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

Supporting Information

Cyclopenta[*b*]naphthalene cyanoacrylate dyes: synthesis and evaluation as fluorescent molecular rotors

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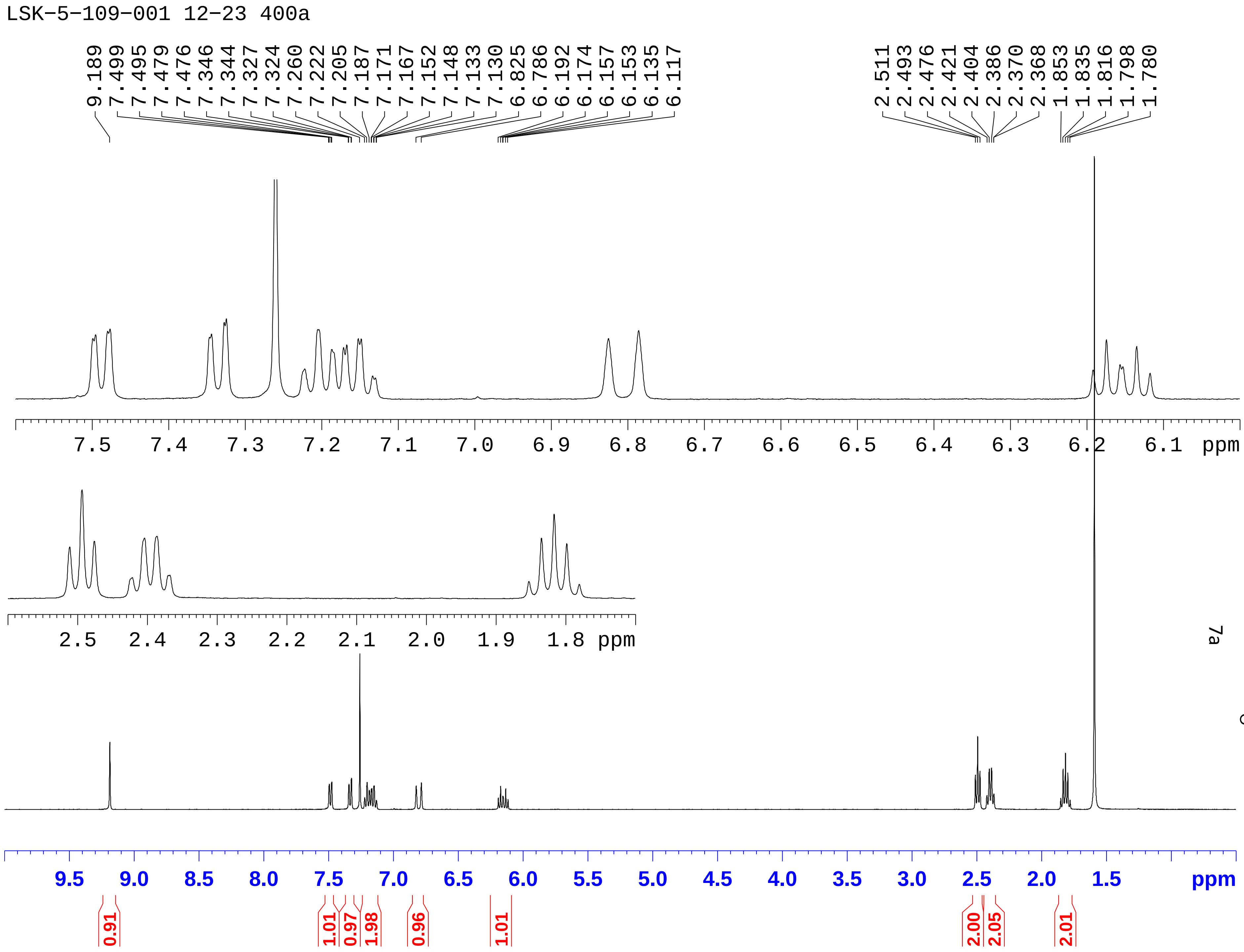
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7.205
7.187
7.171
7.167
7.152
7.148
7.133
7.130
6.825
6.786
6.192
6.174
6.157
6.153
6.135
6.117
2.511
2.493
2.476
2.421
2.404
2.386
2.370
2.368
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1.798
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7.4
7.3
7.2
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3.5
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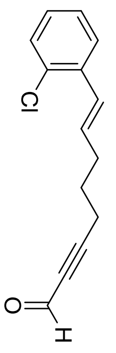
2.01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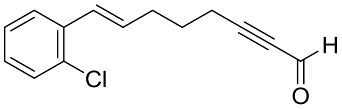
O
H

7a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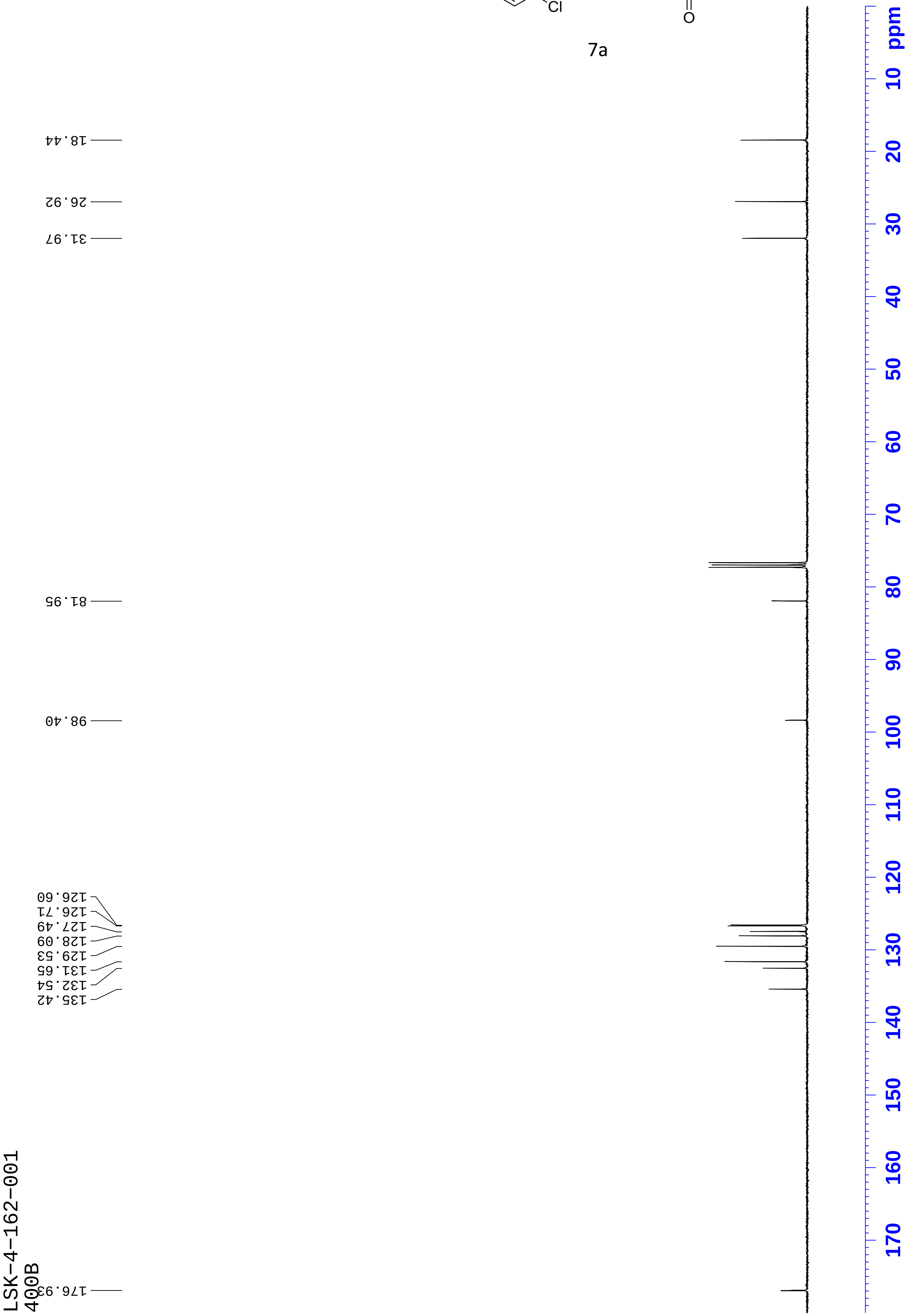
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129.53
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132.54
135.42
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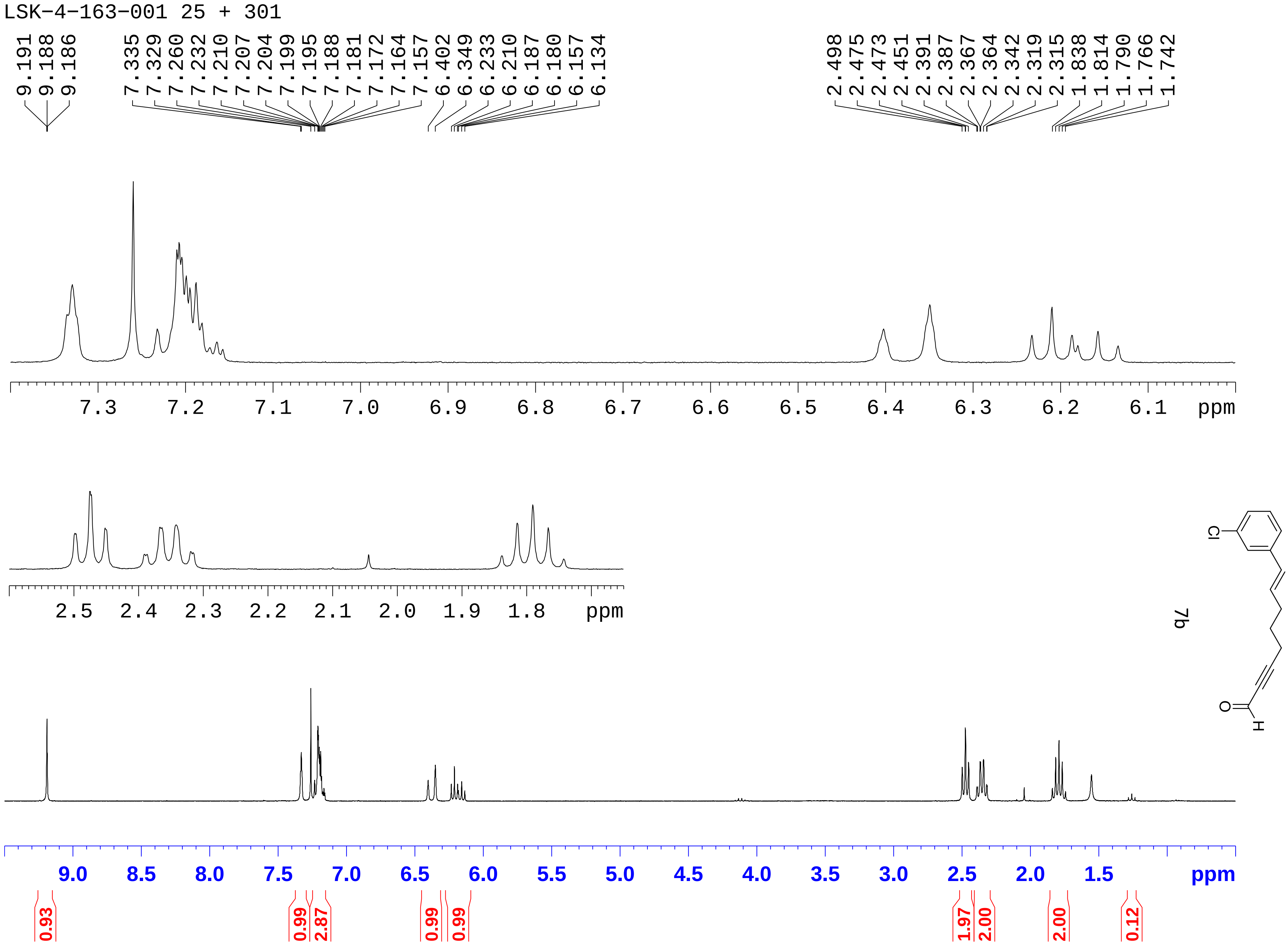
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7.207
7.204
7.199
7.195
7.188
7.181
7.172
7.164
7.157
6.402
6.349
6.233
6.210
6.187
6.180
6.157
6.134
2.498
2.475
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2.451
2.391
2.387
2.367
2.364
2.342
2.319
2.315
1.838
1.814
1.790
1.766
1.742
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
ppm
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
ppm
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6.0
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4.0
3.5
3.0
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1.5
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0.99
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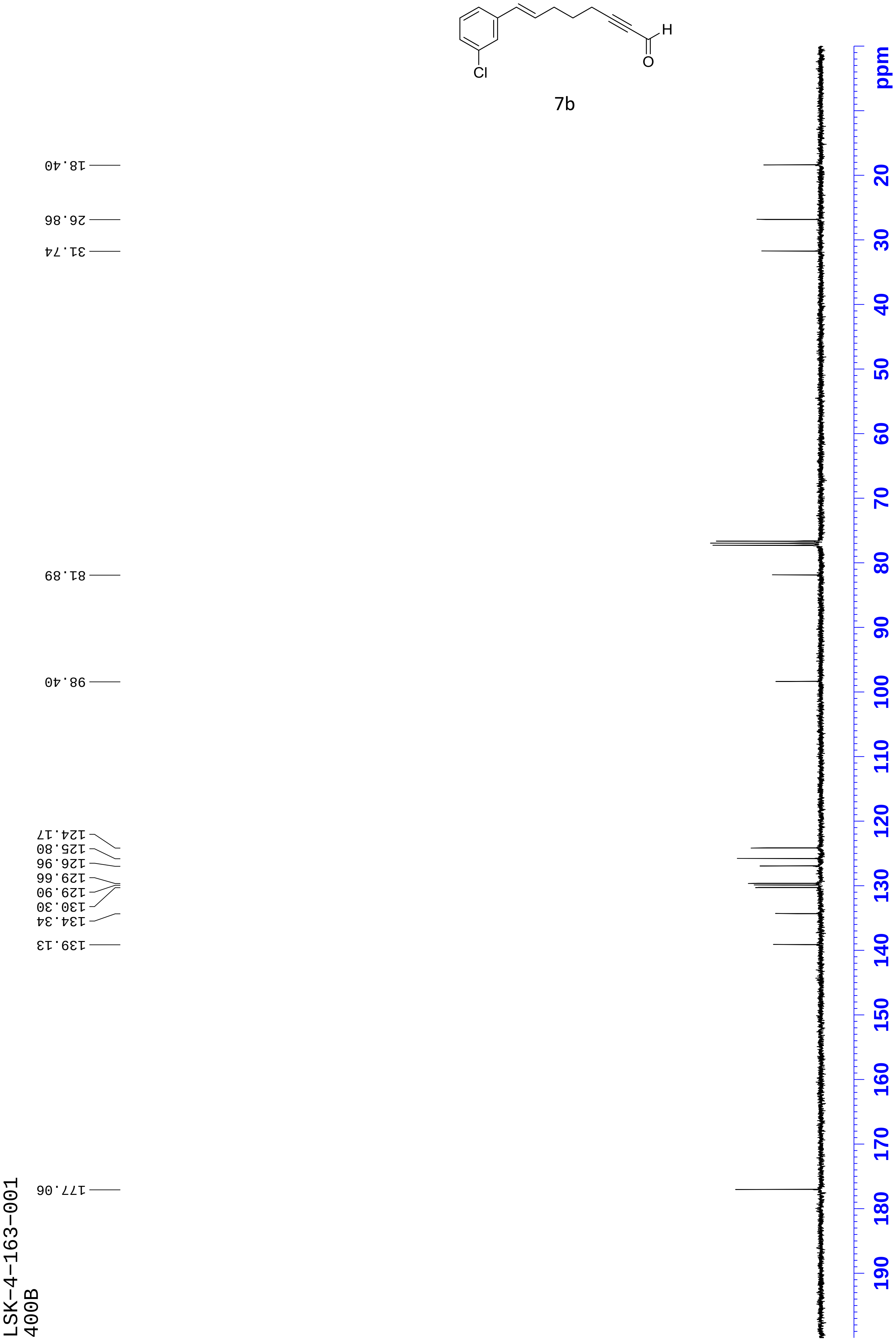
2.00
0.12
Cl
O
H

7b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98.40
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129.66
129.90
130.30
134.34
139.13
177.06
ppm
20
30
40
50
60
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110
120
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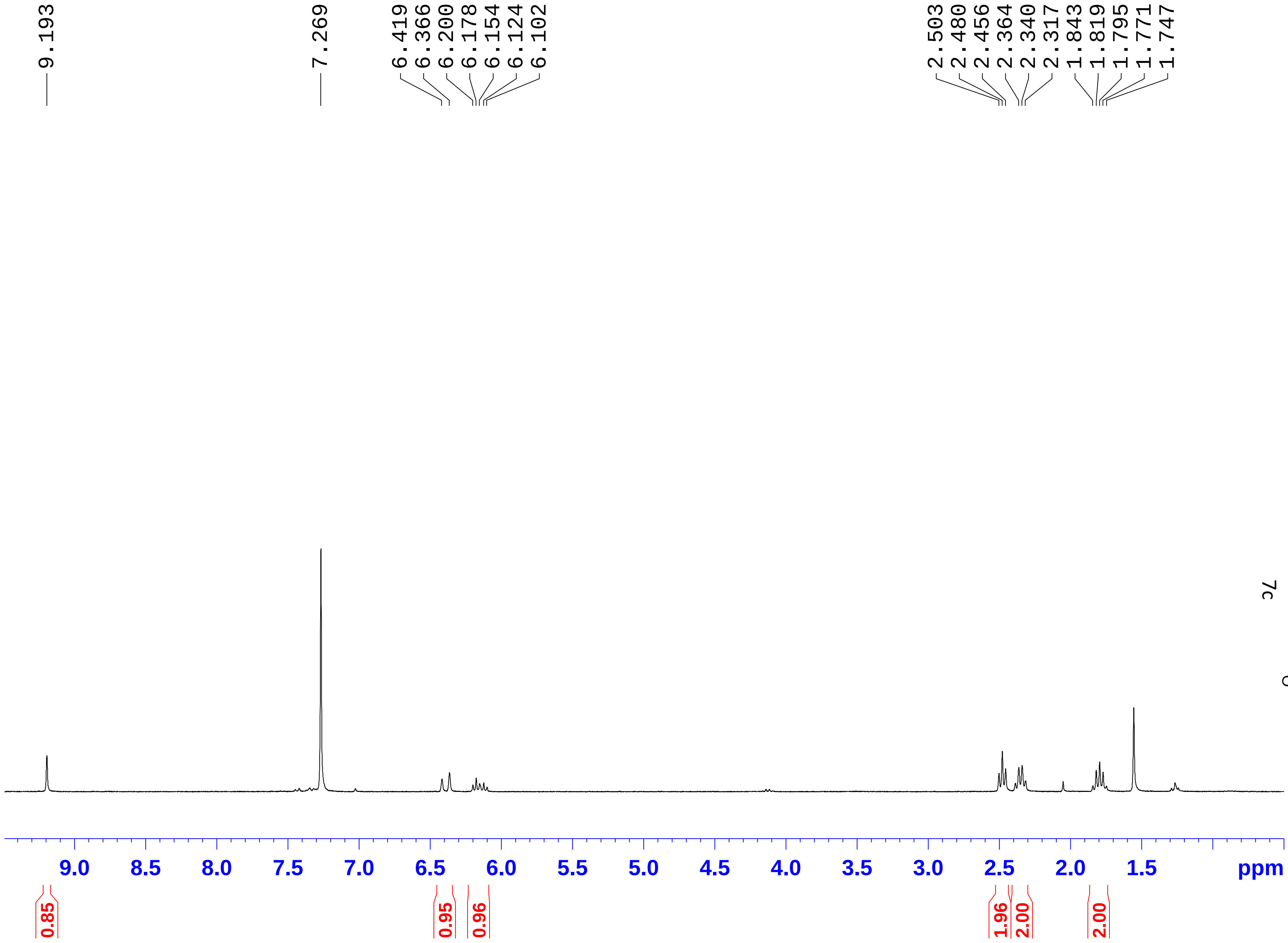
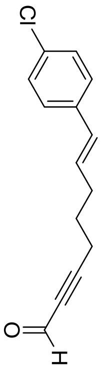
180
190
Cl
H
O

LSK-4-028-001 301





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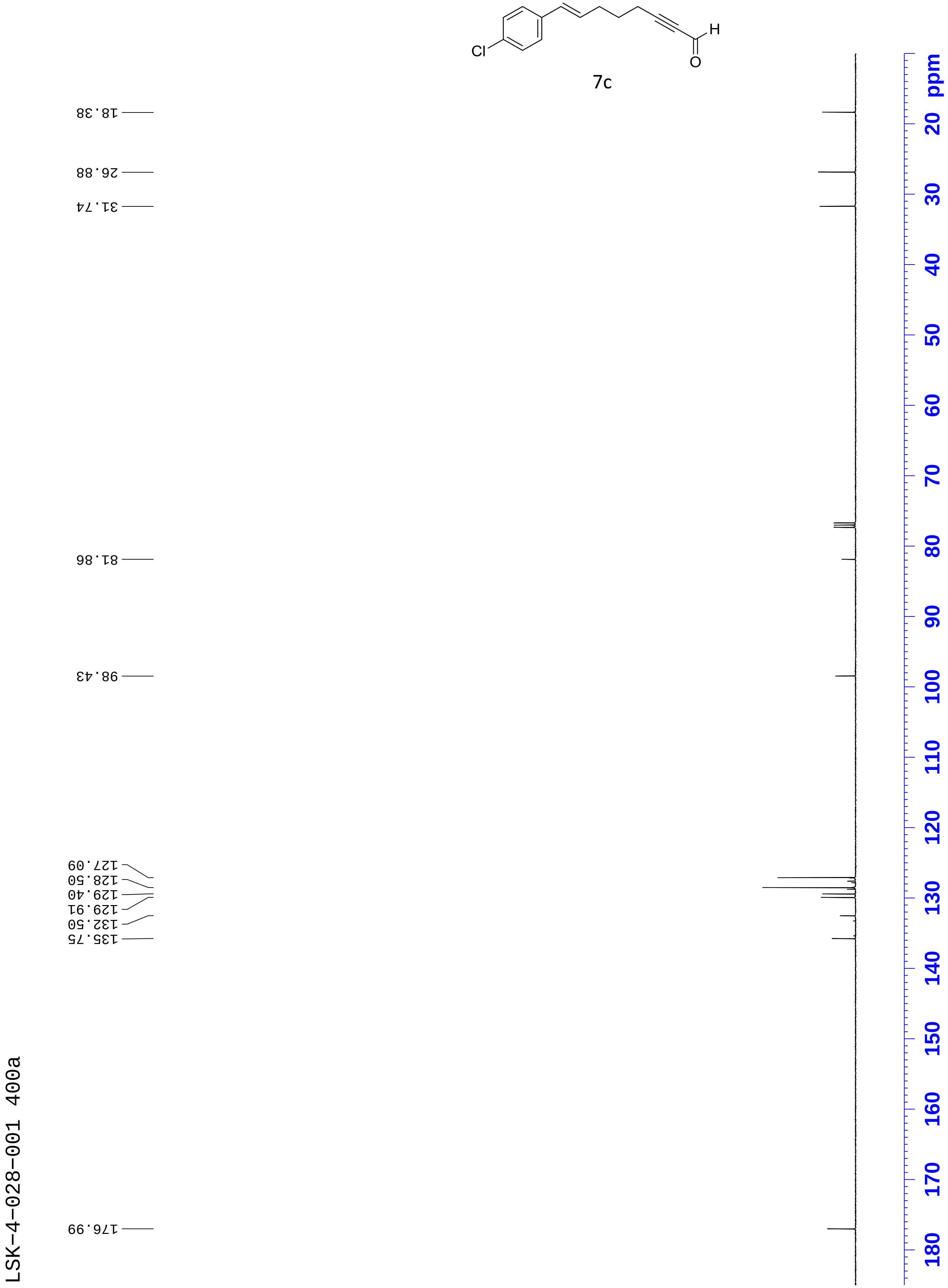

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81.86
98.43
127.09
128.50
129.40
129.91
132.50
135.75
176.99
20 ppm
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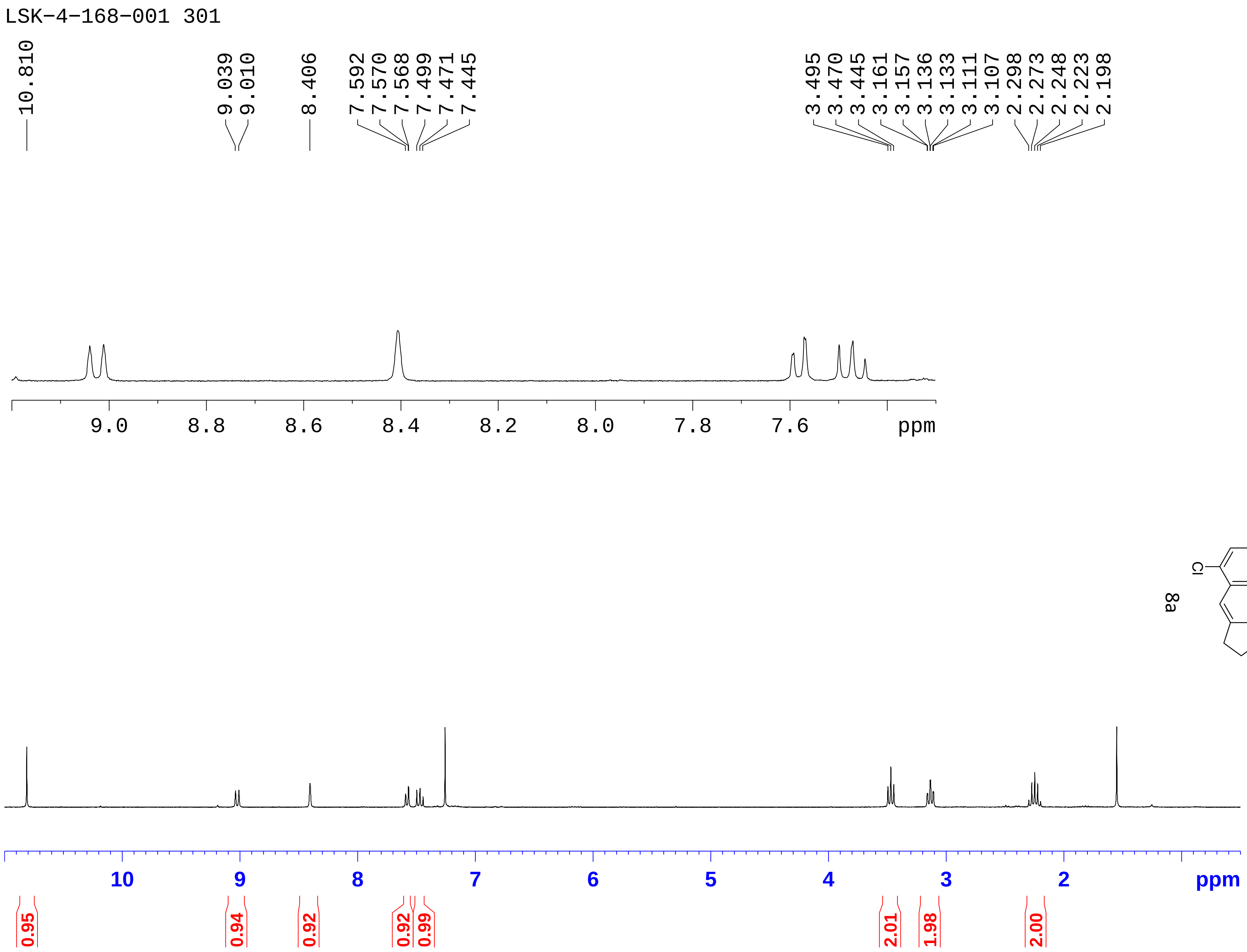
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
Cl
H
O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7.570
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7.499
7.471
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3.495
3.470
3.445
3.161
3.157
3.136
3.133
3.111
3.107
2.298
2.273
2.248
2.223
2.198
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
ppm
10
9
8
7
6
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4
3
2
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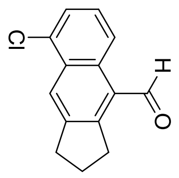
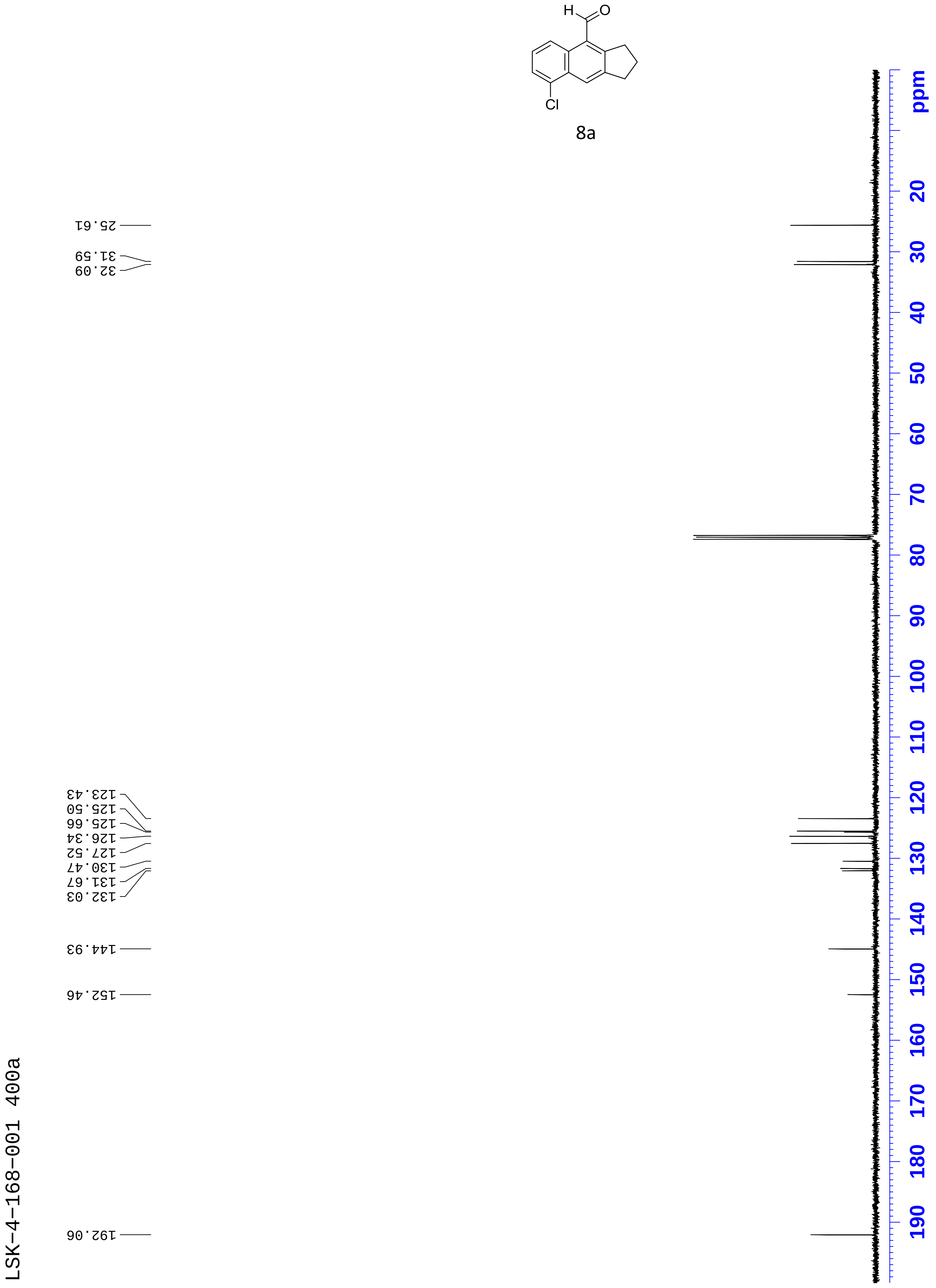
2.00


Cl
H
O

8a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144.93
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126.34
125.66
125.50
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32.09
31.59
25.61
ppm
20
30
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80
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140
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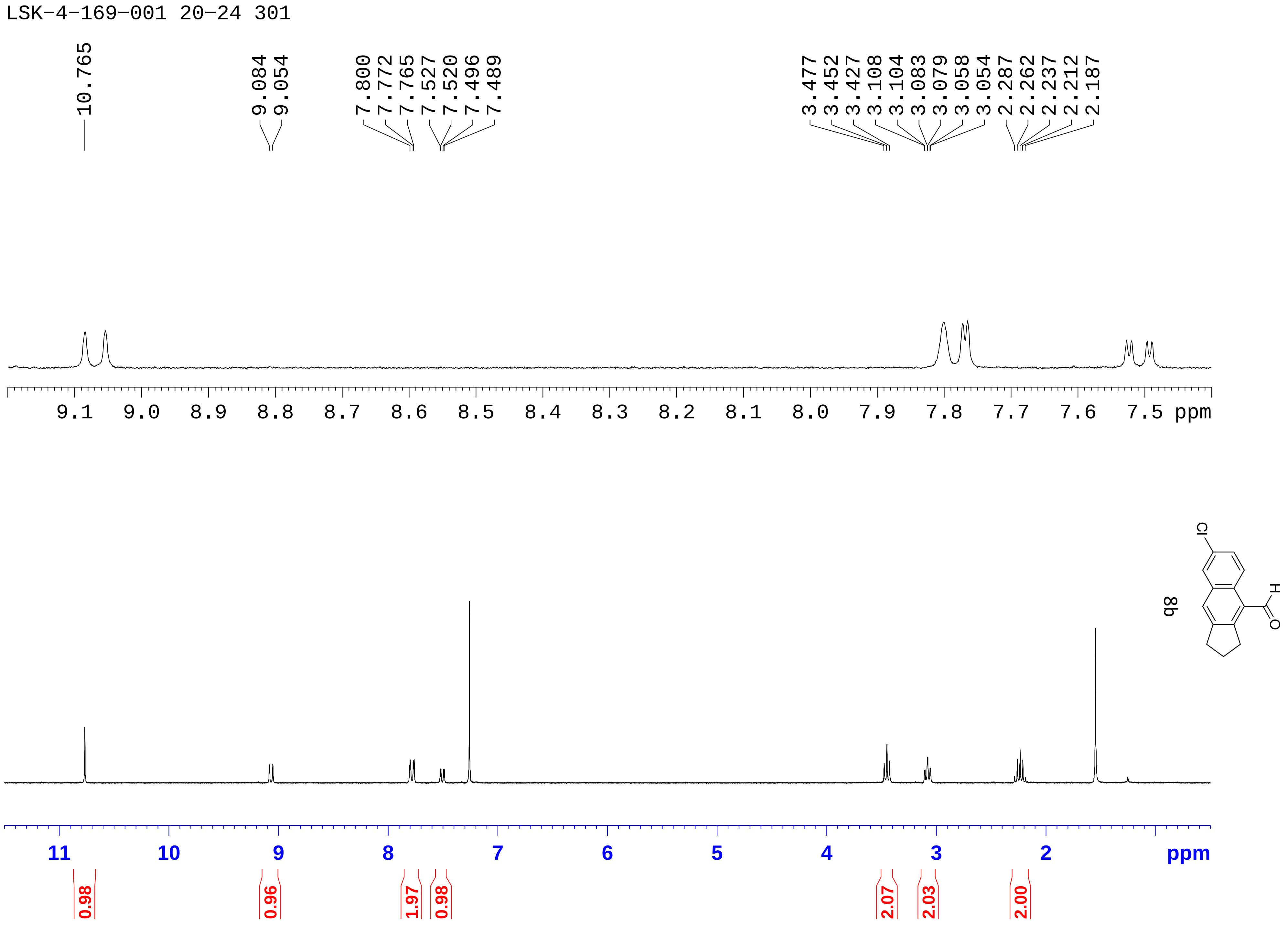
170
180
190
H
O
Cl

8a

LSK-4-169-001 20-24 301
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9.054
7.800
7.772
7.765
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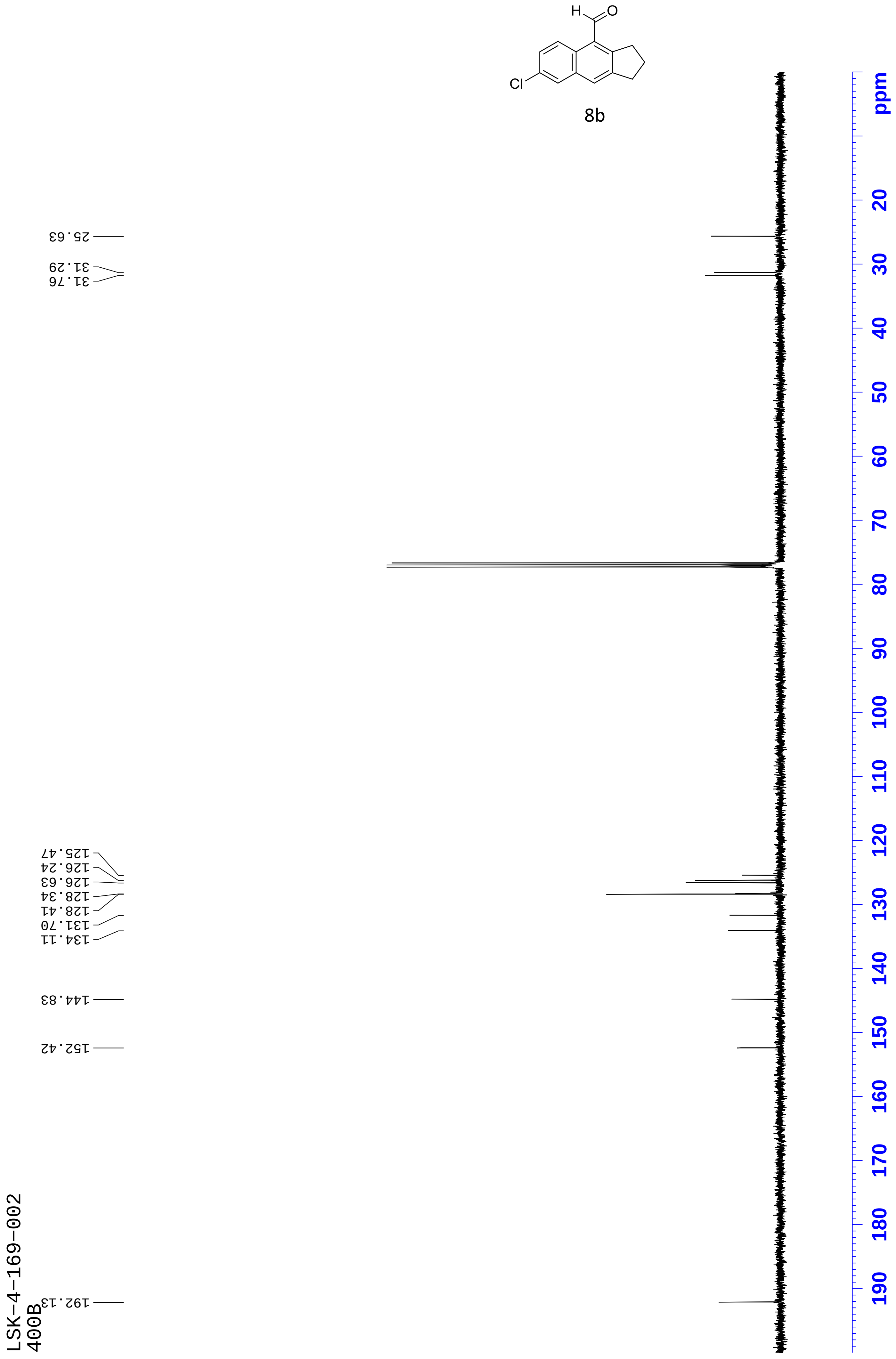
7.520
7.496
7.489
3.477
3.452
3.427
3.108
3.104
3.083
3.079
3.058
3.054
2.287
2.262
2.237
2.212
2.187
9.1
9.0
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5 ppm
Cl
H
O
8b
11
10
9
8
7
6
5
4
3
2
ppm
0.98
0.96
1.97
0.98
2.07
2.03
2.00


H
O
Cl
8b
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128.34
128.41
131.70
134.11
144.83
152.42
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30
40
50
60
70
80
90
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110
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130
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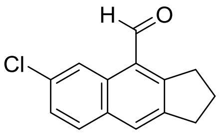

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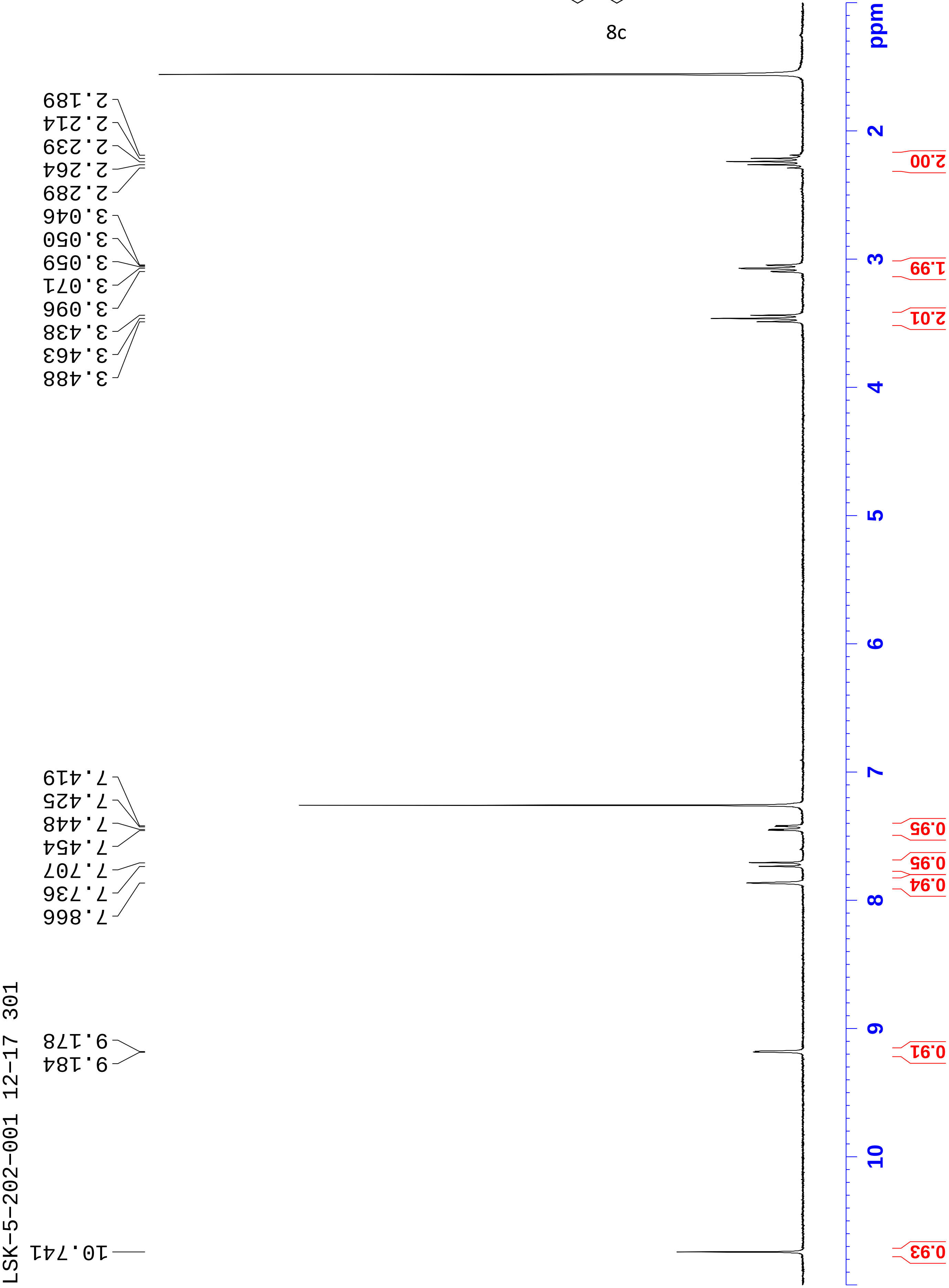
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3.050
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3.438
3.463
3.488
7.419
7.425
7.448
7.454
7.707
7.736
7.866
9.178
9.184
10.741
ppm
2
3
4
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6
7
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9
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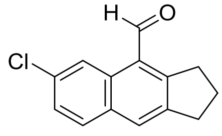
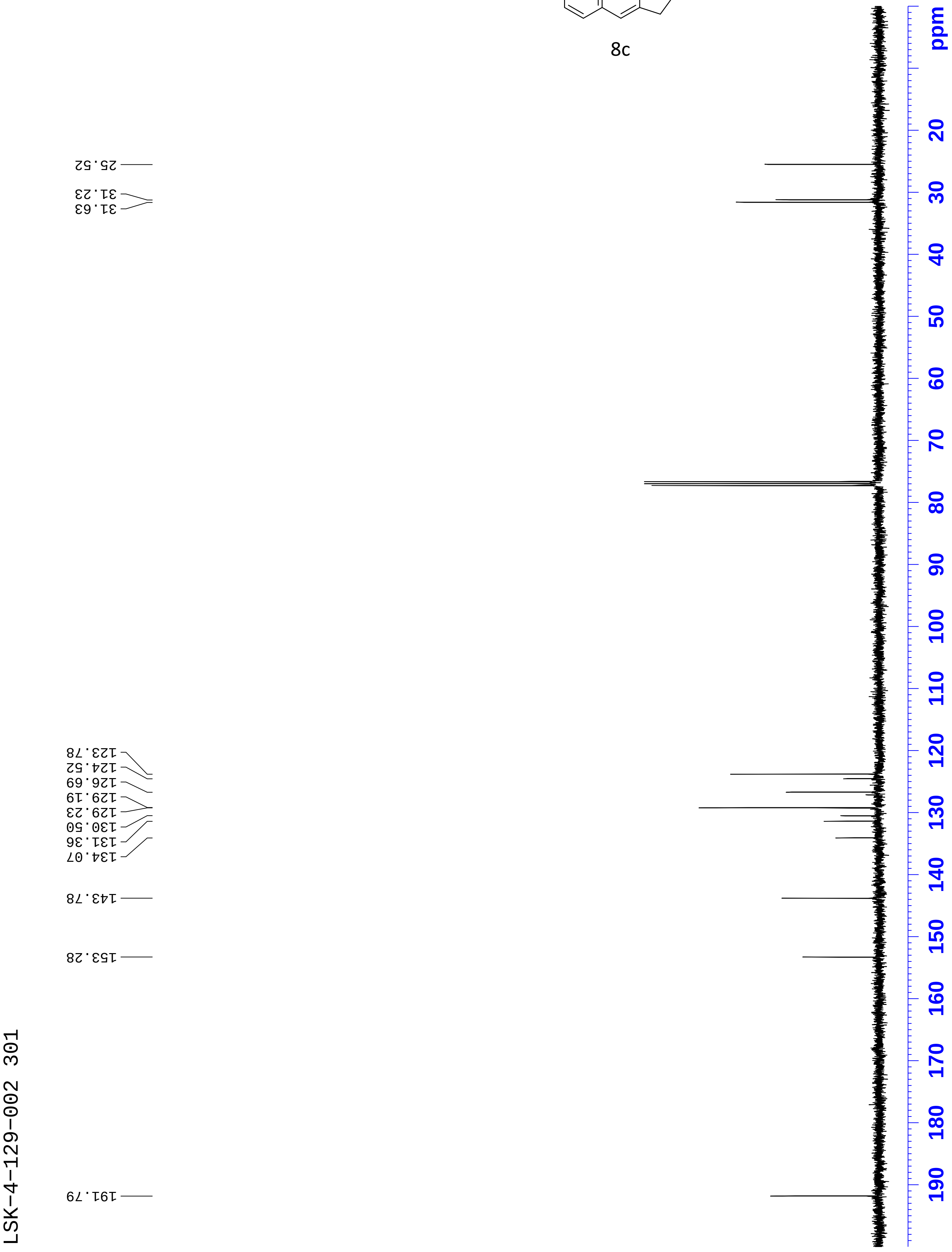
0.94
0.91
0.93


H
O
Cl

8c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31.23
31.63
123.78
124.52
126.69
129.19
129.23
130.50
131.36
134.07
143.78
153.28
191.79
ppm
20
30
40
50
60
70
80
90
100
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120
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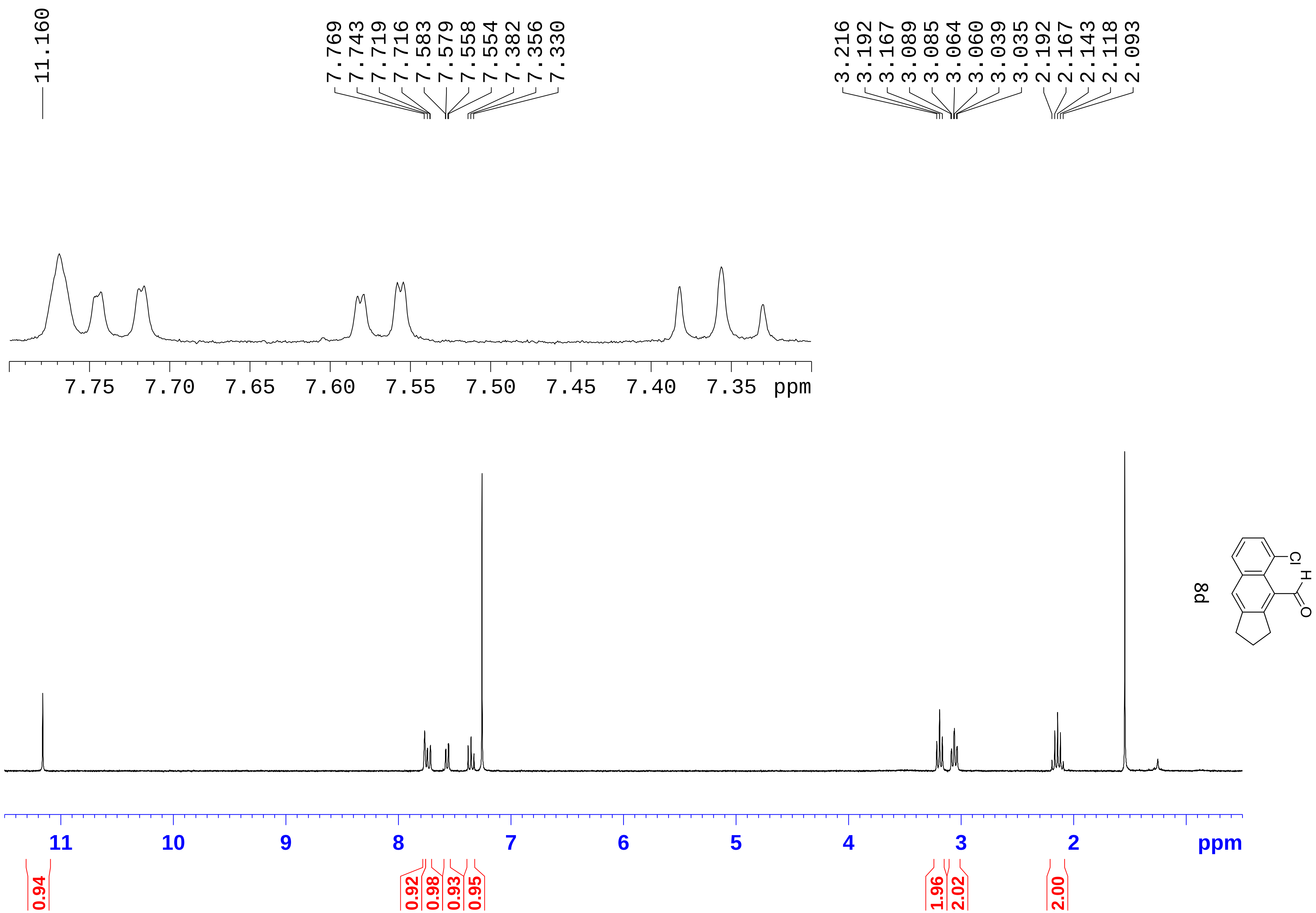
140
150
160
170
180
190

LSK-4-169-001 28-30 301



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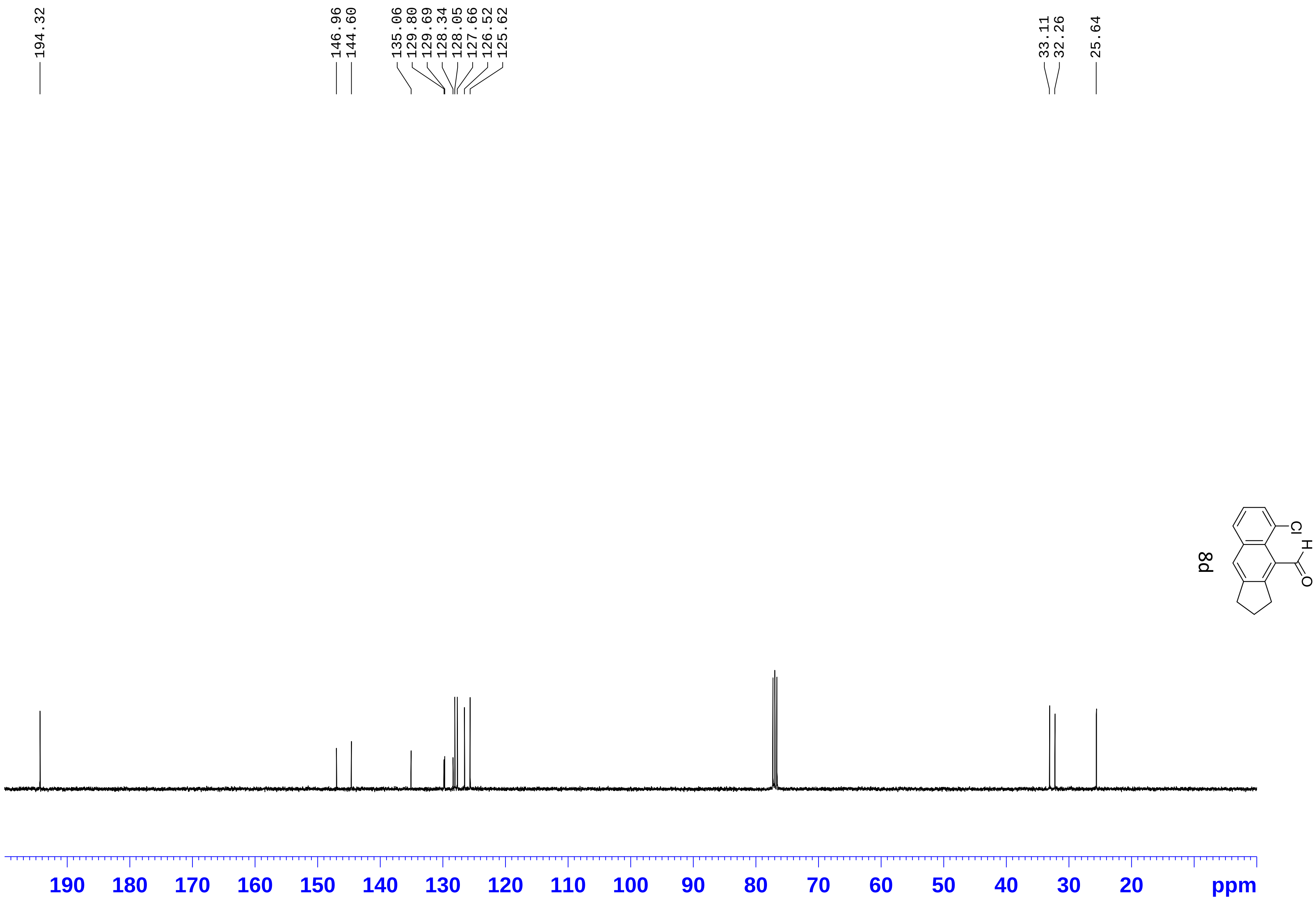

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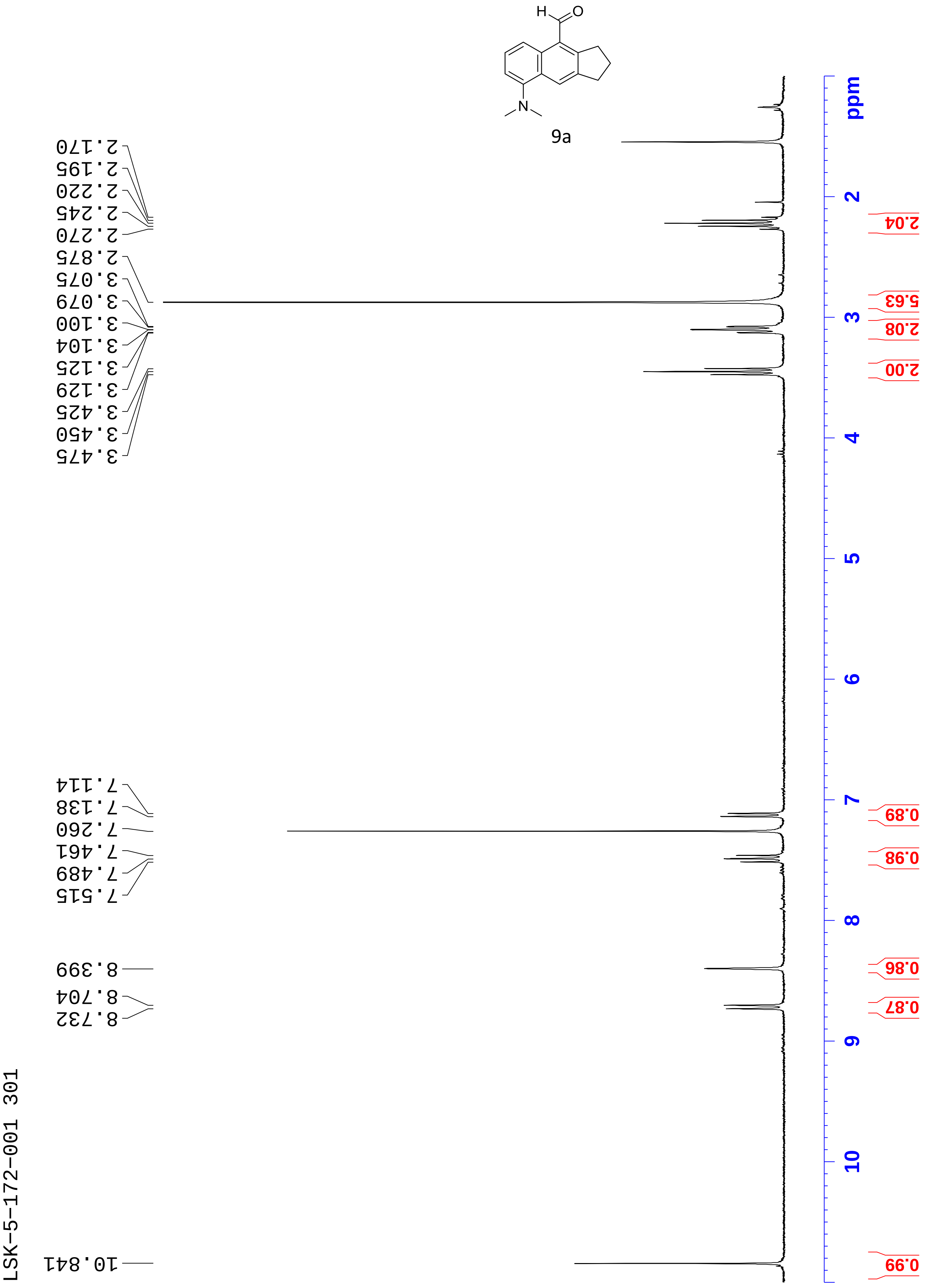
9a

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2.270
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3.079
3.100
3.104
3.125
3.129
3.425
3.450
3.475
7.114
7.138
7.260
7.461
7.489
7.515
8.399
8.704
8.732
10.841
ppm
2
3
4
5
6
7
8
9
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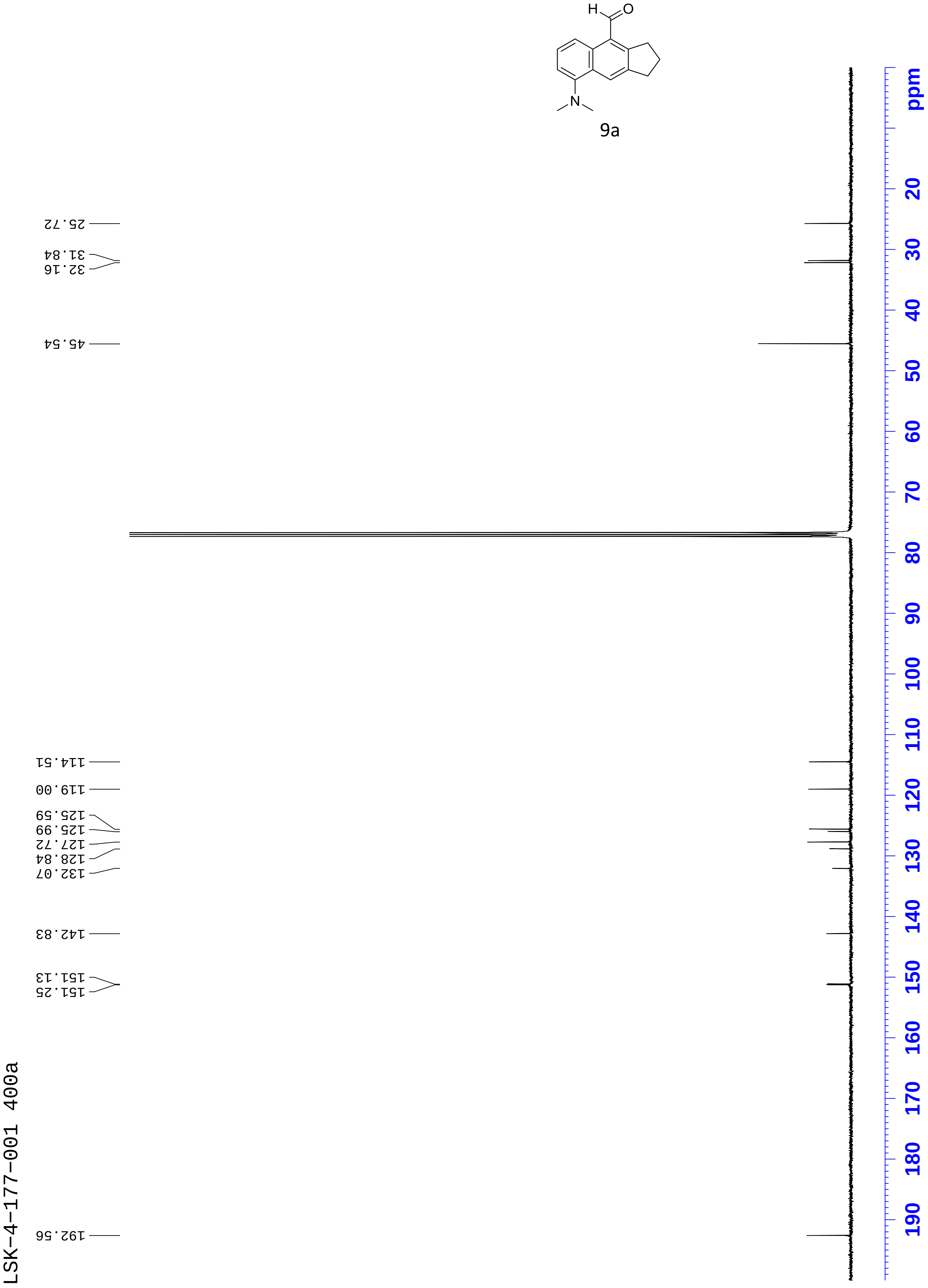
0.98
0.86
0.87
0.99
H
O
N


H
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127.72
128.84
132.07
142.83
151.13
151.25
192.56
ppm
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140
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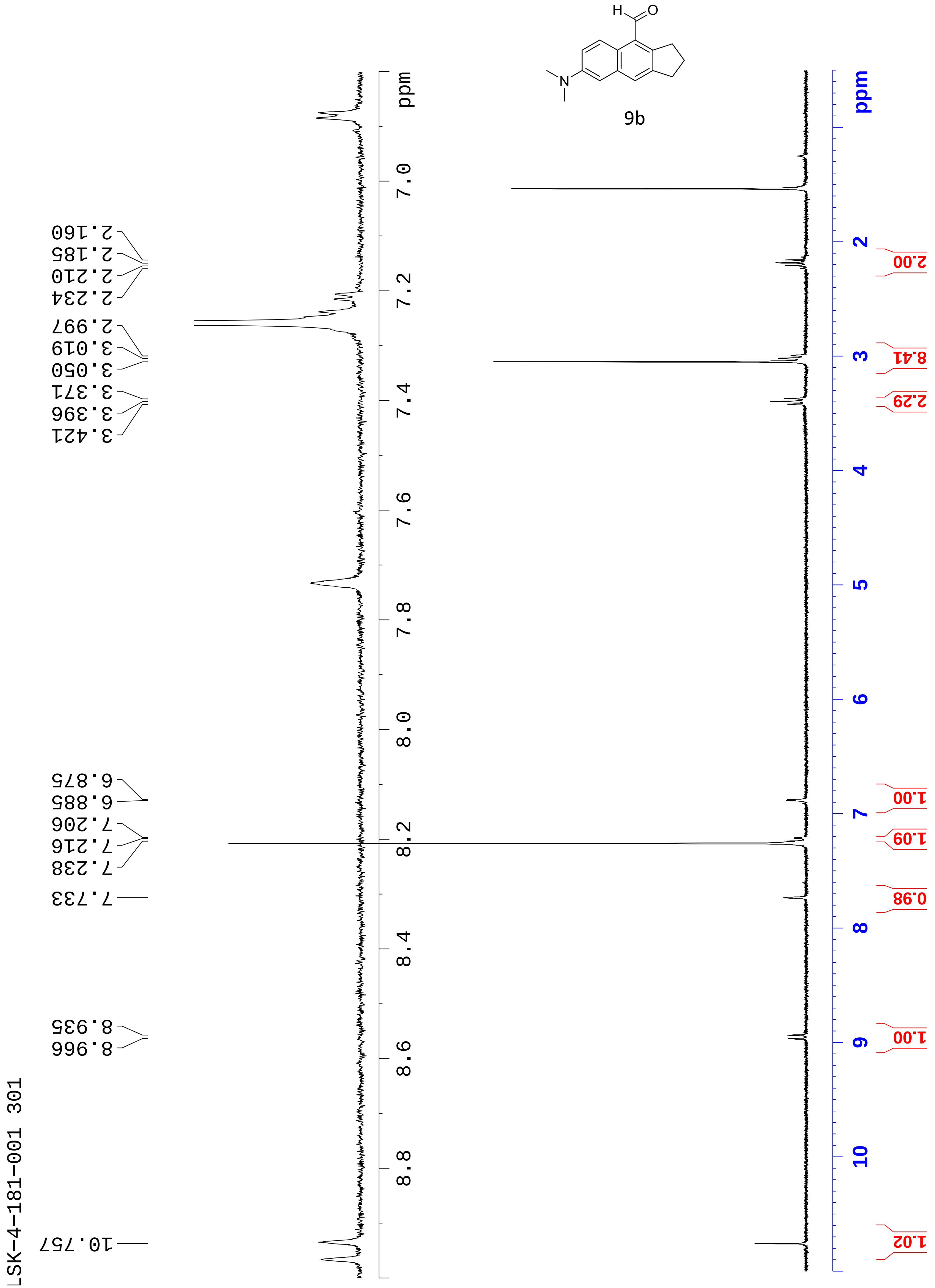
180
190

9a



9b

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7.216
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6.875
3.421
3.396
3.371
3.050
3.019
2.997
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2.210
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2.160
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7.2
7.4
7.6
7.8
8.0
8.2
8.4
8.6
8.8
ppm
2
3
4
5
6
7
8
9
10
2.00
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1.09
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1.00
1.02
H
O
N

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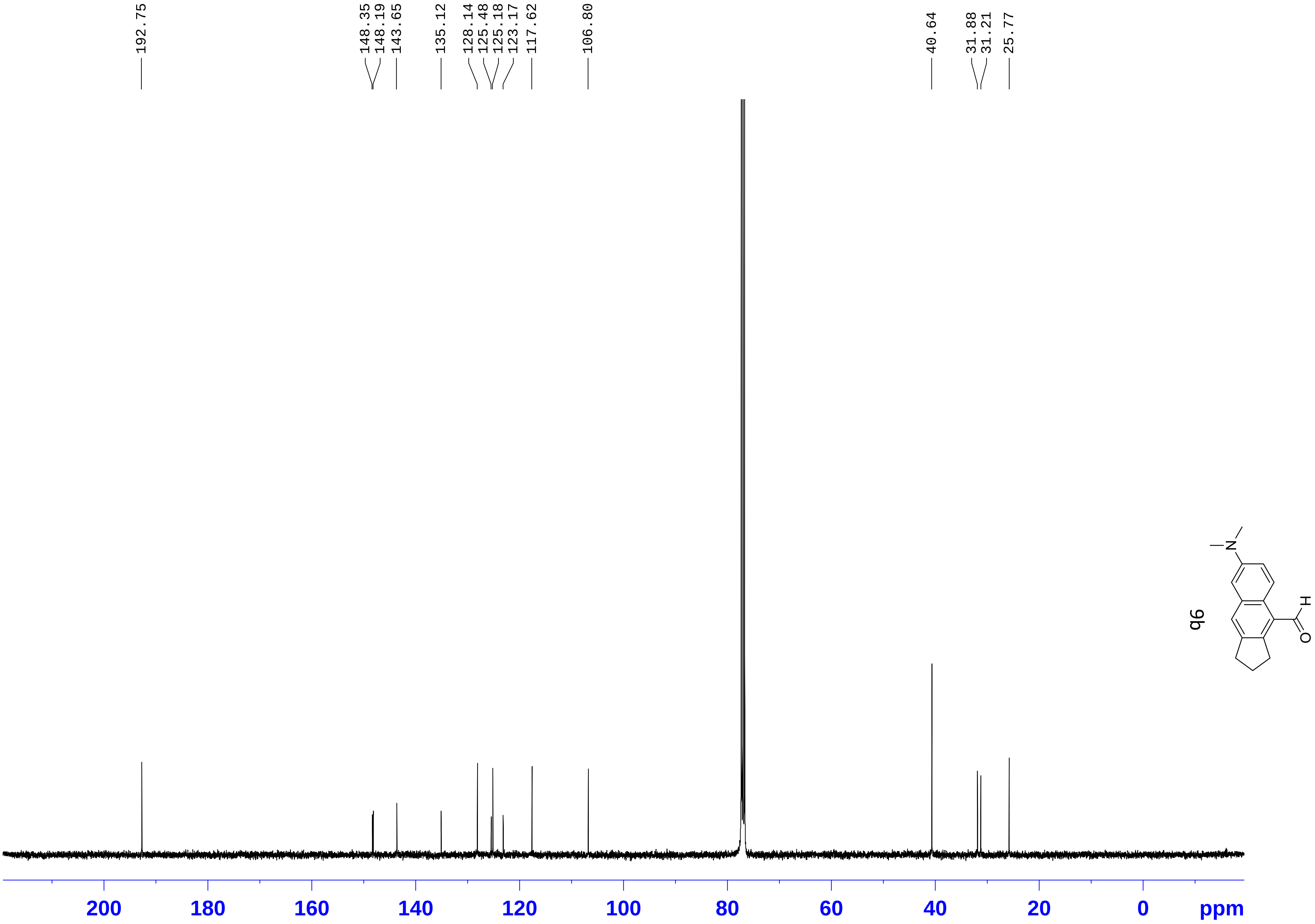

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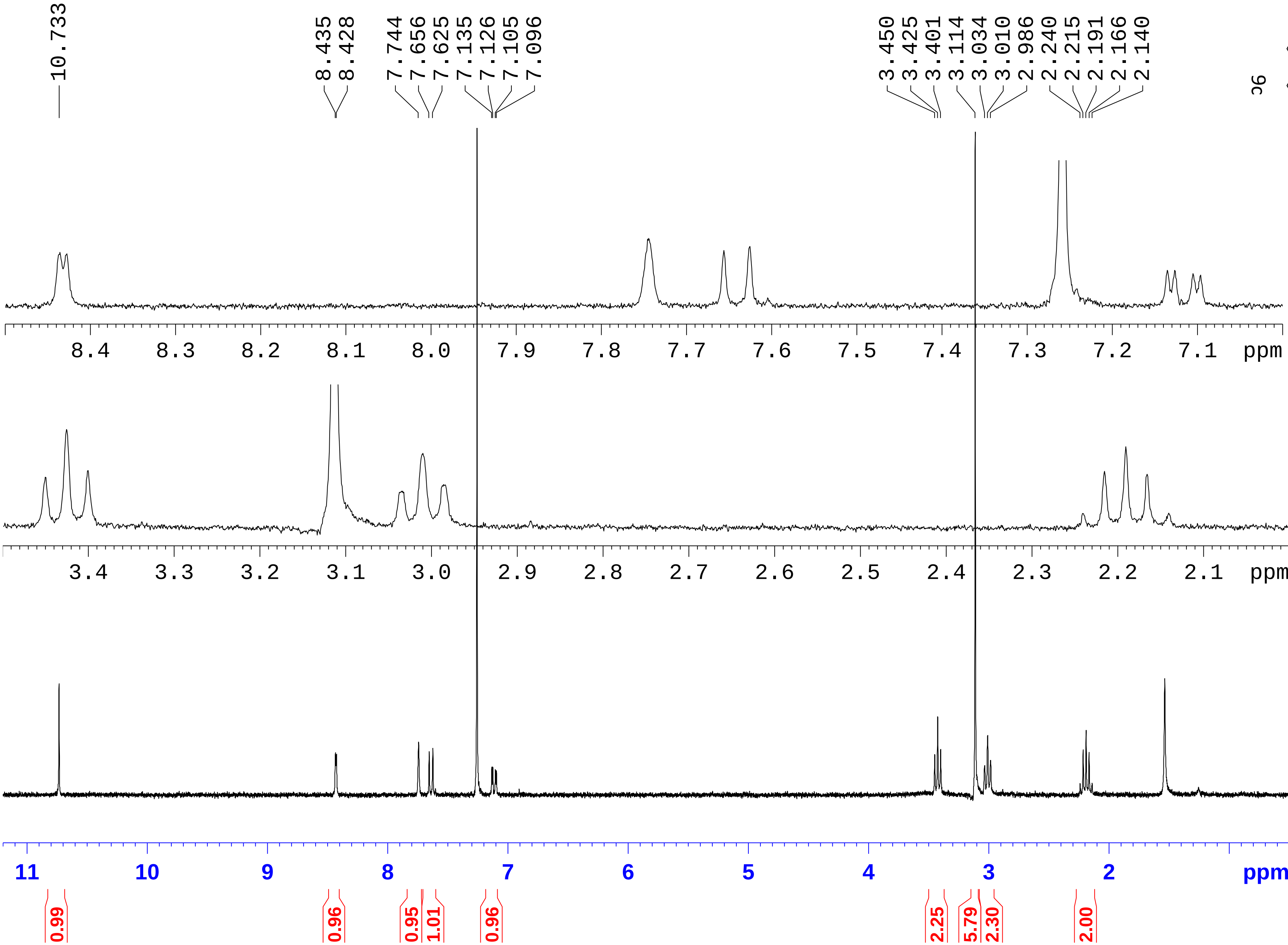

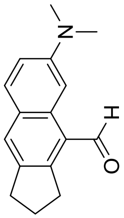

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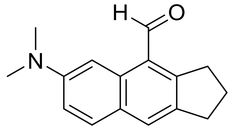

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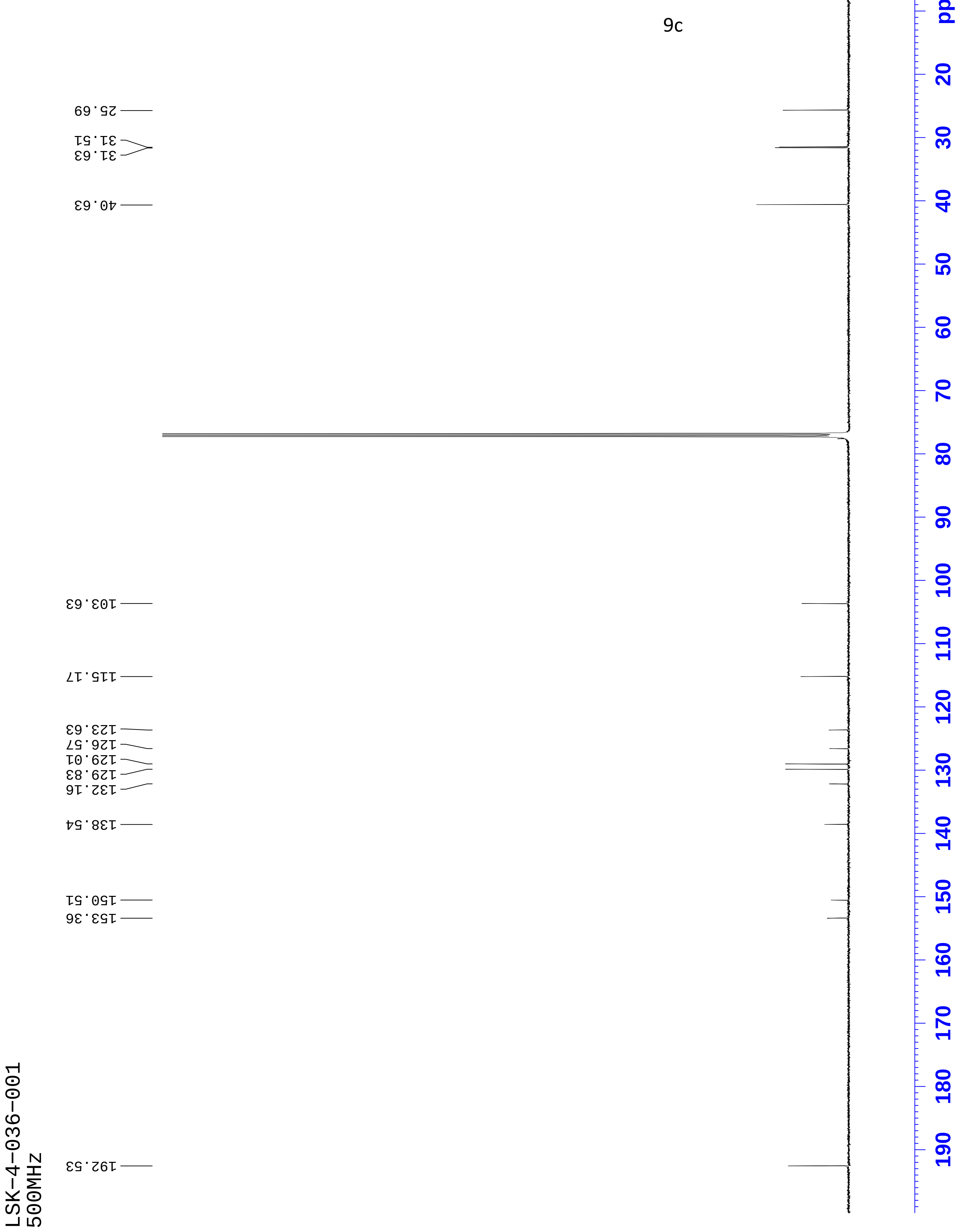
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40.63
103.63
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123.63
126.57
129.01
129.83
132.16
138.54
150.51
153.36
192.53
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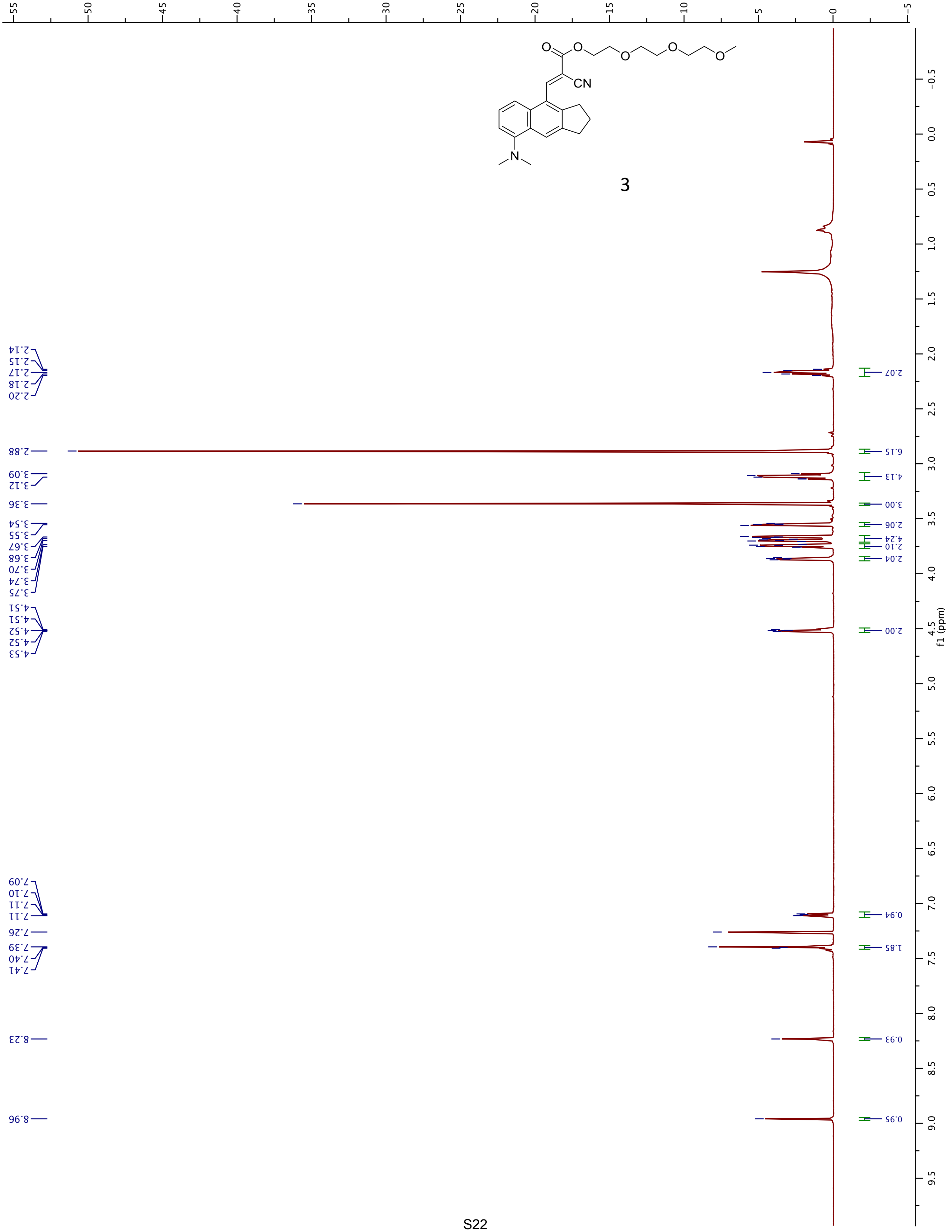
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190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2.14
2.15
2.17
2.18
2.20
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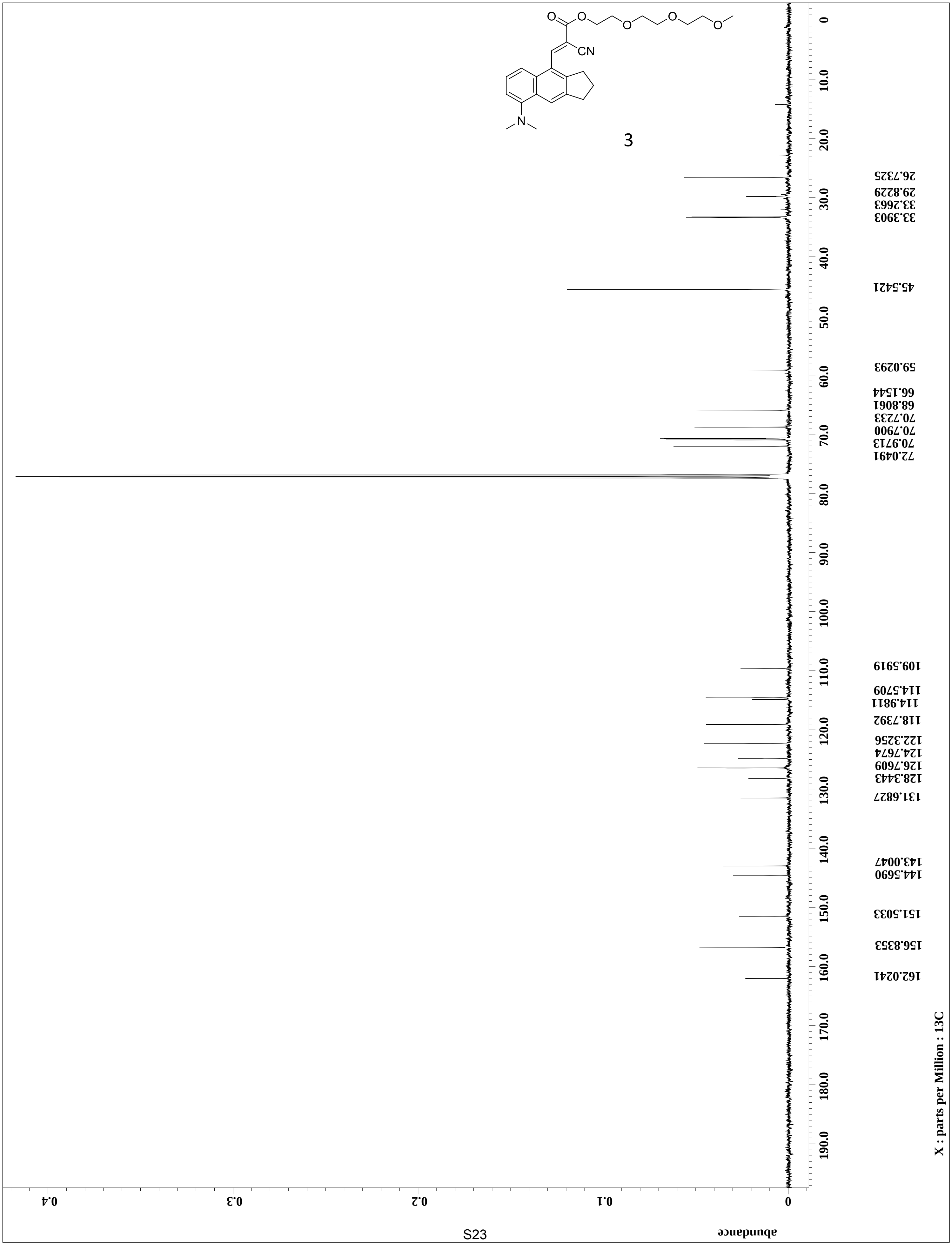
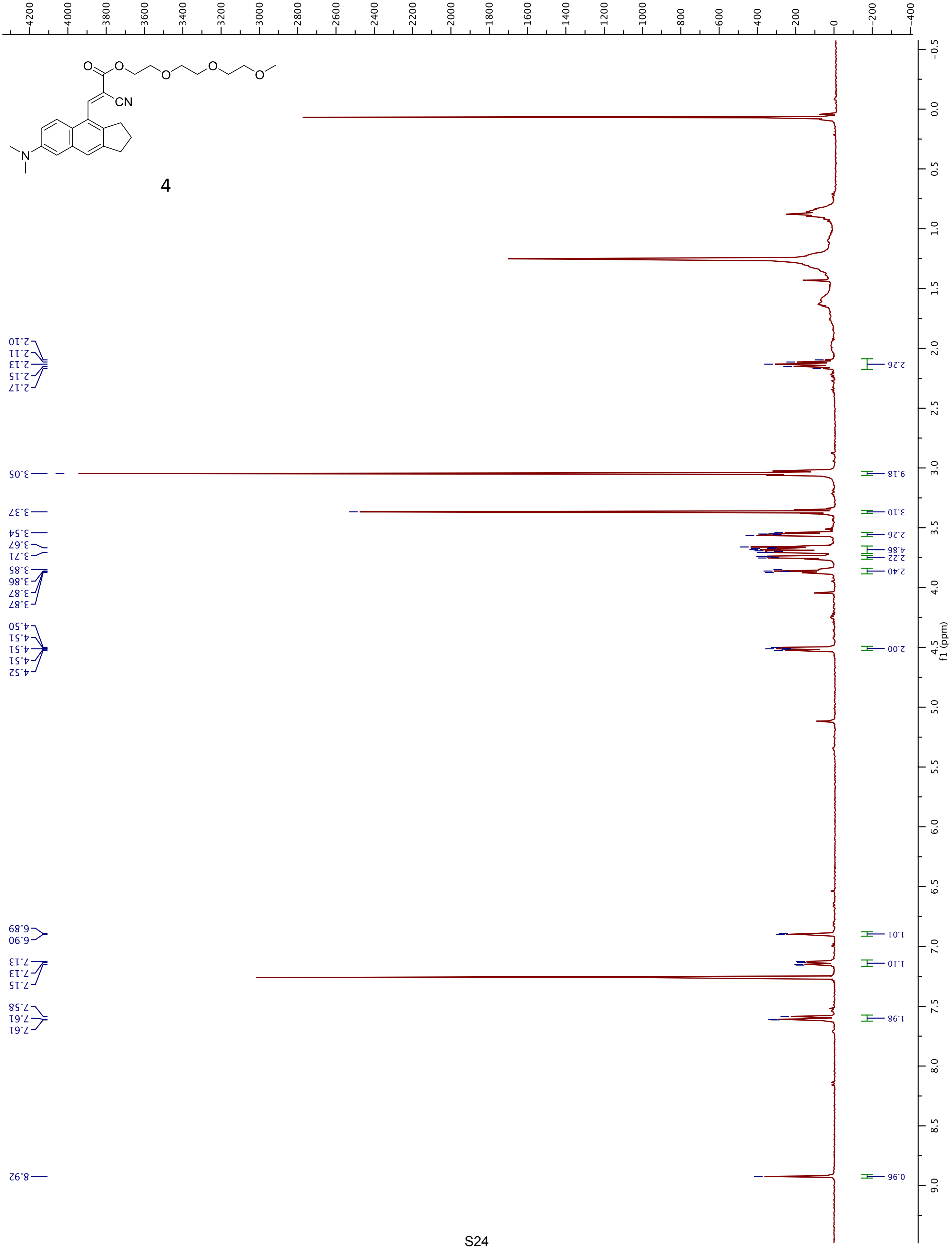
3.09
3.12
3.36
3.54
3.55
3.67
3.68
3.70
3.74
3.75
4.51
4.51
4.52
4.52
4.53
7.09
7.10
7.11
7.11
7.26
7.39
7.40
7.41
8.23
8.96
2.07
6.15
4.13
3.00
2.06
4.24
2.10
2.04
2.00
0.94
1.85
0.93
0.95
f1 (ppm)
O
O
O
O
O
CN
N


3
CN
26.7325
29.8229
33.2663
33.3903
45.5421
59.0293
66.1544
68.8061
70.7233
70.7900
70.9713
72.0491
109.5919
114.5709
114.9811
118.7392
122.3256
124.7674
126.7609
128.3443
131.6827
143.0047
144.5690
151.5033
156.8353
162.0241
X : parts per Million : 13C
abundance



O
O
O
O
O
CN
N
2.10
2.11
2.13
2.15
2.17
3.05
3.37
3.54
3.67
3.71
3.85
3.86
3.87
3.87
4.50
4.51
4.51
4.51
4.52
6.89
6.90
7.13
7.13
7.15
7.58
7.61
7.61
8.92
2.26
9.18
3.10
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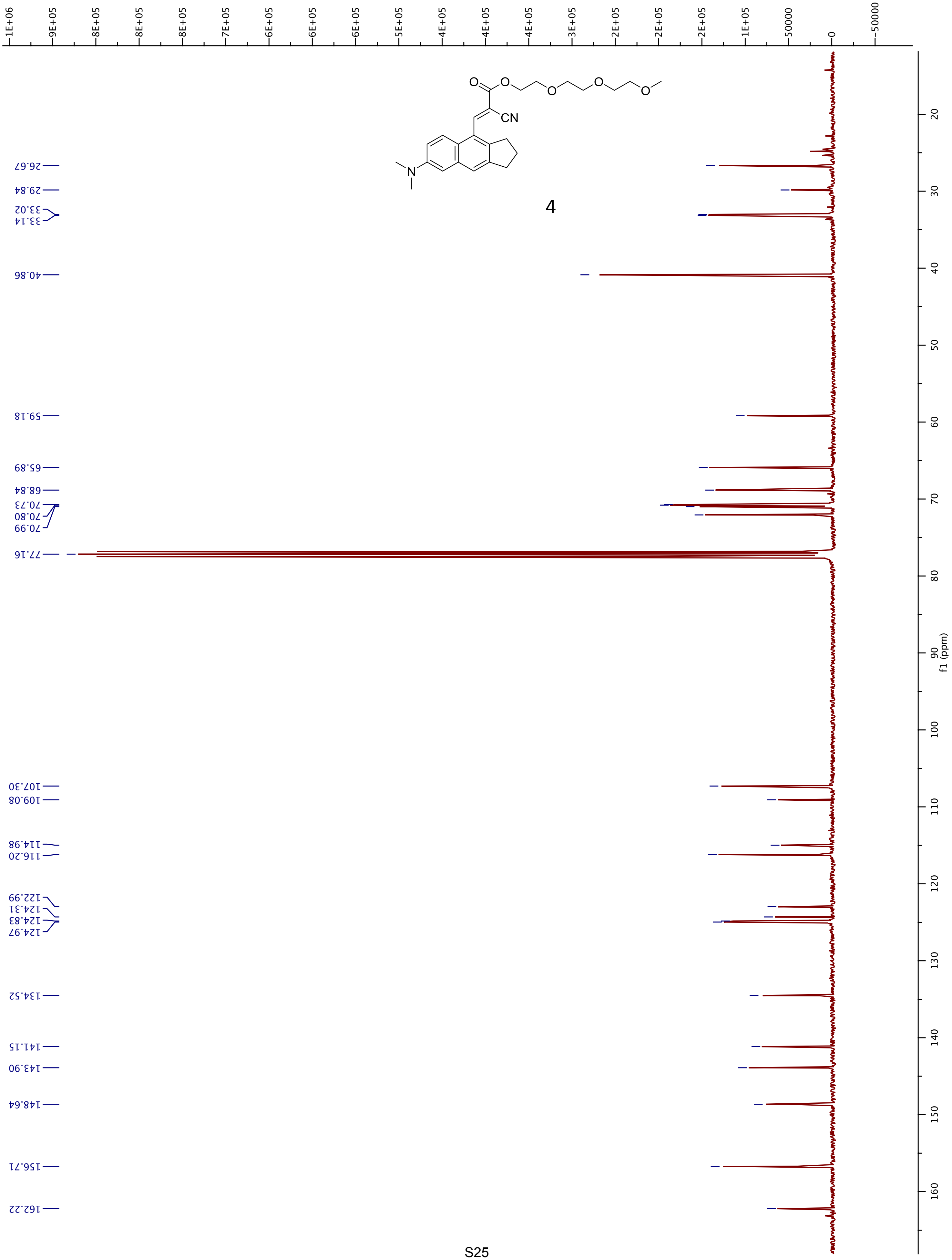
1.01
1.10
1.98
0.96
f1 (ppm)

4


4

26.67
29.84
33.02
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77.16
107.30
109.08
114.98
116.20
122.99
124.31
124.83
124.97
134.52
141.15
143.90
148.64
156.71
162.22
f1 (ppm)
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
1E+06
9E+05
8E+05
8E+05
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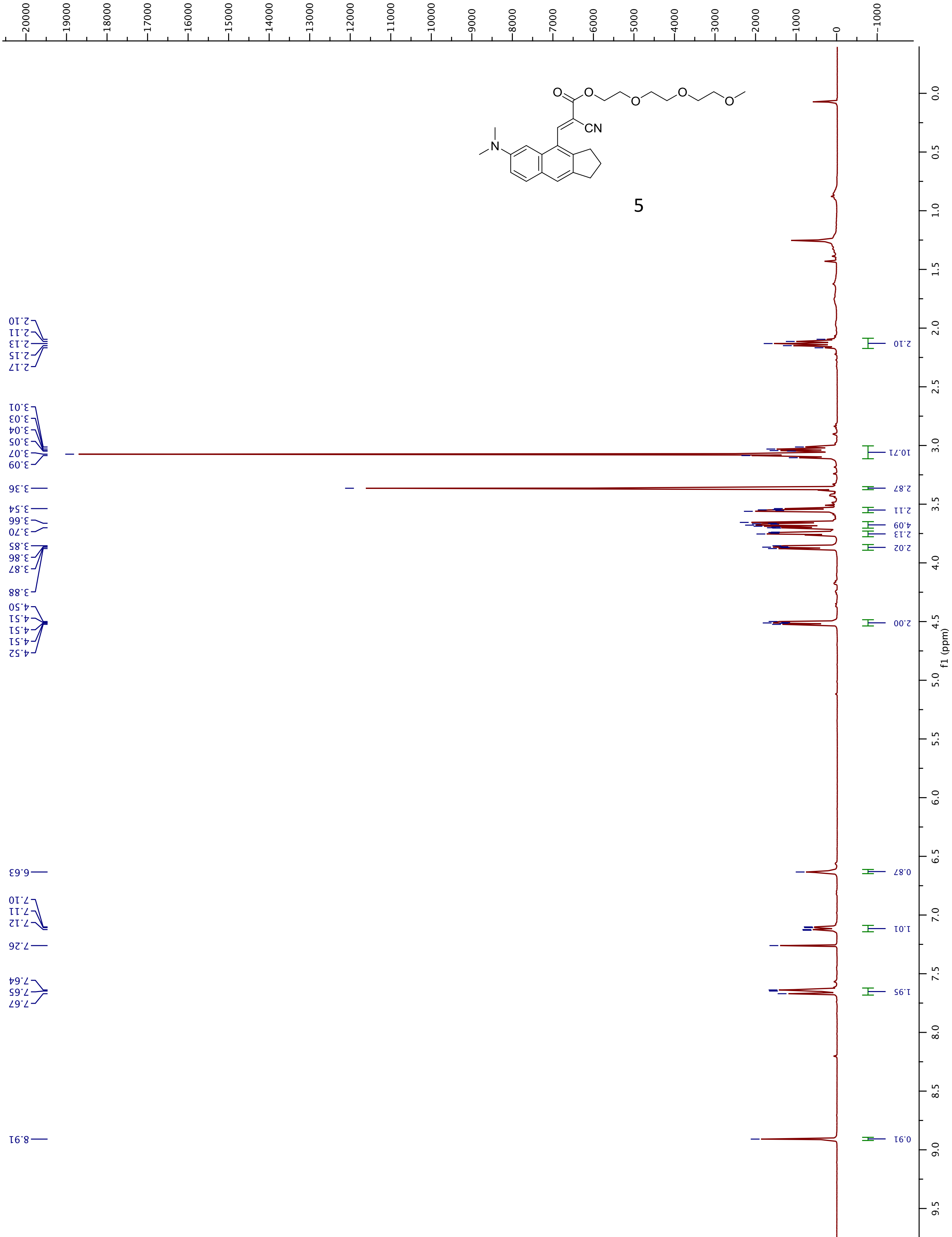
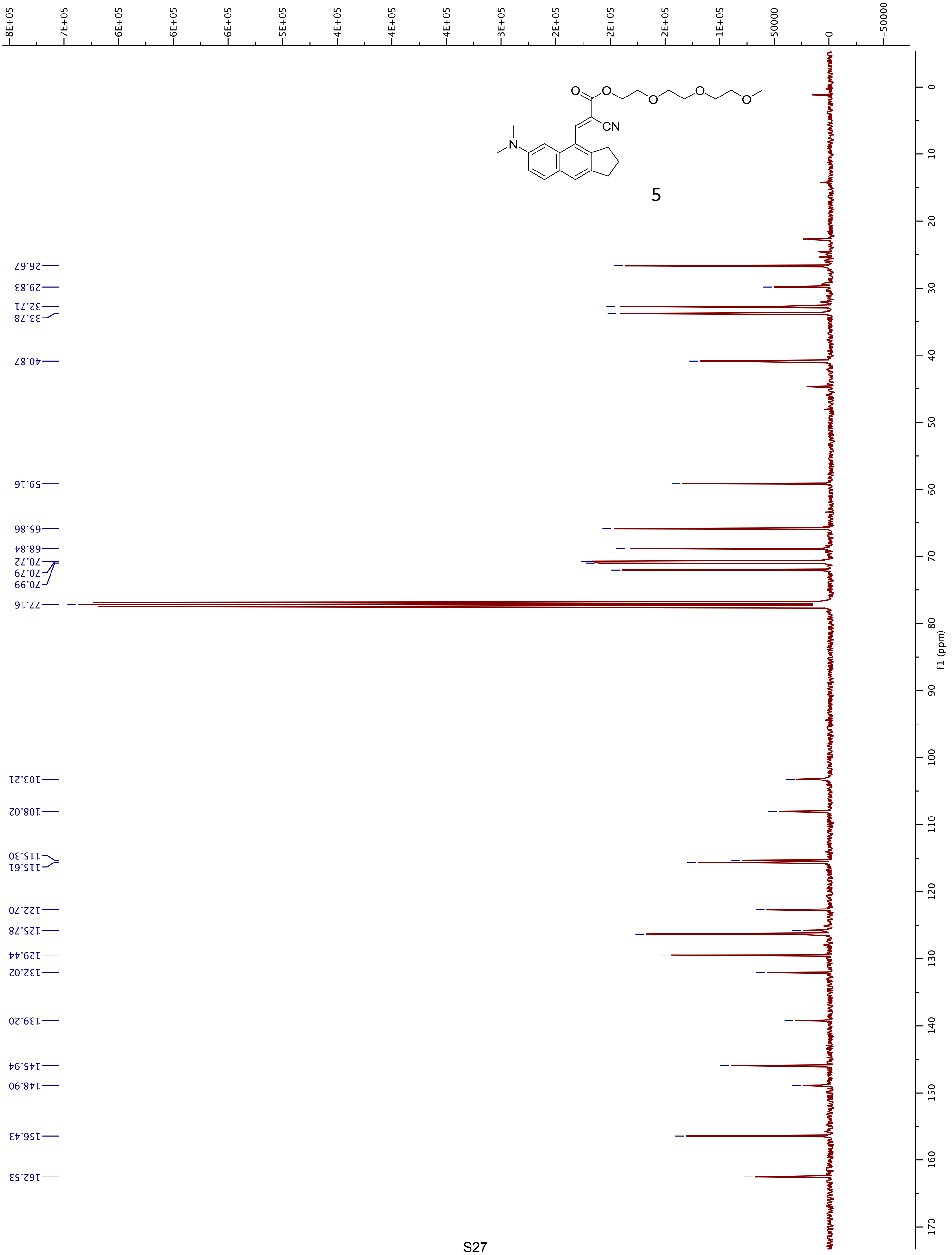
CN
N



5
CN
N
O
2.10
2.11
2.13
2.15
2.17
3.01
3.03
3.04
3.05
3.07
3.09
3.36
3.54
3.66
3.70
3.85
3.86
3.87
3.88
4.50
4.51
4.51
4.51
4.52
6.63
7.10
7.11
7.12
7.26
7.64
7.65
7.67
8.91
2.10
10.71
2.87
2.11
4.09
2.13
2.02
2.00
0.87
1.01
1.95
0.91
f1 (ppm)
0.0
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
8.0
8.5
9.0
9.5
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000


5
O
O
O
O
O
CN
N
26.67
29.83
32.71
33.78
40.87
59.16
65.86
68.84
70.72
70.79
70.99
77.16
103.21
108.02
115.30
115.61
122.70
125.78
129.44
132.02
139.20
145.94
148.90
156.43
162.53
f1 (ppm)
8E+05
7E+05
6E+05
6E+05
6E+05
5E+05
4E+05
4E+05
4E+05
3E+05
2E+05
2E+05
2E+05
1E+05
50000
0
-50000
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170

Isomerization of 5 with DBU

*Isomerization of **5** over time*

After CNCA dye **5** was allowed to stand on a benchtop at rt for several months, the sample was analyzed by ^{1}H NMR spectroscopy and it was noted that isomerization of the alkene had occurred to form a mixture of *trans* and *cis* isomers; neither CNCA dye **3** nor **4** exhibited similar behavior under these conditions. The isomerization of **5** was evident based on the appearance of new resonances in the ^{1}H NMR spectrum that mirrored those of the original *trans* compound (***trans*-5**), but sometimes appeared at different chemical shifts (Figure S1). For example, the aromatic singlet at 8.90 ppm, the vinyl singlet at 6.63 ppm, and the methylene triplet at 4.52 ppm each had mirrored resonances that were shifted up field in the spectrum to 8.20, 6.56, and 4.17 ppm, respectively. Integration of the resonances that were attributed to the *cis* isomer (***cis*-5**) showed a *trans*-**5**:*cis*-**5** ratio of 2.2:1. The remainder of the resonances characteristic of ***cis*-5** were overlapping with those belonging to ***trans*-5**.

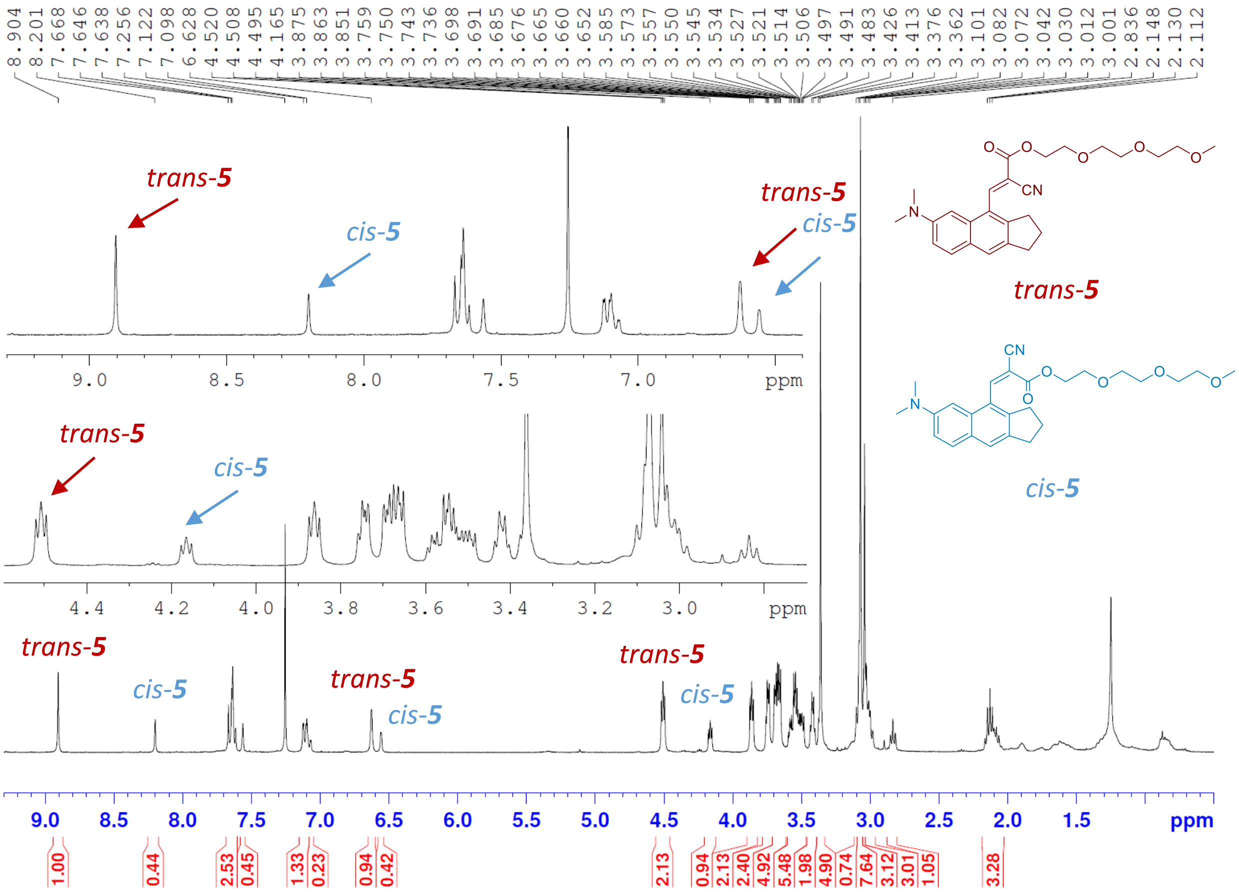


Figure S1. ^{1}H NMR Spectrum of **5** after Several Months

*Treatment of **5** with DBU and K_2CO_3*

In an attempt to isomerize the mixture of ***cis*-** and ***trans*-5** to the original and thermodynamically preferred *trans* compound, the sample was reacted with both 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and K_2CO_3 at 50 °C for several hours. For reaction with DBU, a crude ^{1}H NMR spectrum of the reaction mixture appeared nearly identical to that of ***trans*-5**, with the addition of resonances characteristic of DBU; no *cis* isomer was present (Figure S2). However, after purification by silica gel column chromatography, both isomers were once again noted by ^{1}H NMR spectroscopy in a 3.4:1 ratio of ***trans*-5**:***cis*-5** (Figure S3). The degree of isomerization resulting from purification was not as great as when the sample was allowed to stand on a benchtop at rt for several months (3.4:1 vs. 2.2:1 ratio of ***trans*-5**:***cis*-5**, respectively). In addition to isomerizing under the purification conditions, aldehyde **9c** was isolated in a 1:1 ratio with **5**; **9c** is believed to form via a retro-Knoevenagel reaction that occurred between **5** and water retained by the silica gel.

When a mixture of ***cis*-** and ***trans*-5** was reacted with K_2CO_3 under similar conditions, undesired isomerization occurred to provide additional ***cis*-5**, which yielded a 1.4:1 ratio of ***trans*-5**:***cis*-5** based on ^{1}H NMR spectroscopy of the crude reaction mixture (Figure S4). See Table S1 for a summary of the conditions used and the isomer ratios observed.

*Procedure for reaction of **5** with DBU*

To a NMR tube was added CNCA dye **5** (5 mg, 0.011 mmol), deuterated chloroform (0.5 mL), and DBU (2 µL). The NMR tube was heated at 50 °C in an oil bath for 2 h. A crude ^{1}H NMR spectrum was obtained showing complete conversion of the *cis* to *trans* isomer (Figure S2). The reaction mixture was concentrated under reduced pressure and purified by silica gel flash column chromatography (pipette as column, 40-50% ethyl acetate/hexanes) to yield **5** as a red solid and a 3.4:1 mixture of ***trans***:***cis*** isomers (2 mg, 40% yield, Figure S3). Aldehyde **9c** was also isolated (1 mg, 38% yield). The recovery of the material from the column may have been reduced due to the small amount of the sample being purified.

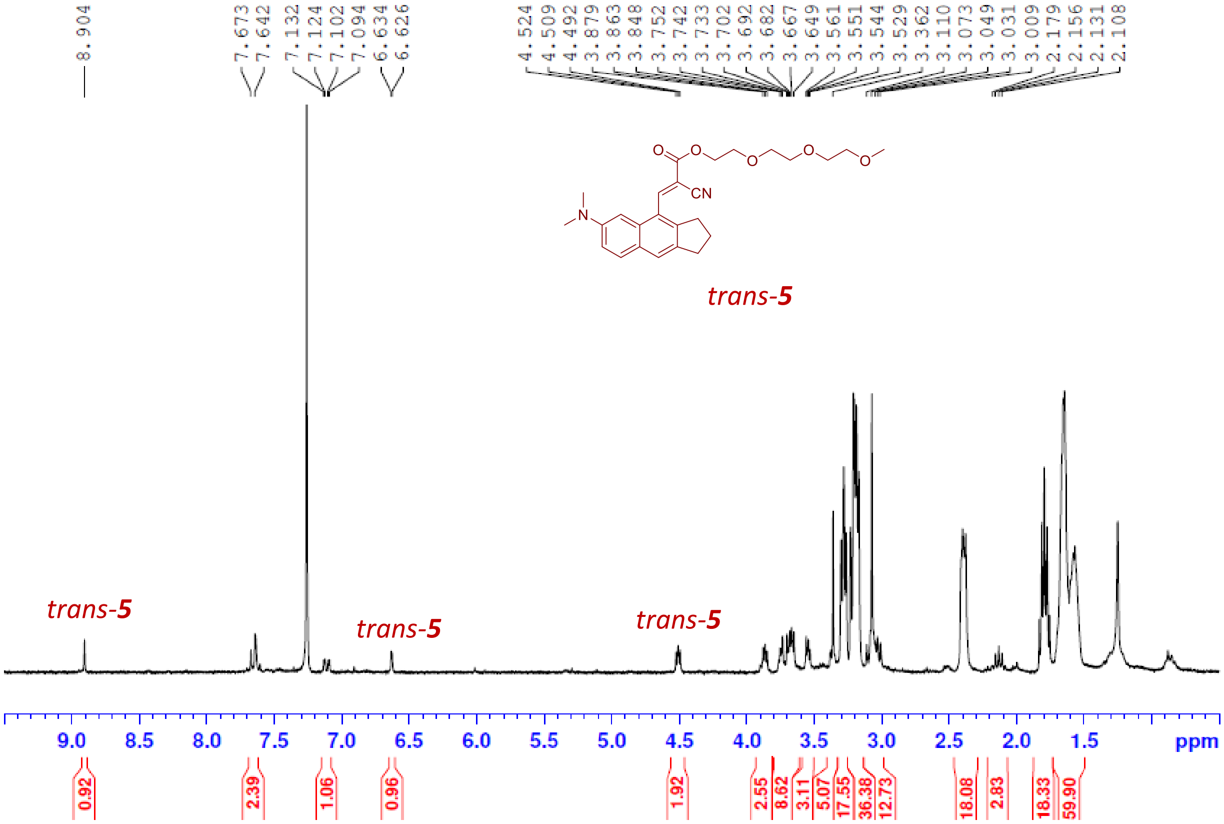


Figure S2. Crude ^{1}H NMR Spectrum of **5** after Treatment with DBU

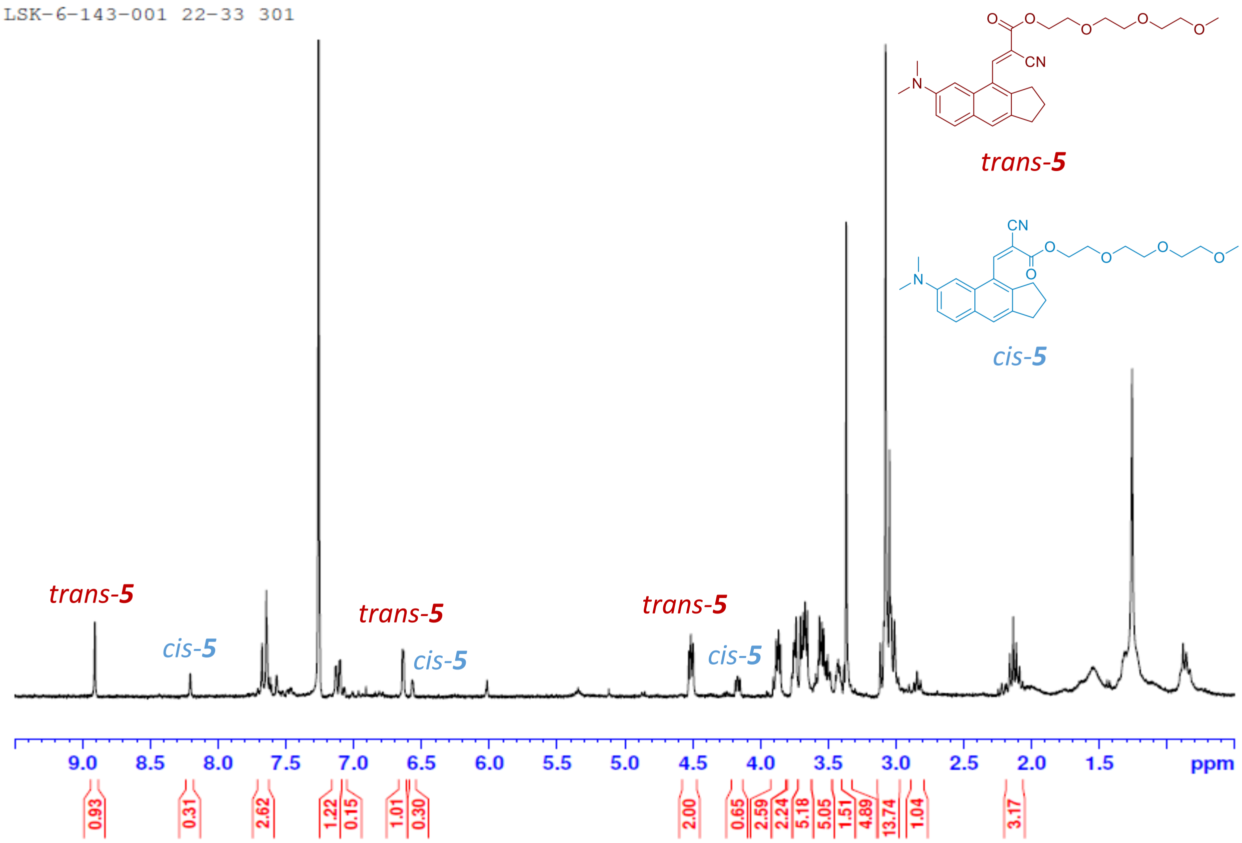


Figure S3. ^{1}H NMR Spectrum of **5** after treatment with DBU and Purification

*Procedure for reaction of **5** with K_2CO_3*

To a NMR tube was added CNCA dye **5** (2 mg), deuterated chloroform (0.7 mL), and K_2CO_3 (1 mg). The NMR tube was heated at 50 °C in an oil bath for 4 h. A crude ^1H NMR spectrum was obtained showing a 1.4:1 mixture of ***trans***:***cis*** isomers (Figure S4). No purification was performed for this experiment.

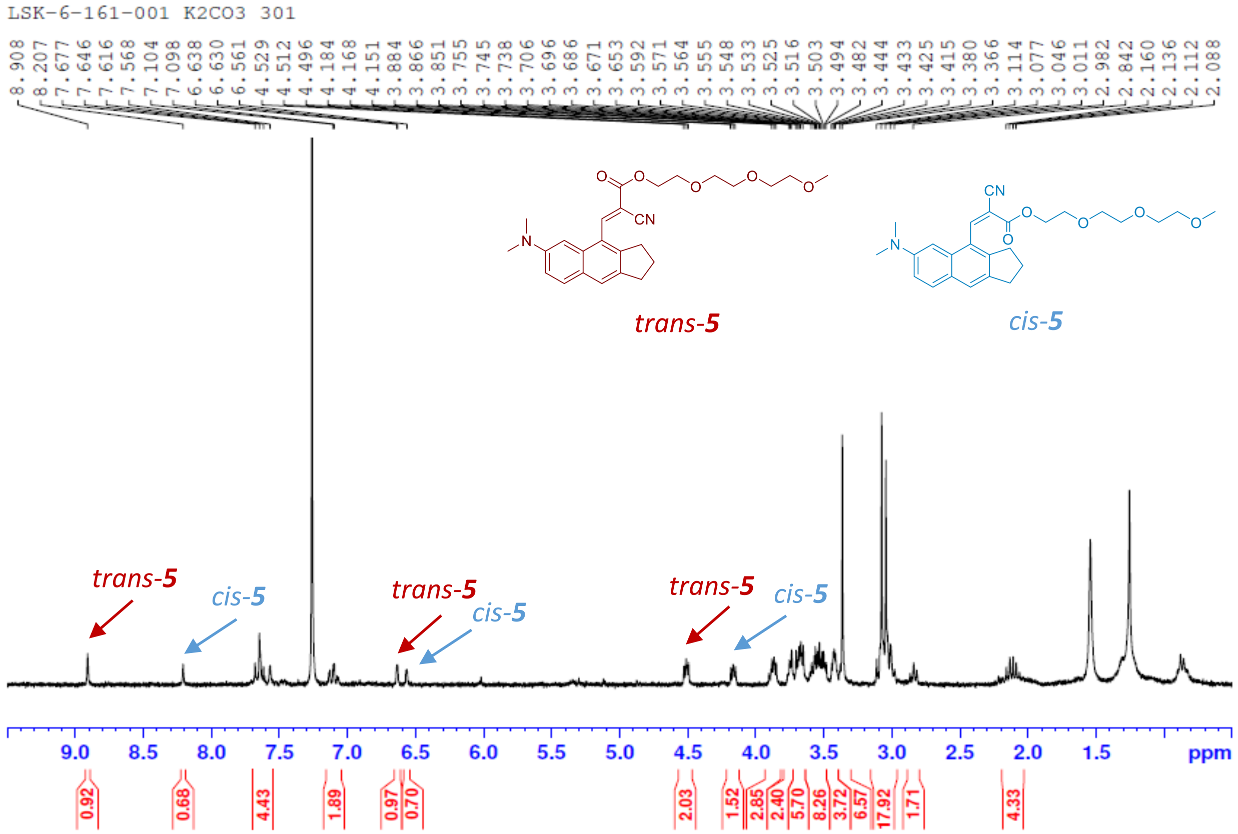


Figure S4. Crude ^1H NMR Spectrum of **5** after treatment with K_2CO_3 and Purification

Table S1. Isomer Distribution of **5** after Treatment of **5** to Various Conditions

entry	conditions used	***trans***-5:***cis***-5[a]
1	several months at rt	2.2:1
2	DBU, $CDCl_3$, 50 °C, 2 h	1:0
	after purification by SiO_2 chromatography	3.4:1
	after SiO_2 column pretreated with 10% Et_3N	1:0
3	K_2CO_3, $CDCl_3$, 50 °C, 4 h	1.4:1

Purification of Isomer Mixture by Silica Gel Column Pretreated with Base

Repetition of the DBU experiment with the original mixture of isomers of **5** (2.2:1 ratio of ***trans*-5**:***cis*-5**), once again showed isomerization of the mixture to exclusively the *trans* isomer during the reaction as observed by ^{1}H NMR spectroscopy. When the reaction mixture was concentrated under reduced pressure and the resulting solid allowed to sit at rt for several days, no isomerization to ***cis*-5** occurred. This crude solid was then subjected to purification by column chromatography on a silica gel column pretreated with 10% Et_3N to reduce the column's acidity. No isomerization to ***cis*-5** occurred under these slightly basic purification conditions, but the retro-Knoevenagel reaction did take place to produce aldehyde **9c** in an approximate 0.5:1 ratio with ***trans*-5** as observed by ^{1}H NMR spectroscopy (Figure S5). The amount of **9c** produced was less than the 1:1 ratio of **9c**:**5** that was isolated when the silica gel column was not pretreated with base. The small scale of this reaction (~2 mg) prevented separation of **9c** from **5** during the purification.

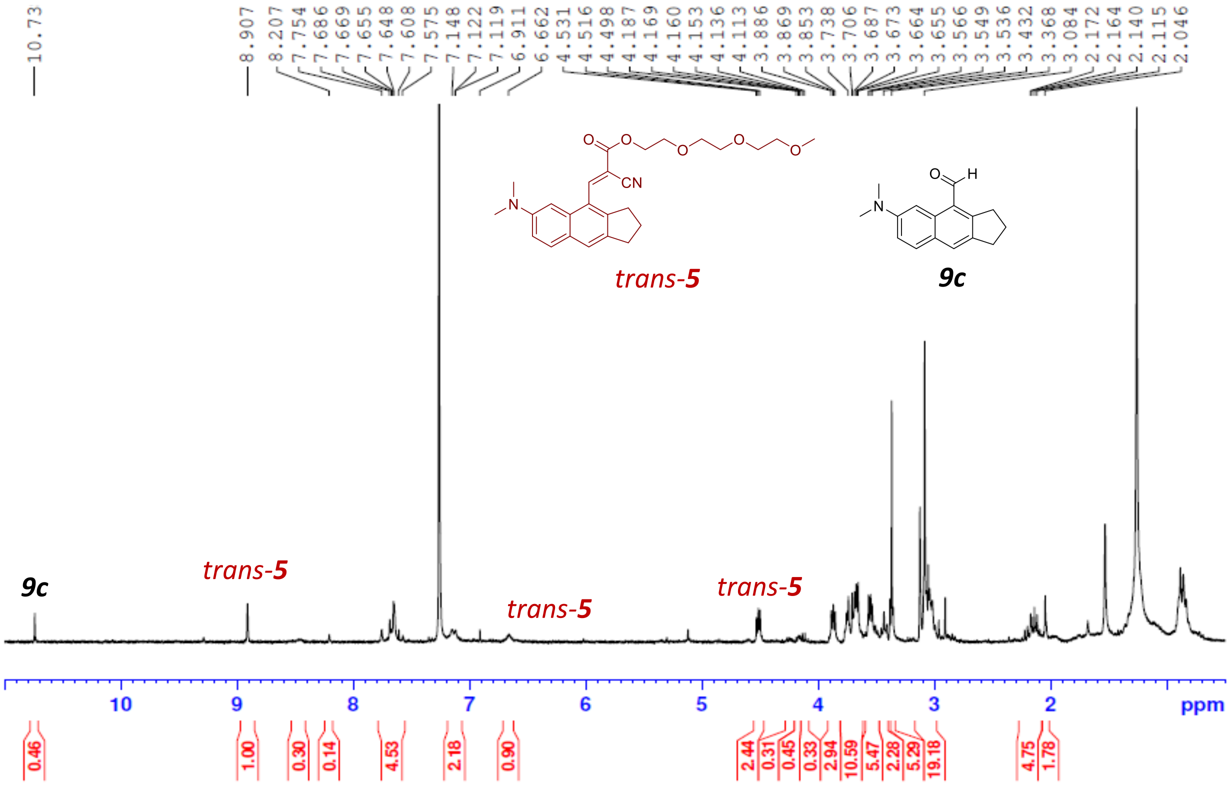


Figure S5. ^{1}H NMR Spectrum of **5** after Purification by Silica Gel Column Pretreated with 10% Et_3N