Supporting Information

Selective demethylation and debenzylation of aryl ethers by magnesium iodide under solvent-free conditions and its application to the total synthesis of natural products

Kai Bao,[a,b] Aixue Fan,[a] Yi Dai,[b] Liang Zhang,[a] Weige Zhang,*[a] Maosheng Cheng[a] and Xinsheng Yao*[b]

[a] School of Pharmaceutical Engineering, Shenyang Pharmaceutical University
[b] Institute of Traditional Chinese Medicine & Natural Products, Jinan University

Tel: +86 24 23986422, +86 20 85225849; E-mail: zhangweige2000@sina.com, yaoxinsheng@vip.tom.com

Table of Contents **Page No.**

1-(4-hydroxy-3,5-dimethoxyphenyl)ethanone (2b)

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.25 (s, 2H, 2,6-H), 5.93 (s, 1H, OH), 3.96 (s, 6H, CH_3O), 2.57 (s, 3H, CH_3CO); MS (ESI, *m/z*): 195 [M-H$^-$]; data consistent with the literature.[1]

4-hydroxy-3,5-dimethoxybenzoic acid (2c)

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.39 (s, 2H, 2,6-H), 3.96 (s, 6H, CH_3O); MS (ESI, *m/z*): 197 [M-H$^-$]; data consistent with the literature.[2]

ethyl 4-hydroxy-3,5-dimethoxybenzoate (2d)

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.33 (s, 2H, 2,6-H), 5.88 (s, 1H, OH), 3.95 (s, 6H, CH_3O), 3.36 (q, 2H, *J* = 7.1 Hz, CH_2), 1.40 (t, 3H, *J* = 7.1 Hz, $CH_2\underline{C}H_3$); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 166.4 (CO), 146.6 (C-3/C-5), 139.2 (C-4), 121.5 (C-1), 106.7 (C-2/C-6), 61.0 ($\underline{C}H_2CH_3$), 56.5 (C-3/C-5 OCH_3), 14.4 ($CH_2\underline{C}H_3$); MS (ESI, *m/z*): 225 [M-H$^-$]; data consistent with the literature.[3]

2,6-dimethoxy-4-methylphenyl acetate (2f')

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 6.41 (s, 2H, 3,5-H), 3.78 (s, 6H, CH_3O), 2.32 (s, 3H, 4-CH_3), 2.31 (s, 3H, CH_3CO); MS (ESI, *m/z*): 223 [M+Na$^+$]; data consistent with the literature.[4]

2-hydroxybenzaldehyde (4a)

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 11.01 (s, 1H, OH), 9.85 (s, 1H, CHO), 7.46-7.54 (m, 2H, 4,6-H), 6.94-7.01 (m, 2H, 3,5-H); MS (ESI, *m/z*): 121 [M-H$^-$]; data consistent with the literature.[5]

3-hydroxybenzaldehyde (4b)

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 9.96 (s, 1H, CHO), 7.40-7.47 (m, 2H, Ar-H), 7.36 (m, 1H, Ar-H), 7.14 (m, 1H, 4-H), 5.55 (s, 1H, OH); MS (ESI, *m/z*): 243 [2M-H$^-$]; data consistent with the literature.[6]

4-hydroxybenzaldehyde (4c)

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 9.87 (s, 1H, CHO), 7.81 (d, 2H, *J* = 8.4 Hz, 2,6-H), 6.96 (m, 2H, 3,5-H), 5.83 (s, 1H, OH), 5.55 (s, 1H, OH); MS (ESI, *m/z*): 243 [2M-H$^-$]; data consistent with the literature.[7]

1-(2-hydroxy-3,4-dimethoxyphenyl)ethanone (4d)

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 12.56 (s, 1H, OH), 7.50 (d, 2H, *J* = 9.0 Hz, 6-H), 6.50 (d, 2H, *J* = 9.0 Hz, 5-H), 3.94 (s, 3H, 4-CH_3O), 3.89 (s, 3H, 3-CH_3O), 2.58 (s, 3H, CH_3CO); MS (ESI, *m/z*): 197 [M+H$^+$]; data consistent with the literature.[8]

2-hydroxy-3-methoxybenzaldehyde (4e)

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 11.87 (s, 1H, OH), 9.92 (s, 1H, CHO), 7.18 (dd, 1H, *J* = 7.8 Hz, 1.3 Hz, 6-H), 7.12 (dd, 1H, *J* = 7.5 Hz, 0.8 Hz, 4-H), 6.97 (dd, 1H, *J* = 7.9 Hz, 7.8 Hz, 5-H), 3.92 (s, 3H, CH_3O); MS (ESI, *m/z*): 151 [M-H$^-$]; data consistent with the literature.[9]

4-hydroxy-3-methoxybenzaldehyde (4f)

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 9.83 (s, 1H, CHO), 7.41-7.44 (m, 2H, 2,6-H), 7.04 (d, 1H, *J* = 8.5 Hz, 5-H), 6.21 (s, 1H, OH), 3.97 (s, 3H, CH_3O); MS (ESI, *m/z*): 151 [M-H$^-$]; data consistent with the literature.[10]

2-hydroxybenzoic acid (4h)

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 10.35 (s, 1H, OH), 7.94 (dd, 1H, *J* = 8.0 Hz, 1.6 Hz, 6-H), 7.54 (m, 1H, 4-H), 7.02 (d, 1H, *J* = 8.4 Hz, 3-H), 6.95 (m, 1H, 5-H); MS (ESI, *m/z*): 139.0 [M+H$^+$], 136.8 [M-H$^-$]; data consistent with the literature.[11]

3-hydroxy-4-methoxybenzaldehyde (6a)

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 9.84 (s, 1H, CHO), 7.43-7.44 (m, 2H, 2,6-H), 6.97 (d, 1H, *J* = 8.6 Hz, 5-H), 5.79 (s, 1H, OH), 3.99 (s, 3H, CH_3O); MS (ESI, *m/z*): 151 [M-H$^-$]; data consistent with the literature.[12]

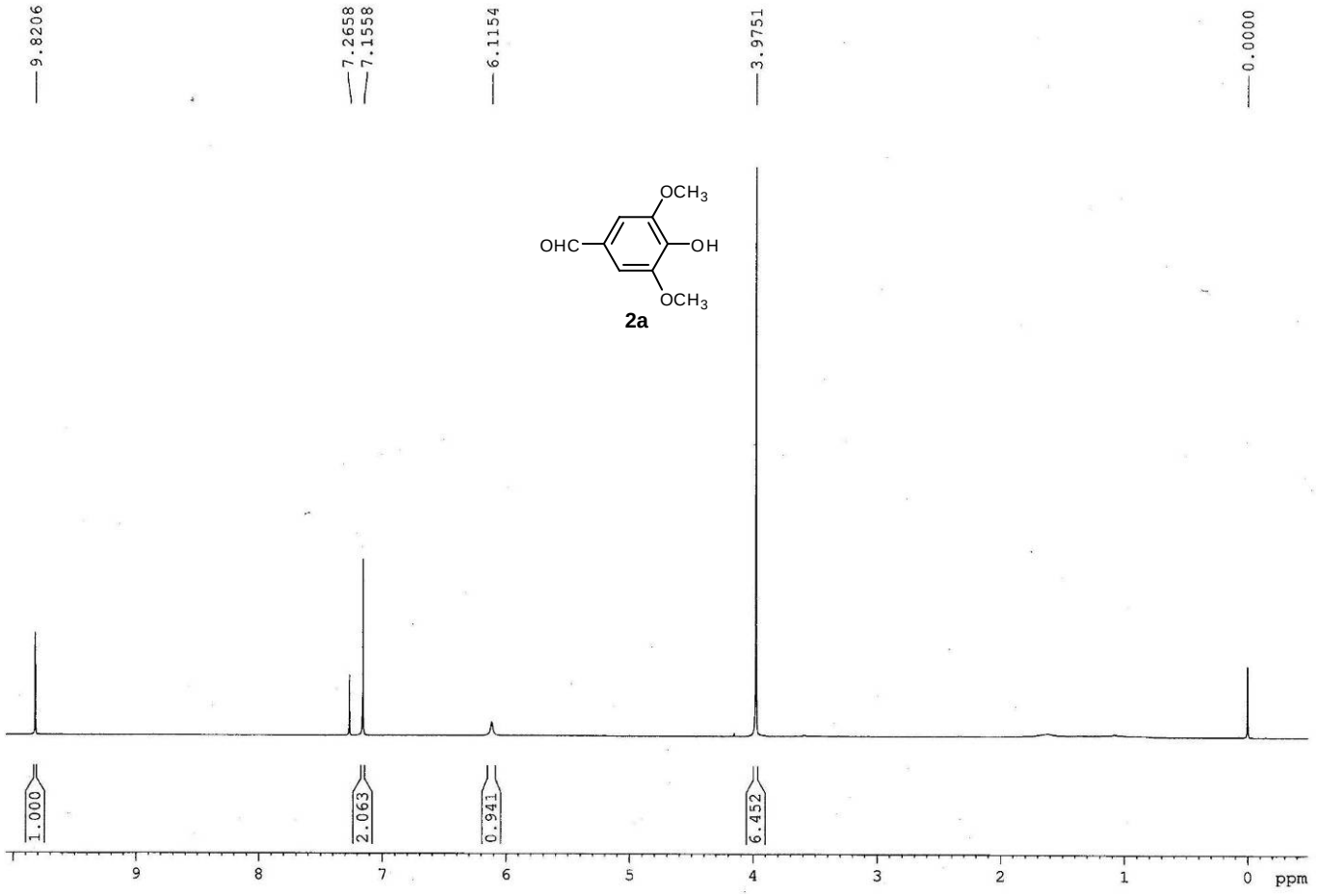
4-hydroxy-3-methoxybenzoic acid (6c)

^{1}H NMR (300 MHz, DMSO, TMS): δ, 7.42 (m, 2H, 2,6-H), 6.83 (d, 1H, *J* = 7.7 Hz, 5-H), 3.79 (s, 3H,

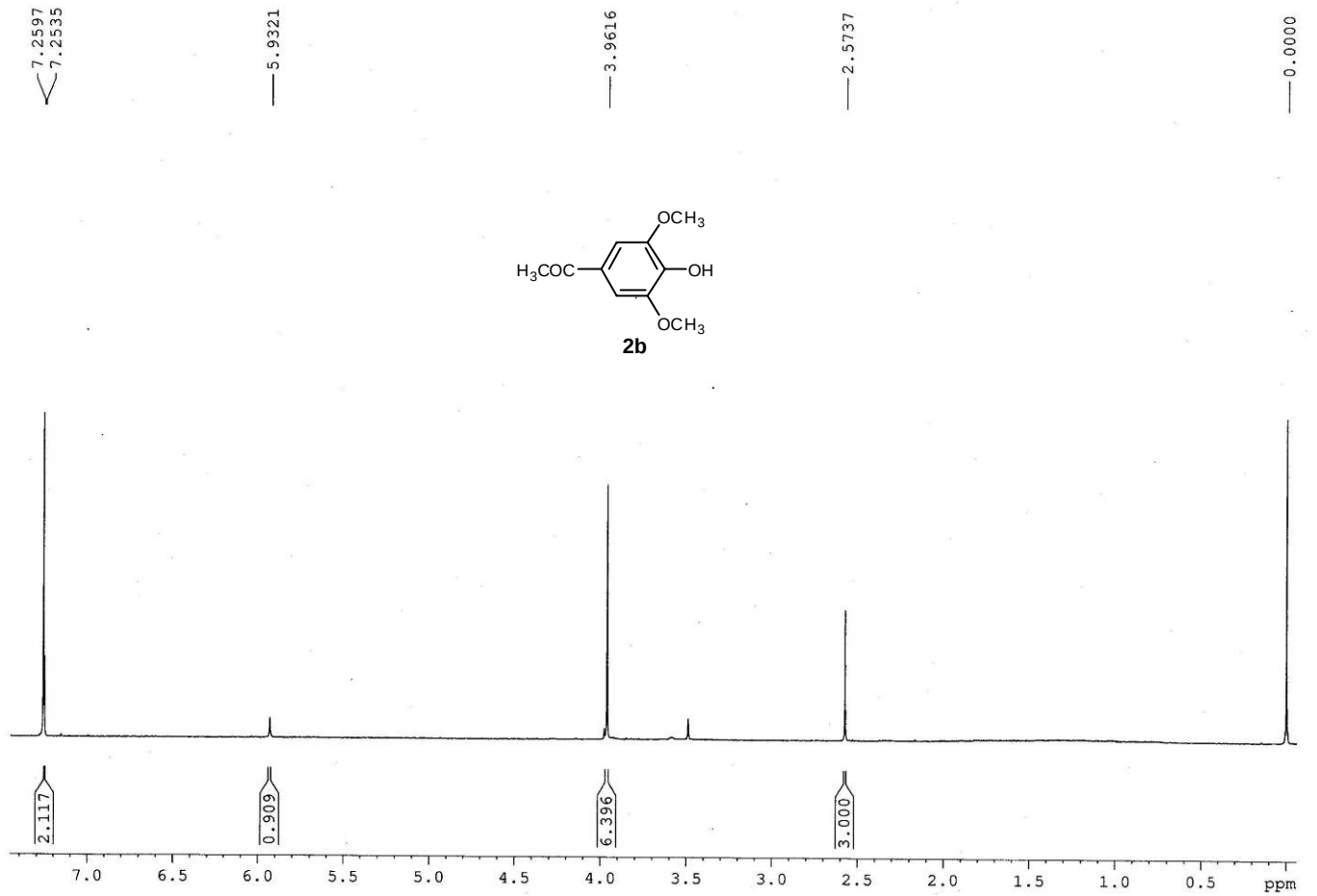
CH_3O); MS (ESI, *m/z*): 167 [M-H^-]; data consistent with the literature.[13]

References

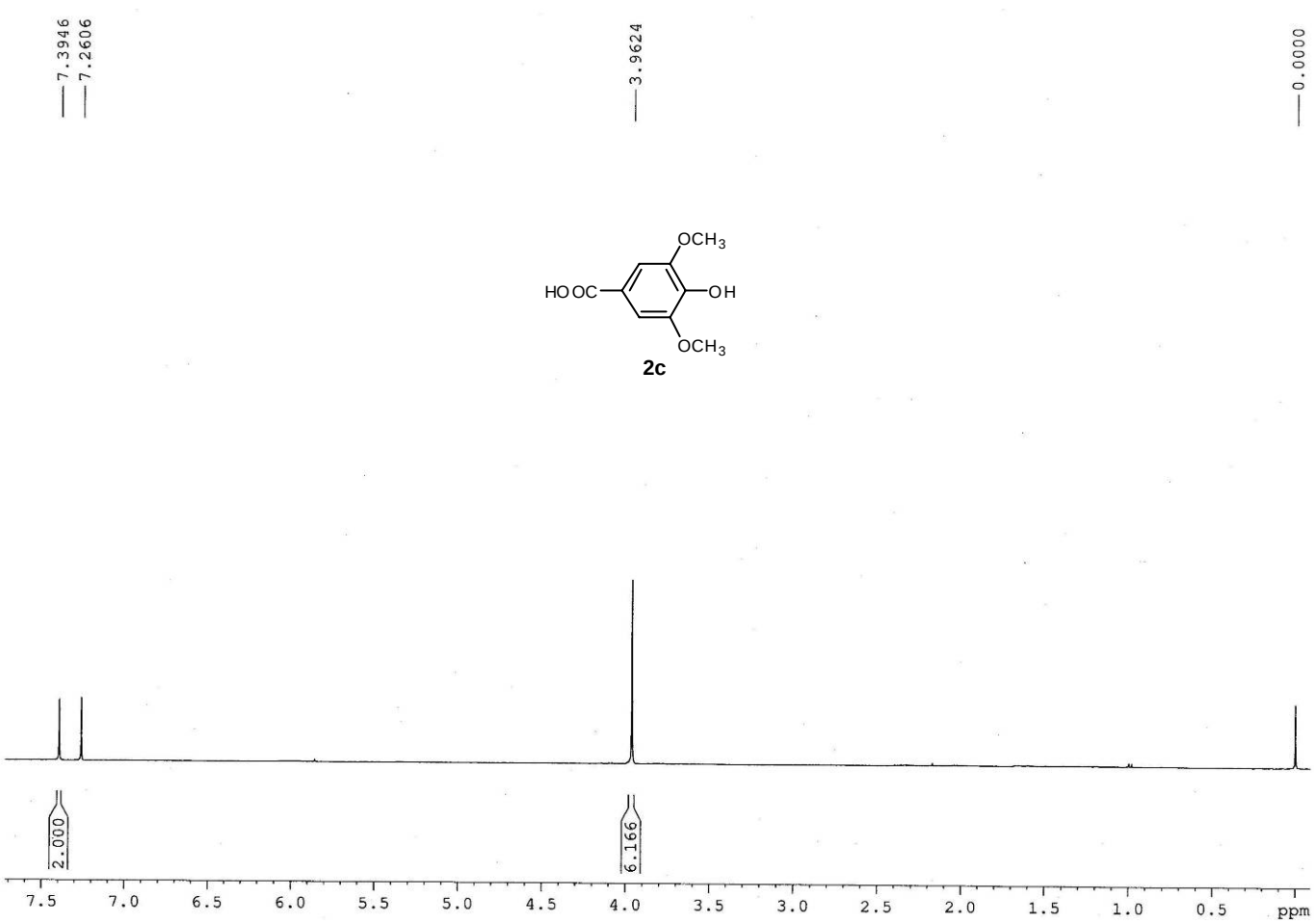
1. J. Cvengroš, S. Neufeind, A. Becker and H. G. Schmalz, *Synlett*., 2008, **13**, 1993–1998.
2. X. K. Zheng, J. Li, W. S. Feng, Y. F. Bi and C. R. Ji, *Yaoxue Xuebao*, 2003, **38**, 268–271.
3. M. T. Bogert and J. Ehrlich, *J. Am. Chem. Soc*., 1919, **41**, 798–810.
4. Y. S. Ovdov, G. M. Frolova, A. K. Dzizenko and V. I. Litvinenko, *Izv. Akad. Nauk. SSSR. Ser. Khim*., 1969, **6**, 1370–1372.
5. S. D. Kim and J. D. Kim, *J. Korean Chem. Soc*., 2003, **47**, 183–188.
6. Y.X. Zhao, Y.Zhou, K. M. O'Boyle and P. V. Murphy, *Bioorg. Med. Chem*., 2008, **16**,6333–6337.
7. J. Magano, M. H. Chen, J. D. Clark and T. Nussbaumer, *J. Org. Chem*., 2006, **71**, 7103–7105.
8. M. M. D. M. Pinto, A. A. L. Mesquita and O. R. Gottlieb, *Phytochemistry*, 1987, **26**, 2045–2048.
9. M. E. Moustafa, *Synth. React. Inorg. Met. Org. Chem*., 2003, **33**, 453–468.
10. W. K. Su and C. Jin, *Synth. Commun*., 2004, **34**, 4199–4205.
11. X. J. Li and Z. Z. Zeng, *Chem. Res. Chin. Univ*., 2006, **22**, 6–10.
12. A. Couture, E. Deniau, P. Grandclaudon and S. Lebrun, *Tetrahedron*: *Asymmetry*, 2003, **14**, 1309–1316.
13. T. Stalin and N. Rajendiran, *J. Mol. Struct*., 2006, **794**, 35–45.


9.8206
7.2658
7.1558
6.1154
3.9751
0.0000
OCH3
OHC
OH
OCH3
1.000
2.063
0.941
6.452
9
8
7
6
5
4
3
2
1
0
ppm

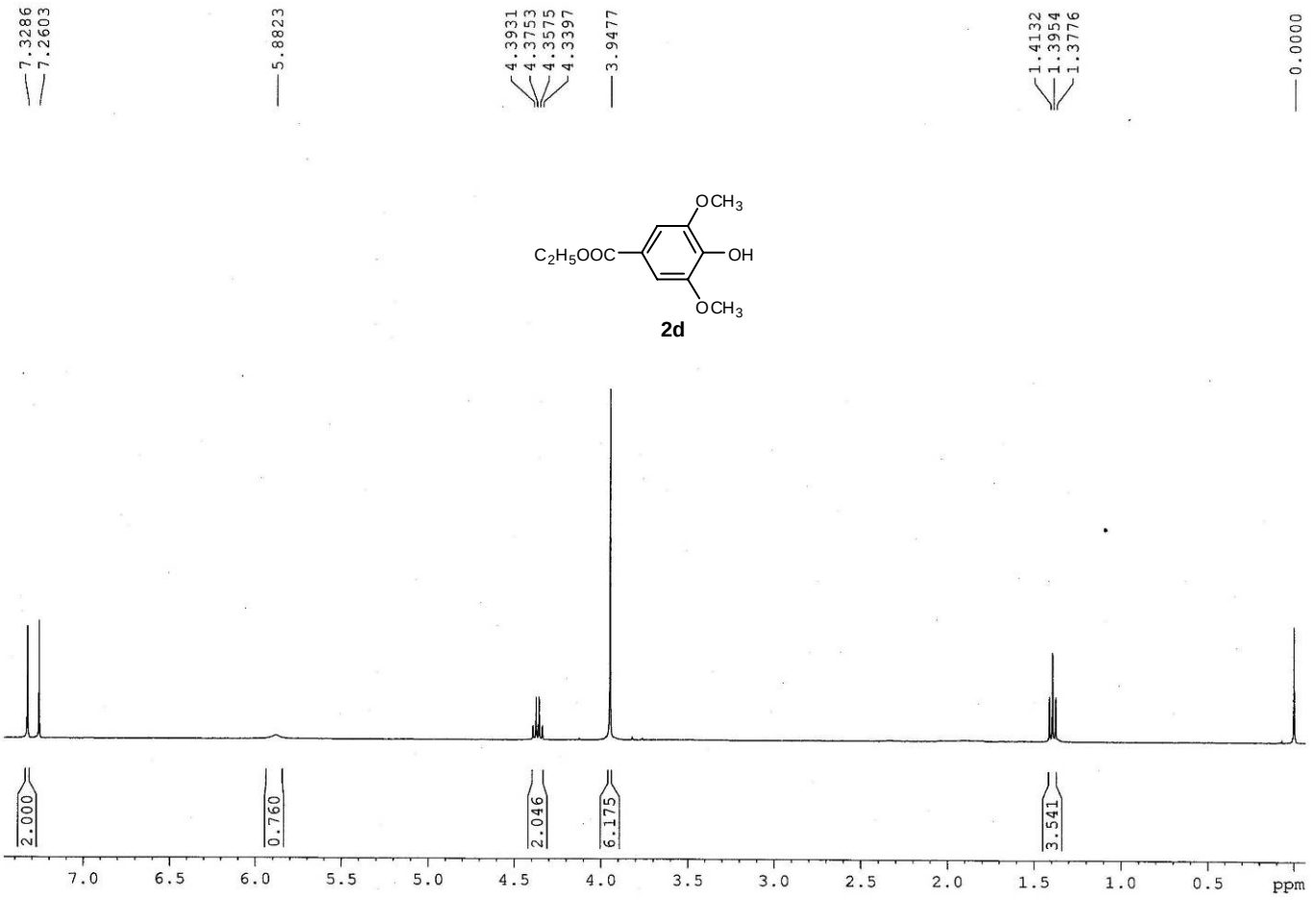
2a


7.2597
7.2535
5.9321
3.9616
2.5737
0.0000
OCH3
H3COC
OH
OCH3
2.117
0.909
6.396
3.000
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
ppm

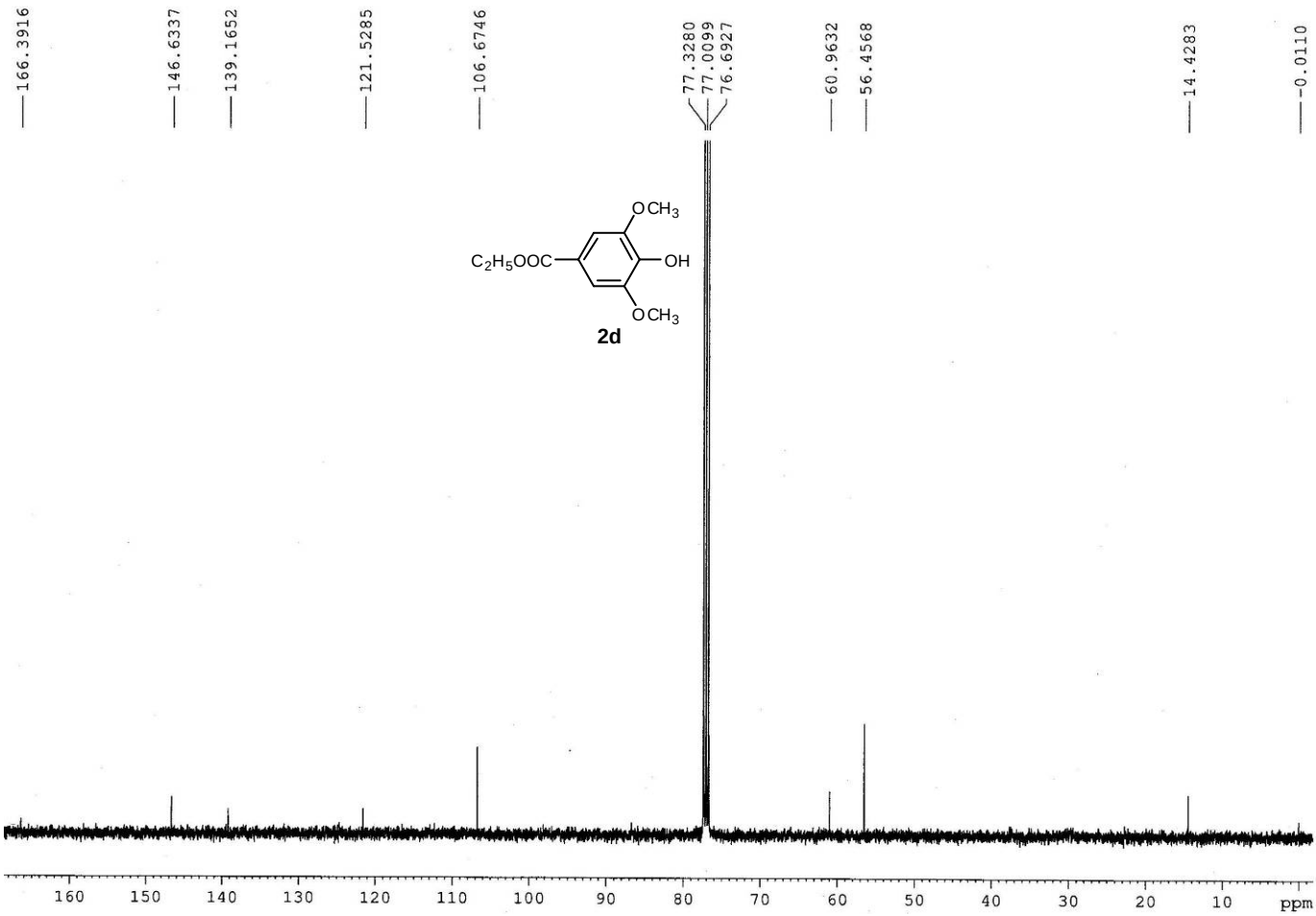
2b

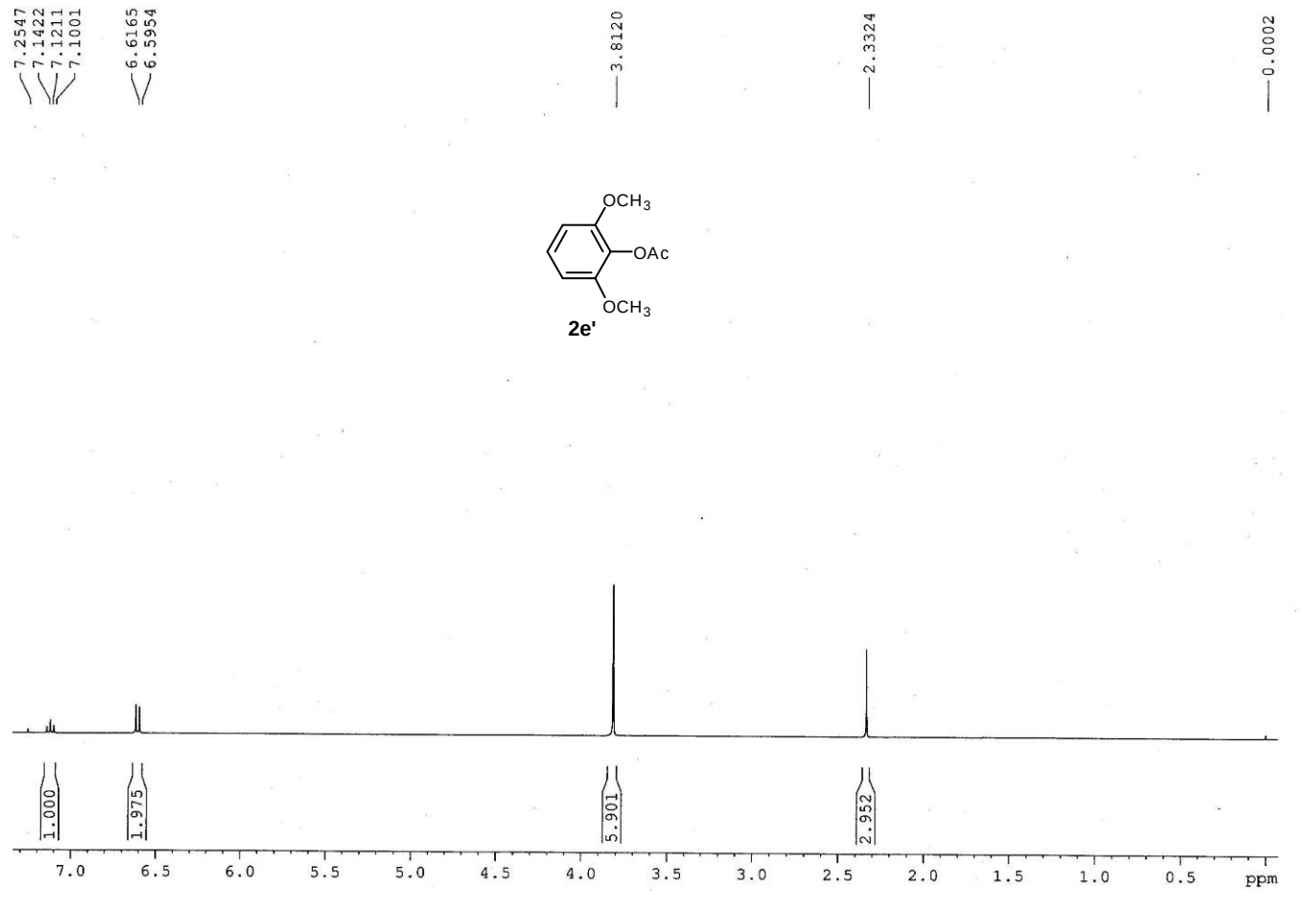

7.3946
7.2606
3.9624
0.0000
OCH3
HOOC
OH
OCH3
2.000
6.166
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

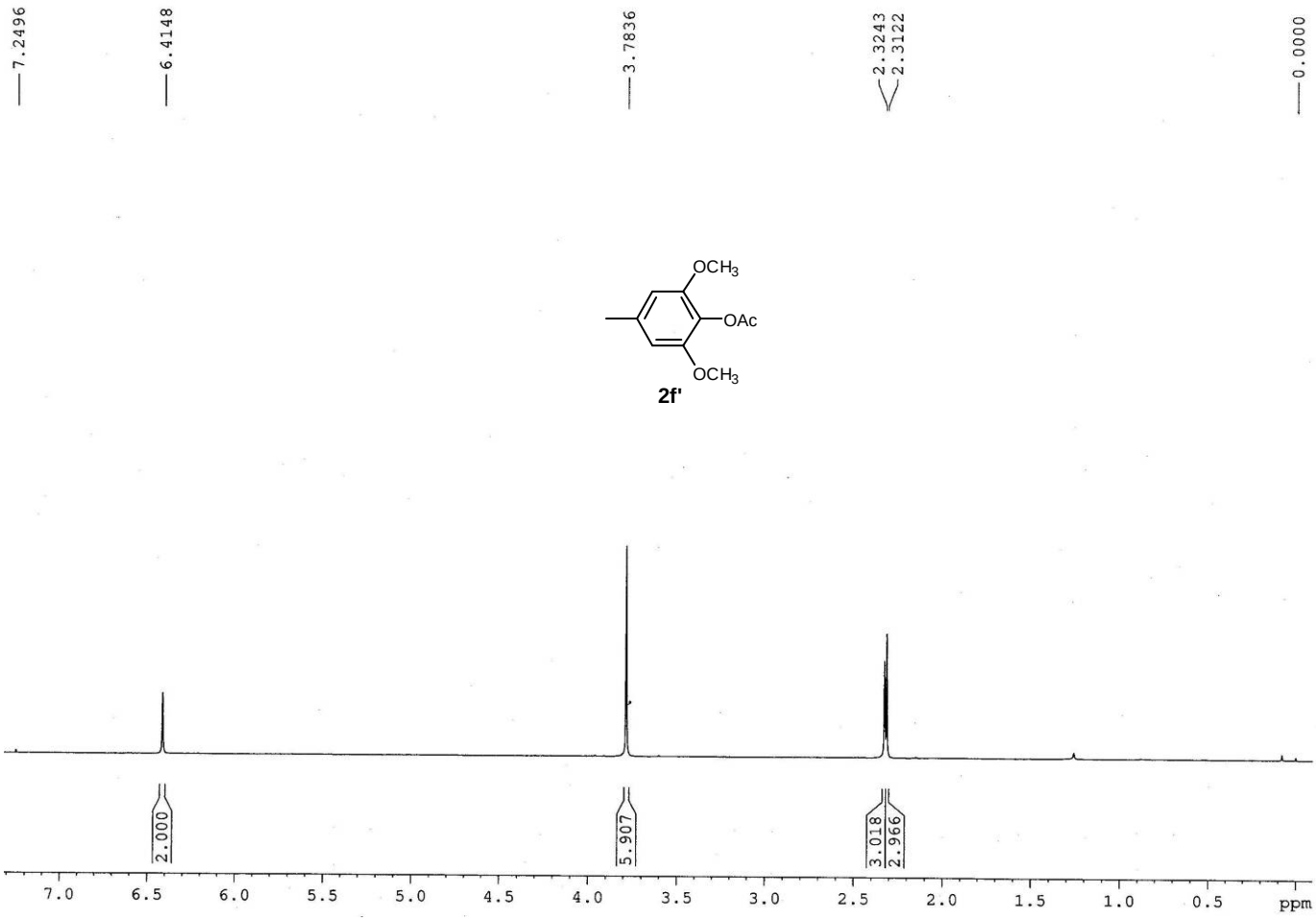
2c


7.3286
7.2603
5.8823
4.3931
4.3753
4.3575
4.3397
3.9477
1.4132
1.3954
1.3776
0.0000
OCH3
C2H5OOC
OH
OCH3
2.000
0.760
2.046
6.175
3.541
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 ppm

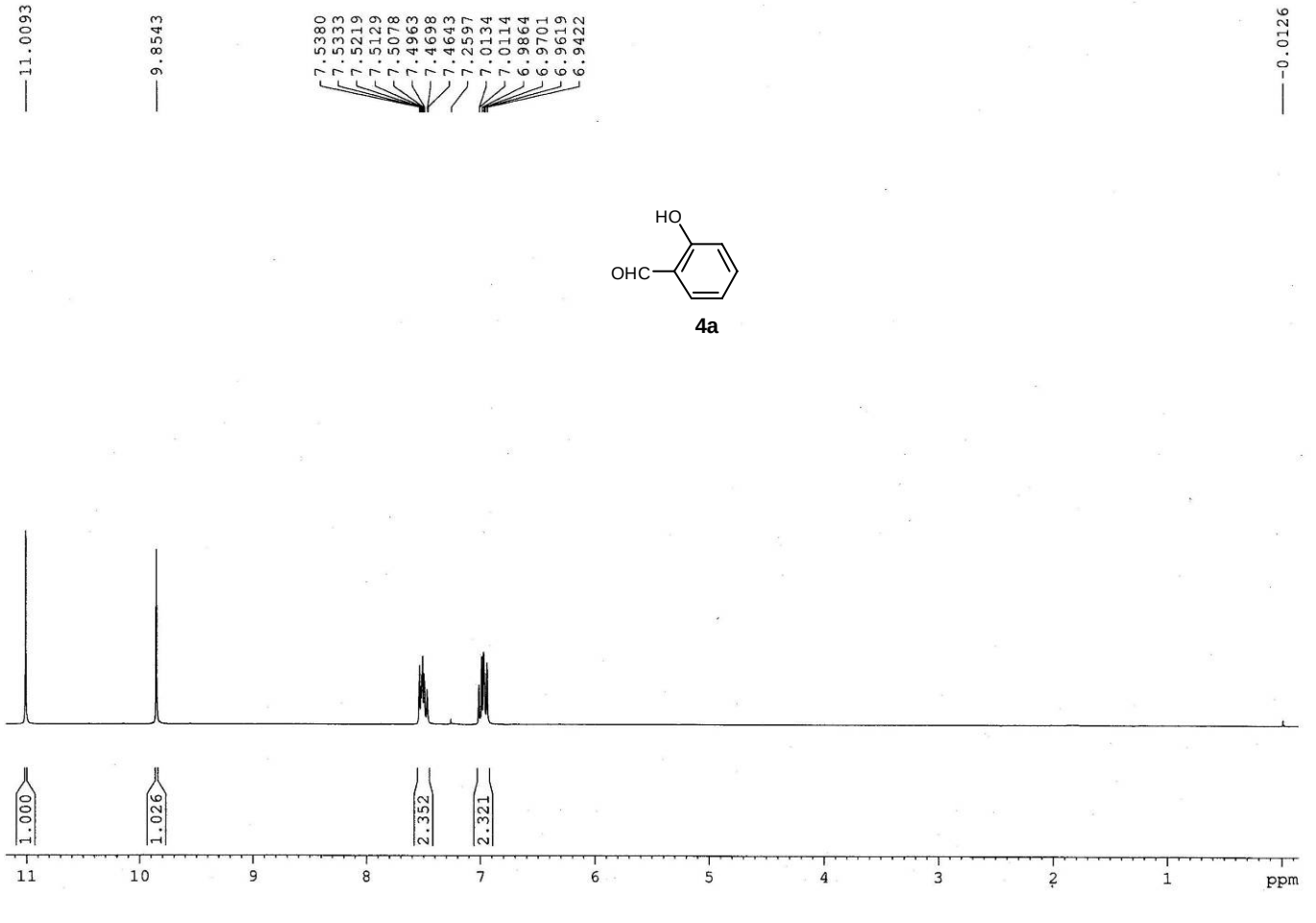
2d


166.3916
146.6337
139.1652
121.5285
106.6746
77.3280
77.0099
76.6927
60.9632
56.4568
14.4283
-0.0110
OCH3
C2H5OOC
OH
OCH3
2d
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.2547
7.1422
7.1211
7.1001
6.6165
6.5954
3.8120
2.3324
0.0002
OCH3
OAc
OCH3
2e'
1.000
1.975
5.901
2.952
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
ppm

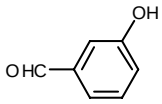

7.2496
6.4148
3.7836
2.3243
2.3122
0.0000
OCH3
OAc
OCH3
2.000
5.907
3.018
2.966
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

2f'

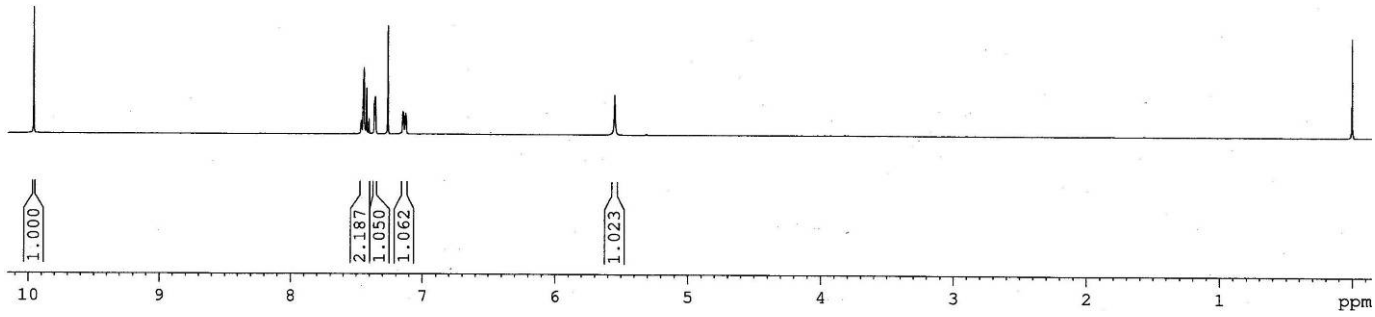

11.0093
9.8543
7.5380
7.5333
7.5219
7.5129
7.5078
7.4963
7.4698
7.4643
7.2597
7.0134
7.0114
6.9864
6.9701
6.9619
6.9422
-0.0126
HO
OHC
1.000
1.026
2.352
2.321
11
10
9
8
7
6
5
4
3
2
1
ppm

4a

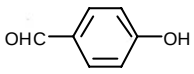

9.9587
7.4686
7.4651
7.4615
7.4498
7.4465
7.4423
7.4231
7.4044
7.3601
7.3566
7.3534
7.1510
7.1468
7.1446
7.1401
7.1323
7.1280
7.1217
5.5488
0.0000


OH
OHC

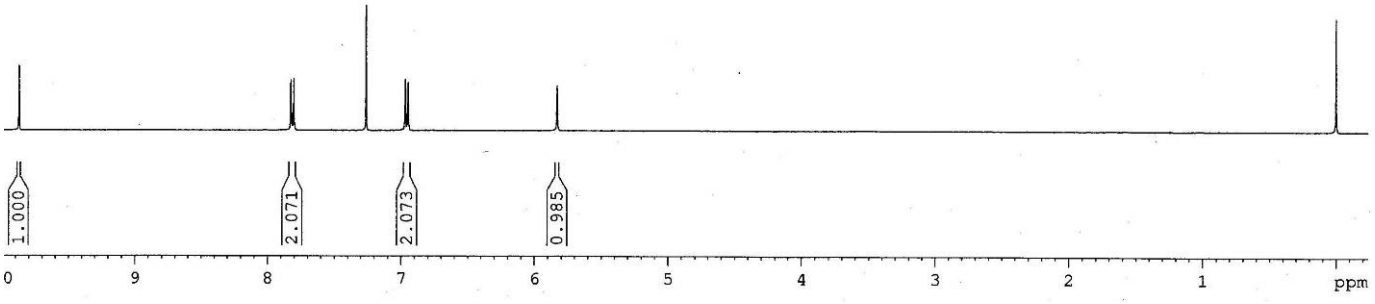
4b

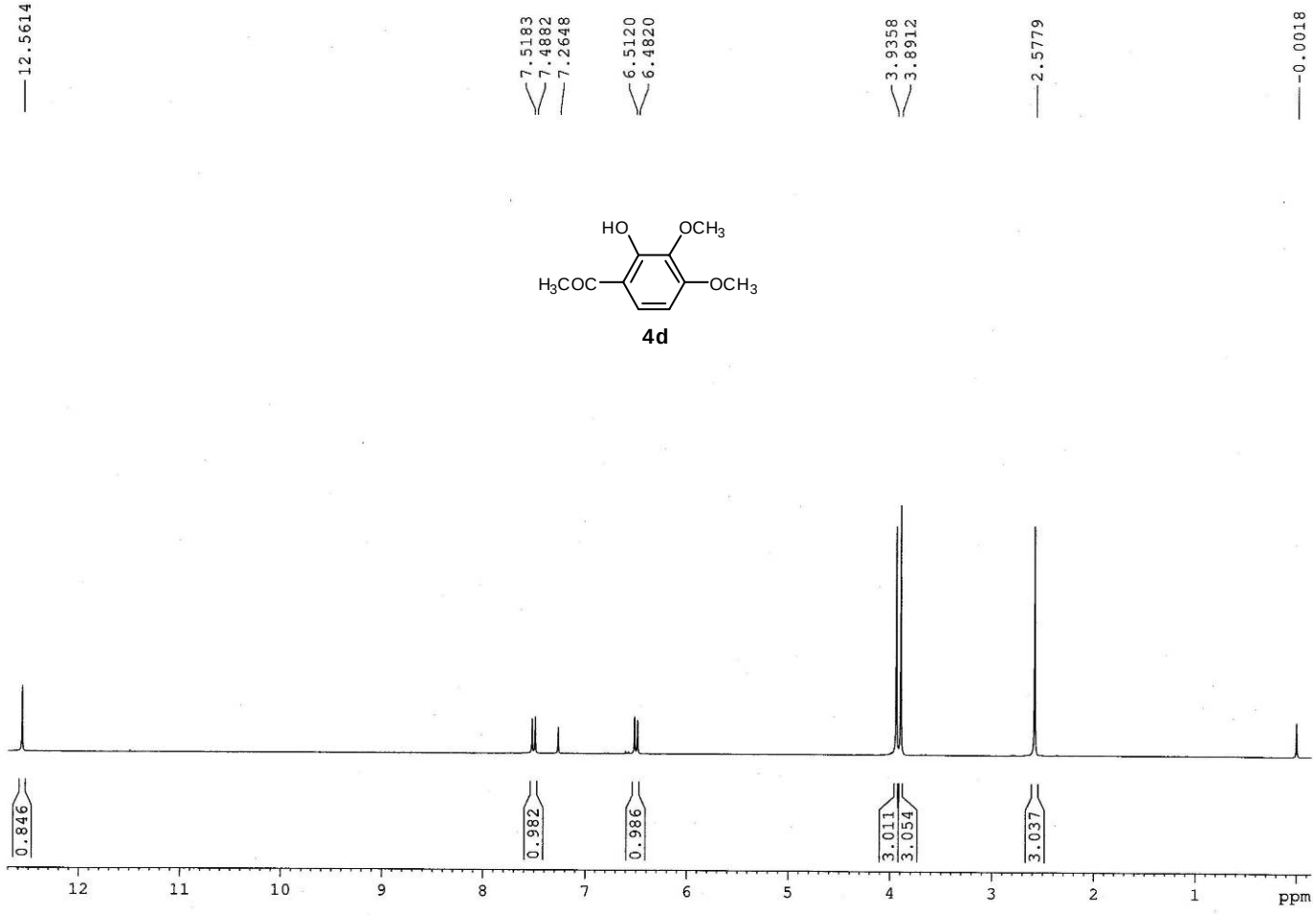

1.000
2.187
1.050
1.062
1.023
10
9
8
7
6
5
4
3
2
1
ppm

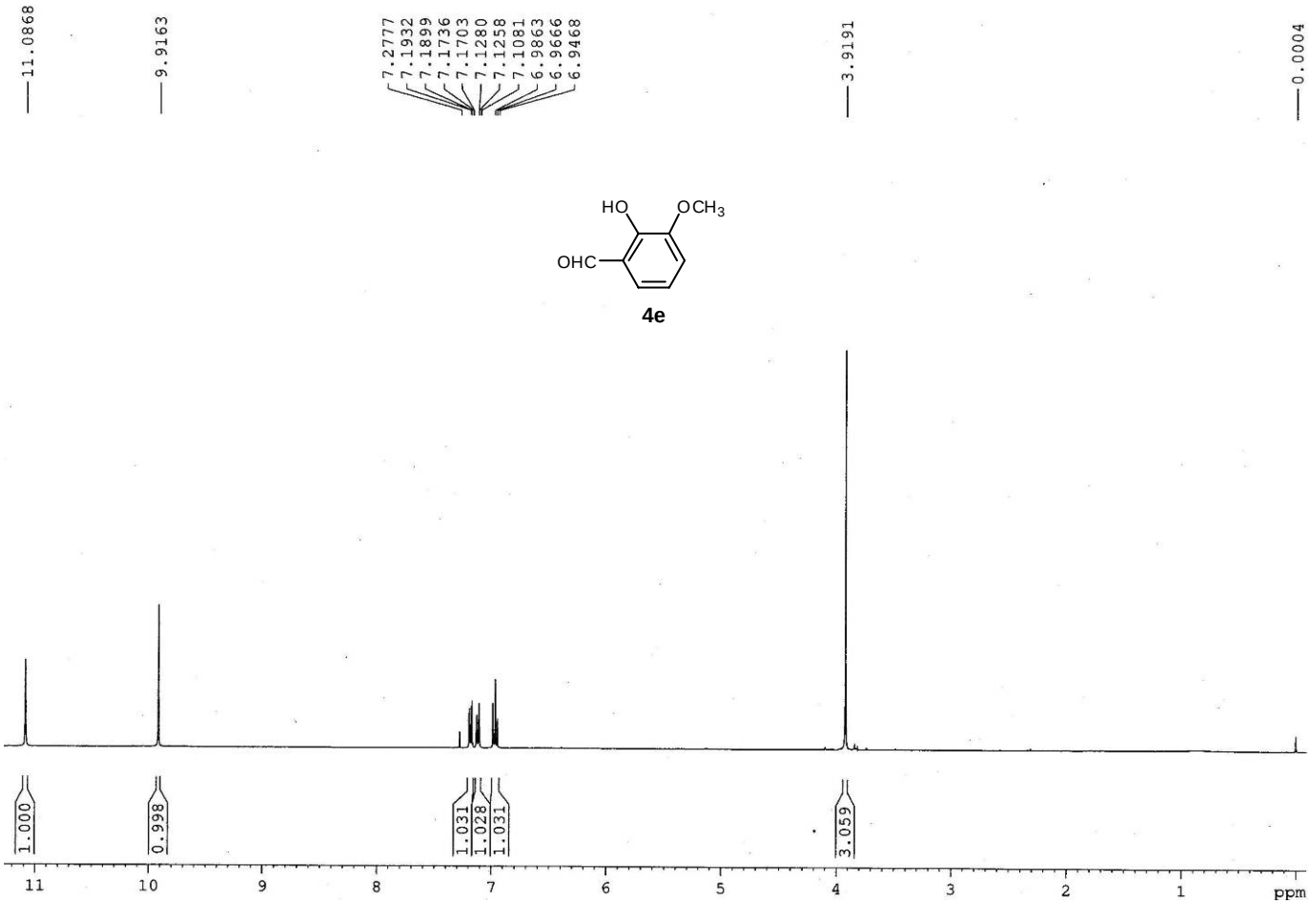

9.8740
7.8243
7.8028
7.2595
6.9679
6.9463
5.8289
-0.0003

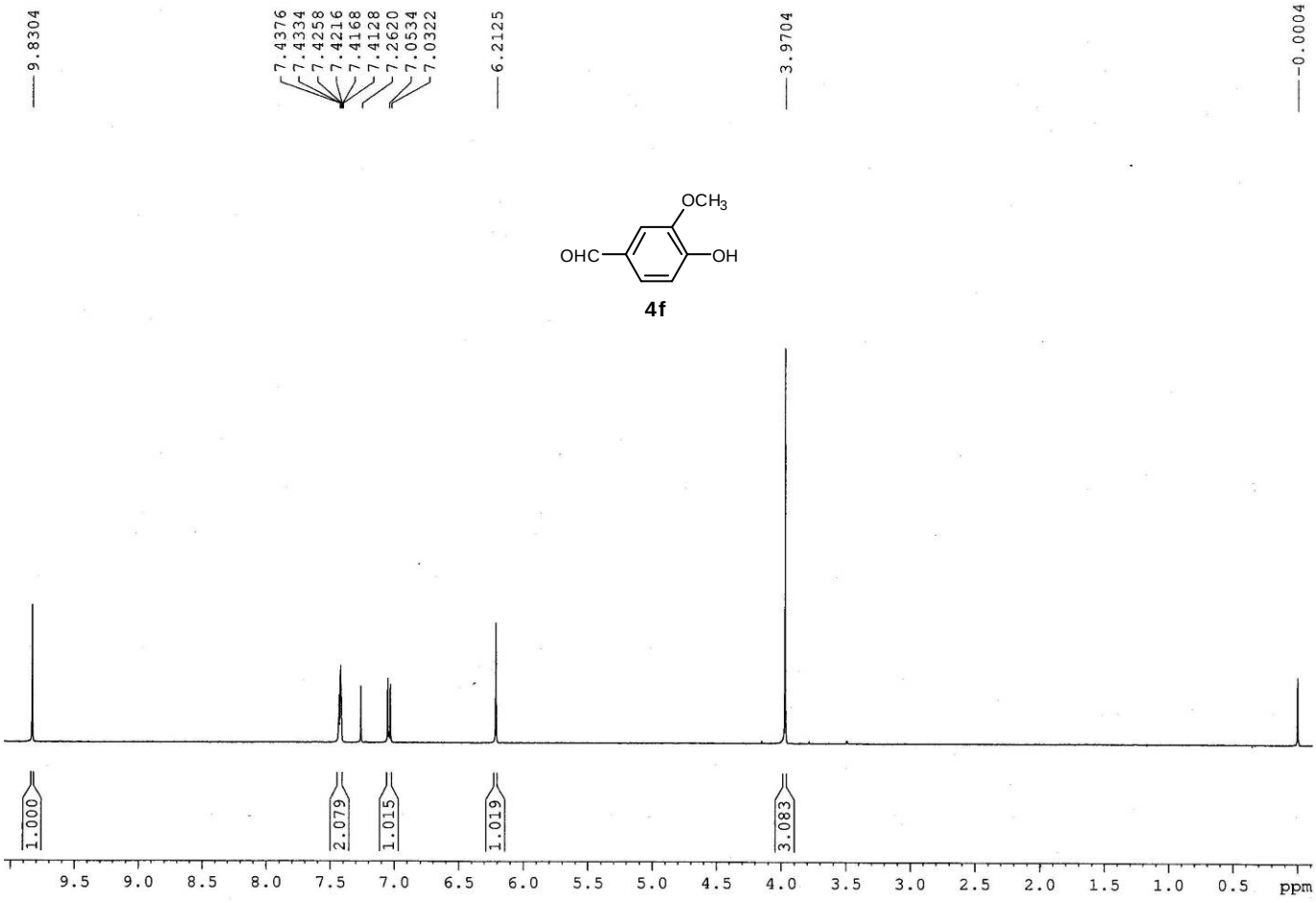

OHC
OH

4c

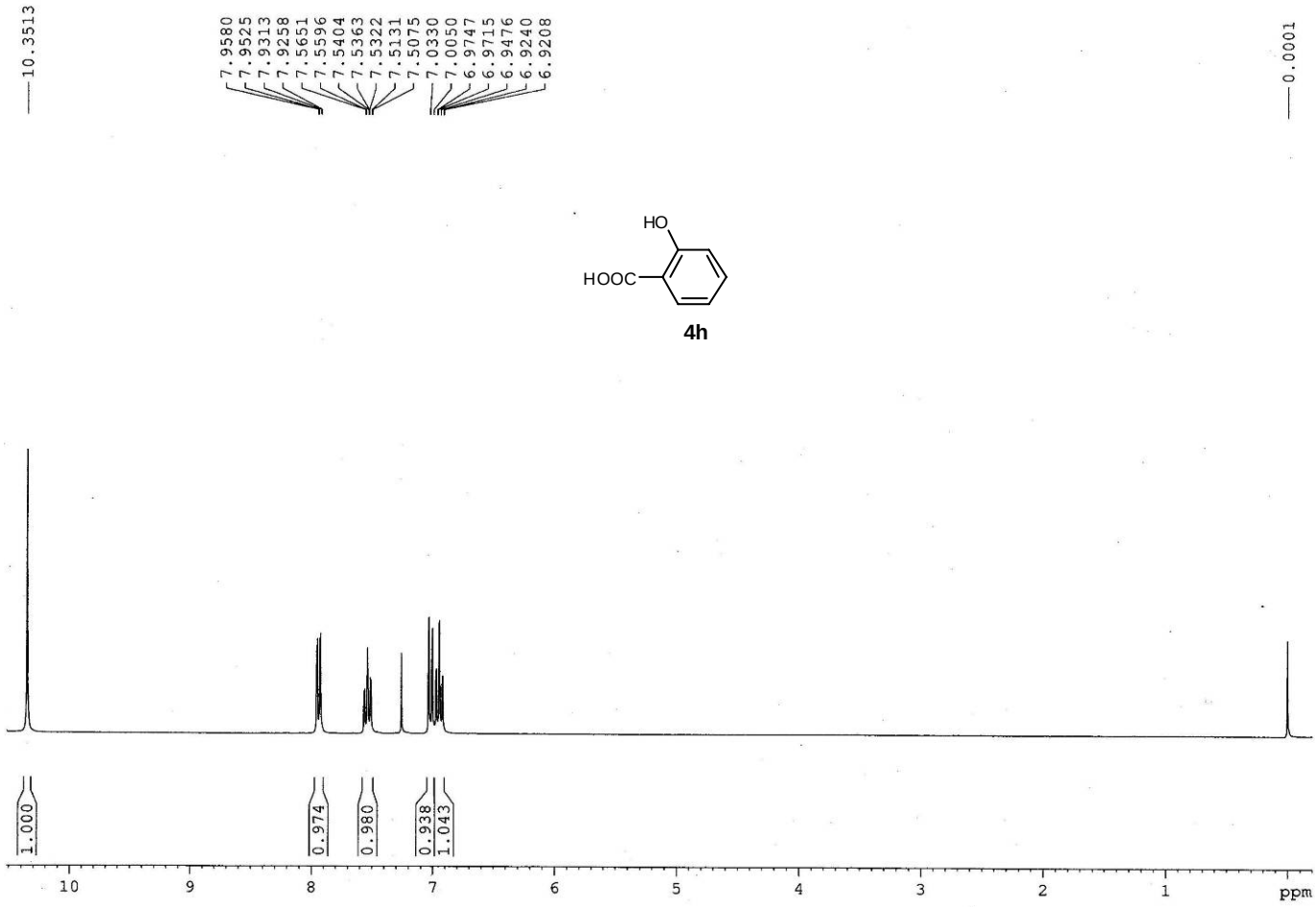

1.000
2.071
2.073
0.985
0
9
8
7
6
5
4
3
2
1
ppm


12.5614
7.5183
7.4882
7.2648
6.5120
6.4820
3.9358
3.8912
2.5779
-0.0018
HO
OCH3
H3COC
OCH3
4d
0.846
0.982
0.986
3.011
3.054
3.037
12
11
10
9
8
7
6
5
4
3
2
1
ppm

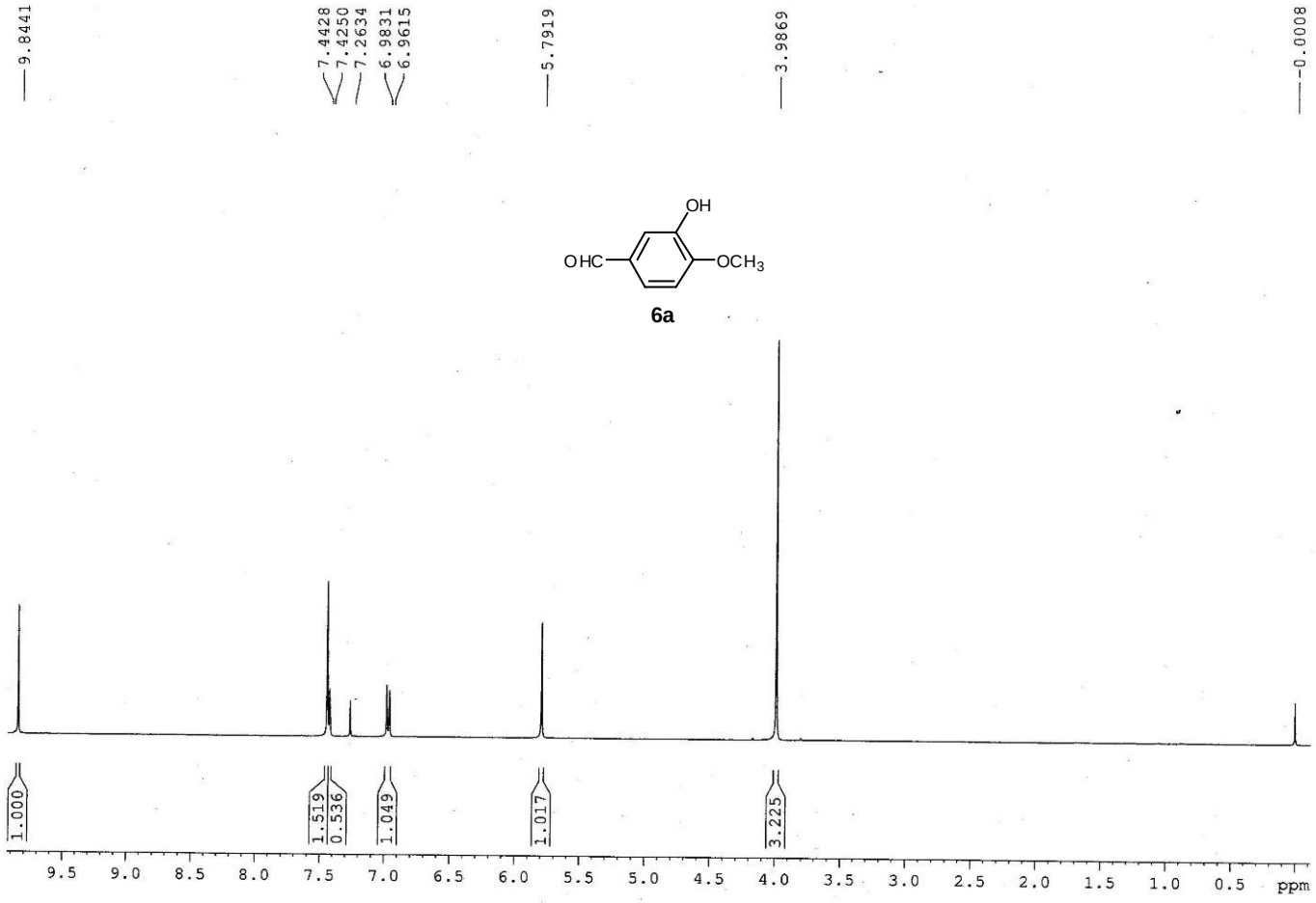

11.0868
9.9163
7.2777
7.1932
7.1899
7.1736
7.1703
7.1280
7.1258
7.1081
6.9863
6.9666
6.9468
3.9191
0.0004
HO
OCH3
OHC
4e
1.000
0.998
1.031
1.028
1.031
3.059
11
10
9
8
7
6
5
4
3
2
1
ppm


9.8304
7.4376
7.4334
7.4258
7.4216
7.4168
7.4128
7.2620
7.0534
7.0322
6.2125
3.9704
0.0004
OCH3
OHC
OH
1.000
2.079
1.015
1.019
3.083
ppm

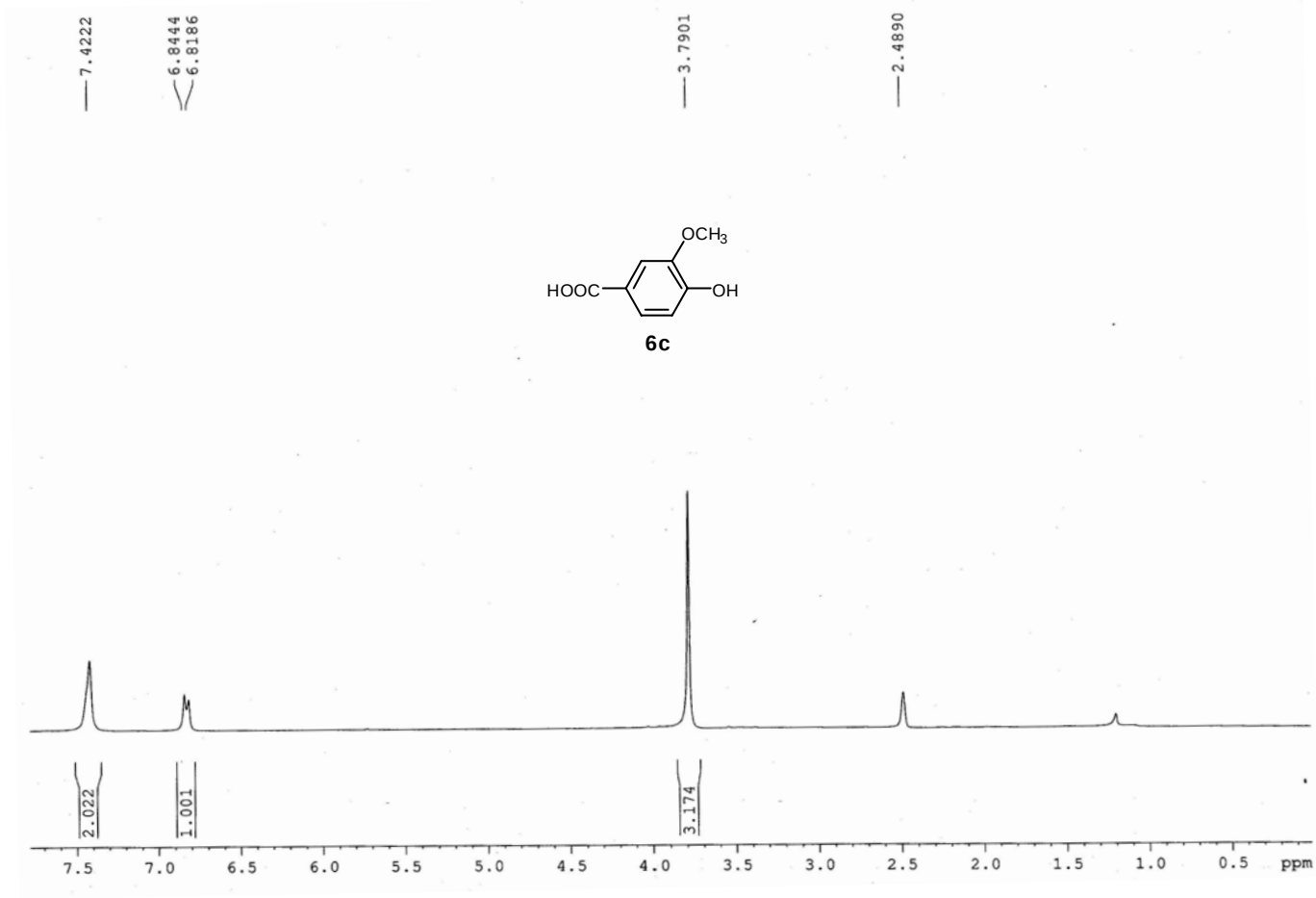
4f


10.3513
7.9580
7.9525
7.9313
7.9258
7.5651
7.5596
7.5404
7.5363
7.5322
7.5131
7.5075
7.0330
7.0050
6.9747
6.9715
6.9476
6.9240
6.9208
0.0001
HO
HOOC
1.000
0.974
0.980
0.938
1.043
ppm

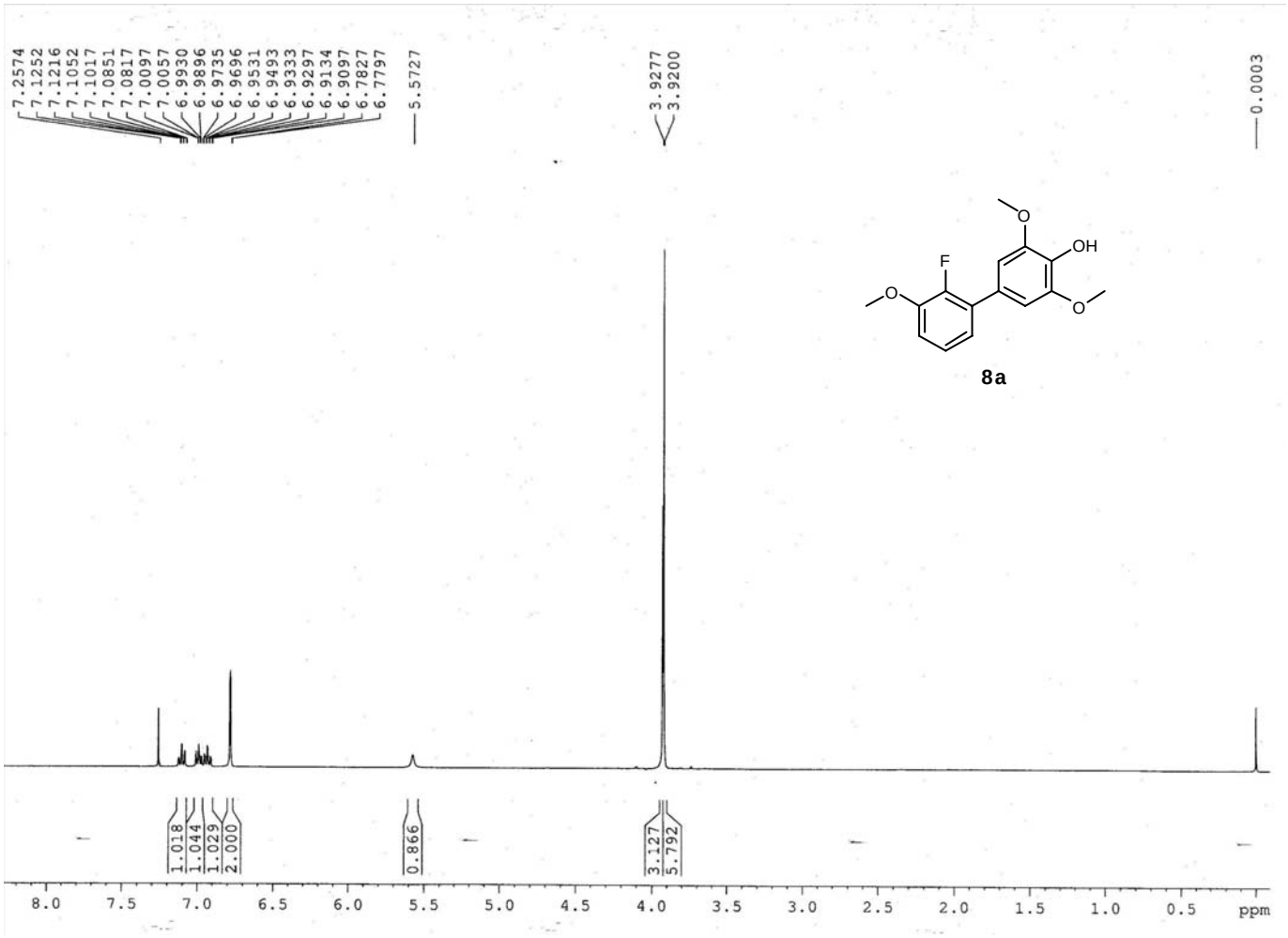
4h


9.8441
7.4428
7.4250
7.2634
6.9831
6.9615
5.7919
3.9869
0.0008
OH
OHC
OCH3
1.000
1.519
0.536
1.049
1.017
3.225
9.5 9.0 8.5 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 ppm

6a

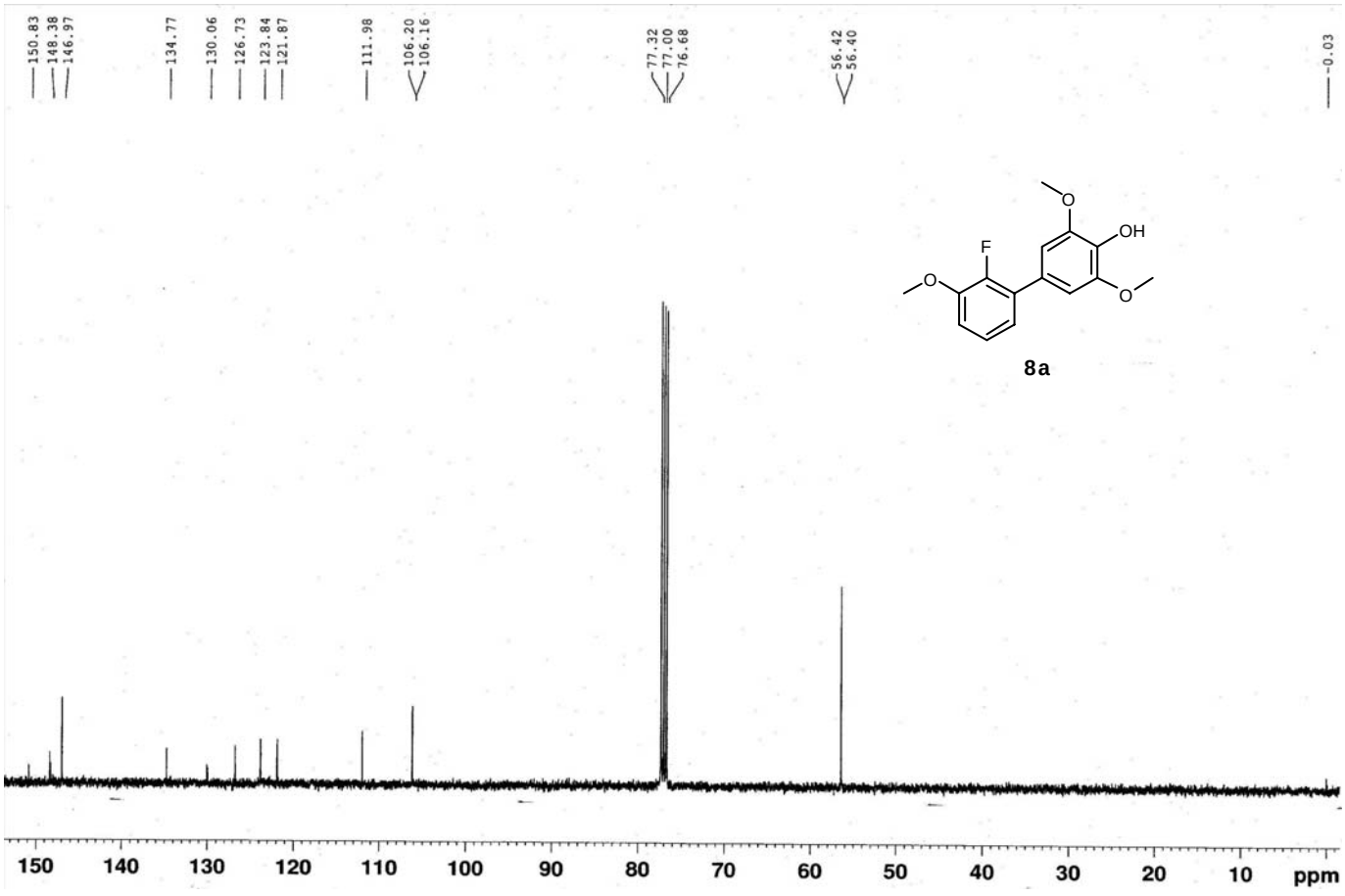

7.4222
6.8444
6.8186
3.7901
2.4890
OCH3
HOOC
OH
2.022
1.001
3.174
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

6c


7.2574
7.1252
7.1216
7.1052
7.1017
7.0851
7.0817
7.0097
7.0057
6.9930
6.9896
6.9735
6.9696
6.9531
6.9493
6.9333
6.9297
6.9134
6.9097
6.7827
6.7797
5.5727
3.9277
3.9200
0.0003
1.018
1.044
1.029
2.000
0.866
3.127
5.792
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
ppm

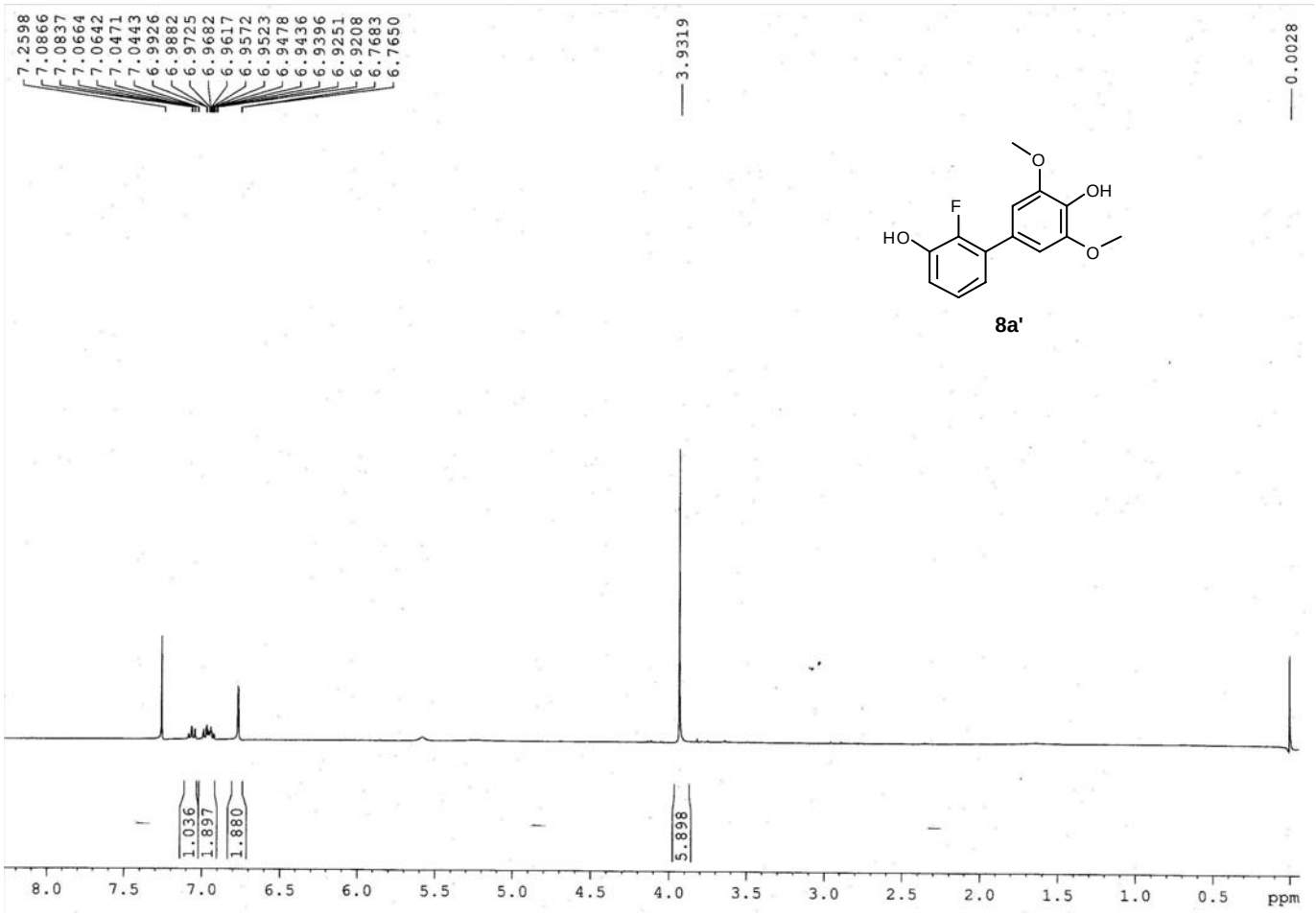
O
OH
F
O
O

8a


150.83
148.38
146.97
134.77
130.06
126.73
123.84
121.87
111.98
106.20
106.16
77.32
77.00
76.68
56.42
56.40
-0.03
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

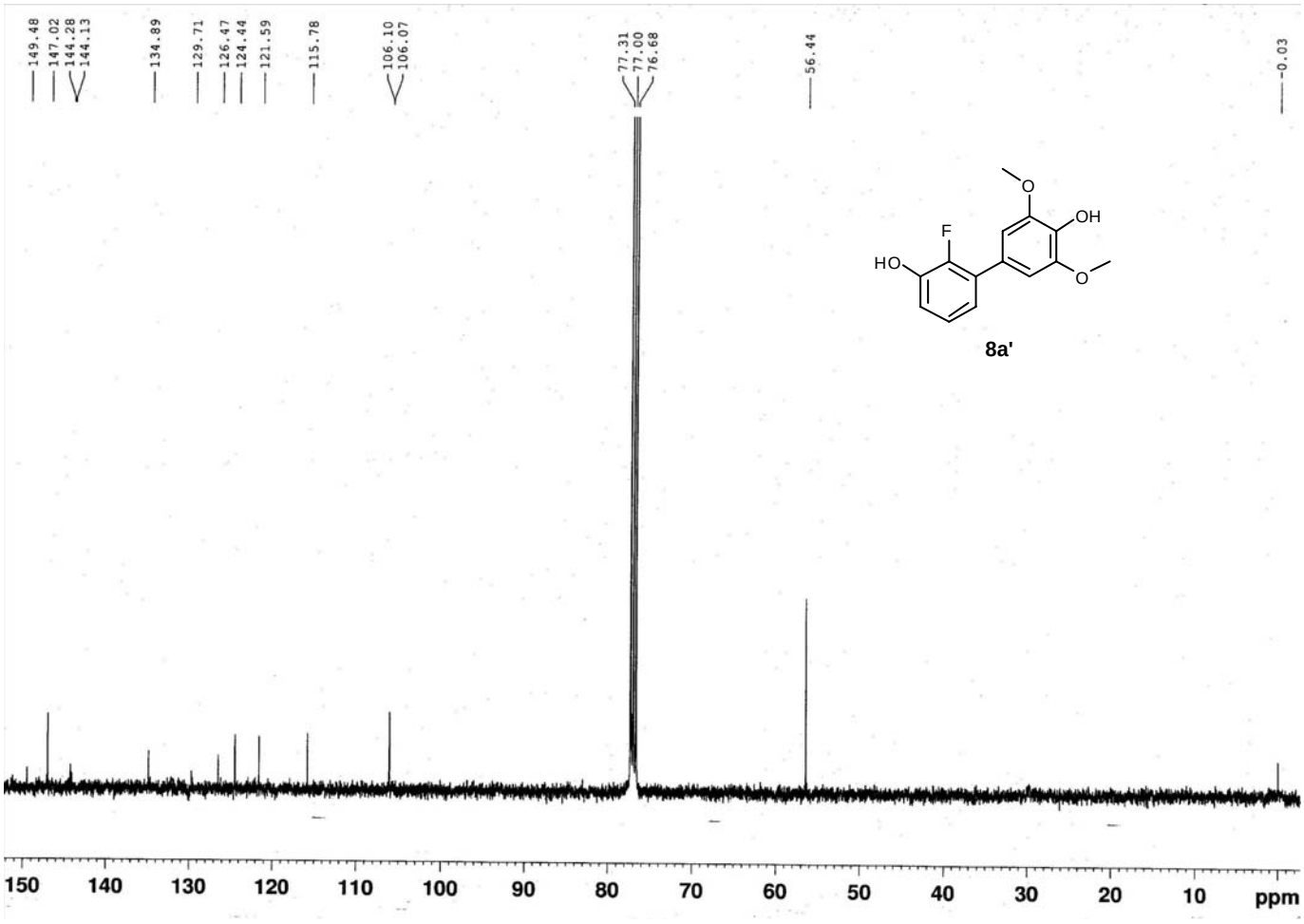
O
OH
F
O
O

8a


7.2598
7.0866
7.0837
7.0664
7.0642
7.0471
7.0443
6.9926
6.9882
6.9725
6.9682
6.9617
6.9572
6.9523
6.9478
6.9436
6.9396
6.9251
6.9208
6.7683
6.7650
3.9319
0.0028
1.036
1.897
1.880
5.898
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
ppm

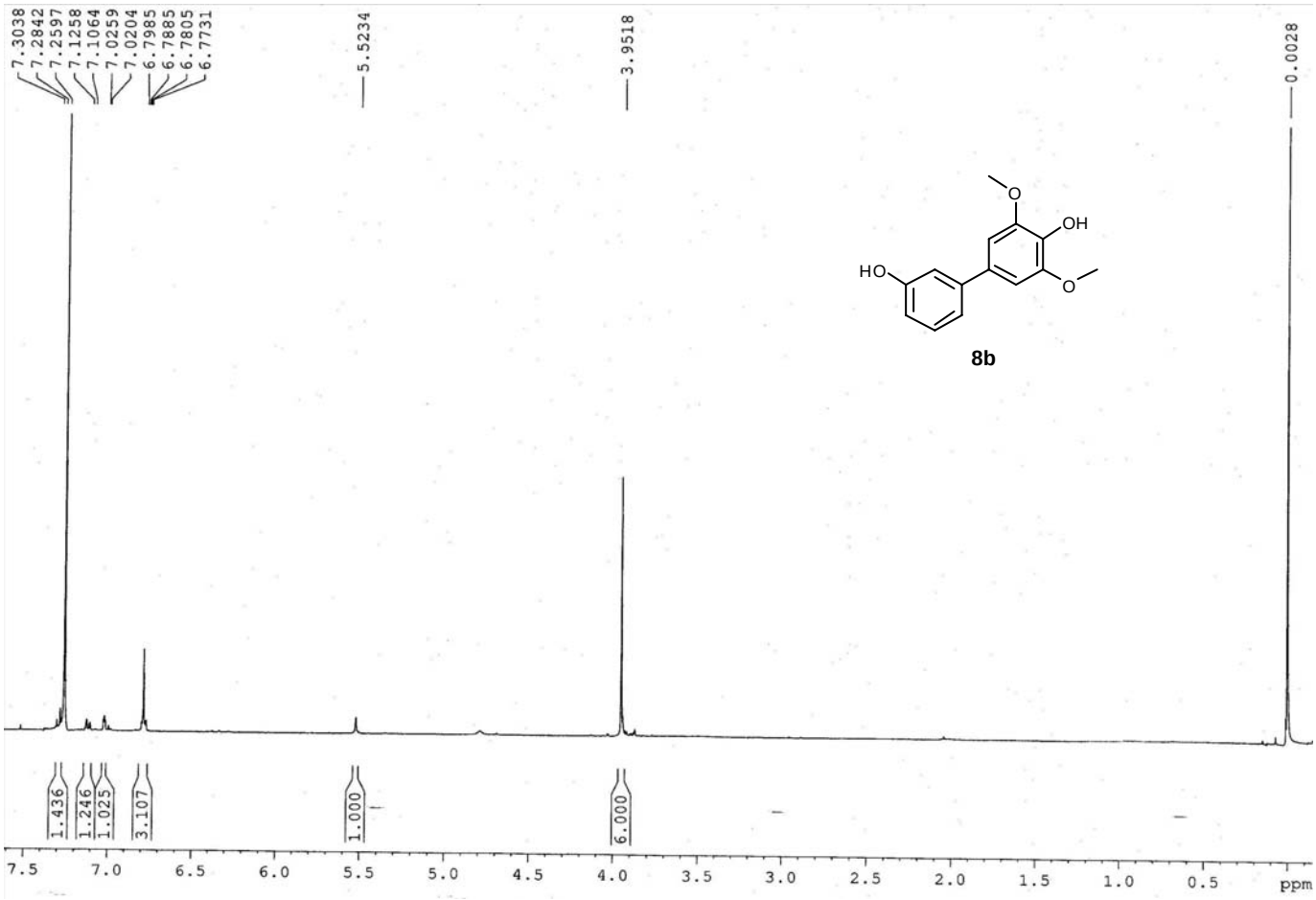
O
OH
F
HO
O

8a'

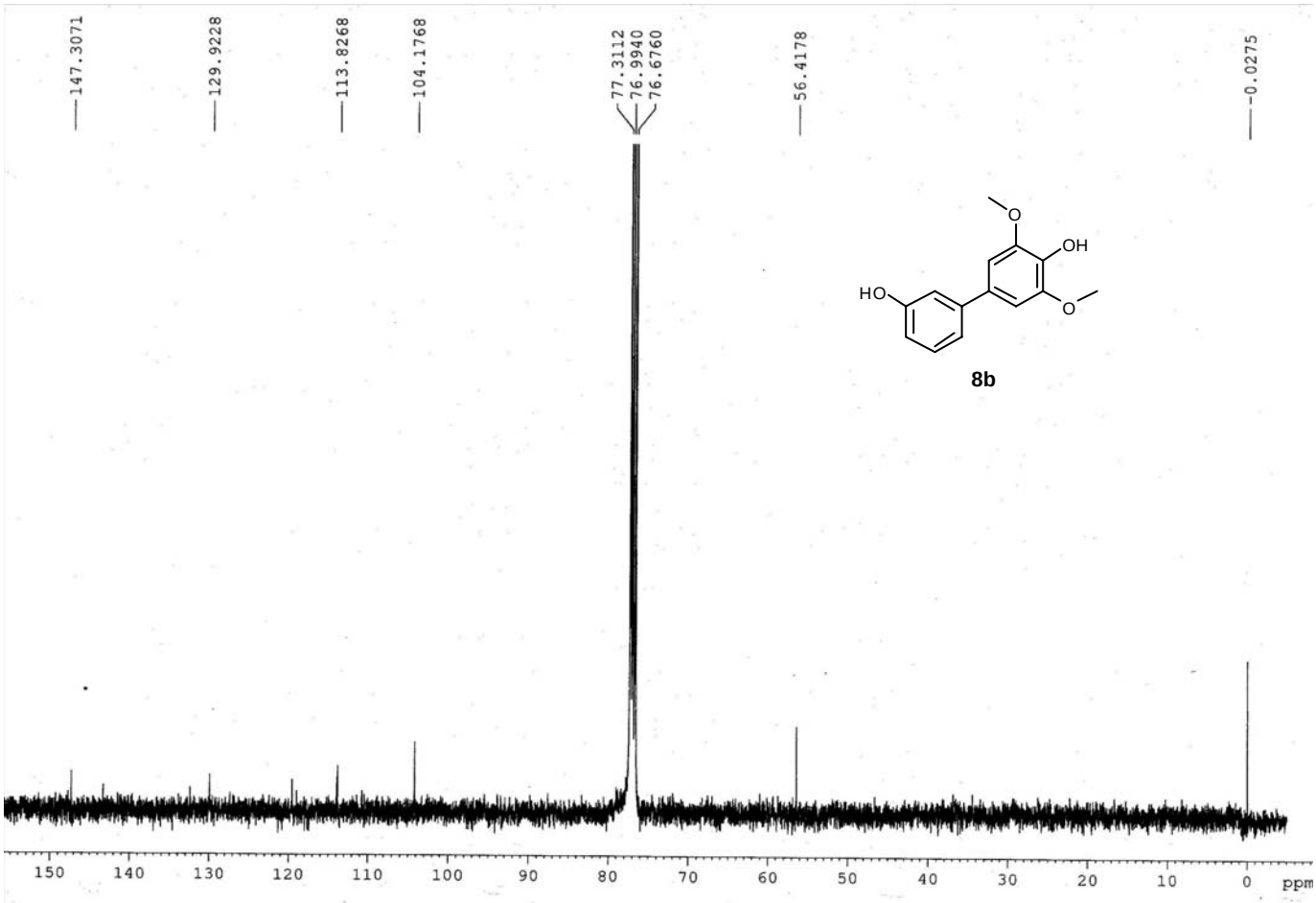

149.48
147.02
144.28
144.13
134.89
129.71
126.47
124.44
121.59
115.78
106.10
106.07
77.31
77.00
76.68
56.44
-0.03
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

O
OH
F
HO
O

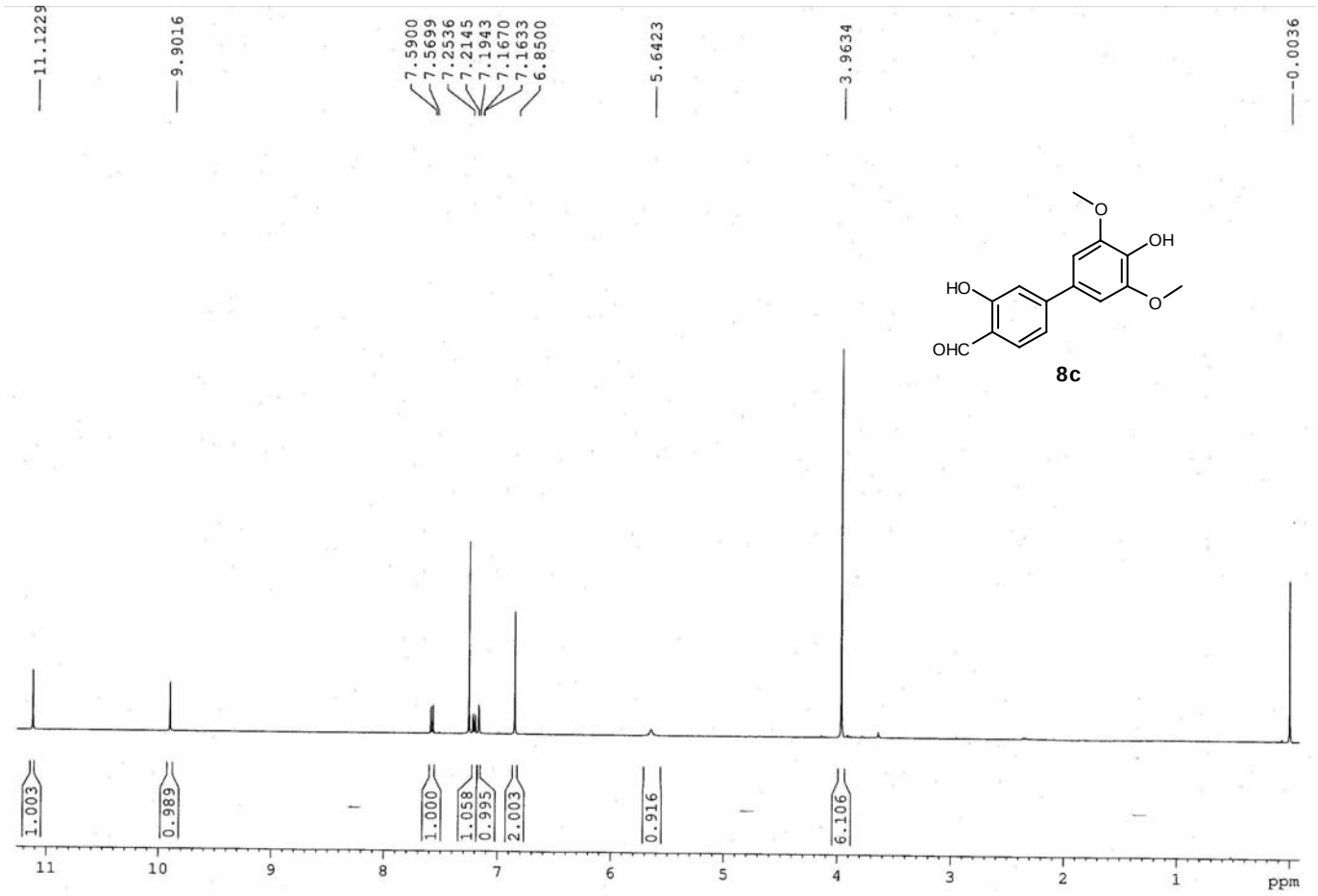
8a'


7.3038
7.2842
7.2597
7.1258
7.1064
7.0259
7.0204
6.7985
6.7885
6.7805
6.7731
5.5234
3.9518
0.0028
1.436
1.246
1.025
3.107
1.000
6.000
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
ppm
O
OH
HO
O

8b

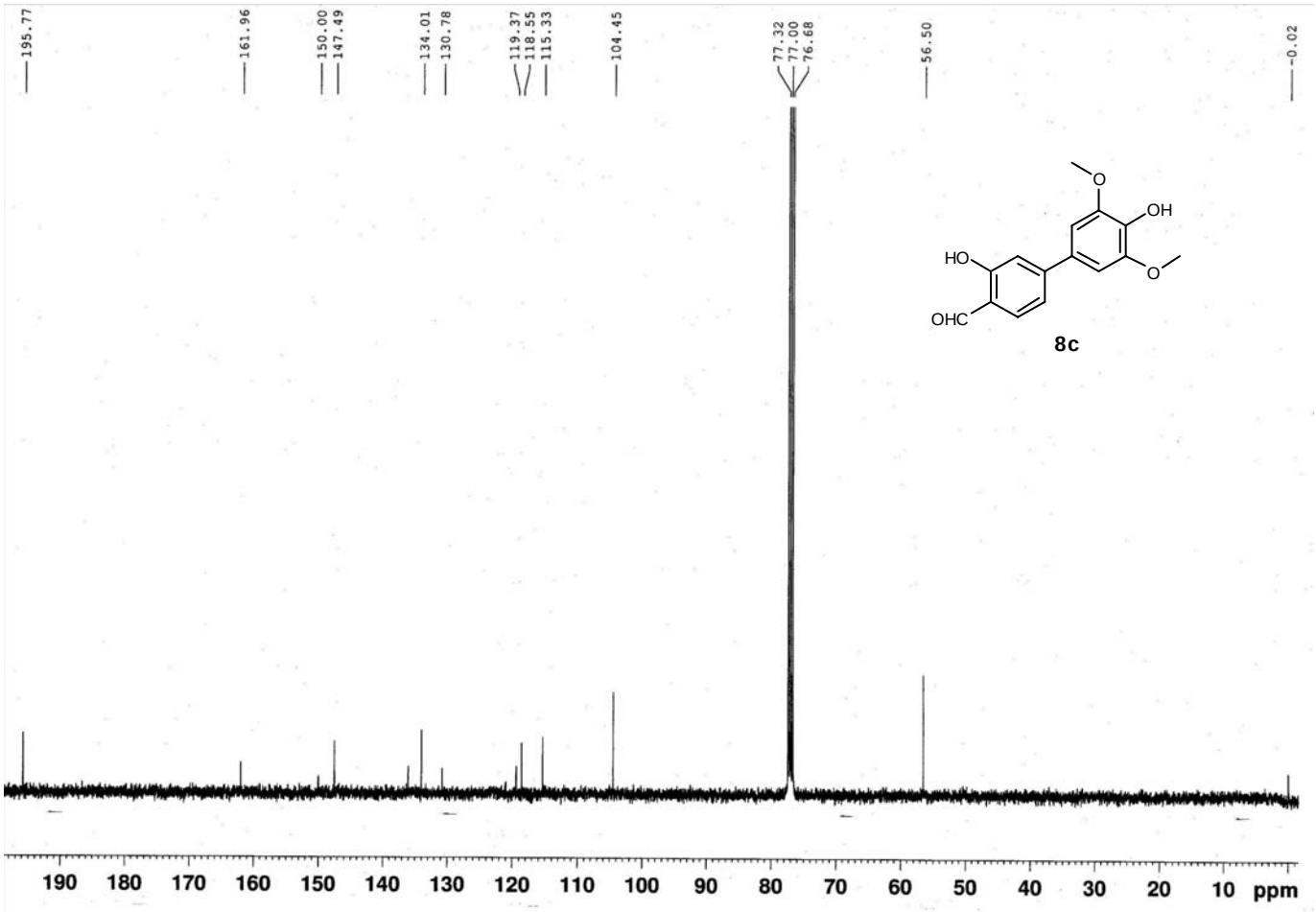

147.3071
129.9228
113.8268
104.1768
77.3112
76.9940
76.6760
56.4178
-0.0275
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
O
OH
HO
O

8b


11.1229
9.9016
7.5900
7.5699
7.2536
7.2145
7.1943
7.1670
7.1633
6.8500
5.6423
3.9634
-0.0036
1.003
0.989
1.000
1.058
0.995
2.003
0.916
6.106
11
10
9
8
7
6
5
4
3
2
1
ppm

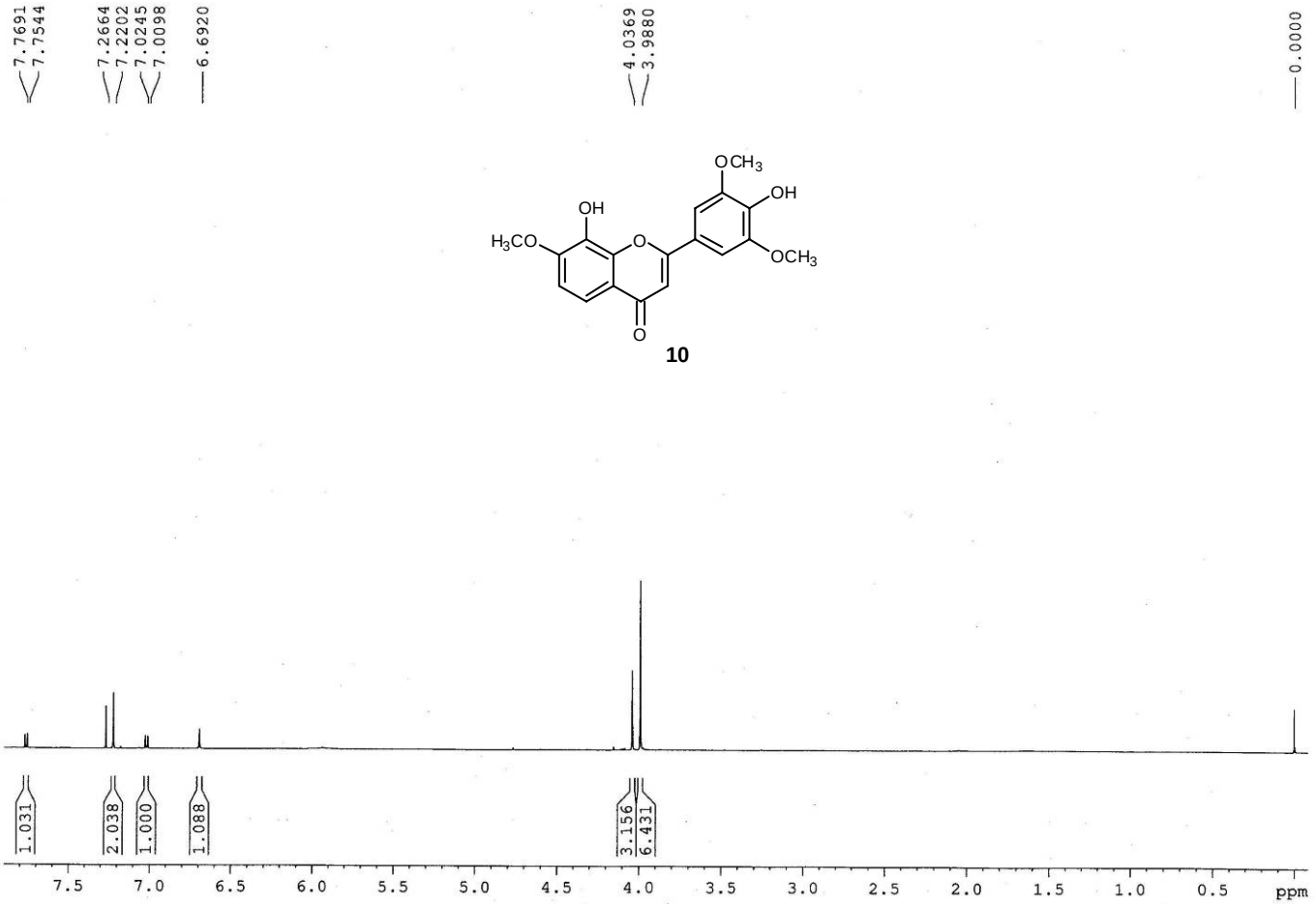
O
OH
HO
O
OHC

8c

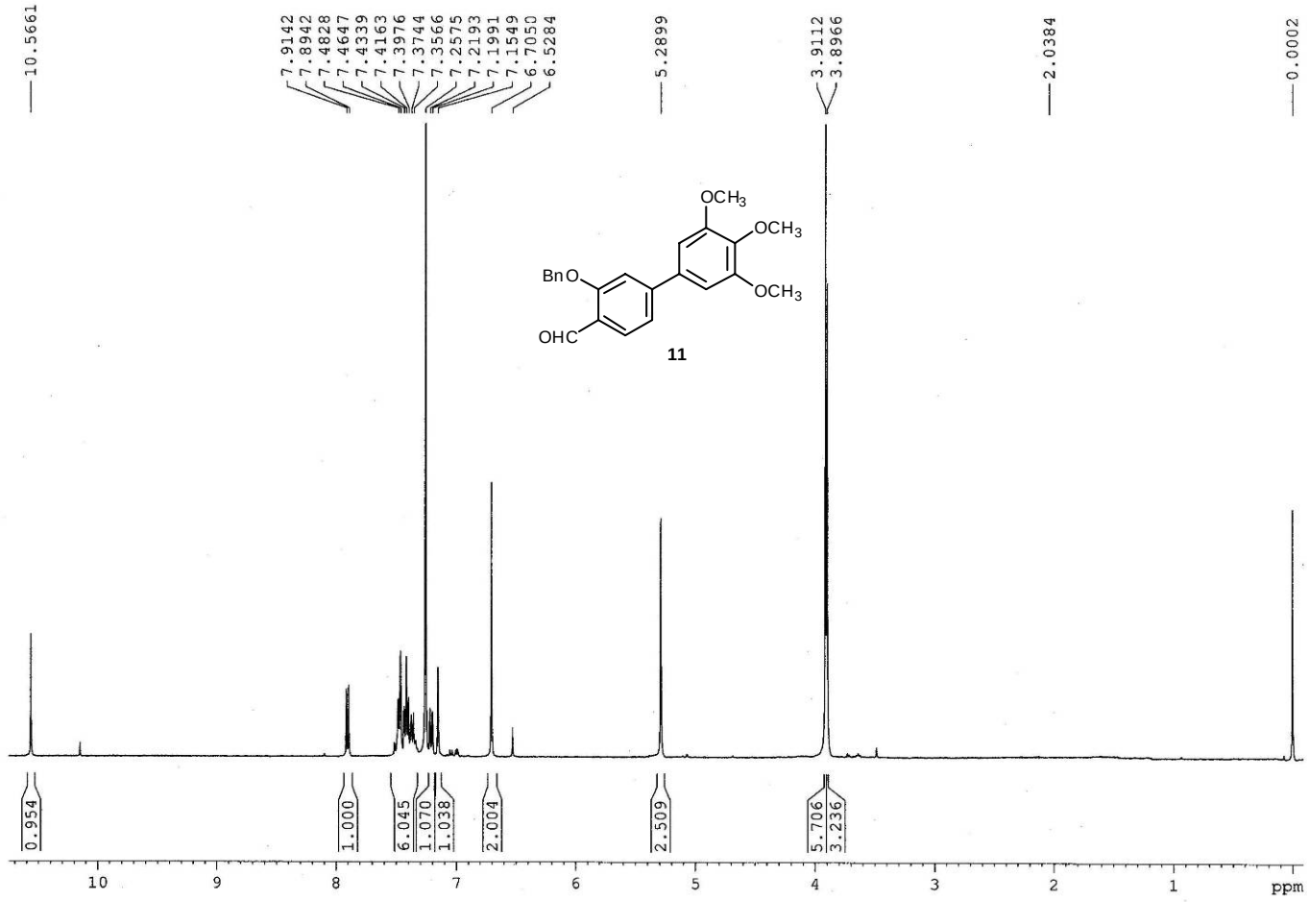

195.77
161.96
150.00
147.49
134.01
130.78
119.37
118.55
115.33
104.45
77.32
77.00
76.68
56.50
-0.02
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

O
OH
HO
O
OHC

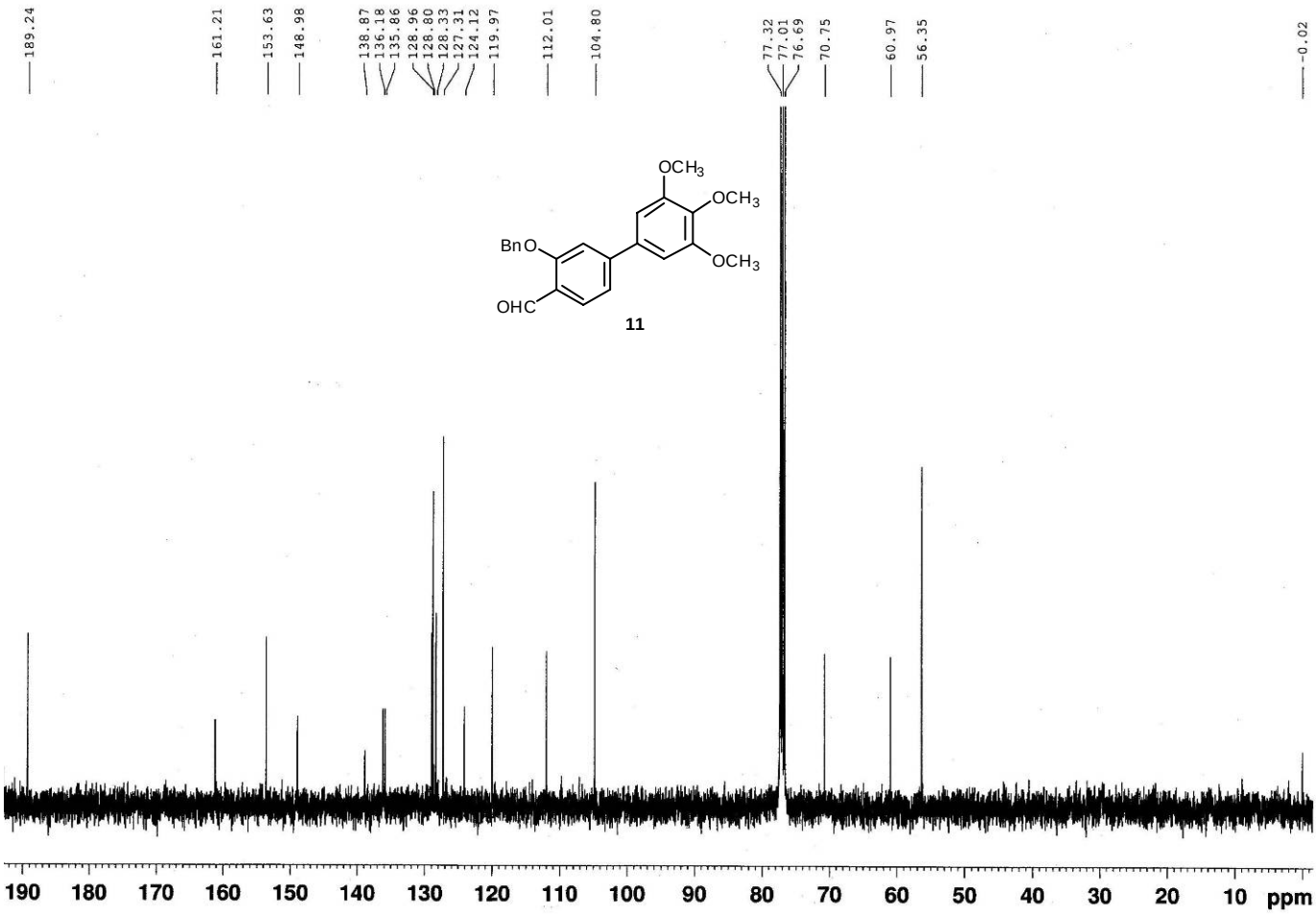
8c

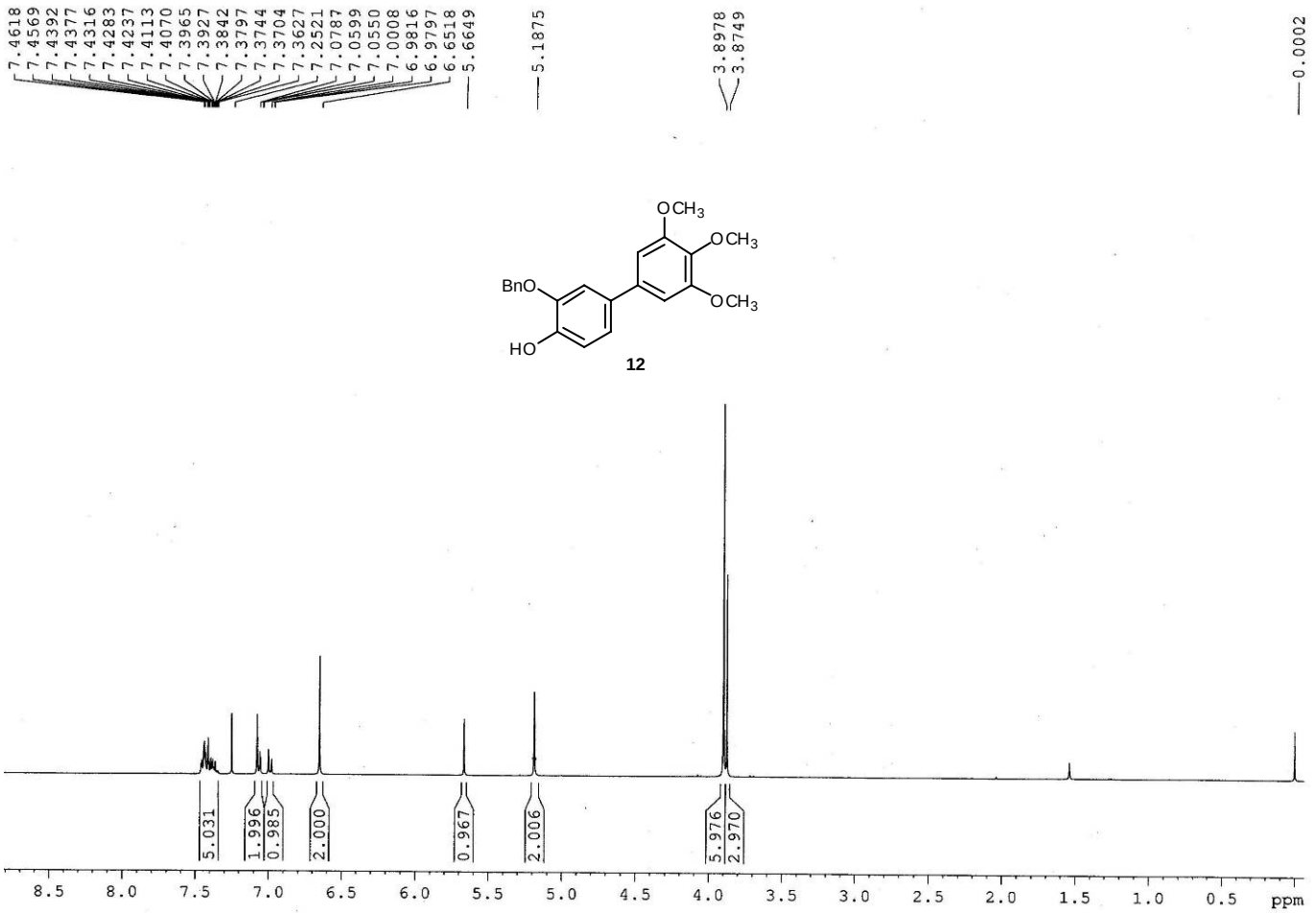

7.7691
7.7544
7.2664
7.2202
7.0245
7.0098
6.6920
4.0369
3.9880
0.0000
OCH3
OH
OH
H3CO
O
OCH3
O
1.031
2.038
1.000
1.088
3.156
6.431
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

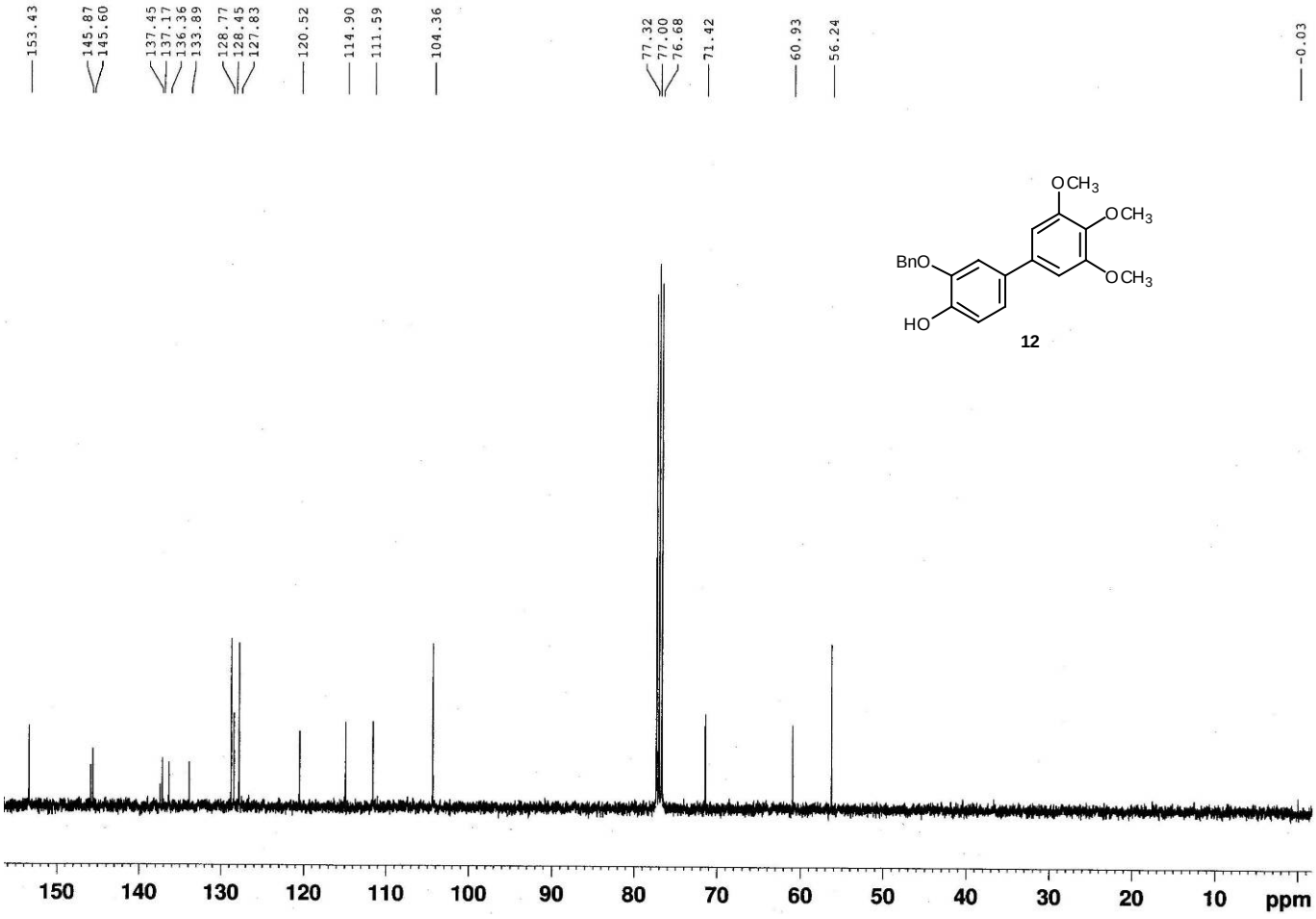
10

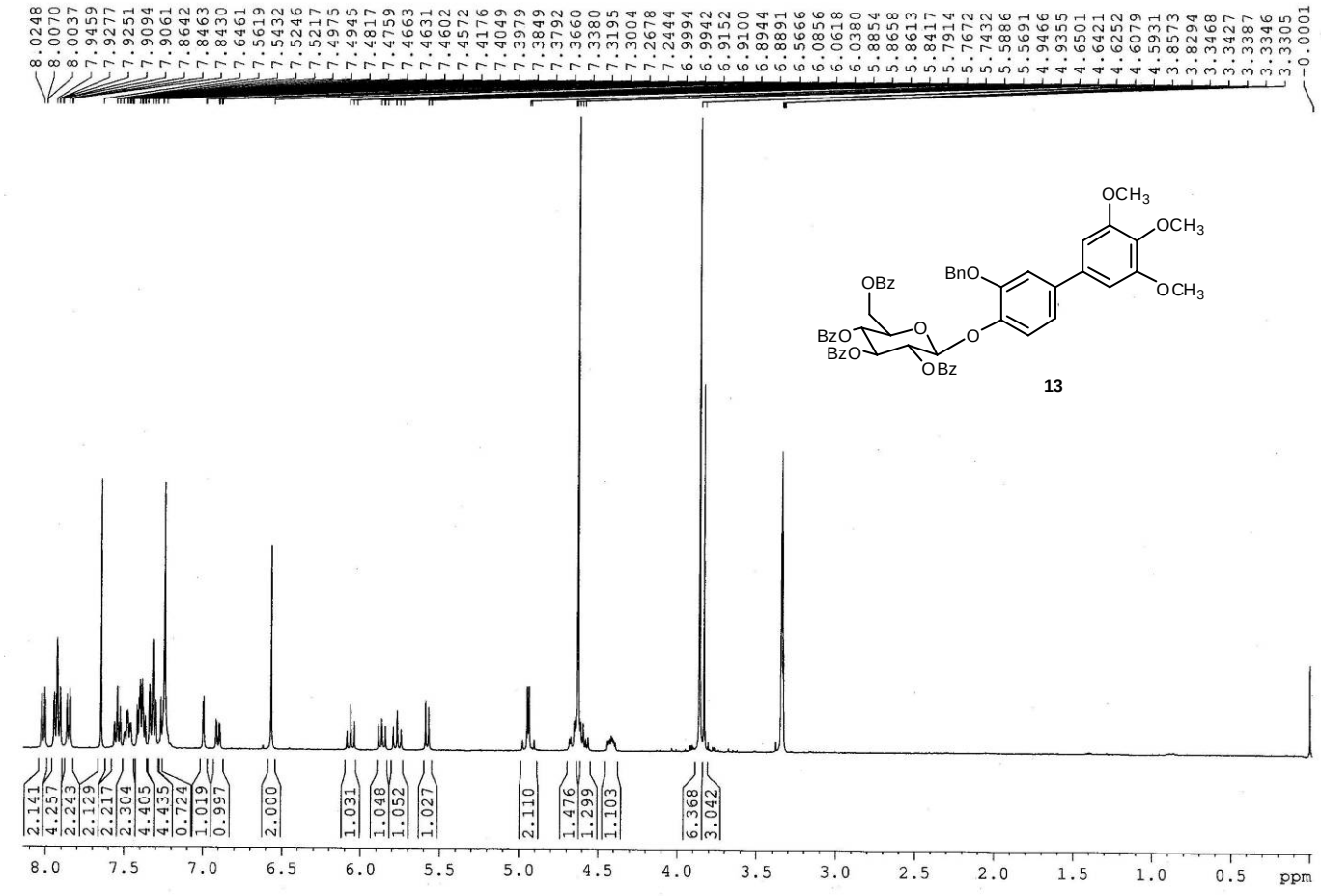

10.5661
7.9142
7.8942
7.4828
7.4647
7.4339
7.4163
7.3976
7.3744
7.3566
7.2575
7.2193
7.1991
7.1549
6.7050
6.5284
5.2899
3.9112
3.8966
2.0384
0.0002
OCH3
OCH3
BnO
OCH3
OHC
0.954
1.000
6.045
1.070
1.038
2.004
2.509
5.706
3.236
10
9
8
7
6
5
4
3
2
1
ppm

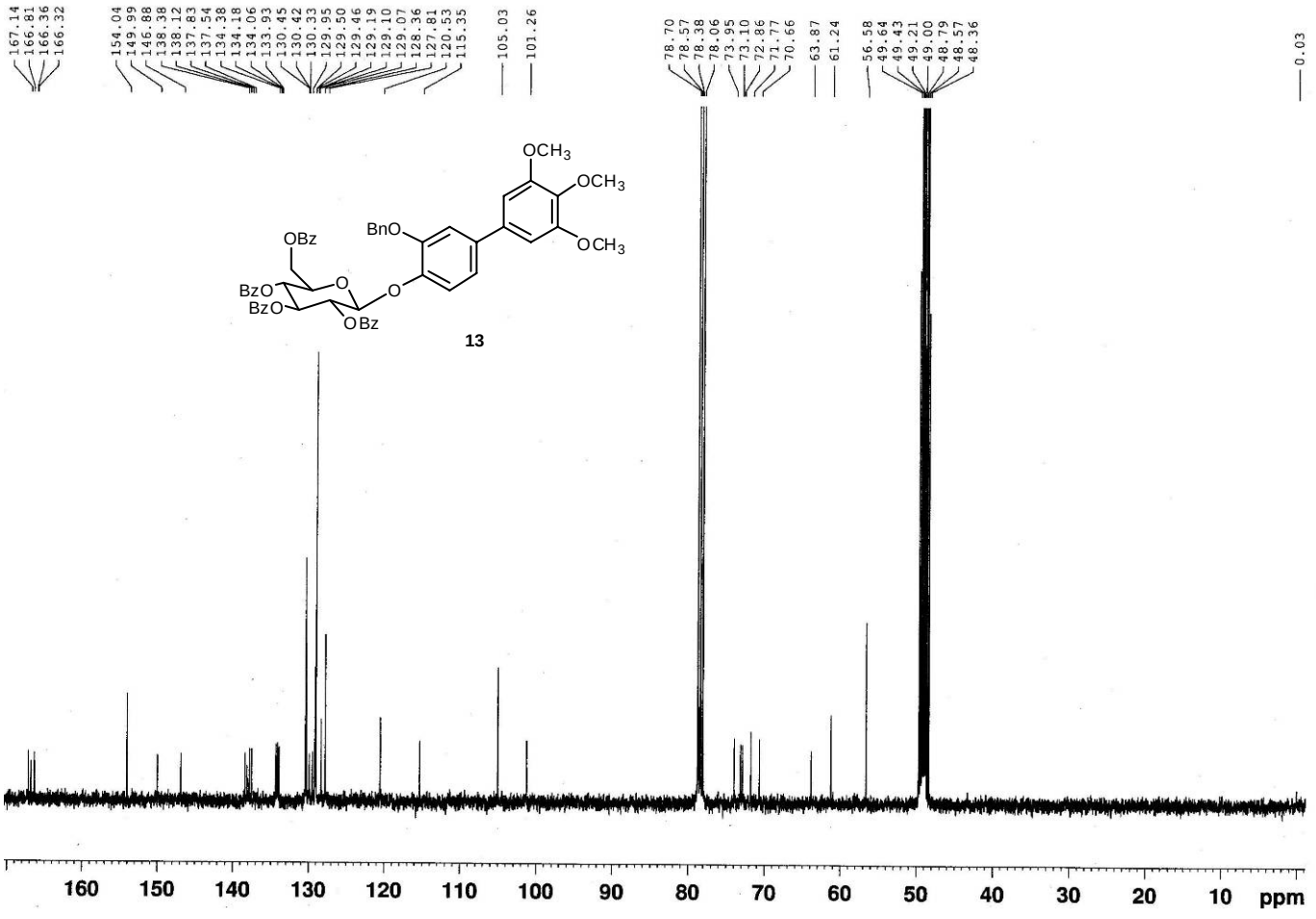
11

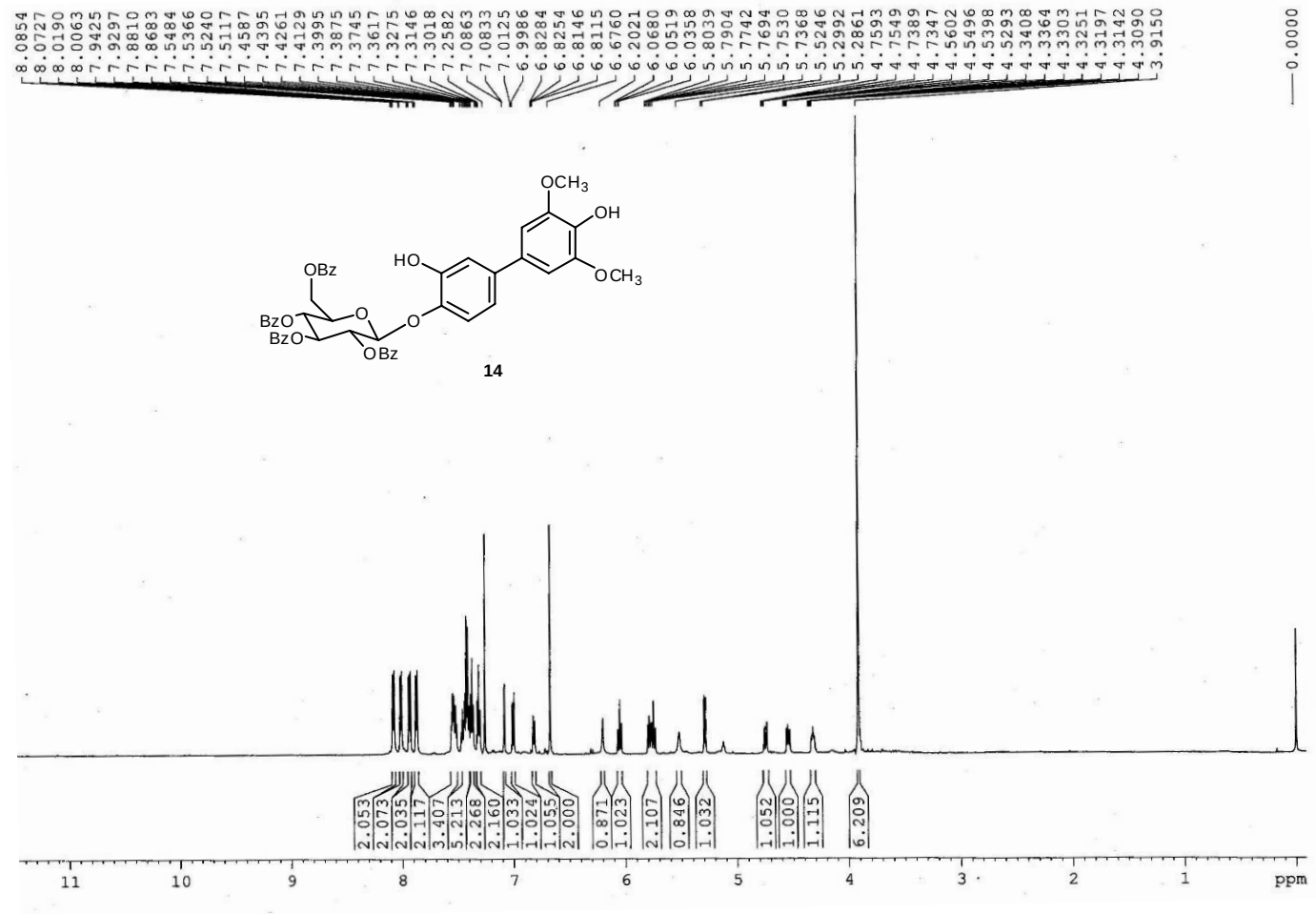

189.24
161.21
153.63
148.98
138.87
136.18
135.86
128.96
128.80
128.33
127.31
124.12
119.97
112.01
104.80
77.32
77.01
76.69
70.75
60.97
56.35
-0.02
OCH3
OCH3
OCH3
BnO
OHC
11
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

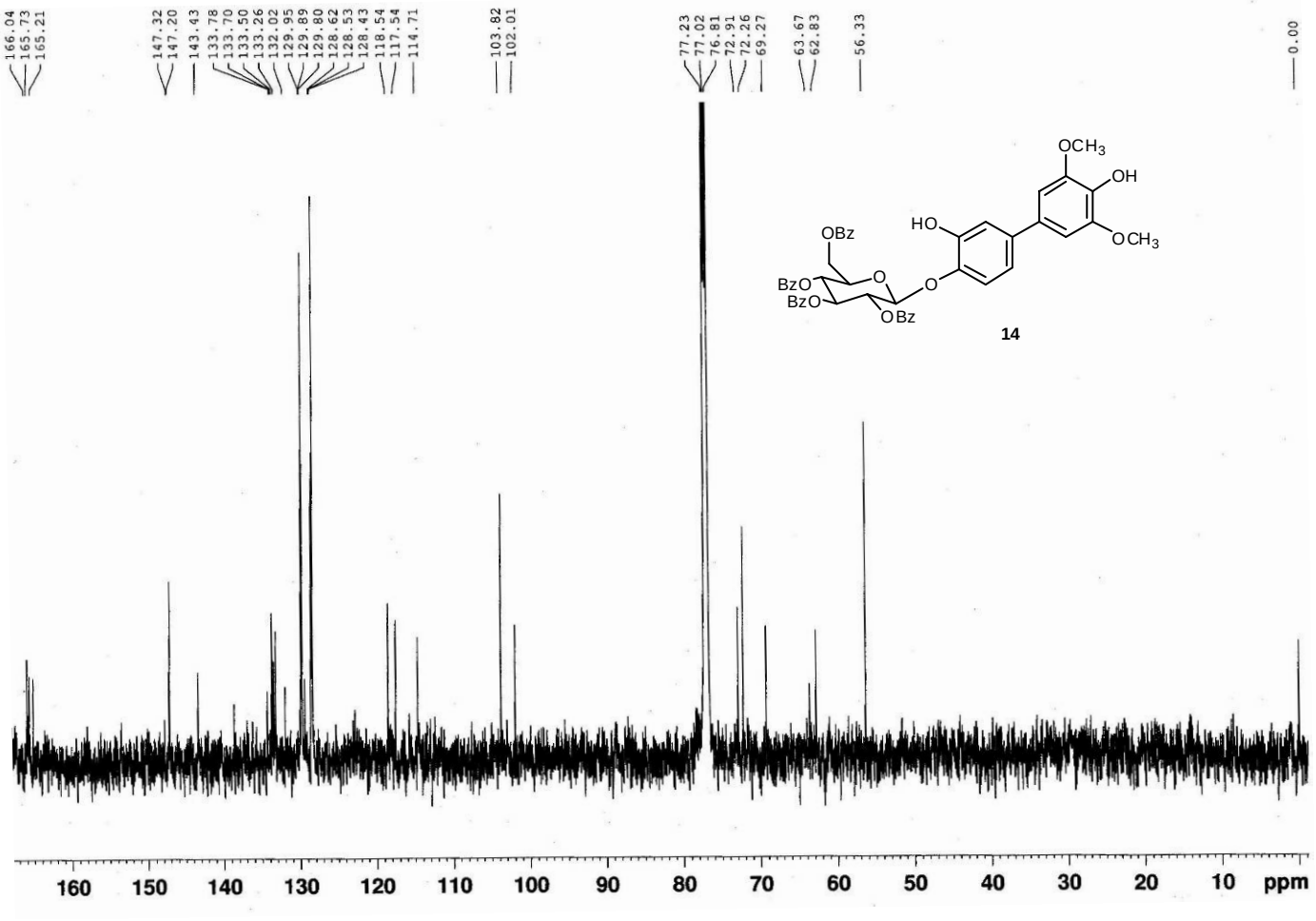

7.4618
7.4569
7.4392
7.4377
7.4316
7.4283
7.4237
7.4113
7.4070
7.3965
7.3927
7.3842
7.3797
7.3744
7.3704
7.3627
7.2521
7.0787
7.0599
7.0550
7.0008
6.9816
6.9797
6.6518
5.6649
5.1875
3.8978
3.8749
0.0002
OCH3
OCH3
OCH3
BnO
HO
12
5.031
1.996
0.985
2.000
0.967
2.006
5.976
2.970
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


153.43
145.87
145.60
137.45
137.17
136.36
133.89
128.77
128.45
127.83
120.52
114.90
111.59
104.36
77.32
77.00
76.68
71.42
60.93
56.24
-0.03
OCH3
OCH3
OCH3
BnO
HO
12
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

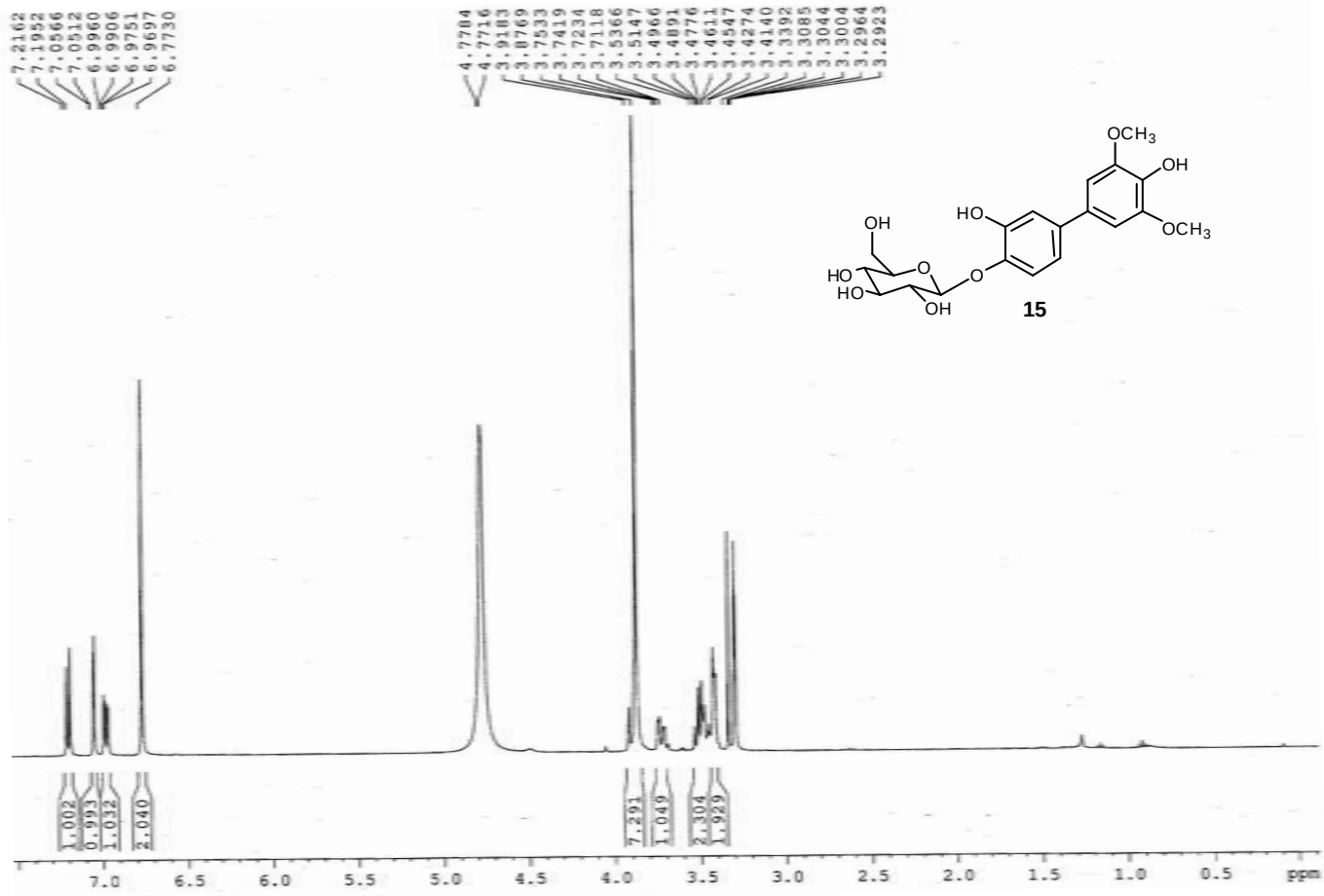

8.0248
8.0070
8.0037
7.9459
7.9277
7.9251
7.9094
7.9061
7.8642
7.8463
7.8430
7.6461
7.5619
7.5432
7.5246
7.5217
7.4975
7.4945
7.4817
7.4759
7.4663
7.4631
7.4602
7.4572
7.4176
7.4049
7.3979
7.3849
7.3792
7.3660
7.3380
7.3195
7.3004
7.2678
7.2444
6.9994
6.9942
6.9152
6.9100
6.8944
6.8891
6.5666
6.0856
6.0618
6.0380
5.8854
5.8658
5.8613
5.8417
5.7914
5.7672
5.7432
5.5886
5.5691
4.9466
4.9355
4.6501
4.6421
4.6252
4.6079
4.5931
3.8573
3.8294
3.3468
3.3427
3.3387
3.3346
3.3305
-0.0001
OCH3
OCH3
OCH3
BnO
OBz
BzO
BzO
OBz
13
2.141
4.257
2.243
2.129
2.217
2.304
4.405
4.435
0.724
1.019
0.997
2.000
1.031
1.048
1.052
1.027
2.110
1.476
1.299
1.103
6.368
3.042
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
ppm


167.14
166.81
166.36
166.32
154.04
149.99
146.88
138.38
138.12
137.83
137.54
134.38
134.18
134.06
133.93
130.45
130.42
130.33
129.95
129.50
129.46
129.19
129.10
129.07
128.36
127.81
120.53
115.35
105.03
101.26
78.70
78.57
78.38
78.06
73.95
73.10
72.86
71.77
70.66
63.87
61.24
56.58
49.64
49.43
49.21
49.00
48.79
48.57
48.36
0.03
OCH3
OCH3
OCH3
BnO
OBz
BzO
BzO
O
O
OBz
13
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

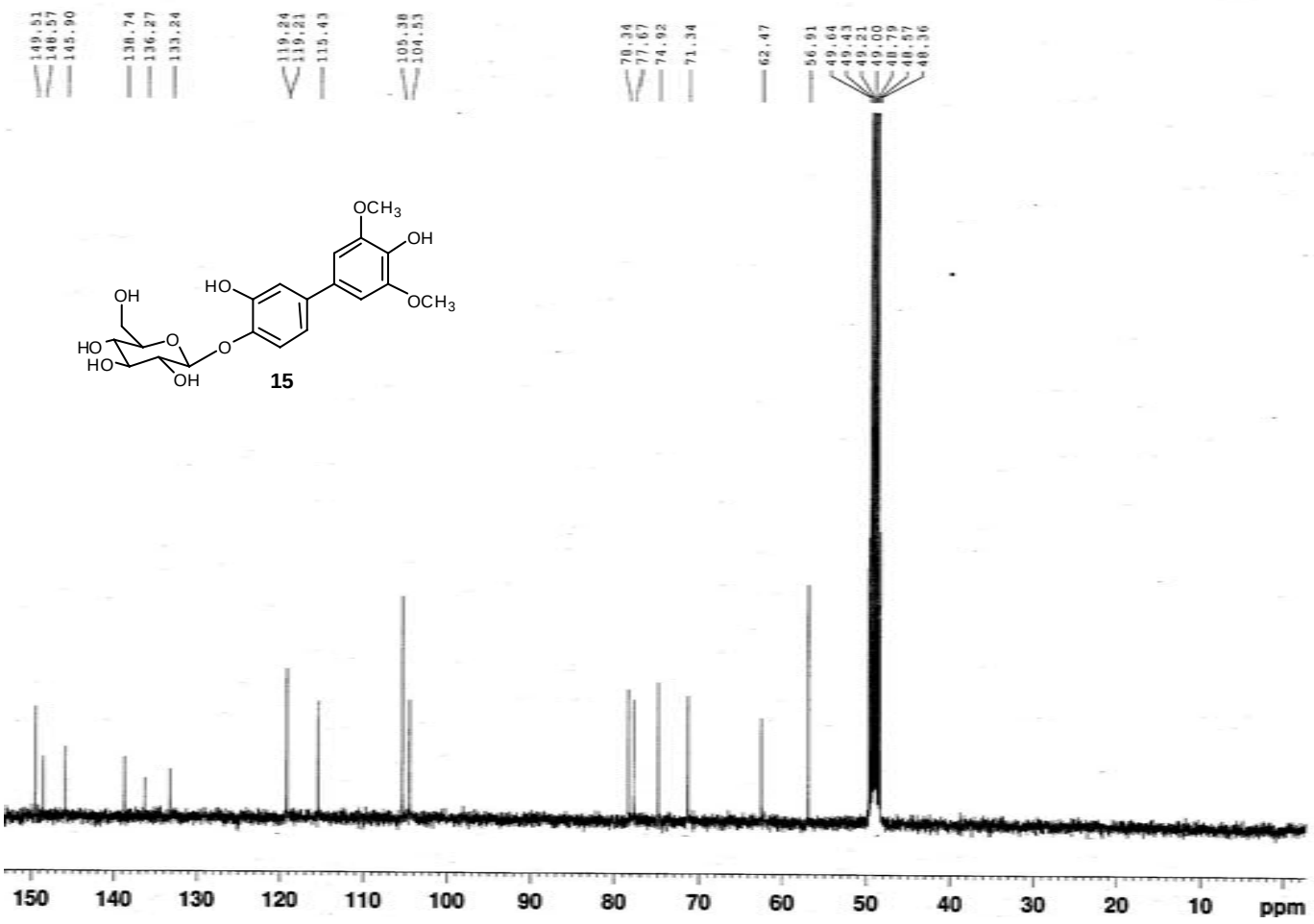

8.0854
8.0727
8.0190
8.0063
7.9425
7.9297
7.8810
7.8683
7.5484
7.5366
7.5240
7.5117
7.4587
7.4395
7.4261
7.4129
7.3995
7.3875
7.3745
7.3617
7.3275
7.3146
7.3018
7.2582
7.0863
7.0833
7.0125
6.9986
6.8284
6.8254
6.8146
6.8115
6.6760
6.2021
6.0680
6.0519
6.0358
5.8039
5.7904
5.7742
5.7694
5.7530
5.7368
5.5246
5.2992
5.2861
4.7593
4.7549
4.7389
4.7347
4.5602
4.5496
4.5398
4.5293
4.3408
4.3364
4.3303
4.3251
4.3197
4.3142
4.3090
3.9150
0.0000
OCH3
OH
HO
OCH3
OBz
BzO
BzO
O
O
OBz
14
2.053
2.073
2.035
2.117
3.407
5.213
2.268
2.160
1.033
1.024
1.055
2.000
0.871
1.023
2.107
0.846
1.032
1.052
1.000
1.115
6.209
11
10
9
8
7
6
5
4
3
2
1
ppm

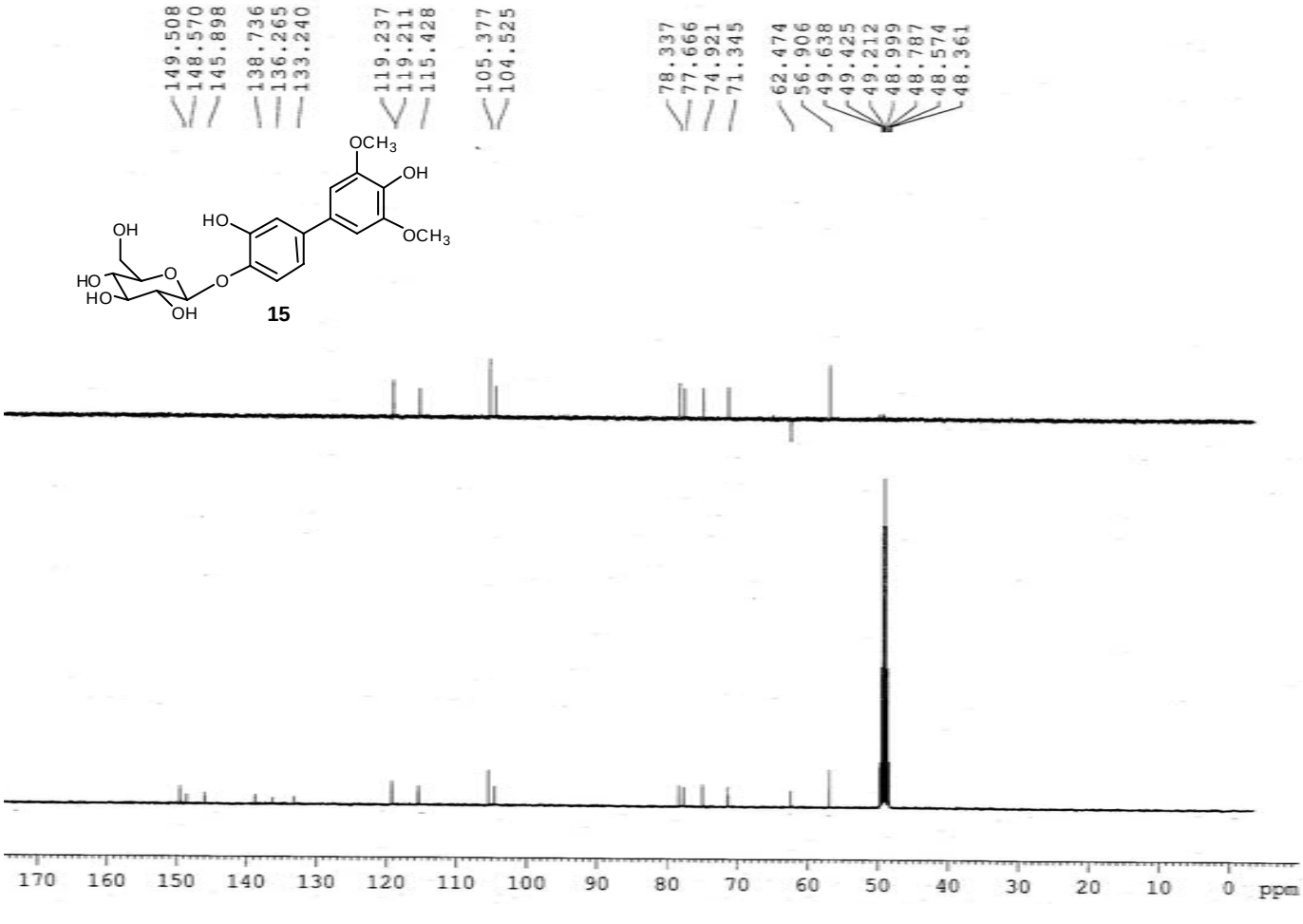

166.04
165.73
165.21
147.32
147.20
143.43
133.78
133.70
133.50
133.26
132.02
129.95
129.89
129.80
128.62
128.53
128.43
118.54
117.54
114.71
103.82
102.01
77.23
77.02
76.81
72.91
72.26
69.27
63.67
62.83
56.33
0.00
OCH3
OH
HO
OCH3
OBz
BzO
BzO
OBz
O
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

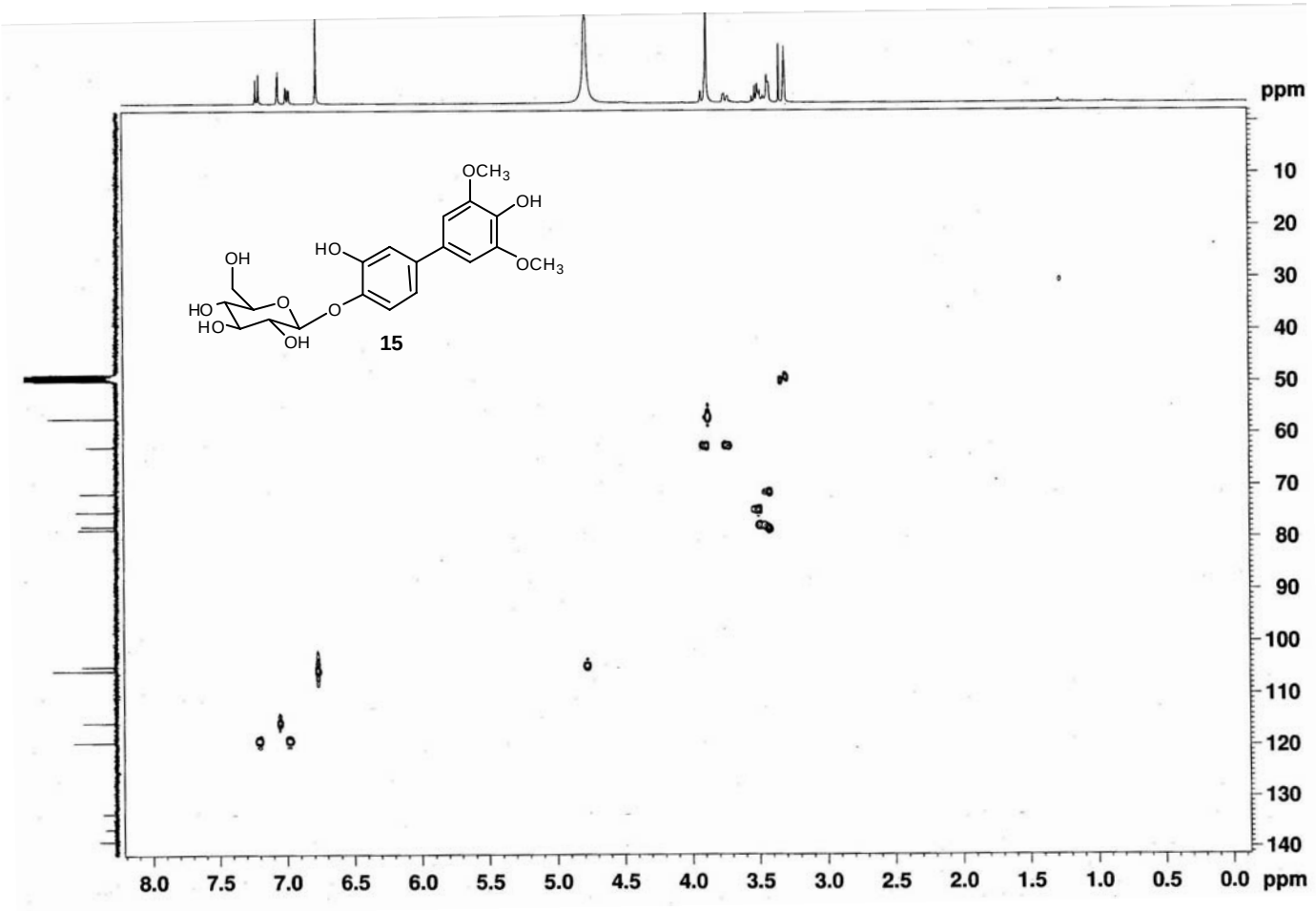
14

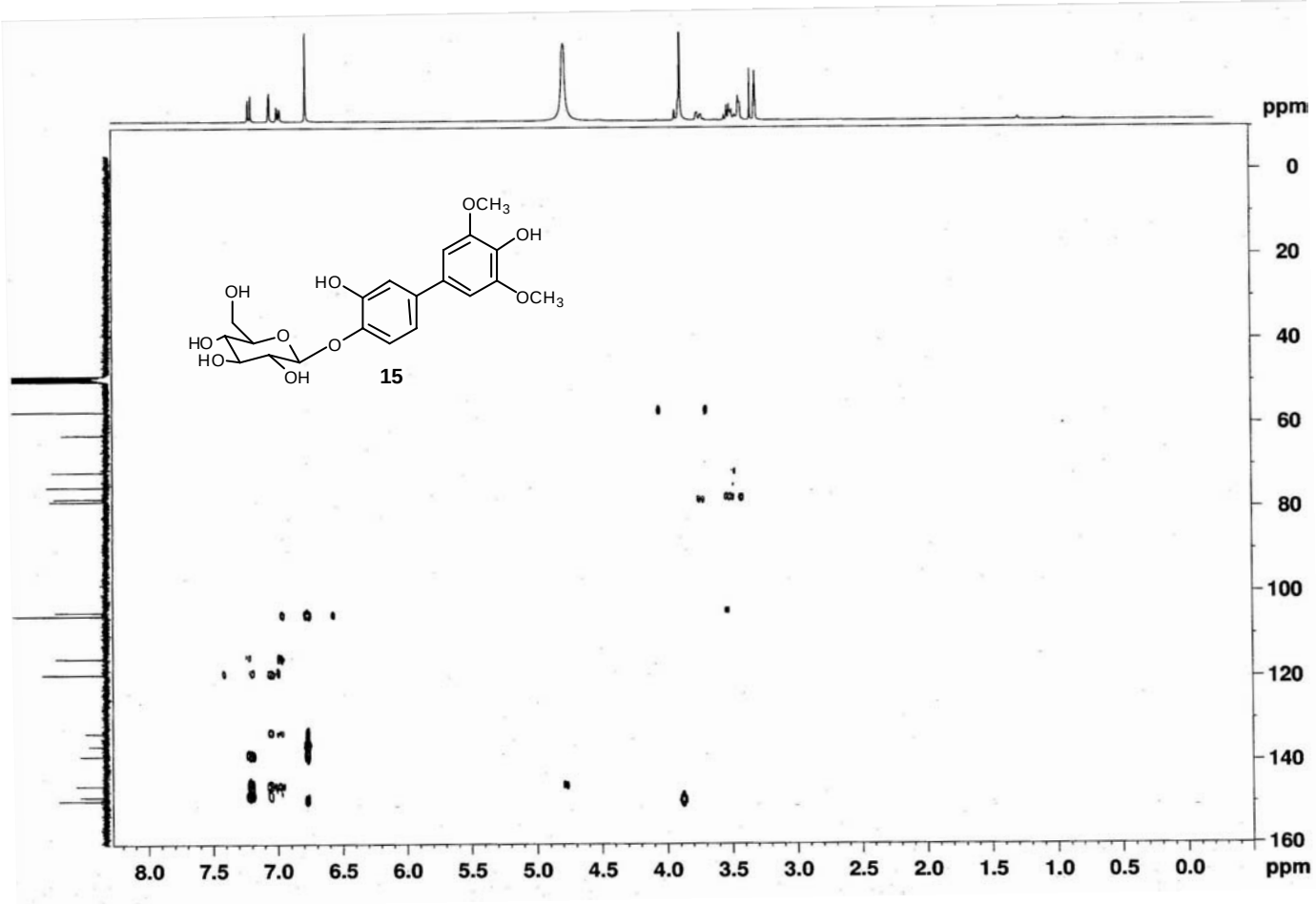

7.2162
7.1952
7.0566
7.0512
6.9960
6.9906
6.9751
6.9697
6.7730
4.7784
4.7716
3.9183
3.8769
3.7533
3.7419
3.7234
3.7118
3.5366
3.5147
3.4966
3.4891
3.4776
3.4611
3.4547
3.4274
3.4140
3.3392
3.3085
3.3044
3.3004
3.2964
3.2923
OCH3
OH
HO
OCH3
OH
HO
HO
OH
O
O
1.002
0.993
1.032
2.040
7.291
1.049
2.304
1.929
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
ppm

15


149.51
148.57
145.90
138.74
136.27
133.24
119.24
119.21
115.43
105.38
104.53
78.34
77.67
74.92
71.34
62.47
56.91
49.64
49.43
49.21
49.00
48.79
48.57
48.36
OCH3
OH
HO
OCH3
OH
HO
HO
O
O
OH
15
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


149.508
148.570
145.898
138.736
136.265
133.240
119.237
119.211
115.428
105.377
104.525
78.337
77.666
74.921
71.345
62.474
56.906
49.638
49.425
49.212
48.999
48.787
48.574
48.361
OCH3
OH
HO
OCH3
OH
HO
HO
O
O
OH
15
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


OCH3
OH
HO
OCH3
OH
HO
HO
O
O
OH
15
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
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
ppm


OCH3
OH
HO
OCH3
OH
HO
HO
O
O
OH
15
ppm
0
20
40
60
80
100
120
140
160
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
ppm