Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

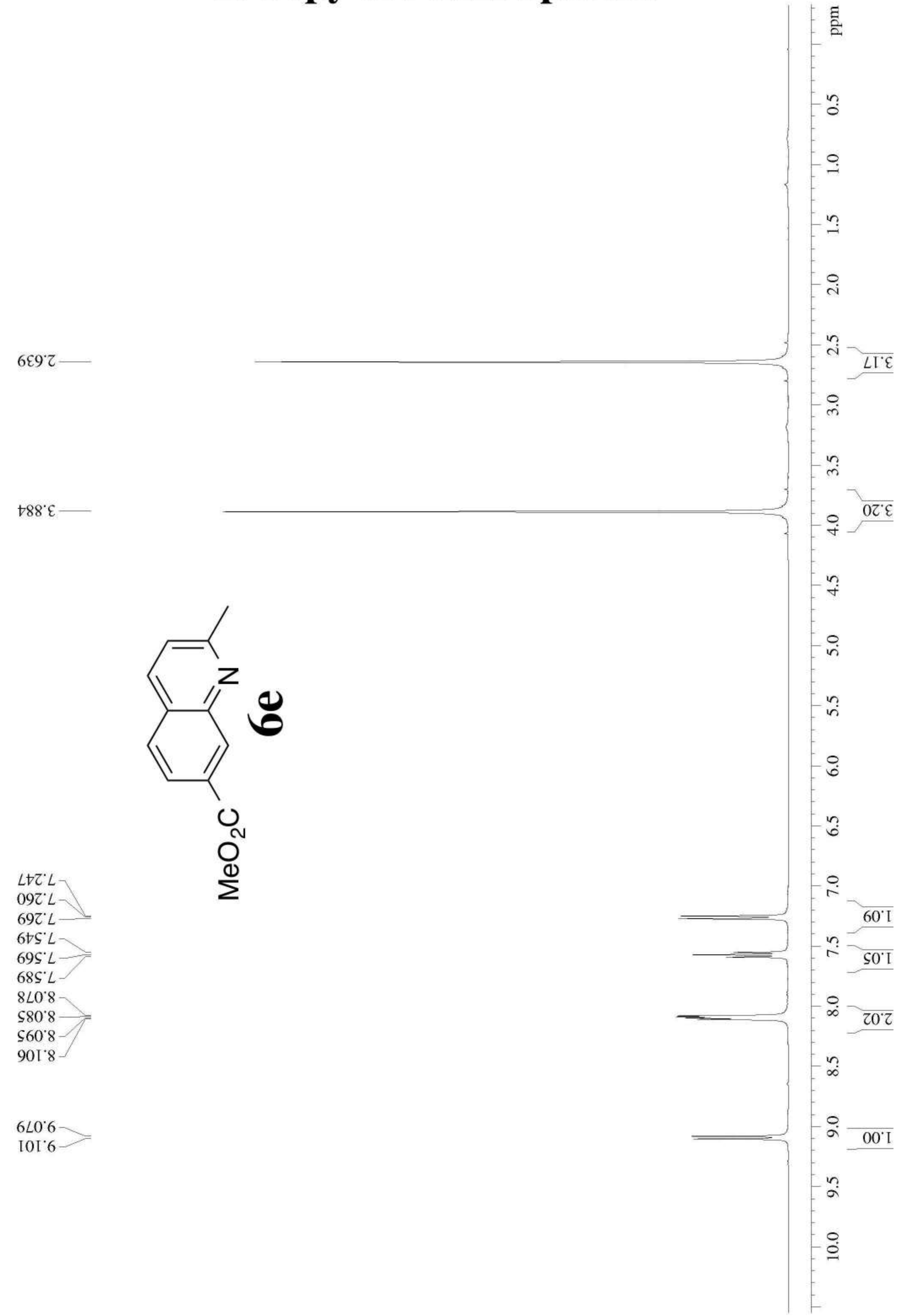
Supporting Information

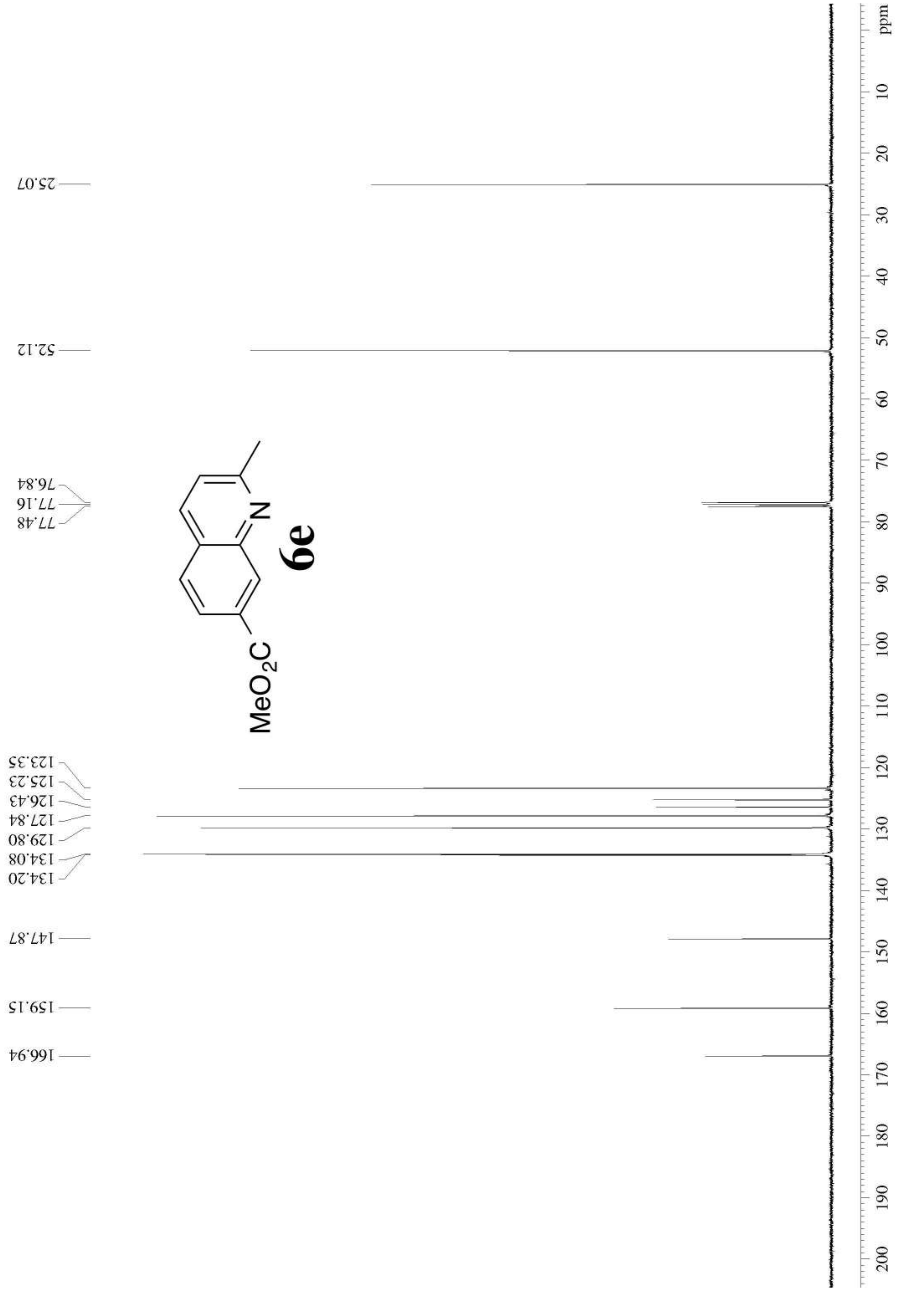
Quinoline-galactose hybrids bind selectively with high affinity to galectin-8 *N*-terminal domain

Kumar Bhaskar Pal,[1] Mukul Mahanti,[1] Xiaoli Huang,[2] Stella Persson,[1] Anders P. Sundin,[1] Fredrik R. Zetterberg,[3] Stina Oredsson,[2] Hakon Leffler,[4] and Ulf J. Nilsson[1]*

Content:

I. Copy of NMR Spectra

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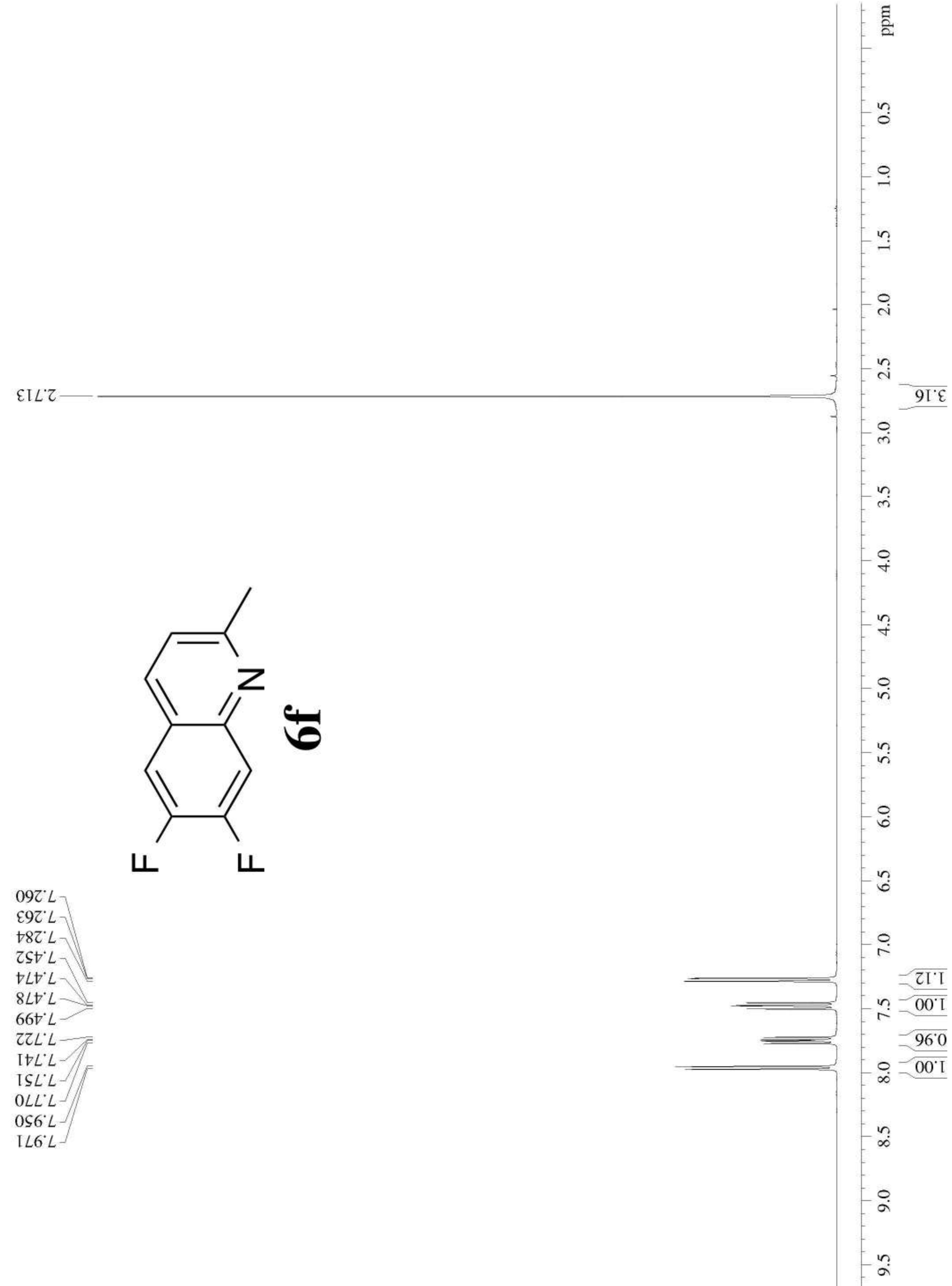
MeO2C
N
6e
ppm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F
F
N
6f
3.16
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1.00
ppm
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2.0
2.5
3.0
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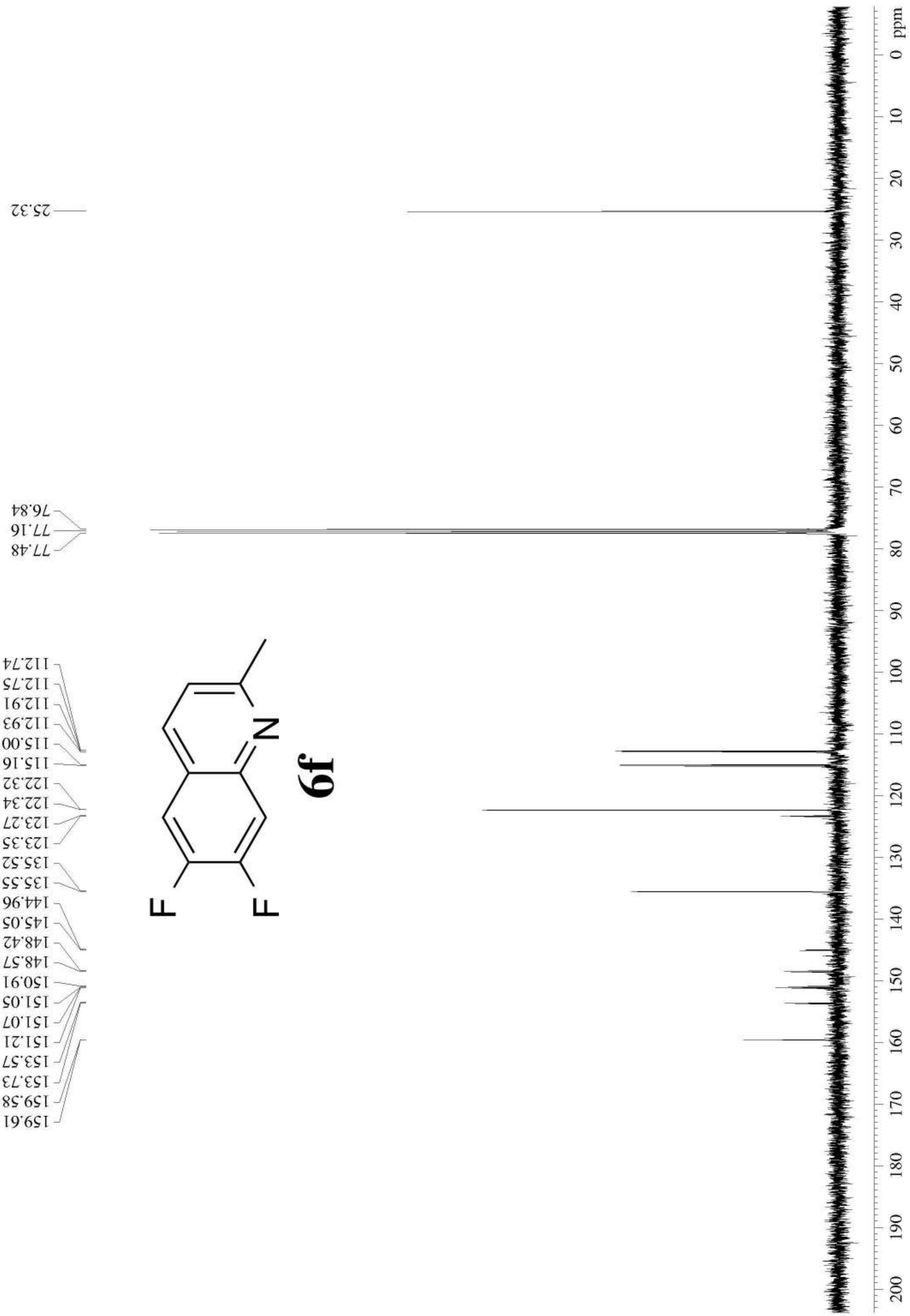
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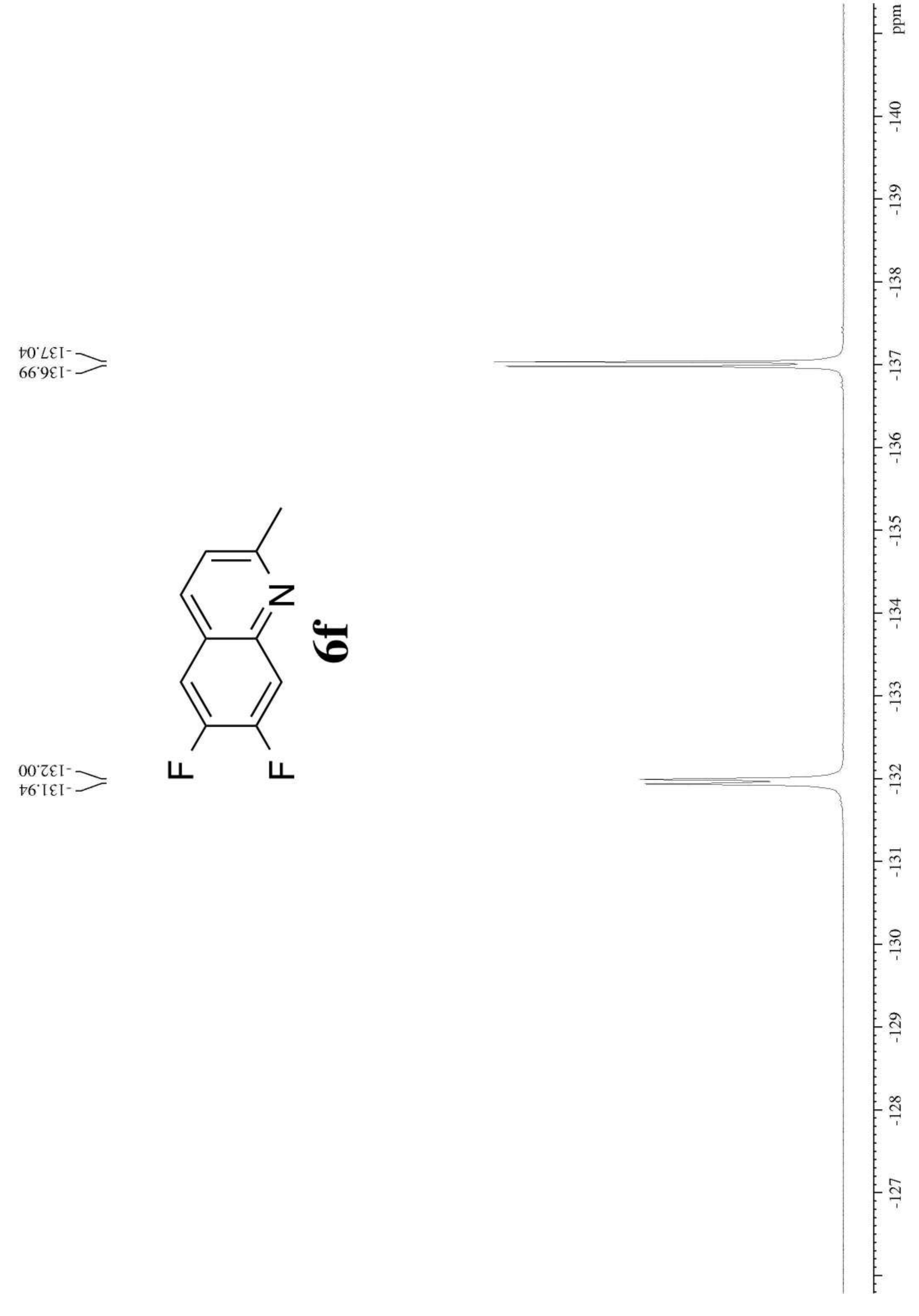

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F
F
N
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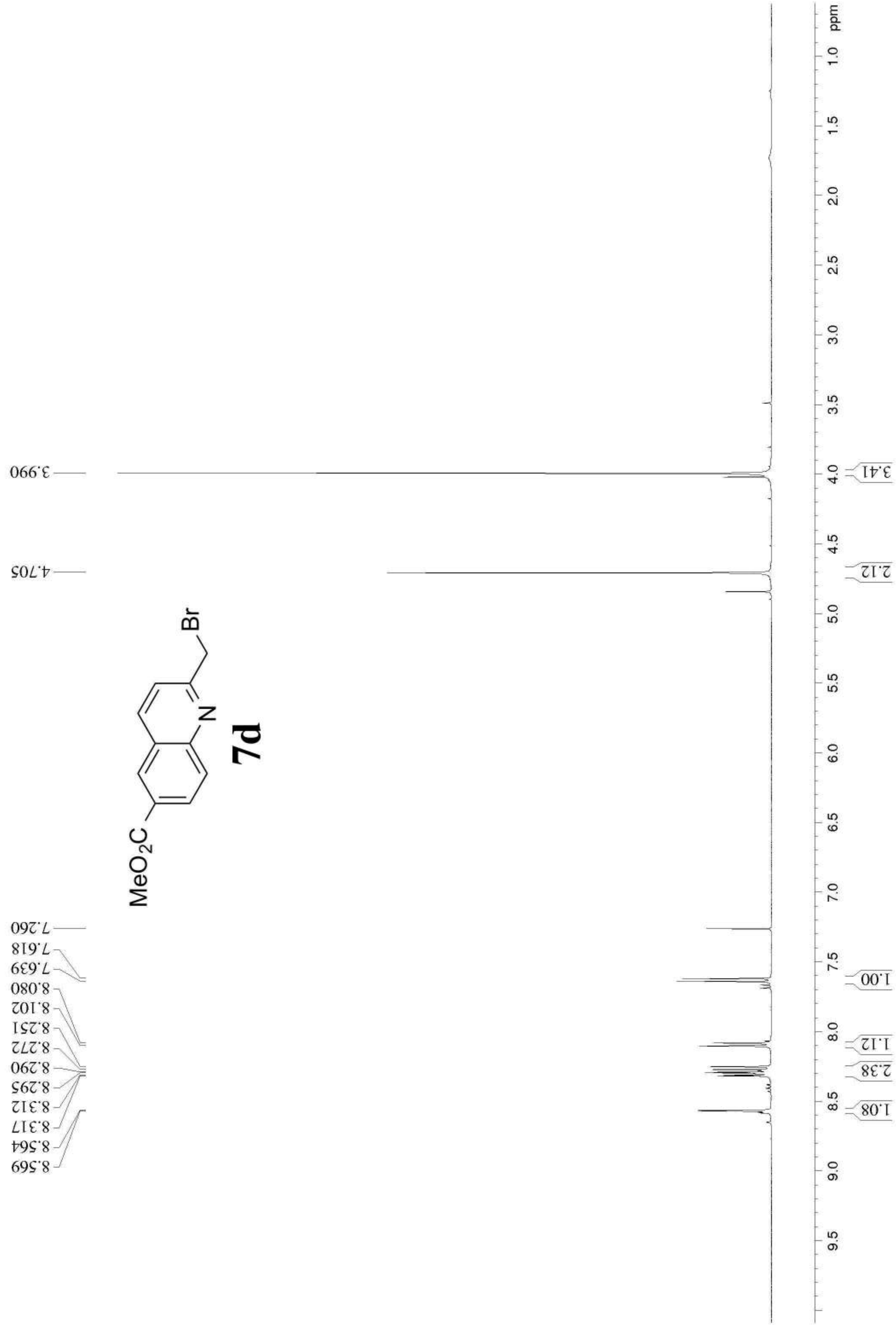

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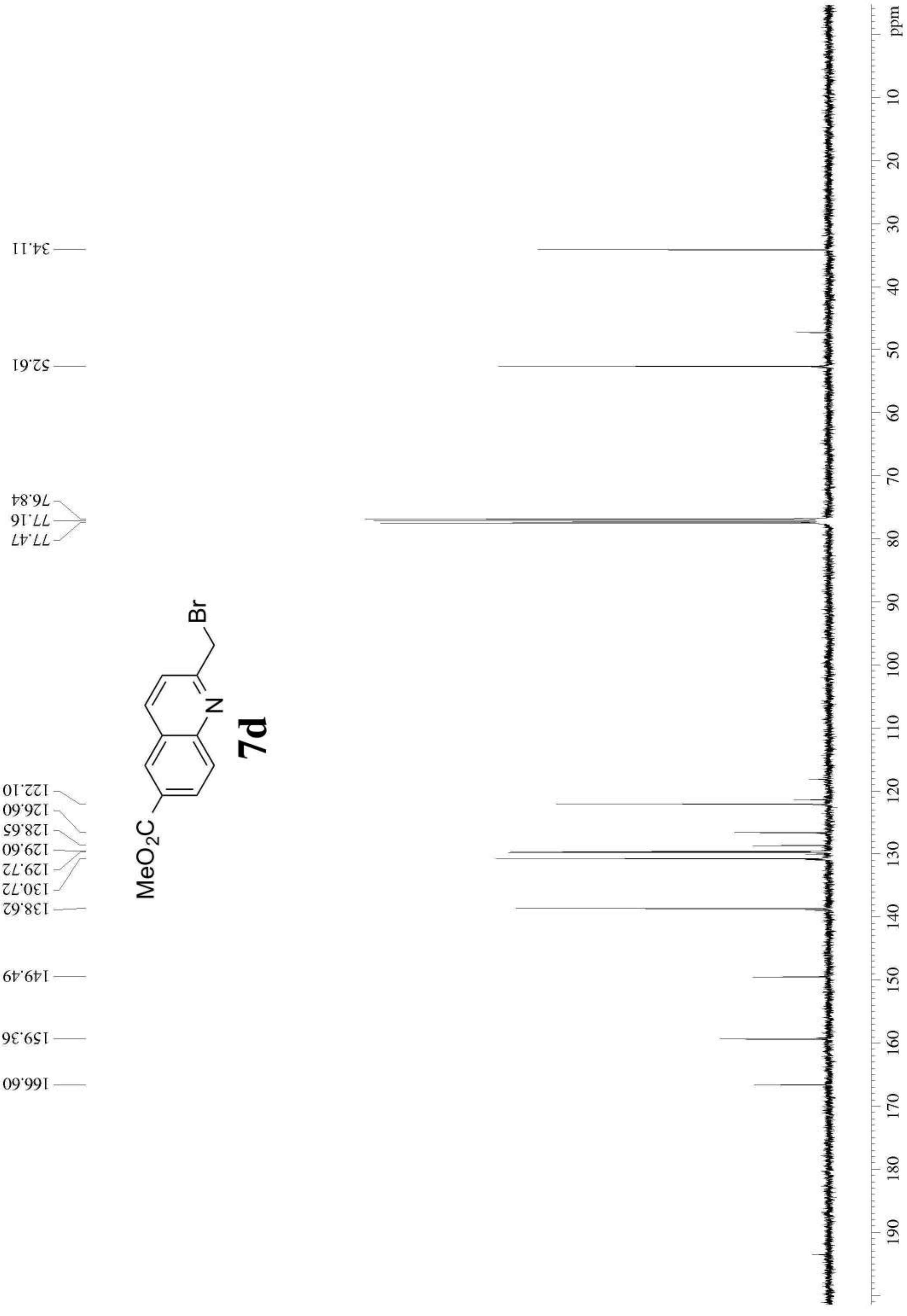

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159.36
166.60
Br
N
MeO2C
7d
ppm


3.980
4.677
7.260
7.631
7.653
7.687
7.705
7.708
7.727
8.204
8.207
8.209
8.225
8.228
8.230
8.235
8.238
8.253
8.257
9.310
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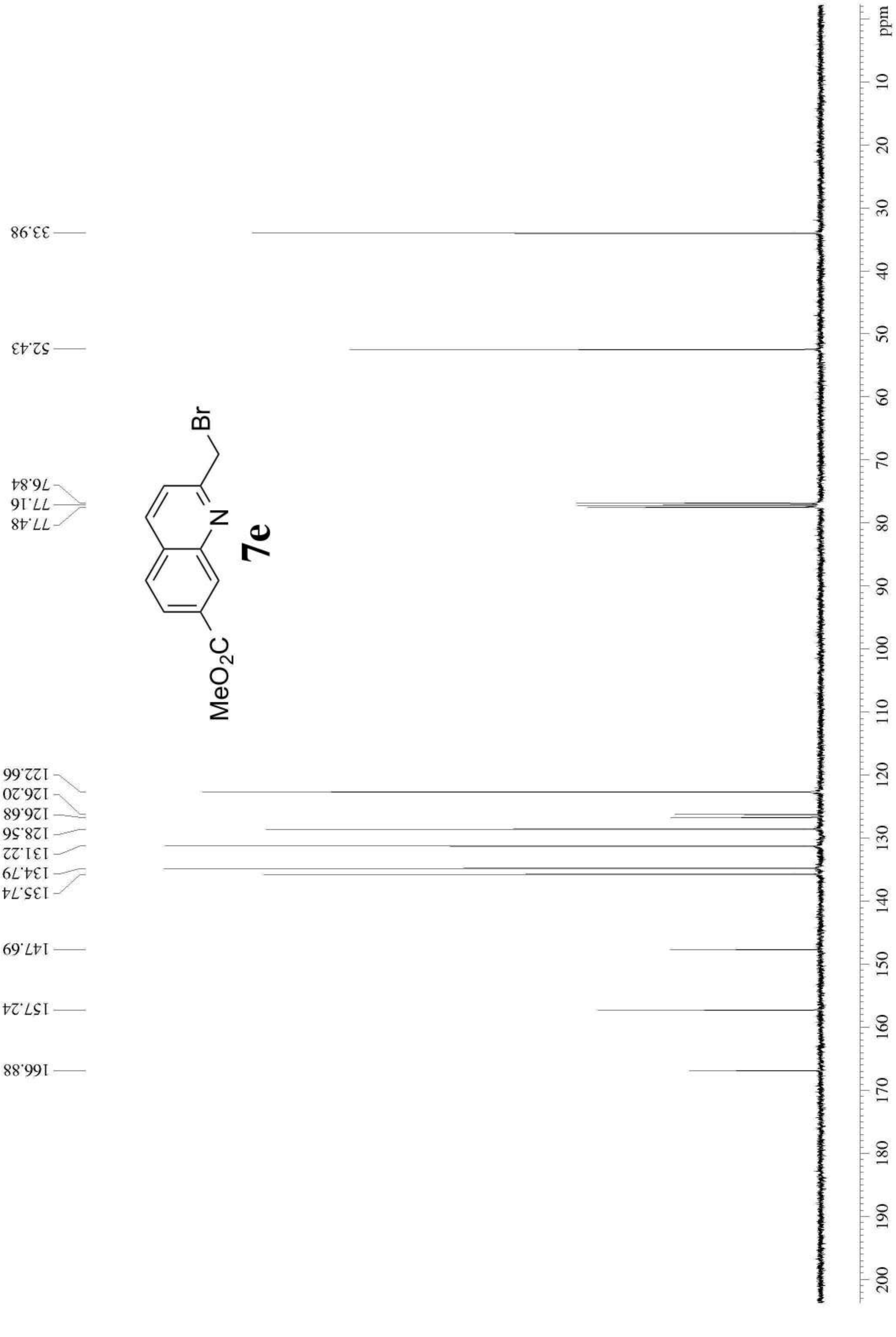

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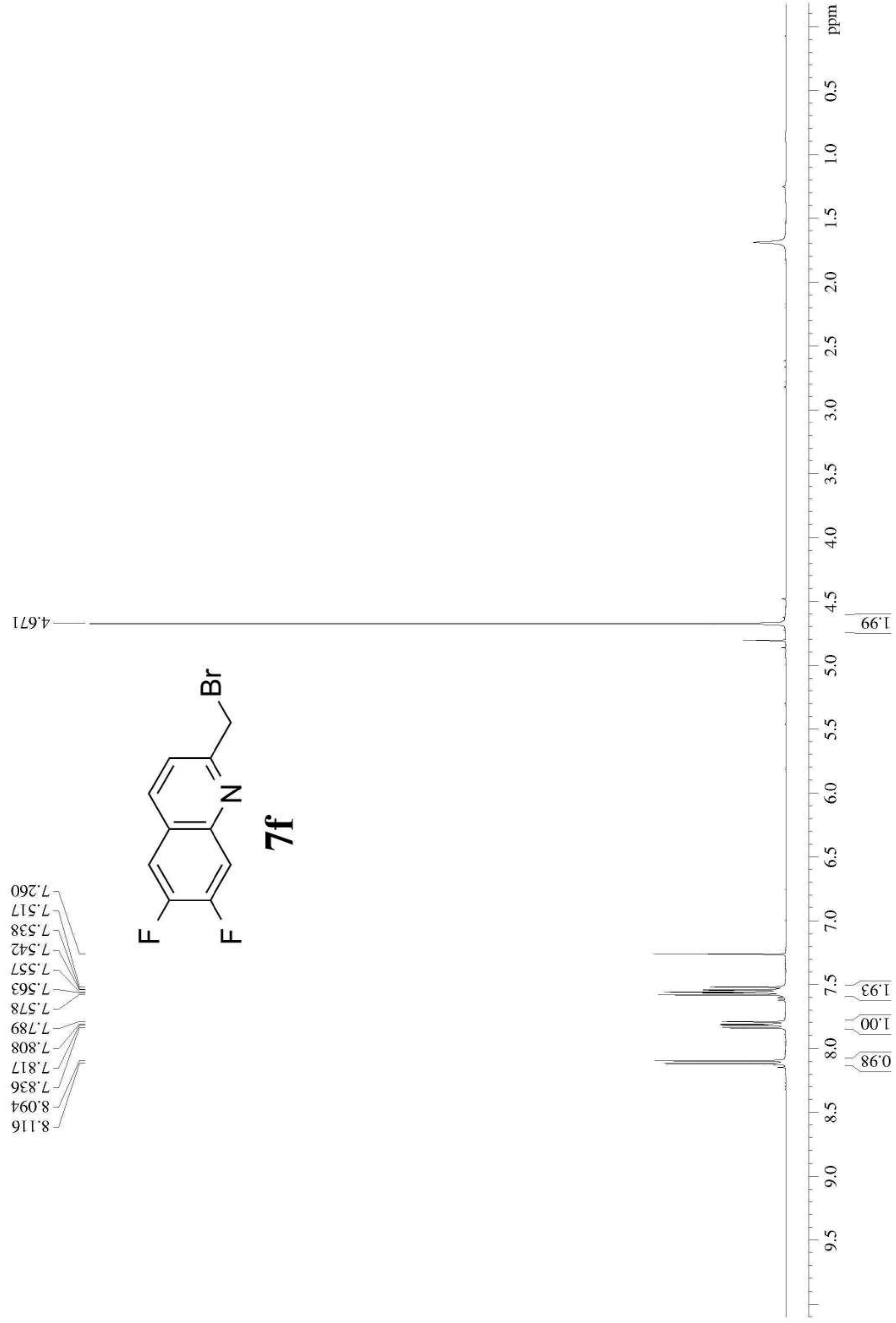

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F
F
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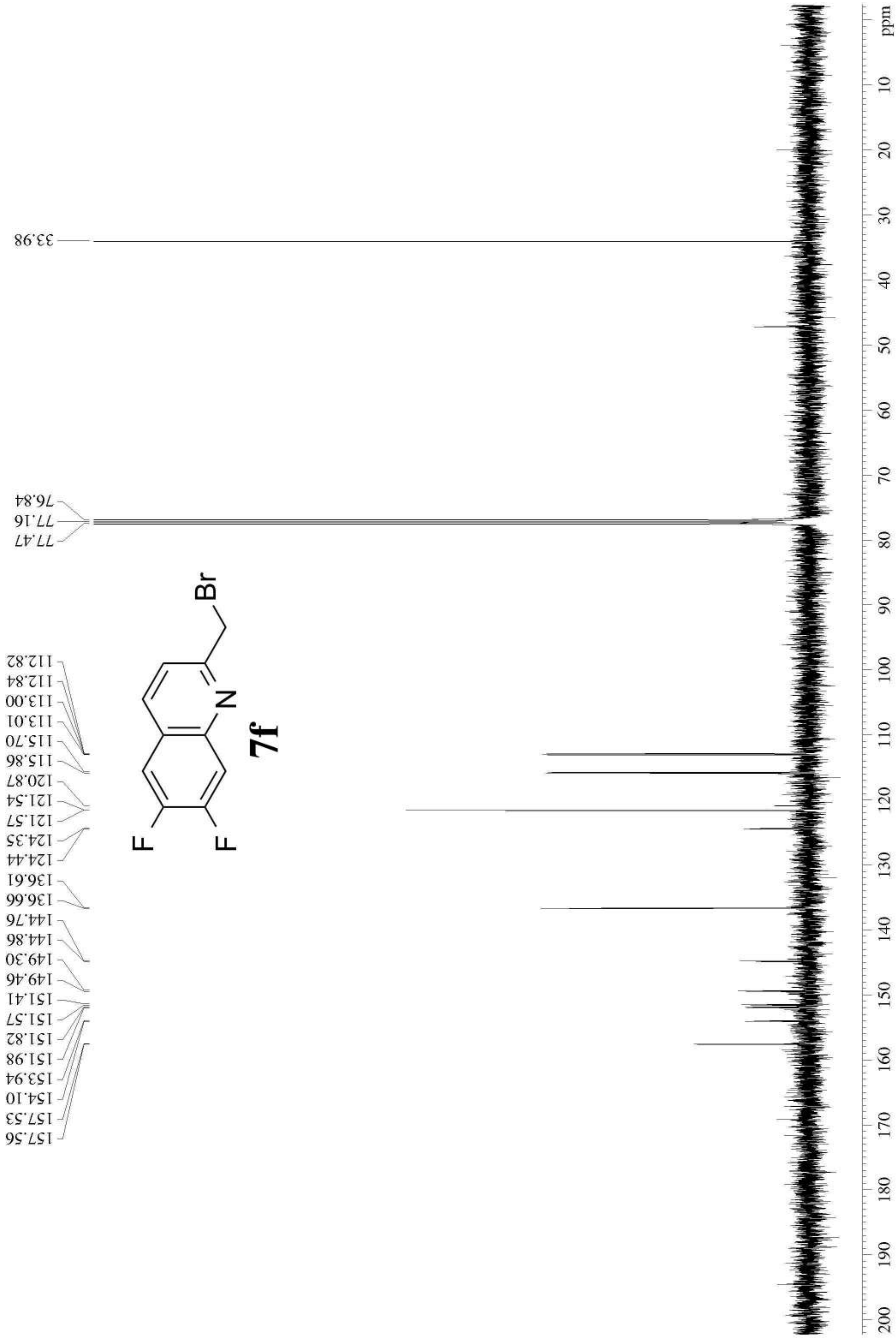
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77.16
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121.57
124.35
124.44
136.61
136.66
144.76
144.86
149.30
149.46
151.41
151.57
151.82
151.98
153.94
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157.56
Br
N
F
F
7f
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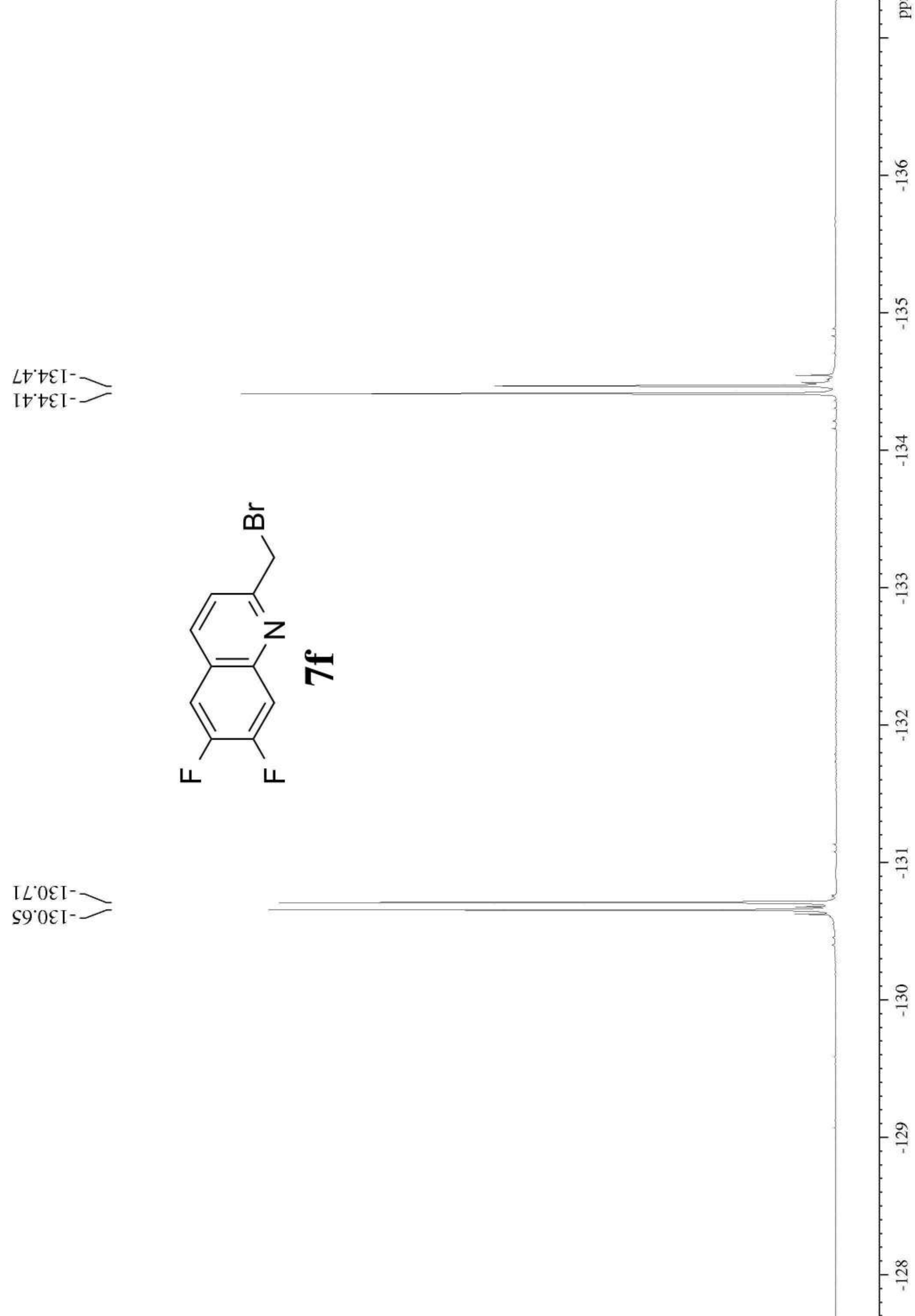
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Br
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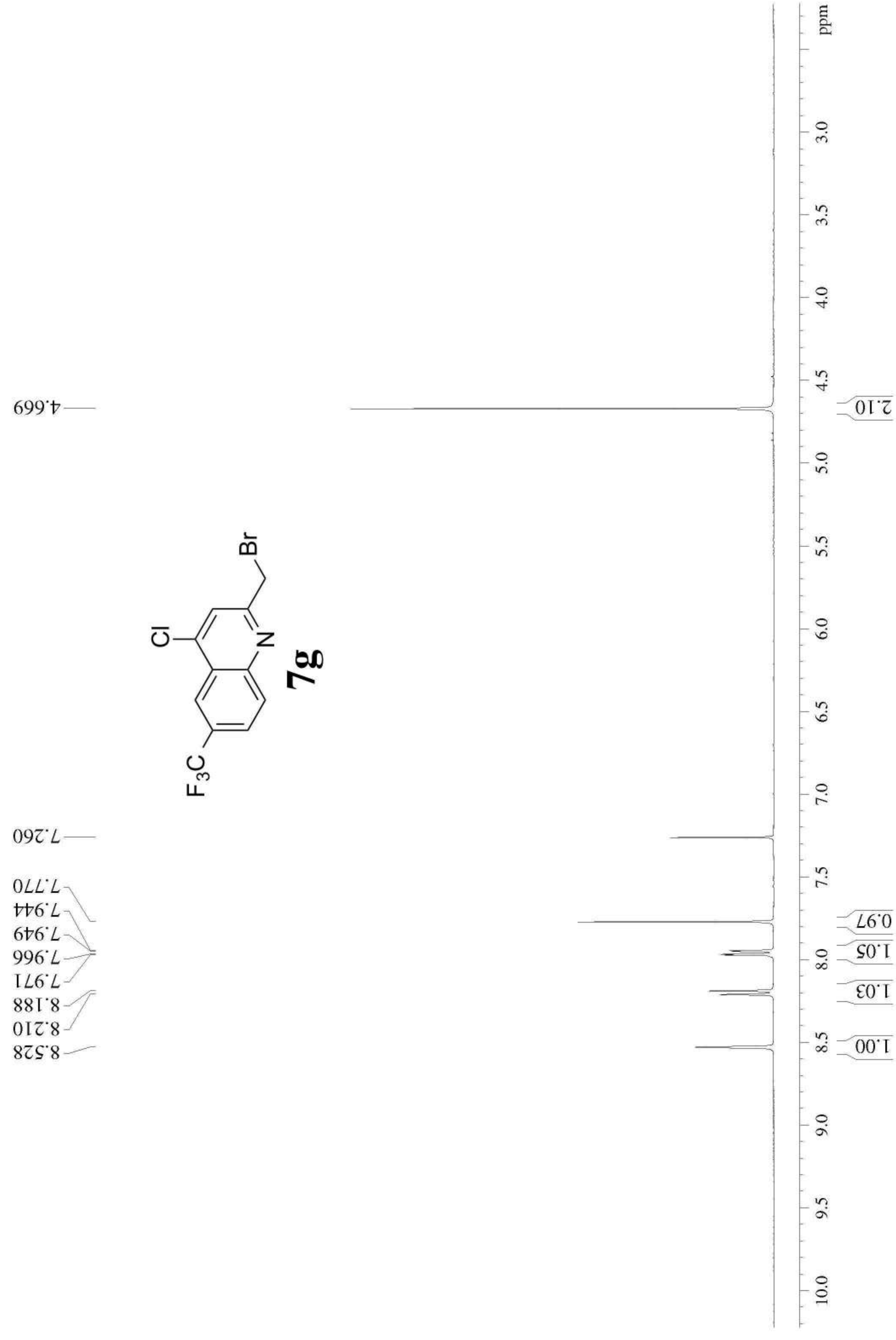
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F3C
7g
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0.97
1.05
1.03
1.00
ppm
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4.0
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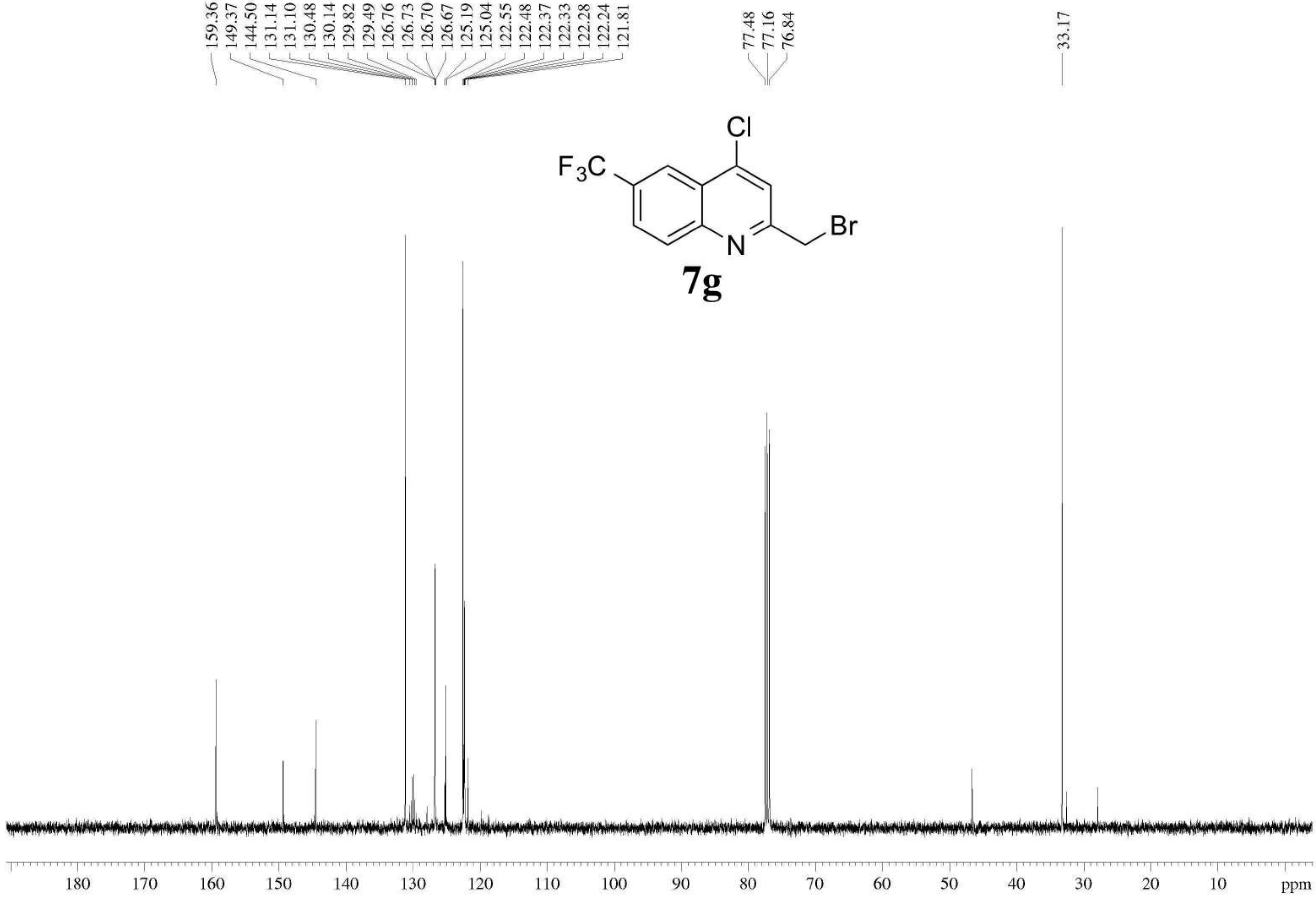
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122.48
122.37
122.33
122.28
122.24
121.81
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33.17
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F_3C
N
Br
7g
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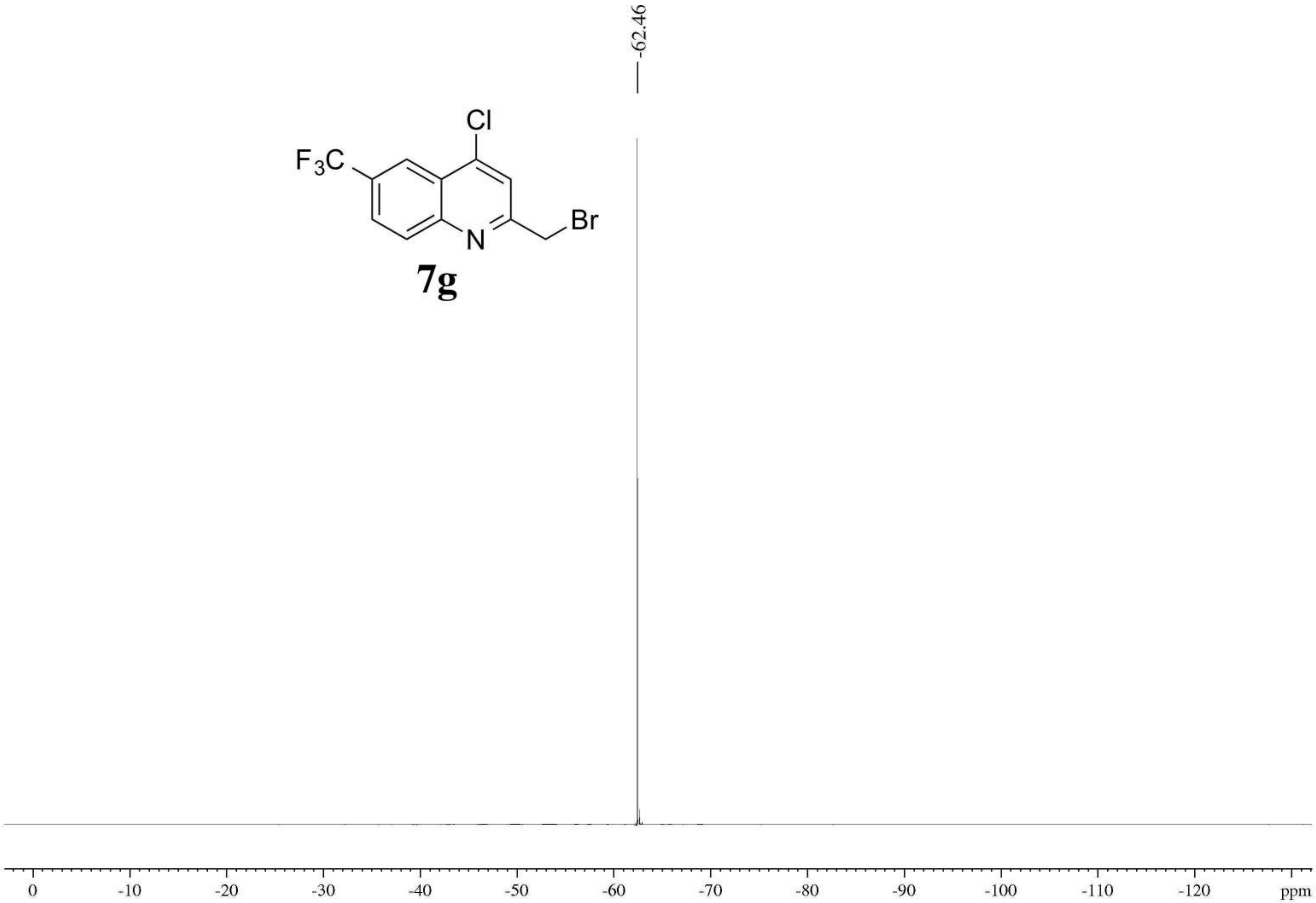

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-40
-50
-60
-70
-80
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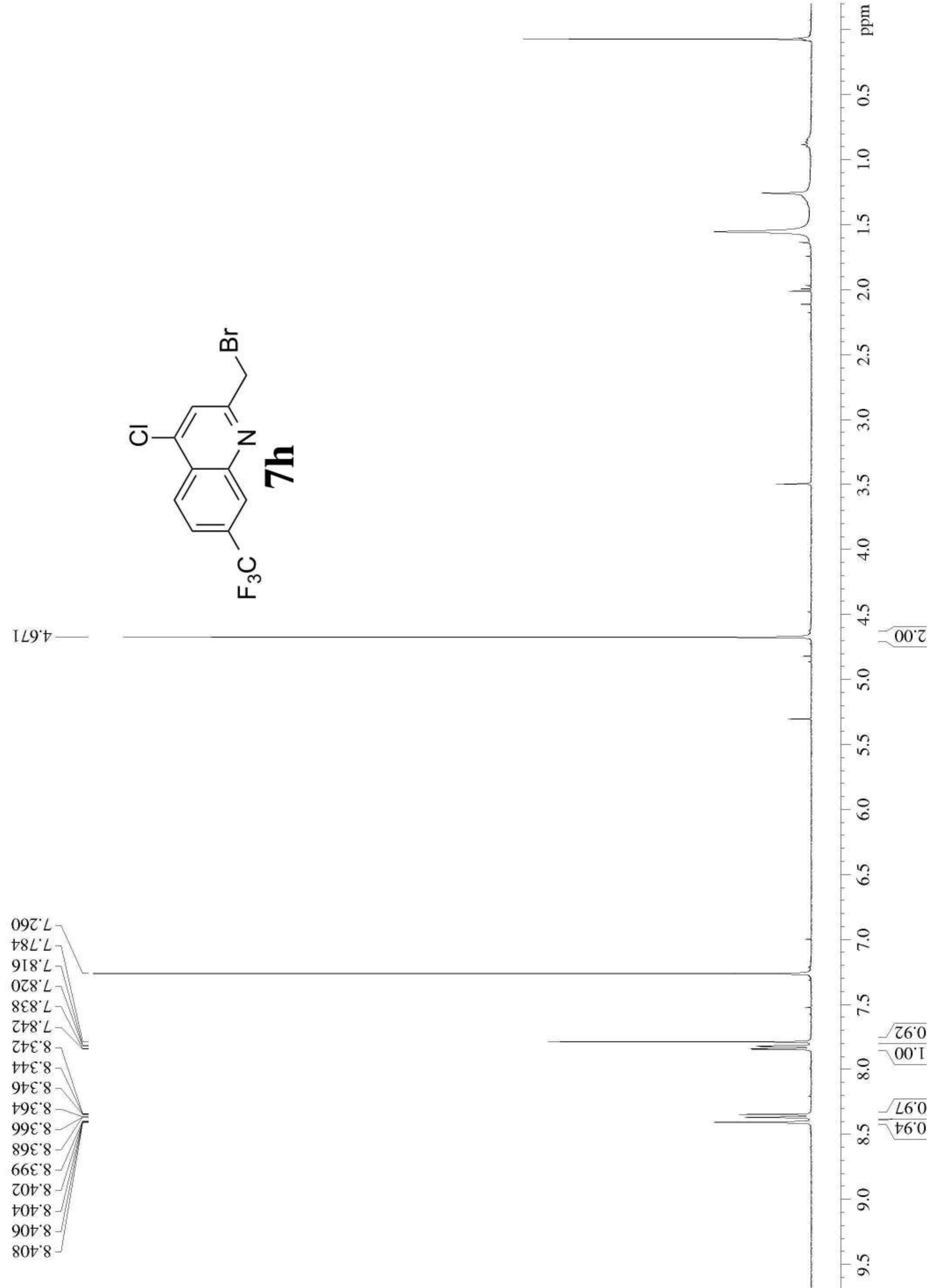
-100
-110
-120
ppm



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Br
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8.346
8.364
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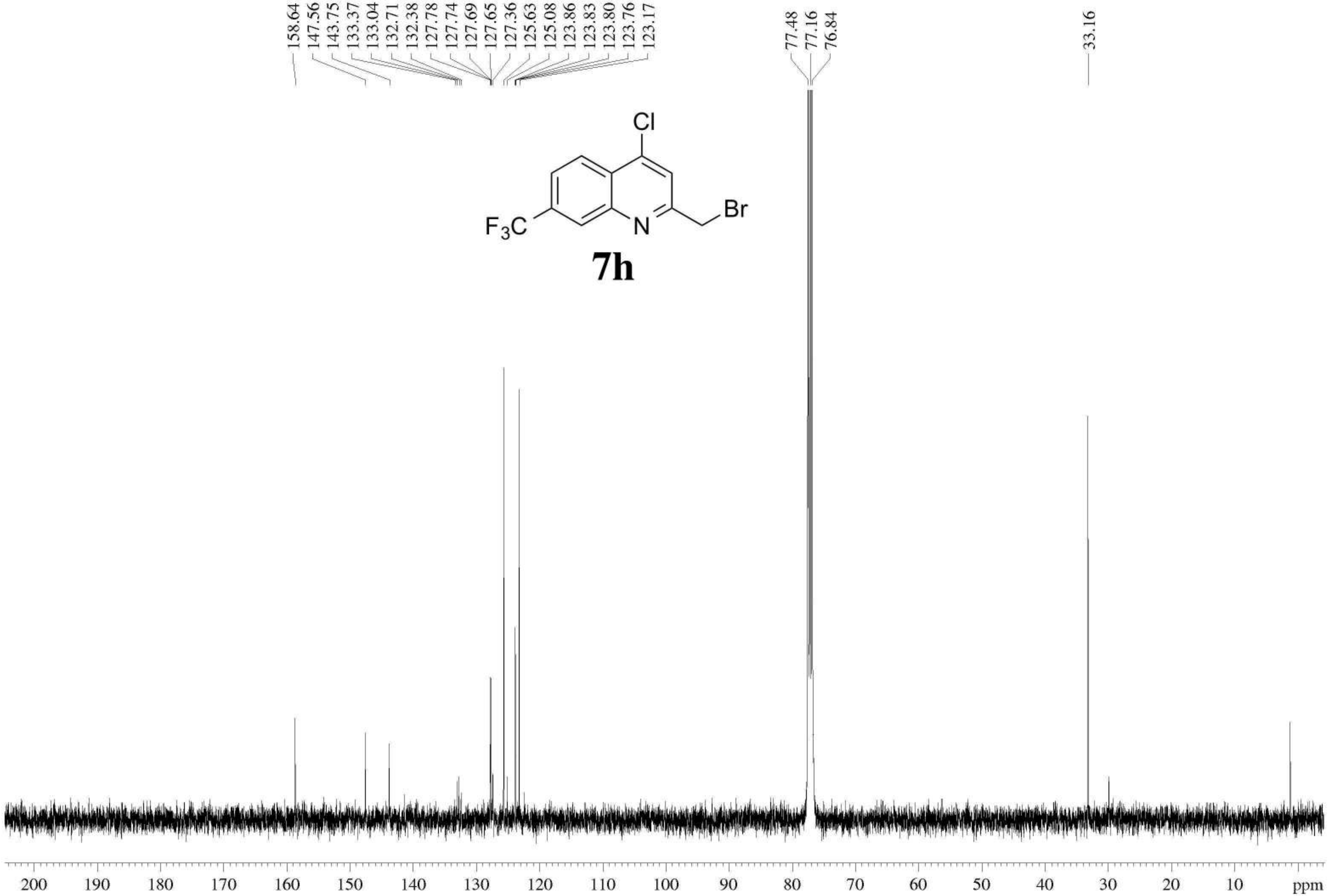
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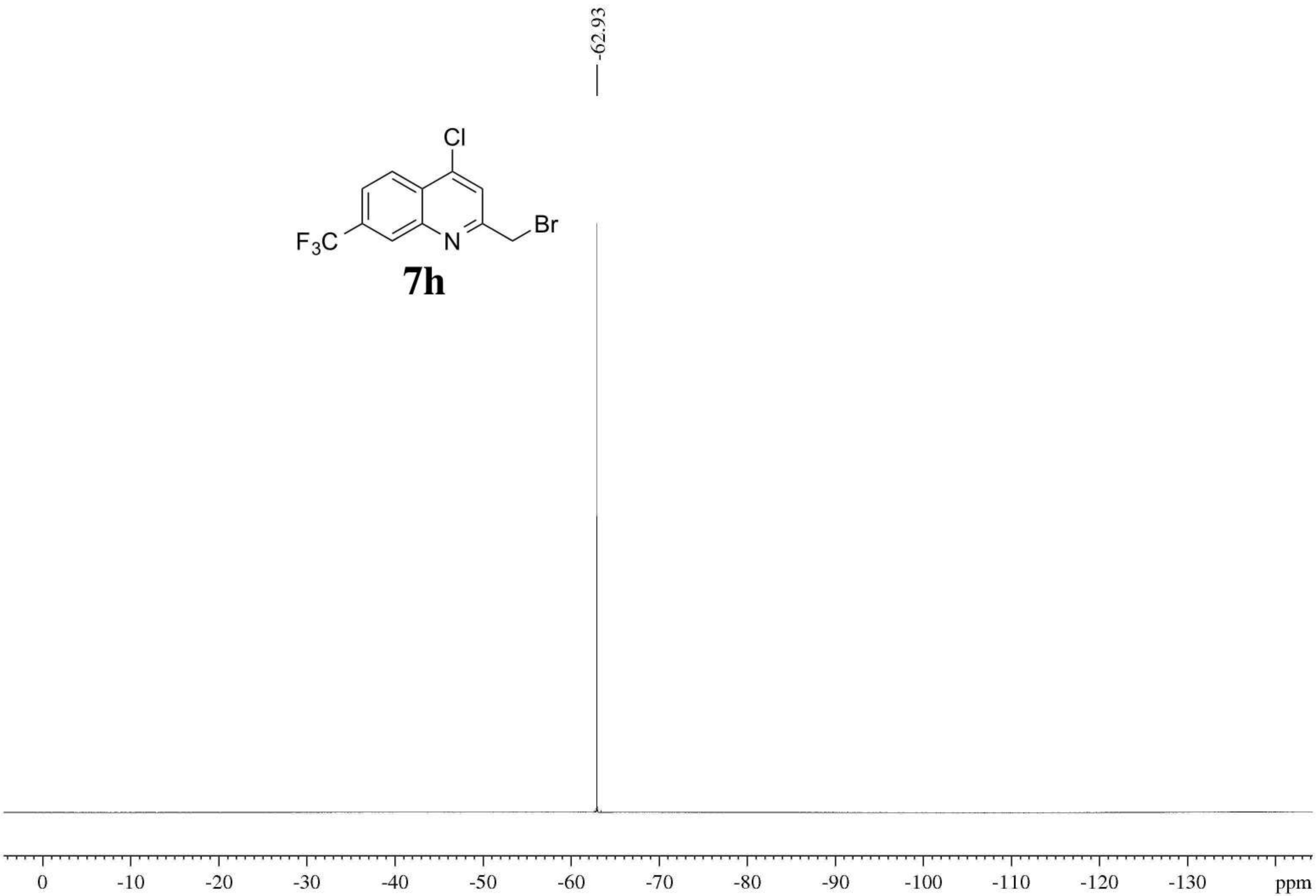
125.08
123.86
123.83
123.80
123.76
123.17
77.48
77.16
76.84
33.16
Cl
F3C
N
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

7h



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-70
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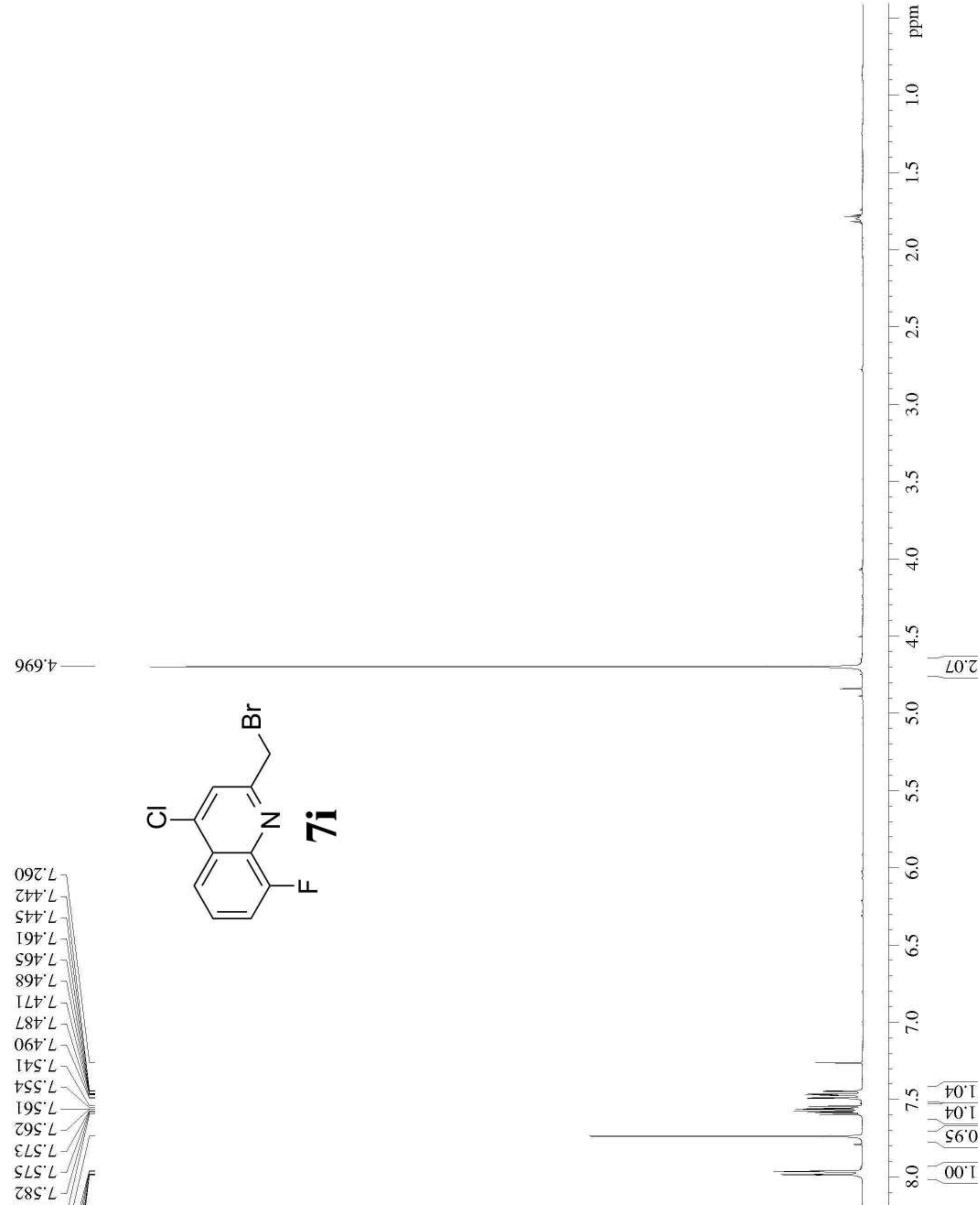
-120
-130
ppm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7.562
7.573
7.575
7.582
7.594
7.735
7.960
7.963
7.966
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F
Br
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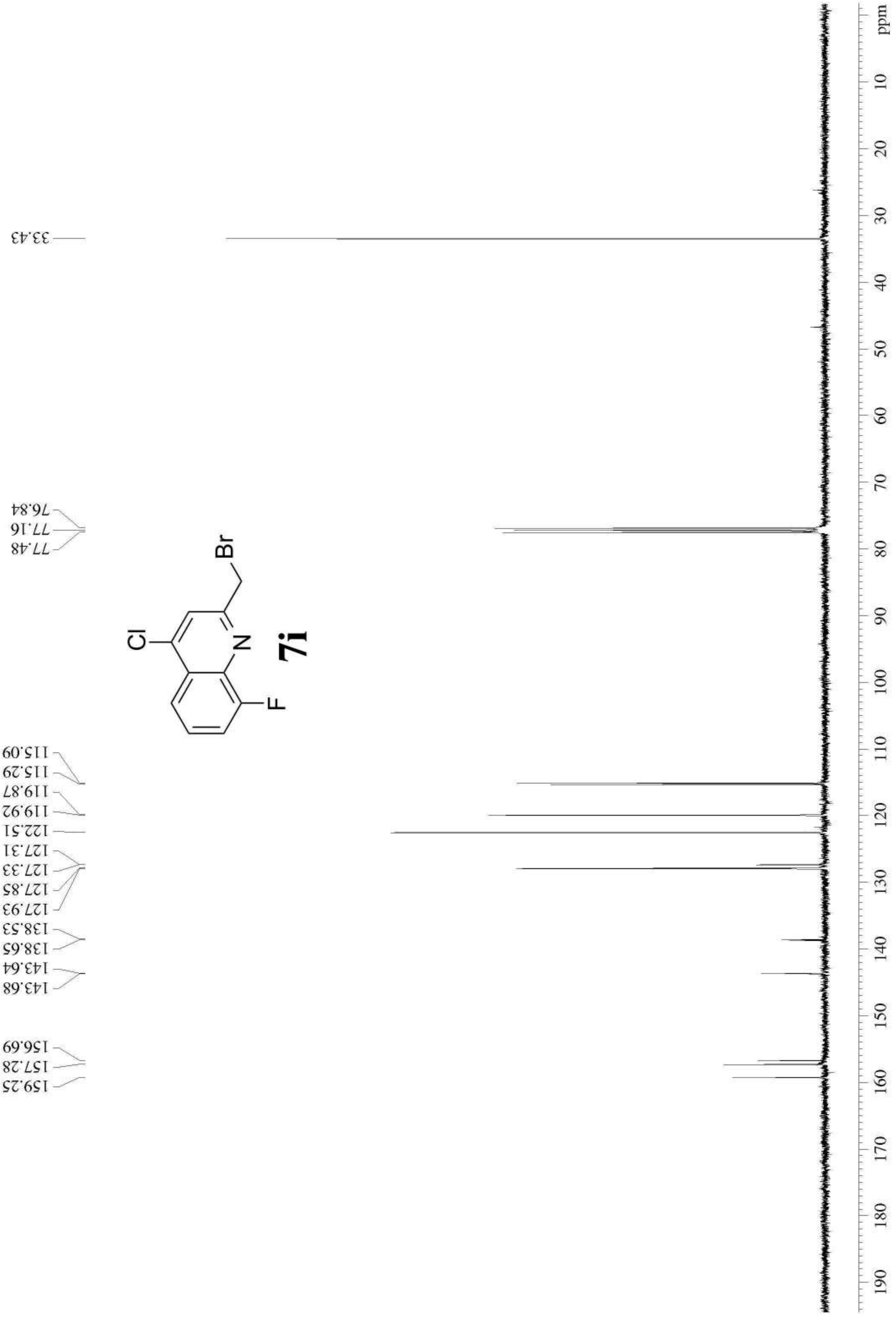
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127.93
138.53
138.65
143.64
143.68
156.69
157.28
159.25
Cl
Br
N
F
7i
ppm
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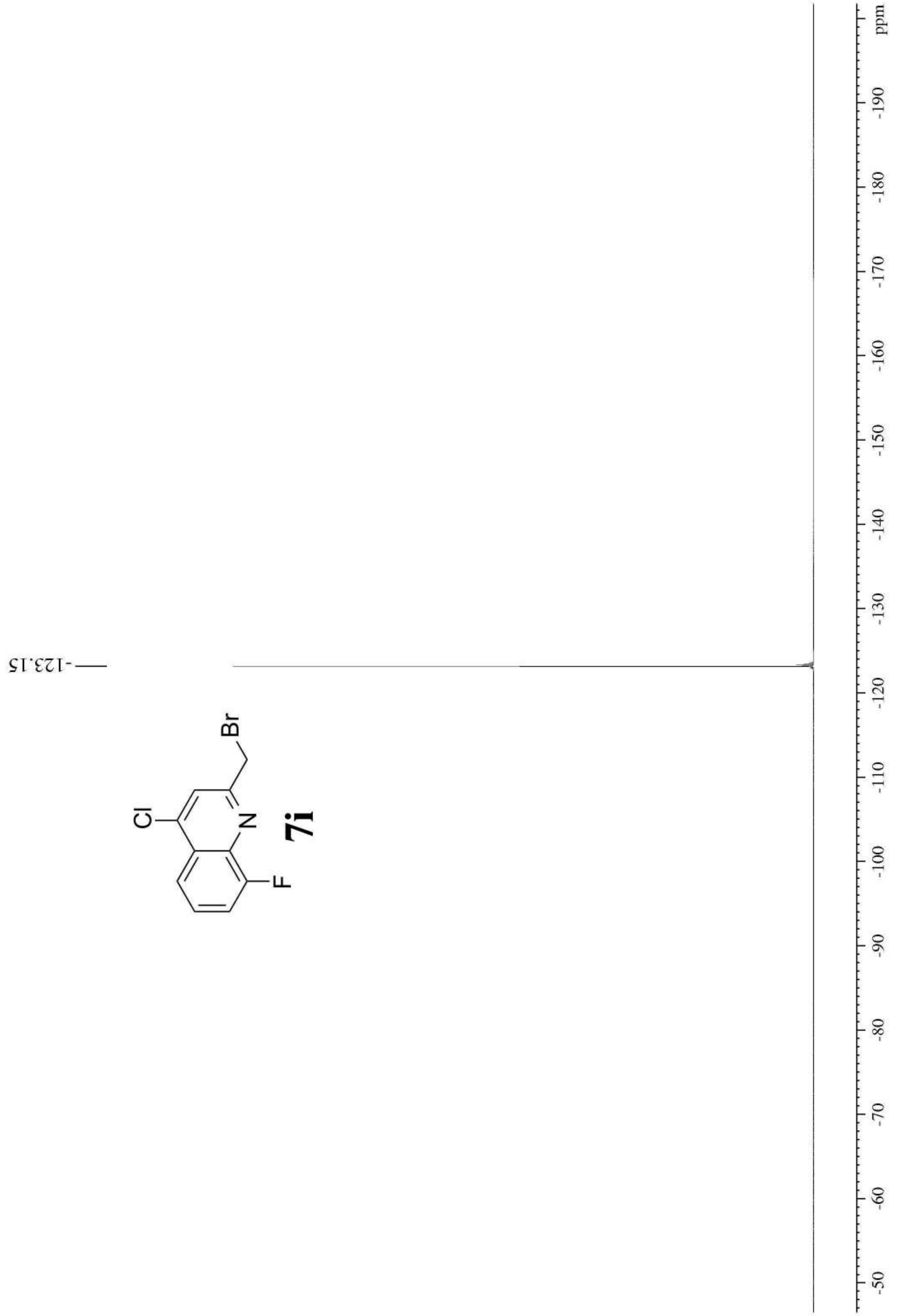
170
180
190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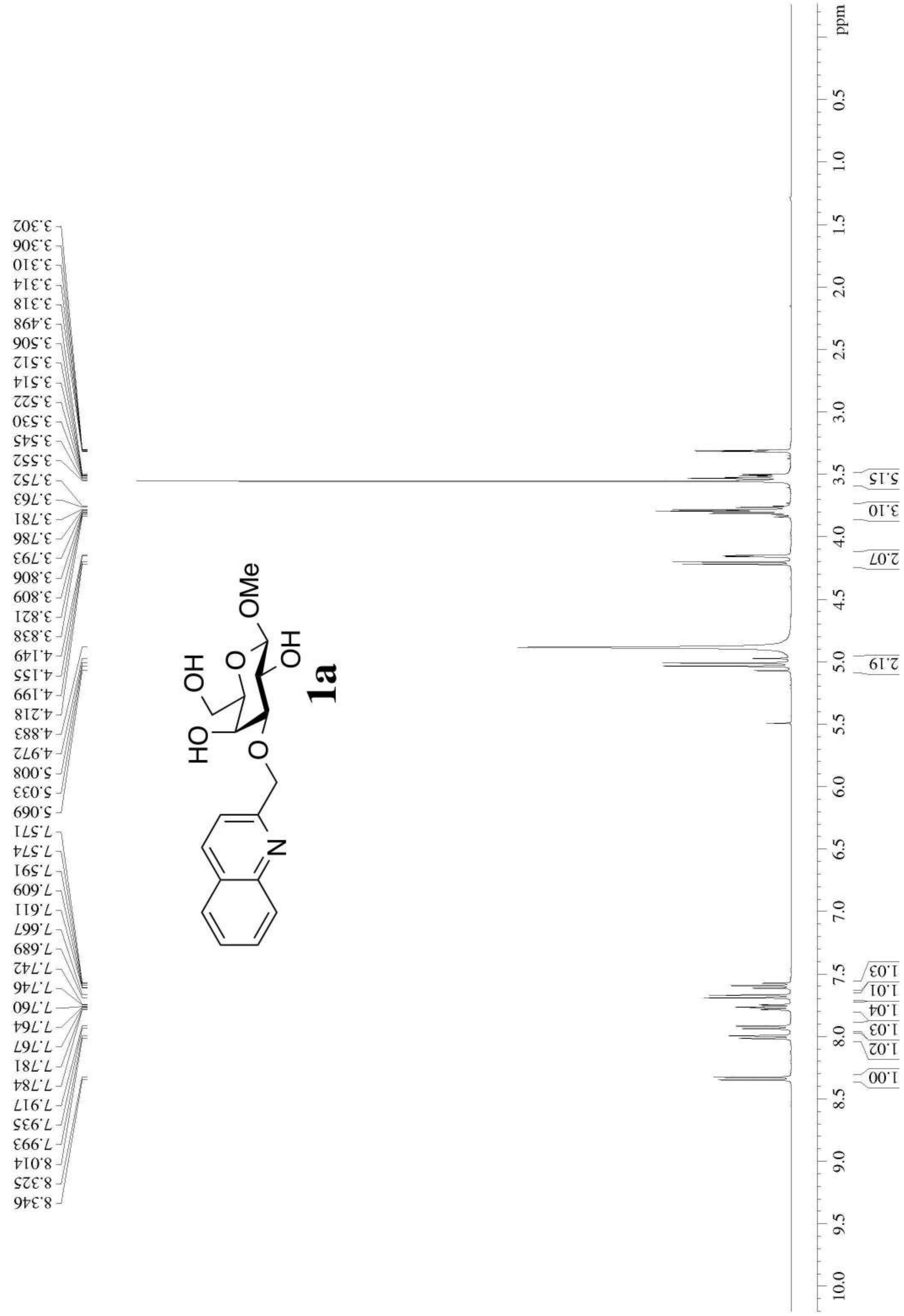
-170
-180
-190
ppm



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3.314
3.318
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3.506
3.512
3.514
3.522
3.530
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3.552
3.752
3.763
3.781
3.786
3.793
3.806
3.809
3.821
3.838
4.149
4.155
4.199
4.218
4.883
4.972
5.008
5.033
5.069
7.571
7.574
7.591
7.609
7.611
7.667
7.689
7.742
7.746
7.760
7.764
7.767
7.781
7.784
7.917
7.935
7.993
8.014
8.325
8.346
HO
OH
O
OMe
OH
O
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2.07
2.19
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1.01
1.04
1.03
1.02
1.00
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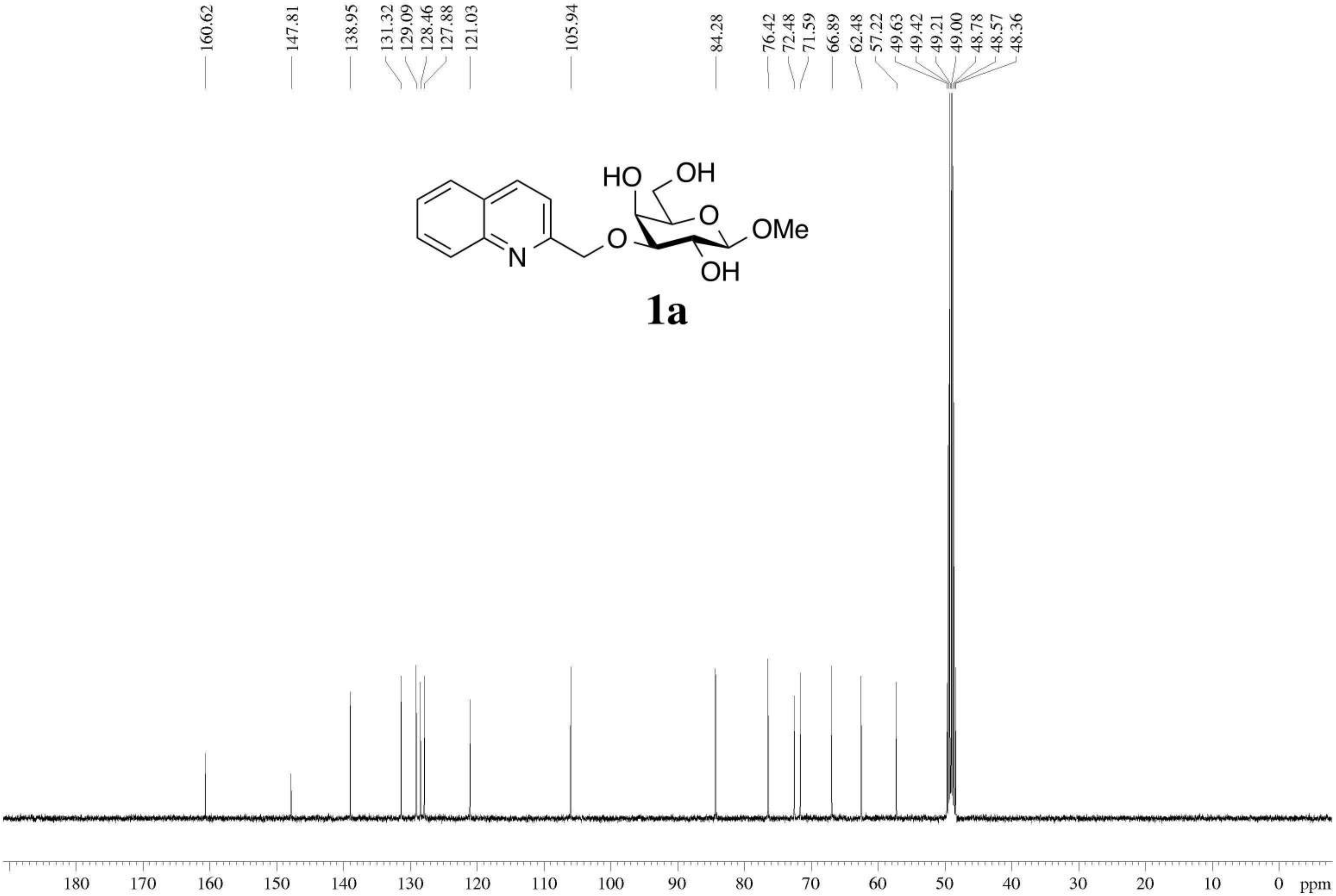
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49.63
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49.21
49.00
48.78
48.57
48.36
HO
OH
O
OMe
N
O
OH
1a
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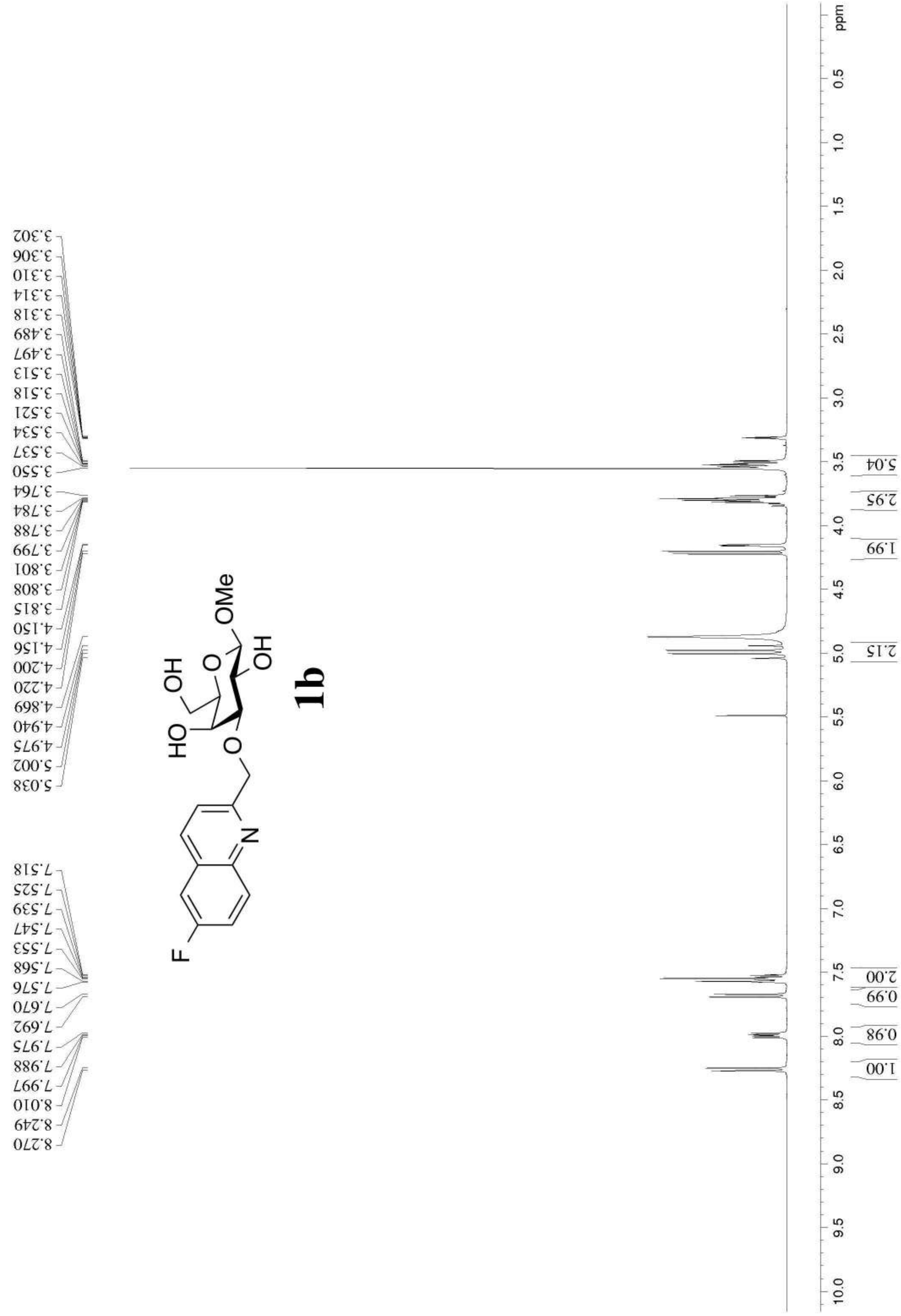

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3.537
3.550
3.764
3.784
3.788
3.799
3.801
3.808
3.815
4.150
4.156
4.200
4.220
4.869
4.940
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5.002
5.038
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7.525
7.539
7.547
7.553
7.568
7.576
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8.249
8.270
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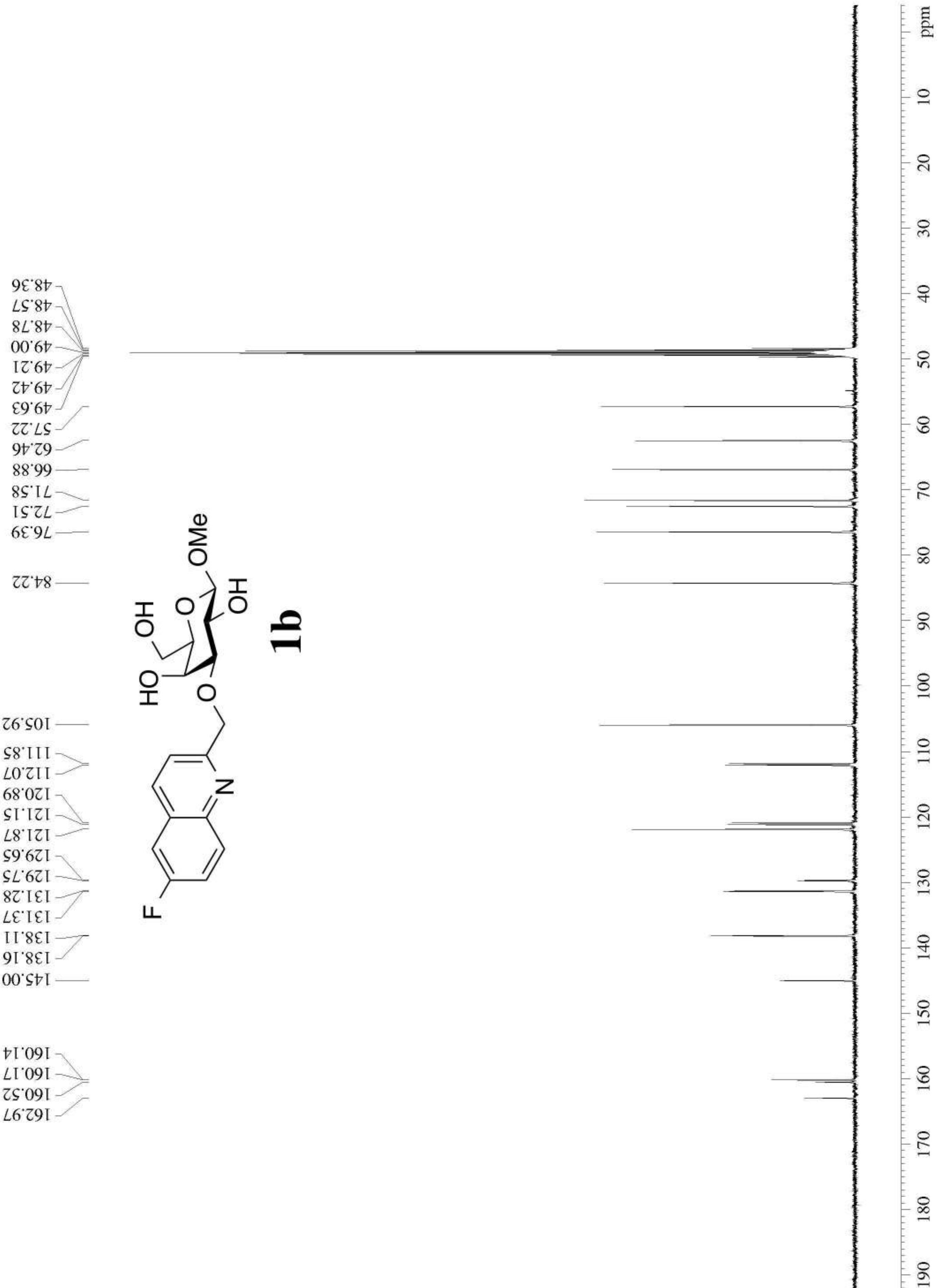
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57.22
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66.88
71.58
72.51
76.39
84.22
105.92
111.85
112.07
120.89
121.15
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129.65
129.75
131.28
131.37
138.11
138.16
145.00
160.14
160.17
160.52
162.97
OMe
HO
OH
N
F
ppm
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170
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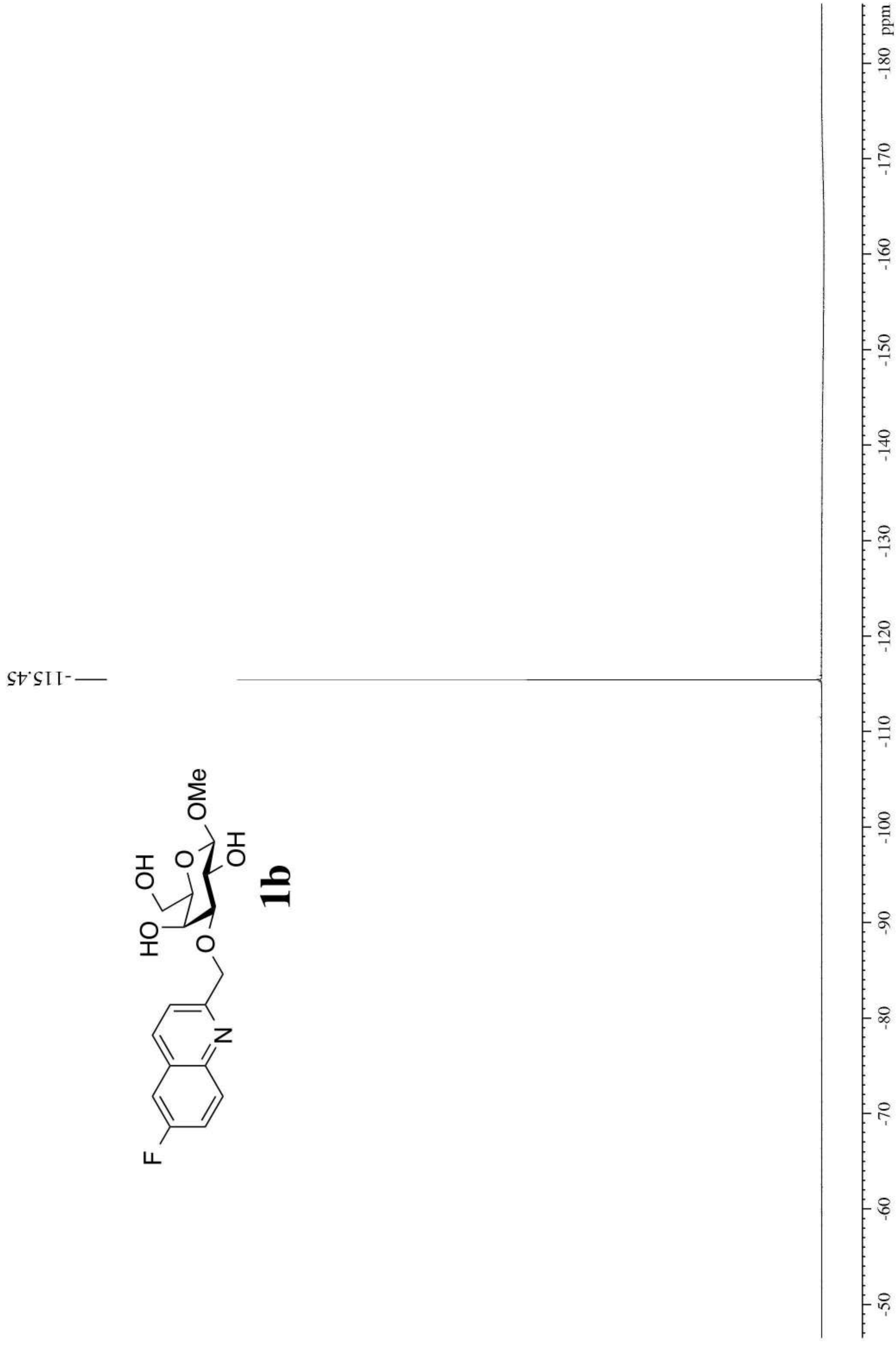
190

1b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OH
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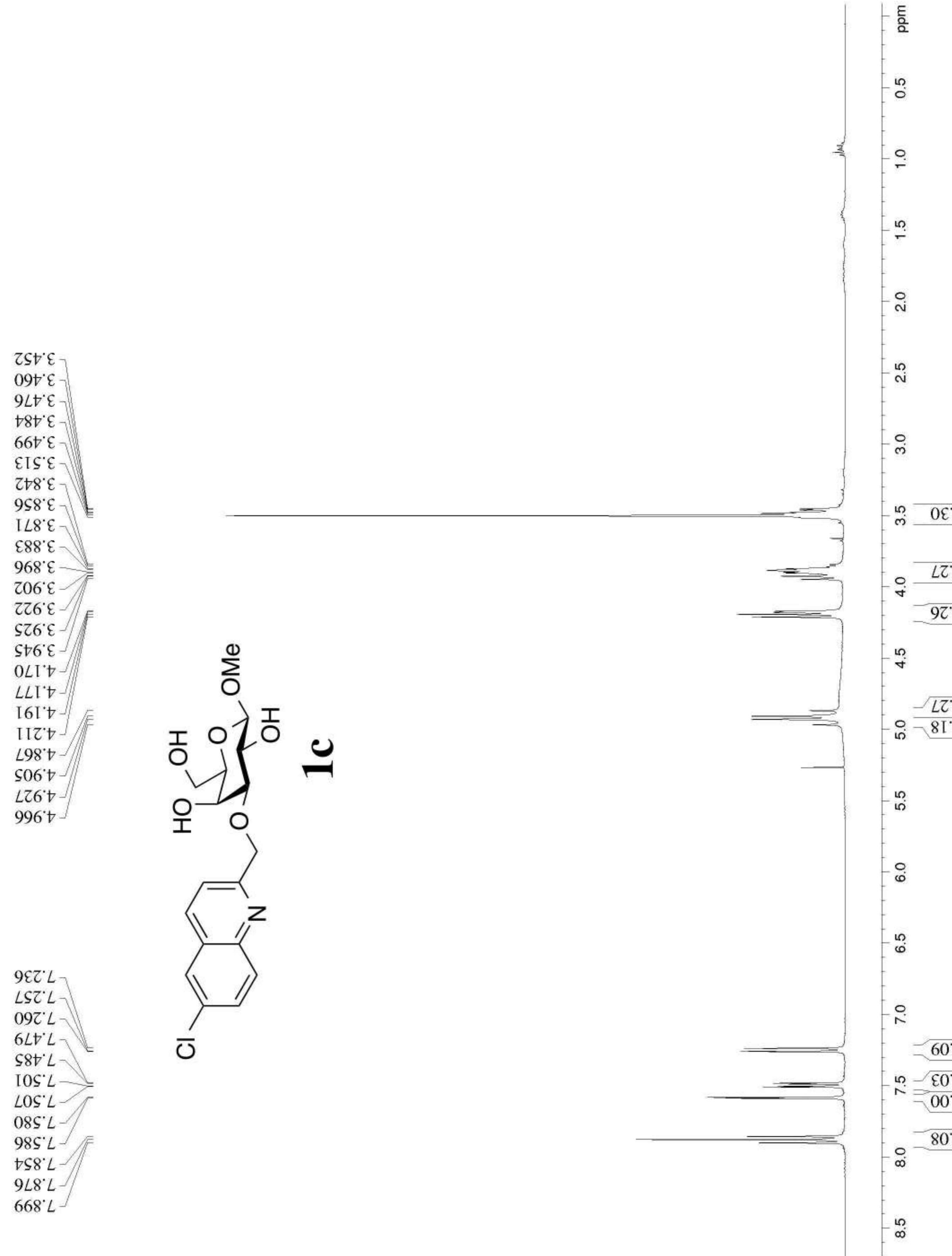
-130
-140
-150
-160
-170
-180 ppm



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3.499
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3.871
3.883
3.896
3.902
3.922
3.925
3.945
4.170
4.177
4.191
4.211
4.867
4.905
4.927
4.966
7.236
7.257
7.260
7.479
7.485
7.501
7.507
7.580
7.586
7.854
7.876
7.899
Cl
N
O
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OH
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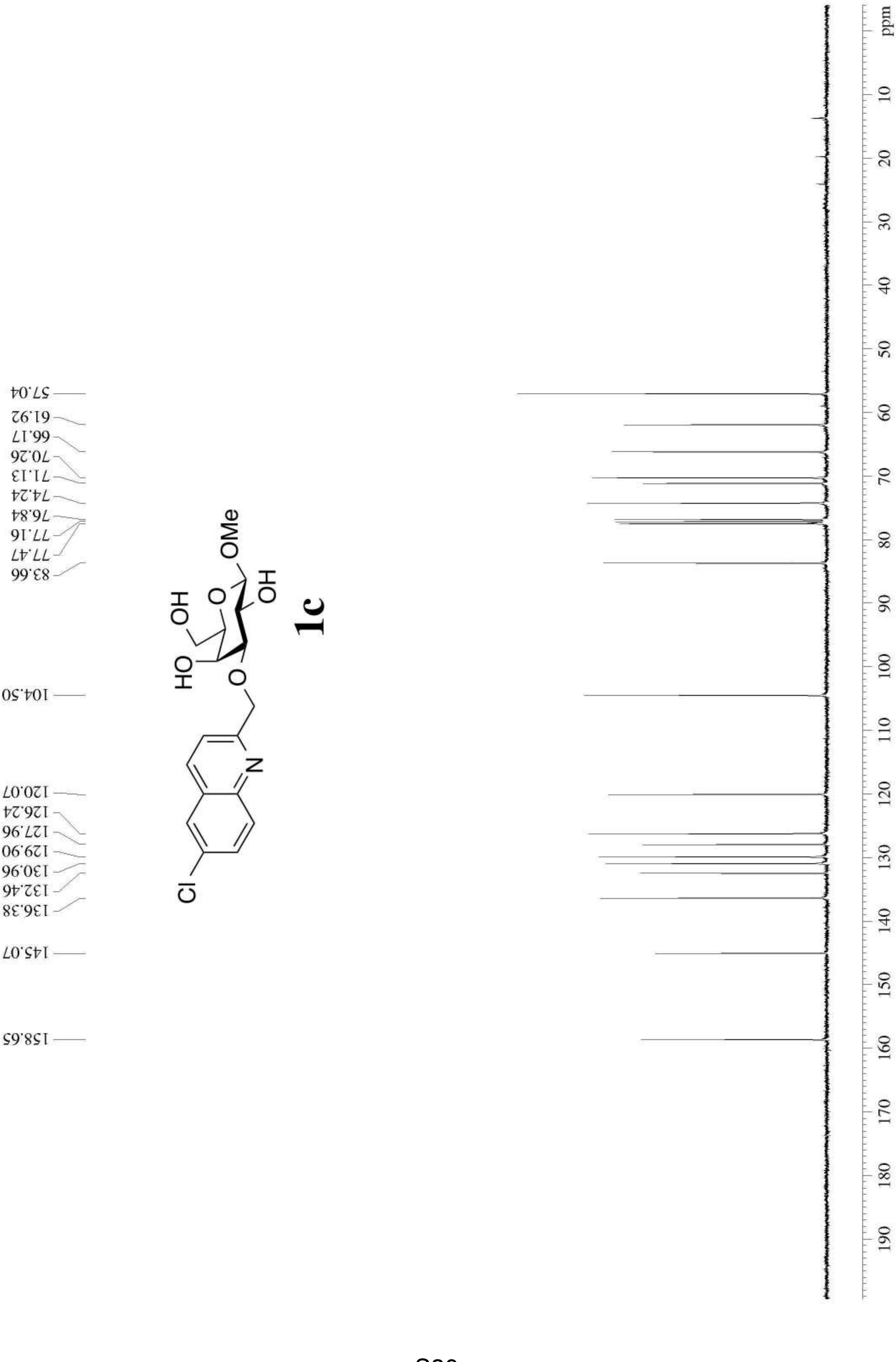
1.00
2.08
ppm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130.96
132.46
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Cl
N
O
HO
OH
OMe
ppm
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100
110
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130
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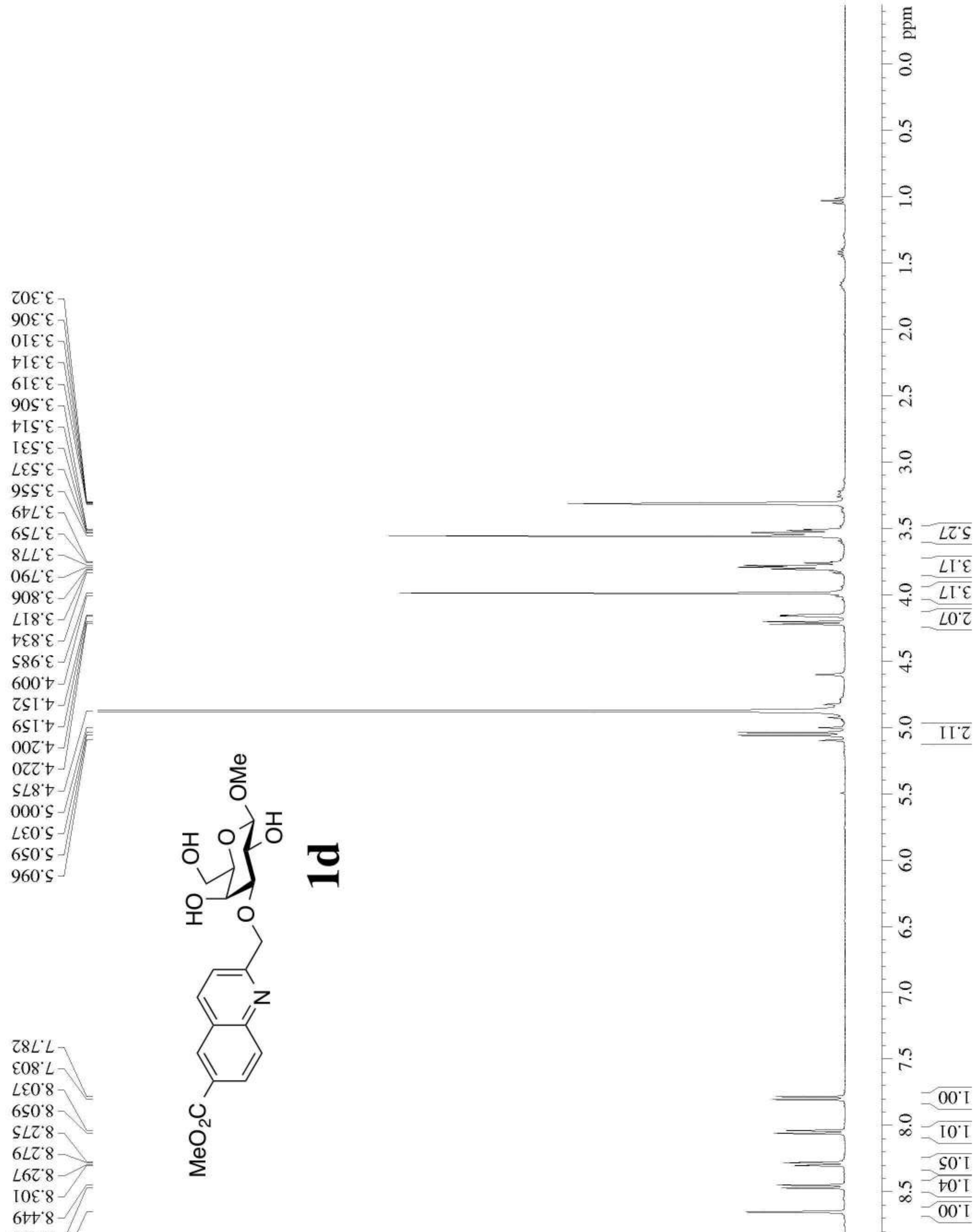
160
170
180
190

1c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3.310
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3.531
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3.759
3.778
3.790
3.806
3.817
3.834
3.985
4.009
4.152
4.159
4.200
4.220
4.875
5.000
5.037
5.059
5.096
7.782
7.803
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8.059
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8.279
8.297
8.301
8.449
8.470
8.652
MeO2C
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O
HO
OH
OMe
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3.17
2.07
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1.04
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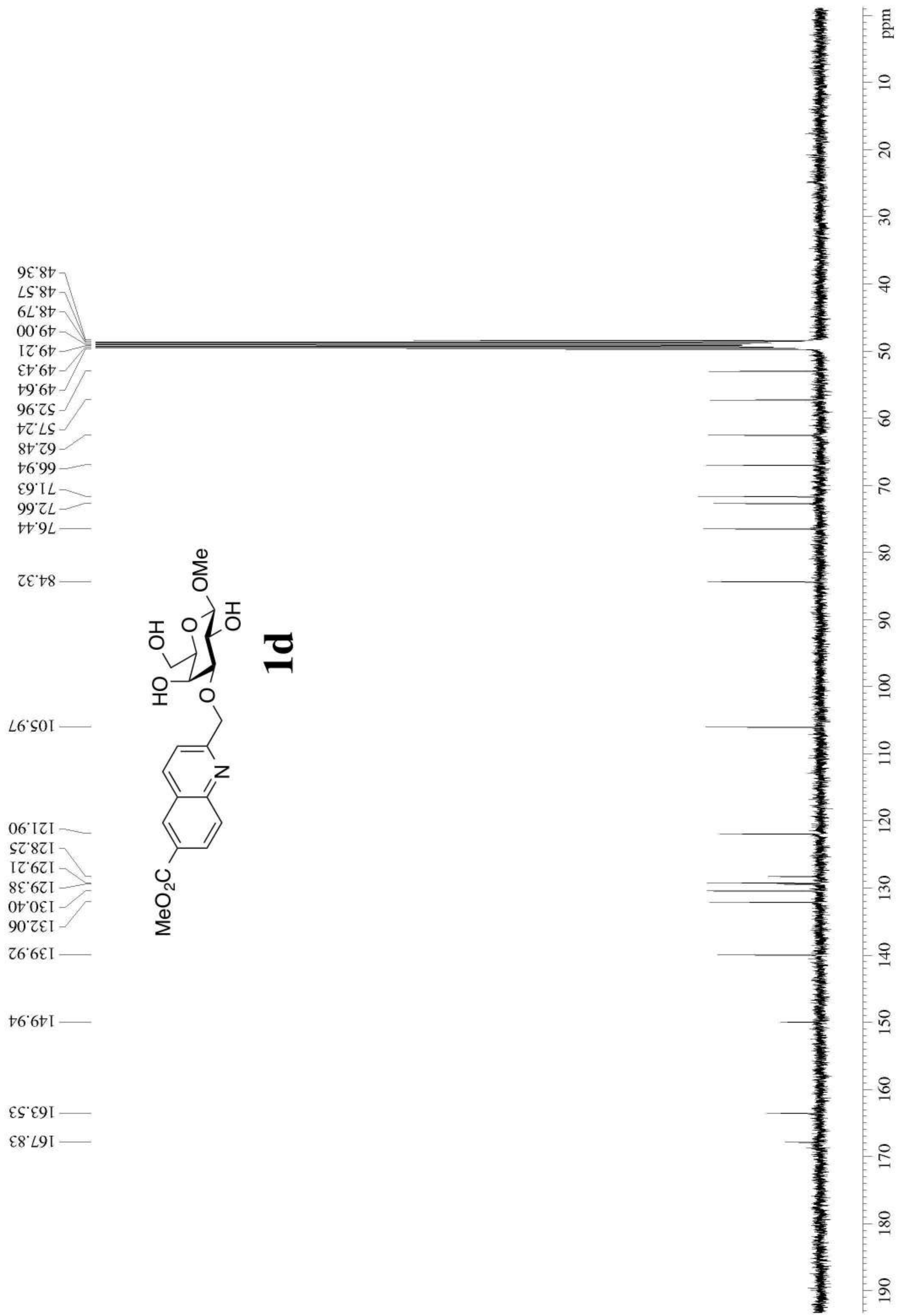
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72.66
76.44
84.32
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128.25
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129.38
130.40
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163.53
167.83
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O
OH
OMe
O
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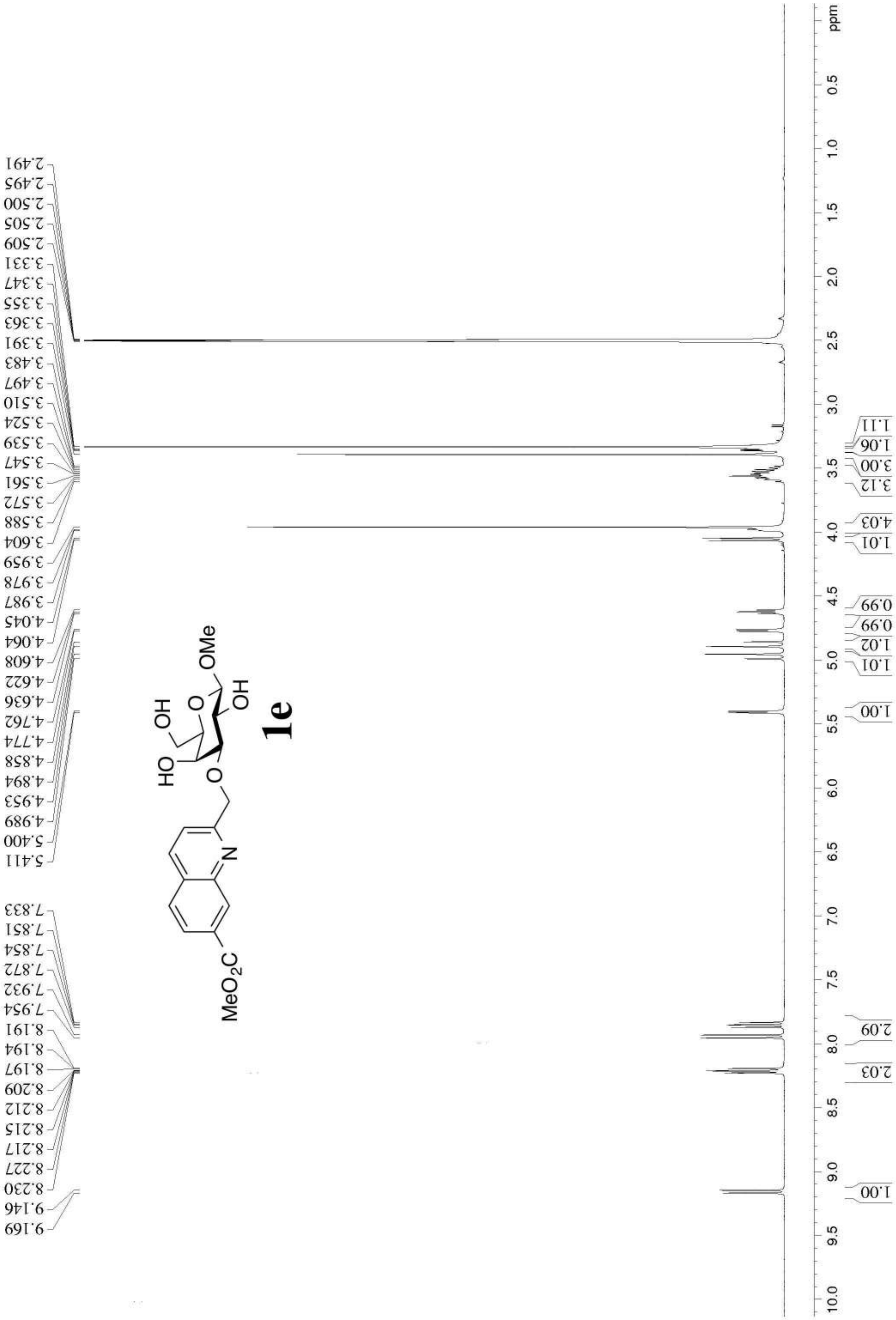
MeO_2C
1d
ppm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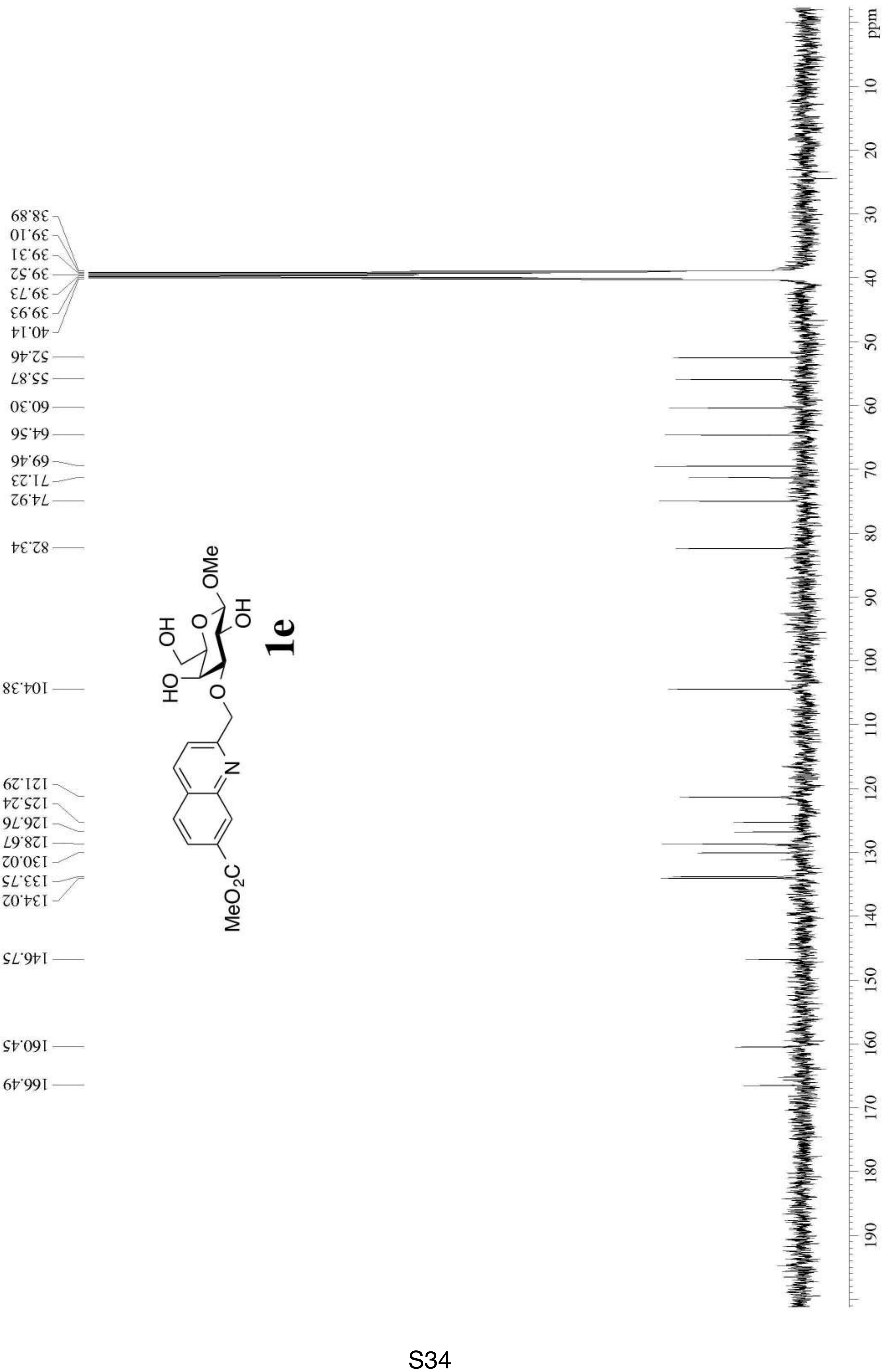

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HO
OH
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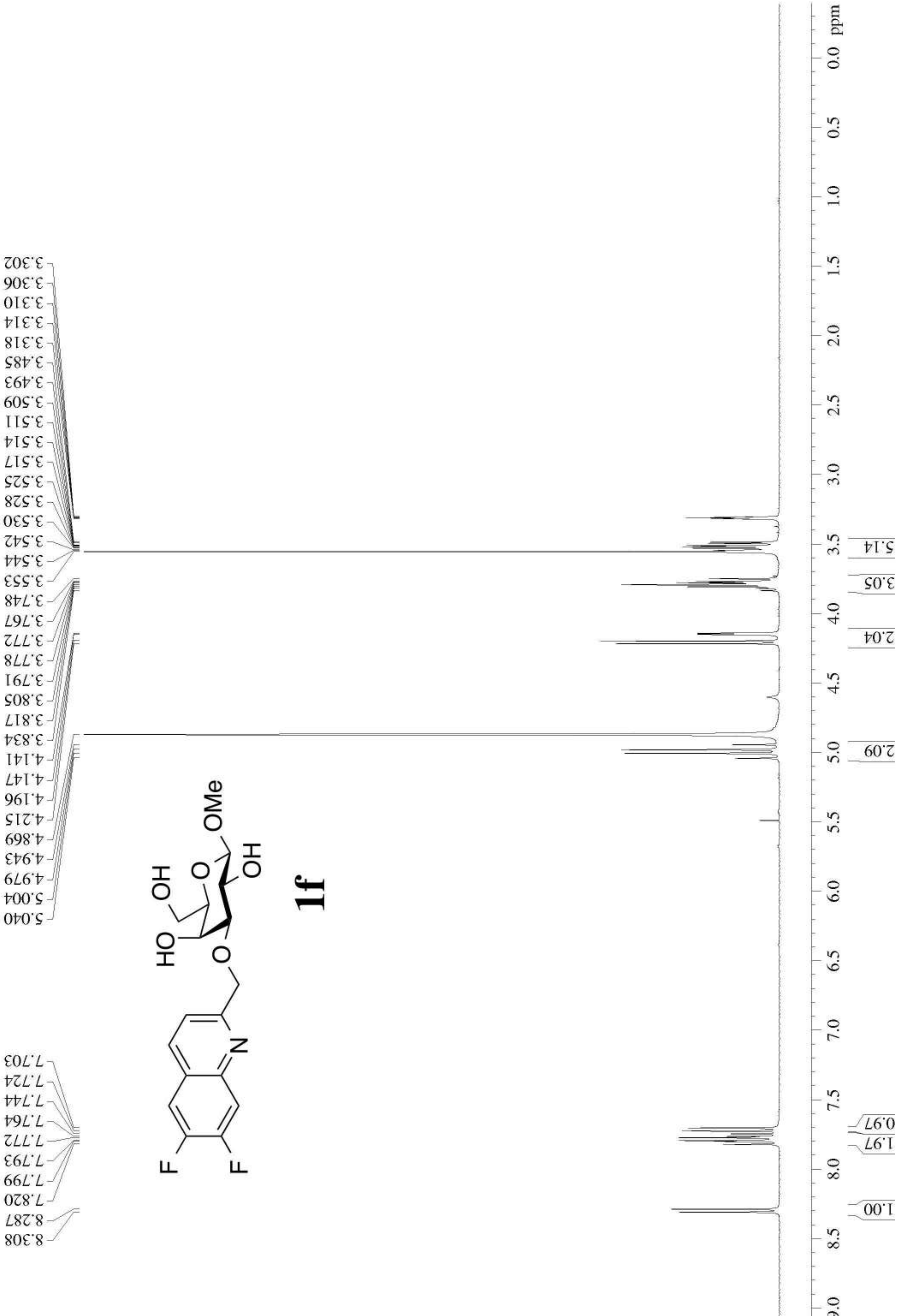
OH
OMe
1e
ppm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F
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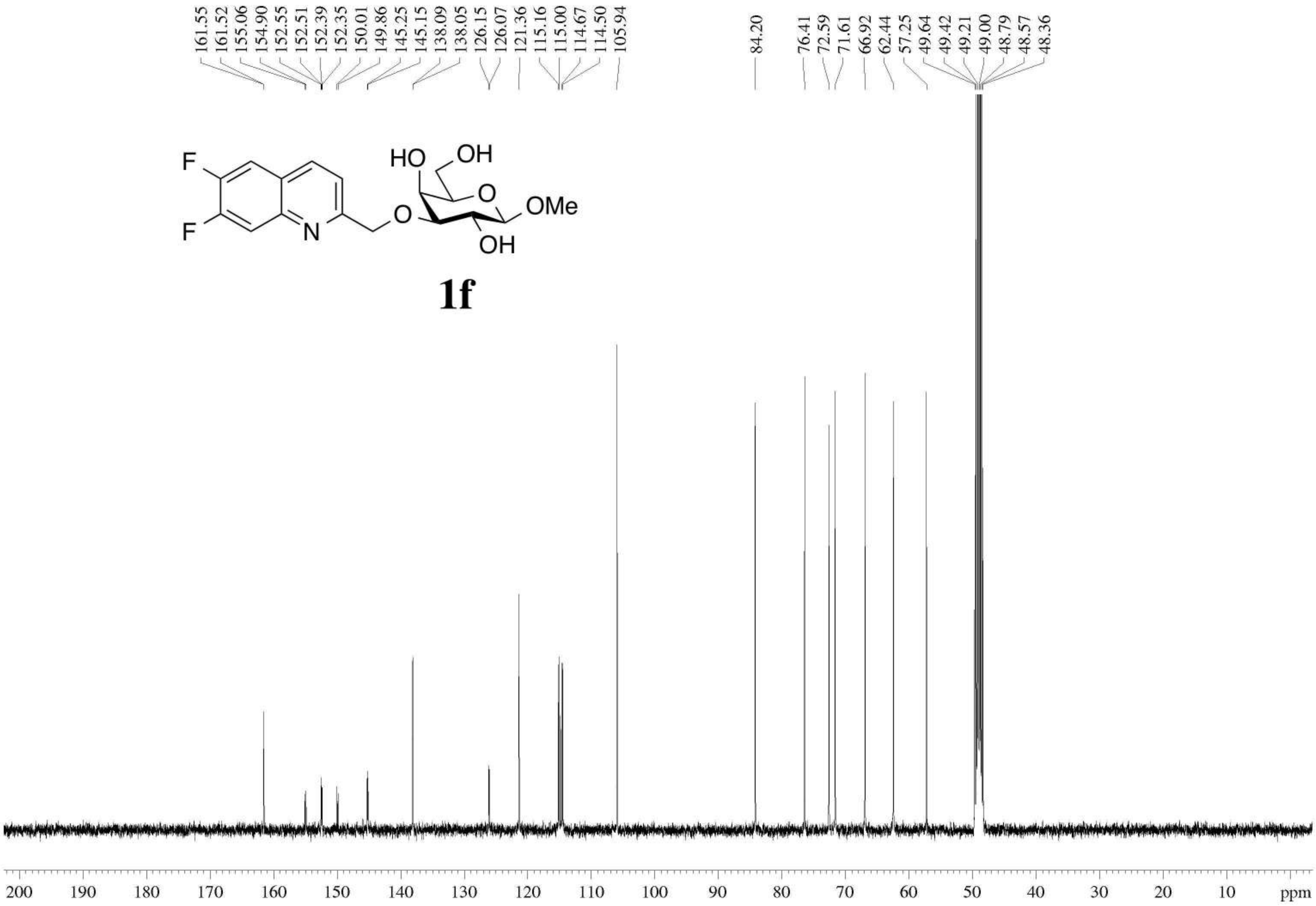
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126.07
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72.59
71.61
66.92
62.44
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49.21
49.00
48.79
48.57
48.36
F
F
N
O
HO
OH
O
OMe
OH
1f
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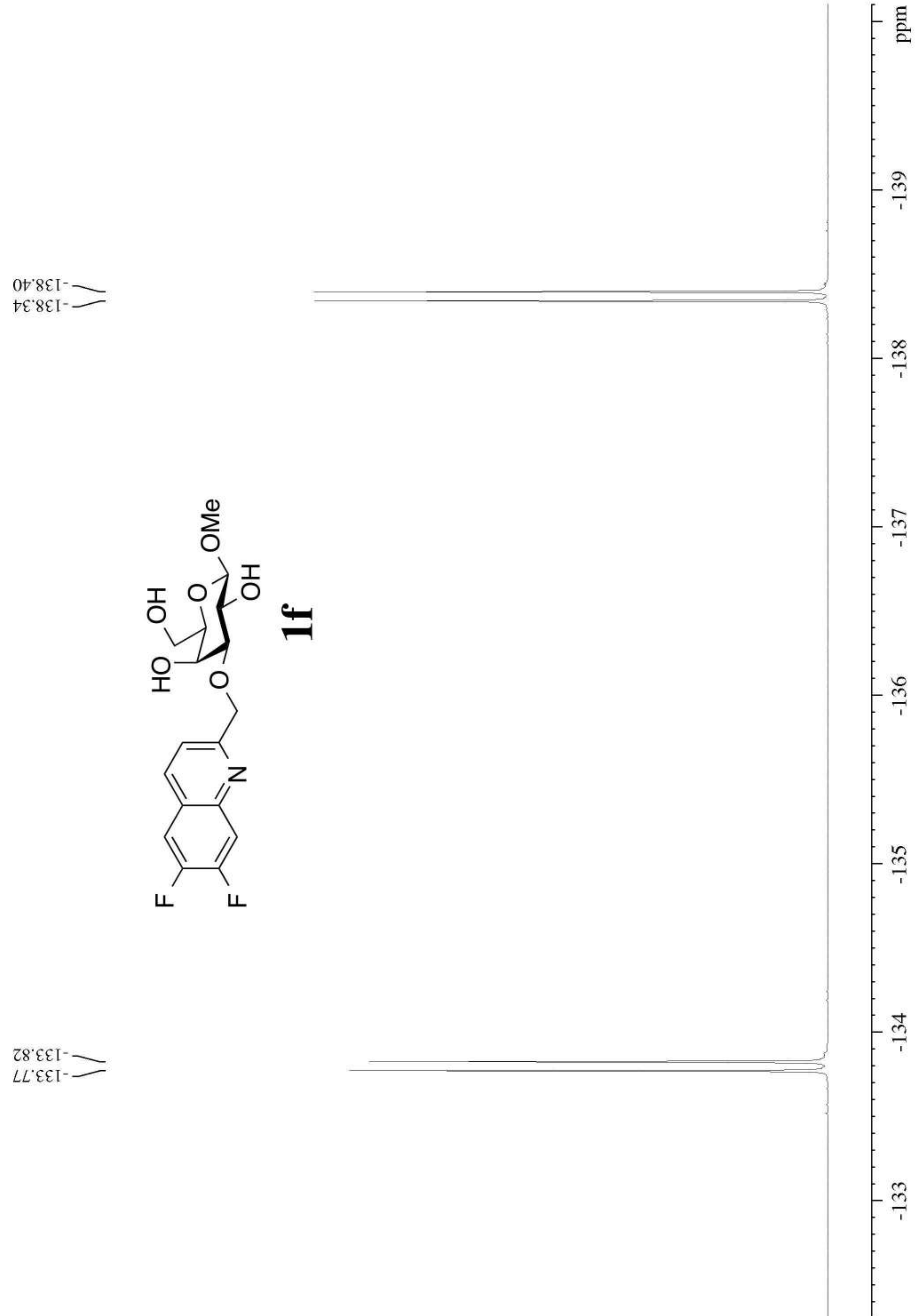
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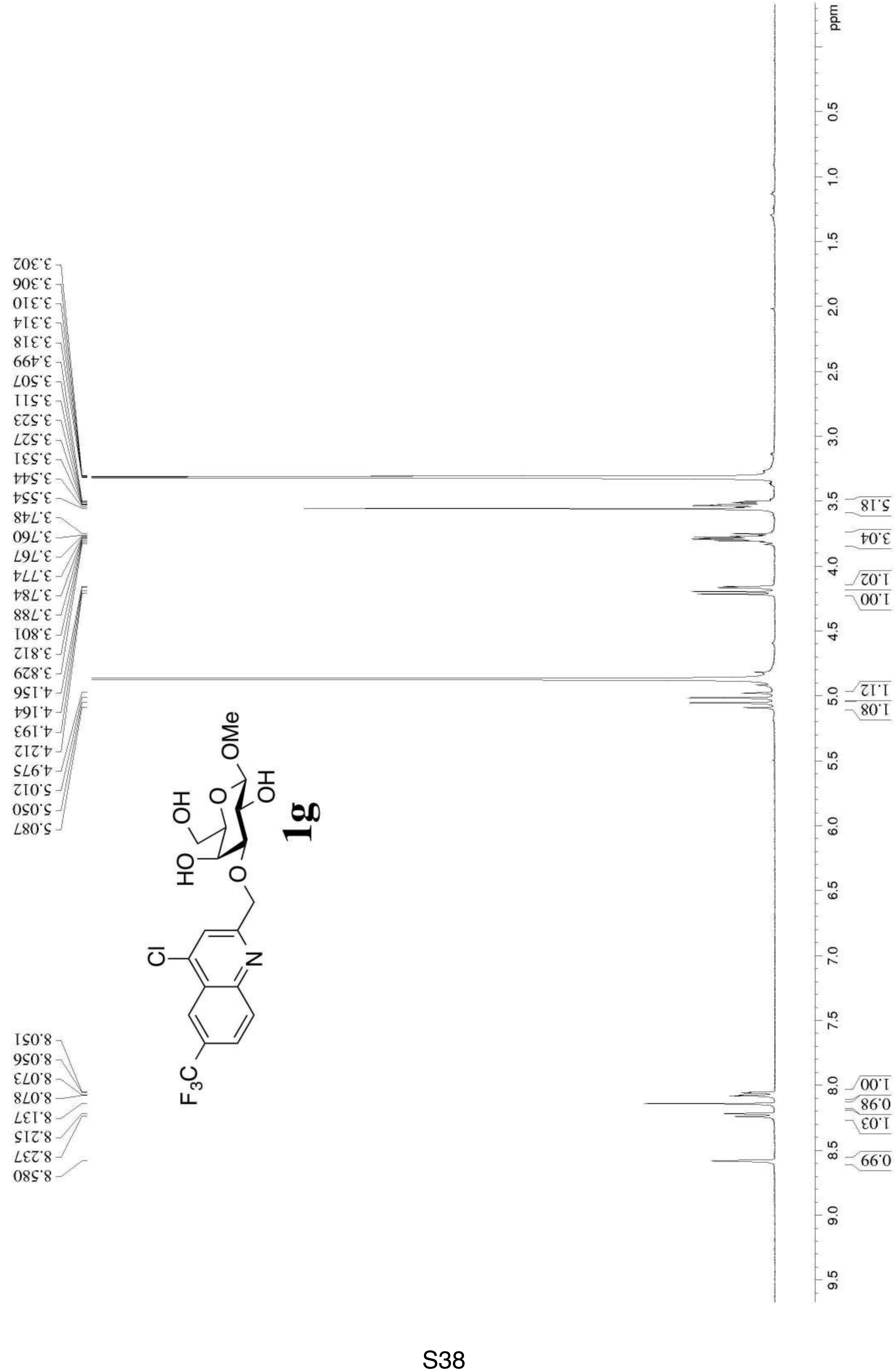
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5.087
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Cl
F3C
N
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HO
OH
O
OMe
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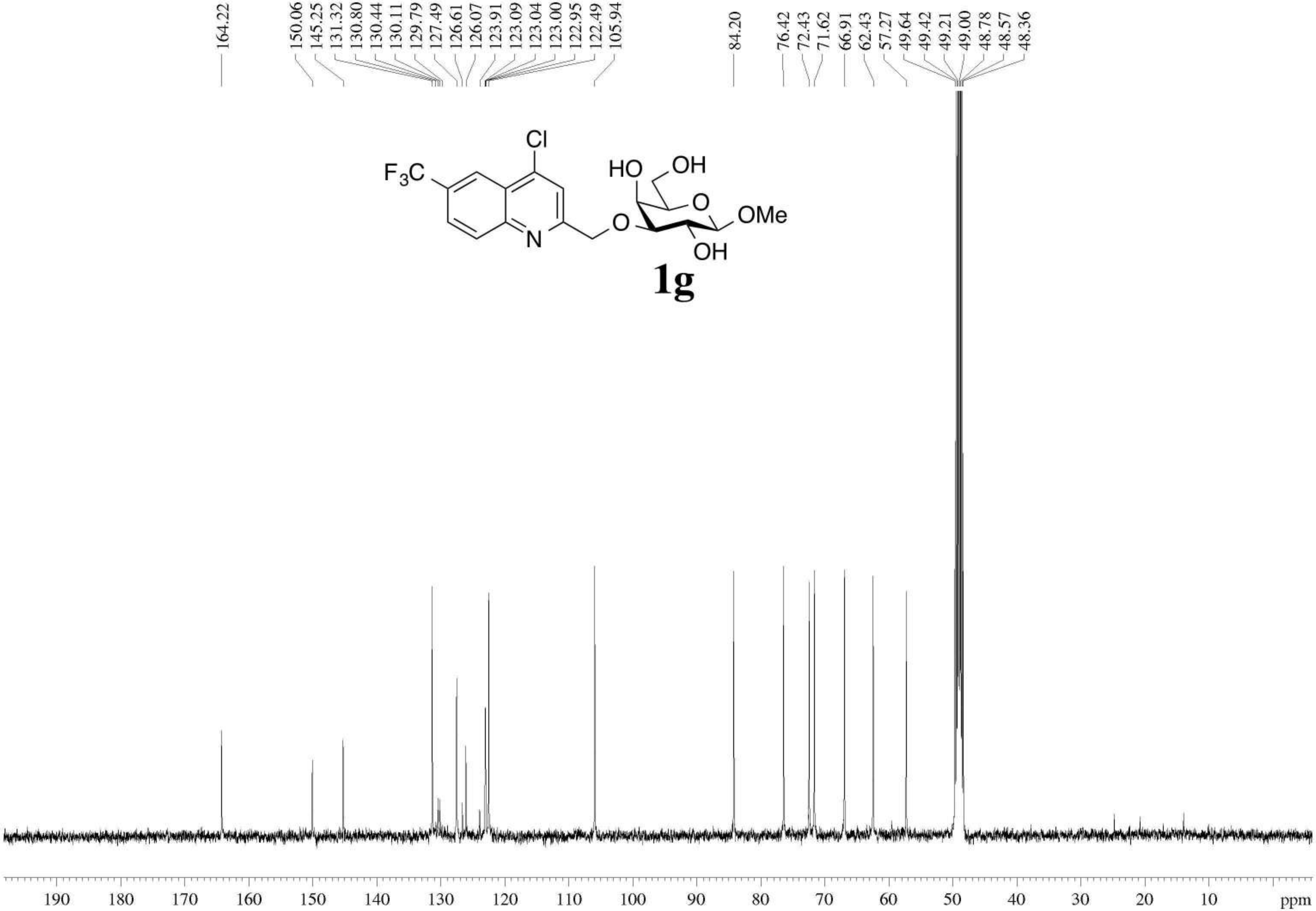
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49.21
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N
O
HO
OH
O
OMe
OH
1g
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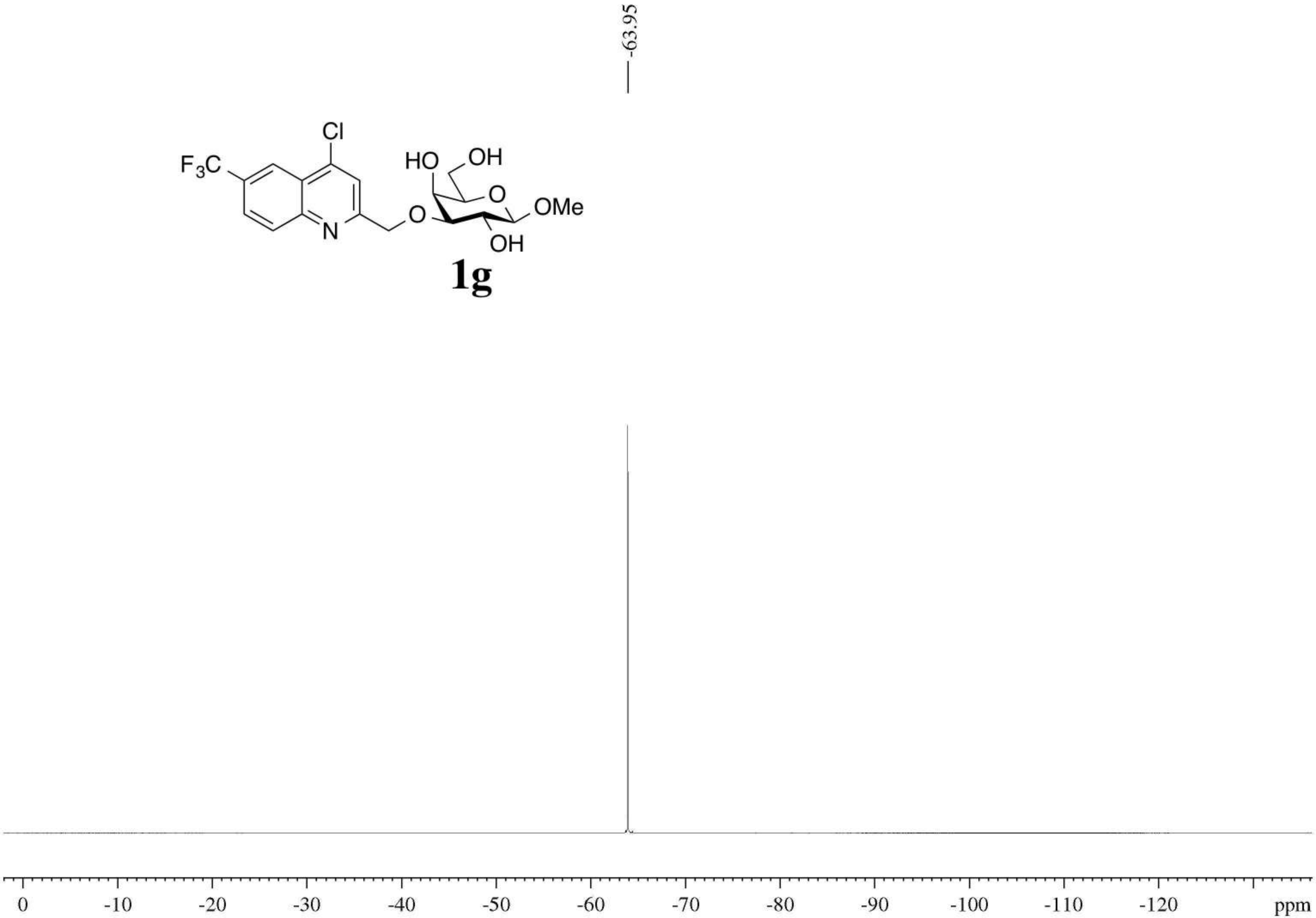

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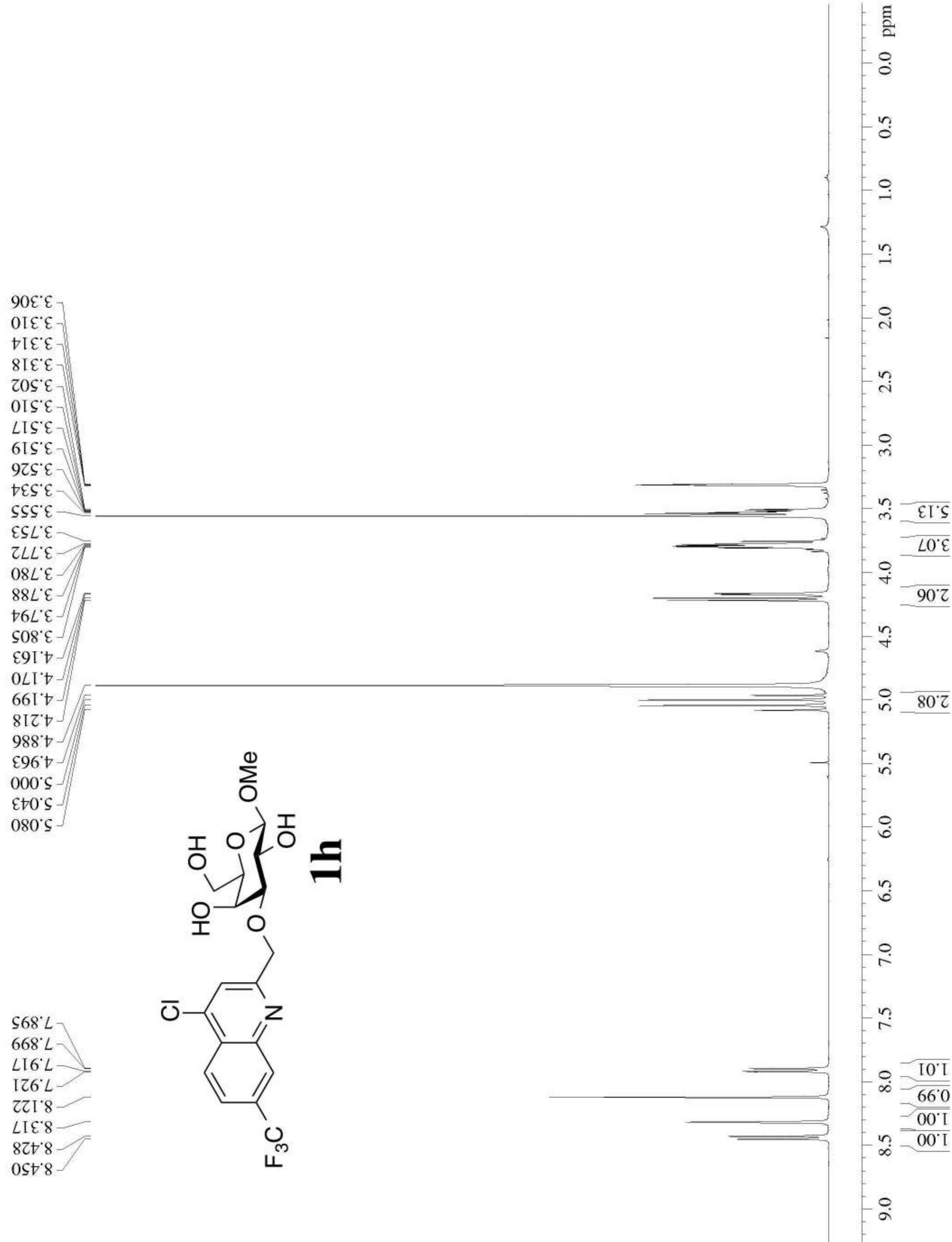
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4.963
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5.080
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Cl
N
F3C
O
HO
OH
O
OMe
OH
1h
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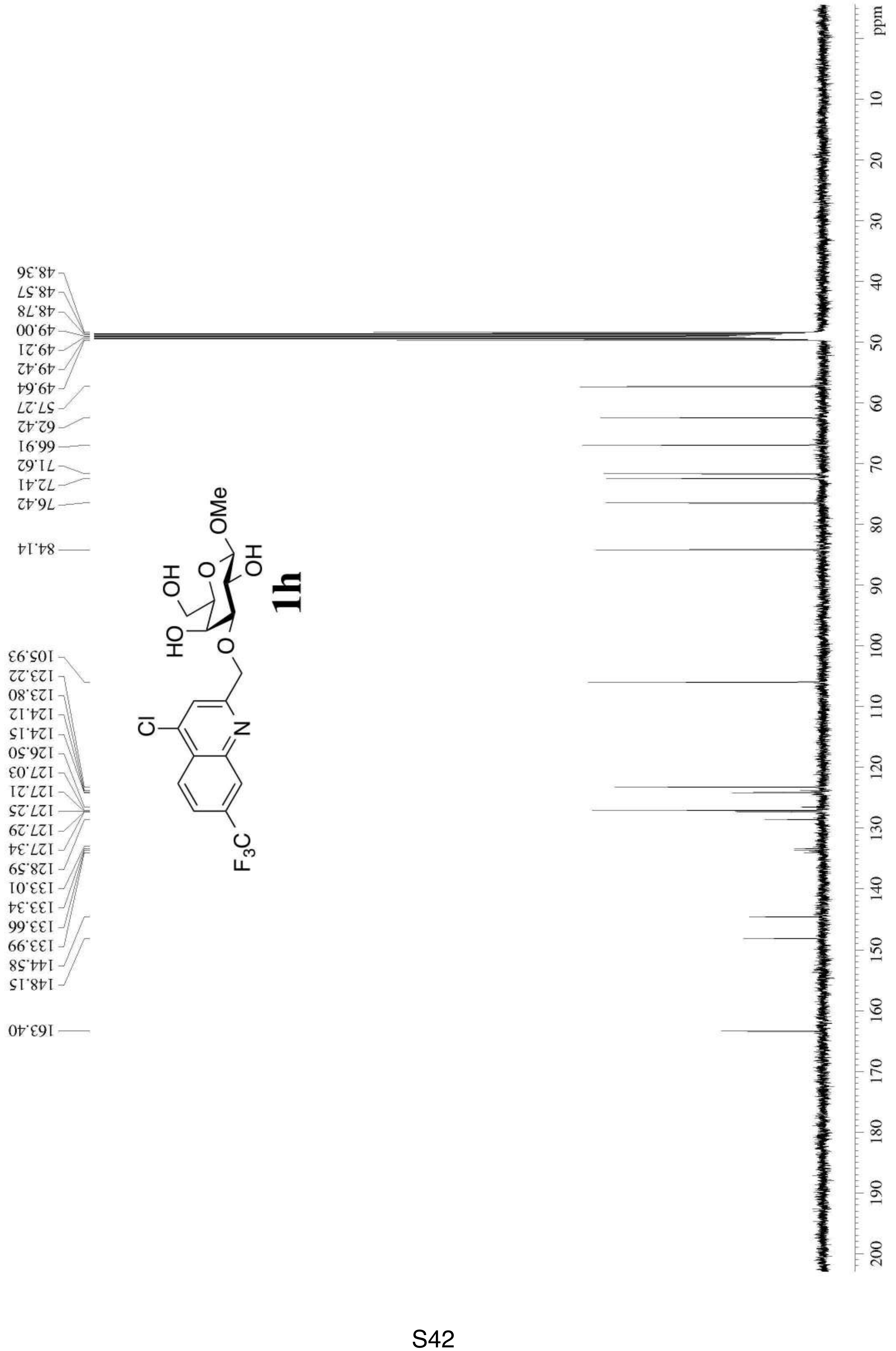
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OH
O
Cl
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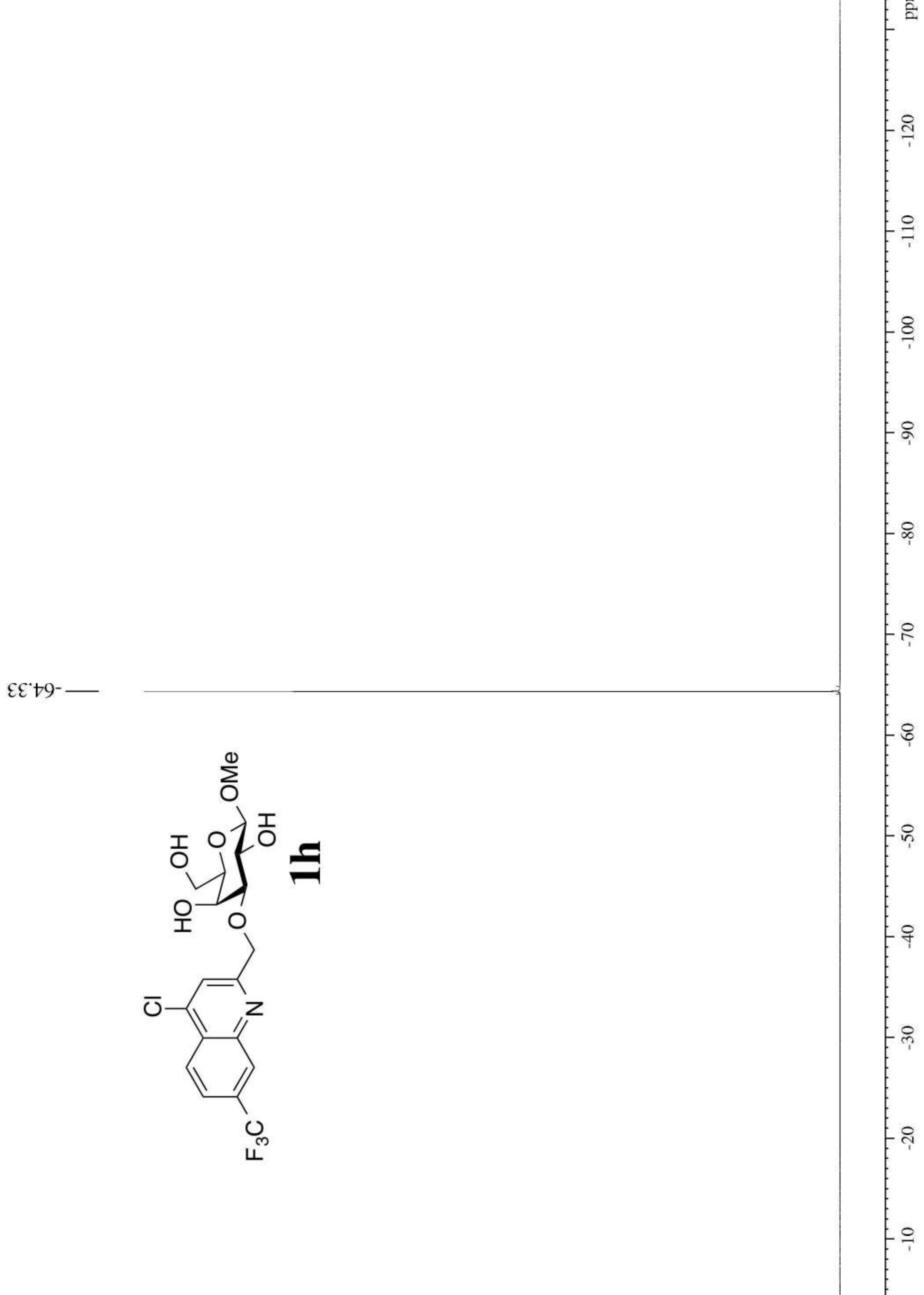
F_3C
1h
ppm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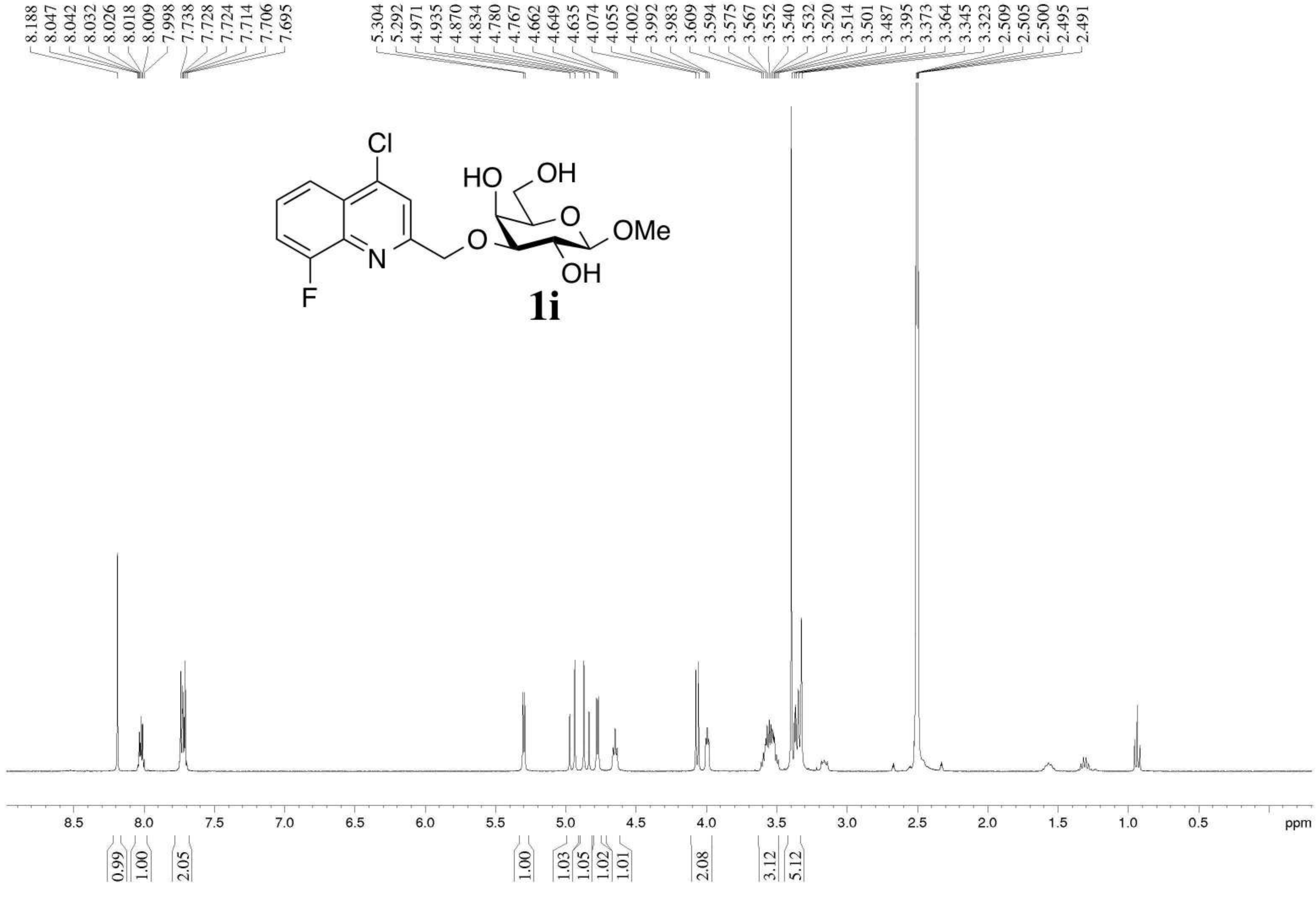
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3.487
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2.505
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Cl
HO
OH
O
OMe
N
OH
F
1i
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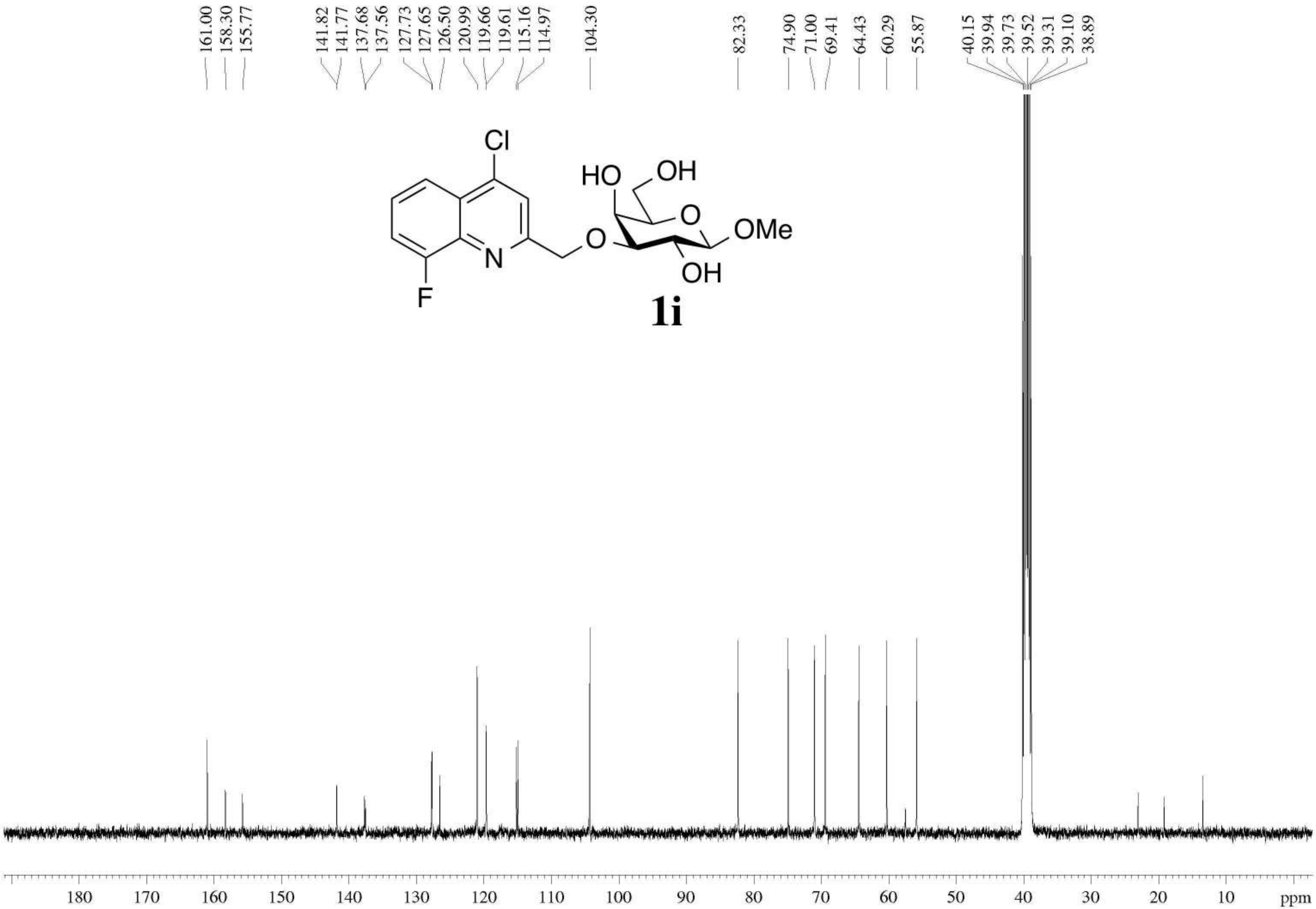
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82.33
74.90
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69.41
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39.94
39.73
39.52
39.31
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O
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N
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OH
F
1i
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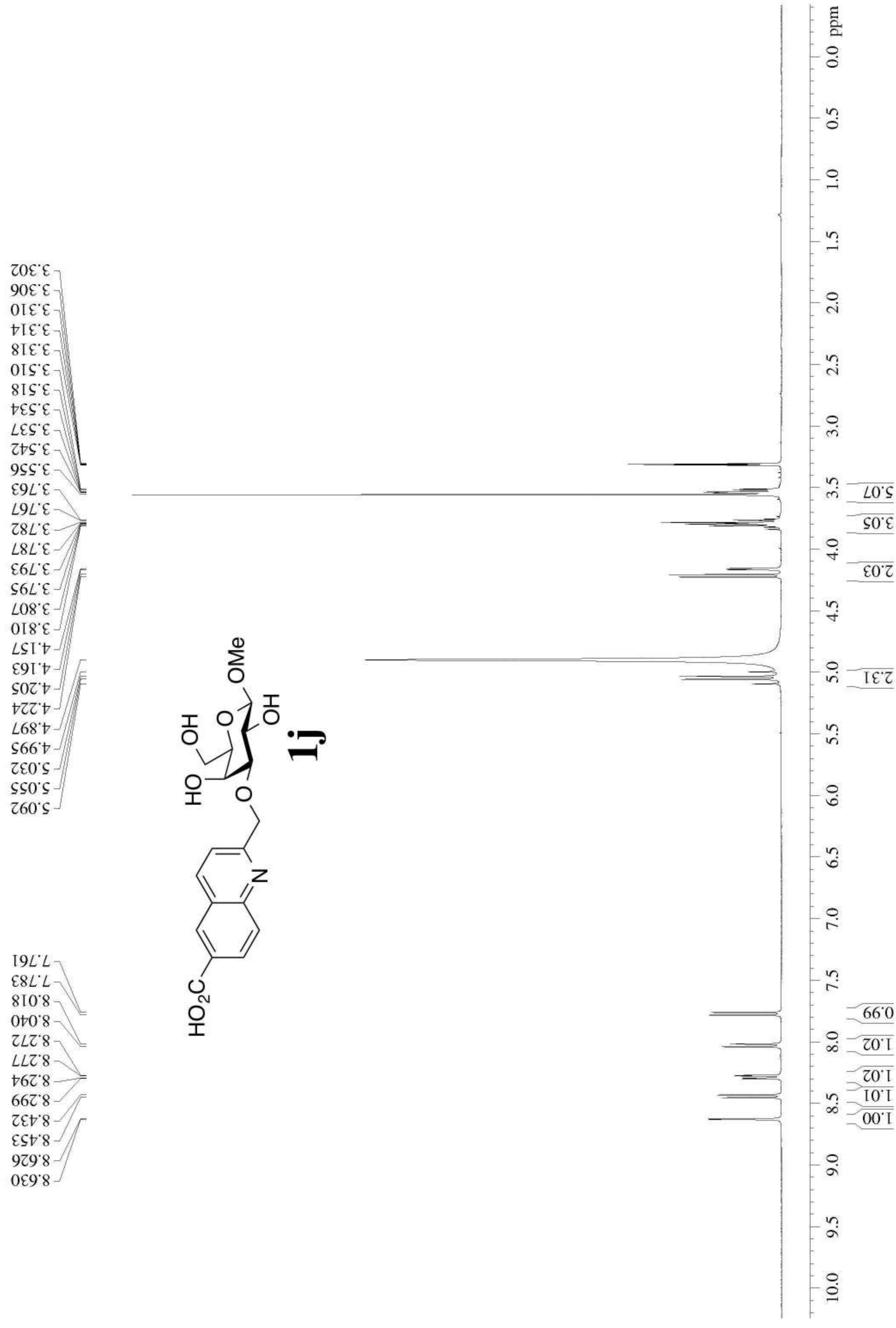
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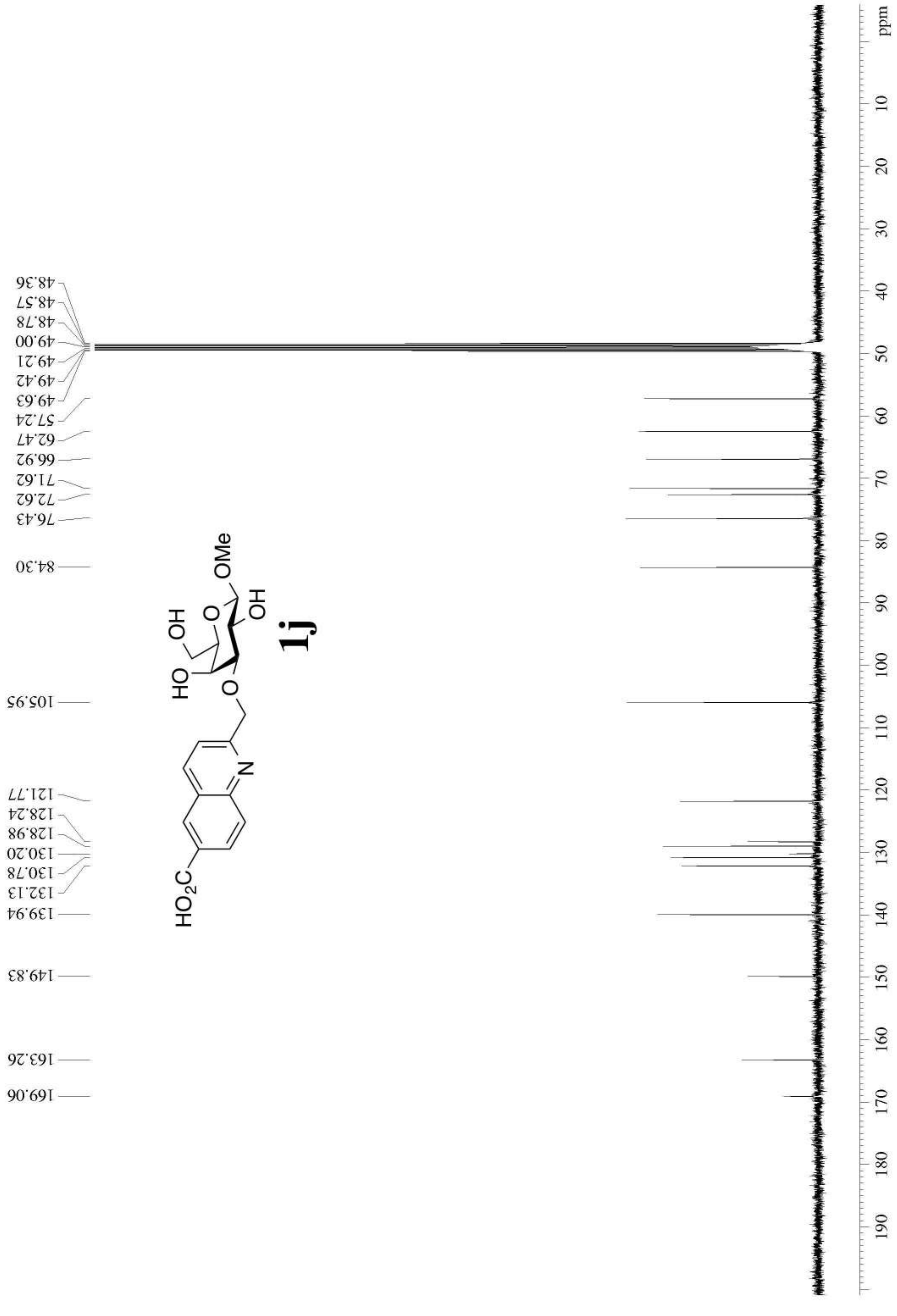
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121.77
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128.98
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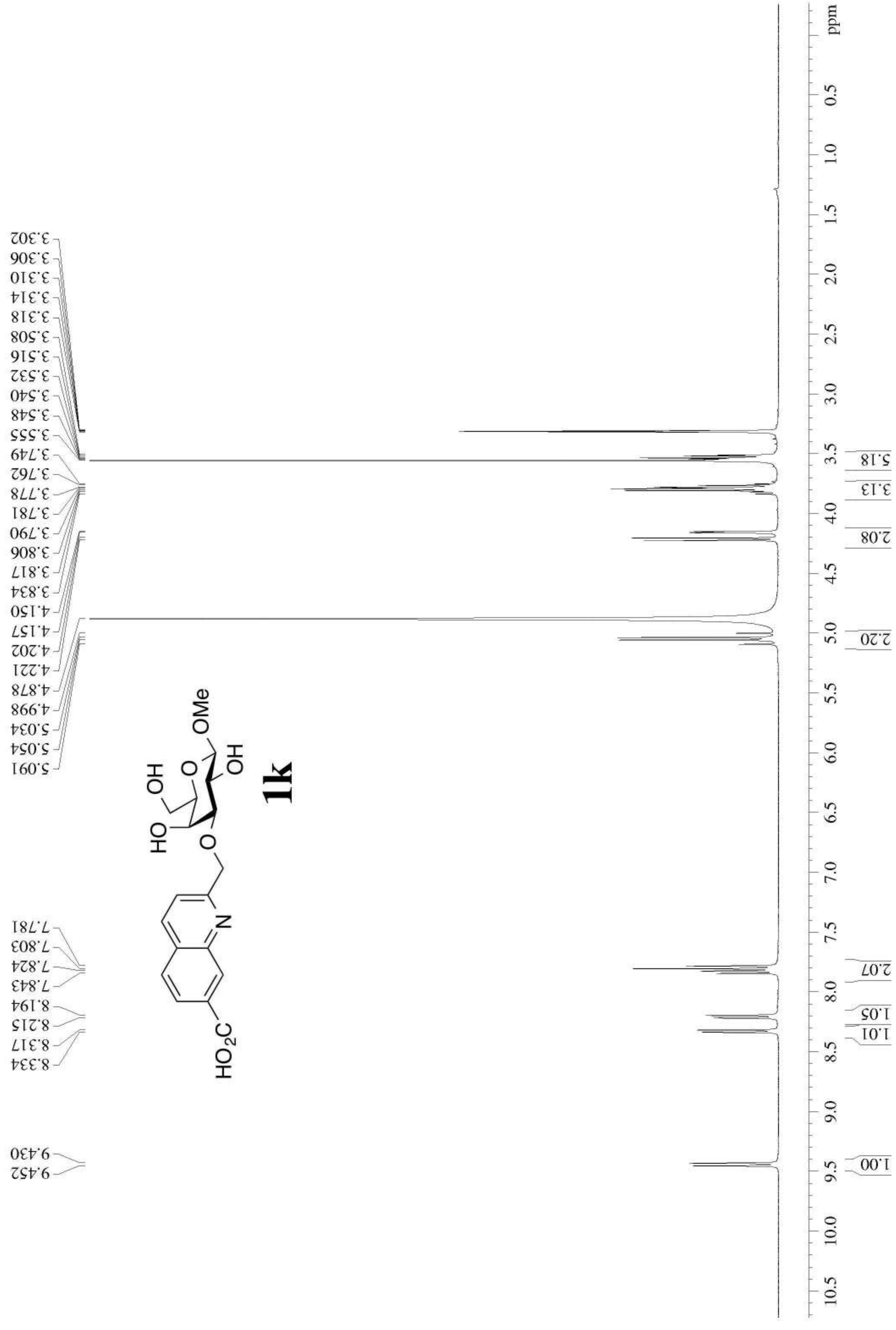
N
HO2C
1j
ppm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HO2C
N
O
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OH
O
OMe
OH
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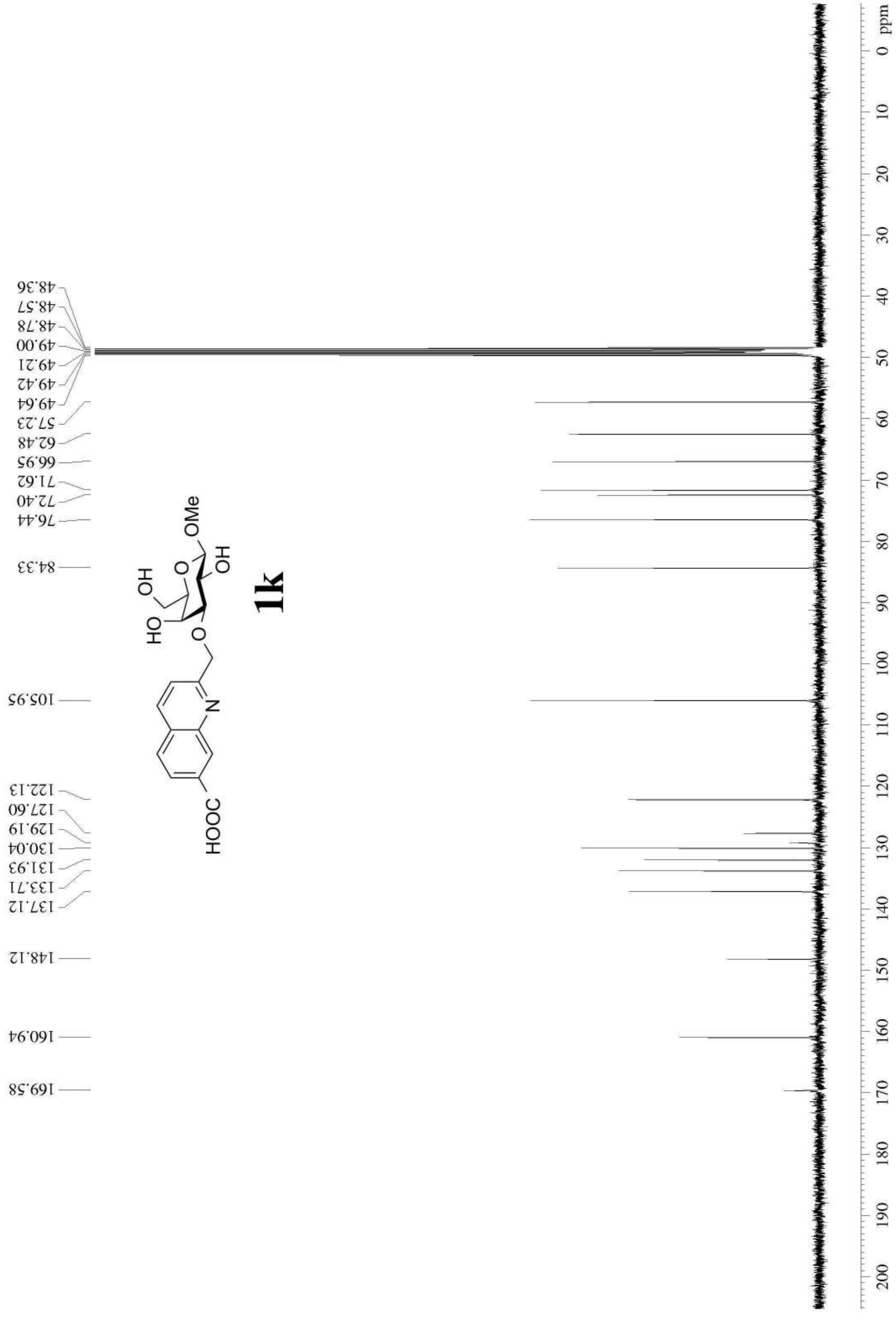
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129.19
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148.12
160.94
169.58
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O
N
HOOC
1k
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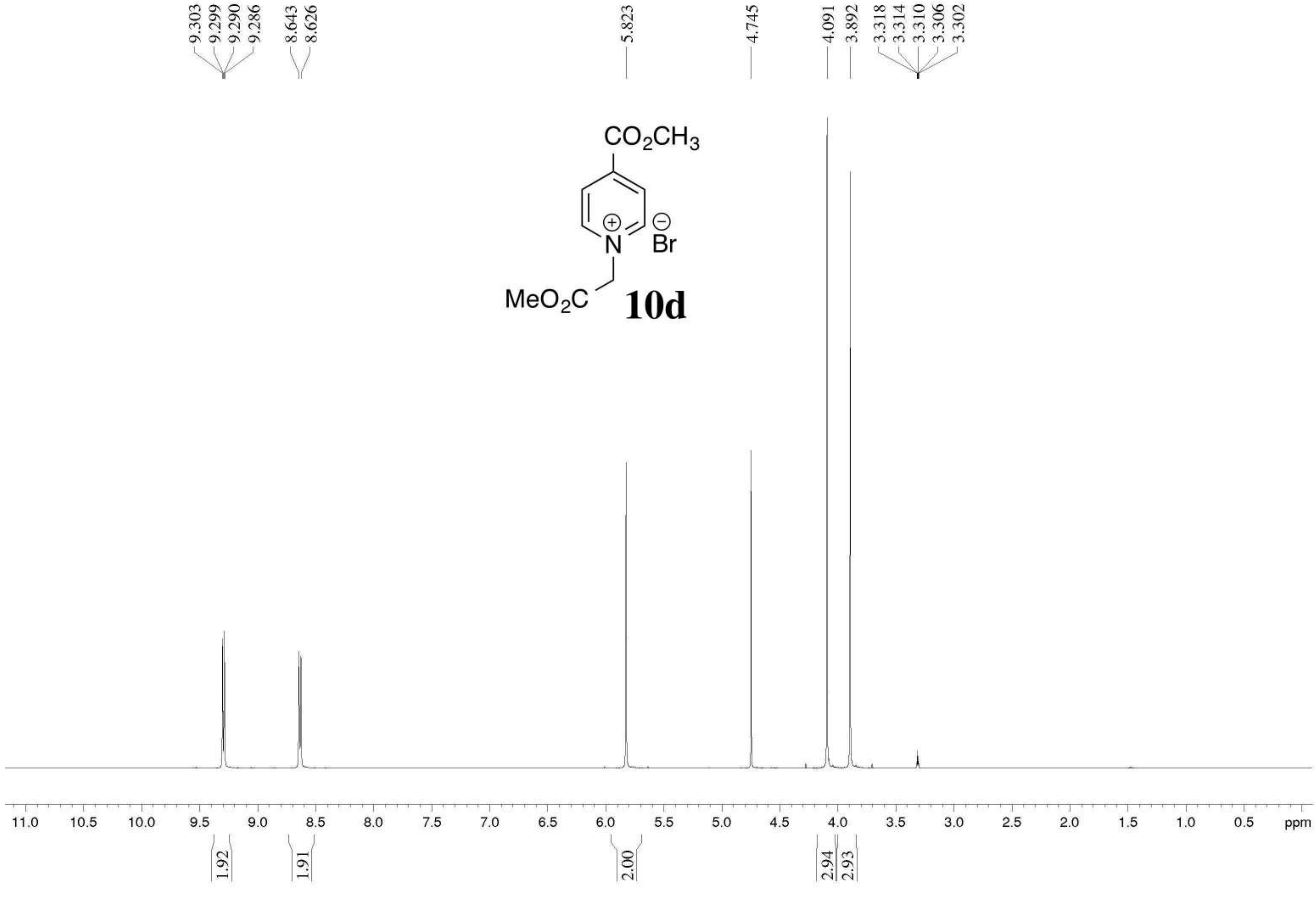
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3.306
3.302
CO2CH3
Br
MeO2C
10d
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10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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4.0
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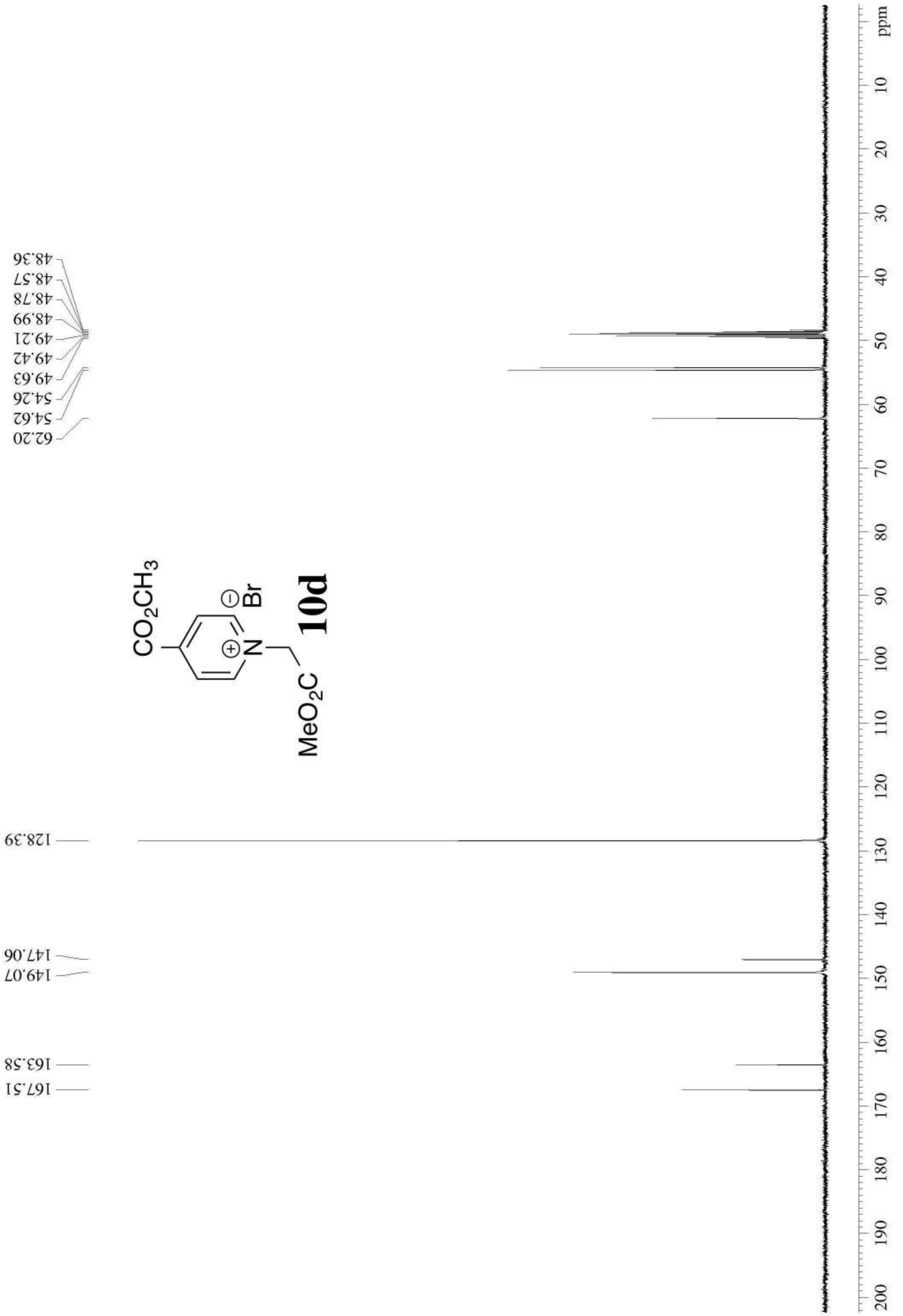
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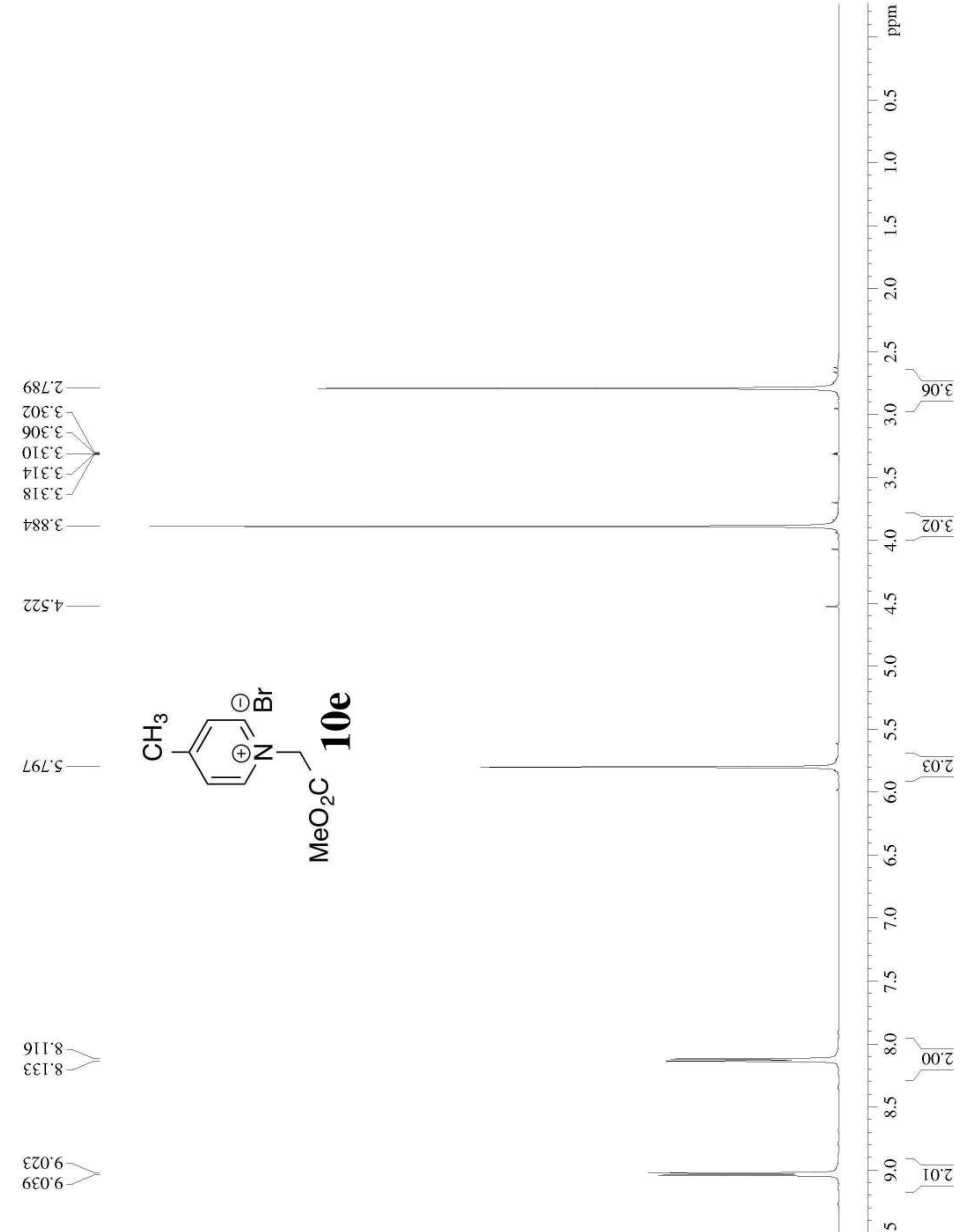
MeO_2C
10d
ppm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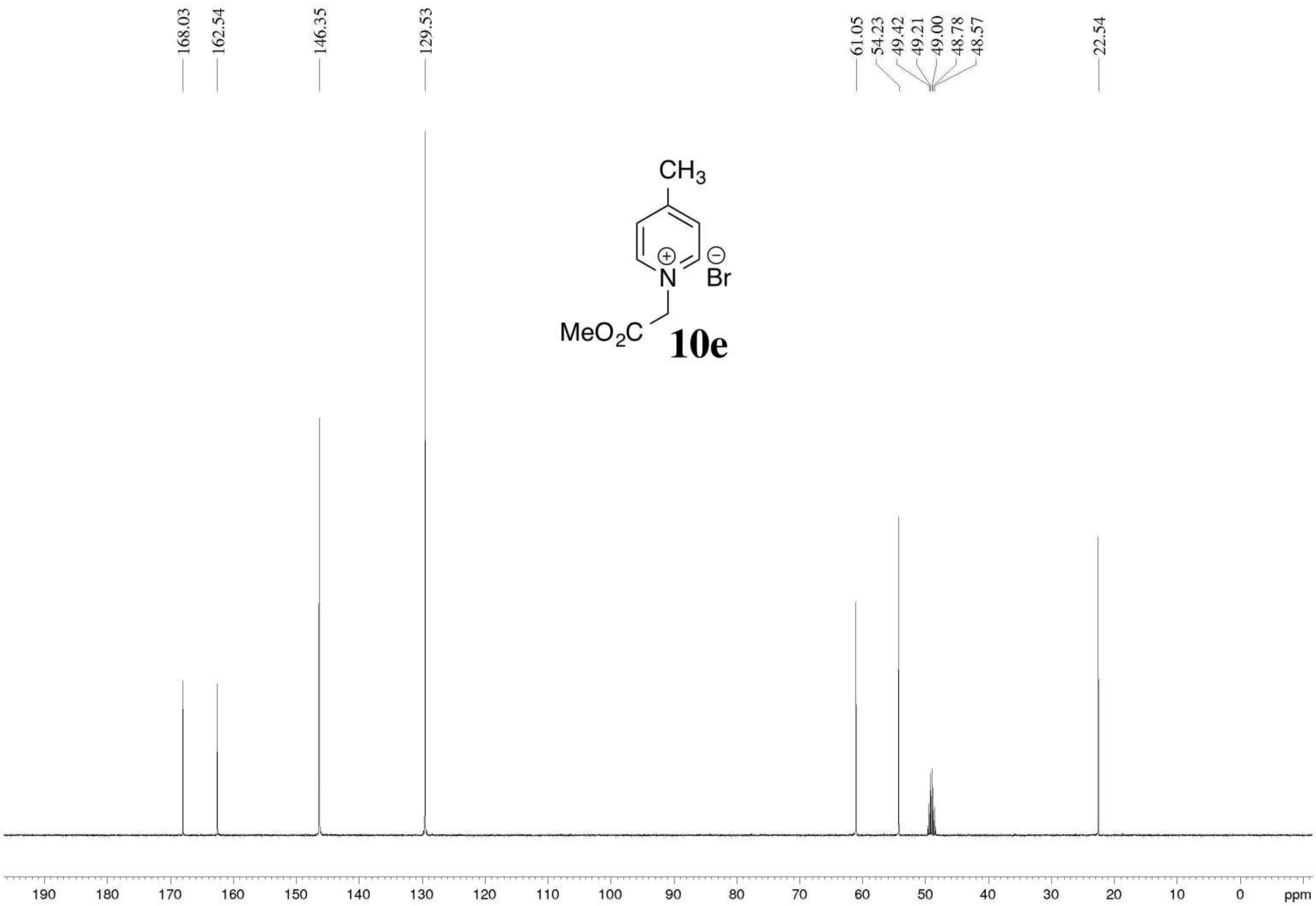
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N
Br
MeO2C
10e
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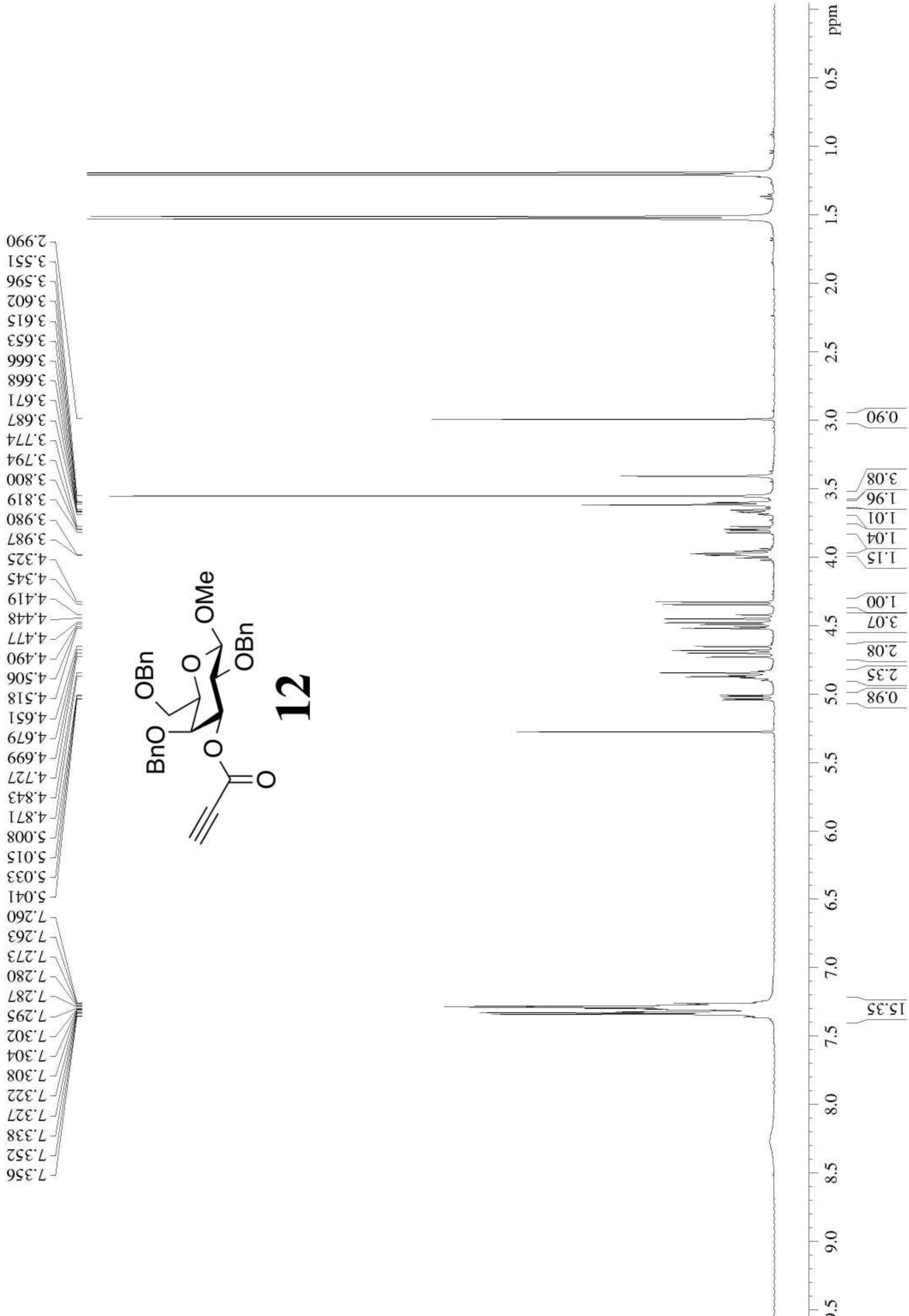
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7.356
BnO
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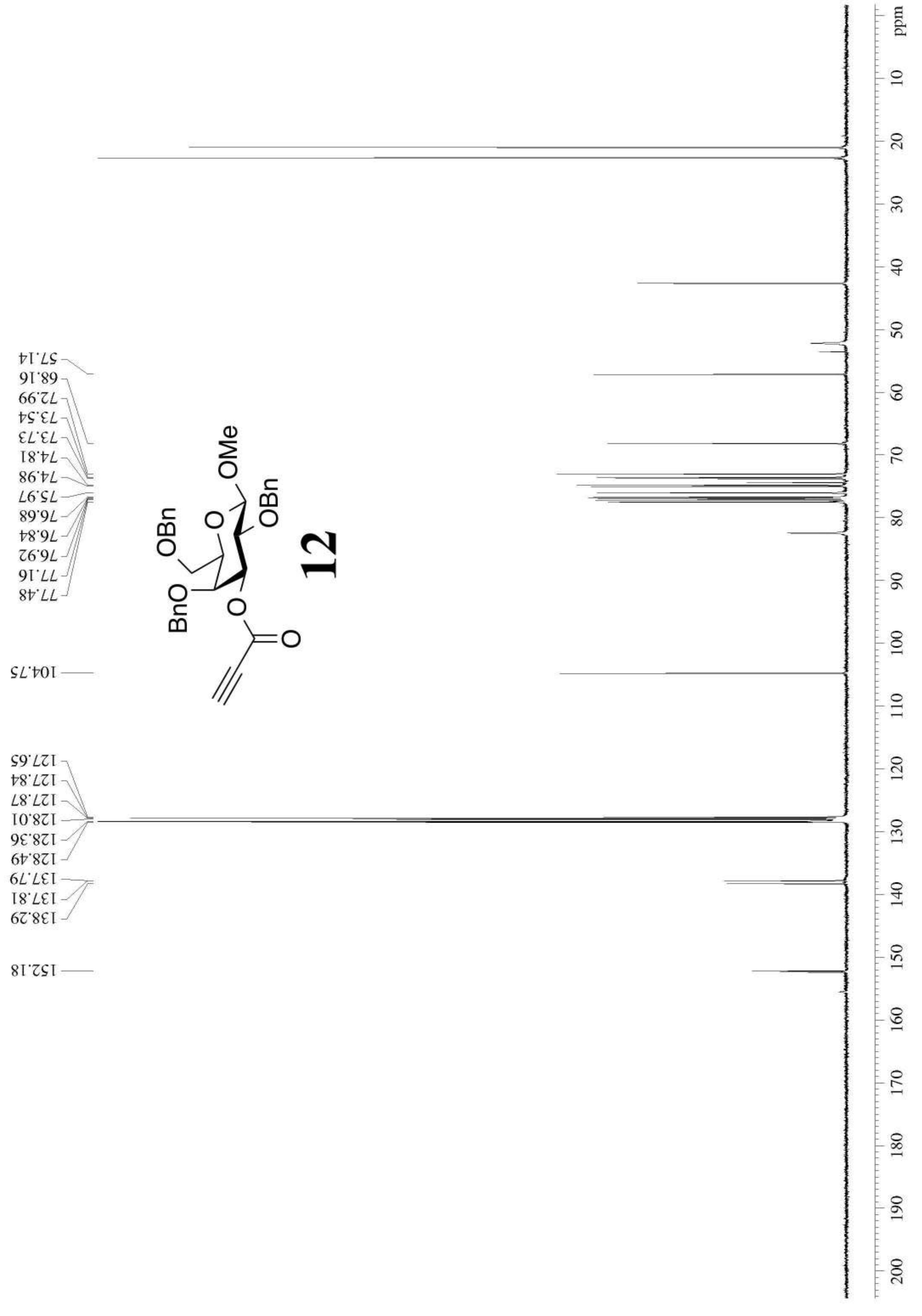
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OBn
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OMe
OBn
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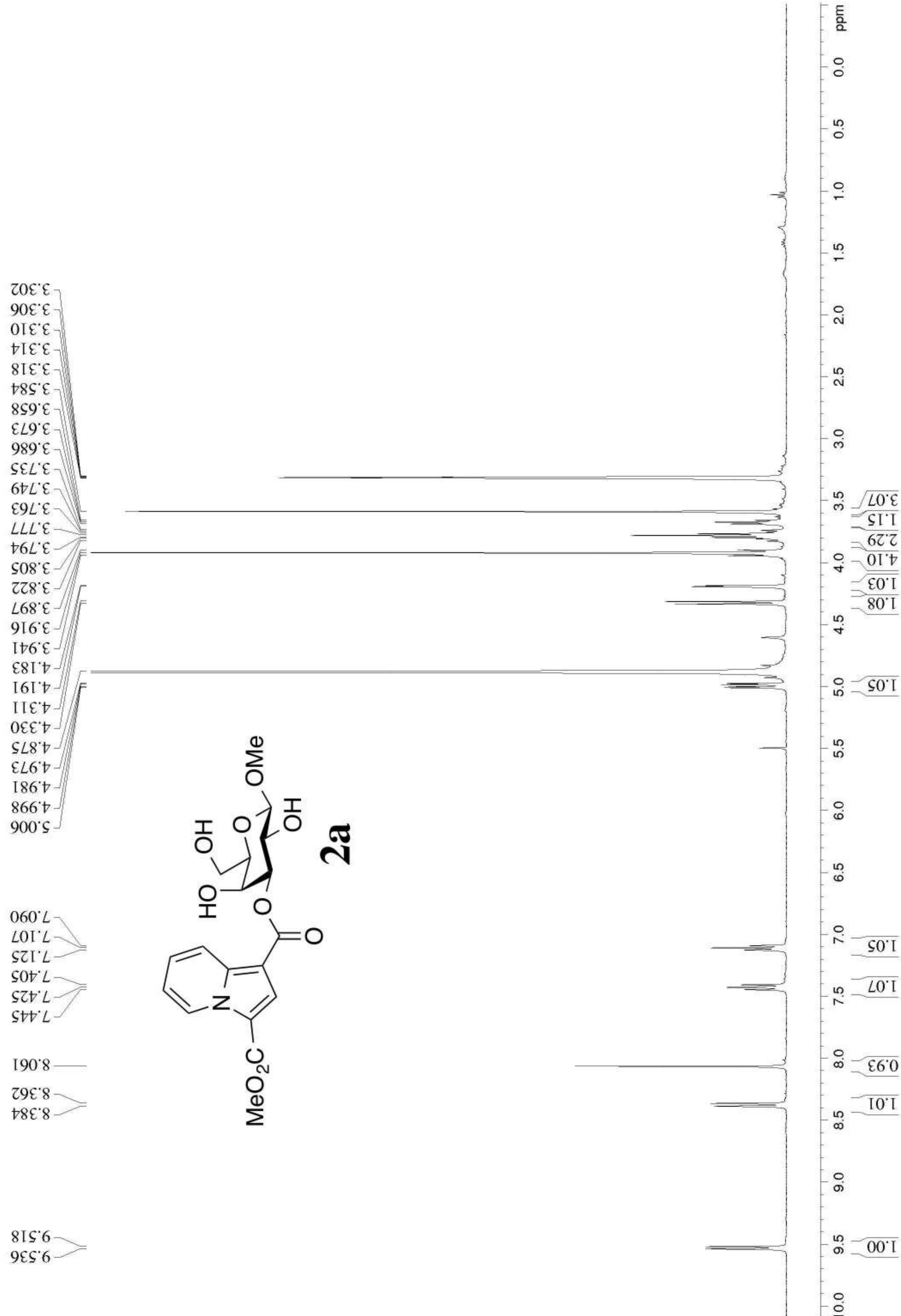
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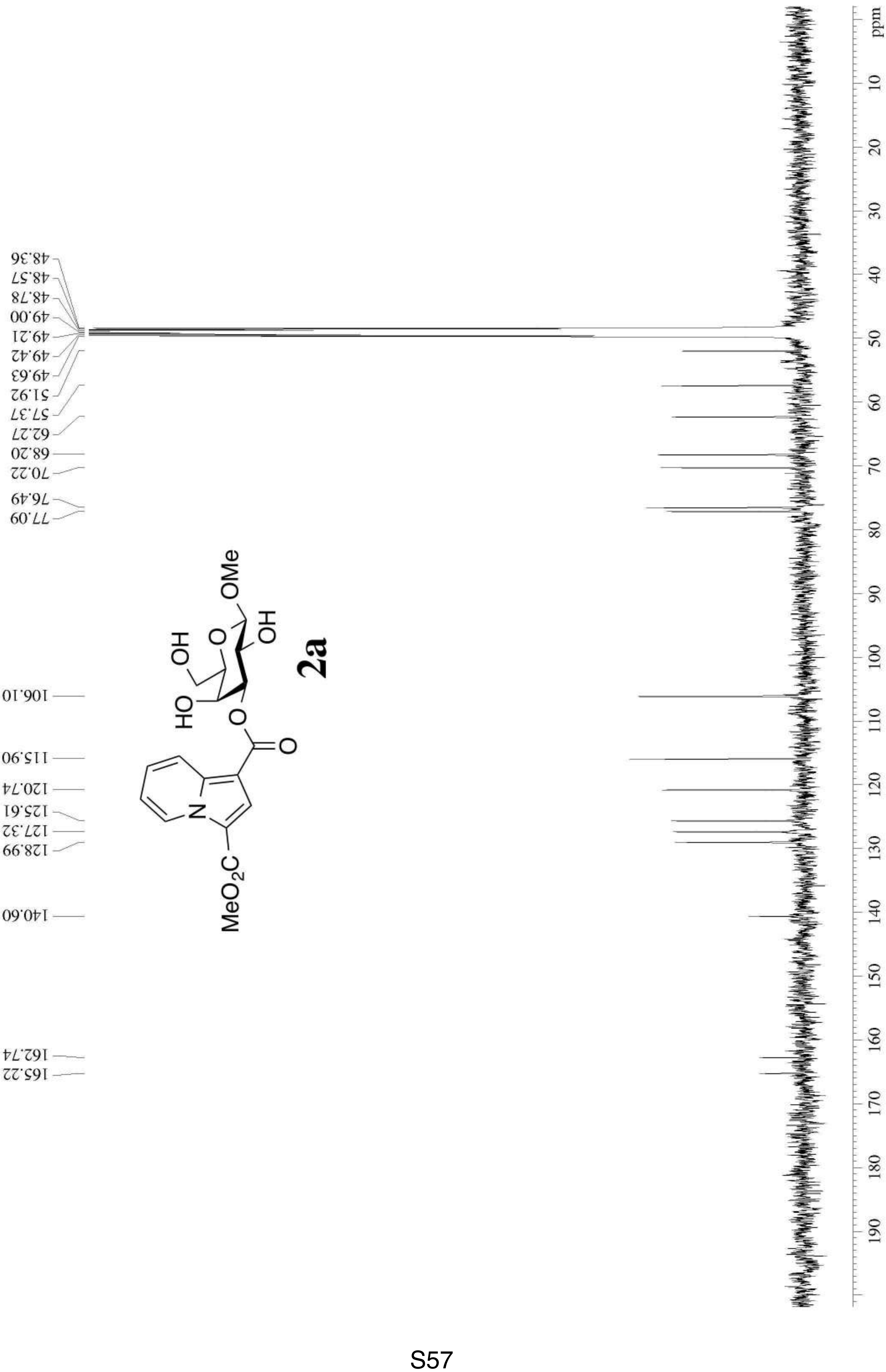
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2a
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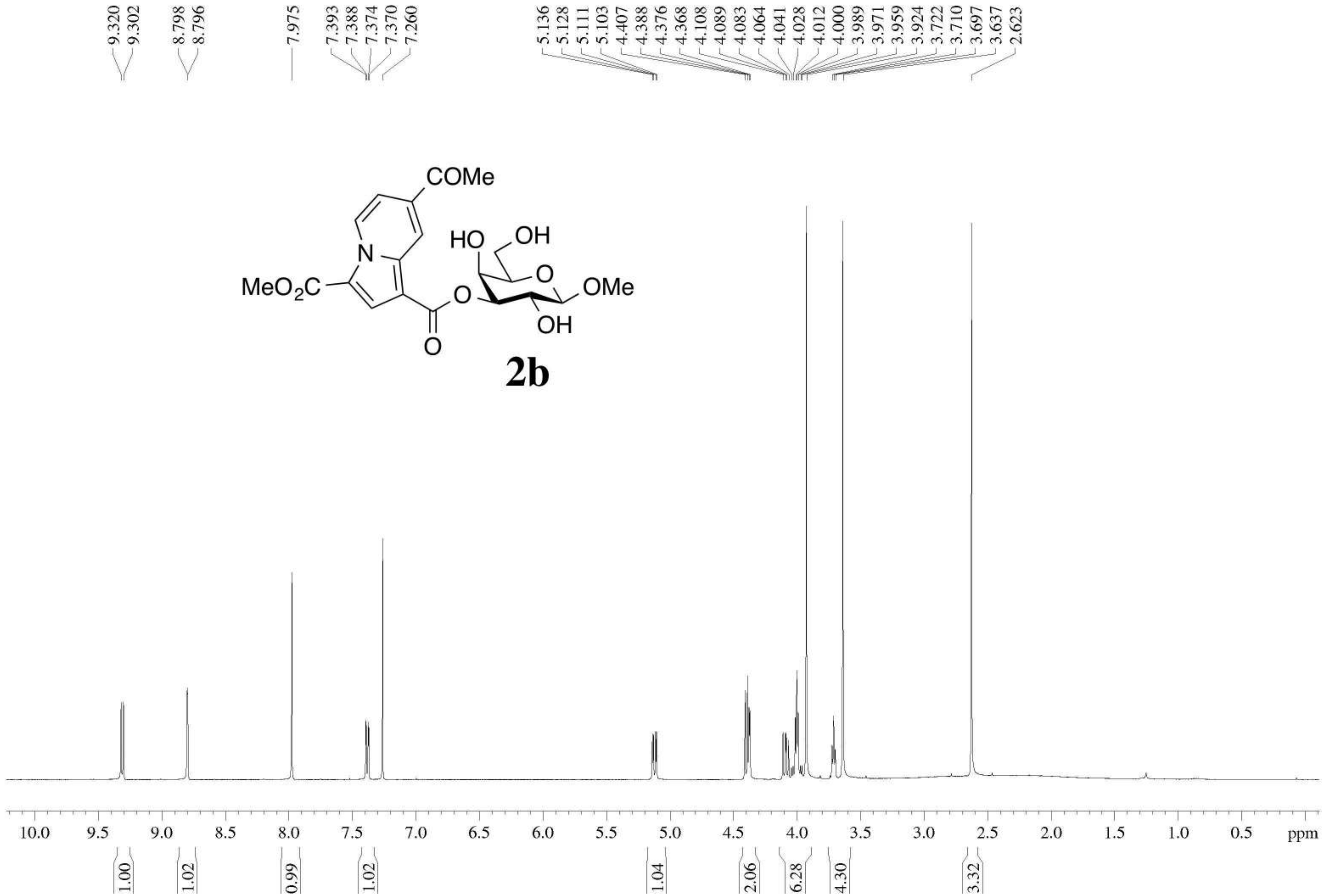
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5.103
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4.388
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4.083
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4.028
4.012
4.000
3.989
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3.959
3.924
3.722
3.710
3.697
3.637
2.623
COMe
MeO2C
N
HO
OH
O
OMe
OH
O
O
2b
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8.0
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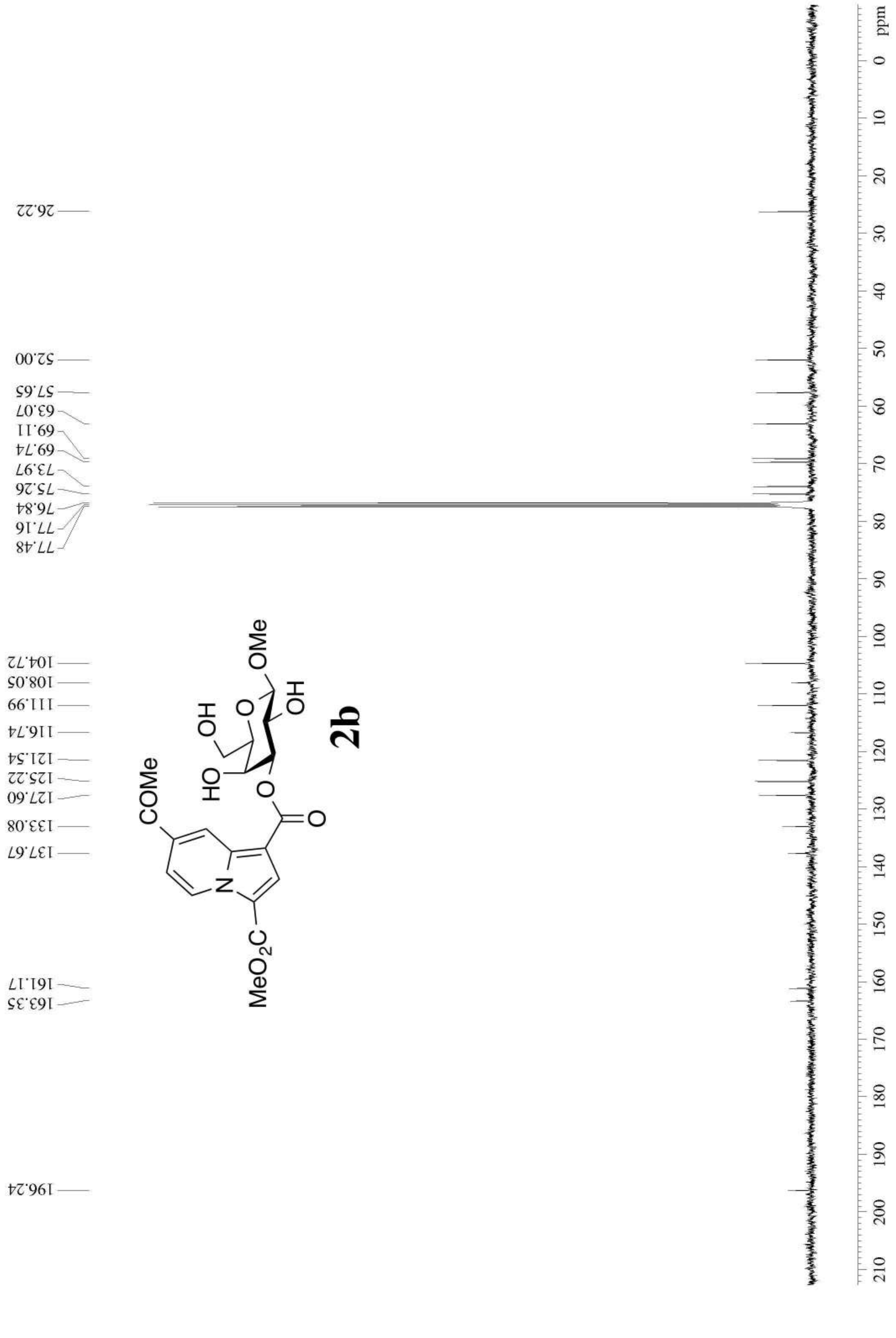
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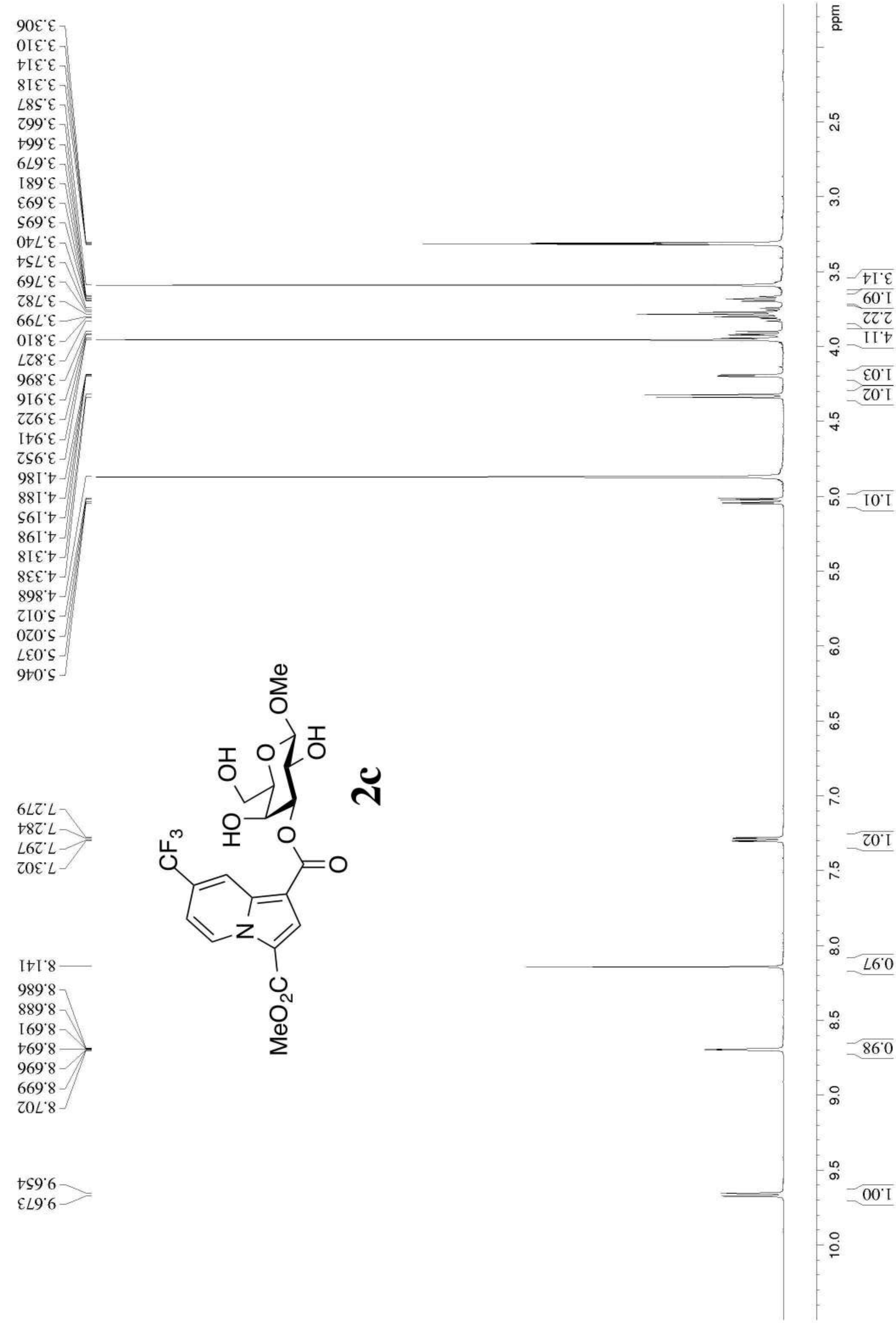
OMe
2b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3.922
3.941
3.952
4.186
4.188
4.195
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4.318
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8.702
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9.673
CF3
HO
OH
O
OMe
HO
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O
N
MeO2C
2c
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2.22
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1.02
1.01
1.02
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0.98
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ppm
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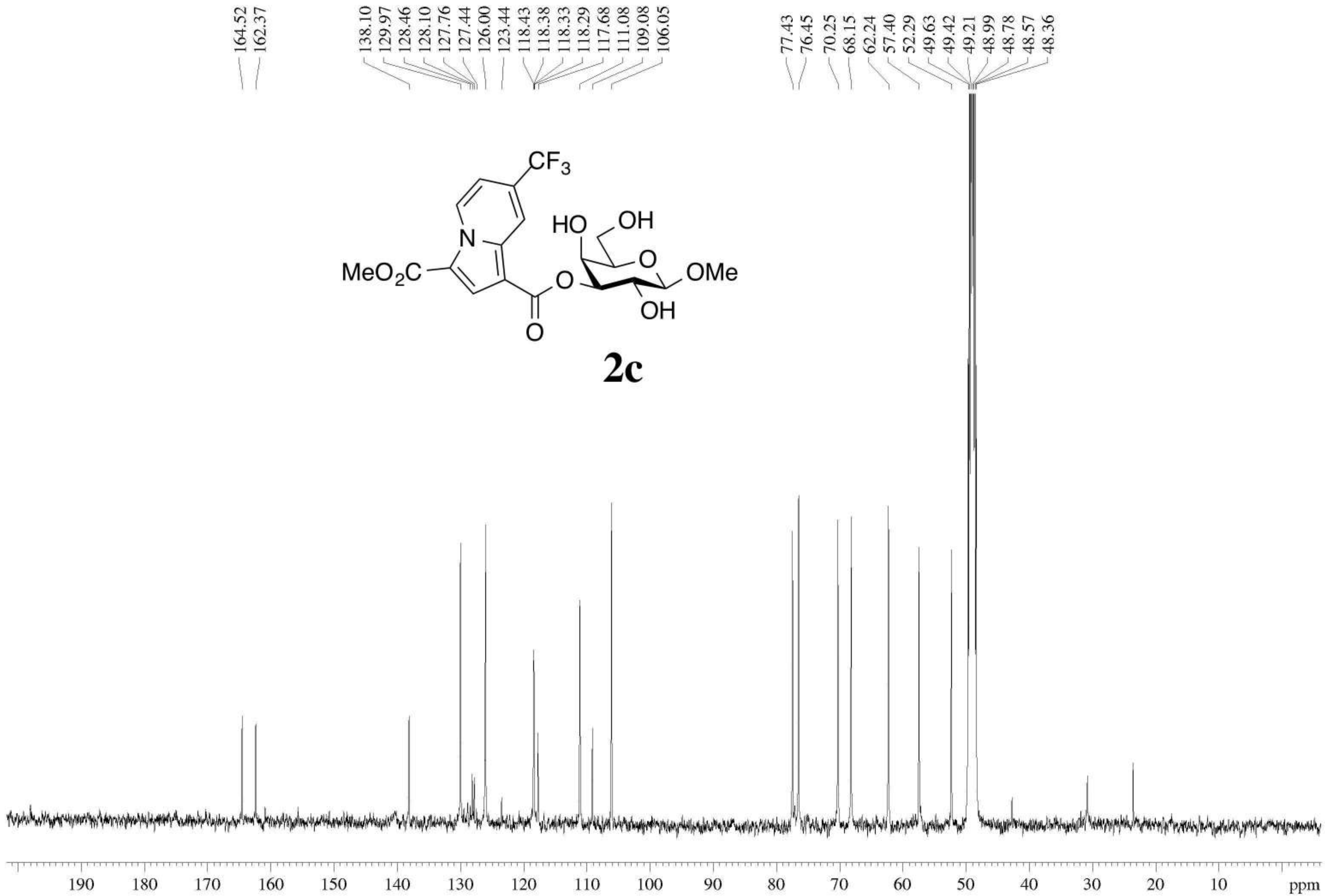
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62.24
57.40
52.29
49.63
49.42
49.21
48.99
48.78
48.57
48.36
CF3
MeO2C
N
HO
OH
O
OMe
OH
O
O
2c
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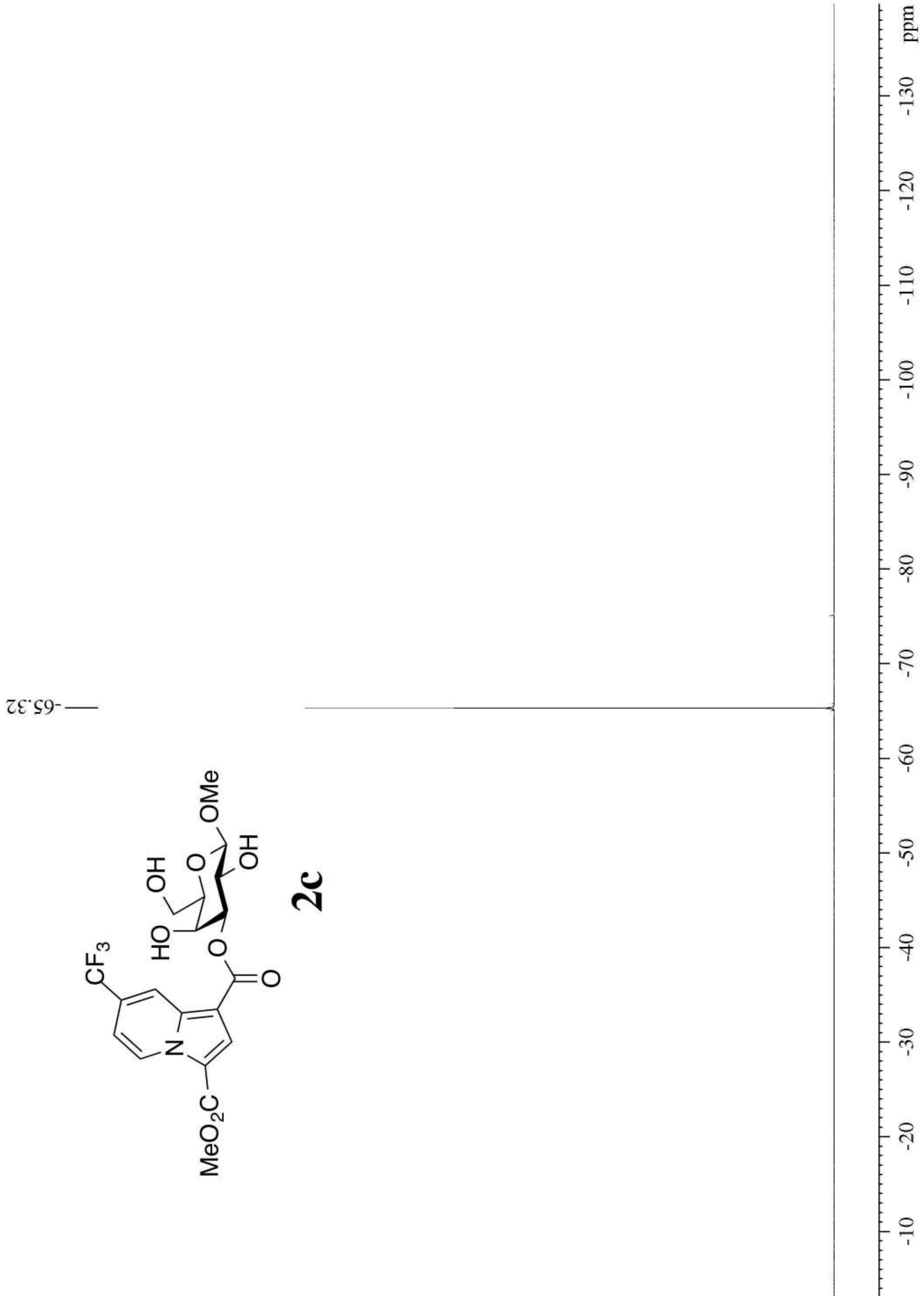
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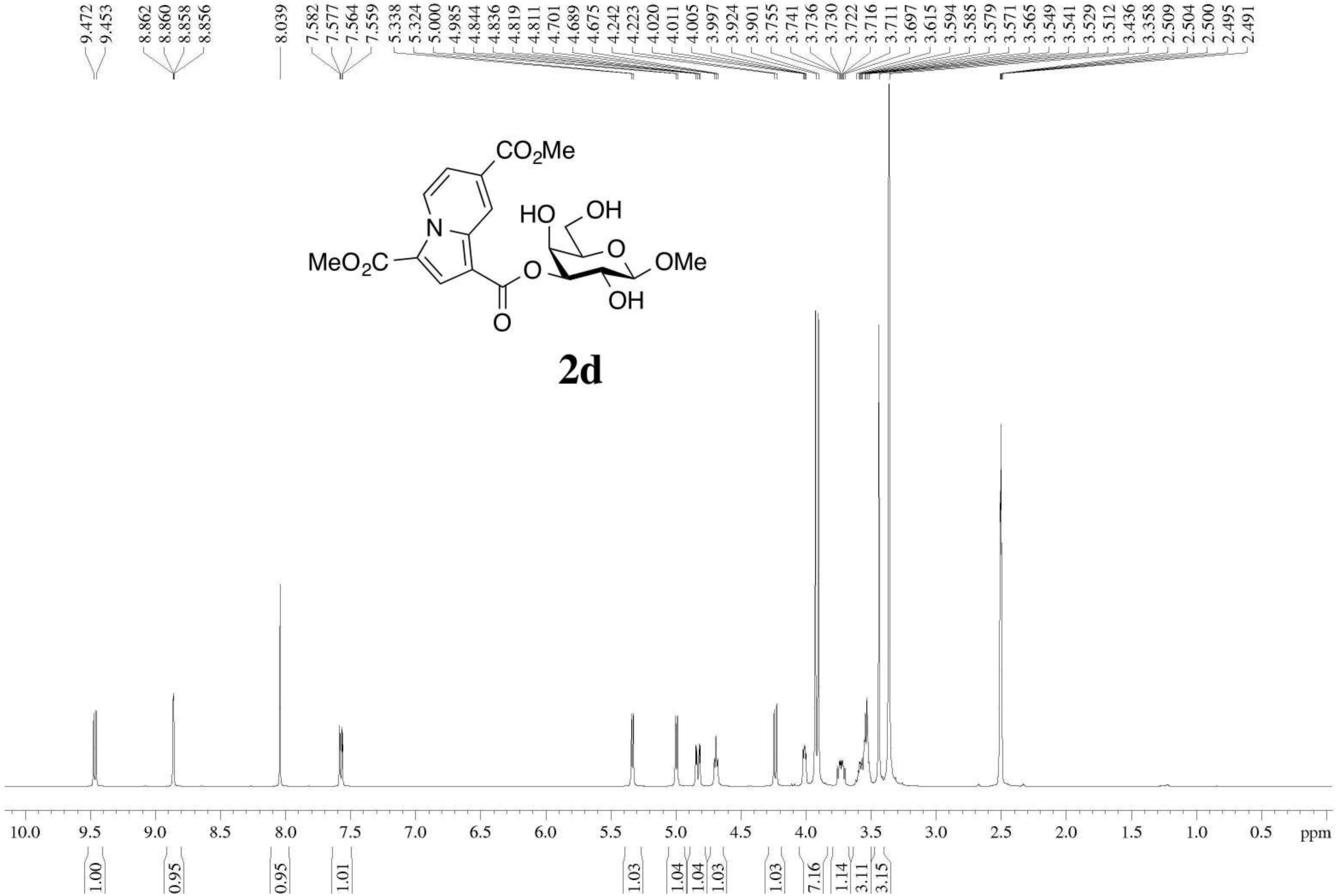
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4.020
4.011
4.005
3.997
3.924
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3.730
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3.716
3.711
3.697
3.615
3.594
3.585
3.579
3.571
3.565
3.549
3.541
3.529
3.512
3.436
3.358
2.509
2.504
2.500
2.495
2.491
CO_2Me
HO
OH
N
O
MeO_2C
O
OMe
OH
O
2d
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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1.03
1.04
1.04
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1.03
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1.14
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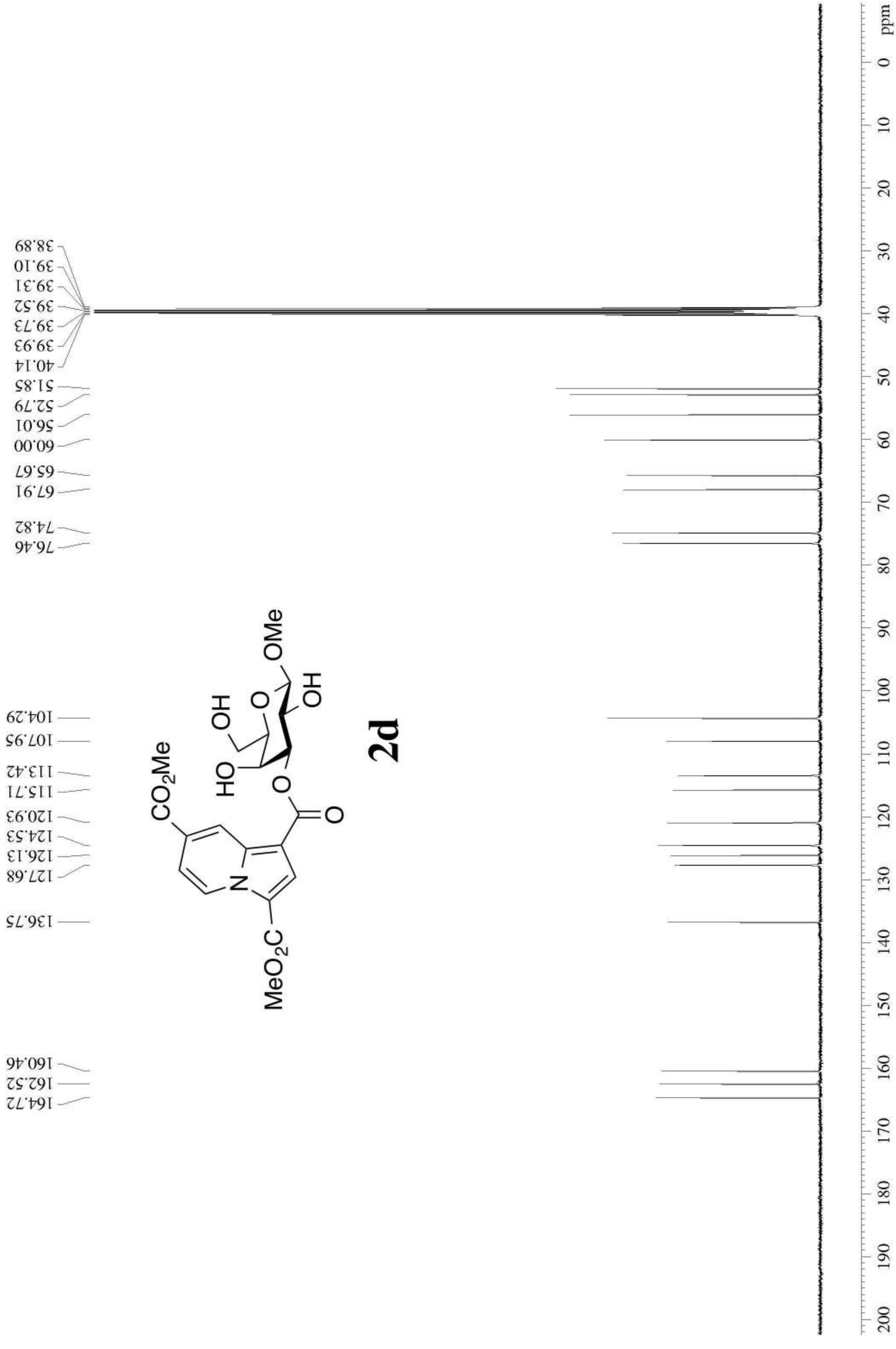
3.15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74.82
76.46
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126.13
127.68
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164.72
CO2Me
HO
OH
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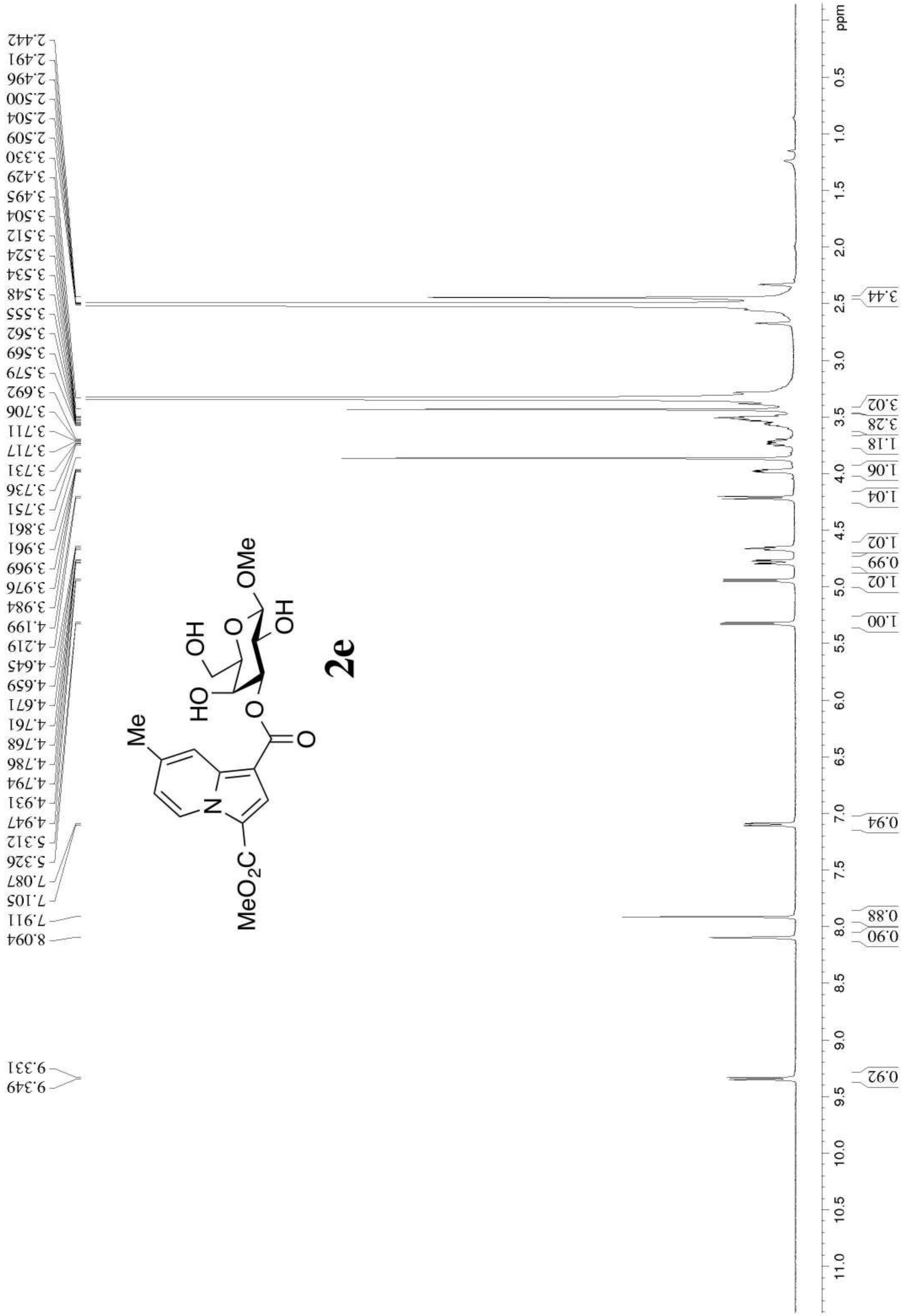
N
MeO2C
2d
ppm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3.534
3.548
3.555
3.562
3.569
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3.711
3.717
3.731
3.736
3.751
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3.961
3.969
3.976
3.984
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4.219
4.645
4.659
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4.761
4.768
4.786
4.794
4.931
4.947
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5.326
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7.105
7.911
8.094
9.331
9.349
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3.28
1.18
1.06
1.04
1.02
0.99
1.02
1.00
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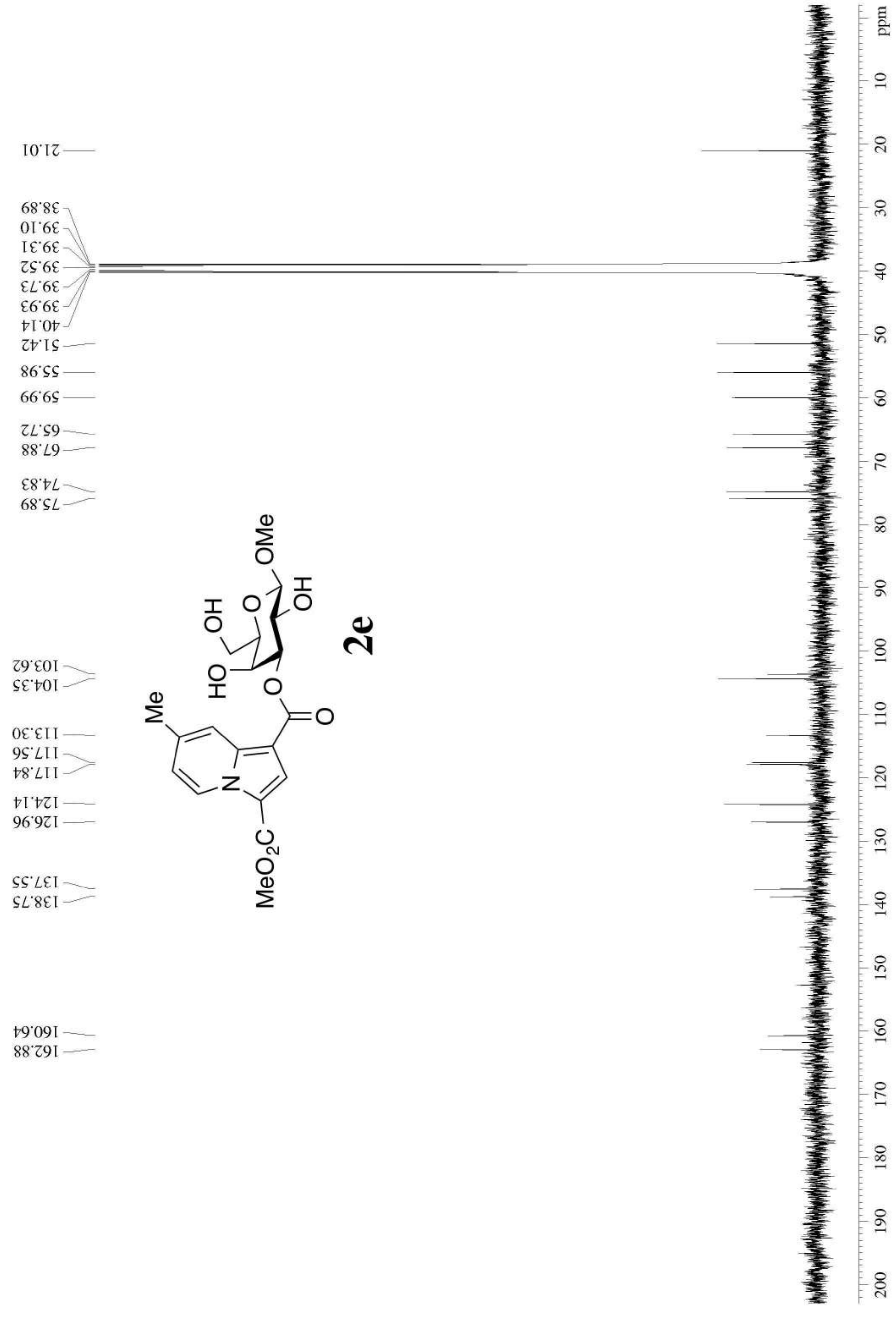
0.92
ppm
Me
HO
OH
O
OMe
OH
O
O
N
MeO2C
2e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75.89
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162.88
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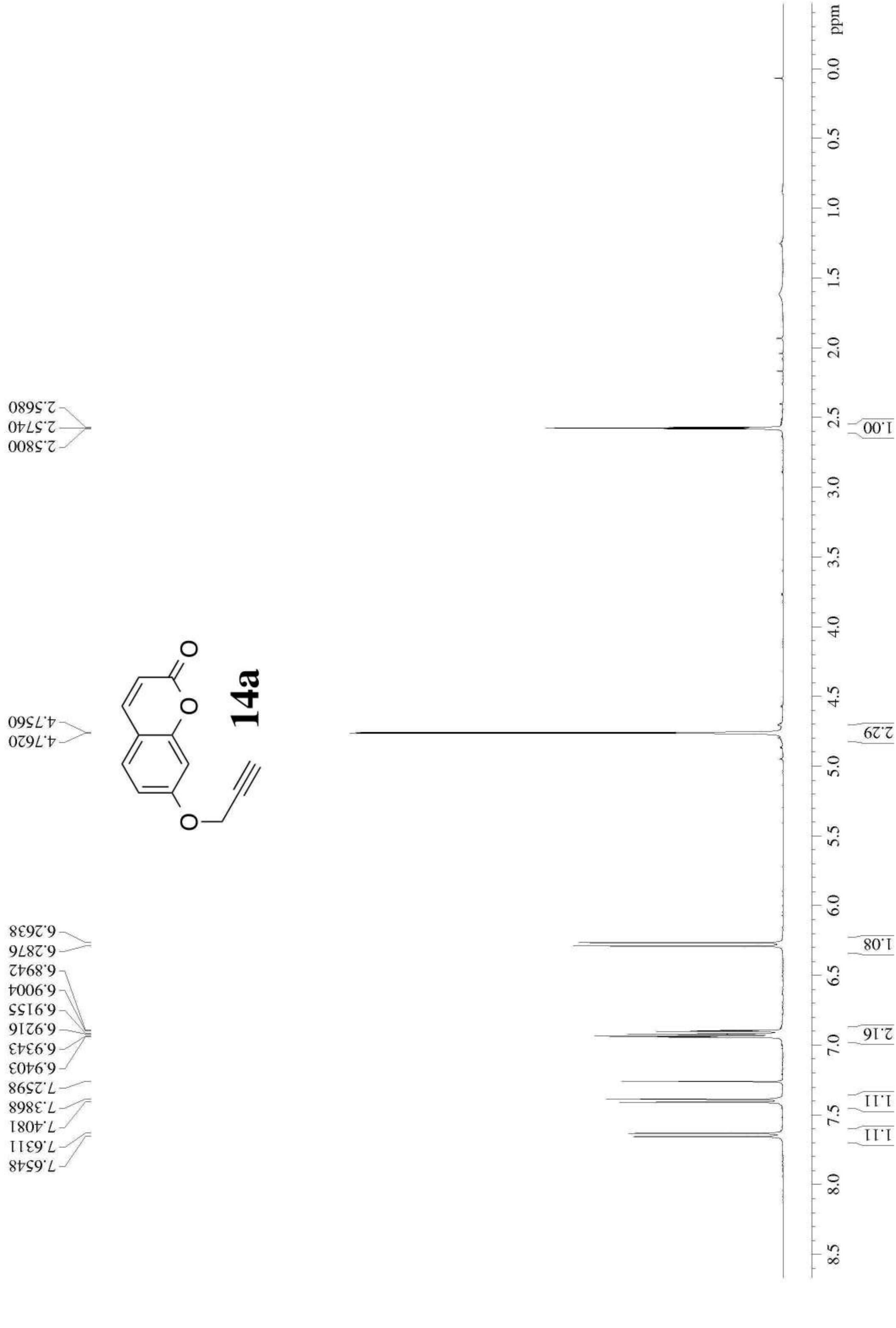
ppm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7.3868
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7.6311
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1.08
2.16
1.11
1.11
ppm
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0.5
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2.0
2.5
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4.0
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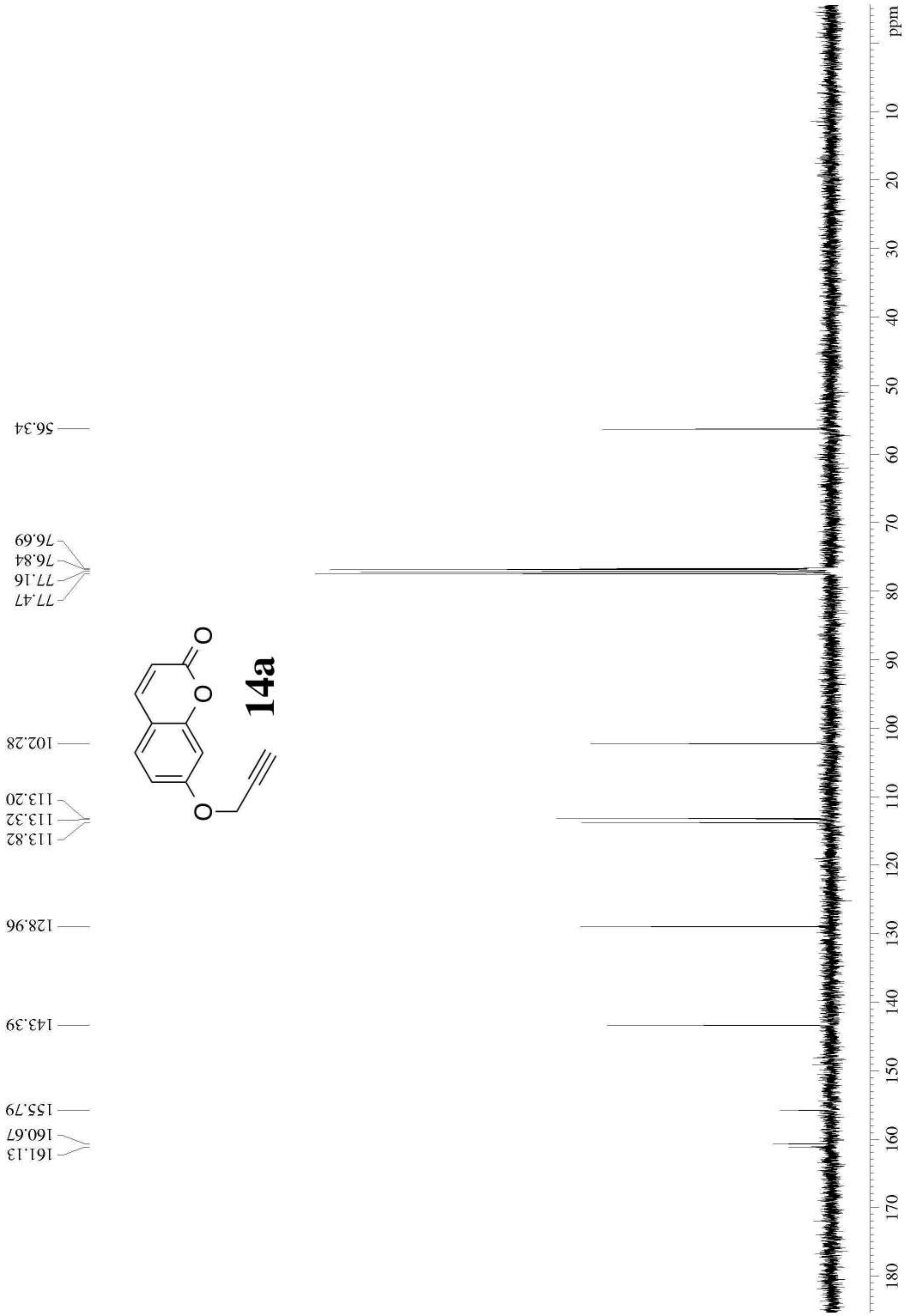
8.5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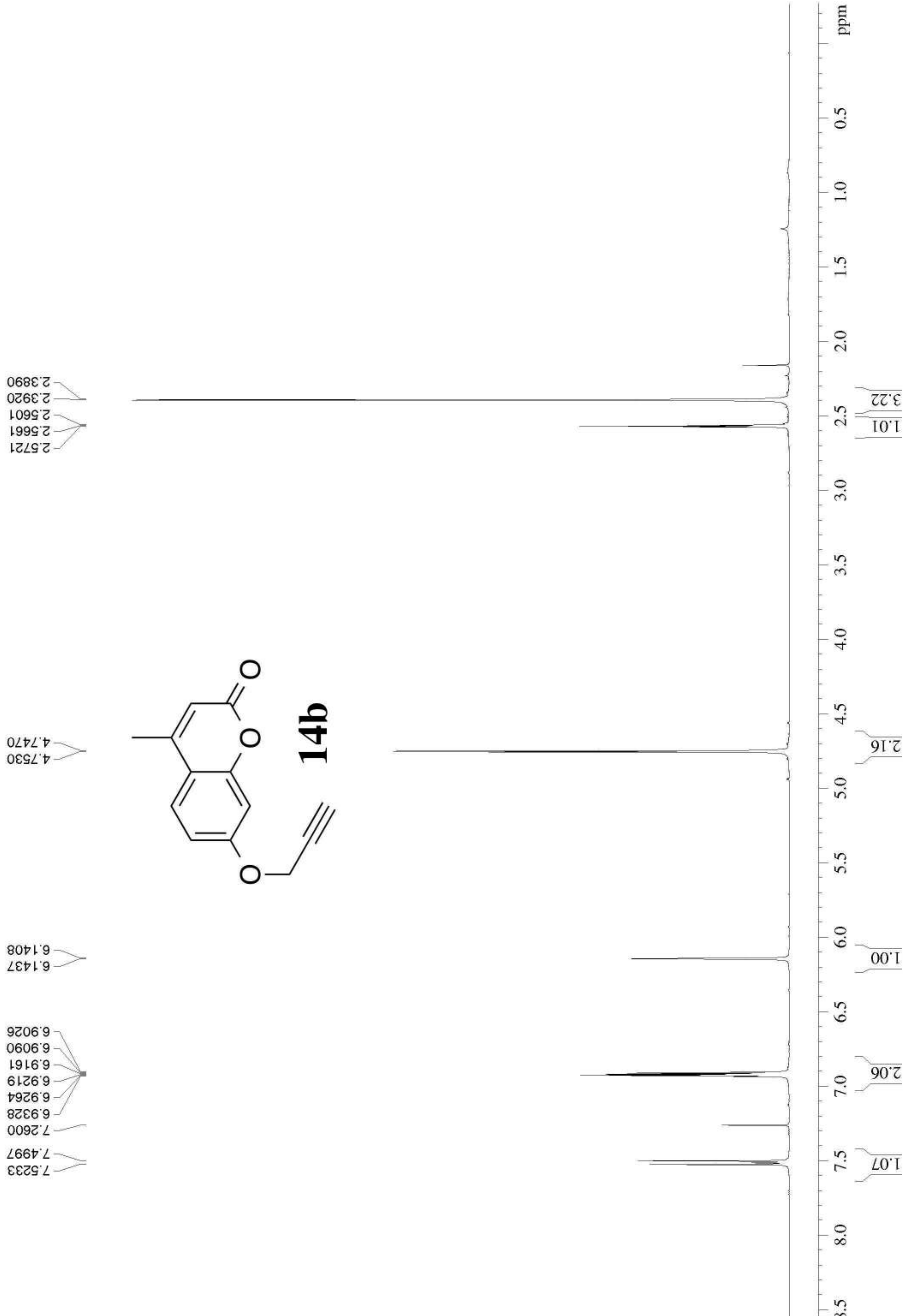

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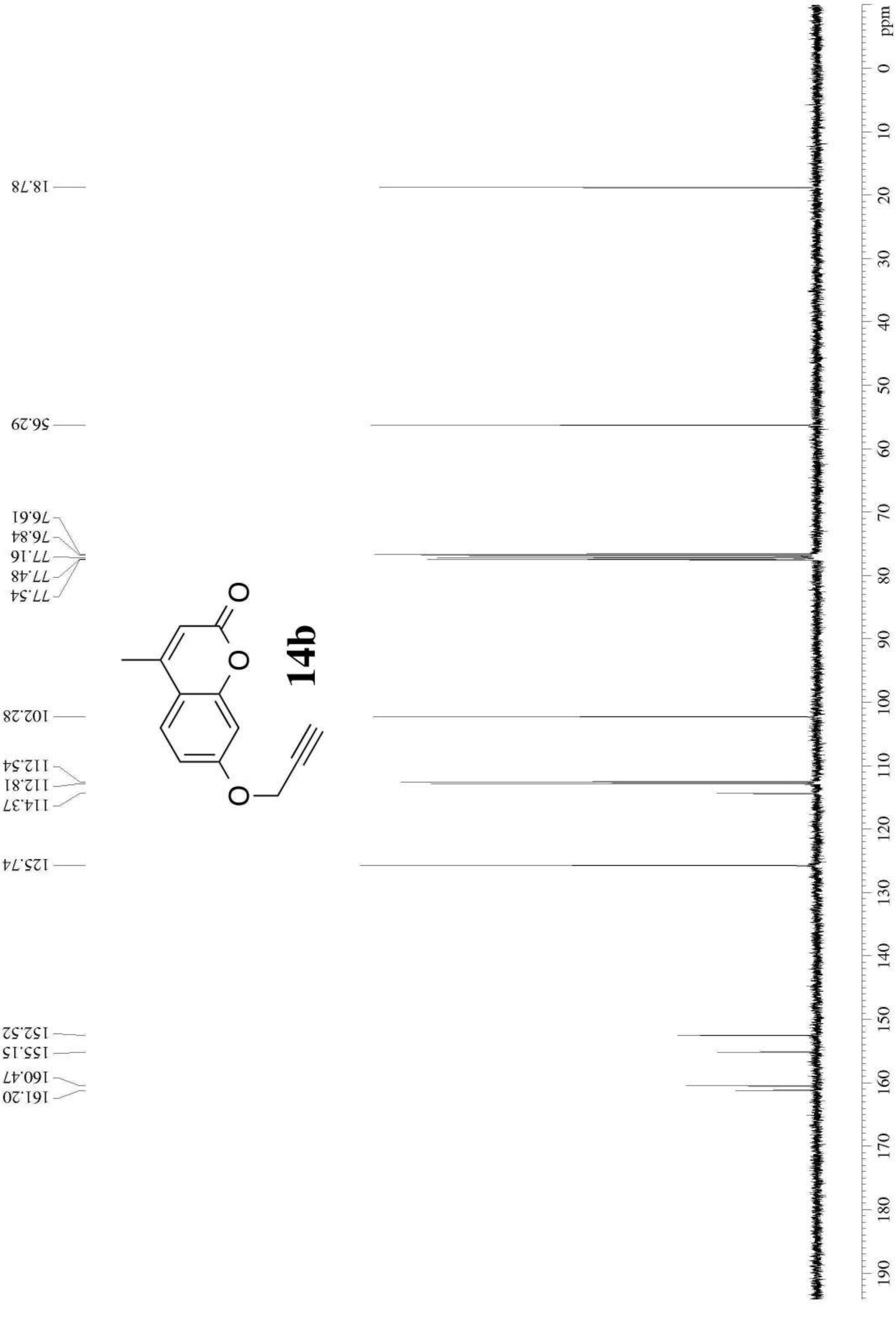
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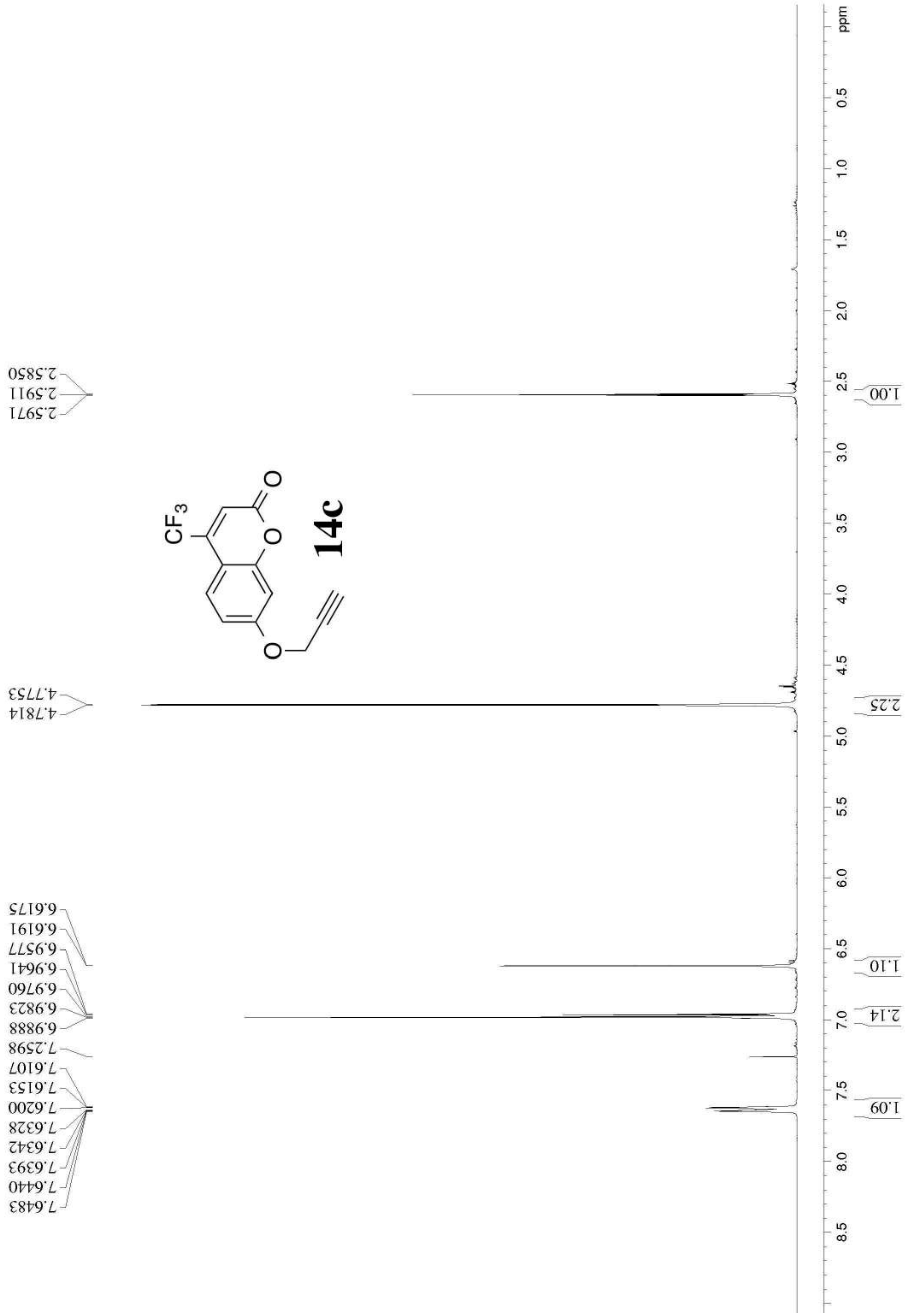
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CF3
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6.9823
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7.6107
7.6153
7.6200
7.6328
7.6342
7.6393
7.6440
7.6483
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ppm
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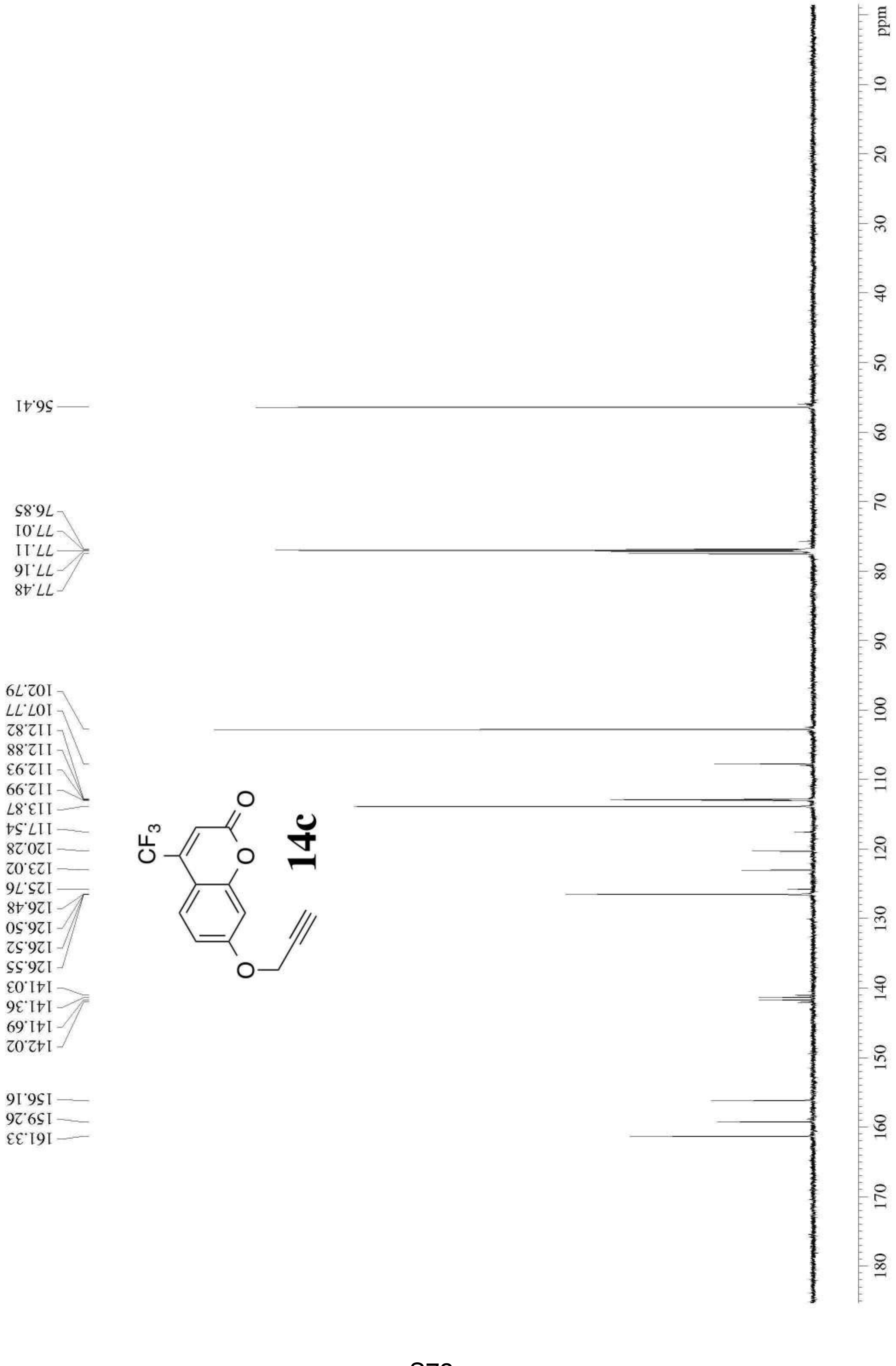

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141.69
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156.16
159.26
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CF3
O
O
O
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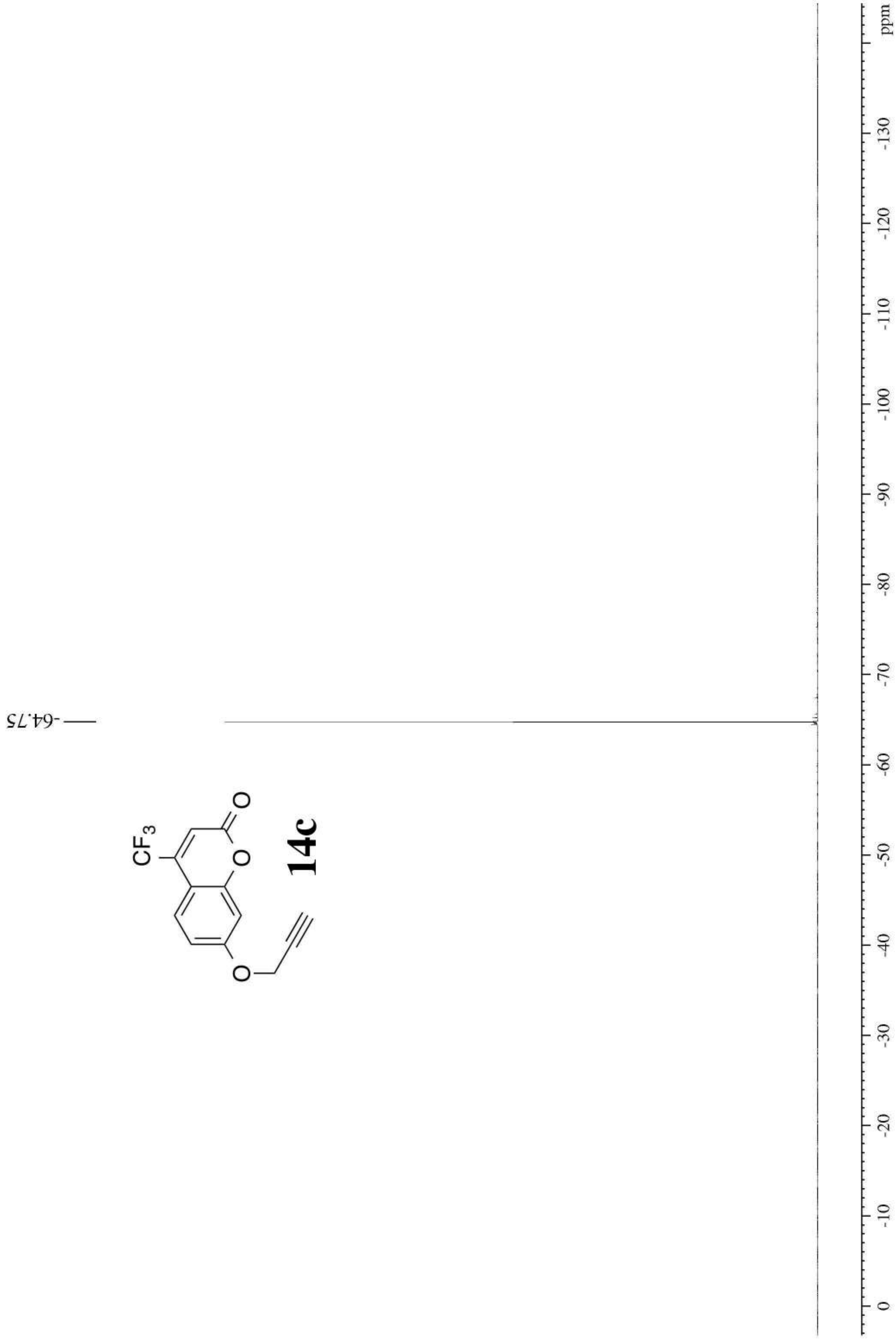

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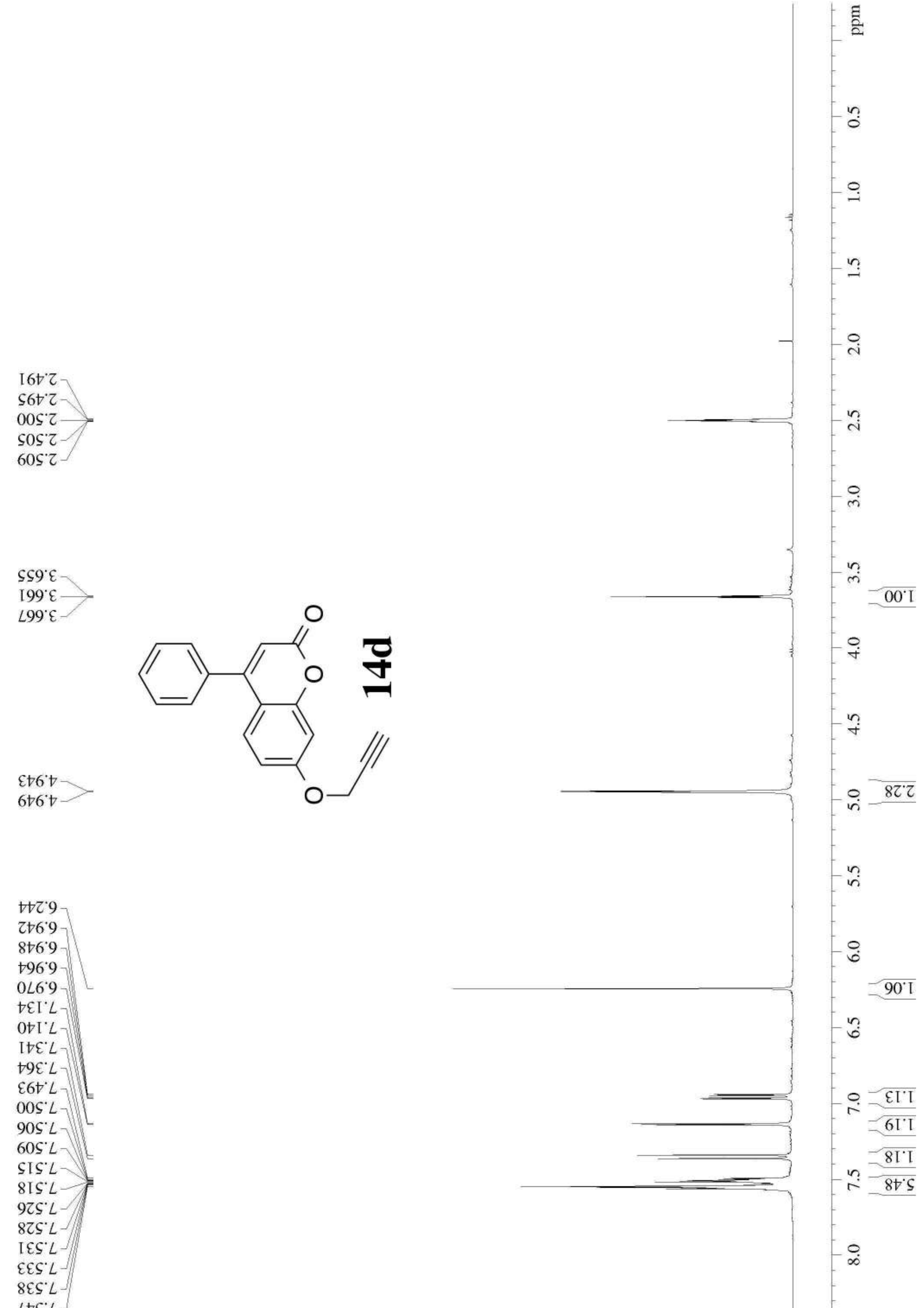
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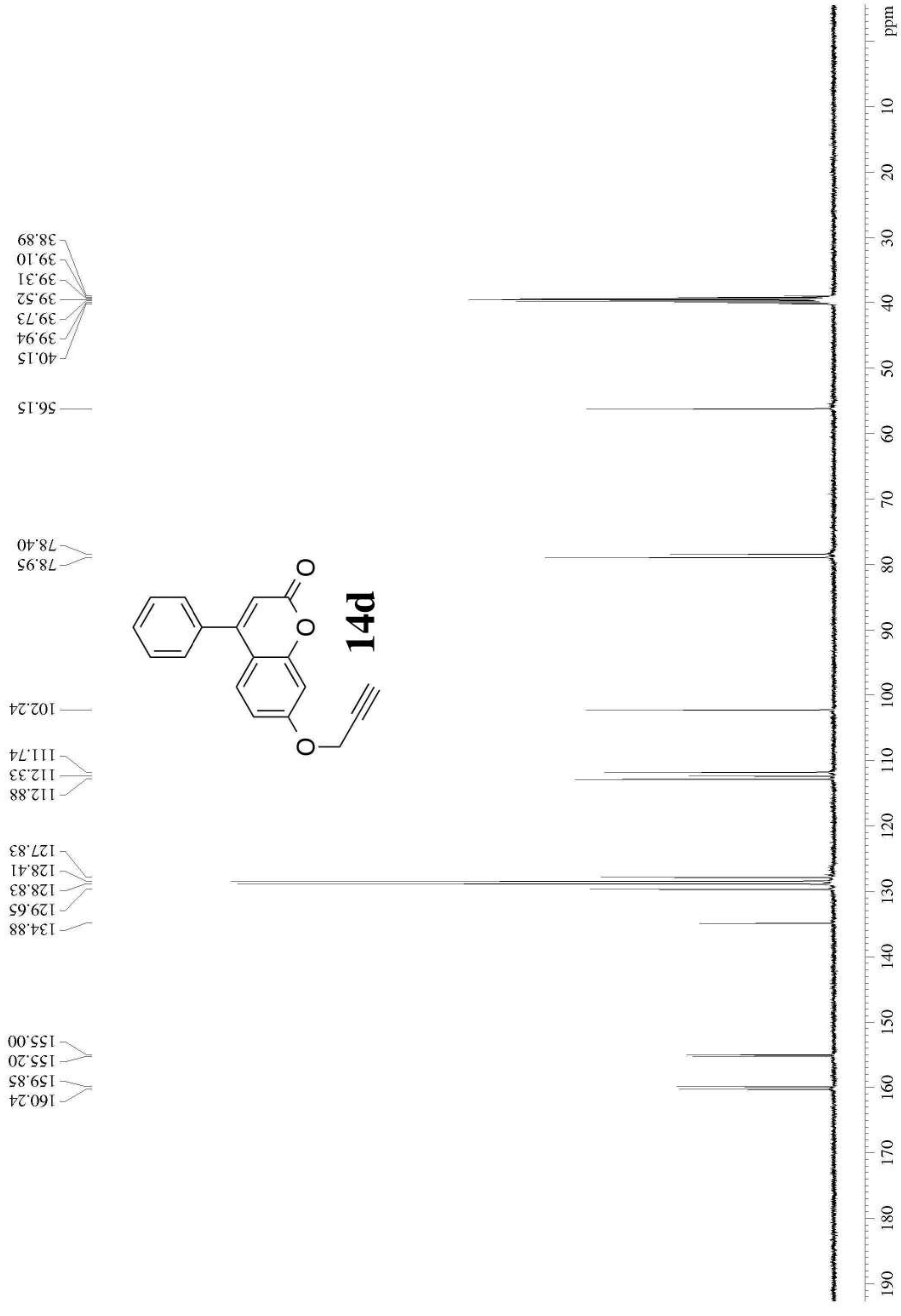
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112.88
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128.41
128.83
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134.88
155.00
155.20
159.85
160.24
14d
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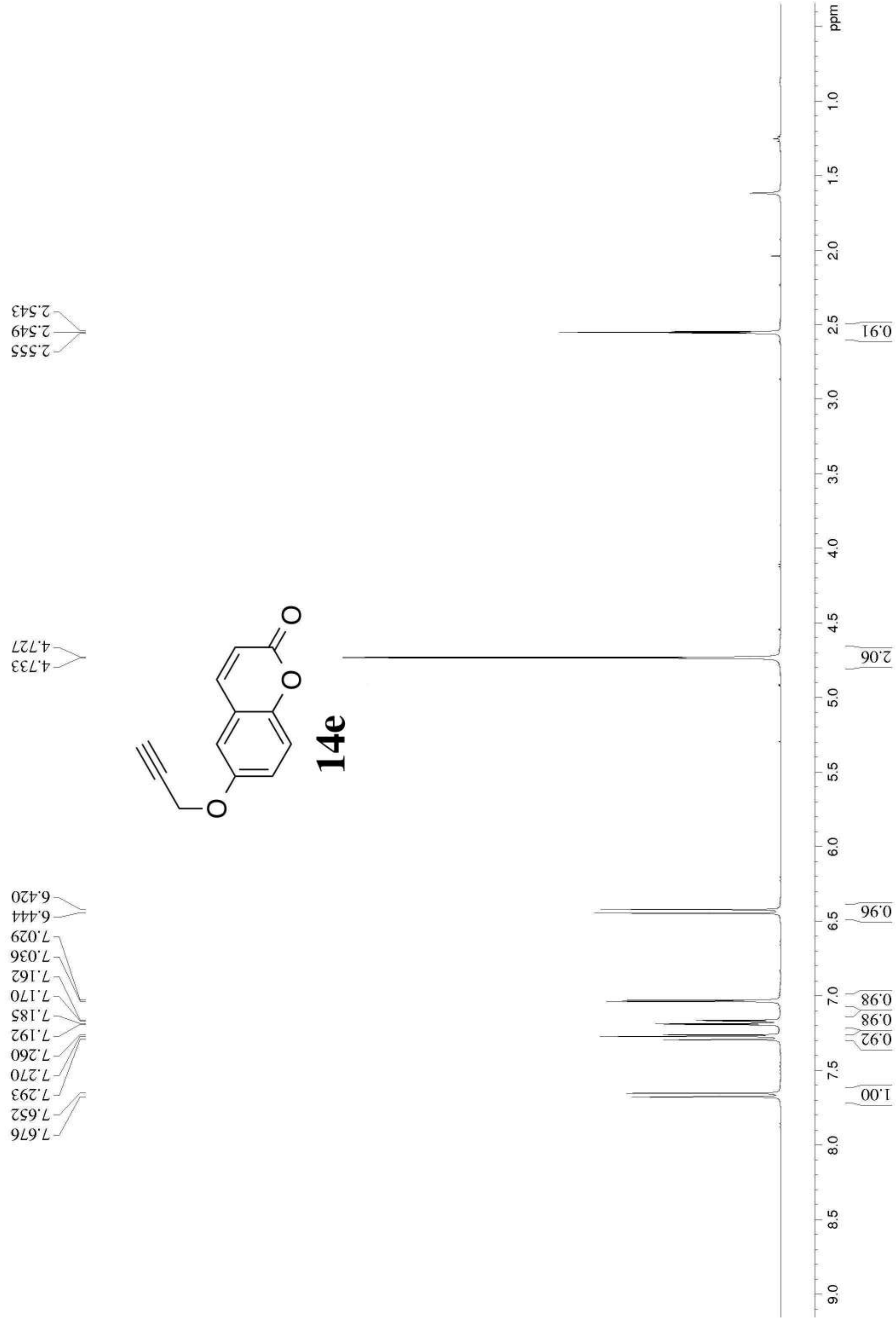
190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7.652
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0.98
0.92
1.00
ppm
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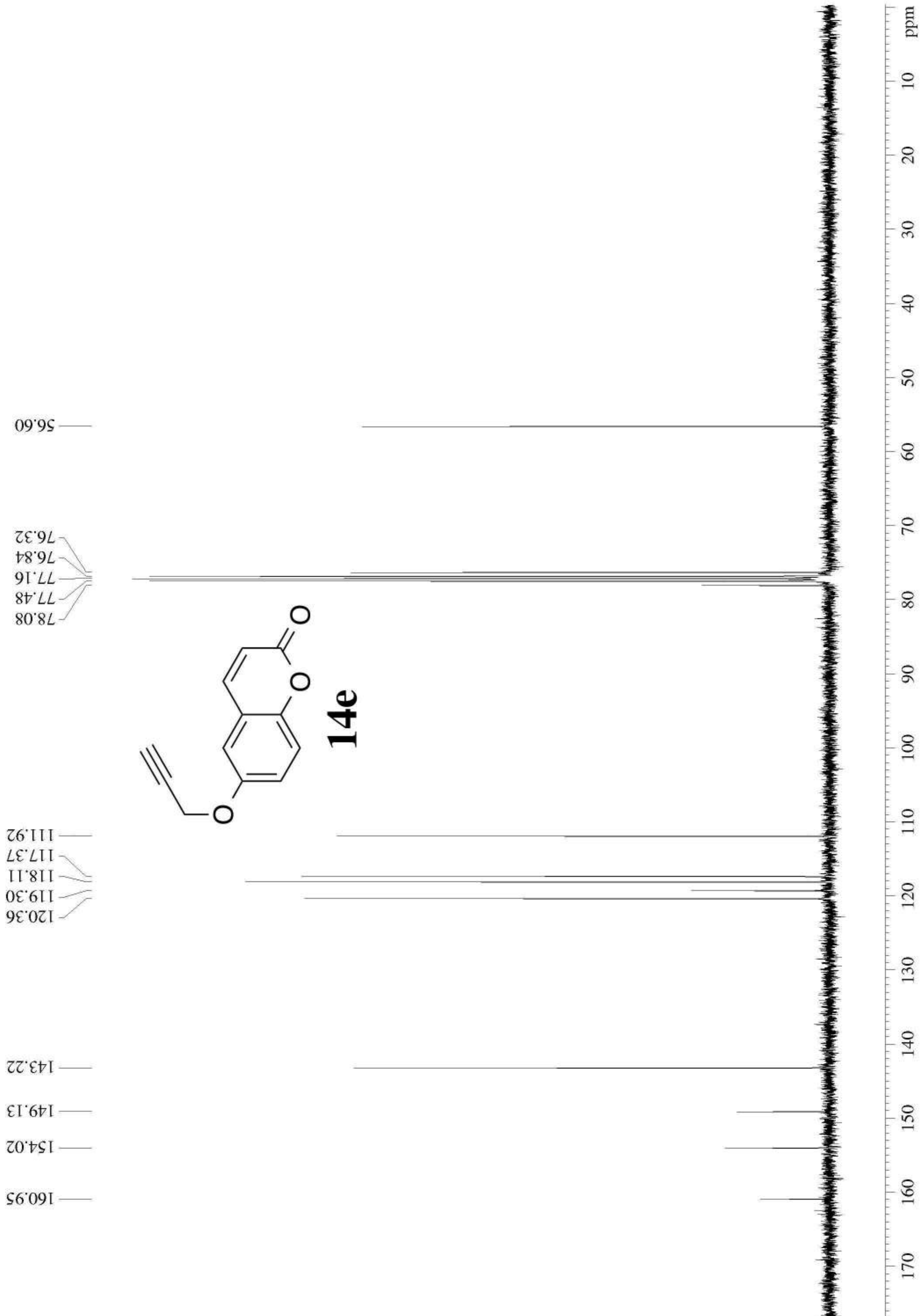
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O
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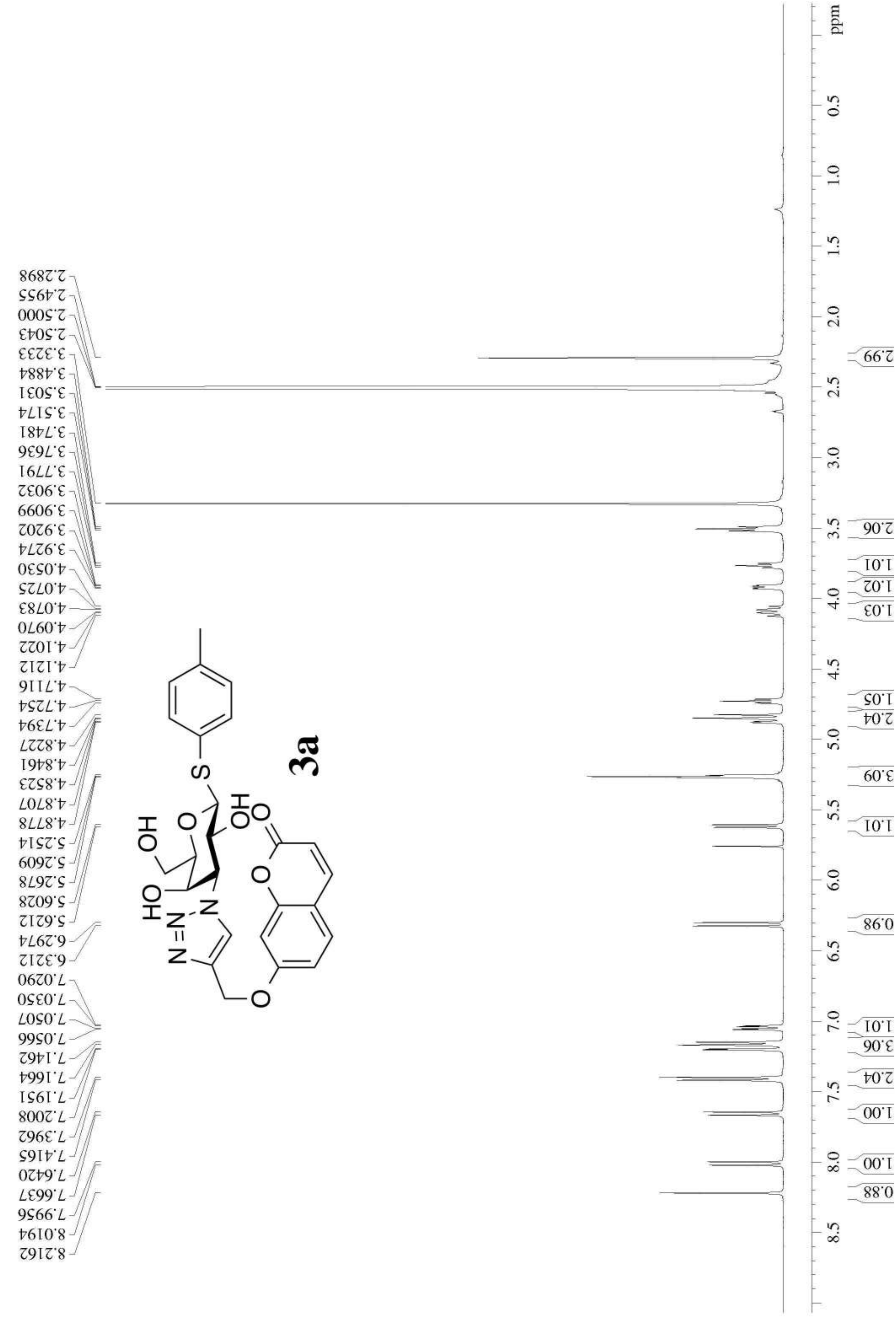
ppm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1.02
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3.06
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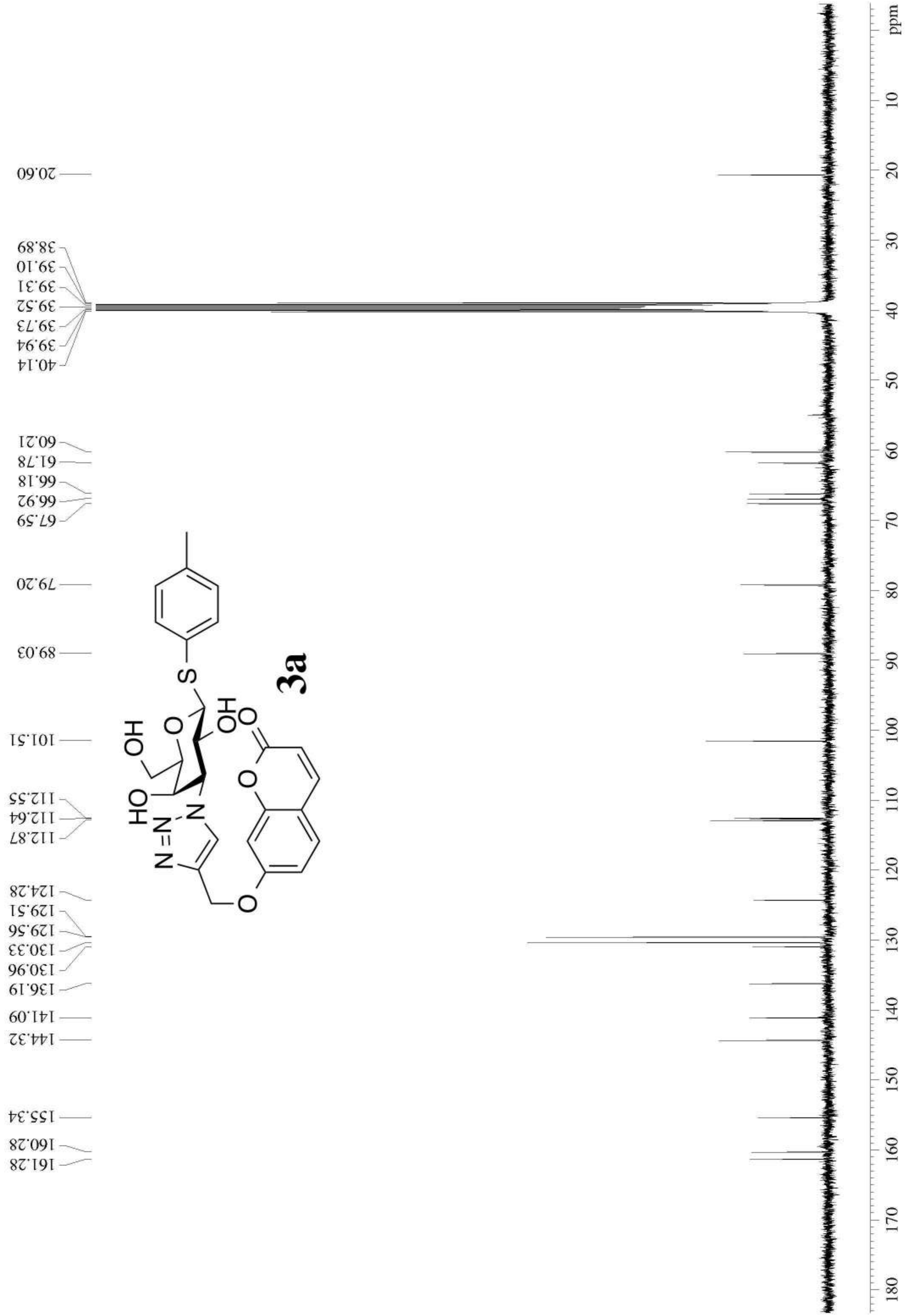

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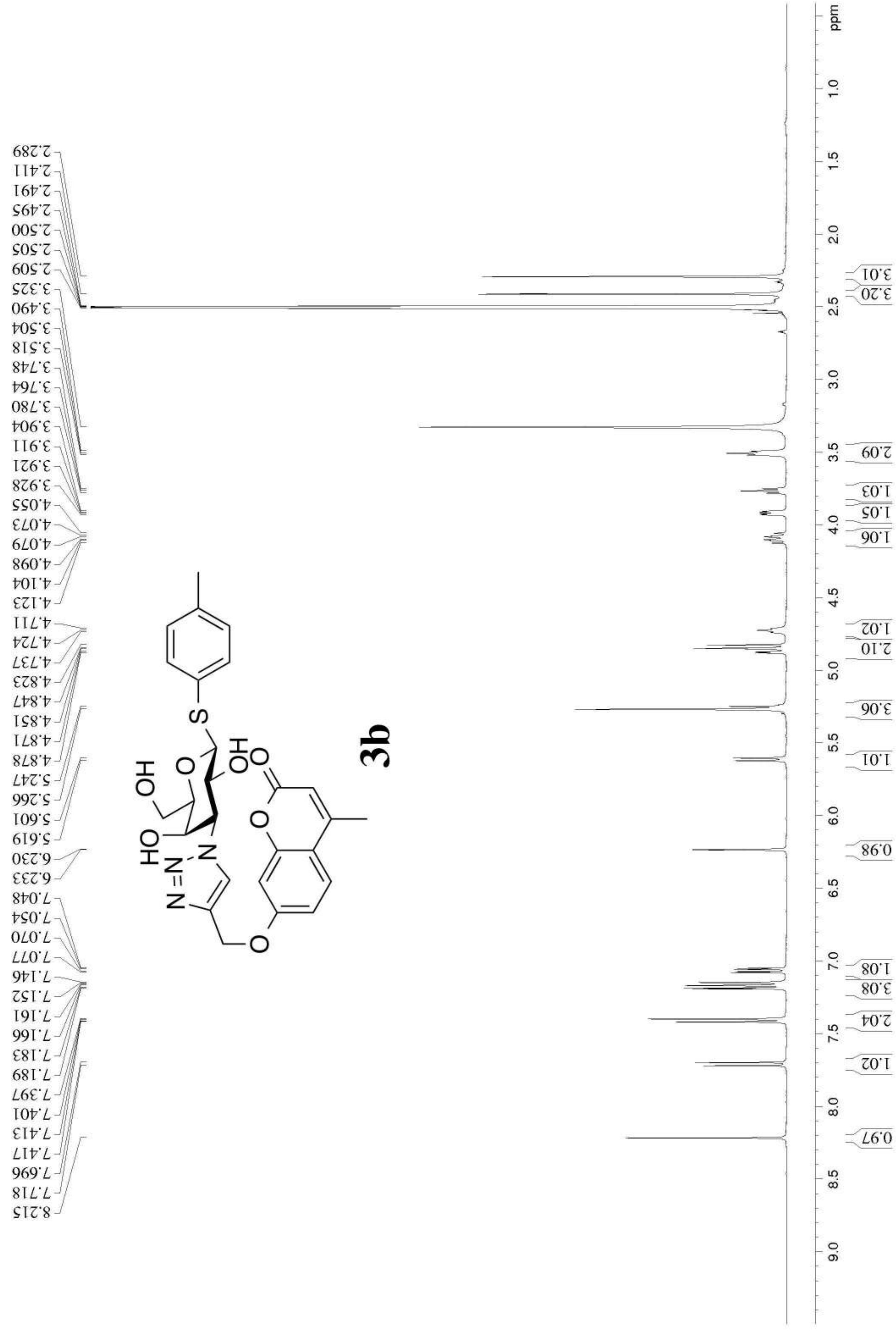

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3b
ppm
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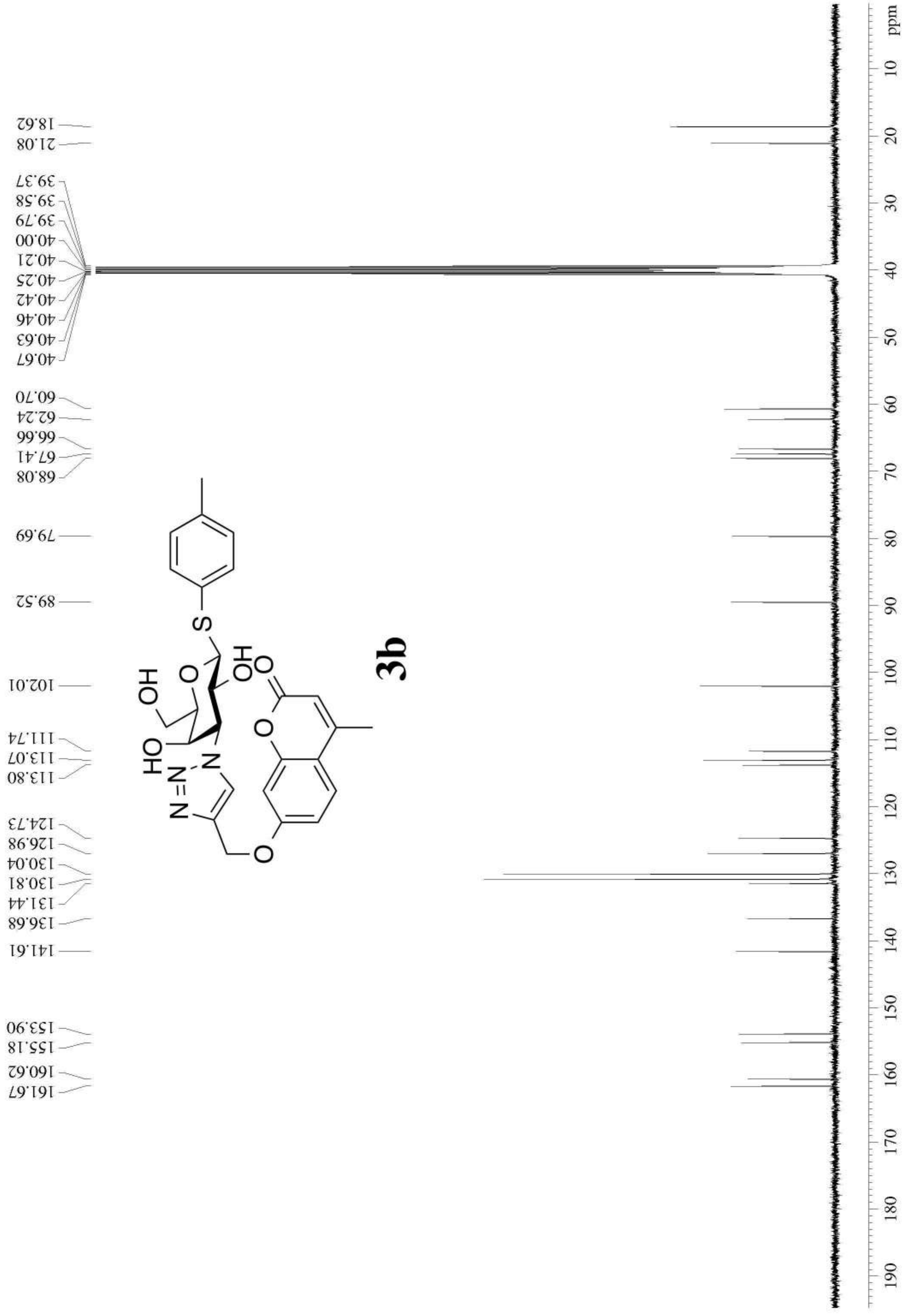
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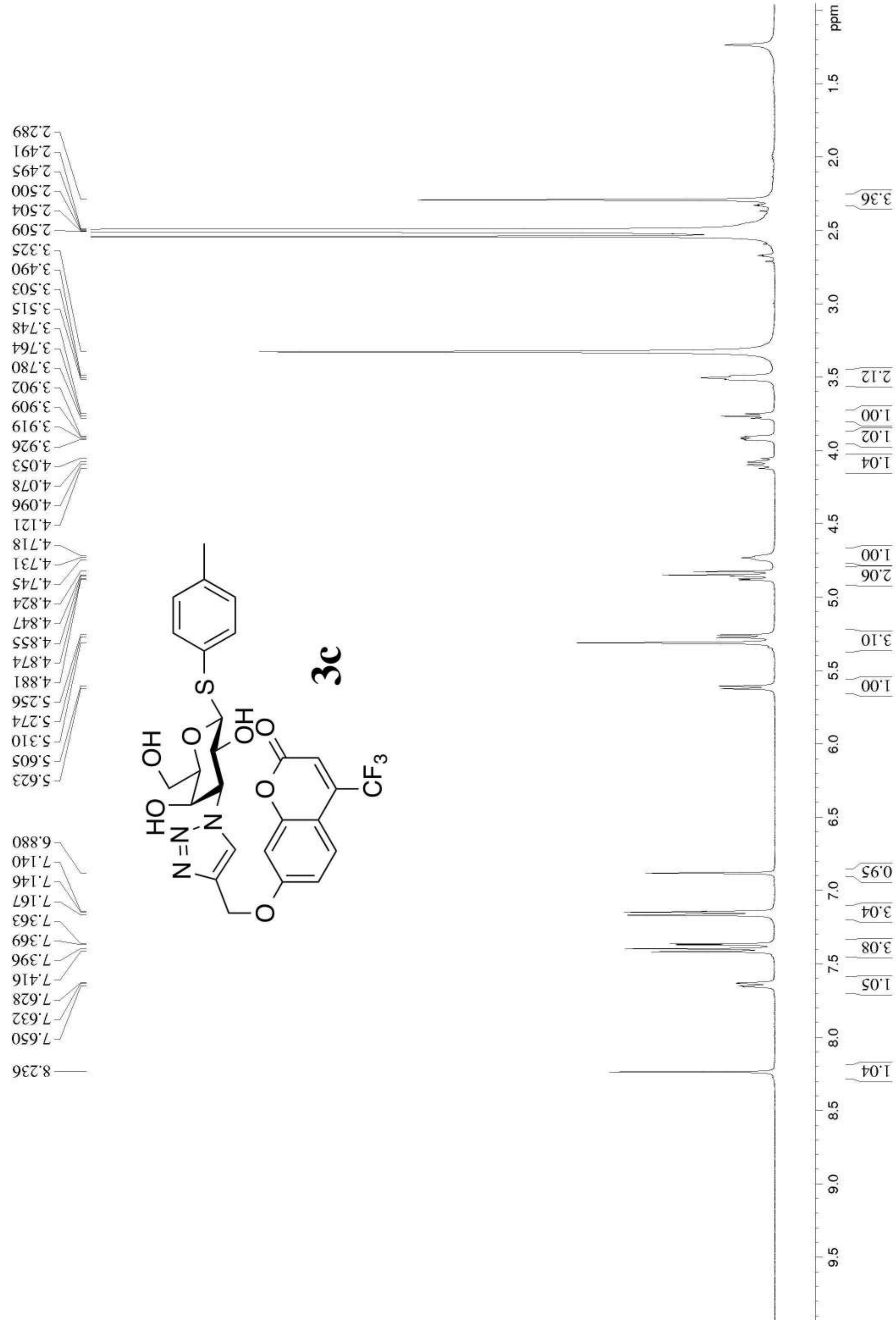
3b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3.902
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3.926
4.053
4.078
4.096
4.121
4.718
4.731
4.745
4.824
4.847
4.855
4.874
4.881
5.256
5.274
5.310
5.605
5.623
6.880
7.140
7.146
7.167
7.363
7.369
7.396
7.416
7.628
7.632
7.650
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3.36
2.12
1.00
1.02
1.04
1.00
2.06
3.10
1.00
0.95
3.04
3.08
1.05
1.04
ppm
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2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
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HO
OH
N
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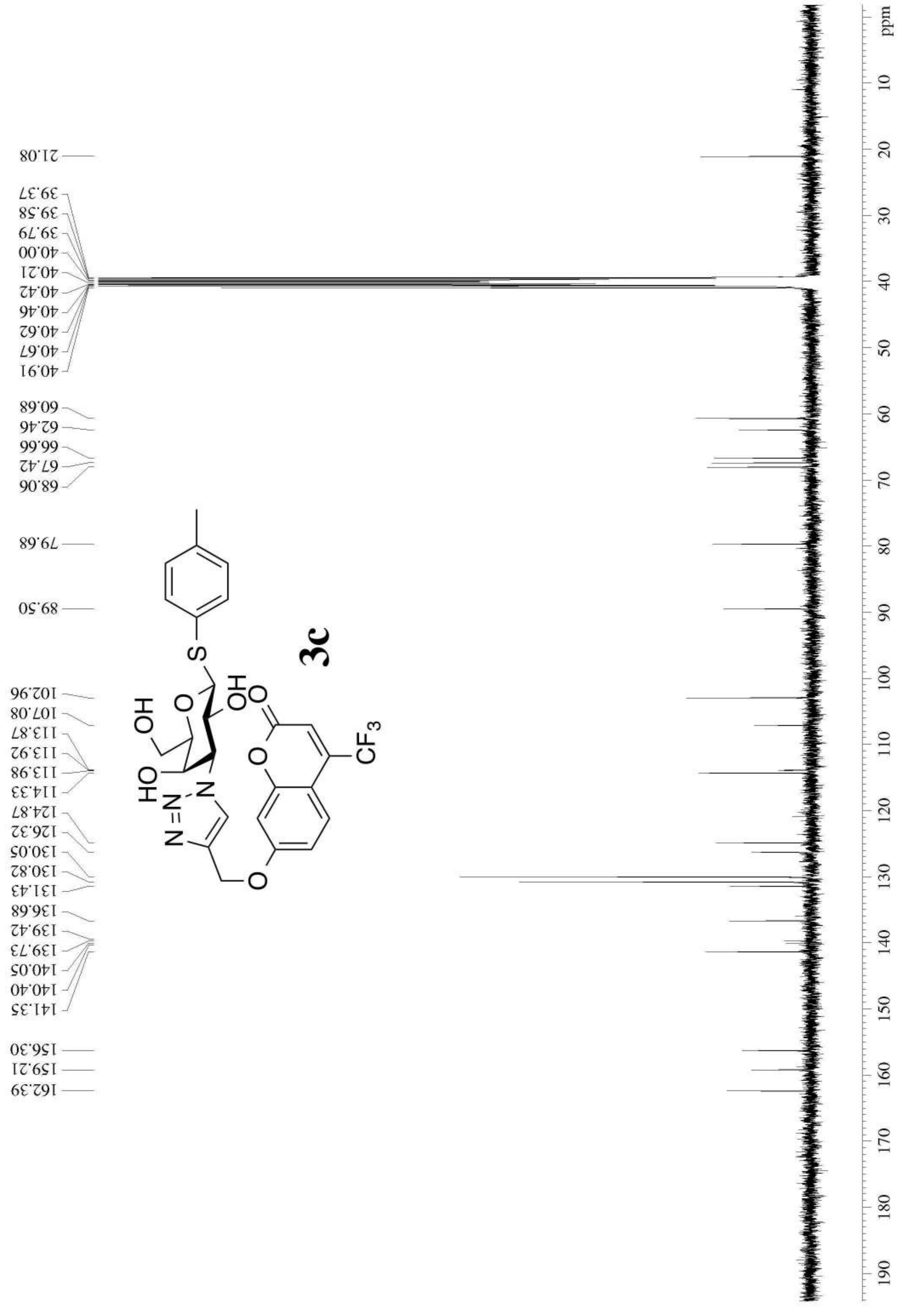
O
O
CF_3

3c



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79.68
89.50
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126.32
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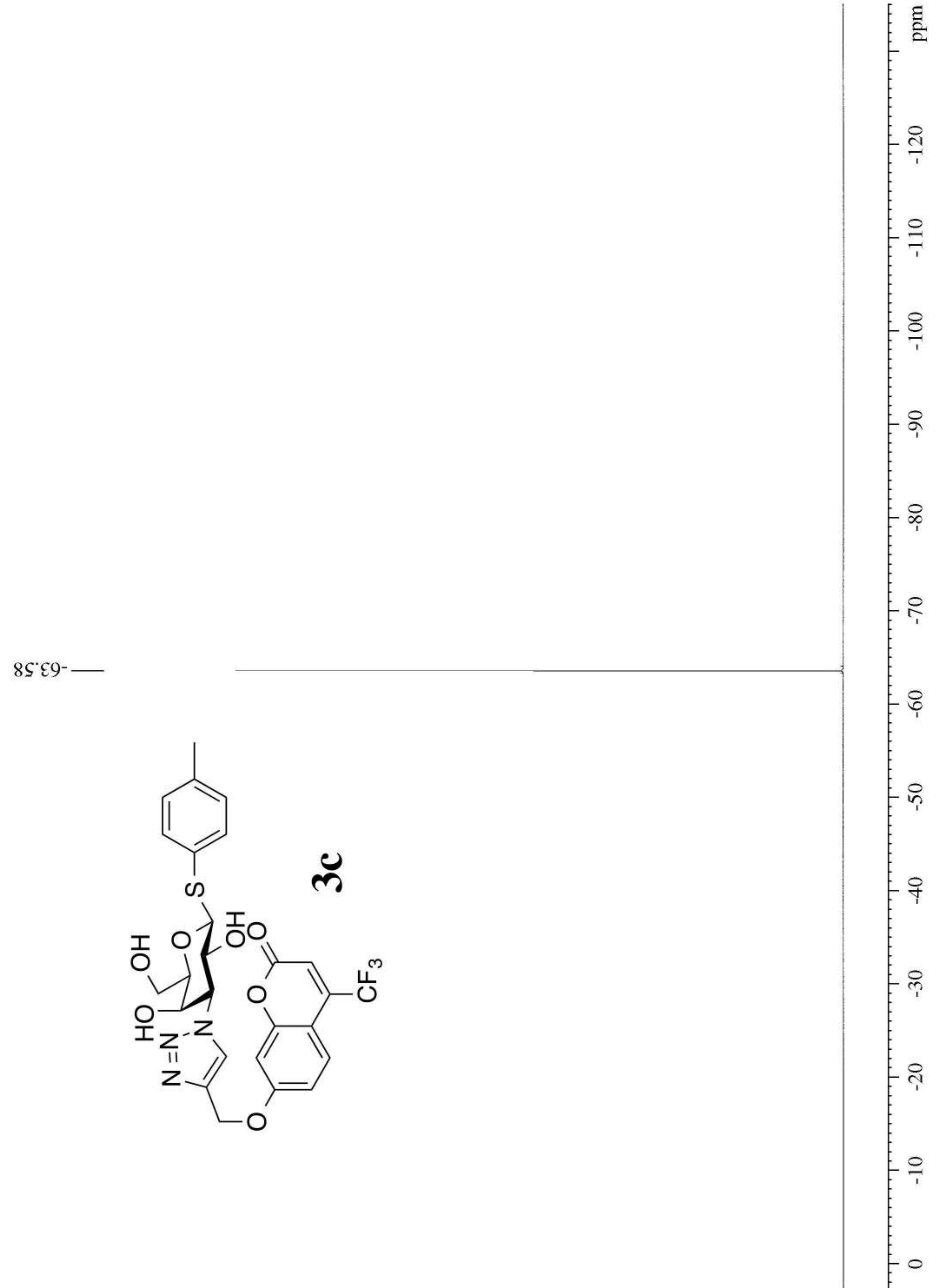
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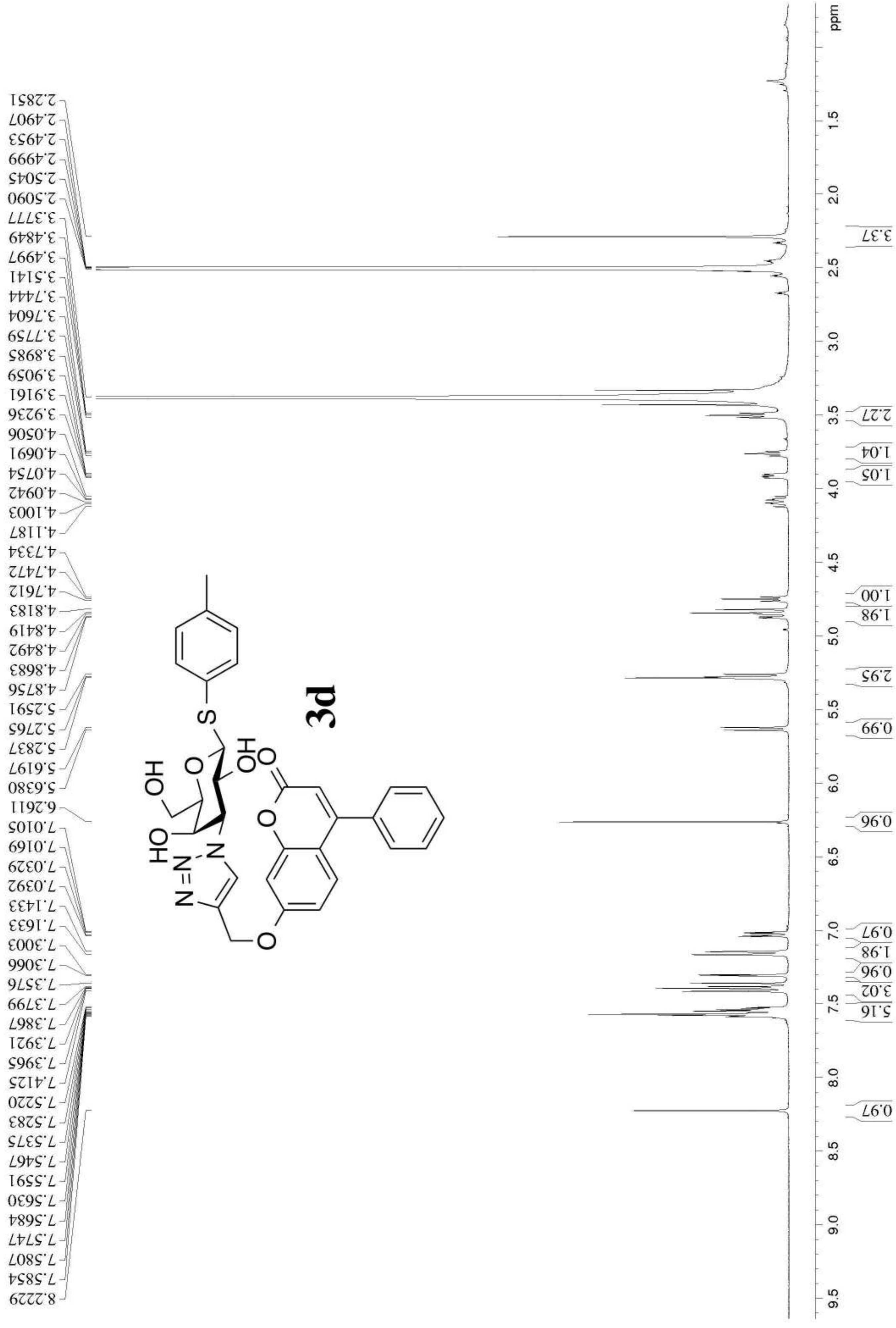
OH
O
S
OH
N=N
N
O
O
O
CF3

3c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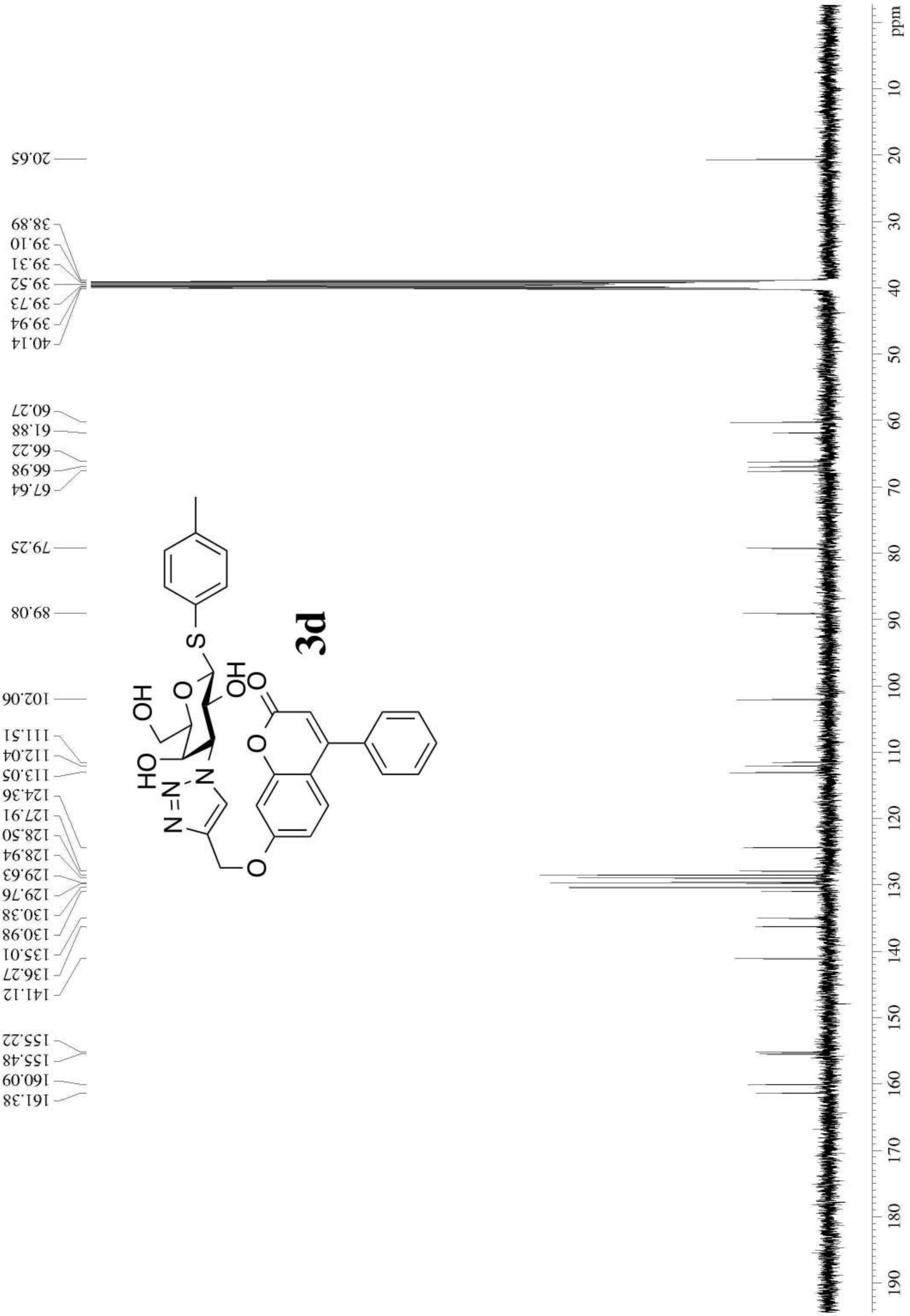
3.37 2.27 1.04 1.05 1.00 1.98 2.95 0.99 0.96 0.97 1.98 0.96 3.02 5.16 0.97
2.2851 2.4907 2.4953 2.4999 2.5045 2.5090 3.3777 3.4849 3.4997 3.5141 3.7444 3.7604 3.7759 3.8985 3.9059 3.9161 3.9236 4.0506 4.0691 4.0754 4.0942 4.1003 4.1187 4.7334 4.7472 4.7612 4.8183 4.8419 4.8492 4.8683 4.8756 5.2591 5.2765 5.2837 5.6197 5.6380 6.2611 7.0105 7.0169 7.0329 7.0392 7.1433 7.1633 7.3003 7.3066 7.3576 7.3799 7.3867 7.3921 7.3965 7.4125 7.5220 7.5283 7.5375 7.5467 7.5591 7.5630 7.5684 7.5747 7.5807 7.5854 8.2229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79.25
89.08
102.06
111.51
112.04
113.05
124.36
127.91
128.50
128.94
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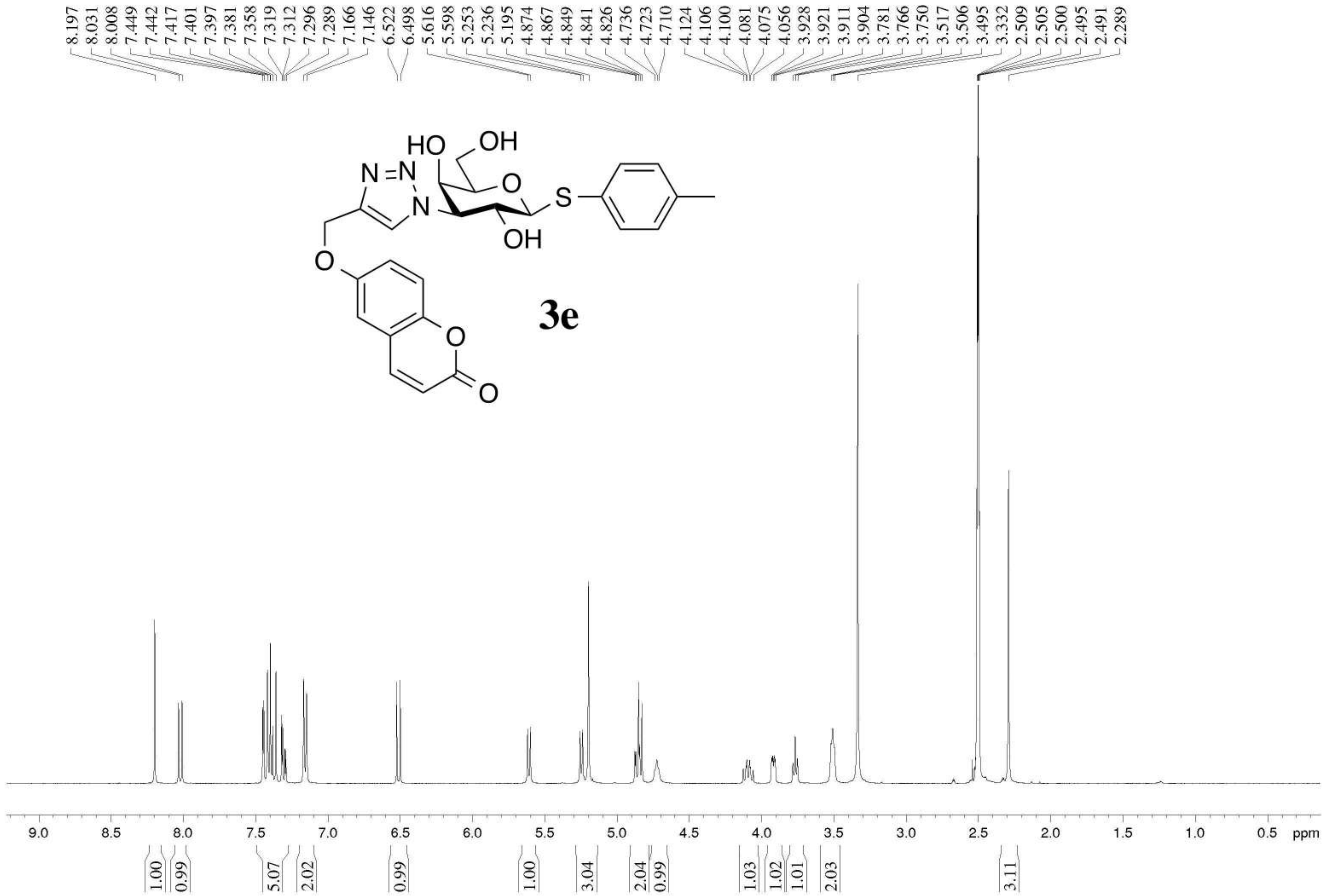
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7.296
7.289
7.166
7.146
6.522
6.498
5.616
5.598
5.253
5.236
5.195
4.874
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4.849
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4.826
4.736
4.723
4.710
4.124
4.106
4.100
4.081
4.075
4.056
3.928
3.921
3.911
3.904
3.781
3.766
3.750
3.517
3.506
3.495
3.332
2.509
2.505
2.500
2.495
2.491
2.289
HO
OH
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N
O
S
OH
O
O
O
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6.5
6.0
5.5
5.0
4.5
4.0
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1.0
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ppm
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0.99
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1.02
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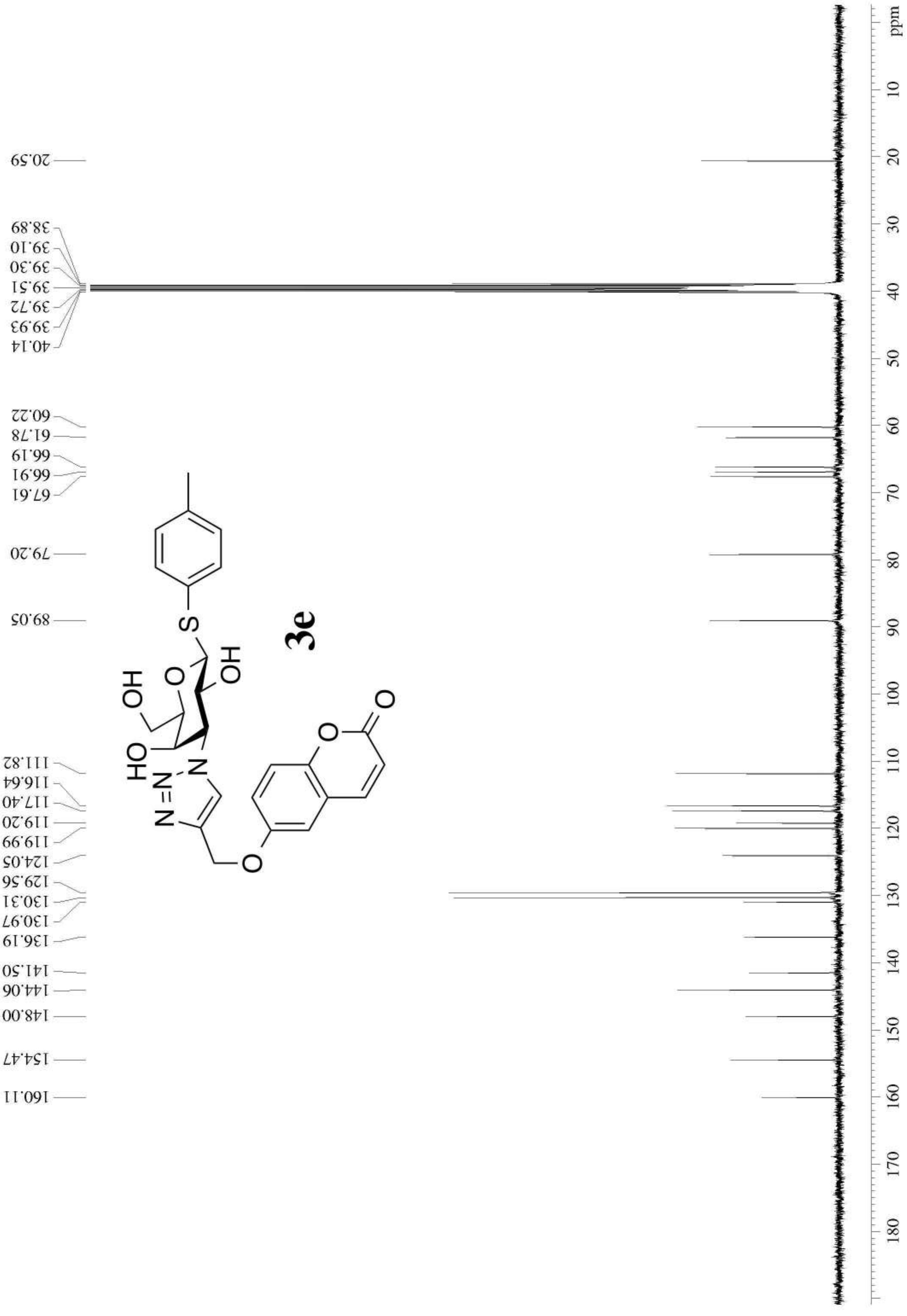
3.11

3e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67.61
79.20
89.05
111.82
116.64
117.40
119.20
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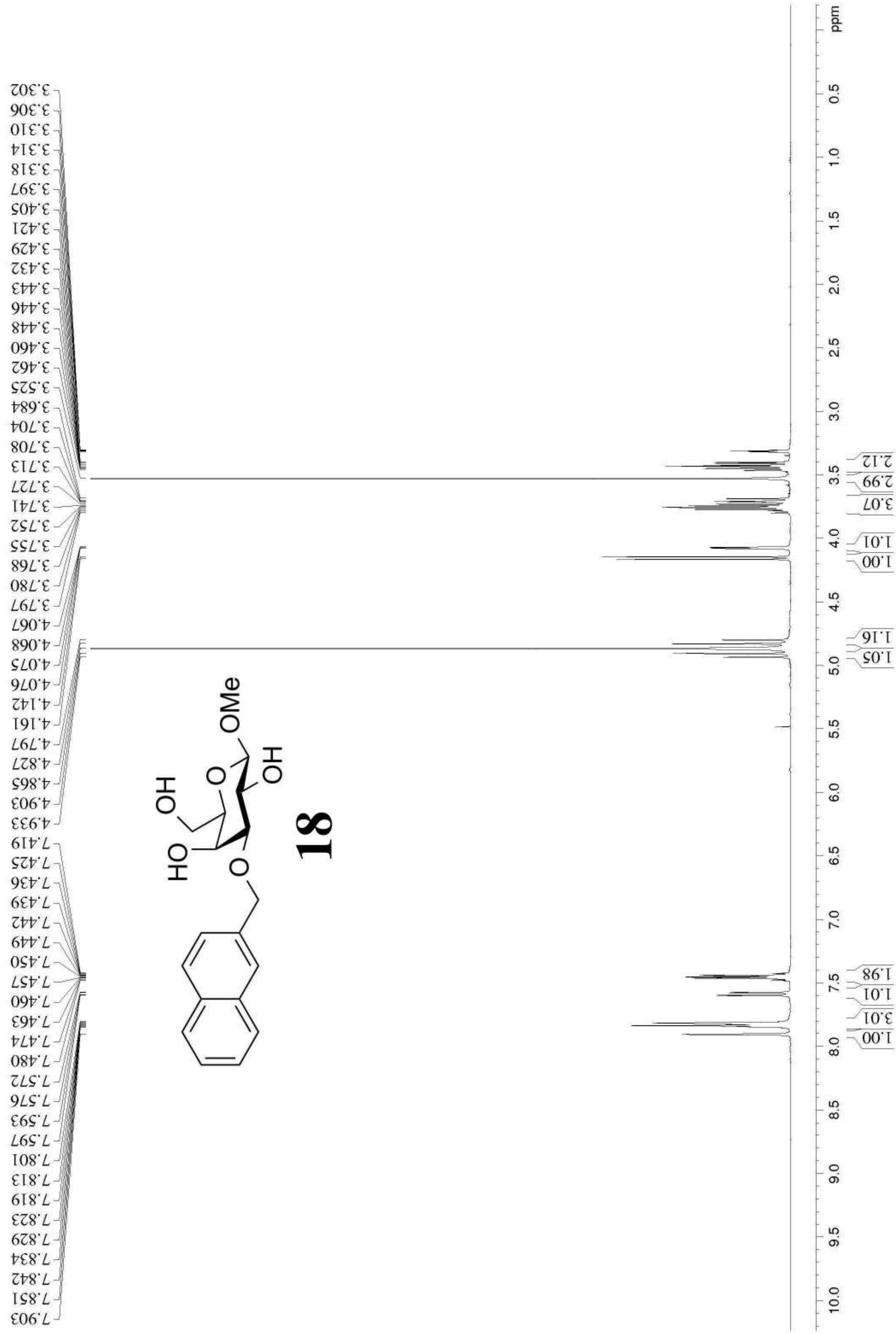
160.11
3e
ppm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3.405
3.421
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3.432
3.443
3.446
3.448
3.460
3.462
3.525
3.684
3.704
3.708
3.713
3.727
3.741
3.752
3.755
3.768
3.780
3.797
4.067
4.068
4.075
4.076
4.142
4.161
4.797
4.827
4.865
4.903
4.933
7.419
7.425
7.436
7.439
7.442
7.449
7.450
7.457
7.460
7.463
7.474
7.480
7.572
7.576
7.593
7.597
7.801
7.813
7.819
7.823
7.829
7.834
7.842
7.851
7.903
OMe
OH
HO
O
18
2.12
2.99
3.07
1.01
1.00
1.16
1.05
1.98
1.01
3.01
1.00
ppm
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1.0
1.5
2.0
2.5
3.0
3.5
4.0
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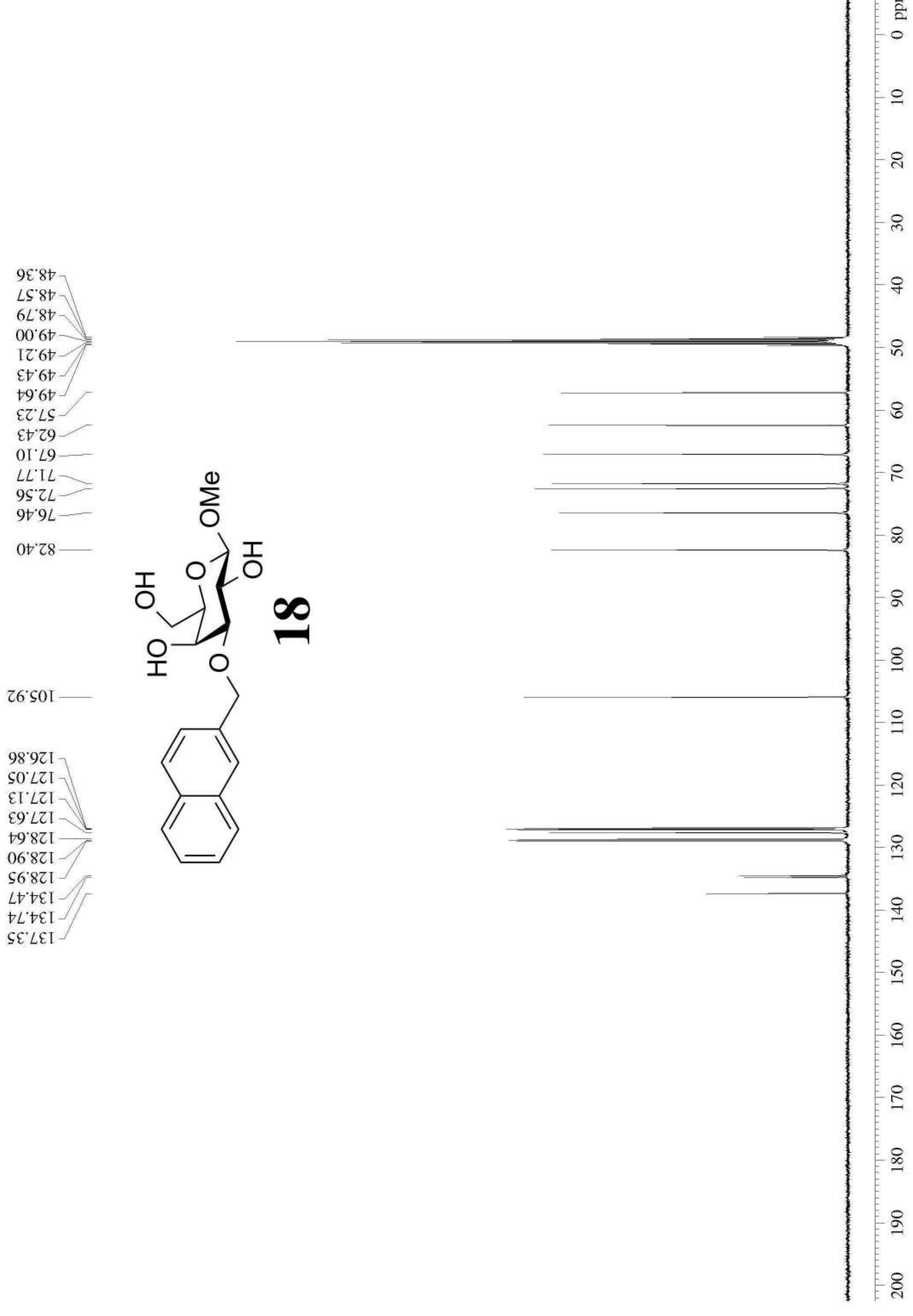
10.0



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76.46
82.40
105.92
126.86
127.05
127.13
127.63
128.64
128.90
128.95
134.47
134.74
137.35
HO
OH
O
OMe
OH
O
18
ppm
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10
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50
60
70
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90
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170
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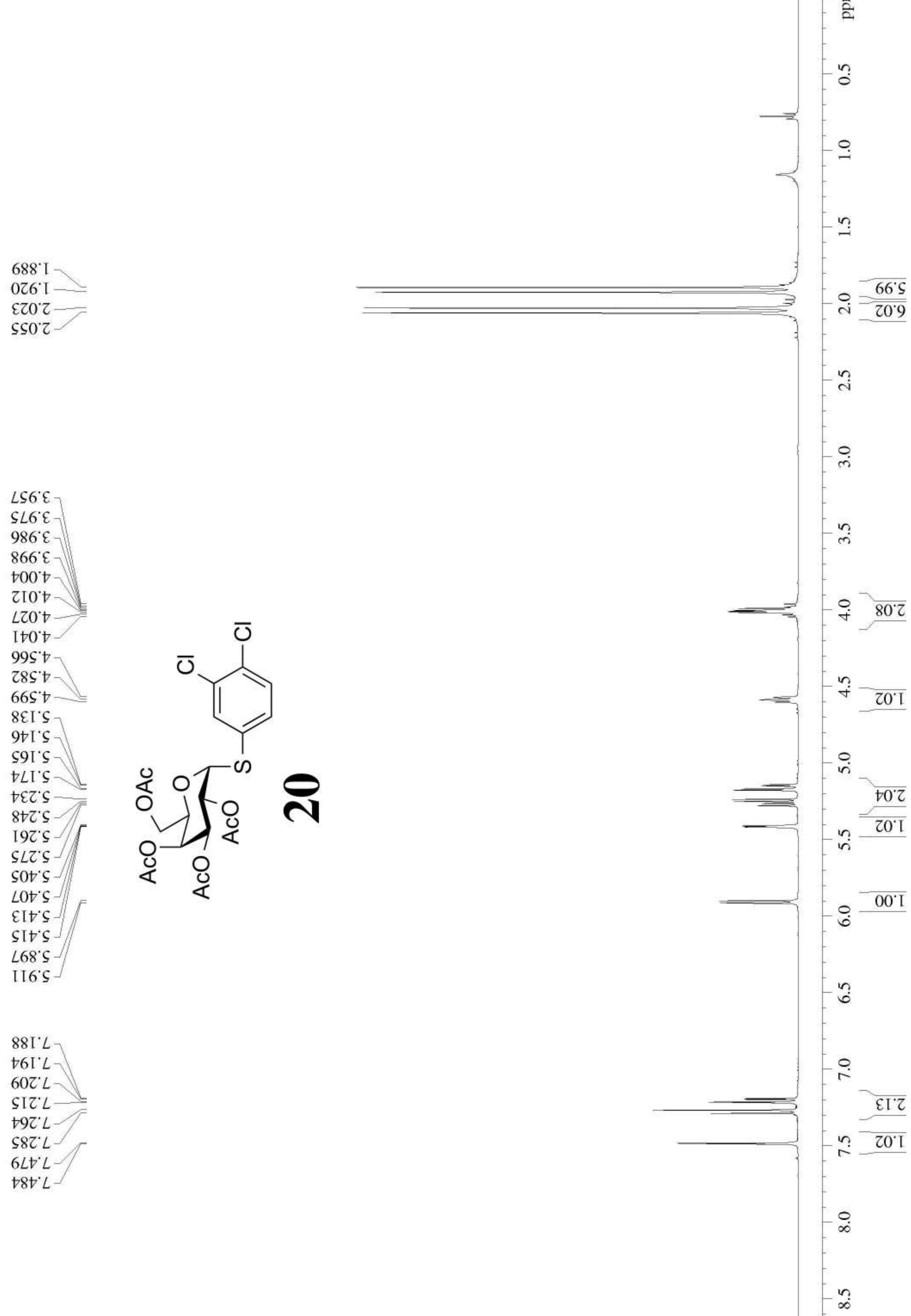
190
200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3.986
3.998
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4.012
4.027
4.041
4.566
4.582
4.599
5.138
5.146
5.165
5.174
5.234
5.248
5.261
5.275
5.405
5.407
5.413
5.415
5.897
5.911
7.188
7.194
7.209
7.215
7.264
7.285
7.479
7.484
AcO
OAc
AcO
AcO
O
S
Cl
Cl
20
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
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8.5
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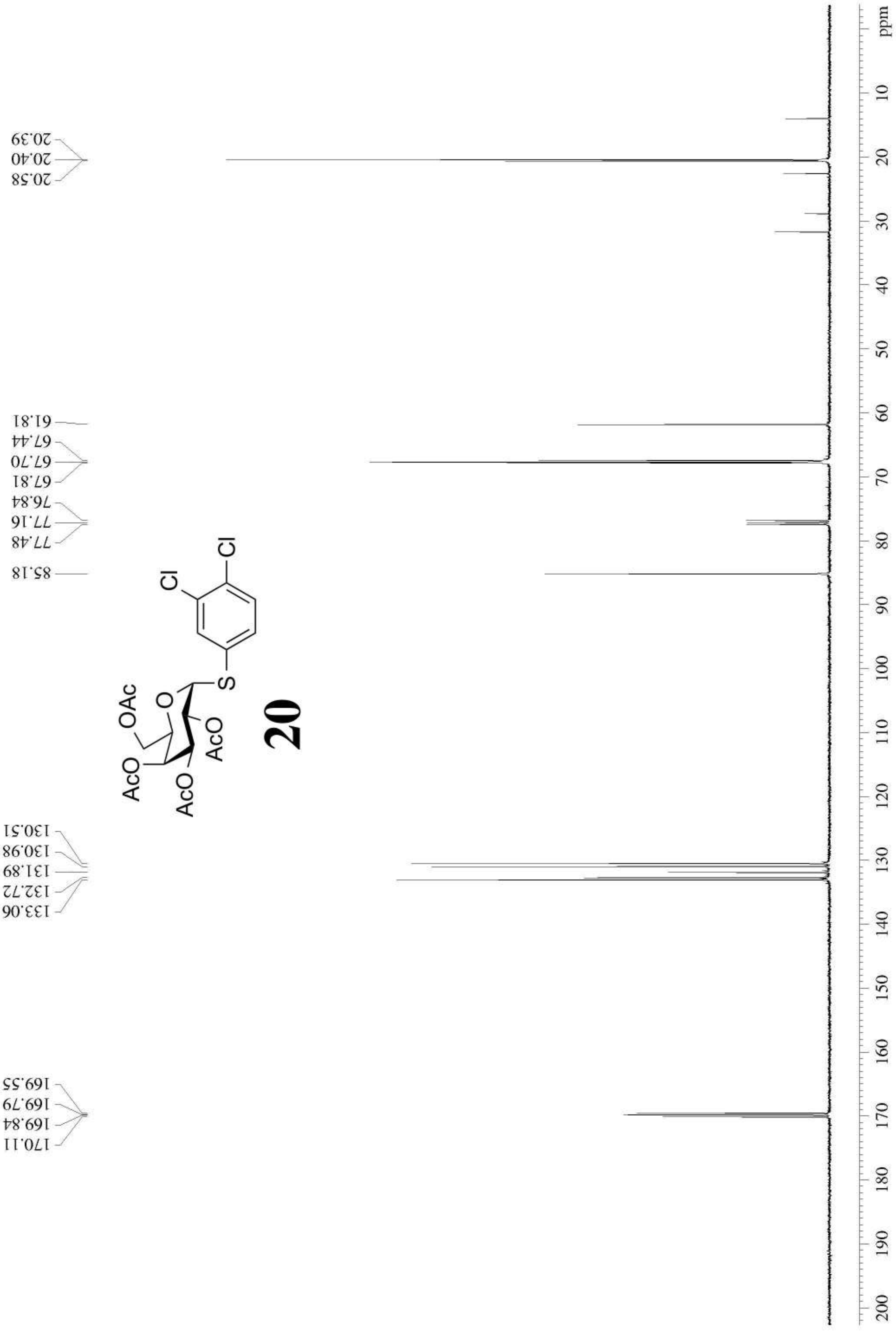
2.08
1.02
2.04
1.02
1.00
2.13
1.02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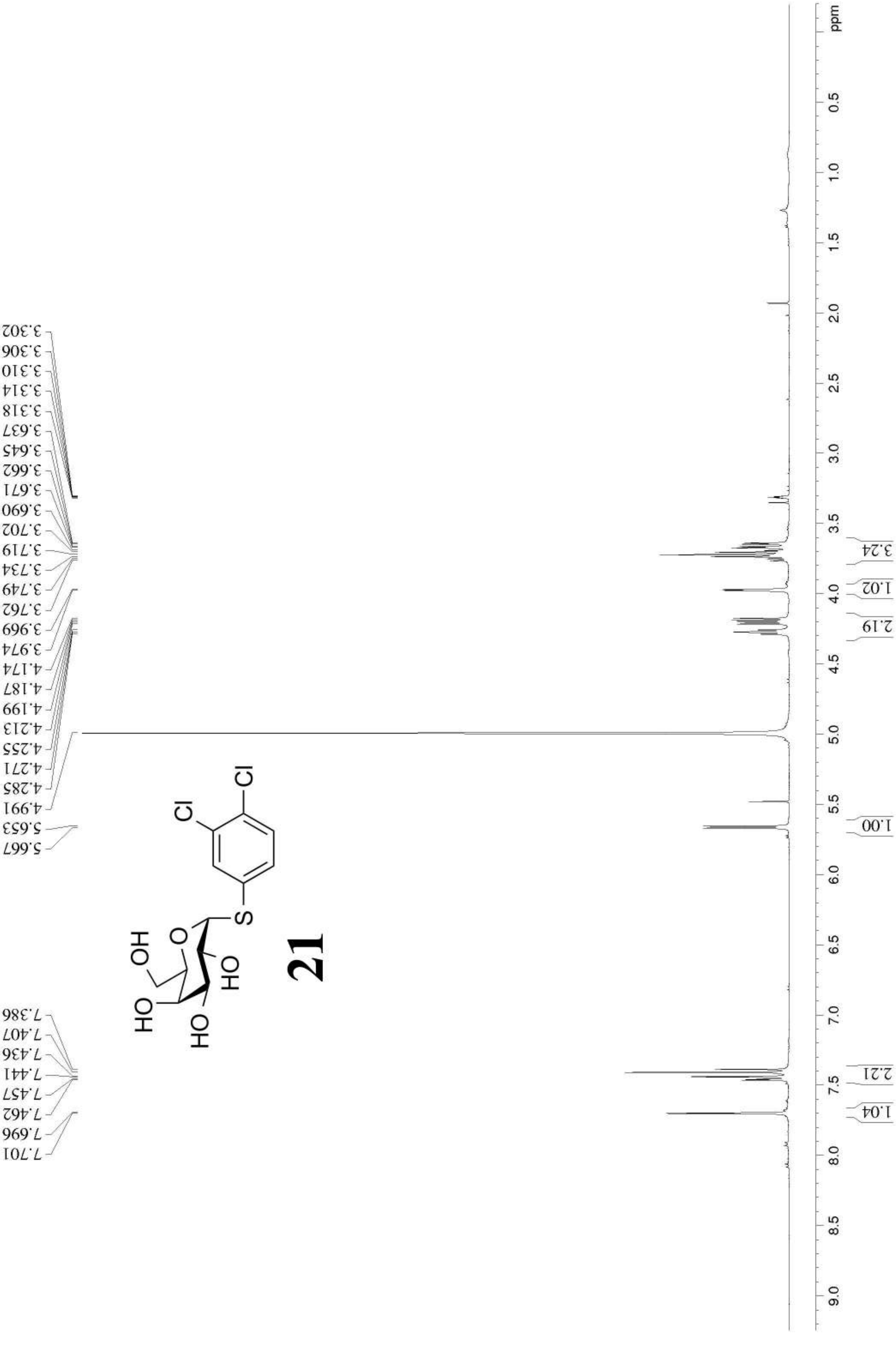
130.51
130.98
131.89
132.72
133.06
169.55
169.79
169.84
170.11
AcO
AcO
OAc
O
AcO
S
Cl
Cl
20
ppm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3.690
3.702
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3.734
3.749
3.762
3.969
3.974
4.174
4.187
4.199
4.213
4.255
4.271
4.285
4.991
5.653
5.667
7.386
7.407
7.436
7.441
7.457
7.462
7.696
7.701
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HO
OH
O
HO
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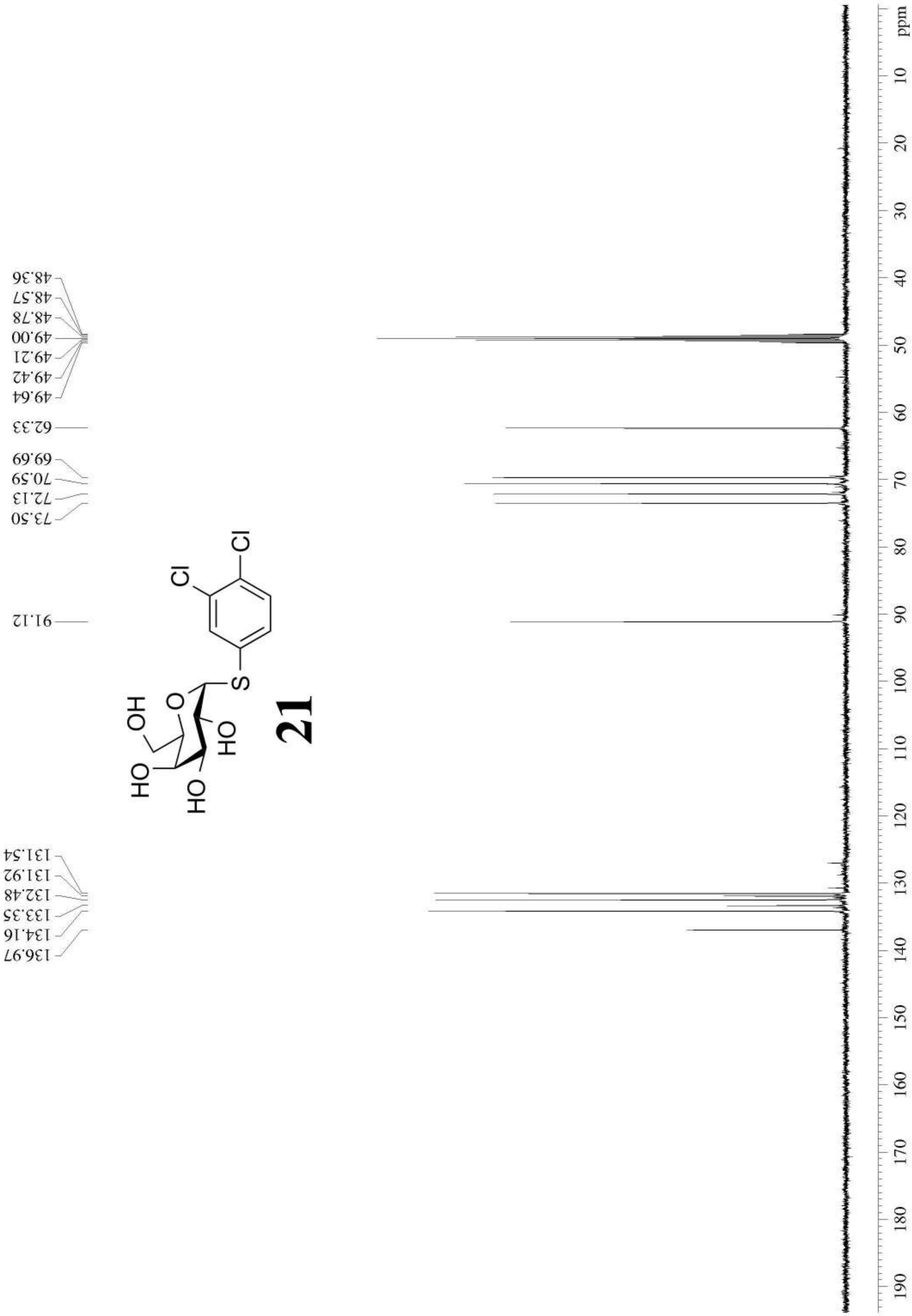
2.21
1.04
ppm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69.69
70.59
72.13
73.50
91.12
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131.92
132.48
133.35
134.16
136.97
Cl
Cl
S
OH
HO
HO
HO
O
21
ppm
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20
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40
50
60
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80
90
100
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120
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150
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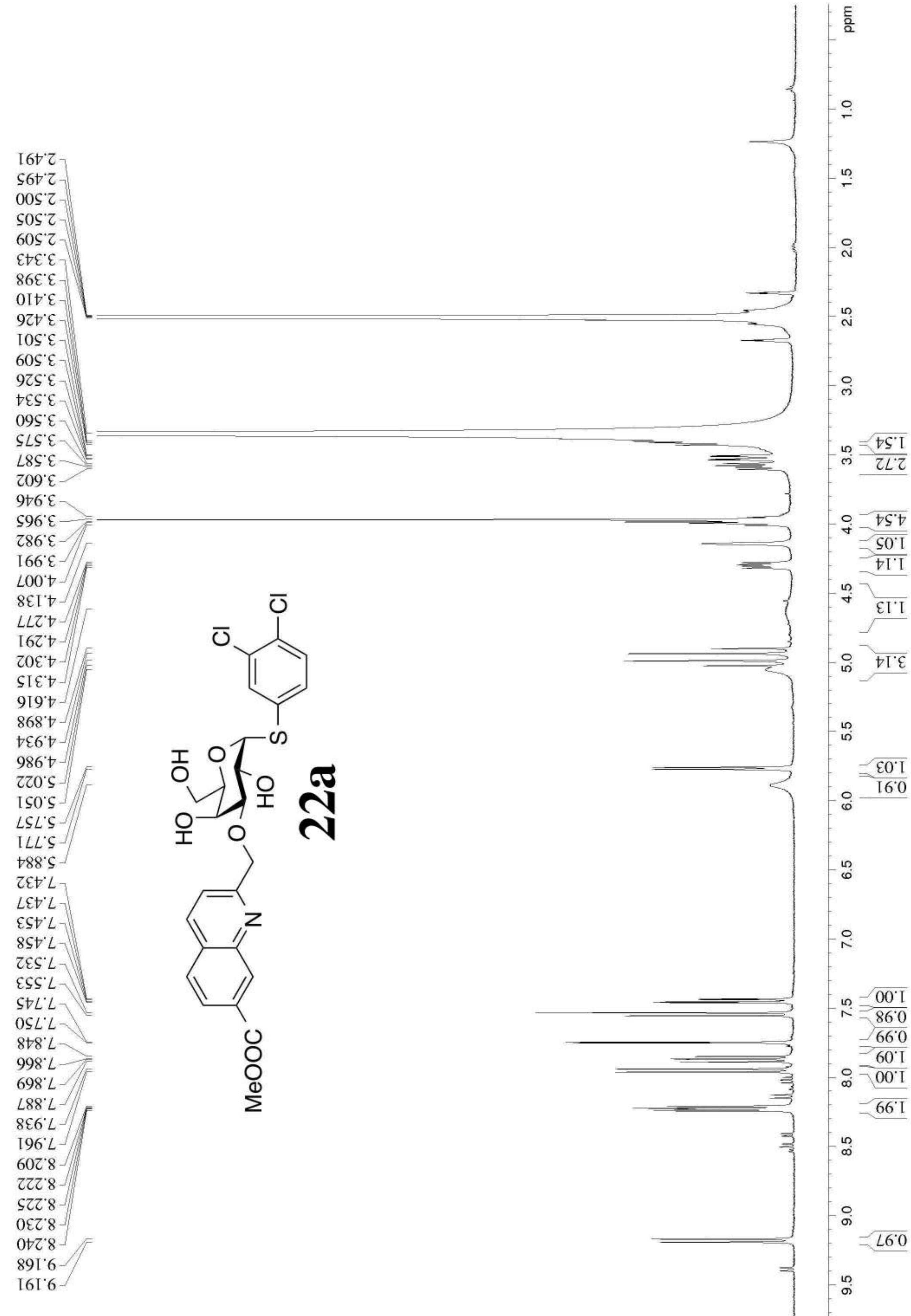
180
190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3.509
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3.534
3.560
3.575
3.587
3.602
3.946
3.965
3.982
3.991
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4.277
4.291
4.302
4.315
4.616
4.898
4.934
4.986
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5.771
5.884
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7.532
7.553
7.745
7.750
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7.866
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7.887
7.938
7.961
8.209
8.222
8.225
8.230
8.240
9.168
9.191
Cl
Cl
S
HO
OH
O
HO
O
N
MeOOC
1.54
2.72
4.54
1.05
1.14
1.13
3.14
1.03
0.91
1.00
0.98
0.99
1.09
1.00
1.99
0.97
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
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6.0
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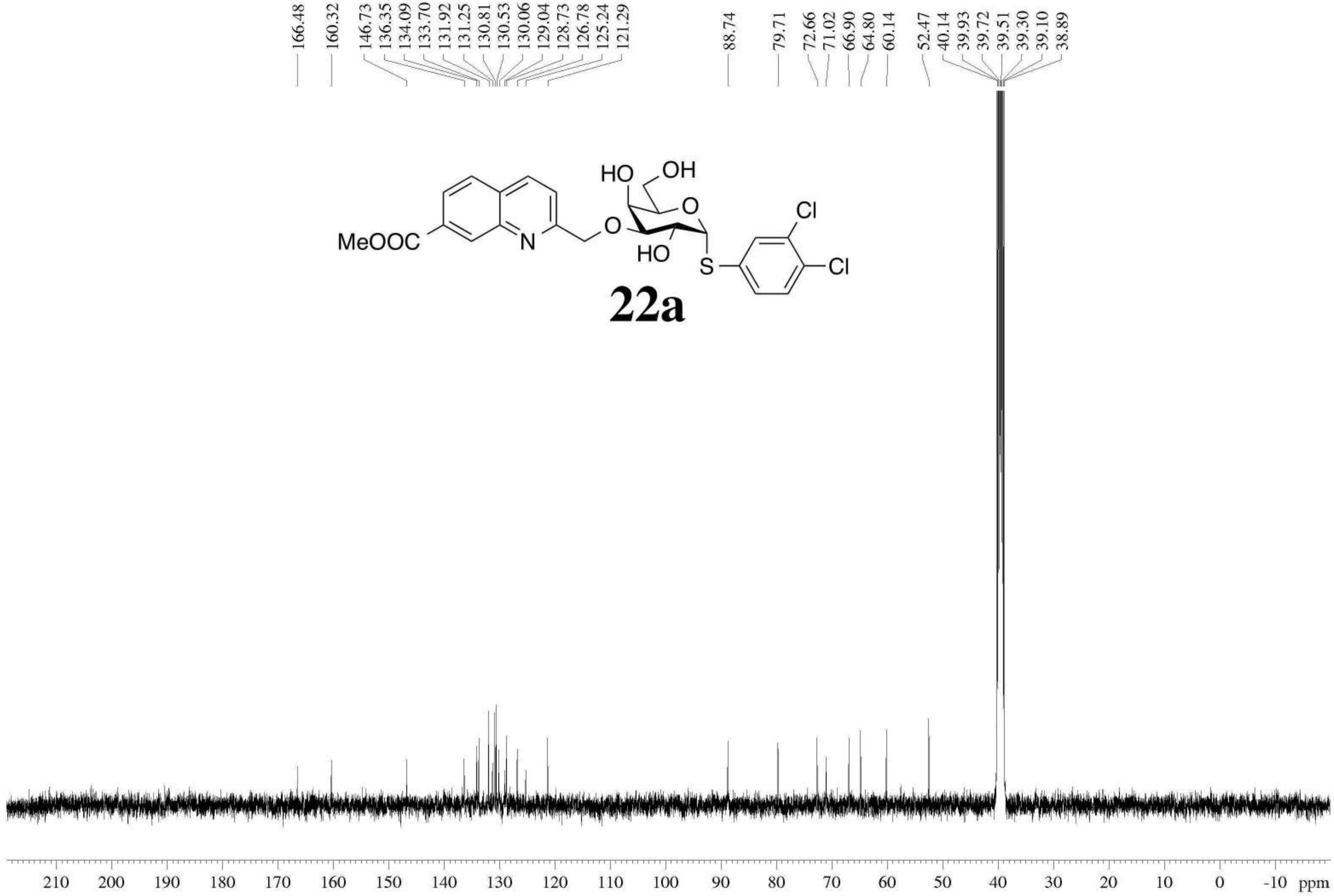
8.0
8.5
9.0
9.5

22a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131.25
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130.53
130.06
129.04
128.73
126.78
125.24
121.29
88.74
79.71
72.66
71.02
66.90
64.80
60.14
52.47
40.14
39.93
39.72
39.51
39.30
39.10
38.89
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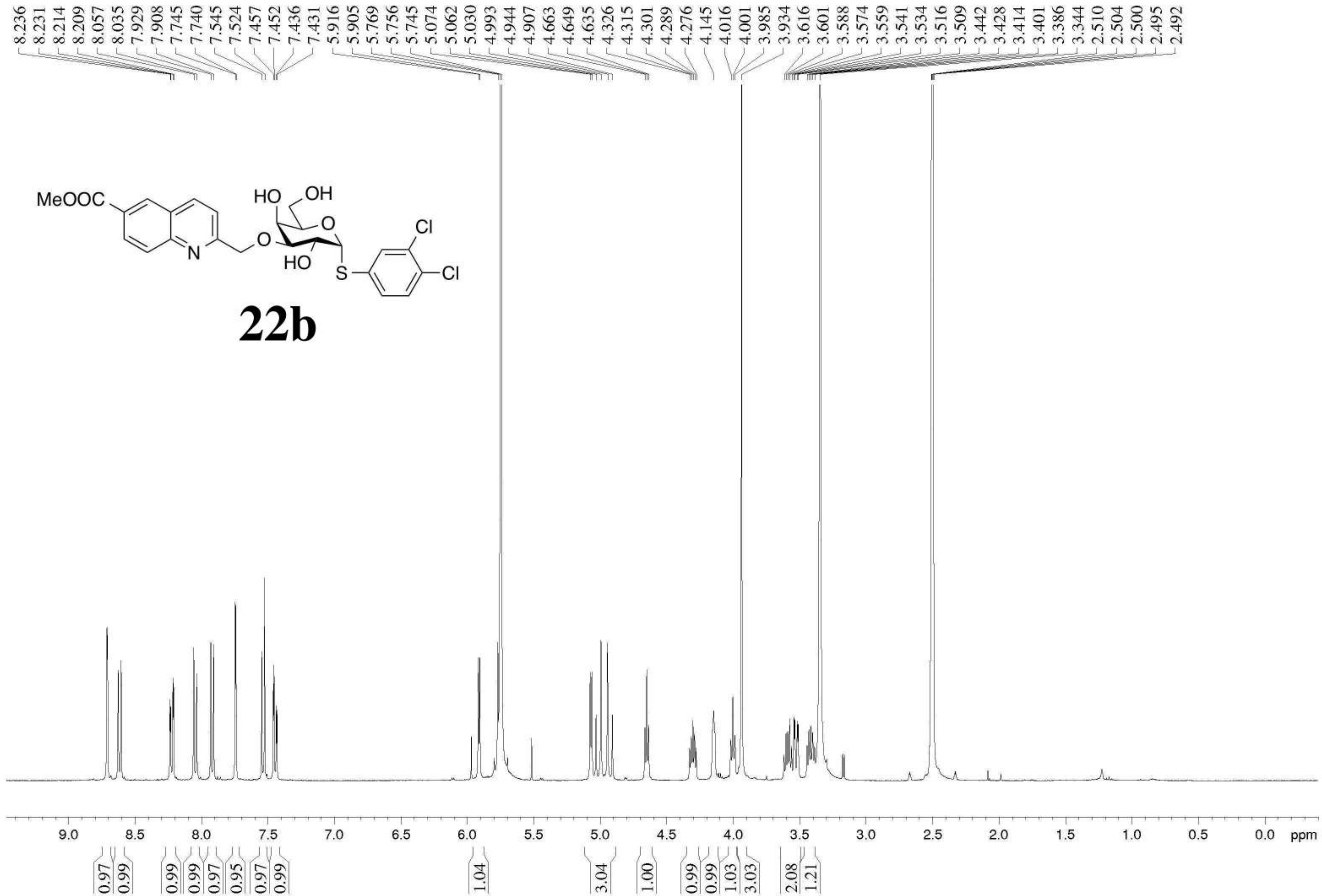
N
O
HO
OH
HO
S
Cl
Cl
22a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm



8.236 8.231 8.214 8.209 8.057 8.035 7.929 7.908 7.745 7.740 7.545 7.524 7.457 7.452 7.436 7.431 5.916 5.905 5.769 5.756 5.745 5.074 5.062 5.030 4.993 4.944 4.907 4.663 4.649 4.635 4.326 4.315 4.301 4.289 4.276 4.145 4.016 4.001 3.985 3.934 3.616 3.601 3.588 3.574 3.559 3.541 3.534 3.516 3.509 3.442 3.428 3.414 3.401 3.386 3.344 2.510 2.504 2.500 2.495 2.492
MeOOC
HO
OH
O
N
O
HO
S
Cl
Cl
22b
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
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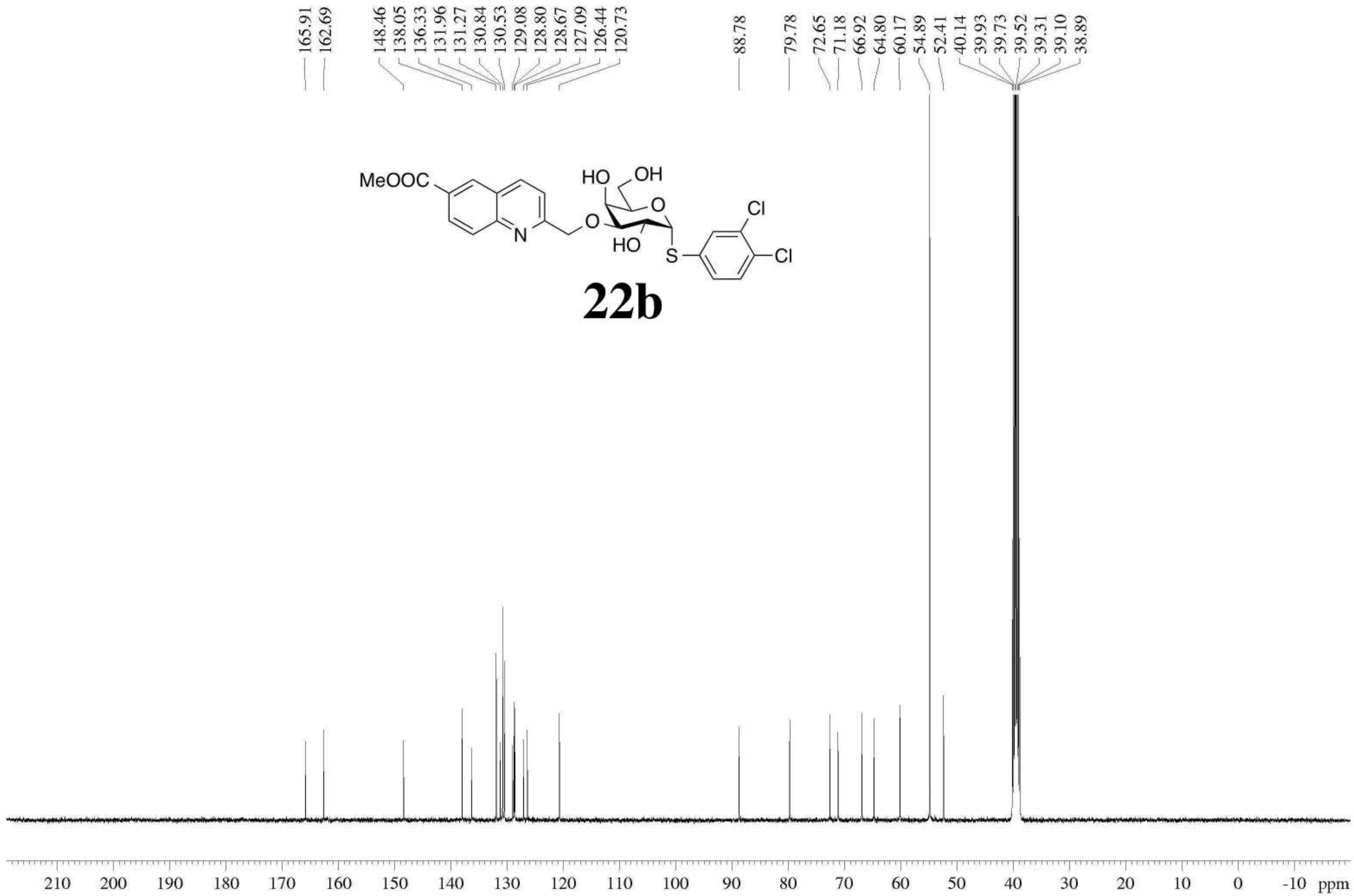
22b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HO
OH
O
N
O
HO
S
Cl
Cl
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162.69
148.46
138.05
136.33
131.96
131.27
130.84
130.53
129.08
128.80
128.67
127.09
126.44
120.73
88.78
79.78
72.65
71.18
66.92
64.80
60.17
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52.41
40.14
39.93
39.73
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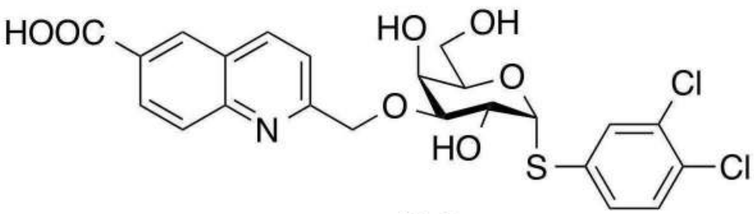
39.31
39.10
38.89
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

22b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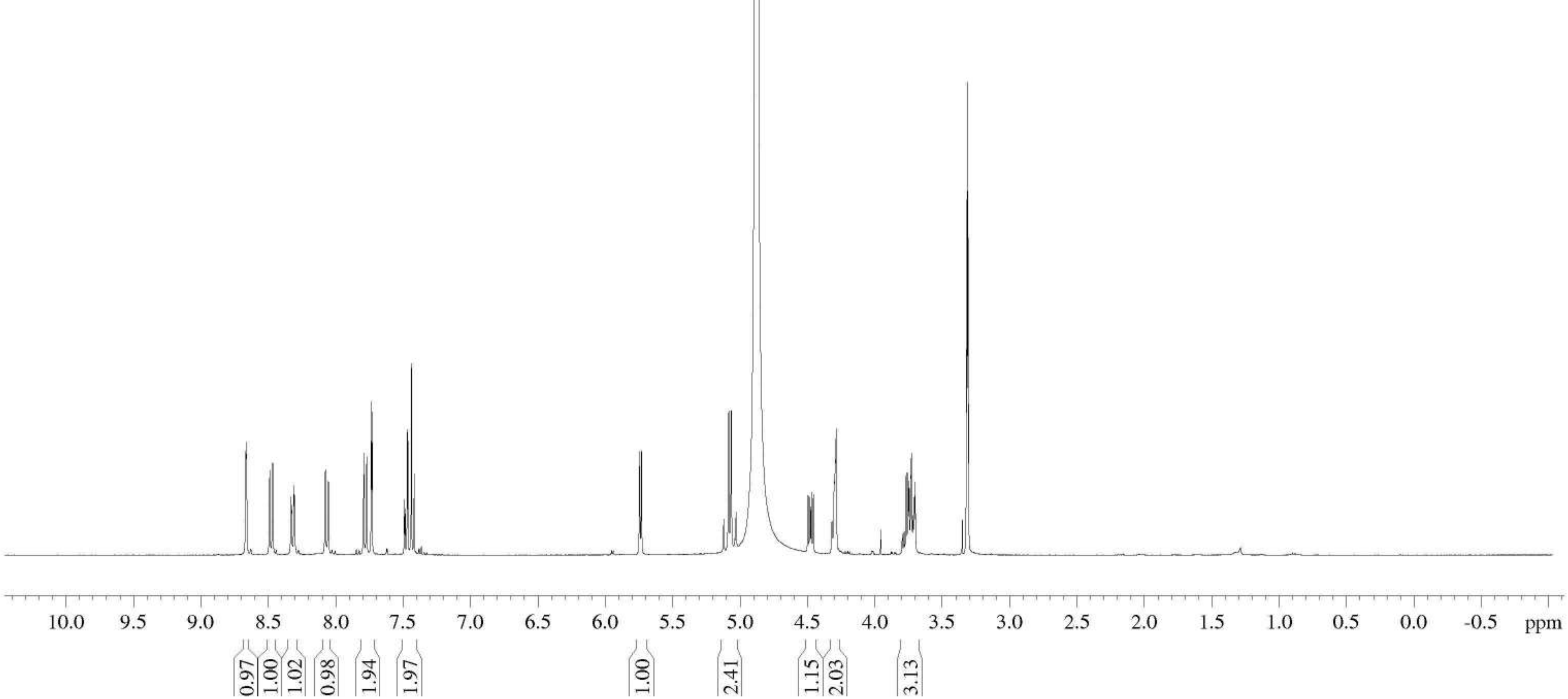
N
O
HO
OH
O
HO
S
Cl
Cl

23a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7.462
7.437
7.416
5.744
5.730
5.119
5.082
5.064
5.027
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4.293
4.290
4.285
3.794
3.781
3.766
3.752
3.744
3.731
3.727
3.715
3.706
3.699
3.318
3.314
3.310
3.306
3.302
10.0
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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
-0.5
ppm
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1.02
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1.97
1.00
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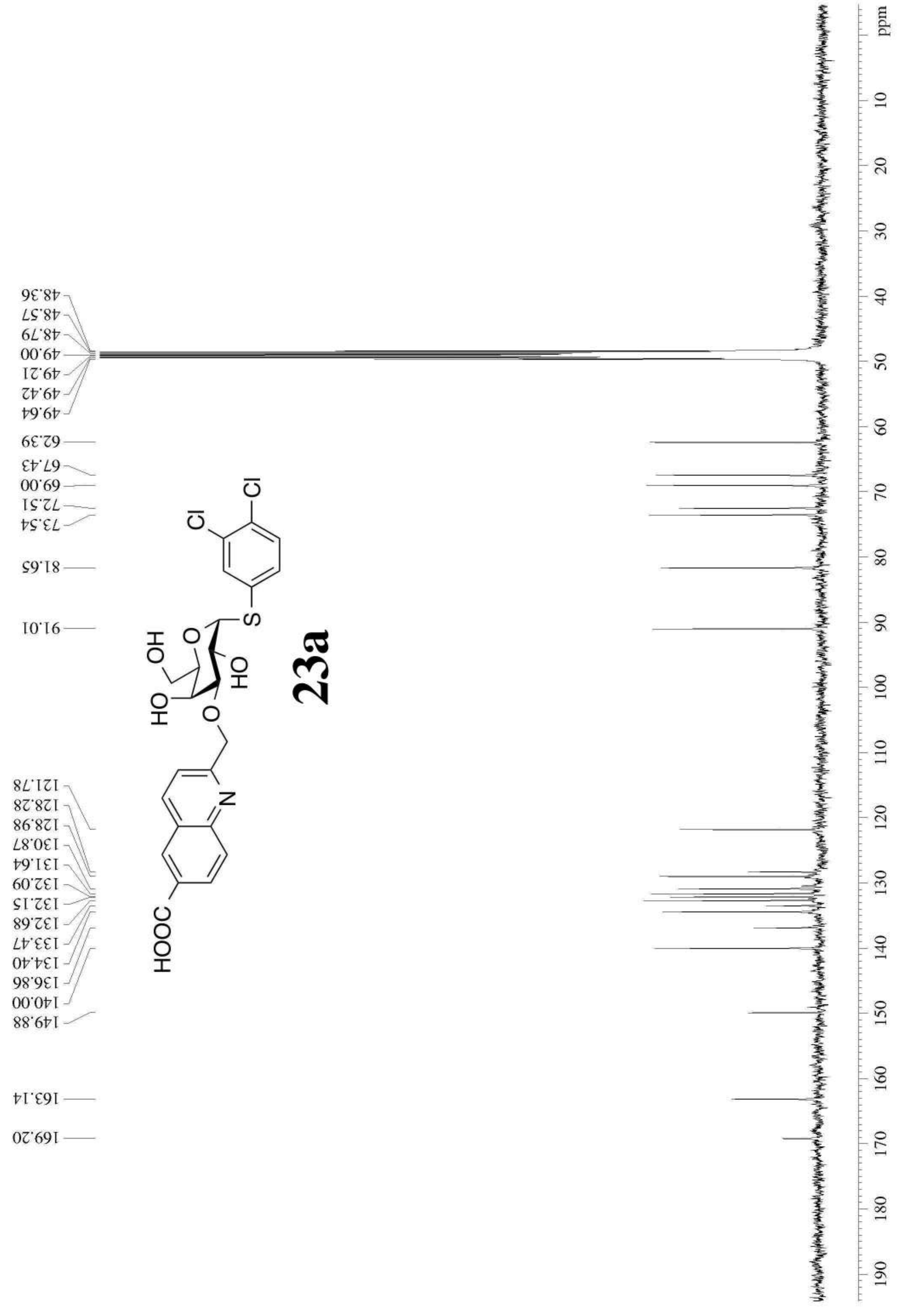
1.15
2.03
3.13



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67.43
69.00
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73.54
81.65
91.01
121.78
128.28
128.98
130.87
131.64
132.09
132.15
132.68
133.47
134.40
136.86
140.00
149.88
163.14
169.20
Cl
Cl
S
O
OH
HO
HO
O
N
HOOC
23a
ppm
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20
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40
50
60
70
80
90
100
110
120
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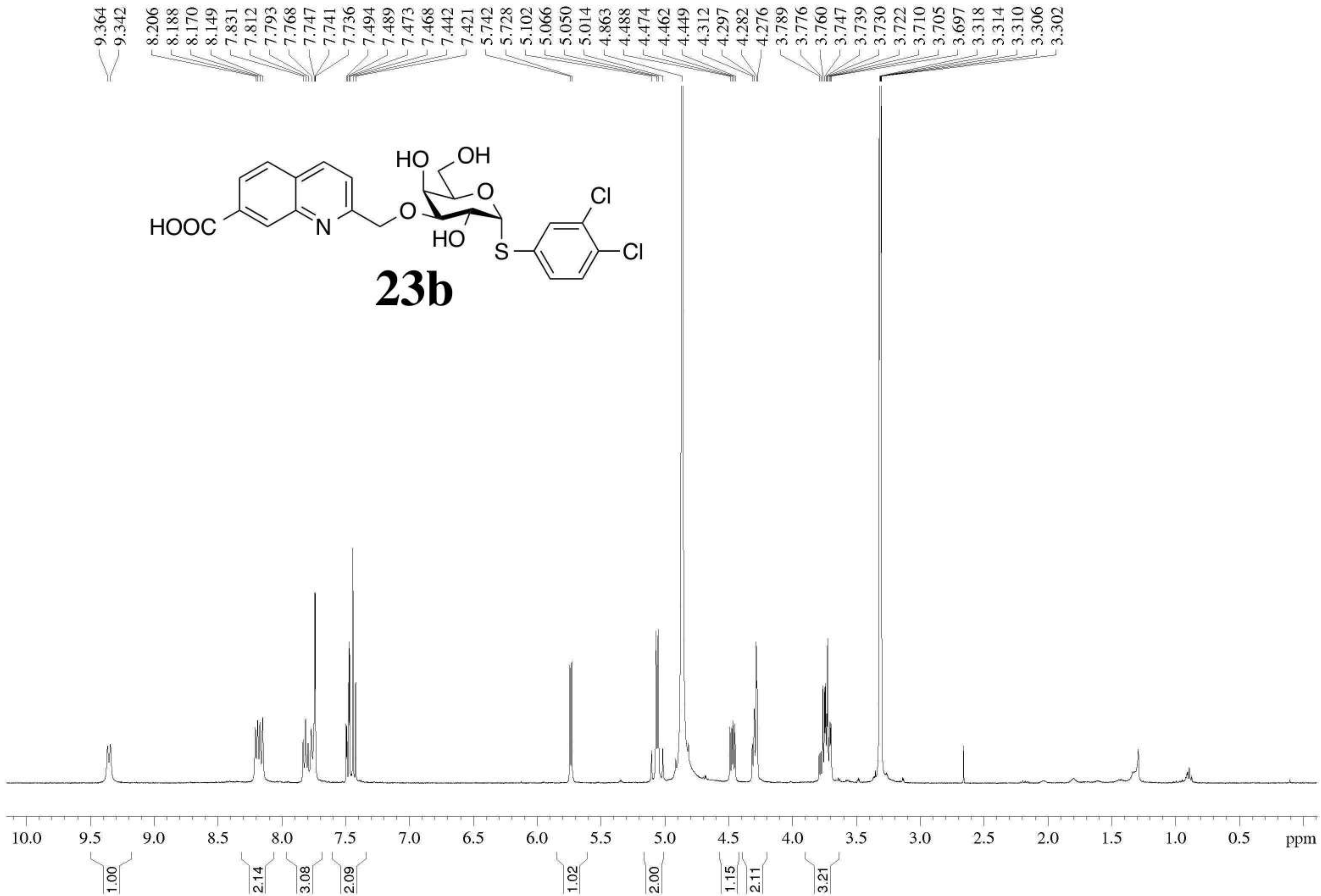
180
190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7.736
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7.489
7.473
7.468
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7.421
5.742
5.728
5.102
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5.050
5.014
4.863
4.488
4.474
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4.297
4.282
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3.730
3.722
3.710
3.705
3.697
3.318
3.314
3.310
3.306
3.302
HO
OH
O
Cl
HOOC
N
O
HO
S
Cl
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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2.09
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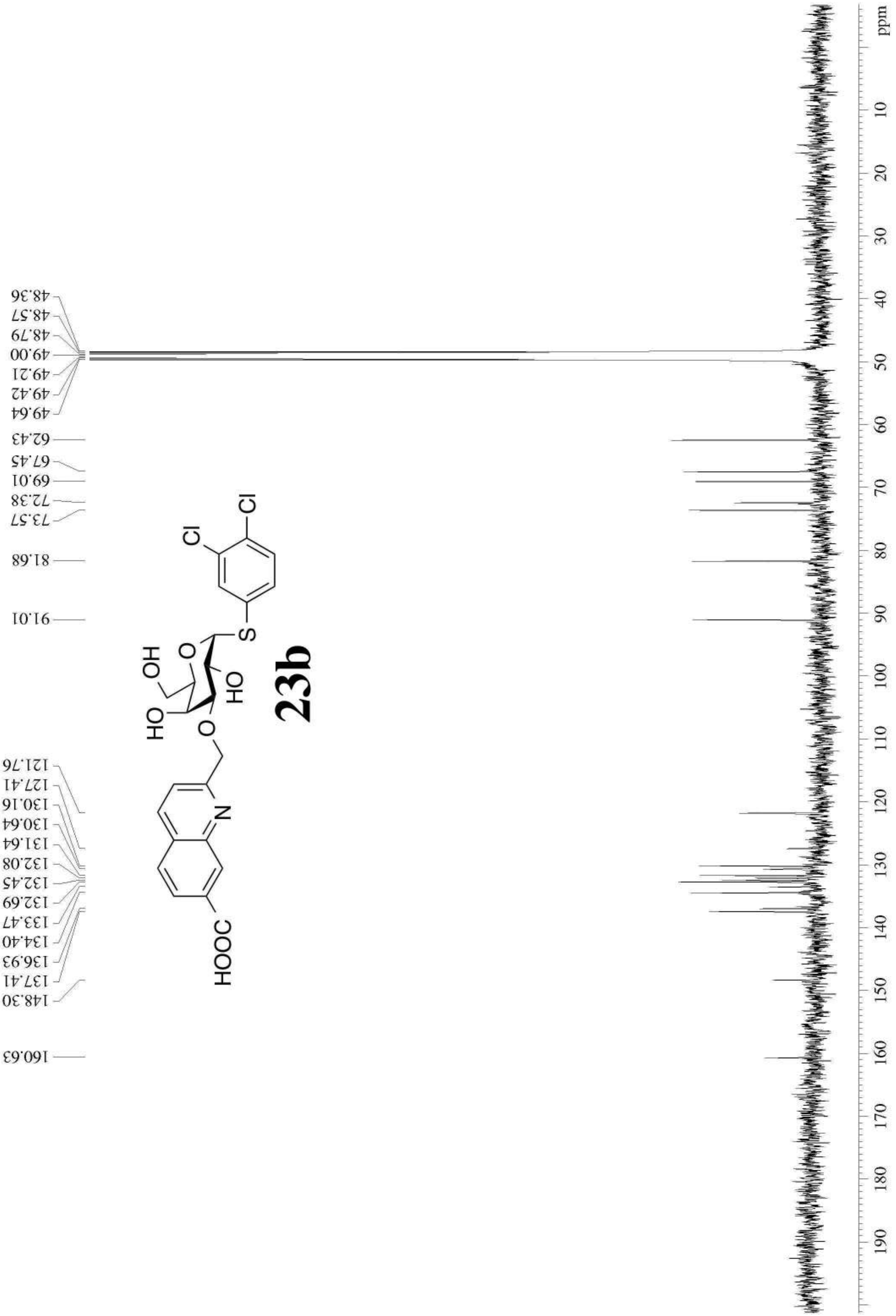
2.00
1.15
2.11
3.21

23b



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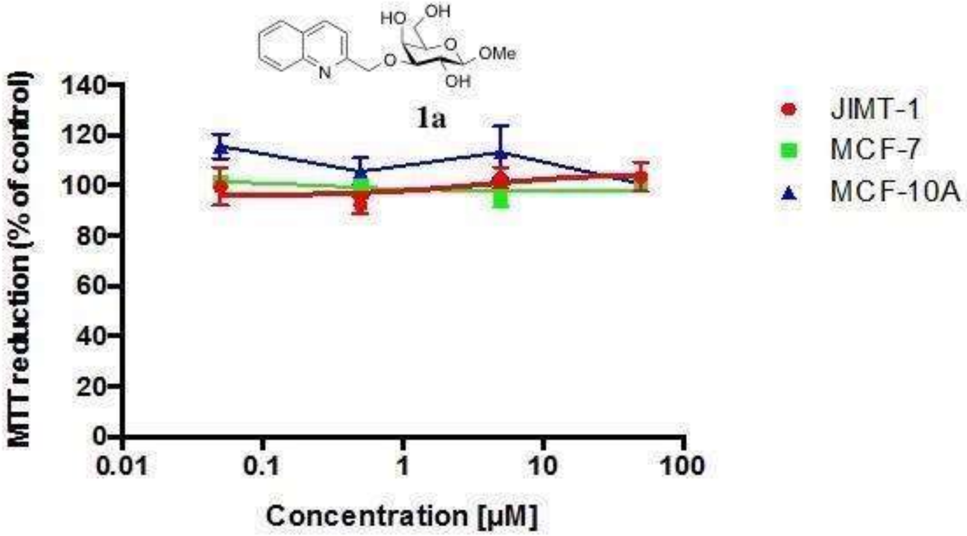
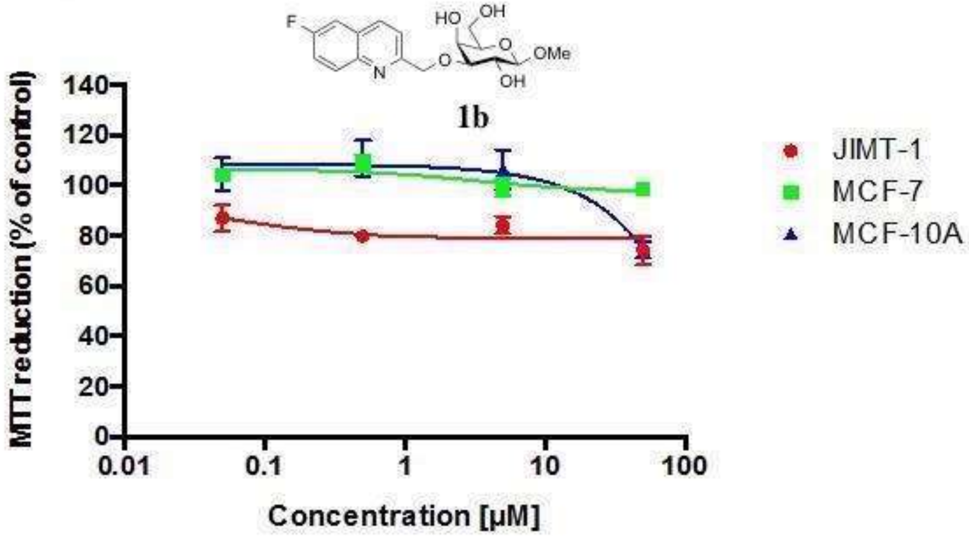
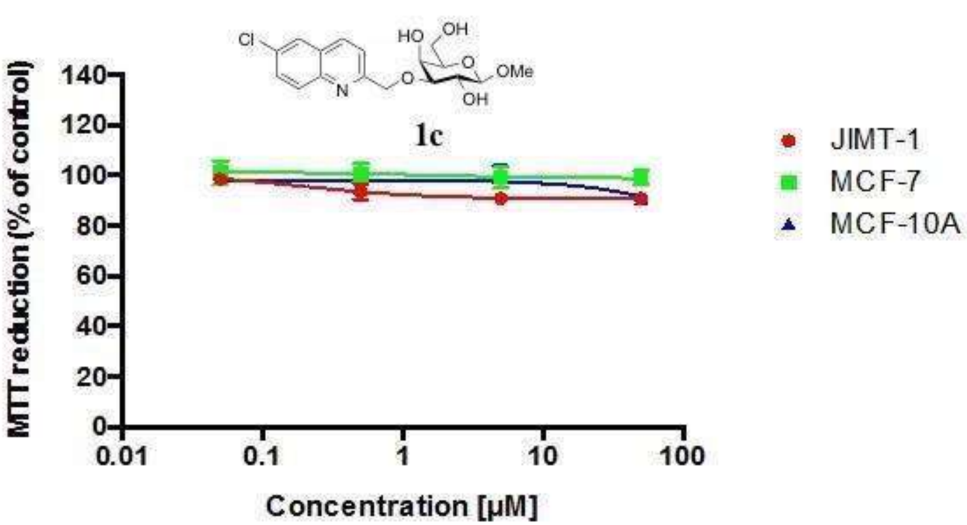
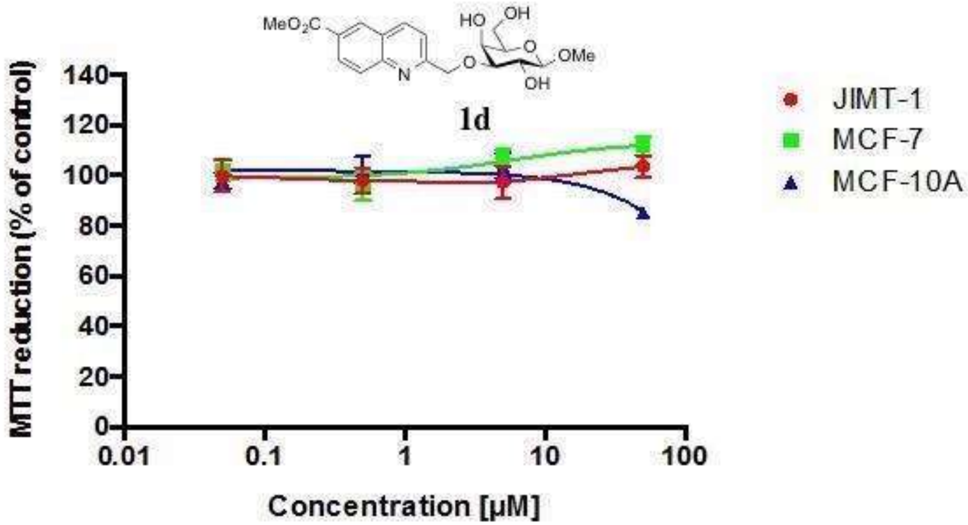
48.79
49.00
49.21
49.42
49.64
62.43
67.45
69.01
72.38
73.57
81.68
91.01
121.76
127.41
130.16
130.64
131.64
132.08
132.45
132.69
133.47
134.40
136.93
137.41
148.30
160.63
HOOC
N
O
HO
OH
HO
S
Cl
Cl
23b
ppm

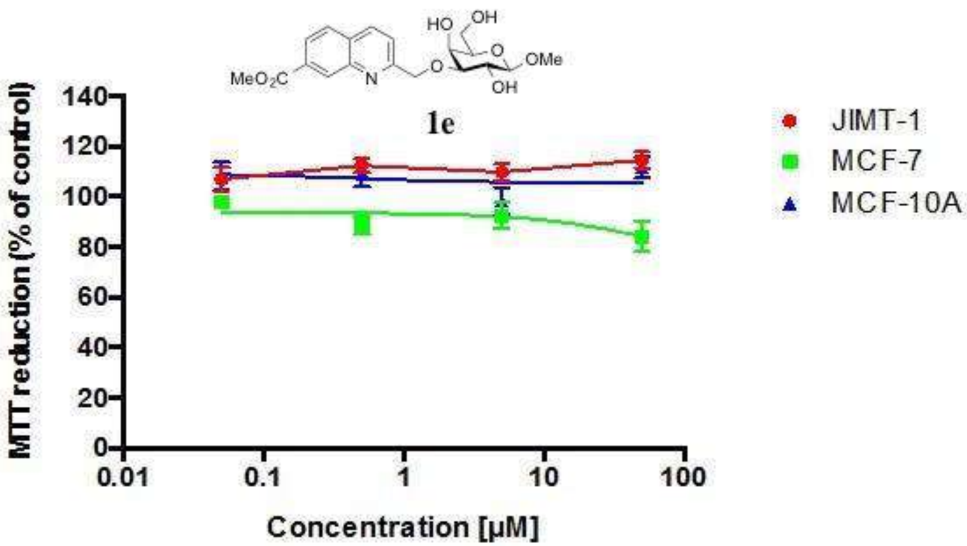
II. Figures of MTT Assay



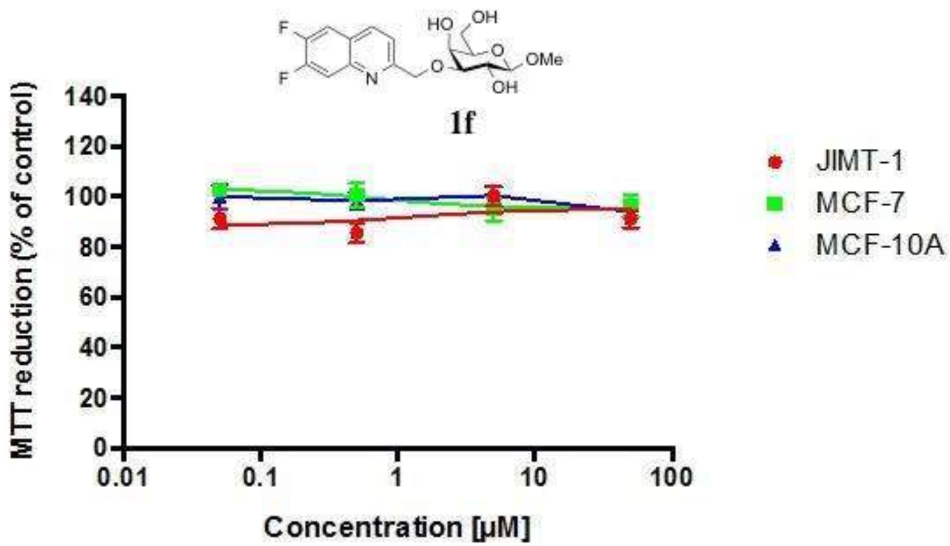




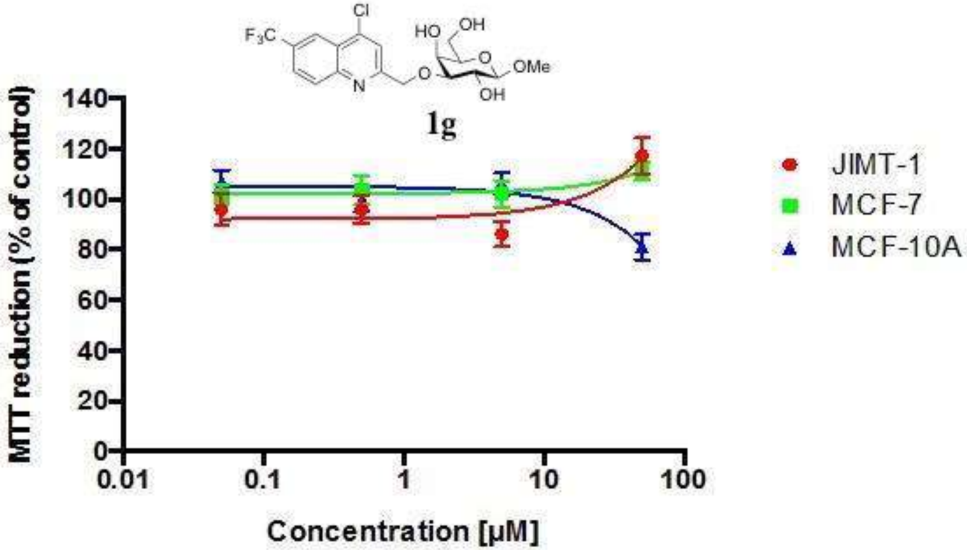




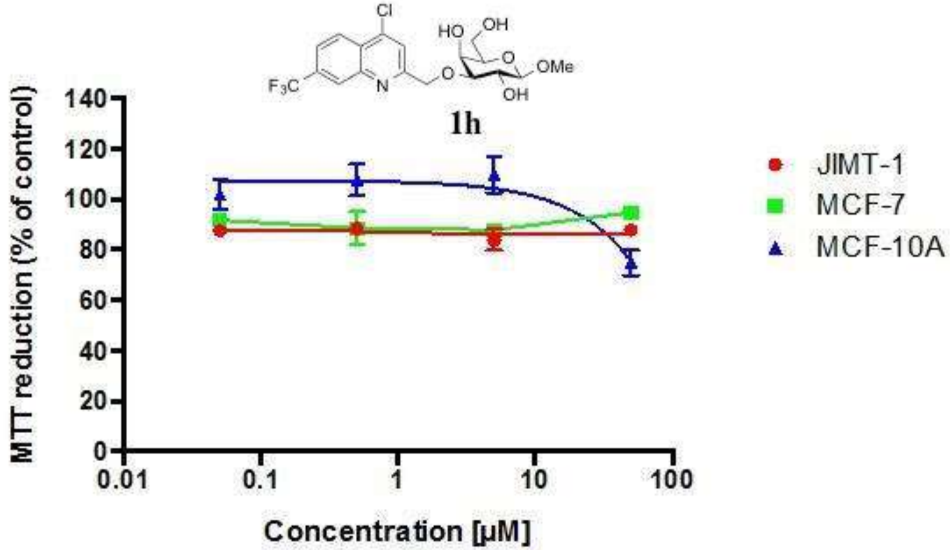
MeO2C
N
O
HO
OH
O
OMe
OH
1e
MTT reduction (% of control)
Concentration [μM]
0
20
40
60
80
100
120
140
0.01
0.1
1
10
100
JIMT-1
MCF-7
MCF-10A



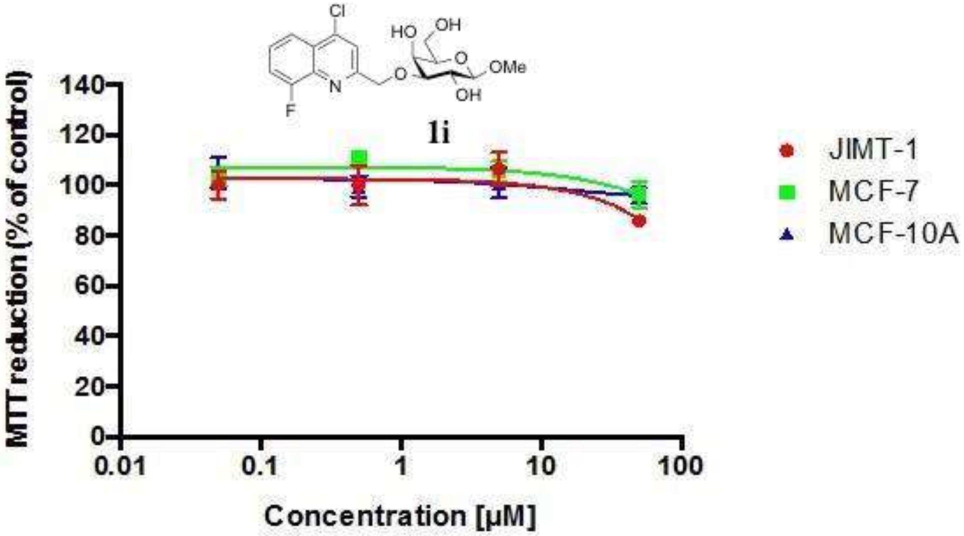
F
F
N
O
HO
OH
O
OMe
OH
1f
MTT reduction (% of control)
Concentration [μM]
0
20
40
60
80
100
120
140
0.01
0.1
1
10
100
JIMT-1
MCF-7
MCF-10A

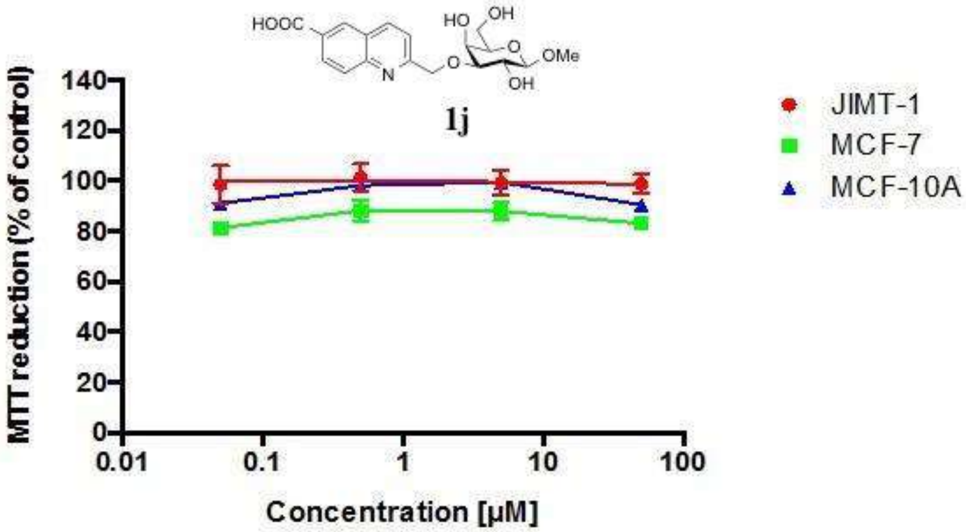


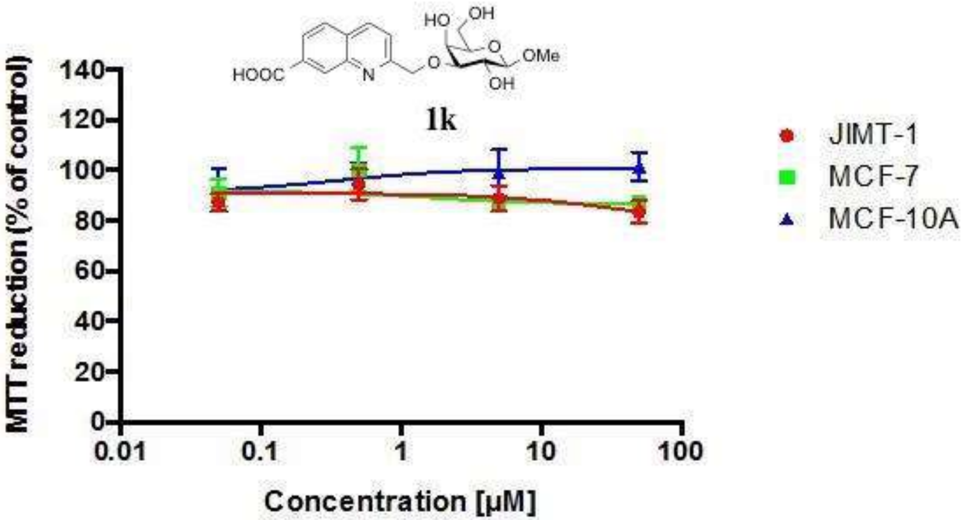
Cl
F3C
N
O
HO
OH
O
OMe
OH
1g
MTT reduction (% of control)
Concentration [μM]
0
20
40
60
80
100
120
140
0.01
0.1
1
10
100
JIMT-1
MCF-7
MCF-10A

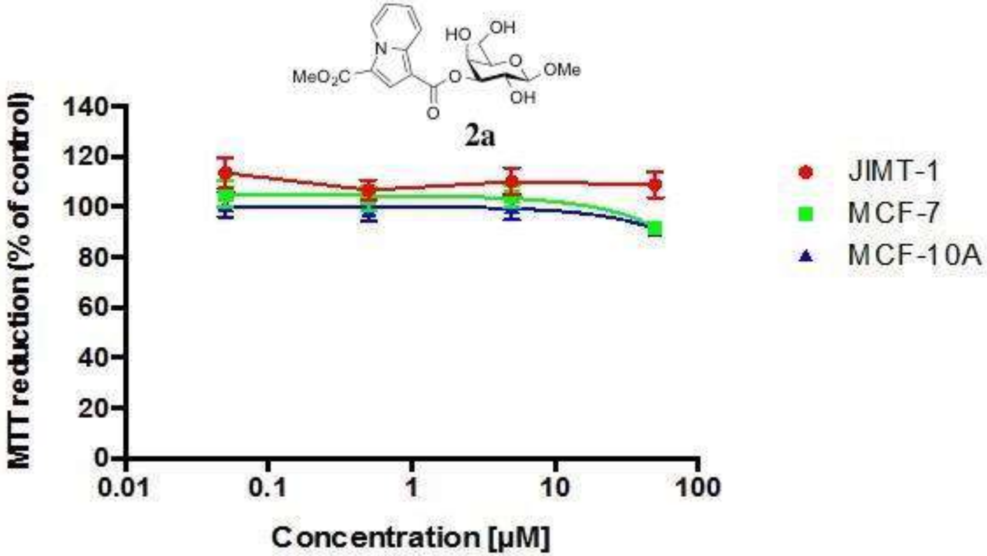


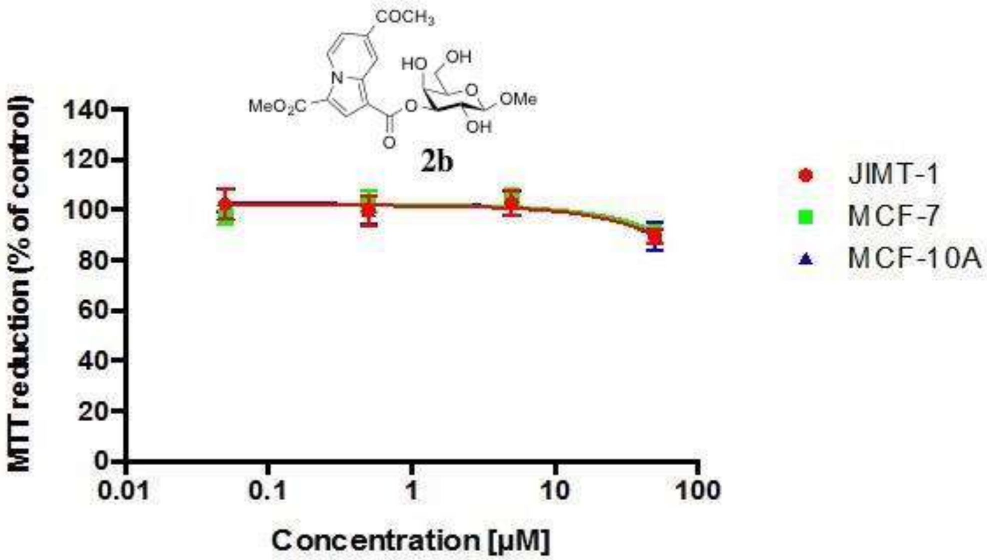
Cl
F3C
N
O
HO
OH
O
OMe
OH
1h
MTT reduction (% of control)
Concentration [μM]
0
20
40
60
80
100
120
140
0.01
0.1
1
10
100
JIMT-1
MCF-7
MCF-10A

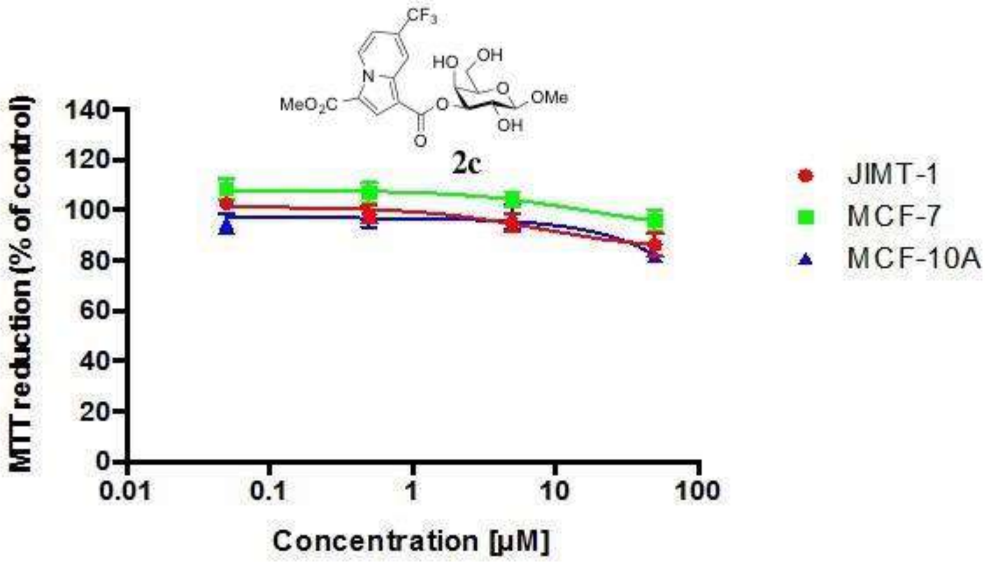

1i
MTT reduction (% of control)
Concentration [μM]
JIMT-1
MCF-7
MCF-10A

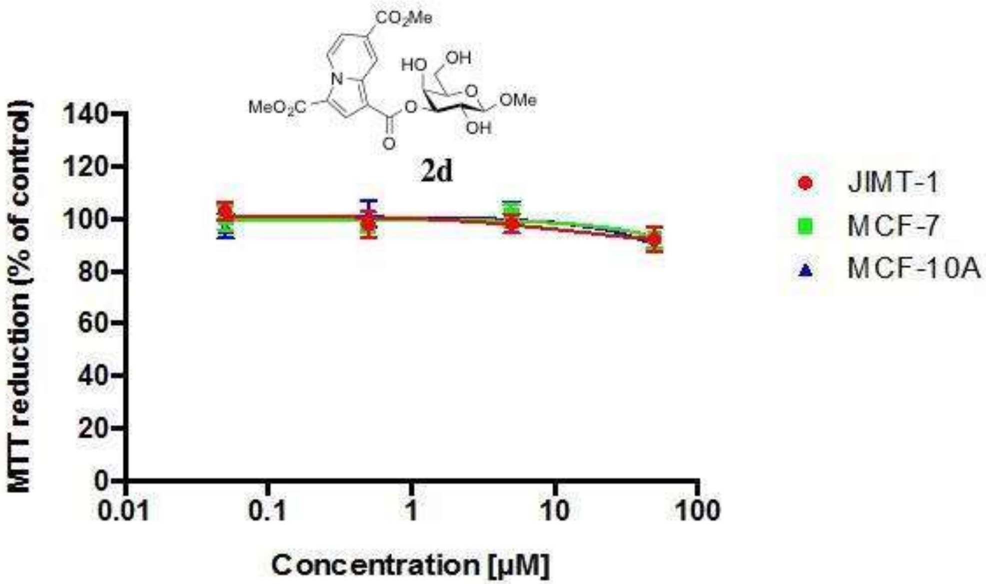

1j
MTT reduction (% of control)
Concentration [μM]
JIMT-1
MCF-7
MCF-10A

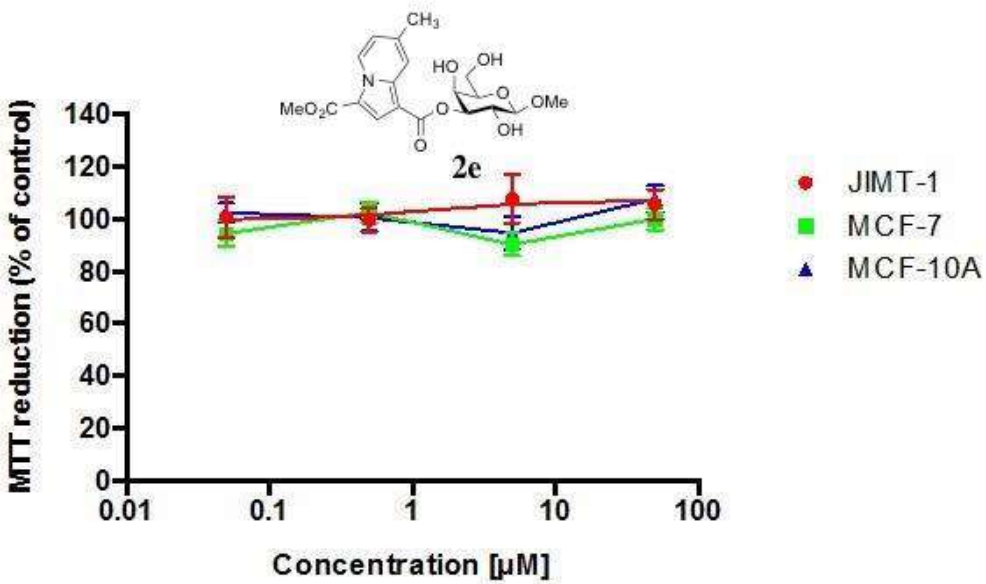

1k
MTT reduction (% of control)
Concentration [μM]
JIMT-1
MCF-7
MCF-10A

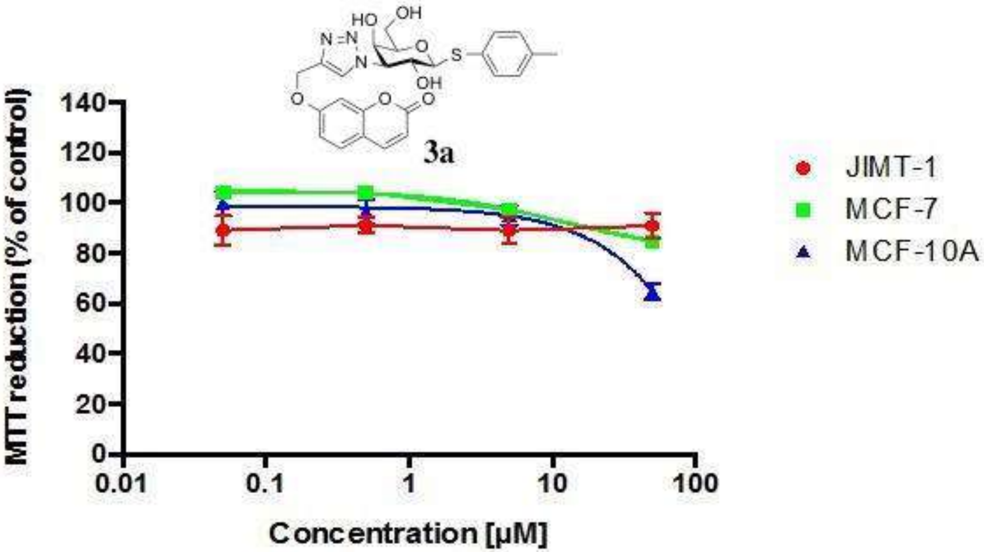

2a
MTT reduction (% of control)
Concentration [μM]
JIMT-1
MCF-7
MCF-10A

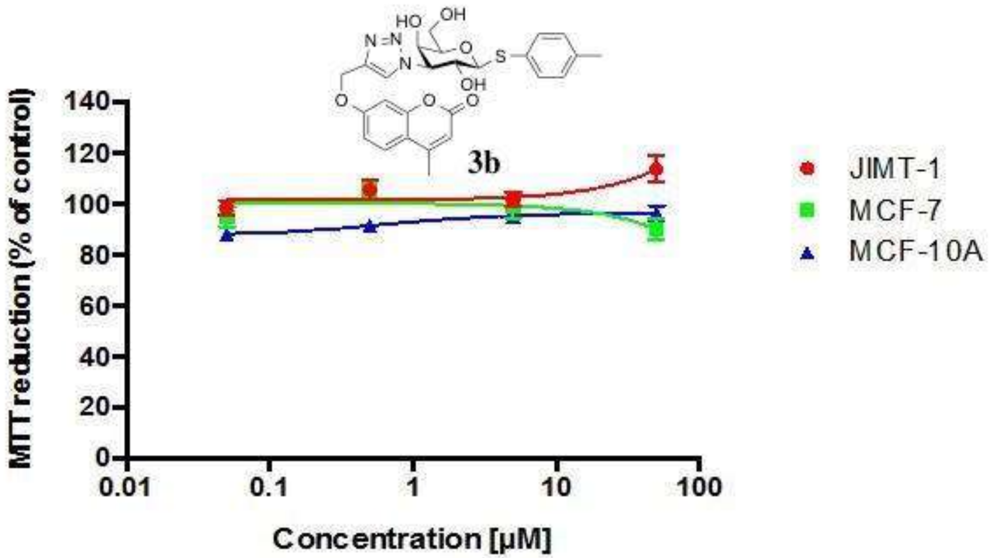

COCH3
HO
OH
MeO2C
OMe
OH
O
2b
MTT reduction (% of control)
140
120
100
80
60
40
20
0
0.01
0.1
1
10
100
Concentration [µM]
JIMT-1
MCF-7
MCF-10A

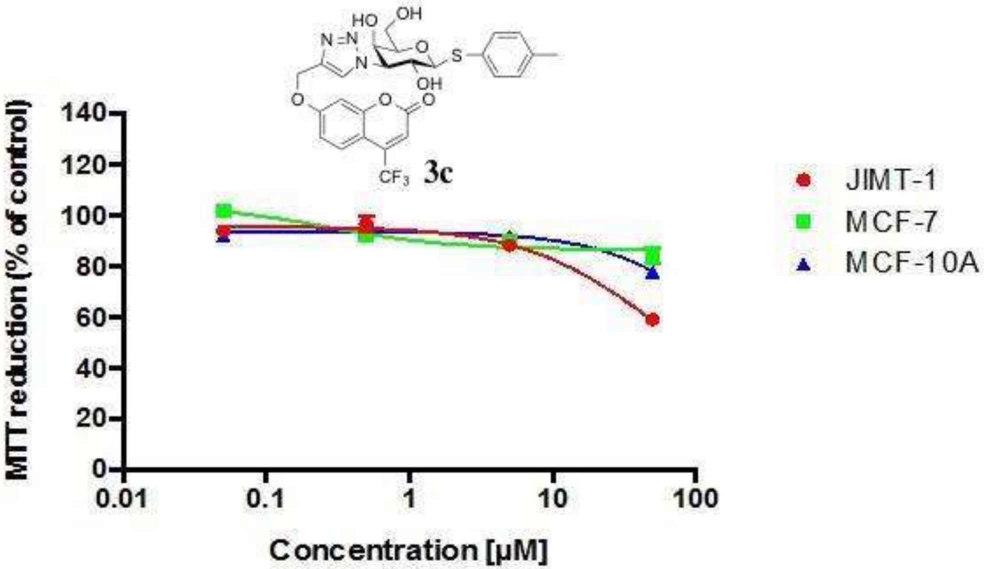

CF3
HO
OH
MeO2C
OMe
OH
O
2c
MTT reduction (% of control)
140
120
100
80
60
40
20
0
0.01
0.1
1
10
100
Concentration [µM]
JIMT-1
MCF-7
MCF-10A

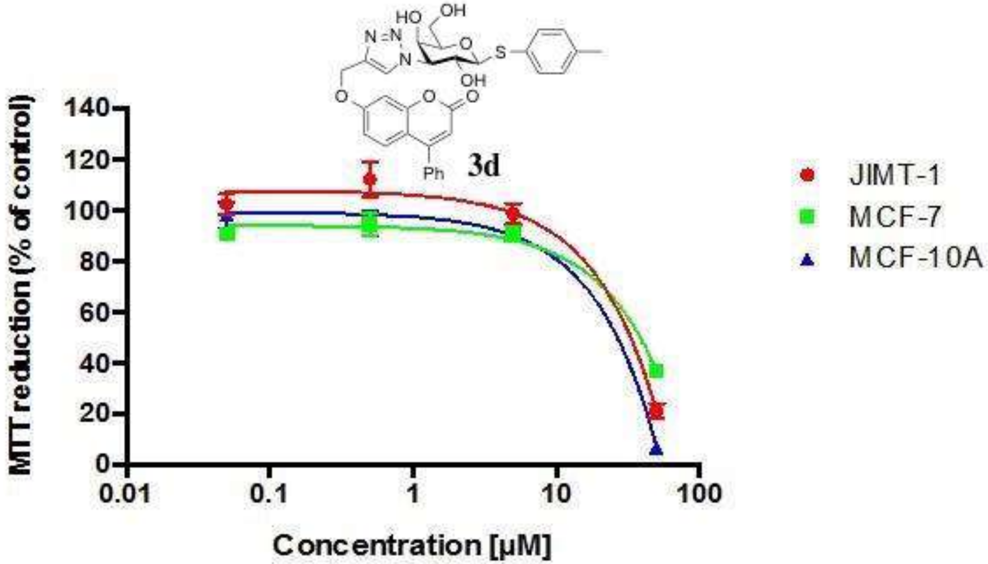

CO2Me
HO
OH
MeO2C
OMe
OH
O
2d
MTT reduction (% of control)
140
120
100
80
60
40
20
0
0.01
0.1
1
10
100
Concentration [µM]
JIMT-1
MCF-7
MCF-10A

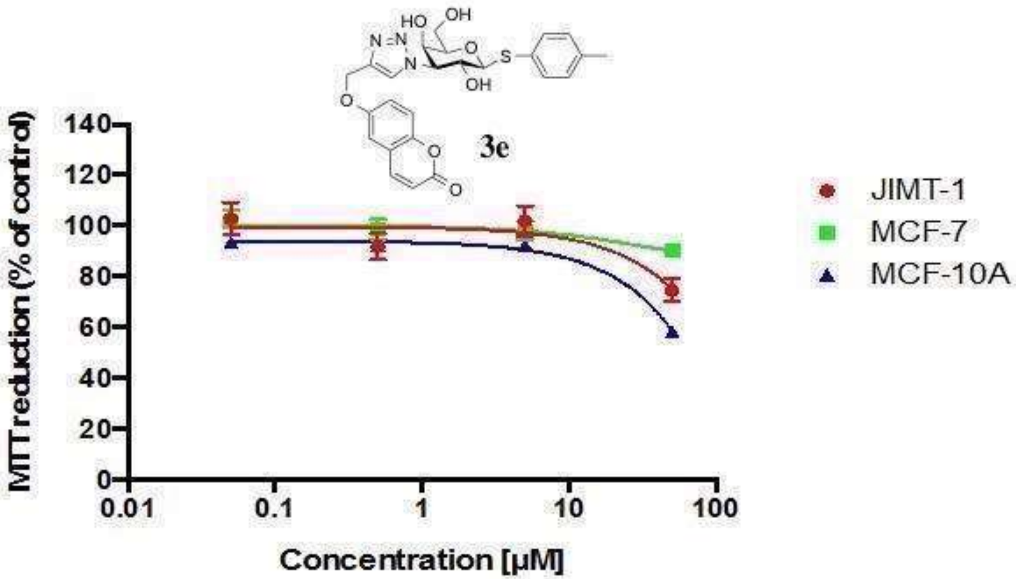

CH3
HO
OH
MeO2C
OMe
OH
O
2e
MTT reduction (% of control)
140
120
100
80
60
40
20
0
0.01
0.1
1
10
100
Concentration [µM]
JIMT-1
MCF-7
MCF-10A

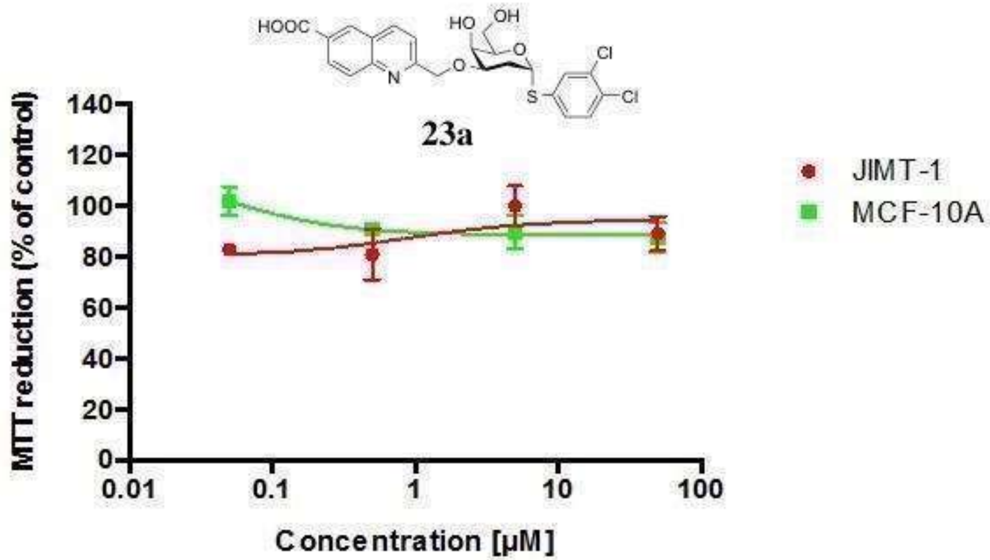

3a
MTT reduction (% of control)
Concentration [μM]
JIMT-1
MCF-7
MCF-10A


3b
MTT reduction (% of control)
Concentration [μM]
JIMT-1
MCF-7
MCF-10A


3c
MTT reduction (% of control)
Concentration [μM]
JIMT-1
MCF-7
MCF-10A


3d
MTT reduction (% of control)
Concentration [μM]
JIMT-1
MCF-7
MCF-10A


3e
MTT reduction (% of control)
140
120
100
80
60
40
20
0
0.01
0.1
1
10
100
Concentration [μM]
JIMT-1
MCF-7
MCF-10A


HOOC
23a
MTT reduction (% of control)
140
120
100
80
60
40
20
0
0.01
0.1
1
10
100
Concentration [μM]
JIMT-1
MCF-10A

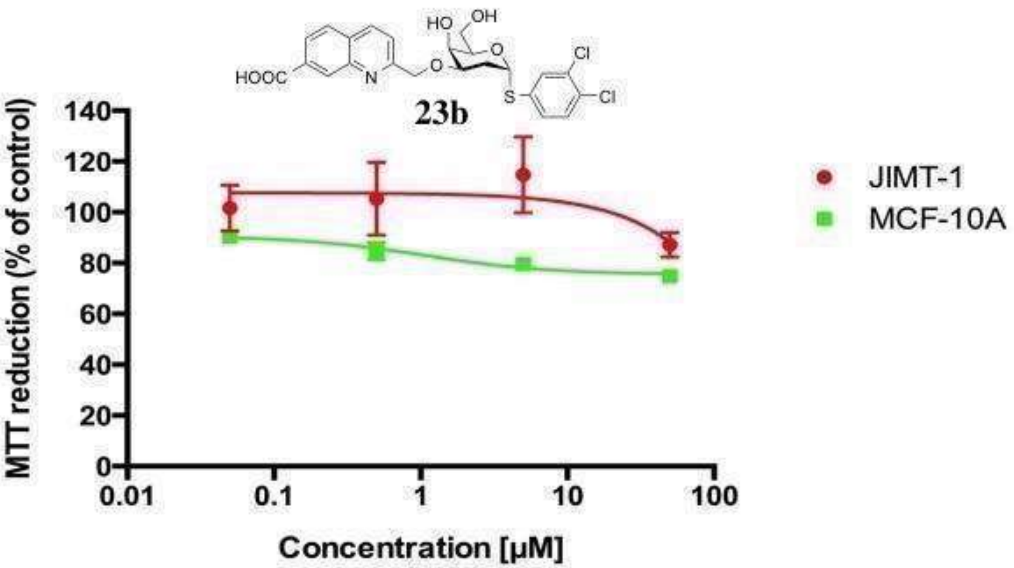
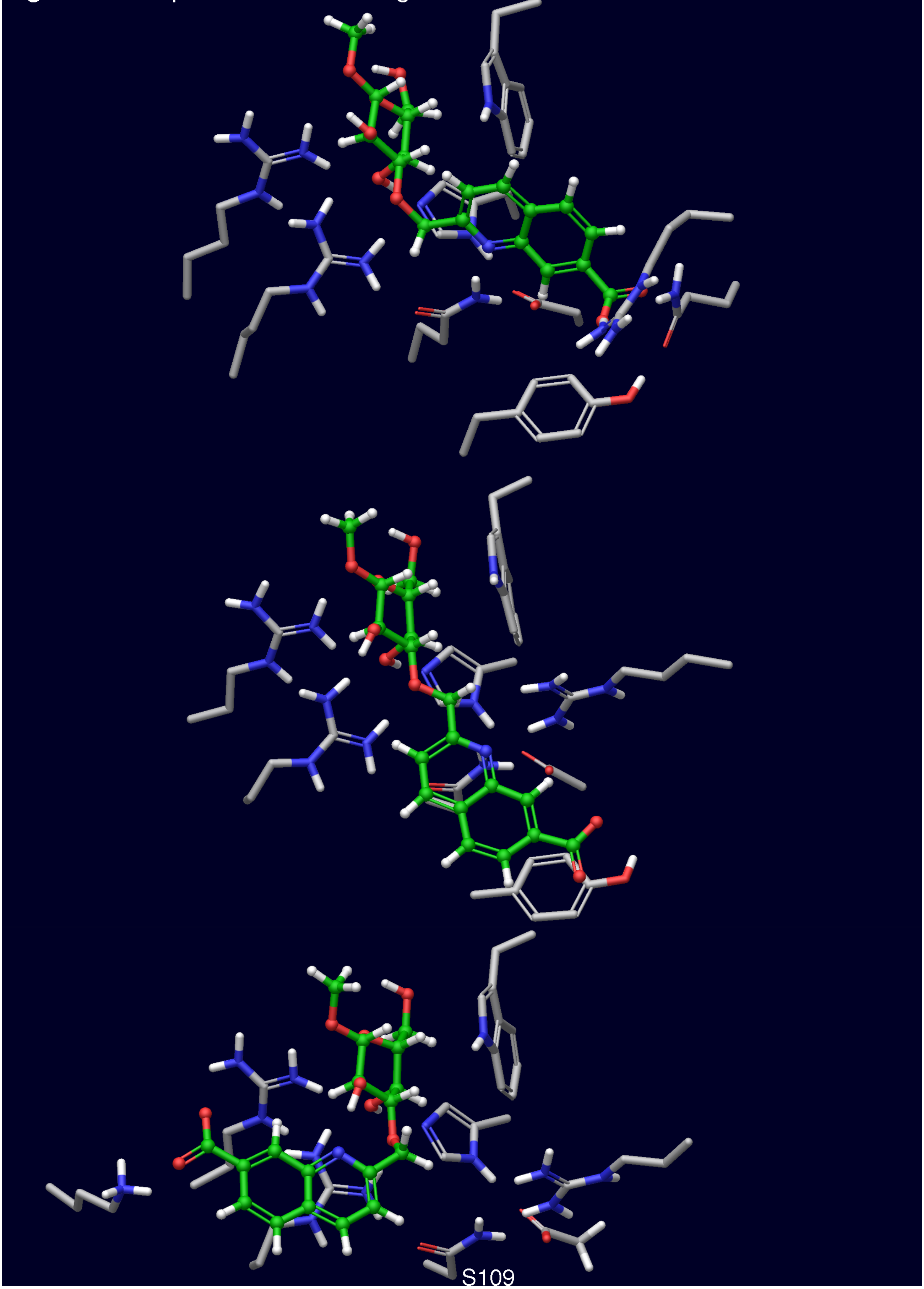

HOOC
23b
MTT reduction (% of control)
140
120
100
80
60
40
20
0
0.01
0.1
1
10
100
Concentration [μM]
JIMT-1
MCF-10A

Figure S1. Representative starting conformations for MD simulations



IV. Synthetic procedures and physical data for quinolines **7e-7i**

Methyl 2-bromomethyl-quinoline-6-carboxylate 7d

The reaction was performed with **6d**[1-2] (552 mg, 2.75 mmol) and NBS (489 mg, 2.75) following the general method *3.4* in the article experimental section. Methyl 2-bromomethyl-quinoline-6-carboxylate **7d** was obtained in 47% yield (360 mg, 1.29 mmol) as a white solid (flash column chromatography heptane/EtOAc 15:1-12:1). ^{1}H NMR ($CDCl_3$, 400 MHz): 8.56 (d, 1H, *J* 2.0 Hz, Ar*H*), 8.30 (dd, 1H, *J* 2.0 Hz, *J* 8.8 Hz, Ar*H*), 8.26 (d, 1H, *J* 8.8 Hz, Ar*H*), 8.09 (d, 1H, *J* 8.8 Hz, Ar*H*), 7.63 (d, 1H, *J* 8.4 Hz, Ar*H*), 4.70 (s, 2H, CH_2Ar), 3.99 (s, 3H, CO_2CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): 166.6 (CO_2CH_3), 159.4, 149.5, 138.6, 130.7, 129.7, 129.6, 128.6, 126.6, 122.1, 52.6 (CH_2Ar), 34.1 (CO_2CH_3). HRMS calcd. for $C_{12}H_{10}BrNO_2$+H^+ $(M+H)^+$: 279.9973, found: 279.9974.

Methyl 2-bromomethyl-quinoline-7-carboxylate 7e

The reaction was performed with **6e** (579 mg, 2.89 mmol) and NBS (514 mg, 2.89) following the general method *3.4* in the article experimental section. Methyl 2-bromomethyl-quinoline-7-carboxylate **7e** was obtained in 49% yield (393 mg, 1.41 mmol) as a white solid (flash column chromatography heptane/EtOAc 15:1-11:1). ^{1}H NMR ($CDCl_3$, 400 MHz): 9.32 (dd, 1H, *J* 0.4 Hz, *J* 8.8 Hz, Ar*H*), 8.26-8.20 (m, 2H, Ar*H*), 7.71 (dd, 1H, *J* 7.2 Hz, *J* 8.4 Hz, Ar*H*), 7.64 (d, 1H, *J* 8.8 Hz, Ar*H*), 4.68 (s, 2H, CH_2Ar), 3.98 (s, 3H, CO_2CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): 166.9 (CO_2CH_3), 157.2, 147.7, 135.7, 134.8, 131.2, 128.6, 126.7, 126.2, 122.7, 52.4 (CH_2Ar), 34.0 (CO_2CH_3). HRMS calcd. for $C_{12}H_{10}BrNO_2$+H^+ $(M+H)^+$: 279.9973, found: 279.9975.

2-Bromomethyl-6,7-difluoro-quinoline 7f

The reaction was performed with **6f** (402 mg, 2.24 mmol) and NBS (400 mg, 2.24) following the general method *3.4* in the article experimental section. 2-Bromomethyl-6,7-difluoro-quinoline **7f** was obtained in 42% yield (242 mg, 0.94 mmol) as a white solid (flash column chromatography heptane/EtOAc 20:1-15:1). ^{1}H NMR ($CDCl_3$, 400 MHz): 8.10 (d, 1H, *J* 8.8 Hz, Ar*H*), 7.81 (dd, 1H, *J* 7.6 Hz, *J* 11.2 Hz, Ar*H*), 8.57 (d, 1H, *J* 8.4 Hz, Ar*H*), 7.54 (dd, 1H, *J* 8.4 Hz, *J* 10.0 Hz Ar*H*), 4.67 (s, 2H, CH_2Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): 157.5 (d, *J* 2.9 Hz), 154.0 (d, *J* 15.8 Hz), 151.7 (dd, *J* 15.9 Hz, *J* 41.3 Hz), 149.4 (d, *J* 16.0 Hz), 144.8 (d, *J* 9.7 Hz), 136.6 (d, *J* 5.1 Hz), 124.3 (d, *J* 9.0 Hz), 121.5 (d, *J* 2.4 Hz), 120.9, 115.8 (d, *J* 16.7 Hz), 112.9 (dd, *J* 1.4 Hz, *J* 17.5 Hz), 34.0. ^{19}F NMR ($CDCl_3$, 376 MHz): -130.7 (d, *J* 20.5 Hz), -130.4 (d, *J* 21.0 Hz). HRMS calcd. for $C_{10}H_6BrF_2N$+H^+ $(M+H)^+$: 257.9730, found: 257.9733.

2-Bromomethyl-4-chloro-6-trifluoromethyl-quinoline 7g

The reaction was performed with **6g** (455 mg, 1.86 mmol) and NBS (331 mg, 1.86 mmol) following the general method *3.4* in the article experimental section. 2-Bromomethyl-4-chloro-6-trifluoromethyl-quinoline **6g** was obtained in 40% yield (240 mg, 0.74 mmol) as a white solid (flash column chromatography, heptane/EtOAc 25:1-20:1). ^{1}H NMR ($CDCl_3$, 400 MHz): 8.53 (s, 1H, Ar*H*), 8.20 (d, 1H, *J* 8.8 Hz, Ar*H*), 7.95 (dd, 1H, *J* 2.0 Hz, *J* 8.8 Hz, Ar*H*), 7.77 (s, 1H, Ar*H*), 4.67 (s, 2H, CH_2Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): 159.4, 149.4, 144.5, 131.14, 131.10, 130.0 (q, *J* 32.7 Hz), 126.7 (q, *J* 2.9 Hz), 125.2, 125.0, 122.55, 122.48, 122.3 (q, *J* 4.5 Hz), 121.8, 33.2 (CH_2Ar). ^{19}F NMR ($CDCl_3$, 376 MHz): -62.5. HRMS calcd. for $C_{11}H_6BrClF_3N$+H^+ $(M+H)^+$: 323.9402, found: 323.9403.

2-Bromomethyl-4-chloro-7-trifluoromethyl-quinoline 7h

The reaction was performed with **6h** (460 mg, 1.88 mmol) and NBS (334 mg, 1.88 mmol) following the general method *3.4* in the article experimental section. 2-Bromomethyl-4-chloro-7-trifluoromethyl-quinoline **7h** was obtained in 37% yield (224 mg, 0.695 mmol) as a white solid (flash column chromatography, heptane/EtOAc 35:1-30:1). ^{1}H NMR ($CDCl_3$, 400 MHz): 8.40 (m, 1H, Ar*H*), 8.35 (m, 1H, Ar*H*), 7.83 (dd, 1H, *J* 1.6 Hz, *J* 8.8 Hz, Ar*H*), 7.78 (s, 1H, Ar*H*), 4.67 (s, 2H, $CH_2C_{10}H_7$). ^{13}C NMR ($CDCl_3$, 100 MHz): 158.6, 147.6, 143.8, 132.9 (q, *J* 33.0 Hz), 127.7 (q, *J* 4.1 Hz), 127.4, 125.6, 125.1, 123.8 (q, *J* 3.0 Hz), 123.2, 33.2 (CH_2Ar). ^{19}F NMR ($CDCl_3$, 376 MHz): -62.9. HRMS calcd. for $C_{11}H_6BrClF_3N$+H^+ $(M+H)^+$: 323.9402, found: 323.9401.

2-Bromomethyl-4-chloro-8-fluoro-quinoline 7i

The reaction was performed with **6i** (421 mg, 2.16 mmol) and NBS (384 mg, 2.16 mmol) following the general method *3.4* in the article experimental section. 2-Bromomethyl-4-chloro-8-fluoro-quinoline **7i** was obtained in 43% yield (253 mg, 0.93 mmol) as a white solid (flash column chromatography, heptane/EtOAc 20:1-16:1). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.97 (m, 1H, Ar*H*), 7.74 (s, 1H, Ar*H*), 7.56 (m, 1H, Ar*H*), 7.46 (m, 1H, Ar*H*), 4.70 (s, 2H, CH_2Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): 159.3, 157.3, 156.7, 143.6 (d, *J* 4.4 Hz), 138.5 (d, *J* 12.0 Hz), 127.8 (d, *J* 8.4 Hz), 127.3 (d, *J* 1.5 Hz), 122.5, 119.9 (d, *J* 4.9 Hz), 115.2 (d, *J* 19.2 Hz), 33.4 (CH_2Ar). ^{19}F NMR ($CDCl_3$, 376 MHz): -123.1. HRMS calcd. for $C_{10}H_6BrClFN$+H^+ $(M+H)^+$: 273.9434, found: 273.9435.

V. Synthetic procedures and physical data for compound **1a-1c** and **1f-1i**

Methyl 3-O-(quinolin-2-ylmethoxy)-β-D-galactopyranoside 1a

The reaction was performed with **8** (45 mg, 0.23 mmol) and **7a** (77 mg, 0.35 mmol) following the general method *3.5* in the article experimental section. The quinoline **1a** was obtained in 81% yield (63 mg, 0.19 mmol) as a colurless oil. $[\alpha]_D^{25}$ +53.6 (*c* 1.5, CH_3OH). ^{1}H NMR (CD_3OD, 400 MHz): 8.33 (d, 1H, *J* 8.4 Hz, Ar*H*), 8.00 (d, 1H, *J* 8.4

Hz, Ar*H*), 7.93 (d, 1H, *J* 7.2 Hz, Ar*H*), 7.76 (m, 1H, Ar*H*), 7.68 (d, 1H, *J* 8.8 Hz, Ar*H*), 7.59 (m, 1H, Ar*H*), 5.05 (d, 1H, *J* 14.4 Hz, $CH_2C_9H_6N$), 4.99 (d, 1H, *J* 14.4 Hz, $CH_2C_9H_6N$), 4.21 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.15 (d, 1H, $J_{3,4}$ 2.4 Hz, H-4), 3.84-3.75 (m, 3H, H-2, H-6a, H-6b), 3.55 (s, 3H, OCH_3), 3.55-3.50 (m, 2H, H-3, H-5). ^{13}C NMR (CD_3OD, 100 MHz): 160.6, 147.8, 138.9, 131.3, 129.1, 128.5, 127.9, 121.0 (Ar*C*), 105.9 (C-1), 84.3, 76.4, 72.5, 71.6, 66.9, 62.5, 57.2 (OCH_3). HRMS calcd. for $C_{17}H_{21}NO_6+H^+$ $(M+H)^+$: 336.1447, found: 336.1455.

Methyl 3-O-((6-fluoro-quinolin-2-yl)-methoxy)-β-D-galactopyranoside 1b

The reaction was performed with **8** (52 mg, 0.27 mmol) and **7b** (96 mg, 0.40 mmol) following the general method *3.5* in the article experimental sectionThe quinoline **1b** was obtained in 75% yield (71 mg, 0.20 mmol) as a white amorphous solid. $[\alpha]_D^{25}$ +61.7 (*c* 0.7, CH_3OH). ^1H NMR (CD_3OD, 400 MHz): 8.26 (d, 1H, *J* 8.4 Hz, Ar*H*), 7.99 (dd, 1H, *J* 5.2 Hz, *J* 8.8 Hz, Ar*H*), 7.68 (d, 1H, *J* 8.8 Hz, Ar*H*), 7.58-7.52 (m, 2H, Ar*H*), 5.02 (d, 1H, *J* 14.4 Hz, $CH_2C_9H_6FN$), 4.95 (d, 1H, *J* 14.4 Hz, $CH_2C_9H_6FN$), 4.21 (d, 1H, *J* 8.0 Hz, H-1), 4.15 (d, 1H, *J* 2.4 Hz, H-4), 3.82-3.76 (m, 3H, H-2, H-6a, H-6b), 3.55 (s, 3H, OCH_3), 3.54-3.49 (m, 2H, H-3, H-5). ^{13}C NMR (CD_3OD, 100 MHz): 163.0, 160.5, 160.1 (d, *J* 9.1 Hz), 145.0, 138.1 (d, *J* 19.4 Hz), 131.3 (d, *J* 34.1 Hz), 129.6 (d, *J* 38.00 Hz), 121.9, 121.0 (d, *J* 97.5 Hz), 112.0 (d, *J* 82.6 Hz) (Ar*C*), 105.9 (C-1), 84.2, 76.4, 72.5, 71.6, 66.9, 62.5, 57.2 (OCH_3). ^{19}F NMR (CD_3OD, 376 MHz): -115.5. HRMS calcd. for $C_{17}H_{20}NO_6F+H^+$ $(M+H)^+$: 354.1353, found: 354.1352.

Methyl 3-O-((4-chloro-quinolin-2-yl)-methoxy)-β-D-galactopyranoside 1c

The reaction was performed with **8** (48 mg, 0.25 mmol) and **7c** (95 mg, 0.37 mmol) following the general method *3.5* in the article experimental section The quinoline **1c** was obtained in 73% yield (67 mg, 0.18 mmol) as a white amorphous solid. $[\alpha]_D^{25}$ +66.1 (*c* 1.1, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): 7.87 (t, 2H, *J* 8.8 Hz, Ar*H*), 7.58 (d, 1H *J* 2.4 Hz, Ar*H*), 7.49 (dd, 1H, *J* 2.4 Hz, *J* 8.8 Hz, Ar*H*), 7.25 (d, 1H, *J* 8.4 Hz, Ar*H*), 4.95 (d, 1H, *J* 15.6 Hz, $CH_2C_9H_6ClN$), 4.89 (d, 1H, *J* 15.6 Hz, $CH_2C_9H_6ClN$), 4.20 (d, 1H, *J* 8.0 Hz, H-1), 4.17 (d, 1H, *J* 2.8 Hz, H-4), 3.94-3.84 (m, 3H, H-2, H-6a, H-6b), 3.51-3.45 (m, 5H, H-3, H-5, OCH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): 158.6, 145.1, 136.4, 132.5, 131.0, 129.9, 128.0, 126.2, 120.1 (Ar*C*), 104.5 (C-1), 83.7, 74.2, 71.1, 70.3, 66.2, 61.9, 57.0 (OCH_3). HRMS calcd. for $C_{17}H_{20}ClNO_6+H^+$ $(M+H)^+$: 370.1057, found: 370.1056.

Methyl 3-O-((6-methoxycarbonyl)quinolin-2-yl)-methoxy)-β-D-galactopyranoside 1d

The reaction was performed with **8** (103 mg, 0.53 mmol) and **7d** (222 mg, 0.80 mmol) following the general method *3.5* in the article experimental section. The quinoline **1d** was obtained in 79% yield (165 mg, 0.42 mmol) as a white solid. $[\alpha]_D^{25}$ +49.9 (*c* 0.8, CH_3OH). ^1H NMR (CD_3OD, 400 MHz): 8.65 (d, 1H, *J* 1.6 Hz, Ar*H*), 8.46 (d, 1H, *J* 8.4 Hz, Ar*H*), 8.29 (dd, 1H, *J* 2.0 Hz, *J* 9.2 Hz, Ar*H*), 7.79 (d, 1H, *J* 8.4 Hz, Ar*H*), 5.08 (d, 1H, *J* 14.8 Hz, $CH_2C_{11}H_8NO_2$), 5.02 (d, 1H, *J* 14.8 Hz, $CH_2C_{11}H_8NO_2$), 4.21 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.15 (dd, 1H, $J_{4,5}$ 0.8 Hz, $J_{3,4}$ 3.2 Hz, H-4), 3.99 (s, 3H, CO_2CH_3), 3.83-3.75 (m, 3H, H-2, H-6a, H-6b), 3.56-3.50 (m, 5H, H-3, H-5, OCH_3). ^{13}C NMR (CD_3OD, 100 MHz): 167.8 ($COCH_3$), 163.5, 149.9, 139.9, 132.1, 130.4, 129.4, 129.2, 128.3, 121.9 (Ar*C*), 106.0 (C-1), 84.3, 76.4, 72.7, 71.6, 66.9, 62.5, 57.2 (OCH_3), 53.0 (CO_2CH_3). HRMS calcd. for $C_{19}H_{23}NO_8+H^+$ $(M+H)^+$: 394.1502, found: 394.1504.

Methyl 3-O-((7-methoxycarbonyl)quinolin-2-yl)-methoxy)-β-D-galactopyranoside 1e

The reaction was performed with **8** (106 mg, 0.545 mmol) and **7e** (229 mg, 0.817 mmol) following the general method *3.5* in the article experimental section. The quinoline **1e** was obtained in 72% yield (155 mg, 0.393 mmol) as a white solid. $[\alpha]_D^{25}$ +46.6 (*c* 0.5, $(CH_3)_2SO$). ^1H NMR ($(CD_3)_2SO$, 400 MHz): 9.16 (d, 1H, *J* 9.2 Hz, Ar*H*), 8.21 (m, 2H, Ar*H*), 7.94 (d, 1H, *J* 8.8 Hz, Ar*H*), 7.85 (dd, 1H, *J* 7.2 Hz, *J* 8.4 Hz, Ar*H*), 5.40 (d, 1H, *J* 4.4 Hz, OH), 4.97 (d, 1H, *J* 14.4 Hz, $CH_2C_{11}H_8NO_2$), 4.87 (d, 1H, *J* 14.4 Hz, $CH_2C_{11}H_8NO_2$), 4.76 (d, 1H, *J* 4.8 Hz, O*H*), 5.08 (t, 1H, *J* 5.6 Hz, O*H*), 4.05 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 3.98 (d, 1H, *J* 3.6 Hz, H-4), 3.96 (s, 3H, CO_2CH_3), 3.60-3.48 (m, 3H, H-2, H-6a, H-6b), 3.39 (s, 3H, OCH_3), 3.36-3.32 (m, 2H, H-3, H-5). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): 166.5 (CO_2CH_3), 160.4, 146.8, 134.0, 133.7, 130.0, 128.7, 126.8, 125.2, 121.3 (Ar*C*), 104.4 (C-1), 82.3, 74.9, 71.2, 69.5, 64.6, 60.3, 55.9 (OCH_3), 52.5 (CO_2CH_3). HRMS calcd. for $C_{19}H_{23}NO_8+H^+$ $(M+H)^+$: 394.1502, found: 394.1501.

Methyl 3-O-((6,7-difluoro-quinolin-2-yl)-methoxy)-β-D-galactopyranoside 1f

The reaction was performed with **8** (41 mg, 0.211 mmol) and **7f** (82 mg, 0.317) following the general method *3.5* in the article experimental section. The quinoline **1f** was obtained in 80% yield (63 mg, 0.169 mmol) as a white amorphous solid. $[\alpha]_D^{25}$ +51.5 (*c* 0.7, CH_3OH). ^1H NMR (CD_3OD, 400 MHz): 8.30 (d, 1H, *J* 8.4 Hz, Ar*H*), 7.82-7.74 (m, 2H), 7.99 (d, 1H, *J* 8.4 Hz, Ar*H*), 5.02 (d, 1H, *J* 14.4 Hz, $CH_2C_9H_2F_2N$), 4.96 (d, 1H, *J* 14.4 Hz, $CH_2C_9H_2F_2N$), 4.21 (d, 1H, *J* 7.6 Hz, H-1), 4.14 (d, 1H, $J_{3,4}$ 3.2 Hz, $J_{4,5}$ 0.8 Hz, H-4), 3.83-3.75 (m, 3H, H-2, H-6a, H-6b), 3.55 (s, 3H, OCH_3), 3.52 (m, 1H, H-5), 3.50 (dd, 1H, $J_{2,3}$ 9.6 Hz, $J_{3,4}$ 3.2 Hz, H-3). ^{13}C NMR (CD_3OD, 100 MHz): 161.5, 155.0 (d, *J* 60.3), 152.4 (dd, *J* 13.0 Hz, *J* 57.9 Hz), 149.9 (d, *J* 58.8), 145.2 (d, *J* 39.5 Hz), 138.1 (d, *J* 16.3 Hz), 126.1 (d, *J* 29.9 Hz), 121.4, 114.8 (dd, *J* 66.4 Hz, *J* 187.7 Hz) (Ar*C*), 105.9 (C-1), 84.2, 76.4, 72.6, 71.6, 66.9, 62.4, 57.2 (OCH_3). ^{19}F NMR (CD_3OD, 376 MHz): -133.8 (d, 20.4 Hz), -138.4 (d, 20.4 Hz). HRMS calcd. for $C_{17}H_{19}NO_6F_2+H^+$ $(M+H)^+$: 372.1259, found: 372.1253.

Methyl 3-O-((4-chloro-6-(trifluoromethyl)-quinolin-2-yl)methoxy)-β-D-galactopyranoside 1g

The reaction was performed with **8** (51 mg, 0.263 mmol) and **7g** (127 mg, 0.394 mmol) following the general method *3.5* in the article experimental section. The quinoline **1g** was obtained in 71% yield (82 mg, 0.186 mmol) as a white amorphous solid. $[\alpha]_D^{25}$ +44.2 (*c* 0.6, CH_3OH). ^1H NMR (CD_3OD, 400 MHz): 8.58 (bs, 1H, Ar*H*), 8.23 (d, 1H, *J* 8.8 Hz, Ar*H*), 8.14 (s, 1H, Ar*H*), 8.06 (dd, 1H, *J* 2.0 Hz, *J* 8.8 Hz, Ar*H*), 5.07 (d, 1H, *J* 14.8 Hz, $CH_2C_{10}H_4ClF_3N$), 4.99 (d, 1H, *J* 14.8 Hz, $CH_2C_{10}H_4ClF_3N$), 4.20 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.16 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 3.83-3.75 (m, 3H, H-2, H-6a, H-6b), 3.55 (s, 3H, OCH_3), 3.54-3.50 (m, 2H, H-3, H-5). ^{13}C NMR (CD_3OD, 100 MHz): 164.2, 150.1, 145.2, 131.3, 130.2 (q, *J* 32.8 Hz), 127.5, 126.6, 126.1, 123.9, 123.2 (q, *J* 3.4 Hz), 122.5 (Ar*C*), 105.9 (C-1), 84.2, 76.4, 72.4, 71.6, 66.9, 62.4, 57.3 (OCH_3). ^{19}F NMR (CD_3OD, 376 MHz): -63.9. HRMS calcd. for $C_{18}H_{19}ClF_3NO_6+H^+$ $(M+H)^+$: 438.0931, found: 438.0933.

Methyl 3-O-((4-chloro-7-(trifluoromethyl)-quinolin-2-yl)methoxy)-β-D-galactopyranoside 1h.

The reaction was performed with **8** (50 mg, 0.26 mmol) and **7h** (125 mg, 0.39 mmol) following the general method *3.5* in the article experimental section. The quinoline **1h** was obtained in 77% yield (87 mg, 0.20 mmol) as a white amorphous solid. $[\alpha]_D^{25}$ +39.9 (*c* 0.5, CH_3OH). ^1H NMR (CD_3OD, 400 MHz): 8.44 (d, 1H, *J* 8.8 Hz, Ar*H*), 8.32 (bs, 1H, Ar*H*), 8.12 (s, 1H, Ar*H*), 7.91 (dd, 1H, *J* 1.6 Hz, *J* 8.8 Hz, Ar*H*), 5.06 (d, 1H, *J* 14.8 Hz, $CH_2C_{10}H_4ClF_3N$), 4.98 (d, 1H, *J* 14.8 Hz, $CH_2C_{10}H_4ClF_3N$), 4.21 (d, 1H, *J* 7.6 Hz, H-1), 4.16 (d, 1H, $J_{3,4}$ 2.8 Hz, H-4), 3.81-3.75 (m, 3H, H-2, H-6a, H-6b), 3.56 (s, 3H, OCH_3), 3.53-3.50 (m, 2H, H-3, H-5). ^{13}C NMR ($CDCl_3$, 100 MHz): 163.4, 148.2, 144.6, 134.0, 133.5 (q, *J* 32.5 Hz), 128.6, 127.3 (q, *J* 4.0 Hz), 127.0, 126.5, 124.1 (d, *J* 3.0 Hz), 123.8, 123.2 (Ar*C*), 105.9 (C-1), 84.1, 76.4, 72.4, 71.6, 66.9, 62.4, 57.3 (OCH_3). ^{19}F NMR (CD_3OD, 376 MHz): -64.3. HRMS calcd. for $C_{18}H_{19}ClF_3NO_6+H^+$ $(M+H)^+$: 438.0931, found: 438.0930.

Methyl 3-O-((4-chloro-7-fluoro-quinolin-2-yl)-methoxy)-β-D-galactopyranoside 1i

The reaction was performed with **8** (43 mg, 0.22 mmol) and **7h** (91 mg, 0.33 mmol) following the general method *3.5* in the article experimental section. The quinoline **1h** was obtained in 73% yield (63 mg, 0.16 mmol) as a white amorphous solid. $[\alpha]_D^{25}$ +60.6 (*c* 0.9, $(CH_3)_2SO$). ^1H NMR ($(CD_3)_2SO$, 400 MHz): 8.19 (s, 1H, Ar*H*), 7.02 (m, 1H), 7.74-7.70 (m, 2H, Ar*H*), 5.29 (d, 1H, *J* 4.8 Hz, O*H*), 4.95 (d, 1H, *J* 14.4 Hz, $CH_2C_9H_4ClFN$), 4.84 (d, 1H, *J* 14.4 Hz, $CH_2C_9H_4ClFN$), 4.77 (d, 1H, *J* 5.2 Hz, O*H*), 4.65 (t, 1H, *J* 5.6 Hz, O*H*), 4.06 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 3.99 (t, 1H, $J_{5,6a}$, $J_{5,6b}$ 4.0 Hz, H-5), 3.61-3.49 (m, 3H, H-2, H-6a, H-6b), 3.40 (s, 3H, OCH_3), 3.37-3.32 (m, 2H, H-3, H-5). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): 161.0, 158.3, 155.8, 141.8 (d, *J* 4.4 Hz), 137.6 (d, *J* 12.3 Hz), 127.6 (d, *J* 8.2 Hz), 126.5, 121.0, 119.6 (d, *J* 4.4 Hz), 115.1 (d, *J* 18.5 Hz) (Ar*C*), 104.3 (C-1), 82.3, 74.9, 71.0, 69.4, 64.4, 60.3, 55.9 (OCH_3). ^{19}F NMR ($(CH_3)_2SO$, 376 MHz): -124.1. HRMS calcd. for $C_{17}H_{19}ClFNO_6+H^+$ $(M+H)^+$: 388.0963, found: 388.0972.

VI. Synthetic procedures and physical data for carboxylates 1j-1k and 23a-23b

Methyl 3-O-(6-carboxyquinolin-2-yl)methoxy)-β-D-galactopyranoside 1j

The reaction was performed with **1d** (37 mg, 0.094 mmol), following general methods *3.6* in the article experimental section. Compound **1j** was obtained in 66% yield (24 mg, 0.062 mmol) as a white amorphous solid. $[\alpha]_D^{25}$ +38.8 (*c* 0.5, CH_3OH). ^1H NMR (CD_3OD, 400 MHz): 8.63 (d, 1H, *J* 1.6 Hz, Ar*H*), 8.44 (d, 1H, *J* 8.4 Hz, Ar*H*), 8.28 (dd, 1H, *J* 2.0 Hz, *J* 8.8 Hz, Ar*H*), 8.03 (d, 1H, *J* 8.8 Hz, Ar*H*), 7.77 (d, 1H, *J* 8.8 Hz, Ar*H*), 5.07 (d, 1H, *J* 14.8 Hz, $CH_2C_{10}H_6NO_2$), 5.01 (d, 1H, *J* 14.8 Hz, $CH_2C_{10}H_6NO_2$), 4.21 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.16 (d, 1H, $J_{3,4}$ 2.4 Hz, H-4), 3.81-3.76 (m, 3H, H-2, H-6a, H-6b), 3.56 (s, 3H, OCH_3), 3.54-3.51 (m, 2H, H-3, H-5). ^{13}C NMR (CD_3OD, 100 MHz): 169.1 (CO_2H), 163.3, 149.8, 139.9, 132.1, 130.8, 130.2, 129.0, 128.2, 121.8 (Ar*C*), 105.9 (C-1), 84.3, 76.4, 72.6, 71.6, 66.9, 62.5, 57.2 (OCH_3). HRMS calcd. for $C_{18}H_{21}NO_8+H^+$ $(M+H)^+$: 380.1345, found: 380.1342.

Methyl 3-O-((7-carboxy)quinolin-2-yl)-methoxy)-β-D-galactopyranoside 1k

The reaction was performed with **1e** (31 mg, 0.079 mmol) following the general methods *3.6* in the article experimental section. Compound **1k** was obtained in 63% yield (19 mg, 0.05 mmol) as a white amorphous solid. $[\alpha]_D^{25}$ +36.3 (*c* 0.7, CH_3OH). ^1H NMR (CD_3OD, 400 MHz): 9.43 (d, 1H, *J* 8.8 Hz, Ar*H*), 8.32 (d, 1H, *J* 6.8 Hz, Ar*H*), 8.20 (d, 1H, *J* 8.4 Hz, Ar*H*), 7.81 (d, 1H, *J* 7.6 Hz, Ar*H*), 7.79 (d, 1H, *J* 8.8 Hz, Ar*H*), 5.07 (d, 1H, *J* 14.4 Hz, $CH_2C_{10}H_6NO_2$), 5.01 (d, 1H, *J* 14.4 Hz, $CH_2C_{10}H_6NO_2$), 4.21 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.15 (d, 1H, $J_{3,4}$ 2.8 Hz, H-4), 3.83-3.75 (m, 3H, H-2, H-6a, H-6b), 3.56-3.51 (m, 2H, H-3, H-5). ^{13}C NMR (CD_3OD, 100 MHz): 169.6 (CO_2H), 160.9, 148.1, 137.1, 133.7, 131.9, 130.0, 129.2, 127.6, 122.1 (Ar*C*), 106.0 (C-1), 84.3, 76.4, 72.4, 71.6, 66.9, 62.5, 57.2 (OCH_3). HRMS calcd. for $C_{18}H_{21}NO_8+H^+$ $(M+H)^+$: 380.1345, found: 380.1356.

3,4-Dichlorophenyl 3-O-(6-carboxy-quinolin-2-yl-methyl)-1-thio-α-D-galactopyranoside 23a

The reaction was performed with **22a** (25 mg, 0.046 mmol) following the general method *3.6* in the article experimental section. Compound **23a** was obtained in 69% yield (17 mg, 0.032 mmol) as a white amorphous solid. $[\alpha]_D^{25}$ +56.7 (*c* 0.6, CH_3OH). ^1H NMR (CD_3OD, 400 MHz): 8.66 (d, 1H, *J* 1.6 Hz, Ar*H*), 8.48 (d, 1H, *J* 8.4 Hz, Ar*H*), 8.31 (dd, 1H, *J* 1.6 Hz, *J* 8.8 Hz, Ar*H*), 8.06 (d, 1H, *J* 8.8 Hz, Ar*H*), 7.78 (d, 1H, *J* 8.8 Hz, Ar*H*), 7.73 (d, 1H, *J* 2.0 Hz, Ar*H*), 7.73 (dd, 1H, *J* 2.4 Hz, *J* 8.4 Hz, Ar*H*), 7.43 (d, 1H, *J* 8.4 Hz, Ar*H*), 5.73 (d, 1H, $J_{1,2}$ 5.6 Hz, H-1), 5.10 (d, 1H, *J* 14.8 Hz, $CH_2C_{10}H_6NO_2$), 5.04 (d, 1H, *J* 14.8 Hz, $CH_2C_{10}H_6NO_2$), 4.47 (dd, 1H, $J_{1,2}$ 5.6 Hz, $J_{2,3}$ 10.4 Hz, H-2), 4.32-4.29 (m, 2H, H-4, H-5), 3.79-3.70 (m, 3H, H-3, H-6a, H-6b). ^{13}C NMR (CD_3OD, 100 MHz): 169.2 (CO_2H), 163.1, 149.9, 140.0, 136.9, 134.4, 133.5, 132.7, 132.14, 132.09, 131.6, 130.9, 129.0, 128.3, 121.8 (Ar*C*), 91.0 (C-1), 81.7, 73.5, 72.5, 69.0, 67.4, 62.4. HRMS calcd. for $C_{23}H_{21}Cl_2NO_7S+H^+$ $(M+H)^+$: 526.0494, found: 526.0497.

3,4-Dichlorophenyl 3-O-(7-carboxy-quinolin-2-yl-methyl)-1-thio-α-D-galactopyranoside 23b

The reaction was performed with **22b** (23 mg, 0.043 mmol) following the general method *3.6* in the article experimental section. Compound **23b** was obtained in 65% yield (15 mg, 0.028 mmol) as a white amorphous solid. $[\alpha]_D^{25}$ +53.2 (*c* 0.5, CH_3OH). ^1H NMR (CD_3OD, 400 MHz): 9.35 (d, 1H, *J* 8.8 Hz, Ar*H*), 8.20 (d, 1H, *J* 7.2 Hz, Ar*H*), 8.16 (d, 1H, *J* 8.4 Hz, Ar*H*), 7.81 (t, 1H, *J* 7.6 Hz, Ar*H*), 7.76 (d, 1H, *J* 8.4 Hz, Ar*H*), 7.74 (d, 1H, *J* 2.0 Hz, Ar*H*), 7.48 (dd, 1H, *J* 2.0 Hz, *J* 8.4 Hz, Ar*H*), 7.43 (d, 1H, *J* 2.0 Hz, Ar*H*), 5.73 (d, 1H, $J_{1,2}$ 5.6 Hz, H-1), 5.08 (d, 1H, *J* 14.4 Hz, $CH_2C_{10}H_6NO_2$), 5.03 (d, 1H, *J* 14.4 Hz, $CH_2C_{10}H_6NO_2$), 4.47 (dd, 1H, $J_{1,2}$ 5.6 Hz, $J_{2,3}$ 10.0 Hz, H-2), 4.31-4.28 (m, 2H, H-4, H-5), 3.79-3.70 (m, 3H, H-3, H-6a, H-6b). ^{13}C NMR (CD_3OD, 100 MHz): 160.6, 148.3, 137.4, 136.9, 134.4, 133.5, 132.7, 132.4, 132.1, 131.6, 130.6, 130.2, 127.4, 121.8 (Ar*C*), 91.0 (C-1), 81.7, 73.6, 72.4, 69.0, 67.4, 62.4. HRMS calcd. for $C_{23}H_{21}Cl_2NO_7S+H^+$ $(M+H)^+$: 526.0494, found: 526.0502.

VII. Synthetic procedures and physical data for pyridinium bromides **10e-10d**

4-Methoxycarbonyl-1-(2-methoxy-2-oxoethyl)-pyridinium bromide 10d

The reaction was performed with methyl isonicotinate (1 mL, 8.46 mmol) following the general method *3.7* in the article experimental section. Compound **10d** was obtained in 61% yield (1.49 g, 5.16 mmol) as a white powder. ^1H NMR (CD_3OD, 400 MHz): 9.29 (dd, 2H, *J* 2.4 Hz, *J* 5.2 Hz, Ar*H*), 8.63 (d, 2H, *J* 6.8 Hz, Ar*H*), 5.82 (s, 2H, $CH_2CO_2CH_3$), 4.09 (s, 3H, CO_2CH_3), 3.89 (s, 3H, CO_2CH_3). ^{13}C NMR (CD_3OD, 100 MHz): 167.5 ($CH_2CO_2CH_3$), 163.6 (CO_2CH_3), 149.1, 147.1, 128.4 (Ar*C*), 62.2 ($CH_2CO_2CH_3$), 54.6 ($CH_2CO_2CH_3$), 54.3 (CO_2CH_3). HRMS calcd. for $C_{10}H_{12}NO_4^+$ $(M+H)^+$: 210.0766, found: 210.0770.

4-Methyl-1-(2-methoxy-2-oxoethyl)-pyridinium bromide 10e

The reaction was performed with 4-methylpyridine (1 mL, 10.27 mmol) following the general method *3.7* in the article experimental section. Compound **10e** was obtained in 54% yield (1.36 g, 5.55 mmol) as a white powder. ^1H NMR (CD_3OD, 400 MHz): 9.03 (d, 2H, *J* 6.4 Hz, Ar*H*), 8.12 (d, 2H, *J* 6.8 Hz, Ar*H*), 5.80 (s, 2H, $CH_2CO_2CH_3$), 3.88 (s, 3H, CO_2CH_3), 2.79 (s, 3H, CO_2CH_3). ^{13}C NMR (CD_3OD, 100 MHz): 168.0 ($CH_2CO_2CH_3$), 162.5, 146.3, 129.5 (Ar*C*), 61.1 (CH_2CO_2Me), 54.2 ($CH_2CO_2CH_3$), 22.5 (CH_3). HRMS calcd. for $C_9H_{12}NO_2^+$ $(M+H)^+$: 166.0868, found: 166.0865.

VIII. Synthetic procedures and physical data for Indolizine **2a-2e**

Methyl 3-O-(1-carboxylato-(3-methyl-indolizine-3-carboxylate)-β-D-galactopyranoside 2a

The reaction was performed with **12** (76 mg, 0.15 mmol) and **10a** (34 mg, 0.15 mmol) following method *3.9* in the article experimental section. The indolizine **2a** was obtained in 25% yield (14.5 mg, 0.037 mmol) as a white amorphous solid. $[\alpha]_D^{25}$ +18.4 (*c* 0.6, CH_3OH). ^1H NMR (CD_3OD, 400 MHz): 9.53 (d, 1H, *J* 7.2 Hz, Ar*H*), 8.37 (d, 1H, *J* 8.8 Hz, Ar*H*), 8.06 (s, 1H, Ar*H*), 7.42 (t, 1H, *J* 8.0 Hz, Ar*H*), 7.10 (t, 1H, *J* 7.2 Hz, Ar*H*), 4.98 (dd, 1H, *J* 10.4 Hz, *J* 3.2 Hz, H-3), 4.32 (d, 1H, *J* 7.6 Hz, H-1), 4.18 (d, 1H, *J* 3.2 Hz, H-4), 3.94-3.90 (m, 4H, H-2, CO_2CH_3), 3.80 (dd, 1H, *J* 6.8 Hz, *J* 11.2 Hz, H-6a), 3.80 (dd, 1H, *J* 5.6 Hz, *J* 11.2 Hz, H-6b), 3.67 (t, 1H, *J* 6.0 Hz, H-5), 3.58 (s, 3H, OCH_3). ^{13}C NMR (CD_3OD, 100 MHz): 165.2 (CO_2CH_3), 162.7, 140.6, 129.0, 127.3, 125.6, 120.7, 115.9 (Ar*C*), 106.1 (C-1), 77.1, 76.5, 70.2, 68.2, 62.3, 57.4 (OCH_3), 51.9 (CO_2CH_3). HRMS calcd. for $C_{18}H_{21}NO_9+H^+$ $(M+H)^+$: 396.1295, found: 396.1286.

Methyl 3-O-(1-carboxylato-(3-methyl-7-acetylindolizine-3-carboxylate)-β-D-galactopyranoside 2b

The reaction was performed with **12** (63 mg, 0.12 mmol) and **10b** (33 mg, 0.12 mmol) following method *3.9* in the article experimental section. The indolizine **2b** was obtained in 27% yield (14.4 mg, 0.033 mmol) as a white amorphous solid. $[\alpha]_D^{25}$ +29.4 (*c* 0.7, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): 9.36 (dd, 1H, *J* 0.8 Hz, *J* 7.2 Hz, Ar*H*), 8.84 (dd, 1H, *J* 0.8 Hz, *J* 1.6 Hz, Ar*H*), 8.01 (s, 1H, Ar*H*), 7.42 (dd, 1H, *J* 2.0 Hz, *J* 7.6 Hz, Ar*H*), 5.13 (dd, 1H, *J* 10.0 Hz, *J* 3.2 Hz, H-3), 4.40 (d, 1H, *J* 7.6 Hz, H-1), 4.37 (dd, 1H, *J* 0.8 Hz, *J* 3.2 Hz, H-4), 4.08 (dd, 1H, *J* 7.6 Hz, *J* 10.0 Hz, H-2), 4.02 (dd, 1H, *J* 6.4 Hz, *J* 12.4 Hz, H-6a), 3.98 (dd, 1H, *J* 4.8 Hz, *J* 12.4 Hz, H-6b), 3.93 (s, 3H, CO_2CH_3), 3.71 (t, 1H, *J* 5.6 Hz, H-5), 3.63 (s, 3H, OCH_3), 2.64 (s, 3H, $COCH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): 196.2 ($COCH_3$), 163.4 (CO_2CH_3), 161.2, 137.7, 133.1, 127.6, 125.2, 121.5, 116.7, 112.0, 108.0 (Ar*C*), 104.7 (C-1), 75.3, 74.0, 69.7, 69.1, 63.1, 57.7 (OCH_3), 52.0 (CO_2CH_3), 26.2 ($COCH_3$). HRMS calcd. for $C_{20}H_{23}NO_{10}+H^+$ $(M+H)^+$: 438.1400, found: 438.1396.

Methyl 3-O-(1-carboxylato-(3-methyl-7-(trifluoromethyl)indolizine-3-carboxylate)-β-D-galactopyranoside 2c

The reaction was performed with **12** (71 mg, 0.14 mmol) and **10c** (41 mg, 0.14 mmol) following method *3.9* in the article experimental section. The indolizine **2c** was obtained in 31% yield (19.7 mg, 0.043 mmol) as a white amorphous solid. $[\alpha]_D^{25}$ +21.3 (*c* 0.7, CH_3OH). ^1H NMR (CD_3OD, 400 MHz): 9.66 (d, 1H, *J* 7.6 Hz, Ar*H*), 8.69 (m, 1H, Ar*H*), 8.14 (s, Ar*H*), 7.29 (dd, 1H, *J* 0.2 Hz, *J* 7.2 Hz, Ar*H*), 5.03 (dd, 1H, *J* 10.0 Hz, *J* 3.2 Hz, H-3), 4.33 (d, 1H, *J* 8.0 Hz, H-1), 4.19 (d, 1H, *J* 1.2 Hz, *J* 3.6 Hz, H-4), 3.95 (s, 3H, CO_2CH_3), 3.92 (dd, 1H, *J* 8.0 Hz, *J* 10.4 Hz, H-2), 3.80 (dd, 1H, *J* 6.8 Hz, *J* 11.2 Hz, H-6a), 3.76 (dd, 1H, *J* 5.6 Hz, *J* 11.2 Hz, H-6b), 3.67 (m, 1H, H-5), 3.59 (s, 3H, OCH_3). ^{13}C NMR

(CD_3OD, 100 MHz): 164.5 (CO_2CH_3), 162.4, 138.1, 130.0, 127.9 (q, *J* 31.7 Hz), 126.0, 123.4, 118.3 (q, *J* 3.8 Hz), 117.7, 111.1 109.1 (Ar*C*), 106.0 (C-1), 77.4, 76.5, 70.3, 68.1, 62.2, 57.4 (OCH_3), 52.3 (CO_2CH_3). ^{19}F NMR (CD_3OD, 376 MHz): -65.3. HRMS calcd. for $C_{19}H_{20}F_3NO_9$+H^+ $(M+H)^+$: 464.1168, found: 464.1168.

Methyl 3-O-(1-carboxylato-(3,7-dimethyl-indolizine-3,7-dicarboxylate)-β-D-galactopyranoside 2d

The reaction was performed with **12** (60 mg, 0.12 mmoL) and **10d** (34 mg, 0.12 mmol) following method *3.9* in the article experimental section. The indolizine **2d** was obtained in 34% yield (17.9 mg, 0.039 mmol) as a white amorphous solid. $[\alpha]_D^{25}$ +23.9 (*c* 0.5, $(CH_3)_2SO$). ^1H NMR ($(CD_3)_2SO$, 400 MHz): 9.46 (d, 1H, *J* 7.6 Hz, Ar*H*), 8.86 (dd, 1H, *J* 0.8 Hz, *J* 1.6 Hz, Ar*H*), 8.04 (s, 1H, Ar*H*), 7.57 (dd, 1H, *J* 2.0 Hz, *J* 7.2 Hz, Ar*H*), 5.33 (d, 1H, *J* 5.6 Hz, O*H*), 4.99 (d, 1H, *J* 6.0 Hz, O*H*), 4.82 (dd, 1H, $J_{2,3}$ 10.0 Hz, $J_{3,4}$ 3.2 Hz, H-3), 4.69 (t, 1H, *J* 5.6 Hz, O*H*), 4.23 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.01 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{4,OH}$ 5.6 Hz, H-4), 3.92 (s, 3H, CO_2CH_3), 3.90 (s, 3H, CO_2CH_3), 3.72 (m, 1H, H-2), 3.62-3.51 (m, 3H, H-5, H-6a, H-6b), 3.44 (s, 3H, OCH_3). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): 164.7 (CO_2CH_3), 162.5 (CO_2CH_3), 160.5, 136.8, 127.7, 126.1, 124.5, 120.9, 115.7, 113.4, 107.9 (Ar*C*), 104.3 (C-1), 76.5, 74.8, 67.9, 65.7, 60.0, 56.0 (OCH_3), 52.8 (CO_2CH_3), 51.9 (CO_2CH_3). HRMS calcd. for $C_{20}H_{23}NO_{11}$+H^+ $(M+H)^+$: 454.1349, found: 454.1354.

Methyl 3-O-(1-carboxylato-(3-methyl-7-methylindolizine-3-carboxylate)-β-D-galactopyranoside 2e

The reaction was performed with **10** (59 mg, 0.114 mmol) and **10e** (15.8 mg, 0.114 mmol) following method *3.9* in the article experimental section. The indolizine **2e** was obtained in 29% yield (13.6 mg, 0.033 mmol) as a white amorphous solid. $[\alpha]_D^{25}$ +20.5 (*c* 0.5, $(CH_3)_2SO$). ^1H NMR ($(CD_3)_2SO$, 400 MHz): 9.34 (d, 1H, *J* 7.2 Hz, Ar*H*), 8.09 (s, 1H, Ar*H*), 7.91 (s, 1H, Ar*H*), 7.10 (d, 1H, *J* 7.2 Hz, Ar*H*), 5.32 (d, 1H, *J* 5.6 Hz, O*H*), 4.94 (d, 1H, *J* 6.4 Hz, O*H*), 4.86 (dd, 1H, $J_{3,4}$ 2.8 Hz, $J_{2,3}$ 10.0 Hz, H-3), 4.65 (t, 1H, *J* 5.6 Hz, O*H*), 4.21 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 3.97 (dd, 1H, $J_{3,4}$ 2.8 Hz, $J_{3,4}$ 6.0 Hz, H-4), 3.86 (s, 3H, CO_2CH_3), 3.72 (m, 1H, H-2), 3.58-3.50 (m, 1H, H-5, H-6a, H-6b), 3.43 (s, 3H, OCH_3), 2.44 (s, 3H, CH_3). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): 162.9 (CO_2CH_3), 160.6 (CO_2Ar), 138.8, 137.6, 127.0, 124.1, 117.8, 117.6, 113.3, 104.4 (Ar*C*), 103.6 (C-1), 75.9, 74.8, 67.9, 65.7, 60.0, 56.0 (OCH_3), 51.4 (CO_2CH_3), 21.0 (CO_2CH_3). HRMS calcd. for $C_{19}H_{23}NO_9$+H^+ $(M+H)^+$: 410.1451, found: 410.1448.

IX. Synthetic procedures and physical data for coumarins **14a-14e**

3.10.1. 7-O-Propargyl-coumarin 14a

The reaction was performed with **13a** (461 mg, 2.84 mmol) and propargyl bromide (635 µL, 4.27 mmol) following the general method *3.10* in the article experimental section to give **14a** in 92% yield (523 mg, 2.61 mmol) as a white solid (flash column chromatography, heptane/EtOAc 4:1 to 1:1). ^1H NMR ($CDCl_3$, 400 MHz): 7.64 (d, 1H, *J* 9.6 Hz, Ar*H*), 7.40 (d, 1H, *J* 8.4 Hz, Ar*H*), 6.93 (d, 1H, *J* 2.4 Hz, Ar*H*), 6.90 (dd, 1H, *J* 2.4 Hz, *J* 8.4 Hz, Ar*H*), 6.27 (d, 1H, *J* 9.6 Hz, Ar*H*), 4.76 (d, 1H, *J* 2.4 Hz, CHC-$CH_2OC_9H_5O_2$), 2.57 (t, 1H, *J* 2.4 Hz, C*H*C-$CH_2OC_9H_5O_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): 161.1, 160.7, 155.8, 143.4, 129.0, 113.8, 113.3, 113.2, 102.3 (Ar*C*), 77.5 (CH*C*-$CH_2OC_{10}H_7O_2$), 76.7 (*C*HC-$CH_2OC_{10}H_7O_2$), 56.3 (CHC-$CH_2OC_{10}H_7O_2$). HRMS calcd. for $C_{12}H_8O_3$+H^+ $(M+H)^+$: 201.0552, found: 201.0553.

3.10.2. 4-Methyl-7-O-propargyl-coumarin 14b

The reaction was performed with **13b** (411 mg, 2.33 mmol) and propargyl bromide (520 mL, 3.5 mmol) following the general method *3.10* in the article experimental section to give **14b** in 94% yield (470 mg, 2.19 mmol) as a white solid (flash column chromatography, heptane/EtOAc 4:1 to 1:1). ^1H NMR ($CDCl_3$, 400 MHz): 7.51 (d, 1H, *J* 9.2 Hz, Ar*H*), 6.93-6.90 (m, 2H, Ar*H*), 6.14 (d, 1H, *J* 1.2 Hz, Ar*H*), 4.75 (d, 1H, *J* 2.4 Hz, CHC-$CH_2OC_{10}H_7O_2$), 2.56 (t, 1H, *J* 2.4 Hz, C*H*C-$CH_2OC_{10}H_7O_2$), 2.39 (d, *J* 1.2 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): 161.2, 160.5, 155.2, 152.5, 125.7, 114.4, 112.8, 112.5, 102.3 (Ar*C*), 77.5 (CH*C*-$CH_2OC_{10}H_7O_2$), 76.6 (*C*HC-$CH_2OC_{10}H_7O_2$), 56.3 (CHC-$CH_2OC_{10}H_7O_2$), 18.8 (CH_3). HRMS calcd. for $C_{13}H_{10}O_3$+H^+ $(M+H)^+$: 215.0708, found: 215.0710.

3.10.3. 4-(Trifluoromethyl)-7-O-propargyl-coumarin 14c

The reaction was performed with **13c** (352 mg, 1.53 mmol) and propargyl bromide (341 mL, 2.29 mmol) following the general method *3.10* in the article experimental section to give **14c** in 90% yield (369 mg, 1.376 mmol) as a white solid (flash column chromatography, heptane/EtOAc 4:1 to 1:1). ^1H NMR ($CDCl_3$, 400 MHz): 7.63 (m, 1H, Ar*H*), 6.99-6.96 (m, 2H, Ar*H*), 6.62 (d, 1H, *J* 0.4 Hz, Ar*H*), 4.78 (d, 1H, *J* 2.4 Hz, CHC-$CH_2OC_{10}H_4F_3O_2$), 2.59 (t, 1H, *J* 2.4 Hz, C*H*C-$CH_2OC_{10}H_4F_3O_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): 161.3, 159.3, 156.2, 141.5 (q, *J* 32.7 Hz), 126.5 (q, *J* 2.2 Hz) (Ar*C*), 121.7 (q, *J* 274.0 Hz, CF_3), 113.9, 112.9 (q, *J* 5.7 Hz), 107.8, 102.8 (Ar*C*), 77.1 (CH*C*-$CH_2OC_{10}H_4F_3O_2$), 77.0 (*C*HC-$CH_2OC_{10}H_4F_3O_2$), 56.4 (CHC-$CH_2OC_{10}H_4F_3O_2$). HRMS calcd. for $C_{13}H_7F_3O_3$+H^+ $(M+H)^+$: 269.0426, found: 269.0425.

3.10.4. 4-Phenyl-7-O-propargyl-coumarin 14d

The reaction was performed with **13d** (515 mg, 2.16 mmol) and propargyl bromide (480 mL, 6.33 mmol) following the general method *3.10* in the article experimental section to give **14d** in 89% yield (531 mg, 1.92 mmol) as a white solid (flash column chromatography, heptane/EtOAc 6:1 to 2:1). ^1H NMR ($(CD_3)_2SO$, 400 MHz): 7.57-7.49 (m, 5H, Ar*H*), 7.35 (d, 1H, *J* 9.2 Hz, Ar*H*), 7.13 (d, 1H, *J* 2.4 Hz, Ar*H*), 6.95 (dd, 1H, *J* 2.4 Hz, *J* 9.2 Hz, Ar*H*), 6.24 (s, 1H, Ar*H*), 4.94 (d, 1H, *J* 2.4 Hz, CHC-$CH_2OC_{15}H_9O_2$), 3.66 (t, 1H, *J* 2.4 Hz, C*H*C-$CH_2OC_{15}H_9O_3$). ^{13}C NMR ($(CD_3)_2SO$, 100

MHz): 160.2, 159.9, 155.2, 155.0, 134.9, 129.7, 128.8, 128.4, 127.8, 112.9, 112.3, 111.7, 102.2 (Ar*C*), 78.9 (*C*HC-$CH_2OC_{15}H_9O_2$), 78.4 (CH*C*-$CH_2OC_{15}H_9O_2$), 56.1 (CHC-*C*$H_2OC_{15}H_9O_2$). HRMS calcd. for $C_{18}H_{12}O_3+H^+$ $(M+H)^+$: 277.0865, found: 277.0863.

3.10.5. 6-O-Propargyl-coumarin 14e

The reaction was performed with **13e** (504 mg, 3.11 mmol) and propargyl bromide (693 µL, 9.14 mmol) following the general method *3.10* in the article experimental section to give **14e** in 93% yield (578 mg, 2.89 mmol) as a white solid (flash column chromatography, heptane/EtOAc 4:1 to 1:1). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.66 (d, 1H, *J* 9.6 Hz, Ar*H*), 7.28 (d, 1H, *J* 9.2 Hz, Ar*H*), 7.17 (dd, 1H, *J* 2.8 Hz, *J* 9.2 Hz, Ar*H*), 7.03 (d, 1H, *J* 2.8 Hz, Ar*H*), 6.43 (d, 1H, *J* 9.6 Hz, Ar*H*), 4.73 (d, 1H, *J* 2.4 Hz, CHC-C*H*$_2OC_9H_5O_2$), 2.55 (t, 1H, *J* 2.4 Hz, C*H*C-$CH_2OC_9H_5O_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): 161.0, 154.0, 149.1, 143.2, 120.4, 119.3, 118.1, 117.4, 111.9 (Ar*C*), 78.1 (CH*C*-$CH_2OC_{10}H_7O_2$), 76.3 (*C*HC-$CH_2OC_{10}H_7O_2$), 56.6 (CHC-*C*$H_2OC_{10}H_7O_2$). HRMS calcd. for $C_{12}H_8O_3+H^+$ $(M+H)^+$: 201.0552, found: 201.0550.

X. Synthetic procedures and physical data for thiogalactosides 3a-3e

3.12.1. p-Tolyl 3-deoxy-3-(4-(7-O-methylene-coumarin)-1H-1,2,3-triazol-1-yl)-1-thio-β-D-galactopyranoside 3a

The reaction was performed with **16** (33 mg, 0.11 mmol) and **14a** (32 mg, 0.16 mmol) following the general method *3.12* in the article experimental section. Compound **3a** was obtained in 63% yield (34 mg, 0.066 mmol) as a white amorphous solid. $[\alpha]_D^{25}$ +70.7 (*c* 0.5, CH_3OH). ^{1}H NMR ($(CD_3)_2SO$, 400 MHz): 8.22 (s, 1H, Ar*H*), 8.01 (d, 1H, *J* 9.2 Hz, Ar*H*), 7.65 (d, 1H, *J* 8.8 Hz, Ar*H*), 7.41 (d, 1H, *J* 8.4 Hz, Ar*H*), 7.20 (d, 1H, *J* 2.4 Hz, Ar*H*), 7.16 (d, 2H, *J* 8.0 Hz, Ar*H*), 7.04 (dd, 1H, *J* 2.4 Hz, *J* 8.8 Hz, Ar*H*), 6.31 (d, 1H, *J* 9.6 Hz, Ar*H*), 5.61 (d, 1H, *J* 7.2 Hz, O*H*), 5.26 (s, 2H, C*H*$_2OC_9H_5O_2$), 5.25 (d, 1H, *J* 6.8 Hz, O*H*), 4.86 (dd, 1H, *J* 2.8 Hz, *J* 10.0 Hz, H-3), 4.83 (d, 1H, $J_{1,2}$ 9.2 Hz, H-1), 4.72 (t, 1H, *J* 5.2 Hz, O*H*), 4.08 (m, 1H, H-2), 3.91 (dd, $J_{3,4}$ 2.8 Hz, $J_{4,OH}$ 6.8 Hz, H-4), 3.76 (t, 1H, $J_{5,6a\text{-}6b}$ 6.0 Hz, H-5), 3.50 (t, 2H, $J_{5,6a\text{-}6b}$ 6.0 Hz, H-6a, H-6b), 2.29 (s, 3H, $SC_6H_4CH_3$). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): 161.3, 160.3, 155.3, 144.3, 141.1, 136.2, 131.0, 130.3, 129.6, 129.5, 124.3, 112.9, 112.6, 101.5 (Ar*C*), 89.0 (C-1), 79.2, 67.6, 66.9, 66.2, 61.8, 60.2 ($SC_6H_4CH_3$), 20.6. HRMS calcd. for $C_{25}H_{25}N_3O_7S+H^+$ $(M+H)^+$: 512.1491, found: 512.1484.

3.12.2. p-Tolyl 3-deoxy-3-(4-(4-methyl-7-O-methylene-coumarin)-1H-1,2,3-triazol-1-yl)-1-thio-β-D-galactopyranoside 3b

The reaction was performed with **16** (38 mg, 0.12 mmol) and **14b** (39 mg, 0.18 mmol) following the general method *3.12* in the article experimental section. Compound **3b** (40 mg, 0.18 mmol) was obtained in 74% yield (48 mg, 0.09 mmol) as a white amorphous solid. $[\alpha]_D^{25}$ +63.2 (*c* 0.6, CH_3OH). ^{1}H NMR ($(CD_3)_2SO$, 400 MHz): 8.21 (s, 1H, Ar*H*), 7.71 (d, 1H, *J* 8.8 Hz, Ar*H*), 7.41 (dd, 2H, *J* 1.6 Hz, *J* 6.4 Hz, Ar*H*), 7.18 (d, 1H, *J* 2.4 Hz, Ar*H*), 7.16 (dd, 2H, *J* 1.6 Hz, *J* 6.4 Hz, Ar*H*), 7.06 (dd, 1H, *J* 2.4 Hz, *J* 8.8 Hz, Ar*H*), 6.23 (d, 1H, *J* 1.2 Hz, Ar*H*), 5.61 (d, 1H, $J_{4,OH}$ 7.2 Hz, O*H*), 5.27 (s, 2H, OC*H*$_2$Ar), 5.26 (d, 1H, *J* 7.6 Hz, O*H*), 4.86 (dd, 1H, $J_{3,4}$ 2.8 Hz, $J_{2,3}$ 10.8 Hz, H-3), 4.83 (d, 1H, $J_{1,2}$ 9.6 Hz, H-1), 4.72 (t, 1H, *J* 5.2 Hz, O*H*), 4.08 (m, 1H, H-2), 3.91 (dd, $J_{3,4}$ 2.8 Hz, $J_{4,OH}$ 7.2 Hz, H-4), 3.76 (t, 1H, $J_{5,6a\text{-}6b}$ 6.0 Hz, H-5), 3.50 (t, 2H, $J_{5,6a\text{-}6b}$ 6.0 Hz, H-6a, H-6b), 2.41 (s, 3H, $OC_9H_4O_2CH_3$), 2.29 (s, 3H, $SC_6H_4CH_3$). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): 161.7, 160.6, 155.2, 153.9, 141.6, 136.7, 131.4, 130.8, 130.0, 127.0, 124.7, 113.8, 113.1, 111.7 (Ar*C*), 102.0 (C-1), 89.5, 79.7, 68.1, 67.4, 66.7, 62.2, 60.7, 21.1 ($SC_6H_4CH_3$), 18.6 ($OC_9H_4O_2CH_3$). HRMS calcd. for $C_{26}H_{27}N_3O_7S+H^+$ $(M+H)^+$: 526.1648, found: 526.1645.

3.12.3. p-Tolyl 3-deoxy-3-(4-(4-(trifluoromethyl)-7-O-methylene-coumarin)-1H-1,2,3-triazol-1-yl)-1-thio-β-D-galactopyranoside, 3c

The reaction was performed with **16** (31 mg, 0.099 mmol) and **14c** (40 mg, 0.149 mmol) following the general method *3.12* in the article experimental section. Compound **3c** was obtained in 85% yield (49 mg, 0.085 mmol) as a white amorphous solid. $[\alpha]_D^{25}$ +76.6 (*c* 0.6, CH_3OH). ^{1}H NMR ($(CD_3)_2SO$, 400 MHz): 8.23 (s, 1H, Ar*H*), 7.64 (dd, 1H, *J* 1.6 Hz, *J* 8.8 Hz, Ar*H*), 7.40 (d, 2H, *J* 8.4 Hz, Ar*H*), 7.35 (d, 1H, *J* 2.8 Hz, Ar*H*), 7.17-7.14 (m, 3H, Ar*H*), 6.88 (s, 1H, Ar*H*), 5.63 (d, 1H, *J* 7.2 Hz, O*H*), 5.31 (s, 2H, C*H*$_2OC_{10}H_4F_3O_2$), 5.27 (d, 1H, *J* 6.8 Hz, O*H*), 4.86 (dd, 1H, *J* 2.8 Hz, *J* 10.4 Hz, H-3), 4.83 (d, 1H, *J* 9.6 Hz, H-1), 4.75 (t, 1H, *J* 6.0 Hz, O*H*), 4.08 (m, 1H, H-2), 3.91 (dd, 1H, *J* 2.8 Hz, *J* 6.4 Hz, H-4), 3.76 (t, 1H, *J* 6.4 Hz, H-5), 3.50 (t, 2H, *J* 6.0 Hz, H-6a, H-6b), 2.29 (s, 3H, $SC_6H_4CH_3$). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): 162.4, 159.2, 156.3, 141.4, 139.9 (q, 31.7 Hz), 136.7, 131.4, 130.8, 130.1, 126.3, 124.9, 123.1, 120.4, 113.9, 113.4 (d, 5.1 Hz), 106.7, 102.5 (Ar*C*), 89.1 (C-1), 79.2, 67.6, 67.0, 66.2, 62.0, 60.3 ($SC_6H_4CH_3$), 20.7. ^{19}F NMR ($CDCl_3$, 100 MHz): HRMS calcd. for $C_{26}H_{24}F_3N_3O_7S+H^+$ $(M+H)^+$: 580.1365, found: 580.1353.

3.12.4. p-Tolyl 3-deoxy-3-(4-(4-phenyl-7-O-methylene-coumarin)-1H-1,2,3-triazol-1-yl)-1-thio-β-D-galactopyranoside 3d

The reaction was performed with **16** (29 mg, 0.093 mmol) and **14d** (39 mg, 0.14 mmol) following the general method *3.12* in the article experimental section. Compound **3d** was obtained in 59% yield (33 mg, 0.055 mmol) as a white amorphous solid. $[\alpha]_D^{25}$ +62.4 (*c* 0.5, CH_3OH). ^{1}H NMR ($(CD_3)_2SO$, 400 MHz): 8.22 (s, 1H, Ar*H*), 7.59-7.52 (m, 5H), 7.40 (d, 2H, *J* 8.0 Hz, Ar*H*), 7.37 (d, 2H, *J* 8.8 Hz, Ar*H*), 7.30 (d, 1H, *J* 2.8 Hz, Ar*H*), 7.15 (d, 2H, *J* 8.0 Hz, Ar*H*), 7.02 (dd, 1H, *J* 2.8 Hz, *J* 8.8 Hz, Ar*H*), 6.26 (s, 1H, Ar*H*), 5.63 (d, 1H, *J* 7.2 Hz, O*H*), 5.28 (s, 2H, C*H*$_2OC_{15}H_9O_2$), 5.27 (d, 1H, *J* 6.8 Hz, O*H*), 4.86 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.8 Hz, H-3), 4.83 (d, 1H, $J_{1,2}$ 9.6 Hz, H-1), 4.74 (t, 1H, *J* 5.6 Hz, O*H*), 4.08 (m, 1H, H-2), 3.91 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{4,OH}$ 6.8 Hz, H-4), 3.76 (t, 1H, $J_{5,6a}$, $J_{5,6b}$ 6.4 Hz, H-5), 3.49 (t, 2H, $J_{5,6a}$, $J_{5,6b}$ 6.4 Hz, H-6a, H-6b), 2.29 (s, 3H, $SC_6H_4CH_3$). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): 161.4, 160.1, 155.5, 155.2, 141.1, 136.2, 135.0, 131.0, 130.4, 129.8, 129.6, 128.9, 128.5, 127.9, 124.4, 113.1, 112.0, 111.5, 102.1 (ArC), 89.1, 79.2, 67.6, 67.0, 66.2, 61.9, 60.3 ($SC_6H_4CH_3$), 20.7. HRMS calcd. for $C_{31}H_{29}N_3O_7S+H^+$ $(M+H)^+$: 588.1804, found: 588.1813.

3.12.5. p-Tolyl 3-deoxy-3-(4-(6-O-methylene-coumarin)-1H-1,2,3-triazol-1-yl)-1-thio-β-D-galactopyranoside 3e

The reaction was performed with **16** (28 mg, 0.09 mmol) and **14e** (27 mg, 0.135 mmol) following the general method *3.12* in the article experimental section. Compound **3b** was obtained in 61% yield (28 mg, 0.055 mmol) as a white solid. $[\alpha]_D^{25}$ +73.8 (*c* 0.5, CH_3OH). ^{1}H NMR ($(CD_3)_2SO$, 400 MHz): 8.20 (s, 1H, Ar*H*), 8.02 (d, 1H, *J* 9.2 Hz, Ar*H*), 7.44 (d, 1H, *J* 2.8 Hz, Ar*H*), 7.41 (d, 2H, *J* 8.0 Hz, Ar*H*), 7.37 (d, 1H, *J* 9.2 Hz, Ar*H*), 7.30 (dd, 1H, *J* 2.8 Hz, *J* 9.2 Hz, Ar*H*), 7.16 (d, 2H, *J* 8.0 Hz, Ar*H*), 5.61 (d, 1H, *J* 7.2 Hz, O*H*), 5.24 (d, 1H, *J* 6.8 Hz, O*H*), 5.2 (s, 2H, $OCH_2C_9H_5O_3$), 4.85 (dd, 1H, $J_{3,4}$ 2.8 Hz, $J_{2,3}$ 10.0 Hz, H-3), 4.84 (d, 1H, *J* 9.2 Hz, H-1), 4.72 (t, 1H, *J* 5.2 Hz, O*H*), 4.09 (m, 1H, H-2), 4.91 (dd, 1H, $J_{3,4}$ 2.8 Hz, $J_{4,OH}$ 7.2 Hz, H-4), 3.76 (t, 1H, *J* 6.4 Hz, H-5), 3.52-3.49 (m, 2H, H-6a, H-6b), 2.29 (s, 3H, $SC_6H_4CH_3$). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): 160.1, 154.5, 148.0, 144.1, 141.5, 136.2, 131.0, 130.3, 129.6, 124.1, 120.0, 119.2, 117.4, 116.7, 111.8 (Ar*C*), 89.1 (C-1), 79.2, 67.6, 66.9, 66.2, 61.8, 60.2, 20.6 ($SC_6H_4CH_3$). HRMS calcd. for $C_{25}H_{25}N_3O_7S+H^+$ $(M+H)^+$: 512.1491, found: 512.1492.

XI. References

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