Synthesis of Cyclopenta-fused Polycyclic Aromatic Hydrocarbons Utilizing Aryl-substituted Anilines

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Supporting Information

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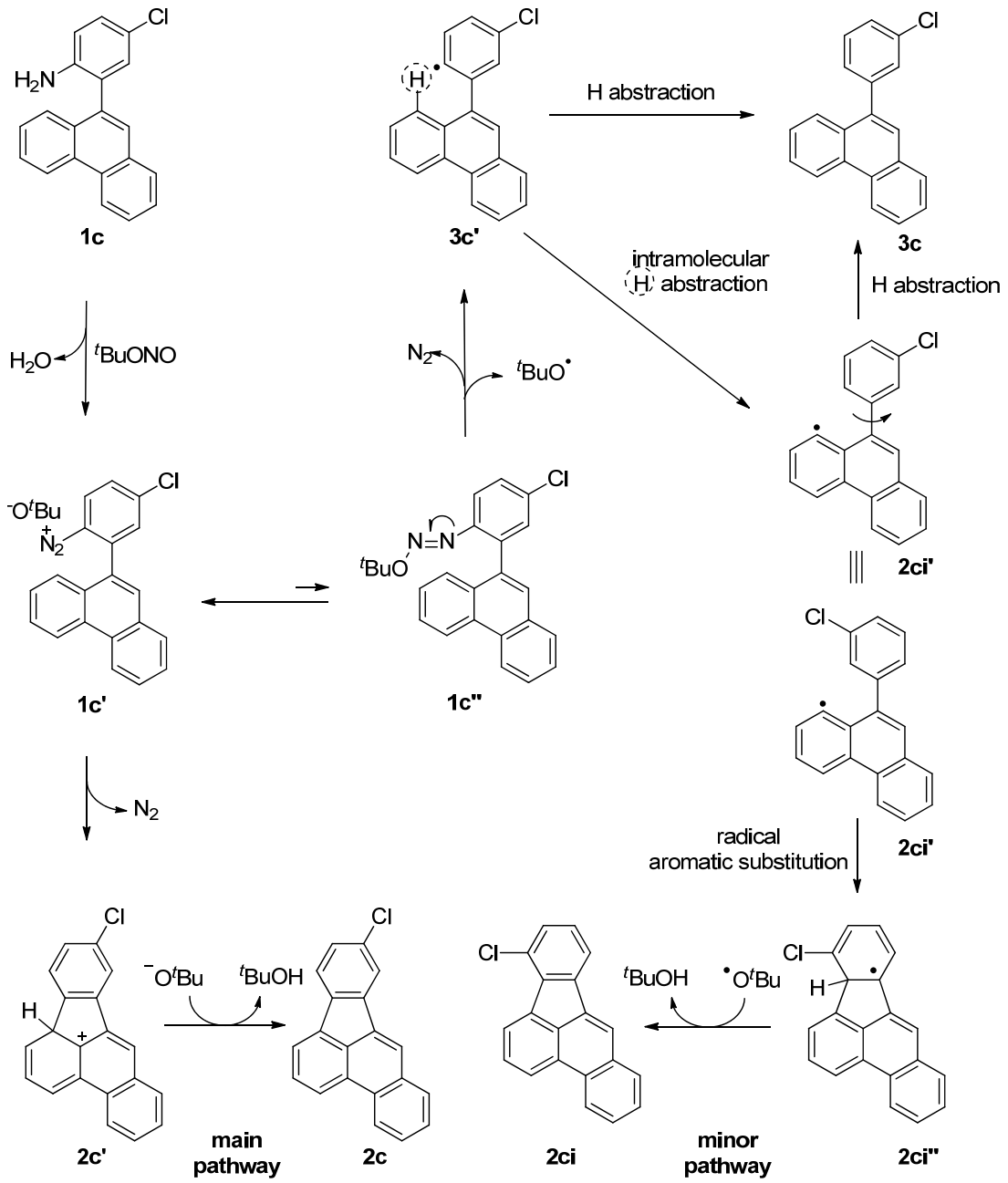
Proposed Mechanism for reaction of 1c



Scheme S1. Proposed Mechanism for reaction of **1c**.

Method for DFT Calculation

Density functional theory (DFT) calculation of orbital coefficients and energy levels

Density functional theory (DFT) calculations were performed with the Gaussian 09 program package[ref S1]. Four diazonium intermediates generated from **8**, **1a**, **6a**, and **13**, are presented in Figure 1, and denoted by **8′**, **1a′**, **6a′**, and **13′**. The intermediates were optimized by the hybrid B3LYP functional and a 6-31G(d) basis set. Solvation effects by acetonitrile were taken into account by the polarization continuum model using the integral equation formalism (IEFPCM).

Ref. S1 Gaussian 09, Revision **E.01**, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

Cartesian coordinates for all the species calculated in this work

C	2.093057	-2.104619	-1.053923
C	1.002359	-1.292998	-0.826288
C	1.159316	0.005990	-0.268363
C	2.490345	0.470820	0.004871
C	3.591361	-0.394764	-0.237331
C	3.400160	-1.658892	-0.746822
H	1.947653	-3.091744	-1.482686
H	0.014523	-1.646788	-1.105786
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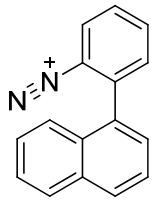

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H	1.779929	3.648994	1.051646
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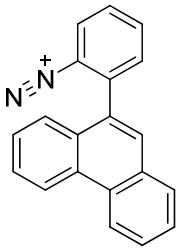

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C	4.609408	-1.164292	0.305616
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C	1.596314	1.070349	-0.241346
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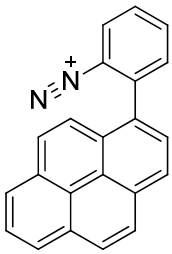

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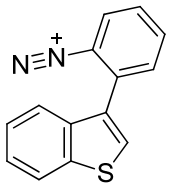

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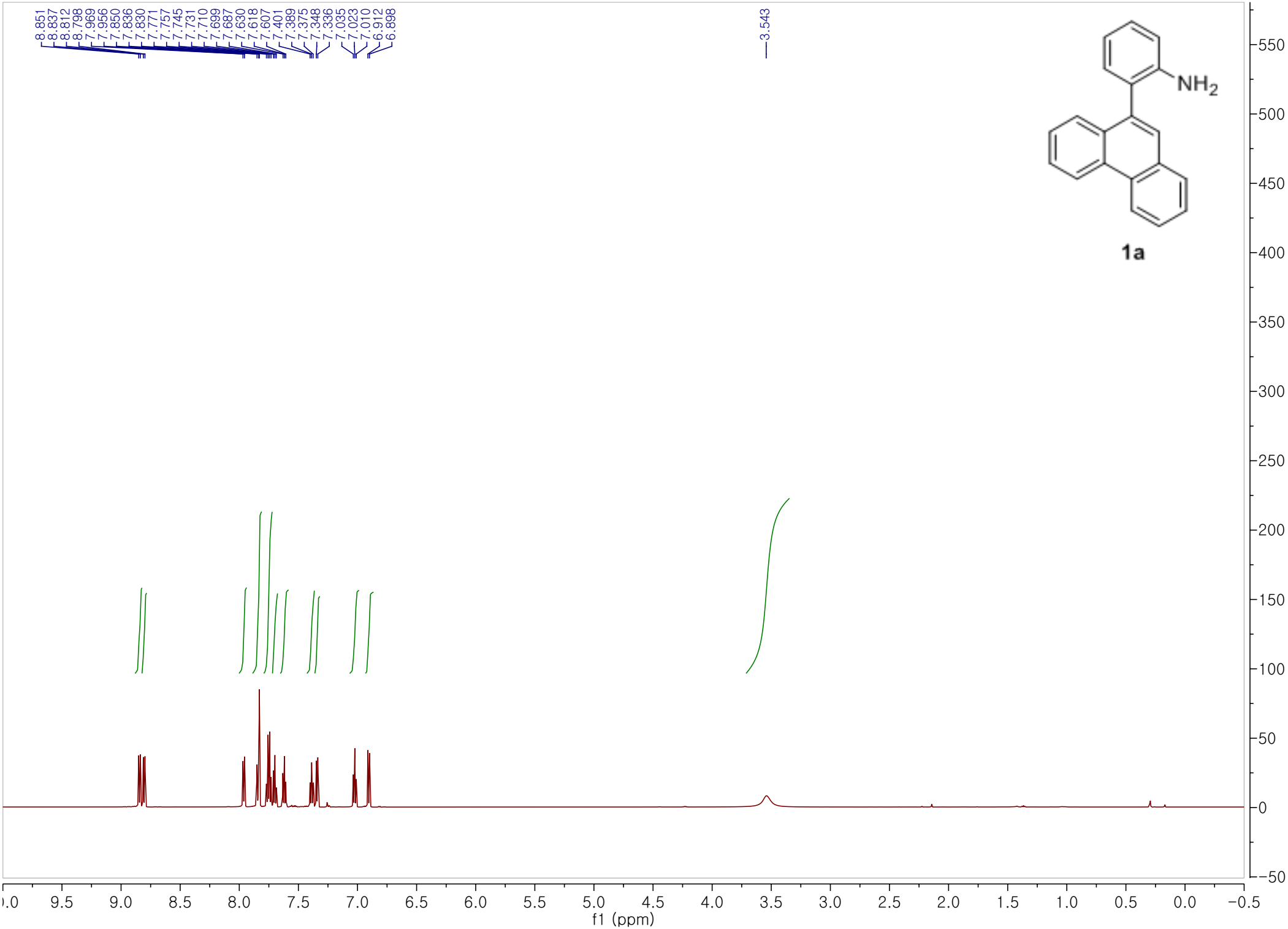
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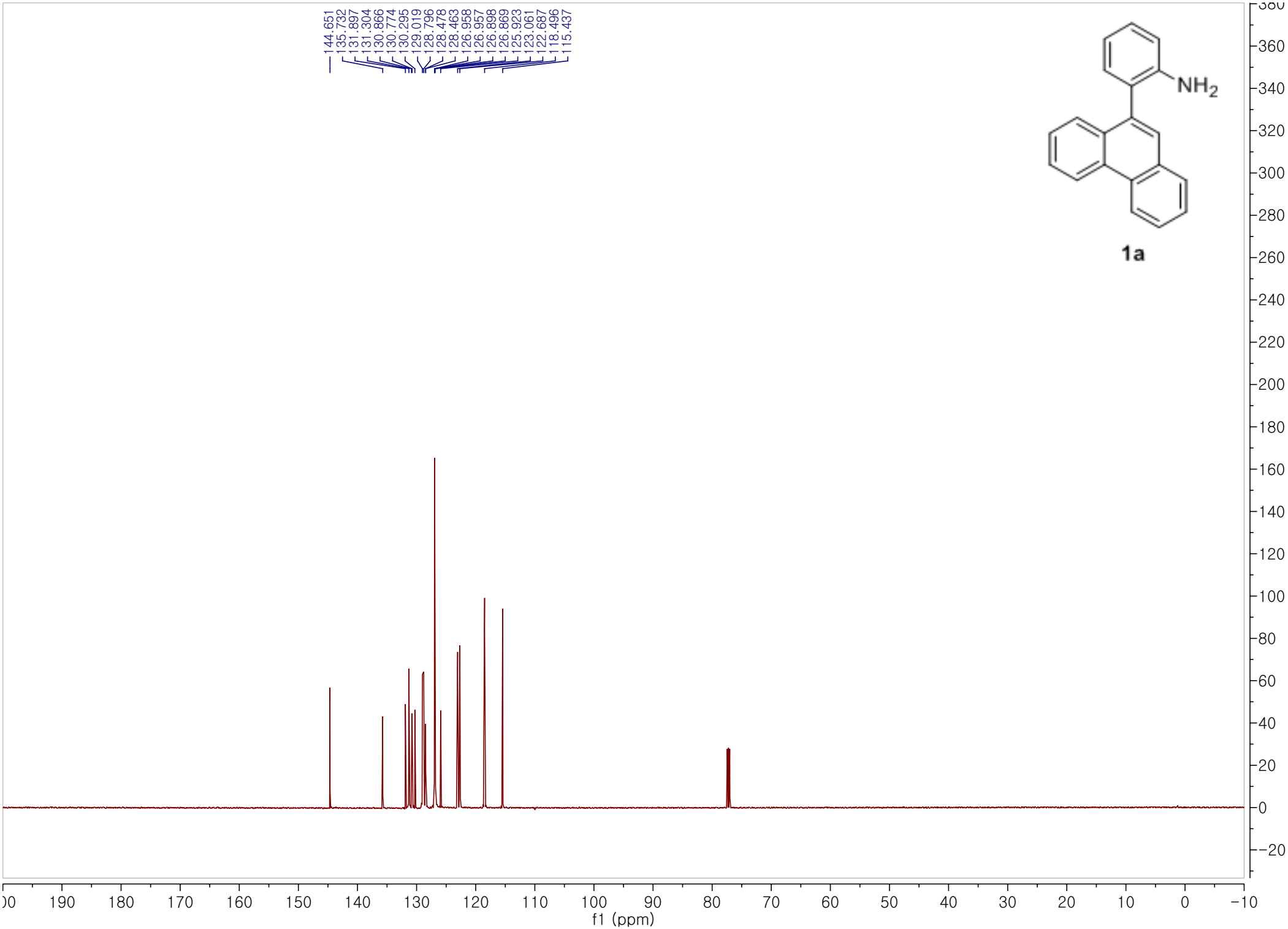
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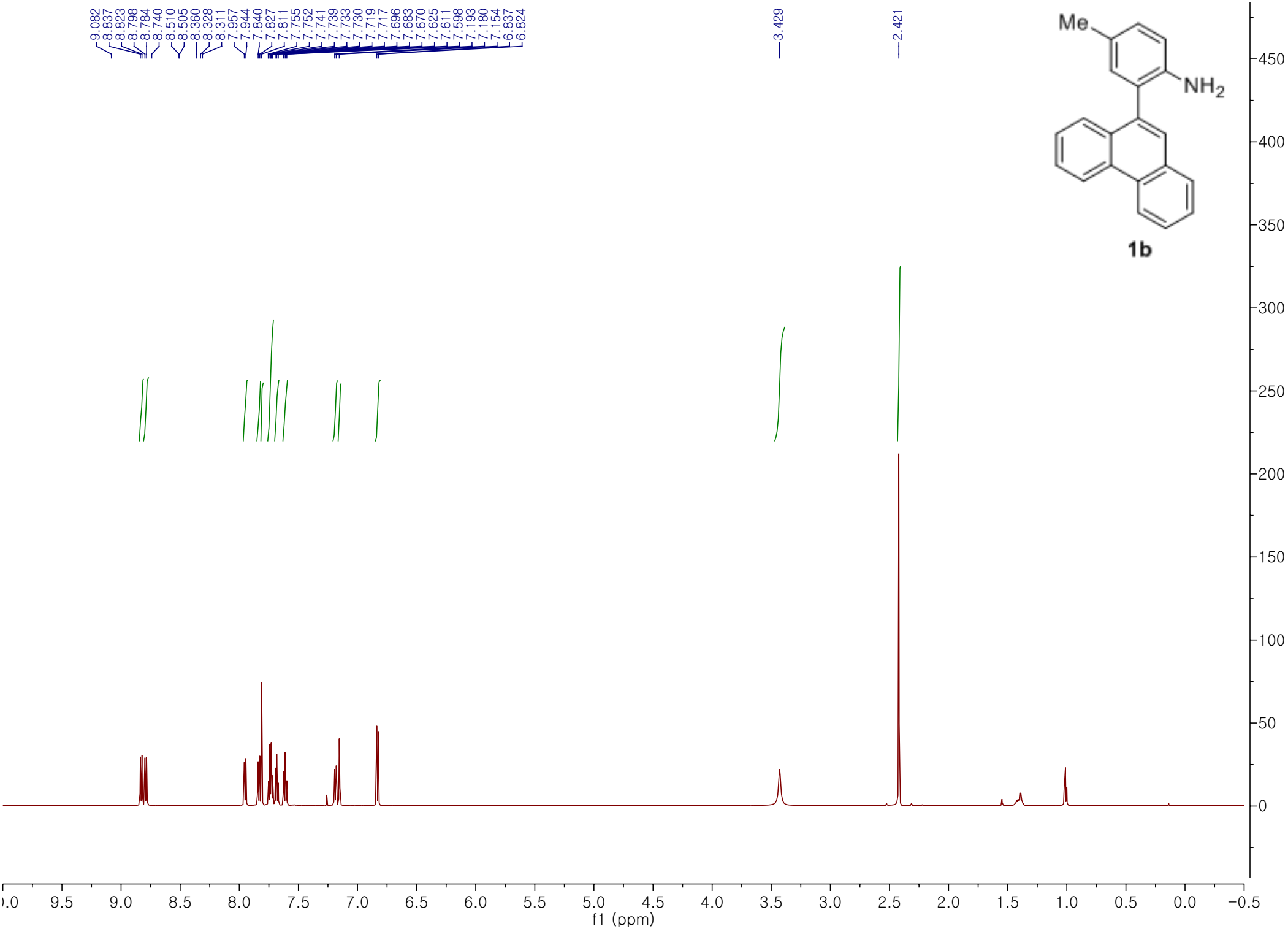
NH2
1a
f1 (ppm)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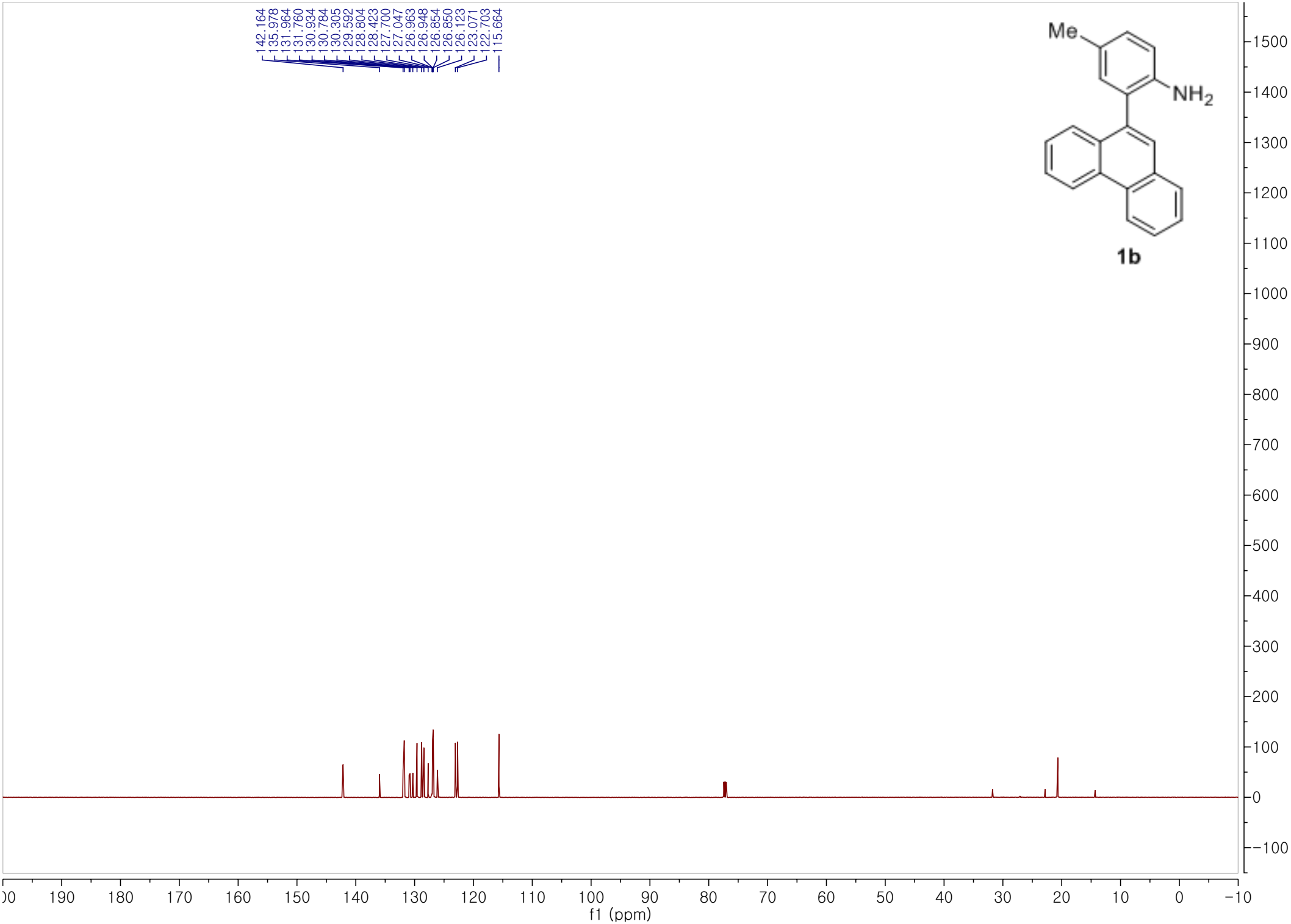
f1 (ppm)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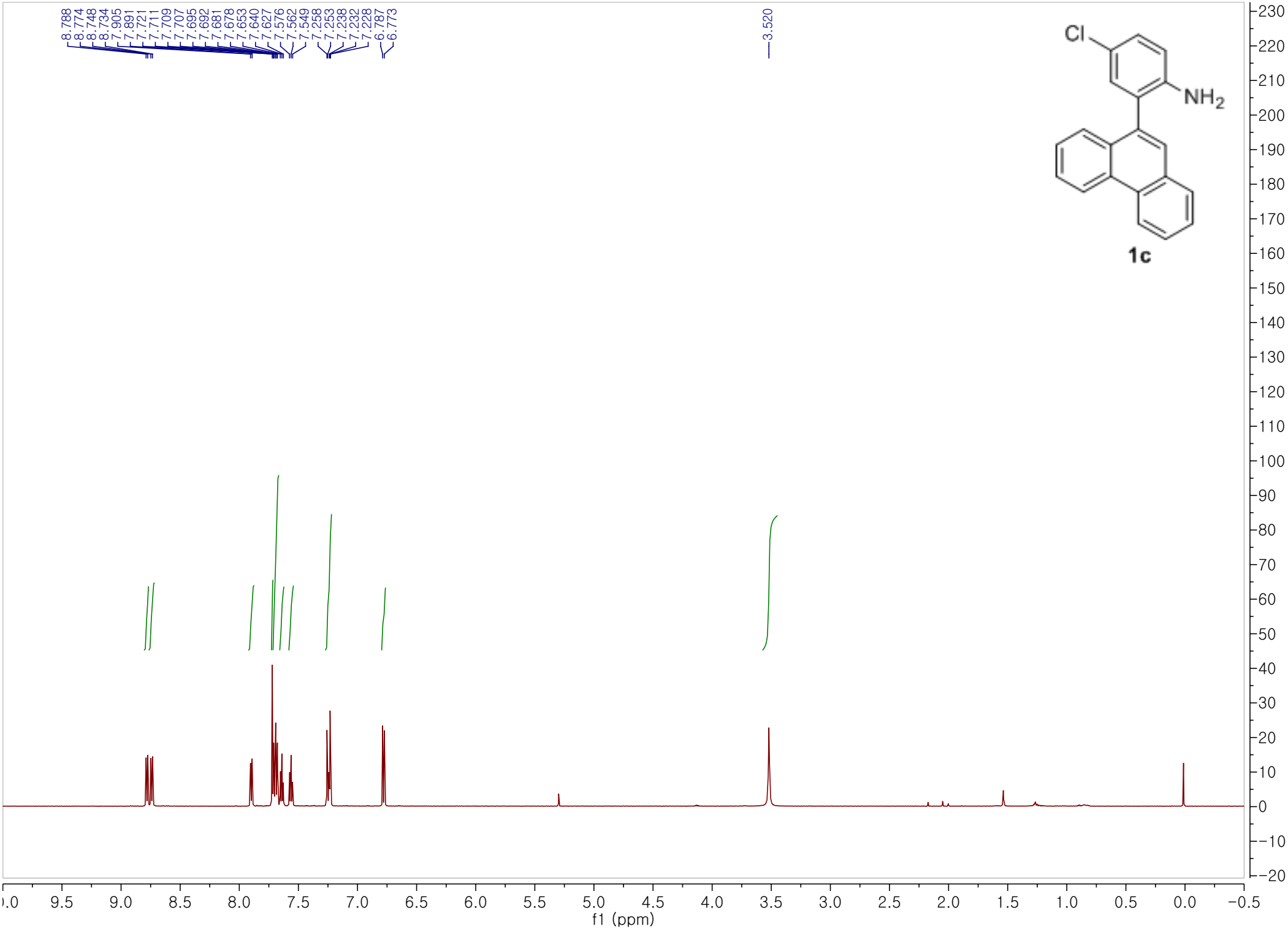
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7.576
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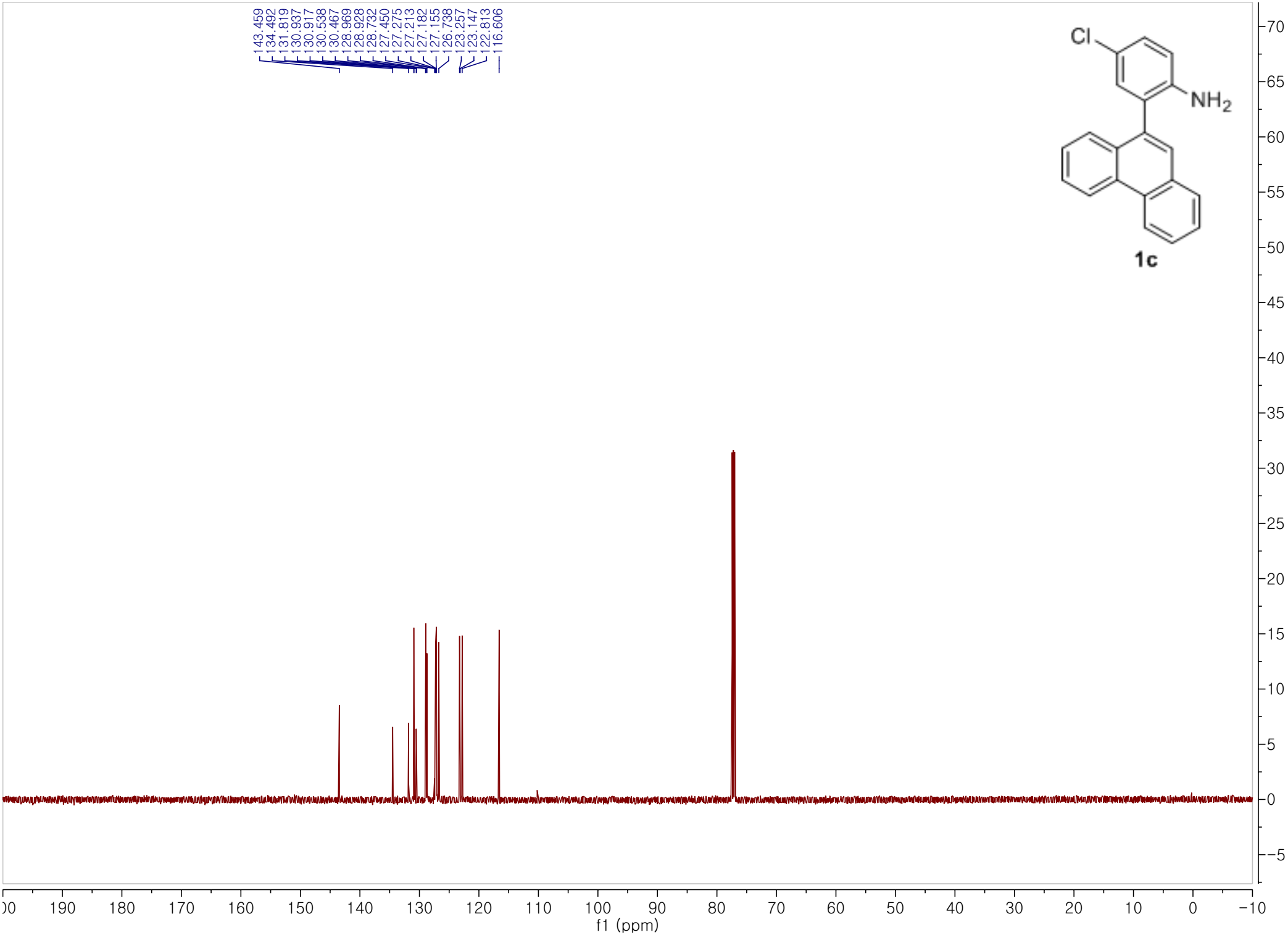
1c
f1 (ppm)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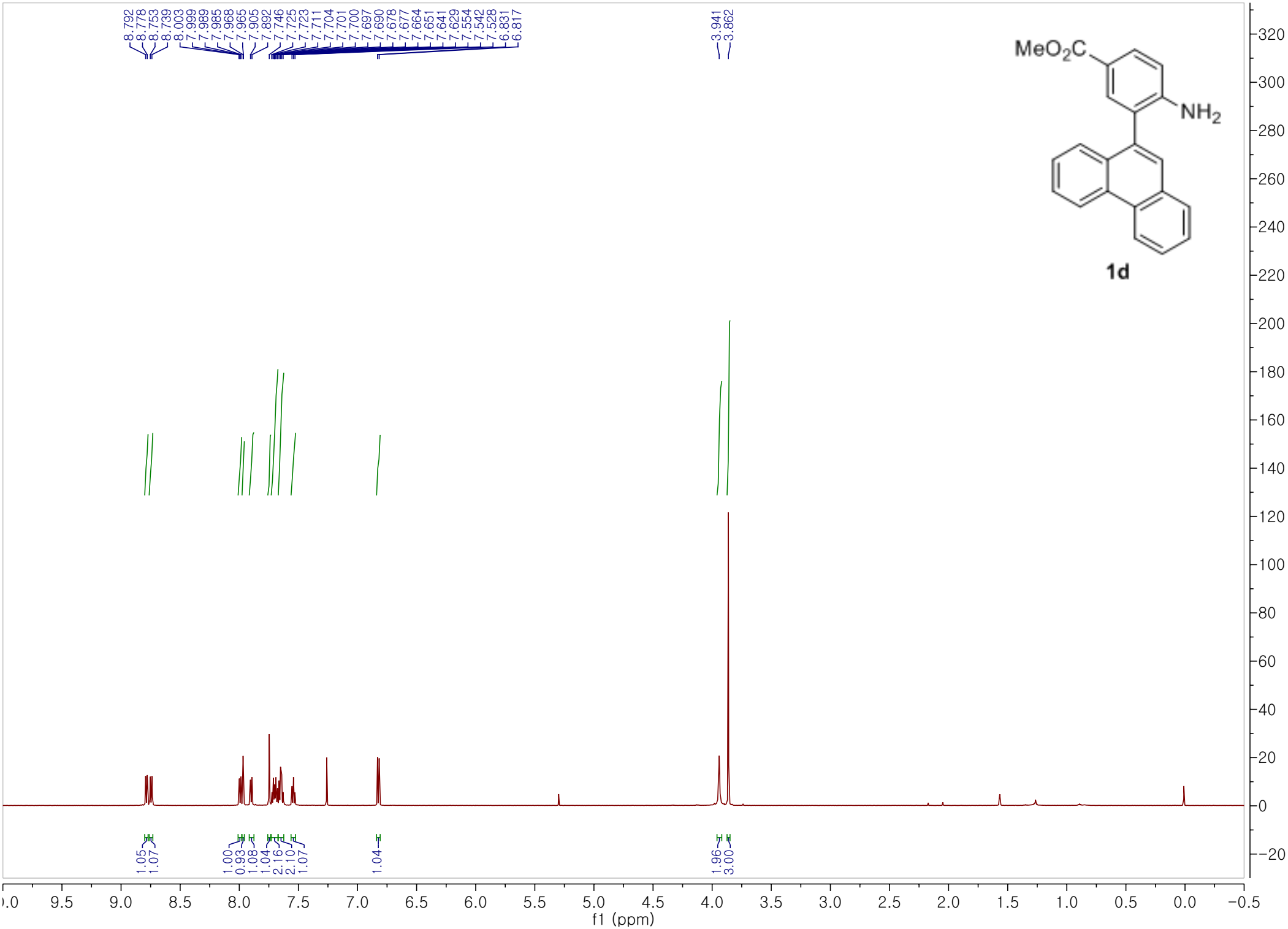
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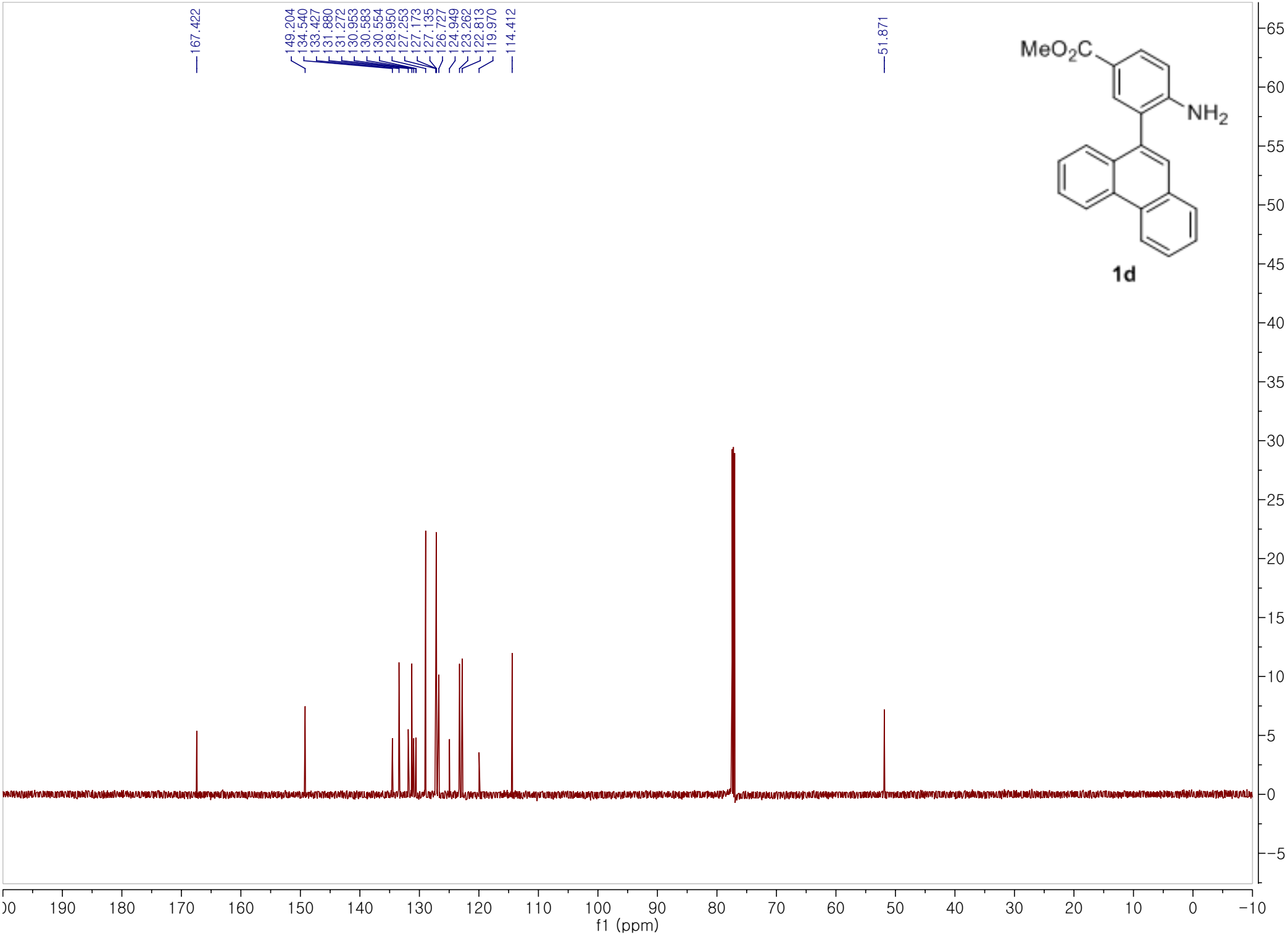
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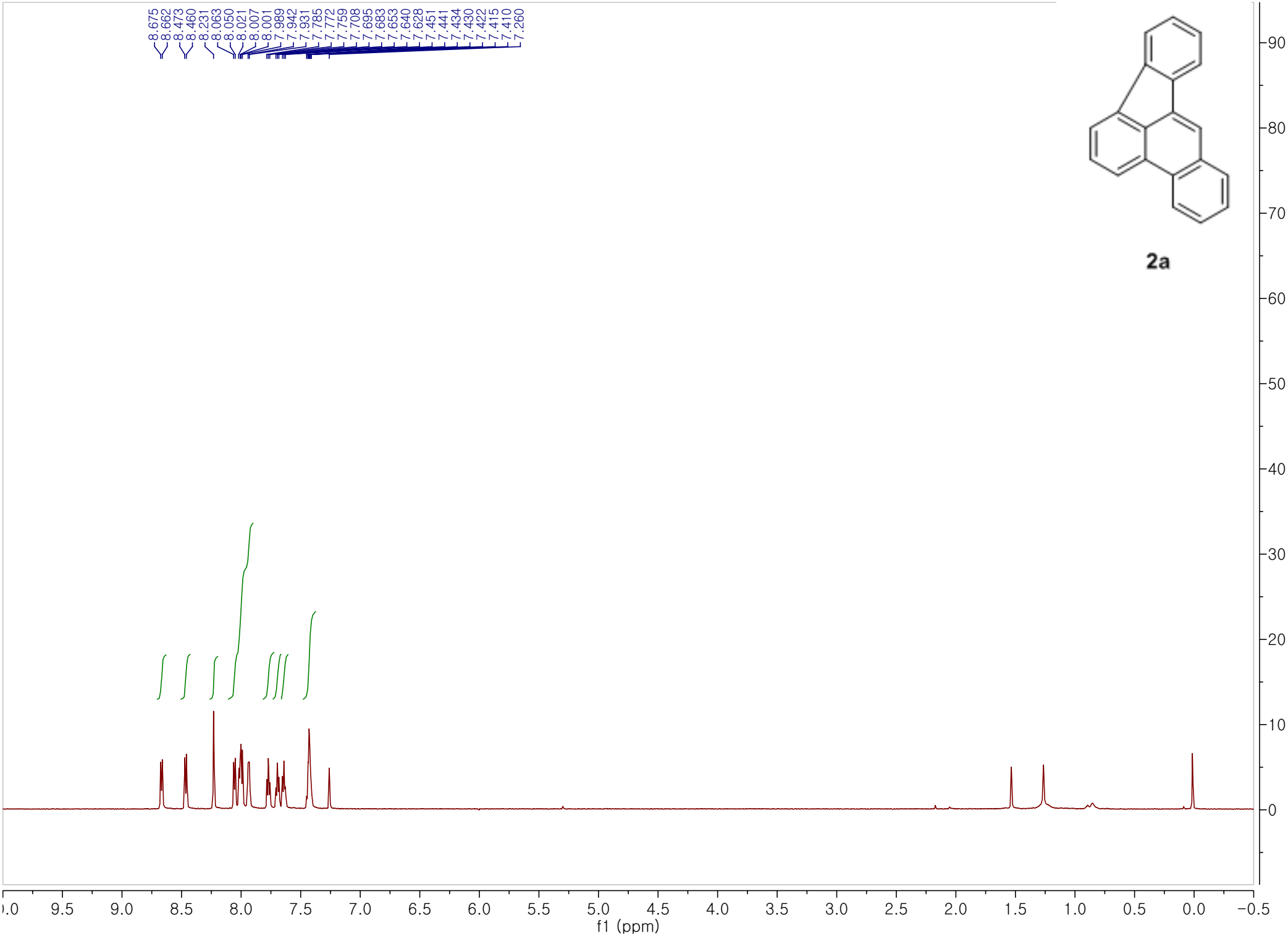
f1 (ppm)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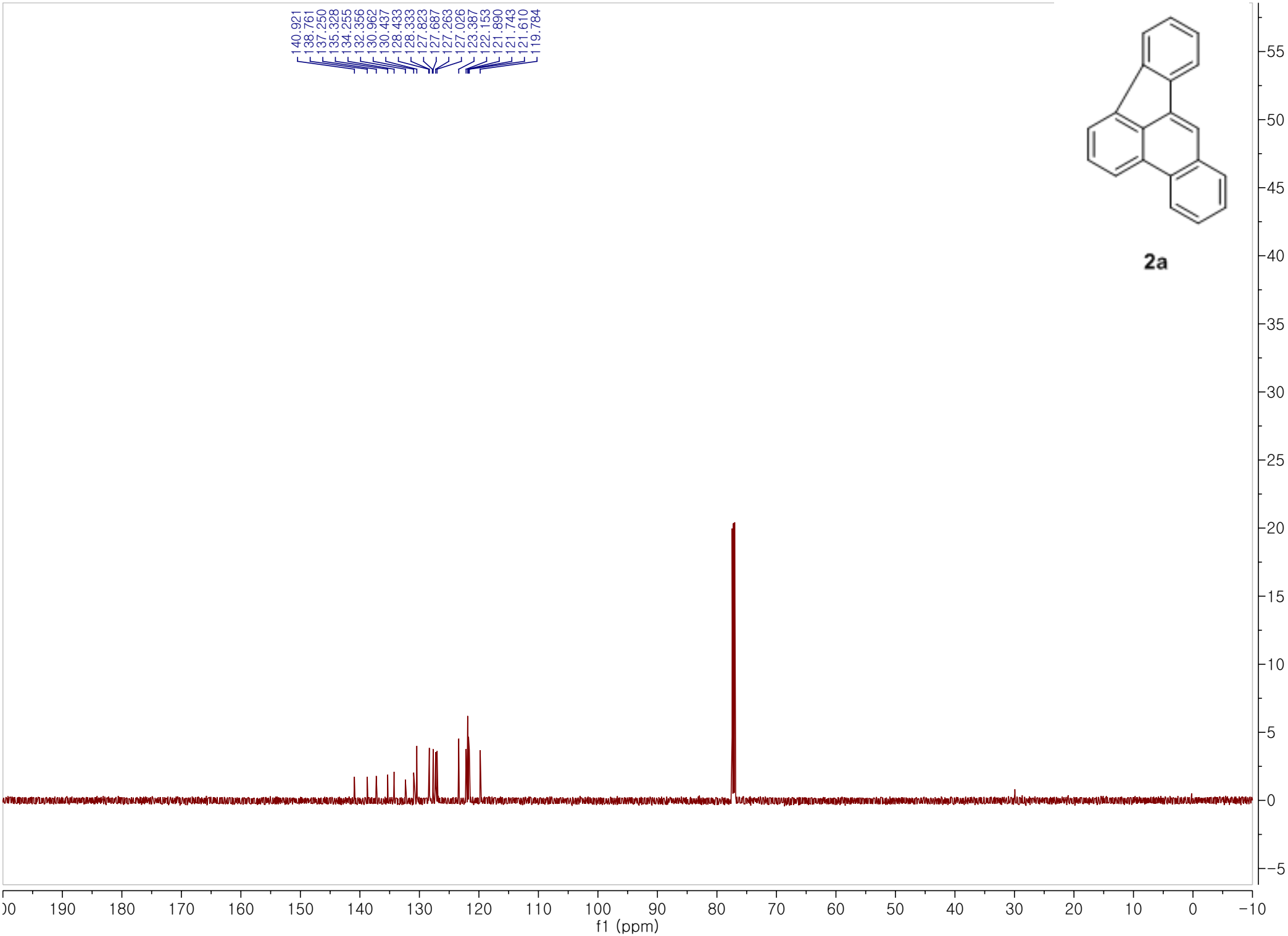
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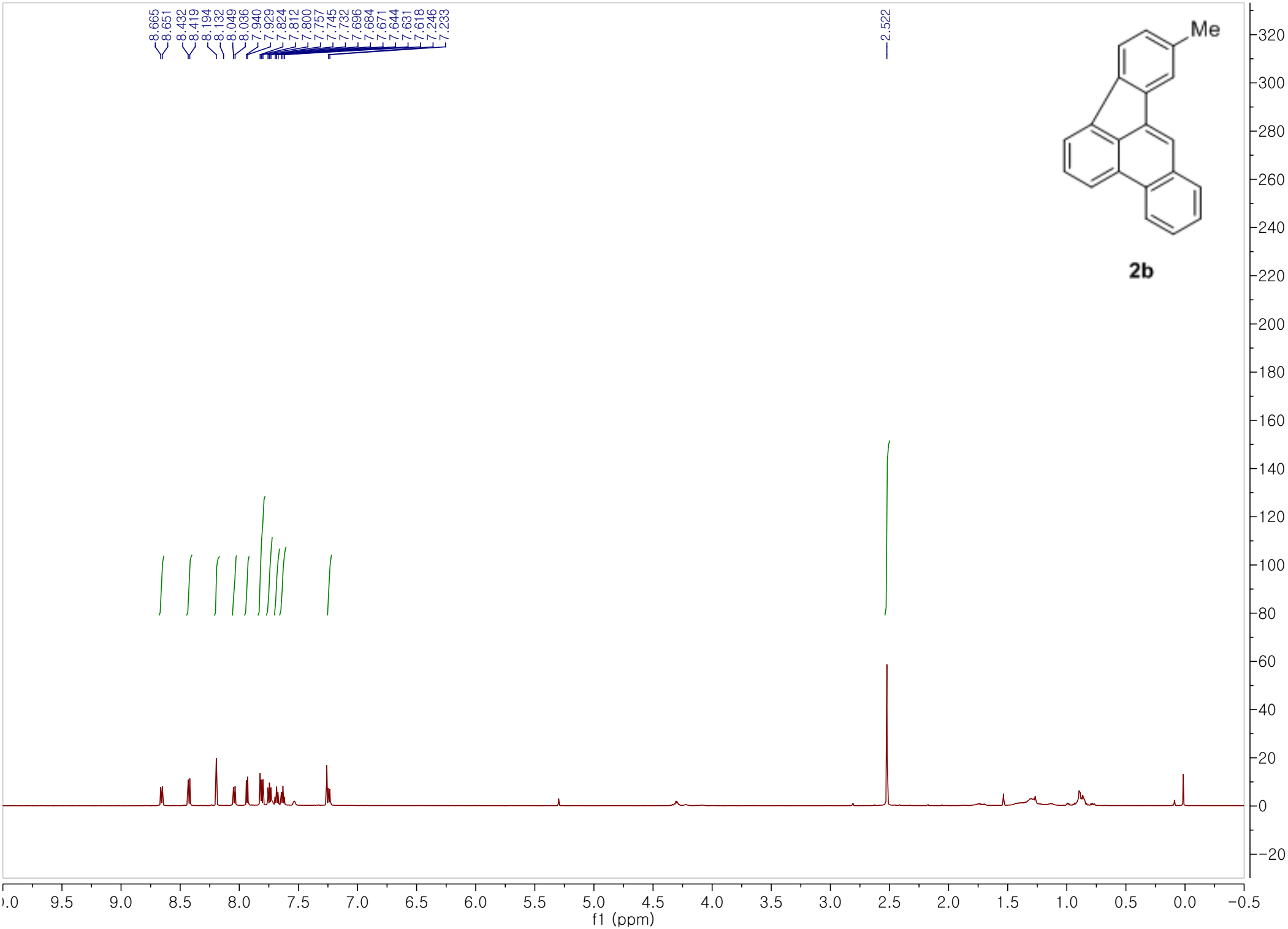
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Me
2b
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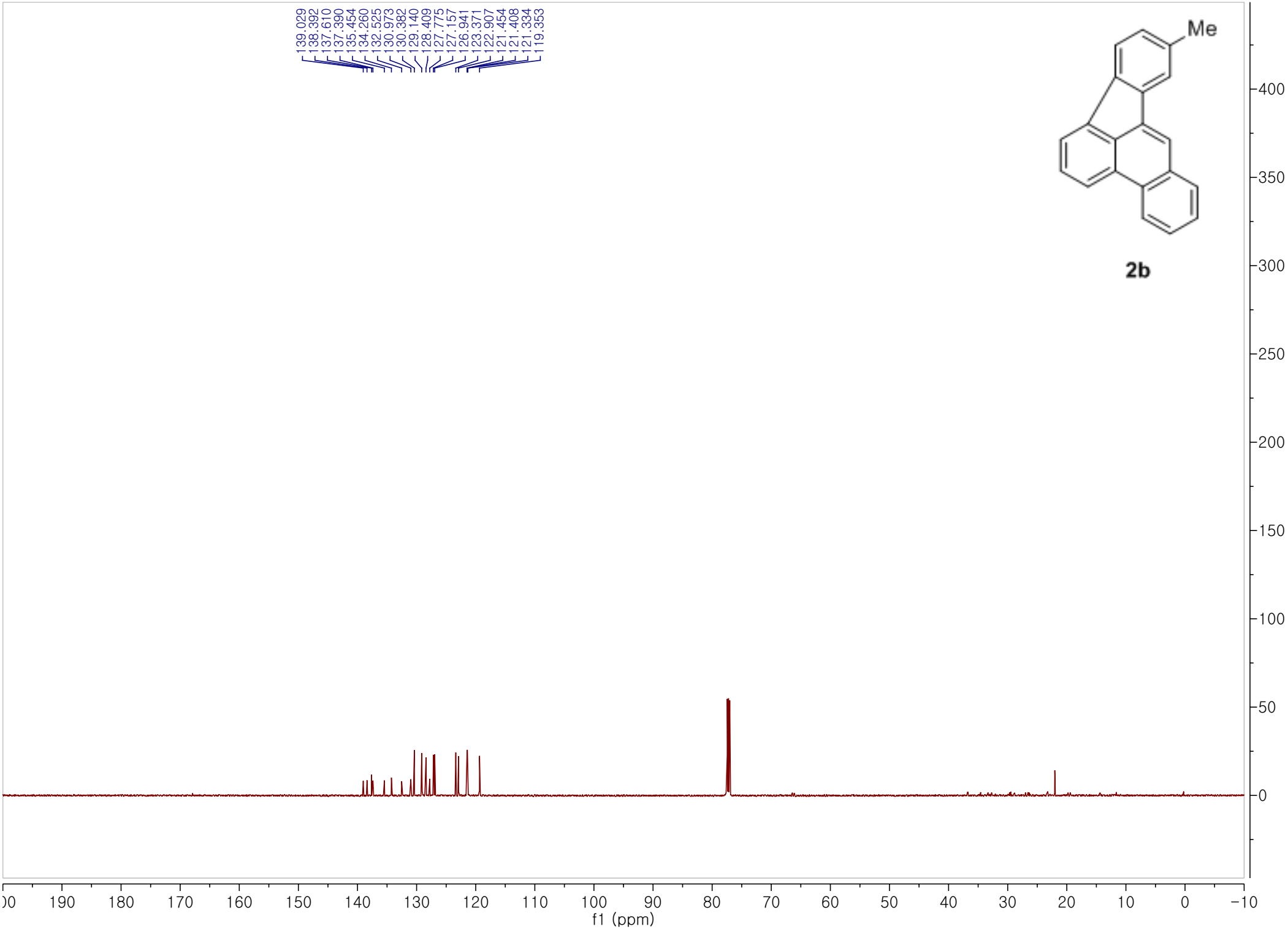
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119.353
Me
2b
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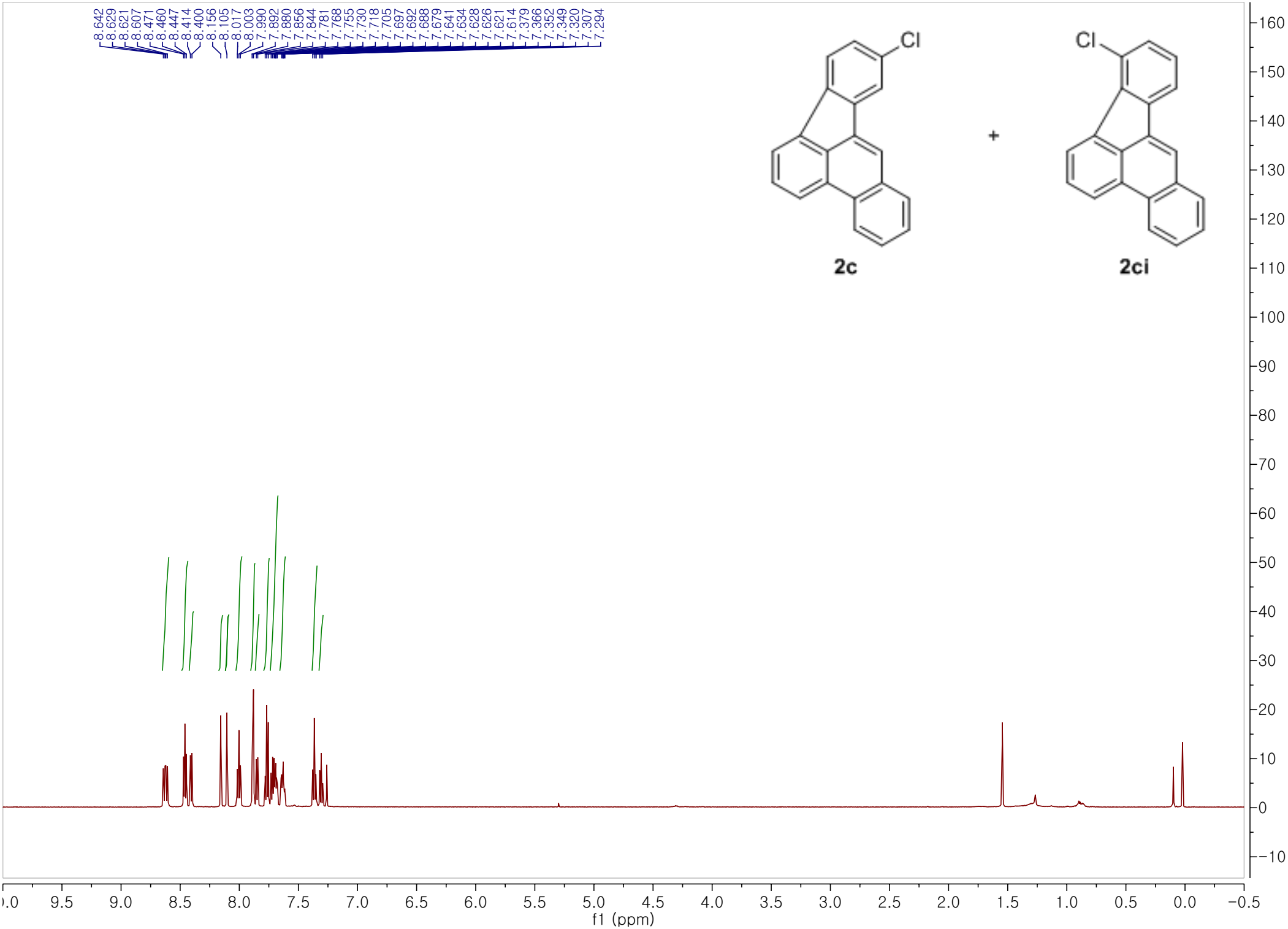
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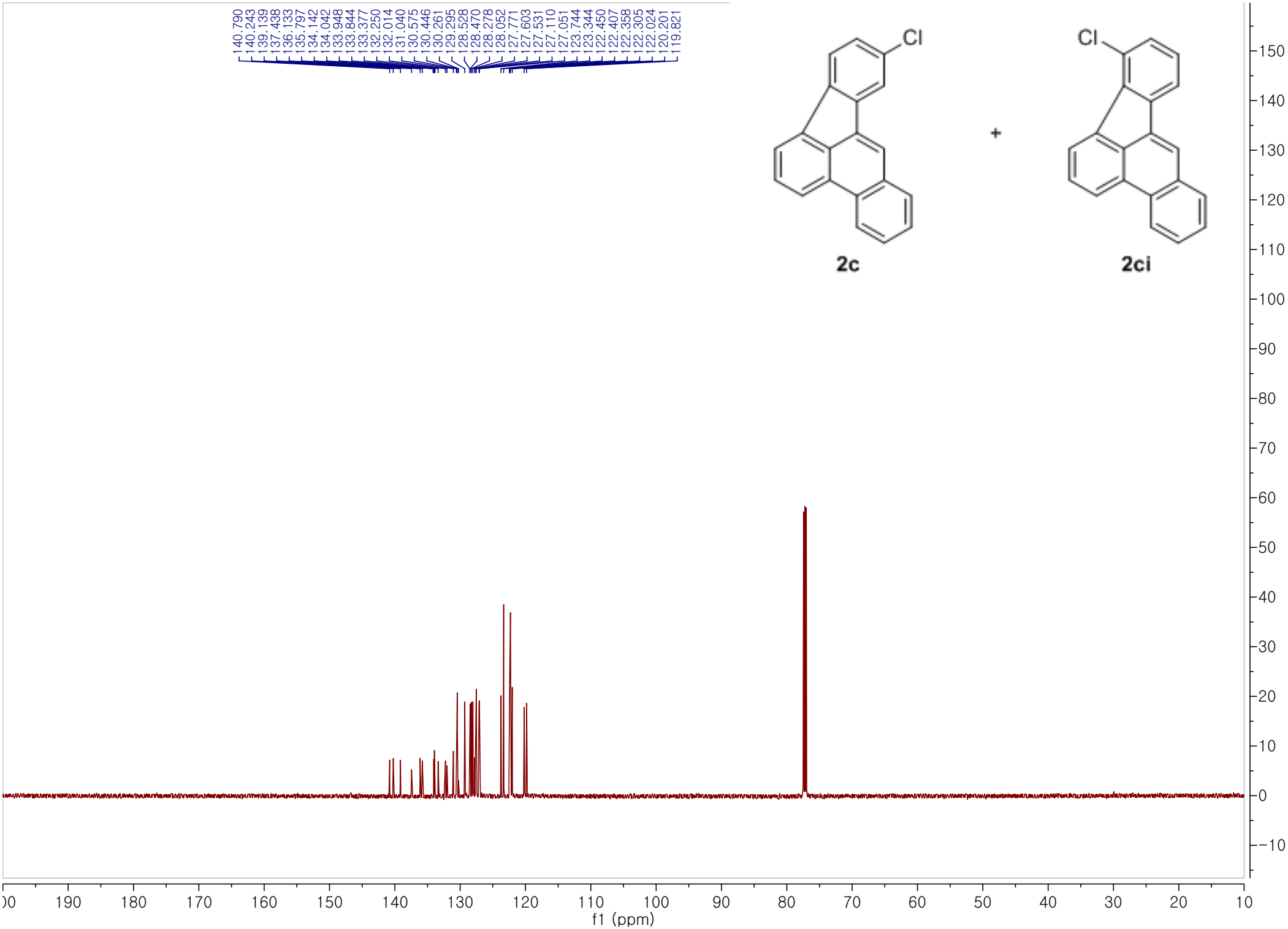
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134.142
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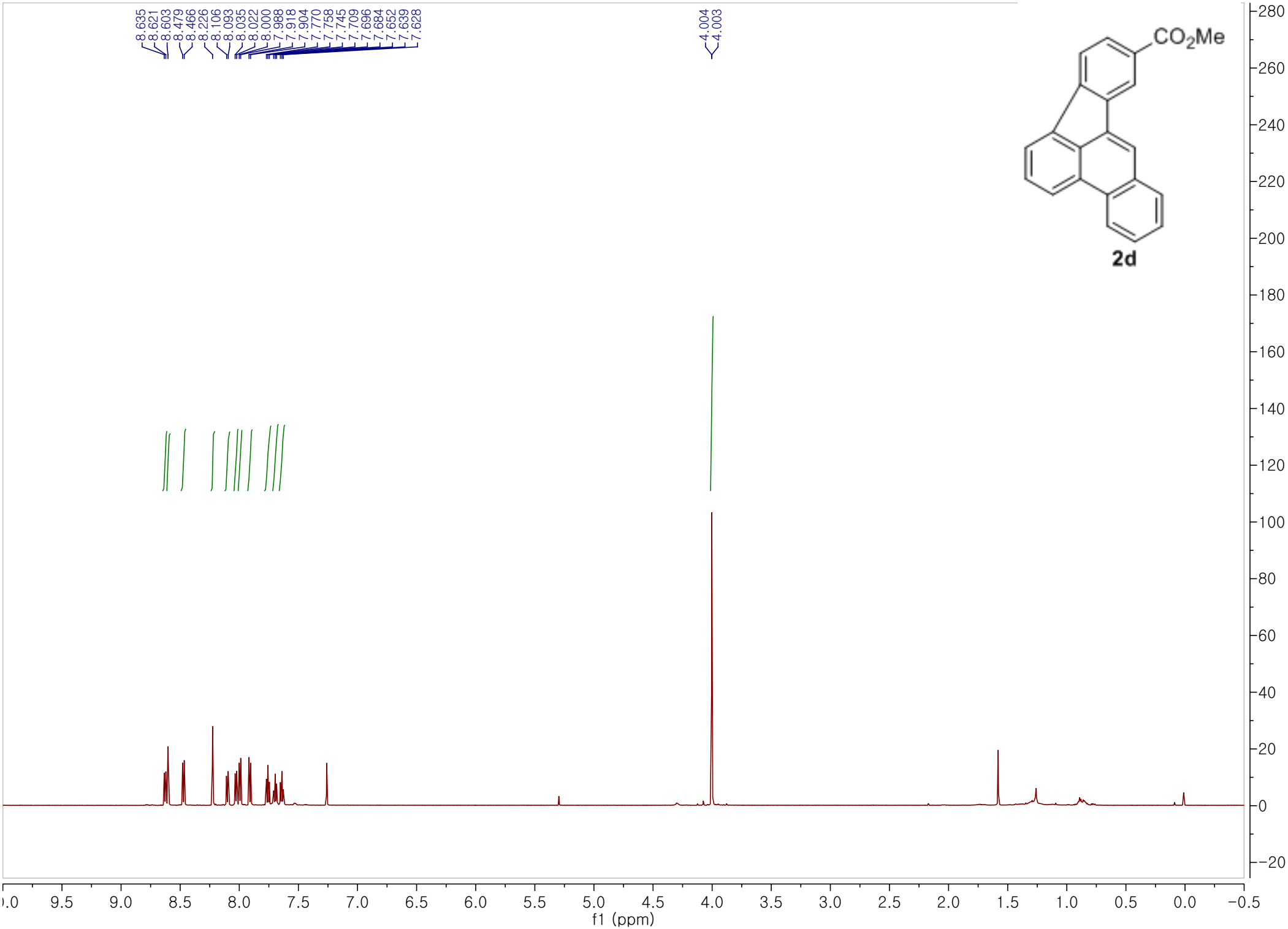
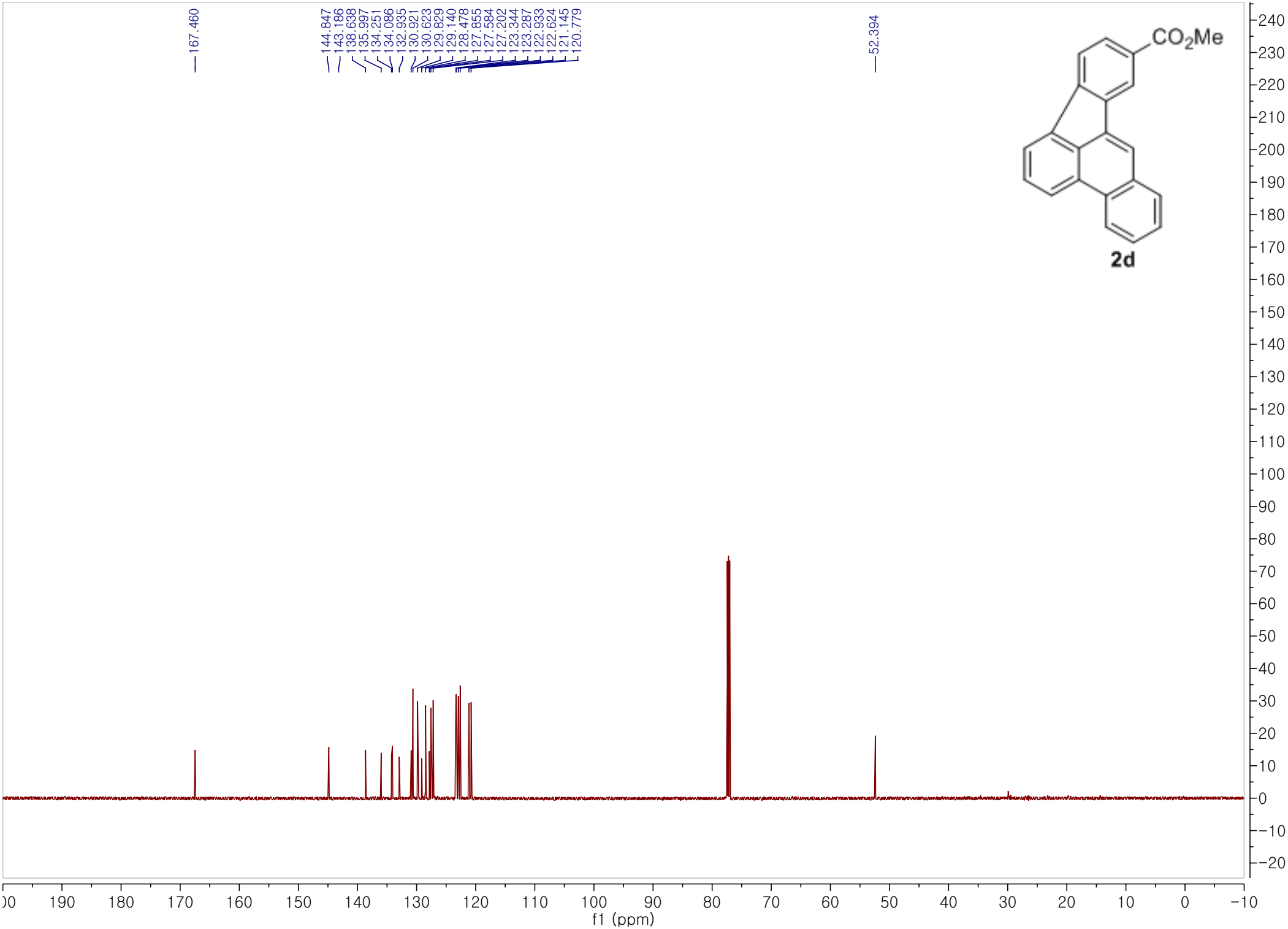
133.948
133.844
133.377
132.250
132.014
131.040
130.575
130.446
130.261
129.295
128.528
128.470
128.278
128.052
127.771
127.603
127.531
127.110
127.051
123.744
123.344
122.450
122.407
122.358
122.305
122.024
120.201
119.821
Cl
2c
+
Cl
2ci
f1 (ppm)


8.635
8.621
8.603
8.479
8.466
8.226
8.106
8.093
8.035
8.022
8.000
7.988
7.918
7.904
7.770
7.758
7.745
7.709
7.696
7.684
7.652
7.639
7.628
4.004
4.003
CO2Me
2d
f1 (ppm)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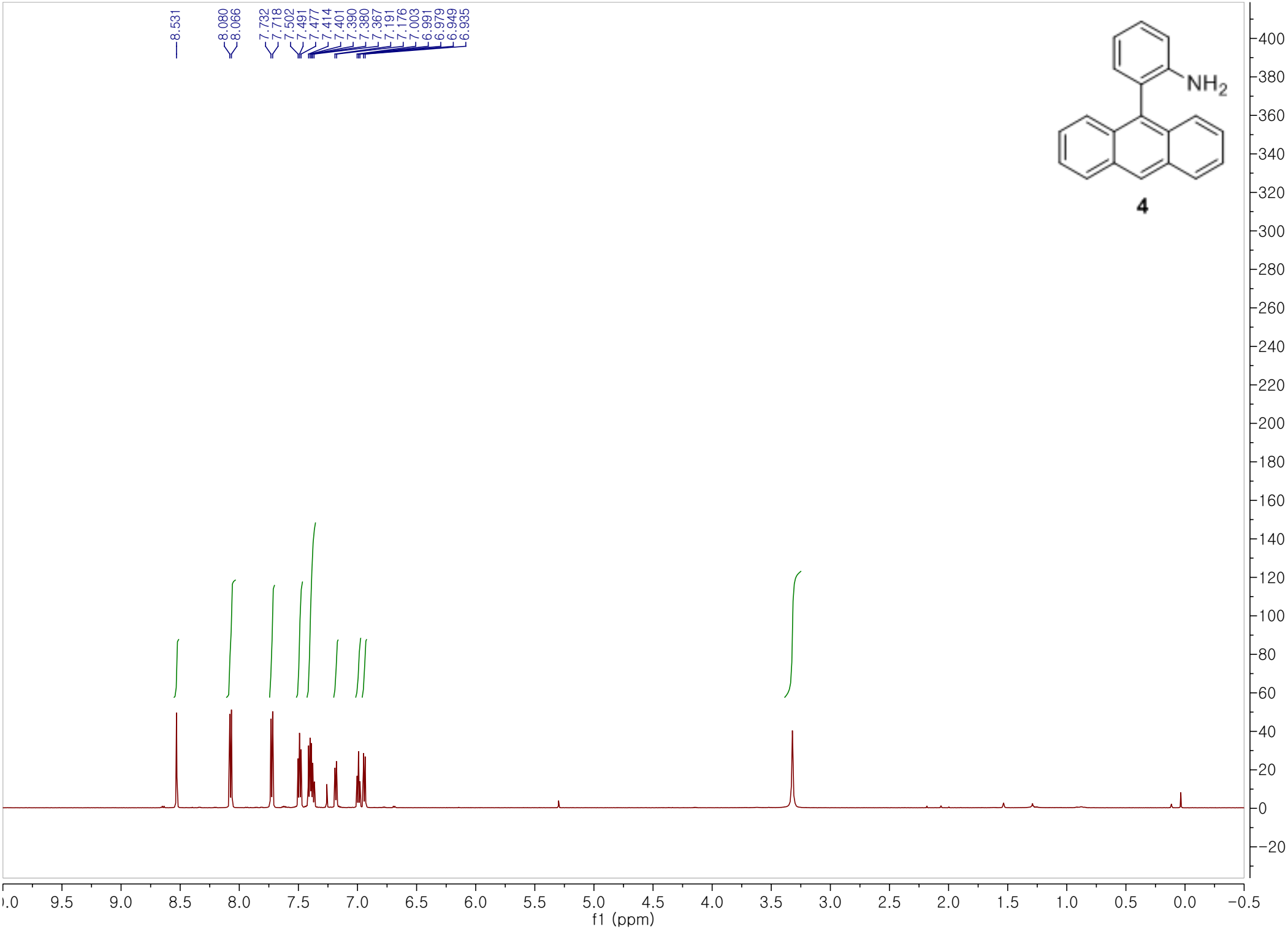
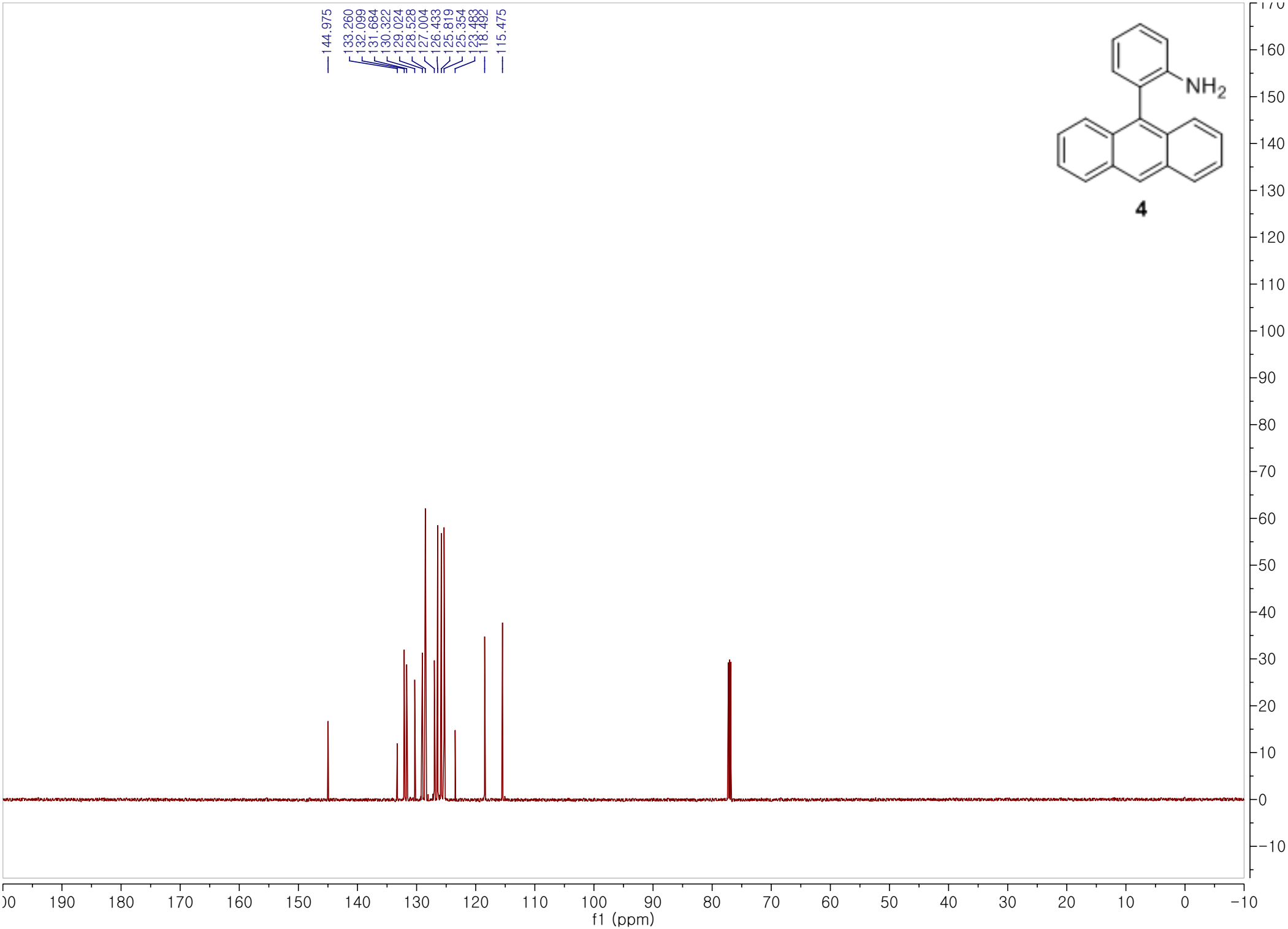
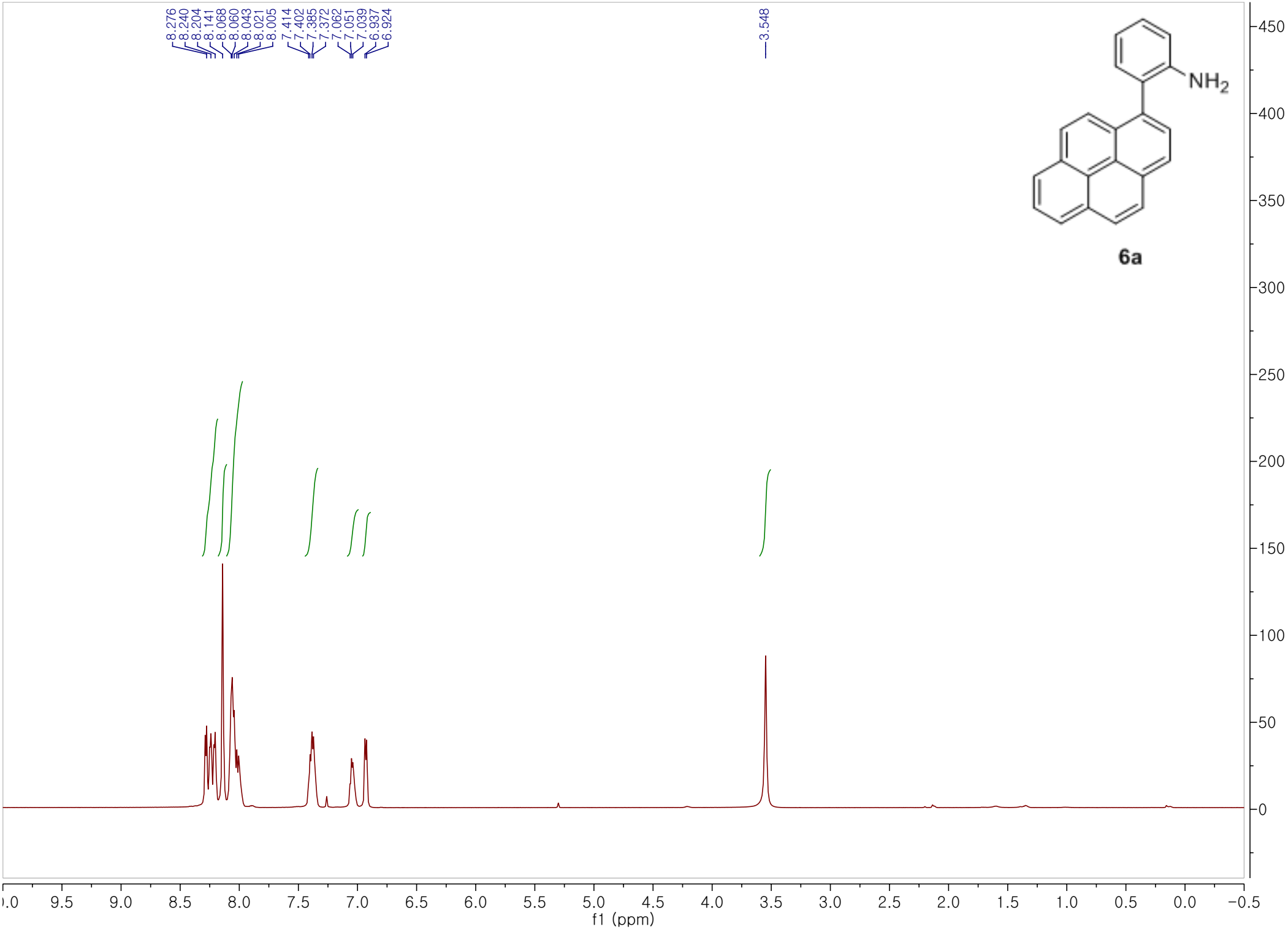
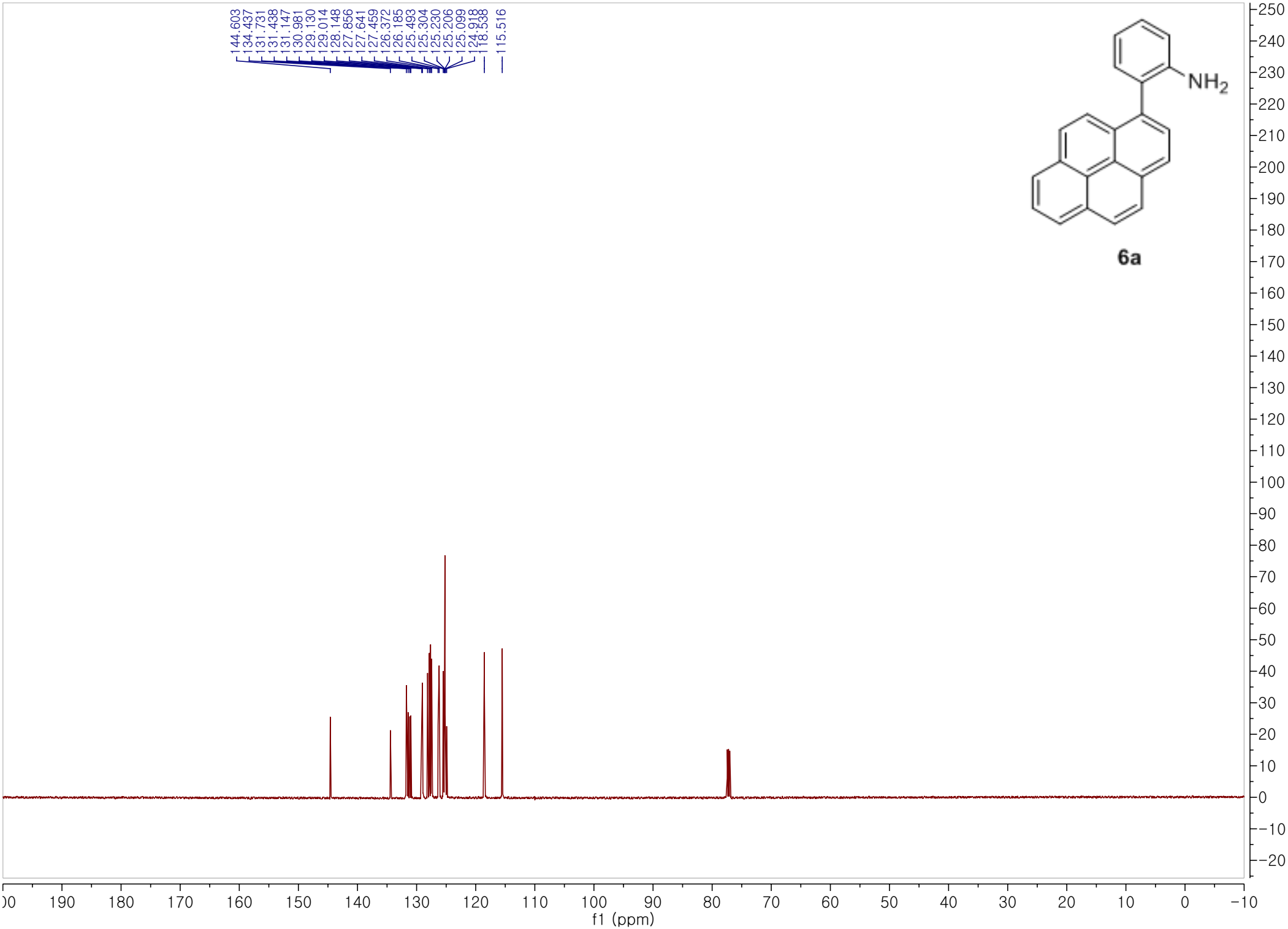
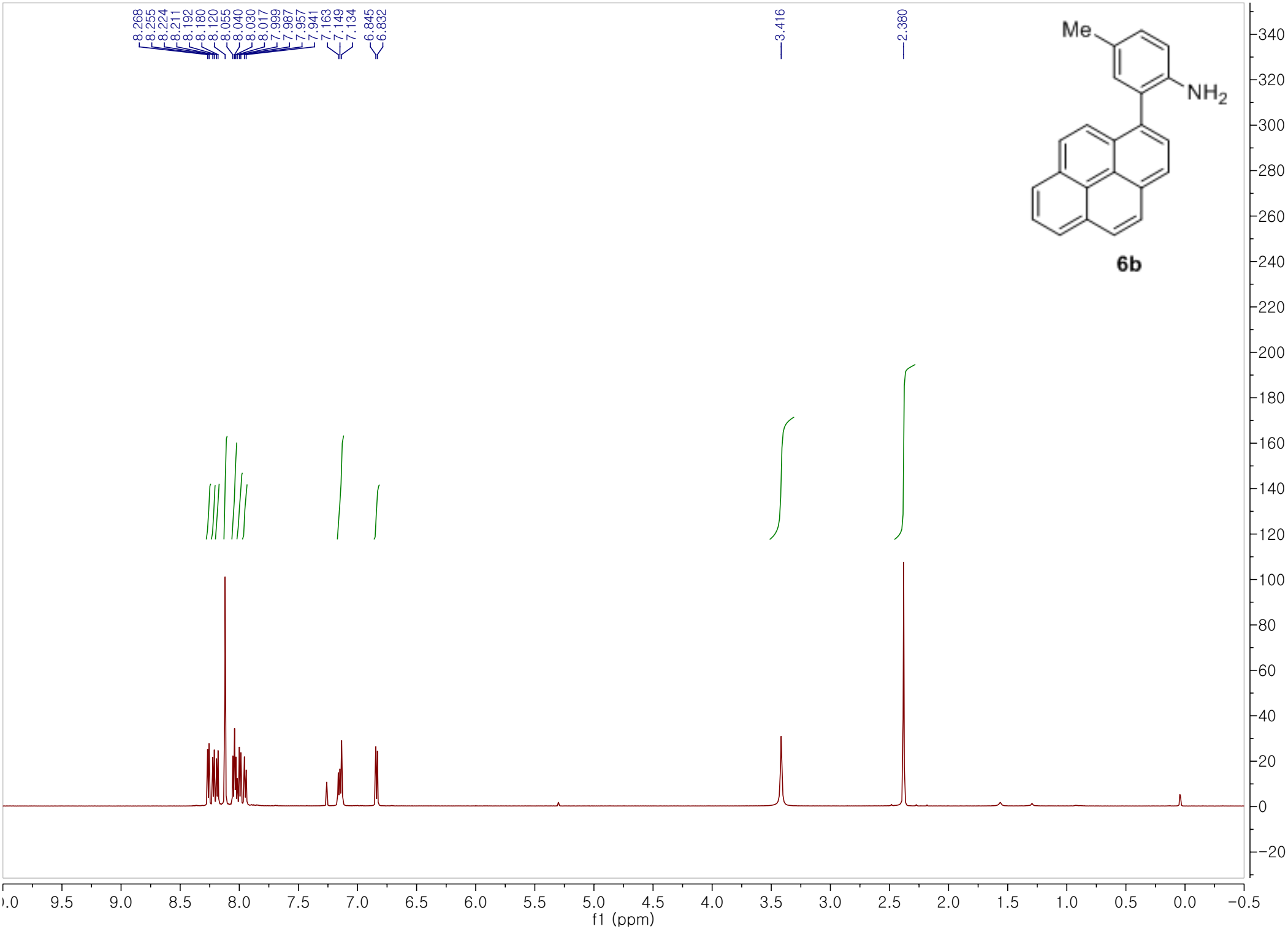
144.847
143.186
138.638
135.997
134.251
134.086
132.935
130.921
130.623
129.829
129.140
128.478
127.855
127.584
127.202
123.344
123.287
122.933
122.624
121.145
120.779
52.394
CO2Me
2d
f1 (ppm)

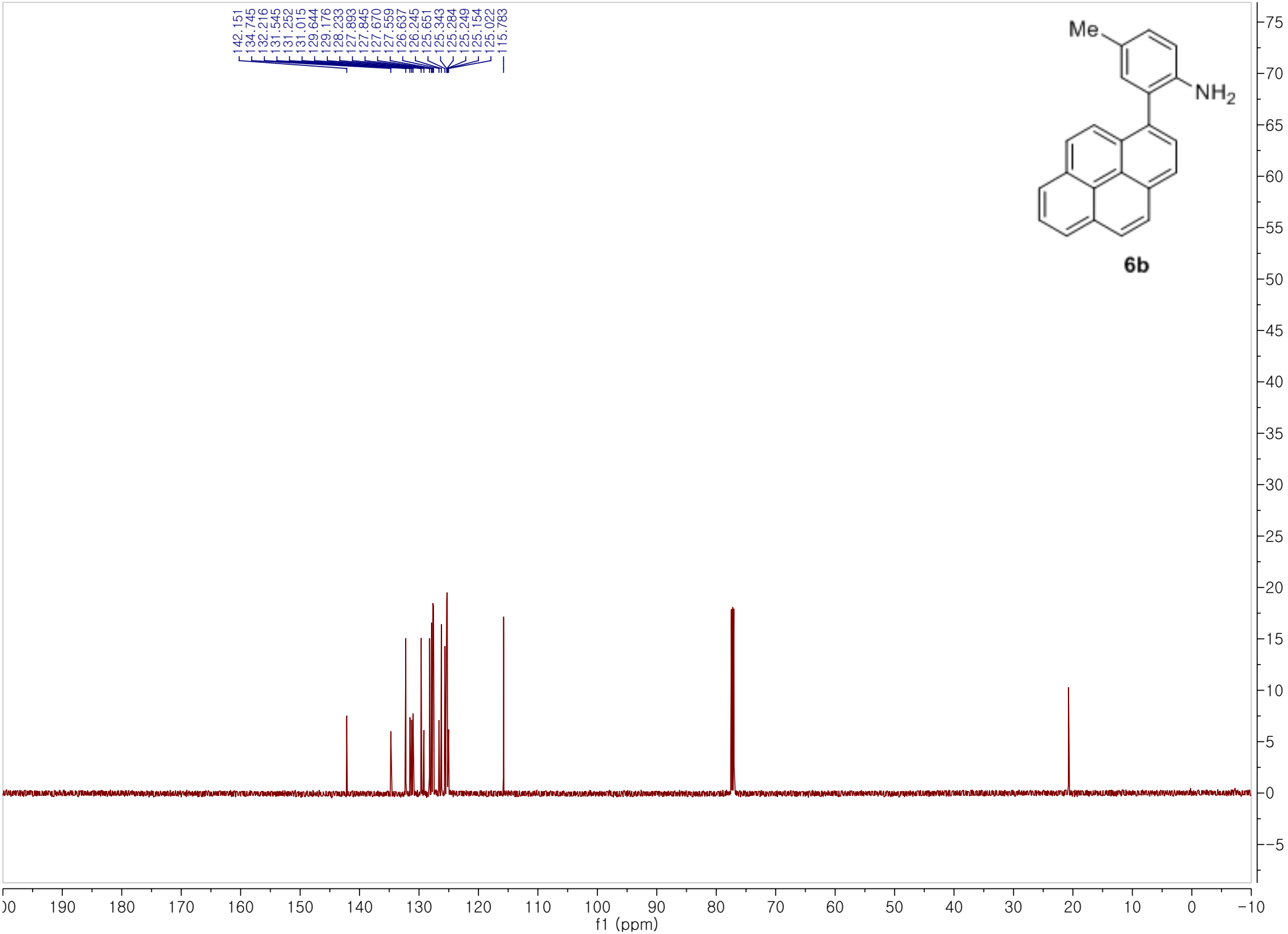

8.531
8.080
8.066
7.732
7.718
7.502
7.491
7.477
7.414
7.401
7.390
7.380
7.367
7.191
7.176
7.003
6.991
6.979
6.949
6.935
NH2
4
f1 (ppm)

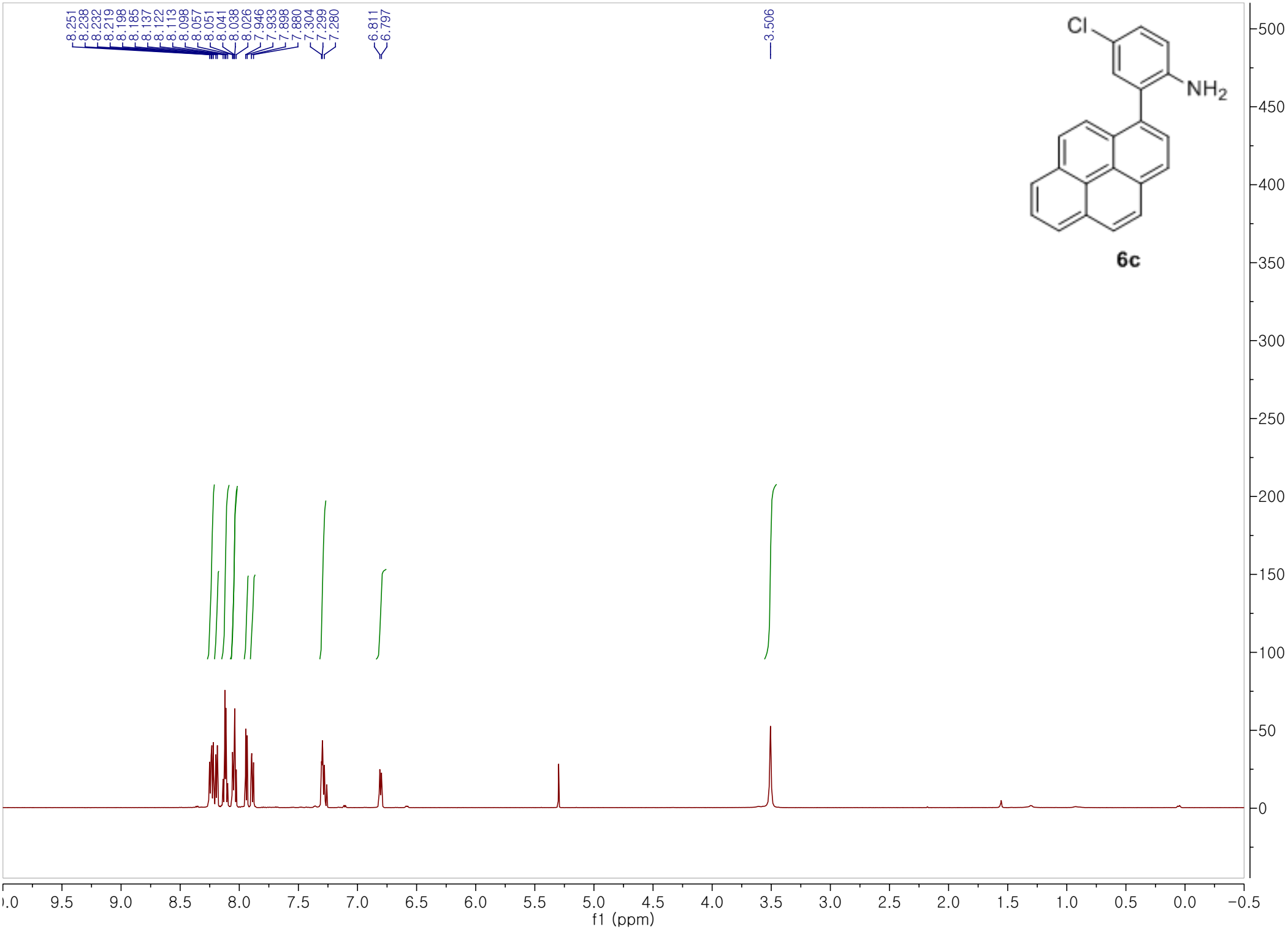

144.975
133.260
132.099
131.684
130.322
129.024
128.528
127.004
126.433
125.819
125.354
123.483
118.492
115.475
NH2
4
f1 (ppm)

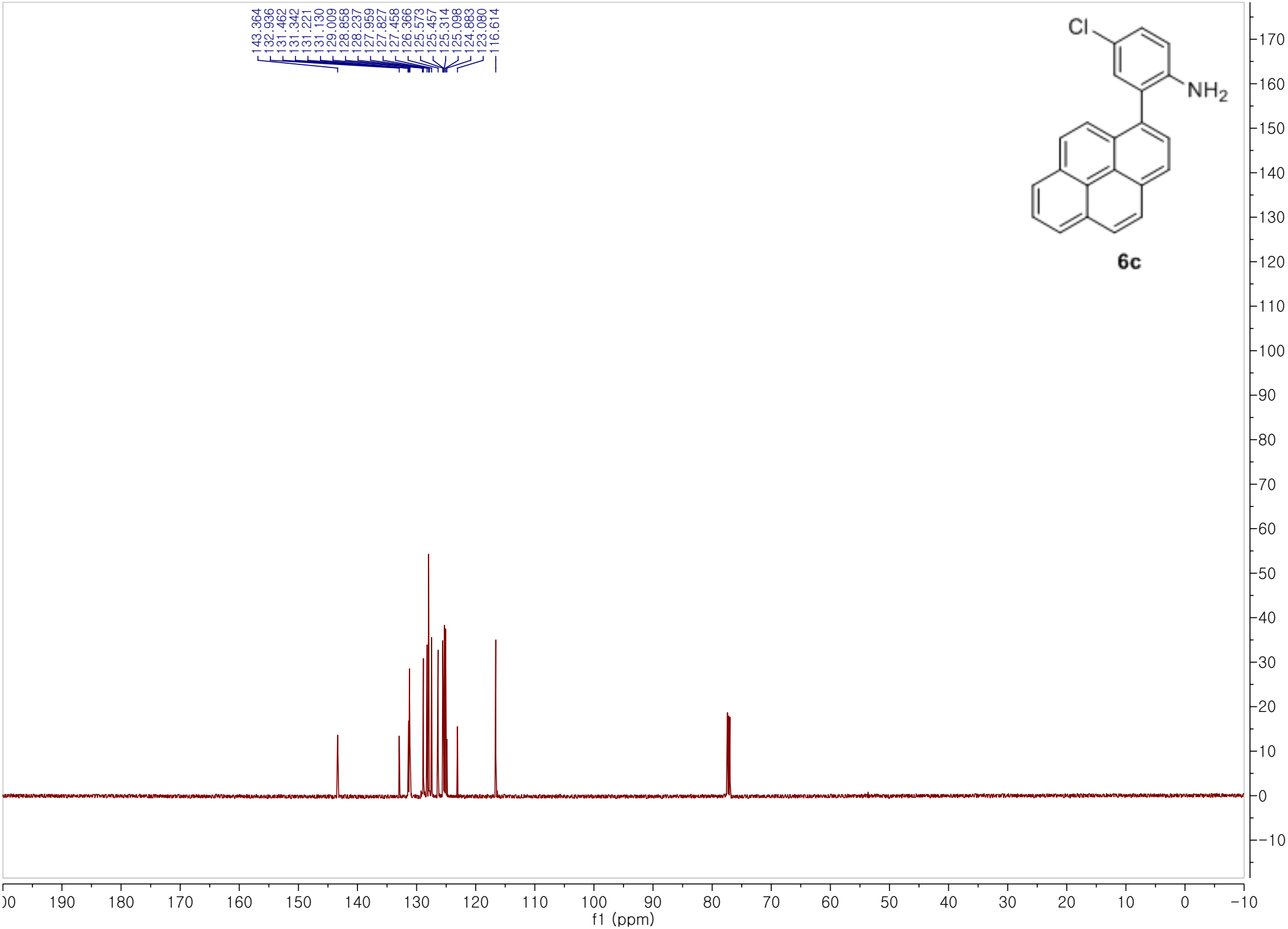

8.276
8.240
8.204
8.141
8.068
8.060
8.043
8.021
8.005
7.414
7.402
7.385
7.372
7.062
7.051
7.039
6.937
6.924
3.548
NH2
6a
f1 (ppm)

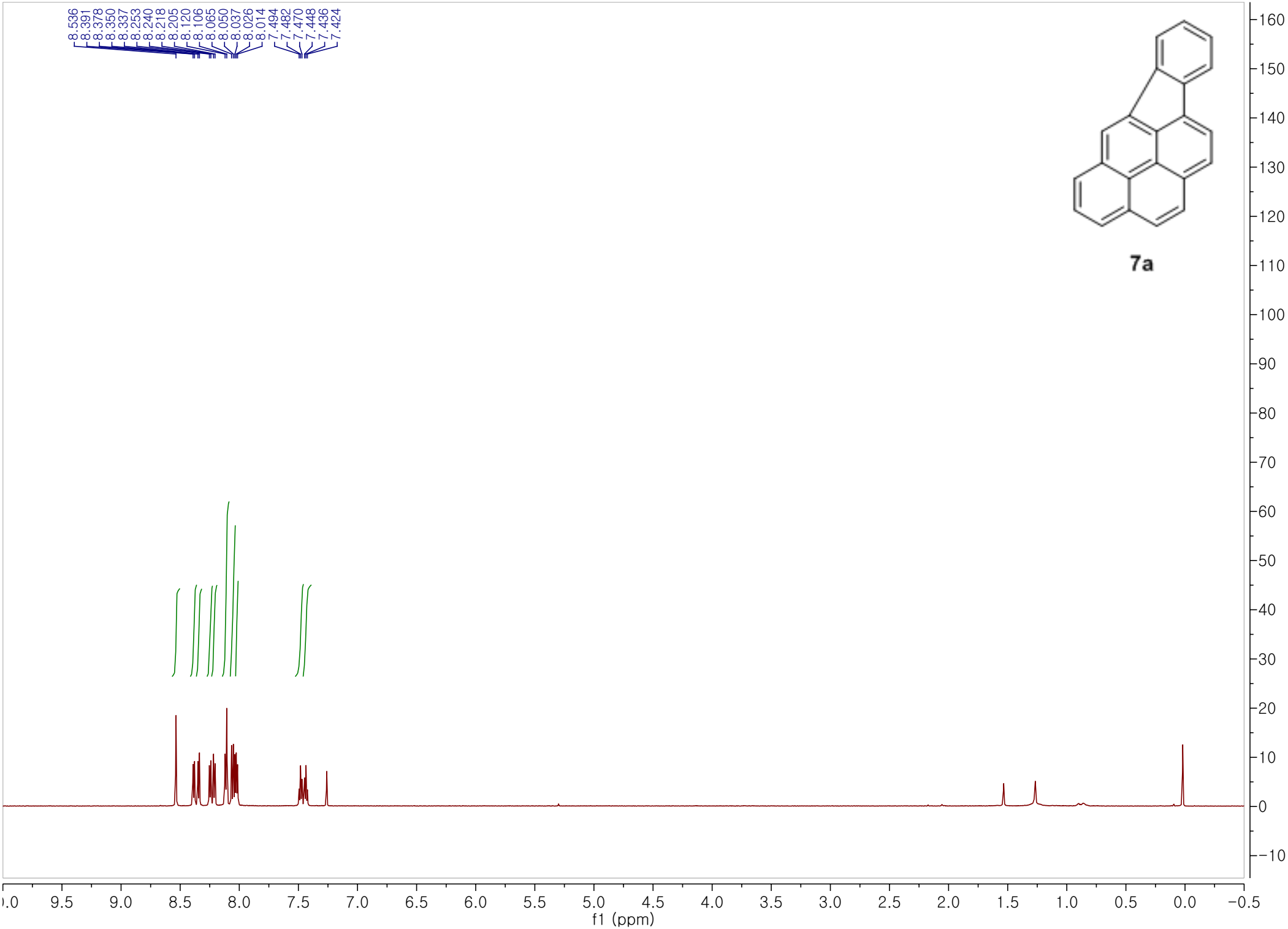

144.603
134.437
131.731
131.438
131.147
130.981
129.130
129.014
128.148
127.856
127.641
127.459
126.372
126.185
125.493
125.304
125.230
125.206
125.099
124.918
118.538
115.516
NH2
6a
f1 (ppm)

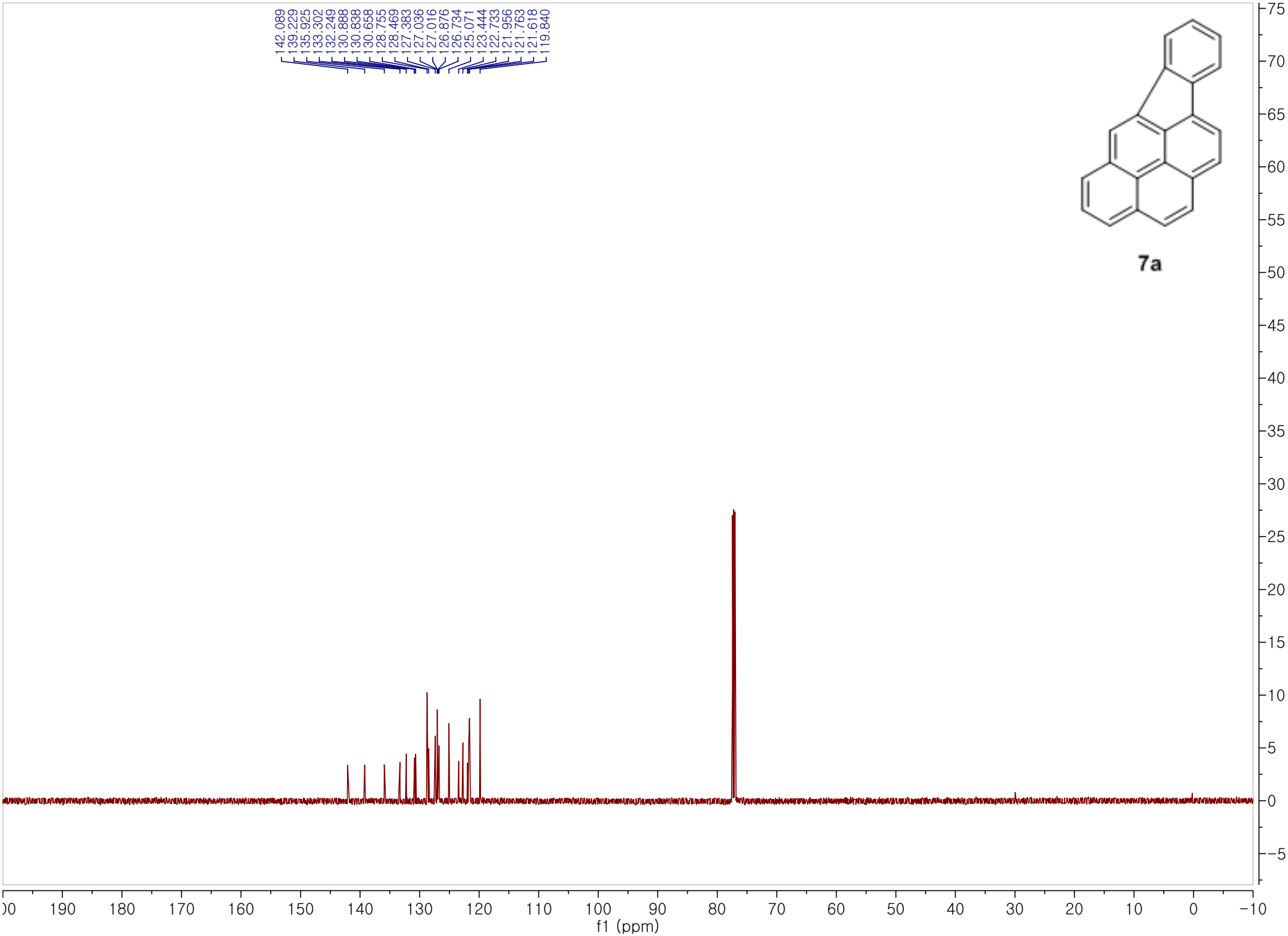

8.268
8.255
8.224
8.211
8.192
8.180
8.120
8.055
8.040
8.030
8.017
7.999
7.987
7.957
7.941
7.163
7.149
7.134
6.845
6.832
3.416
2.380
Me
NH2
6b
f1 (ppm)


142.151
134.745
132.216
131.545
131.252
131.015
129.644
129.176
128.233
127.893
127.845
127.670
127.559
126.637
126.245
125.651
125.343
125.284
125.249
125.154
125.022
115.783
Me
NH2
6b
f1 (ppm)


8.251
8.238
8.232
8.219
8.198
8.185
8.137
8.122
8.113
8.098
8.057
8.051
8.041
8.038
8.026
7.946
7.933
7.898
7.880
7.304
7.299
7.280
6.811
6.797
3.506
Cl
NH2
6c
f1 (ppm)


143.364
132.936
131.462
131.342
131.221
131.130
129.009
128.858
128.237
127.959
127.827
127.458
126.366
125.573
125.457
125.314
125.098
124.883
123.080
116.614
Cl
NH2
6c
f1 (ppm)


8.536
8.391
8.378
8.350
8.337
8.253
8.240
8.218
8.205
8.120
8.106
8.065
8.050
8.037
8.026
8.014
7.494
7.482
7.470
7.448
7.436
7.424
7a
f1 (ppm)


142.089
139.229
135.925
133.302
132.249
130.888
130.838
130.658
128.755
128.469
127.383
127.036
127.016
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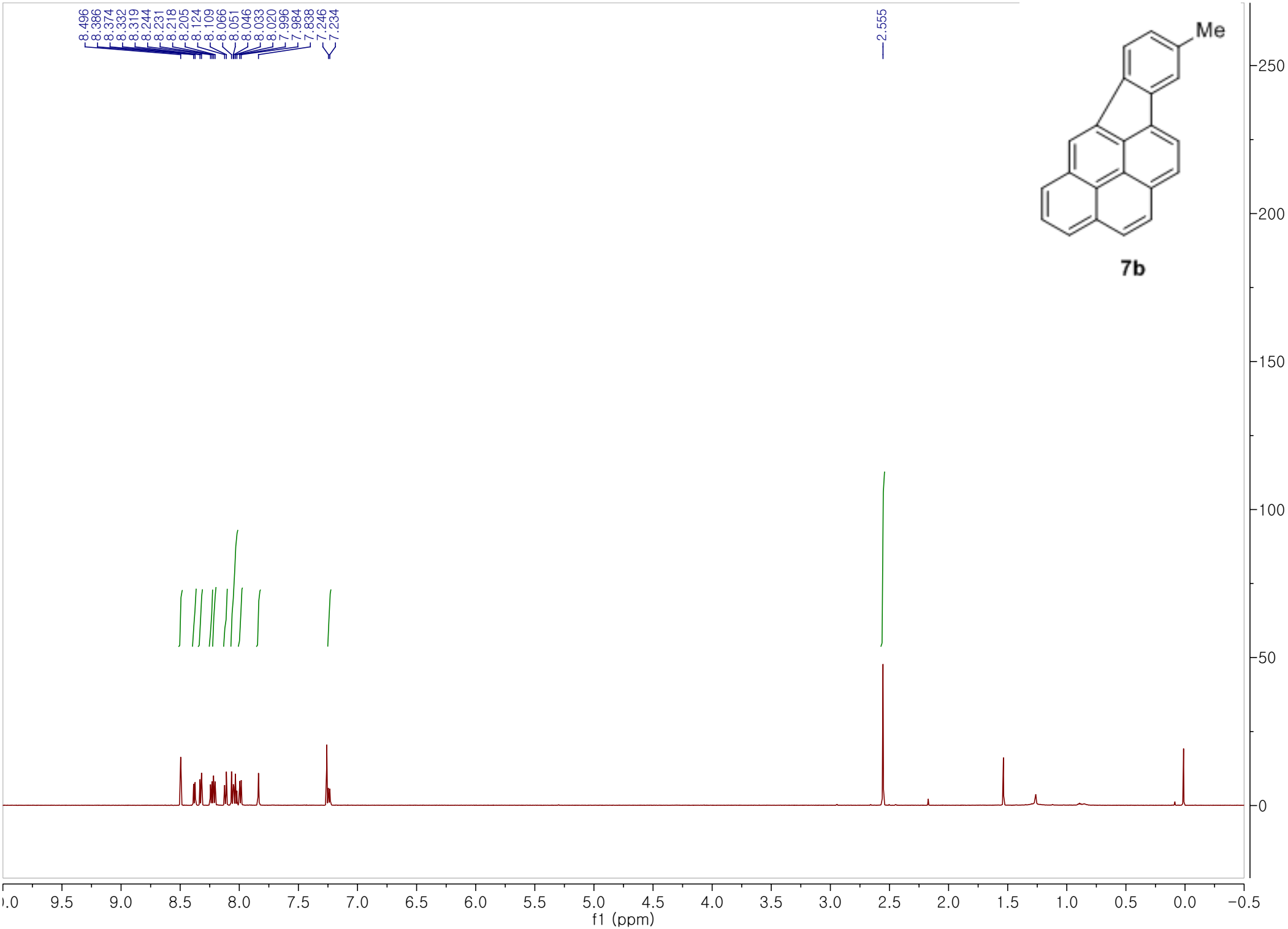
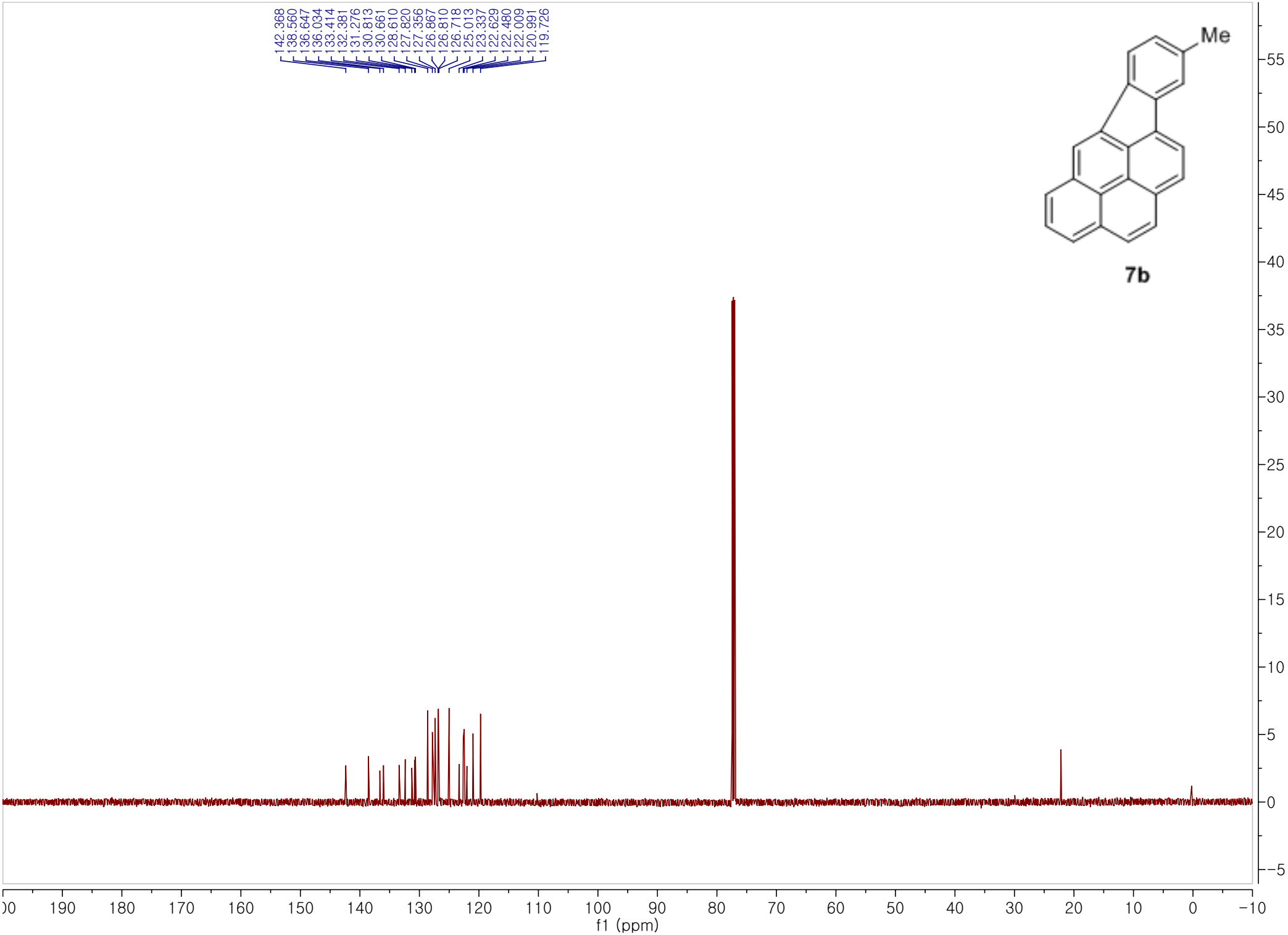
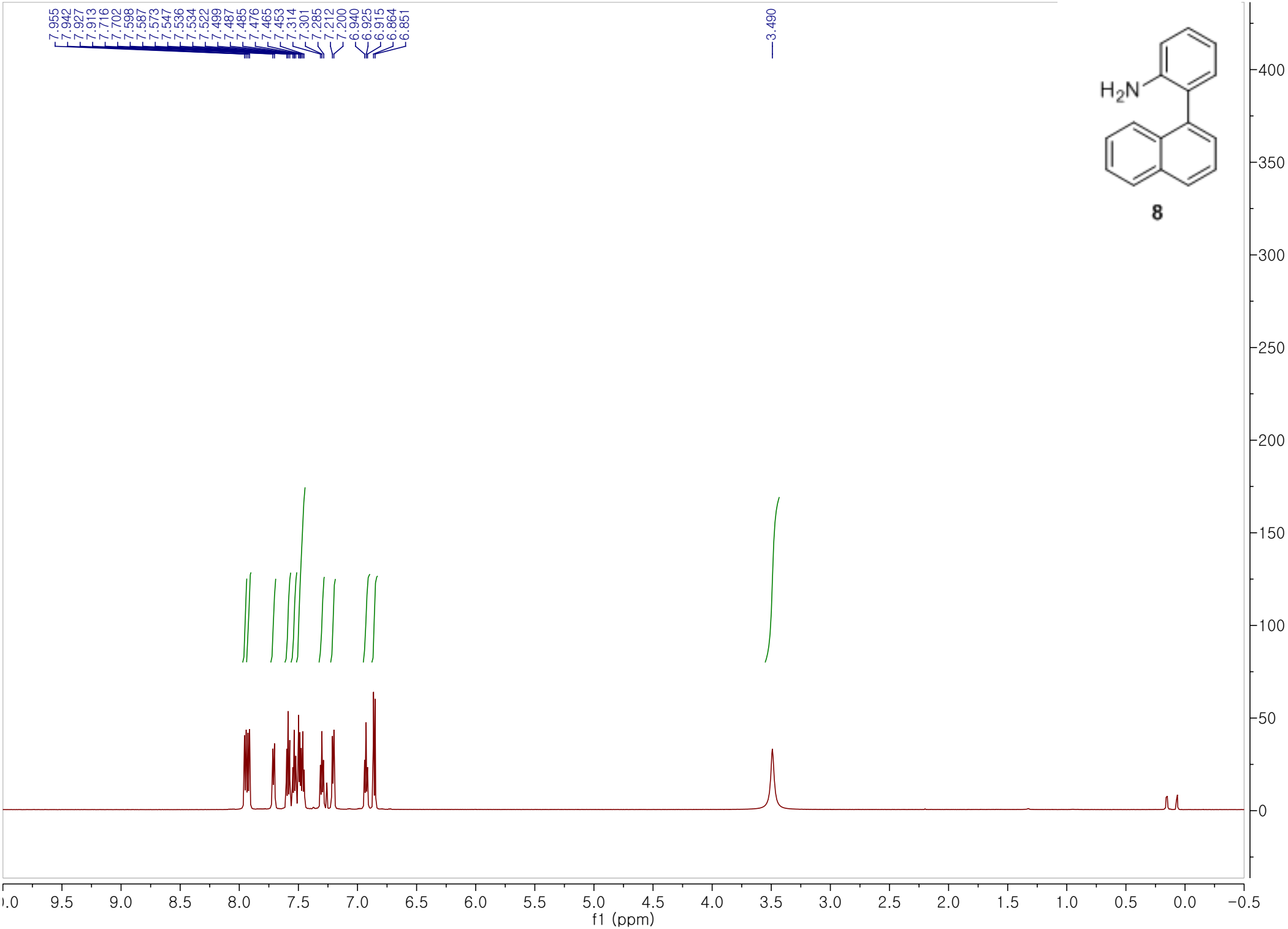
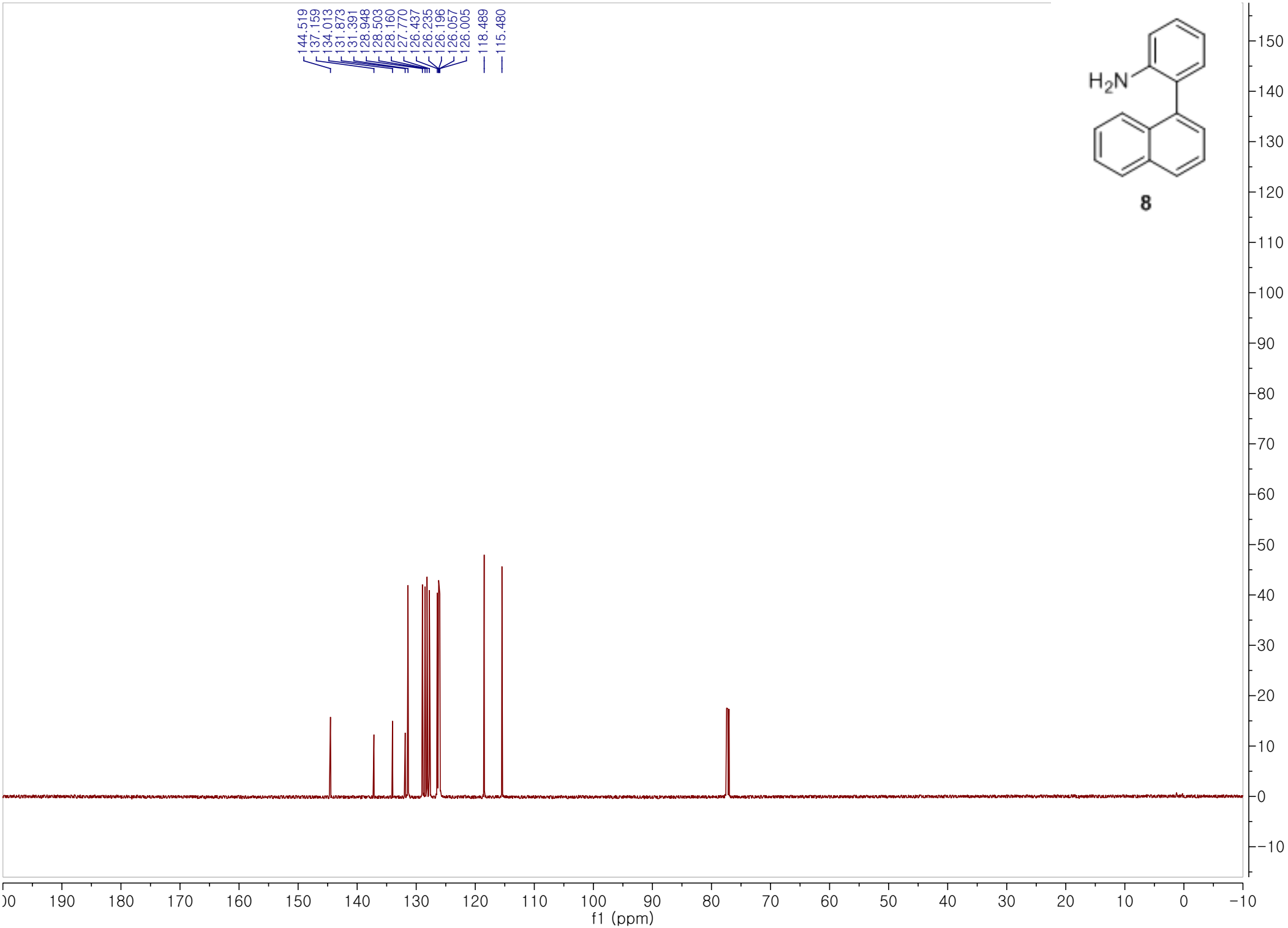
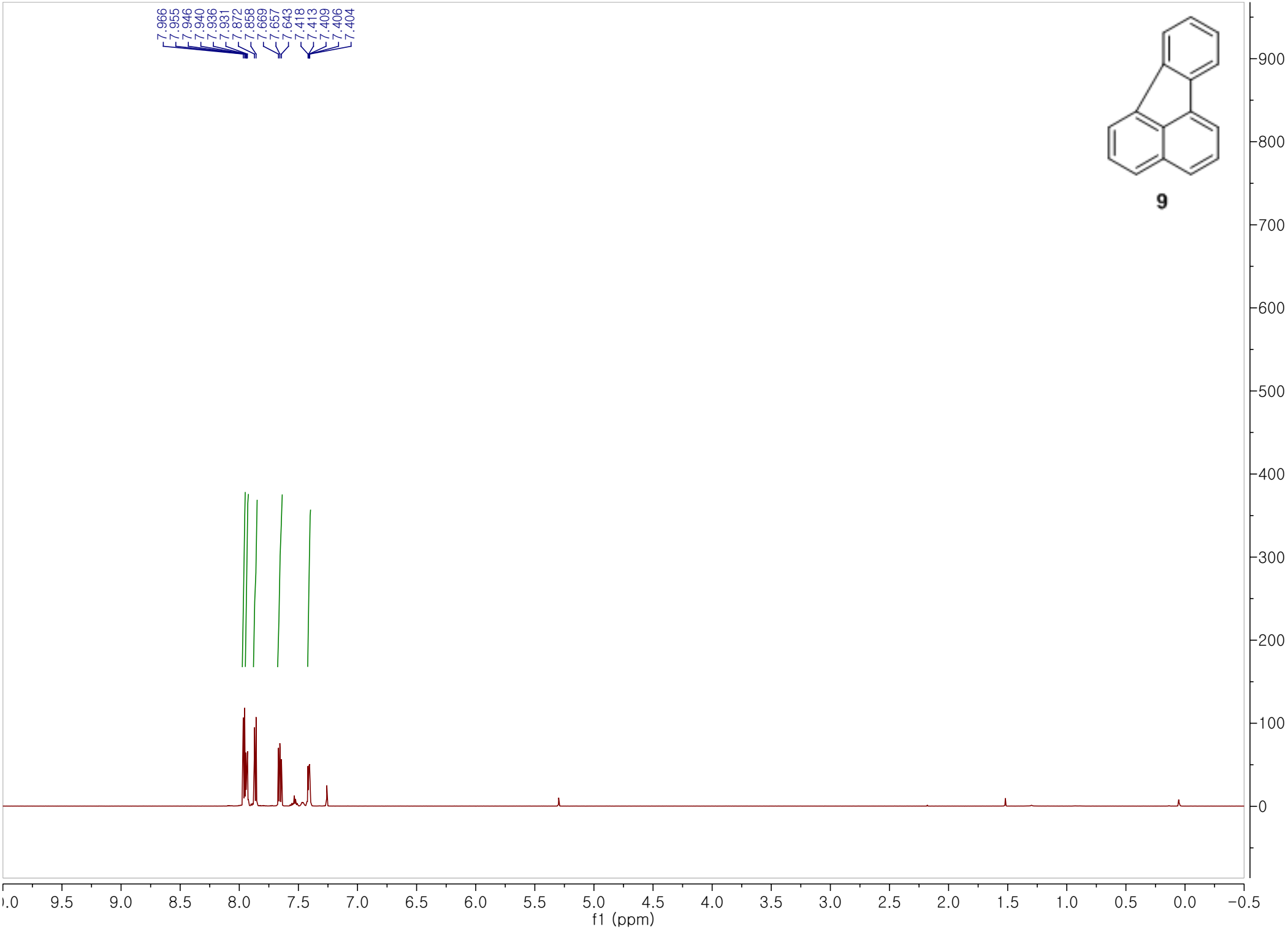
121.763
121.618
119.840
7a
f1 (ppm)

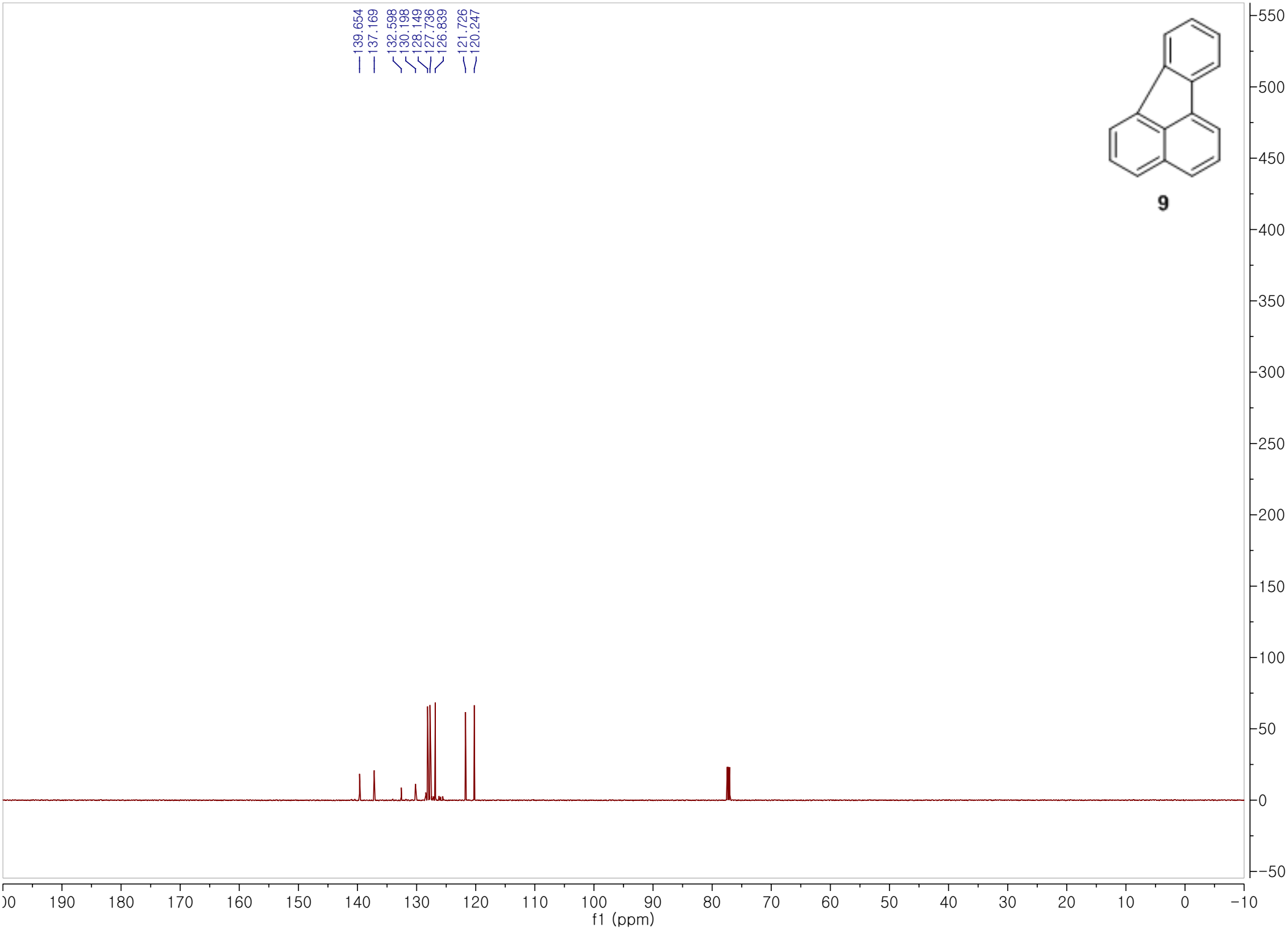

8.496
8.386
8.374
8.332
8.319
8.244
8.231
8.218
8.205
8.124
8.109
8.066
8.051
8.046
8.033
8.020
7.996
7.984
7.838
7.246
7.234
2.555
Me
7b
f1 (ppm)

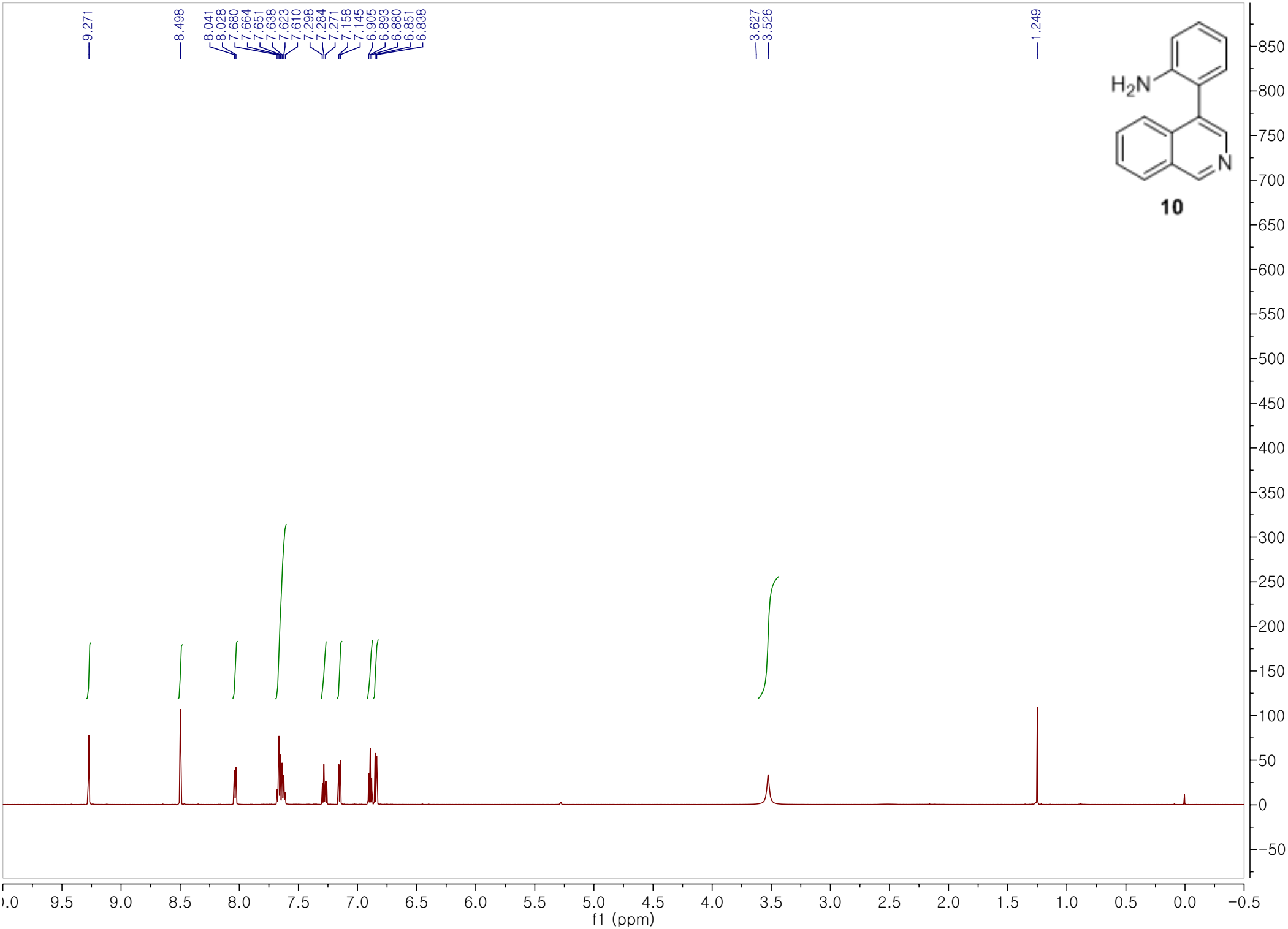

142.368
138.560
136.647
136.034
133.414
132.381
131.276
130.813
130.661
128.610
127.820
127.356
126.867
126.810
126.718
125.013
123.337
122.629
122.480
122.009
120.991
119.726
Me
7b
f1 (ppm)

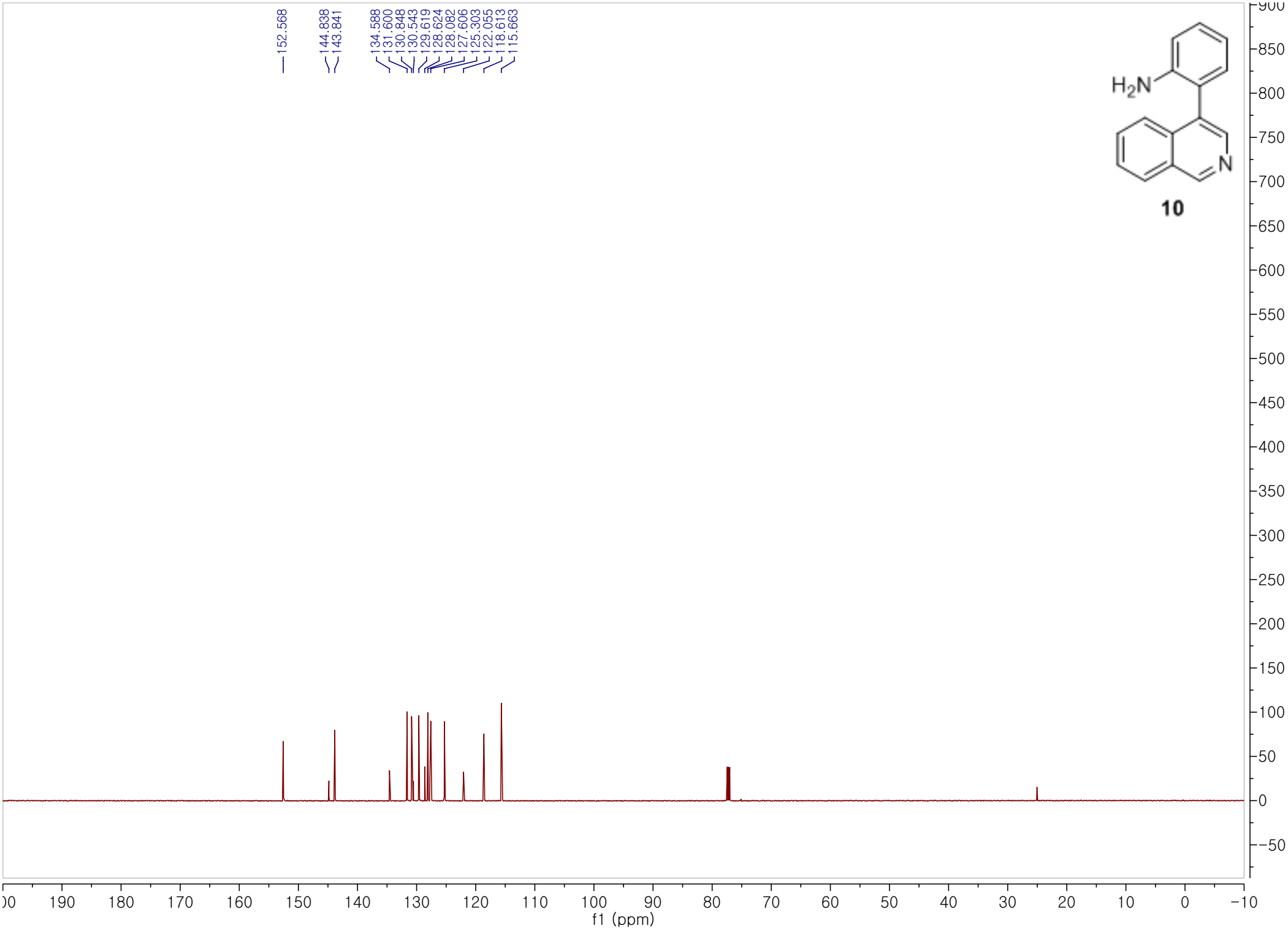

7.955
7.942
7.927
7.913
7.716
7.702
7.598
7.587
7.573
7.547
7.536
7.534
7.522
7.499
7.487
7.485
7.476
7.465
7.453
7.314
7.301
7.285
7.212
7.200
6.940
6.925
6.915
6.864
6.851
3.490
H2N
8
f1 (ppm)


144.519
137.159
134.013
131.873
131.391
128.948
128.503
128.160
127.770
126.437
126.235
126.196
126.057
126.005
118.489
115.480
H_2N
8
f1 (ppm)


7.966
7.955
7.946
7.940
7.936
7.931
7.872
7.858
7.669
7.657
7.643
7.418
7.413
7.409
7.406
7.404
9
900
800
700
600
500
400
300
200
100
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
0.0
−0.5
f1 (ppm)


139.654
137.169
132.598
130.198
128.149
127.736
126.839
121.726
120.247
9
f1 (ppm)


9.271
8.498
8.041
8.028
7.680
7.664
7.651
7.638
7.623
7.610
7.298
7.284
7.271
7.158
7.145
6.905
6.893
6.880
6.851
6.838
3.627
3.526
1.249
H2N
N
10
f1 (ppm)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143.841
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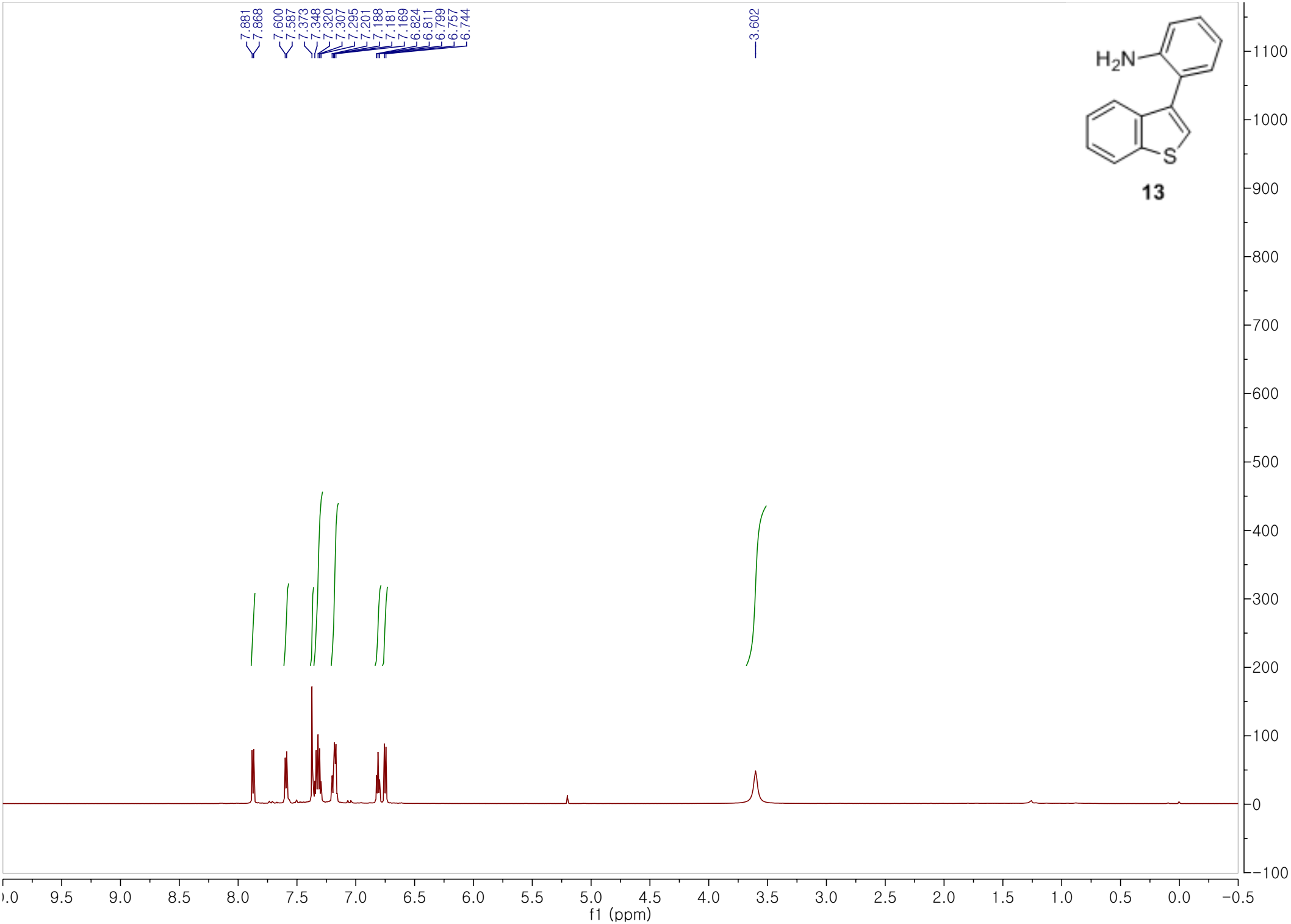
131.600
130.848
130.543
129.619
128.624
128.082
127.606
125.303
122.055
118.613
115.663
H2N
N
10
f1 (ppm)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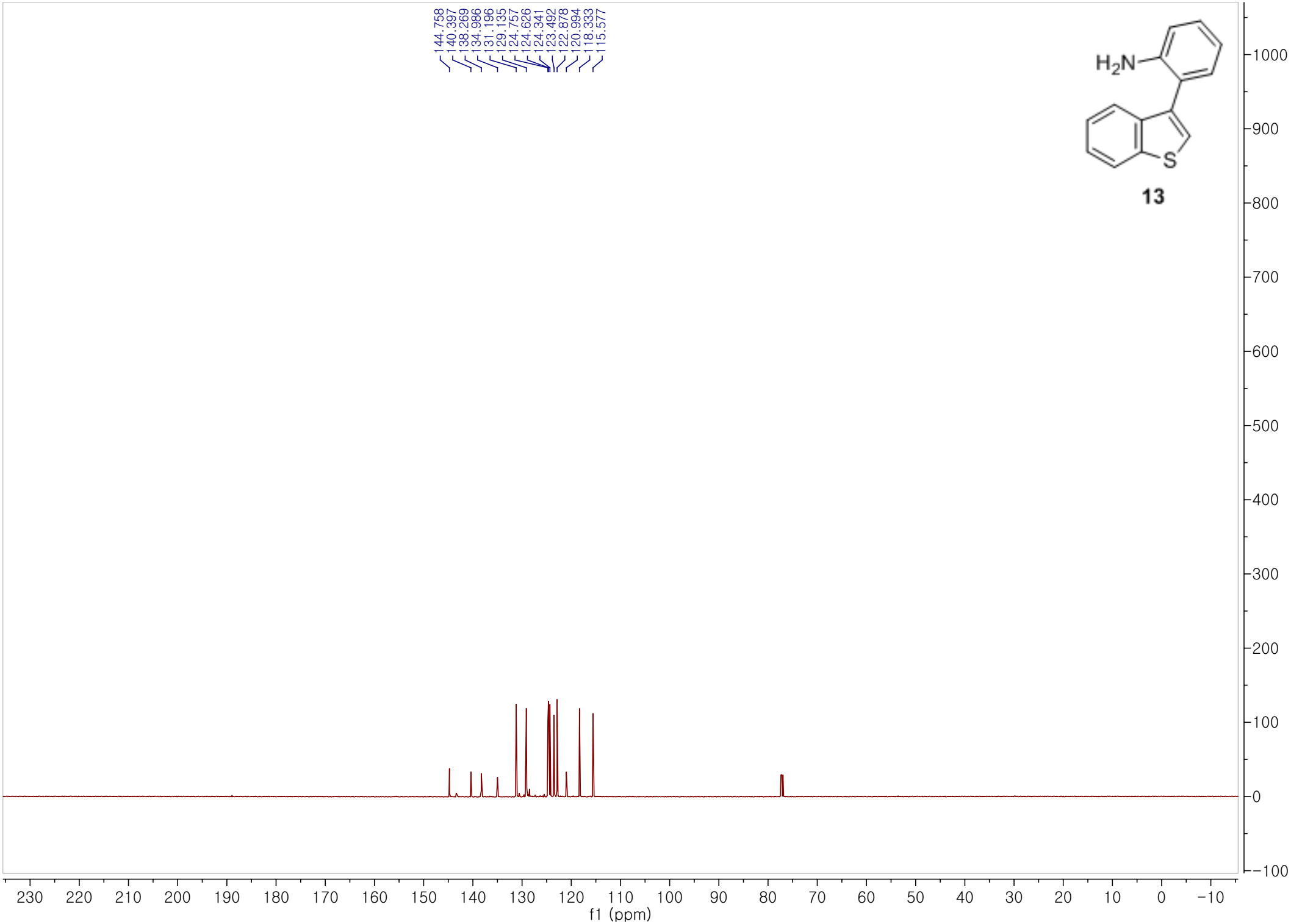
7.600
7.587
7.373
7.348
7.320
7.307
7.295
7.201
7.188
7.181
7.169
6.824
6.811
6.799
6.757
6.744
3.602
H2N
S
13
f1 (ppm)


144.758
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138.269
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131.196
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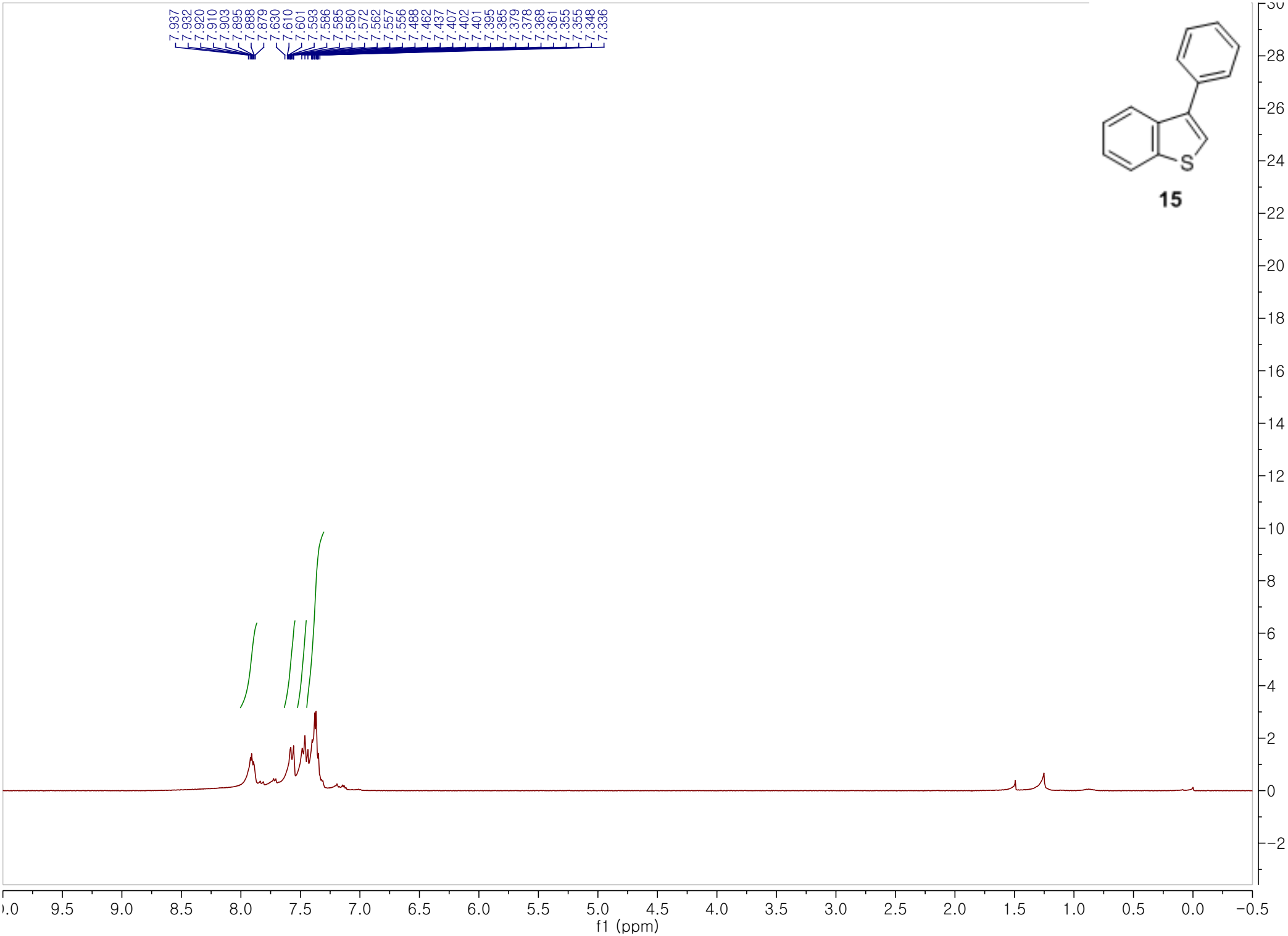
124.757
124.626
124.341
123.492
122.878
120.994
118.333
115.577
H2N
S
13
f1 (ppm)


7.937
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7.910
7.903
7.895
7.888
7.879
7.630
7.610
7.601
7.593
7.586
7.585
7.580
7.572
7.562
7.557
7.556
7.488
7.462
7.437
7.407
7.402
7.401
7.395
7.385
7.379
7.378
7.368
7.361
7.355
7.355
7.348
7.336
S
15
f1 (ppm)