Supporting Information

A Ball-Milling Strategy for the Synthesis of Benzothiazole Benzimidazole and Benzoxazole Derivatives under Solvent-Free Conditions

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General

All chemicals and solvents were used as received without any purification. The Fritsch "Pulverisette 7 premium line" (Fritsch GmbH, Idar-oberstein, Germany) planetary ball mill was employed as a reaction chamber with 80 mL grinding cups (tungsten carbide) and milling balls (20×5 mm; tungsten carbide). Prior to the reaction, all vessels and milling balls were cleaned several times with acetone followed by aqua regia to avoid any contamination. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a JNM-ECS400 JEOL spectrophotometer in DMSO-d_6 or $CDCl_3$ solvent using TMS as an internal reference. The splitting patterns are indicated as s (singlet), bs (broad singlet), d (doublet), dd (doublet of doublet), t (triplet), and m (multiplet). Fourier transform infrared (FT-IR) spectra of the entitled compounds were recorded in the range of 4000-600 cm^{-1} using a Bruker Tensor 27 spectrophotometer. For solid samples, KBr pellets were prepared for IR measurement, and neat sample was used for liquids. The PANalytical X'PERT PRO diffractometer was employed for analysis of the crystal structure of ZnO powder, operated at 45 KV, 40 mA using Ni-filtered Cu K_α radiation with a scan speed of 10º/min for 2θ in a range from 10 to 75. For XRD analysis, air-dried fine powder samples were prepared in a uniform thin layer on a zero background sample holder. The morphology and elemental (EDX) composition were visualized by scanning electron microscopy (SEM, JEOL JSM-6610LV) using a voltage of 15 KV. A dilute solution of ZnO (100 µM) in ethanol was placed on carbon tape and was dried at room temperature under vacuum. The Metrohm Microtrac Ultra Nanotrac Particle Size Analyzer (Dynamic Light Scattering) was used to measure the hydrodynamic diameter of ZnO particles using a DMSO/water (5:5, v/v) system as the dispersion medium. N_2 absorption measurements were carried out on an Autosorb-IQ Quantachrome Instruments volumetric adsorption analyzer. The sample was degassed at 200 ºC for 3 h in the degassing port. The Brunauer-Emmett-Teller (BET) model from a linear part of the BET plot ($P/P_{O:}$ 0.05-0.3) was employed for the surface area calculation.

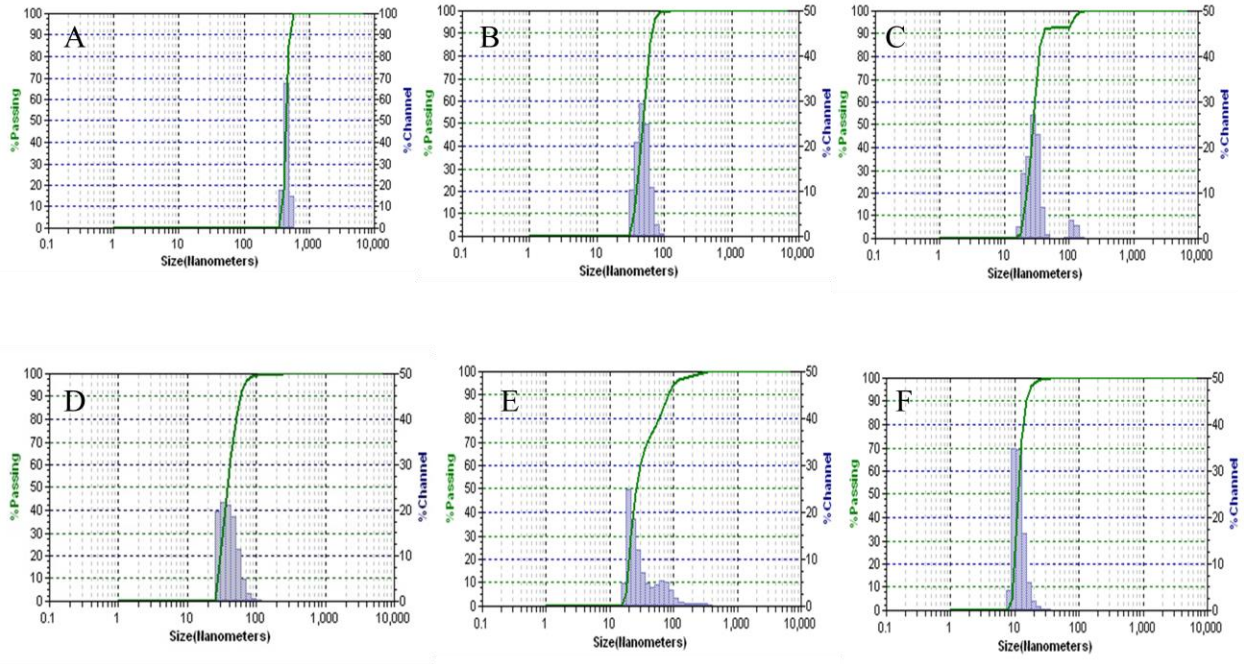


Figure S1. A dynamic light scattering (DLS) study of six different catalysts indicating the size of the ZnO nanoparticles (nm) (A) NPs-**1**, (B) NPs-**2**, (C) NPs-**3**, (D) NPs-**4**, (E) NPs-**5**, and (F) NPs-**6**.

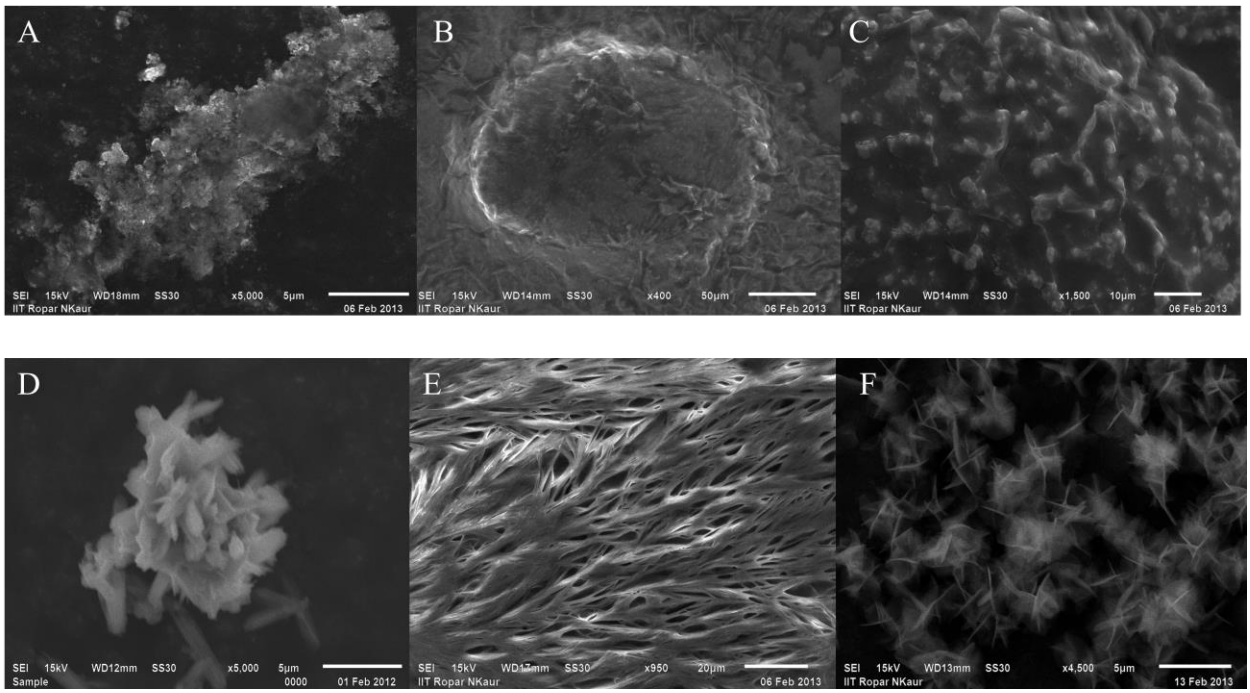


Figure S2. SEM images of six different catalysts showing the size of ZnO nanoparticles (nm) (A) NPs-**1**, (B) NPs-**2**, (C) NPs-**3**, (D) NPs-**4**, (E) NPs-**5**, and (F) NPs-**6**.

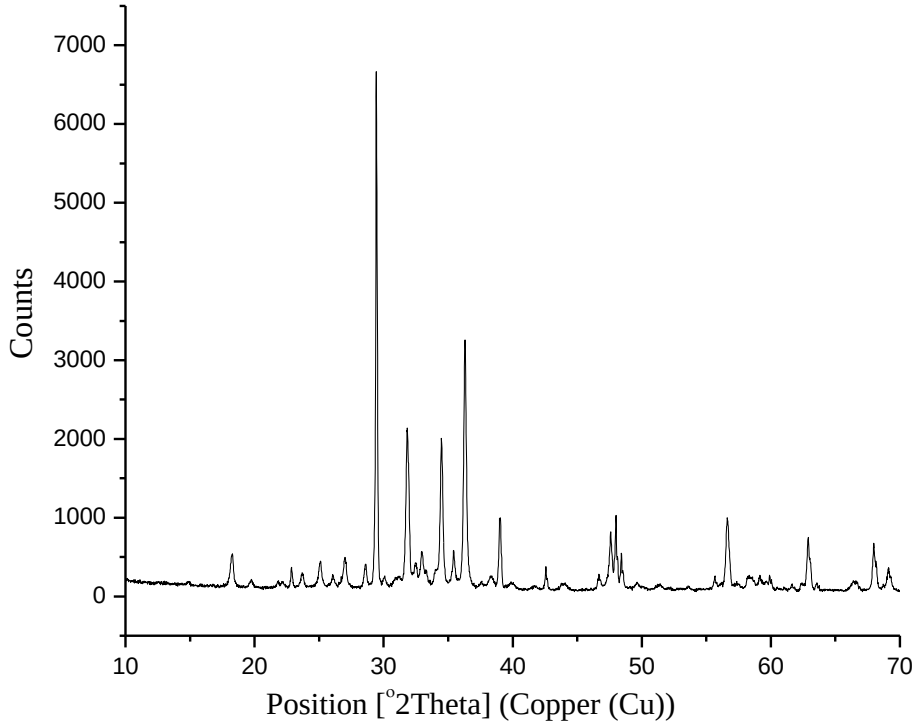


Figure S3. XRD pattern of NPs-**6**.

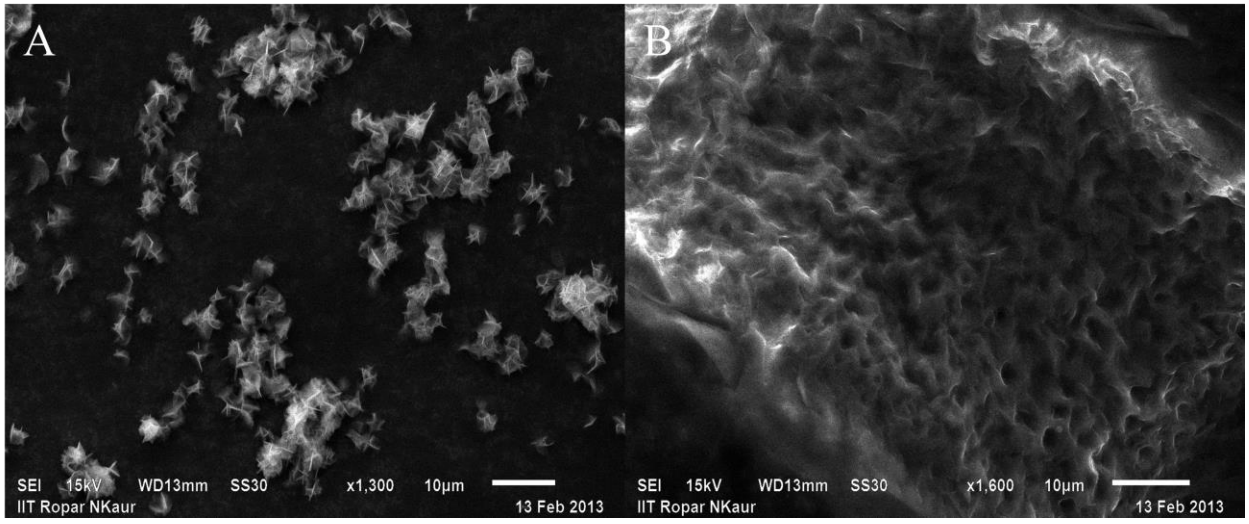


Figure S4. SEM image of catalyst NPs-**6** (A) before reaction and (B) after the fifth reaction.

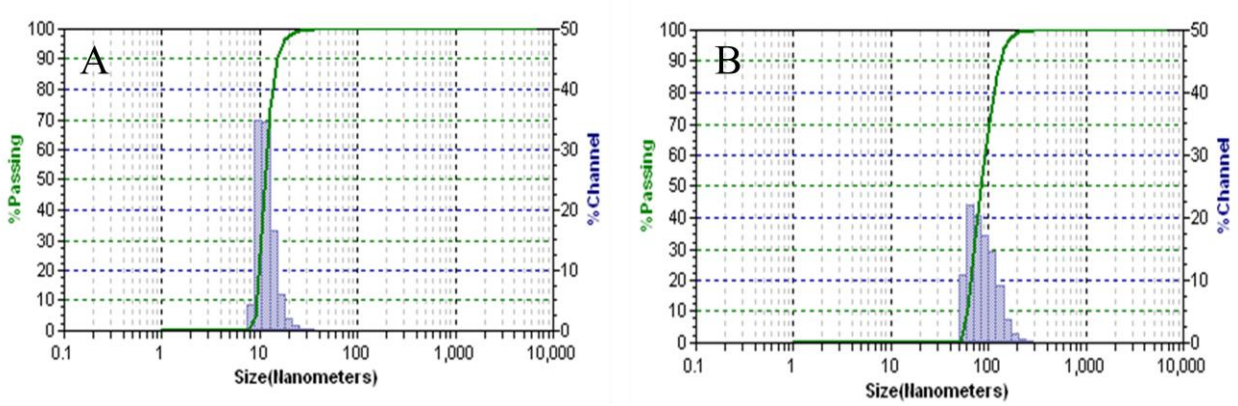


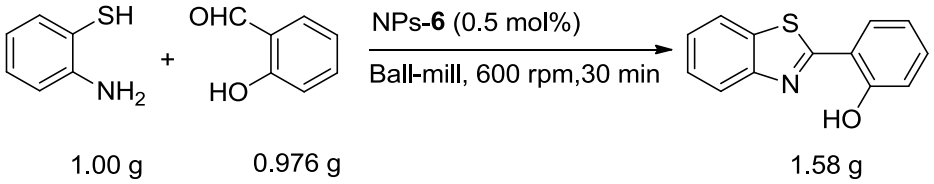
Figure S5. Size measurement of catalyst NPs-**6** (A) before reaction and (B) after the fifth reaction.

Table S1. Ecoscale calculation for the reaction of 2-aminothiophenol with 2-hydroxybenzaldehyde.[a]

	Detail of parameters	Penalty Points[b]
1. Yield	87%	6.5
2. Cost of reactants to obtain 10 mmol of product		
	2-aminothiophenol (1.25 g)	0
	2-hydroxybenzaldehyde (1.22 g)	0
	ZnO nanoparticles (0.5 mol%, 81 mg)	0
	methanol (10 mL)	0
3. Safety		
	2-aminothiophenol	5 (T)
	2-hydroxybenzaldehyde	5 (T)
	ZnO	5 (N)
	methanol	10 (F, T)
4. Technical setup		
	ball-mill	2
5. Temperature/Time		
	room temperature, < 1h	0
	annealing for ZnO, Heating > 1h	3
6. Work-up and Purification		
	adding solvent	0
	simple filtration	0

[a]The reaction was performed on a 10 mmol scale.
[b]The total of all penalties was 36.5, which gave a score of 63.5 (100 - 36.5), which is indicative of an acceptable synthesis.

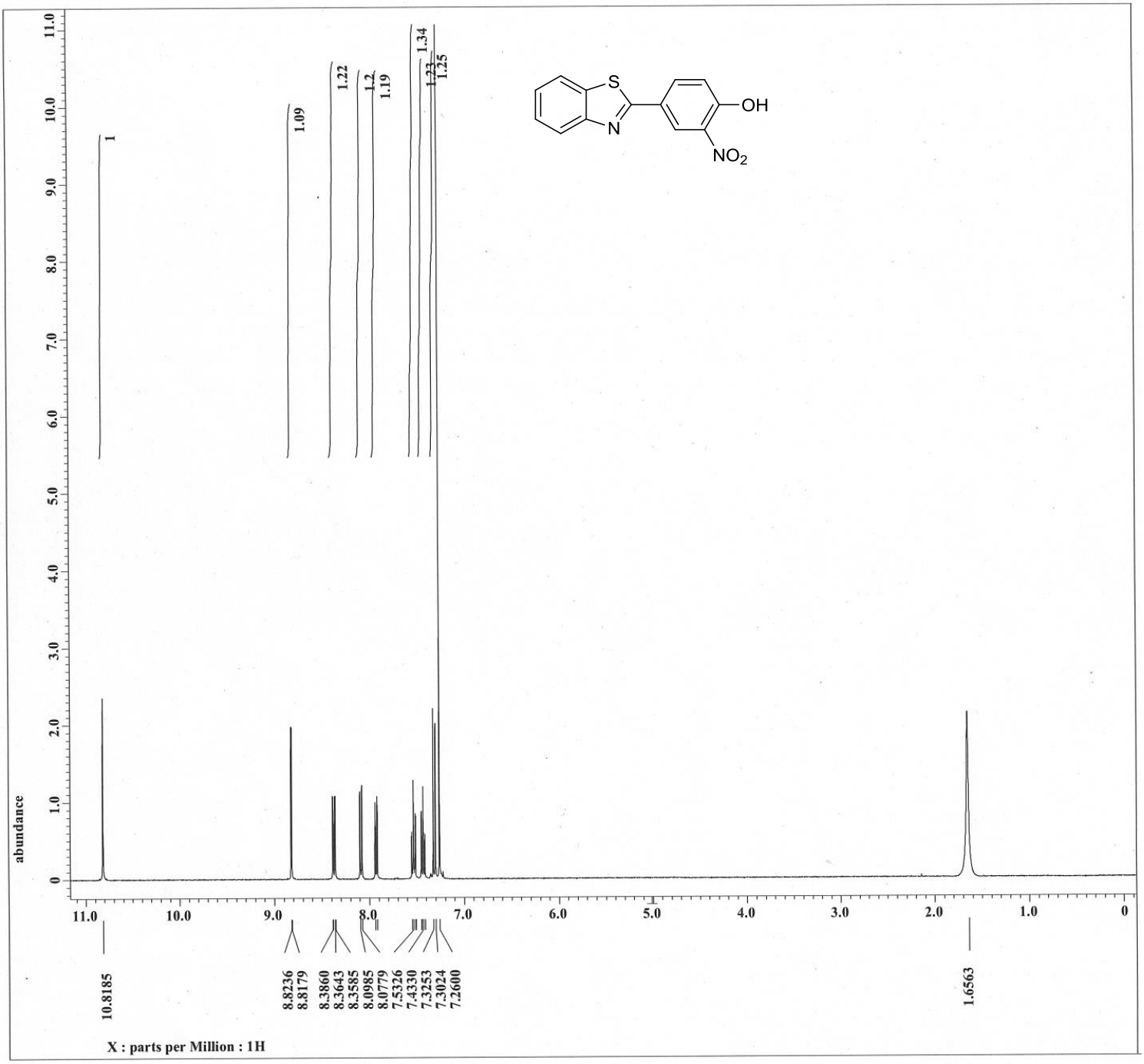
Table S2. Calculation of E-factor and mass intensities for the reaction of 2-aminothiophenol with 2-hydroxybenzaldehyde .[a]

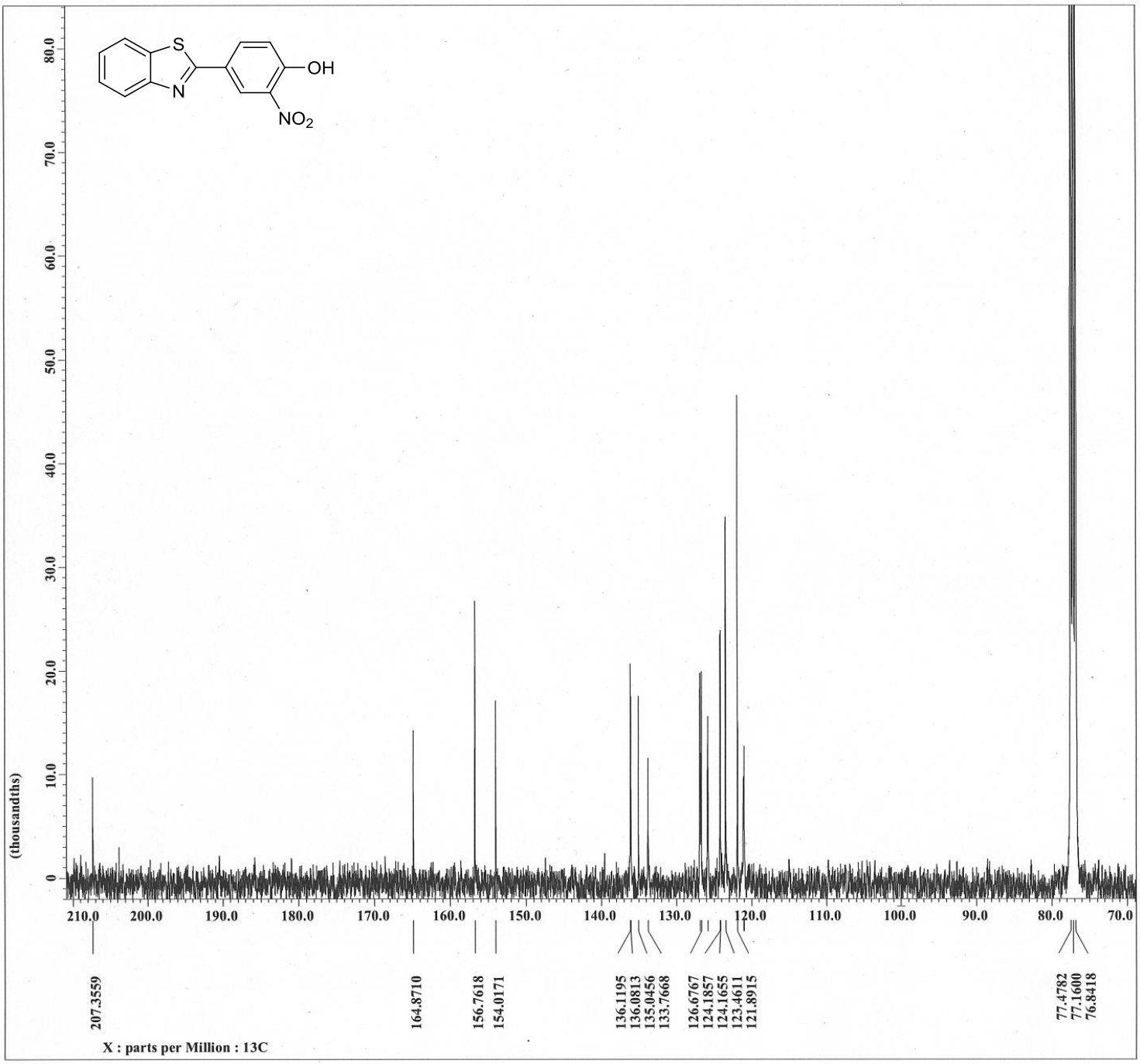


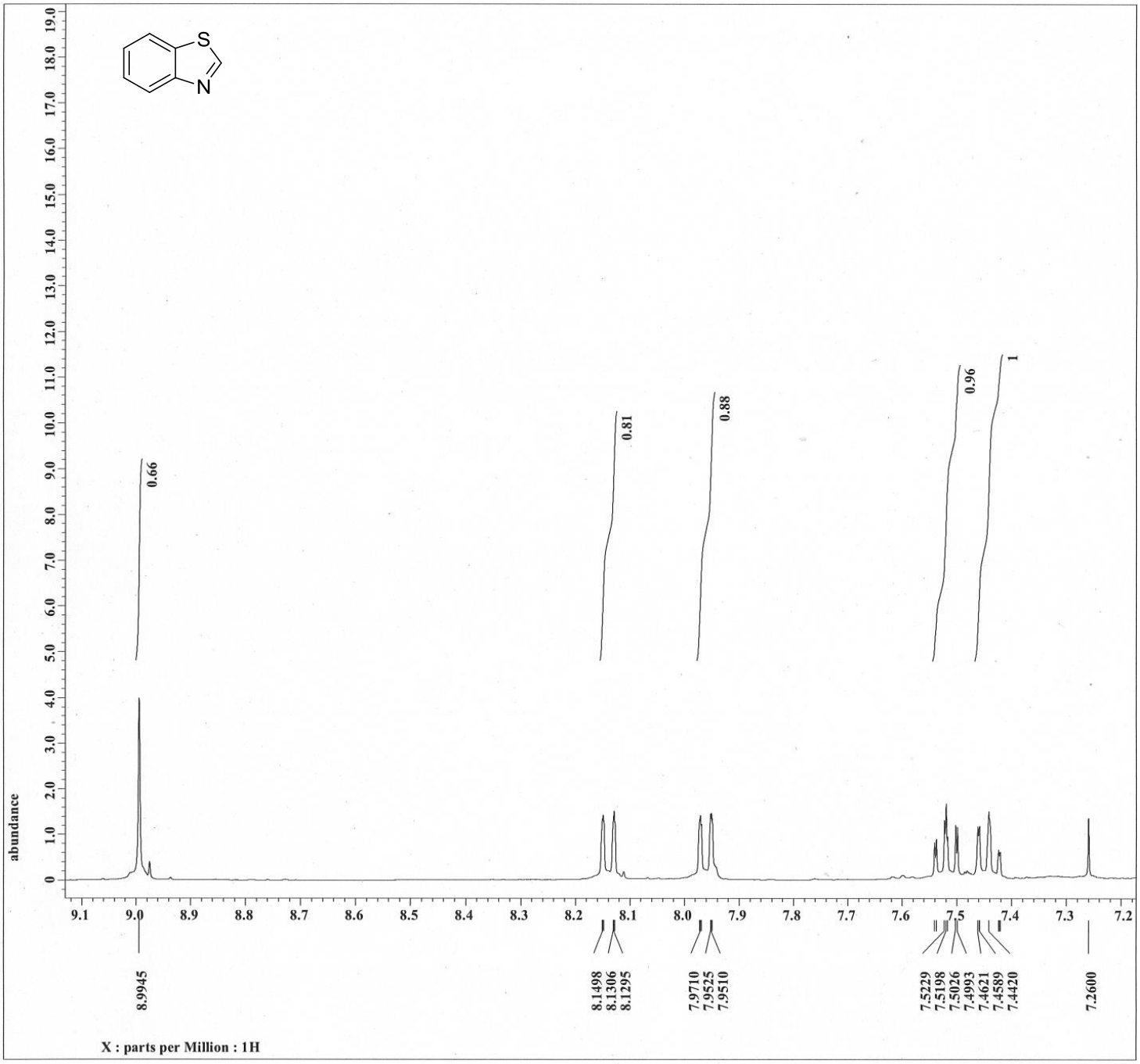
1.00 g 0.976 g 1.58 g

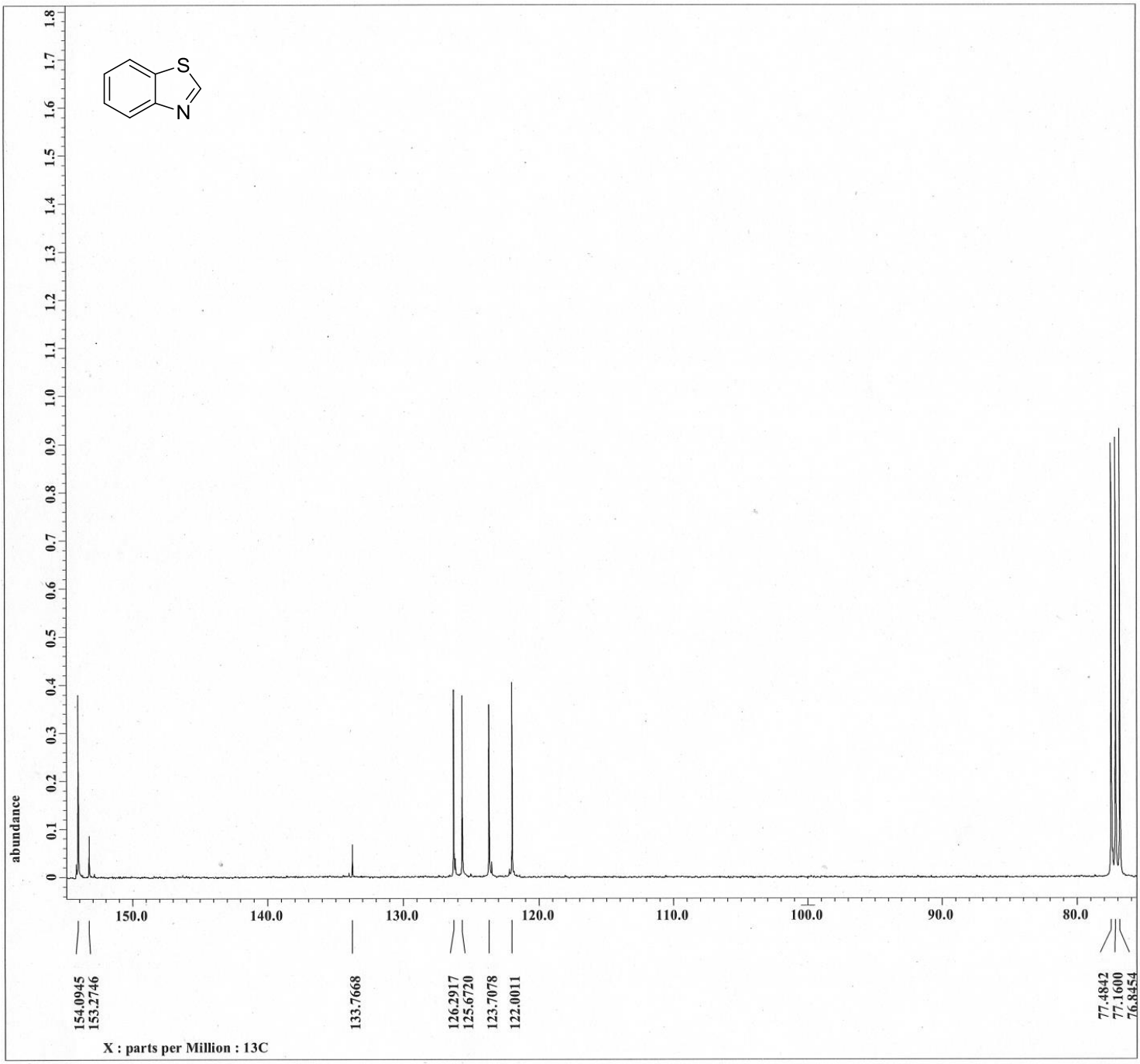
Total amount of reactants: 1.00 g + 0.976 g = 1.98 g
Amount of final product: 1.58 g
Amount of waste: (1.98 g - 1.58 g) = 0.40 g
E-Factor = Amount of waste/Amount of product = 0.40 g/1.58 g = 0.25
Mass intensity (MI) = 1.25

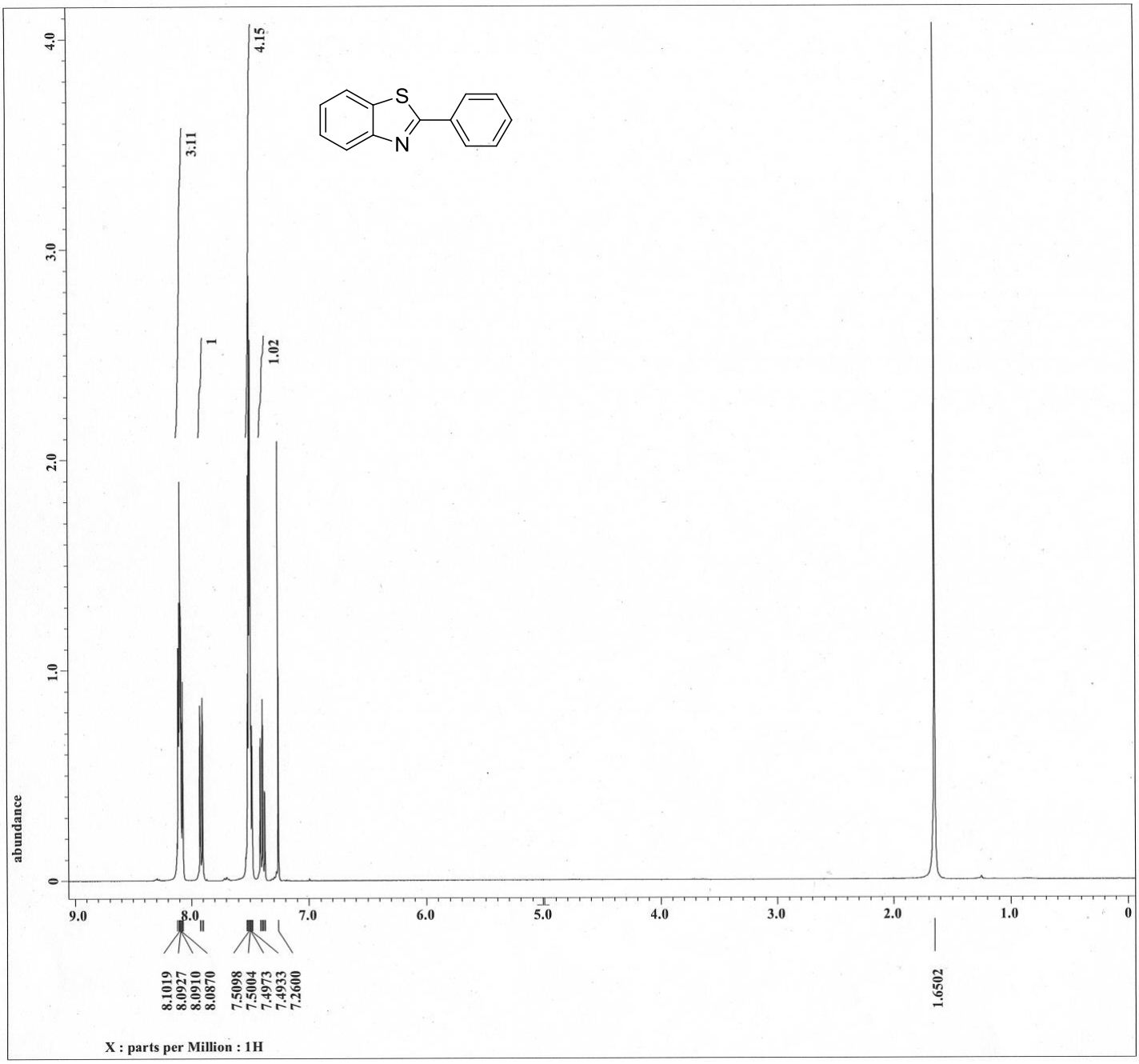
[a]The calculation was performed for 8 mmol scale.

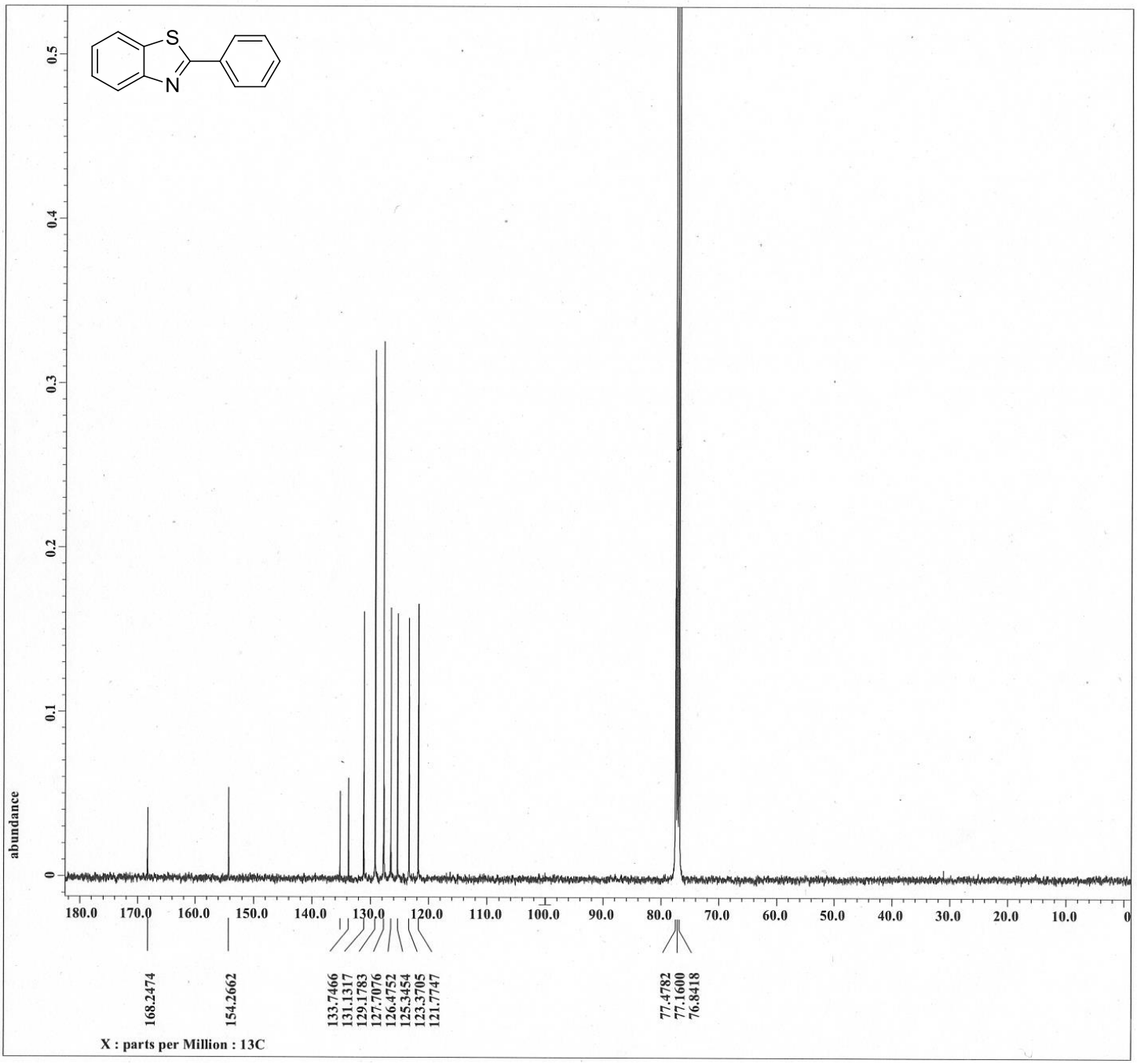

abundance
X : parts per Million : 1H
1
1.09
1.22
1.2
1.19
1.34
1.33
1.25
S
N
OH
NO2
10.8185
8.8236
8.8179
8.3860
8.3643
8.3585
8.0985
8.0779
7.5326
7.4330
7.3253
7.3024
7.2600
1.6563

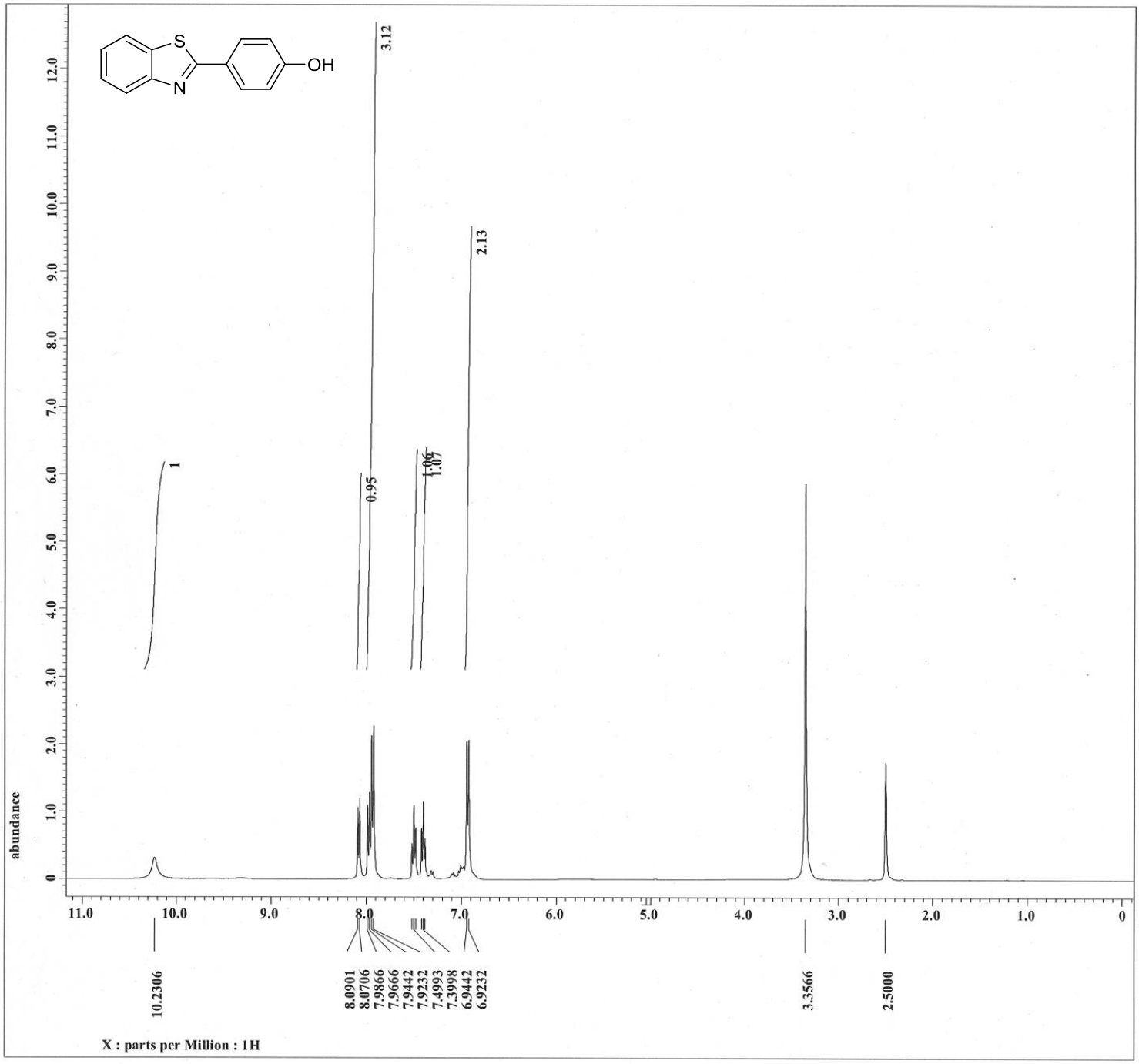

S
N
OH
NO2
(thousandths)
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
207.3559
164.8710
156.7618
154.0171
136.1195
136.0813
135.0456
133.7668
126.6767
124.1857
124.1655
123.4611
121.8915
77.4782
77.1600
76.8418
X : parts per Million : 13C

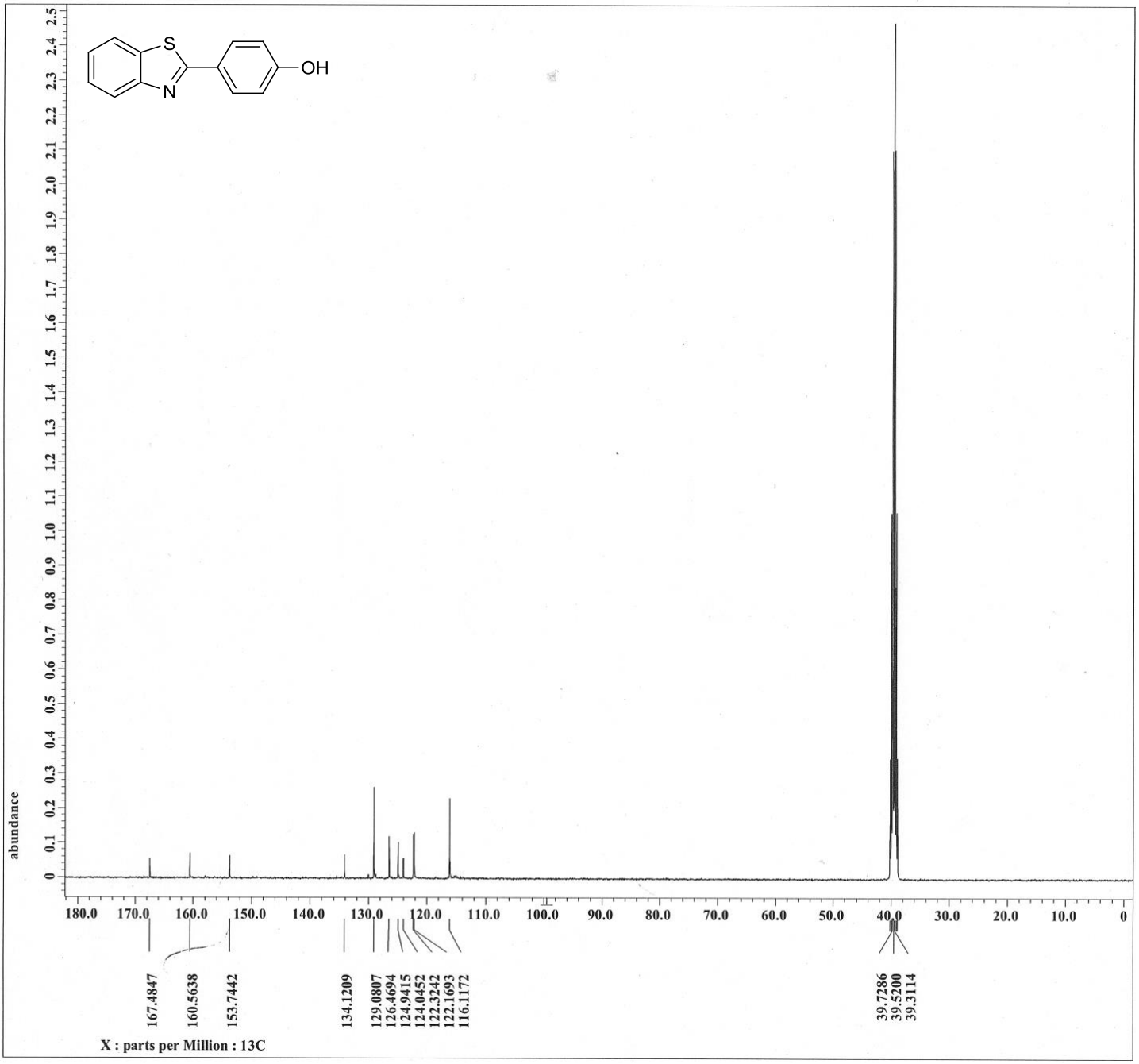

S
N
abundance
0.66
0.81
0.88
0.96
1
8.9945
8.1498
8.1306
8.1295
7.9710
7.9525
7.9510
7.5229
7.5198
7.5026
7.4993
7.4621
7.4589
7.4420
7.2600
X : parts per Million : 1H

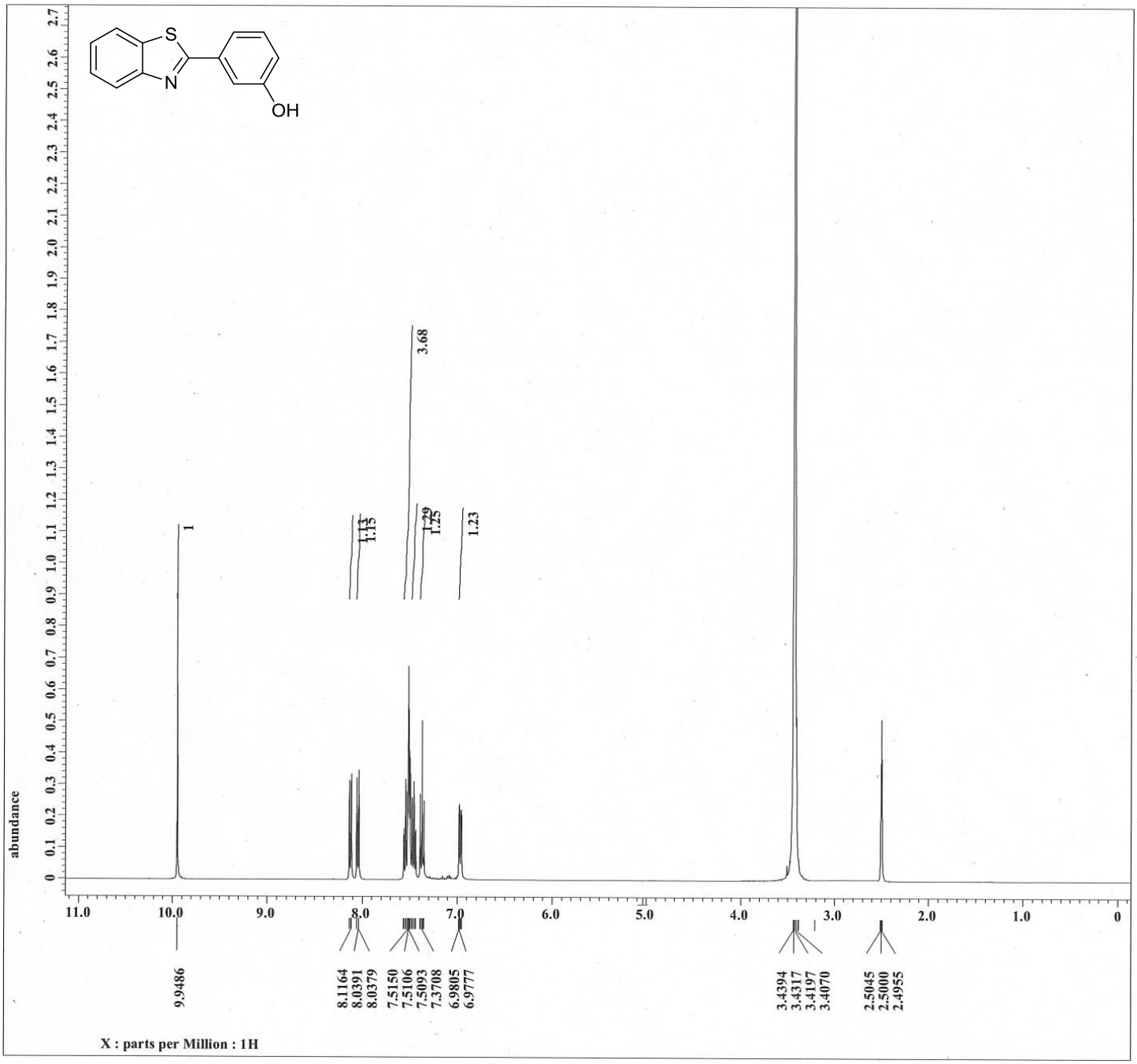

S
N
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
154.0945
153.2746
133.7668
126.2917
125.6720
123.7078
122.0011
77.4842
77.1600
76.8454
X : parts per Million : 13C

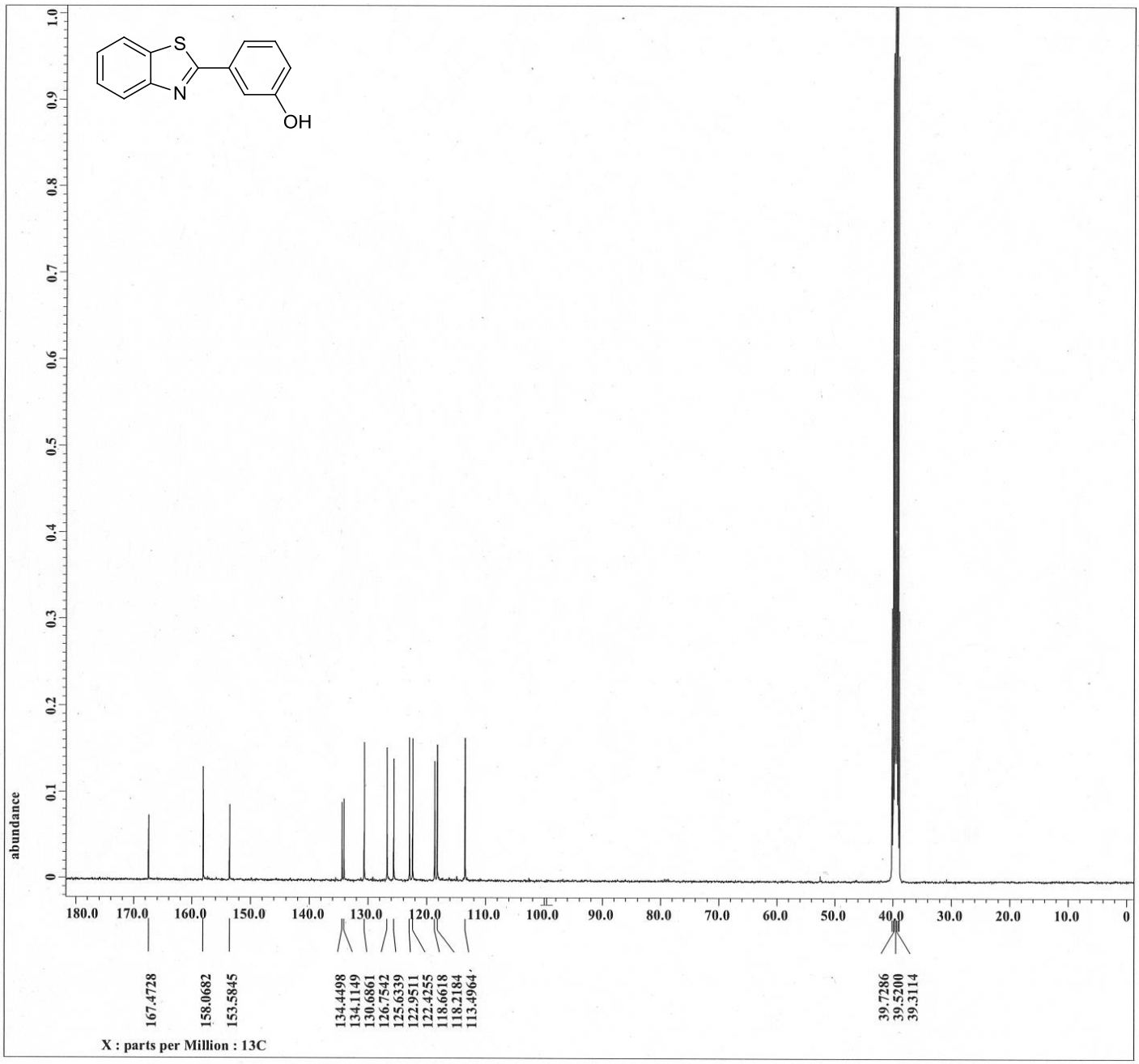

4.15
3.11
1
1.02
S
N
abundance
4.0
3.0
2.0
1.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.1019
8.0927
8.0910
8.0870
7.5098
7.5004
7.4973
7.4933
7.2600
1.6502
X : parts per Million : 1H

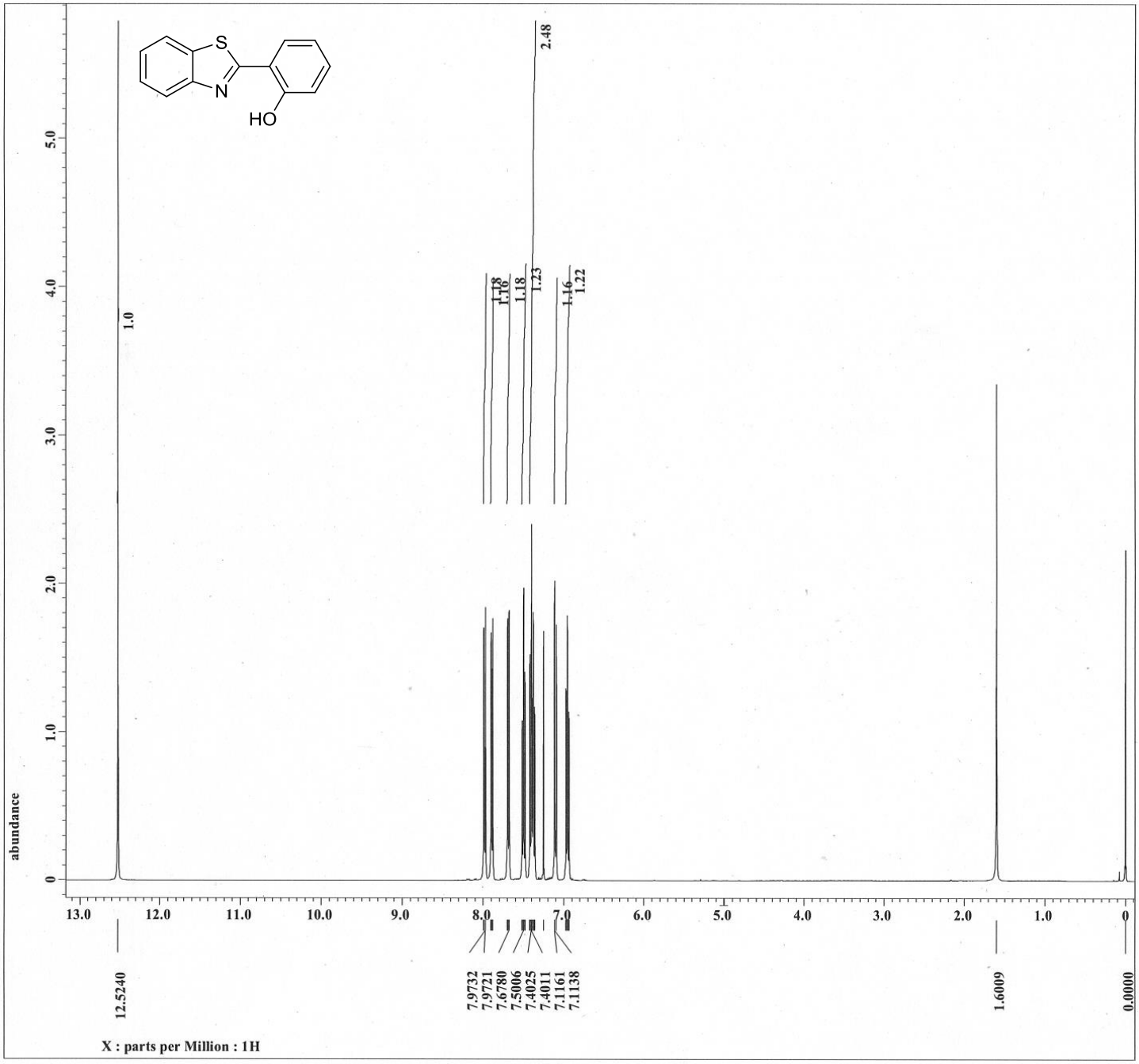

S
N
abundance
0
0.1
0.2
0.3
0.4
0.5
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.2474
154.2662
133.7466
131.1317
129.1783
127.7076
126.4752
125.3454
123.3705
121.7747
77.4782
77.1600
76.8418
X : parts per Million : 13C

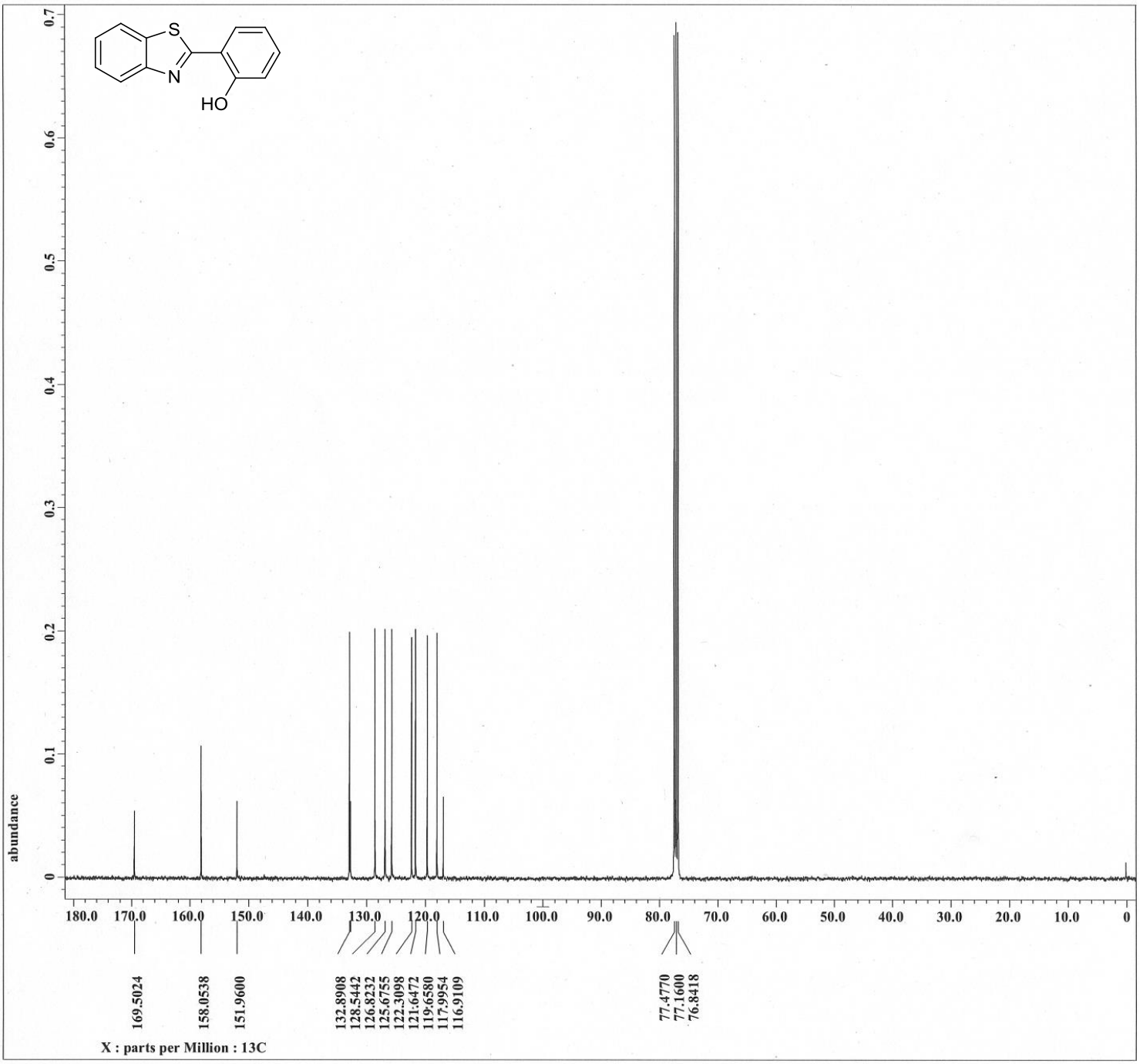

S
N
OH
abundance
X : parts per Million : 1H
10.2306
8.0901
8.0706
7.9866
7.9666
7.9442
7.9232
7.4993
7.3998
6.9442
6.9232
3.3566
2.5000

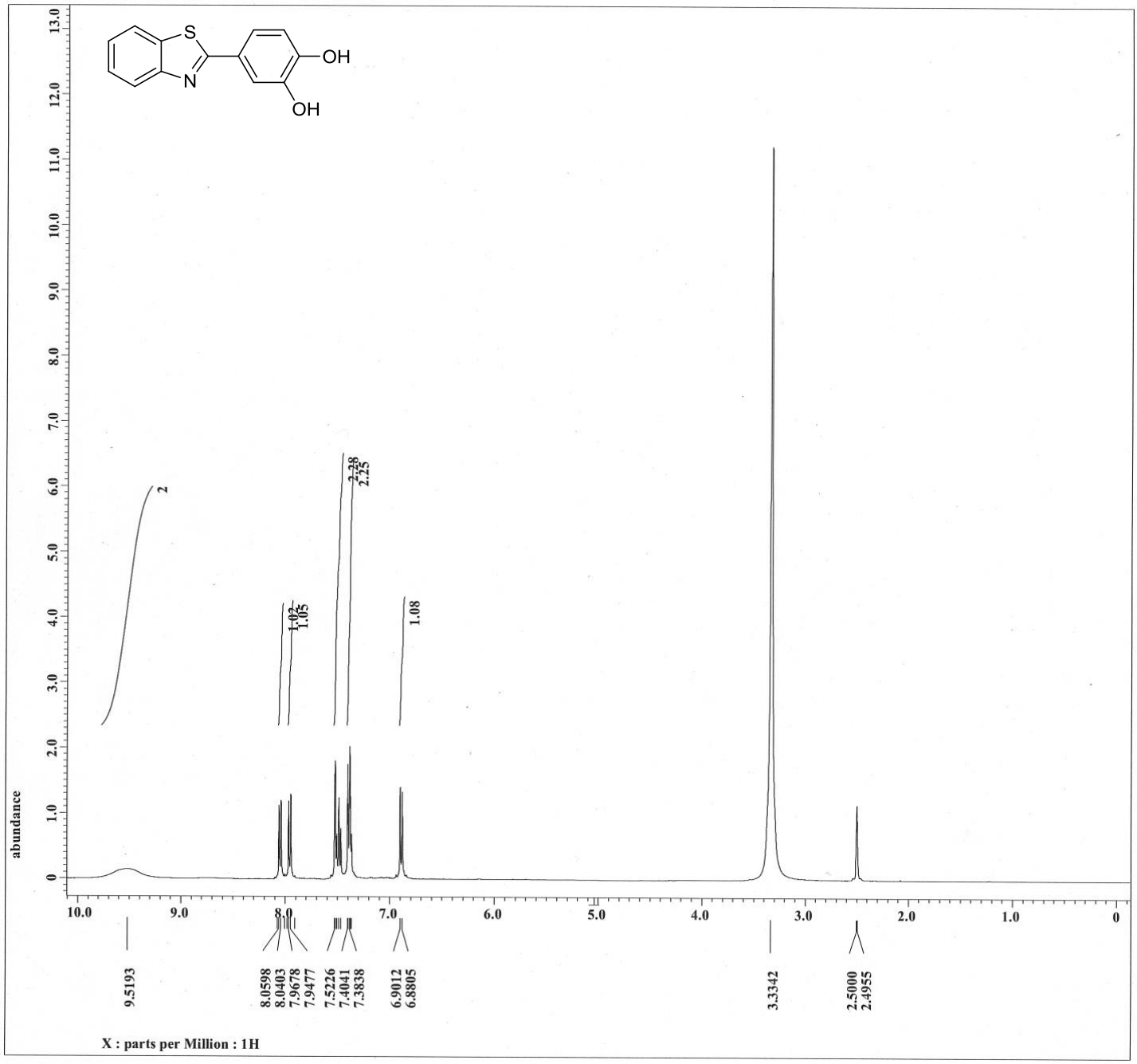

S
N
OH
abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
167.4847
160.5638
153.7442
134.1209
129.0807
126.4694
124.9415
124.0452
122.3242
122.1693
116.1172
39.7286
39.5200
39.3114
X : parts per Million : 13C

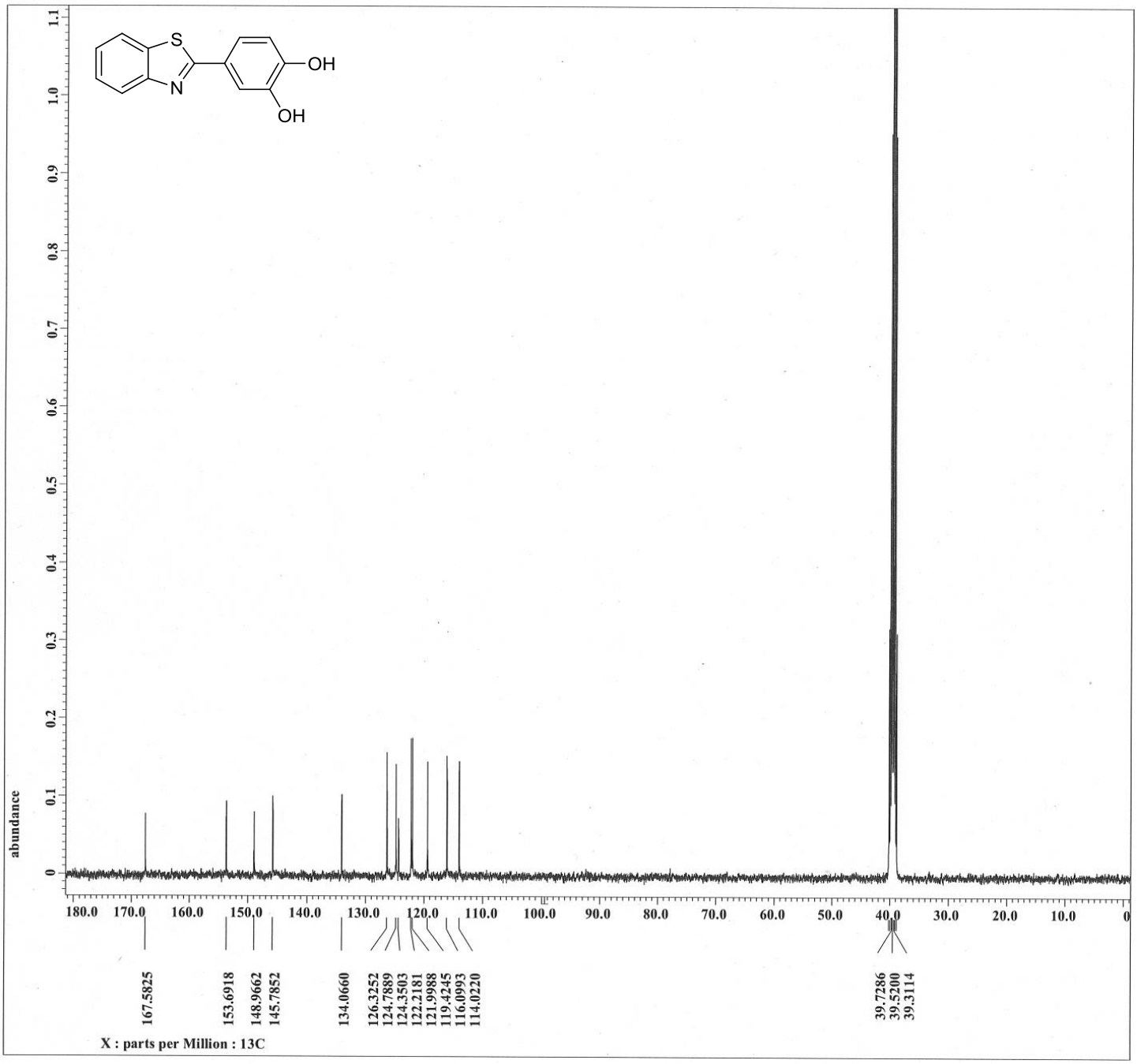

S
N
OH
abundance
3.68
1
1.13
1.15
1.29
1.25
1.23
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.9486
8.1164
8.0391
8.0379
7.5150
7.5106
7.5093
7.3708
6.9805
6.9777
3.4394
3.4317
3.4197
3.4070
2.5045
2.5000
2.4955
X : parts per Million : 1H

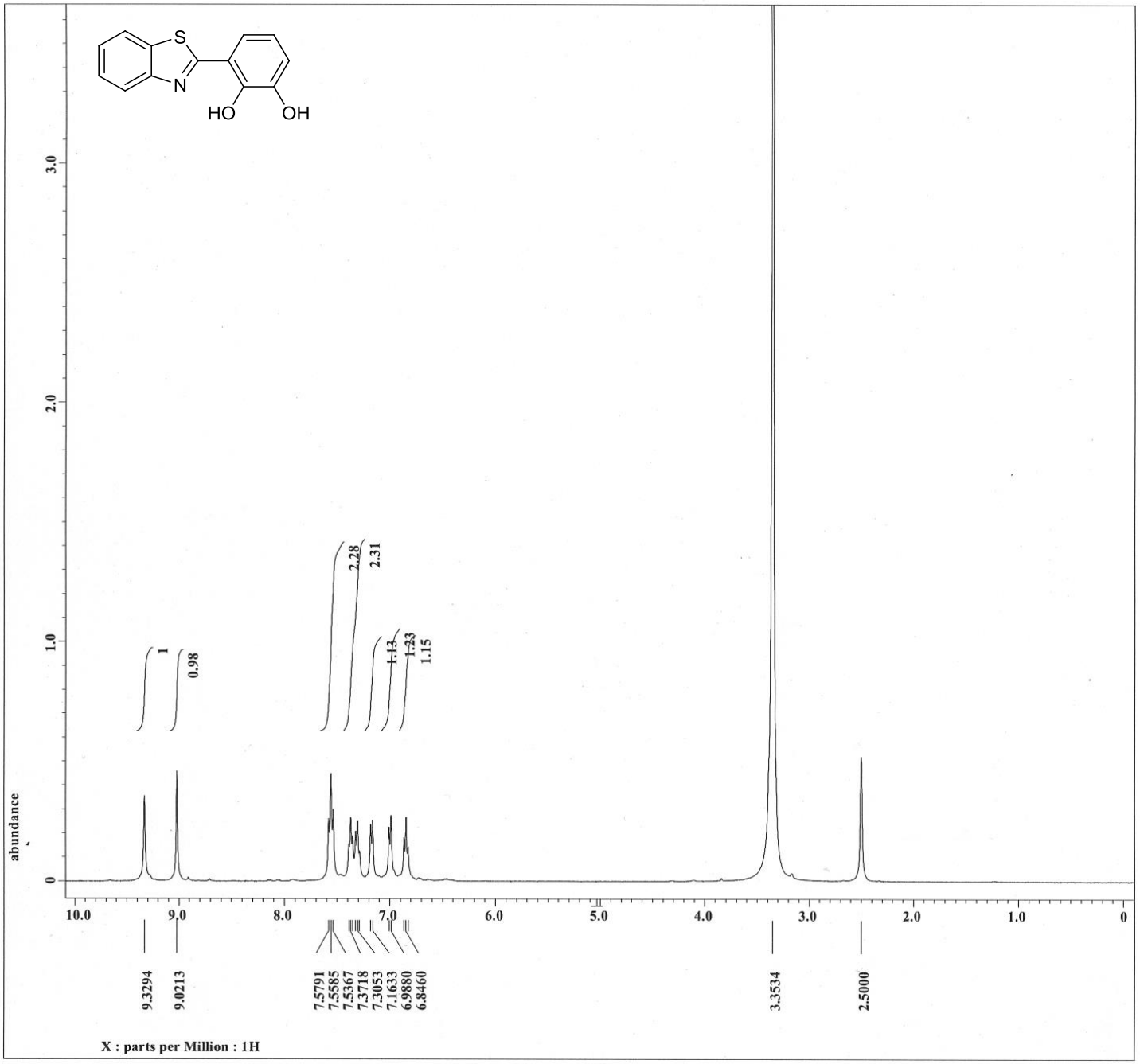

S
N
OH
abundance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.4728
158.0682
153.5845
134.4498
134.1149
130.6861
126.7542
125.6339
122.9511
122.4255
118.6618
118.2184
113.4964
39.7286
39.5200
39.3114
X : parts per Million : 13C


S
N
HO
2.48
1.0
1.18
1.16
1.18
1.23
1.16
1.22
abundance
5.0
4.0
3.0
2.0
1.0
0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
12.5240
7.9732
7.9721
7.6780
7.5006
7.4025
7.4011
7.1161
7.1138
1.6009
0.0000
X : parts per Million : 1H


S
N
HO
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
169.5024
158.0538
151.9600
132.8908
128.5442
126.8232
125.6755
122.3098
121.6472
119.6580
117.9954
116.9109
77.4770
77.1600
76.8418
X : parts per Million : 13C


S
N
OH
OH
abundance
2
2.28
2.25
1.02
1.05
1.08
9.5193
8.0598
8.0403
7.9678
7.9477
7.5226
7.4041
7.3838
6.9012
6.8805
3.3342
2.5000
2.4955
X : parts per Million : 1H


S
N
OH
OH
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
167.5825
153.6918
148.9662
145.7852
134.0660
126.3252
124.7889
124.3503
122.2181
121.9988
119.4245
116.0993
114.0220
39.7286
39.5200
39.3114
X : parts per Million : 13C


S
N
HO
OH
abundance
3.0
2.0
1.0
0
1
0.98
2.28
2.31
1.13
1.23
1.15
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.3294
9.0213
7.5791
7.5585
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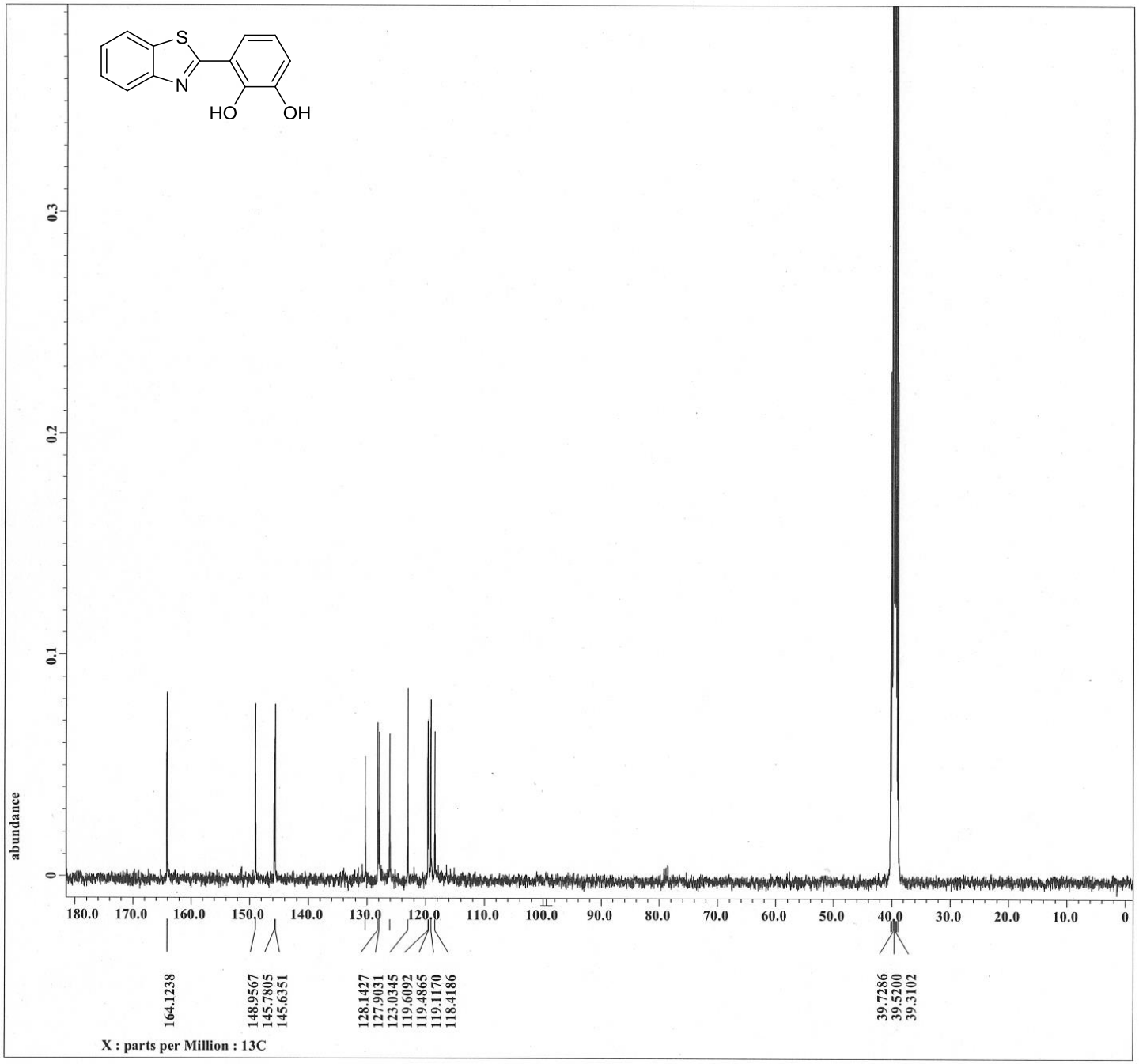
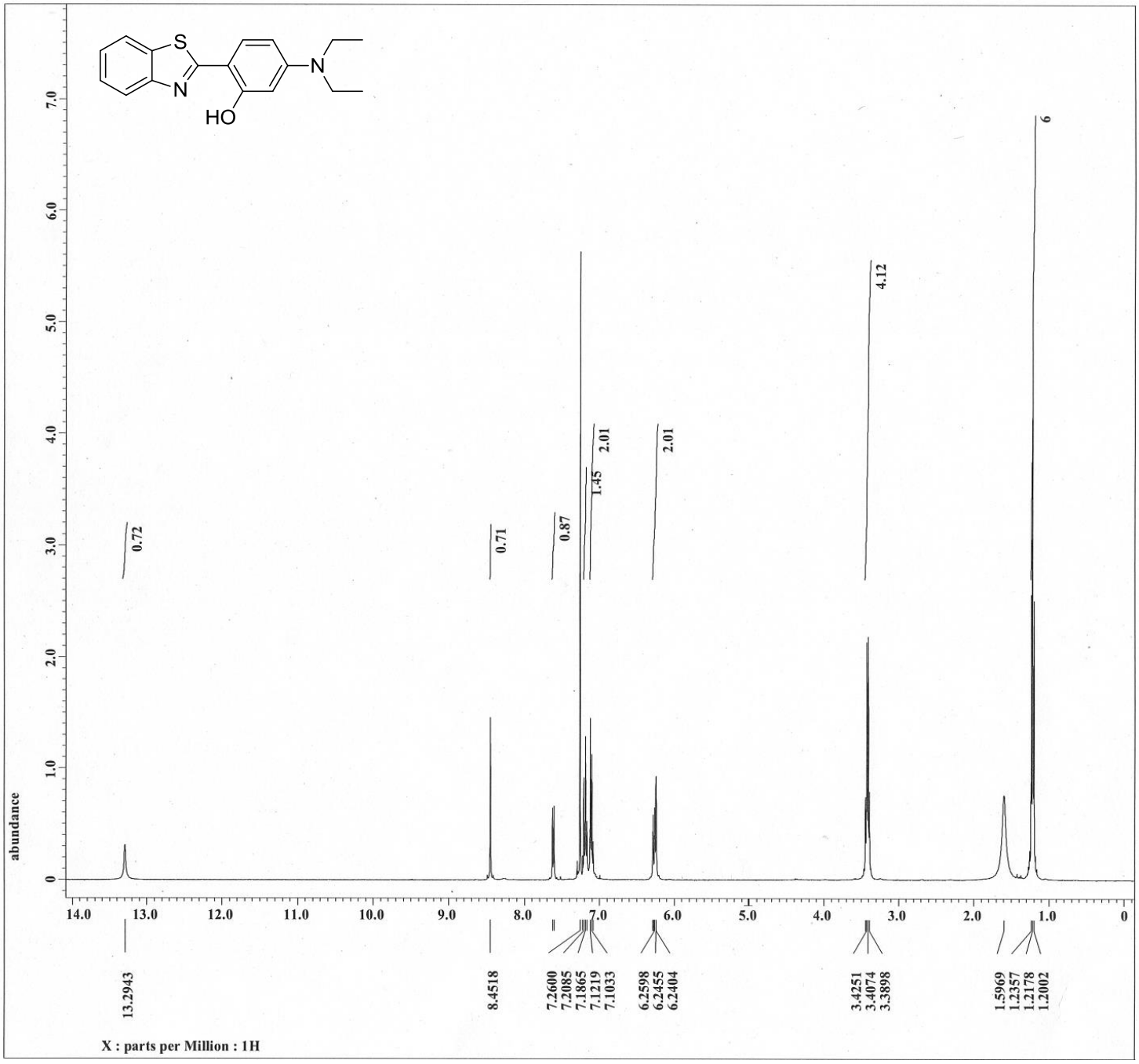
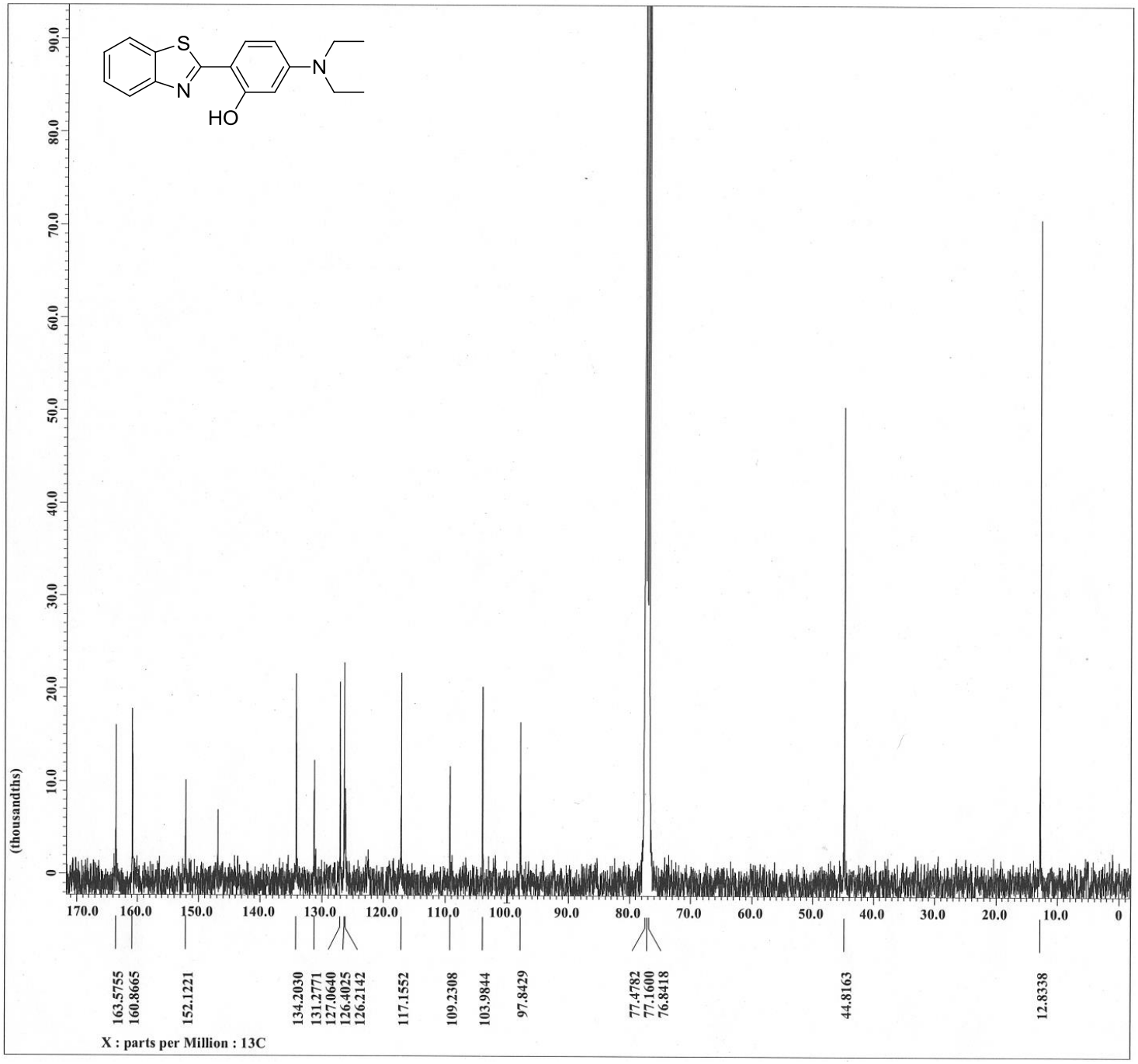
7.3053
7.1633
6.9880
6.8460
3.3534
2.5000
X : parts per Million : 1H


S
N
HO
OH
abundance
0
0.1
0.2
0.3
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
164.1238
148.9567
145.7805
145.6351
128.1427
127.9031
123.0345
119.6092
119.4865
119.1170
118.4186
39.7286
39.5200
39.3102
X : parts per Million : 13C


S
N
N
HO
abundance
0.72
0.71
0.87
1.45
2.01
2.01
4.12
6
13.2943
8.4518
7.2600
7.2085
7.1865
7.1219
7.1033
6.2598
6.2455
6.2404
3.4251
3.4074
3.3898
1.5969
1.2357
1.2178
1.2002
X : parts per Million : 1H


S
N
N
HO
(thousandths)
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
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134.2030
131.2771
127.0640
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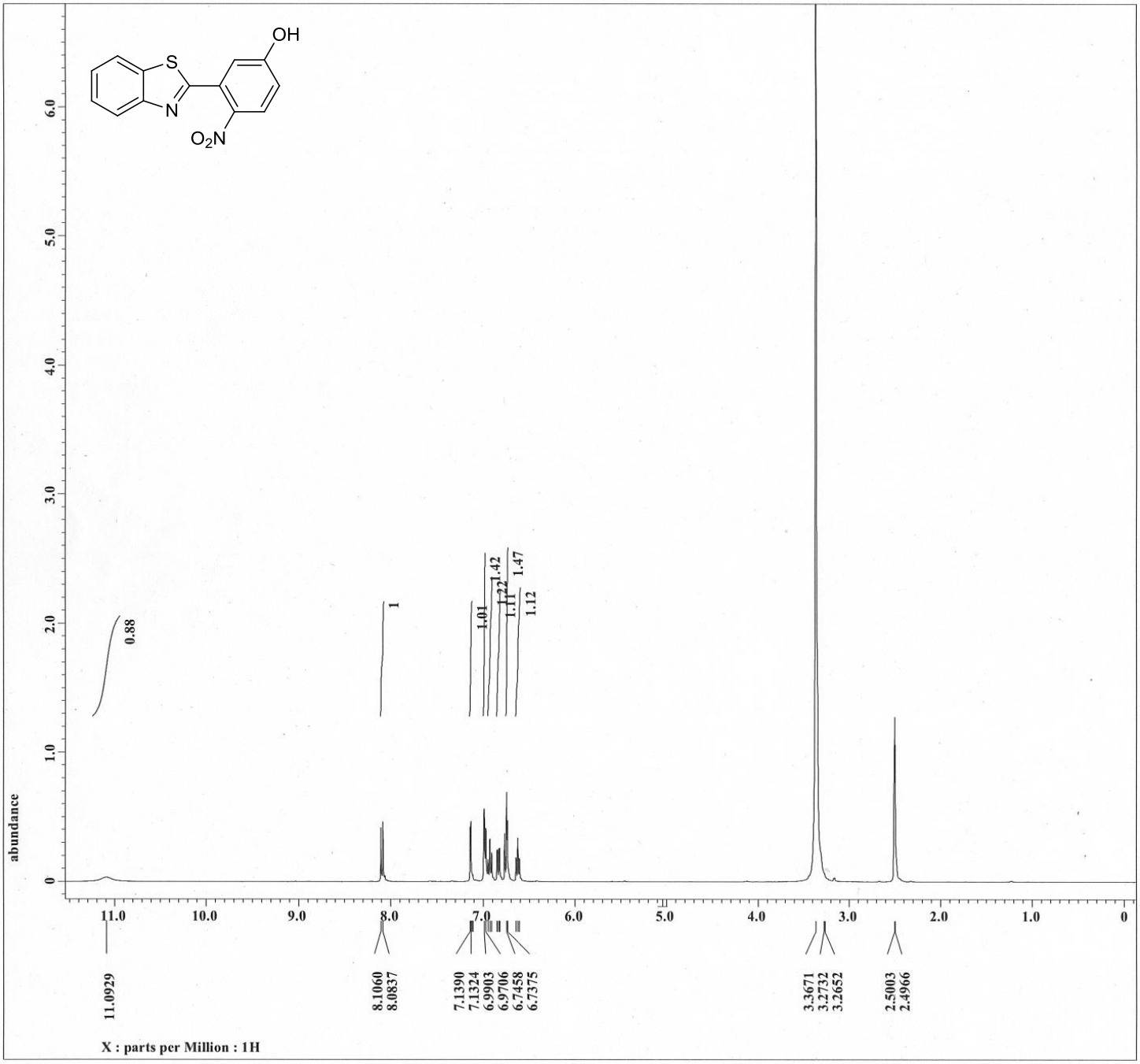
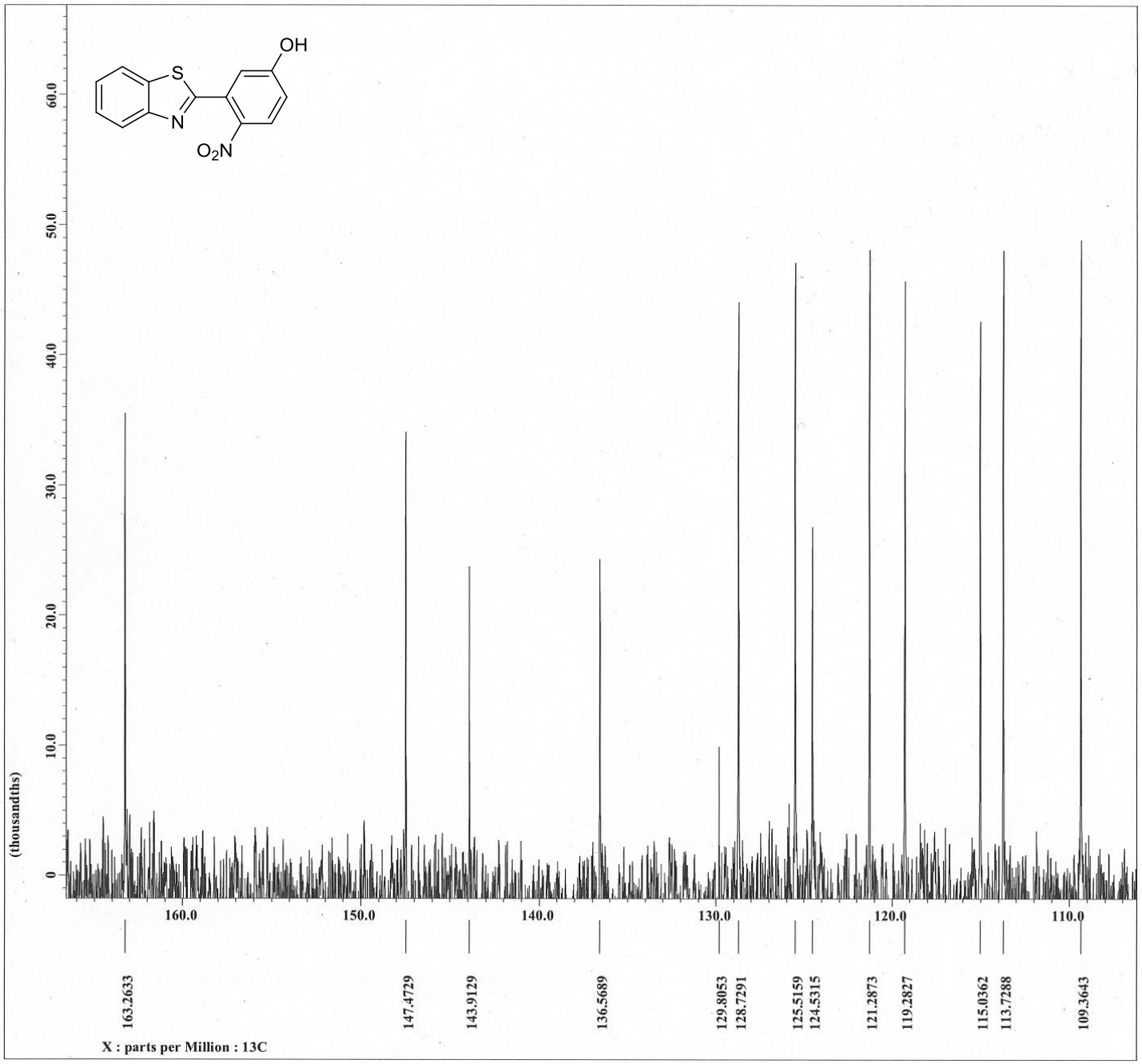
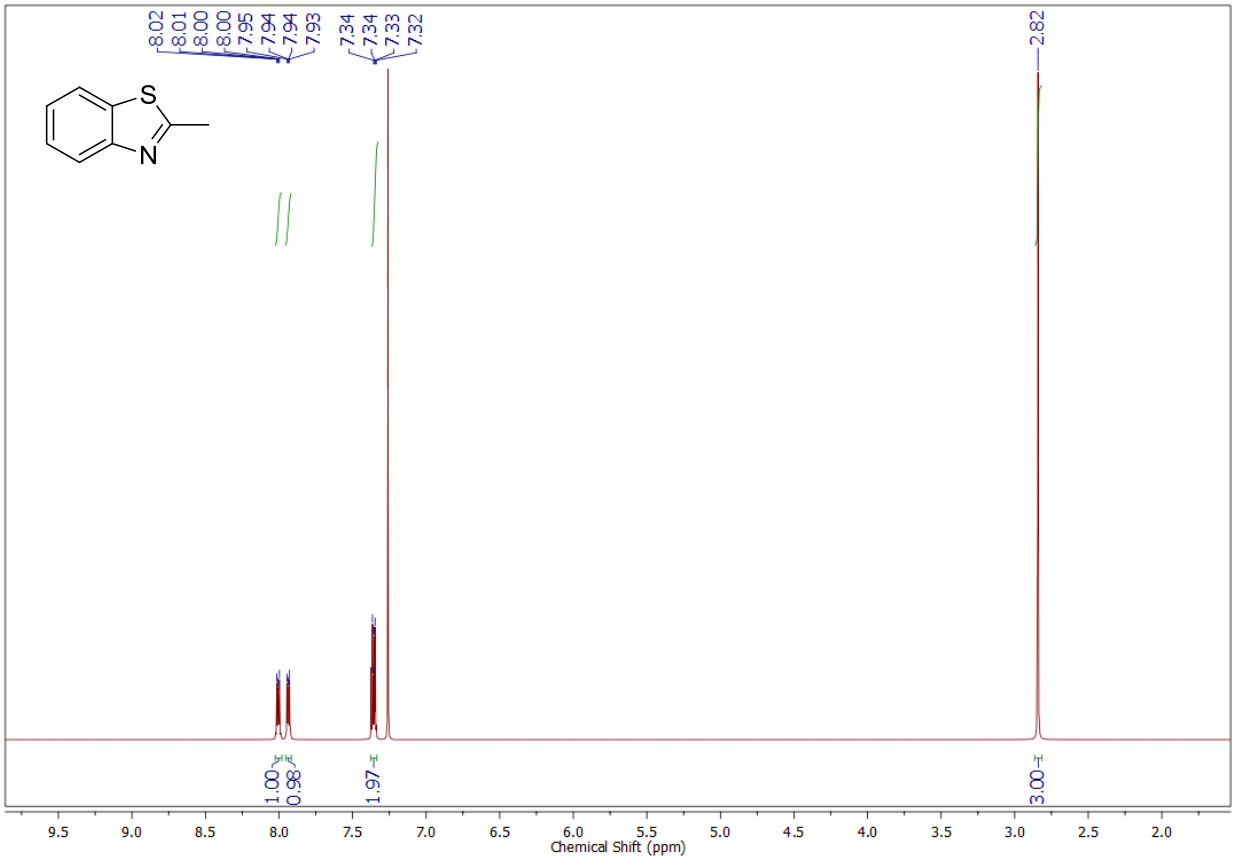
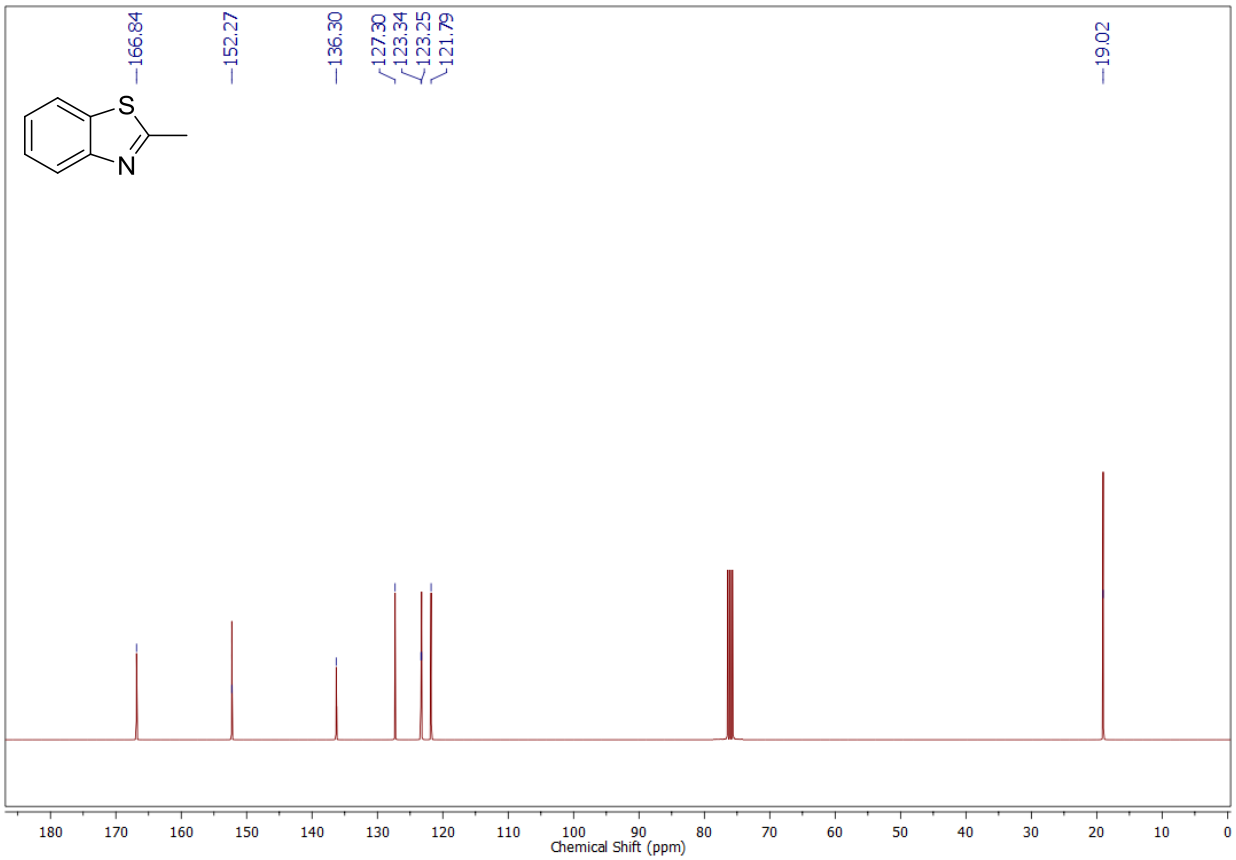
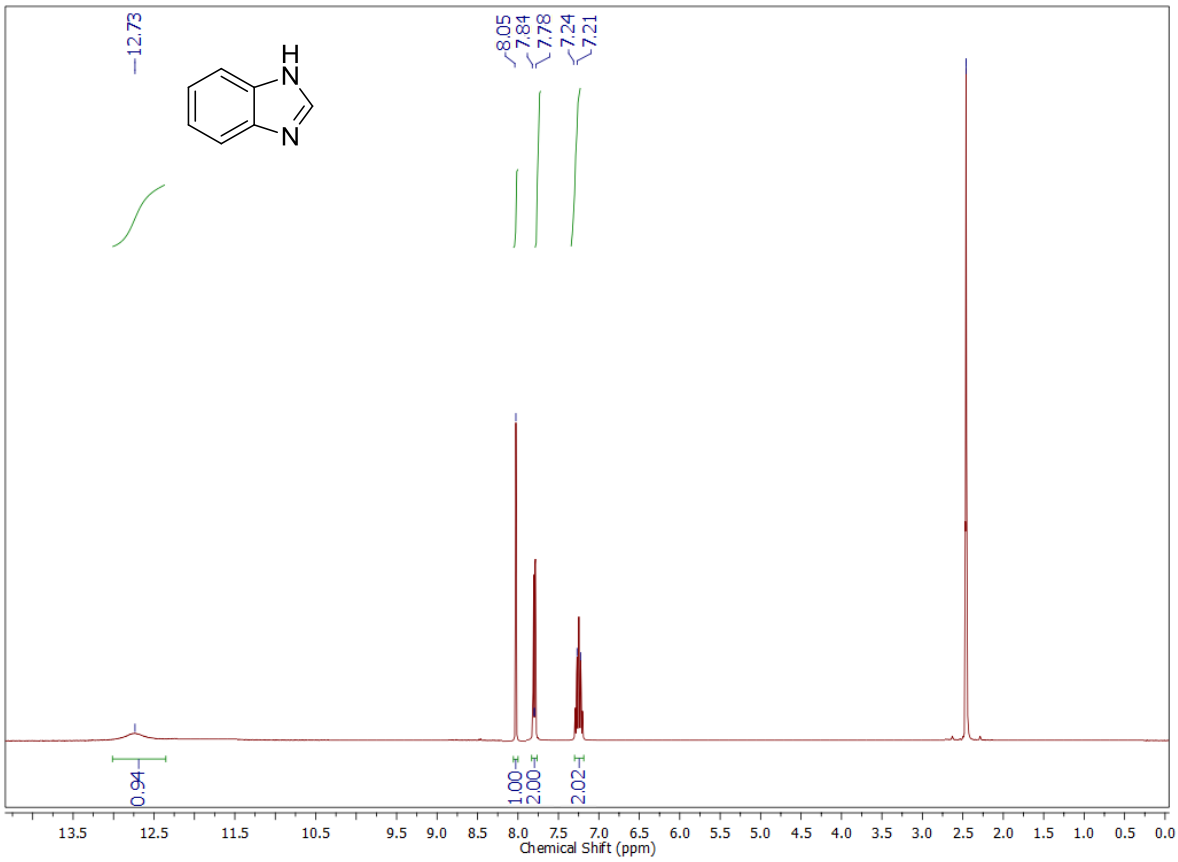
126.2142
117.1552
109.2308
103.9844
97.8429
77.4782
77.1600
76.8418
44.8163
12.8338
X : parts per Million : 13C

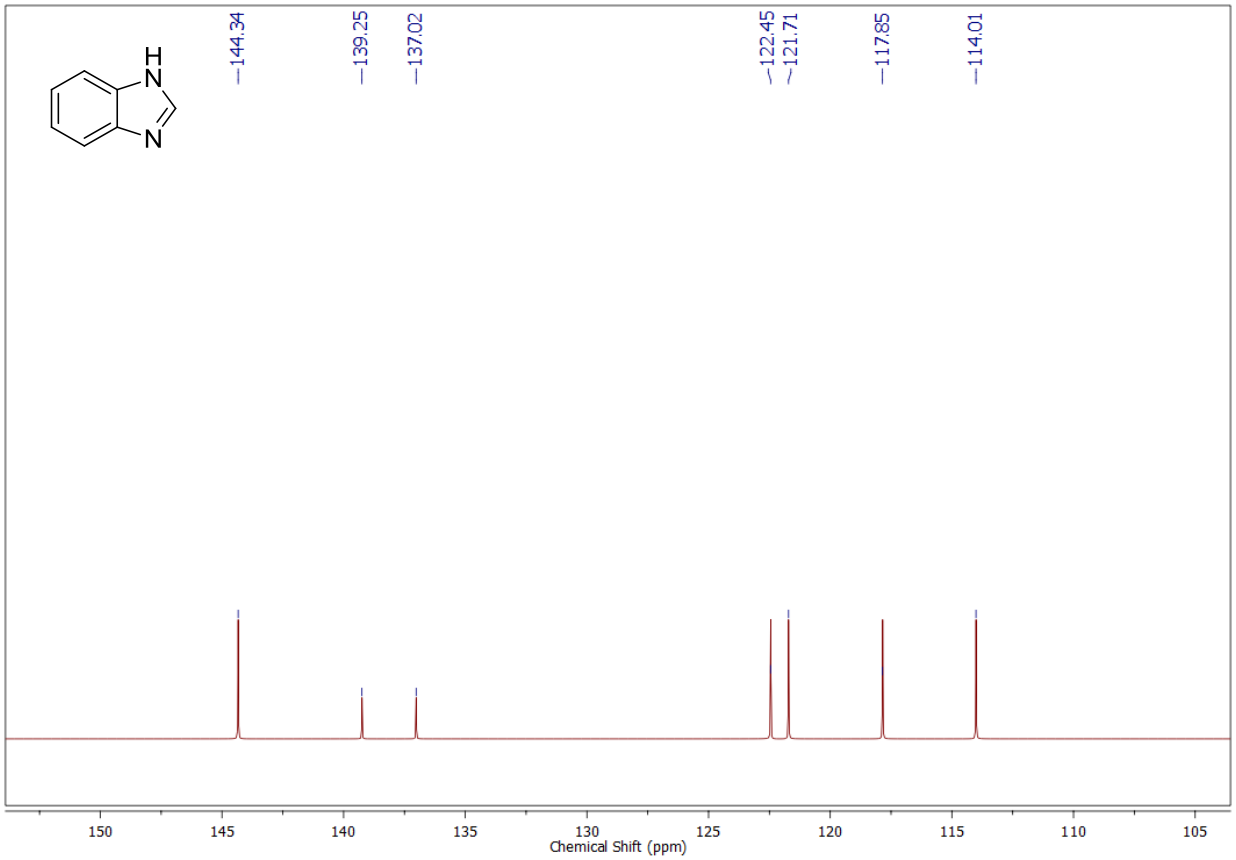

OH
S
N
O_2N
abundance
0.88
1
1.01
1.42
1.22
1.11
1.47
1.12
11.0929
8.1060
8.0837
7.1390
7.1324
6.9903
6.9706
6.7458
6.7375
3.3671
3.2732
3.2652
2.5003
2.4966
X : parts per Million : 1H

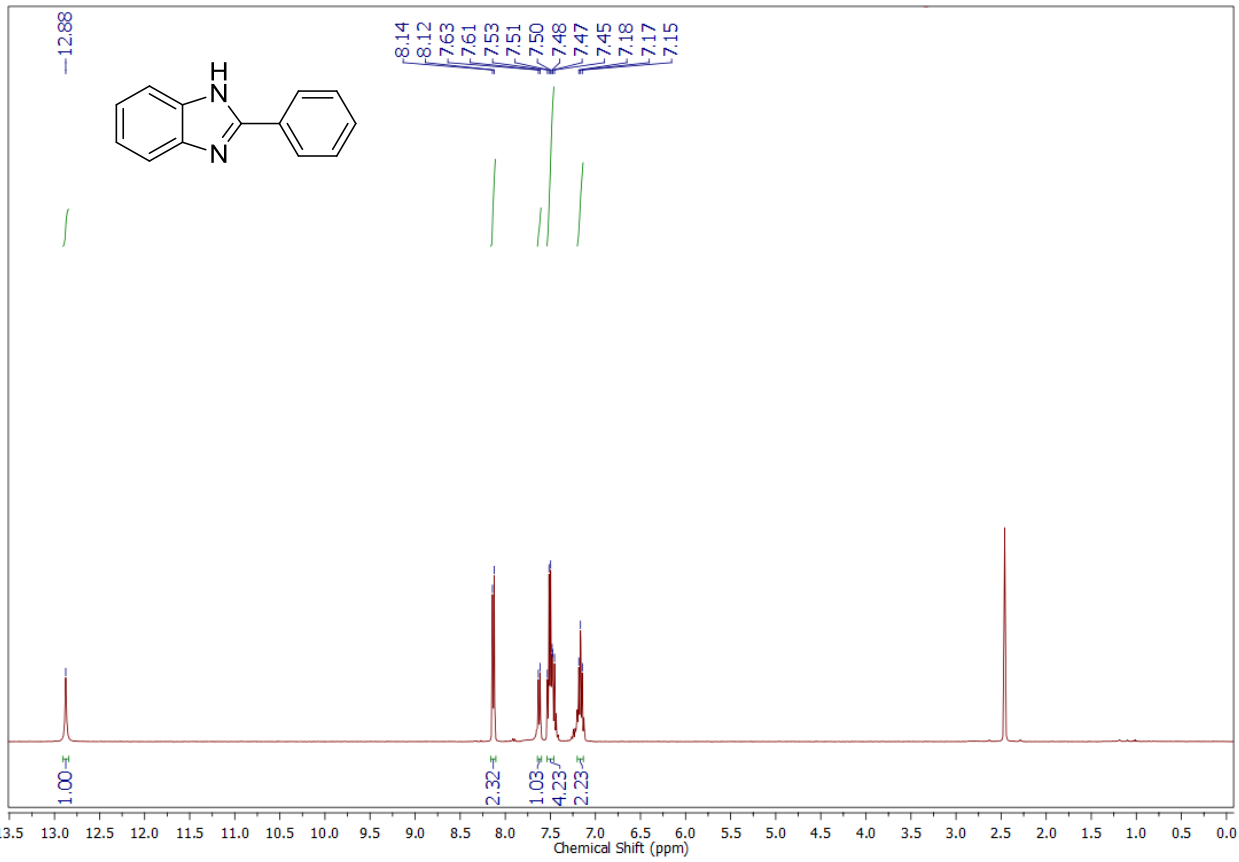

OH
S
N
O2N
60.0
50.0
40.0
30.0
20.0
10.0
0
(thousandths)
160.0
150.0
140.0
130.0
120.0
110.0
163.2633
147.4729
143.9129
136.5689
129.8053
128.7291
125.5159
124.5315
121.2873
119.2827
115.0362
113.7288
109.3643
X : parts per Million : 13C

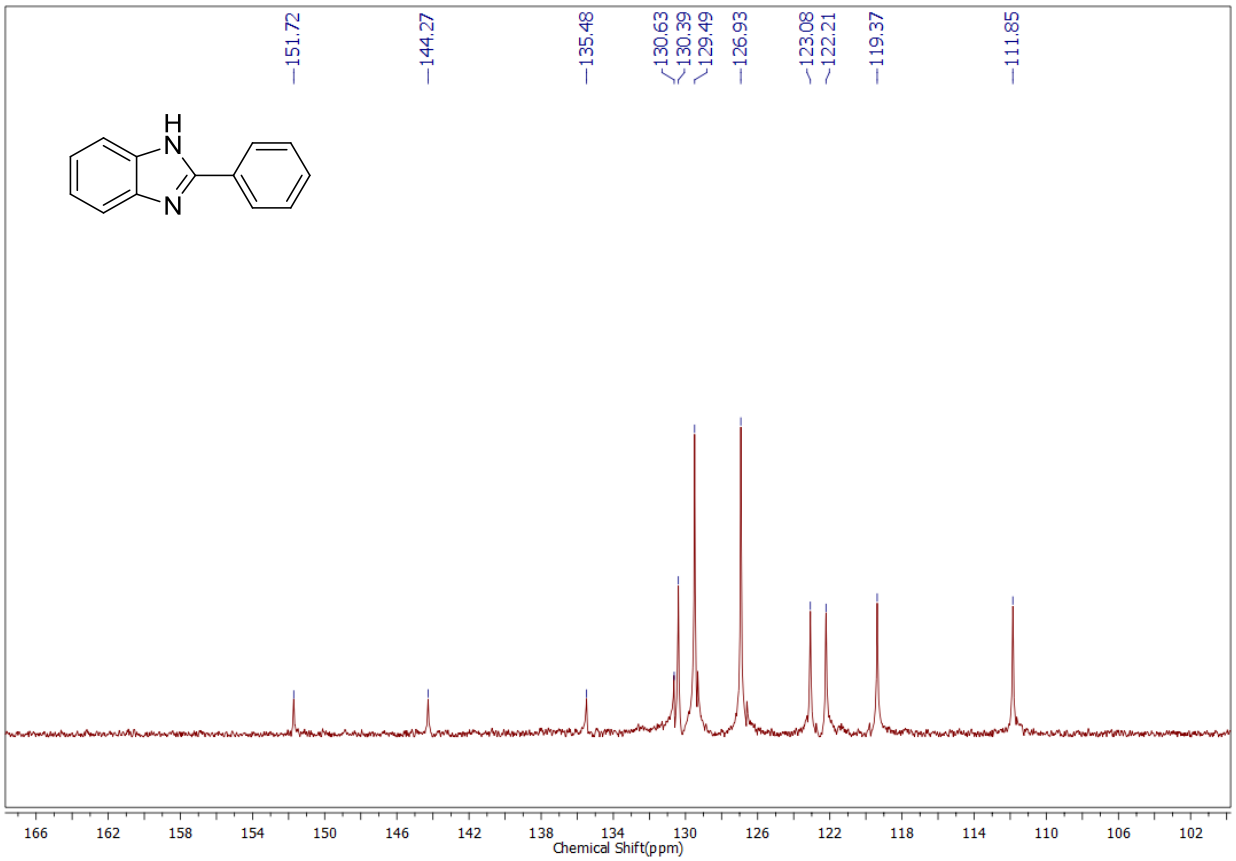

8.02
8.01
8.00
8.00
7.95
7.94
7.94
7.93
7.34
7.34
7.33
7.32
2.82
S
N
1.00
0.98
1.97
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
Chemical Shift (ppm)

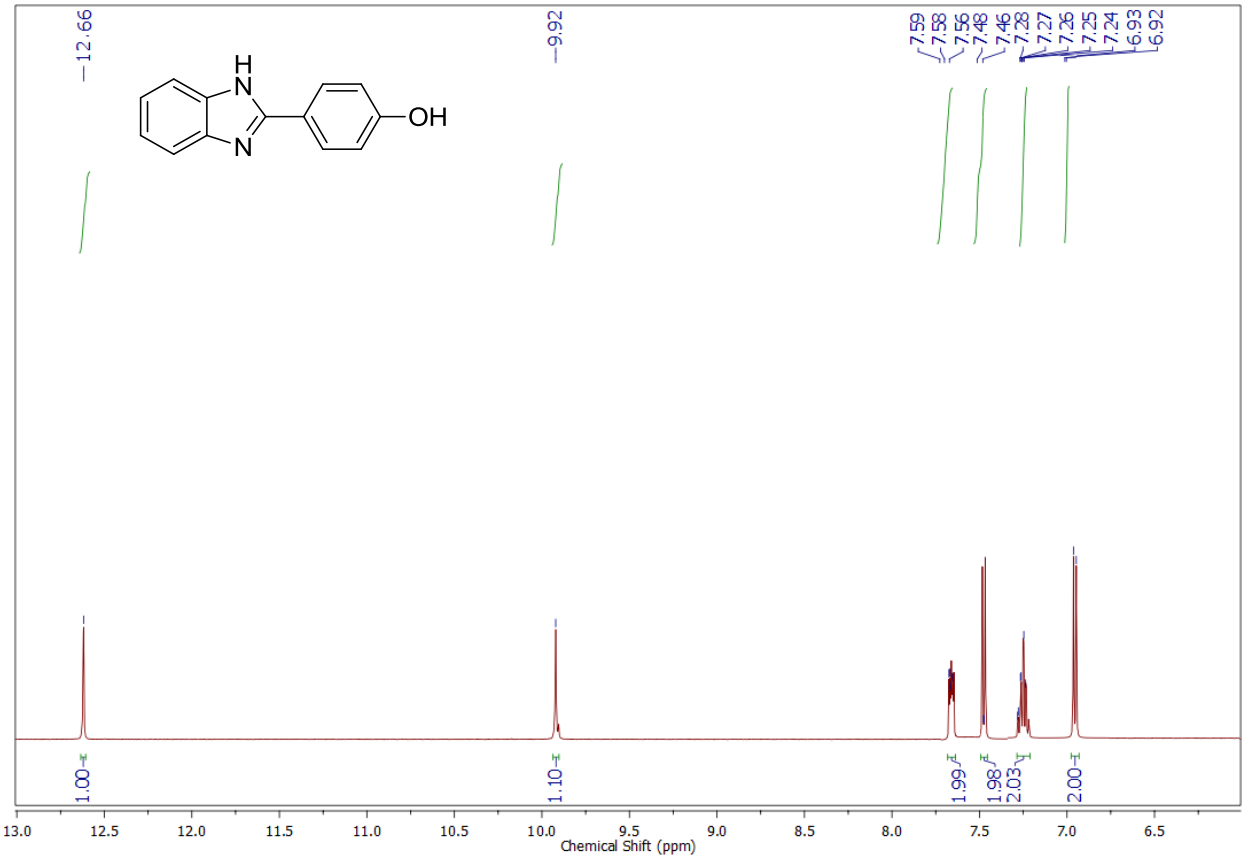

166.84
152.27
136.30
127.30
123.34
123.25
121.79
19.02
S
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

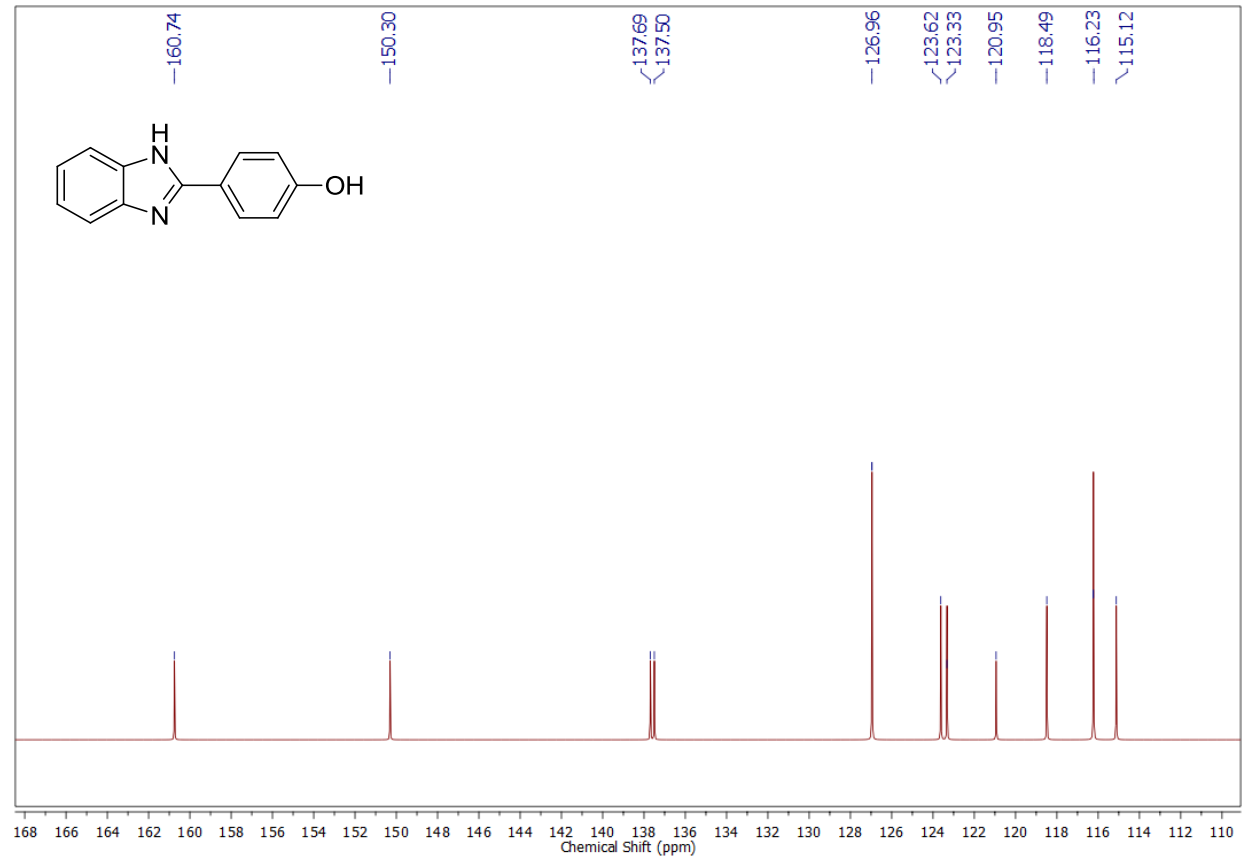

12.73
8.05
7.84
7.78
7.24
7.21
0.94
1.00
2.00
2.02
Chemical Shift (ppm)

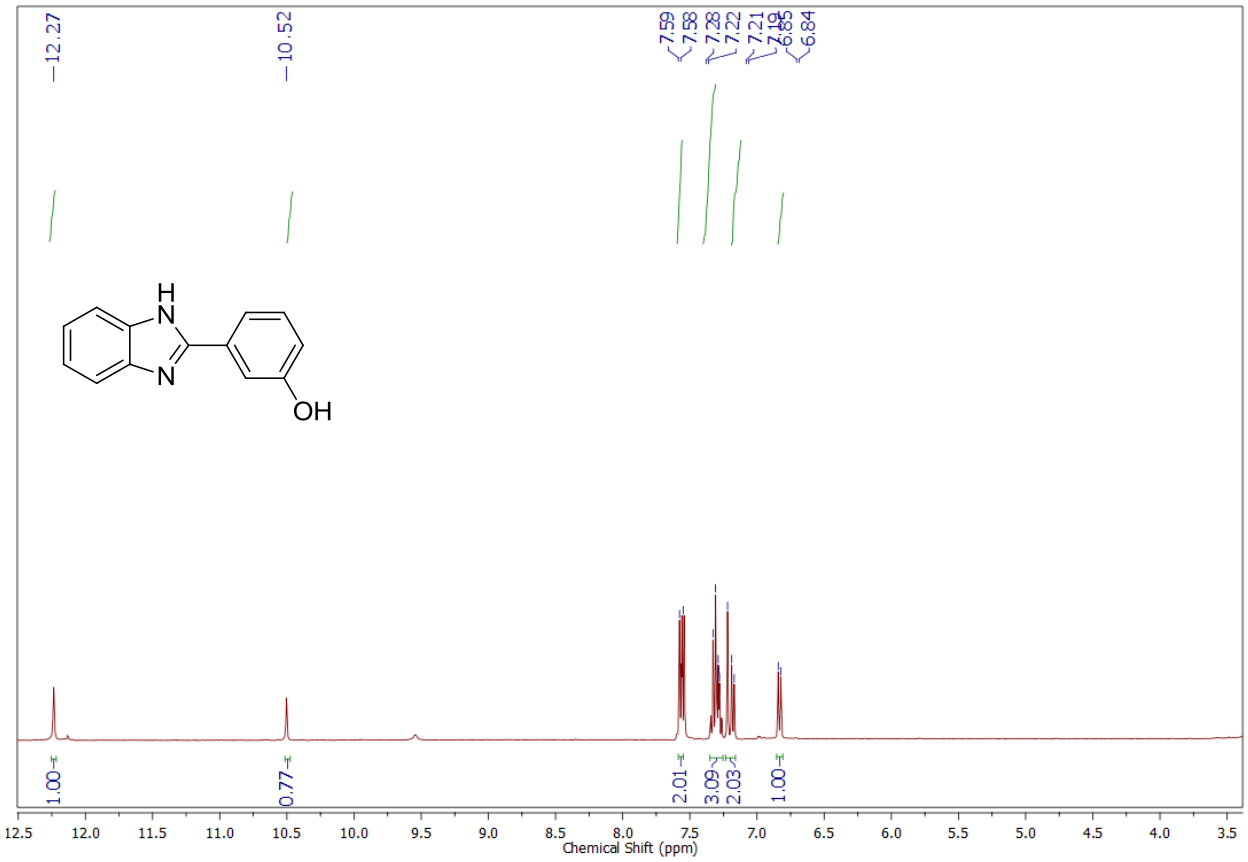

144.34
139.25
137.02
122.45
121.71
117.85
114.01
Chemical Shift (ppm)

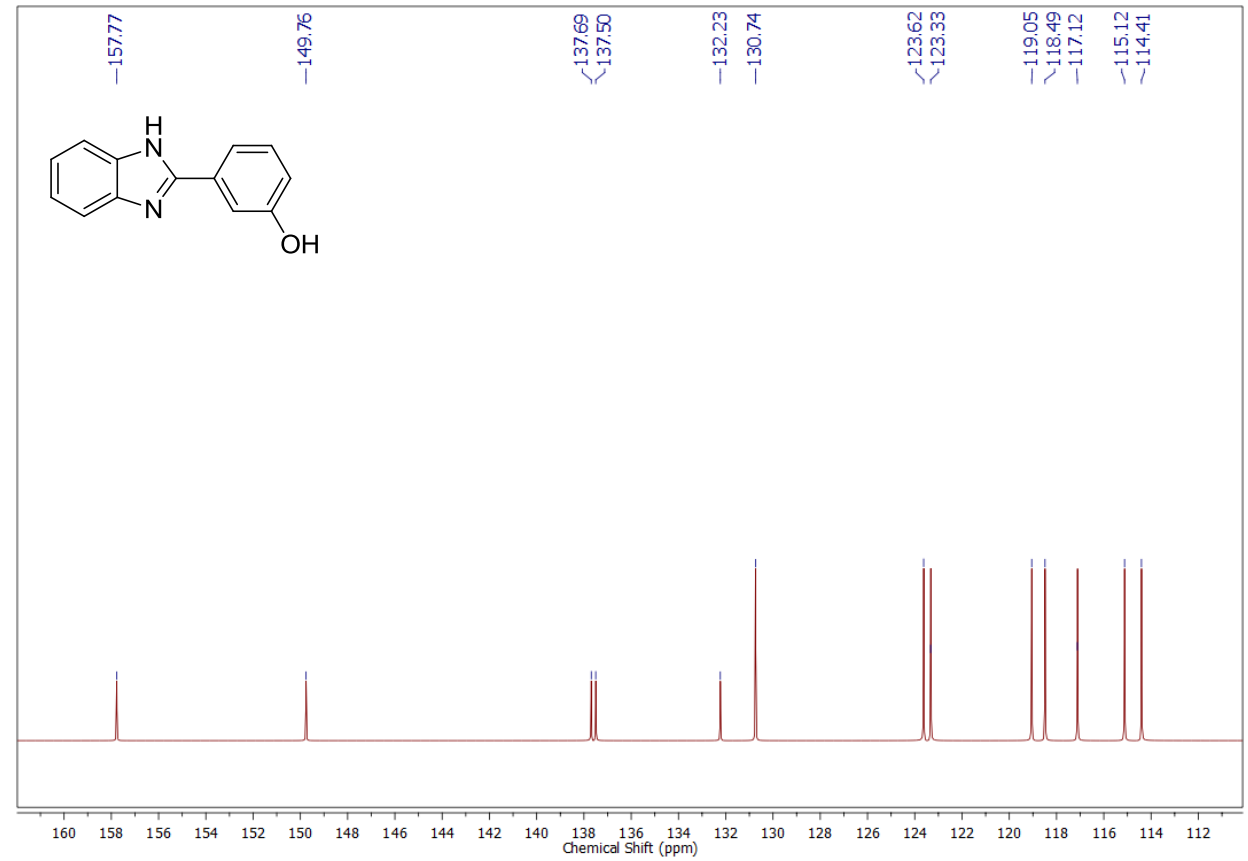

12.88
8.14
8.12
7.63
7.61
7.53
7.51
7.50
7.48
7.47
7.45
7.18
7.17
7.15
1.00
2.32
1.03
4.23
2.23
Chemical Shift (ppm)

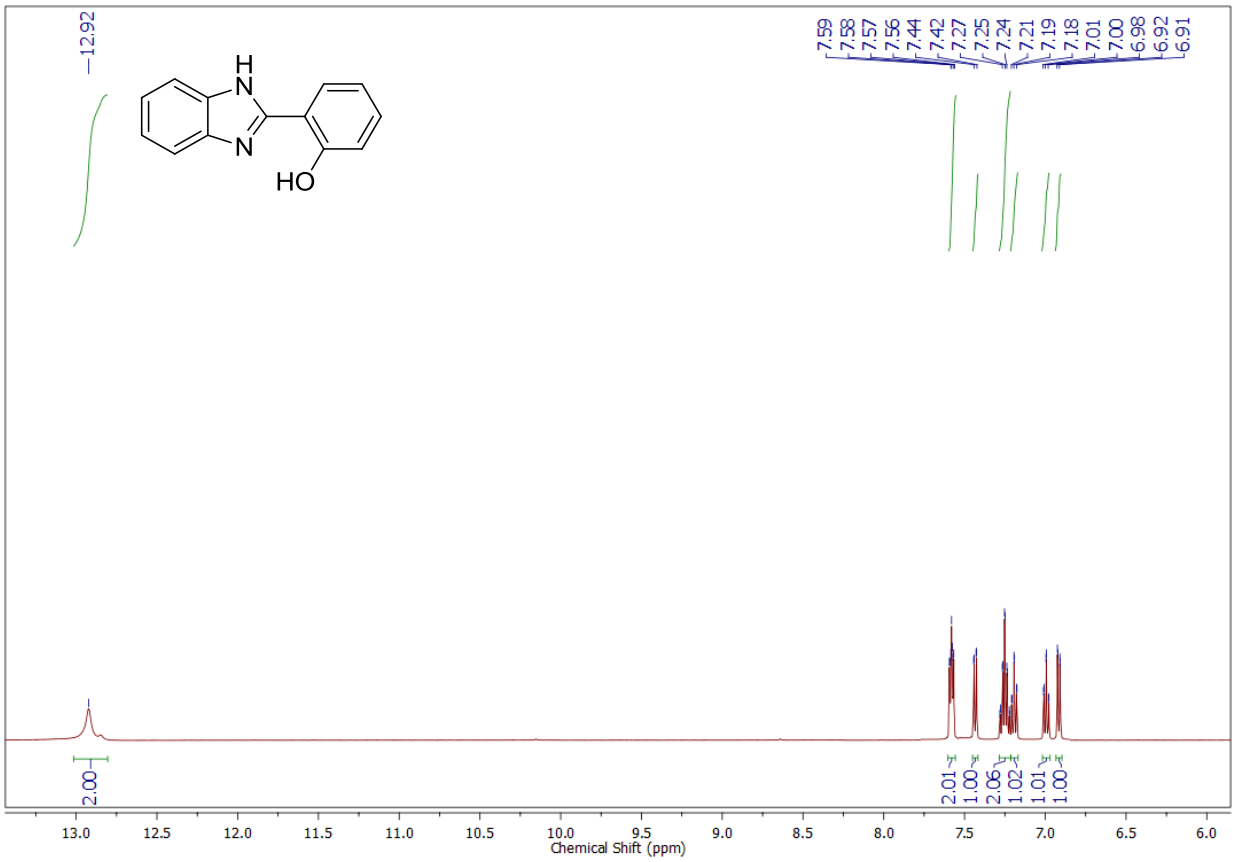

151.72
144.27
135.48
130.63
130.39
129.49
126.93
123.08
122.21
119.37
111.85
Chemical Shift(ppm)

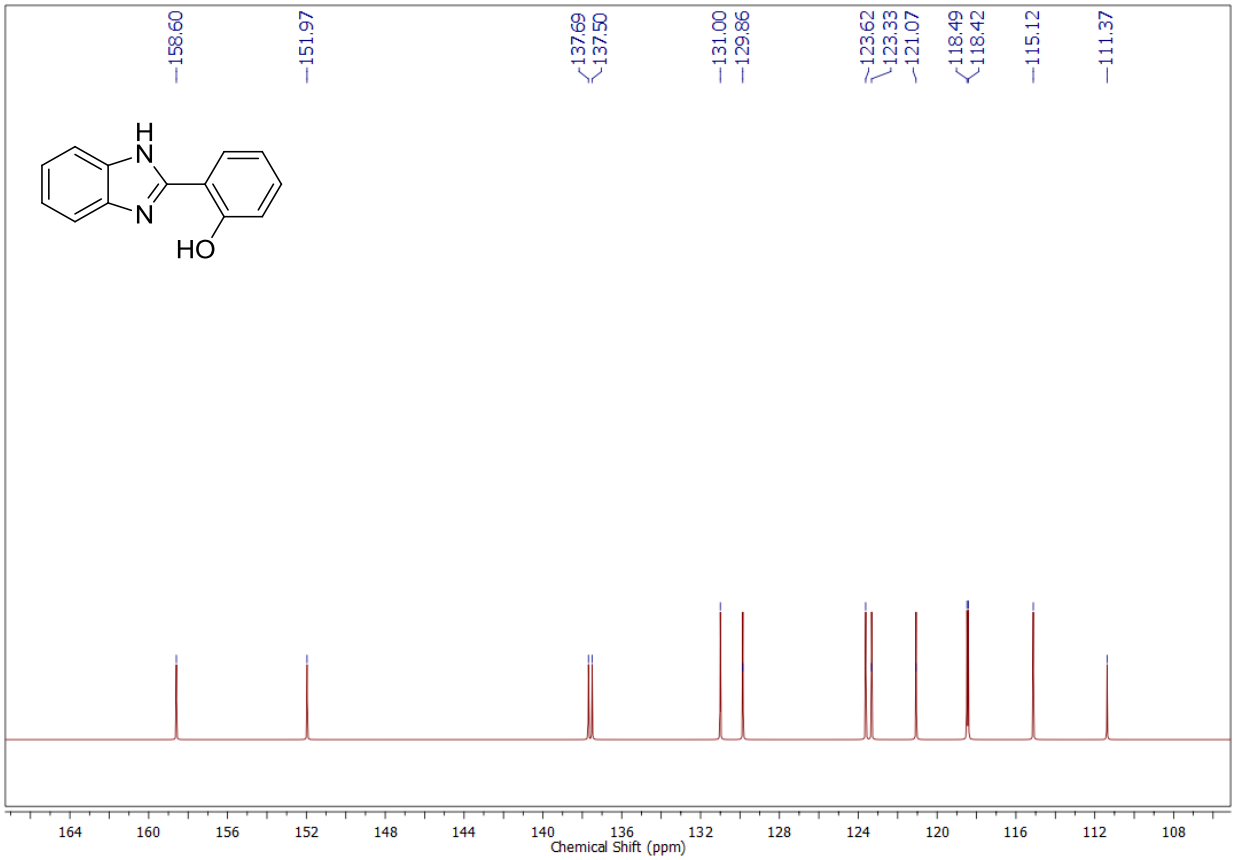

12.66
9.92
7.59
7.58
7.56
7.48
7.46
7.28
7.27
7.26
7.25
7.24
6.93
6.92
OH
1.00
1.10
1.99
1.98
2.03
2.00
Chemical Shift (ppm)

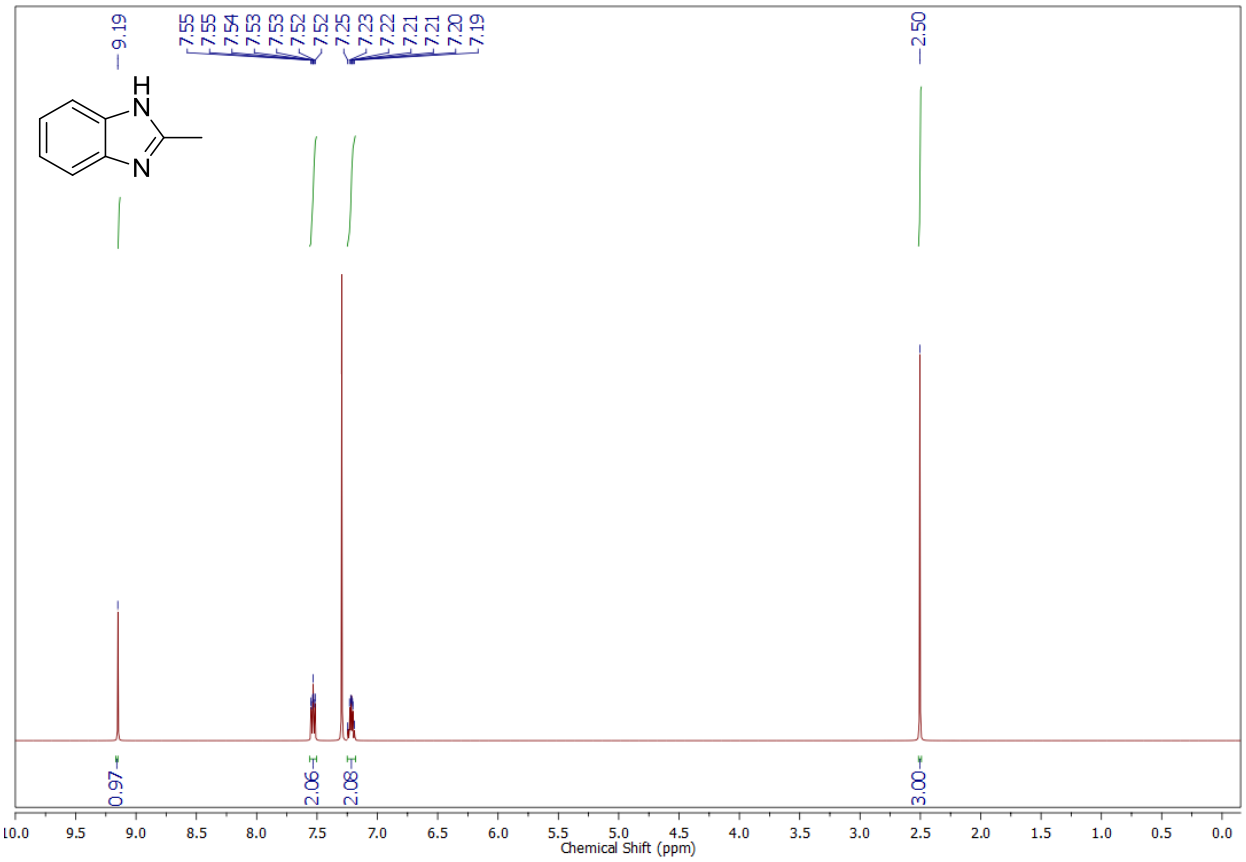

160.74
150.30
137.69
137.50
126.96
123.62
123.33
120.95
118.49
116.23
115.12
OH
Chemical Shift (ppm)

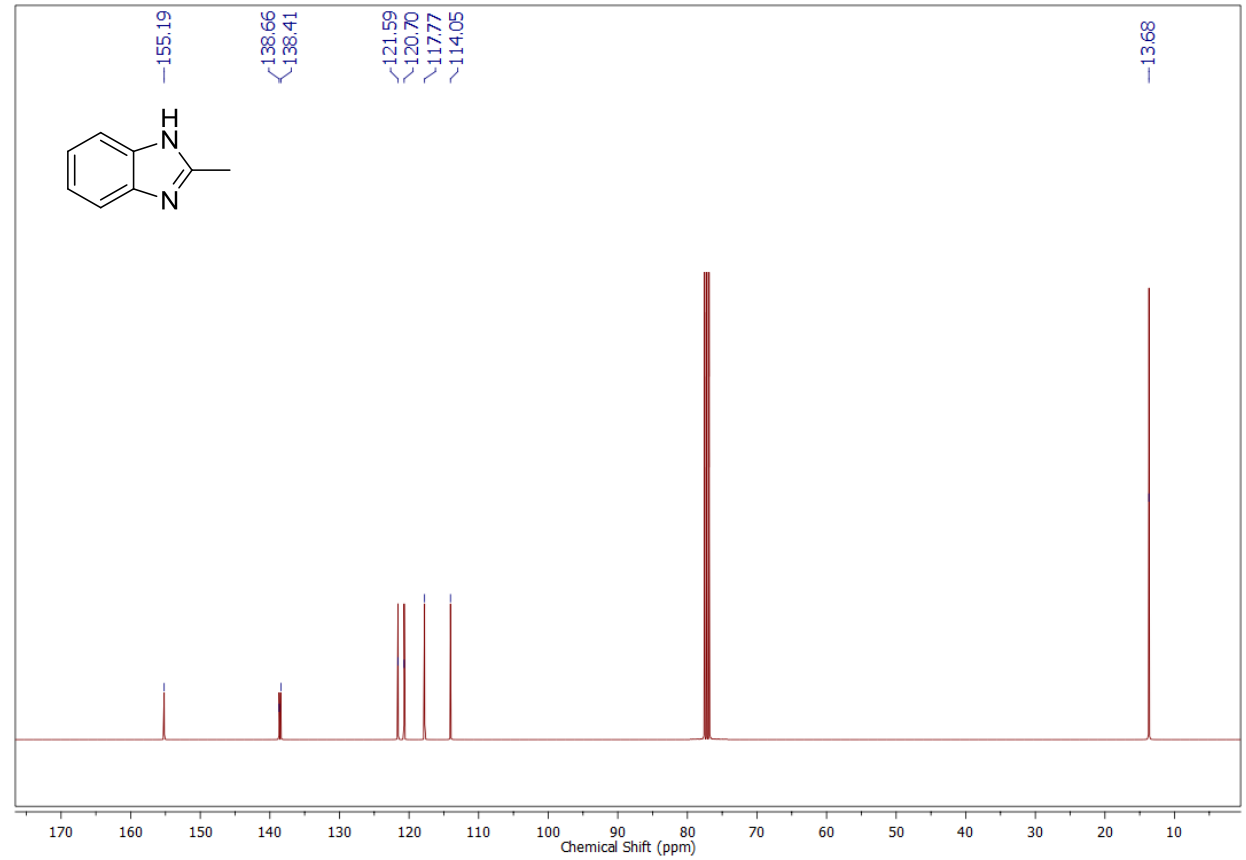

12.27
10.52
7.59
7.58
7.28
7.22
7.21
7.19
6.85
6.84
H
N
N
OH
1.00
0.77
2.01
3.09
2.03
1.00
Chemical Shift (ppm)

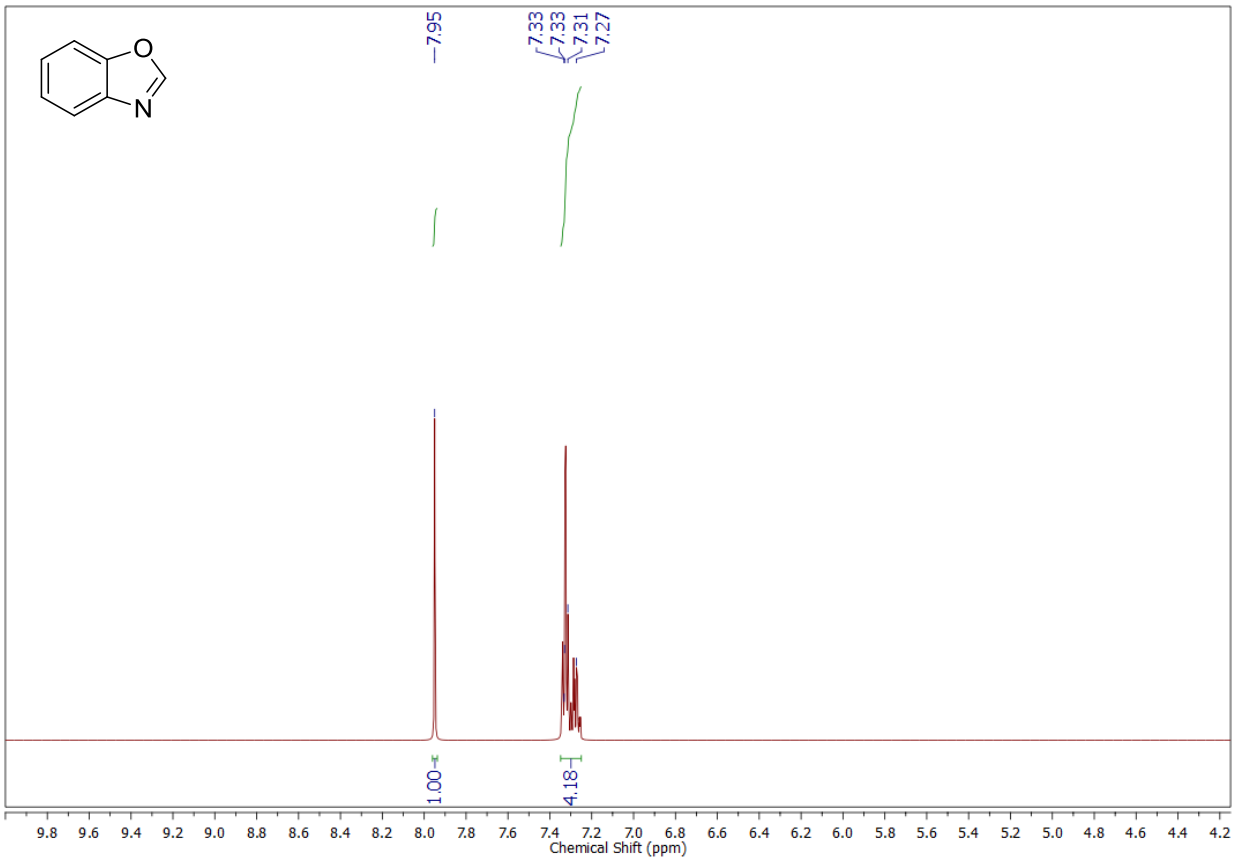

157.77
149.76
137.69
137.50
132.23
130.74
123.62
123.33
119.05
118.49
117.12
115.12
114.41
H
N
N
OH
Chemical Shift (ppm)

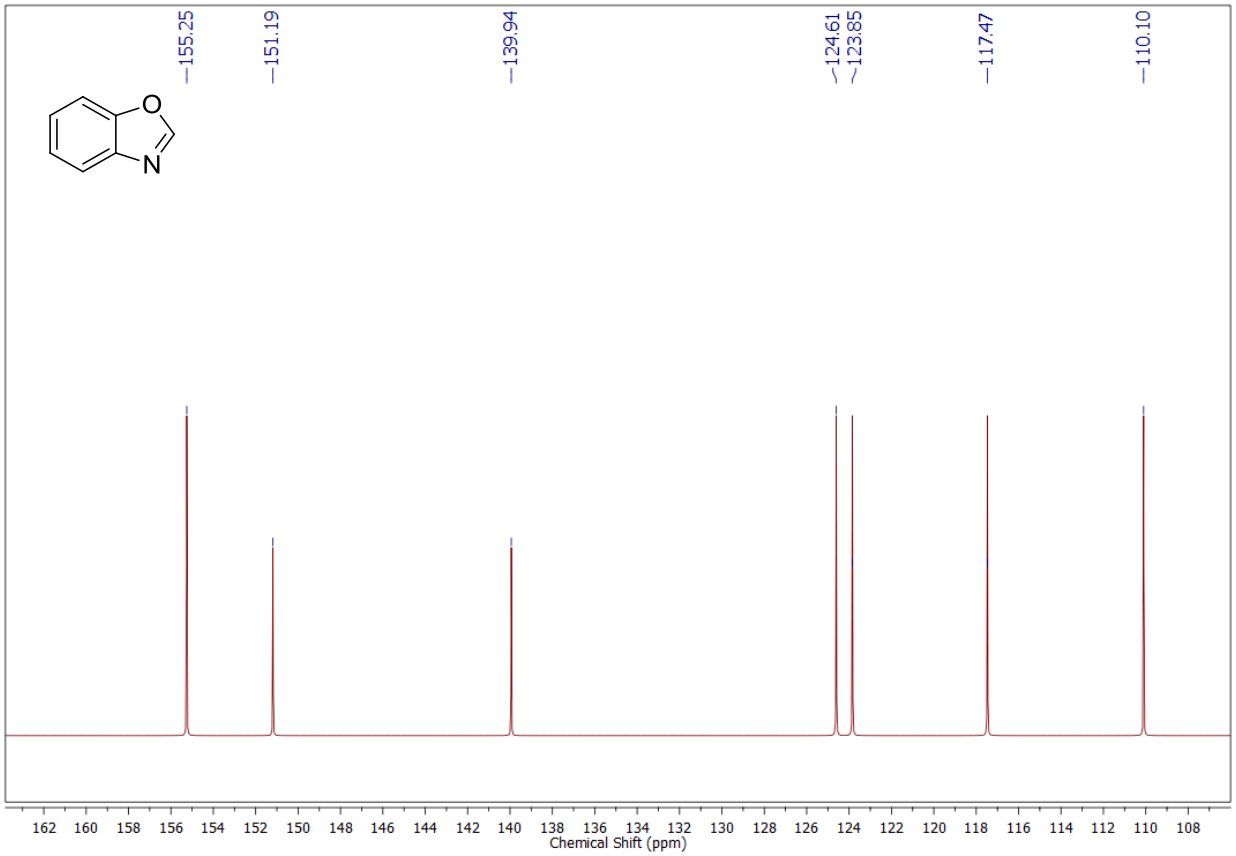

12.92
7.59
7.58
7.57
7.56
7.44
7.42
7.27
7.25
7.24
7.21
7.19
7.18
7.01
7.00
6.98
6.92
6.91
H
N
N
HO
2.00
2.01
1.00
2.06
1.02
1.01
1.00
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
Chemical Shift (ppm)

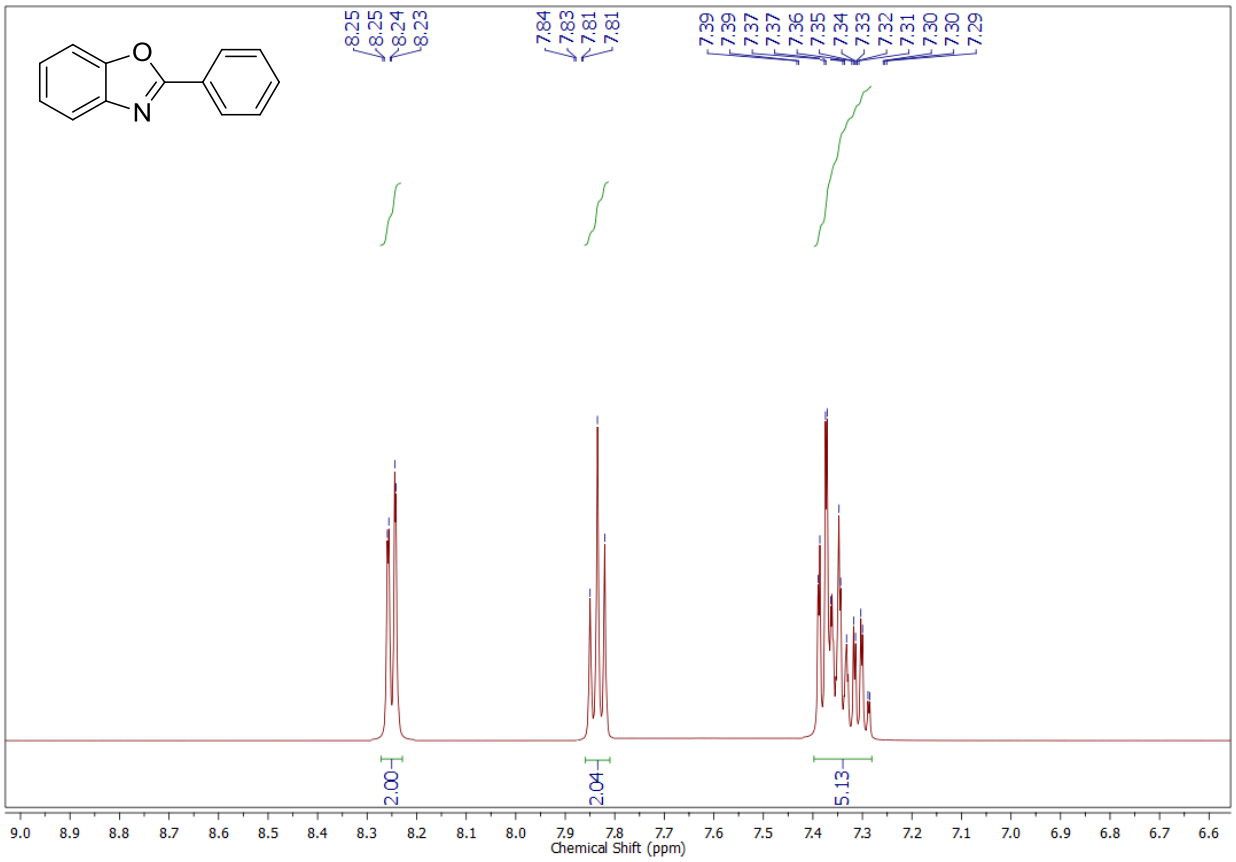

158.60
151.97
137.69
137.50
131.00
129.86
123.62
123.33
121.07
118.49
118.42
115.12
111.37
H
N
N
HO
164
160
156
152
148
144
140
136
132
128
124
120
116
112
108
Chemical Shift (ppm)

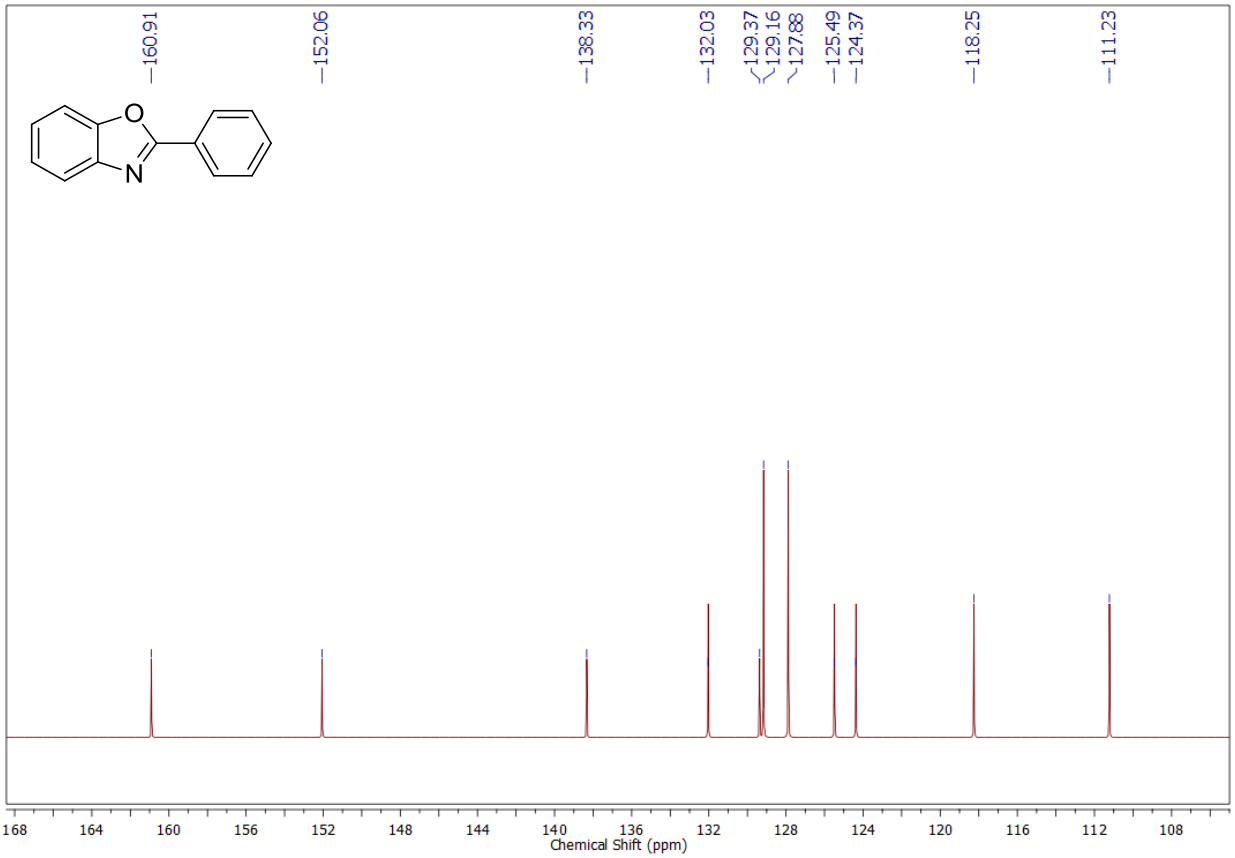

9.19
7.55
7.55
7.54
7.53
7.53
7.52
7.52
7.25
7.23
7.22
7.21
7.21
7.20
7.19
2.50
0.97
2.06
2.08
3.00
Chemical Shift (ppm)

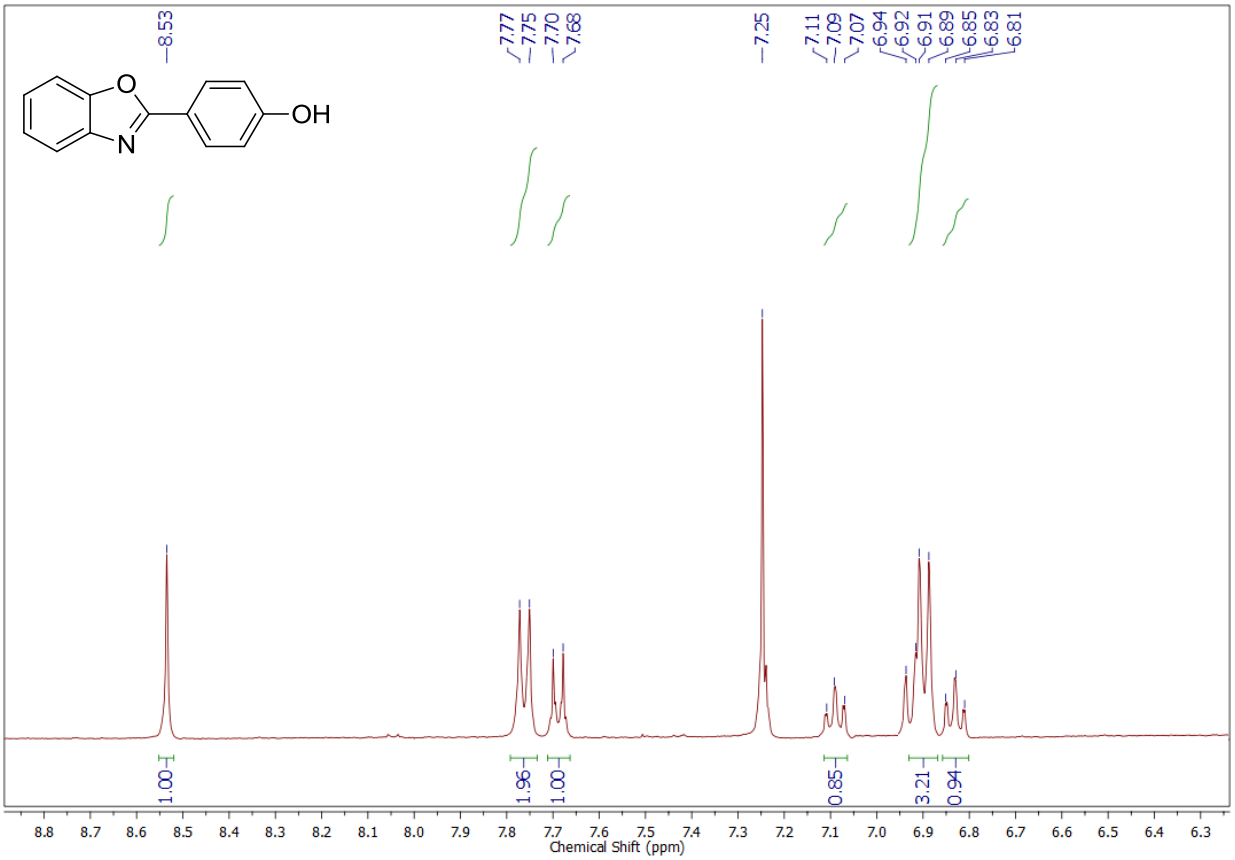

155.19
138.66
138.41
121.59
120.70
117.77
114.05
13.68
Chemical Shift (ppm)

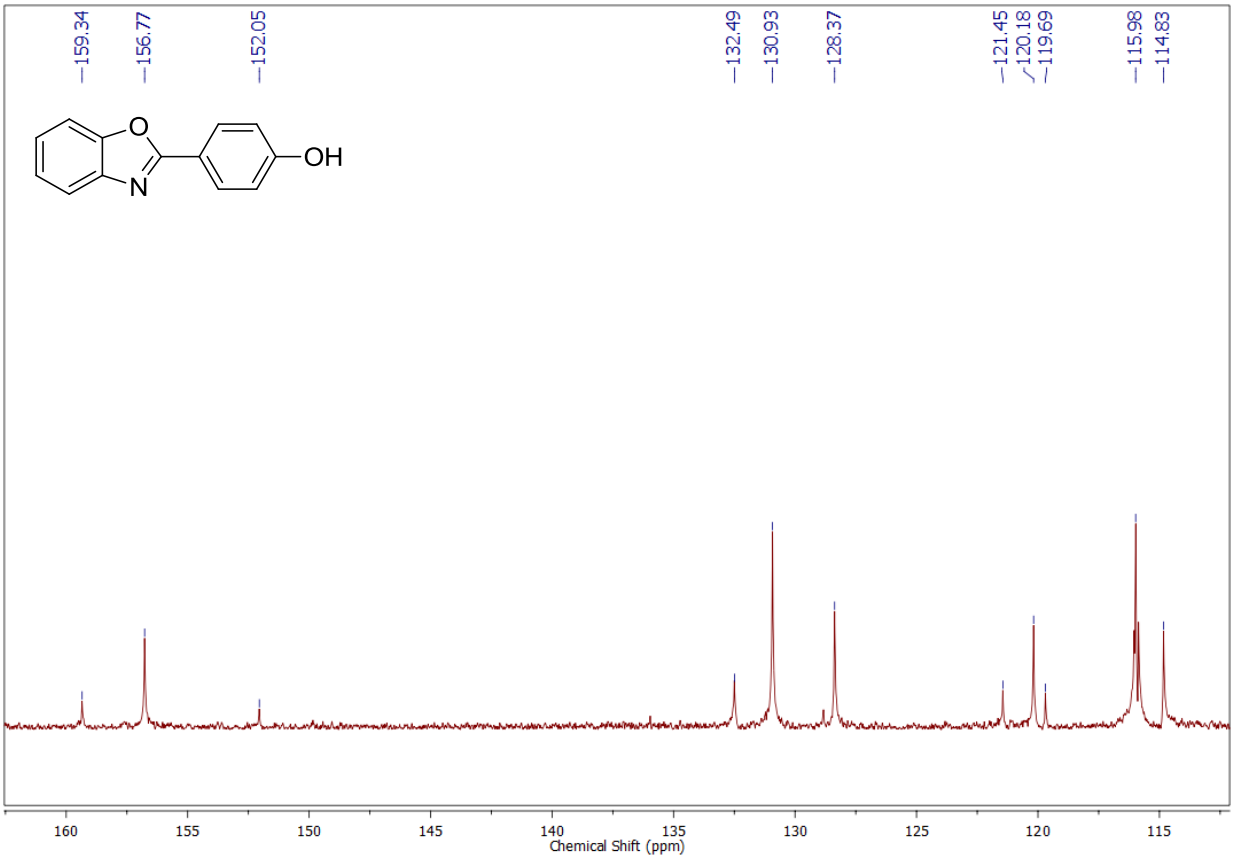

7.95
7.33
7.33
7.31
7.27
1.00
4.18
Chemical Shift (ppm)

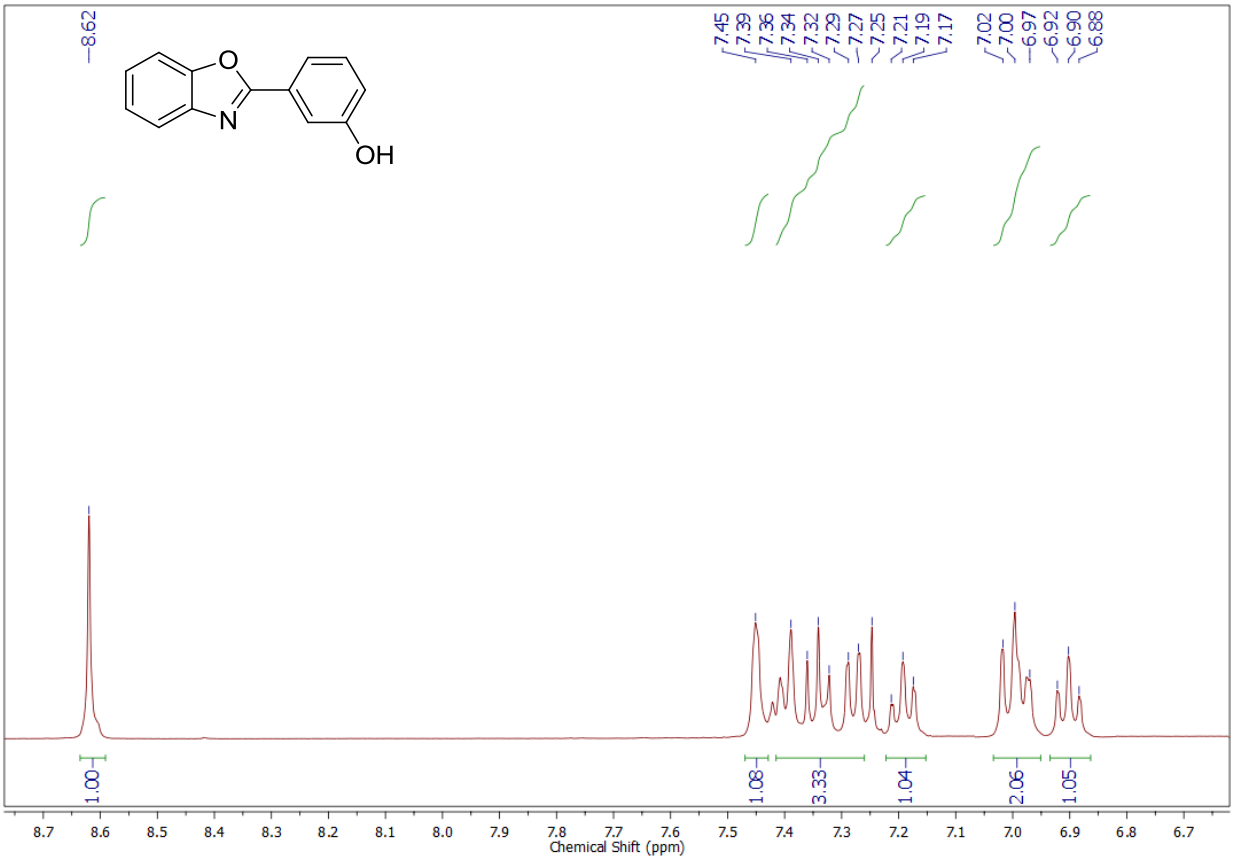

155.25
151.19
139.94
124.61
123.85
117.47
110.10
Chemical Shift (ppm)

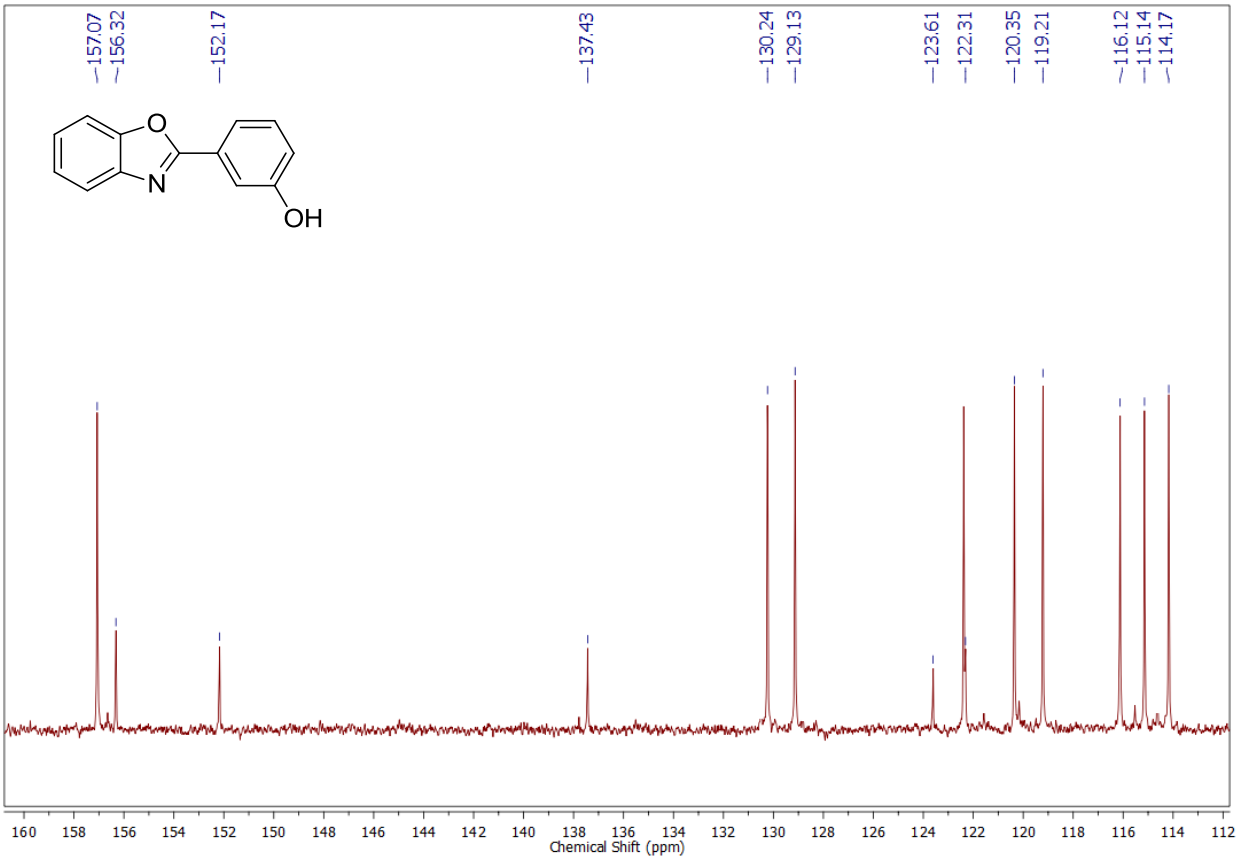

8.25
8.25
8.24
8.23
7.84
7.83
7.81
7.81
7.39
7.39
7.37
7.37
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.30
7.29
2.00
2.04
5.13
9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
Chemical Shift (ppm)

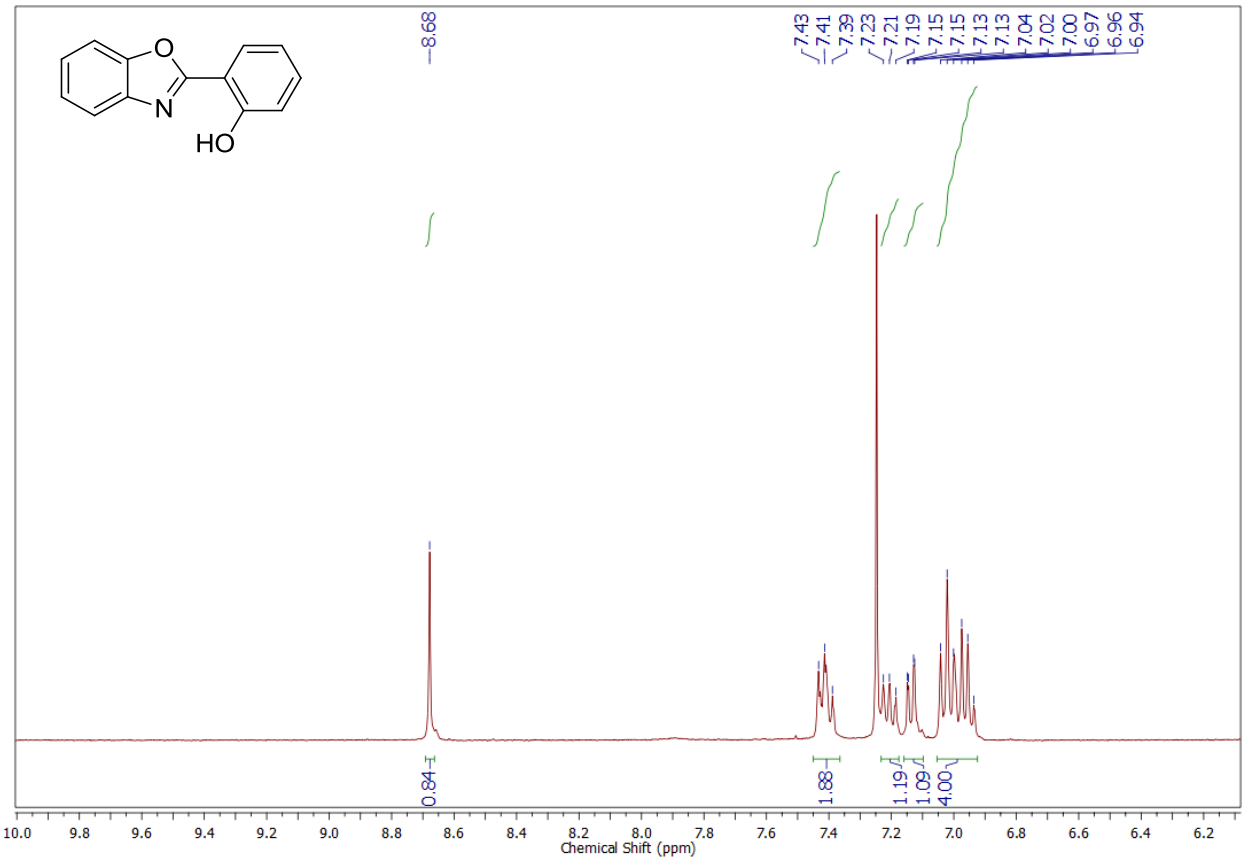

160.91
152.06
138.33
132.03
129.37
129.16
127.88
125.49
124.37
118.25
111.23
168 164 160 156 152 148 144 140 136 132 128 124 120 116 112 108
Chemical Shift (ppm)

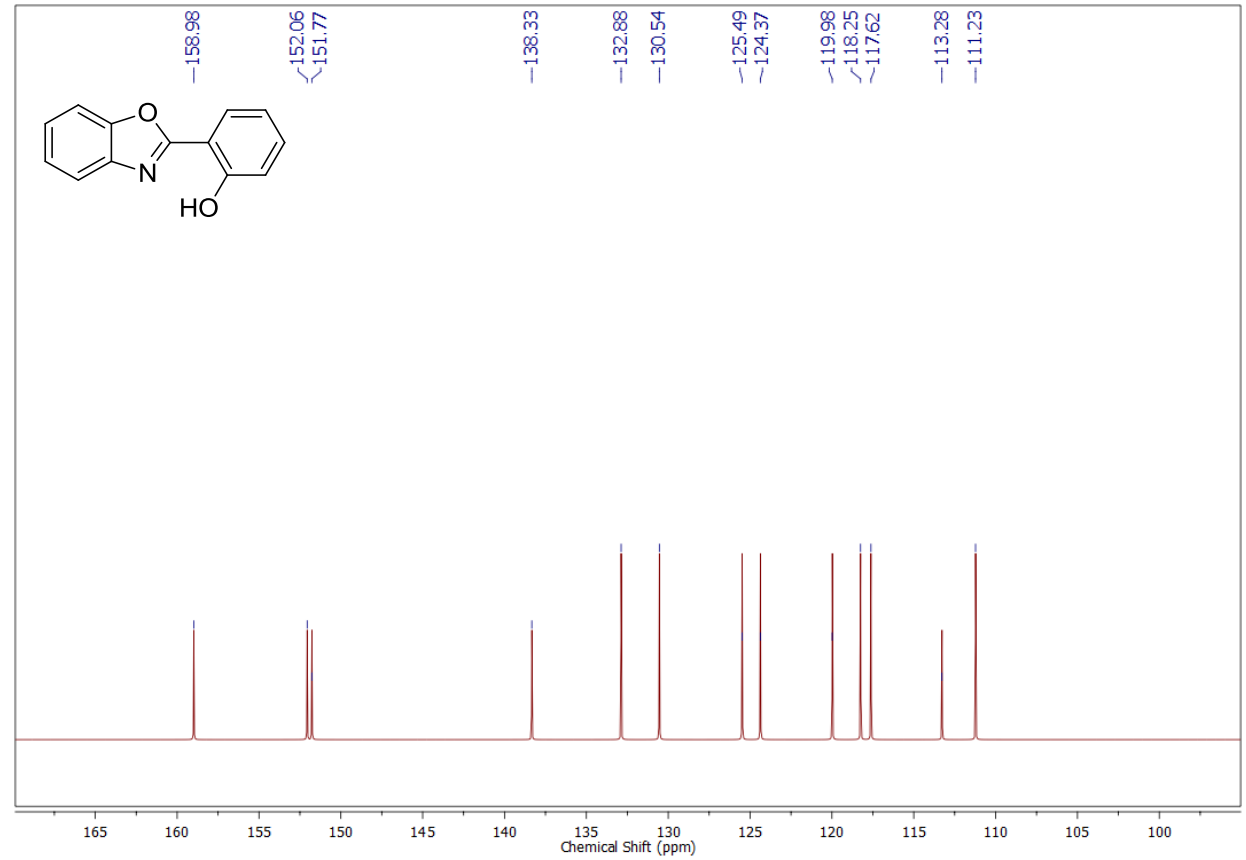

8.53
7.77
7.75
7.70
7.68
7.25
7.11
7.09
7.07
6.94
6.92
6.91
6.89
6.85
6.83
6.81
OH
1.00
1.96
1.00
0.85
3.21
0.94
Chemical Shift (ppm)

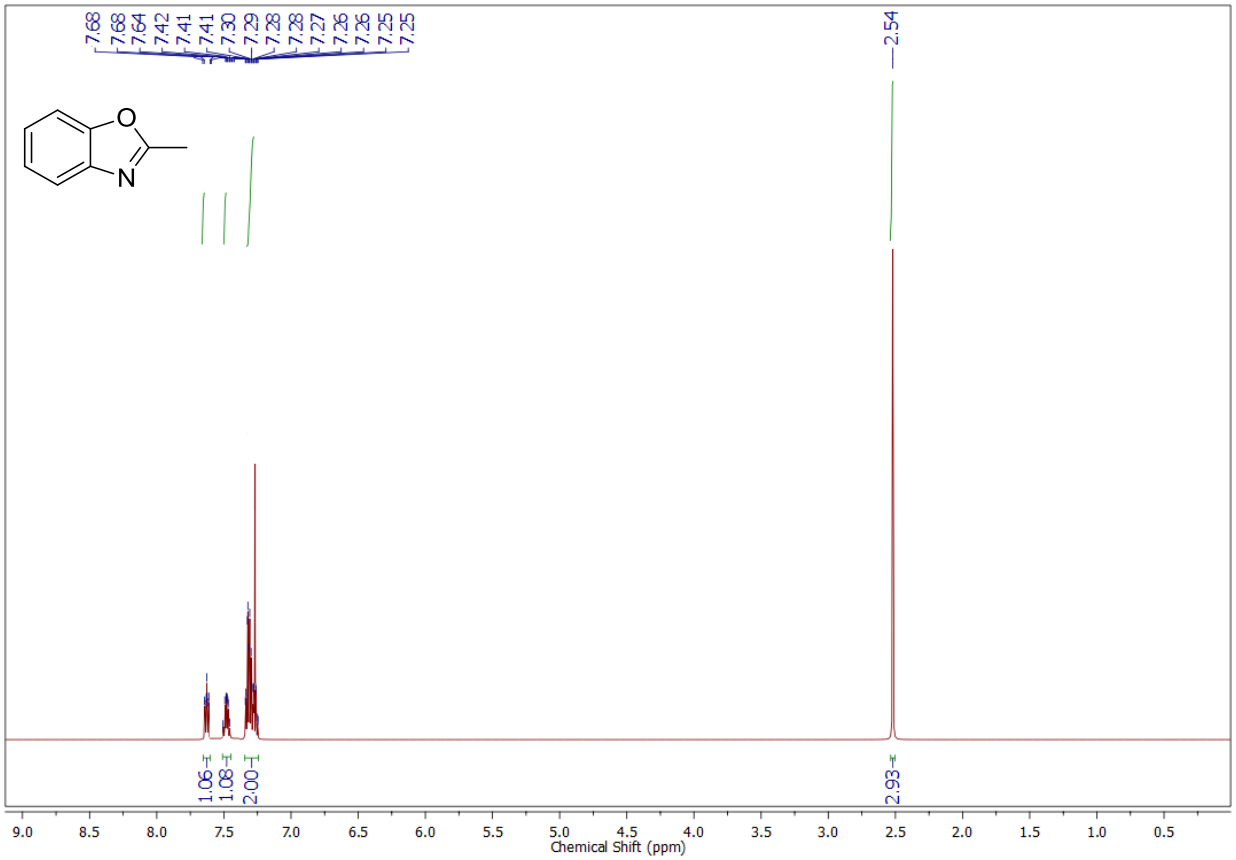

159.34
156.77
152.05
132.49
130.93
128.37
121.45
120.18
119.69
115.98
114.83
OH
Chemical Shift (ppm)

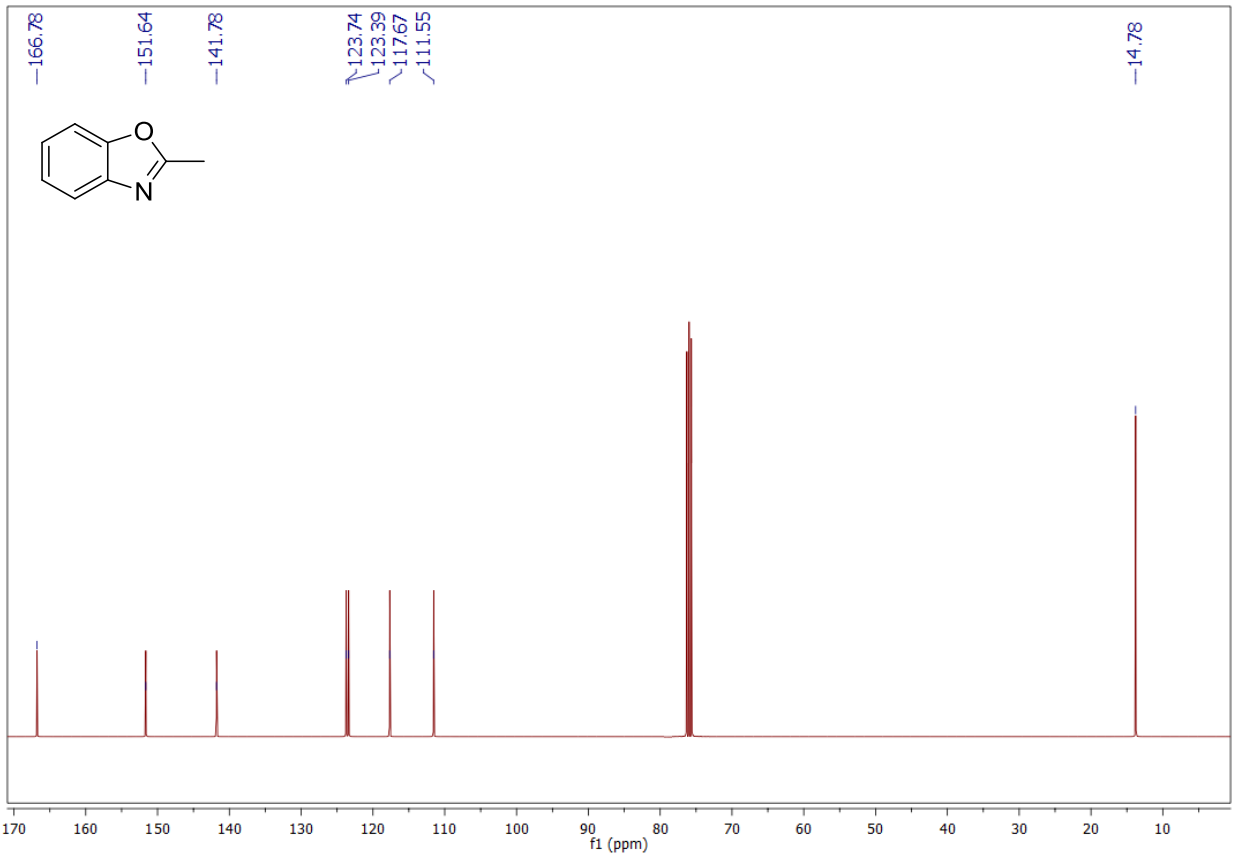

8.62
7.45
7.39
7.36
7.34
7.32
7.29
7.27
7.25
7.21
7.19
7.17
7.02
7.00
6.97
6.92
6.90
6.88
O
N
OH
1.00
1.08
3.33
1.04
2.06
1.05
8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
Chemical Shift (ppm)


157.07
156.32
152.17
137.43
130.24
129.13
123.61
122.31
120.35
119.21
116.12
115.14
114.17
O
N
OH
160 158 156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112
Chemical Shift (ppm)


8.68
7.43
7.41
7.39
7.23
7.21
7.19
7.15
7.15
7.13
7.13
7.04
7.02
7.00
6.97
6.96
6.94
0.84
1.88
1.19
1.09
4.00
Chemical Shift (ppm)


158.98
152.06
151.77
138.33
132.88
130.54
125.49
124.37
119.98
118.25
117.62
113.28
111.23
Chemical Shift (ppm)


7.68
7.68
7.64
7.42
7.41
7.41
7.30
7.29
7.28
7.28
7.27
7.26
7.26
7.25
7.25
2.54
1.06
1.08
2.00
2.93
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
Chemical Shift (ppm)


166.78
151.64
141.78
123.74
123.39
117.67
111.55
14.78
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)