Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Syn-selective Crotylation of Aldehydes Using Bismuth-Crotyl Bromide-(1-Butyl-3-methylimidazolium Bromide) Combination: Some Synthetic Applications

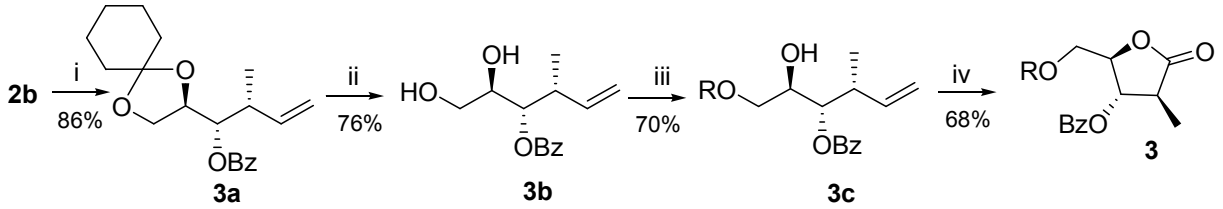
Dibakar Goswami, Mrunesh Koli, Sucheta Chatterjee, Subrata Chattopadhyay and Anubha Sharma*

Bio-Organic Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

Fax: +91 22 25505151; e-mail: anubhas@barc.gov.in

Supplementary materials

Content



i) Et_3N/ BzCN/ CH_2Cl_2/ 0 ^oC/ 3h, ii) Aqueous 80% TFA/0 ^oC/3 h, iii)TBDPSCl/imidazole/ CH_2Cl_2/0 ^oC/4 h, iv) O_3/ NaOH-MeOH/ CH_2Cl_2/-40 ^oC- 0 ^oC/ 7h.

Synthesis of γ-lactone 3

Experimental section.

(3*R*,4*S*,5*R*)-4-Benzoyloxy-5,6-cyclohexylidenedioxy-3-methyl-1-hexene 3a. To a well stirred and cooled (0 ^oC) solution of **2b** (0.55 g, 2.43 mmol) and Et_3N (0.51 mL, 3.65 mmol) in CH_2Cl_2 (15 mL) was added BzCN (380 mg, 2.92 mmol) in CH_2Cl_2 (10 mL) in 20 min. After completion of the reaction (*cf*. TLC, 3 h) the reaction mixture was poured into H_2O (15 mL), the organic layer separated, and the aqueous layer extracted with $CHCl_3$ (2 × 10 mL). The combined organic extracts were washed with H_2O (2 × 10 mL) and brine (1 × 5 mL), and dried. Solvent removal in vacuo followed by column chromatography (silica gel, 5-15% EtOAc/hexane) of the residue gave **3a** (690

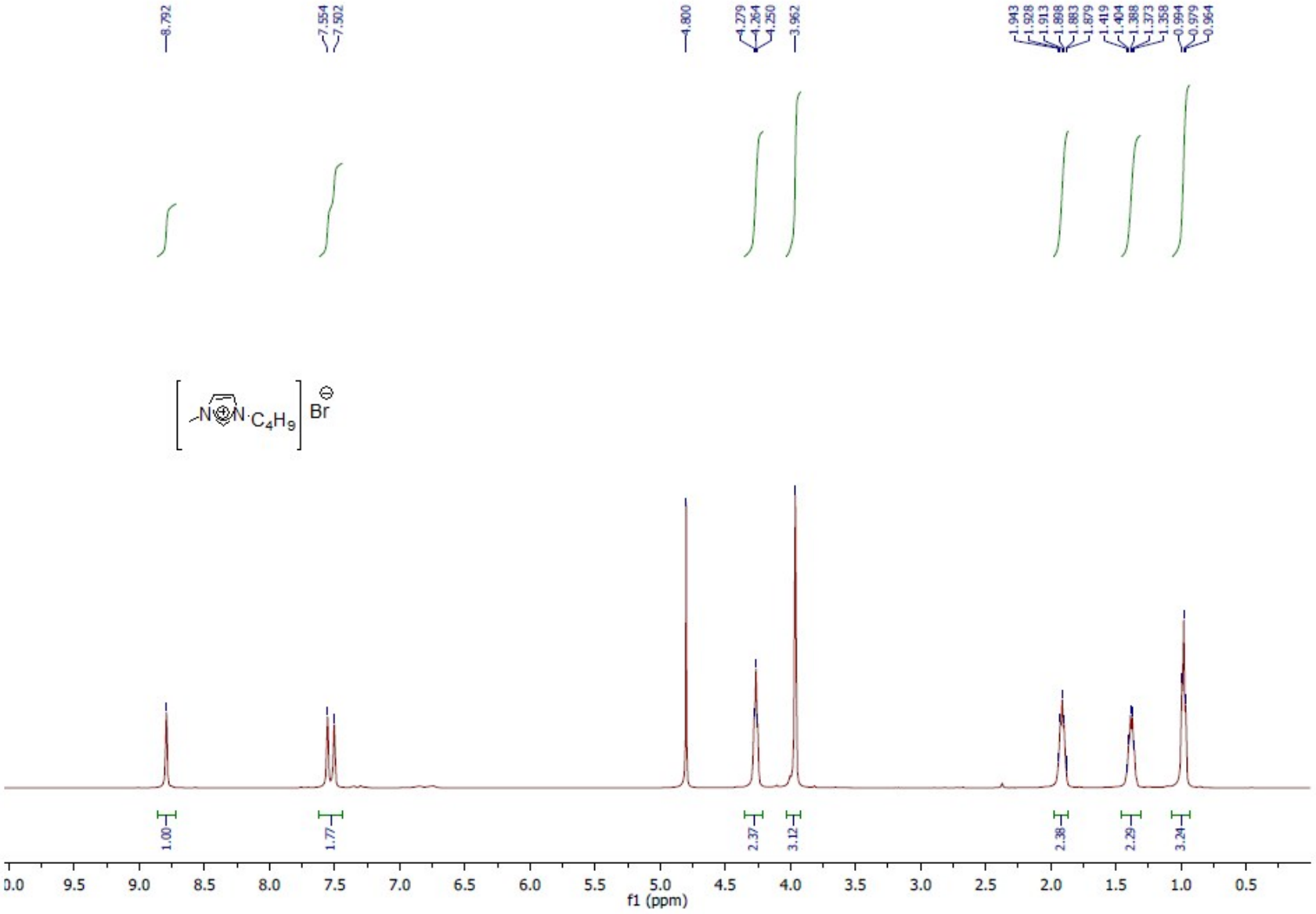
mg, 86%). colorless oil; $[\alpha]_D^{24}$ +12.6 (*c* 1.2 in $CHCl_3$); ν_{max}/cm^{-1} 1720, 984; δ_H (500 MHz, $CDCl_3$) 1.13 (3H, d, *J* = 6.8 Hz), 1.30-1.38 (2H, m), 1.46-1.57 (8H, m), 2.57-2.61 (1H, m) 3.93-4.04 (2H, m), 4.29-4.33 (1H, m), 5.02-5.09 (2H, m), 5.31-5.33 (1H, m), 5.79-5.84 (1H, m), 7.41-7.56 (3H, m), 8.02-8.04 (2H, m); δ_C (125 MHz, $CDCl_3$) 15.1, 23.7, 25.0, 35.0, 36.0, 39.6, 65.3, 74.8, 75.8, 109.8, 115.5, 128.3, 129.6, 132.9, 139.4, 165.8. Anal. Calc. for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93%. Found: C, 72.52; H, 8.20%.

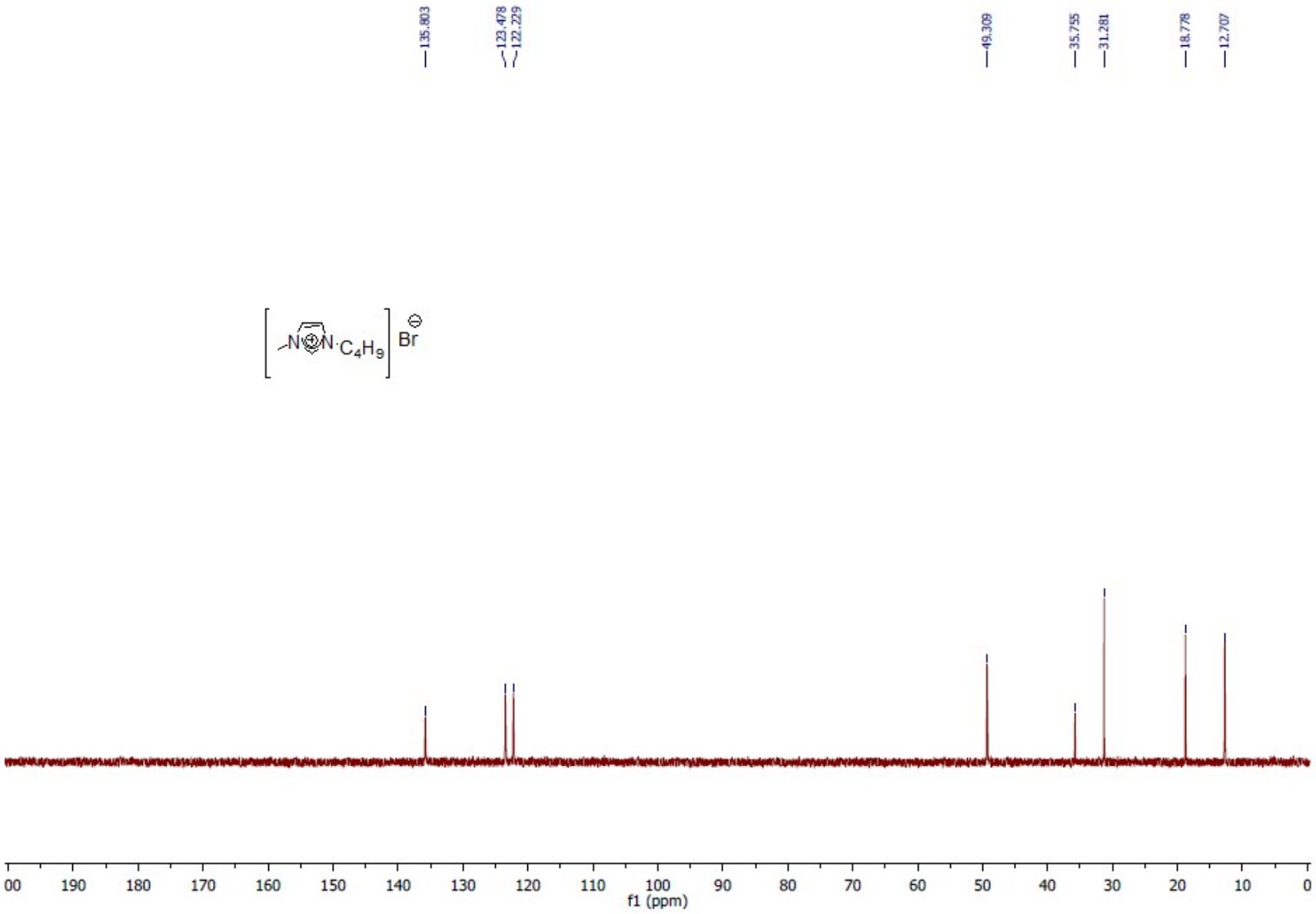
(*2R,3S,4R*)-3-Benzoyloxy-4-methyl-5-hexene-1,2-diol 3b. To a stirred and cooled (0 °C) solution of **3a** (550 mg, 1.67 mmol) in CH_2Cl_2 (10 mL) was added aqueous TFA (8 mL) in portions. After stirring the mixture for 3 h, when the reaction was complete (*cf*. TLC), $NaHCO_3$ was added to decompose excess TFA, followed by H_2O (5 mL), and the mixture extracted with $CHCl_3$ (2 × 10 mL). The combined organic extracts were washed with H_2O (2 × 10 mL) and brine (1 × 5 mL), and dried. Removal of solvent in vacuo followed by column chromatography (silica gel, 5% $CHCl_3$/MeOH) of the residue afforded **3b** (320 mg, 76%). colorless thick oil; $[\alpha]_D^{24}$ +4.8 (*c* 1.0 in $CHCl_3$); ν_{max}/cm^{-1} 3412, 1724, 926; δ_H (500 MHz, $CDCl_3$) 1.20 (3H, d, *J* = 6.5 Hz), 2.67 (2H, br s), 2.84-2.86 (1H, m), 3.59-3.63 (1H, m), 3.70-3.73 (1H, m), 3.83-3.86 (1H, m), 5.04 (1H, dd, *J* = 10.5, 1.5 Hz), 5.10-5.15 (2H, m), 5.79-5.87 (1H, m), 7.44-7.47 (2H, m), 7.57-7.61 (1H, m), 8.01-8.04 (2H, m); δ_C (125 MHz, $CDCl_3$) 13.8, 38.1, 62.4, 70.7, 76.4, 115.4, 128.5, 129.7, 129.8, 133.5, 140.0, 167.3. Anal. Calc. for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25%. Found: C, 67.40; H, 7.15%.

(2*R*,3*S*,4*R*)-3-Benzoyloxy-1-*tert*-butyldiphenylsilyloxy-4-methyl-hex-5-en-2-ol 3c. A cooled (0 °C) solution of **3b** (250 mg, 1.0 mmol), TBDPSCl (0.26 mL, 1.0 mmol), imidazole (82 mg, 1.2 mmol) and DMAP (10 mol%) in CH_2Cl_2 (10 mL) was stirred for 4 h. On completion (*cf*. TLC), H_2O (10 mL) was added to the mixture, which was extracted with $CHCl_3$ (2 × 10 mL). The combined organic extracts were washed with H_2O (2 × 10 mL) and brine (1 × 5 mL), dried and concentrated in vacuo. The residue was subjected to column chromatography (silica gel, 5-15% EtOAc/hexane) to afford **3c** (340 mg, 70%). colorless oil; $[\alpha]_D^{24}$ +14.8 (*c* 0.8 in $CHCl_3$); ν_{max}/cm^{-1} 3500, 1723; δ_H (500 MHz, $CDCl_3$) 0.89 (3H, d, *J* = 7.0 Hz), 1.01 (9H, s), 2.36-2.42 (2H, m merged with br s), 3.42-3.45 (1H, m), 3.97-3.99 (1H, m), 4.38-4.40 (2H, m), 4.84-4.96 (2H, m), 5.41-5.49 (1H, m), 7.28-7.35 (4H, m), 7.55-7.65 (9H, m), 7.73-7.75 (2H, m); δ_C (125 MHz,

$CDCl_3$) 17.1, 24.7, 37.5, 63.4, 71.0, 74.4, 113.4, 125.6, 125.8, 125.9, 126.3, 127.8, 127.9, 128.1, 130.9, 132.9, 133.6, 133.9, 134.0, 138.3, 164.8. Anal. Calc. for $C_{30}H_{36}O_4Si$: C, 73.73; H, 7.43%. Found: C, 73.58; H, 7.59%.

(3*R*,4*S*,5*R*)-(4-Benzoyloxy-3-methyl-5-*tert*-butyldiphenylsilyloxymethyl) dihydro-2(3*H*)-furanone 3. Ozone was bubbled for 20 min through a solution of **3c** (250 mg, 0.51 mmol) and methanolic NaOH (1.0 mL, 2.5 M) in CH_2Cl_2 (20 mL) at -78 ^oC. After stirring the mixture for 3 h at the same temperature, it was diluted with $CHCl_3$ (15 mL) and H_2O (10 mL), brought to room temperature, the organic layer separated and the aqueous layer extracted with $CHCl_3$ (2 × 10 mL). The combined organic extracts were washed with H_2O (2 × 10 mL) and brine (1 × 5 mL), and dried. Removal of solvent in vacuo followed by column chromatography (silica gel, 5-15% $CHCl_3$/MeOH) of the residue afforded **3** (170 mg, 68%); colorless oil; $[\alpha]_D^{24}$ +21.4 (*c* 1.1 in $CHCl_3$) (lit.[9a] $[\alpha]_D^{24}$ +21.1 (*c* 0.721 in $CHCl_3$)); ν_{max}/cm^{-1} 1739, 1692; δ_H (500 MHz, $CDCl_3$) 0.93 (3H, d, *J* = 6.5 Hz), 1.19 (9H, s), 2.92-2.97 (1H, m), 3.84-3.87 (2H, m), 4.64-4.78 (1H, m), 5.84 (1H, dd, *J* = 12.5, 9.5 Hz), 7.28-7.34 (4H, m), 7.47-7.90 (9H, m), 8.02-8.04 (2H, m); δ_C (125 MHz, $CDCl_3$) 10.2, 19.6, 27.2, 49.7, 70.0, 75.0, 82.2, 125.6, 125.8, 125.9, 126.3, 127.7, 127.8, 130.9, 132.9, 133.9, 134.0, 165.4, 176.7. Anal. Calc. for $C_{29}H_{32}O_5Si$: C, 71.28; H, 6.60%. Found: C, 71.24; 6.84%.


8.792
7.554
7.502
4.800
4.279
4.264
4.250
3.962
1.943
1.928
1.913
1.898
1.883
1.879
1.419
1.404
1.388
1.373
1.358
0.994
0.979
0.964
Br
1.00
1.77
2.37
3.12
2.38
2.29
3.24
f1 (ppm)

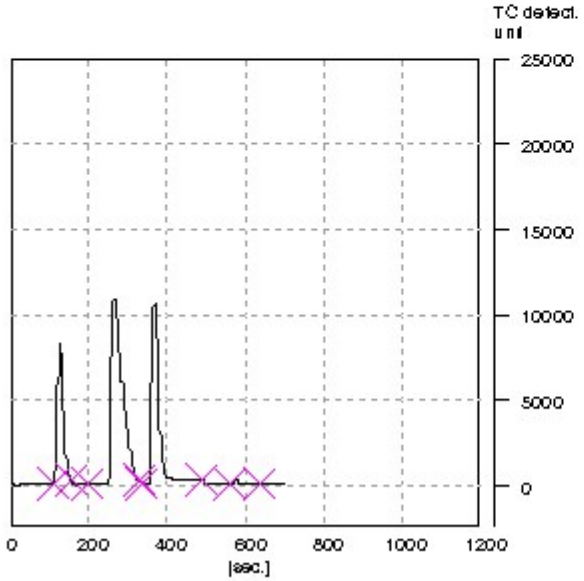

135.803
123.478
122.229
49.309
35.755
31.281
18.778
12.707
Br
f1 (ppm)

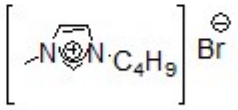
Document: rakes20-1-2017 (VarioMICRO) from: 2/6/2017 11:35:58 AM

analytic functional testing
varioMICRO CHNS
serial number: 15103026

Graphic report

	Weight [mg]	Name	Method	N Area	C Area	H Area	S Area	N [%]	C [%]	H [%]	S [%]	C/N ratio	C/H ratio
20	3.0860	DG IL	2mgChem80s	14 555	35 111	19 103	38	12.71	43.61	7.202	0.000	3.4306	6.0548





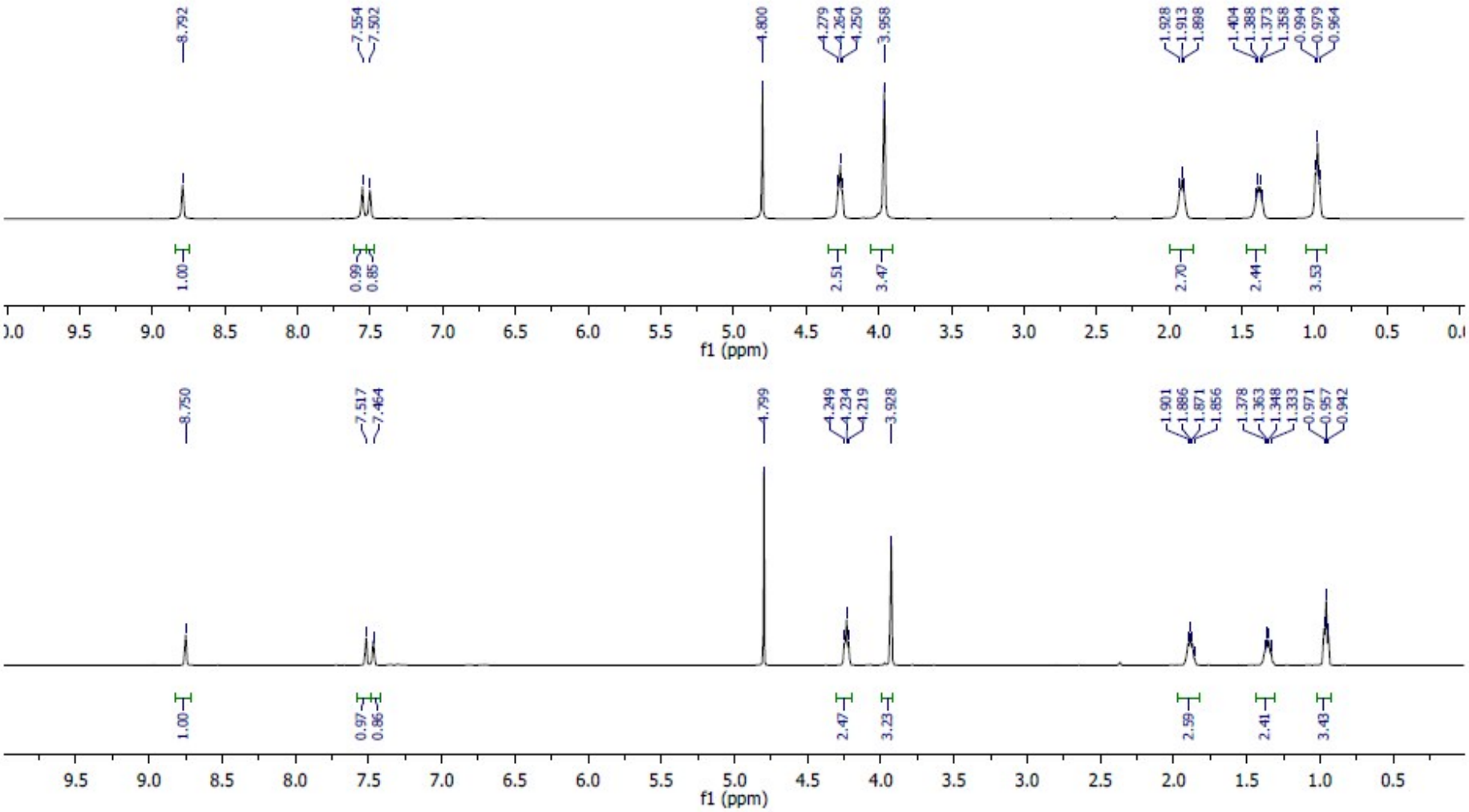


Fig. 1. ^{1}H NMR spectra of (**a**) [bmim][Br] and (**b**) [bmim][Br] + Bi (after 10 min) recorded in D_2O.

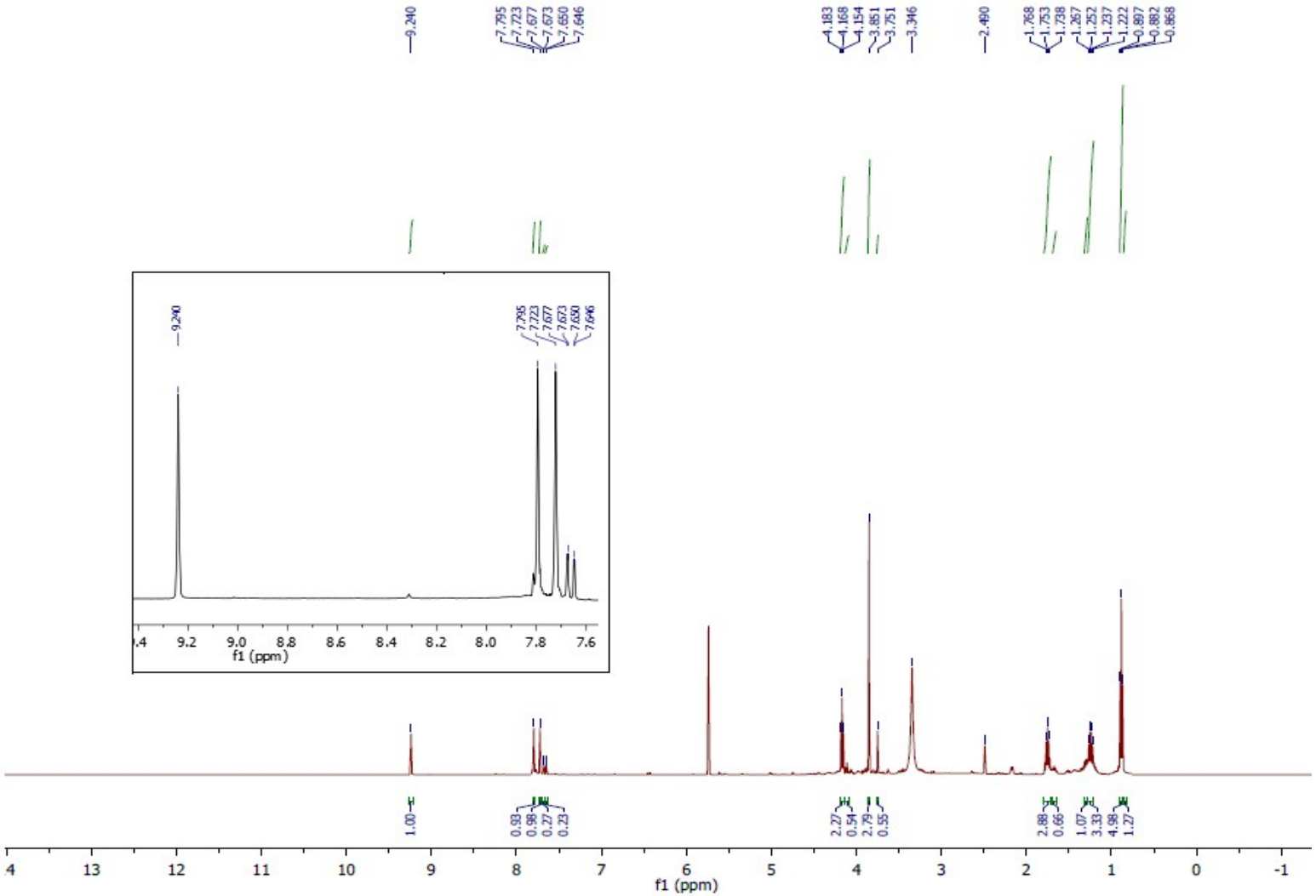


Fig. 2. Formation of the Bi-carbene as revealed from the ^{1}H NMR spectrum (recorded in DMSO-d_6) of a mixture of Bi and [bmim][Br] after incubating for 1 h.

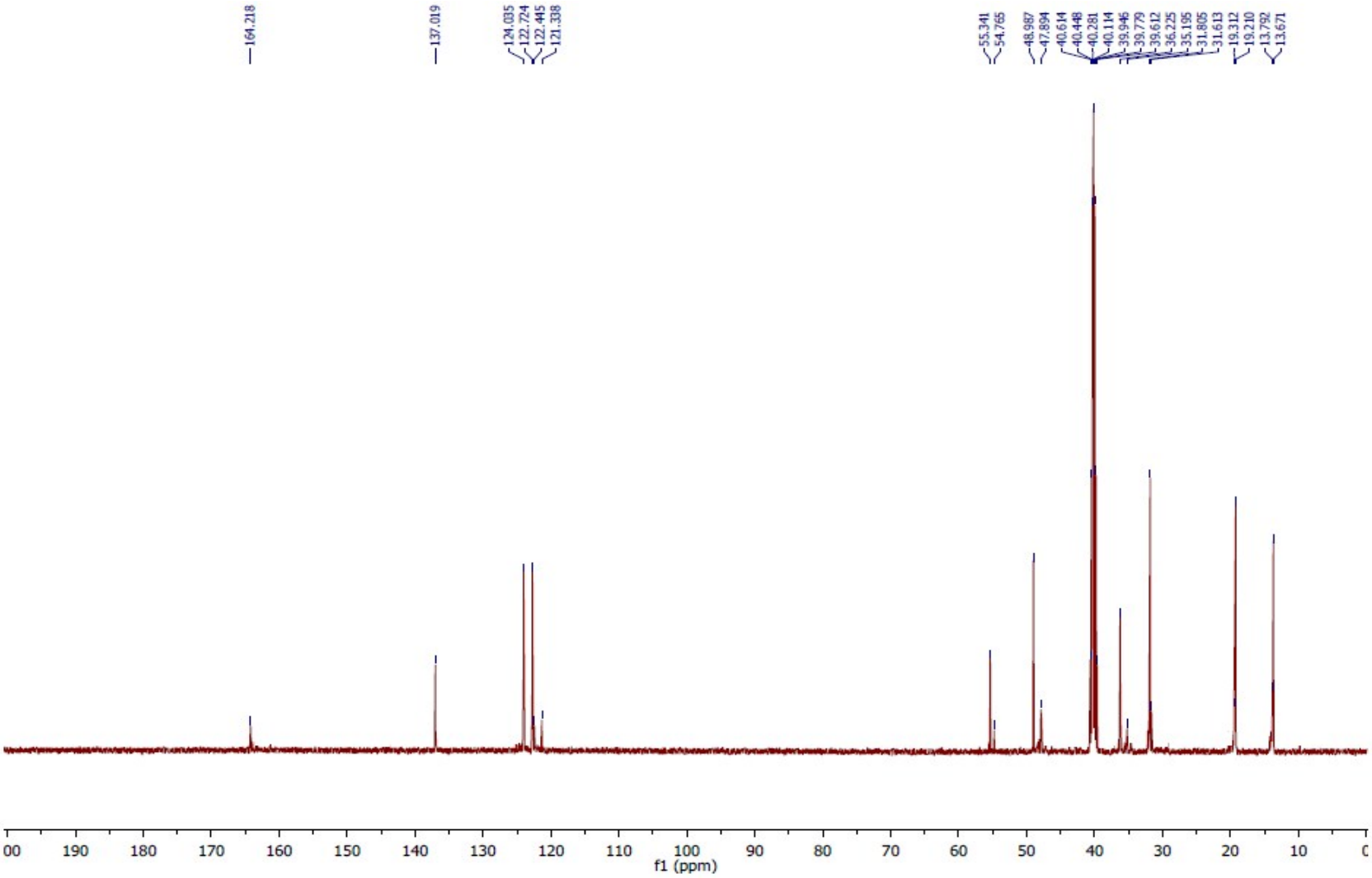


Fig. 3. Formation of the Bi-carbene as revealed from the ^{13}C NMR spectrum (recorded in DMSO-d_6) of a mixture of Bi and [bmim][Br] after incubating for 1 h.

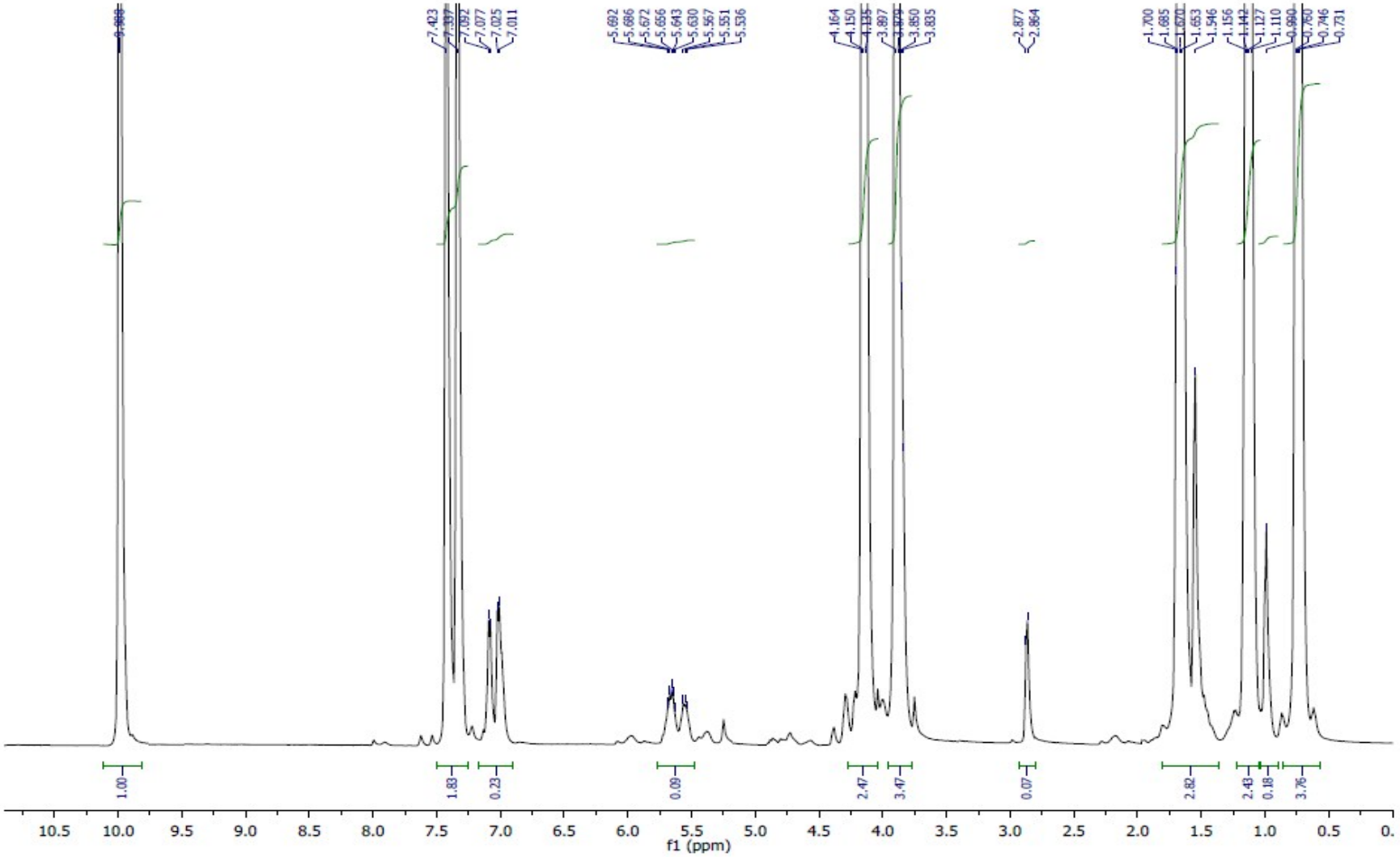


Fig. 4. Formation of the crotyl-Bi species (**I**) as revealed from the ^{1}H NMR spectrum (recorded in CD_2Cl_2 at -70 ^{o}C) of a mixture of Bi and crotyl bromide in [bmim][Br] after stirring for 1.5 h.

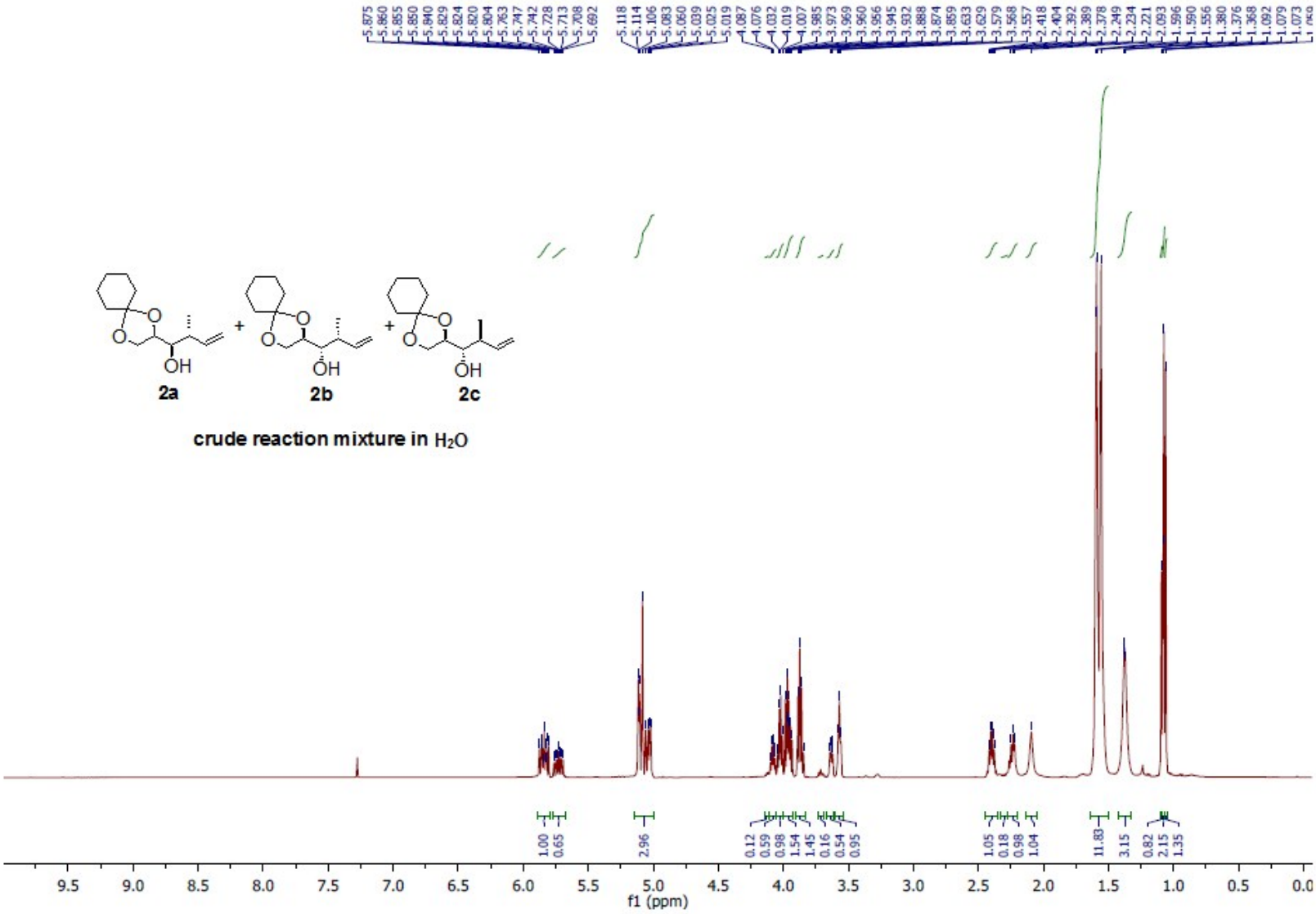


Fig. 5. ^{1}H NMR spectrum (recorded in $CDCl_3$) of the crude reaction mixture obtained from crotylation of **1** in H_2O.

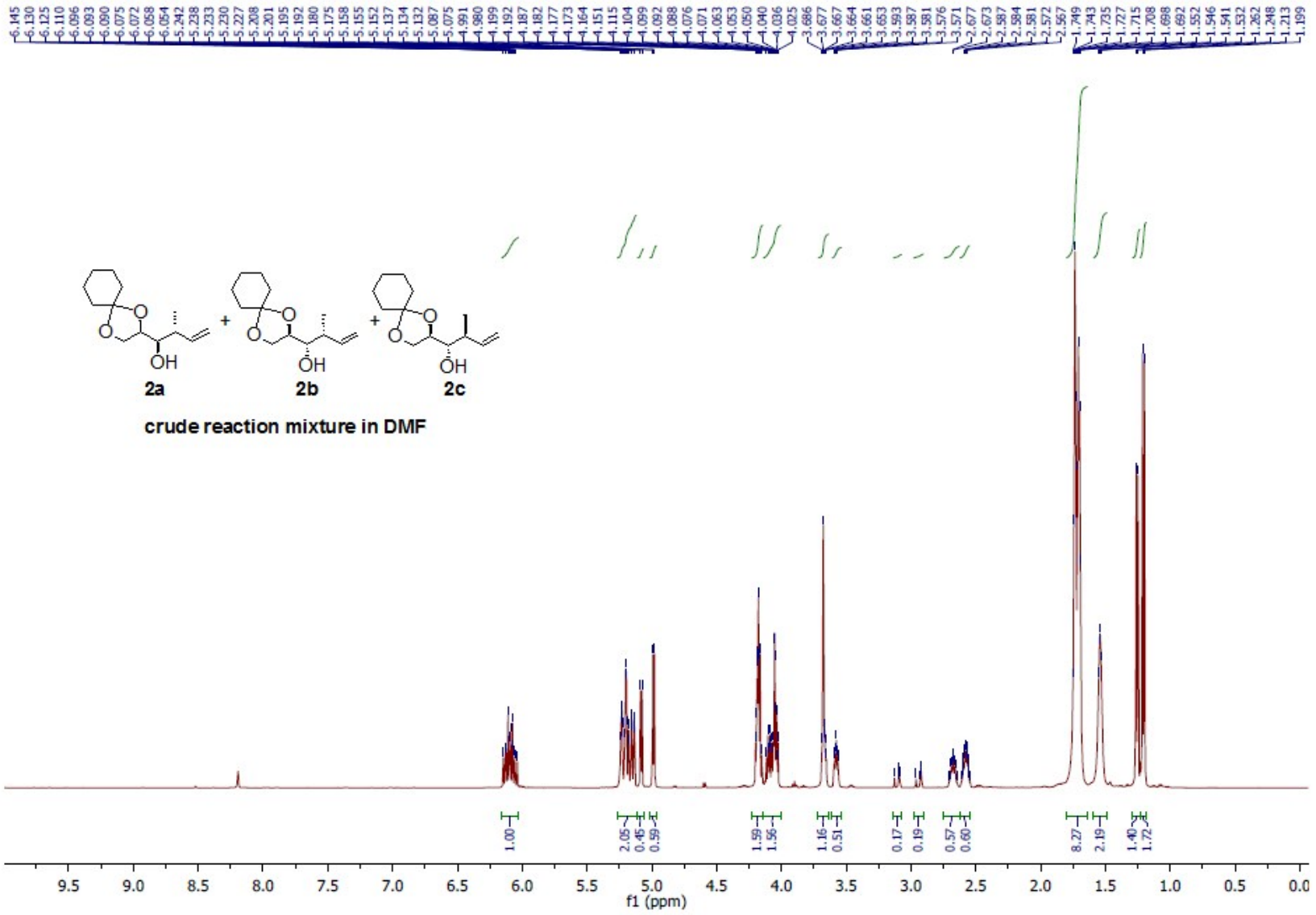


Fig. 6. ^{1}H NMR spectrum (recorded in DMF-d_7) of the crude reaction mixture obtained from crotylation of **1** in DMF.

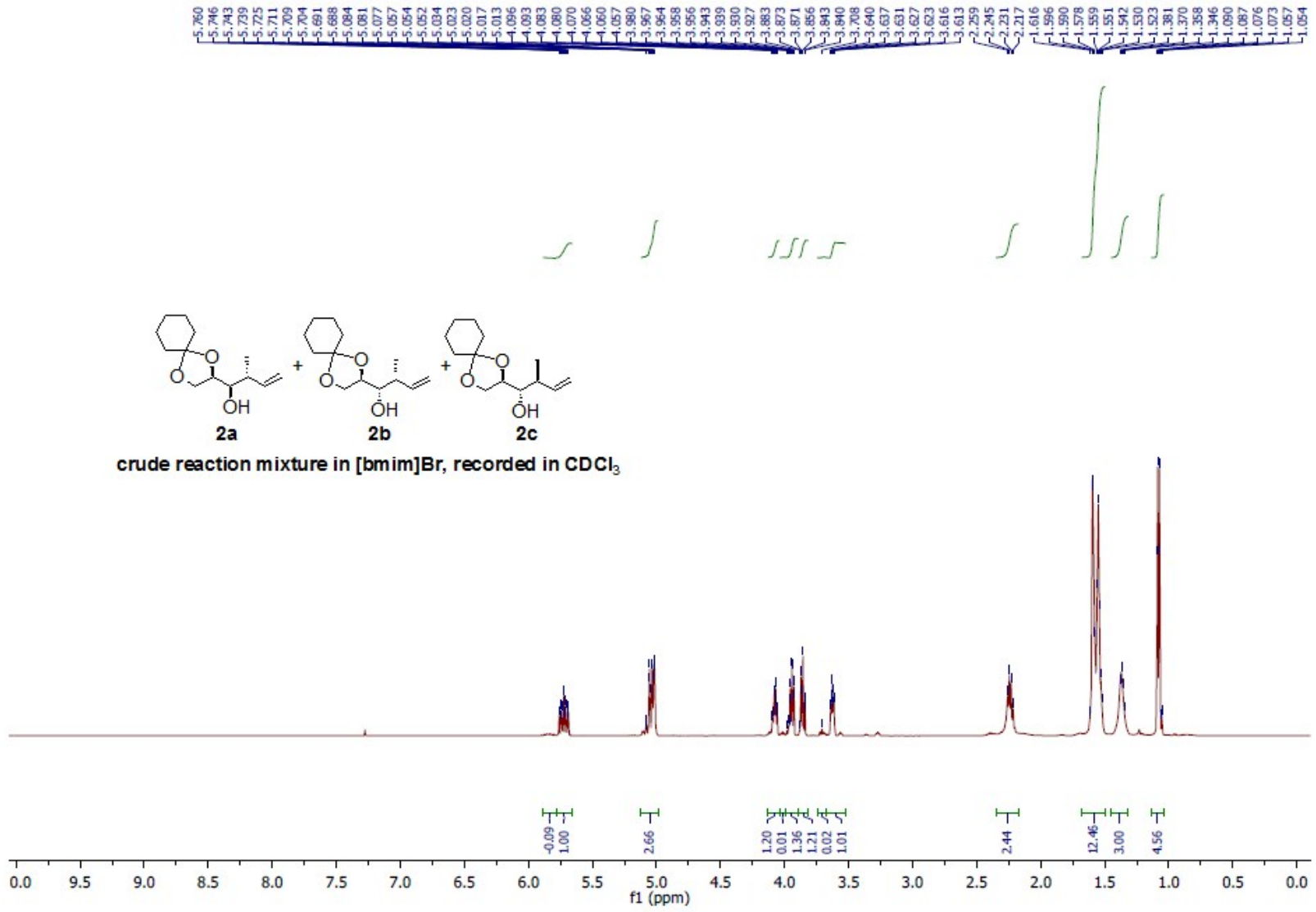


Fig. 7. ^{1}H NMR spectrum (recorded in $CDCl_3$) of the Et_2O extract of the crude reaction mixture obtained from crotylation of **1** in [bmim][Br].

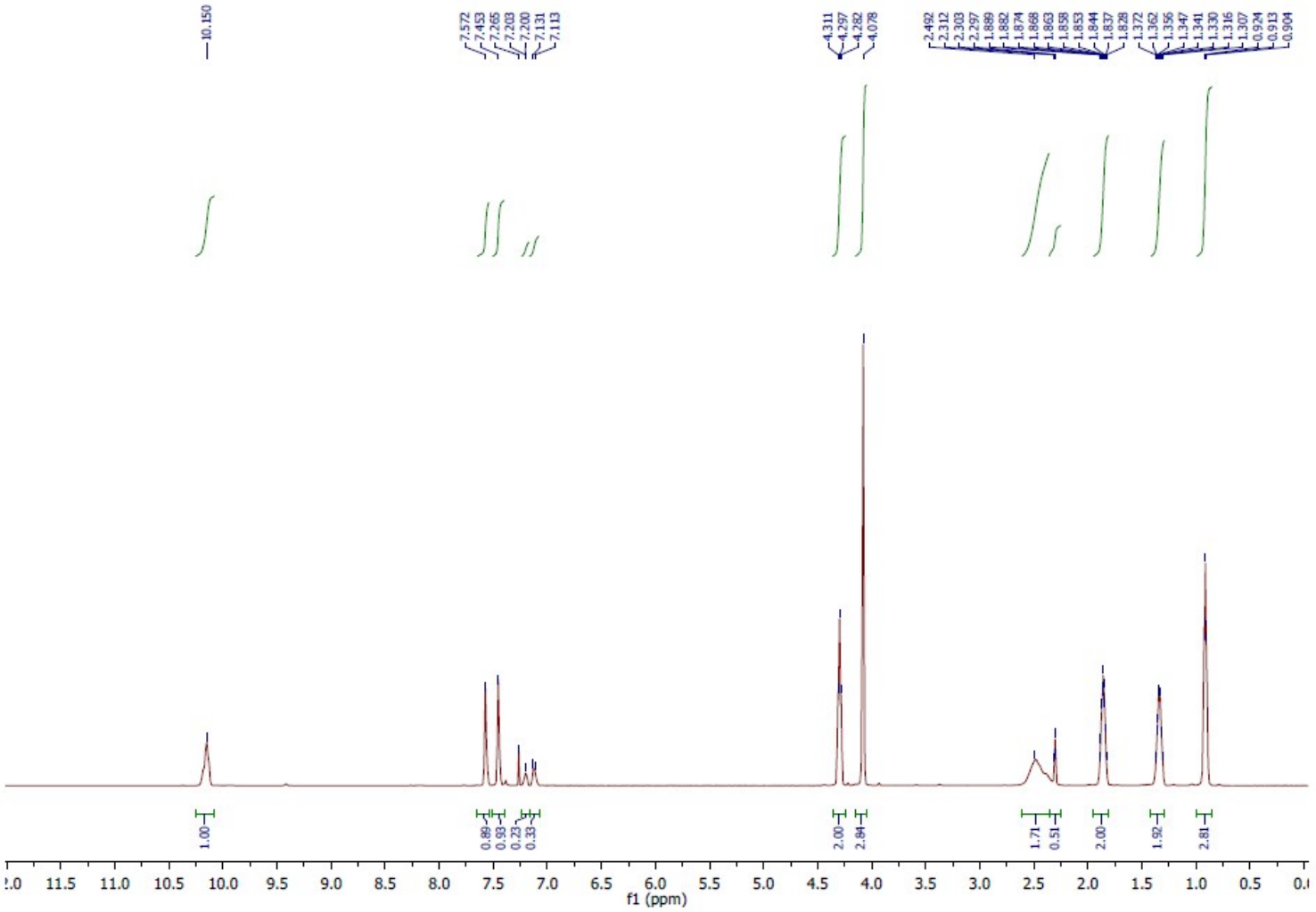
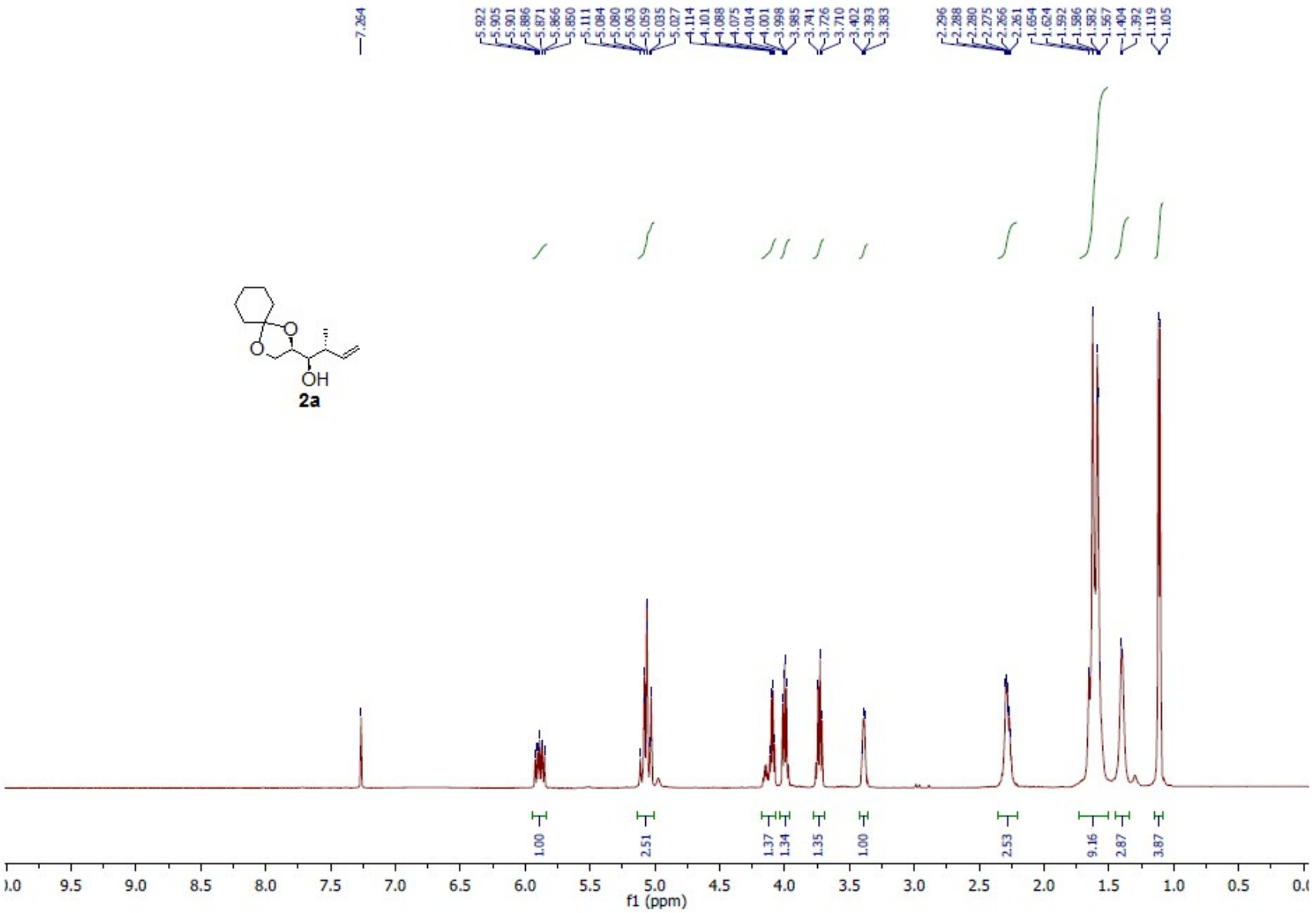
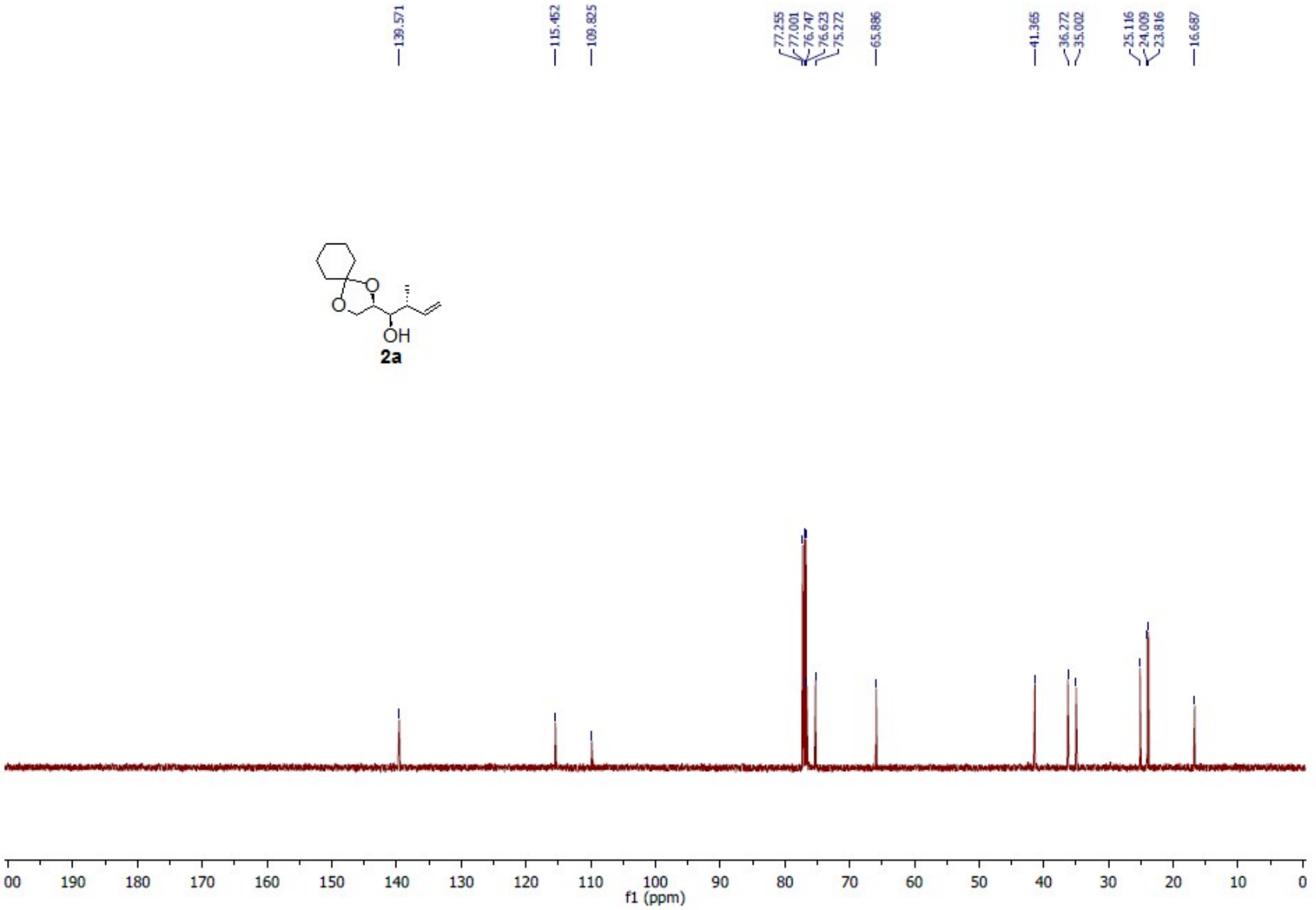
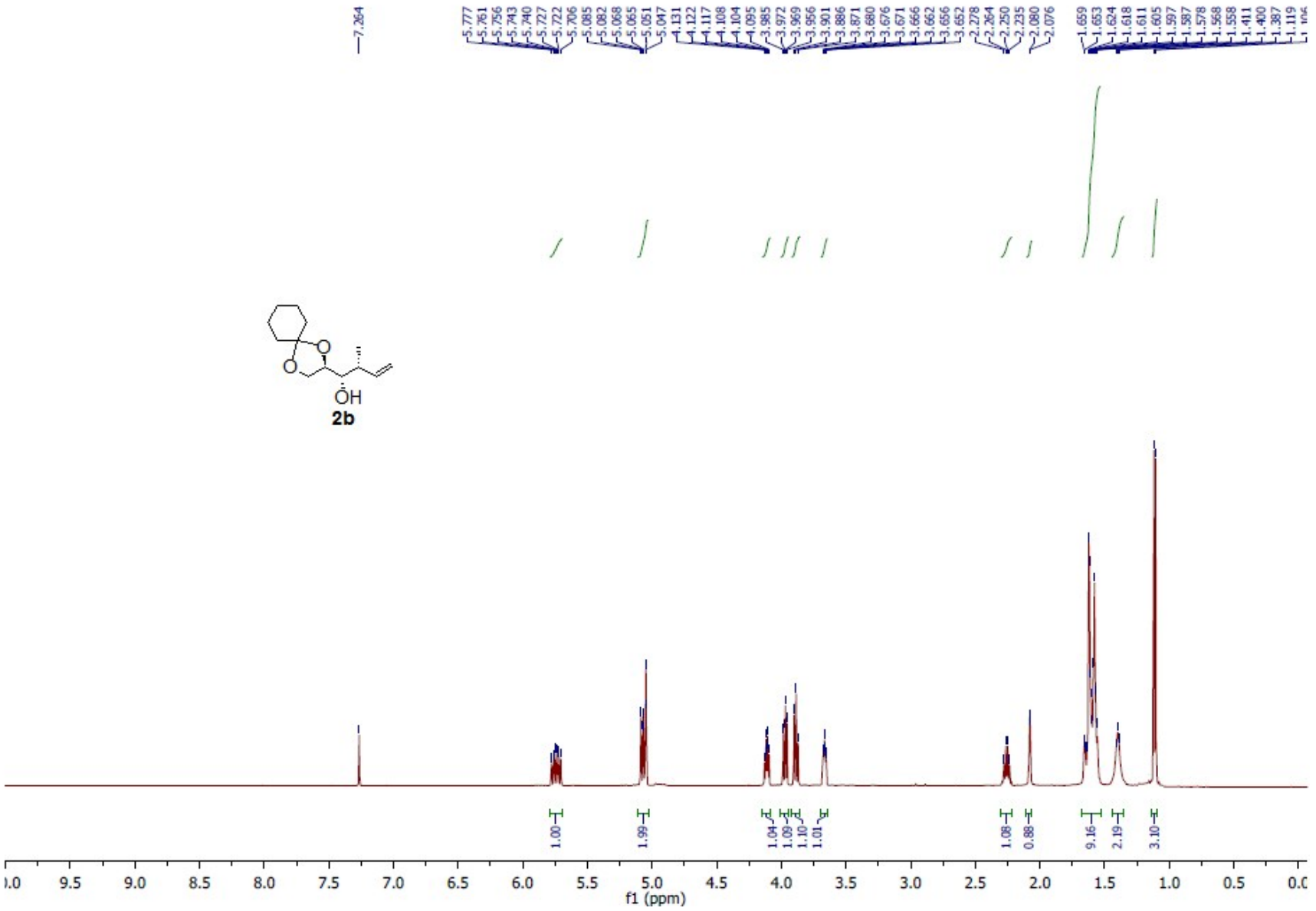
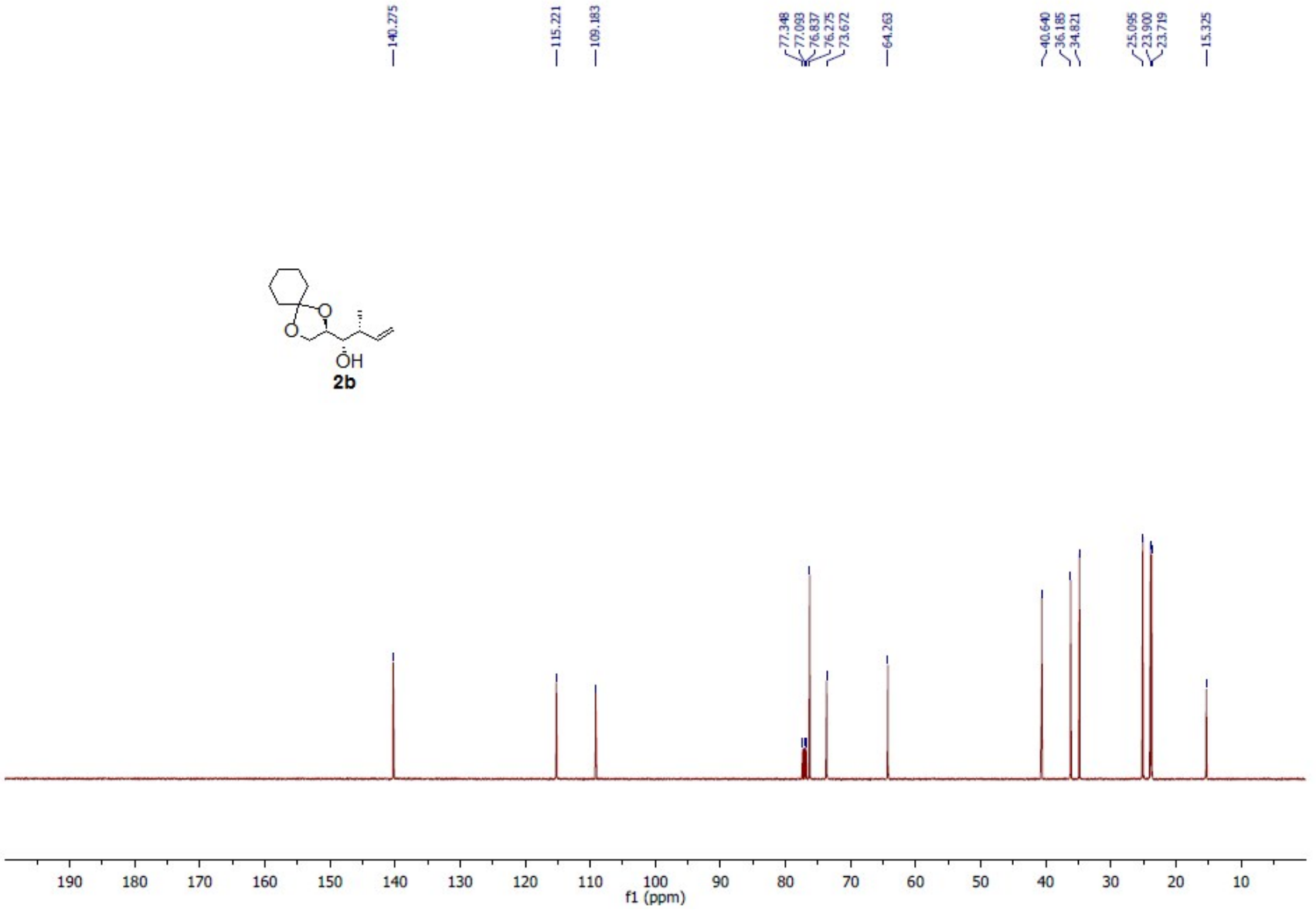


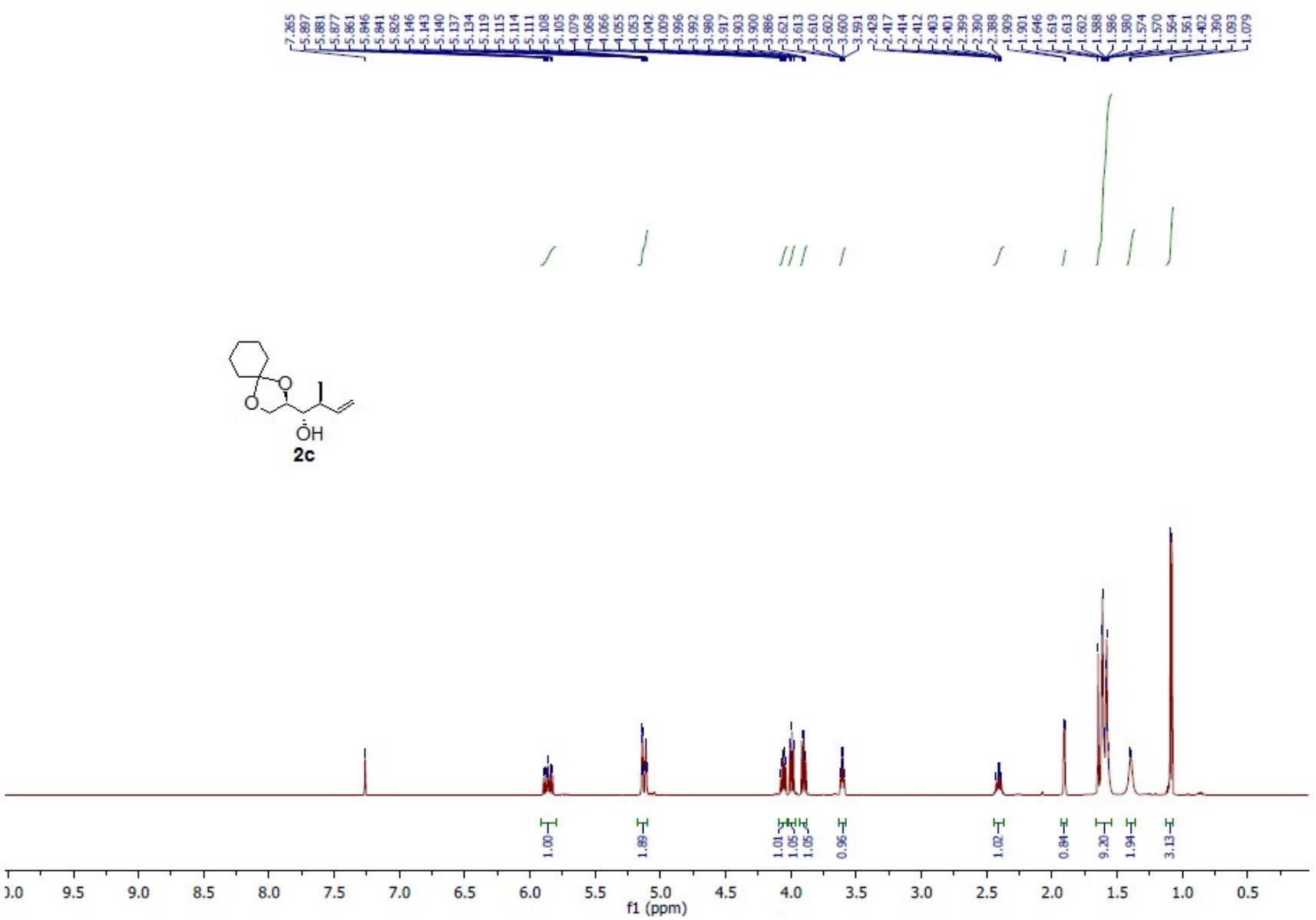
Fig. 8. Representative ^{1}H NMR spectrum (recorded in $CDCl_3$) of the residual [bmim][Br], left after extracting the reaction medium with Et_2O, showing that no product was left unextracted from the RTIL.

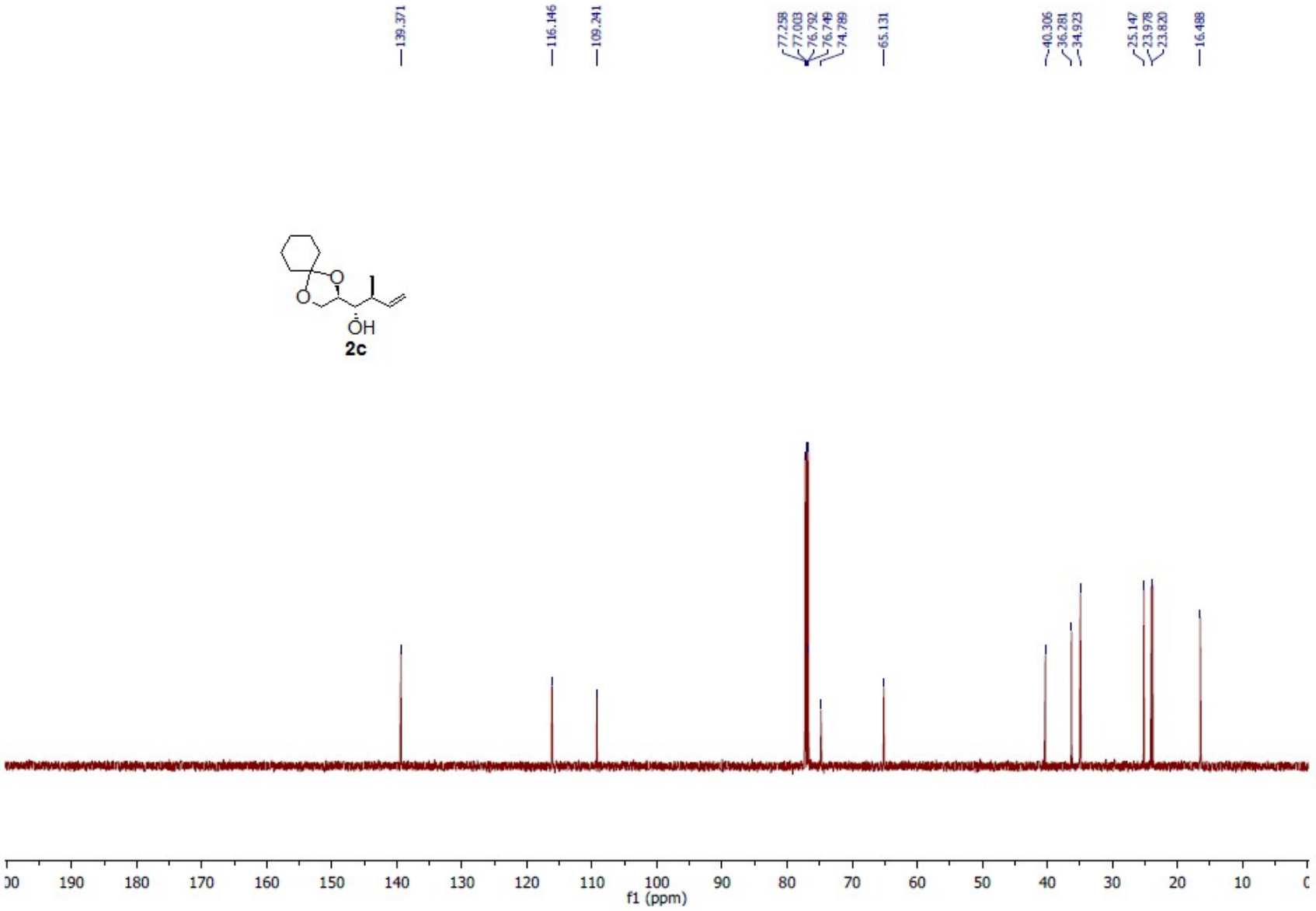

7.264
5.922
5.905
5.901
5.886
5.871
5.866
5.850
5.111
5.084
5.080
5.063
5.059
5.035
5.027
4.114
4.101
4.088
4.075
4.014
4.001
3.998
3.985
3.741
3.726
3.710
3.402
3.393
3.383
2.296
2.288
2.280
2.275
2.266
2.261
1.654
1.624
1.592
1.586
1.582
1.567
1.404
1.392
1.119
1.105
OH
2a
1.00
2.51
1.37
1.34
1.35
1.00
2.53
9.16
2.87
3.87
f1 (ppm)

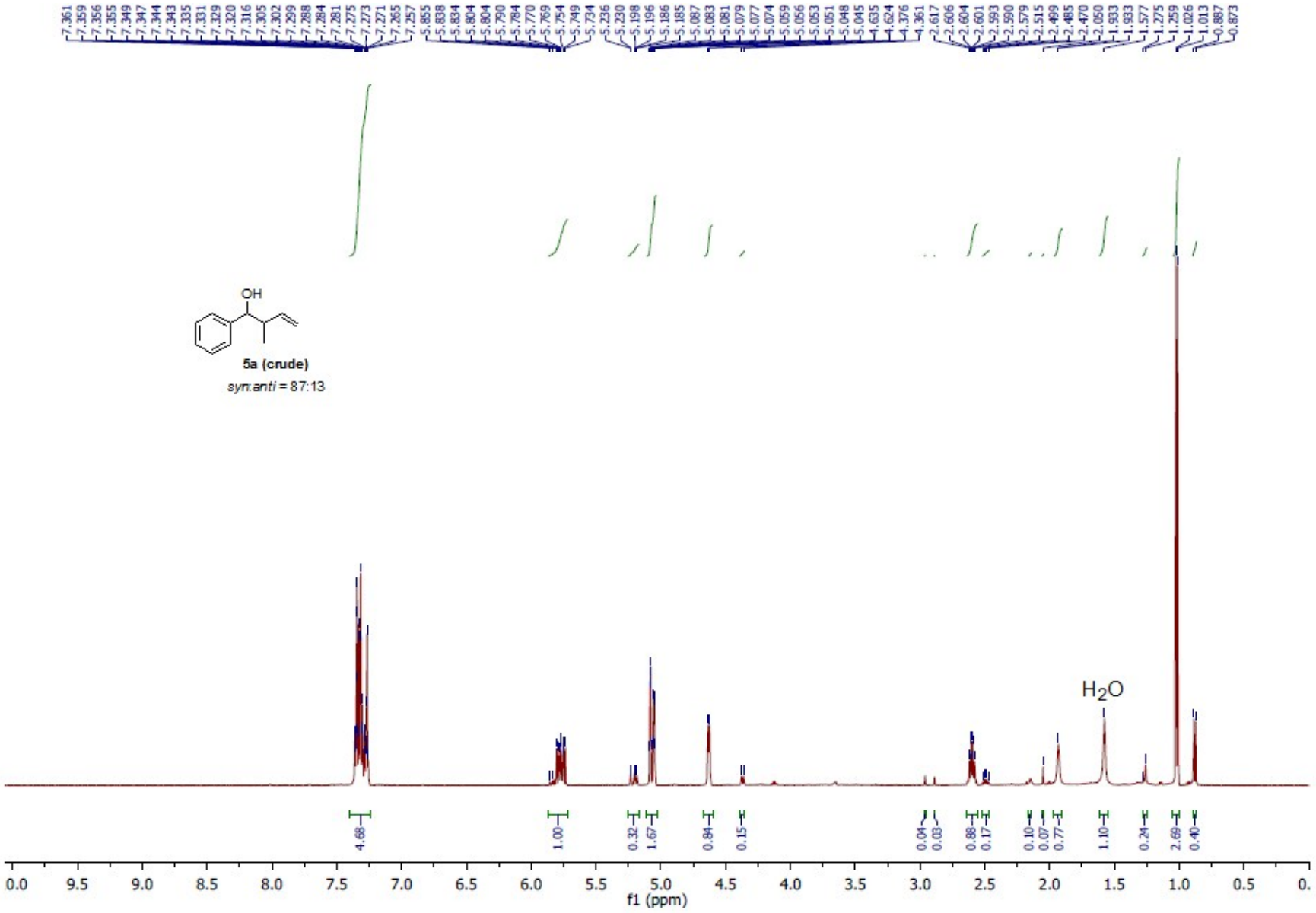

139.571
115.452
109.825
77.255
77.001
76.747
76.623
75.272
65.886
41.365
36.272
35.002
25.116
24.009
23.816
16.687
O
O
OH
2a
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

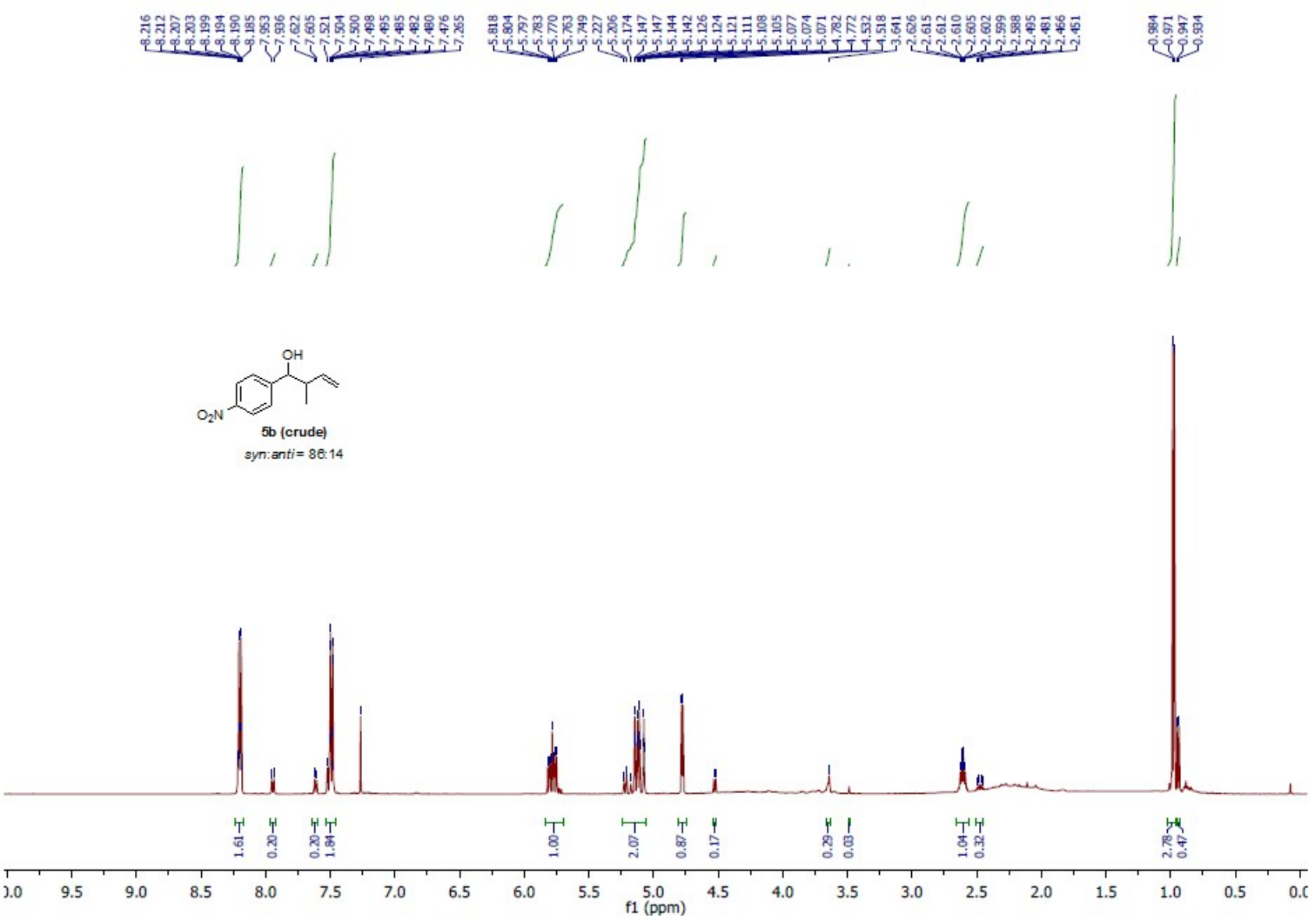

7.264
5.777
5.761
5.756
5.743
5.740
5.727
5.722
5.706
5.085
5.082
5.068
5.065
5.051
5.047
4.131
4.122
4.117
4.108
4.104
4.095
3.985
3.972
3.969
3.956
3.901
3.886
3.871
3.680
3.676
3.671
3.666
3.662
3.656
3.652
2.278
2.264
2.250
2.235
2.080
2.076
1.659
1.653
1.624
1.618
1.611
1.605
1.597
1.587
1.578
1.568
1.558
1.411
1.400
1.387
1.119
OH
2b
1.00
1.99
1.04
1.09
1.10
1.01
1.08
0.88
9.16
2.19
3.10
f1 (ppm)

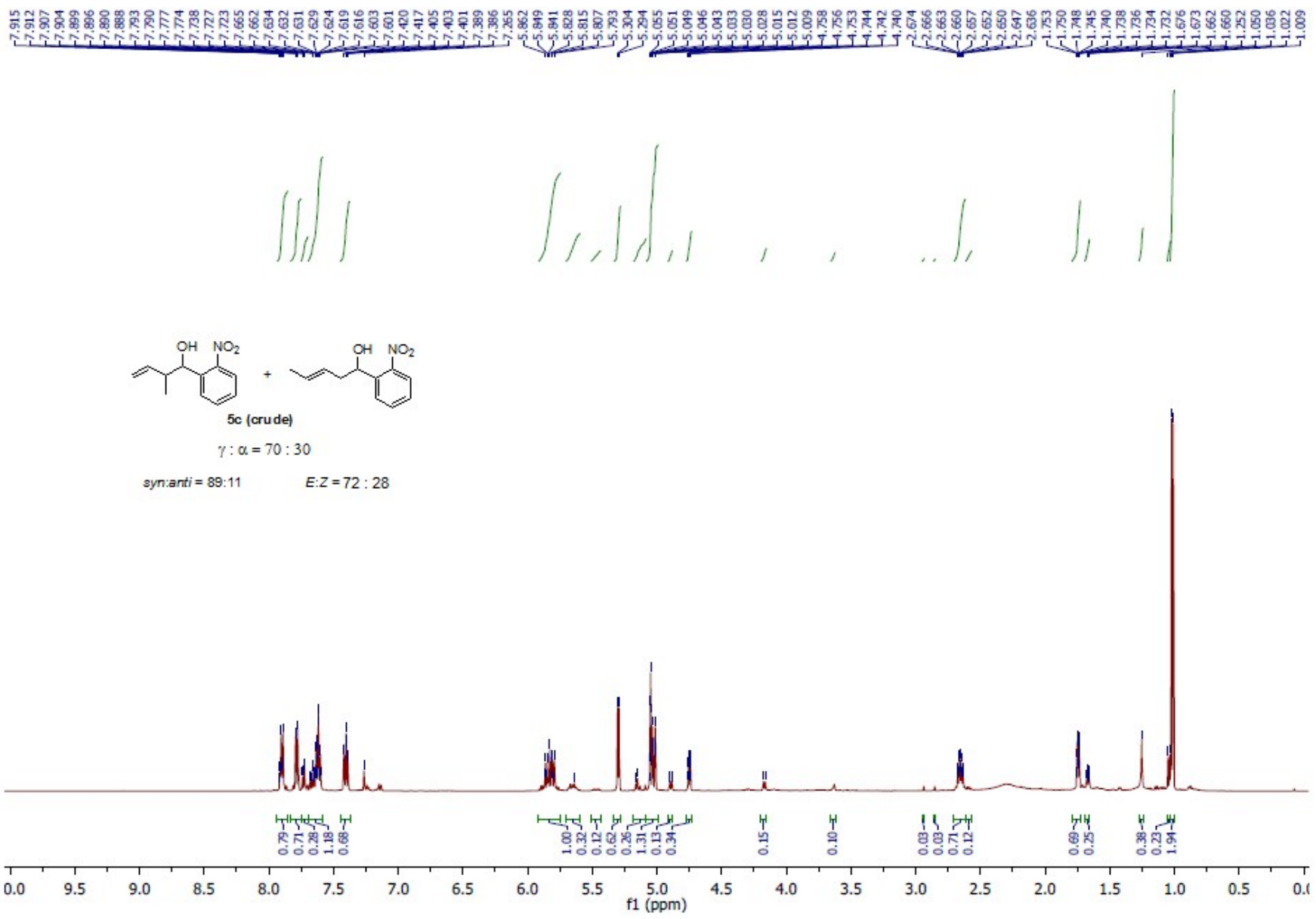

140.275
115.221
109.183
77.348
77.093
76.837
76.275
73.672
64.263
40.640
36.185
34.821
25.095
23.900
23.719
15.325
OH
2b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

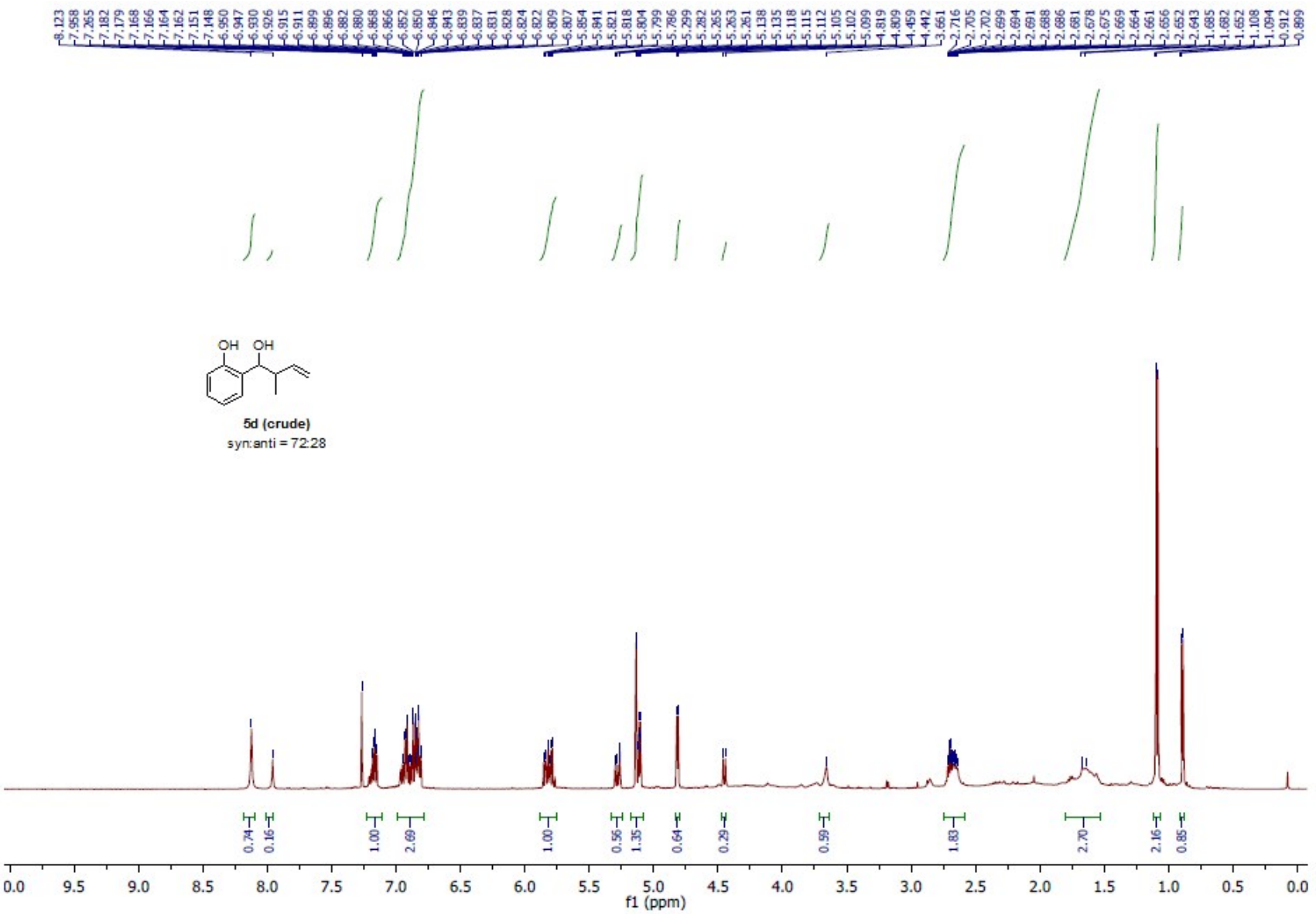

7.265
5.897
5.881
5.877
5.861
5.846
5.841
5.826
5.146
5.143
5.140
5.137
5.134
5.119
5.115
5.114
5.111
5.108
5.105
4.079
4.068
4.066
4.055
4.053
4.042
4.009
3.996
3.992
3.980
3.917
3.903
3.900
3.886
3.621
3.613
3.610
3.602
3.600
3.591
2.428
2.417
2.414
2.412
2.403
2.401
2.399
2.390
2.388
1.909
1.901
1.646
1.619
1.613
1.602
1.588
1.586
1.580
1.574
1.570
1.564
1.561
1.402
1.390
1.093
1.079
O
O
OH
2c
1.00
1.89
1.01
1.05
1.05
0.96
1.02
0.84
9.20
1.94
3.13
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
f1 (ppm)

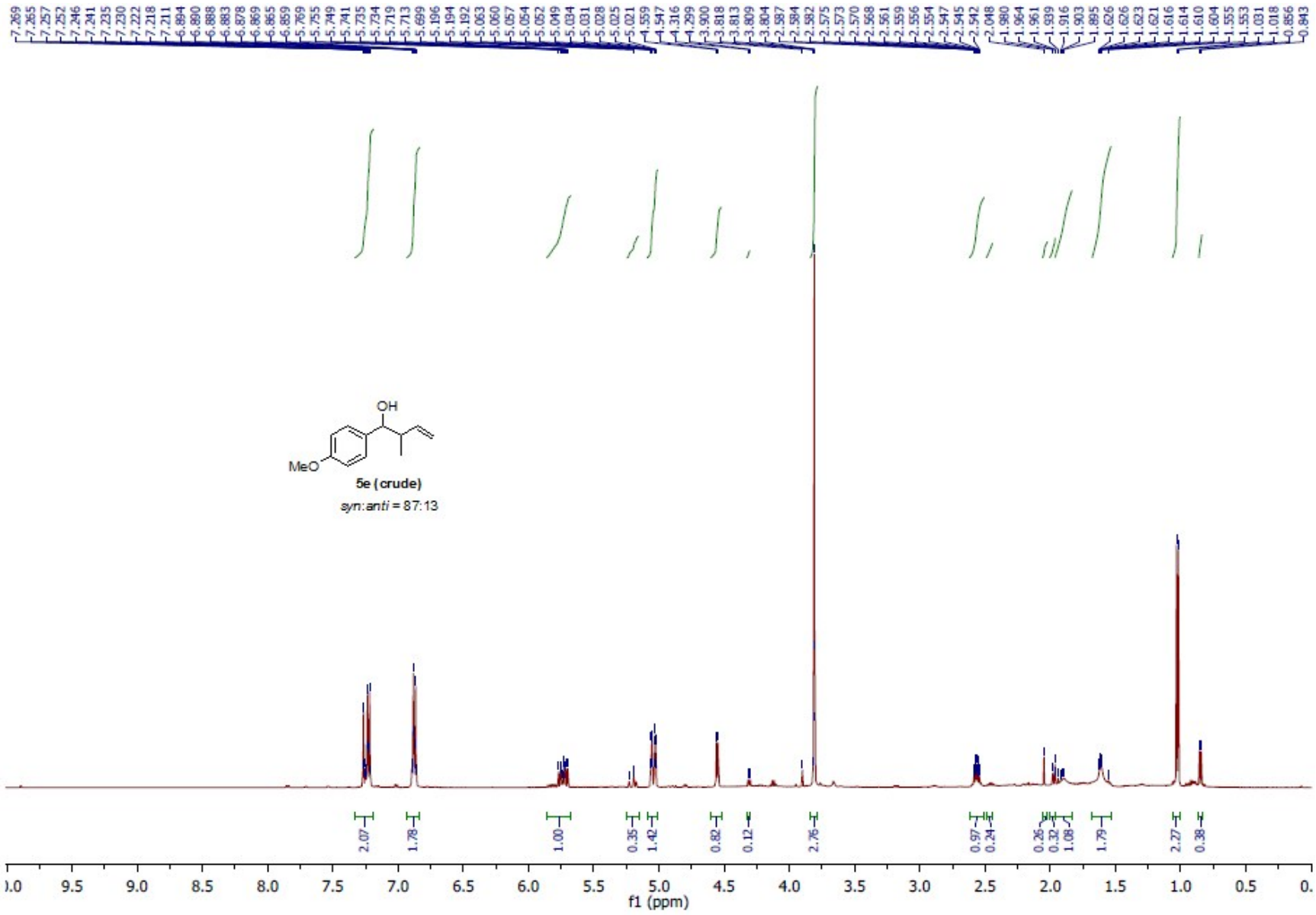

139.371
116.146
109.241
77.258
77.003
76.792
76.749
74.789
65.131
40.306
36.281
34.923
25.147
23.978
23.820
16.488
OH
2c
f1 (ppm)

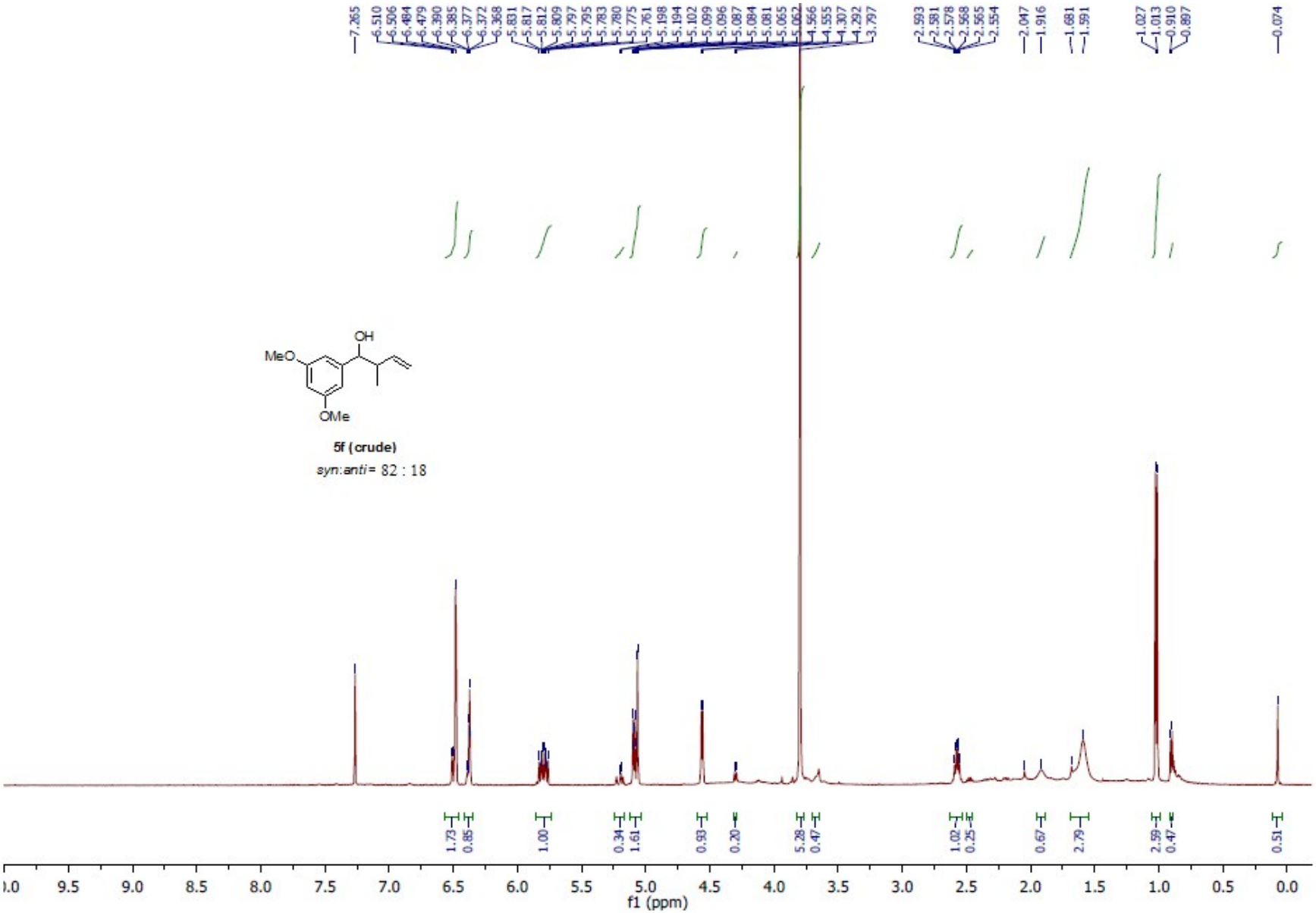

OH
5a (crude)
syn:anti = 87:13
H2O
f1 (ppm)

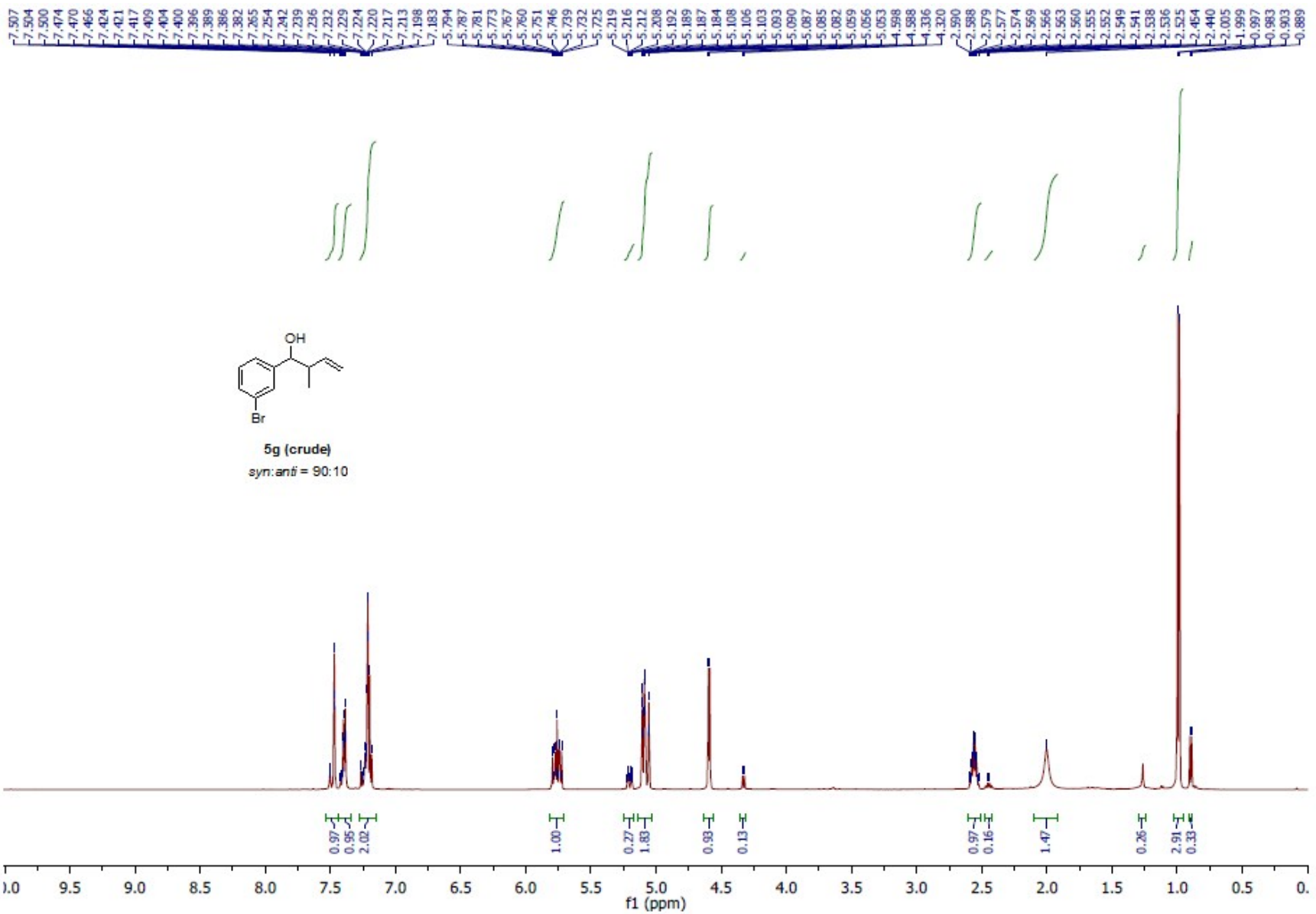

8.216
8.212
8.207
8.203
8.199
8.194
8.190
8.185
7.953
7.936
7.622
7.605
7.521
7.504
7.500
7.498
7.495
7.485
7.482
7.480
7.476
7.265
5.818
5.804
5.797
5.783
5.770
5.763
5.749
5.227
5.206
5.174
5.147
5.147
5.144
5.142
5.126
5.124
5.121
5.111
5.108
5.105
5.077
5.074
5.071
4.782
4.772
4.532
4.518
3.641
2.626
2.615
2.612
2.610
2.605
2.602
2.599
2.588
2.495
2.481
2.466
2.451
0.984
0.971
0.947
0.934
OH
O2N
5b (crude)
syn:anti = 86:14
1.61
0.20
0.20
1.84
1.00
2.07
0.87
0.17
0.29
0.03
1.04
0.32
2.78
0.47
f1 (ppm)

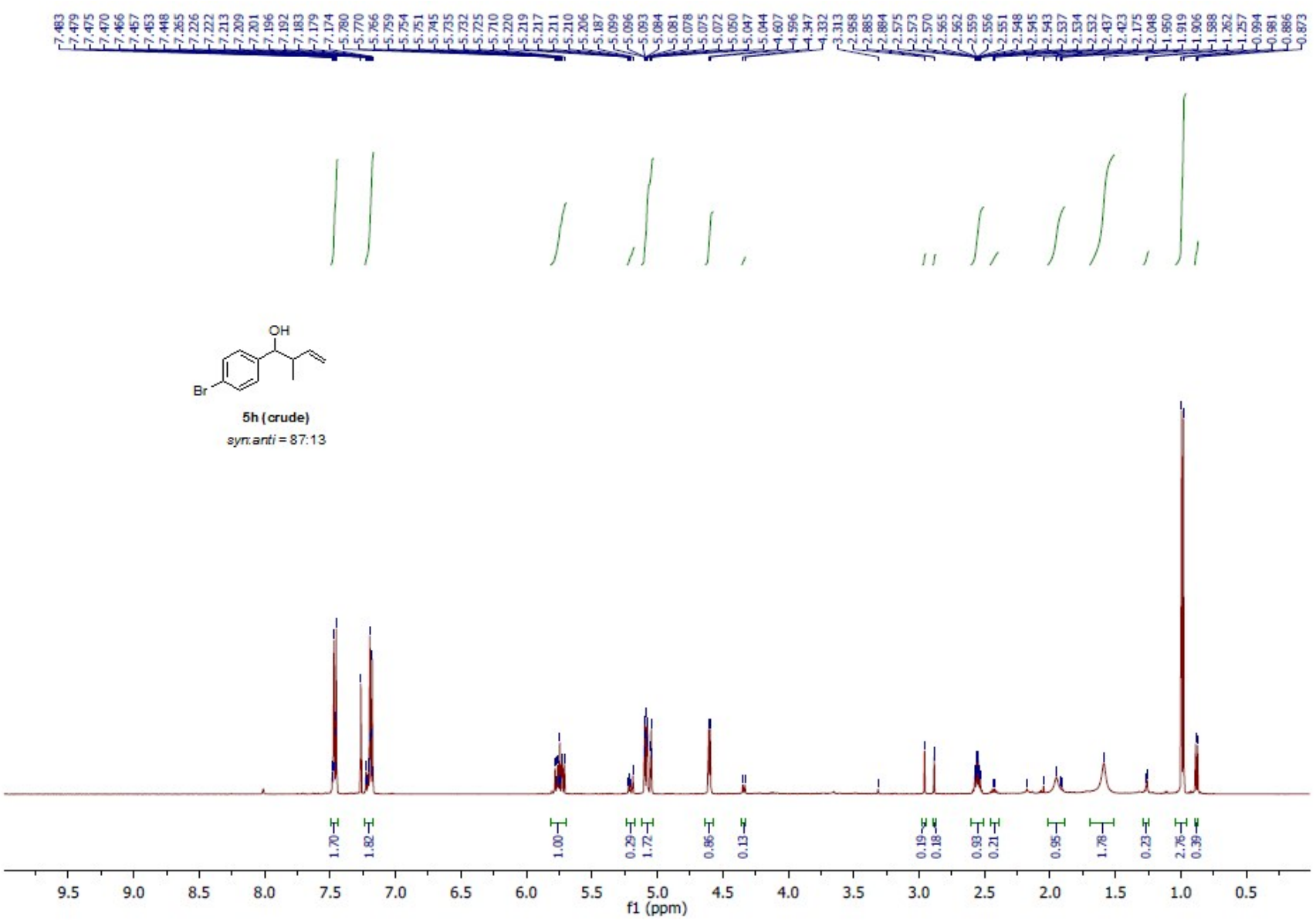

7.915 7.912 7.907 7.904 7.899 7.896 7.890 7.888 7.793 7.790 7.777 7.774 7.738 7.727 7.723 7.665 7.662 7.634 7.632 7.631 7.629 7.624 7.619 7.616 7.603 7.601 7.420 7.417 7.405 7.403 7.401 7.389 7.386 7.265 5.862 5.849 5.841 5.828 5.815 5.807 5.793 5.304 5.294 5.055 5.051 5.049 5.046 5.043 5.033 5.030 5.028 5.015 5.012 5.009 4.758 4.756 4.753 4.744 4.742 4.740 2.674 2.666 2.663 2.660 2.657 2.652 2.650 2.647 2.636 1.753 1.750 1.748 1.745 1.740 1.738 1.736 1.734 1.732 1.676 1.673 1.662 1.660 1.252 1.050 1.036 1.022 1.009
OH NO2
+
OH NO2
5c (crude)
γ : α = 70 : 30
syn:anti = 89:11
E:Z = 72 : 28
0.79 0.71 0.28 1.18 0.68 1.00 0.32 0.12 0.62 0.26 1.31 0.13 0.34 0.15 0.10 0.03 0.03 0.71 0.12 0.69 0.25 0.38 0.23 1.94
0.0 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
f1 (ppm)

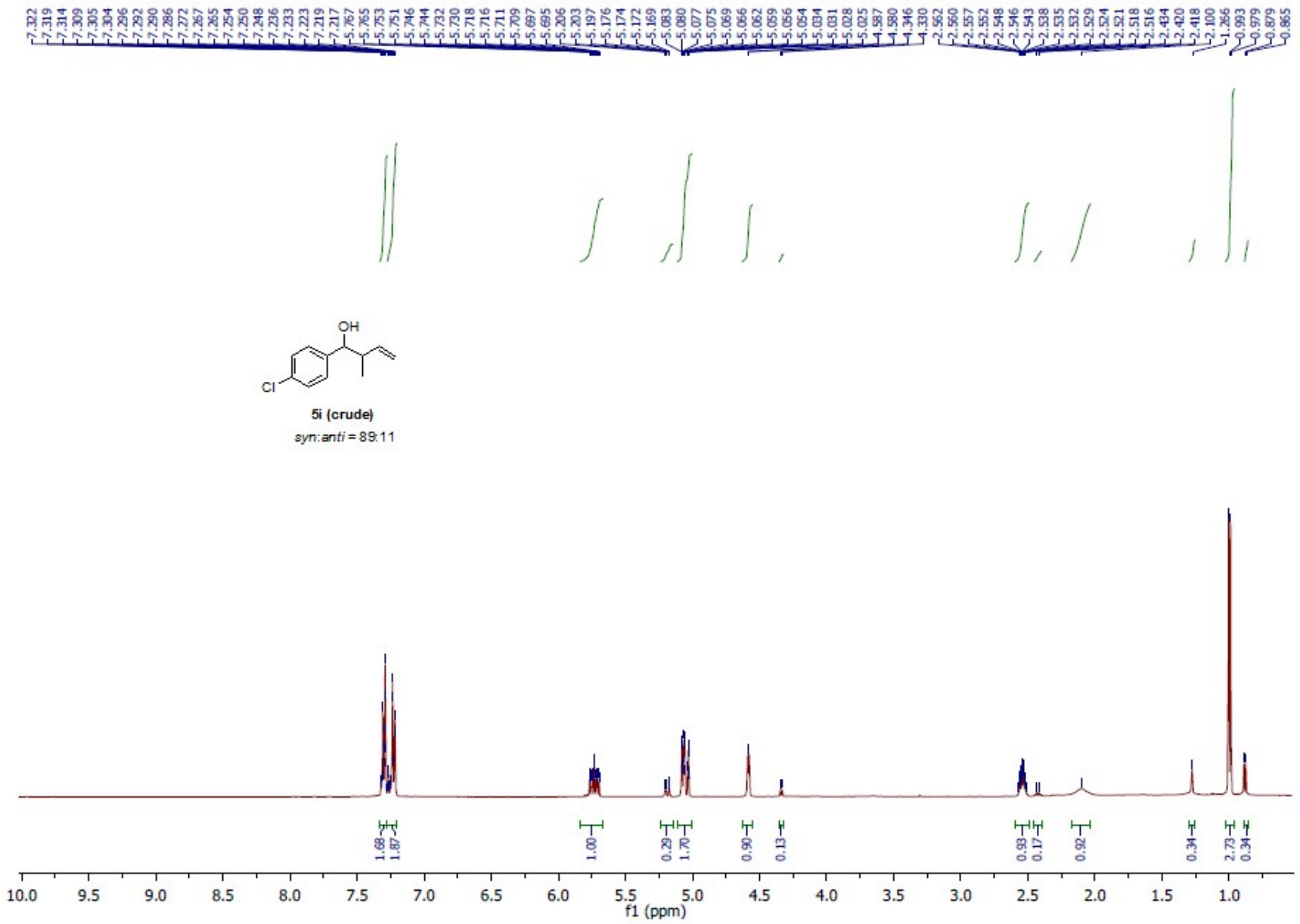

OH OH
5d (crude)
syn:anti = 72:28
f1 (ppm)

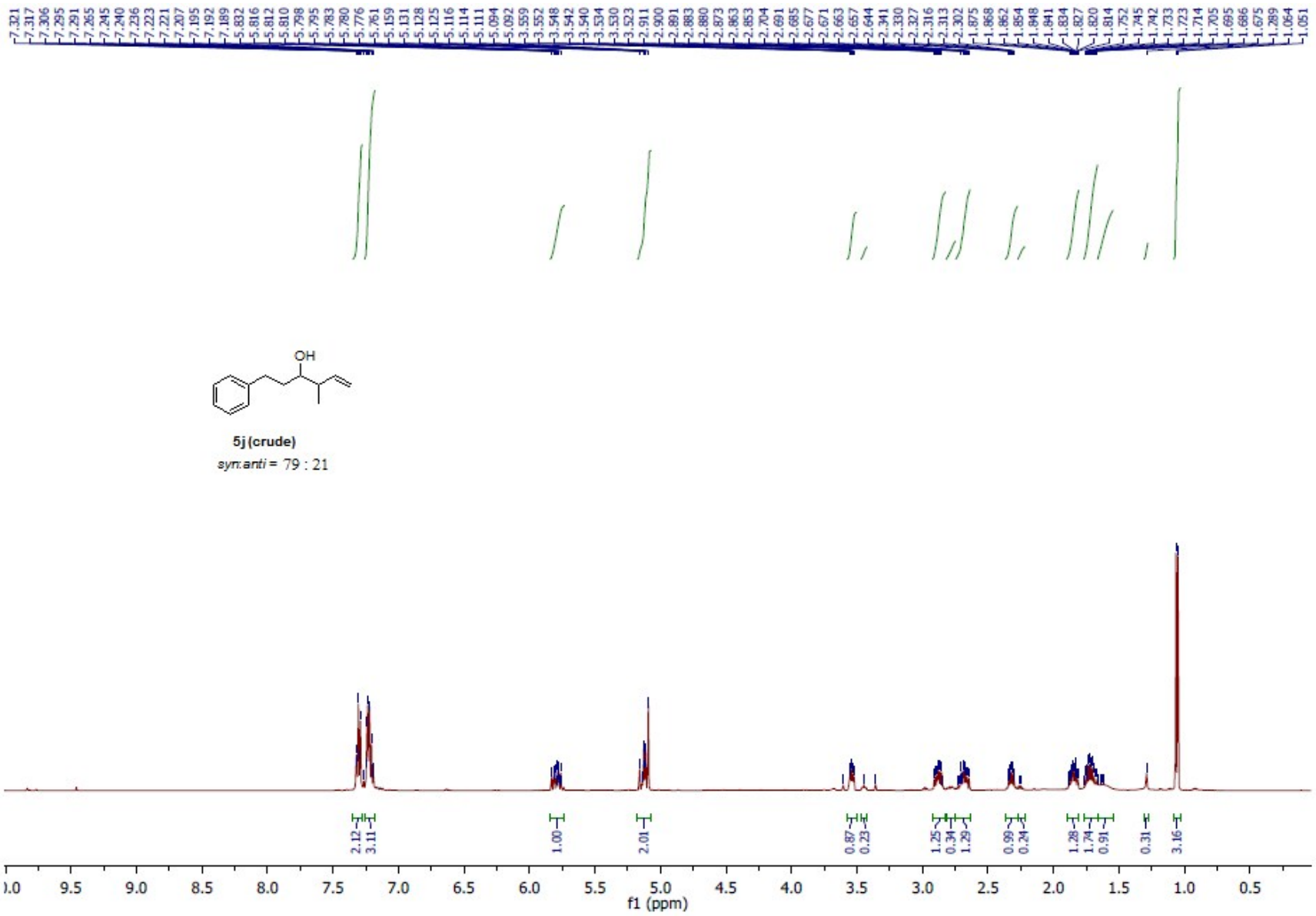

OH
MeO
5e (crude)
syn:anti = 87:13
f1 (ppm)

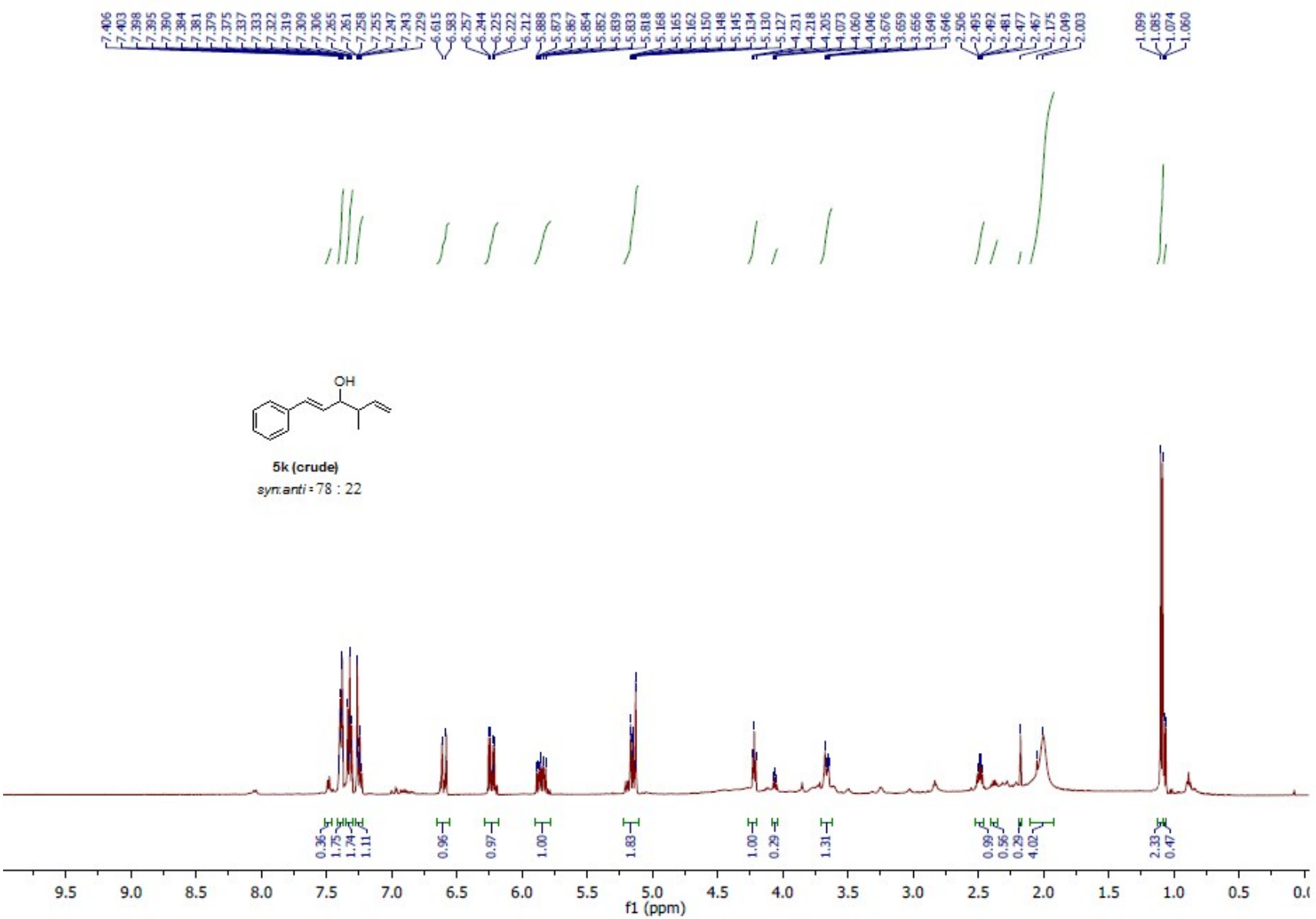

7.265
6.510
6.506
6.484
6.479
6.390
6.385
6.377
6.372
6.368
5.831
5.817
5.812
5.809
5.797
5.795
5.783
5.780
5.775
5.761
5.198
5.194
5.102
5.099
5.096
5.087
5.084
5.081
5.065
5.062
4.566
4.555
4.307
4.292
3.797
2.593
2.581
2.578
2.568
2.565
2.554
2.047
1.916
1.681
1.591
1.027
1.013
0.910
0.897
0.074
OH
MeO
OMe
5f (crude)
syn:anti = 82 : 18
1.73
0.85
1.00
0.34
1.61
0.93
0.20
5.28
0.47
1.02
0.25
0.67
2.79
2.59
0.47
0.51
f1 (ppm)

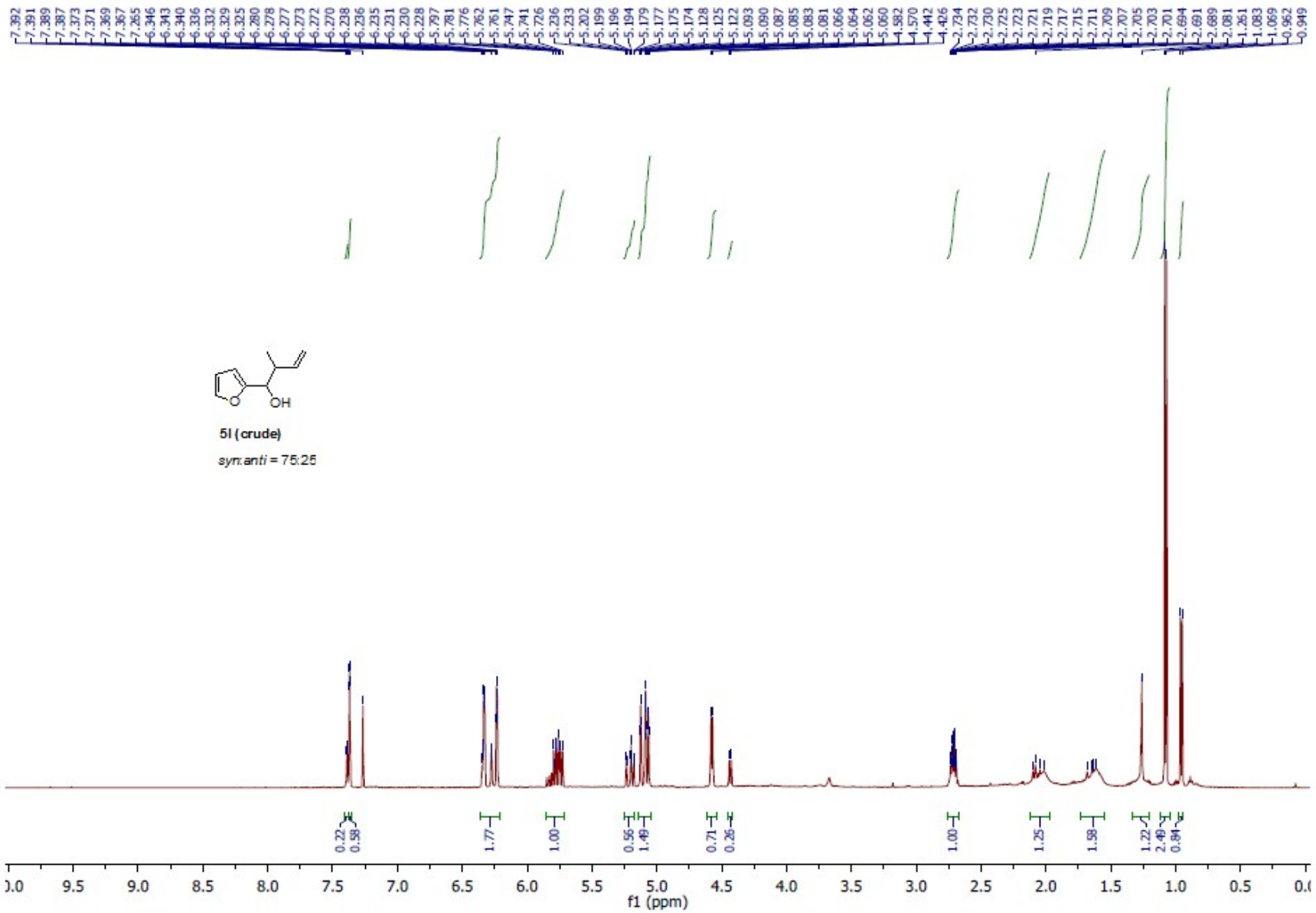

OH
Br
5g (crude)
syn:anti = 90:10
f1 (ppm)

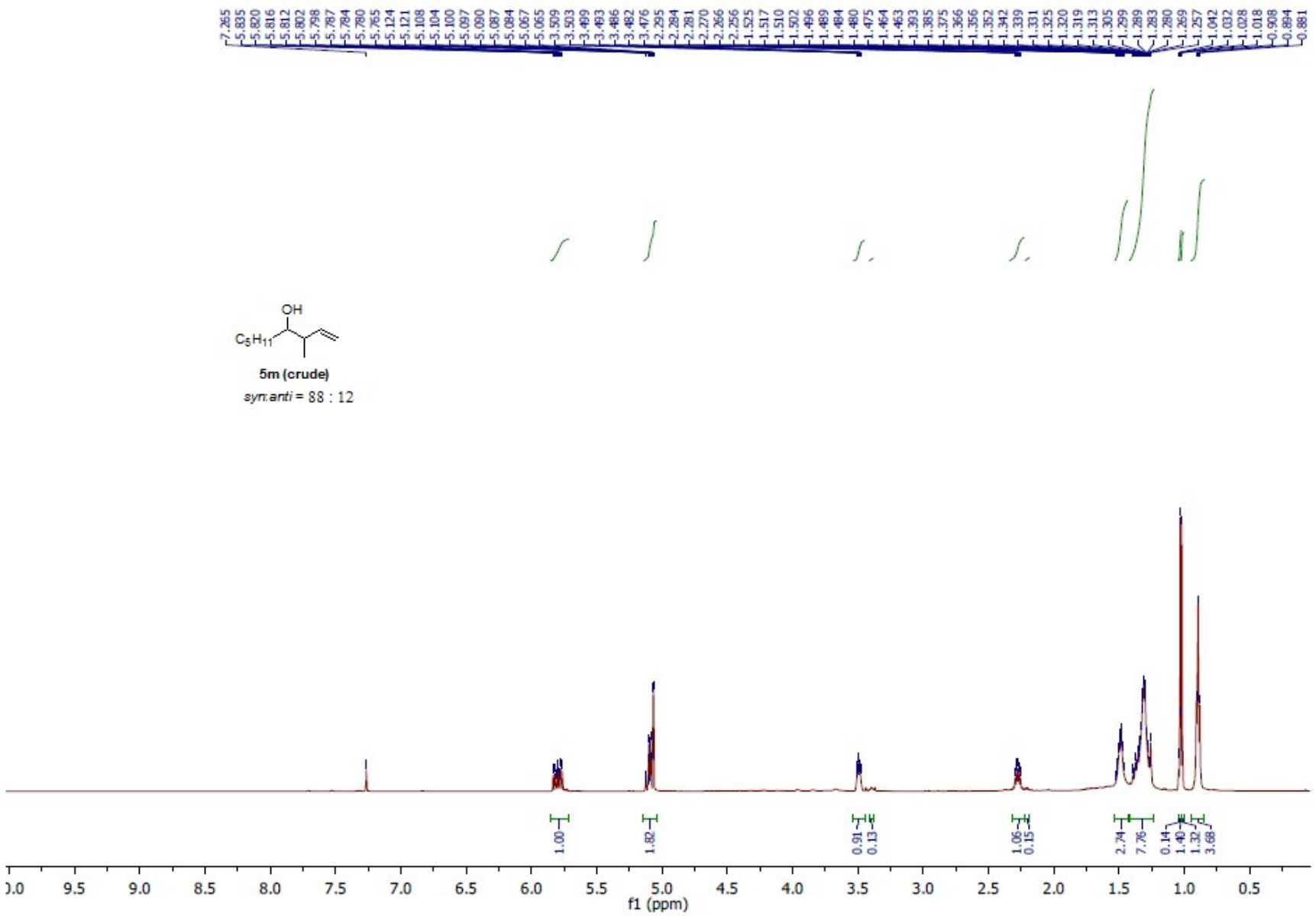

OH
Br
5h (crude)
syn:anti = 87:13
f1 (ppm)

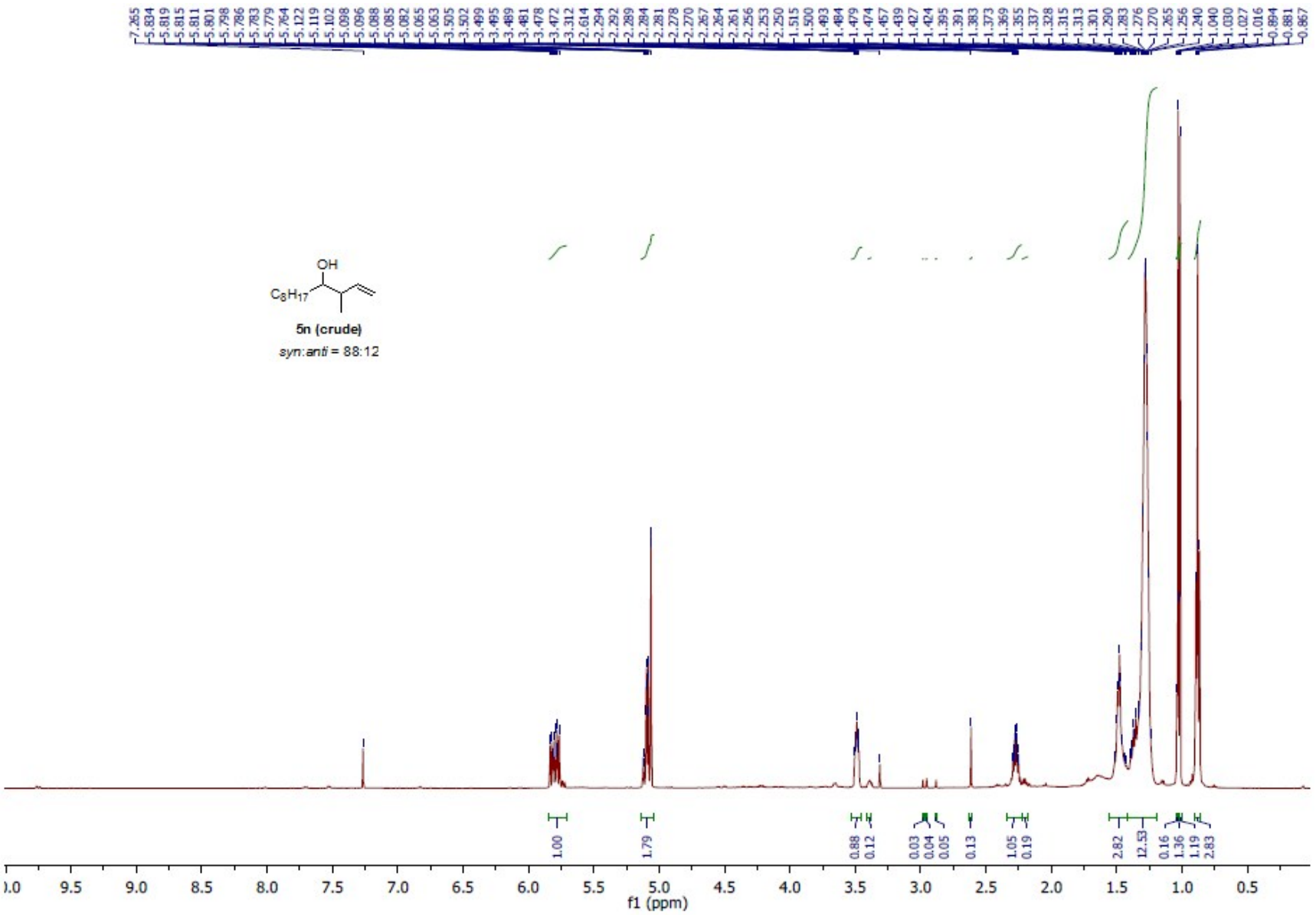

OH
Cl
5i (crude)
syn:anti = 89:11
f1 (ppm)

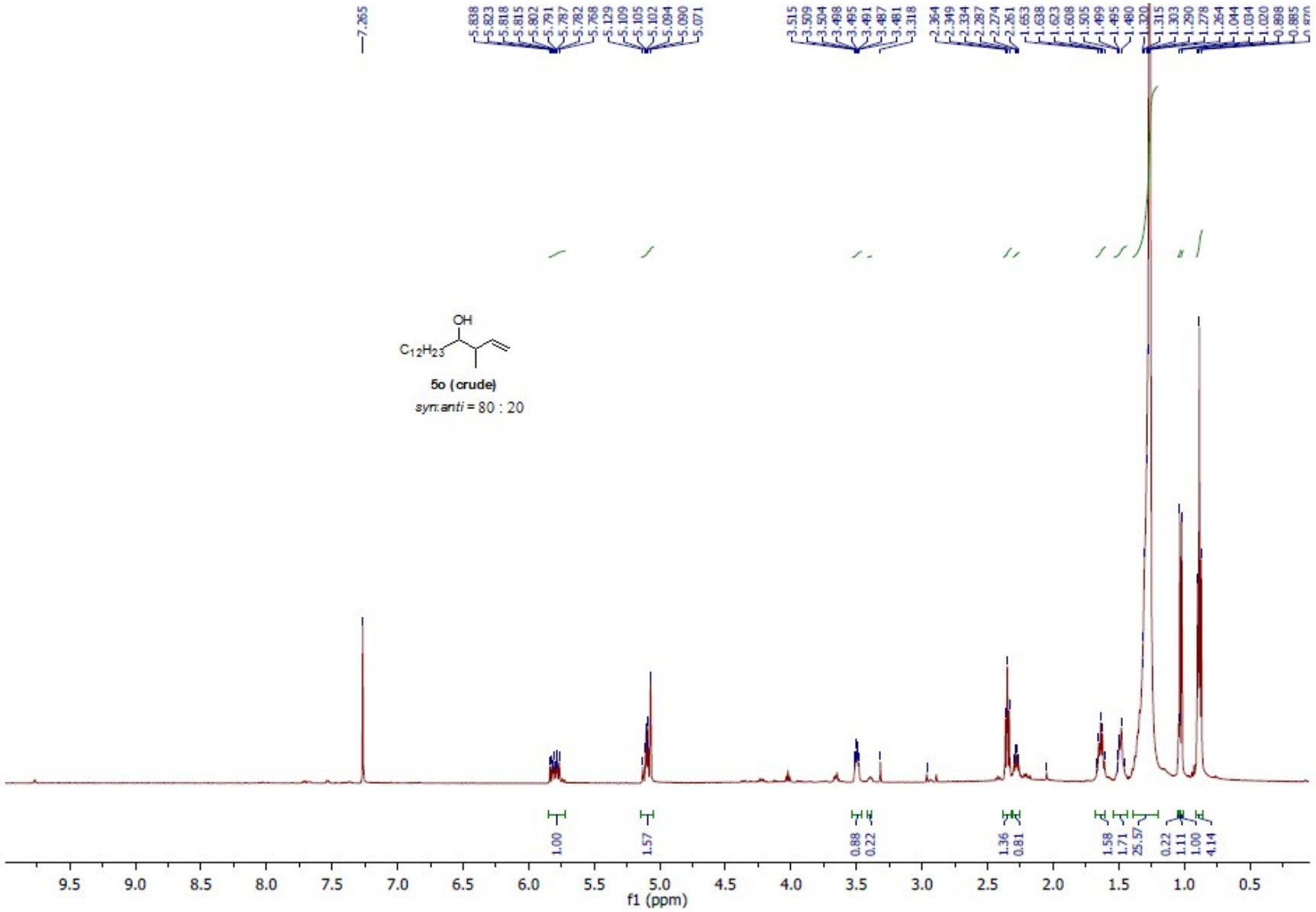

OH
5j (crude)
syn:anti = 79 : 21
f1 (ppm)

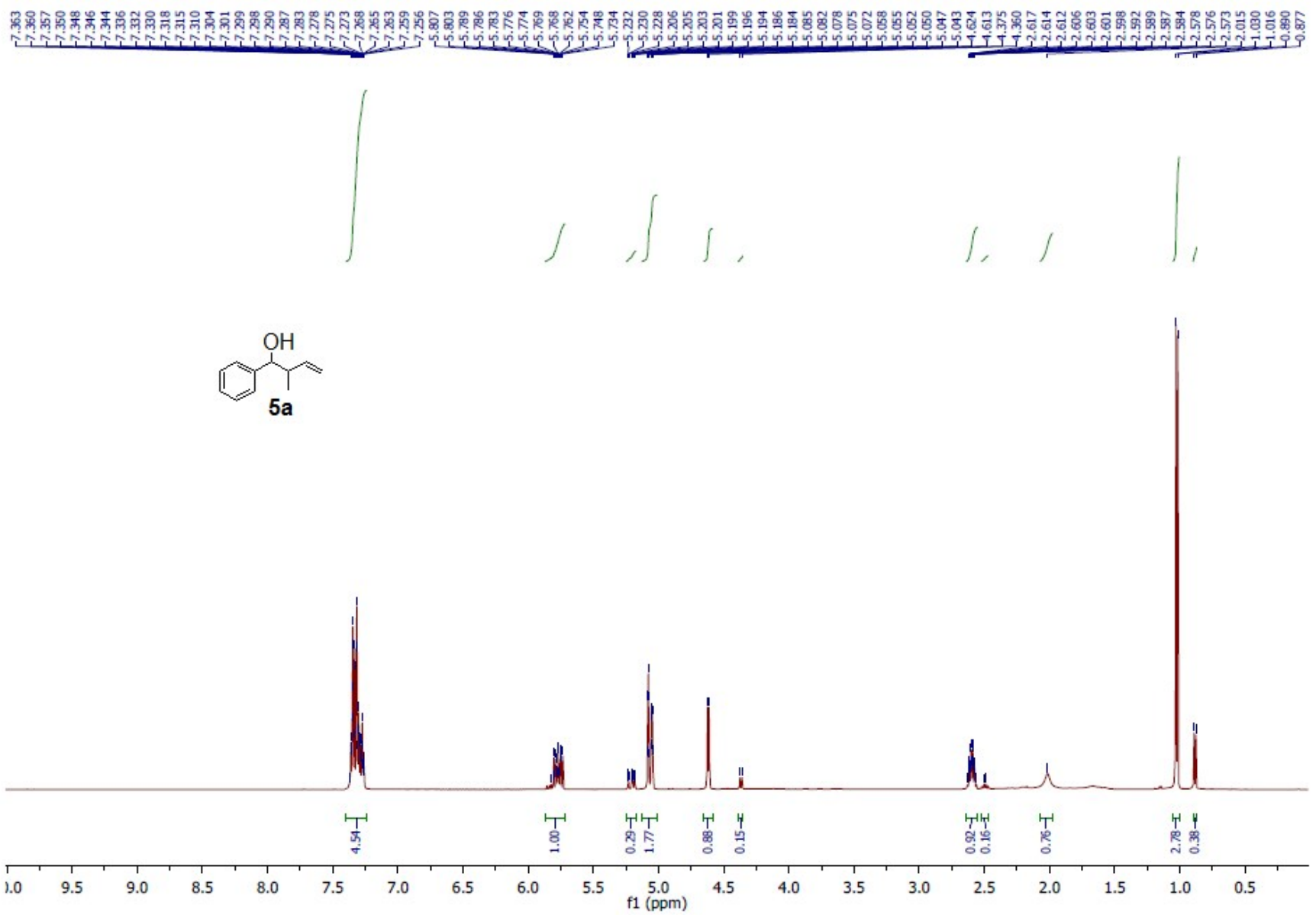

7.406
7.403
7.398
7.395
7.390
7.384
7.381
7.379
7.375
7.337
7.333
7.322
7.319
7.309
7.306
7.265
7.261
7.258
7.255
7.247
7.243
7.229
6.615
6.583
6.257
6.244
6.225
6.222
6.212
5.888
5.873
5.867
5.854
5.852
5.839
5.833
5.818
5.168
5.165
5.162
5.150
5.148
5.145
5.134
5.130
5.127
4.231
4.218
4.205
4.073
4.060
4.046
3.676
3.659
3.656
3.649
3.646
2.506
2.495
2.492
2.481
2.477
2.467
2.175
2.049
2.003
1.099
1.085
1.074
1.060
OH
5k (crude)
syn:anti = 78 : 22
0.36
1.75
1.74
1.11
0.96
0.97
1.00
1.83
1.00
0.29
1.31
0.99
0.56
0.29
4.02
2.33
0.47
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
f1 (ppm)

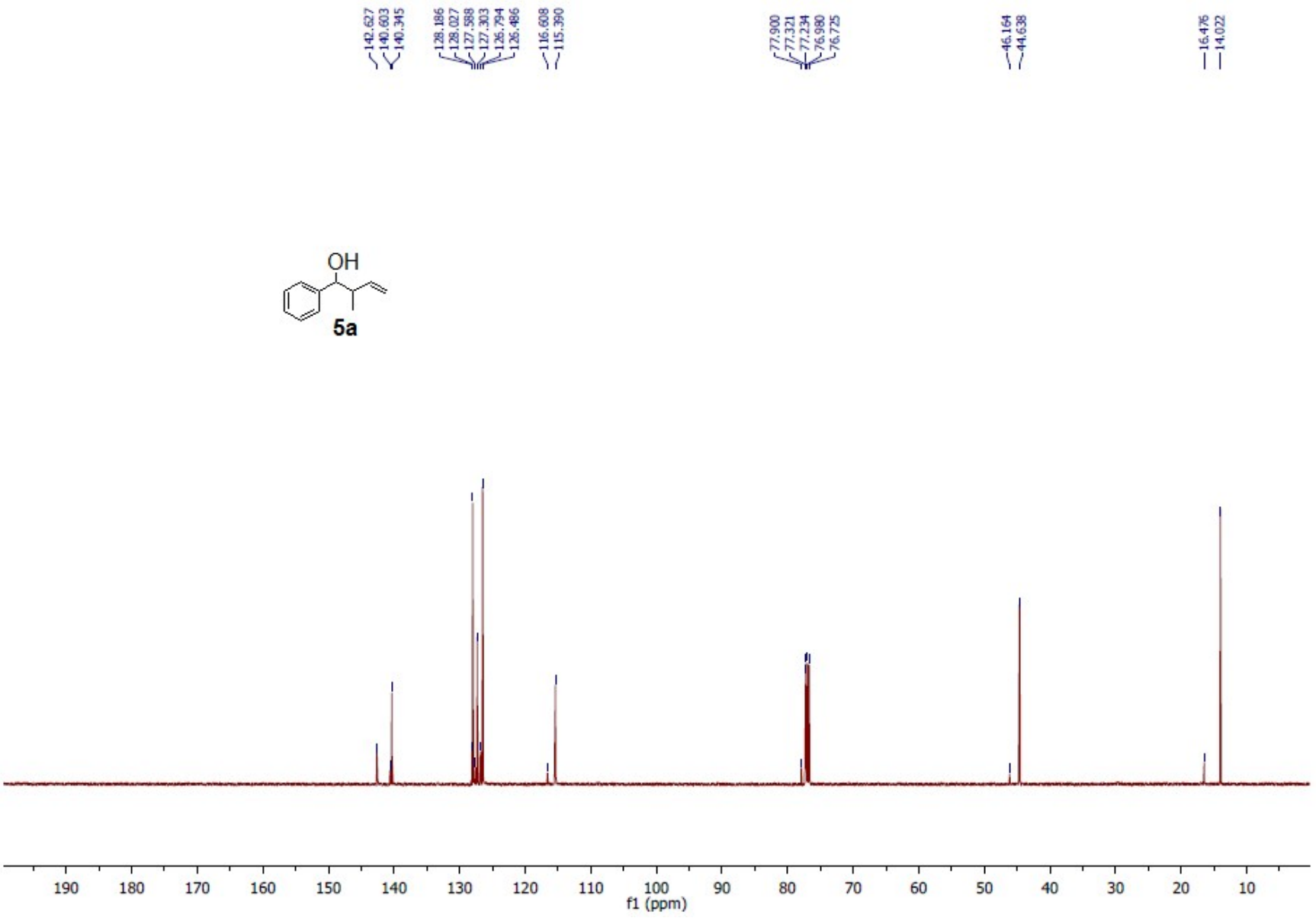

7.392
7.391
7.389
7.387
7.373
7.371
7.369
7.367
7.265
6.346
6.343
6.340
6.336
6.332
6.329
6.325
6.280
6.278
6.277
6.273
6.272
6.270
6.238
6.236
6.235
6.231
6.230
6.228
5.797
5.781
5.776
5.762
5.761
5.747
5.741
5.726
5.236
5.233
5.202
5.199
5.196
5.194
5.179
5.177
5.175
5.174
5.128
5.125
5.122
5.093
5.090
5.087
5.085
5.083
5.081
5.066
5.064
5.062
5.060
4.582
4.570
4.442
4.426
2.734
2.732
2.730
2.725
2.723
2.721
2.719
2.717
2.715
2.711
2.709
2.707
2.705
2.703
2.701
2.694
2.691
2.689
2.081
1.261
1.083
1.069
0.962
0.949
O
OH
5l (crude)
syn:anti = 75:25
0.22
0.58
1.77
1.00
0.56
1.49
0.71
0.26
1.00
1.25
1.58
1.22
2.49
0.84
f1 (ppm)


7.265
5.835
5.820
5.816
5.812
5.802
5.798
5.787
5.784
5.780
5.765
5.124
5.121
5.108
5.104
5.100
5.097
5.090
5.087
5.084
5.067
5.065
3.509
3.503
3.499
3.493
3.486
3.482
3.476
2.295
2.284
2.281
2.270
2.266
2.256
1.525
1.517
1.510
1.502
1.496
1.489
1.484
1.480
1.475
1.464
1.463
1.393
1.385
1.375
1.366
1.356
1.352
1.342
1.339
1.331
1.325
1.320
1.319
1.313
1.305
1.299
1.289
1.283
1.280
1.269
1.257
1.042
1.032
1.028
1.018
0.908
0.894
0.881
OH
C5H11
5m (crude)
syn:anti = 88 : 12
1.00
1.82
0.91
0.13
1.06
0.15
2.74
7.76
0.14
1.40
1.32
3.68
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
f1 (ppm)


OH
C8H17
5n (crude)
syn:anti = 88:12
f1 (ppm)


7.265
5.838
5.823
5.818
5.815
5.802
5.791
5.787
5.782
5.768
5.129
5.109
5.105
5.102
5.094
5.090
5.071
3.515
3.509
3.504
3.498
3.495
3.491
3.487
3.481
3.318
2.364
2.349
2.334
2.287
2.274
2.261
1.653
1.638
1.623
1.608
1.505
1.499
1.495
1.480
1.320
1.315
1.303
1.290
1.278
1.264
1.044
1.034
1.020
0.898
0.885
OH
C12H23
5o (crude)
syn:anti = 80 : 20
1.00
1.57
0.88
0.22
1.36
0.81
1.58
1.71
25.57
0.22
1.11
1.00
4.14
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
f1 (ppm)


OH
5a
4.54
1.00
0.29
1.77
0.88
0.15
0.92
0.16
0.76
2.78
0.38
f1 (ppm)

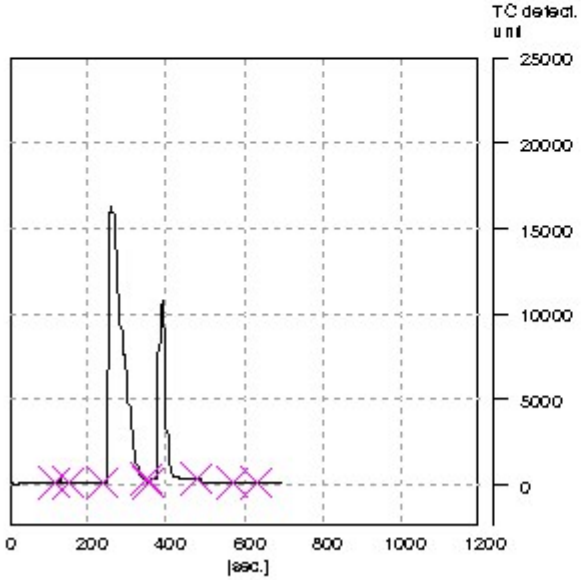

142.627
140.603
140.345
128.186
128.027
127.588
127.303
126.794
126.486
116.608
115.390
77.900
77.321
77.234
76.980
76.725
46.164
44.638
16.476
14.022
OH
5a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

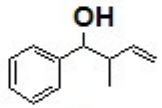
Document: crt-18-1-17 (VarioMICRO) from: 2/2/2017 4:32:07 PM

analytic functional testing
varioMICRO CHNS
serial number: 15103026

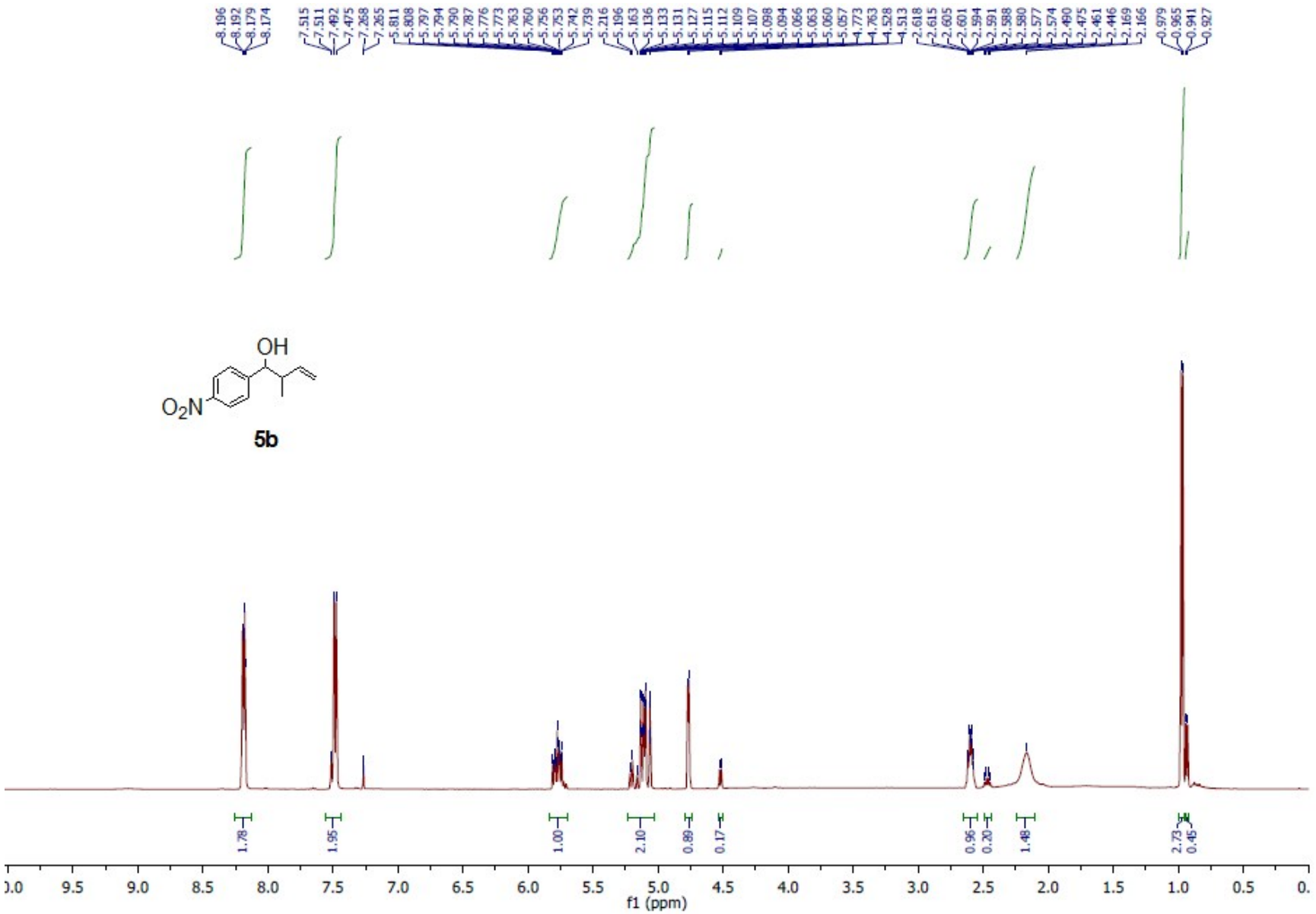
Graphic report

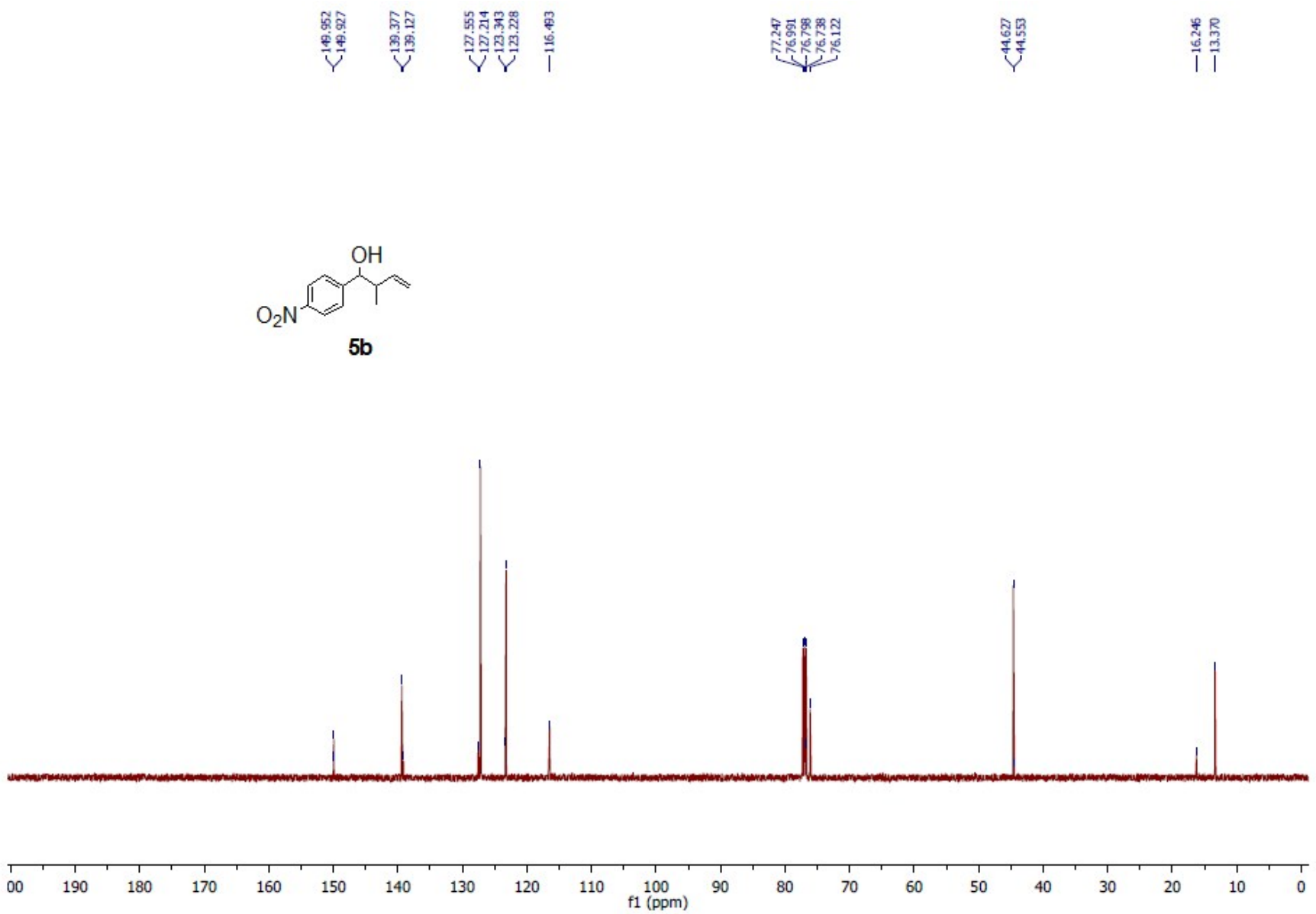
	Weight [mg]	Name	Method	N Area	C Area	H Area	S Area	N [%]	C [%]	H [%]	S [%]	C/N ratio	C/H ratio
15	3.2050	Ph-CHO	2mgChem80s	61	65 357	23 117	29	0.00	81.77	8.947	0.000	0.0000	9.1396





5a

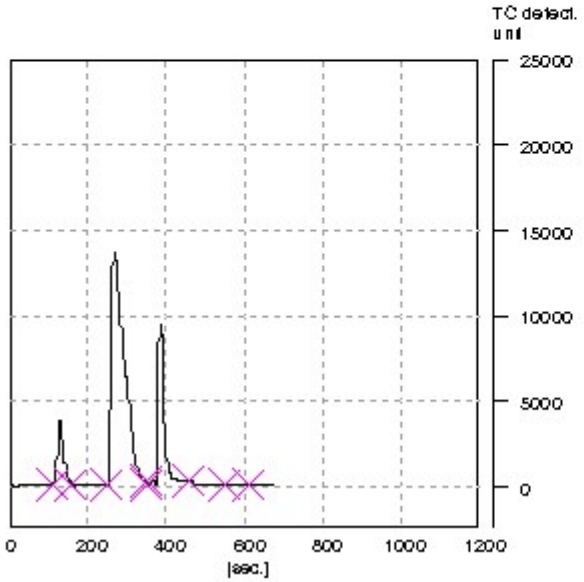

8.196
8.192
8.179
8.174
7.515
7.511
7.492
7.475
7.268
7.265
5.811
5.808
5.797
5.794
5.790
5.787
5.776
5.773
5.763
5.760
5.756
5.753
5.742
5.739
5.216
5.196
5.163
5.136
5.133
5.131
5.127
5.115
5.112
5.109
5.107
5.098
5.094
5.066
5.063
5.060
5.057
4.773
4.763
4.528
4.513
2.618
2.615
2.605
2.601
2.594
2.591
2.588
2.580
2.577
2.574
2.490
2.475
2.461
2.446
2.169
2.166
0.979
0.965
0.941
0.927
OH
O2N
5b
1.78
1.95
1.00
2.10
0.89
0.17
0.96
0.20
1.48
2.73
0.45
f1 (ppm)

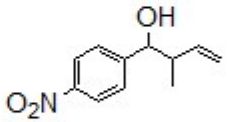

149.952
149.927
139.377
139.127
127.555
127.214
123.343
123.228
116.493
77.247
76.991
76.798
76.738
76.122
44.627
44.553
16.246
13.370
OH
O2N
5b
f1 (ppm)

analytic functional testing
varioMICRO CHNS
serial number: 15103026

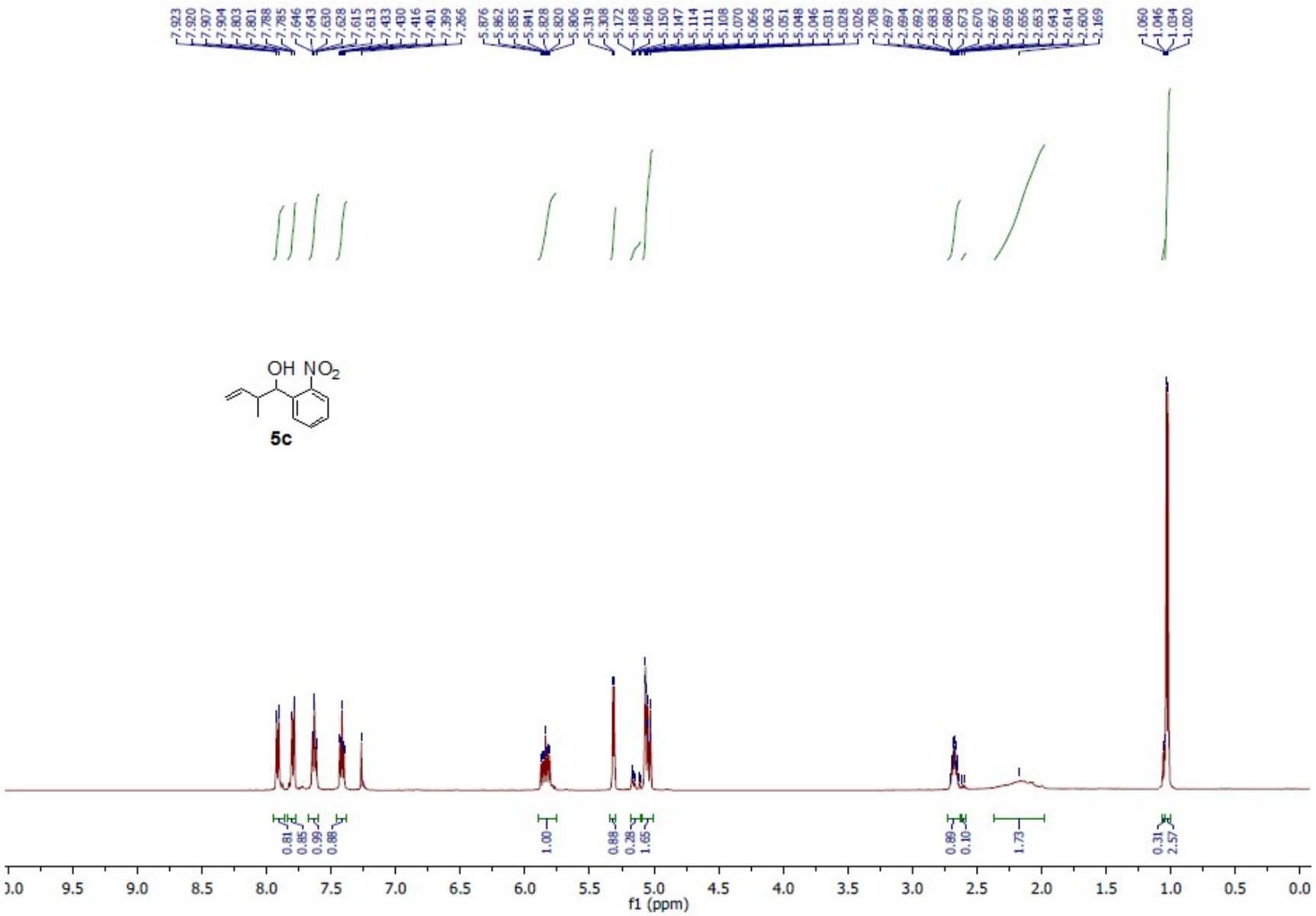
Graphic report

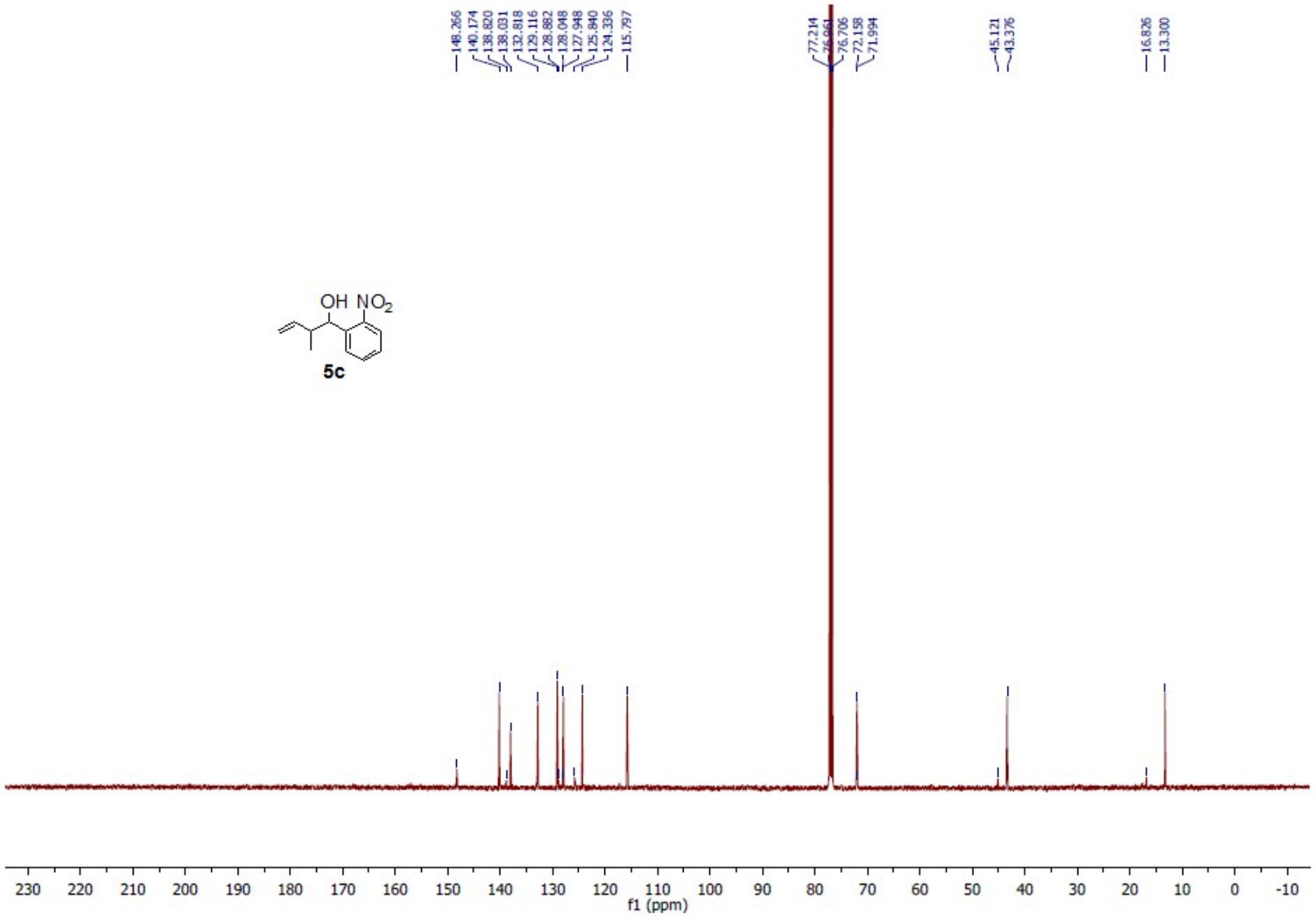
	Weight [mg]	Name	Method	N Area	C Area	H Area	S Area	N [%]	C [%]	H [%]	S [%]	C/N ratio	C/H ratio
16	3.2230	4-NO2	2mgChem80s	7 613	51 321	16 618	35	6.63	63.95	6.527	0.000	9.6461	9.7980





5b

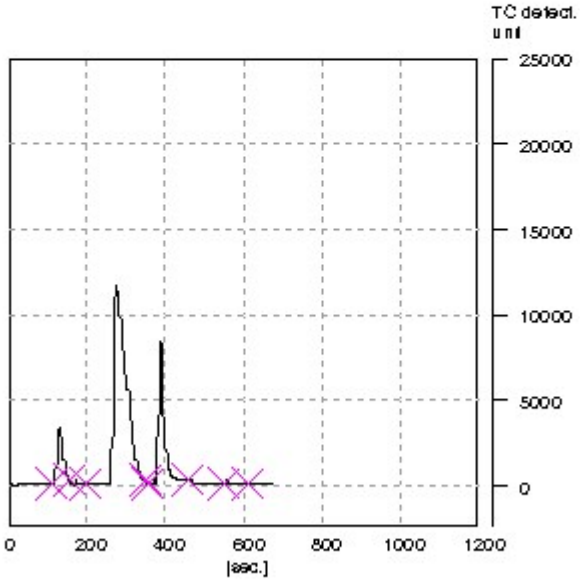

OH NO2
5c
f1 (ppm)

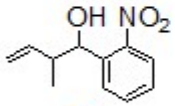

148.266
140.174
138.820
138.031
132.818
129.116
128.882
128.048
127.948
125.840
124.336
115.797
77.214
76.961
76.706
72.158
71.994
45.121
43.376
16.826
13.300
OH NO2
5c
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

analytic functional testing
varioMICRO CHNS
serial number: 15103026

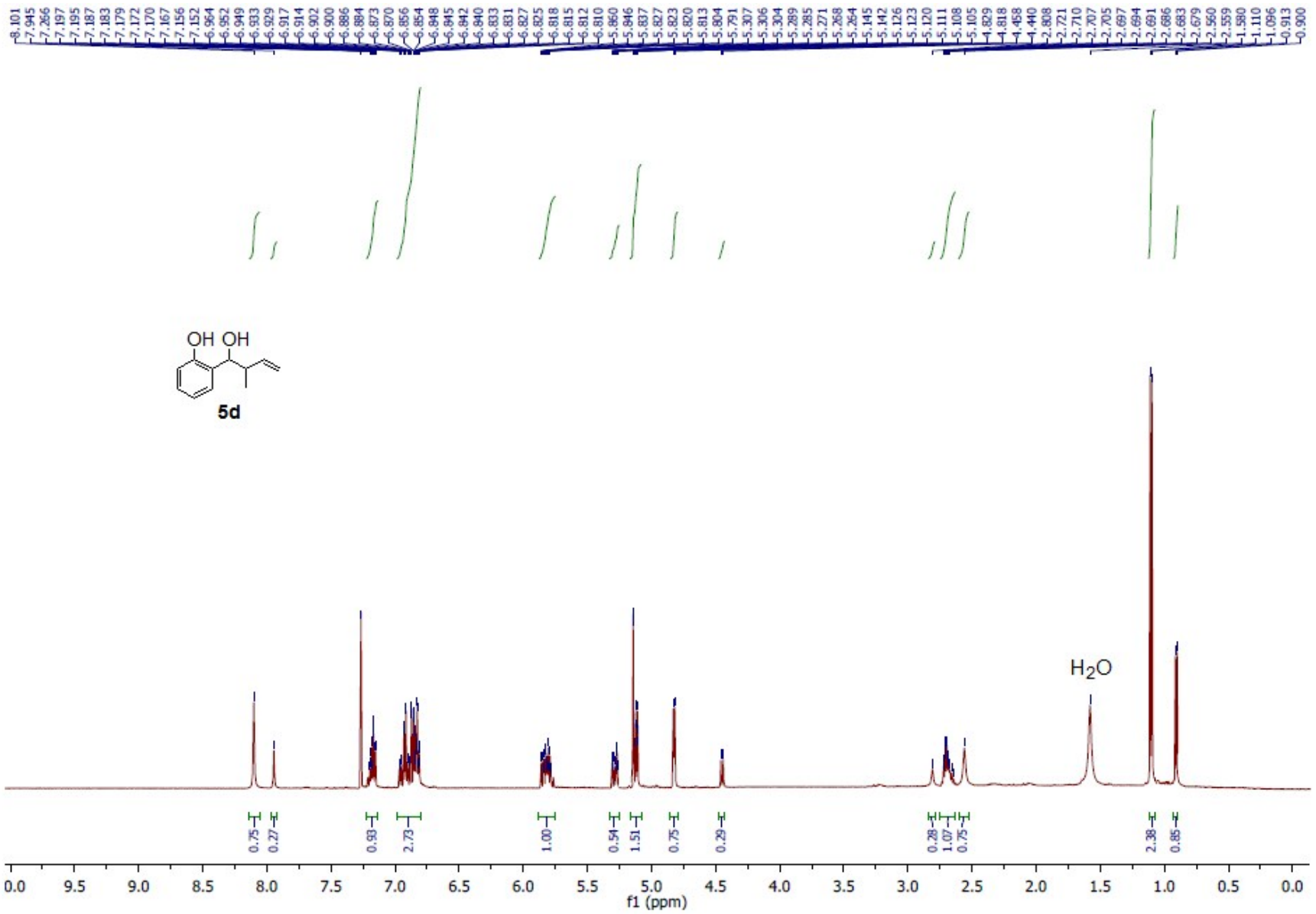
Graphic report

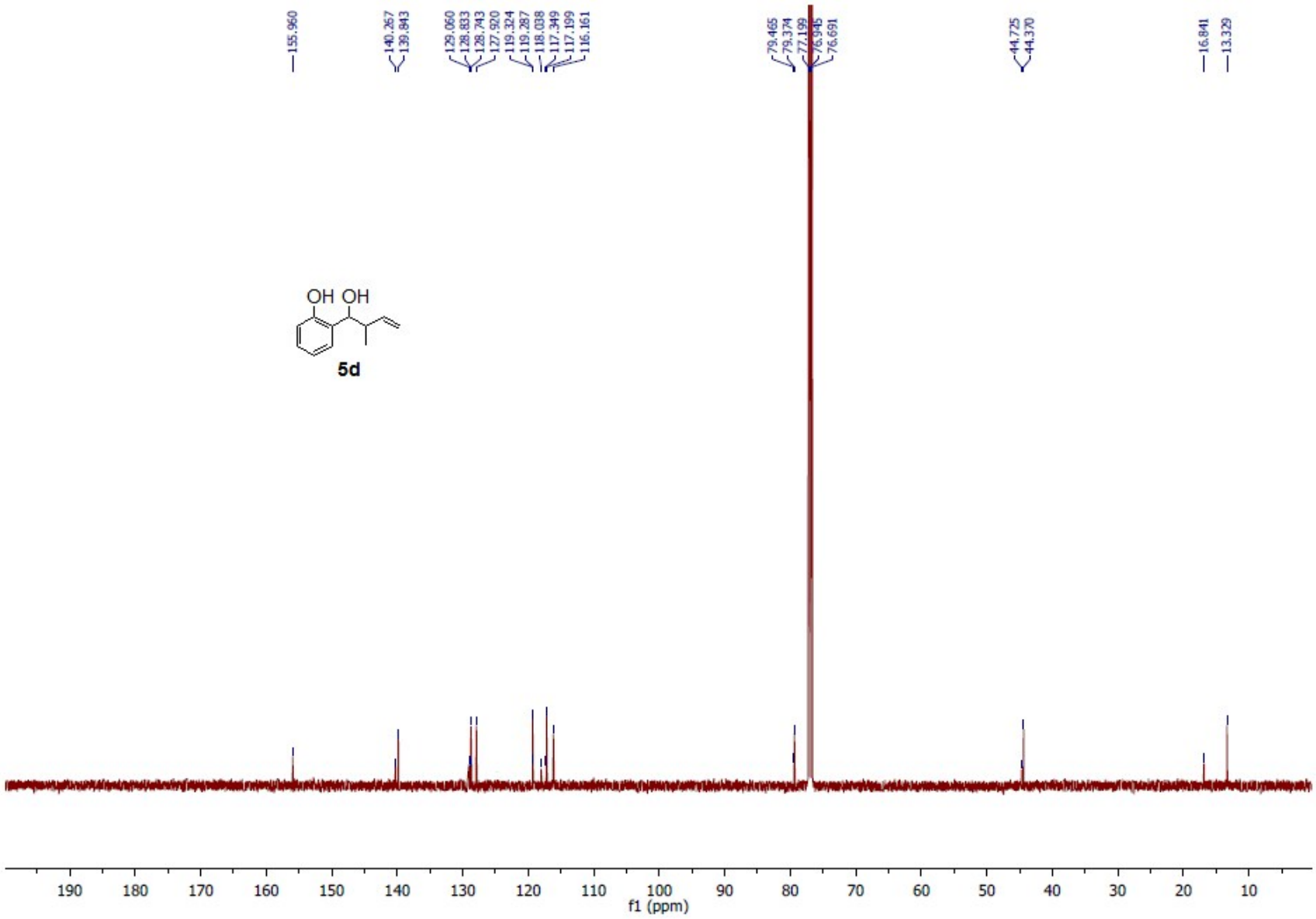
	Weight [mg]	Name	Method	N Area	C Area	H Area	S Area	N [%]	C [%]	H [%]	S [%]	C/N ratio	C/H ratio
10	2.6810	2-NO2-	2mgChem80s	6 088	42 743	13 390	27	6.37	64.09	6.403	0.000	10.0660	10.0101





5c


OH OH
5d
H2O
f1 (ppm)

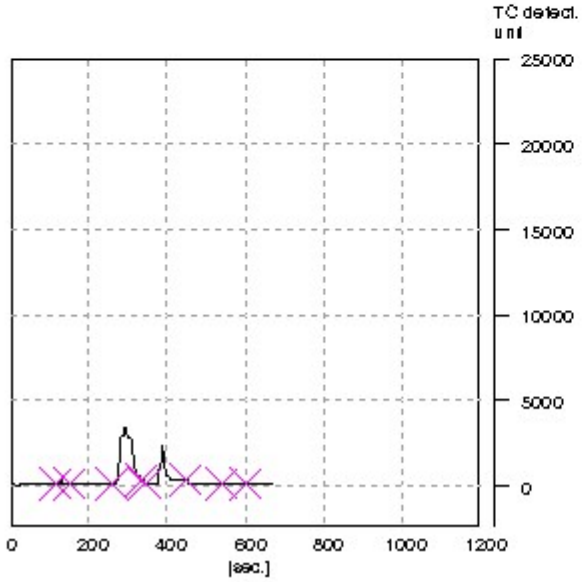

155.960
140.267
139.843
129.060
128.833
128.743
127.920
119.324
119.287
118.038
117.349
117.199
116.161
79.465
79.374
77.199
76.945
76.691
44.725
44.370
16.841
13.329
OH OH
5d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

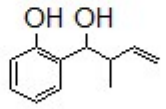
Document: crt-18-1-17 (VarioMICRO) from: 2/2/2017 4:32:07 PM

analytic functional testing
varioMICRO CHNS
serial number: 15103026

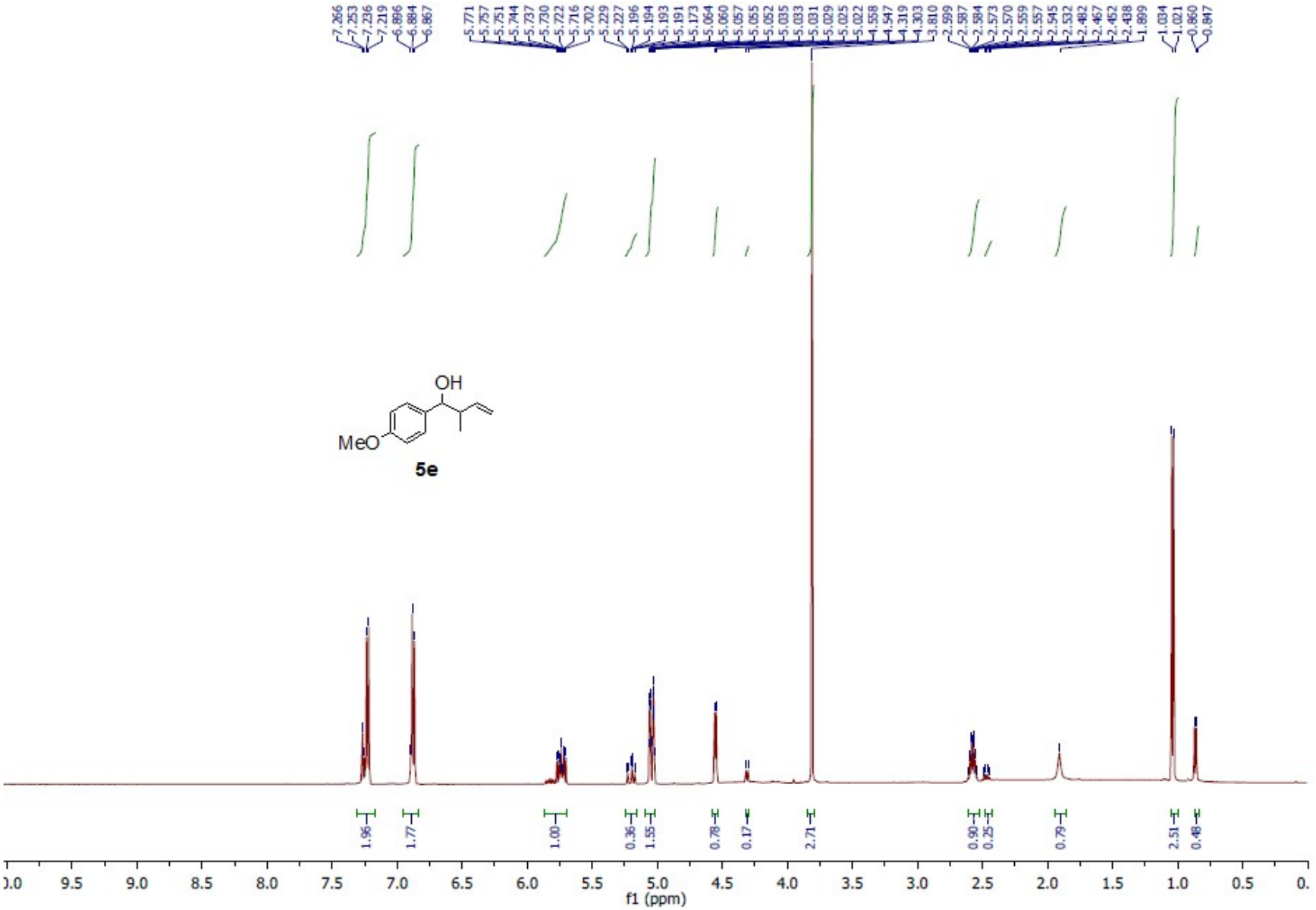
Graphic report

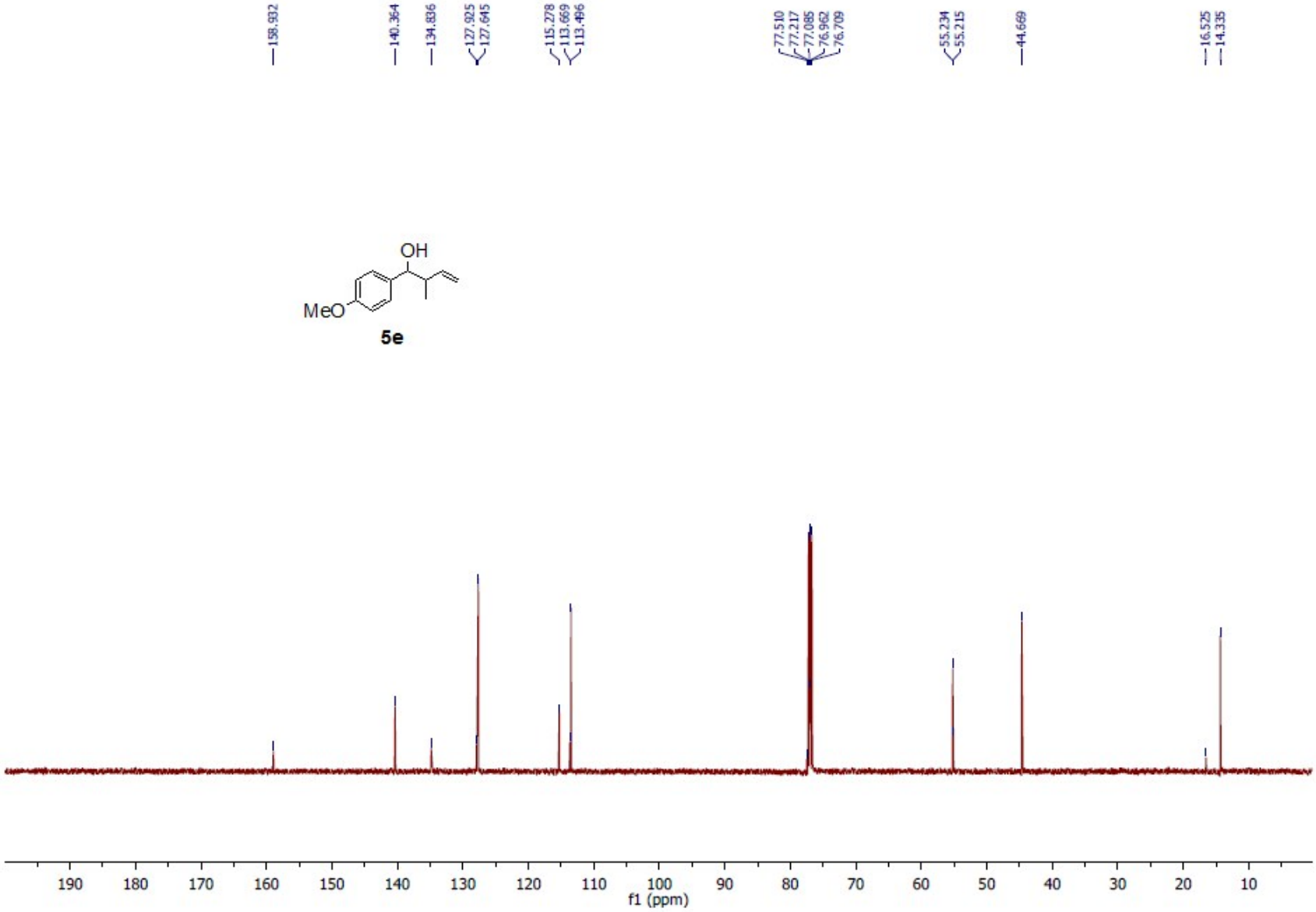
	Weight [mg]	Name	Method	N Area	C Area	H Area	S Area	N [%]	C [%]	H [%]	S [%]	C/N ratio	C/H ratio
21	0.5780	2-OH	2mgChem80s	64	10 747	3 336	32	0.00	74.41	7.736	0.000	0.0000	9.6186





5d


OH
MeO
5e
f1 (ppm)

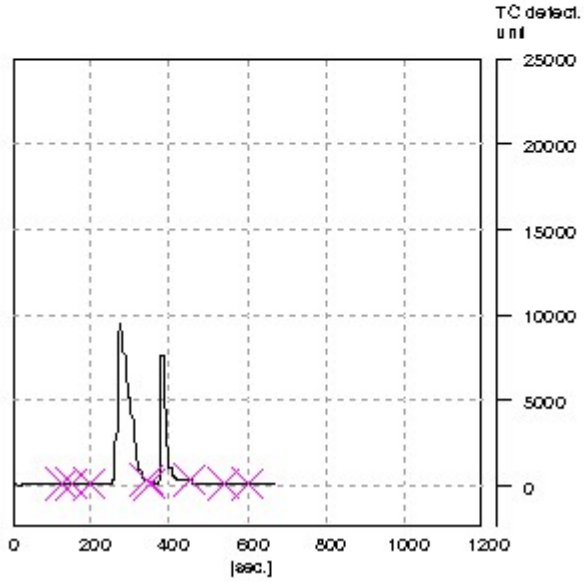

158.932
140.364
134.836
127.925
127.645
115.278
113.669
113.496
77.510
77.217
77.085
76.962
76.709
55.234
55.215
44.669
16.525
14.335
OH
MeO
5e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

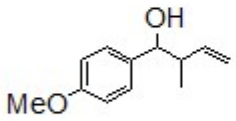
Document: crt-18-1-17 (VarioMICRO) from: 2/2/2017 4:32:07 PM

analytic functional testing
varioMICRO CHNS
serial number: 15103026

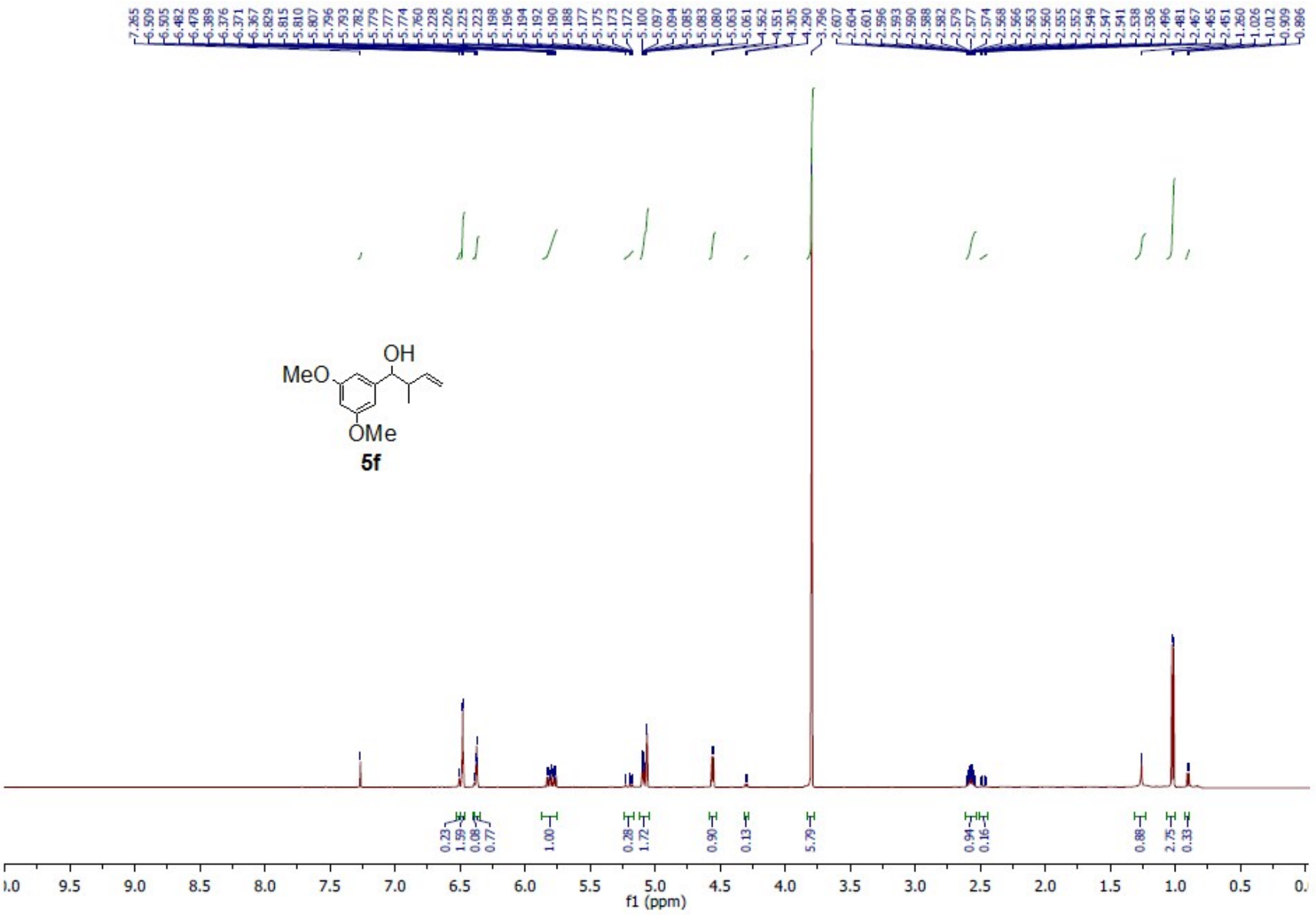
Graphic report

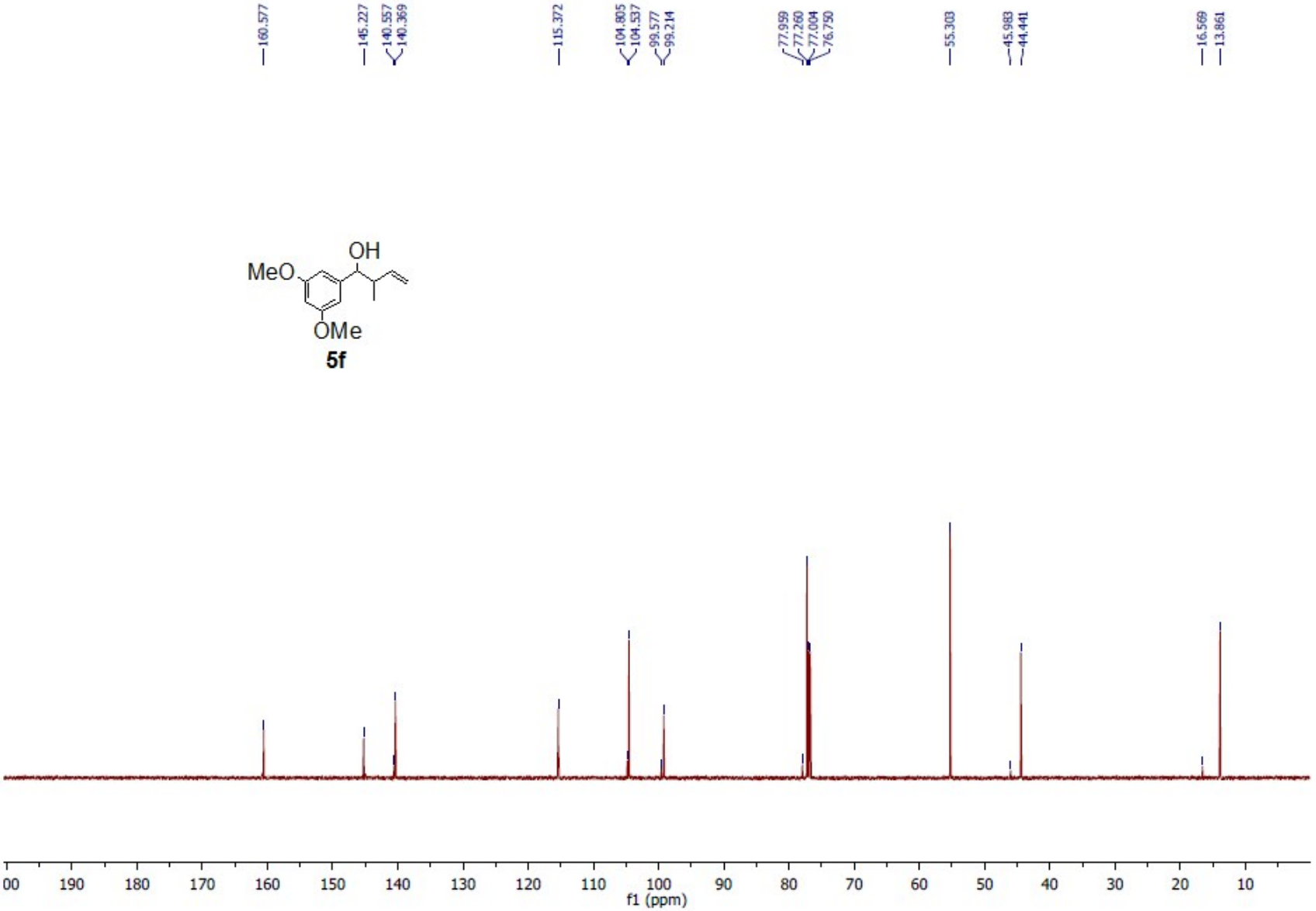
	Weight [mg]	Name	Method	N Area	C Area	H Area	S Area	N [%]	C [%]	H [%]	S [%]	C/N ratio	C/H ratio
12	1.7690	4-OMe	2mgChem80s	68	32 898	11 987	30	0.00	74.80	8.737	0.000	0.0000	8.5612





5e


MeO
OH
OMe
5f
f1 (ppm)

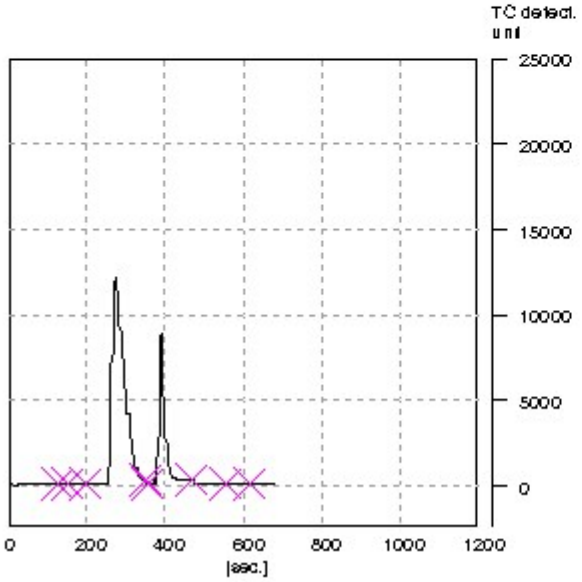

160.577
145.227
140.557
140.369
115.372
104.805
104.537
99.577
99.214
77.959
77.260
77.004
76.750
55.303
45.983
44.441
16.569
13.861
OH
MeO
OMe
5f
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

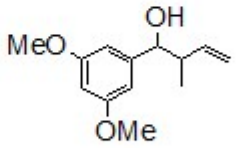
Document: crt-18-1-17 (VarioMICRO) from: 2/2/2017 4:32:07 PM

analytic functional testing
varioMICRO CHNS
serial number: 15103026

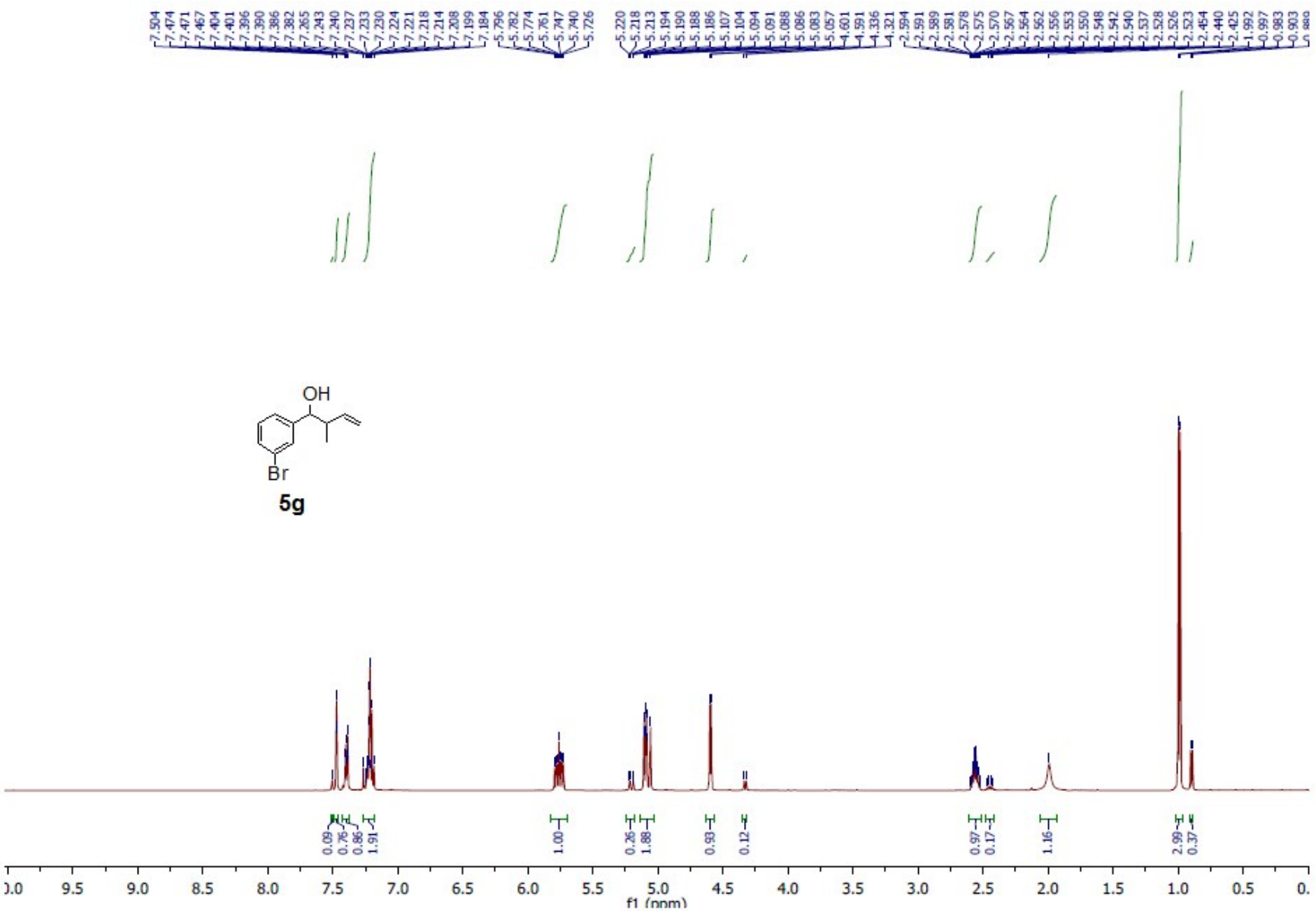
Graphic report

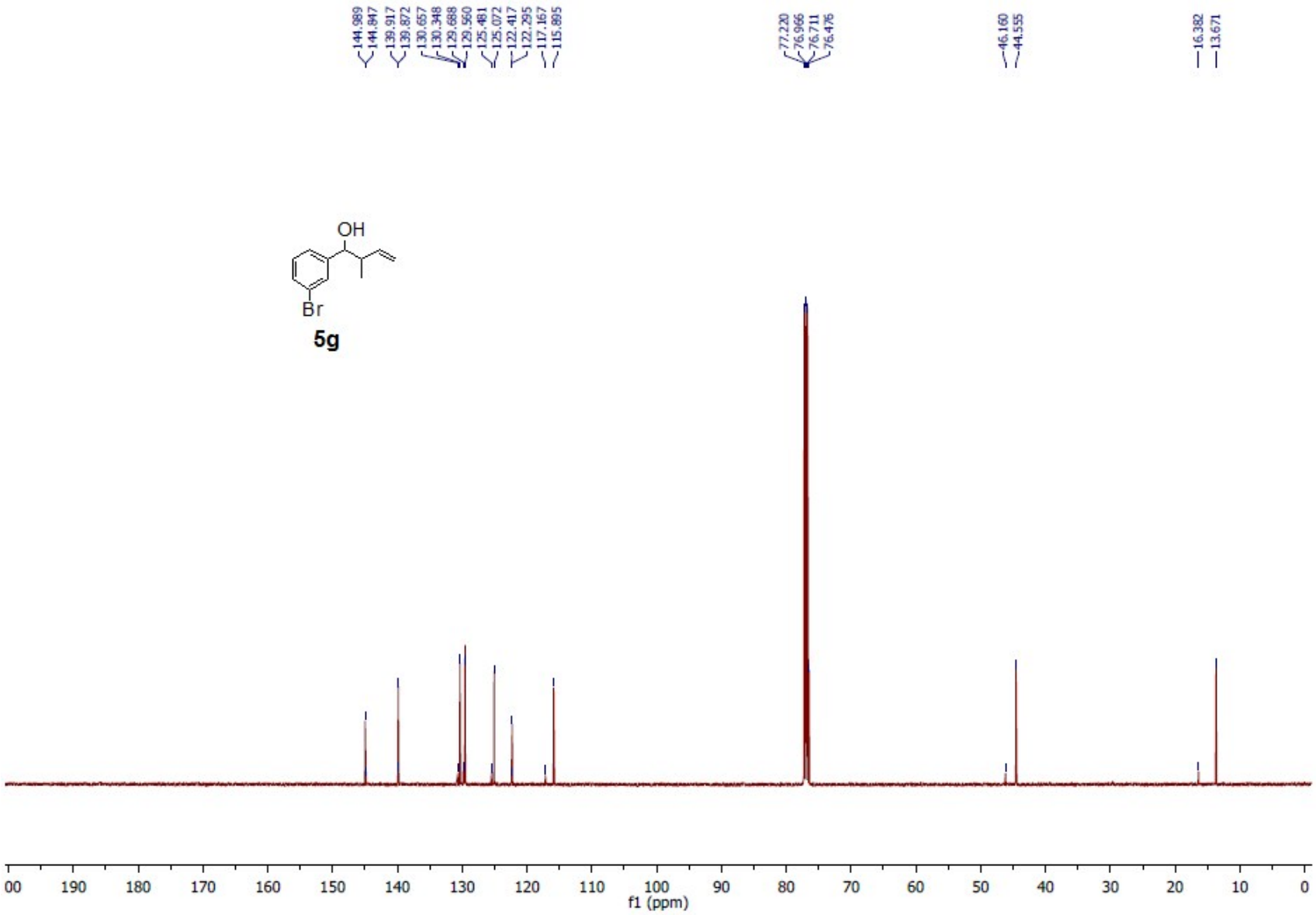
	Weight [mg]	Name	Method	N Area	C Area	H Area	S Area	N [%]	C [%]	H [%]	S [%]	C/N ratio	C/H ratio
17	2.4270	MK-78 E	2mgChem80s	56	42 610	15 094	28	0.00	70.58	7.919	0.000	0.0000	8.9131





5f


OH
Br
5g
0.09
0.76
0.86
1.91
1.00
0.26
1.88
0.93
0.12
0.97
0.17
1.16
2.99
0.37
f1 (ppm)

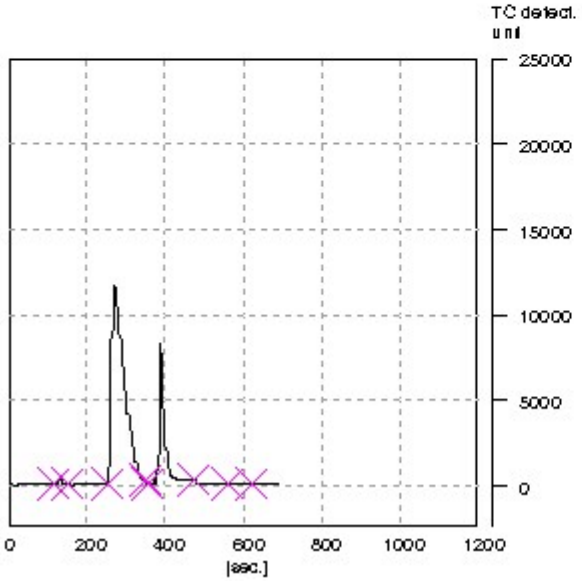

144.989
144.847
139.917
139.872
130.657
130.348
129.688
129.560
125.481
125.072
122.417
122.295
117.167
115.895
77.220
76.966
76.711
76.476
46.160
44.555
16.382
13.671
OH
Br
5g
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

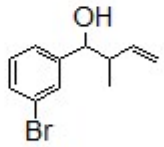
Document: crt-18-1-17 (VarioMICRO) from: 2/2/2017 4:32:07 PM

analytic functional testing
varioMICRO CHNS
serial number: 15103026

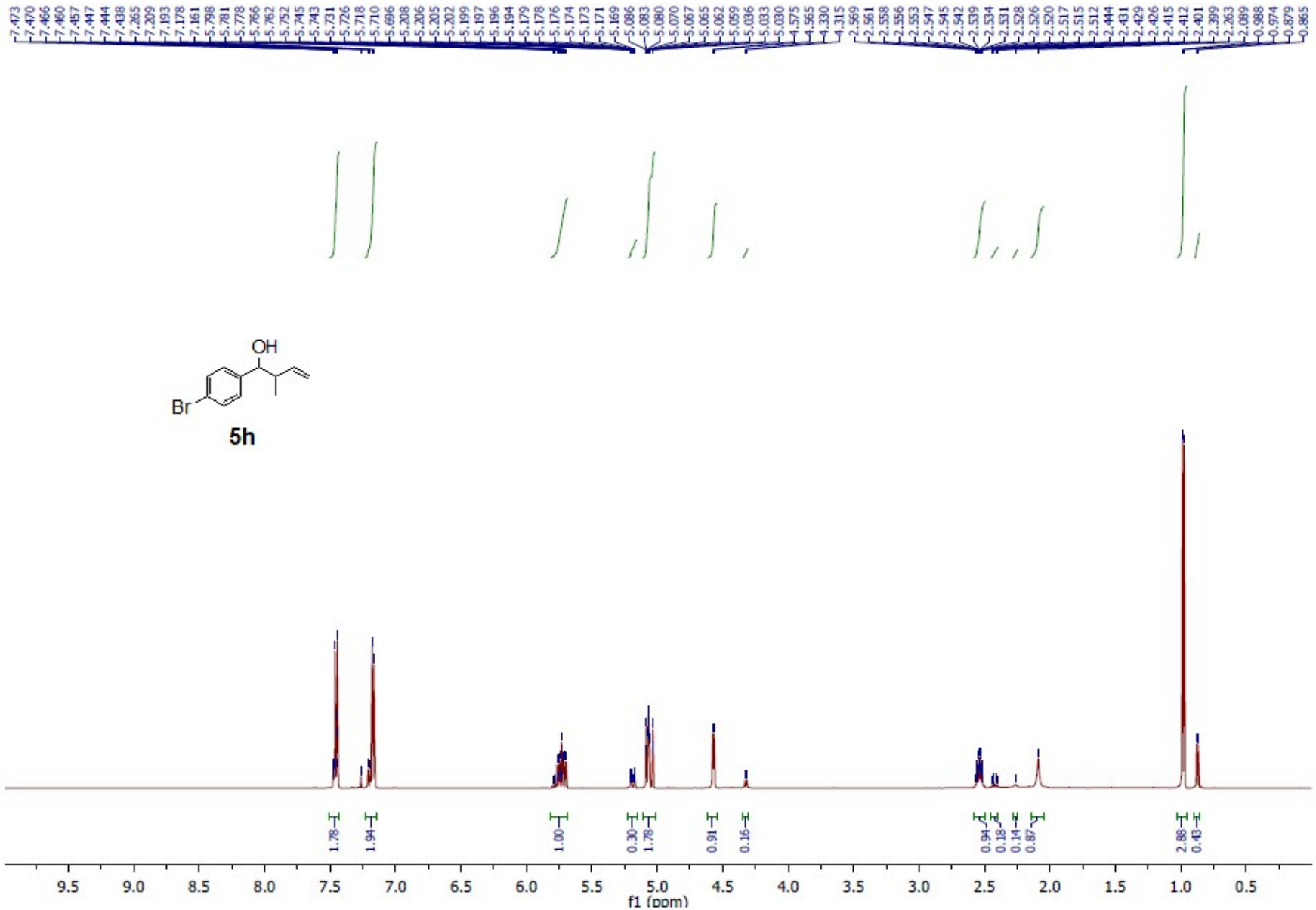
Graphic report

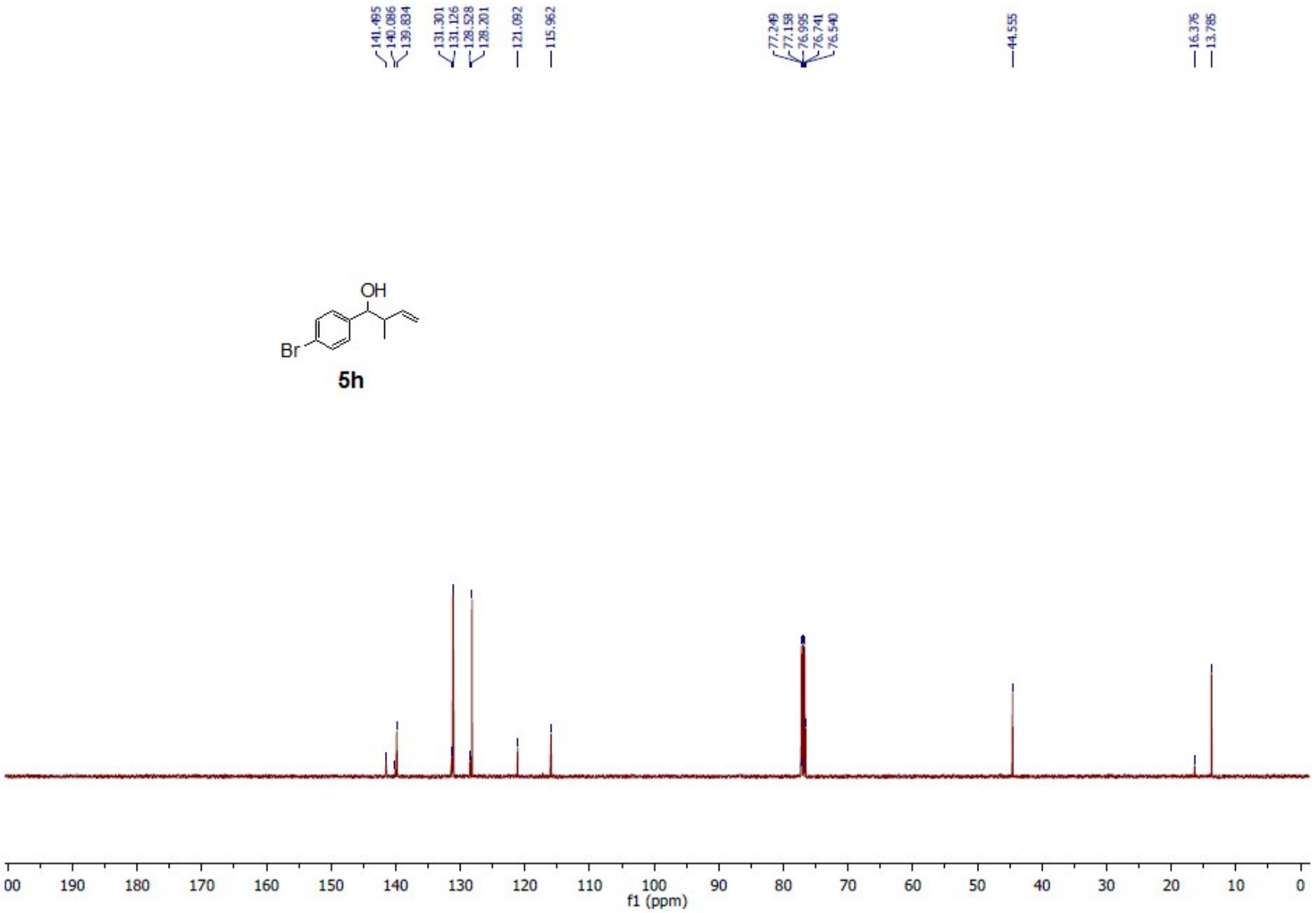
	Weight [mg]	Name	Method	N Area	C Area	H Area	S Area	N [%]	C [%]	H [%]	S [%]	C/N ratio	C/H ratio
24	3.1570	3-Br	2mgChem80s	63	43 046	13 335	35	0.00	54.81	5.416	0.000	0.0000	10.1201





5g


OH
Br
5h
1.78
1.94
1.00
0.30
1.78
0.91
0.16
0.94
0.18
0.14
0.87
2.88
0.43
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
f1 (ppm)

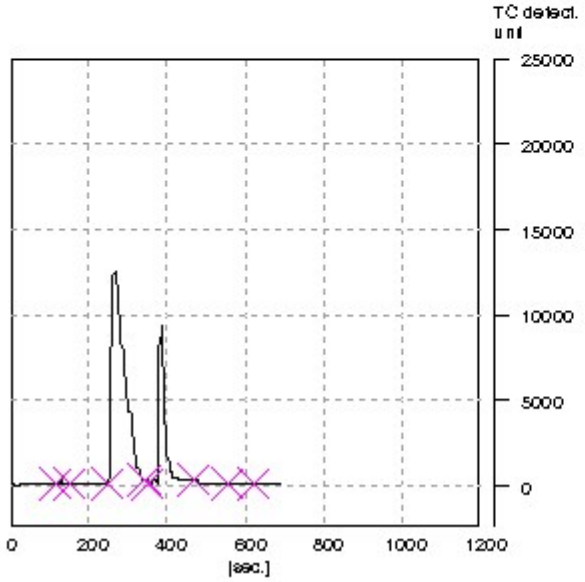

141.495
140.086
139.834
131.301
131.126
128.528
128.201
121.092
115.962
77.249
77.158
76.995
76.741
76.540
44.555
16.376
13.785
OH
Br
5h
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

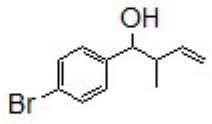
Document: crt-18-1-17 (VarioMICRO) from: 2/2/2017 4:32:07 PM

analytic functional testing
varioMICRO CHNS
serial number: 15103026

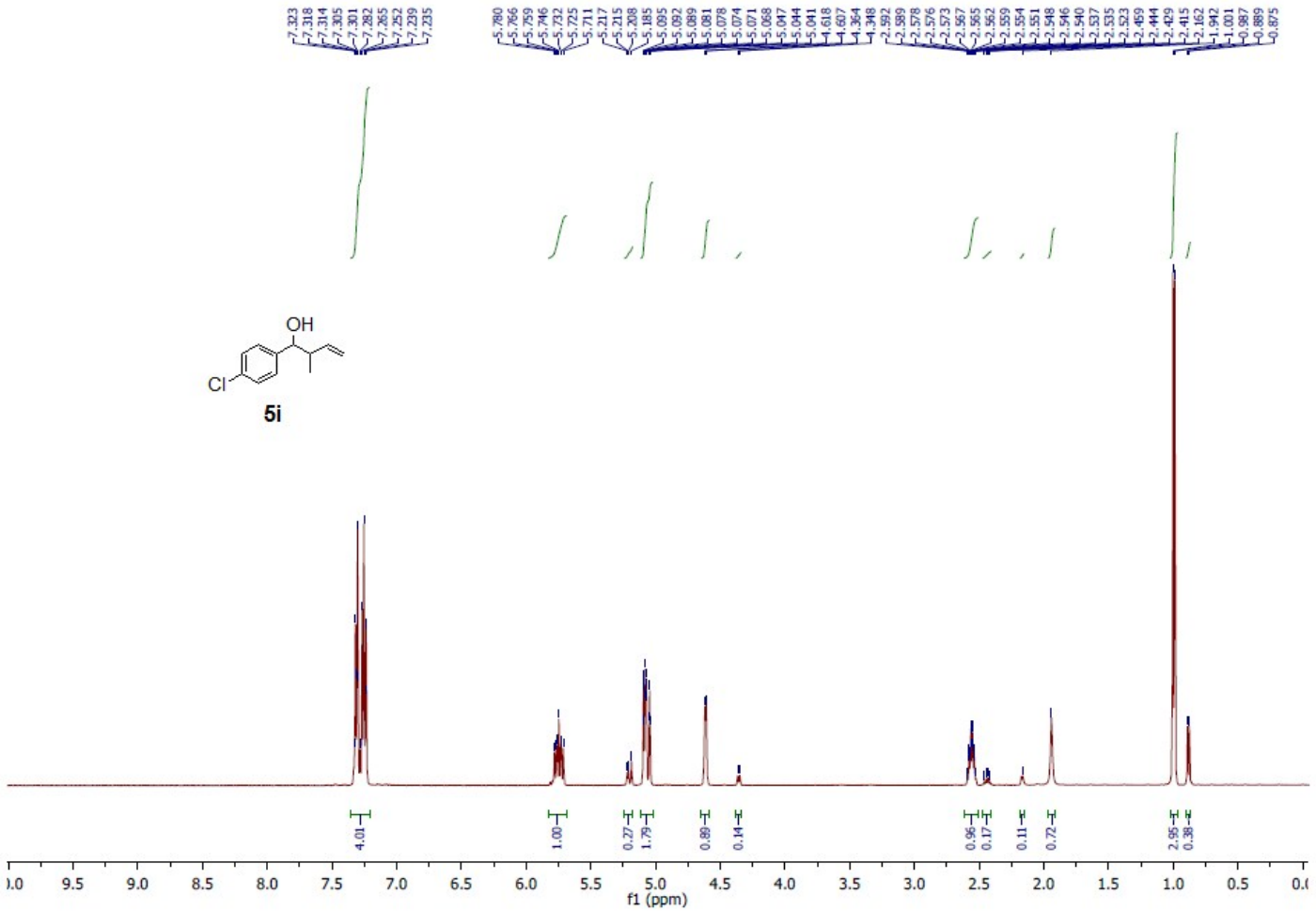
Graphic report

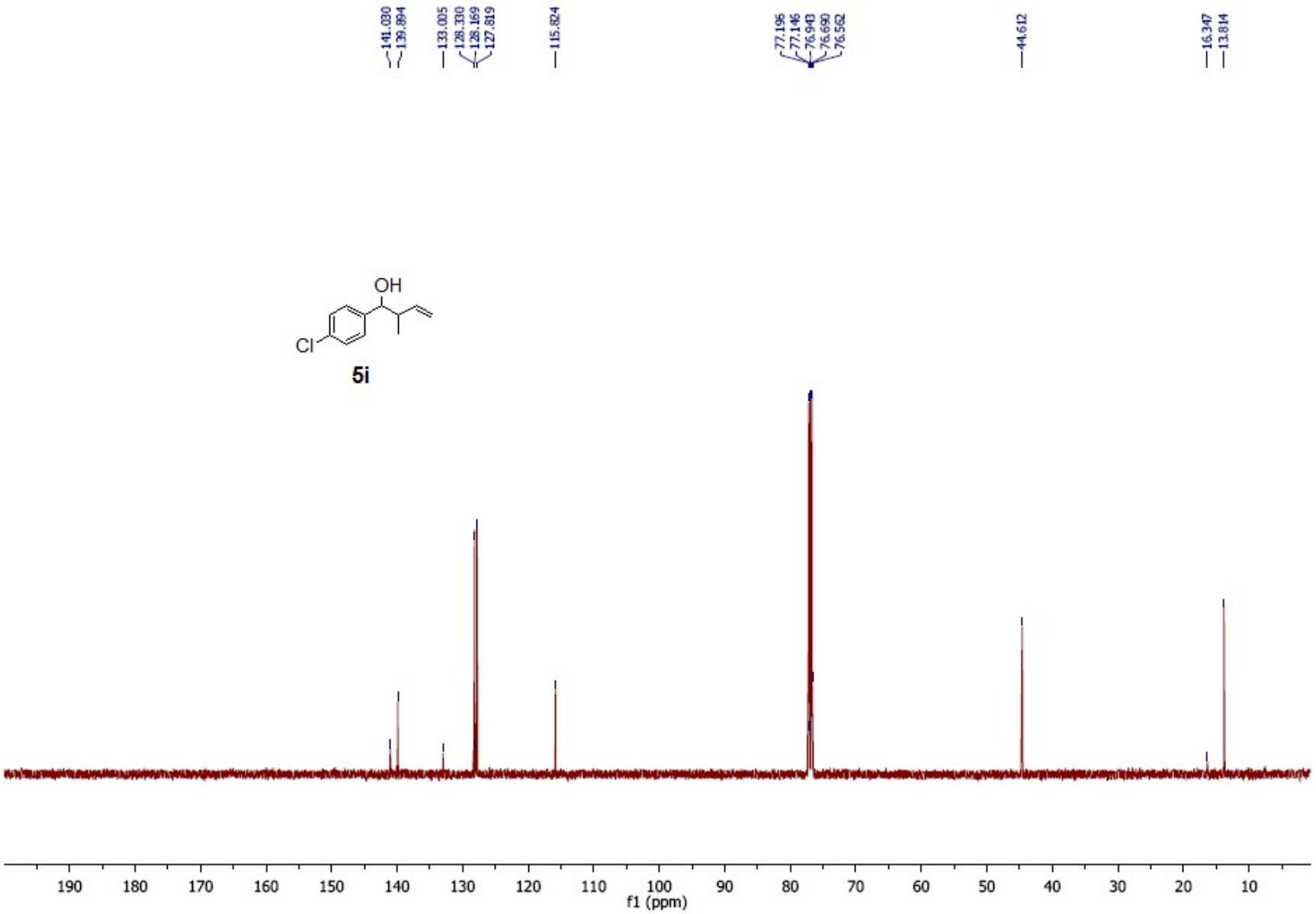
	Weight [mg]	Name	Method	N Area	C Area	H Area	S Area	N [%]	C [%]	H [%]	S [%]	C/N ratio	C/H ratio
23	3.5050	4-Br	2mgChem80s	60	47 590	14 974	29	0.00	54.56	5.442	0.000	0.0000	10.0244





5h


OH
Cl
5i
f1 (ppm)

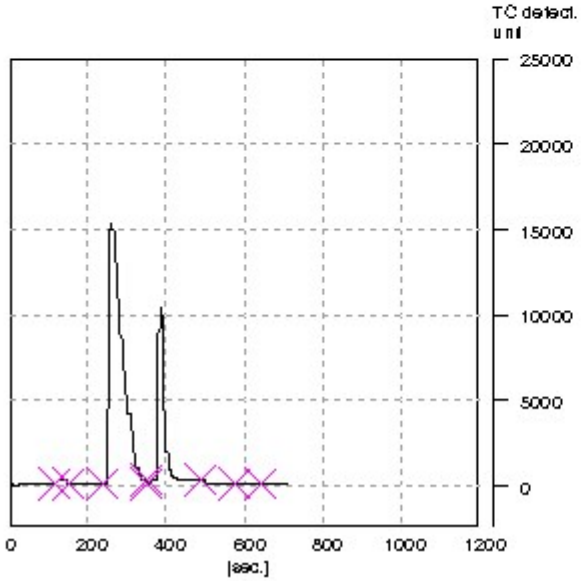

141.030
139.894
133.005
128.330
128.169
127.819
115.824
77.196
77.146
76.943
76.690
76.562
44.612
16.347
13.814
OH
Cl
5i
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

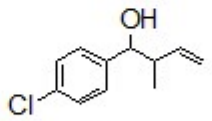
Document: crt-18-1-17 (VarioMICRO) from: 2/2/2017 4:32:07 PM

analytic functional testing
varioMICRO CHNS
serial number: 15103026

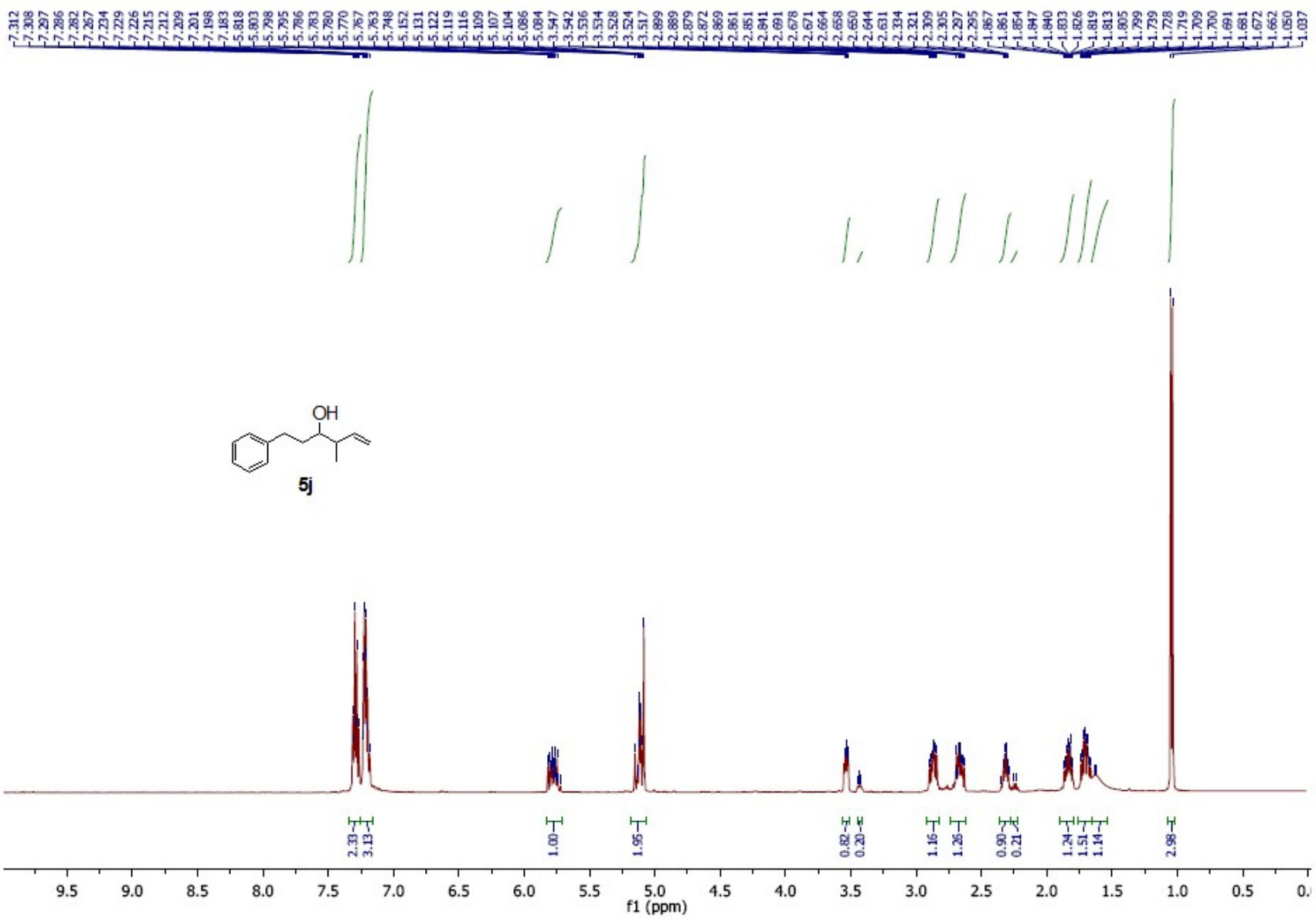
Graphic report

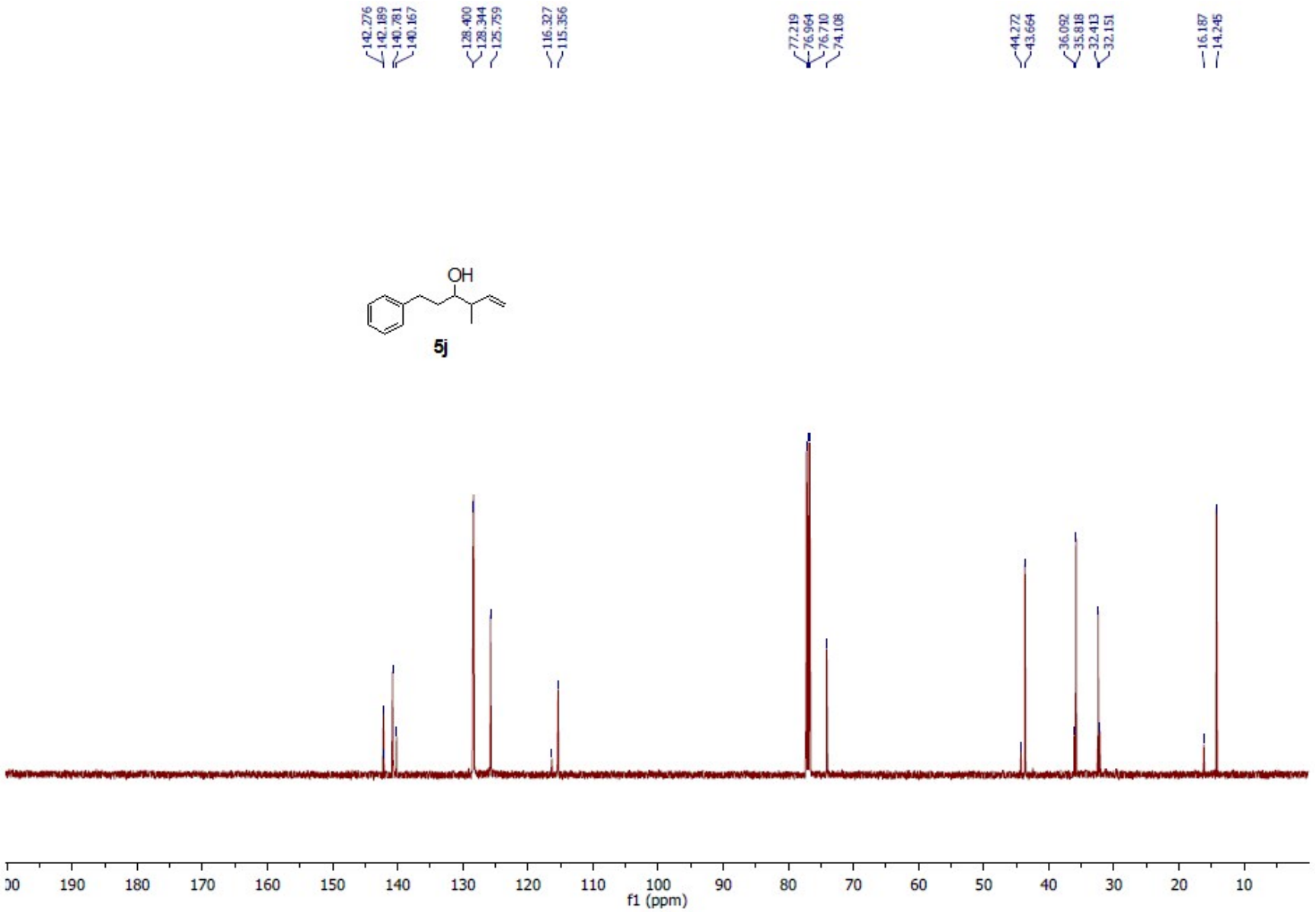
	Weight [mg]	Name	Method	N Area	C Area	H Area	S Area	N [%]	C [%]	H [%]	S [%]	C/N ratio	C/H ratio
22	3.5650	4-Cl	2mgChem80s	67	59 826	18 820	31	0.00	67.33	6.631	0.000	0.0000	10.1540





5i


OH
5j
f1 (ppm)

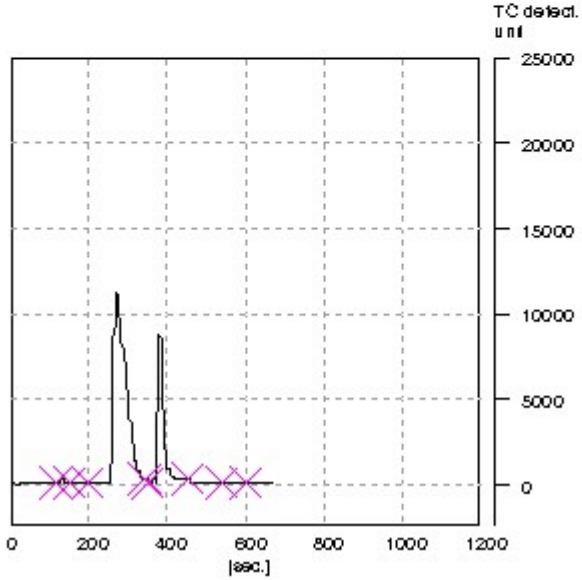

142.276
142.189
140.781
140.167
128.400
128.344
125.759
116.327
115.356
77.219
76.964
76.710
74.108
44.272
43.664
36.092
35.818
32.413
32.151
16.187
14.245
OH
5j
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

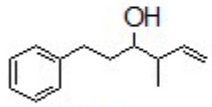
Document: crt-18-1-17 (VarioMICRO) from: 2/2/2017 4:32:07 PM

analytic functional testing
varioMICRO CHNS
serial number: 15103026

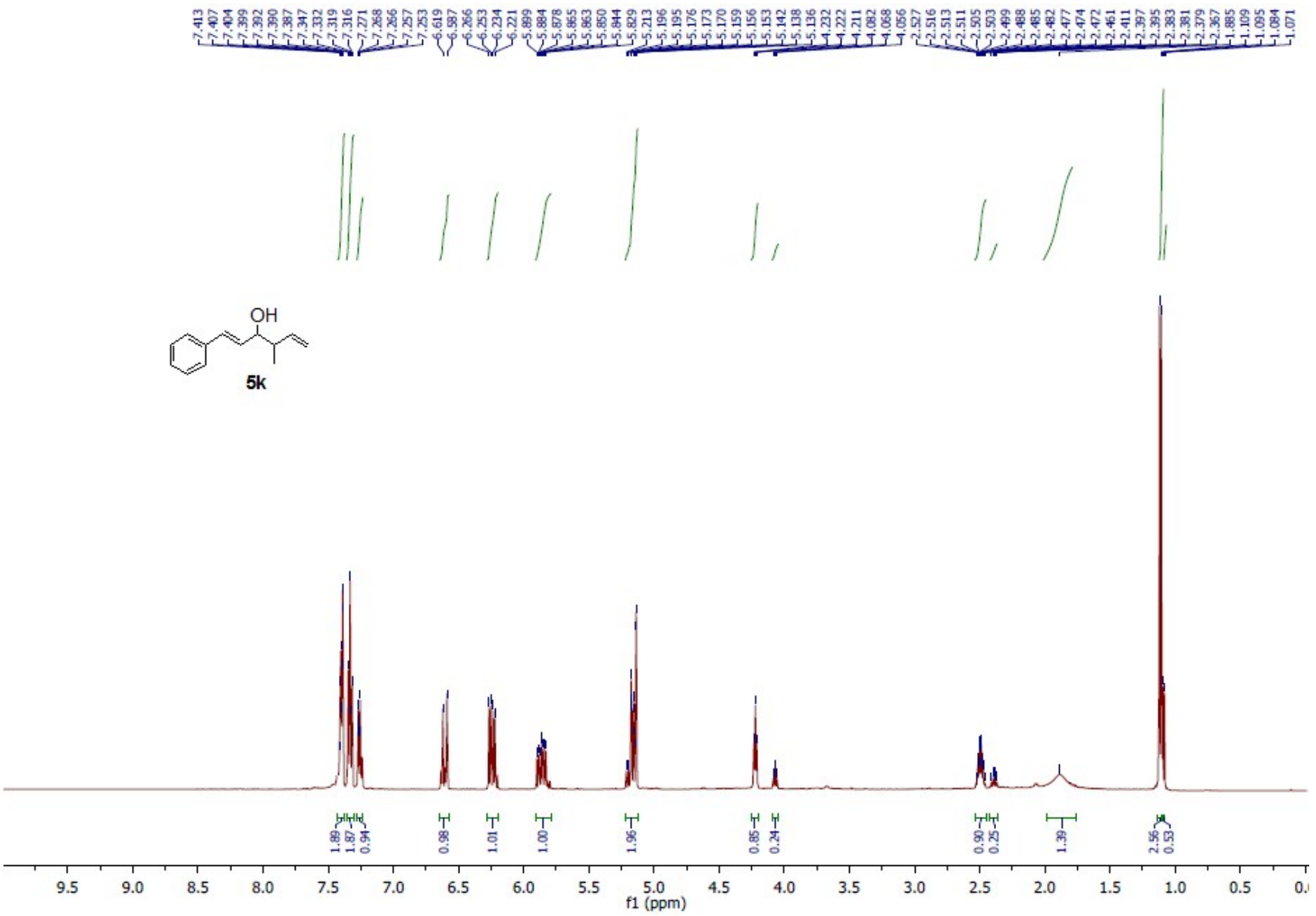
Graphic report

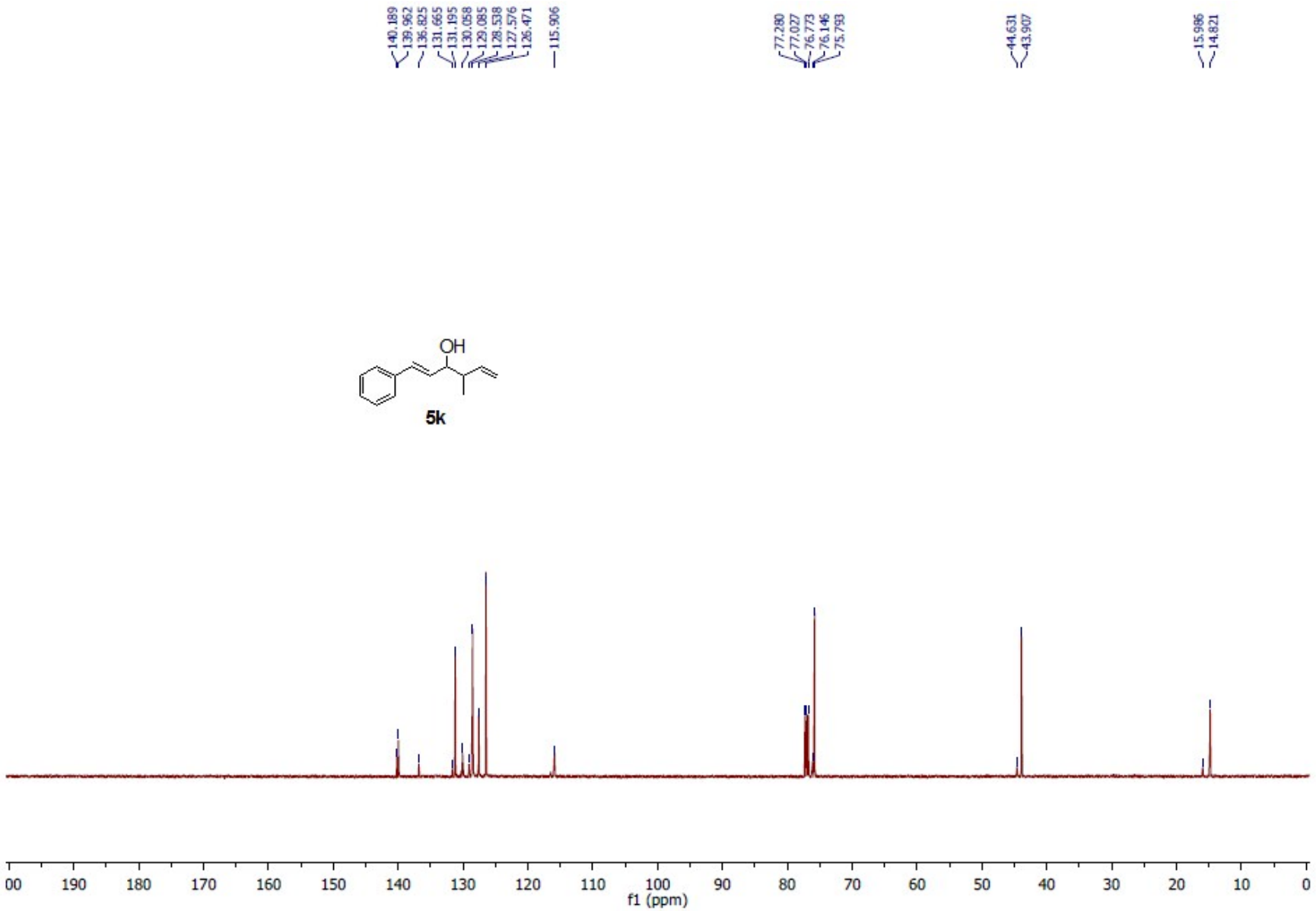
	Weight [mg]	Name	Method	N Area	C Area	H Area	S Area	N [%]	C [%]	H [%]	S [%]	C/N ratio	C/H ratio
13	1.9820	Ph-CH2-Ch2	2mgChem80s	63	40 329	14 236	28	0.00	81.82	9.177	0.000	0.0000	8.9158





5j


OH
5k
f1 (ppm)

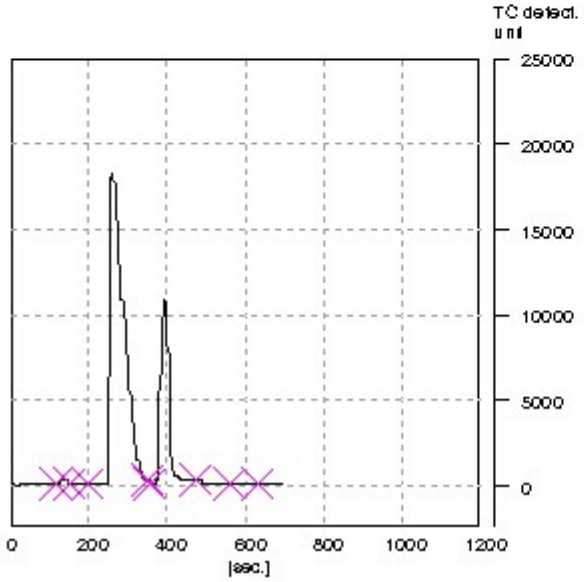

140.189
139.962
136.825
131.665
131.195
130.058
129.085
128.538
127.576
126.471
115.906
77.280
77.027
76.773
76.146
75.793
44.631
43.907
15.986
14.821
OH
5k
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

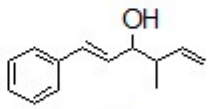
Document: crt-18-1-17 (VarioMICRO) from: 2/2/2017 4:32:07 PM

analytic functional testing
varioMICRO CHNS
serial number: 15103026

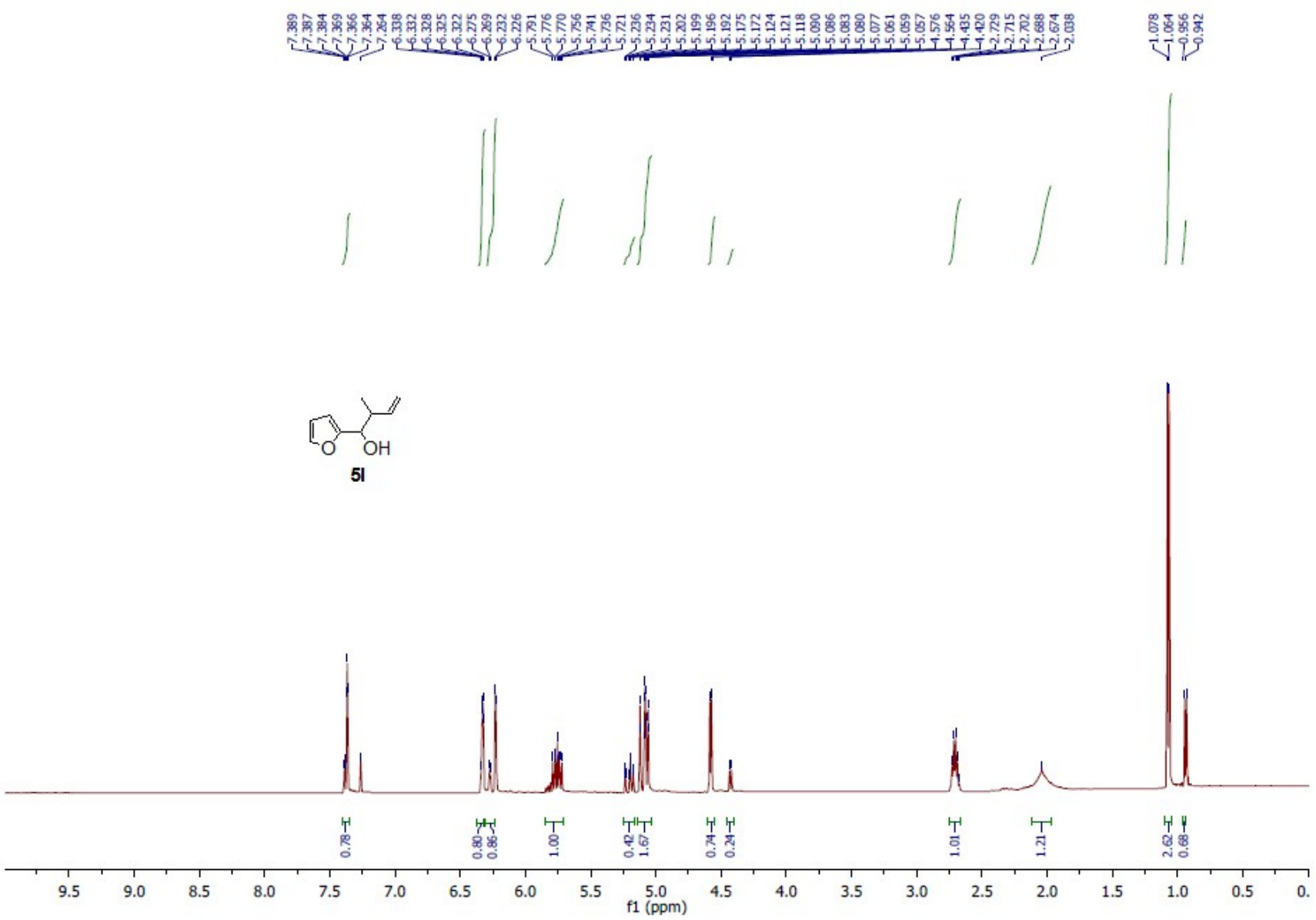
Graphic report

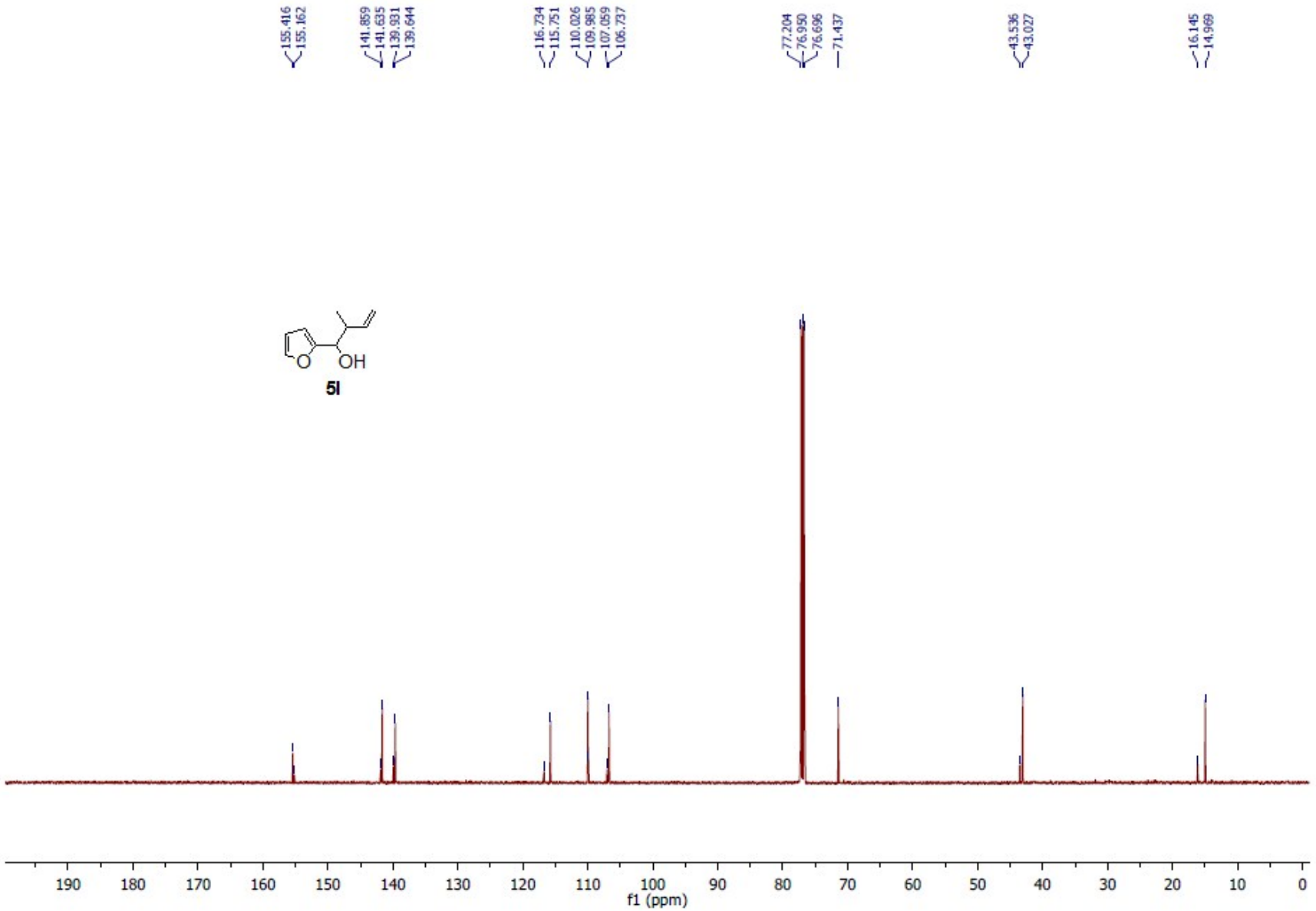
	Weight [mg]	Name	Method	N Area	C Area	H Area	S Area	N [%]	C [%]	H [%]	S [%]	C/N ratio	C/H ratio
11	3.6480	Cinnamal	2mgChem80s	61	75 455	25 679	25	0.00	82.88	8.683	0.000	0.0000	9.5446





5k


7.389
7.387
7.384
7.369
7.366
7.364
7.264
6.338
6.332
6.328
6.325
6.322
6.275
6.269
6.232
6.226
5.791
5.776
5.770
5.756
5.741
5.736
5.721
5.236
5.234
5.231
5.202
5.199
5.196
5.192
5.175
5.172
5.124
5.121
5.118
5.090
5.086
5.083
5.080
5.077
5.061
5.059
5.057
4.576
4.564
4.435
4.420
2.729
2.715
2.702
2.688
2.674
2.038
1.078
1.064
0.956
0.942
O
OH
5l
0.78
0.80
0.86
1.00
0.42
1.67
0.74
0.24
1.01
1.21
2.62
0.68
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
0.
f1 (ppm)

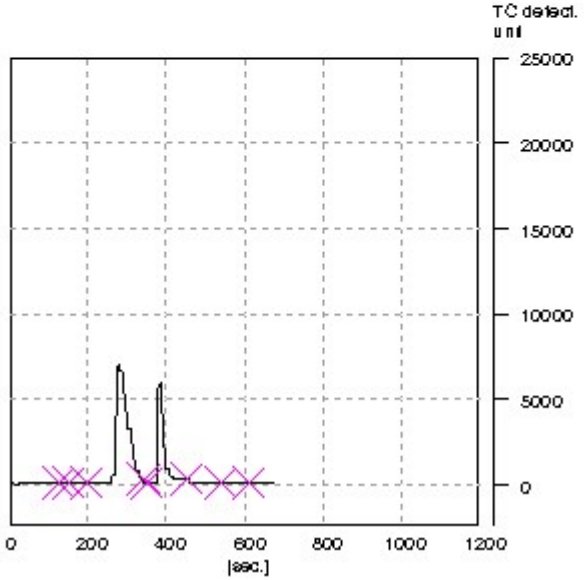

155.416
155.162
141.859
141.635
139.931
139.644
116.734
115.751
110.026
109.985
107.059
106.737
77.204
76.950
76.696
71.437
43.536
43.027
16.145
14.969
O
OH
5l
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

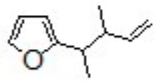
Document: crt-18-1-17 (VarioMICRO) from: 2/2/2017 4:32:07 PM

analytic functional testing
varioMICRO CHNS
serial number: 15103026

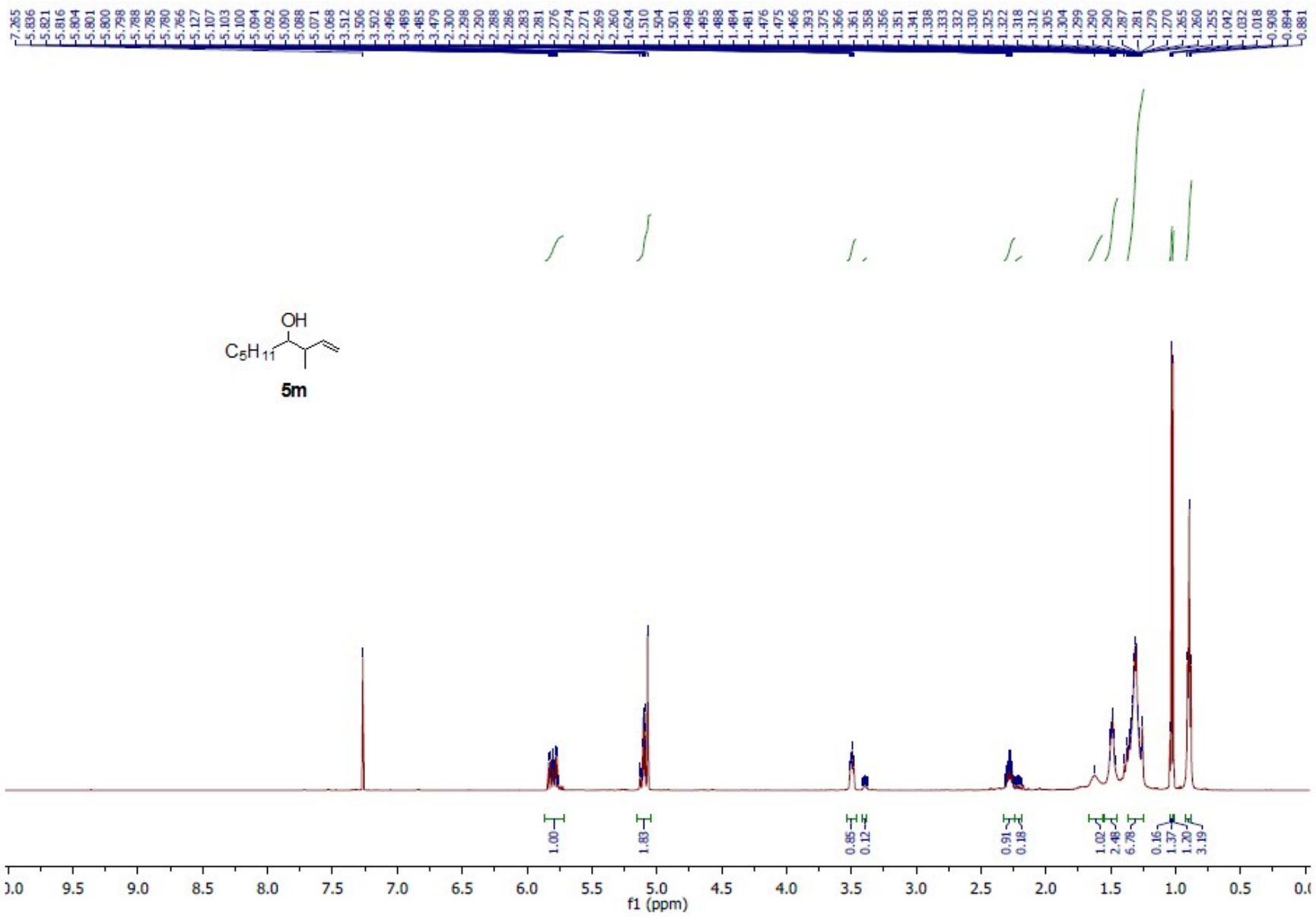
Graphic report

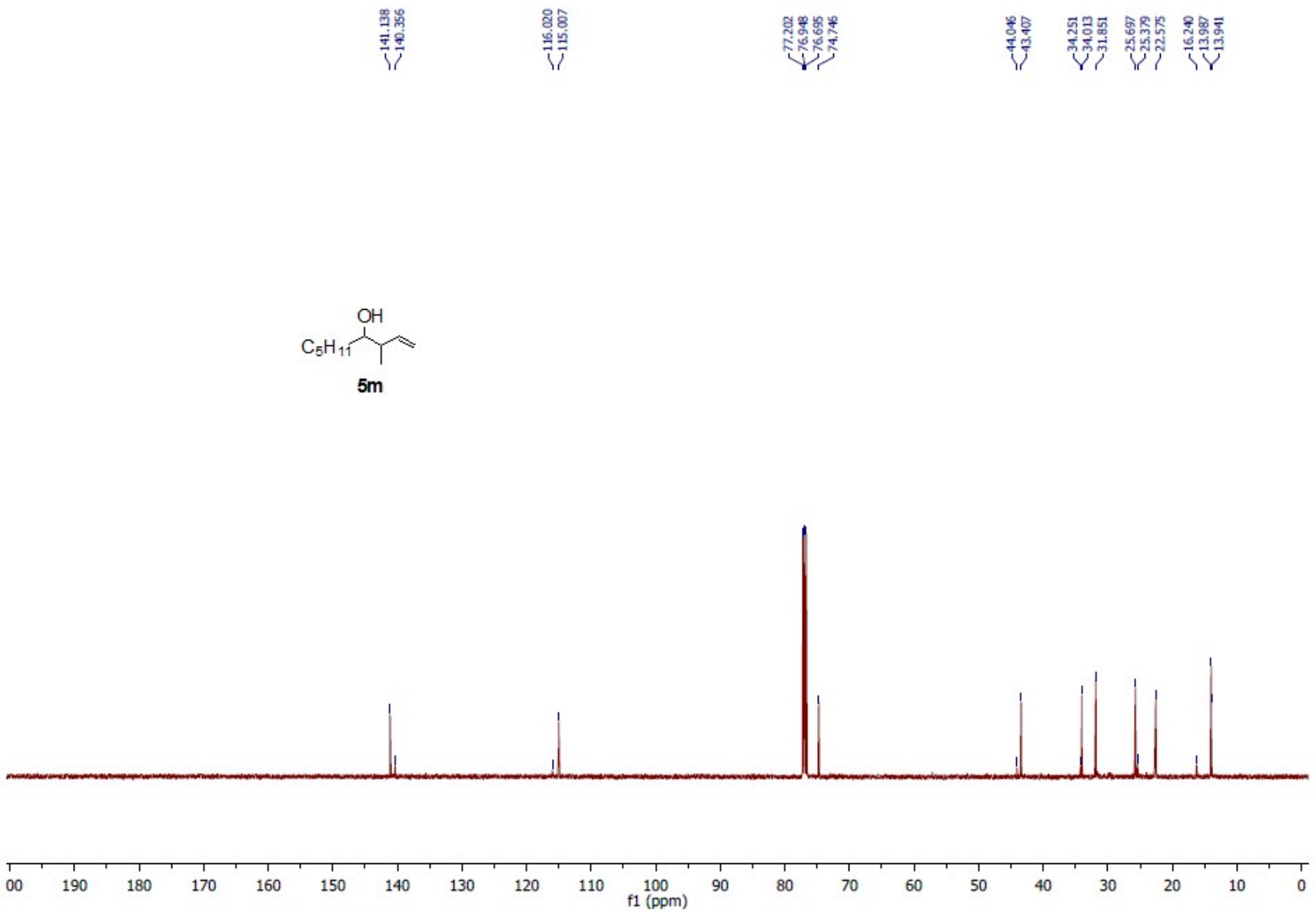
	Weight [mg]	Name	Method	N Area	C Area	H Area	S Area	N [%]	C [%]	H [%]	S [%]	C/N ratio	C/H ratio
19	1.3420	2-Furfural	2mgChem80s	51	23 696	8 254	33	0.00	70.91	8.045	0.000	0.0000	8.8141





5l


OH
C5H11
5m
1.00
1.83
0.85
0.12
0.91
0.18
1.02
2.48
6.78
0.16
1.37
1.20
3.19
f1 (ppm)

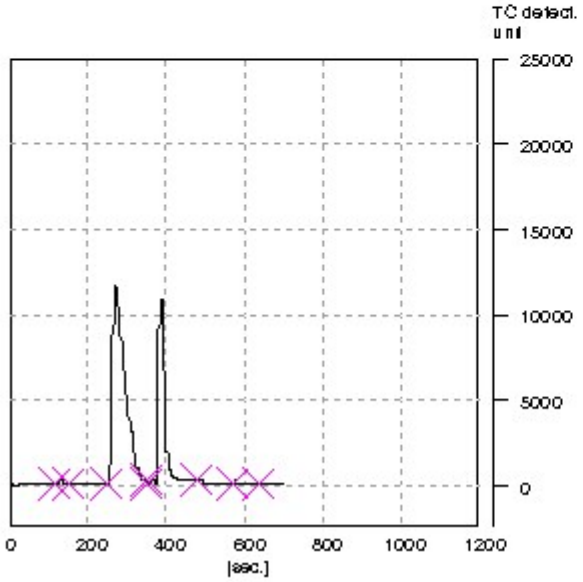

141.138
140.356
116.020
115.007
77.202
76.948
76.695
74.746
44.046
43.407
34.251
34.013
31.851
25.697
25.379
22.575
16.240
13.987
13.941
OH
C5H11
5m
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

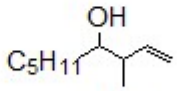
Document: crt-18-1-17 (VarioMICRO) from: 2/2/2017 4:32:07 PM

analytic functional testing
varioMICRO CHNS
serial number: 15103026

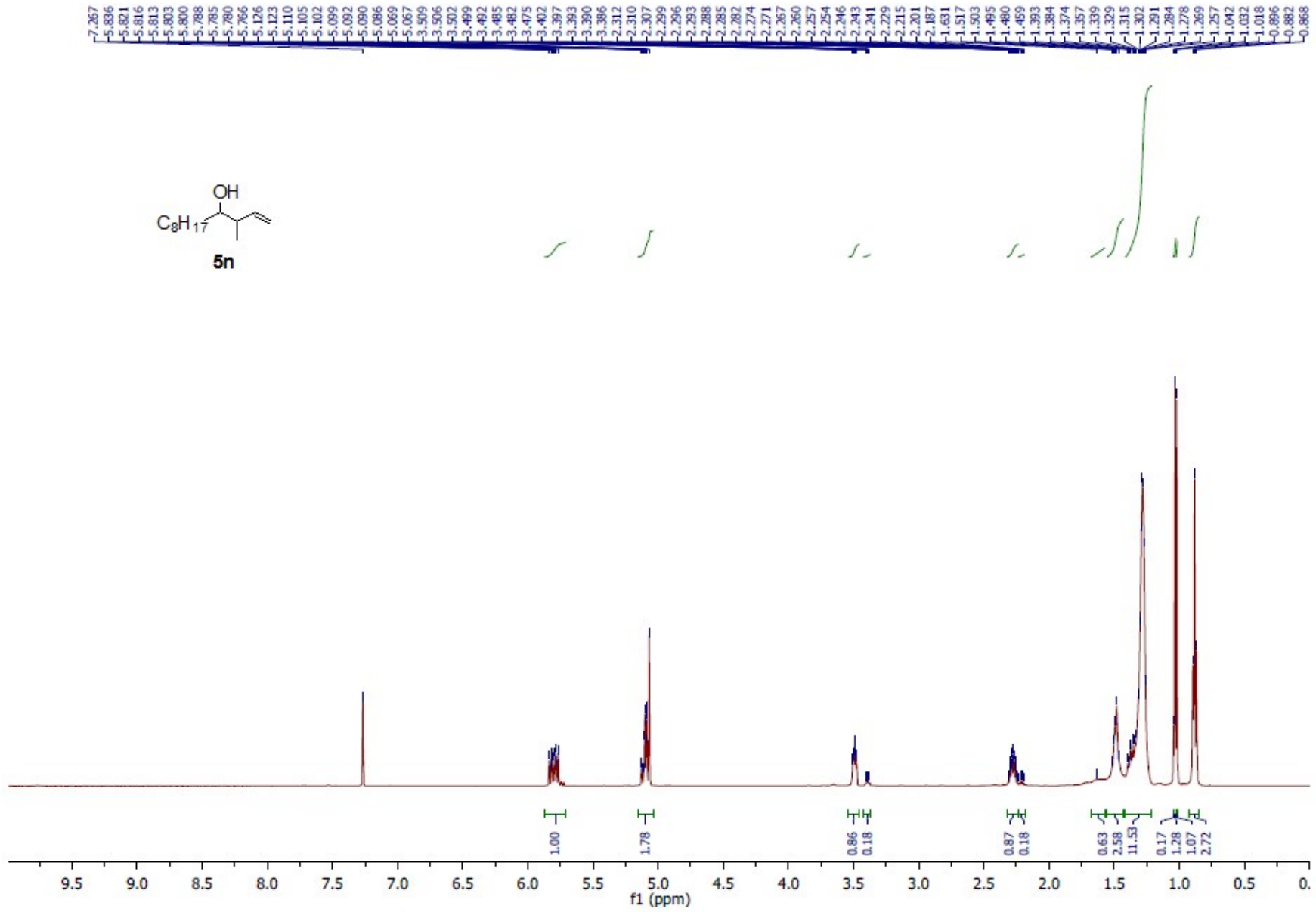
Graphic report

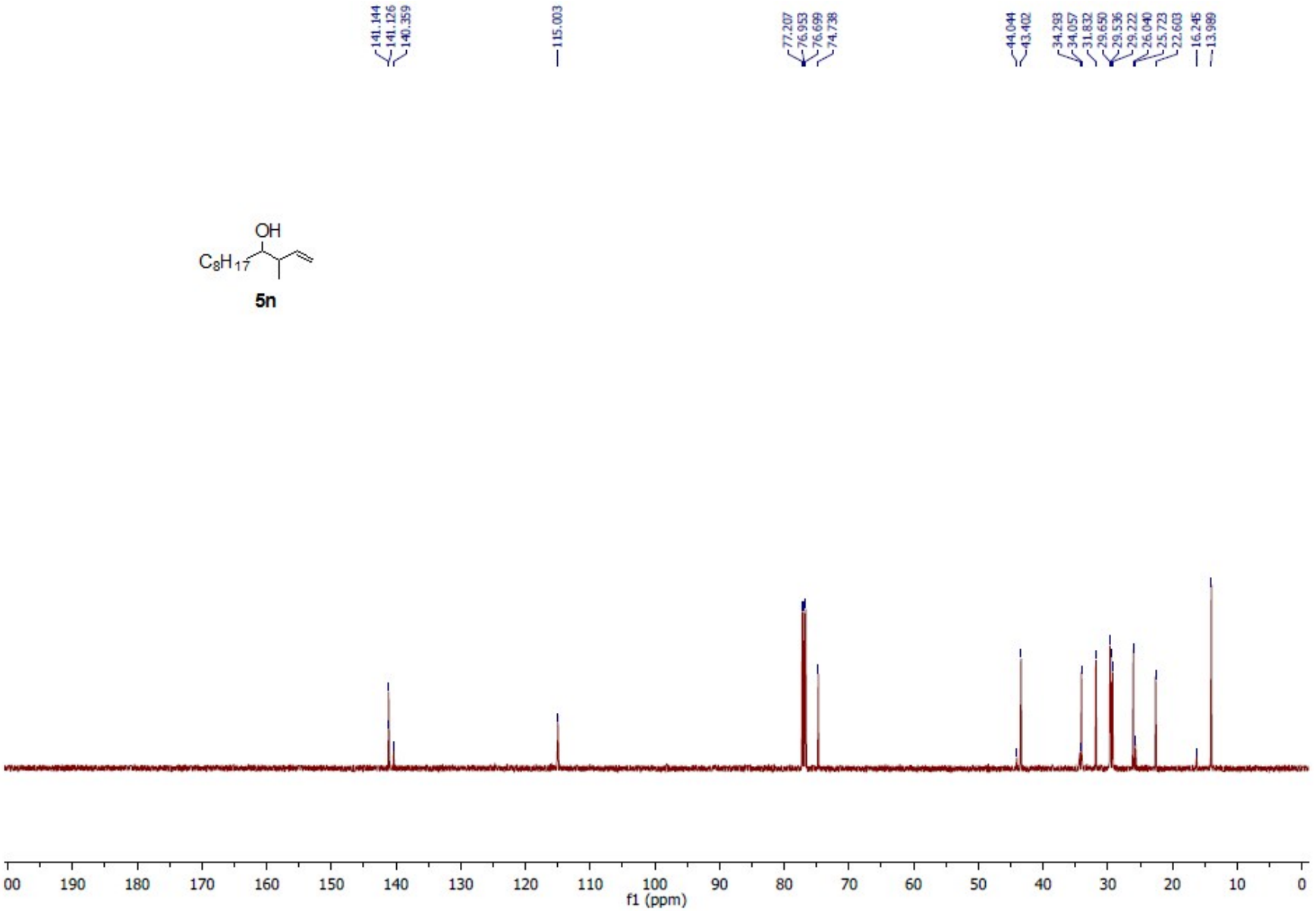
	Weight [mg]	Name	Method	N Area	C Area	H Area	S Area	N [%]	C [%]	H [%]	S [%]	C/N ratio	C/H ratio
18	2.2060	Hexanal	2mgChem80s	68	42 204	22 881	29	0.00	76.92	12.874	0.000	0.0000	5.9748





5m


OH
C8H17
5n
1.00
1.78
0.86
0.18
0.87
0.18
0.63
2.58
11.53
0.17
1.28
1.07
2.72
f1 (ppm)

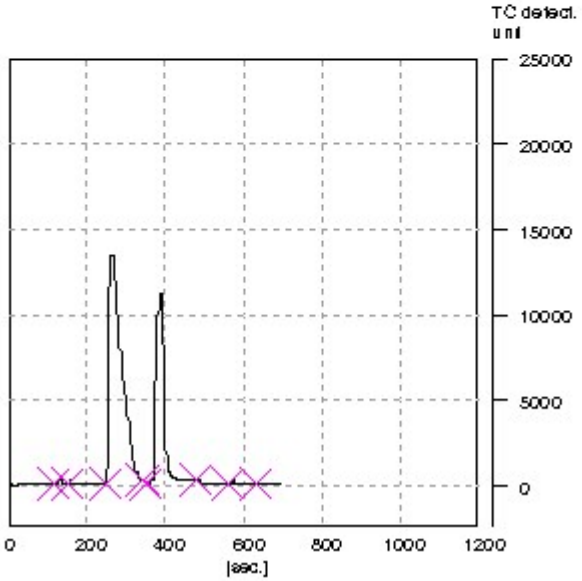

141.144
141.126
140.359
115.003
77.207
76.953
76.699
74.738
44.044
43.402
34.293
34.057
31.832
29.650
29.536
29.222
26.040
25.723
22.603
16.245
13.989
OH
C8H17
5n
f1 (ppm)

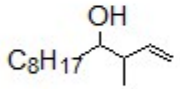
Document: crt-18-1-17 (VarioMICRO) from: 2/2/2017 4:32:07 PM

analytic functional testing
varioMICRO CHNS
serial number: 15103026

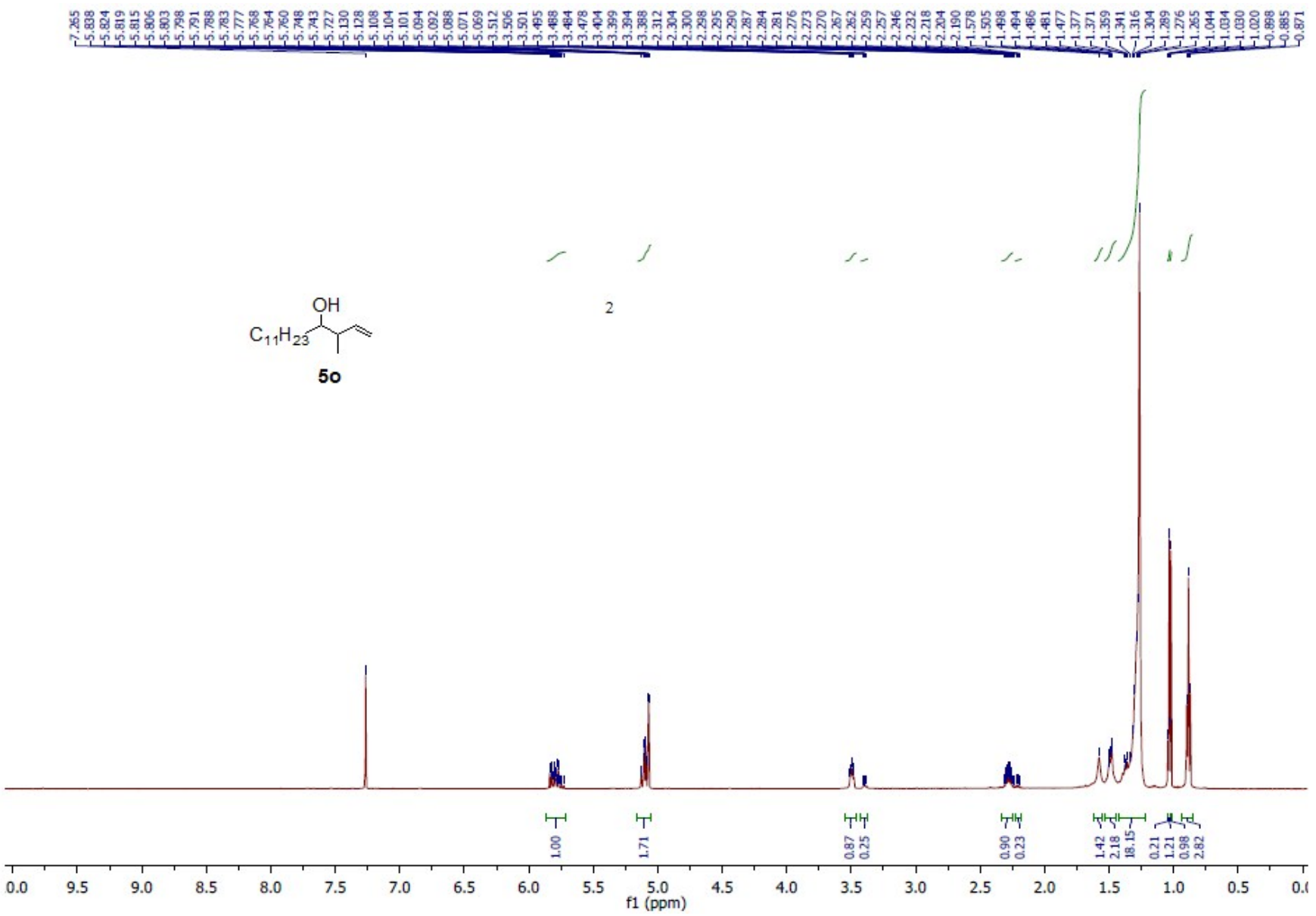
Graphic report

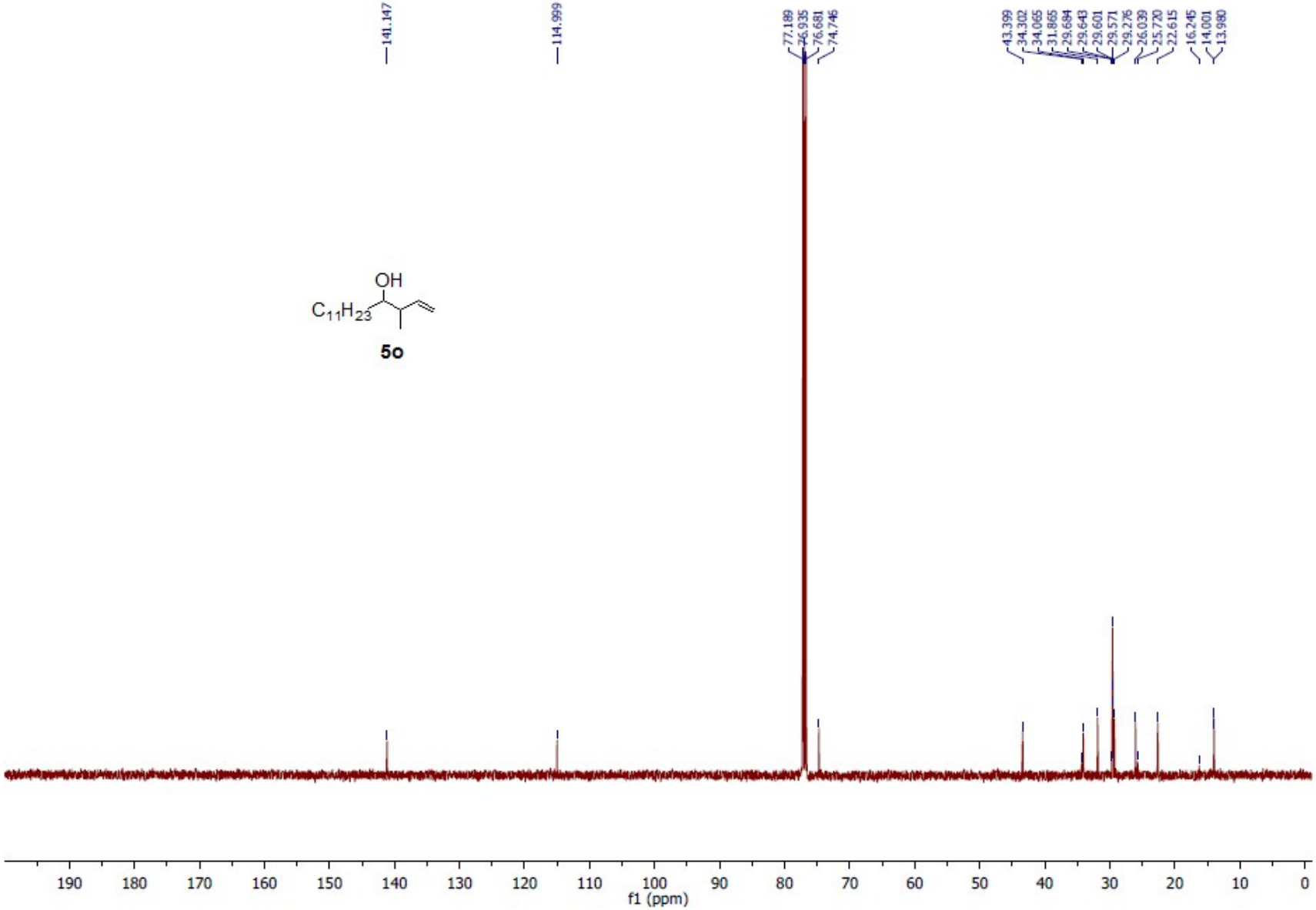
	Weight [mg]	Name	Method	N Area	C Area	H Area	S Area	N [%]	C [%]	H [%]	S [%]	C/N ratio	C/H ratio
14	2.5480	Nonanal	2mgChem80s	62	50 158	26 830	31	0.00	79.07	12.963	0.000	0.0000	6.0997





5n


OH
$C_{11}H_{23}$
5o
2
1.00
1.71
0.87
0.25
0.90
0.23
1.42
2.18
18.15
0.21
1.21
0.98
2.82
0.0
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
f1 (ppm)

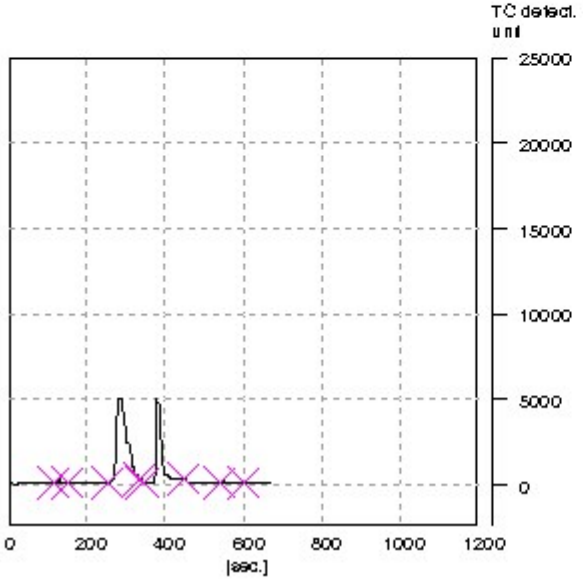

141.147
114.999
77.189
76.935
76.681
74.746
43.399
34.302
34.065
31.865
29.684
29.643
29.601
29.571
29.276
26.039
25.720
22.615
16.245
14.001
13.980
OH
C11H23
5o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

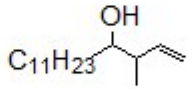
Document: crt-18-1-17 (VarioMICRO) from: 2/2/2017 4:32:07 PM

analytic functional testing
varioMICRO CHNS
serial number: 15103026

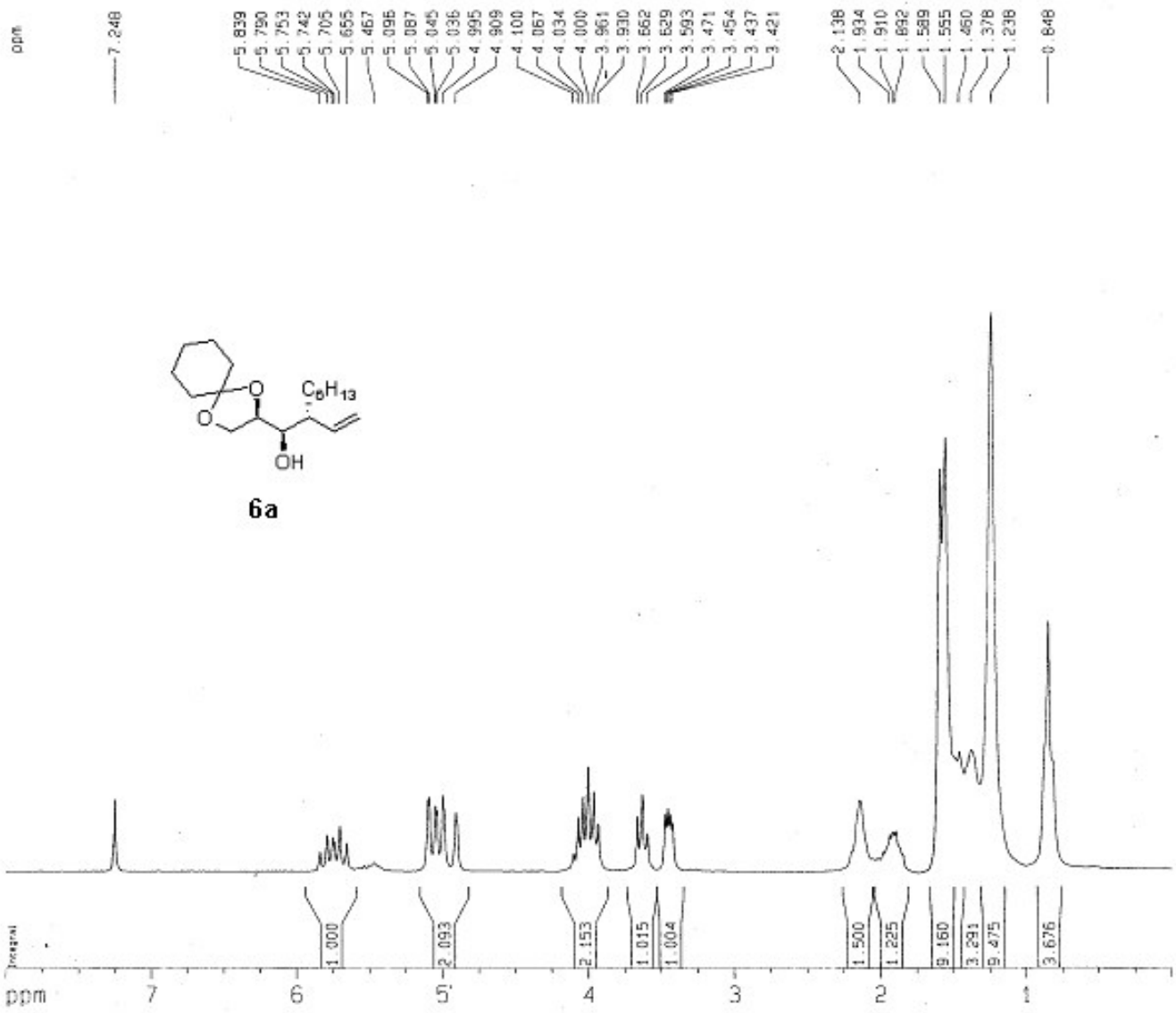
Graphic report

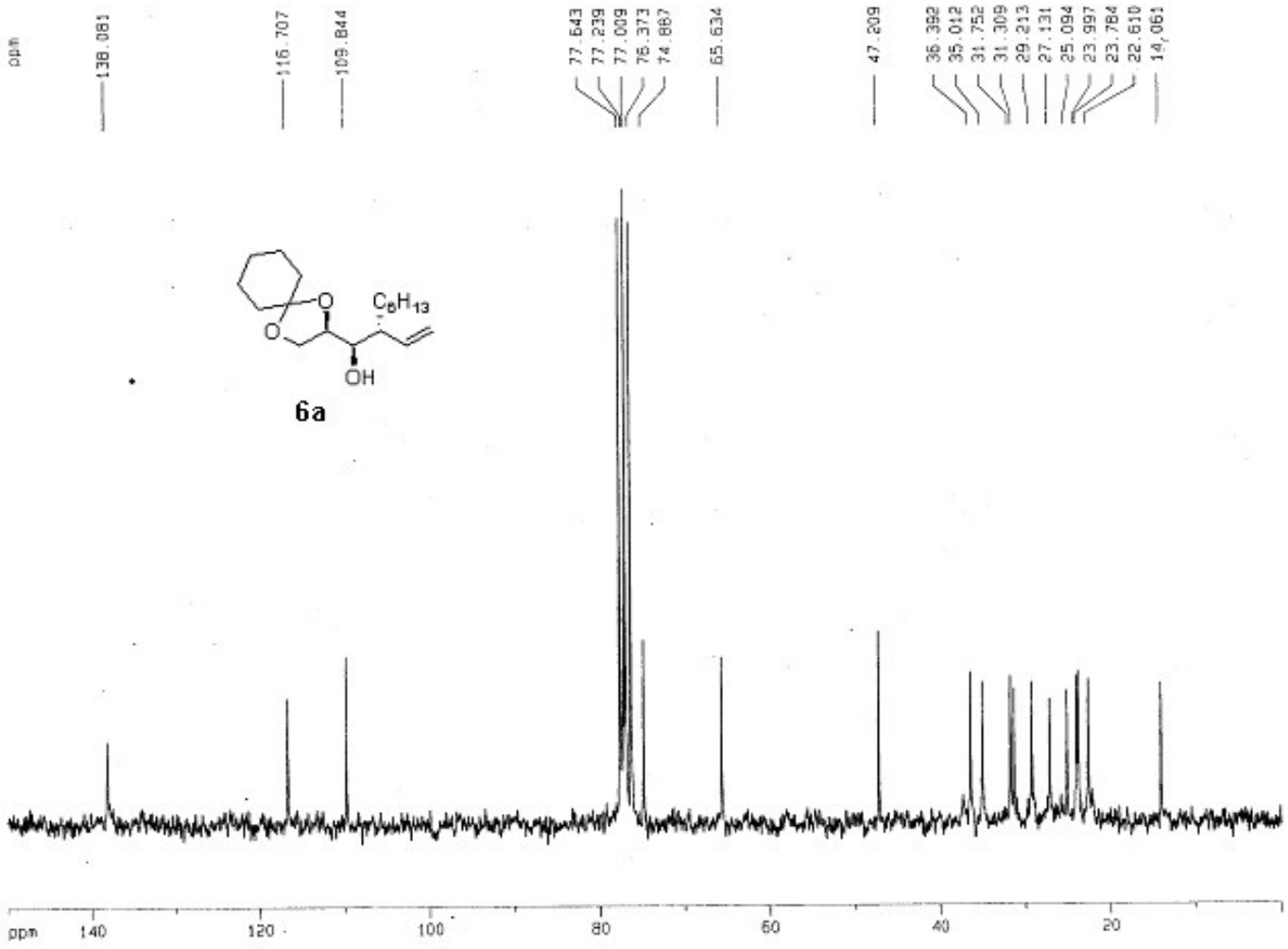
	Weight [mg]	Name	Method	N Area	C Area	H Area	S Area	N [%]	C [%]	H [%]	S [%]	C/N ratio	C/H ratio
20	0.7780	Dodecanal	2mgChem80s	62	15 582	8 086	30	0.00	80.25	13.601	0.000	0.0000	5.9001

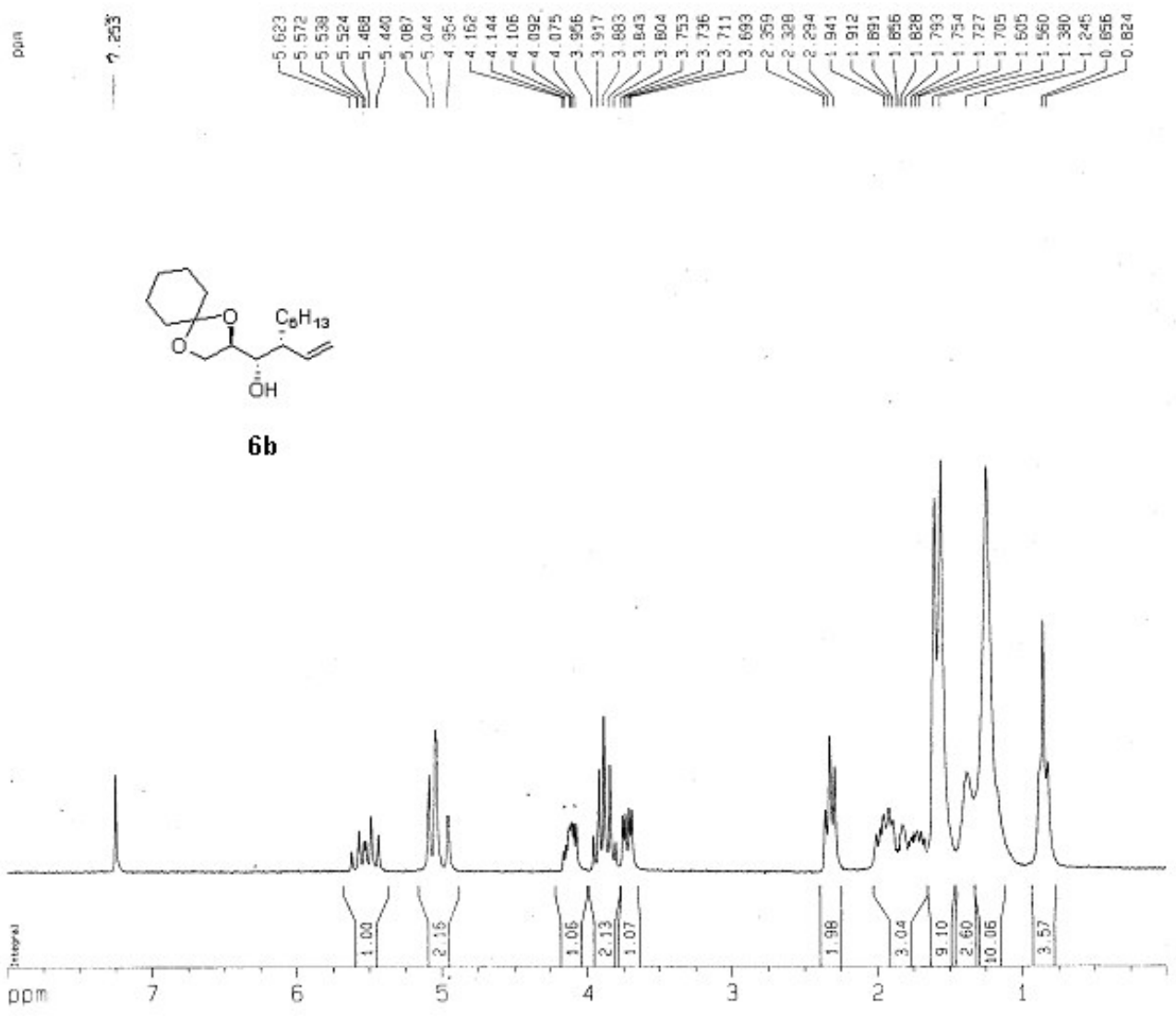


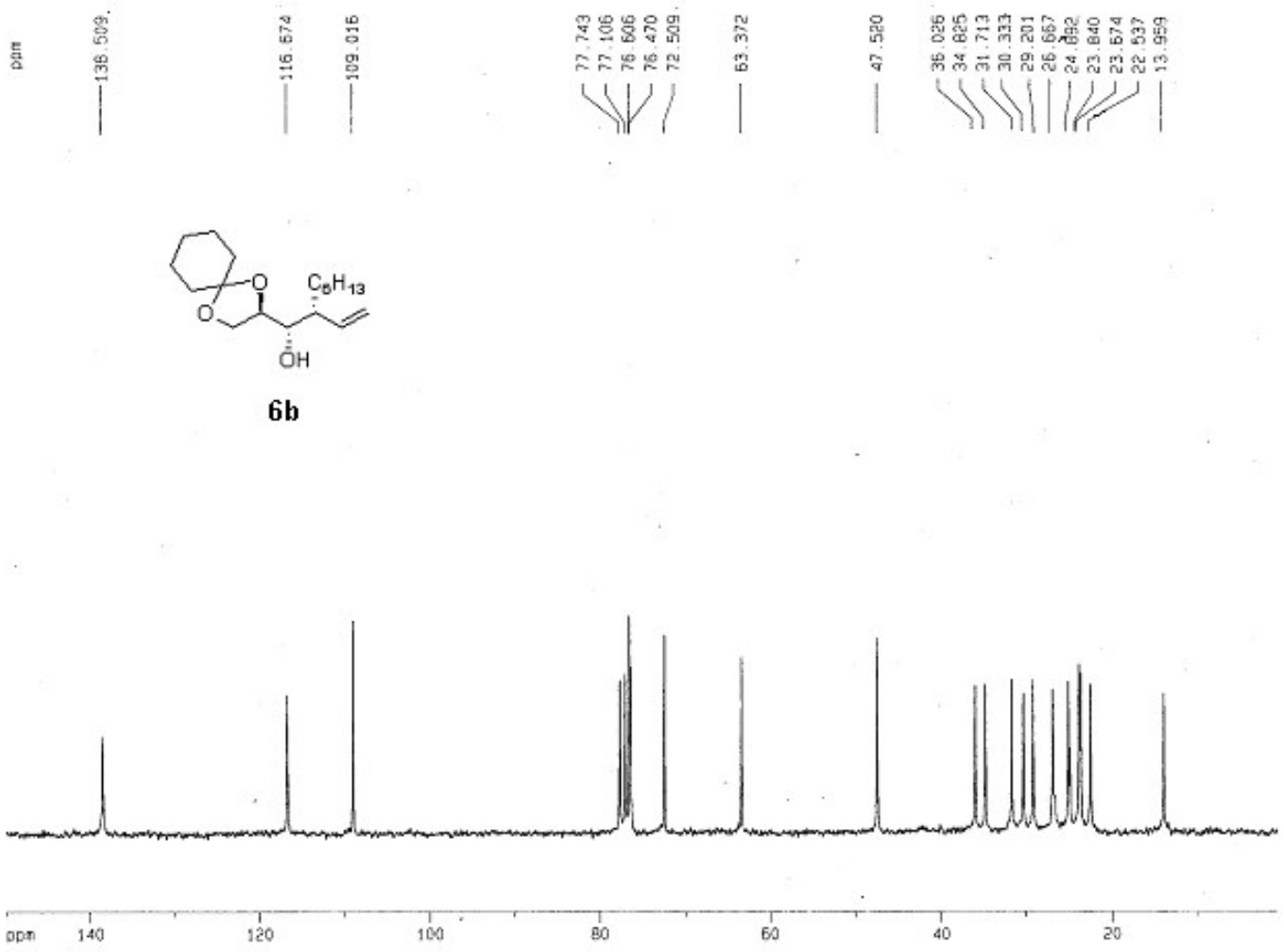


5o

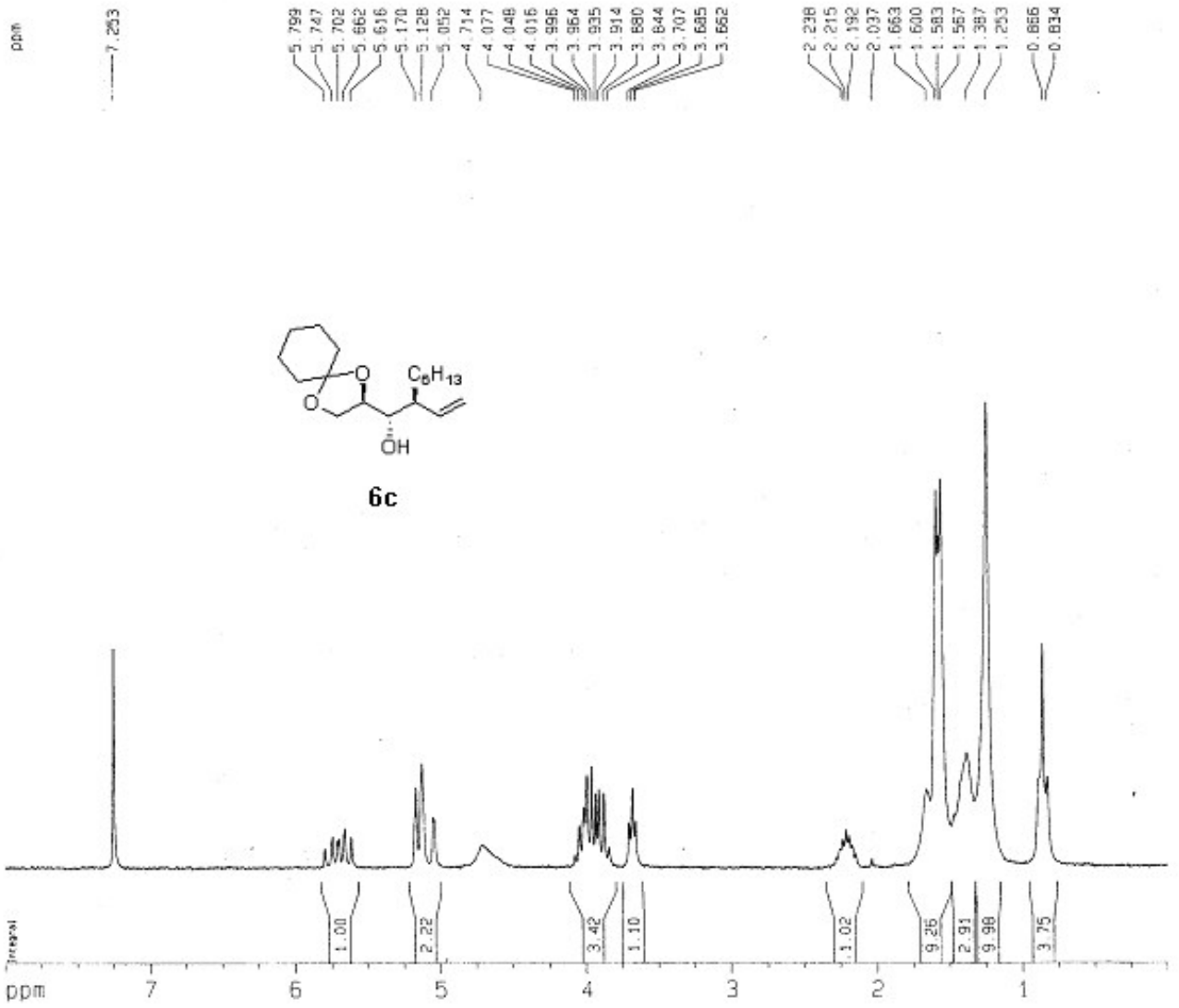

ppm
7.248
5.839
5.790
5.753
5.742
5.705
5.655
5.467
5.096
5.087
5.045
5.036
4.995
4.909
4.100
4.067
4.034
4.000
3.961
3.930
3.662
3.629
3.593
3.471
3.454
3.437
3.421
2.138
1.934
1.910
1.892
1.589
1.555
1.460
1.378
1.238
0.848
C6H13
O
O
OH
6a
1.000
2.093
2.153
1.015
1.004
1.500
1.225
9.160
3.291
9.475
3.676
ppm
7
6
5
4
3
2

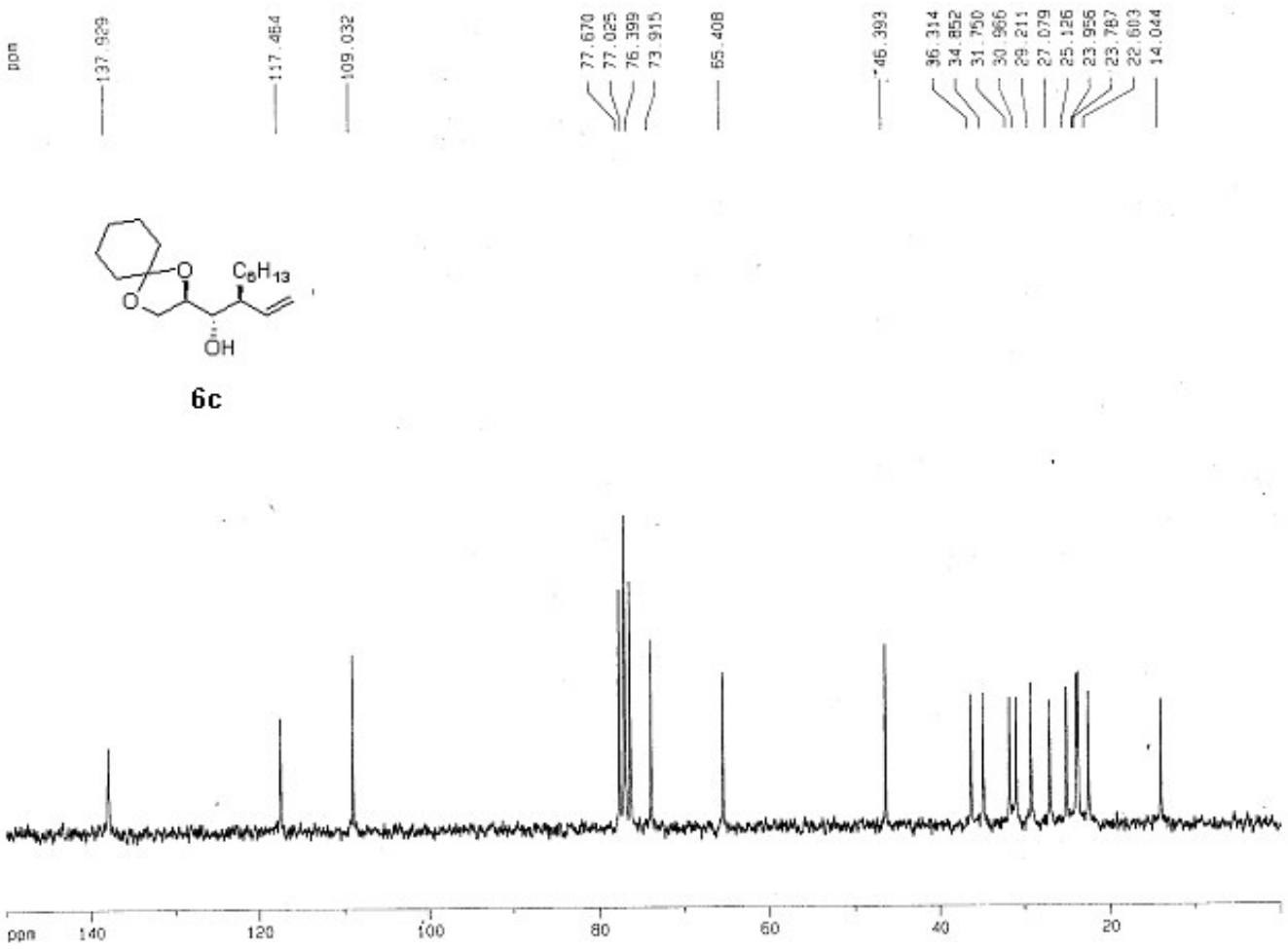

ppm
138.081
116.707
109.844
77.643
77.239
77.009
76.373
74.867
65.634
47.209
36.392
35.012
31.752
31.309
29.213
27.131
25.094
23.997
23.784
22.610
14.061
O
O
C_6H_{13}
OH
6a
ppm
140
120
100
80
60
40
20


ppm
7.253
5.623
5.572
5.538
5.524
5.468
5.440
5.087
5.044
4.954
4.162
4.144
4.106
4.092
4.075
3.956
3.917
3.883
3.843
3.804
3.753
3.736
3.711
3.693
2.359
2.328
2.294
1.941
1.912
1.891
1.856
1.828
1.793
1.754
1.727
1.705
1.605
1.560
1.380
1.245
0.856
0.824
C6H13
O
O
OH
6b
Integral
1.00
2.15
1.06
2.13
1.07
1.98
3.04
9.10
2.60
10.06
3.57
ppm
7
6
5
4
3
2
1

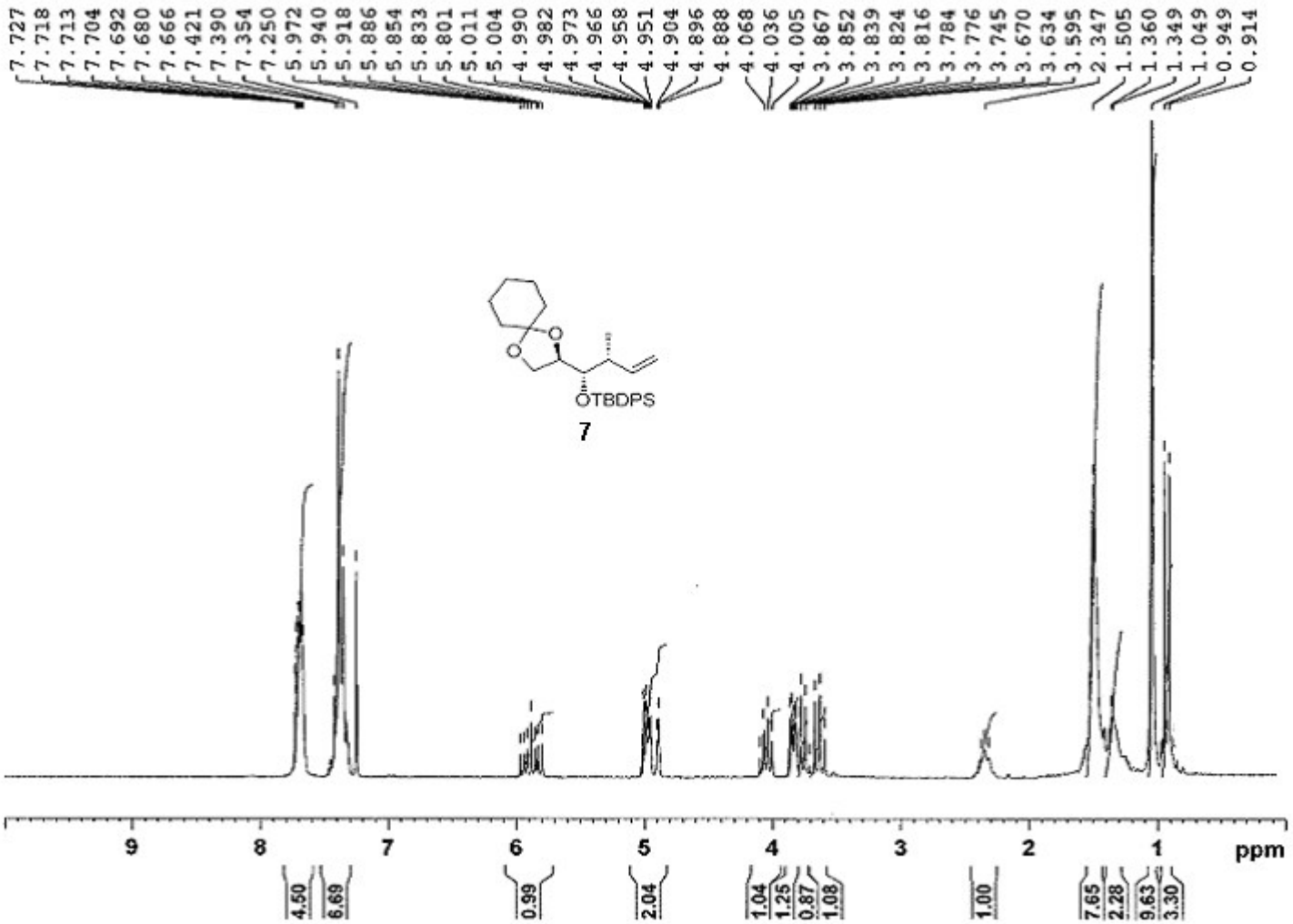

ppm
138.509
116.674
109.016
77.743
77.106
76.606
76.470
72.509
63.372
47.580
36.026
34.825
31.713
30.333
29.201
26.667
24.892
23.840
23.674
22.537
13.959
C_6H_{13}
O
O
OH
ppm
140
120
100
80
60
40
20

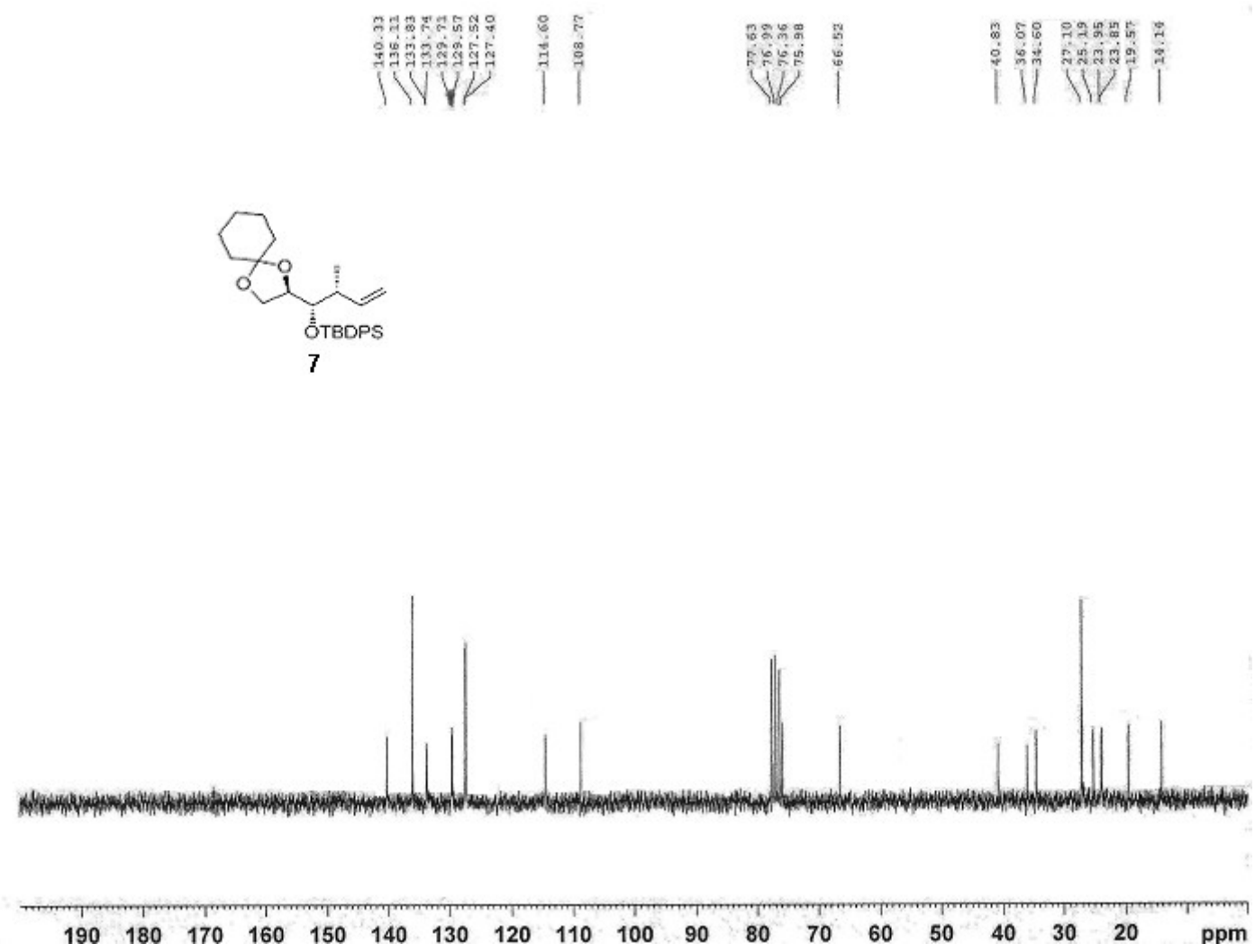
6b

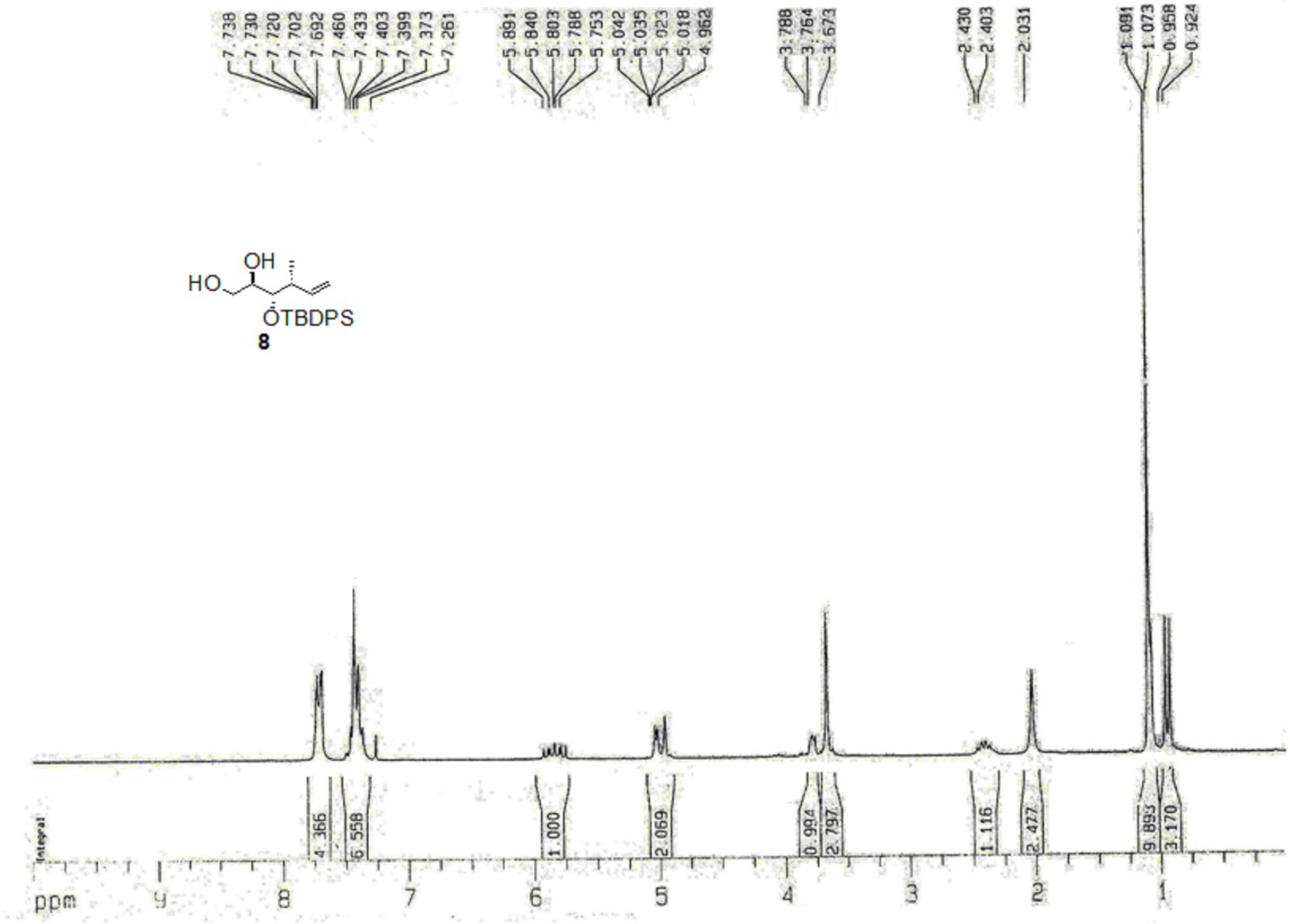

ppm
7.253
5.799
5.747
5.702
5.662
5.616
5.170
5.128
5.052
4.714
4.077
4.048
4.016
3.996
3.964
3.935
3.914
3.880
3.844
3.707
3.685
3.662
2.238
2.215
2.192
2.037
1.663
1.600
1.583
1.567
1.387
1.253
0.866
0.834
O
O
C6H13
OH
6c
Integral
1.00
2.22
3.42
1.10
1.02
9.26
2.91
9.98
3.75
ppm
7
6
5
4
3
2
1

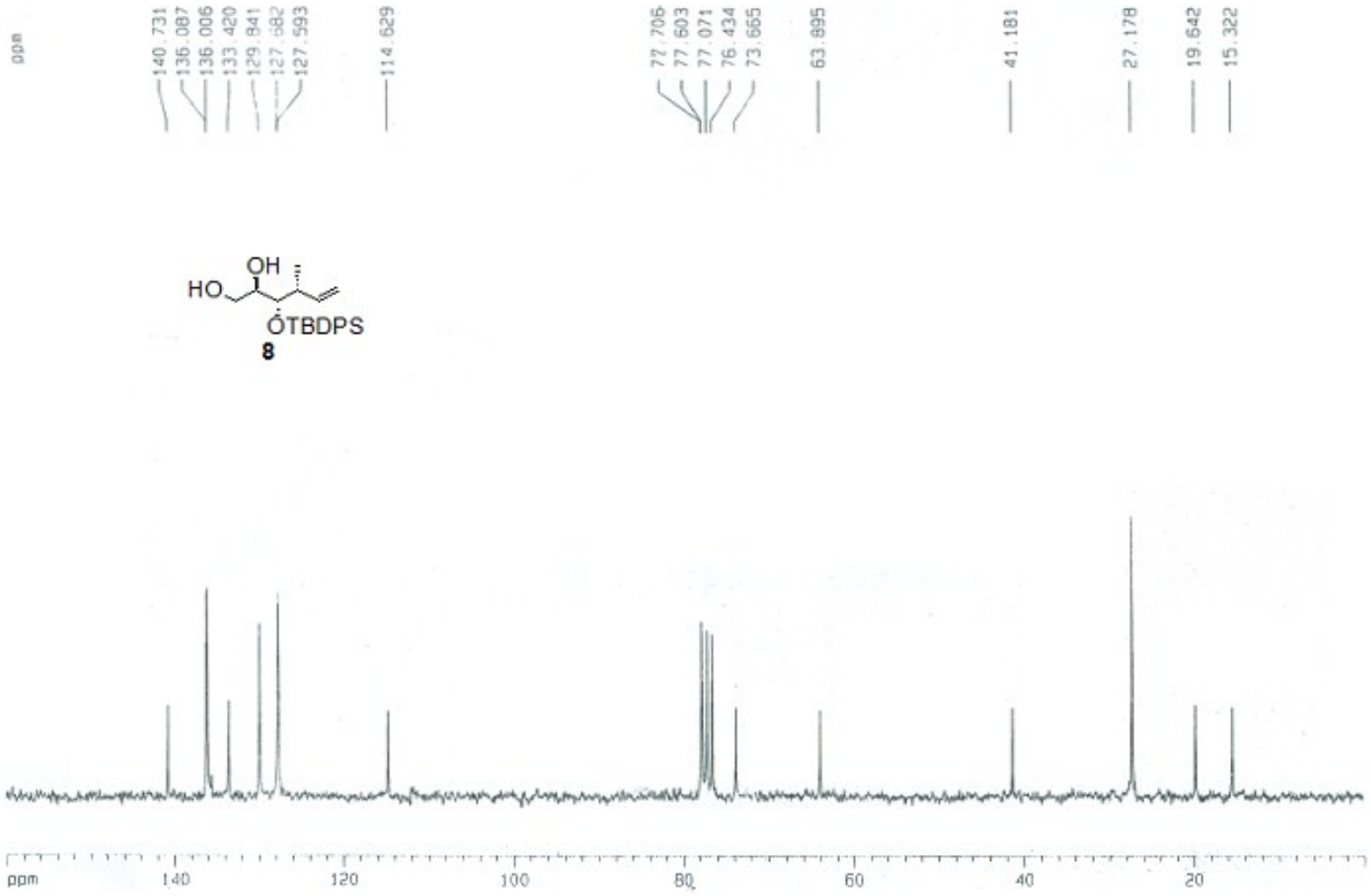

ppm
137.929
117.464
109.032
77.670
77.025
76.399
73.915
65.408
46.393
36.314
34.852
31.750
30.966
29.211
27.079
25.126
23.956
23.787
22.603
14.044
C_6H_{13}
O
O
OH
ppm
140
120
100
80
60
40
20

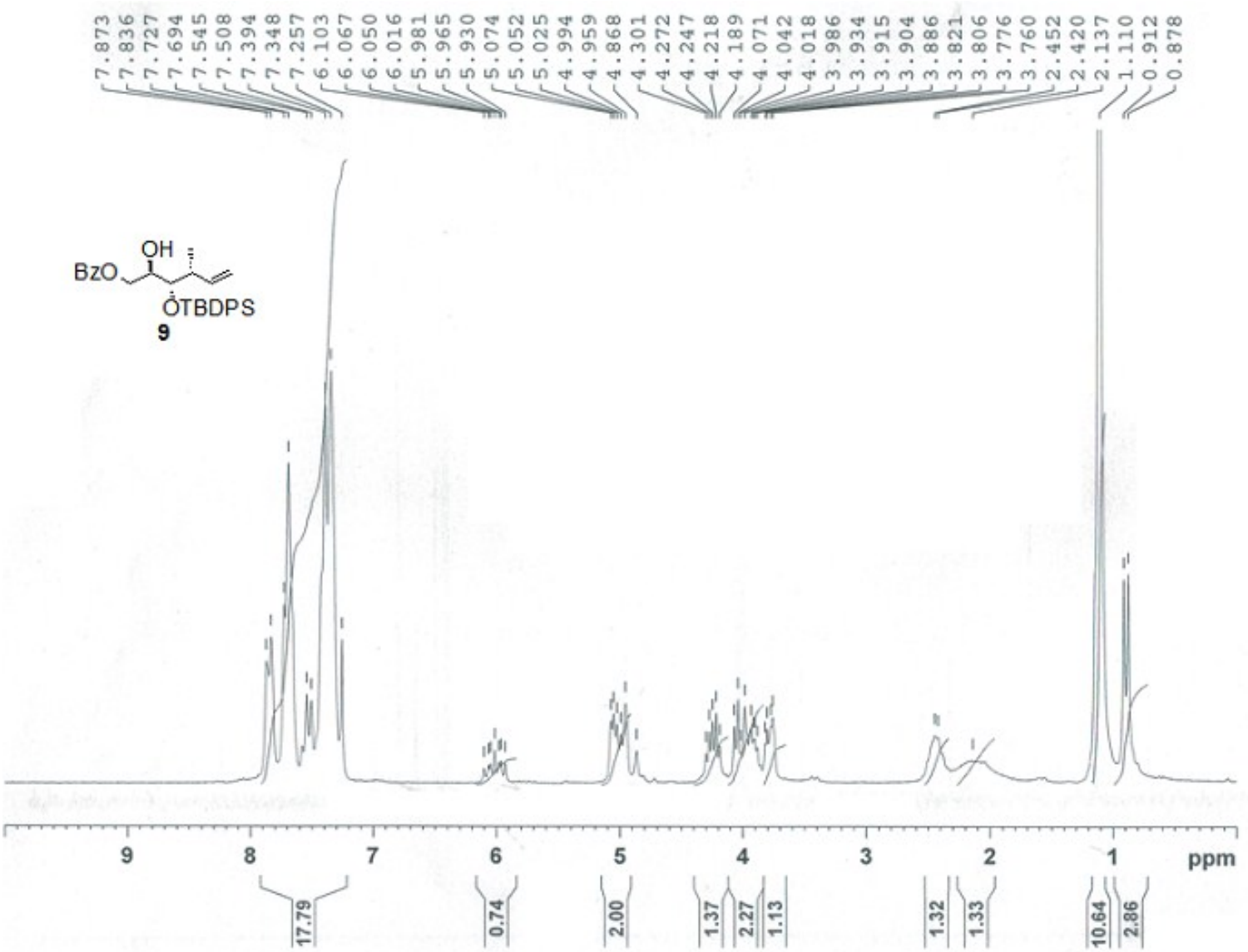
6c

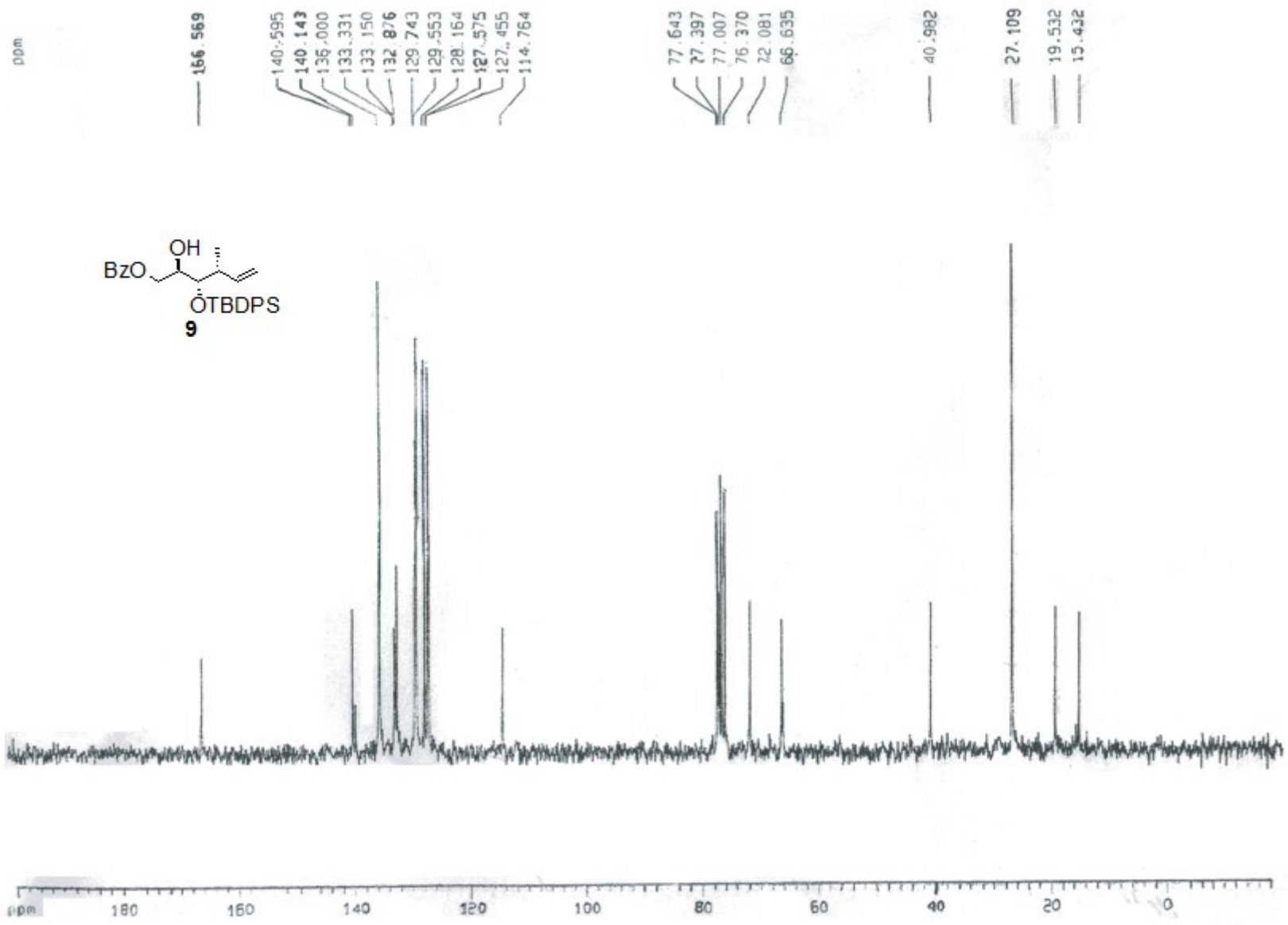

7.727
7.718
7.713
7.704
7.692
7.680
7.666
7.421
7.390
7.354
7.250
5.972
5.940
5.918
5.886
5.854
5.833
5.801
5.011
5.004
4.990
4.982
4.973
4.966
4.958
4.951
4.904
4.896
4.888
4.068
4.036
4.005
3.867
3.852
3.839
3.824
3.816
3.784
3.776
3.745
3.670
3.634
3.595
2.347
1.505
1.360
1.349
1.049
0.949
0.914
OTBDPS
7
9
8
7
6
5
4
3
2
1
ppm
4.50
6.69
0.99
2.04
1.04
1.25
0.87
1.08
1.00
7.65
2.28
9.63
3.30

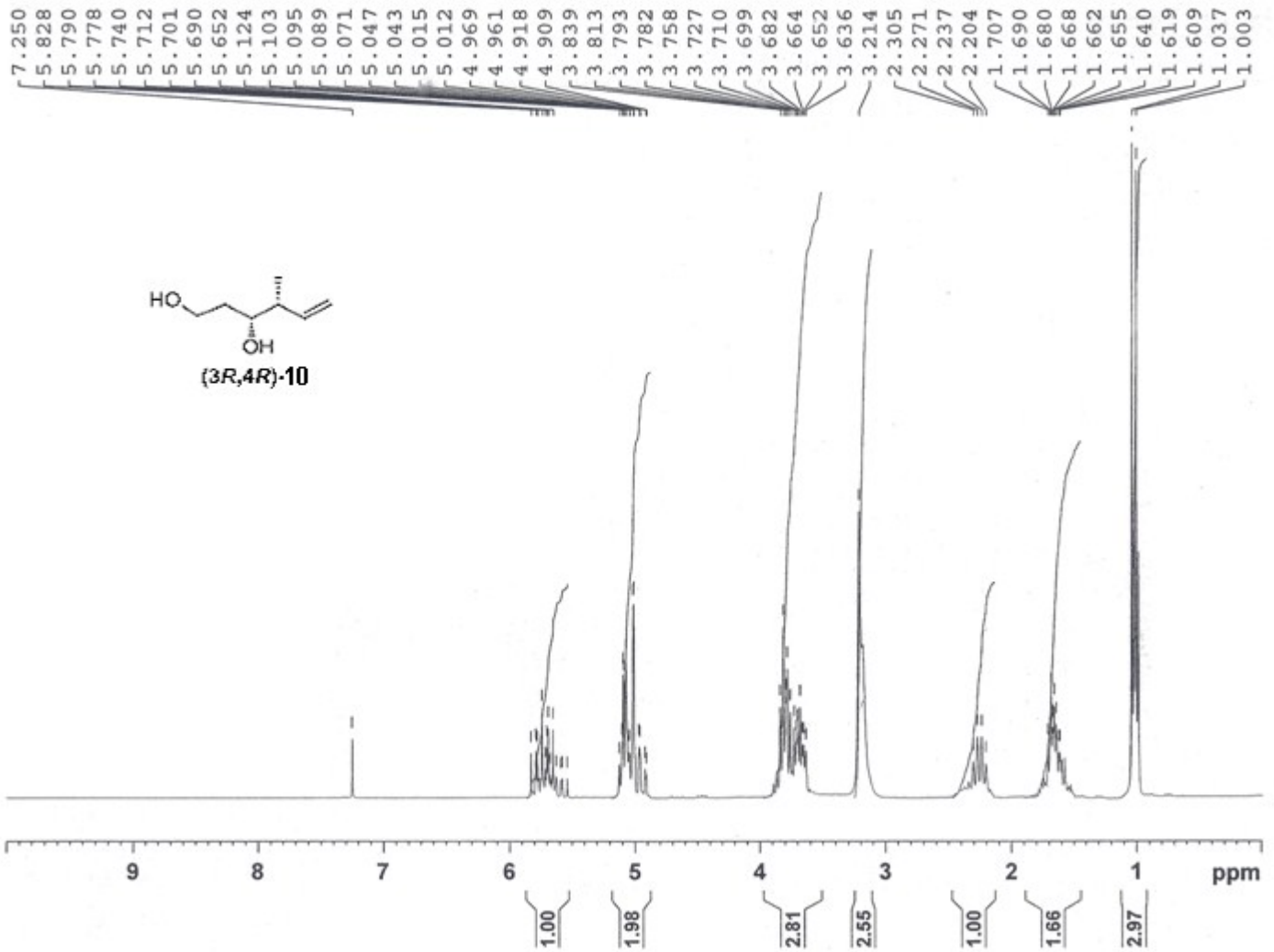

140.33
136.11
133.83
133.74
129.71
129.57
127.52
127.40
114.60
108.77
77.63
76.99
76.36
75.98
66.52
40.83
36.07
34.60
27.10
25.19
23.95
23.85
19.57
14.14
OTBDPS
7
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

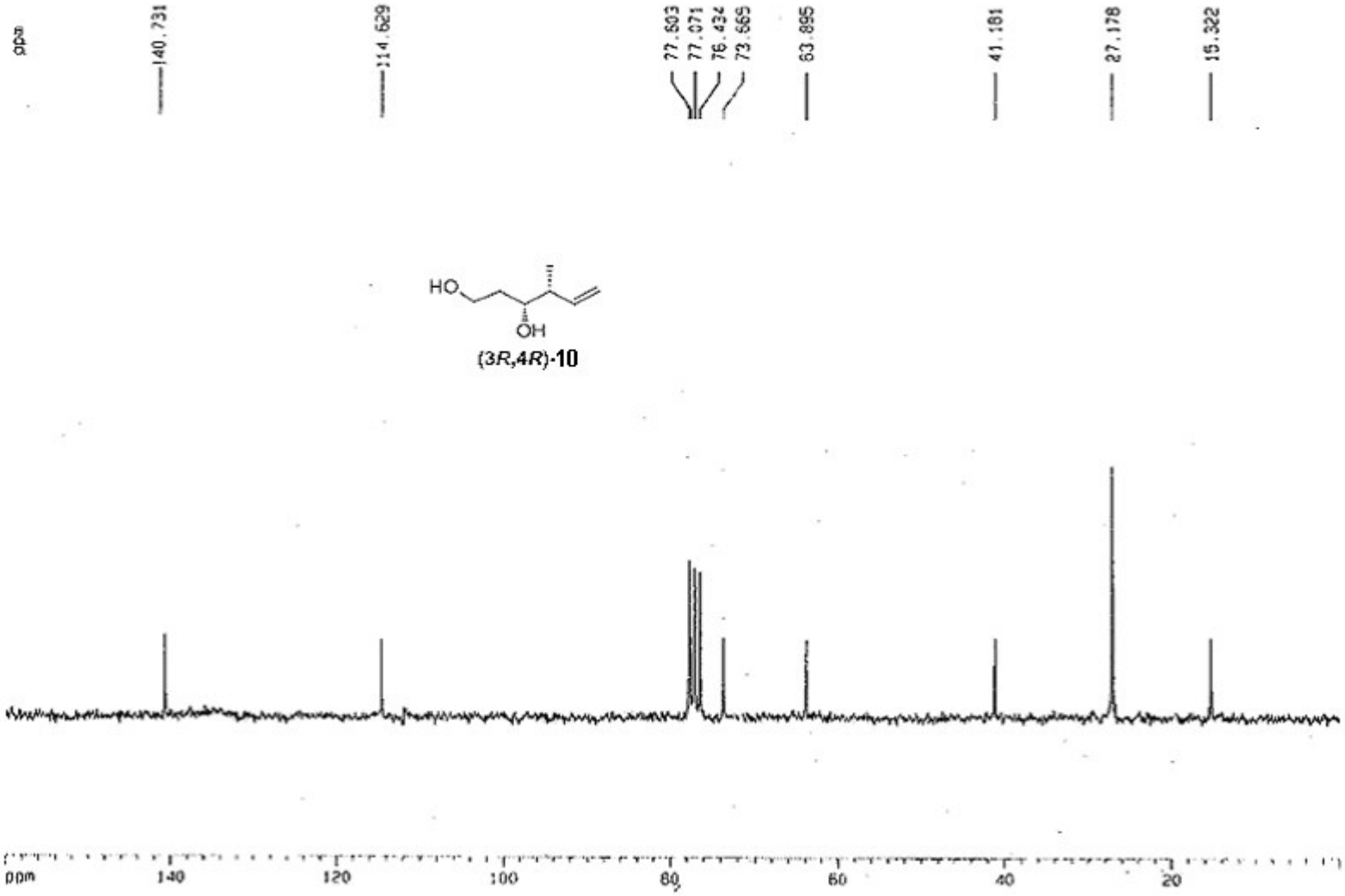

7.738
7.730
7.720
7.702
7.692
7.460
7.433
7.403
7.399
7.373
7.261
5.891
5.840
5.803
5.788
5.753
5.042
5.035
5.023
5.018
4.962
3.788
3.764
3.673
2.430
2.403
2.031
1.081
1.073
0.958
0.924
OH
HO
OTBDPS
8
Integral
4.366
6.558
1.000
2.069
0.994
2.797
1.116
2.477
9.893
3.170
ppm
9
8
7
6
5
4
3
2
1

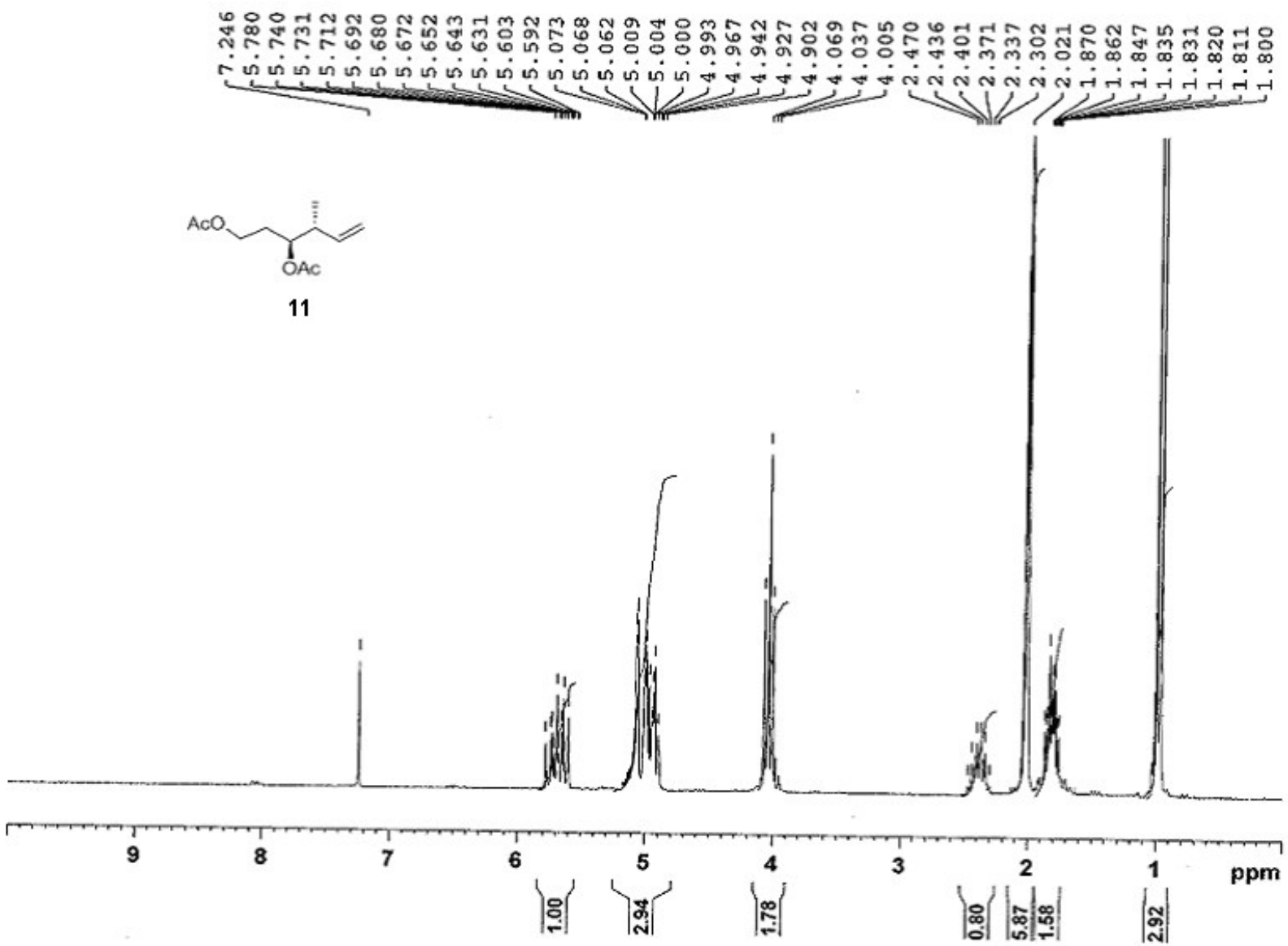

ppm
140.731
136.087
136.006
133.420
129.841
127.682
127.593
114.629
77.706
77.603
77.071
76.434
73.665
63.695
41.181
27.178
19.642
15.322
OH
HO
OTBDPS
8
ppm
140
120
100
80
60
40
20

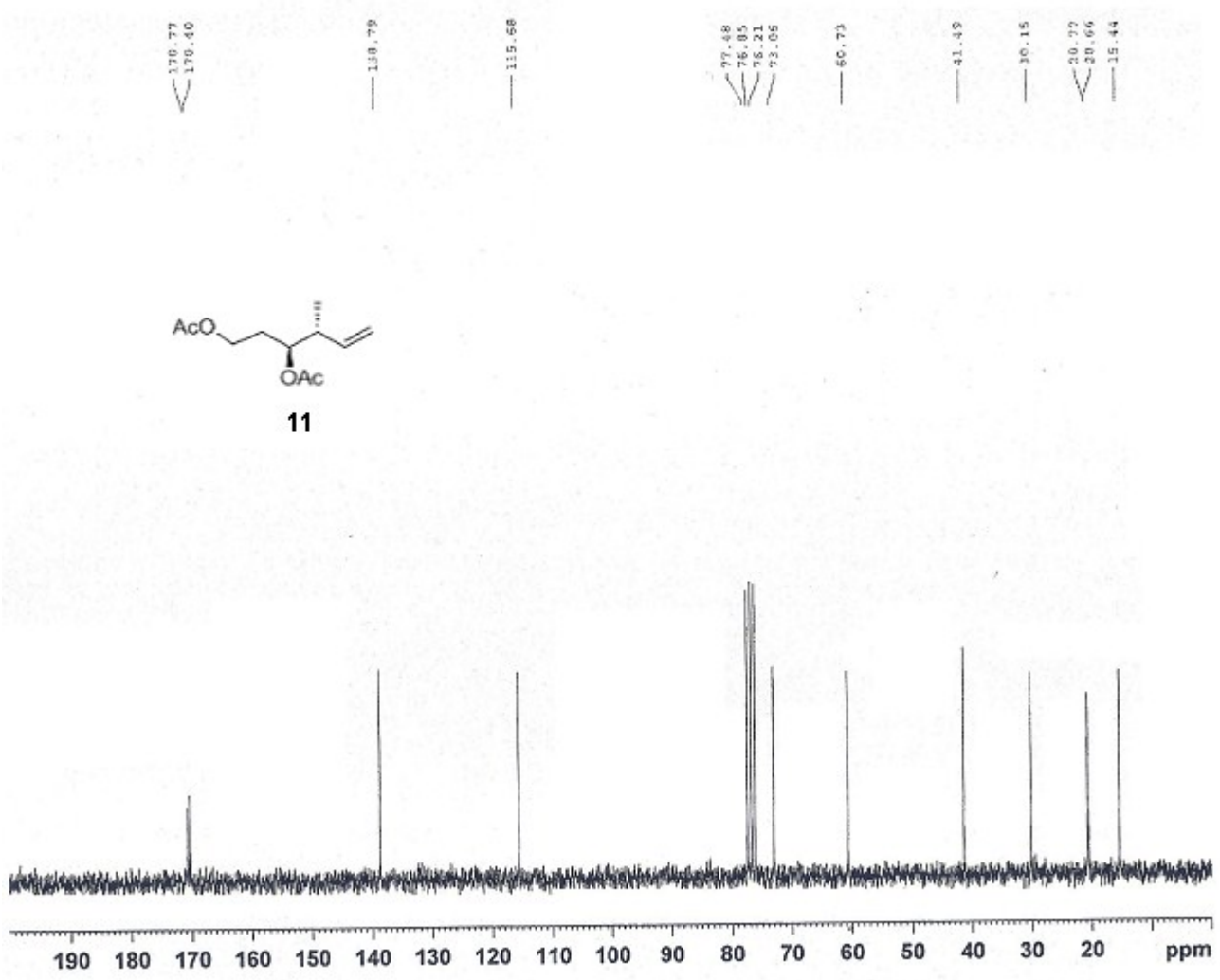

7.873
7.836
7.727
7.694
7.545
7.508
7.394
7.348
7.257
6.103
6.067
6.050
6.016
5.981
5.965
5.930
5.074
5.052
5.025
4.994
4.959
4.868
4.301
4.272
4.247
4.218
4.189
4.071
4.042
4.018
3.986
3.934
3.915
3.904
3.886
3.821
3.806
3.776
3.760
2.452
2.420
2.137
1.110
0.912
0.878
OH
BzO
OTBDPS
9
9
8
7
6
5
4
3
2
1
ppm
17.79
0.74
2.00
1.37
2.27
1.13
1.32
1.33
10.64
2.86

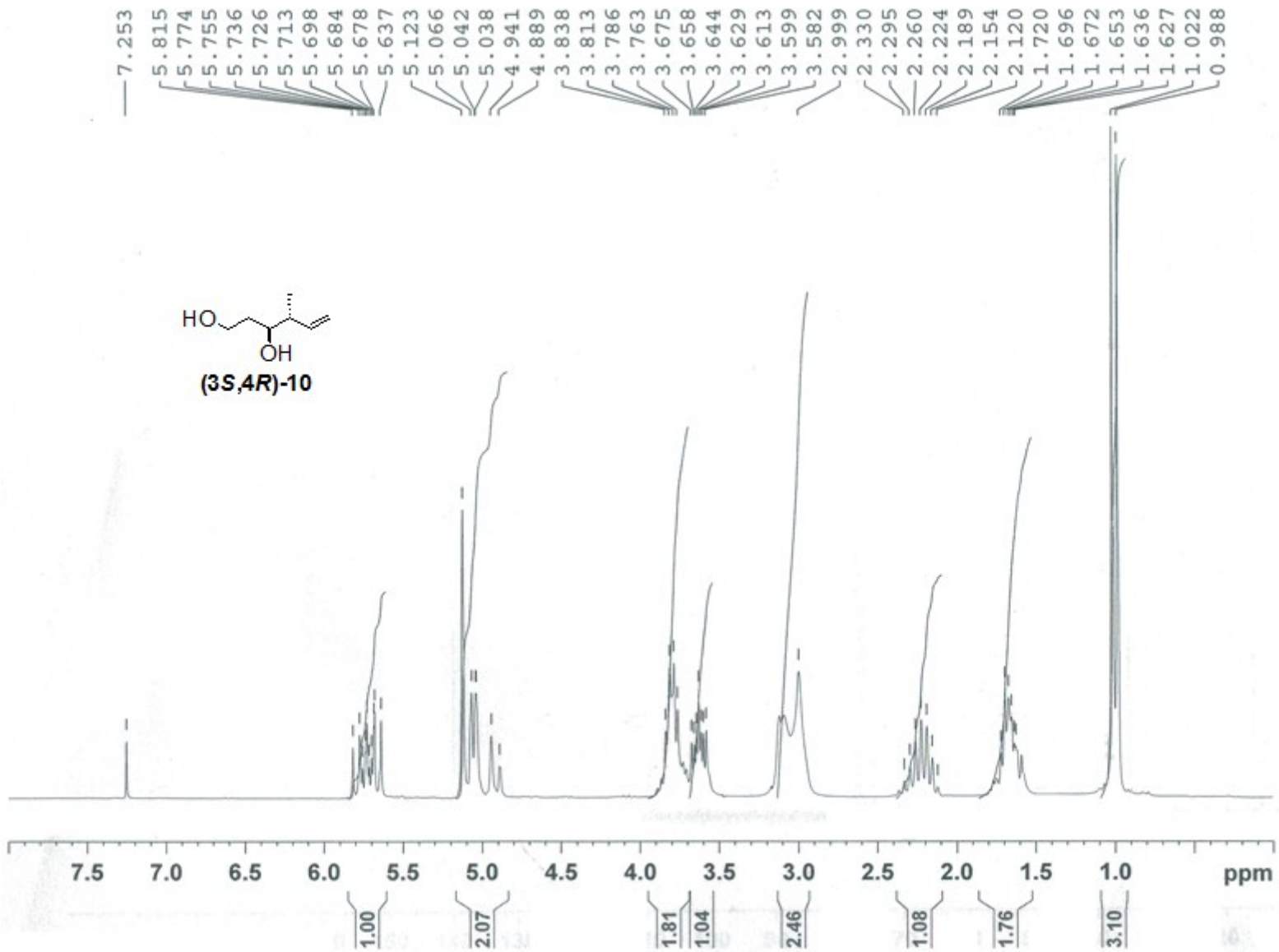

ppm
166.569
140.595
140.143
136.000
133.331
133.150
132.876
129.743
129.553
128.164
127.575
127.455
114.764
77.643
77.397
77.007
76.370
72.081
66.635
40.982
27.109
19.532
15.432
OH
BzO
ÖTBDPS
9
ppm
180
160
140
120
100
80
60
40
20
0

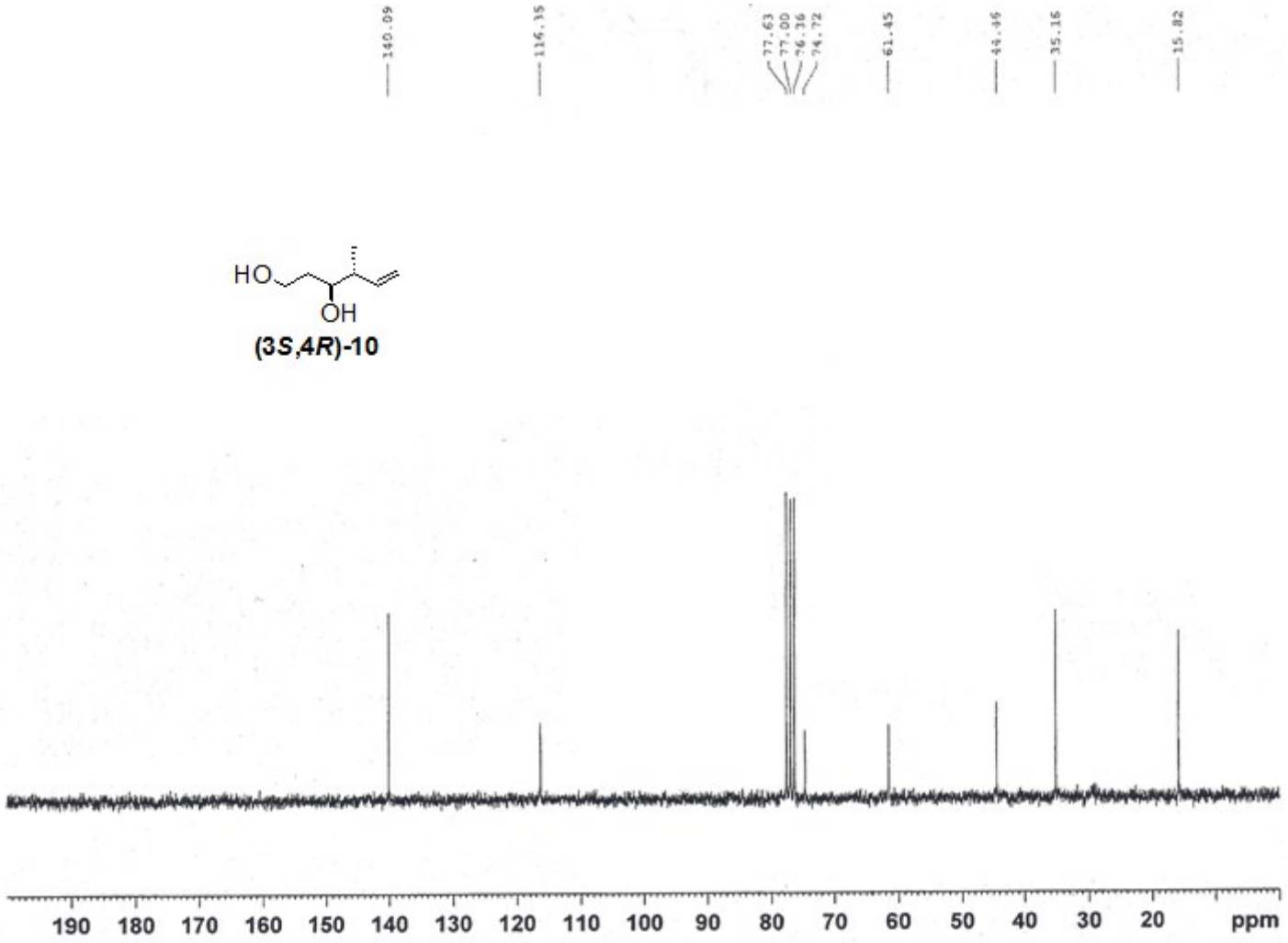

7.250
5.828
5.790
5.778
5.740
5.712
5.701
5.690
5.652
5.124
5.103
5.095
5.089
5.071
5.047
5.043
5.015
5.012
4.969
4.961
4.918
4.909
3.839
3.813
3.793
3.782
3.758
3.727
3.710
3.699
3.682
3.664
3.652
3.636
3.214
2.305
2.271
2.237
2.204
1.707
1.690
1.680
1.668
1.662
1.655
1.640
1.619
1.609
1.037
1.003
HO
OH
(3R,4R)-10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.98
2.81
2.55
1.00
1.66
2.97

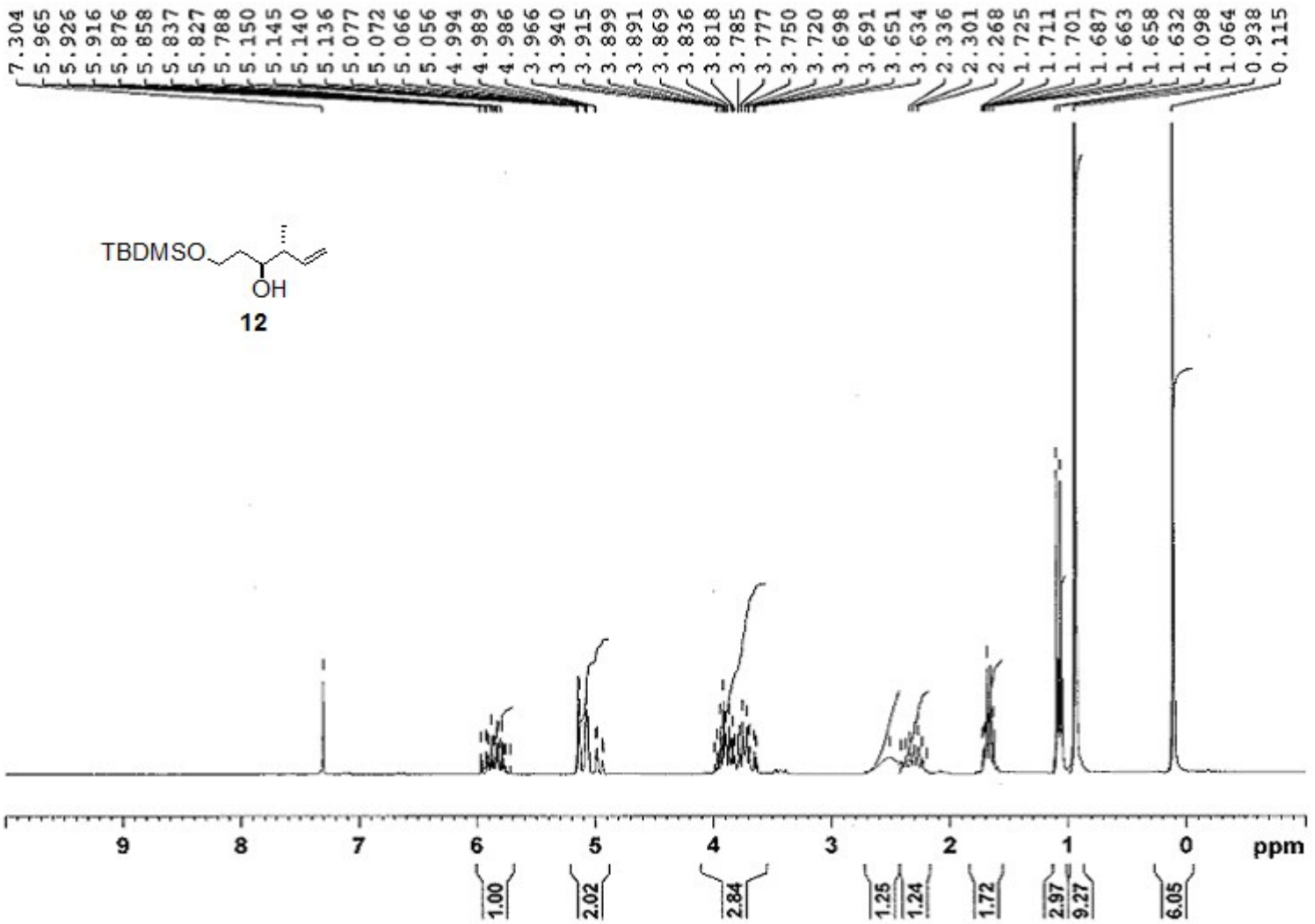

ppm
140.731
114.629
77.603
77.071
76.434
73.669
63.895
41.181
27.178
15.322
HO
OH
(3R,4R)-10
ppm
140
120
100
80
60
40
20

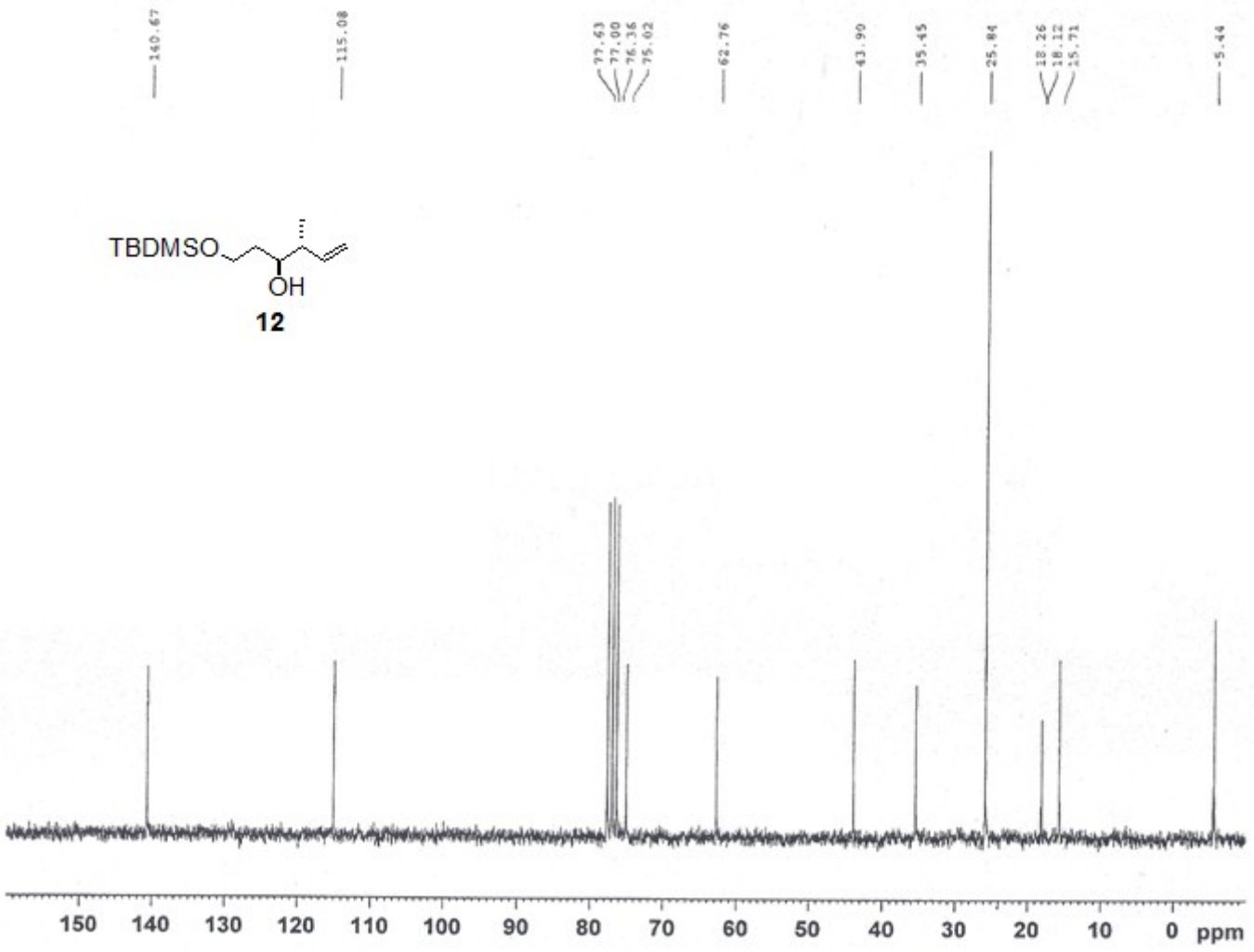

7.246
5.780
5.740
5.731
5.712
5.692
5.680
5.672
5.652
5.643
5.631
5.603
5.592
5.073
5.068
5.062
5.009
5.004
5.000
4.993
4.967
4.942
4.927
4.902
4.069
4.037
4.005
2.470
2.436
2.401
2.371
2.337
2.302
2.021
1.870
1.862
1.847
1.835
1.831
1.820
1.811
1.800
AcO
OAc
11
9
8
7
6
5
4
3
2
1
ppm
1.00
2.94
1.78
0.80
5.87
1.58
2.92

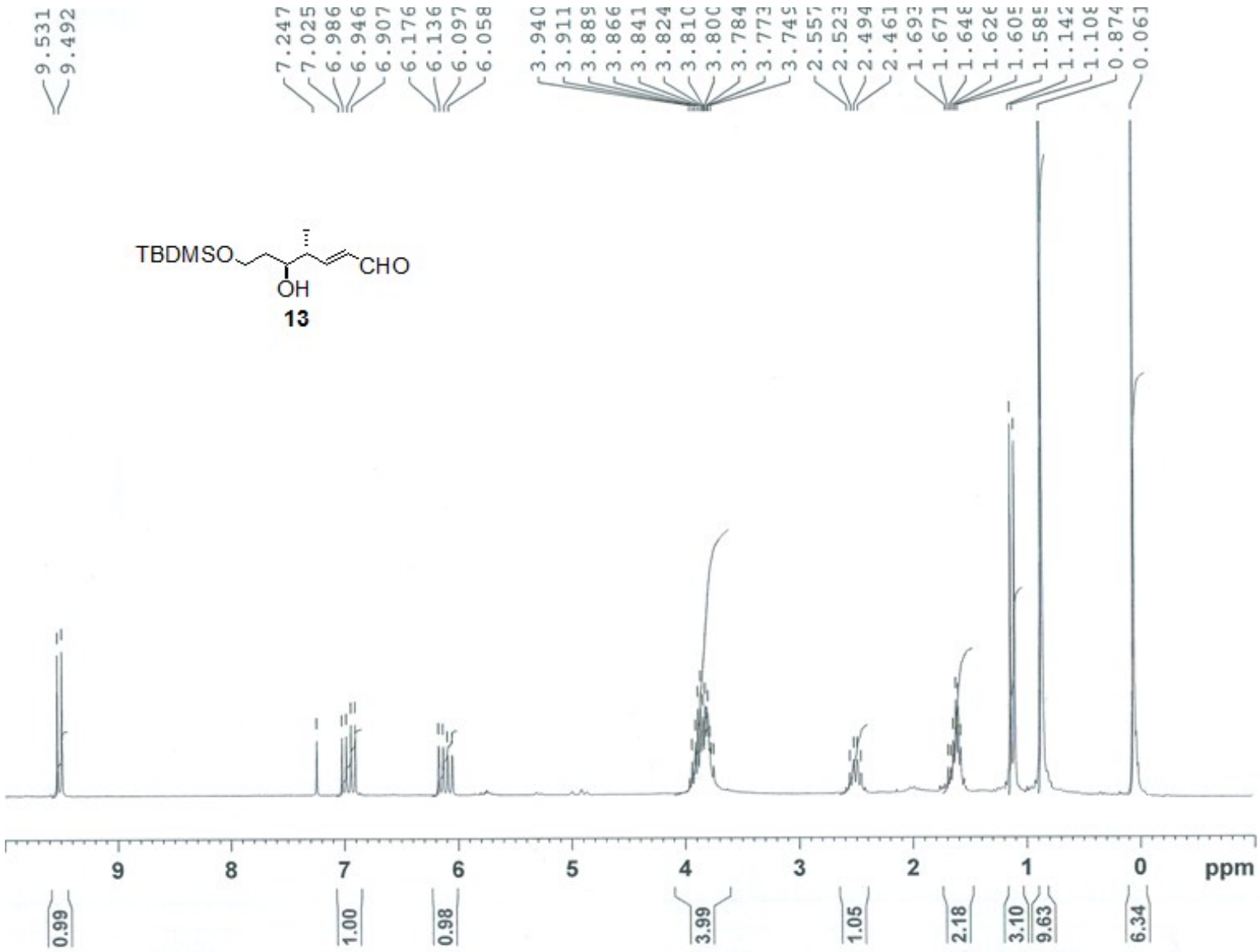

170.77
170.40
138.79
115.68
77.48
76.85
75.21
73.05
60.73
41.49
30.15
20.77
20.66
15.44
AcO
OAc
11
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.253
5.815
5.774
5.755
5.736
5.726
5.713
5.698
5.684
5.678
5.637
5.123
5.066
5.042
5.038
4.941
4.889
3.838
3.813
3.786
3.763
3.675
3.658
3.644
3.629
3.613
3.599
3.582
2.999
2.330
2.295
2.260
2.224
2.189
2.154
2.120
1.720
1.696
1.672
1.653
1.636
1.627
1.022
0.988
HO
OH
(3S,4R)-10
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
ppm
1.00
2.07
1.81
1.04
2.46
1.08
1.76
3.10

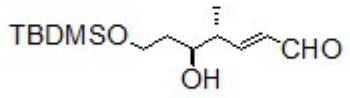

140.09
116.35
77.63
77.00
76.36
74.72
61.45
44.46
35.16
15.82
HO
OH
(3S,4R)-10
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.304
5.965
5.926
5.916
5.876
5.858
5.837
5.827
5.788
5.150
5.145
5.140
5.136
5.077
5.072
5.066
5.056
4.994
4.989
4.986
3.966
3.940
3.915
3.899
3.891
3.869
3.836
3.818
3.785
3.777
3.750
3.720
3.698
3.691
3.651
3.634
2.336
2.301
2.268
1.725
1.711
1.701
1.687
1.663
1.658
1.632
1.098
1.064
0.938
0.115
TBDMSO
OH
12
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.02
2.84
1.25
1.24
1.72
2.97
9.27
6.05

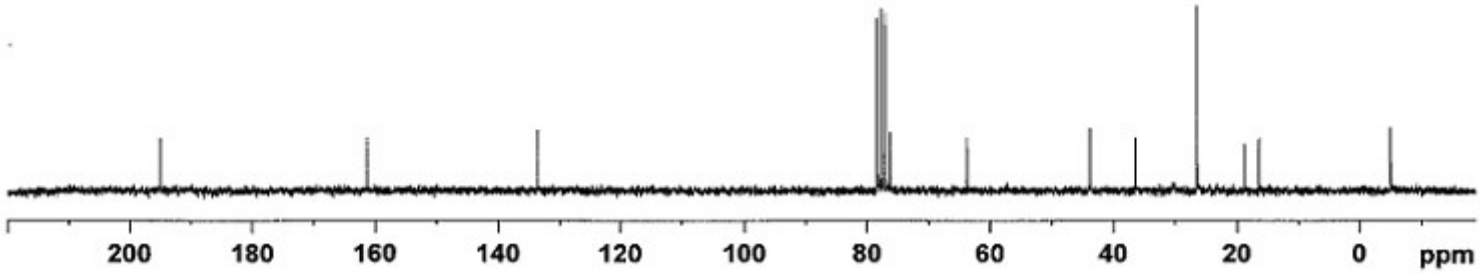

140.67
115.08
77.63
77.00
76.36
75.02
62.76
43.90
35.45
25.84
18.26
18.12
15.71
-5.44
TBDMSO
OH
12
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


9.531
9.492
7.247
7.025
6.986
6.946
6.907
6.176
6.136
6.097
6.058
3.940
3.911
3.889
3.866
3.841
3.824
3.810
3.800
3.784
3.773
3.749
2.557
2.523
2.494
2.461
1.693
1.671
1.648
1.626
1.605
1.585
1.142
1.108
0.874
0.061
TBDMSO
OH
CHO
13
9
8
7
6
5
4
3
2
1
0
ppm
0.99
1.00
0.98
3.99
1.05
2.18
3.10
9.63
6.34

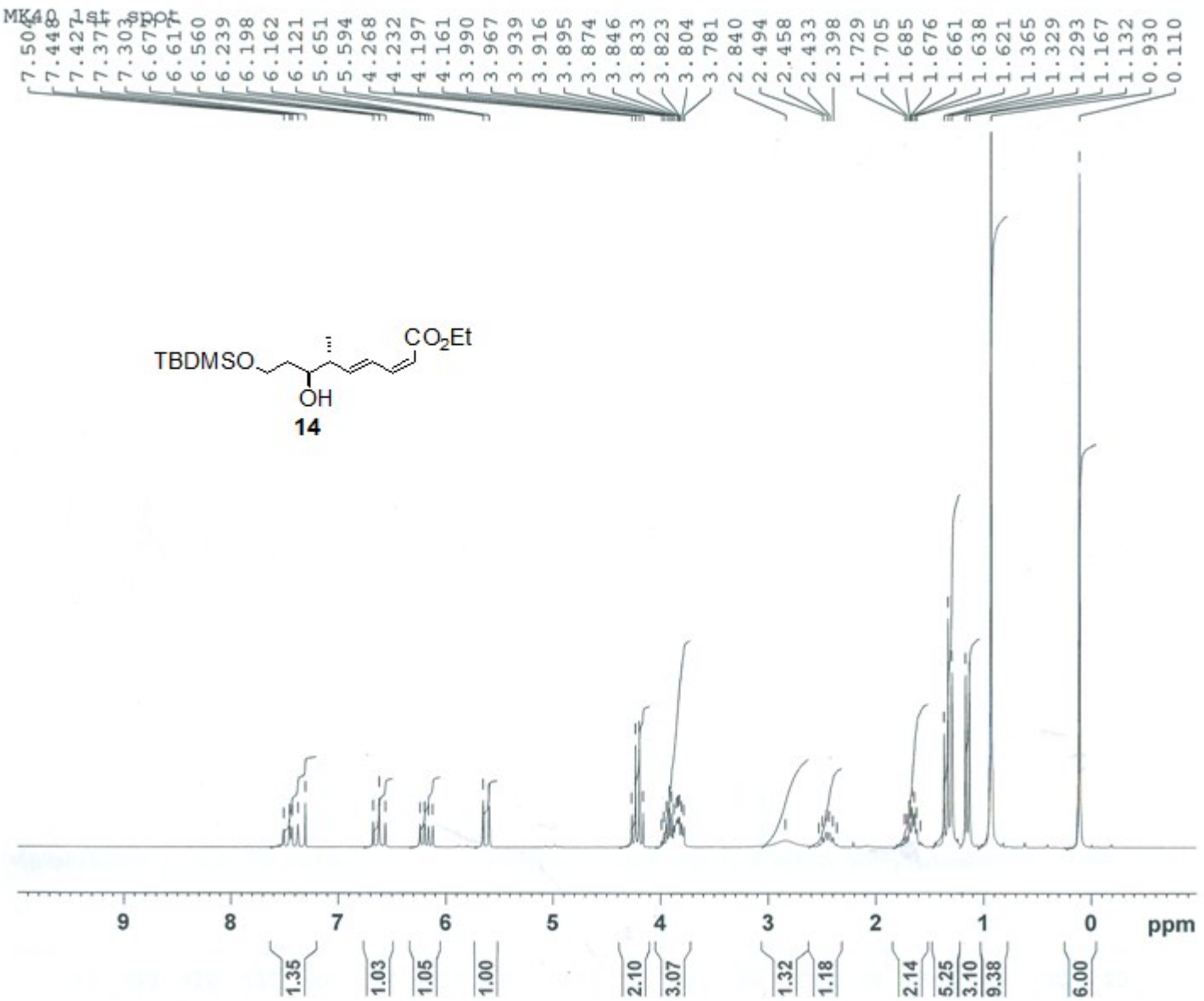

195.04
161.34
133.61
78.40
77.76
77.13
76.27
63.79
43.91
36.46
26.54
18.80
16.42
-4.86
-4.89

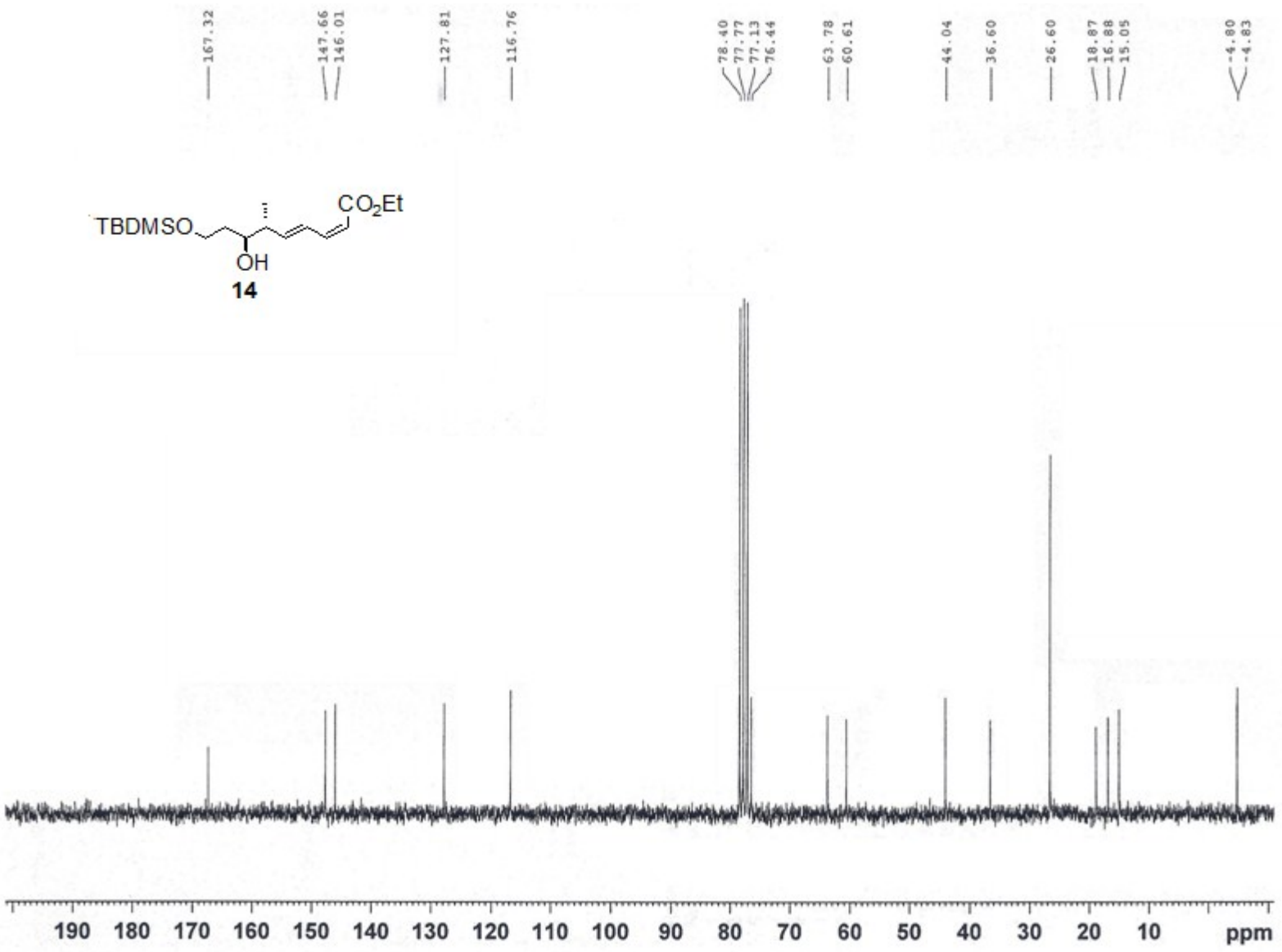

TBDMSO
CHO
OH

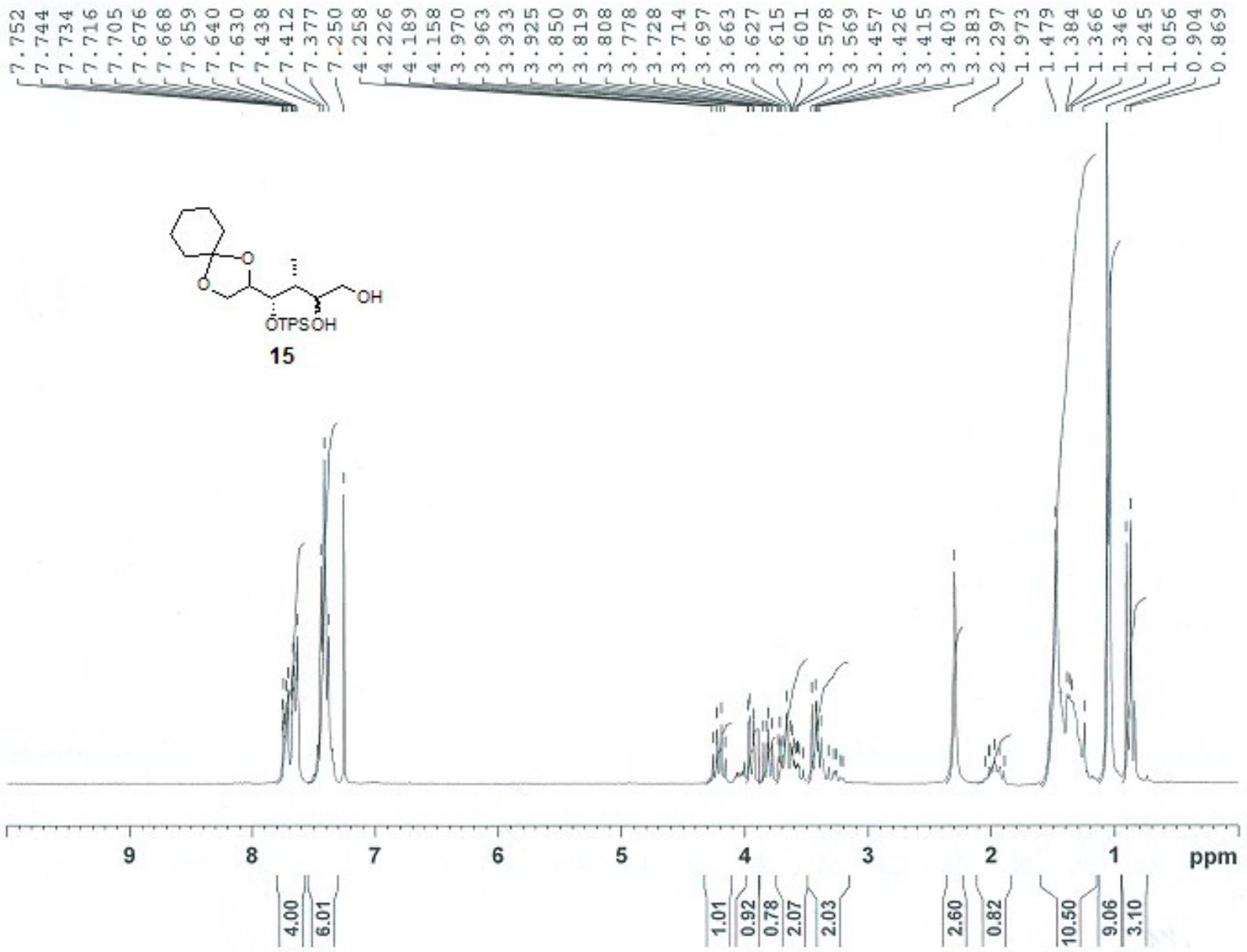
13

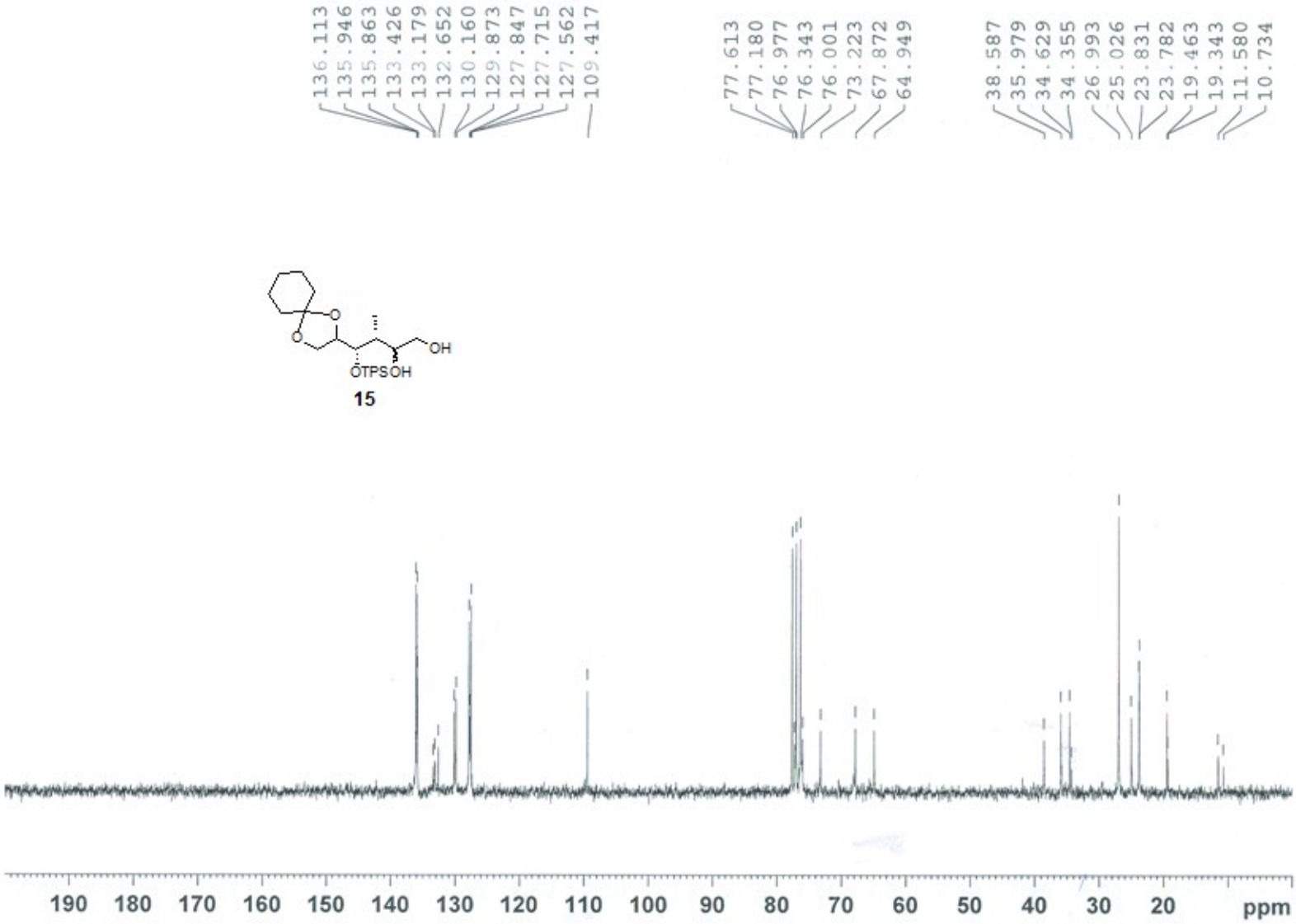

200
180
160
140
120
100
80
60
40
20
0
ppm

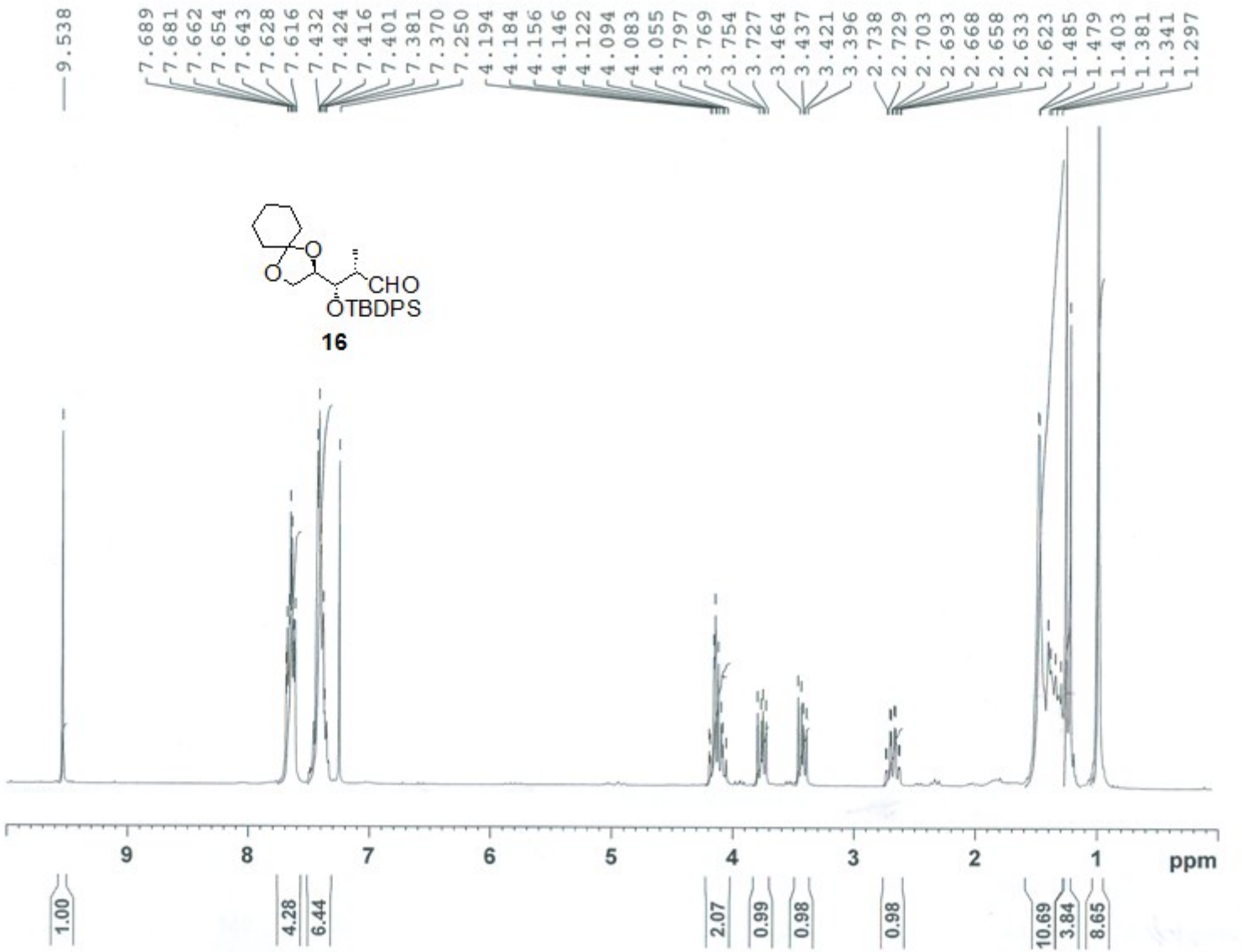
1

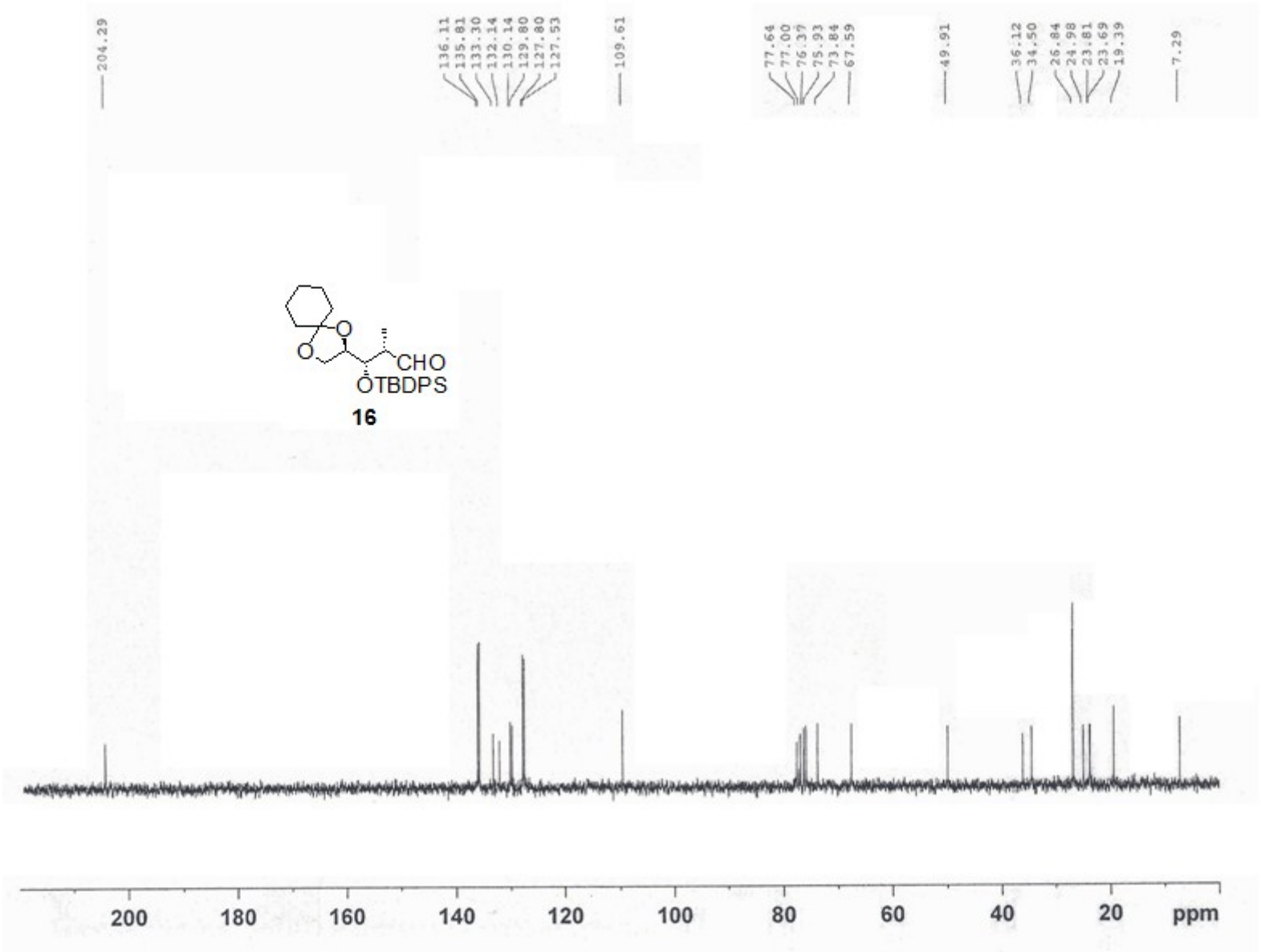

MK40 1st H spot
7.504
7.448
7.427
7.371
7.303
6.677
6.617
6.560
6.239
6.198
6.162
6.121
5.651
5.594
4.268
4.232
4.197
4.161
3.990
3.967
3.939
3.916
3.895
3.874
3.846
3.833
3.823
3.804
3.781
2.840
2.494
2.458
2.433
2.398
1.729
1.705
1.685
1.676
1.661
1.638
1.621
1.365
1.329
1.293
1.167
1.132
0.930
0.110
TBDMSO
CO2Et
OH
14
9
8
7
6
5
4
3
2
1
0
ppm
1.35
1.03
1.05
1.00
2.10
3.07
1.32
1.18
2.14
5.25
3.10
9.38
6.00

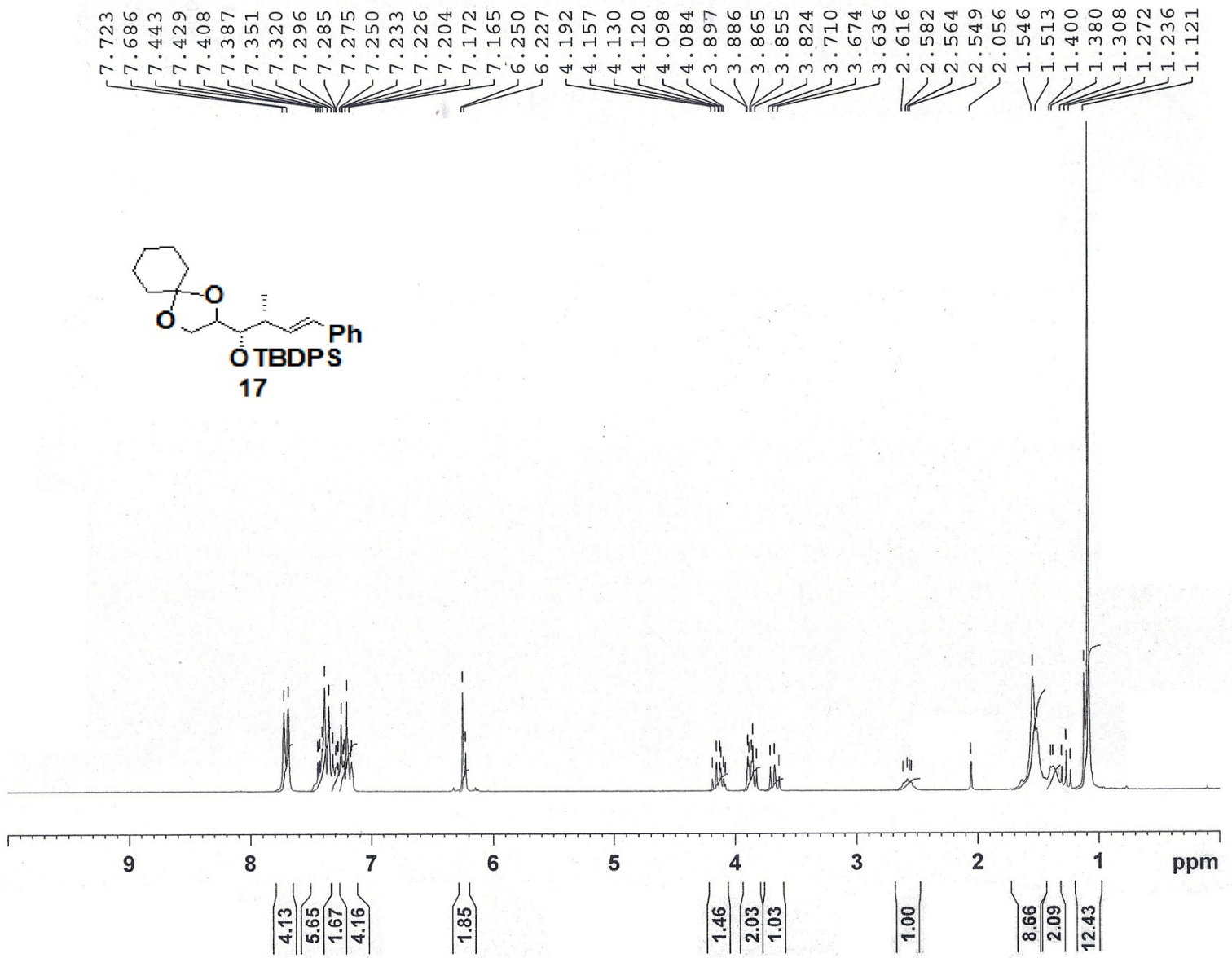

167.32
147.66
146.01
127.81
116.76
78.40
77.77
77.13
76.44
63.78
60.61
44.04
36.60
26.60
18.87
16.88
15.05
-4.80
-4.83
TBDMSO
OH
CO2Et
14
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

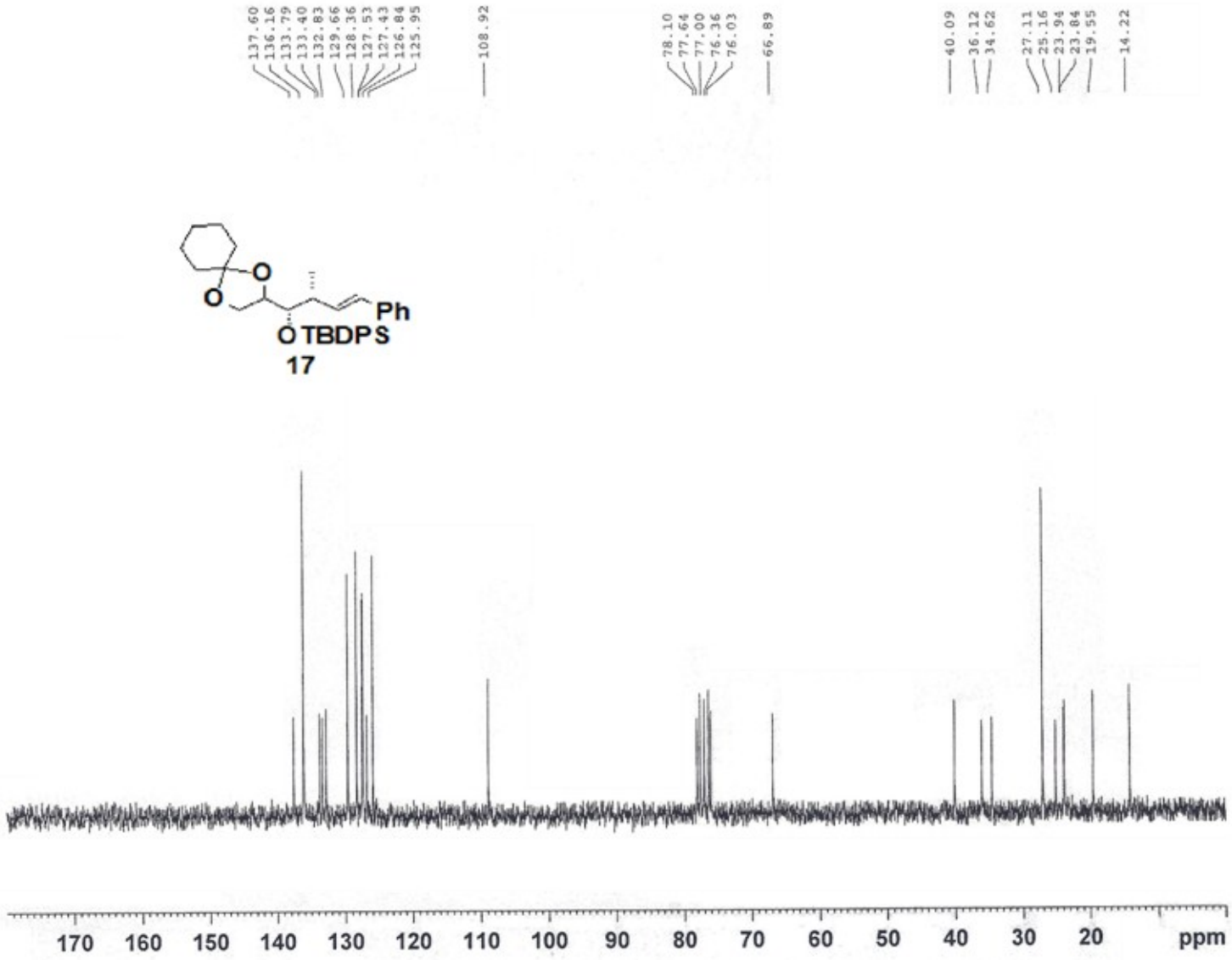

7.752
7.744
7.734
7.716
7.705
7.676
7.668
7.659
7.640
7.630
7.438
7.412
7.377
7.250
4.258
4.226
4.189
4.158
3.970
3.963
3.933
3.925
3.850
3.819
3.808
3.778
3.728
3.714
3.697
3.663
3.627
3.615
3.601
3.578
3.569
3.457
3.426
3.415
3.403
3.383
2.297
1.973
1.479
1.384
1.366
1.346
1.245
1.056
0.904
0.869
OH
OTPSOH
15
9
8
7
6
5
4
3
2
1
ppm
4.00
6.01
1.01
0.92
0.78
2.07
2.03
2.60
0.82
10.50
9.06
3.10

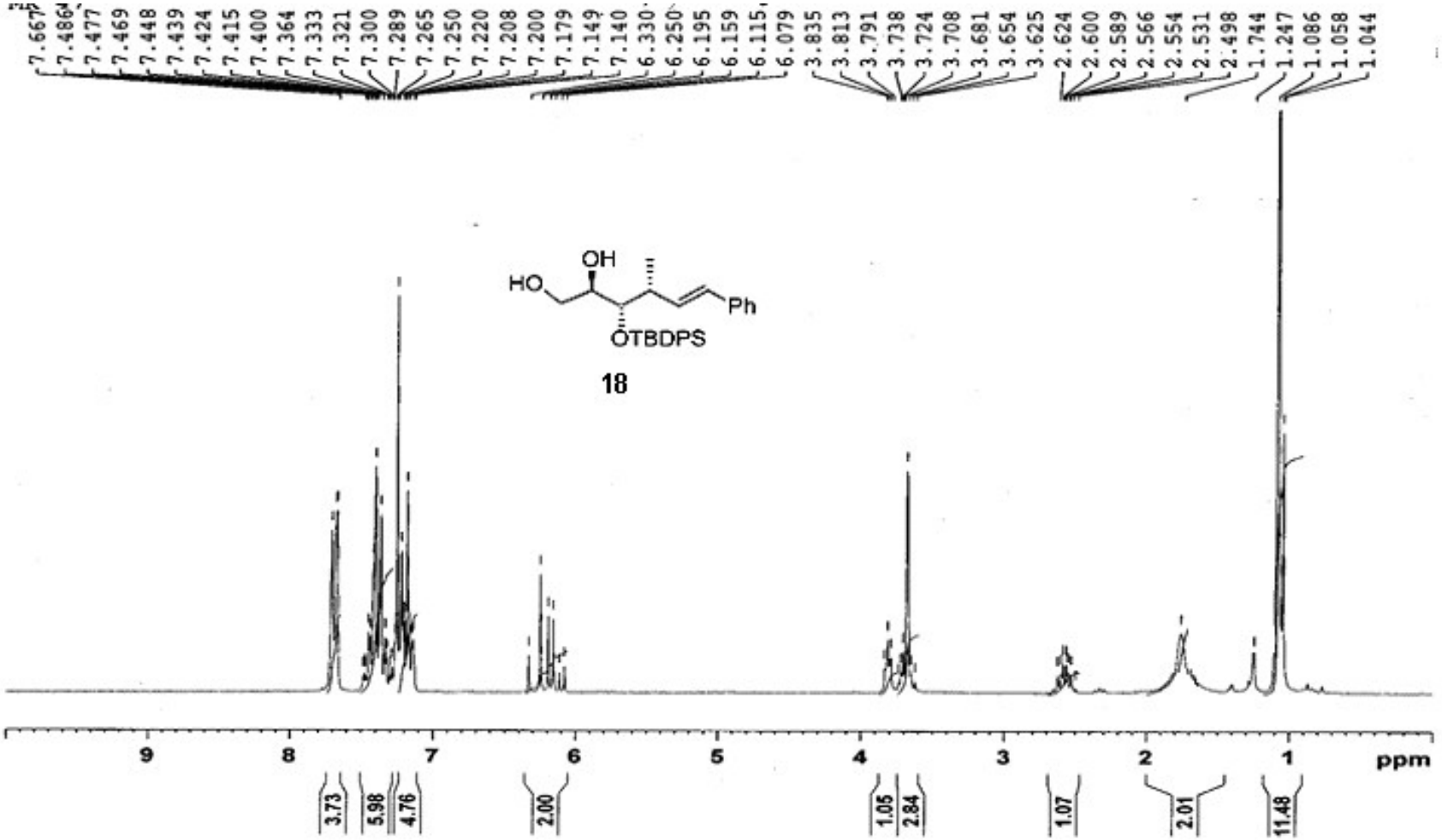

136.113
135.946
135.863
133.426
133.179
132.652
130.160
129.873
127.847
127.715
127.562
109.417
77.613
77.180
76.977
76.343
76.001
73.223
67.872
64.949
38.587
35.979
34.629
34.355
26.993
25.026
23.831
23.782
19.463
19.343
11.580
10.734
OH
OTPSOH
15
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

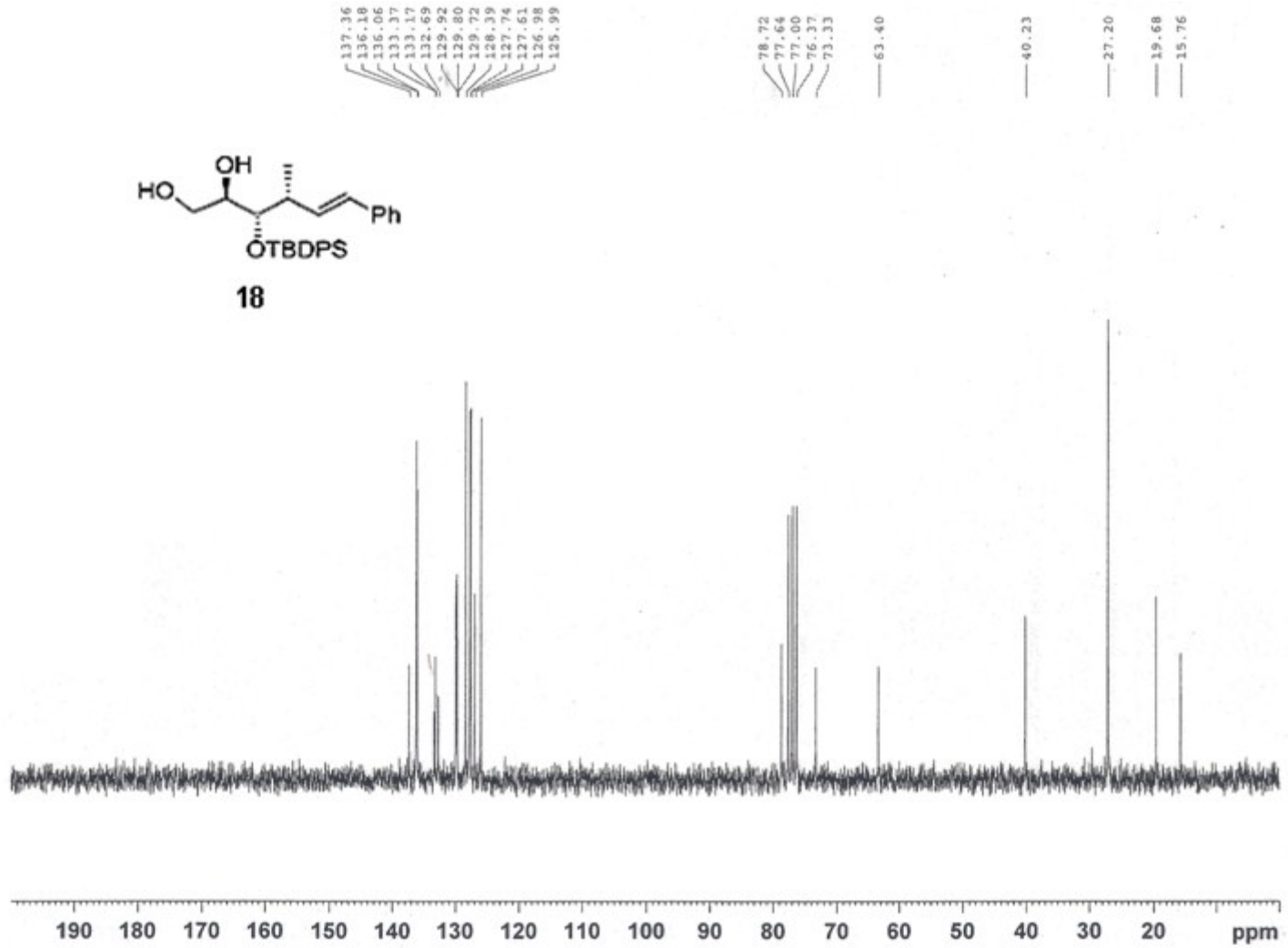

9.538
7.689
7.681
7.662
7.654
7.643
7.628
7.616
7.432
7.424
7.416
7.401
7.381
7.370
7.250
4.194
4.184
4.156
4.146
4.122
4.094
4.083
4.055
3.797
3.769
3.754
3.727
3.464
3.437
3.421
3.396
2.738
2.729
2.703
2.693
2.668
2.658
2.633
2.623
1.485
1.479
1.403
1.381
1.341
1.297
O
O
CHO
OTBDPS
16
9
8
7
6
5
4
3
2
1
ppm
1.00
4.28
6.44
2.07
0.99
0.98
0.98
10.69
3.84
8.65

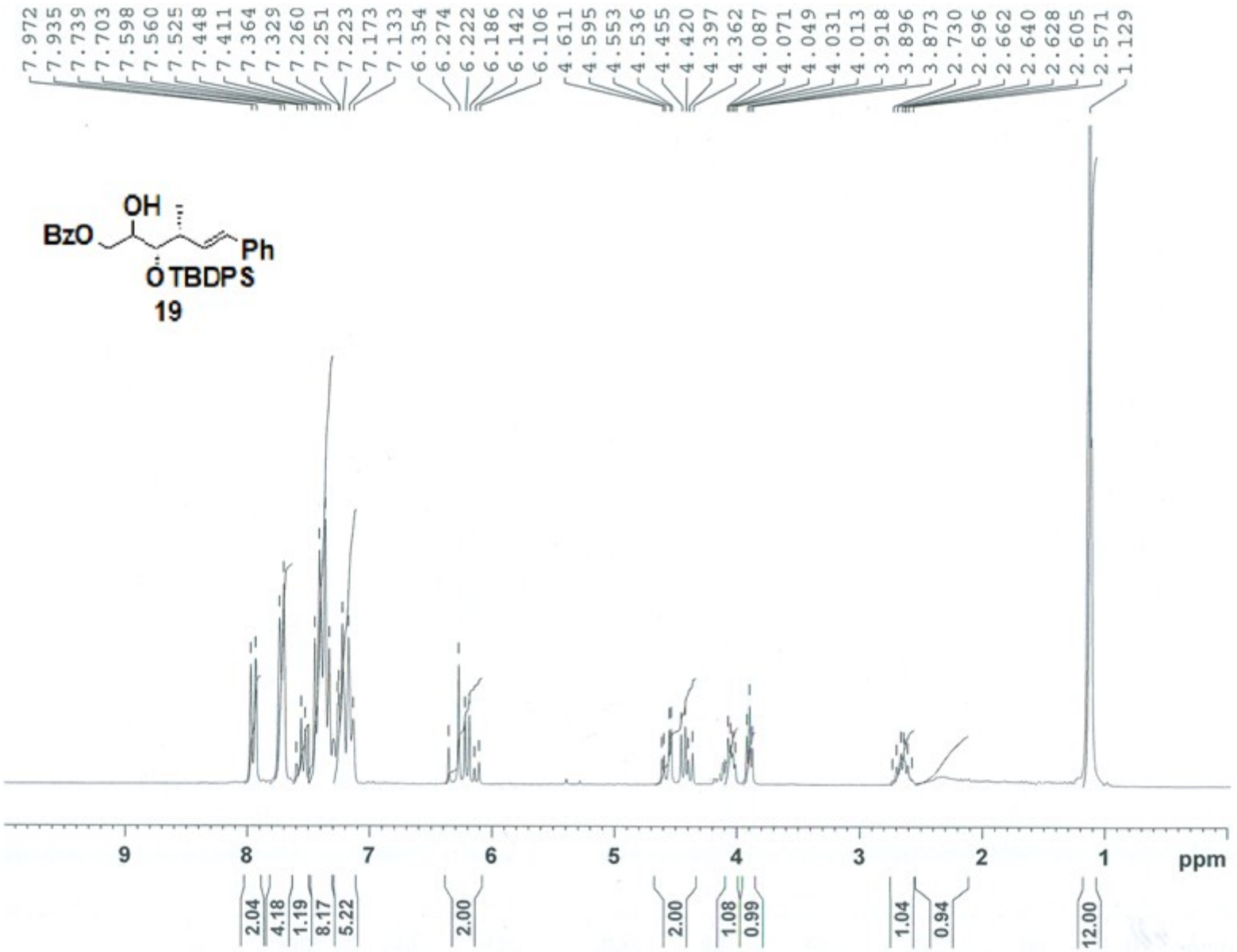

204.29
136.11
135.81
133.30
132.14
130.14
129.80
127.80
127.53
109.61
77.64
77.00
76.37
75.93
73.84
67.59
49.91
36.12
34.50
26.84
24.98
23.81
23.69
19.39
7.29
O
O
CHO
OTBDPS
16
200
180
160
140
120
100
80
60
40
20
ppm

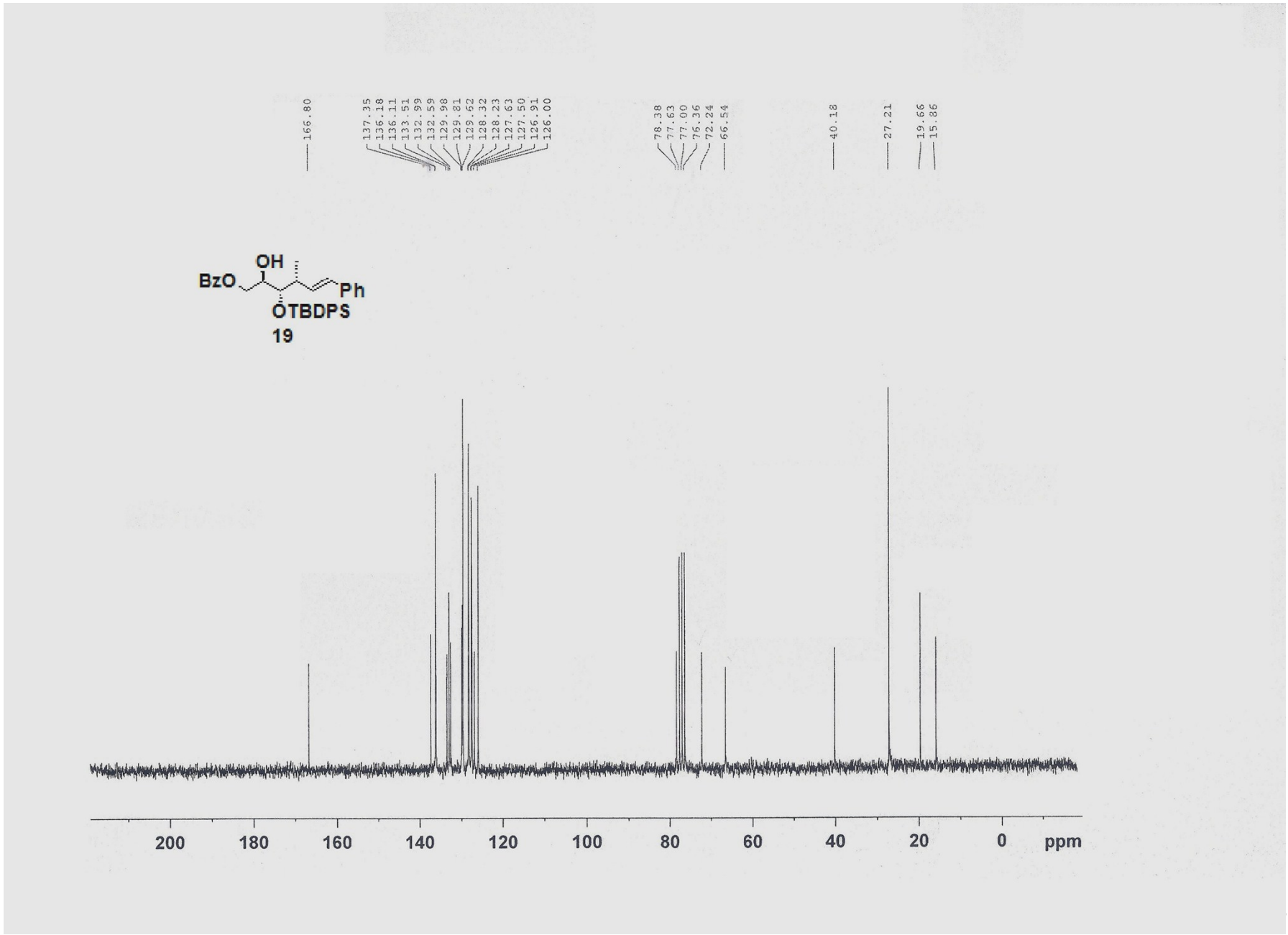

7.723
7.686
7.443
7.429
7.408
7.387
7.351
7.320
7.296
7.285
7.275
7.250
7.233
7.226
7.204
7.172
7.165
6.250
6.227
4.192
4.157
4.130
4.120
4.098
4.084
3.897
3.886
3.865
3.855
3.824
3.710
3.674
3.636
2.616
2.582
2.564
2.549
2.056
1.546
1.513
1.400
1.380
1.308
1.272
1.236
1.121
O
O
Ph
OTBDPS
17
9
8
7
6
5
4
3
2
1
ppm
4.13
5.65
1.67
4.16
1.85
1.46
2.03
1.03
1.00
8.66
2.09
12.43

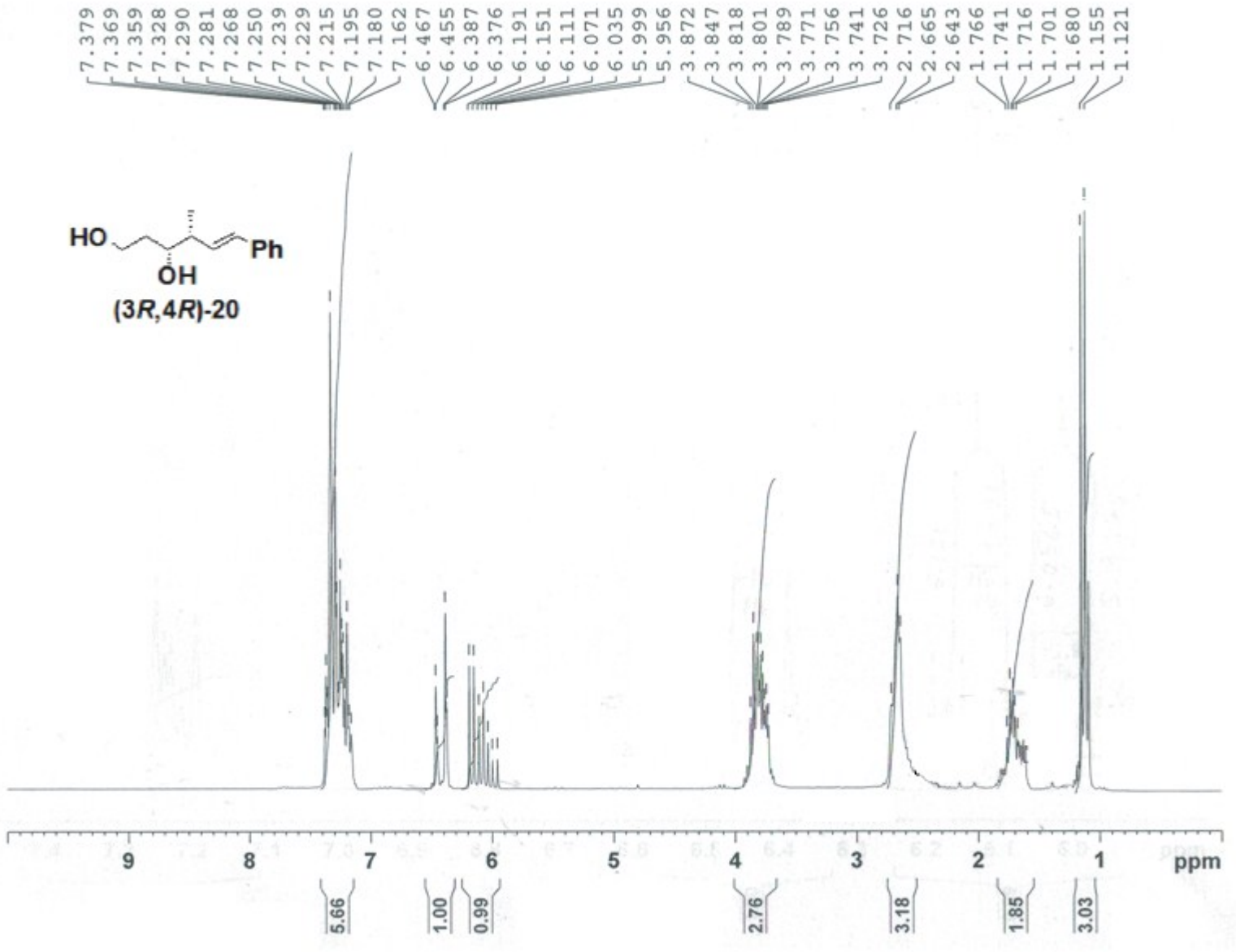

137.60
136.16
133.79
133.40
132.83
129.66
128.36
127.53
127.43
126.84
125.95
108.92
78.10
77.64
77.00
76.36
76.03
66.89
40.09
36.12
34.62
27.11
25.16
23.94
23.84
19.55
14.22
O
O
Ph
OTBDPS
17
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

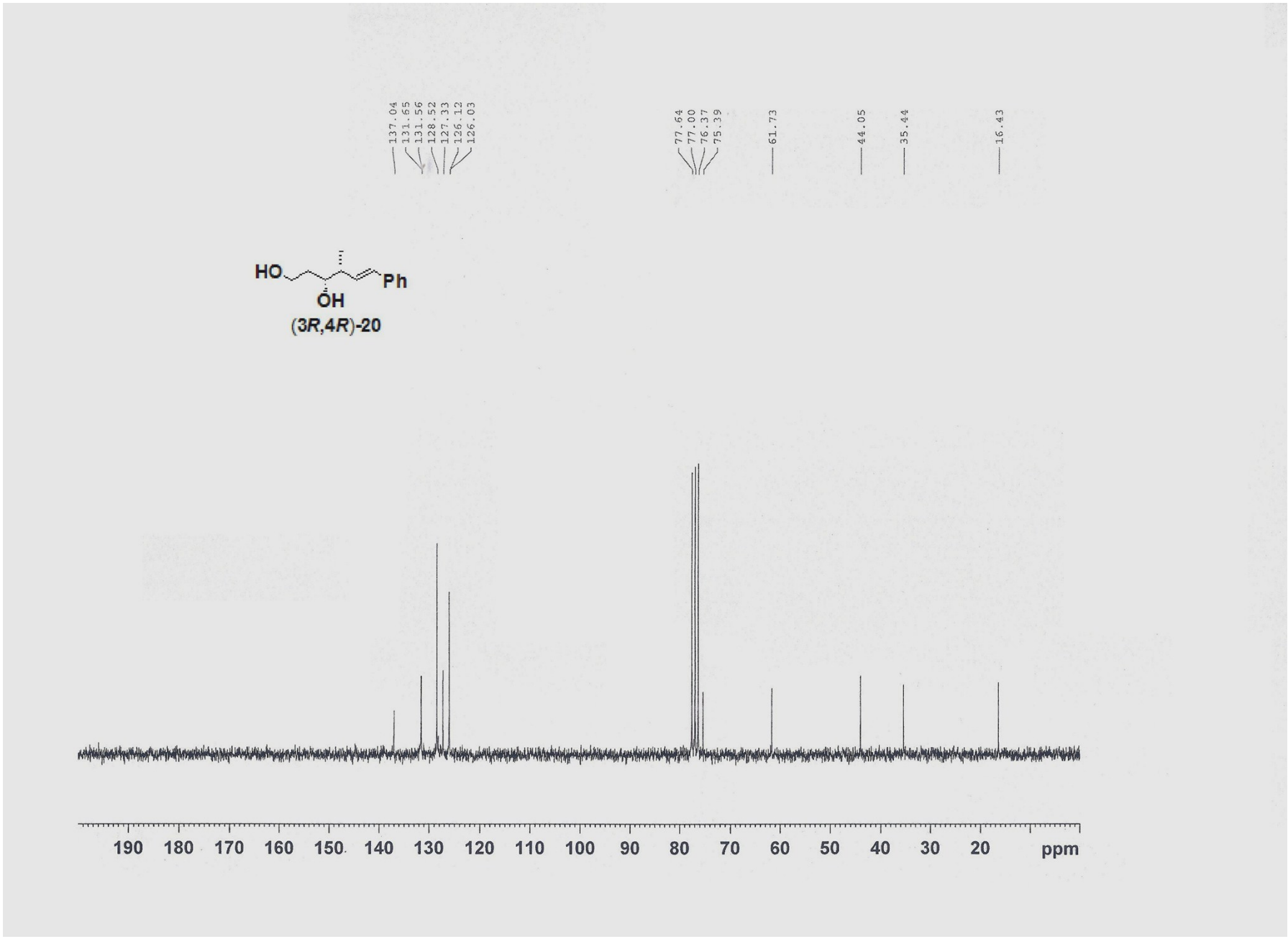

7.667
7.486
7.477
7.469
7.448
7.439
7.424
7.415
7.400
7.364
7.333
7.321
7.300
7.289
7.265
7.250
7.220
7.208
7.200
7.179
7.149
7.140
6.330
6.250
6.195
6.159
6.115
6.079
3.835
3.813
3.791
3.738
3.724
3.708
3.681
3.654
3.625
2.624
2.600
2.589
2.566
2.554
2.531
2.498
1.744
1.247
1.086
1.058
1.044
OH
HO
Ph
OTBDPS
18
9
8
7
6
5
4
3
2
1
ppm
3.73
5.98
4.76
2.00
1.05
2.84
1.07
2.01
11.48

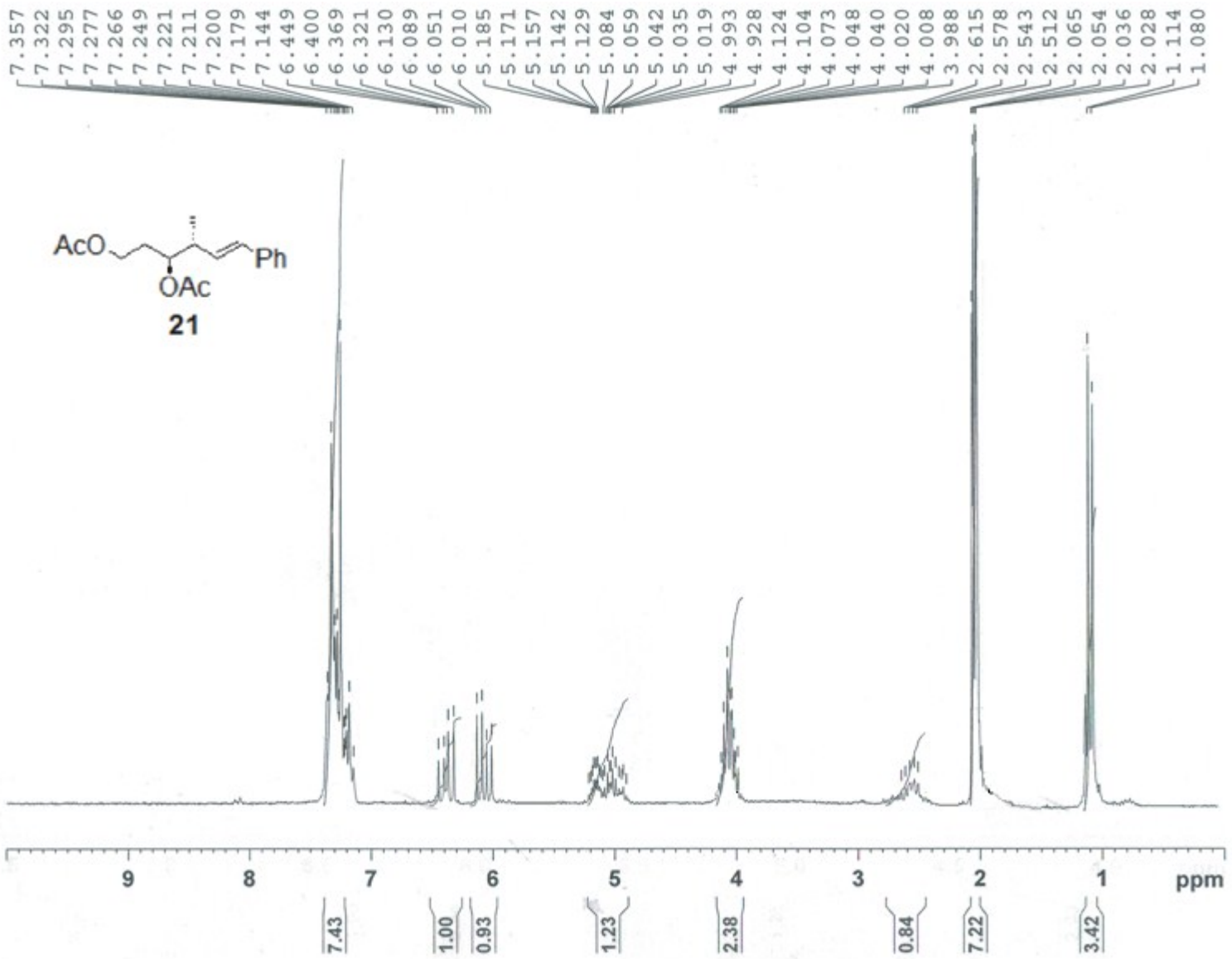

137.36
136.18
136.06
133.37
133.17
132.69
129.92
129.80
129.72
128.39
127.74
127.61
126.98
125.99
78.72
77.64
77.00
76.37
73.33
63.40
40.23
27.20
19.68
15.76
OH
HO
Ph
OTBDPS
18
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

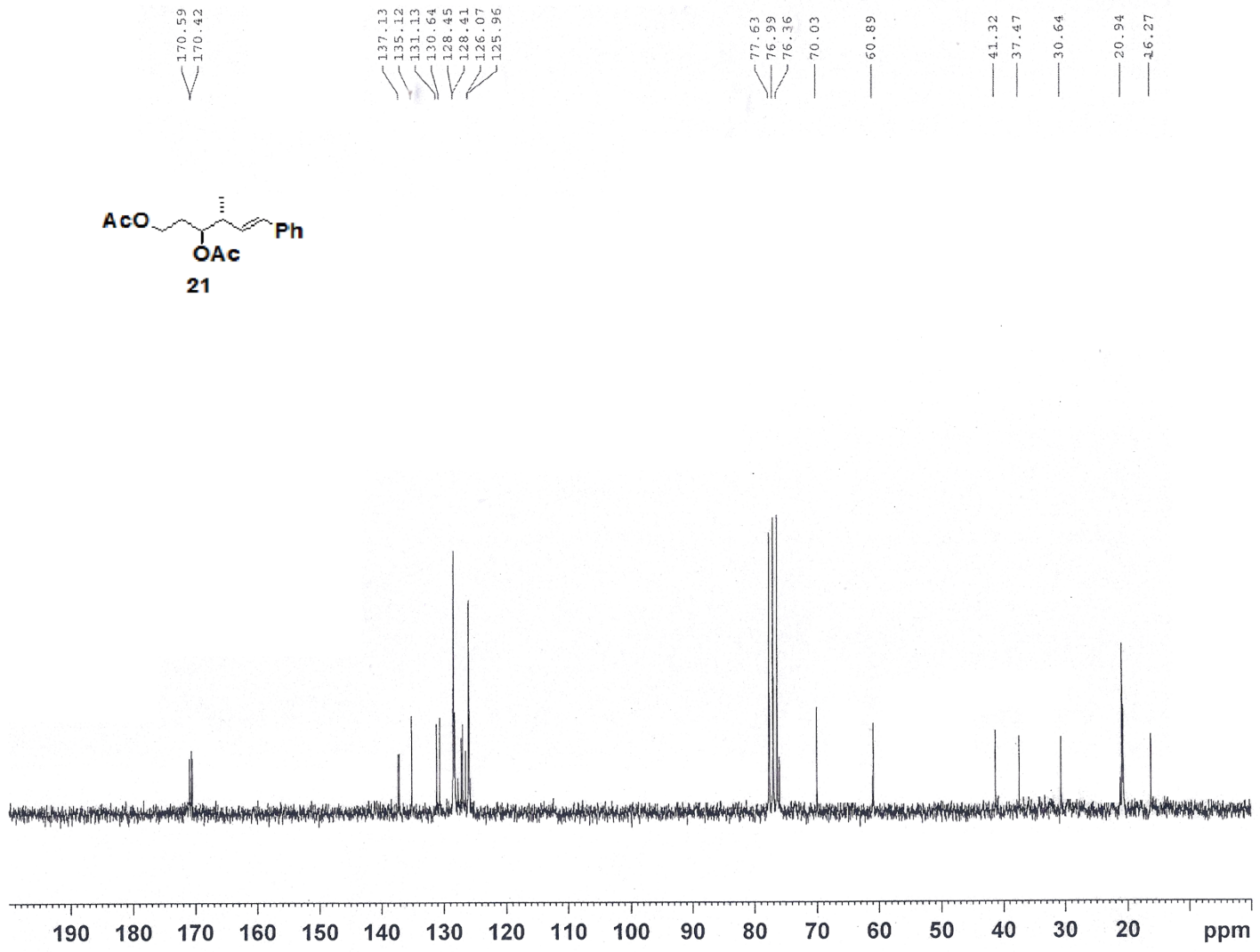

7.972
7.935
7.739
7.703
7.598
7.560
7.525
7.448
7.411
7.364
7.329
7.260
7.251
7.223
7.173
7.133
6.354
6.274
6.222
6.186
6.142
6.106
4.611
4.595
4.553
4.536
4.455
4.420
4.397
4.362
4.087
4.071
4.049
4.031
4.013
3.918
3.896
3.873
2.730
2.696
2.662
2.640
2.628
2.605
2.571
1.129
OH
BzO
Ph
OTBDPS
19
9
8
7
6
5
4
3
2
1
ppm
2.04
4.18
1.19
8.17
5.22
2.00
2.00
1.08
0.99
1.04
0.94
12.00

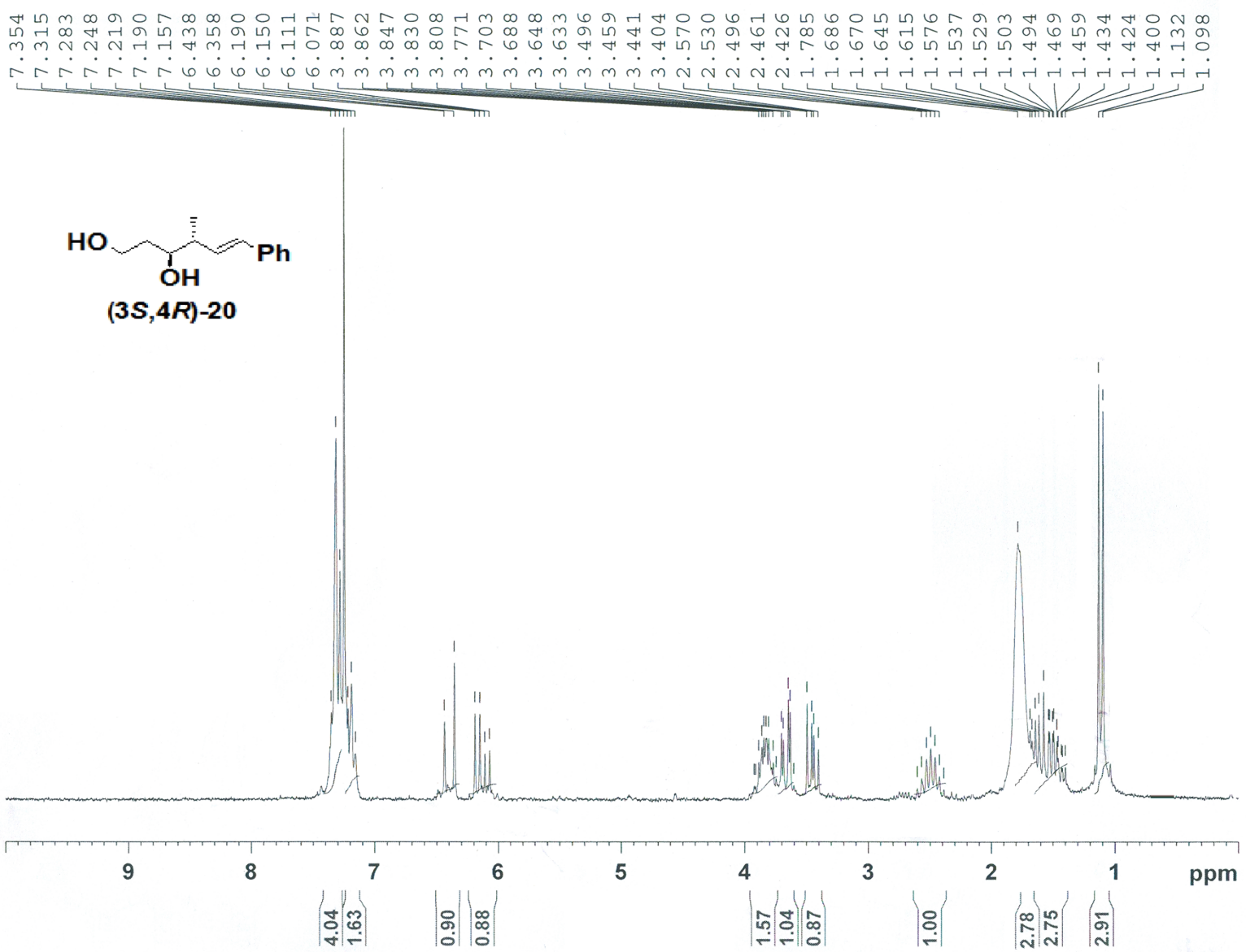

166.80
137.35
136.18
136.11
133.51
132.99
132.59
129.98
129.81
129.62
128.32
128.23
127.63
127.50
126.91
126.00
78.38
77.63
77.00
76.36
72.24
66.54
40.18
27.21
19.66
15.86
OH
BzO
Ph
OTBDPS
19
200
180
160
140
120
100
80
60
40
20
0
ppm

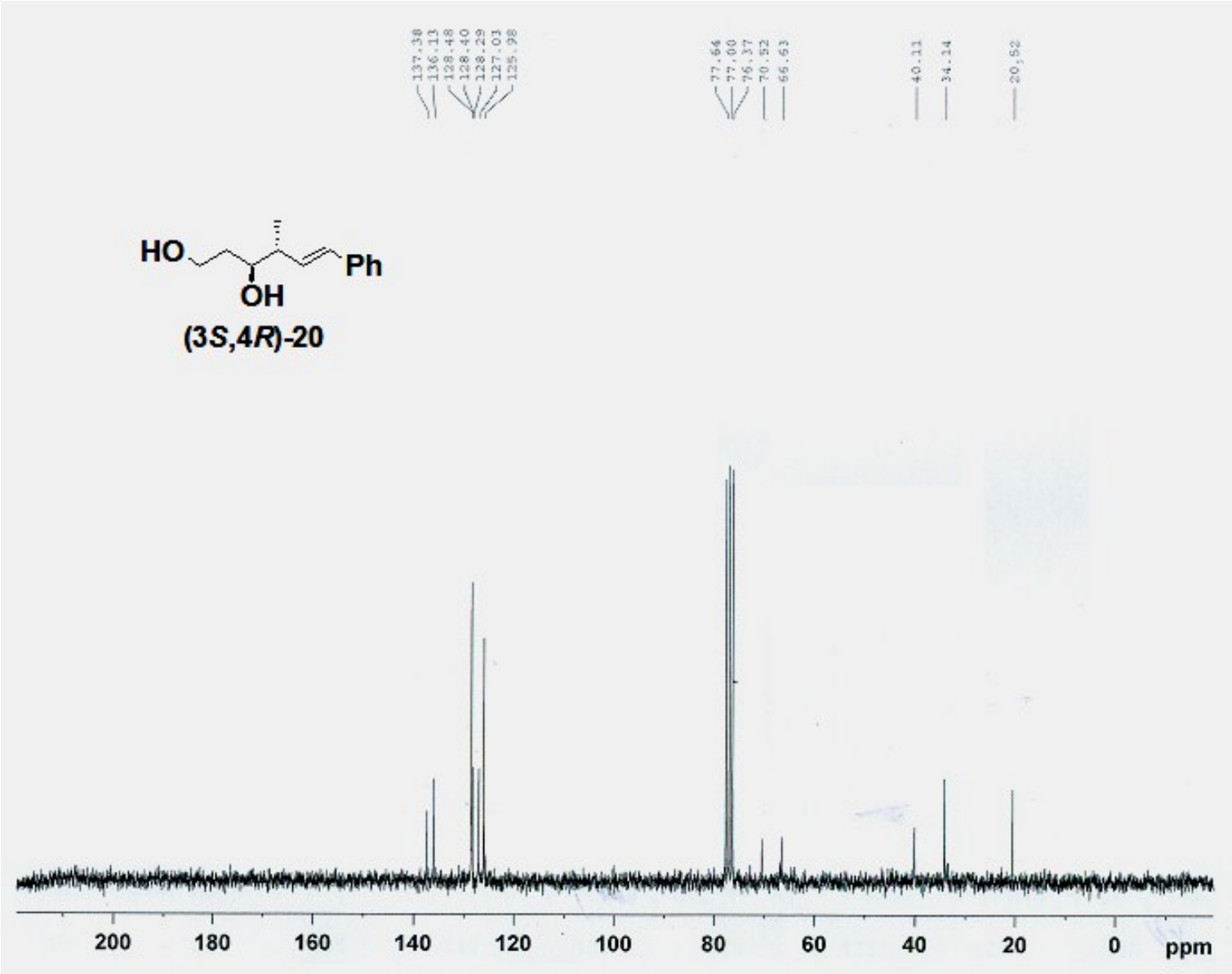

7.379
7.369
7.359
7.328
7.290
7.281
7.268
7.250
7.239
7.229
7.215
7.195
7.180
7.162
6.467
6.455
6.387
6.376
6.191
6.151
6.111
6.071
6.035
5.999
5.956
3.872
3.847
3.818
3.801
3.789
3.771
3.756
3.741
3.726
2.716
2.665
2.643
1.766
1.741
1.716
1.701
1.680
1.155
1.121
HO
Ph
OH
(3R,4R)-20
9
8
7
6
5
4
3
2
1
ppm
5.66
1.00
0.99
2.76
3.18
1.85
3.03

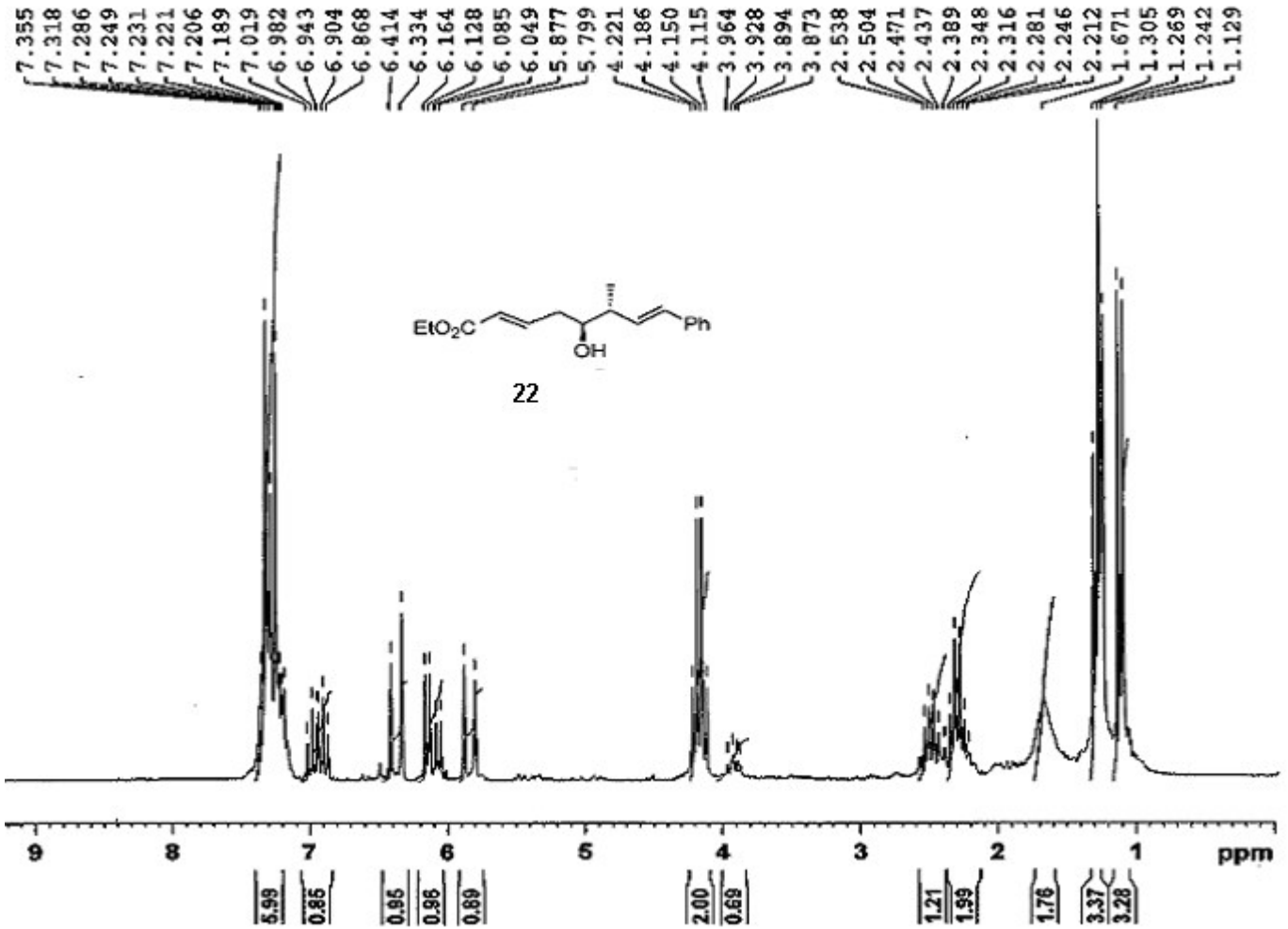

137.04
131.65
131.56
128.52
127.33
126.12
126.03
77.64
77.00
76.37
75.39
61.73
44.05
35.44
16.43
HO
OH
Ph
(3R,4R)-20
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

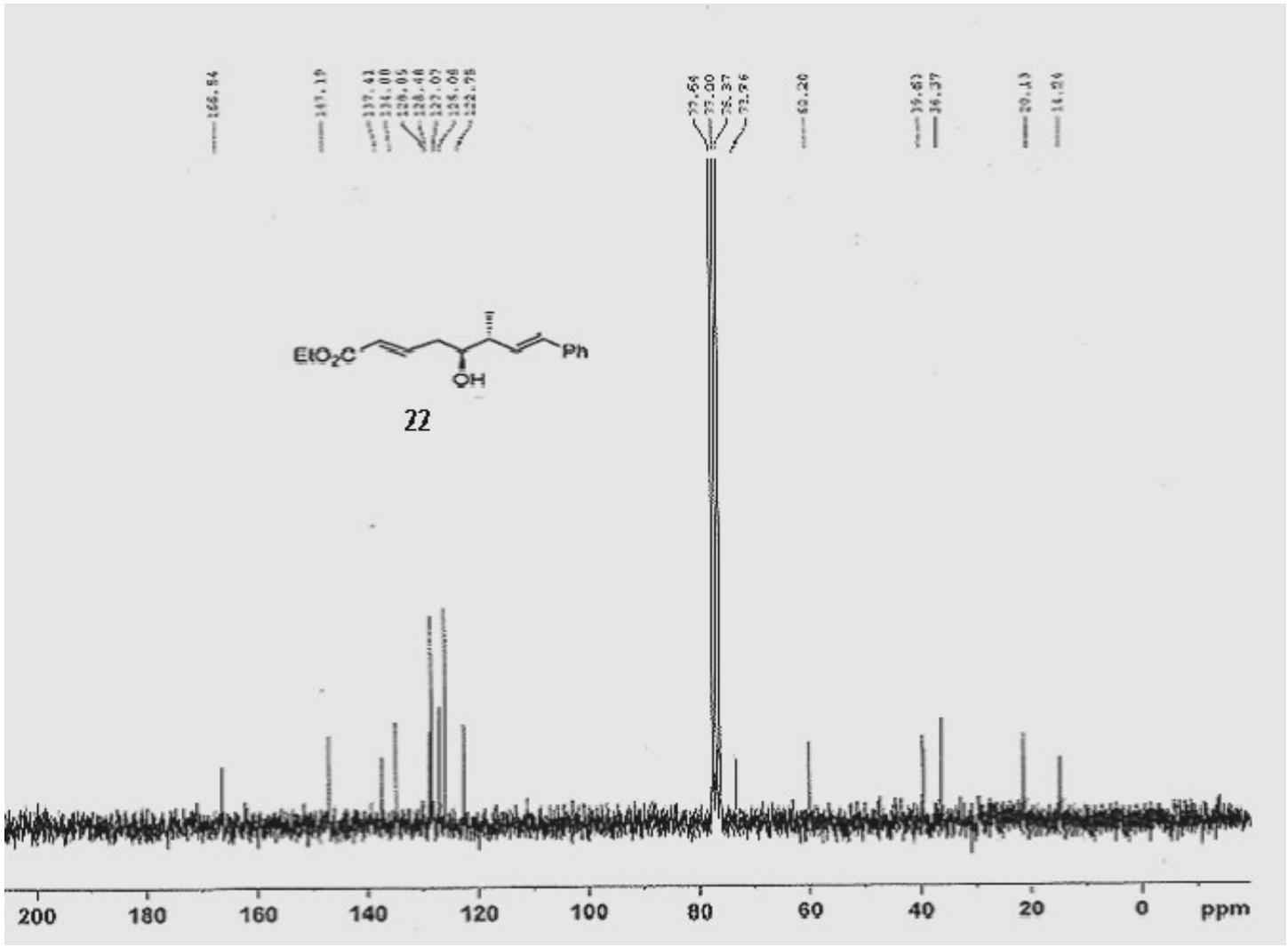

7.357
7.322
7.295
7.277
7.266
7.249
7.221
7.211
7.200
7.179
7.144
6.449
6.400
6.369
6.321
6.130
6.089
6.051
6.010
5.185
5.171
5.157
5.142
5.129
5.084
5.059
5.042
5.035
5.019
4.993
4.928
4.124
4.104
4.073
4.048
4.040
4.020
4.008
3.988
2.615
2.578
2.543
2.512
2.065
2.054
2.036
2.028
1.114
1.080
AcO
OAc
Ph
21
9
8
7
6
5
4
3
2
1
ppm
7.43
1.00
0.93
1.23
2.38
0.84
7.22
3.42

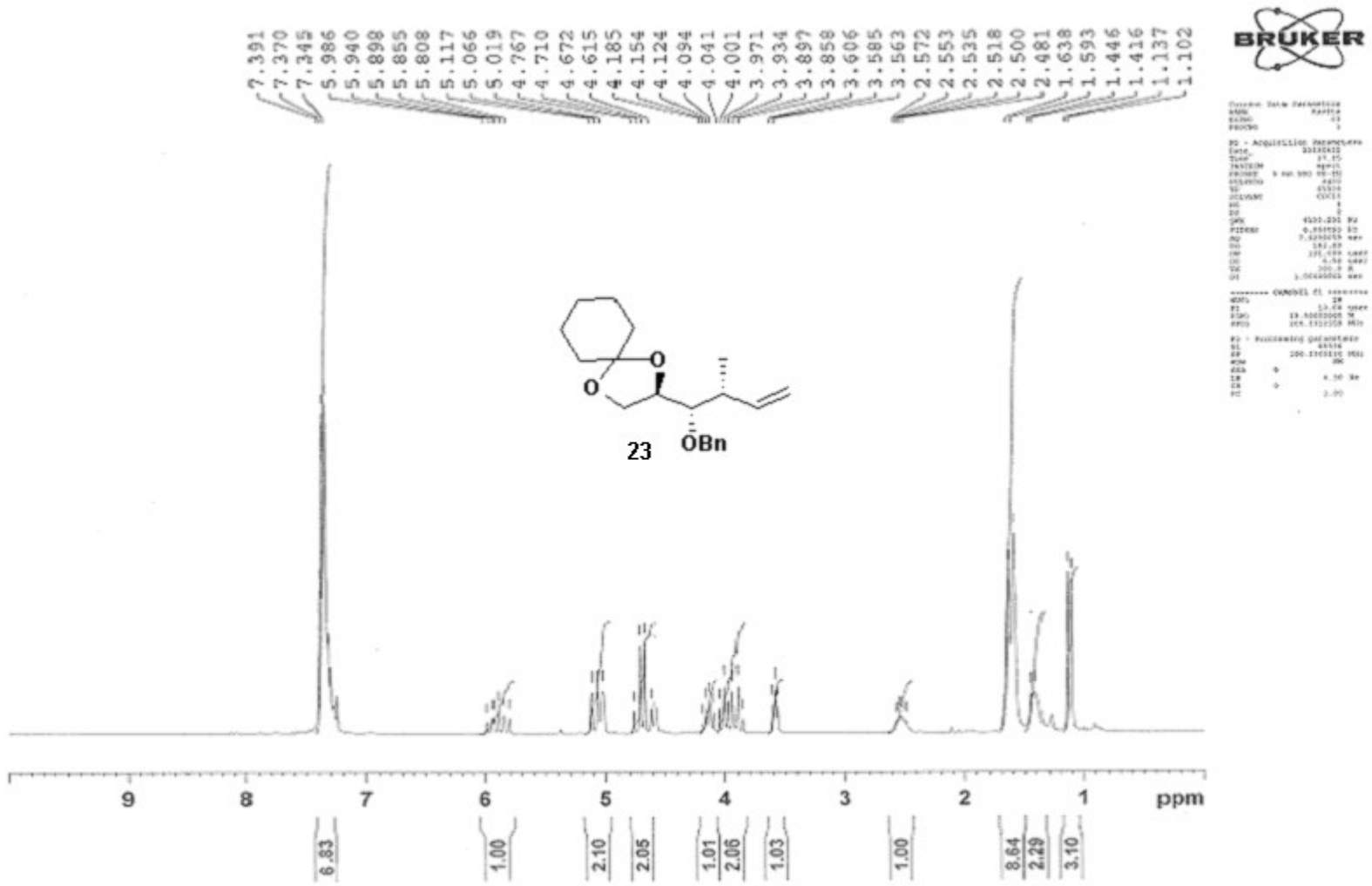

170.59
170.42
137.13
135.12
131.13
130.64
128.45
128.41
126.07
125.96
77.63
76.99
76.36
70.03
60.89
41.32
37.47
30.64
20.94
16.27
AcO
OAc
Ph
21
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

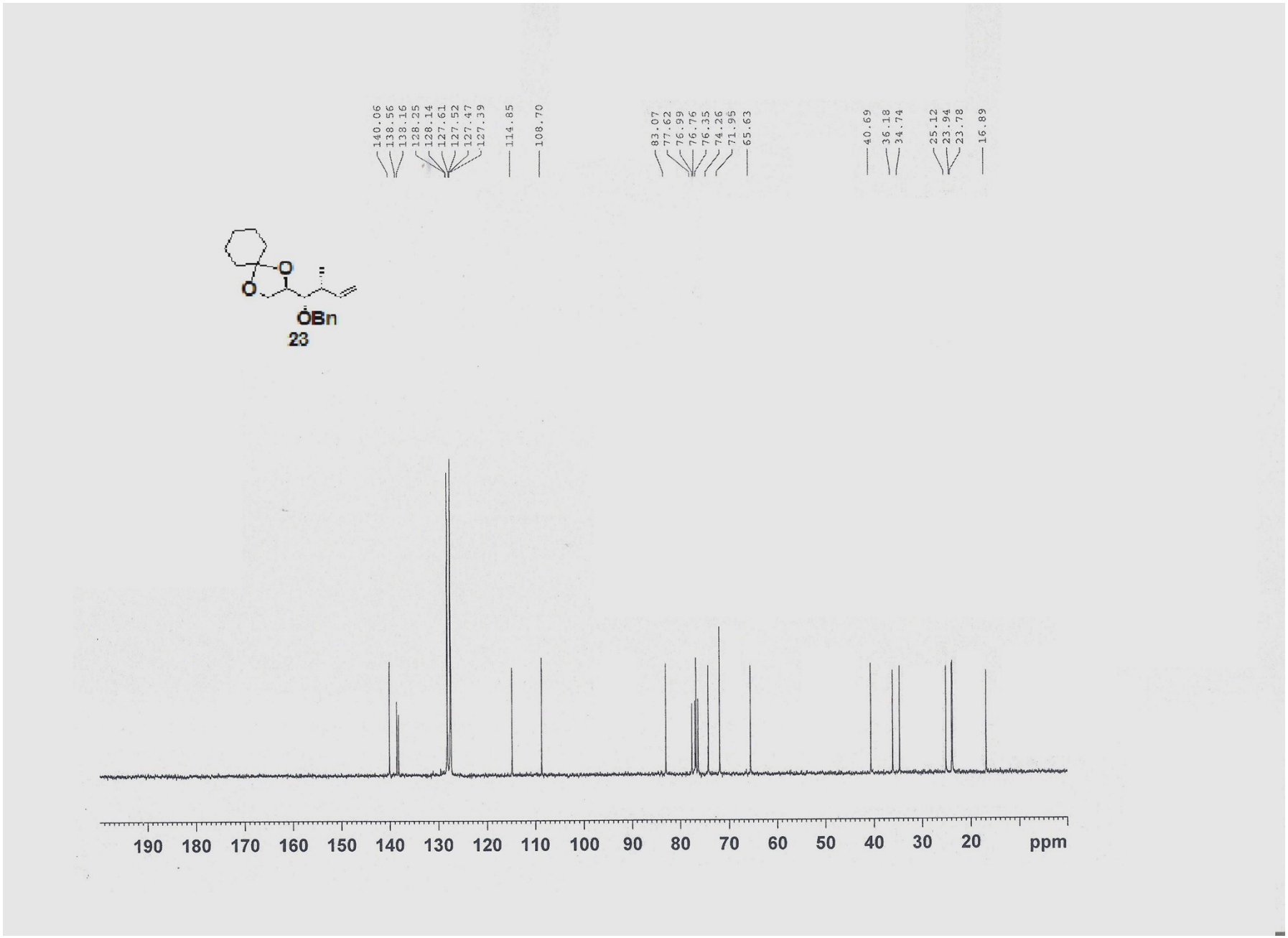

7.354
7.315
7.283
7.248
7.219
7.190
7.157
6.438
6.358
6.190
6.150
6.111
6.071
3.887
3.862
3.847
3.830
3.808
3.771
3.703
3.688
3.648
3.633
3.496
3.459
3.441
3.404
2.570
2.530
2.496
2.461
2.426
1.785
1.686
1.670
1.645
1.615
1.576
1.537
1.529
1.503
1.494
1.469
1.459
1.434
1.424
1.400
1.132
1.098
HO
Ph
OH
(3S,4R)-20
9
8
7
6
5
4
3
2
1
ppm
4.04
1.63
0.90
0.88
1.57
1.04
0.87
1.00
2.78
2.75
2.91

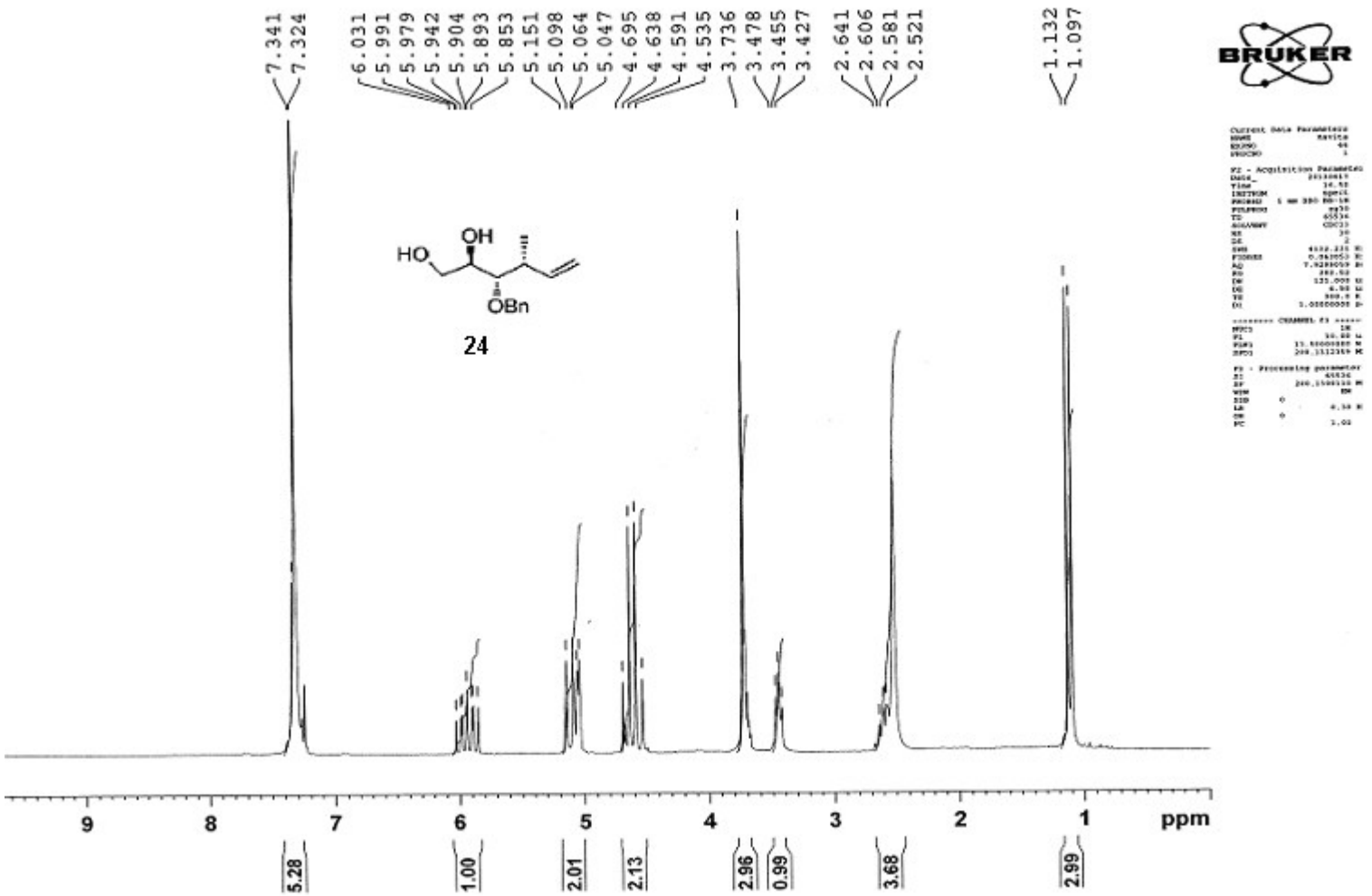

137.38
136.13
128.48
128.40
128.29
127.03
125.98
77.64
77.00
76.37
70.52
66.63
40.11
34.14
20.52
HO
Ph
OH
(3S,4R)-20
200
180
160
140
120
100
80
60
40
20
0
ppm

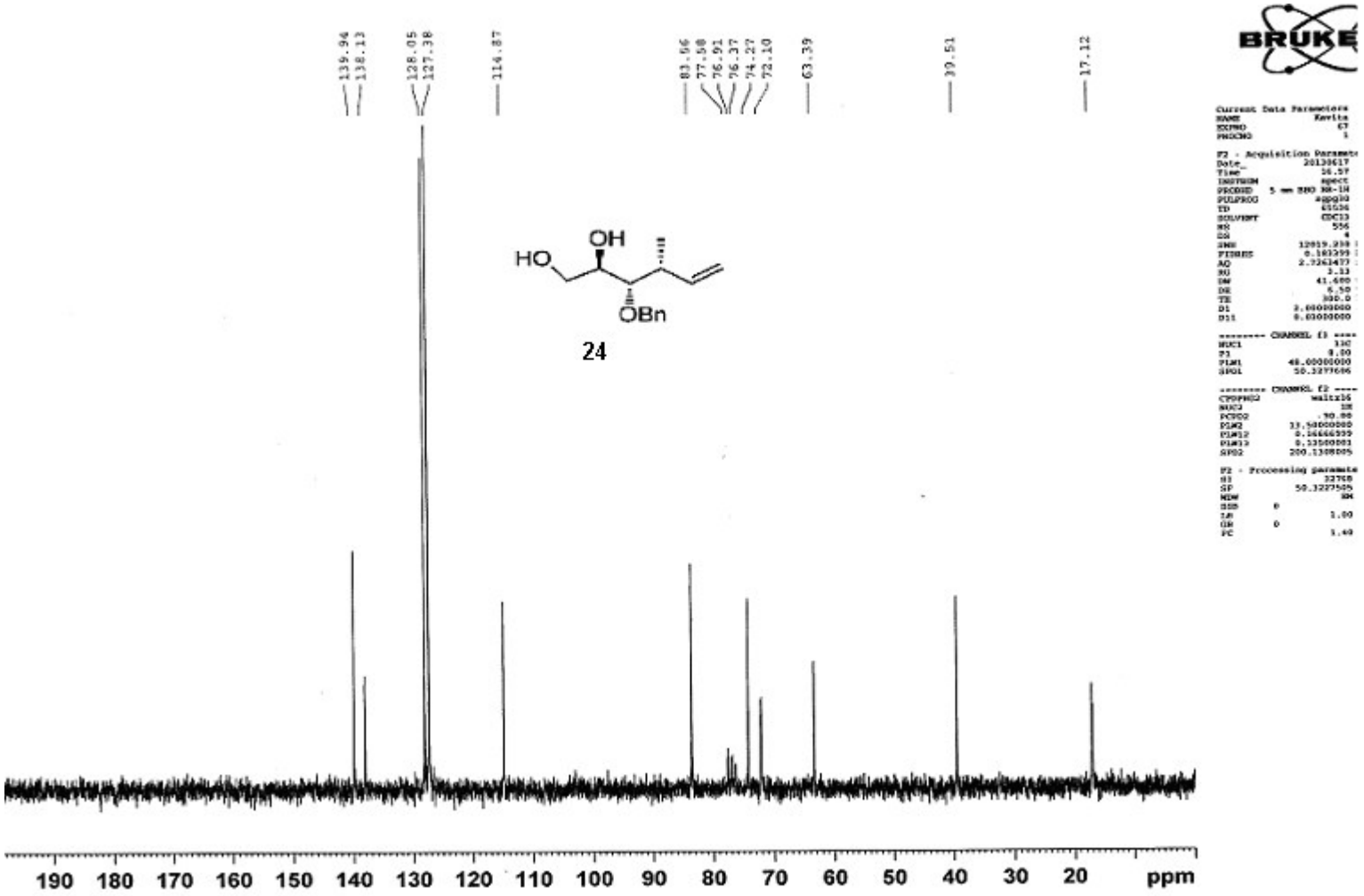

7.355
7.318
7.286
7.249
7.231
7.221
7.206
7.189
7.019
6.982
6.943
6.904
6.868
6.414
6.334
6.164
6.128
6.085
6.049
5.877
5.799
4.221
4.186
4.150
4.115
3.964
3.928
3.894
3.873
2.538
2.504
2.471
2.437
2.389
2.348
2.316
2.281
2.246
2.212
1.671
1.305
1.269
1.242
1.129
EtO2C
Ph
OH
22
9
8
7
6
5
4
3
2
1
ppm
5.99
0.85
0.95
0.96
0.89
2.00
0.69
1.21
1.99
1.76
3.37
3.28

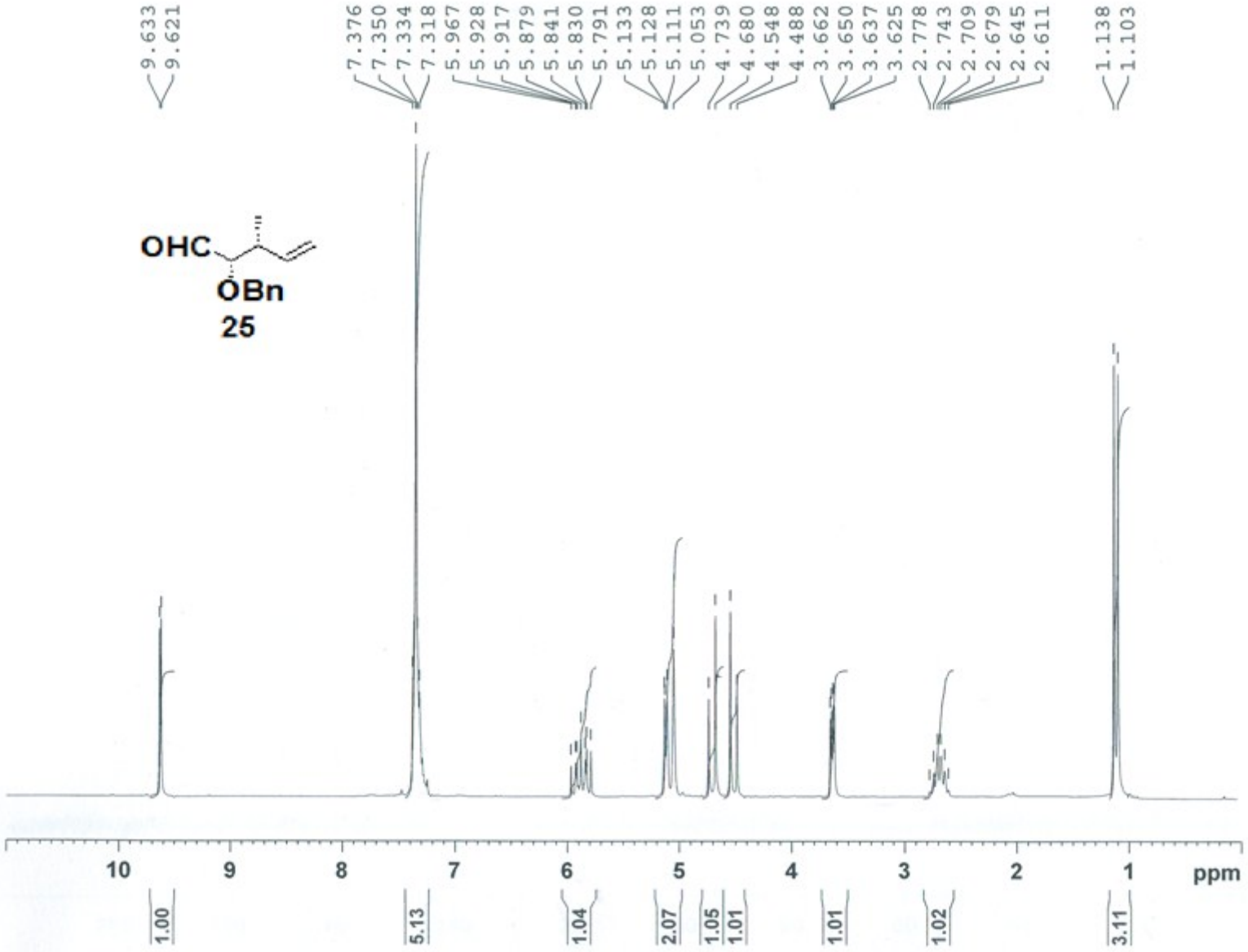

166.84
147.19
137.41
134.00
129.05
128.46
127.07
125.08
122.78
77.64
77.00
76.37
73.76
60.26
39.63
36.37
20.13
14.24
EtO2C
Ph
OH
22
200
180
160
140
120
100
80
60
40
20
0
ppm

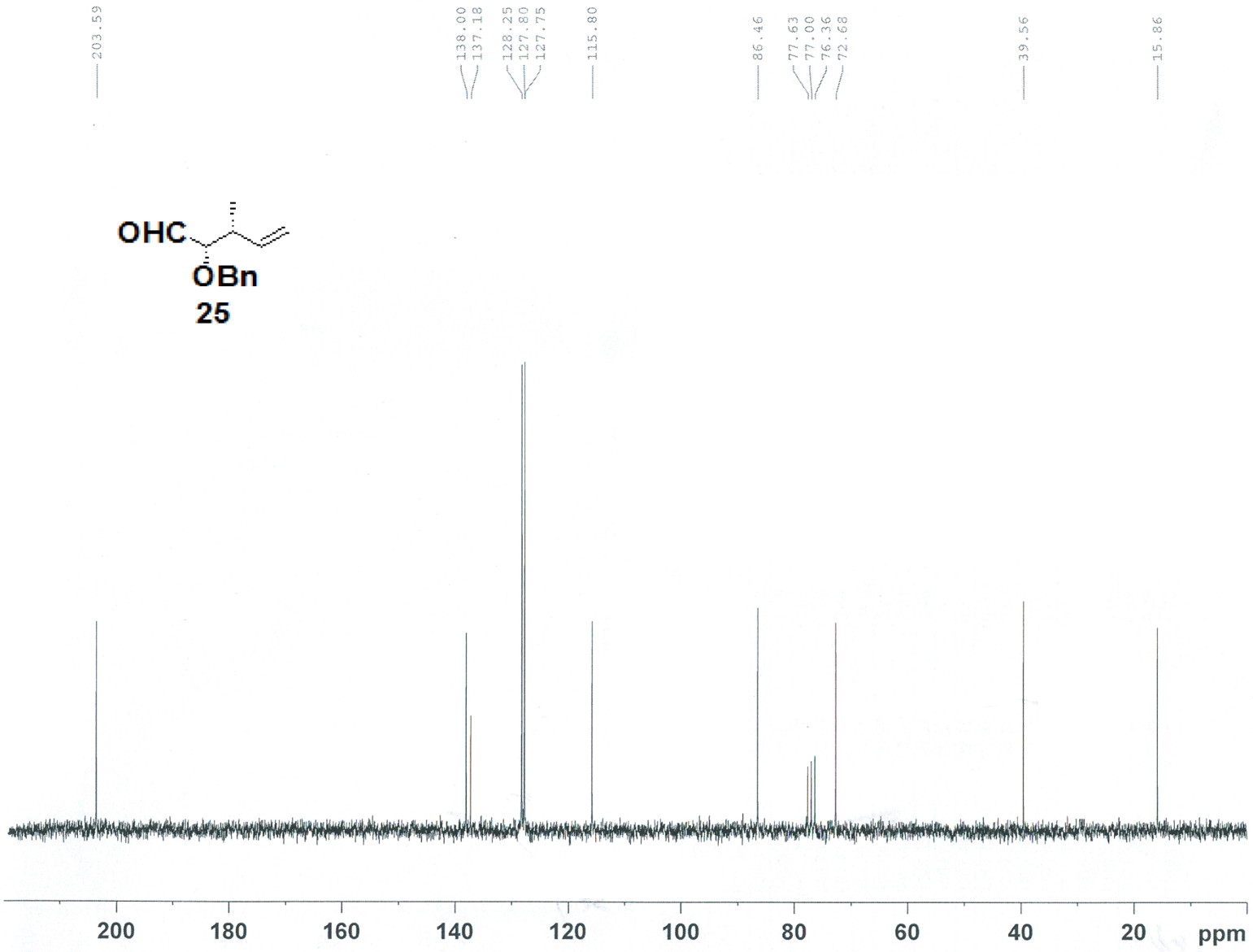

7.391
7.370
7.345
5.986
5.940
5.898
5.855
5.808
5.117
5.066
5.019
4.767
4.710
4.672
4.615
4.185
4.154
4.124
4.094
4.041
4.001
3.971
3.934
3.897
3.858
3.606
3.585
3.563
2.572
2.553
2.535
2.518
2.500
2.481
1.638
1.593
1.446
1.416
1.137
1.102
BRUKER
O
O
OBn
23
9
8
7
6
5
4
3
2
1
ppm
6.83
1.00
2.10
2.05
1.01
2.06
1.03
1.00
8.64
2.29
3.10

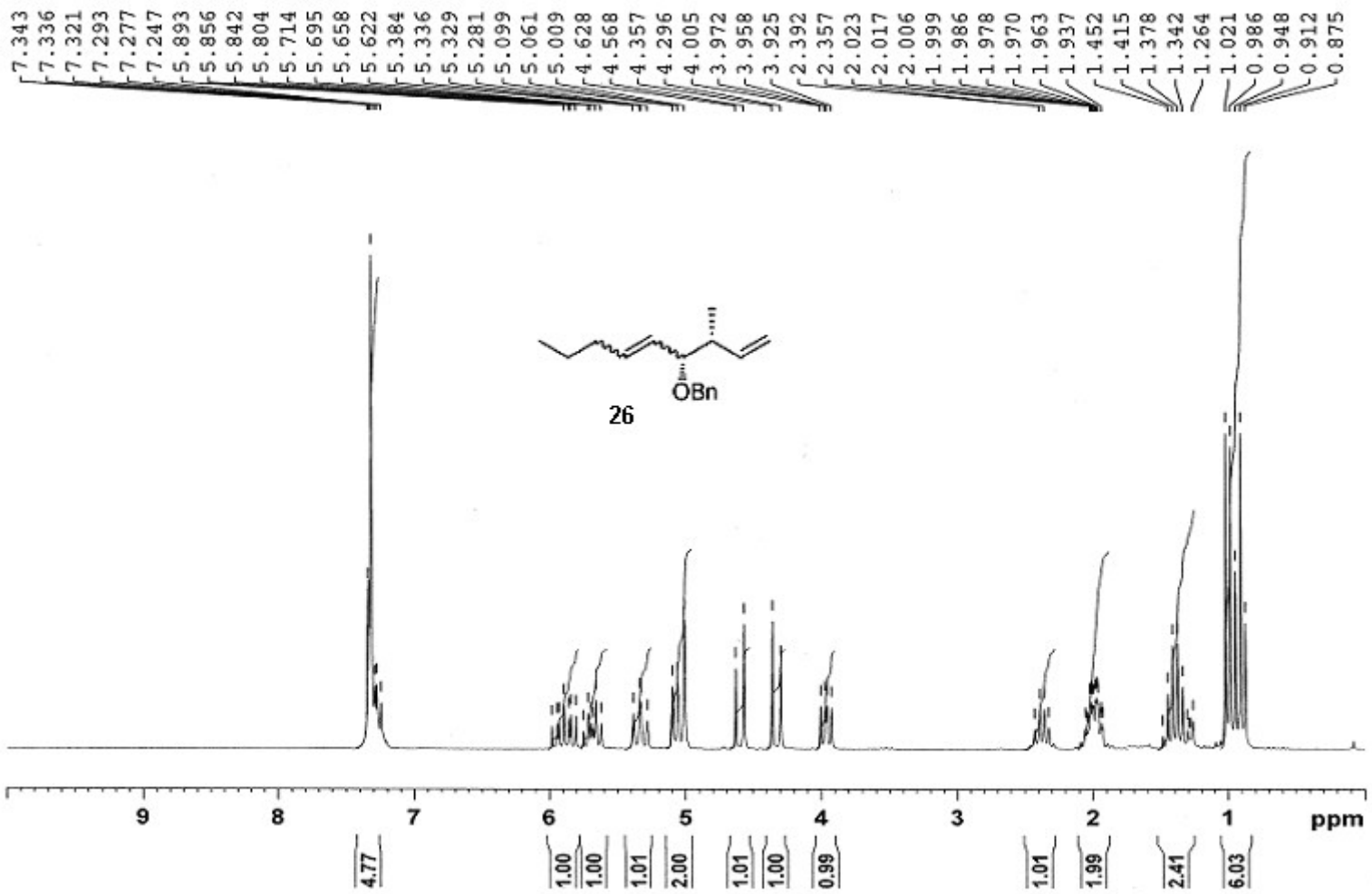

140.06
138.56
138.16
128.25
128.14
127.61
127.52
127.47
127.39
114.85
108.70
83.07
77.62
76.99
76.76
76.35
74.26
71.95
65.63
40.69
36.18
34.74
25.12
23.94
23.78
16.89
OBn
23
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

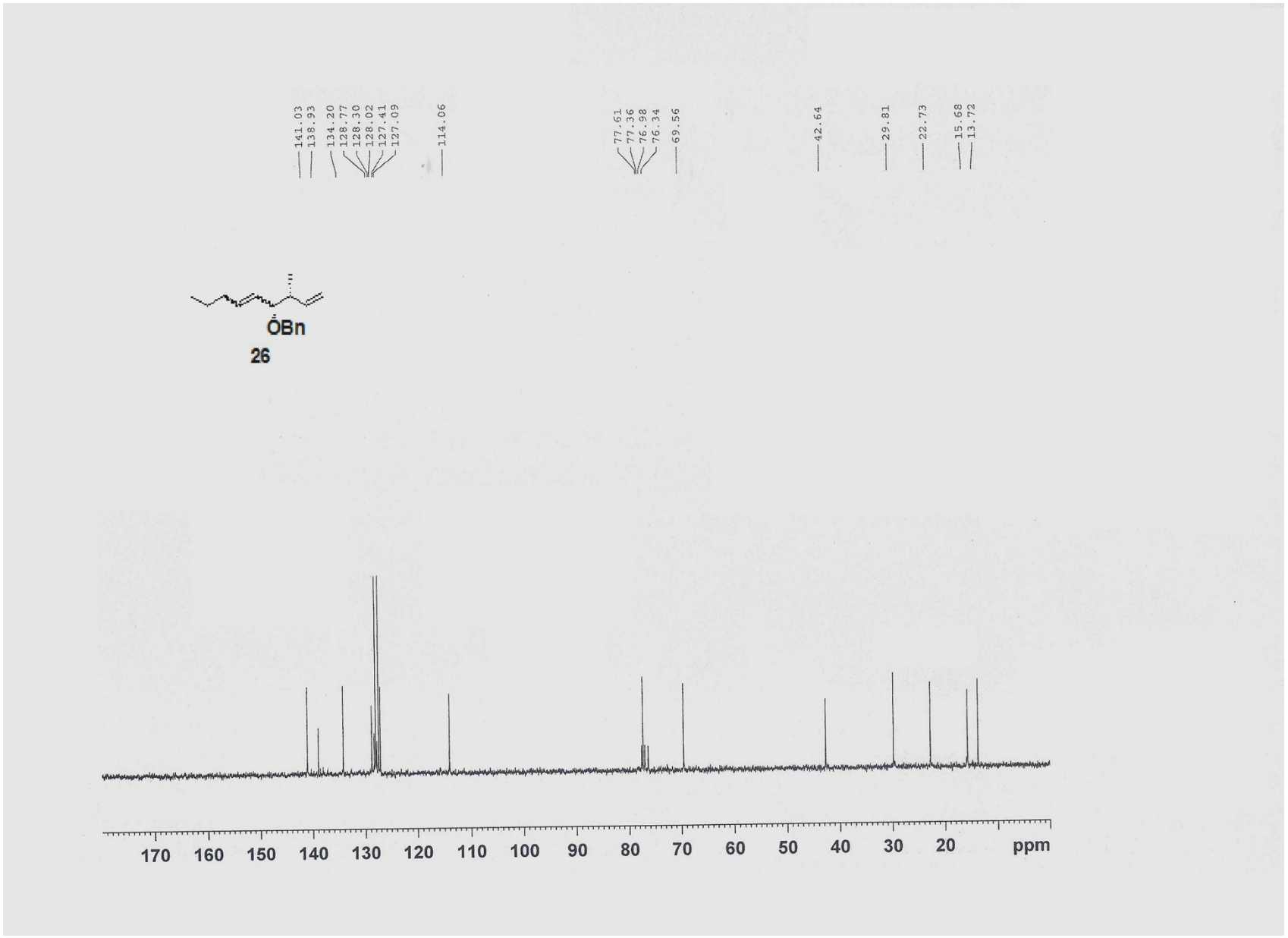

7.341
7.324
6.031
5.991
5.979
5.942
5.904
5.893
5.853
5.151
5.098
5.064
5.047
4.695
4.638
4.591
4.535
3.736
3.478
3.455
3.427
2.641
2.606
2.581
2.521
1.132
1.097
HO
OH
OBn
24
9
8
7
6
5
4
3
2
1
ppm
5.28
1.00
2.01
2.13
2.96
0.99
3.68
2.99

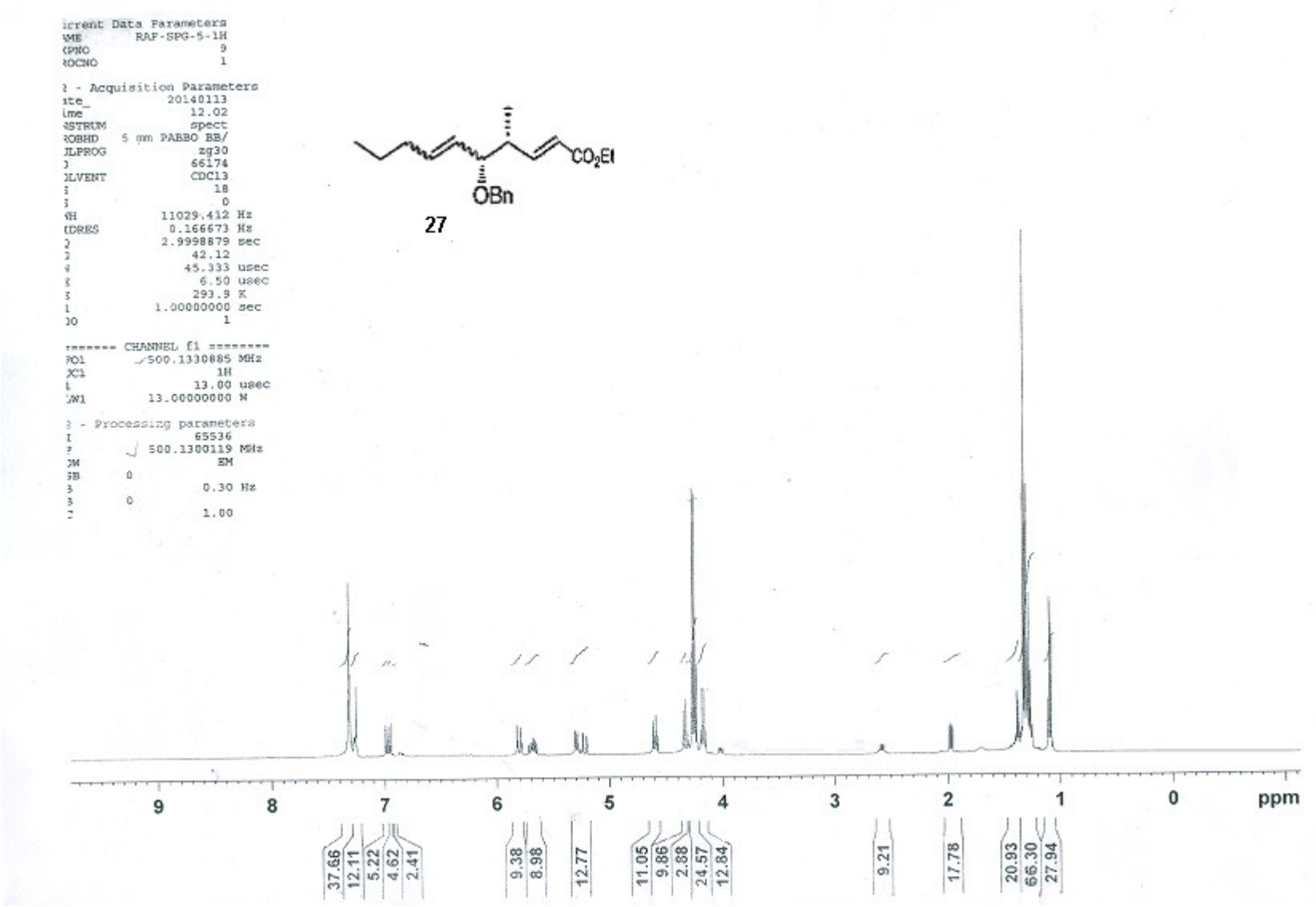

139.94
138.13
128.05
127.38
114.87
83.66
77.68
76.91
76.37
74.27
72.10
63.39
39.51
17.12
HO
OH
OBn
24
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

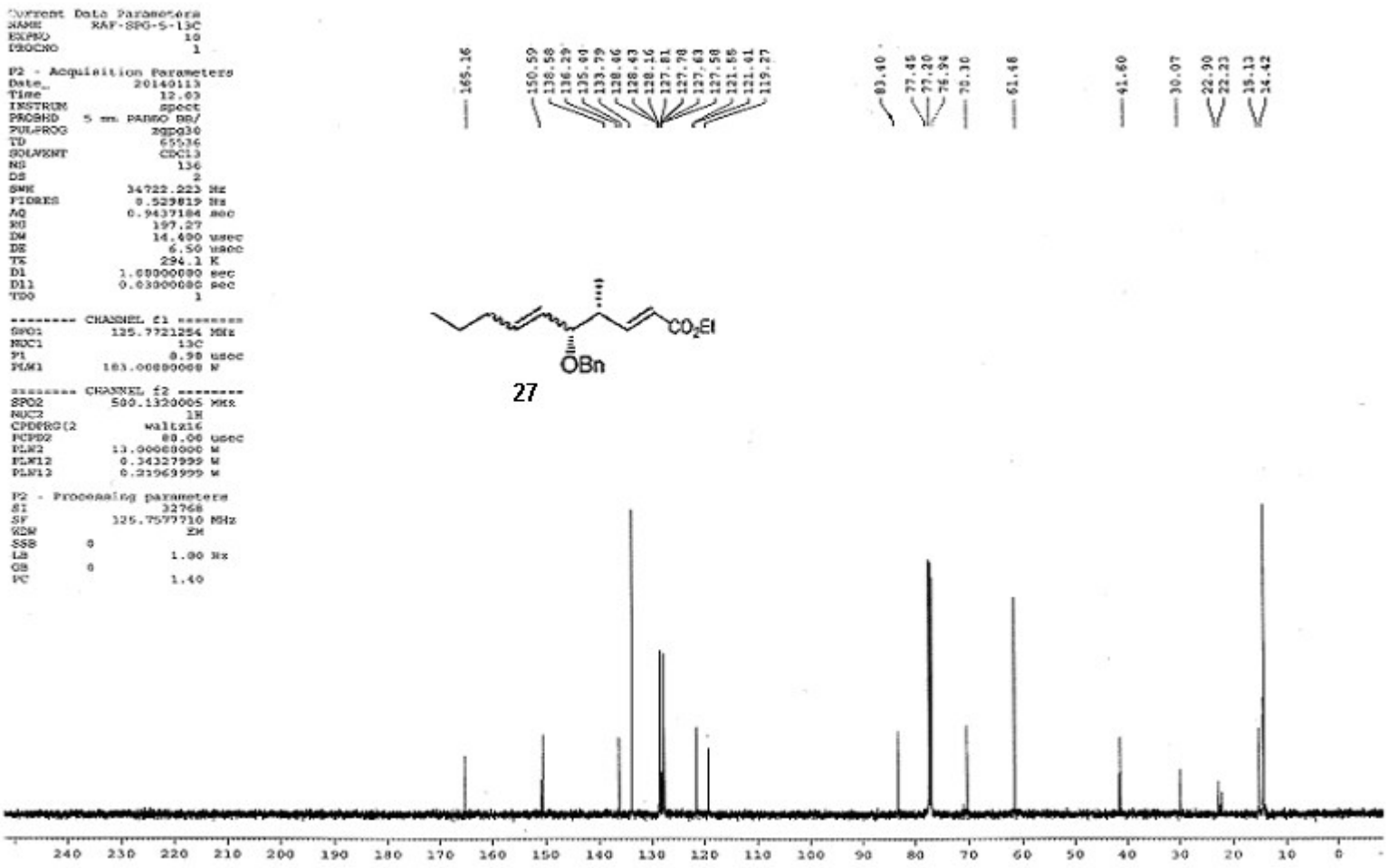

9.633
9.621
7.376
7.350
7.334
7.318
5.967
5.928
5.917
5.879
5.841
5.830
5.791
5.133
5.128
5.111
5.053
4.739
4.680
4.548
4.488
3.662
3.650
3.637
3.625
2.778
2.743
2.709
2.679
2.645
2.611
1.138
1.103
OHC
OBn
25
10
9
8
7
6
5
4
3
2
1
ppm
1.00
5.13
1.04
2.07
1.05
1.01
1.01
1.02
3.11


203.59
138.00
137.18
128.25
127.80
127.75
115.80
86.46
77.63
77.00
76.36
72.68
39.56
15.86
OHC
OBn
25
200
180
160
140
120
100
80
60
40
20
ppm

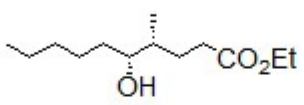

7.343
7.336
7.321
7.293
7.277
7.247
5.893
5.856
5.842
5.804
5.714
5.695
5.658
5.622
5.384
5.336
5.329
5.281
5.099
5.061
5.009
4.628
4.568
4.357
4.296
4.005
3.972
3.958
3.925
2.392
2.357
2.023
2.017
2.006
1.999
1.986
1.978
1.970
1.963
1.937
1.452
1.415
1.378
1.342
1.264
1.021
0.986
0.948
0.912
0.875
OBn
26
9
8
7
6
5
4
3
2
1
ppm
4.77
1.00
1.00
1.01
2.00
1.01
1.00
0.99
1.01
1.99
2.41
6.03


141.03
138.93
134.20
128.77
128.30
128.02
127.41
127.09
114.06
77.61
77.36
76.98
76.34
69.56
42.64
29.81
22.73
15.68
13.72
ÖBn
26
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

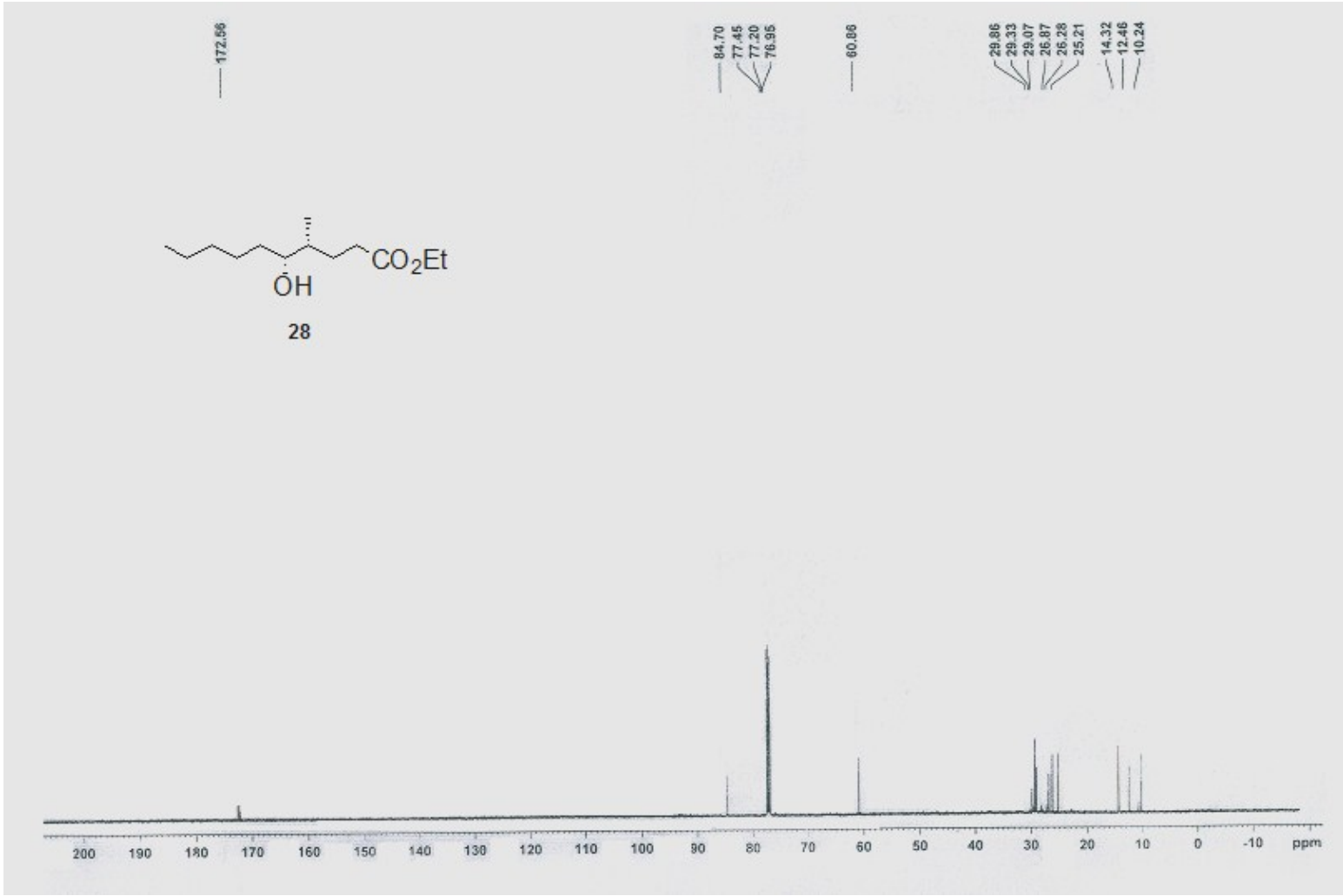

irrent Data Parameters
AME RAF-SPG-5-1H
CPNO 9
ROCNO 1
2 - Acquisition Parameters
ate_ 20140113
ime 12.02
NSTRUM spect
ROBHD 5 mm PABBO BB/
ULPROG zg30
D 66174
OLVENT CDCl3
S 18
S 0
SH 11029.412 Hz
IDRES 0.166673 Hz
D1 2.9998879 sec
D3 42.12
P1 45.333 usec
P2 6.50 usec
TE 293.9 K
D1 1.00000000 sec
NO 1
======= CHANNEL f1 ========
FO1 500.1330885 MHz
NC1 1H
P1 13.00 usec
PW1 13.00000000 W
3 - Processing parameters
SI 65536
F 500.1300119 MHz
WM EM
SSB 0
LB 0.30 Hz
GB 0
C1 1.00
CO2Et
OBn
27
9
8
7
6
5
4
3
2
1
0
ppm
37.66
12.11
5.22
4.62
2.41
9.38
8.98
12.77
11.05
9.86
2.88
24.57
12.84
9.21
17.78
20.93
66.30
27.94

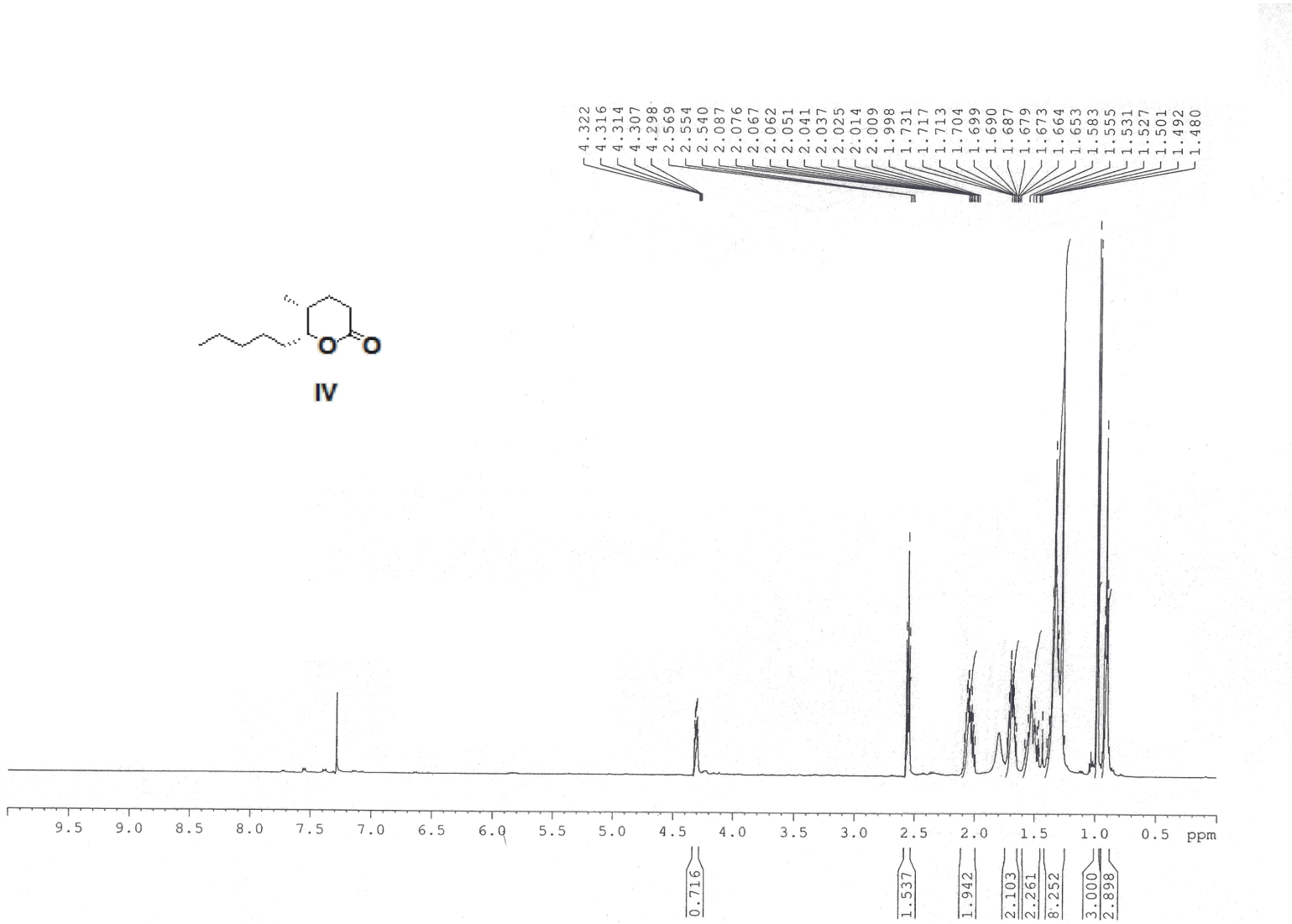

Current Data Parameters
NAME RAF-SPG-S-13C
EXPNO 10
PROCNO 1
P2 - Acquisition Parameters
Date_ 20140113
Time 12.03
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 136
DS 2
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437184 sec
RG 197.27
DW 14.400 usec
DE 6.50 usec
TE 294.1 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7721256 MHz
NUC1 13C
P1 8.90 usec
PLW1 163.00890060 W
======== CHANNEL f2 ========
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.00060000 W
PLW12 0.34327999 W
PLW13 0.21969999 W
P2 - Processing parameters
SI 32768
SF 125.7577710 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
165.16
150.59
138.58
136.29
135.40
133.79
128.46
128.43
128.16
127.81
127.78
127.63
127.58
121.55
121.41
119.27
83.40
77.48
77.20
76.94
70.30
61.48
41.60
30.07
22.90
22.23
15.13
14.42
CO2Et
OBn
27
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

```
Current Data Parameters
NAME          SSK-SC-2-1H
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20140126
Time               10.58
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    24
DS                     0
SWH            10000.000 Hz
FIDRES             0.152588 Hz
AQ             3.2767999 sec
RG                 53.37
DW                 50.000 usec
DE                  6.50 usec
TE                293.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          500.1330885 MHz
NUC1                   1H
P1                  13.00 usec
PLW1          13.00000000 W

F2 - Processing parameters
SI                 65536
SF            500.1300121 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

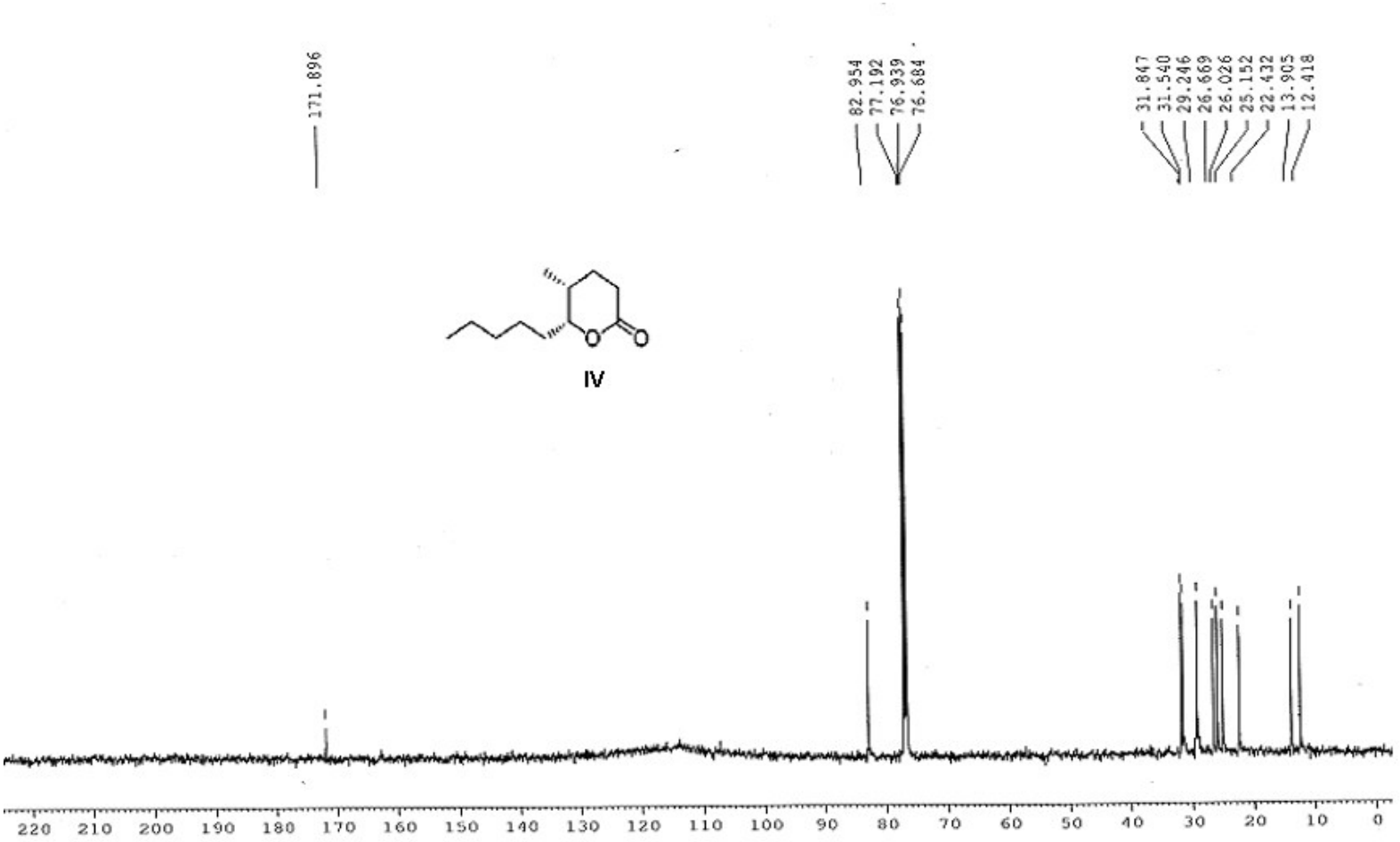


28


172.56
84.70
77.45
77.20
76.95
60.86
29.86
29.33
29.07
26.87
26.28
25.21
14.32
12.46
10.24
CO2Et
OH
28
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm


4.322
4.316
4.314
4.307
4.298
2.569
2.554
2.540
2.087
2.076
2.067
2.062
2.051
2.041
2.037
2.025
2.014
2.009
1.998
1.731
1.717
1.713
1.704
1.699
1.690
1.687
1.679
1.673
1.664
1.653
1.583
1.555
1.531
1.527
1.501
1.492
1.480
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
0.716
1.537
1.942
2.103
2.261
8.252
3.000
2.898

IV


171.896
82.954
77.192
76.939
76.684
31.847
31.540
29.246
26.669
26.026
25.152
22.432
13.905
12.418
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

IV