Supporting Information

Heterocyclization of N-(1-chloro-2,2,2-trifluoroethylidene)carbamates with β-enaminoesters – a novel synthetic strategy to functionalized trifluoromethylated pyrimidines

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X-ray Structure determination for compound ***5a****.*

Crystal data: $C_{10}H_{11}B_2F_3N_2O_3$, M 285.83, monoclinic, space group $P2_1/c$, a = 4.8955(6), b = 11.0400(15), c = 21.316(3) Å, β = 93.177(4)º, V = 1150.3(3)Å^3, Z = 4, d_c = 1.56 g·cm^{-3}, μ = 0.148 mm^{-1}, F(000) = 584, crystal size ca. 0.19 x 0.27 x 0.35 mm. All crystallographic measurements were performed at room temperature on a Bruker Smart Apex II diffractometer operating in the ω and φ scans mode. The intensity data were collected within the $\theta_{max} \leq 26.38°$ using Mo-K_α radiation (λ = 0.71078 Å). The intensities of 5640 reflections were collected (2164 unique reflections, R_{merg} = 0.0202).

The structure was solved by direct methods and refined by the full-matrix least-squares technique in the anisotropic approximation for non-hydrogen atoms using the Bruker SHELXTL program package[1]. All hydrogen atoms were refined isotropically. In the refinement 2164 reflections (1539 reflections with $I \geq 2\sigma(I)$) were used. Convergence was obtained at R1 = 0.0588 and wR2 = 0.1039, for all reflection and R1 = 0.0374 and wR2 = 0.0921, GOF = 1.007 for observed (207 parameters; observed/variable ratio 7.4; the largest and minimal peaks in the final difference map 0.18 and –0.18 e/Å^3, weighting scheme is as follows: $\omega = 1/[\sigma^2(Fo^2) + 0.0509P^2+0.2021P]$, where $P = (Fo^2 + 2Fc^2)/3$). Full crystallographic details have been deposited

at Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for these materials should quote the full literature citation and reference number CCDC 878801.

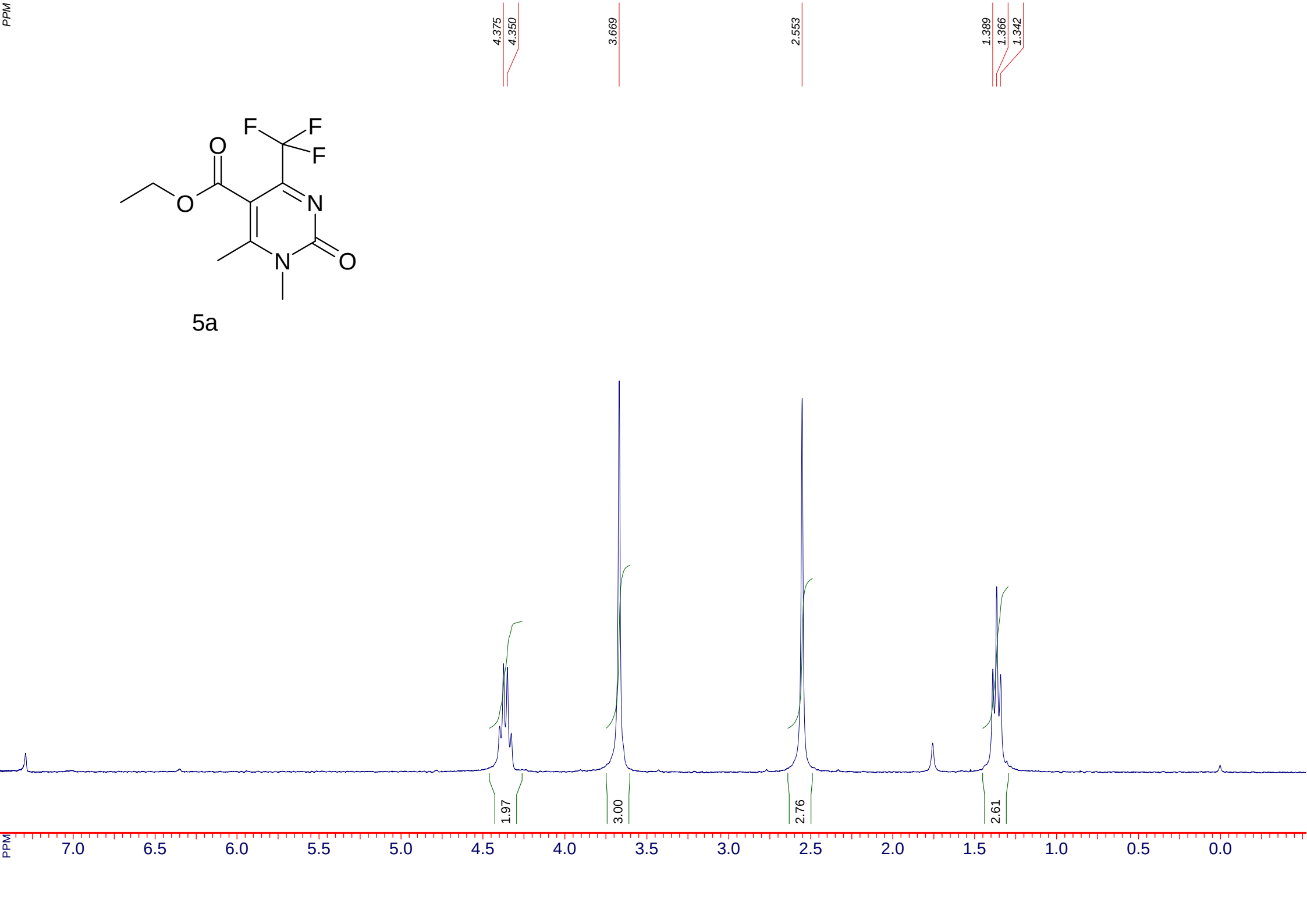
X-ray Structure determination for compound ***5l****.*

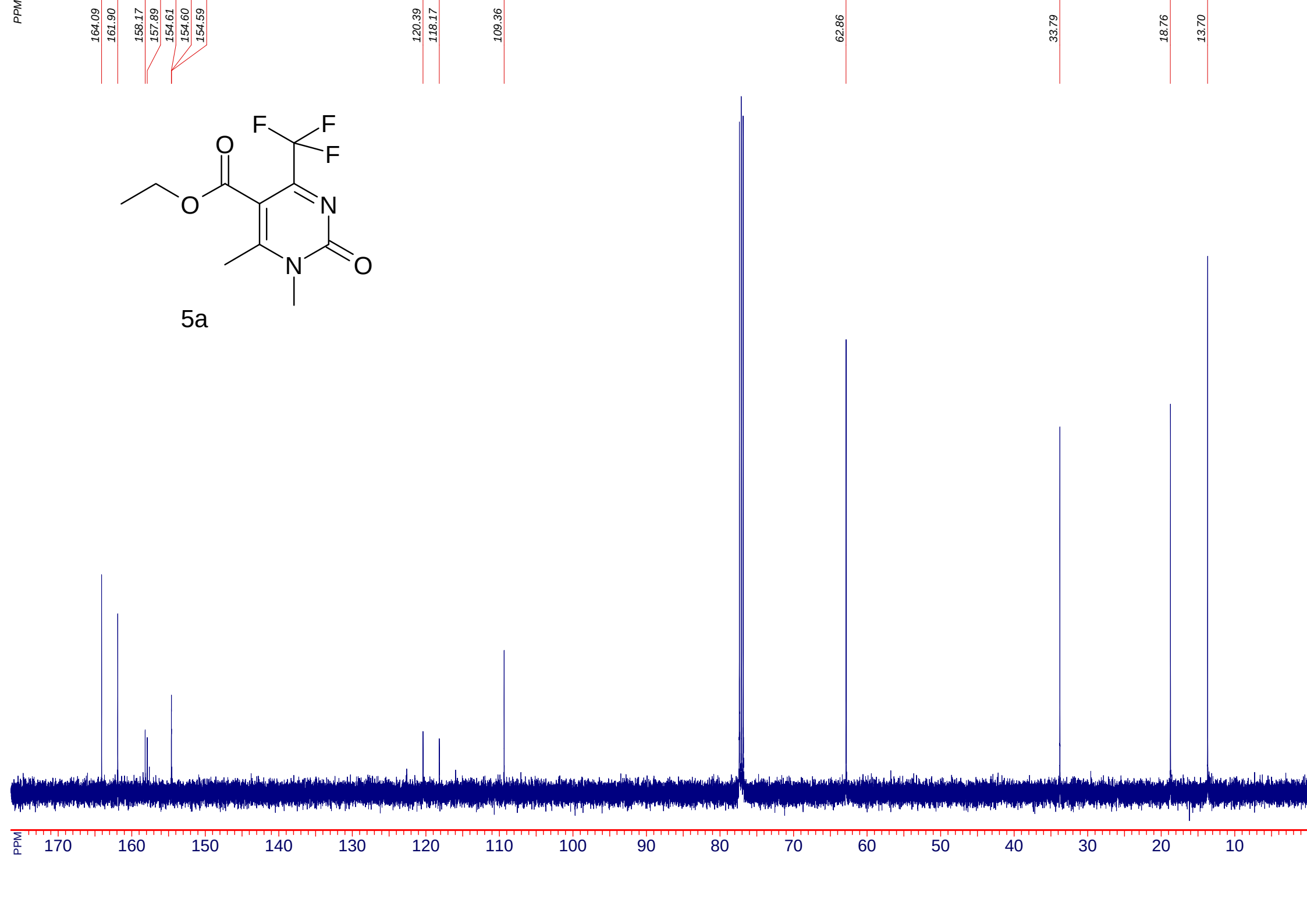
Crystal data: $C_{35}H_{30}F_6N_4O_6$, M 716.63, monoclinic, space group $P2_1/c$, a = 20.2101(4), b = 11.0539(2), c = 15.0422(3) Å, β = 100.384(1)º, V = 3305.40(11)Å^3, Z = 4, d_c = 1.44 g·cm^{-3}, μ = 0.121 mm^{-1}, F(000) = 1480, crystal size ca. 0.19 x 0.27 x 0.35 mm. All crystallographic measurements were performed at room temperature on a Bruker Smart Apex II diffractometer operating in the ω and φ scans mode. The intensity data were collected within the range $\theta \leq 28.94°$ using Mo-K_α radiation (λ = 0.71078 Å). The intensities of 35627 reflections were collected (8636 unique reflections, R_{merg} = 0.0509).

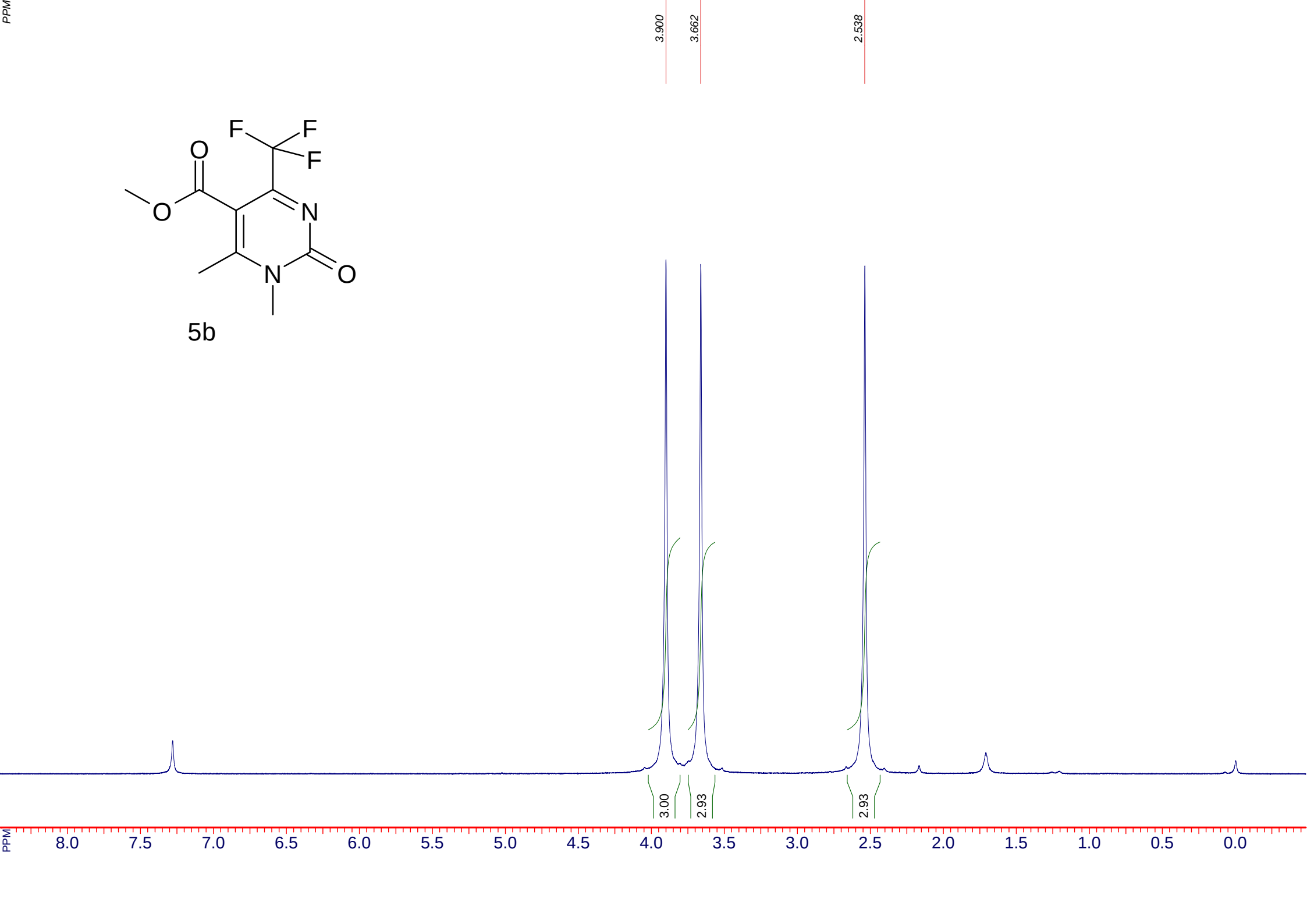
The structure was solved by direct methods and refined by the full-matrix least-squares technique in the anisotropic approximation for non-hydrogen atoms using the Bruker SHELXTL program package[1]. The Et group one of the independent molecule is disordered over two position with occupancy of 50%. The hydrogen atoms that supported N atoms where found in difference Fourier maps and refined isotropically, rest ones is placed geometrically and refined as "riding" model. In the refinement 8636 reflections (4990 reflections with $I \geq 2\sigma(I)$) were used. Convergence was obtained at R1 = 0.1126 and wR2 = 0.1924, for all reflection and R1 = 0.0565 and wR2 = 0.1544, GOF = 1.061 for observed (467 parameters; observed/variable ratio 10.7; the largest and minimal peaks in the final difference map 0.64 and –0.36 e/Å^3, weighting scheme is as follows: $\omega = 1/[\sigma^2(Fo^2) + (0.1P)^2]$, where $P = (Fo^2 + 2Fc^2)/3$). Full crystallographic details have been deposited at Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for these materials should quote the full literature citation and reference number CCDC 878802.

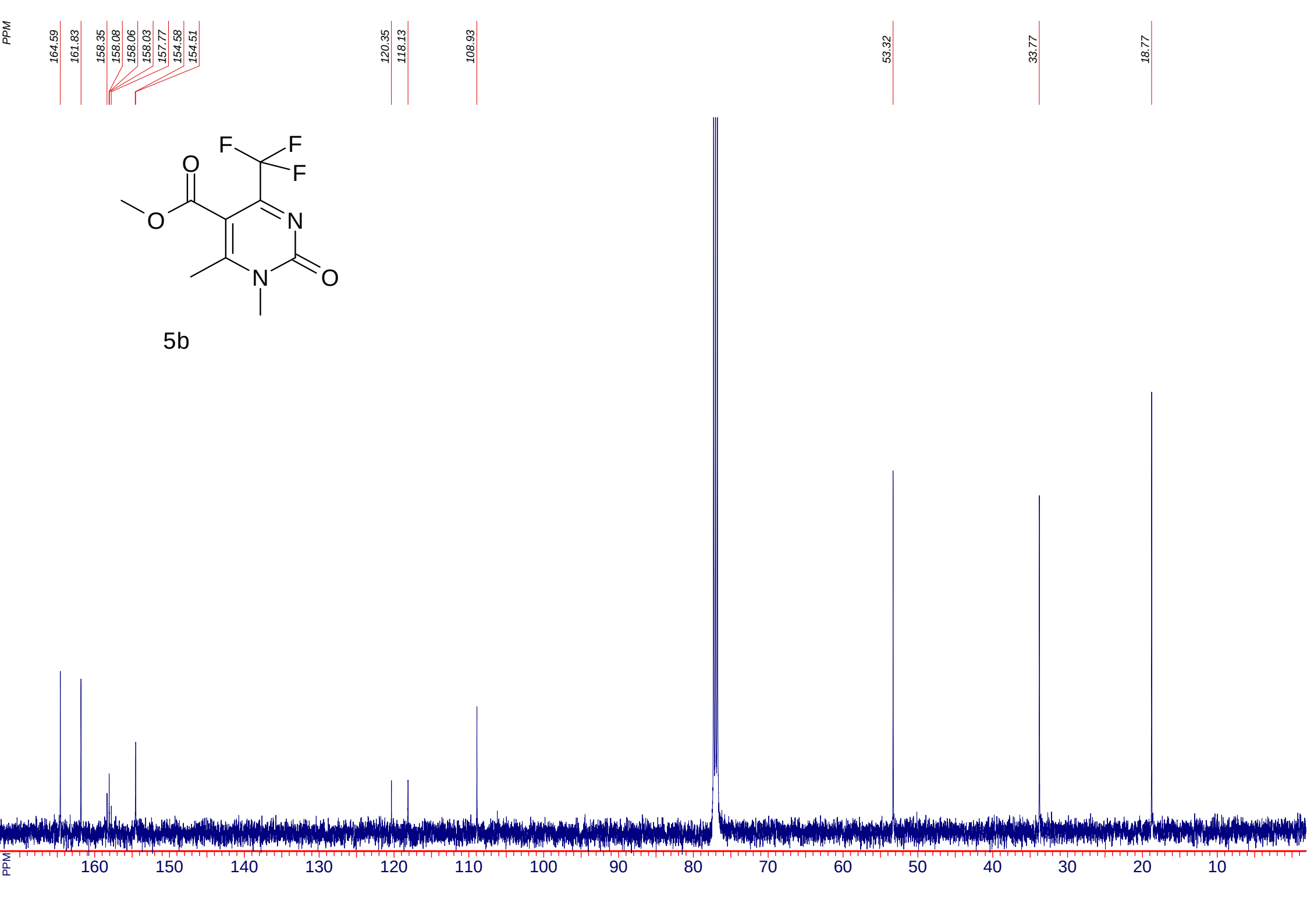
1.Sheldrick, G. M. (2008). *Acta Cryst.* A **64**, 112-122.

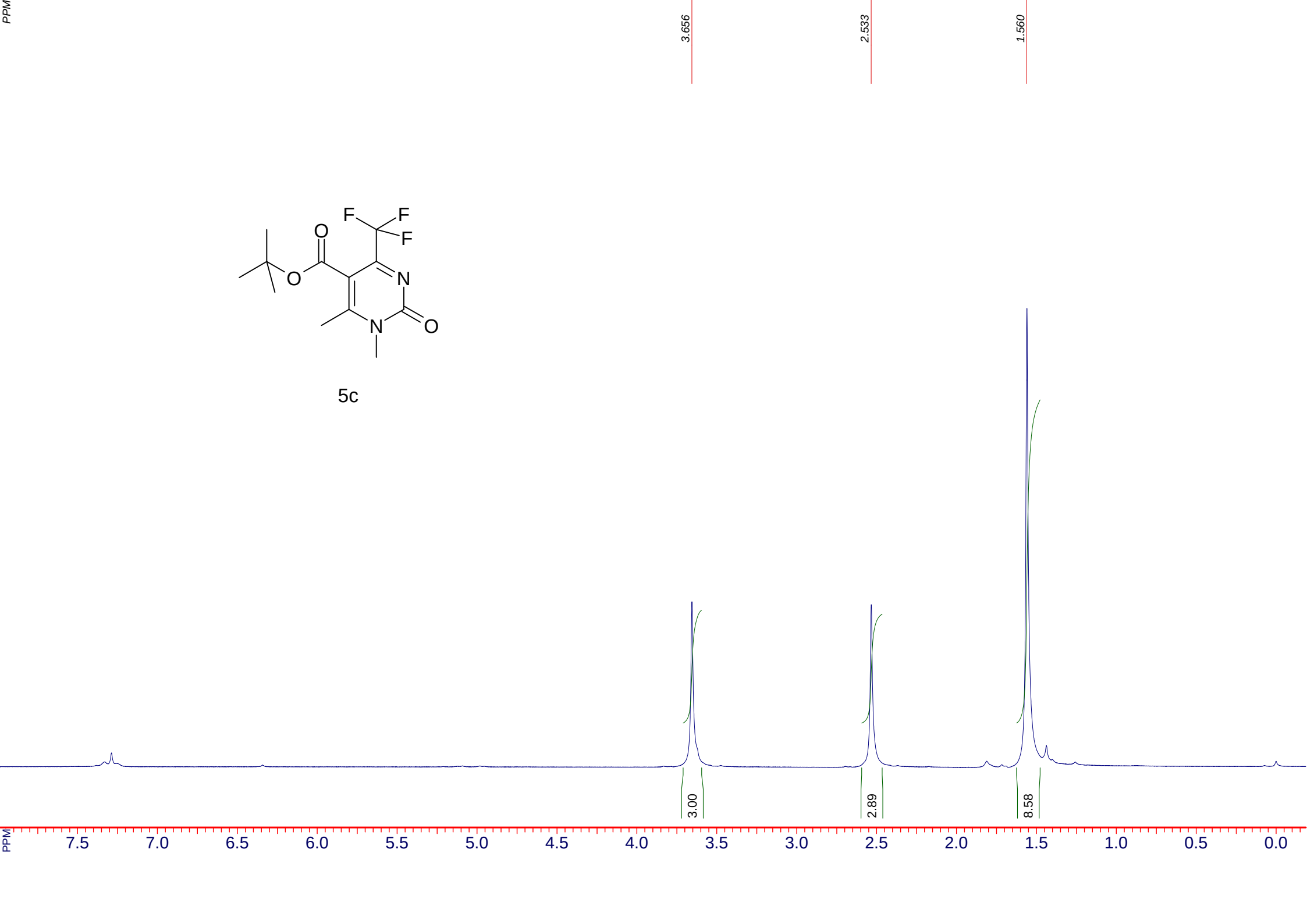
^{1}H and ^{13}C–NMR spectra of compounds 5, 7, 9-12, 14

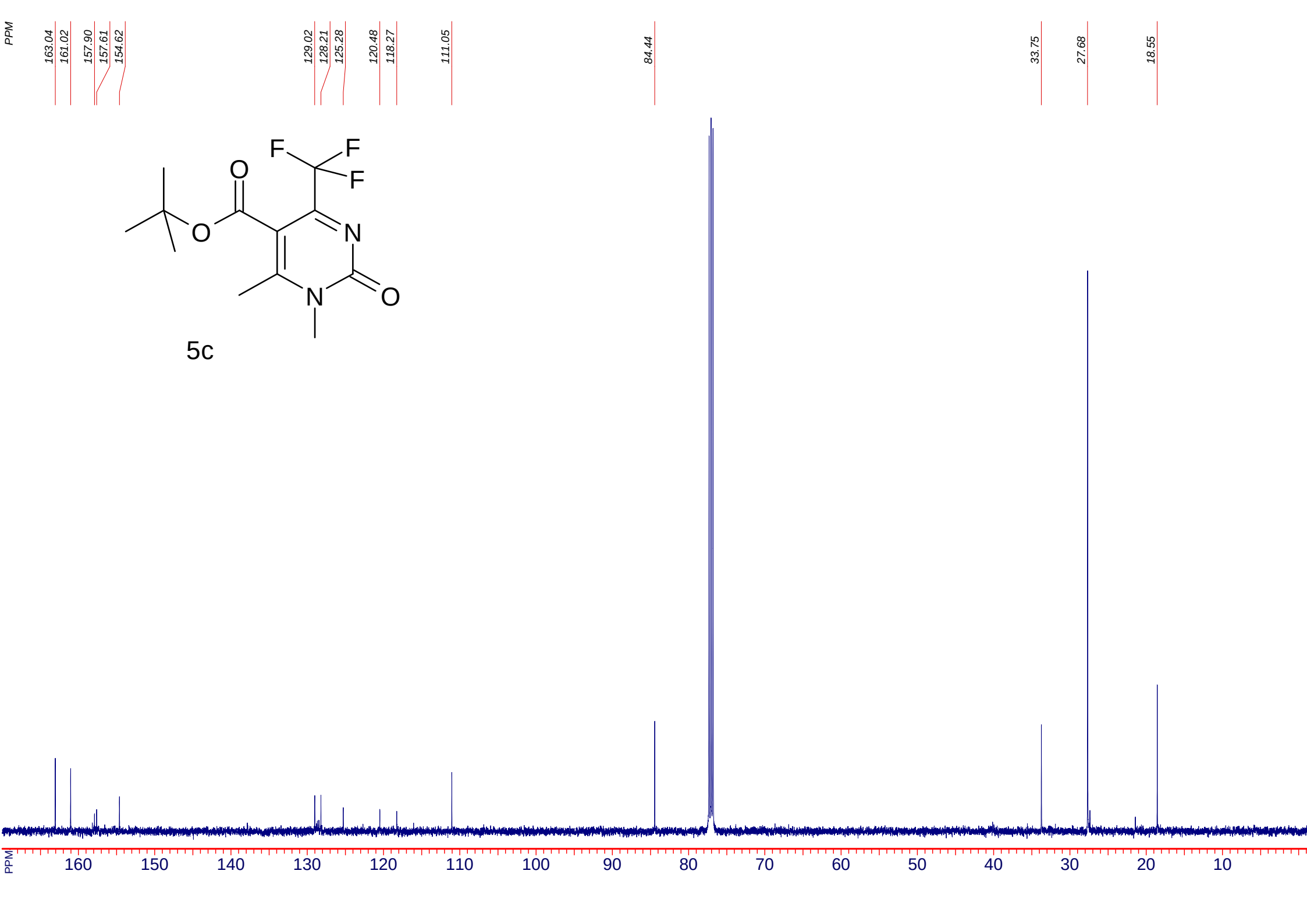

PPM
4.375
4.350
3.669
2.553
1.389
1.366
1.342
F
F
F
O
O
N
N
O
5a
1.97
3.00
2.76
2.61
PPM
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

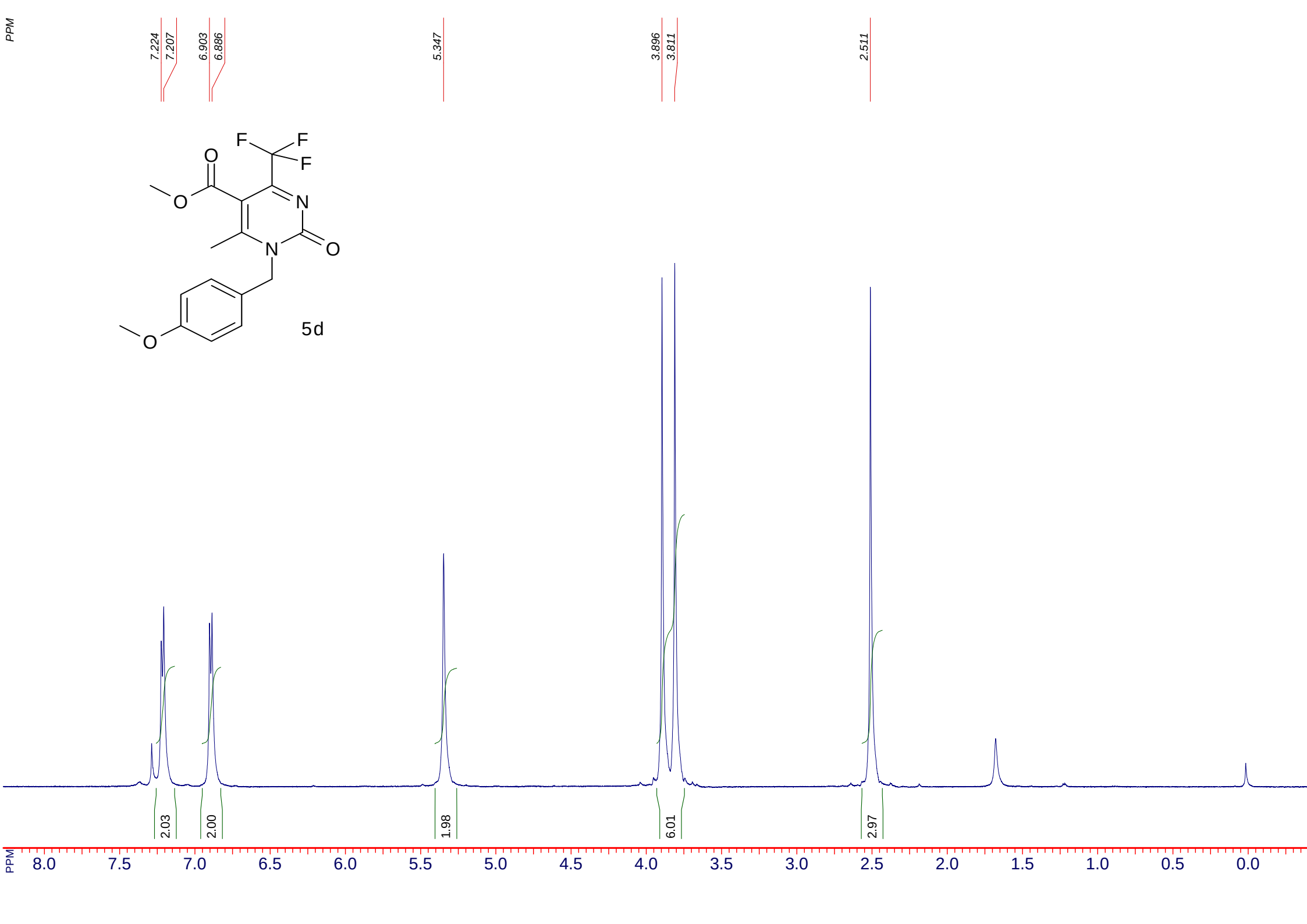

PPM
164.09
161.90
158.17
157.89
154.61
154.60
154.59
120.39
118.17
109.36
62.86
33.79
18.76
13.70
F
F
F
O
O
N
N
O
5a
PPM
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

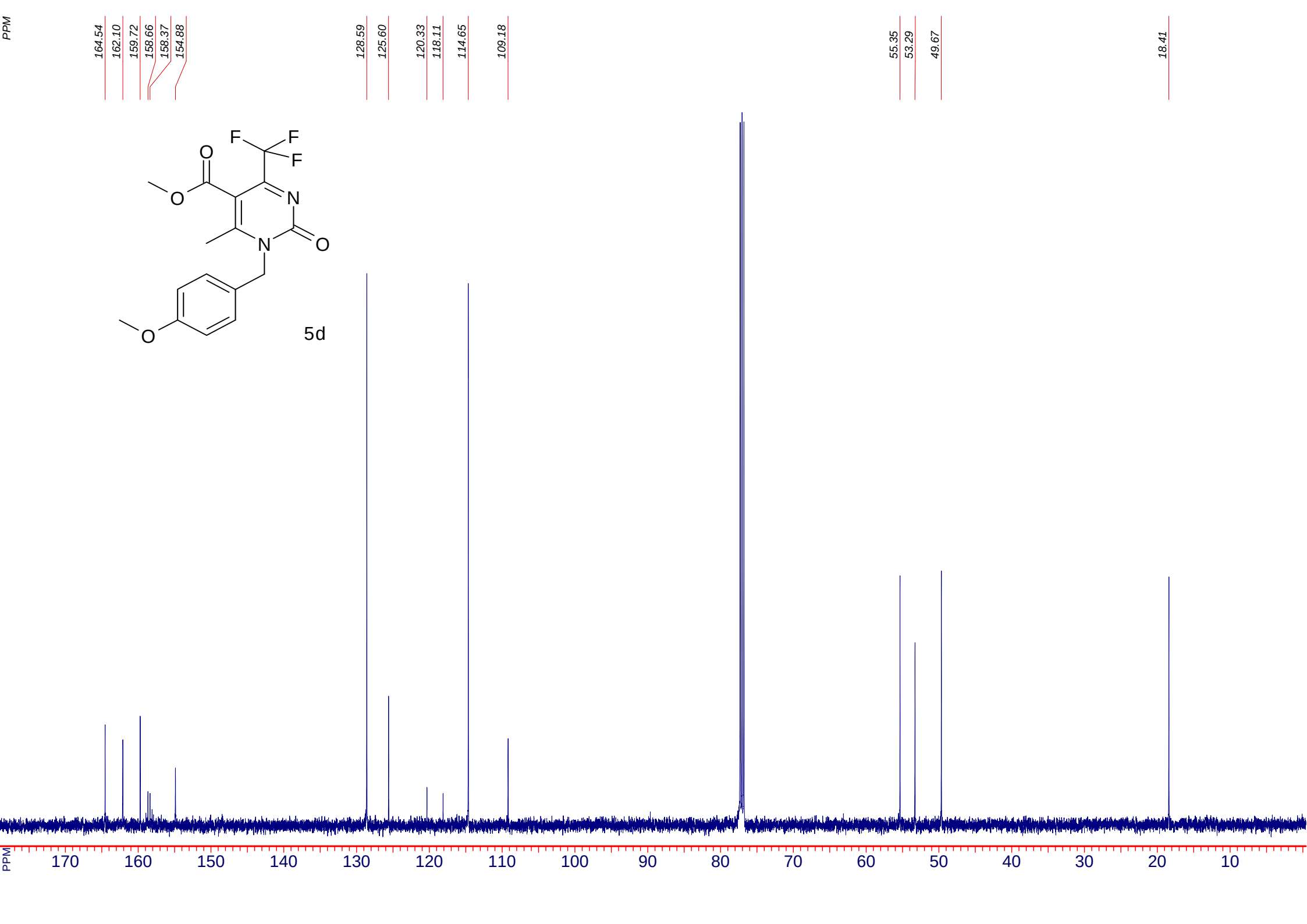

PPM
3.900
3.662
2.538
F
F
F
O
O
N
N
O
5b
3.00
2.93
2.93
PPM
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

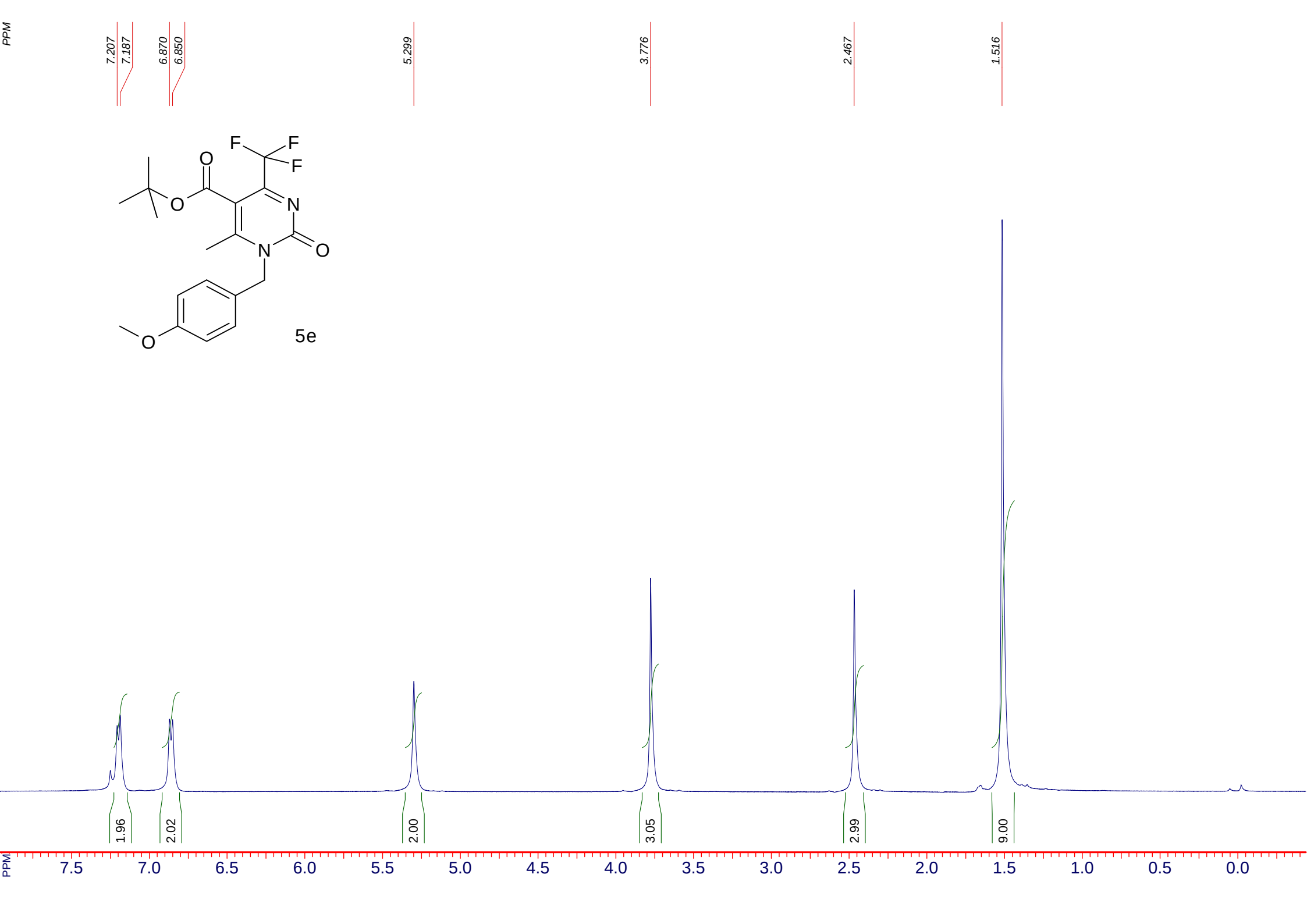

PPM
164.59
161.83
158.35
158.08
158.06
158.03
157.77
154.58
154.51
120.35
118.13
108.93
53.32
33.77
18.77
F
F
F
O
O
N
N
O
5b
PPM
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

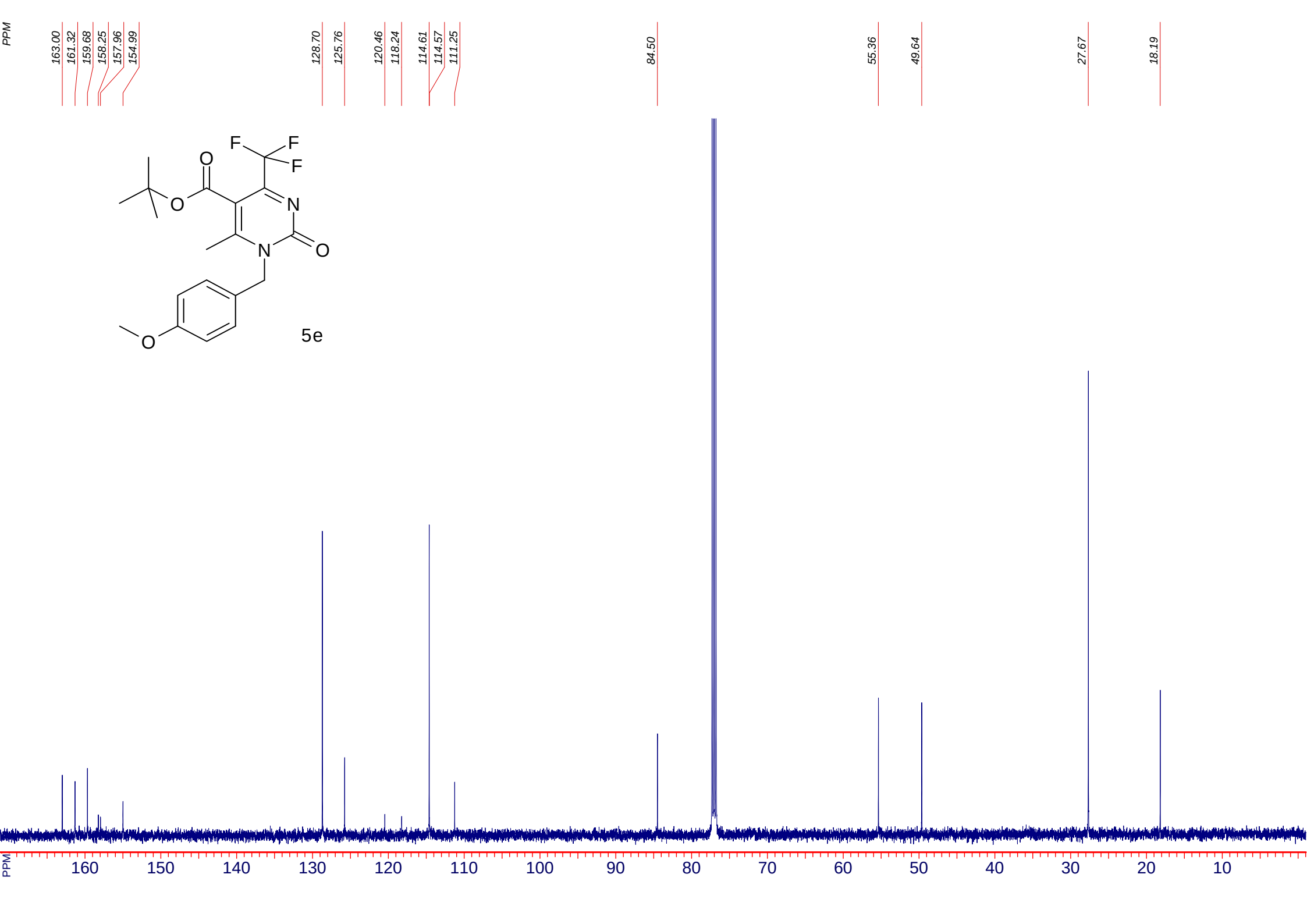

PPM
3.656
2.533
1.560
F
F
F
O
O
N
N
O
5c
3.00
2.89
8.58
PPM
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

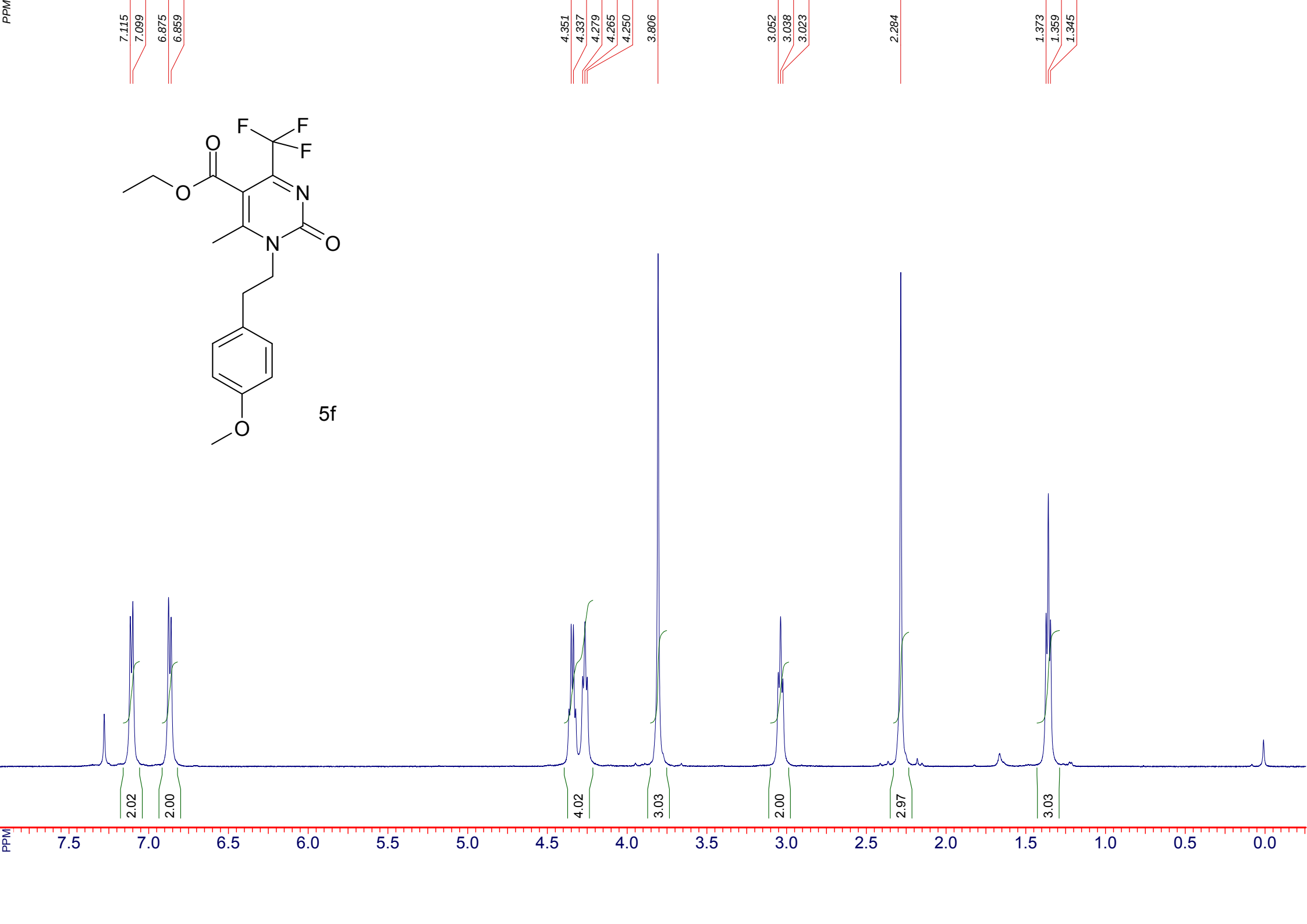

PPM
163.04
161.02
157.90
157.61
154.62
129.02
128.21
125.28
120.48
118.27
111.05
84.44
33.75
27.68
18.55
F
F
F
O
O
N
N
O
5c
PPM
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

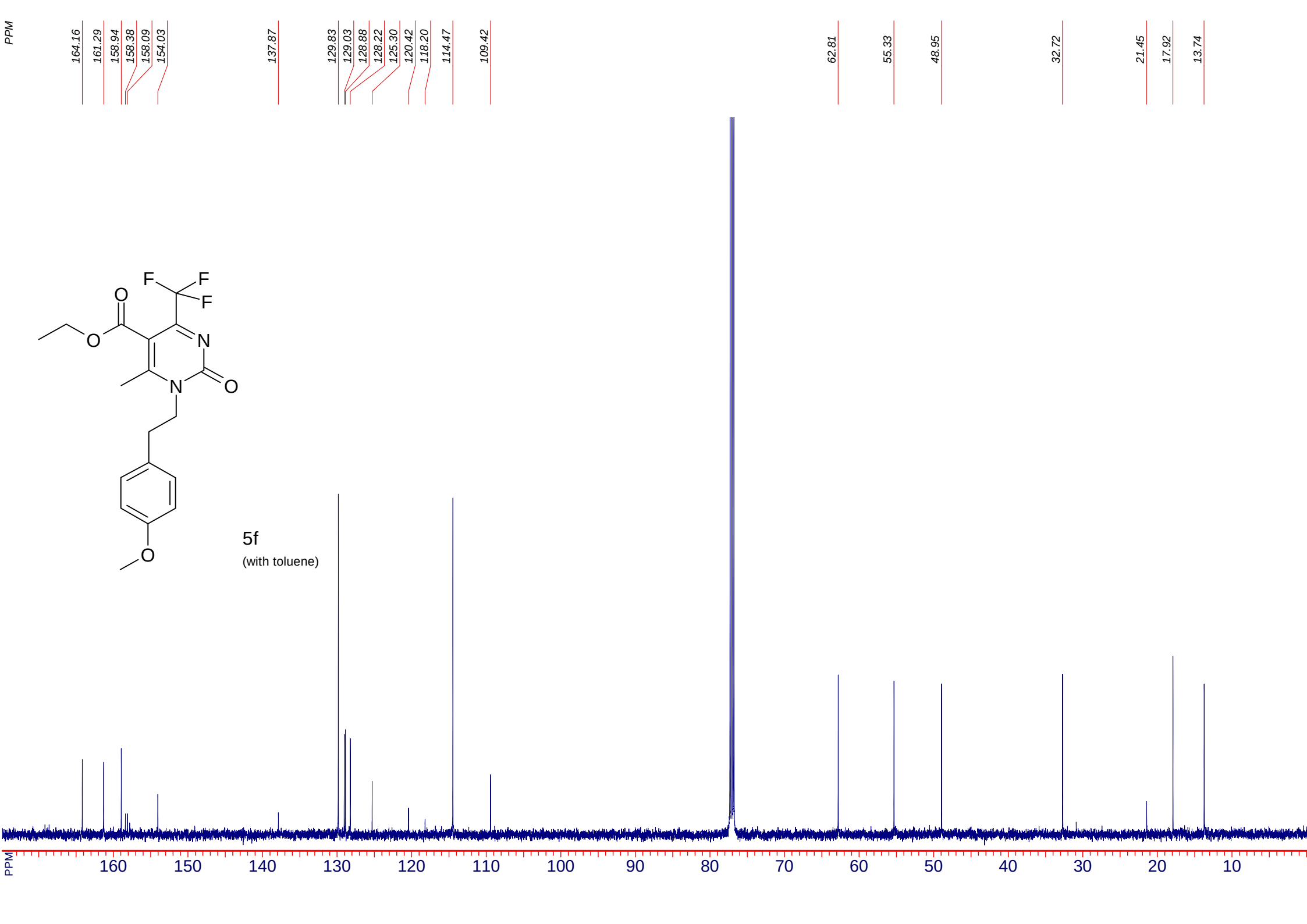

PPM
7.224
7.207
6.903
6.886
5.347
3.896
3.811
2.511
F
F
F
O
O
N
N
O
O
5d
2.03
2.00
1.98
6.01
2.97
PPM
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

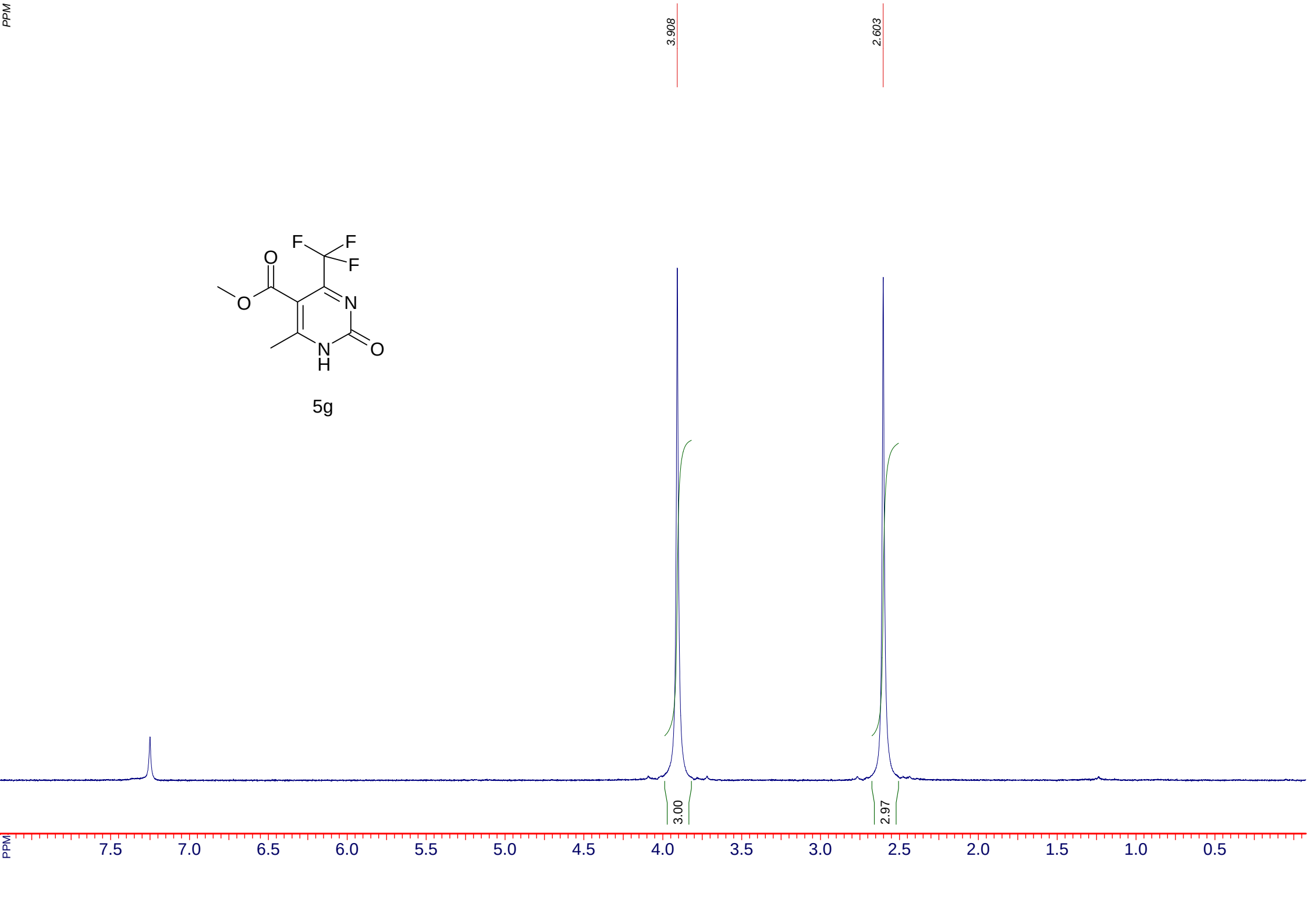

PPM
164.54
162.10
159.72
158.66
158.37
154.88
128.59
125.60
120.33
118.11
114.65
109.18
55.35
53.29
49.67
18.41
F
F
F
O
O
N
N
O
O
5d
PPM
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

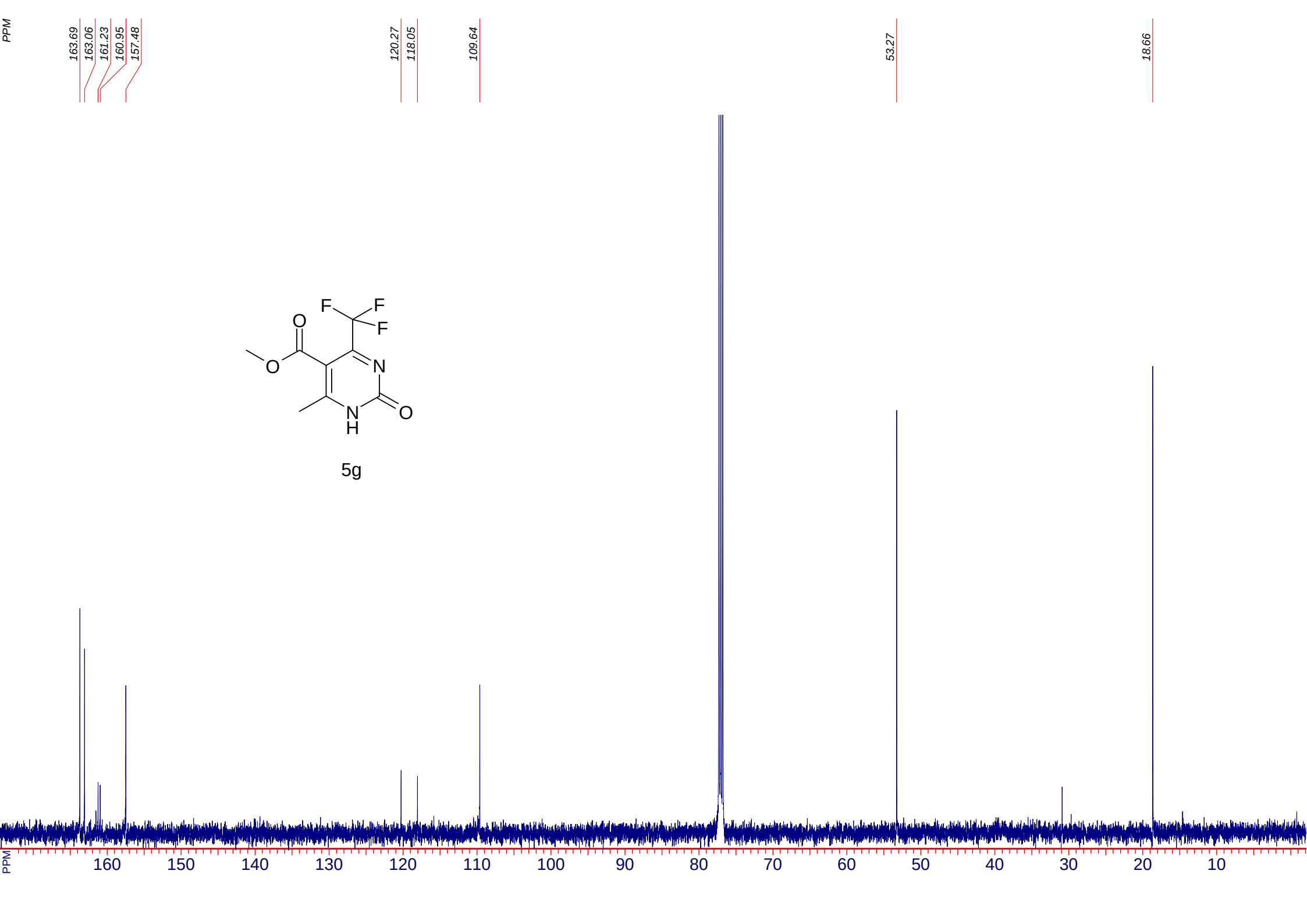

PPM
7.207
7.187
6.870
6.850
5.299
3.776
2.467
1.516
F
F
F
O
O
N
N
O
O
5e
1.96
2.02
2.00
3.05
2.99
9.00
PPM
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

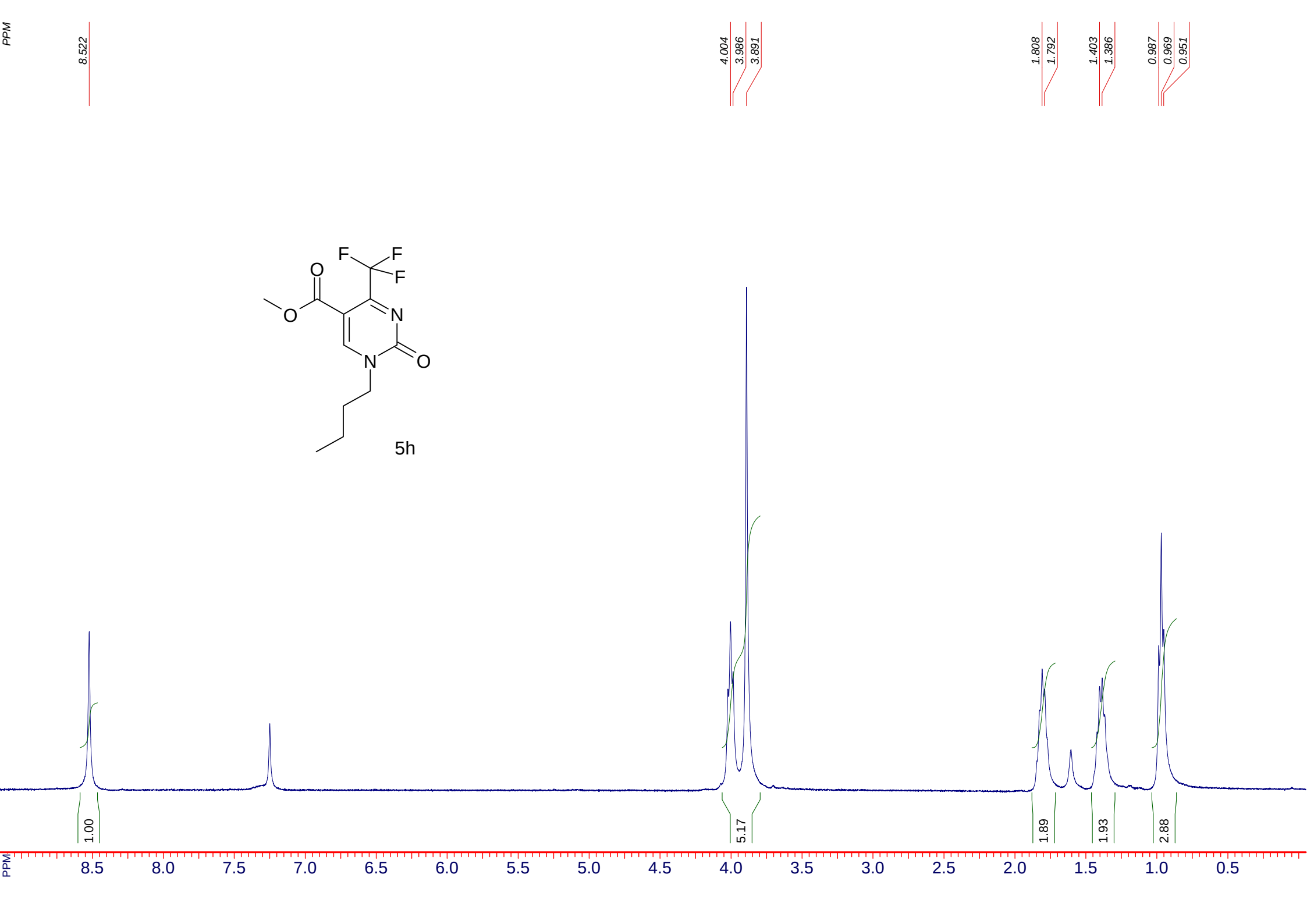

PPM
163.00
161.32
159.68
158.25
157.96
154.99
128.70
125.76
120.46
118.24
114.61
114.57
111.25
84.50
55.36
49.64
27.67
18.19
F
F
F
O
O
N
N
O
O
5e
PPM
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

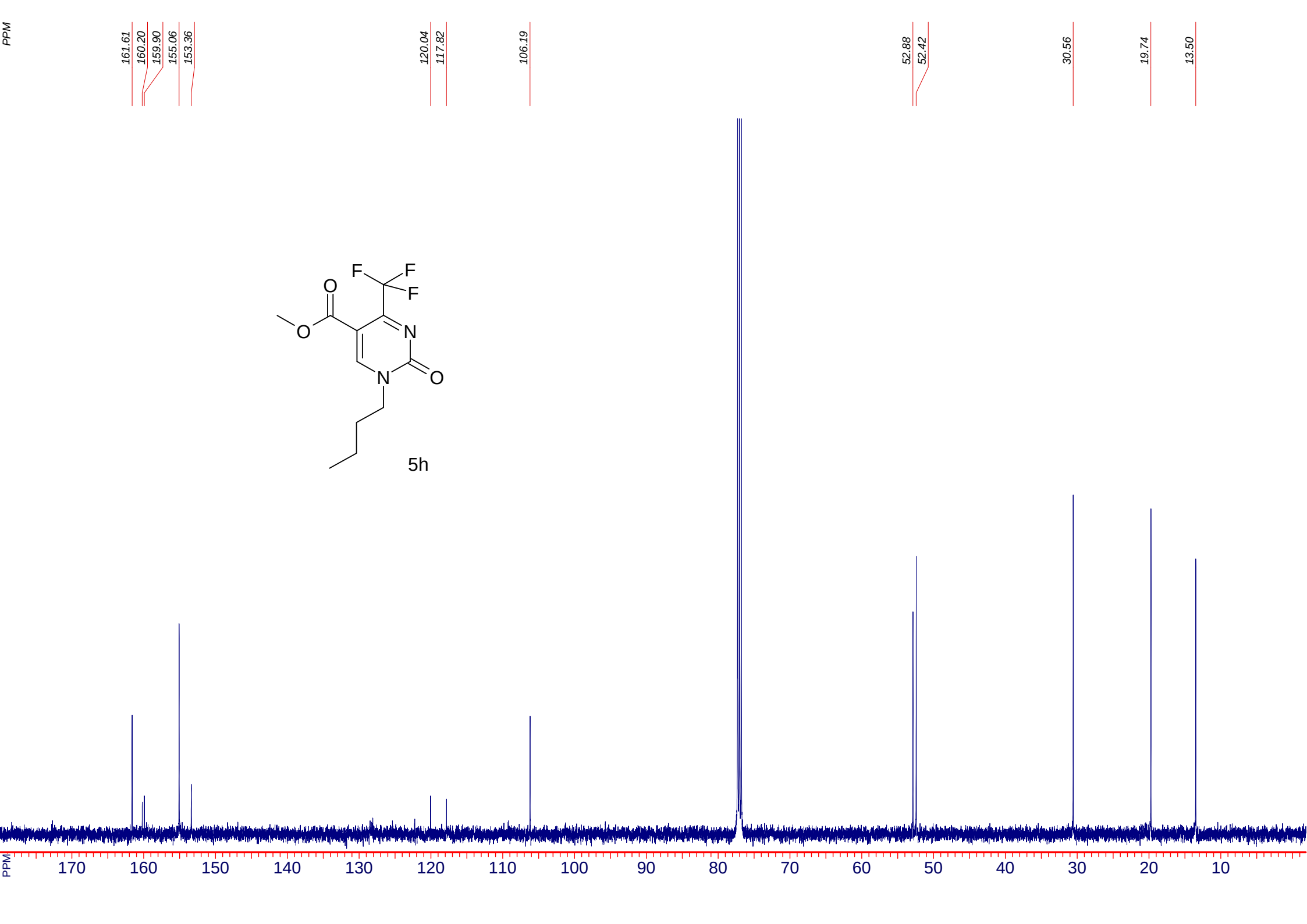

PPM
7.115
7.099
6.875
6.859
4.351
4.337
4.279
4.265
4.250
3.806
3.052
3.038
3.023
2.284
1.373
1.359
1.345
F
F
F
O
O
N
N
O
O
5f
2.02
2.00
4.02
3.03
2.00
2.97
3.03
PPM
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

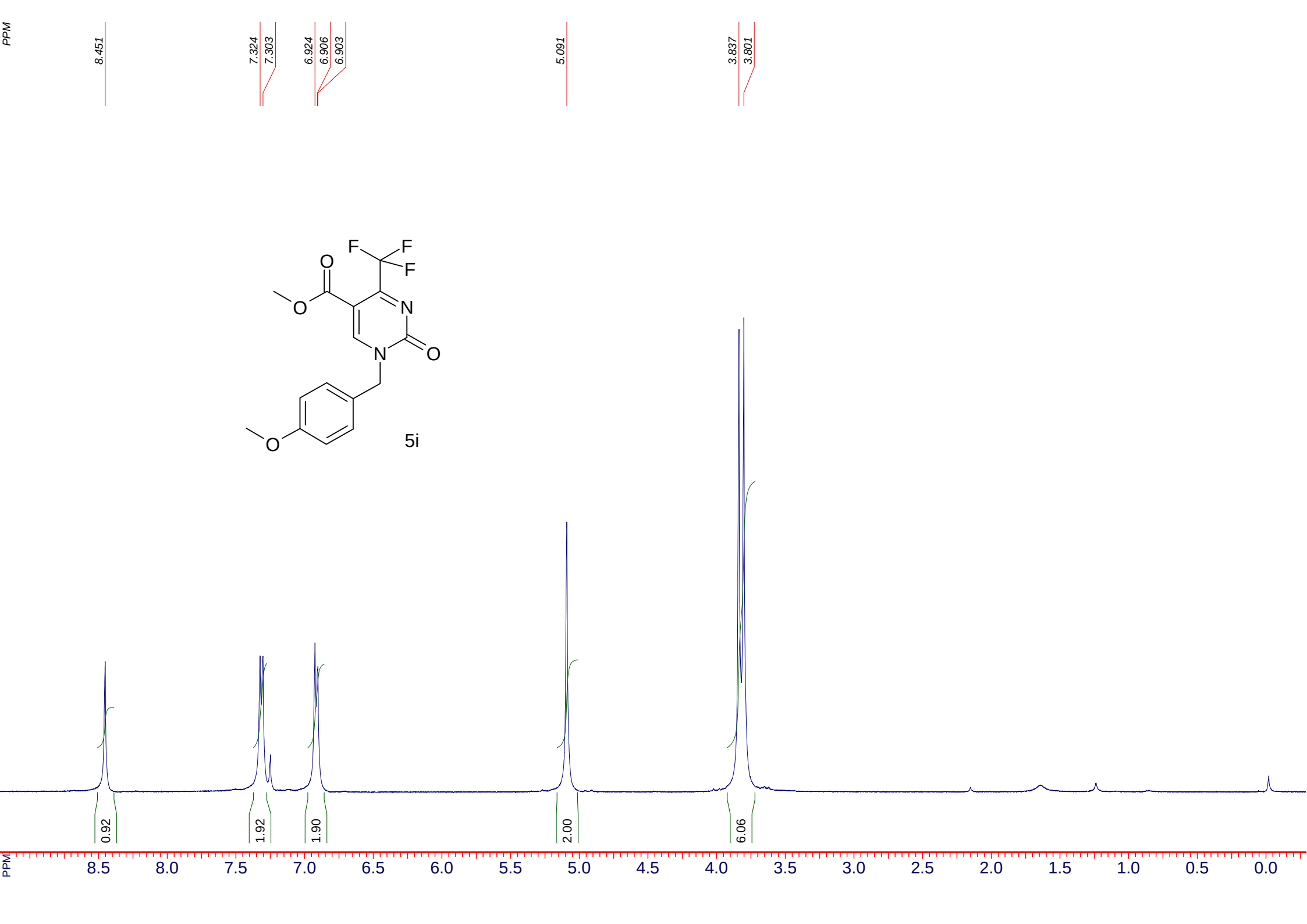

PPM
164.16
161.29
158.94
158.38
158.09
154.03
137.87
129.83
129.03
128.88
128.22
125.30
120.42
118.20
114.47
109.42
62.81
55.33
48.95
32.72
21.45
17.92
13.74
F
F
F
O
O
N
N
O
O
5f
(with toluene)
PPM
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


PPM
3.908
2.603
F
F
F
O
O
N
N
H
O
5g
3.00
2.97
PPM
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


PPM
163.69
163.06
161.23
160.95
157.48
120.27
118.05
109.64
53.27
18.66
F
F
F
O
O
N
N
H
O
5g
PPM
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


PPM
8.522
4.004
3.986
3.891
1.808
1.792
1.403
1.386
0.987
0.969
0.951
F
F
F
O
O
N
N
O
5h
1.00
5.17
1.89
1.93
2.88
PPM
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


PPM
161.61
160.20
159.90
155.06
153.36
120.04
117.82
106.19
52.88
52.42
30.56
19.74
13.50
F
F
F
O
O
N
N
O
5h
PPM
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


PPM
8.451
7.324
7.303
6.924
6.906
6.903
5.091
3.837
3.801
F
F
F
O
O
N
N
O
O
5i
0.92
1.92
1.90
2.00
6.06
PPM
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
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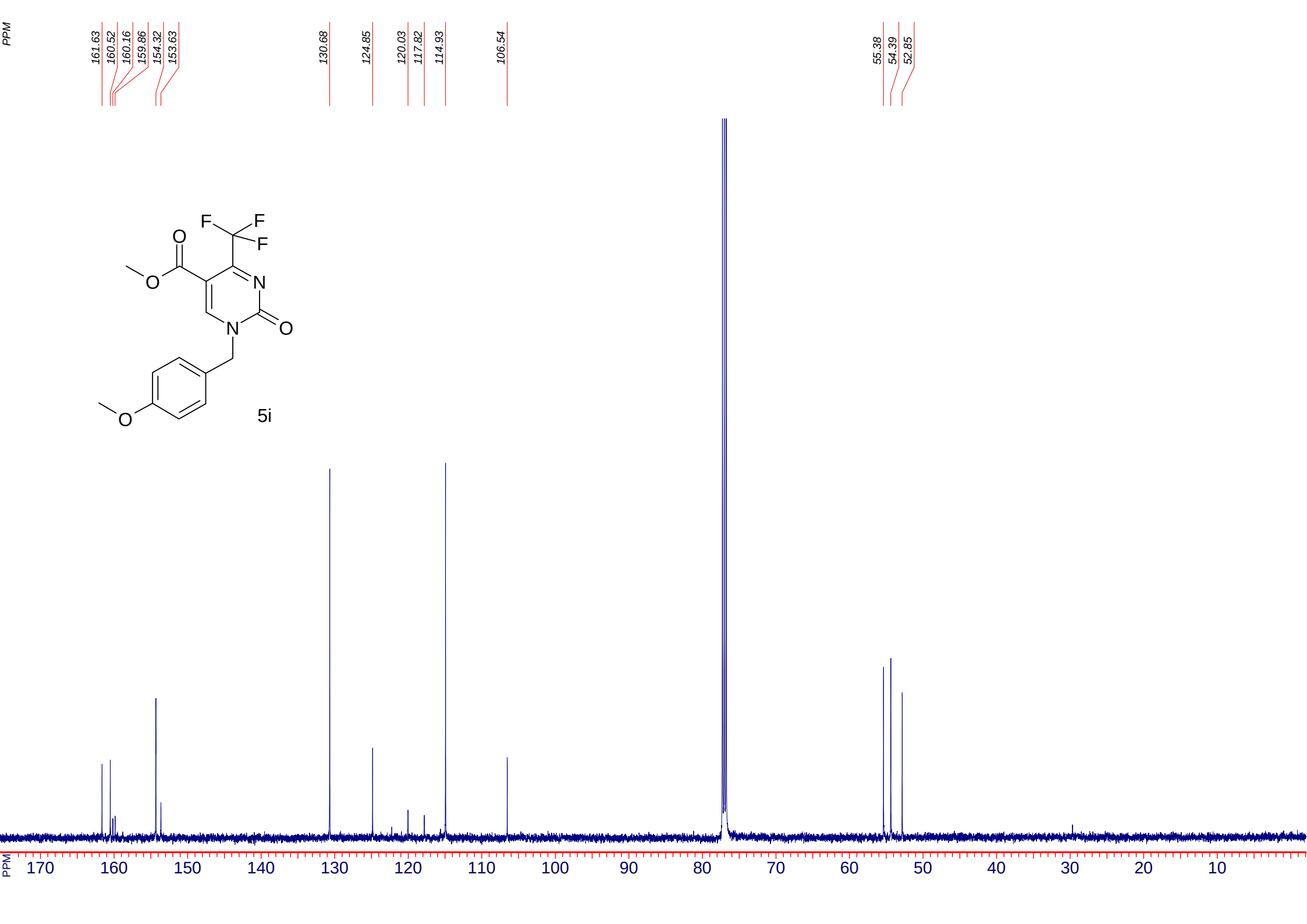
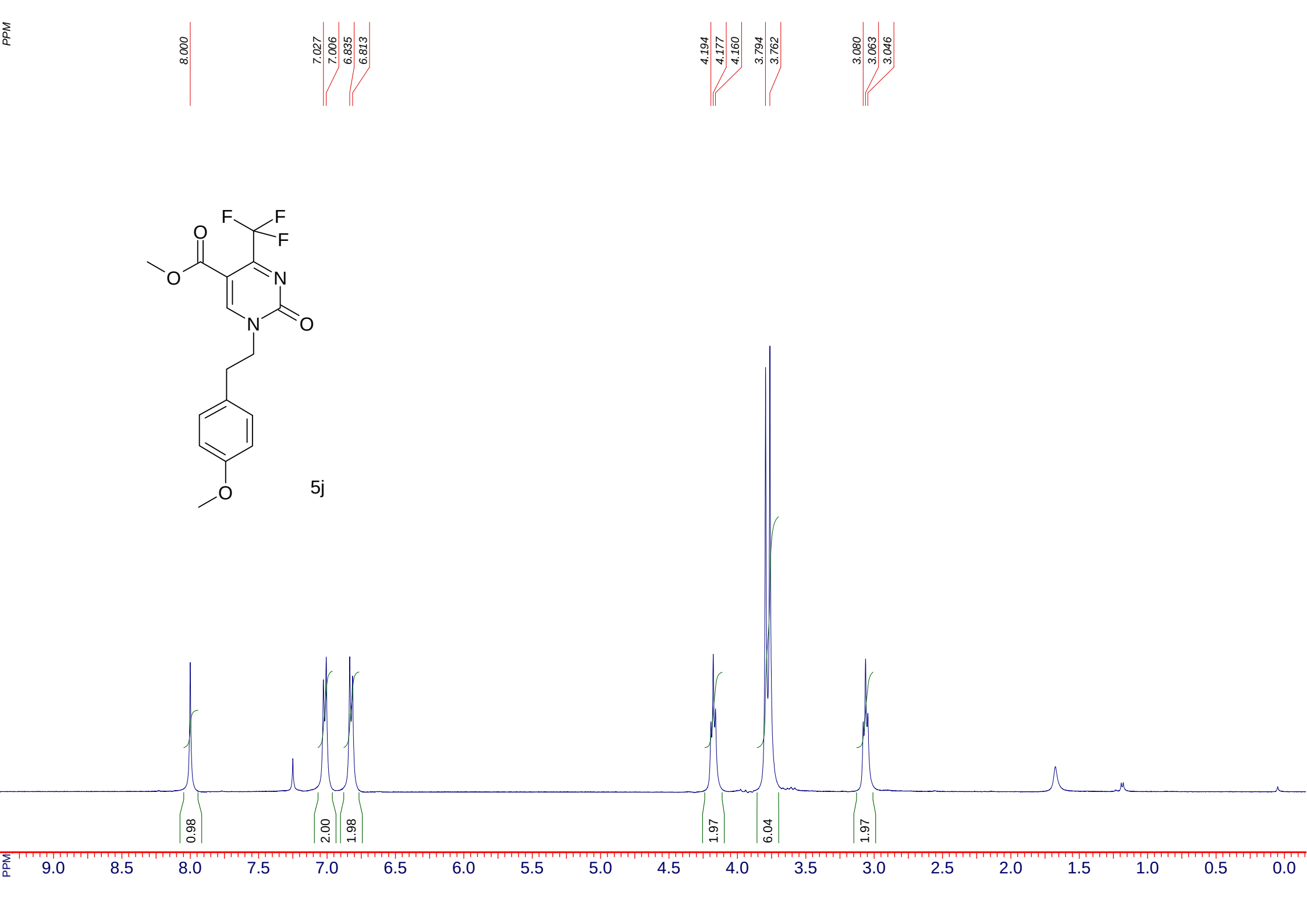
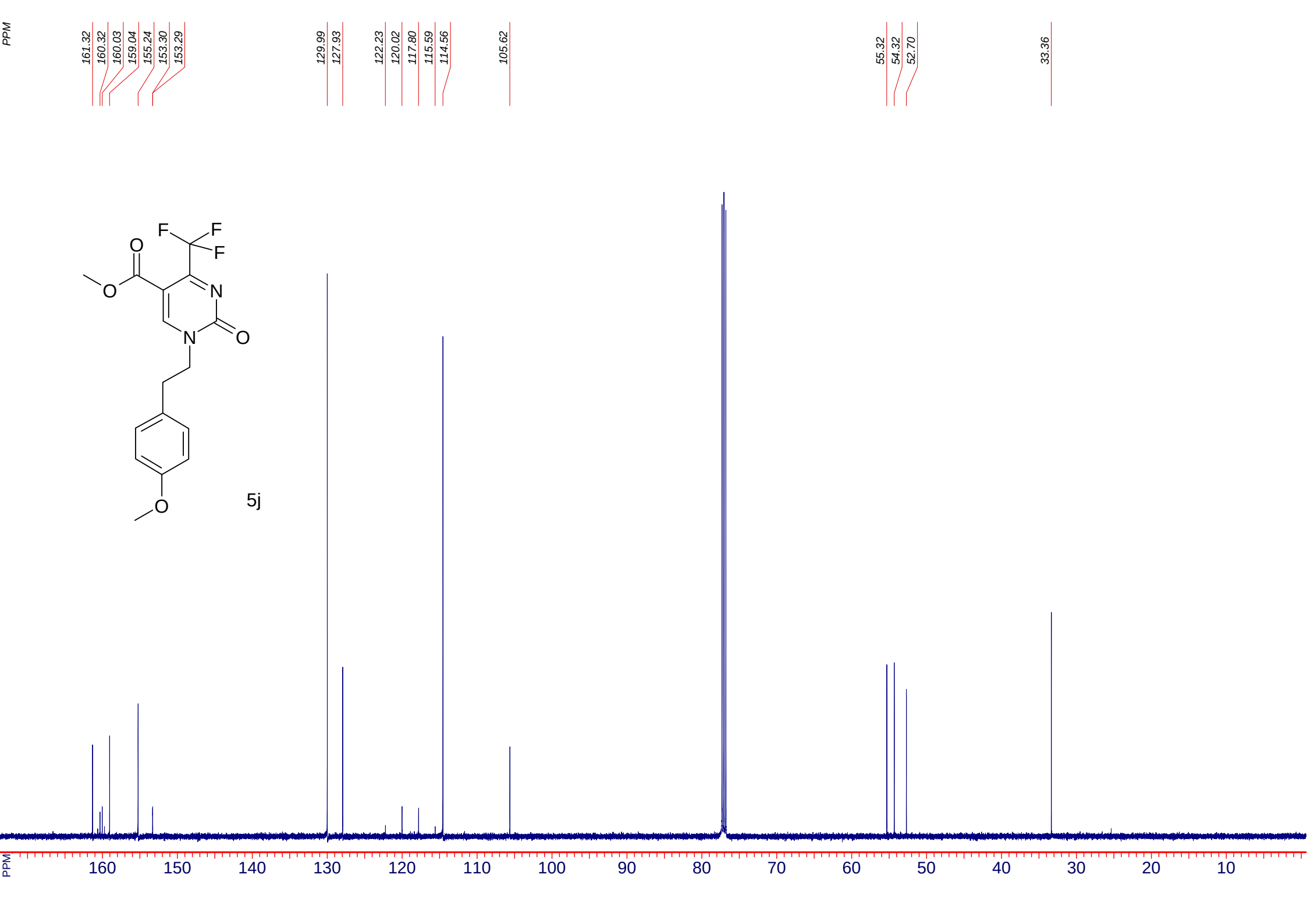
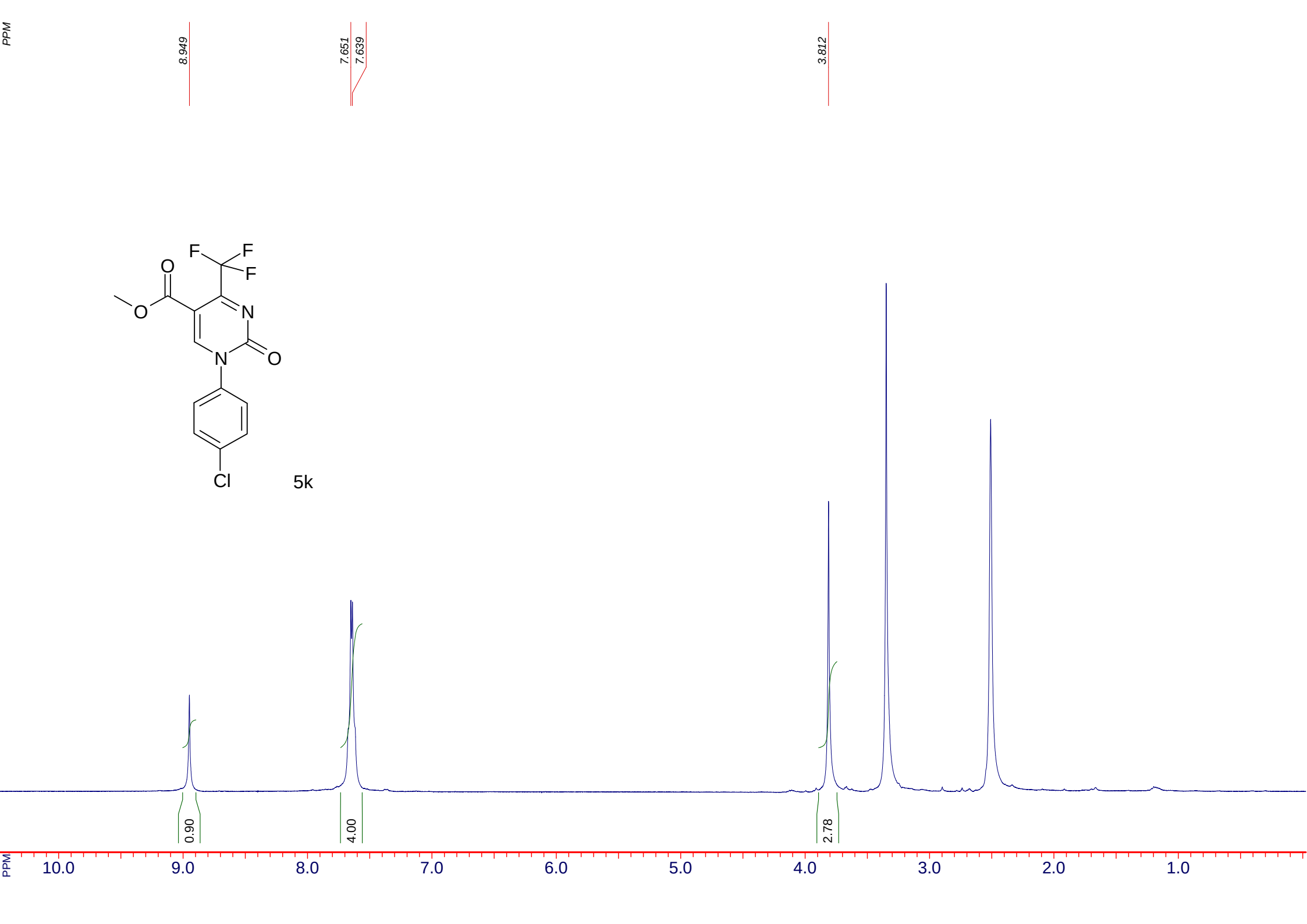
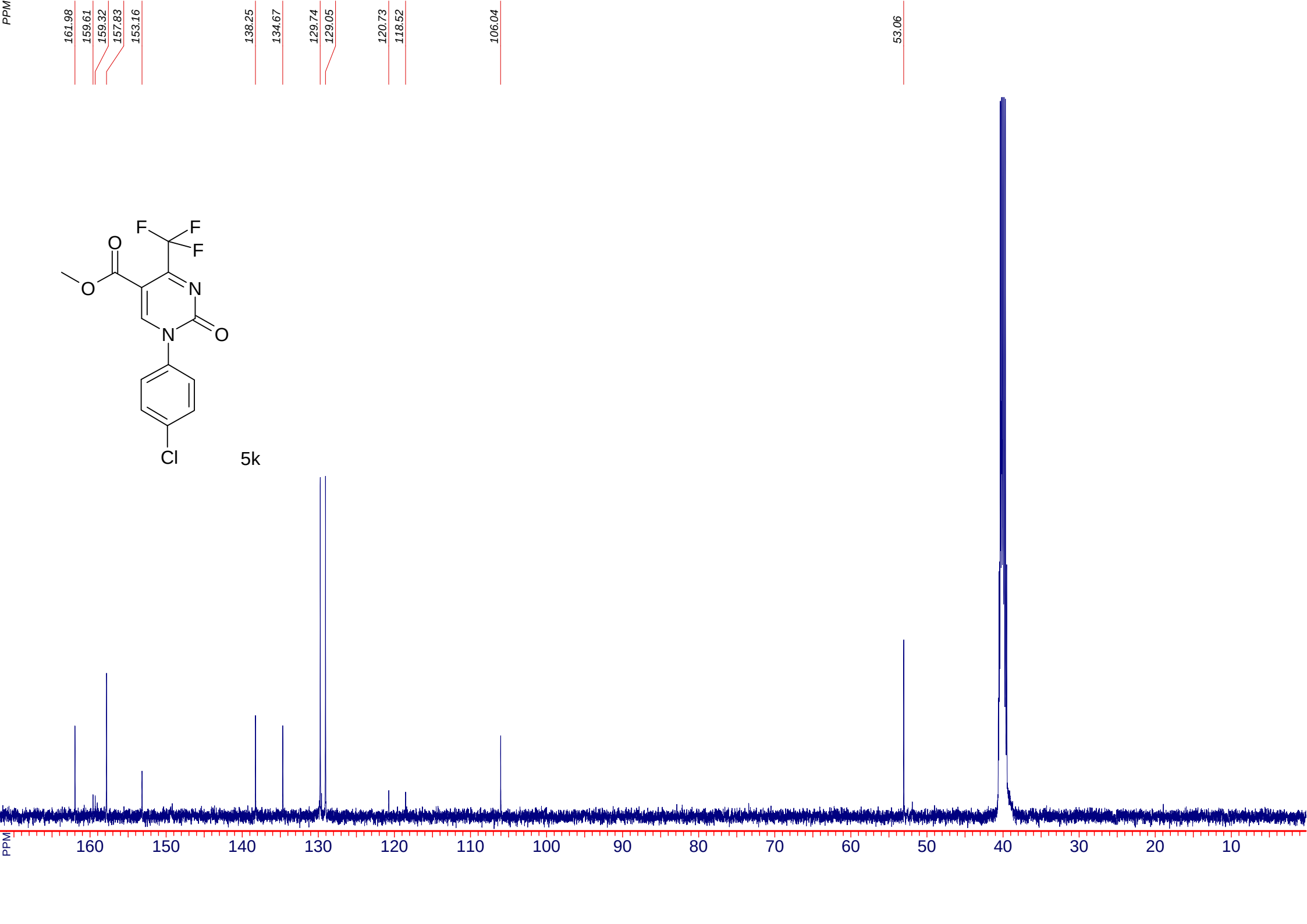
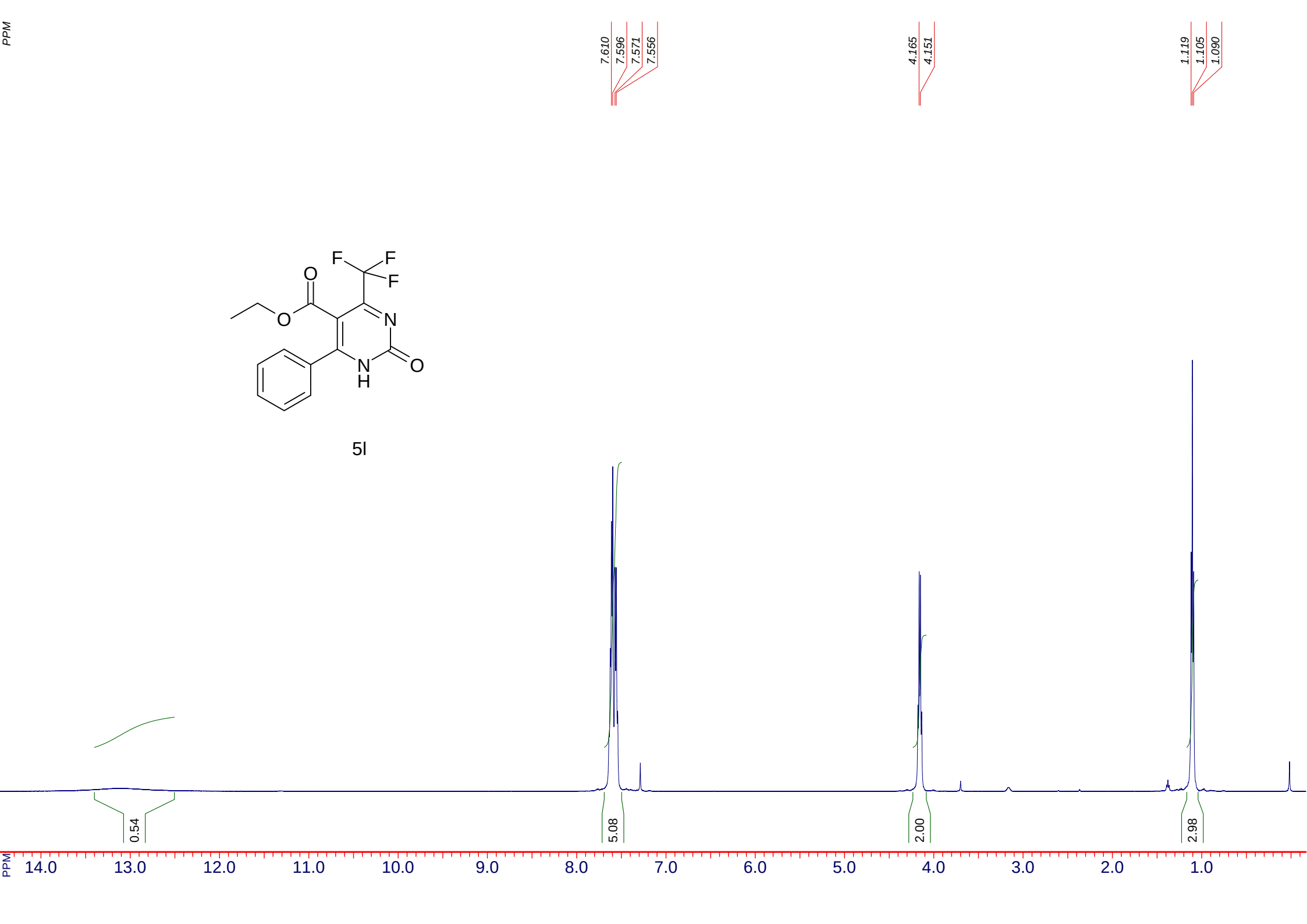

PPM
161.63
160.52
160.16
159.86
154.32
153.63
130.68
124.85
120.03
117.82
114.93
106.54
55.38
54.39
52.85
F
F
F
O
O
N
N
O
O
5i
PPM
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


PPM
8.000
7.027
7.006
6.835
6.813
4.194
4.177
4.160
3.794
3.762
3.080
3.063
3.046
F
F
F
O
O
N
N
O
O
5j
0.98
2.00
1.98
1.97
6.04
1.97
PPM
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
0.0


PPM
161.32
160.32
160.03
159.04
155.24
153.30
153.29
129.99
127.93
122.23
120.02
117.80
115.59
114.56
105.62
55.32
54.32
52.70
33.36
F
F
F
O
O
N
N
O
O
5j
PPM
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


PPM
8.949
7.651
7.639
3.812
F
F
F
O
O
N
N
O
Cl
5k
0.90
4.00
2.78
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


PPM
161.98
159.61
159.32
157.83
153.16
138.25
134.67
129.74
129.05
120.73
118.52
106.04
53.06
F
F
F
O
O
N
N
O
Cl
5k
PPM
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


PPM
7.610
7.596
7.571
7.556
4.165
4.151
1.119
1.105
1.090
F
F
F
O
O
N
N
H
O
5l
0.54
5.08
2.00
2.98
PPM
14.0
13.0
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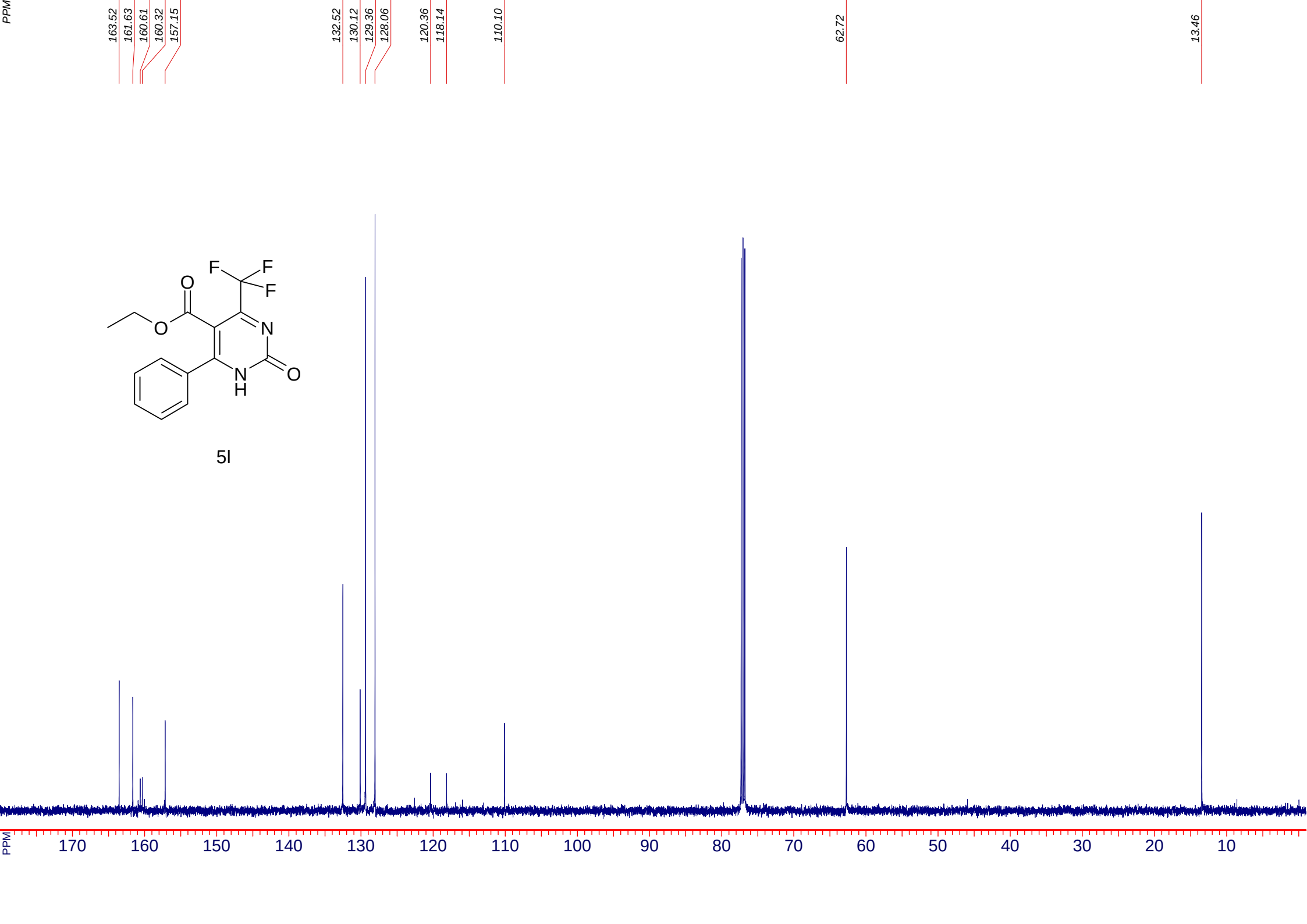
PPM
163.52
161.63
160.61
160.32
157.15
132.52
130.12
129.36
128.06
120.36
118.14
110.10
62.72
13.46
F
F
F
O
O
N
N
H
O
5l
PPM
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120
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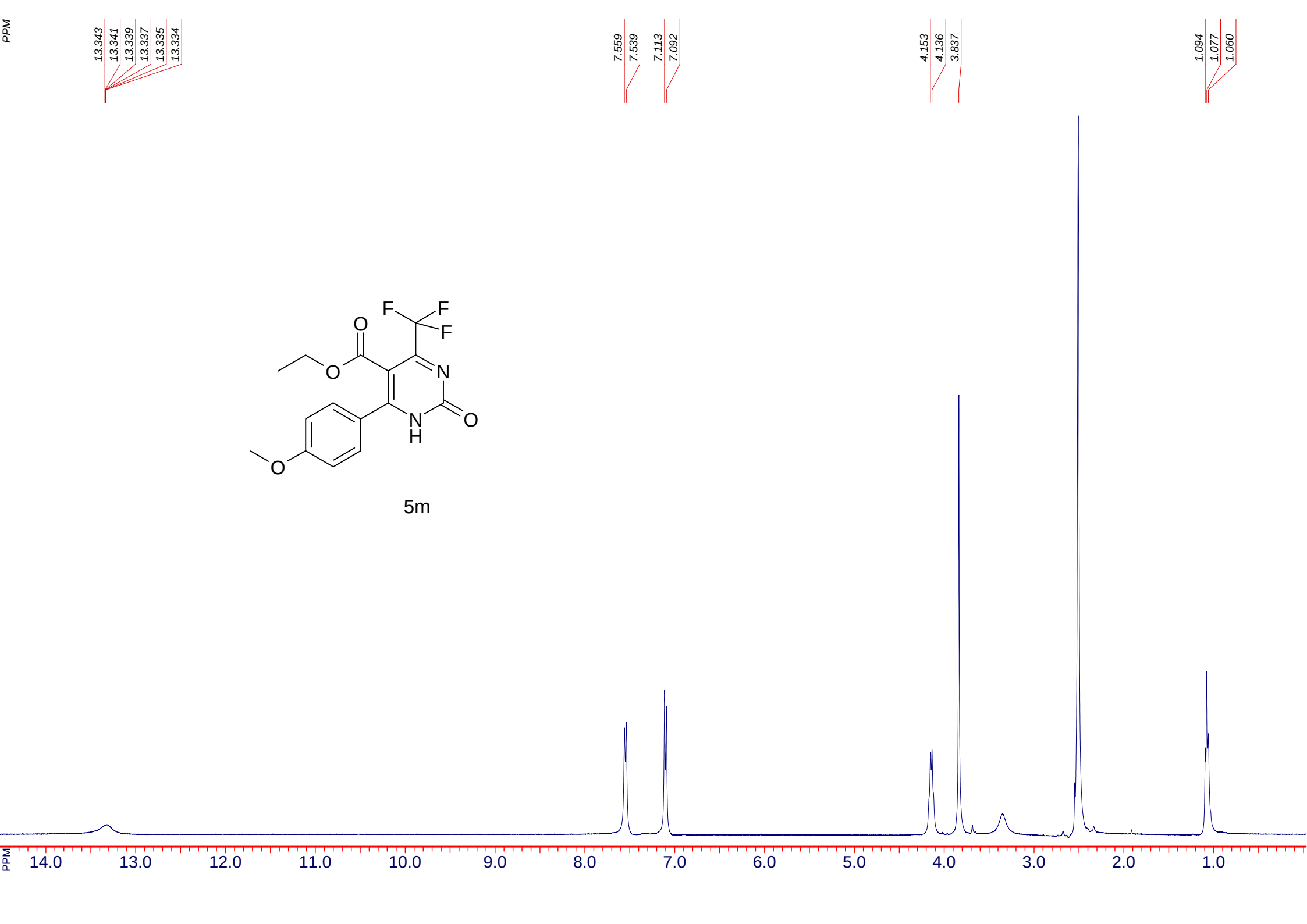
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13.337
13.335
13.334
7.559
7.539
7.113
7.092
4.153
4.136
3.837
1.094
1.077
1.060
F
F
F
O
O
N
N
H
O
O
5m
PPM
14.0
13.0
12.0
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10.0
9.0
8.0
7.0
6.0
5.0
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2.0
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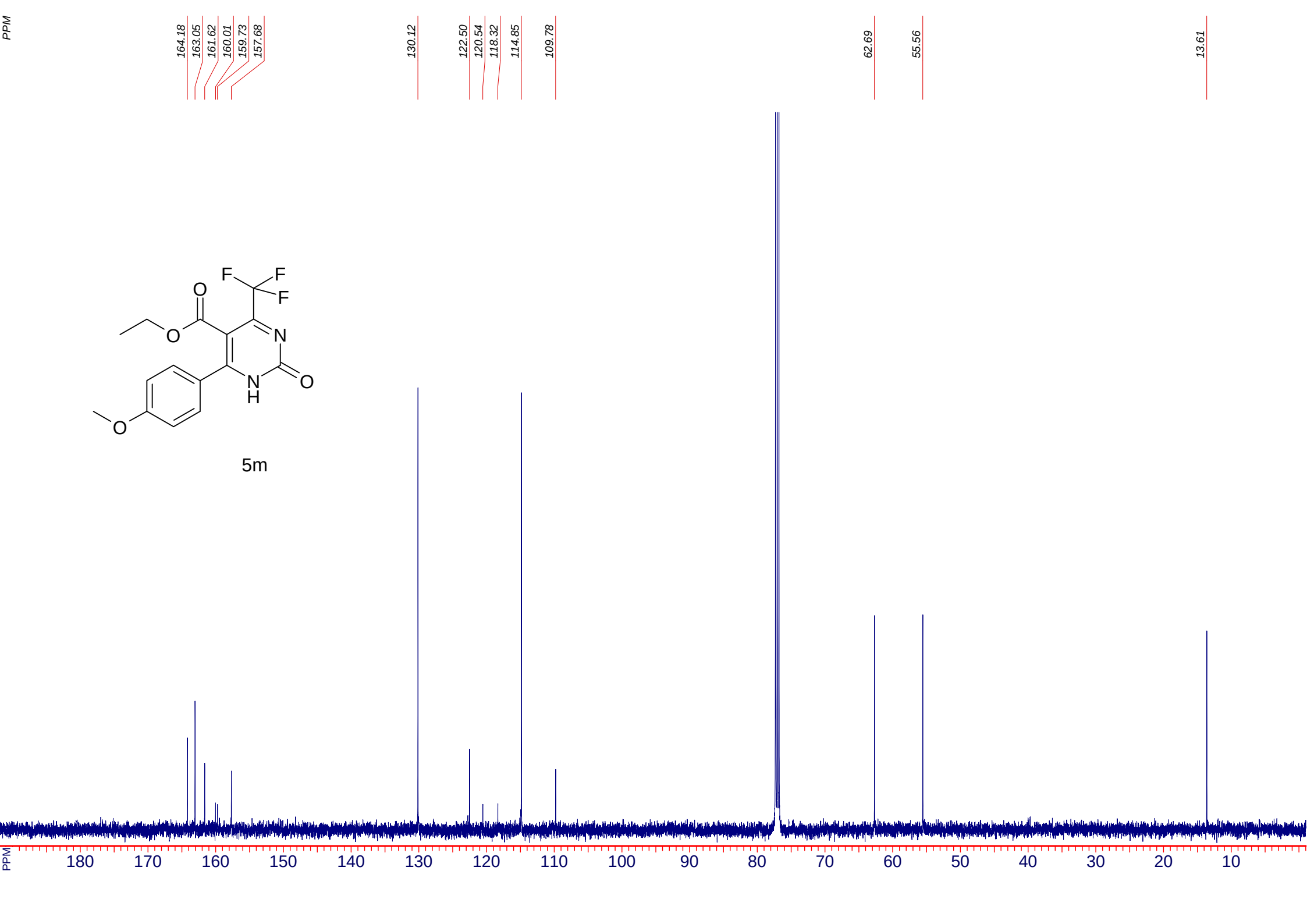
PPM
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160.01
159.73
157.68
130.12
122.50
120.54
118.32
114.85
109.78
62.69
55.56
13.61
F
F
F
O
O
N
N
H
O
O
5m
PPM
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160
150
140
130
120
110
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80
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30
20
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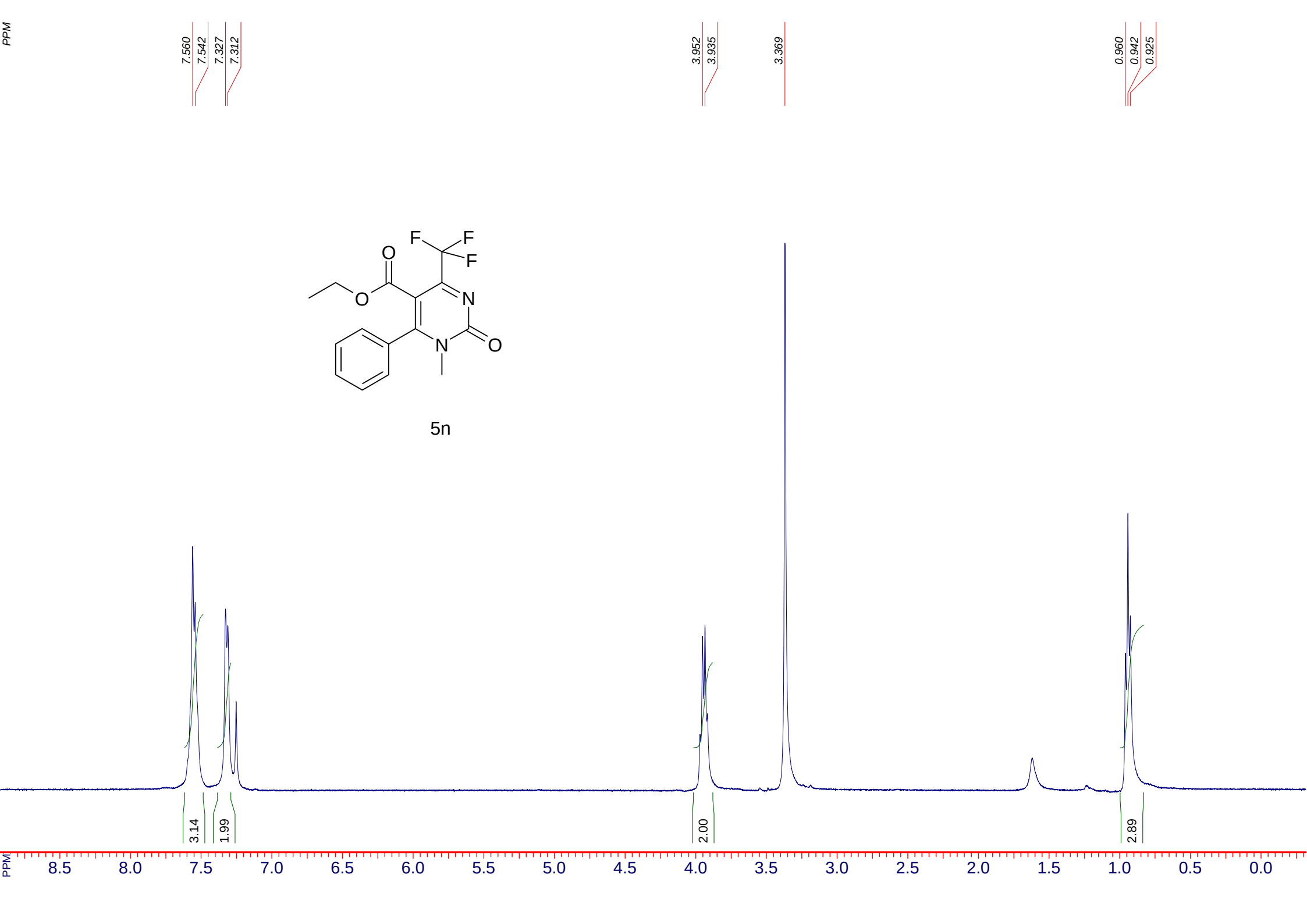
PPM
7.560
7.542
7.327
7.312
3.952
3.935
3.369
0.960
0.942
0.925
F
F
F
O
O
N
N
O
5n
3.14
1.99
2.00
2.89
PPM
8.5
8.0
7.5
7.0
6.5
6.0
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4.5
4.0
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3.0
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2.0
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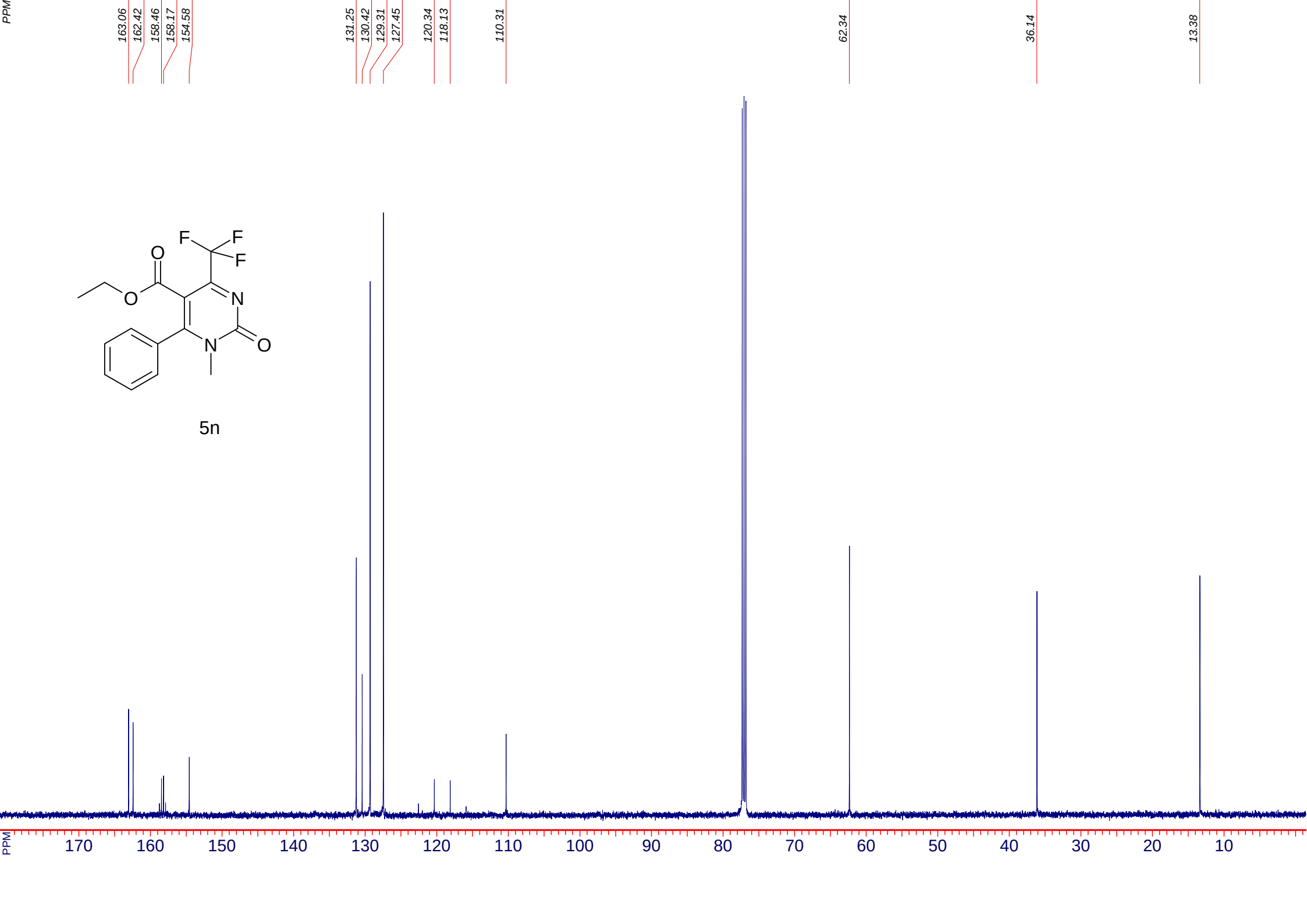
PPM
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158.46
158.17
154.58
131.25
130.42
129.31
127.45
120.34
118.13
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62.34
36.14
13.38
F
F
F
O
O
N
N
O
5n
PPM
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160
150
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130
120
110
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80
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20
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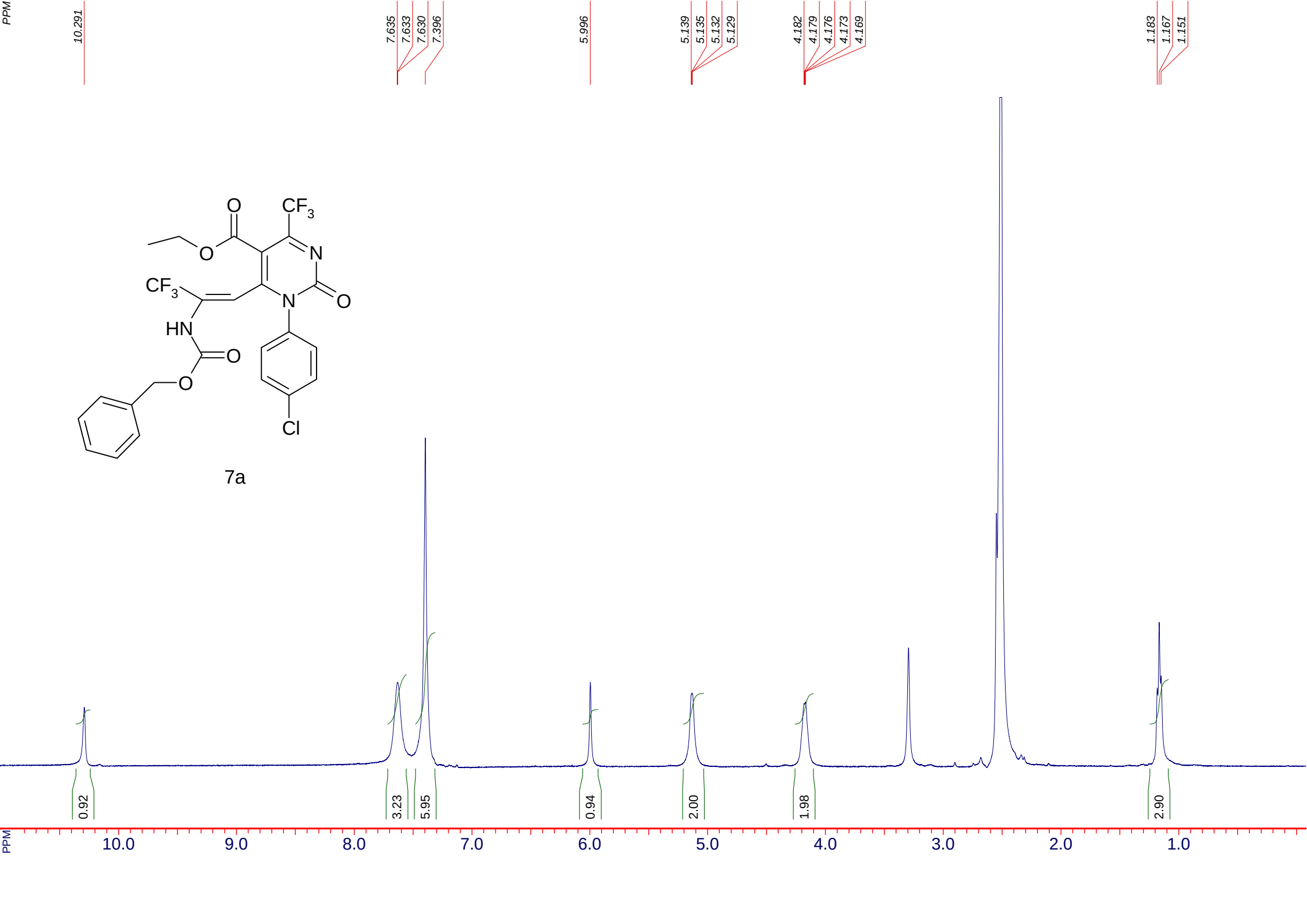
PPM
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7.635
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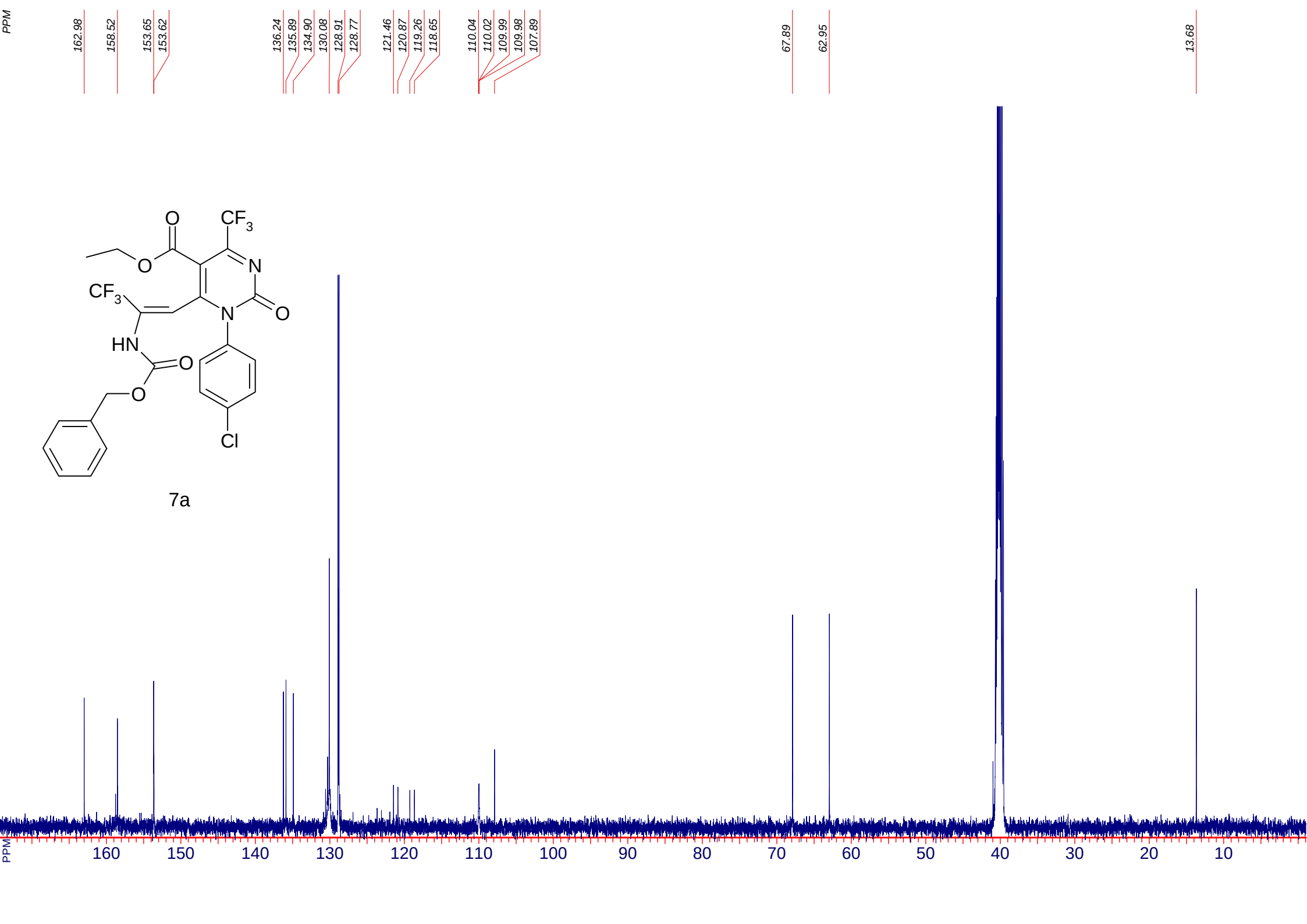
7.630
7.396
5.996
5.139
5.135
5.132
5.129
4.182
4.179
4.176
4.173
4.169
1.183
1.167
1.151
O
CF3
O
N
CF3
N
O
HN
O
O
Cl
7a
0.92
3.23
5.95
0.94
2.00
1.98
2.90
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


PPM
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158.52
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153.62
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134.90
130.08
128.91
128.77
121.46
120.87
119.26
118.65
110.04
110.02
109.99
109.98
107.89
67.89
62.95
13.68
O
CF3
O
N
CF3
N
O
HN
O
O
Cl
7a
PPM
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150
140
130
120
110
100
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80
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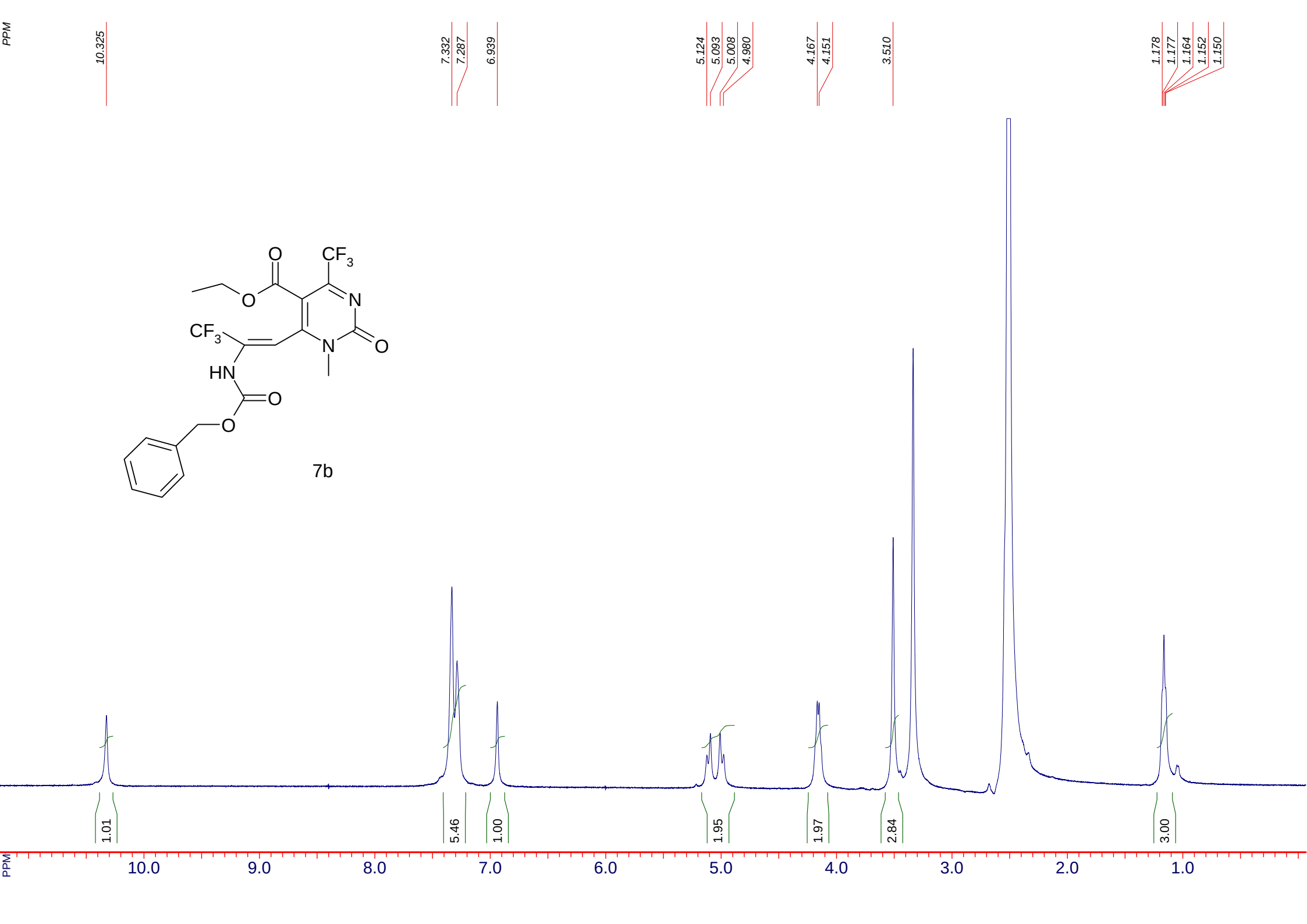
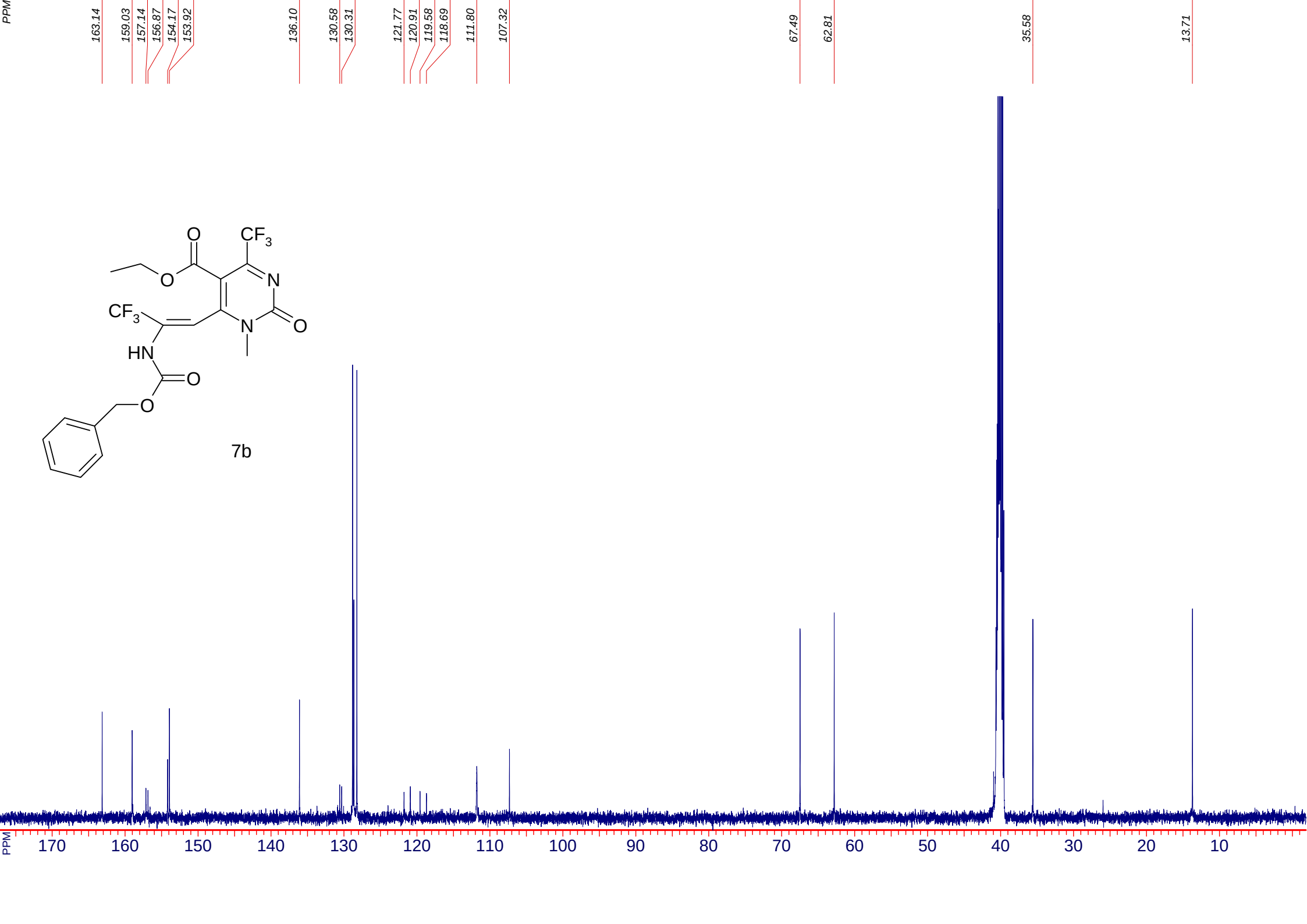
20
10


PPM
10.325
7.332
7.287
6.939
5.124
5.093
5.008
4.980
4.167
4.151
3.510
1.178
1.177
1.164
1.152
1.150
O
CF3
O
N
CF3
N
O
HN
O
O
7b
1.01
5.46
1.00
1.95
1.97
2.84
3.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


PPM
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157.14
156.87
154.17
153.92
136.10
130.58
130.31
121.77
120.91
119.58
118.69
111.80
107.32
67.49
62.81
35.58
13.71
O
CF3
O
N
CF3
N
O
HN
O
O
7b
PPM
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160
150
140
130
120
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100
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80
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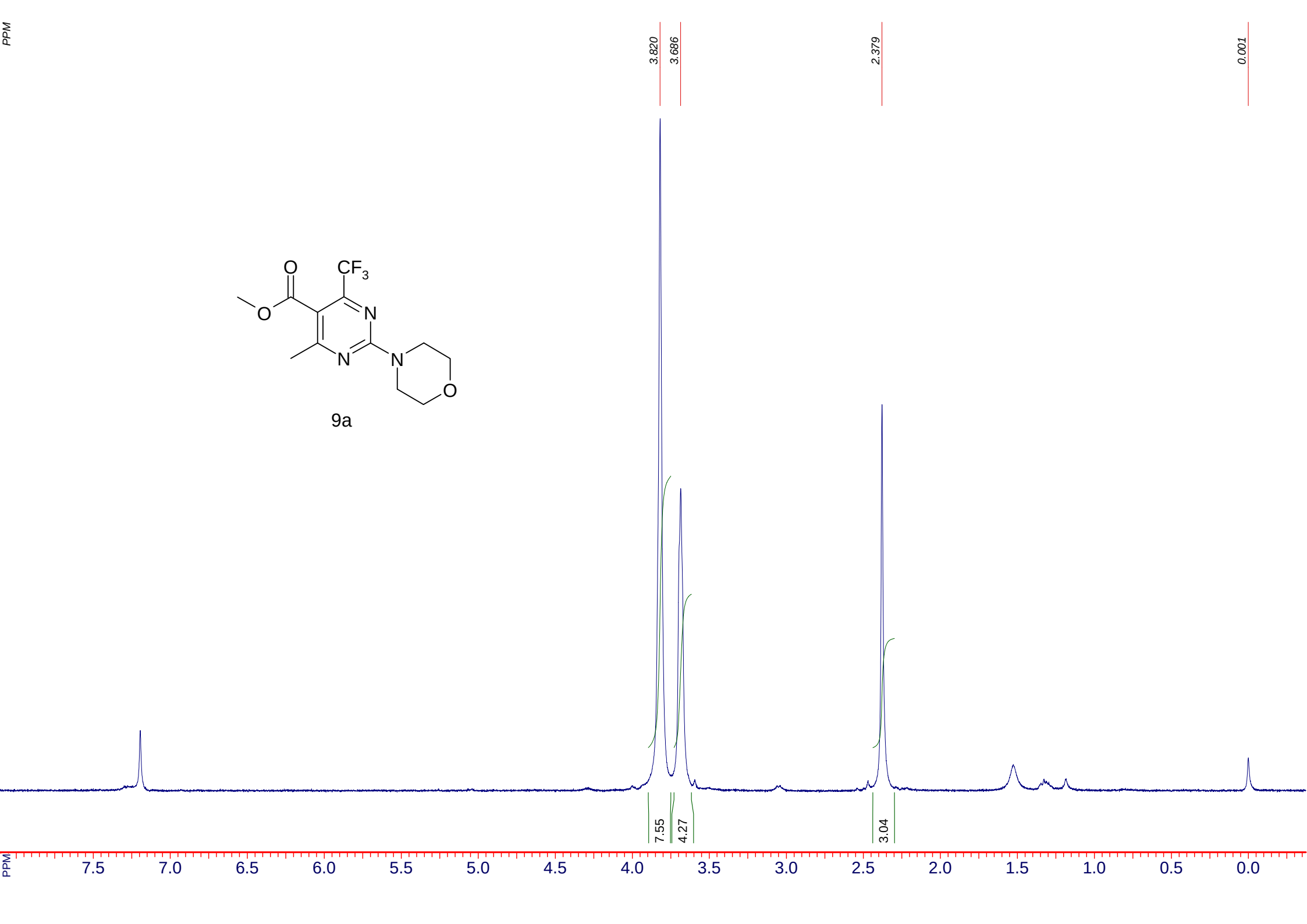
40
30
20
10


PPM
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3.686
2.379
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CF3
O
N
N
N
O
9a
7.55
4.27
3.04
PPM
7.5
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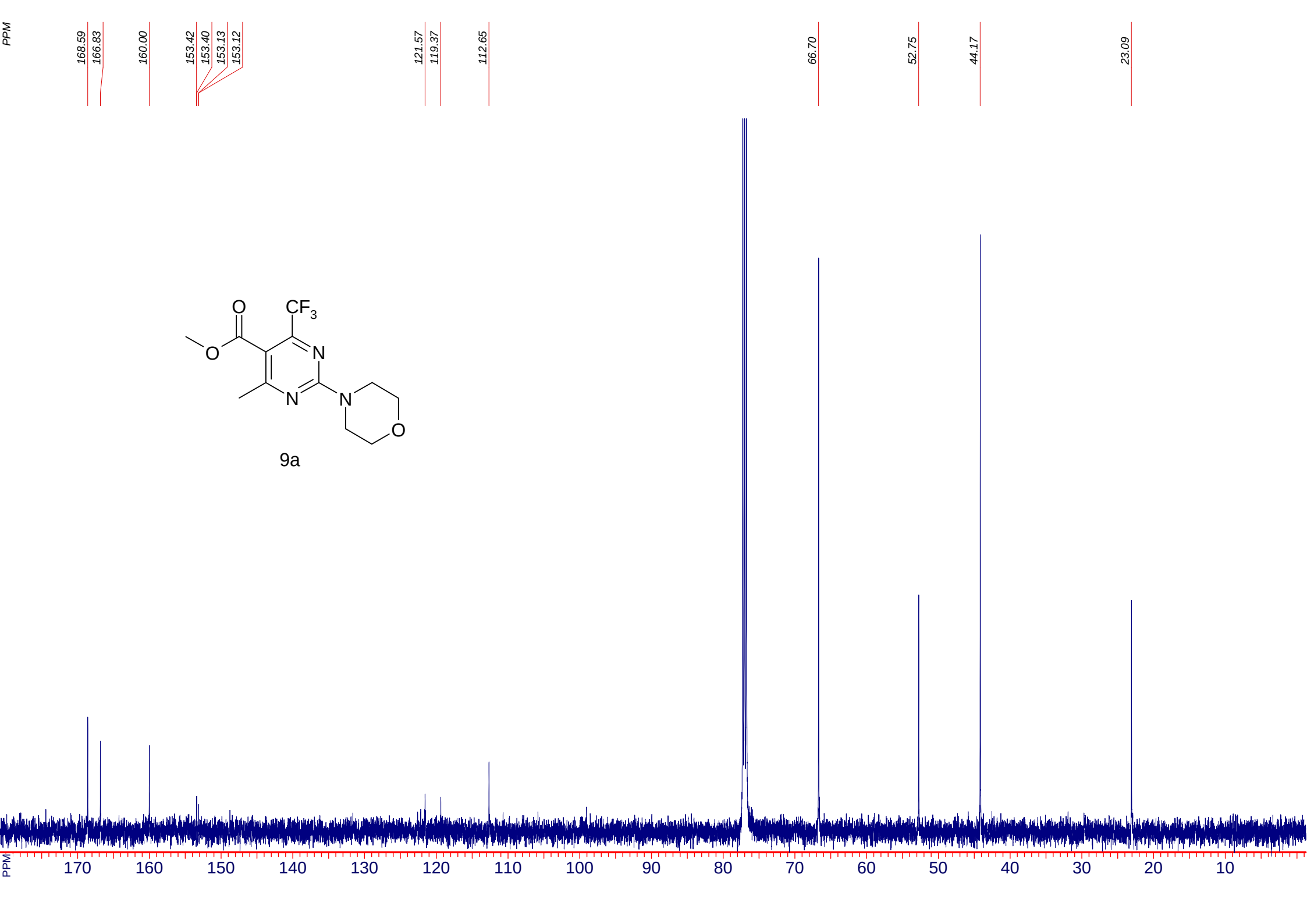
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


PPM
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153.40
153.13
153.12
121.57
119.37
112.65
66.70
52.75
44.17
23.09
O
CF3
O
N
N
N
O
9a
PPM
170
160
150
140
130
120
110
100
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80
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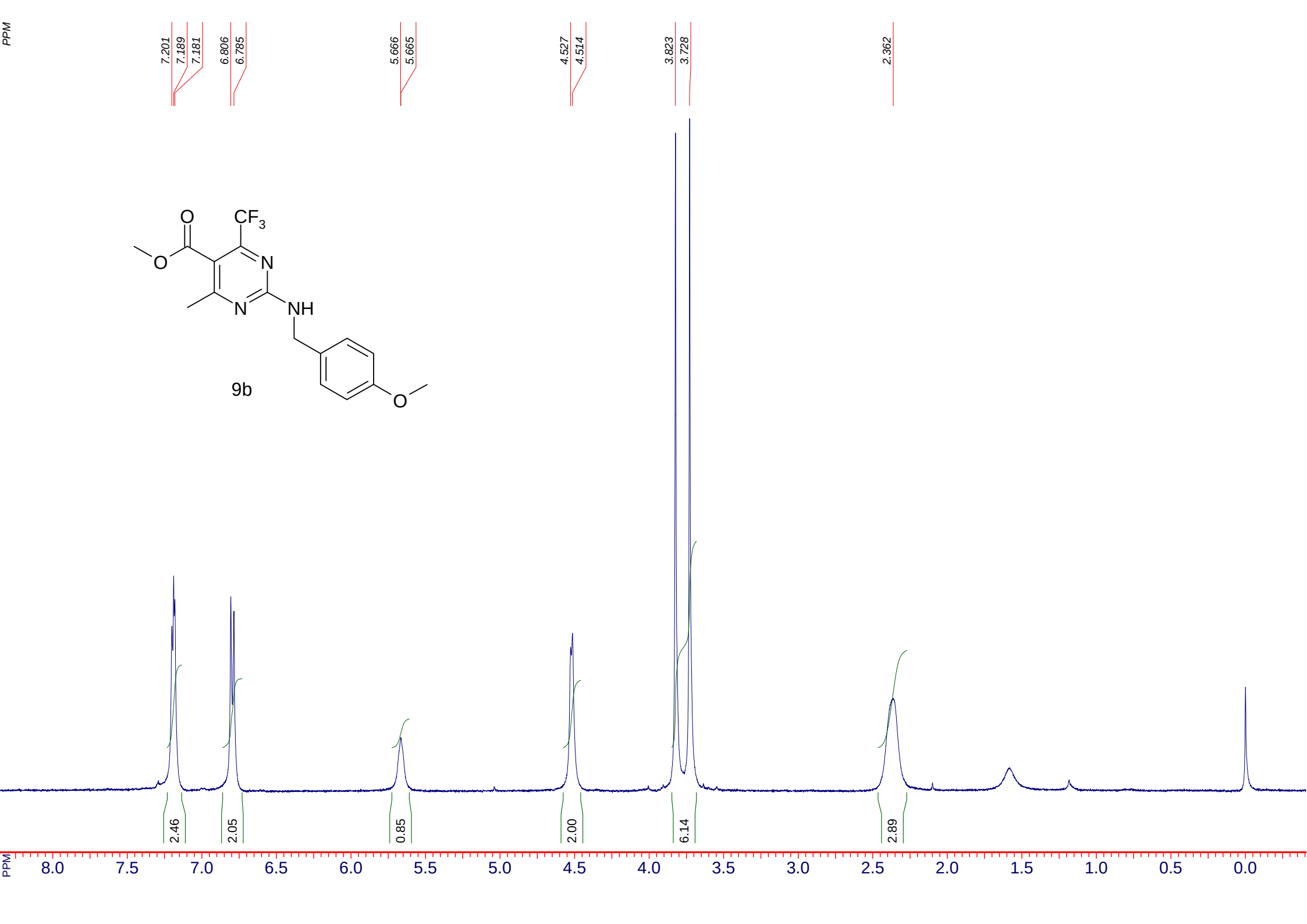
60
50
40
30
20
10


PPM
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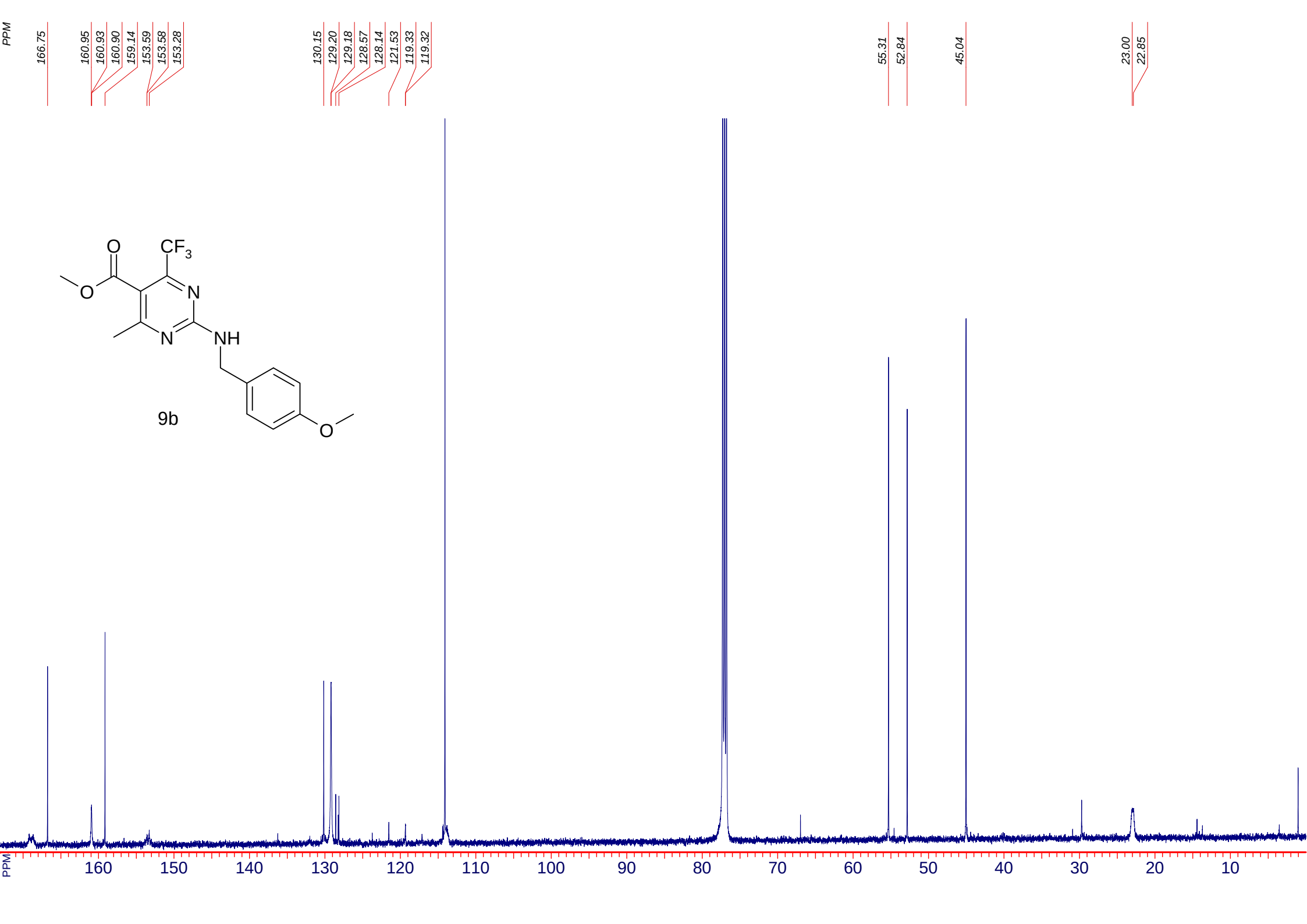
7.189
7.181
6.806
6.785
5.666
5.665
4.527
4.514
3.823
3.728
2.362
O
CF3
O
N
N
NH
O
9b
2.46
2.05
0.85
2.00
6.14
2.89
PPM
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


PPM
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160.95
160.93
160.90
159.14
153.59
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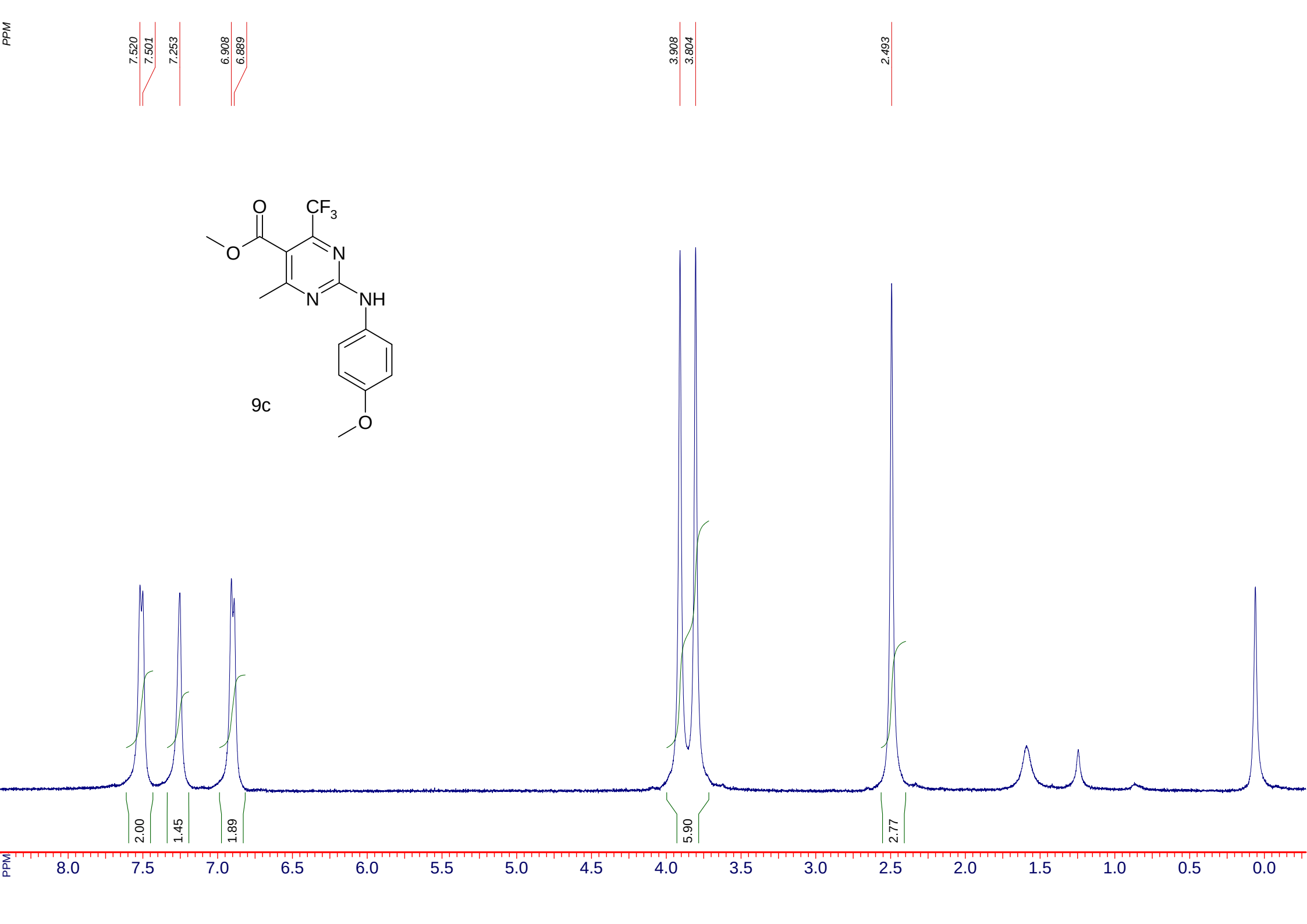
153.28
130.15
129.20
129.18
128.57
128.14
121.53
119.33
119.32
55.31
52.84
45.04
23.00
22.85
O
CF3
O
N
N
NH
O
9b
PPM
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


PPM
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7.501
7.253
6.908
6.889
3.908
3.804
2.493
O
CF3
O
N
N
NH
O
9c
2.00
1.45
1.89
5.90
2.77
PPM
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
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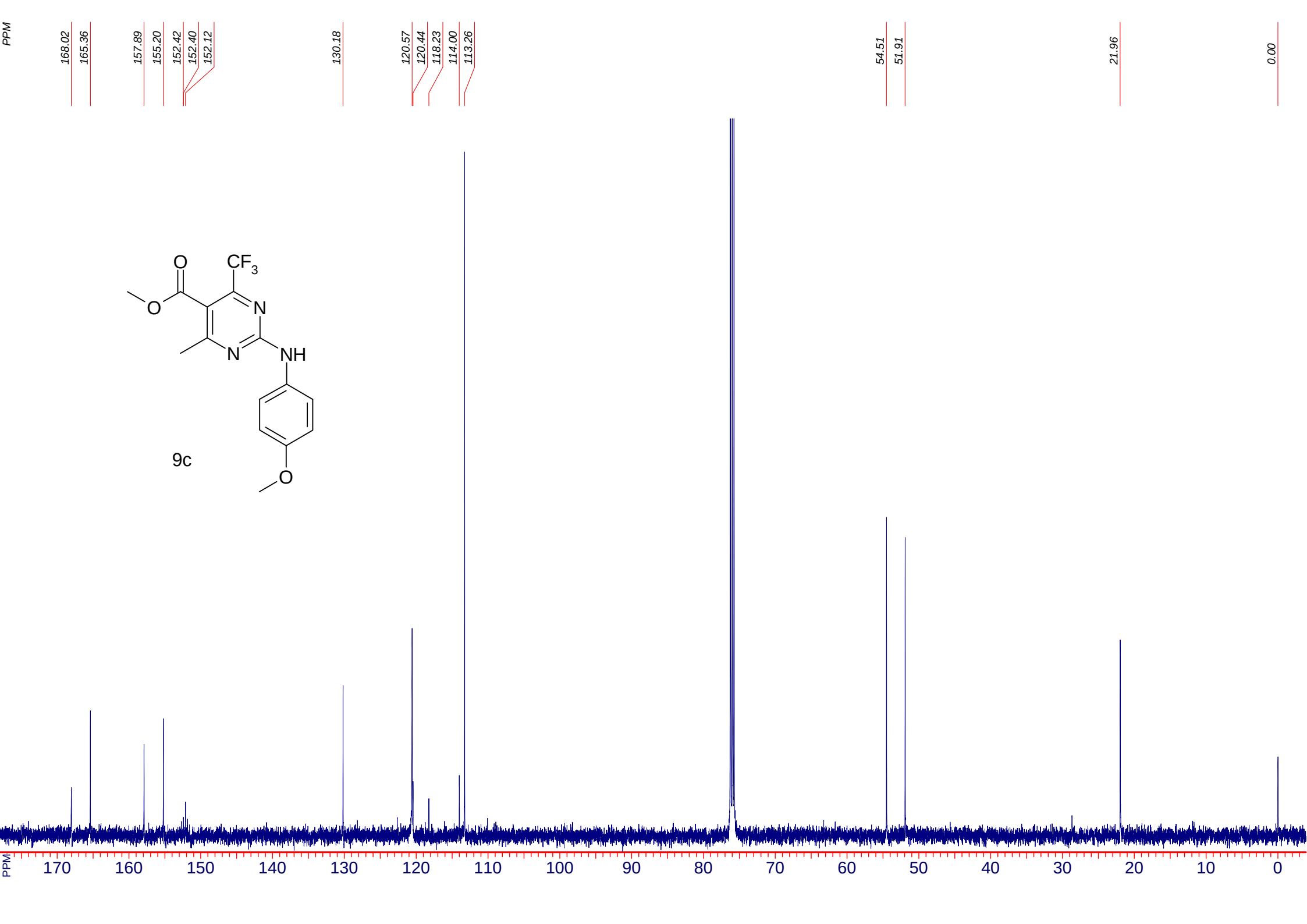
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152.40
152.12
130.18
120.57
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118.23
114.00
113.26
54.51
51.91
21.96
0.00
O
CF3
O
N
N
NH
O
9c
PPM
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150
140
130
120
110
100
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70
60
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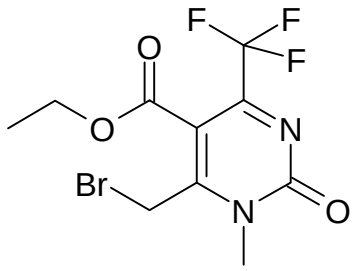
30
20
10
0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O
O
N
Br
N
O

10

PPM
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4.332
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1.325
1.309
2.00
2.04
2.97
2.92
PPM
8.0
7.5
7.0
6.5
6.0
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4.5
4.0
3.5
3.0
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2.0
1.5
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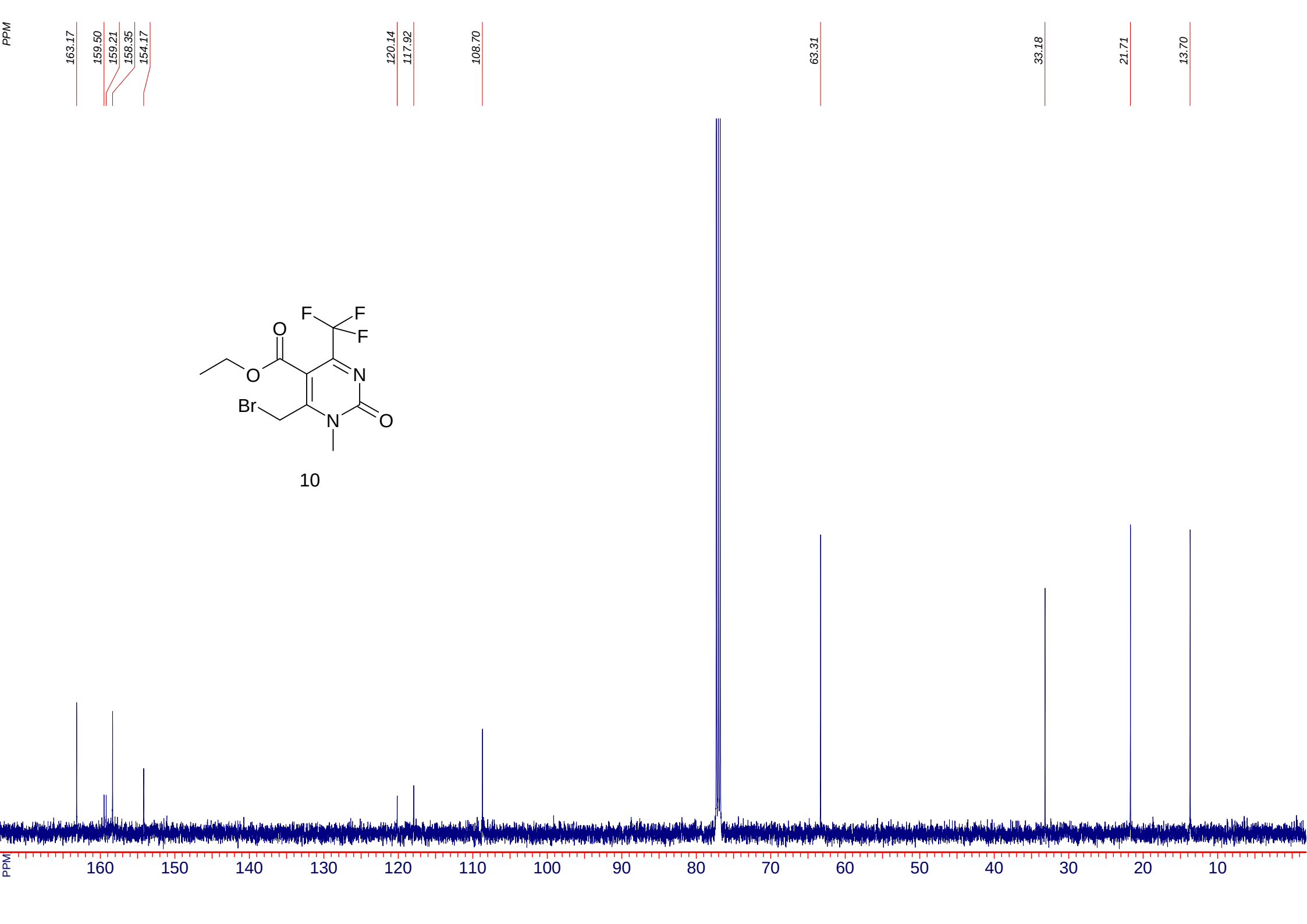
PPM
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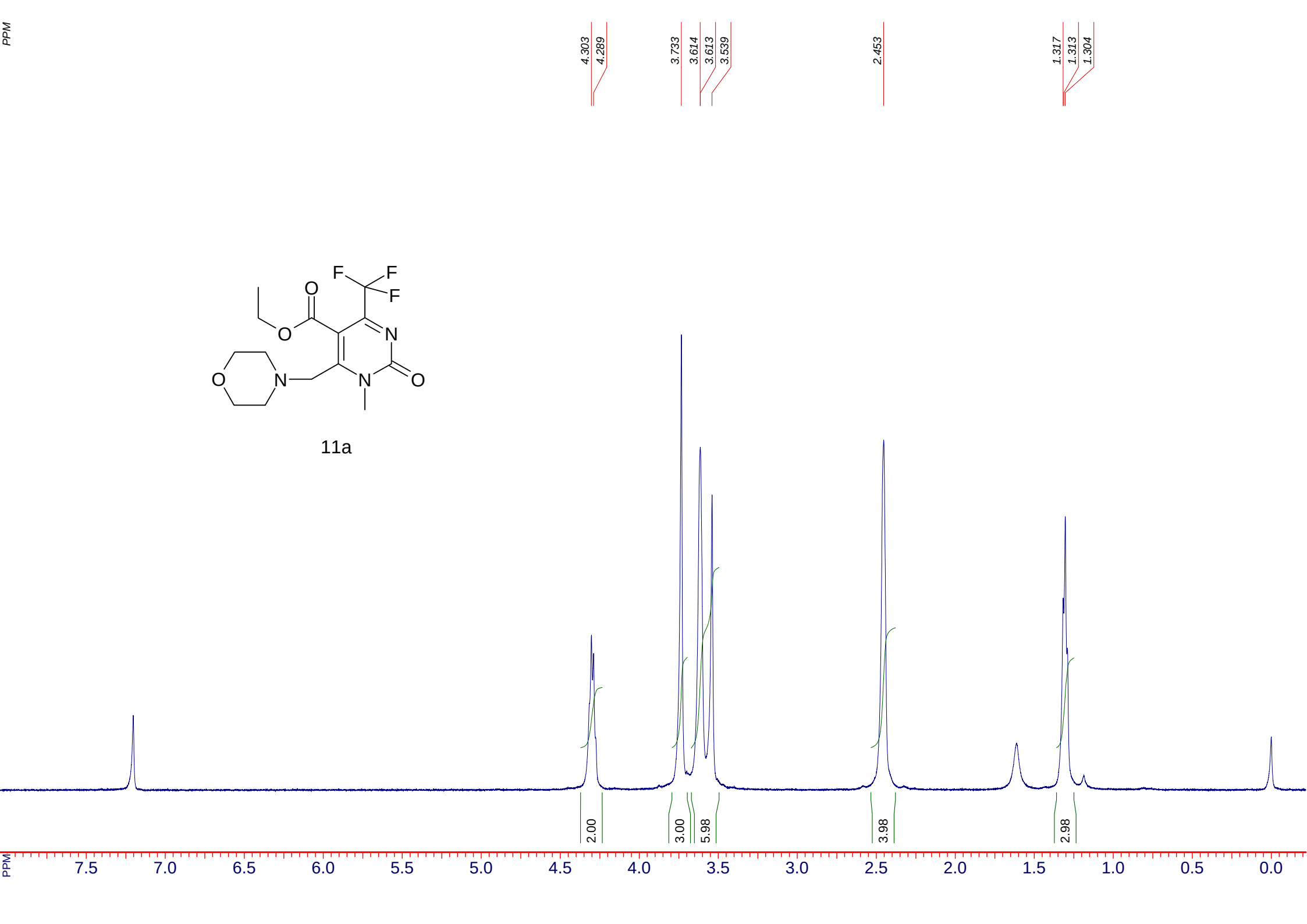
159.50
159.21
158.35
154.17
120.14
117.92
108.70
63.31
33.18
21.71
13.70
F
F
F
O
O
N
Br
N
O
10
PPM
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


PPM
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4.289
3.733
3.614
3.613
3.539
2.453
1.317
1.313
1.304
F
F
F
O
O
N
O
N
N
O
2.00
3.00
5.98
3.98
2.98
PPM
7.5
7.0
6.5
6.0
5.5
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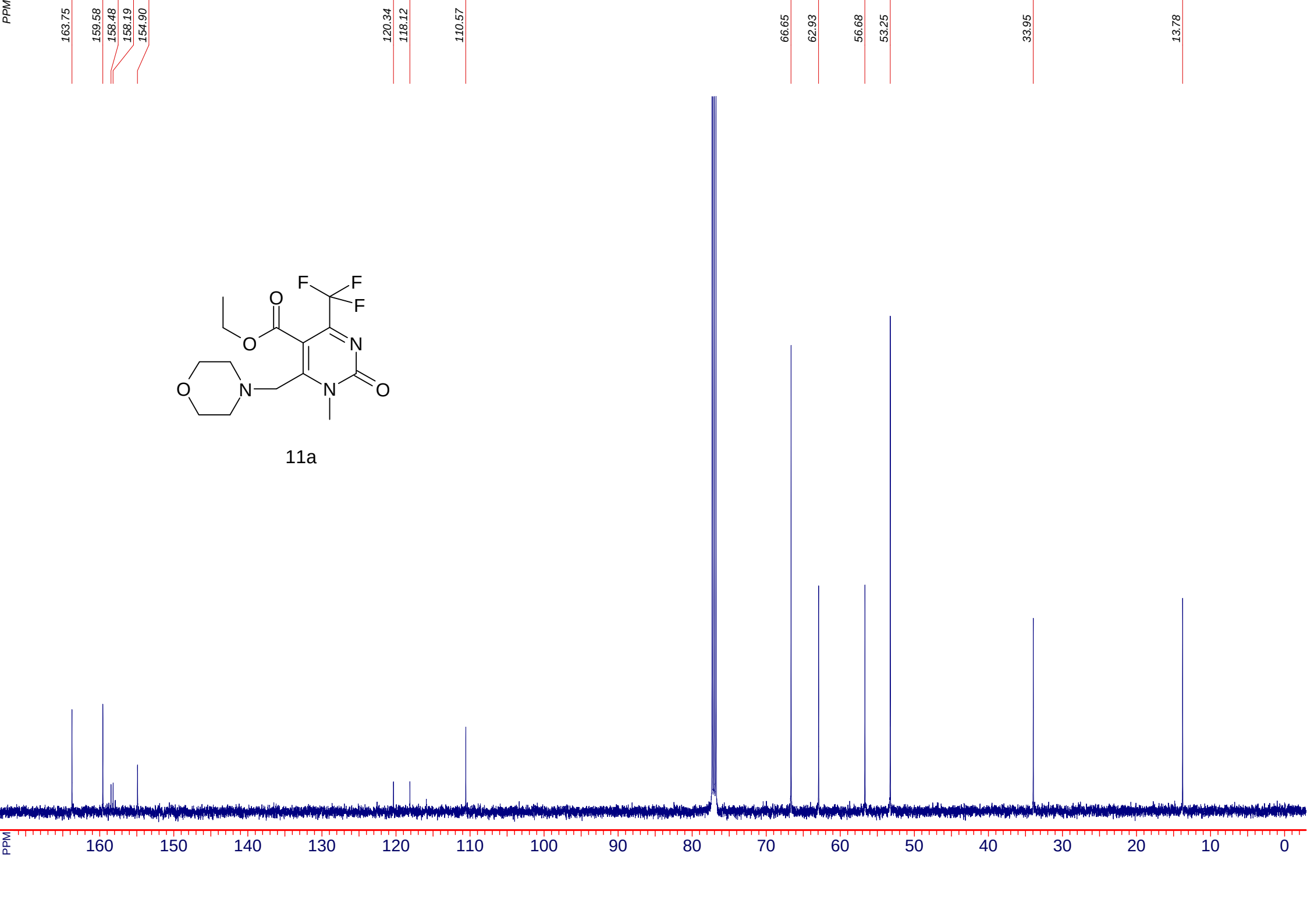
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

11a


PPM
163.75
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158.48
158.19
154.90
120.34
118.12
110.57
66.65
62.93
56.68
53.25
33.95
13.78
F
F
F
O
O
N
O
N
N
O
11a
PPM
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150
140
130
120
110
100
90
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70
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30
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10
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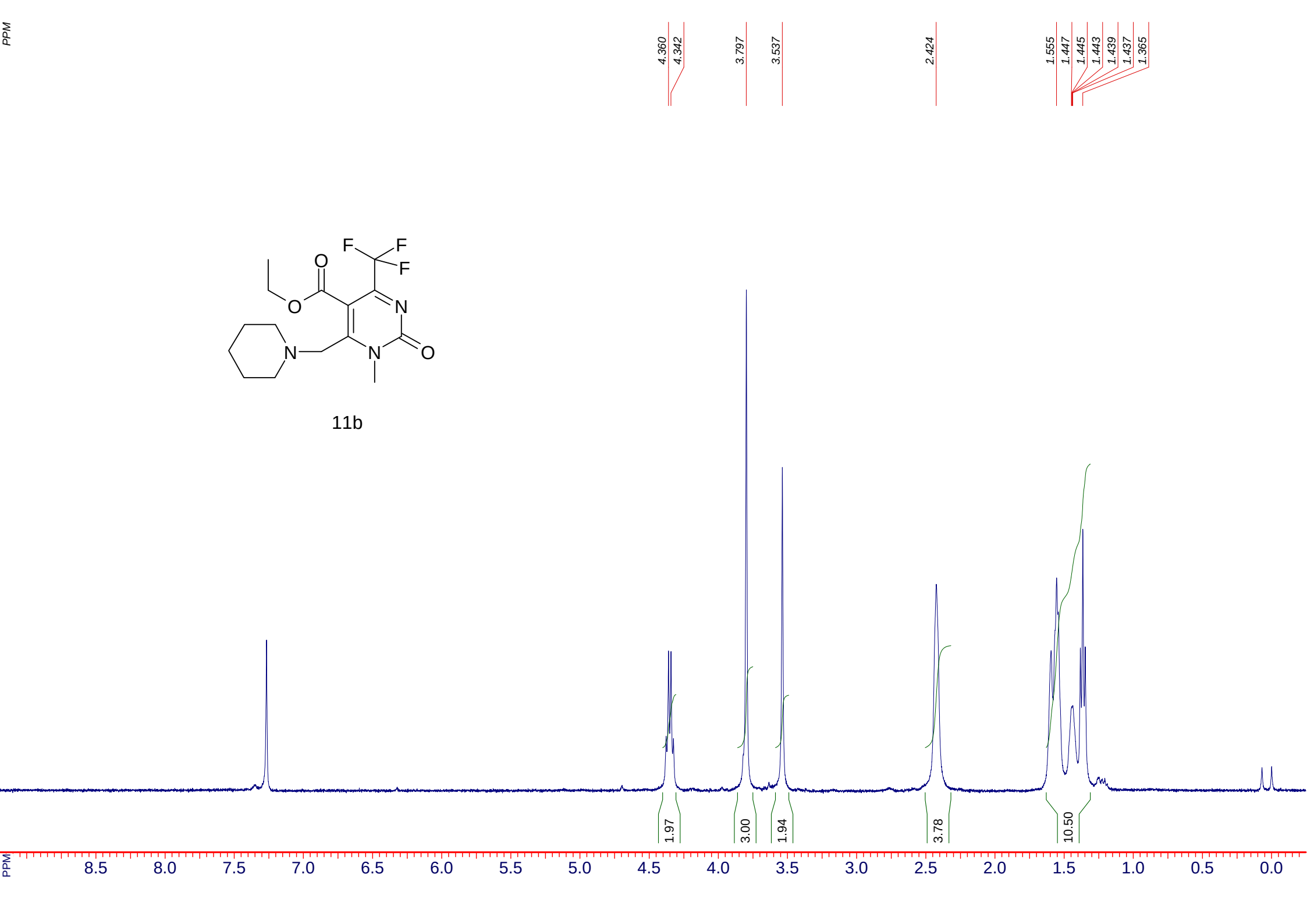
PPM
4.360
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3.537
2.424
1.555
1.447
1.445
1.443
1.439
1.437
1.365
F
F
F
O
O
N
N
N
O
11b
1.97
3.00
1.94
3.78
10.50
PPM
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
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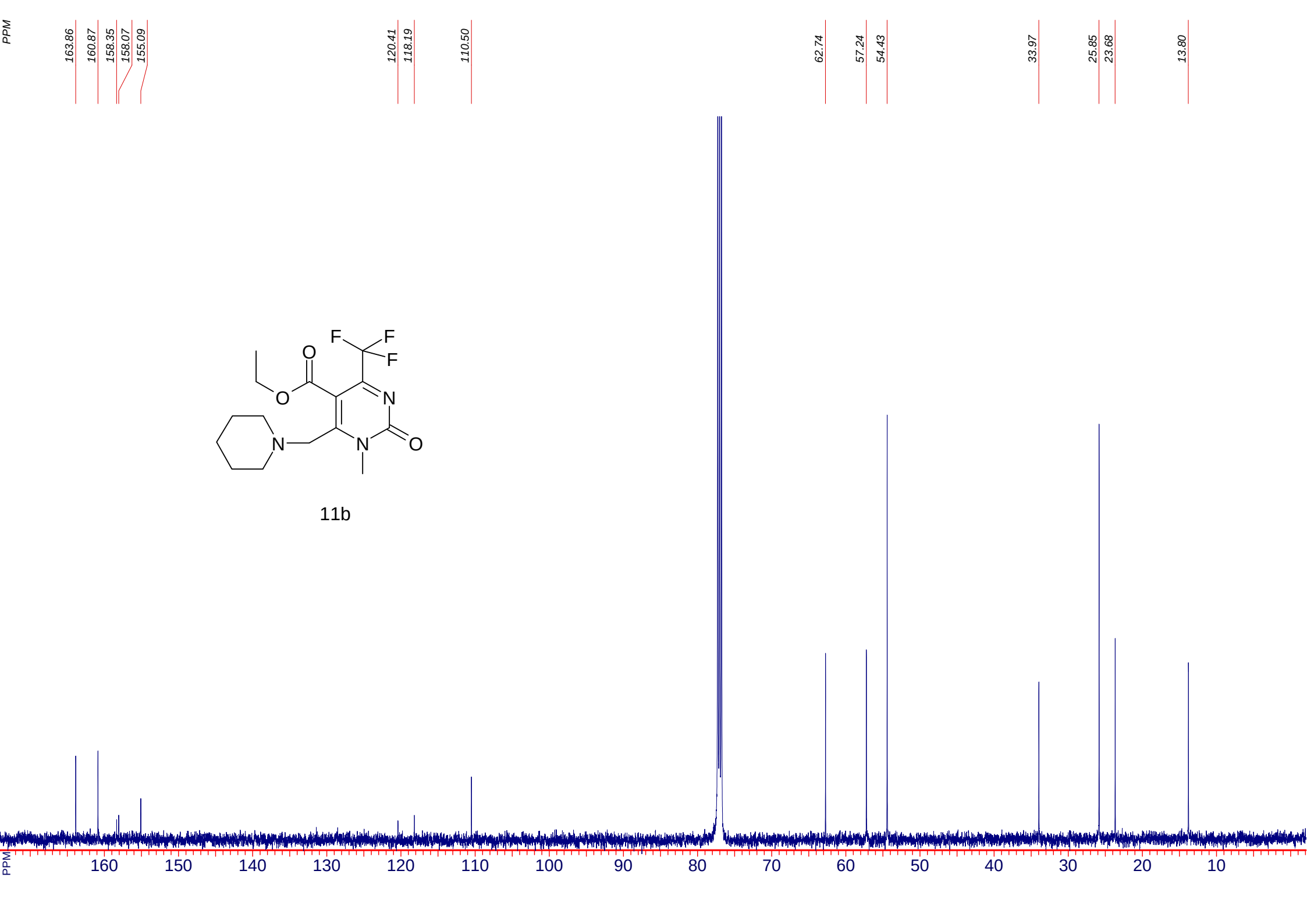
PPM
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158.07
155.09
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110.50
62.74
57.24
54.43
33.97
25.85
23.68
13.80
F
F
F
O
O
N
N
N
O
11b
PPM
160
150
140
130
120
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100
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80
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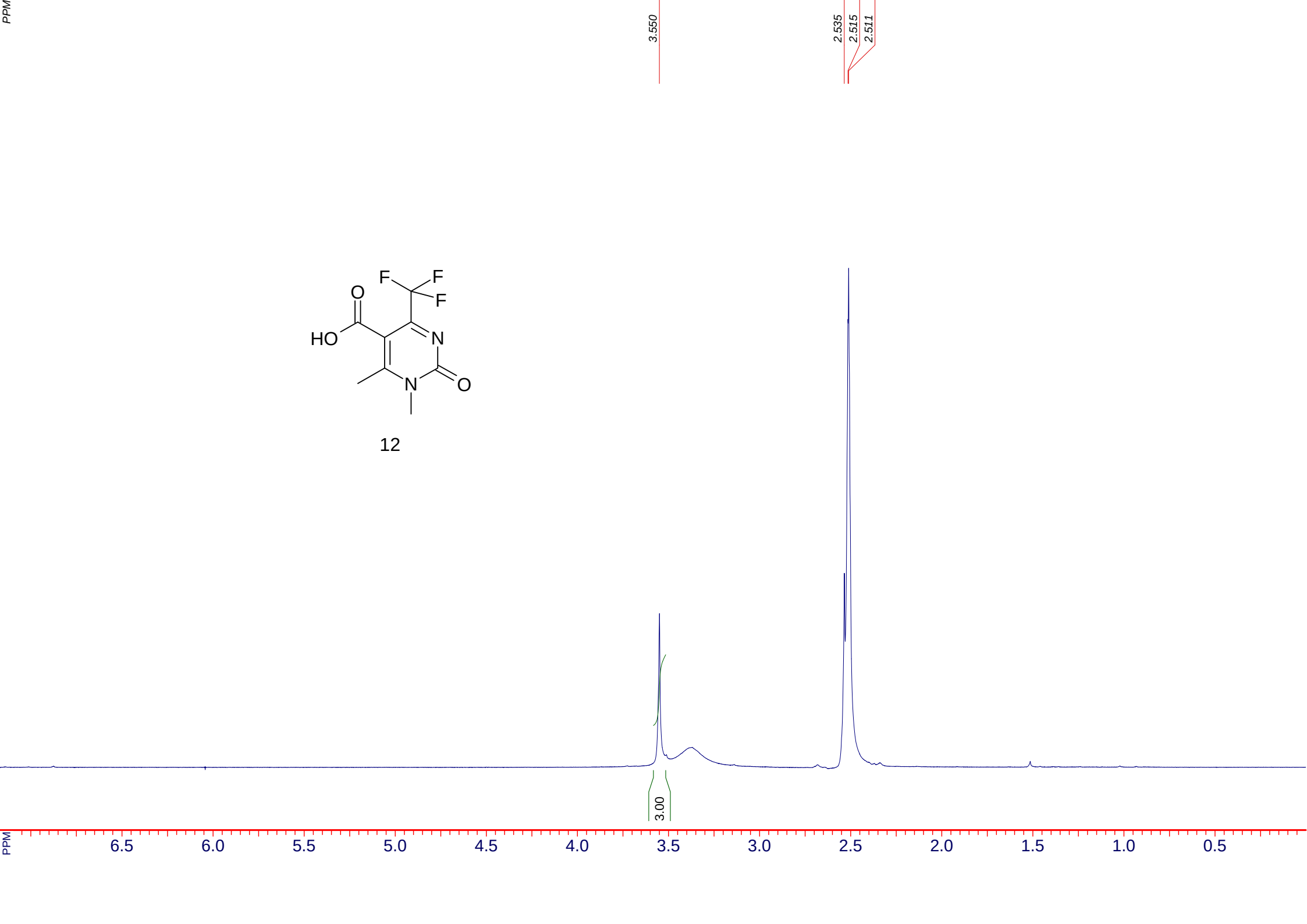
PPM
3.550
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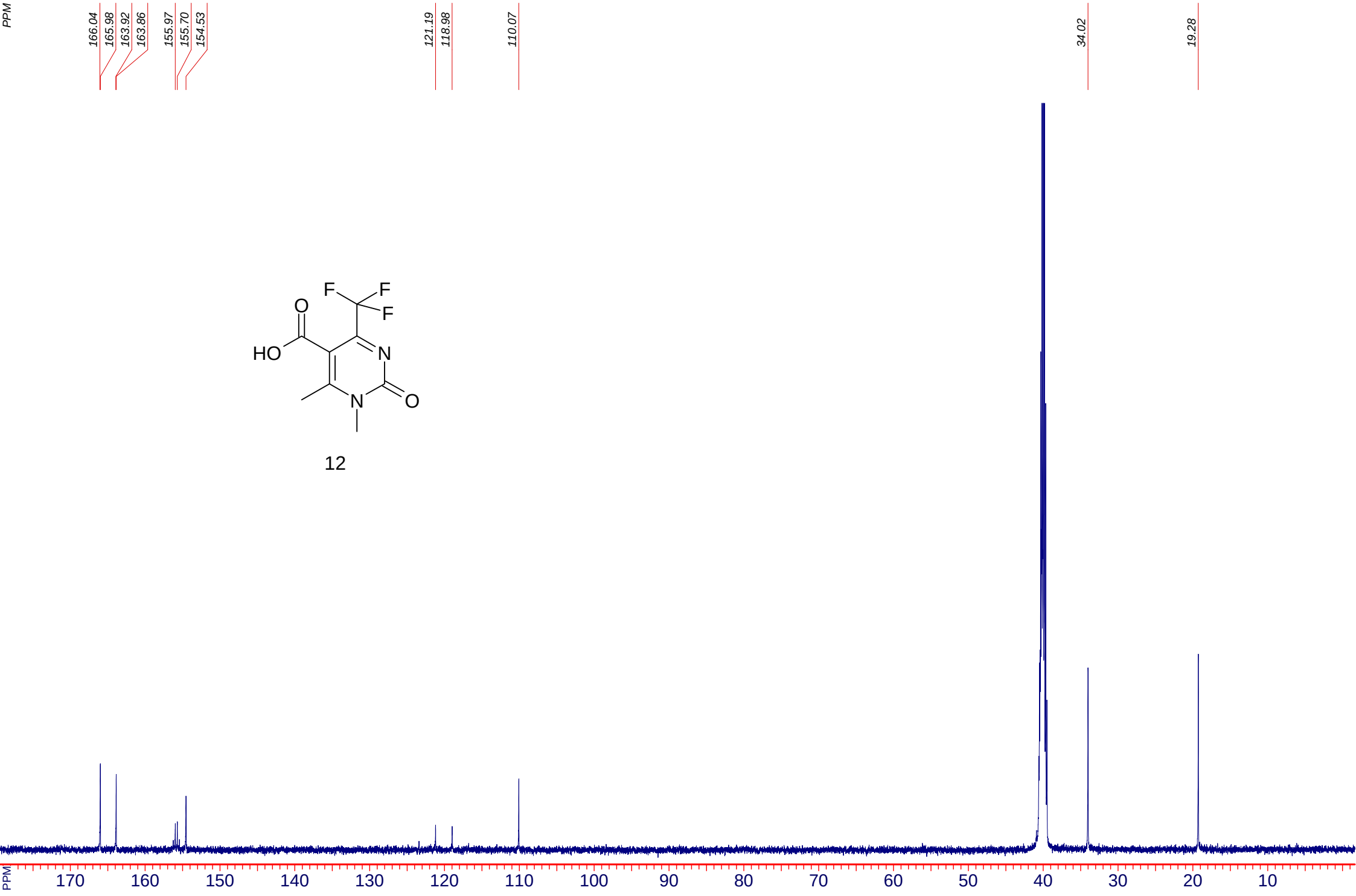
2.515
2.511
F
F
F
O
HO
N
N
O
12
3.00
PPM
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


PPM
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163.92
163.86
155.97
155.70
154.53
121.19
118.98
110.07
34.02
19.28
F
F
F
O
HO
N
N
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PPM
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150
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80
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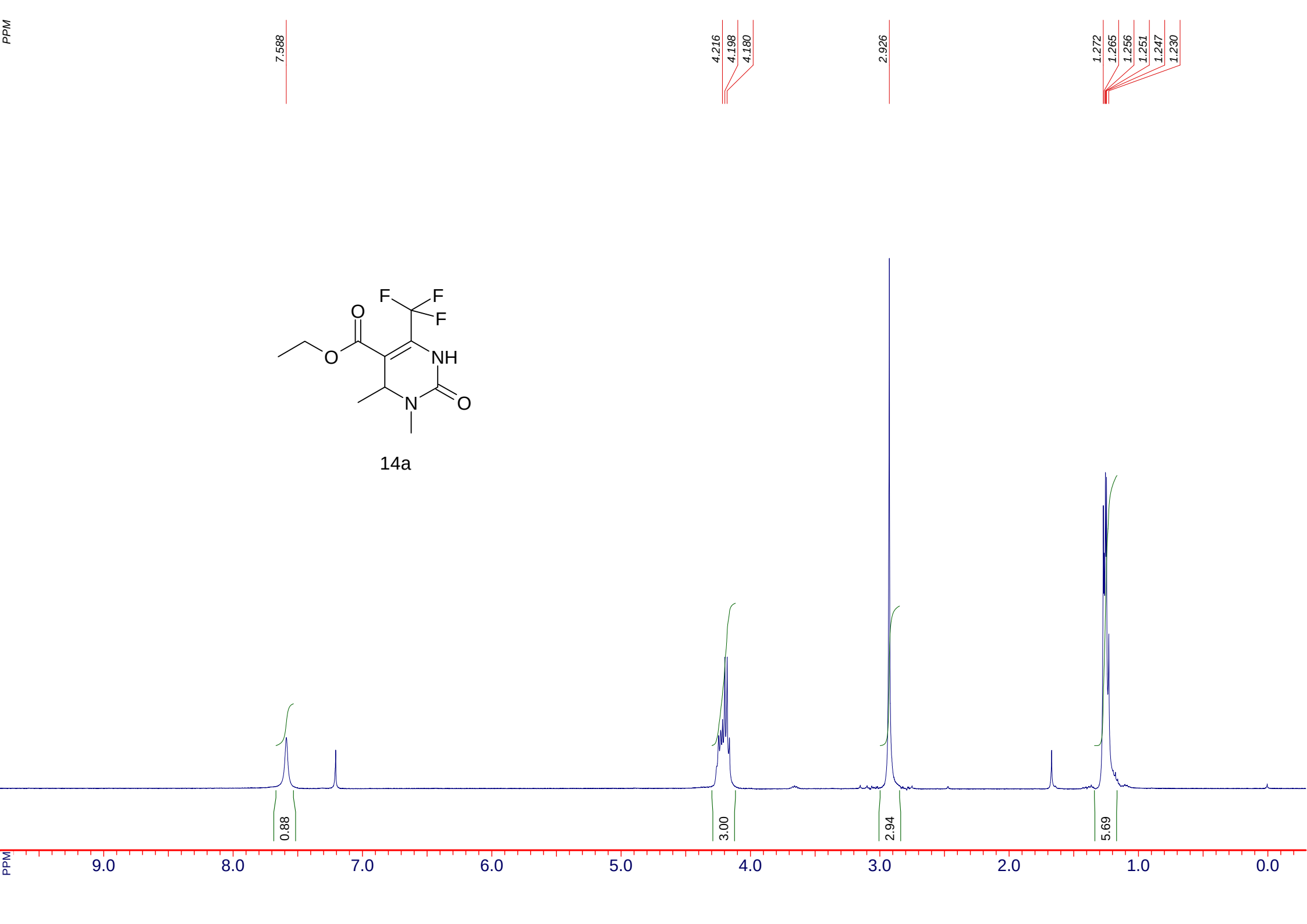
PPM
7.588
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4.180
2.926
1.272
1.265
1.256
1.251
1.247
1.230
F
F
F
O
O
NH
N
O
14a
0.88
3.00
2.94
5.69
PPM
9.0
8.0
7.0
6.0
5.0
4.0
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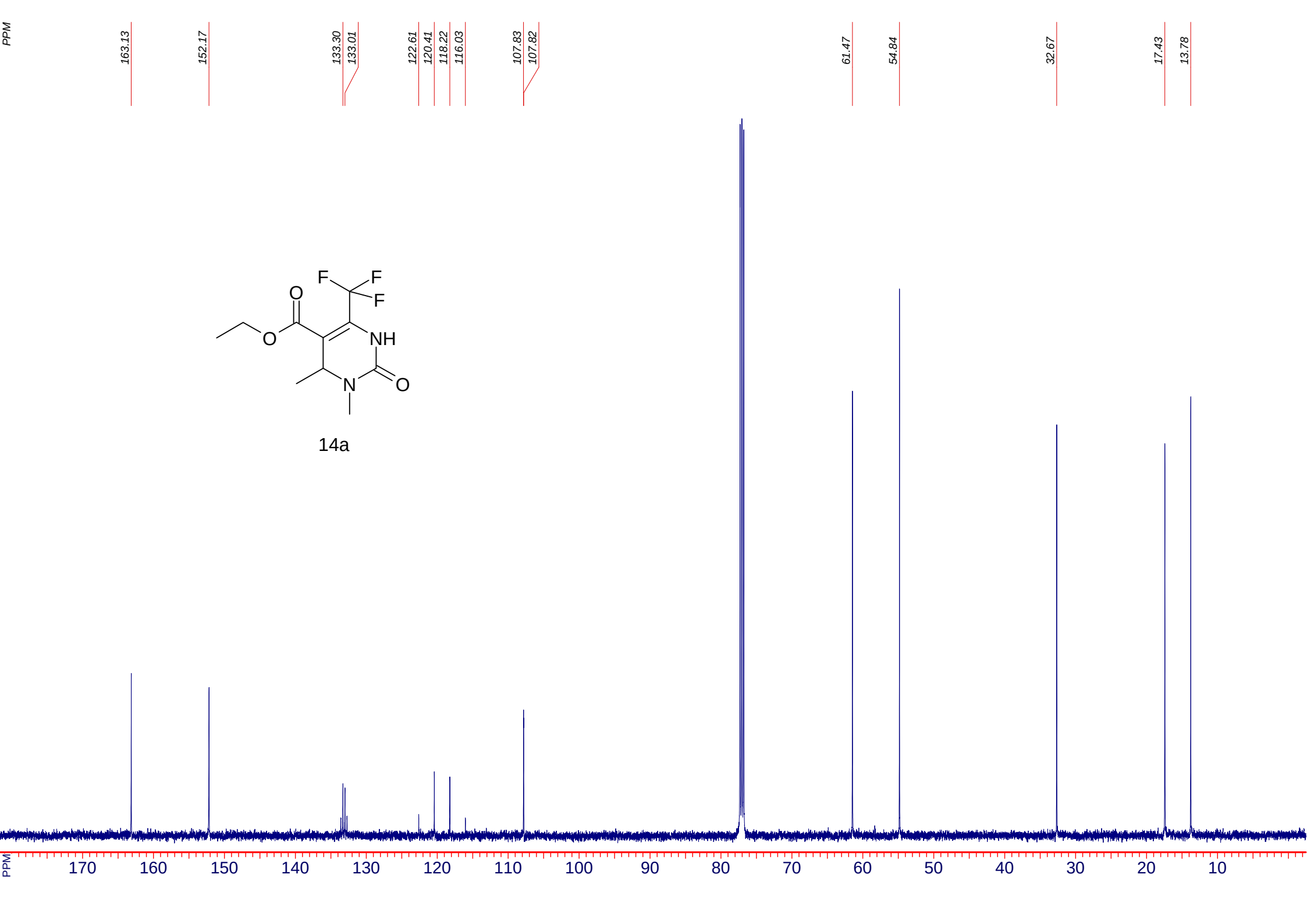
2.0
1.0
0.0


PPM
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133.30
133.01
122.61
120.41
118.22
116.03
107.83
107.82
61.47
54.84
32.67
17.43
13.78
F
F
F
O
O
NH
N
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14a
PPM
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160
150
140
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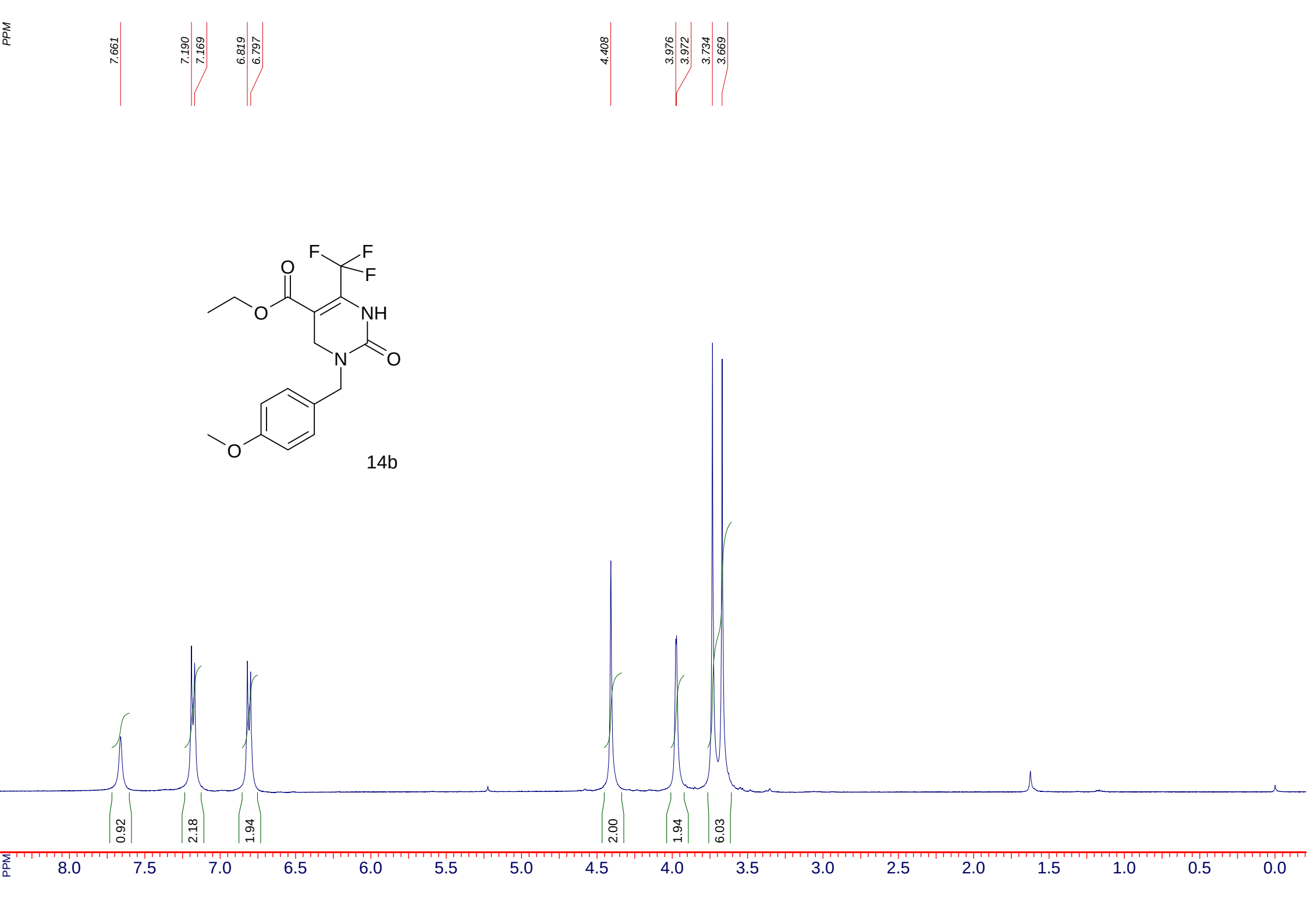
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4.408
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3.972
3.734
3.669
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F
F
O
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NH
N
O
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14b
0.92
2.18
1.94
2.00
1.94
6.03
PPM
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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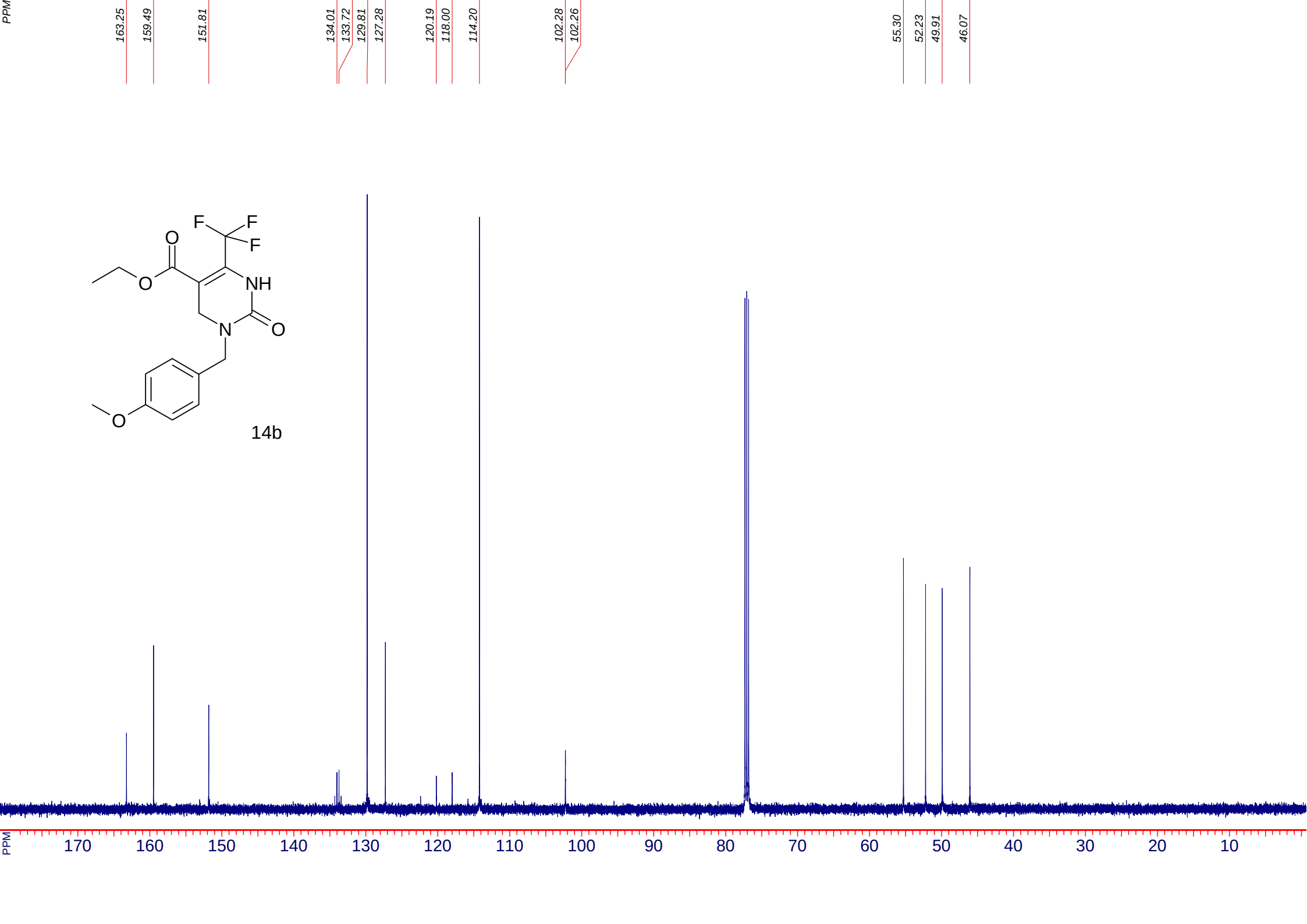
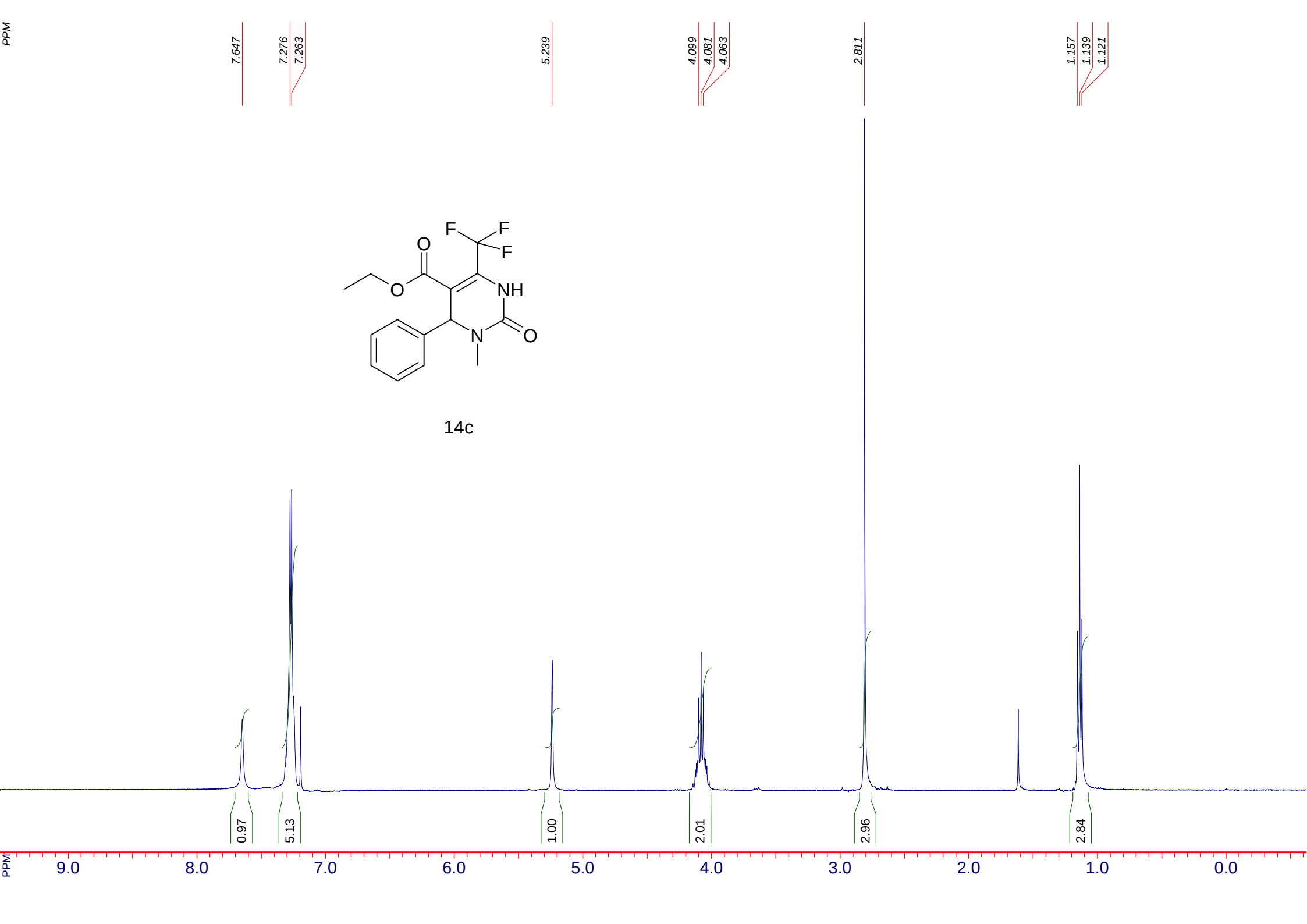
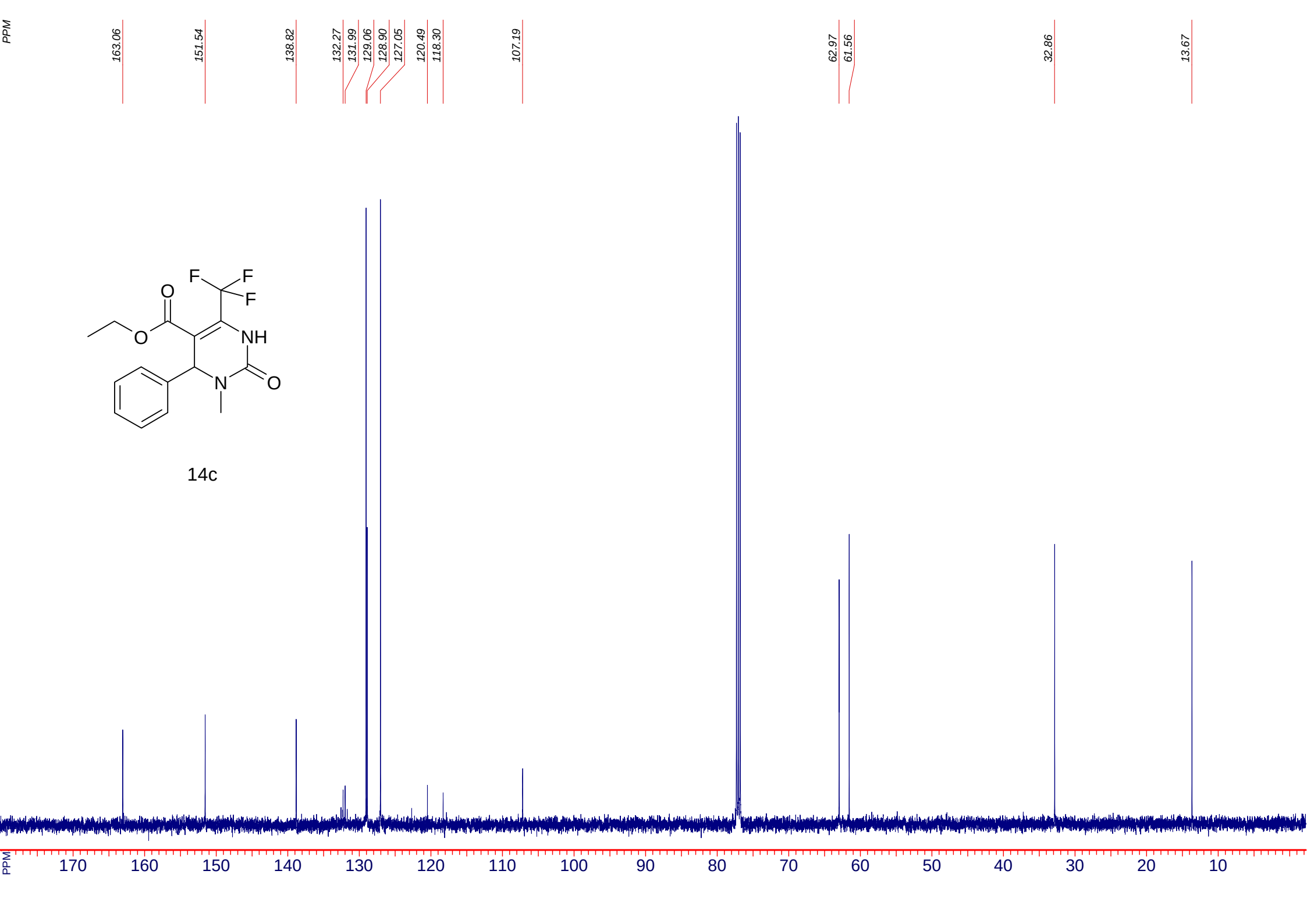

PPM
163.25
159.49
151.81
134.01
133.72
129.81
127.28
120.19
118.00
114.20
102.28
102.26
55.30
52.23
49.91
46.07
F
F
F
O
O
NH
N
O
O
14b
PPM
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


PPM
7.647
7.276
7.263
5.239
4.099
4.081
4.063
2.811
1.157
1.139
1.121
F
F
F
O
O
NH
N
O
14c
0.97
5.13
1.00
2.01
2.96
2.84
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


PPM
163.06
151.54
138.82
132.27
131.99
129.06
128.90
127.05
120.49
118.30
107.19
62.97
61.56
32.86
13.67
F
F
F
O
O
NH
N
O
14c
PPM
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10