Supporting Information

Catalytic Asymmetric Total Syntheses of (–)-Galanthamine and (–) -Lycoramine

Qing Zhang,[†] Fu-Min Zhang,*[,†] Chang-Sheng Zhang,[†] Si-Zhan Liu,[†] Jin-Miao Tian,[‡] Shao-Hua Wang,[†] Xiao-Ming Zhang[†] and Yong-Qiang Tu*[,†,‡]

[†]*State Key Laboratory of Applied Organic Chemistry & College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P. R. China.*

[‡]*School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, P. R. China.*

Correspondence and requests for materials should be addressed to Y.-Q.T. (email: tuyq@lzu.edu.cn; tuyq@sjtu.edu.cn) or to F.-M.Z. (email: zhangfm@lzu.edu.cn).

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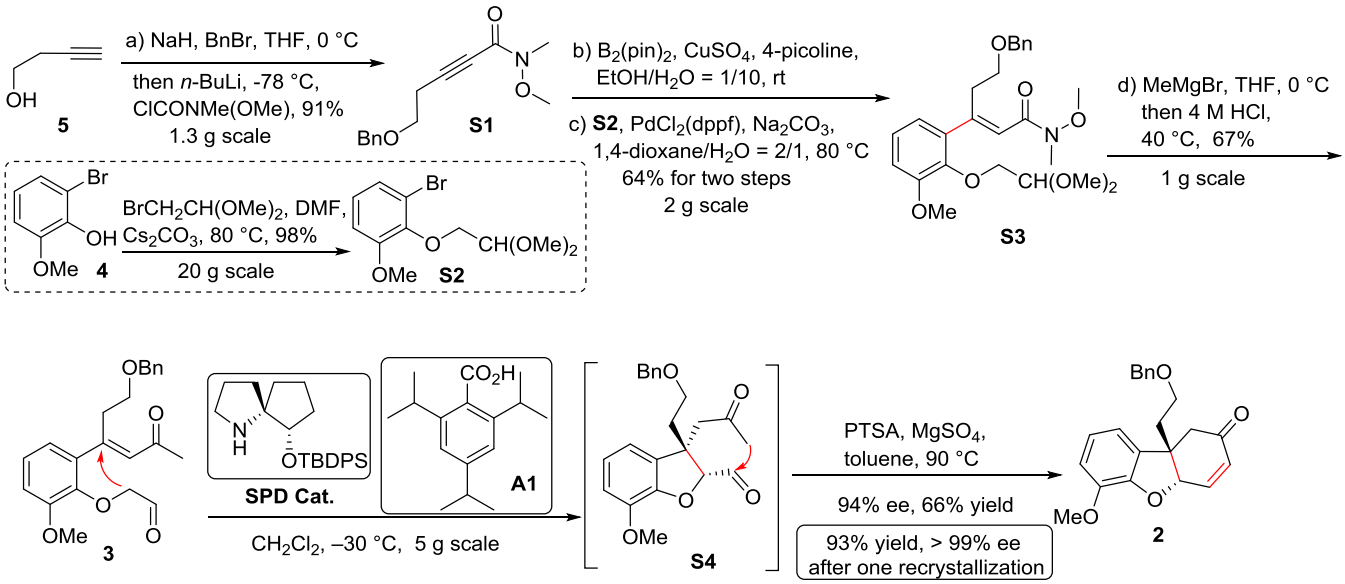
1. The Preparation of the Tricycle Compound 2

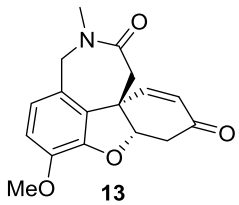
The tricycle compound **2** was readily prepared from commercially available 3-butyn-1-ol **5** through our previously reported six-step protocol[1].



Scheme S1. The synthetic route of compound **2**

2. The Comparison of NMR Spectral Data

2.1 The comparison of NMR spectral data of compound 13 (Zhou's Intermediate)



13

Zhou's Intermediate

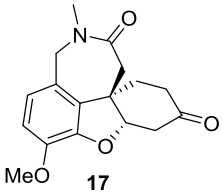
Table S1 Comparison of ^{1}H NMR Spectral Data of Compound 13 (Zhou's Intermediate)

A: Qi-Lin Zhou's Report[2]	B: Our Synthetic One	Error (B–A)
δ (ppm, 400 MHz,$CDCl_3$)	δ (ppm, 600 MHz,$CDCl_3$)	Δδ/ppm
6.74 (s, 2H)	6.78 – 6.71 (m, 2H)	-
6.38 (dd, *J* = 10.4, 2.4 Hz, 1H)	6.39 (dd, *J* = 10.2, 2.3 Hz, 1H)	0.01
6.04 (d, *J* = 10.4 Hz, 1H)	6.06 (d, *J* = 10.2 Hz, 1H)	0.02
4.84 (br, 1H)	4.85 (q, *J* = 2.8 Hz, 1H)	0.01
4.49 (d, *J* = 16.2 Hz, 1H)	4.50 (d, *J* = 16.2 Hz, 1H)	0.01
4.40 (d, *J* = 16.2 Hz, 1H)	4.41 (d, *J* = 16.2 Hz, 1H)	0.01
3.85 (s, 3H)	3.86 (s, 3H)	0.01
3.16 (d, *J* = 17.6 Hz, 1H)	3.17 (dd, *J* = 17.9, 2.9 Hz, 1H)	0.01
3.04 (s, 3H)	3.06 (s, 3H)	0.02
2.99 (d, *J* = 13.8 Hz, 1H)	3.02 (d, *J* = 13.9 Hz, 1H)	0.03
2.95 (d, *J* = 13.8 Hz, 1H)	2.96 (d, *J* = 13.8 Hz, 1H)	0.01
2.81 (dd, *J* = 17.9, 3.0 Hz, 1H)	2.82 (dd, *J* = 17.9, 3.2 Hz, 1H)	0.01

Table S2 Comparison of ^{13}C NMR Spectral Data of Compound 13 (Zhou's Intermediate)

A: Qi-Lin Zhou's Report[2]	B: Our Synthetic One	Error (A–B)
δ (ppm, 100 MHz,$CDCl_3$)	δ (ppm, 150 MHz,$CDCl_3$)	Δδ/ppm
193.6	193.5	0.1
170.1	170.0	0.1
147.7	147.8	-0.1
144.9	145.0	0.1
144.7	144.6	-0.1
129.8	129.9	-0.1
127.8	127.8	0
124.9	124.9	0
120.3	120.2	0.1
112.7	112.9	-0.2
87.1	87.1	0
56.3	56.3	0
52.0	52.0	0
43.8	43.9	-0.1
40.6	40.7	-0.1
36.4	36.4	0
36.0	36.0	0

2.2 The comparison of NMR spectral data of compound 17 (Zhou's Intermediate)



17

Zhou's Intermediate

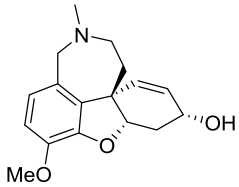
Table S3 Comparison of ^{1}H NMR Spectral Data of Compound 17 (Zhou's Intermediate)

A: Qi-Lin Zhou's Report[2]	**B: Our Synthetic One**	**Error (A–B)**
δ (ppm, 400 MHz,$CDCl_3$)	δ (ppm, 600 MHz,$CDCl_3$)	Δδ/ppm
6.73 (dd, *J* = 18.4, 8.2 Hz, 2H)	6.70 (dd, *J* = 18.4, 8.2 Hz, 2H)	0.03
4.85 (br, 1H)	4.83 (t, J = 3.0 Hz, 1H)	0.02
4.42 (dd, *J* = 20.4, 16.4 Hz, 2H)	4.42 (dd, J = 25.2, 16.8 Hz, 2H)	0
3.86 (s, 3H)	3.85 (s, 3H)	0.01
3.09–2.98 (m, 5H)	3.06–3.02 (m, 1H)	-
-	3.02 (s, 3H)	-
-	2.99 (d, J = 13.8 Hz, 1H)	-
2.87 (d, *J* = 13.8 Hz, 1H)	2.85 (d, J = 13.8 Hz, 1H)	0.02
2.75 (dd, *J* = 17.6, 2.8 Hz, 1H)	2.73 (dd, J = 17.6, 2.9 Hz, 1H)	0.02
2.39–2.34 (m, 1H)	2.39–2.34 (m, 1H)	0
2.34–2.23 (m, 1H)	2.30–2.24 (m, 1H)	0.04
2.04–2.00 (m, 2H)	2.04–2.01 (m, 2H)	-0.01

Table S4 Comparison of ^{13}C NMR Spectral Data of Compound 13 (Zhou's Intermediate)

A: Qi-Lin Zhou's Report[2]	B: Our Synthetic One	Error (A–B)
δ (ppm, 100 MHz,$CDCl_3$)	δ (ppm, 150 MHz,$CDCl_3$)	Δδ/ppm
207.5	207.3	0.2
171.4	171.3	0.1
146.8	146.9	-0.1
144.5	144.5	0
132.5	132.6	-0.1
124.9	124.9	0
120.1	120.0	0.1
112.2	112.5	-0.3
88.4	88.4	0
56.2	56.3	-0.1
52.1	52.1	0
43.5	43.6	-0.1
42.2	42.3	-0.1
39.4	39.4	0
36.2	36.2	0
35.8	35.8	0
32.7	32.7	0

2.3 The comparison of NMR spectral data of (–)-Galanthamine



(–)-Galanthamine (**1a**)

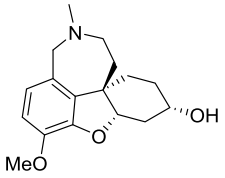
Table S5 Comparison of ^{1}H NMR Spectral Data of (–)-Galanthamine

A: Yanxing Jia's Report[3]	B: Our Synthetic One	Error (B–A)
δ (ppm, 400 MHz,$CDCl_3$)	δ (ppm, 400 MHz,$CDCl_3$)	Δδ/ppm
6.66 (d, *J* = 8.4 Hz, 1H)	6.67 (d, *J* = 8.2 Hz, 1H)	0.01
6.63 (d, *J* = 8.4 Hz, 1H)	6.63 (d, *J* = 8.2 Hz, 1H)	0
6.08-5.99 (m, 2H)	6.07–5.99 (m, 2H)	0.01
4.61 (br s, 1H)	4.62 (s, 1H)	0.01
4.14 (t, *J* = 4.3 Hz, 1H)	4.15–4.11 (m, 2H)	0.01
4.10 (d, *J* = 15.2 Hz, 1H)	-	0.01
3.83 (s, 3H)	3.84 (s, 3H)	0.01
3.69 (d, *J* = 15.1 Hz, 1H)	3.72 (d, *J* = 15.1 Hz, 1H)	0.03
3.28 (m, 1H)	3.31 (t, *J* = 13.1 Hz, 1H)	0.03
3.06 (m, 1H)	3.08 (d, *J* = 14.6 Hz, 1H)	0.02
2.69 (m, 1H)	2.69 (dd, *J* = 15.7, 3.4 Hz, 1H)	0
2.41 (s, 3H)	2.43 (s, 3H)	0.02
2.12-1.98 (m, 2H)	2.10 (td, *J* = 13.5, 3.1 Hz, 1H)	-
-	2.01 (ddd, *J* = 15.7, 5.0, 2.4 Hz, 1H)	-
1.58 (m, 1H)	1.61 (dd, *J* = 13.8, 2.3 Hz, 1H)	0.03

Table S6 Comparison of ^{13}C NMR Spectral Data of (–)-Galanthamine

A: Yanxing Jia's Report[3]	B: Our Synthetic One	Error (B–A)
δ (ppm, 100 MHz,$CDCl_3$)	δ (ppm, 100 MHz,$CDCl_3$)	Δδ/ppm
145.8	145.9	0.1
144.2	144.3	0.1
133.0	133.0	0
127.7	127.8	0.1
126.8	126.6	-0.2
122.1	122.2	0.1
111.2	111.3	0.1
88.7	88.7	0
62.1	62.0	-0.1
60.6	60.4	-0.2
55.9	55.9	0
53.8	53.7	-0.1
48.2	48.1	-0.1
42.0	41.7	-0.3
33.8	33.5	-0.3
29.9	29.9	0

2.4 The comparison of NMR spectral data of (–)-Lycoramine



(–)-Lycoramine (**1b**)

Table S7 Comparison of ^{1}H NMR Spectral Data of (–)-Lycoramine

A: Yanxing Jia's Report[3]	B: Our Synthetic One	Error (B–A)
δ (ppm, 400 MHz,$CDCl_3$)	δ (ppm, 600 MHz,$CDCl_3$)	Δδ/ppm
6.65 (d, *J* = 8.2 Hz, 1H)	6.66 (d, *J* = 8.2 Hz, 1H)	0.01
6.60 (d, *J* = 8.2 Hz, 1H)	6.61 (d, *J* = 8.2 Hz, 1H)	0.01
4.37 (t, *J* = 3.0 Hz, 1H)	4.38 (s, 1H)	0.01
4.08 (m, 1H)	4.09 (s, 1H)	0.01
4.04 (d, *J* = 15.0 Hz, 1H)	4.05 (d, *J* = 15.0 Hz, 1H)	0.01
3.85 (s, 3H)	3.86 (s, 3H)	0.01
3.65 (d, *J* = 15.0 Hz, 1H)	3.67 (d, *J* = 15.0 Hz, 1H)	0.02
3.24 (m, 1H)	3.26 (t, *J* = 13.5 Hz, 1H)	0.02
3.07 (m, 1H)	3.08 (d, *J* = 14.3 Hz, 1H)	0.01
2.50 (m, 1H)	2.51 (d, *J* = 16.1 Hz, 1H)	0.01
2.38 (s, 3H)	2.40 (s, 3H)	0.02
2.00-1.66 (m, 6H)	2.01–1.67 (m, 6H)	0.01
1.57 (m, 1H)	1.60–1.54 (m, 1H)	-

Table S8 Comparison of ^{13}C NMR Spectral Data of (–)-Lycoramine

A: Yanxing Jia's Report[3]	B: Our Synthetic One	Error (B–A)
δ (ppm, 100 MHz,$CDCl_3$)	δ (ppm, 150 MHz,$CDCl_3$)	Δδ/ppm
146.0	146.1	0.1
144.2	144.3	0.1
136.2	136.2	0
128.0	127.9	-0.1
122.0	122.0	0
110.7	111.0	0.3
89.9	89.9	0
65.4	65.4	0
60.2	60.2	0
55.9	55.9	0
53.9	54.0	0.1
46.7	46.7	0
41.5	41.5	0
31.5	31.6	0.1
30.9	31.1	0.2
27.6	27.7	0.1
23.7	23.8	0.1

3. References

(1) Zhang, Q.; Zhang, F.-M.; Zhang, C.-S.; Liu, S.-Z.; Tian, J.-M.; Wang, S.-H.; Zhang, X.-M.; Tu, Y.-Q. Enantioselective synthesis of *cis*-hydrobenzofurans bearing all-carbon quaternary stereocenters and application to total synthesis of (–)-morphine. *Nat. Commun.* **2019**, *10*, 2507.

(2) Chen, J.-Q.; Xie, J.-H.; Bao, D.-H.; Liu, S.; Zhou, Q.-L. Total synthesis of (–)-galanthamine and (–)-lycoramine *via* catalytic asymmetric hydrogenation and intramolecular reductive Heck cyclization. *Org. Lett.* **2012**, *14*, 2714-2717.

(3) Li, L.; Yang, Q.; Wang, Y.; Jia, Y. Catalytic asymmetric total synthesis of (–)-galanthamine and (–)-lycoramine. *Angew. Chem. Int. Ed.* **2015**, *54*, 6255-6259

4. Copies of the HPLC Chromatograms and NMR Spectra

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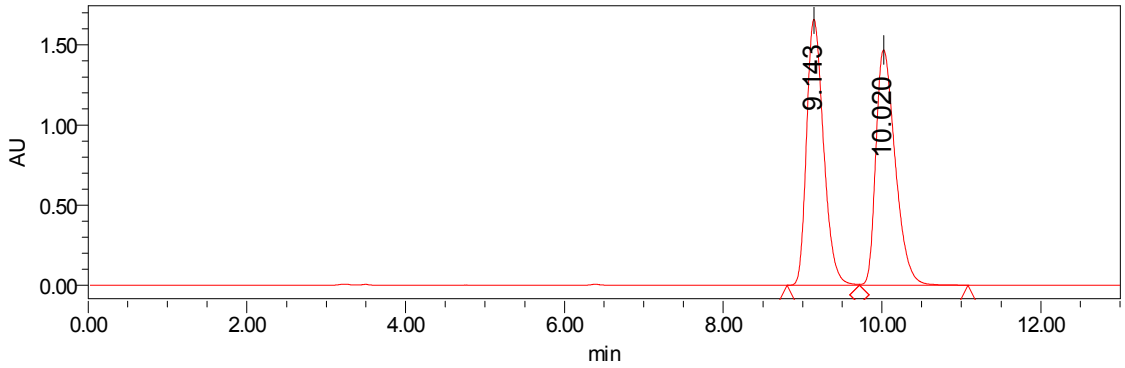
Column: 10.00 ul



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2	10.020	24801963.547	50.213	1466889

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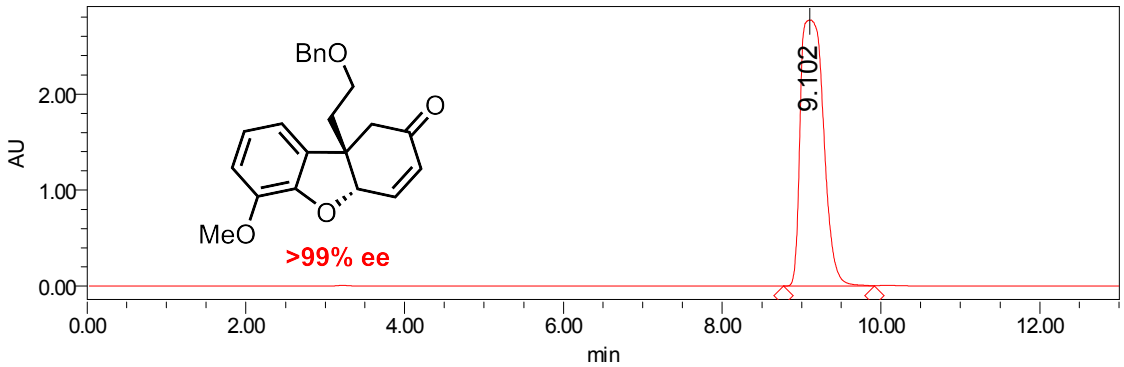

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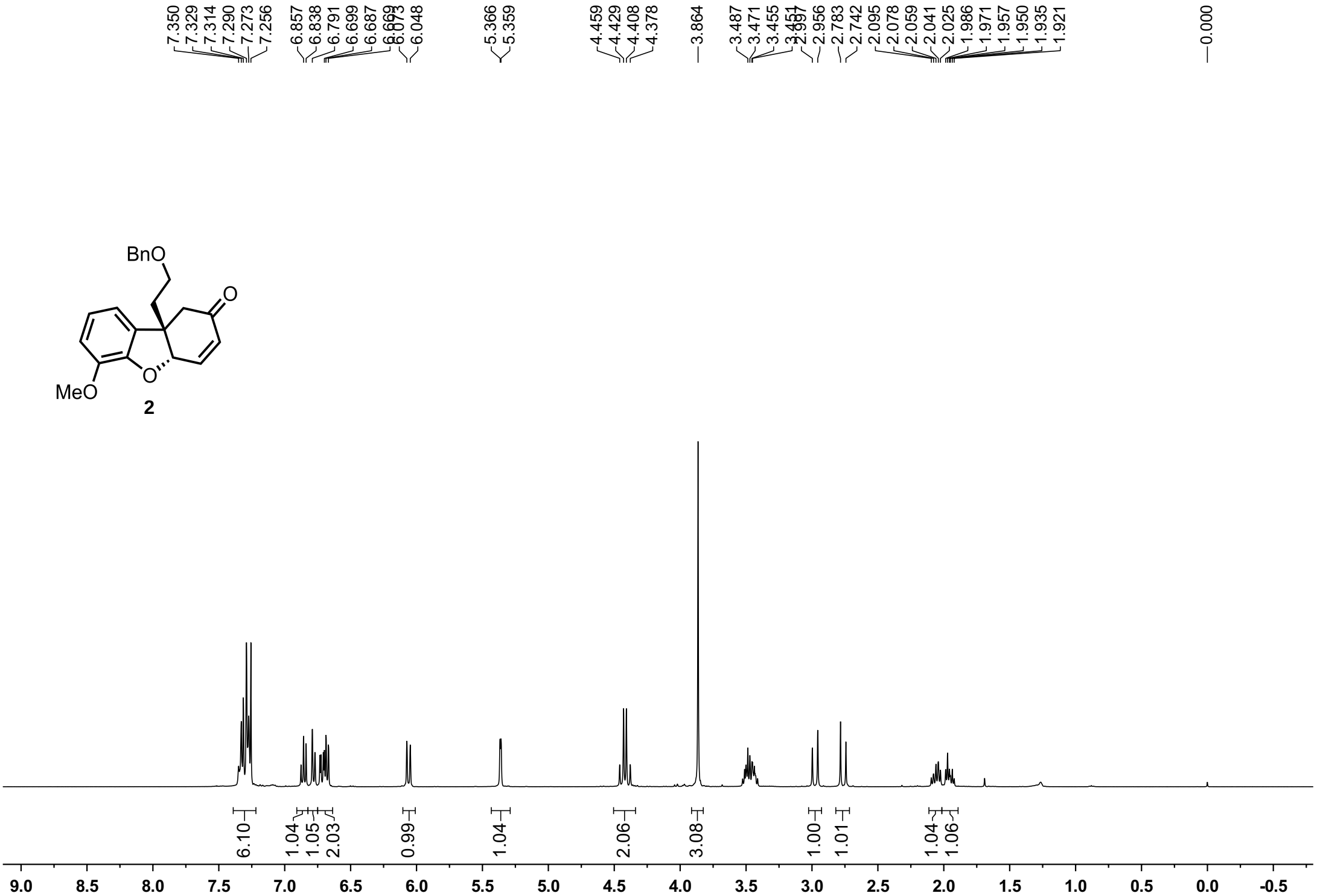
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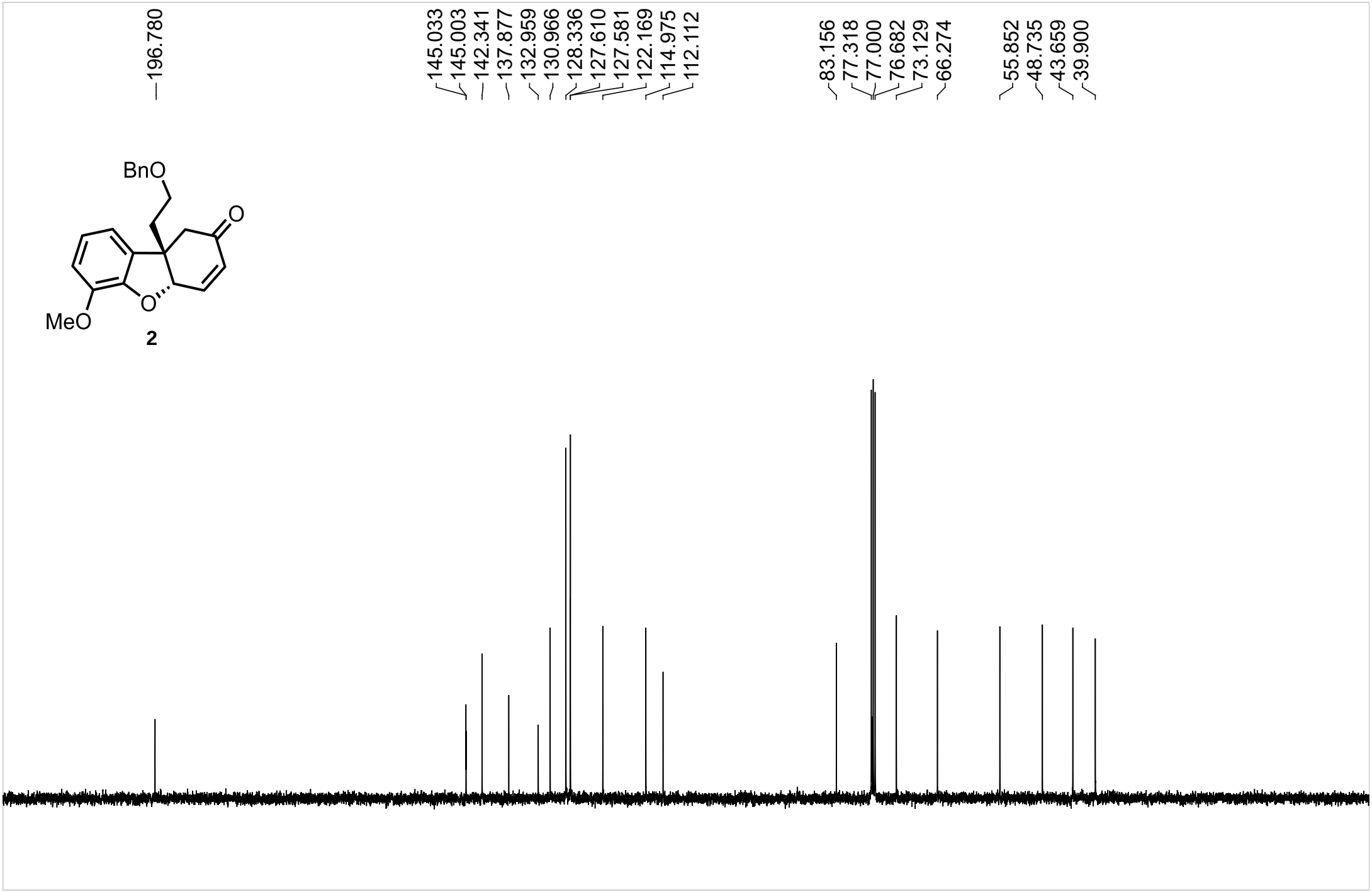
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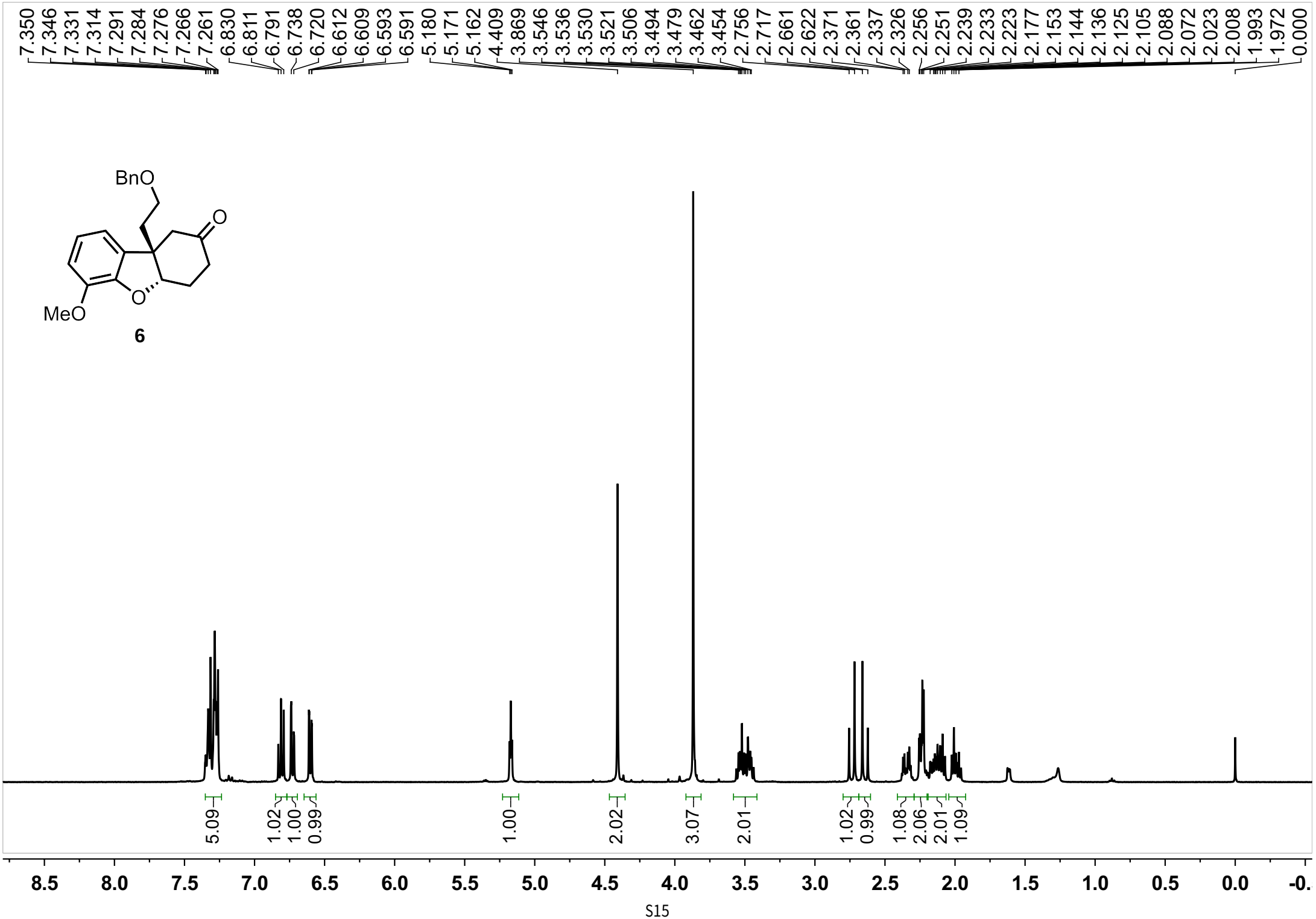
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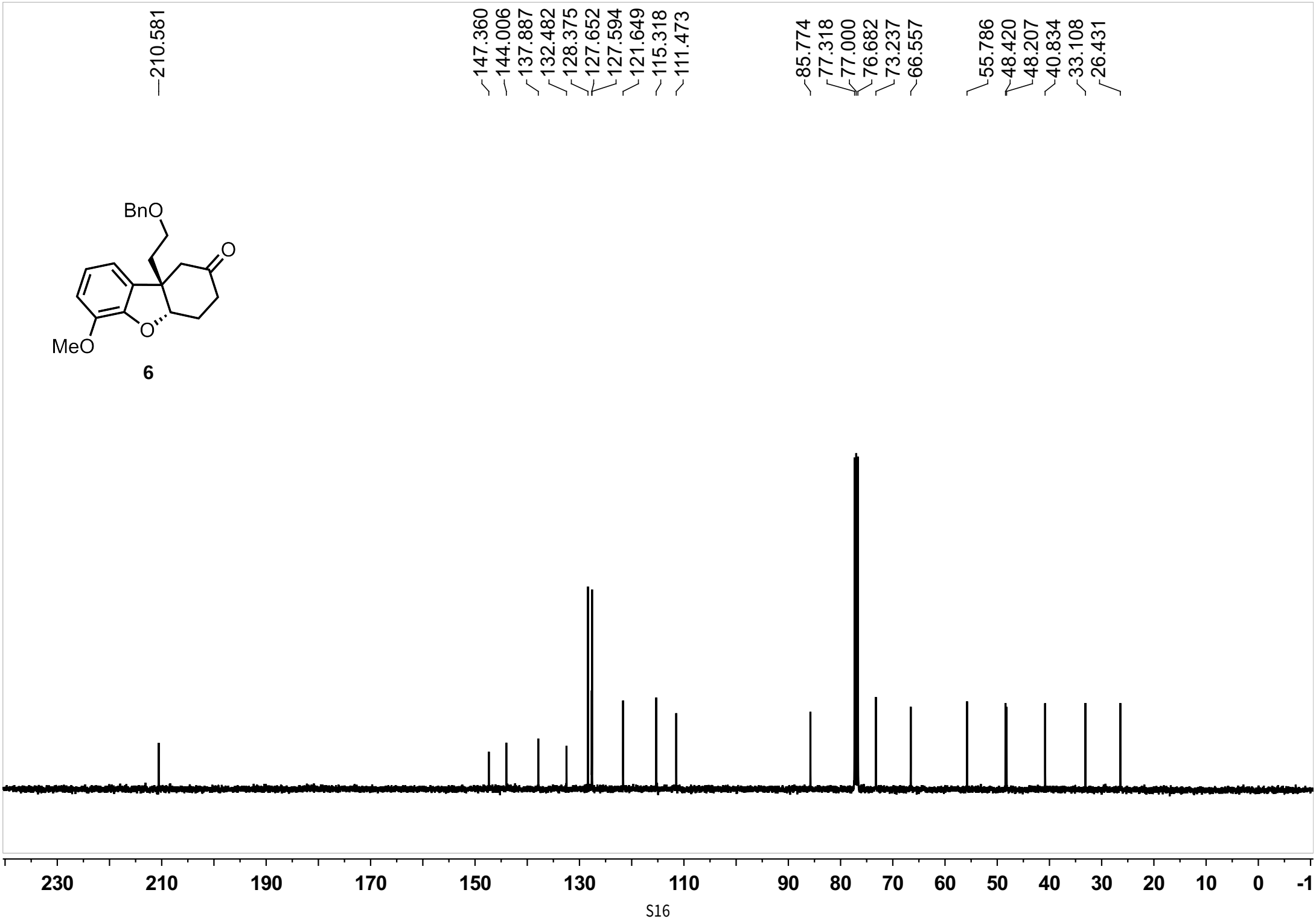
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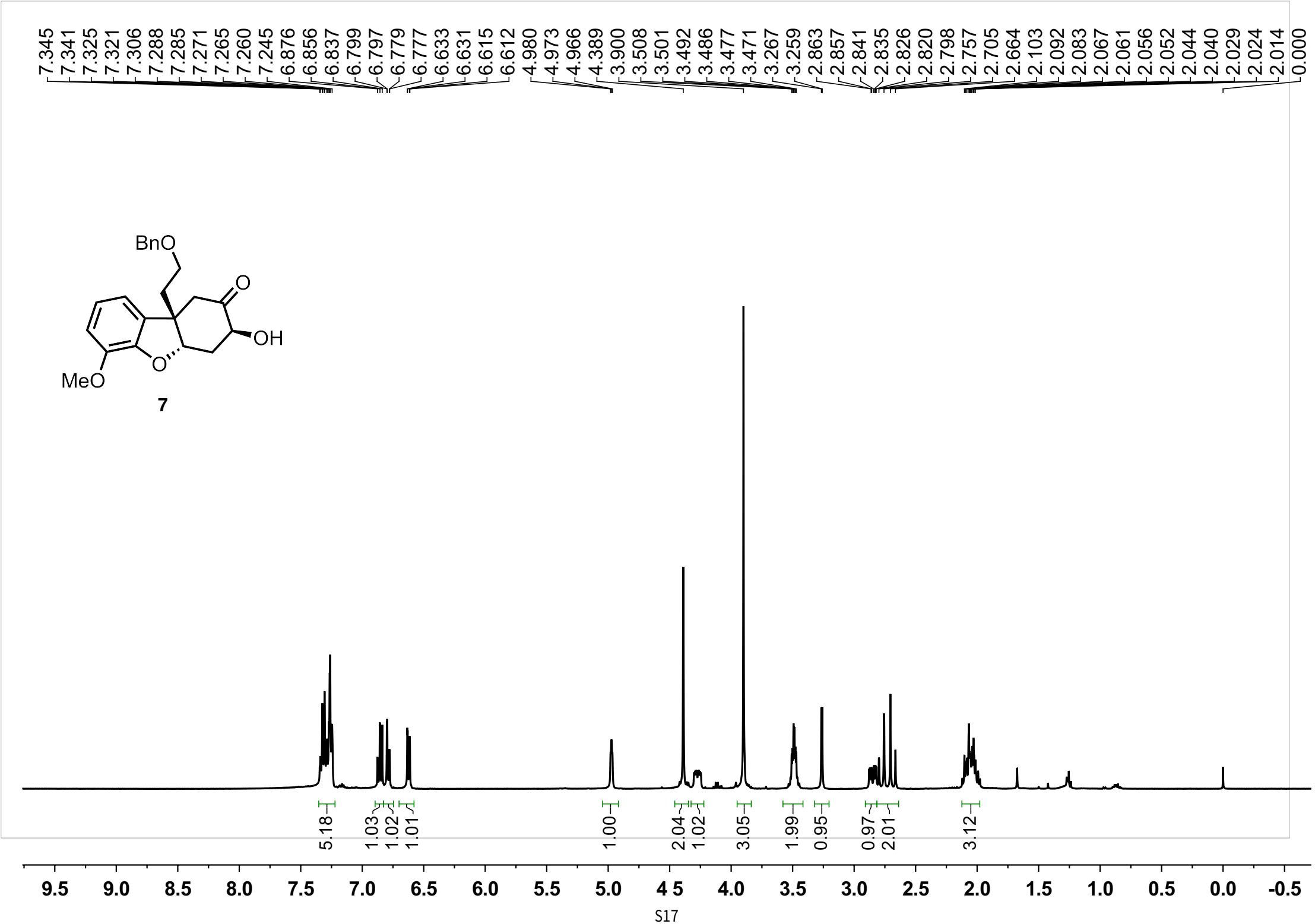
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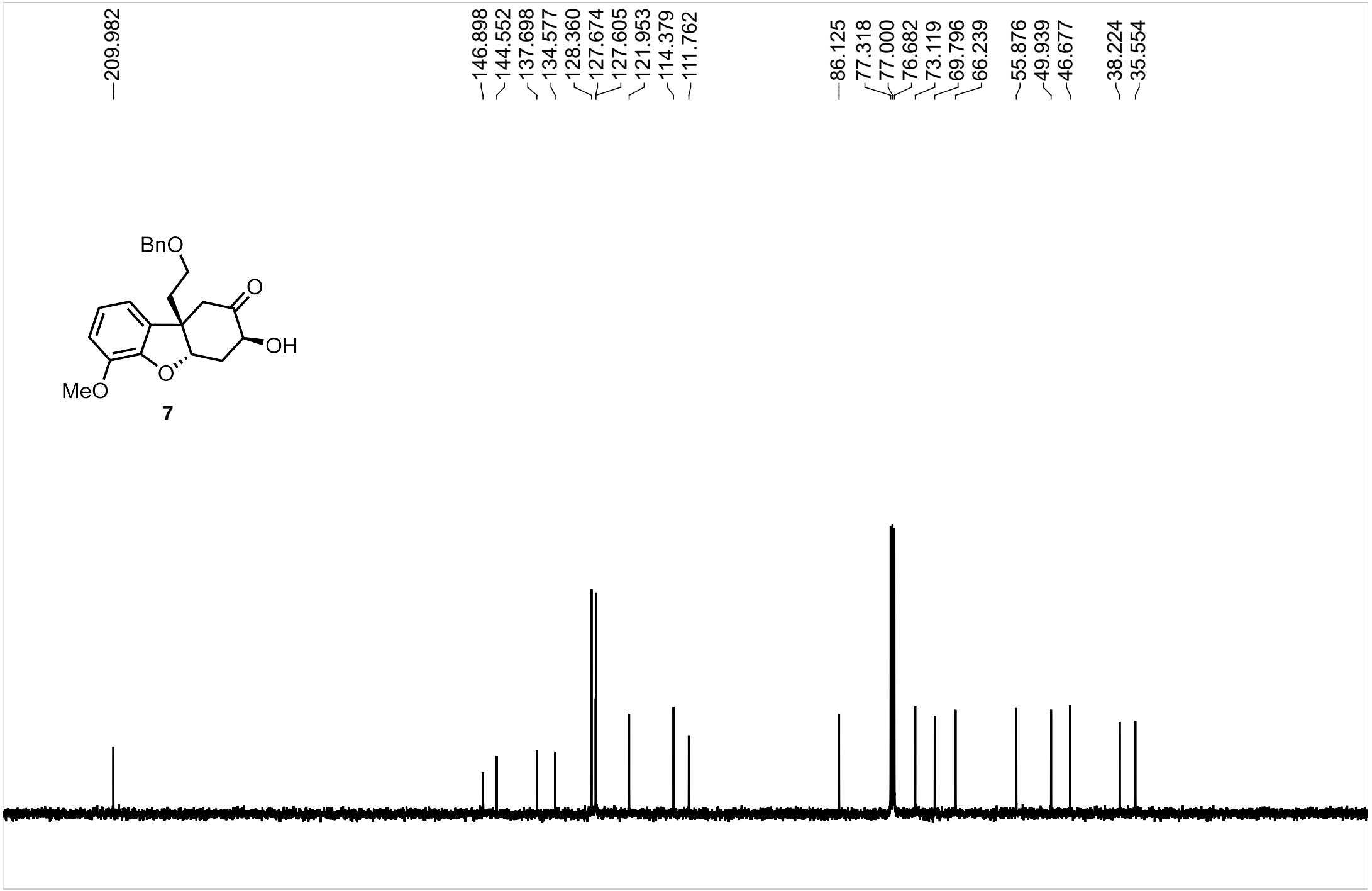
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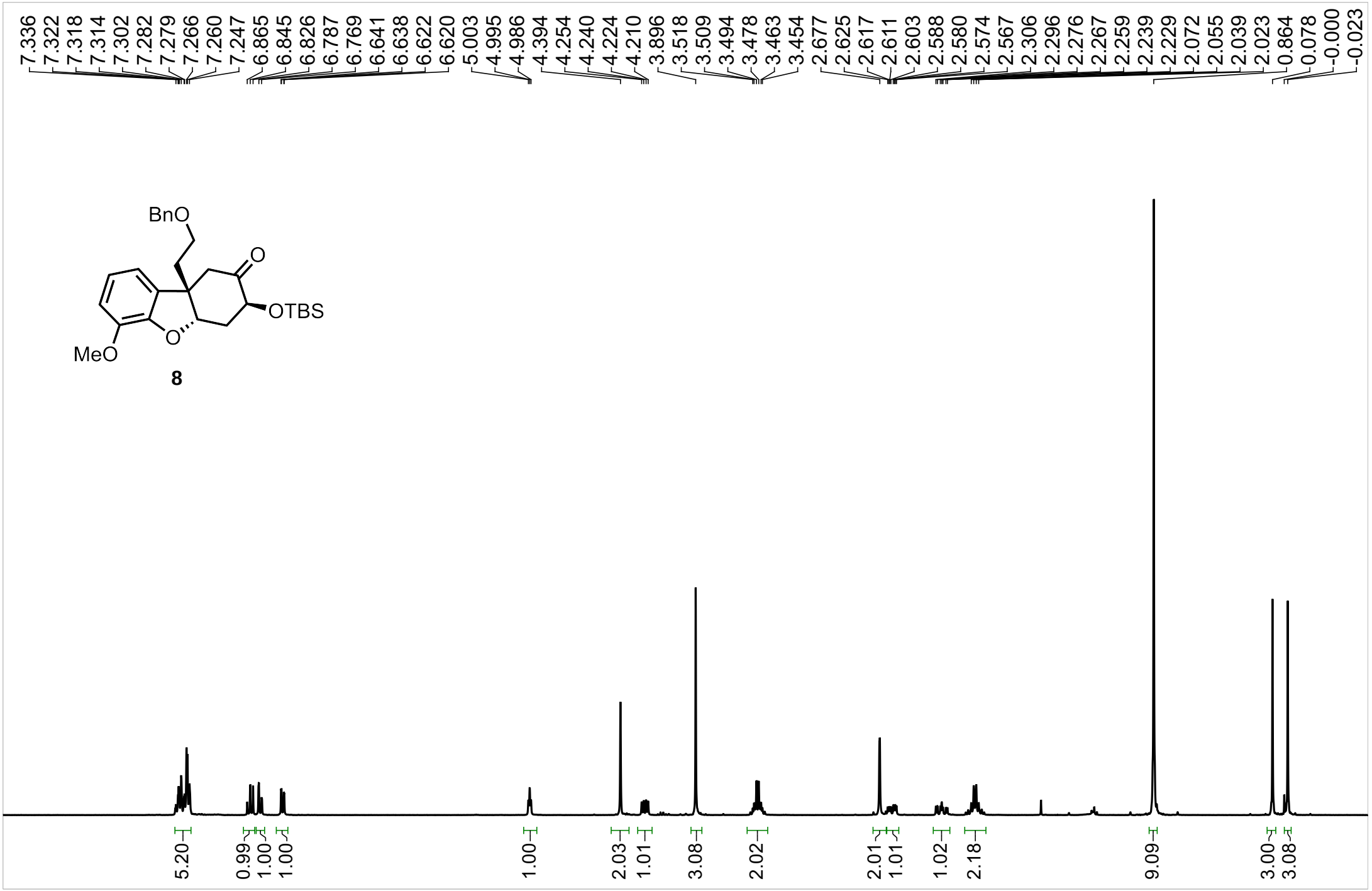
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7.260
7.247
6.865
6.845
6.826
6.787
6.769
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6.638
6.622
6.620
5.003
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4.254
4.240
4.224
4.210
3.896
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3.509
3.494
3.478
3.463
3.454
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2.617
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2.039
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-0.023
BnO
O
OTBS
O
MeO
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1.00
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1.01
3.08
2.02
2.01
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1.02
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3.00
3.08
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6.0
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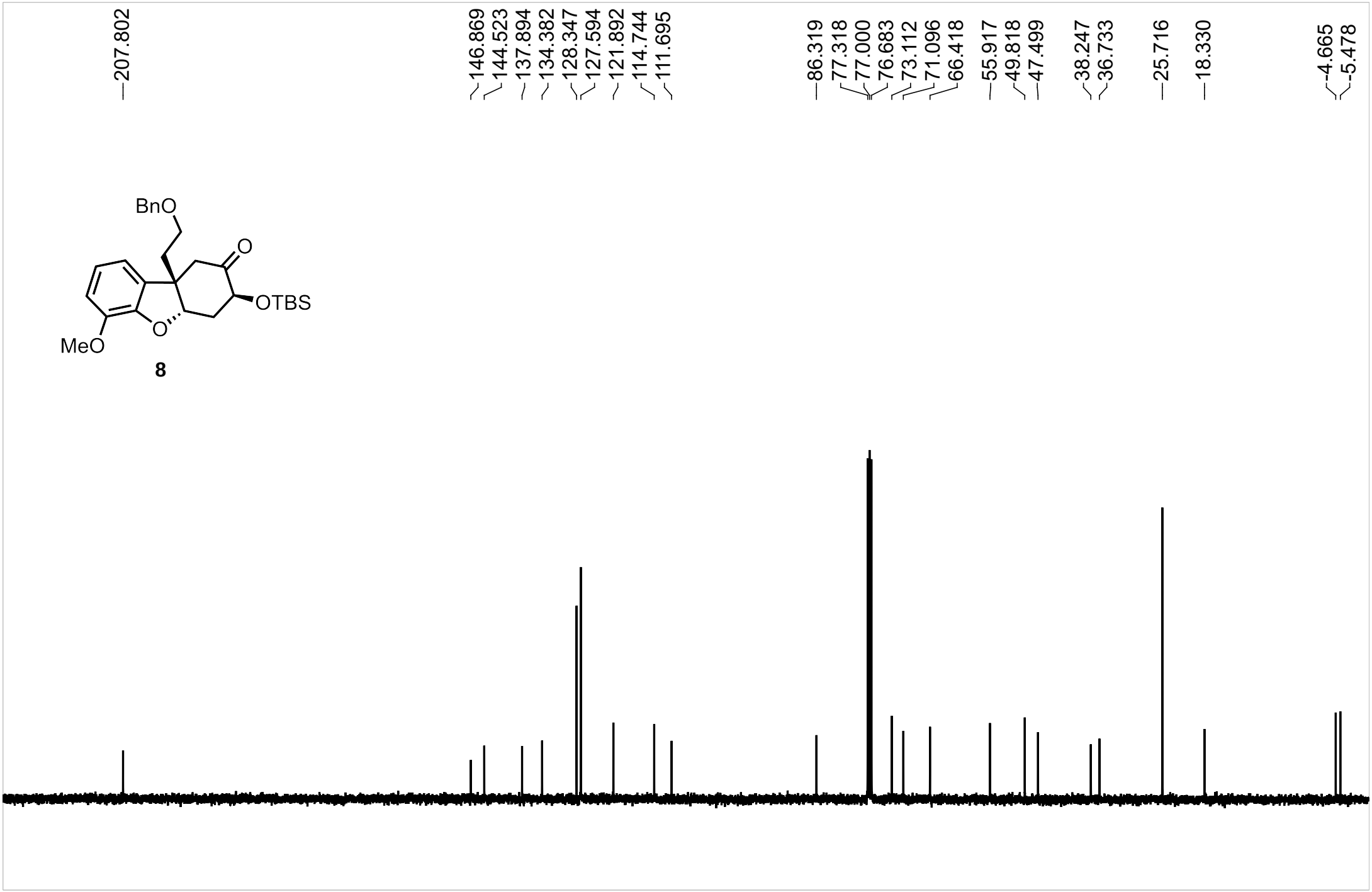
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47.499
38.247
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25.716
18.330
-4.665
-5.478
BnO
O
OTBS
O
MeO
8
220
210
200
190
180
170
160
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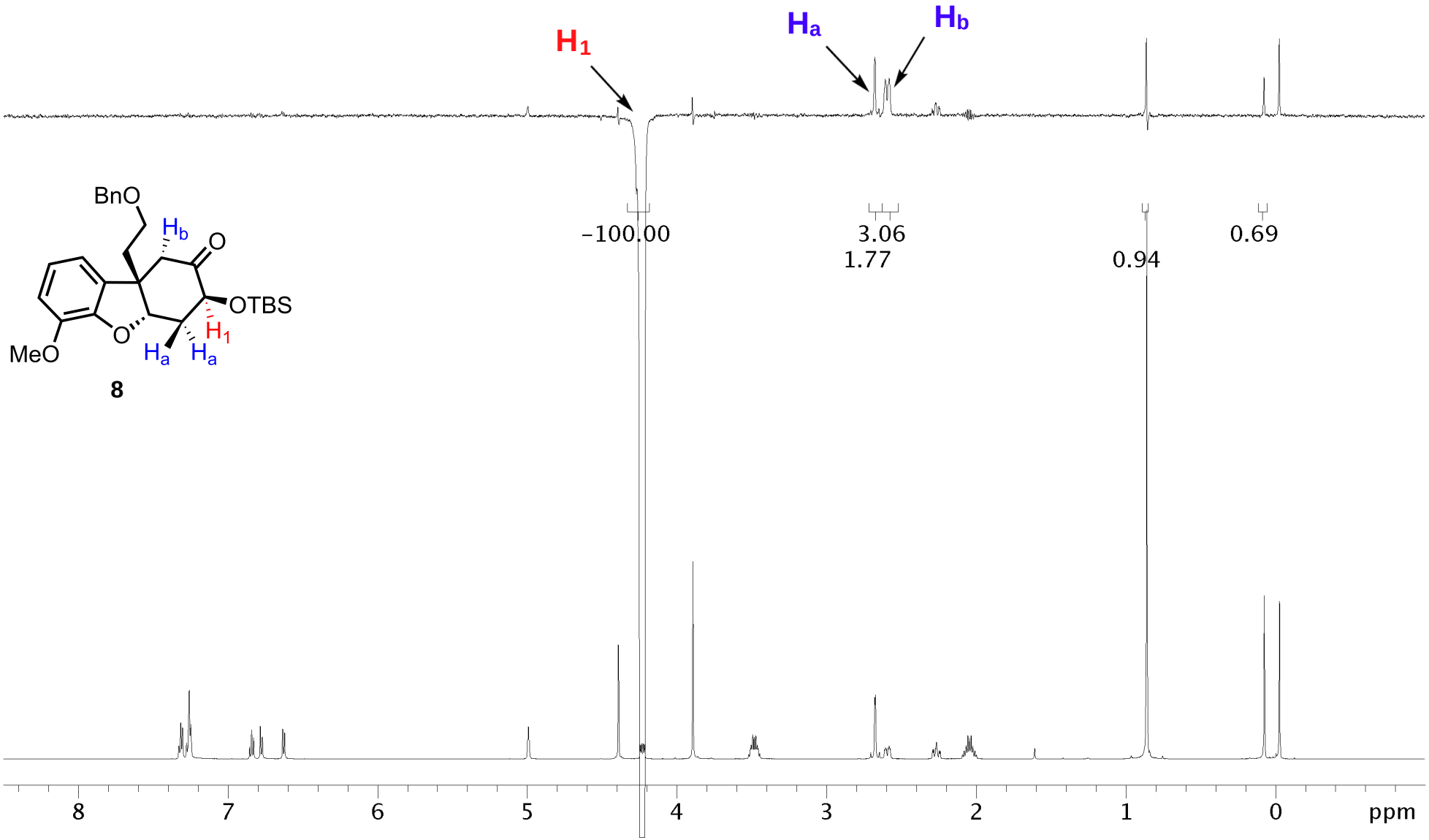
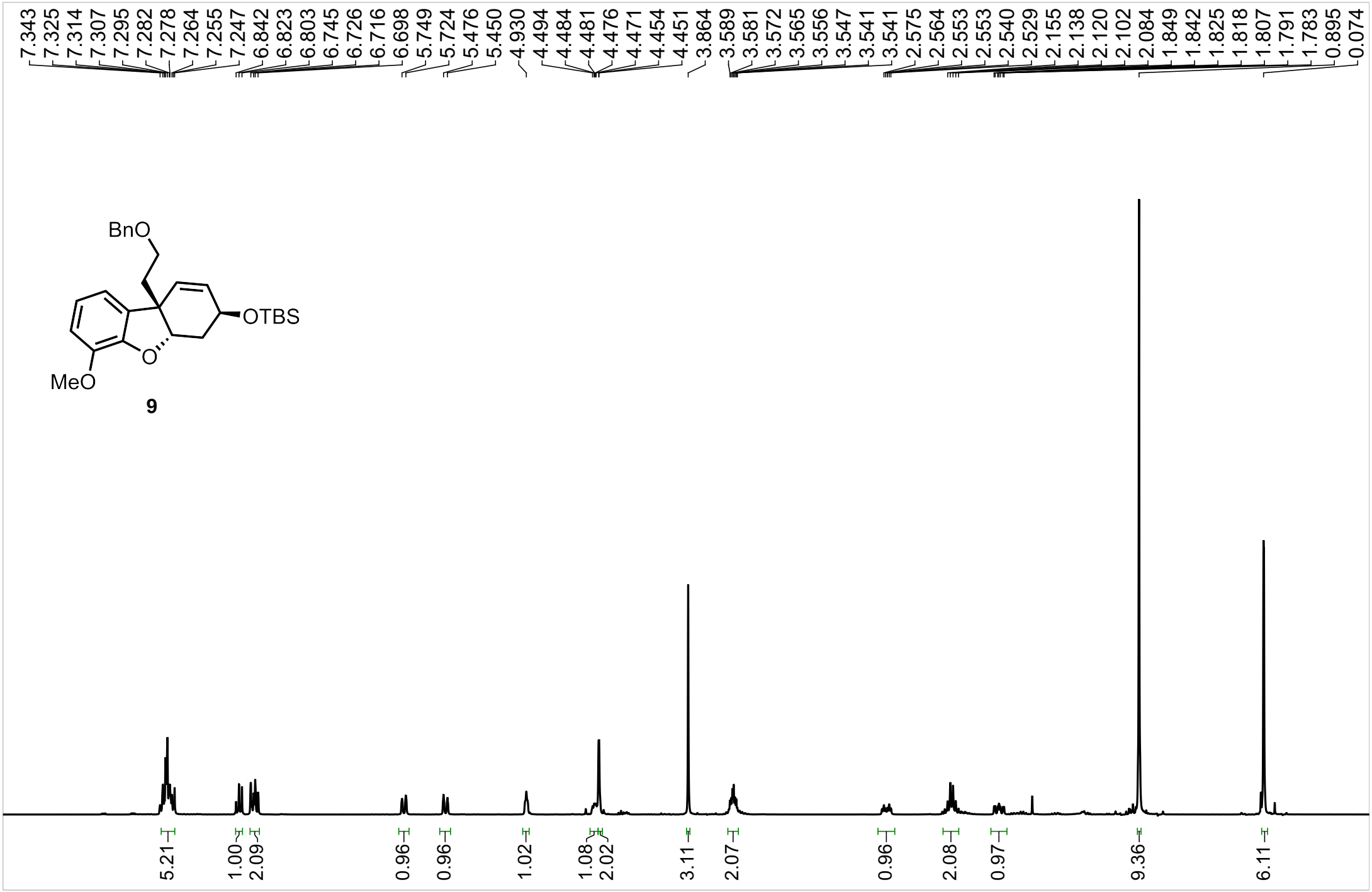
1D-NOESY Experiment

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6.745
6.726
6.716
6.698
5.749
5.724
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5.450
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4.484
4.481
4.476
4.471
4.454
4.451
3.864
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3.581
3.572
3.565
3.556
3.547
3.541
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2.575
2.564
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2.553
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2.529
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2.120
2.102
2.084
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1.842
1.825
1.818
1.807
1.791
1.783
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0.074
BnO
OTBS
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MeO
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1.08
2.02
3.11
2.07
0.96
2.08
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6.11
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6.0
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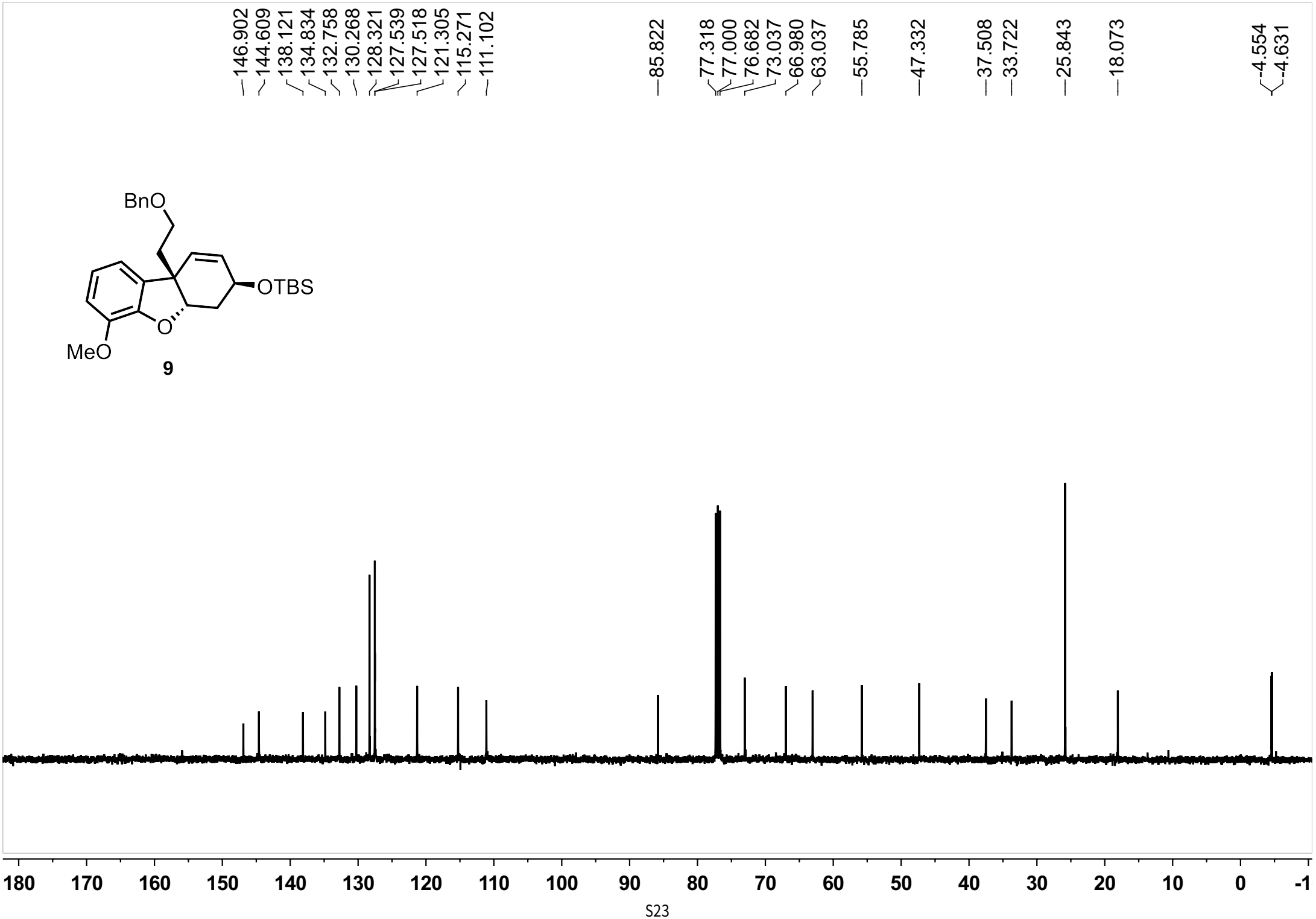
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77.318
77.000
76.682
73.037
66.980
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37.508
33.722
25.843
18.073
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-4.631
BnO
OTBS
O
MeO
9
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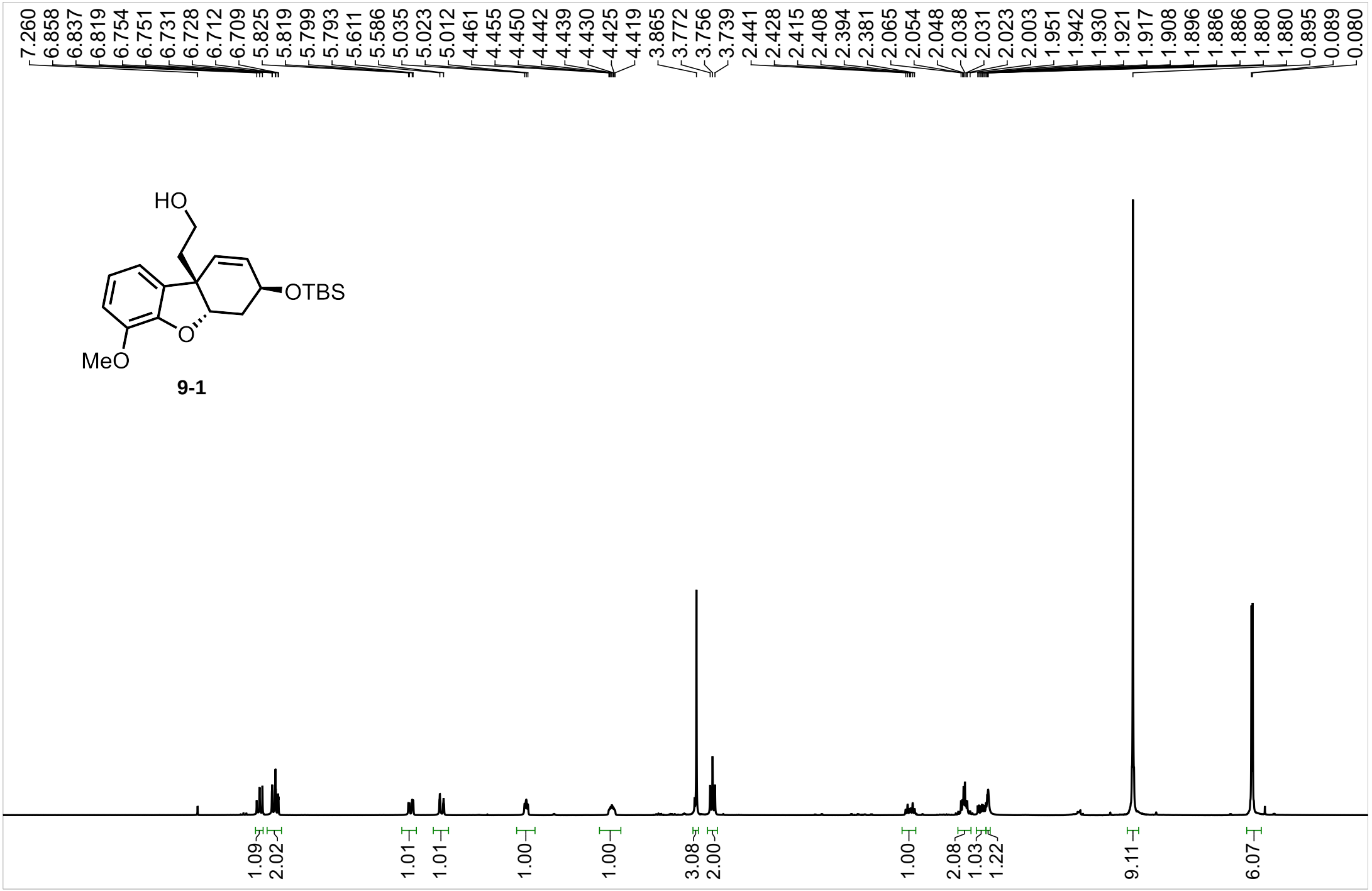
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5.793
5.611
5.586
5.035
5.023
5.012
4.461
4.455
4.450
4.442
4.439
4.430
4.425
4.419
3.865
3.772
3.756
3.739
2.441
2.428
2.415
2.408
2.394
2.381
2.065
2.054
2.048
2.038
2.031
2.023
2.003
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1.942
1.930
1.921
1.917
1.908
1.896
1.886
1.886
1.880
1.880
0.895
0.089
0.080
HO
OTBS
O
MeO
9-1
1.09
2.02
1.01
1.01
1.00
1.00
3.08
2.00
1.00
2.08
1.03
1.22
9.11
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7.0
6.5
6.0
5.5
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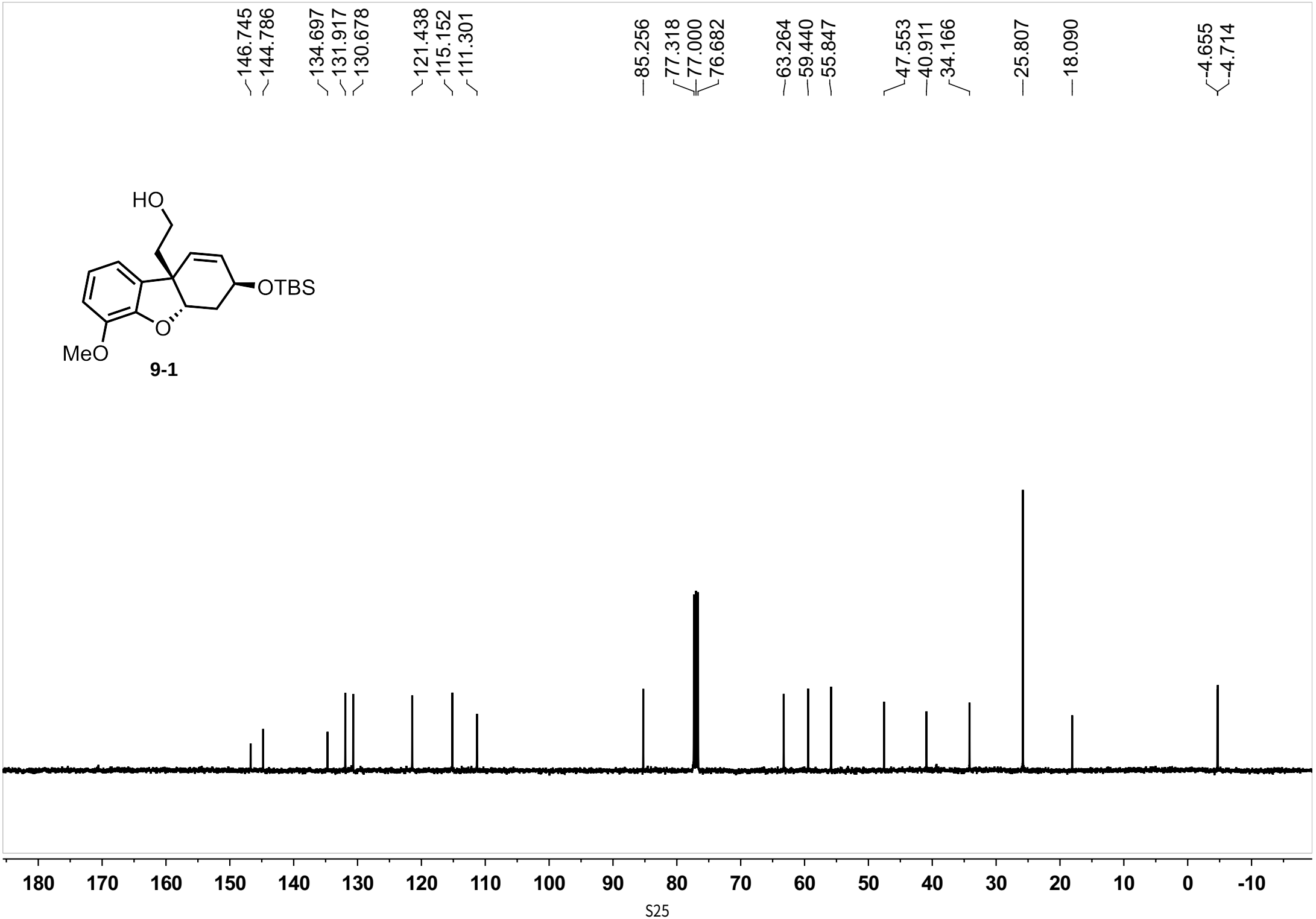
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111.301
85.256
77.318
77.000
76.682
63.264
59.440
55.847
47.553
40.911
34.166
25.807
18.090
-4.655
-4.714
HO
OTBS
O
MeO
9-1
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130
120
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20
10
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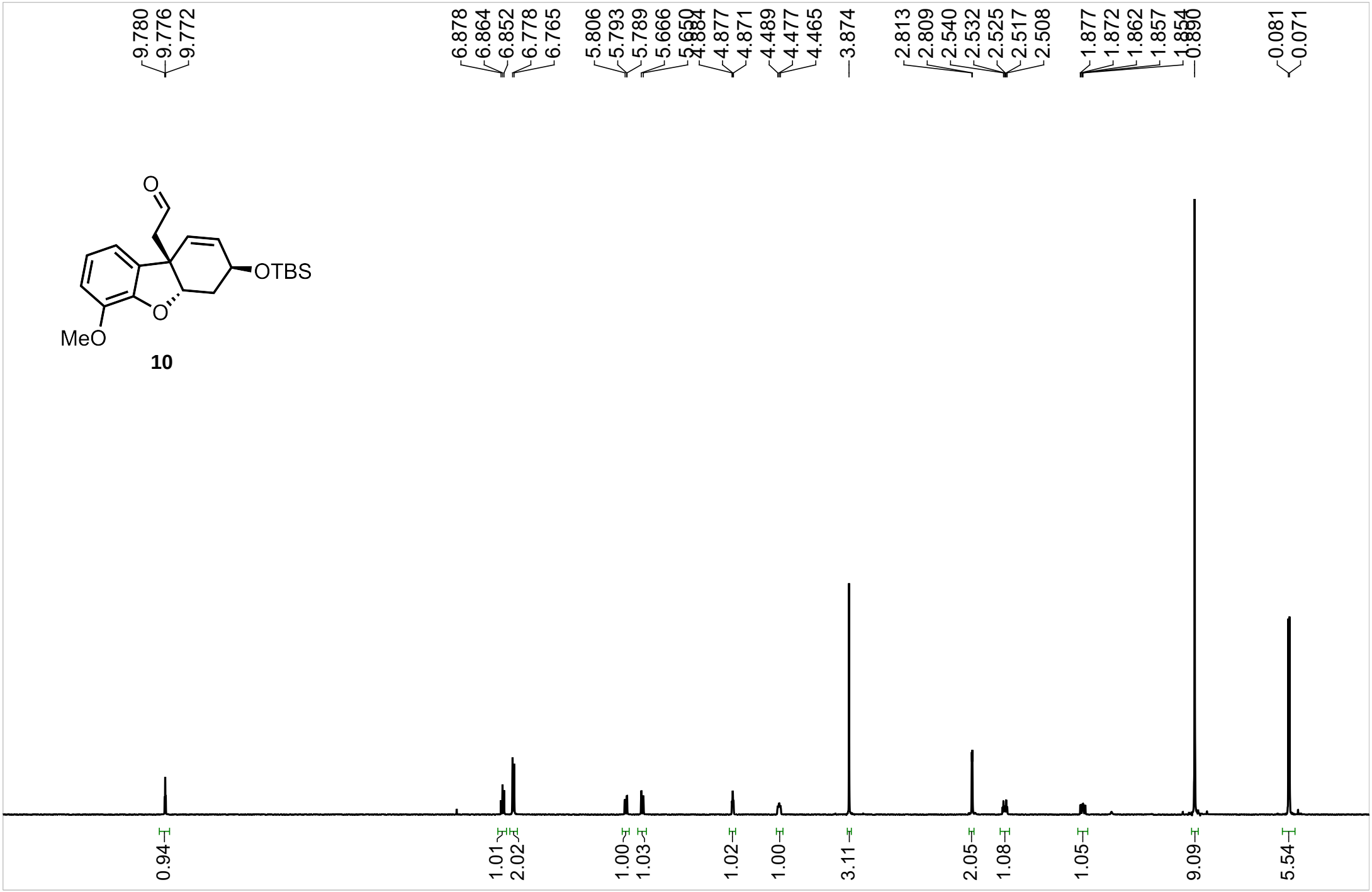
-10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6.765
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5.793
5.789
5.666
4.877
4.871
4.489
4.477
4.465
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2.813
2.809
2.540
2.532
2.525
2.517
2.508
1.877
1.872
1.862
1.857
0.081
0.071
O
OTBS
O
MeO
10
0.94
1.01
2.02
1.00
1.03
1.02
1.00
3.11
2.05
1.08
1.05
9.09
5.54
10.5
9.5
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8.0
7.5
7.0
6.5
6.0
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2.0
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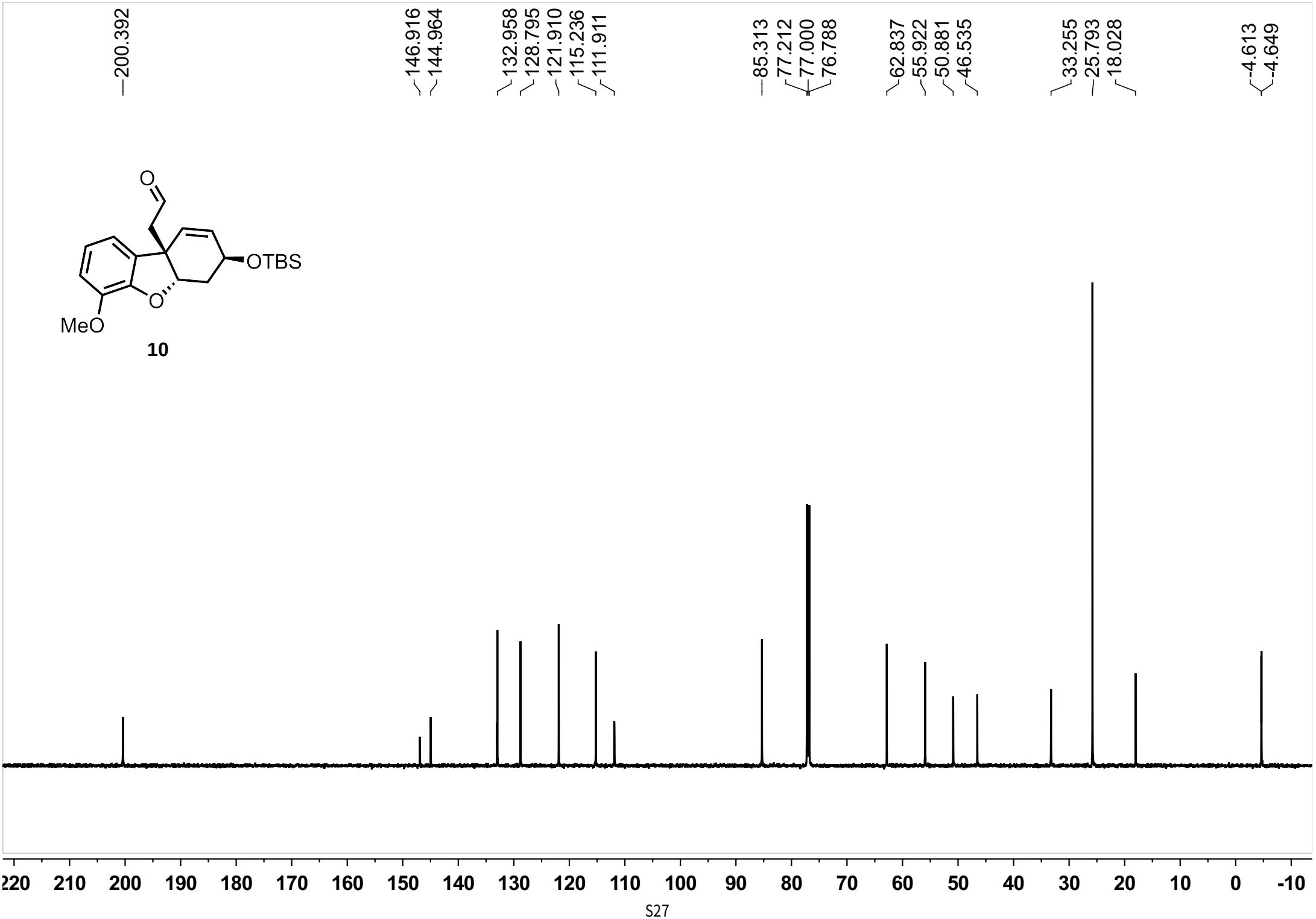
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62.837
55.922
50.881
46.535
33.255
25.793
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O
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O
MeO
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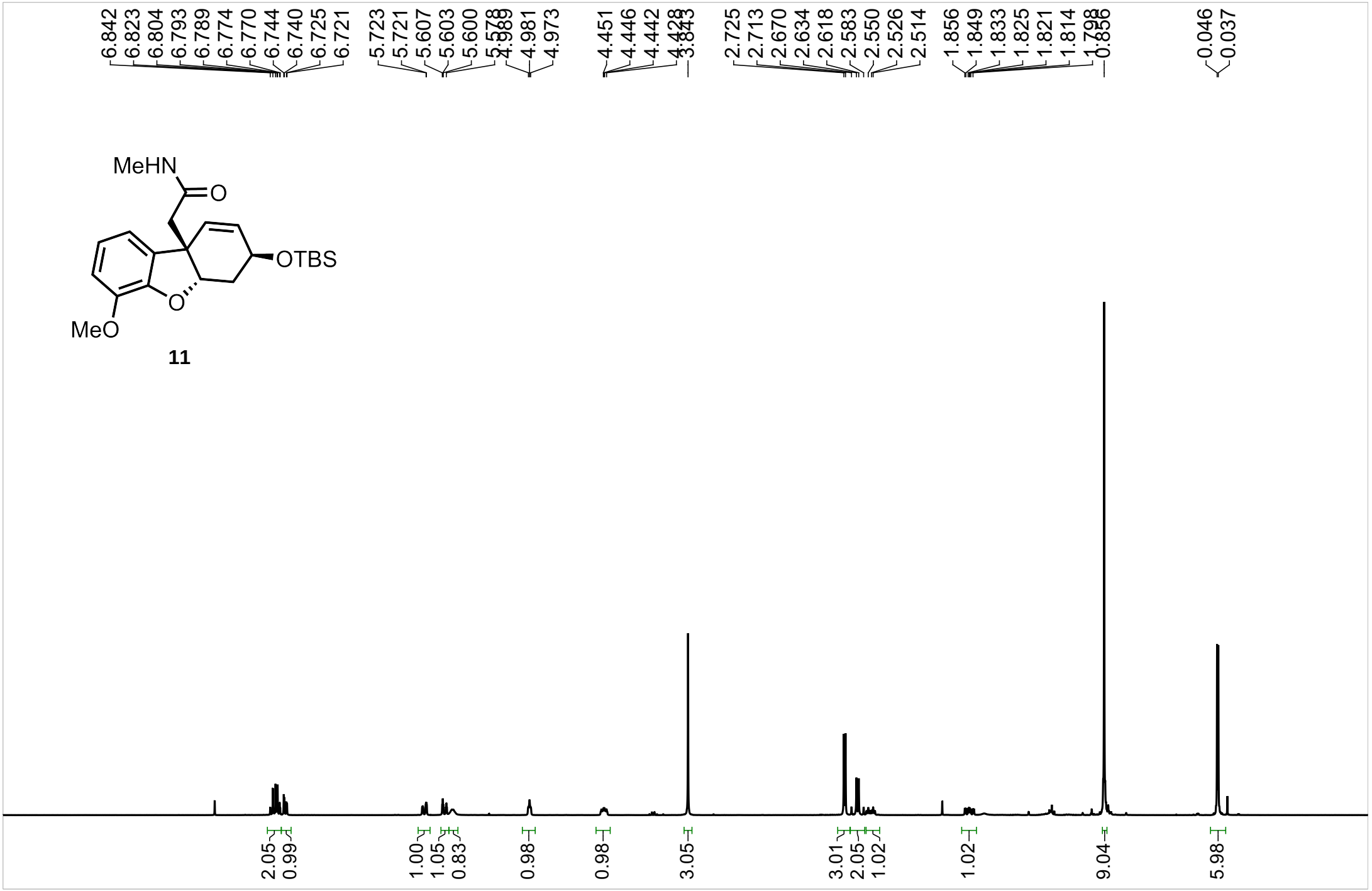
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5.607
5.603
5.600
5.578
4.989
4.981
4.973
4.451
4.446
4.442
4.428
3.843
2.725
2.713
2.670
2.634
2.618
2.583
2.550
2.526
2.514
1.856
1.849
1.833
1.825
1.821
1.814
1.798
0.856
0.046
0.037
MeHN
O
OTBS
O
MeO
11
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1.00
1.05
0.83
0.98
0.98
3.05
3.01
2.05
1.02
1.02
9.04
5.98
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5.5
5.0
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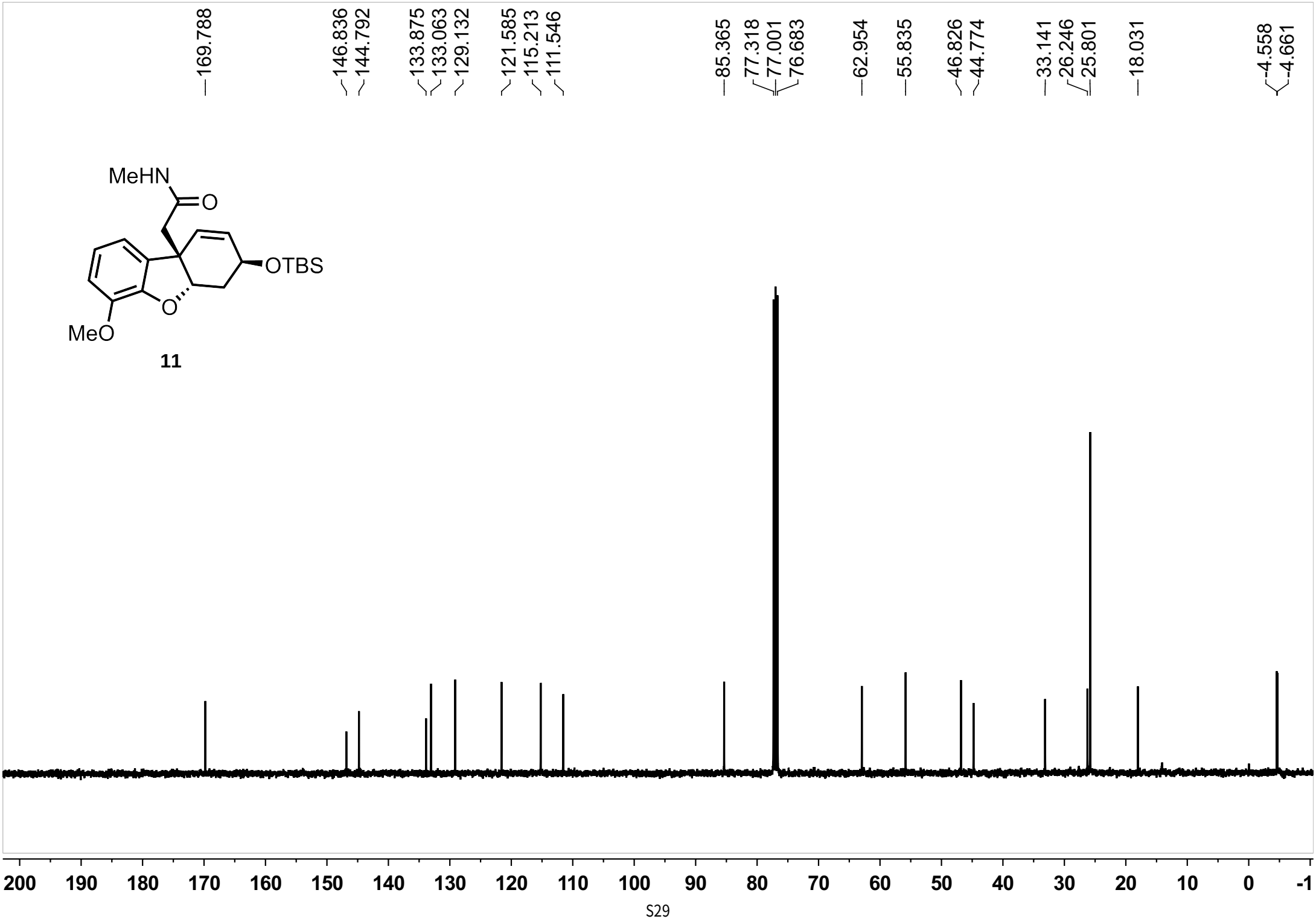
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76.683
62.954
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46.826
44.774
33.141
26.246
25.801
18.031
-4.558
-4.661
MeHN
O
OTBS
O
MeO
11
200
190
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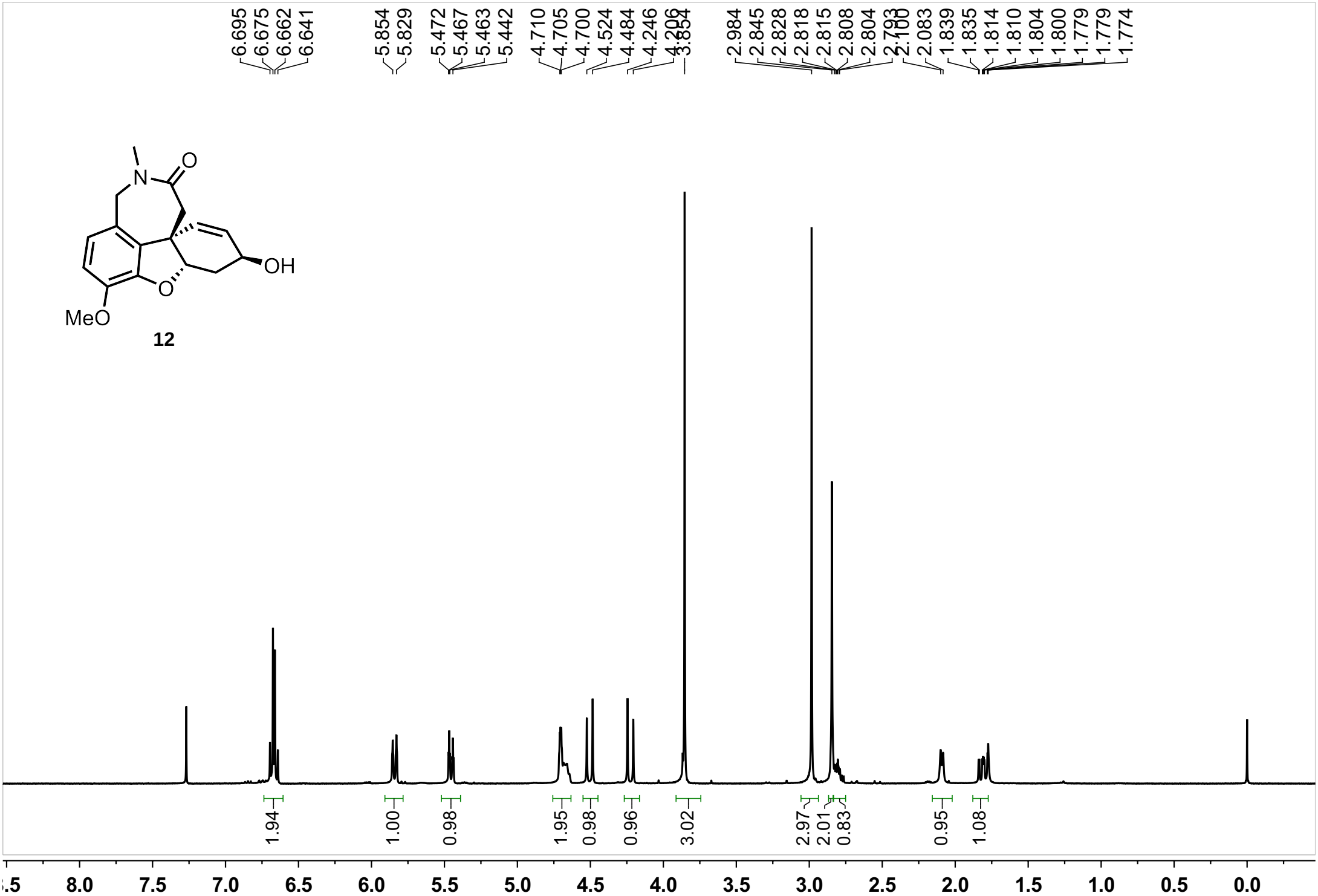
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4.700
4.524
4.484
4.246
4.206
3.854
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2.845
2.828
2.818
2.815
2.808
2.804
2.793
2.100
2.083
1.839
1.835
1.814
1.810
1.804
1.800
1.779
1.779
1.774
N
O
OH
O
MeO
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0.98
1.95
0.98
0.96
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2.97
2.01
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0.95
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6.0
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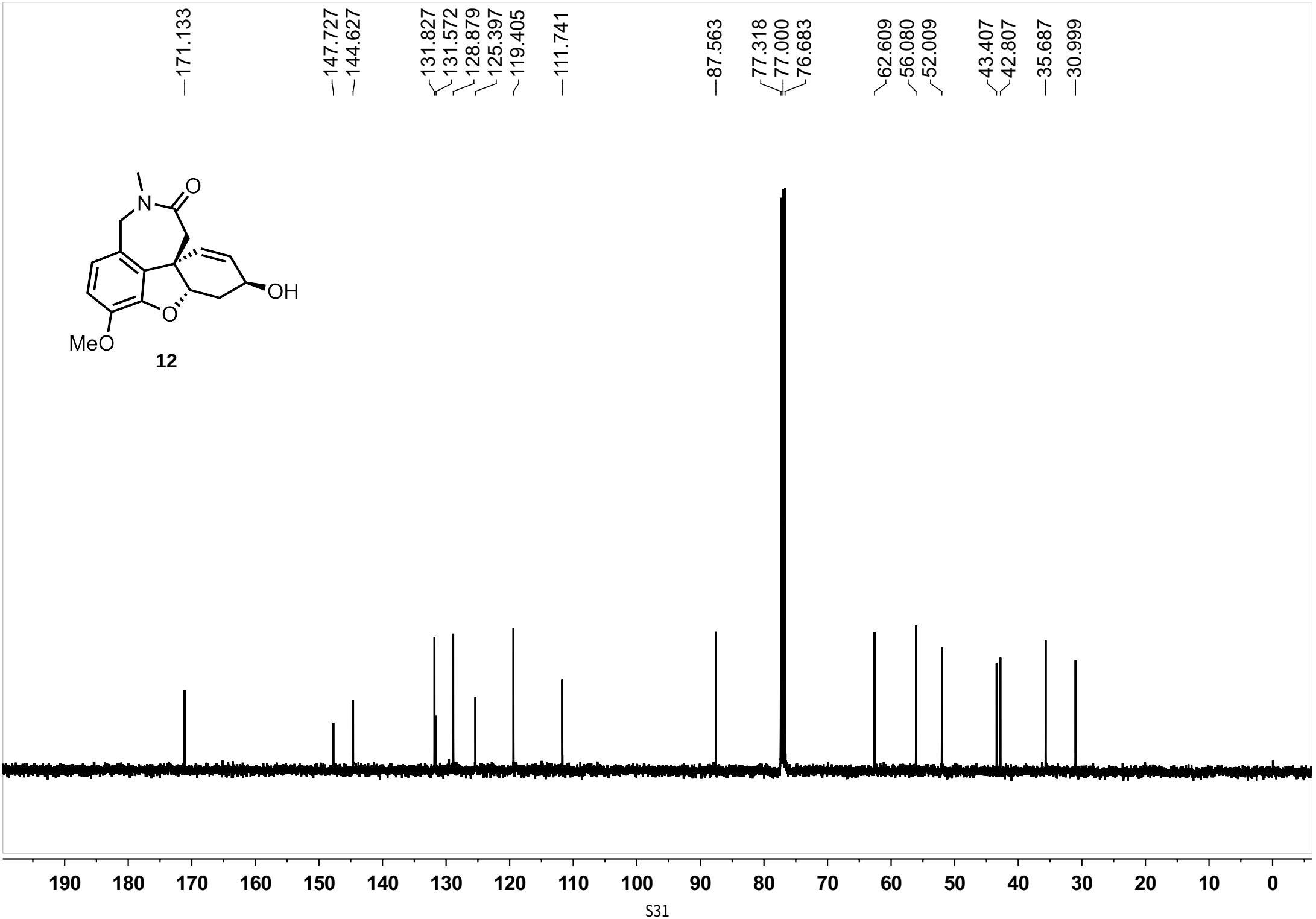
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43.407
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OH
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MeO
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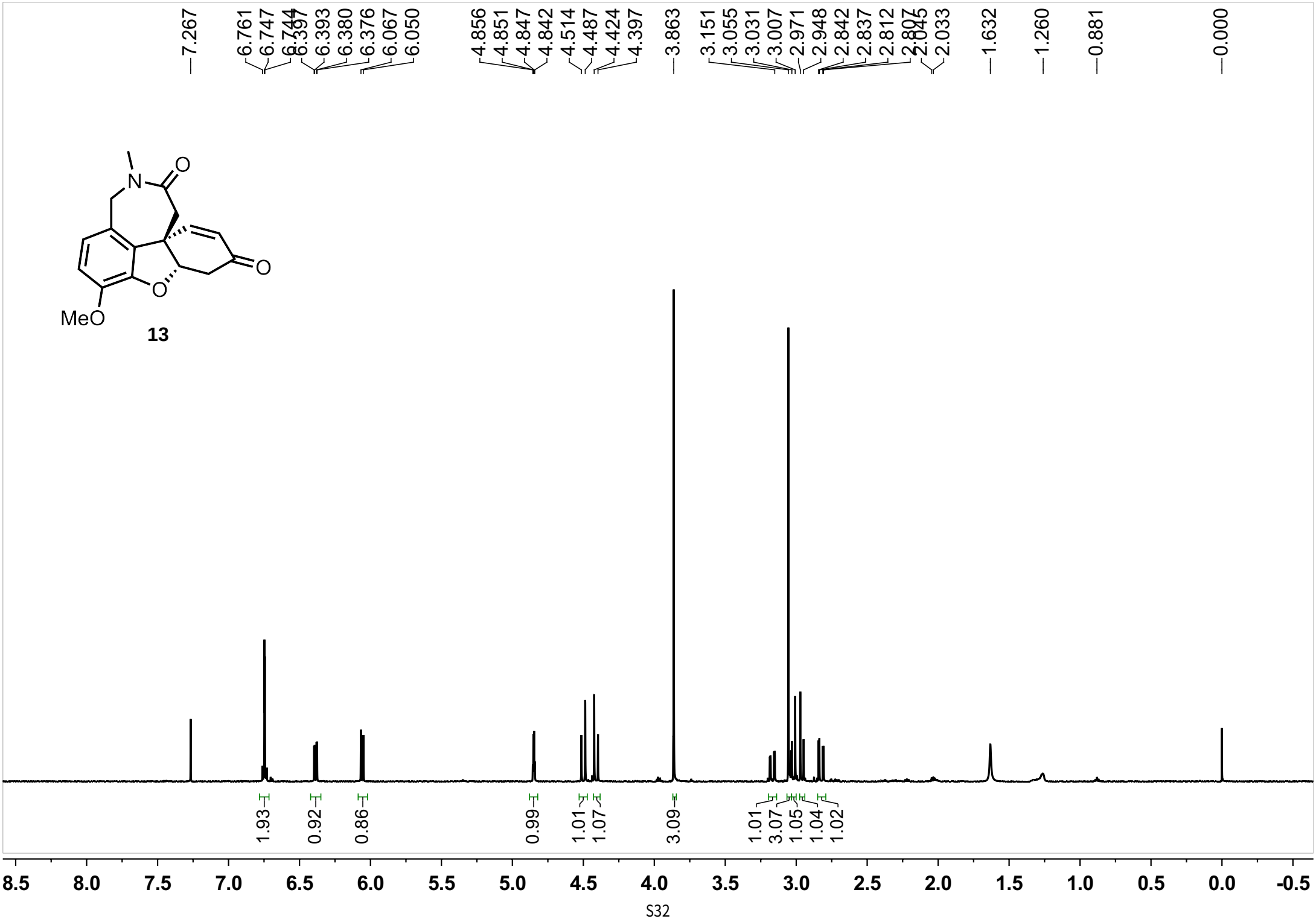
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3.055
3.031
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2.971
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2.842
2.837
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2.807
2.045
2.033
1.632
1.260
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O
O
MeO
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1.07
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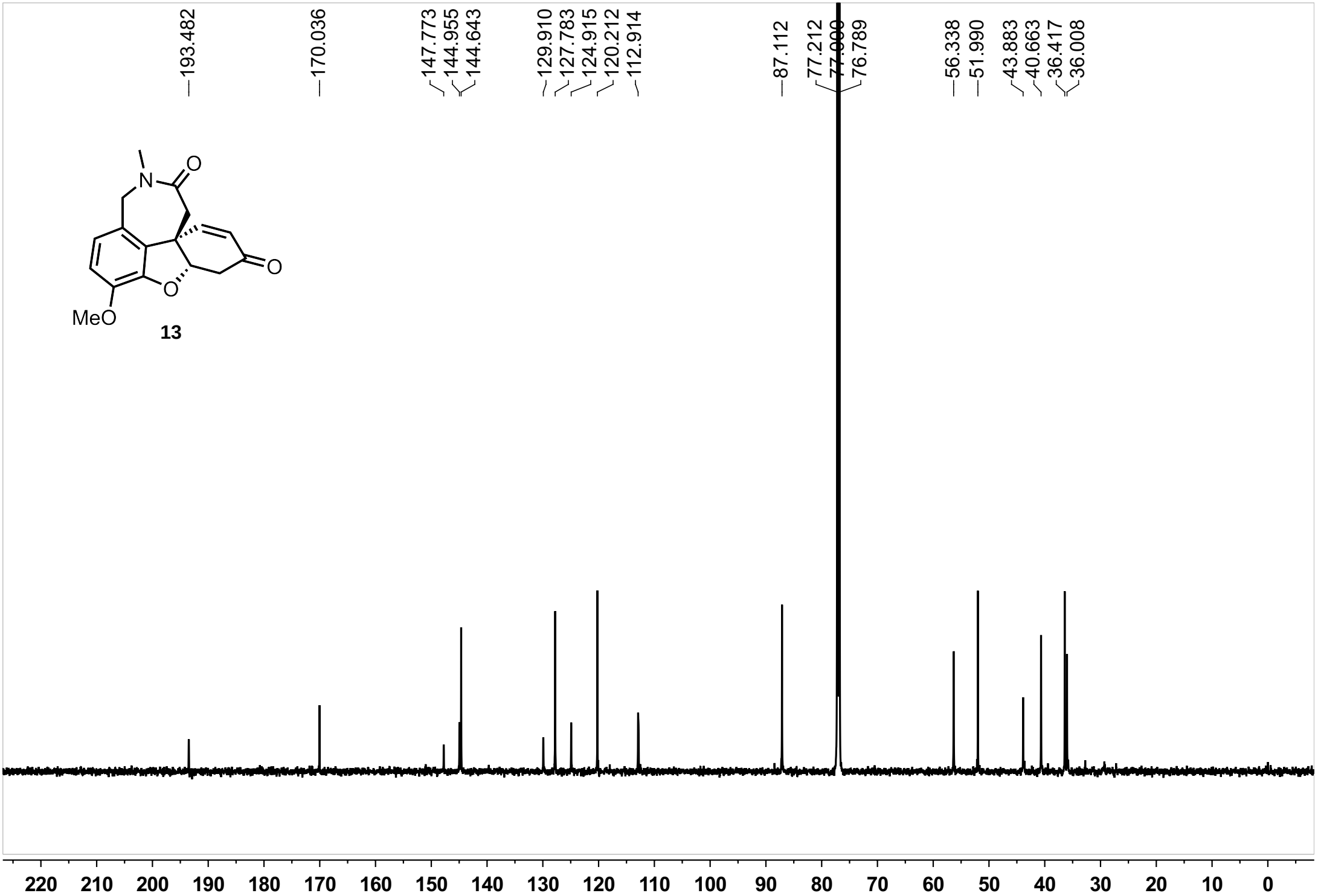
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77.000
76.789
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51.990
43.883
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36.008
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O
O
MeO
13
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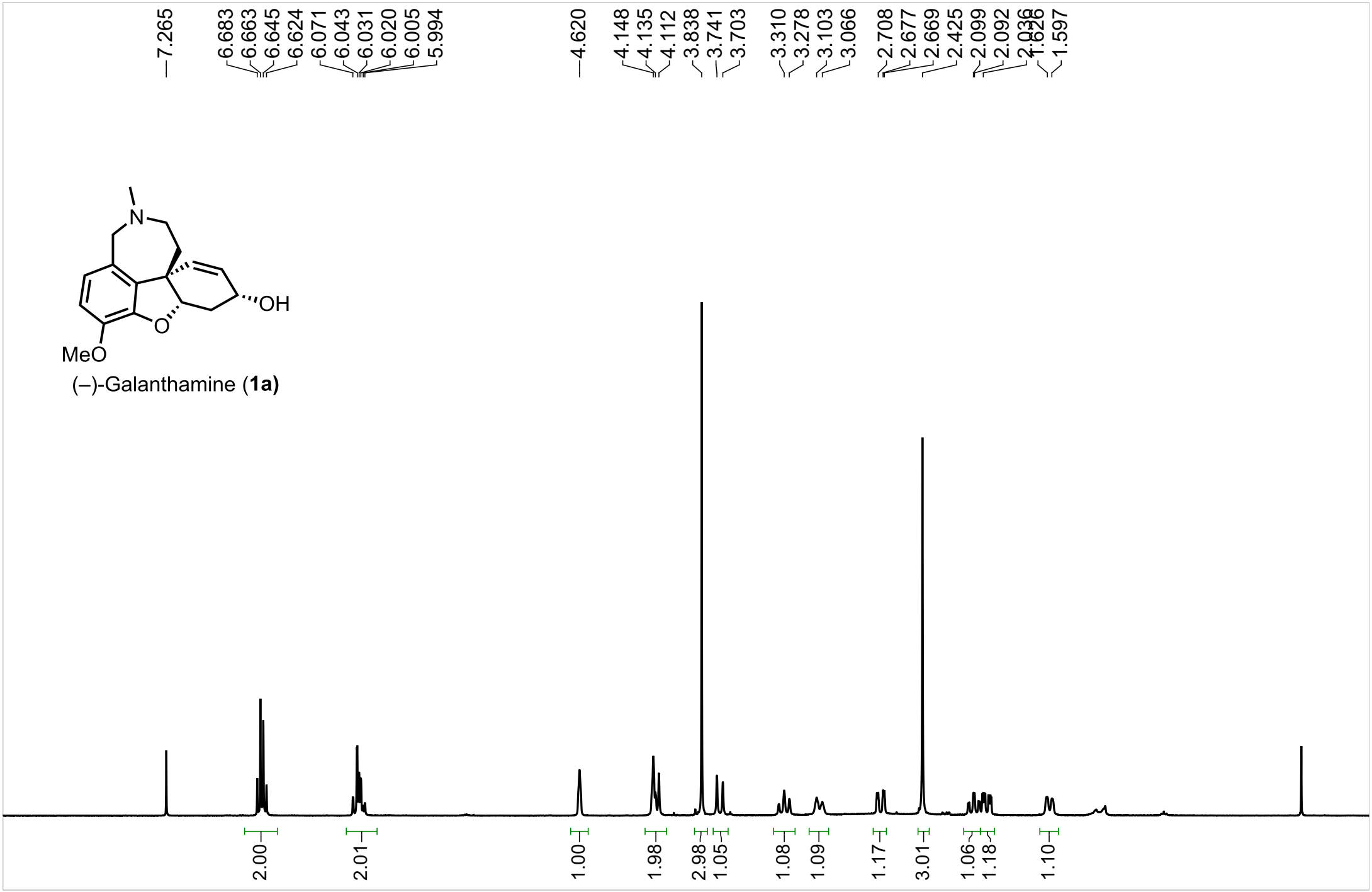
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3.066
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2.669
2.425
2.099
2.092
2.036
1.626
1.597
N
OH
O
MeO
(–)-Galanthamine (1a)
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2.01
1.00
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2.98
1.05
1.08
1.09
1.17
3.01
1.06
1.18
1.10
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7.0
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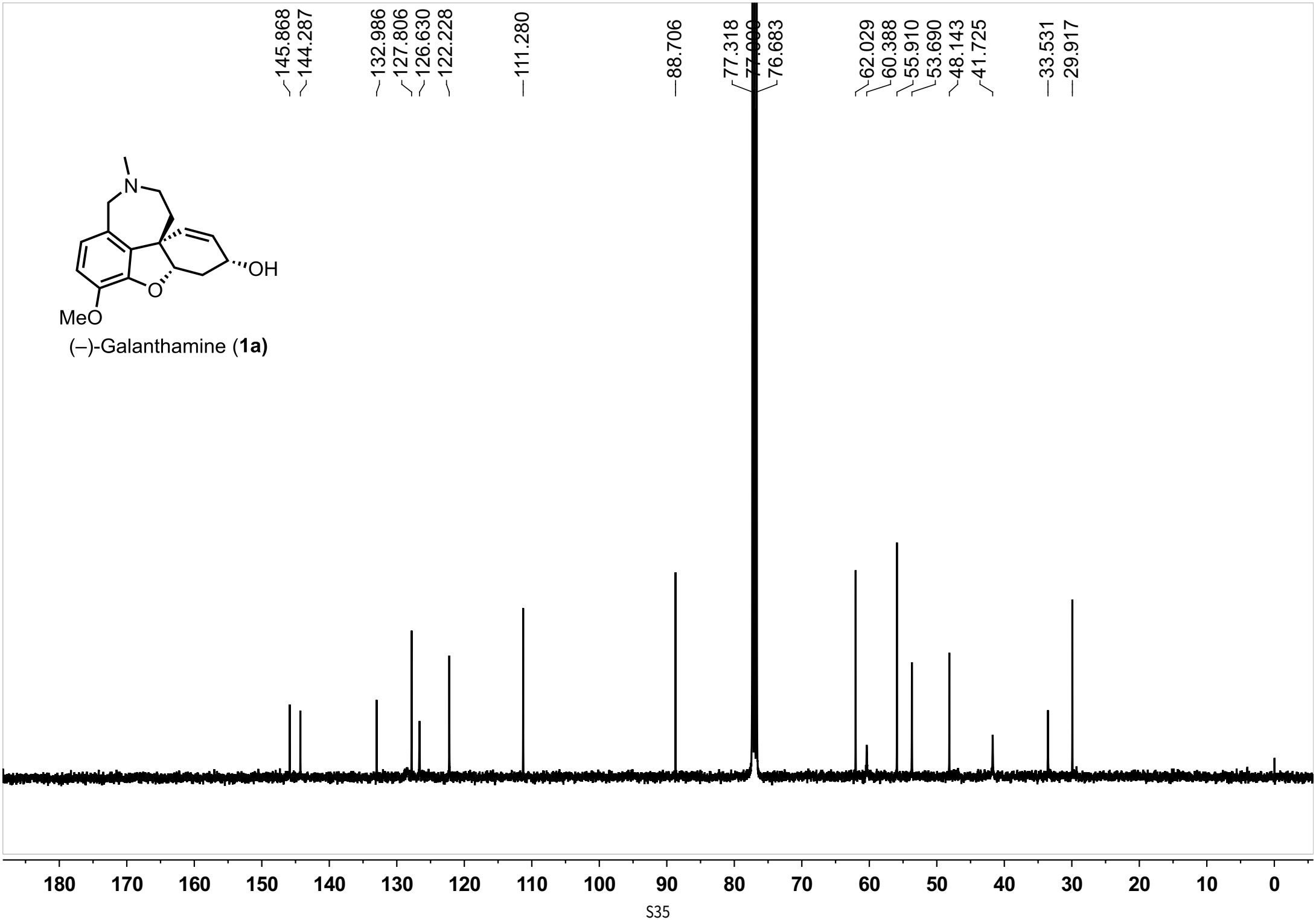
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55.910
53.690
48.143
41.725
33.531
29.917
N
OH
O
MeO
(–)-Galanthamine (1a)
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170
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150
140
130
120
110
100
90
80
70
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50
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30
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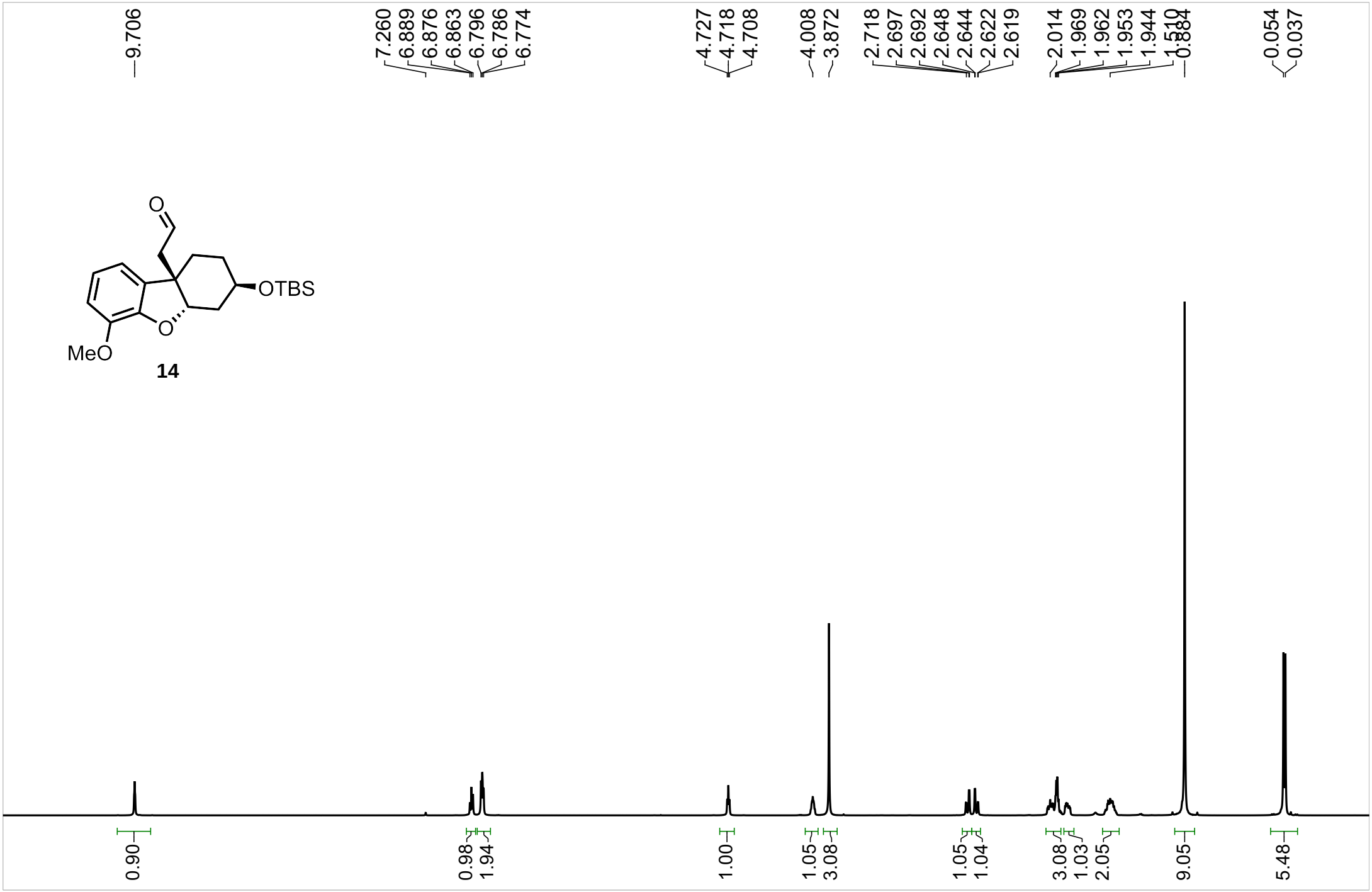
10
0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2.697
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2.644
2.622
2.619
2.014
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1.962
1.953
1.944
1.510
0.884
0.054
0.037
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OTBS
O
MeO
14
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0.98
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1.00
1.05
3.08
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1.04
3.08
1.03
2.05
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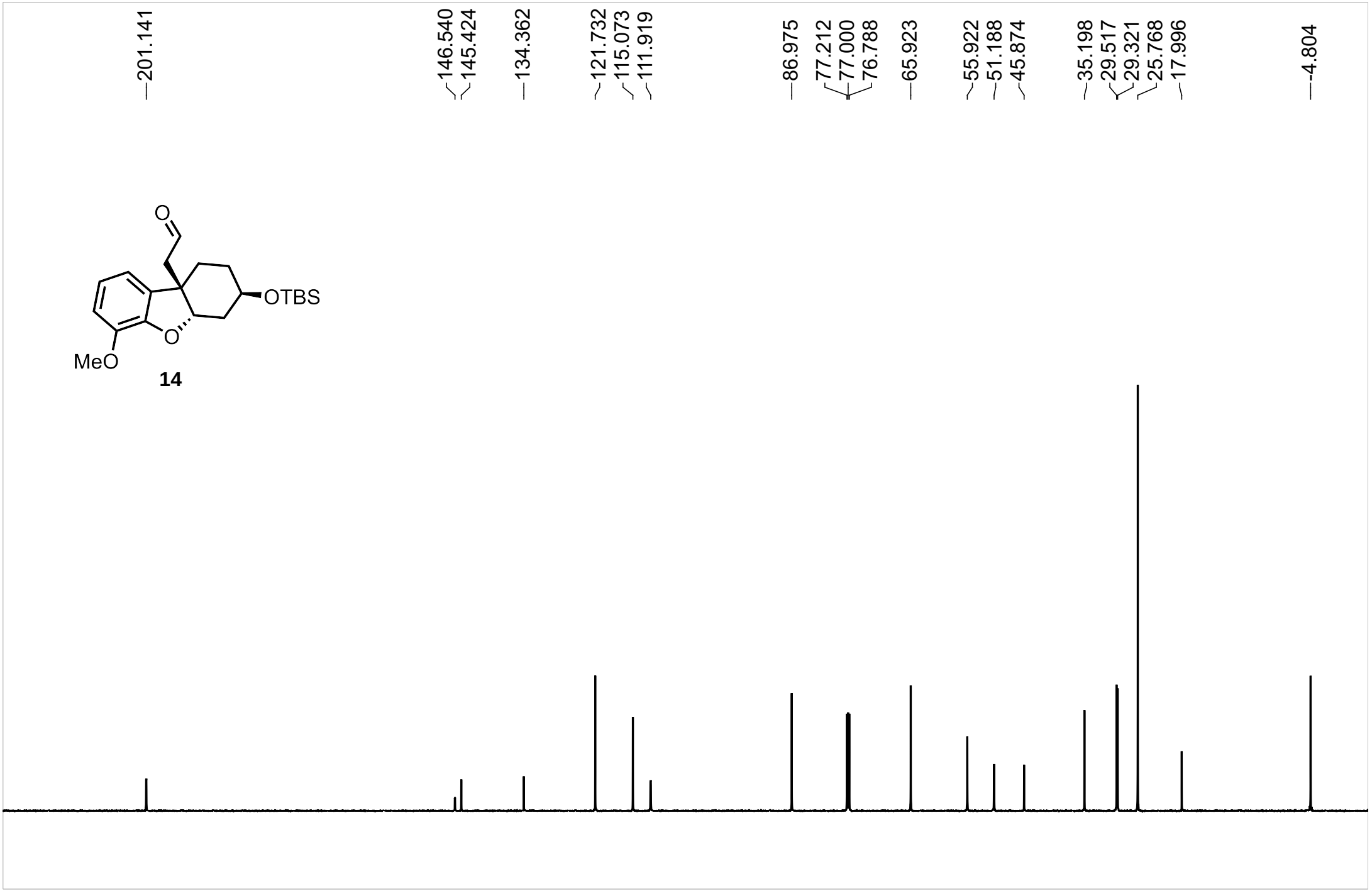
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51.188
45.874
35.198
29.517
29.321
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-4.804
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OTBS
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MeO
14
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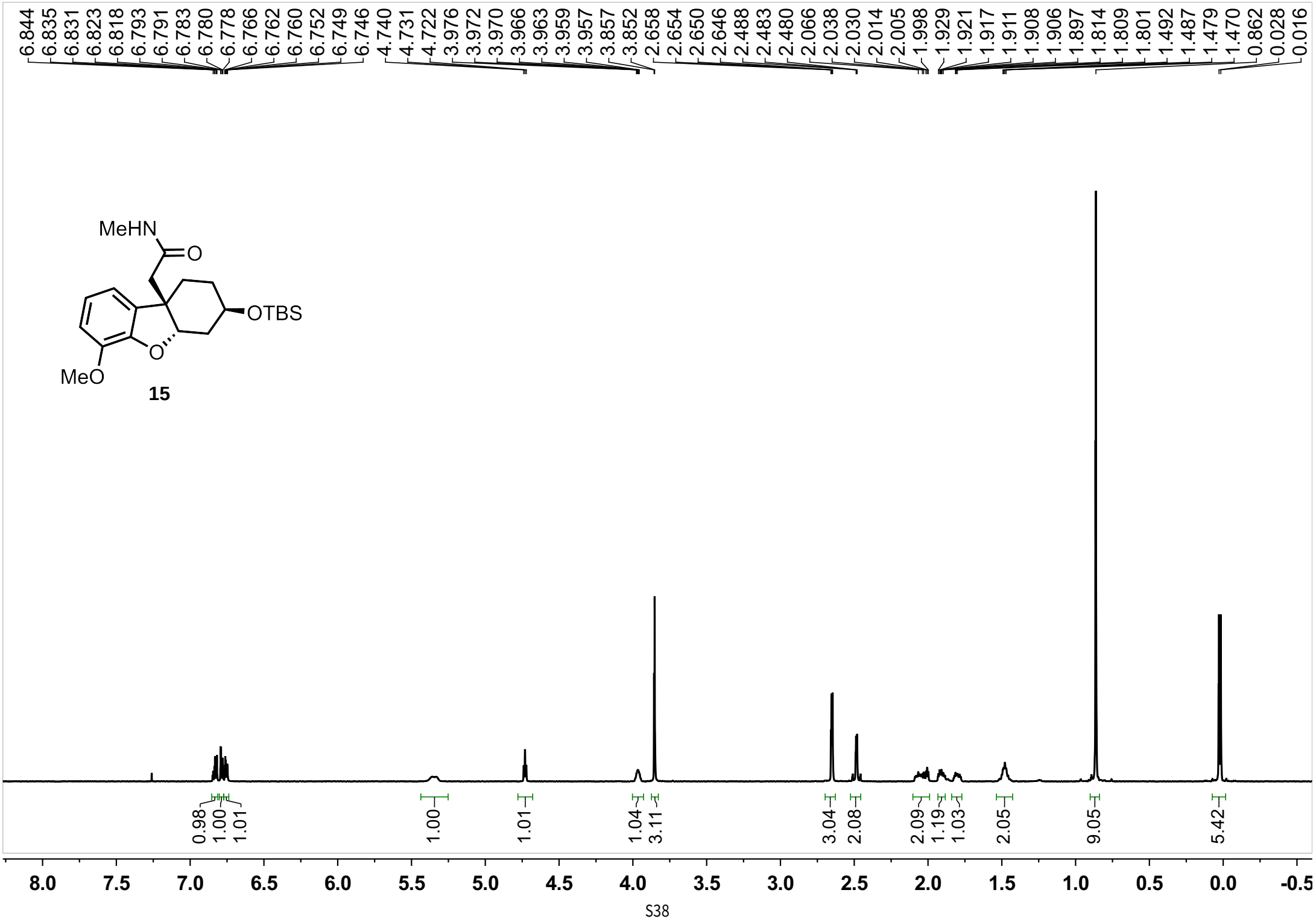
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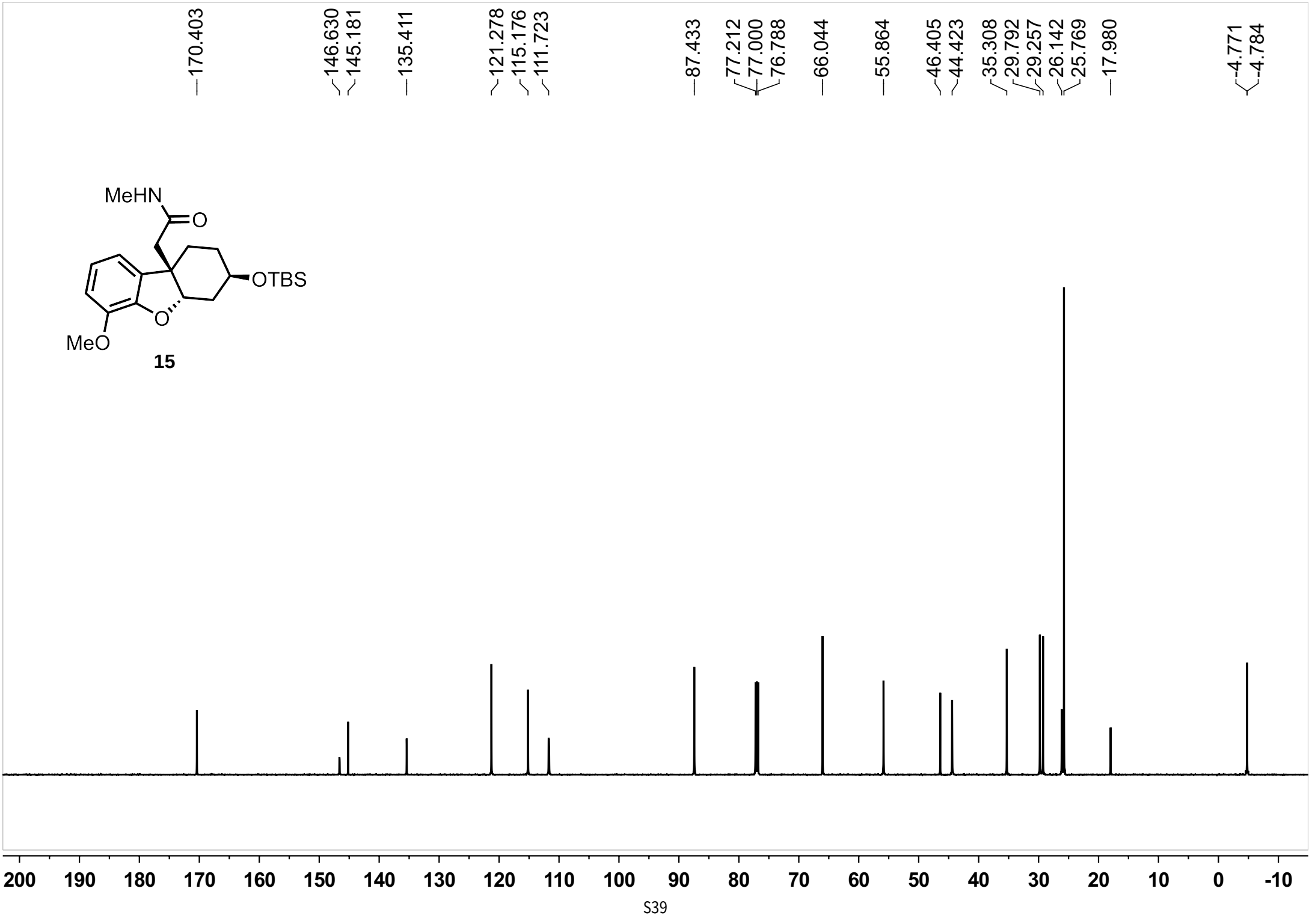
MeHN
O
OTBS
O
MeO
15
0.98 1.00 1.01 1.00 1.01 1.04 3.11 3.04 2.08 2.09 1.19 1.03 2.05 9.05 5.42
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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55.864
46.405
44.423
35.308
29.792
29.257
26.142
25.769
17.980
-4.771
-4.784
MeHN
O
OTBS
O
MeO
15
200
190
180
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110
100
90
80
70
60
50
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30
20
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0
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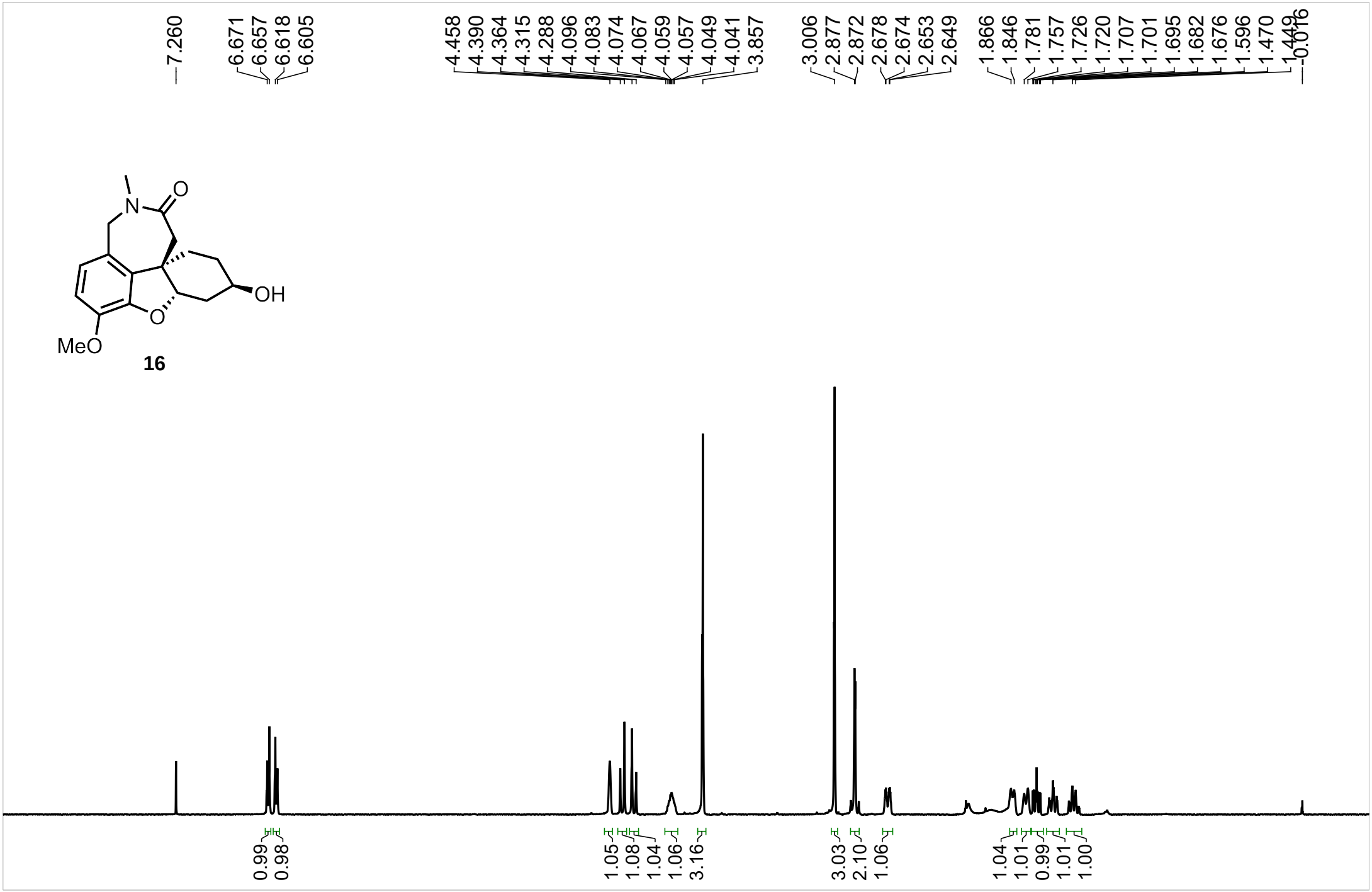
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6.671
6.657
6.618
6.605
4.458
4.390
4.364
4.315
4.288
4.096
4.083
4.074
4.067
4.059
4.057
4.049
4.041
3.857
3.006
2.877
2.872
2.678
2.674
2.653
2.649
1.866
1.846
1.781
1.757
1.726
1.720
1.707
1.701
1.695
1.682
1.676
1.596
1.470
1.449
-0.016
N
O
OH
O
MeO
16
0.99
0.98
1.05
1.08
1.04
1.06
3.16
3.03
2.10
1.06
1.04
1.01
0.99
1.01
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
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2.0
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1.0
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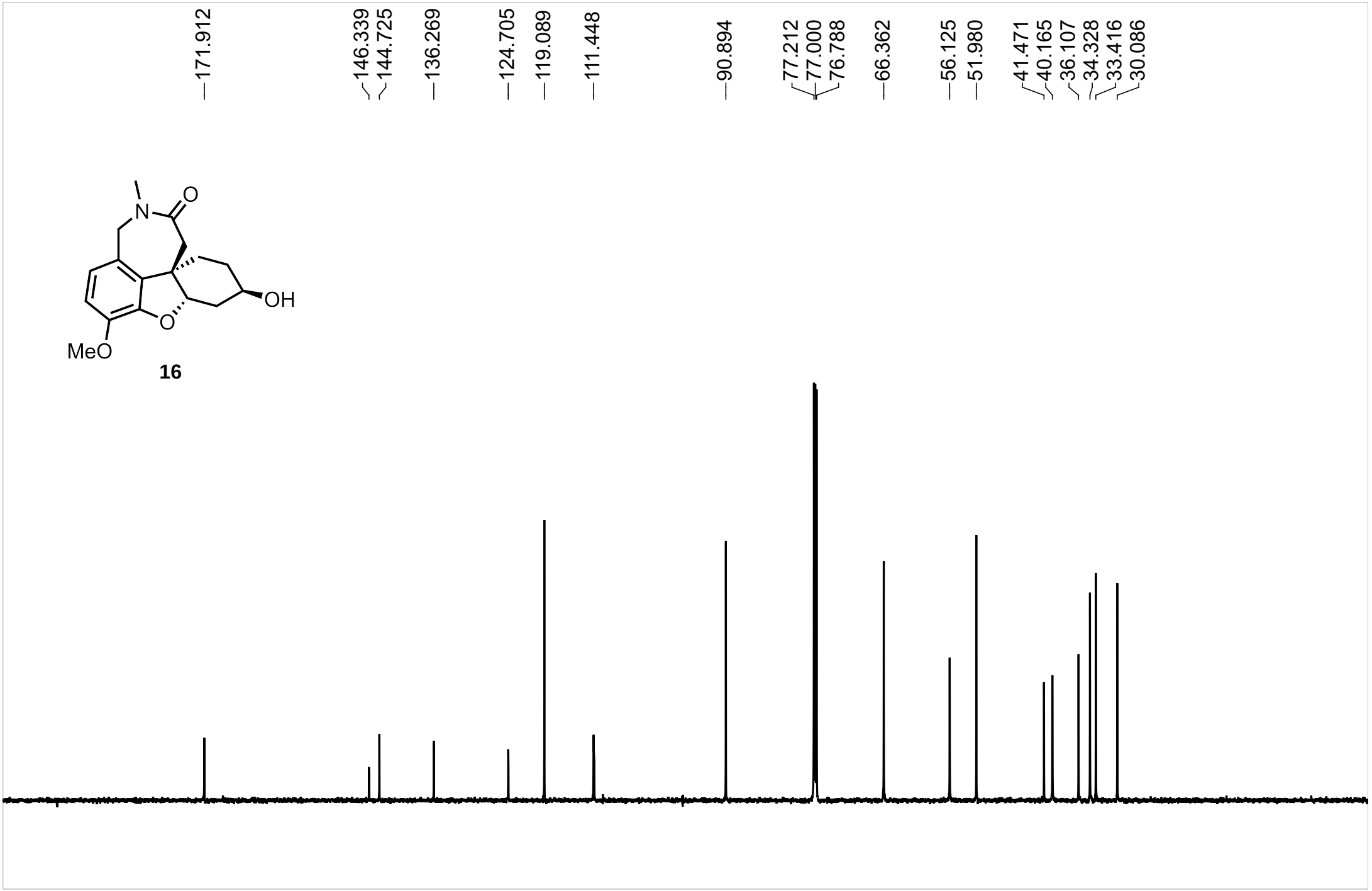
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144.725
136.269
124.705
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111.448
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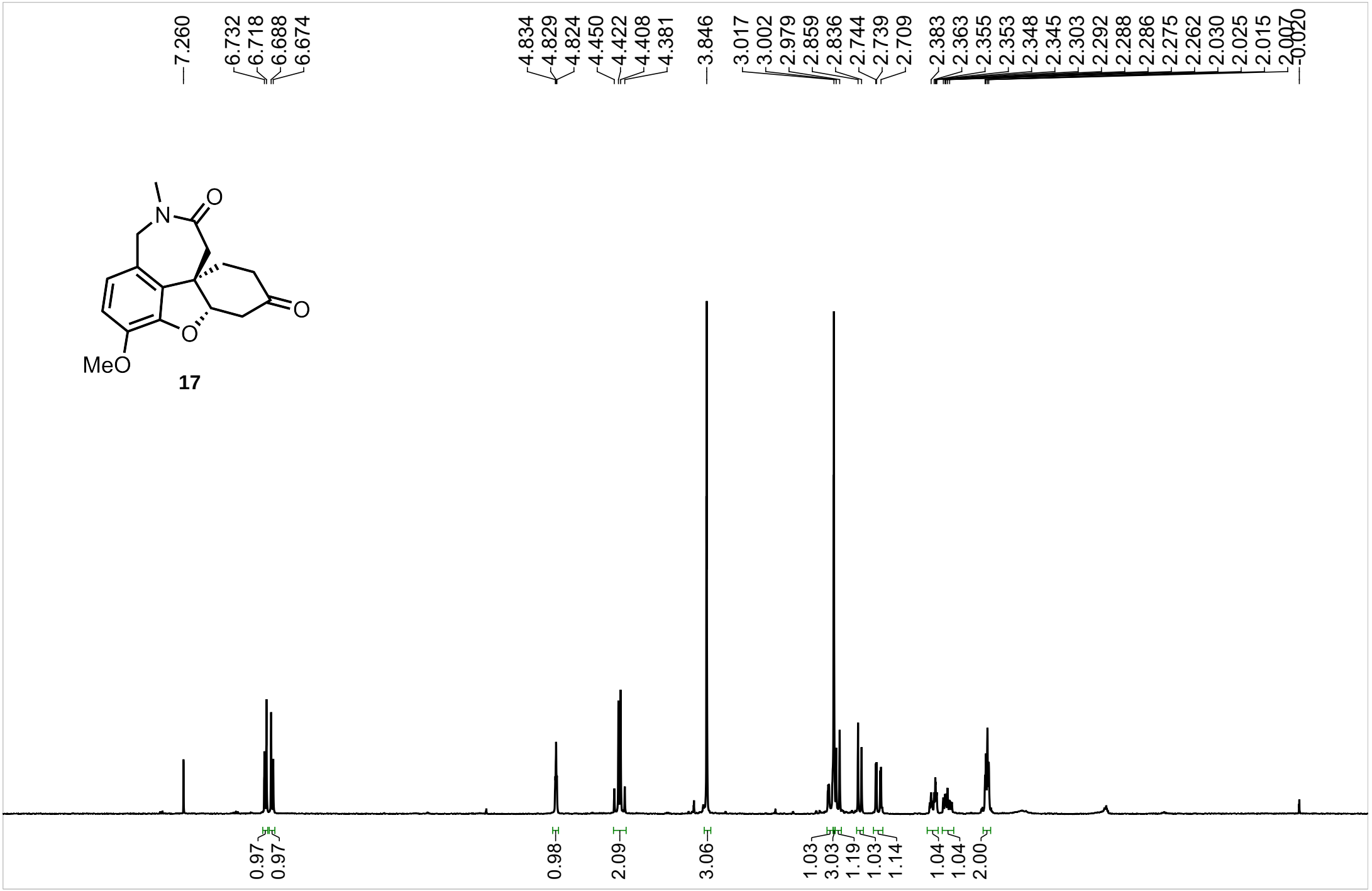
77.000
76.788
66.362
56.125
51.980
41.471
40.165
36.107
34.328
33.416
30.086
N
O
OH
O
MeO
16
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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6.674
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4.829
4.824
4.450
4.422
4.408
4.381
3.846
3.017
3.002
2.979
2.859
2.836
2.744
2.739
2.709
2.383
2.363
2.355
2.353
2.348
2.345
2.303
2.292
2.288
2.286
2.275
2.262
2.030
2.025
2.015
2.007
0.020
N
O
O
O
MeO
17
0.97
0.97
0.98
2.09
3.06
1.03
3.03
1.19
1.03
1.14
1.04
1.04
2.00
8.0
7.5
7.0
6.5
6.0
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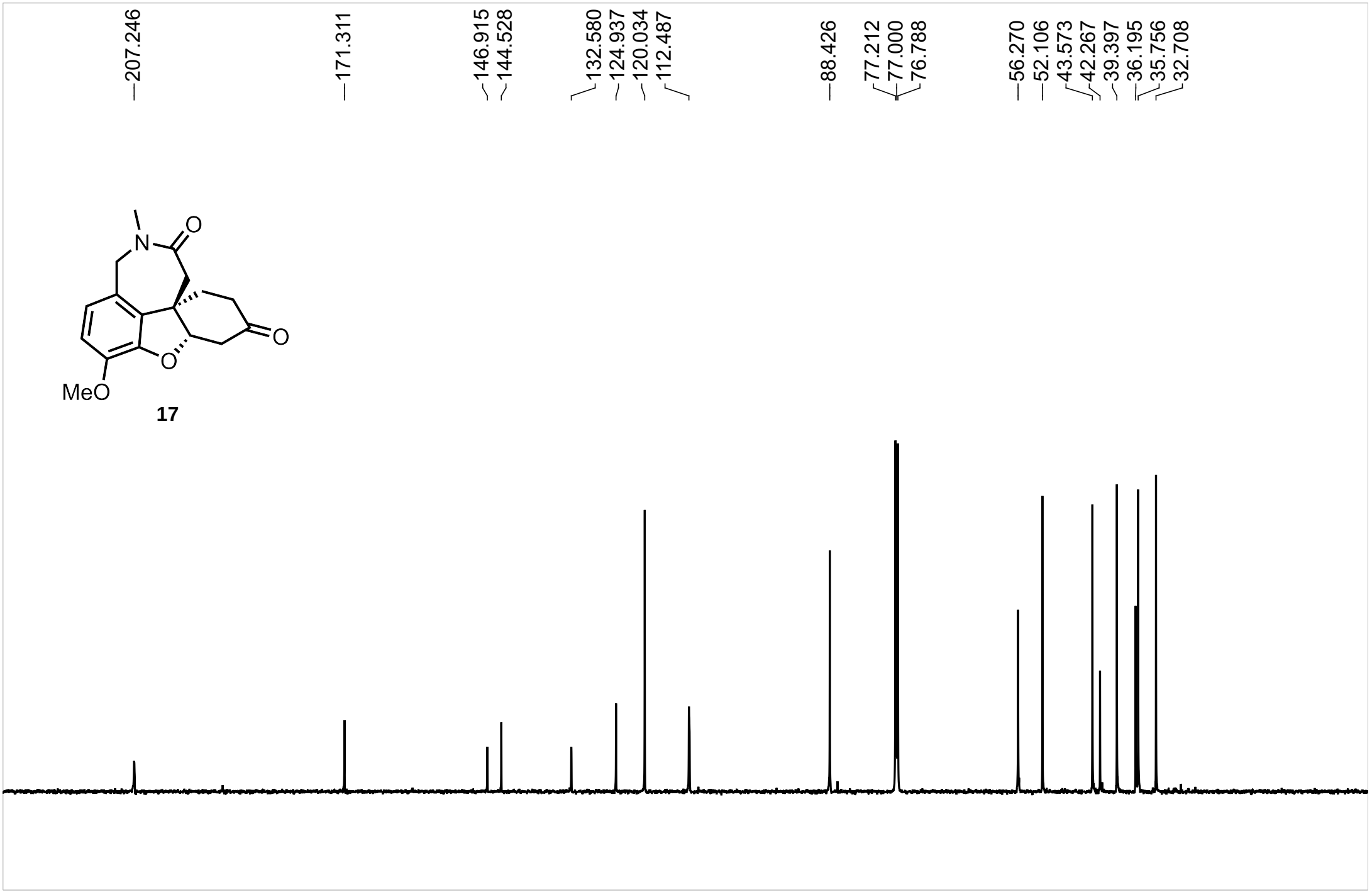
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124.937
120.034
112.487
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77.212
77.000
76.788
56.270
52.106
43.573
42.267
39.397
36.195
35.756
32.708
N
O
O
O
MeO
17
220
210
200
190
180
170
160
150
140
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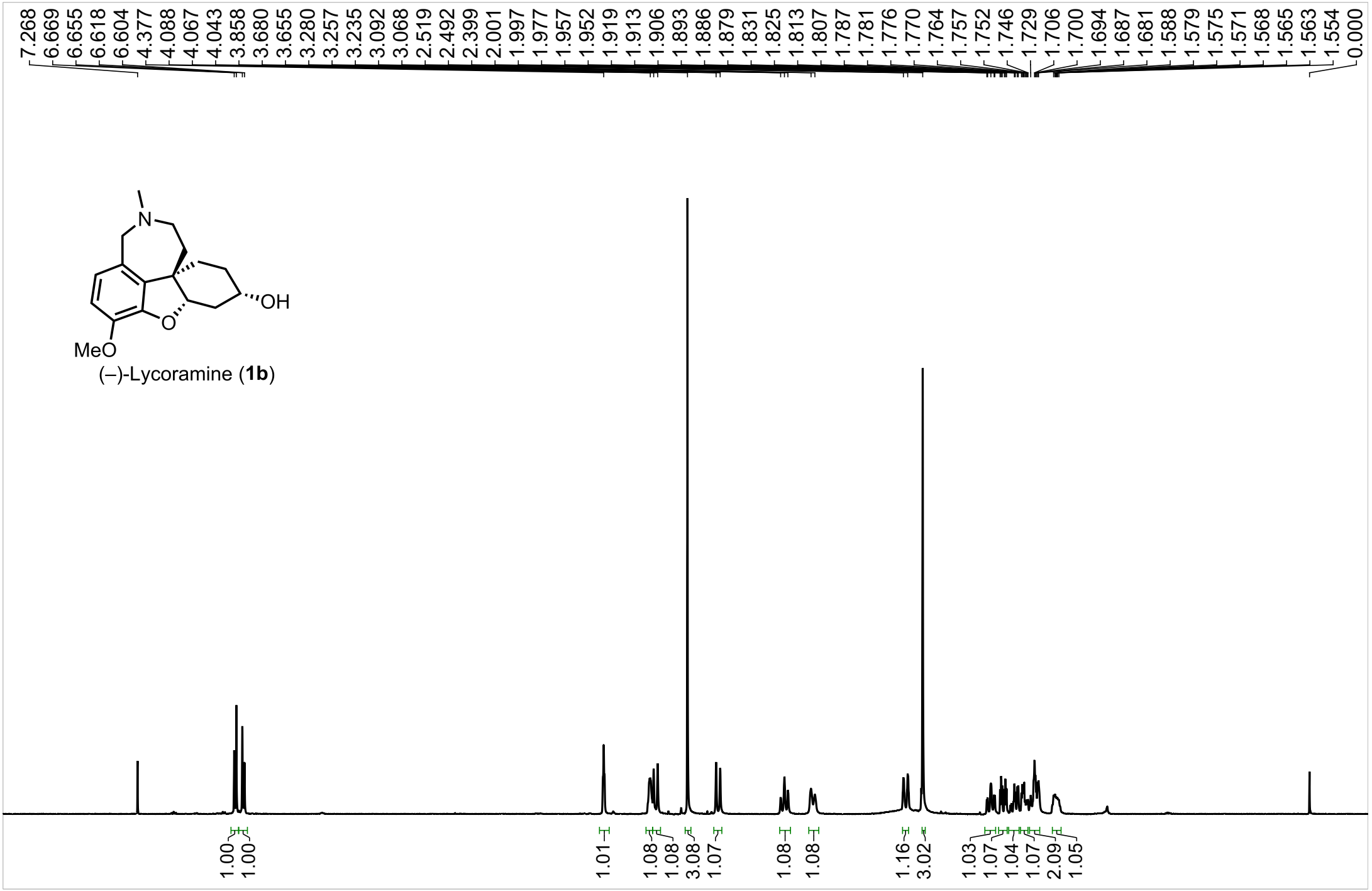
120
110
100
90
80
70
60
50
40
30
20
10
0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6.669
6.655
6.618
6.604
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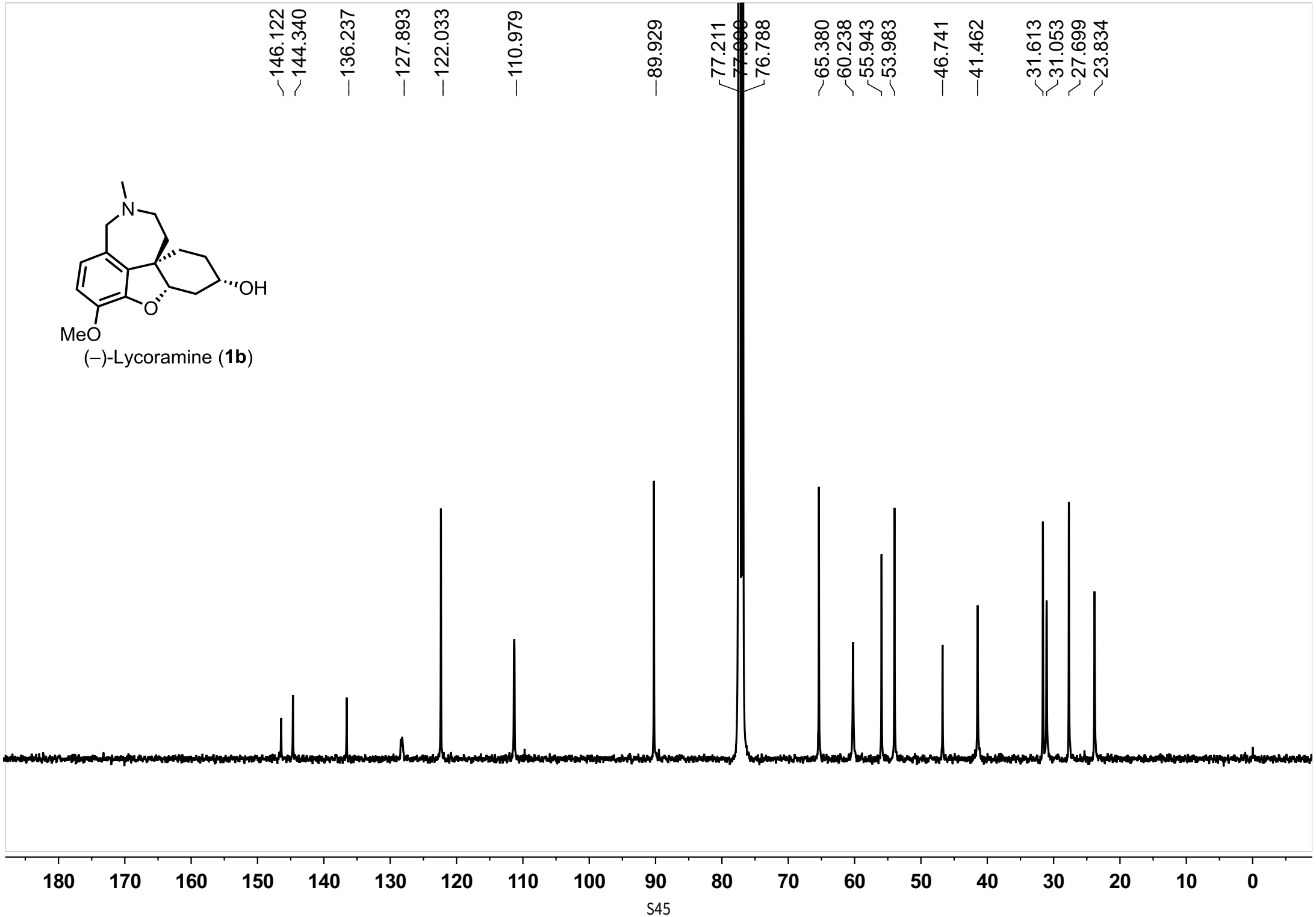
4.088
4.067
4.043
3.858
3.680
3.655
3.280
3.257
3.235
3.092
3.068
2.519
2.492
2.399
2.001
1.997
1.977
1.957
1.952
1.919
1.913
1.906
1.893
1.886
1.879
1.831
1.825
1.813
1.807
1.787
1.781
1.776
1.770
1.764
1.757
1.752
1.746
1.729
1.706
1.700
1.694
1.687
1.681
1.588
1.579
1.575
1.571
1.568
1.565
1.563
1.554
0.000
N
OH
O
MeO
(–)-Lycoramine (1b)
1.00
1.00
1.01
1.08
1.08
3.08
1.07
1.08
1.08
1.16
3.02
1.03
1.07
1.04
1.07
2.09
1.05
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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136.237
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122.033
110.979
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77.211
77.000
76.788
65.380
60.238
55.943
53.983
46.741
41.462
31.613
31.053
27.699
23.834
N
OH
O
MeO
(–)-Lycoramine (1b)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0