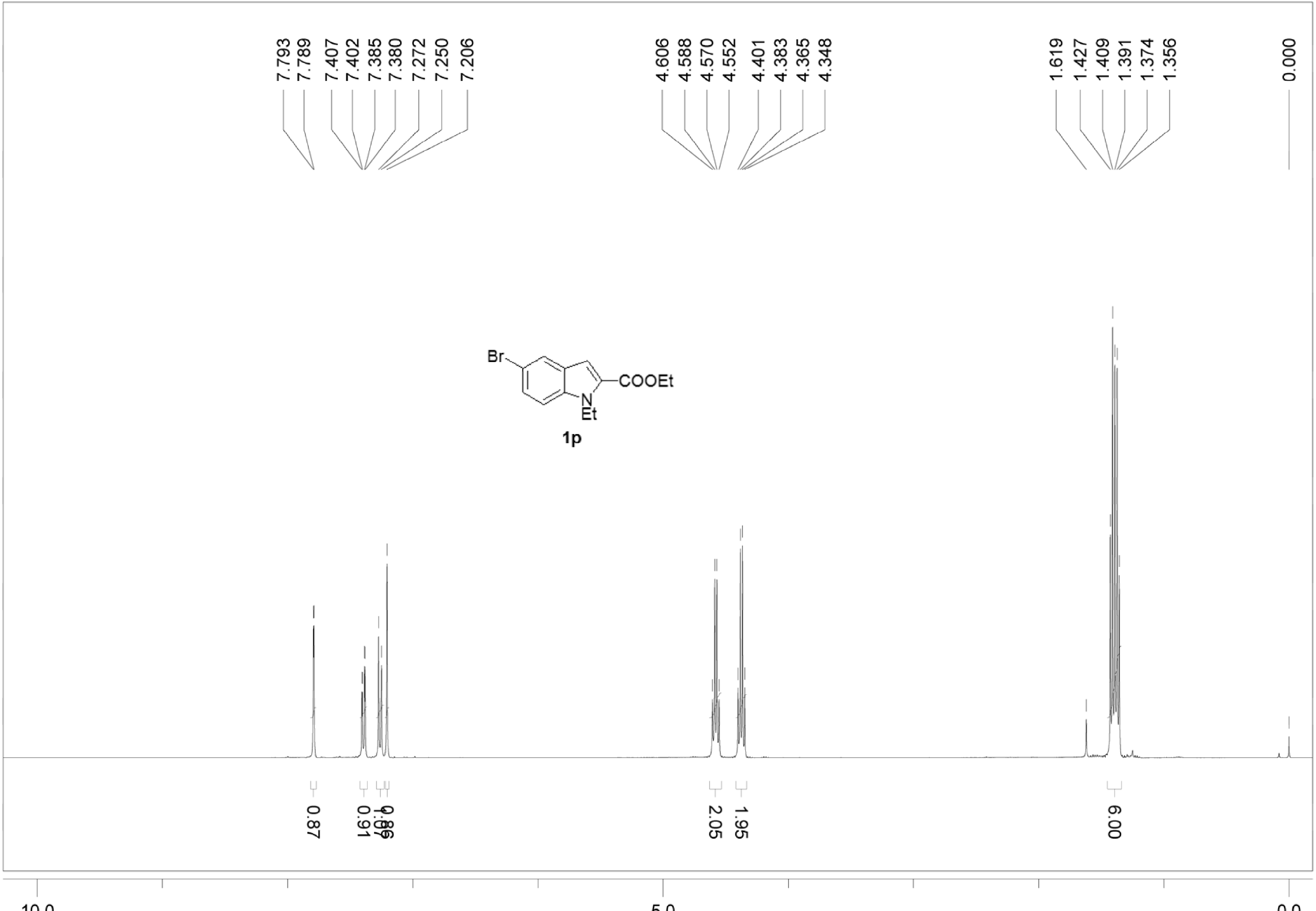
Copper-Catalyzed Regioselective C-H Sulfonyloxylation of Electron-Rich Arenes with *p*-Toluenesulfonic Acid and Sulfonyloxylation of Aryl(mesityl)iodonium Sulfonates

He Huang,† Yang Wu,† Wen Zhang, Chun Feng, Bi-Qin Wang,* Wan-Fei Cai, Ping Hu, Ke-Qing Zhao, and Shi-Kai Xiang*

College of Chemistry and Materials Science, Sichuan Normal University, Chengdu 610068, People's Republic of China

E-mail: xiangsk@hotmail.com; wangbiqin1964@126.com
†He Huang and Yang Wu contributed equally to this work

Supporting Information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4.552
4.401
4.383
4.365
4.348
1.619
1.427
1.409
1.391
1.374
1.356
0.000
Br
COOEt
N
Et
1p
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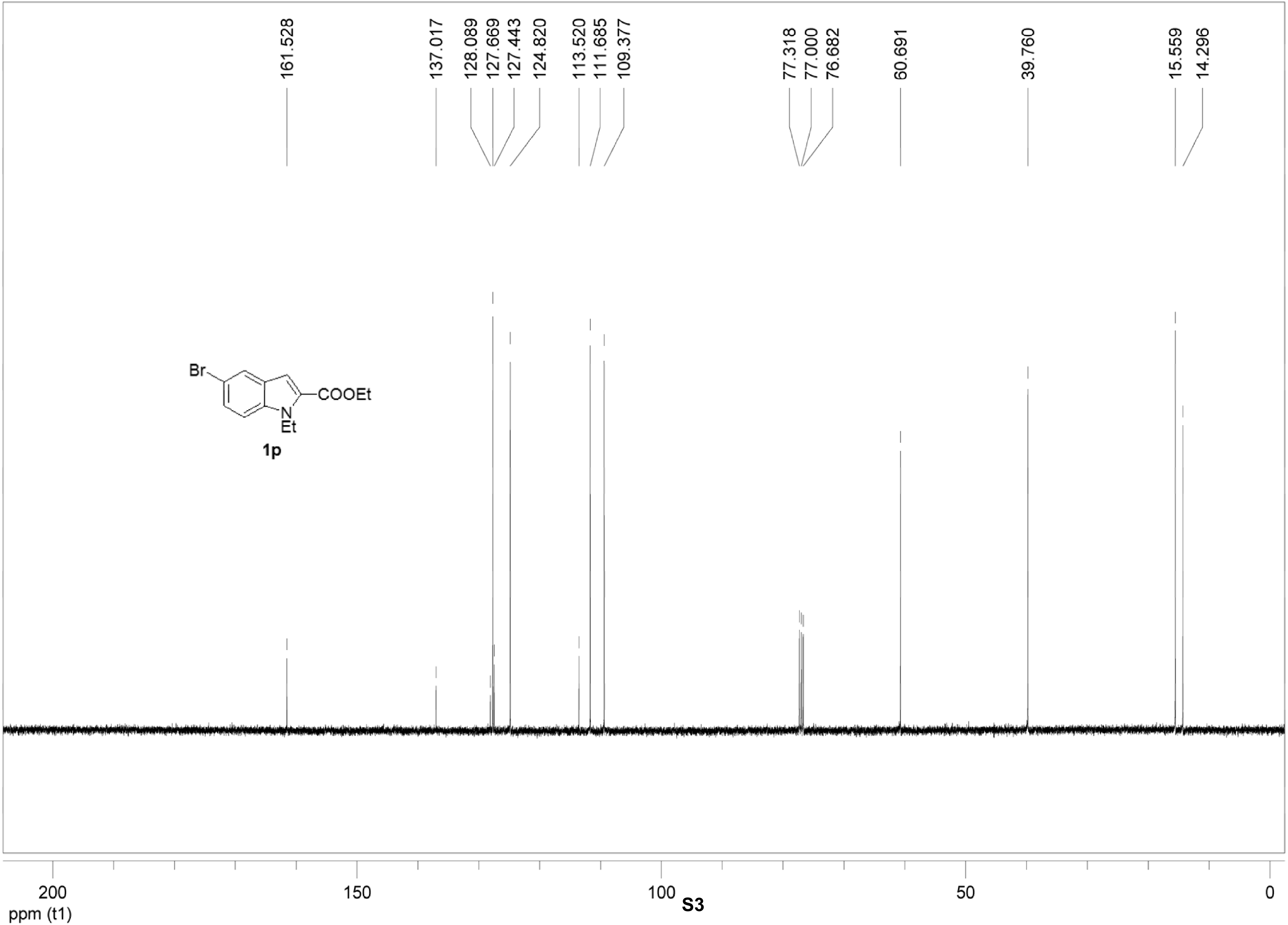
ppm (t1)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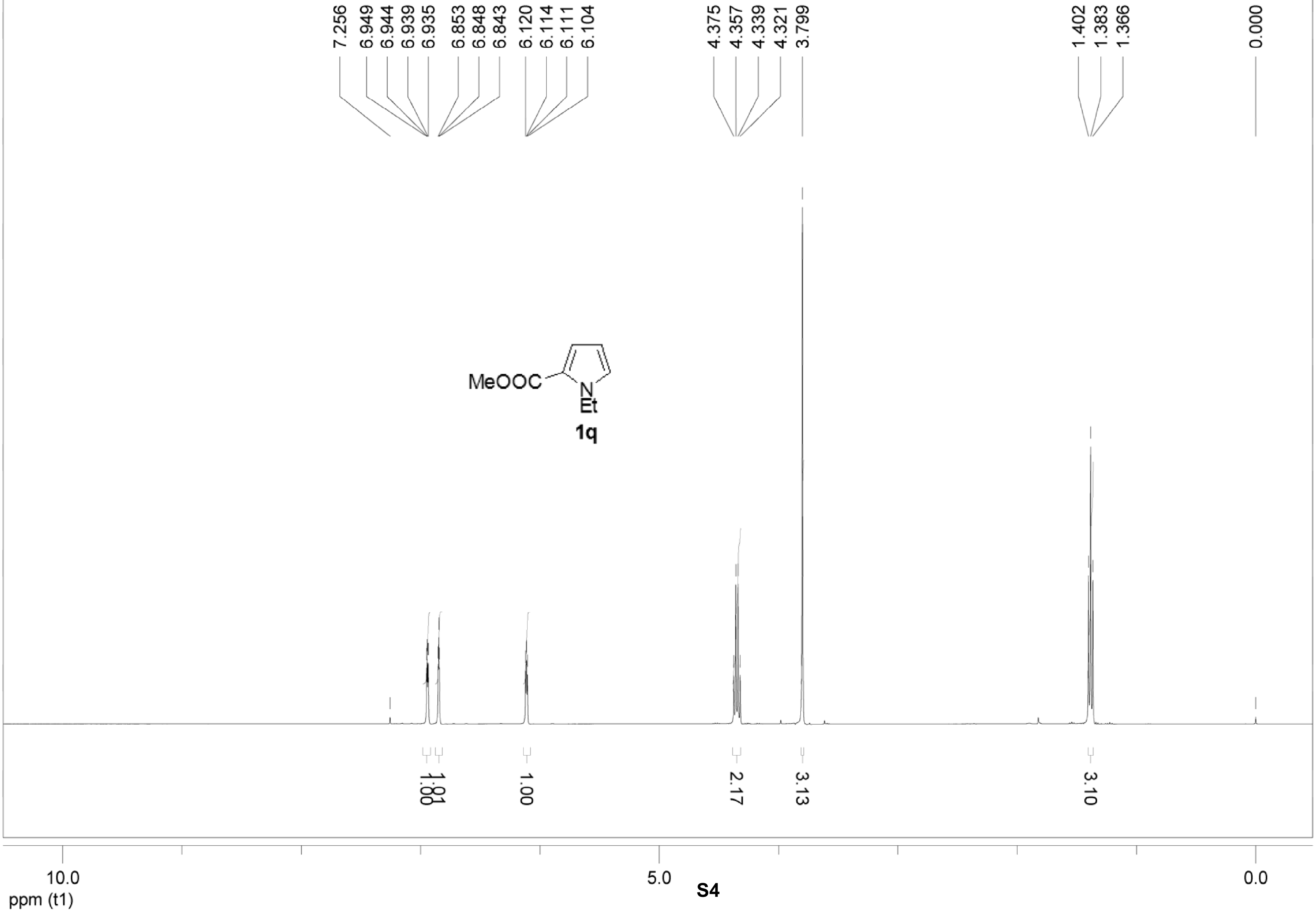
ppm (t1)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4.321
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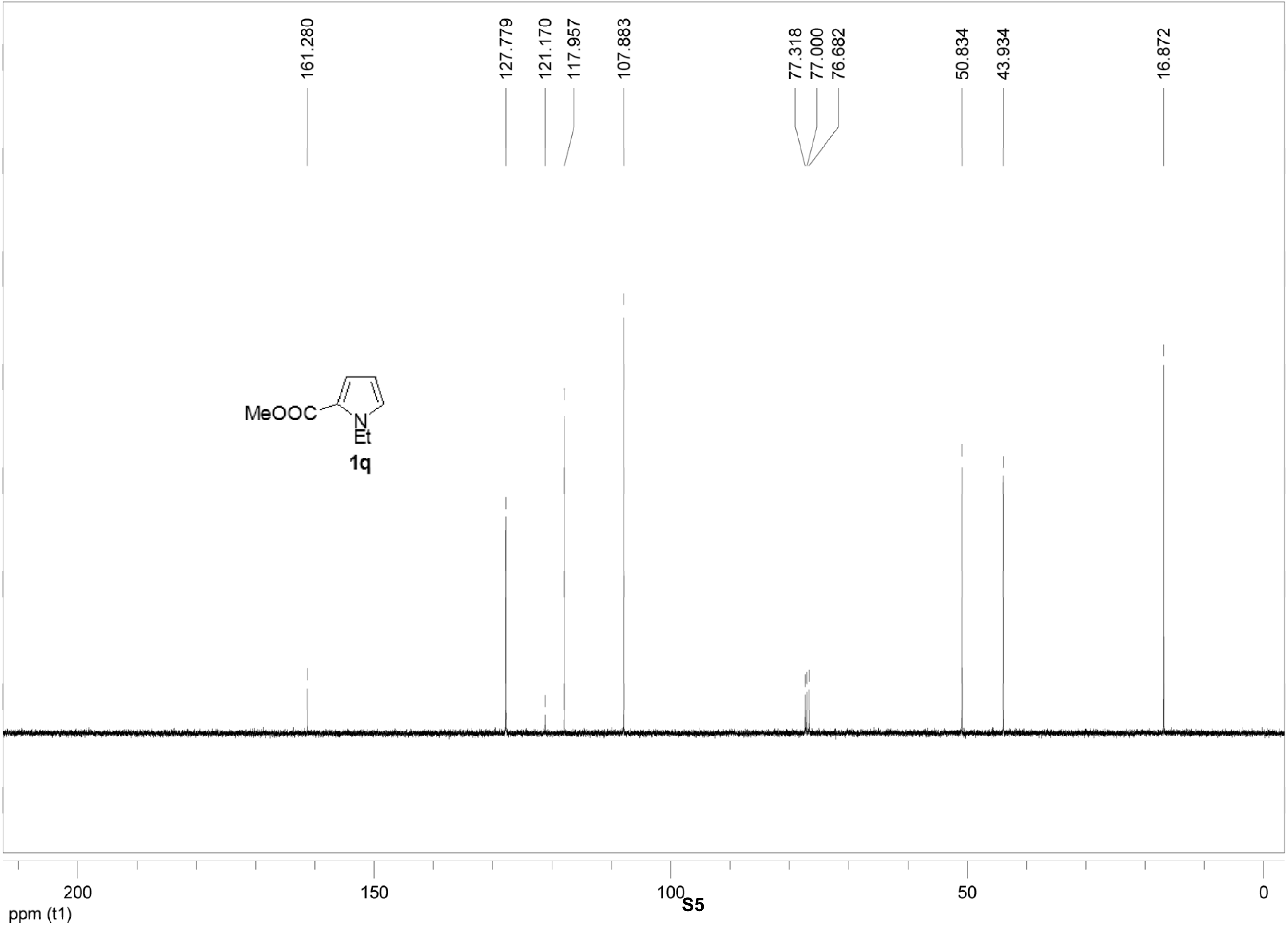
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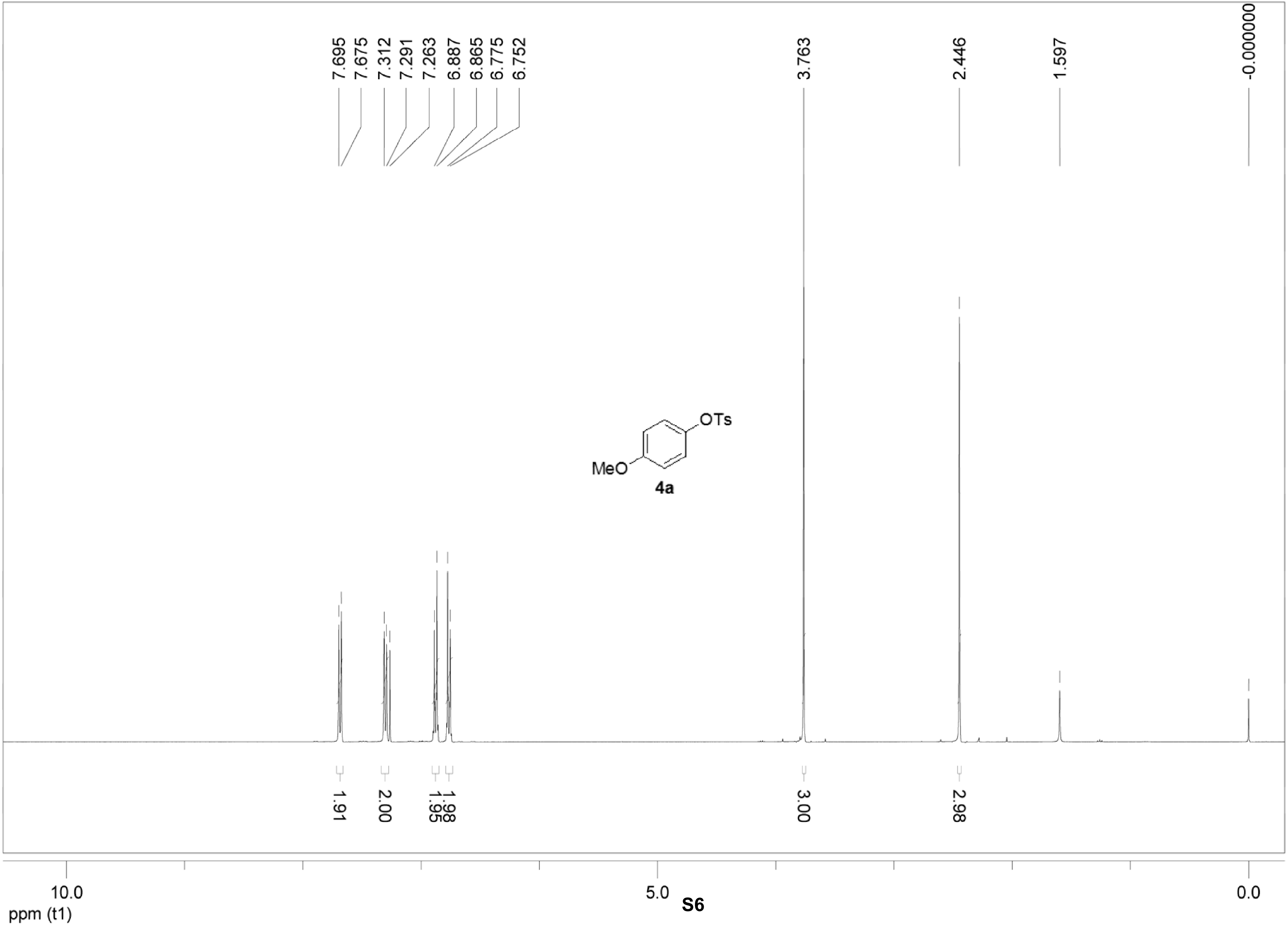
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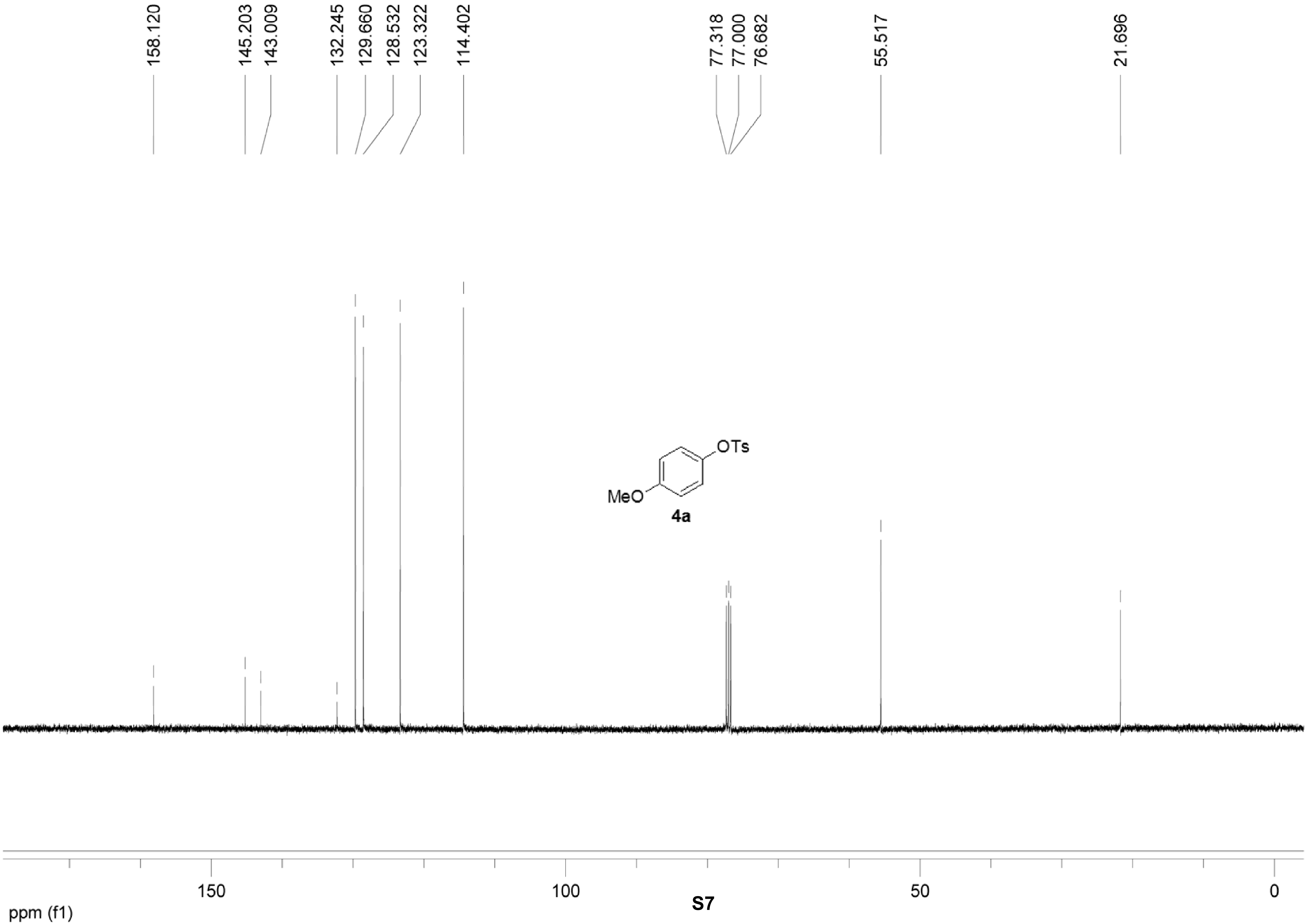
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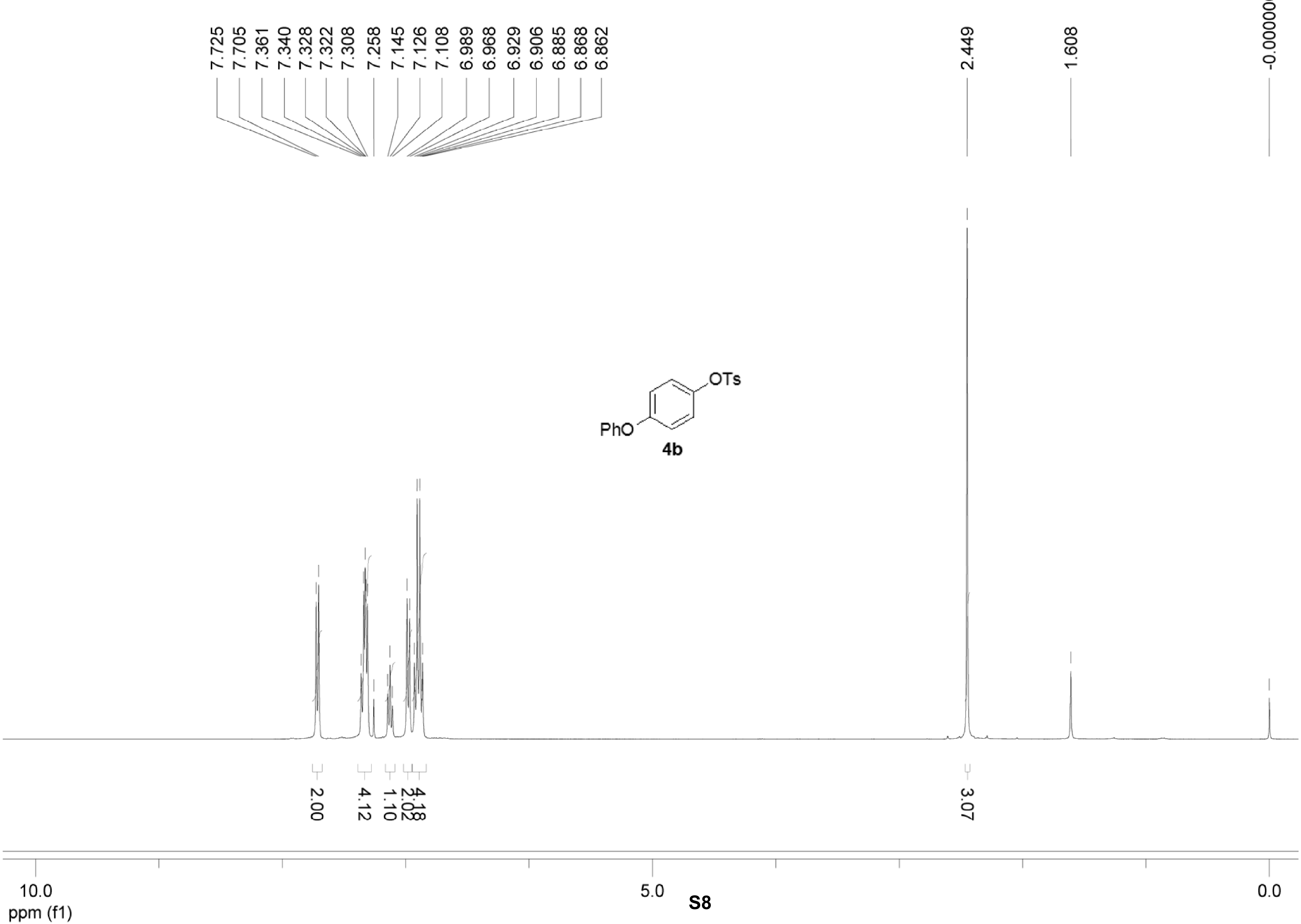
ppm (f1)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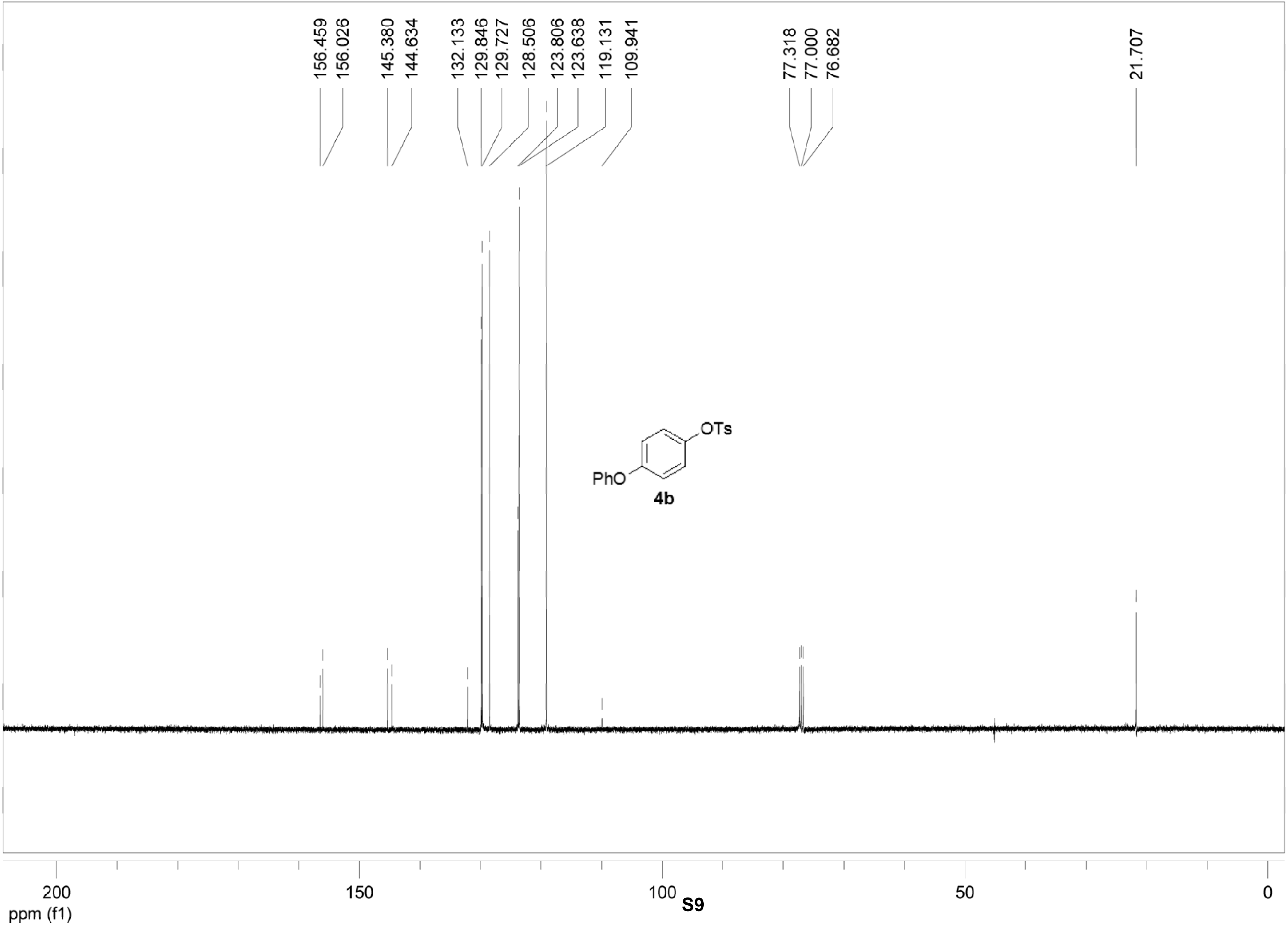
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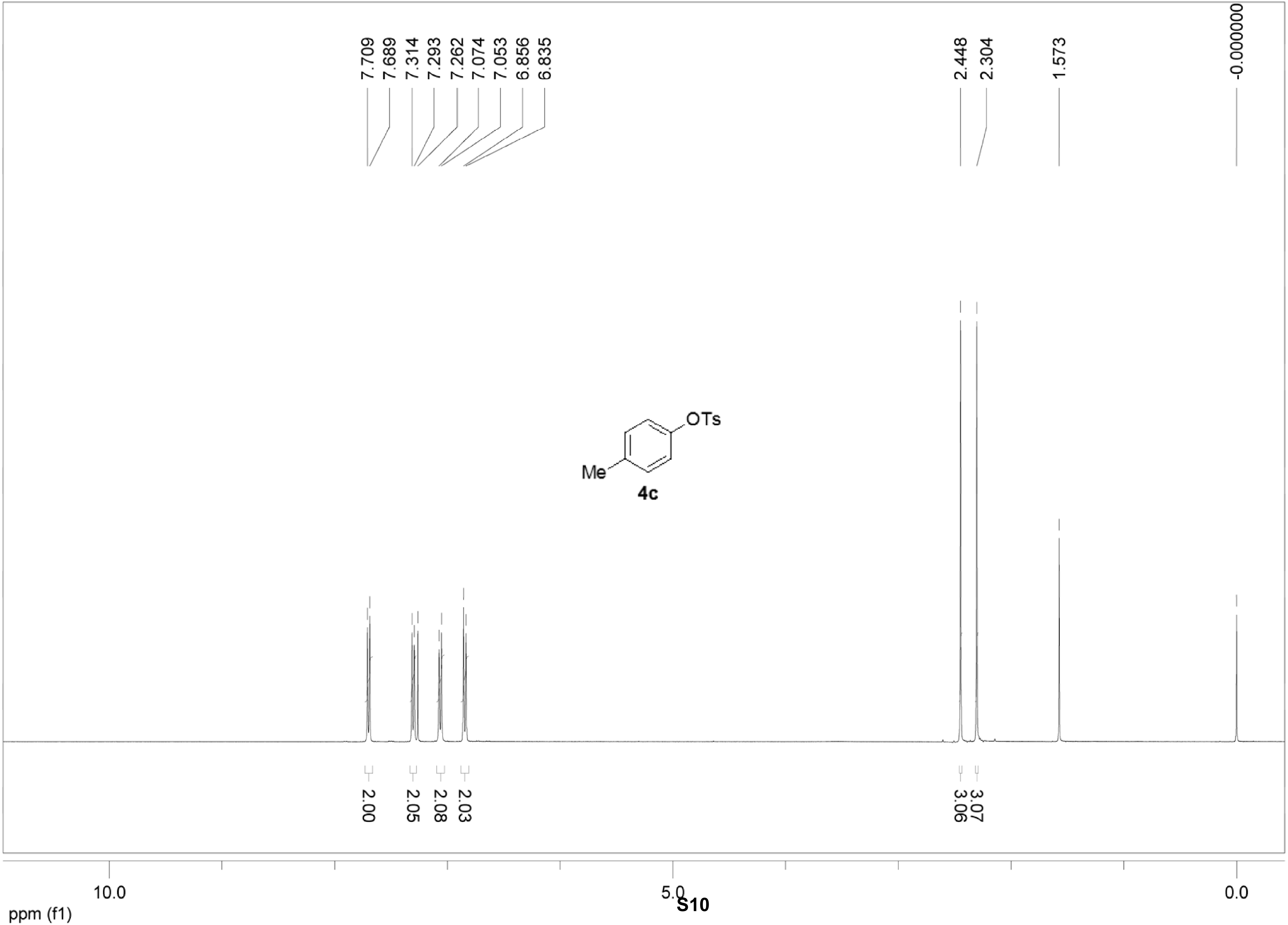
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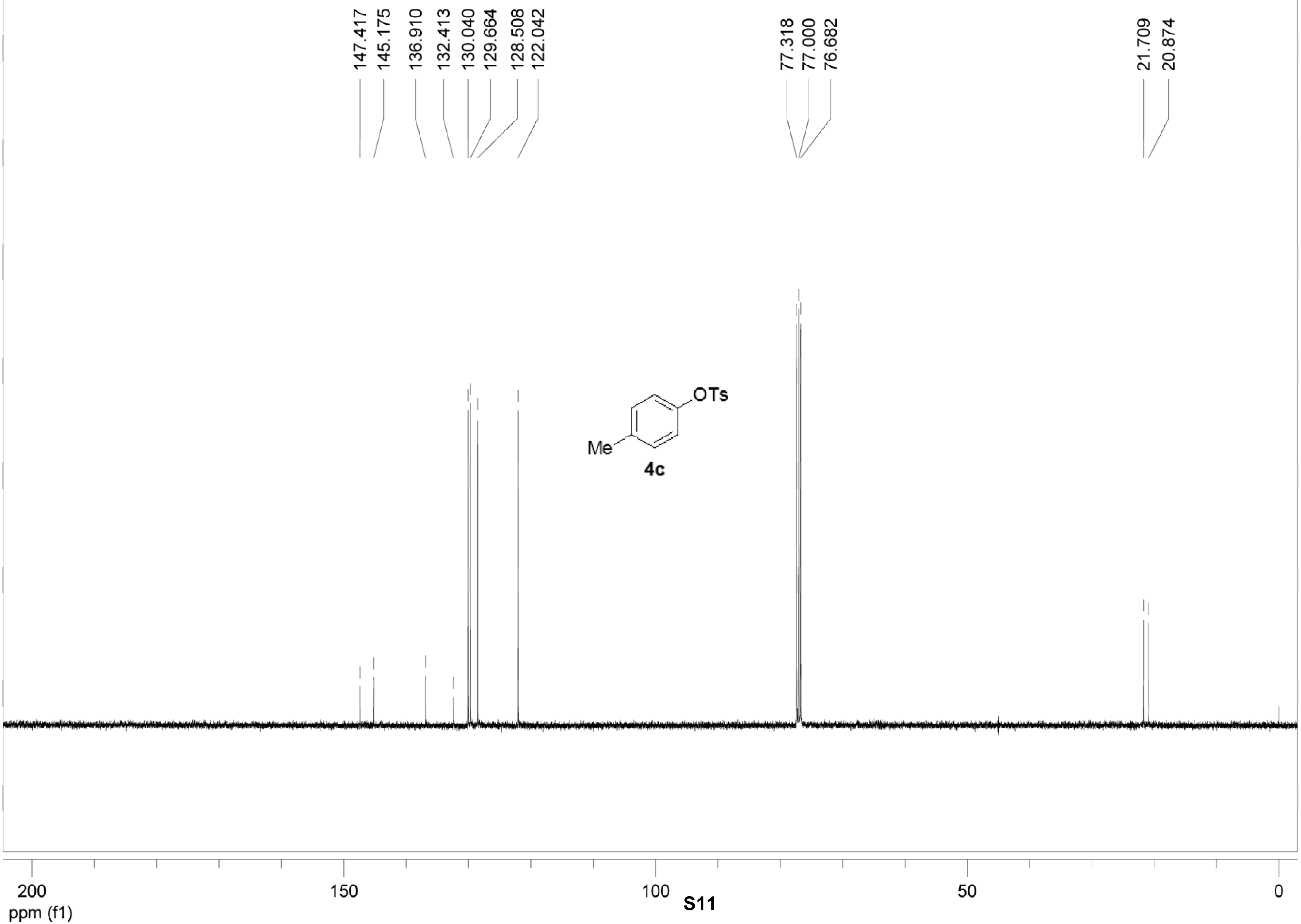
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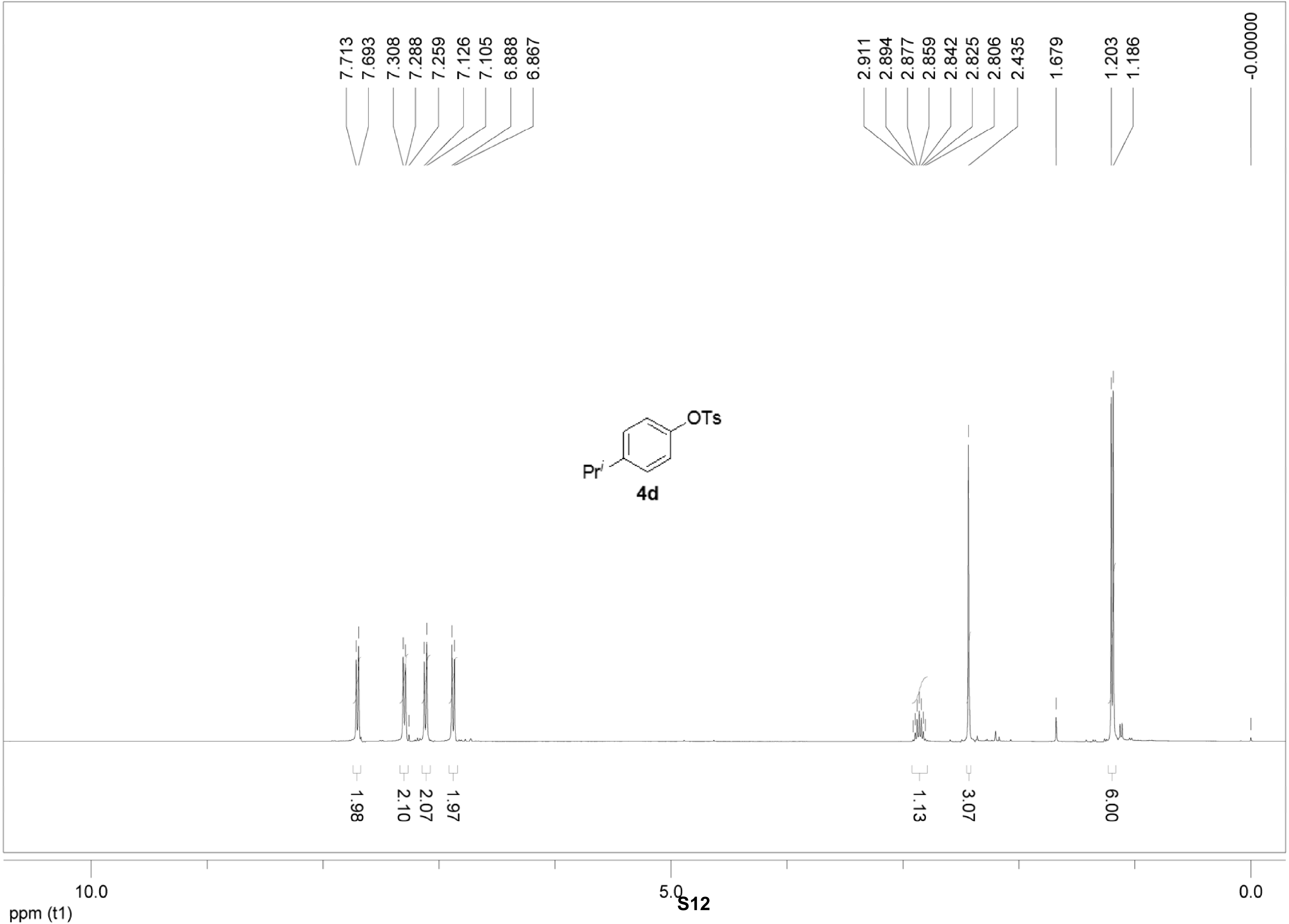
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OTs
Pr^i
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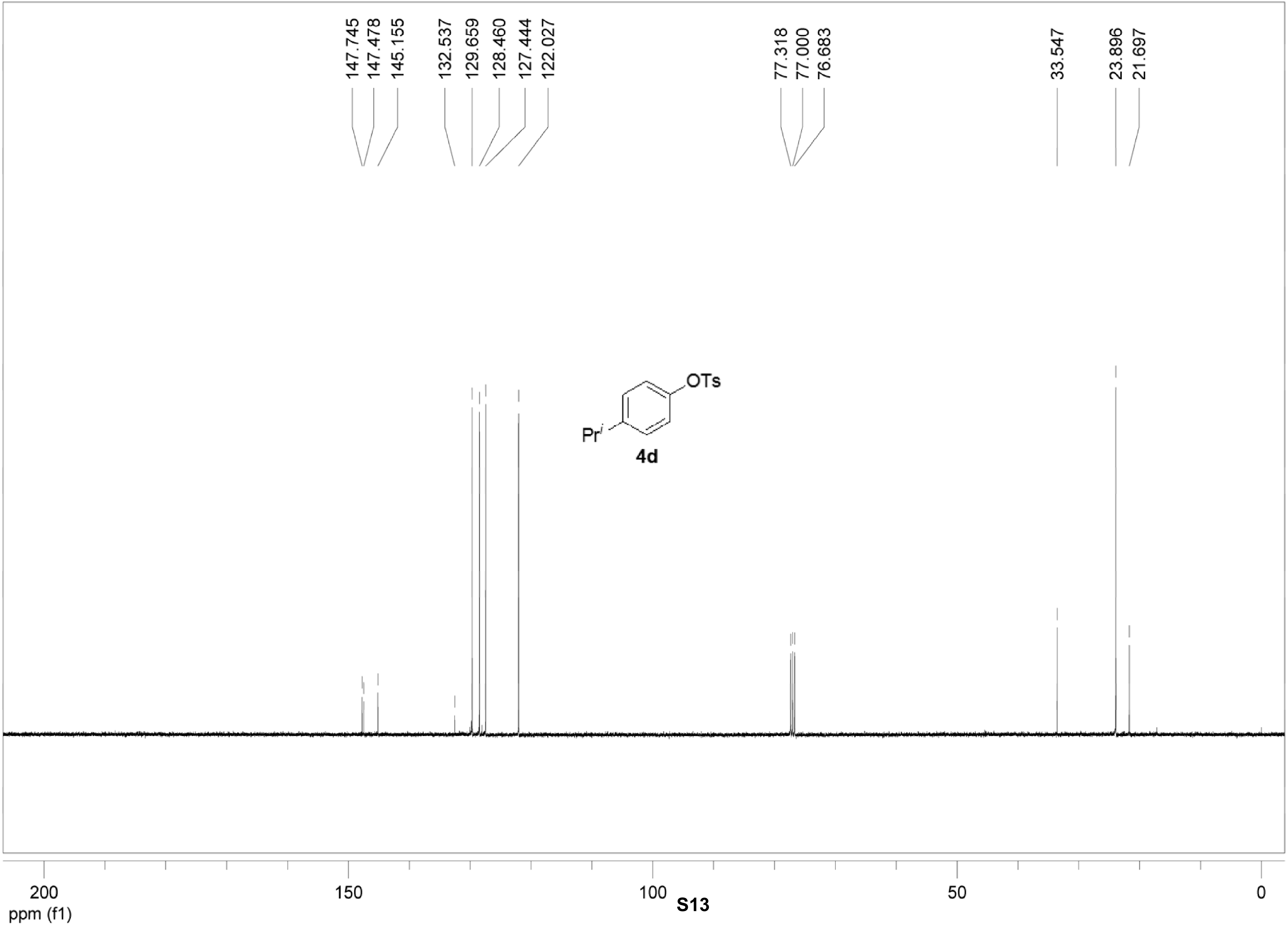
ppm (t1)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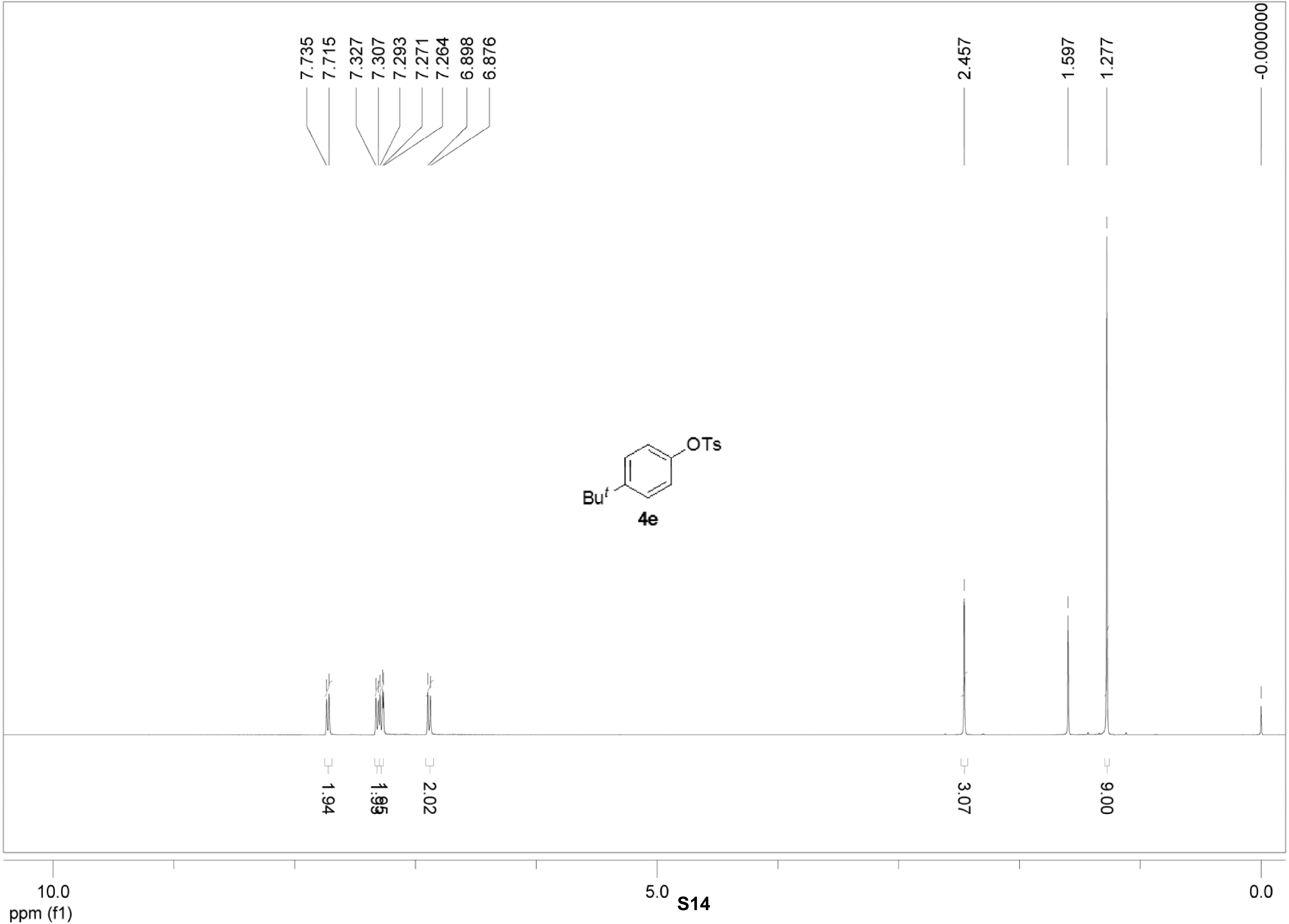
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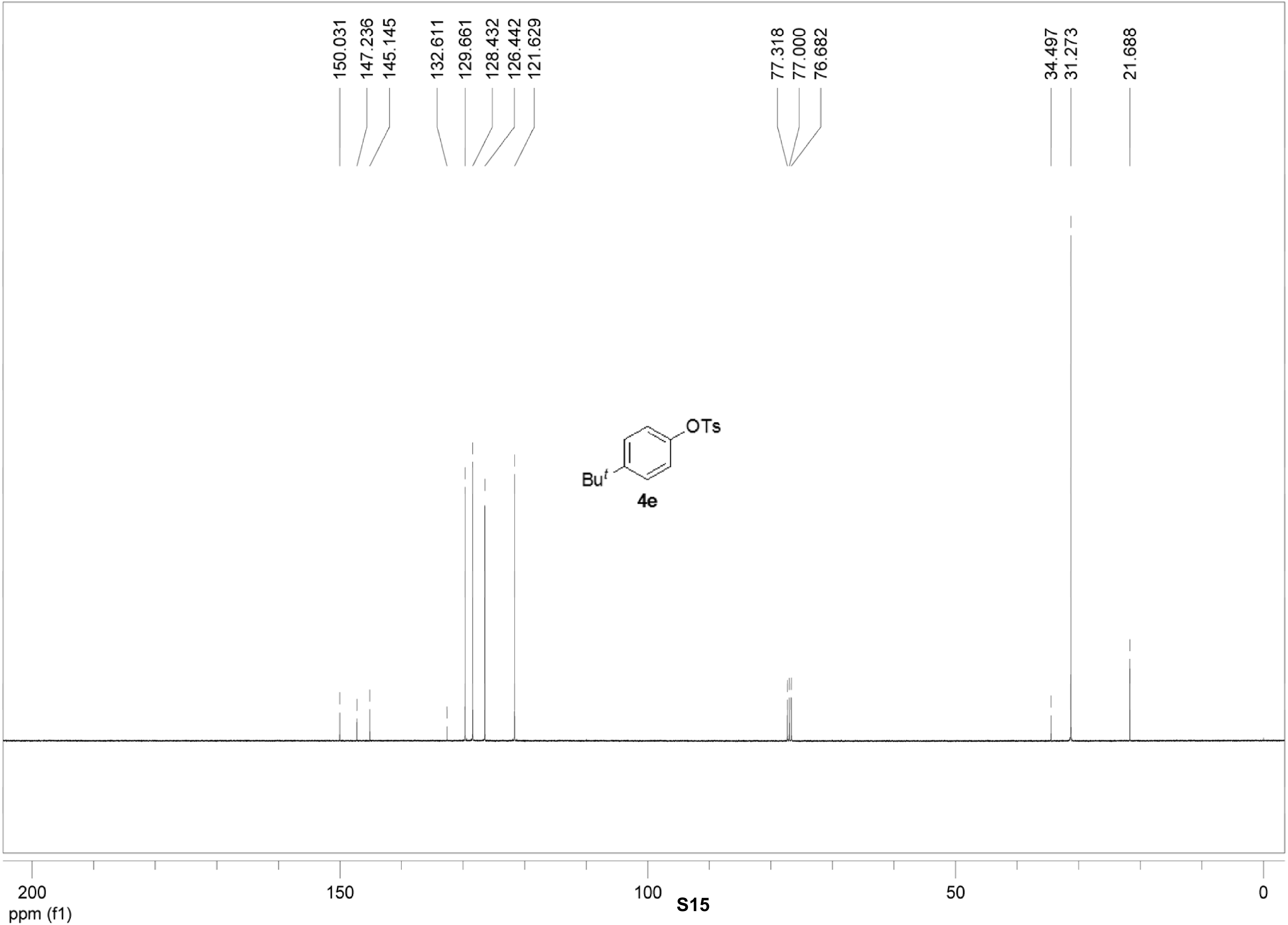
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Bu^t
4e
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50
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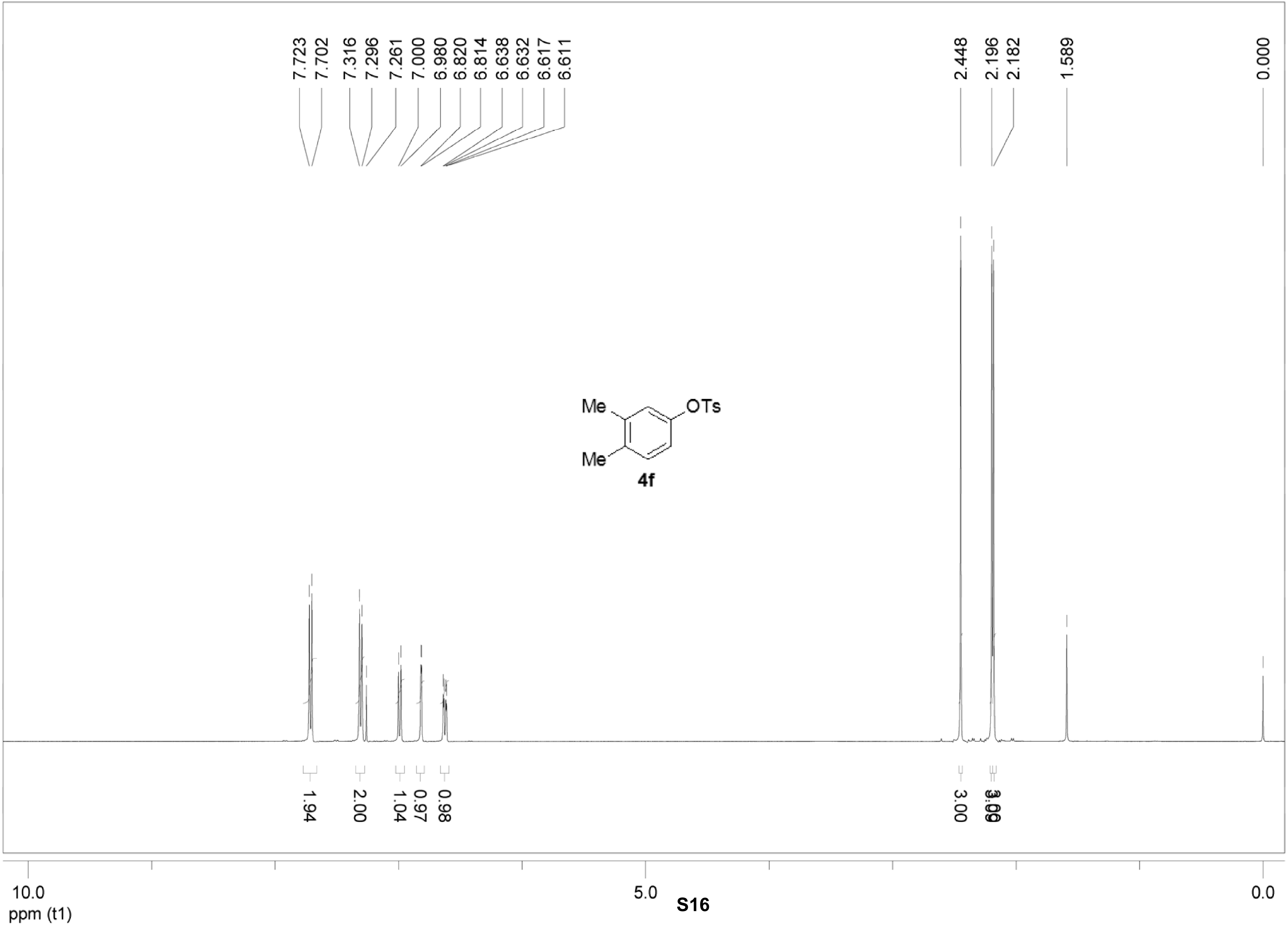
ppm (f1)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6.611
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2.196
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0.000
Me
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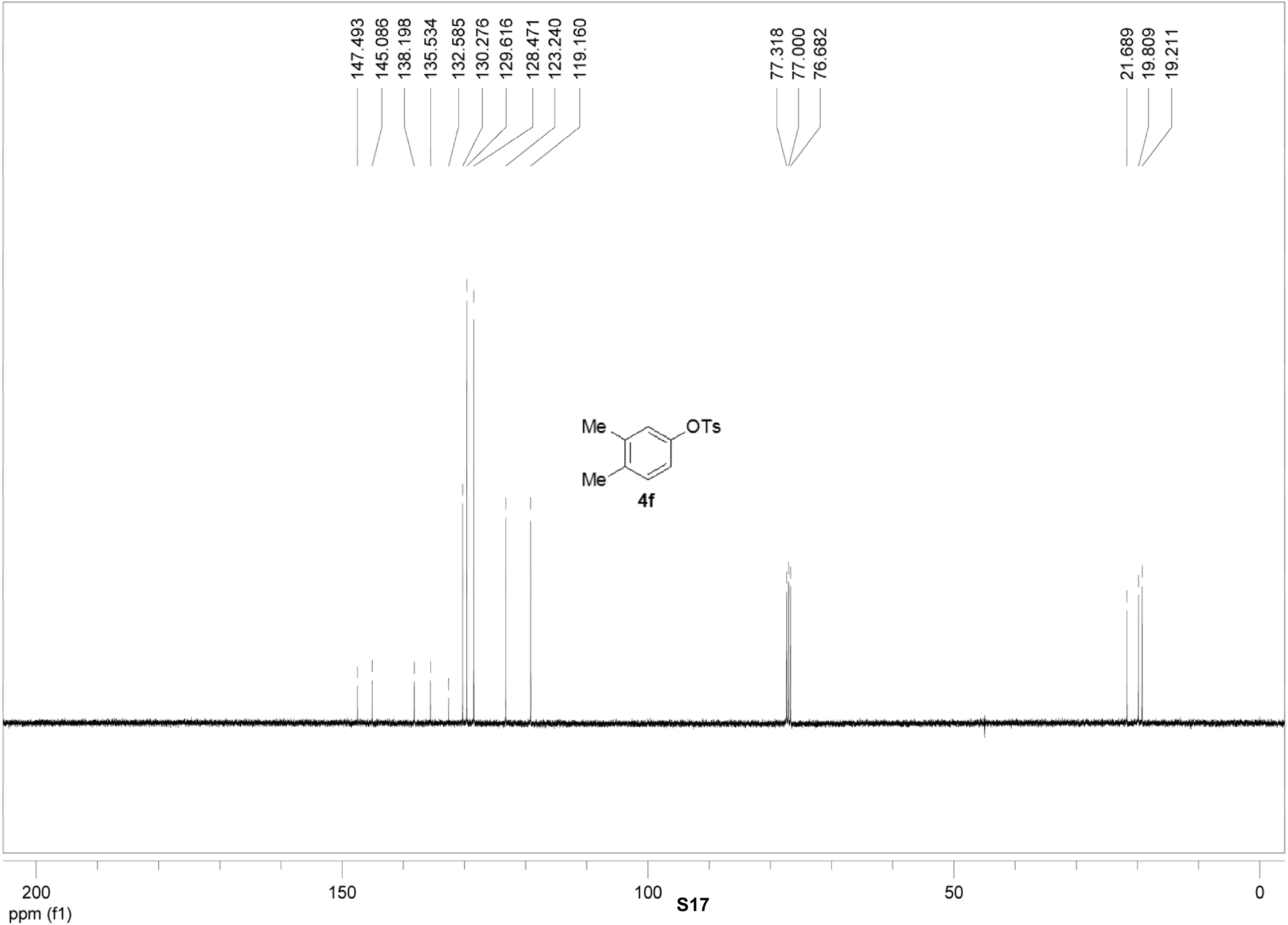
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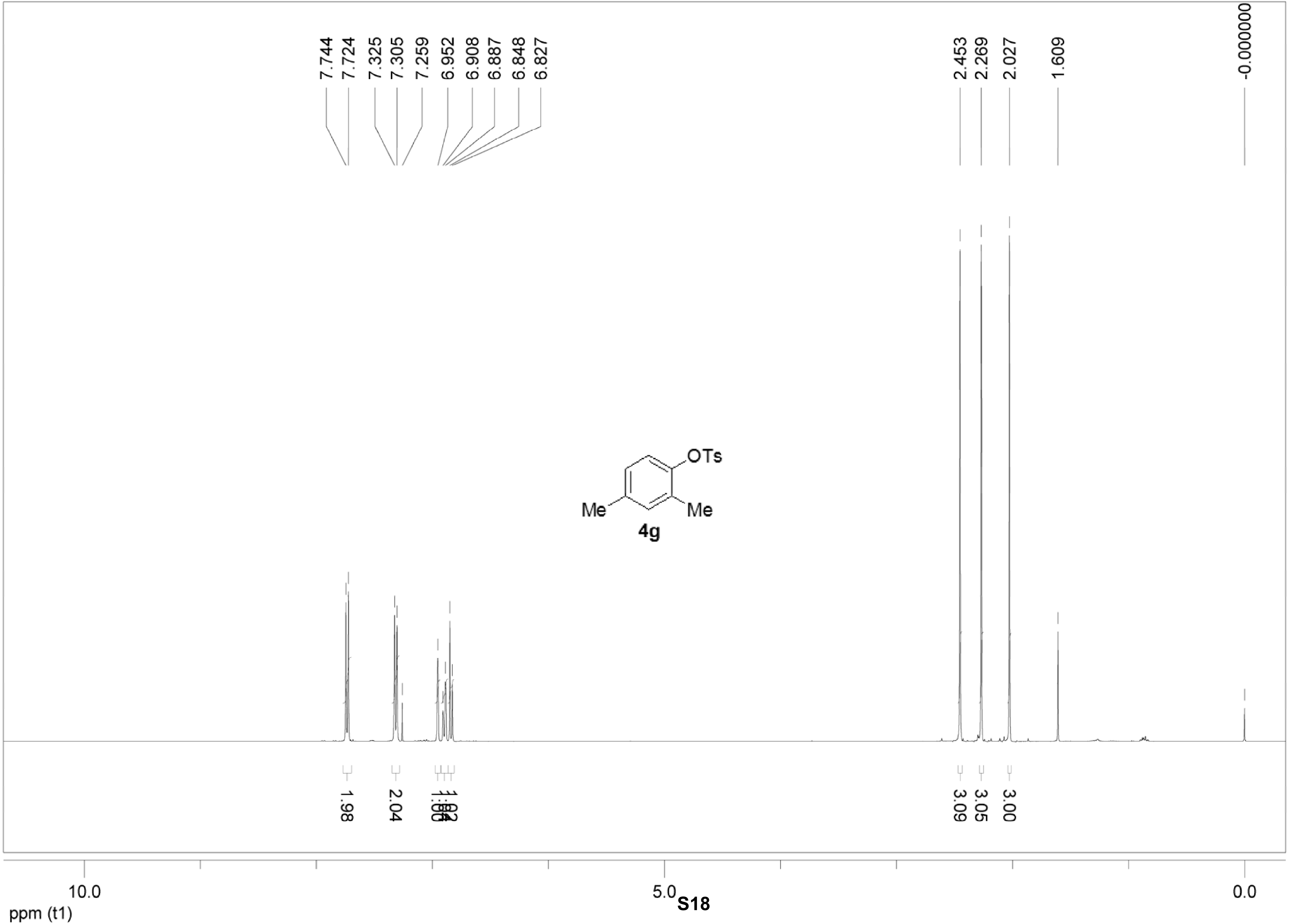
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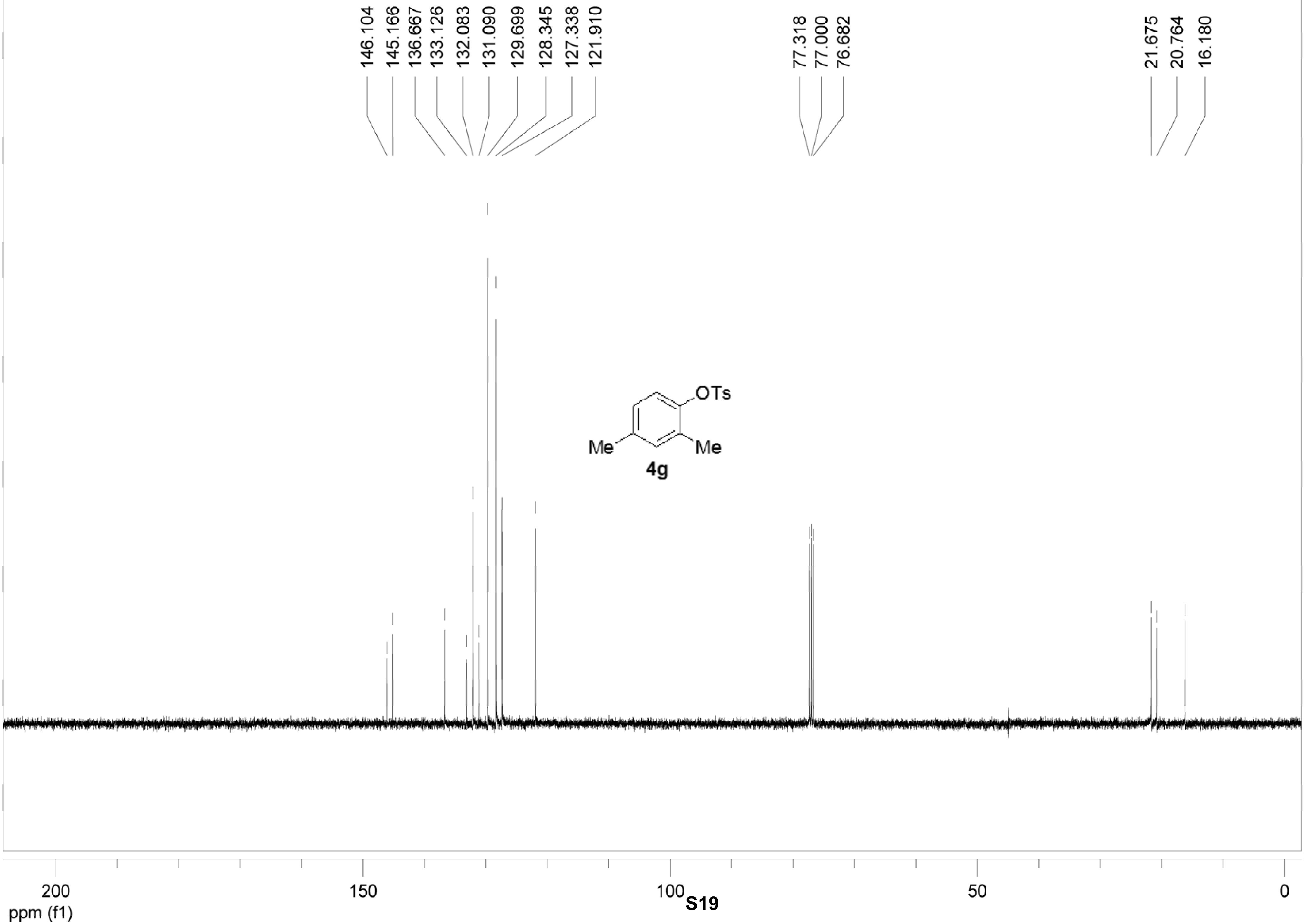
ppm (t1)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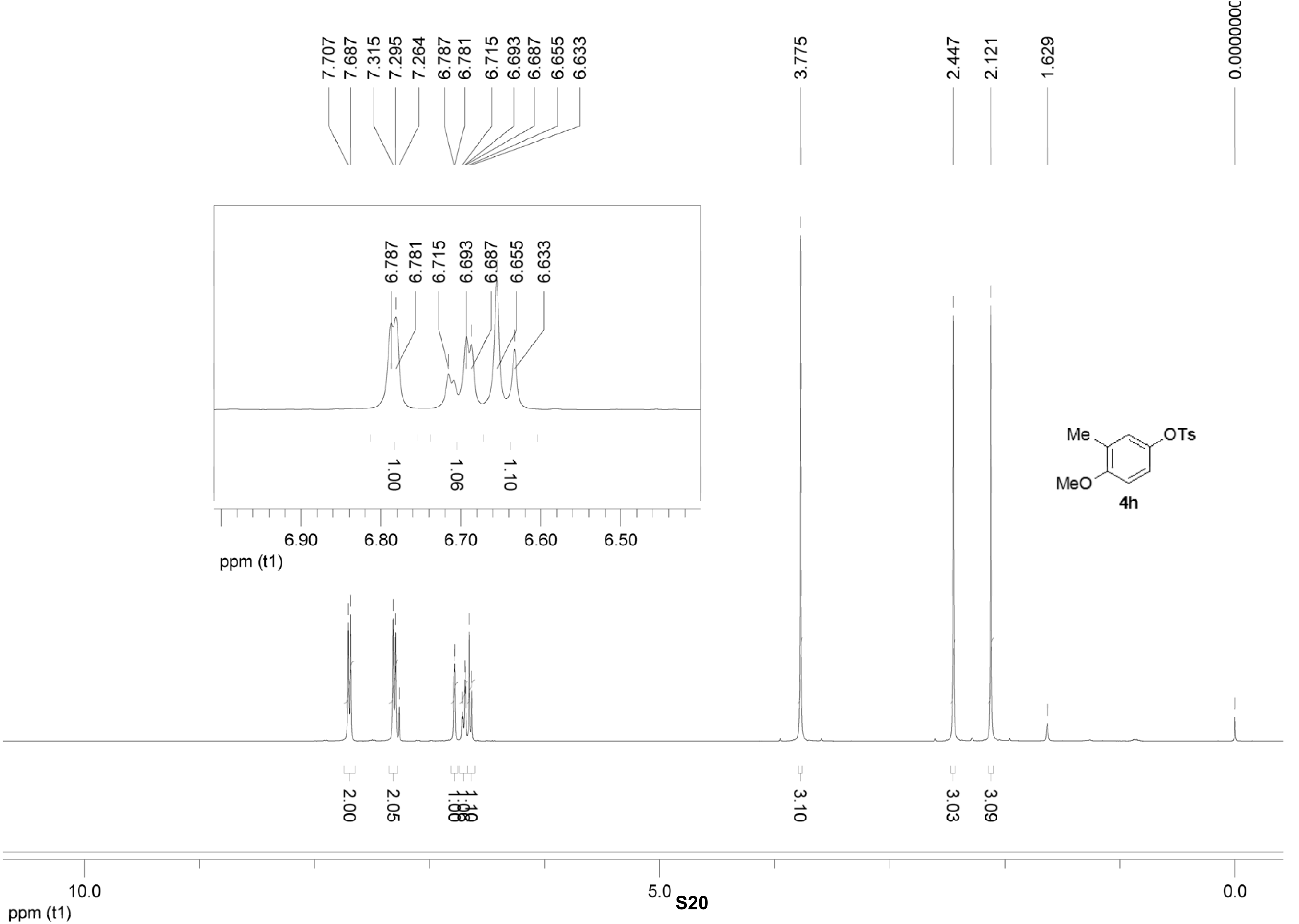
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6.60
6.50
ppm (t1)
Me
OTs
MeO
4h
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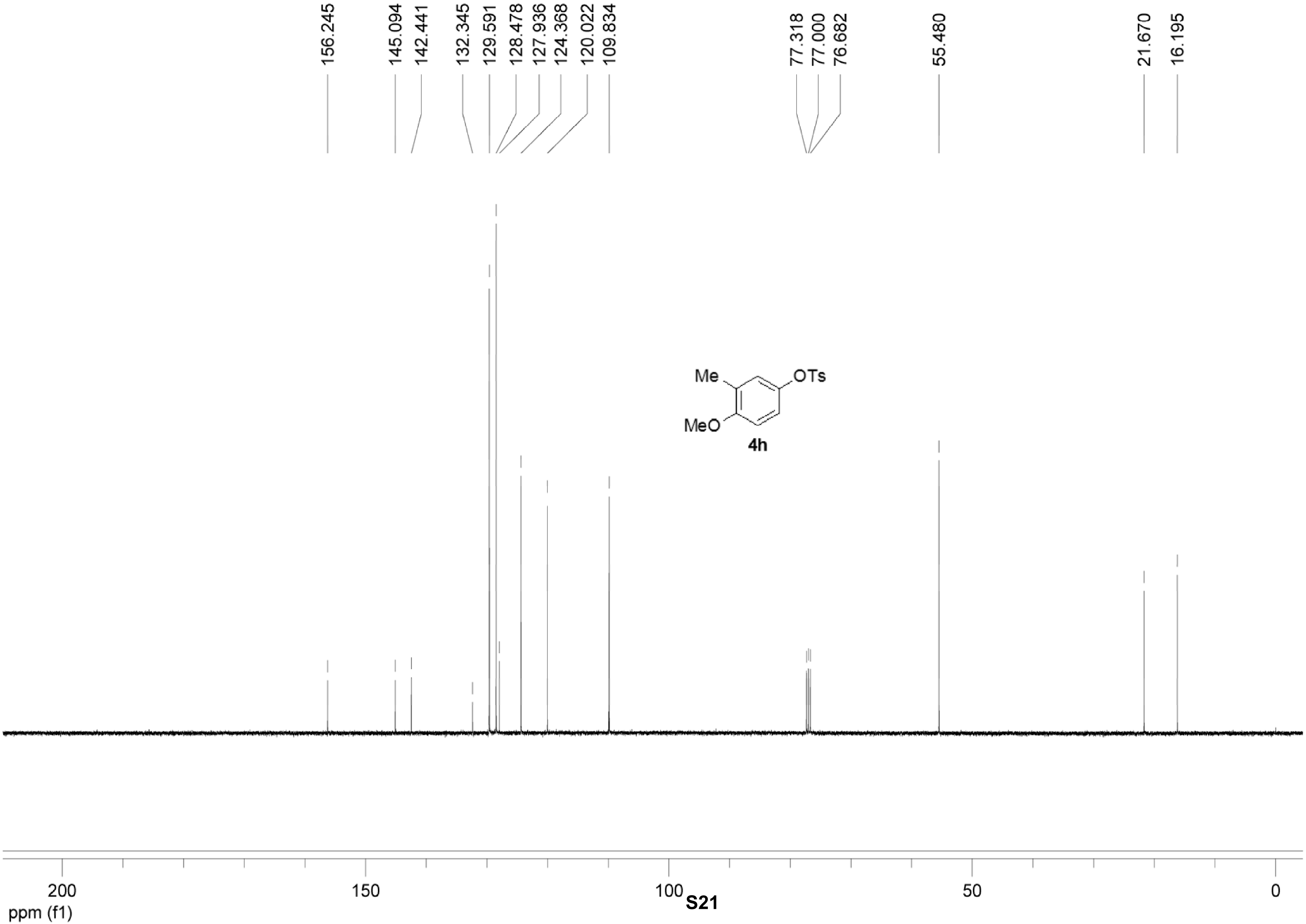
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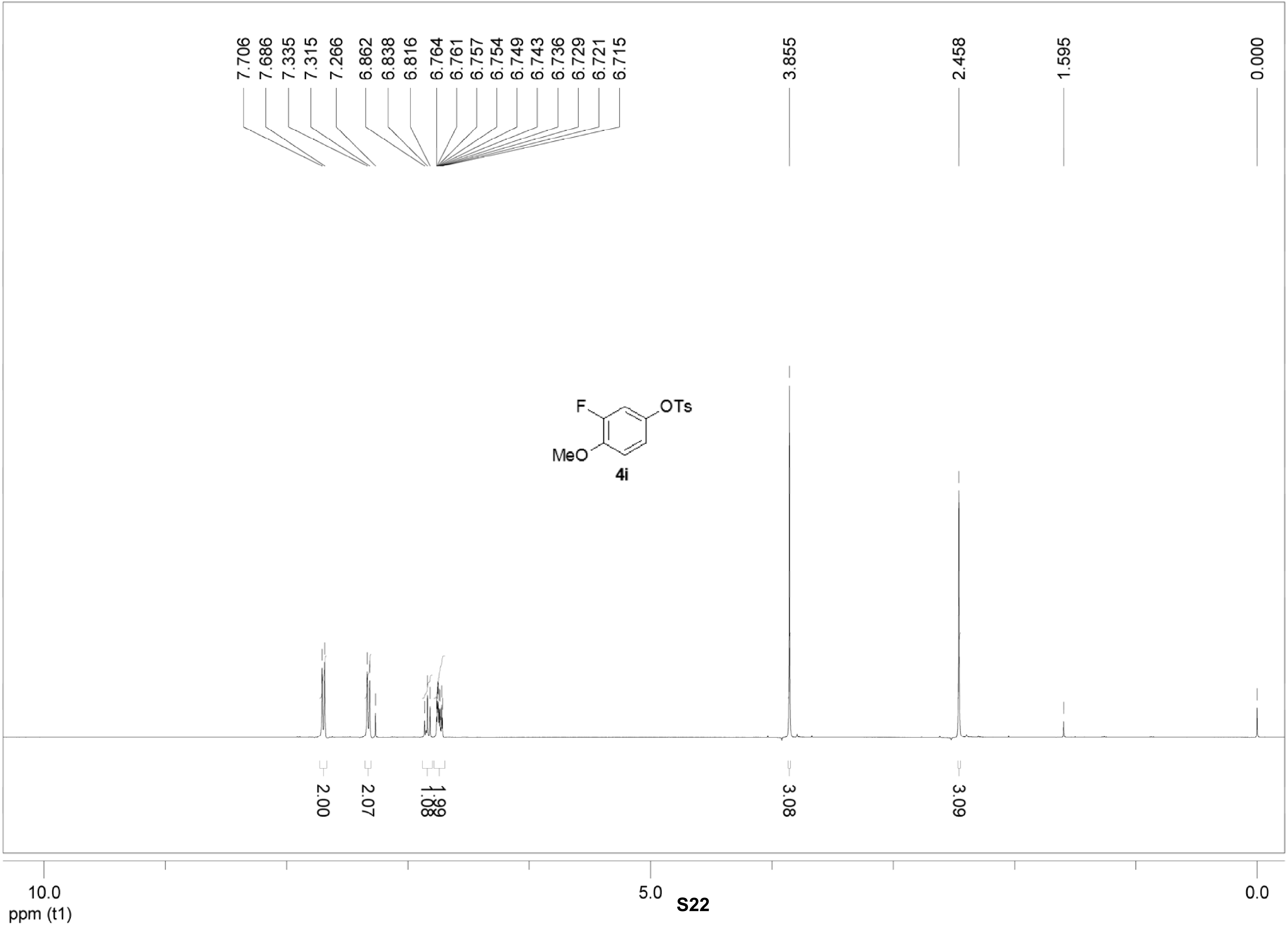
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0.000
F
OTs
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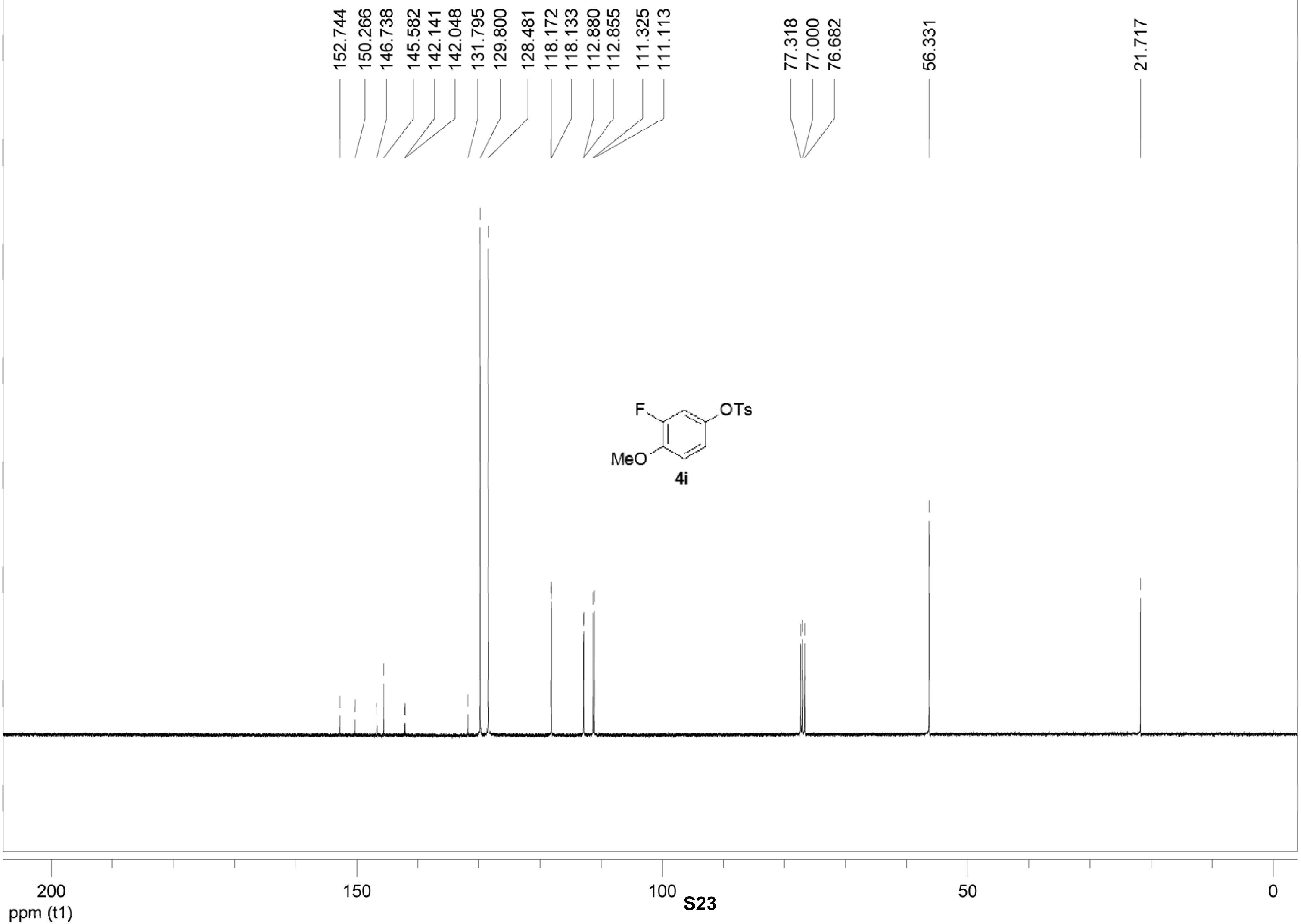

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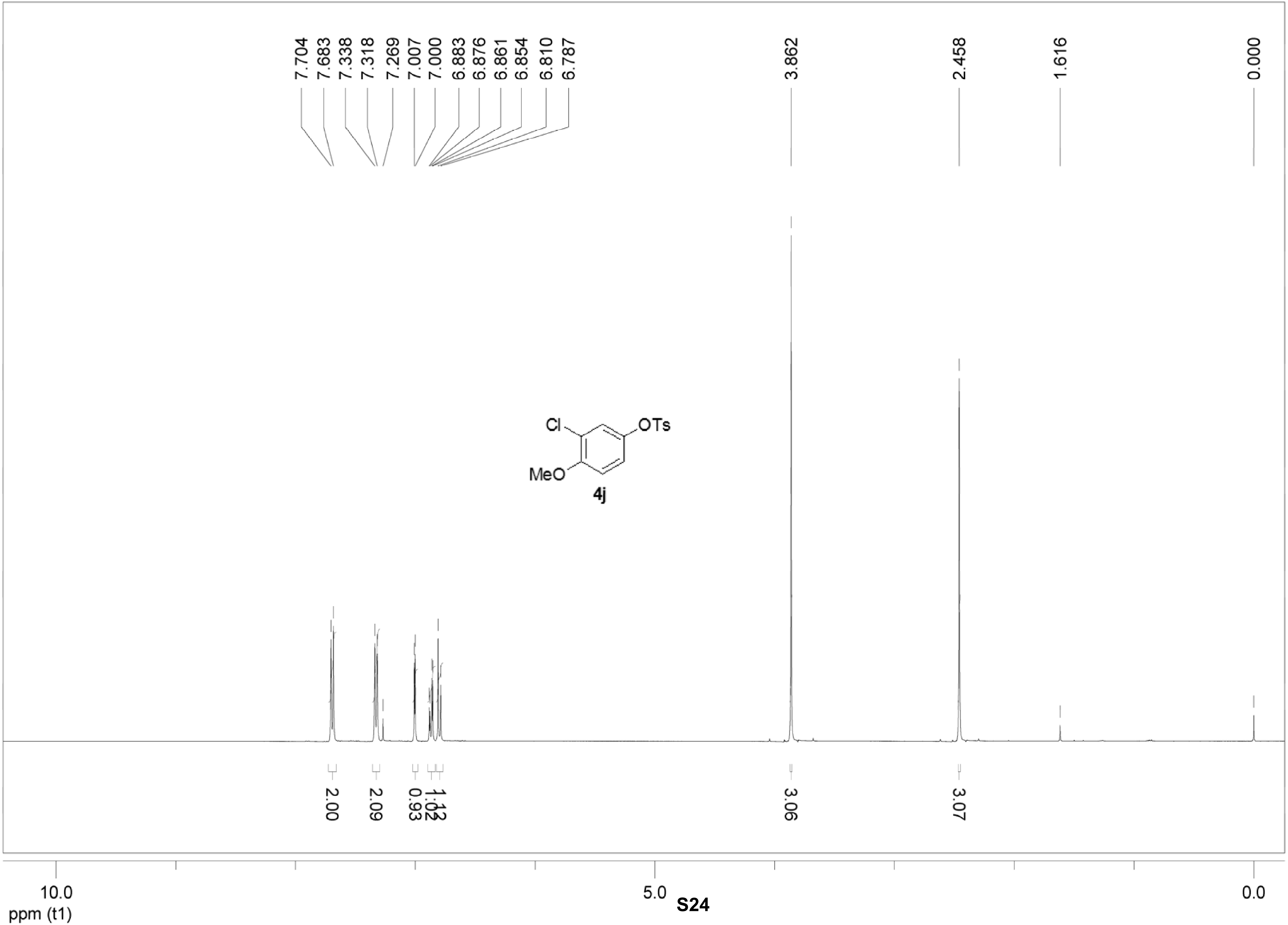
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MeO
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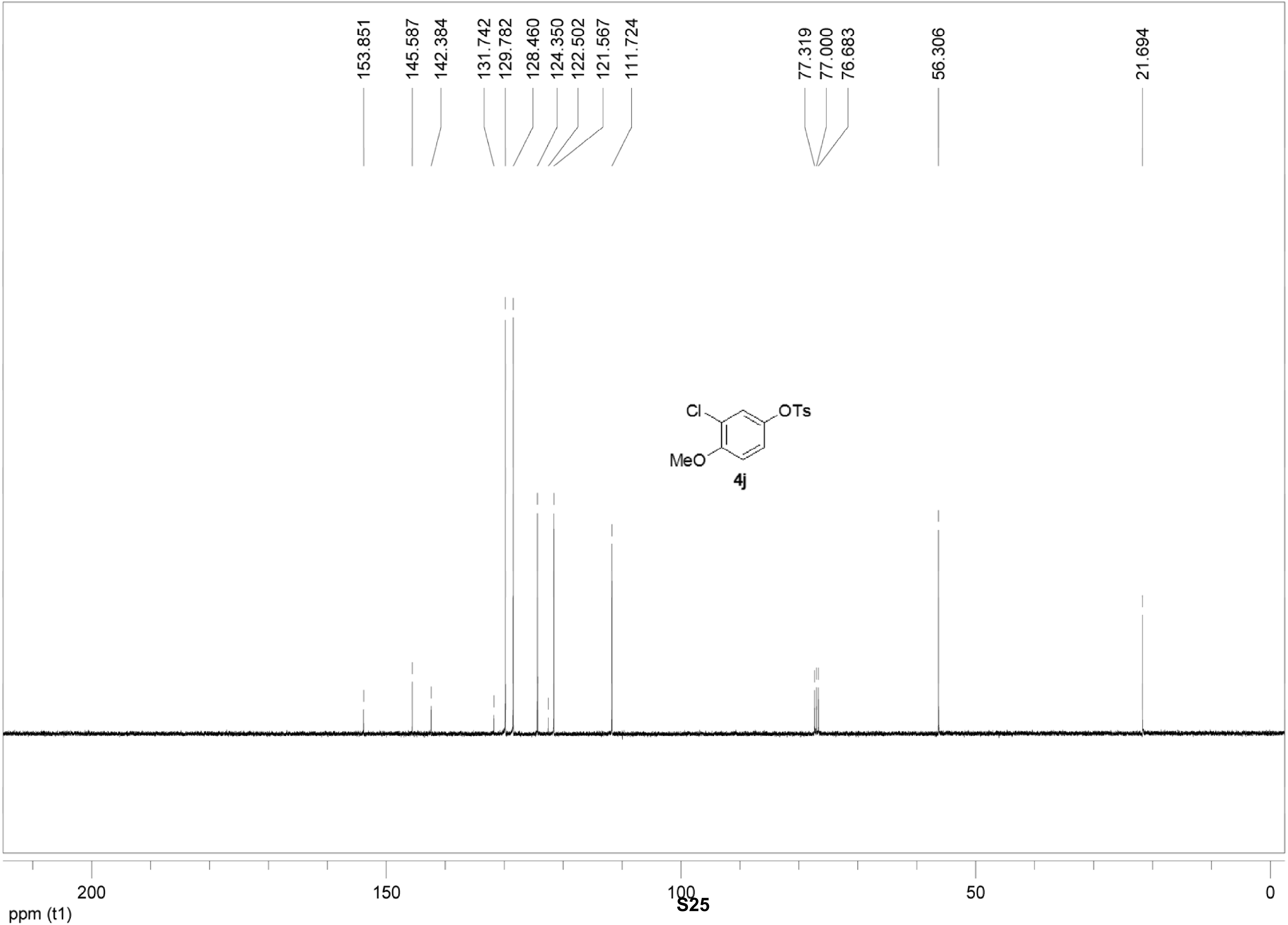
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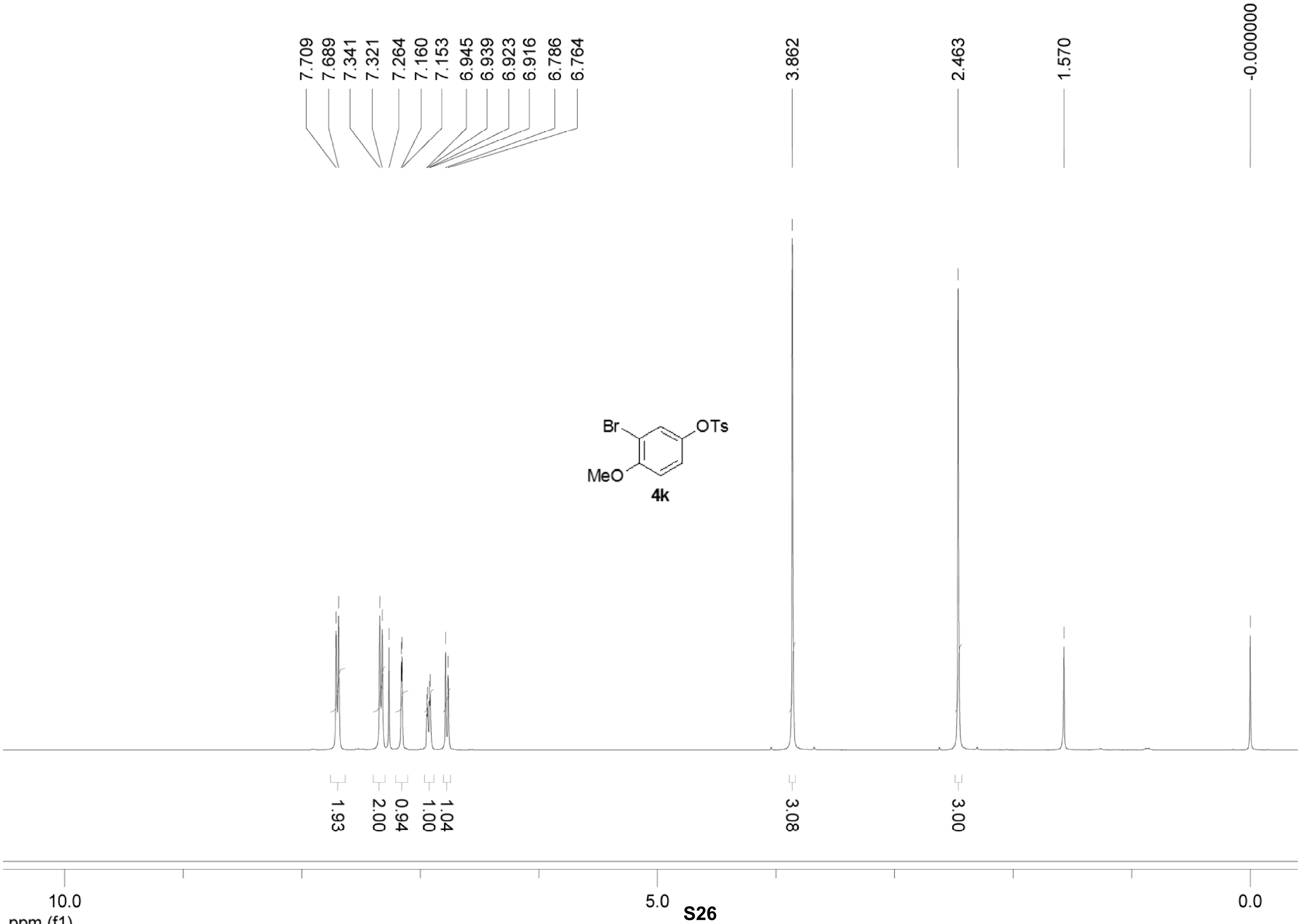
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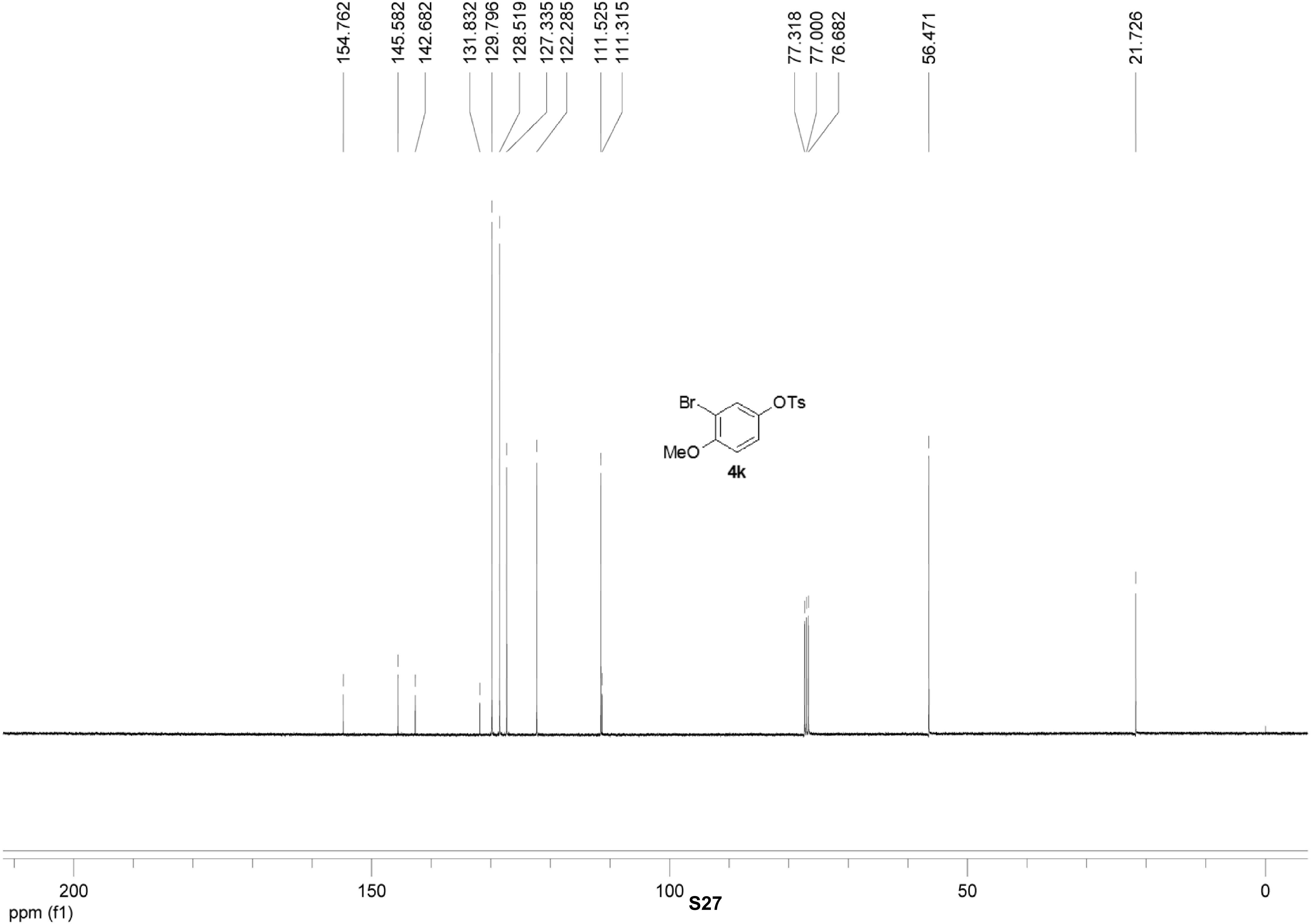
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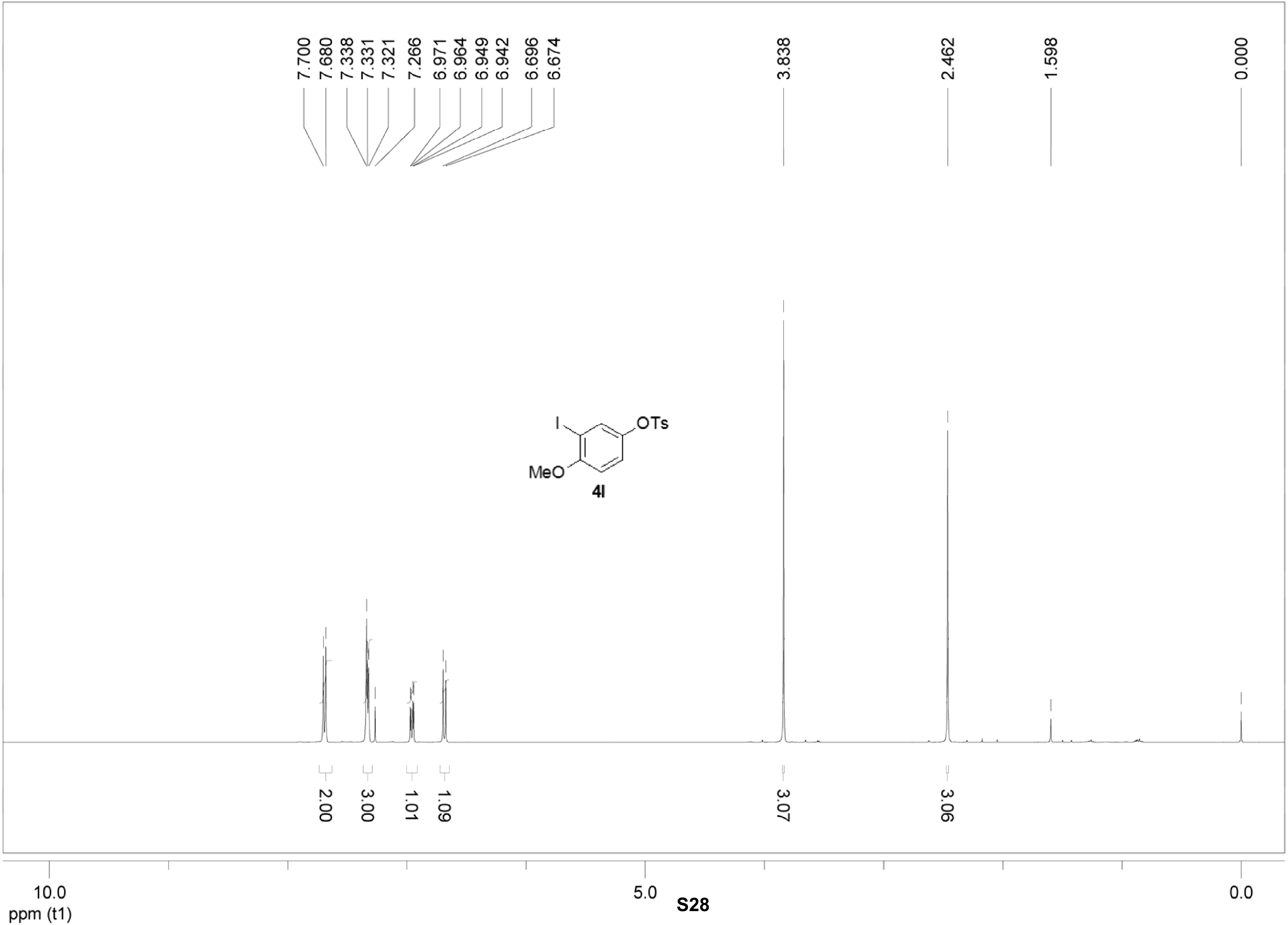
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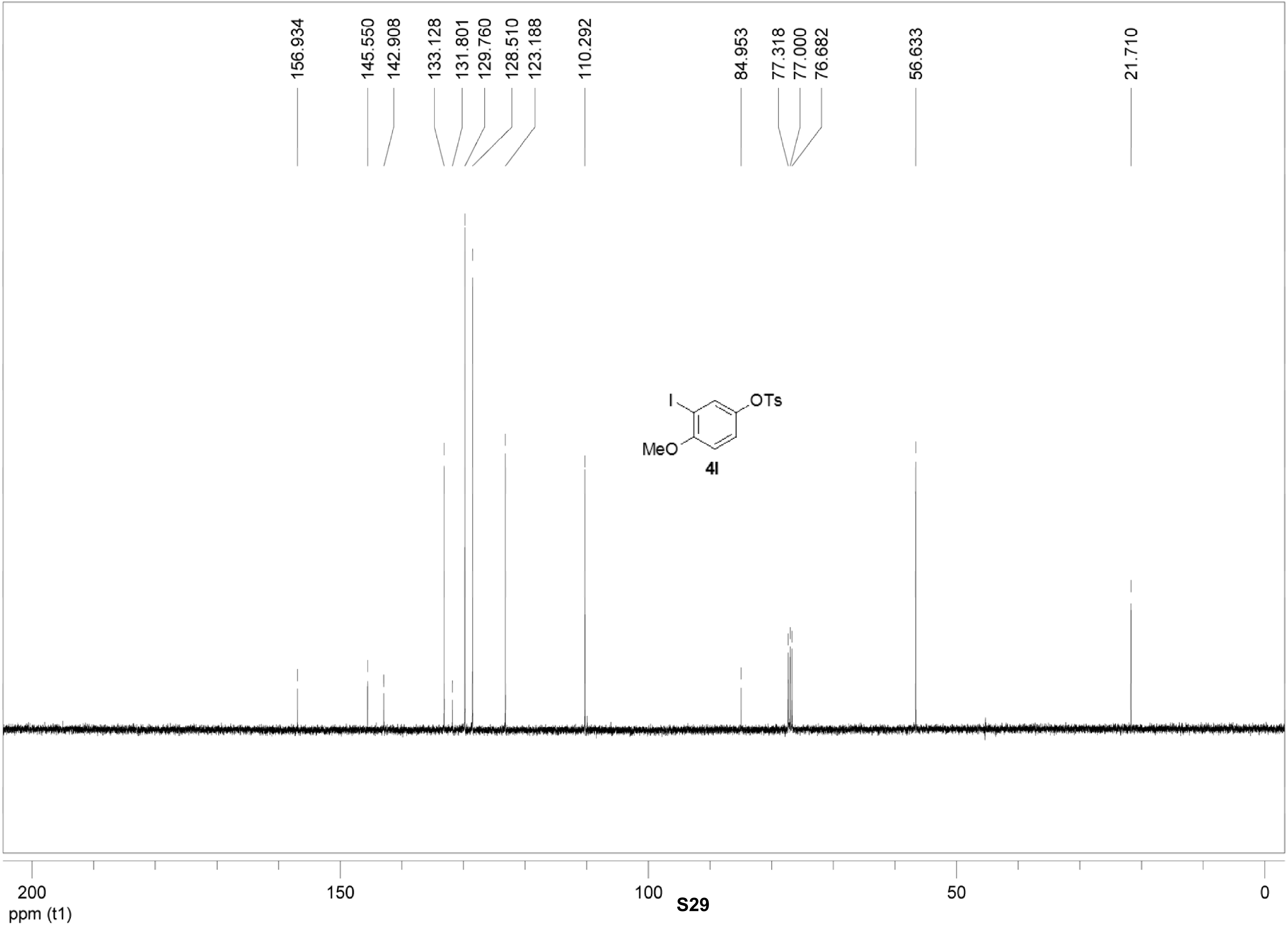
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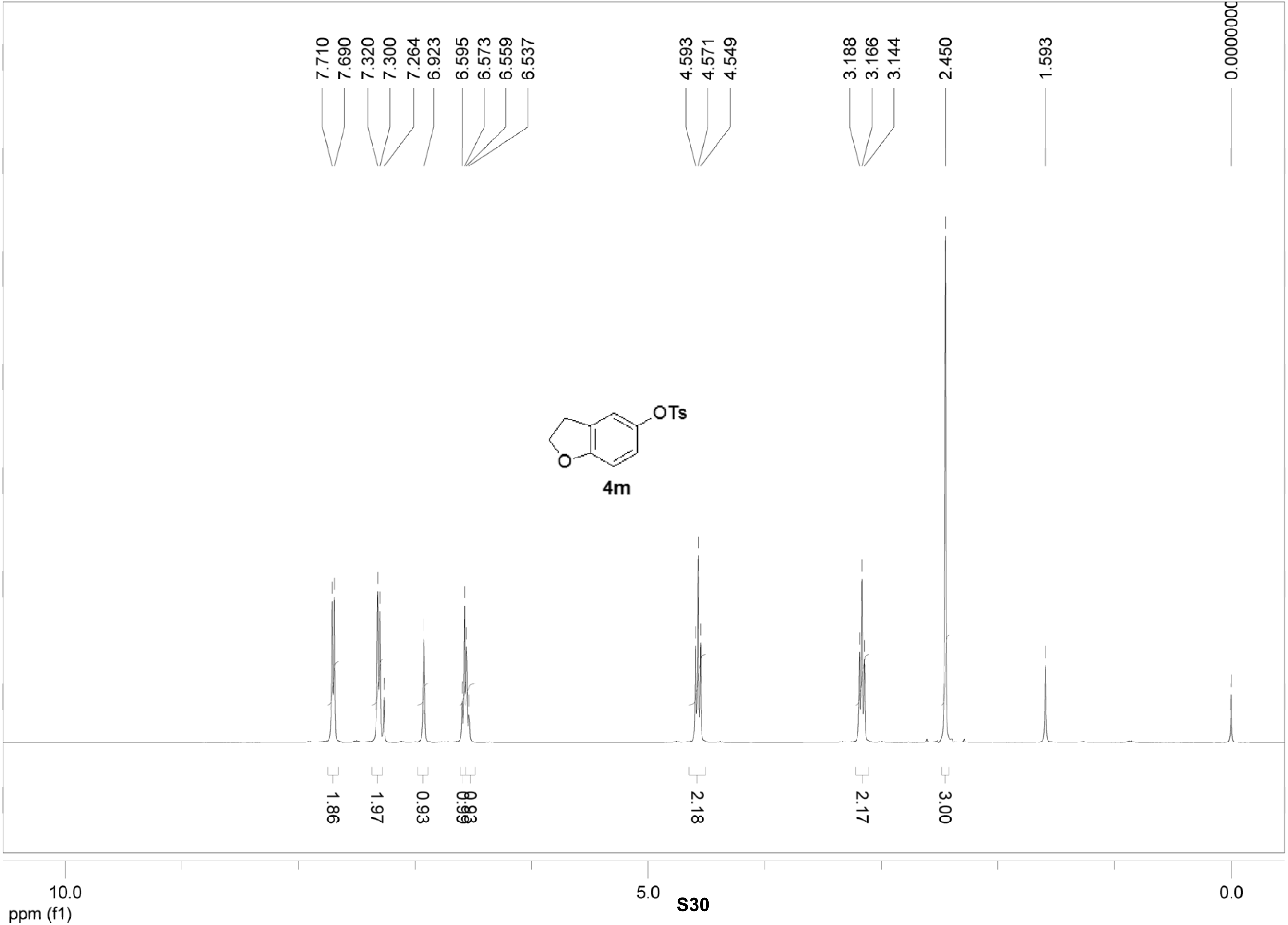
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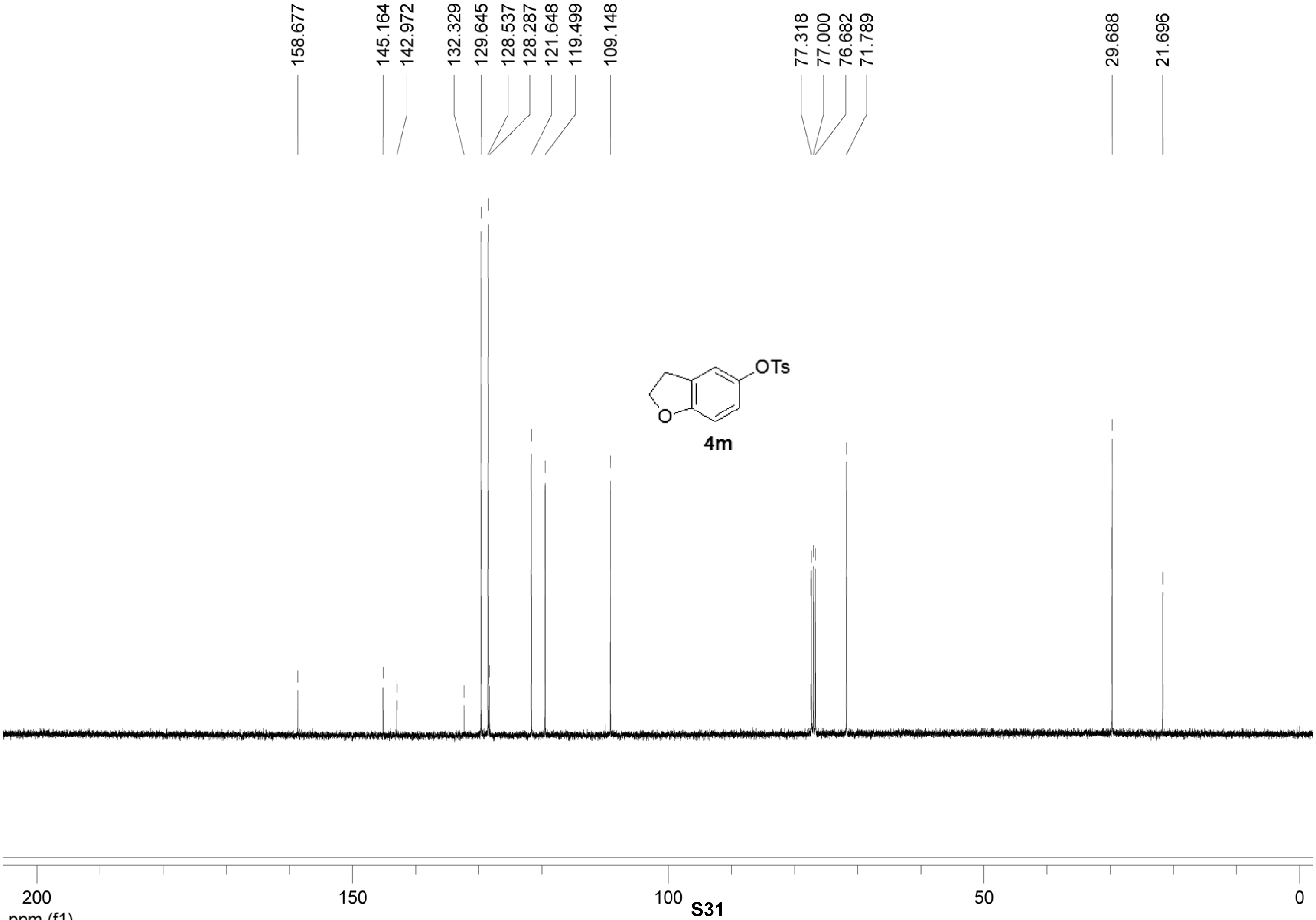
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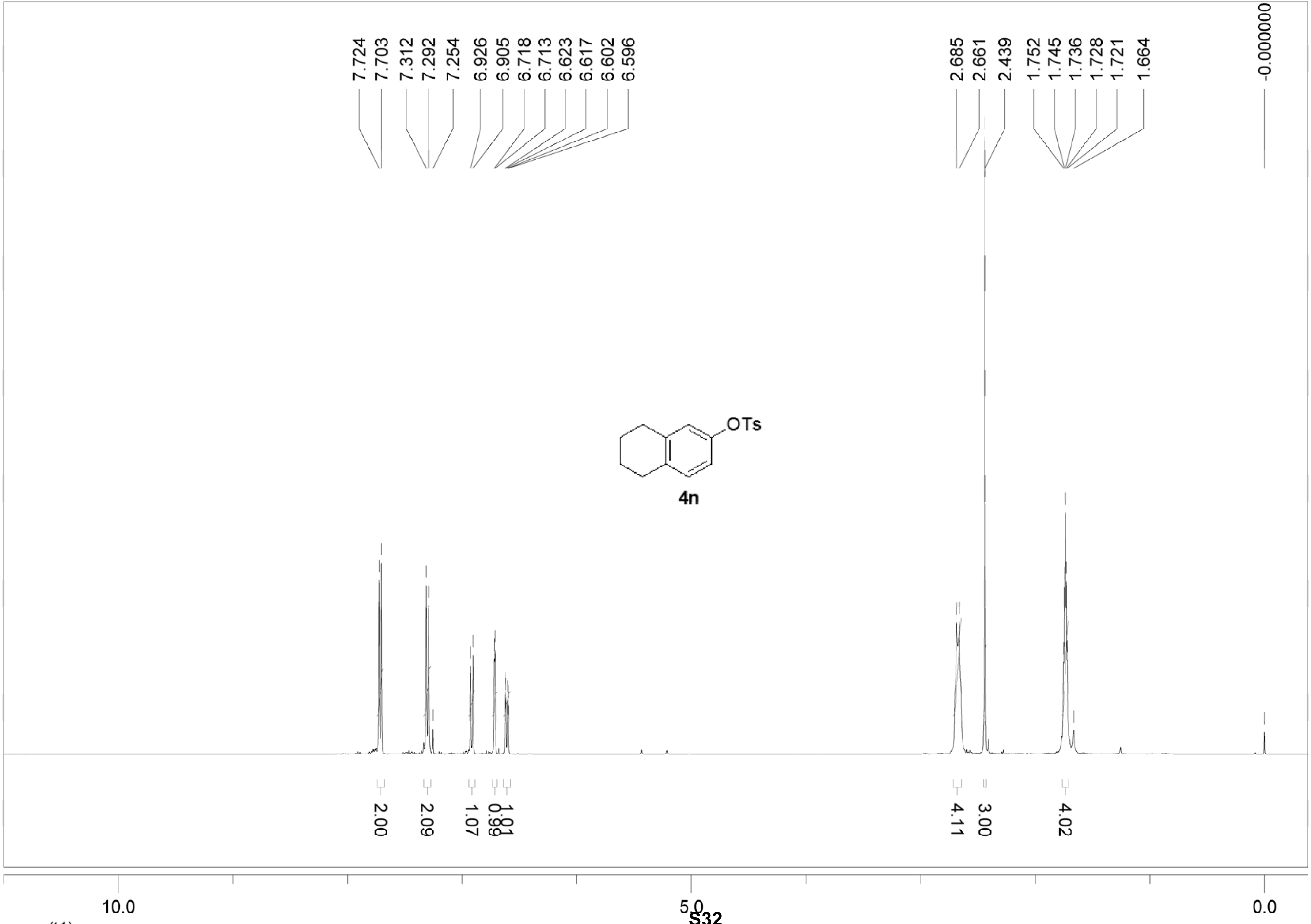
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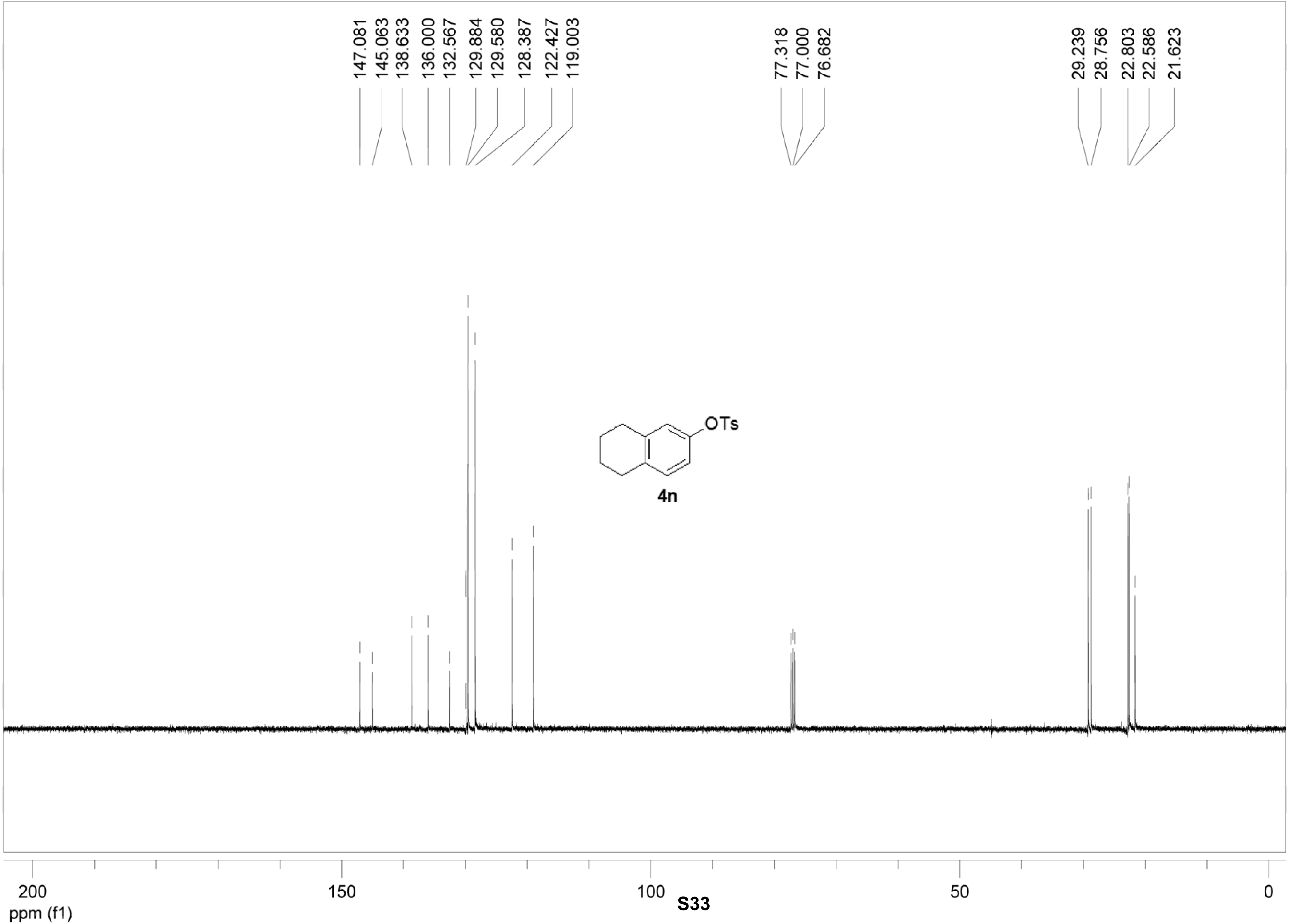
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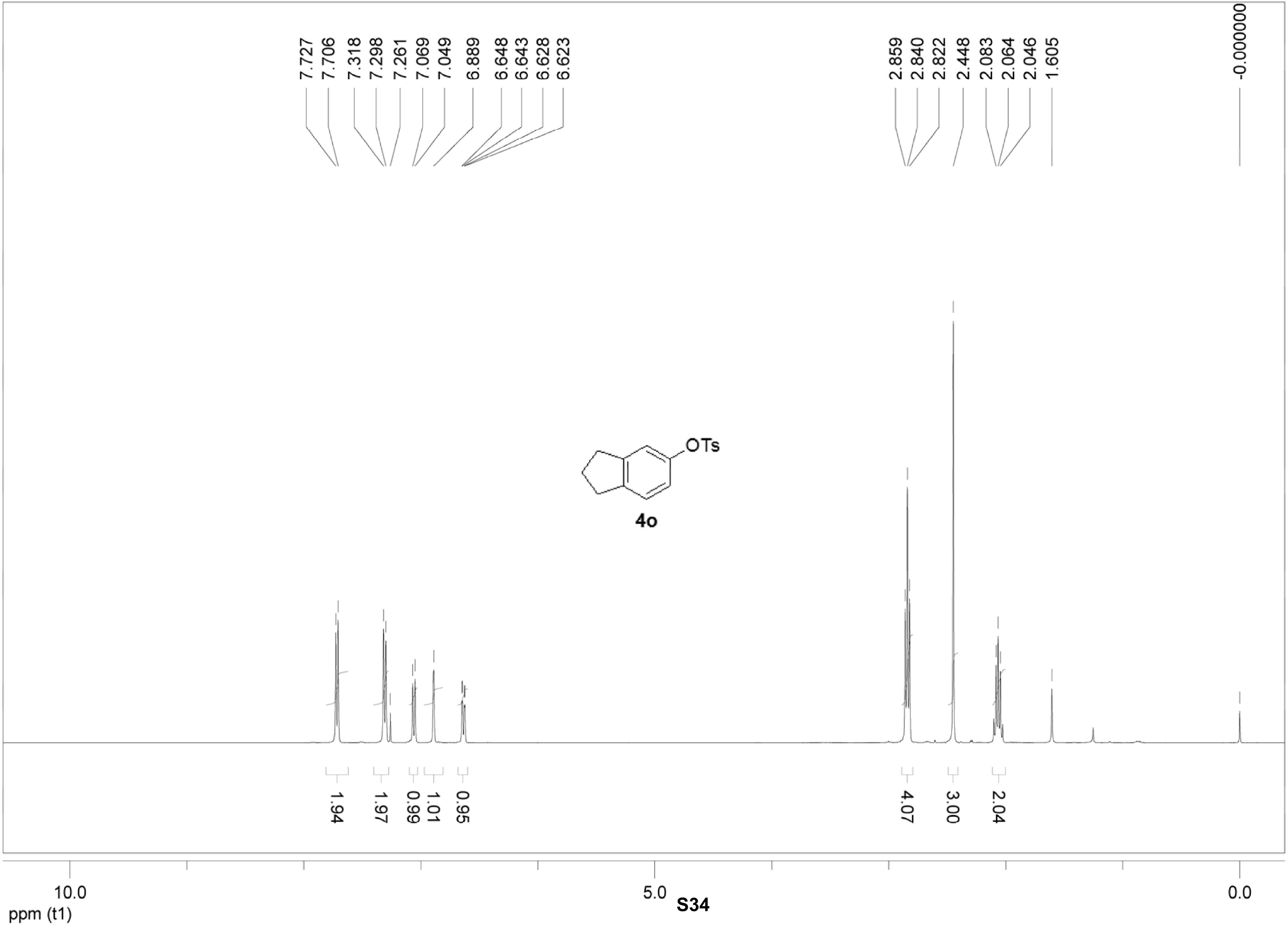
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OTs
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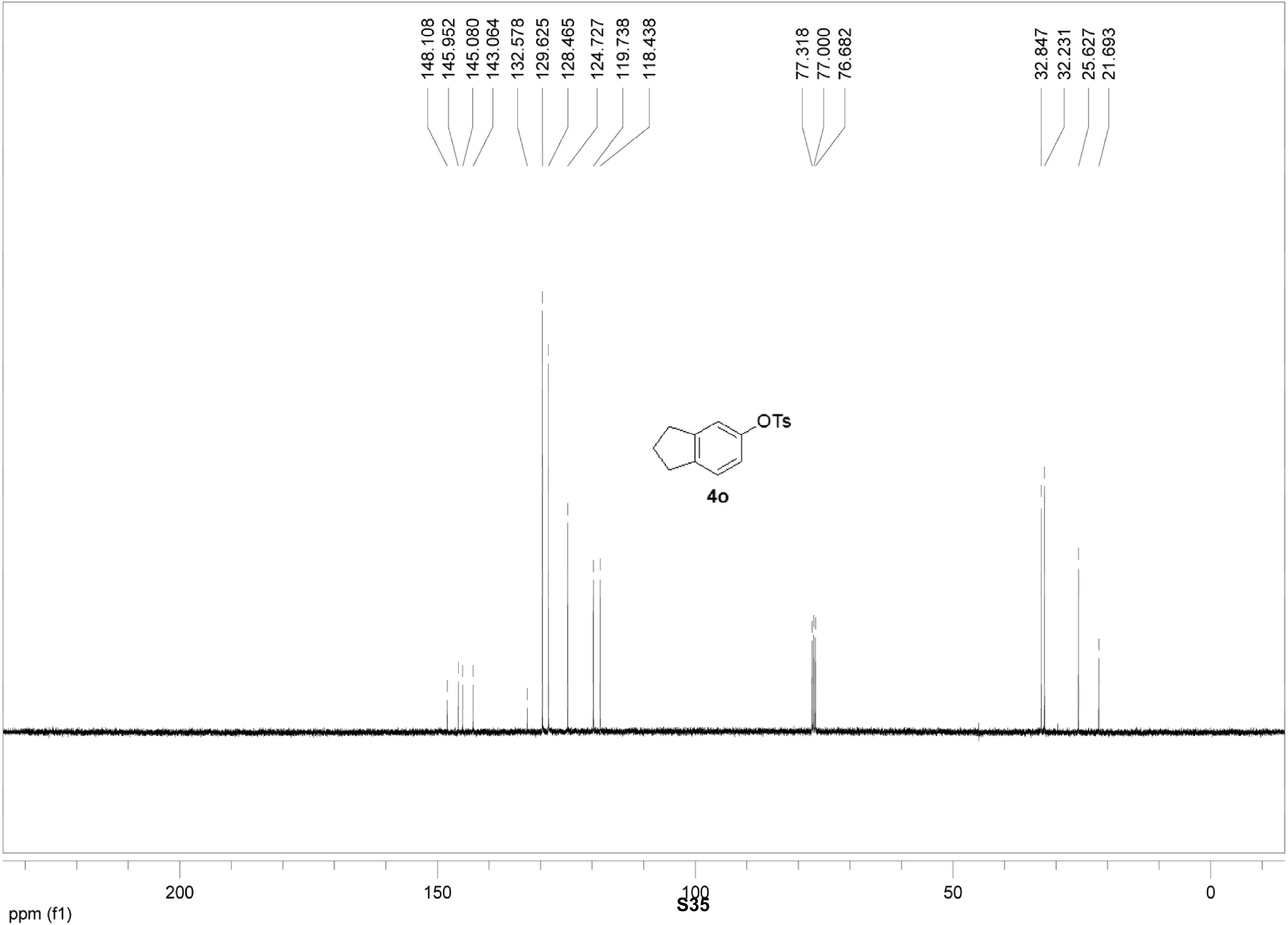
0.99
1.01
0.95
4.07
3.00
2.04
10.0
5.0
0.0
ppm (t1)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128.465
124.727
119.738
118.438
77.318
77.000
76.682
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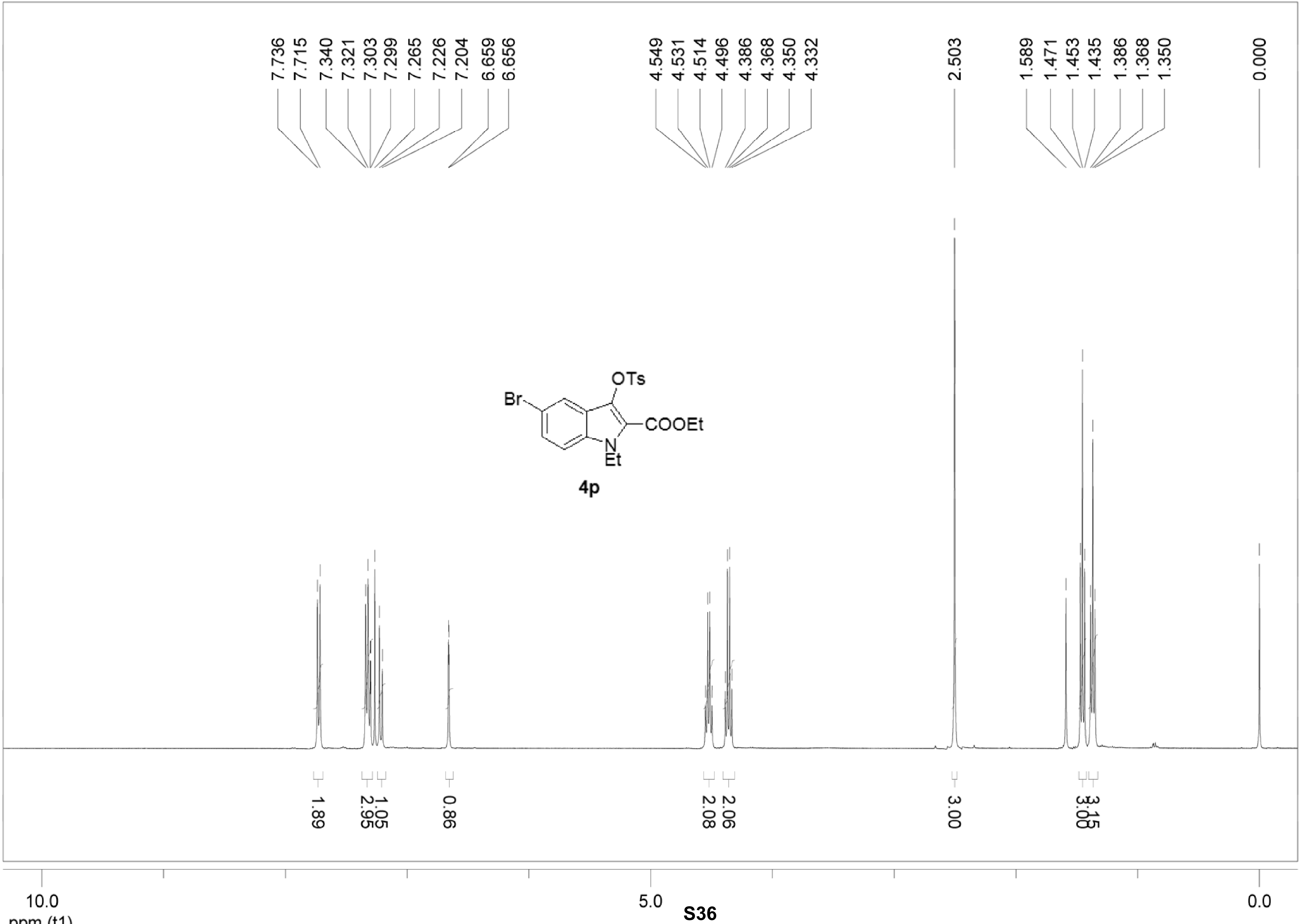
32.231
25.627
21.693
OTs
4o
200
150
100
50
0
ppm (f1)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7.321
7.303
7.299
7.265
7.226
7.204
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6.656
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4.531
4.514
4.496
4.386
4.368
4.350
4.332
2.503
1.589
1.471
1.453
1.435
1.386
1.368
1.350
0.000
OTs
Br
COOEt
N
Et
4p
1.89
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2.06
3.00
3.00
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10.0
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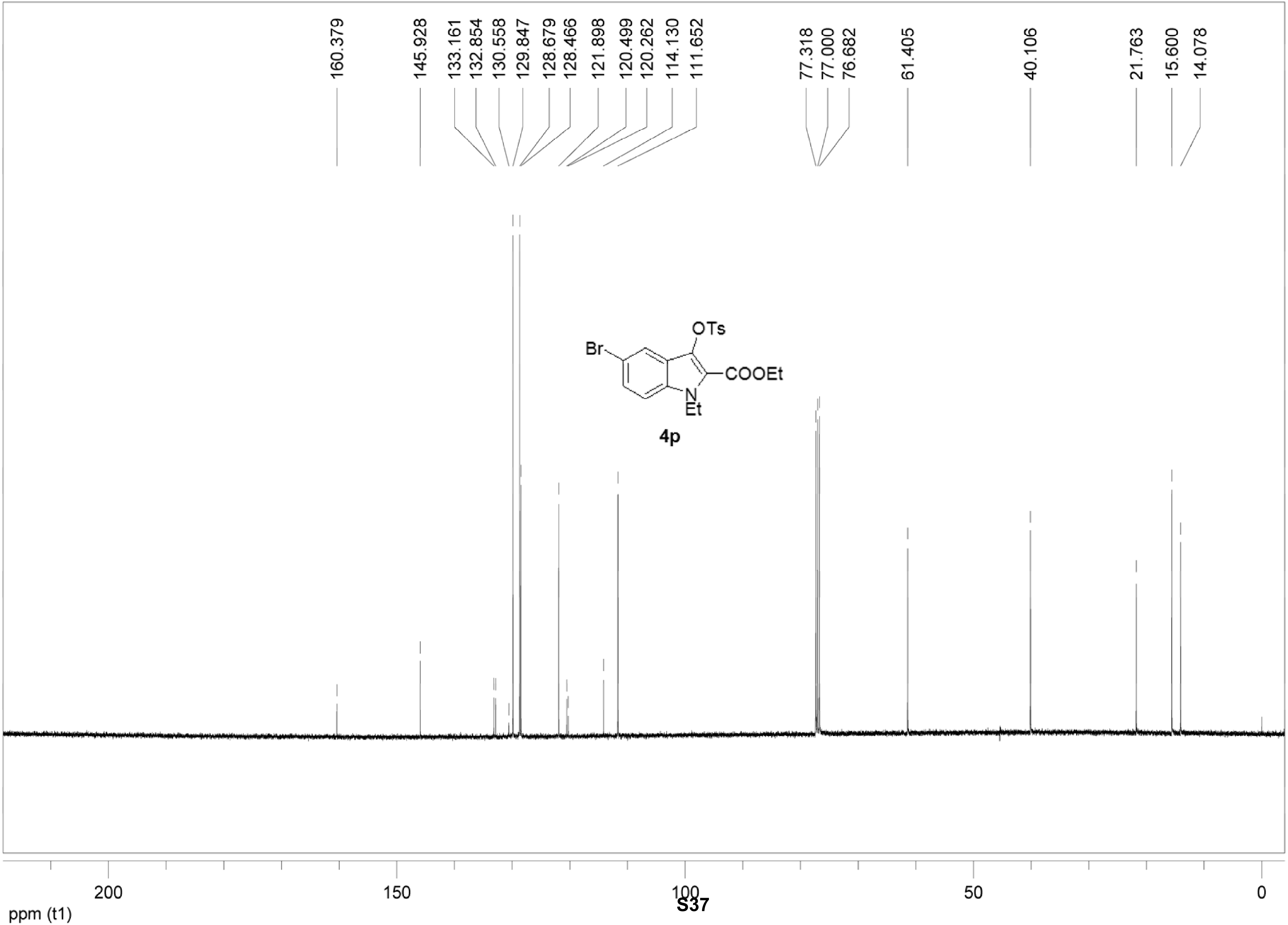
ppm (t1)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128.679
128.466
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120.262
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111.652
77.318
77.000
76.682
61.405
40.106
21.763
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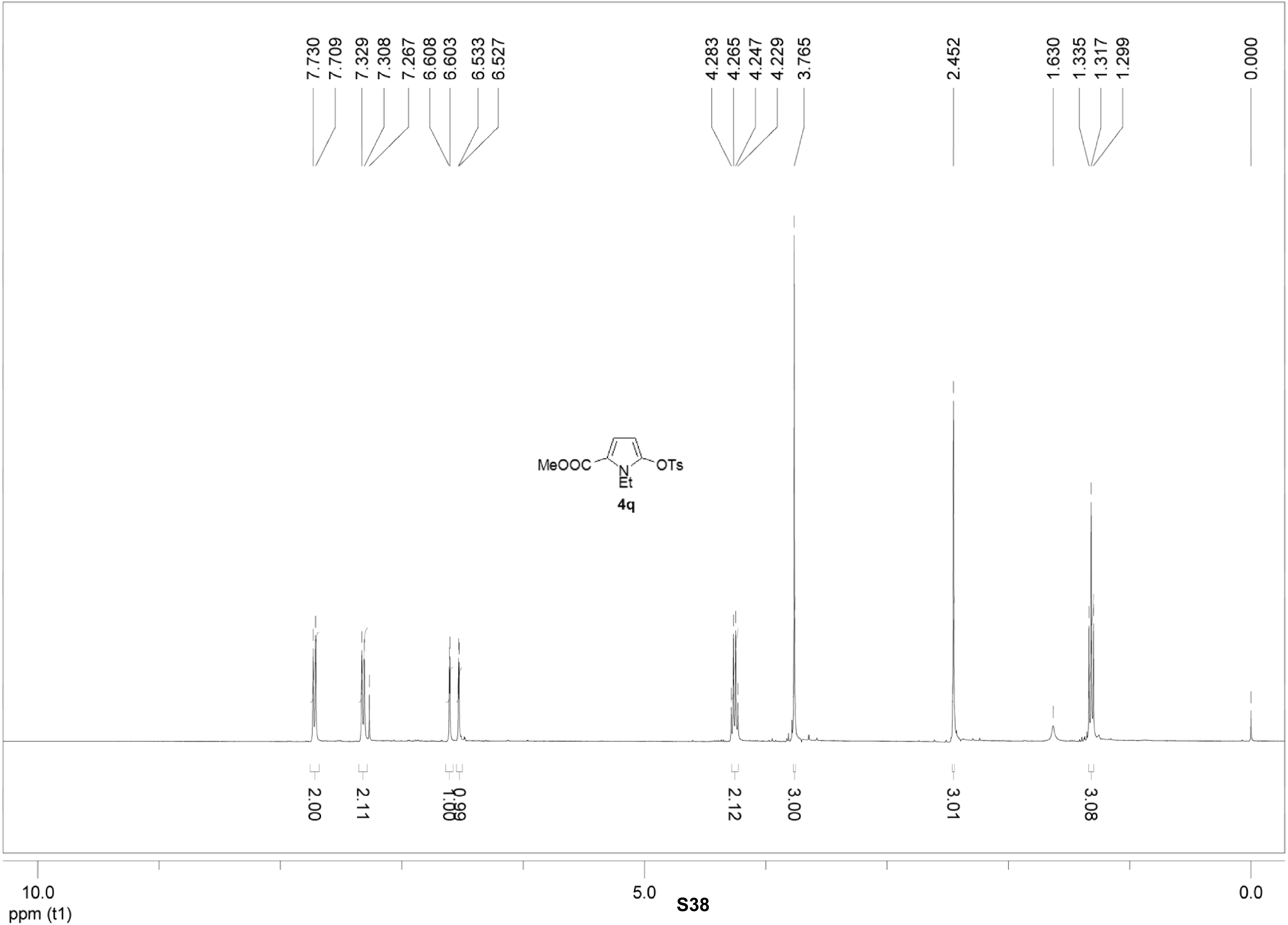
14.078
OTs
Br
COOEt
N
Et
4p
200
150
100
50
0
ppm (t1)



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7.308
7.267
6.608
6.603
6.533
6.527
4.283
4.265
4.247
4.229
3.765
2.452
1.630
1.335
1.317
1.299
0.000
MeOOC
N
Et
OTs
4q
2.00
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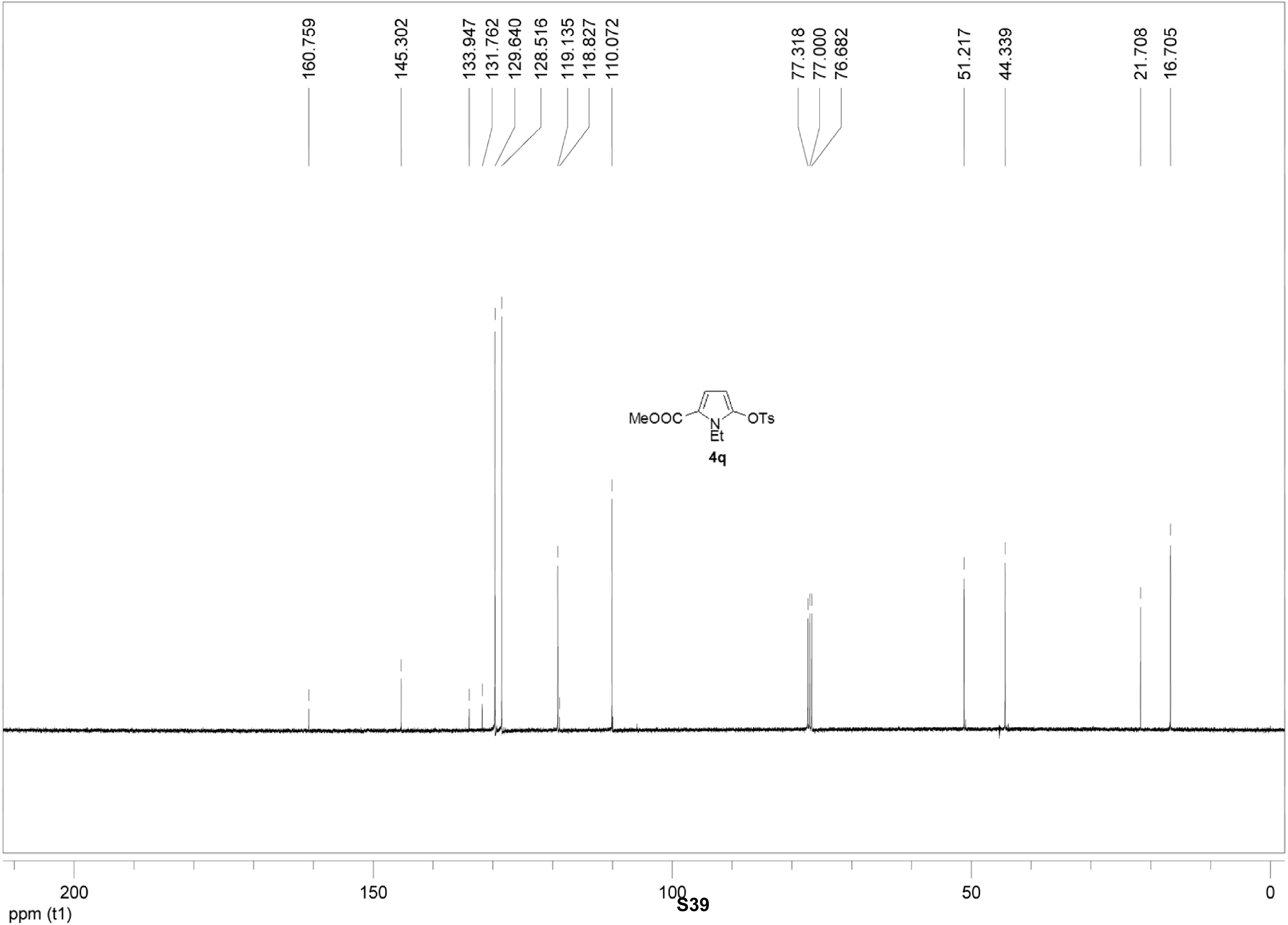
2.12
3.00
3.01
3.08
10.0
ppm (t1)
5.0
0.0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119.135
118.827
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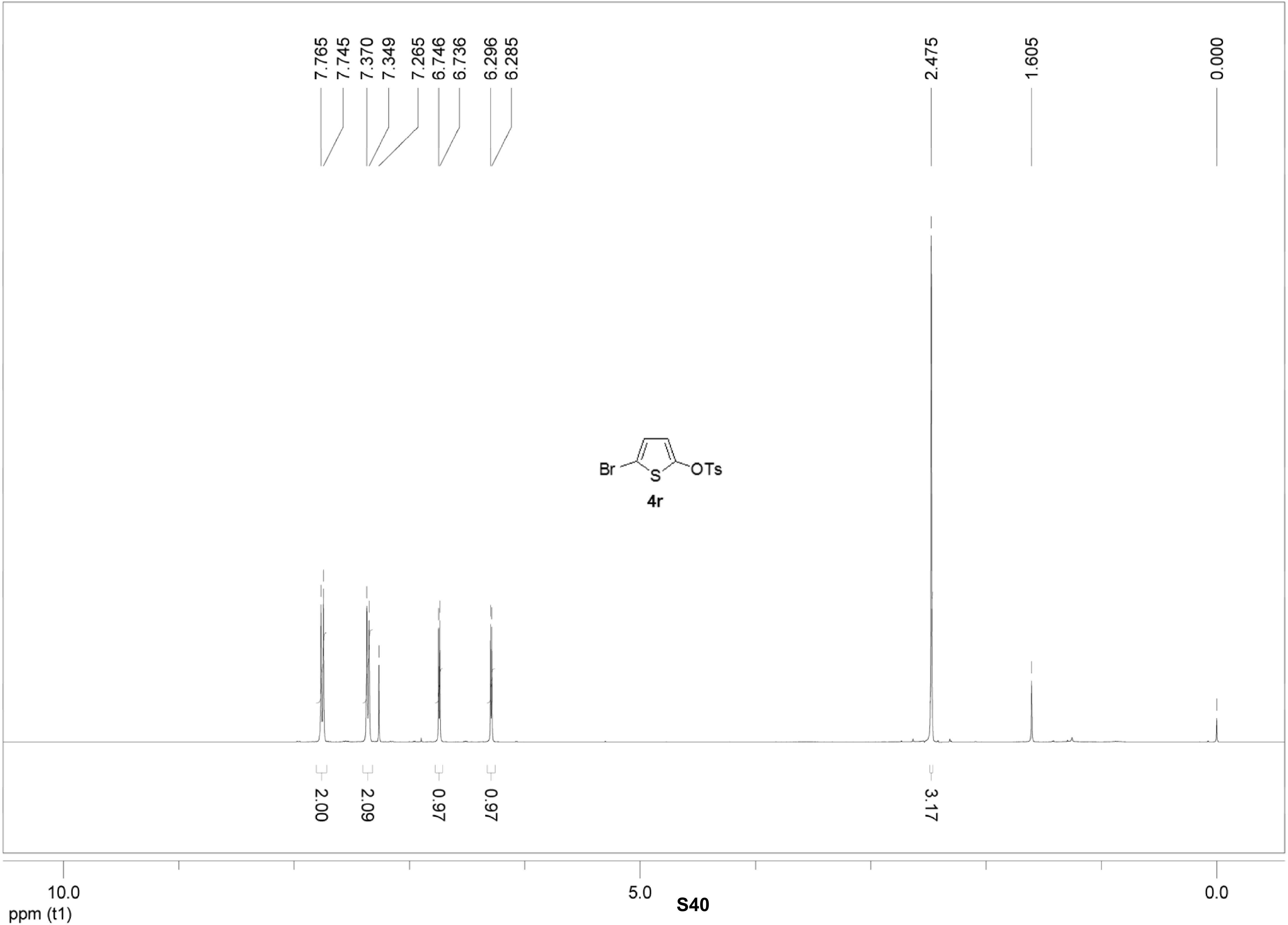
Et
OTs
4q
200
150
100
50
0
ppm (t1)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7.265
6.746
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6.296
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2.475
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0.000
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S
OTs
4r
2.00
2.09
0.97
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3.17
10.0
5.0
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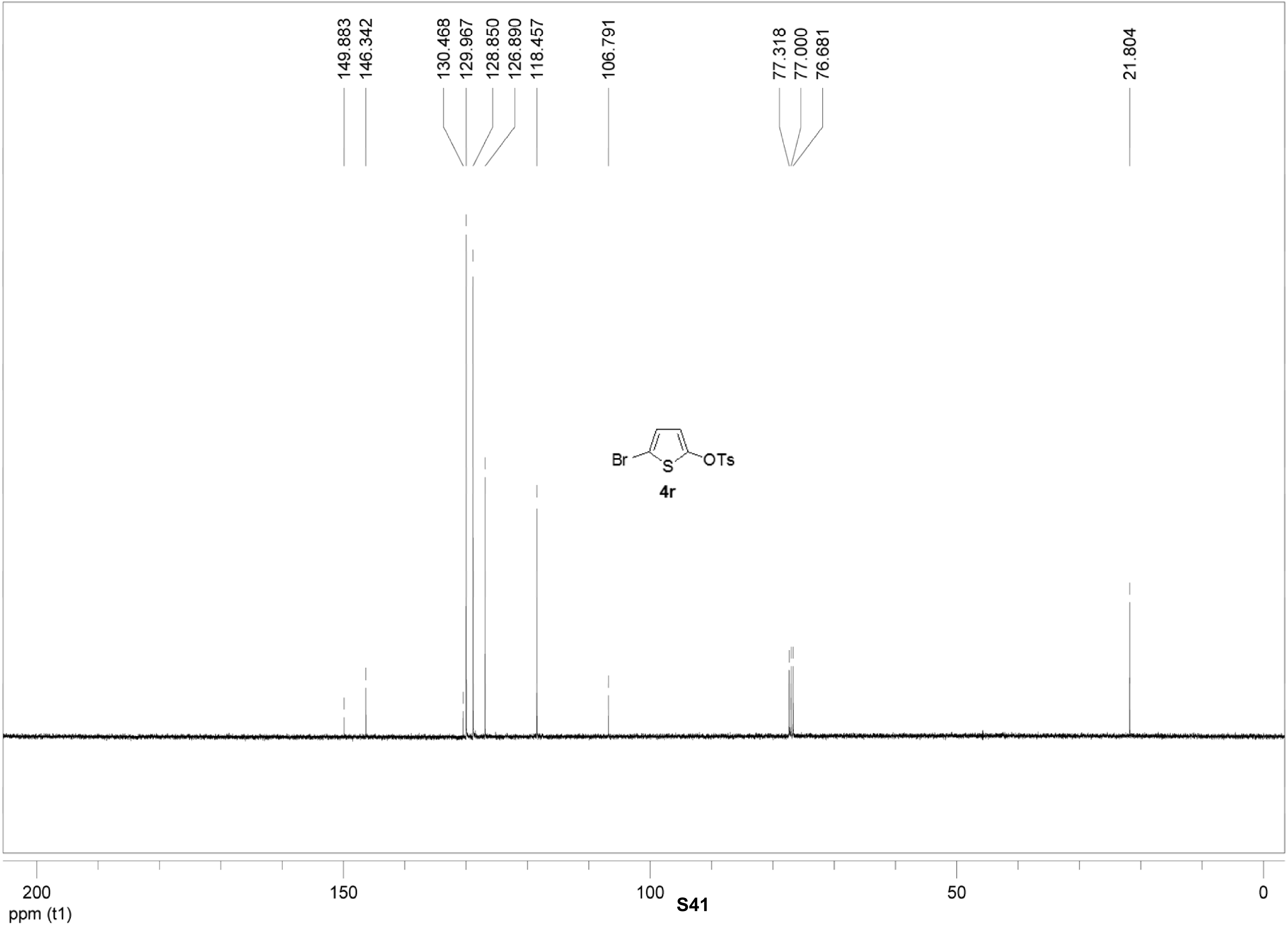
ppm (t1)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76.681
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S
OTs
4r
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50
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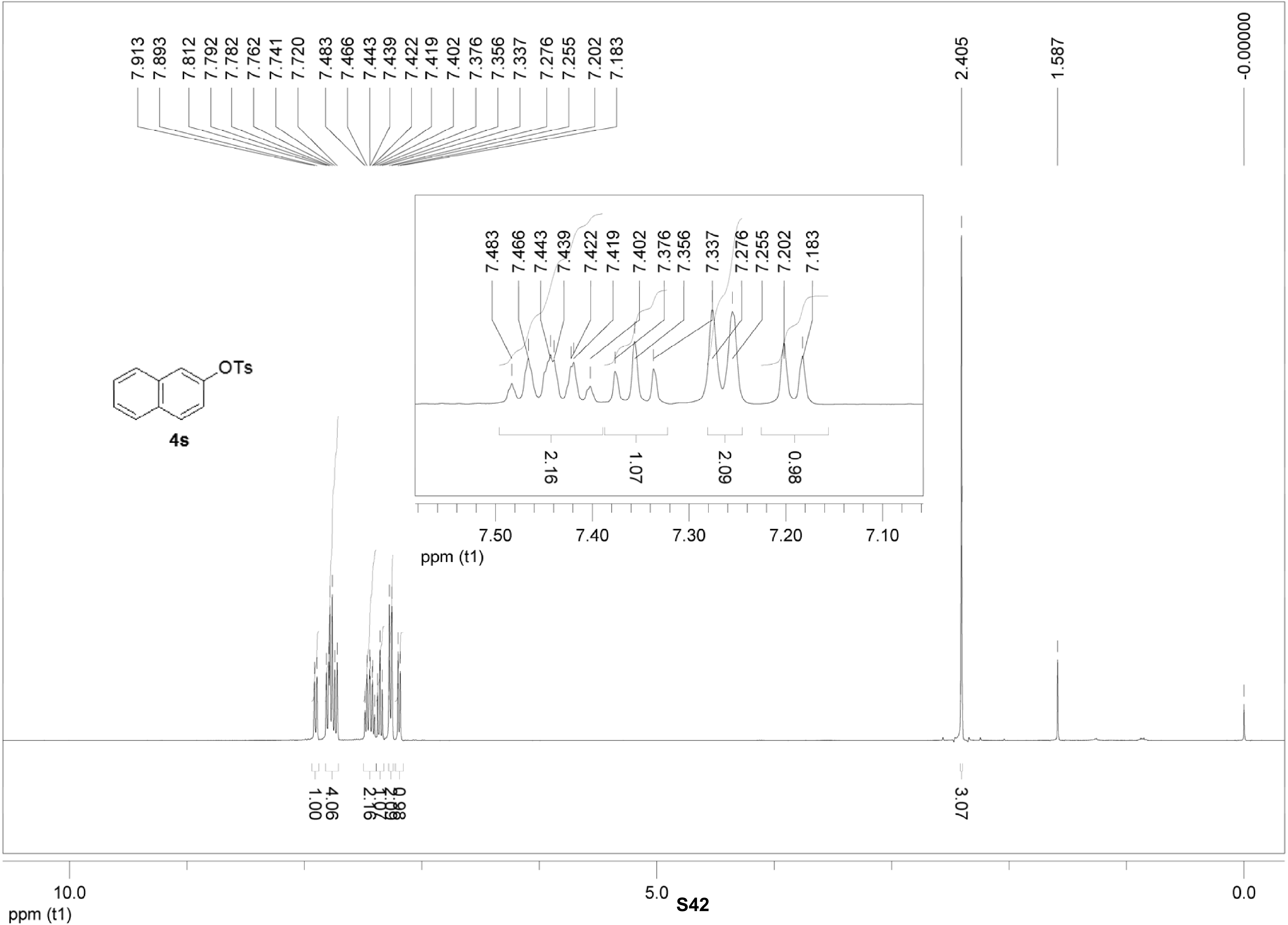
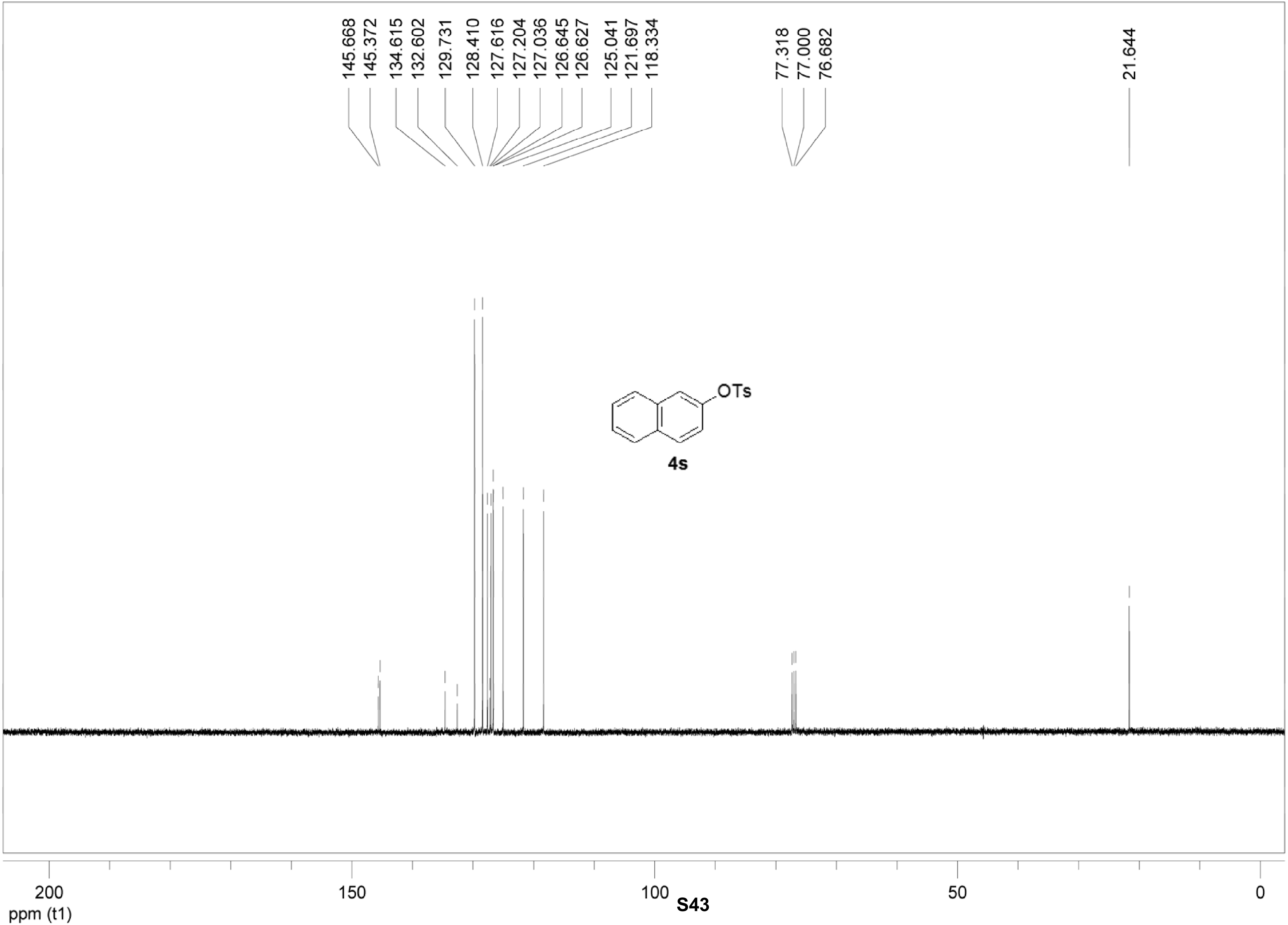
ppm (t1)


OTs
4s
ppm (t1)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127.616
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126.627
125.041
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77.000
76.682
21.644
OTs
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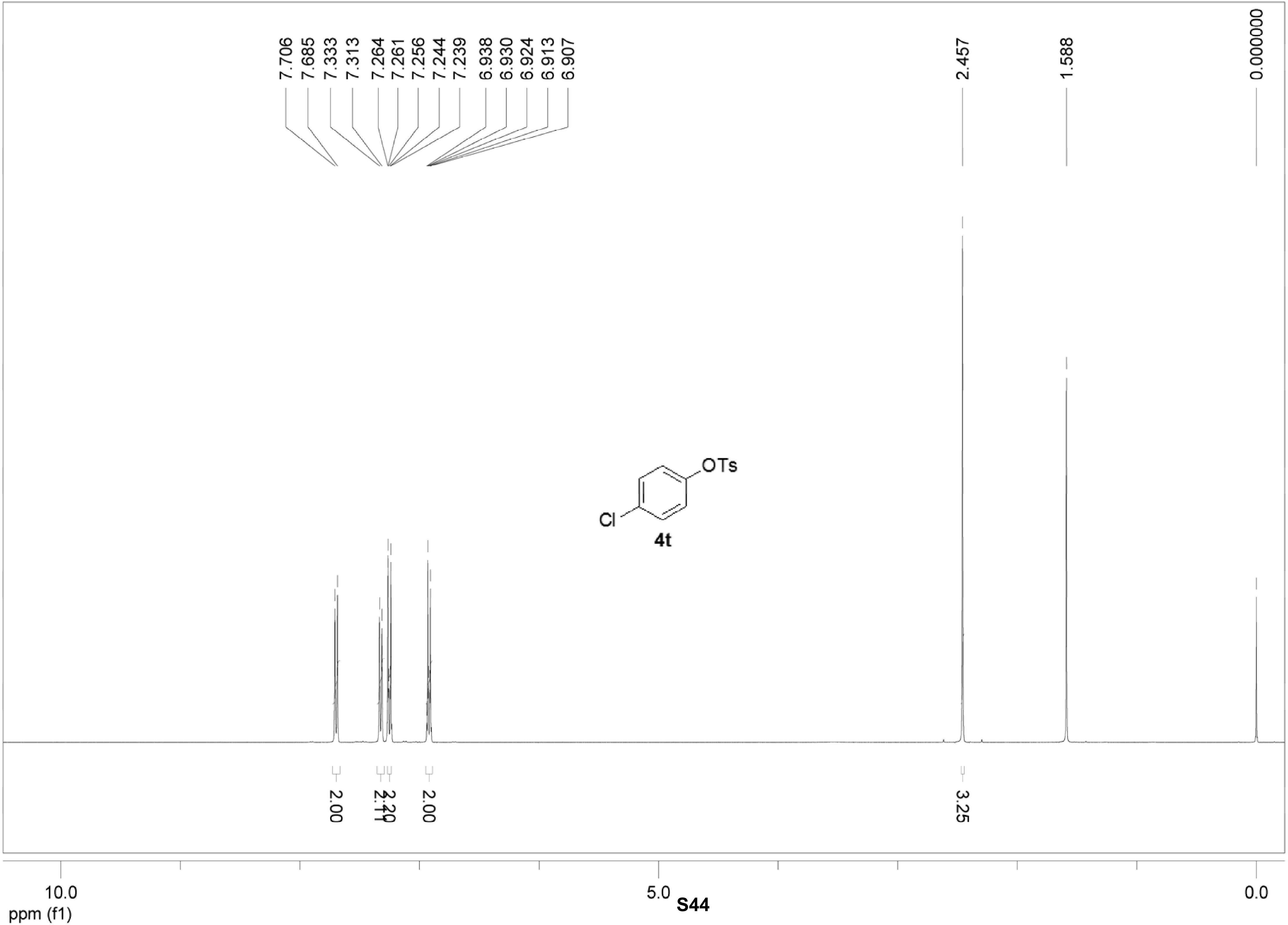
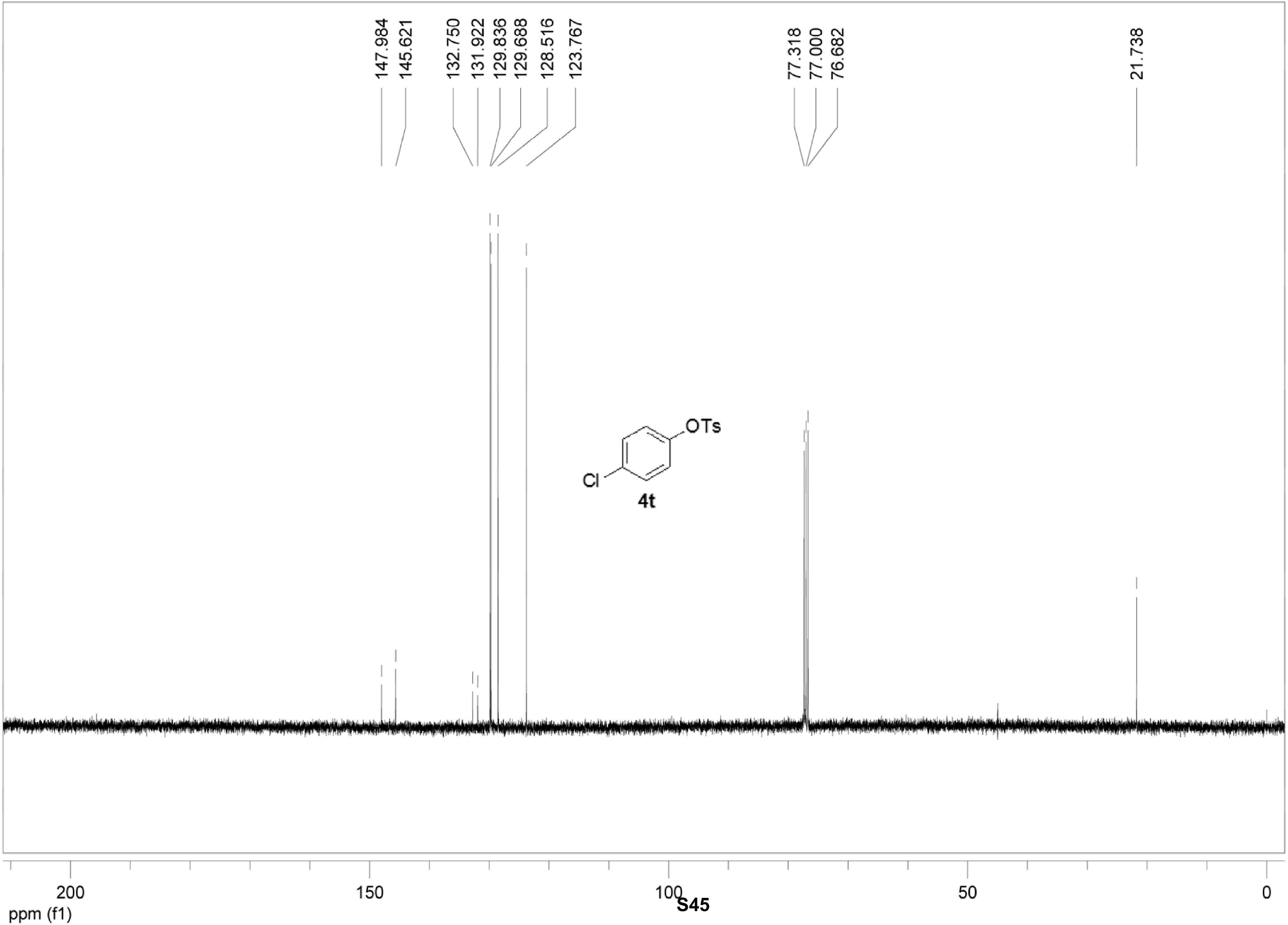
200
150
100
50
0
ppm (t1)


7.706
7.685
7.333
7.313
7.264
7.261
7.256
7.244
7.239
6.938
6.930
6.924
6.913
6.907
2.457
1.588
0.000000
OTs
Cl
4t
2.00
2.11
2.20
2.00
3.25
10.0
5.0
0.0
ppm (f1)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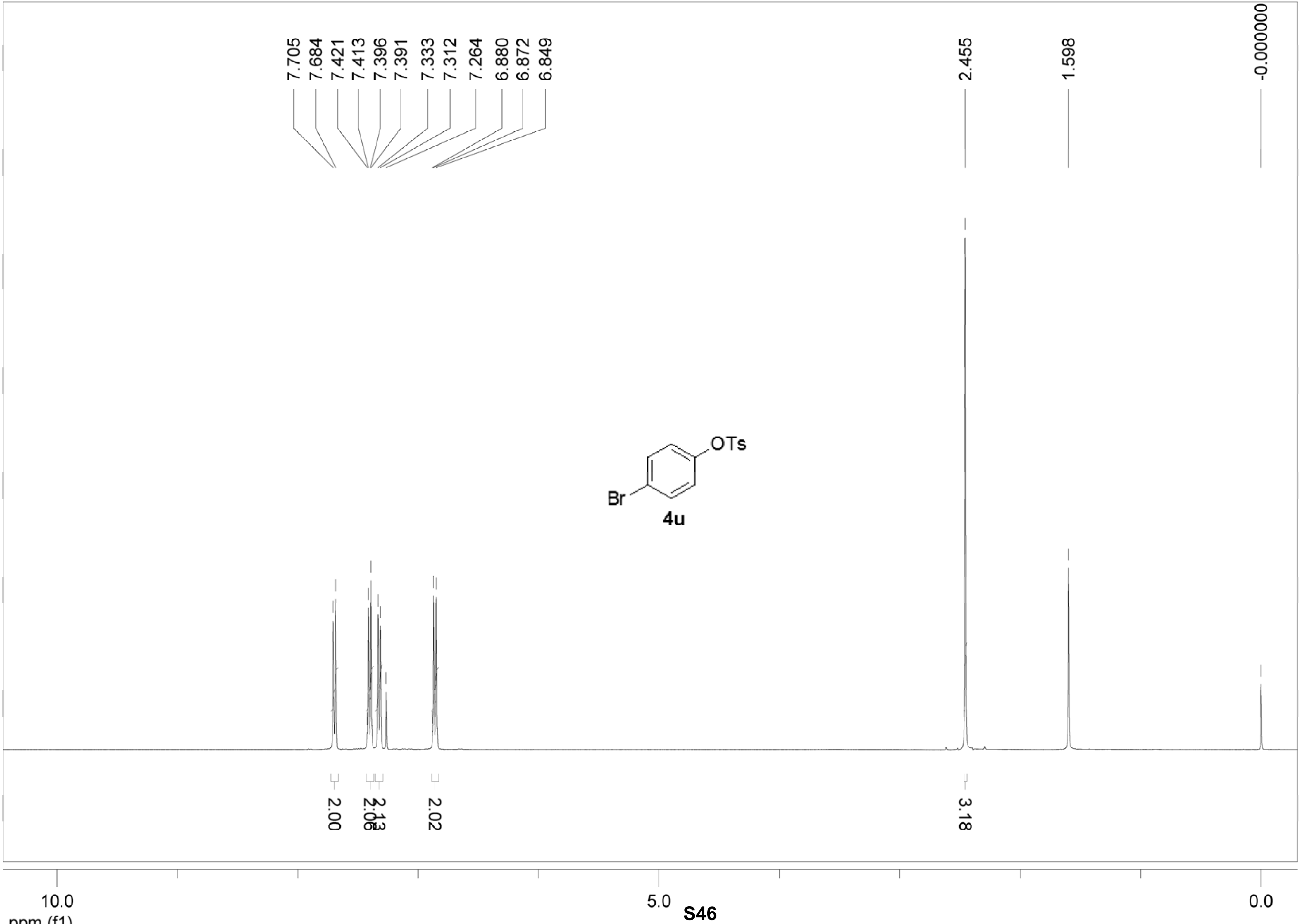
145.621
132.750
131.922
129.836
129.688
128.516
123.767
77.318
77.000
76.682
21.738
OTs
Cl
4t
200
150
100
50
0
ppm (f1)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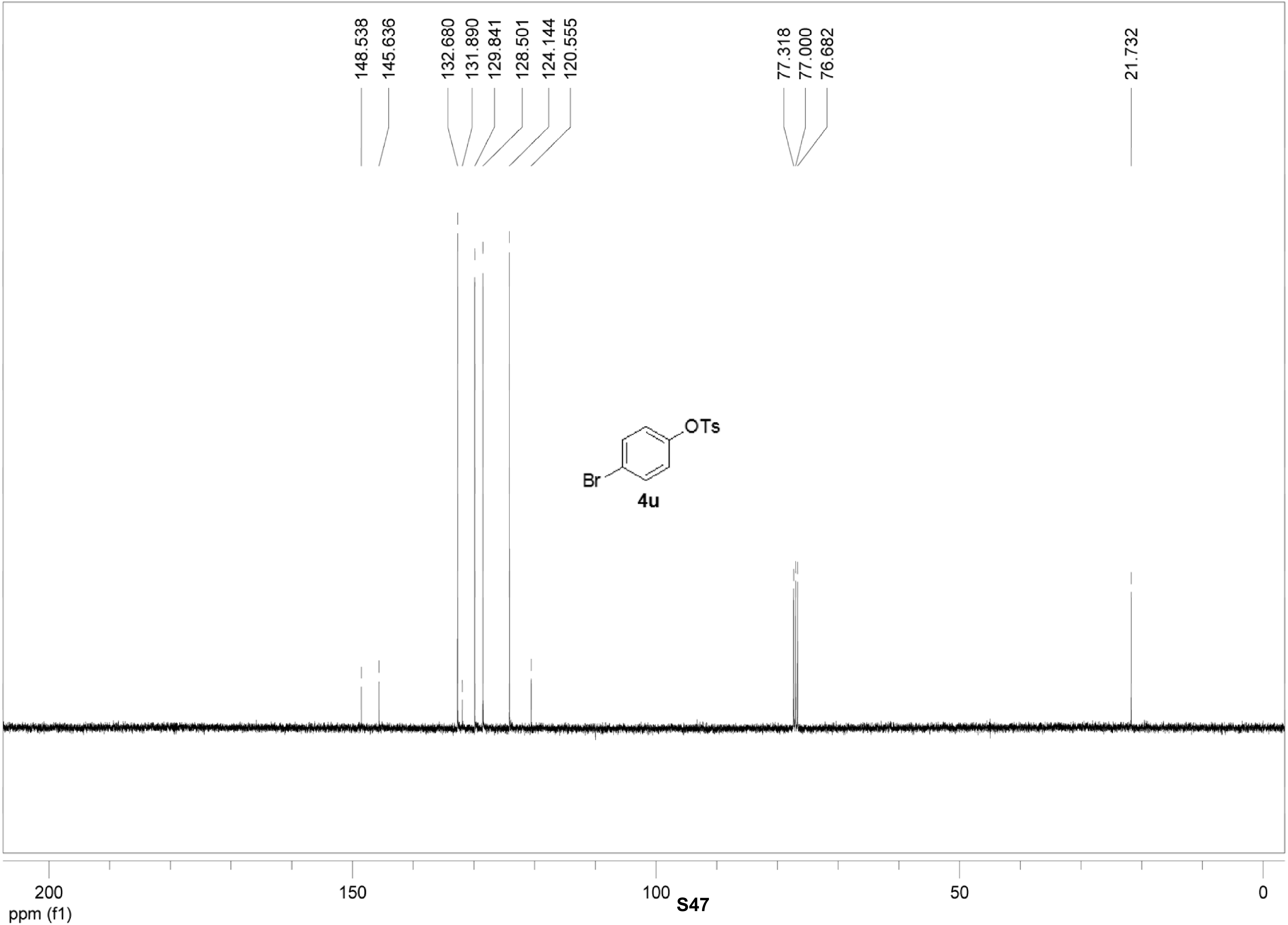
7.684
7.421
7.413
7.396
7.391
7.333
7.312
7.264
6.880
6.872
6.849
2.455
1.598
-0.000000
OTs
Br
4u
2.00
2.06
2.13
2.02
3.18
10.0
5.0
0.0
ppm (f1)


148.538
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131.890
129.841
128.501
124.144
120.555
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77.000
76.682
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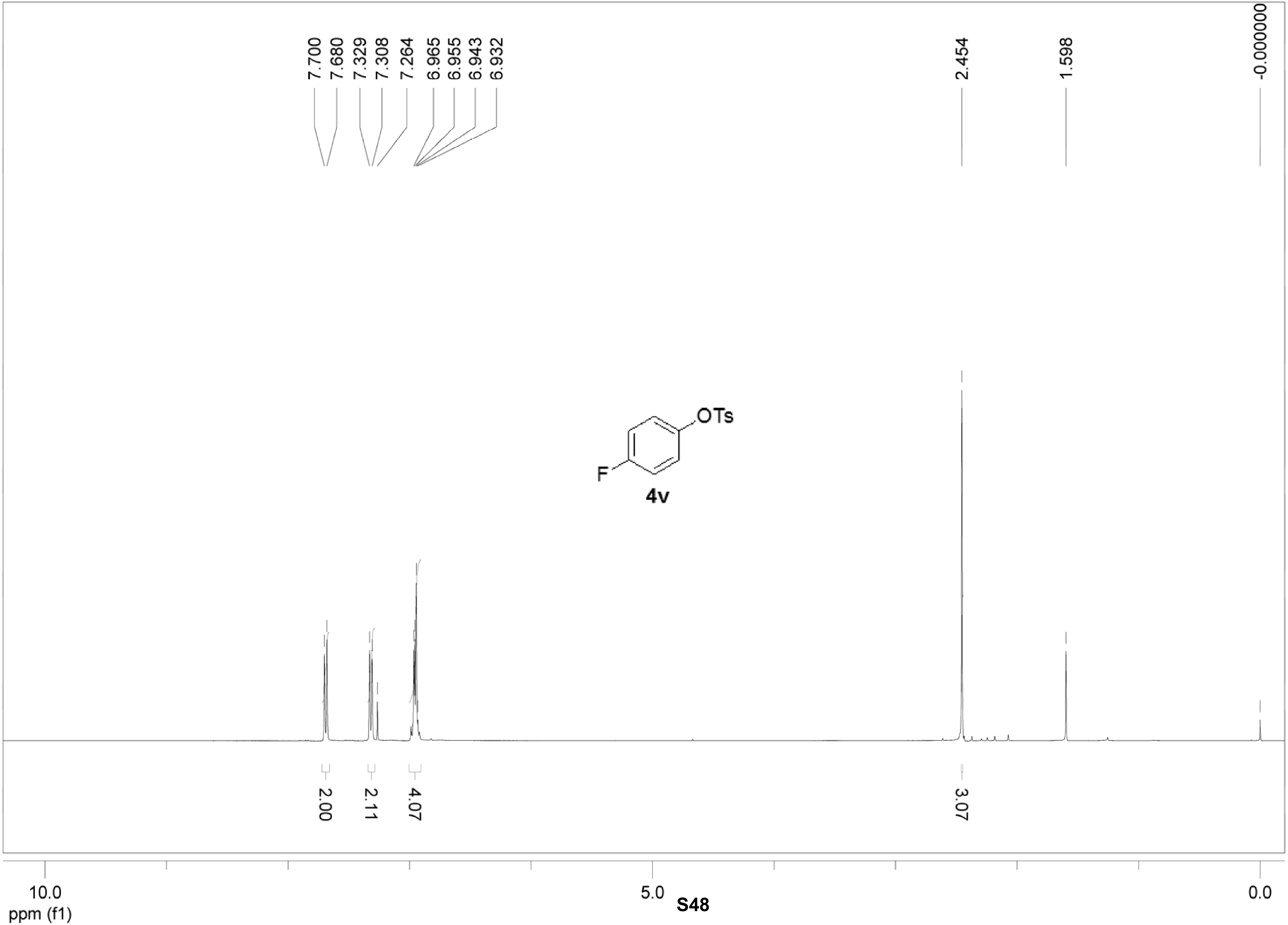
Br
4u
200
150
100
50
0
ppm (f1)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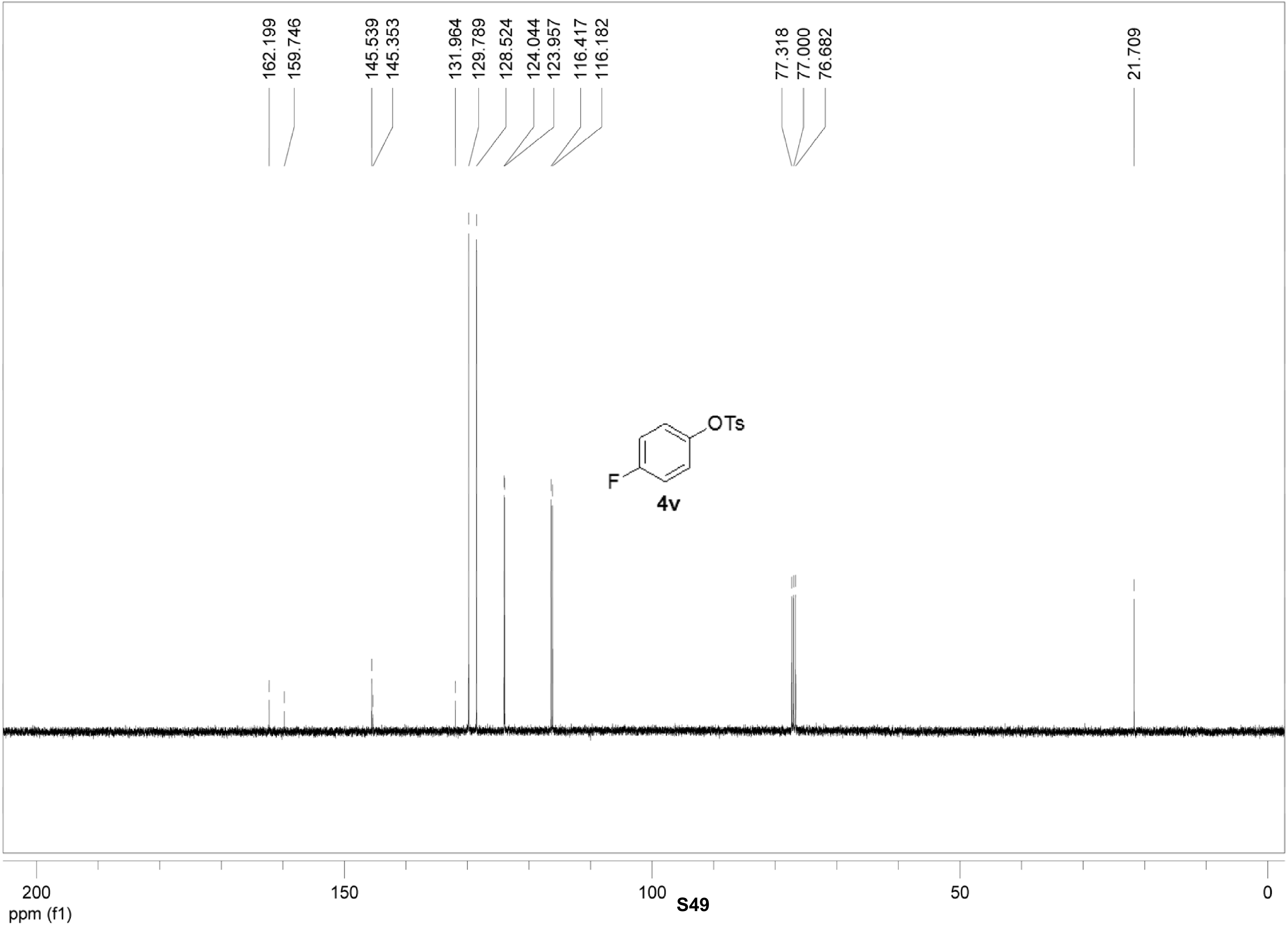
7.680
7.329
7.308
7.264
6.965
6.955
6.943
6.932
2.454
1.598
-0.000000
OTs
F
4v
2.00
2.11
4.07
3.07
10.0
5.0
0.0
ppm (f1)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145.539
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128.524
124.044
123.957
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77.000
76.682
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OTs
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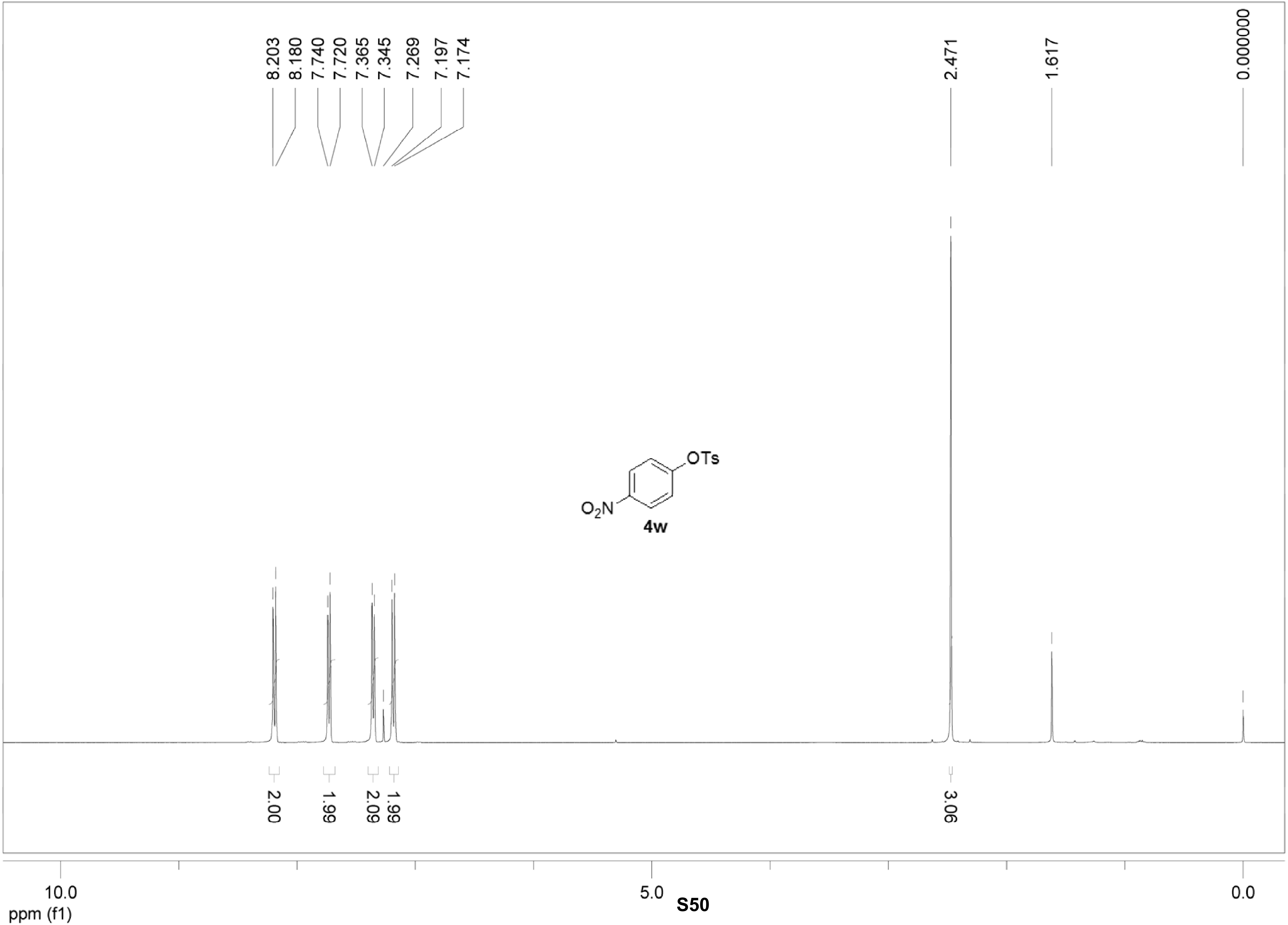
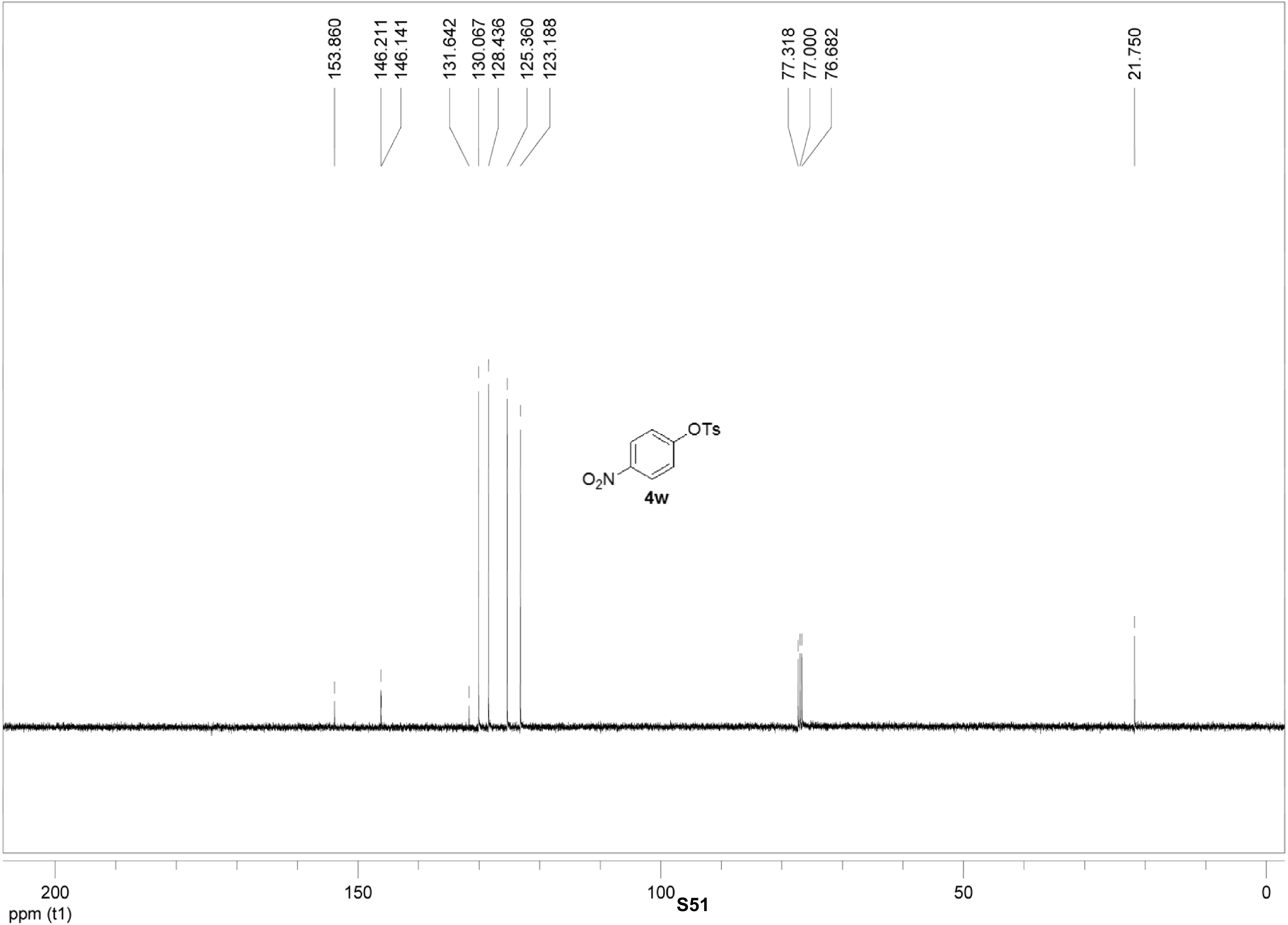
4v
200
150
100
50
0
ppm (f1)


8.203
8.180
7.740
7.720
7.365
7.345
7.269
7.197
7.174
2.471
1.617
0.000000
OTs
O2N
4w
2.00
1.99
2.09
1.99
3.06
10.0
5.0
0.0
ppm (f1)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128.436
125.360
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77.000
76.682
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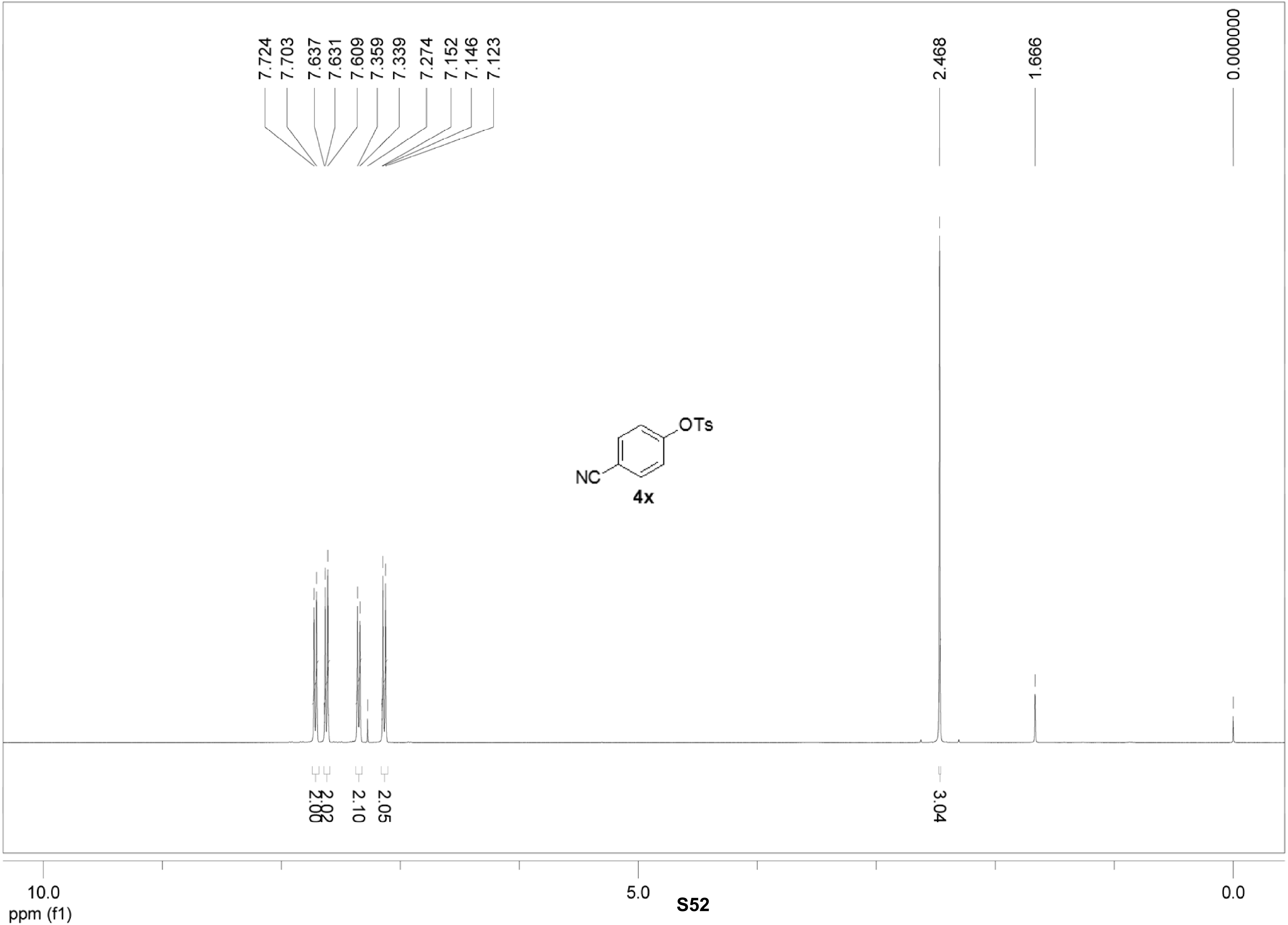
4w
200
150
100
50
0
ppm (t1)


7.724
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7.637
7.631
7.609
7.359
7.339
7.274
7.152
7.146
7.123
2.468
1.666
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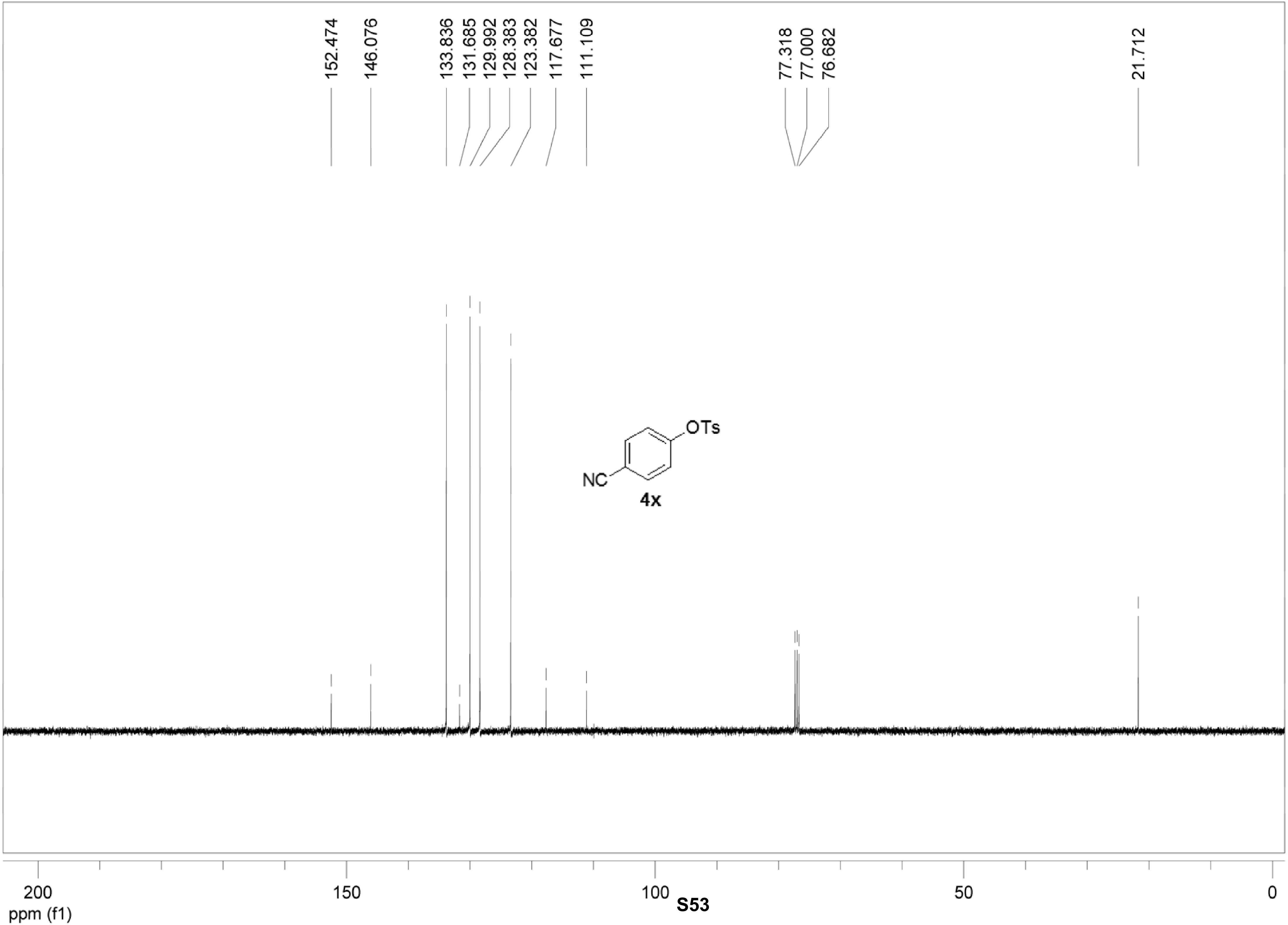
OTs
NC
4x
2.02
2.10
2.05
3.04
10.0
5.0
0.0
ppm (f1)


152.474
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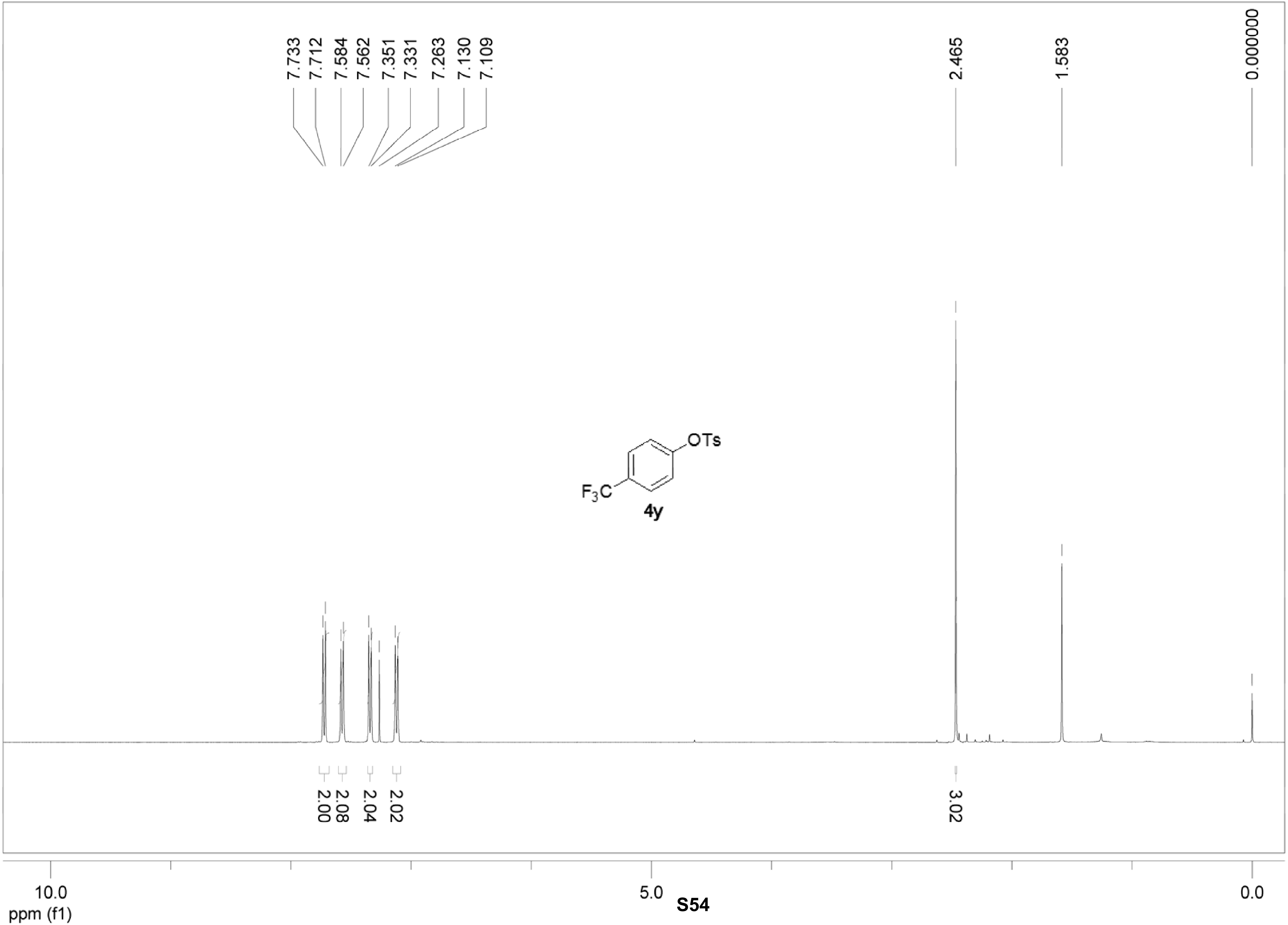
4x
200
150
100
50
0
ppm (f1)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7.562
7.351
7.331
7.263
7.130
7.109
2.465
1.583
0.000000
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F3C
4y
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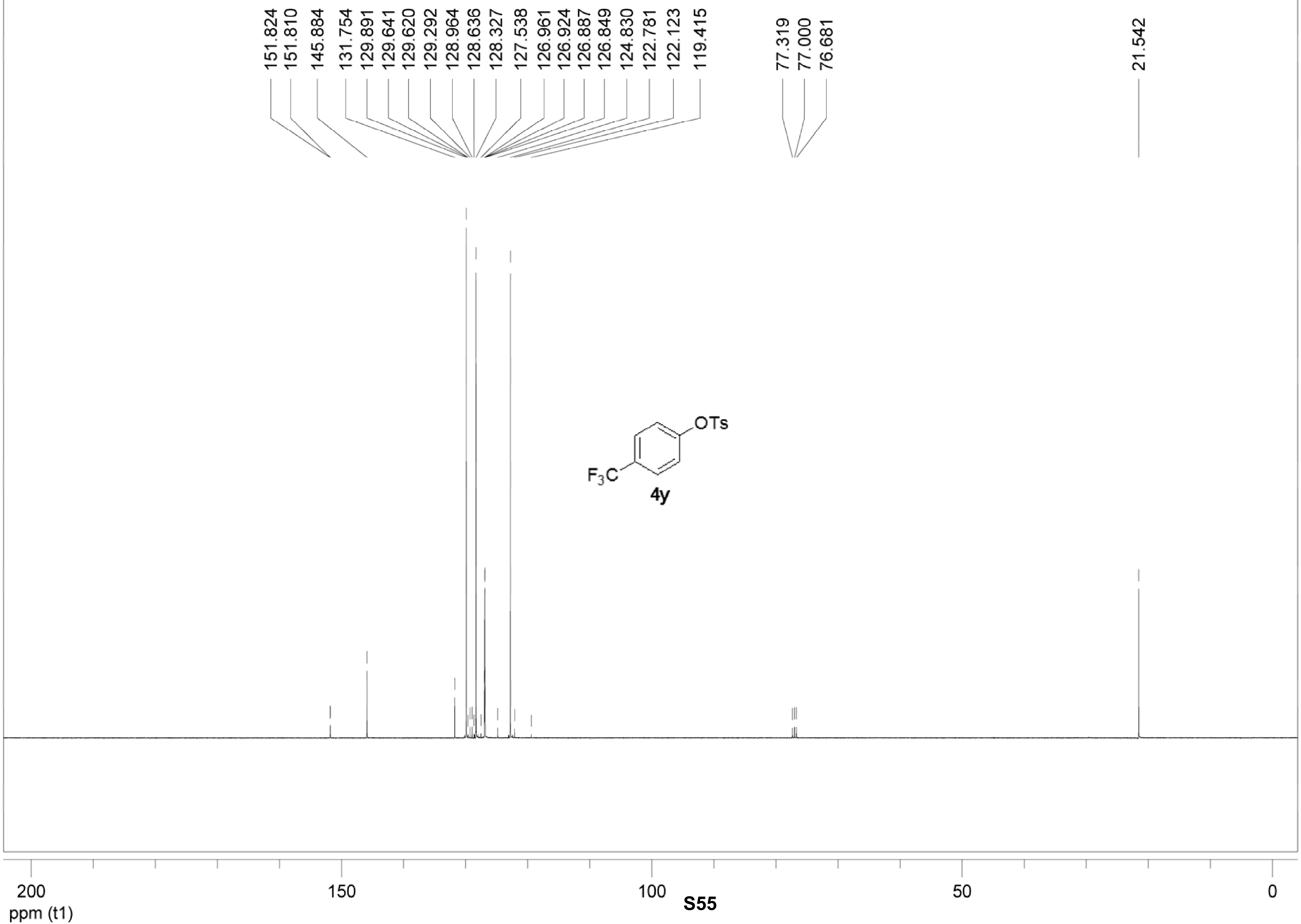
2.08
2.04
2.02
3.02
10.0
5.0
0.0
ppm (f1)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129.620
129.292
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128.636
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127.538
126.961
126.924
126.887
126.849
124.830
122.781
122.123
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77.000
76.681
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4y
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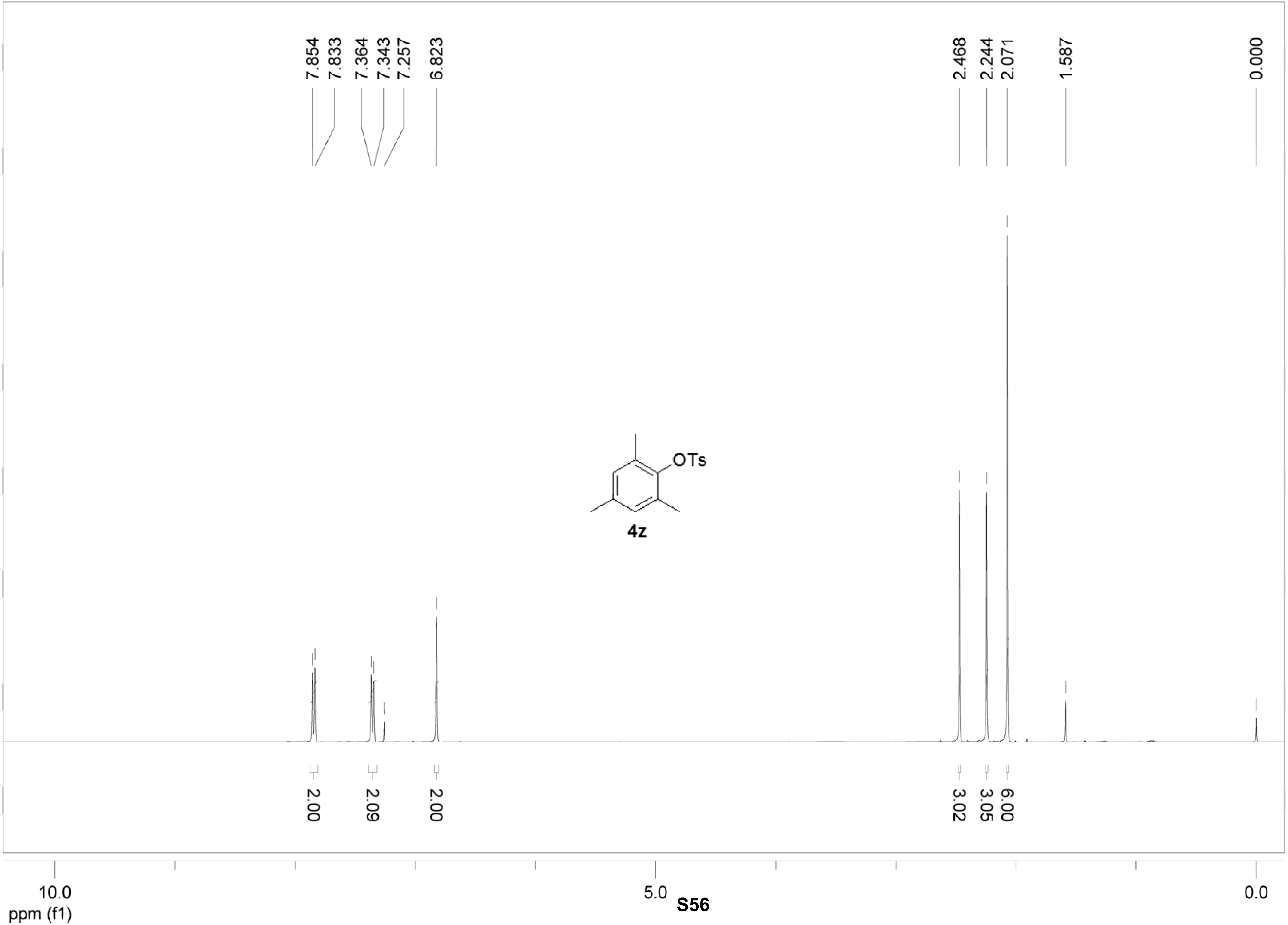
150
100
50
0
ppm (t1)



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2.244
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1.587
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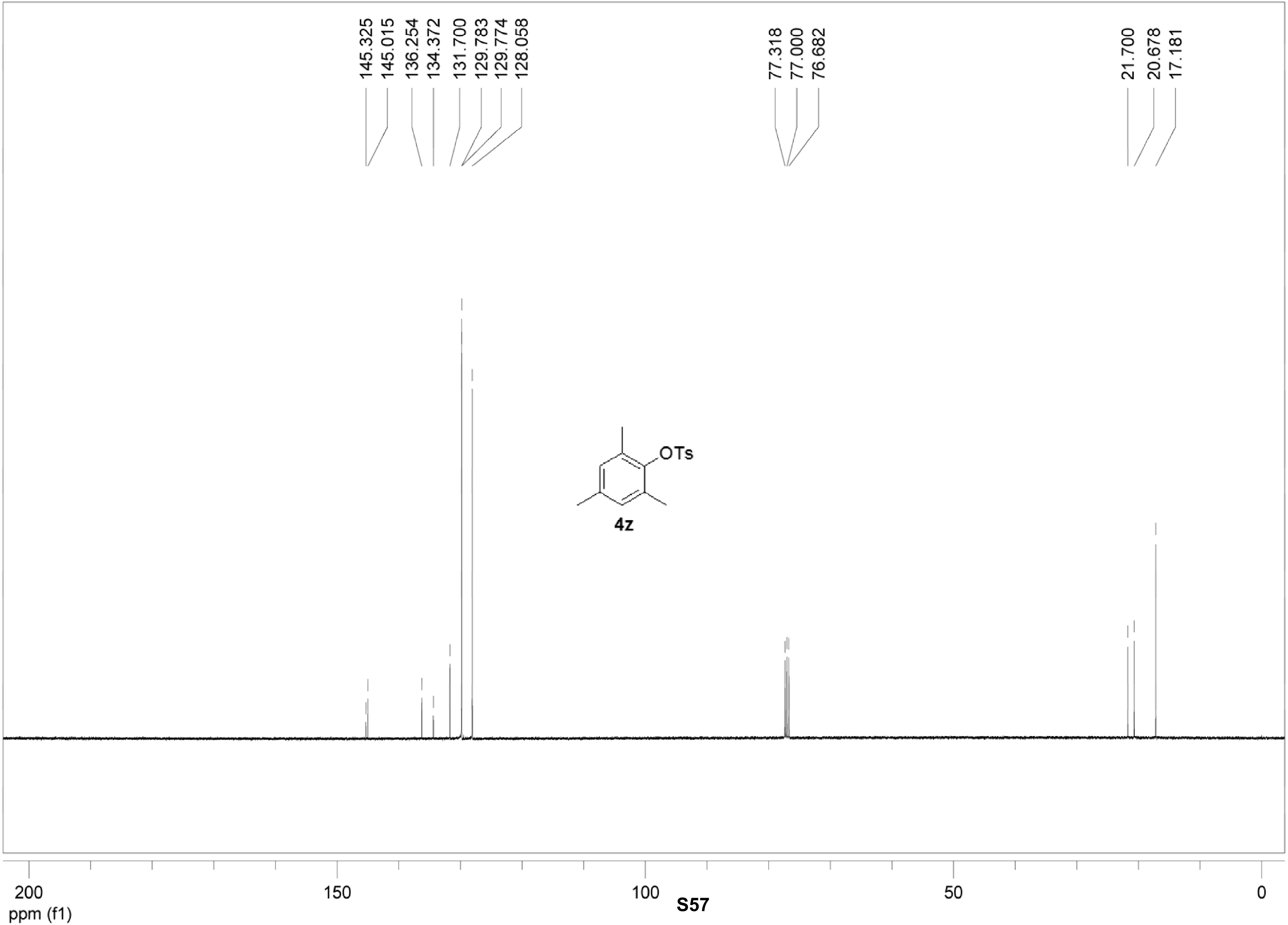
2.09
2.00
3.02
3.05
6.00
10.0
5.0
0.0
ppm (f1)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136.254
134.372
131.700
129.783
129.774
128.058
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76.682
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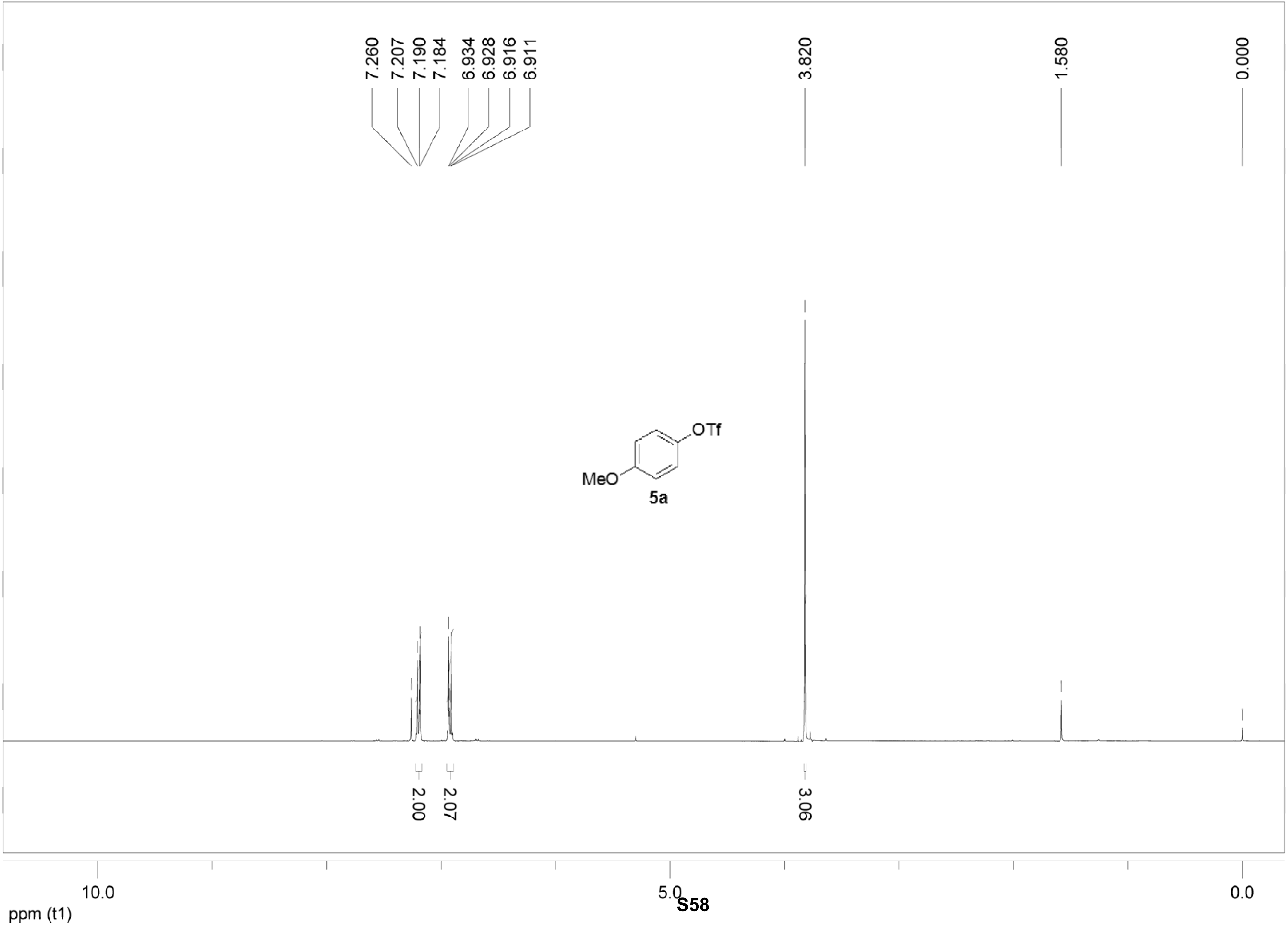
100
50
0
ppm (f1)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7.190
7.184
6.934
6.928
6.916
6.911
3.820
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OTf
MeO
5a
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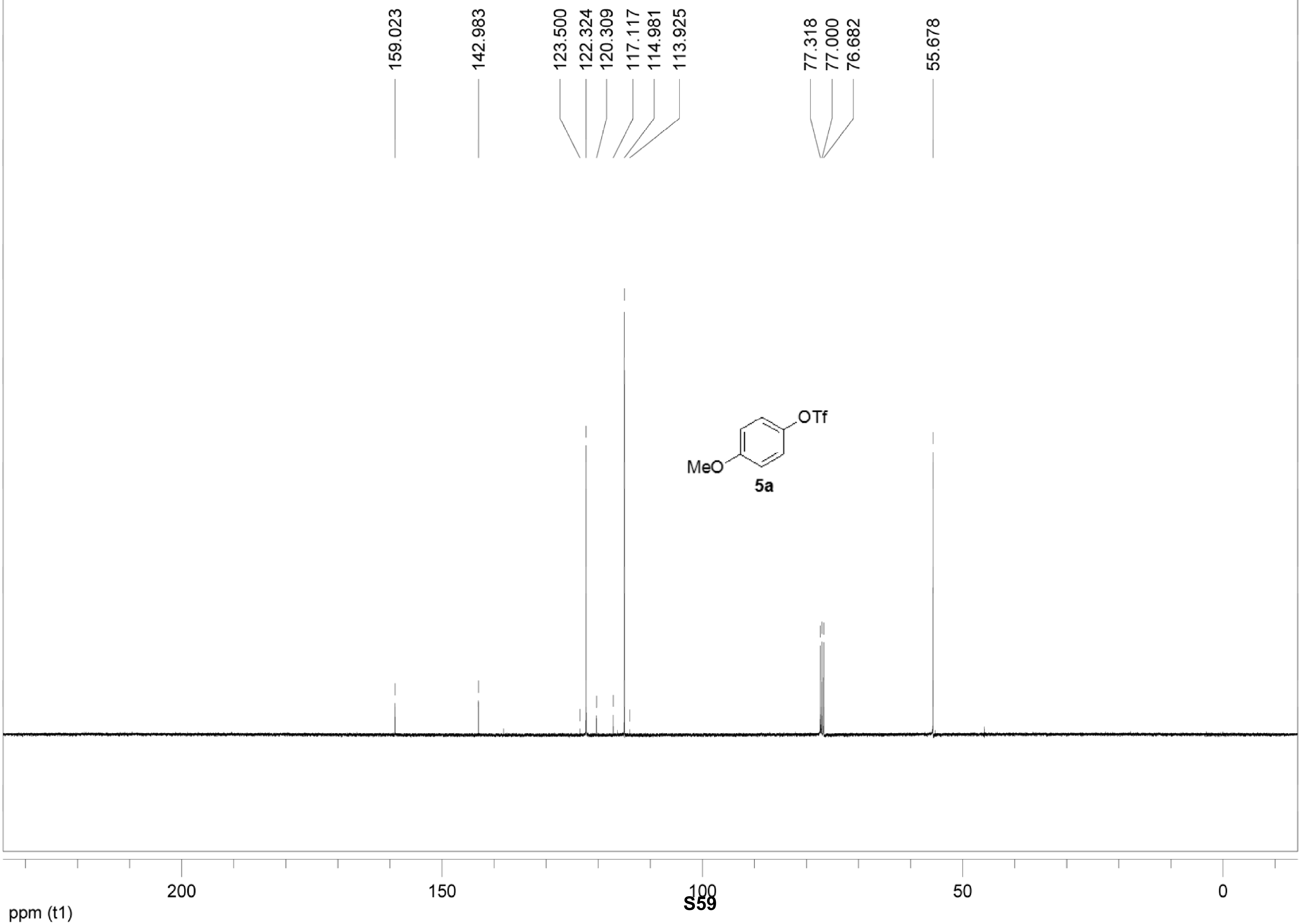
2.07
3.06
10.0
5.0
0.0
ppm (t1)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122.324
120.309
117.117
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77.000
76.682
55.678
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MeO
5a
200
150
100
50
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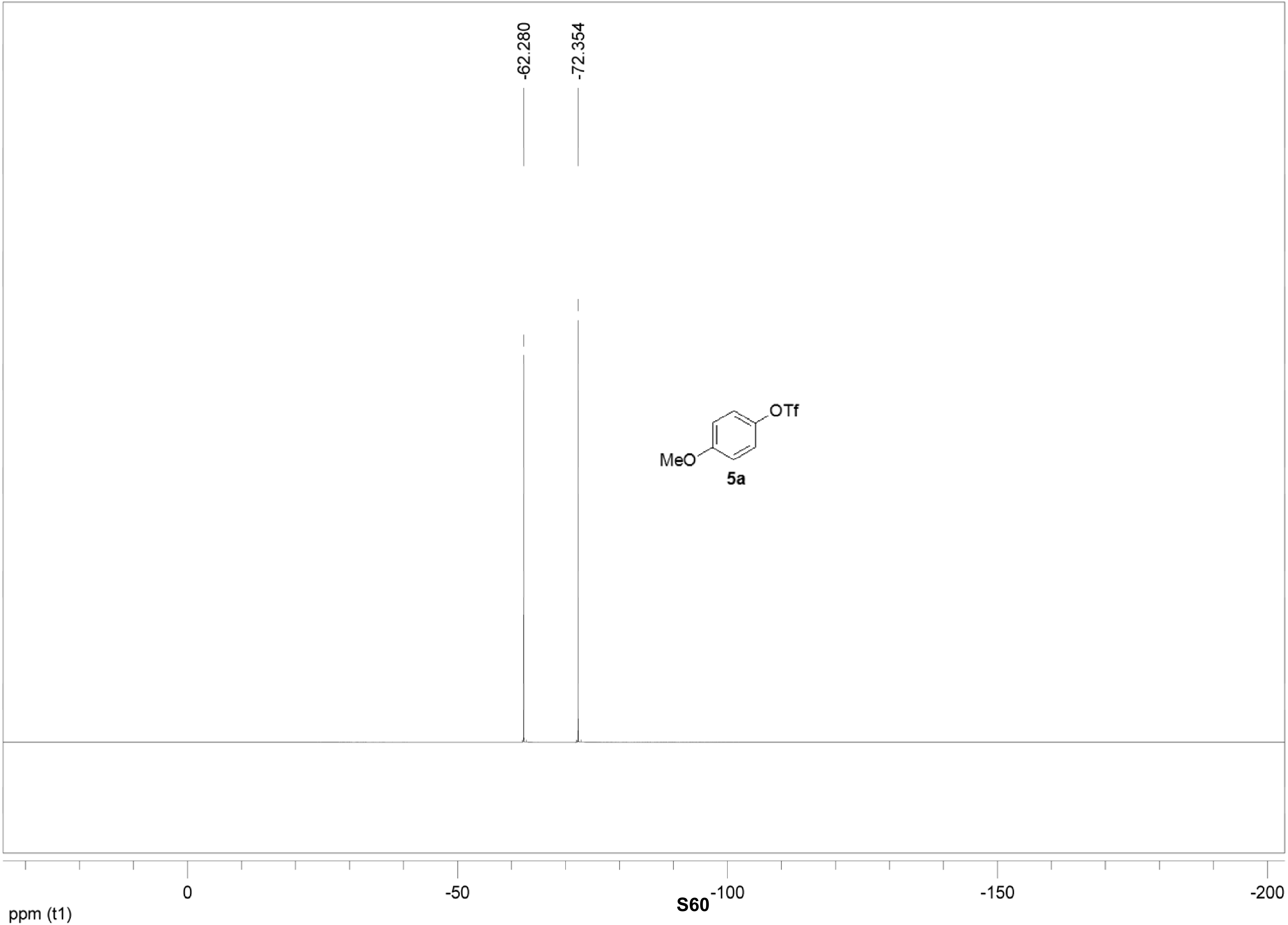
ppm (t1)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MeO
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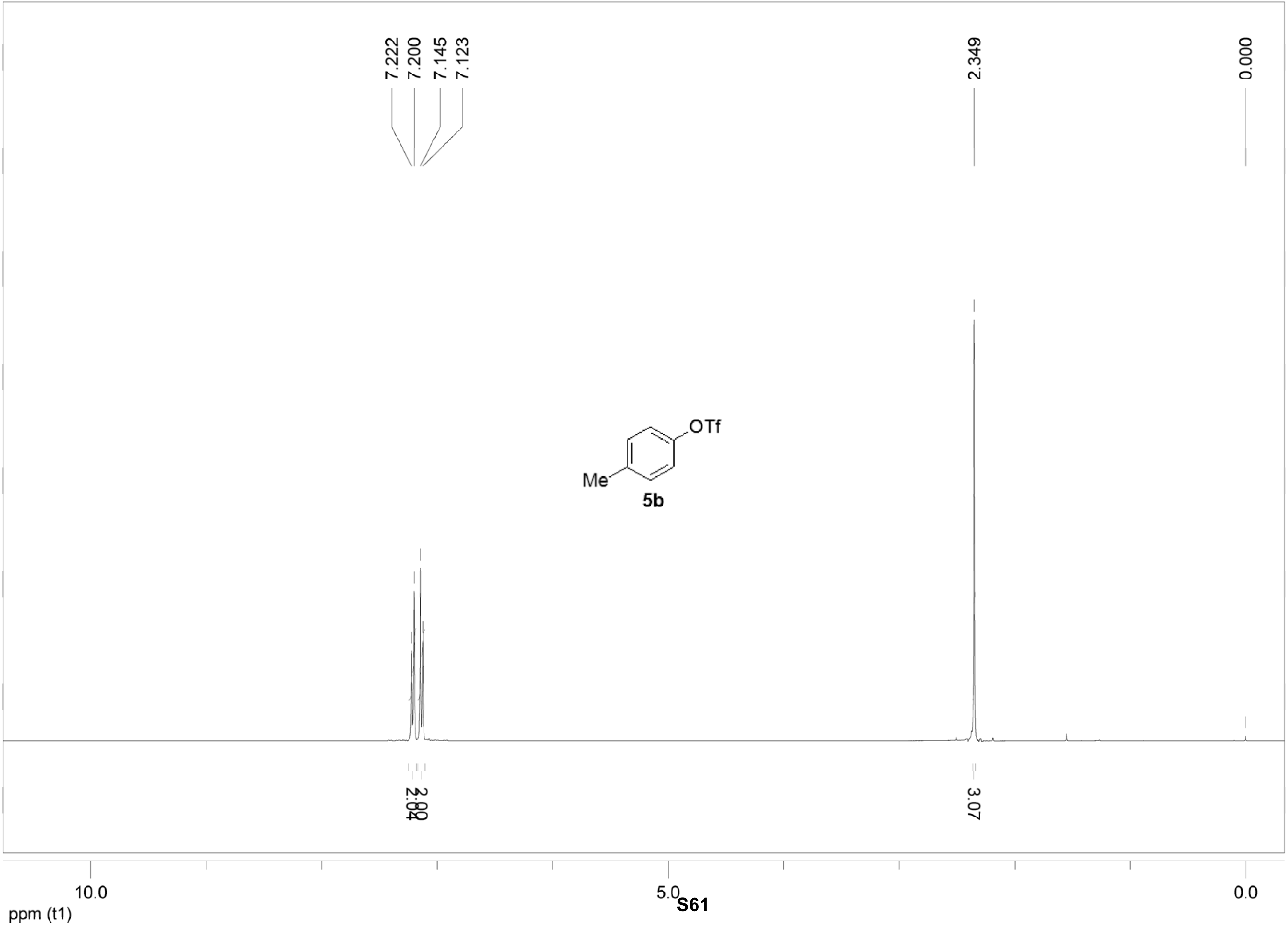
-150
-200
ppm (t1)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7.200
7.145
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Me
5b
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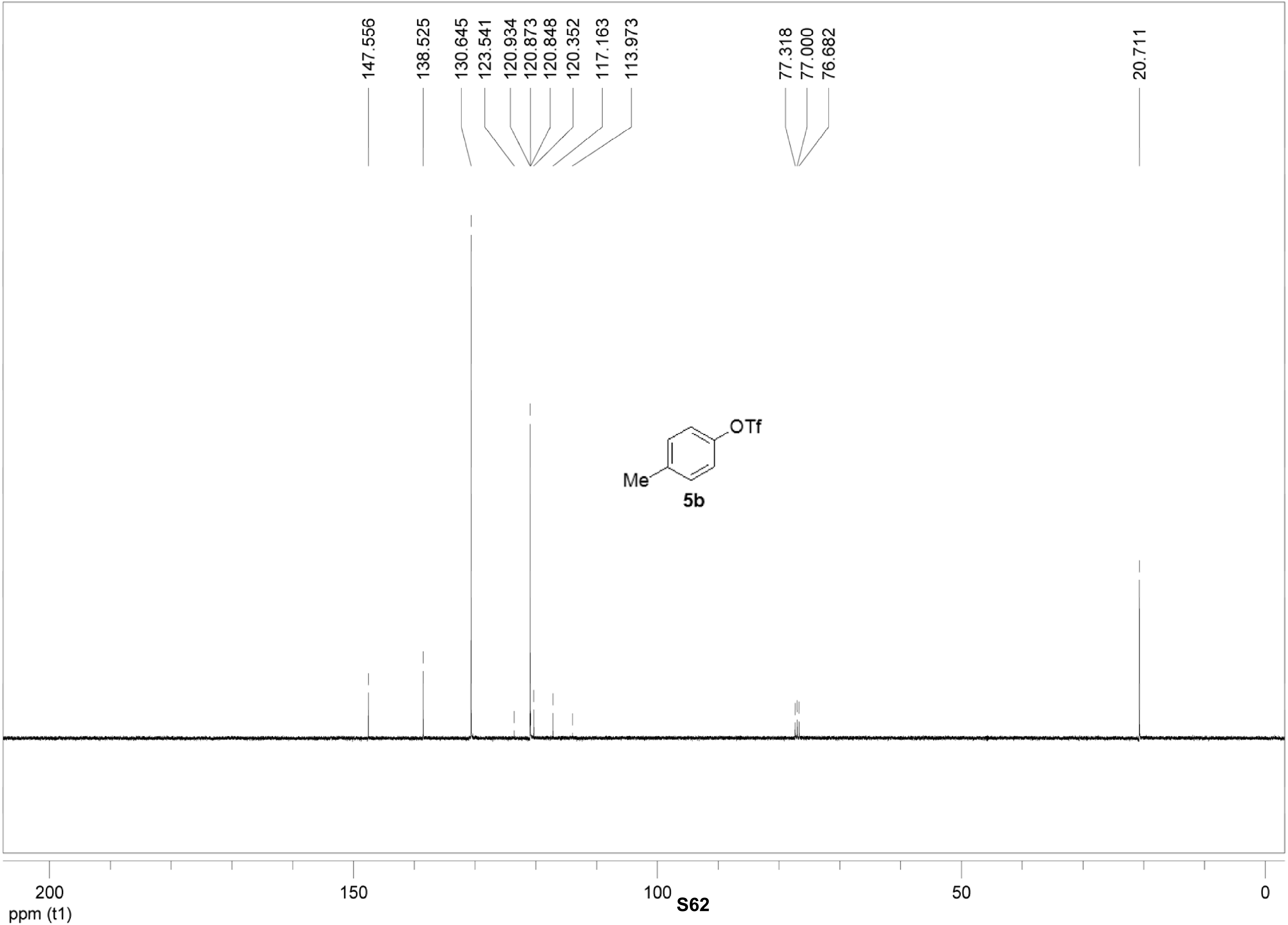
10.0
5.0
0.0
ppm (t1)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120.352
117.163
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77.000
76.682
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100
50
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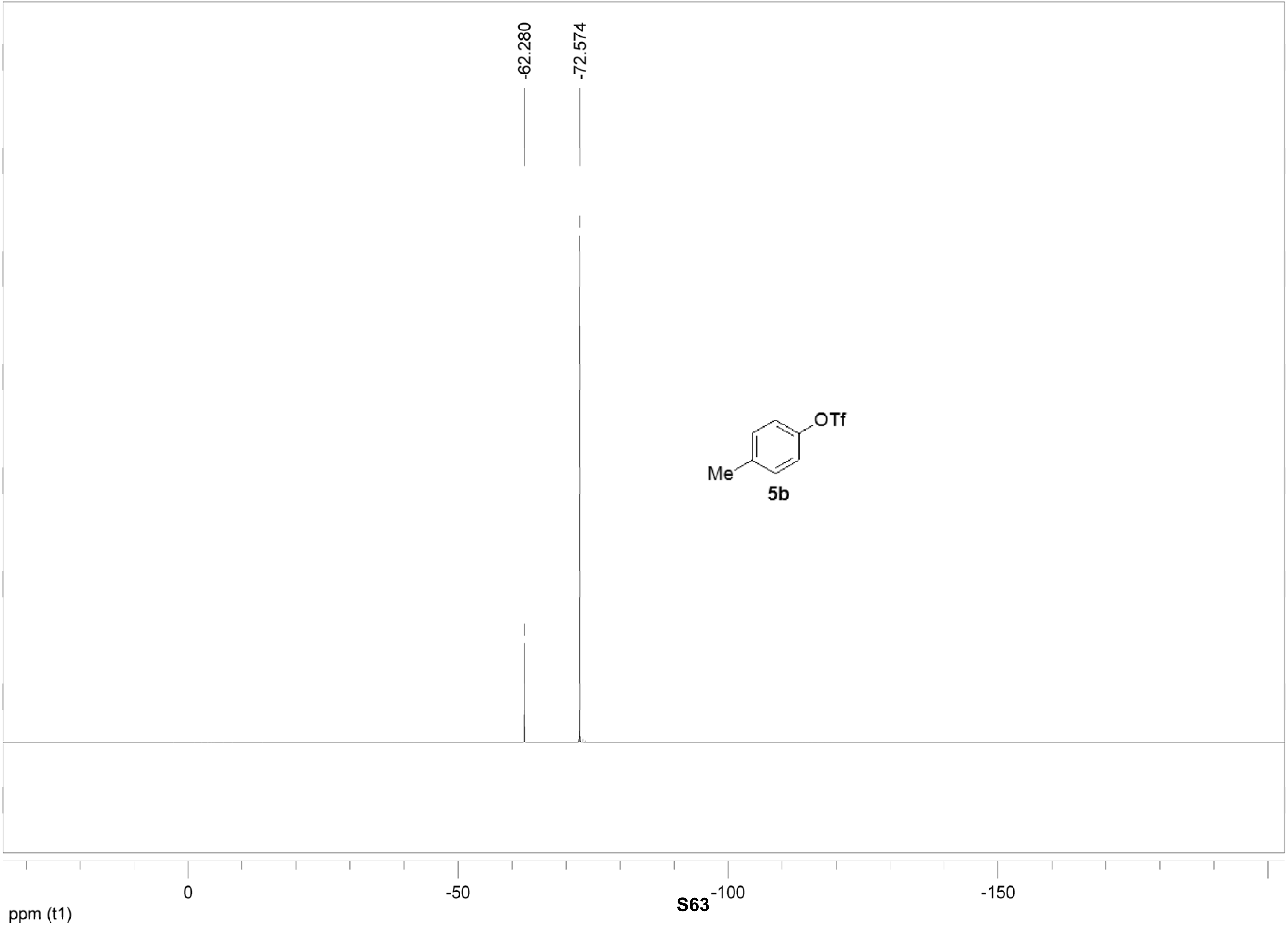
ppm (t1)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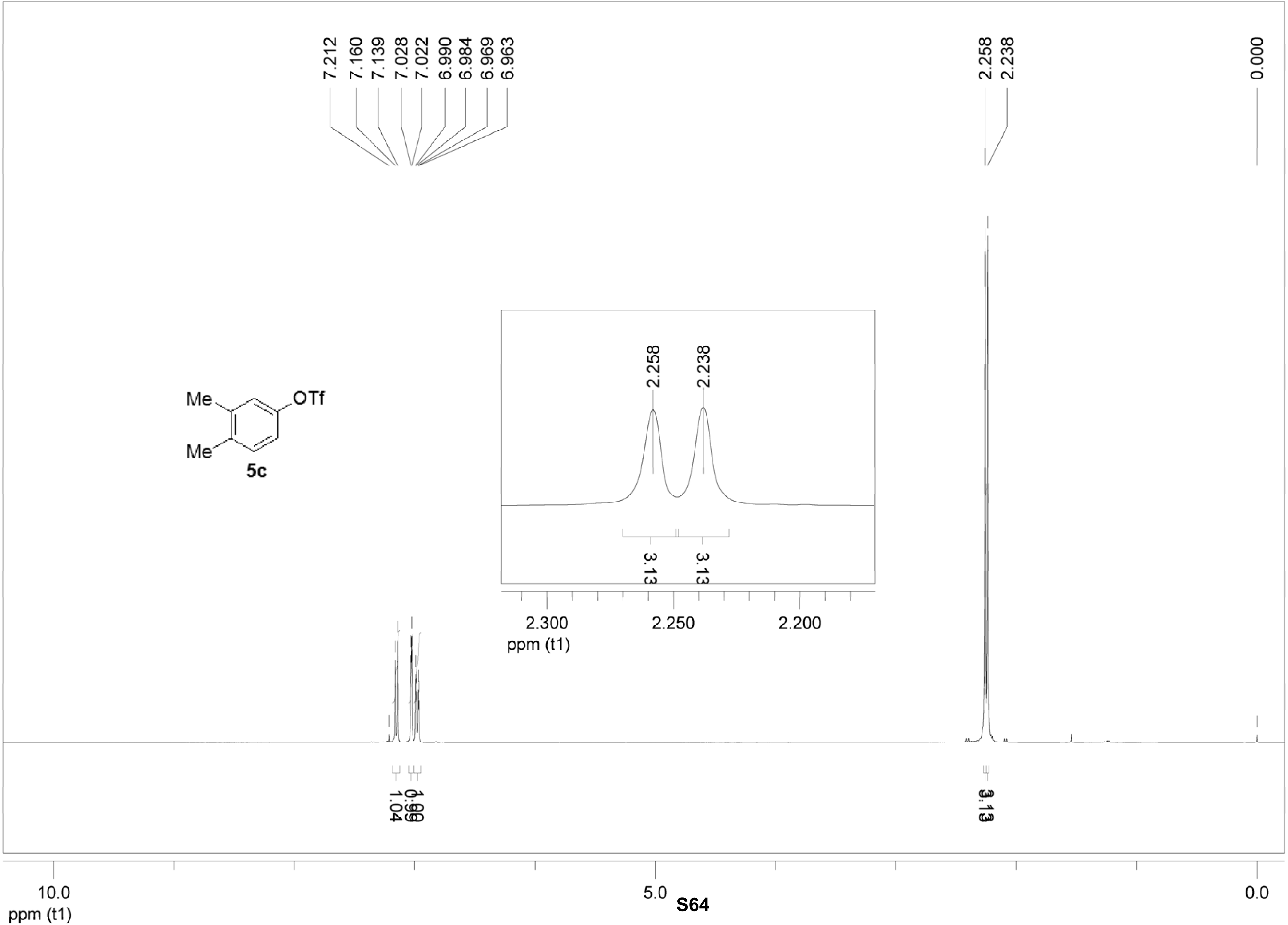
ppm (t1)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7.139
7.028
7.022
6.990
6.984
6.969
6.963
2.258
2.238
0.000
Me
Me
OTf
5c
2.258
2.238
3.13
3.13
2.300
2.250
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1.00
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3.13
10.0
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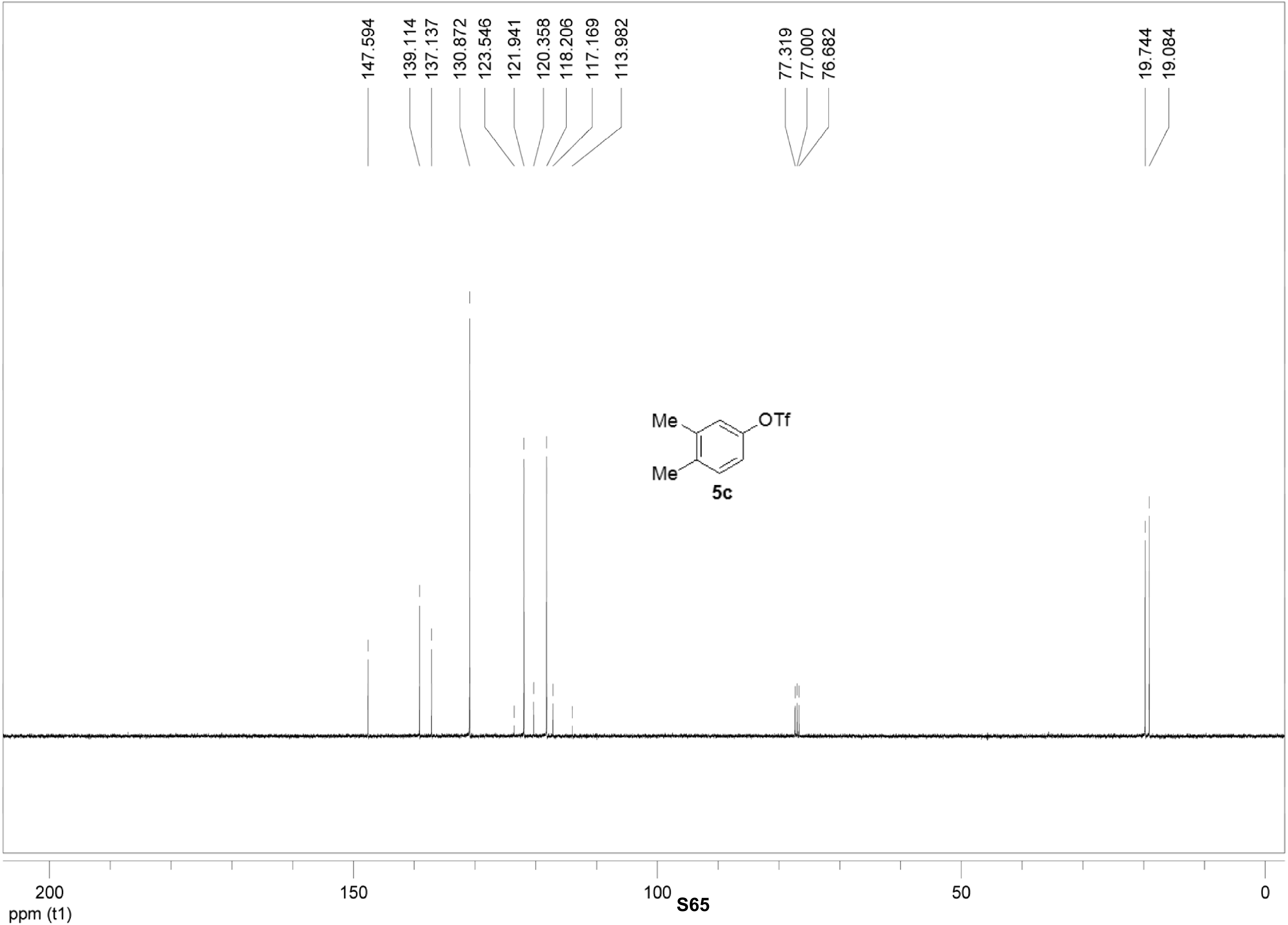
ppm (t1)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137.137
130.872
123.546
121.941
120.358
118.206
117.169
113.982
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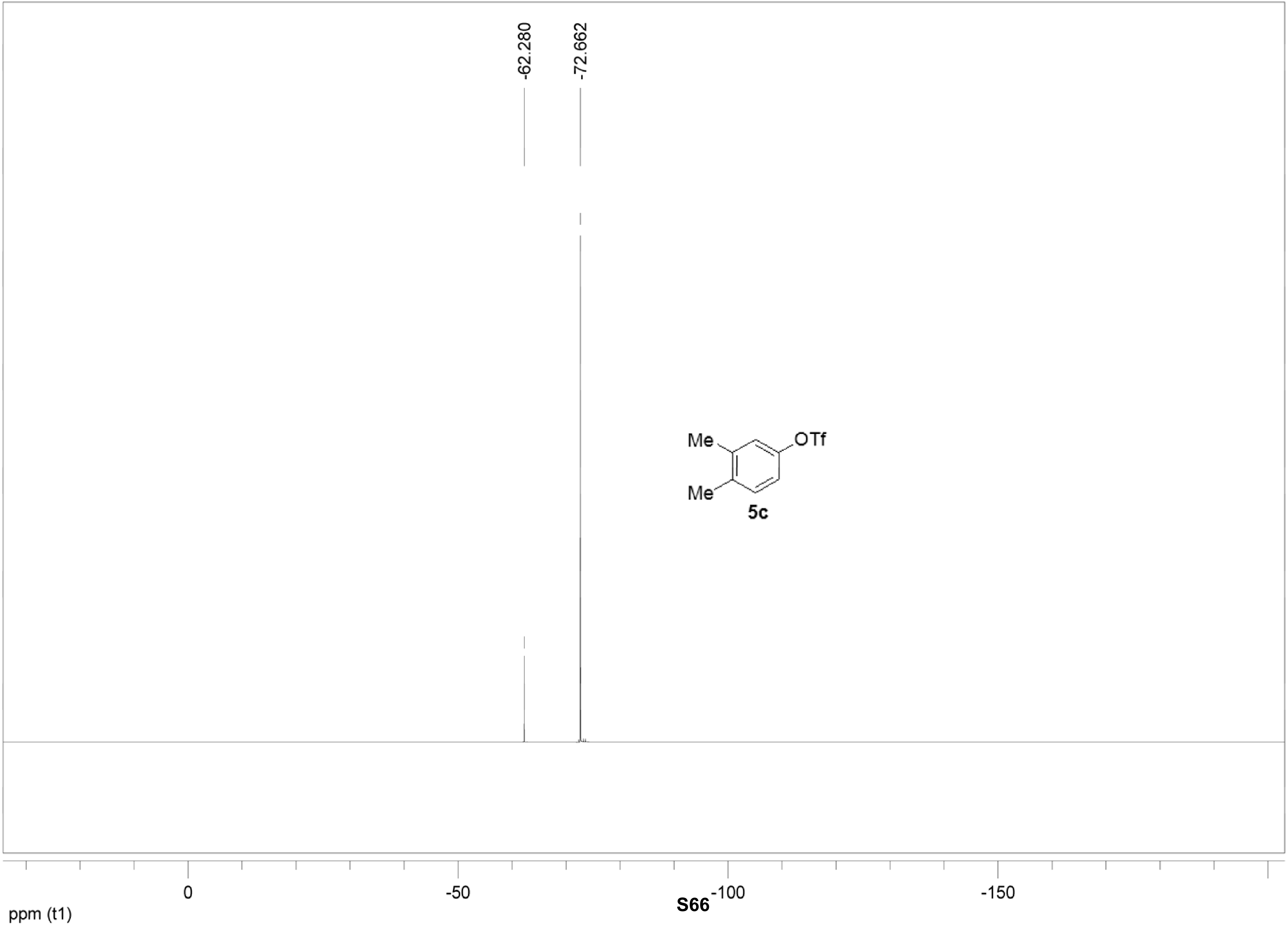
19.084
Me
Me
OTf
5c
200
150
100
50
0
ppm (t1)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Me
OTf
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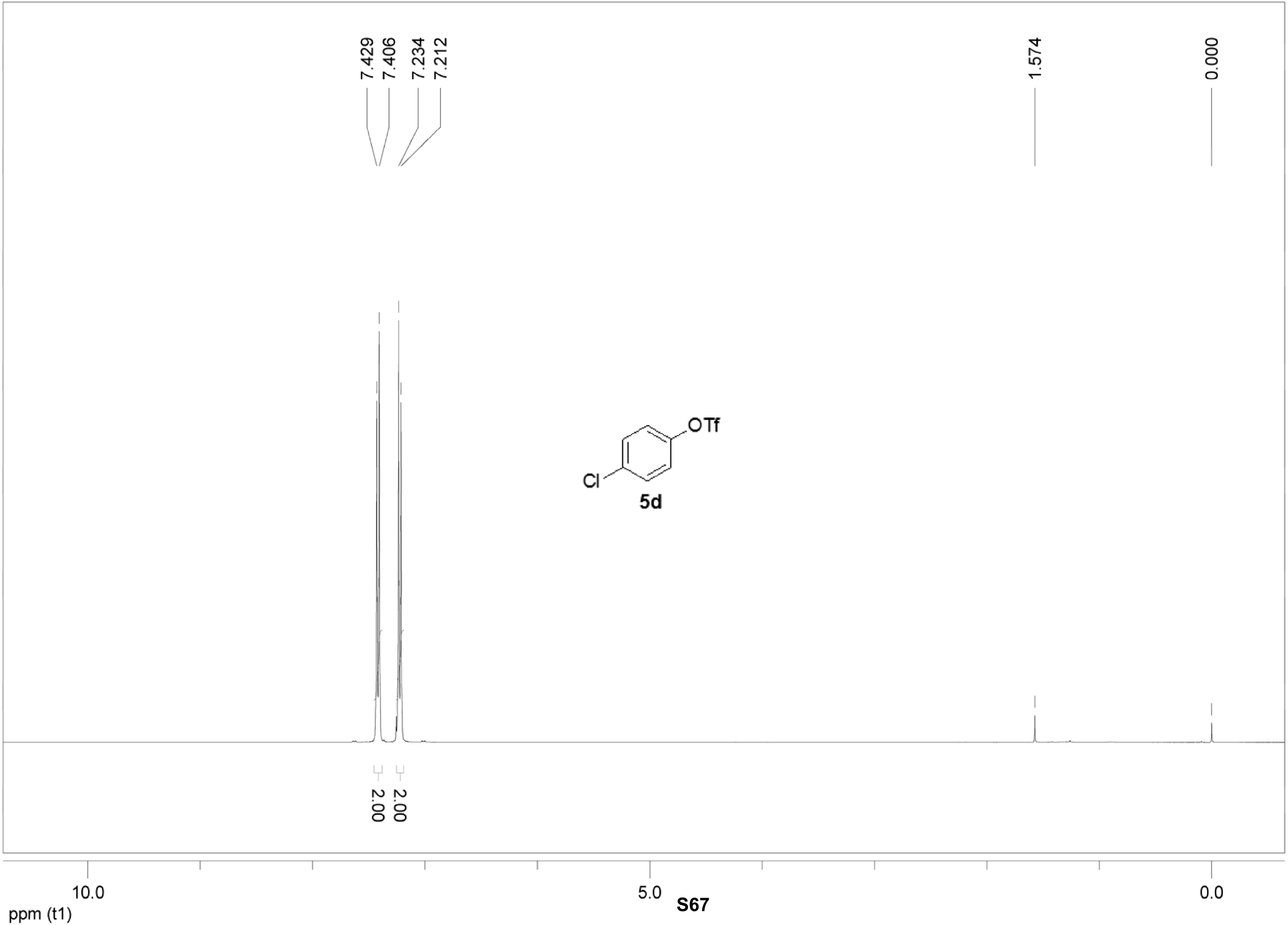
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Cl
5d
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2.00
10.0
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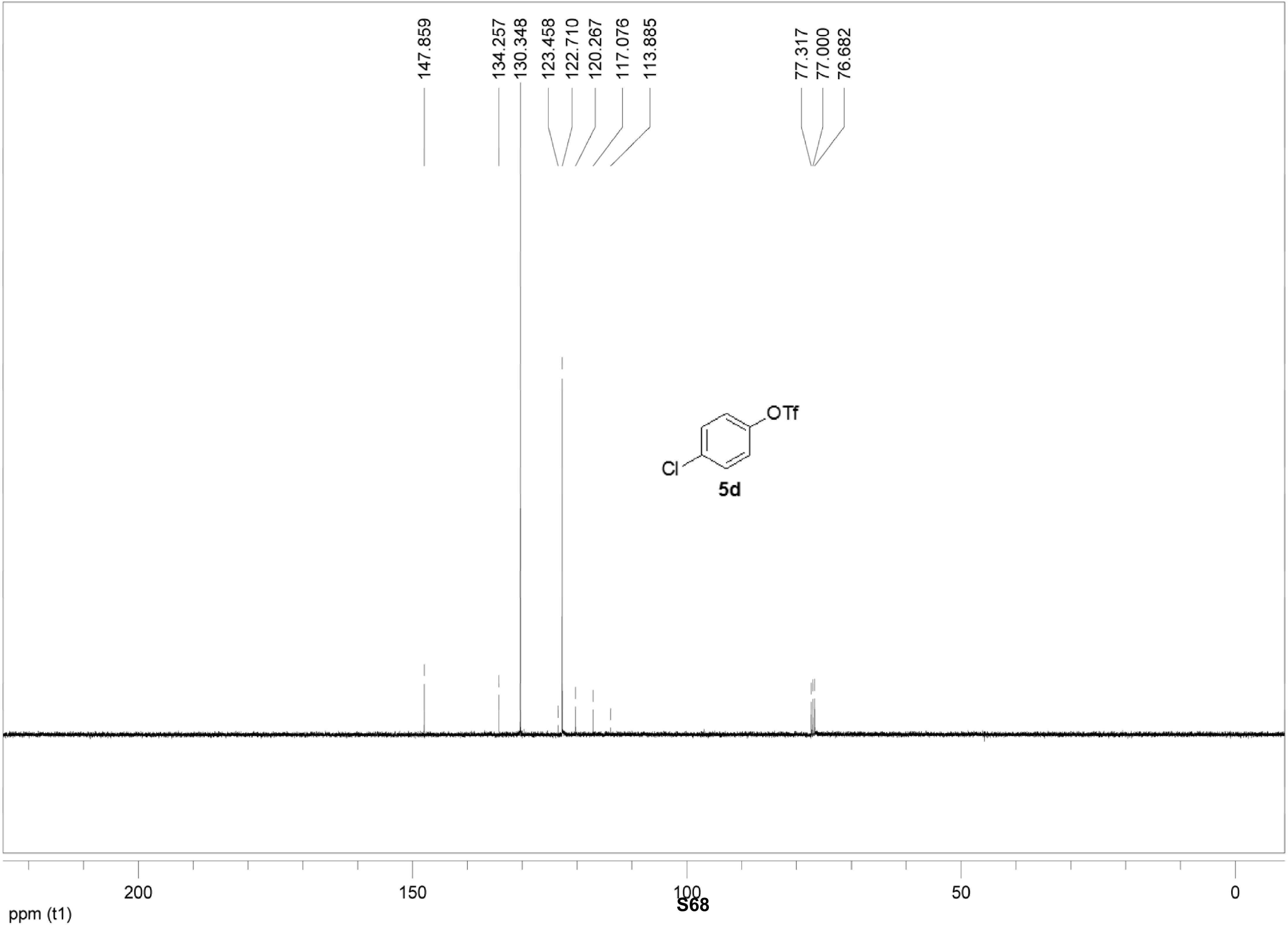
ppm (t1)


147.859
134.257
130.348
123.458
122.710
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77.000
76.682
OTf
Cl
5d
200
150
100
50
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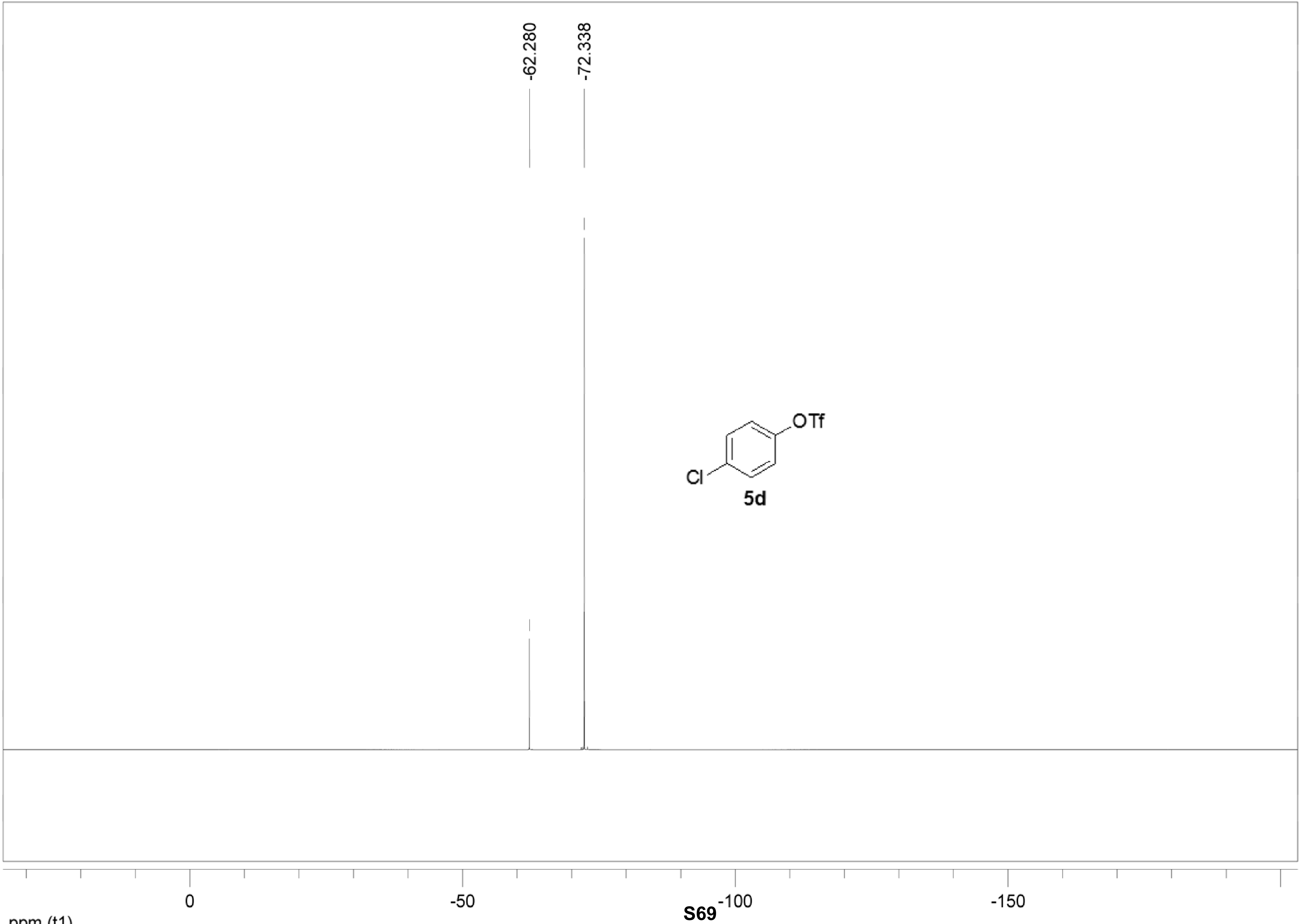
ppm (t1)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-72.338
OTf
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5d
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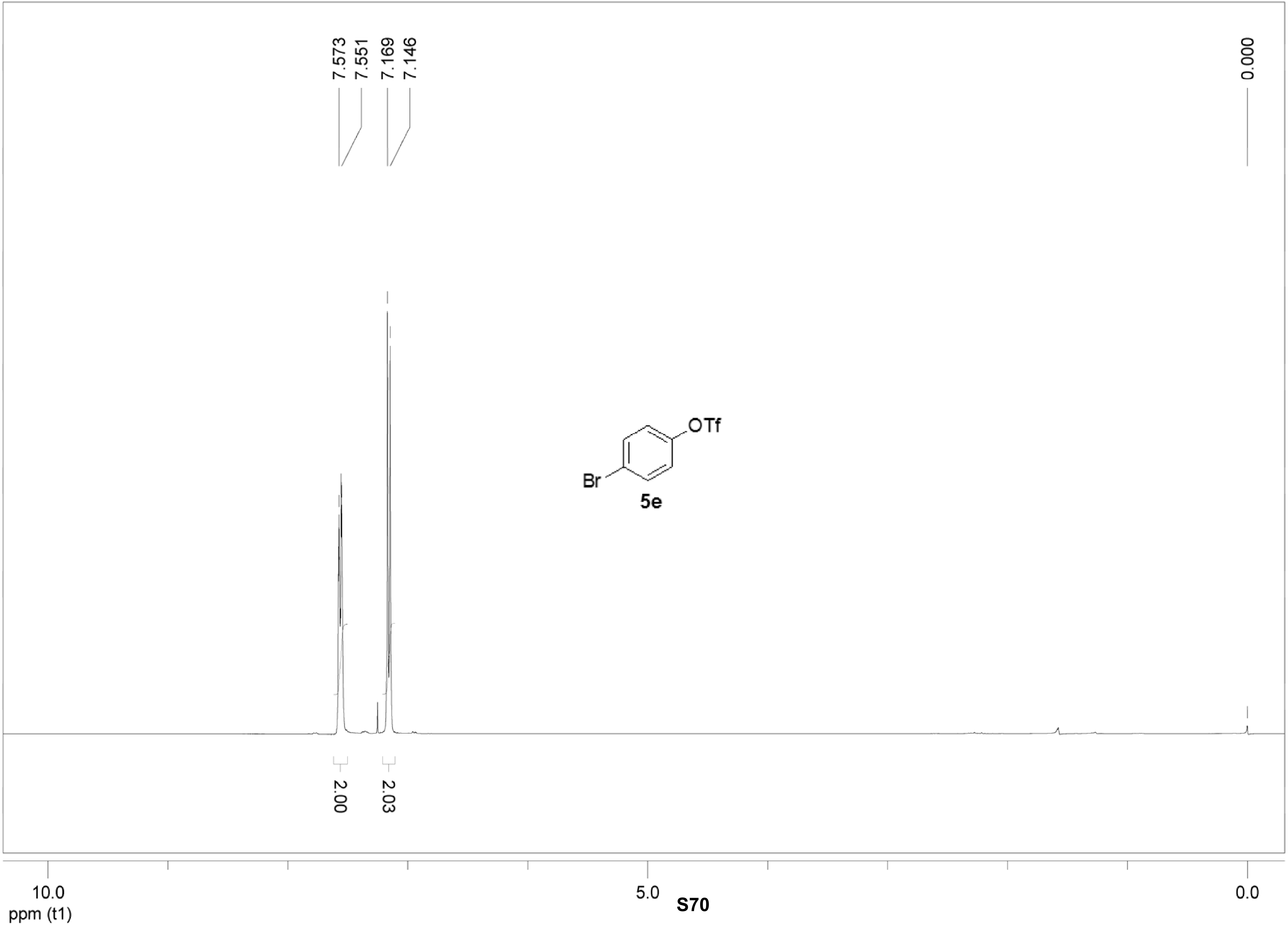
ppm (t1)


7.573
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Br
5e
2.00
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5.0
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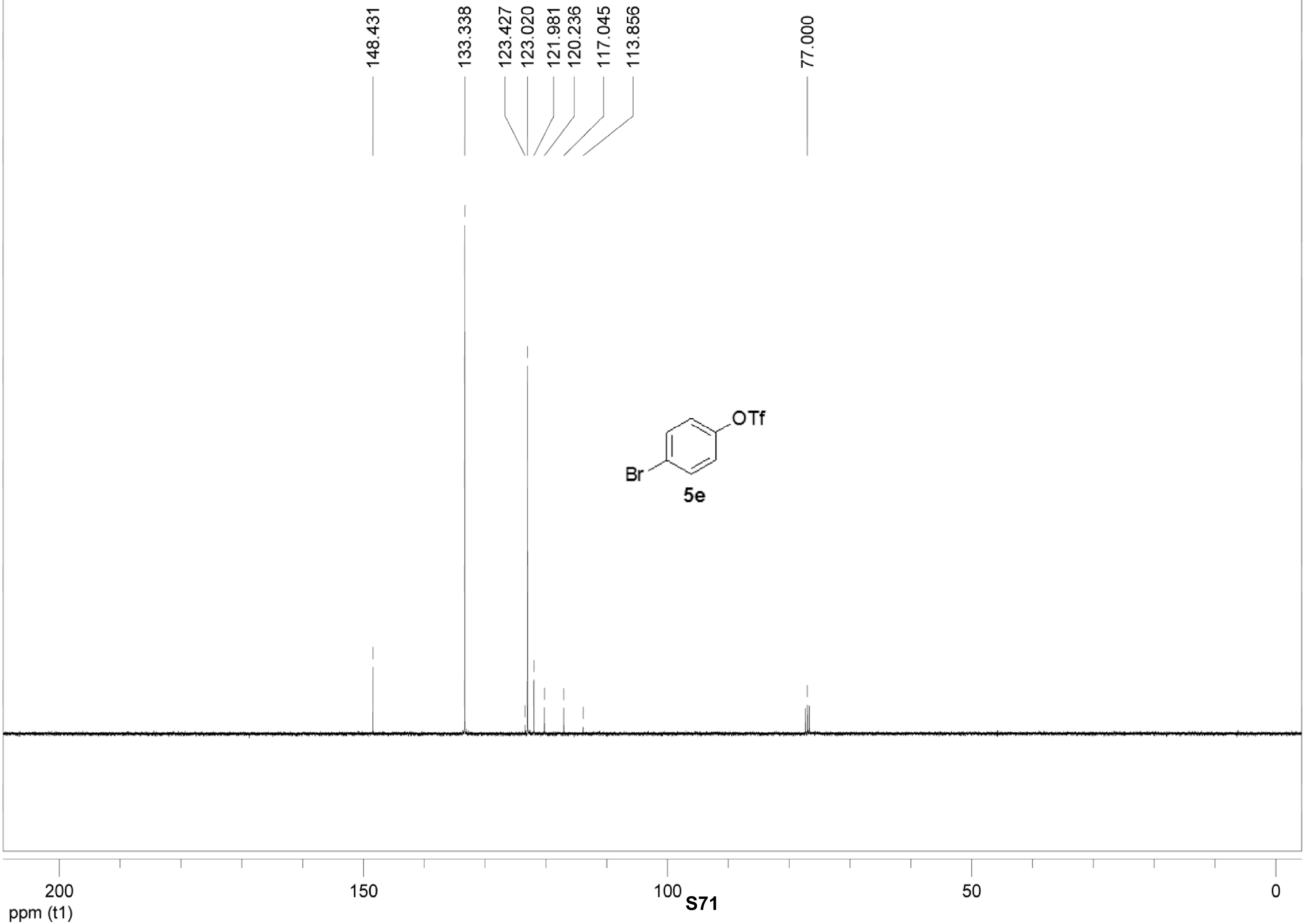
ppm (t1)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123.020
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Br
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200
150
100
50
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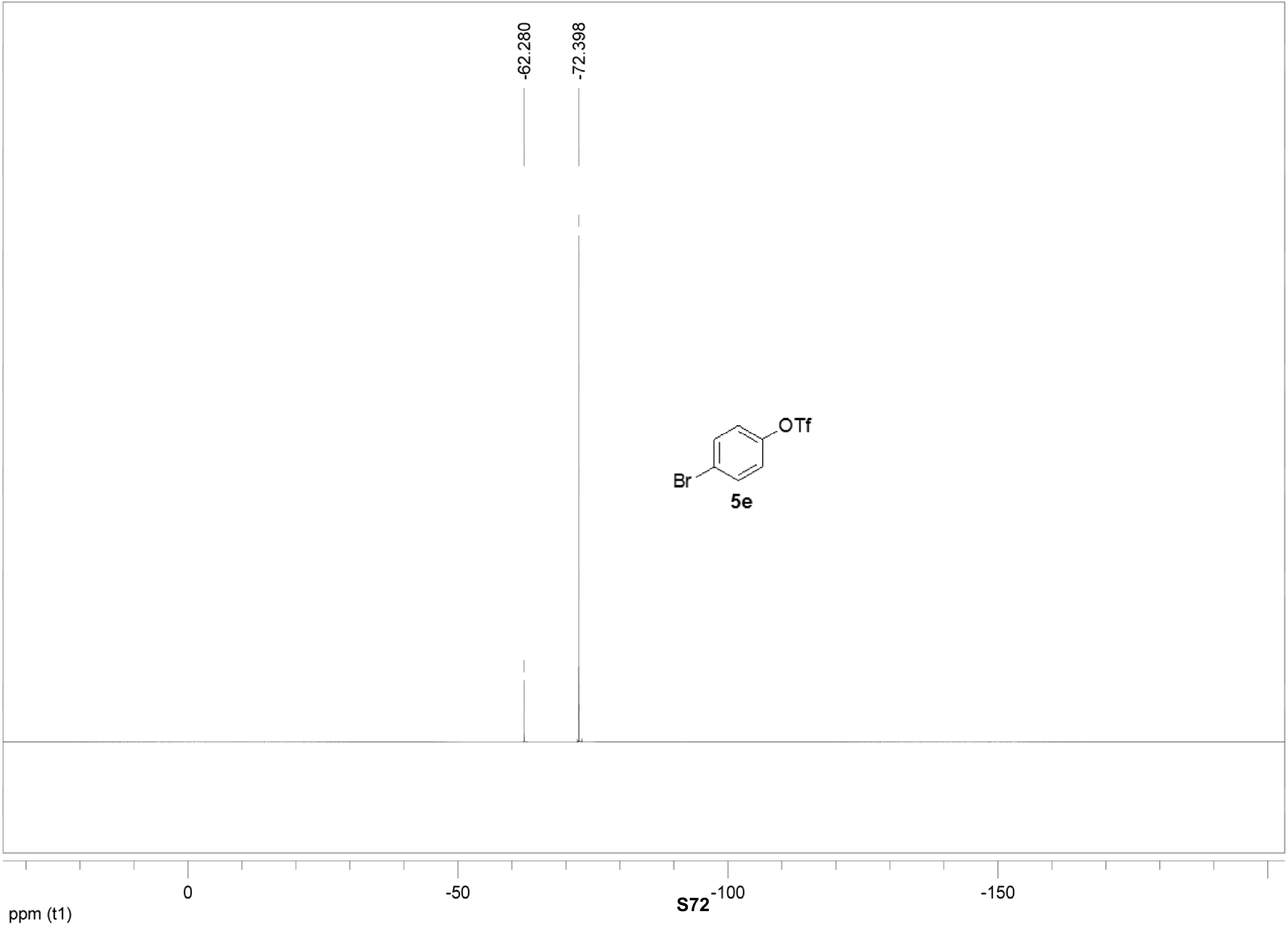
ppm (t1)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5e
0
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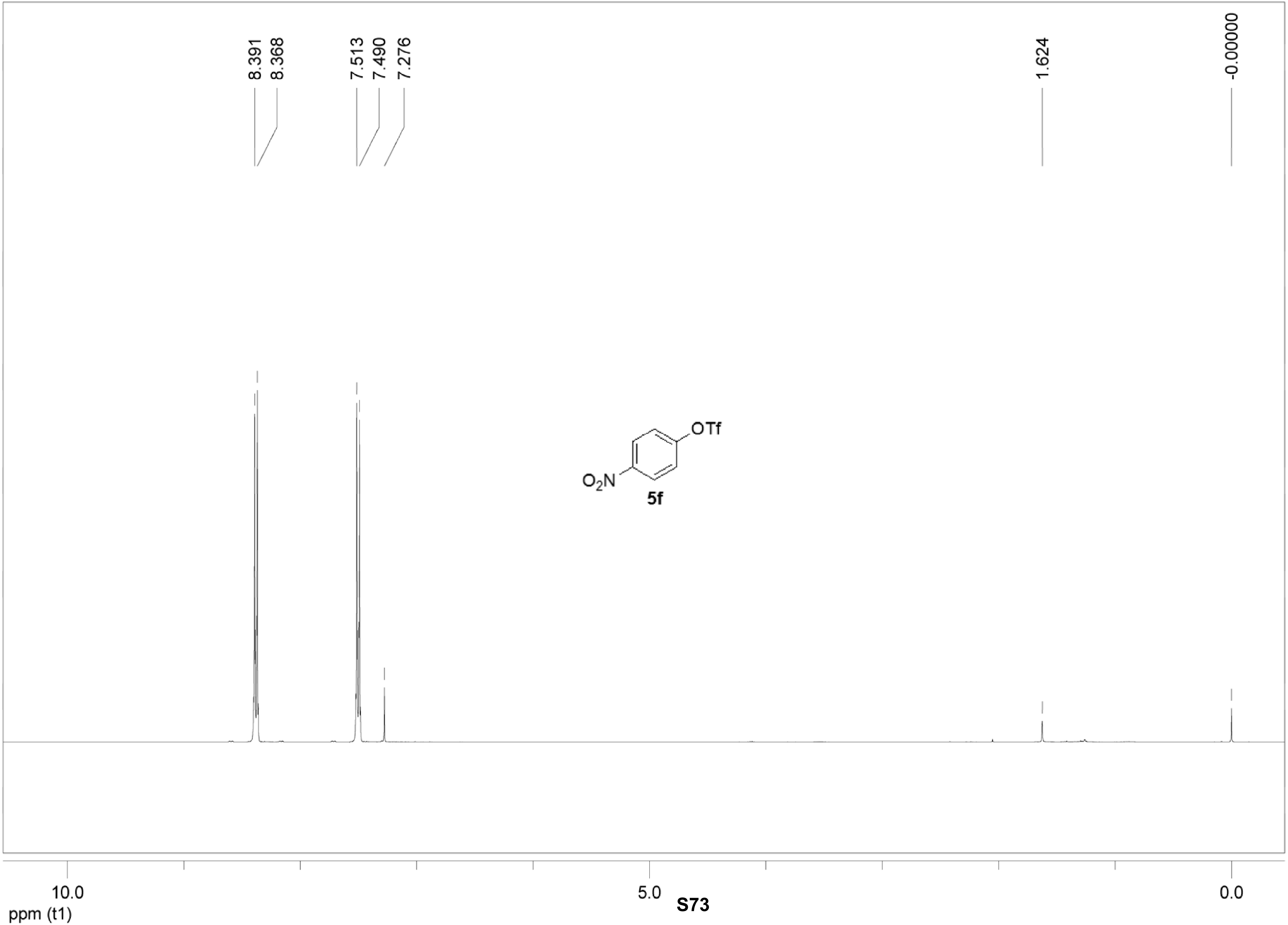
ppm (t1)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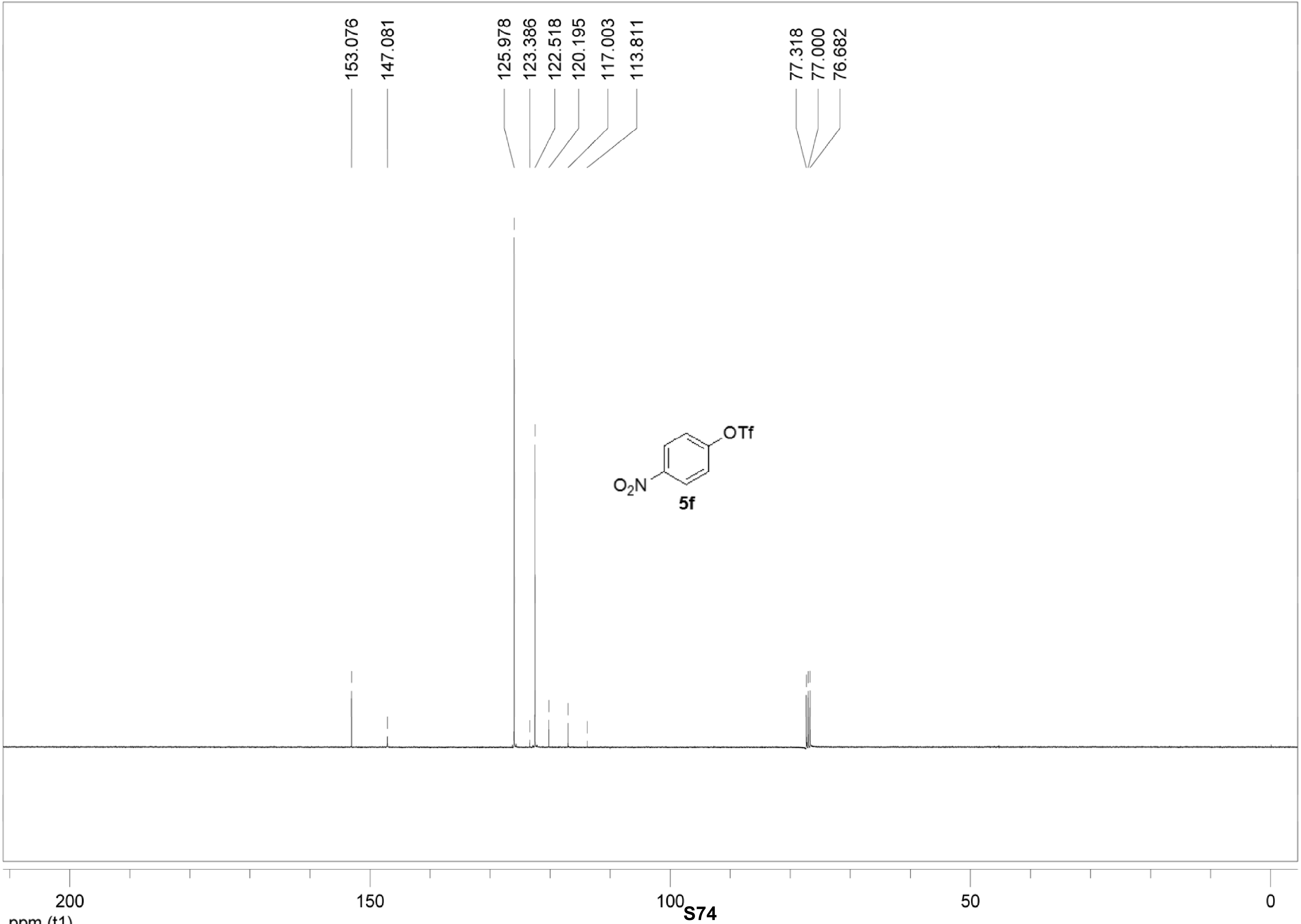
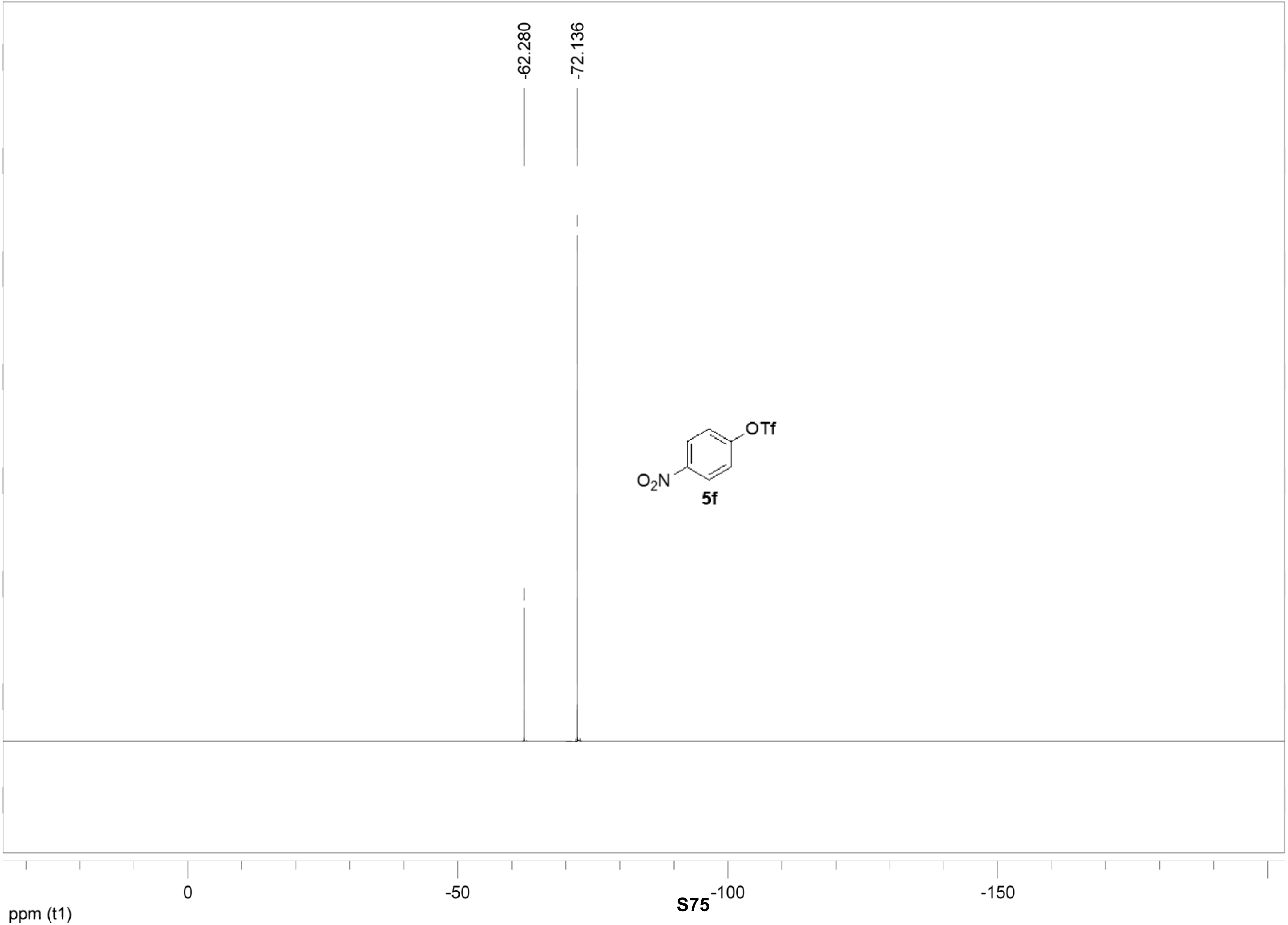
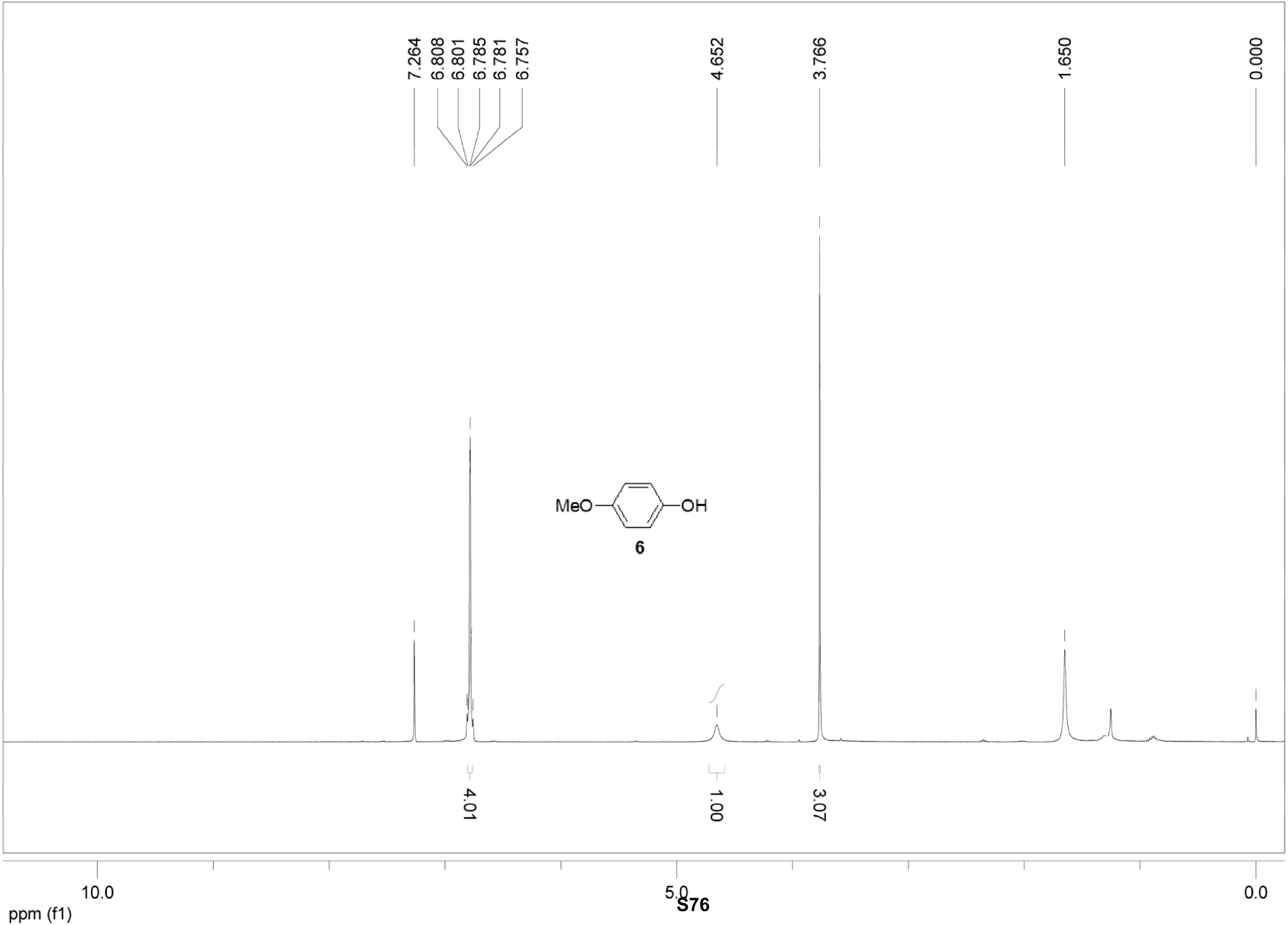
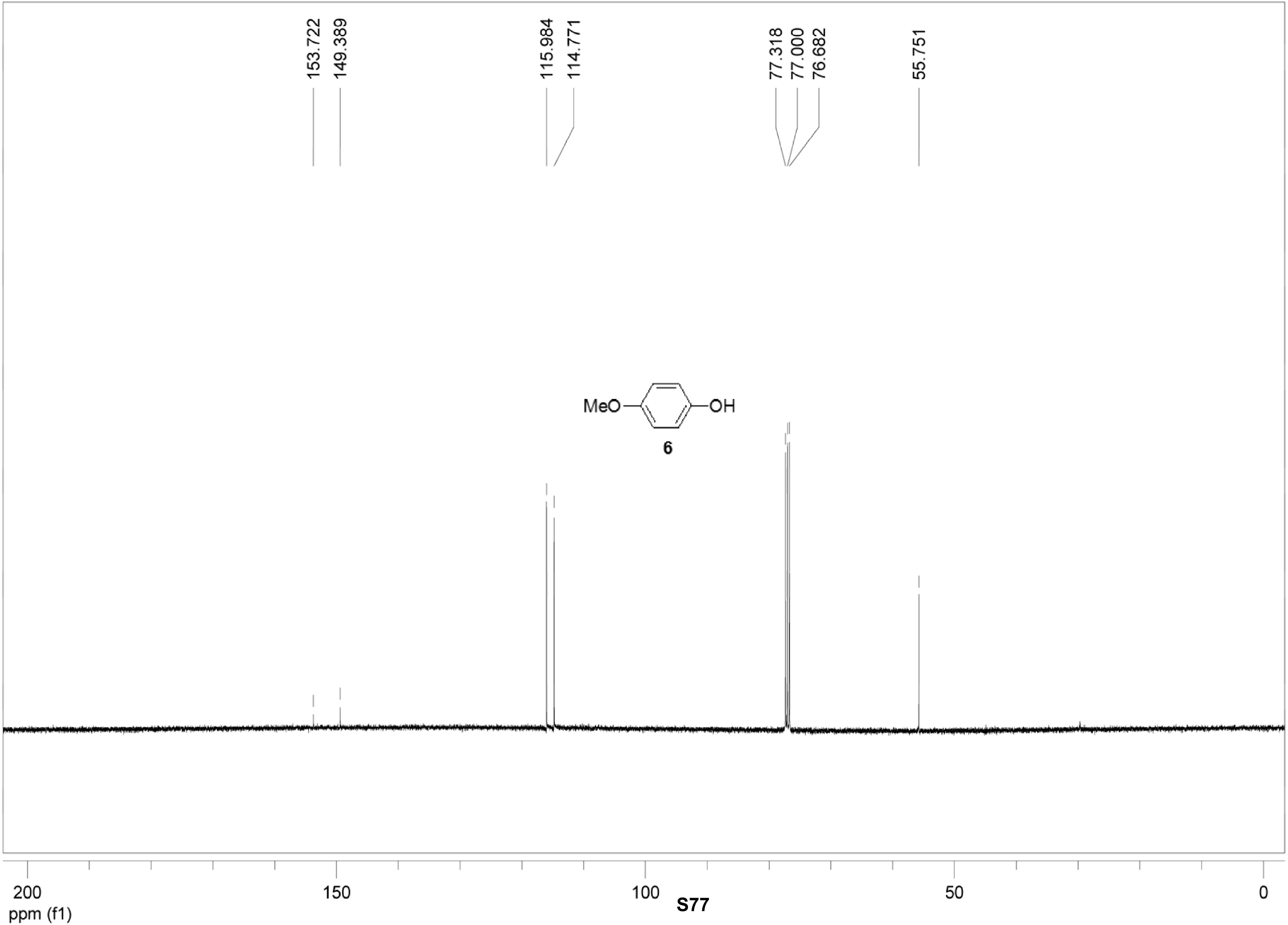
7.513
7.490
7.276
1.624
-0.00000
OTf
O2N
5f
10.0
5.0
0.0
ppm (t1)

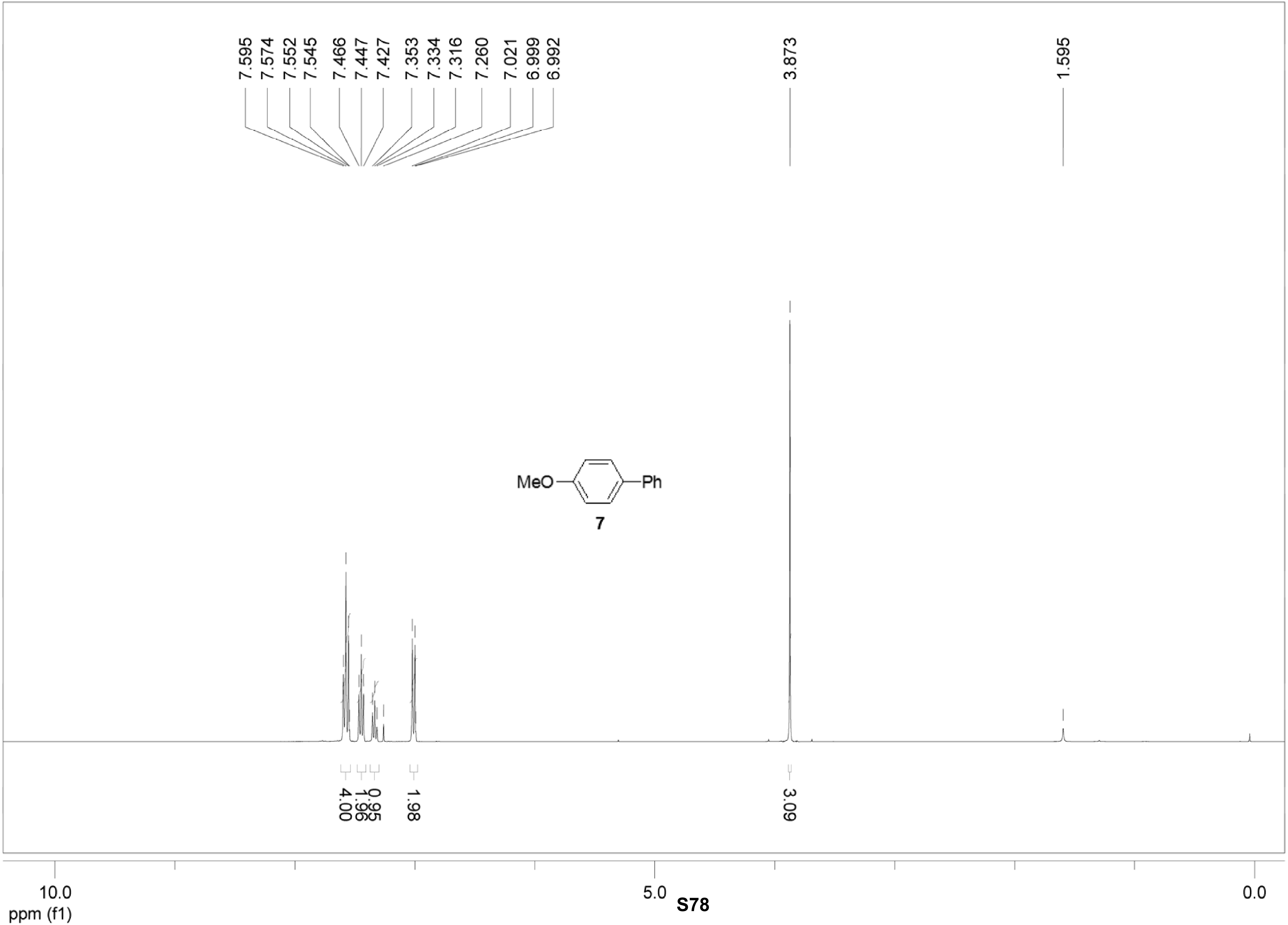

153.076
147.081
125.978
123.386
122.518
120.195
117.003
113.811
77.318
77.000
76.682
OTf
O_2N
5f
200
150
100
50
0
ppm (t1)

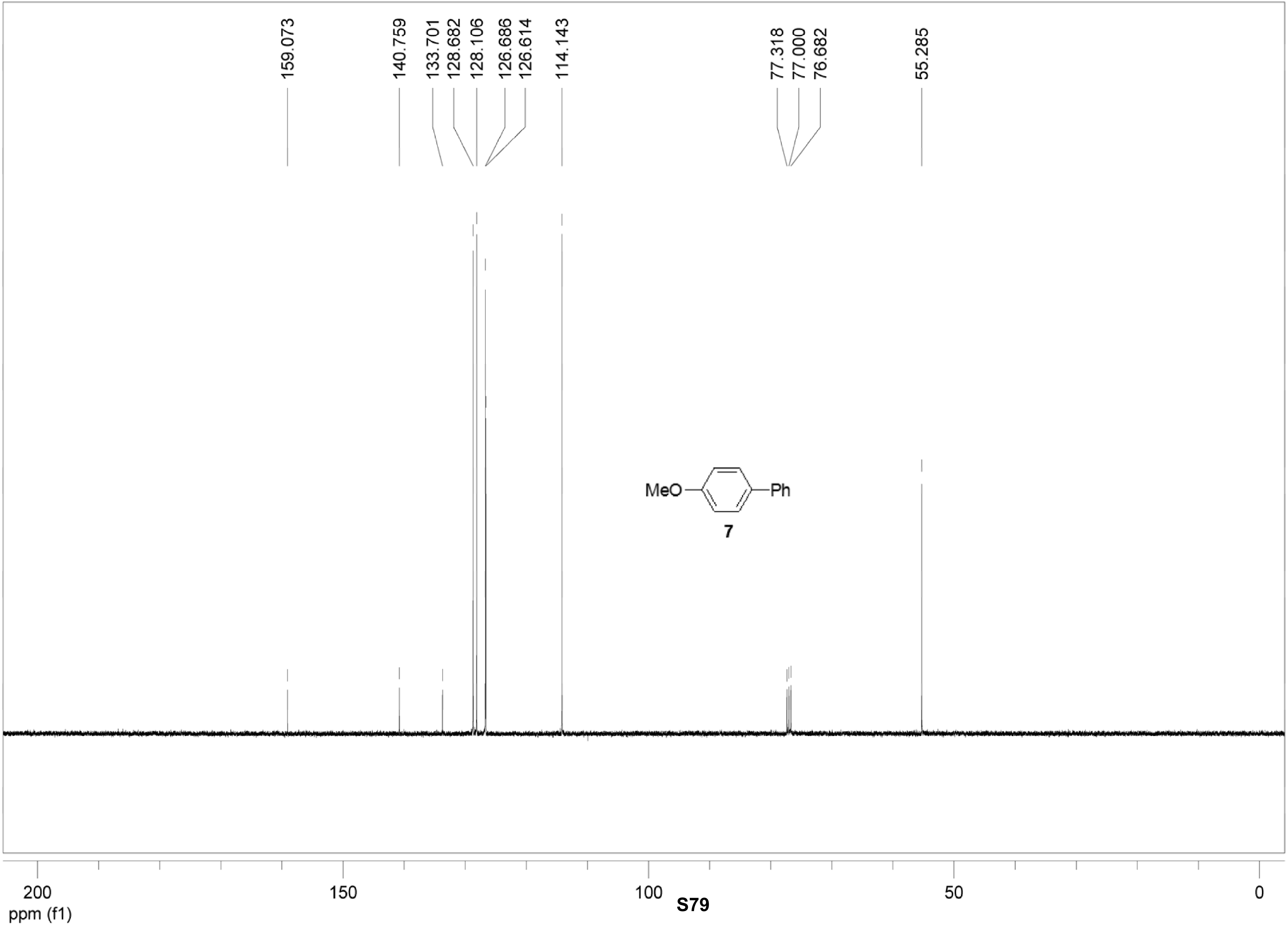

-62.280
-72.136
OTf
O2N
5f
0
-50
-100
-150
ppm (t1)


7.264
6.808
6.801
6.785
6.781
6.757
4.652
3.766
1.650
0.000
MeO
OH
6
4.01
1.00
3.07
10.0
5.0
0.0
ppm (f1)



153.722
149.389
115.984
114.771
77.318
77.000
76.682
55.751
MeO
OH
6
200
150
100
50
0
ppm (f1)


7.595
7.574
7.552
7.545
7.466
7.447
7.427
7.353
7.334
7.316
7.260
7.021
6.999
6.992
3.873
1.595
MeO
Ph
7
4.00
1.96
0.95
1.98
3.09
10.0
5.0
0.0
ppm (f1)


159.073
140.759
133.701
128.682
128.106
126.686
126.614
114.143
77.318
77.000
76.682
55.285
MeO
Ph
7
200
150
100
50
0
ppm (f1)