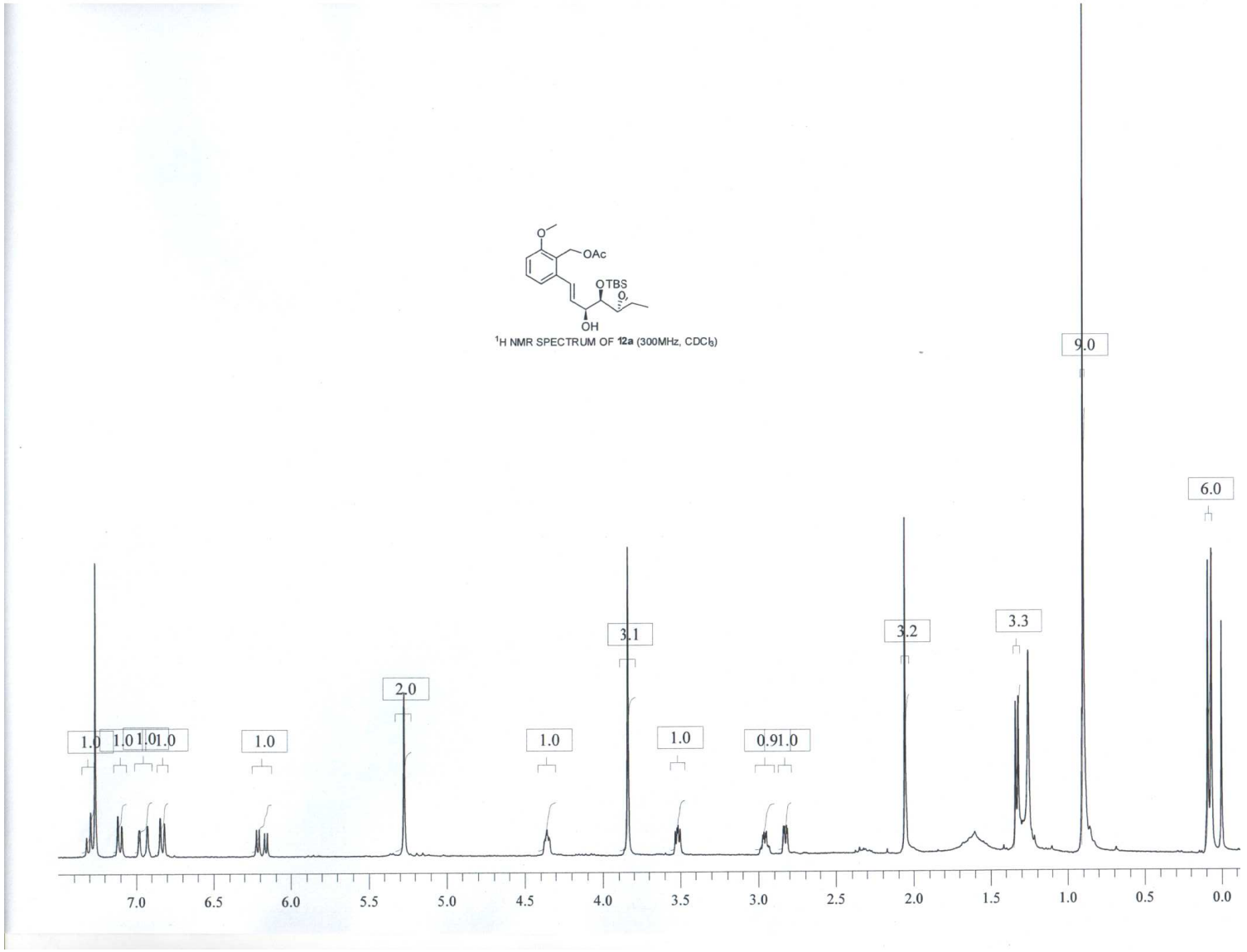
^{1}H NMR SPECTRUM OF **6** (300MHz, $CDCl_3$)



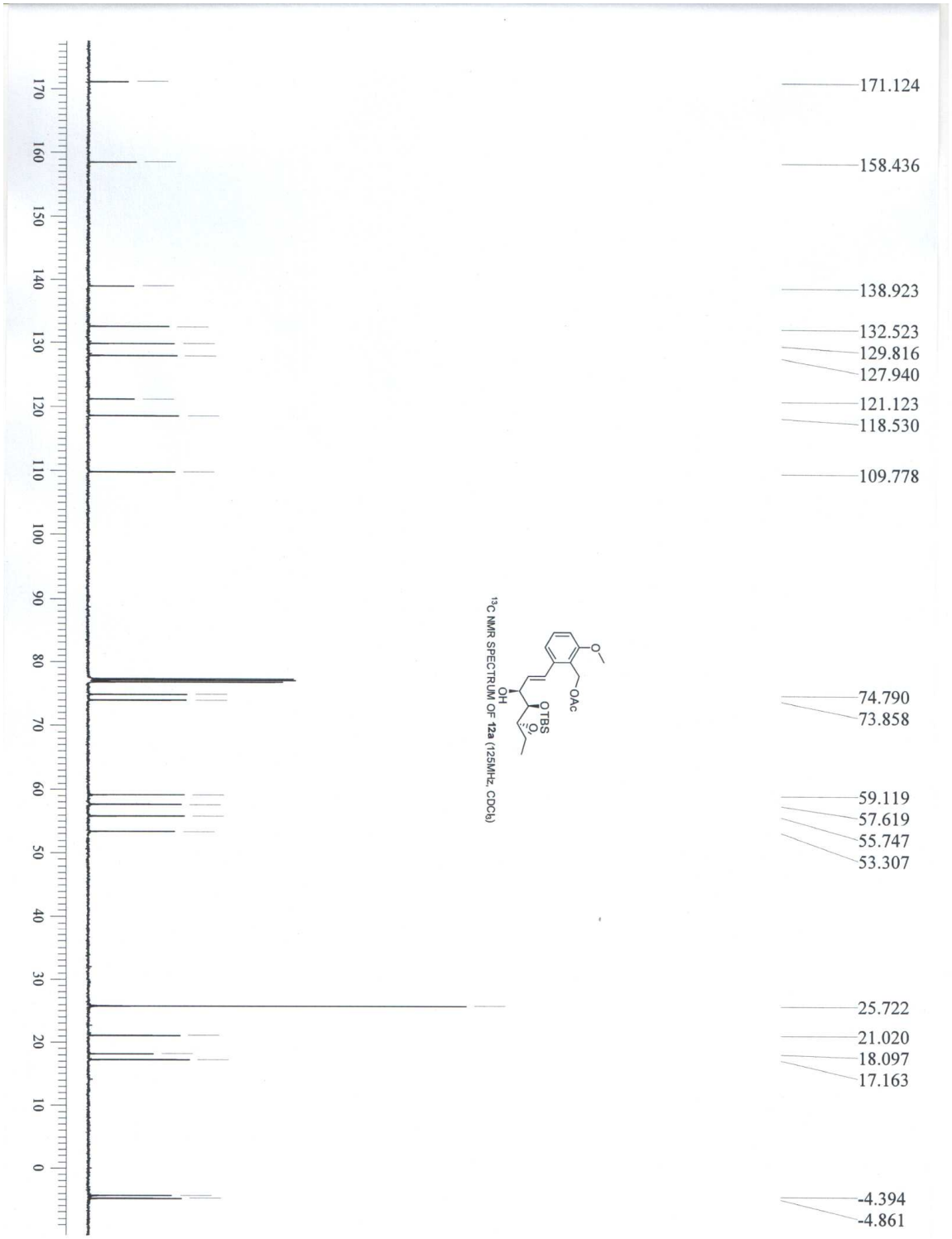

191.569
170.606
158.314
135.860
130.089
124.835
122.673
116.121
56.041
55.688
20.699
200
175
150
125
100
75
50
25
0
OAc
O
H
O
^{13}C NMR SPECTRUM OF 6 (125MHz, CDCl$_3$)

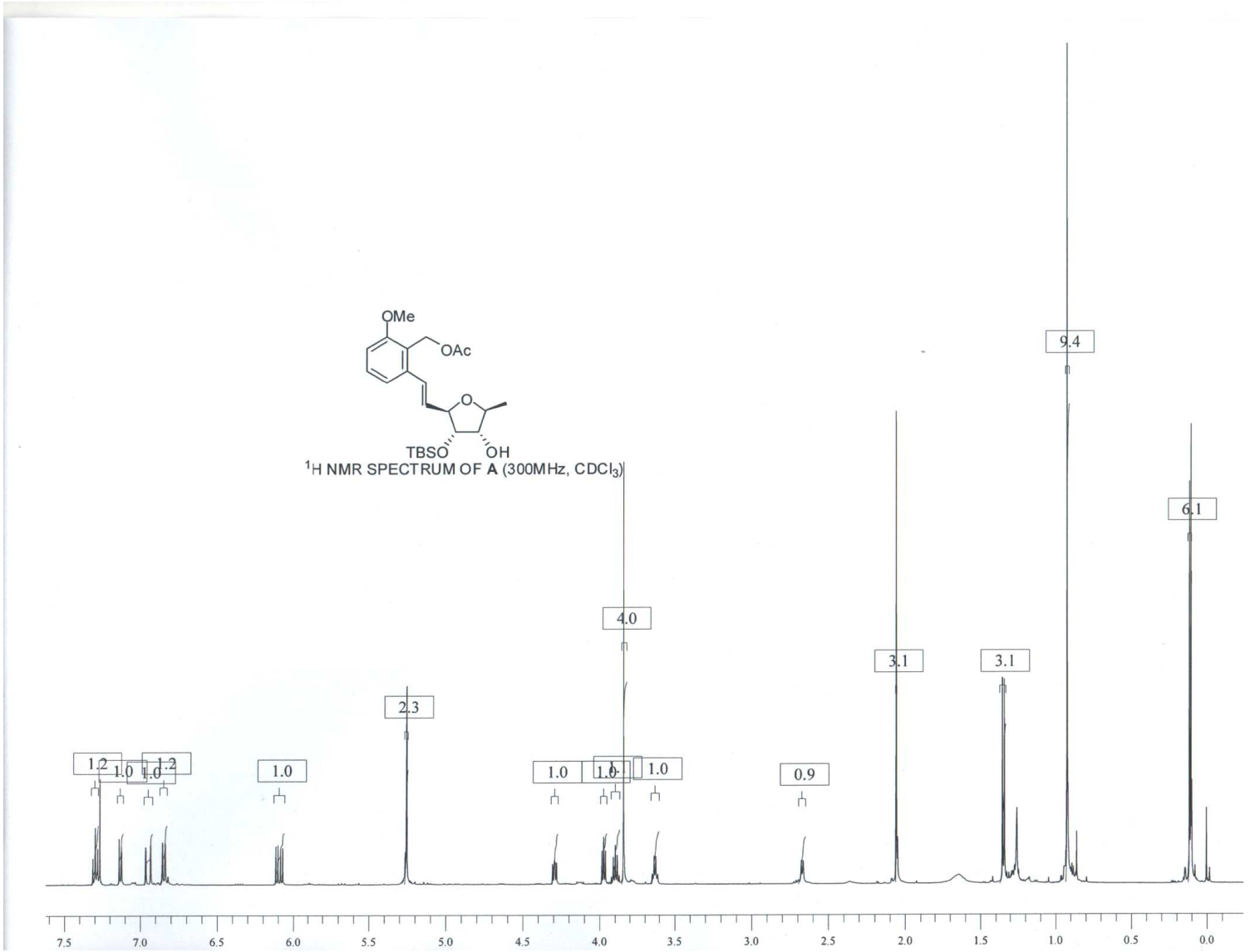

OAc
OTBS
O
O
O
^{1}H NMR SPECTRUM OF 4 (300MHz, CDCl$_3$)
1.0
1.4
1.0
1.1
1.0
2.0
0.9
3.1
1.0
0.9
3.0
3.2
9.2
6.2
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

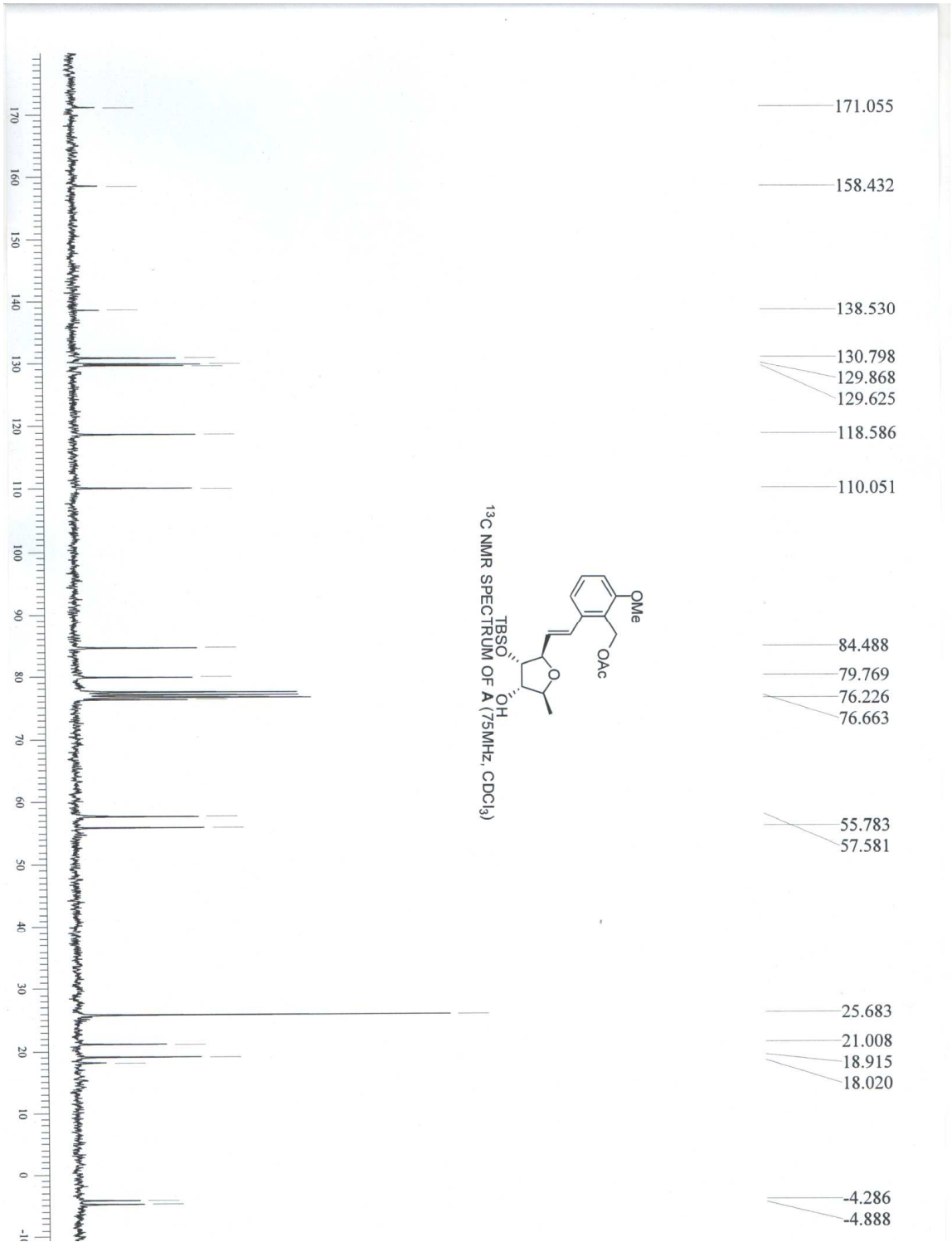

198.255
170.538
158.355
140.722
136.297
129.903
123.609
118.704
112.337
123.506
76.743
59.301
56.907
55.716
50.778
25.544
20.698
18.107
16.847
-5.098
-5.249
200
175
150
125
100
75
50
25
0
OAc
OTBS
O
O
^{13}C NMR SPECTRUM OF 4 (125MHz, CDCl$_3$)

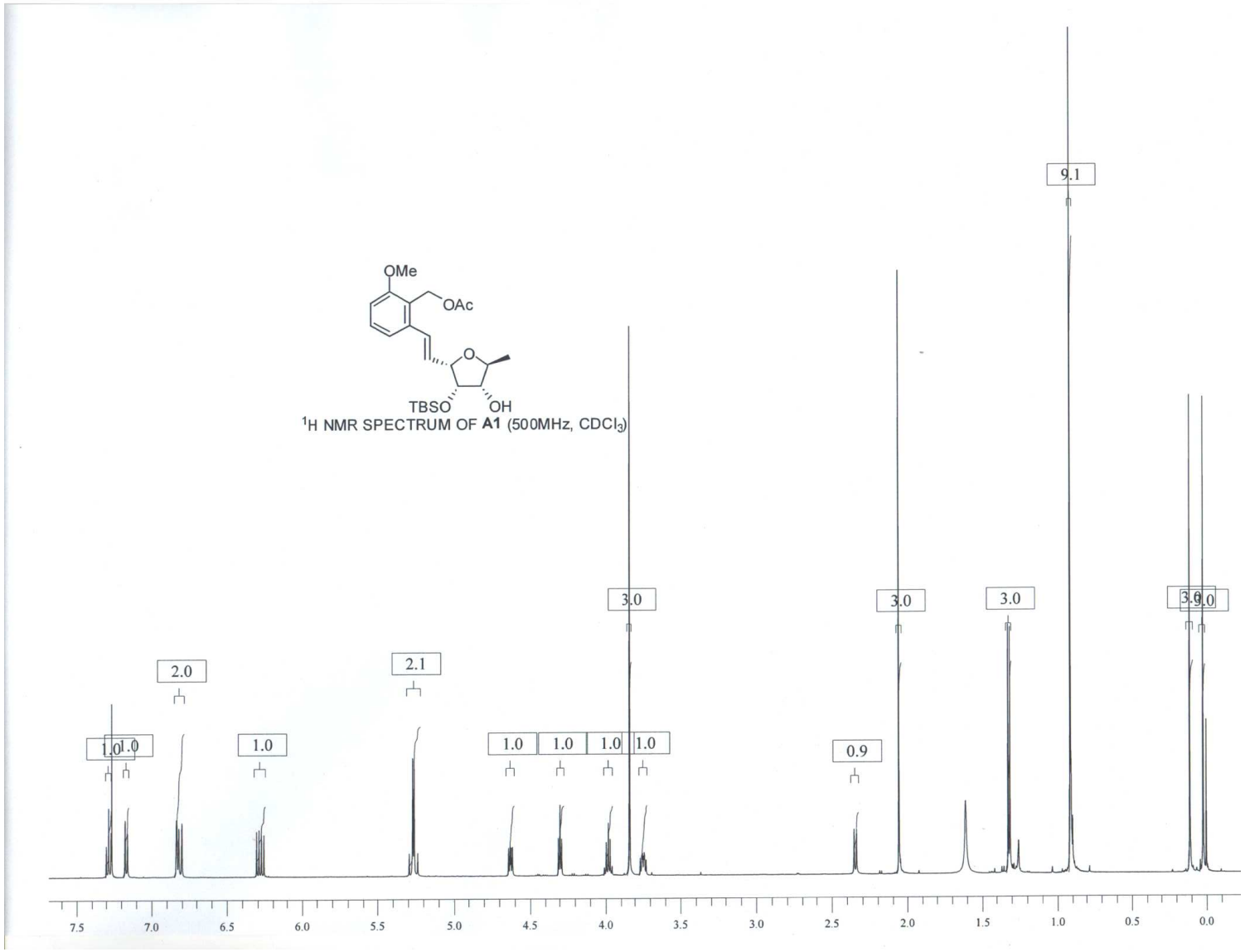


^{1}H NMR SPECTRUM OF **12a** (300MHz, $CDCl_3$)

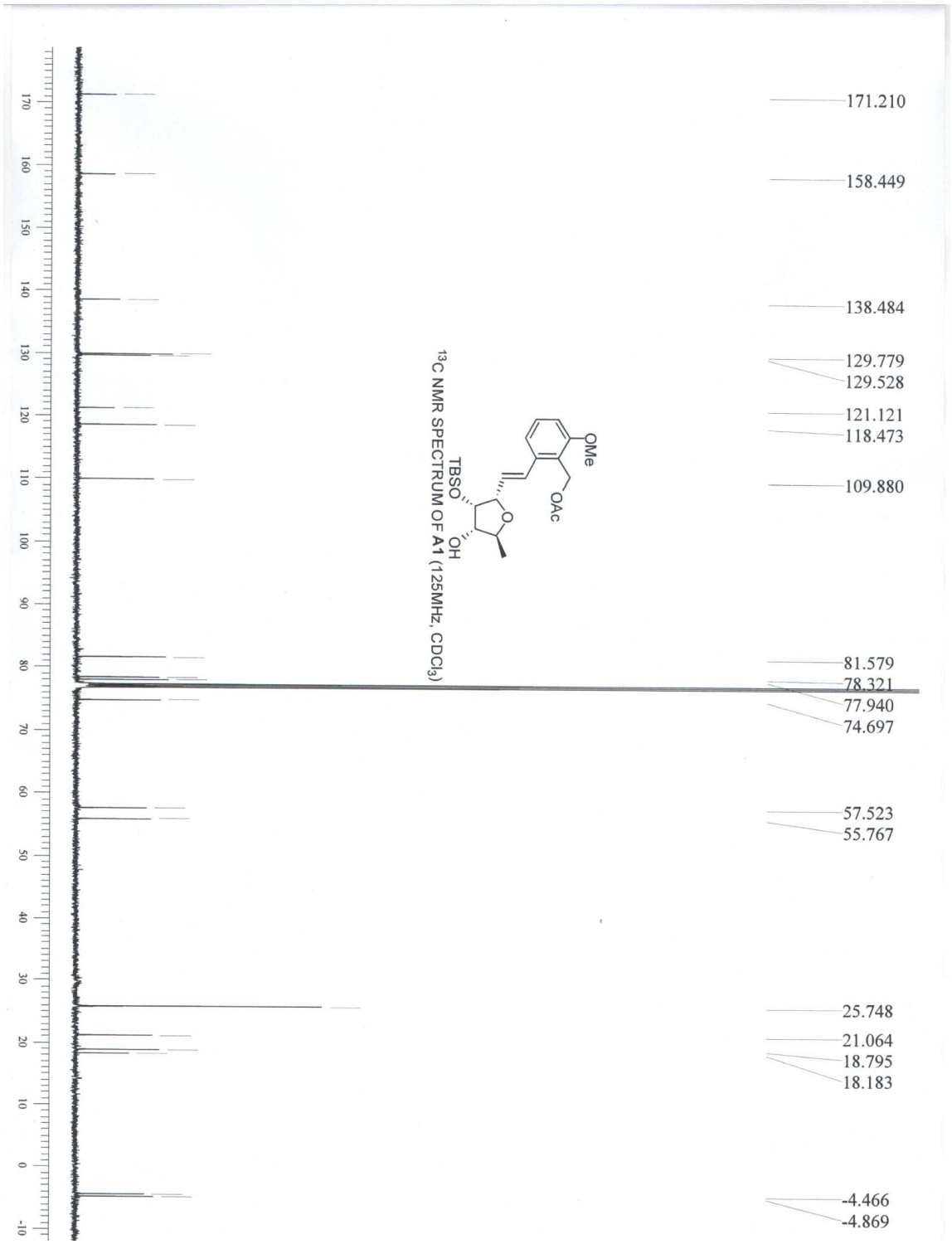

171.124
158.436
138.923
132.523
129.816
127.940
121.123
118.530
109.778
74.790
73.858
59.119
57.619
55.747
53.307
25.722
21.020
18.097
17.163
-4.394
-4.861
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
OH
OTBS
O
OAc
O
13C NMR SPECTRUM OF 12a (125MHz, CDCl3)

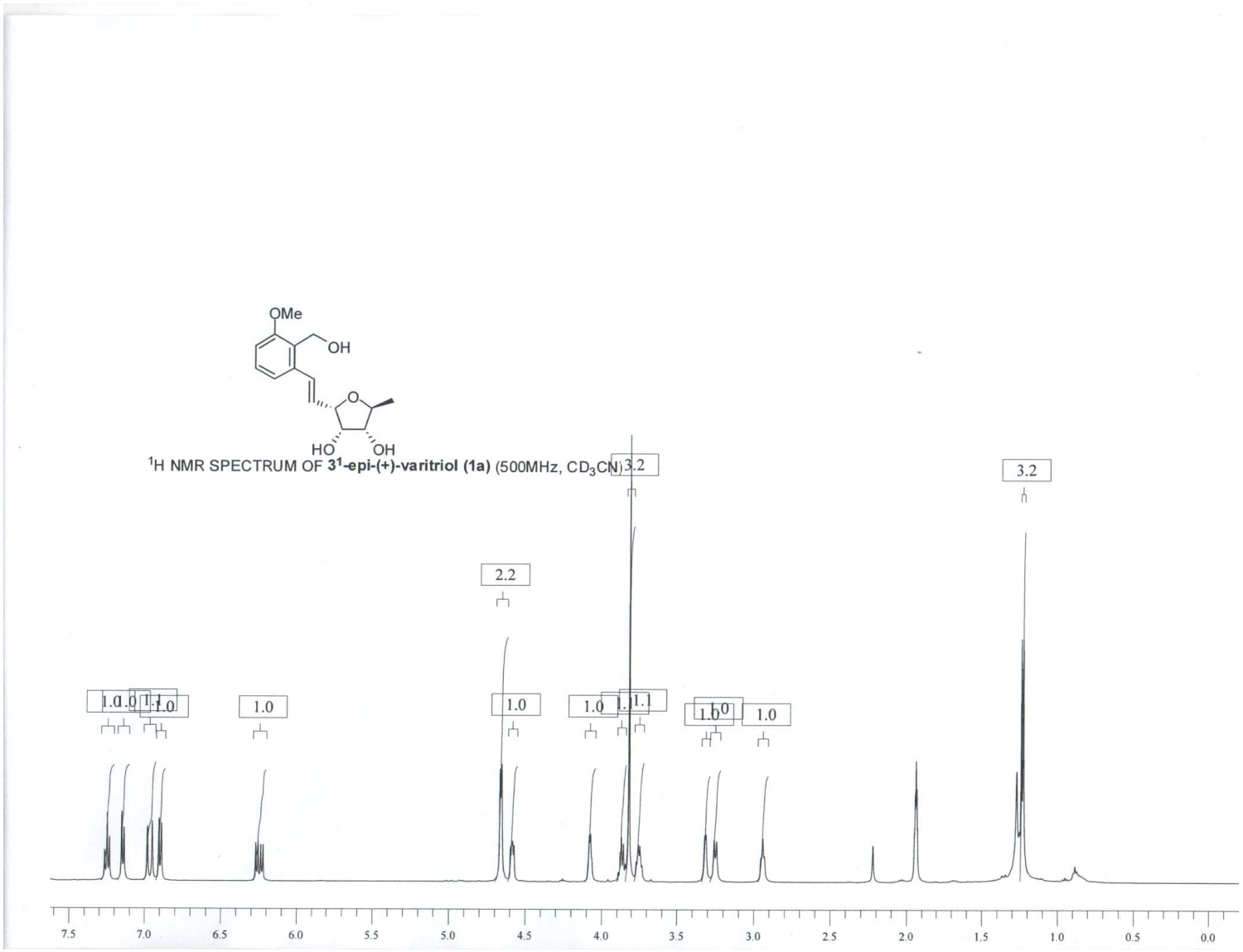

OMe
OAc
O
TBSO
OH
^{1}H NMR SPECTRUM OF **A** (300MHz, $CDCl_3$)
1.2
1.0
1.0
1.2
1.0
2.3
1.0
1.0
1.0
4.0
1.0
0.9
3.1
3.1
9.4
6.1
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


171.055
158.432
138.530
130.798
129.868
129.625
118.586
110.051
84.488
79.769
76.226
76.663
55.783
57.581
25.683
21.008
18.915
18.020
-4.286
-4.888
OMe
OAc
TBSO
OH
O
13C NMR SPECTRUM OF A (75MHz, CDCl3)

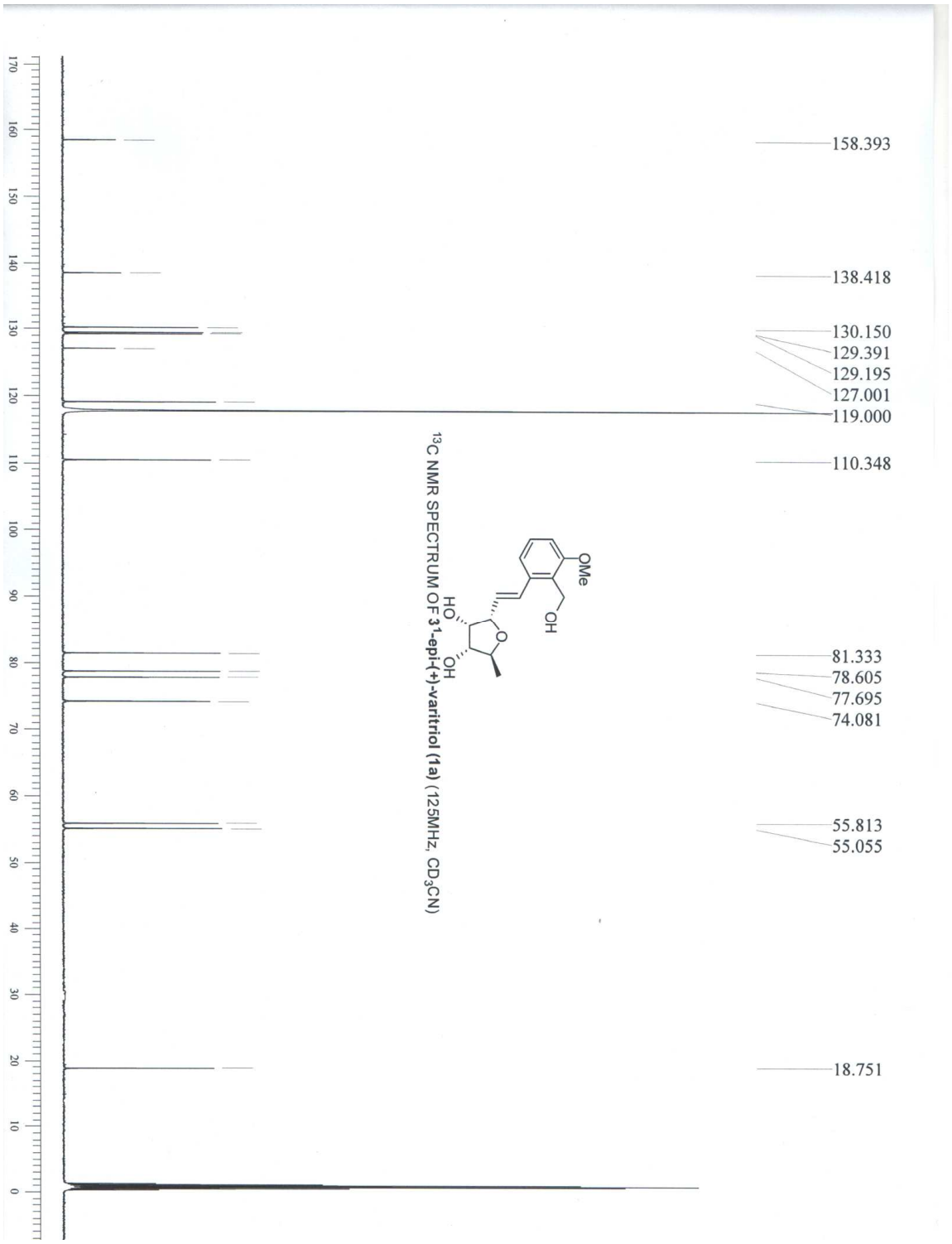


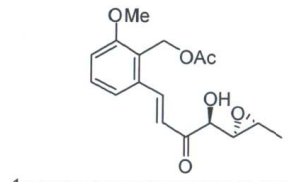
^{1}H NMR SPECTRUM OF **A1** (500MHz, $CDCl_3$)


171.210
158.449
138.484
129.779
129.528
121.121
118.473
109.880
81.579
78.321
77.940
74.697
57.523
55.767
25.748
21.064
18.795
18.183
-4.466
-4.869
OMe
OAc
TBSO
OH
^{13}C NMR SPECTRUM OF A1 (125MHz, CDCl$_3$)

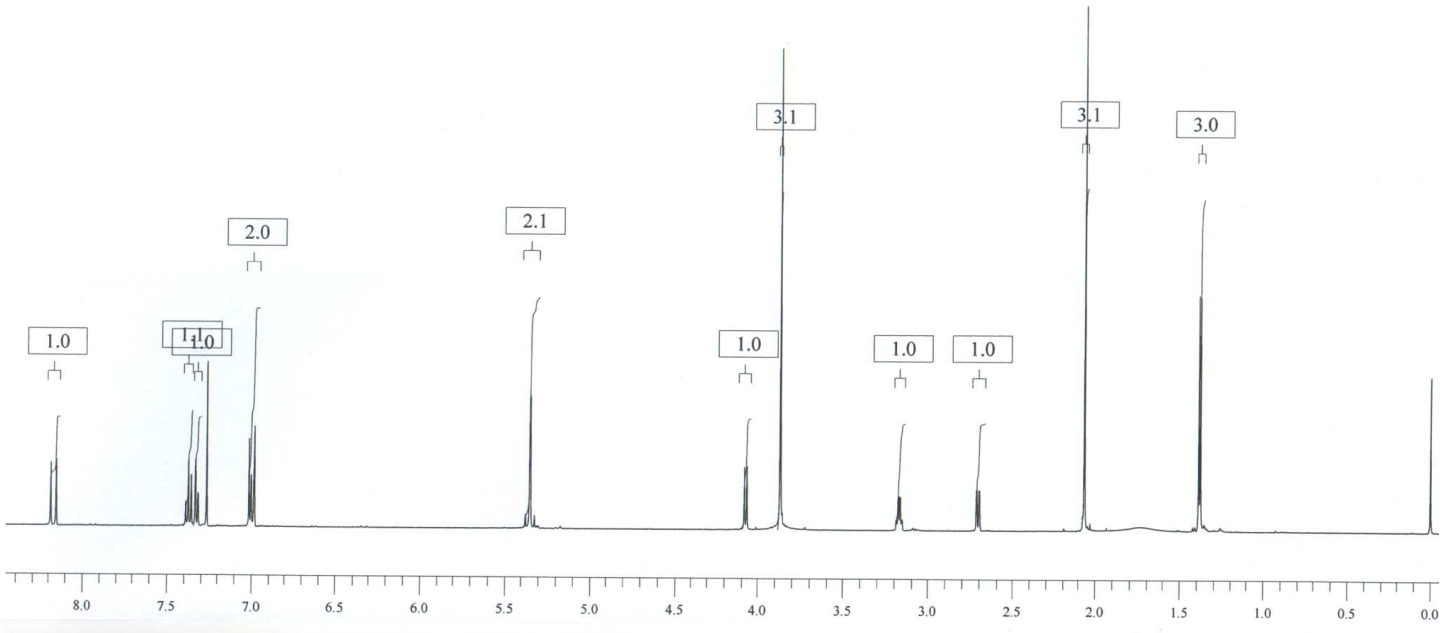


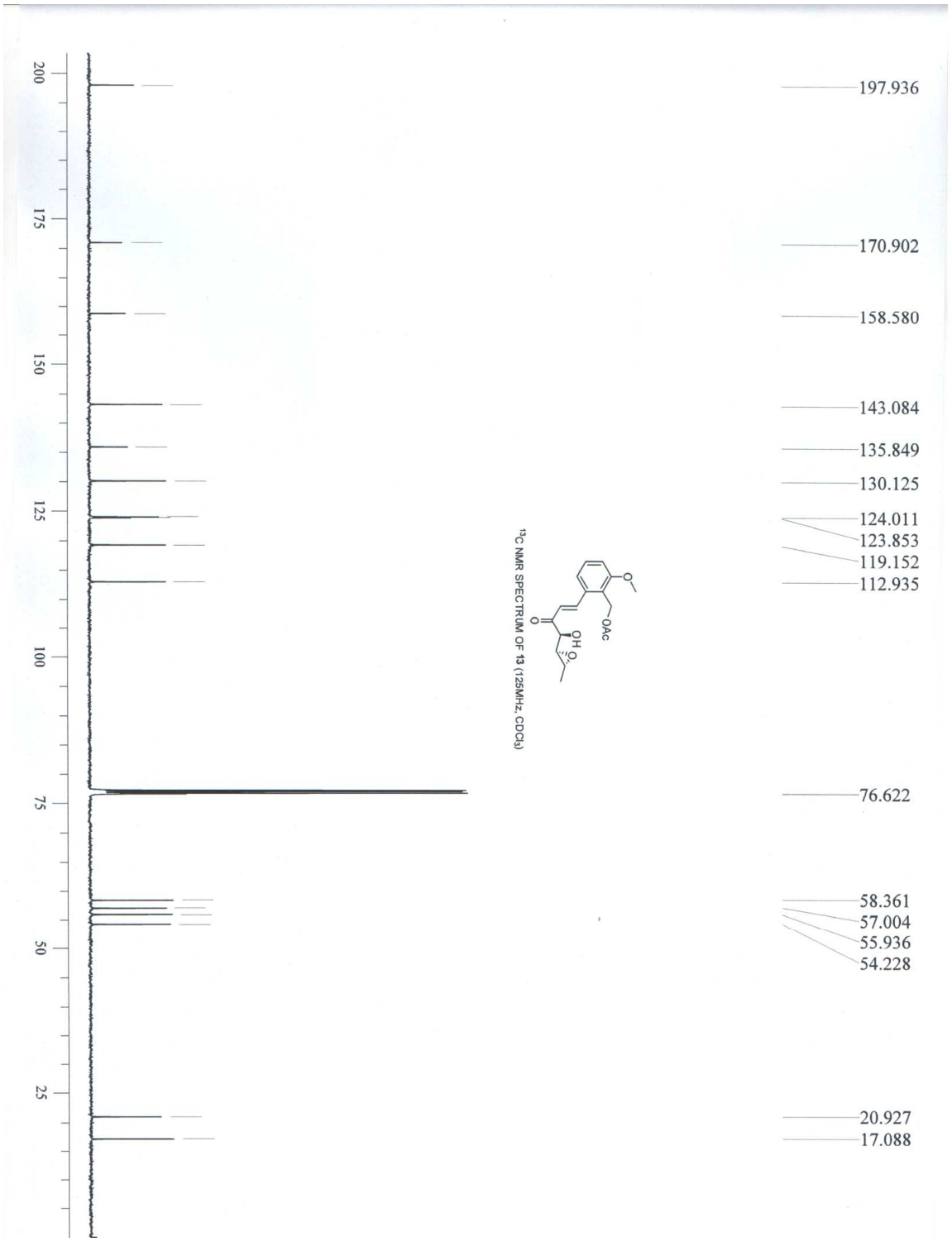
^{1}H NMR SPECTRUM OF **3^1-epi-(+)-varitriol (1a)** (500MHz, CD_3CN)


158.393
138.418
130.150
129.391
129.195
127.001
119.000
110.348
81.333
78.605
77.695
74.081
55.813
55.055
18.751
OMe
OH
HO
OH
O
^{13}C NMR SPECTRUM OF 3'-epi-(+)-varitriol (1a) (125MHz, CD$_3$CN)

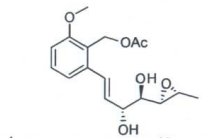


^{1}H NMR SPECTRUM OF **13** (500MHz,$CDCl_3$)

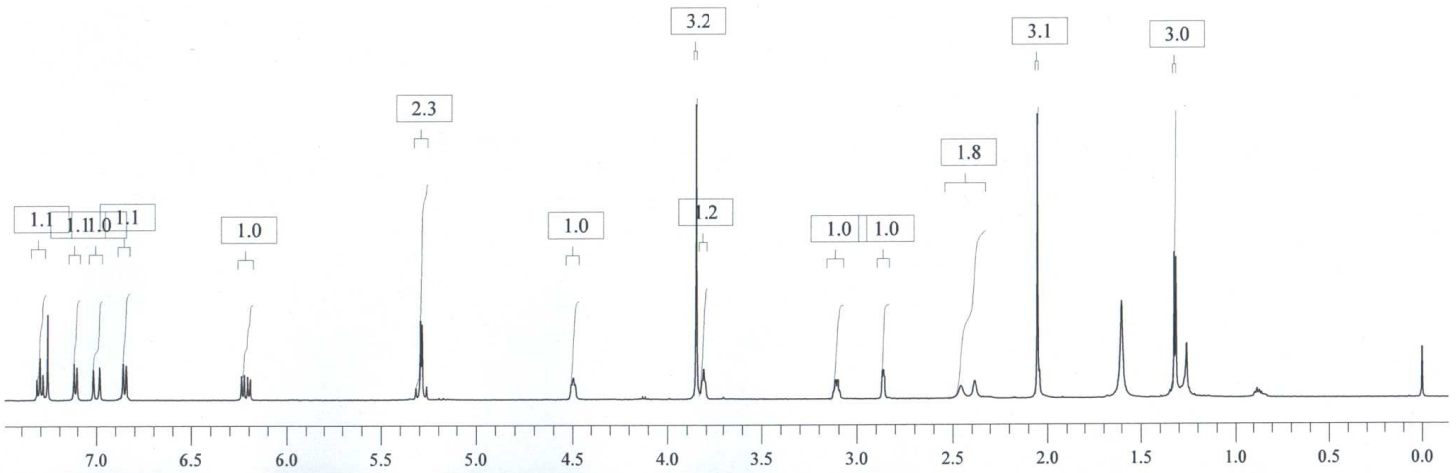


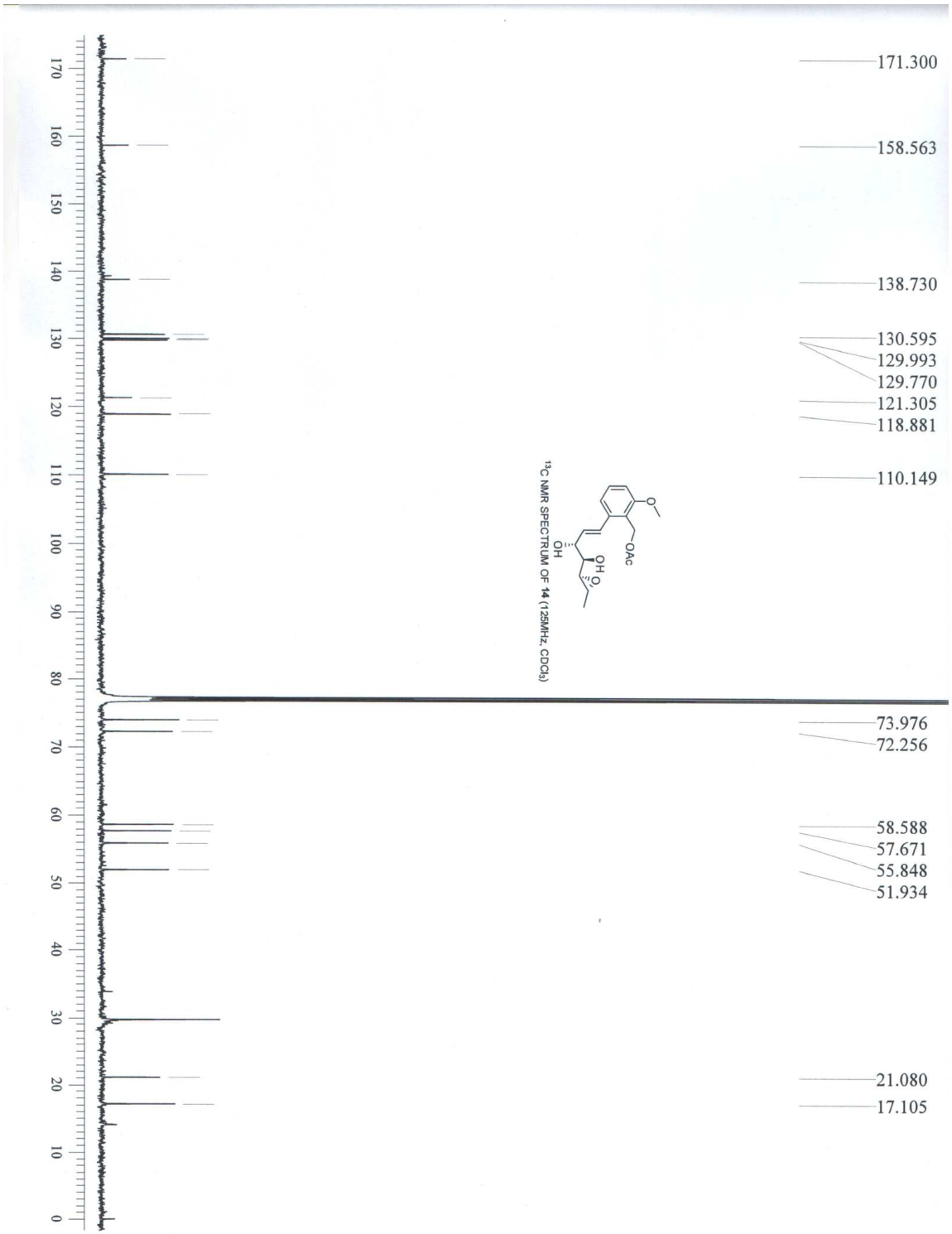


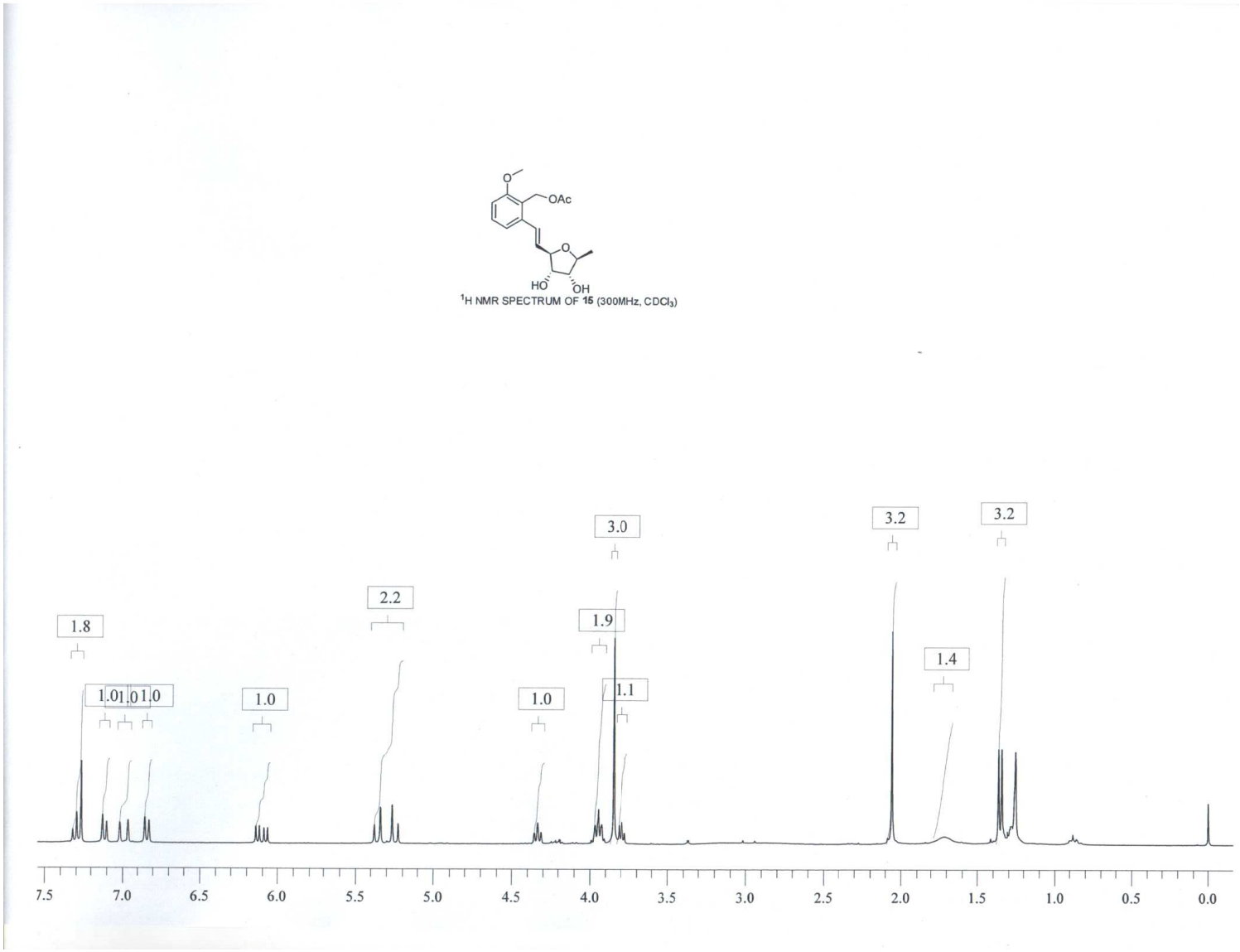
^{13}C NMR SPECTRUM OF **13** (125MHz, $CDCl_3$)

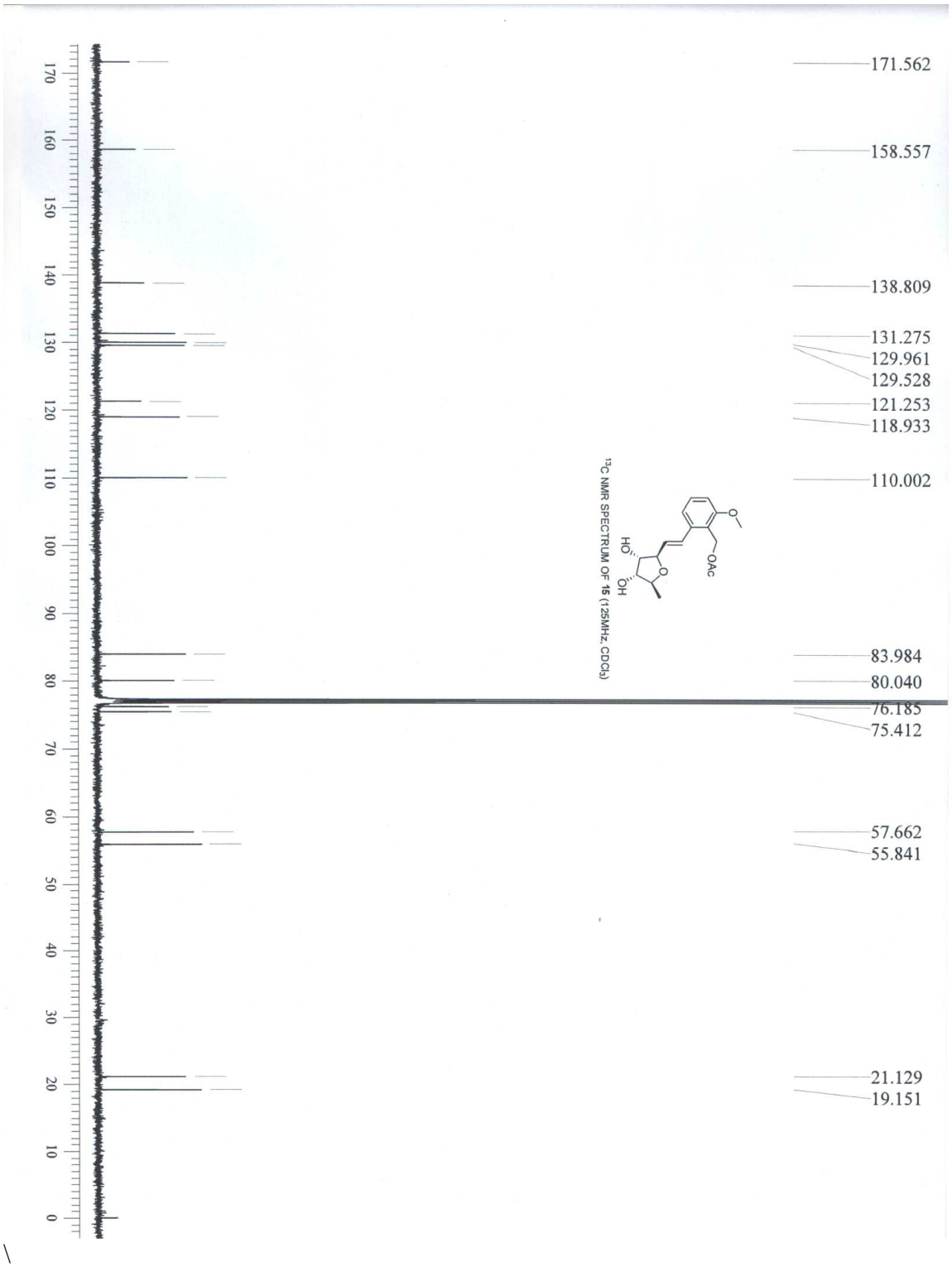


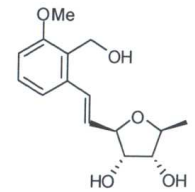
^{1}H NMR SPECTRUM OF **14** (500MHz, $CDCl_3$)



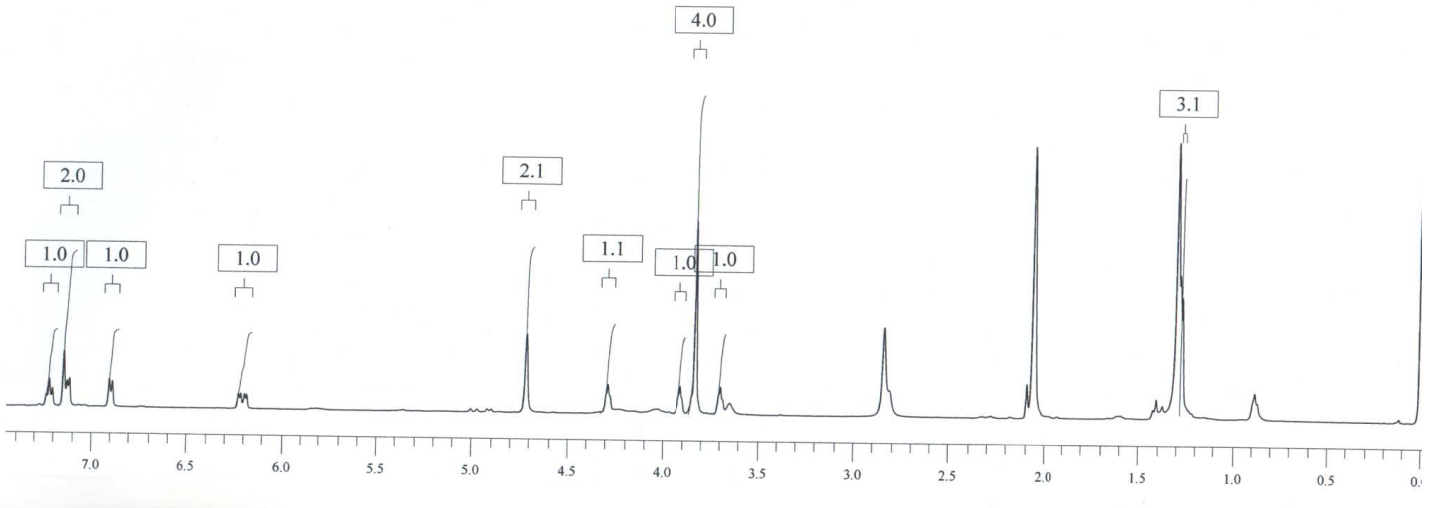

171.300
158.563
138.730
130.595
129.993
129.770
121.305
118.881
110.149
73.976
72.256
58.588
57.671
55.848
51.934
21.080
17.105
OAc
OH
O
OH
O
^{13}C NMR SPECTRUM OF 14 (125MHz, CDCl$_3$)

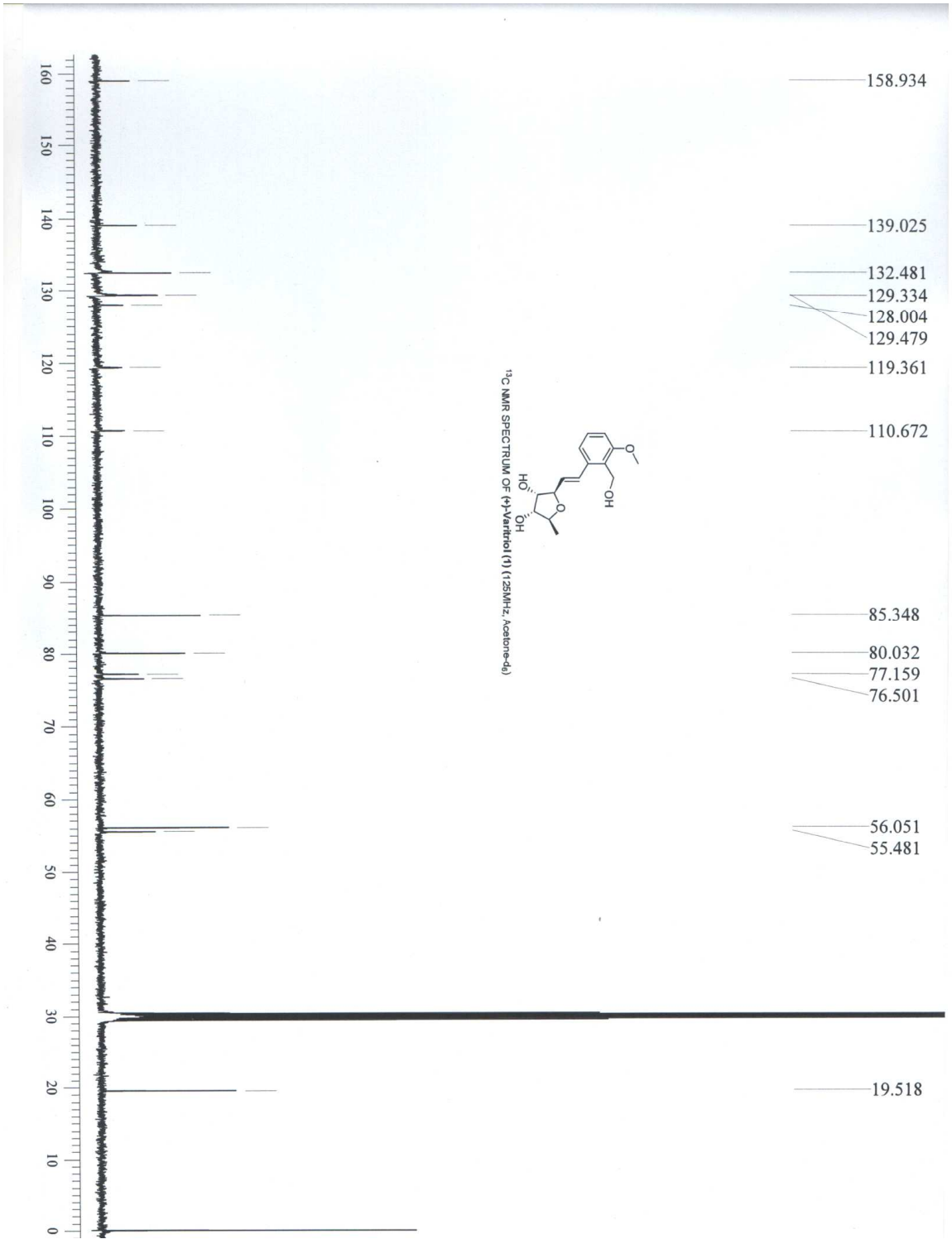

OAc
HO
OH
^{1}H NMR SPECTRUM OF 15 (300MHz, CDCl$_3$)
1.8
1.0
1.0
1.0
1.0
1.0
2.2
1.0
3.0
1.9
1.1
3.2
1.4
3.2
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

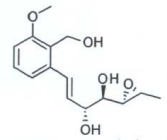

171.562
158.557
138.809
131.275
129.961
129.528
121.253
118.933
110.002
83.984
80.040
76.185
75.412
57.662
55.841
21.129
19.151
^{13}C NMR SPECTRUM OF 15 (125MHz, CDCl$_3$)
HO
OH
O
OAc
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



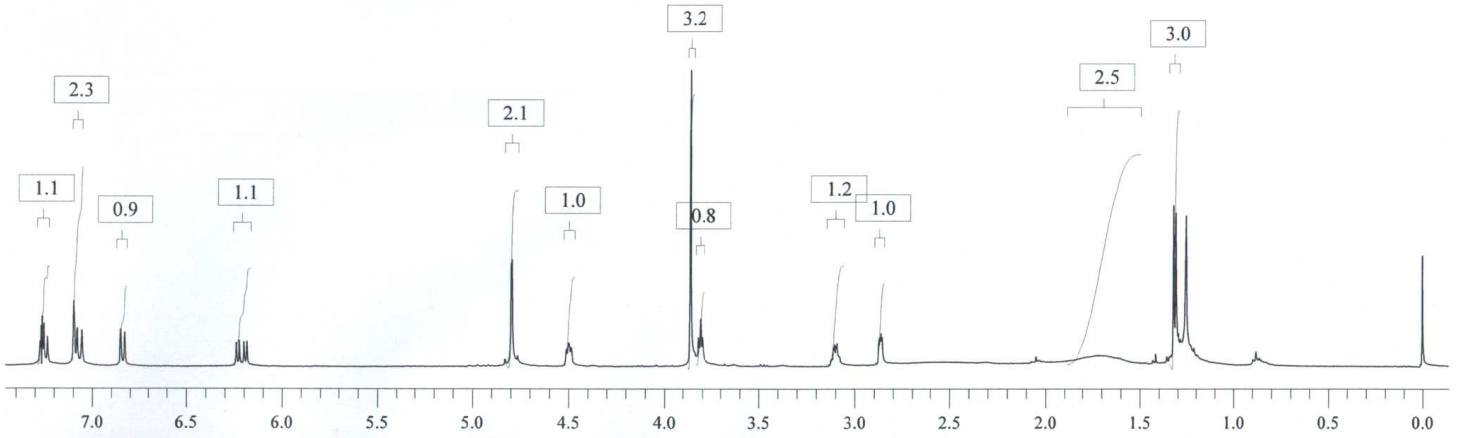
^{1}H NMR SPECTRUM OF **(+)-varitriol (1)**(500MHz,Acetone-d_6)

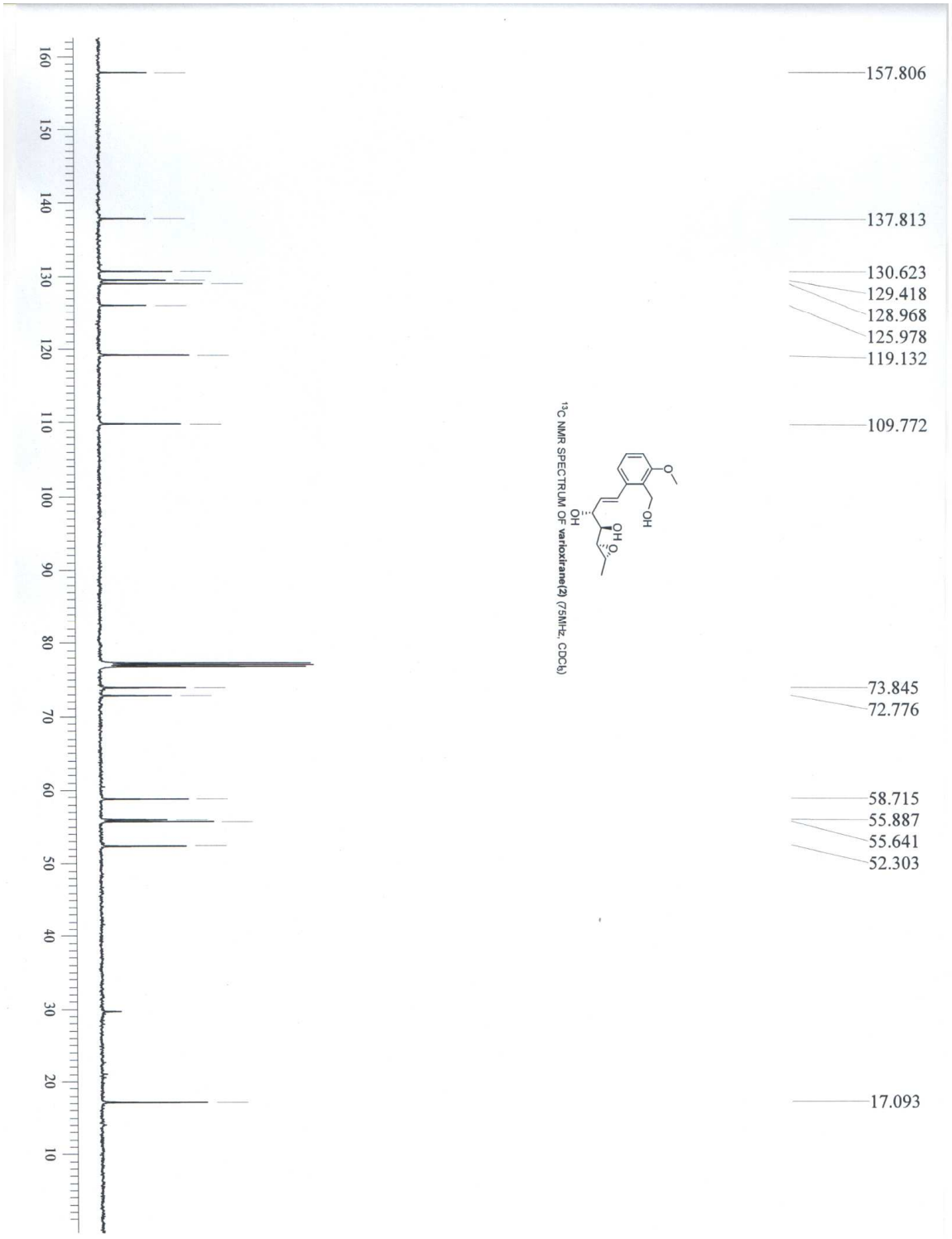


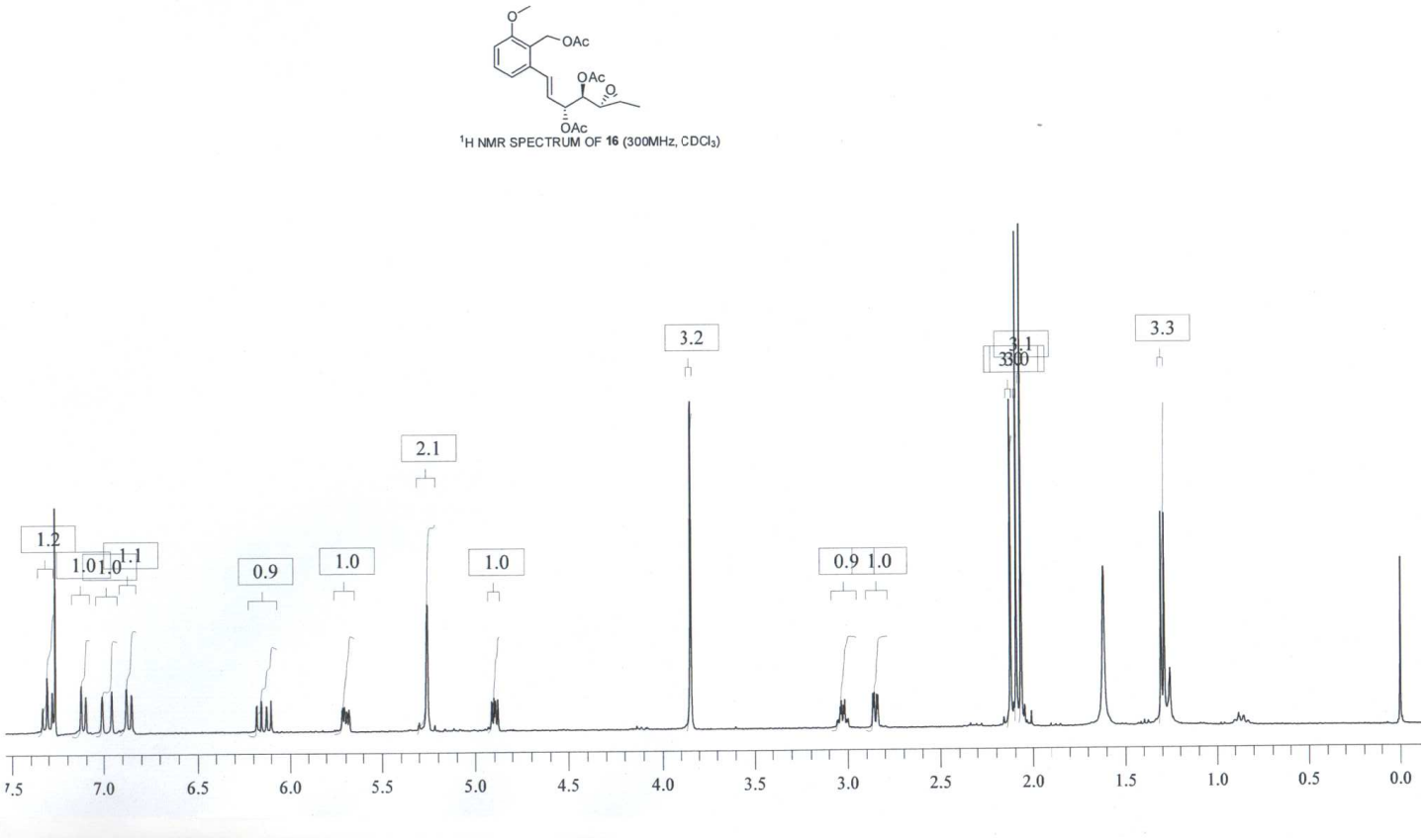

158.934
139.025
132.481
129.334
128.004
129.479
119.361
110.672
85.348
80.032
77.159
76.501
56.051
55.481
19.518
^{13}C NMR SPECTRUM OF (+)-Varitriol (1) (125MHz, Acetone-d$_6$)
HO
OH
O
OH
O



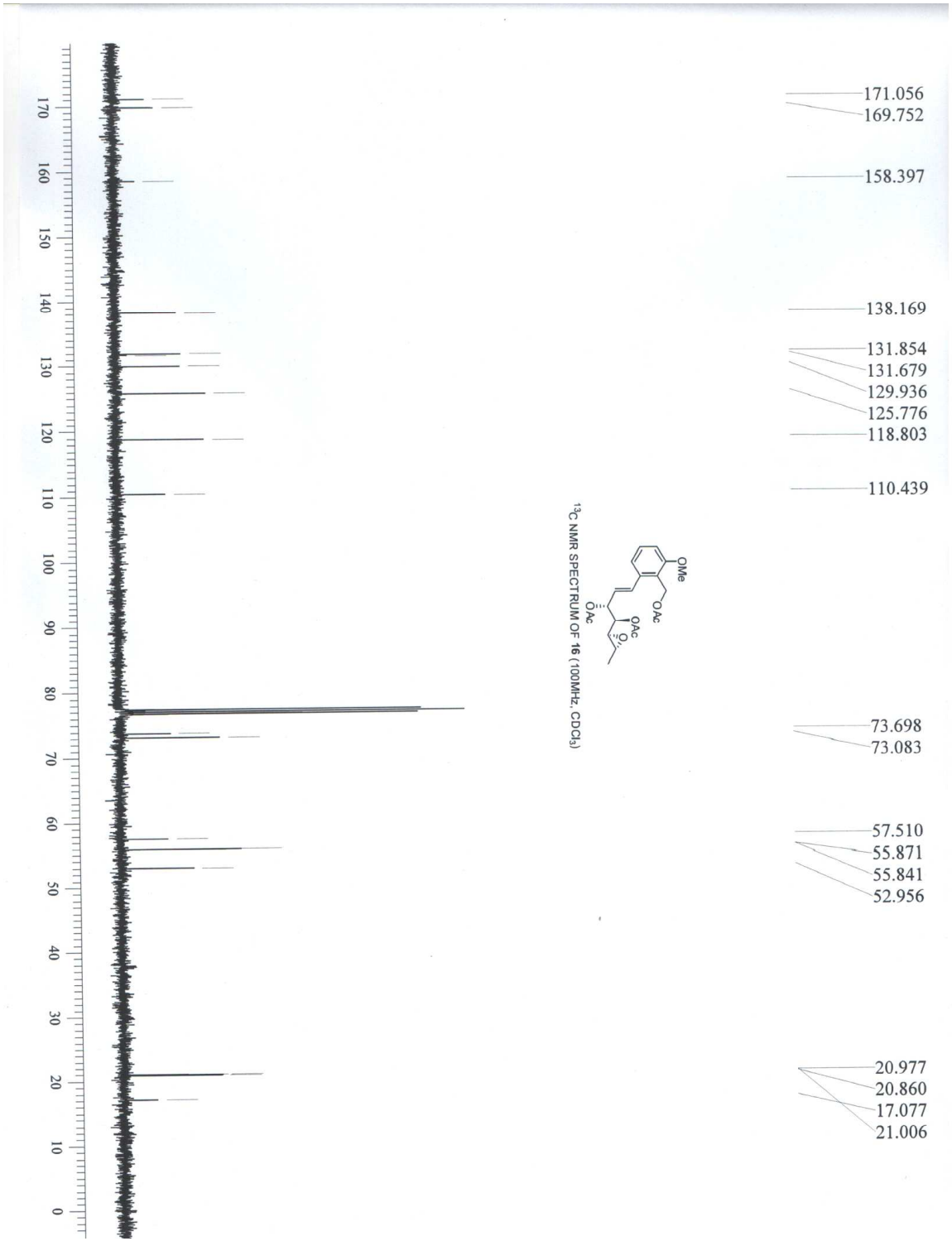
^{1}H NMR SPECTRUM OF **varioxirane(2)** (400MHz, $CDCl_3$)

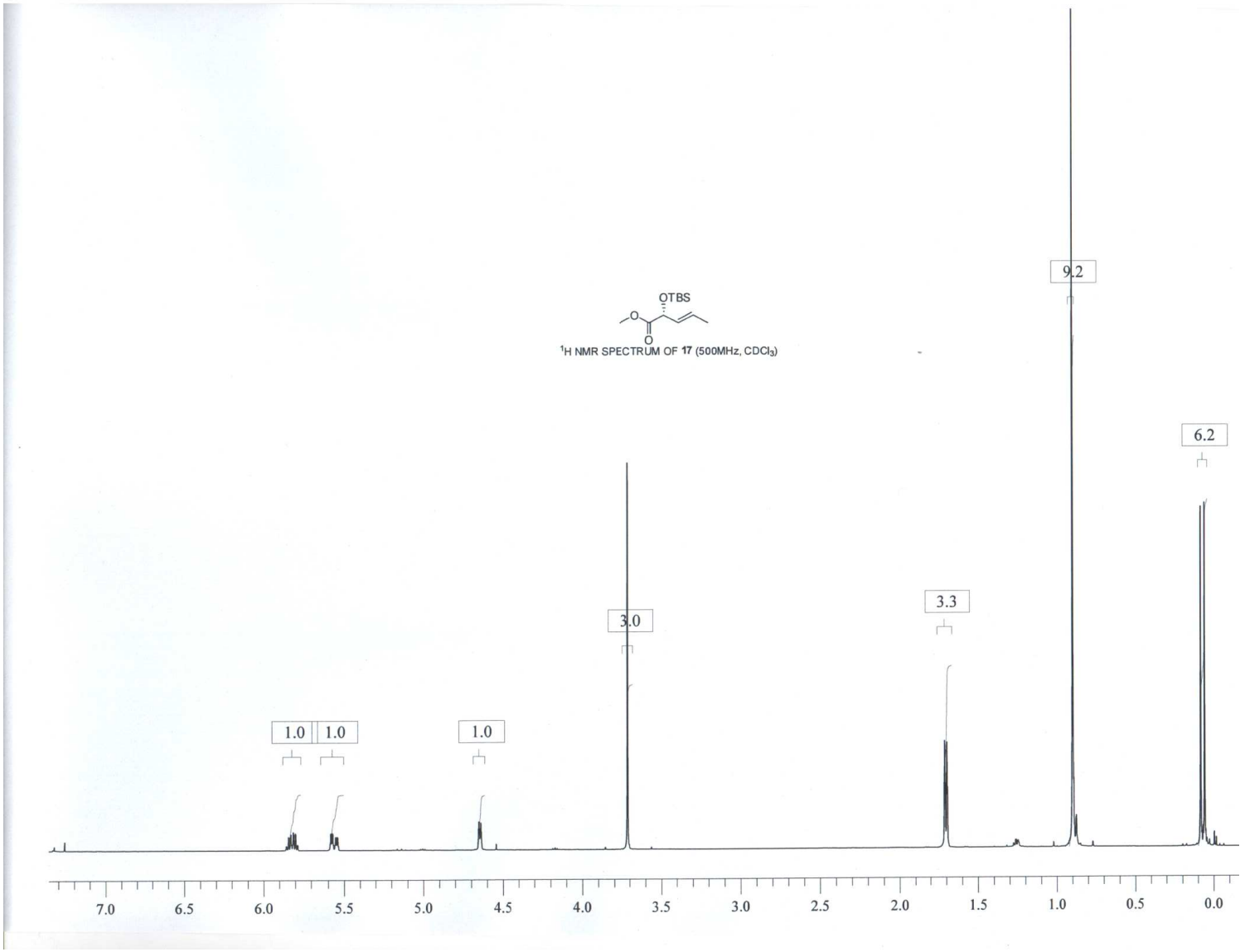



157.806
137.813
130.623
129.418
128.968
125.978
119.132
109.772
73.845
72.776
58.715
55.887
55.641
52.303
17.093
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
OH
OH
O
OH
O
13C NMR SPECTRUM OF variooxirane(2) (75MHz, CDCl3)

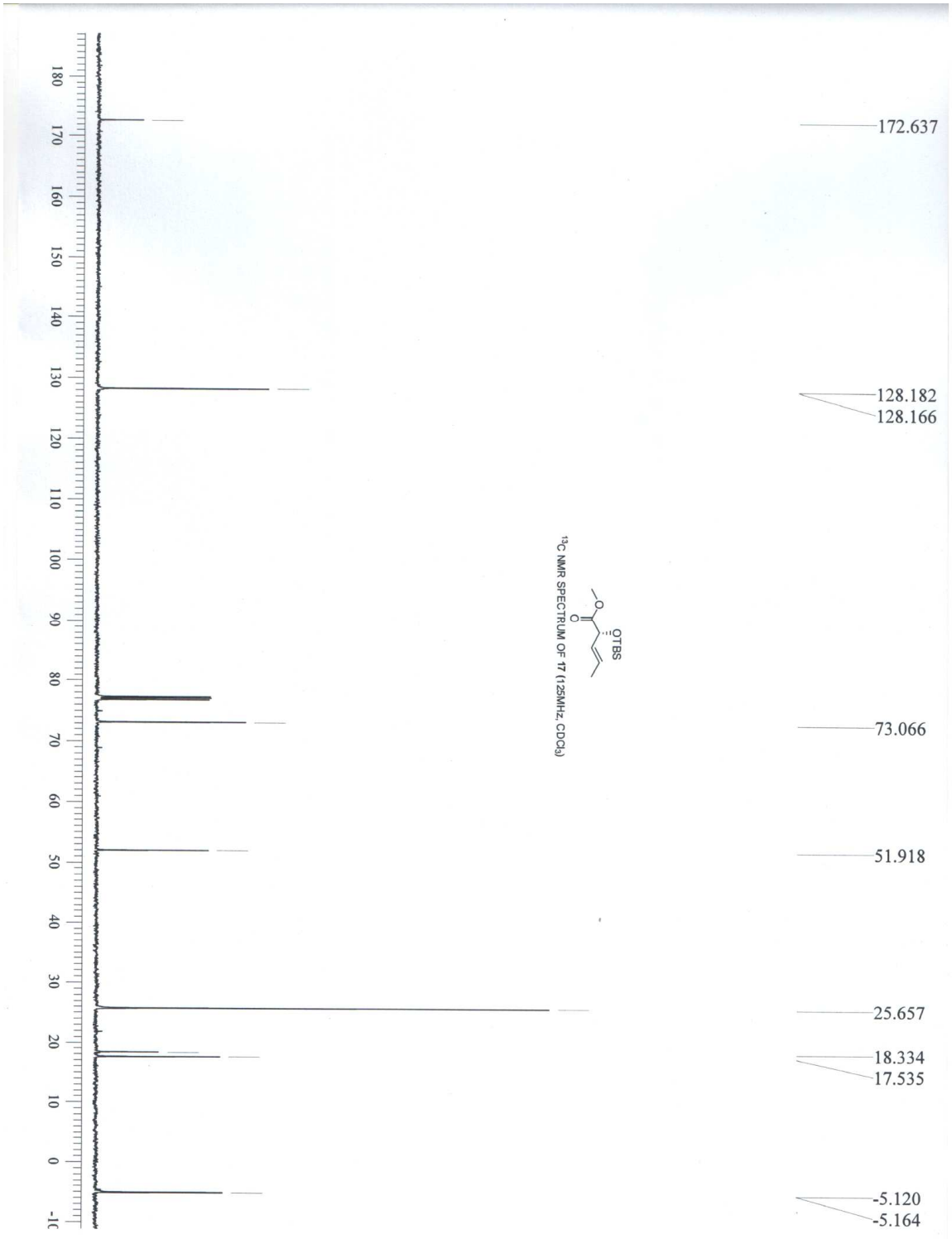


^{1}H NMR SPECTRUM OF **16** (300MHz, $CDCl_3$)

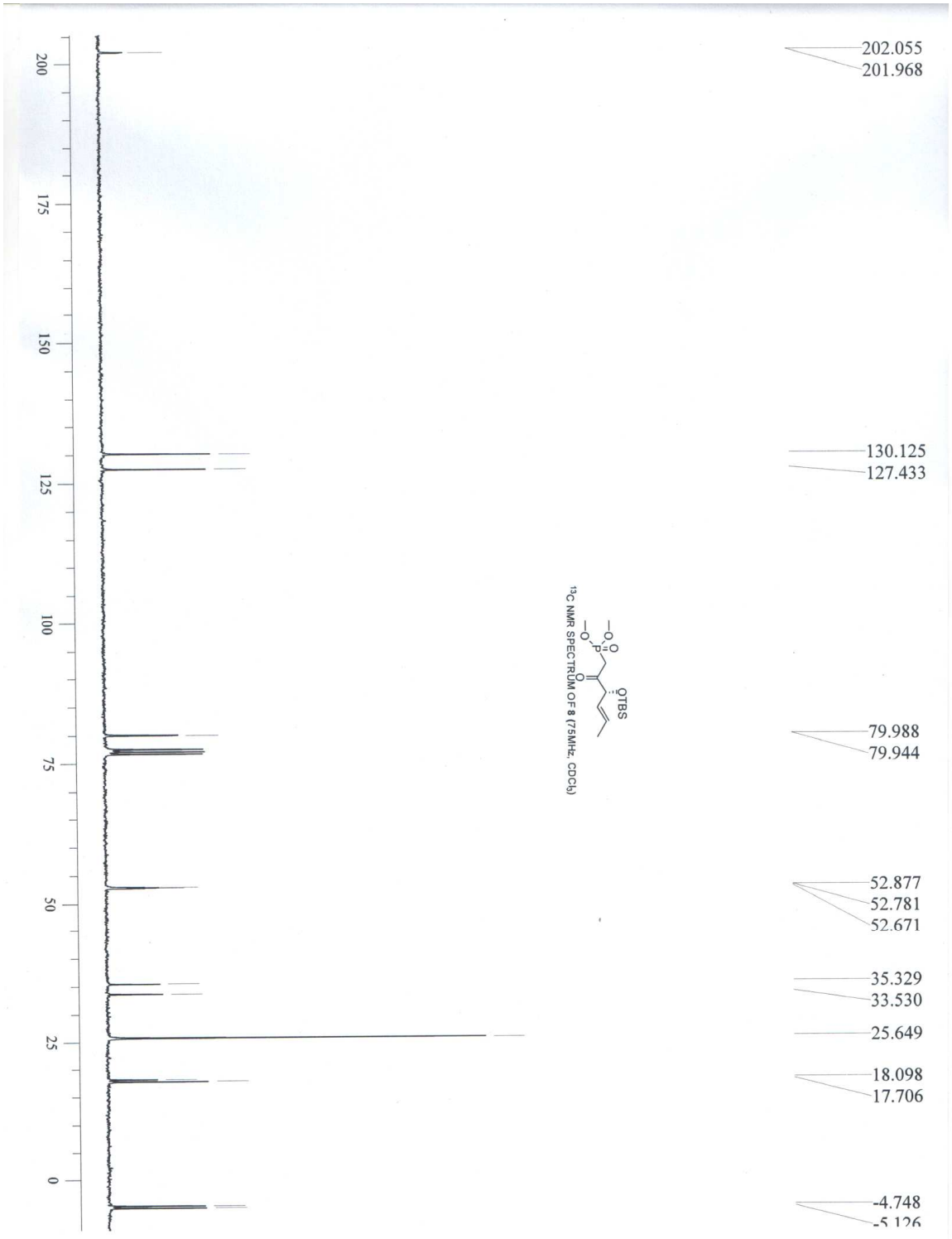

171.056
169.752
158.397
138.169
131.854
131.679
129.936
125.776
118.803
110.439
73.698
73.083
57.510
55.871
55.841
52.956
20.977
20.860
17.077
21.006
OMe
OAc
OAc
OAc
^{13}C NMR SPECTRUM OF 16 (100MHz, CDCl$_3$)

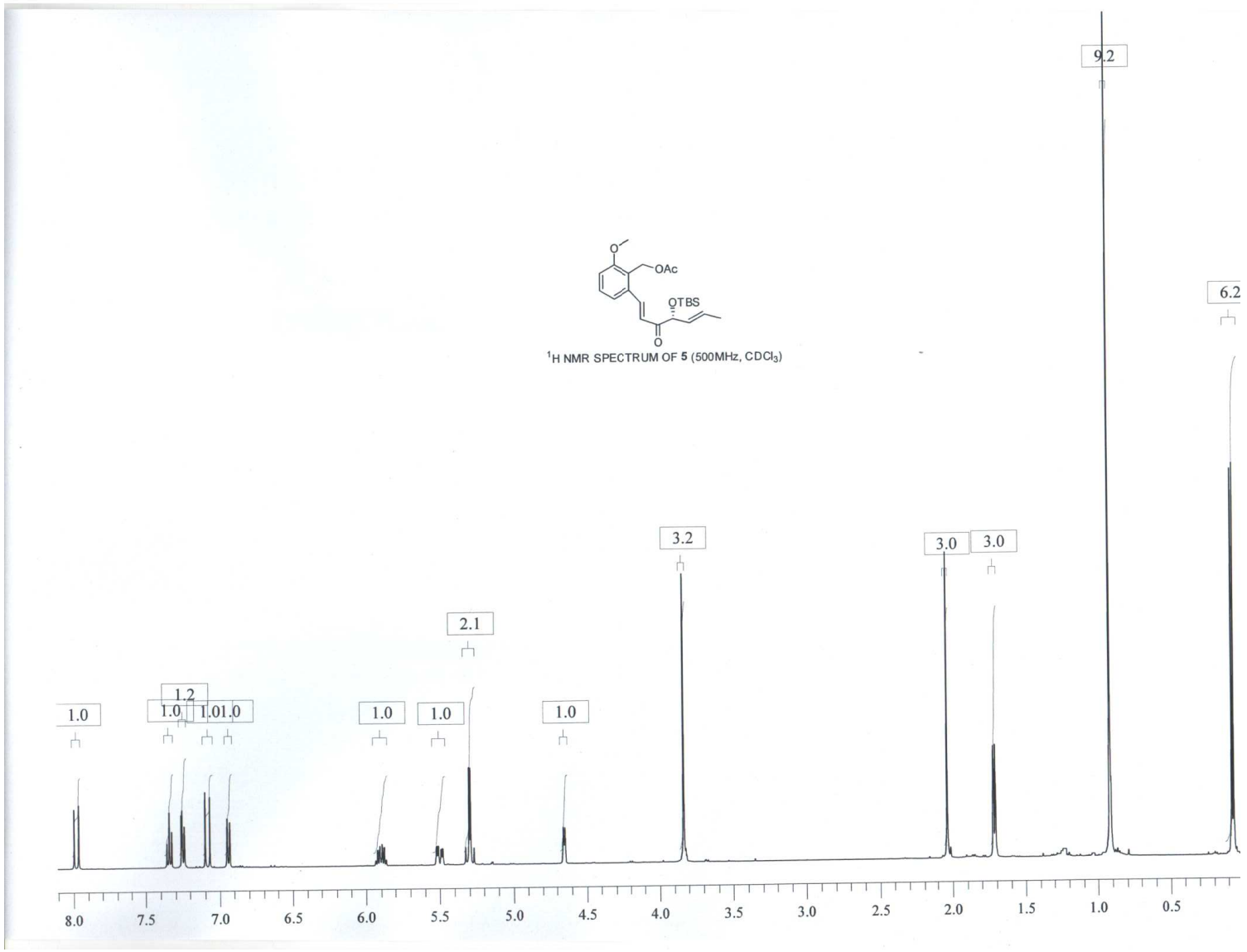


^{1}H NMR SPECTRUM OF **17** (500MHz, $CDCl_3$)

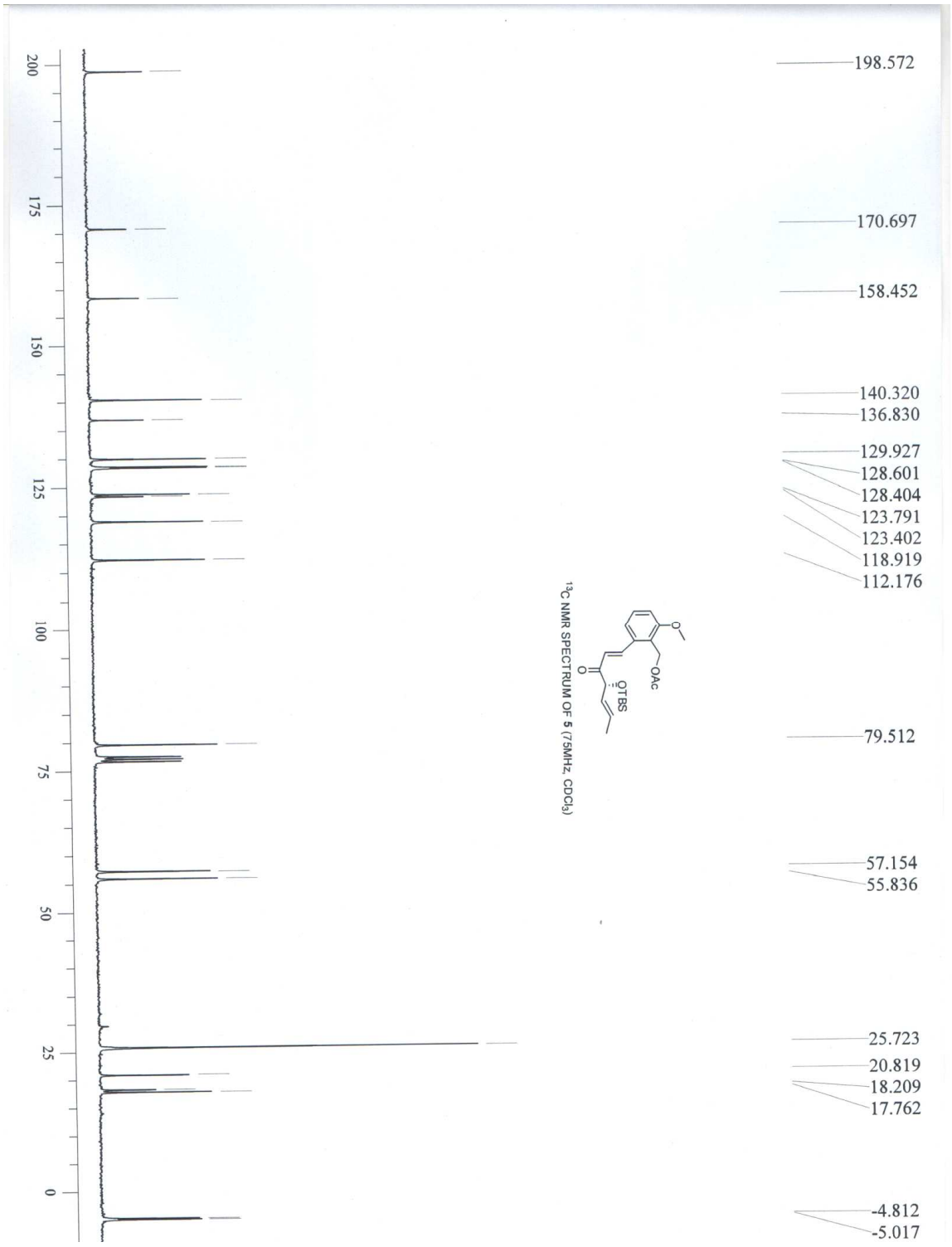

^{13}C NMR SPECTRUM OF 17 (125MHz, CDCl$_3$)
OTBS
172.637
128.182
128.166
73.066
51.918
25.657
18.334
17.535
-5.120
-5.164

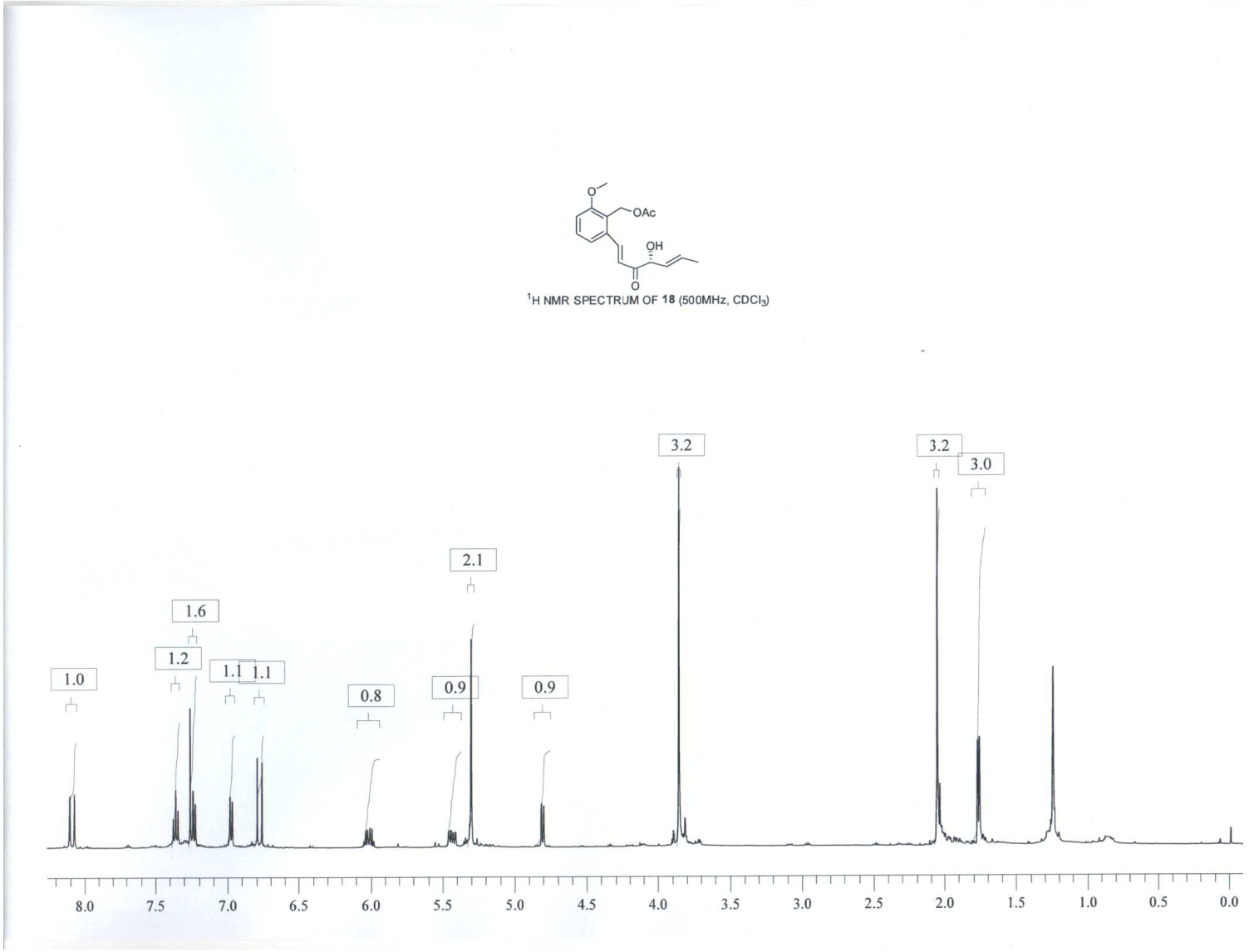
OTBS
^{1}H NMR SPECTRUM OF 8 (400MHz, CDCl$_3$)
1.0
0.9
1.0
6.0
2.2
3.0
9.0
6.0
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

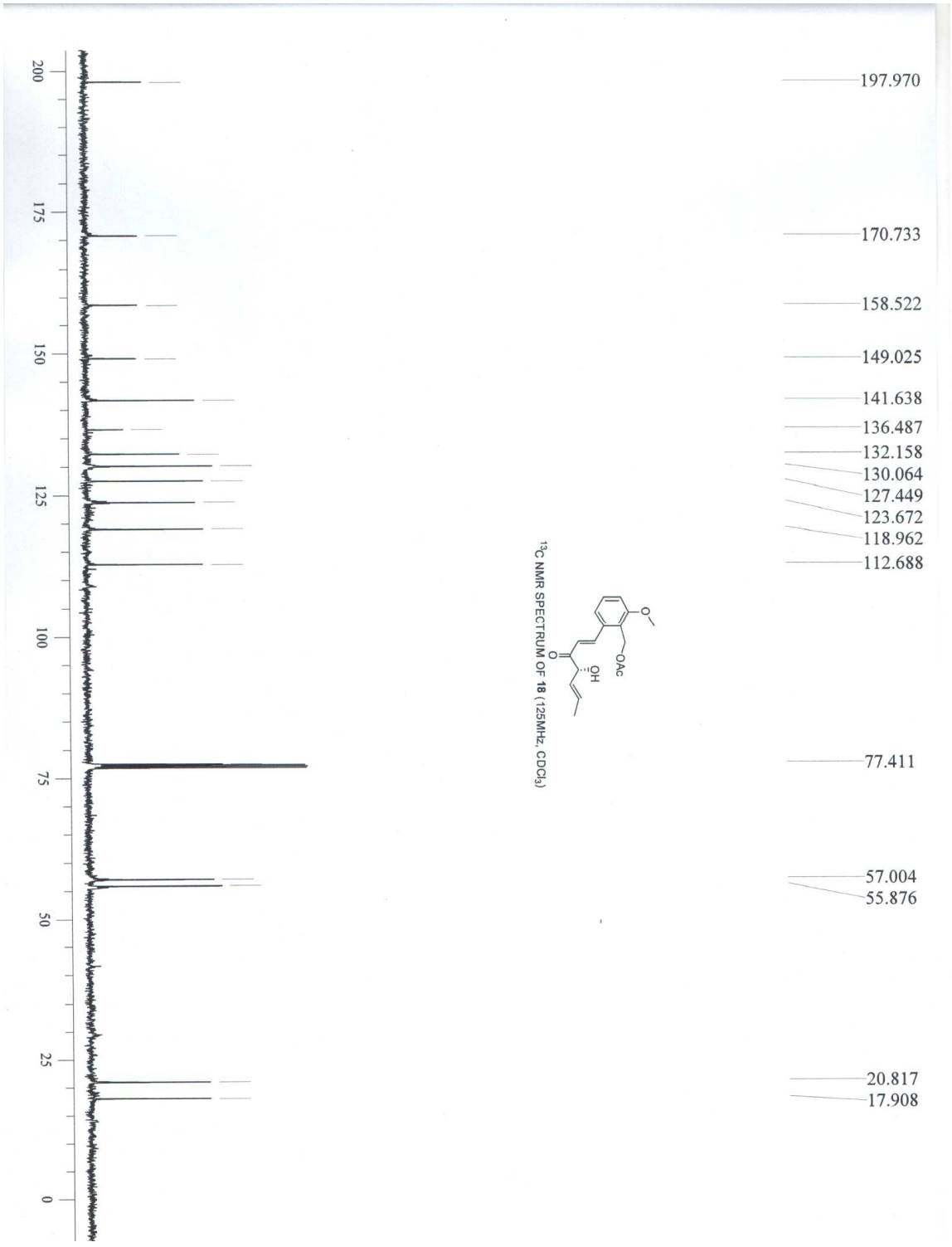

202.055
201.968
130.125
127.433
79.988
79.944
52.877
52.781
52.671
35.329
33.530
25.649
18.098
17.706
-4.748
-5.126
200
175
150
125
100
75
50
25
0
OTBS
^{13}C NMR SPECTRUM OF 8 (75MHz, CDCl$_3$)



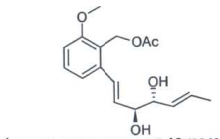
^{1}H NMR SPECTRUM OF **5** (500MHz, $CDCl_3$)


198.572
170.697
158.452
140.320
136.830
129.927
128.601
128.404
123.791
123.402
118.919
112.176
79.512
57.154
55.836
25.723
20.819
18.209
17.762
-4.812
-5.017
200
175
150
125
100
75
50
25
0
OAc
OTBS
O
O
13C NMR SPECTRUM OF 5 (75MHz, CDCl3)

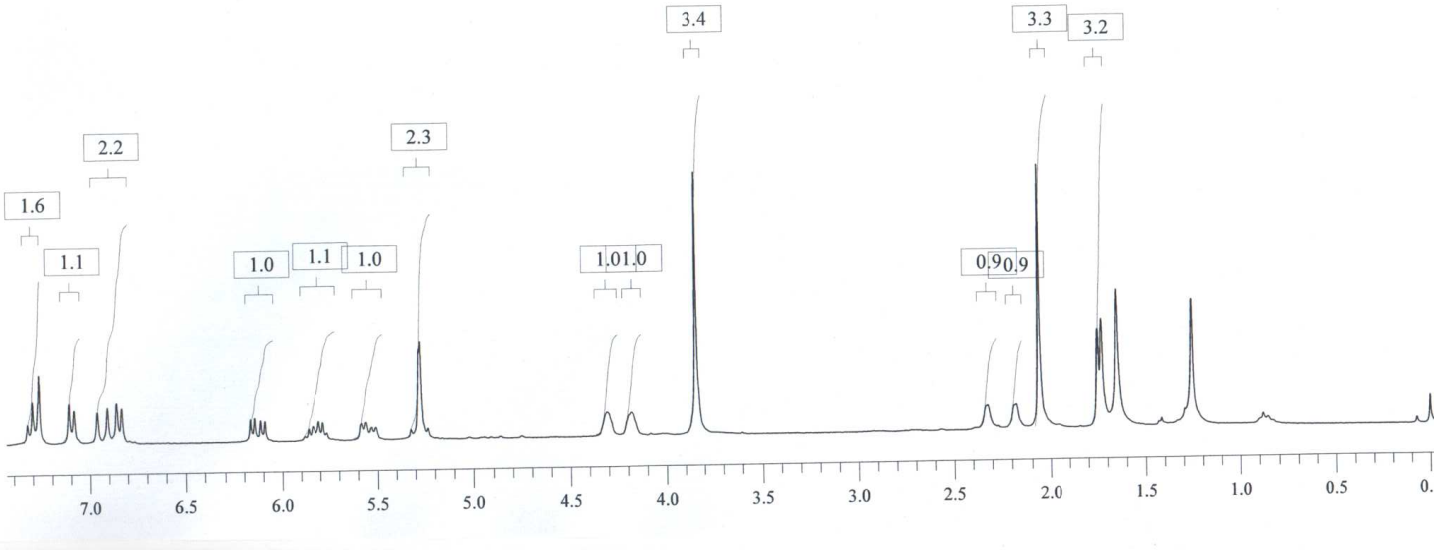

OAc
OH
O
^{1}H NMR SPECTRUM OF **18** (500MHz, $CDCl_3$)
1.0
1.2
1.6
1.1
1.1
0.8
0.9
2.1
0.9
3.2
3.2
3.0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

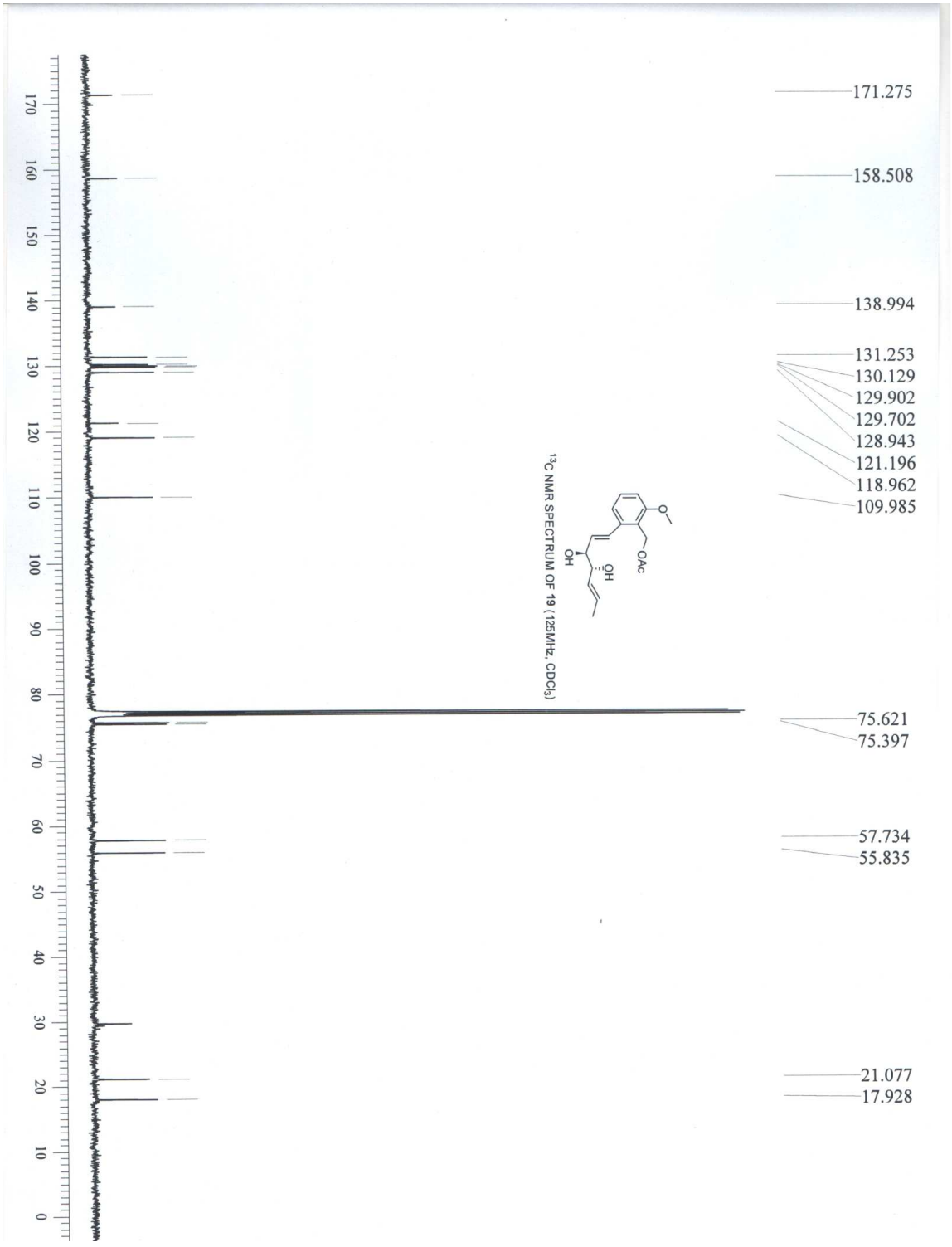


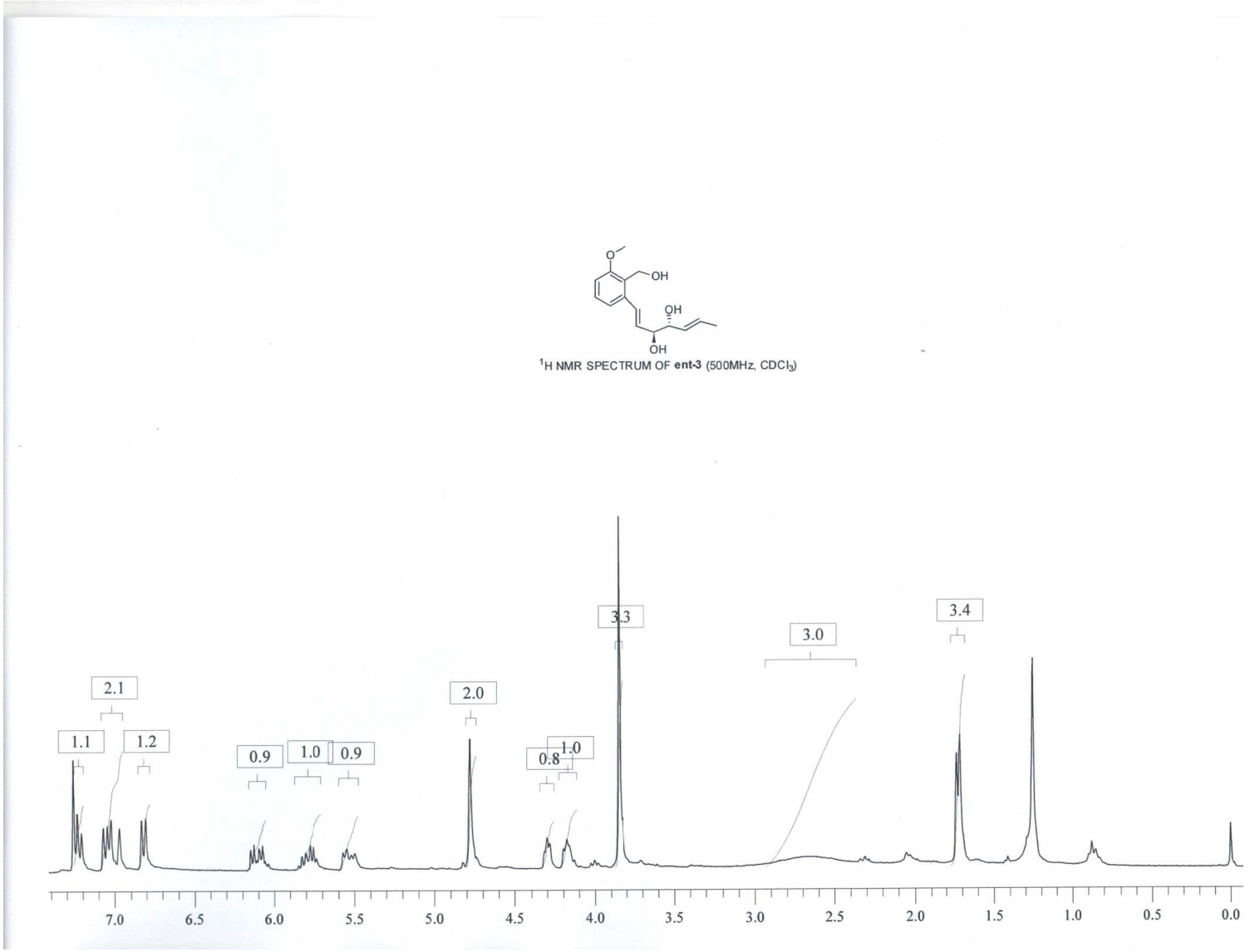
^{13}C NMR SPECTRUM OF **18** (125MHz, $CDCl_3$)



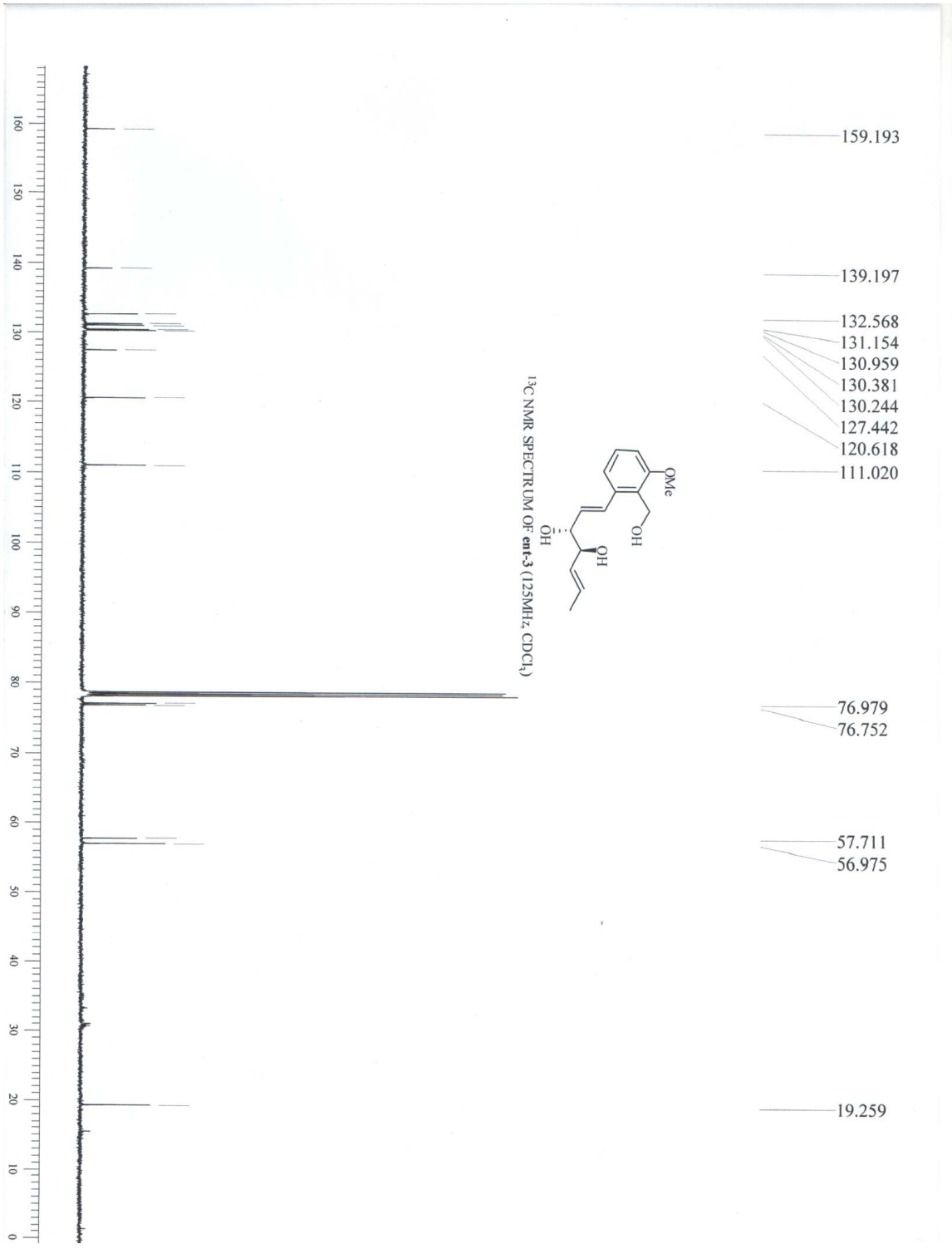
^{1}H NMR SPECTRUM OF **19** (300MHz, $CDCl_3$)



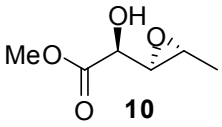

171.275
158.508
138.994
131.253
130.129
129.902
129.702
128.943
121.196
118.962
109.985
75.621
75.397
57.734
55.835
21.077
17.928
OAc
OH
OH
^{13}C NMR SPECTRUM OF 19 (125MHz, CDCl$_3$)



^{1}H NMR SPECTRUM OF **ent-3** (500MHz, $CDCl_3$)


159.193
139.197
132.568
131.154
130.959
130.381
130.244
127.442
120.618
111.020
76.979
76.752
57.711
56.975
19.259
OMe
OH
OH
OH
^{13}C NMR SPECTRUM OF **ent-3** (125MHz, $CDCl_3$)

HPLC Chromatograms



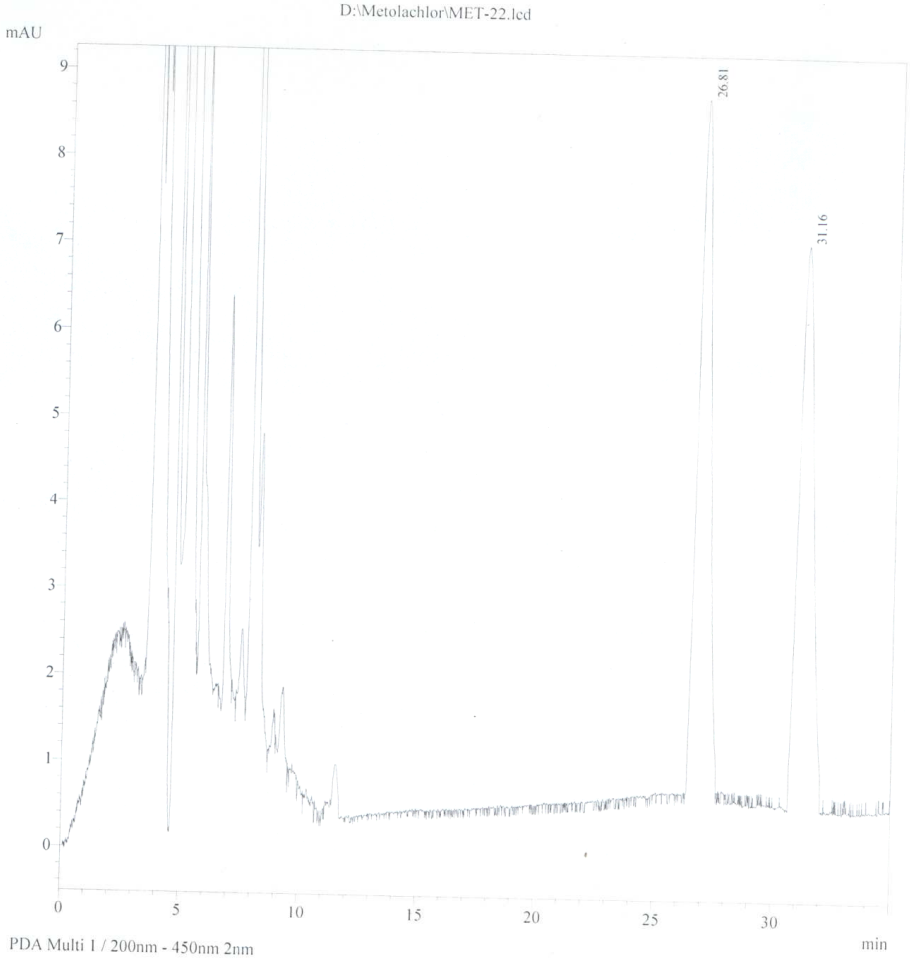
10

HPLC Chromatogram of (±)-10

INDIAN INSTITUTE OF CHEMICAL TECHNOLOGY
CROP PROTECTION CHEMICALS DIVISION

Acquired by	: T RAMESH BABU
Sample Name	: GS
Sample ID	: RR-B Racemic
Data Filename	: MET-22.lcd
Method Filename	: ramesh.lcm
Date Acquired	: 05/07/2013

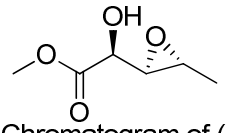
D:\Metolachlor\MET-22.lcd



1 PDA Multi 1 / 200nm - 450nm 2nm

PDA Ch1 200nm - 450nm 2nm

Peak#	Ret. Time	Area	Area %
1	26.81	303960	51.78
2	31.16	283017	48.22
Total		586976	100.00

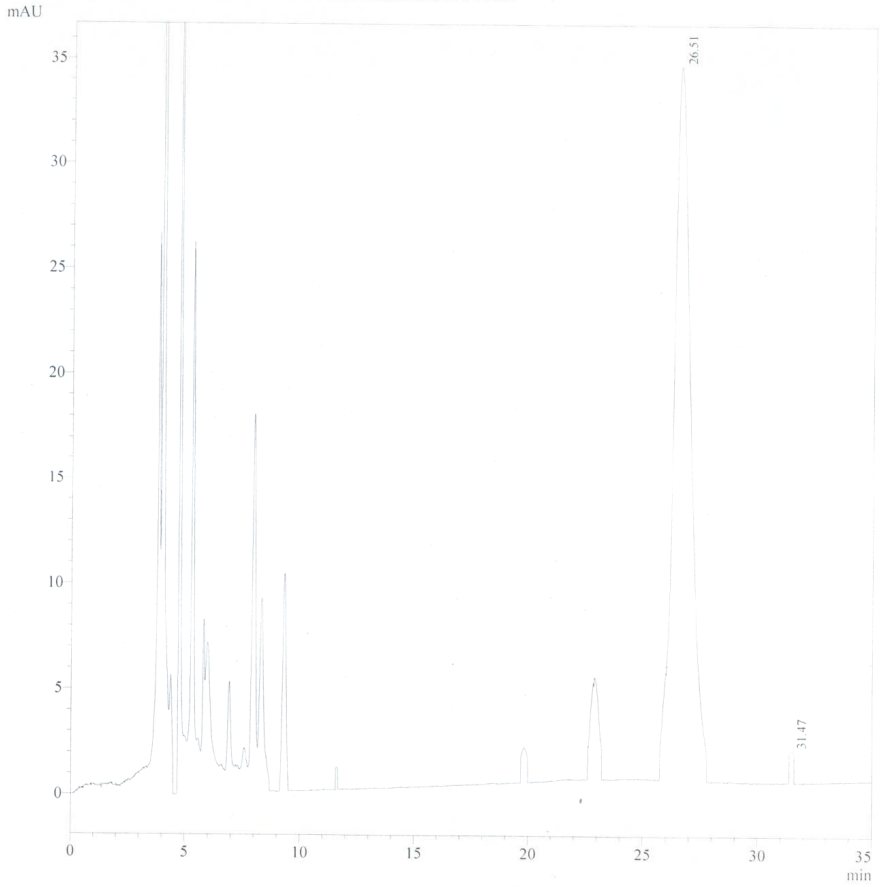


HPLC Chromatogram of (+)-10

INDIAN INSTITUTE OF CHEMICAL TECHNOLOGY
CROP PROTECTION CHEMICALS DIVISION

Acquired by	: T RAMESH BABU
Sample Name	: GS
Sample ID	: PURE
Data Filename	: MET-21.lcd
Method Filename	: ramesh.lcm
Date Acquired	: 05/07/2013

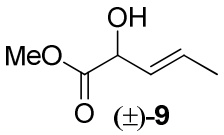
D:\Metolachlor\MET-21.lcd



PDA Ch1 200nm - 450nm 2nm

Peak#	Ret. Time	Area	Area %
1	26.51	1748278	98.89
2	31.47	19675	1.11
Total		1767953	100.00

HPLC Chromatogram of (±)-9

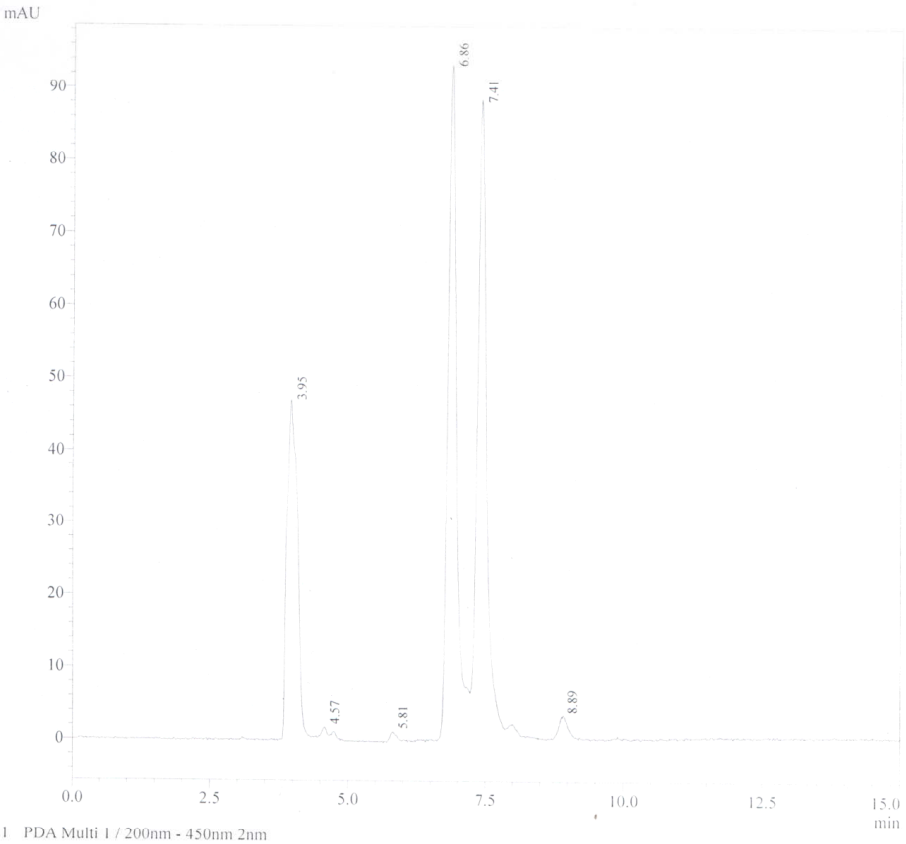


(±)-**9**

INDIAN INSTITUTE OF CHEMICAL TECHNOLOGY
CROP PROTECTION CHEMICALS DIVISION

Acquired by : T RAMESH BABU
Sample Name : GS-R
Sample ID : Racemic 90:10
Data Filename : alcohol 135.lcd
Method Filename : ramesh.lcm
Date Acquired : 22/01/2013

D:\SUDHAKAR\alcohol 135.lcd

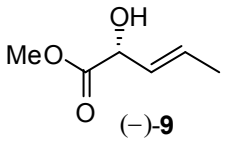


1 PDA Multi 1 / 200nm - 450nm 2nm

PDA Ch1 200nm - 450nm 2nm

Peak#	Ret. Time	Area	Area %
1	3.95	639546	22.47
2	4.57	10584	0.37
3	5.81	10444	0.37
4	6.86	1044726	36.71
5	7.41	1099014	38.62
6	8.89	41330	1.45
Total		2845644	100.00

HPLC Chromatogram of (□)-**9**, after 8 h reaction time

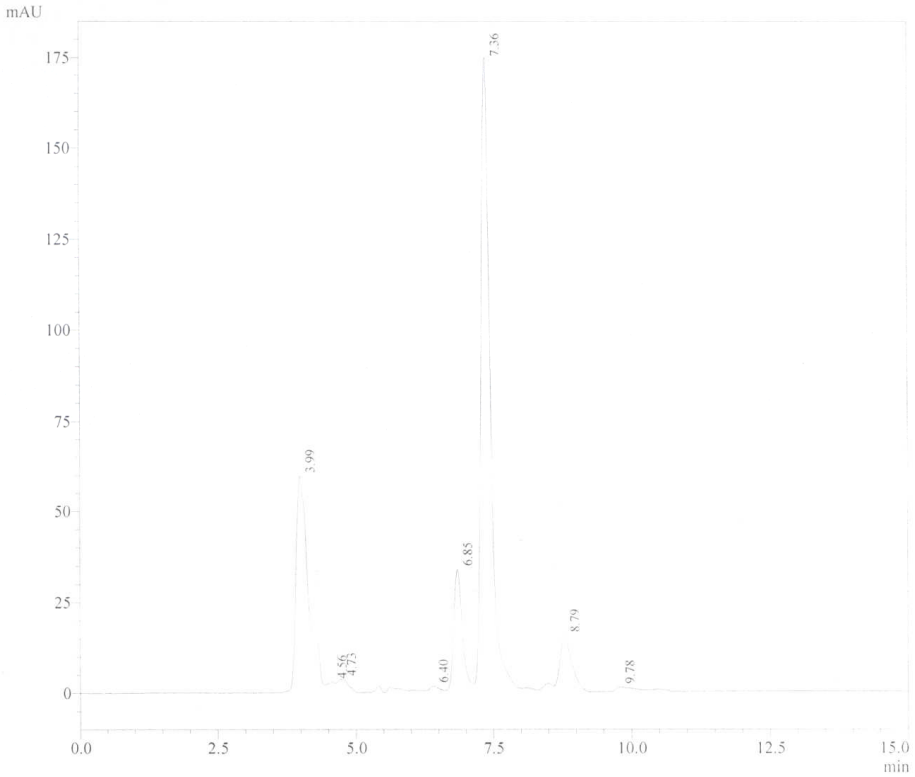


(−)-**9**

INDIAN INSTITUTE OF CHEMICAL TECHNOLOGY
CROP PROTECTION CHEMICALS DIVISION

Acquired by : T RAMESH BABU
Sample Name : GS
Sample ID : 3 0.2 eg
Data Filename : alcohol 139.lcd
Method Filename : ramesh.lcm
Date Acquired : 07/02/2013

D:\SUDHAKAR\alcohol 139.lcd

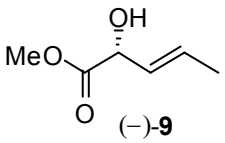


1 PDA Multi 1 / 200nm - 450nm 2nm

PDA Ch1 200nm - 450nm 2nm

Peak#	Ret. Time	Area	Area %
1	3.99	932596	24.74
2	4.56	25757	0.68
3	4.73	55418	1.47
4	6.40	21773	0.58
5	6.85	377482	10.02
6	7.36	2098558	55.68
7	8.79	228051	6.05
8	9.78	29284	0.78
Total		3768920	100.00

HPLC Chromatogram of (□)-**9**, after 10 h reaction time

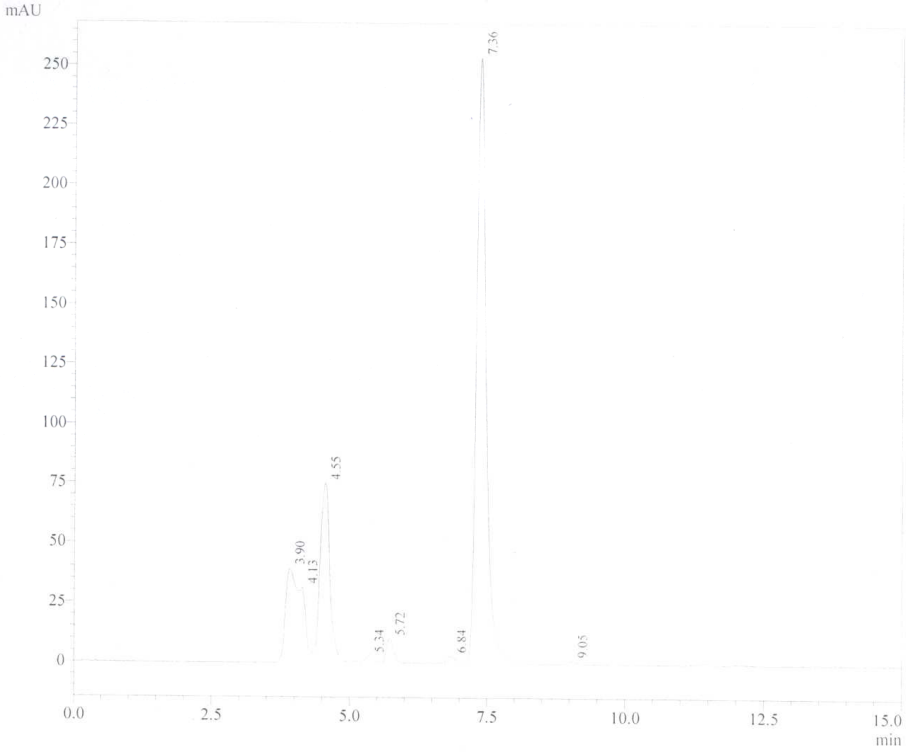


(−)-**9**

INDIAN INSTITUTE OF CHEMICAL TECHNOLOGY
CROP PROTECTION CHEMICALS DIVISION

Acquired by : T RAMESH BABU
Sample Name : GS
Sample ID : 1-500mg-10hrs
Data Filename : alcohol 142.lcd
Method Filename : ramesh.lcm
Date Acquired : 25/04/2013

D:\SUDHAKAR\alcohol 142.lcd

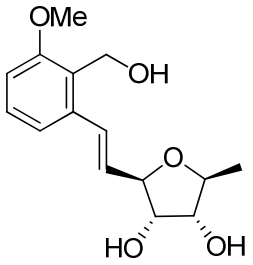


PDA Ch1 200nm - 450nm 2nm

Peak#	Ret. Time	Area	Area %
1	3.90	604892	11.75
2	4.13	217555	4.23
3	4.55	933027	18.13
4	5.34	27667	0.54
5	5.72	114345	2.22
6	6.84	44061	0.86
7	7.36	3183631	61.86
8	9.05	21093	0.41
Total		5146270	100.00

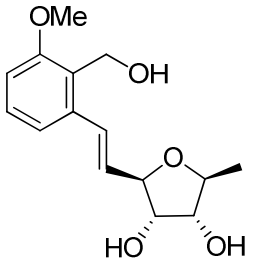
Tabular comparison of natural and synthetic compounds

^{1}H and ^{13}C NMR tabular comparison between the natural and synthetic of varitriol (**1**) in CD_3COCD_3:



(+)-varitriol (**1**)

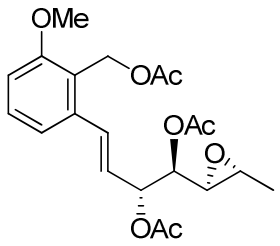
1 δ_H [ppm] (multiplicity; *J* [Hz])		
S.No	**Natural (300 MHz, CD_3COCD_3)**	**Synthetic (500 MHz, CD_3COCD_3)**
1	7.22 (t, 8.0, 1H)	7.23 (t, 8.0, 1H)
2	7.14 (br d, 15.8, 1H)	7.13 (d, 15.8, 1H)
3	7.13 (dd, 8.0, 1.0, 1H)	7.12 (d, 8.0, 1H)
4	6.89 (dd, 8.0, 1.0, 1H)	6.90 (d, 8.0, 1H)
5	6.19 (dd, 15.8, 6.7, 1H)	6.21 (dd, 15.8, 6.7, 1H)
6	4.72 (br s, 2H)	4.72 (s, 2H)
7	4.62 (bs s, 1H)	4.29(t, 6.7, 1H)
8	4.41 (bs s, 1H)	4.23 (br s, 1H)
9	4.32 (br t, 6.4, 1H)	4.03(br s, 1H)
10	3.94 (br q, 5.3, 1H)	3.91 (m, 1H)
11	3.84 (quintuplet, 6.0, 1H)	3.84 (m, 1H)
12	3.82 (s, 3H)	3.83 (s, 3H)
13	3.80-3.70 (br, 1H)	3.70 (m, 1H)
14	3.74 (br q, 5.4, 1H)	3.65 (br s, 1H)
15	1.27 (d, 6.2, 3H)	1.28 (d, 6.2, 3H)



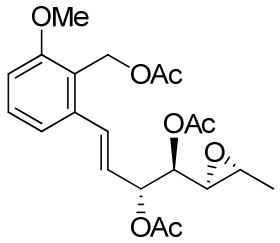
(+)-varitriol (**1**)

1 δ_C [ppm]		
S.No	**Natural (100 MHz, CD_3COCD_3)**	**Synthetic (500 MHz, CD_3COCD_3)**
1	158.9	158.9
2	139.0	139.0
3	132.3	132.4
4	129.4	129.4
5	129.3	129.3
6	127.9	128.0
7	119.3	119.3
8	110.7	110.6
9	85.2	85.3
10	80.1	80.0
11	77.2	77.2
12	76.5	76.5
13	56.0	56.0
14	55.5	55.5
15	19.5	19.5

^{1}H and ^{13}C NMR tabular comparison between the derivative reported and synthetic triacetylvarioxirane **(16)** in $CDCl_3$:

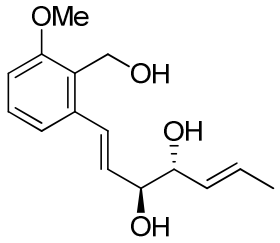


16 δ_H [ppm] (multiplicity; *J* [Hz])		
S.No	**Natural (300 MHz, $CDCl_3$)**	**Synthetic (300 MHz, $CDCl_3$)**
1	7.31 (t, 8.0, 1H)	7.31 (t, 8.3, 1H)
2	7.11 (br d, 8.0, 1H)	7.11 (d, 8.3, 1H)
3	6.98 (br d, 15.8, 1H)	6.98 (d, 15.8, 1H)
4	6.86 (dd, 8.0, 1.0, 1H)	6.86 (d, 8.3, 1H)
5	6.14 (dd, 15.8, 7.5, 1H)	6.14 (dd, 15.8, 7.5, 1H)
6	5.70 (ddd, 7.5, 3.7, 1.2 1H)	5.70 (ddd, 7.5, 3.7, 1.5 1H)
7	5.26 (d, 1.2, 2H)	5.26 (s, 2H)
8	4.89 (dd, 6.0, 3.7, 1H)	4.90 (dd, 6.0, 3.7, 1H)
9	3.84 (s, 3H)	3.84 (s, 3H)
10	3.02 (dq, 5.2, 2.1, 1H)	3.03 (dq, 5.3, 2.2, 1H)
11	2.85 (dd, 6.0, 2.1, 1H)	2.85 (dd, 6.0, 2.2, 1H)
12	2.12 (s, 3H)	2.12 (s, 3H)
13	2.09 (s, 3H)	2.09 (s, 3H)
14	2.06 (s, 3H)	2.07 (s, 3H)
15	1.29 (d, 5.2, 3H)	1.30 (d, 5.3, 3H)

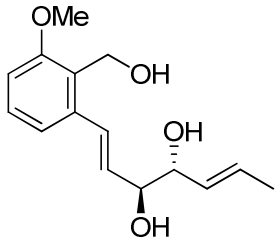


16 δ_C [ppm]		
S.No	**Natural (100 MHz, $CDCl_3$)**	**Synthetic (100 MHz, $CDCl_3$)**
1	171.1	171.0
2	169.9	169.8
3	169.8	169.7
4	158.6	158.4
5	138.4	138.2
6	132.0	131.9
7	131.9	131.7
8	130.0	129.9
9	126.0	125.8
10	119.0	118.8
11	110.6	110.4
12	73.8	73.7
13	73.2	73.1
14	57.6	57.5
15	56.0	55.9
16	-	55.8
17	53.0	52.9
18	27.1	-
19	21.1	21.0
20	21.0	20.9
21	20.9	20.8
22	17.2	17.1

^{1}H and ^{13}C NMR tabular comparison between the natural **3** and synthetic ***ent*-3** in $CDCl_3$:



***ent*-3 δ_H [ppm] (multiplicity; *J* [Hz])**		
S.No	**Natural (100 MHz, $CDCl_3$)**	**Synthetic (500 MHz, $CDCl_3$)**
1	7.18 (t, 8.0, 1H)	7.18 (t, 8.0, 1H)
2	7.00 (d, 8.0, 1H)	7.01 (d, 8.0,1H)
3	6.94(d, 16.0, 1H)	6.94 (d, 16.0, 1H)
4	6.76 (d, 8.0, 1H)	6.76 (d, 8.0, 1H)
5	6.06 (dd, 16.0, 1H)	6.06 (dd, 16.0, 4.5, 1H)
6	5.74 (dq, 15.0, 6.0, 1H)	5.74 (dq, 15.2, 6.4, 1H)
7	5.45 (dd, 15.0,6.0, 1H)	5.48 (dd, 15.2,4.5, 1H)
8	4.72 (s, 2H)	4.73 (ABq, 12.0, 2H)
9	4.24 (m, 1H)	4.24 (t, 6.4, 1H)
10	4.12 (m, 1H)	4.12 (m, 1H)
11	3.80 (s, 3H)	3.80(s, 3H)
12	3.00-2.68 (br, 2H)	2.60 (br s, 2H)1.
13	1.69 (d, 6.0, 3H)	1.67 (d, 6.4, 3H)



ent-3 δ_C [ppm]		
S.No	**Natural ($CDCl_3$)**	**Synthetic (125 MHz, $CDCl_3$)**
1	159.2	159.2
2	139.6	139.2
3	132.8	132.6
4	131.5	131.2
5	130.0	130.9
6	129.7	130.4
7	128.8	130.2
8	127.0	127.4
9	119.6	120.6
10	110.6	110.0
11	76.8	76.9
12	-	76.7
13	56.0	57.7
14	55.5	57.0
15	18.0	19.2