Supporting Information 2

Stereoselective Radical Amination of Electron-Deficient C(sp^3)–H Bonds by Co(II)-Based Metalloradical Catalysis: Direct Synthesis of α-Amino Acid Derivatives via α-C–H Amination

Hongjian Lu,[†,‡] Yang Hu,[†] Huiling Jiang,[†] Lukasz Wojtas,[†] X. Peter Zhang*[,†]

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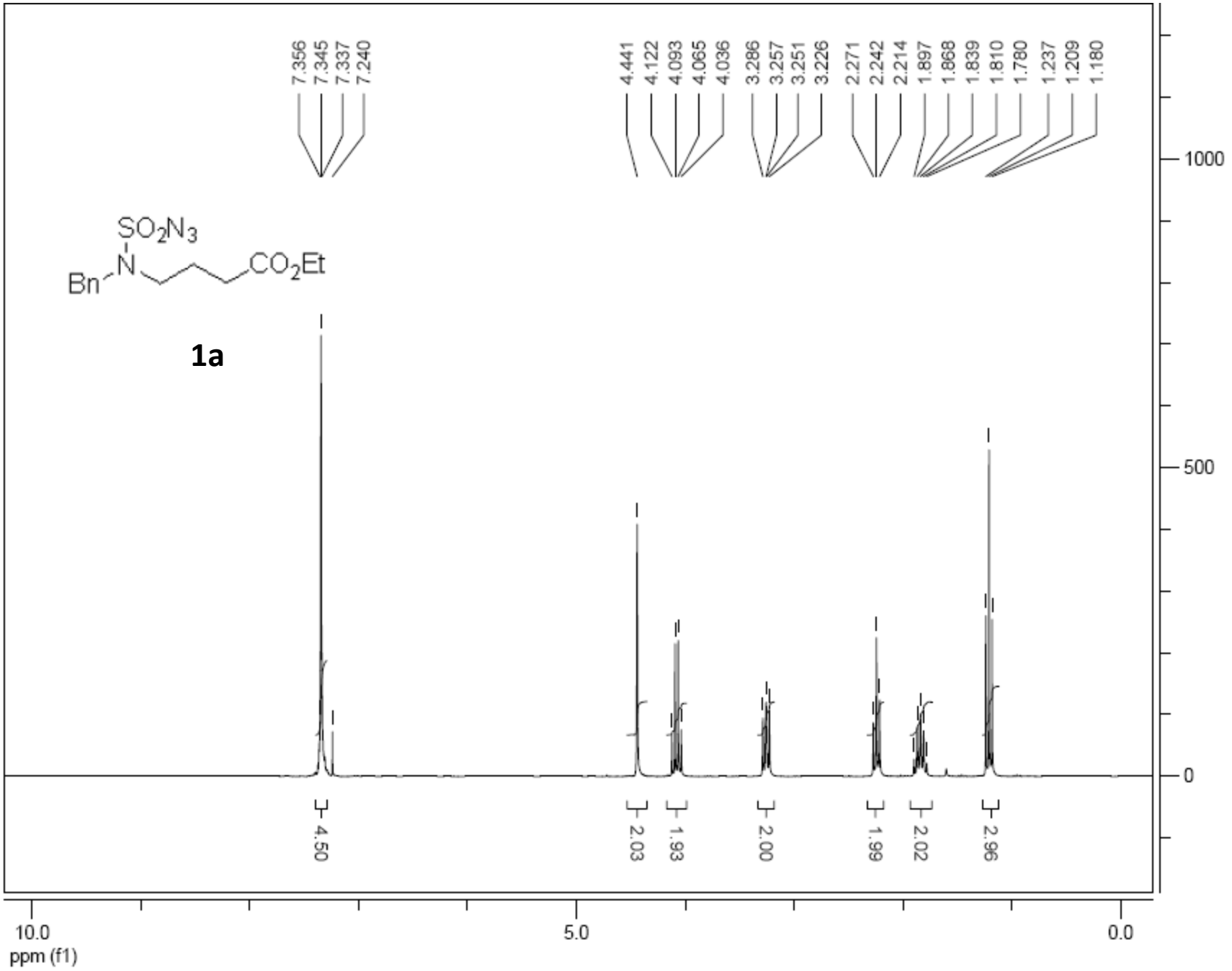
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4.065
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3.226
2.271
2.242
2.214
1.897
1.868
1.839
1.810
1.780
1.237
1.209
1.180
SO2N3
N
Bn
CO2Et
1a
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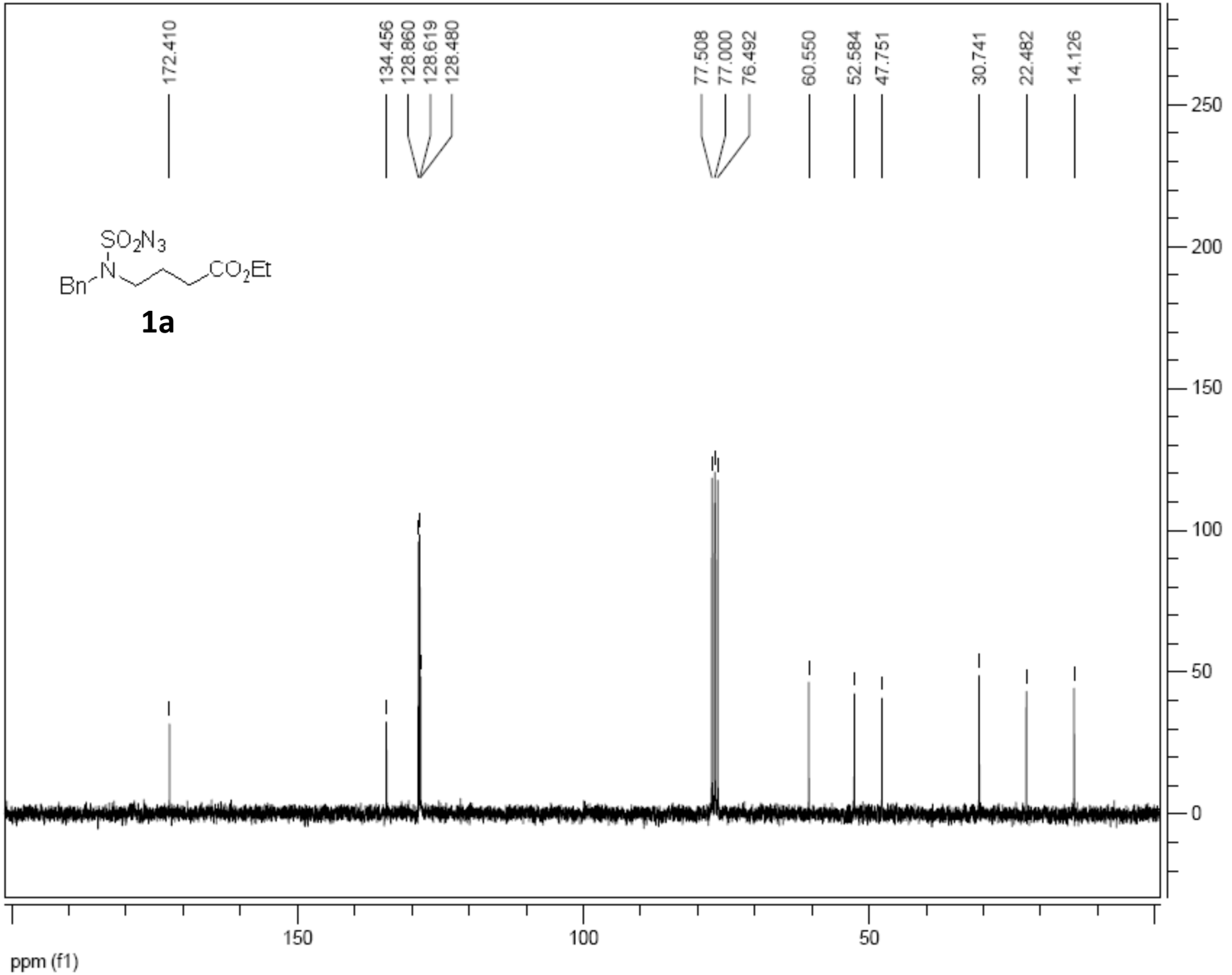
2.00
1.99
2.02
2.96
10.0
5.0
0.0
ppm (f1)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76.492
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30.741
22.482
14.126
SO2N3
N
Bn
CO2Et
1a
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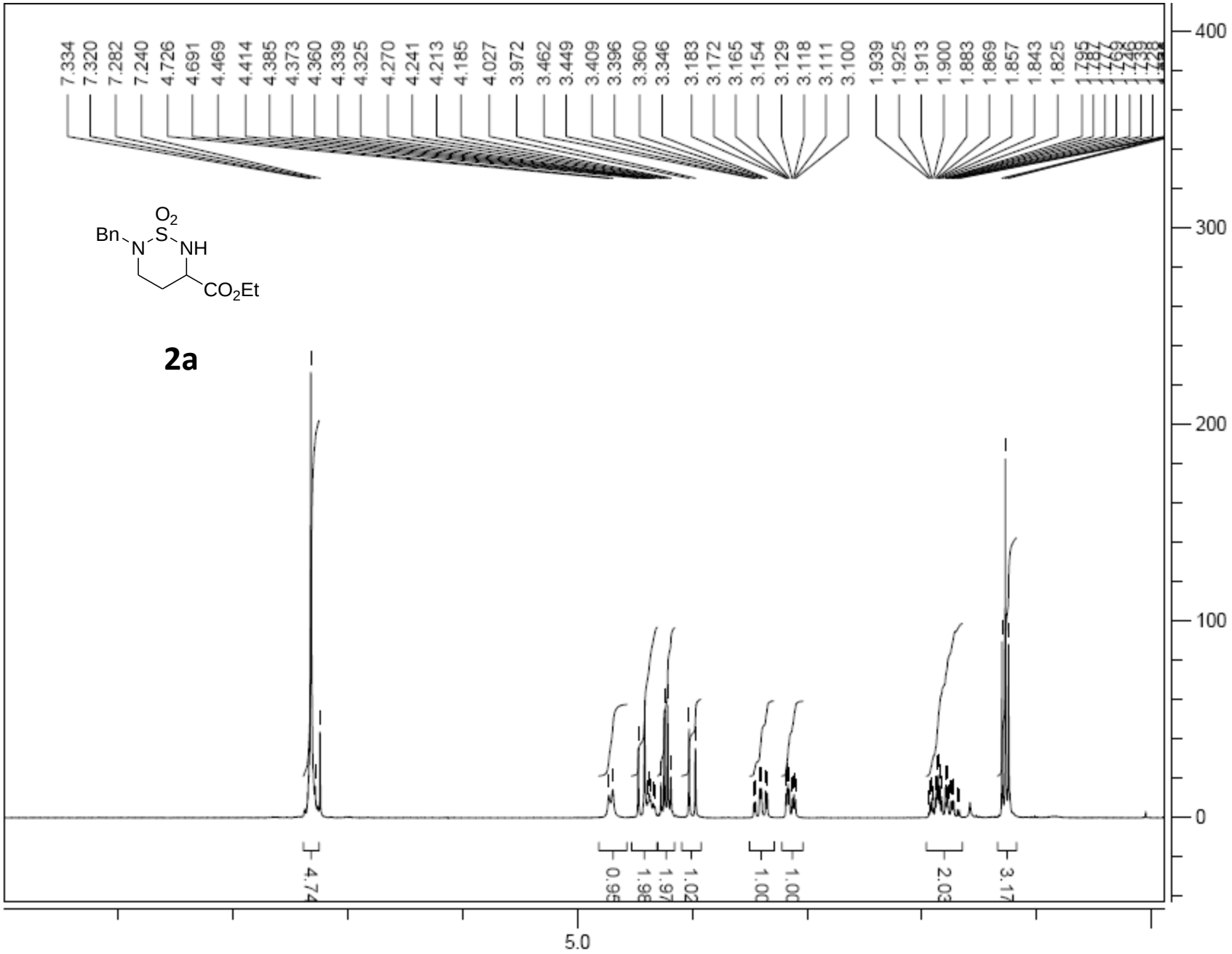
200
150
100
50
0
150
100
50
ppm (f1)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4.360
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4.325
4.270
4.241
4.213
4.185
4.027
3.972
3.462
3.449
3.409
3.396
3.360
3.346
3.183
3.172
3.165
3.154
3.129
3.118
3.111
3.100
1.939
1.925
1.913
1.900
1.883
1.869
1.857
1.843
1.825
Bn
N
O2
S
NH
CO2Et
2a
400
300
200
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1.00
2.03
3.17
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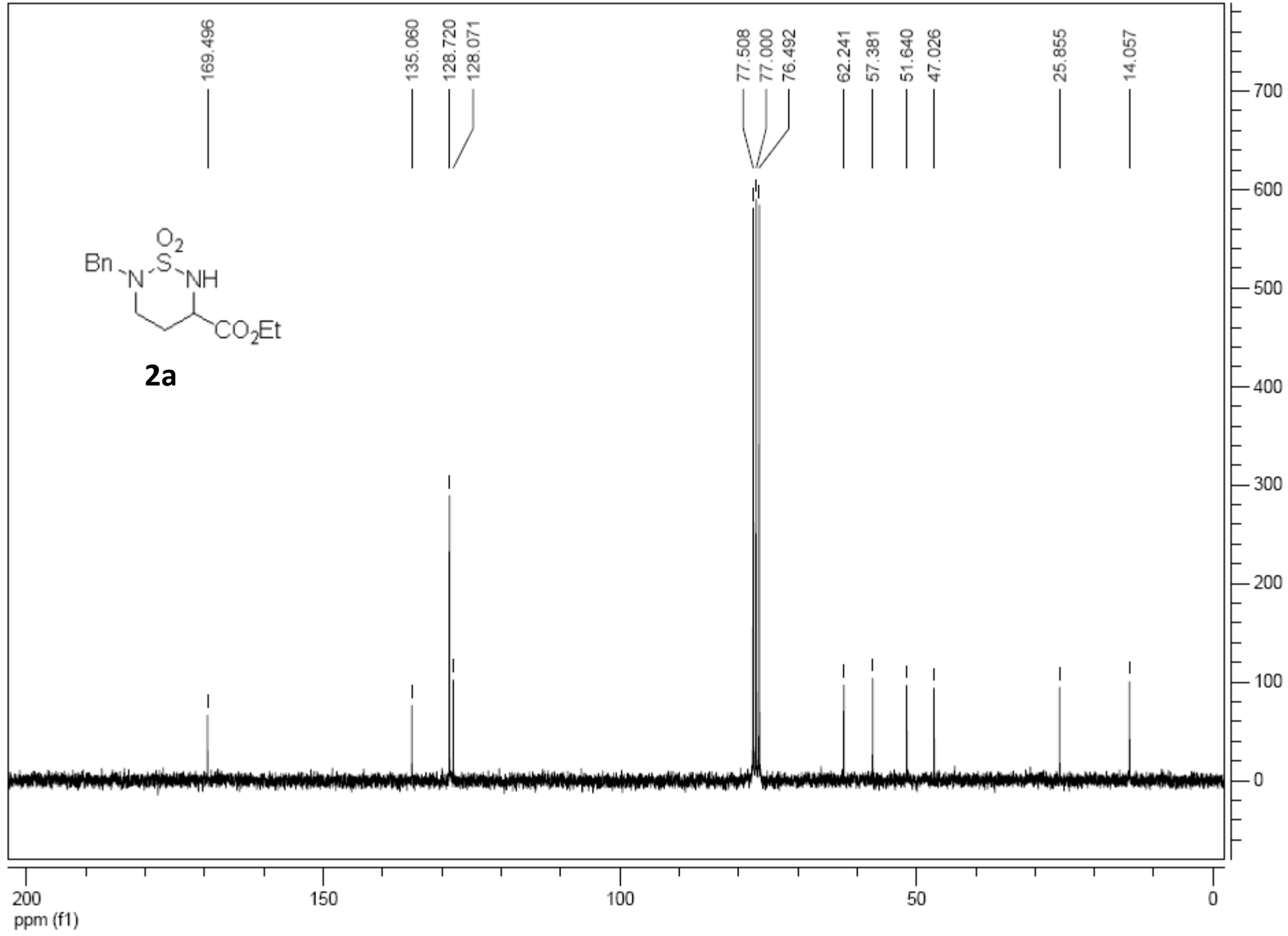
ppm (f1)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14.057
O2
S
Bn
N
NH
CO2Et
2a
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600
500
400
300
200
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0
200
150
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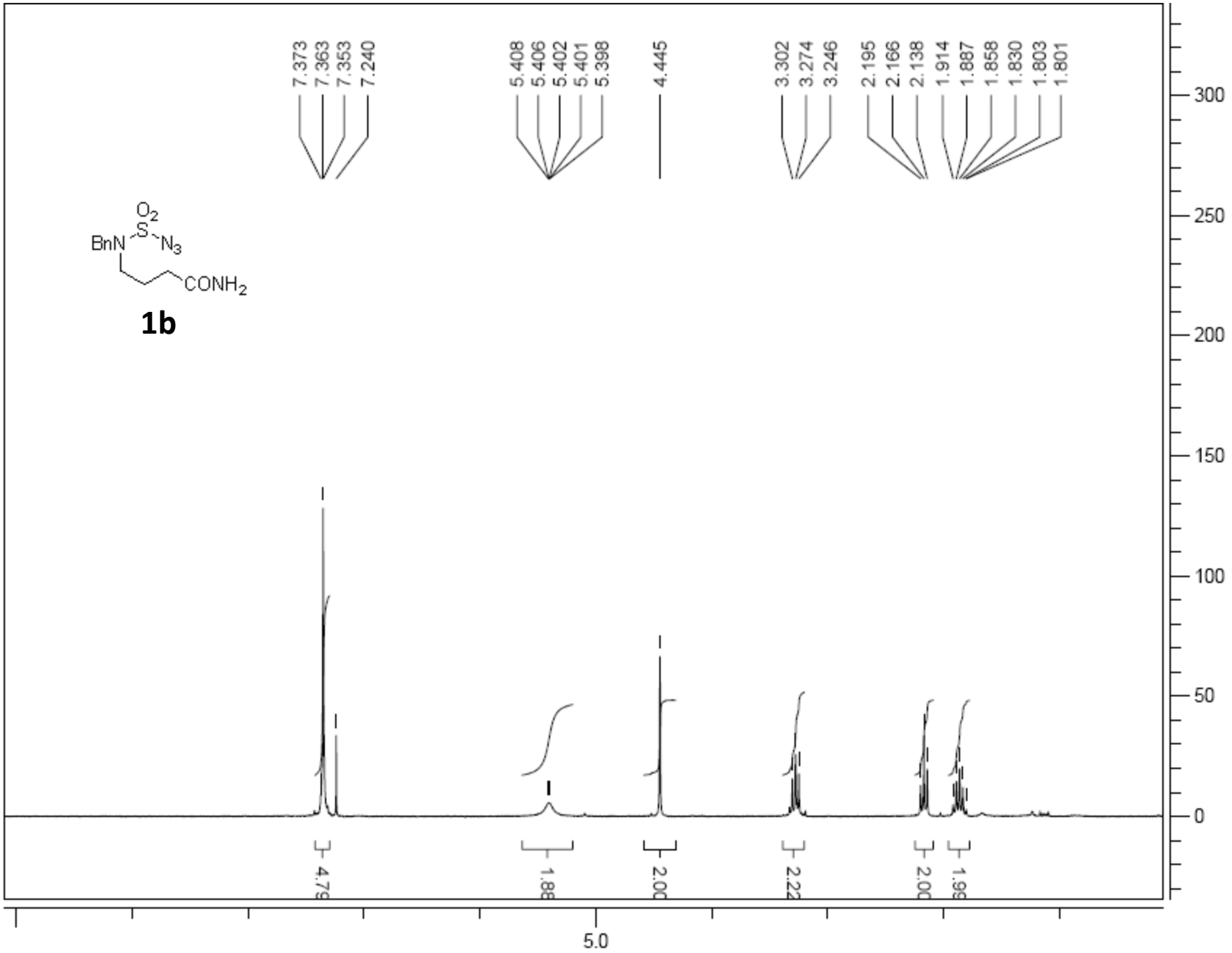
ppm (f1)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5.402
5.401
5.398
4.445
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3.274
3.246
2.195
2.166
2.138
1.914
1.887
1.858
1.830
1.803
1.801
BnN
O2
S
N3
CONH2
1b
4.75
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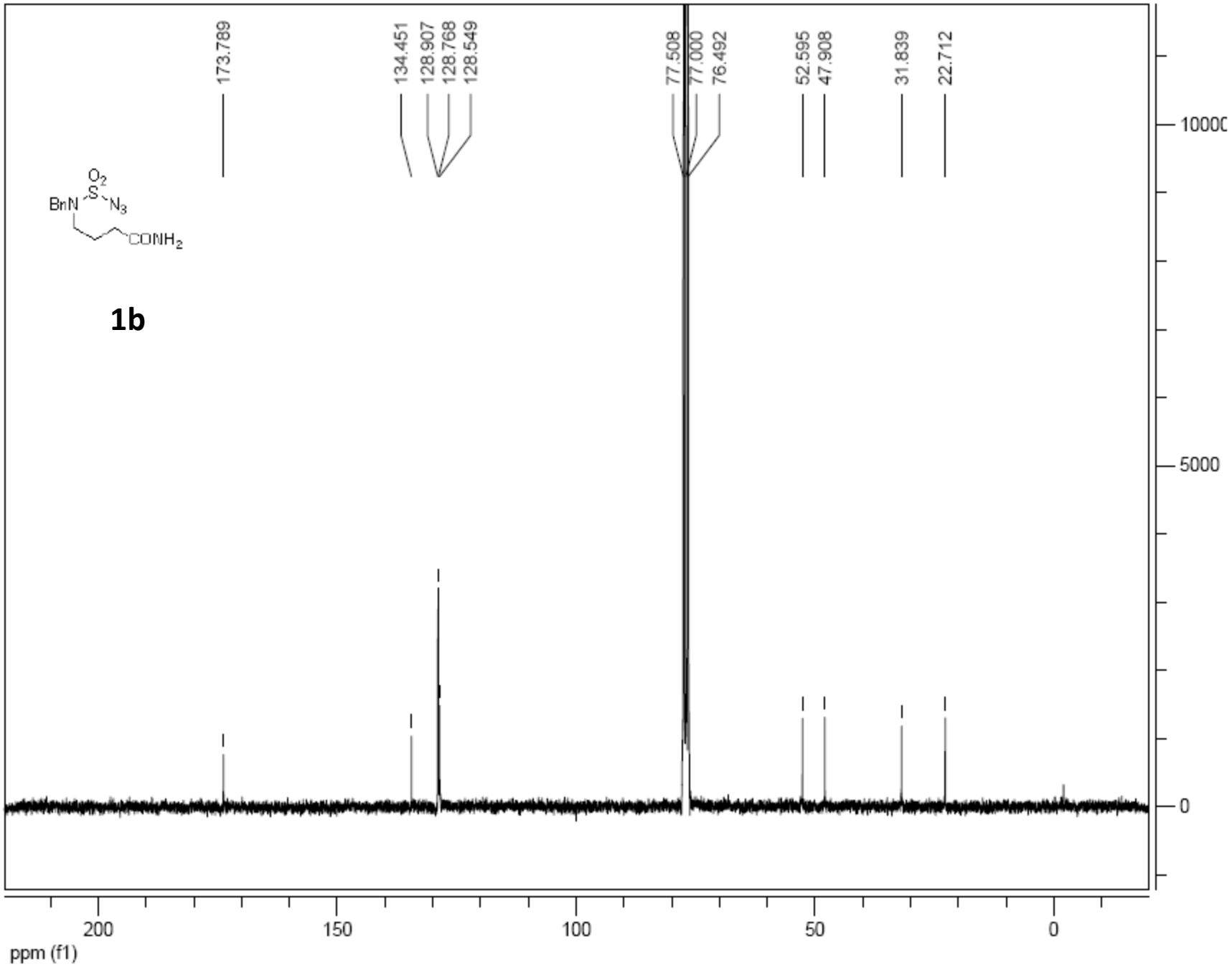
2.22
2.00
1.96
300
250
200
150
100
50
0
5.0
ppm (t1)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77.000
76.492
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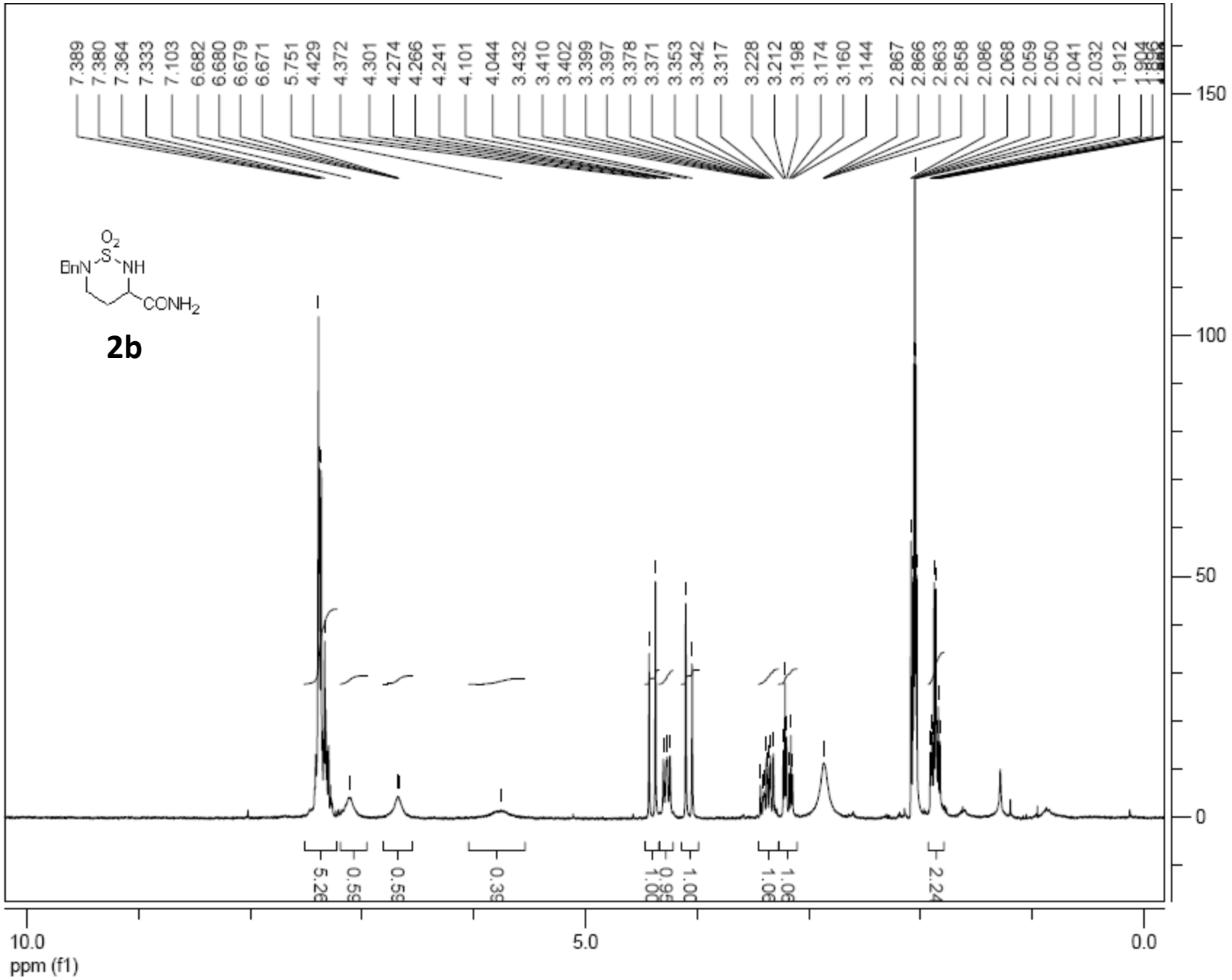
47.908
31.839
22.712
BnN
O2
S
N3
CONH2
1b
10000
5000
0
200
150
100
50
0
ppm (f1)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6.679
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5.751
4.429
4.372
4.301
4.274
4.266
4.241
4.101
4.044
3.432
3.410
3.402
3.399
3.397
3.378
3.371
3.353
3.342
3.317
3.228
3.212
3.198
3.174
3.160
3.144
2.867
2.866
2.863
2.858
2.086
2.068
2.059
2.050
2.041
2.032
1.912
EtN
O2
S
NH
CONH2
2b
150
100
50
0
5.26
0.59
0.59
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0.95
1.00
1.06
1.06
2.24
10.0
5.0
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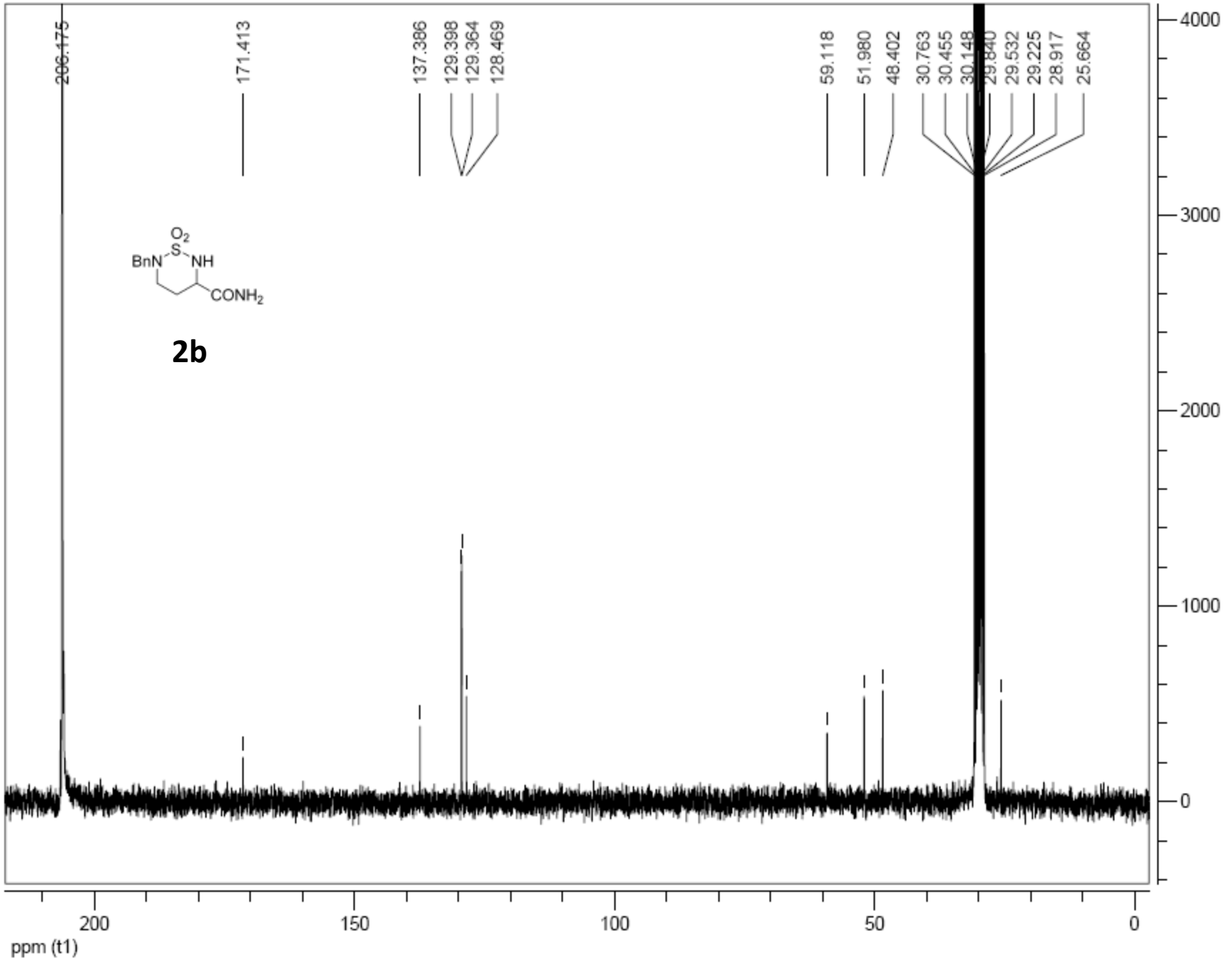
ppm (f1)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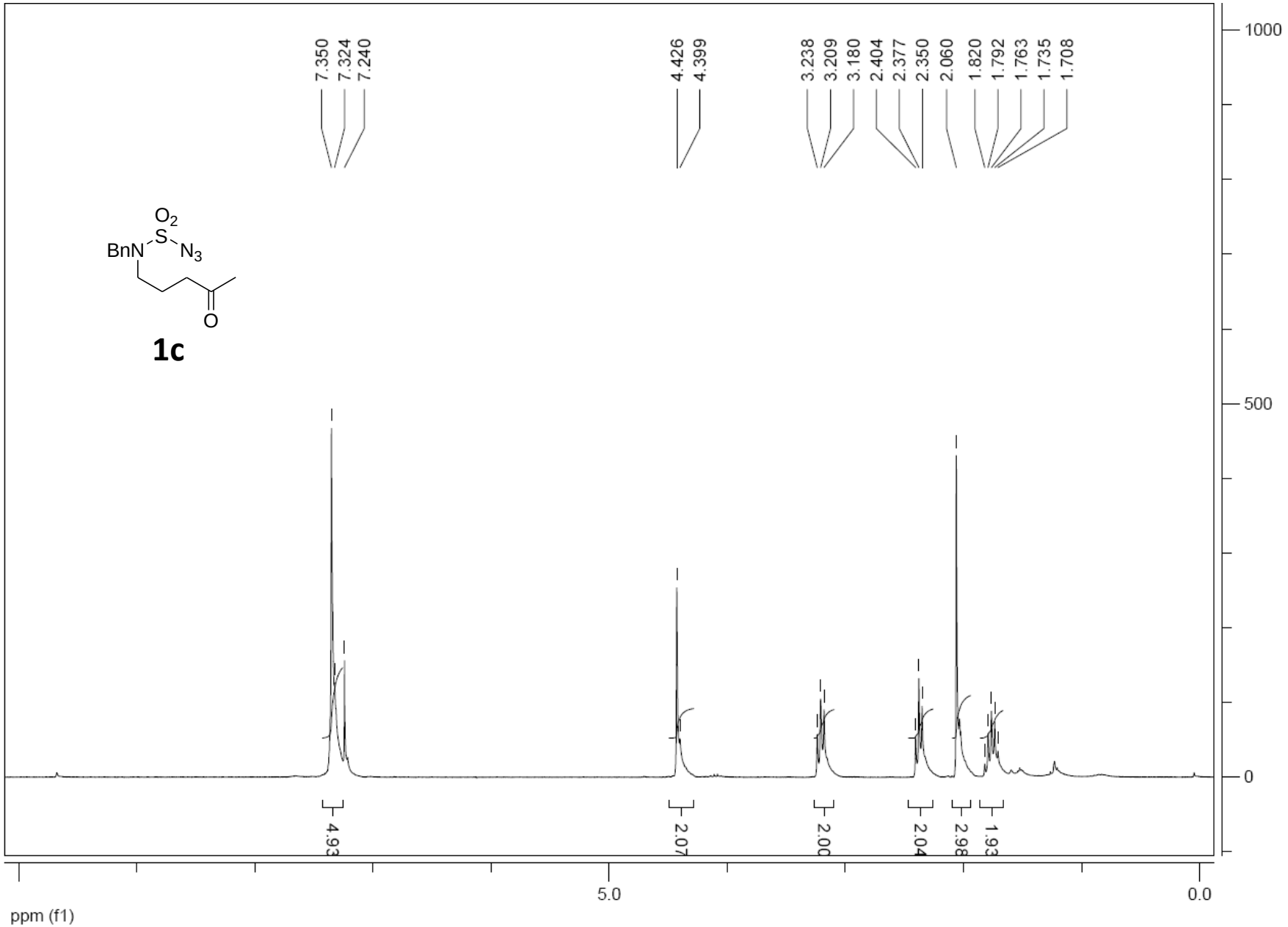
29.840
29.532
29.225
28.917
25.664
4000
3000
2000
1000
0
200
150
100
50
0
ppm (t1)
O2
S
BnN
NH
CONH2

2b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2.350
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1.820
1.792
1.763
1.735
1.708
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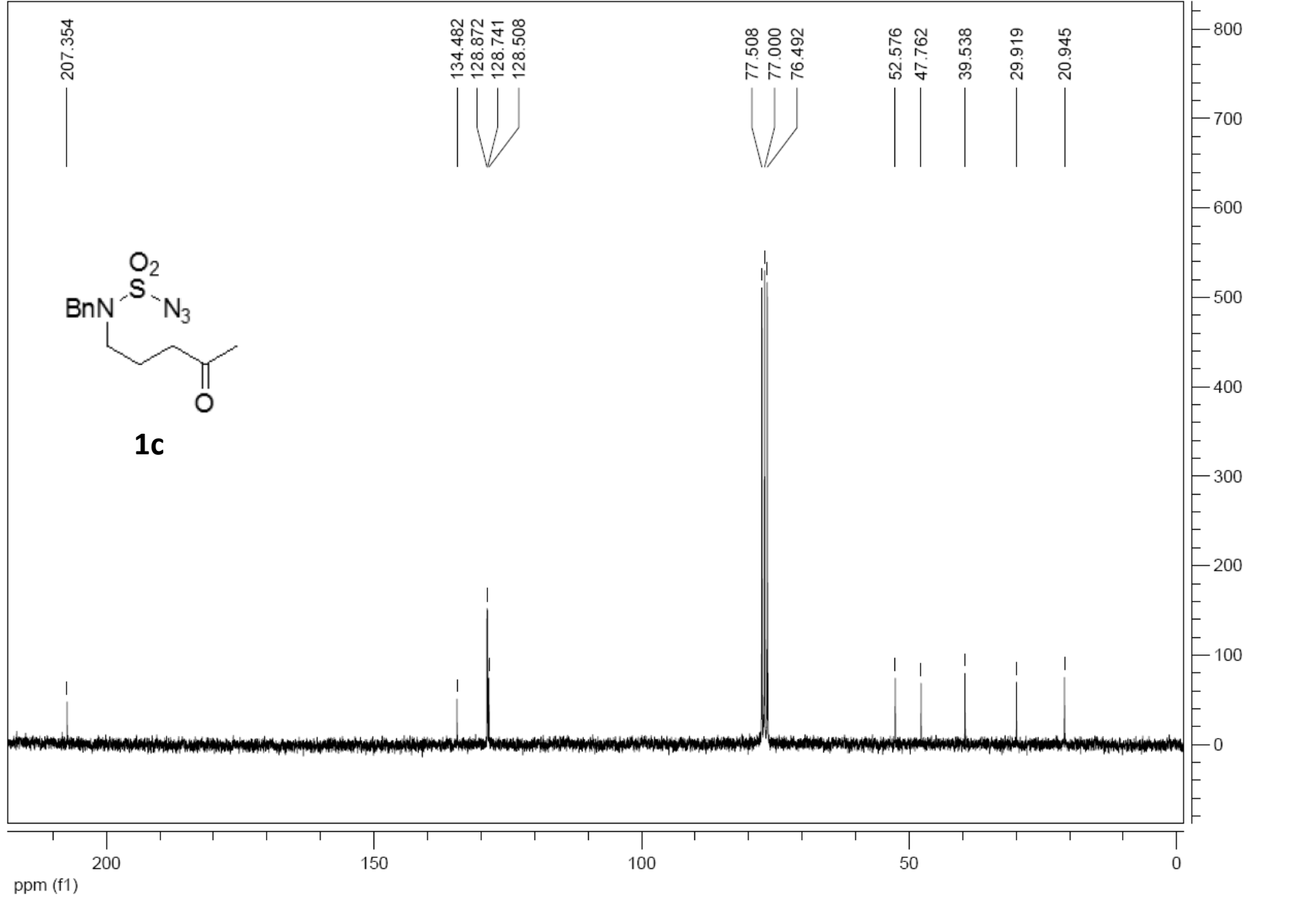
2.07
2.00
2.04
2.98
1.93
5.0
0.0
ppm (f1)

1c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77.000
76.492
52.576
47.762
39.538
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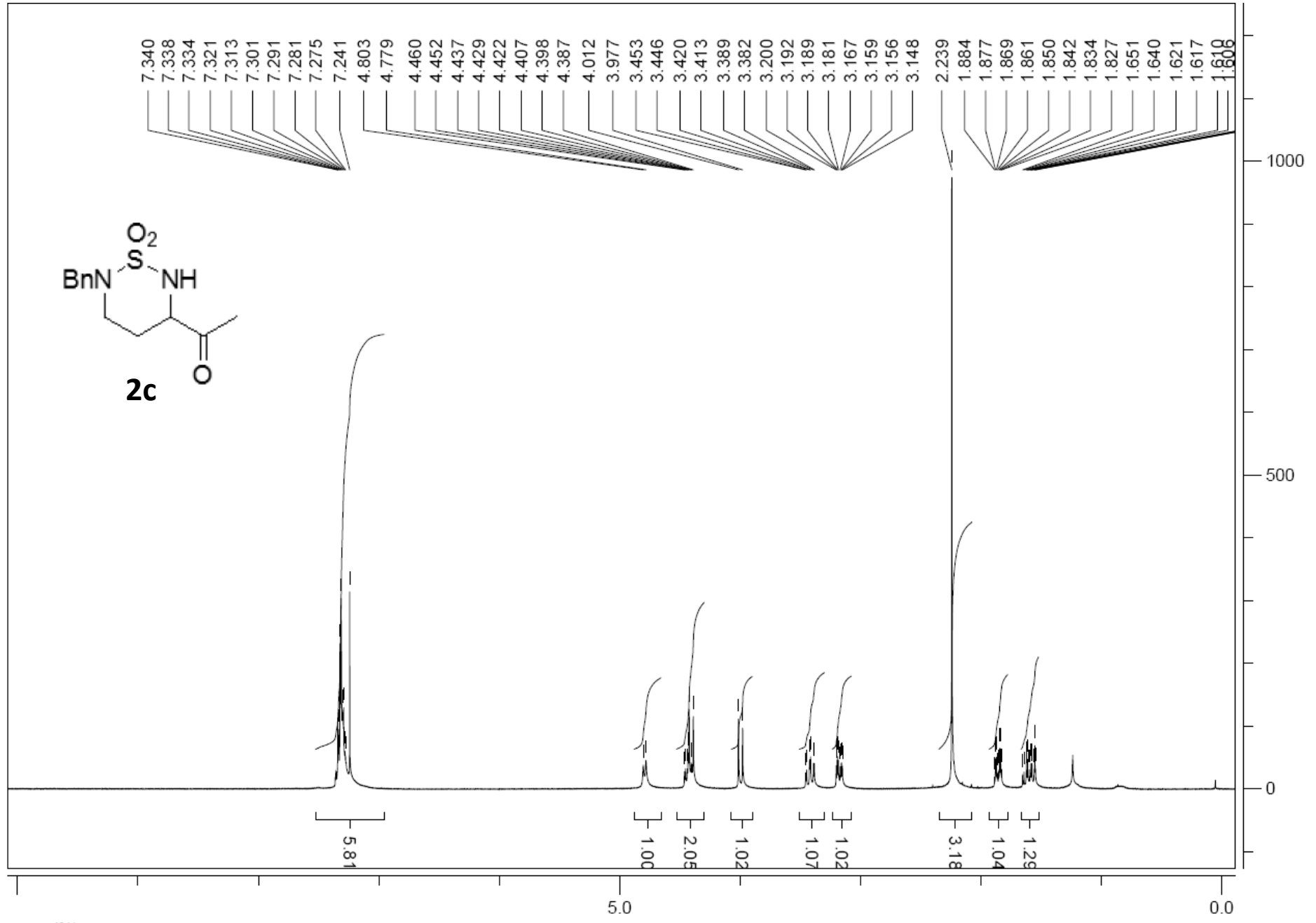
20.945
O2
S
BnN
N3
O
1c
800
700
600
500
400
300
200
100
0
200
150
100
50
0
ppm (f1)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7.281
7.275
7.241
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4.460
4.452
4.437
4.429
4.422
4.407
4.398
4.387
4.012
3.977
3.453
3.446
3.420
3.413
3.389
3.382
3.200
3.192
3.189
3.181
3.167
3.159
3.156
3.148
2.239
1.884
1.877
1.869
1.861
1.850
1.842
1.834
1.827
1.651
1.640
1.621
1.617
1.610
1.606
1000
500
0
5.81
1.00
2.05
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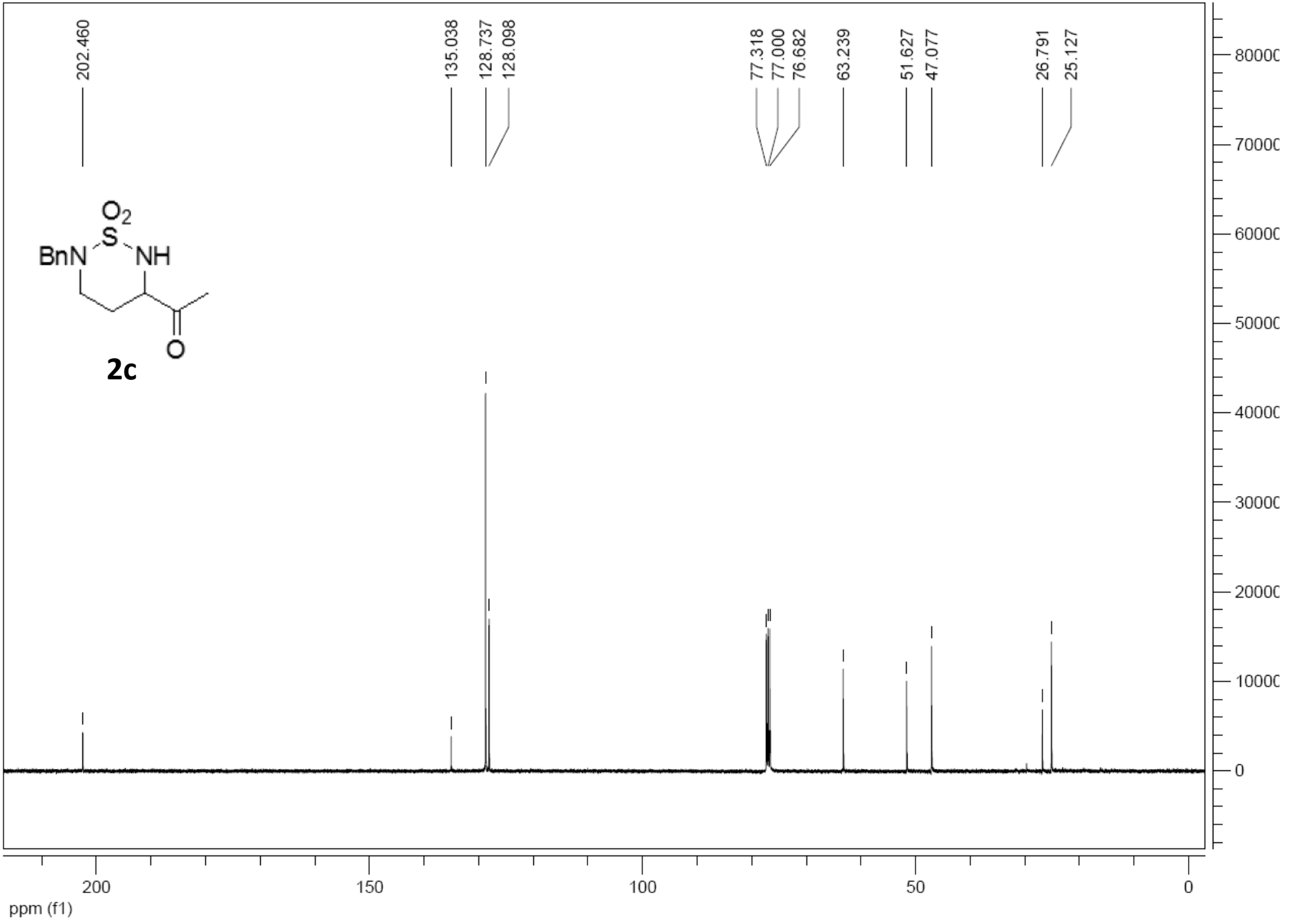
1.07
1.02
3.18
1.04
1.29
5.0
0.0
ppm (f1)

2c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76.682
63.239
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26.791
25.127
O2
S
BnN
NH
O
2c
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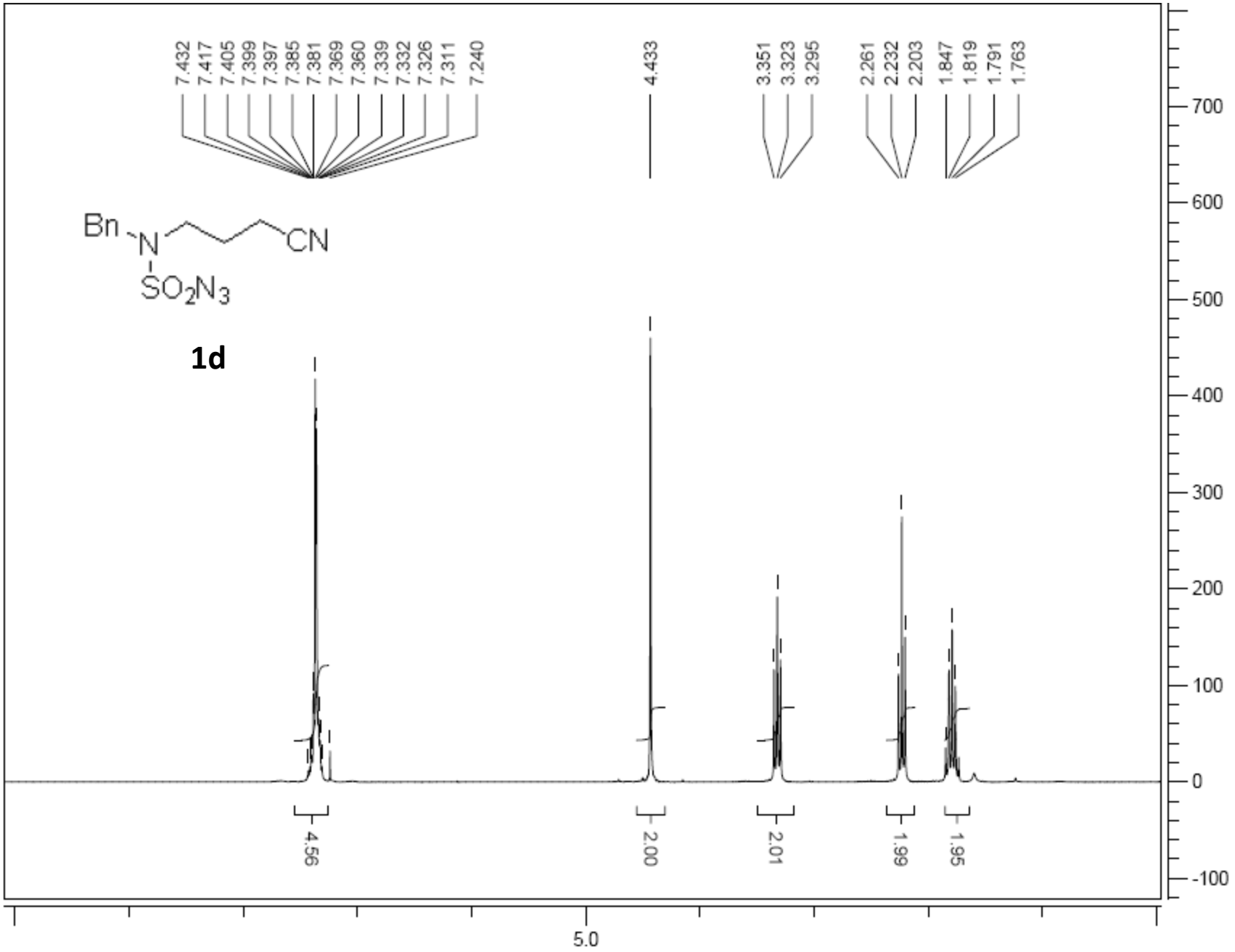
7000
6000
5000
4000
3000
2000
1000
0
200
150
100
50
0
ppm (f1)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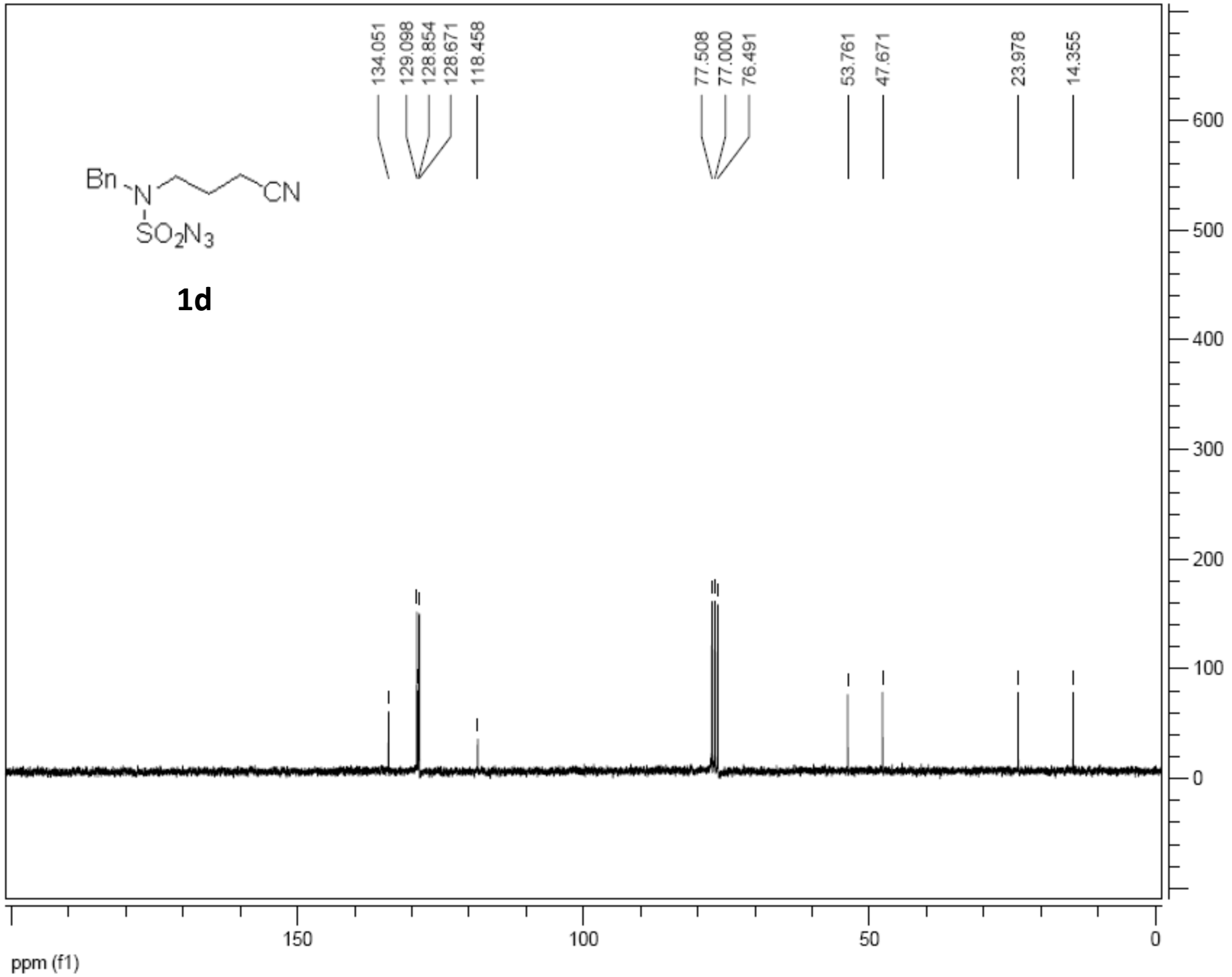
7.240
4.433
3.351
3.323
3.295
2.261
2.232
2.203
1.847
1.819
1.791
1.763
Bn
N
CN
SO2N3
1d
4.96
2.00
2.01
1.99
1.95
700
600
500
400
300
200
100
0
-100
5.0
ppm (f1)


134.051
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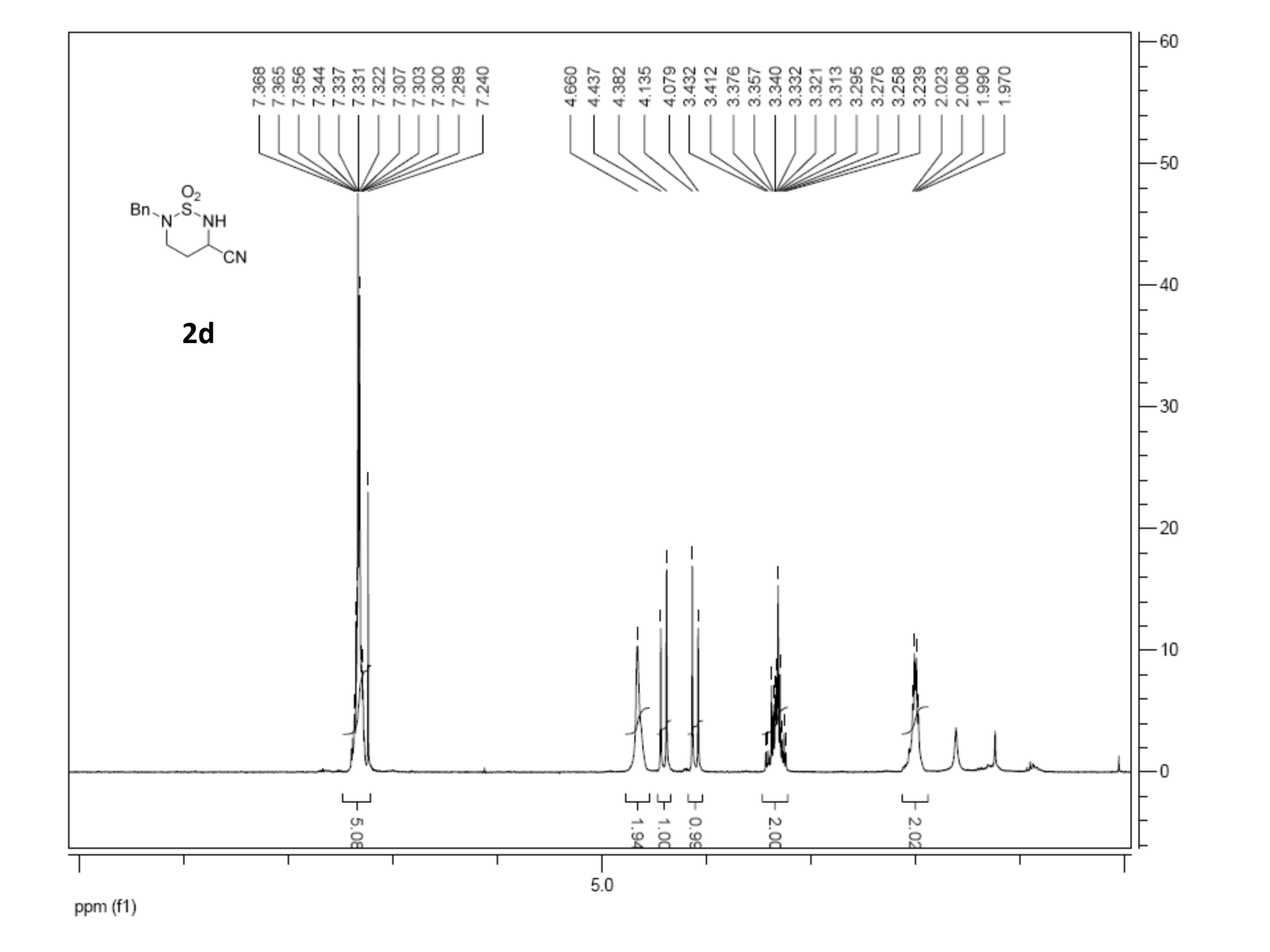
77.000
76.491
53.761
47.671
23.978
14.355
Bn
N
CN
SO2N3
1d
600
500
400
300
200
100
0
150
100
50
0
ppm (f1)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4.660
4.437
4.382
4.135
4.079
3.432
3.412
3.376
3.357
3.340
3.332
3.321
3.313
3.295
3.276
3.258
3.239
2.023
2.008
1.990
1.970
Bn
N
S
O2
NH
CN
2d
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1.00
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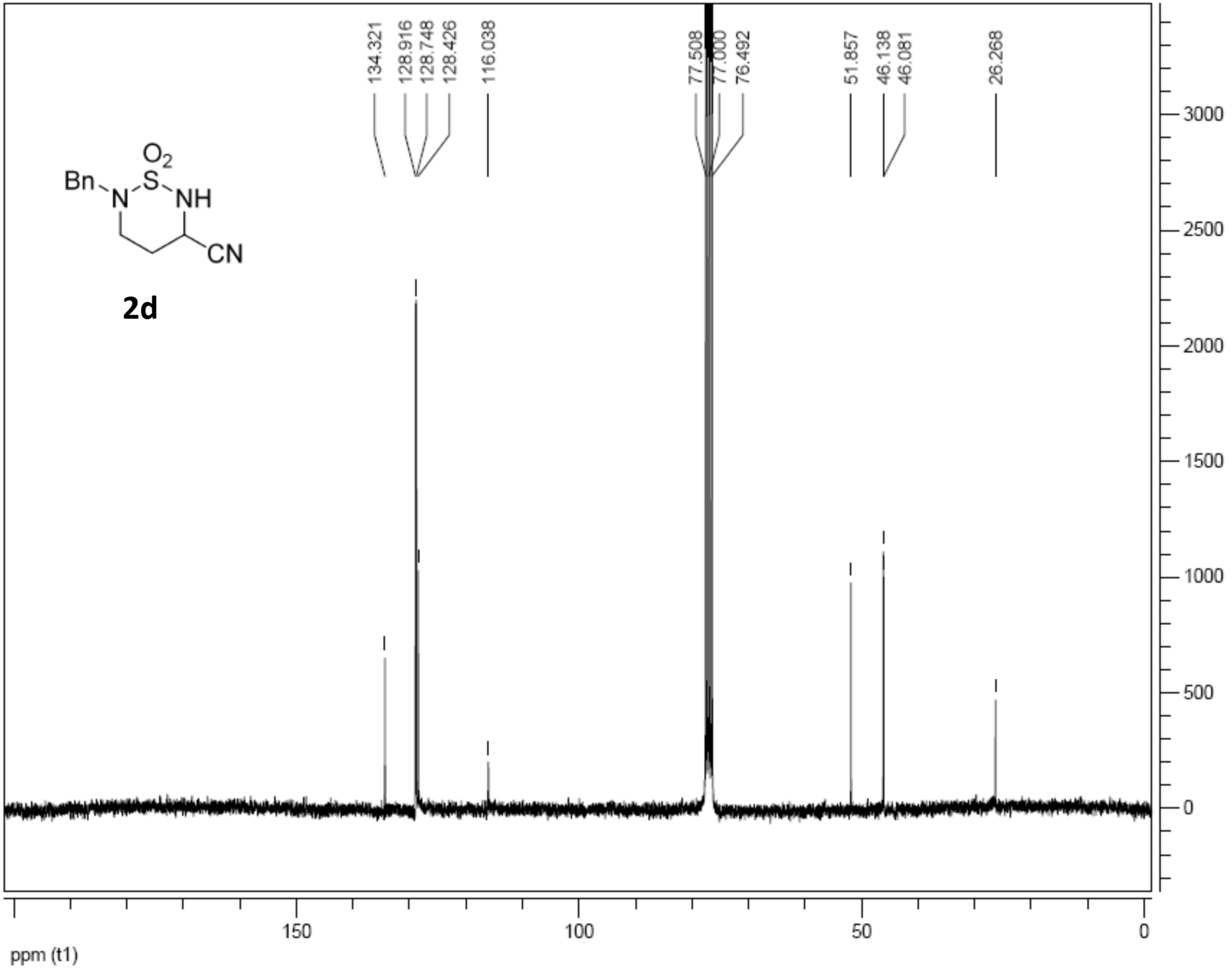
2.00
2.02
5.0
ppm (f1)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77.000
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46.138
46.081
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Bn
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S
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O2
CN
2d
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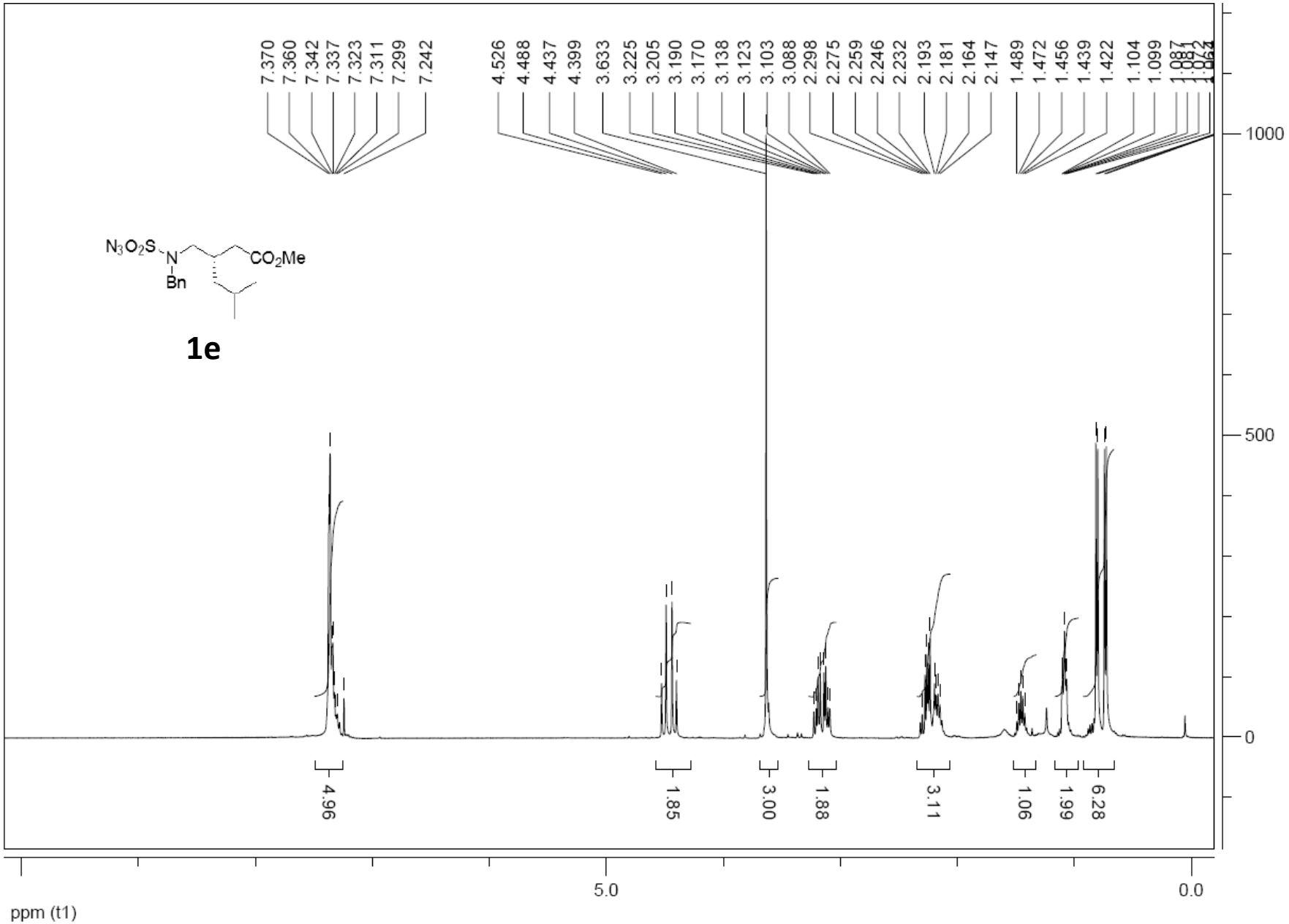
2500
2000
1500
1000
500
0
150
100
50
0
ppm (t1)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3.205
3.190
3.170
3.138
3.123
3.103
3.088
2.298
2.275
2.259
2.246
2.232
2.193
2.181
2.164
2.147
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1.472
1.456
1.439
1.422
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500
0
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1.99
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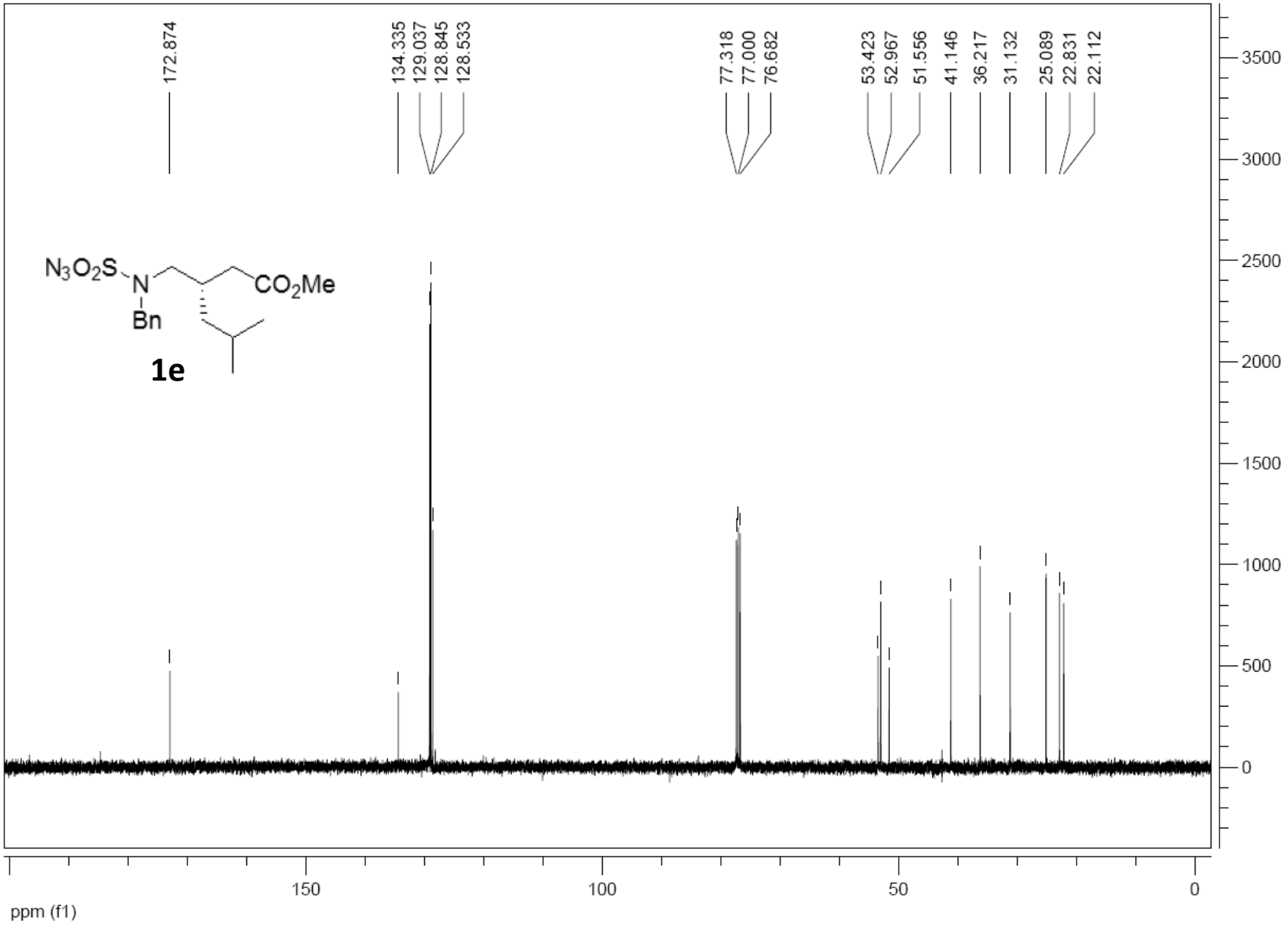
5.0
0.0
ppm (t1)

1e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36.217
31.132
25.089
22.831
22.112
N3O2S
N
Bn
CO2Me
1e
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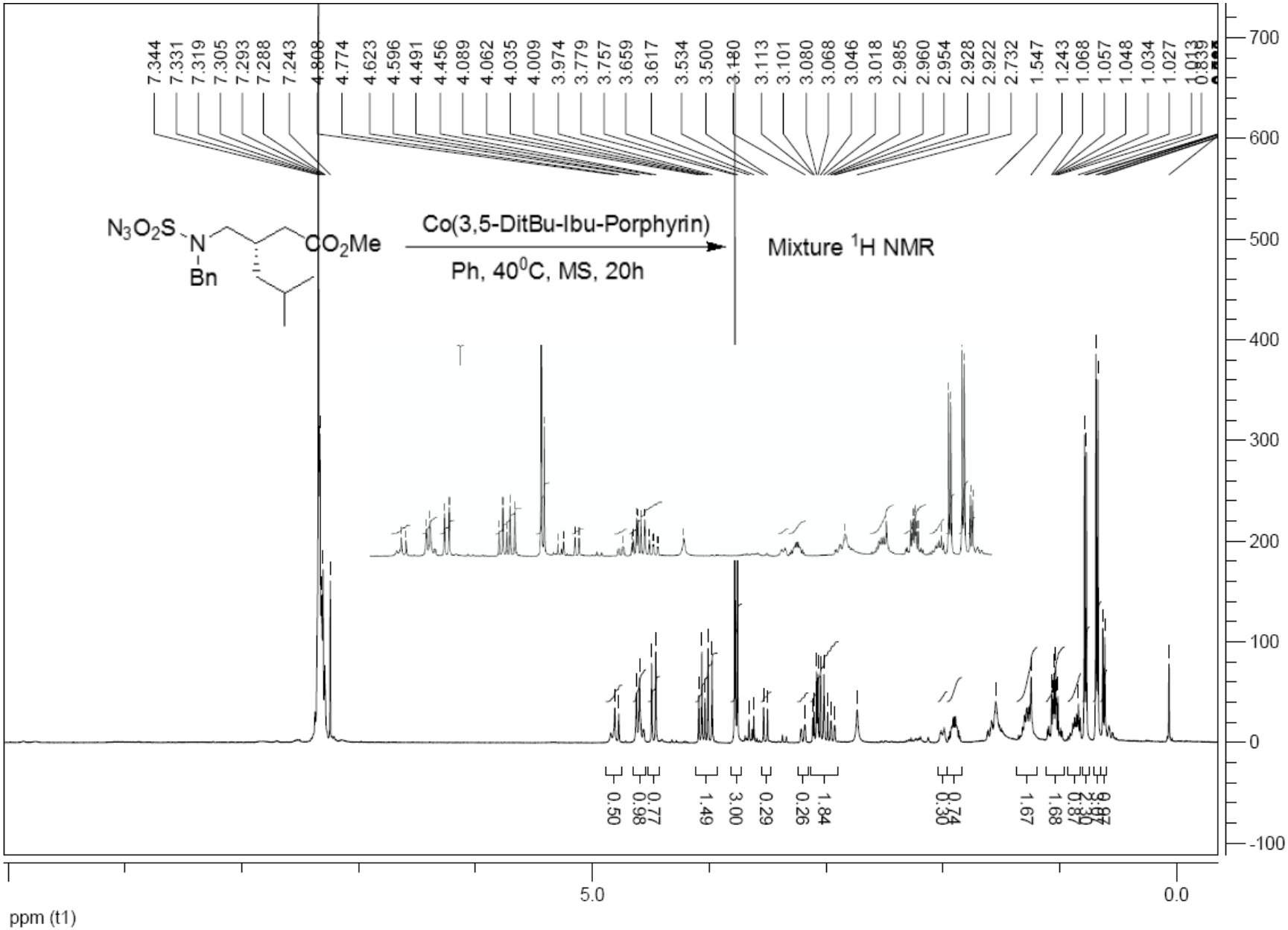
2500
2000
1500
1000
500
0
150
100
50
0
ppm (f1)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4.456
4.089
4.062
4.035
4.009
3.974
3.779
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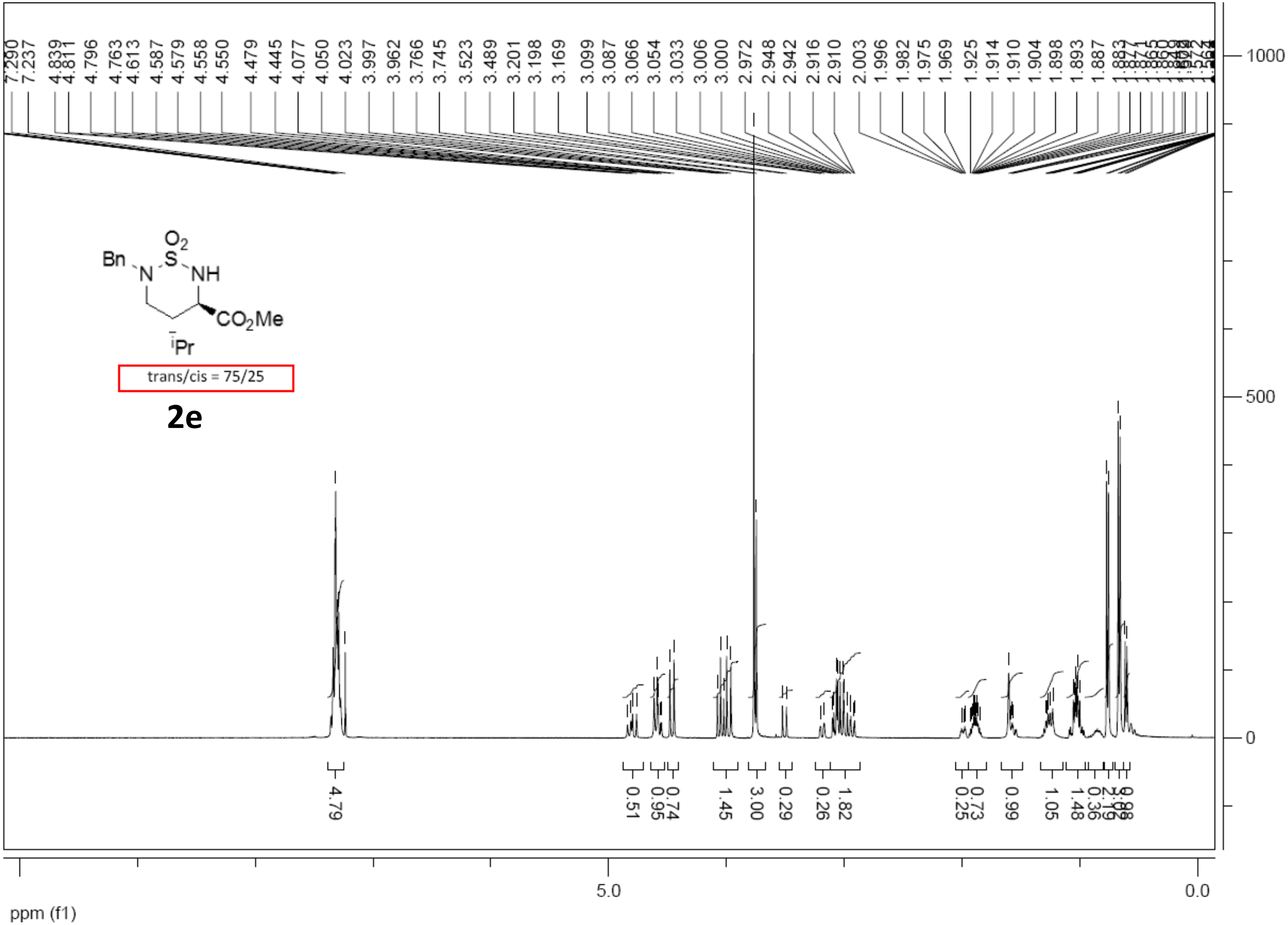
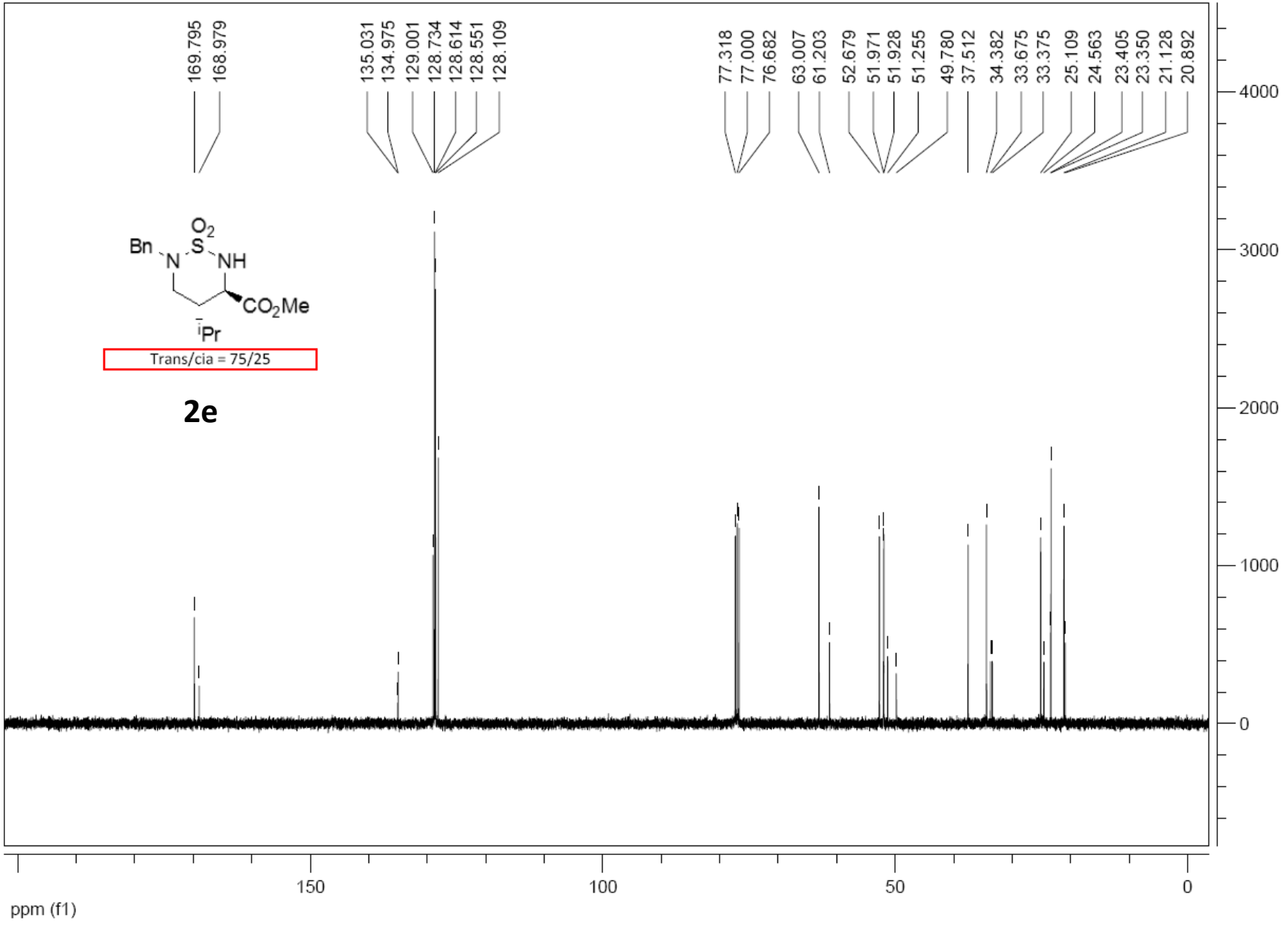
3.659
3.617
3.534
3.500
3.180
3.113
3.101
3.080
3.068
3.046
3.018
2.985
2.960
2.954
2.928
2.922
2.732
1.547
1.243
1.068
1.057
1.048
1.034
1.027
N3O2S
N
Bn
CO2Me
Co(3,5-DitBu-Ibu-Porphyrin)
Ph, 40⁰C, MS, 20h
Mixture 1H NMR
0.50
0.98
0.77
1.49
3.00
0.29
0.26
1.84
0.30
0.74
1.97
1.68
6.87
700
600
500
400
300
200
100
0
-100
5.0
0.0
ppm (t1)



Bn
O_2
S
N
NH
CO_2Me
^iPr
trans/cis = 75/25
2e
1000
500
0
4.79
0.51
0.95
0.74
1.45
3.00
0.29
0.26
1.82
0.25
0.73
0.99
1.05
1.48
0.36
5.0
0.0
ppm (f1)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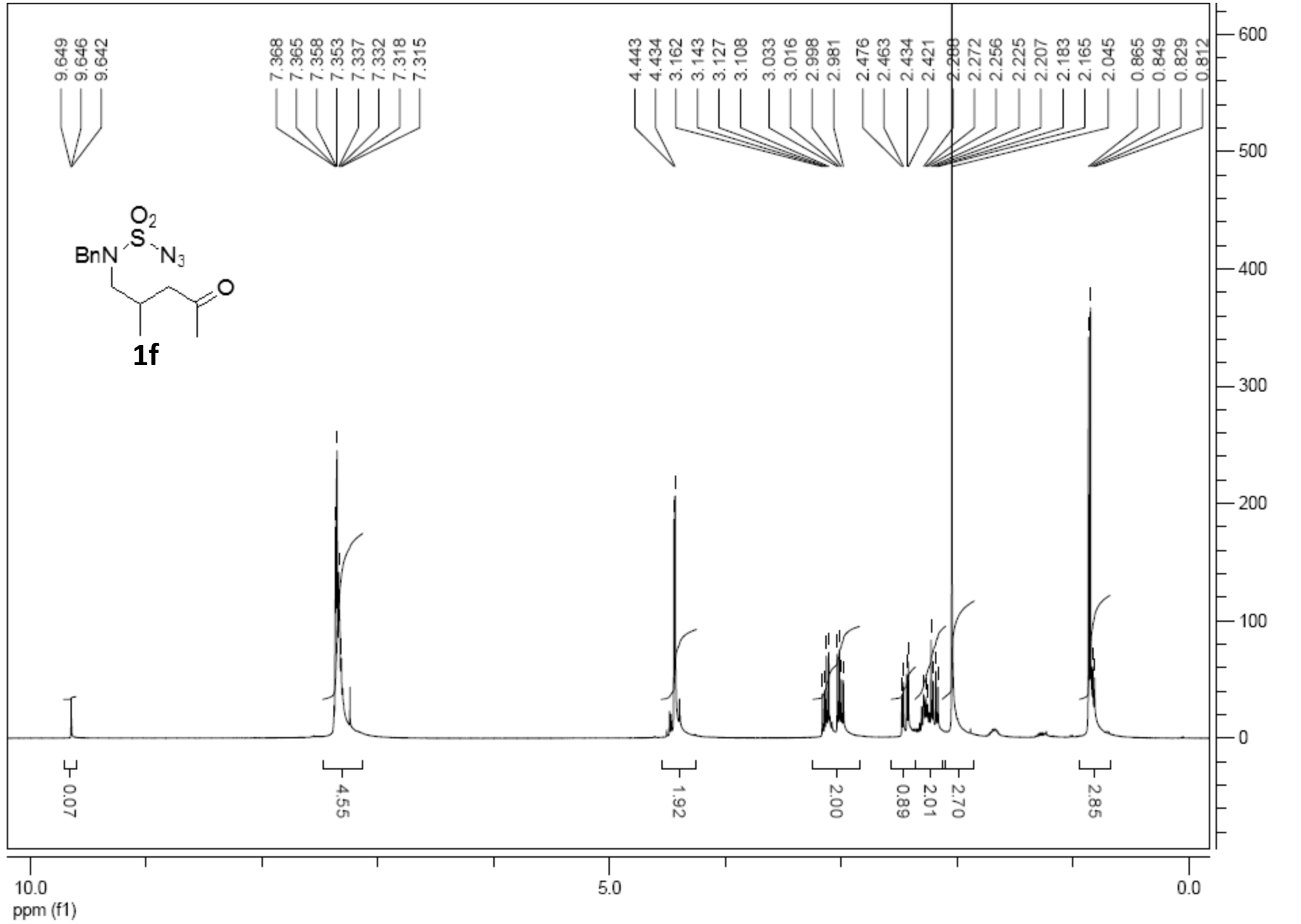
128.614
128.551
128.109
77.318
77.000
76.682
63.007
61.203
52.679
51.971
51.928
51.255
49.780
37.512
34.382
33.675
33.375
25.109
24.563
23.405
23.350
21.128
20.892
Bn
N
S
O2
NH
CO2Me
iPr
Trans/cia = 75/25
2e
4000
3000
2000
1000
0
150
100
50
0
ppm (f1)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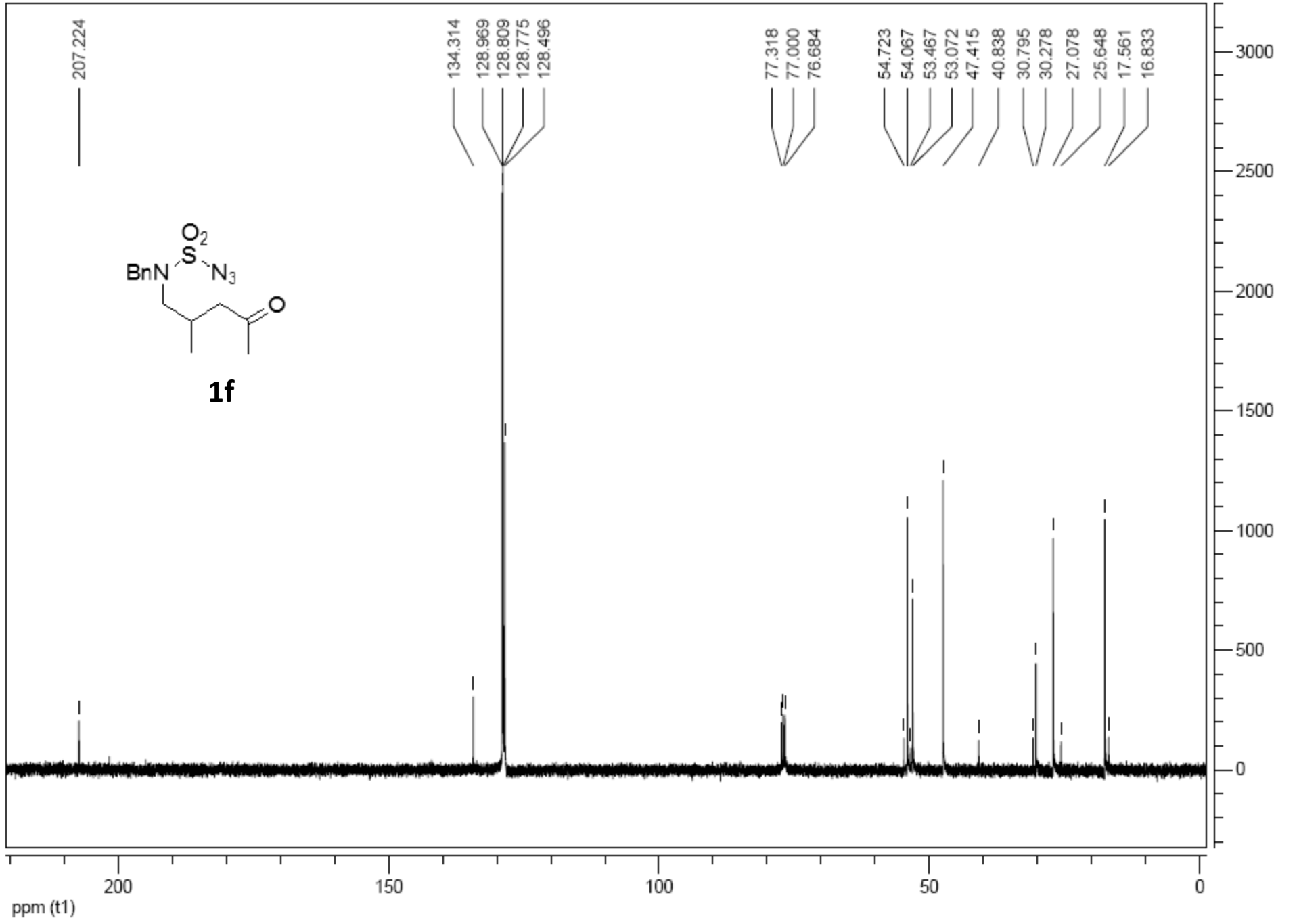
7.318
7.315
4.443
4.434
3.162
3.143
3.127
3.108
3.033
3.016
2.998
2.981
2.476
2.463
2.434
2.421
2.288
2.272
2.256
2.225
2.207
2.183
2.165
2.045
0.865
0.849
0.829
0.812
BnN
O2
S
N3
O
1f
0.07
4.55
1.92
2.00
0.89
2.01
2.70
2.85
600
500
400
300
200
100
0
10.0
5.0
0.0
ppm (f1)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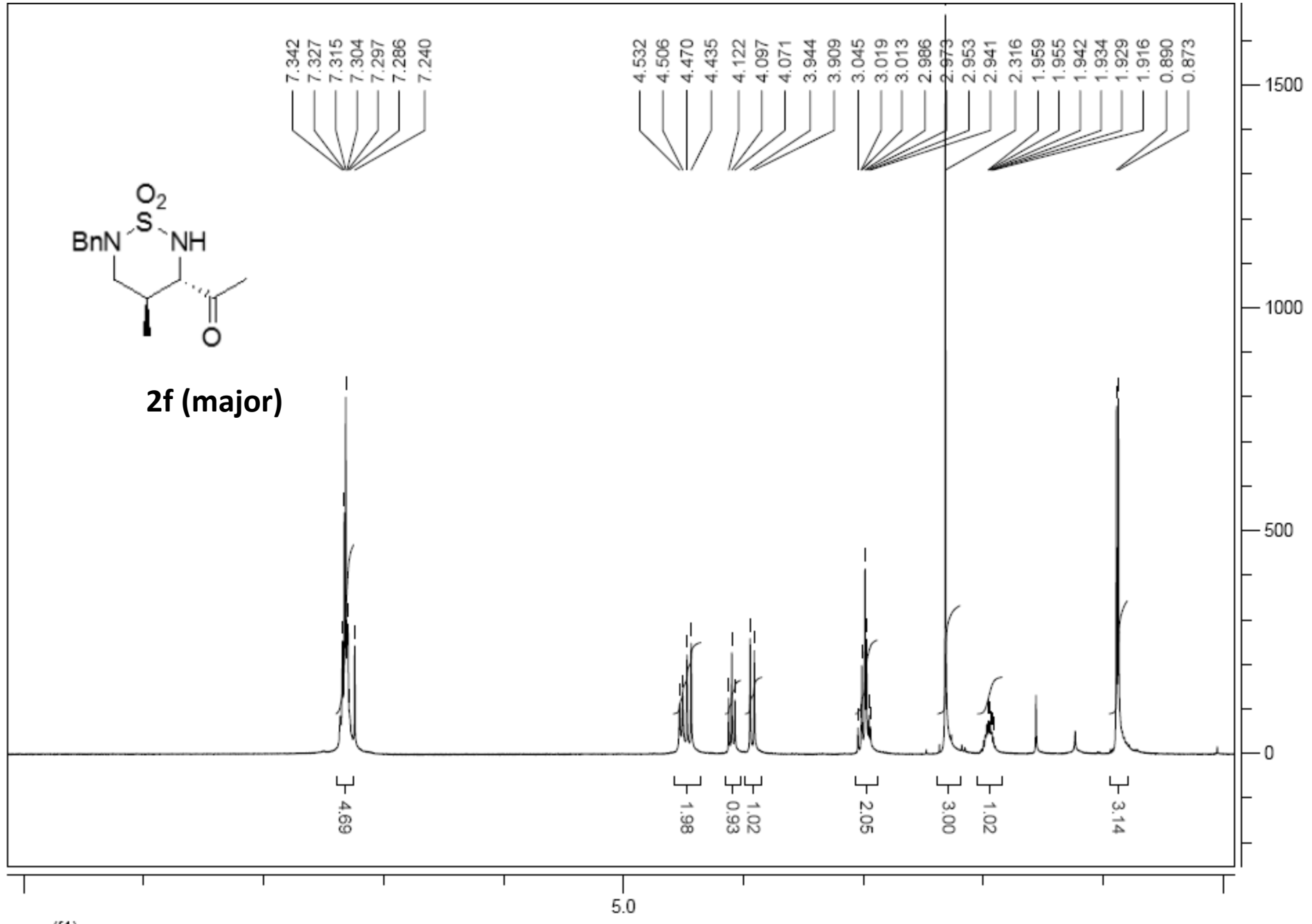
53.072
47.415
40.838
30.795
30.278
27.078
25.648
17.561
16.833
O2
S
BnN
N3
O
1f
3000
2500
2000
1500
1000
500
0
200
150
100
50
0
ppm (t1)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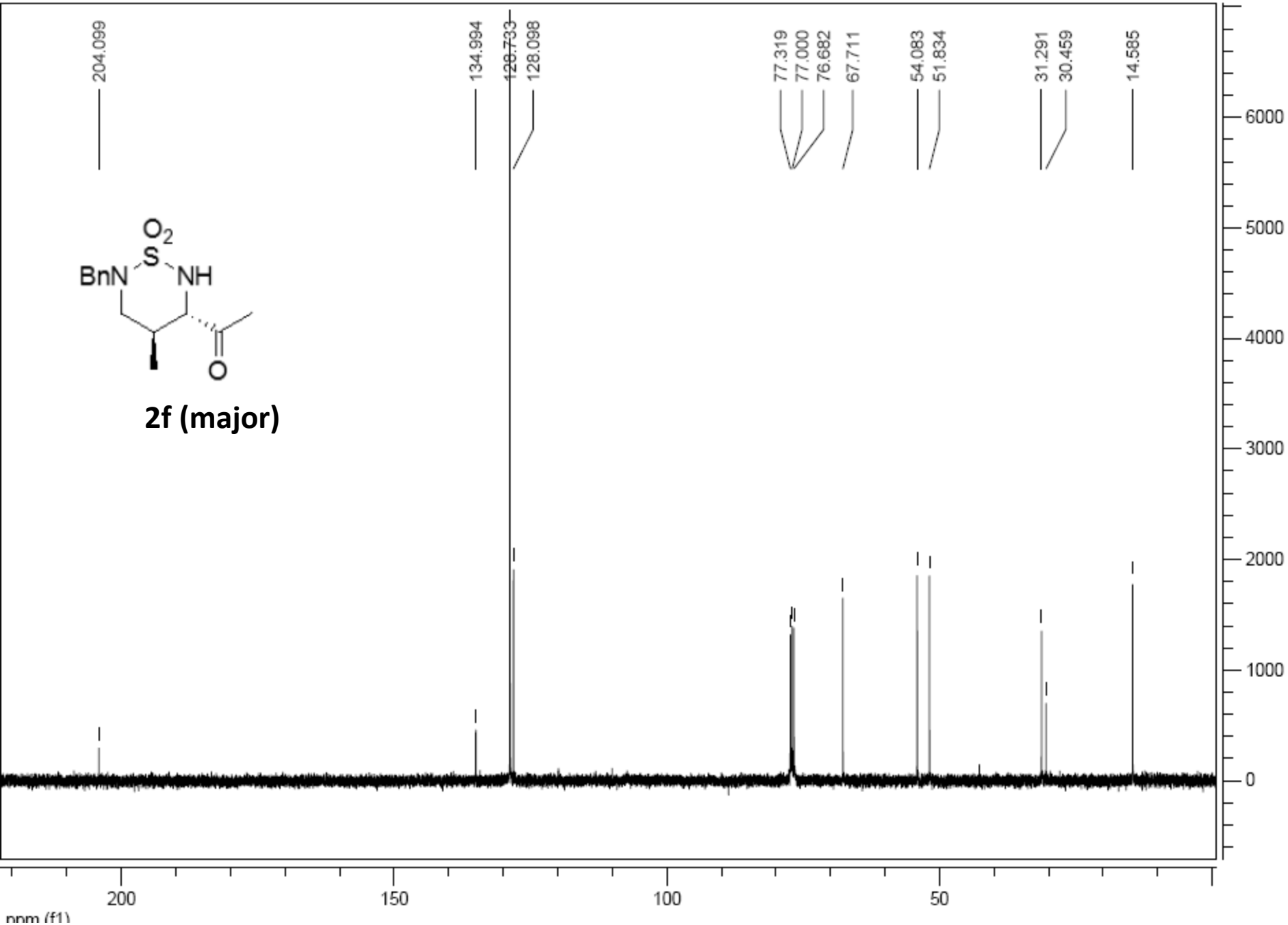
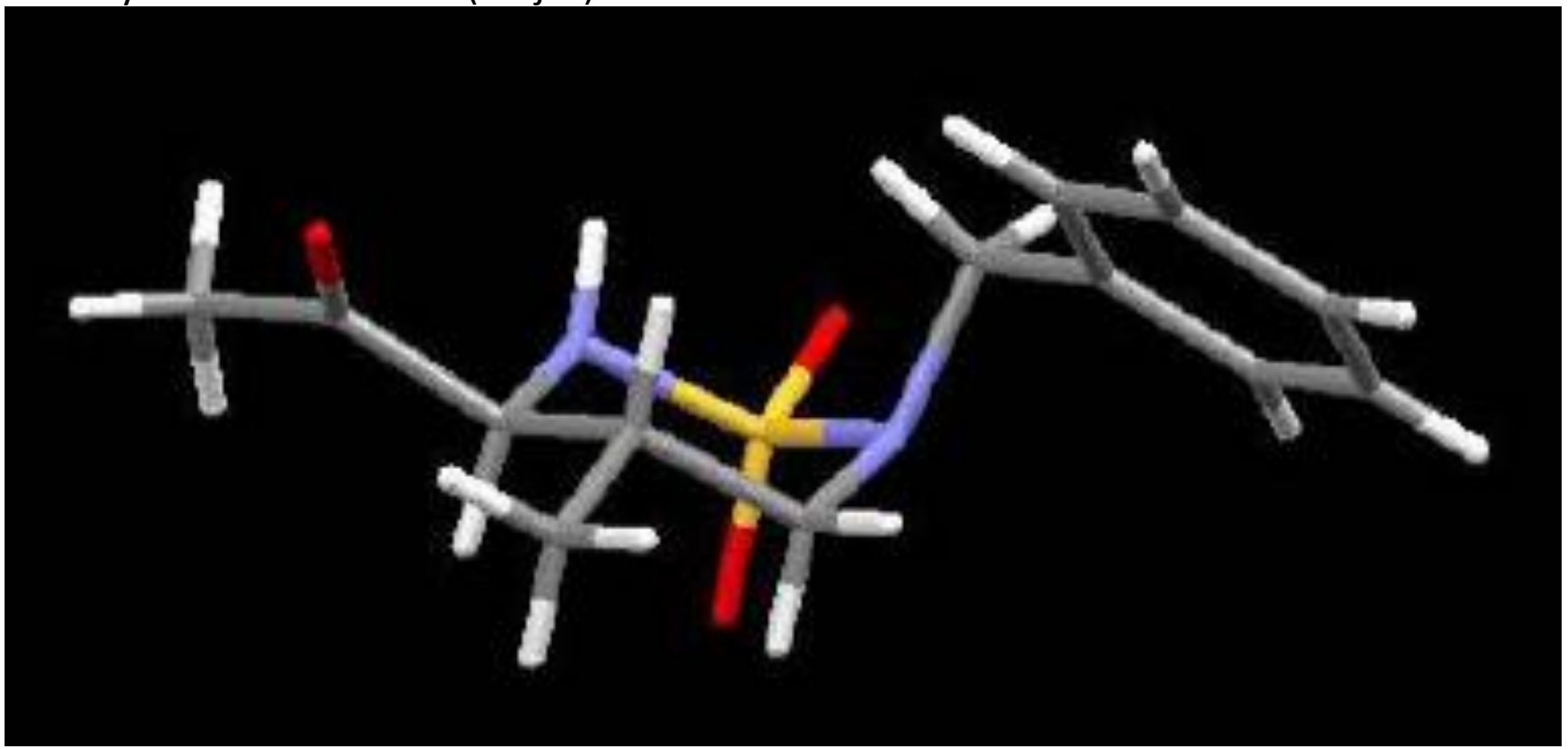
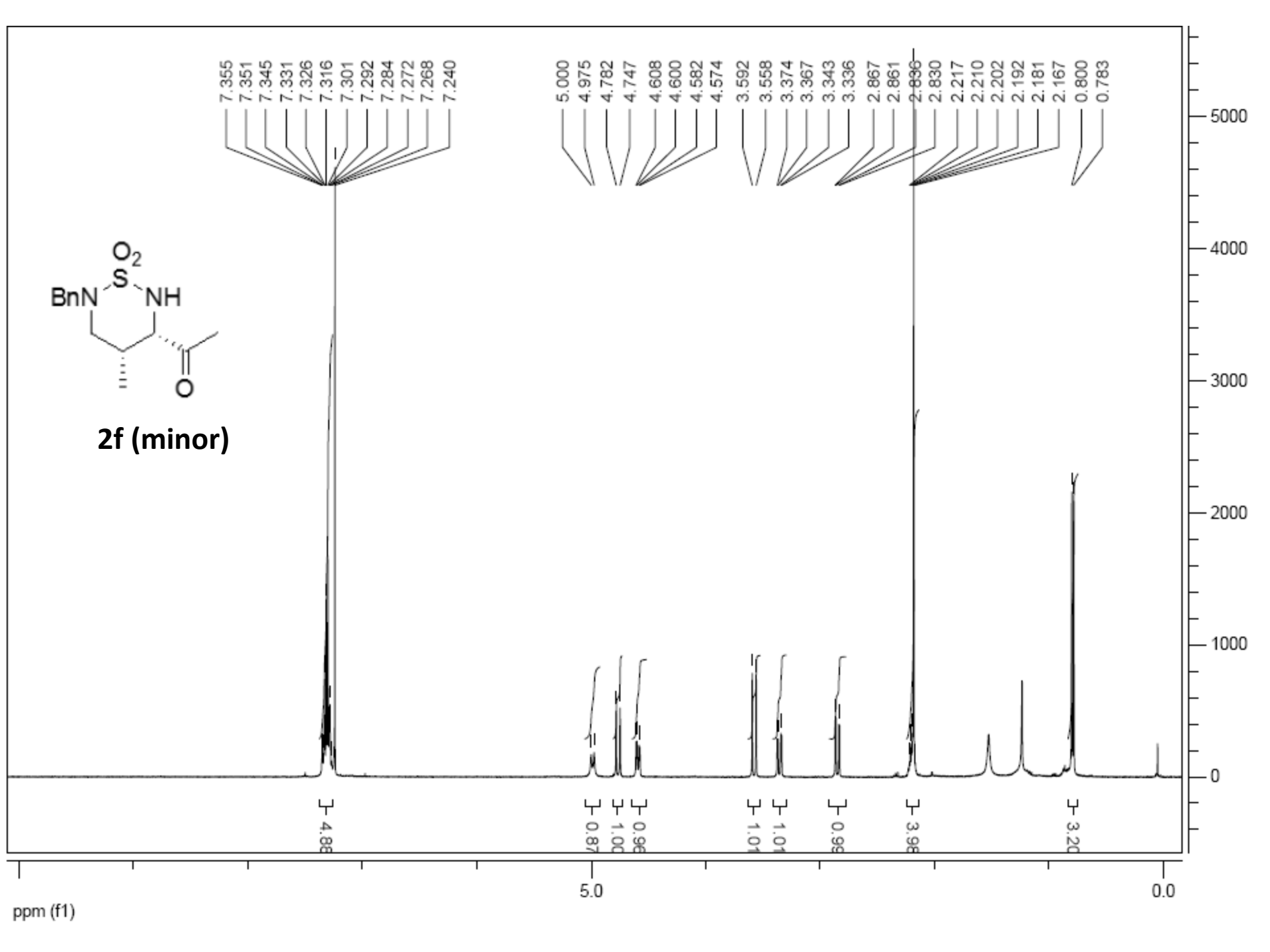
2.986
2.973
2.953
2.941
2.316
1.959
1.955
1.942
1.934
1.929
1.916
0.890
0.873
O2
S
BnN
NH
O
2f (major)
4.69
1.98
0.93
1.02
2.05
3.00
1.02
3.14
1500
1000
500
0
5.0
ppm (f1)

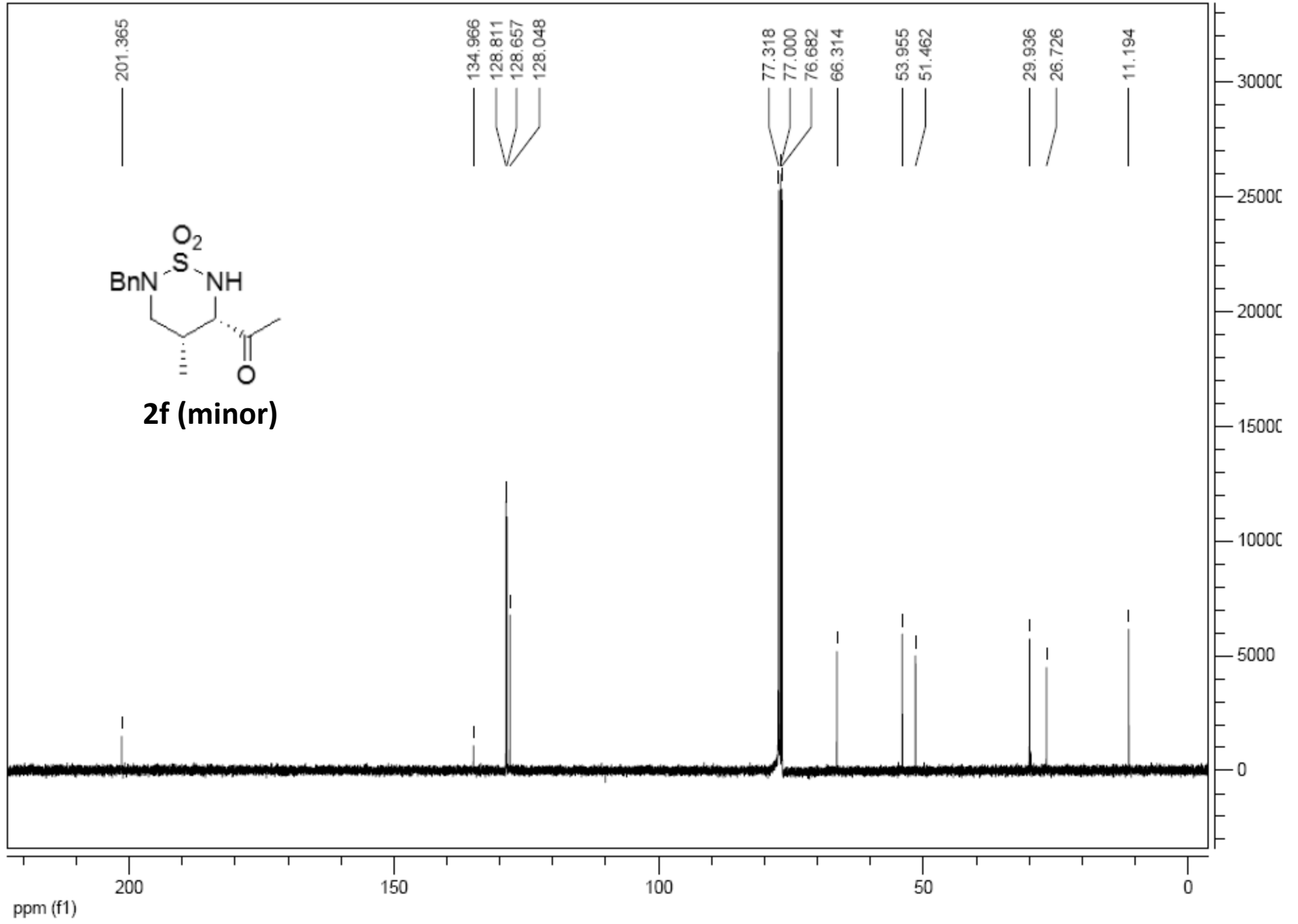

204.099
134.994
129.733
128.098
77.319
77.000
76.682
67.711
54.083
51.834
31.291
30.459
14.585
O2
S
BnN
NH
O
6000
5000
4000
3000
2000
1000
0
200
150
100
50
ppm (f1)

2f (major)

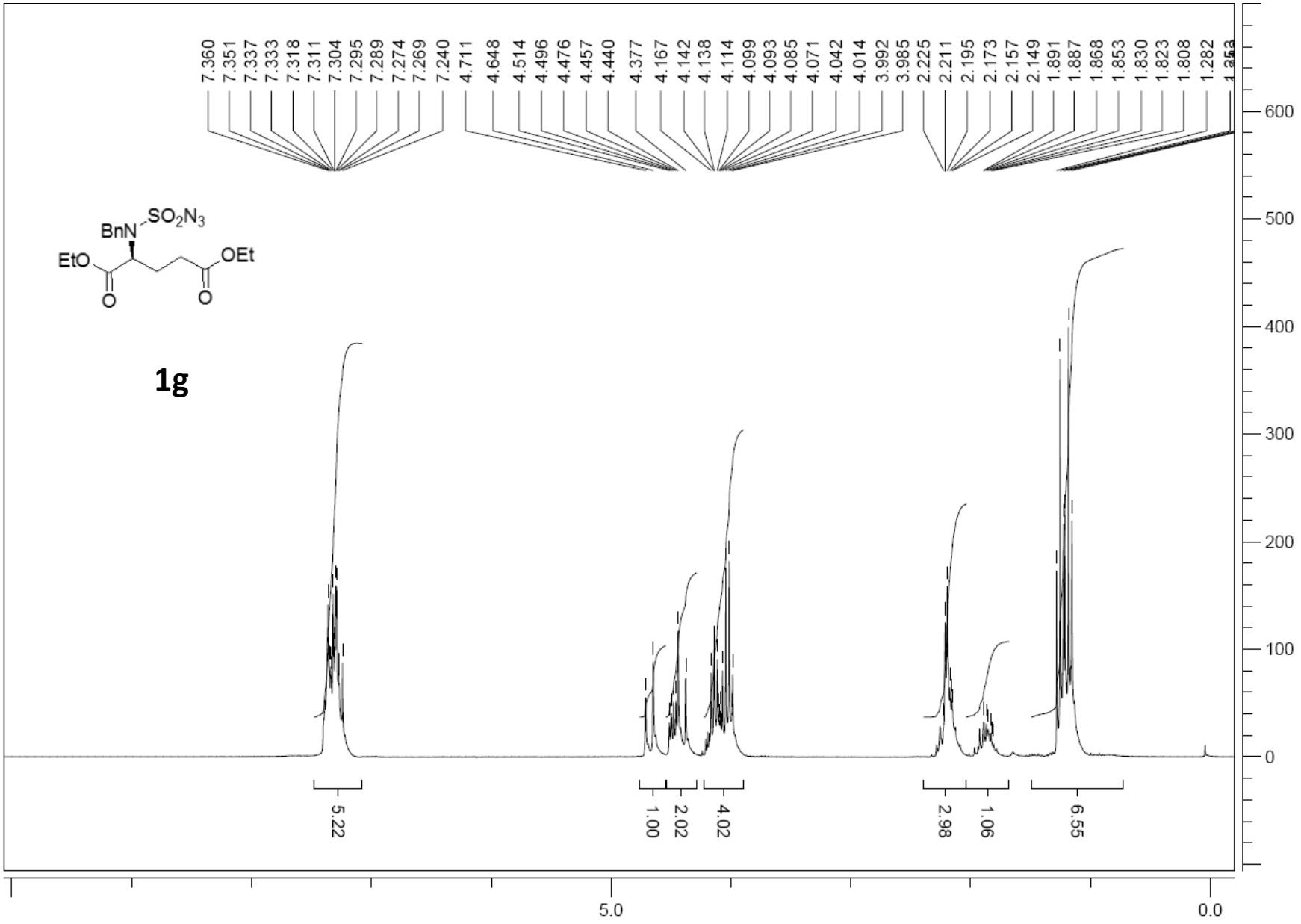
Crystal Structure of **2f**(major)

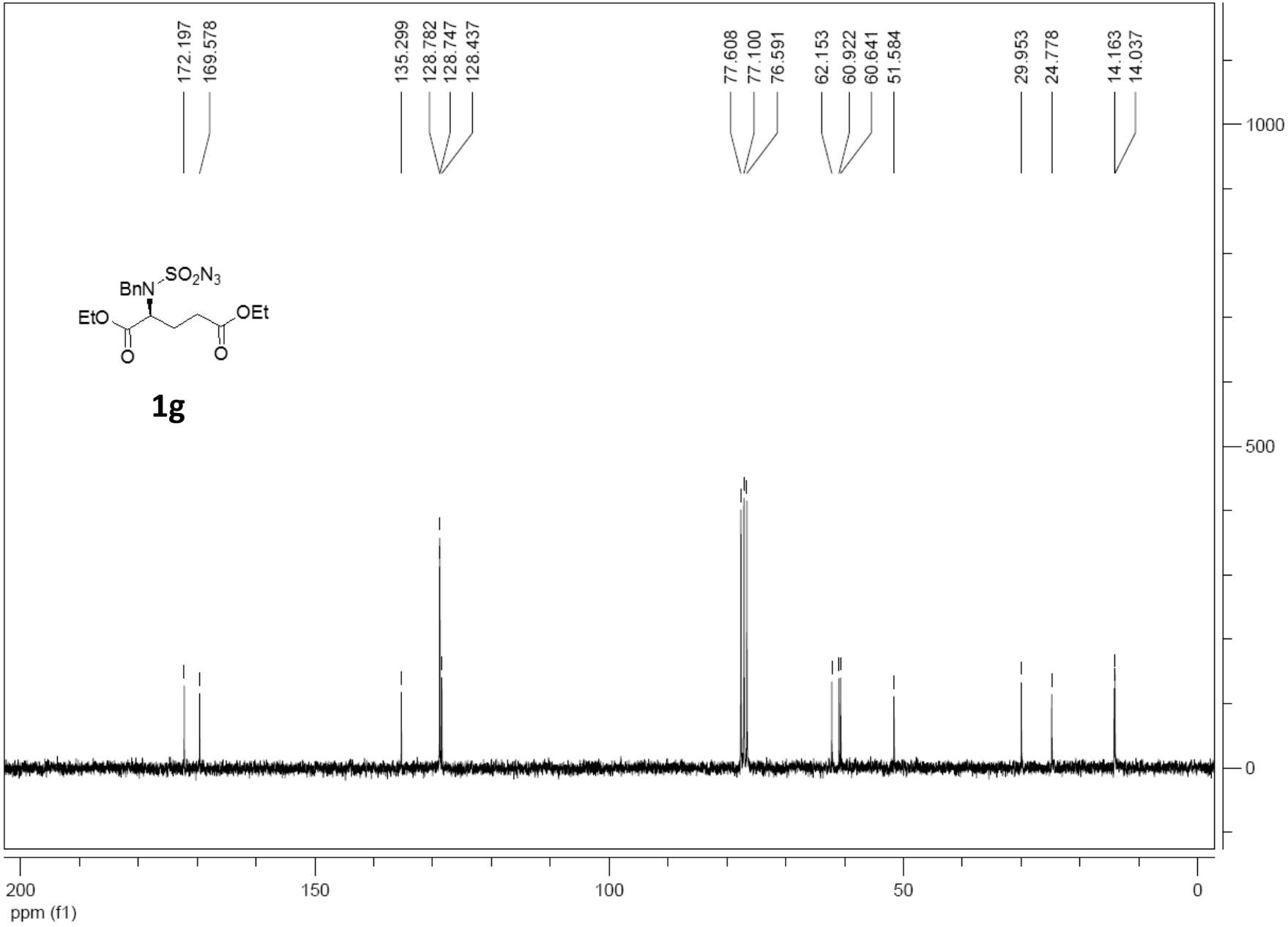


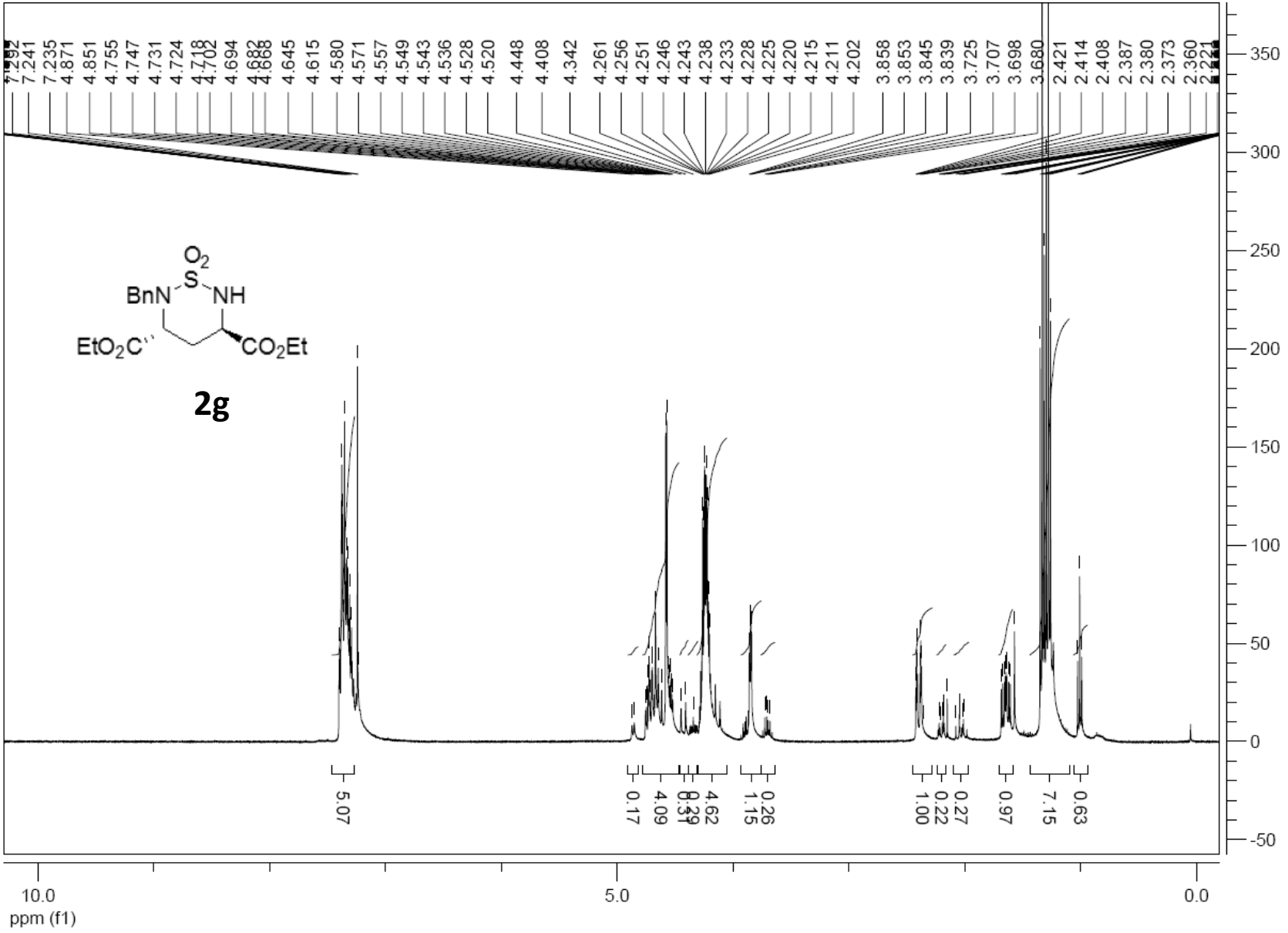

7.355
7.351
7.345
7.331
7.326
7.316
7.301
7.292
7.284
7.272
7.268
7.240
5.000
4.975
4.782
4.747
4.608
4.600
4.582
4.574
3.592
3.558
3.374
3.367
3.343
3.336
2.867
2.861
2.836
2.830
2.217
2.210
2.202
2.192
2.181
2.167
0.800
0.783
O2
S
BnN
NH
O
2f (minor)
5000
4000
3000
2000
1000
0
5.0
0.0
ppm (f1)

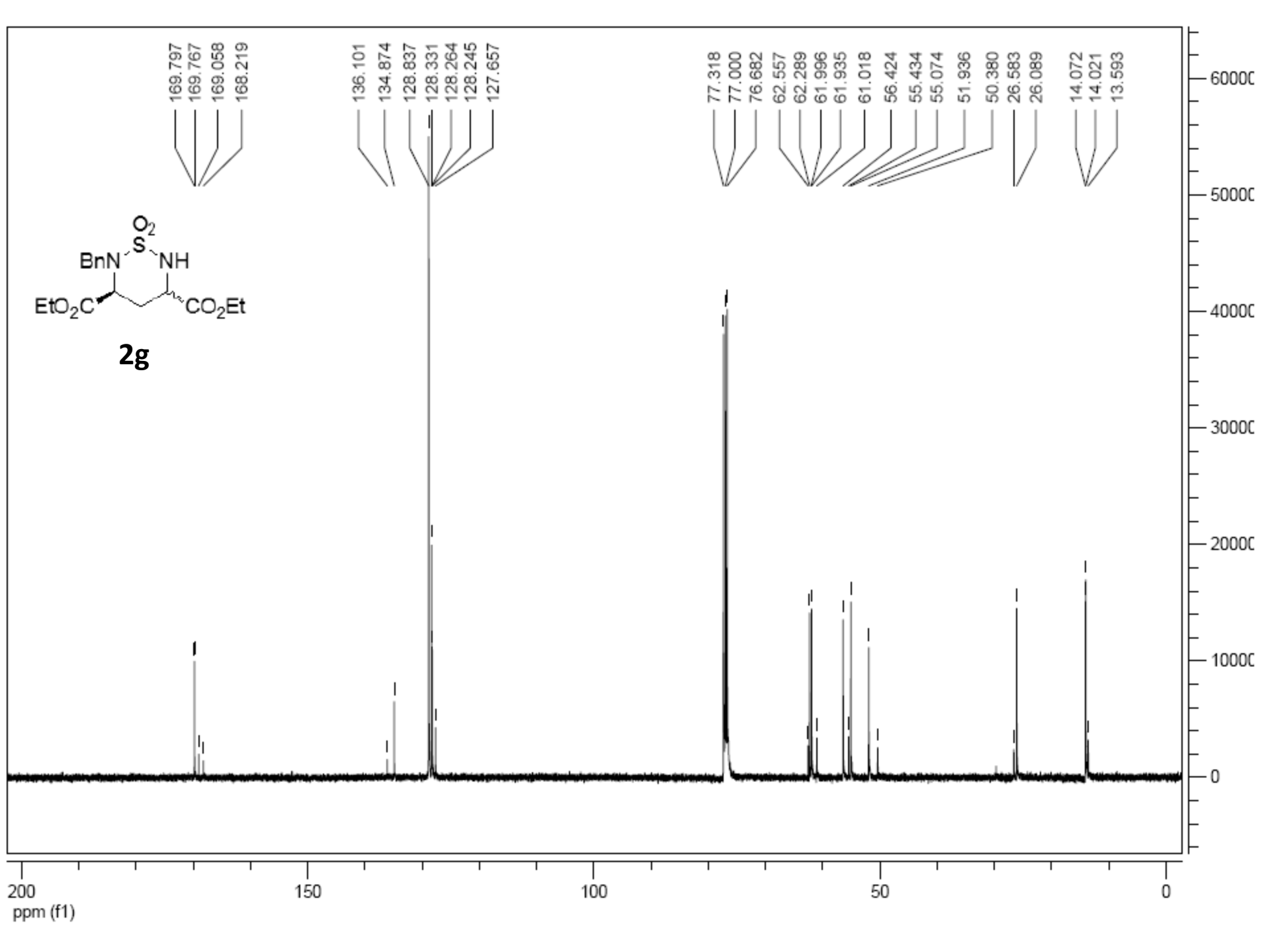

201.365
134.966
128.811
128.657
128.048
77.318
77.000
76.682
66.314
53.955
51.462
29.936
26.726
11.194
O2
S
BnN
NH
O
3000
2500
2000
1500
1000
5000
0
200
150
100
50
0
ppm (f1)

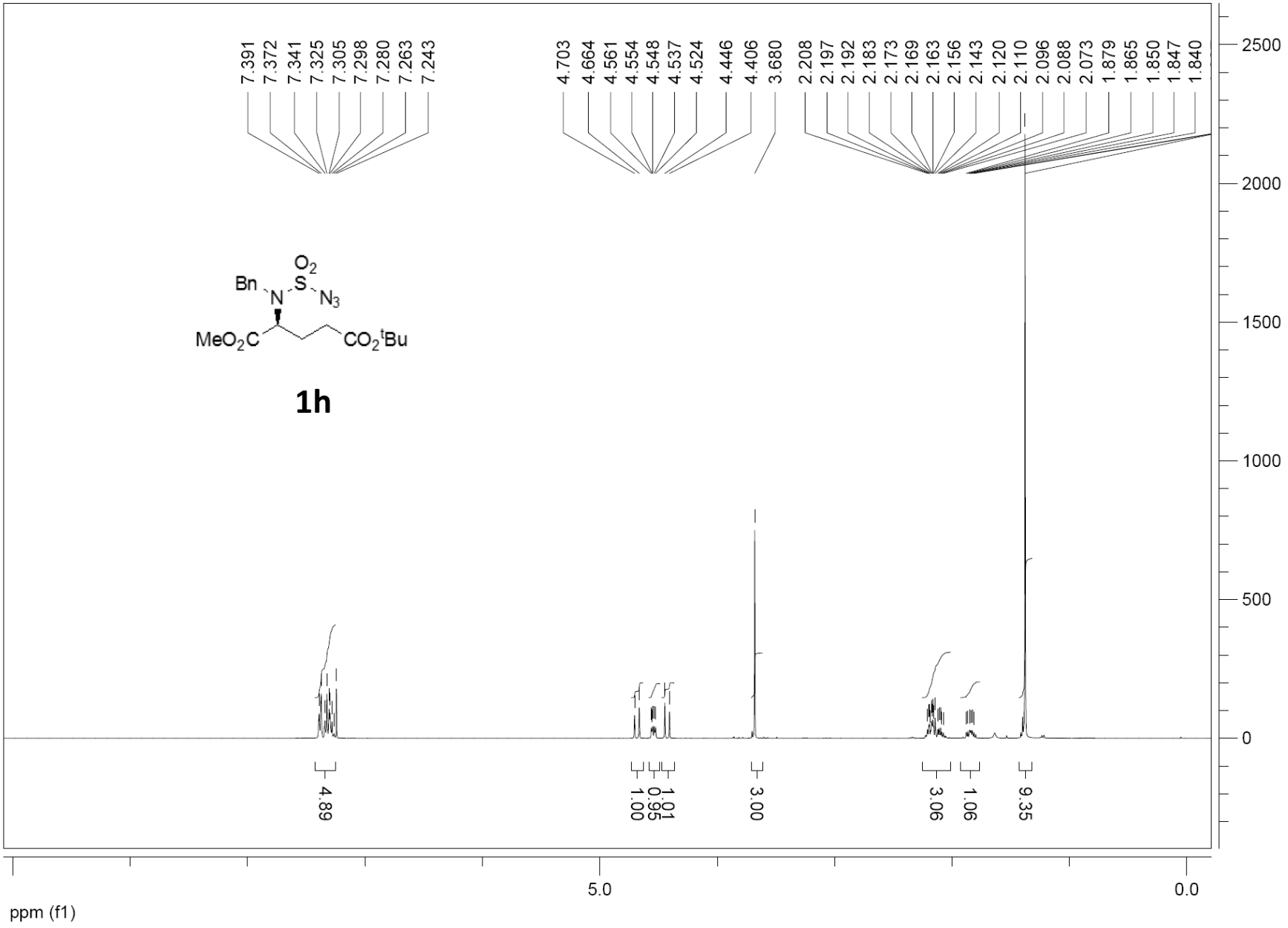
2f (minor)

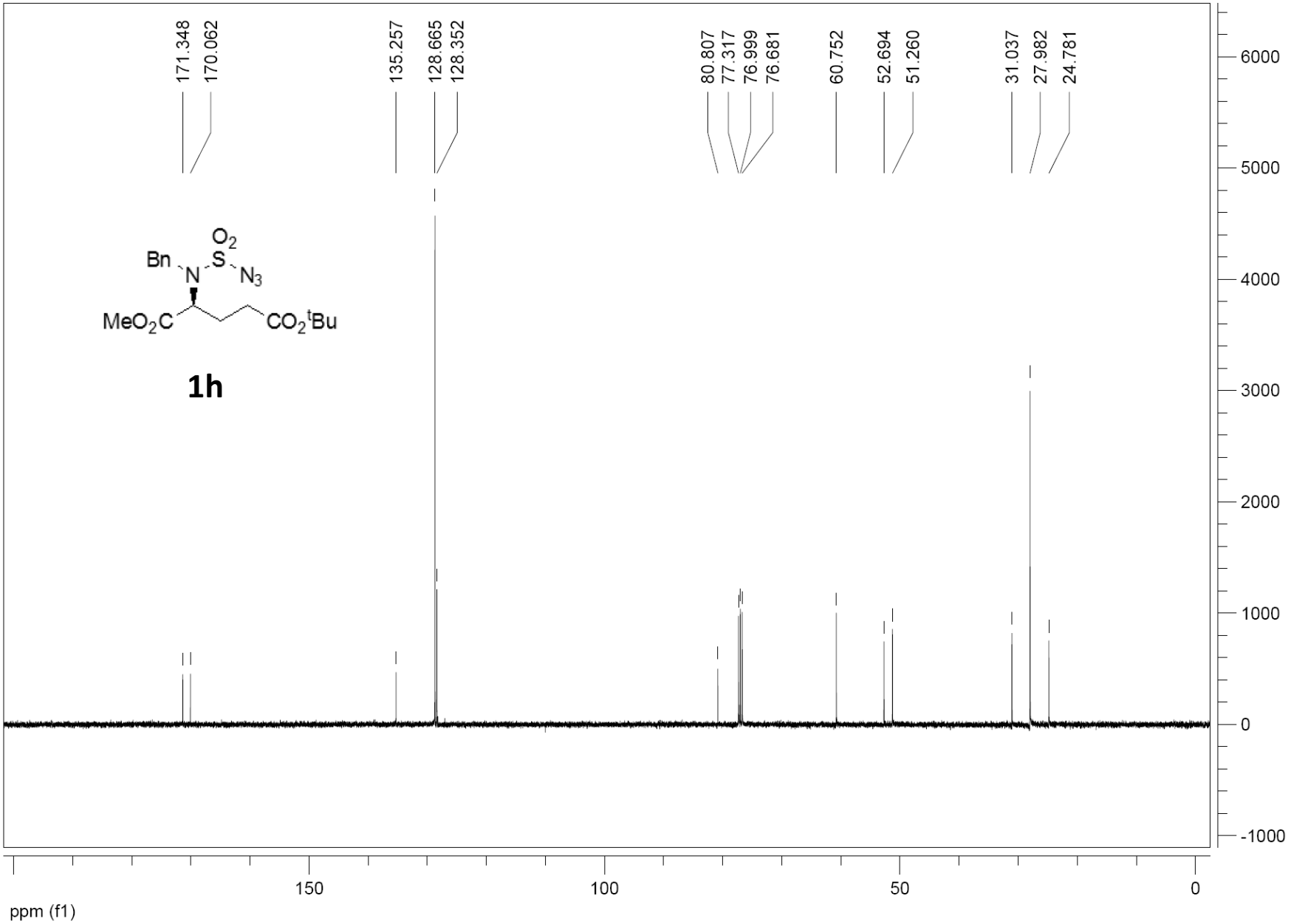

7.360
7.351
7.337
7.333
7.318
7.311
7.304
7.295
7.289
7.274
7.269
7.240
4.711
4.648
4.514
4.496
4.476
4.457
4.440
4.377
4.167
4.142
4.138
4.114
4.099
4.093
4.085
4.071
4.042
4.014
3.992
3.985
2.225
2.211
2.195
2.173
2.157
2.149
1.891
1.887
1.868
1.853
1.830
1.823
1.808
1.282
BnN
SO2N3
EtO
OEt
O
O
1g
600
500
400
300
200
100
0
5.22
1.00
2.02
4.02
2.98
1.06
6.55
5.0
0.0
ppm (f1)

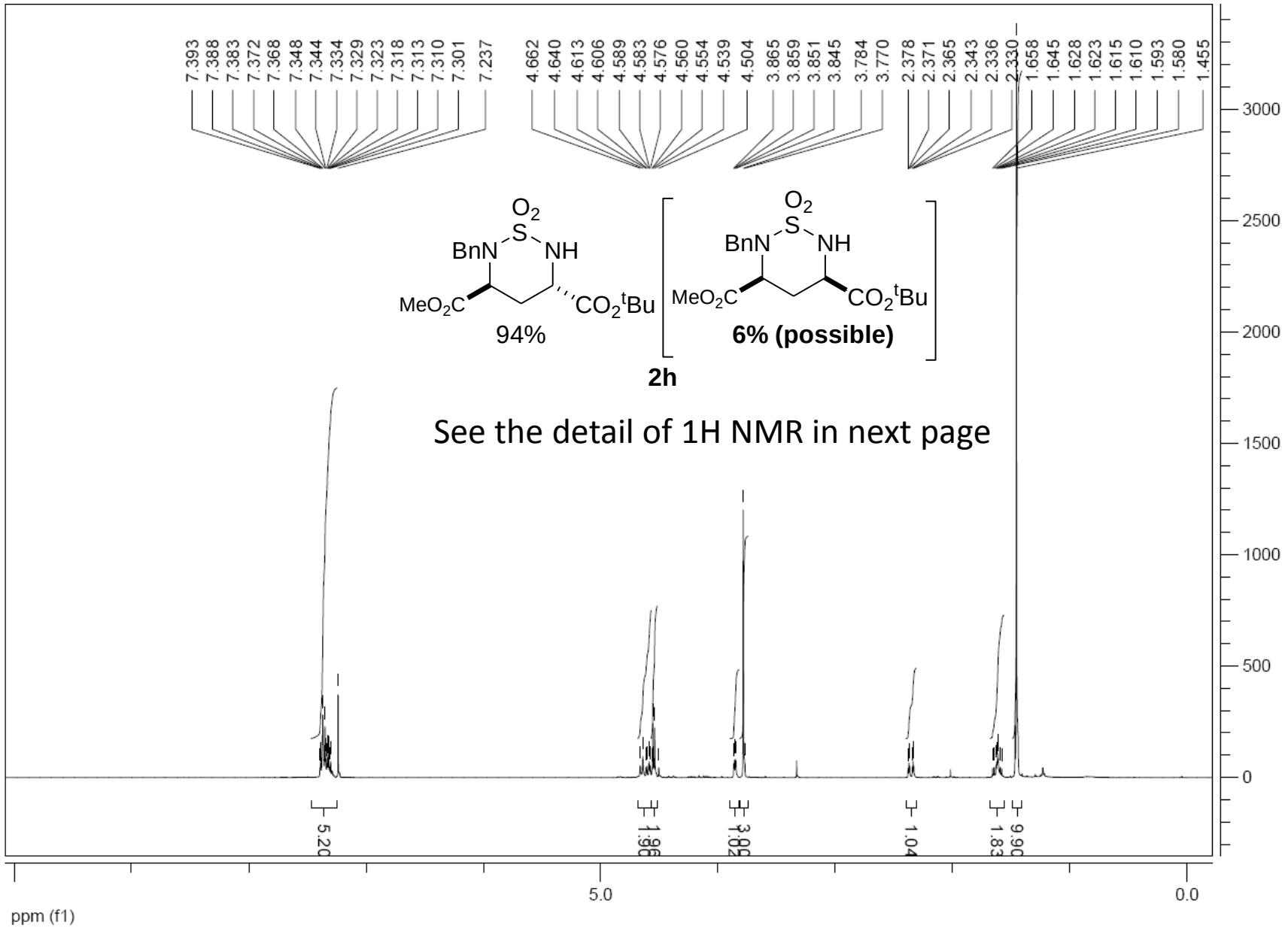

172.197
169.578
135.299
128.782
128.747
128.437
77.608
77.100
76.591
62.153
60.922
60.641
51.584
29.953
24.778
14.163
14.037
BnN
SO2N3
EtO
OEt
O
O
1g
1000
500
0
200
150
100
50
0
ppm (f1)

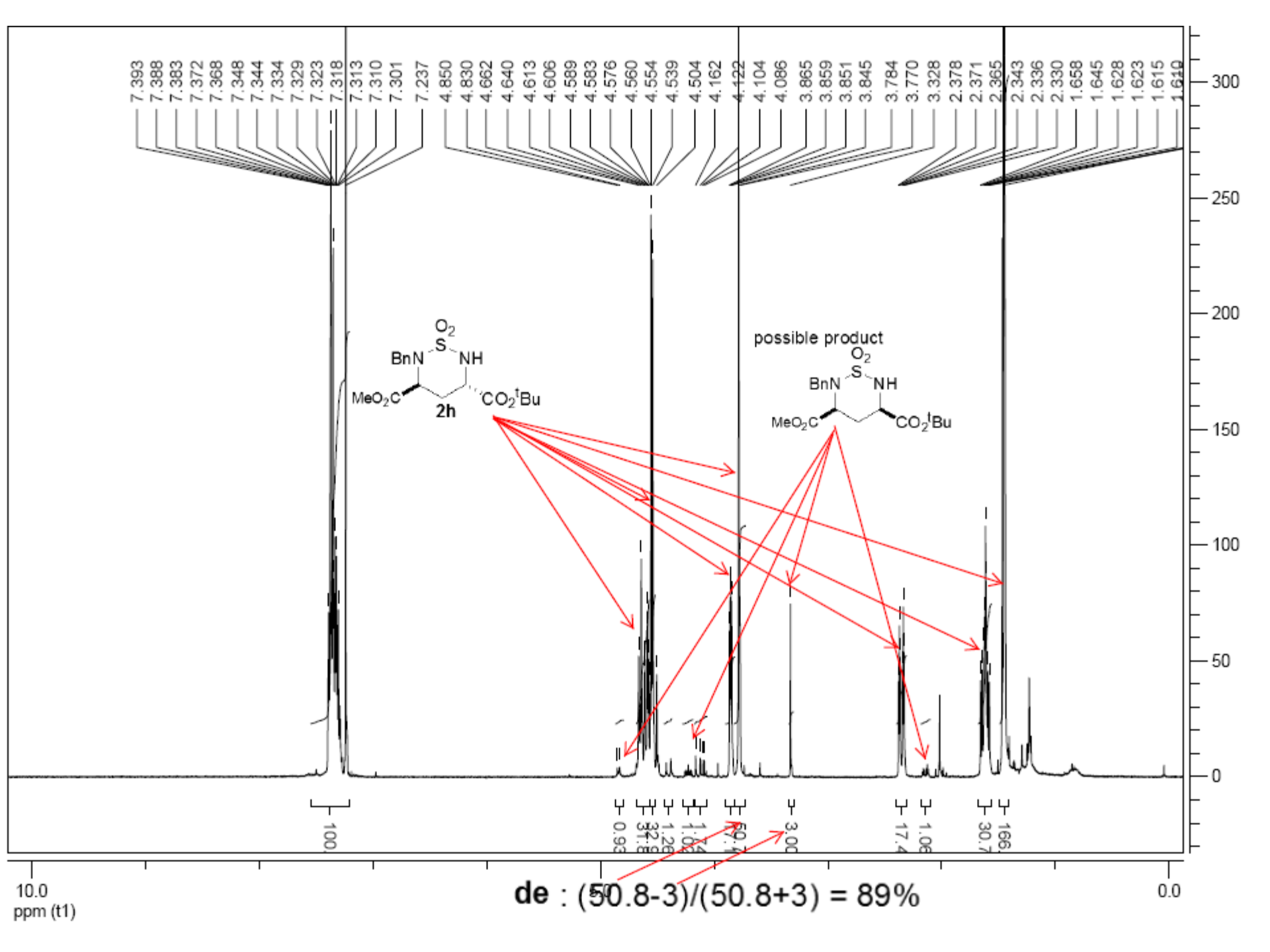

O2
S
BnN
NH
EtO2C
CO2Et
2g
7.241
7.235
4.871
4.851
4.755
4.747
4.731
4.724
4.718
4.702
4.694
4.645
4.615
4.580
4.571
4.557
4.549
4.543
4.536
4.528
4.520
4.448
4.408
4.342
4.261
4.256
4.251
4.246
4.243
4.238
4.233
4.228
4.225
4.220
4.215
4.211
4.202
3.858
3.853
3.845
3.839
3.725
3.707
3.698
3.680
2.421
2.414
2.408
2.387
2.380
2.373
2.360
5.07
0.17
4.09
4.62
1.15
0.26
1.00
0.22
0.27
0.97
7.15
0.63
350
300
250
200
150
100
50
0
-50
10.0
5.0
0.0
ppm (f1)

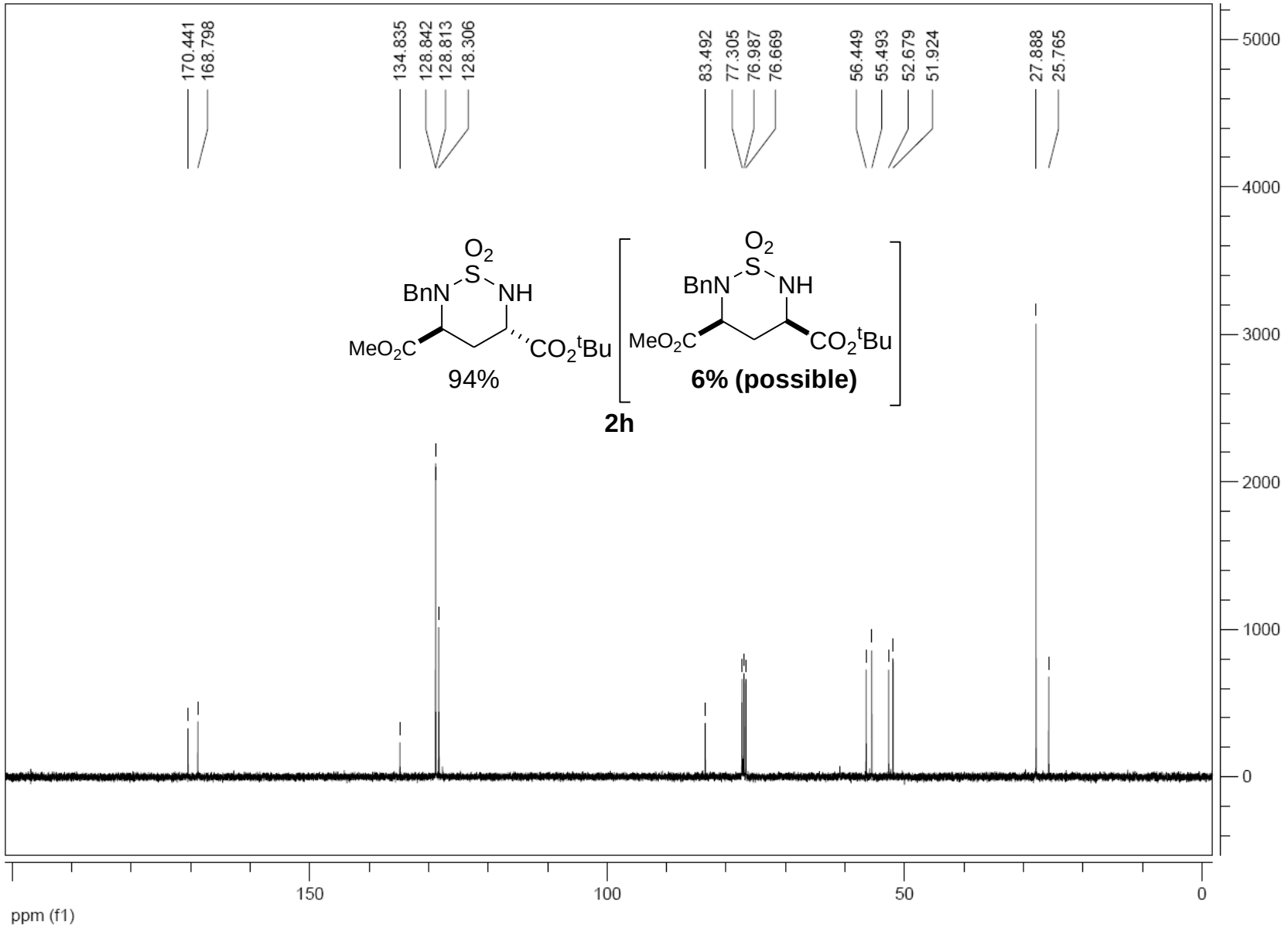

169.797
169.767
169.058
168.219
136.101
134.874
128.837
128.331
128.264
128.245
127.657
77.318
77.000
76.682
62.557
62.289
61.996
61.935
61.018
56.424
55.434
55.074
51.936
50.380
26.583
26.089
14.072
14.021
13.593
BnN
O2
S
NH
EtO2C
CO2Et
2g
6000
5000
4000
3000
2000
1000
0
200
150
100
50
0
ppm (f1)

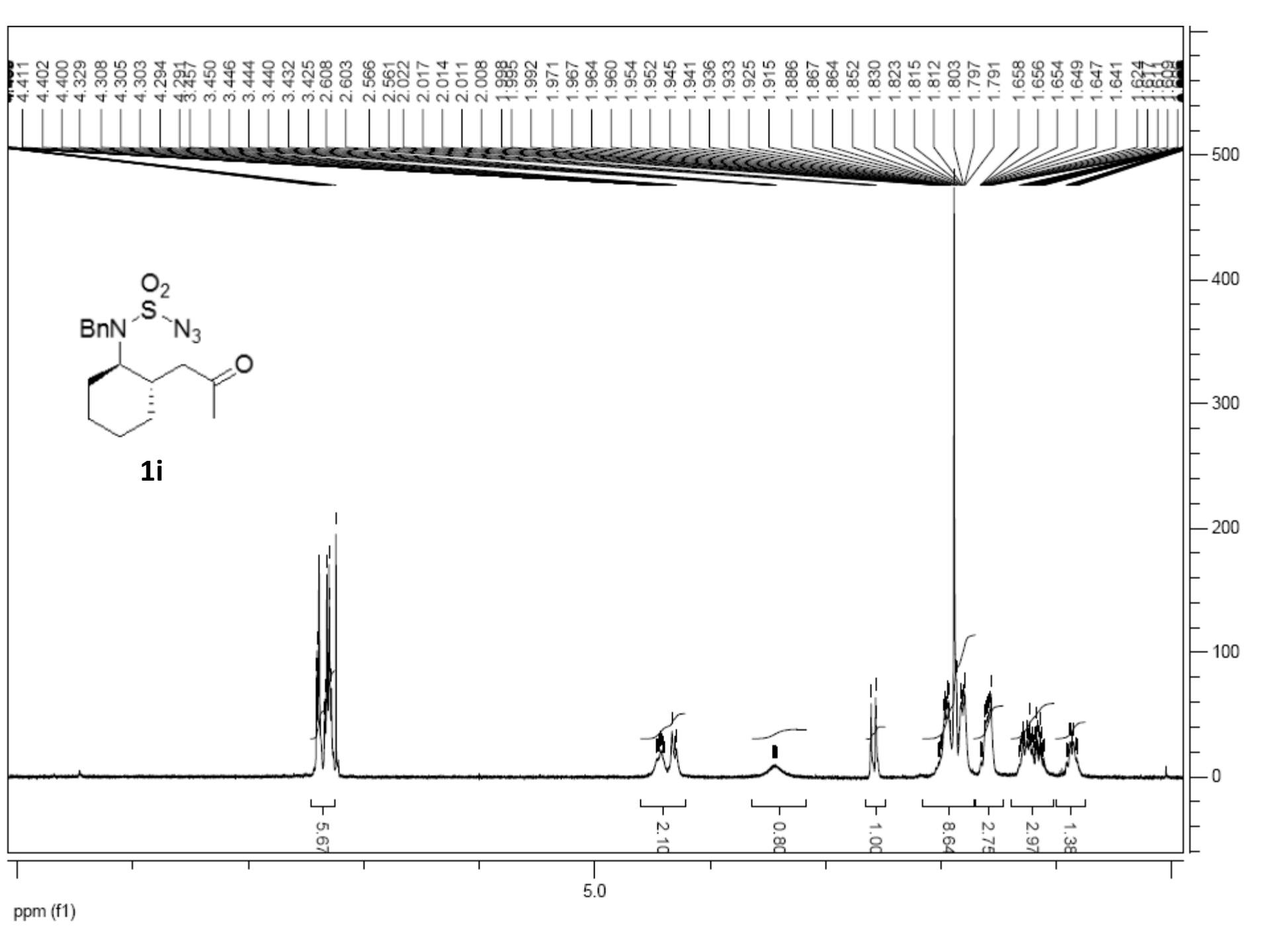

7.391
7.372
7.341
7.325
7.305
7.298
7.280
7.263
7.243
4.703
4.664
4.561
4.554
4.548
4.537
4.524
4.446
4.406
3.680
2.208
2.197
2.192
2.183
2.173
2.169
2.163
2.156
2.143
2.120
2.110
2.096
2.088
2.073
1.879
1.865
1.850
1.847
1.840
Bn
N
O2
S
N3
MeO2C
CO2tBu
1h
2500
2000
1500
1000
500
0
4.89
1.00
0.95
1.01
3.00
3.06
1.06
9.35
5.0
0.0
ppm (f1)

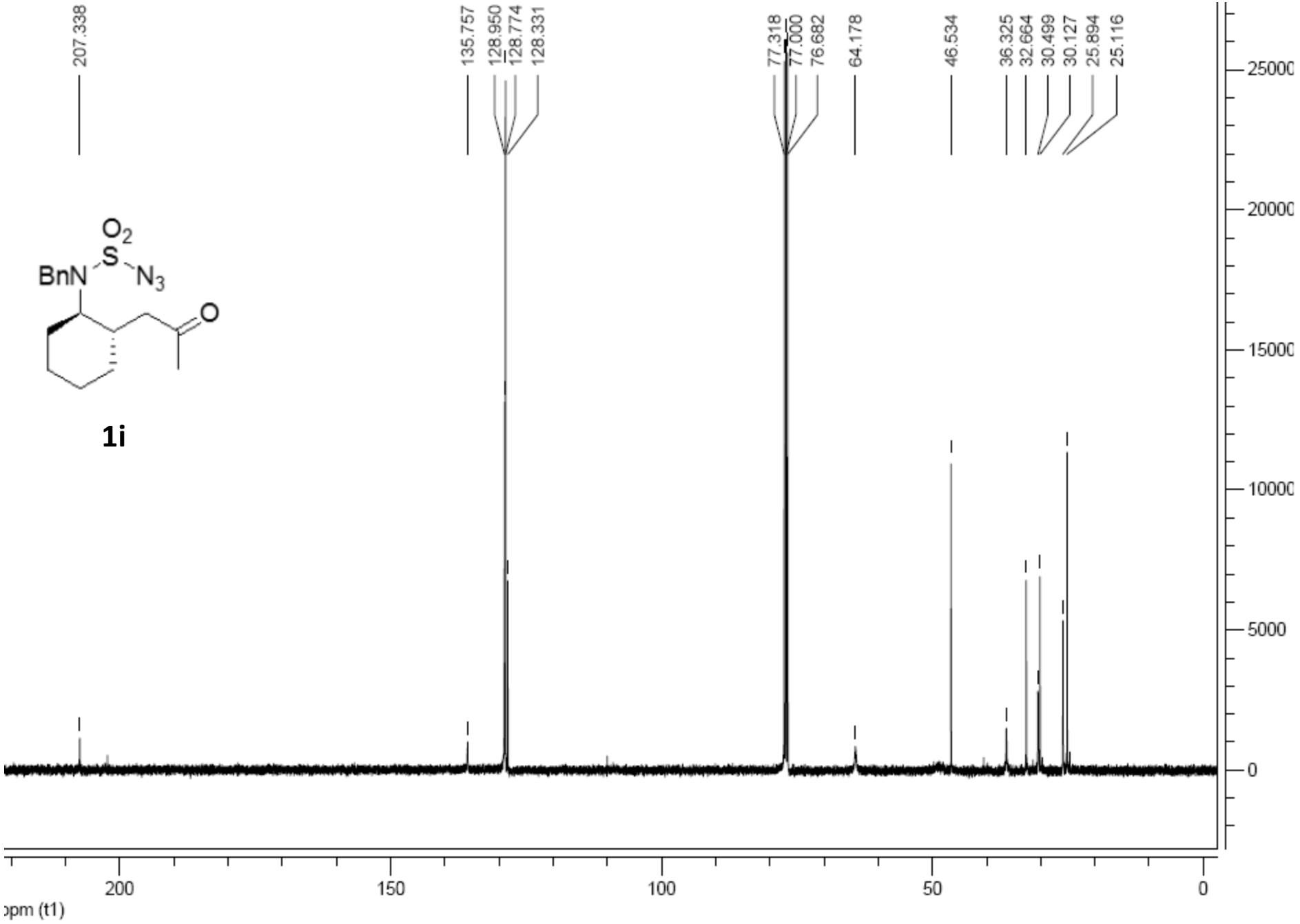

171.348
170.062
135.257
128.665
128.352
80.807
77.317
76.999
76.681
60.752
52.694
51.260
31.037
27.982
24.781
Bn
N
S
O2
N3
MeO2C
CO2tBu
1h
6000
5000
4000
3000
2000
1000
0
-1000
150
100
50
0
ppm (f1)

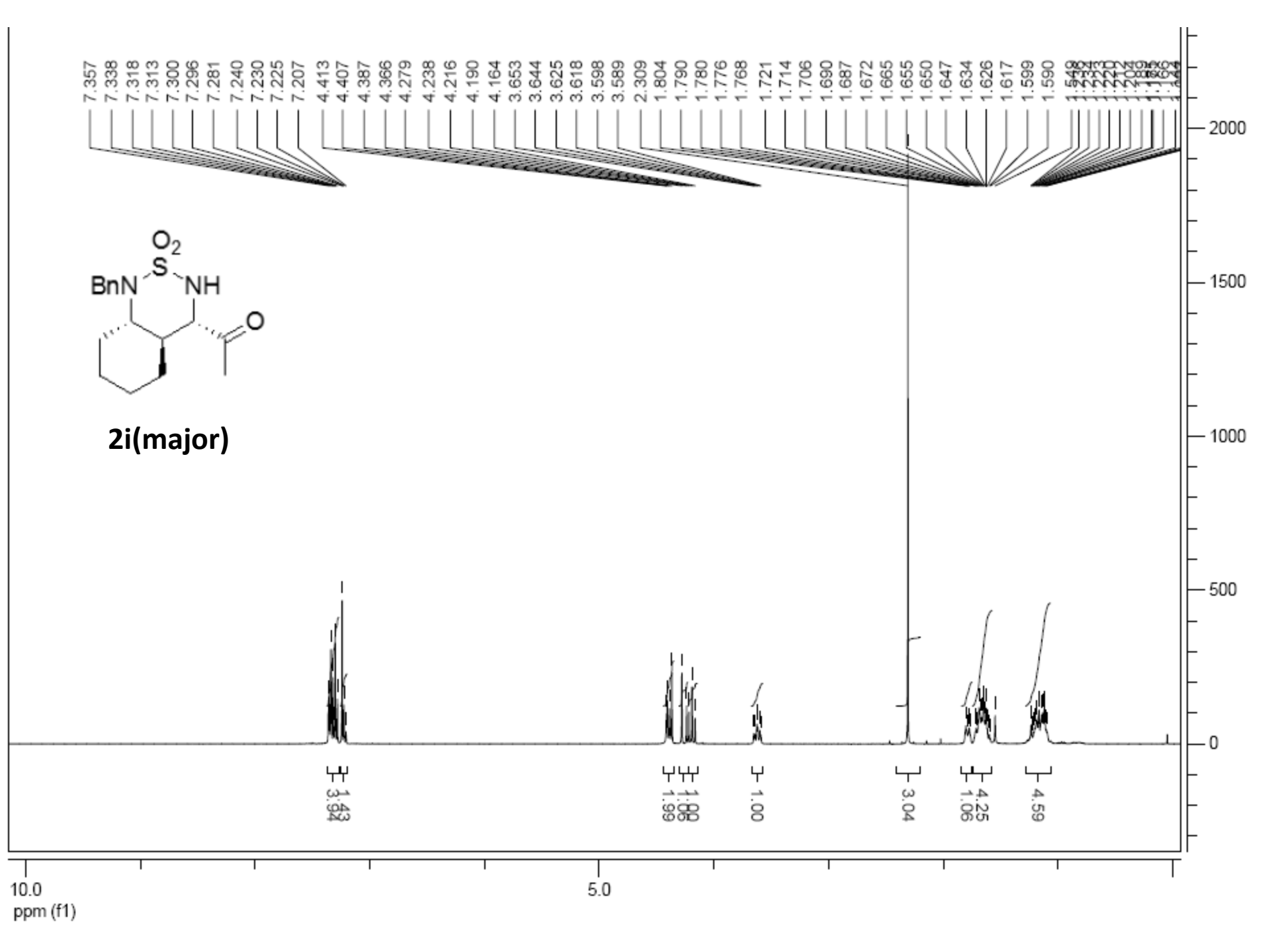

7.393
7.388
7.383
7.372
7.368
7.348
7.344
7.334
7.329
7.323
7.318
7.313
7.310
7.301
7.237
4.662
4.640
4.613
4.606
4.589
4.583
4.576
4.560
4.554
4.539
4.504
3.865
3.859
3.851
3.845
3.784
3.770
2.378
2.371
2.365
2.343
2.336
2.330
1.658
1.645
1.628
1.623
1.615
1.610
1.593
1.580
1.455
O2
S
BnN
NH
MeO2C
CO2tBu
94%
6% (possible)
2h
See the detail of 1H NMR in next page
3000
2500
2000
1500
1000
500
0
5.20
1.96
3.00
1.02
1.04
1.83
9.90
5.0
0.0
ppm (f1)


7.393
7.388
7.383
7.372
7.368
7.348
7.344
7.334
7.329
7.323
7.318
7.313
7.310
7.301
7.237
4.850
4.830
4.662
4.640
4.613
4.606
4.589
4.583
4.576
4.560
4.554
4.539
4.504
4.162
4.122
4.104
4.086
3.865
3.859
3.851
3.845
3.784
3.770
3.328
2.378
2.371
2.365
2.343
2.336
2.330
1.658
1.645
1.628
1.623
1.615
1.610
2h
possible product
BnN
NH
MeO2C
CO2tBu
300
250
200
150
100
50
0
10.0
ppm (t1)
0.0
de : (50.8-3)/(50.8+3) = 89%

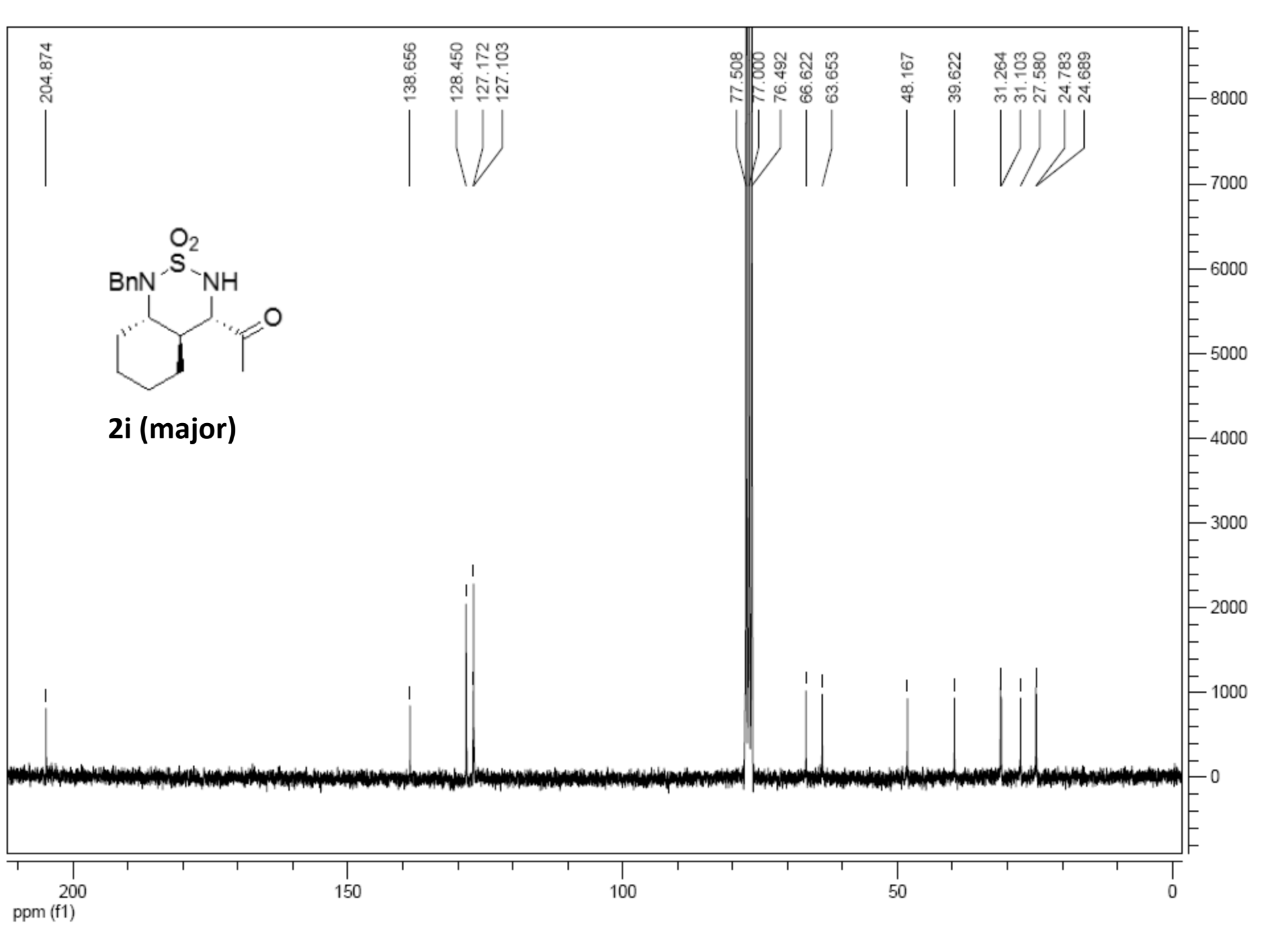

170.441
168.798
134.835
128.842
128.813
128.306
83.492
77.305
76.987
76.669
56.449
55.493
52.679
51.924
27.888
25.765
5000
4000
3000
2000
1000
0
150
100
50
0
ppm (f1)
O2
S
BnN
NH
MeO2C
CO2tBu
94%
6% (possible)
2h


4.411
4.402
4.400
4.329
4.308
4.305
4.303
4.294
4.291
4.257
3.450
3.446
3.444
3.440
3.432
3.425
2.608
2.603
2.566
2.561
2.022
2.017
2.014
2.011
2.008
1.992
1.971
1.967
1.964
1.960
1.954
1.952
1.945
1.941
1.936
1.933
1.925
1.915
1.886
1.867
1.864
1.852
1.830
1.823
1.815
1.812
1.803
1.797
1.791
1.658
1.656
1.654
1.649
1.647
1.641
O2
S
BnN
N3
O
1i
500
400
300
200
100
0
5.67
2.10
0.80
1.00
8.64
2.75
2.97
1.38
5.0
ppm (f1)


207.338
135.757
128.950
128.774
128.331
77.318
77.000
76.682
64.178
46.534
36.325
32.664
30.499
30.127
25.894
25.116
O2
S
BnN
N3
O
1i
25000
20000
15000
10000
5000
0
200
150
100
50
0
ppm (t1)

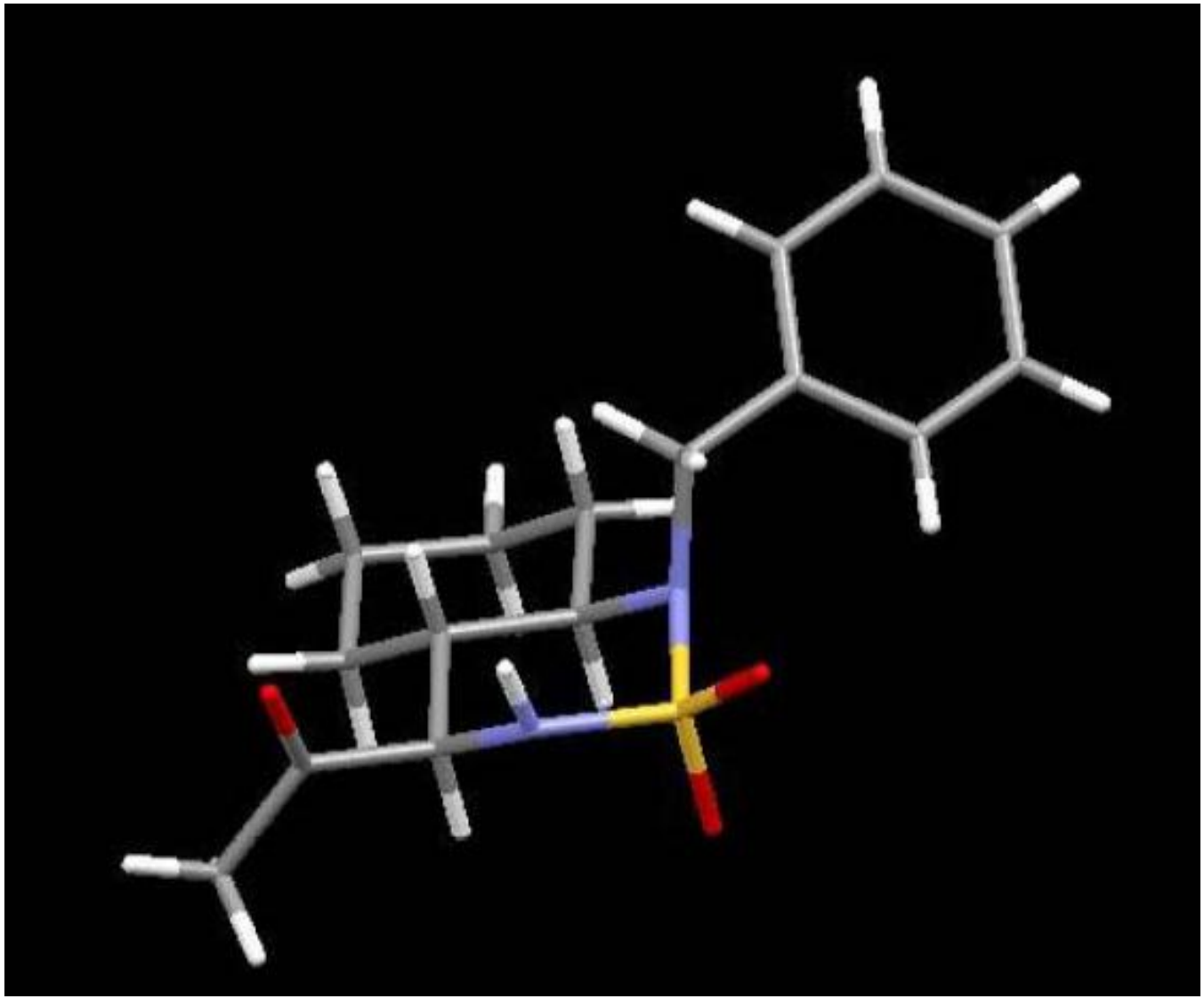

7.357
7.338
7.318
7.313
7.300
7.296
7.281
7.240
7.230
7.225
7.207
4.413
4.407
4.387
4.366
4.279
4.238
4.216
4.190
4.164
3.653
3.644
3.625
3.618
3.598
3.589
2.309
1.804
1.790
1.780
1.776
1.768
1.721
1.714
1.706
1.690
1.687
1.672
1.665
1.655
1.650
1.647
1.634
1.626
1.617
1.599
1.590
O2
S
BnN
NH
O
2000
1500
1000
500
0
3.94
1.43
1.99
1.00
1.00
1.00
3.04
1.06
4.25
4.59
10.0
5.0
ppm (f1)

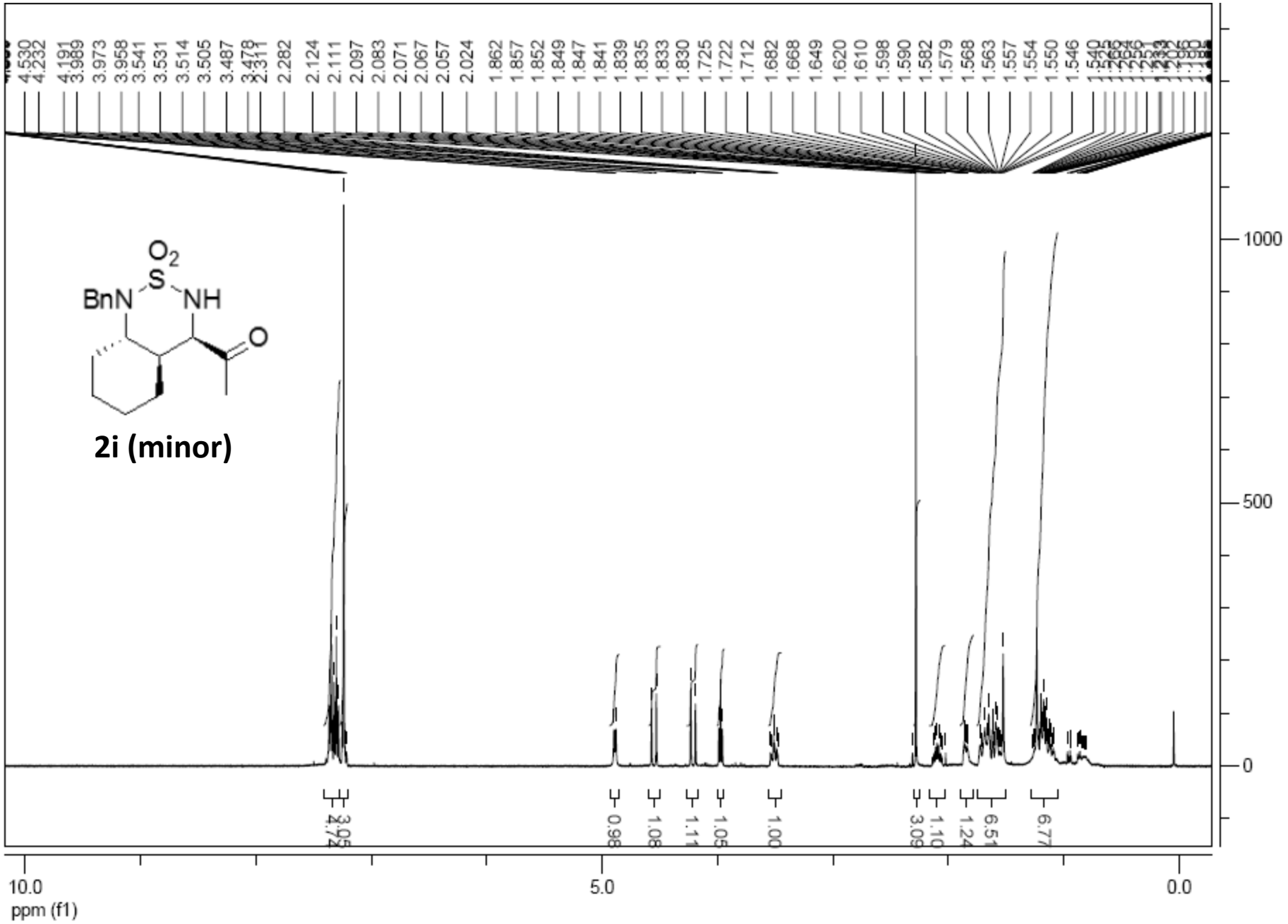
2i(major)

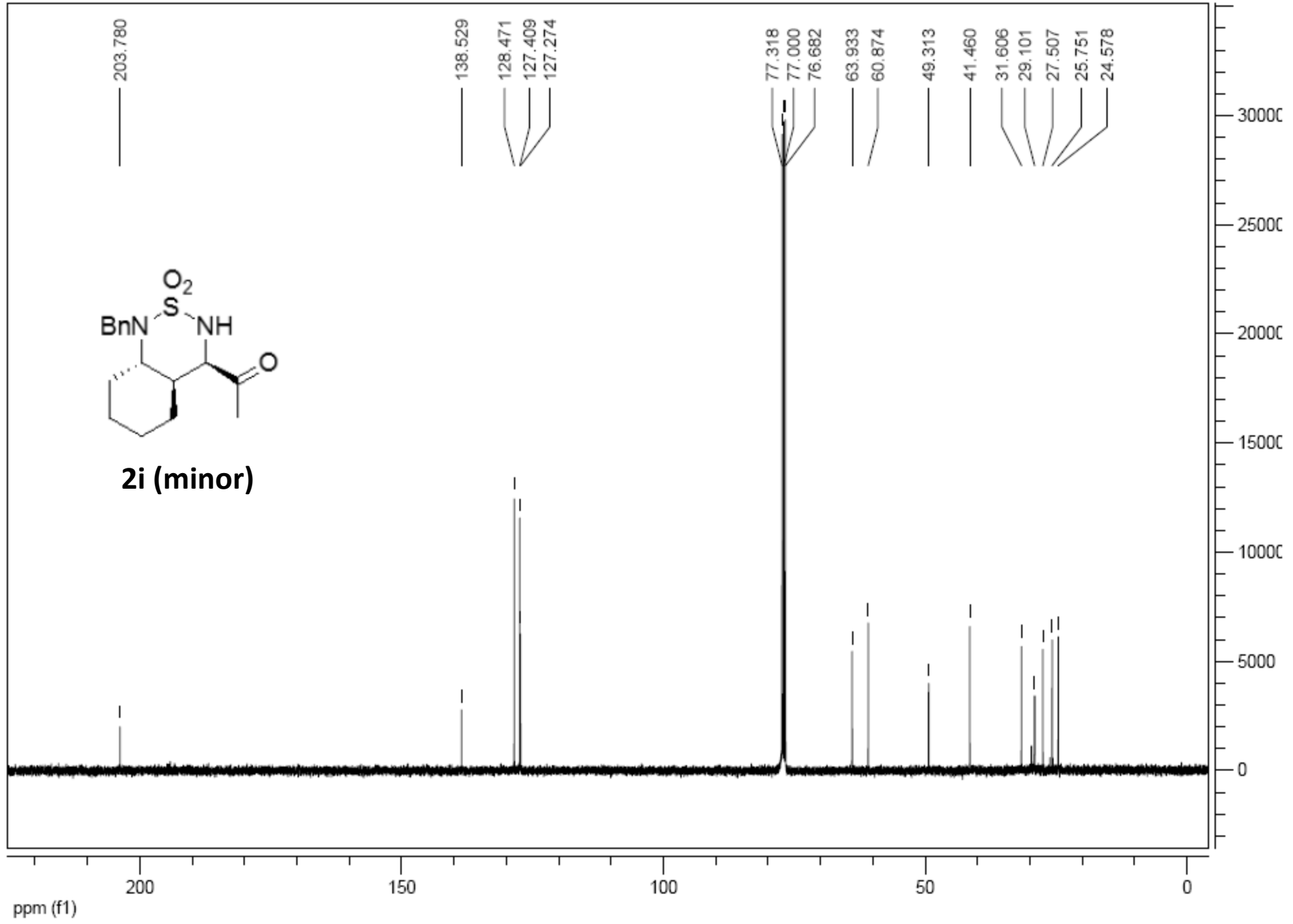

204.874
138.656
128.450
127.172
127.103
77.508
77.000
76.492
66.622
63.653
48.167
39.622
31.264
31.103
27.580
24.783
24.689
O2
S
BnN
NH
O
8000
7000
6000
5000
4000
3000
2000
1000
0
200
150
100
50
0
ppm (f1)

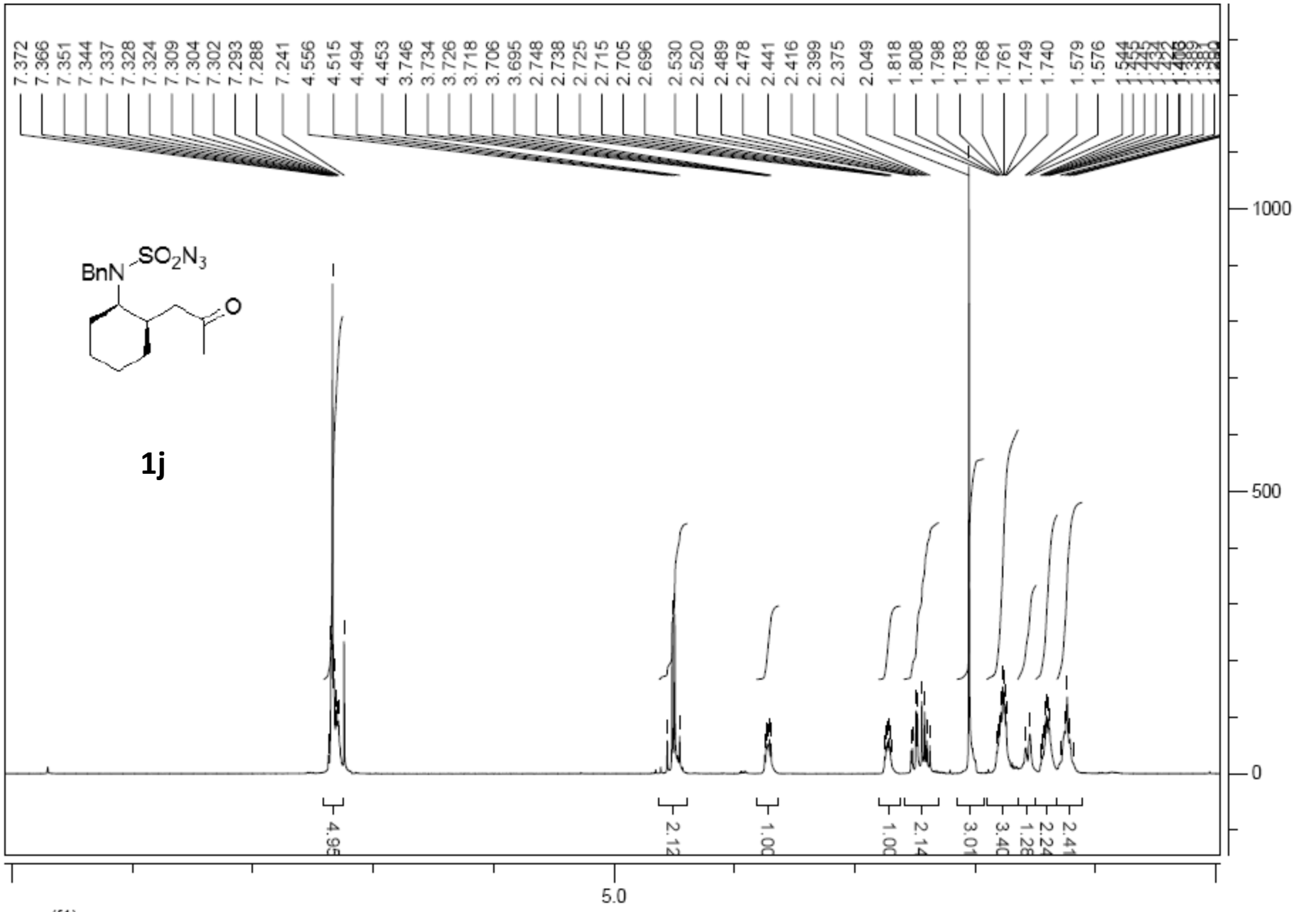
2i (major)

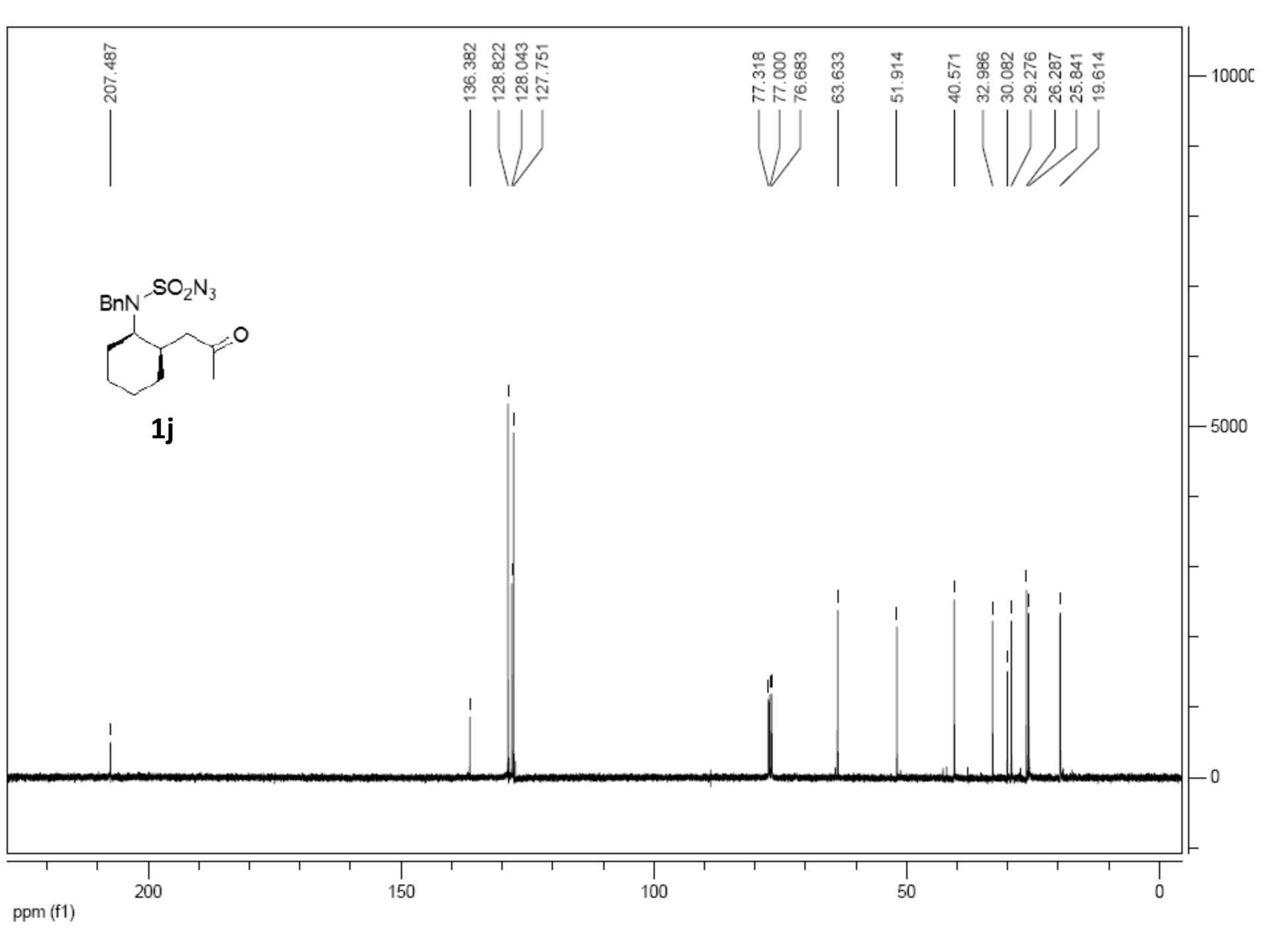
Crystal Structure of **2i**(major)

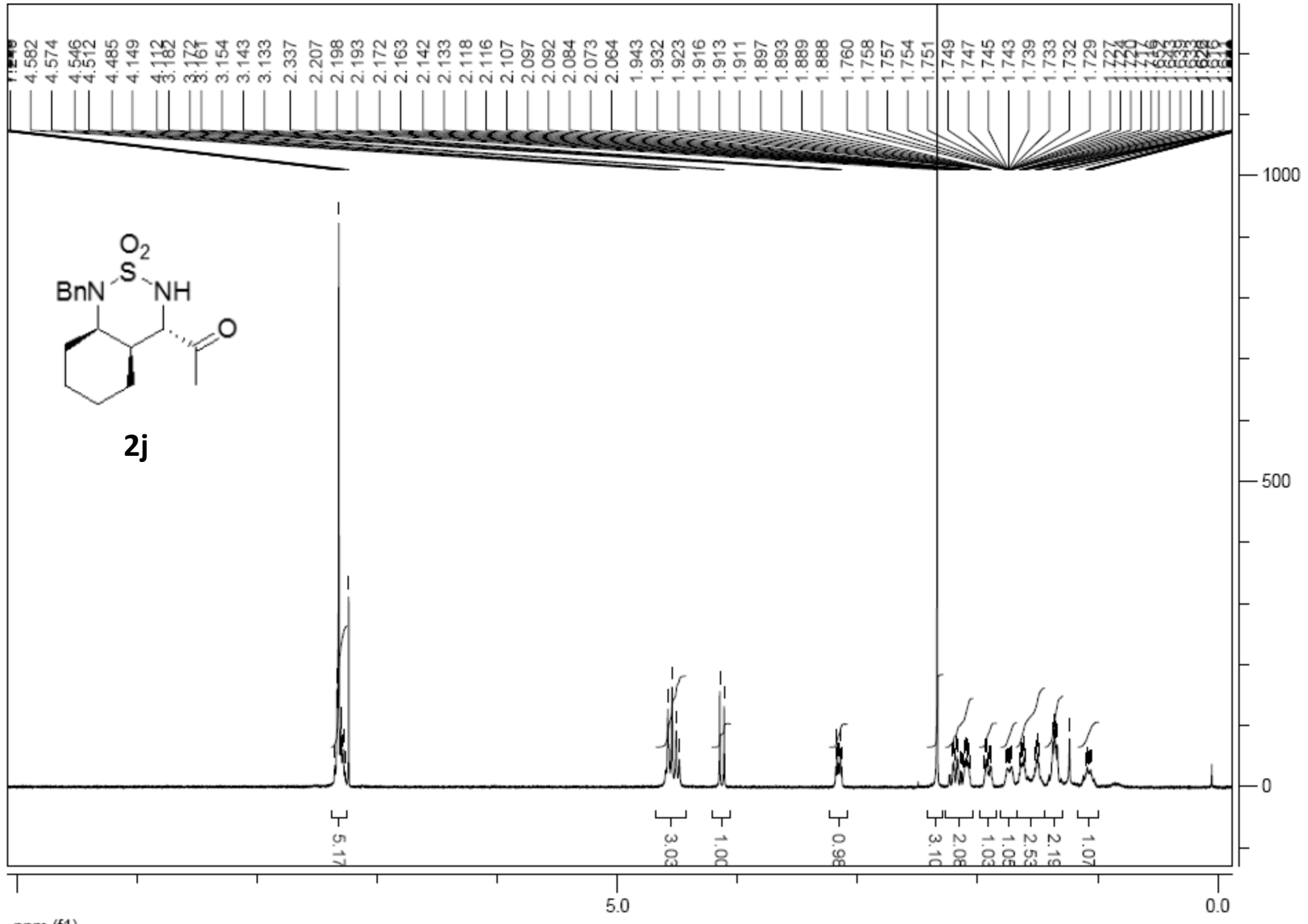



4.530
4.232
4.191
3.989
3.973
3.958
3.541
3.531
3.514
3.505
3.487
3.478
3.311
2.282
2.124
2.111
2.097
2.083
2.071
2.067
2.057
2.024
1.862
1.857
1.852
1.849
1.847
1.841
1.839
1.835
1.833
1.830
1.725
1.722
1.712
1.682
1.668
1.649
1.620
1.610
1.598
1.590
1.582
1.579
1.568
1.563
1.557
1.554
1.550
1.546
O2
S
BnN
NH
O
2i (minor)
1000
500
0
4.74
3.05
0.98
1.08
1.11
1.05
1.00
3.09
1.10
1.24
6.51
6.77
10.0
5.0
0.0
ppm (f1)

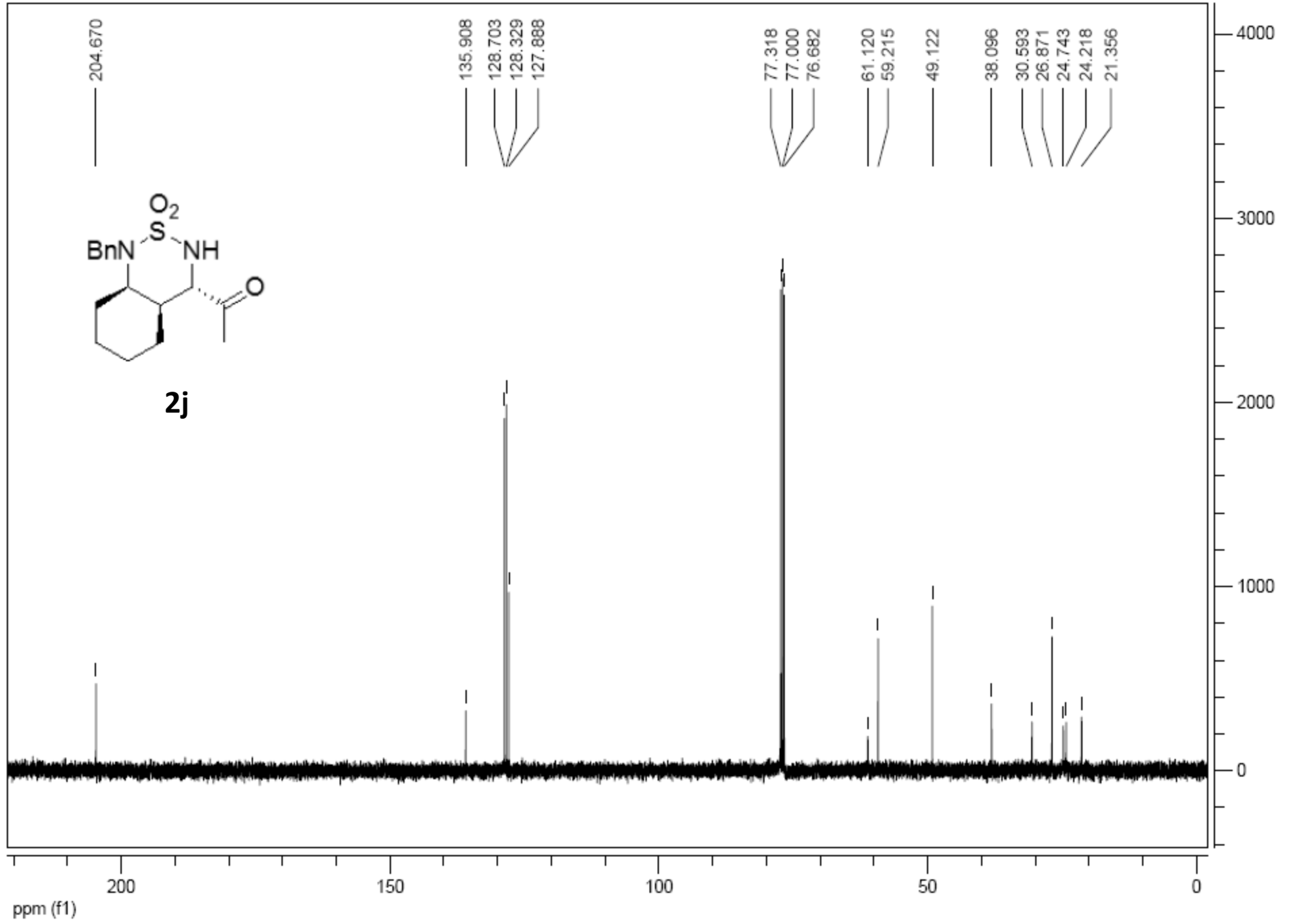

203.780
138.529
128.471
127.409
127.274
77.318
77.000
76.682
63.933
60.874
49.313
41.460
31.606
29.101
27.507
25.751
24.578
O2
S
BnN
NH
O
2i (minor)
3000
2500
2000
1500
1000
5000
0
200
150
100
50
0
ppm (f1)


7.372
7.366
7.351
7.344
7.337
7.328
7.324
7.309
7.304
7.302
7.293
7.288
7.241
4.556
4.515
4.494
4.453
3.746
3.734
3.726
3.718
3.706
3.695
2.748
2.738
2.725
2.715
2.705
2.696
2.530
2.520
2.489
2.478
2.441
2.416
2.399
2.375
2.049
1.818
1.808
1.798
1.783
1.768
1.761
1.749
1.740
1.579
1.576
BnN
SO2N3
O
1j
1000
500
0
4.95
2.12
1.00
1.00
2.14
3.01
3.40
1.28
2.24
2.41
5.0
ppm (f1)

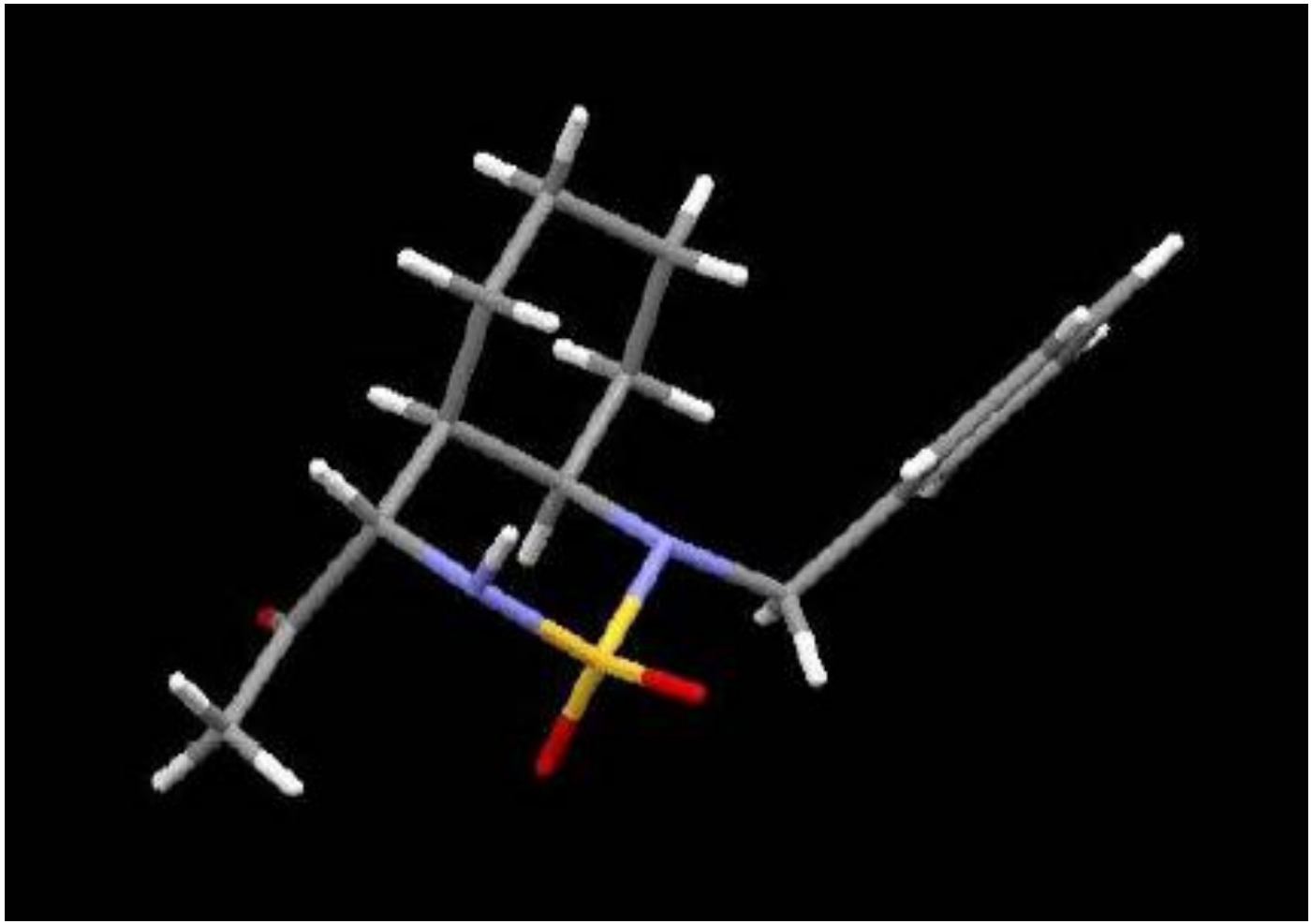

207.487
136.382
128.822
128.043
127.751
77.318
77.000
76.683
63.633
51.914
40.571
32.986
30.082
29.276
26.287
25.841
19.614
BnN
SO2N3
O
1j
10000
5000
0
200
150
100
50
0
ppm (f1)

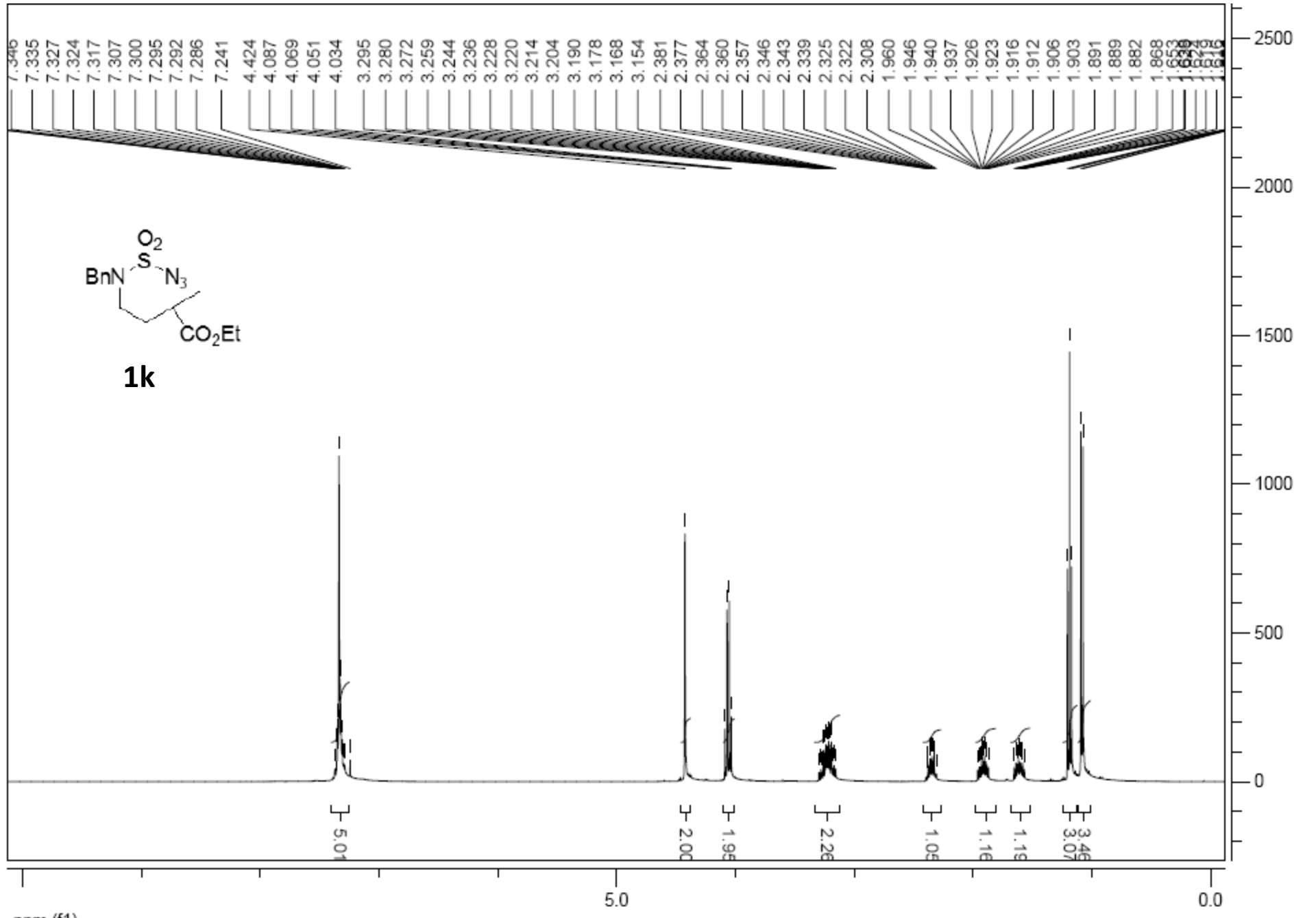

4.582
4.574
4.546
4.512
4.485
4.149
4.112
3.182
3.154
3.143
3.133
2.337
2.207
2.198
2.193
2.172
2.163
2.142
2.133
2.118
2.116
2.107
2.097
2.092
2.084
2.073
2.064
1.943
1.932
1.923
1.916
1.913
1.911
1.897
1.893
1.889
1.888
1.760
1.758
1.757
1.754
1.751
1.749
1.747
1.745
1.743
1.739
1.733
1.732
1.729
1000
500
0
5.17
3.03
1.00
0.98
3.10
2.08
1.03
1.05
2.53
2.19
1.07
5.0
0.0
ppm (f1)

2j

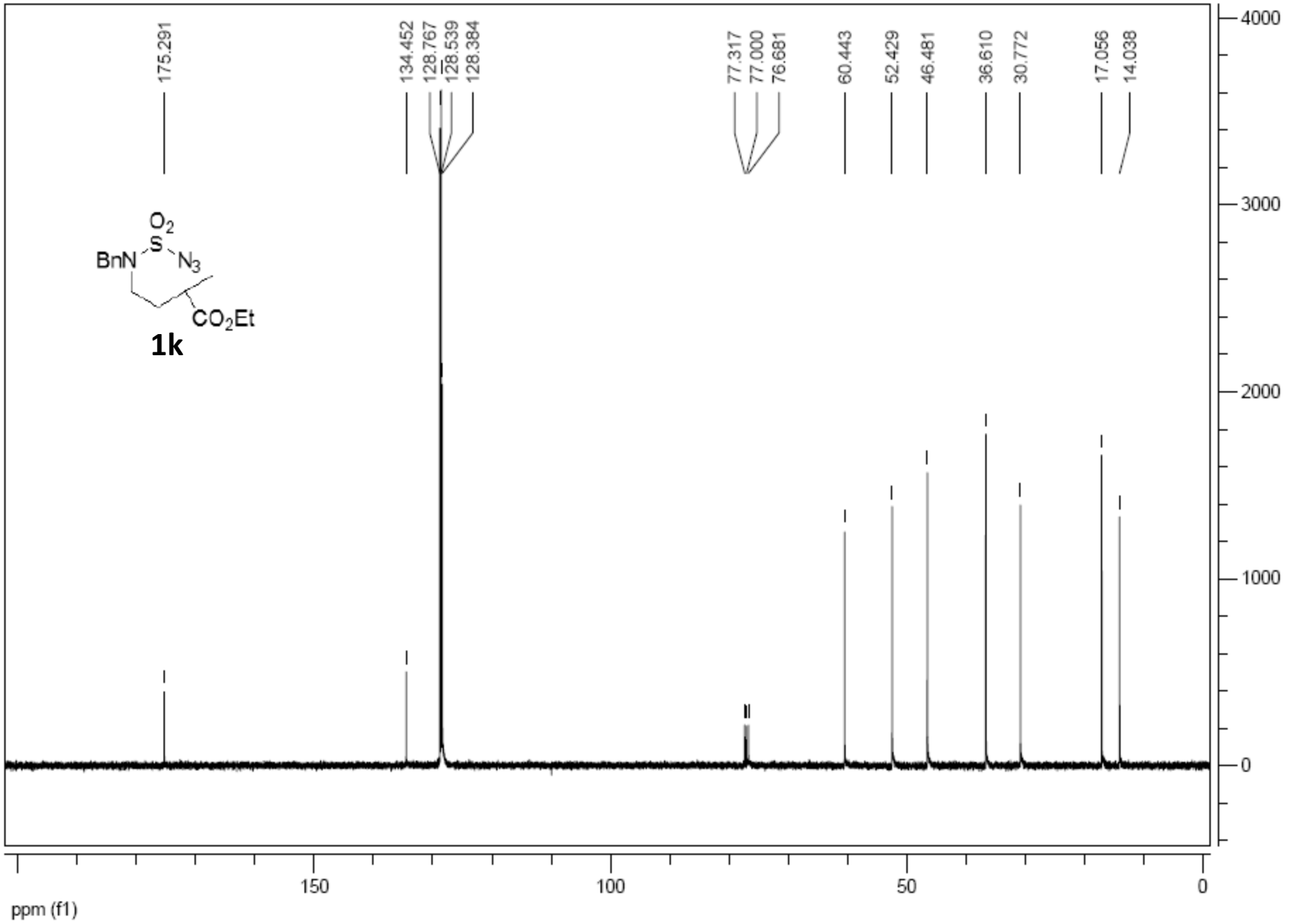

204.670
135.908
128.703
128.329
127.888
77.318
77.000
76.682
61.120
59.215
49.122
38.096
30.593
26.871
24.743
24.218
21.356
O2
S
BnN
NH
O
2j
4000
3000
2000
1000
0
200
150
100
50
0
ppm (f1)

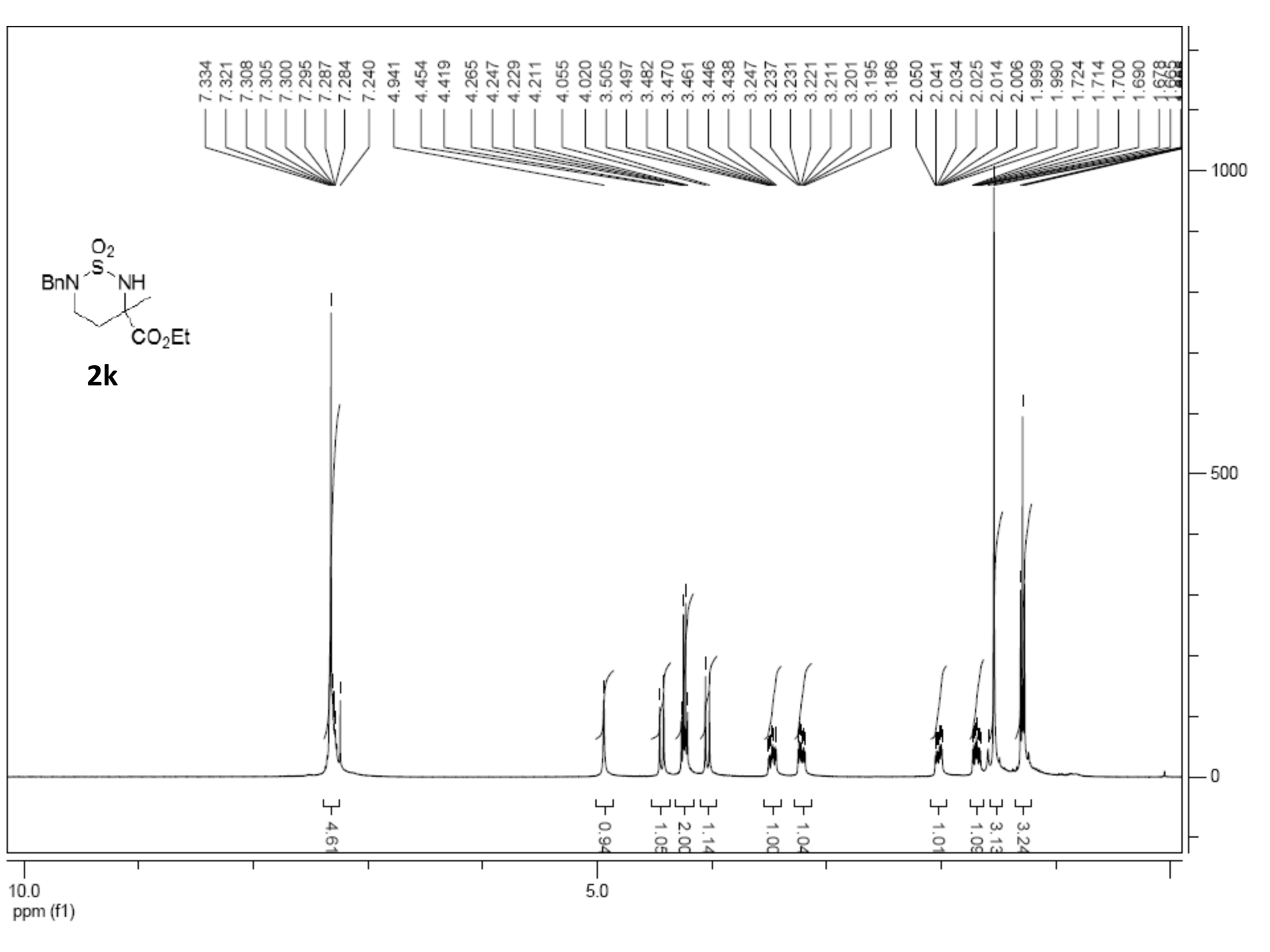
Crystal Structure of **2j**

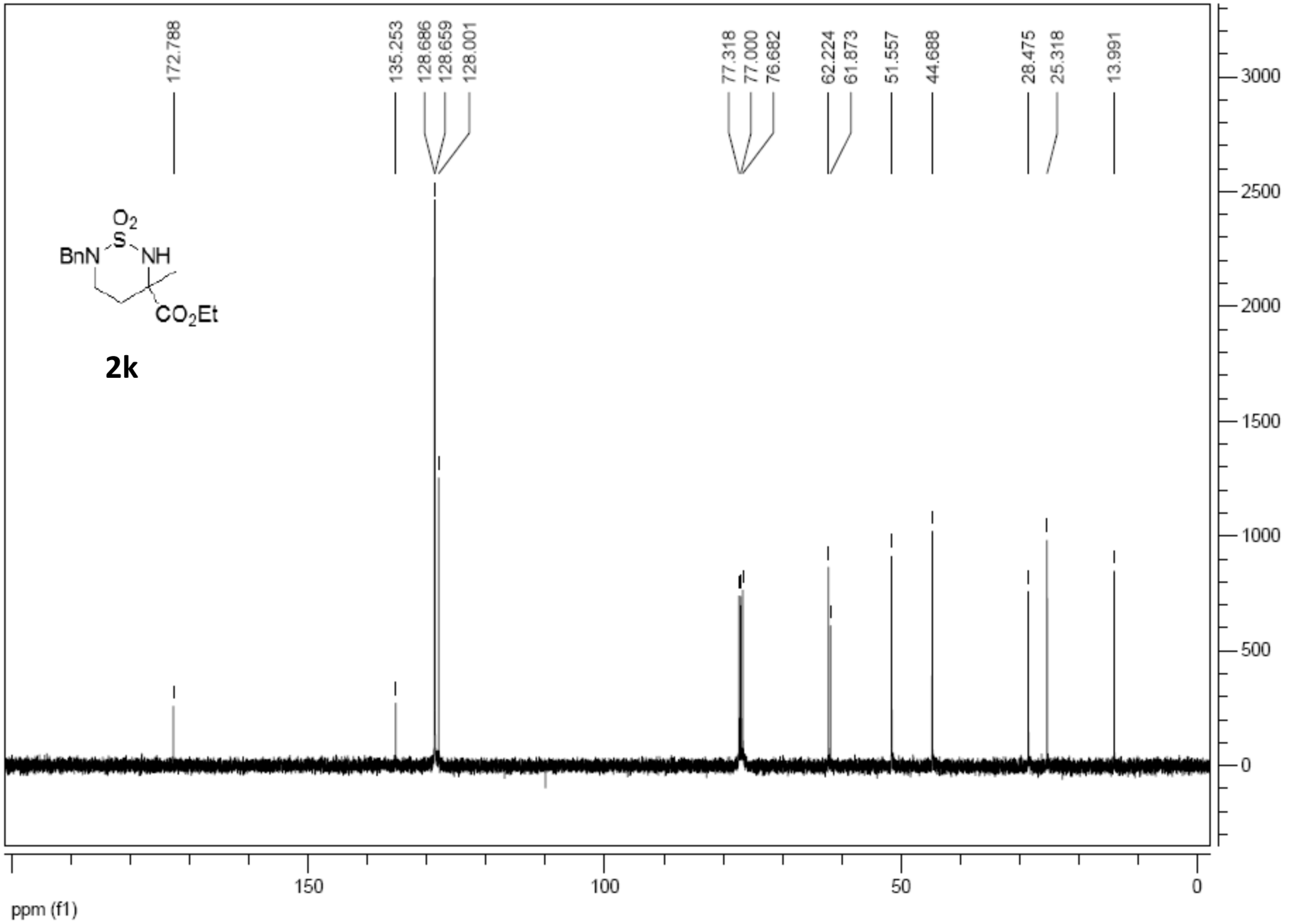


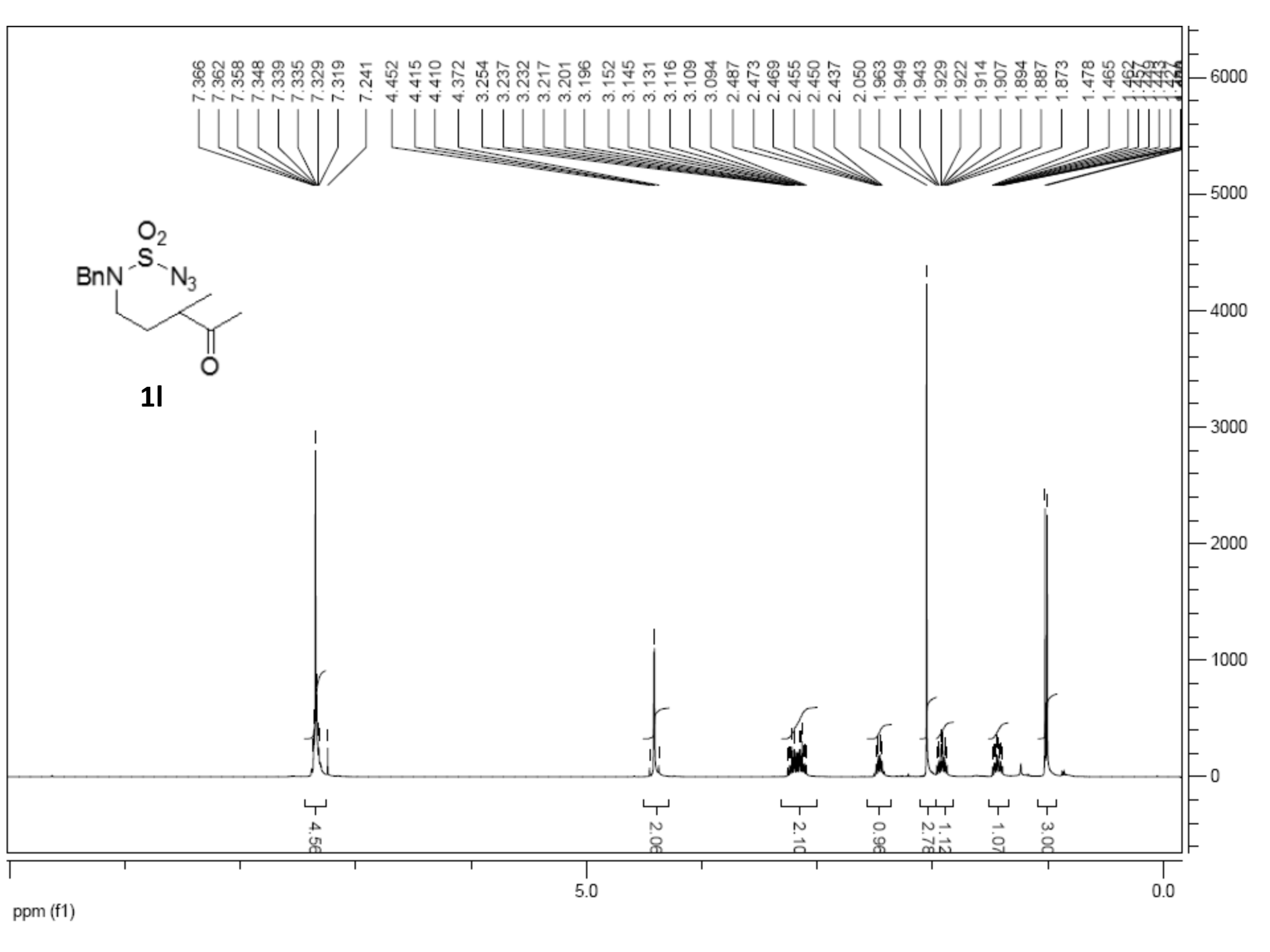

7.345
7.335
7.327
7.324
7.317
7.307
7.300
7.295
7.292
7.286
7.241
4.424
4.087
4.069
4.051
4.034
3.295
3.280
3.272
3.259
3.244
3.236
3.228
3.220
3.214
3.204
3.190
3.178
3.168
3.154
2.381
2.377
2.364
2.360
2.357
2.346
2.343
2.339
2.325
2.322
2.308
1.960
1.946
1.940
1.937
1.926
1.923
1.916
1.912
1.906
1.903
1.891
1.889
1.882
1.868
2500
2000
1500
1000
500
0
5.01
2.00
1.95
2.26
1.05
1.16
1.19
3.07
5.0
0.0
ppm (f1)

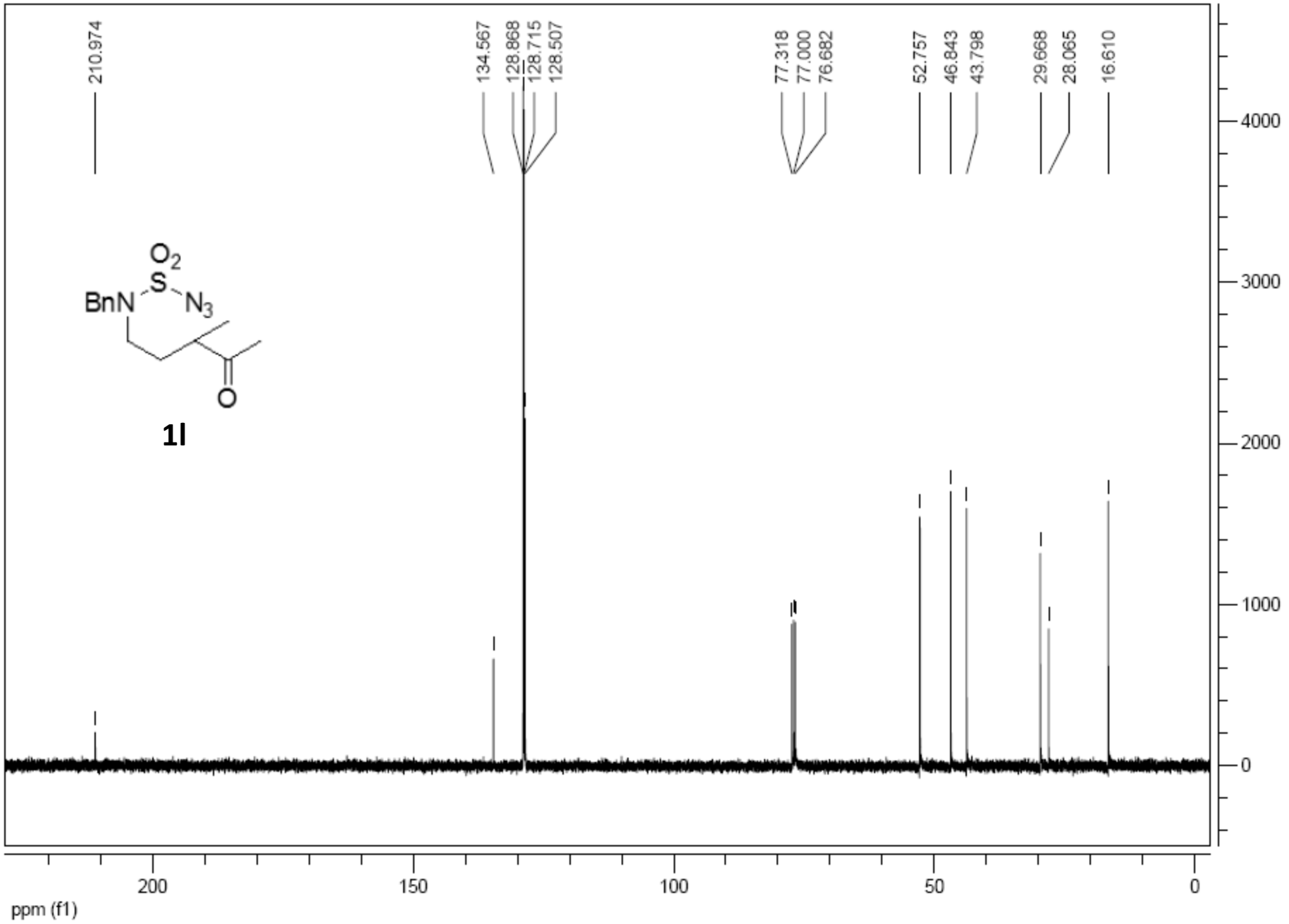
1k

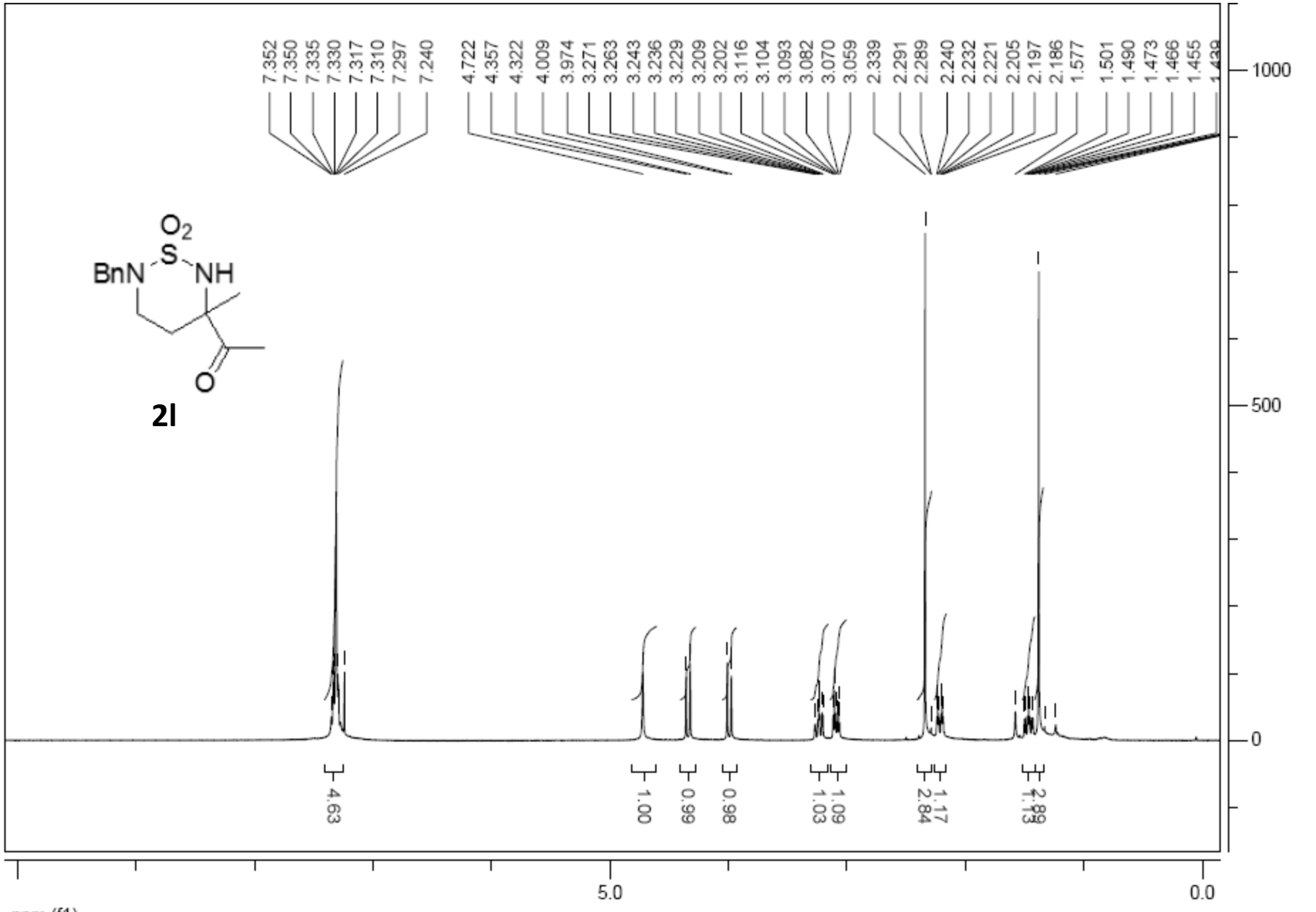

175.291
134.452
128.767
128.539
128.384
77.317
77.000
76.681
60.443
52.429
46.481
36.610
30.772
17.056
14.038
BnN
S
O2
N3
CO2Et
1k
4000
3000
2000
1000
0
150
100
50
0
ppm (f1)

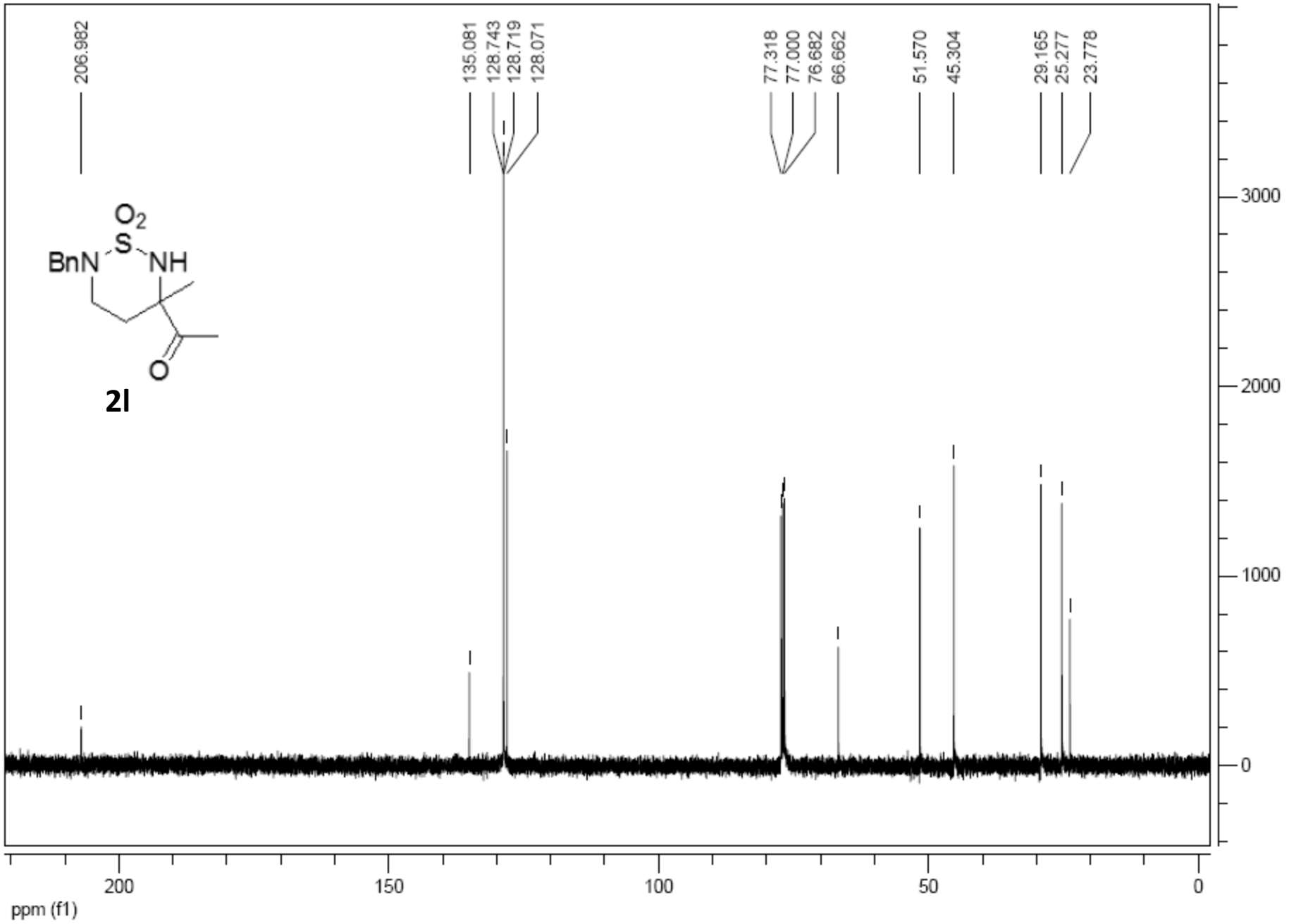

7.334
7.321
7.308
7.305
7.300
7.295
7.287
7.284
7.240
4.941
4.454
4.419
4.265
4.247
4.229
4.211
4.055
4.020
3.505
3.497
3.482
3.470
3.461
3.446
3.438
3.247
3.237
3.231
3.221
3.211
3.201
3.195
3.186
2.050
2.041
2.034
2.025
2.014
2.006
1.999
1.990
1.724
1.714
1.700
1.690
1.678
O2
S
BnN
NH
CO2Et
2k
1000
500
0
4.61
0.94
1.05
2.00
1.14
1.00
1.04
1.01
1.09
3.13
3.24
10.0
5.0
ppm (f1)

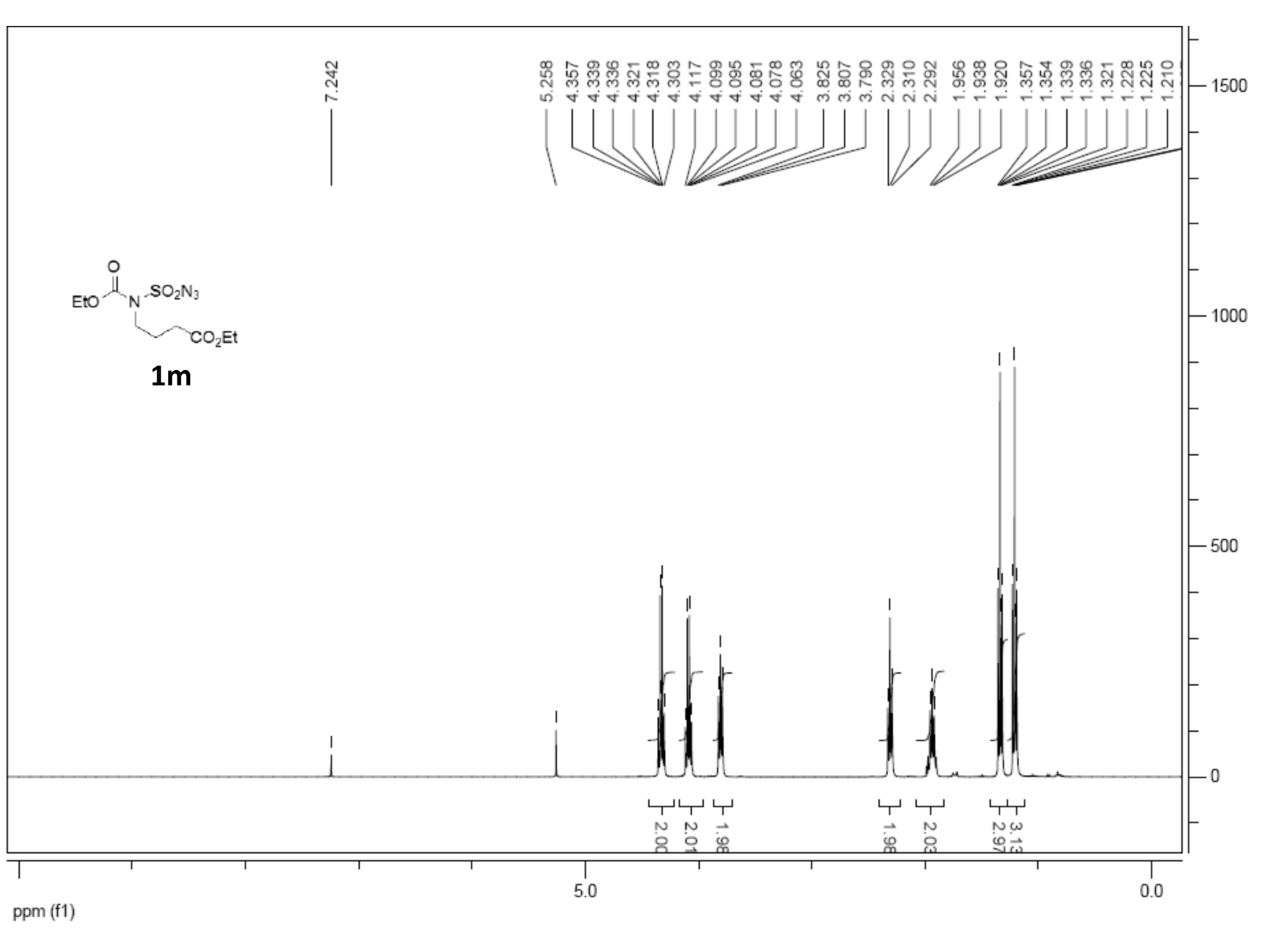

172.788
135.253
128.686
128.659
128.001
77.318
77.000
76.682
62.224
61.873
51.557
44.688
28.475
25.318
13.991
O2
S
BnN
NH
CO2Et
2k
3000
2500
2000
1500
1000
500
0
150
100
50
0
ppm (f1)

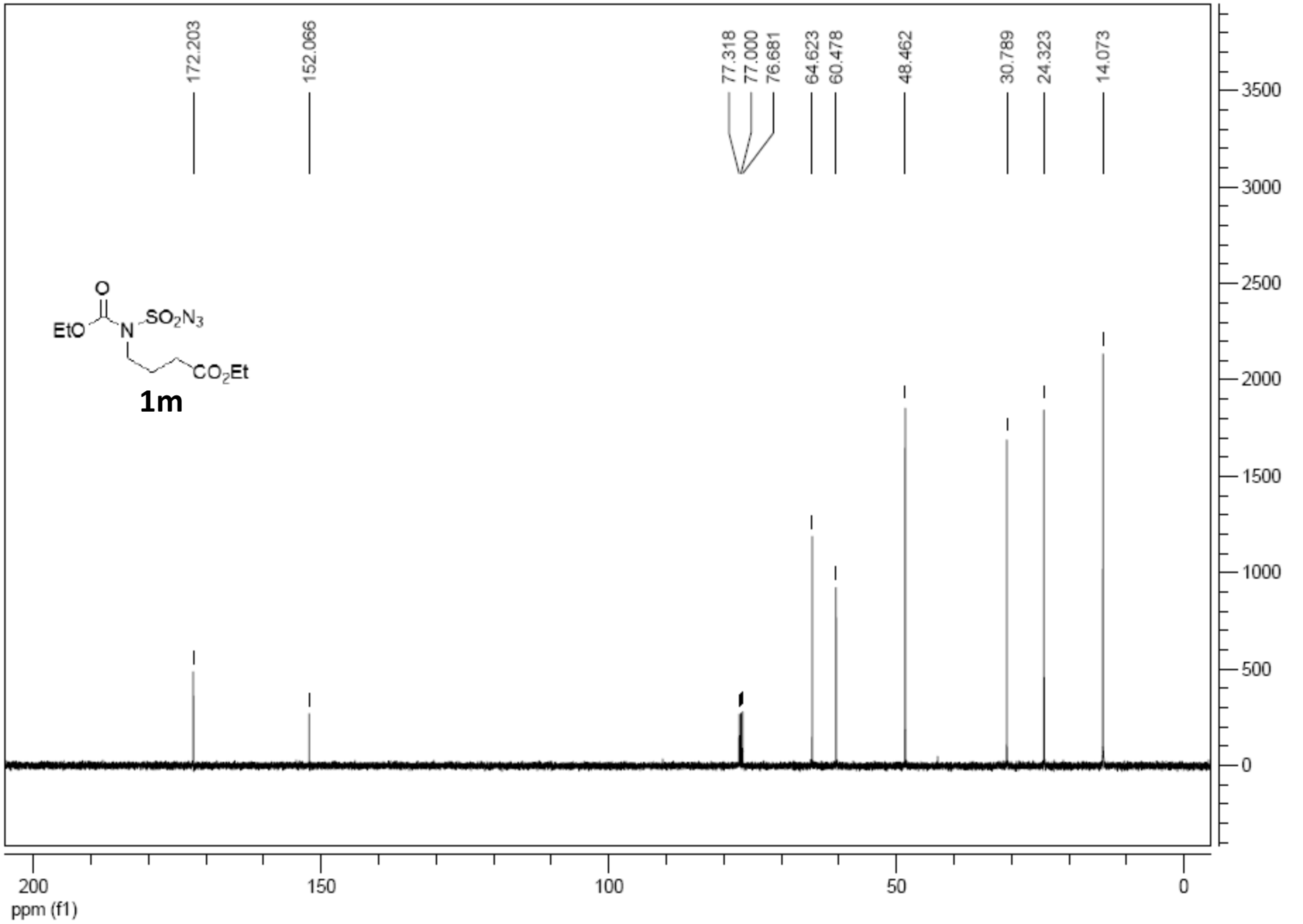

7.366
7.362
7.358
7.348
7.339
7.335
7.329
7.319
7.241
4.452
4.415
4.410
4.372
3.254
3.237
3.232
3.217
3.201
3.196
3.152
3.145
3.131
3.116
3.109
3.094
2.487
2.473
2.469
2.455
2.450
2.437
2.050
1.963
1.949
1.943
1.929
1.922
1.914
1.907
1.894
1.887
1.873
1.478
1.465
6000
5000
4000
3000
2000
1000
0
O2
S
BnN
N3
O
1l
4.56
2.06
2.10
0.96
2.78
1.12
1.07
3.00
5.0
0.0
ppm (f1)

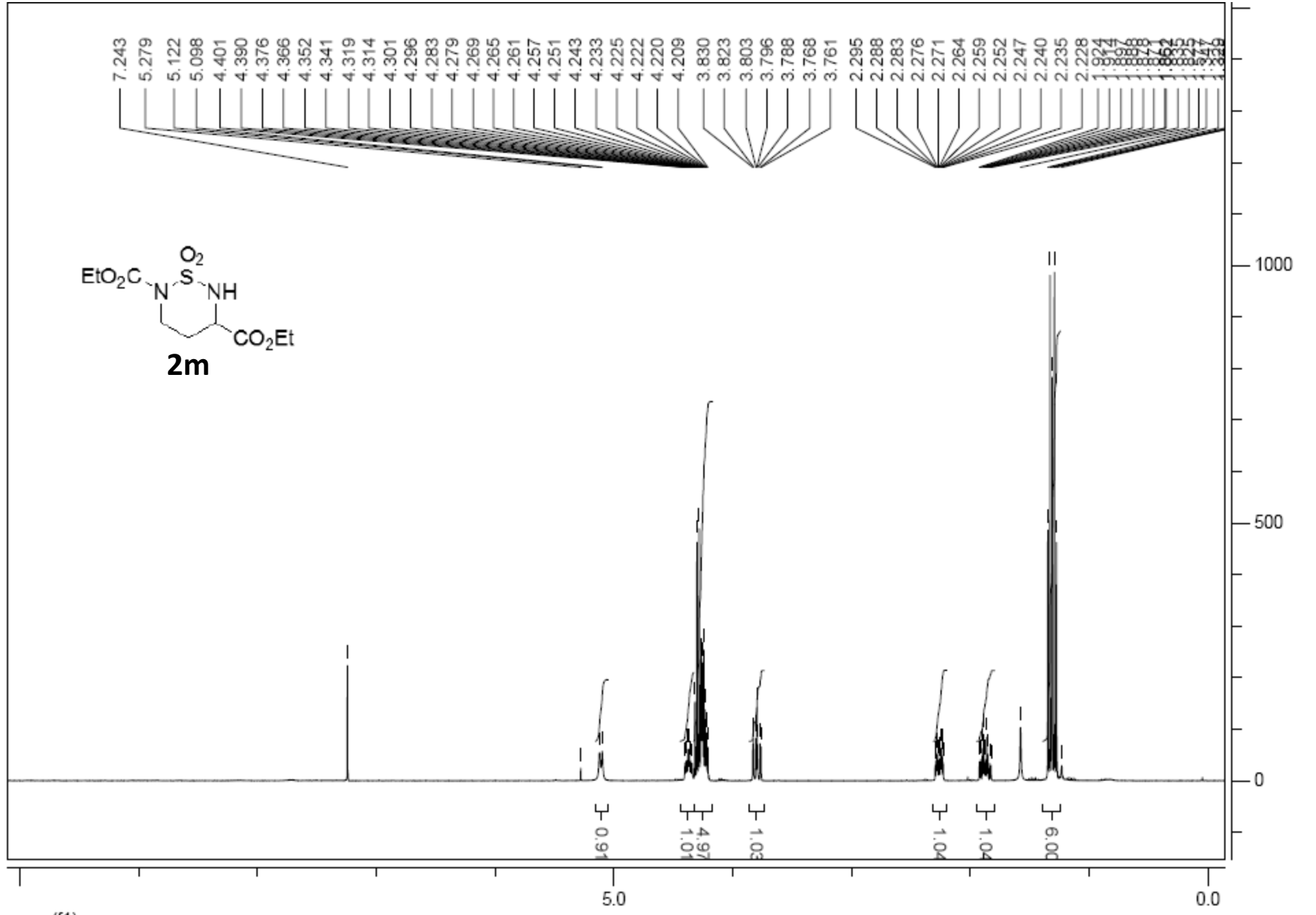

210.974
134.567
128.868
128.715
128.507
77.318
77.000
76.682
52.757
46.843
43.798
29.668
28.065
16.610
O2
S
BnN
N3
O
1l
4000
3000
2000
1000
0
200
150
100
50
0
ppm (f1)

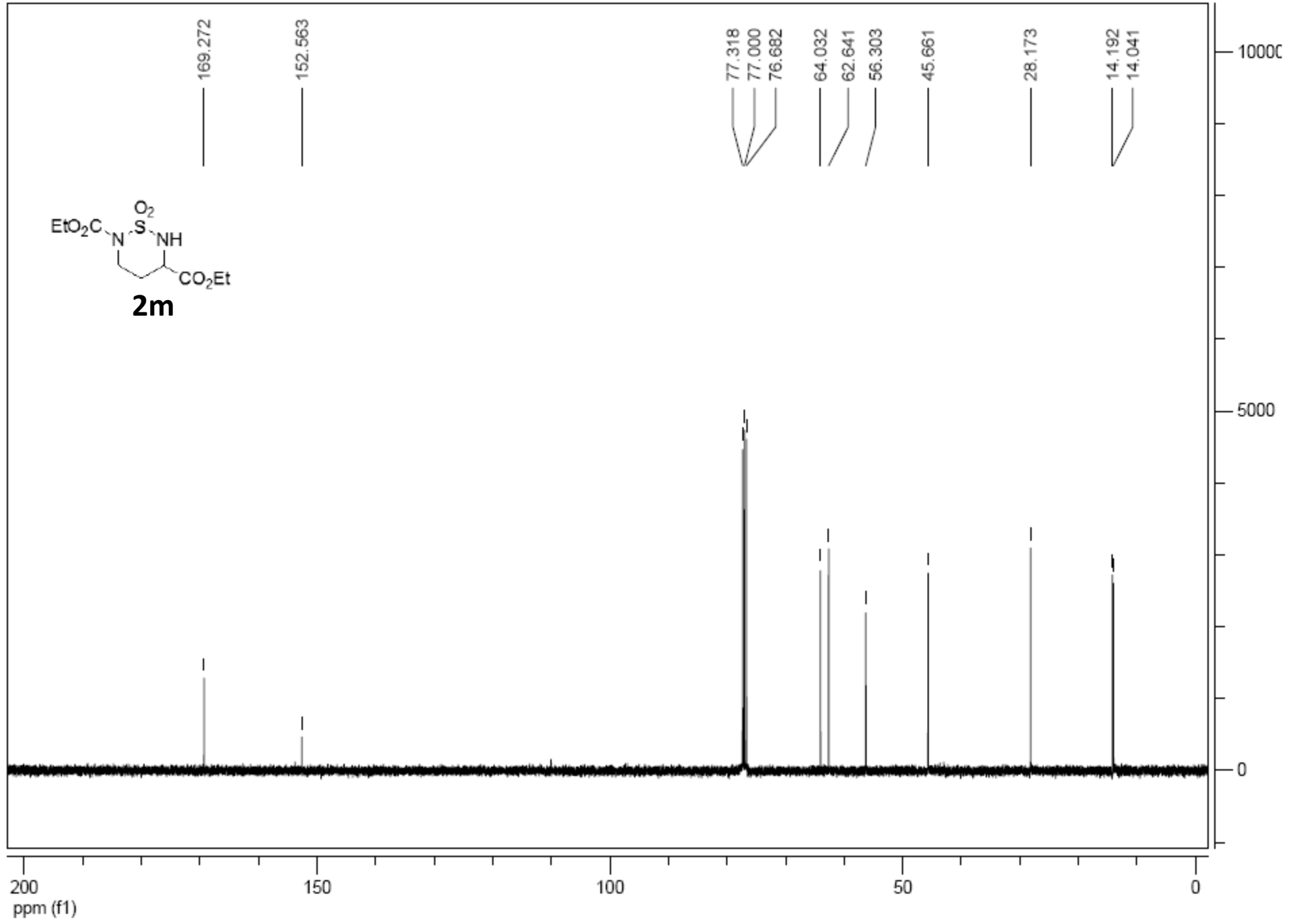

7.352
7.350
7.335
7.330
7.317
7.310
7.297
7.240
4.722
4.357
4.322
4.009
3.974
3.271
3.263
3.243
3.236
3.229
3.209
3.202
3.116
3.104
3.093
3.082
3.070
3.059
2.339
2.291
2.289
2.240
2.232
2.221
2.205
2.197
2.186
1.577
1.501
1.490
1.473
1.466
1.455
1.439
O2
S
BnN
NH
O
2l
1000
500
0
4.63
1.00
0.99
0.98
1.03
1.09
2.84
1.17
1.13
2.89
5.0
0.0
ppm (f1)

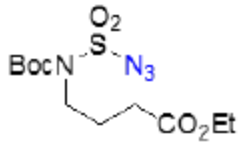

206.982
135.081
128.743
128.719
128.071
77.318
77.000
76.682
66.662
51.570
45.304
29.165
25.277
23.778
O2
S
BnN
NH
O
2l
3000
2000
1000
0
200
150
100
50
0
ppm (f1)


7.242
5.258
4.357
4.339
4.336
4.321
4.318
4.303
4.117
4.099
4.095
4.081
4.078
4.063
3.825
3.807
3.790
2.329
2.310
2.292
1.956
1.938
1.920
1.357
1.354
1.339
1.336
1.321
1.228
1.225
1.210
1500
1000
500
0
EtO
O
N
SO2N3
CO2Et
1m
2.00
2.01
1.98
1.98
2.03
2.97
3.13
5.0
0.0
ppm (f1)


172.203
152.066
77.318
77.000
76.681
64.623
60.478
48.462
30.789
24.323
14.073
EtO
O
N
SO2N3
CO2Et
1m
3500
3000
2500
2000
1500
1000
500
0
200
150
100
50
0
ppm (f1)

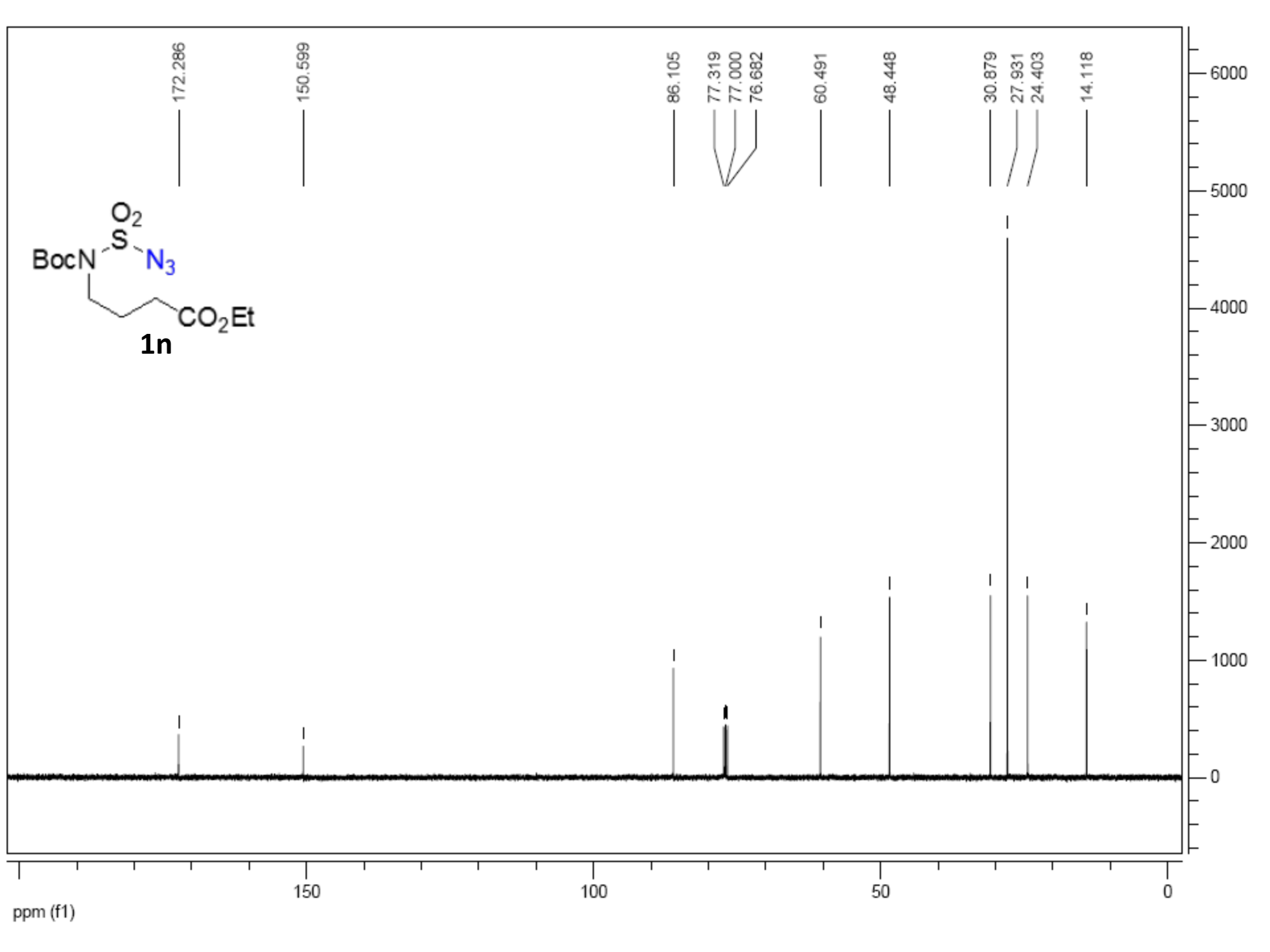

7.243
5.279
5.122
5.098
4.401
4.390
4.376
4.366
4.352
4.341
4.319
4.314
4.301
4.296
4.283
4.279
4.269
4.265
4.261
4.257
4.251
4.243
4.233
4.225
4.222
4.220
4.209
3.830
3.823
3.803
3.796
3.788
3.768
3.761
2.295
2.288
2.283
2.276
2.271
2.264
2.259
2.252
2.247
2.240
2.235
2.228
1.924
O2
EtO2C
N
S
NH
CO2Et
2m
1000
500
0
0.96
1.01
4.97
1.03
1.04
1.04
6.00
5.0
0.0
ppm (f1)

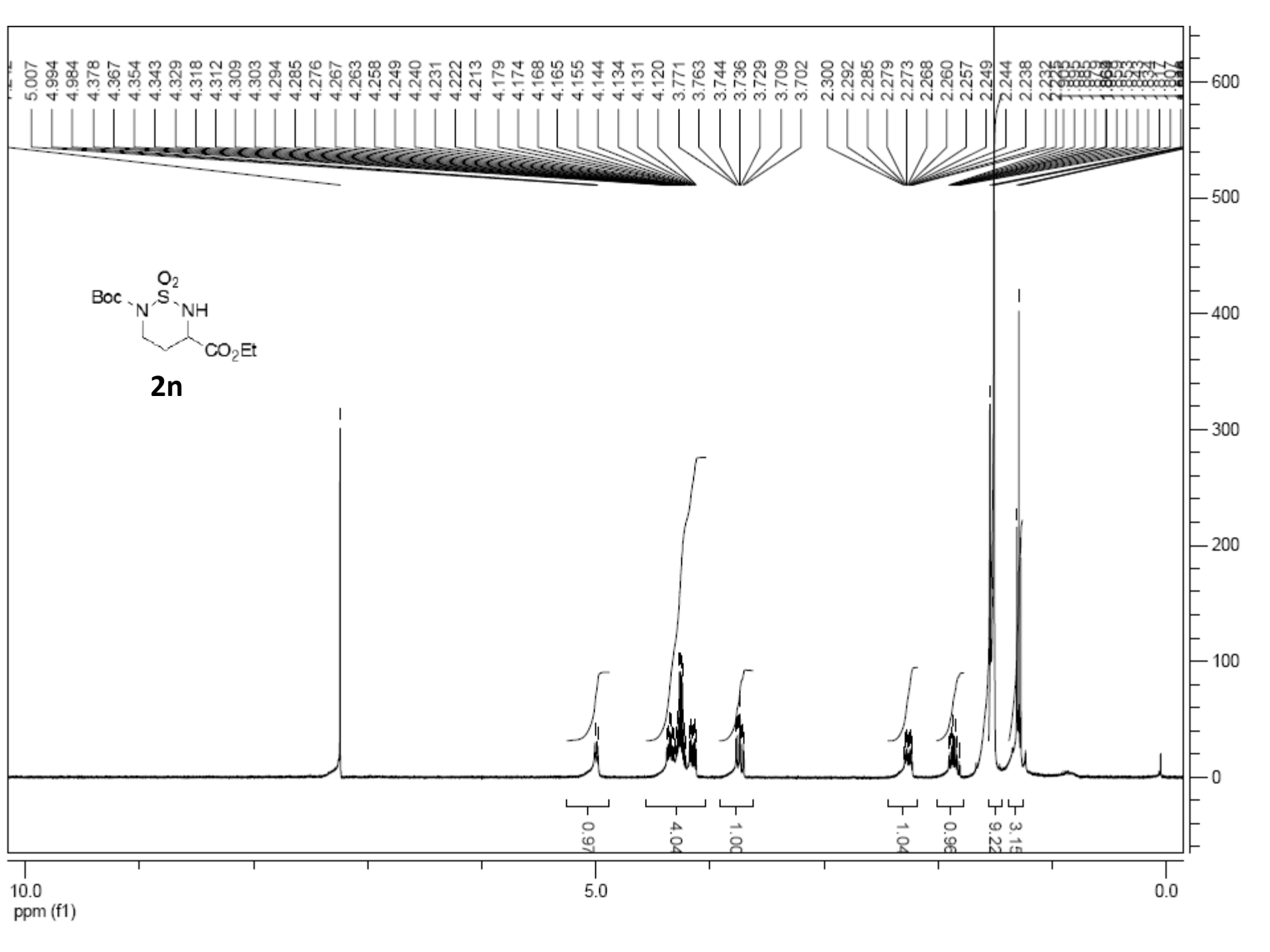

169.272
152.563
77.318
77.000
76.682
64.032
62.641
56.303
45.661
28.173
14.192
14.041
EtO2C
O2
S
N
NH
CO2Et
2m
10000
5000
0
200
150
100
50
0
ppm (f1)

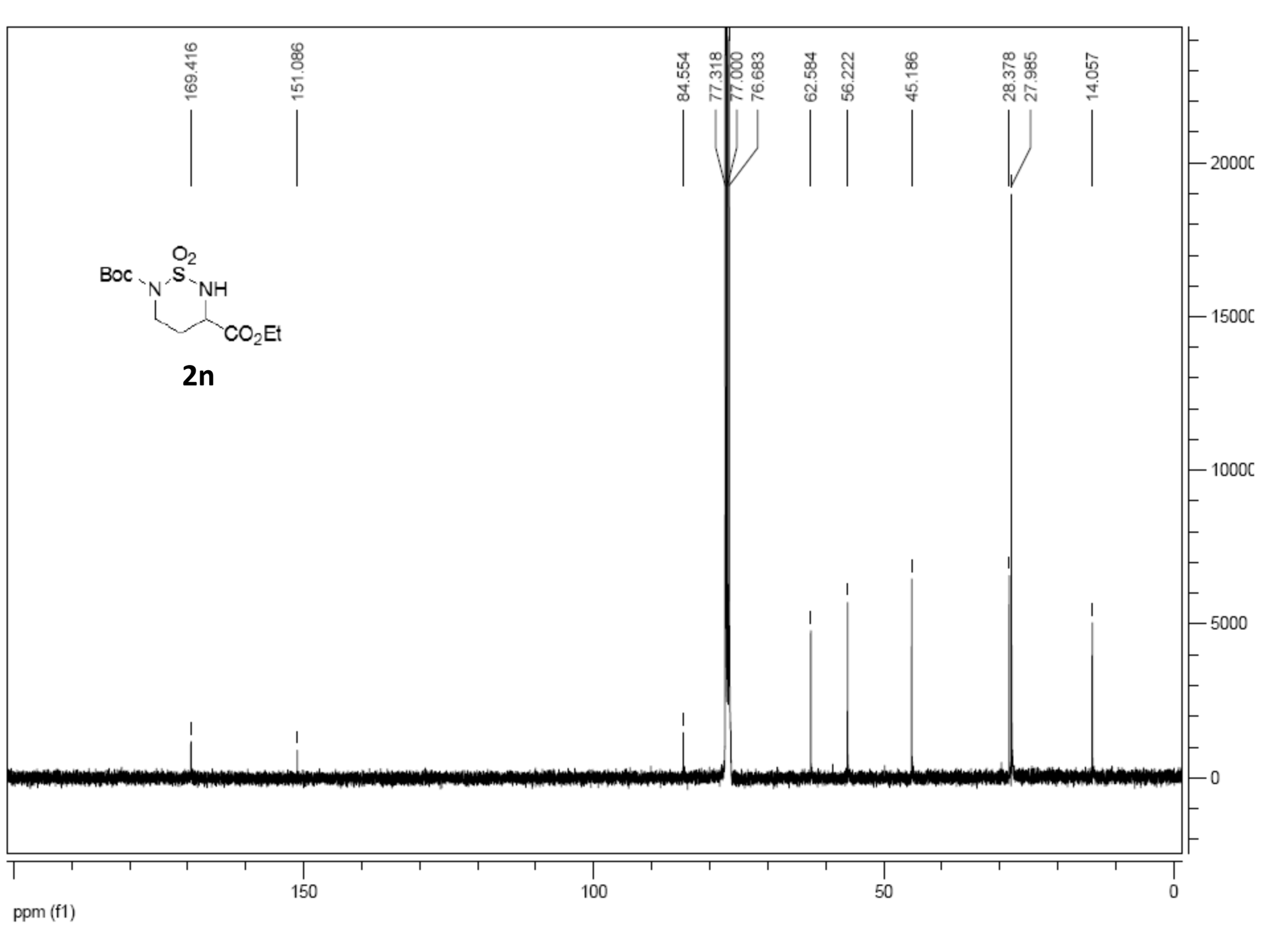

O2
S
BocN
N3
CO2Et

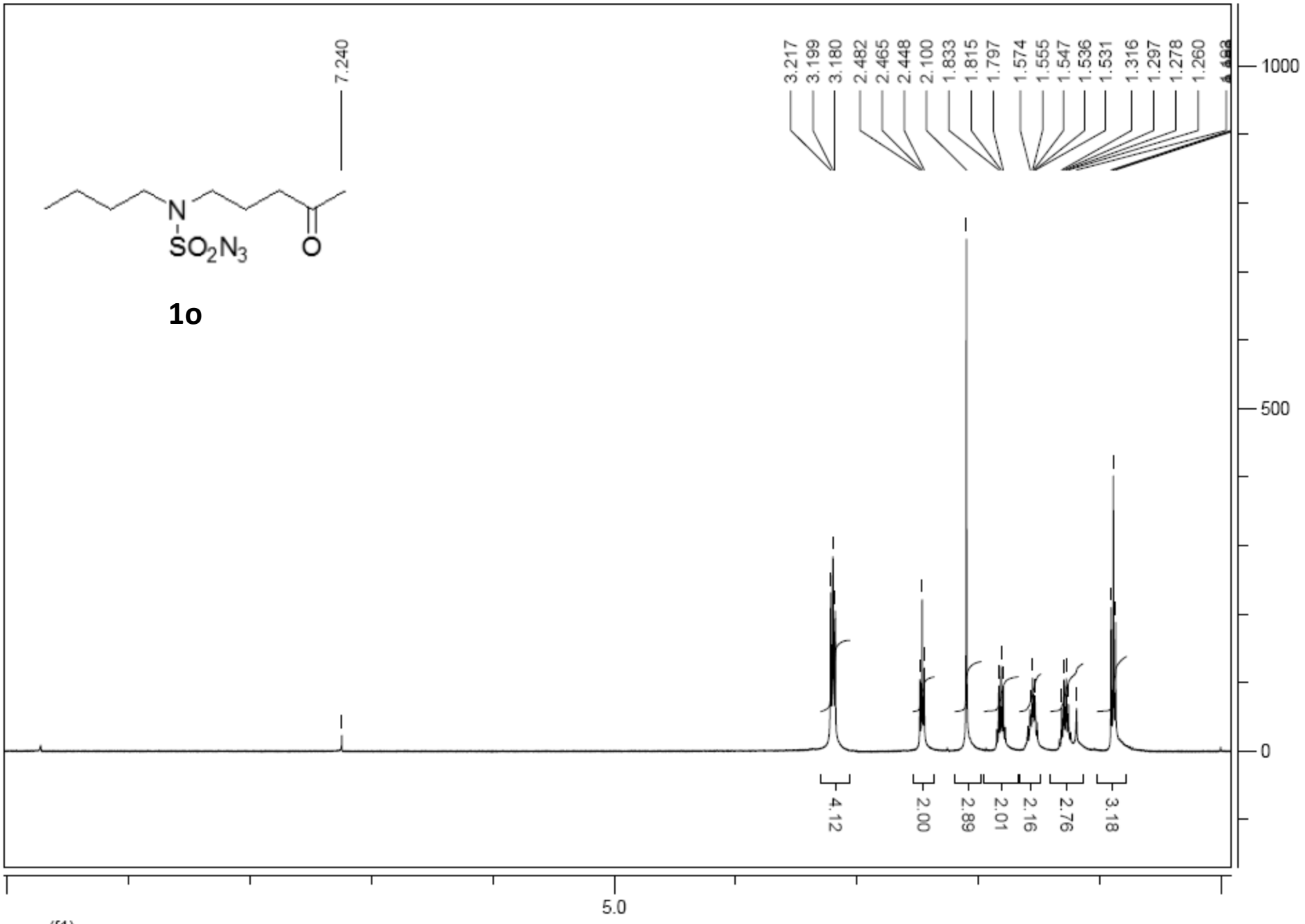
1n

7.242
4.127
4.109
4.092
4.074
3.780
3.762
3.744
2.328
2.309
2.291
1.969
1.951
1.933
1.915
1.897
1.529
1.238
1.221
1.203
1.89
2.02
2.00
2.05
6.00
2.87
8000
7000
6000
5000
4000
3000
2000
1000
0
10.0
5.0
0.0
ppm (f1)

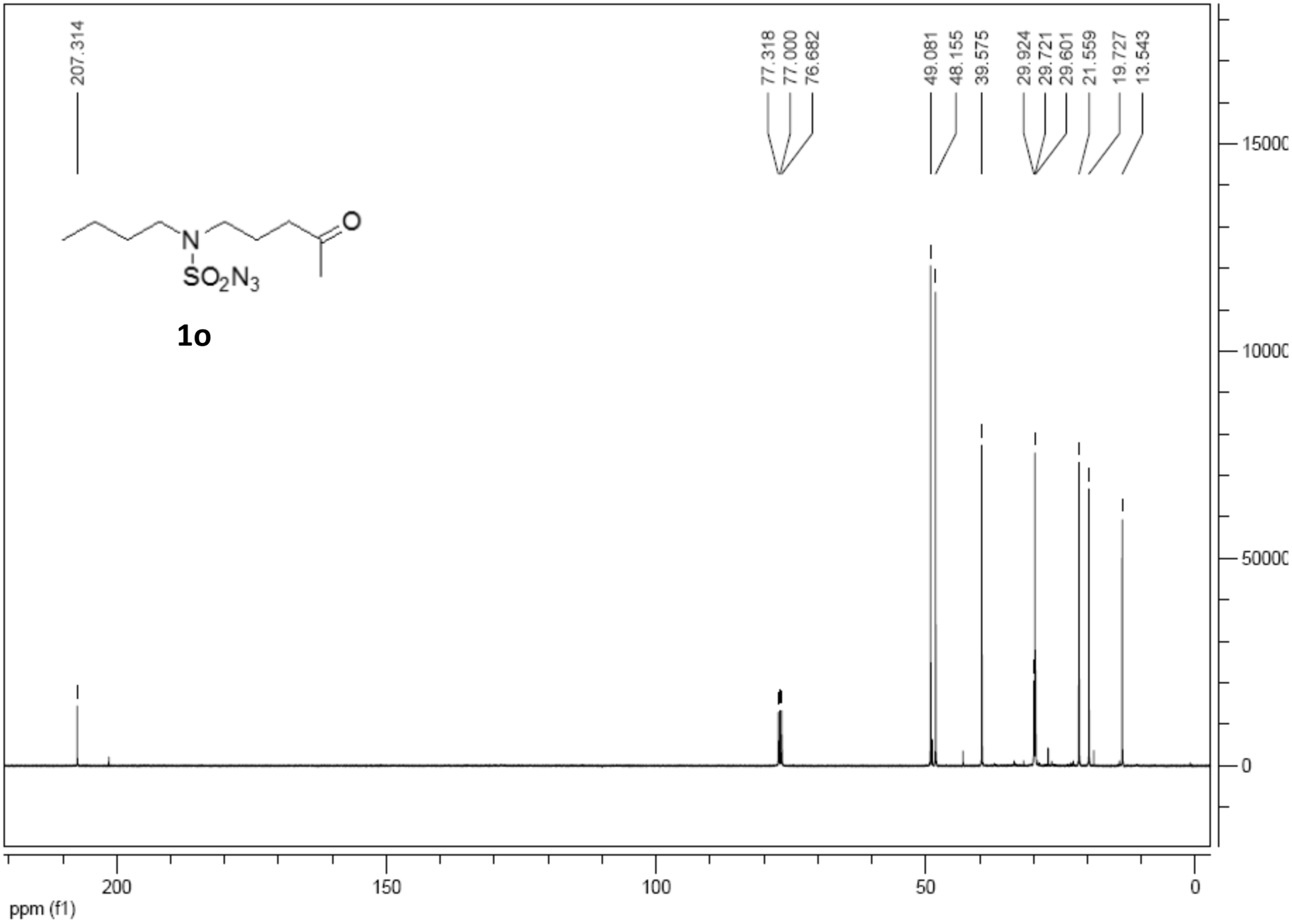

172.286
150.599
86.105
77.319
77.000
76.682
60.491
48.448
30.879
27.931
24.403
14.118
O2
S
BocN
N3
CO2Et
1n
6000
5000
4000
3000
2000
1000
0
150
100
50
0
ppm (f1)

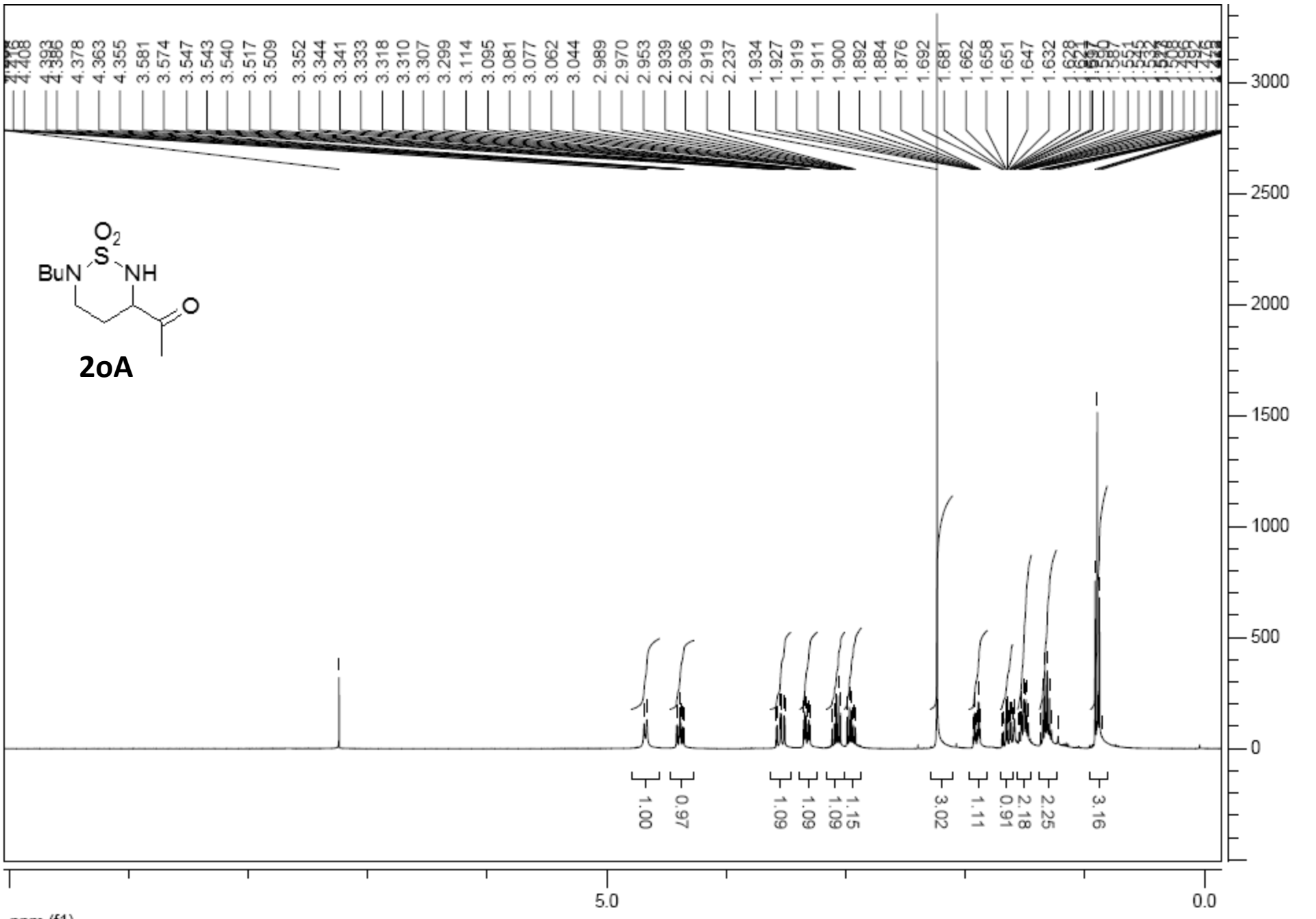

5.007
4.994
4.984
4.378
4.367
4.354
4.343
4.329
4.318
4.312
4.309
4.303
4.294
4.285
4.276
4.267
4.263
4.258
4.249
4.240
4.231
4.222
4.213
4.179
4.174
4.168
4.165
4.155
4.144
4.134
4.131
4.120
3.771
3.763
3.744
3.736
3.729
3.709
3.702
2.300
2.292
2.285
2.279
2.273
2.268
2.260
2.257
2.249
2.244
2.238
Boc
N
S
O2
NH
CO2Et
2n
0.97
4.04
1.00
1.04
0.96
9.22
3.15
600
500
400
300
200
100
0
10.0
5.0
0.0
ppm (f1)


169.416
151.086
84.554
77.318
77.000
76.683
62.584
56.222
45.186
28.378
27.985
14.057
Boc
N
S
O2
NH
CO2Et
2n
2000
1500
1000
5000
0
150
100
50
0
ppm (f1)


7.240
3.217
3.199
3.180
2.482
2.465
2.448
2.100
1.833
1.815
1.797
1.574
1.555
1.547
1.536
1.531
1.316
1.297
1.278
1.260
1000
500
0
4.12
2.00
2.89
2.01
2.16
2.76
3.18
5.0
ppm (f1)

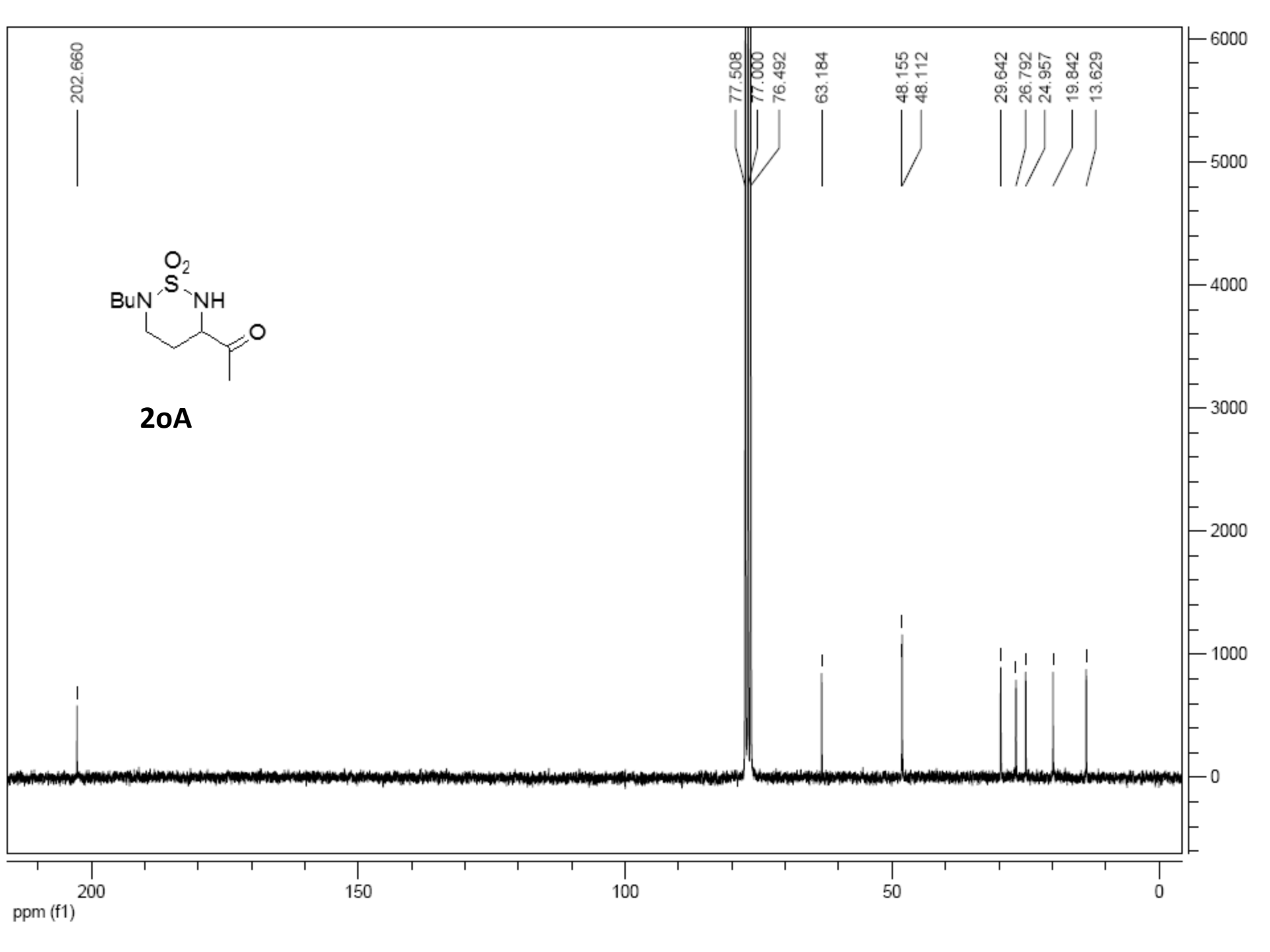
1o


207.314
77.318
77.000
76.682
49.081
48.155
39.575
29.924
29.721
29.601
21.559
19.727
13.543
O
N
SO2N3
1o
15000
10000
5000
0
200
150
100
50
0
ppm (f1)

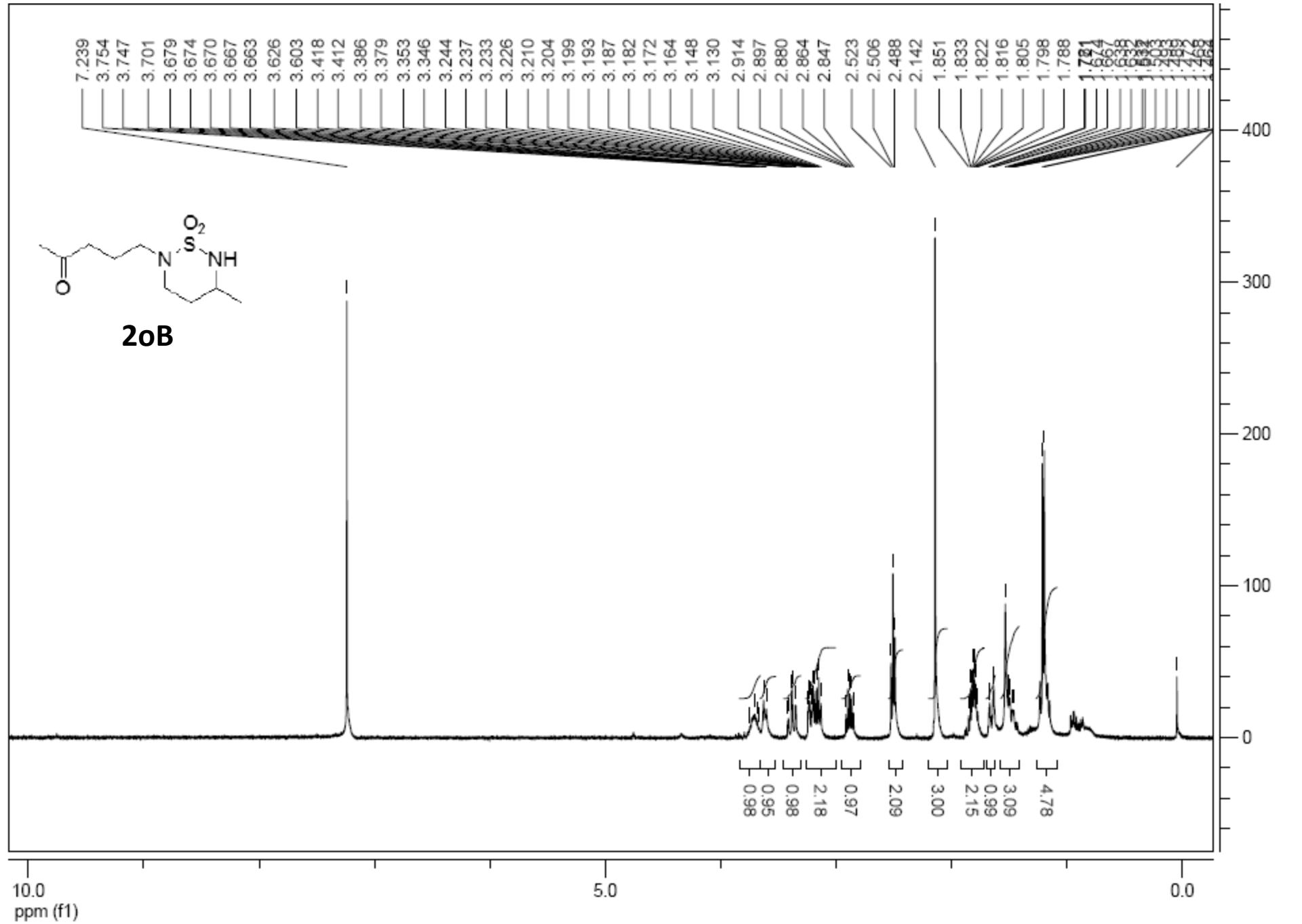

4.408
4.393
4.386
4.378
4.363
4.355
3.581
3.574
3.547
3.543
3.540
3.517
3.509
3.352
3.344
3.341
3.333
3.318
3.310
3.307
3.299
3.114
3.095
3.081
3.077
3.062
3.044
2.989
2.970
2.953
2.939
2.936
2.919
2.237
1.934
1.927
1.919
1.911
1.900
1.892
1.884
1.876
1.692
1.681
1.662
1.658
1.651
1.647
1.632
1.628
1.587
1.551
3000
2500
2000
1500
1000
500
0
1.00
0.97
1.09
1.00
1.09
1.15
3.02
1.11
0.91
2.18
2.25
3.16
5.0
0.0
ppm (f1)

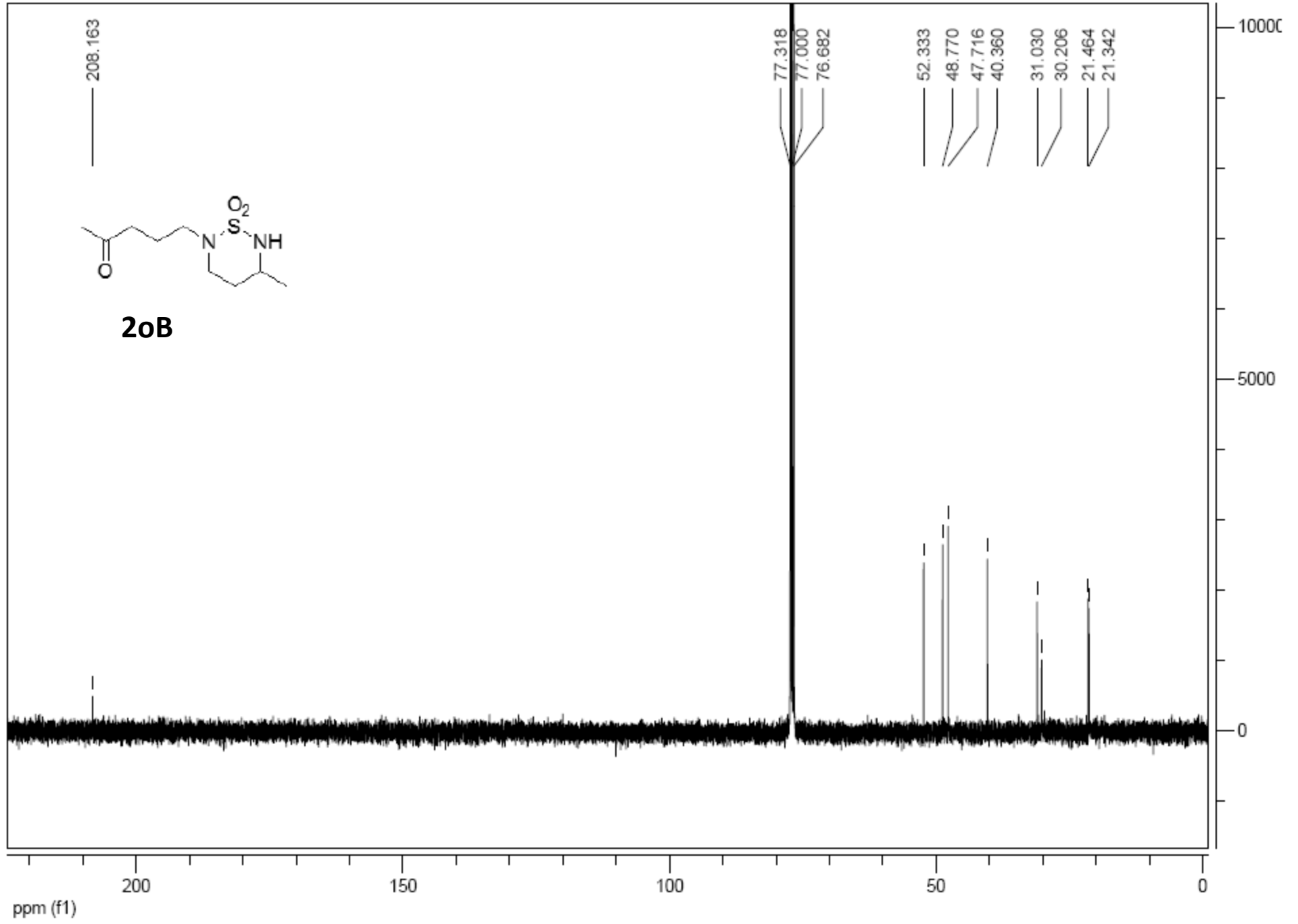
O2
S
BuN
NH
O

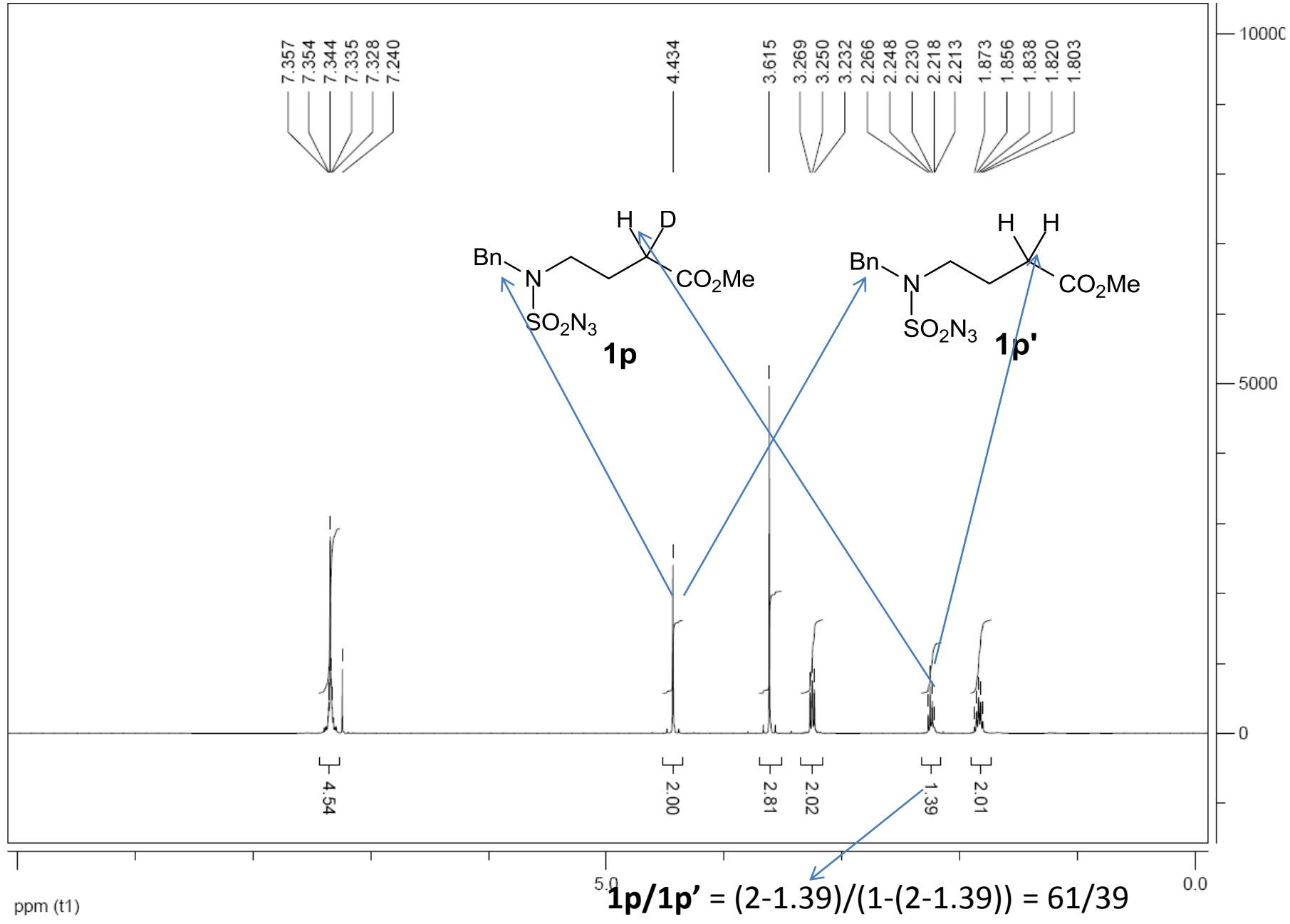
2oA


202.660
77.508
77.000
76.492
63.184
48.155
48.112
29.642
26.792
24.957
19.842
13.629
O2
S
BuN
NH
O
6000
5000
4000
3000
2000
1000
0
200
150
100
50
0
ppm (f1)

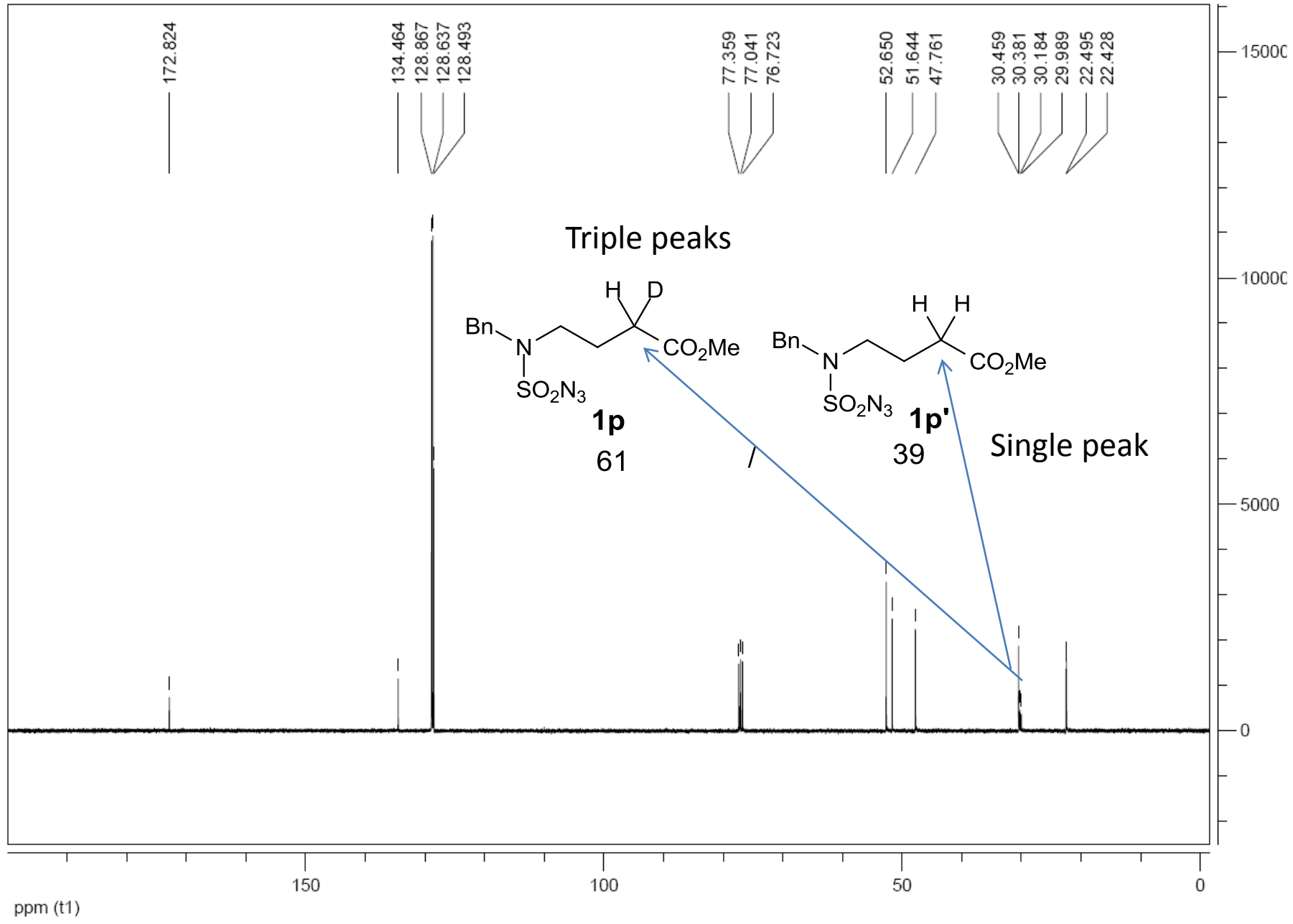
2oA

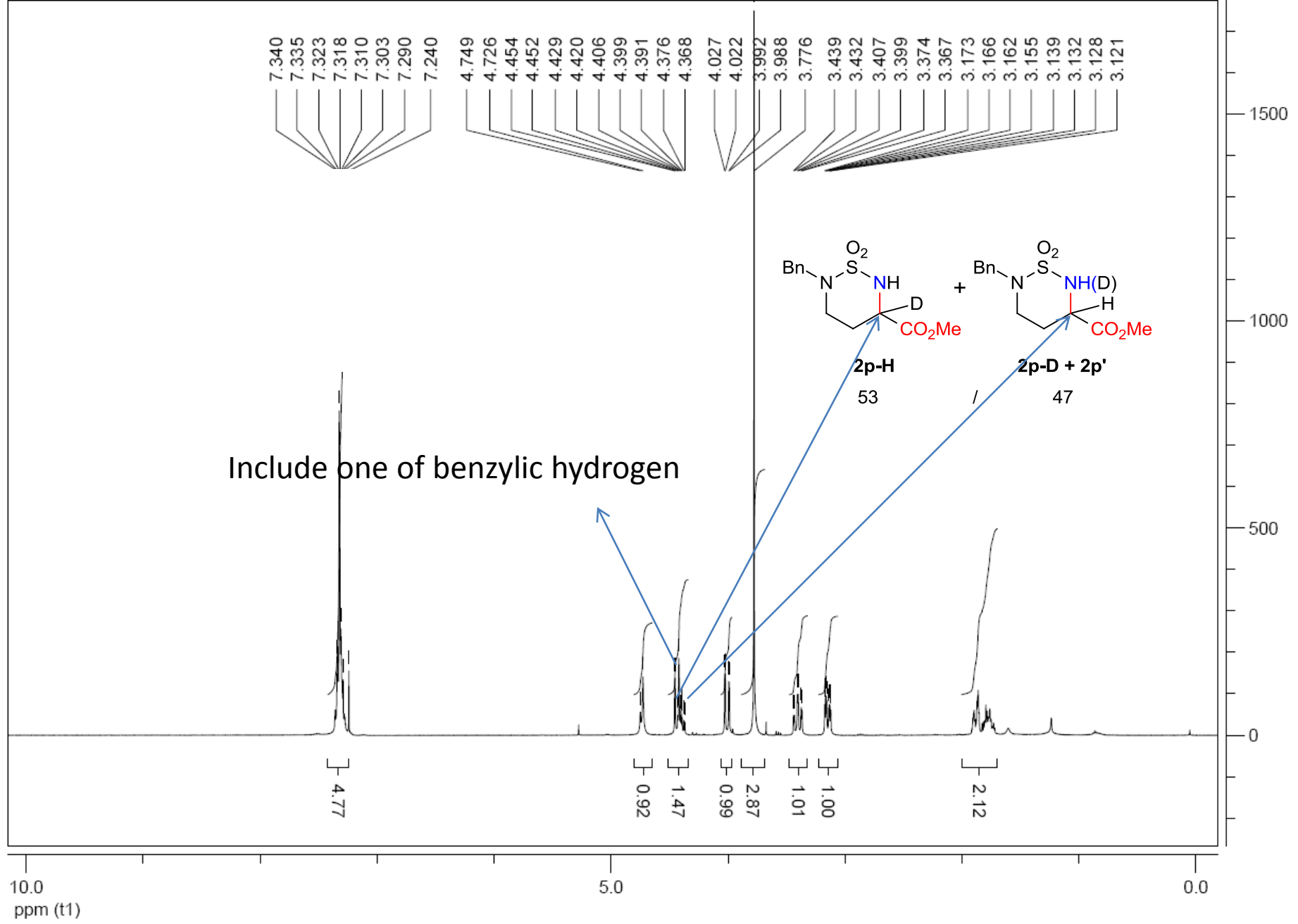

7.239
3.754
3.747
3.701
3.679
3.674
3.670
3.667
3.663
3.626
3.603
3.418
3.412
3.386
3.379
3.353
3.346
3.244
3.237
3.233
3.226
3.210
3.204
3.199
3.193
3.187
3.182
3.172
3.164
3.148
3.130
2.914
2.897
2.880
2.864
2.847
2.523
2.506
2.488
2.142
1.851
1.833
1.822
1.816
1.805
1.798
1.788
O2
S
N
NH
O
2oB
0.98
0.95
0.98
2.18
0.97
2.09
3.00
2.15
0.99
3.09
4.78
400
300
200
100
0
10.0
5.0
0.0
ppm (f1)

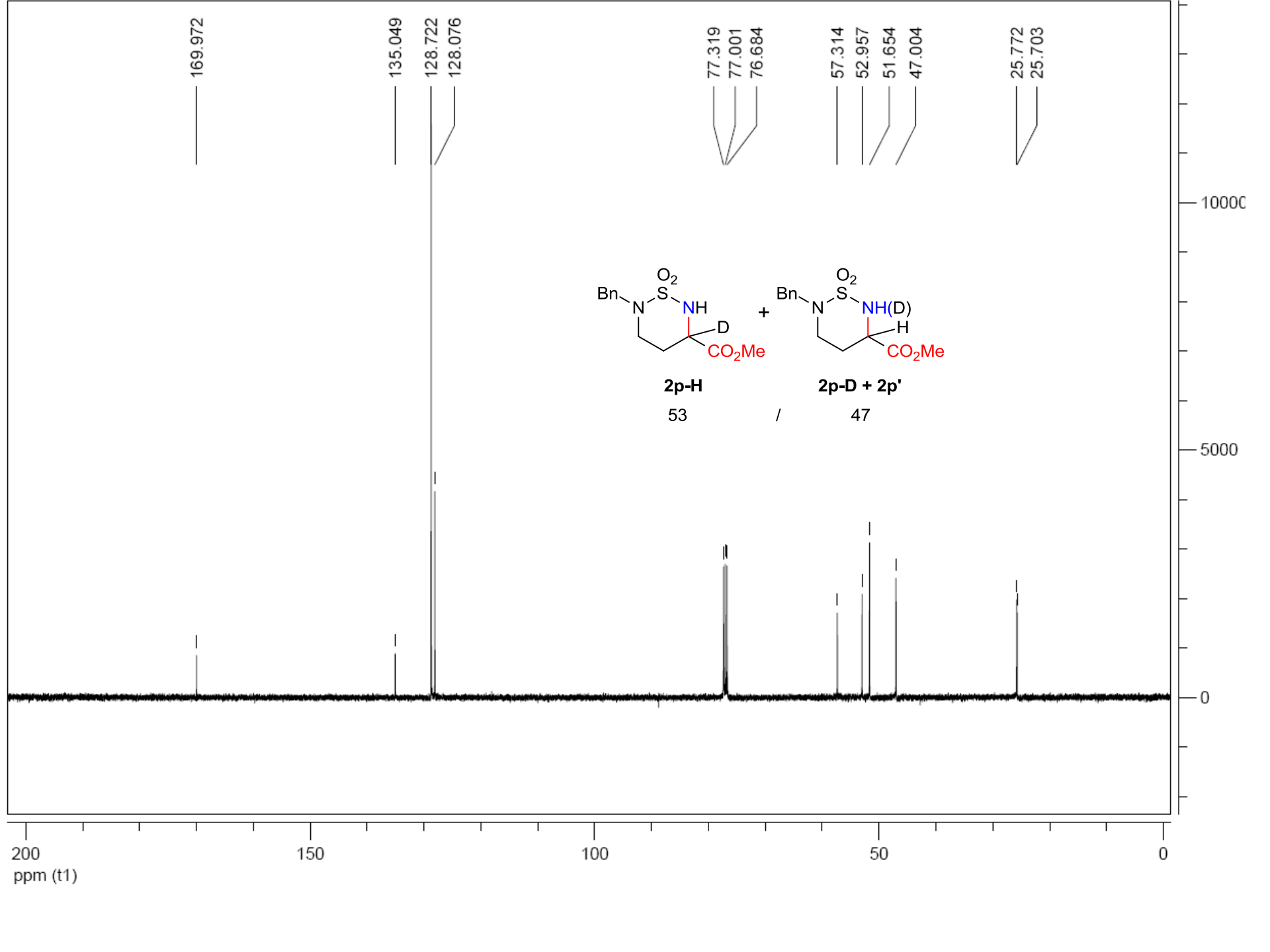

208.163
77.318
77.000
76.682
52.333
48.770
47.716
40.360
31.030
30.206
21.464
21.342
O2
S
N
NH
O
2oB
10000
5000
0
200
150
100
50
0
ppm (f1)

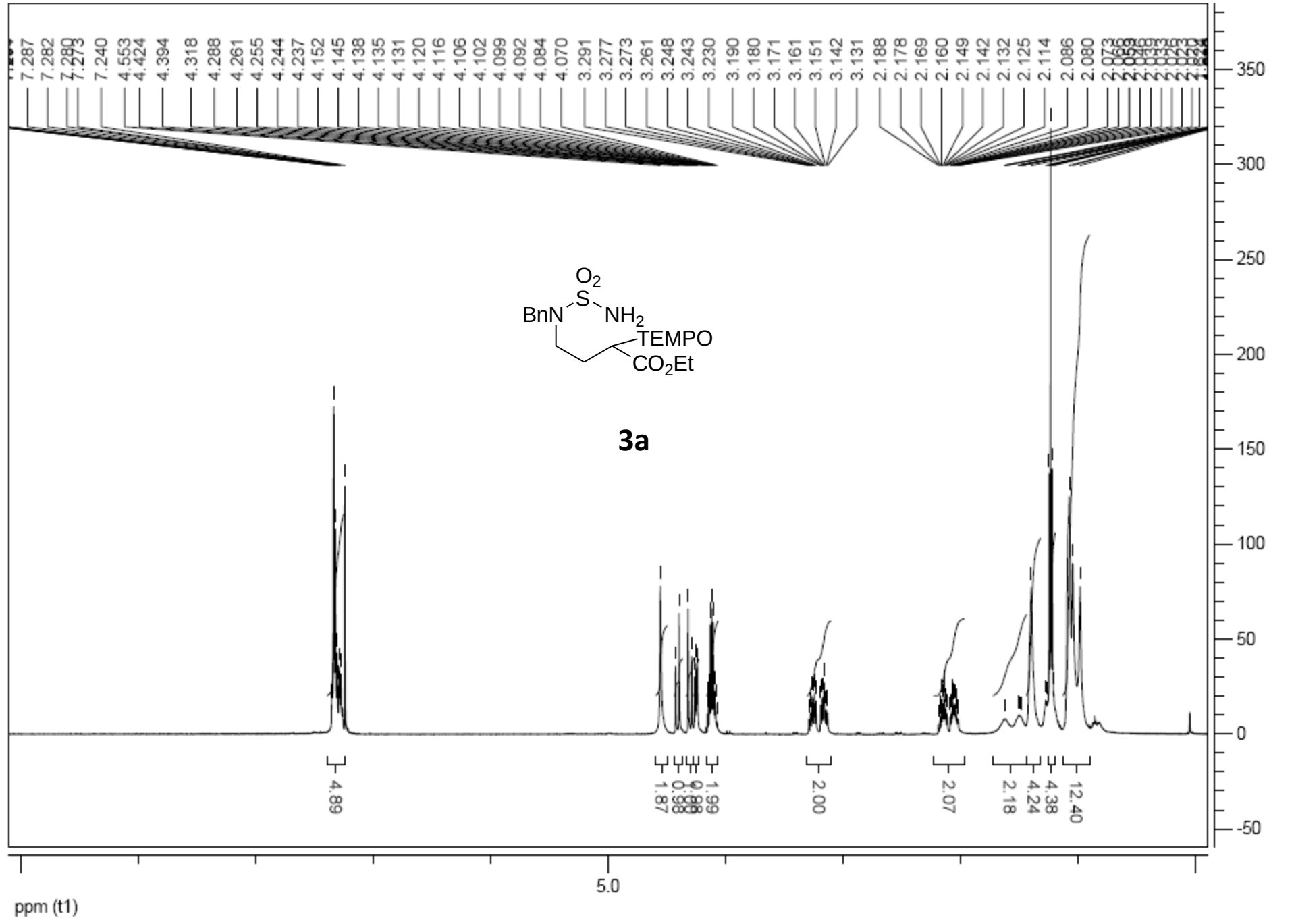


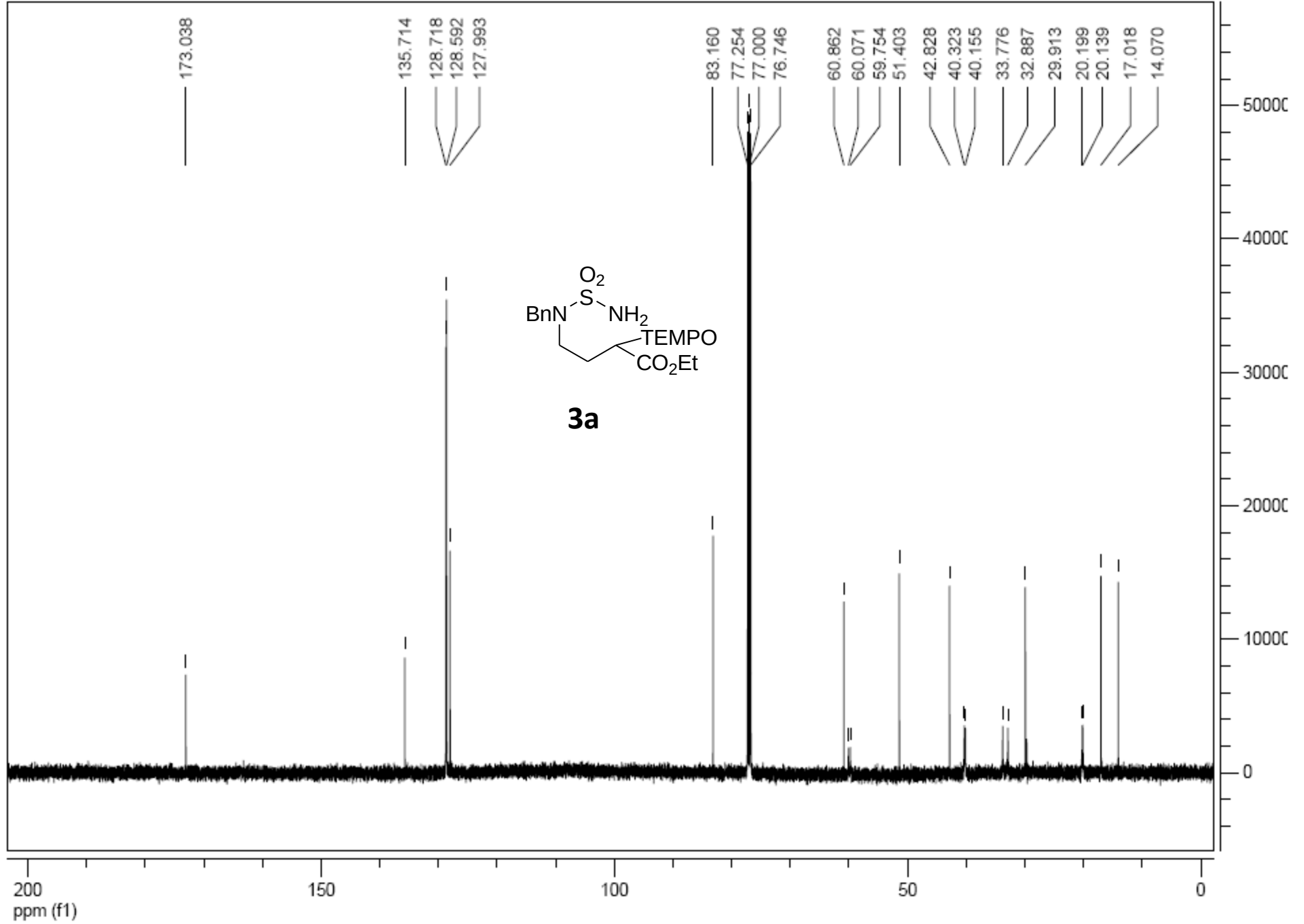
1p/1p' = (2-1.39)/(1-(2-1.39)) = 61/39

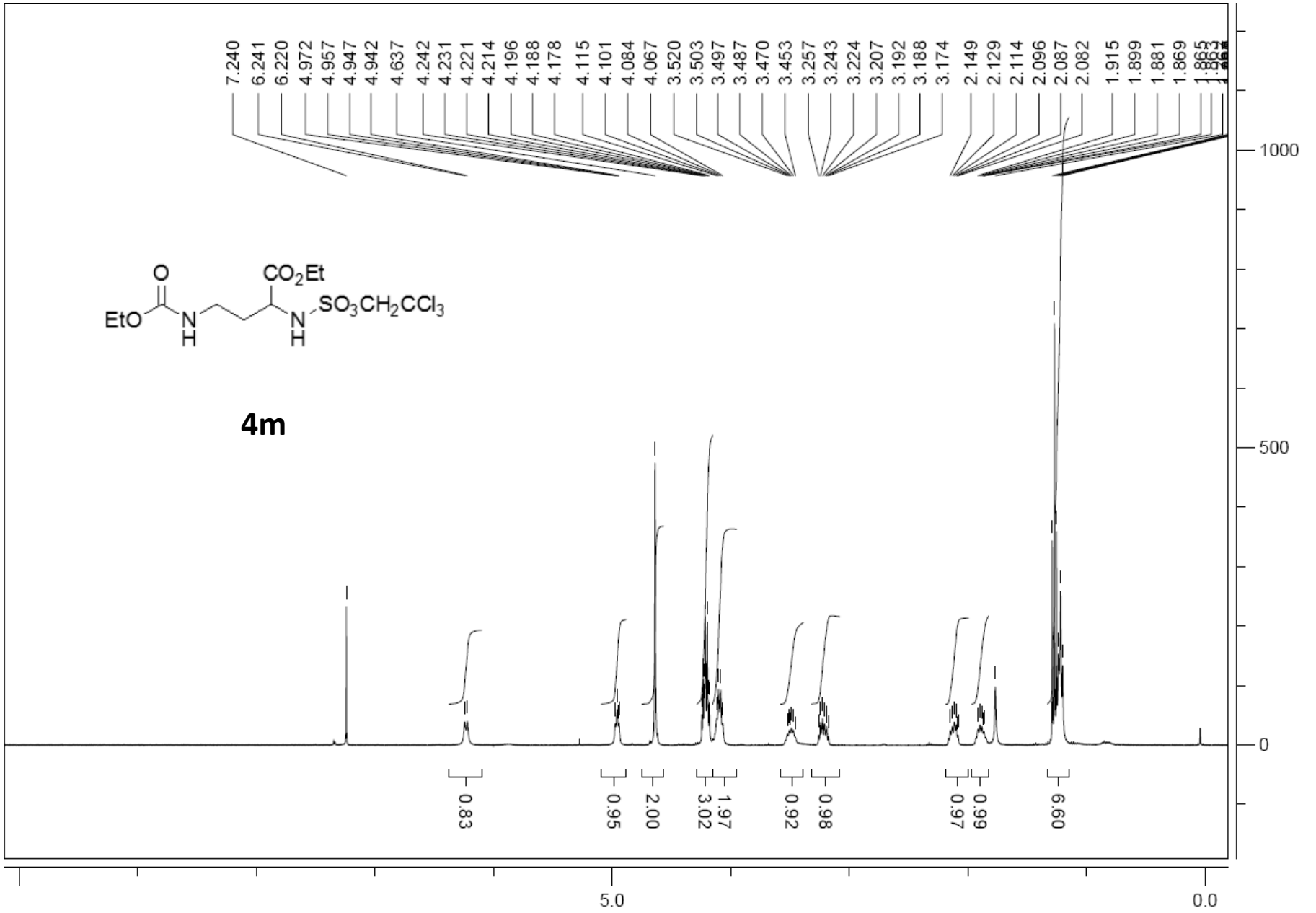

172.824
134.464
128.867
128.637
128.493
77.359
77.041
76.723
52.650
51.644
47.761
30.459
30.381
30.184
29.989
22.495
22.428
Triple peaks
H
D
Bn
N
SO2N3
CO2Me
1p
61
H
H
Bn
N
SO2N3
CO2Me
1p'
39
Single peak
15000
10000
5000
0
150
100
50
0
ppm (t1)

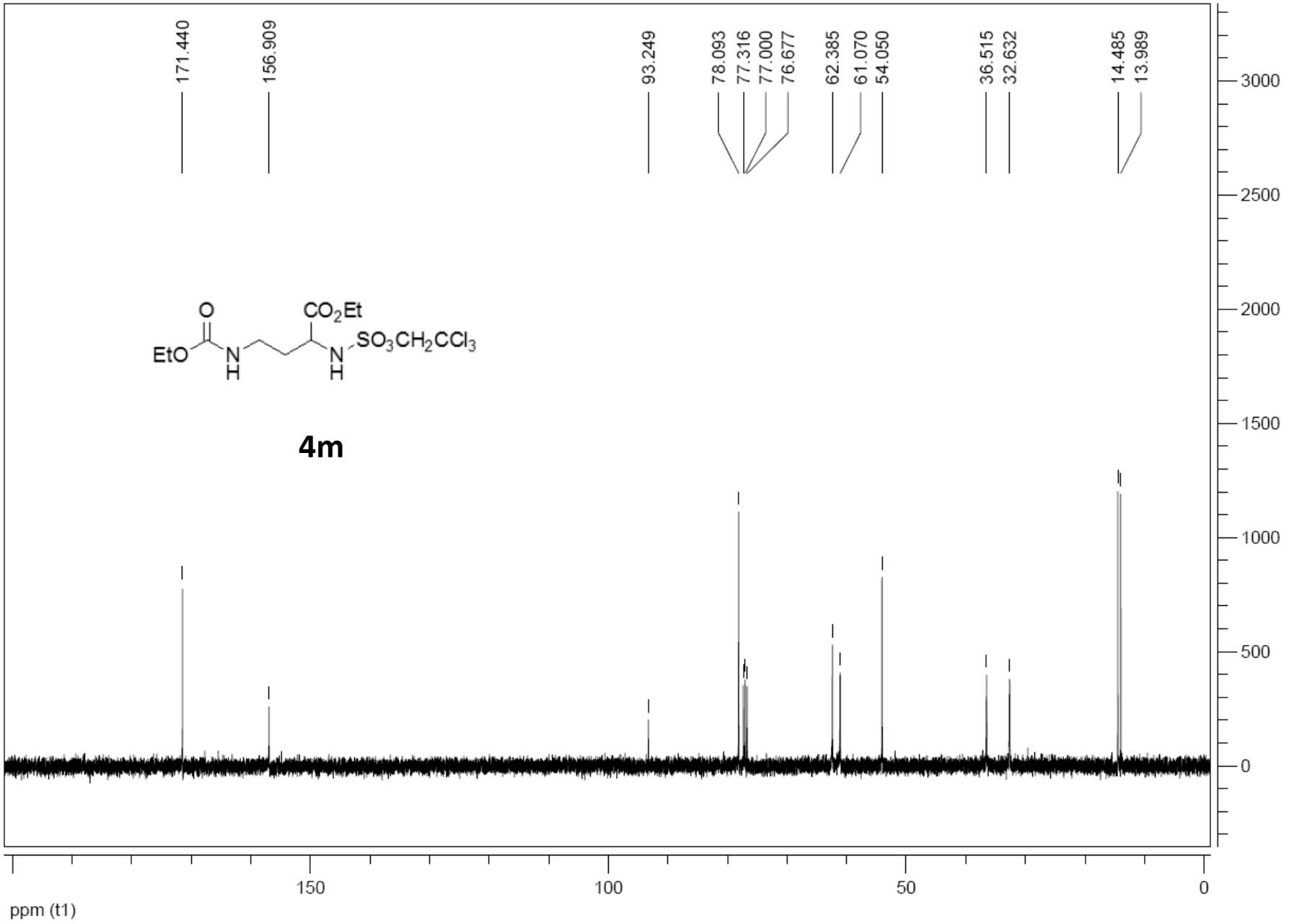

7.340
7.335
7.323
7.318
7.310
7.303
7.290
7.240
4.749
4.726
4.454
4.452
4.429
4.420
4.406
4.399
4.391
4.376
4.368
4.027
4.022
3.992
3.988
3.776
3.439
3.432
3.407
3.399
3.374
3.367
3.173
3.166
3.162
3.155
3.139
3.132
3.128
3.121
Bn
N
S
O2
NH
D
CO2Me
+
NH(D)
H
2p-H
53
/
2p-D + 2p'
47
Include one of benzylic hydrogen
4.77
0.92
1.47
0.99
2.87
1.01
1.00
2.12
1500
1000
500
0
10.0
5.0
0.0
ppm (t1)


169.972
135.049
128.722
128.076
77.319
77.001
76.684
57.314
52.957
51.654
47.004
25.772
25.703
10000
5000
0
Bn
N
S
O2
NH
D
CO2Me
+
Bn
N
S
O2
NH(D)
H
CO2Me
2p-H
2p-D + 2p'
53
/
47
200
150
100
50
0
ppm (t1)


7.287
7.282
7.280
7.273
7.240
4.553
4.424
4.394
4.318
4.288
4.261
4.255
4.244
4.237
4.152
4.145
4.138
4.135
4.131
4.120
4.116
4.106
4.102
4.099
4.092
4.084
4.070
3.291
3.277
3.273
3.261
3.248
3.243
3.230
3.190
3.180
3.171
3.161
3.151
3.142
3.131
2.188
2.178
2.169
2.160
2.149
2.142
2.132
2.125
2.114
2.086
2.080
O2
S
BnN
NH2
TEMPO
CO2Et
3a
4.89
1.87
1.69
2.00
2.07
2.18
4.24
4.38
12.40
350
300
250
200
150
100
50
0
-50
5.0
ppm (t1)


173.038
135.714
128.718
128.592
127.993
83.160
77.254
77.000
76.746
60.862
60.071
59.754
51.403
42.828
40.323
40.155
33.776
32.887
29.913
20.199
20.139
17.018
14.070
O2
S
BnN
NH2
TEMPO
CO2Et
3a
50000
40000
30000
20000
10000
0
200
150
100
50
0
ppm (f1)


7.240
6.241
6.220
4.972
4.957
4.947
4.942
4.637
4.242
4.231
4.221
4.214
4.196
4.188
4.178
4.115
4.101
4.084
4.067
3.520
3.503
3.497
3.487
3.470
3.453
3.257
3.243
3.224
3.207
3.192
3.188
3.174
2.149
2.129
2.114
2.096
2.087
2.082
1.915
1.899
1.881
1.869
1000
500
0
O
CO2Et
EtO
N
H
N
H
SO3CH2CCl3
4m
0.83
0.95
2.00
3.02
1.97
0.92
0.98
0.97
0.99
6.60
5.0
0.0
ppm (f1)


171.440
156.909
93.249
78.093
77.316
77.000
76.677
62.385
61.070
54.050
36.515
32.632
14.485
13.989
O
CO2Et
EtO
N
H
N
H
SO3CH2CCl3
4m
3000
2500
2000
1500
1000
500
0
150
100
50
0
ppm (t1)