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

Supporting Information

Intramolecular Direct Aldol Reactions of Sugar 2,7-Diketones: Syntheses of Hydroxylated Cycloalka(e)nones

Tony K. M. Shing,* Hau M. Cheng

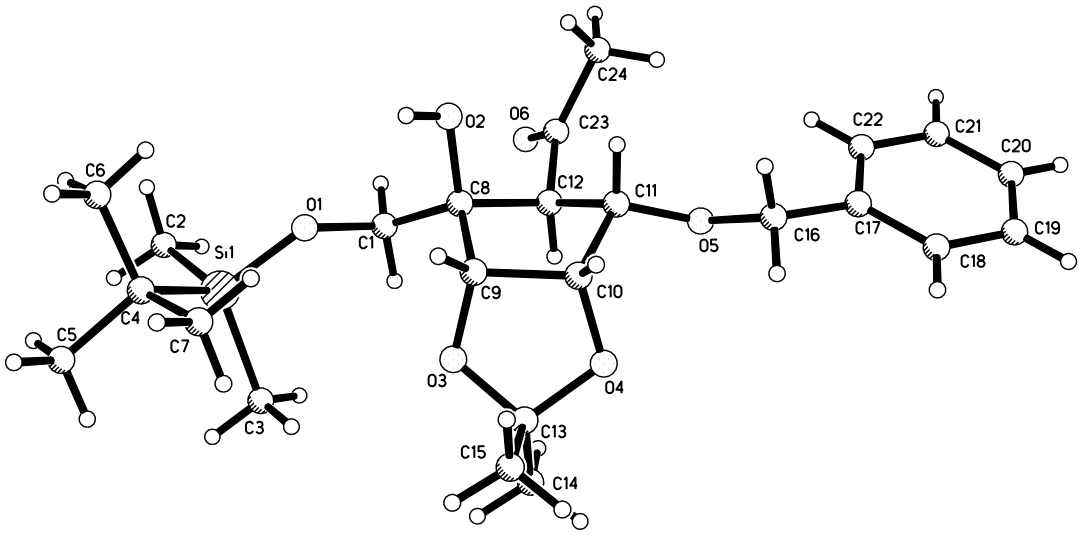
Departments of Chemistry, Center of Novel Functional Molecules

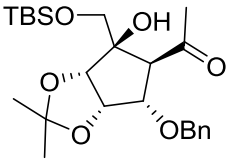
The Chinese University of Hong Kong, Shatin, Hong Kong.

Contents

General experimental Procedures

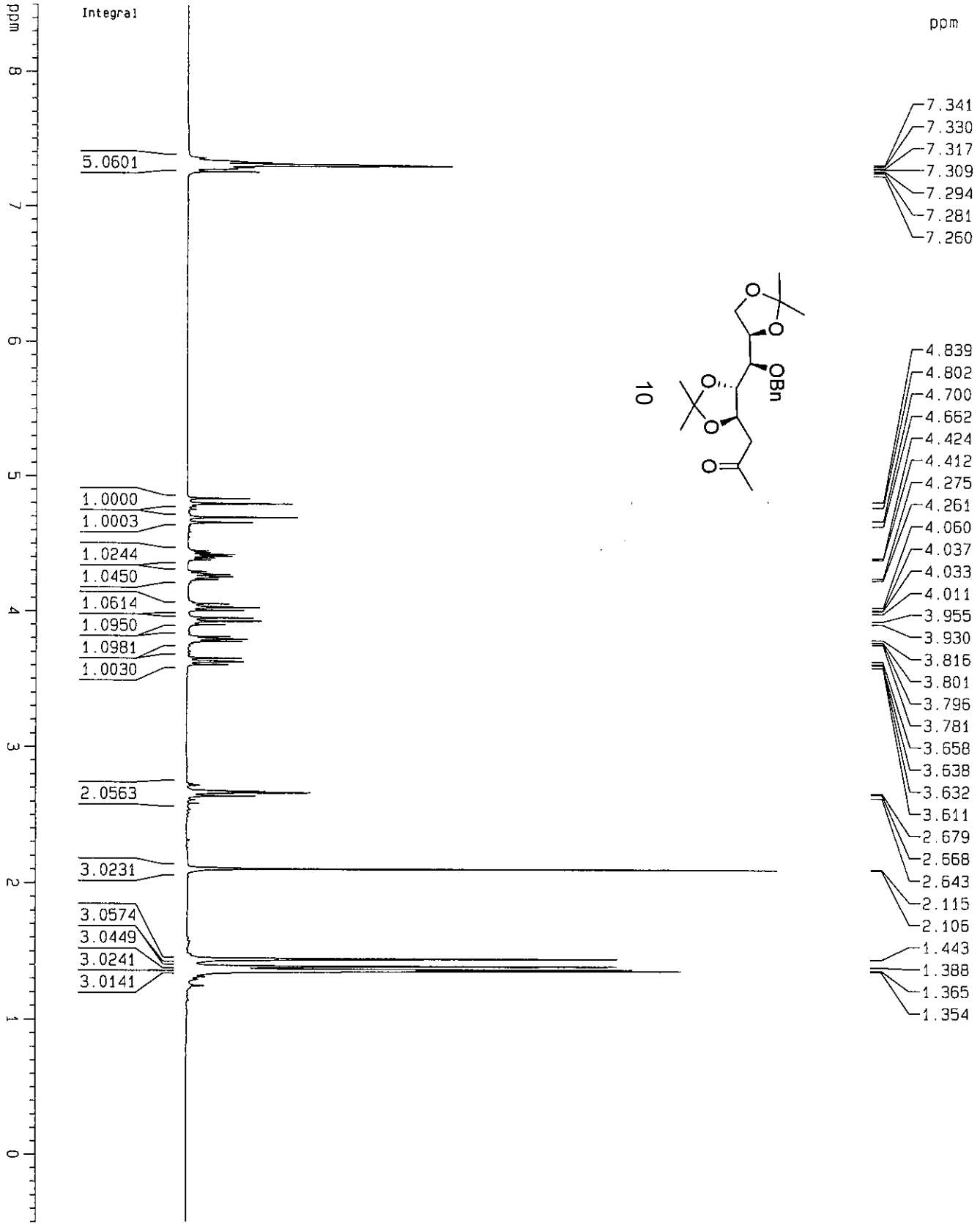
Melting points were uncorrected. Optical rotations were obtained with a polarimeter operating at 589nm. Infrared spectra (IR) were recorded with a FT-IR spectrophotometer as thin film on potassium bromide discs. Nuclear magnetic resonance (NMR) spectra were measured at 300.13 MHz (^{1}H) or at 75.47 MHz (^{13}C) in $CDCl_3$ solutions, unless stated otherwise. All chemical shifts were recorded in ppm relative to tetramethylsilane (δ= 0.0). Spin-spin coupling constants (*J* value) recorded in Hz were measured directly from the spectra. All reactions were monitored by analytical thin-layer chromatography (TLC) on aluminium-precoated plates of silica gel with detection by spraying with 5% (w/v) dodecamolybdophosphoric acid in ethanol or 5% (w/v) ninhydrin in ethanol and subsequent heating. Silica gel (230–400 mesh) was used for flash chromatography. All reagents and solvents were general reagent grade unless otherwise stated. DMF was dried by magnesium sulfate, filtered and was then freshly distilled under reduced pressure. Acetonitrile was freshly distilled from P_2O_5 under nitrogen. THF was freshly distilled from Na/benzophenone ketyl under nitrogen. Dichloromethane and chloroform were freshly distilled from P_2O_5 under nitrogen. Diethyl ether was freshly distilled from K/benzophenone ketyl under nitrogen. Other reagents were purchased from commercial suppliers and were used without purification.

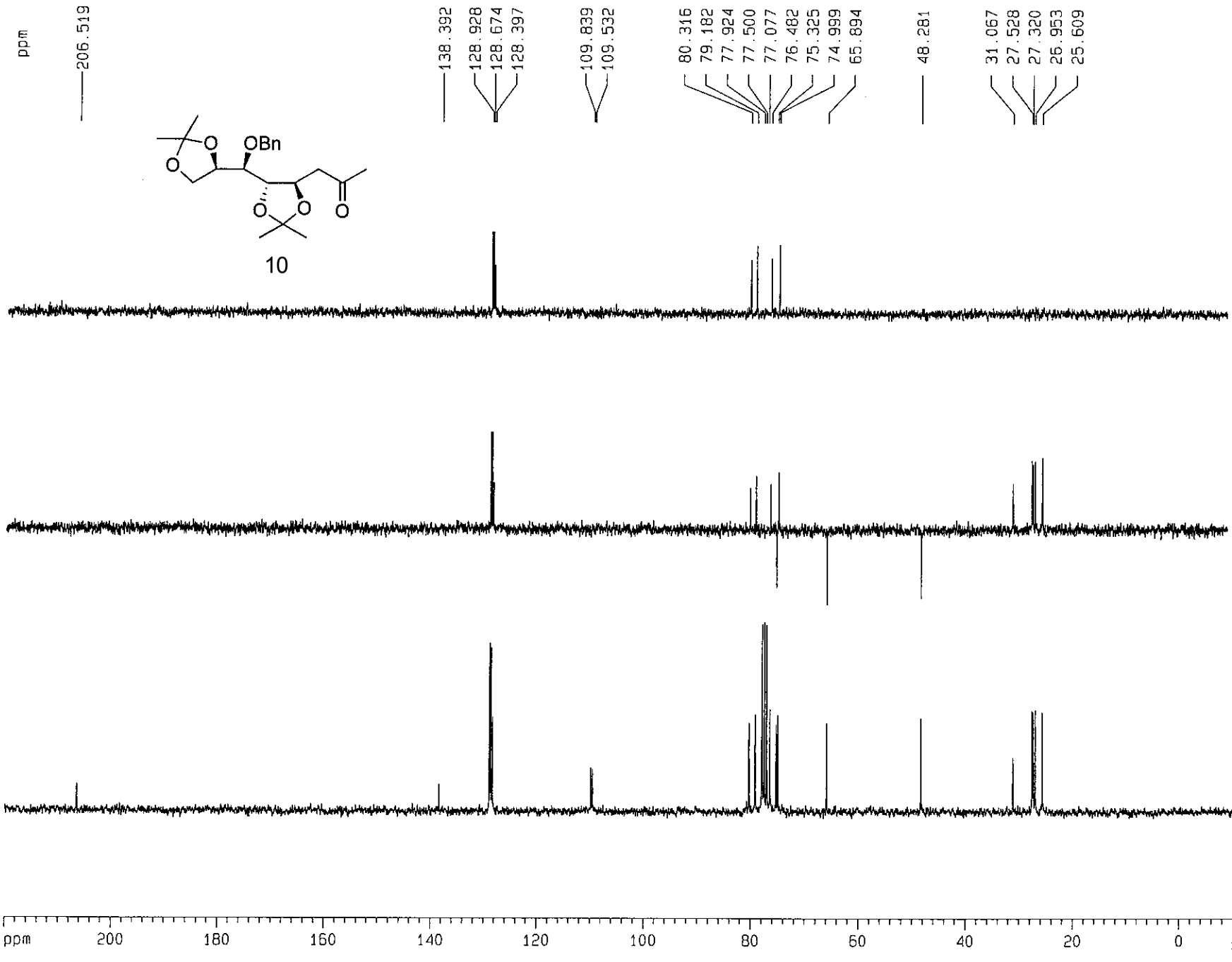


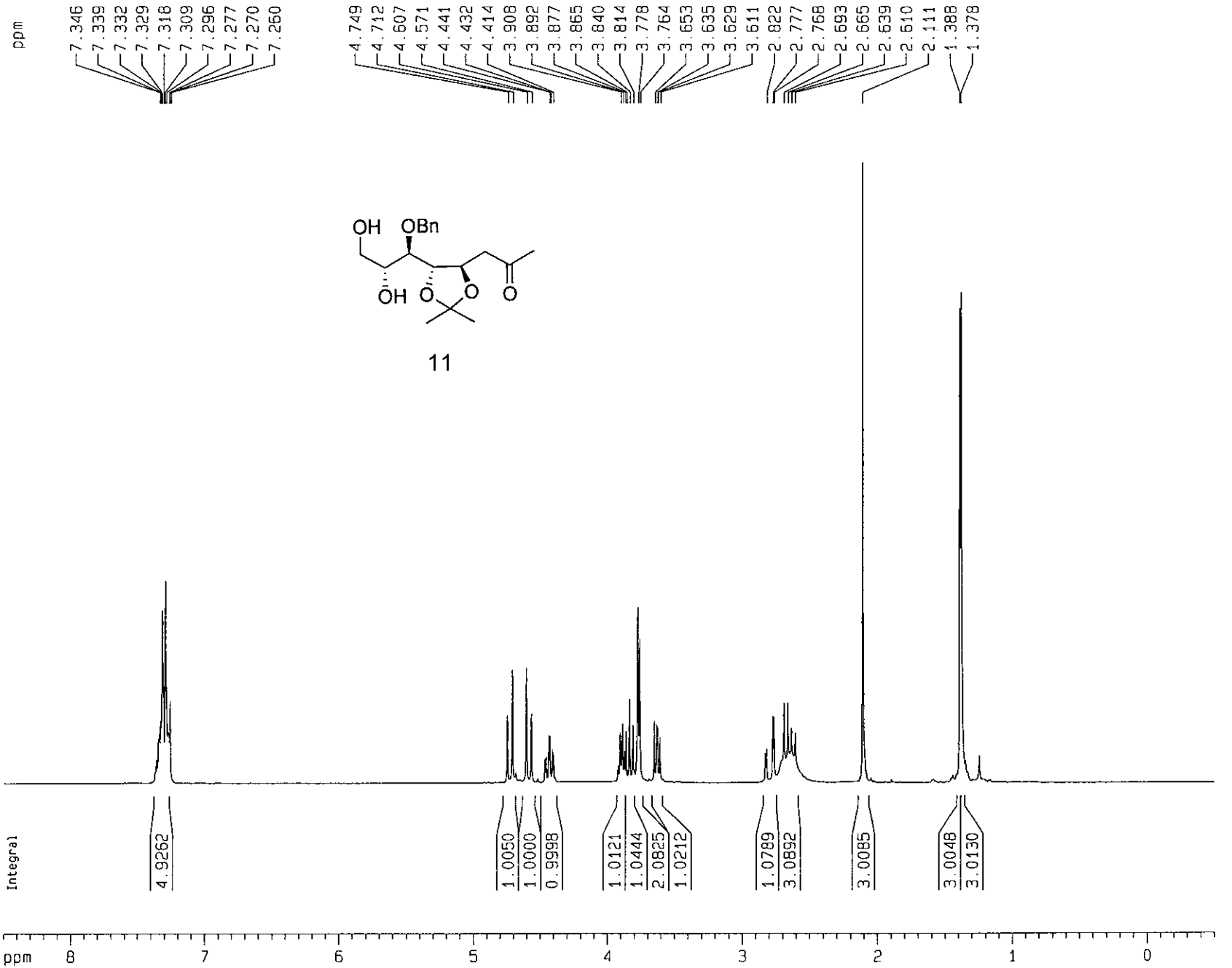


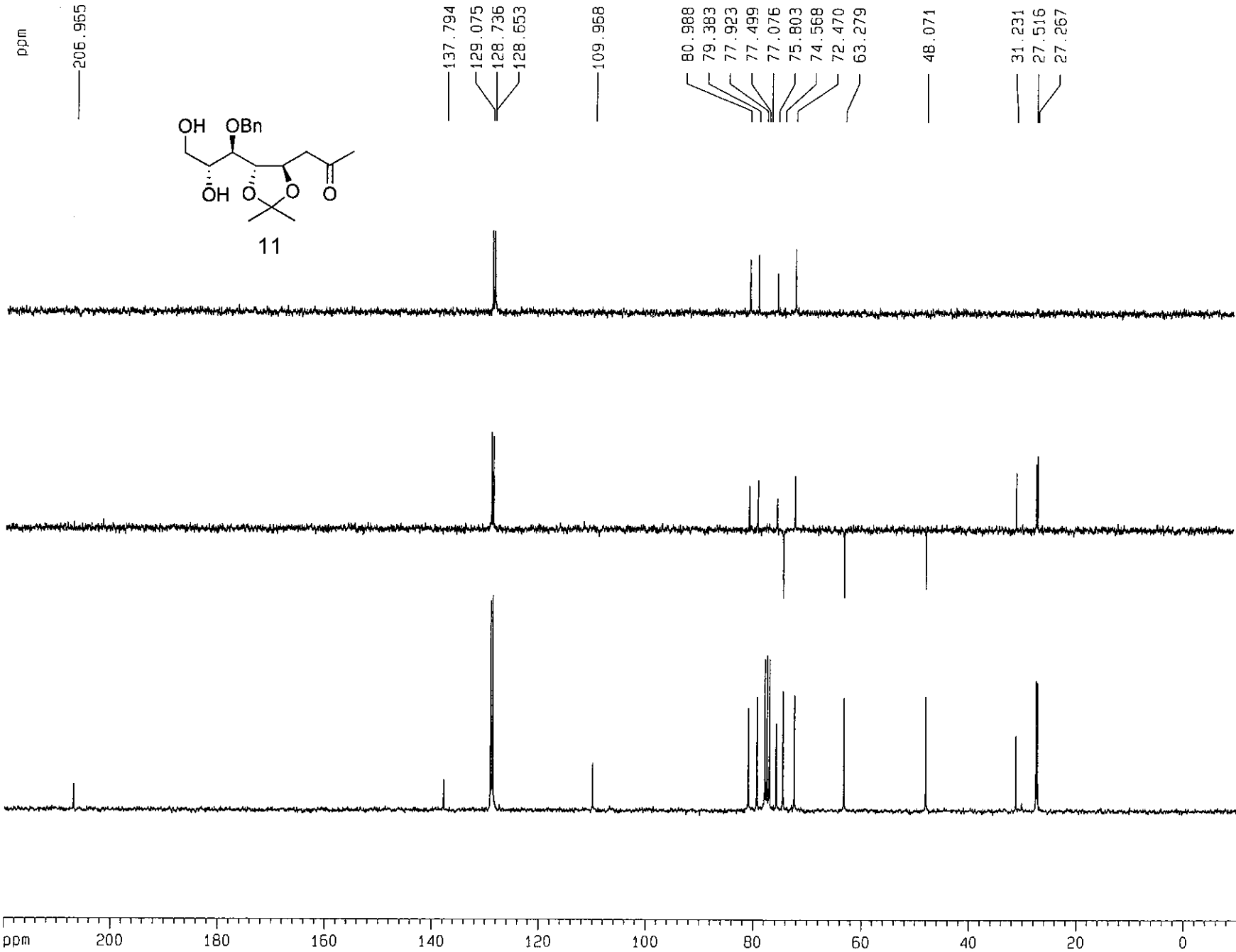
27

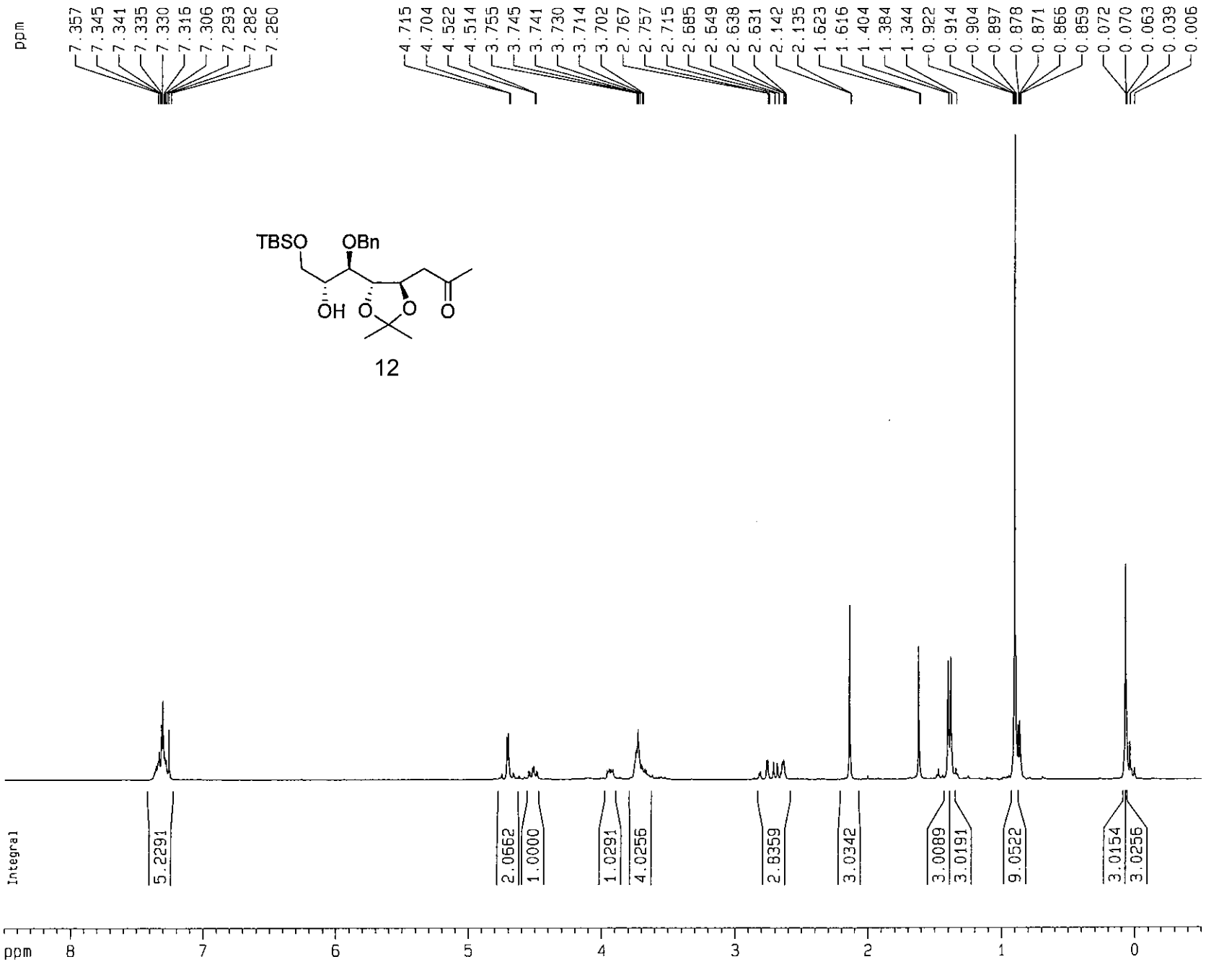
Figure S1. X-ray crystallographic structure of **27**.

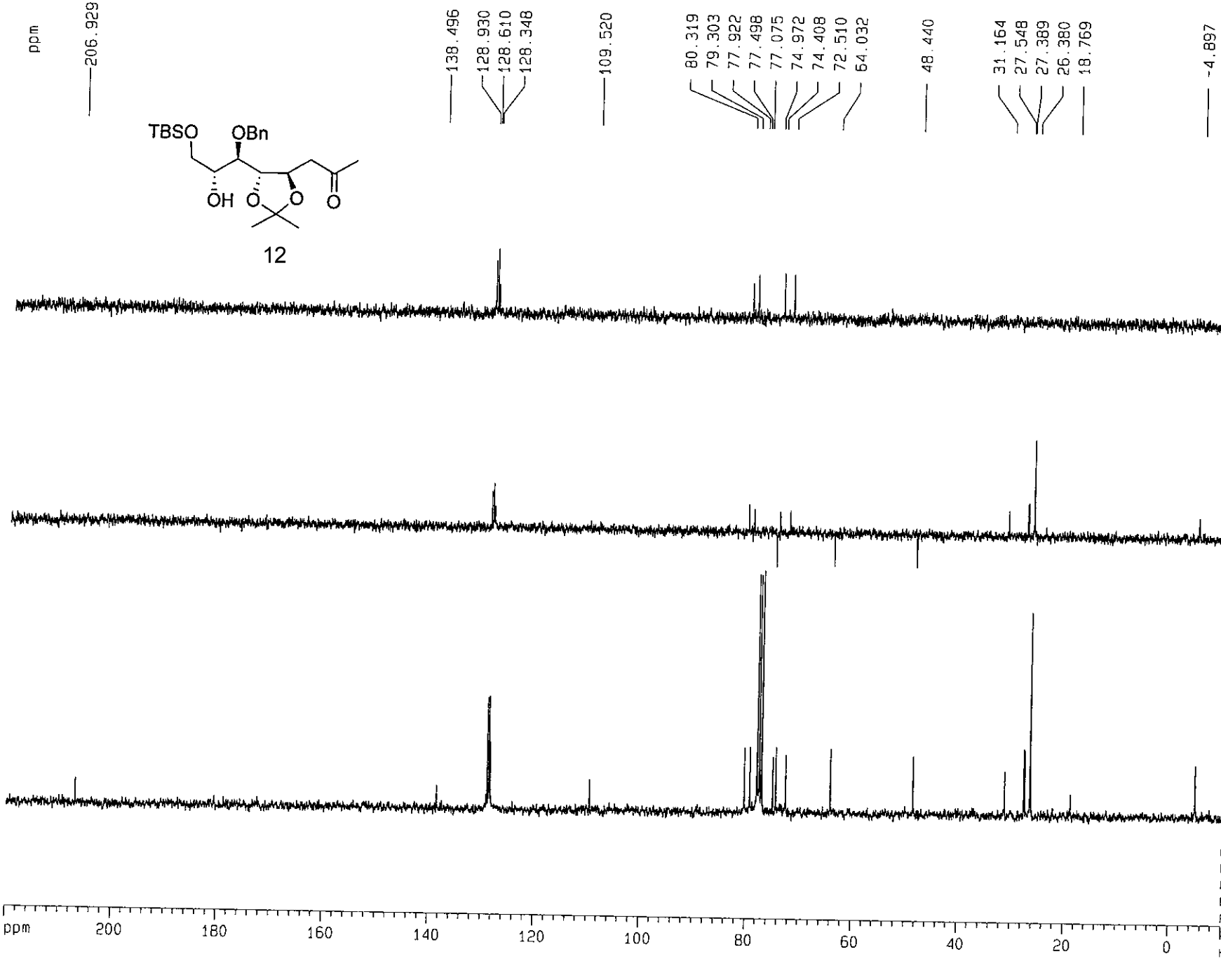

Integral
ppm
5.0601
1.0000
1.0003
1.0244
1.0450
1.0614
1.0950
1.0981
1.0030
2.0563
3.0231
3.0574
3.0449
3.0241
3.0141
10
OBn
ppm
7.341
7.330
7.317
7.309
7.294
7.281
7.260
4.839
4.802
4.700
4.662
4.424
4.412
4.275
4.261
4.060
4.037
4.033
4.011
3.955
3.930
3.816
3.801
3.796
3.781
3.658
3.638
3.632
3.611
2.679
2.668
2.643
2.115
2.105
1.443
1.388
1.365
1.354

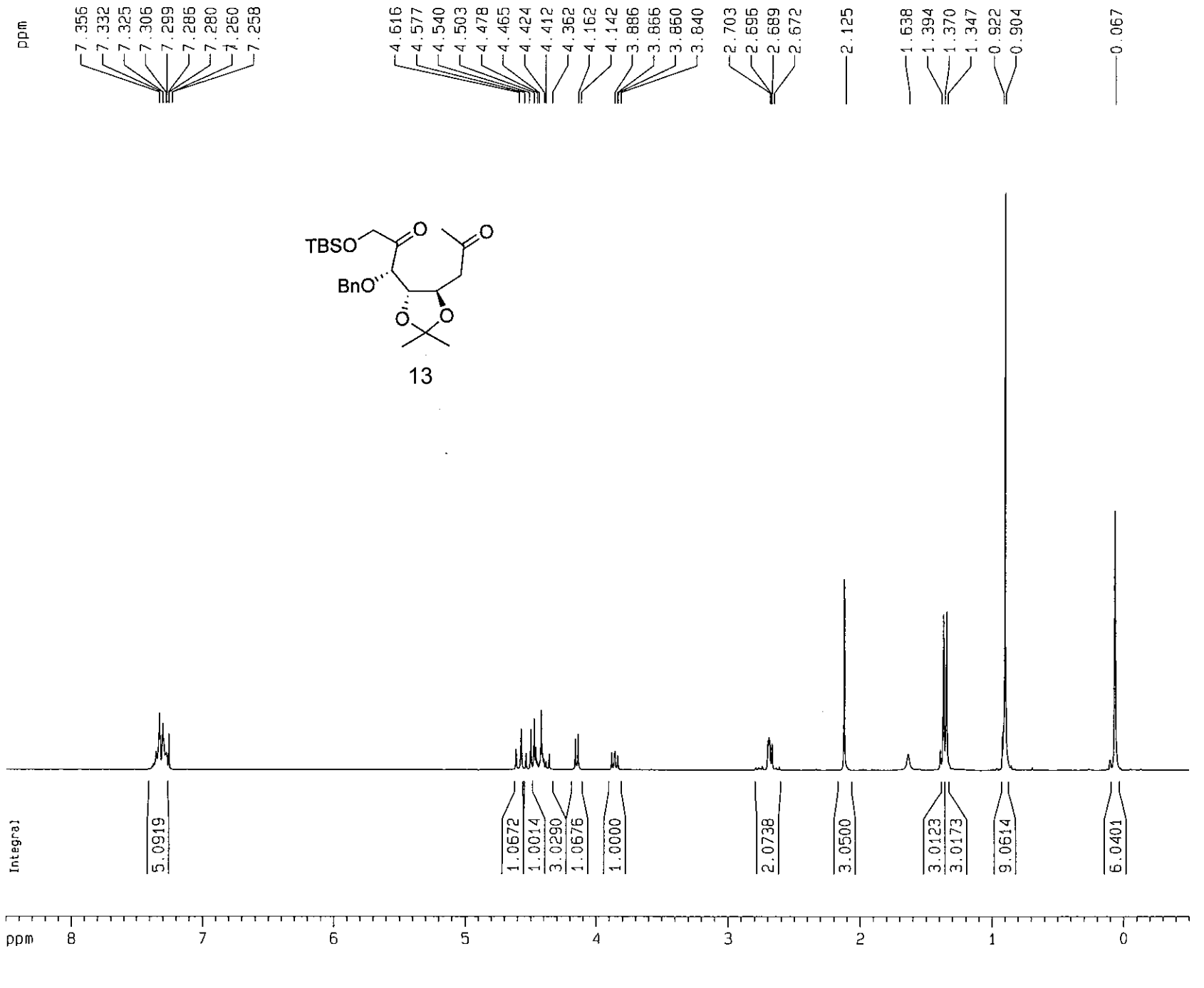

ppm
206.519
138.392
128.928
128.674
128.397
109.839
109.532
80.316
79.182
77.924
77.500
77.077
76.482
75.325
74.999
65.894
48.281
31.067
27.528
27.320
26.953
25.609
OBn
O
O
O
O
O
10
ppm
200
180
160
140
120
100
80
60
40
20
0

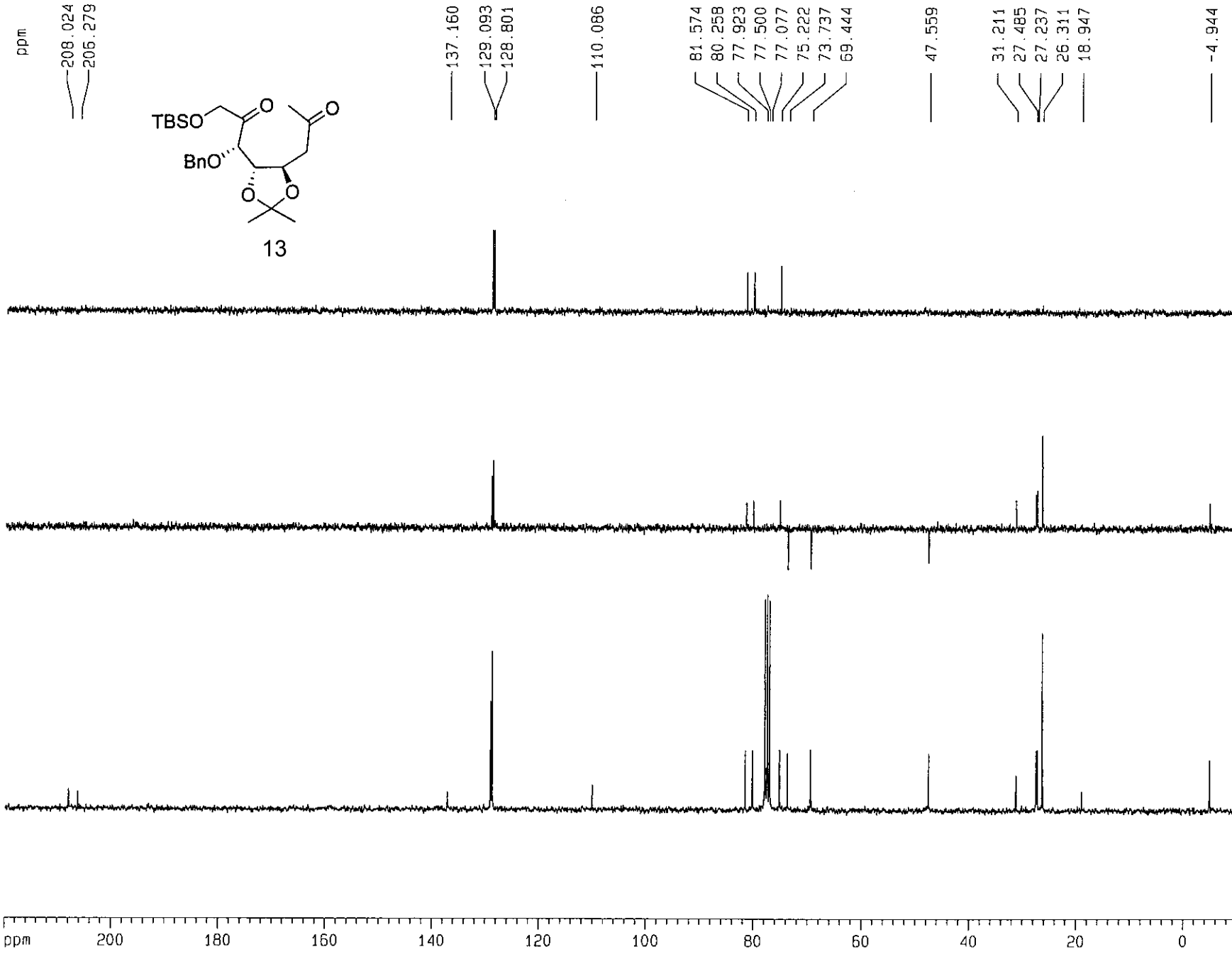

ppm
7.346
7.339
7.332
7.329
7.318
7.309
7.296
7.277
7.270
7.260
4.749
4.712
4.607
4.571
4.441
4.432
4.414
3.908
3.892
3.877
3.865
3.840
3.814
3.778
3.764
3.653
3.635
3.629
3.611
2.822
2.777
2.768
2.693
2.665
2.639
2.610
2.111
1.388
1.378
OH
OBn
OH
O
O
O
11
Integral
4.9262
1.0050
1.0000
0.9998
1.0121
1.0444
2.0825
1.0212
1.0789
3.0892
3.0085
3.0048
3.0130
ppm
8
7
6
5
4
3
2
1
0

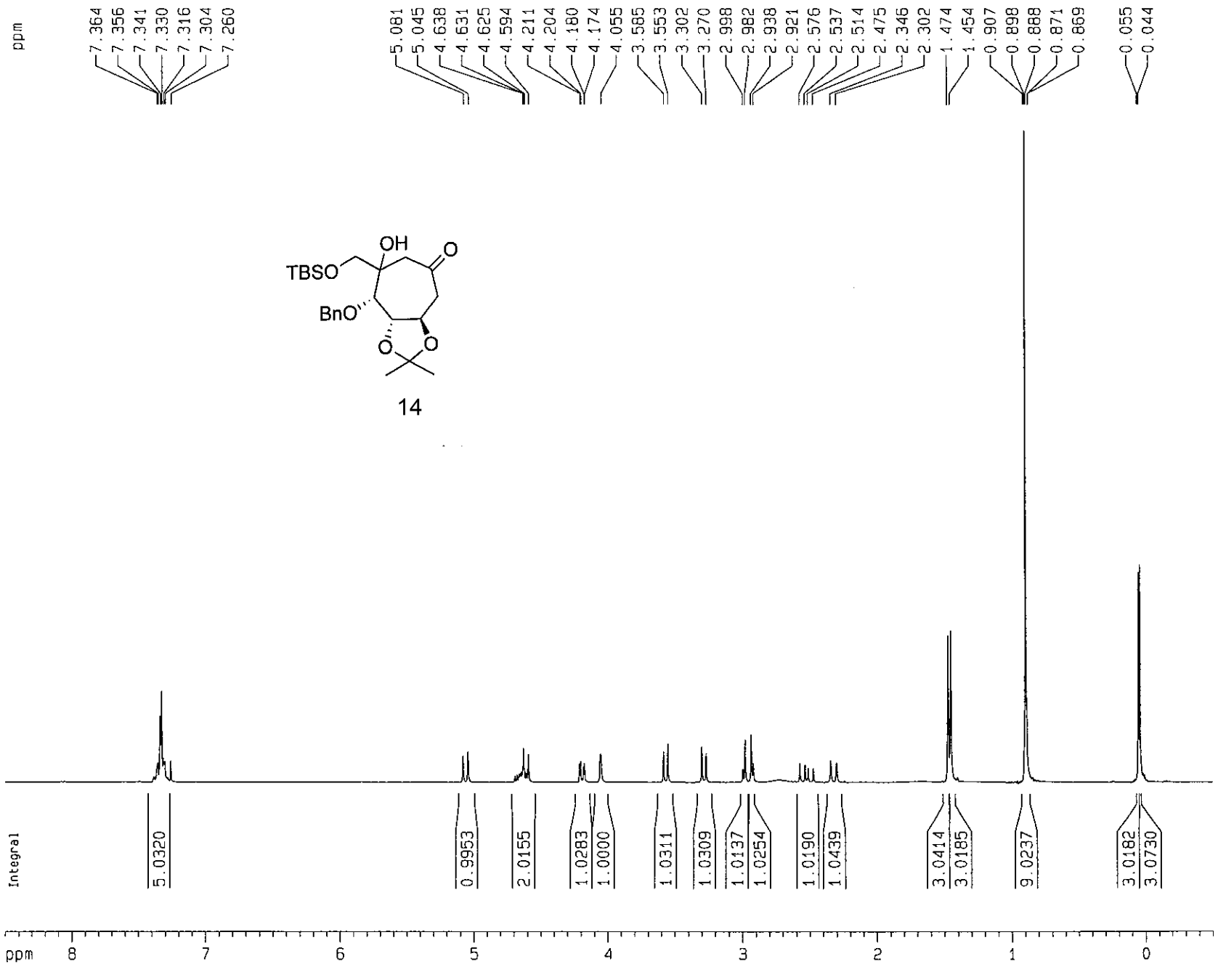

ppm
206.965
137.794
129.075
128.736
128.653
109.968
80.988
79.383
77.923
77.499
77.076
75.803
74.568
72.470
63.279
48.071
31.231
27.516
27.267
OH
OBn
OH
O
O
O
11
ppm
200
180
160
140
120
100
80
60
40
20
0

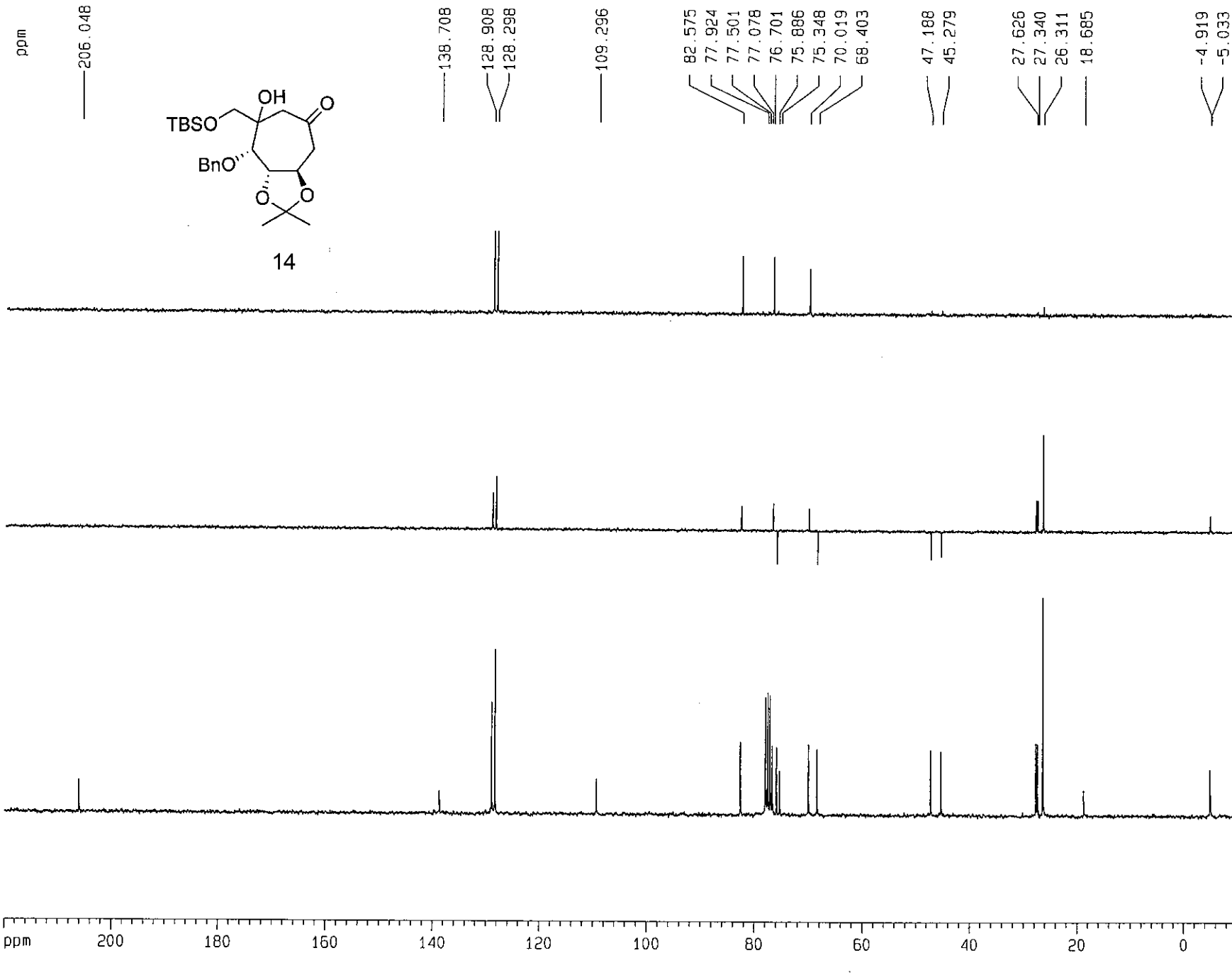

ppm
7.357
7.345
7.341
7.335
7.330
7.316
7.306
7.293
7.282
7.260
4.715
4.704
4.522
4.514
3.755
3.745
3.741
3.730
3.714
3.702
2.767
2.757
2.715
2.685
2.649
2.638
2.631
2.142
2.135
1.623
1.616
1.404
1.384
1.344
0.922
0.914
0.904
0.897
0.878
0.871
0.866
0.859
0.072
0.070
0.063
0.039
0.006
TBSO
OBn
OH
O
O
O
12
Integral
5.2291
2.0662
1.0000
1.0291
4.0256
2.8359
3.0342
3.0089
3.0191
9.0522
3.0154
3.0256
ppm
8
7
6
5
4
3
2
1
0

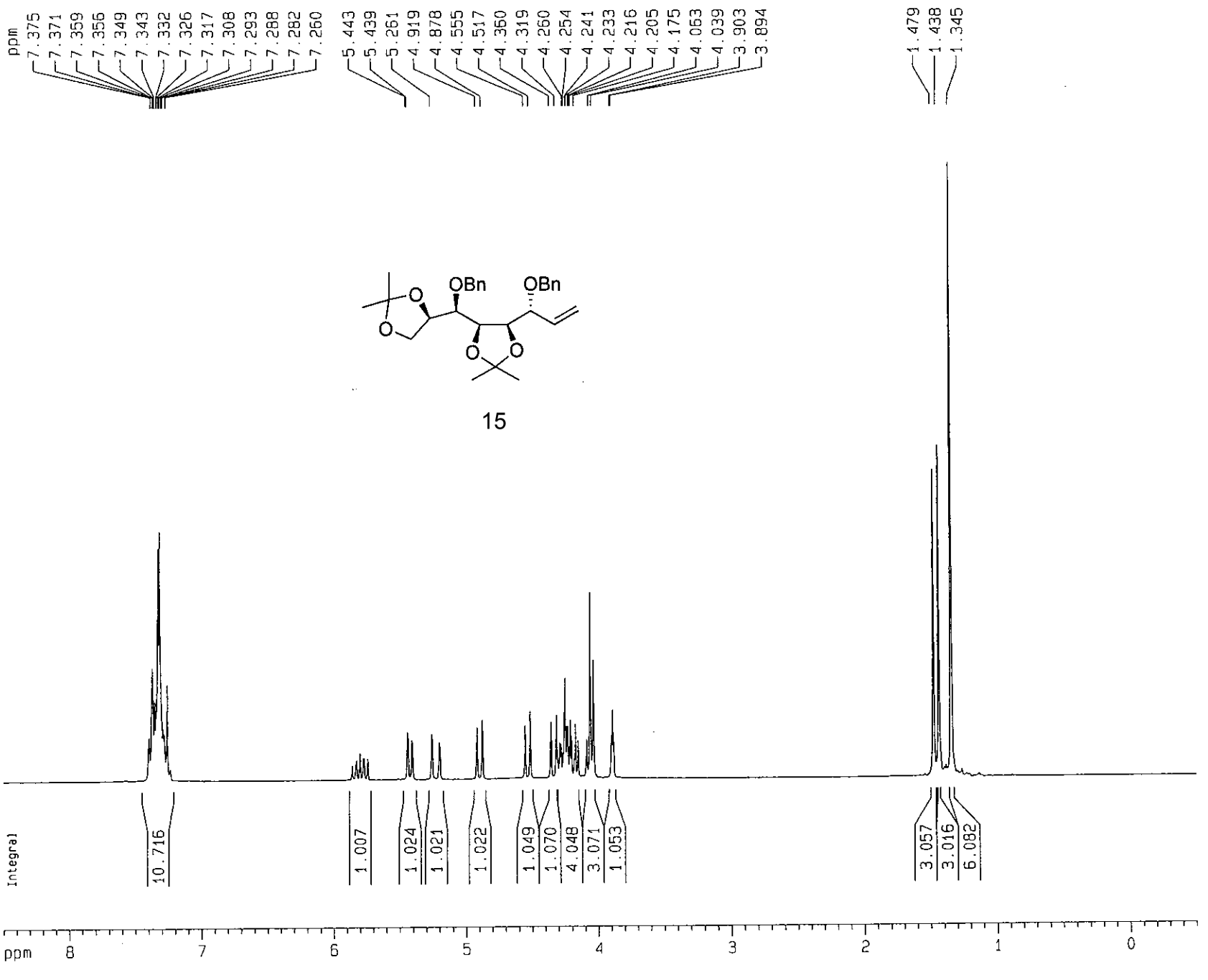

ppm
206.929
138.496
128.930
128.610
128.348
109.520
80.319
79.303
77.922
77.498
77.075
74.972
74.408
72.510
64.032
48.440
31.164
27.548
27.389
26.380
18.769
-4.897
TBSO
OBn
OH
O
O
O
12
ppm
200
180
160
140
120
100
80
60
40
20
0

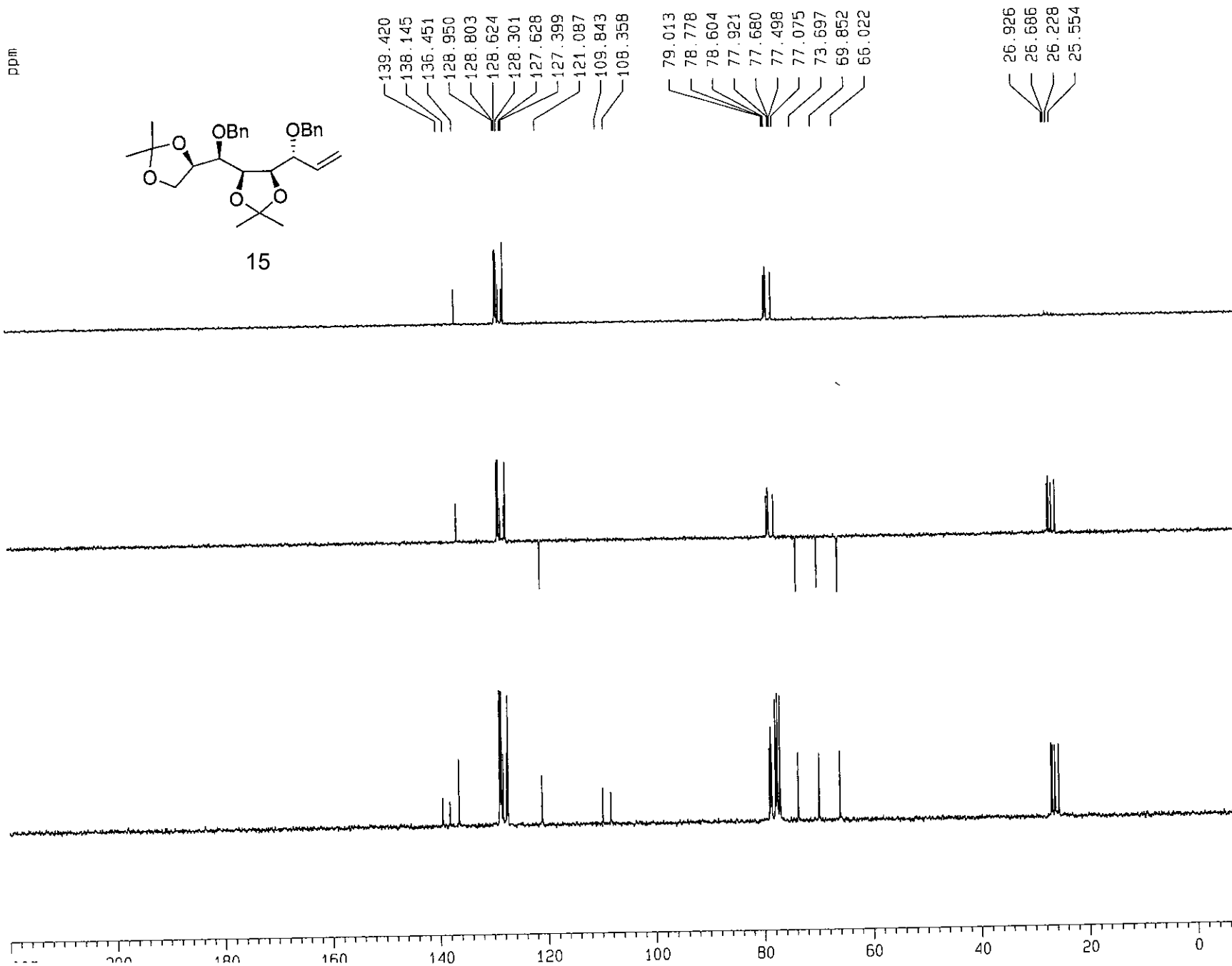

ppm
7.356
7.332
7.325
7.306
7.299
7.286
7.280
7.260
7.258
4.616
4.577
4.540
4.503
4.478
4.465
4.424
4.412
4.362
4.162
4.142
3.886
3.866
3.860
3.840
2.703
2.695
2.689
2.672
2.125
1.638
1.394
1.370
1.347
0.922
0.904
0.067
TBSO
BnO
O
O
O
O
13
Integral
5.0919
1.0672
1.0014
3.0290
1.0676
1.0000
2.0738
3.0500
3.0123
3.0173
9.0614
6.0401
ppm
8
7
6
5
4
3
2
1
0


ppm
208.024
206.279
137.160
129.093
128.801
110.086
81.574
80.258
77.923
77.500
77.077
75.222
73.737
69.444
47.559
31.211
27.485
27.237
26.311
18.947
-4.944
TBSO
BnO
O
O
O
O
13
ppm
200
180
160
140
120
100
80
60
40
20
0

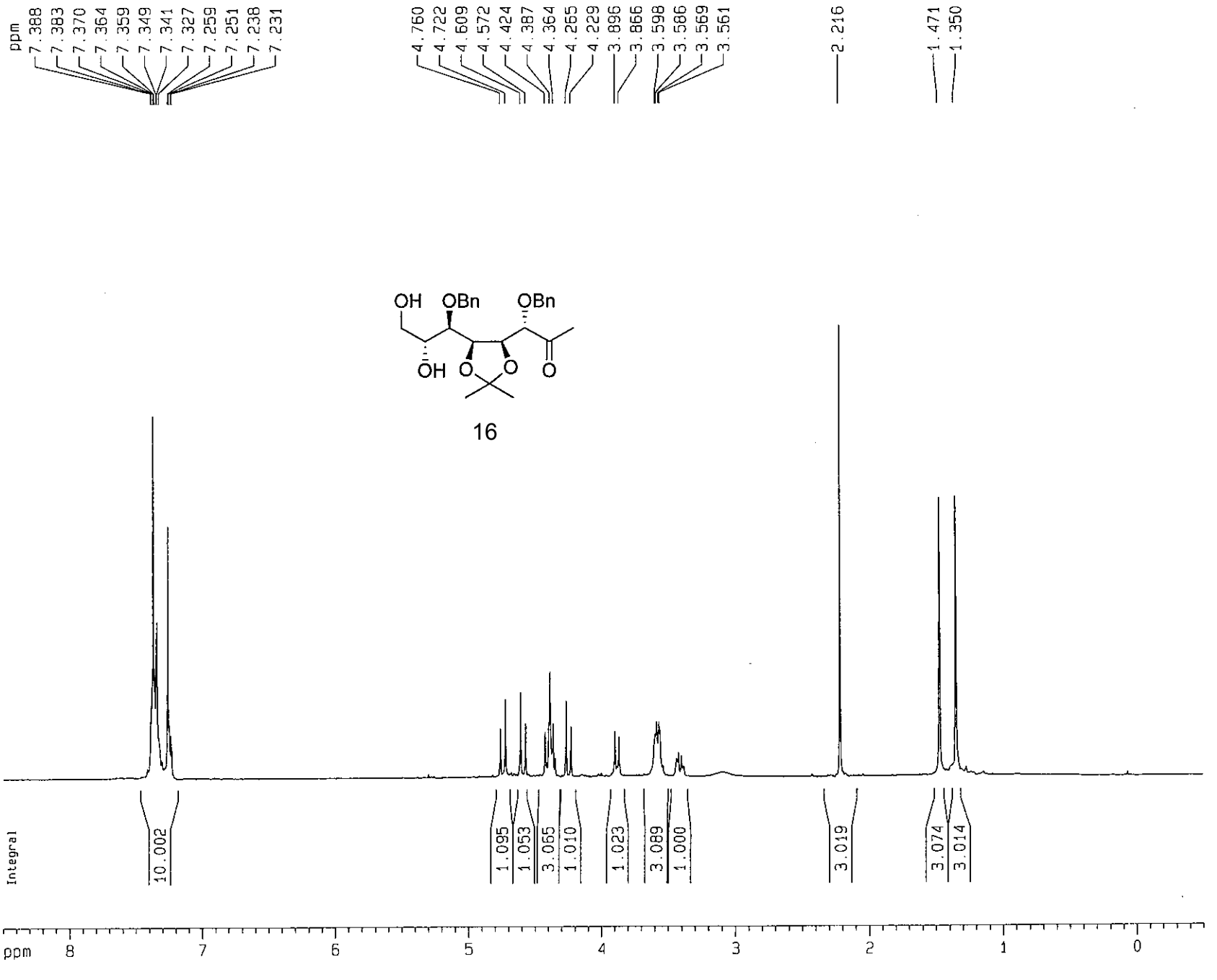

ppm
7.364
7.356
7.341
7.330
7.316
7.304
7.260
5.081
5.045
4.638
4.631
4.625
4.594
4.211
4.204
4.180
4.174
4.055
3.585
3.553
3.302
3.270
2.998
2.982
2.938
2.921
2.576
2.537
2.514
2.475
2.346
2.302
1.474
1.454
0.907
0.898
0.888
0.871
0.869
0.055
0.044
OH
O
TBSO
BnO
O
O
14
Integral
5.0320
0.9953
2.0155
1.0283
1.0000
1.0311
1.0309
1.0137
1.0254
1.0190
1.0439
3.0414
3.0185
9.0237
3.0182
3.0730
ppm
8
7
6
5
4
3
2
1
0

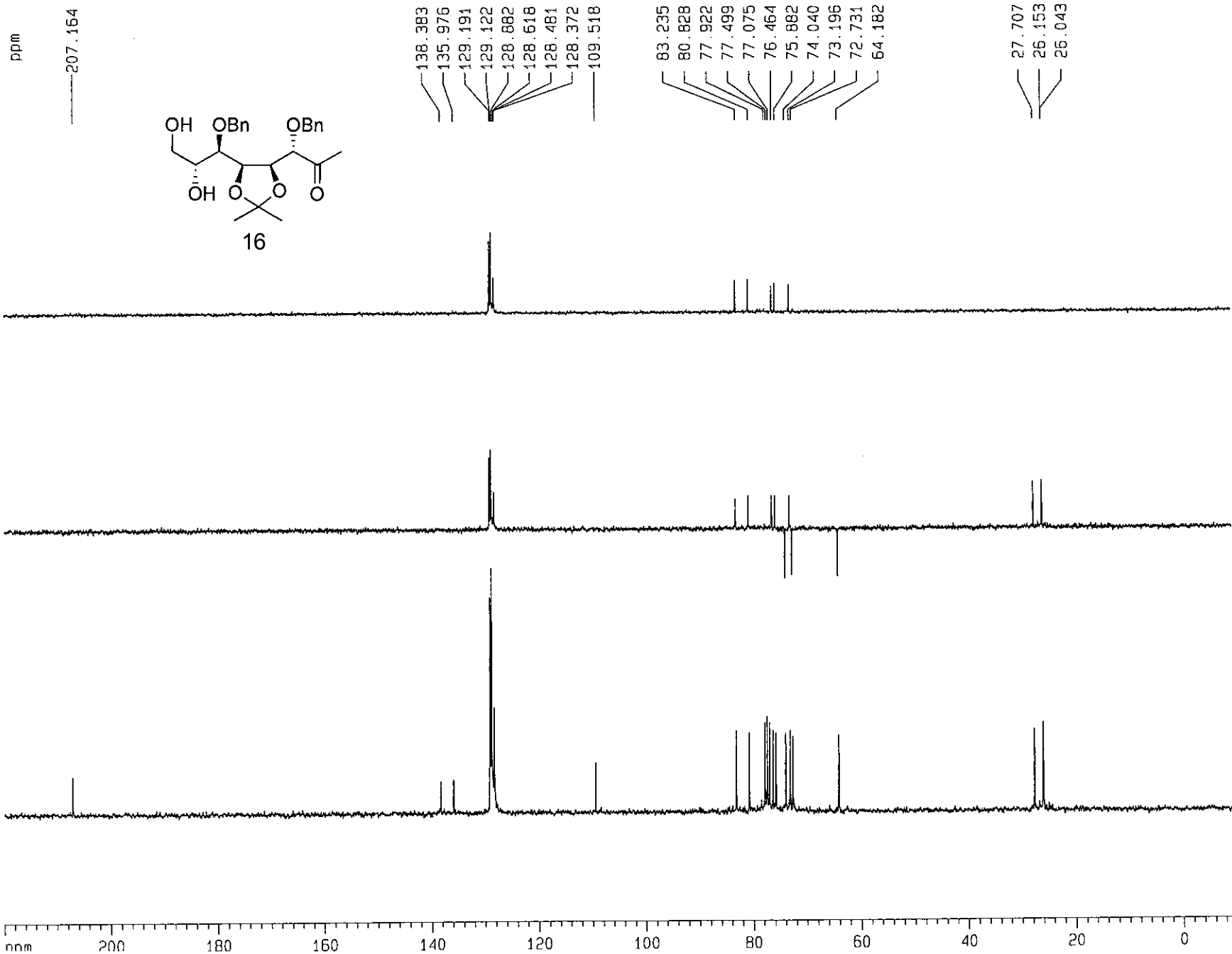

ppm
206.048
138.708
128.908
128.298
109.296
82.575
77.924
77.501
77.078
76.701
75.886
75.348
70.019
68.403
47.188
45.279
27.626
27.340
26.311
18.685
-4.919
-5.033
OH
O
TBSO
BnO
O
O
14
ppm
200
180
160
140
120
100
80
60
40
20
0

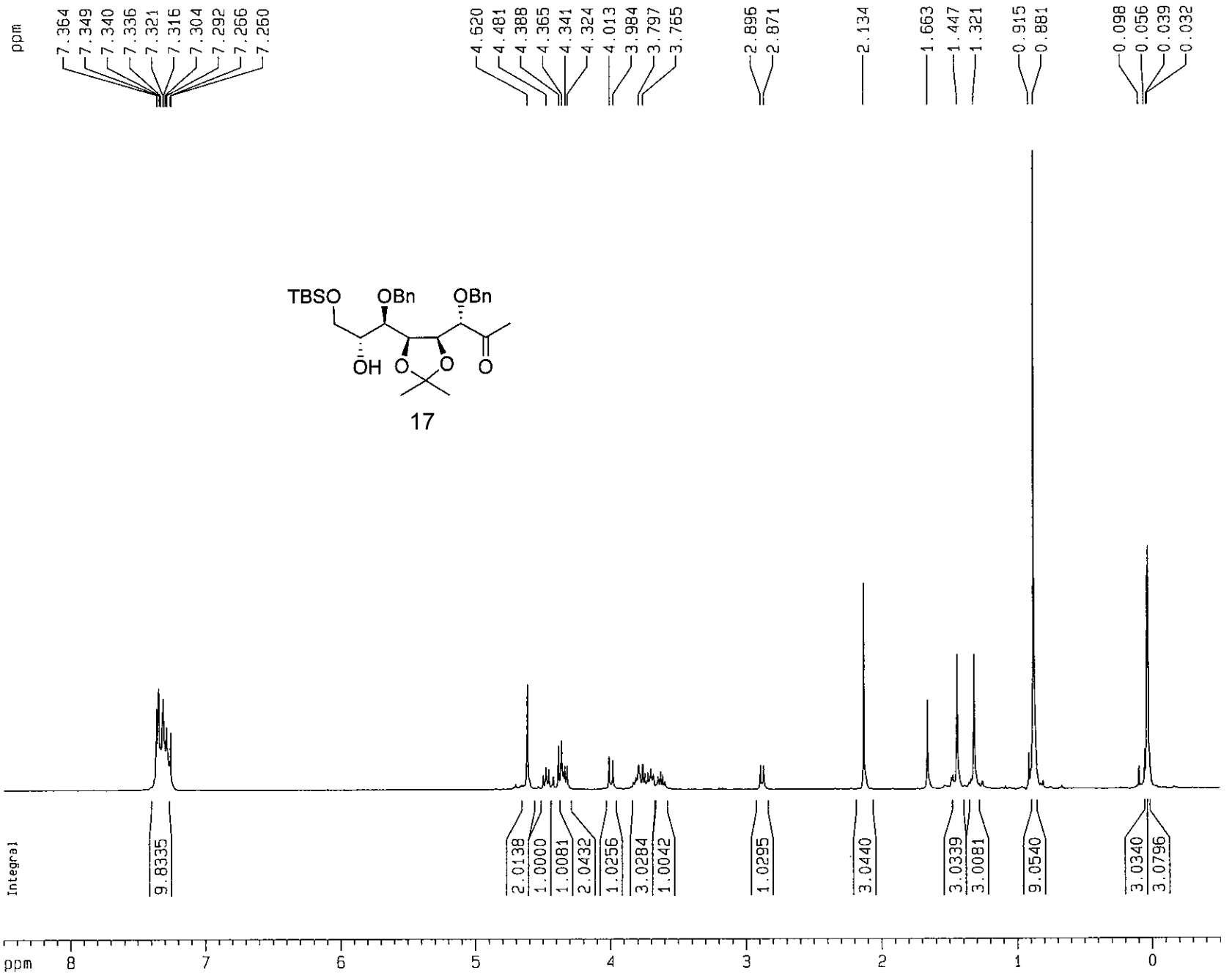

ppm
7.375
7.371
7.359
7.356
7.349
7.343
7.332
7.326
7.317
7.308
7.293
7.288
7.282
7.260
5.443
5.439
5.261
4.919
4.878
4.555
4.517
4.360
4.319
4.260
4.254
4.241
4.233
4.216
4.205
4.175
4.063
4.039
3.903
3.894
1.479
1.438
1.345
OBn
OBn
15
Integral
10.716
1.007
1.024
1.021
1.022
1.049
1.070
4.048
3.071
1.053
3.057
3.016
6.082
ppm
8
7
6
5
4
3
2
1
0

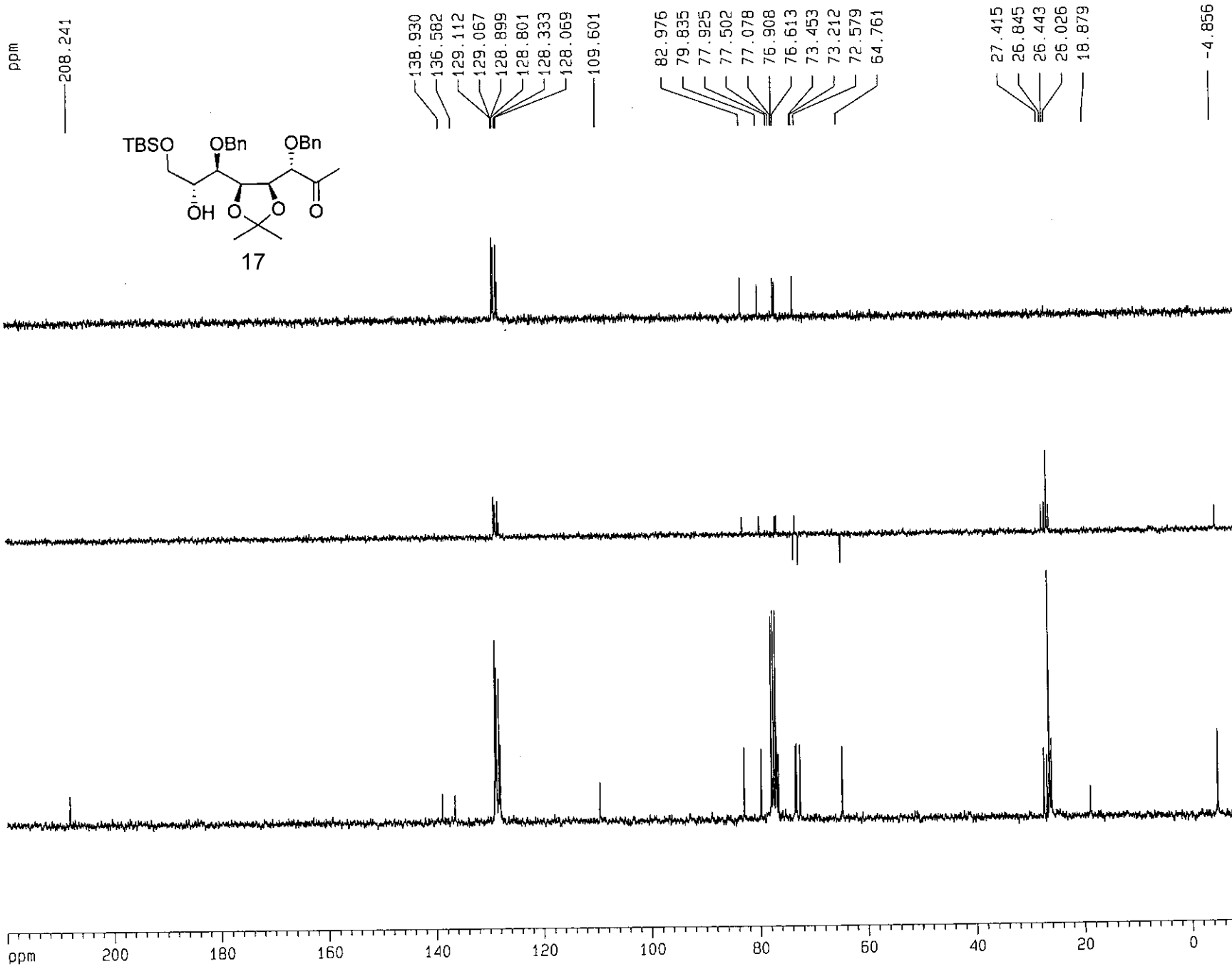

ppm
139.420
138.145
136.451
128.950
128.803
128.624
128.301
127.628
127.399
121.087
109.843
108.358
79.013
78.778
78.604
77.921
77.680
77.498
77.075
73.697
69.852
66.022
26.926
26.686
26.228
25.554
OBn
OBn
O
O
O
O
200
180
160
140
120
100
80
60
40
20
0

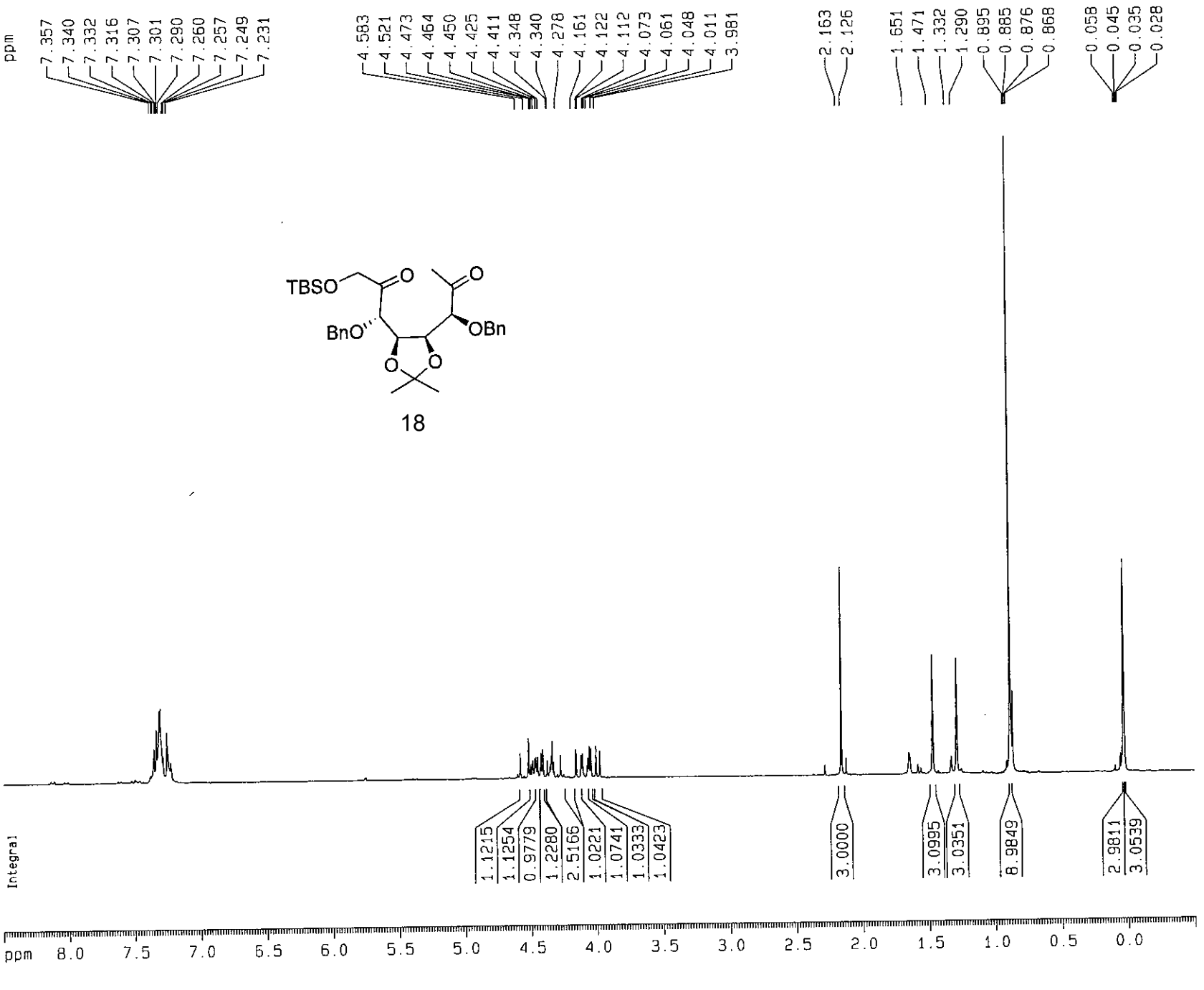
15

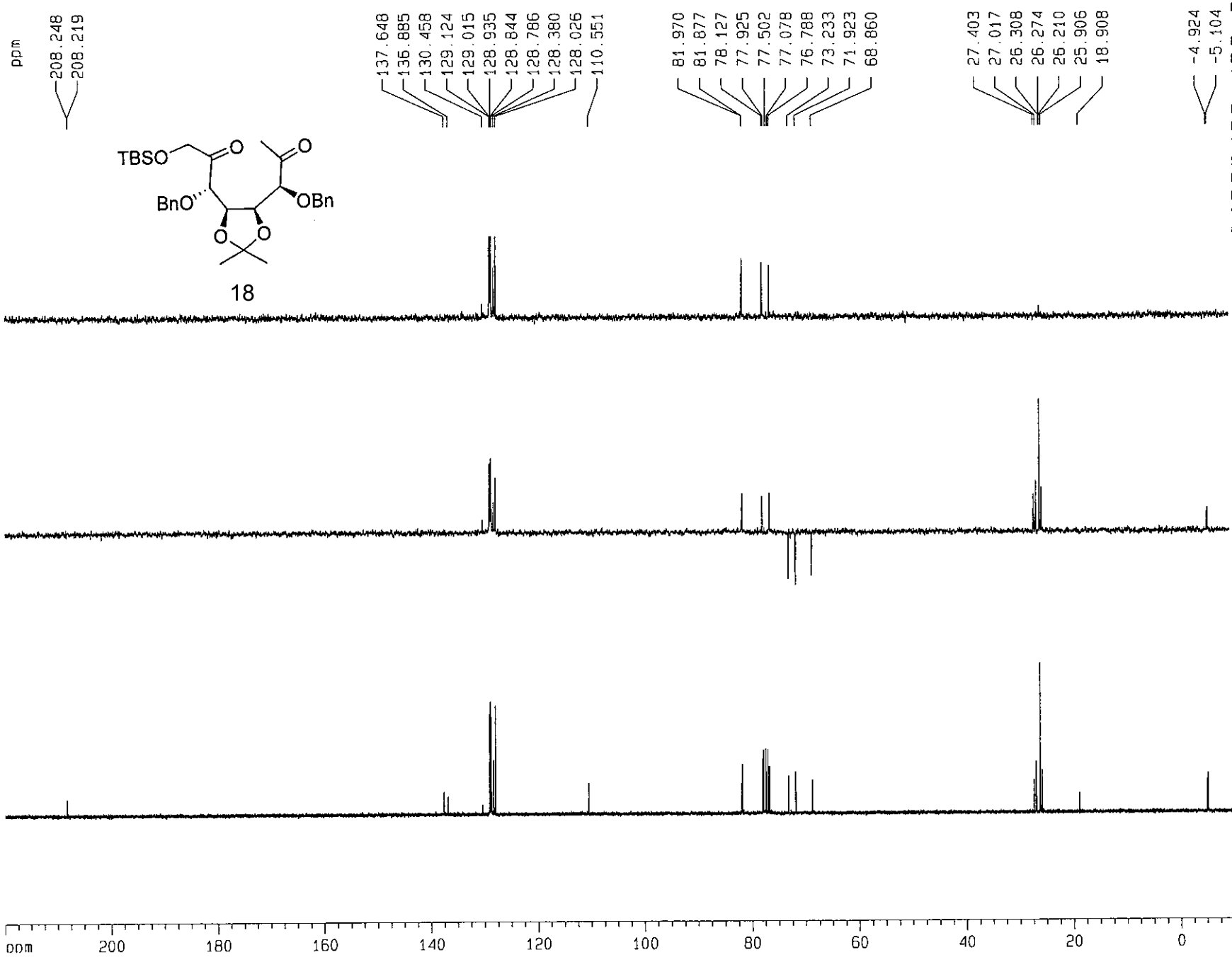

ppm
7.388
7.383
7.370
7.364
7.359
7.349
7.341
7.327
7.259
7.251
7.238
7.231
4.760
4.722
4.609
4.572
4.424
4.387
4.364
4.265
4.229
3.896
3.866
3.598
3.586
3.569
3.561
2.216
1.471
1.350
OH
OBn
OBn
OH
O
O
O
16
Integral
10.002
1.095
1.053
3.065
1.010
1.023
3.089
1.000
3.019
3.074
3.014
ppm
8
7
6
5
4
3
2
1
0


ppm
207.164
138.383
135.976
129.191
129.122
128.882
128.618
128.481
128.372
109.518
83.235
80.828
77.922
77.499
77.075
76.464
75.882
74.040
73.196
72.731
64.182
27.707
26.153
26.043
OH
OBn
OBn
OH
O
O
O
16
ppm
200
180
160
140
120
100
80
60
40
20
0

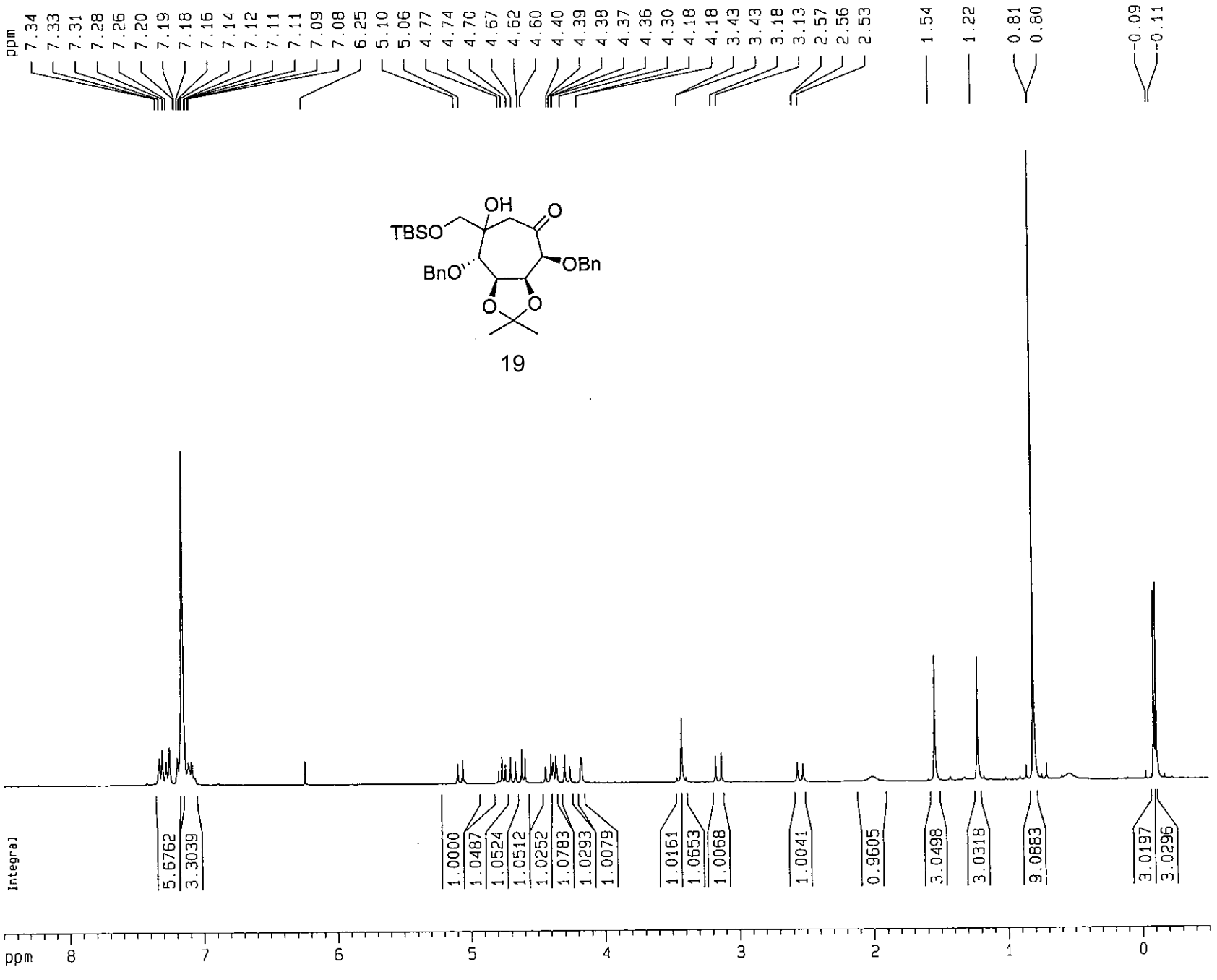

ppm
7.364
7.349
7.340
7.336
7.321
7.316
7.304
7.292
7.266
7.260
4.620
4.481
4.388
4.365
4.341
4.324
4.013
3.984
3.797
3.765
2.896
2.871
2.134
1.663
1.447
1.321
0.915
0.881
0.098
0.056
0.039
0.032
TBSO
OBn
OBn
OH
O
O
O
17
Integral
9.8335
2.0138
1.0000
1.0081
2.0432
1.0256
3.0284
1.0042
1.0295
3.0440
3.0339
3.0081
9.0540
3.0340
3.0796
ppm
8
7
6
5
4
3
2
1
0


ppm
208.241
138.930
136.582
129.112
129.067
128.899
128.801
128.333
128.069
109.601
82.976
79.835
77.925
77.502
77.078
76.908
76.613
73.453
73.212
72.579
64.761
27.415
26.845
26.443
26.026
18.879
-4.856
TBSO
OBn
OBn
OH
O
O
O
17
ppm
200
180
160
140
120
100
80
60
40
20
0

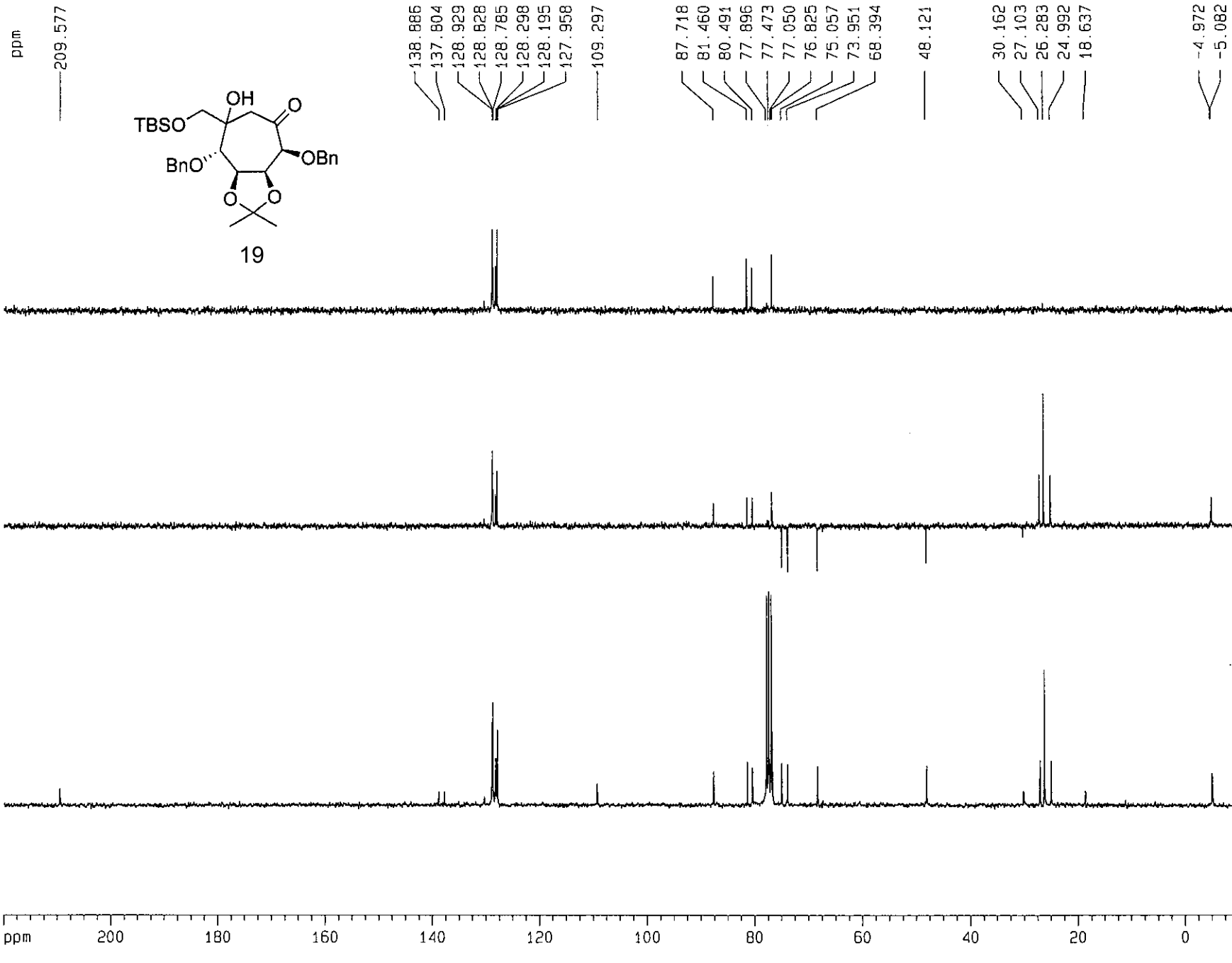

ppm
7.357
7.340
7.332
7.316
7.307
7.301
7.290
7.260
7.257
7.249
7.231
4.583
4.521
4.473
4.464
4.450
4.425
4.411
4.348
4.340
4.278
4.161
4.122
4.112
4.073
4.061
4.048
4.011
3.981
2.163
2.126
1.651
1.471
1.332
1.290
0.895
0.885
0.876
0.868
0.058
0.045
0.035
0.028
TBSO
O
O
BnO
OBn
O
O
18
Integral
1.1215
1.1254
0.9779
1.2280
2.5166
1.0221
1.0741
1.0333
1.0423
3.0000
3.0995
3.0351
8.9849
2.9811
3.0539
ppm
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

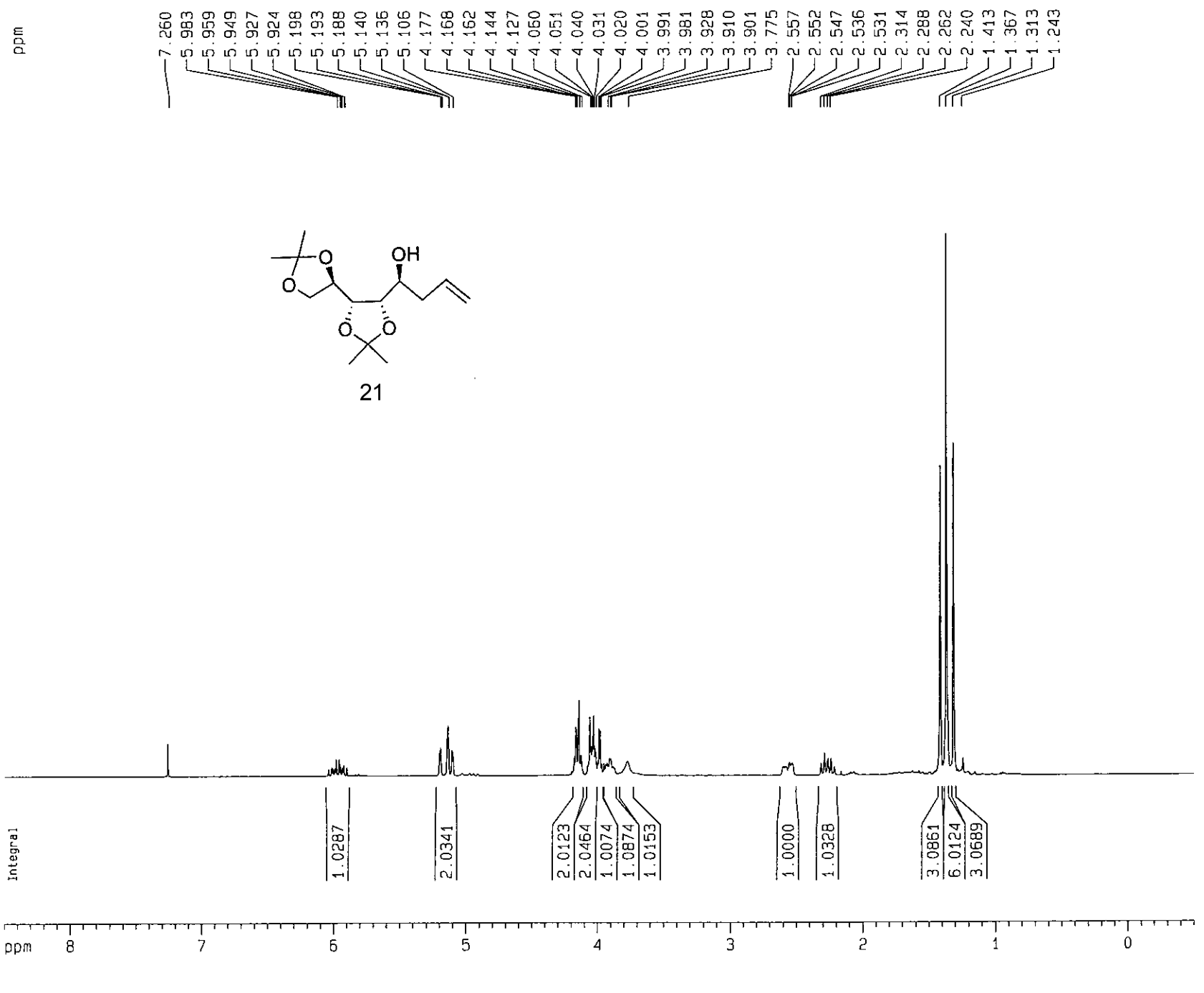

ppm
208.248
208.219
137.648
136.885
130.458
129.124
129.015
128.935
128.844
128.786
128.380
128.026
110.551
81.970
81.877
78.127
77.925
77.502
77.078
76.788
73.233
71.923
68.860
27.403
27.017
26.308
26.274
26.210
25.906
18.908
-4.924
-5.104
TBSO
BnO
OBn
O
O
O
O
18
ppm
200
180
160
140
120
100
80
60
40
20
0

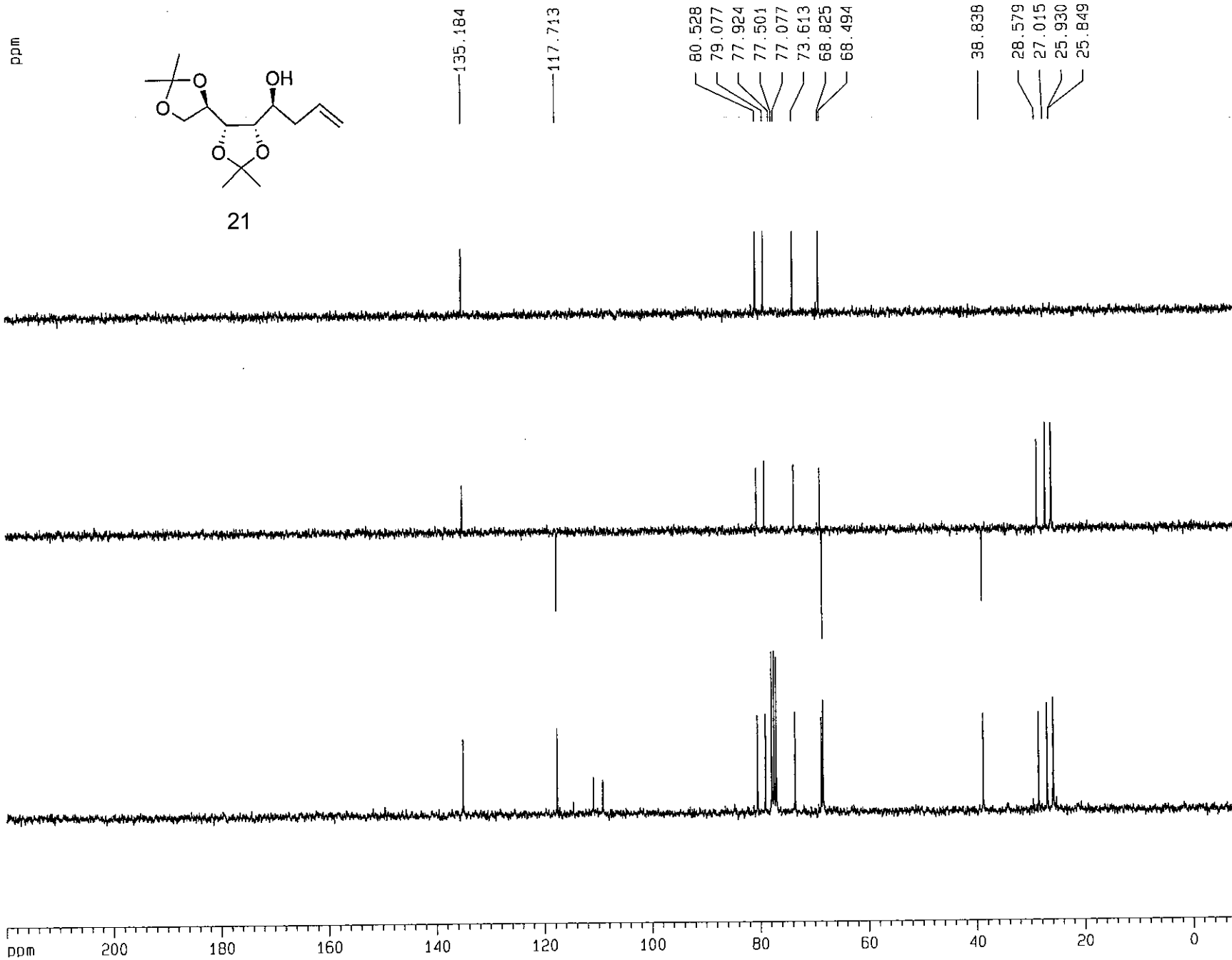
Solvent: C_6D_6:$CDCl_3$, 8:1

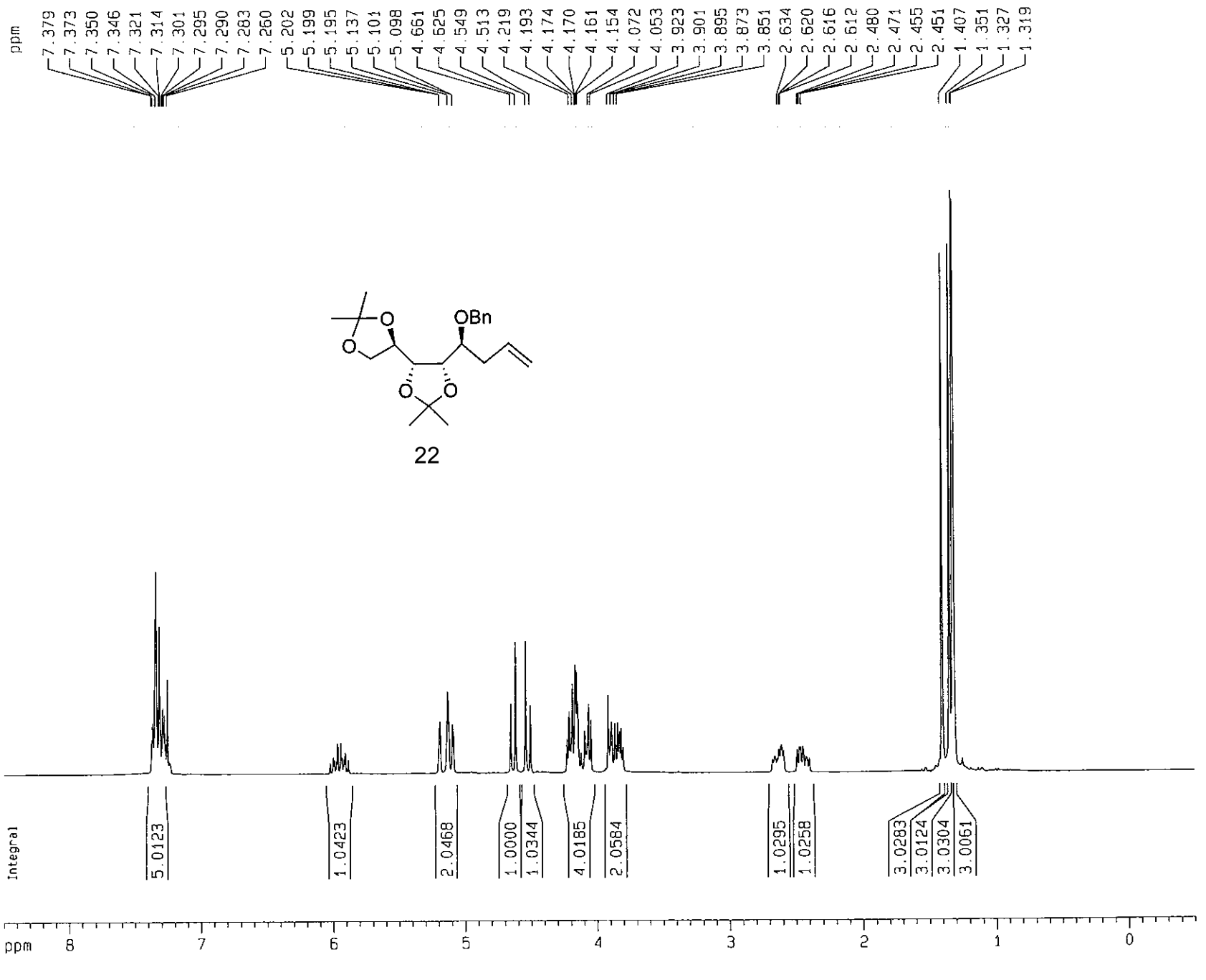


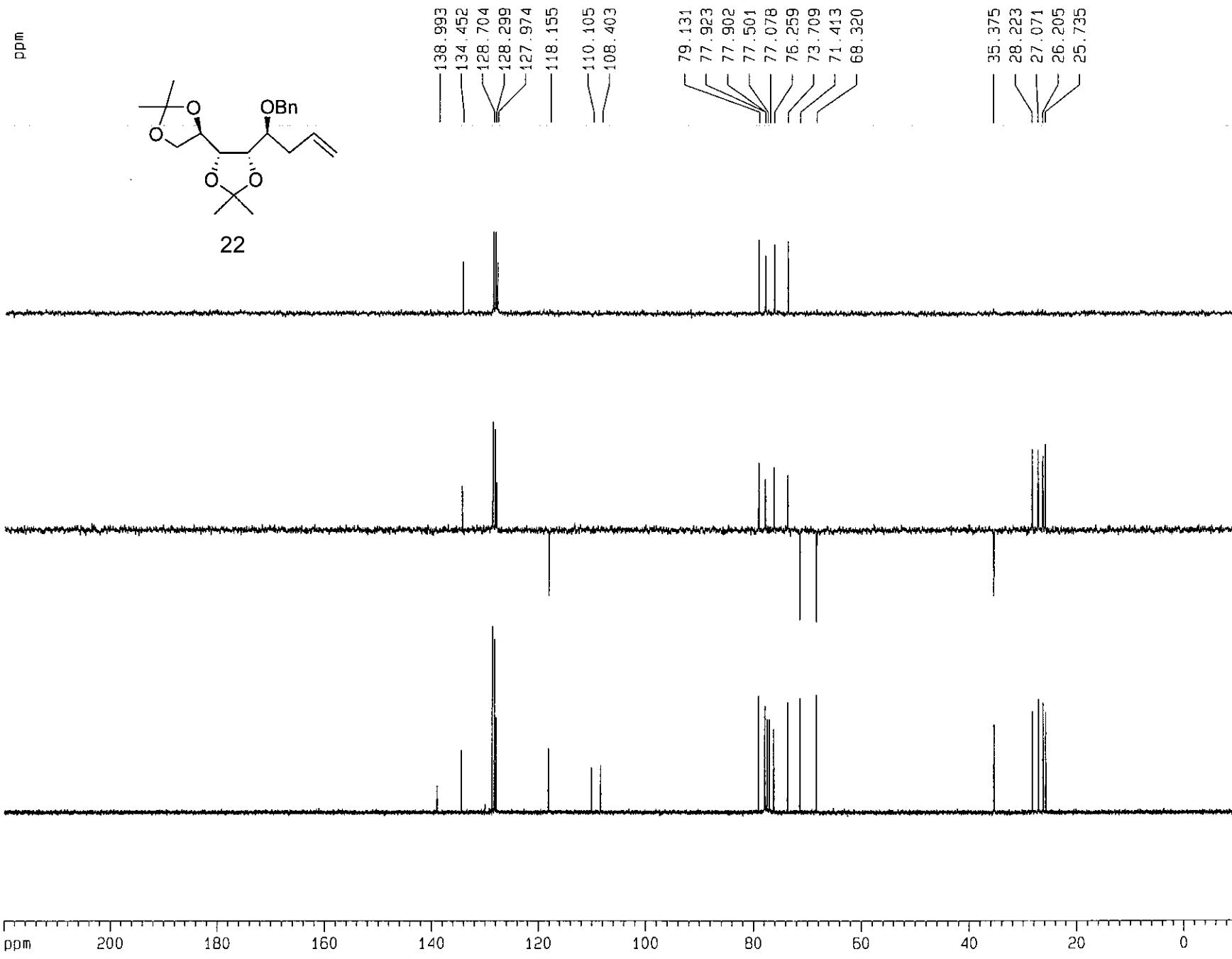
19

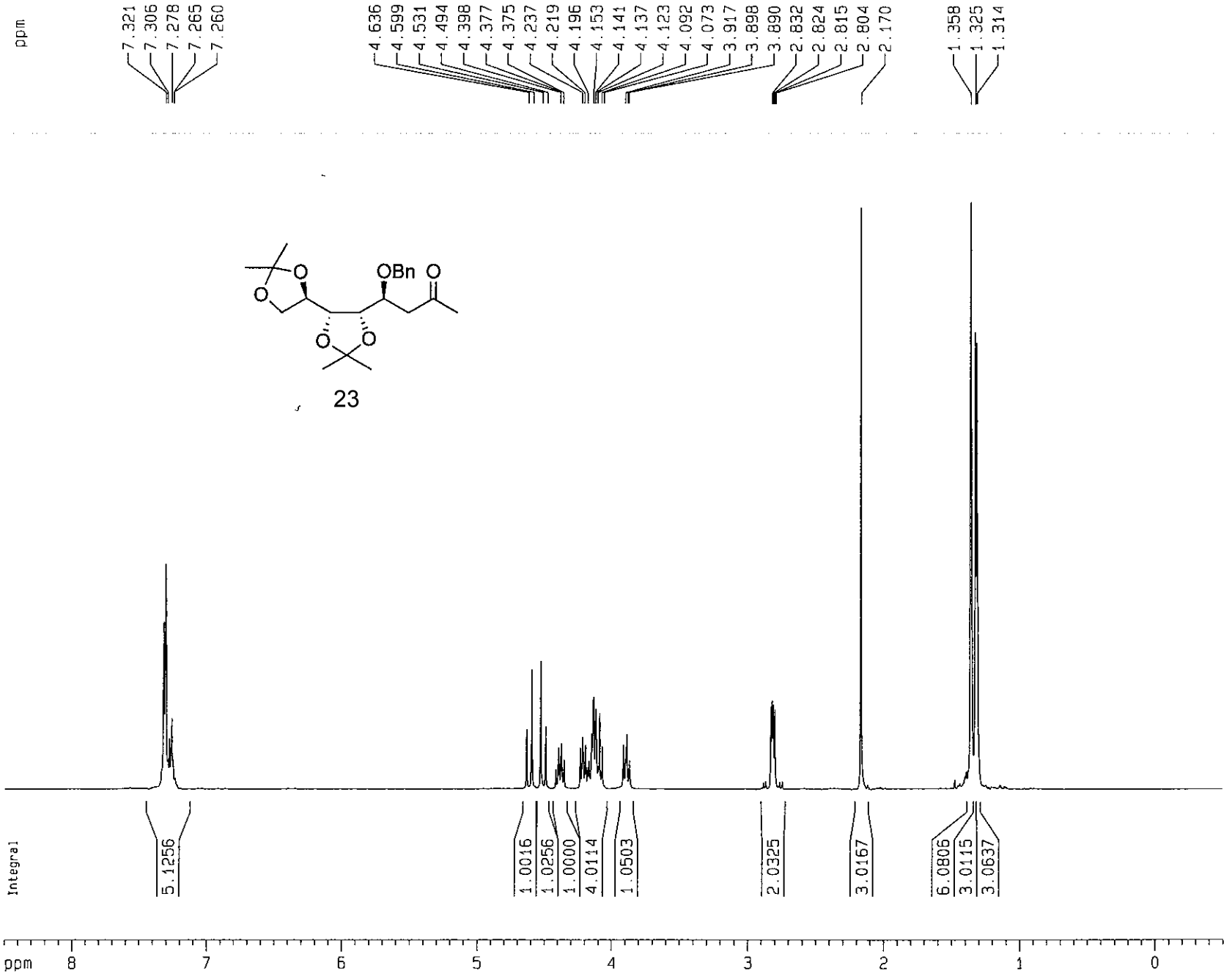

ppm
209.577
138.886
137.804
128.929
128.828
128.785
128.298
128.195
127.958
109.297
87.718
81.460
80.491
77.896
77.473
77.050
76.825
75.057
73.951
68.394
48.121
30.162
27.103
26.283
24.992
18.637
-4.972
-5.082
OH
O
TBSO
BnO
OBn
O
O
19
ppm
200
180
160
140
120
100
80
60
40
20
0

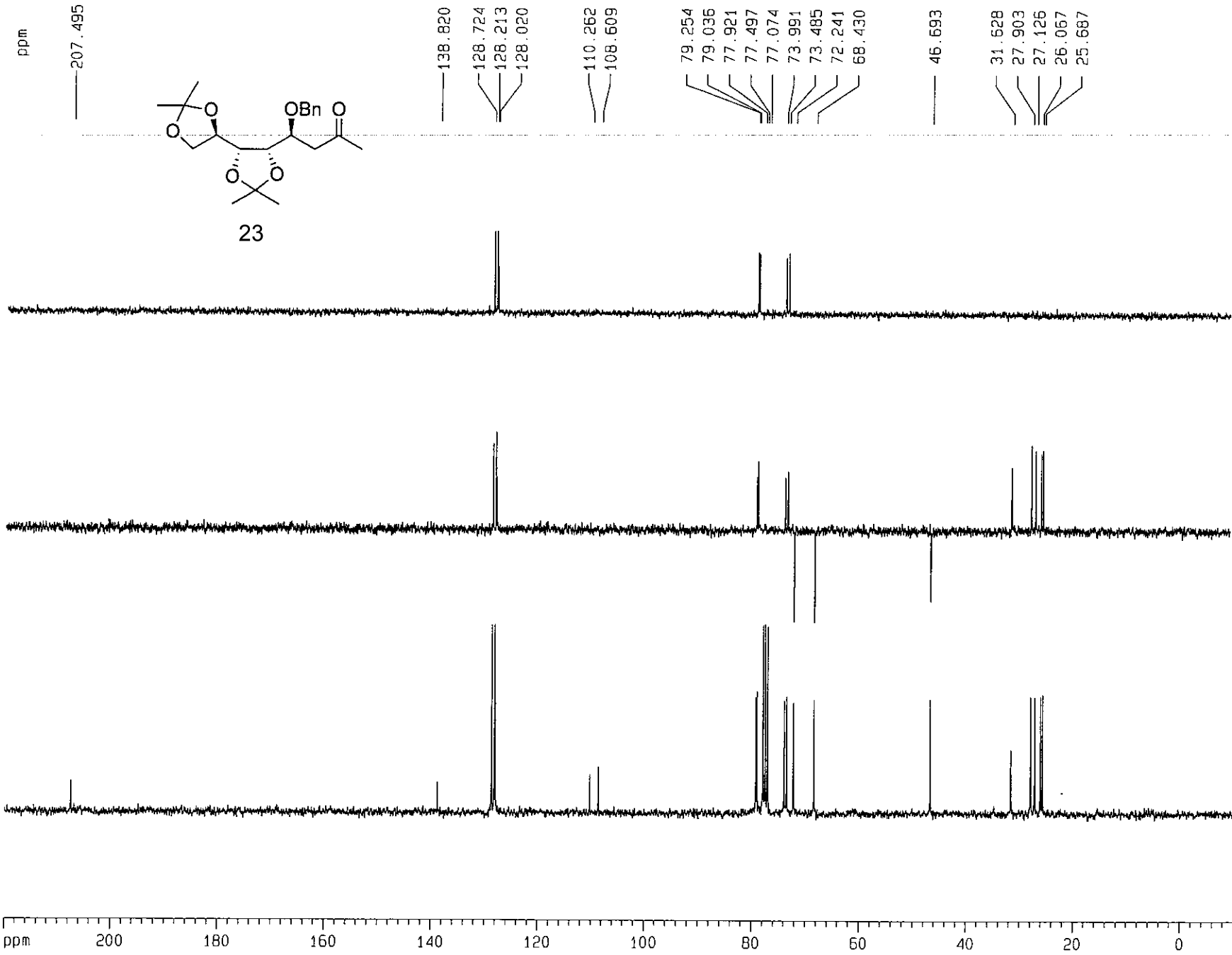

ppm
7.260
5.983
5.959
5.949
5.927
5.924
5.198
5.193
5.188
5.140
5.136
5.106
4.177
4.168
4.162
4.144
4.127
4.060
4.051
4.040
4.031
4.020
4.001
3.991
3.981
3.928
3.910
3.901
3.775
2.557
2.552
2.547
2.536
2.531
2.314
2.288
2.262
2.240
1.413
1.367
1.313
1.243
OH
O
O
O
O
21
Integral
1.0287
2.0341
2.0123
2.0464
1.0074
1.0874
1.0153
1.0000
1.0328
3.0861
6.0124
3.0689
ppm
8
7
6
5
4
3
2
1
0


ppm
135.184
117.713
80.528
79.077
77.924
77.501
77.077
73.613
68.825
68.494
38.838
28.579
27.015
25.930
25.849
OH
O
O
O
O
21
ppm
200
180
160
140
120
100
80
60
40
20
0

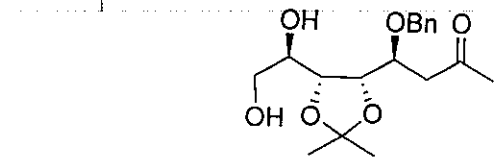

ppm
7.379
7.373
7.350
7.346
7.321
7.314
7.301
7.295
7.290
7.283
7.260
5.202
5.199
5.195
5.137
5.101
5.098
4.661
4.625
4.549
4.513
4.219
4.193
4.174
4.170
4.161
4.154
4.072
4.053
3.923
3.901
3.895
3.873
3.851
2.634
2.620
2.616
2.612
2.480
2.471
2.455
2.451
1.407
1.351
1.327
1.319
OBn
22
Integral
5.0123
1.0423
2.0468
1.0000
1.0344
4.0185
2.0584
1.0295
1.0258
3.0283
3.0124
3.0304
3.0061
ppm
8
7
6
5
4
3
2
1
0


ppm
138.993
134.452
128.704
128.299
127.974
118.155
110.105
108.403
79.131
77.923
77.902
77.501
77.078
76.259
73.709
71.413
68.320
35.375
28.223
27.071
26.205
25.735
OBn
O
O
O
O
22
ppm
200
180
160
140
120
100
80
60
40
20
0

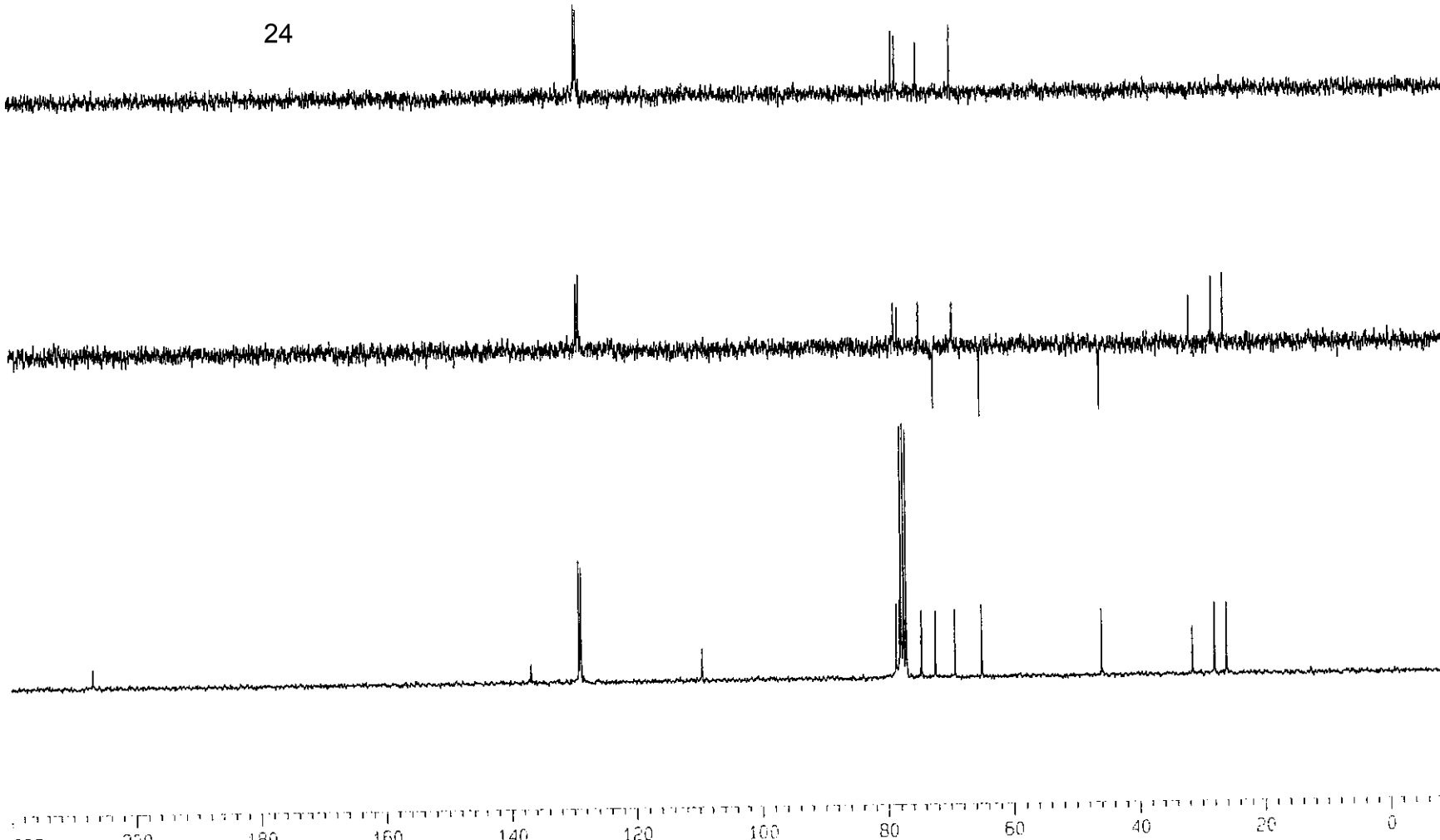

ppm
7.321
7.306
7.278
7.265
7.260
4.636
4.599
4.531
4.494
4.398
4.377
4.375
4.237
4.219
4.196
4.153
4.141
4.137
4.123
4.092
4.073
3.917
3.898
3.890
2.832
2.824
2.815
2.804
2.170
1.358
1.325
1.314
OBn
O
O
O
O
O
23
Integral
5.1256
1.0016
1.0256
1.0000
4.0114
1.0503
2.0325
3.0167
6.0806
3.0115
3.0637
ppm
8
7
6
5
4
3
2
1
0

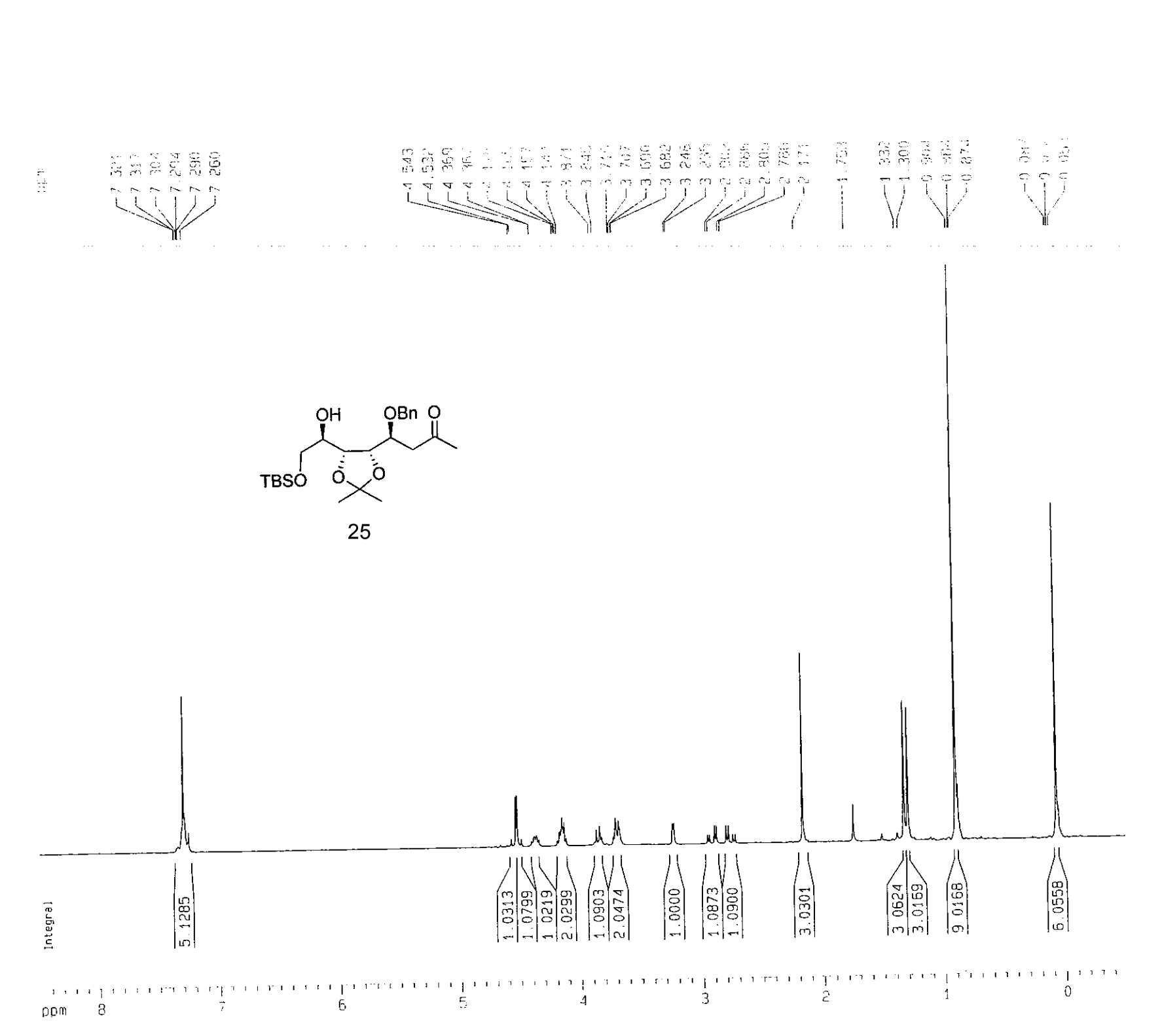

ppm
207.495
138.820
128.724
128.213
128.020
110.262
108.609
79.254
79.036
77.921
77.497
77.074
73.991
73.485
72.241
68.430
46.693
31.628
27.903
27.126
26.067
25.687
OBn
O
O
O
O
23
ppm
200
180
160
140
120
100
80
60
40
20
0

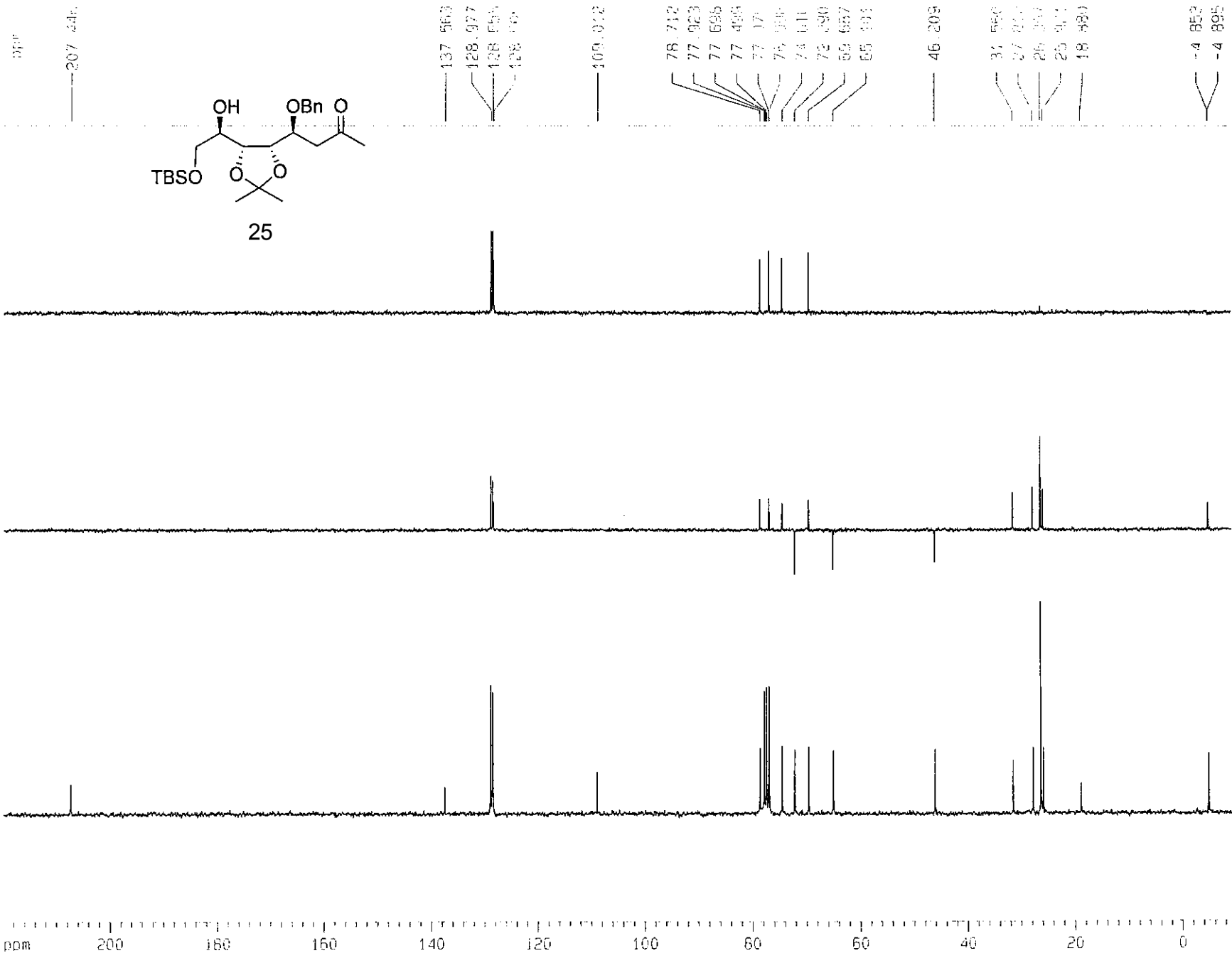
ppm
Integral
7.360
7.355
7.334
7.315
7.298
7.292
7.288
7.260
4.549
4.529
4.493
4.366
4.338
4.117
4.091
4.067
3.846
3.835
3.810
3.799
3.787
3.757
3.657
3.639
3.621
3.603
3.048
3.032
2.991
2.975
2.791
2.774
2.734
2.717
2.189
1.326
1.309
5.0535
3.0196
3.0179
3.0156
1.0970
1.0493
1.0018
2.0788
2.0120
1.0000
1.0711
1.0159
OBn
O
OH
HO
O
O
24

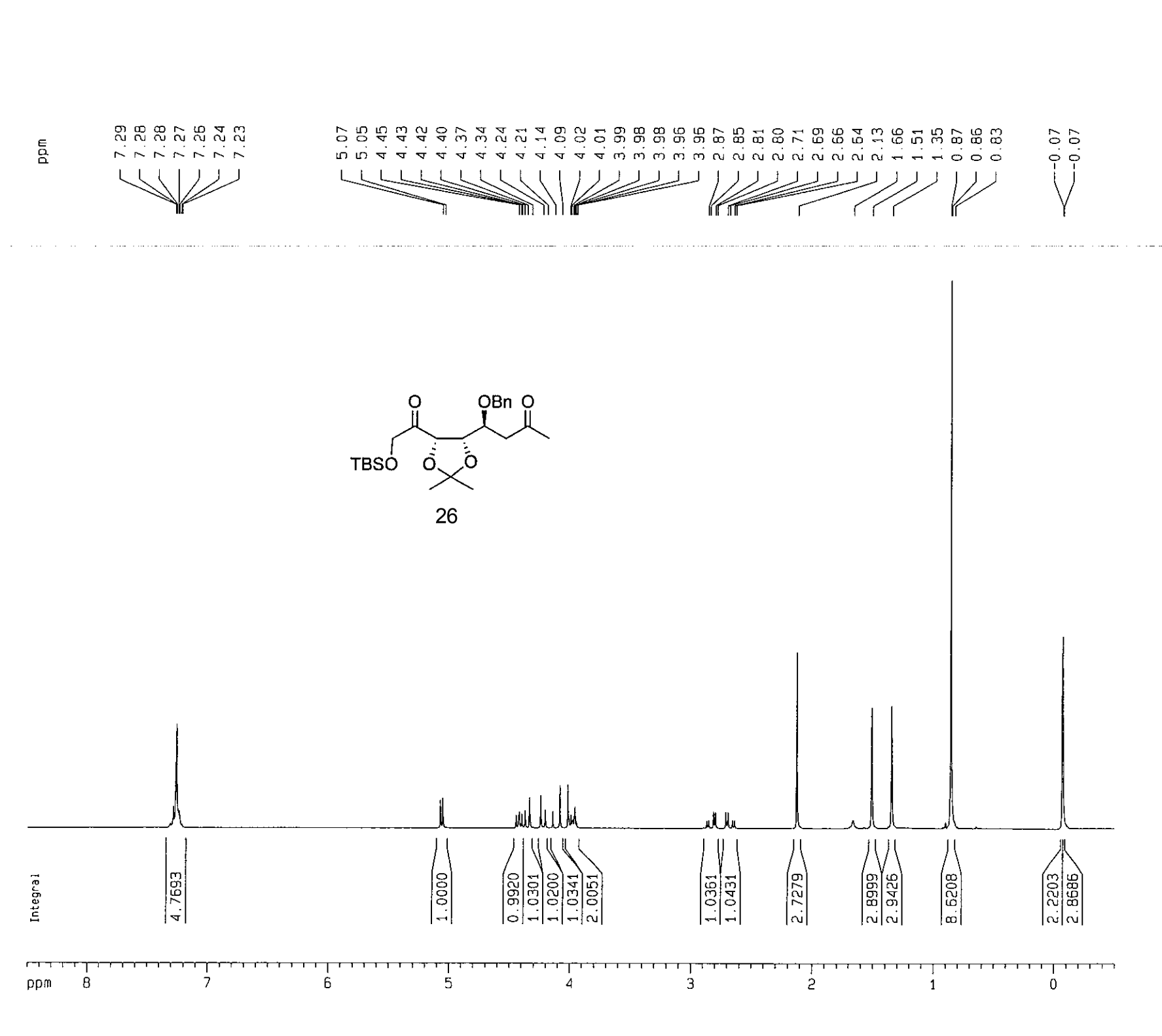


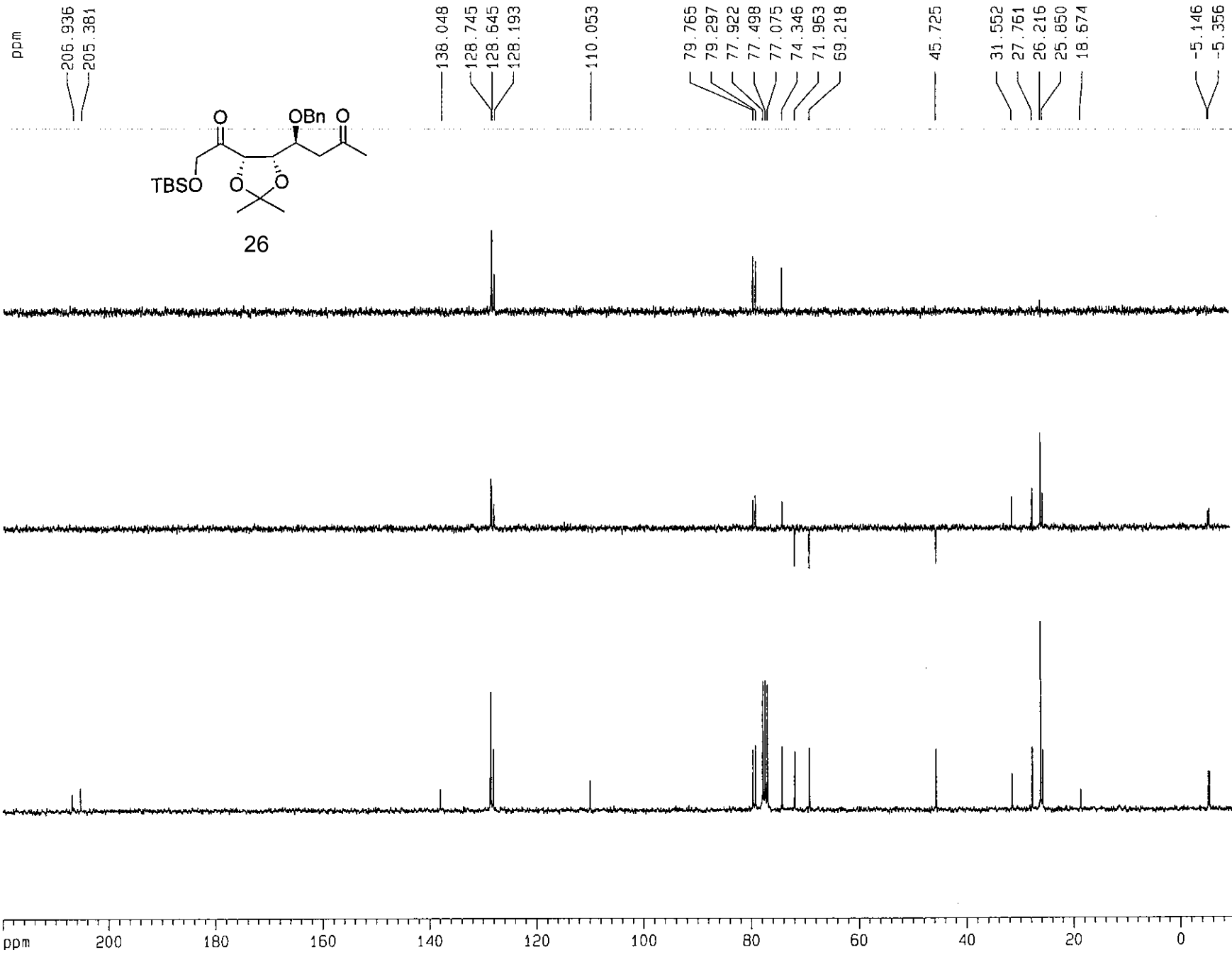
24

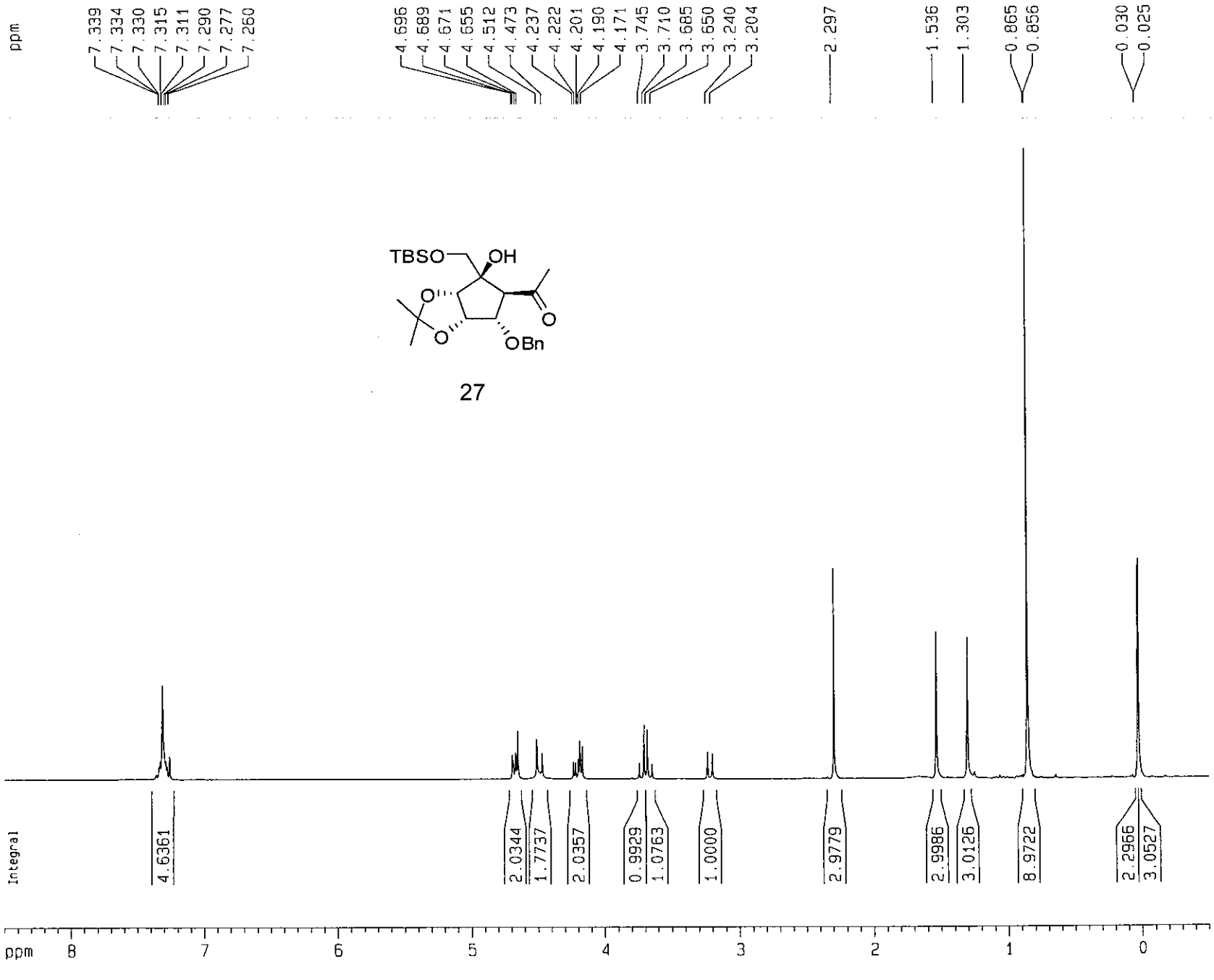



OH
OBn
O
TBSO
O
O
25
Integral
5.1285
1.0313
1.0799
1.0219
2.0299
1.0903
2.0474
1.0000
1.0873
1.0900
3.0301
3.0624
3.0169
9.0168
6.0558
ppm
8
7
6
5
4
3
2
1
0

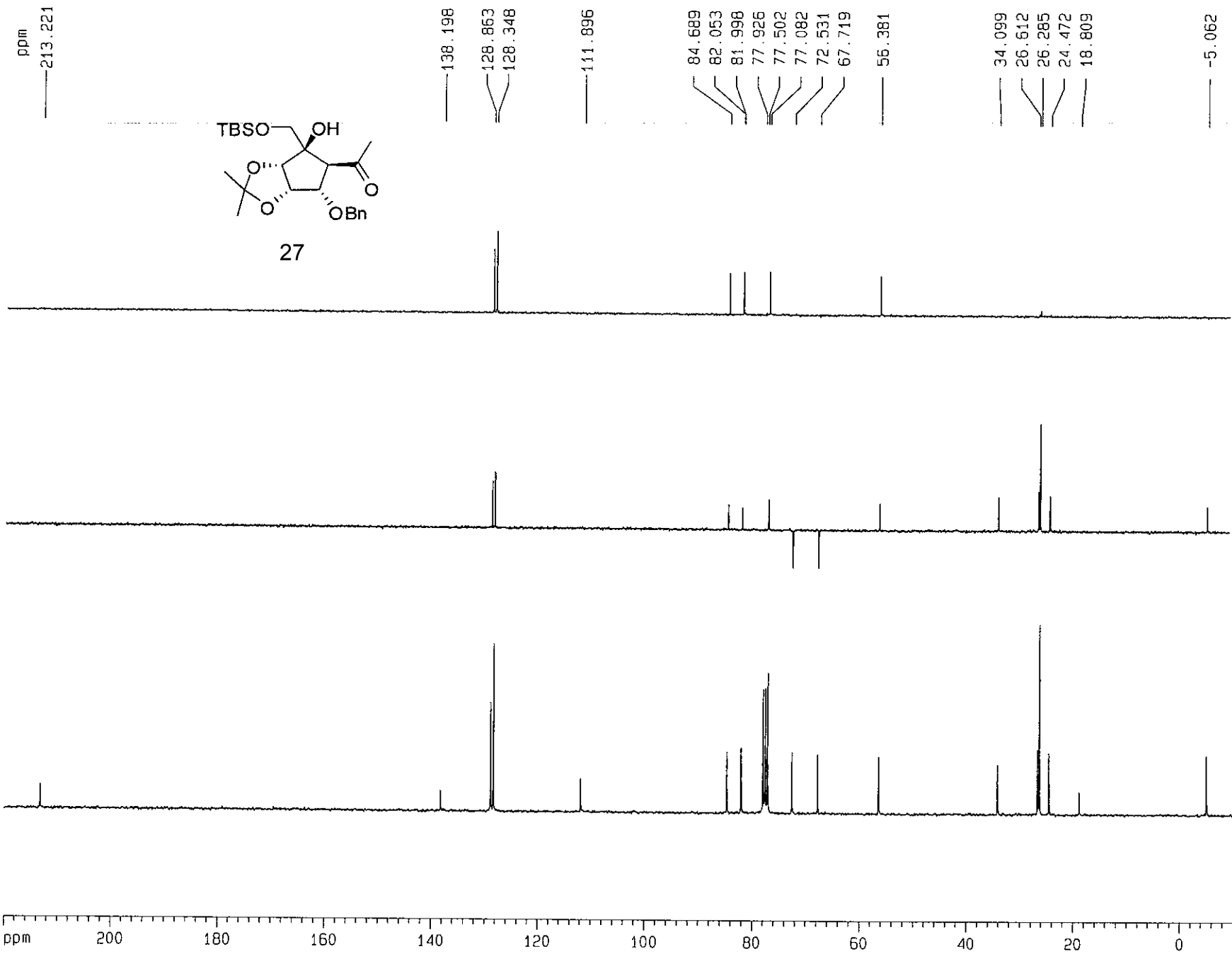

OH
OBn
O
TBSO
O
O
25
ppm
200
180
160
140
120
100
80
60
40
20
0

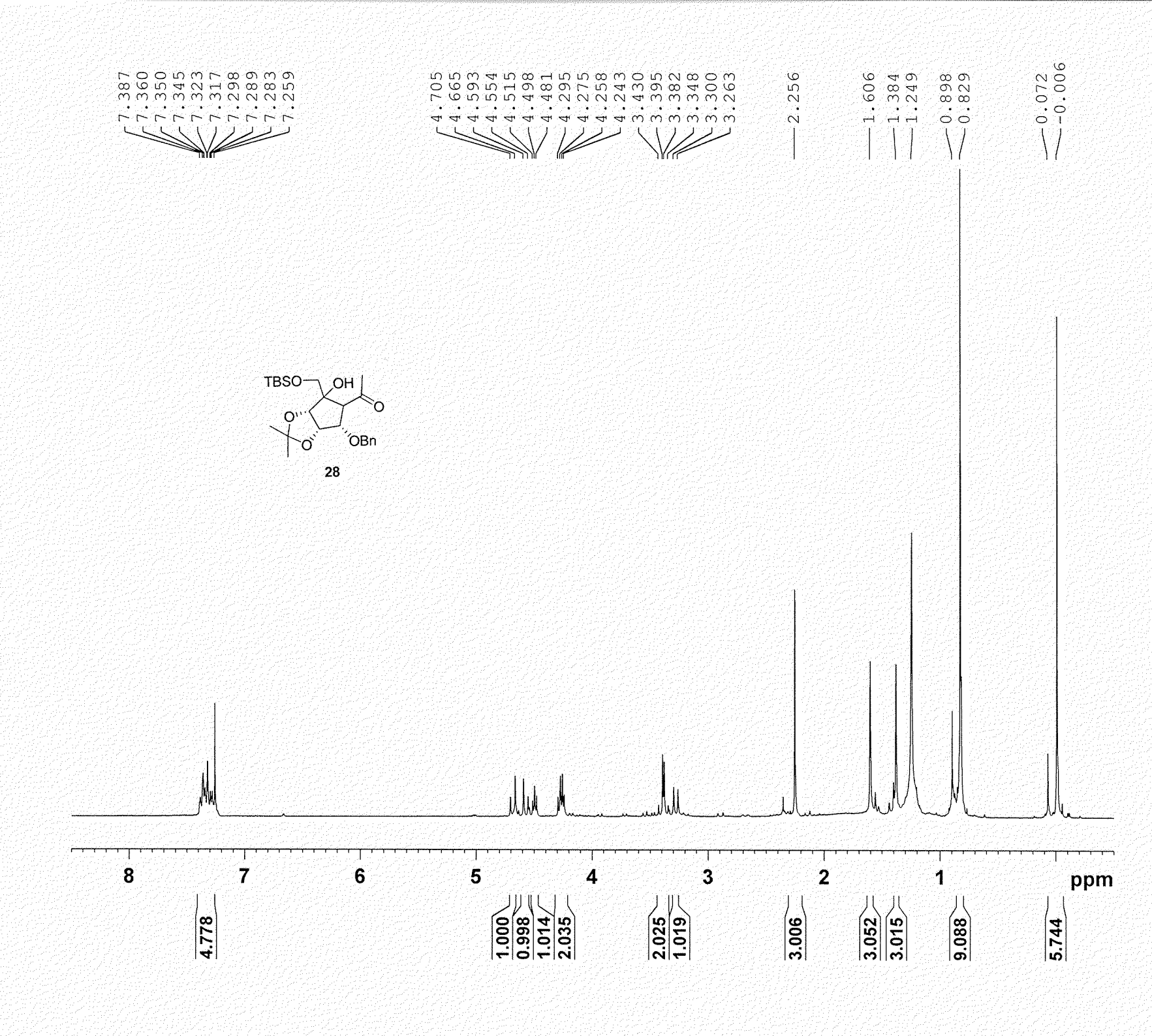

ppm
7.29
7.28
7.28
7.27
7.26
7.24
7.23
5.07
5.05
4.45
4.43
4.42
4.40
4.37
4.34
4.24
4.21
4.14
4.09
4.02
4.01
3.99
3.98
3.98
3.96
3.96
2.87
2.85
2.81
2.80
2.71
2.69
2.66
2.64
2.13
1.66
1.51
1.35
0.87
0.86
0.83
-0.07
-0.07
O
OBn
O
TBSO
O
O
26
Integral
4.7693
1.0000
0.9920
1.0301
1.0200
1.0341
2.0051
1.0361
1.0431
2.7279
2.8999
2.9426
8.6208
2.2203
2.8686
ppm
8
7
6
5
4
3
2
1
0

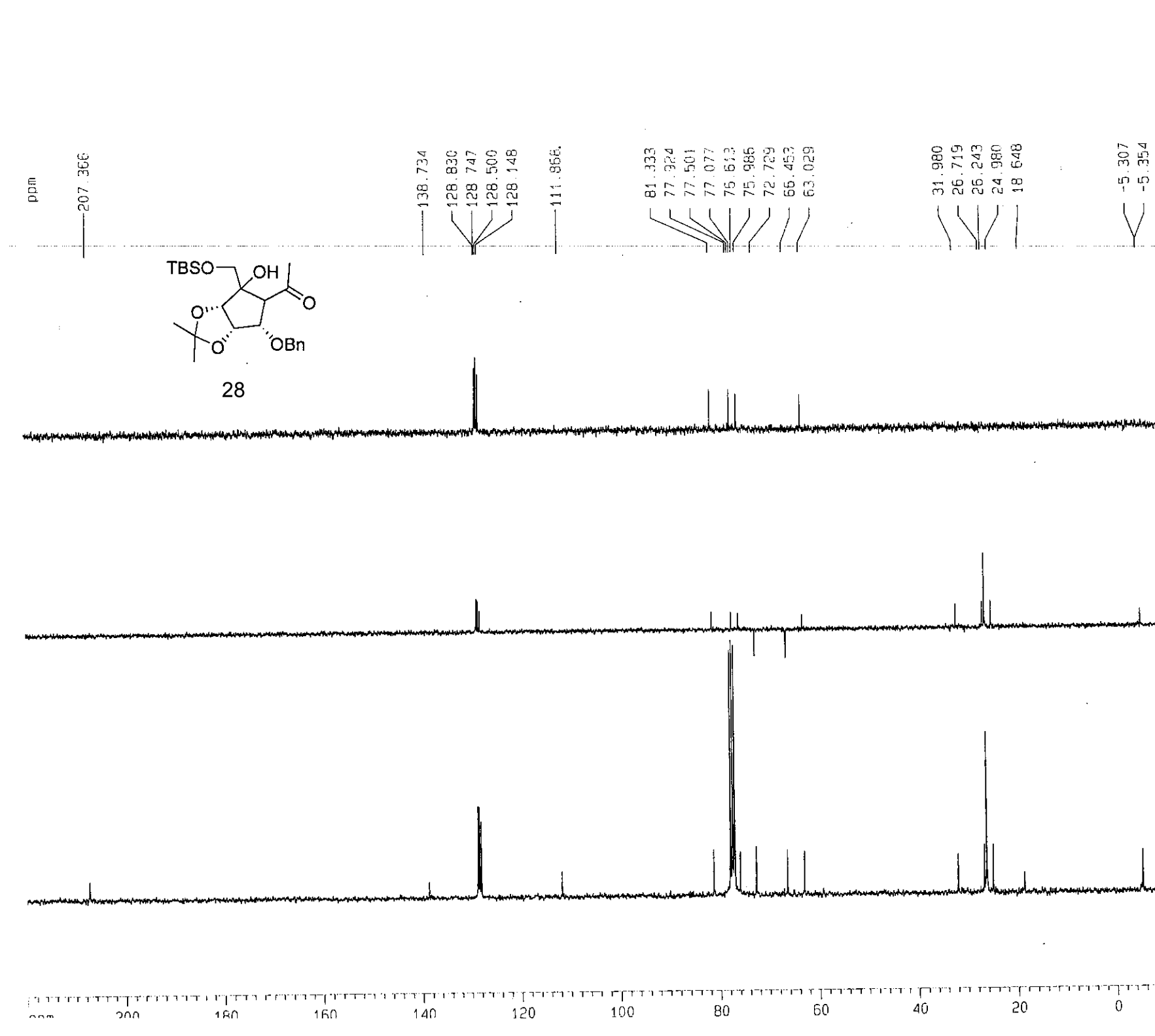

ppm
206.936
205.381
138.048
128.745
128.645
128.193
110.053
79.765
79.297
77.922
77.498
77.075
74.346
71.963
69.218
45.725
31.552
27.761
26.215
25.850
18.674
-5.146
-5.356
O
OBn
O
TBSO
O
O
26
ppm
200
180
160
140
120
100
80
60
40
20
0

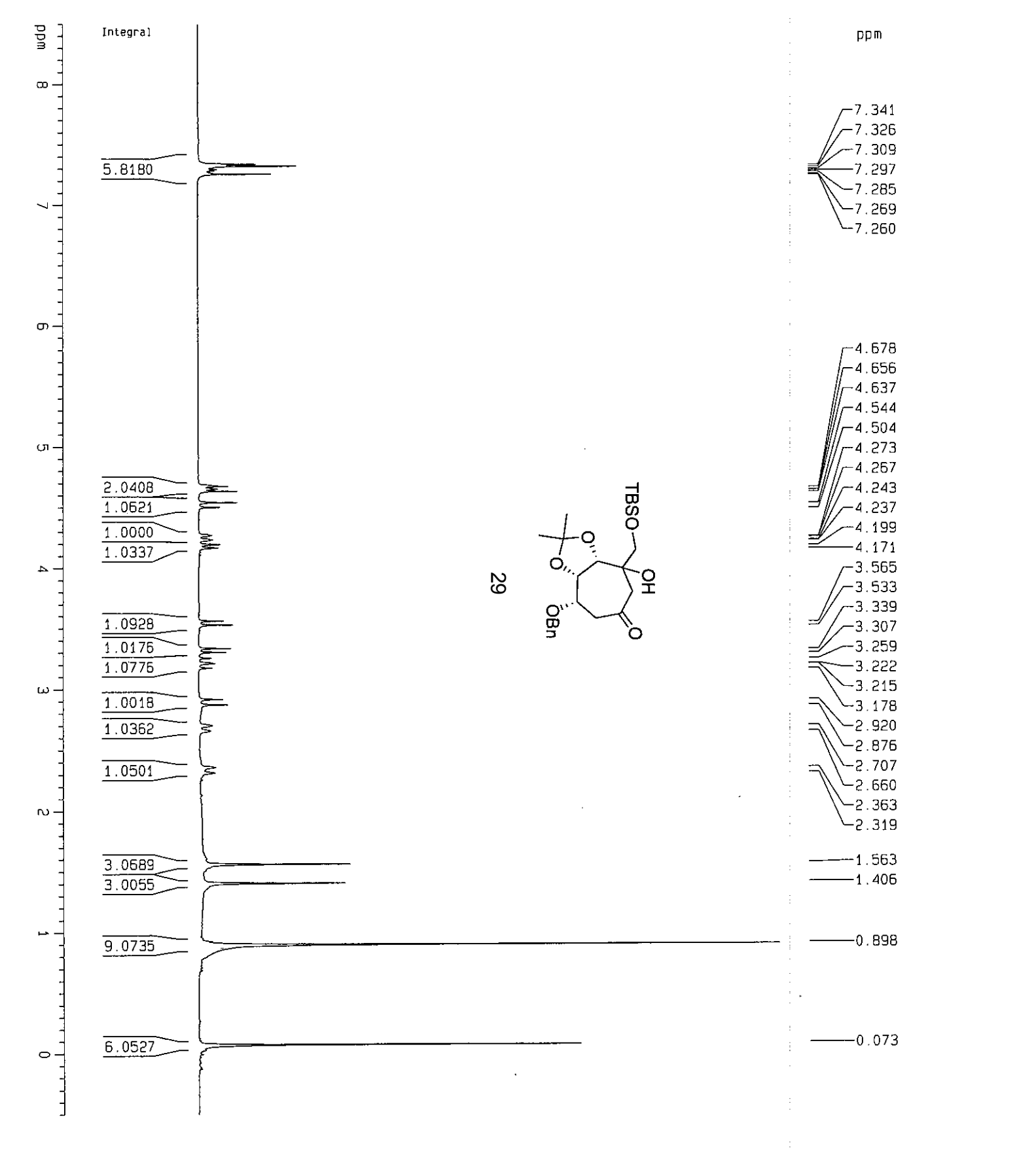

ppm
7.339
7.334
7.330
7.315
7.311
7.290
7.277
7.260
4.696
4.689
4.671
4.655
4.512
4.473
4.237
4.222
4.201
4.190
4.171
3.745
3.710
3.685
3.650
3.240
3.204
2.297
1.536
1.303
0.865
0.856
0.030
0.025
TBSO
OH
O
O
O
OBn
Integral
4.6361
2.0344
1.7737
2.0357
0.9929
1.0763
1.0000
2.9779
2.9986
3.0126
8.9722
2.2966
3.0527
ppm
8
7
6
5
4
3
2
1
0

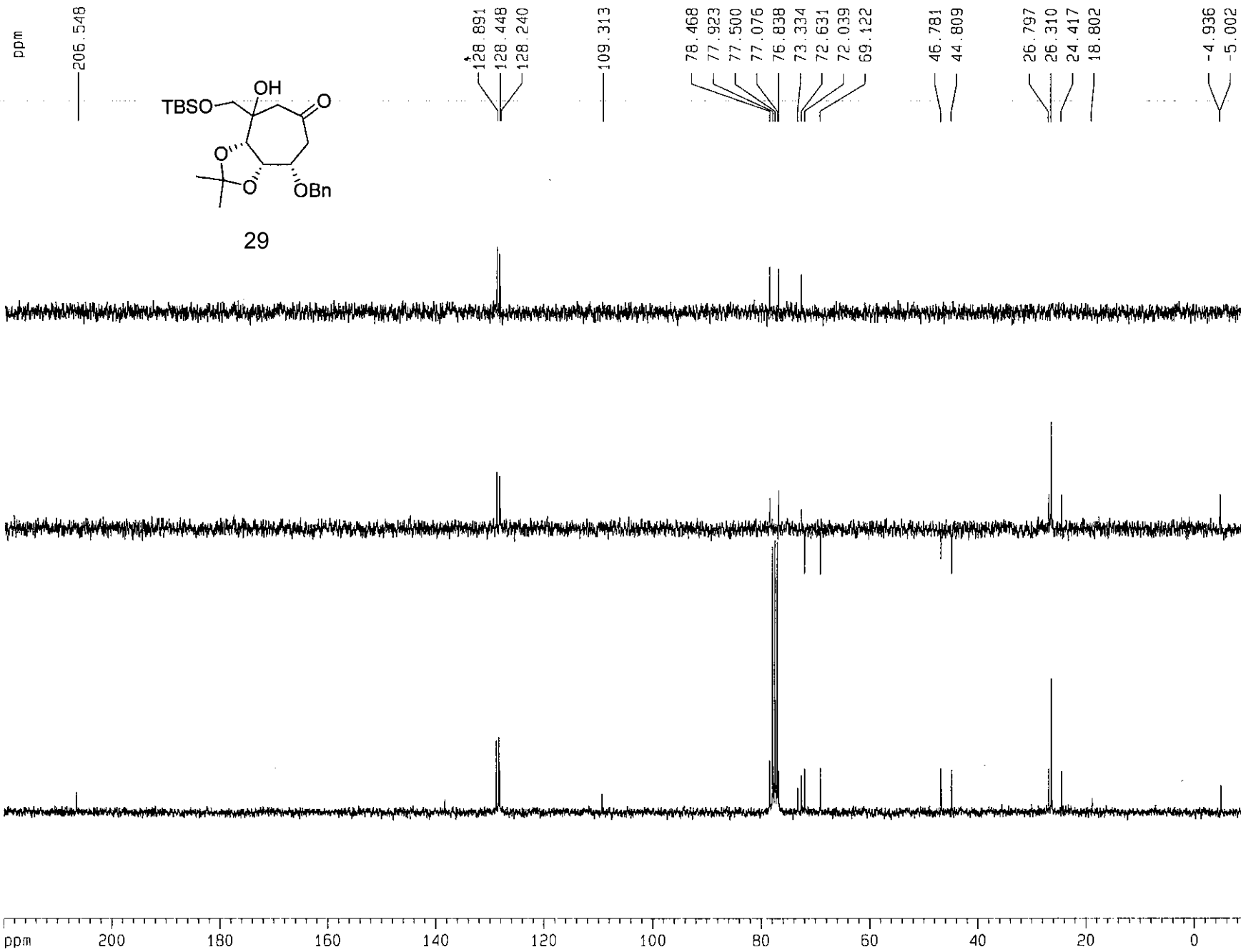
27

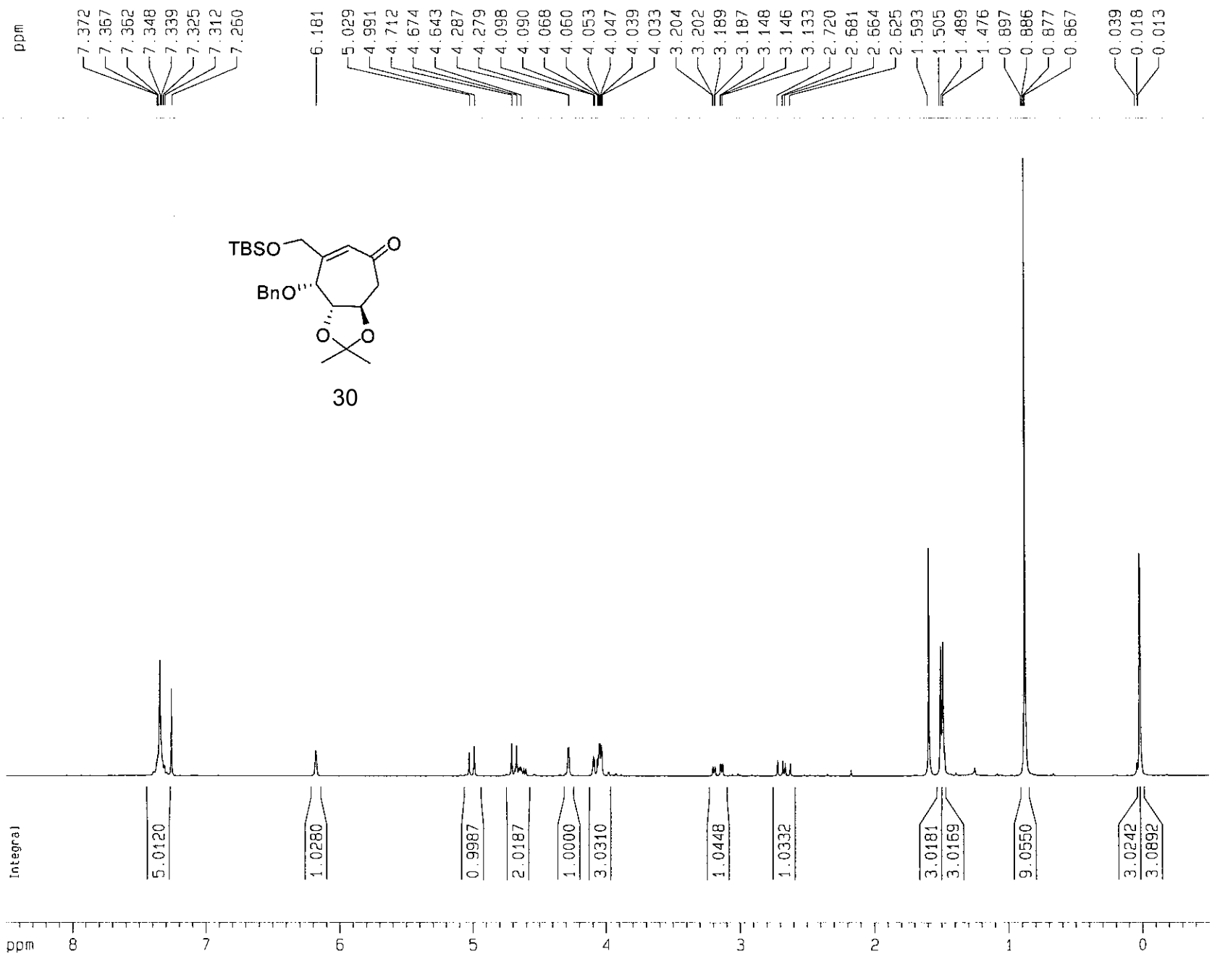

ppm
213.221
138.198
128.863
128.348
111.896
84.689
82.053
81.998
77.926
77.502
77.082
72.531
67.719
56.381
34.099
26.612
26.285
24.472
18.809
-5.062
TBSO
OH
O
O
O
OBn
27
ppm
200
180
160
140
120
100
80
60
40
20
0

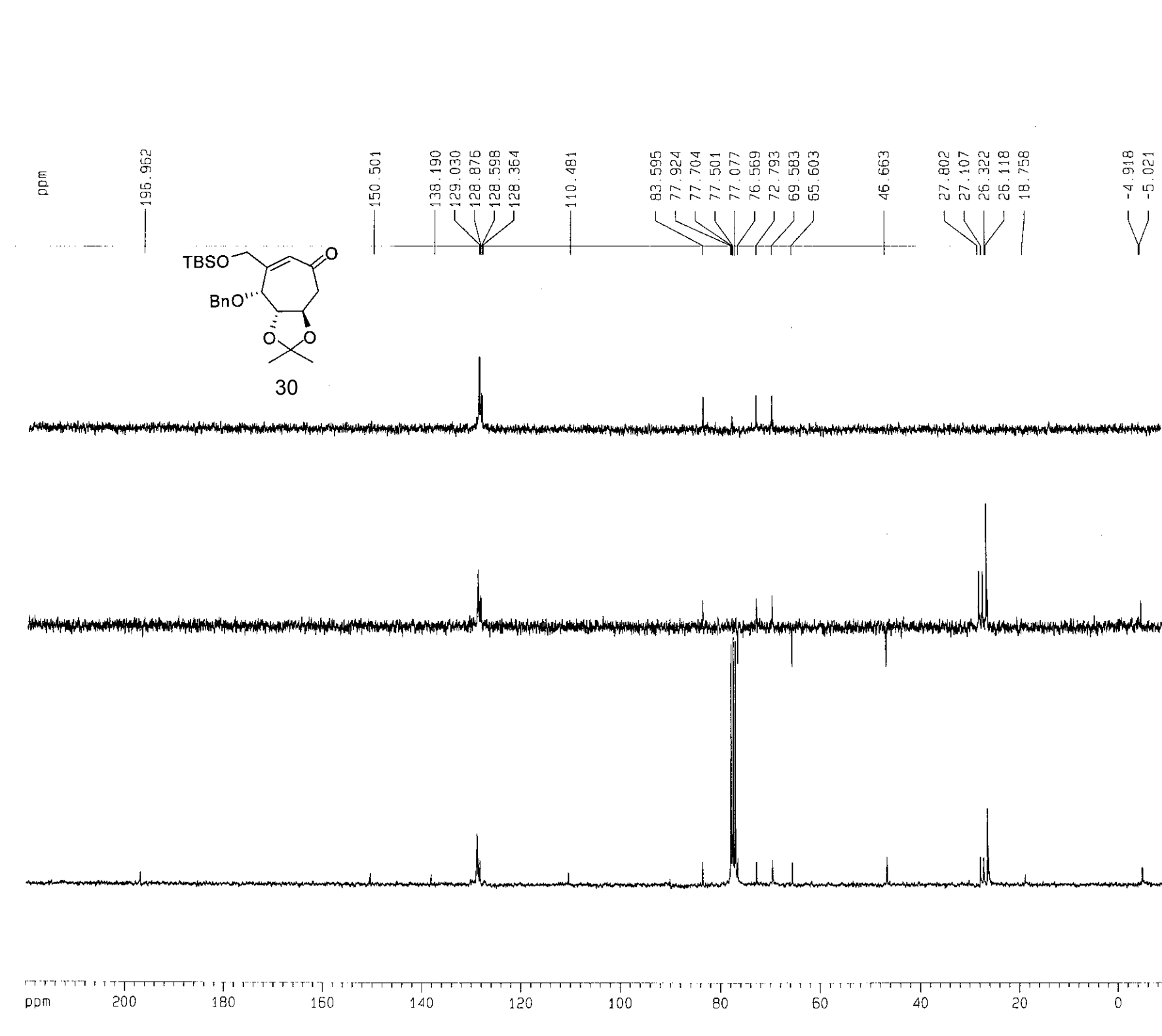

7.387
7.360
7.350
7.345
7.323
7.317
7.298
7.289
7.283
7.259
4.705
4.665
4.593
4.554
4.515
4.498
4.481
4.295
4.275
4.258
4.243
3.430
3.395
3.382
3.348
3.300
3.263
2.256
1.606
1.384
1.249
0.898
0.829
0.072
-0.006
TBSO
OH
O
O
O
OBn
28
8
7
6
5
4
3
2
1
ppm
4.778
1.000
0.998
1.014
2.035
2.025
1.019
3.006
3.052
3.015
9.088
5.744

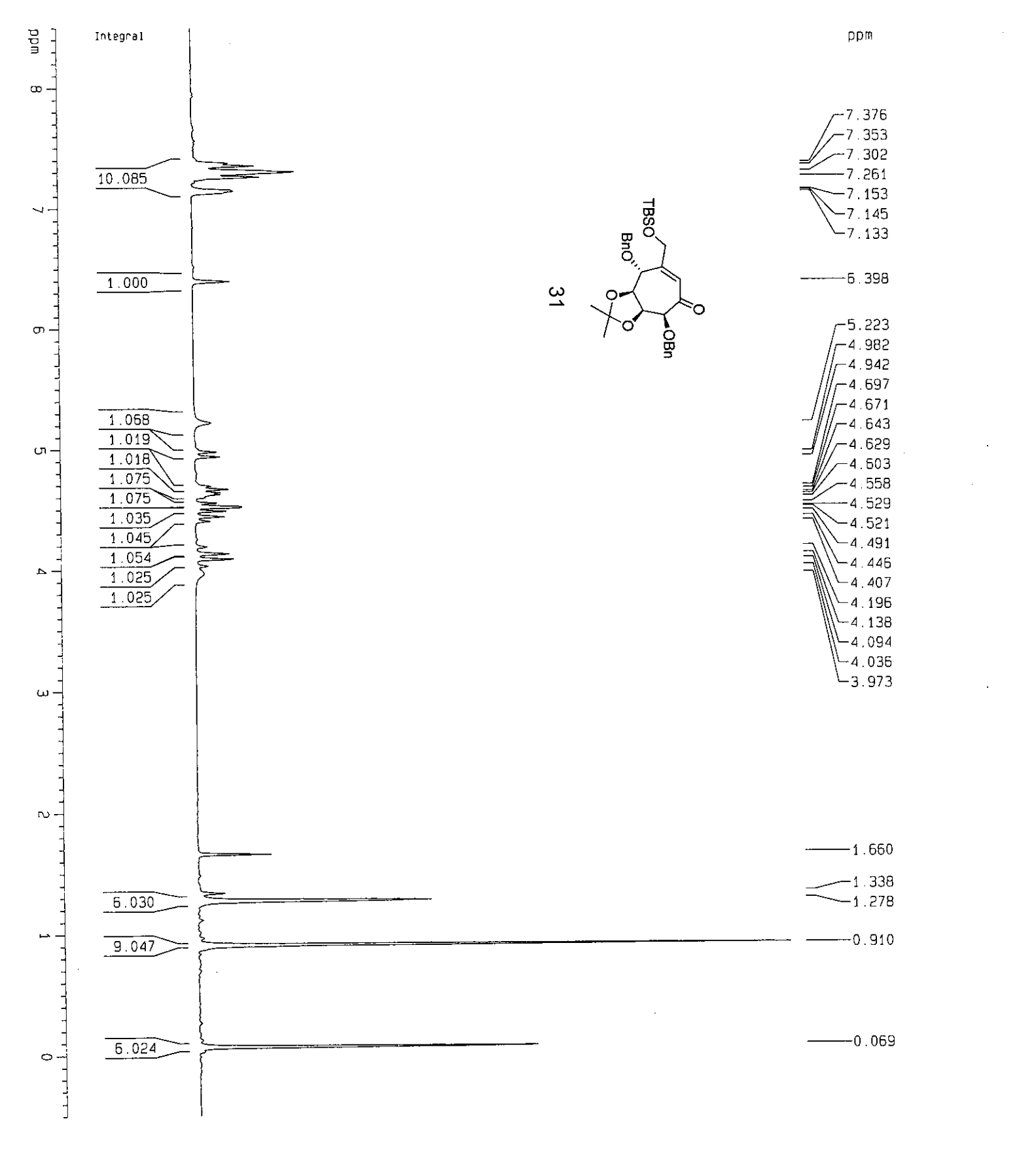

ppm
207.366
138.734
128.830
128.747
128.500
128.148
111.868
81.333
77.324
77.501
77.077
75.613
75.986
72.729
66.453
63.029
31.980
26.719
26.243
24.980
18.648
-5.307
-5.354
TBSO
OH
O
O
O
OBn
28
200
180
160
140
120
100
80
60
40
20
0

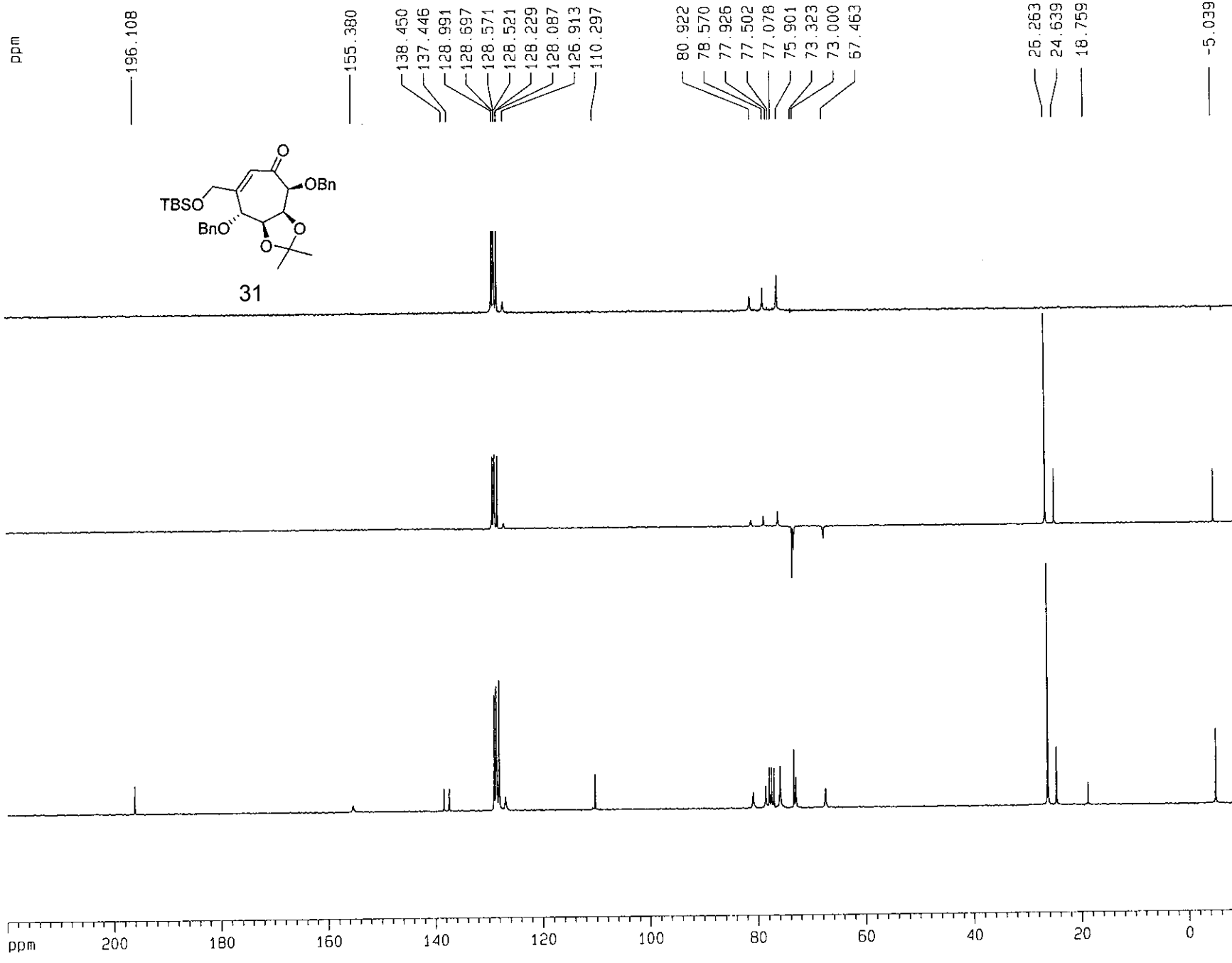

Integral
ppm
5.8180
2.0408
1.0621
1.0000
1.0337
1.0928
1.0176
1.0776
1.0018
1.0362
1.0501
3.0689
3.0055
9.0735
6.0527
29
TBSO
OH
OBn
O
O
O
ppm
7.341
7.326
7.309
7.297
7.285
7.269
7.260
4.678
4.656
4.637
4.544
4.504
4.273
4.267
4.243
4.237
4.199
4.171
3.565
3.533
3.339
3.307
3.259
3.222
3.215
3.178
2.920
2.876
2.707
2.660
2.363
2.319
1.563
1.406
0.898
0.073

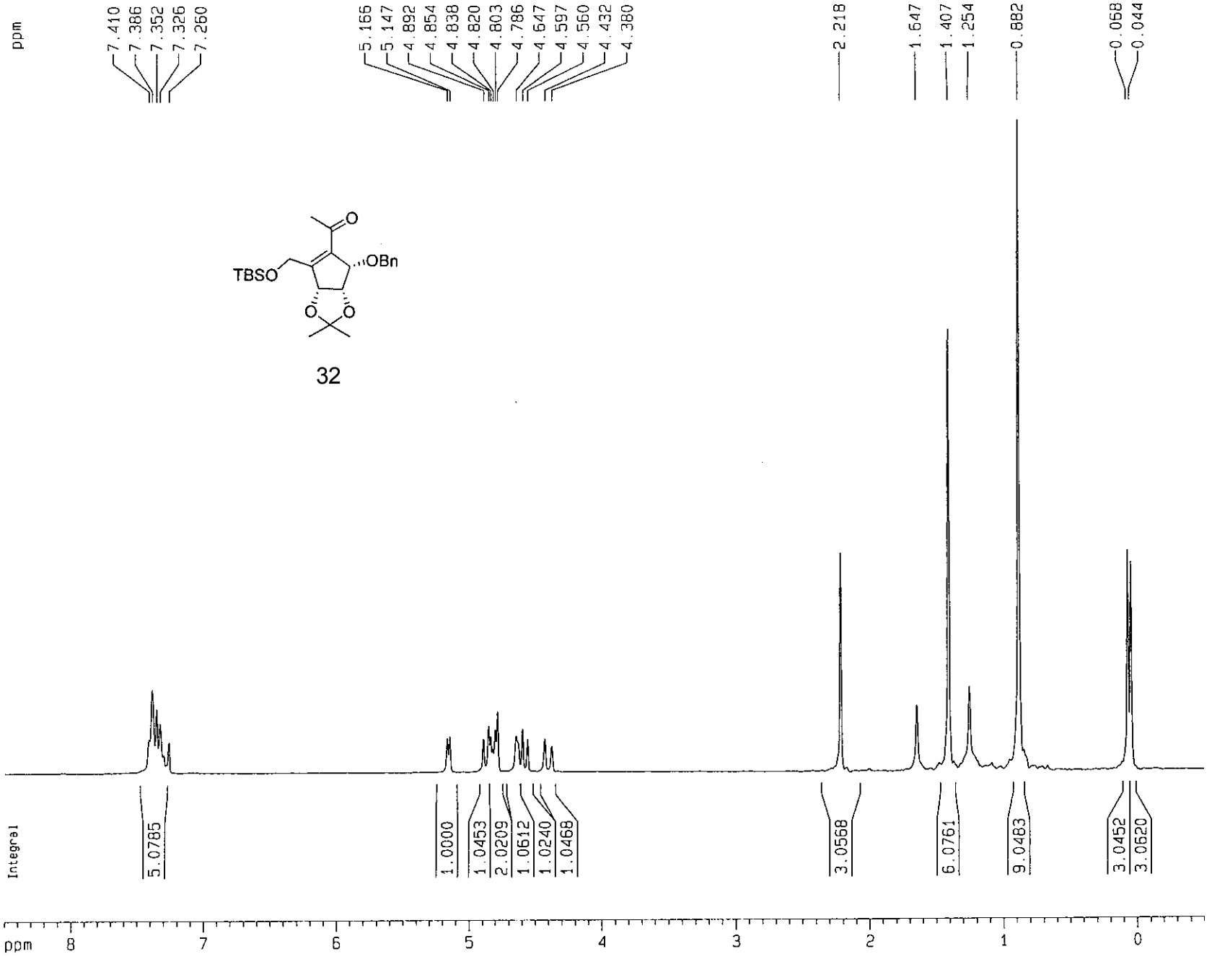

ppm
206.548
128.891
128.448
128.240
109.313
78.468
77.923
77.500
77.076
76.838
73.334
72.631
72.039
69.122
46.781
44.809
26.797
26.310
24.417
18.802
-4.936
-5.002
TBSO
OH
O
O
O
OBn
29
ppm
200
180
160
140
120
100
80
60
40
20
0

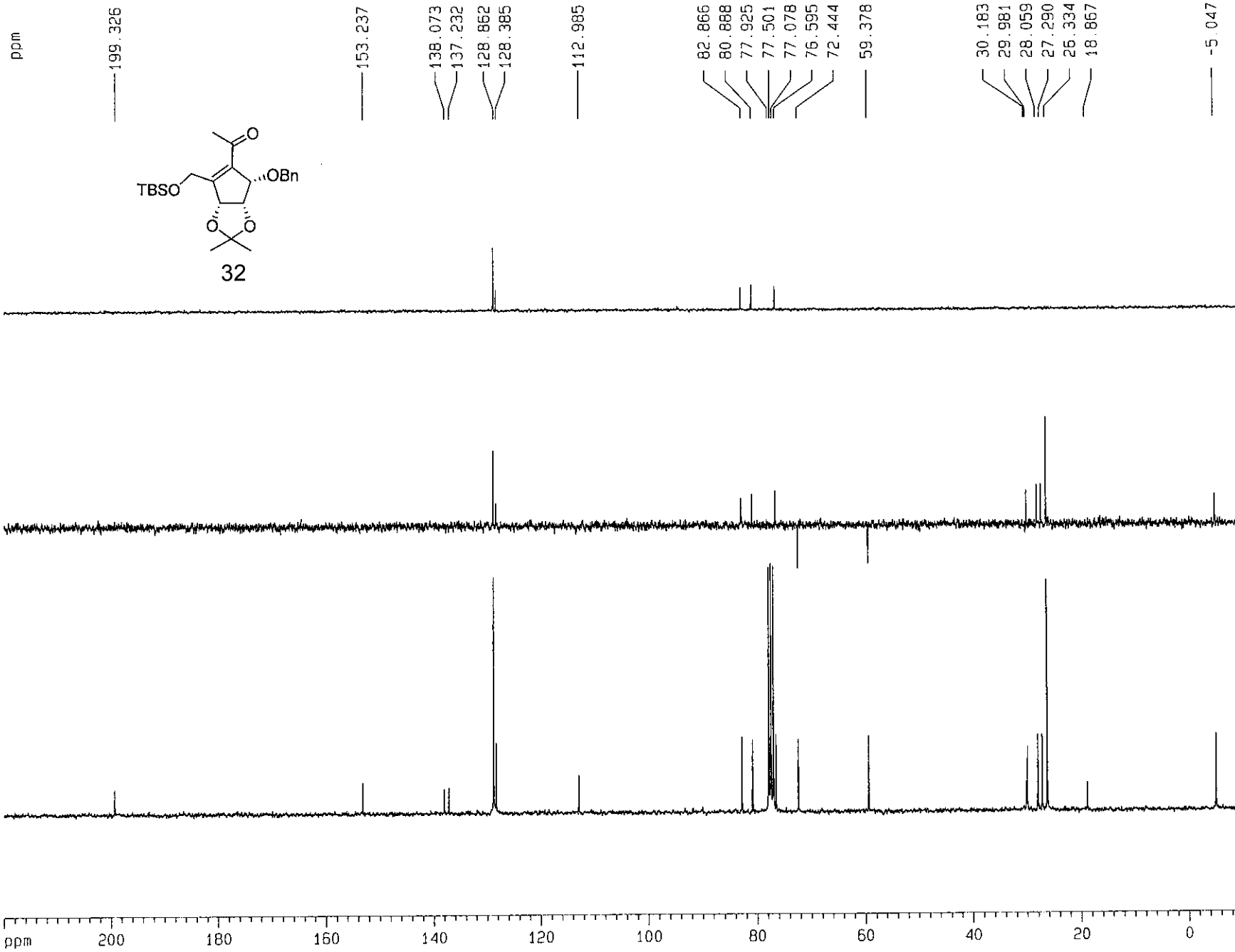

ppm
7.372
7.367
7.362
7.348
7.339
7.325
7.312
7.260
6.181
5.029
4.991
4.712
4.674
4.643
4.287
4.279
4.098
4.090
4.068
4.060
4.053
4.047
4.039
4.033
3.204
3.202
3.189
3.187
3.148
3.146
3.133
2.720
2.681
2.664
2.625
1.593
1.505
1.489
1.476
0.897
0.886
0.877
0.867
0.039
0.018
0.013
TBSO
BnO
O
O
O
30
Integral
5.0120
1.0280
0.9987
2.0187
1.0000
3.0310
1.0448
1.0332
3.0181
3.0169
9.0550
3.0242
3.0892
ppm
8
7
6
5
4
3
2
1
0


ppm
196.962
150.501
138.190
129.030
128.876
128.598
128.364
110.481
83.595
77.924
77.704
77.501
77.077
76.569
72.793
69.583
65.603
46.663
27.802
27.107
26.322
26.118
18.758
-4.918
-5.021
TBSO
BnO
O
O
O
30
ppm
200
180
160
140
120
100
80
60
40
20
0


Integral
ppm
10.085
1.000
1.068
1.019
1.018
1.075
1.075
1.035
1.045
1.054
1.025
1.025
6.030
9.047
6.024
7.376
7.353
7.302
7.261
7.153
7.145
7.133
6.398
5.223
4.982
4.942
4.697
4.671
4.643
4.629
4.603
4.558
4.529
4.521
4.491
4.446
4.407
4.196
4.138
4.094
4.036
3.973
1.660
1.338
1.278
0.910
0.069
TBSO
BnO
OBn
O
31


ppm
196.108
155.380
138.450
137.446
128.991
128.697
128.571
128.521
128.229
128.087
126.913
110.297
80.922
78.570
77.926
77.502
77.078
75.901
73.323
73.000
67.463
26.263
24.639
18.759
-5.039
TBSO
BnO
OBn
O
31
ppm
200
180
160
140
120
100
80
60
40
20
0


ppm
7.410
7.386
7.352
7.326
7.260
5.166
5.147
4.892
4.854
4.838
4.820
4.803
4.786
4.647
4.597
4.560
4.432
4.380
2.218
1.647
1.407
1.254
0.882
0.068
0.044
TBSO
OBn
O
O
O
32
Integral
5.0785
1.0000
1.0453
2.0209
1.0612
1.0240
1.0468
3.0568
6.0761
9.0483
3.0452
3.0620
ppm
8
7
6
5
4
3
2
1
0


ppm
199.326
153.237
138.073
137.232
128.862
128.385
112.985
82.866
80.888
77.925
77.501
77.078
76.595
72.444
59.378
30.183
29.981
28.059
27.290
26.334
18.867
-5.047
O
OBn
TBSO
O
O
32
ppm
200
180
160
140
120
100
80
60
40
20
0