# C-H Bond Functionalization via Hydride Transfer: Formation of α-Arylated Piperidines and 1,2,3,4-Tetrahydroisoquinolines via Stereoselective Intramolecular Amination of Benzylic C-H Bonds

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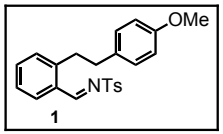
*3000 Broadway, New York, New York, 10027*

## Supporting Information

NMR Spectra for HT-amination Substrates and **S6**

| Substrate | Proton Spectrum | Carbon Spectrum |
|---|---|---|
| ***N*-(2-(4-methoxyphenethyl)benzylidene)-4-methylbenzenesulfonamide (1).** | **3** | **4** |
| **5-(4-methoxyphenyl)-2,2-dimethylpentanal (4).** | **5** | **6** |
| **1-(3-(4-methoxyphenyl)propyl)cyclohexanecarbaldehyde (6).** | **7** | **8** |
| **5-(4-methoxyphenyl)-3,3-dimethylpentanal (8).** | **9** | **10** |
| **5-(4-methoxyphenyl)-3-methylpentanal (10).** | **11** | **12** |
| **2,2-dimethyl-5-phenylpentanal (16).** | **13** | **14** |
| **5-(4-methoxyphenyl)-2-methylpentanal (18).** | **15** | **16** |
| **5-(4-methoxyphenyl)-3-phenylpentanal (20).** | **17** | **18** |
| **5-(2-methoxyphenyl)-2-methylpentanal (22).** | **19** | **20** |
| **5-(3-methoxyphenyl)-2-methylpentanal (24).** | **21** | **22** |
| **5-fluoro-2-(4-methoxyphenethyl)benzaldehyde (28).** | **23** | **24** |
| **4-fluoro-2-(4-methoxyphenethyl)benzaldehyde (30).** | **25** | **26** |
| **4,5-difluoro-2-(4-methoxyphenethyl)benzaldehyde (32).** | **27** | **28** |
| **1-(4-methoxyphenethyl)naphthalene-2-carbaldehyde (34).** | **29** | **30** |
| **2-(2-(biphenyl-4-yl)ethyl)benzaldehyde (38).** | **31** | **32** |
| **2-(4-methoxy-2-methylphenethyl)benzaldehyde (40).** | **33** | **34** |
| **2-(2-(6-methoxynaphthalen-2-yl)ethyl)benzaldehyde (42).** | **35** | **36** |
| **(*S*)-5-(4-methoxyphenyl)-2-methylpentanal (S5).** | **37** | **38** |
| **(*S*)-2-(methoxymethyl)-*N*-((*S*)-5-(4-methoxyphenyl)-2-methylpentylidene)pyrrolidin-1-amine (S6).** | **39** | **40** |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7.258
7.251
7.226
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6.975
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6.821
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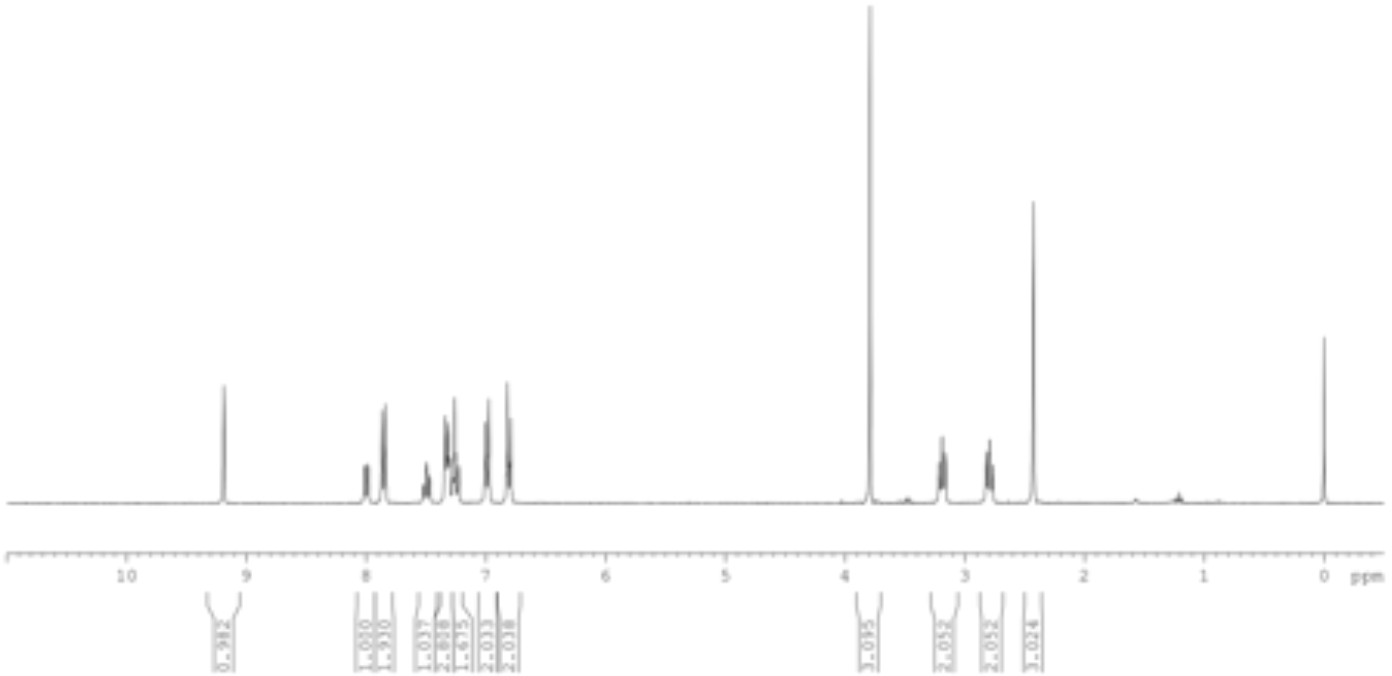
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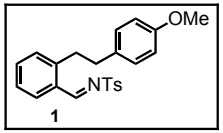


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144.551
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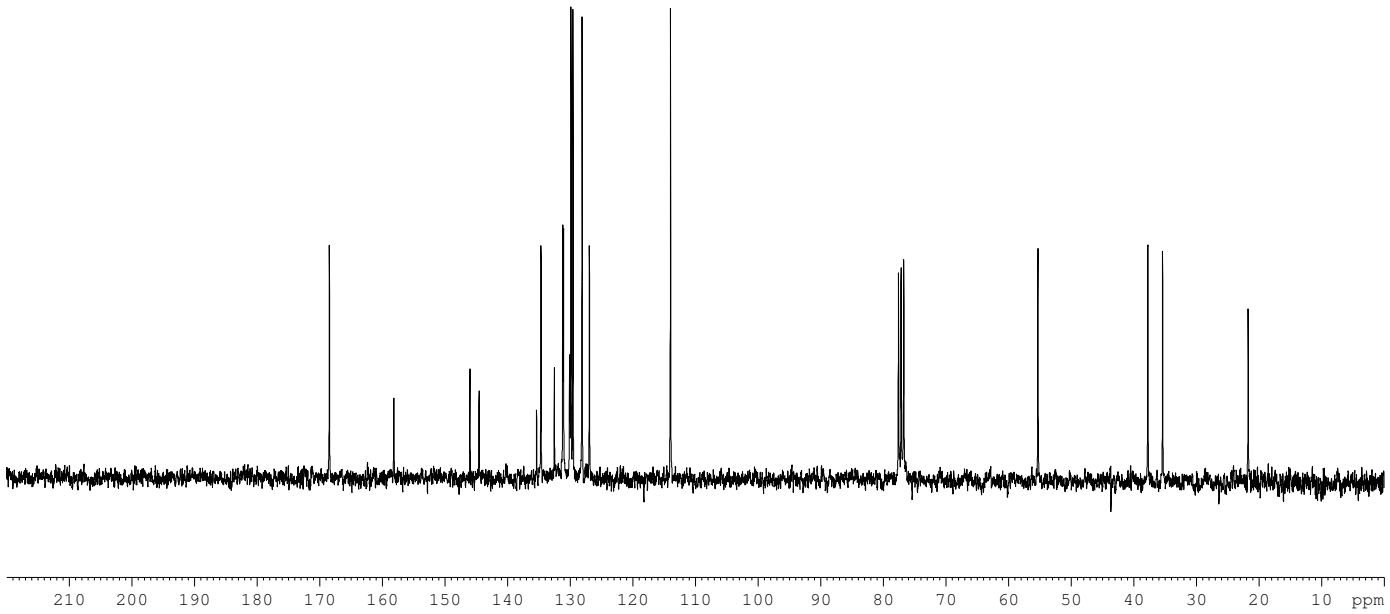

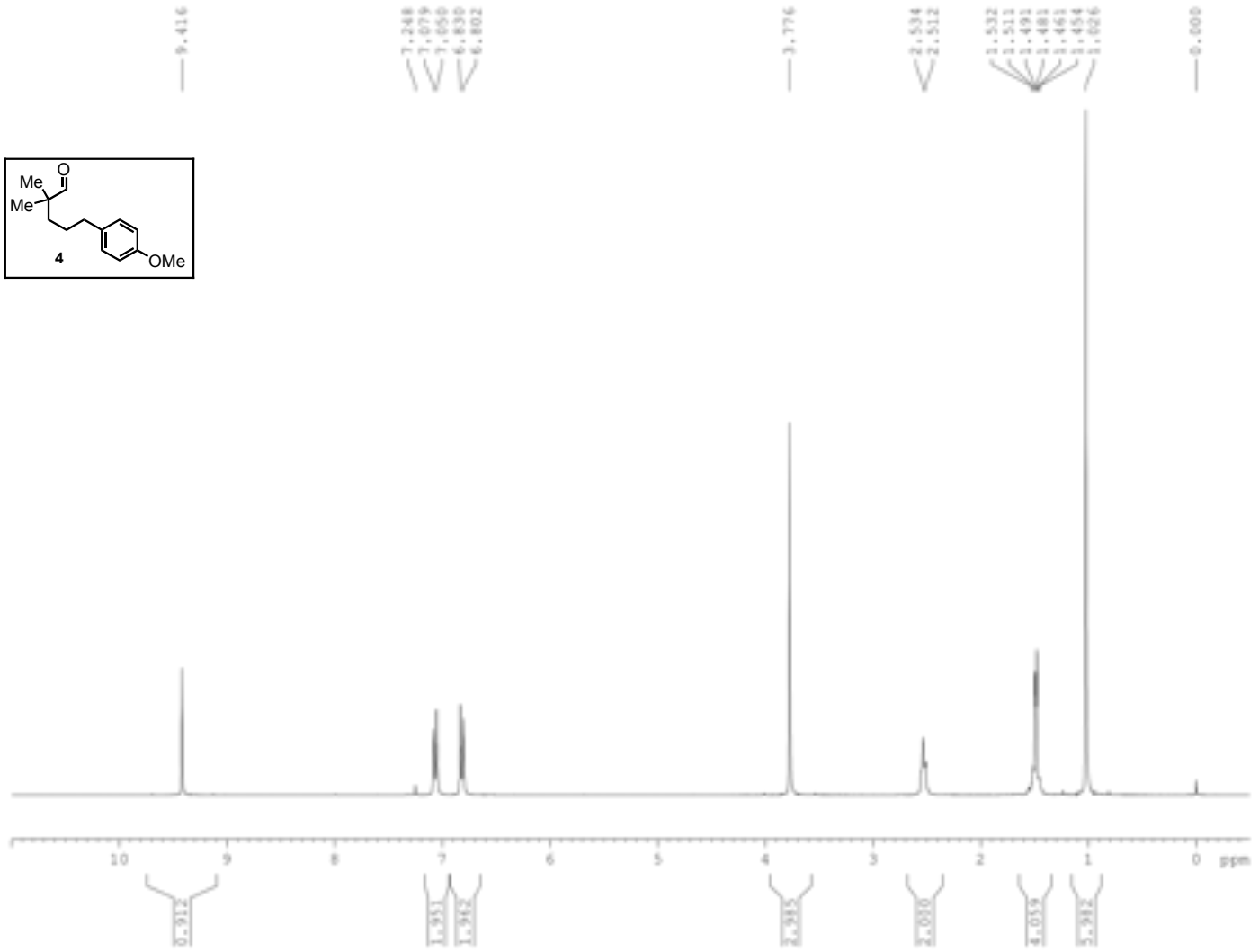
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Me
O
OMe
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7
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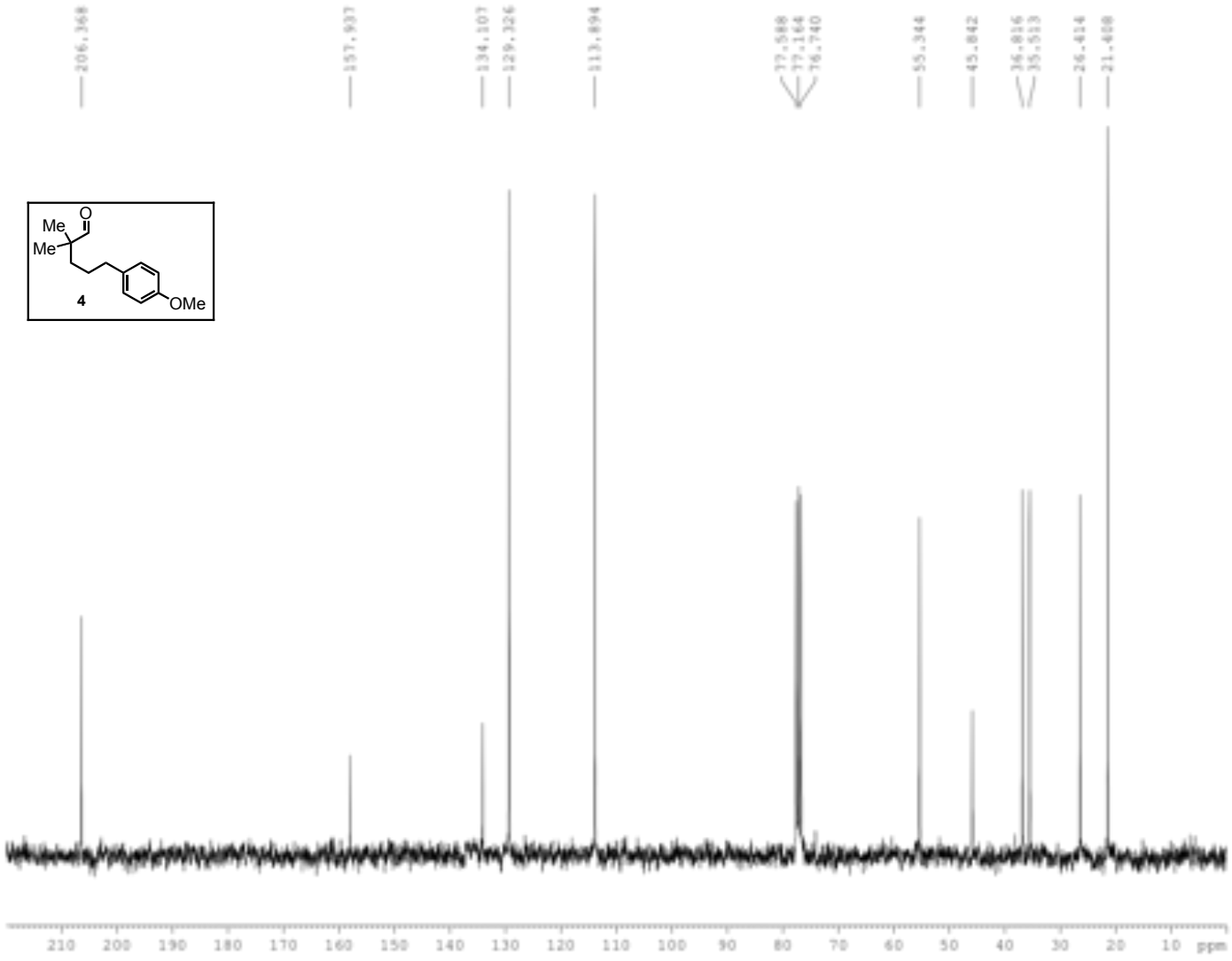
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Me
O
OMe
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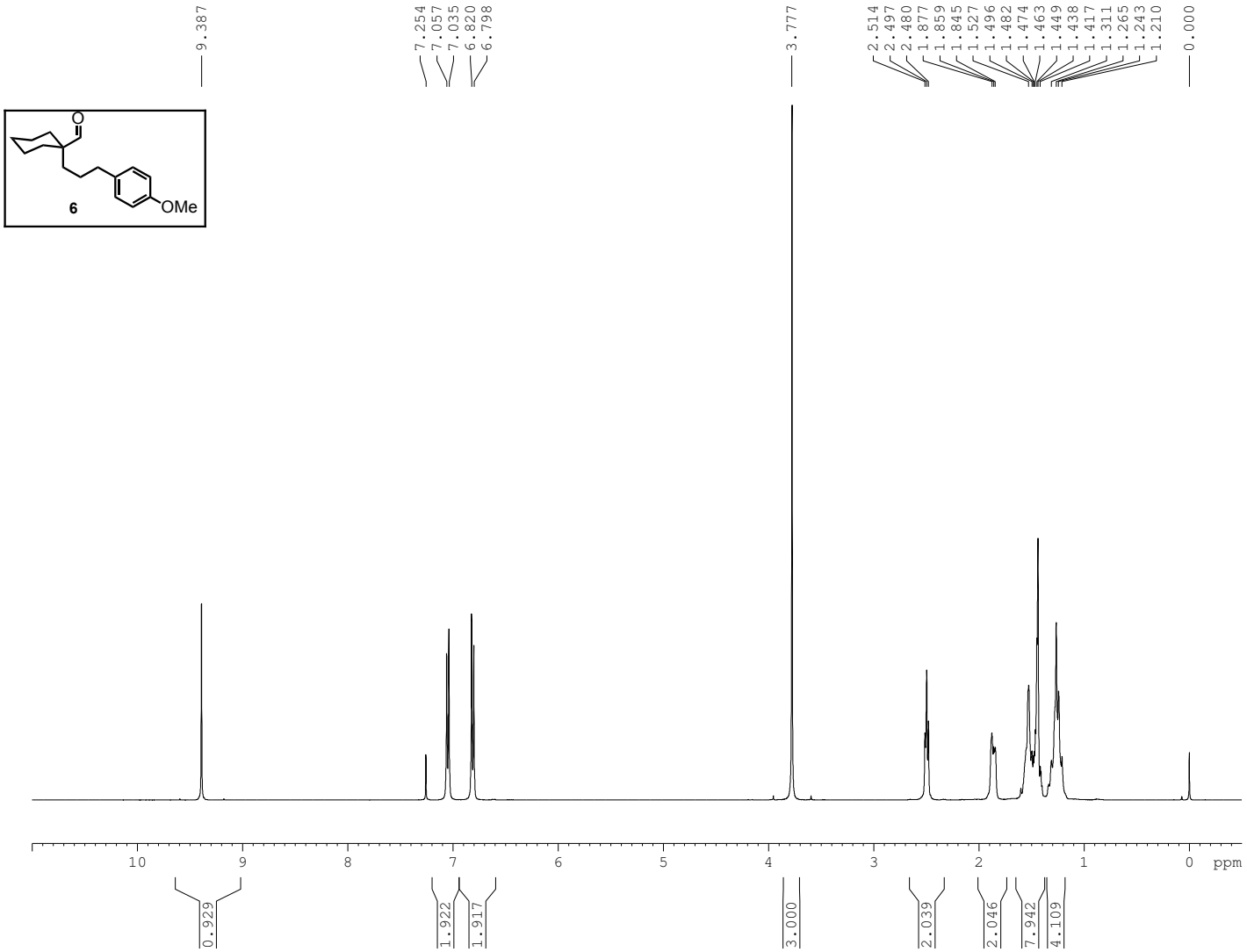
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1.463
1.449
1.438
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OMe
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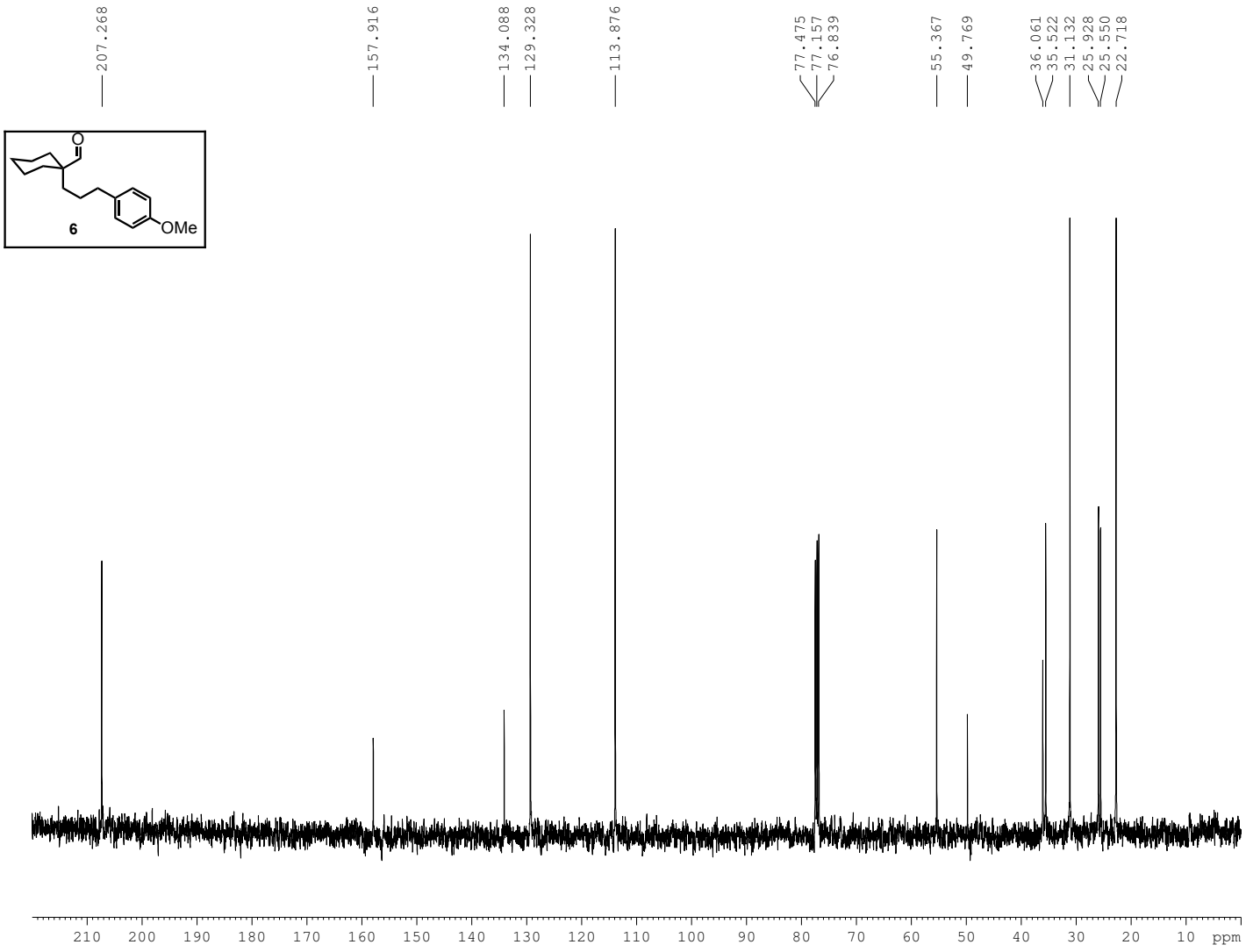
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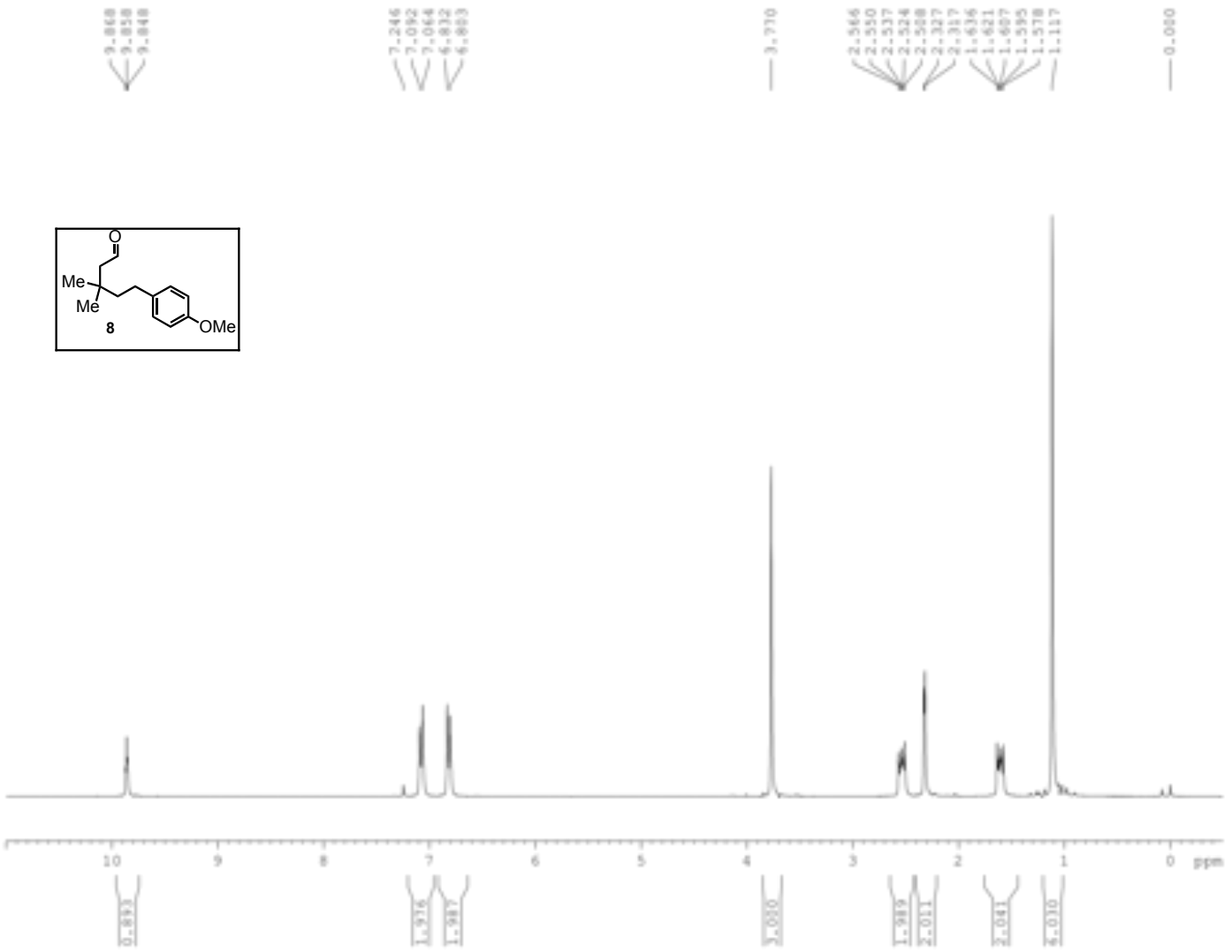
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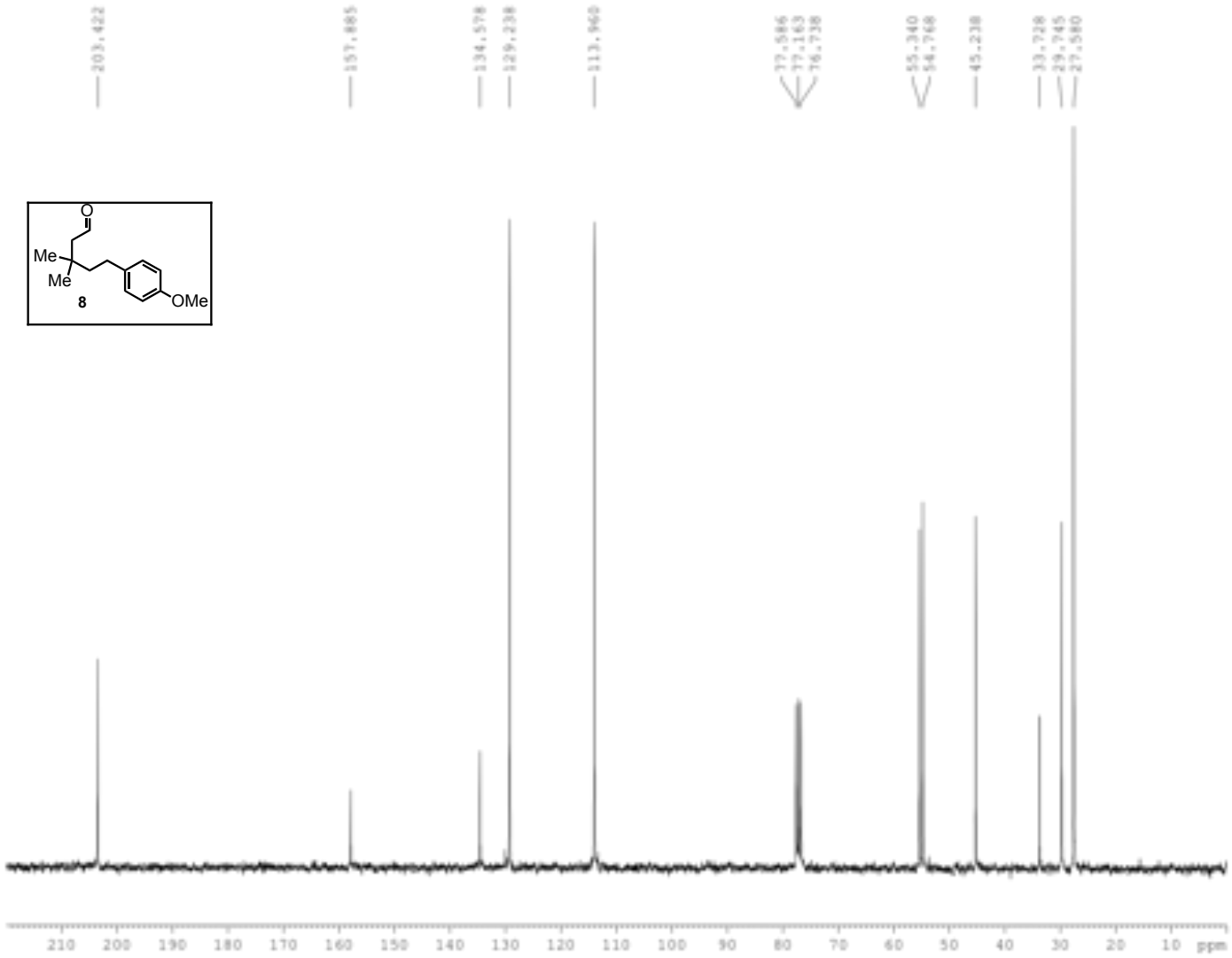
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OMe
8
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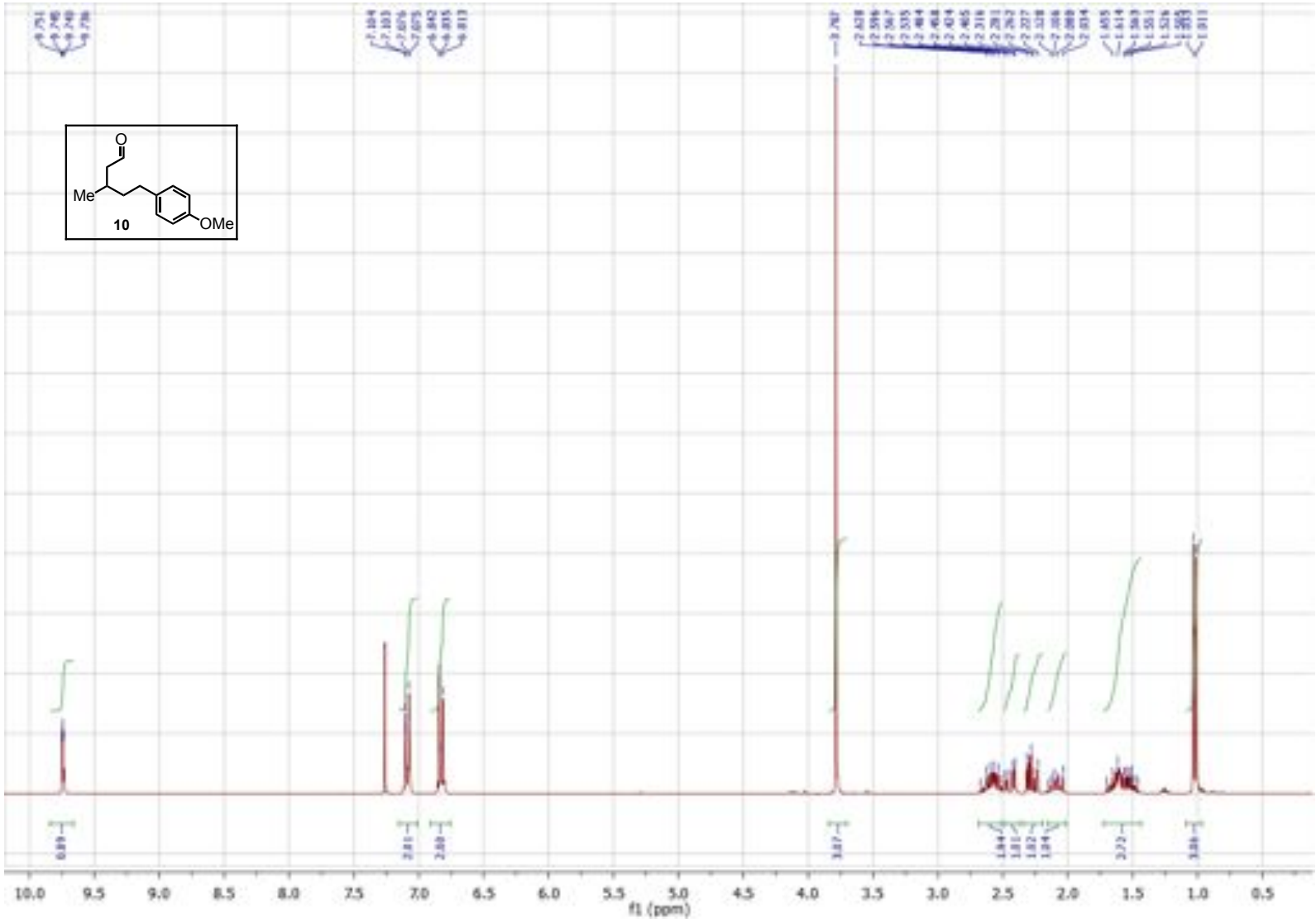
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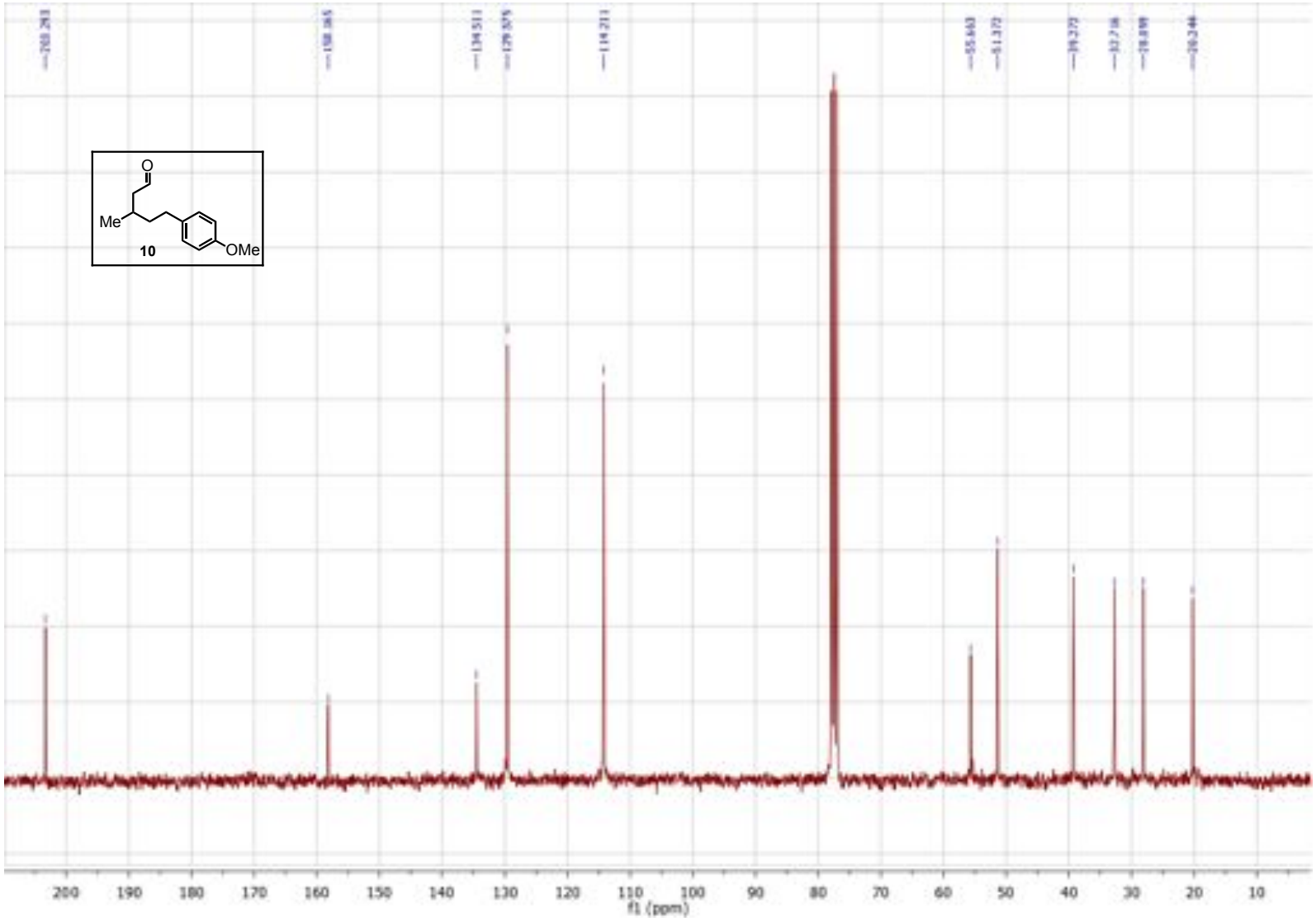
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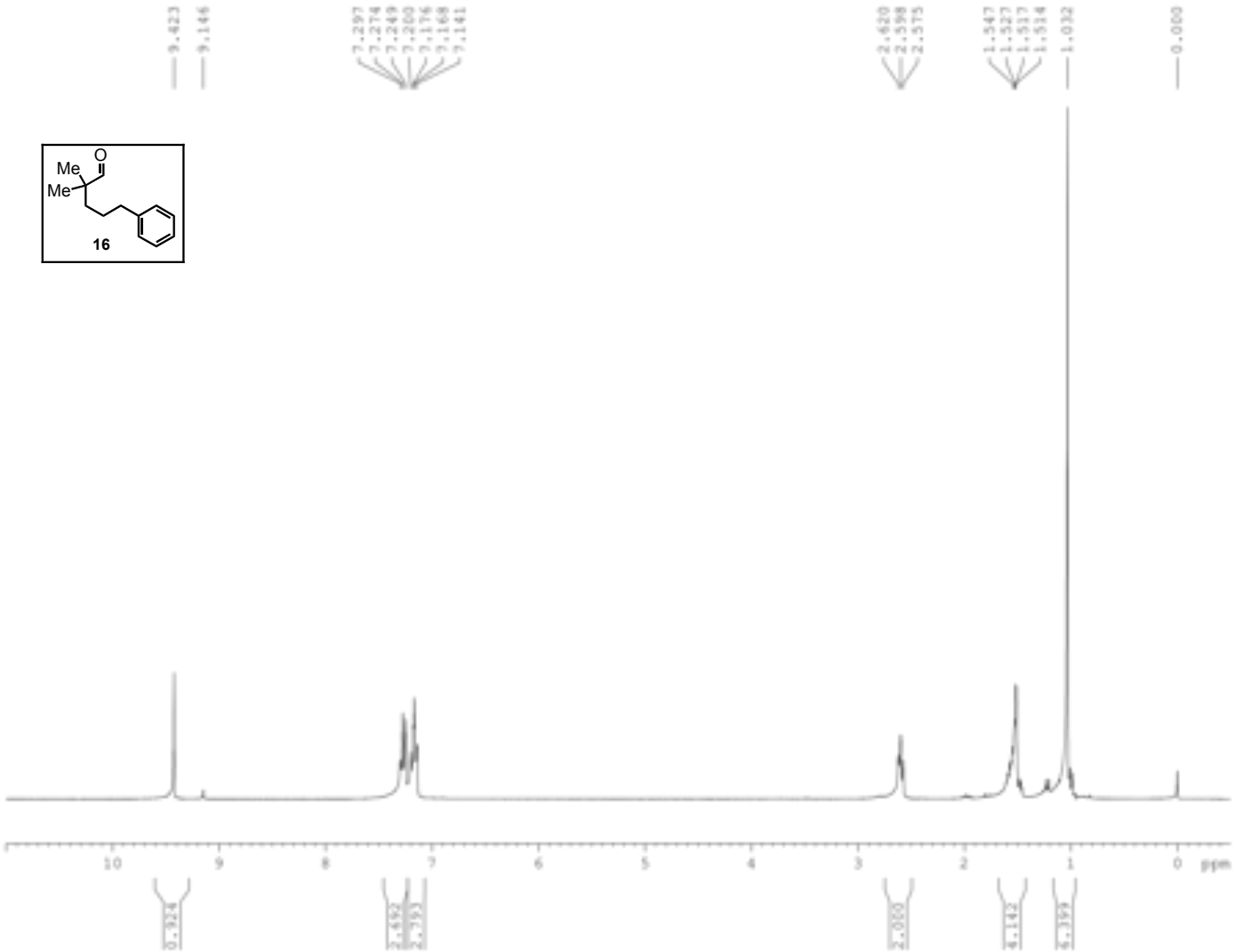
f1 (ppm)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1.517
1.514
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Me
Me
O
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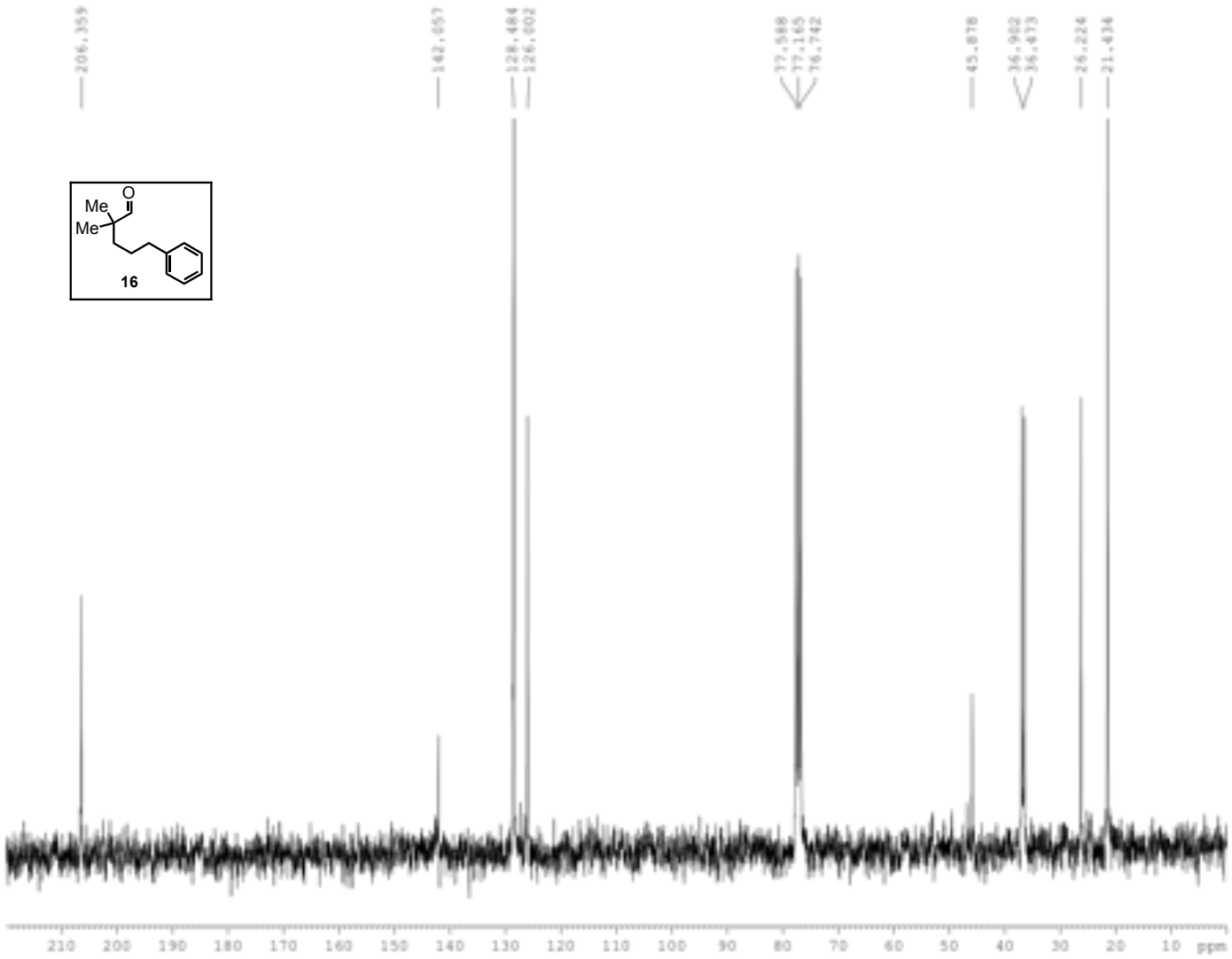
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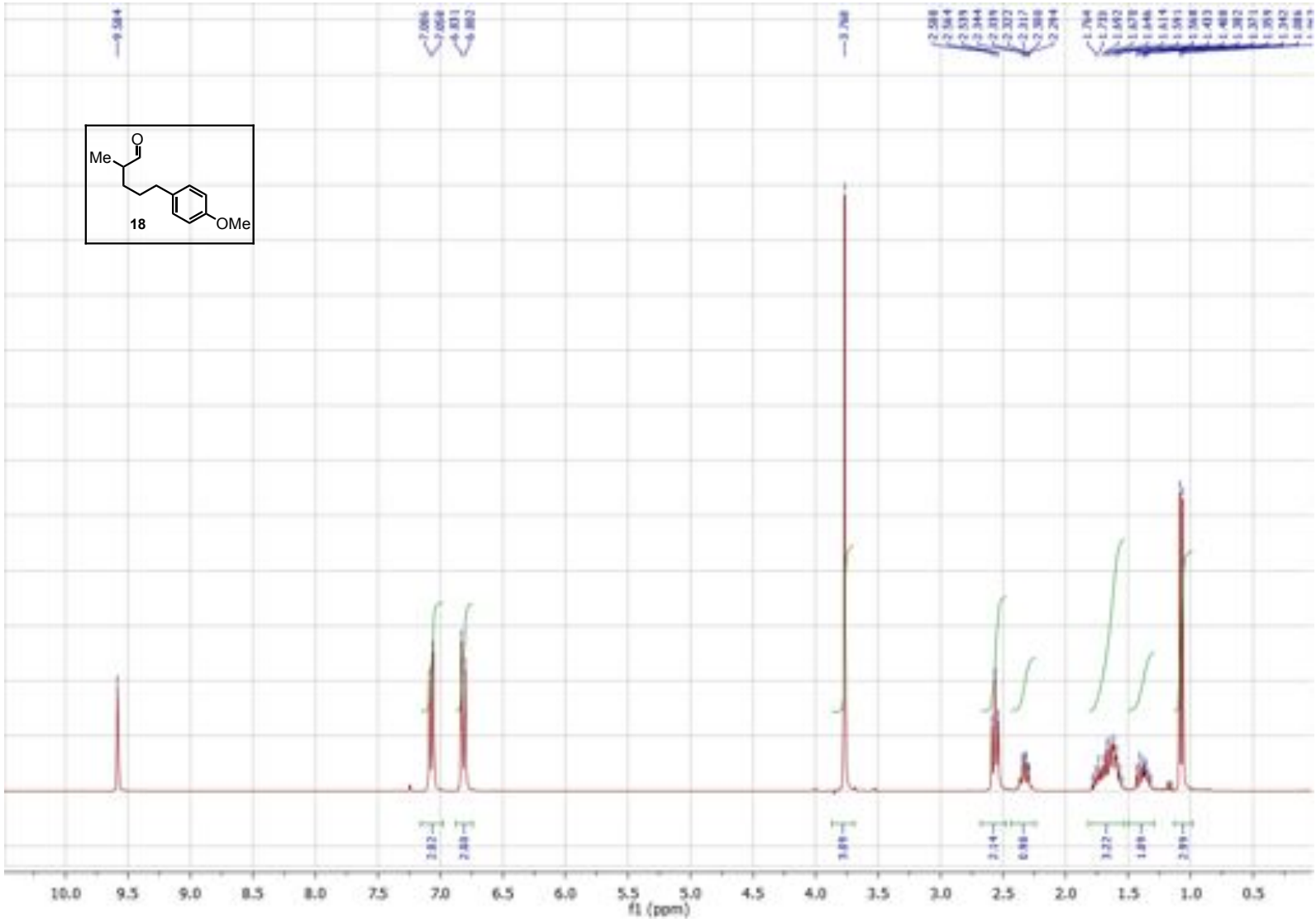
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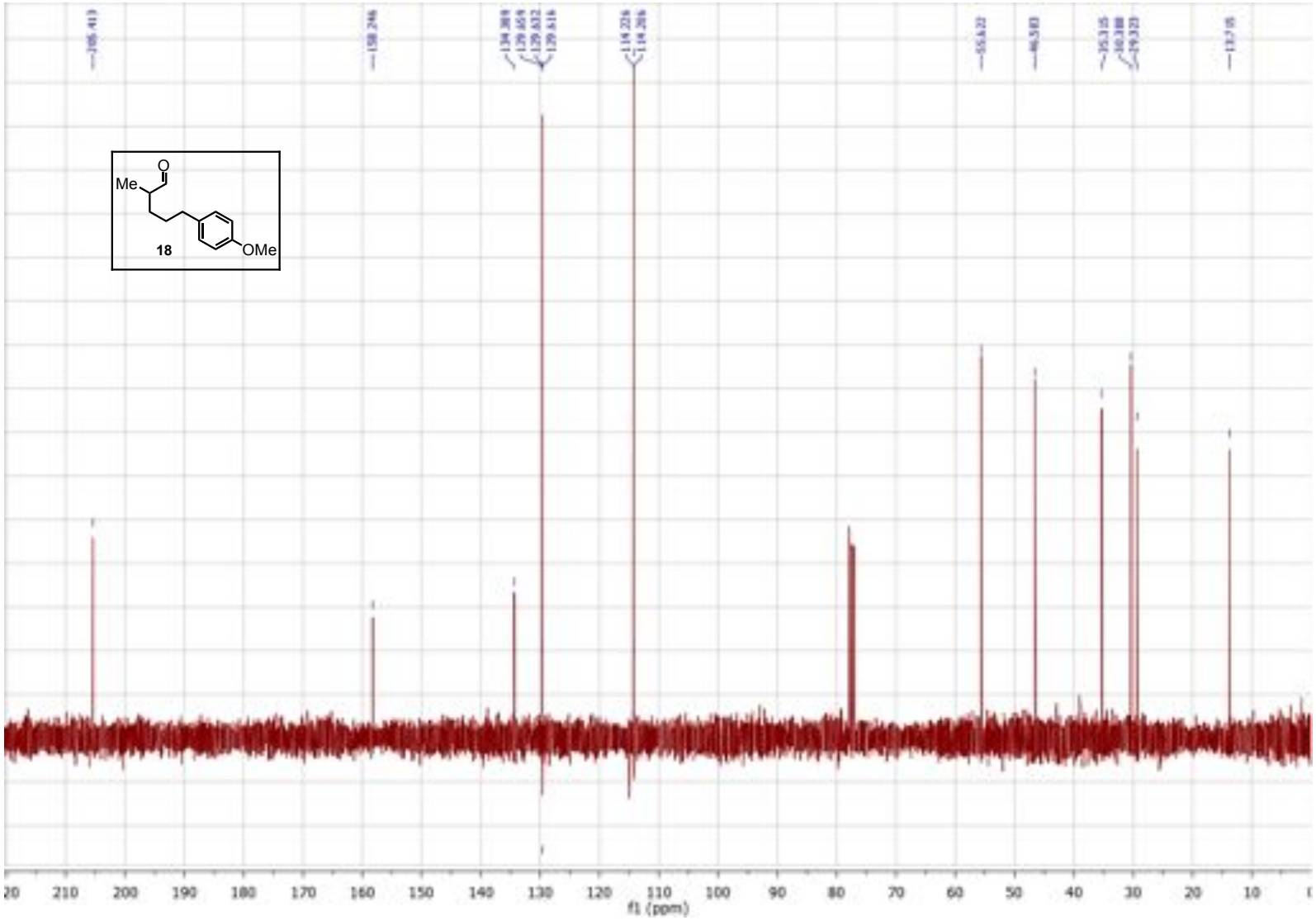
f1 (ppm)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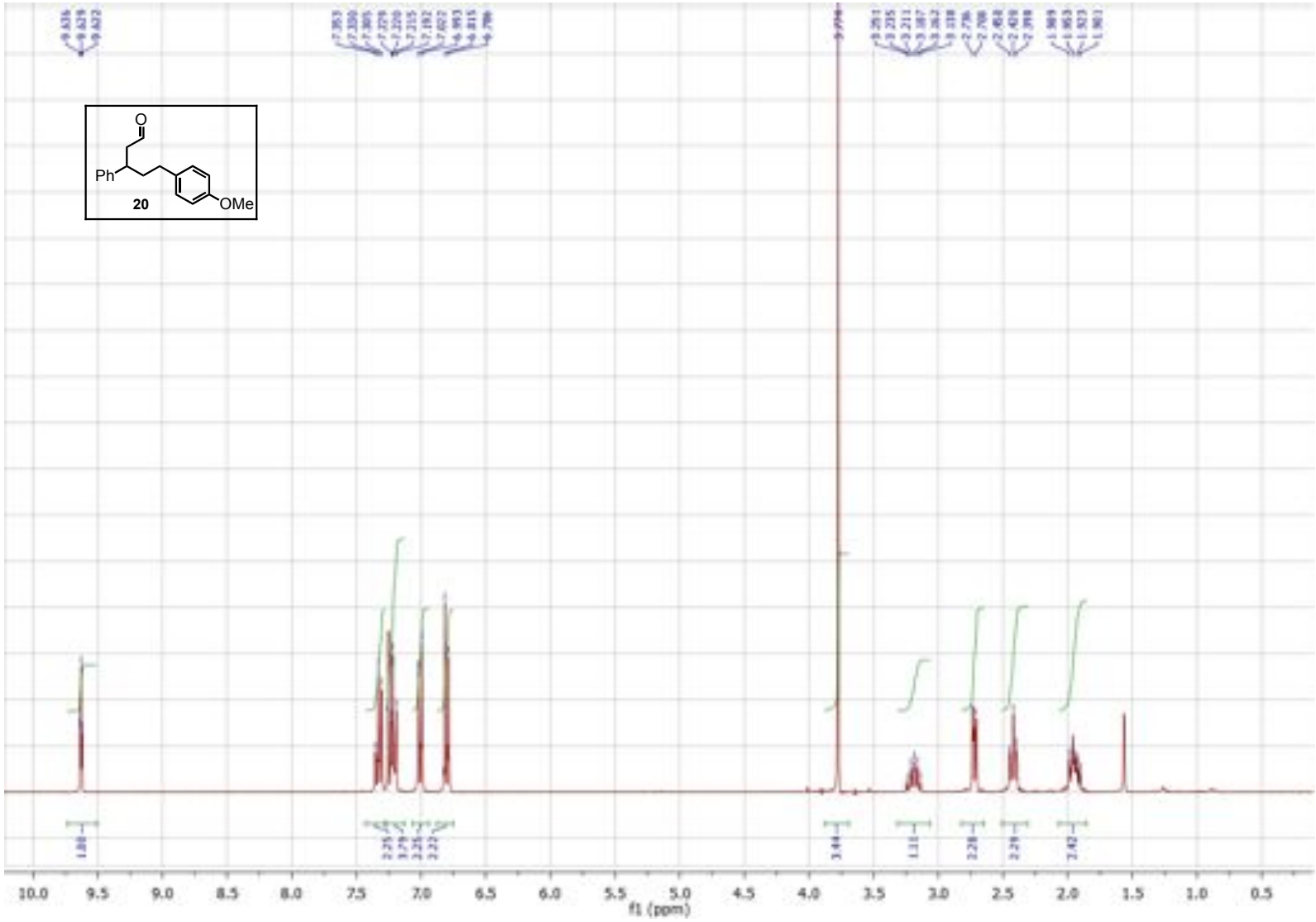
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Ph
OMe
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6.5
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3.0
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1.5
1.0
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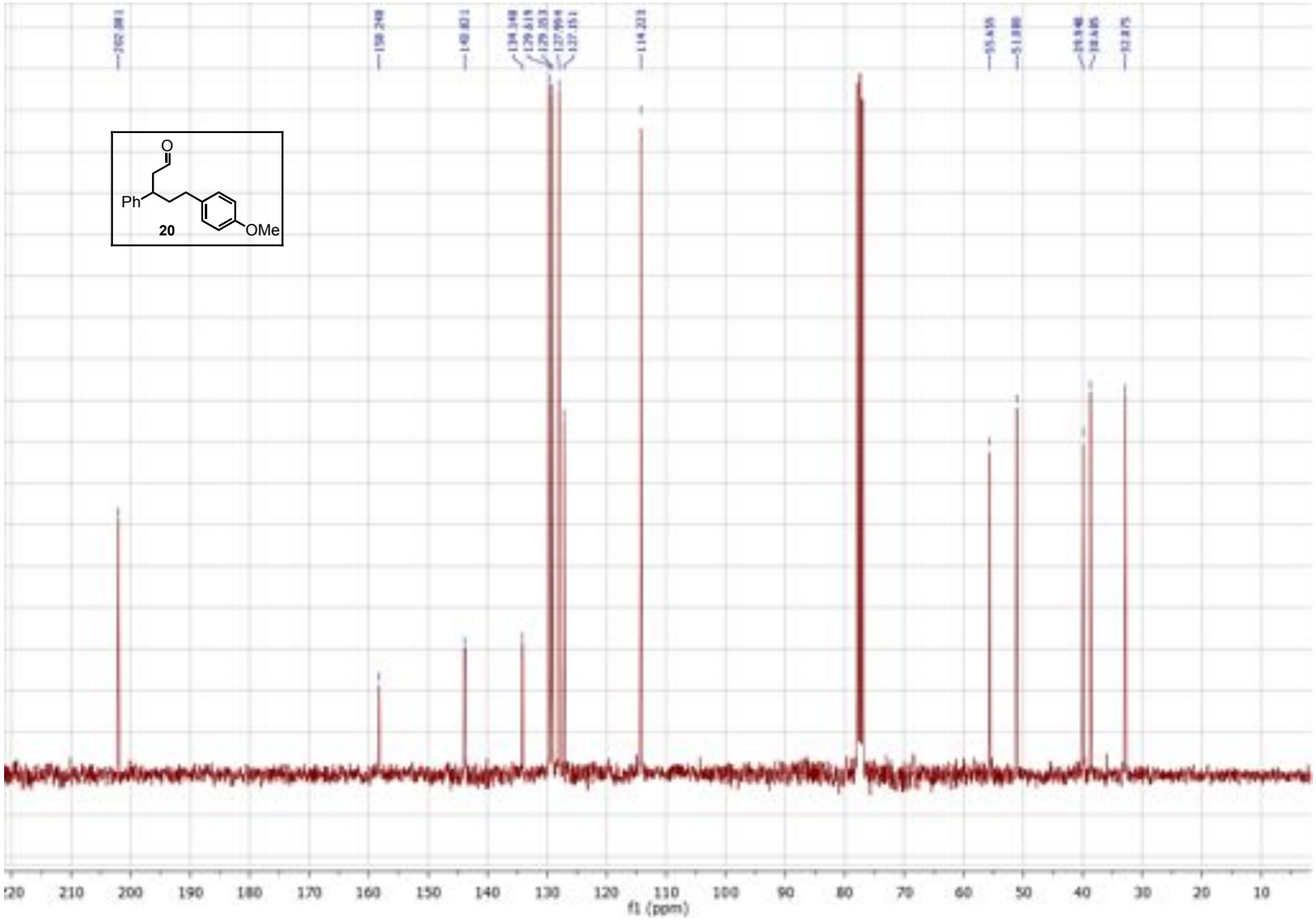
f1 (ppm)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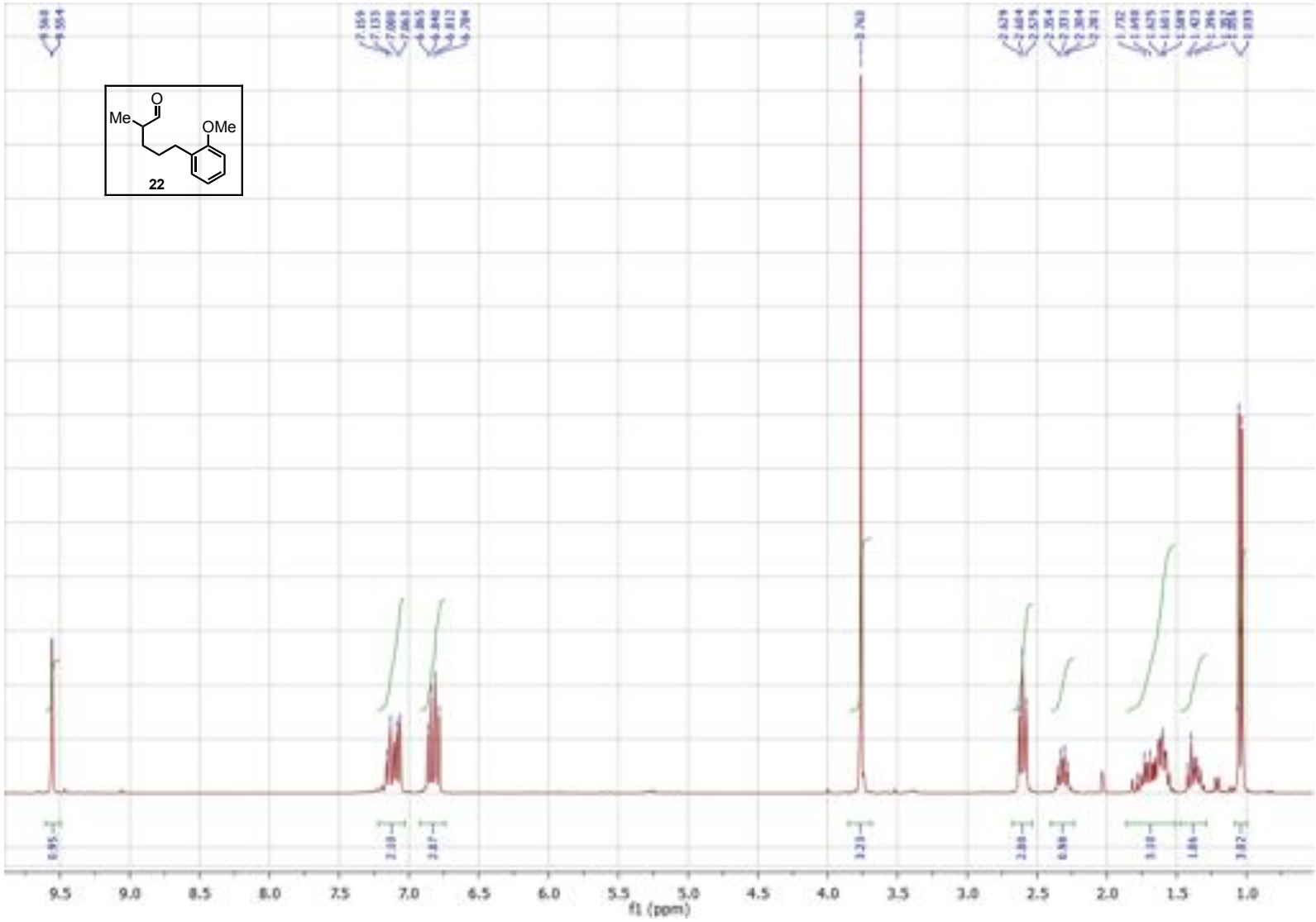
Ph
20
OMe
f1 (ppm)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Me
OMe
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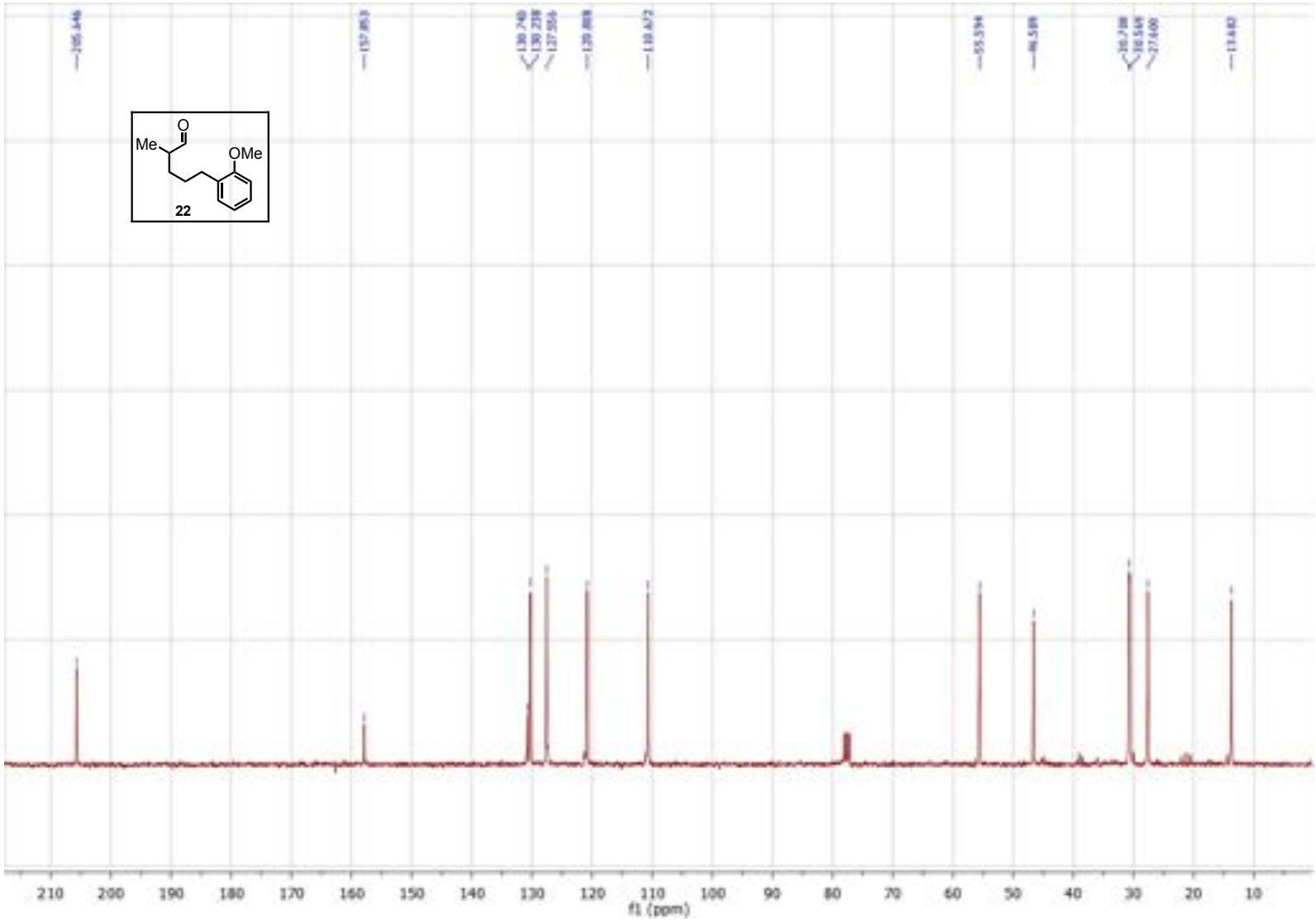
f1 (ppm)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OMe
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200
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140
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120
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100
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80
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60
50
40
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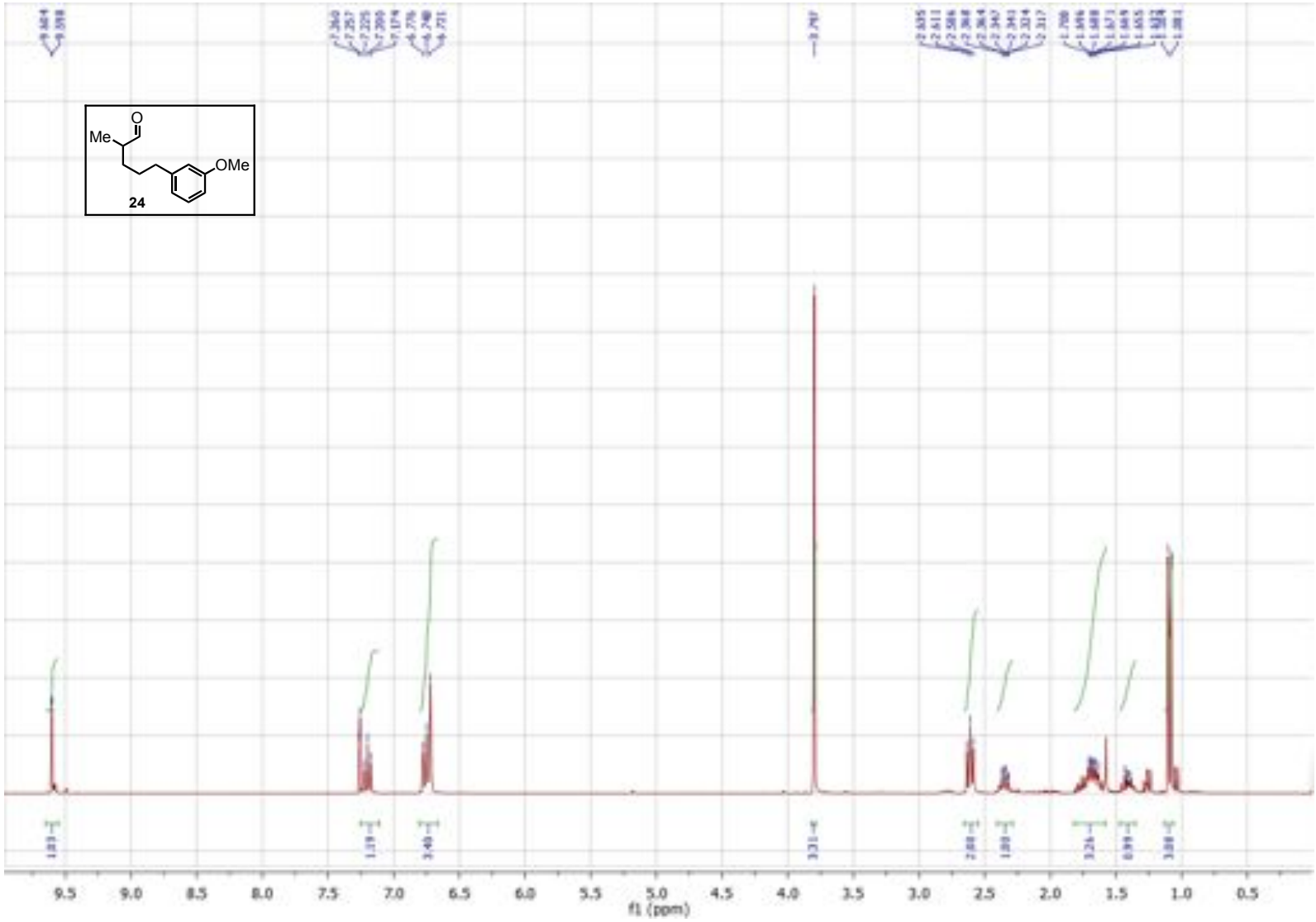
20
10
f1 (ppm)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OMe
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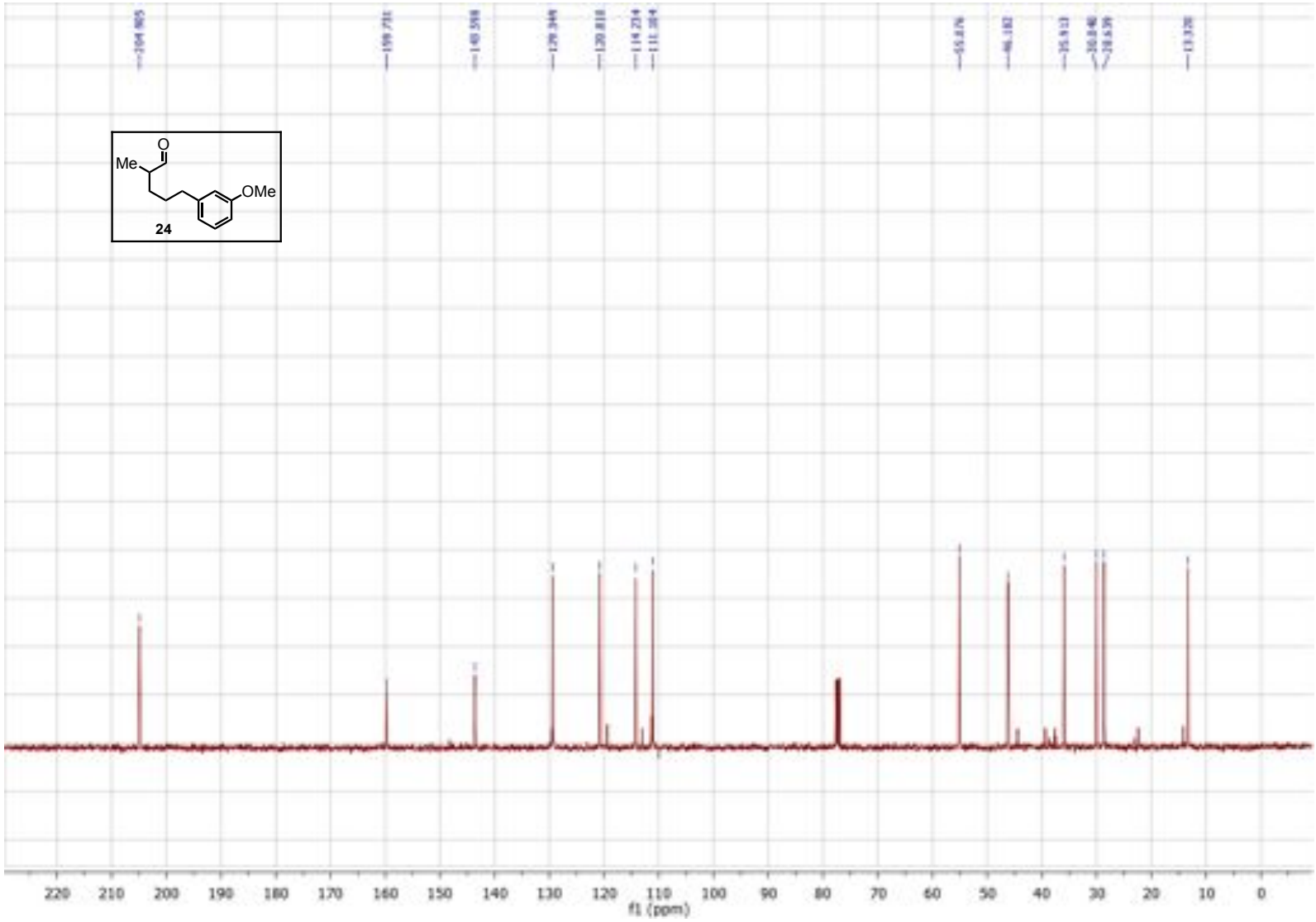
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50
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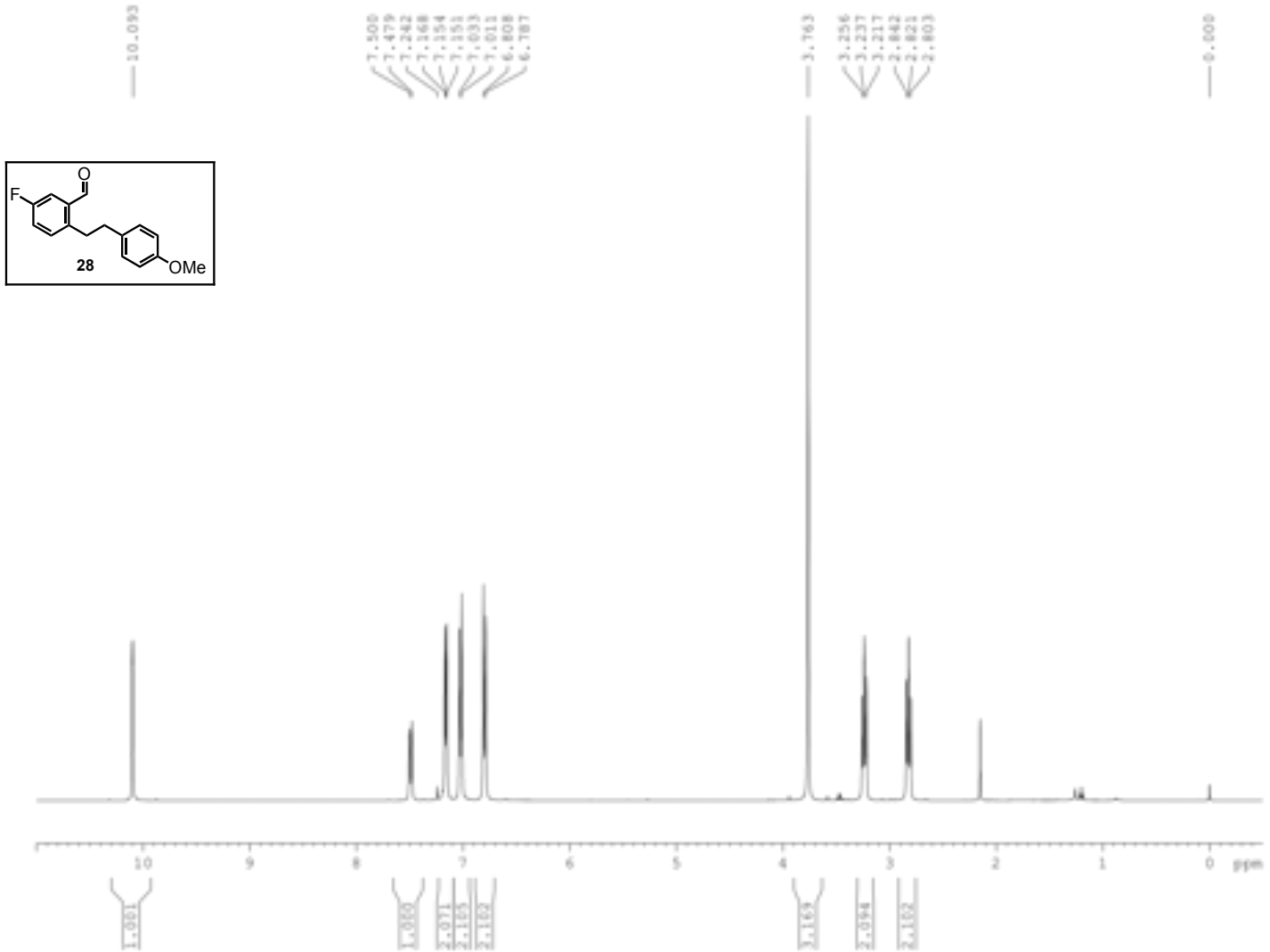
f1 (ppm)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3.237
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2.821
2.803
0.000
O
F
28
OMe
10
9
8
7
6
5
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ppm
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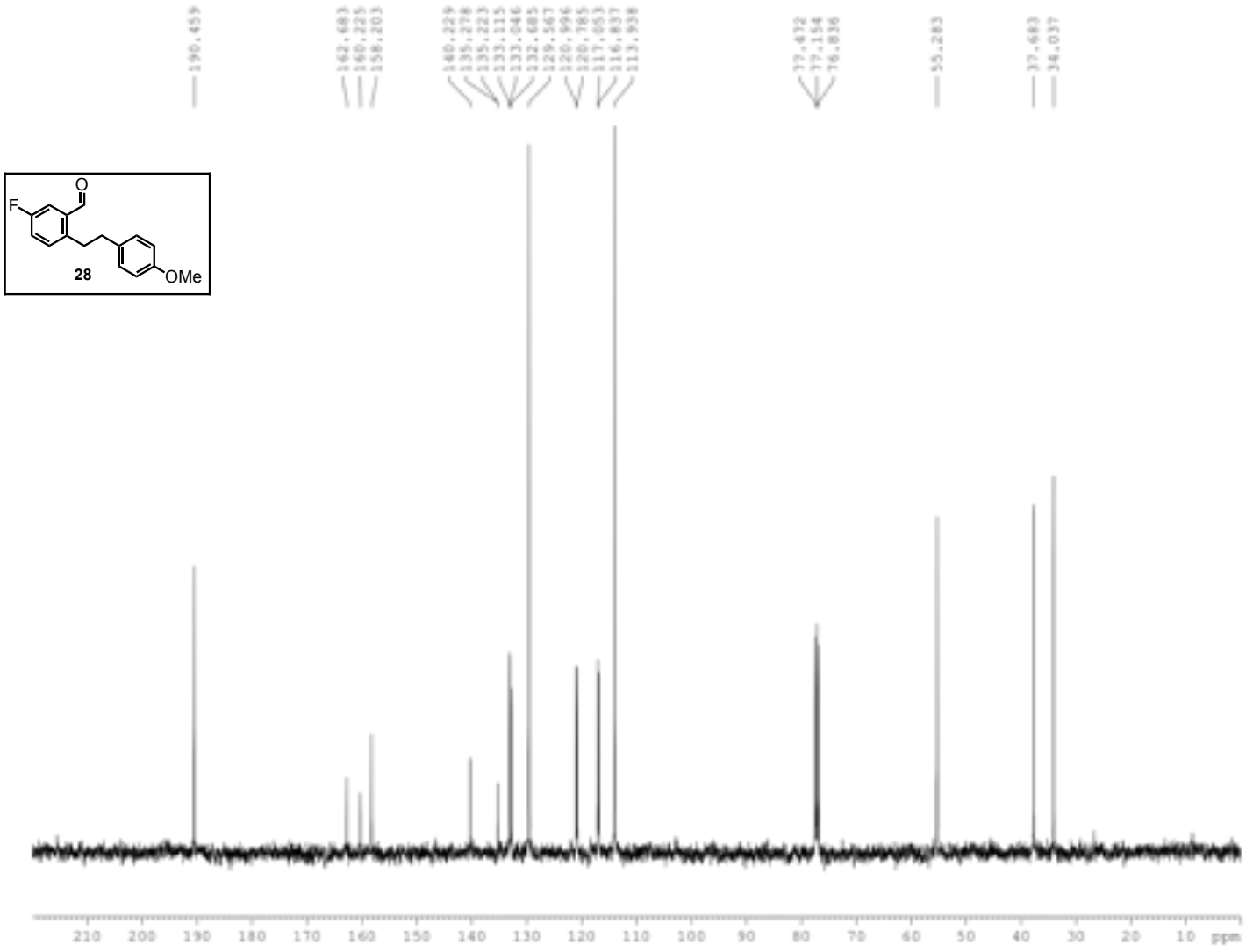
2.102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117.053
116.837
113.958
77.472
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O
F
28
OMe
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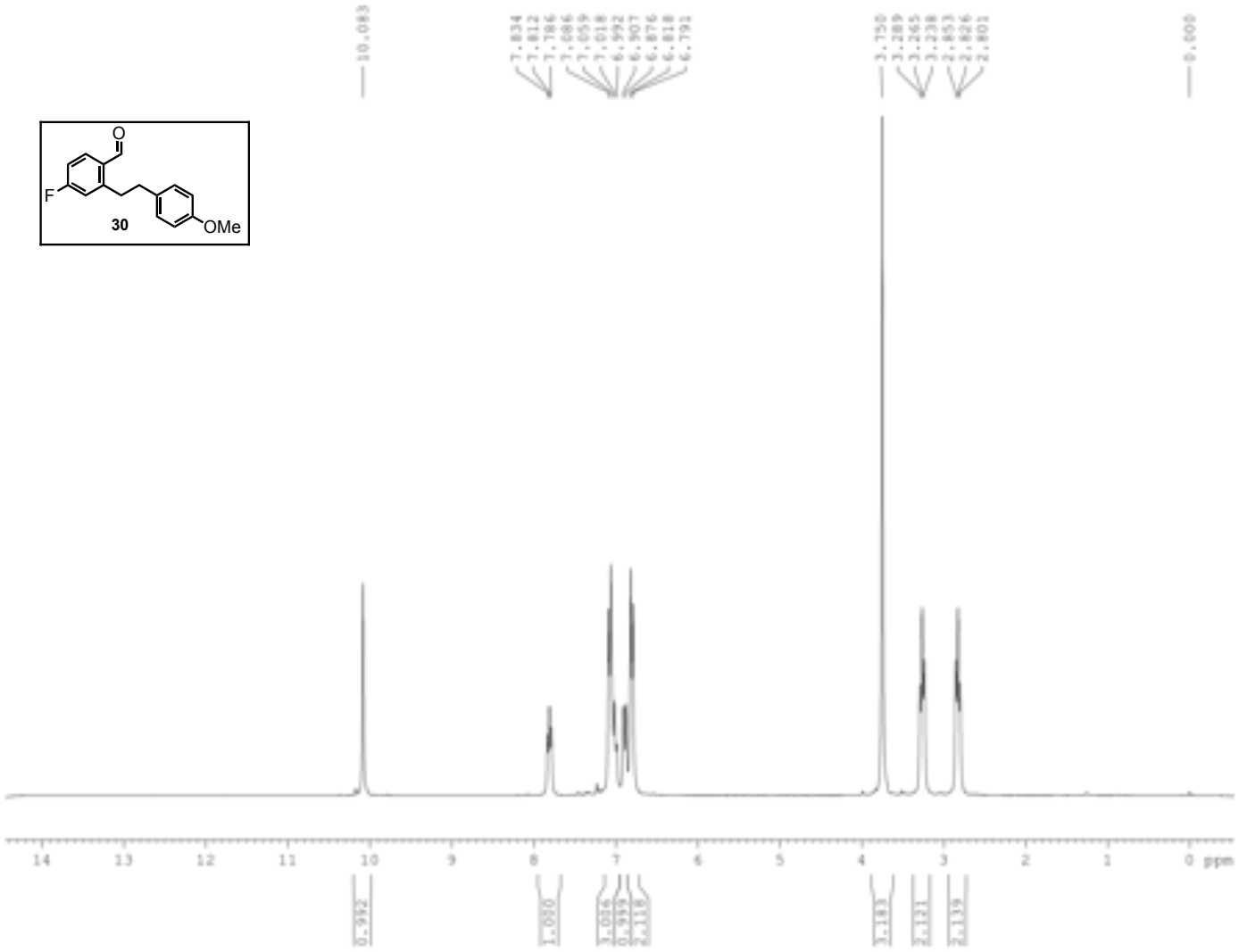
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3.265
3.238
2.853
2.826
2.801
0.000
O
F
OMe
30
14
13
12
11
10
9
8
7
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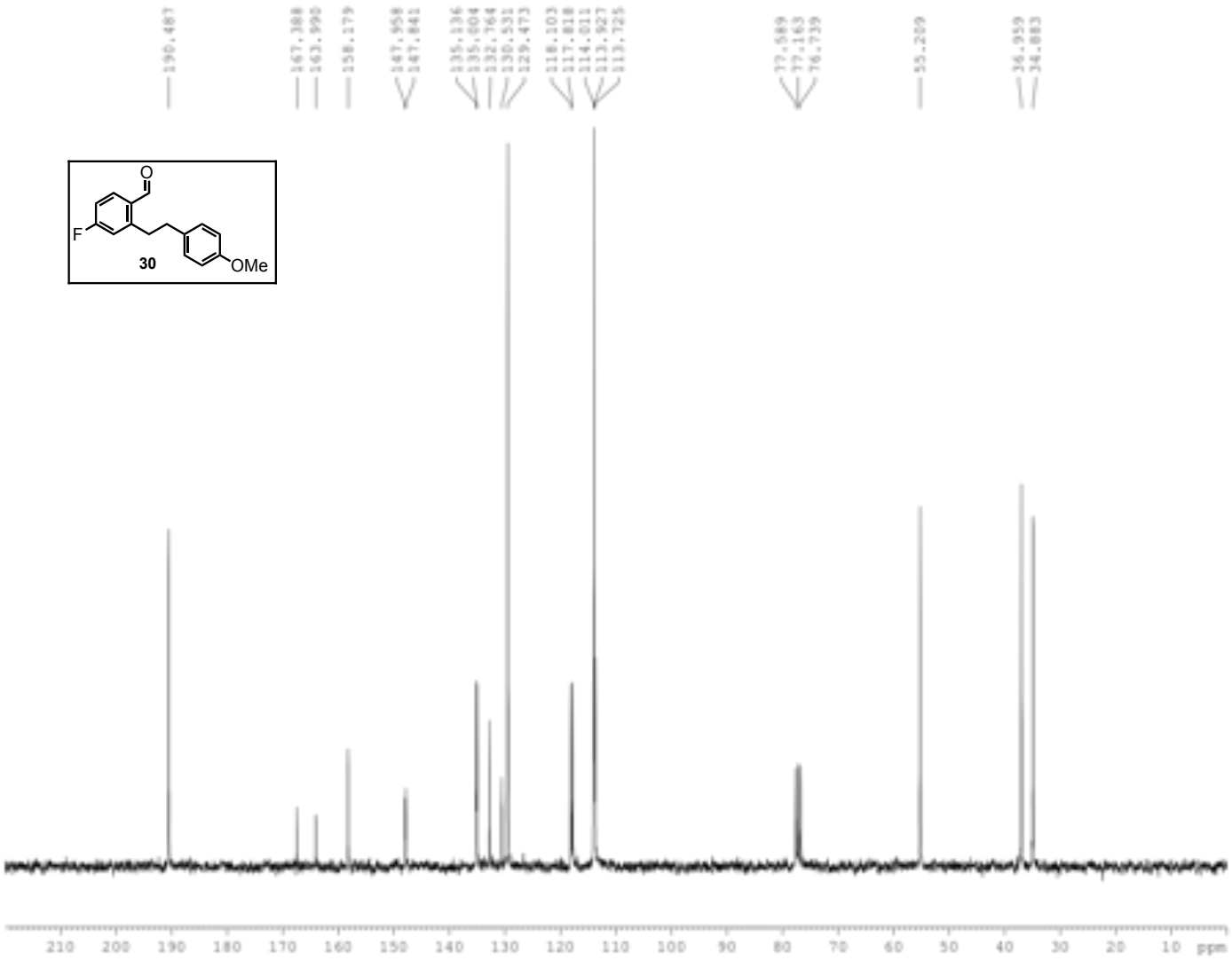
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F
30
OMe
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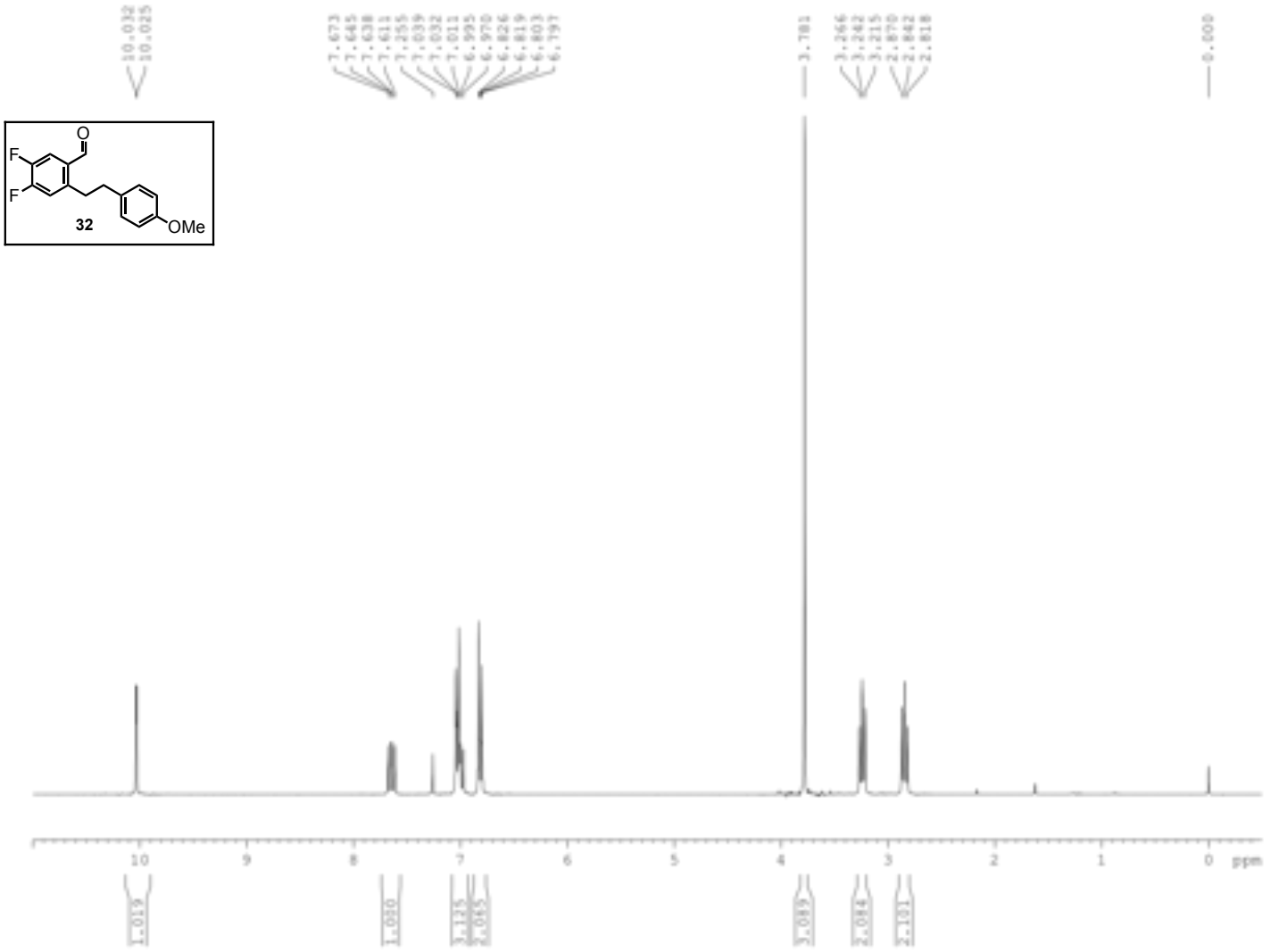
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6.819
6.803
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3.242
3.215
2.870
2.842
2.818
0.000
F
F
O
32
OMe
10
9
8
7
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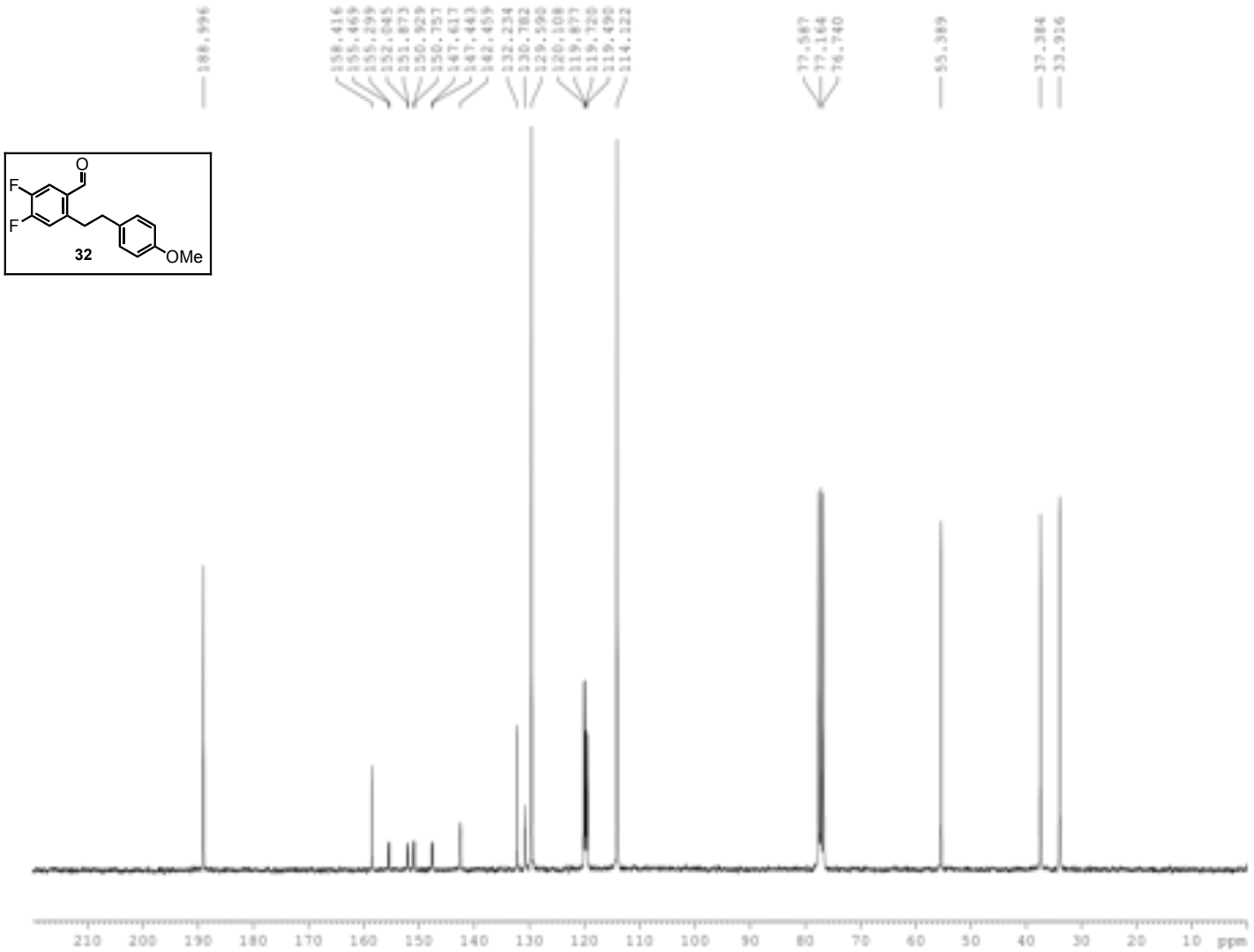
2.101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129.590
120.108
119.877
119.720
119.490
114.122
77.587
77.164
76.740
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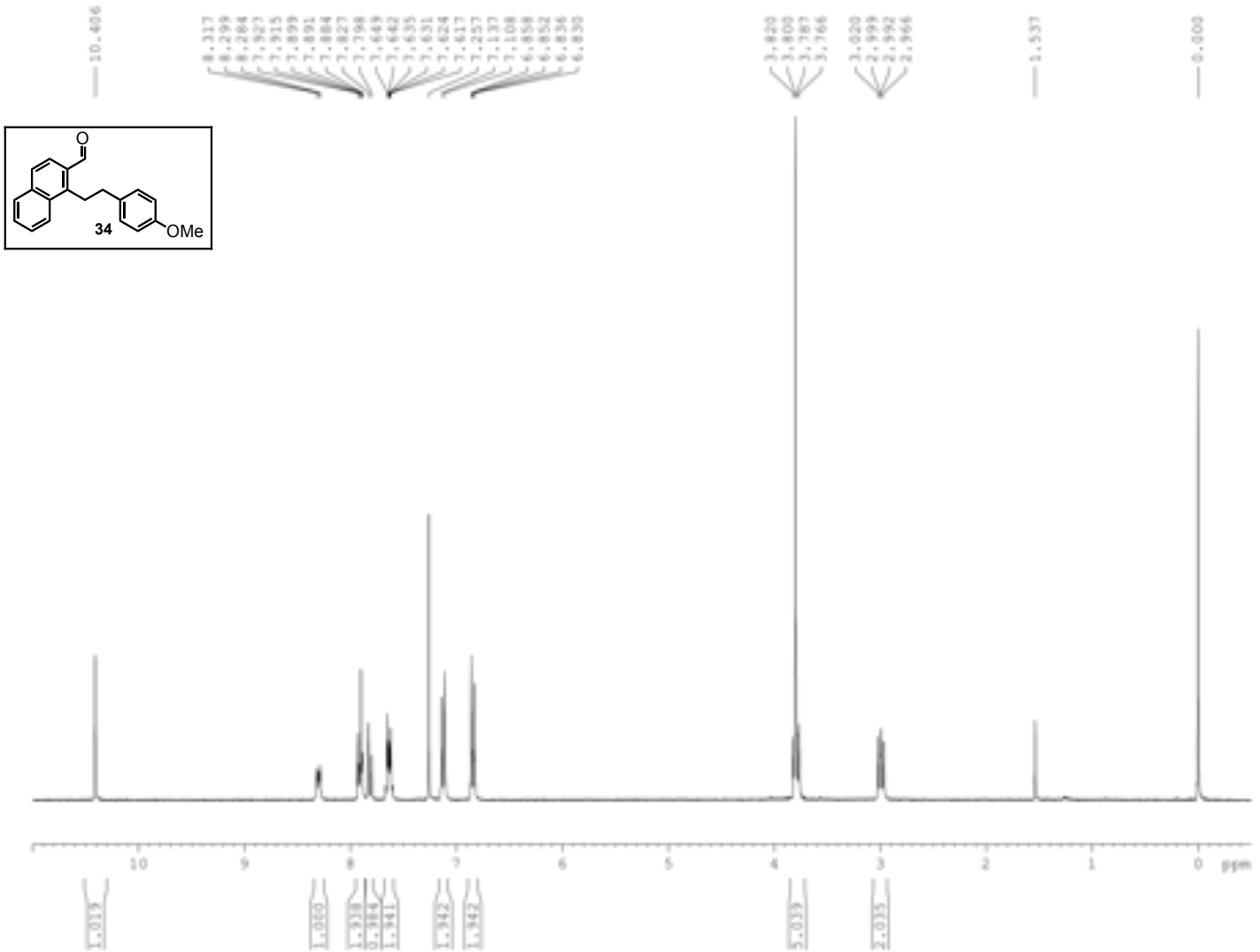
33.916
F
F
O
OMe
32
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.827
7.798
7.649
7.642
7.635
7.631
7.624
7.617
7.257
7.137
7.108
6.858
6.852
6.836
6.830
3.820
3.800
3.787
3.766
3.020
2.999
2.992
2.966
1.537
0.000
O
34
OMe
10
9
8
7
6
5
4
3
2
1
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ppm
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1.000
1.938
0.994
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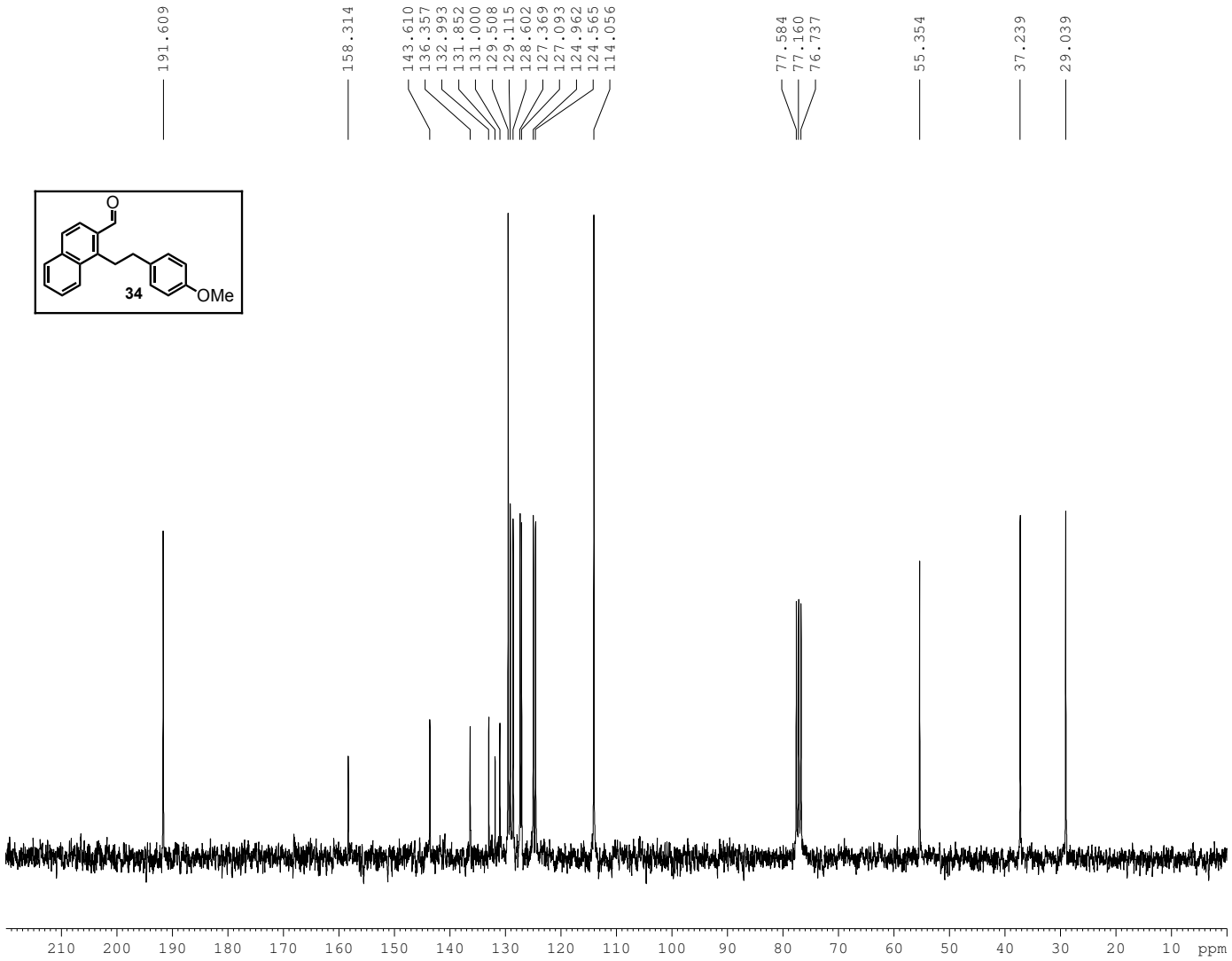
1.942
1.942
5.039
2.035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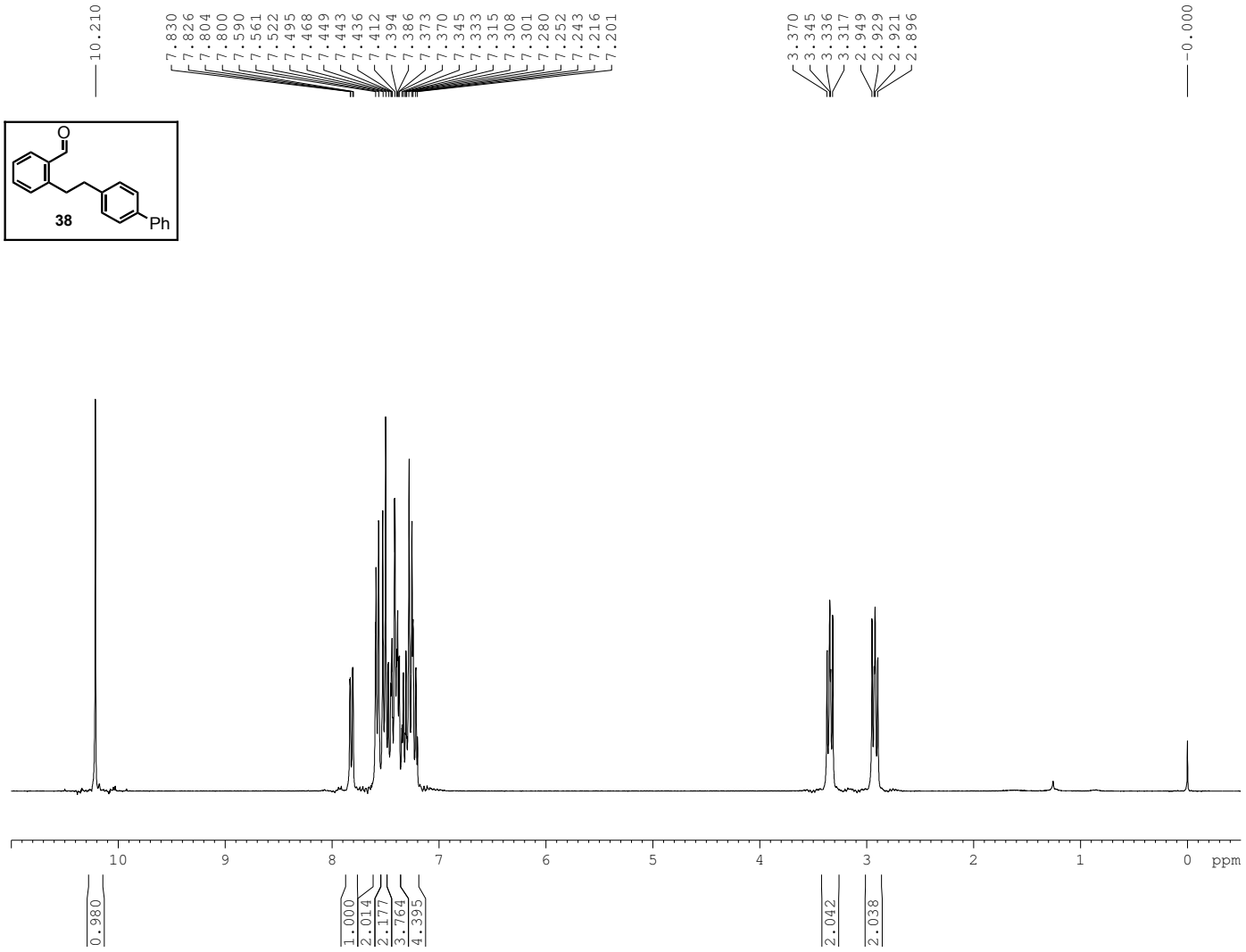
158.314
143.610
136.357
132.993
131.852
131.000
129.508
129.115
128.602
127.369
127.093
124.962
124.565
114.056
77.584
77.160
76.737
55.354
37.239
29.039
O
34
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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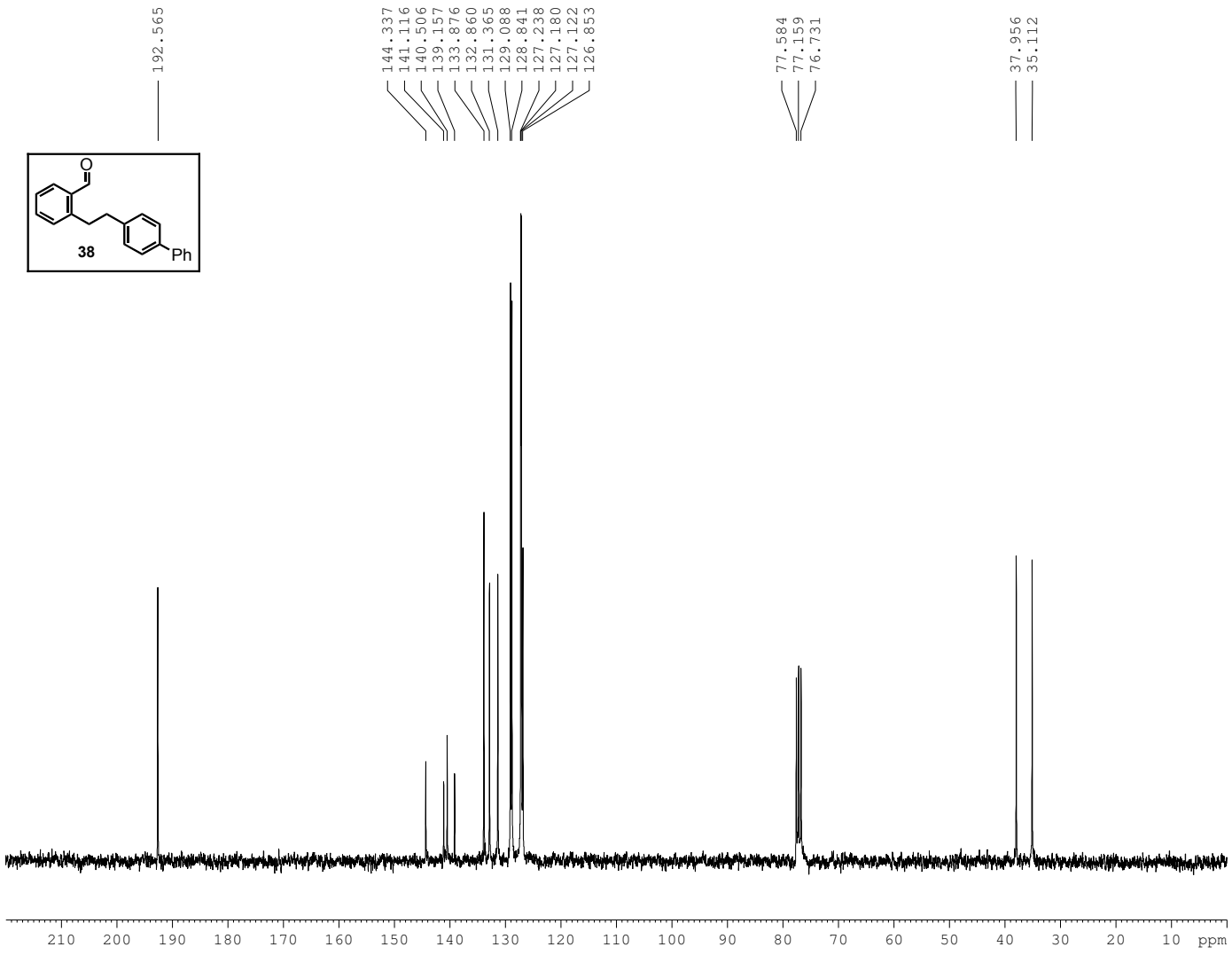
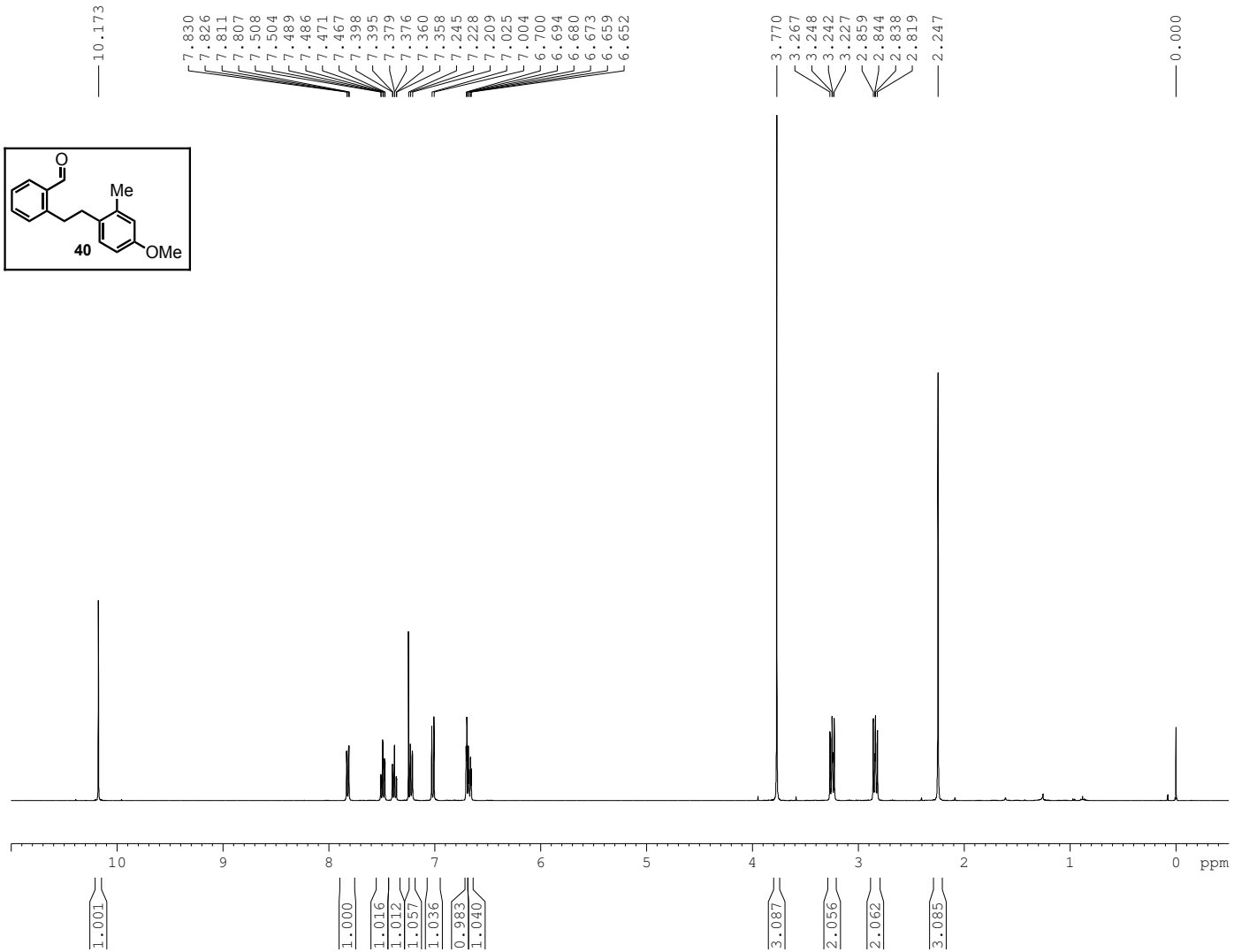
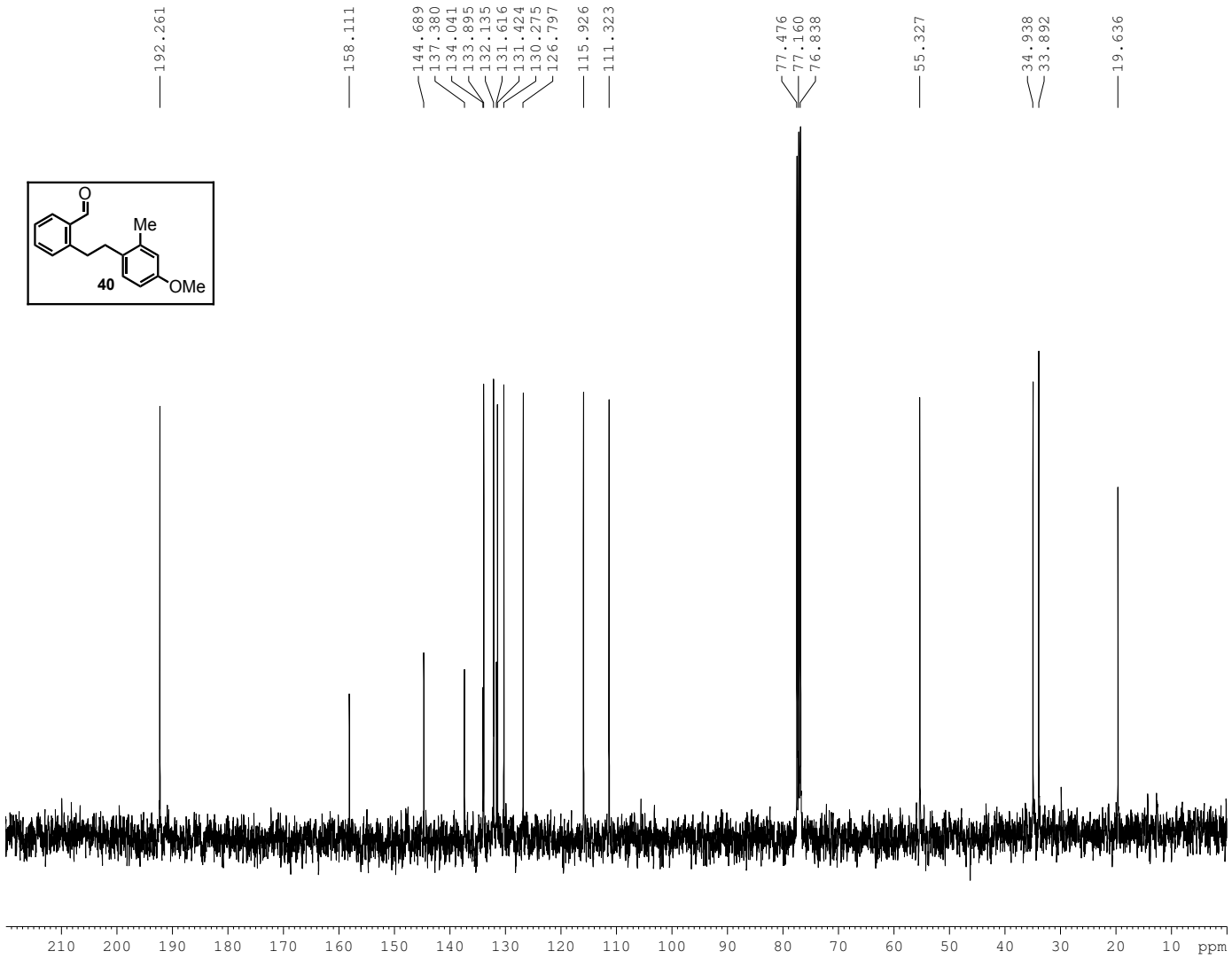
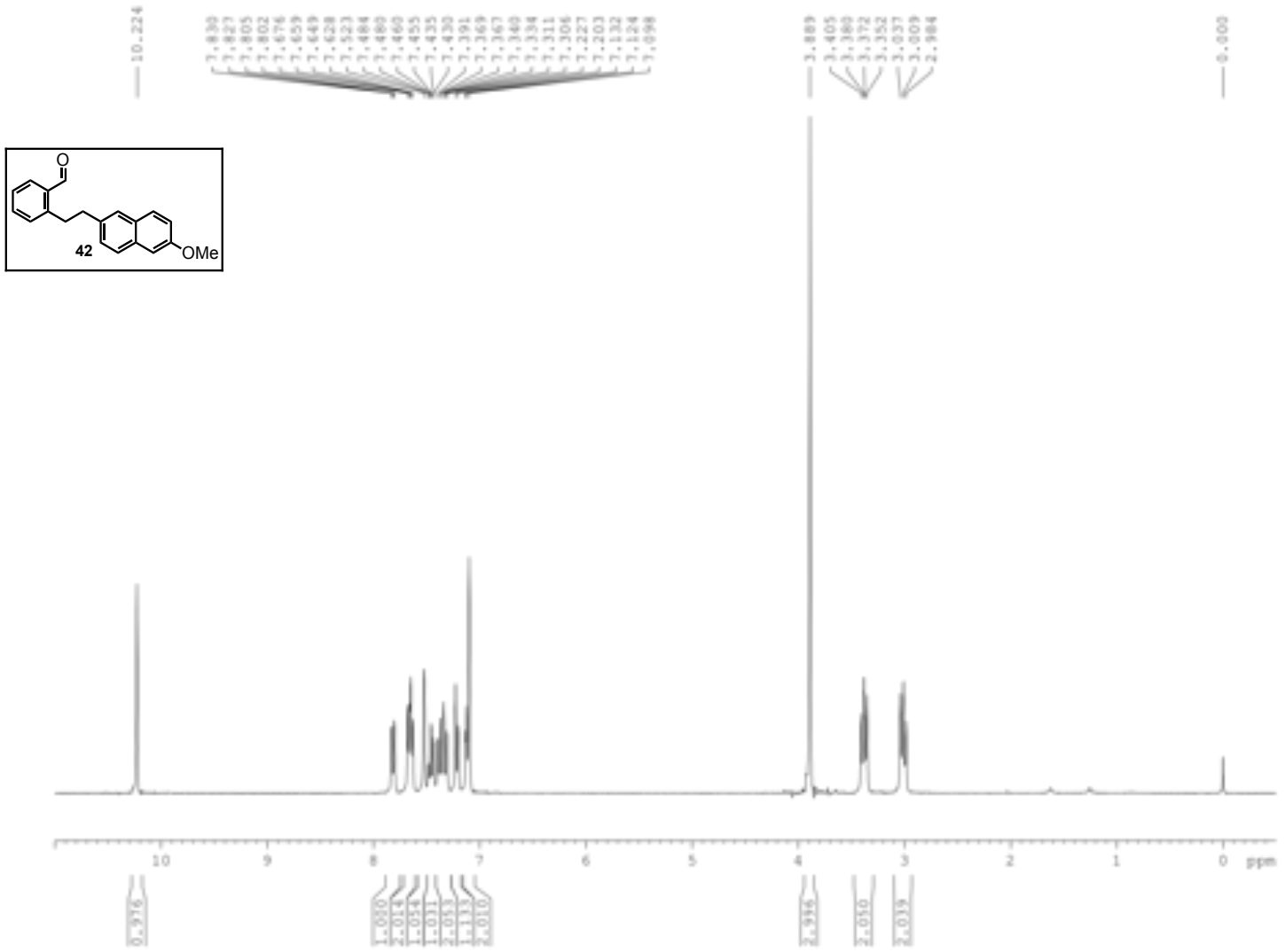
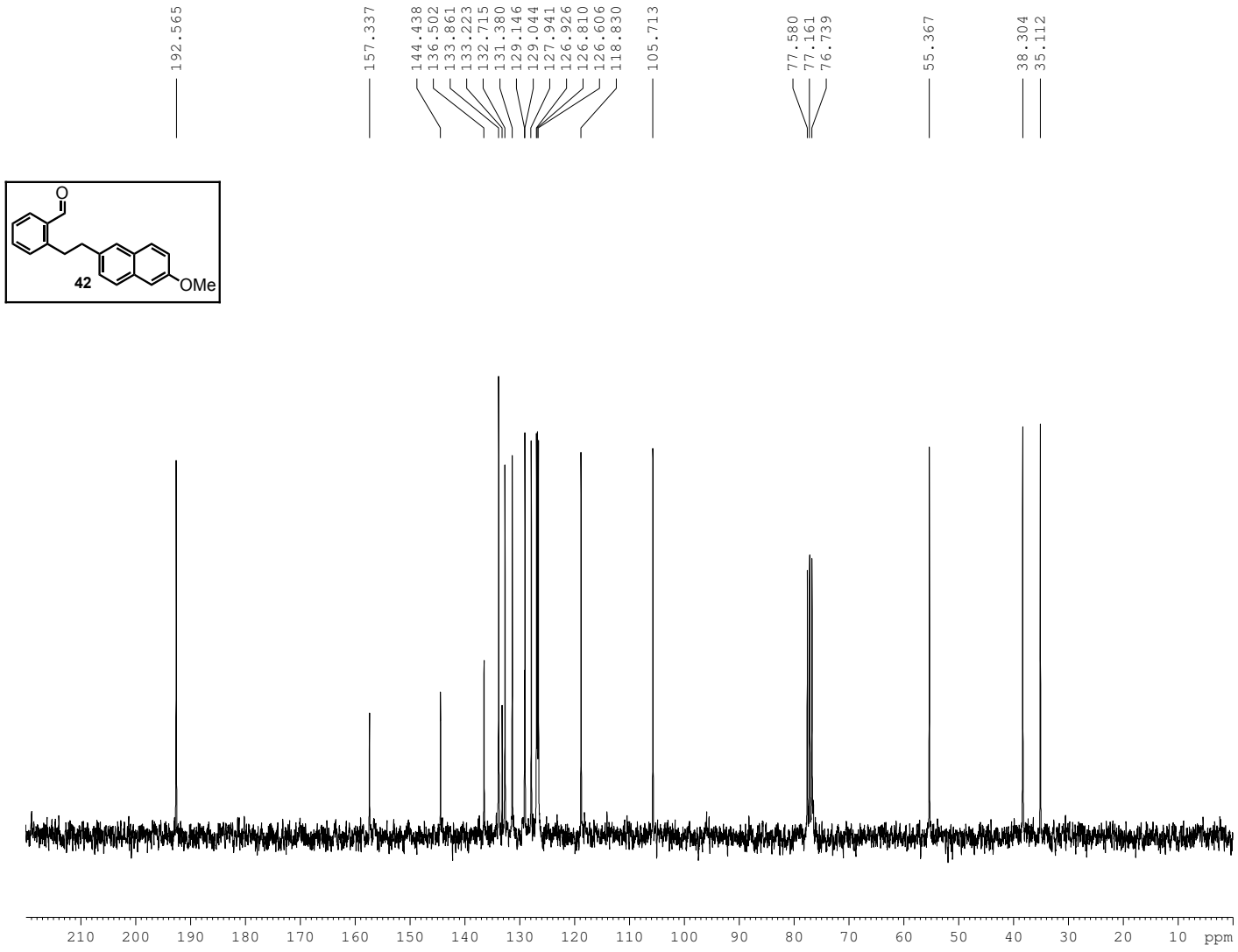
7.830
7.826
7.804
7.800
7.590
7.561
7.522
7.495
7.468
7.449
7.443
7.436
7.412
7.394
7.386
7.373
7.370
7.345
7.333
7.315
7.308
7.301
7.280
7.252
7.243
7.216
7.201
3.370
3.345
3.336
3.317
2.949
2.929
2.921
2.896
0.000
O
38
Ph
10
9
8
7
6
5
4
3
2
1
0
ppm
0.980
1.000
2.014
2.177
3.764
4.395
2.042
2.038

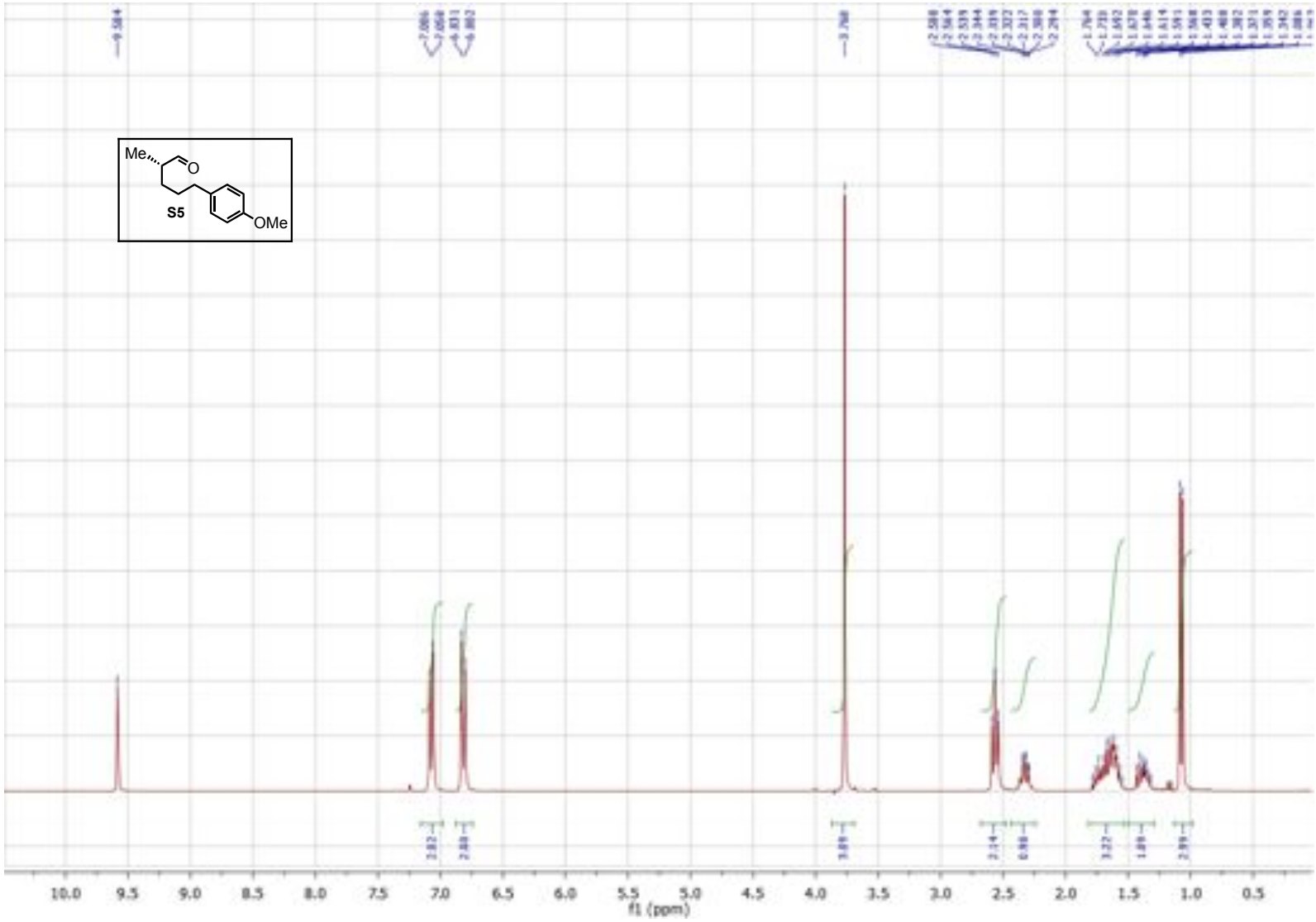

192.565
144.337
141.116
140.506
139.157
133.876
132.860
131.365
129.088
128.841
127.238
127.180
127.122
126.853
77.584
77.159
76.731
37.956
35.112
O
38
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

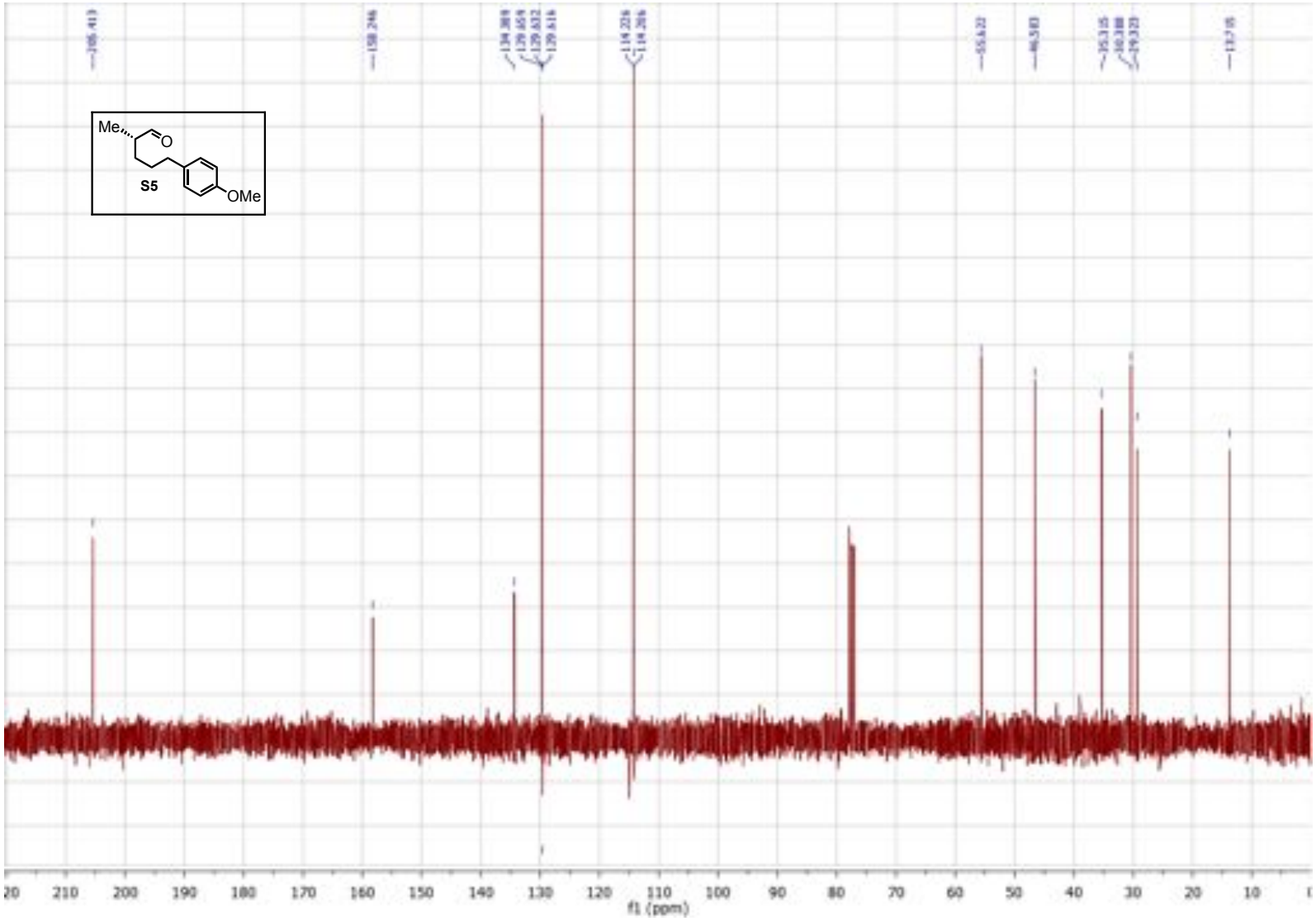

10.173
7.830
7.826
7.811
7.807
7.508
7.504
7.489
7.486
7.471
7.467
7.398
7.395
7.379
7.376
7.360
7.358
7.245
7.228
7.209
7.025
7.004
6.700
6.694
6.680
6.673
6.659
6.652
3.770
3.267
3.248
3.242
3.227
2.859
2.844
2.838
2.819
2.247
0.000
O
Me
OMe
40
10
9
8
7
6
5
4
3
2
1
0
ppm
1.001
1.000
1.016
1.012
1.057
1.036
0.983
1.040
3.087
2.056
2.062
3.085

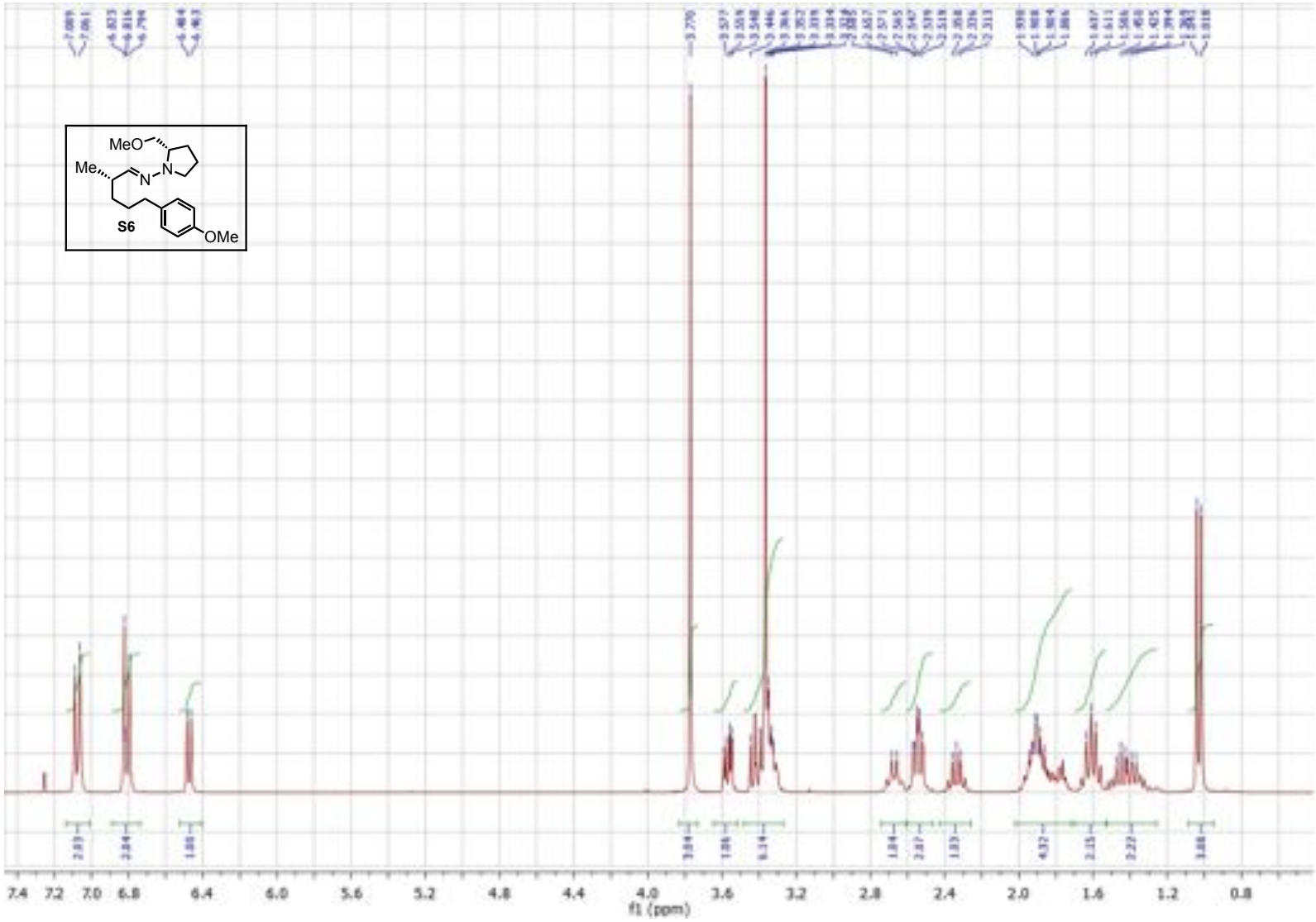

192.261
158.111
144.689
137.380
134.041
133.895
132.135
131.616
131.424
130.275
126.797
115.926
111.323
77.476
77.160
76.838
55.327
34.938
33.892
19.636
O
Me
40
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

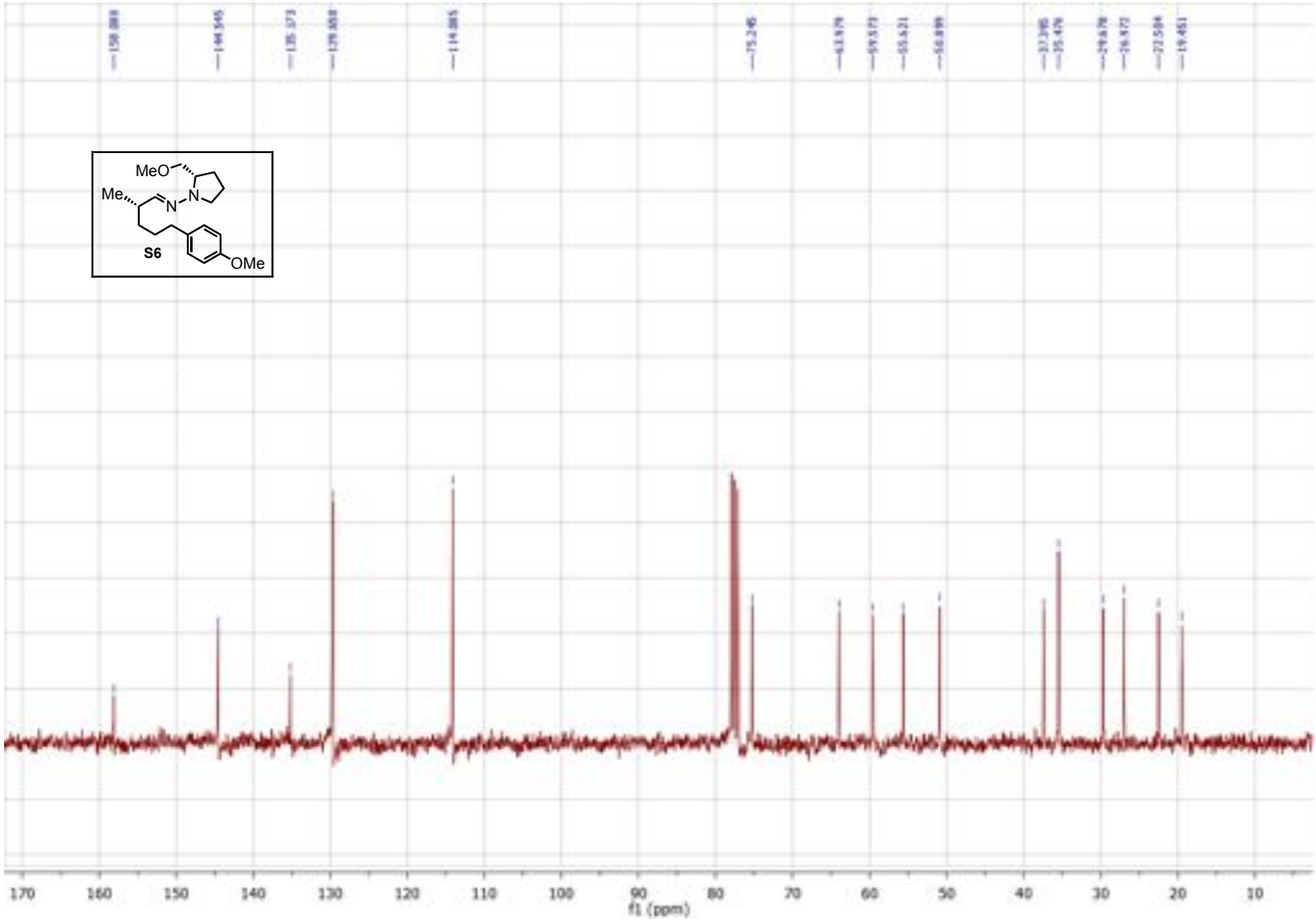

10.224
7.830
7.827
7.805
7.802
7.676
7.659
7.649
7.628
7.523
7.484
7.480
7.460
7.455
7.435
7.430
7.391
7.369
7.367
7.340
7.334
7.311
7.306
7.227
7.203
7.132
7.124
7.098
3.889
3.405
3.380
3.372
3.352
3.037
3.009
2.984
0.000
O
42
OMe
10
9
8
7
6
5
4
3
2
1
0
ppm
0.976
1.080
2.014
1.054
1.011
2.053
4.115
2.010
2.936
2.050
2.019


192.565
157.337
144.438
136.502
133.861
133.223
132.715
131.380
129.146
129.044
127.941
126.926
126.810
126.606
118.830
105.713
77.580
77.161
76.739
55.367
38.304
35.112
O
42
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Me
O
S5
OMe
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


Me
O
S5
OMe
f1 (ppm)


MeO
Me
N
N
S6
OMe
f1 (ppm)


MeO
Me
N
N
S6
OMe
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)