

Supporting Information

Nickel-Catalyzed Suzuki–Miyaura Coupling of Heteroaryl Ethers with Arylboronic Acids

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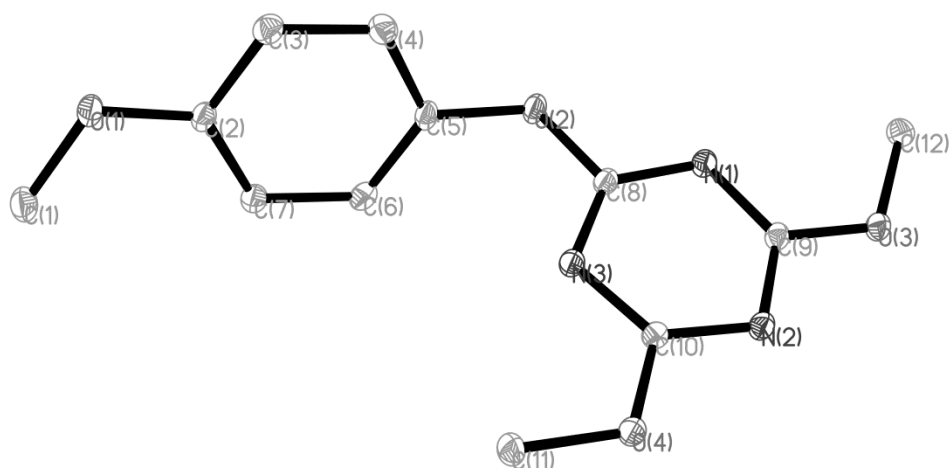
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General Comments

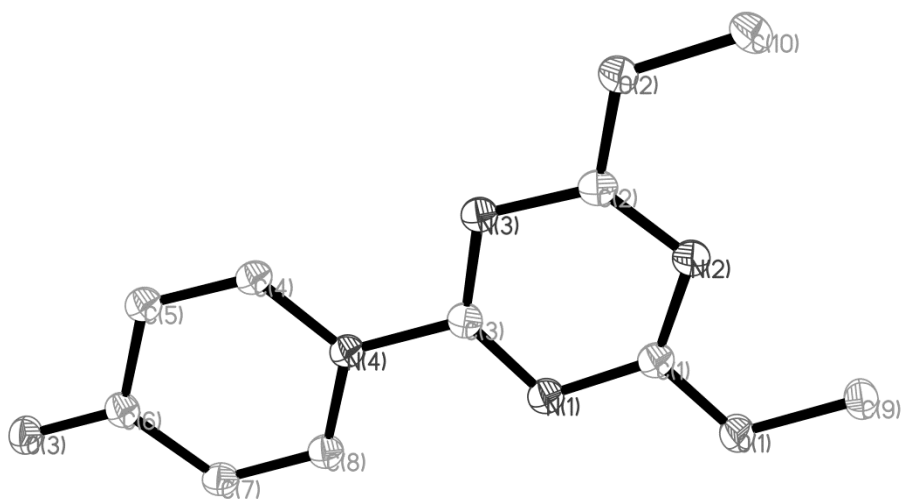
¹H and ¹³C Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker AV400 spectrometer at ambient temperature in CDCl₃ (Cambridge Isotope Laboratories, Inc). ESI-MS were recorded on Thermo Finnigan LCQ Advantage spectrometers. HRMS were recorded on Varian 7.0T FTICR-MS. Melt points of compounds were recorded with uncorrected thermometers. Flash column chromatography was performed on silica gel 60 (230-400 mesh). Crystallographic data was collected on a Bruker SMART CCD areadetector diffractometer with graphite-monochromated Mo K α radiation (λ 10.71073 Å). Diffraction measurements were made at room temperature. An absorption correction by SADABS was applied to the intensity data. The structures were solved by Patterson method. The remaining non-hydrogen atoms were determined from the successive difference Fourier syntheses. All nonhydrogen atoms were refined anisotropically except those mentioned otherwise. The hydrogen atoms were generated geometrically and refined with isotropic thermal parameters. The structures were refined on F² by full-matrix least-squares methods using the SHELXTL-97 program package [G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures. University of Göttingen, Göttingen, Germany, 1997].

Crystal Structures and X-ray Diffraction Analysis Data

Single crystals for X-ray diffraction analysis of compounds **3a** and **3y** were obtained from a concentration solution of ethanol. The crystallographic data for both compounds and selected bond distances and angles were outlined in Table 1 and in Table 2, respectively.



Compound **3a**



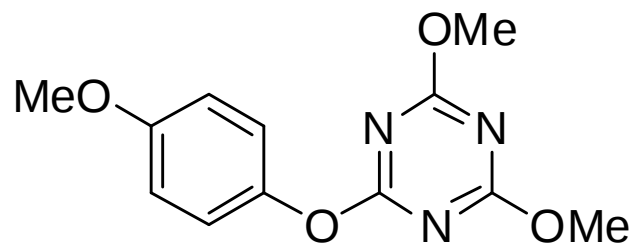
Compound 3y

Table 1. Crystallographic data for compounds **3a** and **3y**.

	3a	3y
chemical formula	C ₁₂ H ₁₃ N ₃ O ₄	C ₁₀ H ₁₂ N ₄ O ₄
space group	<i>P2(1)/c</i>	<i>Pnma</i>
cryst syst	monoclinic	orthorhombic
<i>a</i> , Å	7.902(2)	8.055(16)
<i>b</i> , Å	6.4016(16)	6.5780(12)
<i>c</i> , Å	24.337(6)	22.091(3)
<i>α</i> , deg	90.00	90.00
<i>β</i> , deg	94.076 (5) ^o	90.00
<i>γ</i> , deg	90.00	90.00
<i>Z</i>	4	4
<i>D</i> _{calc.} , g cm ⁻³	1.424	1.431
<i>μ</i> (Mo), mm ⁻¹	0.11	0.11
<i>F</i> (000)	552	528
<i>θ</i> range, deg	2.58 to 27.9	1.84 to 27.82
no. of reflns. collected	12181	11554
no. of unique reflns/ <i>R</i> _{int}	2922/0.033	1505/0.083
no. of params/restraints	175/0	118/0
final <i>R</i> indices	<i>R</i> ₁ = 0.0355,	<i>R</i> ₁ = 0.0467,
[<i>I</i> > 2σ (<i>I</i>)]	<i>wR</i> ₂ = 0.0984	<i>wR</i> ₂ = 1118
<i>R</i> indices (all indices)	<i>R</i> ₁ = 0.0406,	<i>R</i> ₁ = 0.0616,
	<i>wR</i> ₂ = 0.1023	<i>wR</i> ₂ = 0.1221
goodness-of-fit on <i>F</i> ²	1.050	0.987

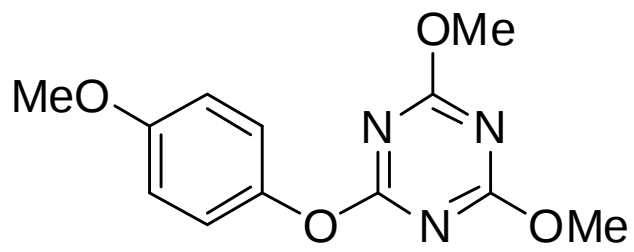
Table 2. Selected bond distances (Å) and angles (°) for compounds **3a** and **3y**.

3a		3y	
C(5)–O(2)	1.4114(11)	N(4)–C(3)	1.434(2)
C(8)–O(2)	1.3489(12)	N(1)–C(3)	1.333(2)
C(2)–O(1)	1.3635(11)	N(3)–C(3)	1.333(2)
C(9)–O(3)	1.3329(12)	C(1)–O(1)	1.336(2)
C(10)–O(4)	1.3245(12)	C(2)–O(2)	1.333(2)
C(5)–O(2)–C(8)	118.53(8)	N(3)–C(3)–N(4)	115.33(16)
O(2)–C(5)–C(4)	117.18(9)	N(2)–C(3)–N(4)	116.38(16)

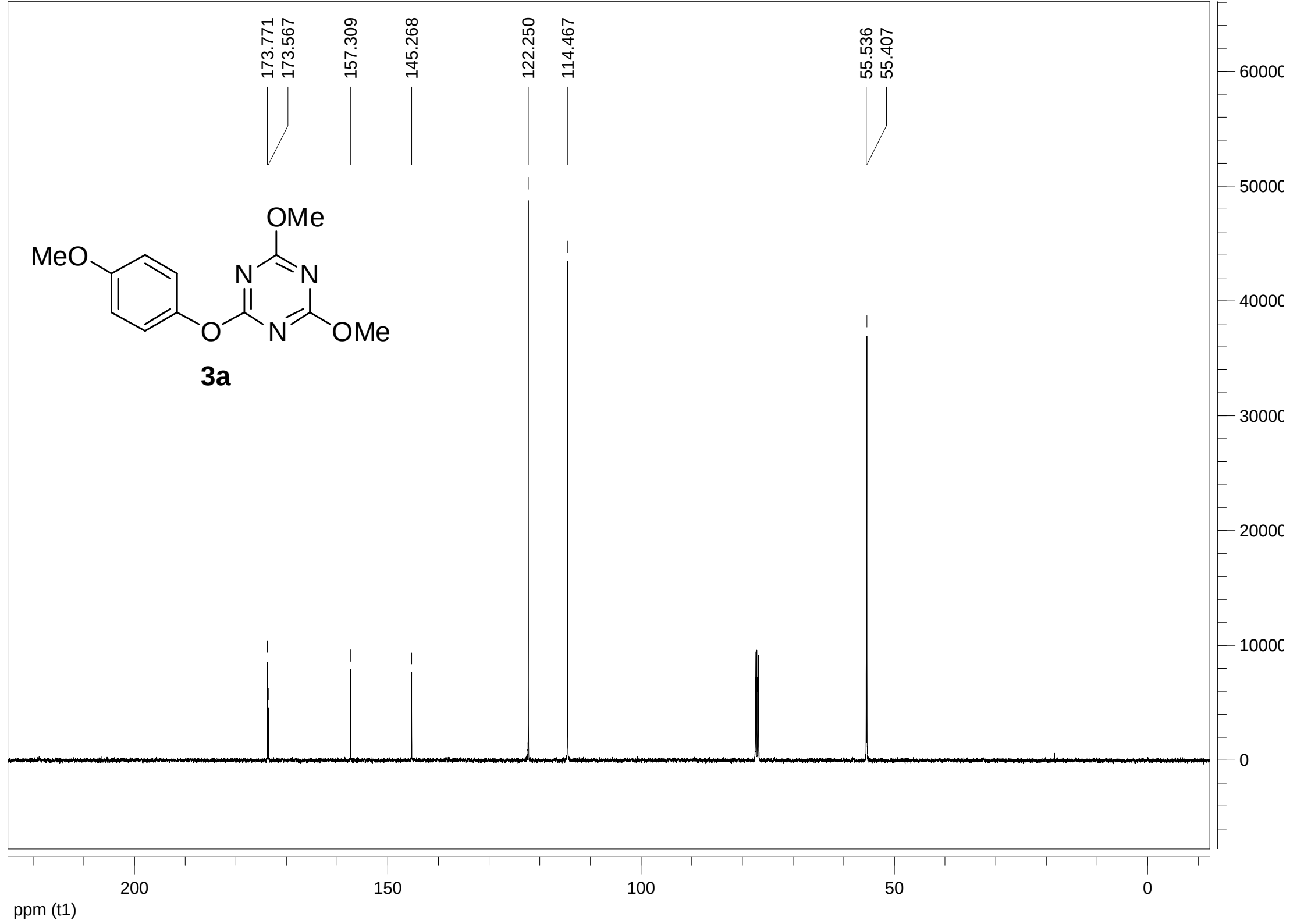
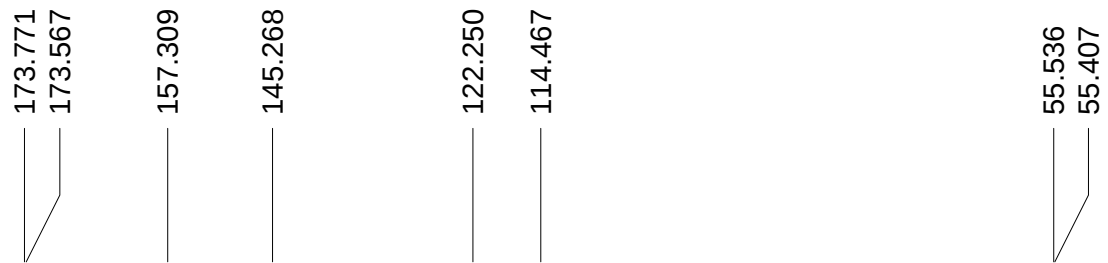


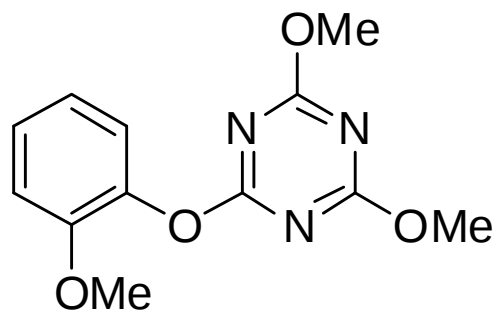
3a



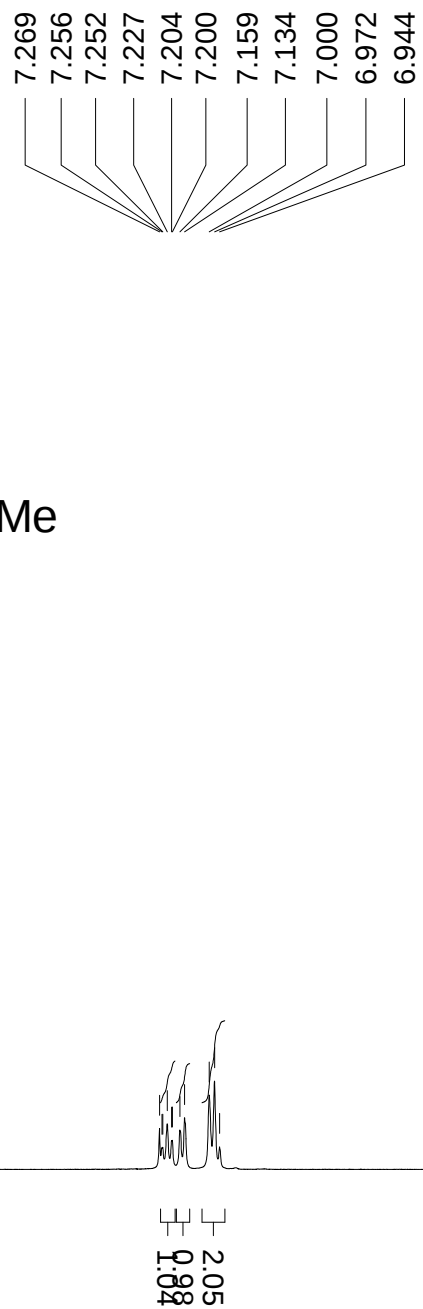


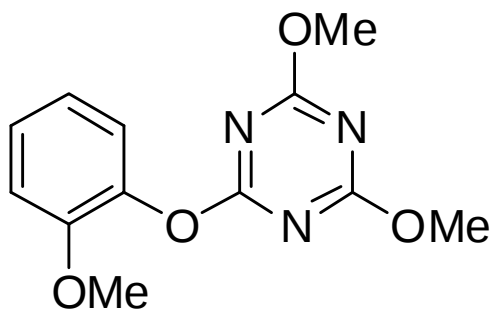
3a





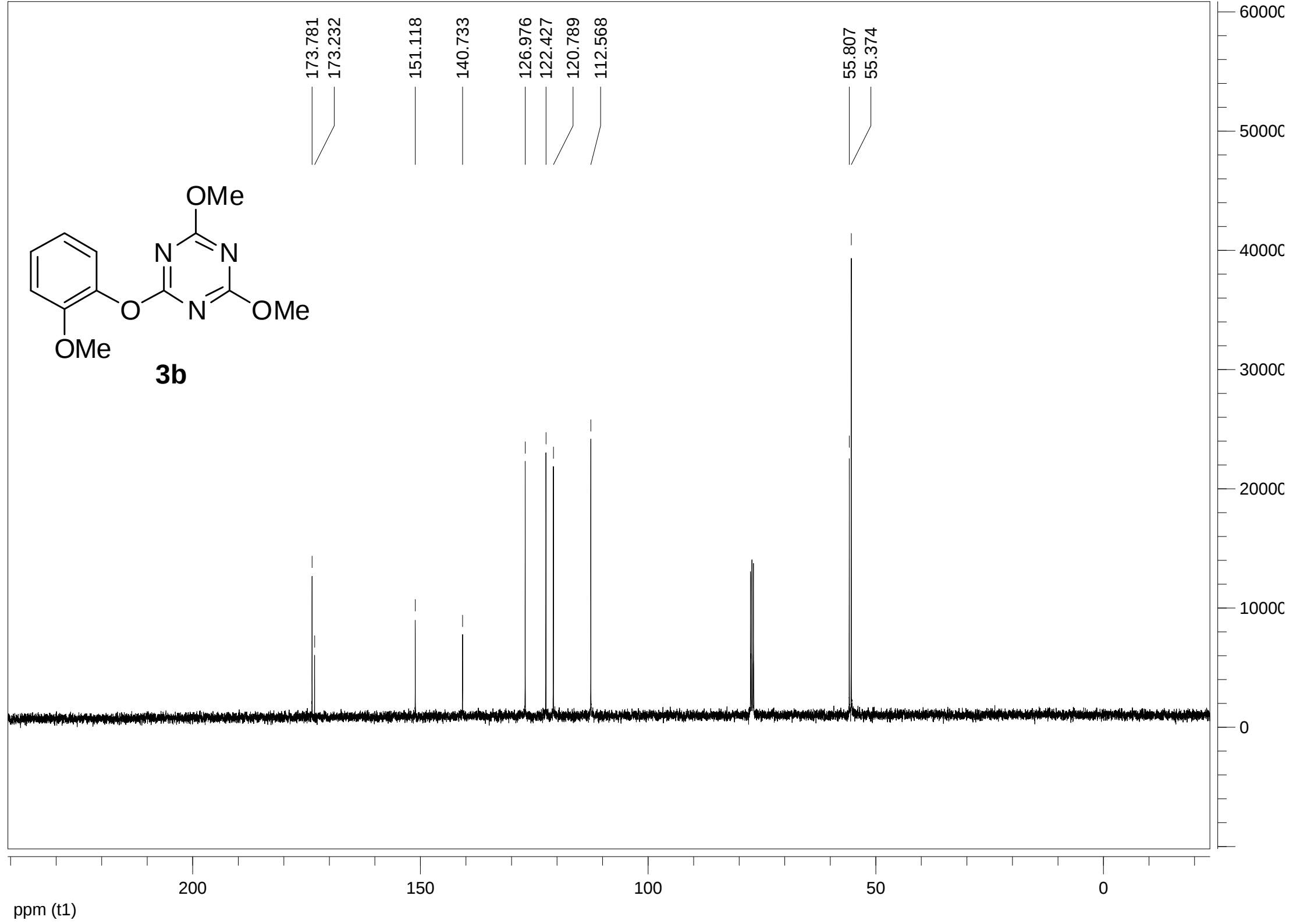
3b

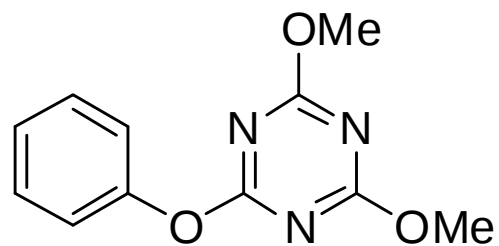




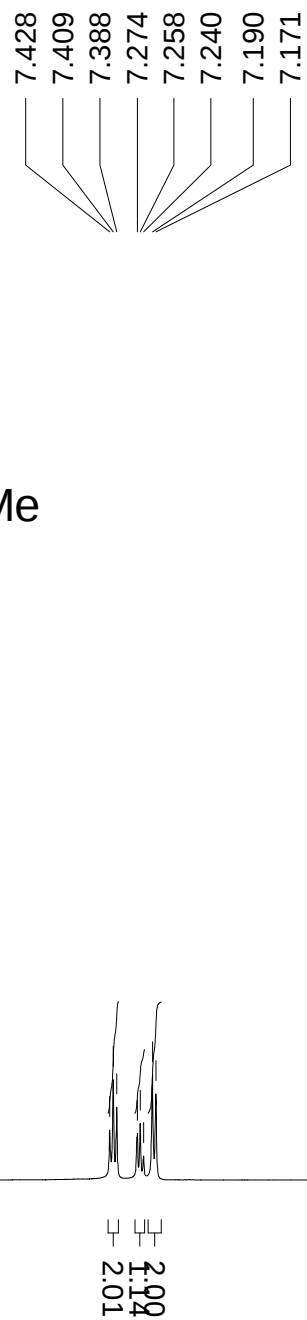
3b

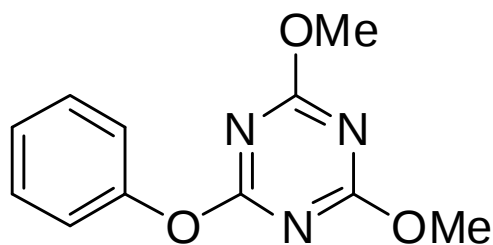
173.781	151.118	126.976	55.807
173.232	140.733	122.427	55.374
		120.789	
		112.568	



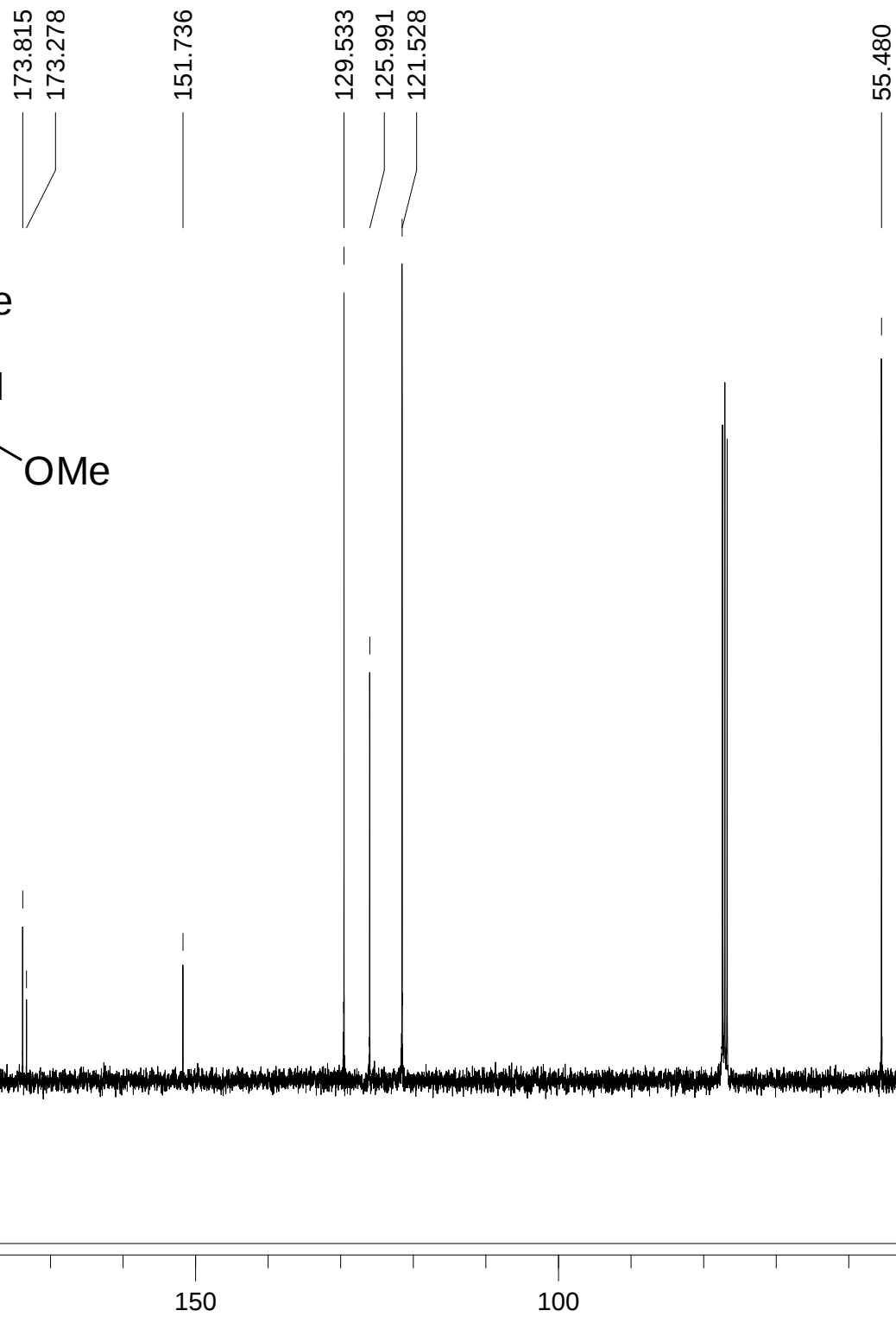


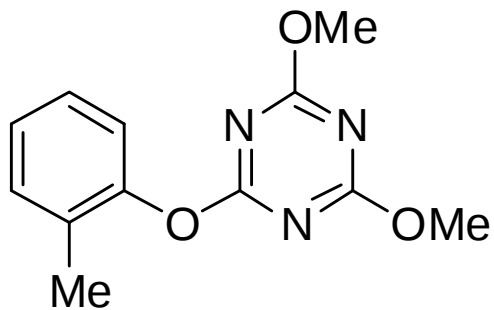
3c





3c





3d

7.271
7.259
7.241
7.227
7.208
7.186
7.183
7.168
7.081
7.061

3.983

2.192

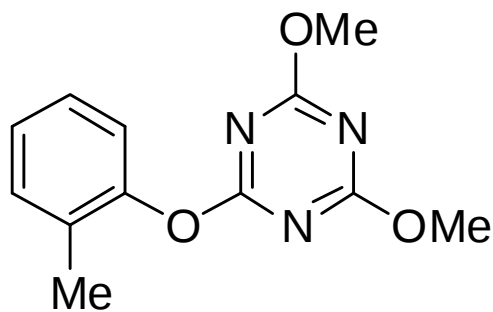
88.7
88.6
88.5

90.9
6.05

00.8
3.00

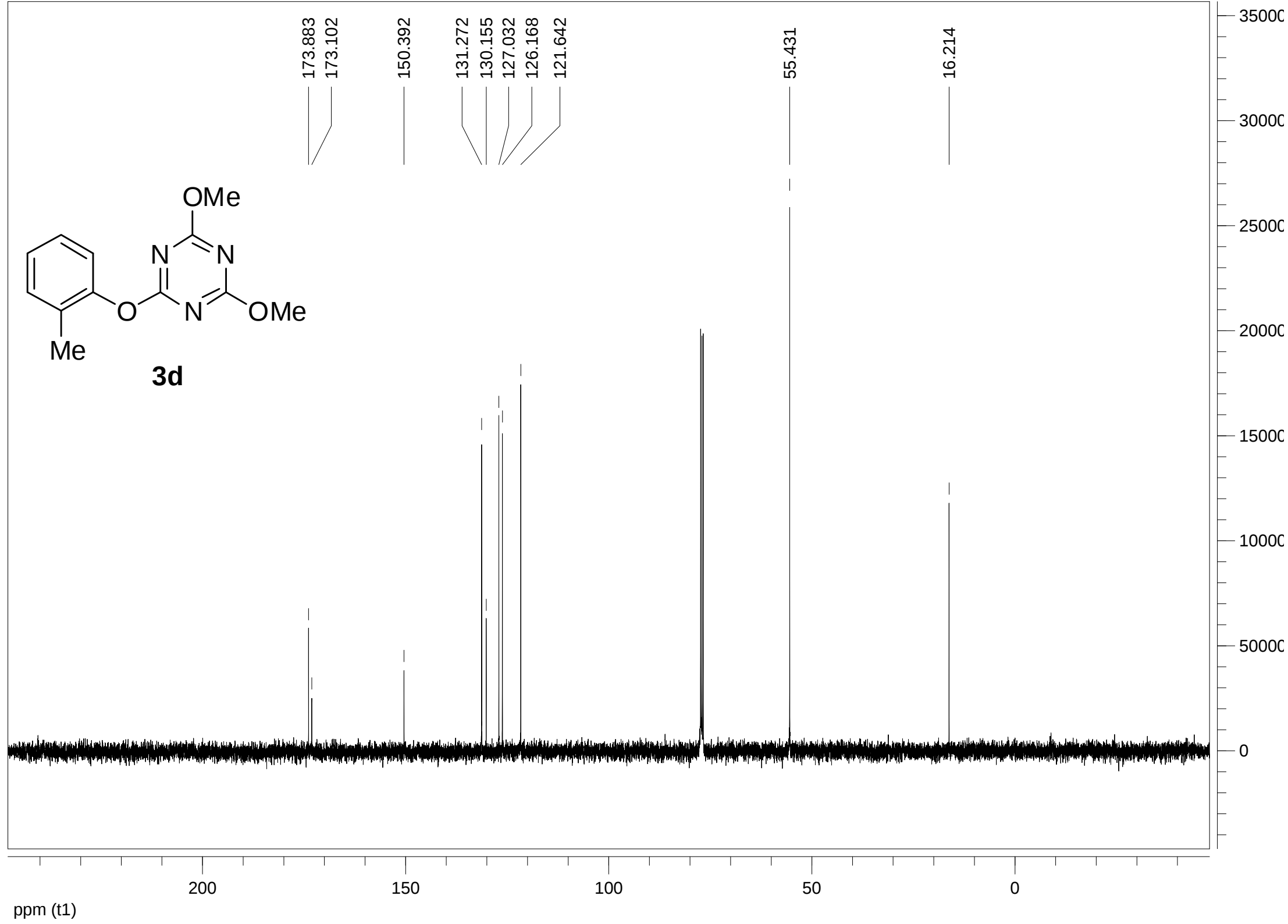
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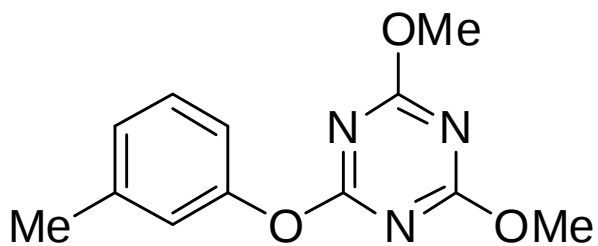
5000C
4000C
3000C
2000C
1000C
0



3d

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173.102
150.392
131.272
130.155
127.032
126.168
121.642
55.431
16.214





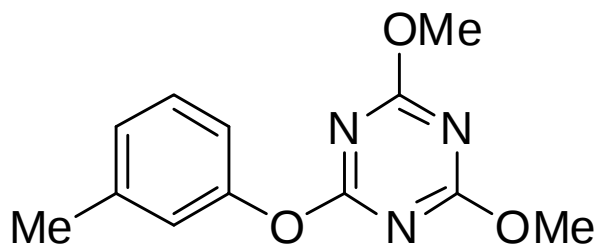
3e



10.0
ppm (t1)

5.0

0.0



3e

173.795
173.333
151.680
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118.495

55.459

21.358

4000C

3000C

2000C

1000C

0

200

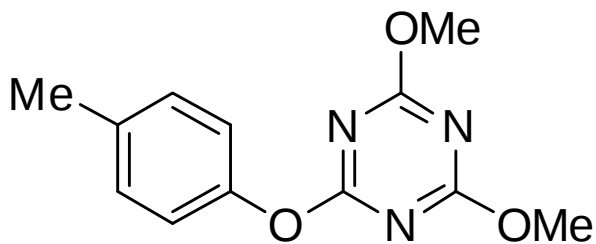
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100

50

0

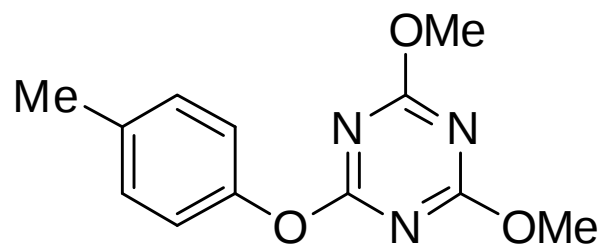
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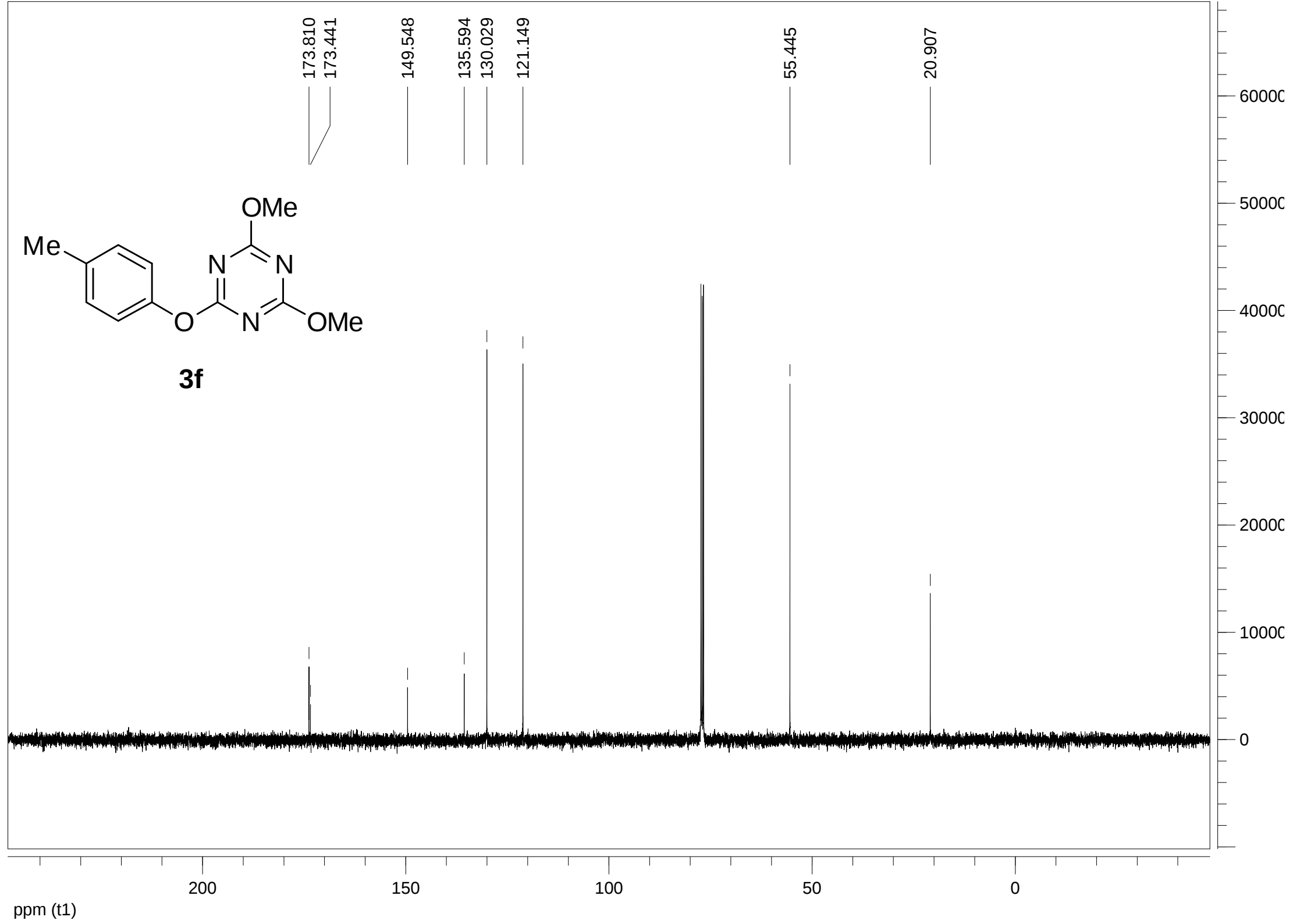
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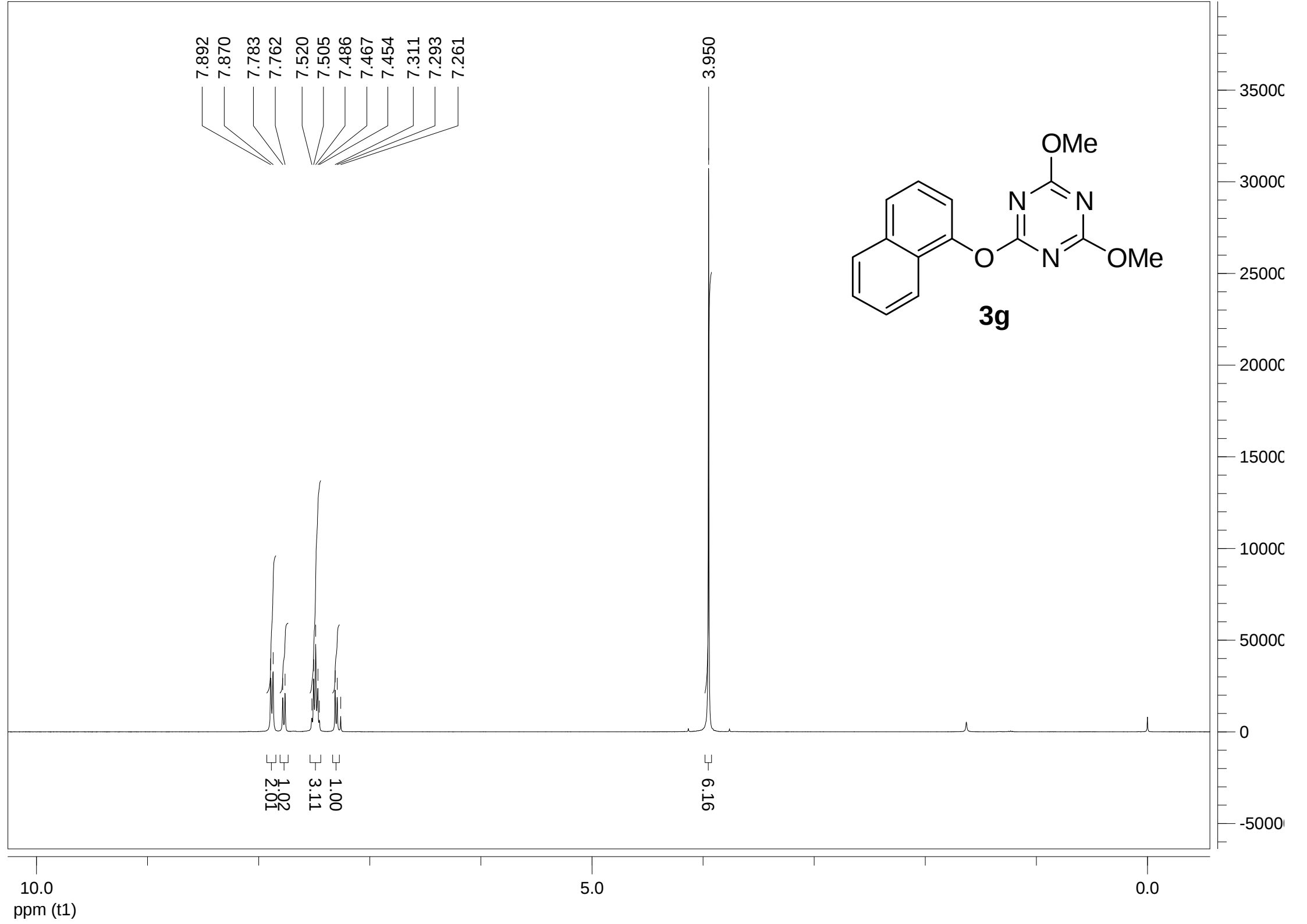


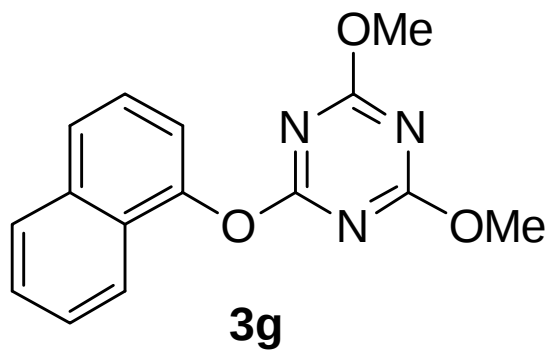
ppm (t1)



3f







173.939
173.808
147.747
134.781
128.009
126.828
126.500
126.274
125.472
121.408
117.978
55.491

5000C

4000C

3000C

2000C

1000C

0

200

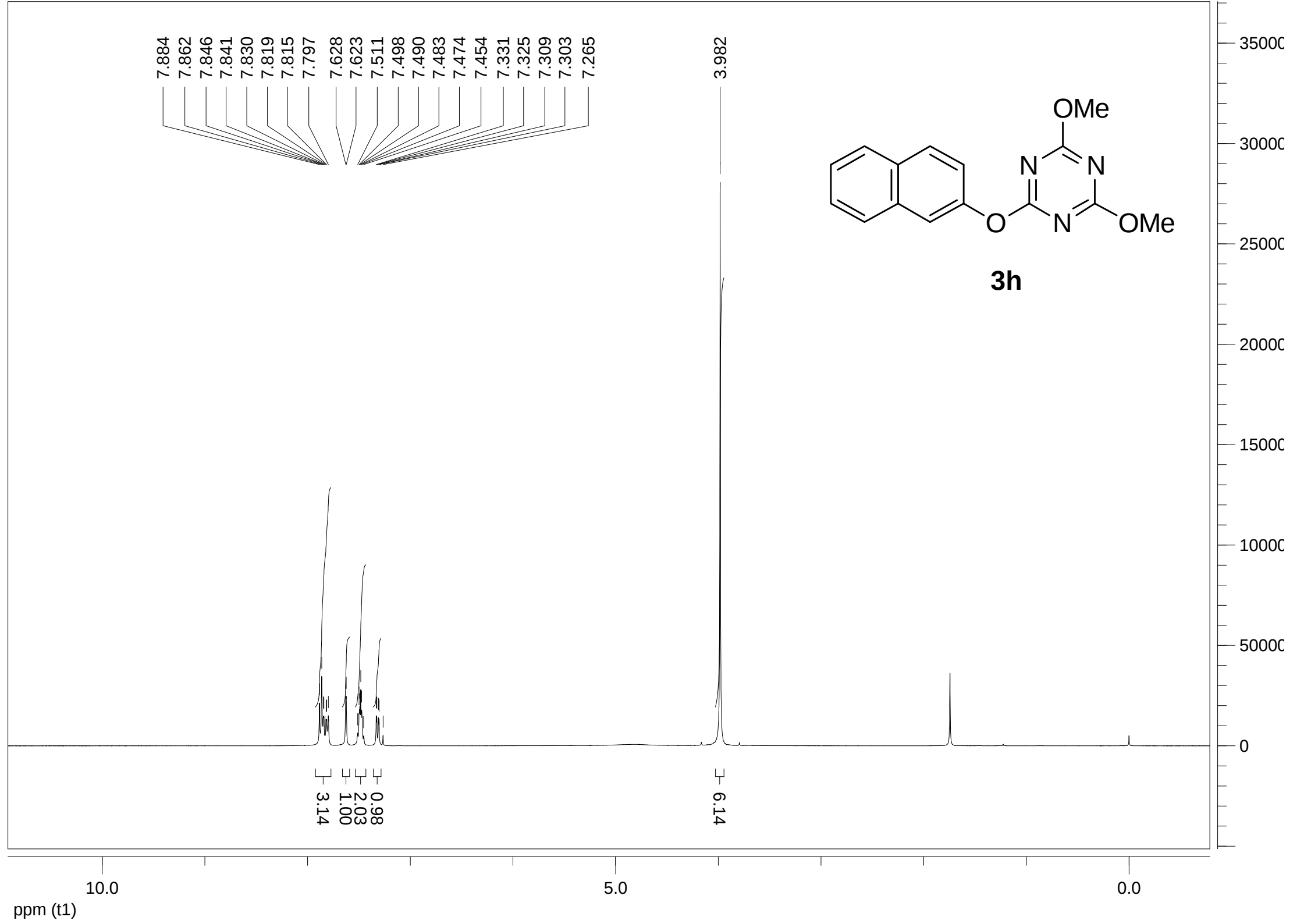
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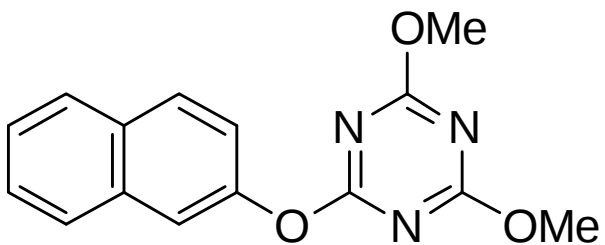
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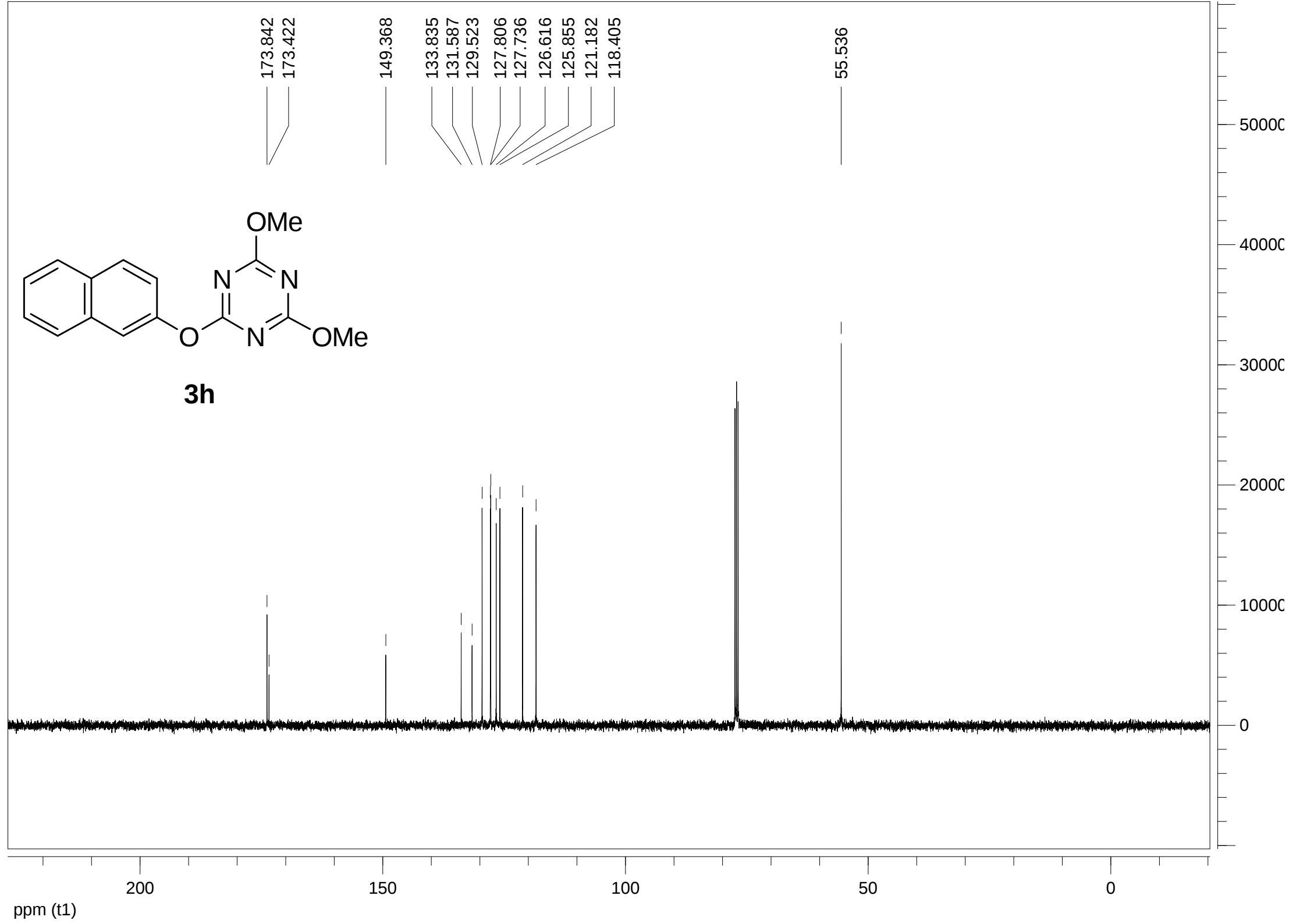
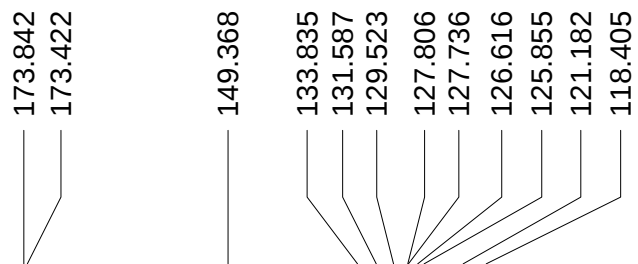
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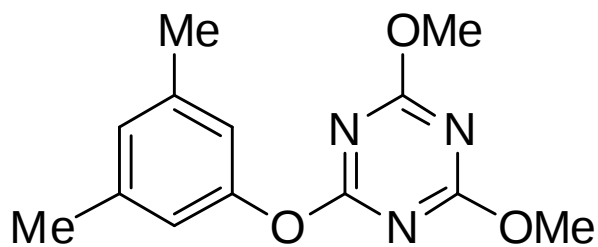
ppm (t1)





3h





3i

7.264
6.883
6.775

4.000

2.322

0.000

35000

30000

25000

20000

15000

10000

50000

0

1.08
1.08

6.10

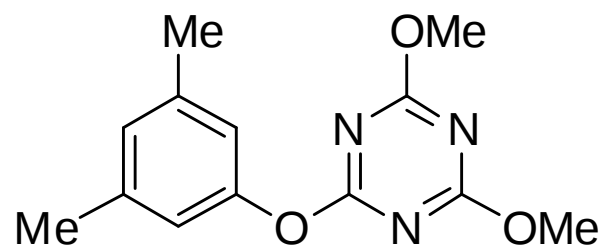
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10.0

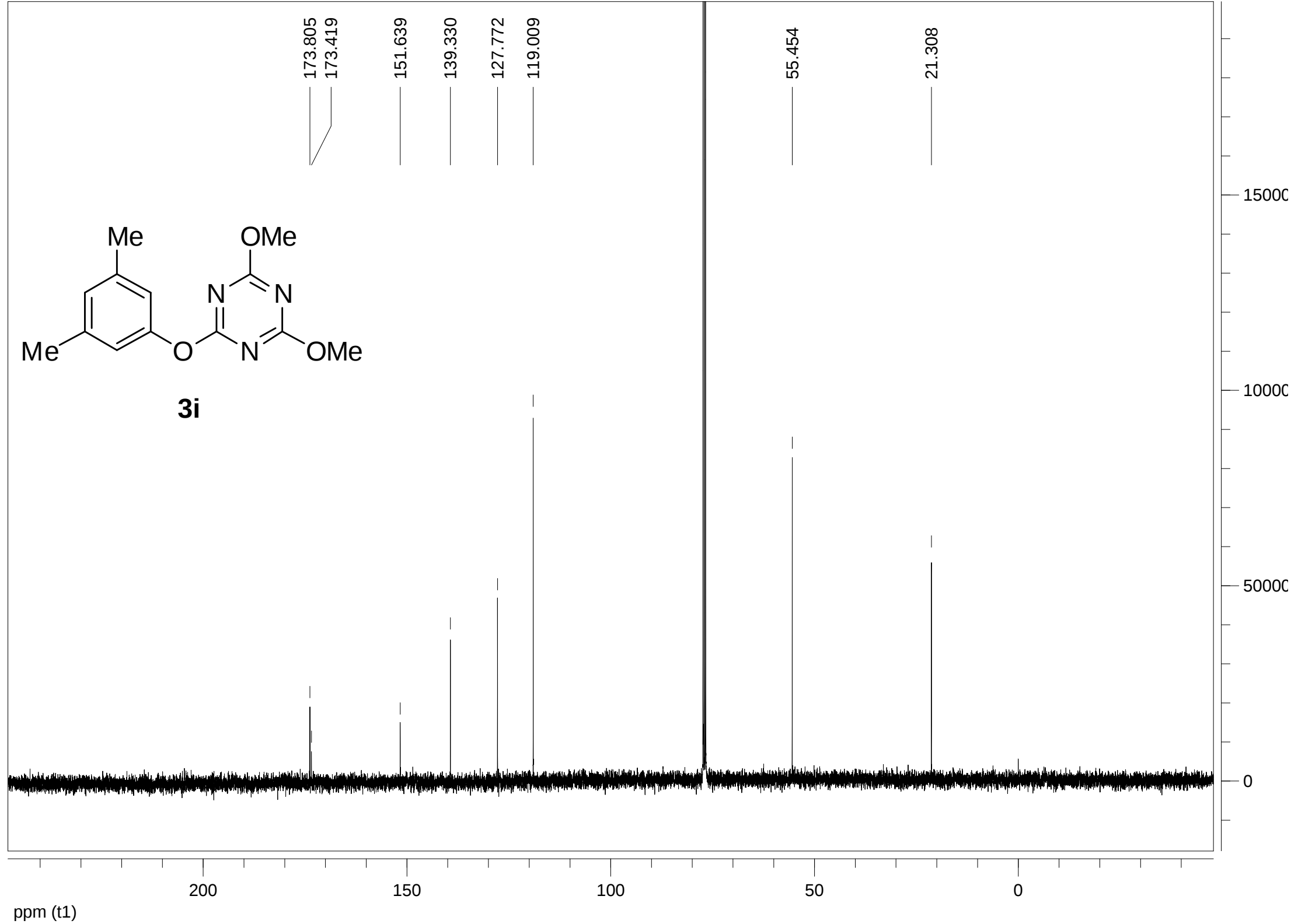
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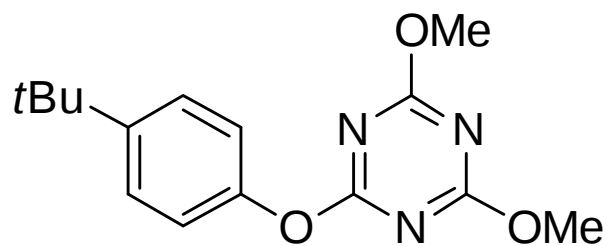
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ppm (t1)



3i





3j

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7.394
7.266
7.112
7.090

4.009

1.328

2.00

2.00

6.09

9.11

10.0
ppm (t1)

5.0

0.0

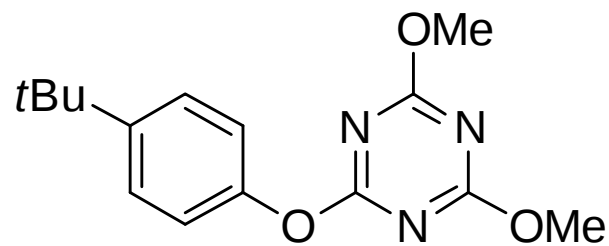
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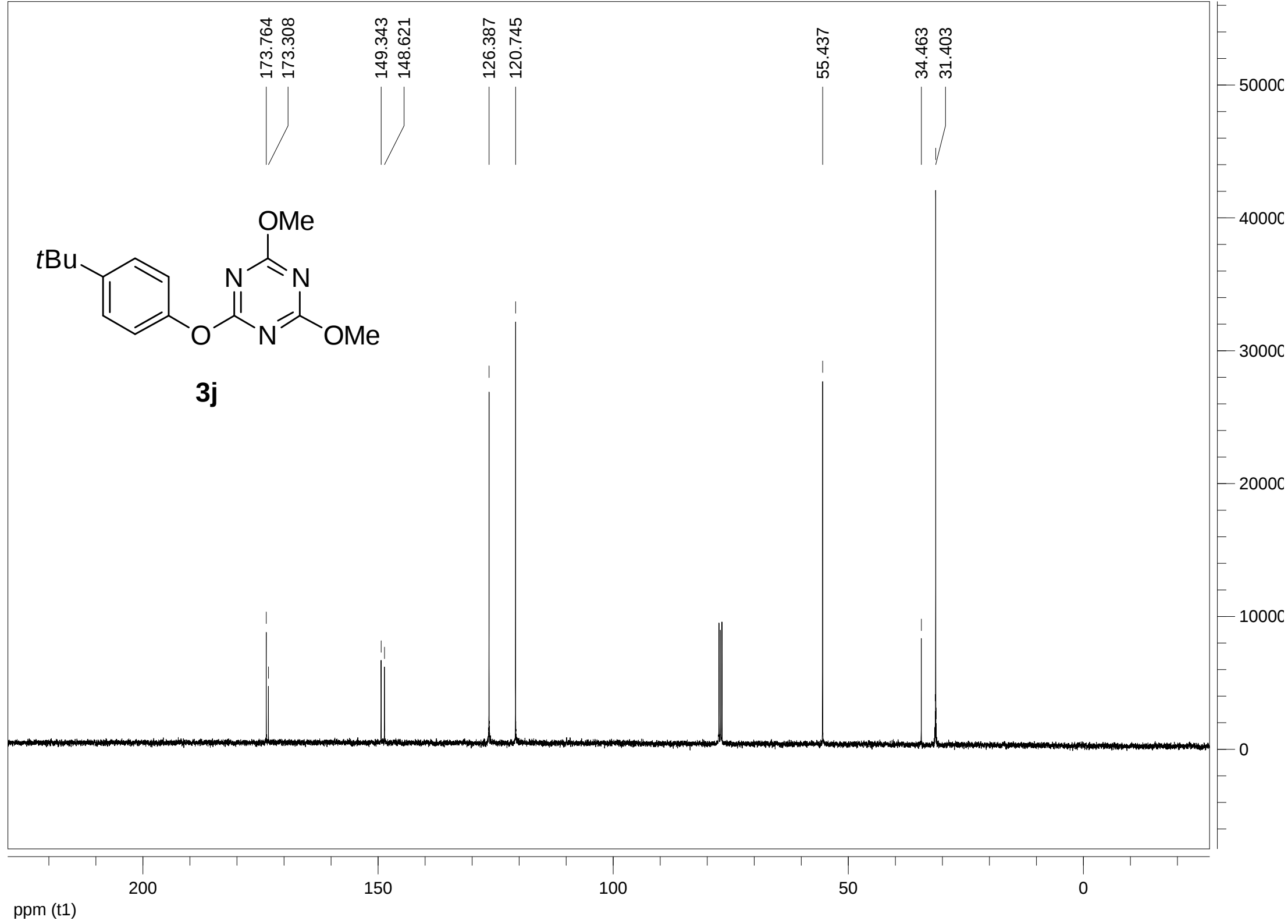
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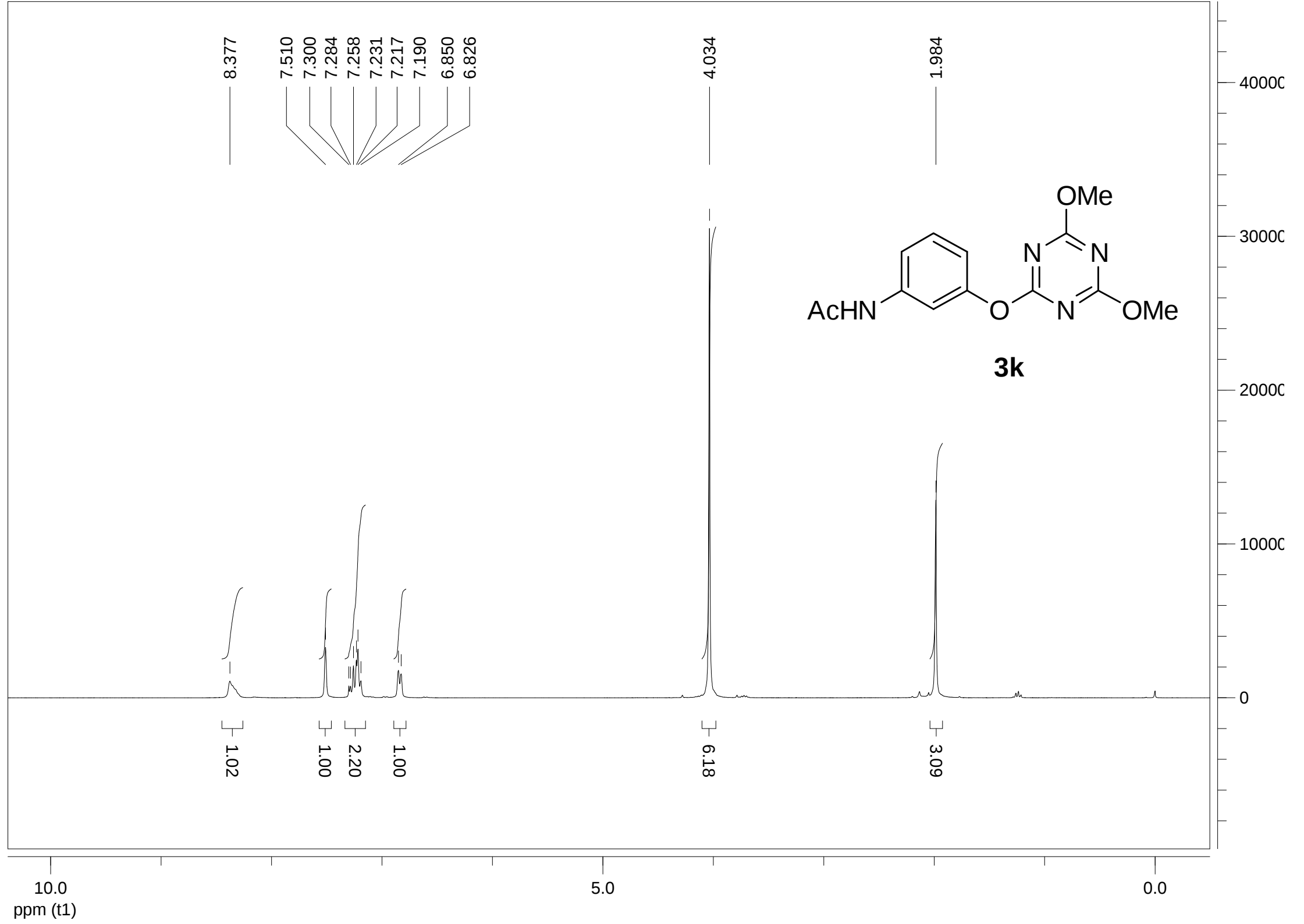
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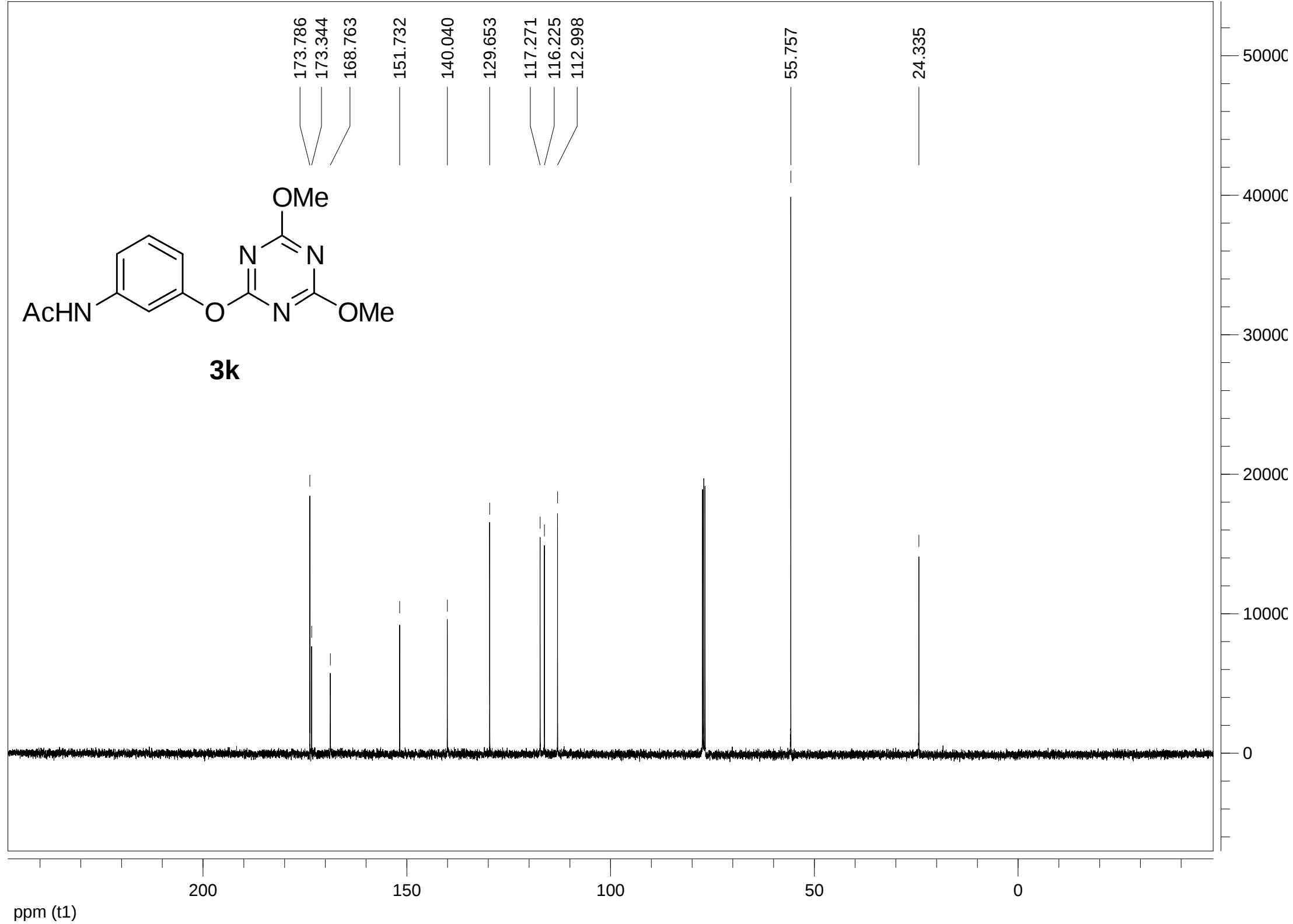
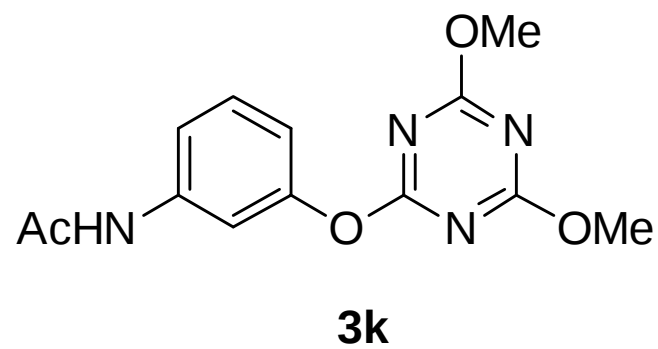
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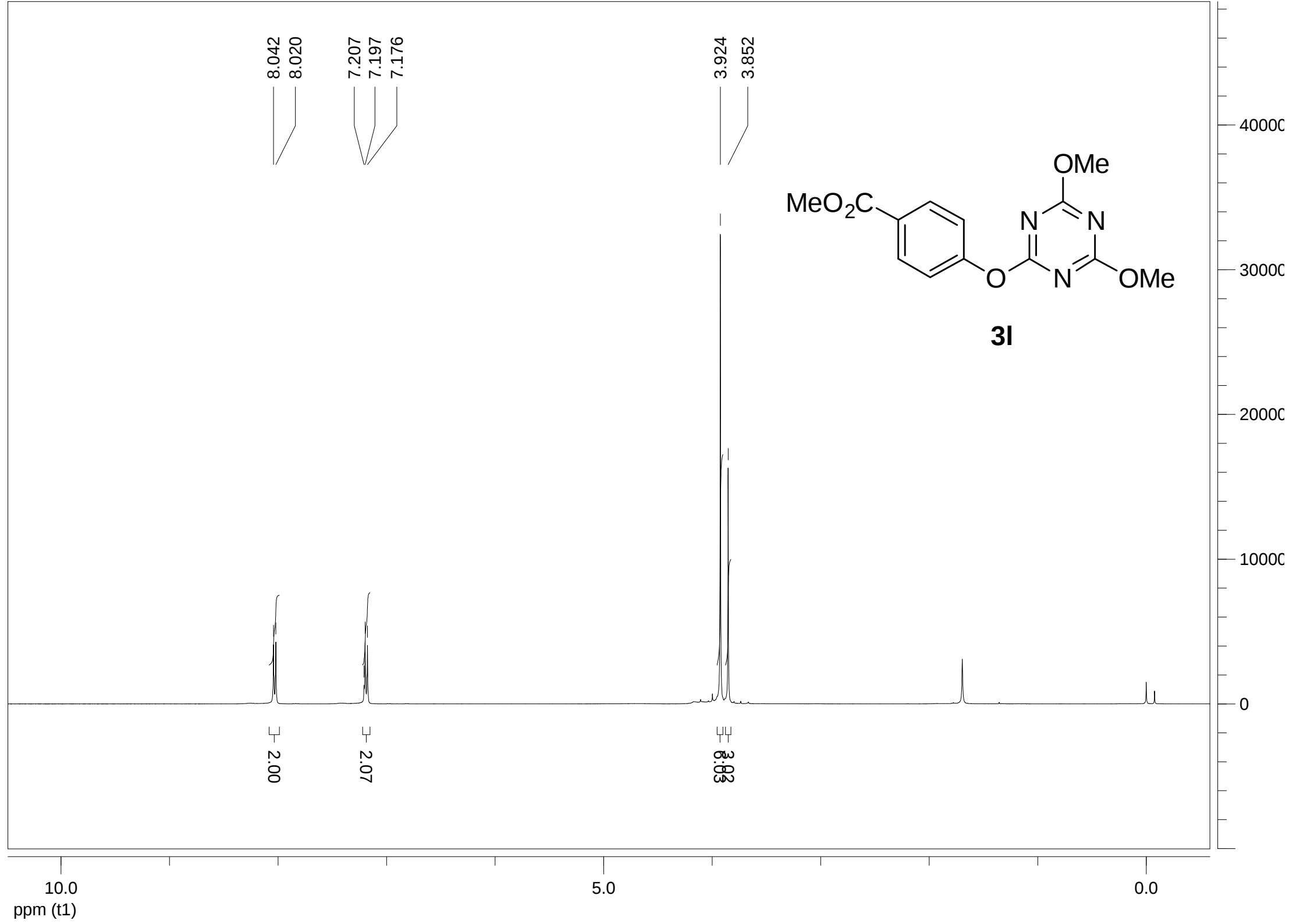


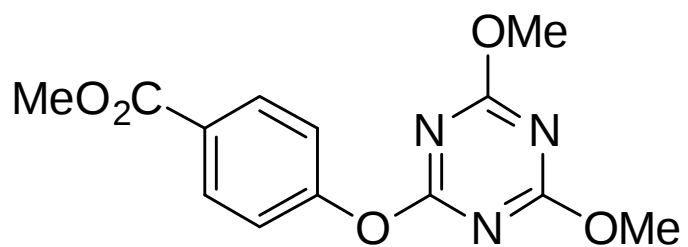
3j









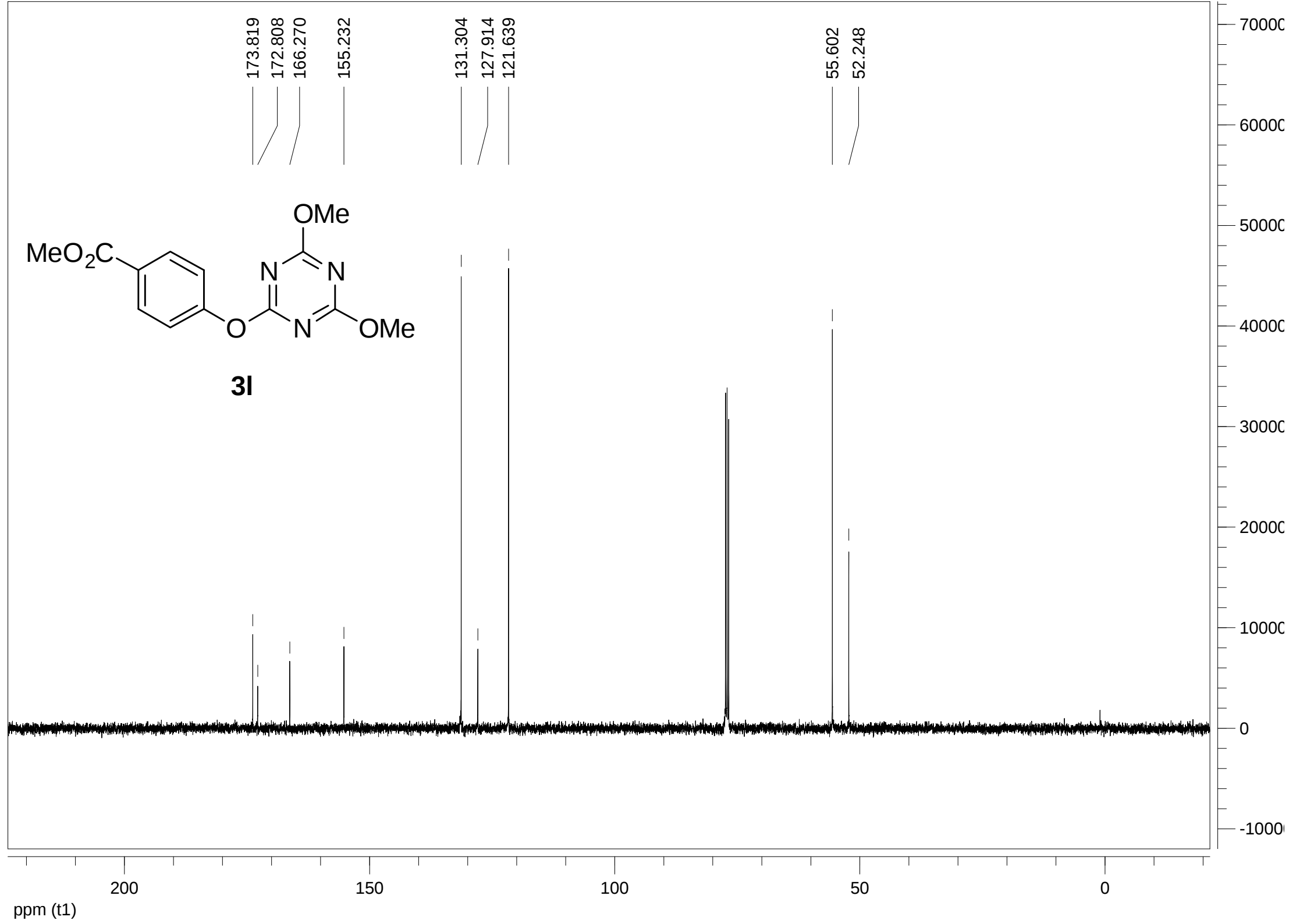


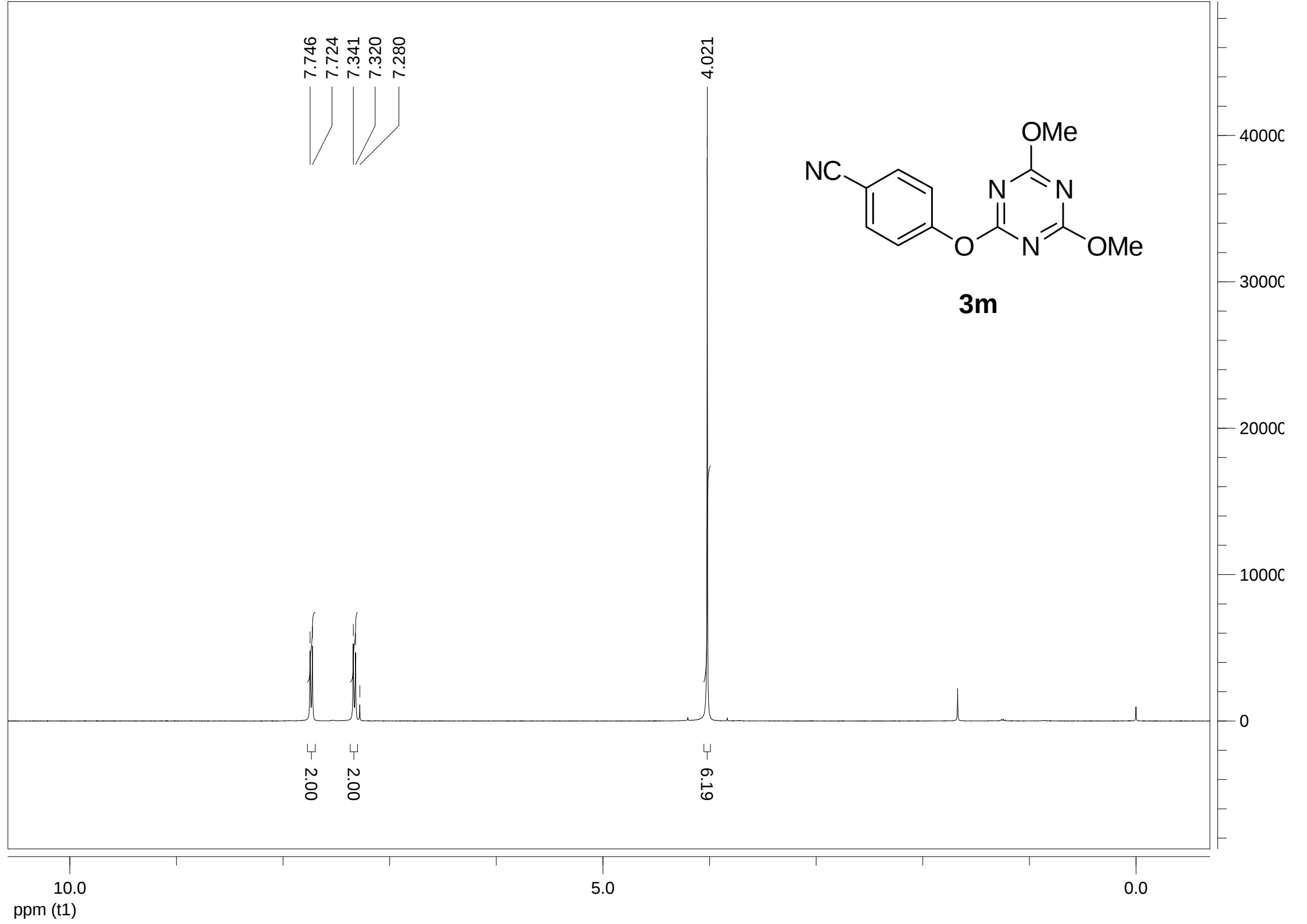
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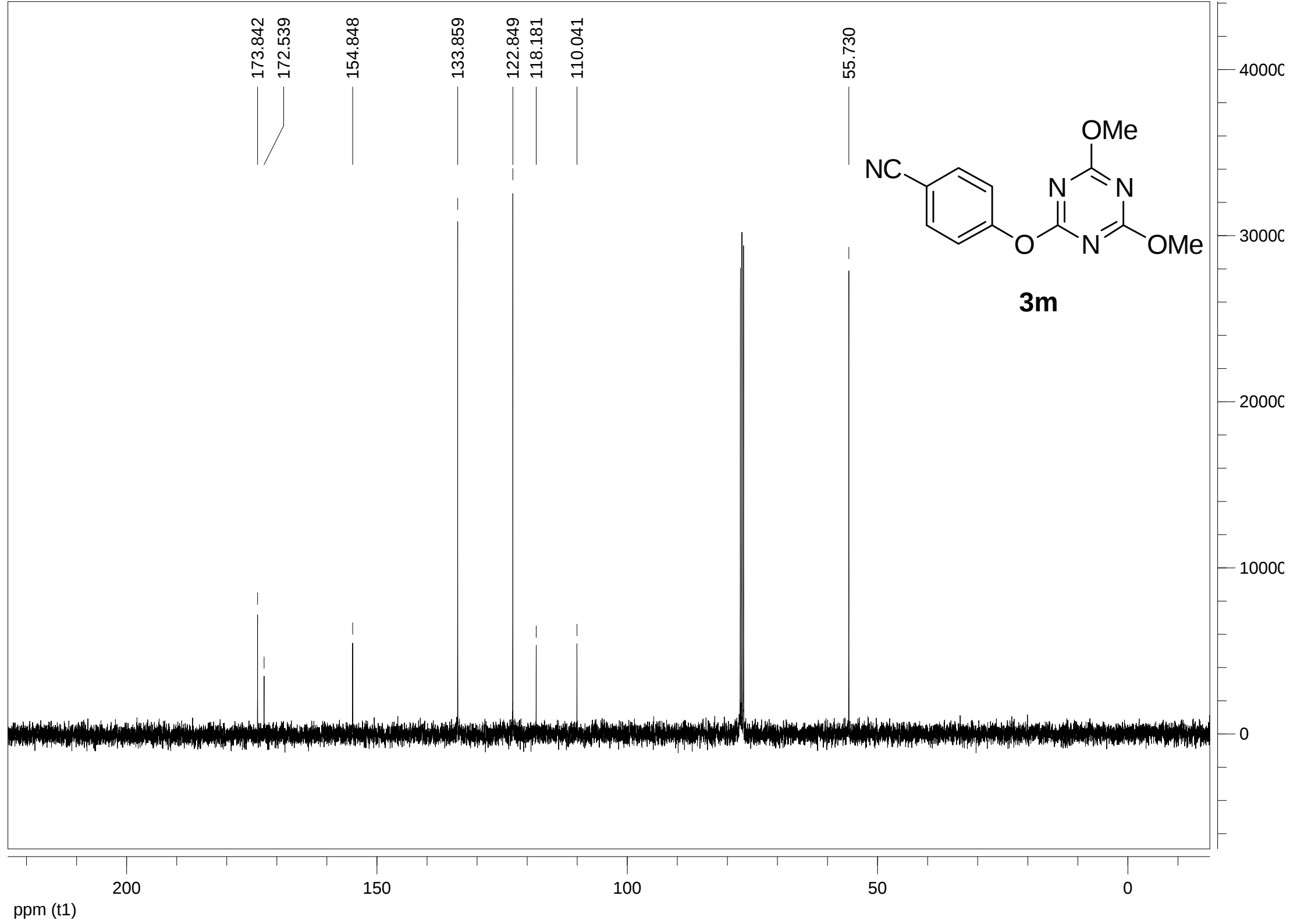
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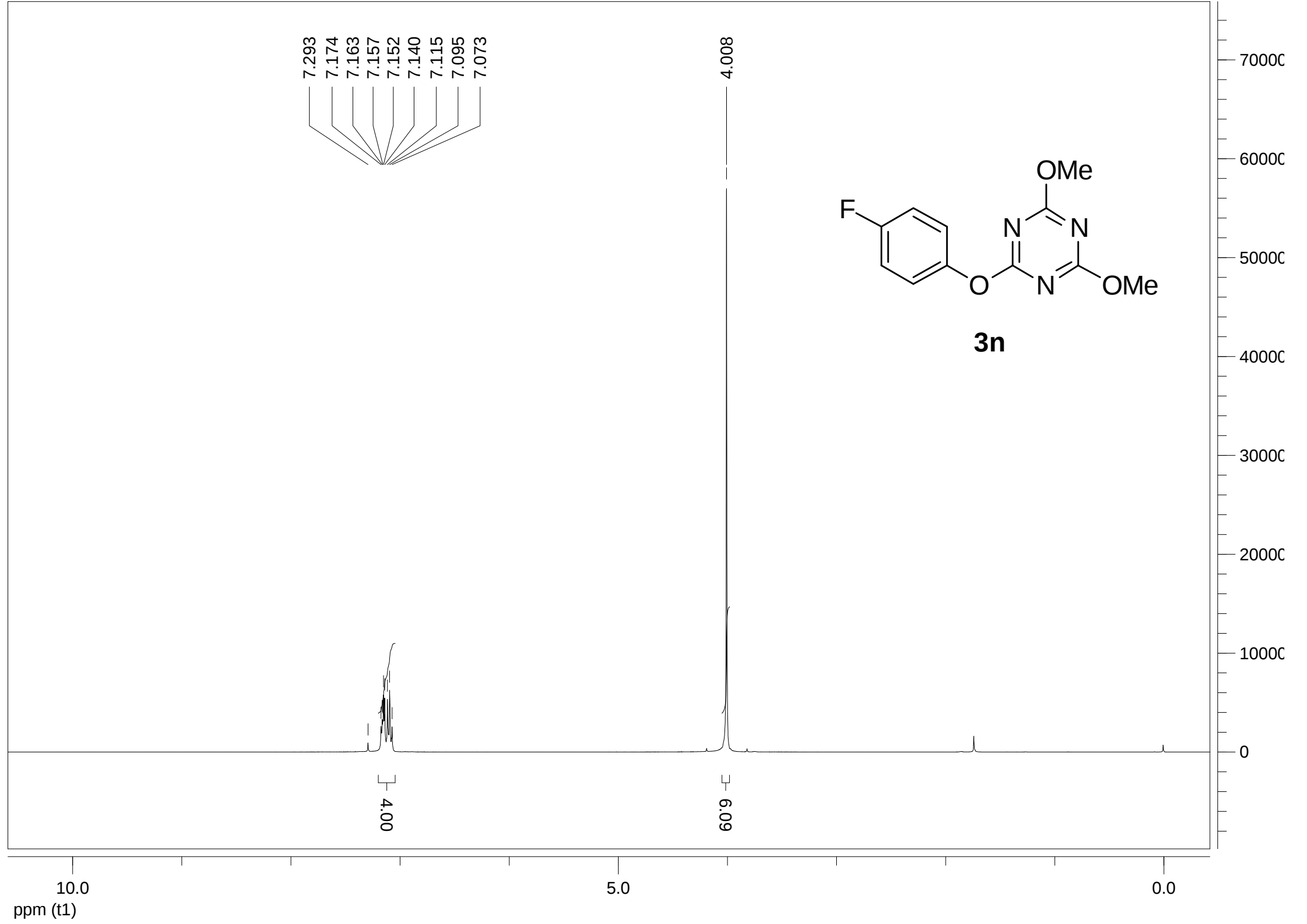
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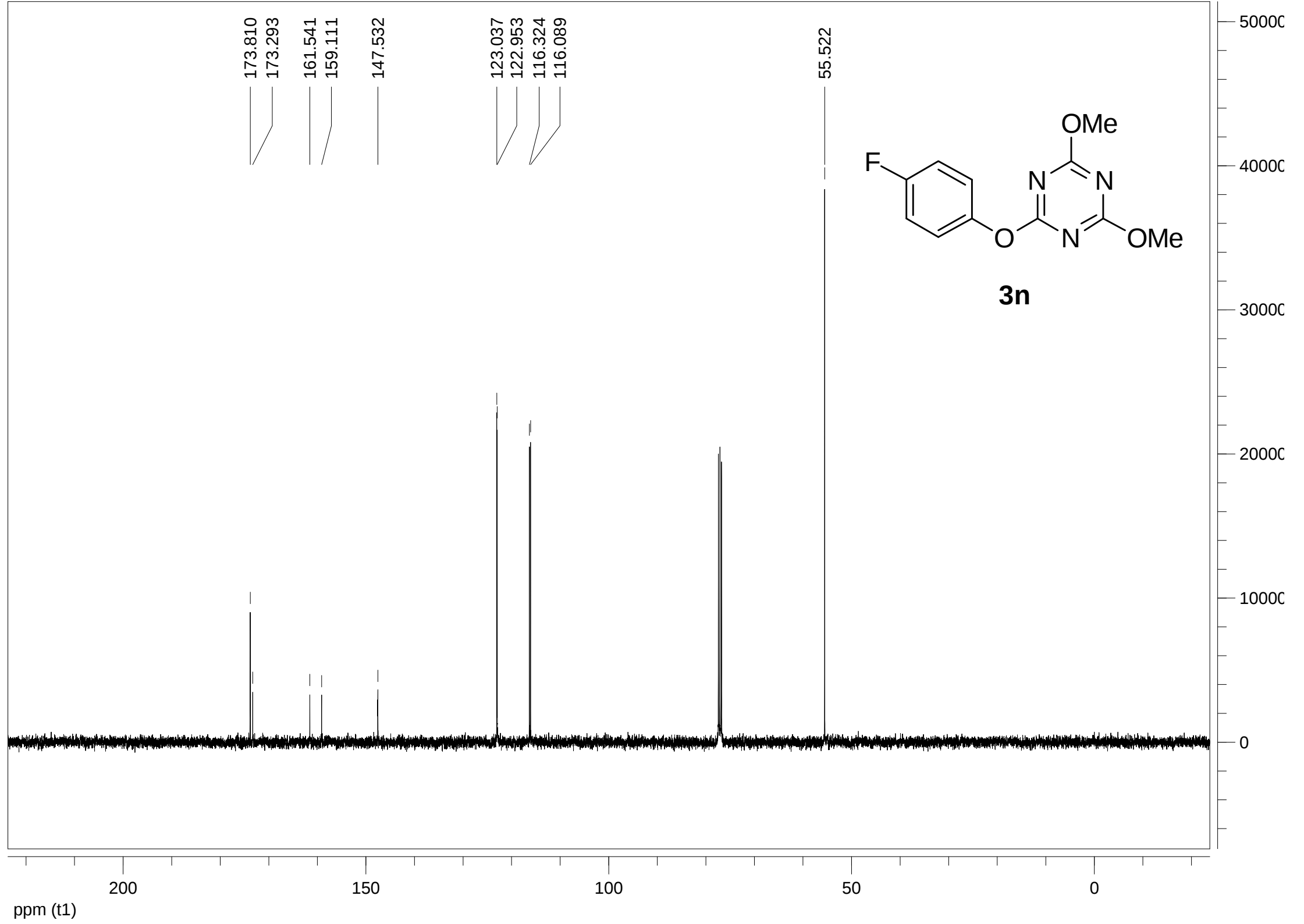
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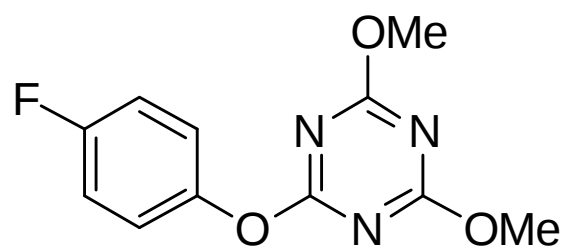












3n

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ppm (t1)

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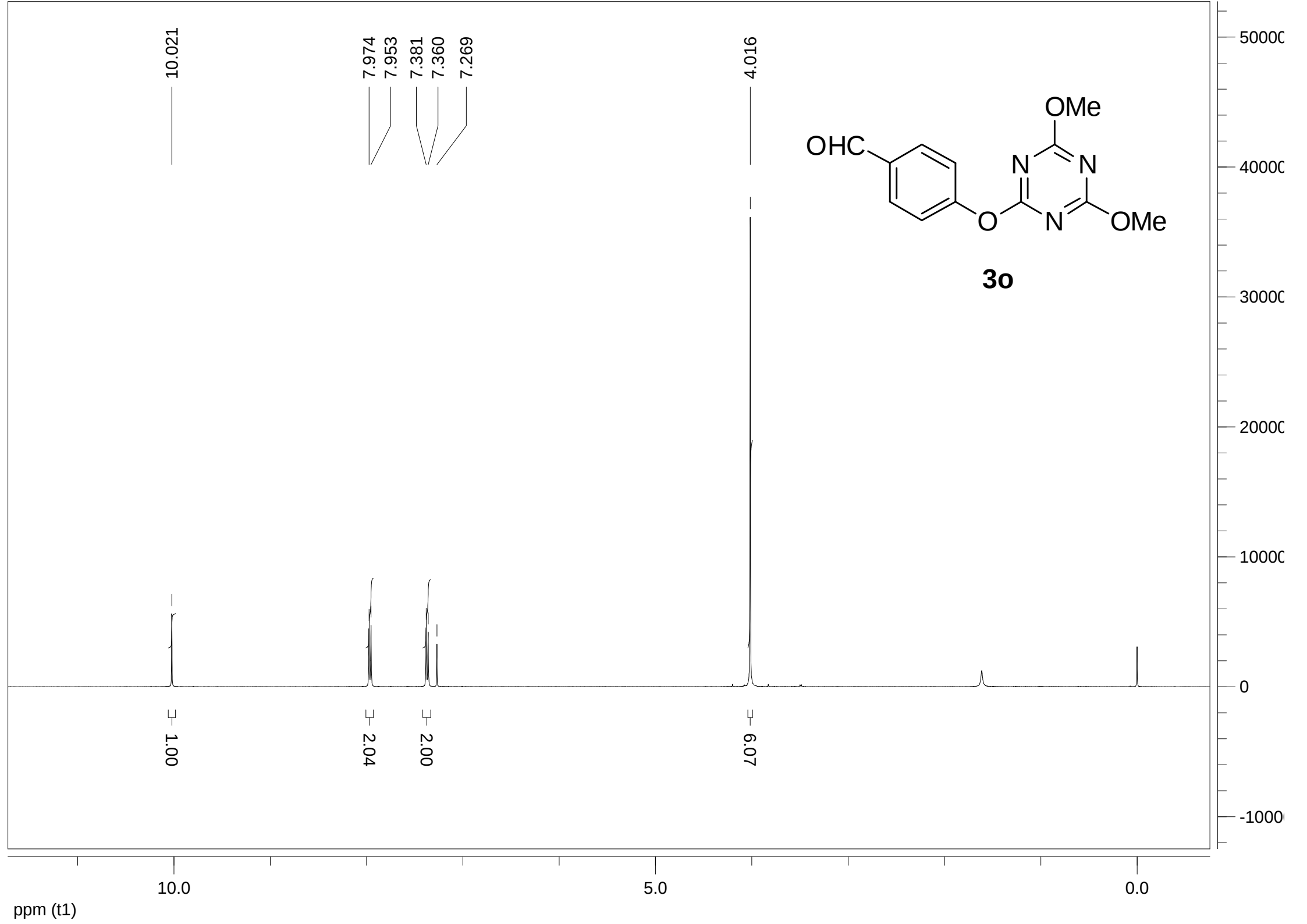
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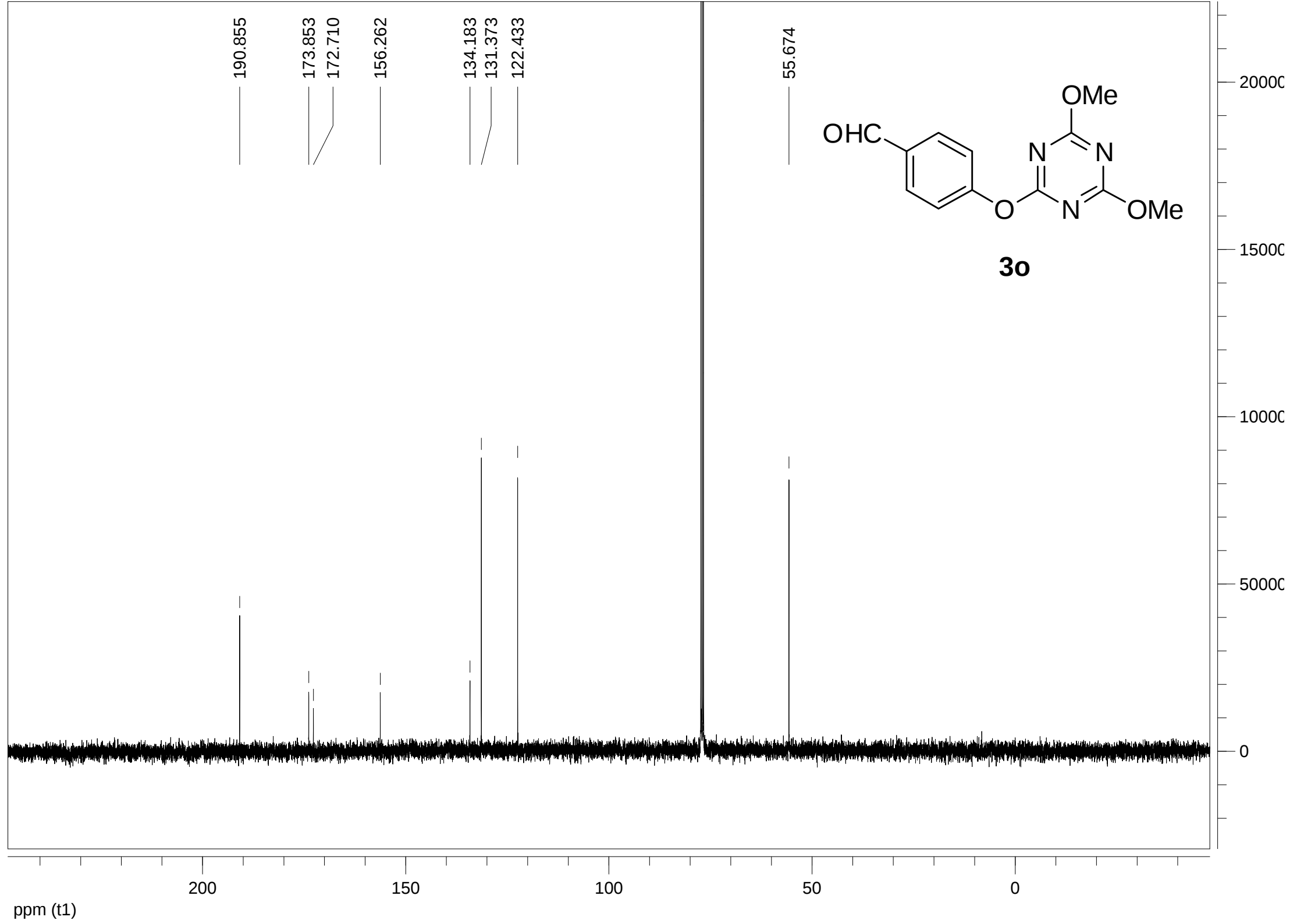
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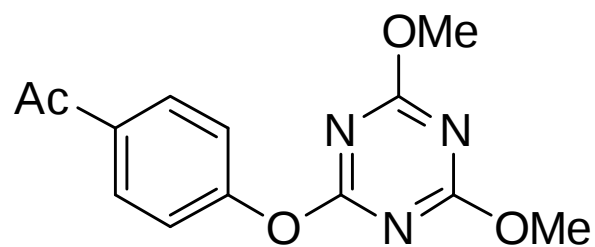
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60000

70000



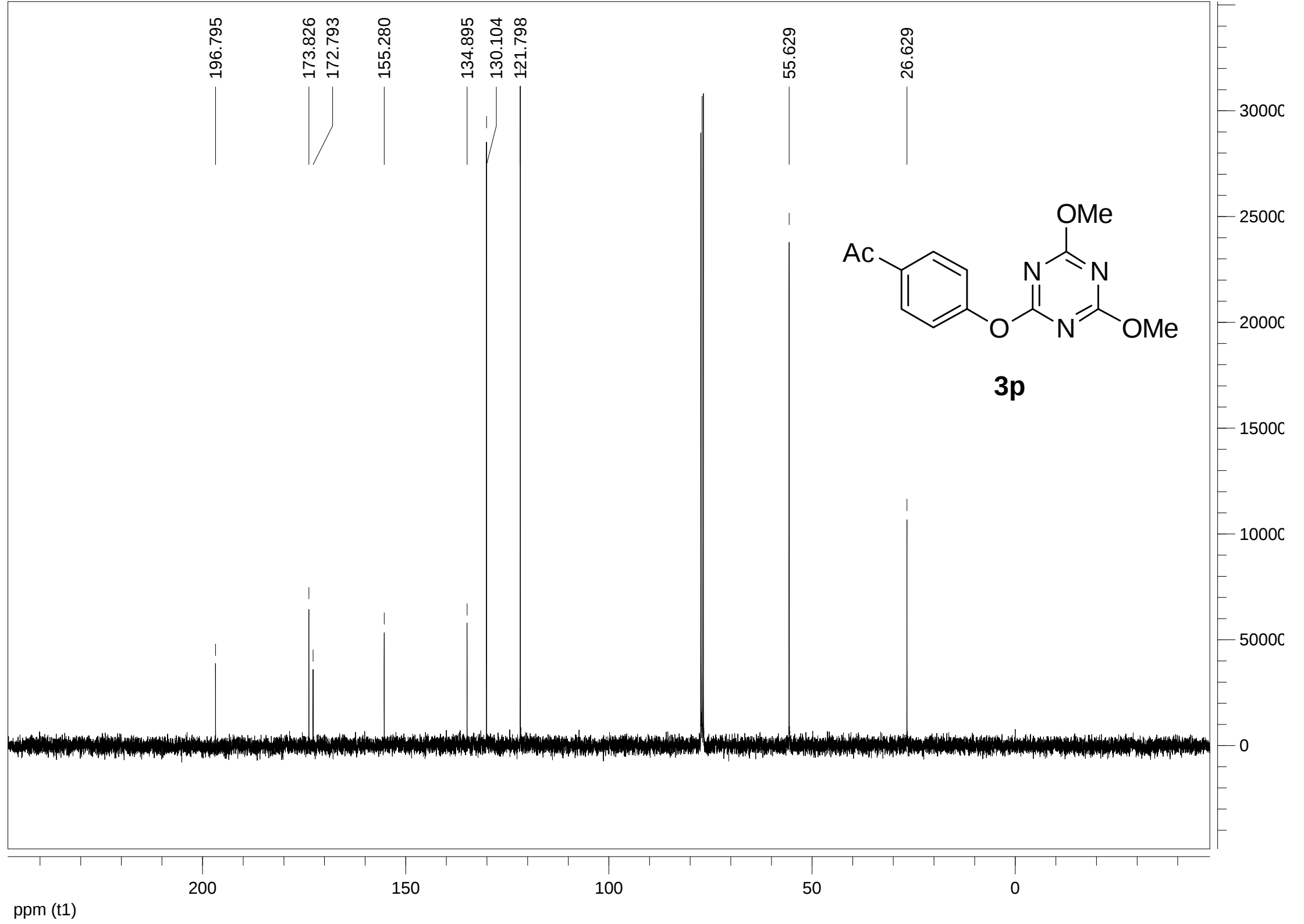


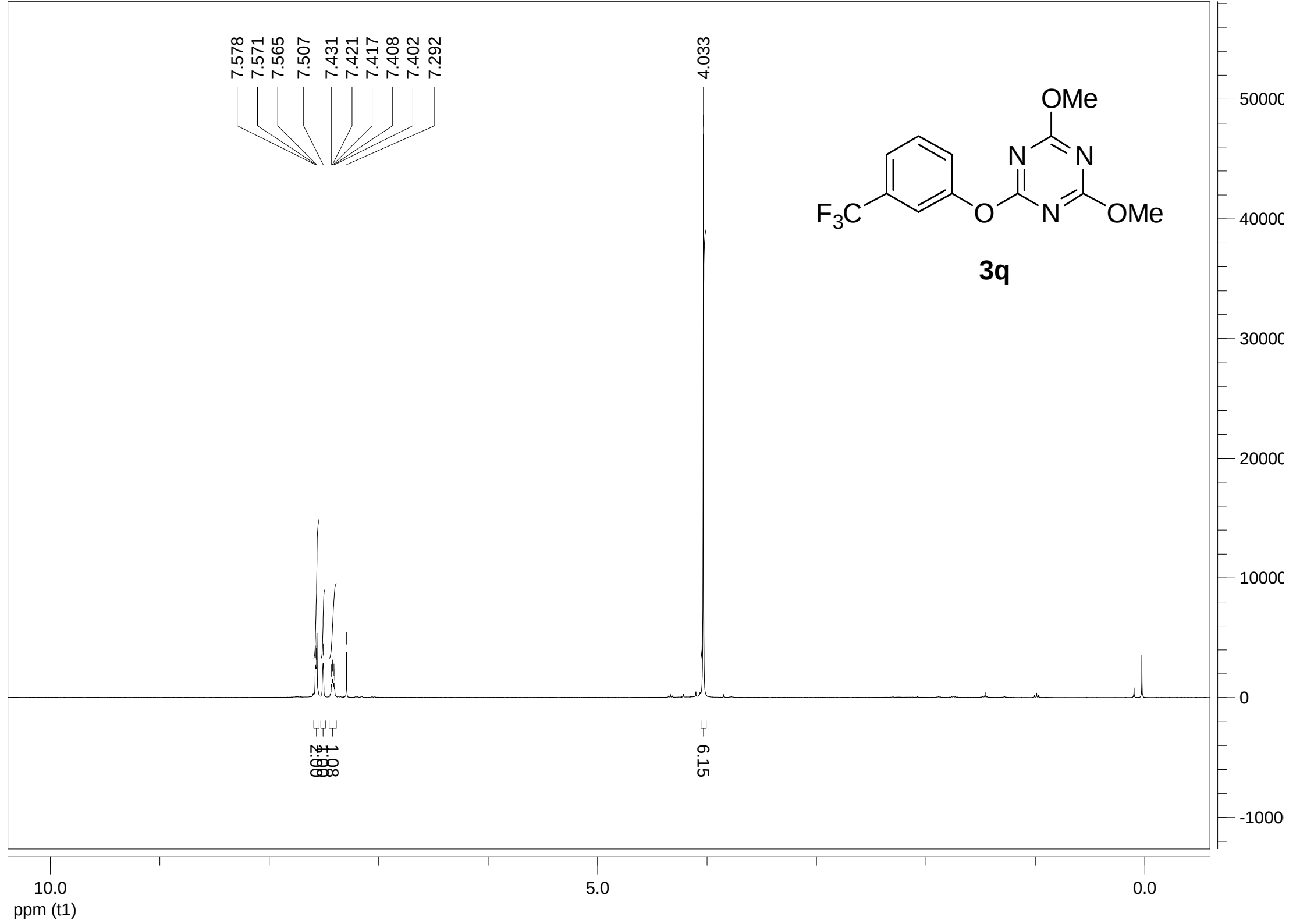
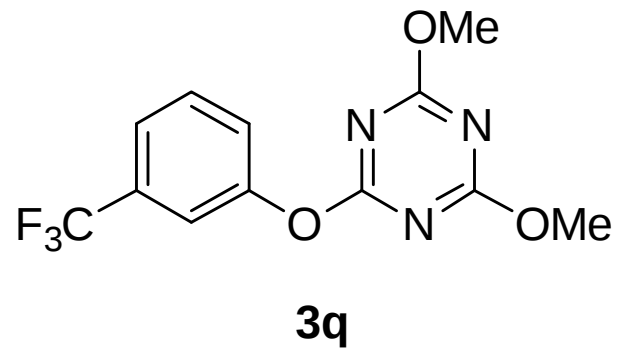


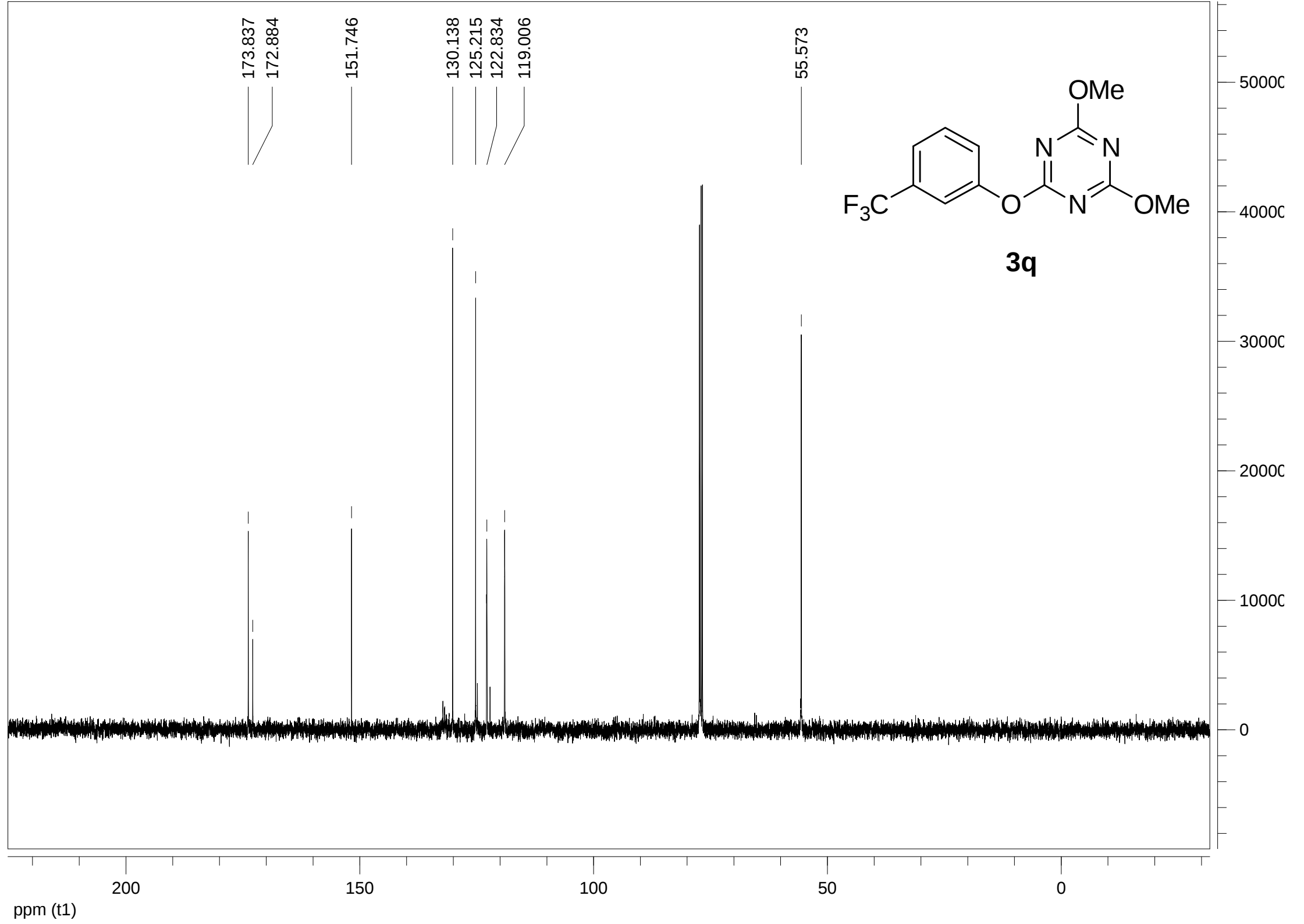
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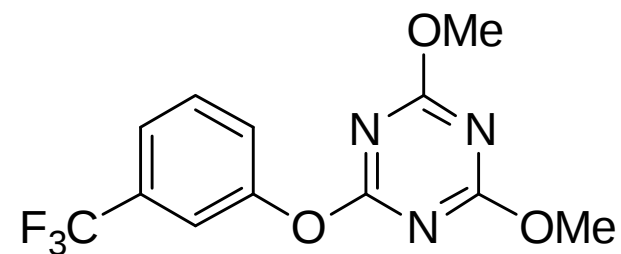


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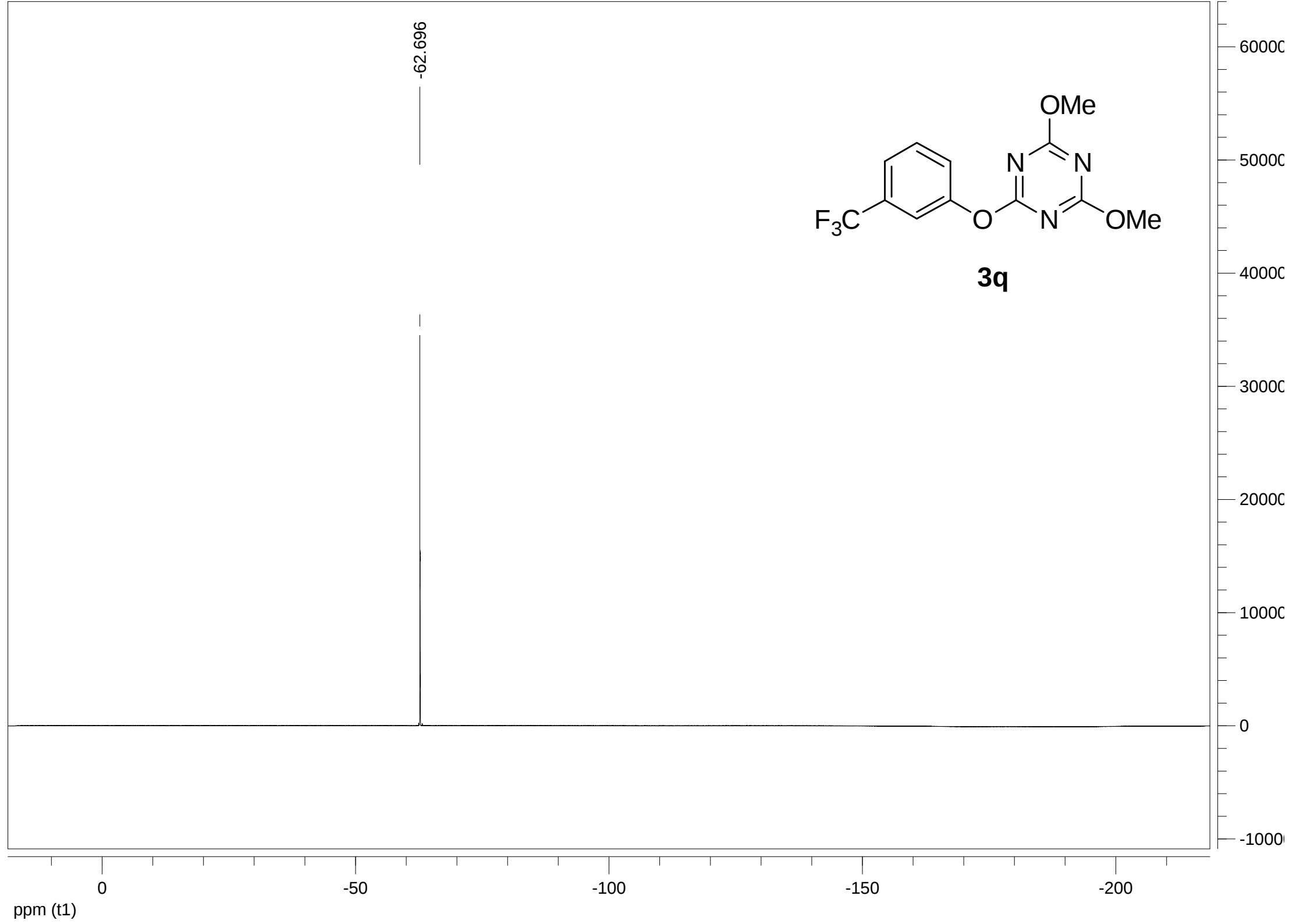


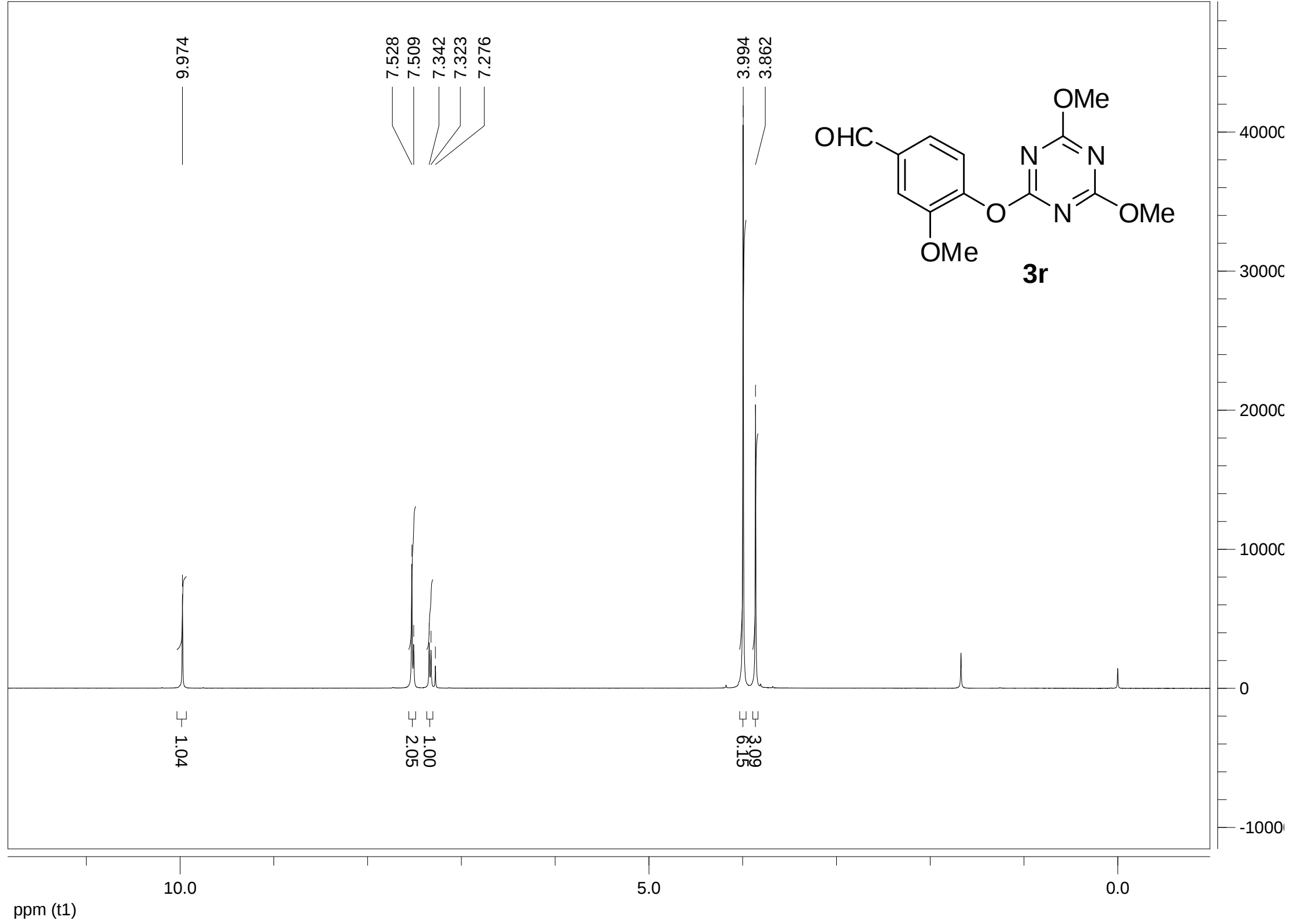


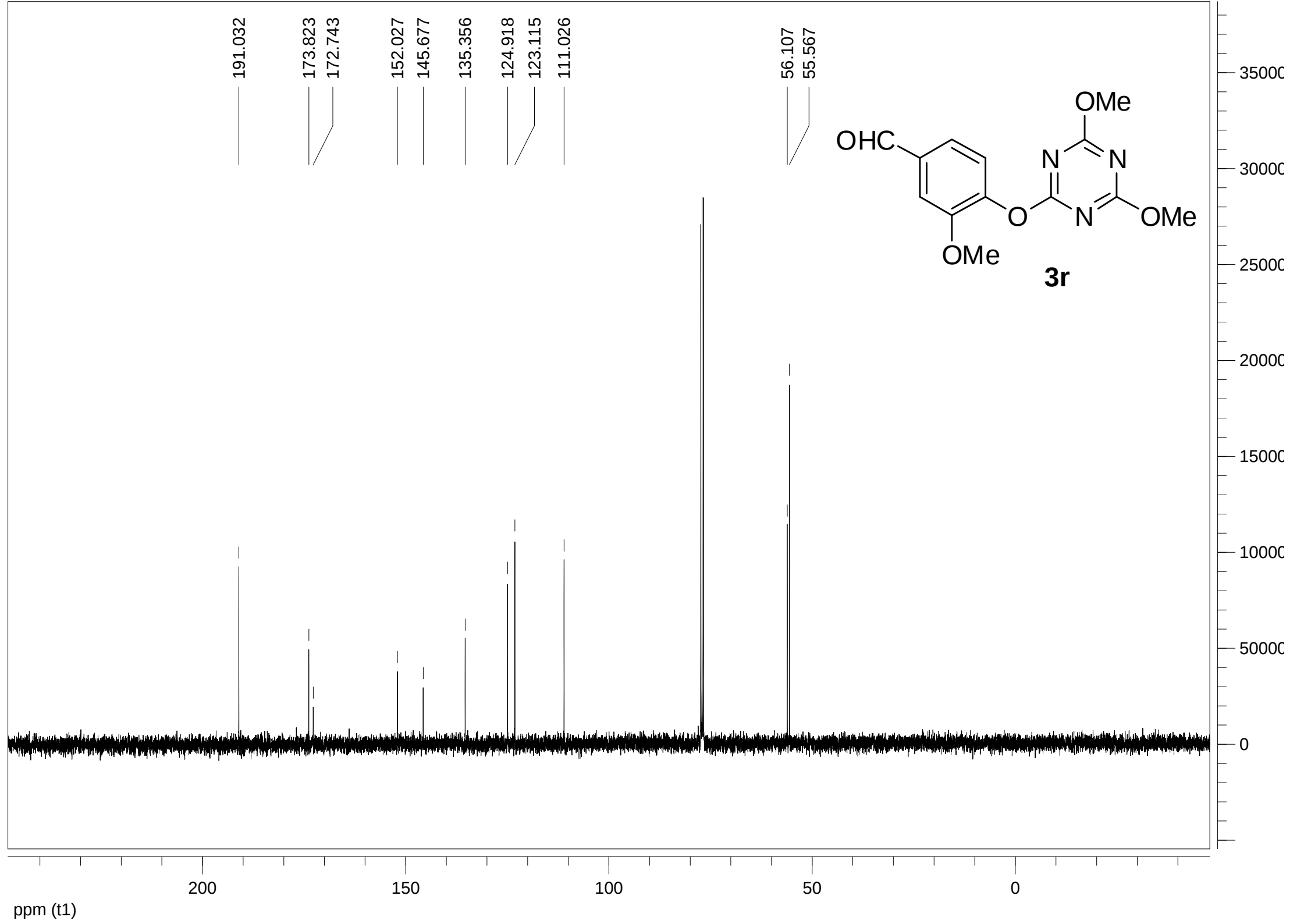


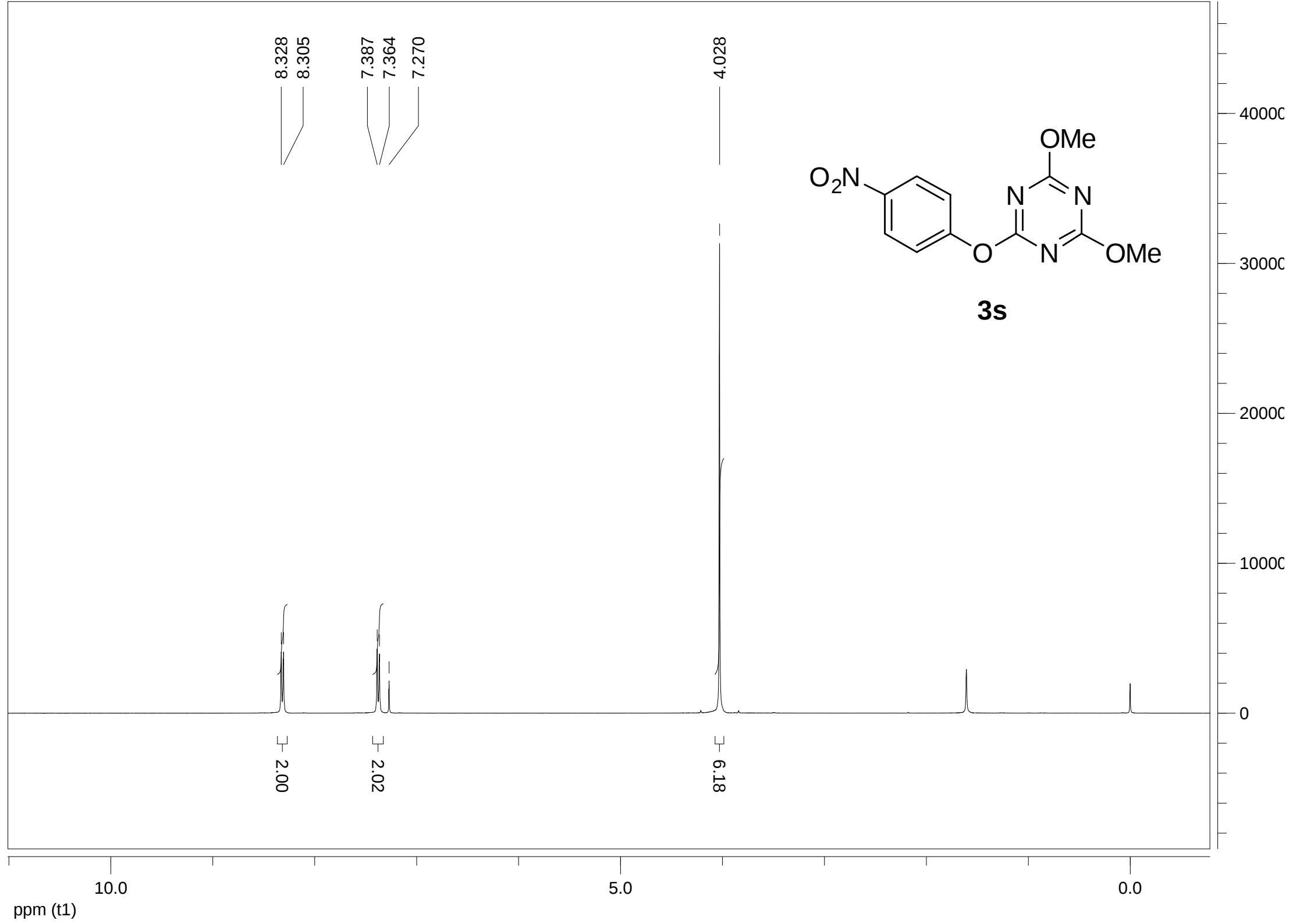
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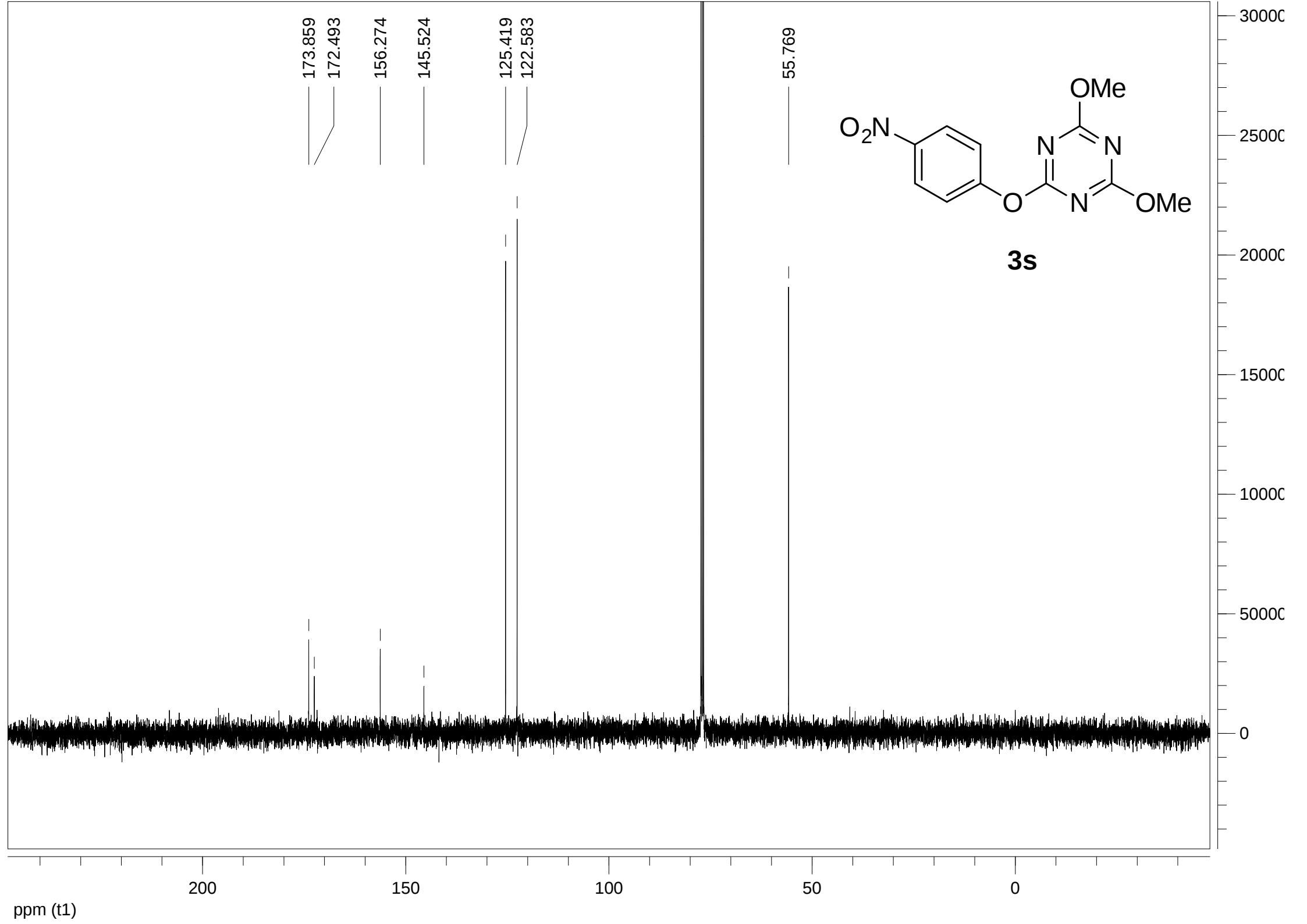
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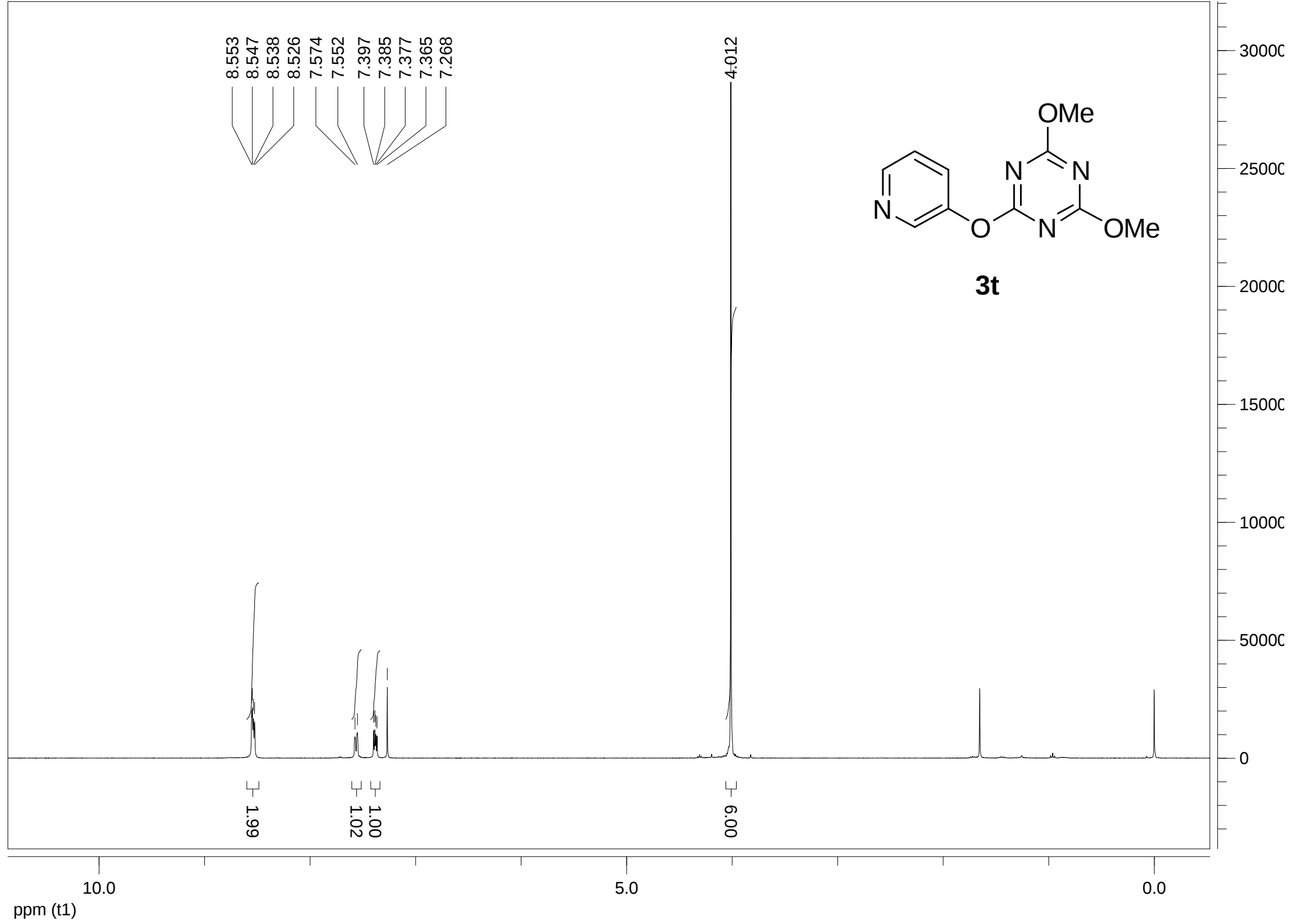


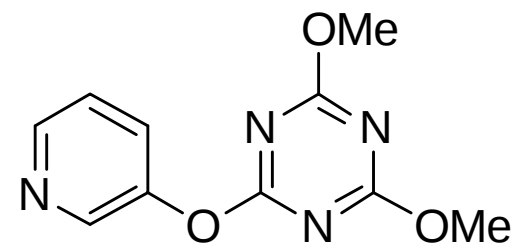




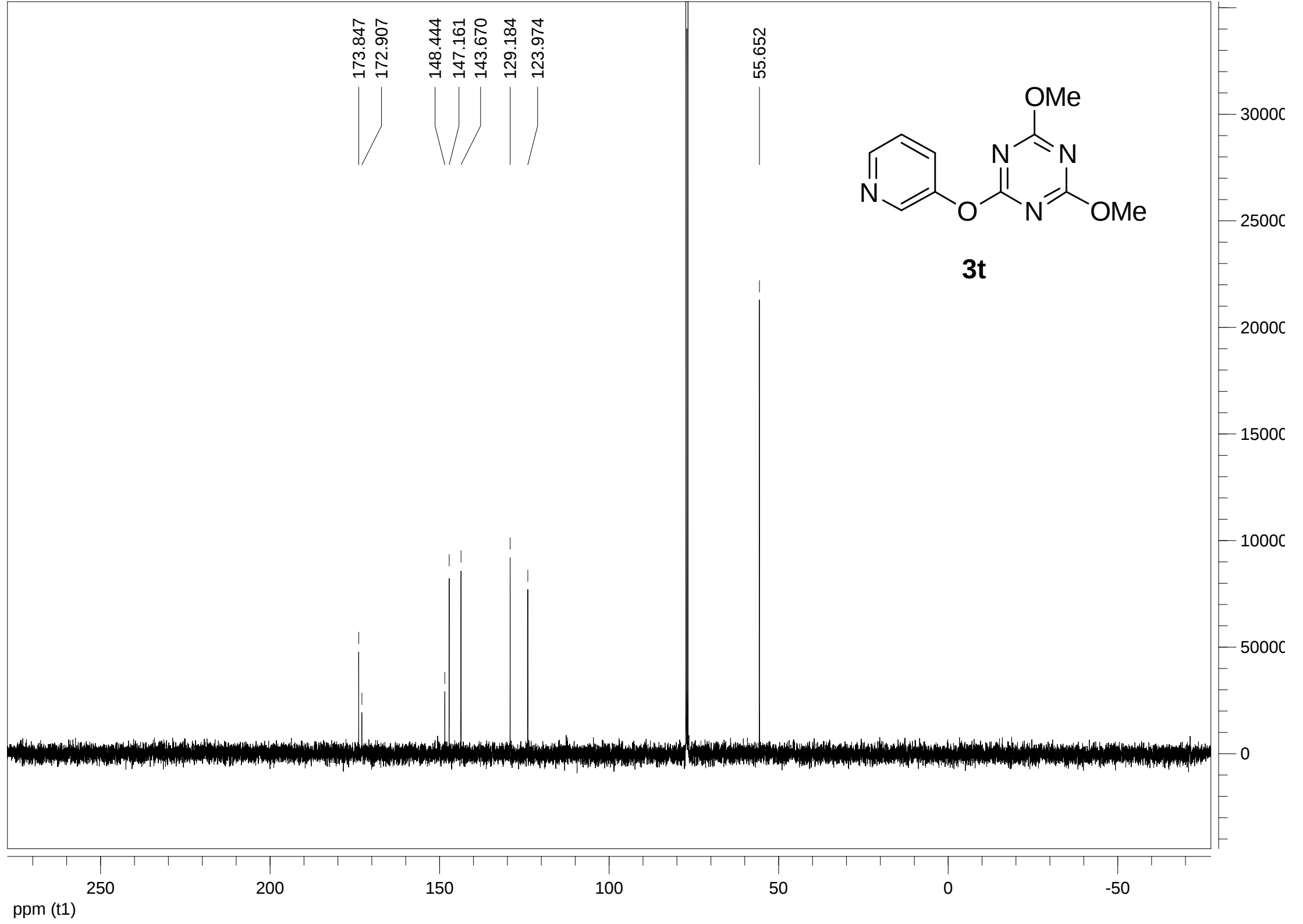


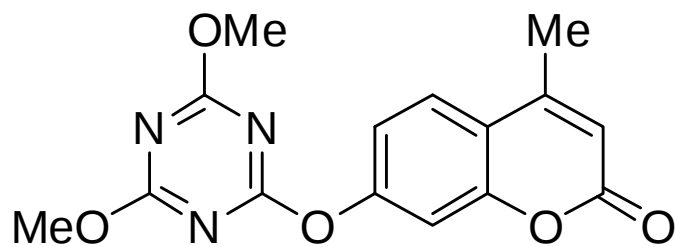






3t





3u

7.683
7.662
7.293
7.248
7.243
7.199
7.194
7.178
7.172
6.317

4.049

2.476

1.07

1.06

1.05

6.09

3.13

50000

40000

30000

20000

10000

0

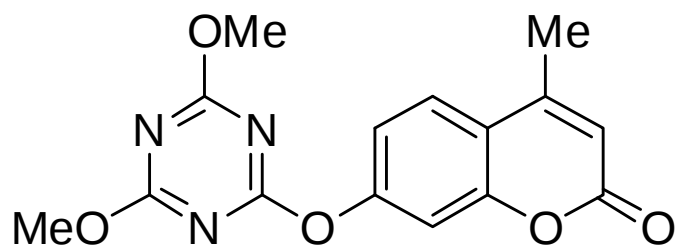
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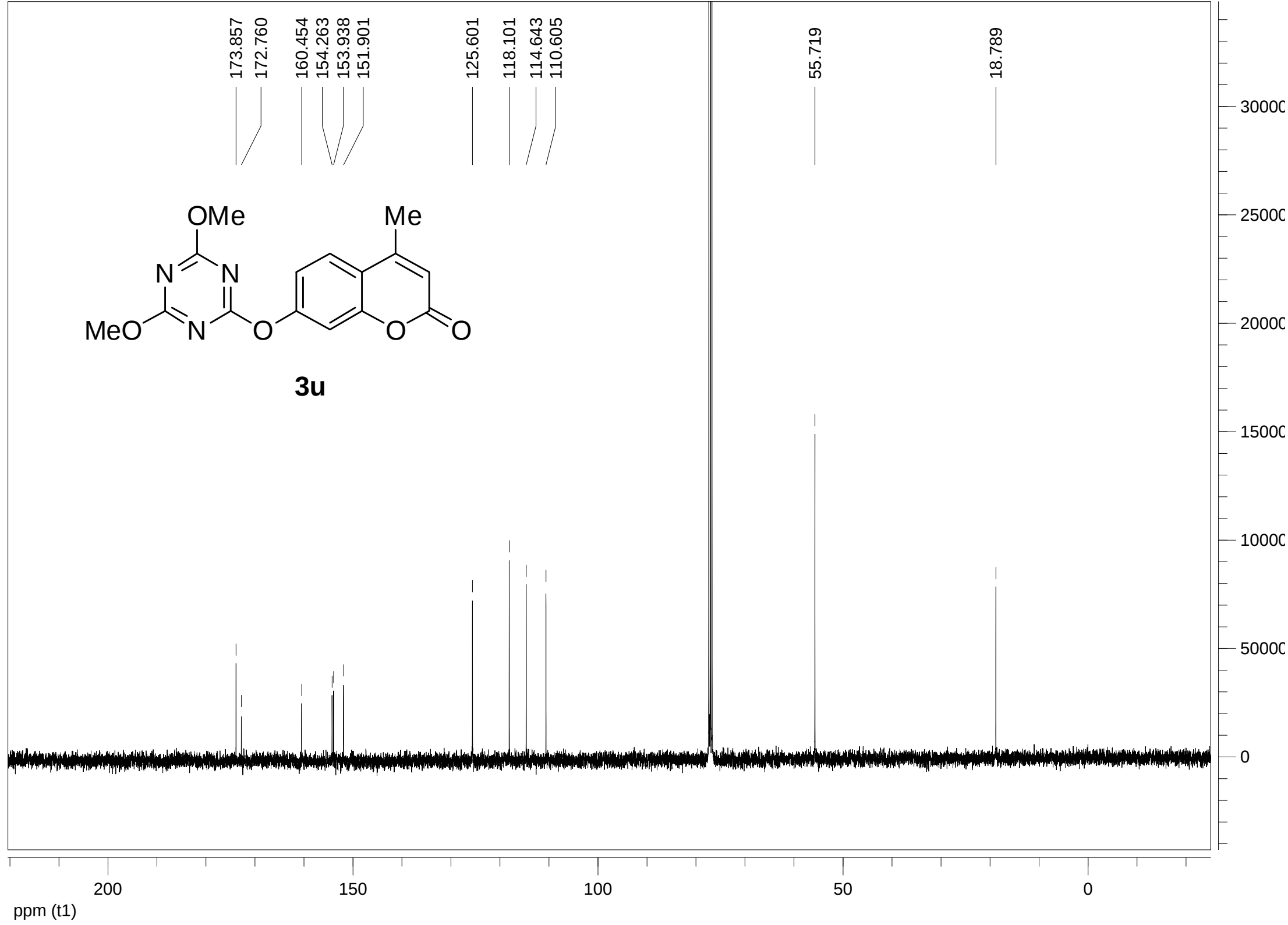
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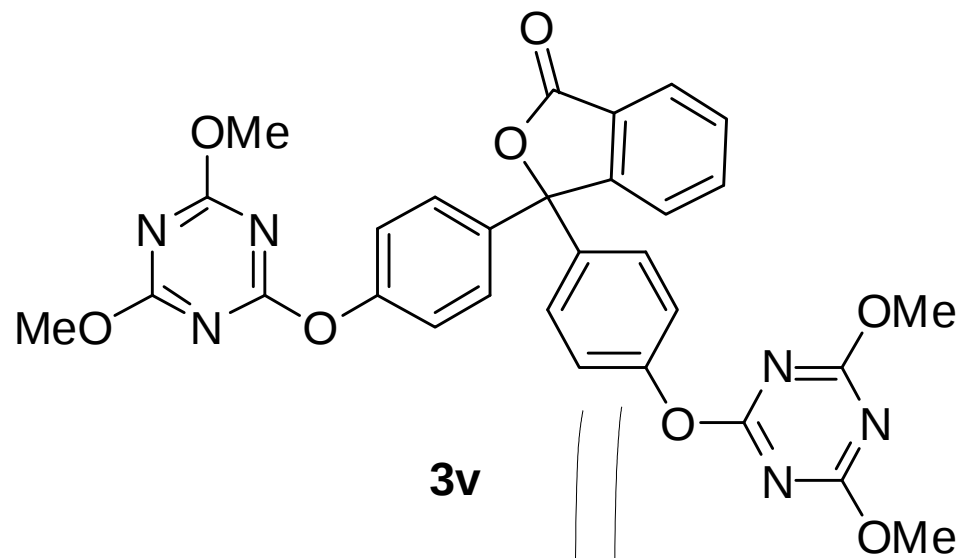
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ppm (t1)



3u





3v

7.979
7.960
7.757
7.739
7.720
7.610
7.600
7.591
7.582
7.563
7.420
7.398
7.275
7.194
7.173

5.005

1.00
1.07
2.07
4.03
4.07

12.19

5000C

4000C

3000C

2000C

1000C

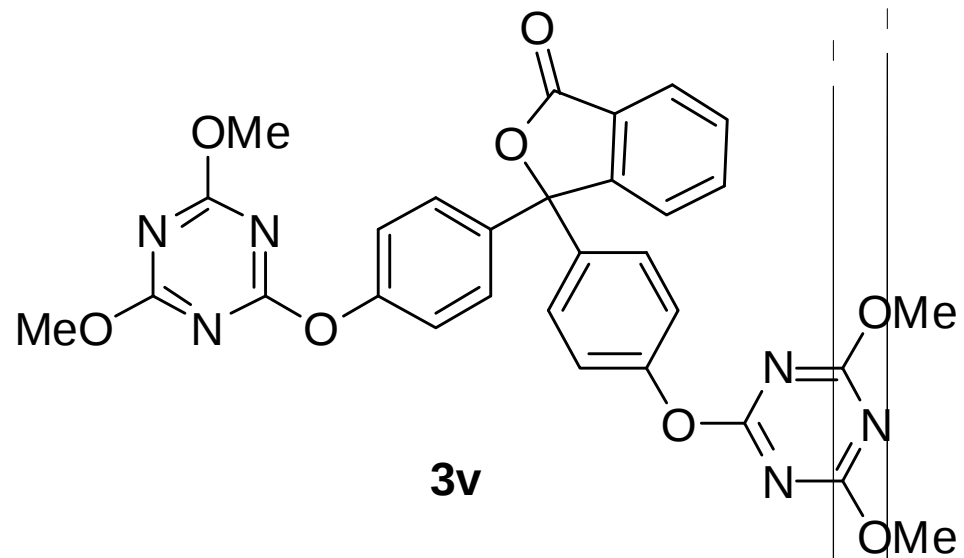
0

10.0

5.0

0.0

ppm (t1)



3v

173.791
172.912
169.396
151.804
151.542
138.189
134.404
129.690
128.861
128.532
128.383
126.221
125.513
124.164
121.664
121.486
115.428
90.746

55.605

4000C

3000C

2000C

1000C

0

200

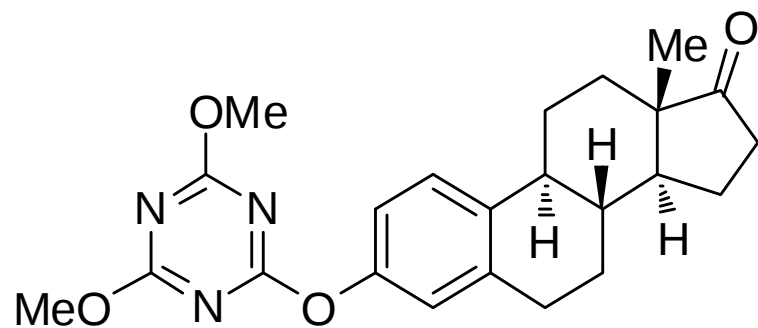
150

100

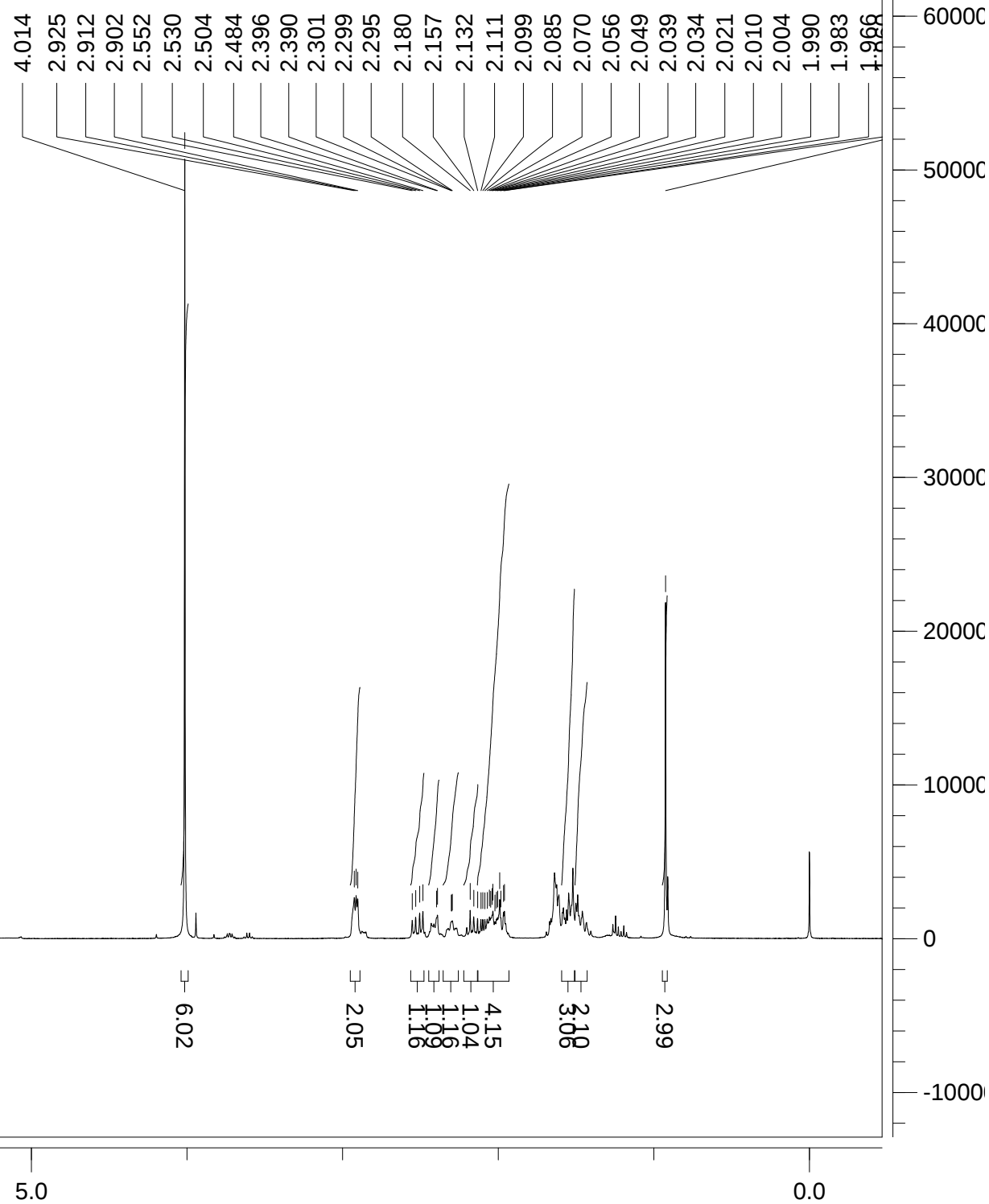
50

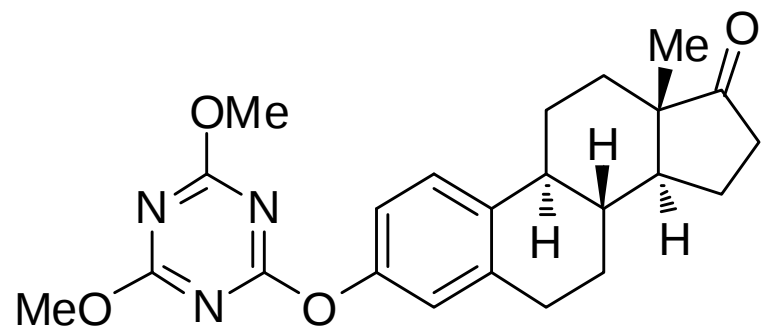
0

ppm (t1)

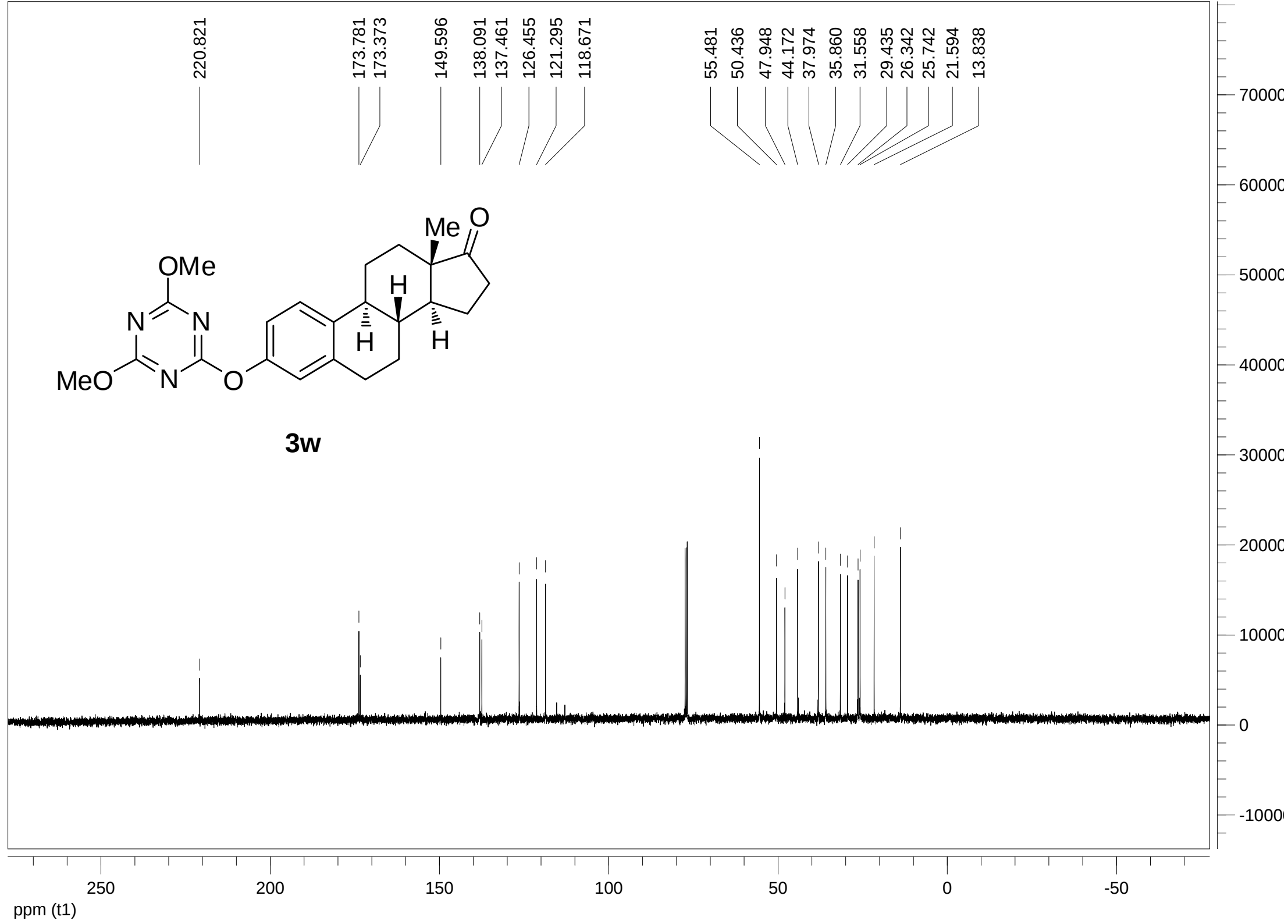


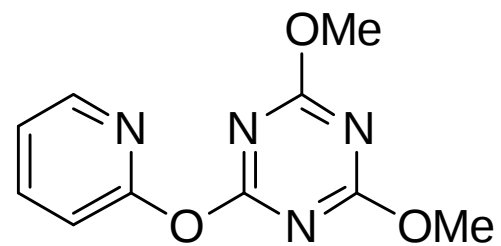
3w



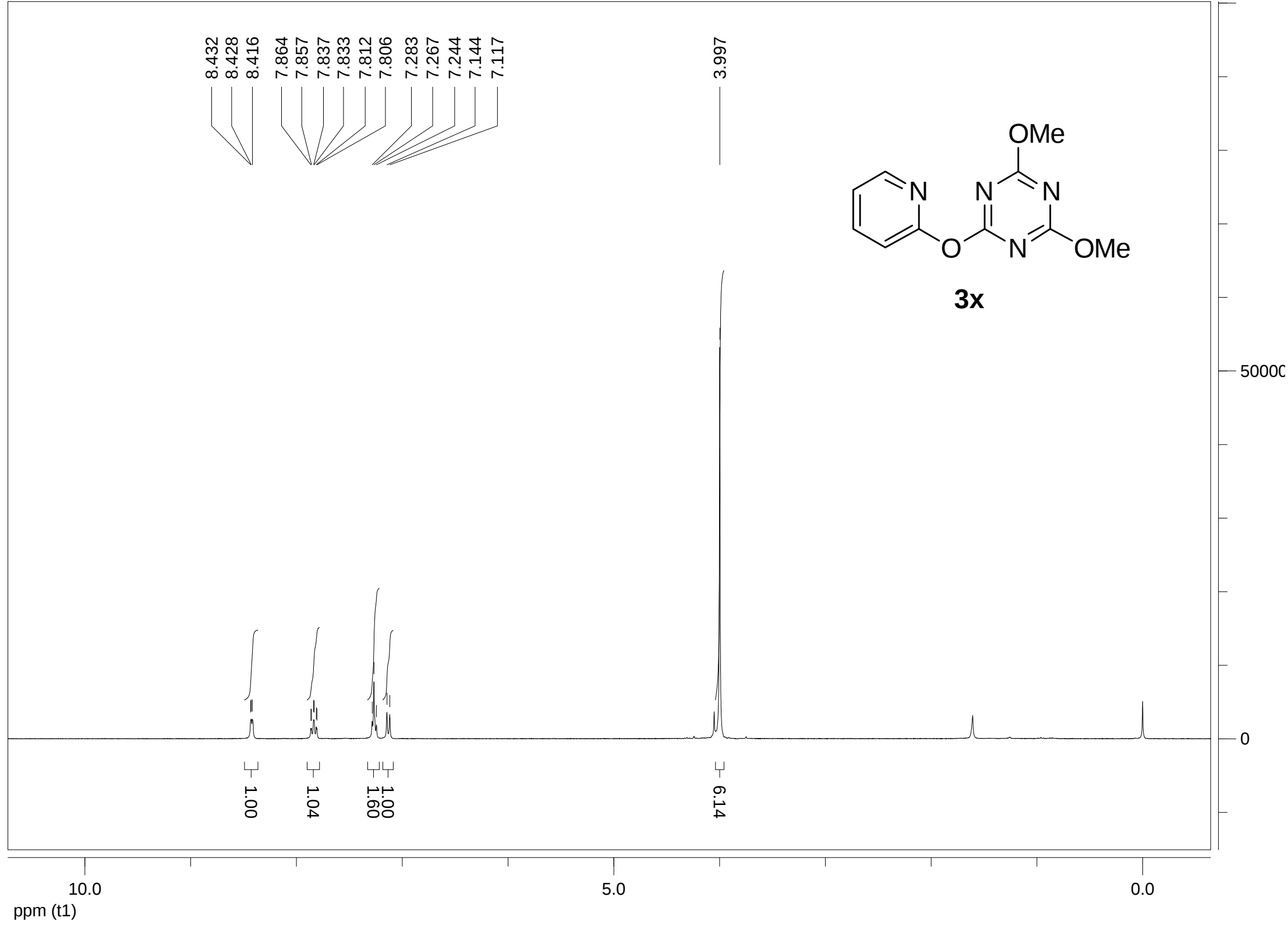


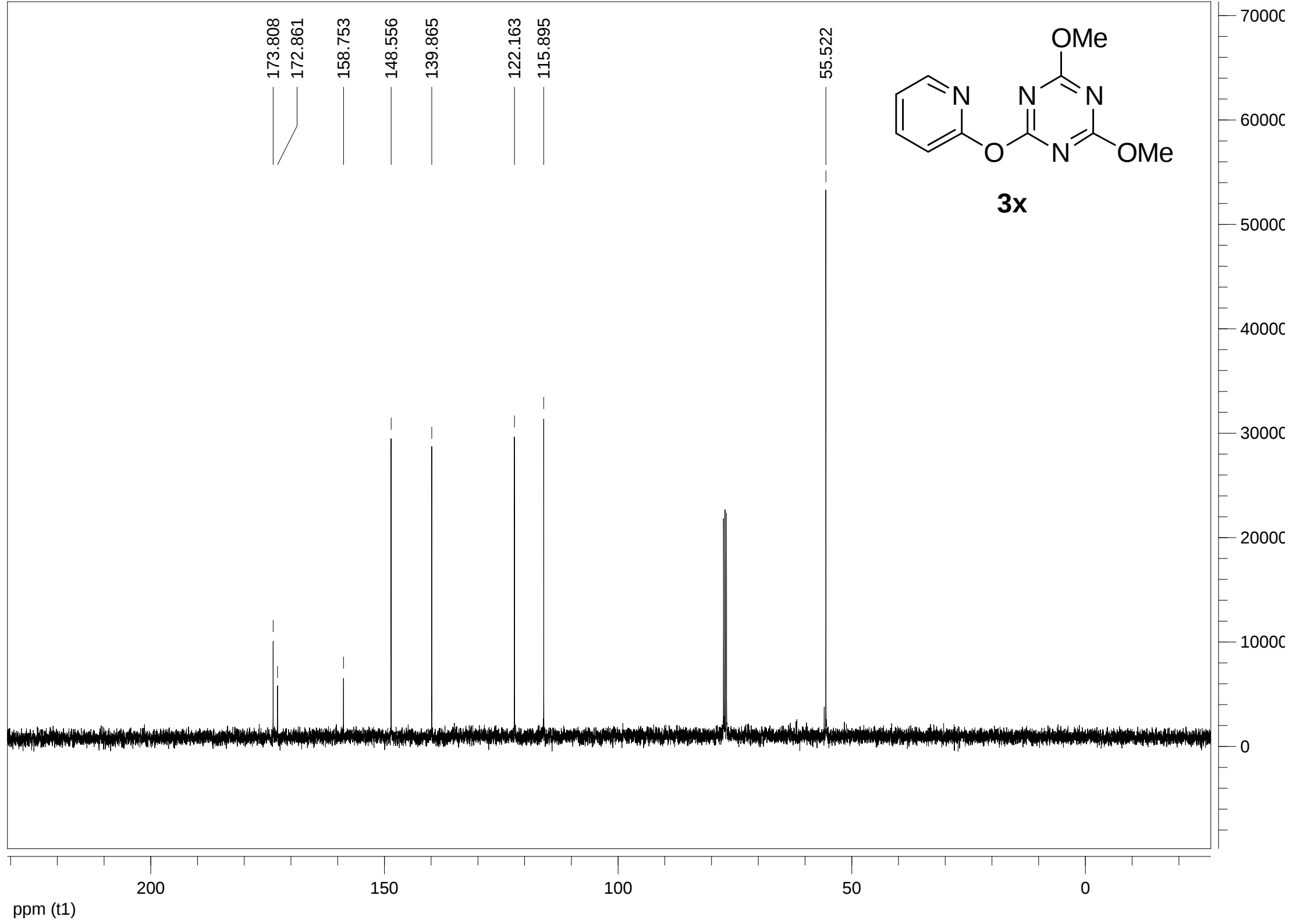
3w

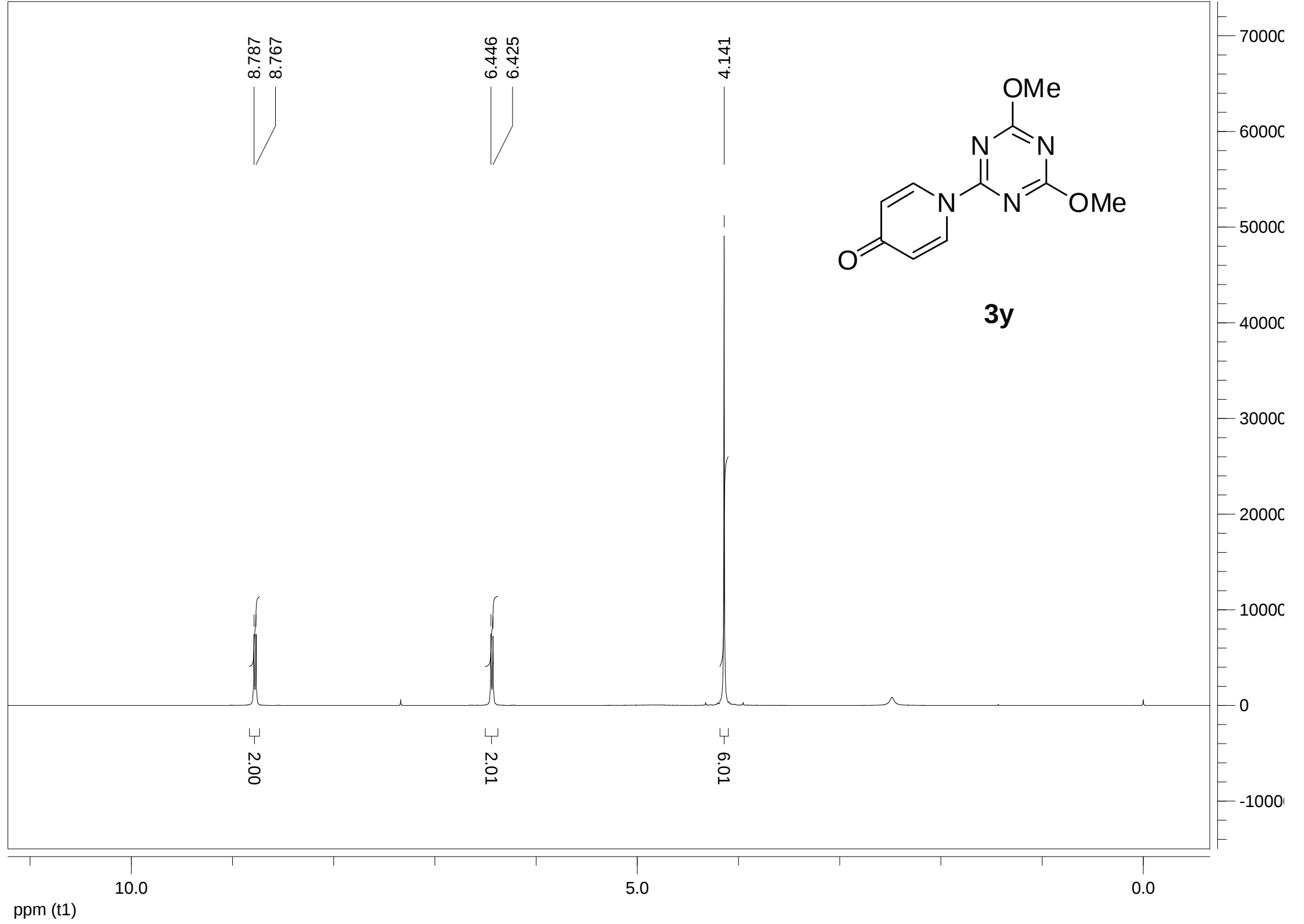


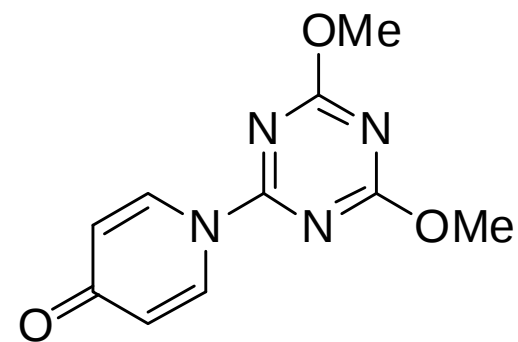


3x

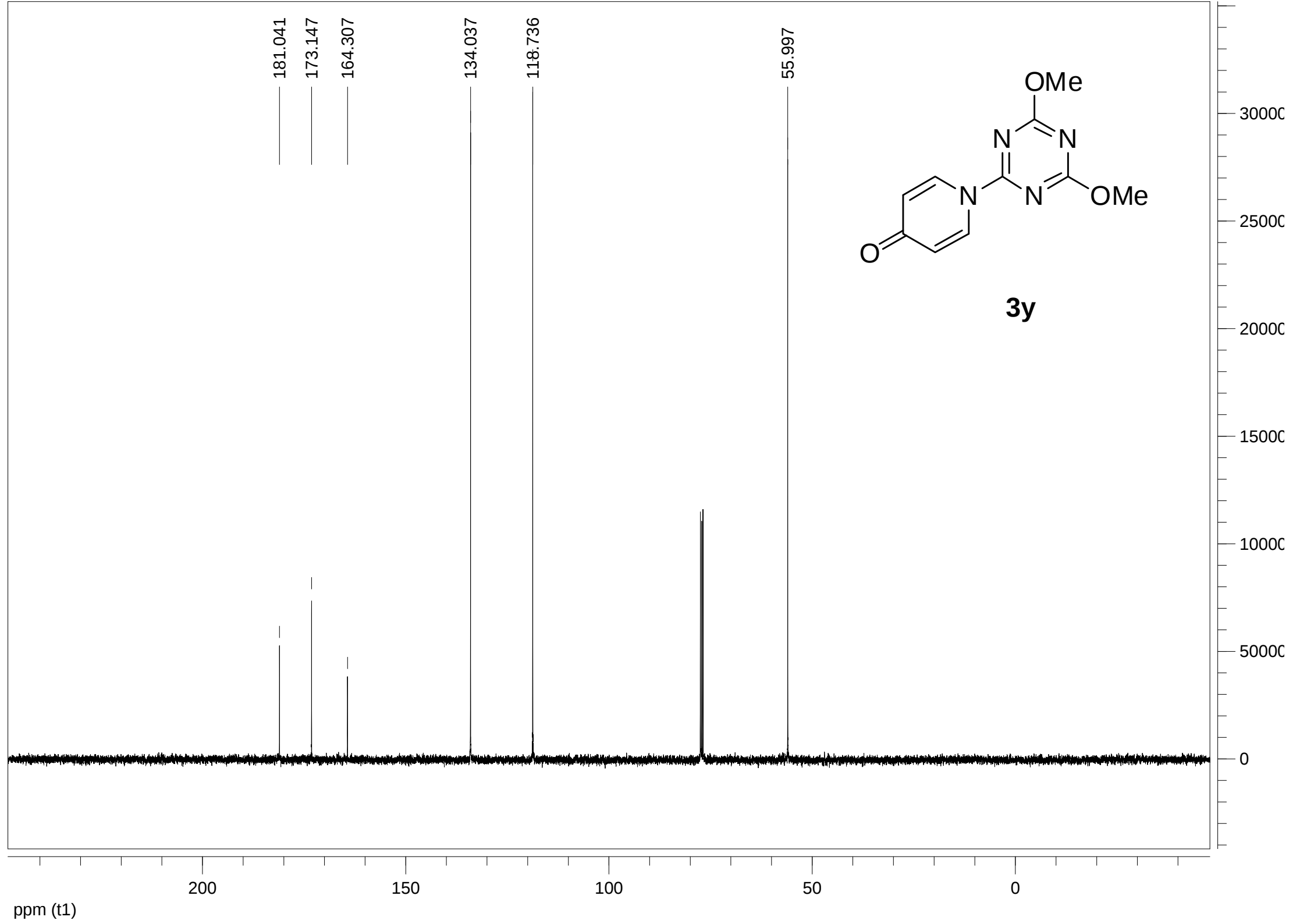


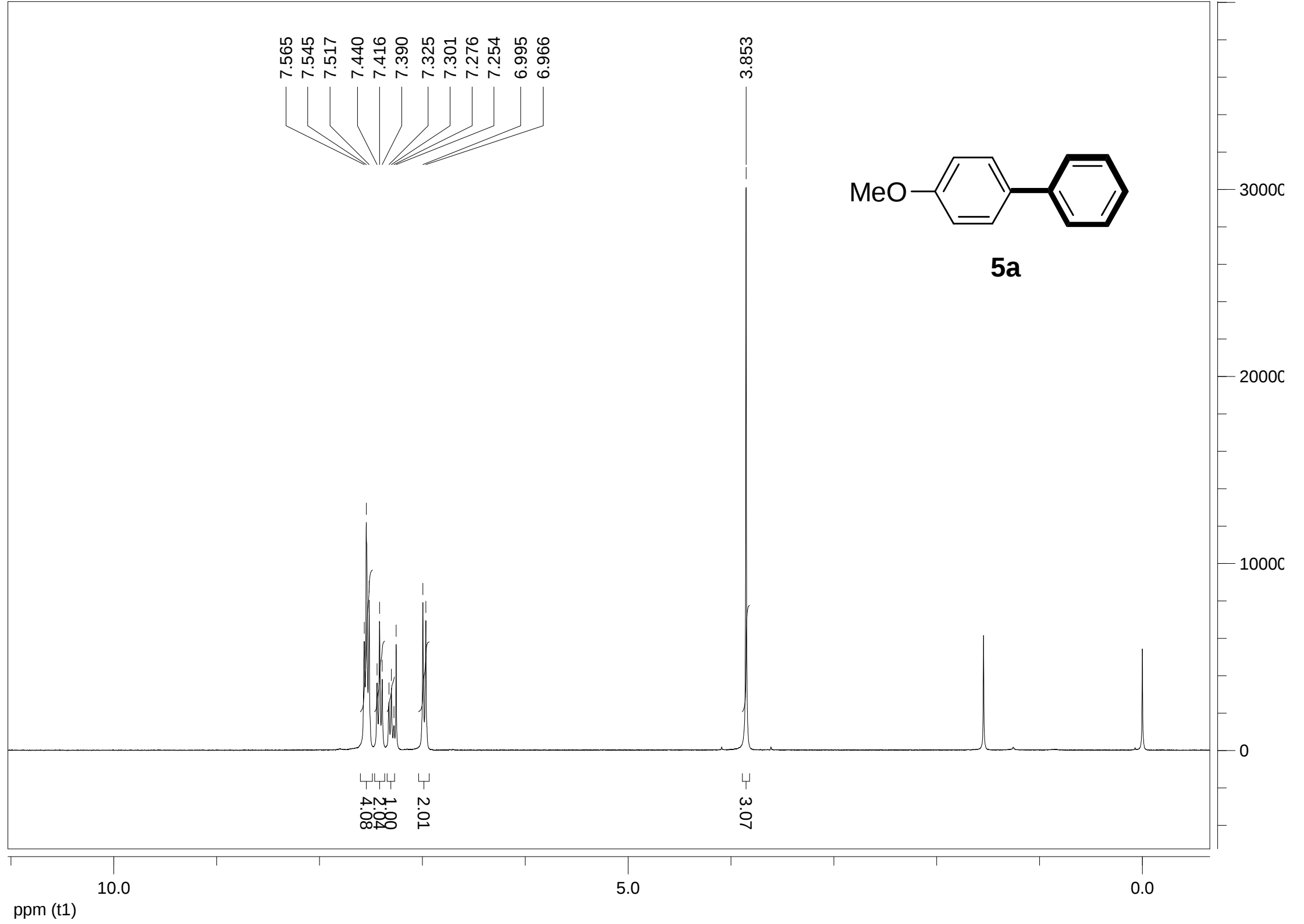


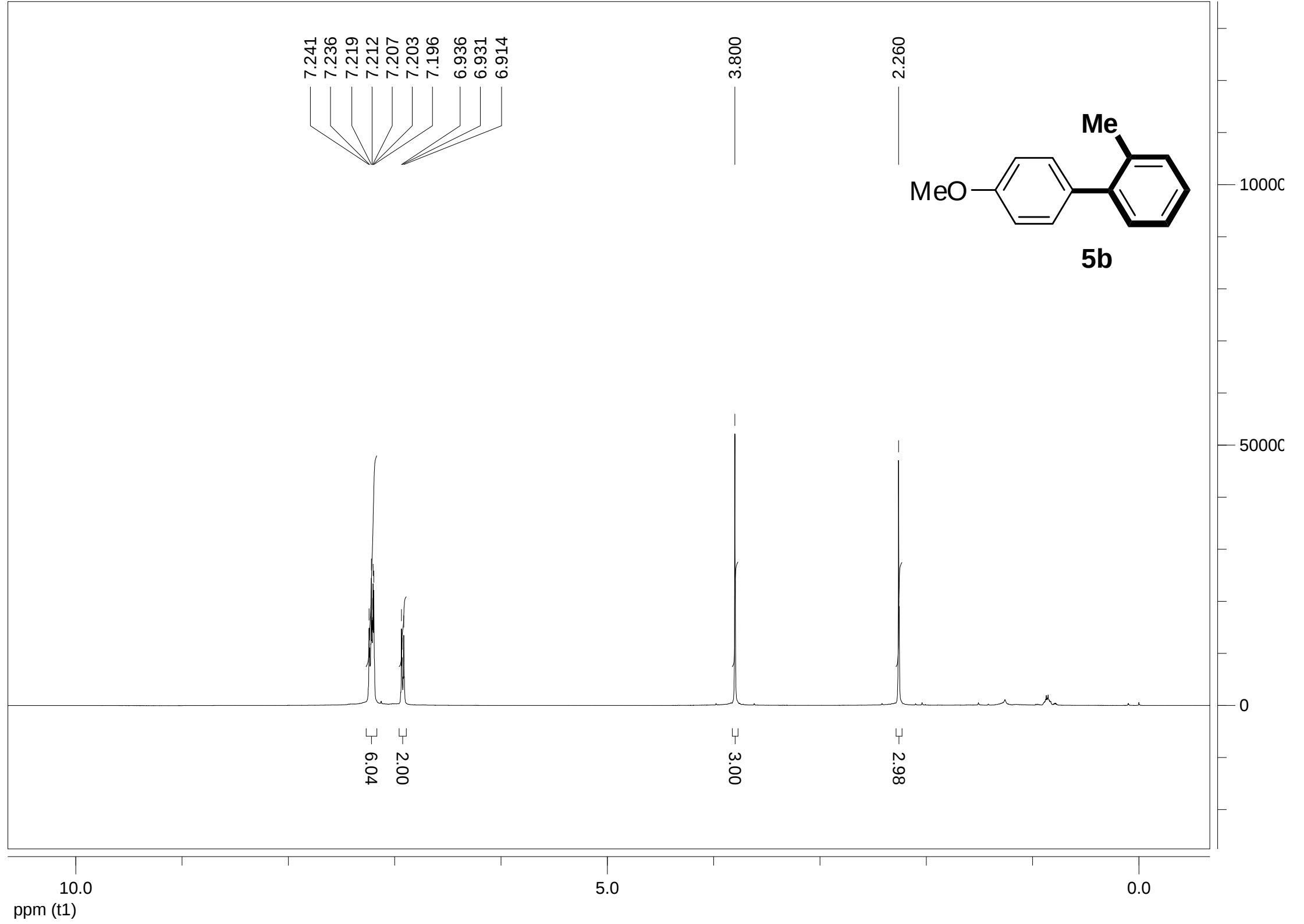


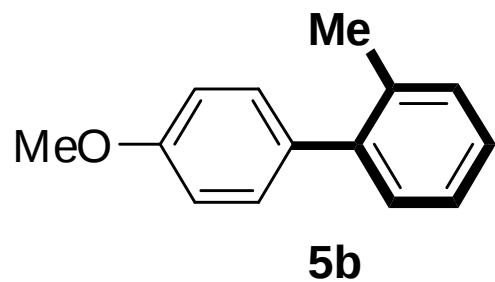


3y





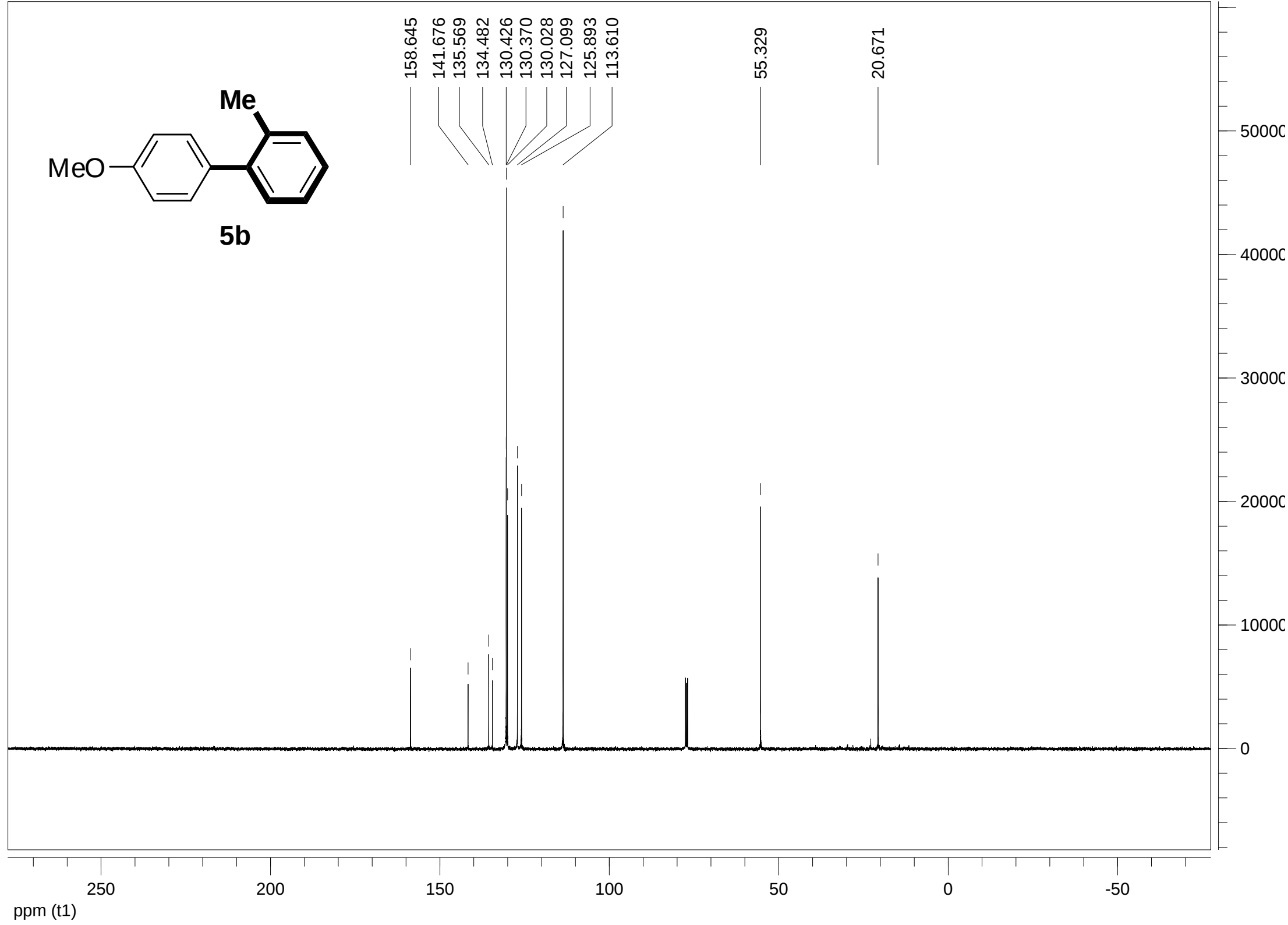


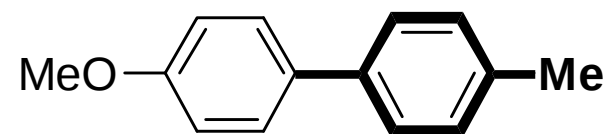


158.645
141.676
135.569
134.482
130.426
130.370
130.028
127.099
125.893
113.610

55.329

20.671





5c

7.513
7.491
7.452
7.432
7.226
7.206
6.967
6.945

3.826

2.374

10000

50000

0

2.03
2.04
2.05

2.95

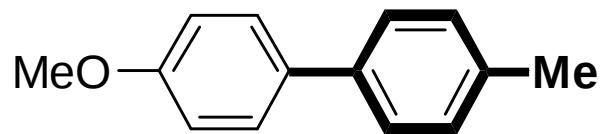
3.00

10.0

5.0

0.0

ppm (t1)



5c

157.880
136.918
135.304
132.694
128.398
126.908
125.539
113.109

54.284

20.012

50000

0

200

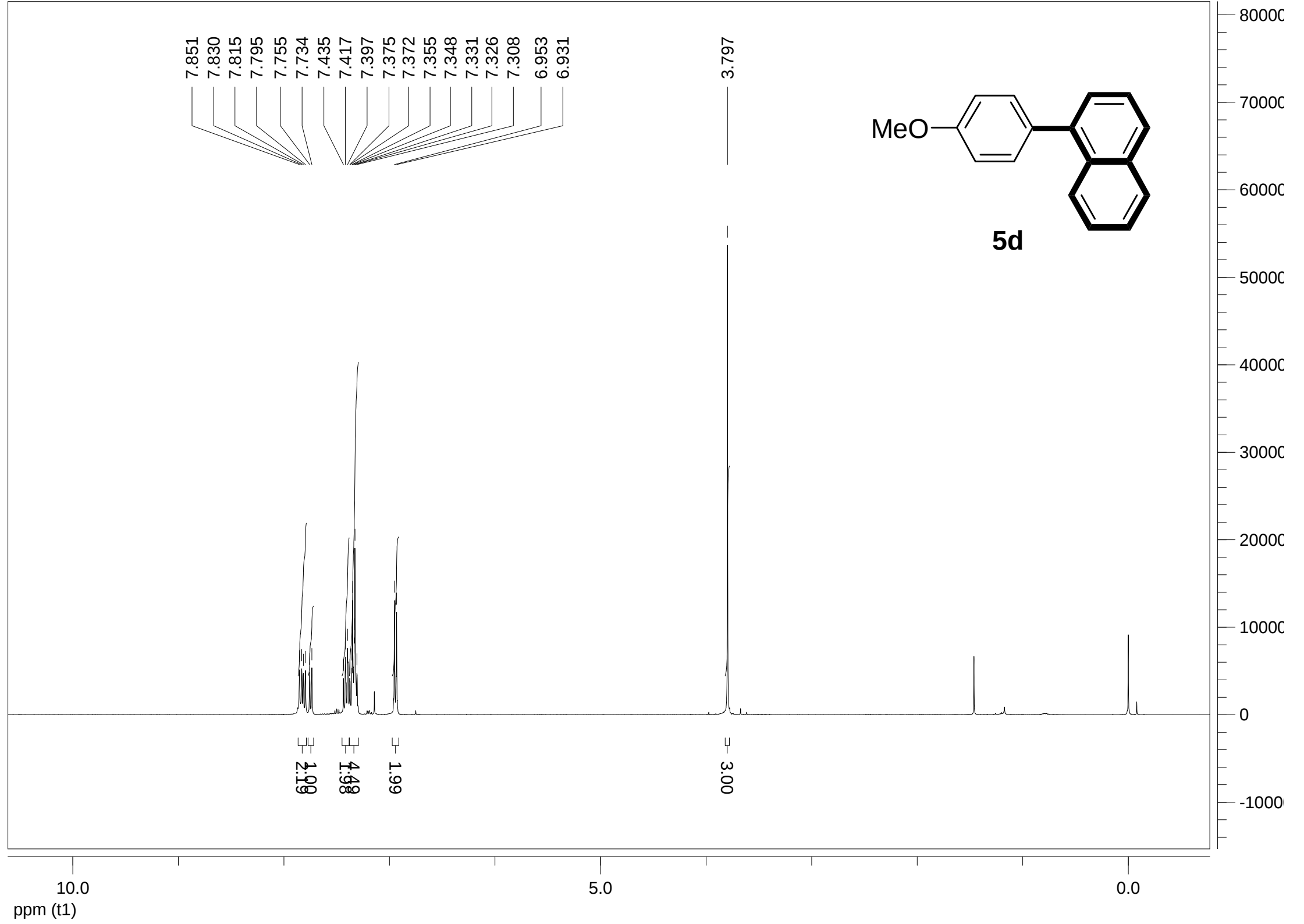
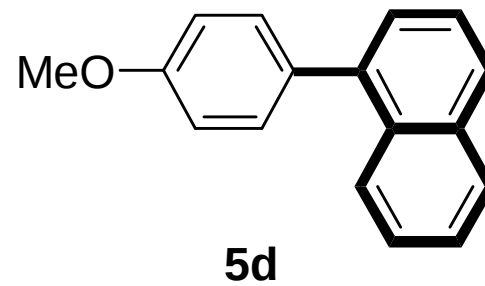
150

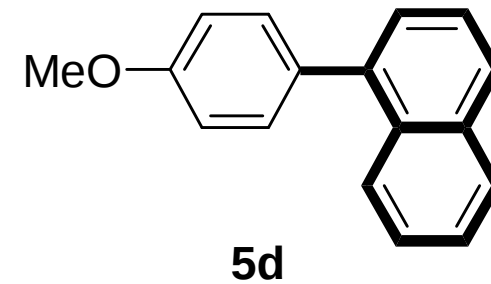
100

50

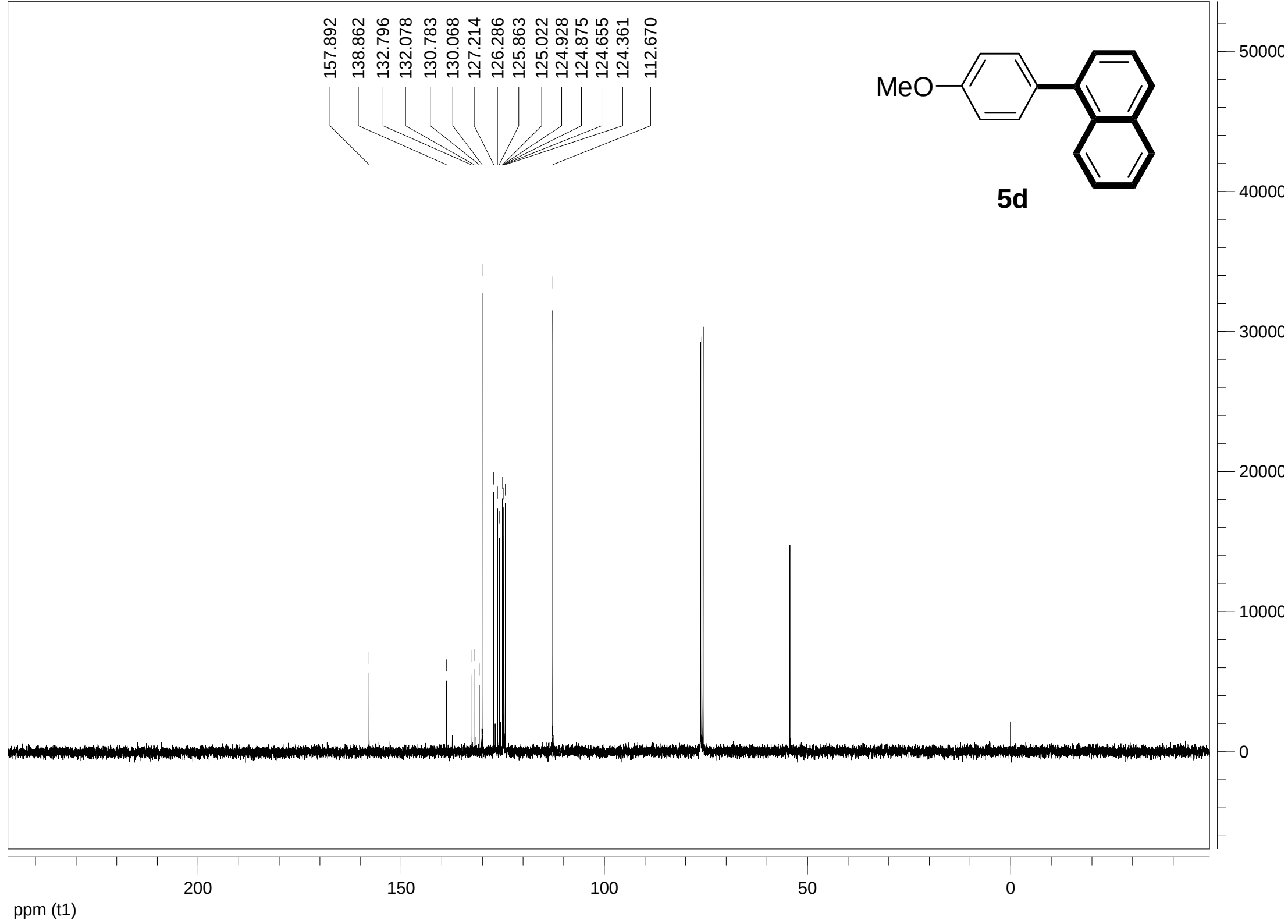
0

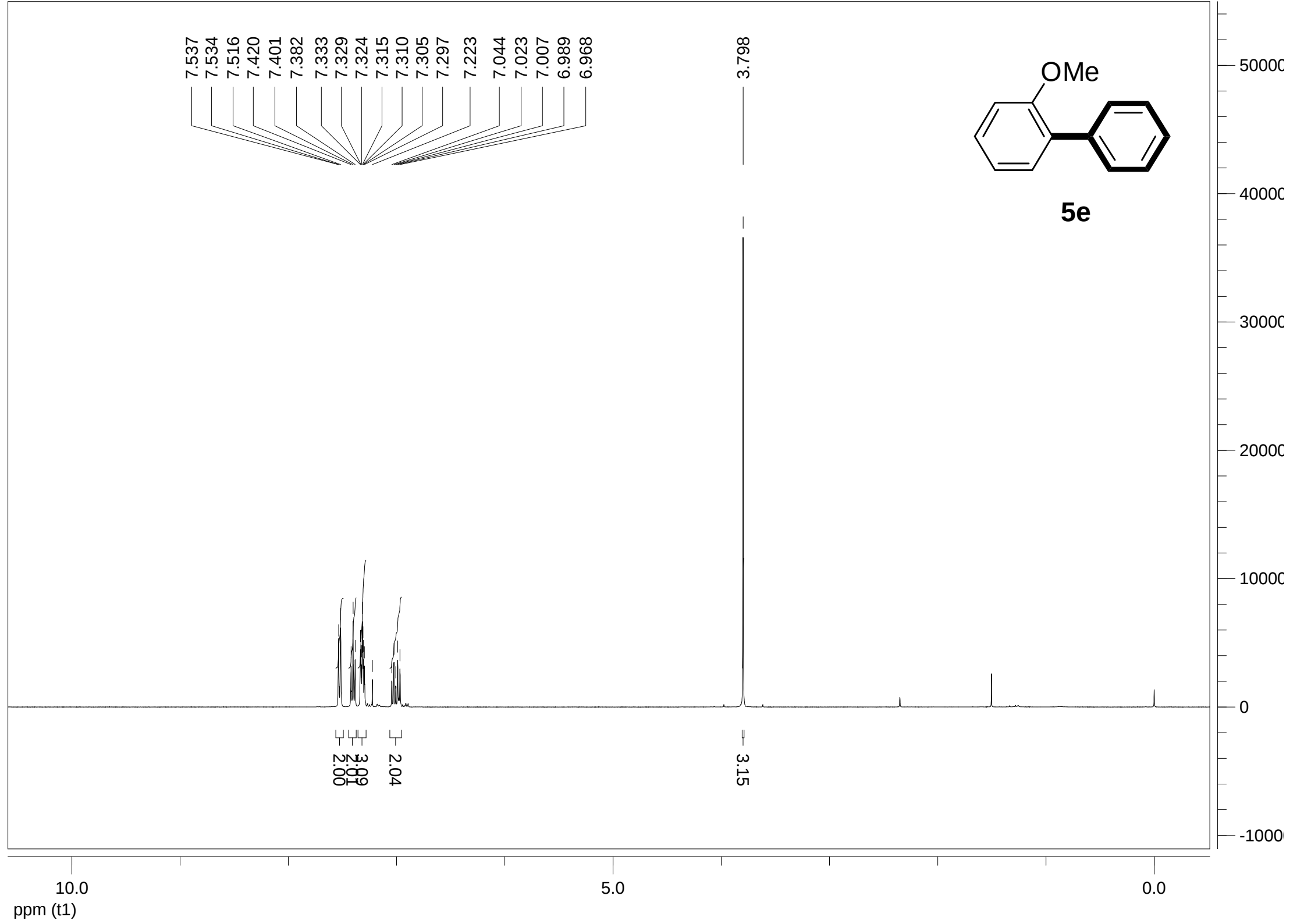
ppm (t1)

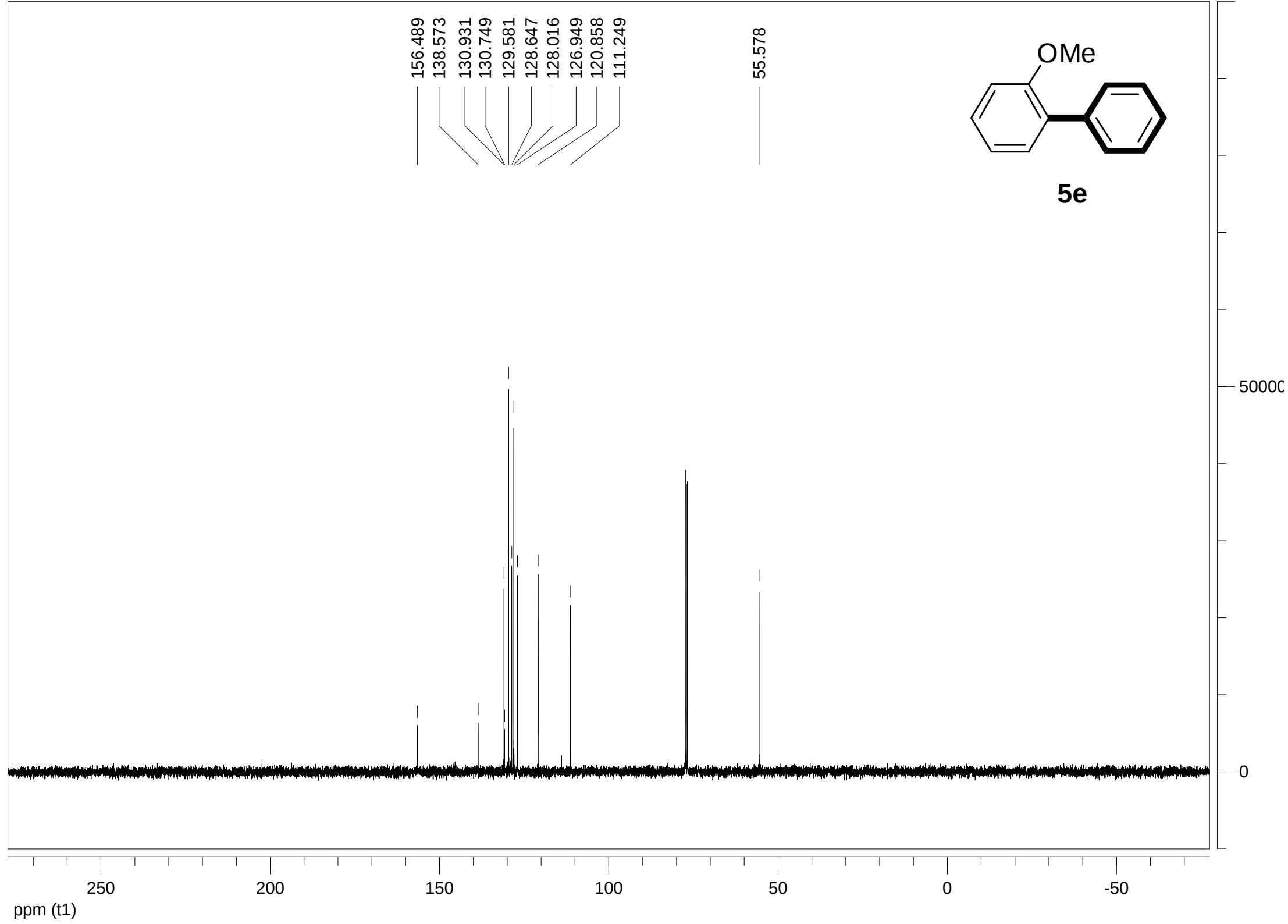


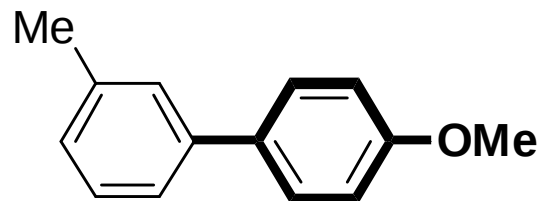


157.892
138.862
132.796
132.078
130.783
130.068
127.214
126.286
125.863
125.022
124.928
124.875
124.655
124.361
112.670

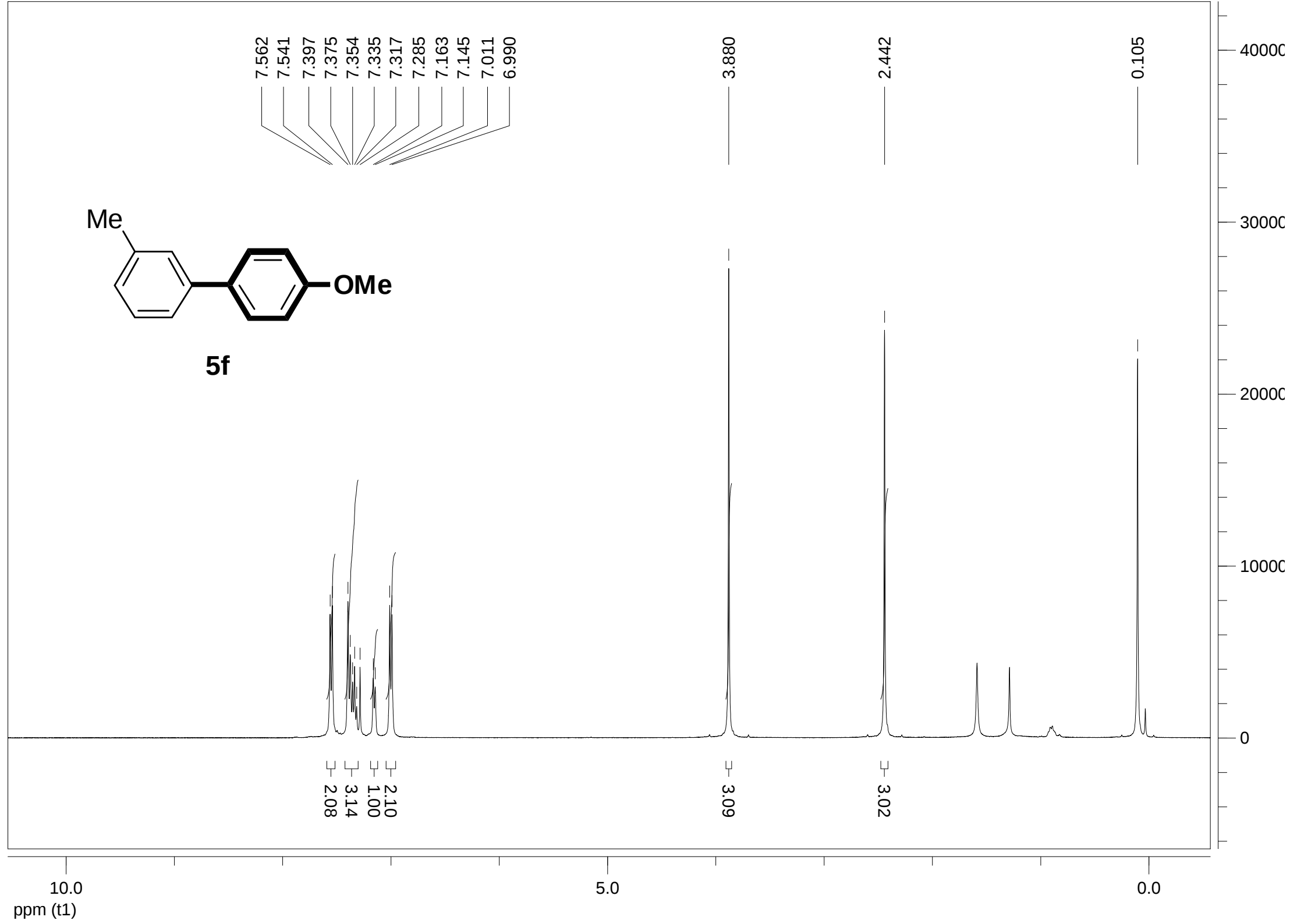


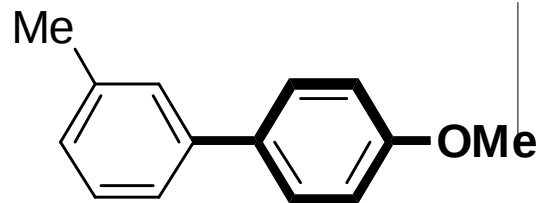






5f



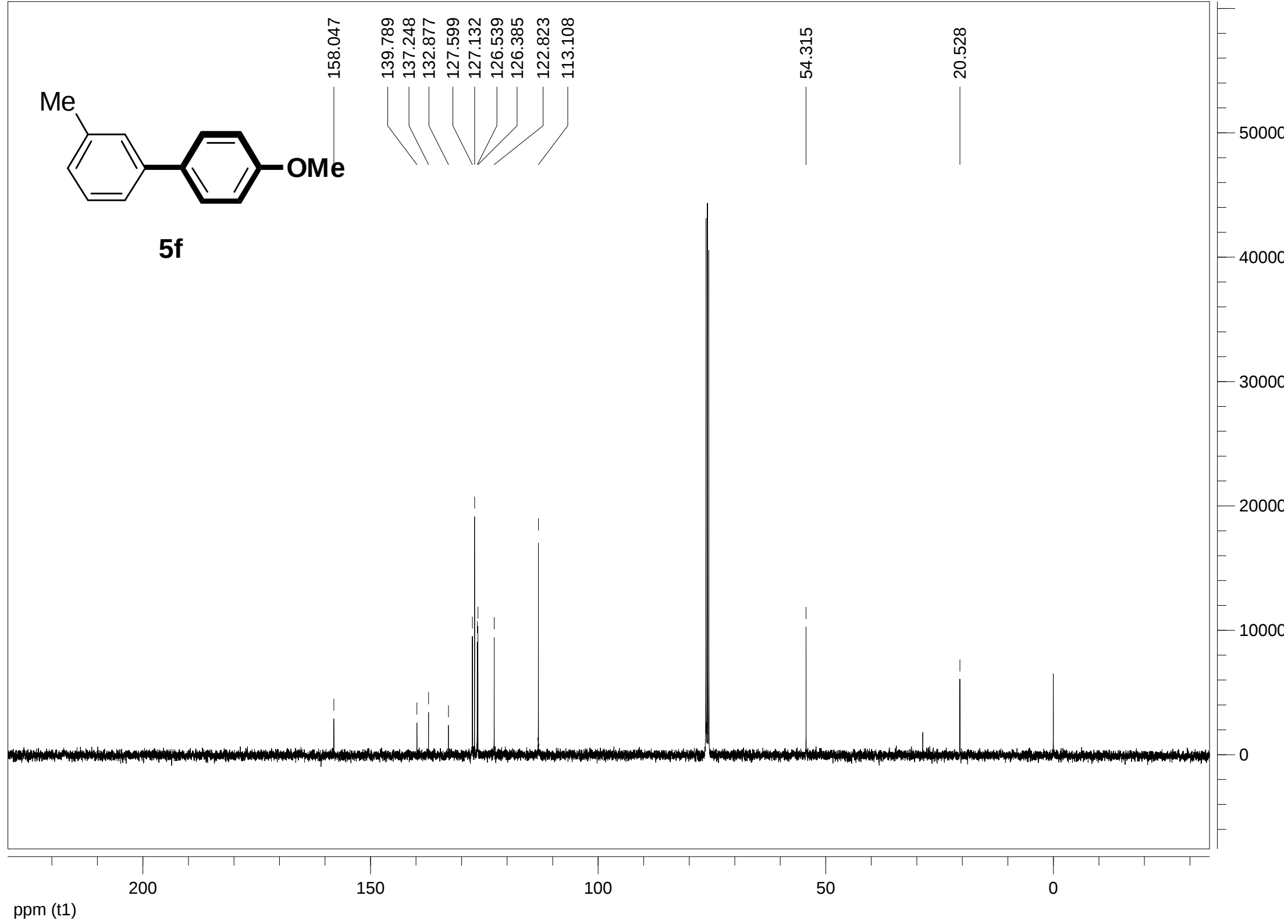


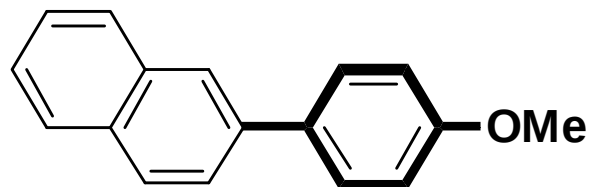
5f

158.047
139.789
137.248
132.877
127.599
127.132
126.539
126.385
122.823
113.108

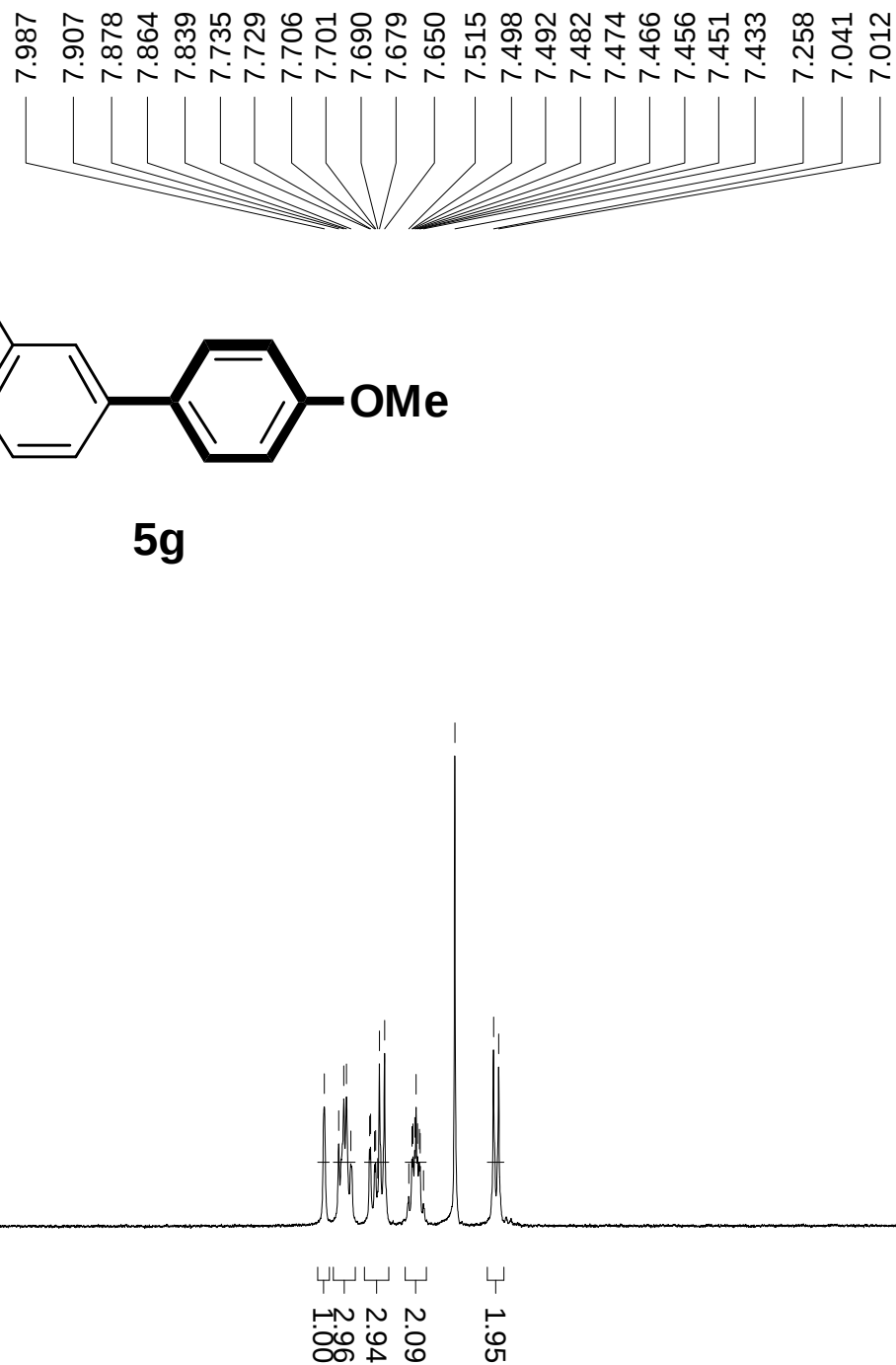
54.315

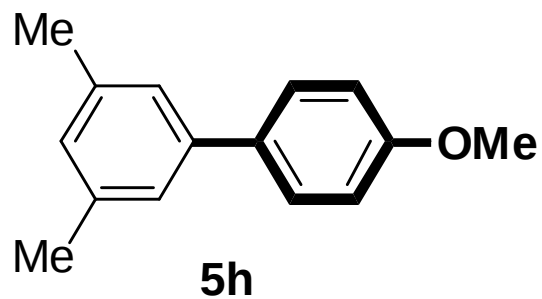
20.528





5g





3500C

3000C

2500C

2000C

1500C

1000C

5000C

0

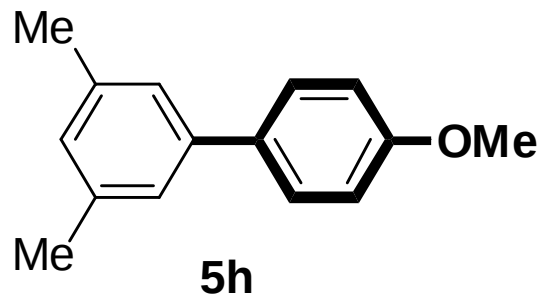
-5000C

10.0

ppm (t1)

5.0

0.0



159.041
140.869
138.237
134.034
128.361
128.201
124.739
114.106

55.360

21.462

4000C

3000C

2000C

1000C

0

200

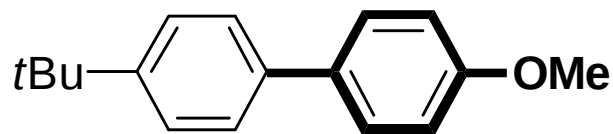
150

100

50

0

ppm (t1)



5i

7.624
7.602
7.580
7.544
7.523
7.064
7.043

3.914

1.453

86.3
2.09

60.7
2.09

11.8
3.11

00.6
9.00

10.0
ppm (t1)

5.0

0.0

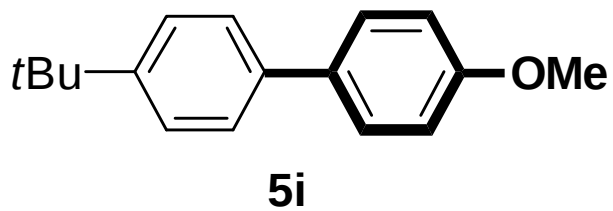
4000C

3000C

2000C

1000C

0

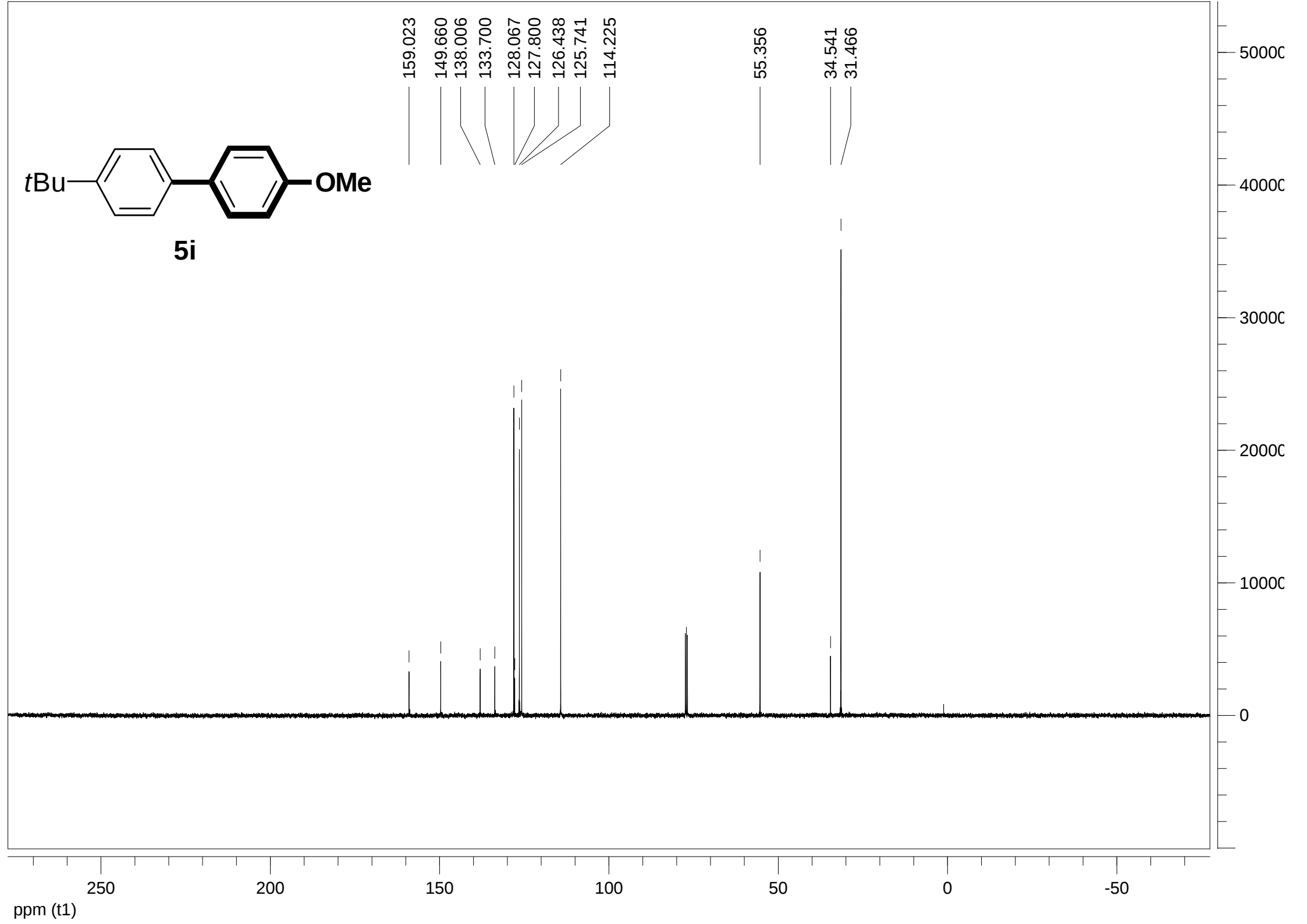


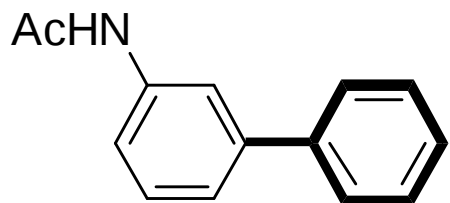
159.023
149.660
138.006
133.700
128.067
127.800
126.438
125.741
114.225

55.356

34.541

31.466





5j

7.760
7.617
7.597
7.550
7.531
7.477
7.458
7.439
7.413
7.394
7.378
7.360
7.294

2.230

3500C
3000C
2500C
2000C
1500C
1000C
500C
0

00.1
80.7
40.9

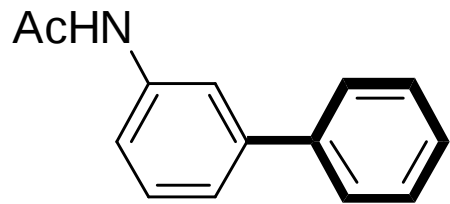
00.3

10.0

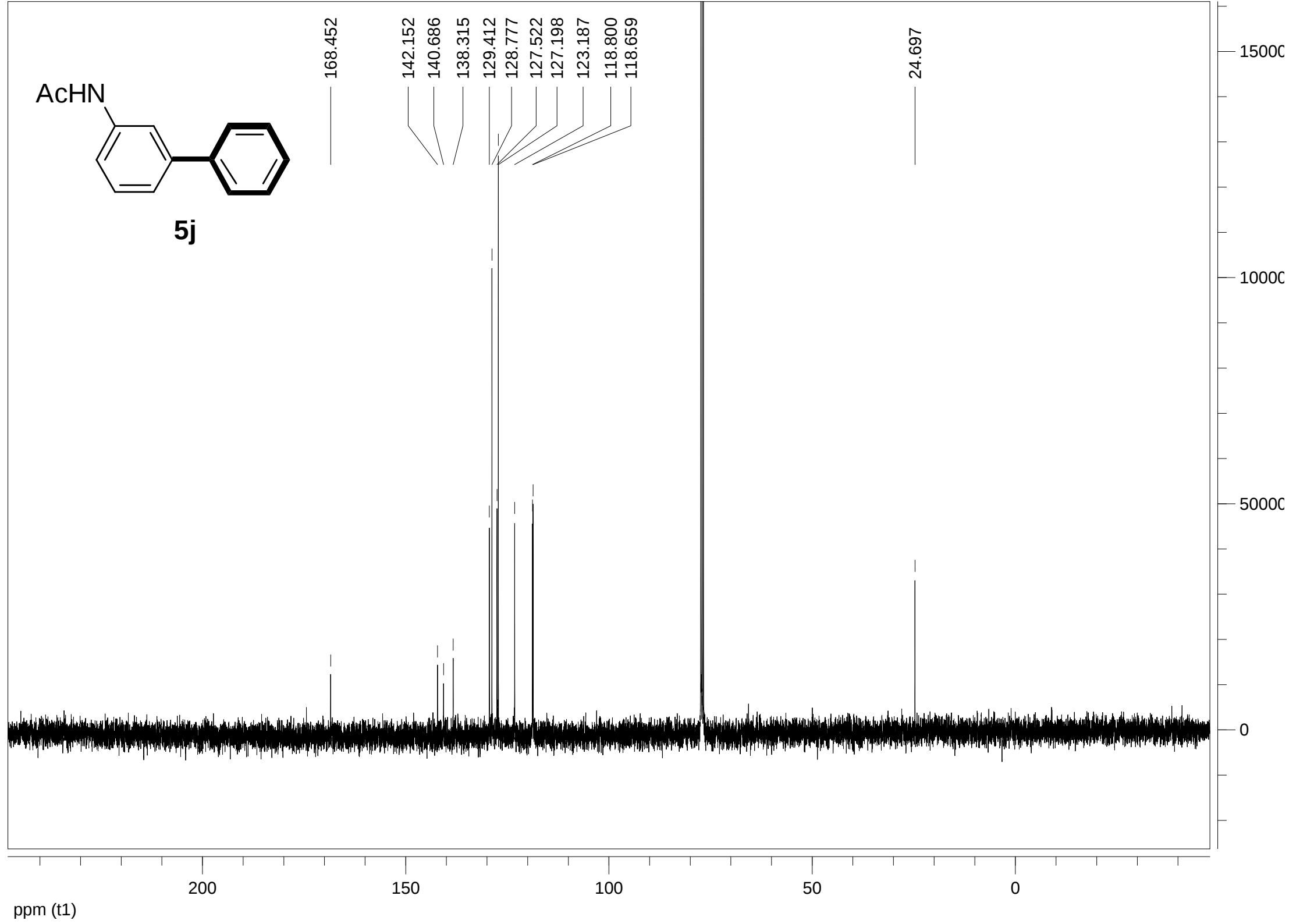
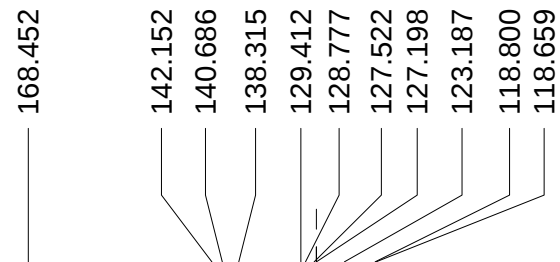
5.0

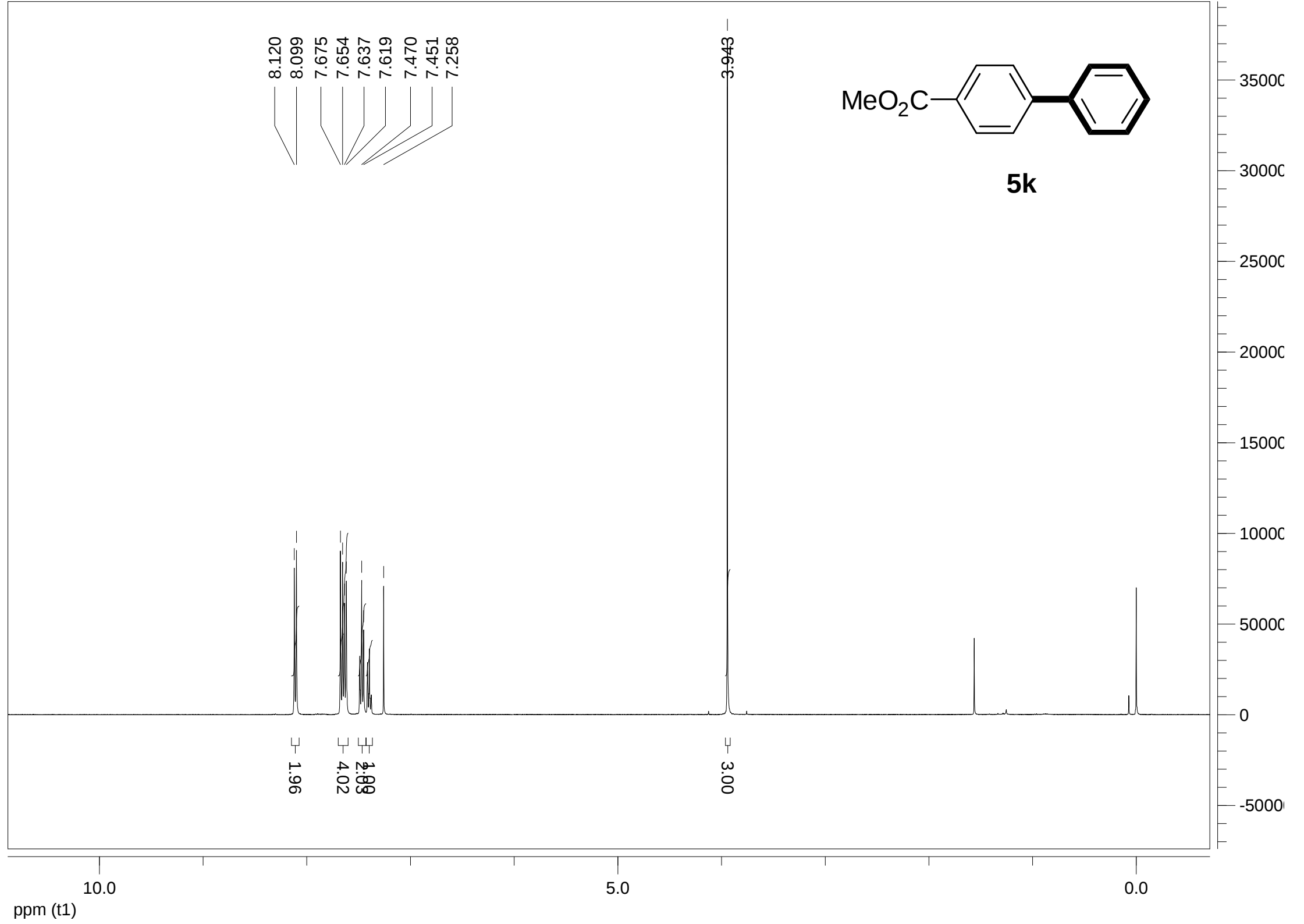
0.0

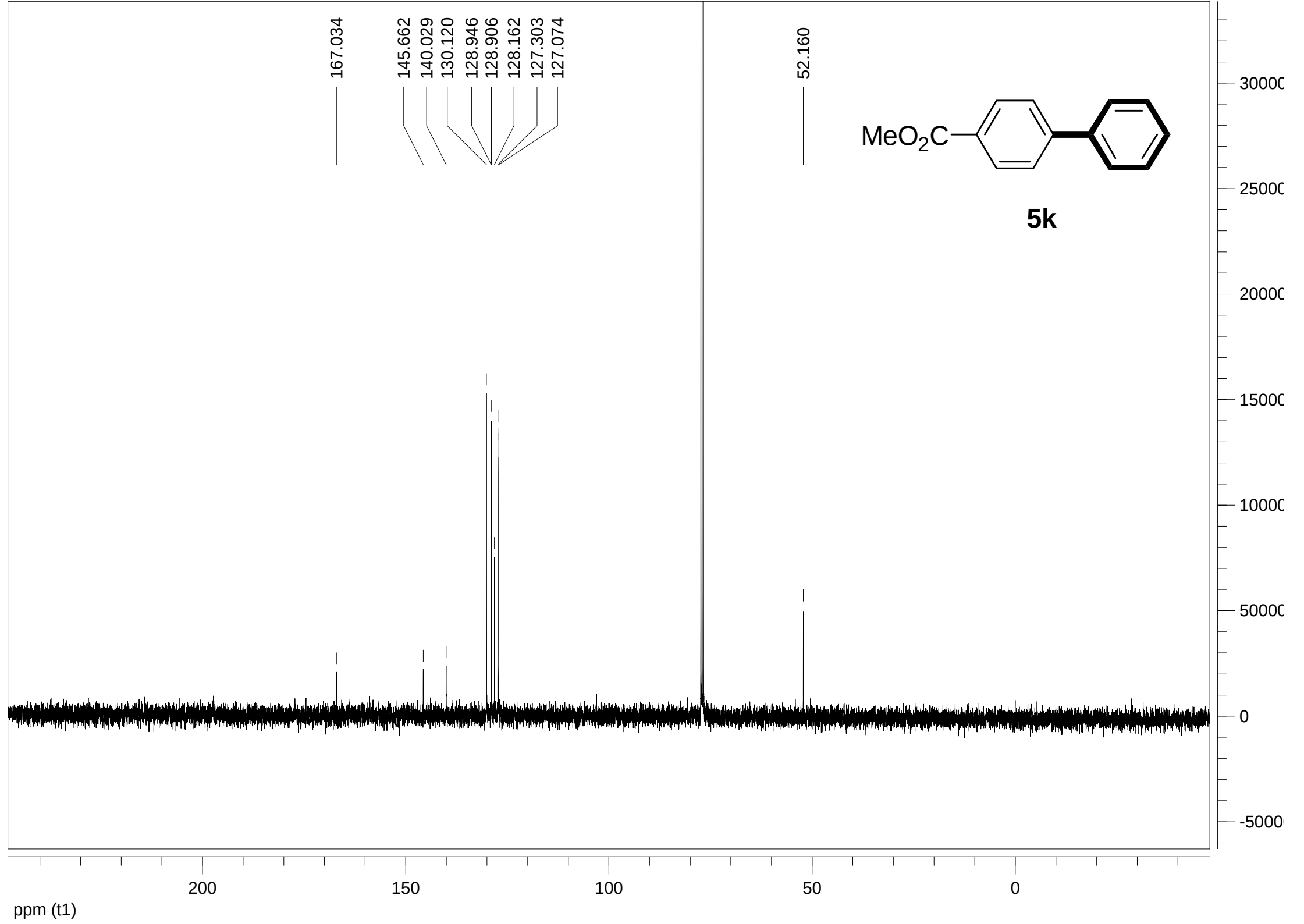
ppm (t1)

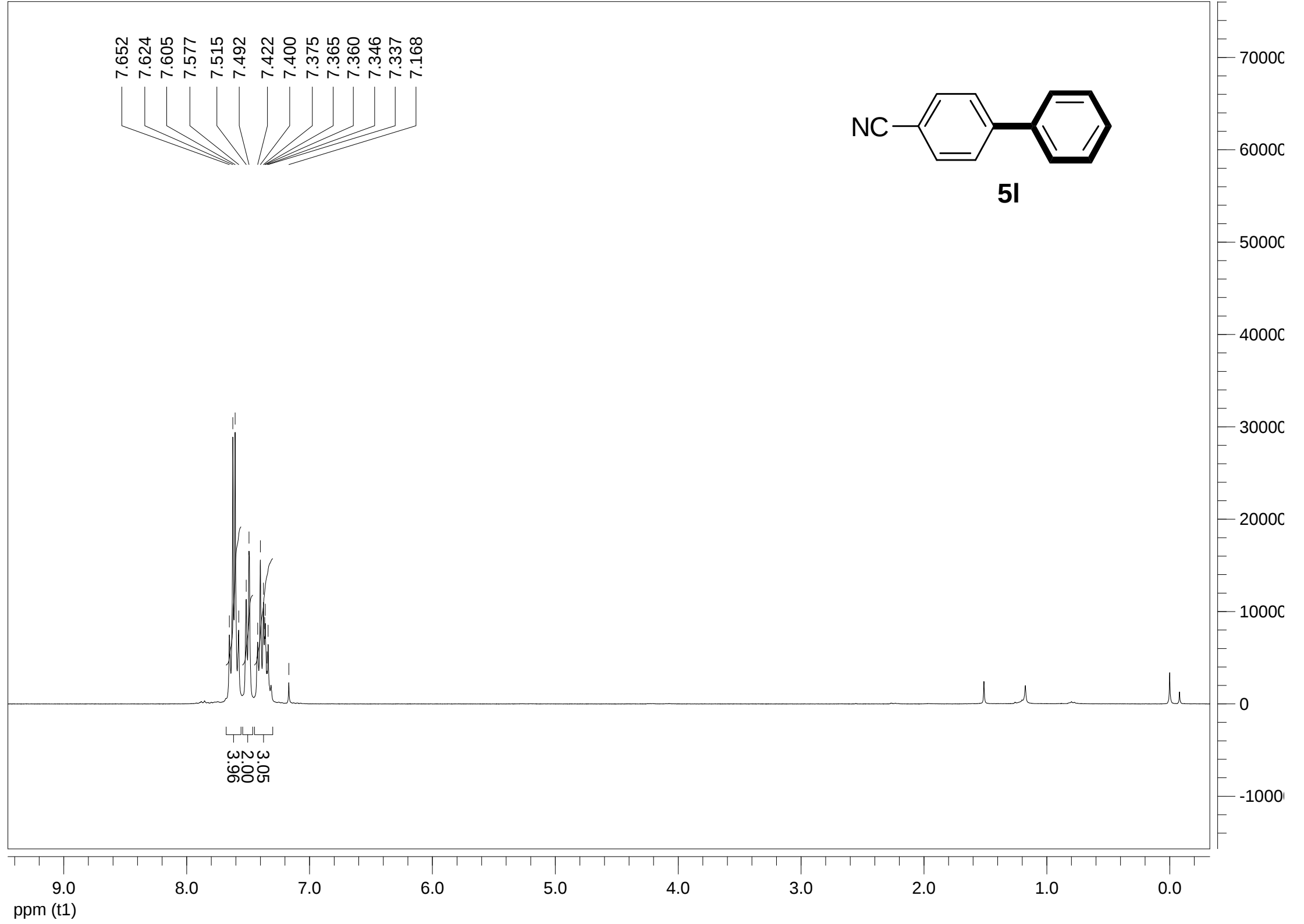


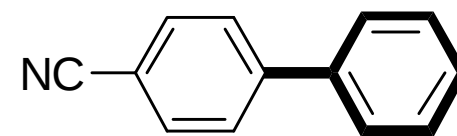
5j





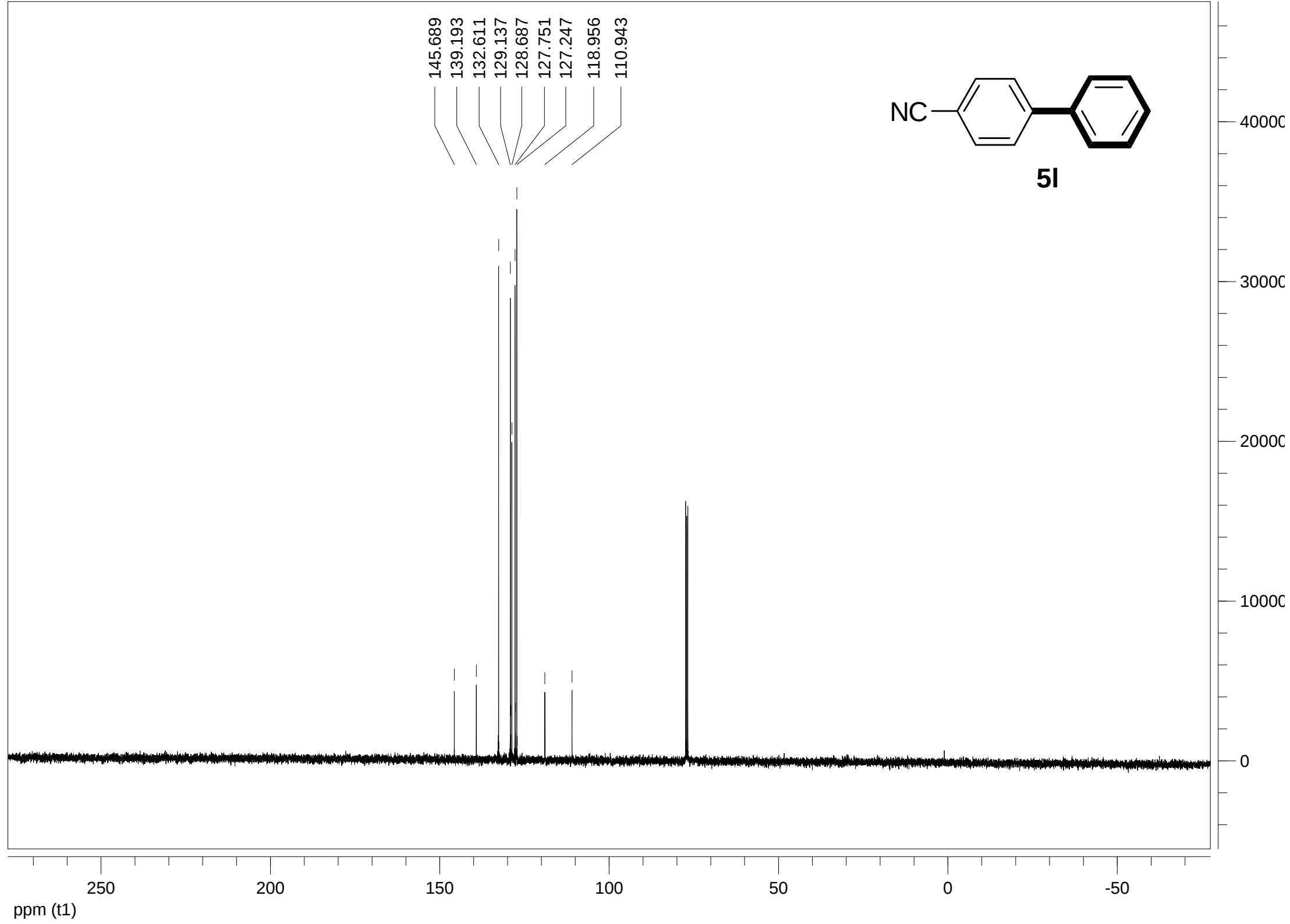


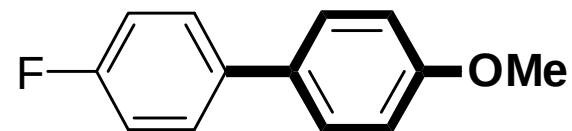




5l

145.689
139.193
132.611
129.137
128.687
127.751
127.247
118.956
110.943





5m

7.503
7.474
7.454
7.247
7.115
7.093
7.072
6.976
6.955

3.843

4.04

2.07
2.00

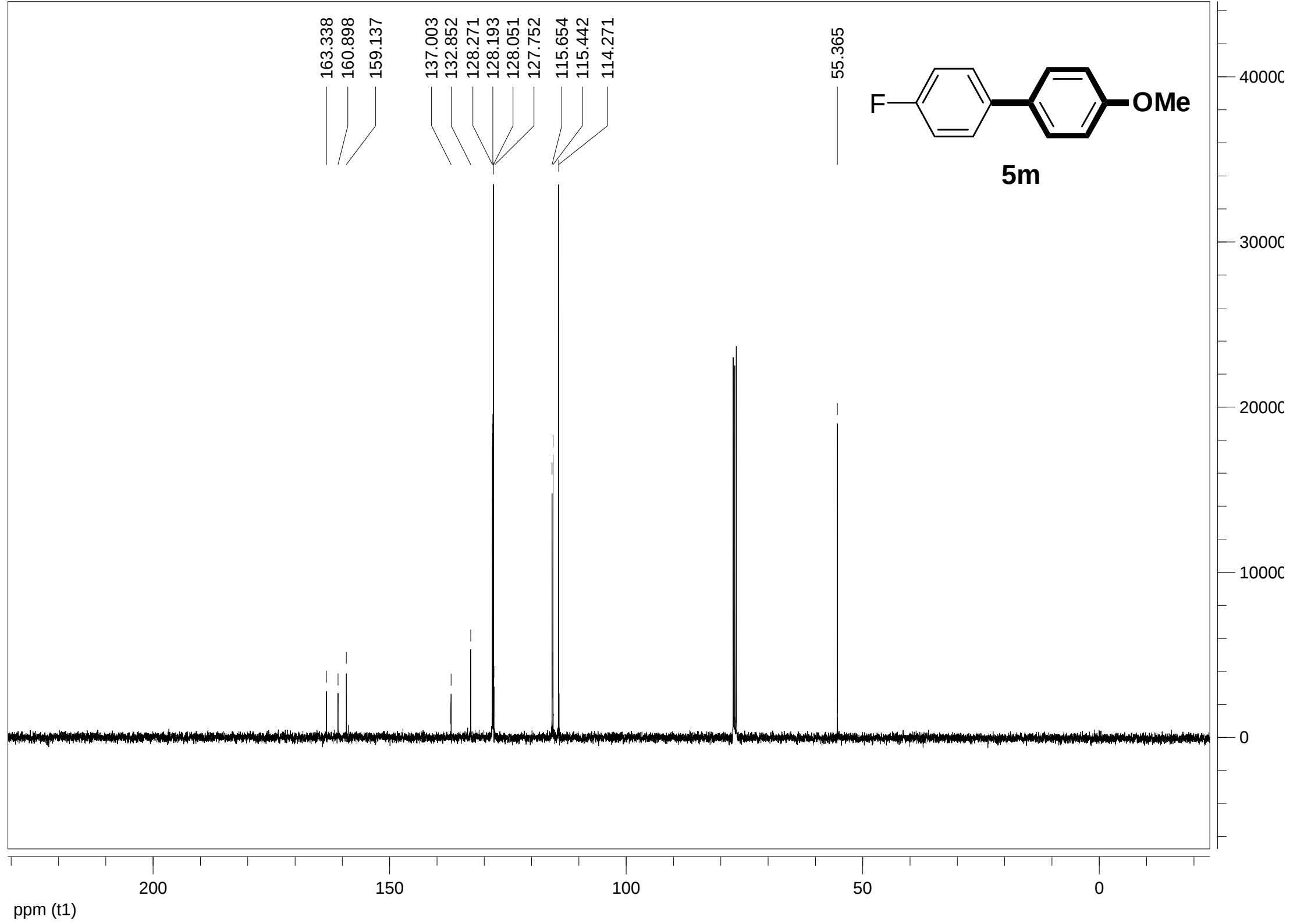
3.11

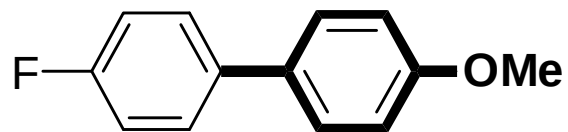
7000
6000
5000
4000
3000
2000
1000
0
-1000

10.0
ppm (t1)

5.0

0.0





5m

-116.707

5000C

0

ppm (t1)

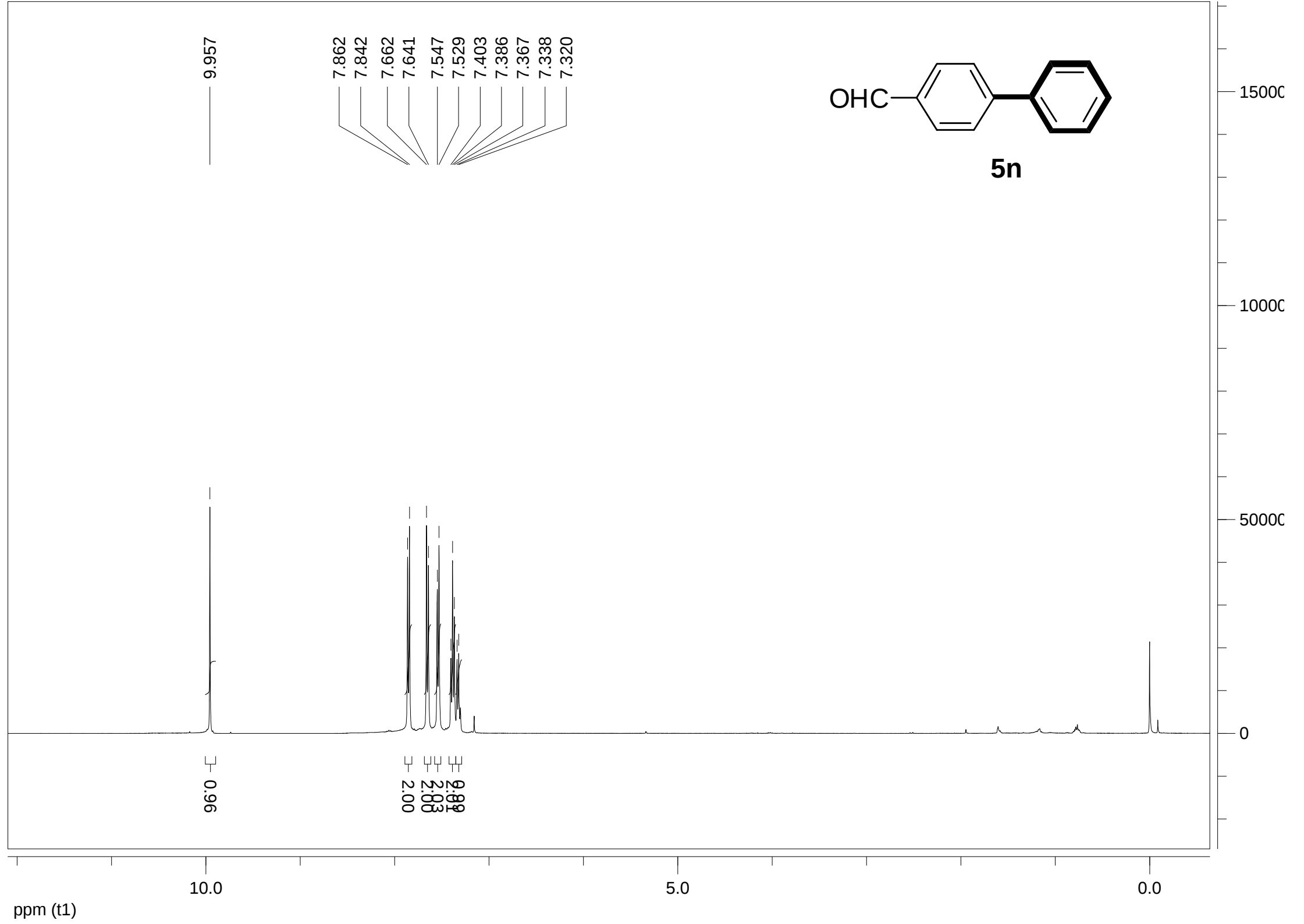
0

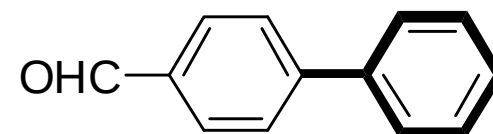
-50

-100

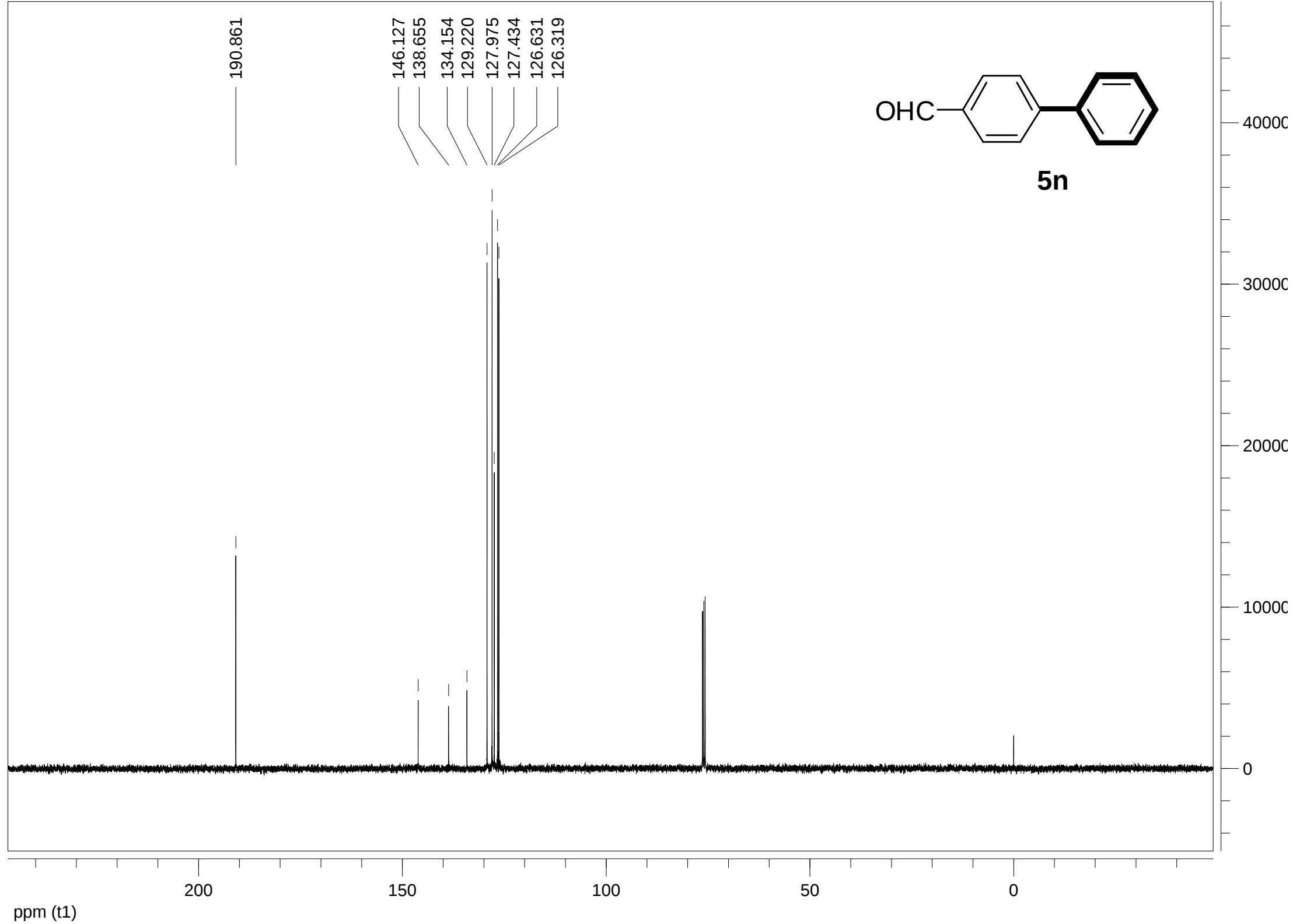
-150

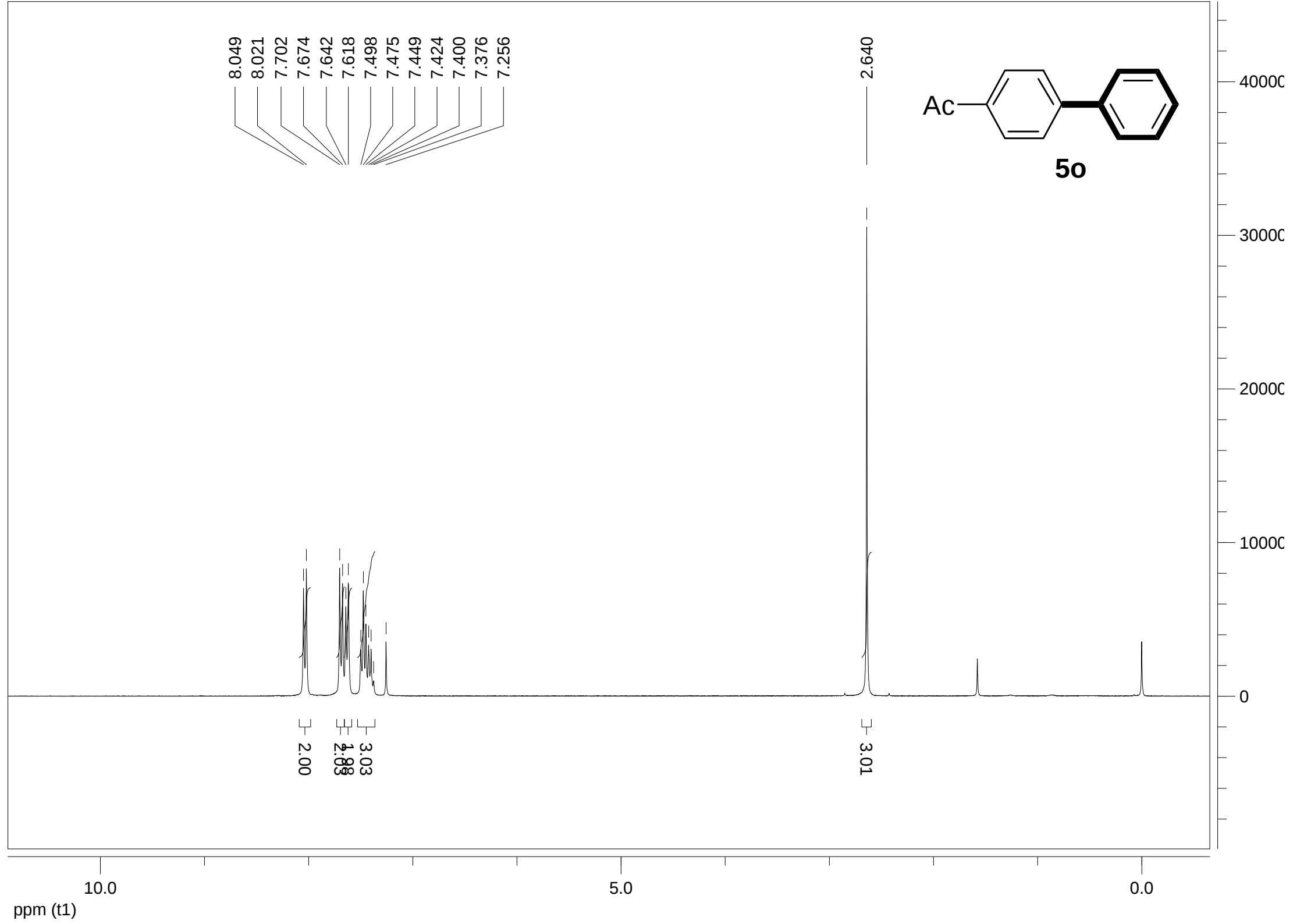
-200

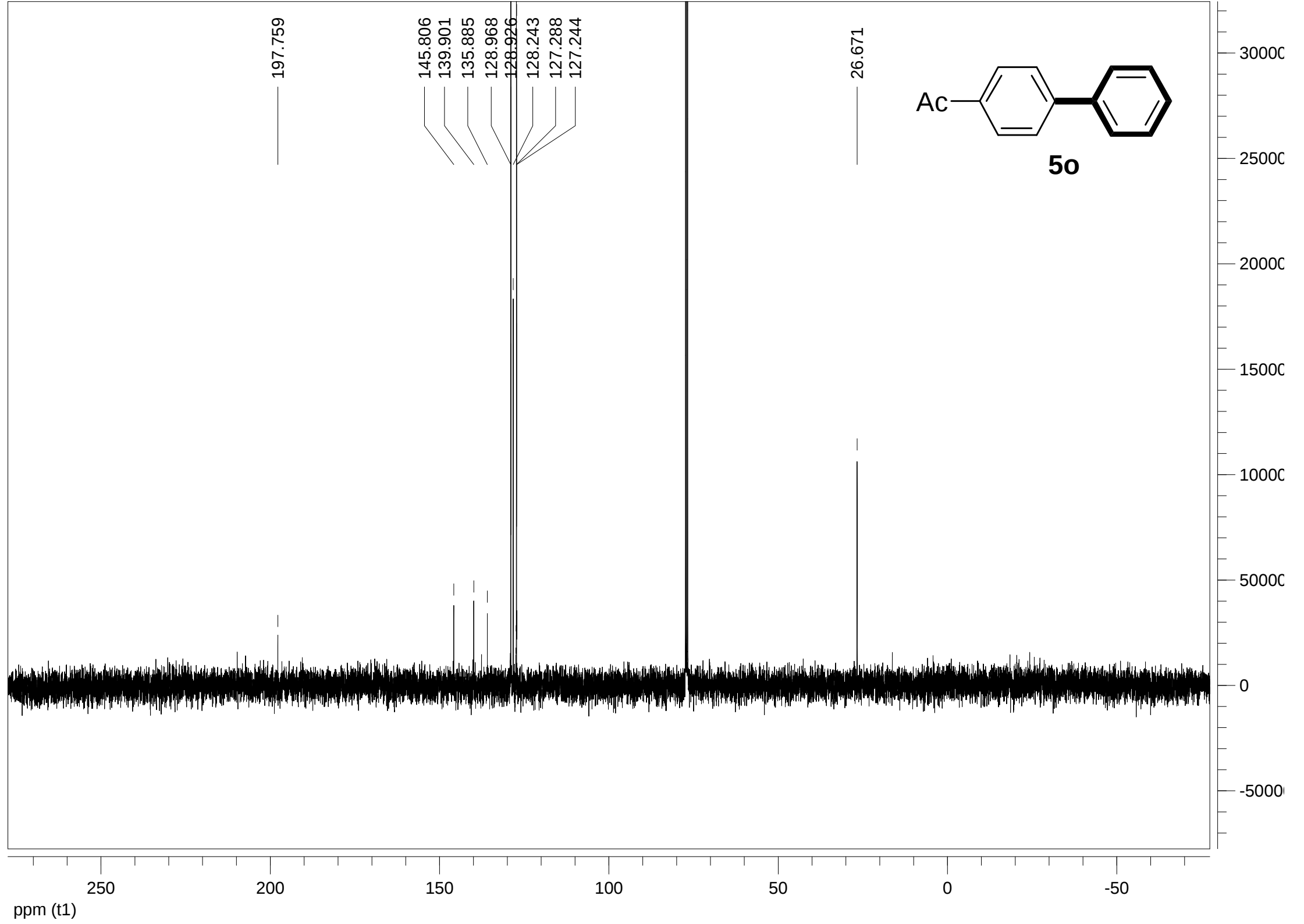


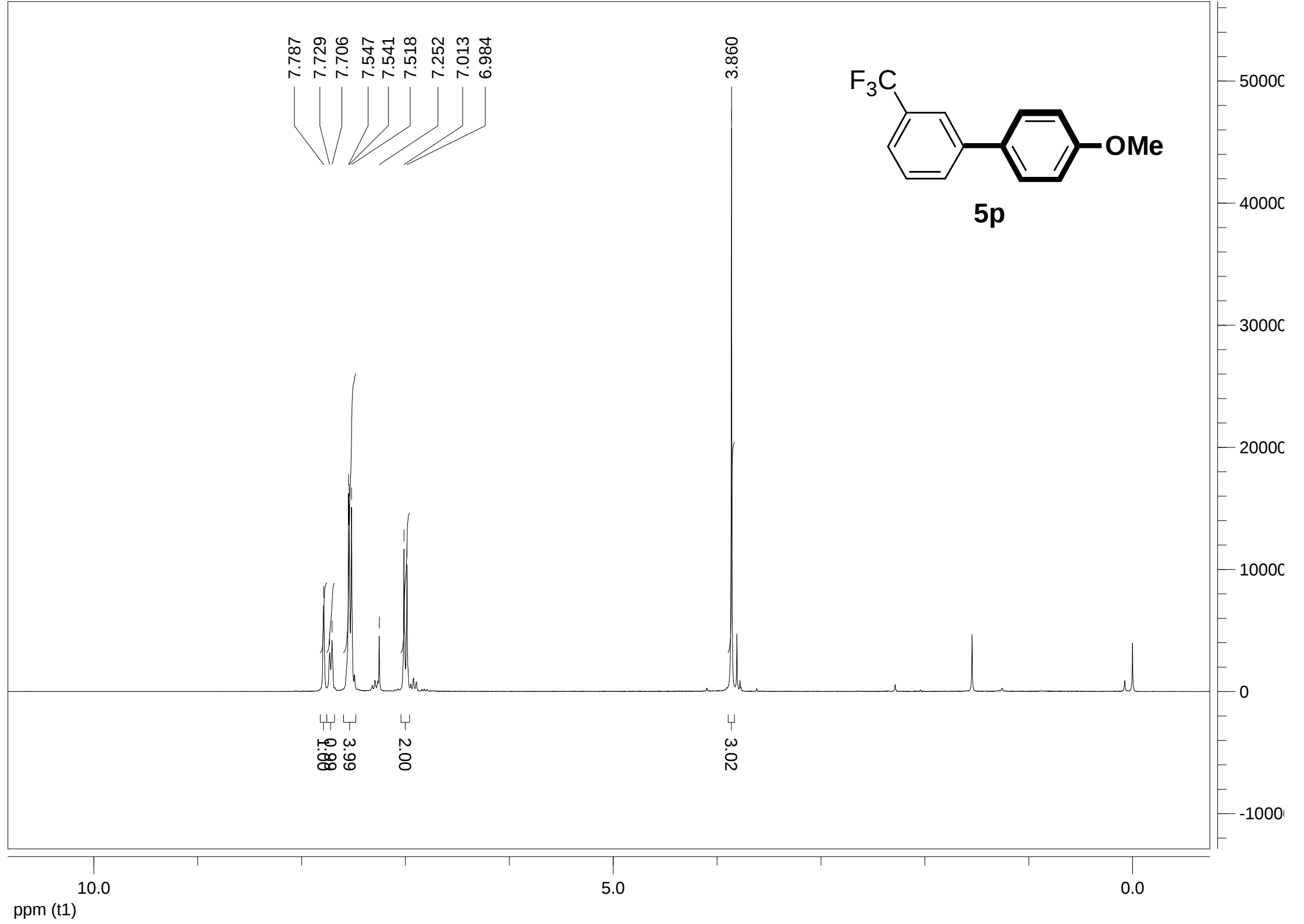


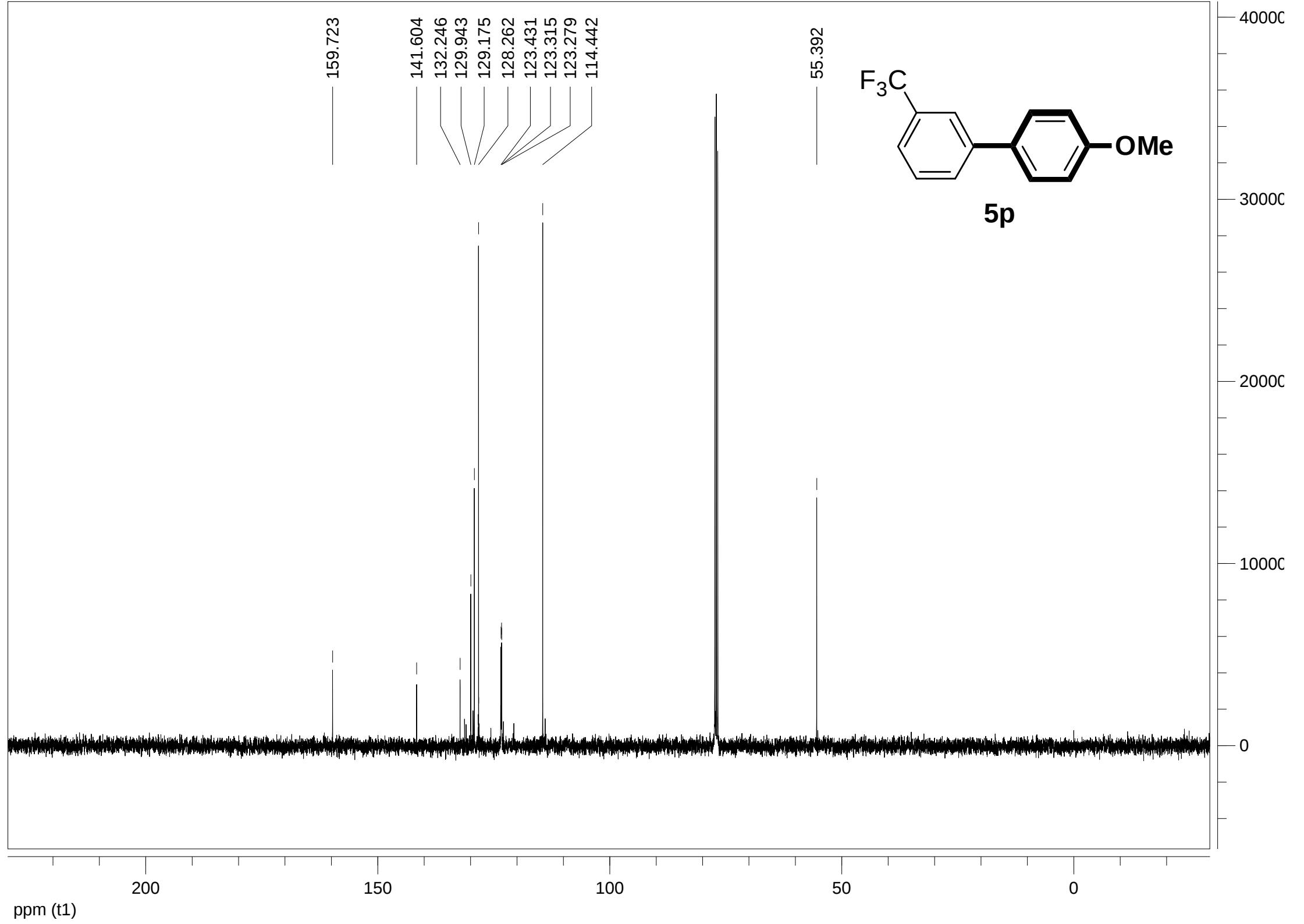
5n

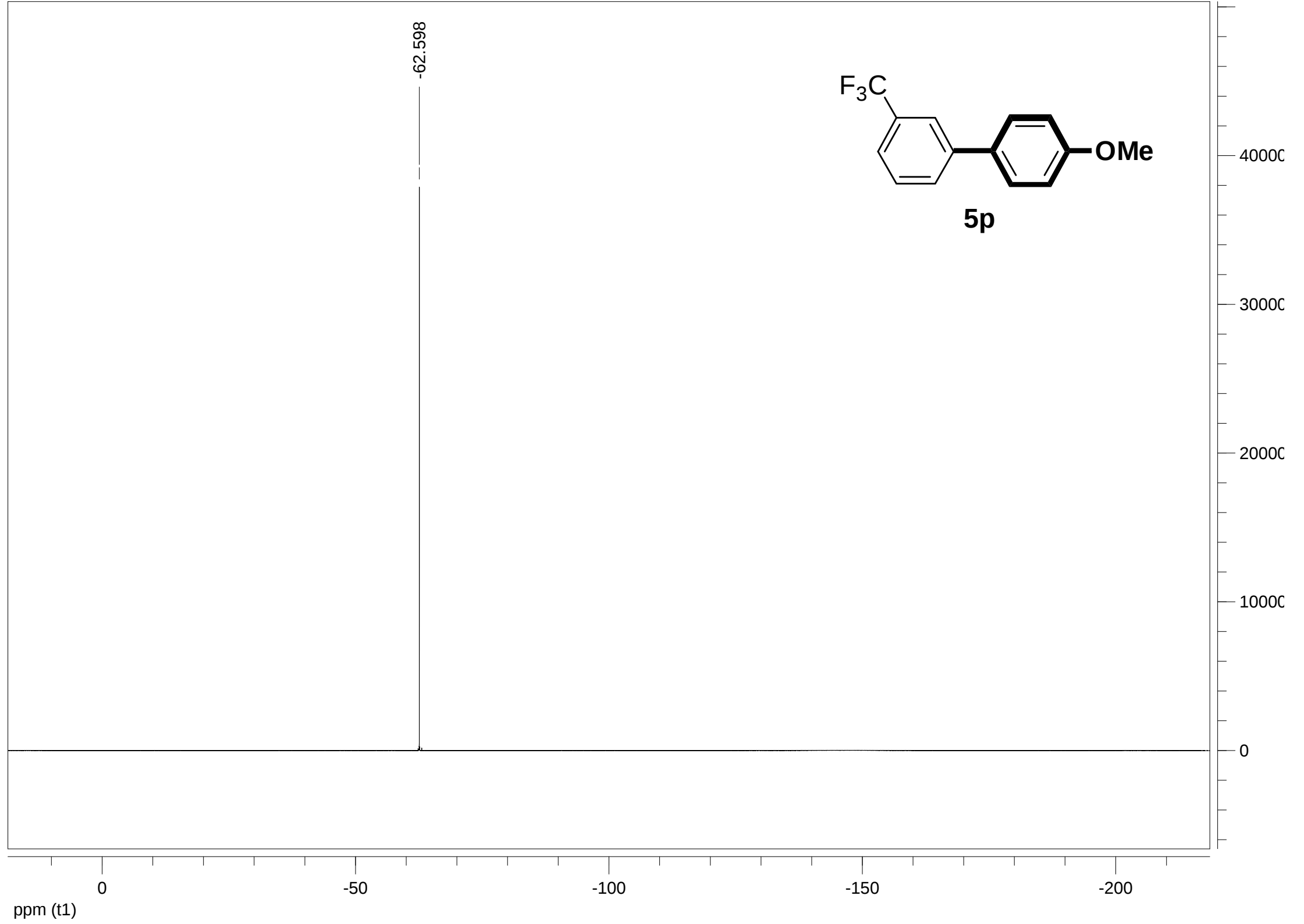


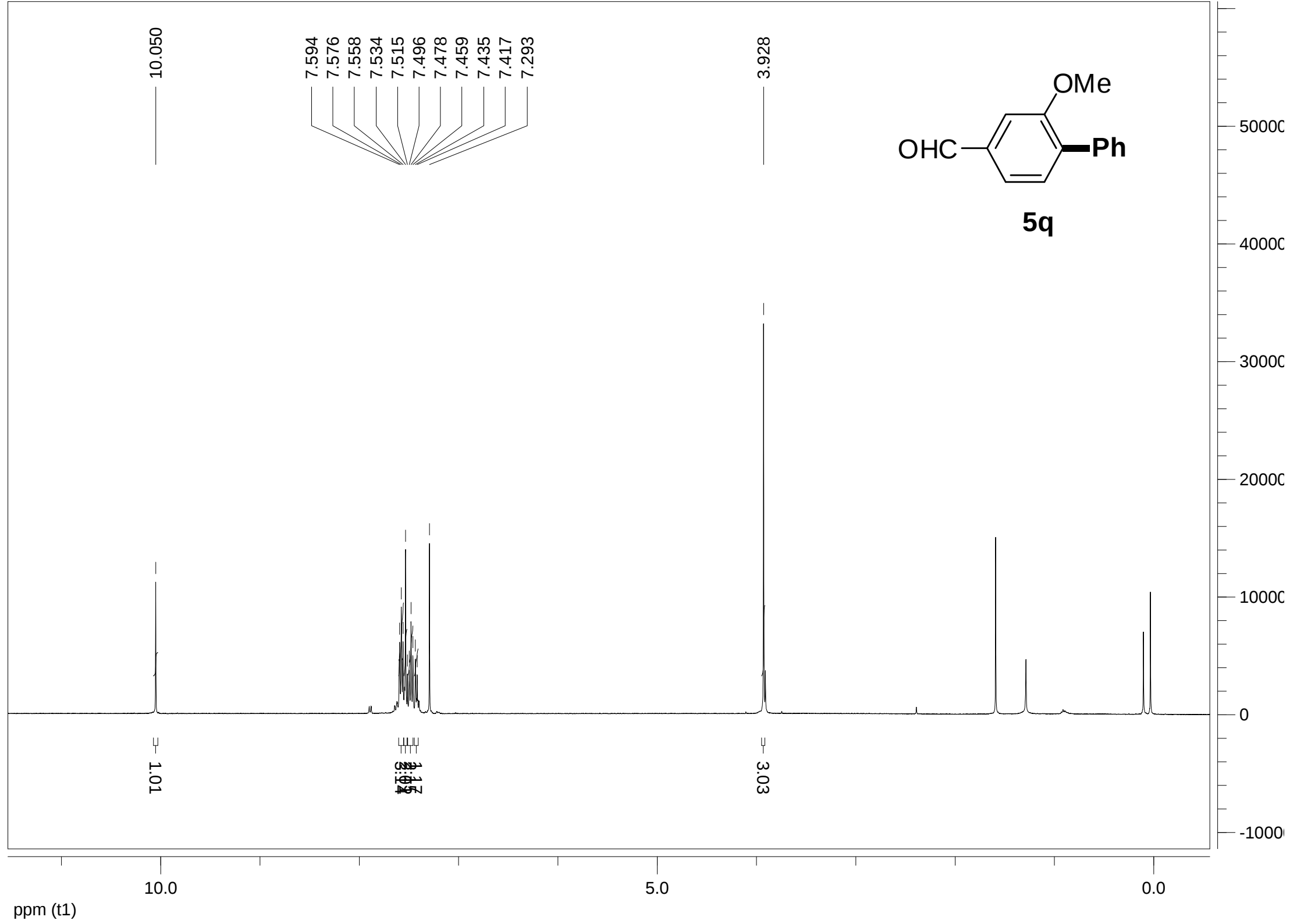


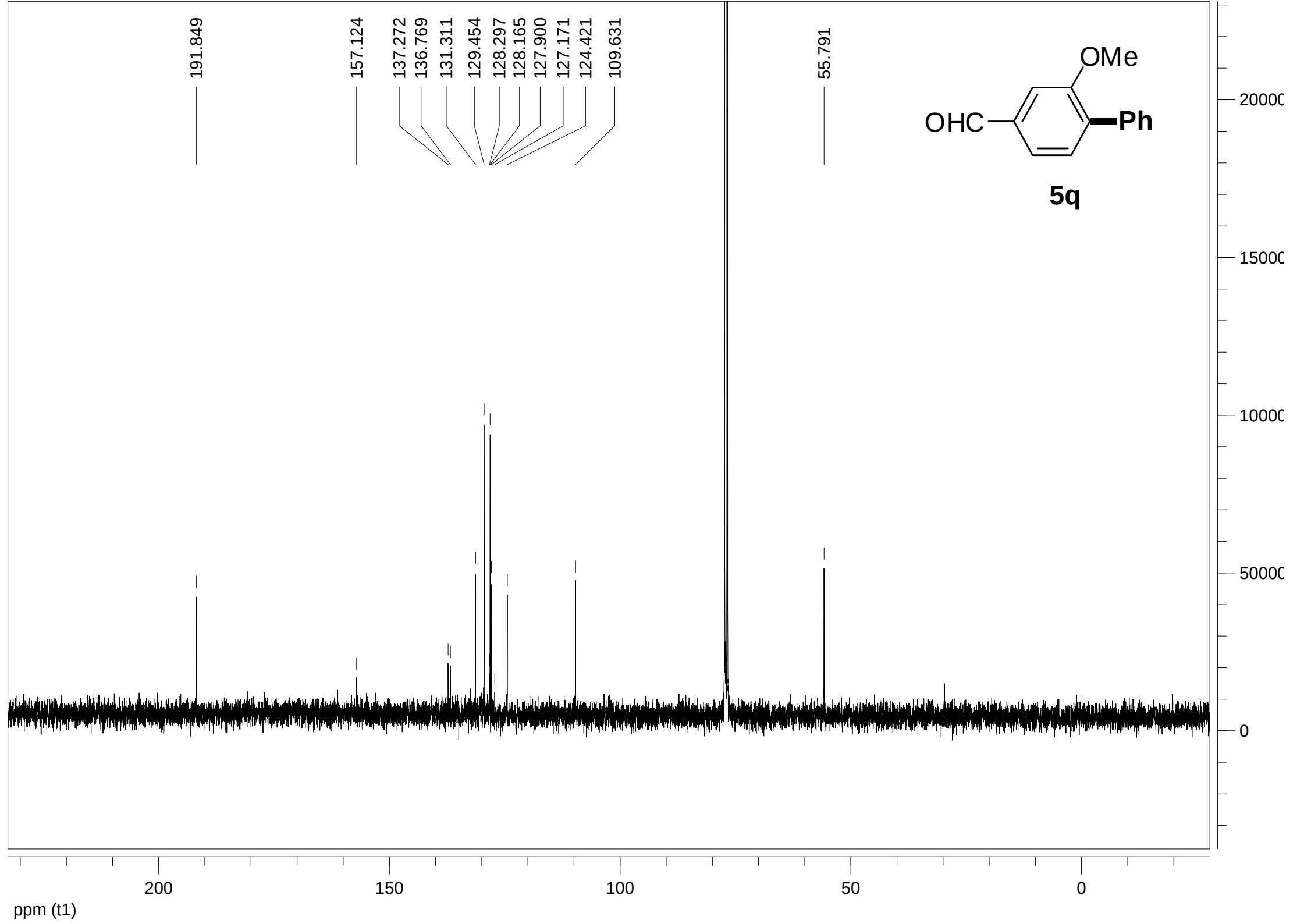


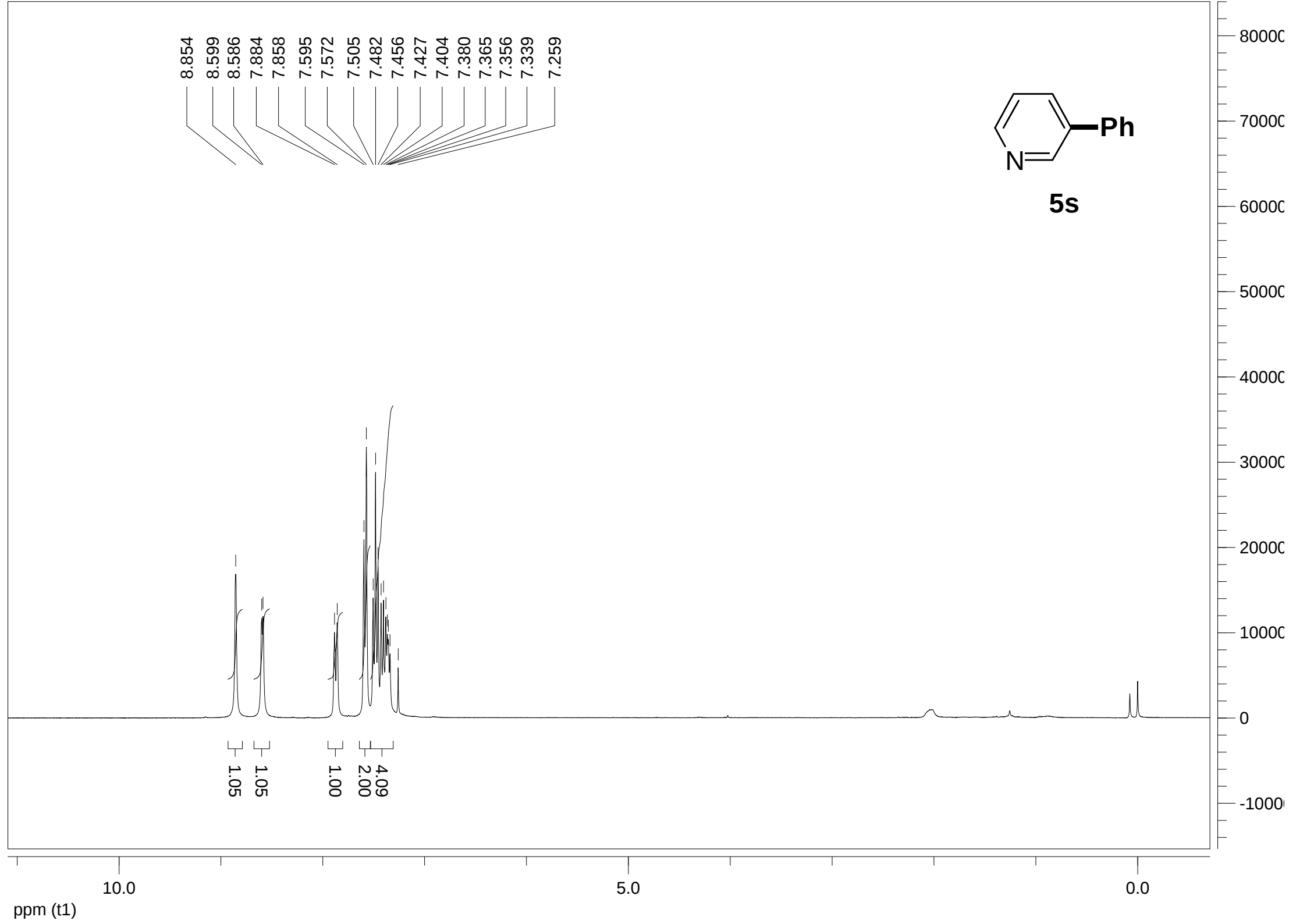


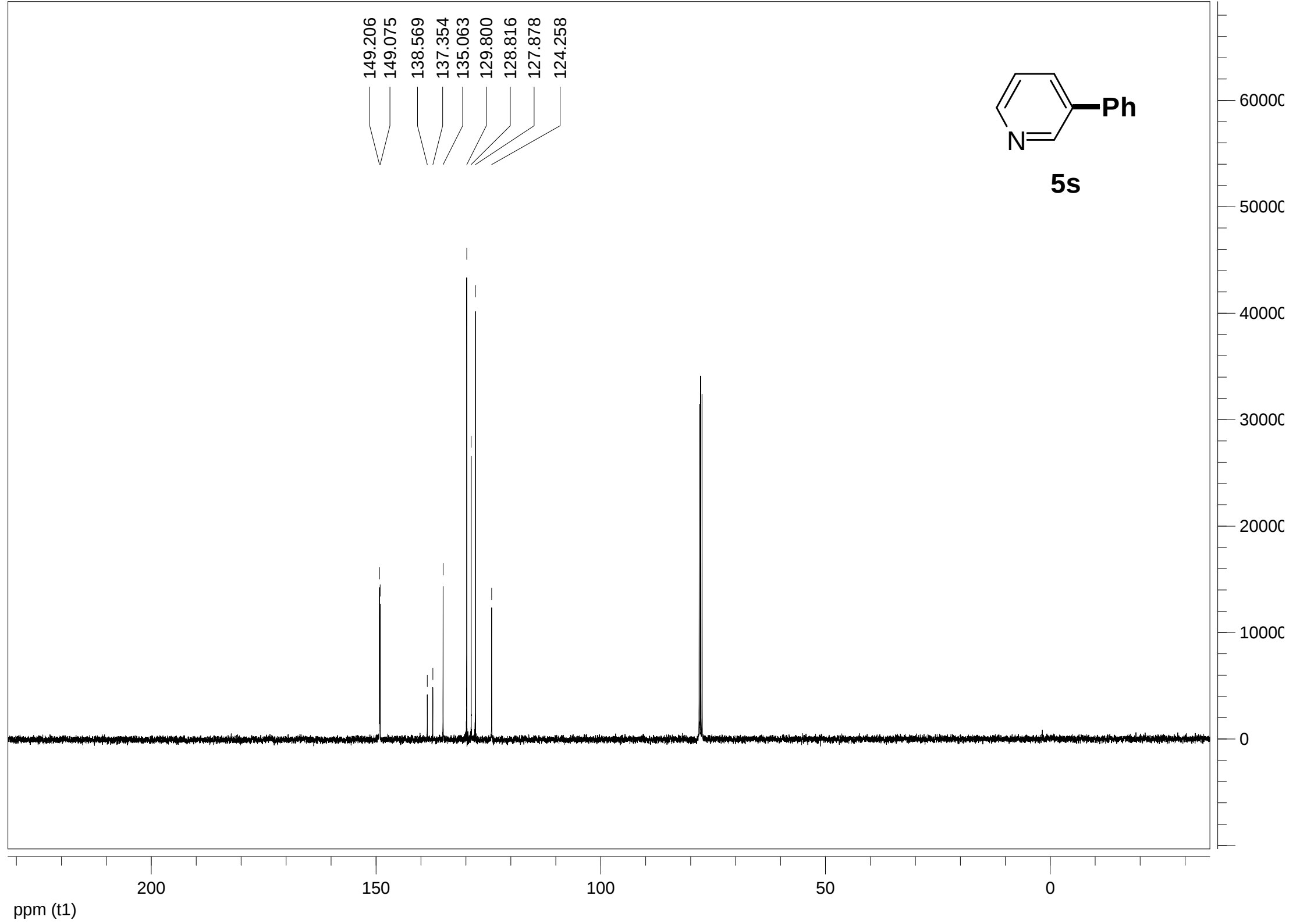


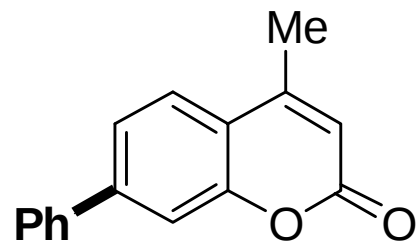












5t

160.948
153.964
152.197
144.914
139.126
129.117
128.535
127.224
124.970
123.066
118.941
115.182
114.816

18.675

6000C

5000C

4000C

3000C

2000C

1000C

0

ppm (t1)

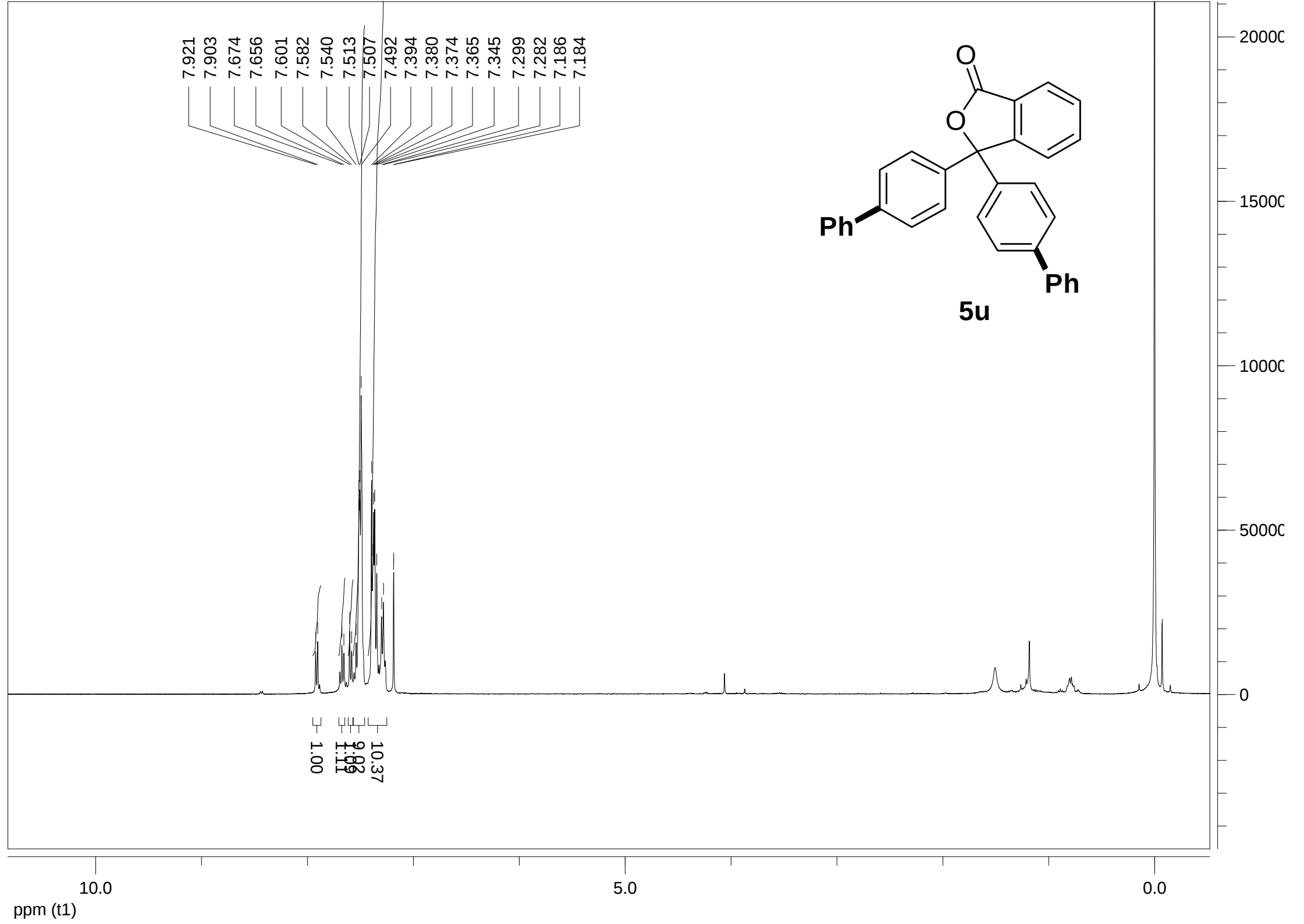
200

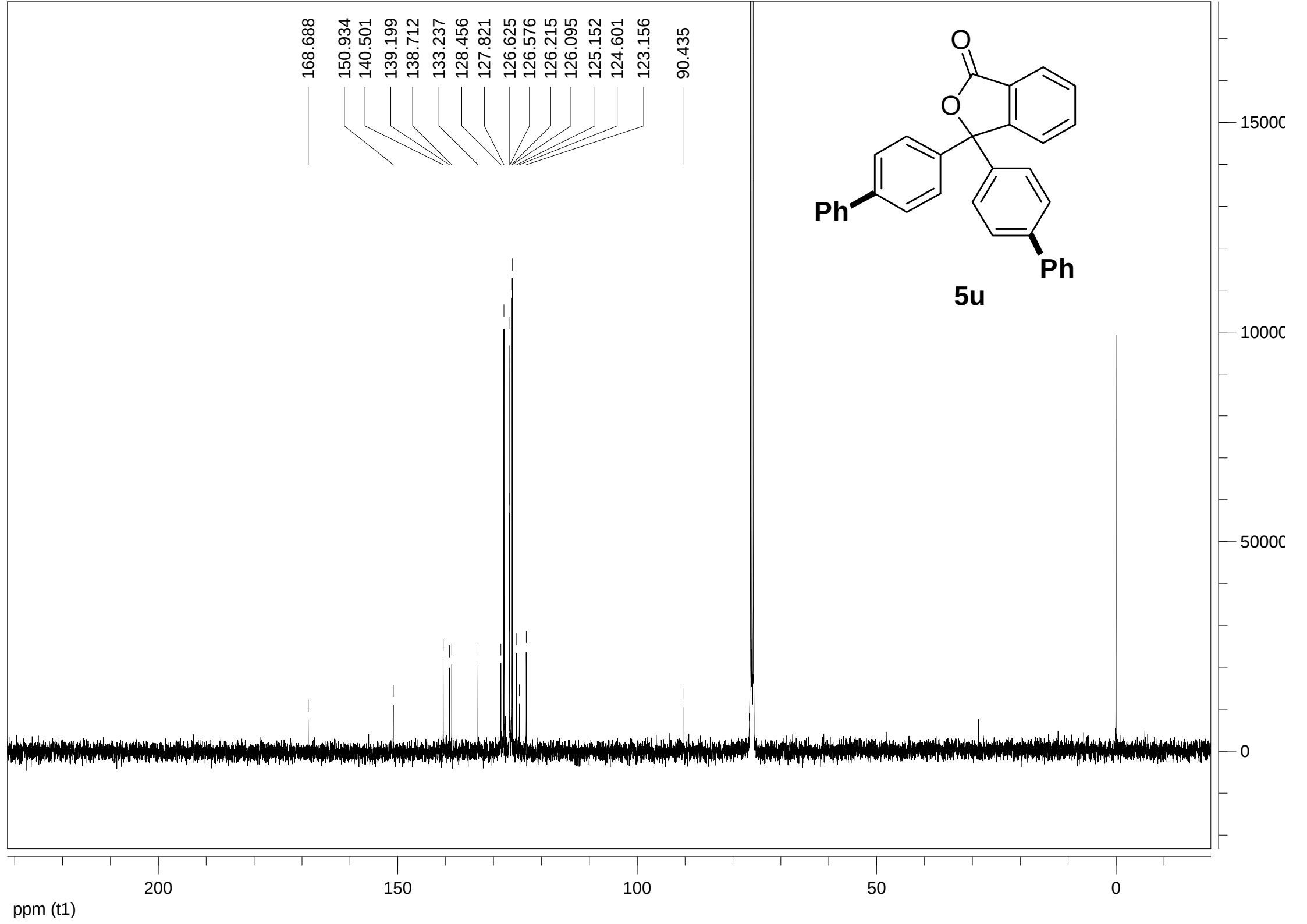
150

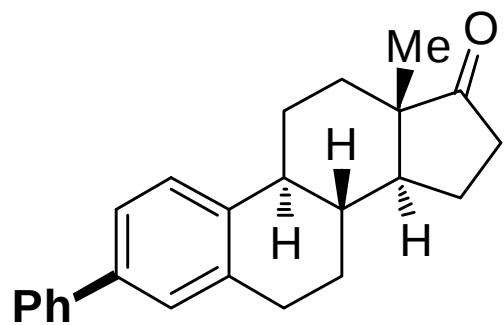
100

50

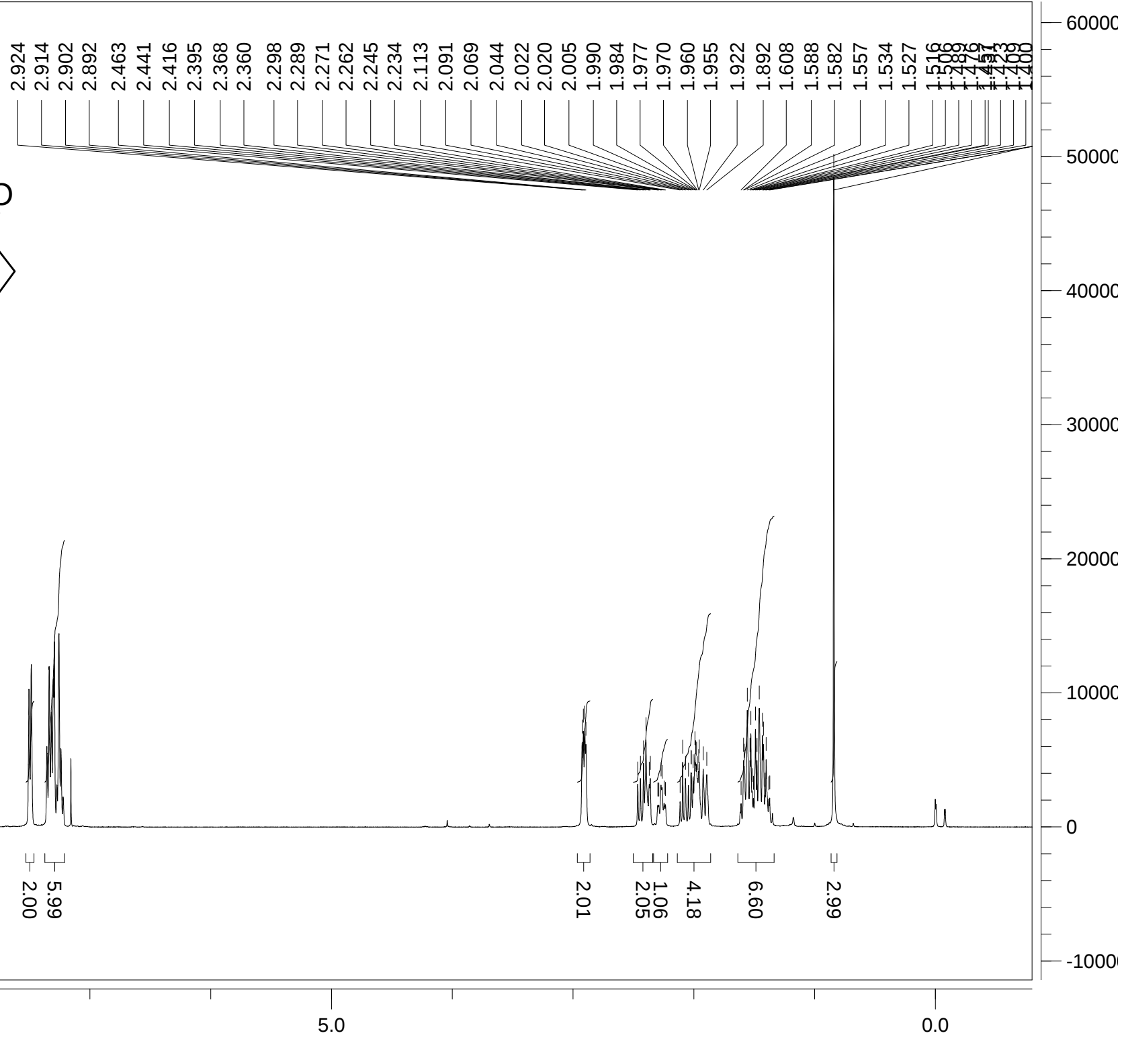
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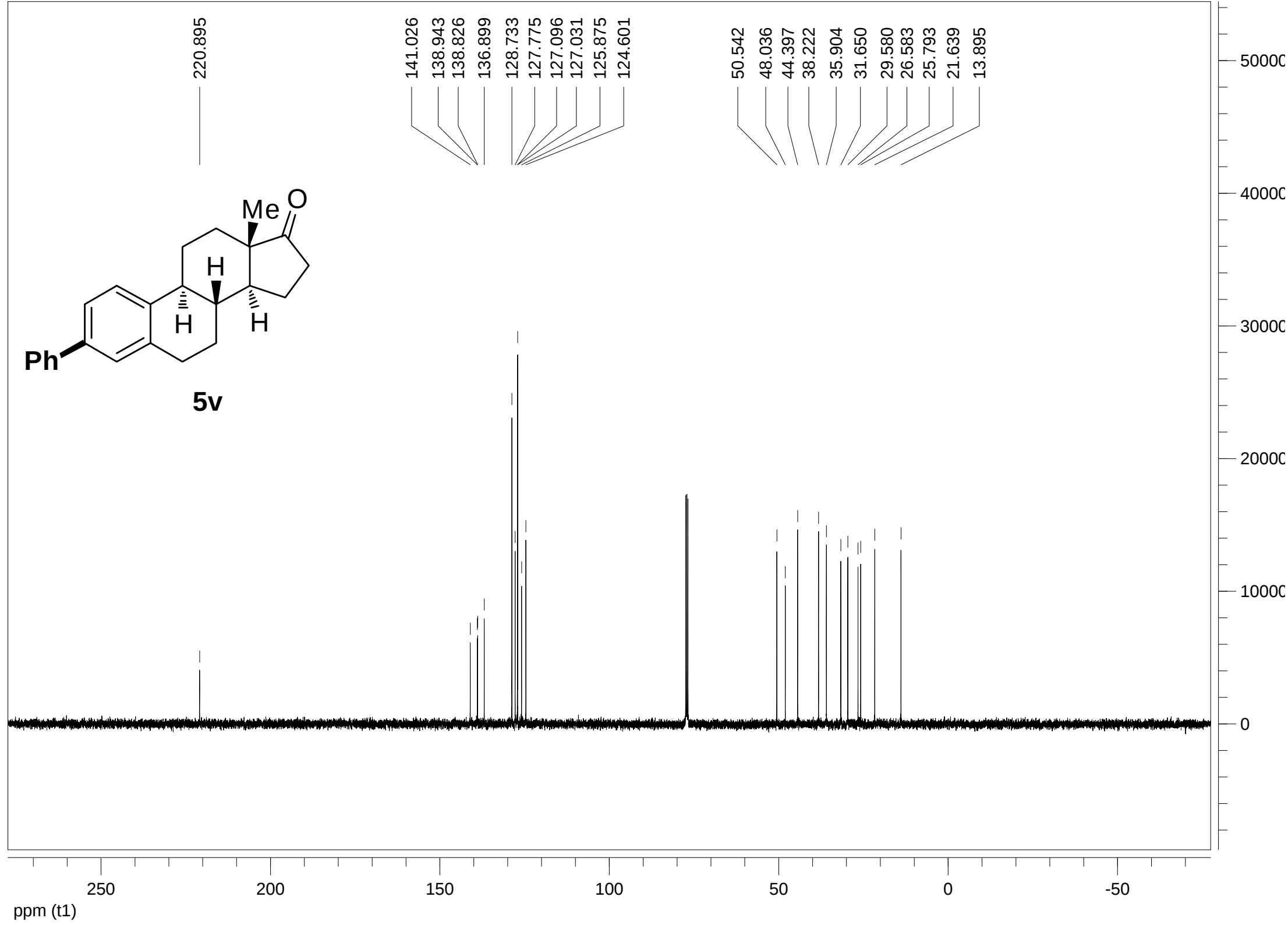
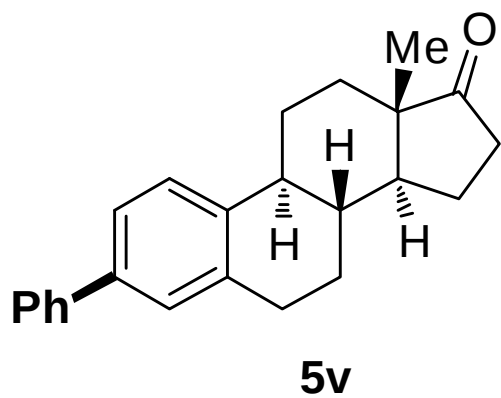


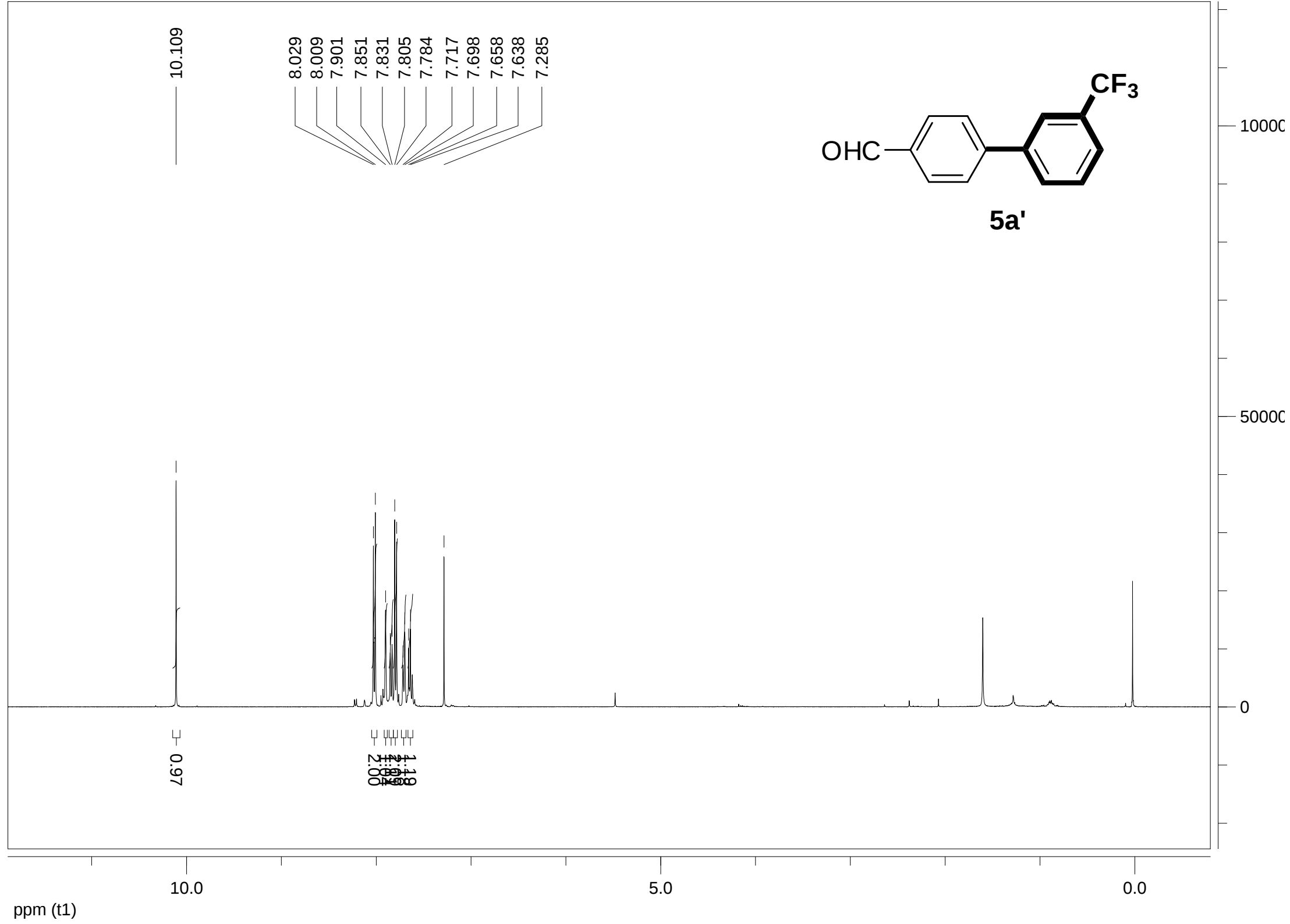
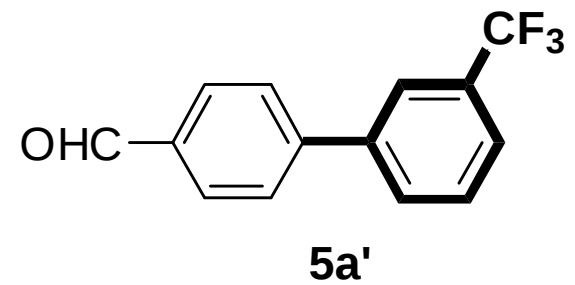


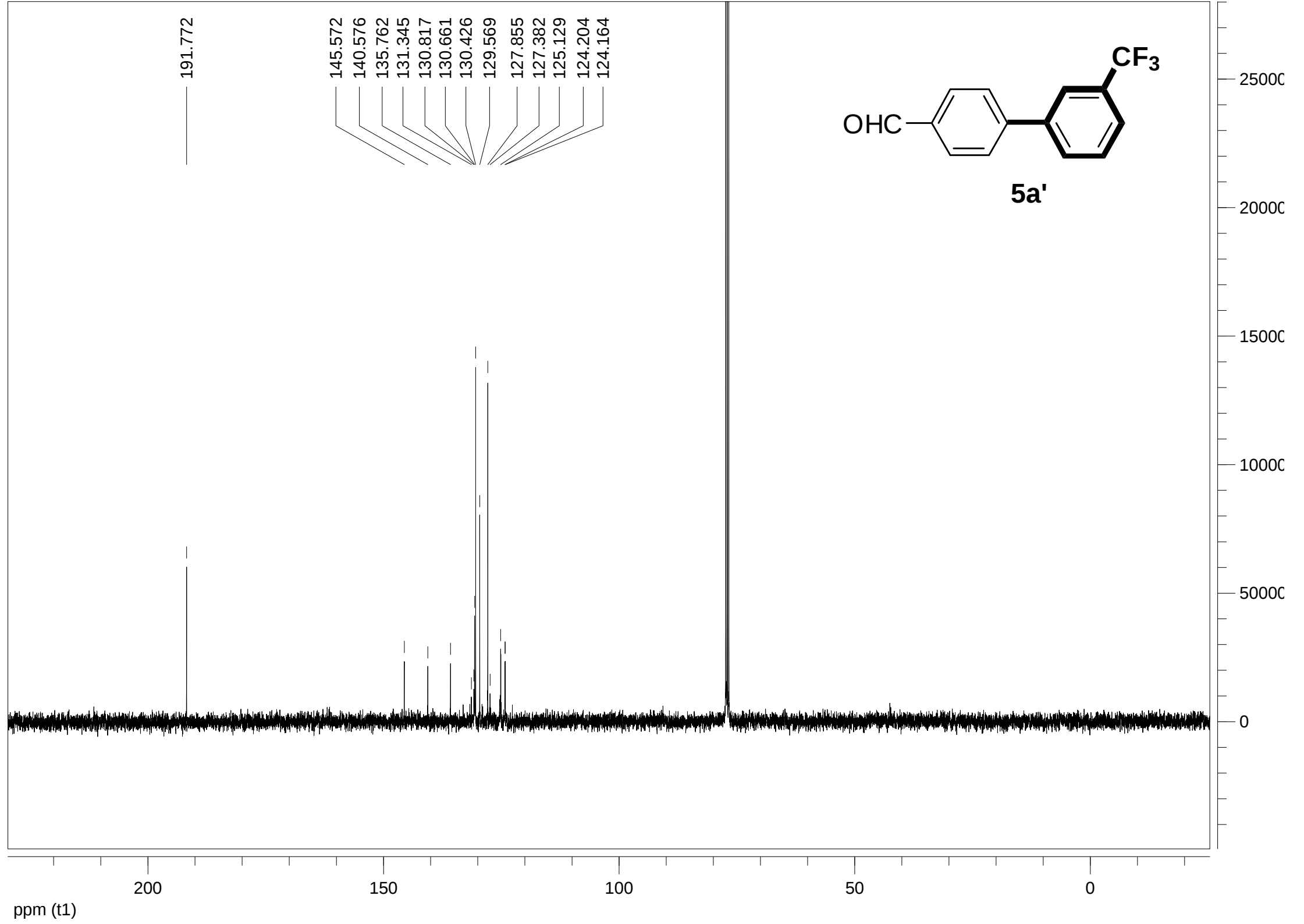


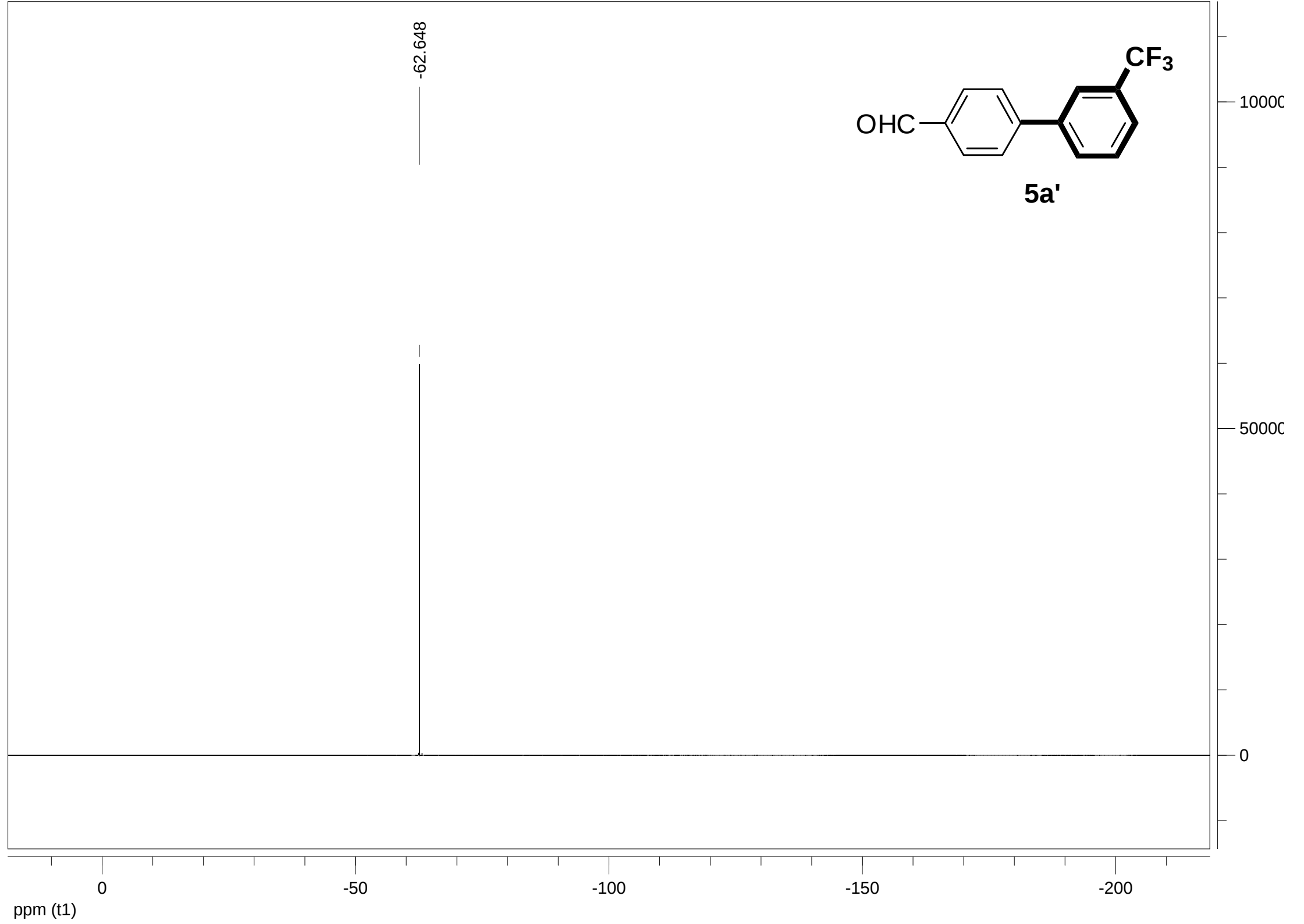
5v

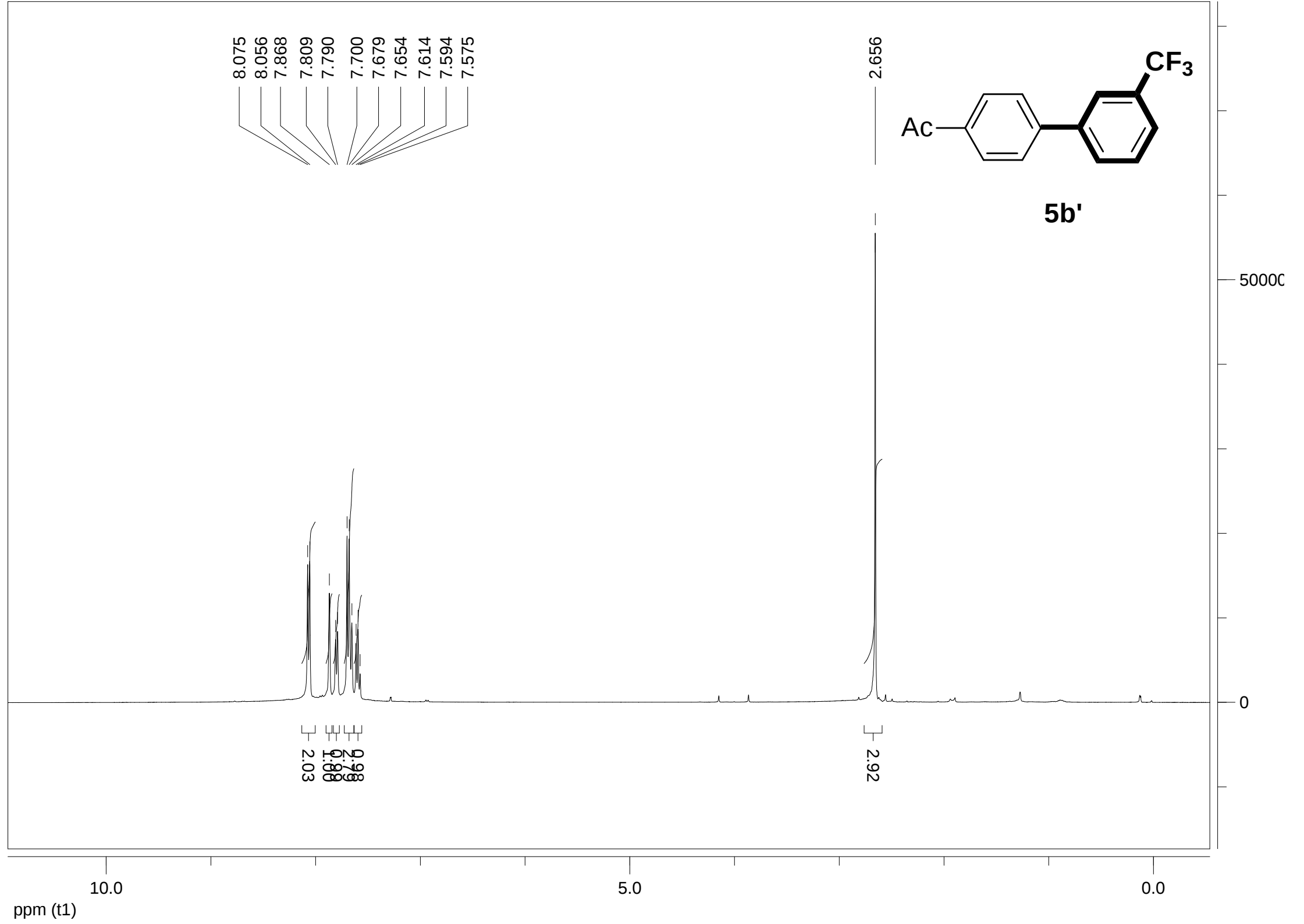


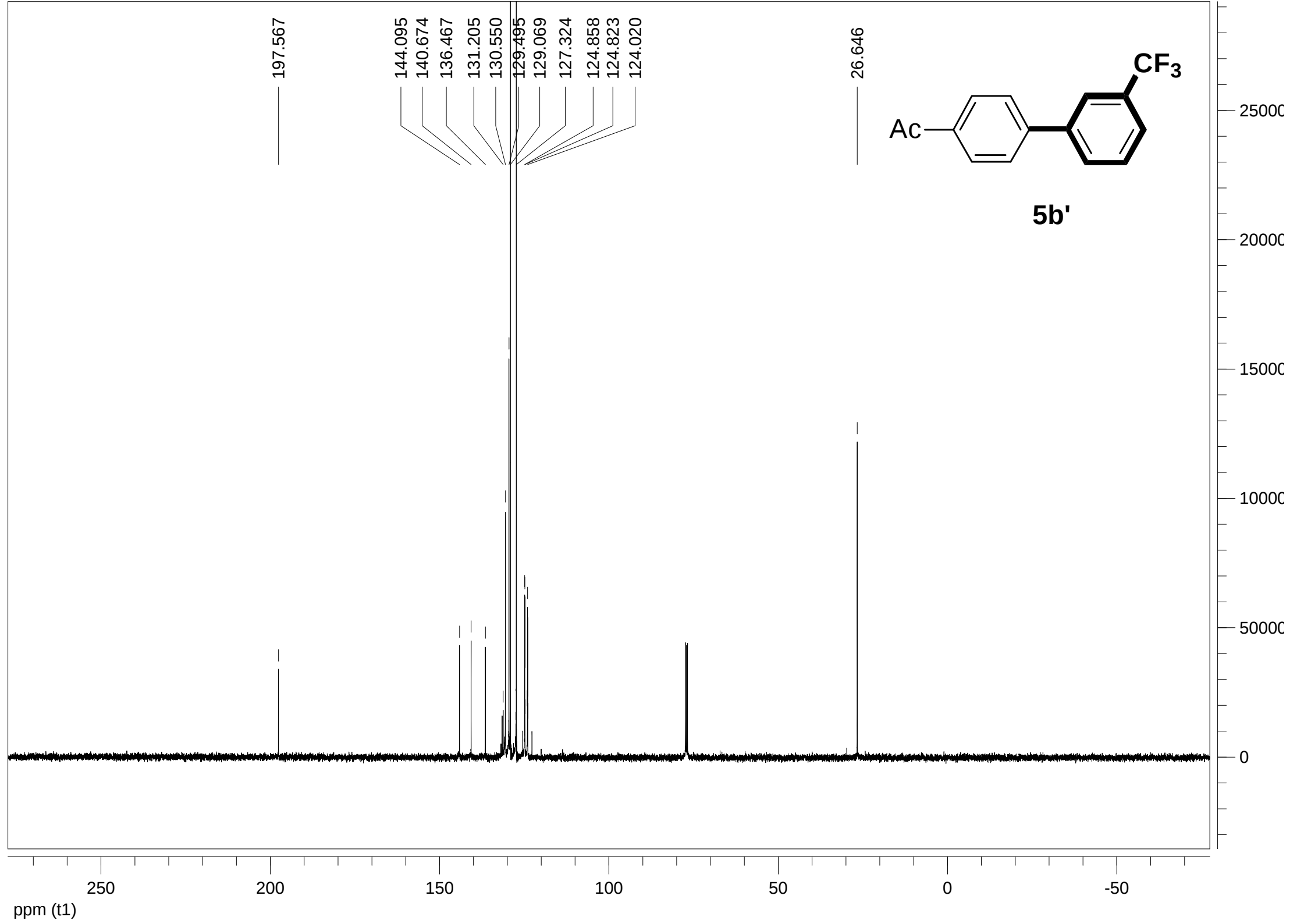


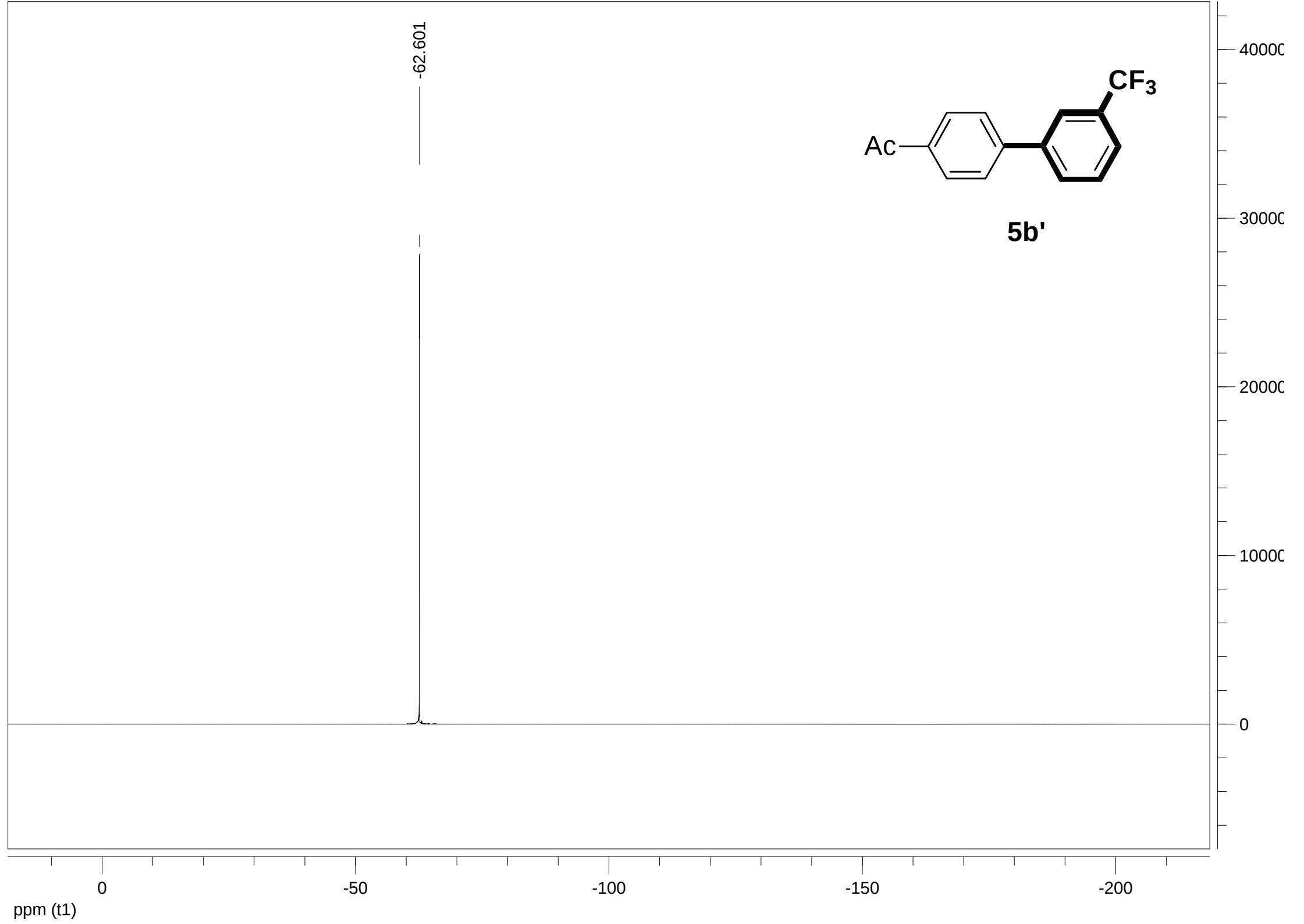


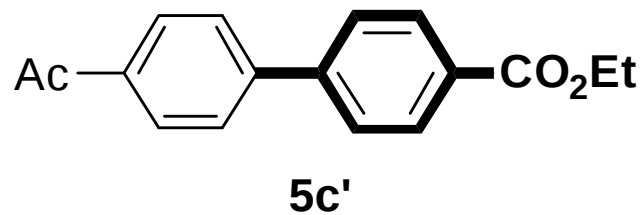










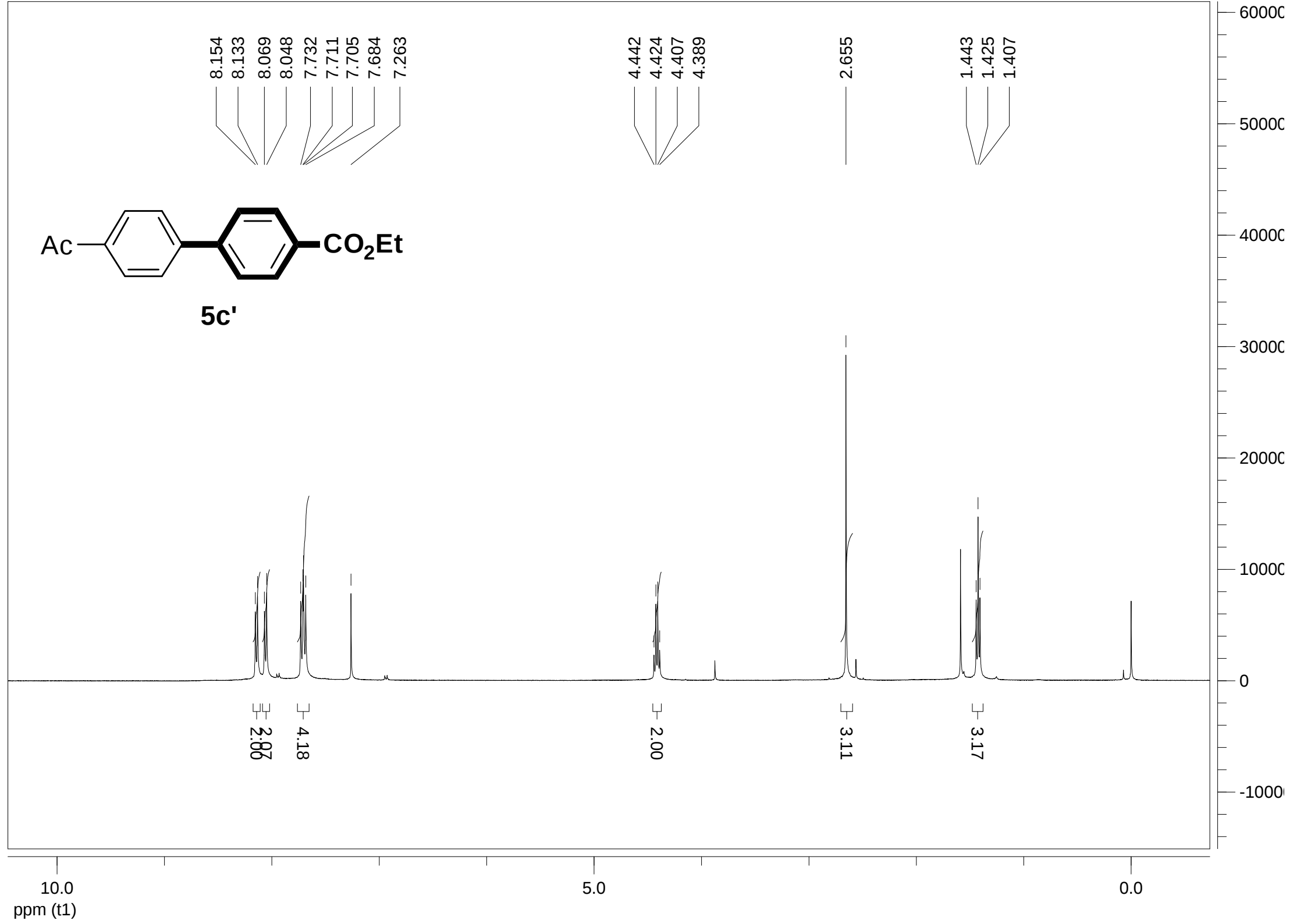


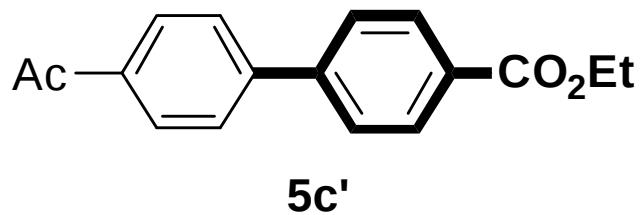
8.154
 8.133
 8.069
 8.048
 7.732
 7.711
 7.705
 7.684
 7.263

4.442
 4.424
 4.407
 4.389

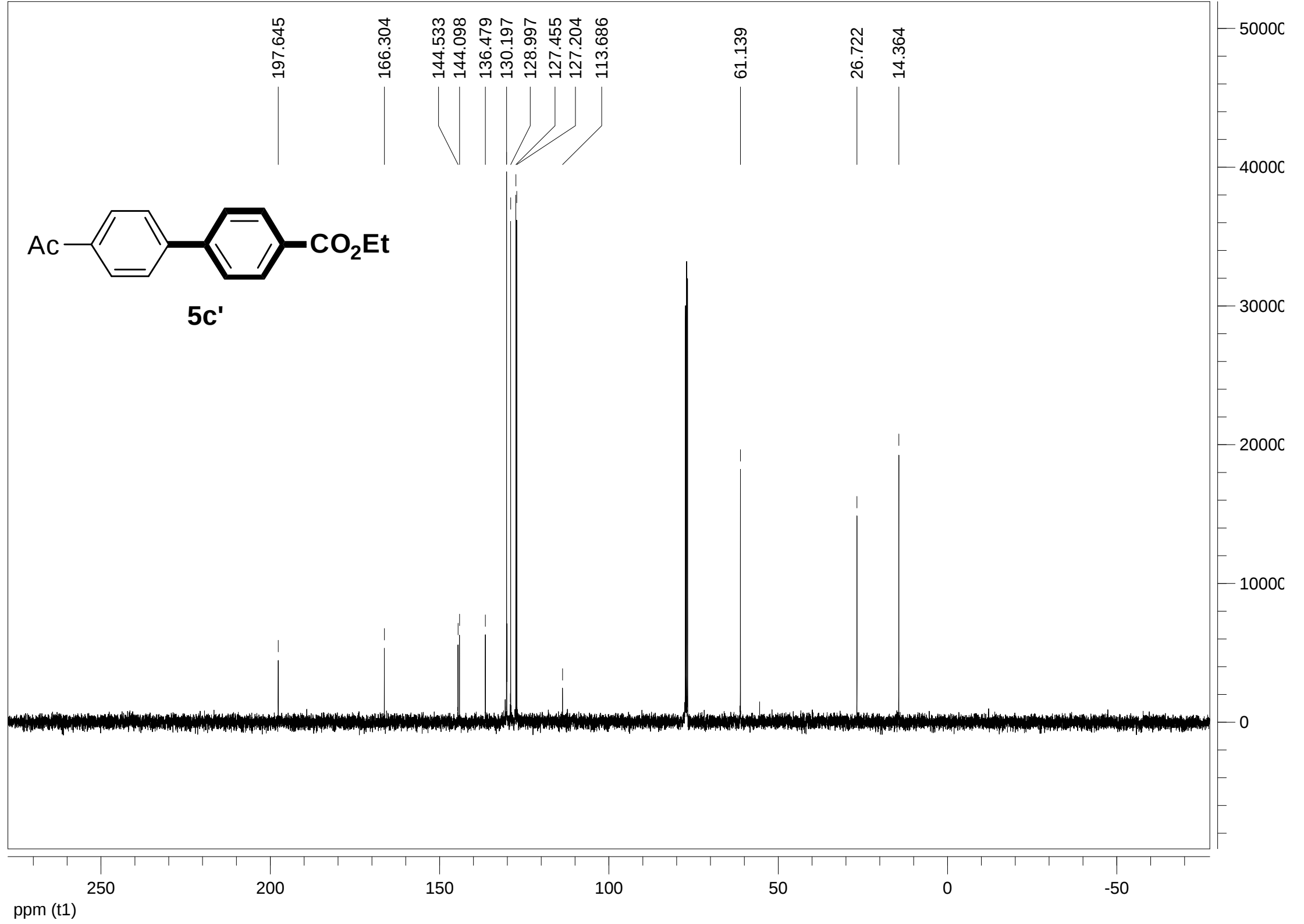
2.655

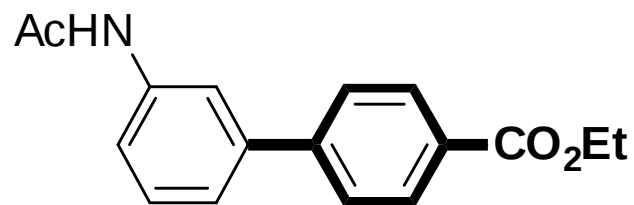
1.443
 1.425
 1.407



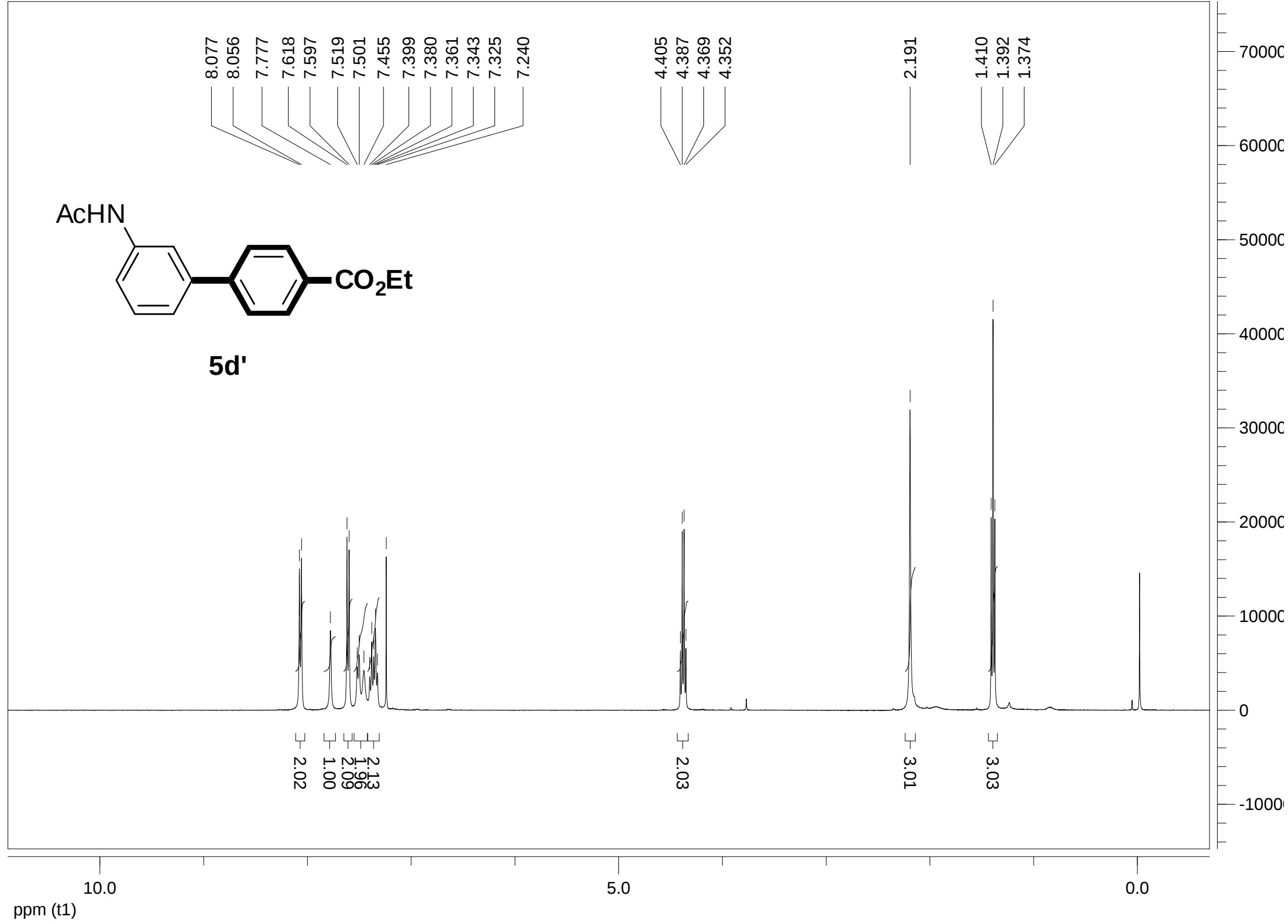


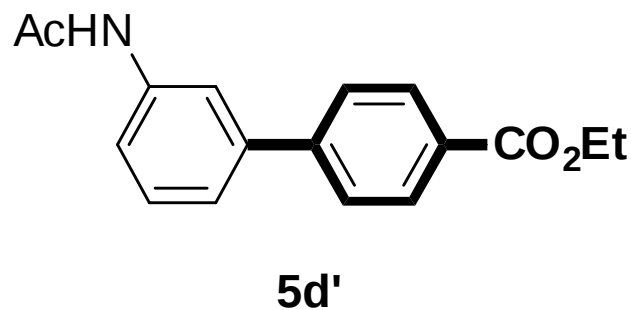
197.645
166.304
144.533
144.098
136.479
130.197
128.997
127.455
127.204
113.686
61.139
26.722
14.364





5d'





168.486
166.539
145.006
140.952
138.500
130.050
129.564
129.452
127.071
123.227
119.532
118.739

61.038

24.703

14.368

20000

15000

10000

50000

0

ppm (t1)

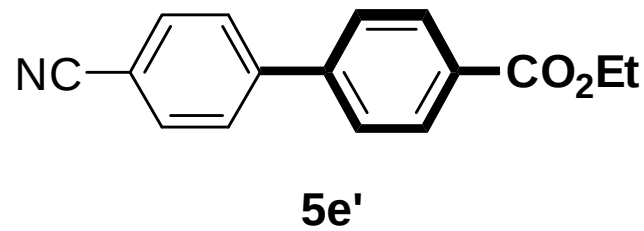
200

150

100

50

0



8.187
 8.166
 7.798
 7.777
 7.754
 7.733
 7.692
 7.671
 7.286

4.468
 4.450
 4.432
 4.415

1.466
 1.448
 1.431

10000

50000

0

2.00

2.00

2.04

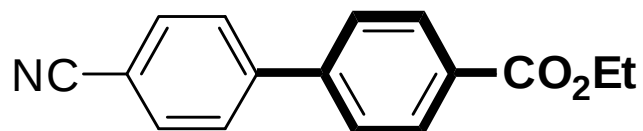
2.99

10.0

5.0

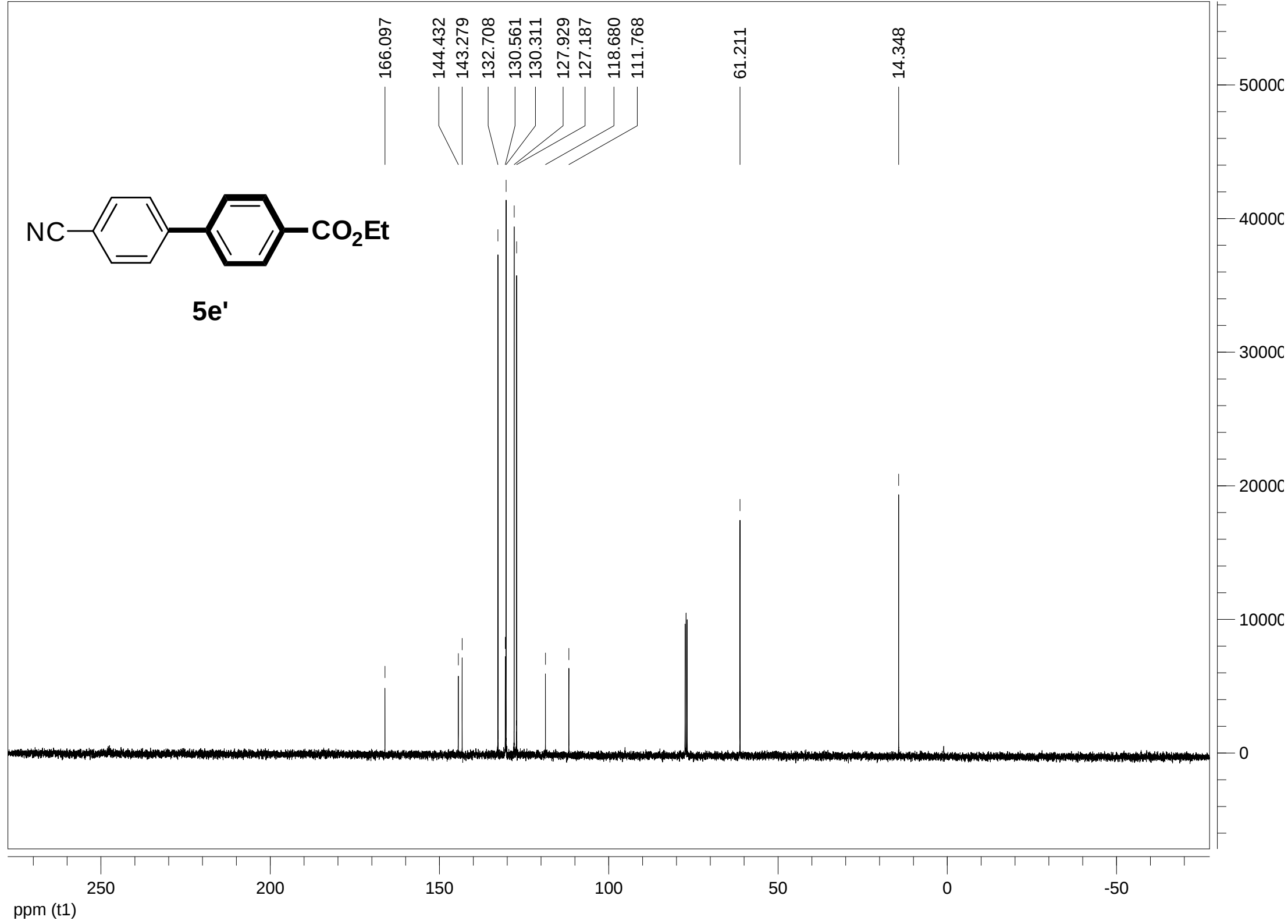
0.0

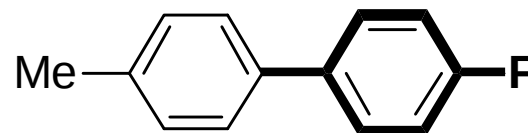
ppm (t1)



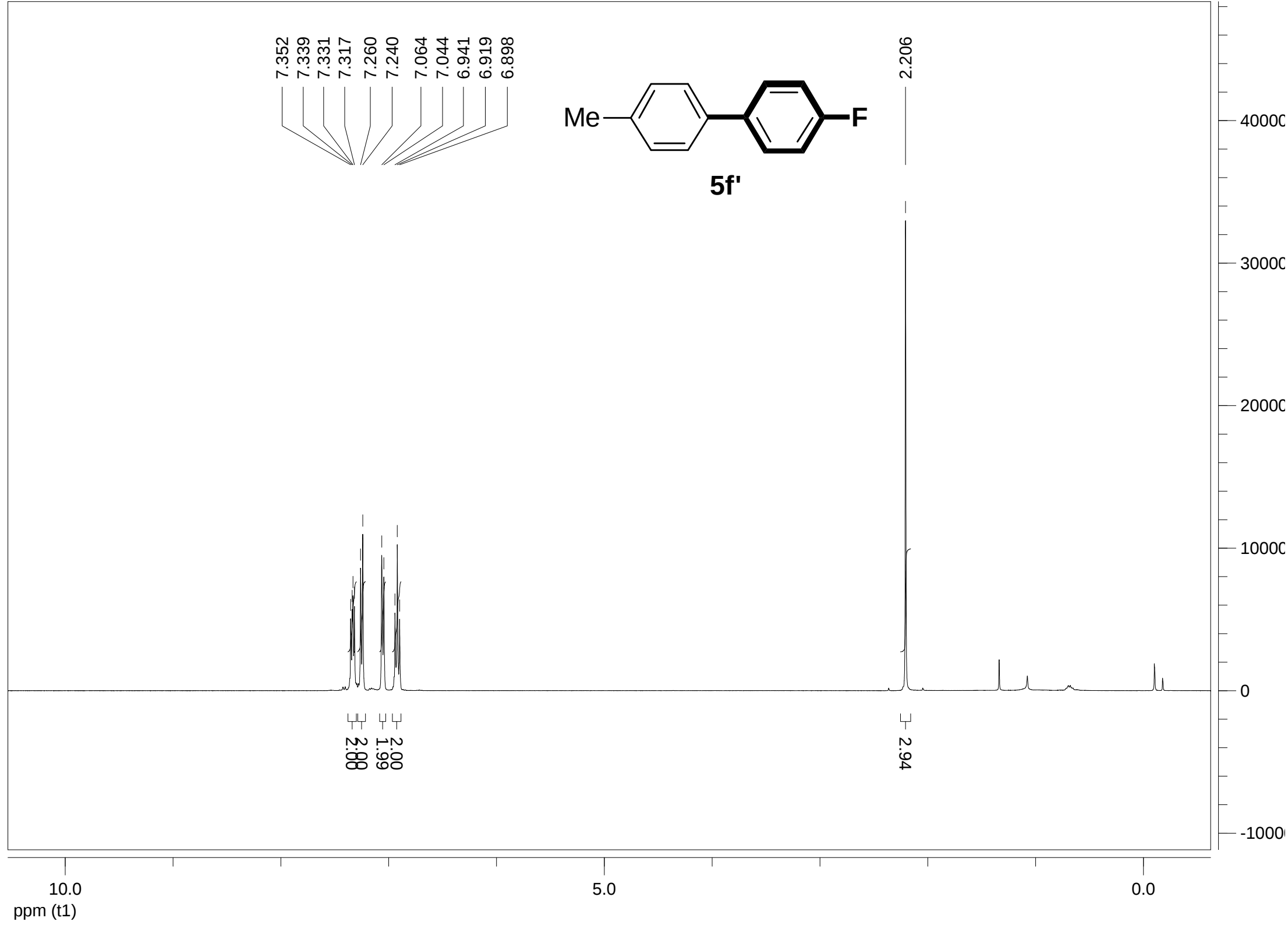
5e'

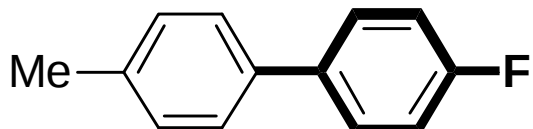
166.097
144.432
143.279
132.708
130.561
130.311
127.929
127.187
118.680
111.768
61.211
14.348





5f'

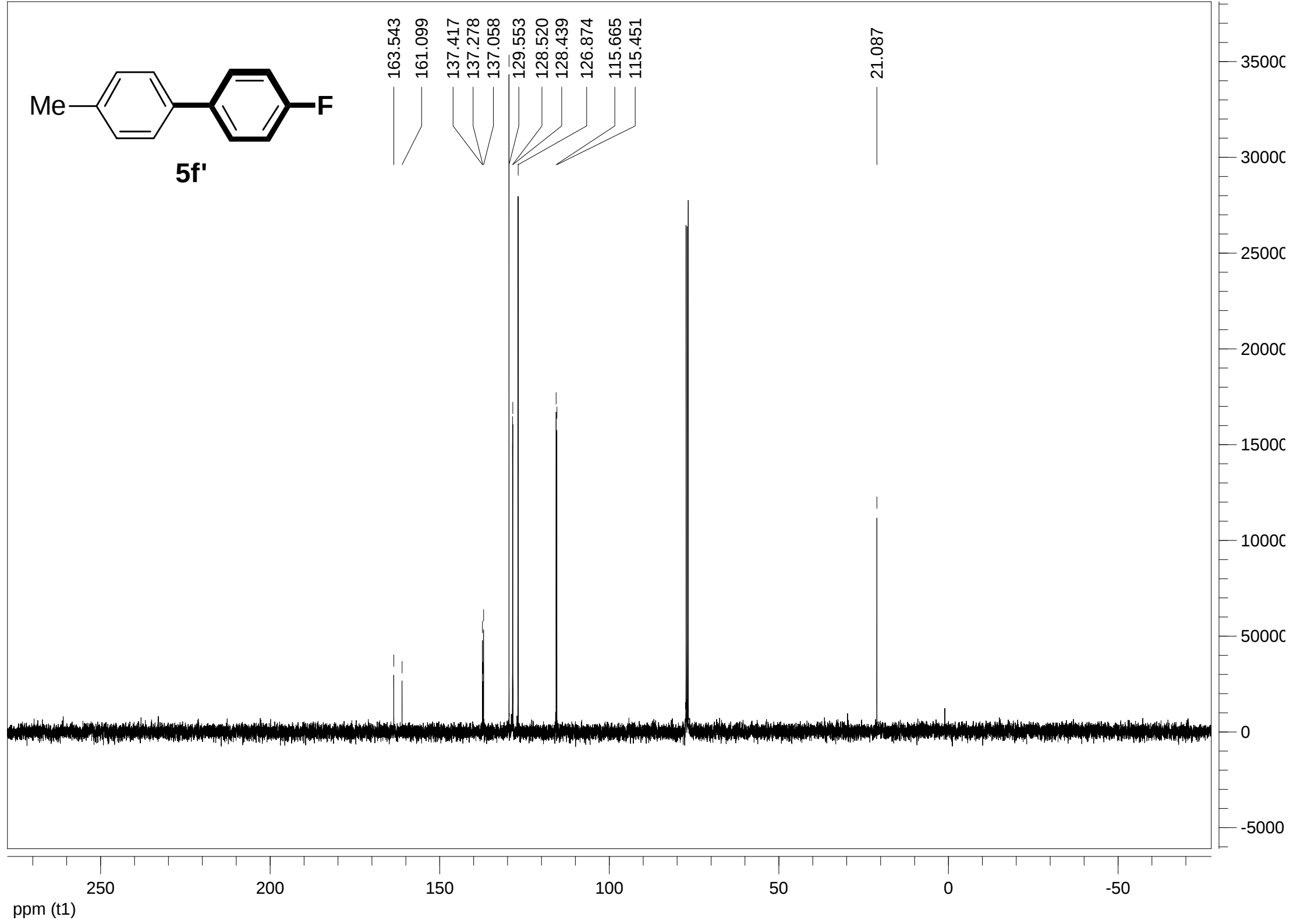


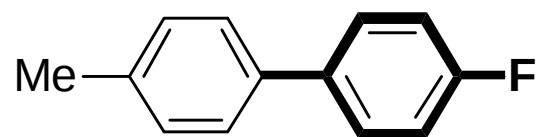


5f'

163.543
161.099
137.417
137.278
137.058
129.553
128.520
128.439
126.874
115.665
115.451

21.087





5f'

-116.273

5000C

0

ppm (t1)

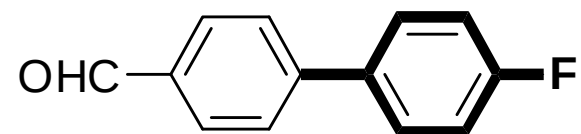
0

-50

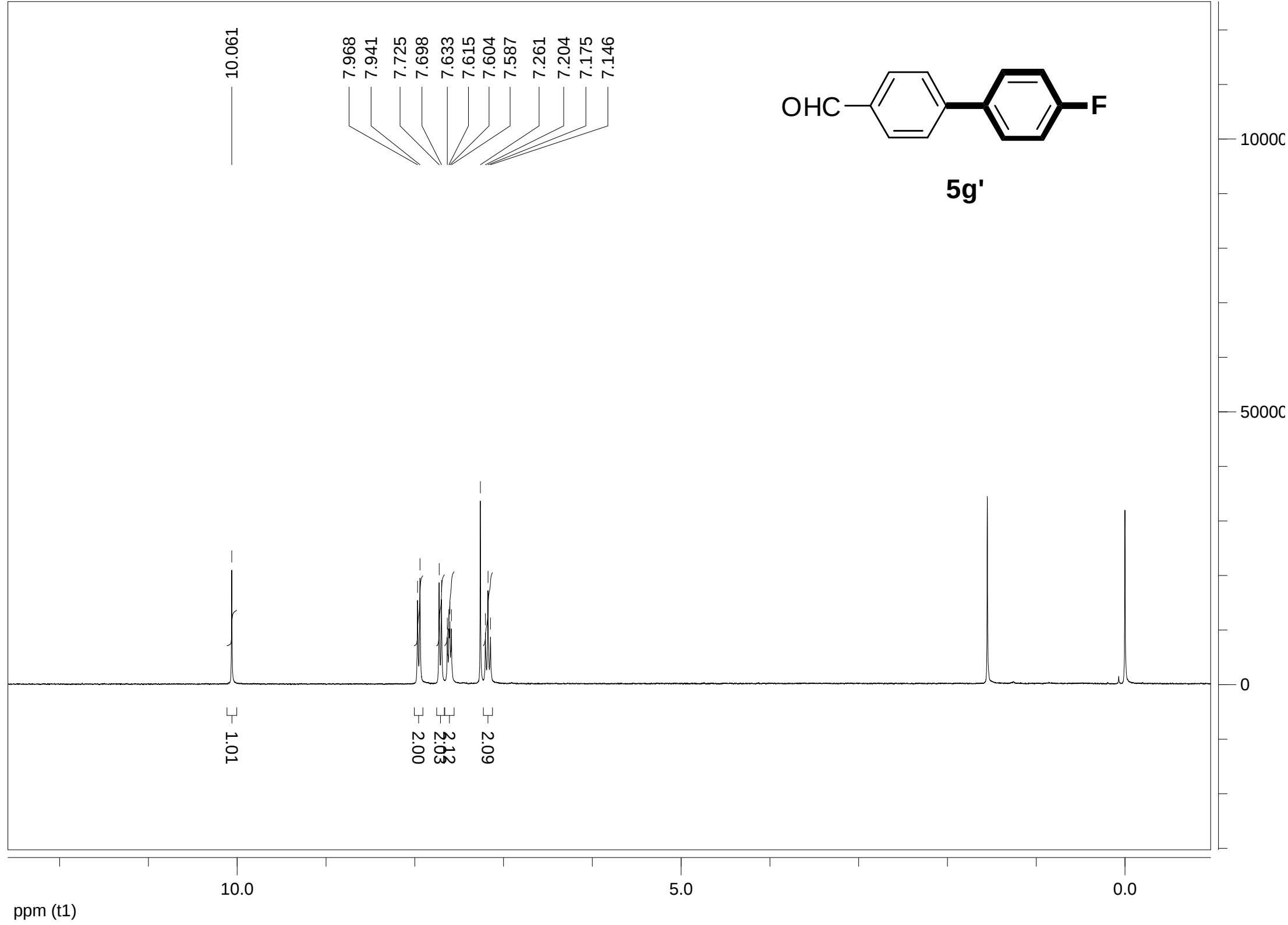
-100

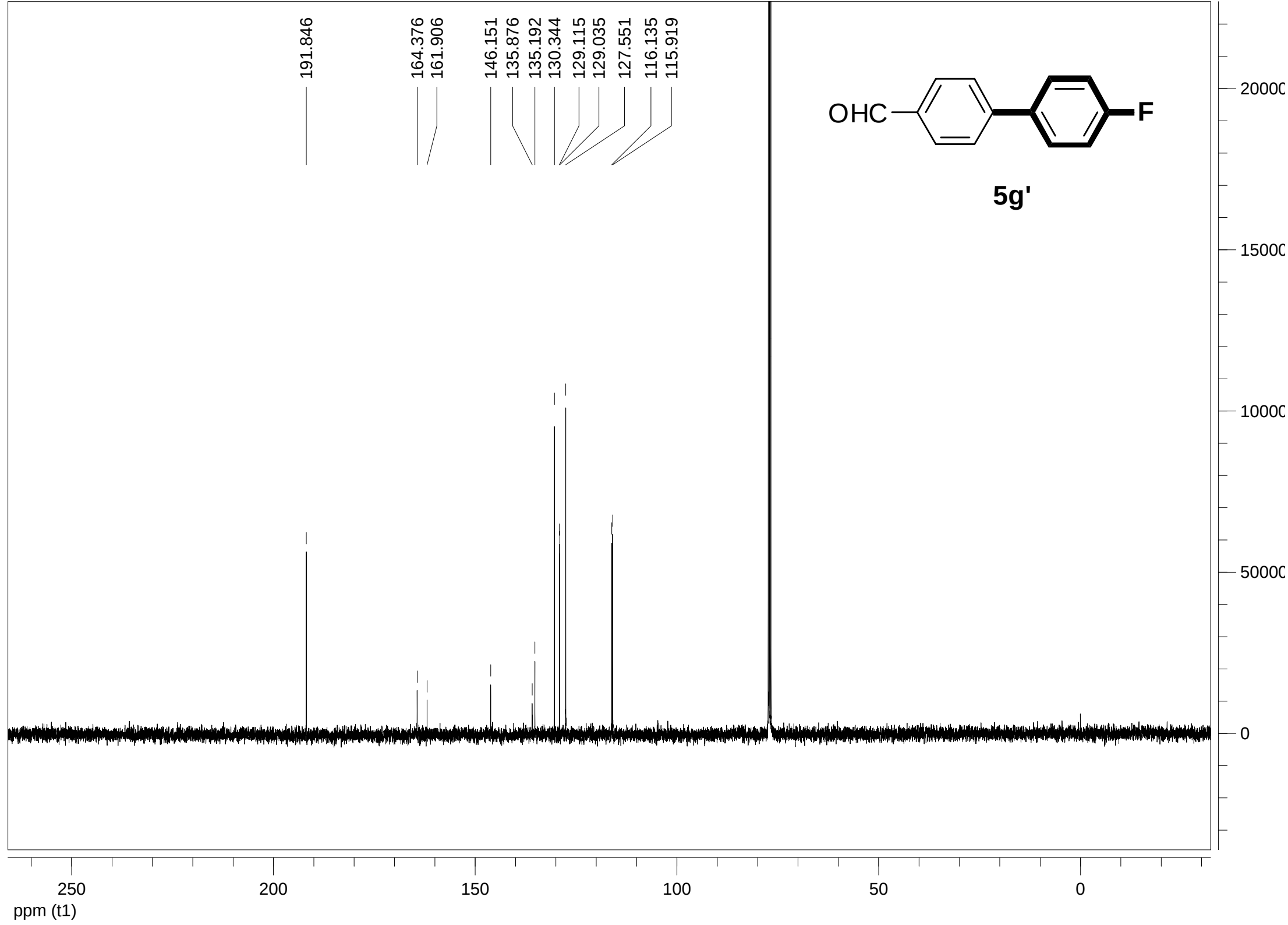
-150

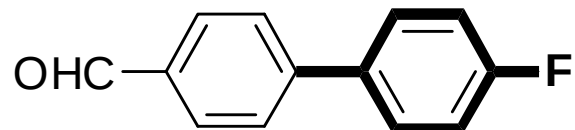
-200



5g'







5g'

-113.561

5000C

4000C

3000C

2000C

1000C

0

0

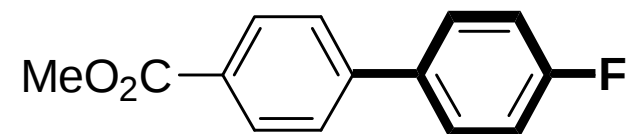
-50

-100

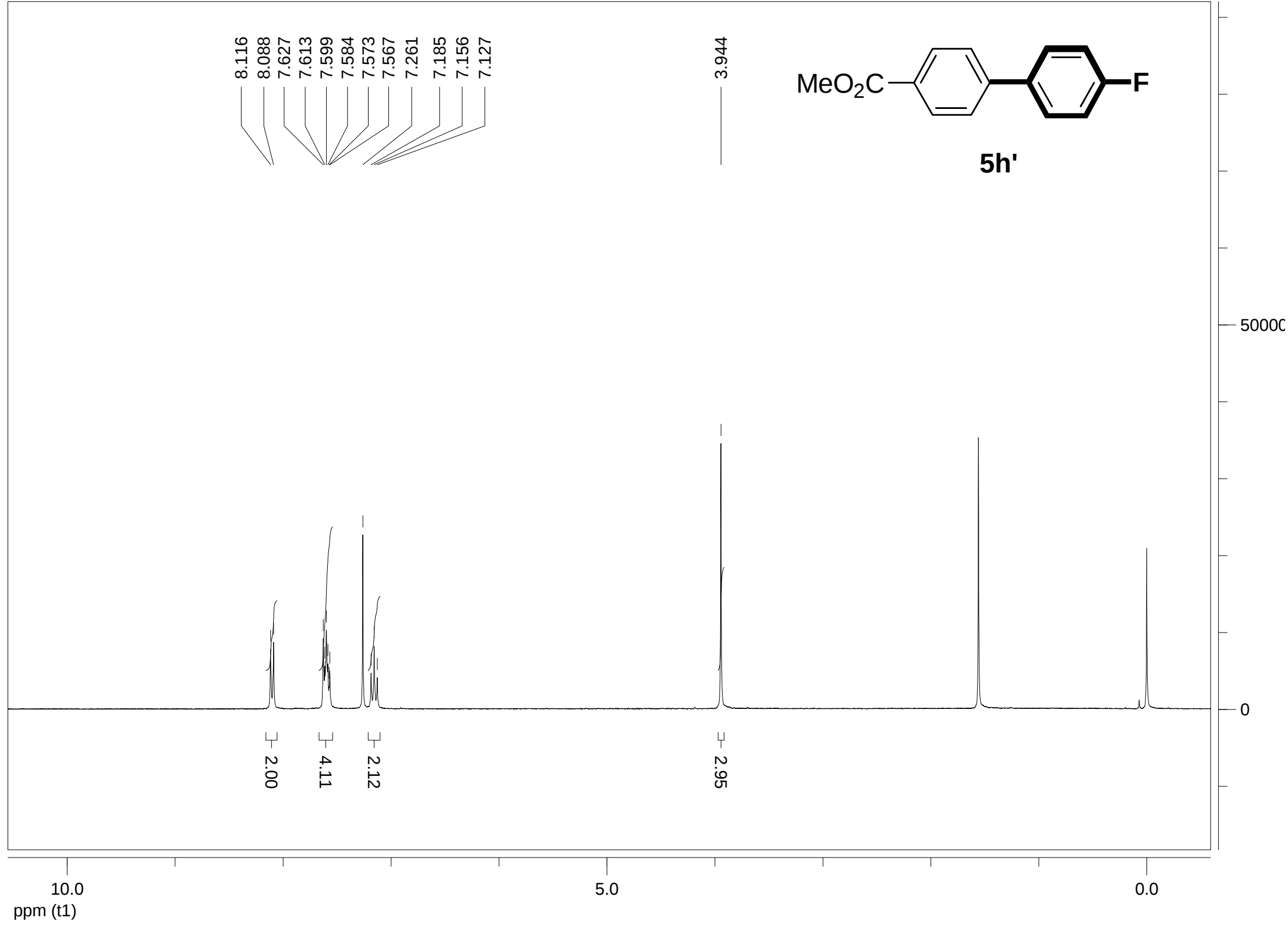
-150

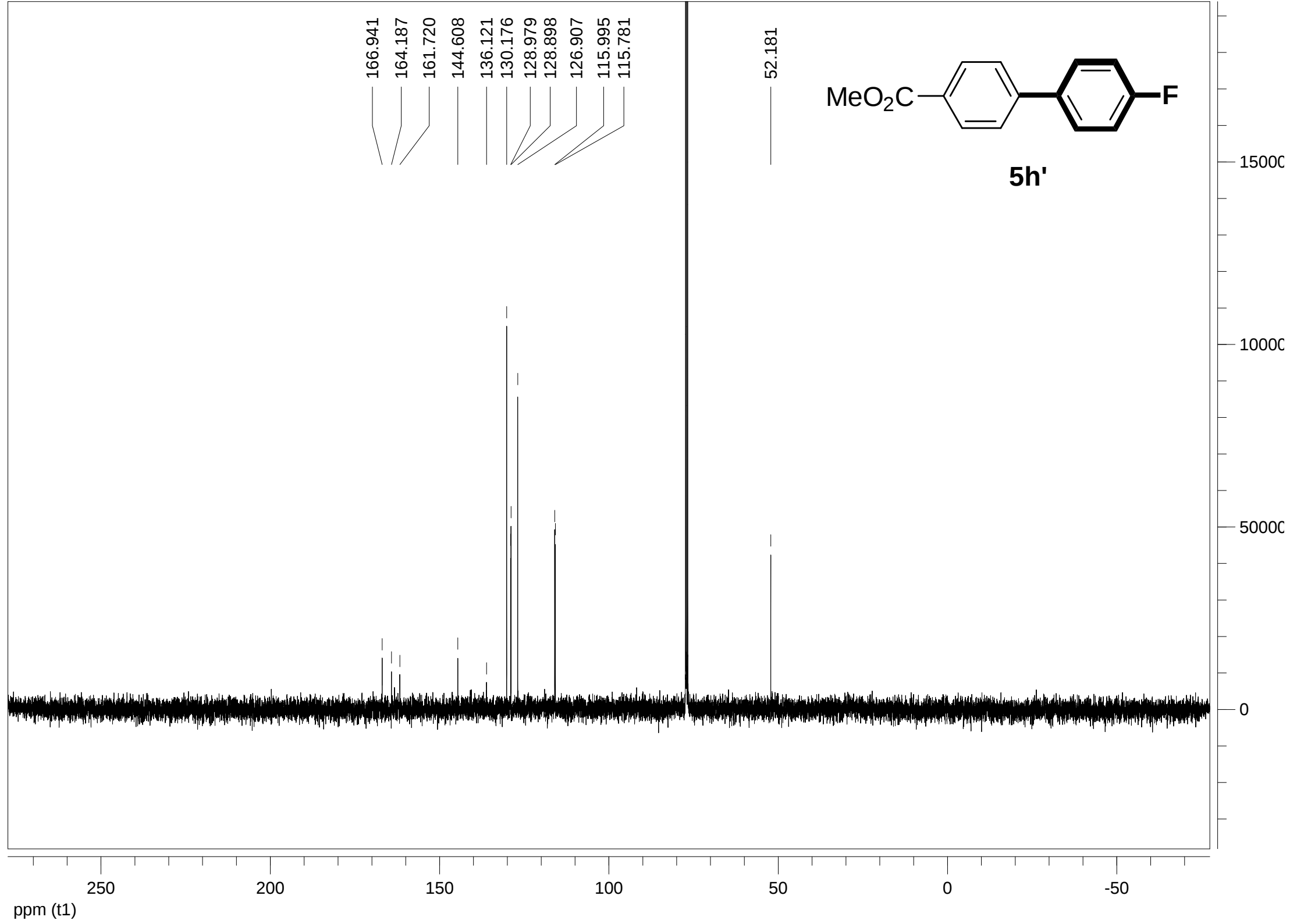
-200

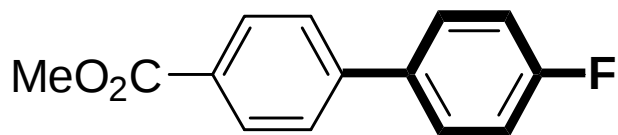
ppm (t1)



5h'







5h'

-114.217

ppm (t1)

0

-50

-100

-150

-200

7000C

6000C

5000C

4000C

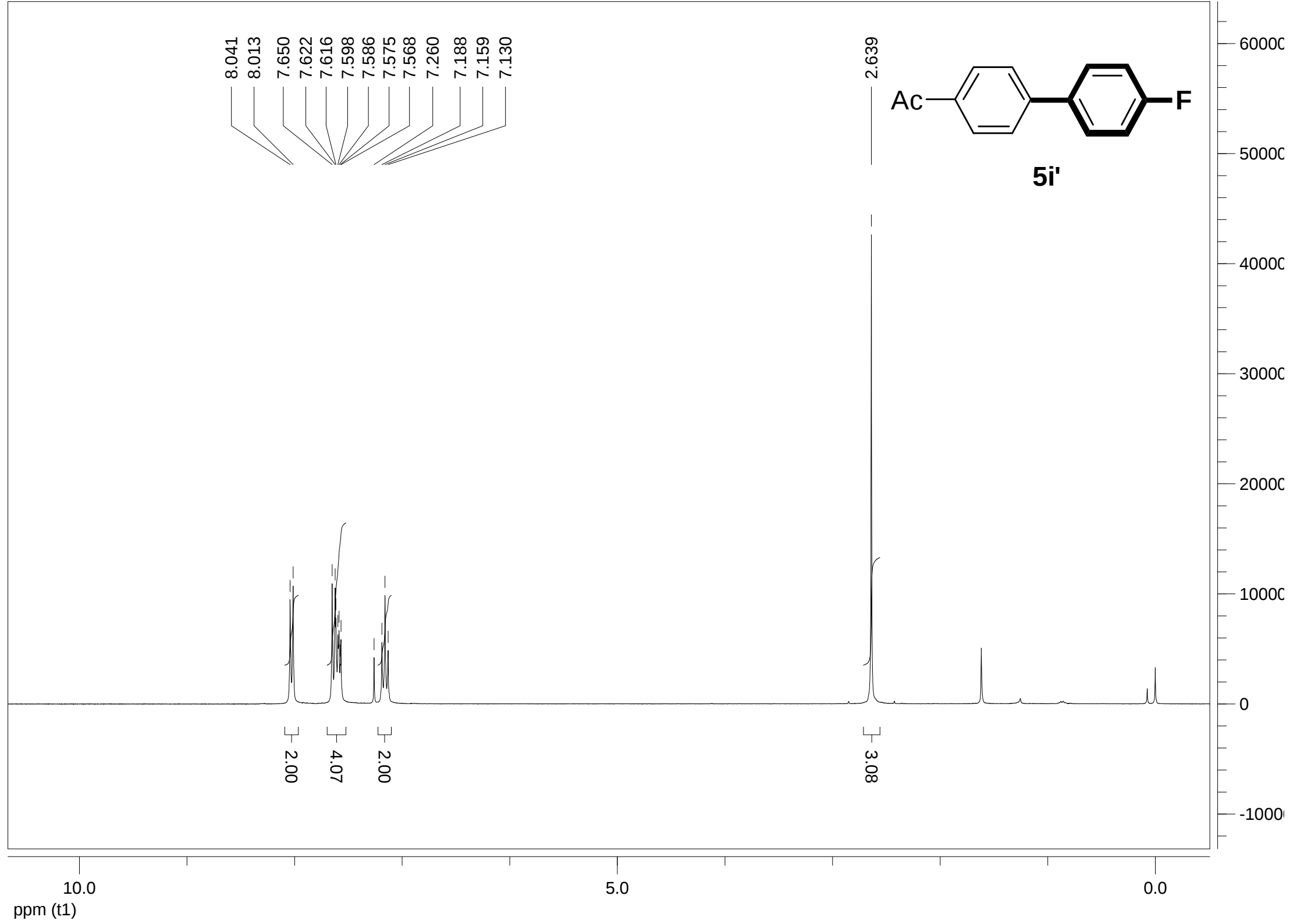
3000C

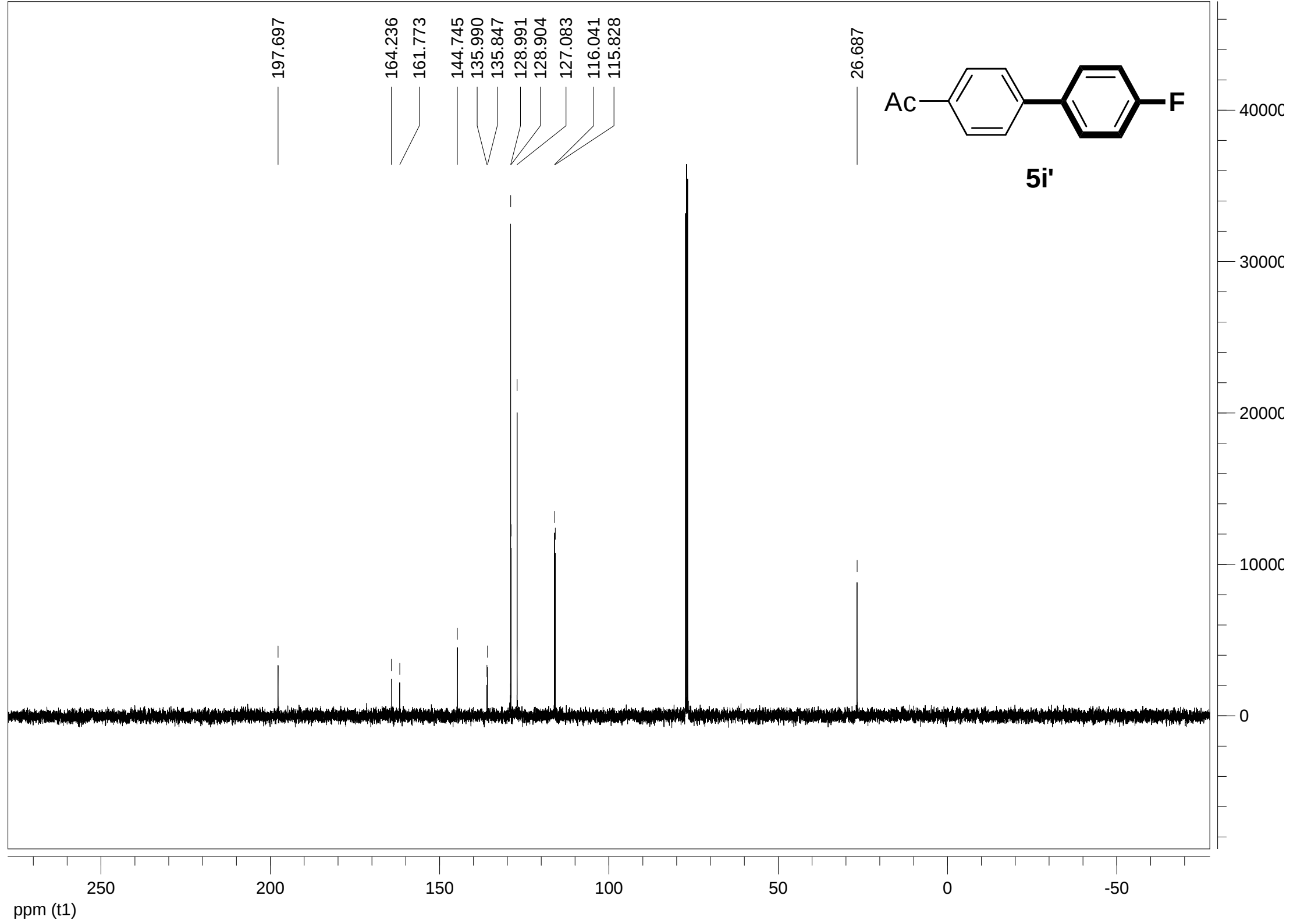
2000C

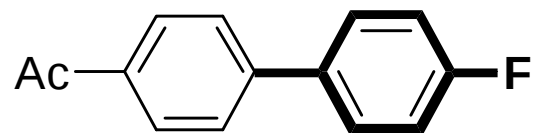
1000C

0

-1000C







5i'

-114.007

1000C

5000C

0

0

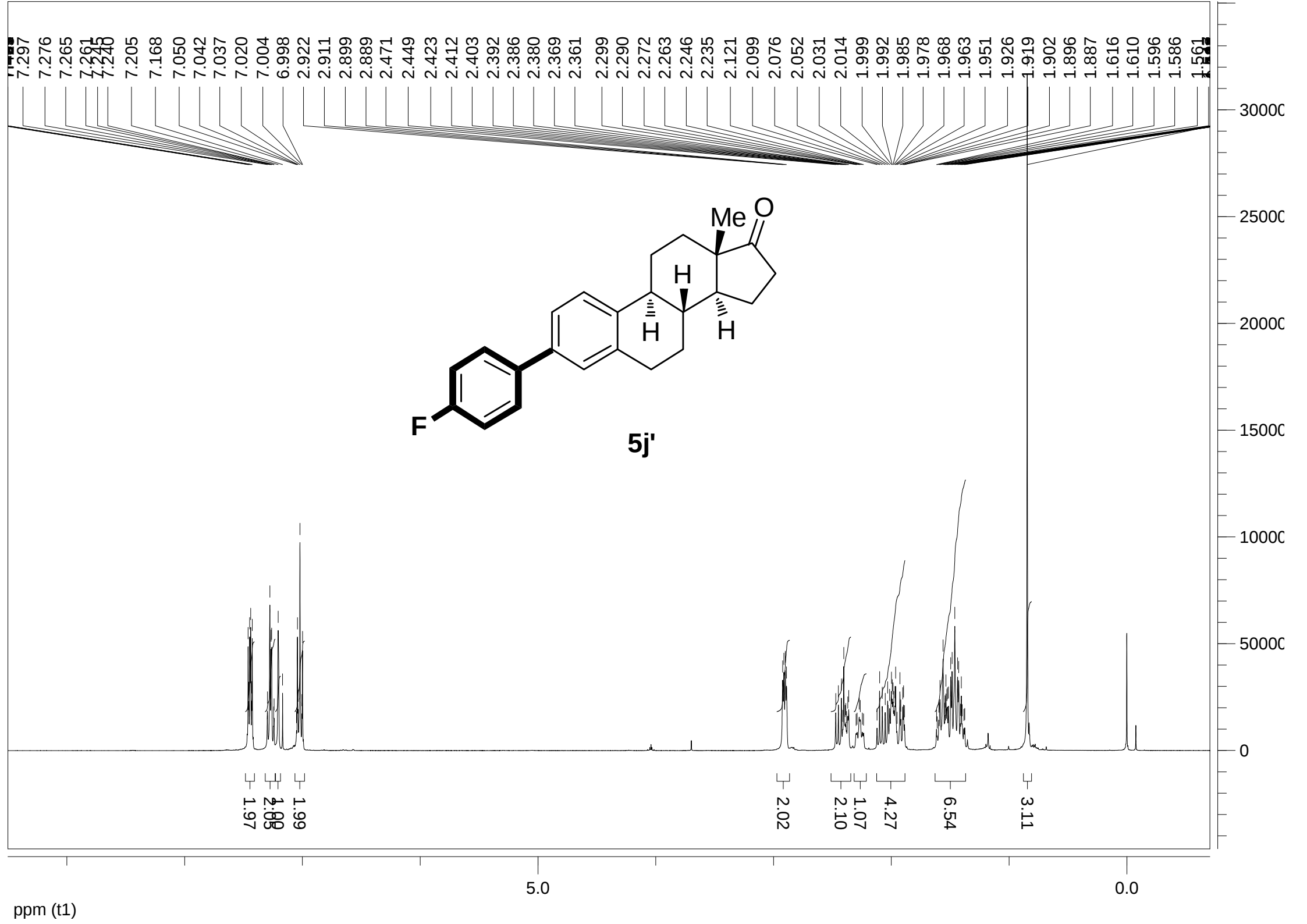
-50

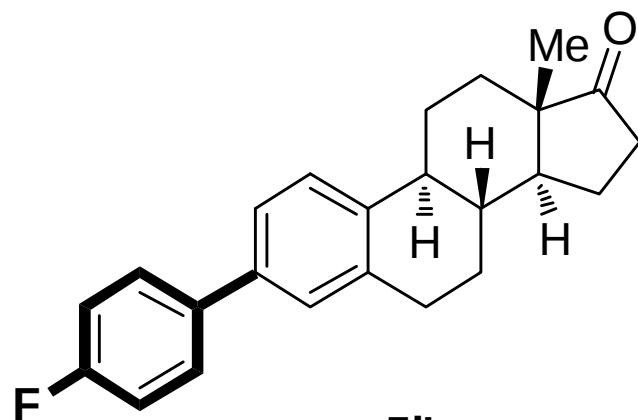
-100

-150

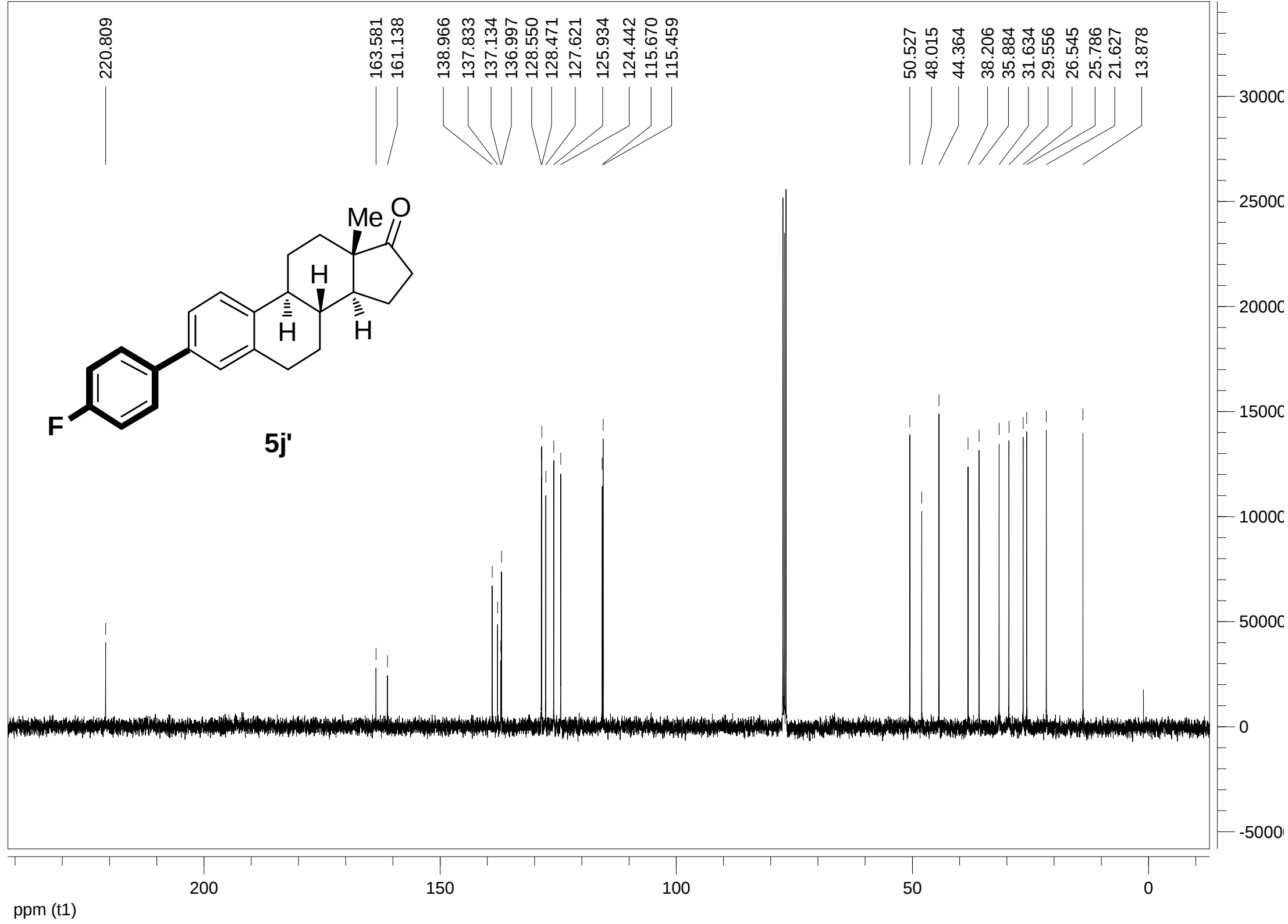
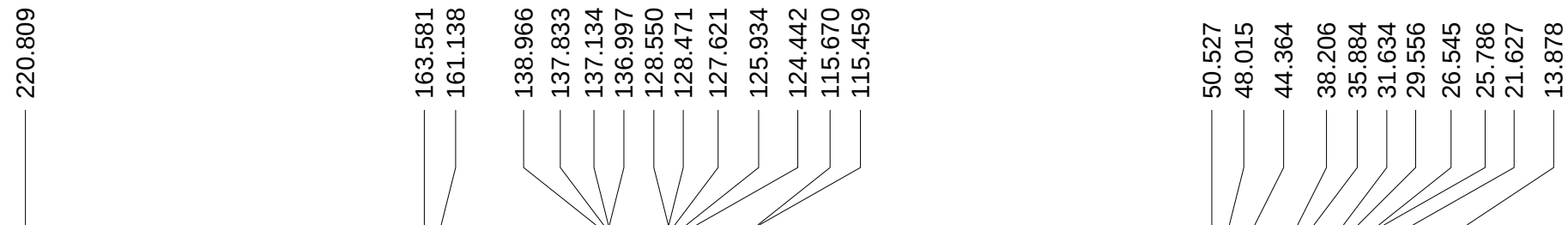
-200

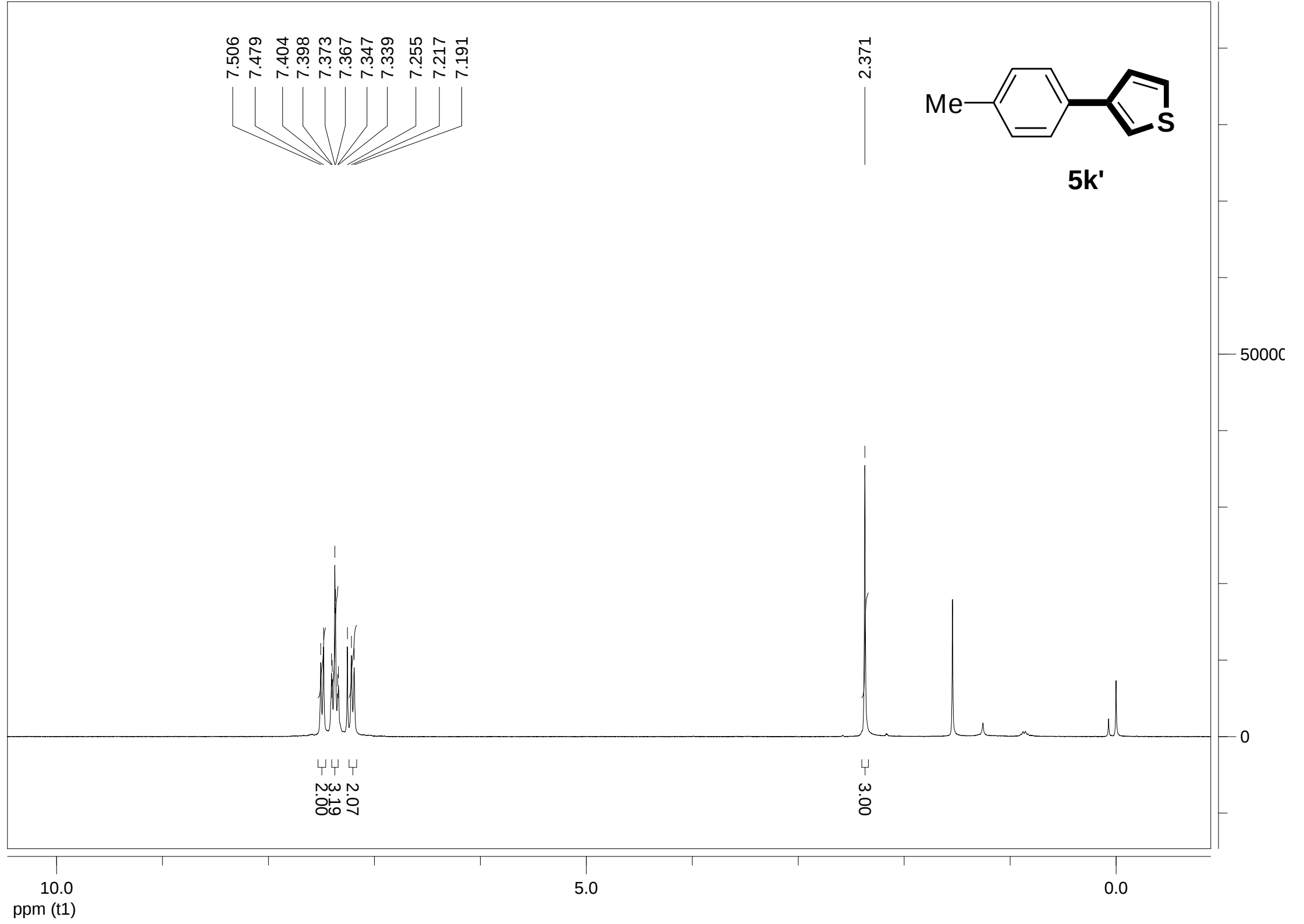
ppm (t1)

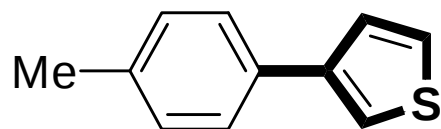




5j'







5k'

142.355
136.879
133.091
129.490
126.339
126.057
119.790
119.655

21.150

10000

50000

0

ppm (t1)

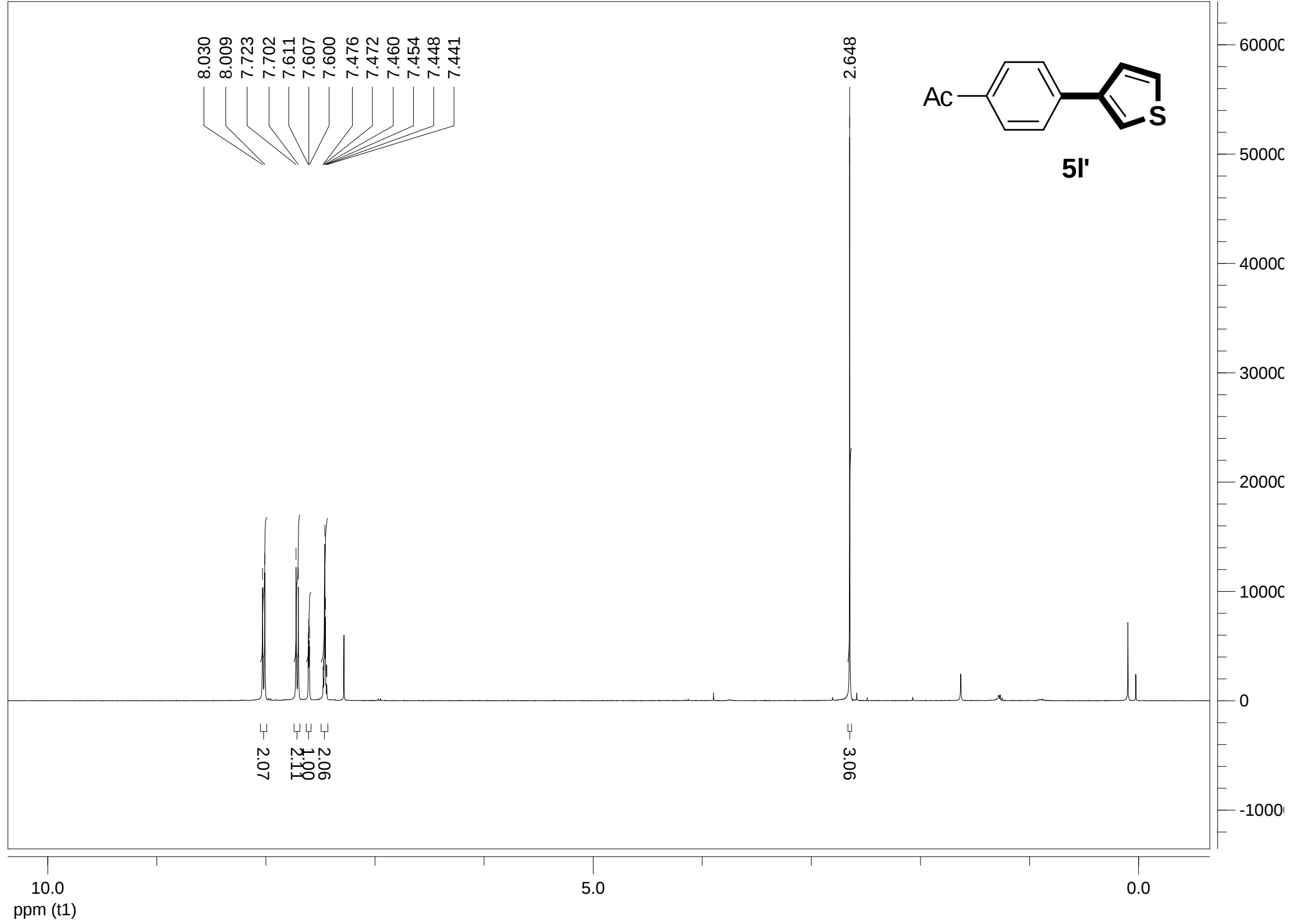
200

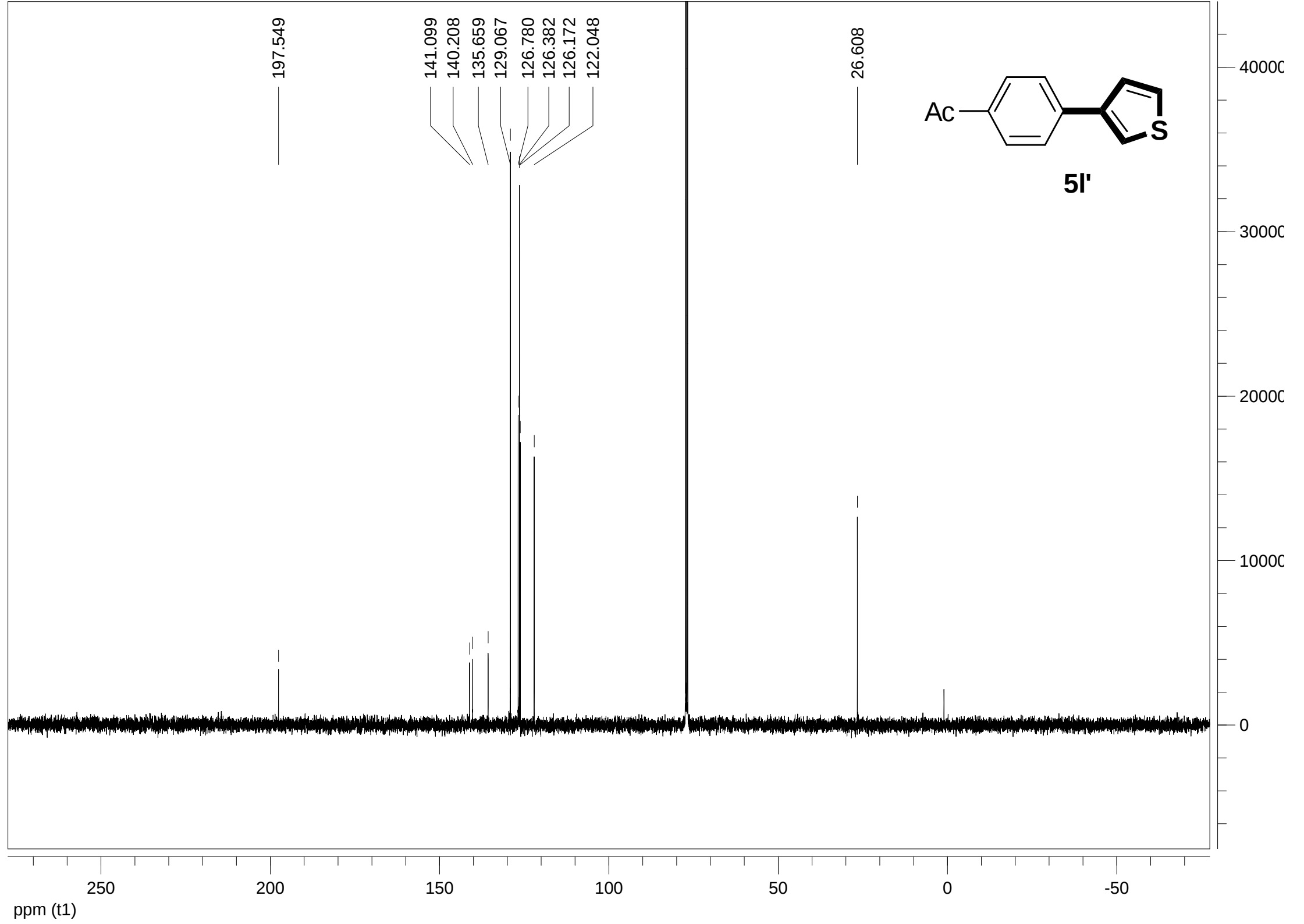
150

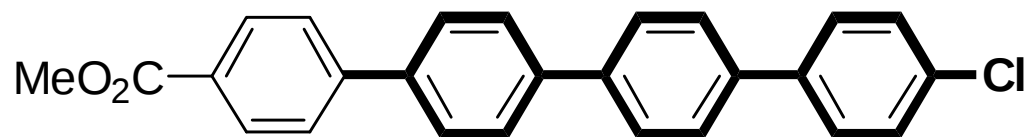
100

50

0







8.136
8.115
7.713
7.698
7.665
7.645
7.630
7.579
7.558
7.443
7.422
7.257

3.949

0.073

80.2

60.8

50.3

00.3

3000C

2000C

1000C

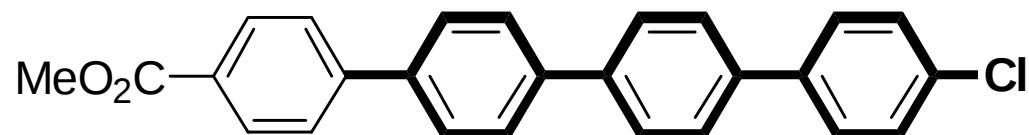
0

10.0

5.0

0.0

ppm (t1)



165.931
143.868
138.712
138.143
137.829
132.665
129.158
128.010
127.820
127.258
127.228
126.729
126.614
126.441
126.410
126.013
125.878

51.145

0.0000

3000

2500

2000

1500

1000

500

0

200

150

100

50

0

ppm (t1)

