Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Online Material for

A General Route for Synthesis of *N*-Aryl Phenoxazines via Copper(I)-Catalyzed *N*-, *N*-, and *O*-Arylations of 2-Aminophenols

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Experimental Section

All melting points were determined on a Yanaco melting point apparatus and were uncorrected. IR spectra were recorded as KBr pellets on a Nicolet FT-IR 5DX spectrometer. All spectra of ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were recorded on a JEOL JNM-ECA 300 spectrometer in $CDCl_3$ (otherwise as indicated). TMS was used as an internal reference and *J* values are given in Hz. HRMS were obtained on a Bruker microTOF-Q II spectrometer.

The substituted 2-[*N*-(2-chlorophenyl)amino]-phenols **5b** (R = H), **5c** (R = 4-Me), **5d** (R = 3-Me) and **5e** (R = 4-Cl) were prepared by the procedure reported in literature (D. Maiti, S. L. Buchwald, *J. Am. Chem. Soc.* **2009**, *131*, 17423–17429) and their analytical data are as following.

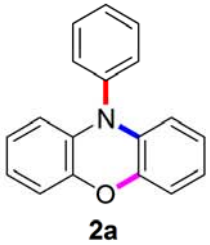
2-(2-Chlorophenylamino)phenol (5b). White solid, 82%, mp 49-50 ^{o}C; IR ν 3506, 3376, 1591, 1497 cm^{-1}; ^{1}H NMR δ 7.34 (d, *J* = 7.9, 1H), 7.19-7.03 (m, 4H), 6.94-6.91 (m, 1H), 6.80-6.75 (m, 1H), 6.60 (d, *J* = 8.2, 1H), 5.85 (s, 0.89H), 5.73 (s, 0.83H) ppm; ^{13}C NMR δ 152.1, 142.1, 129.4, 127.8, 127.5, 127.4, 126.4, 121.1, 120.7, 120.2, 115.6, 114.7 ppm; HRMS (ESI-TOF) (*m/z*): Calcd for $C_{12}H_{10}ClNO$, $[M+H]^{+}$ 220.0524; found 220.0520.

2-(2-Chlorophenylamino)-4-methylphenol (5c). Brown solid, 85%, mp 74-75 ^{o}C; IR ν 3495, 3345, 2967, 2862, 1589, 1496 cm^{-1}; ^{1}H NMR δ 7.33 (d, *J* = 7.9, 1H), 7.09-7.03 (m, 1H), 6.98-6.89 (m, 3H), 6.80-6.74 (m, 1H), 6.60 (d, *J* = 8.3, 1H), 5.69 (s, 0.90H), 5.60 (s, 0.96H), 2.25 (s, 3H) ppm; ^{13}C NMR δ 149.7, 142.2, 130.5, 129.4, 128.0, 127.8, 127.0, 126.8, 120.6, 120.0, 115.3, 114.7, 20.5 ppm; HRMS (ESI-TOF) (*m/z*): Calcd for $C_{13}H_{12}ClNO$, $[M+H]^{+}$ 234.0680; found 234.0674.

2-(2-Chlorophenylamino)-3-methylphenol (5d). White solid, 79%, mp 90-91 ^{o}C; IR ν 3448, 3359, 2950, 2856, 1595, 1498, 1474 cm^{-1}; ^{1}H NMR δ 7.34 (d, *J* = 7.9, 1H), 7.18-7.12 (m, 1H), 7.06-7.00 (m, 1H), 6.91 (d, *J* = 7.5, 1H), 6.82-6.74 (m, 2H), 6.33 (d, *J* = 7.9, 1H), 6.16 (s, 0.97H), 5.50 (s, 0.82H), 2.10 (s, 3H) ppm; ^{13}C NMR δ 154.1,

142.2, 137.2, 129.4, 128.4, 128.0, 125.3, 122.3, 120.1, 120.0, 113.8, 112.6, 17.5 ppm; HRMS (ESI-TOF) (*m/z*): Calcd for $C_{13}H_{12}ClNO$, $[M+H]^+$ 234.0680; found 234.0678.

2-(2-Chlorophenylamino)-4-chlorophenol (5e). White solid, 74%, mp 81-83 ^oC; IR ν 3416, 3182, 1608, 1527 cm^{-1}; ^1H NMR δ 7.36 (d, J = 7.9, 1H), 7.17-7.07 (m, 3H), 6.68 (d, J = 8.6, 1H), 6.86-6.80 (m, 1H), 6.70 (d, J = 7.9, 1H), 5.78 (s, 0.96H), 5.63 (s, 0.98H) ppm; ^{13}C NMR δ 149.9, 141.0, 129.6, 128.9, 127.9, 126.5, 125.5, 124.9, 121.3, 121.0, 116.5, 115.3 ppm; HRMS (ESI-TOF) (*m/z*): Calcd for $C_{12}H_9Cl_2NO$, $[M+H]^+$ 254.0134; found 254.0132.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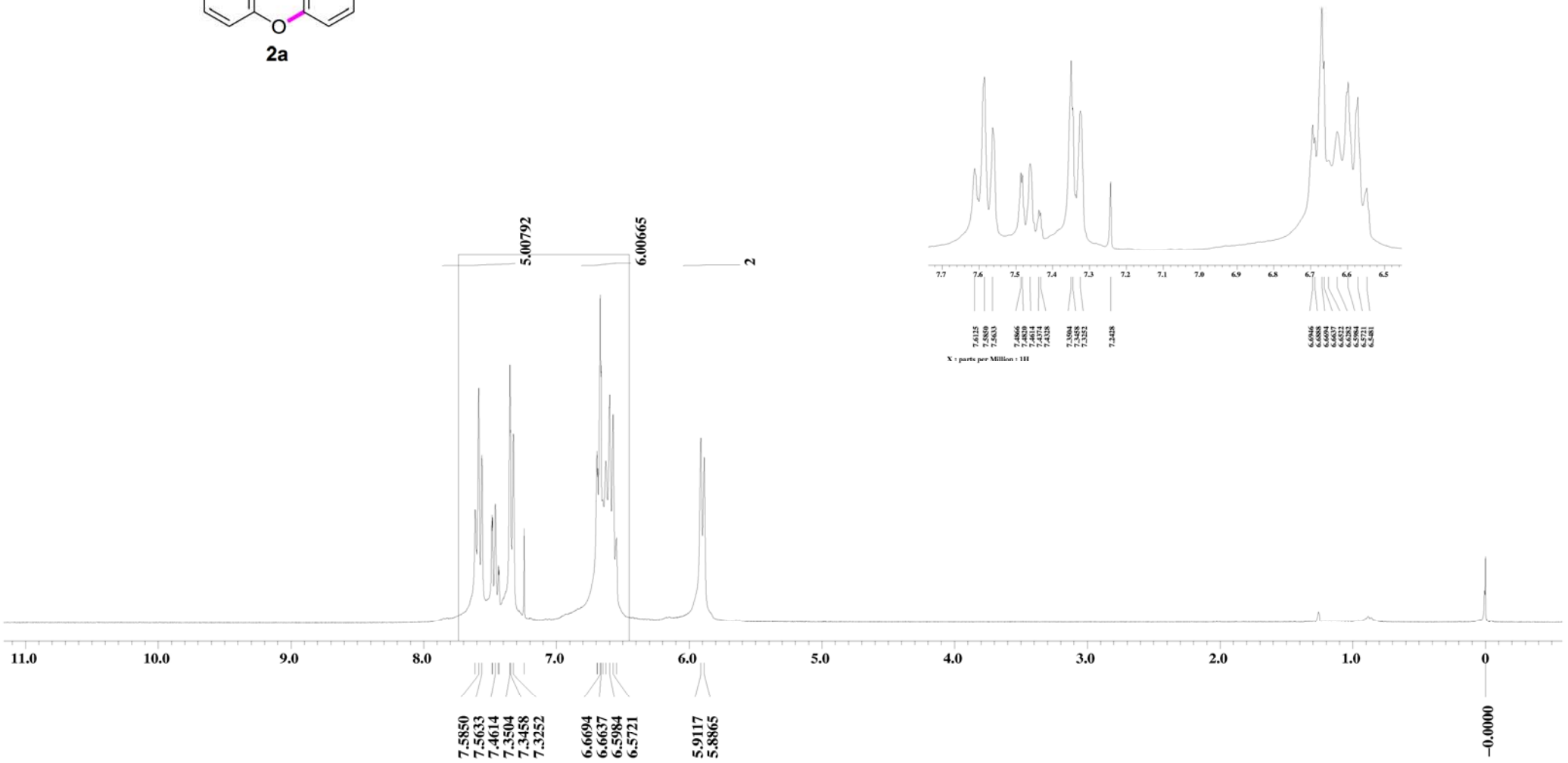
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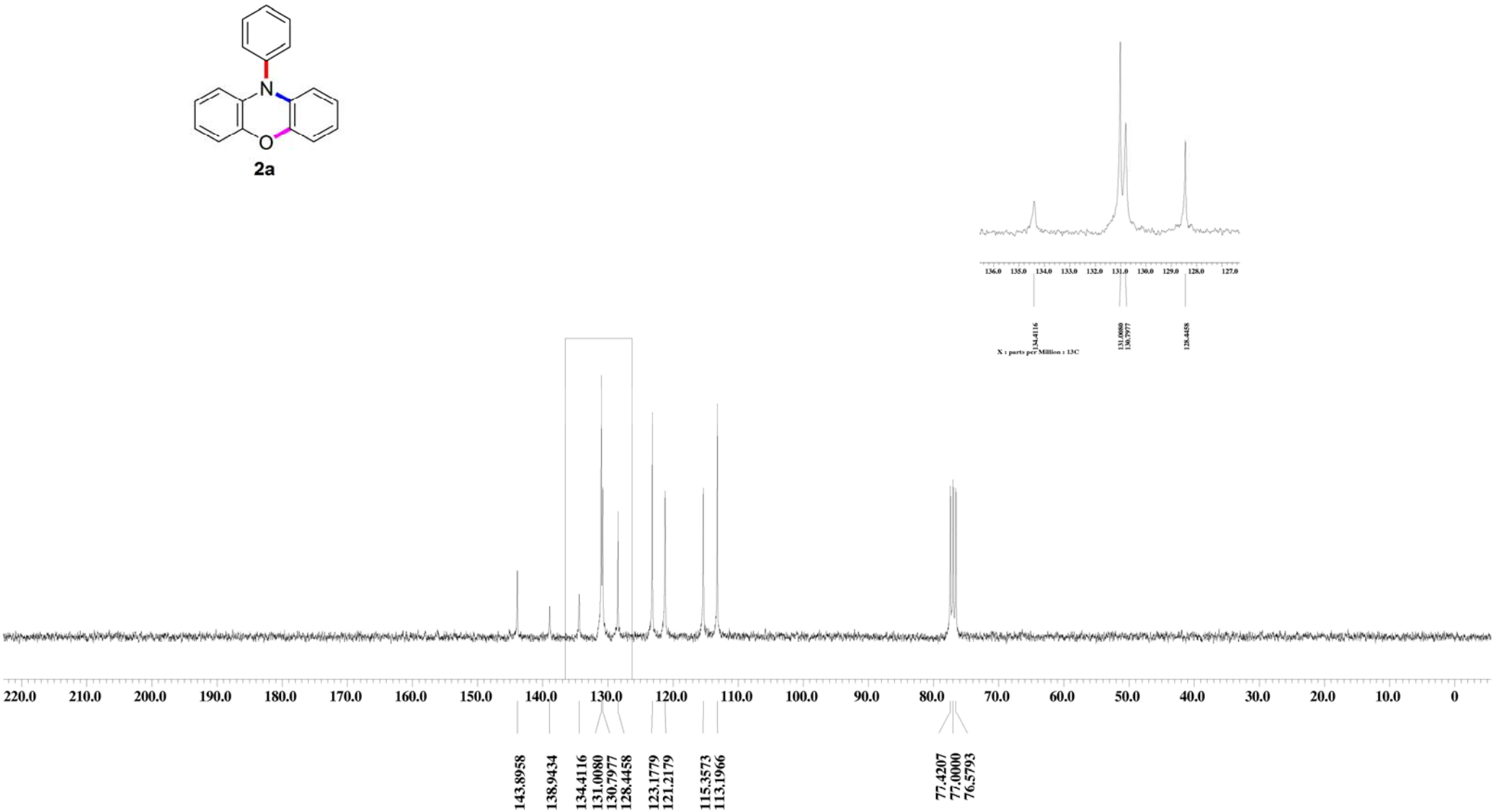
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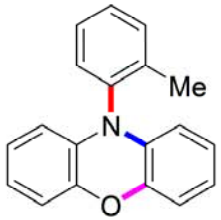
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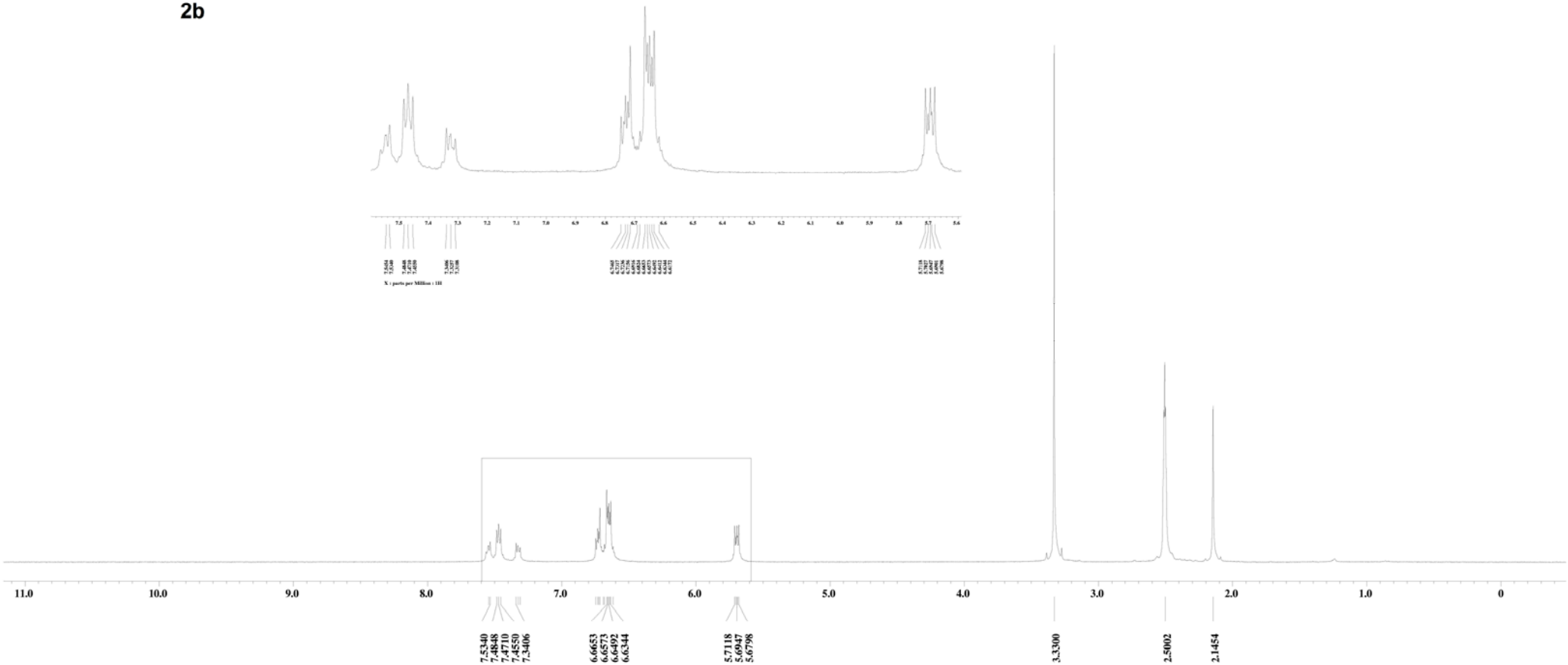
2b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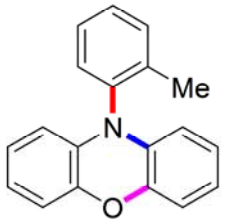
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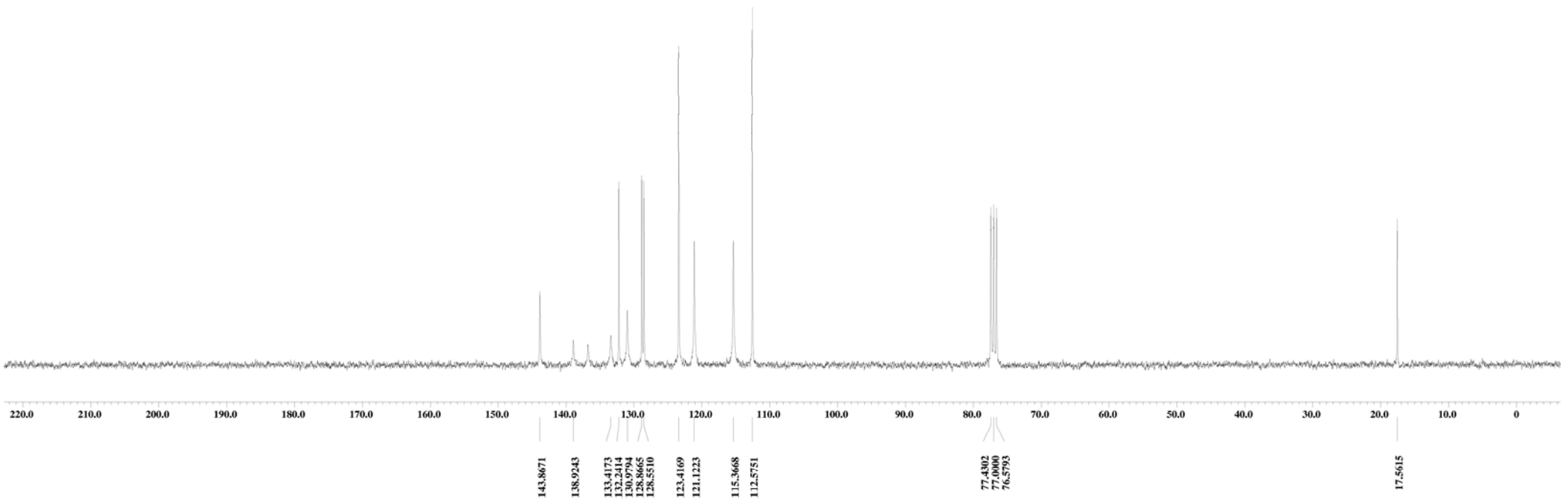
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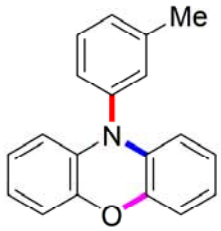
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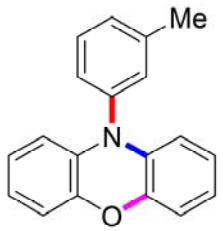
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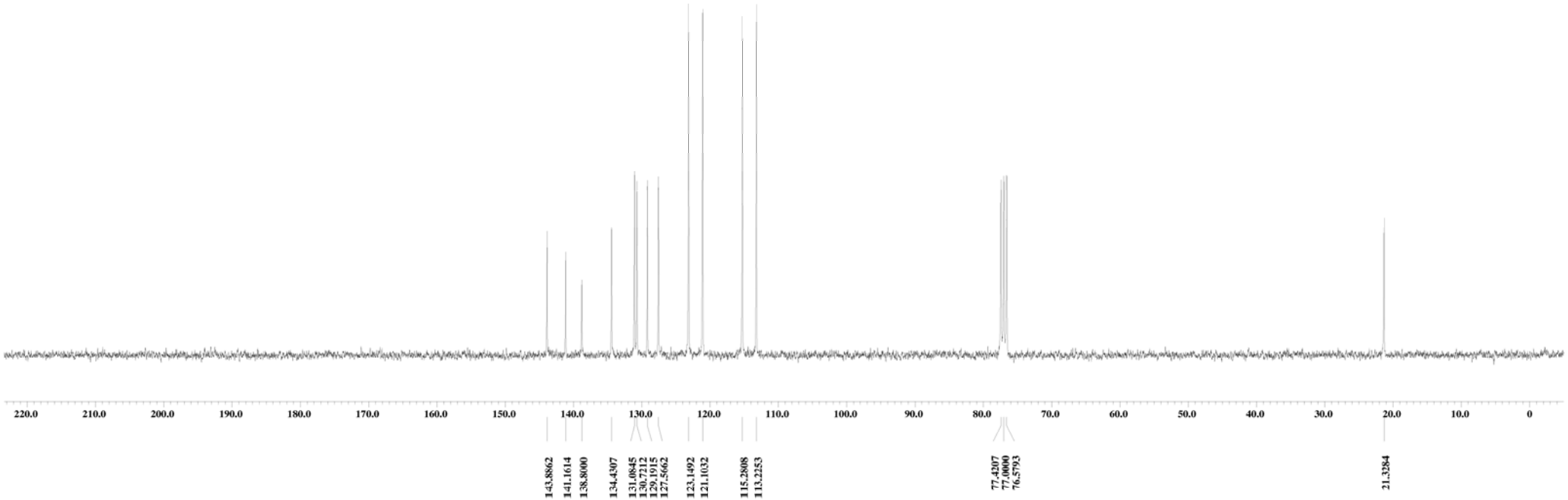
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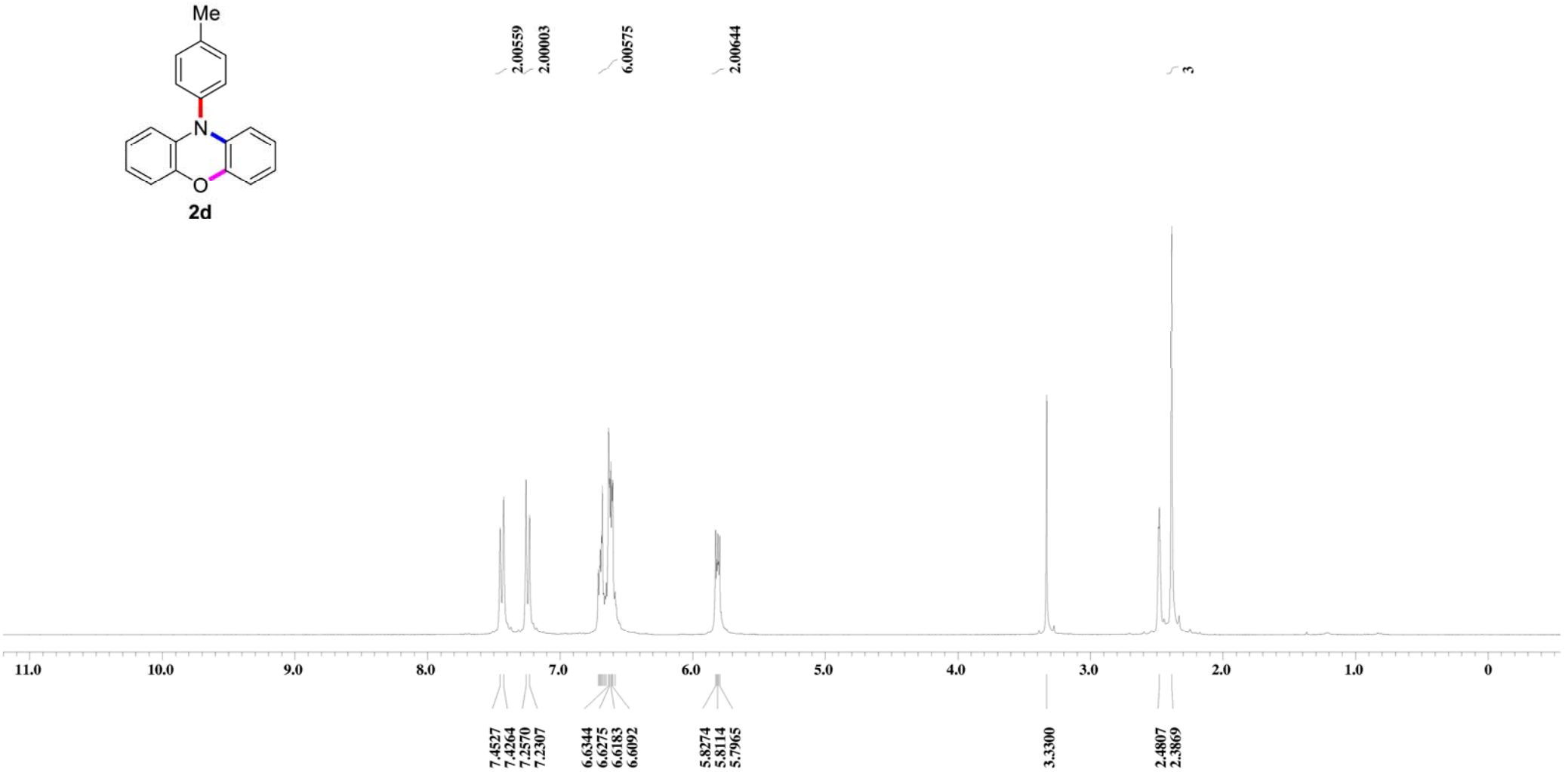
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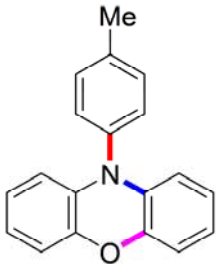
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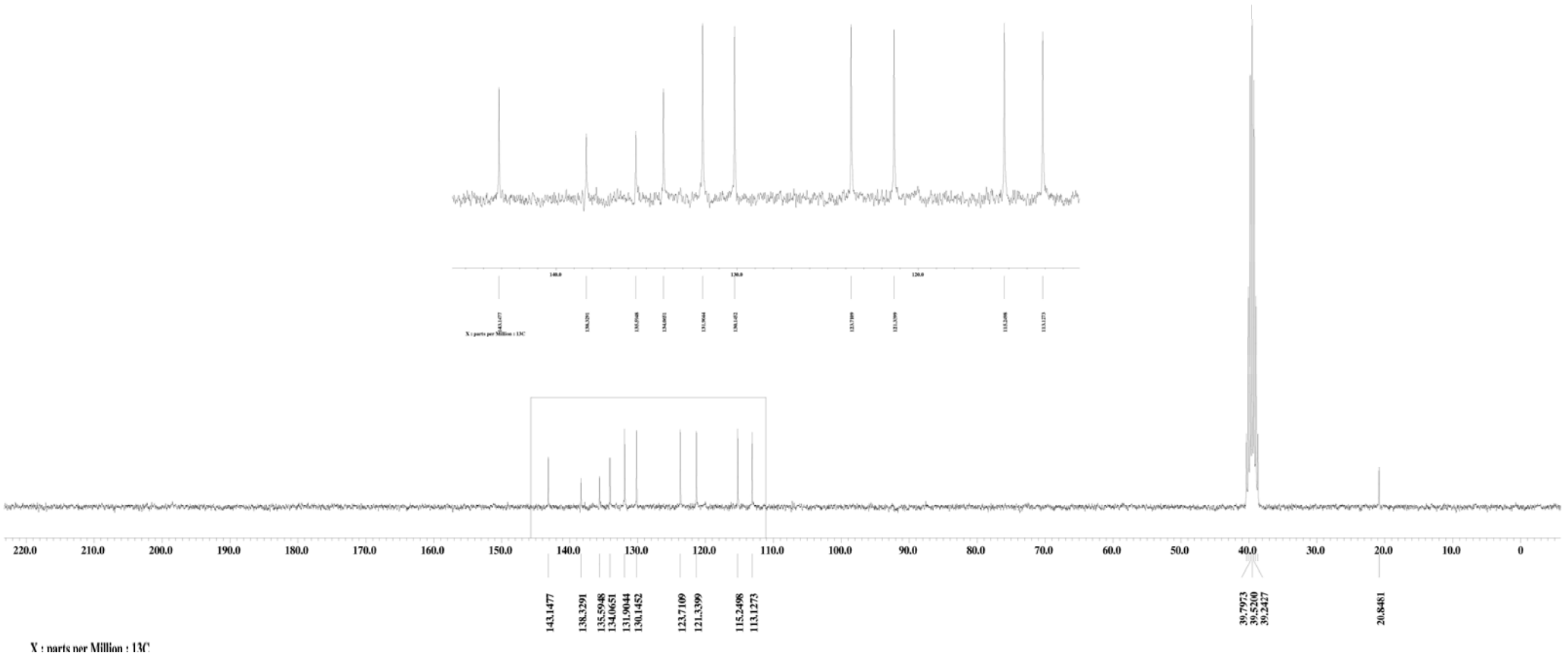
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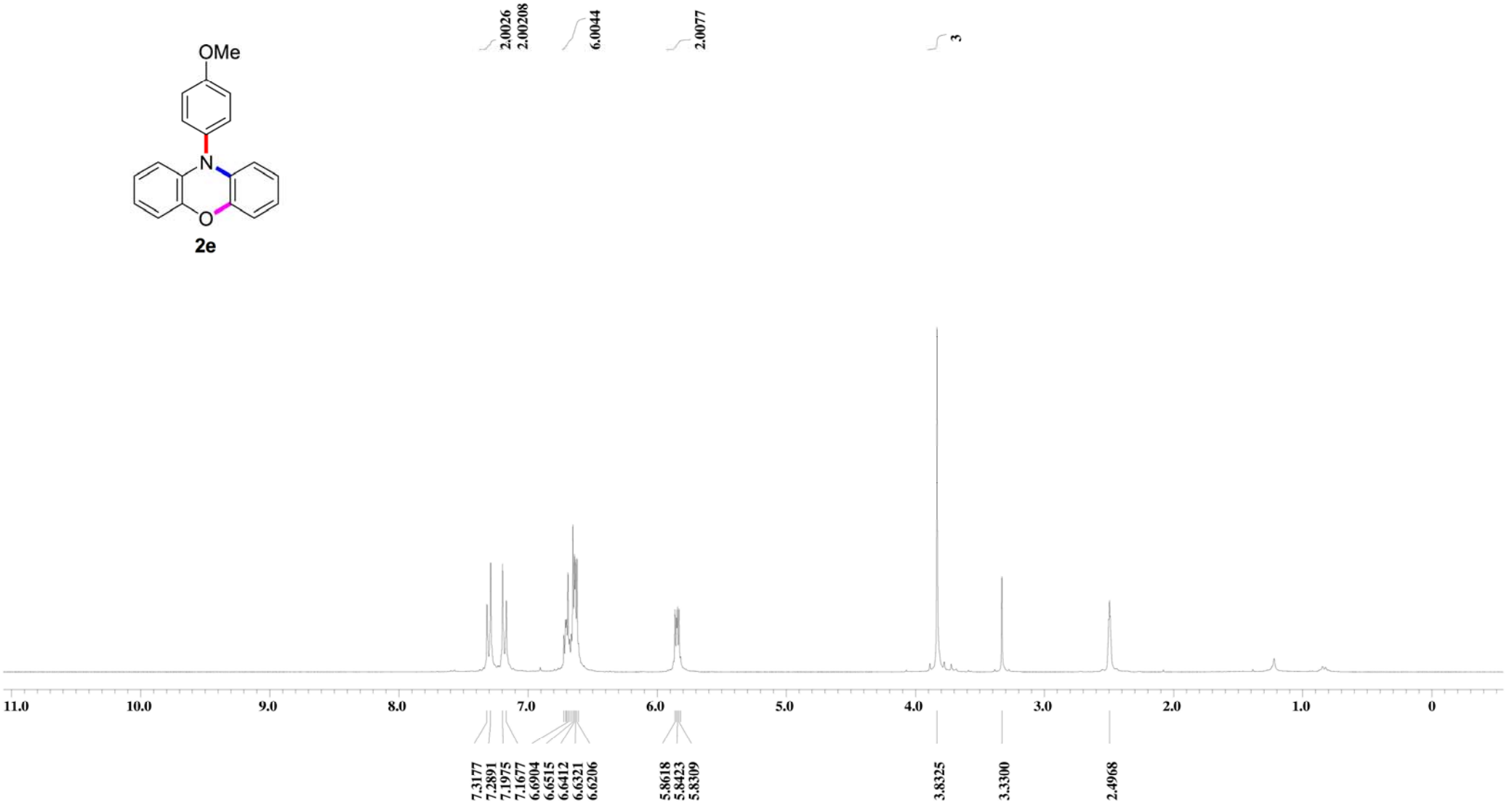
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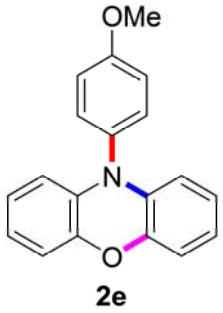
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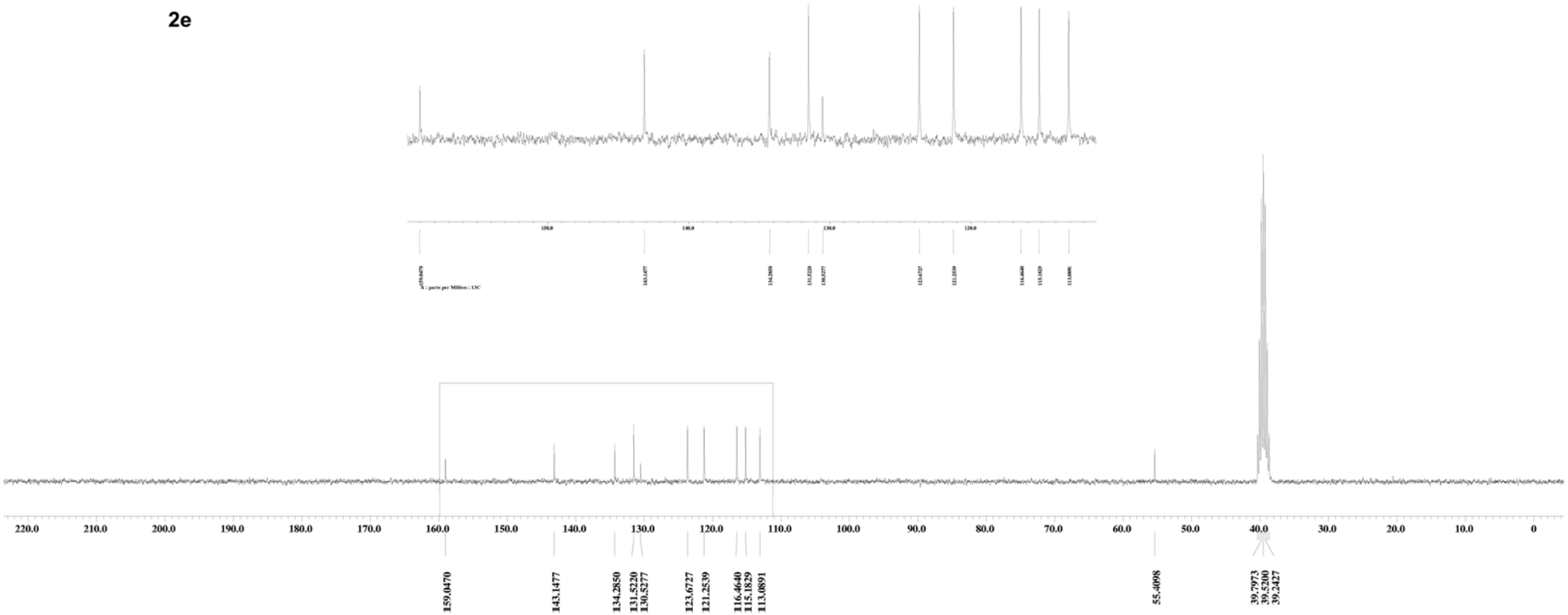
2e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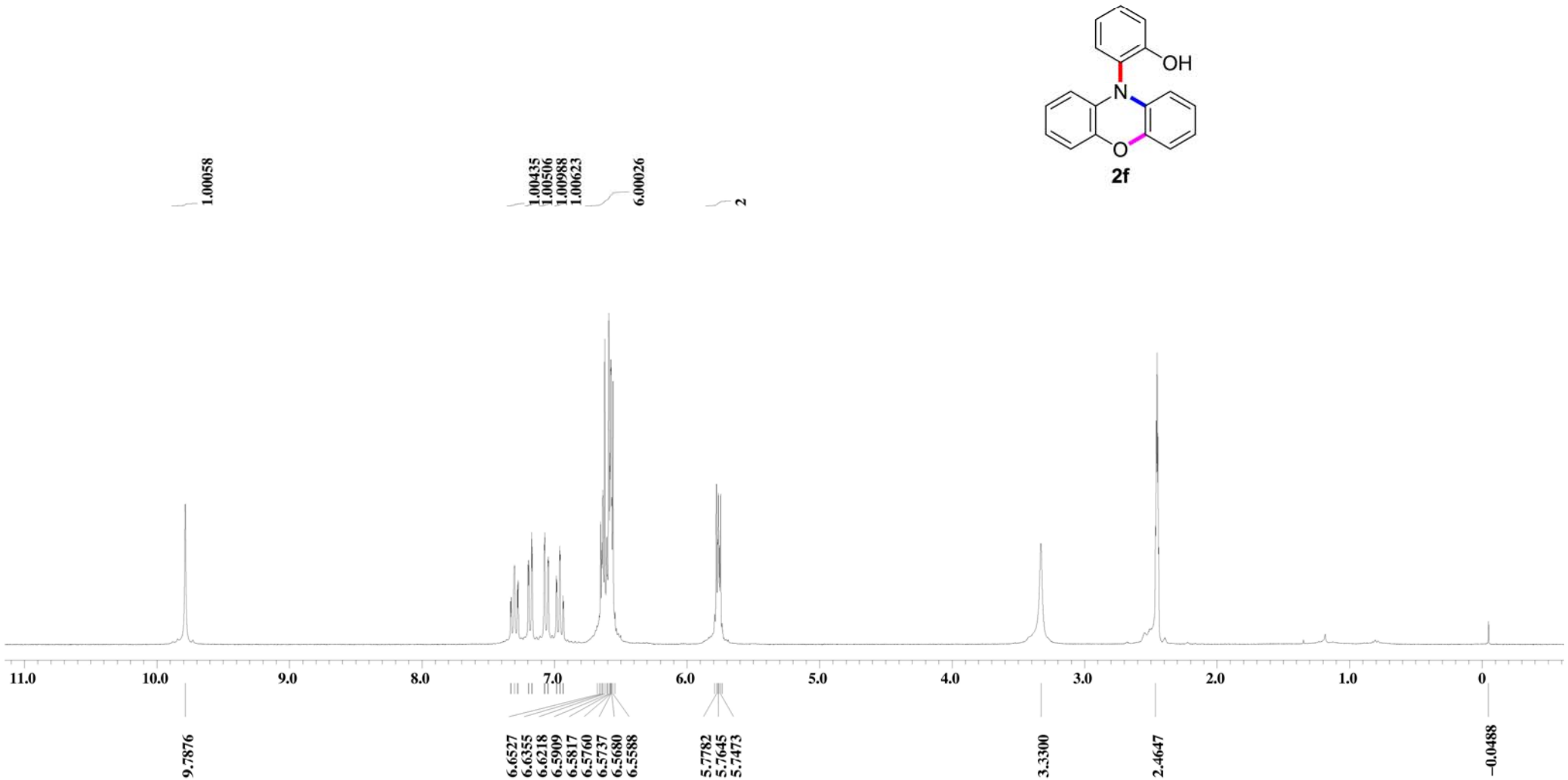
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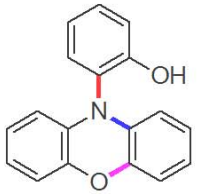
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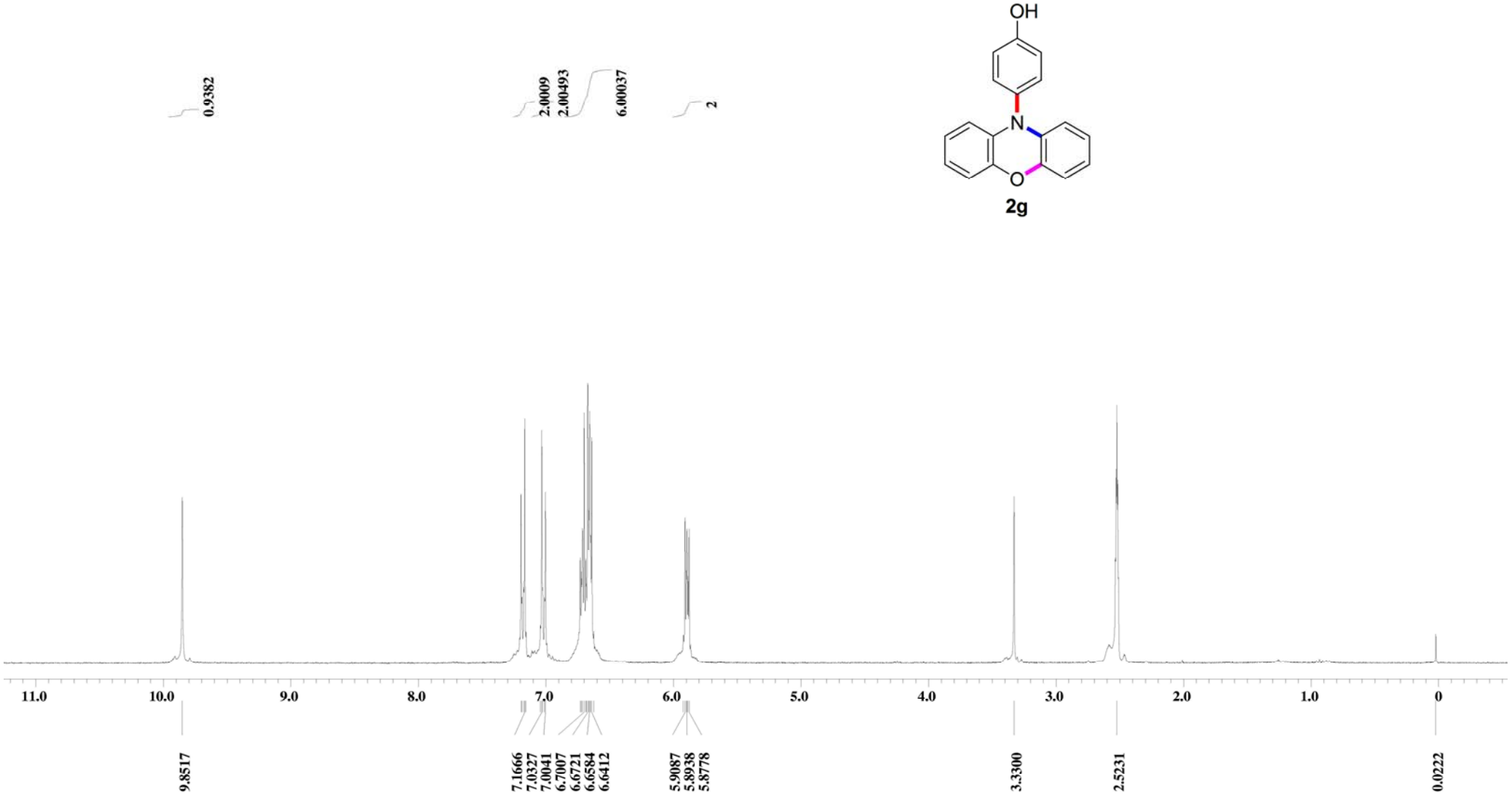
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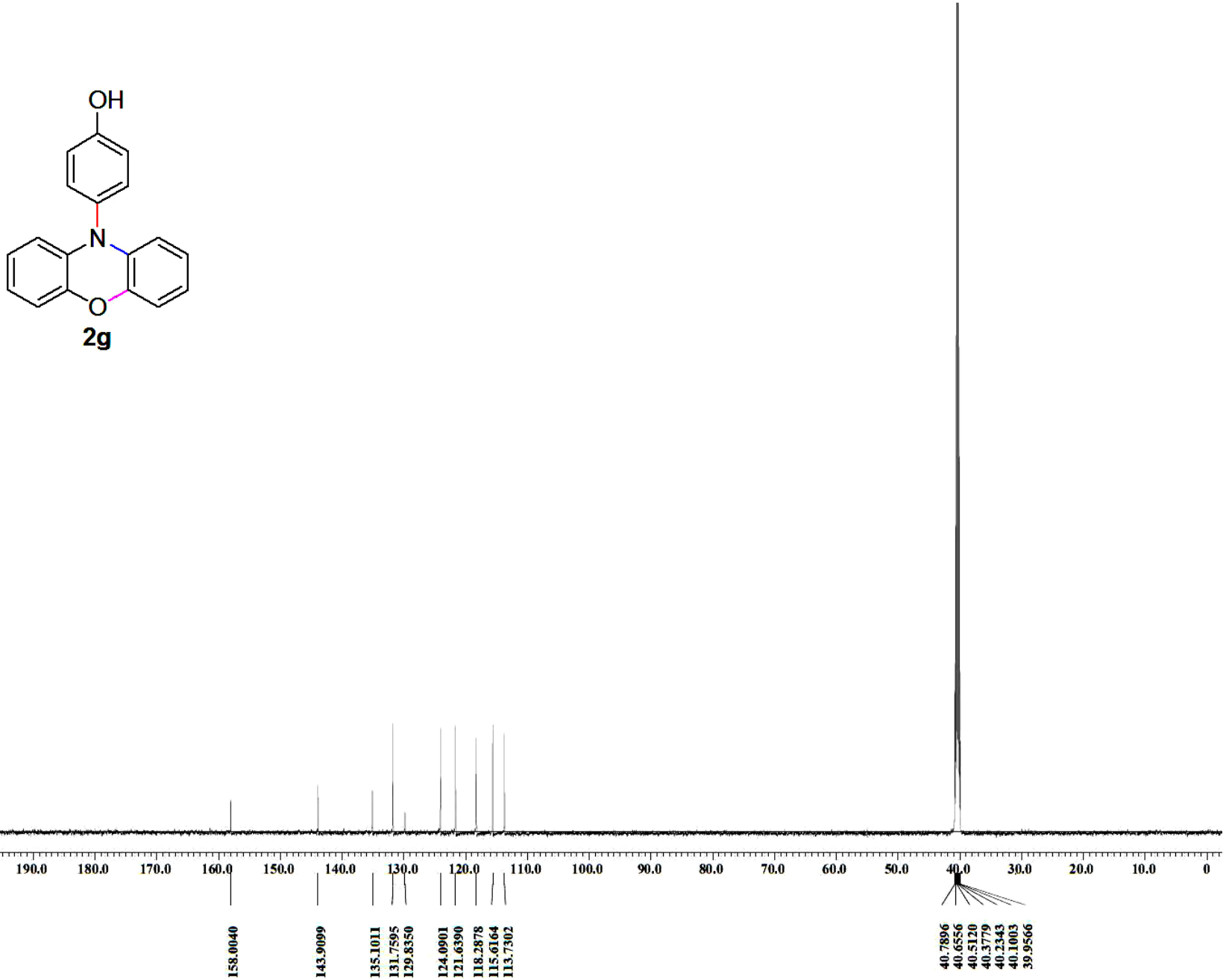
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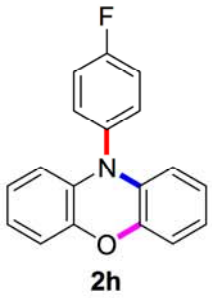
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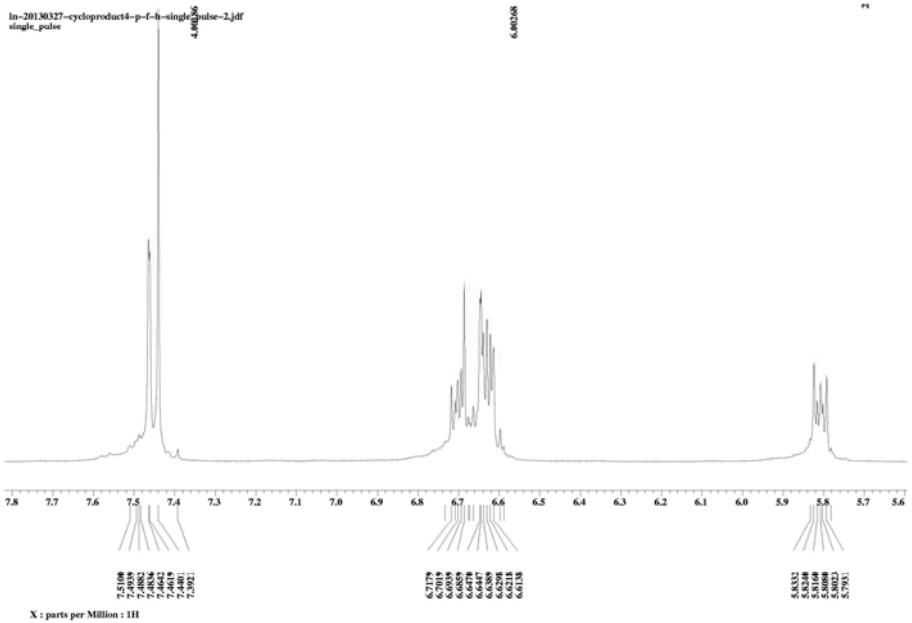
O

2h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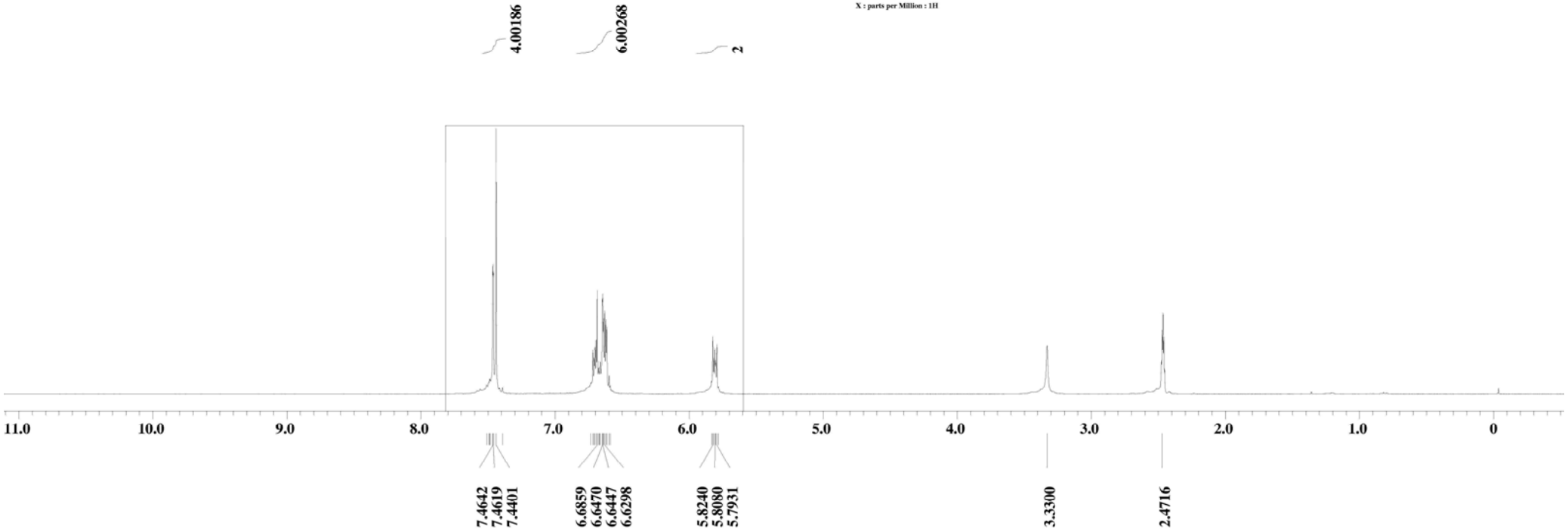
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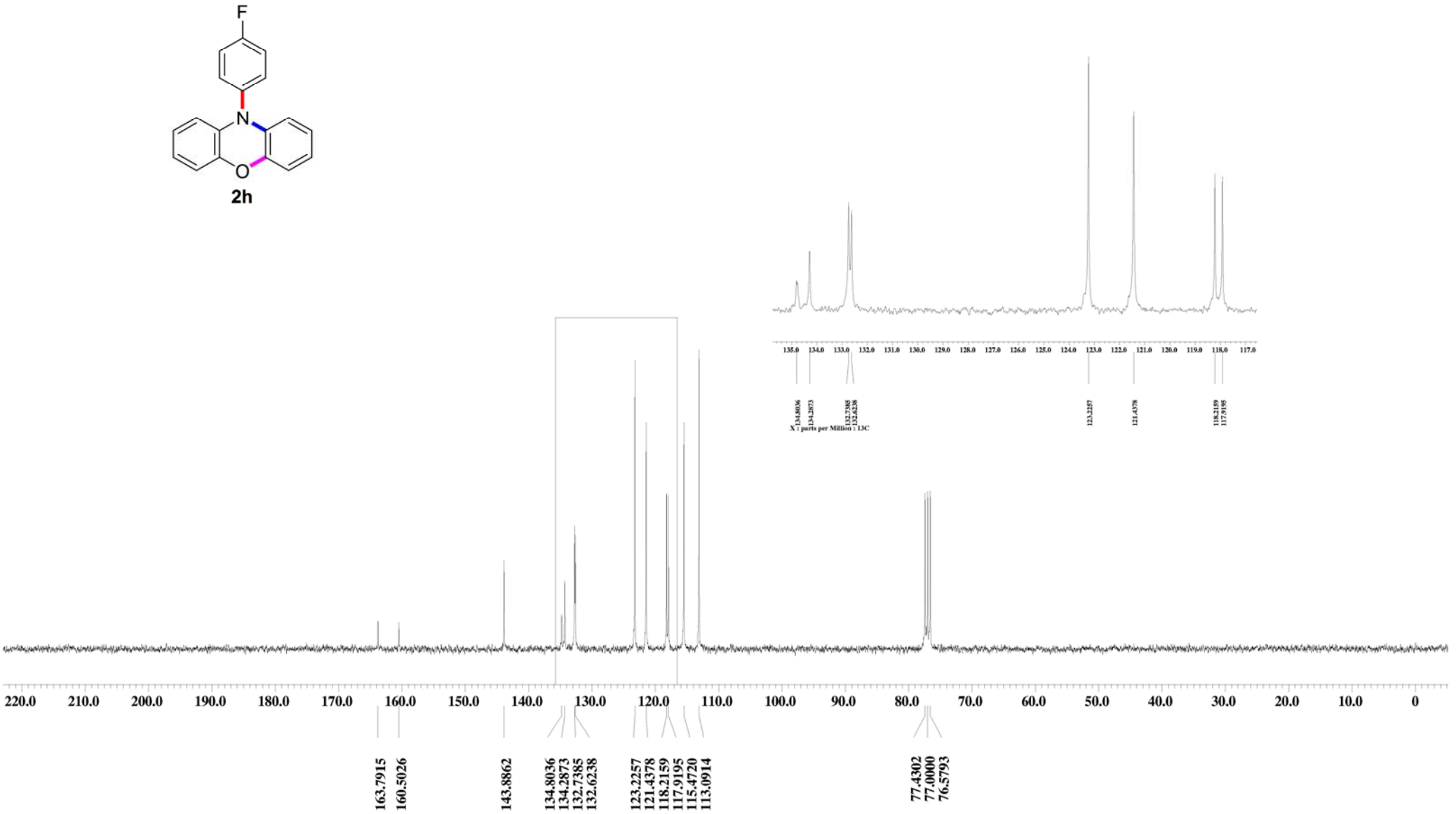
F
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O
2h
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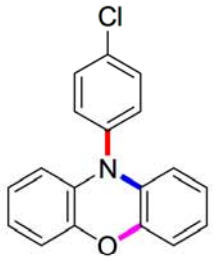
Cl
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O

2i

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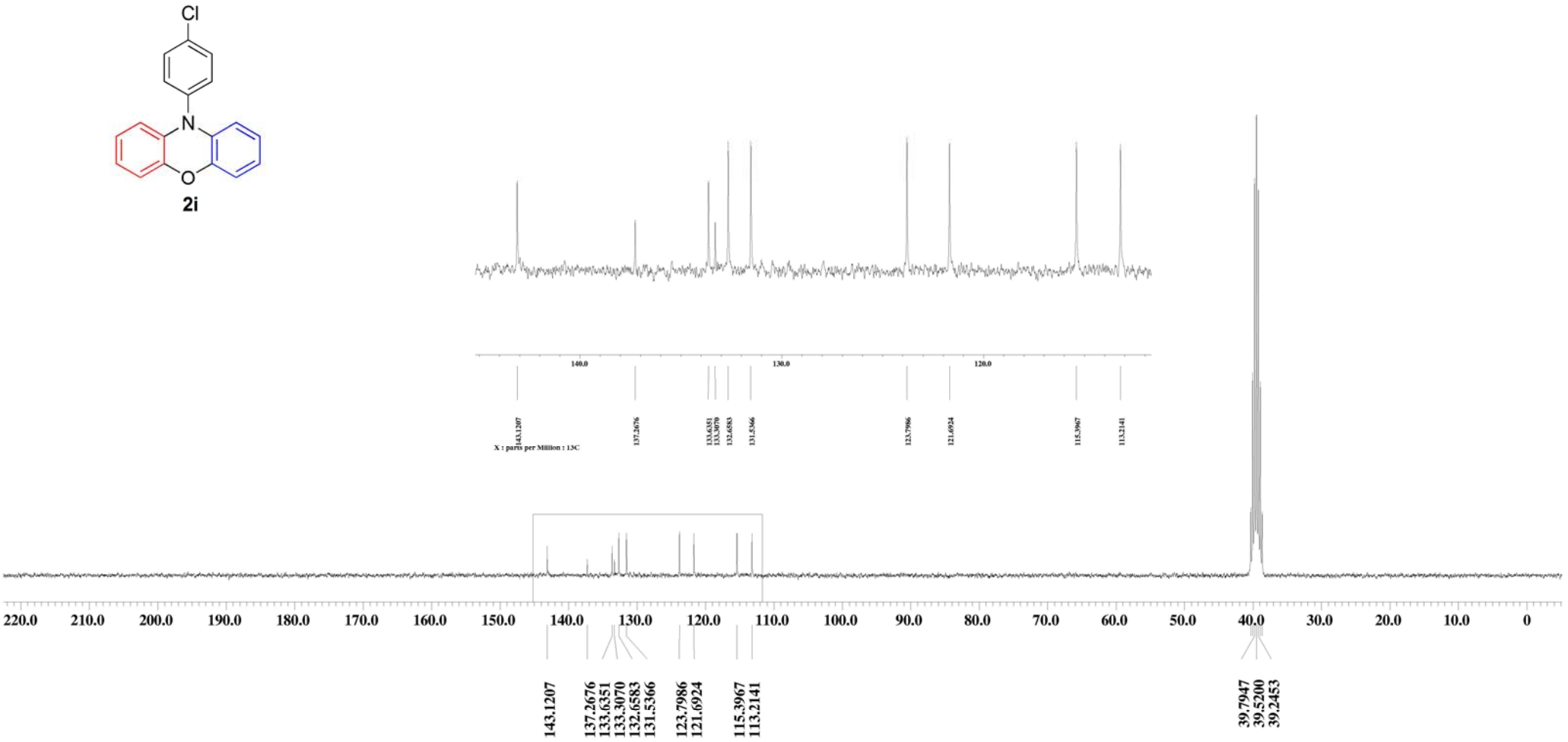
Cl
N
O
2i
140.0
130.0
120.0
143.1207
137.2676
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133.3070
132.6583
131.5366
123.7986
121.6924
115.3967
113.2141
X : parts per Million : 13C
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
143.1207
137.2676
133.6351
133.3070
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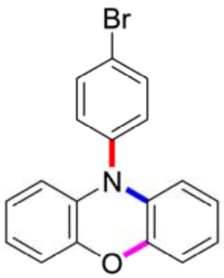
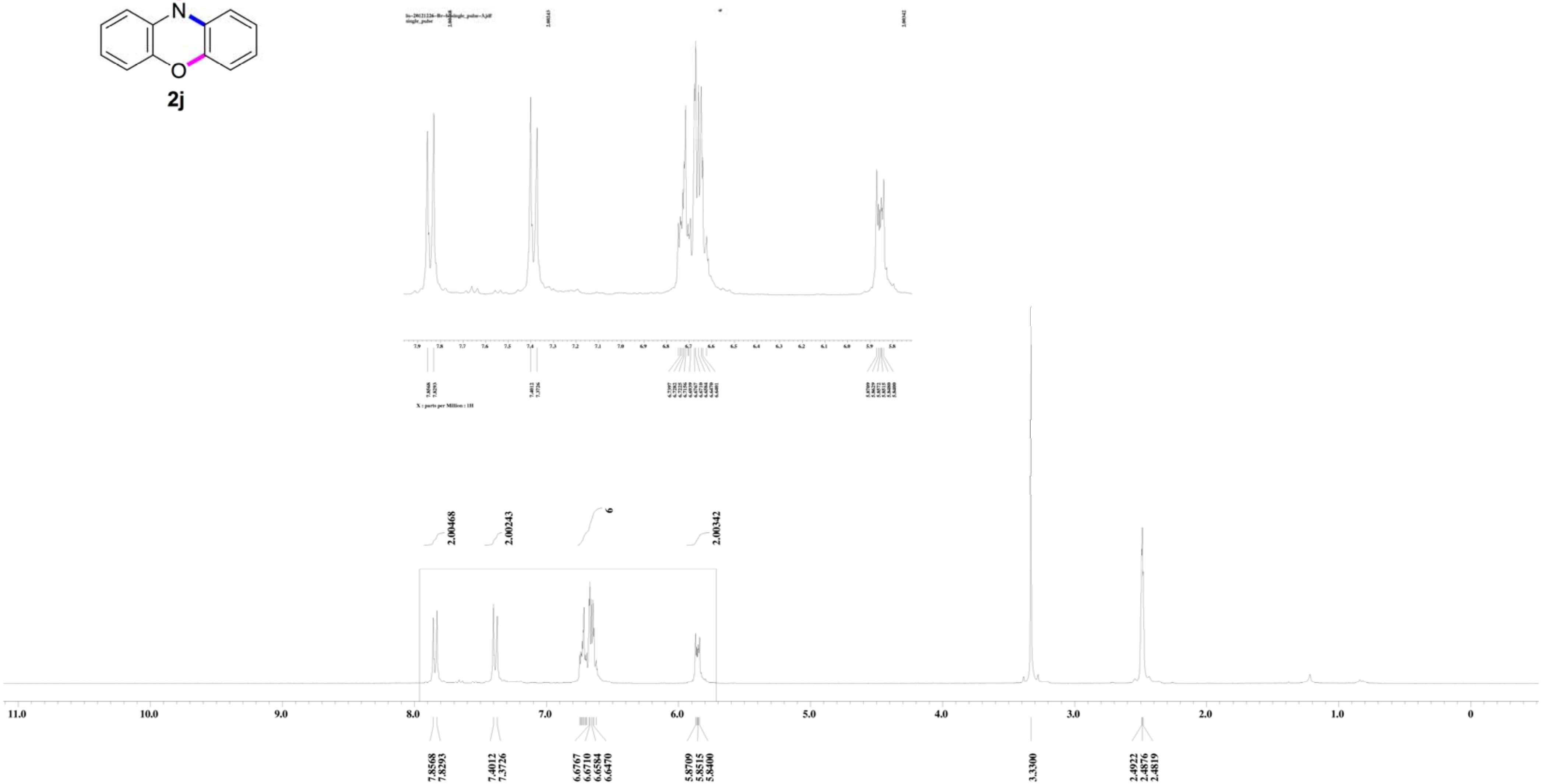
131.5366
123.7986
121.6924
115.3967
113.2141
39.7947
39.5200
39.2453



2j



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6
2.00342
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8.0
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5.0
4.0
3.0
2.0
1.0
0
7.8568
7.8293
7.4012
7.3726
6.6767
6.6710
6.6584
6.6470
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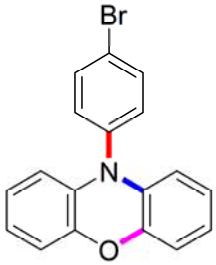
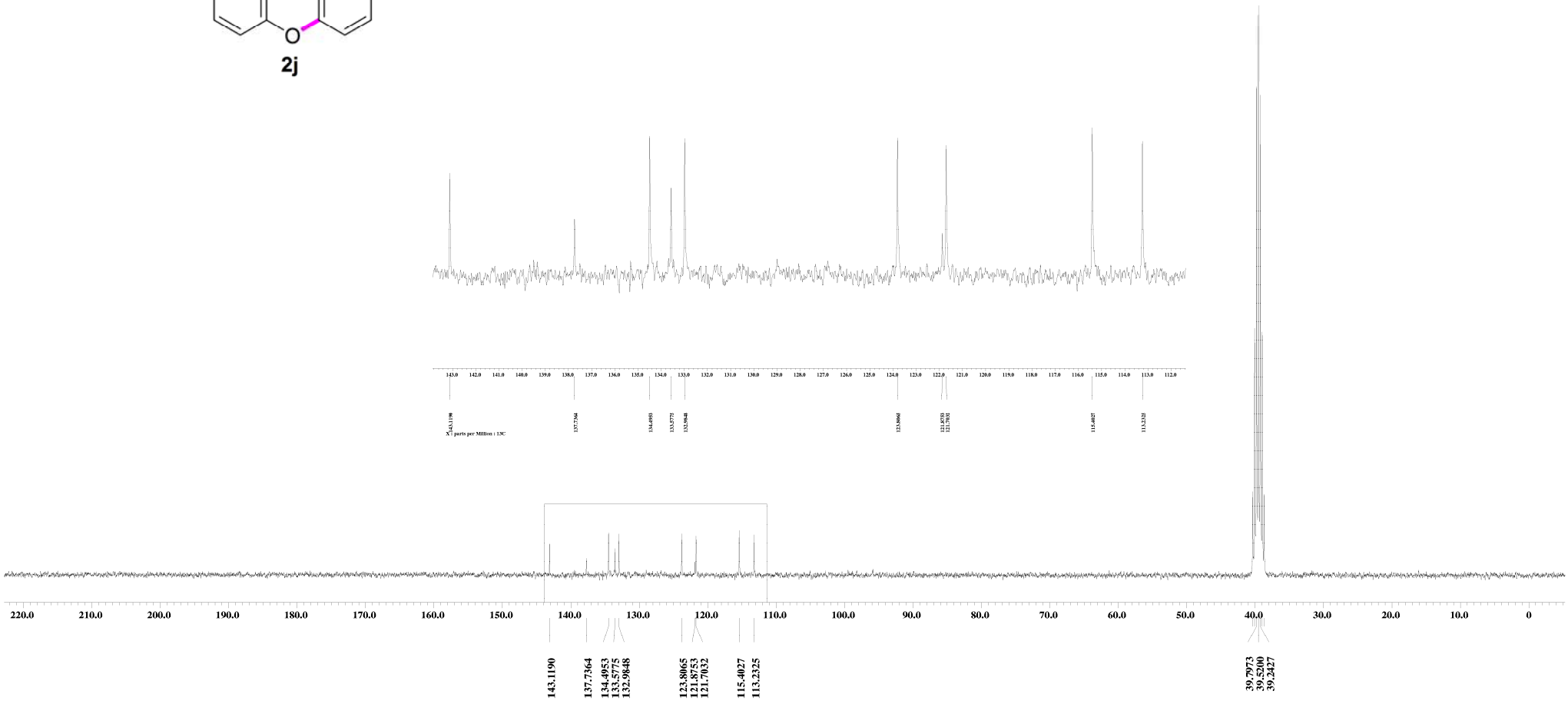
5.8515
5.8400
3.3300
2.4922
2.4876
2.4819
X : parts per Million : 1H


Br
N
O

2j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134.4953
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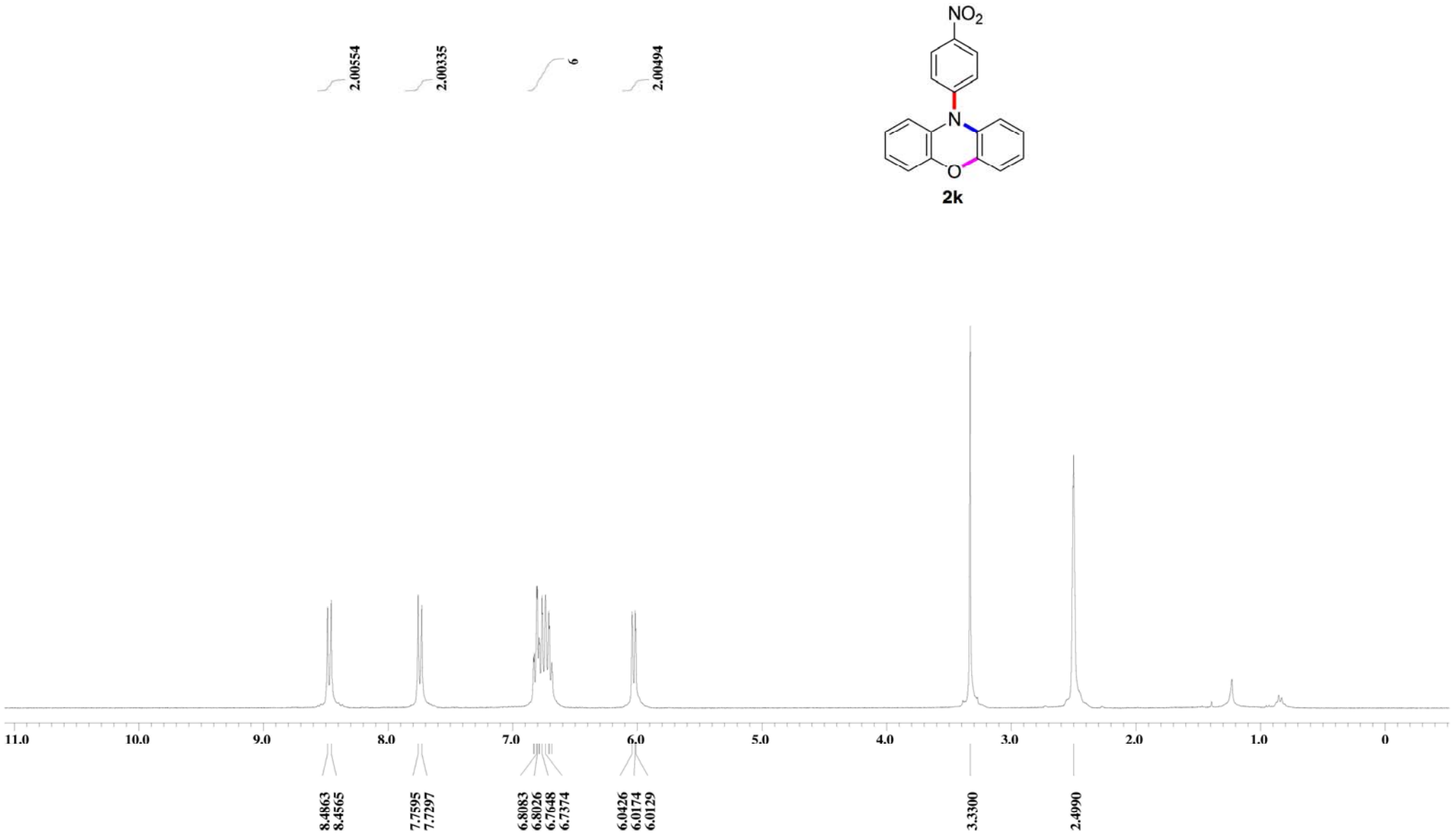
123.8065
121.8753
121.7032
115.4027
113.2325
39.7973
39.5200
39.2427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2.00335
6
2.00494
NO2
N
O
2k
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.4863
8.4565
7.7595
7.7297
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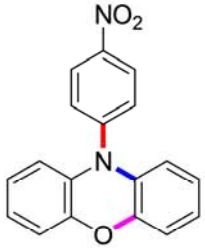
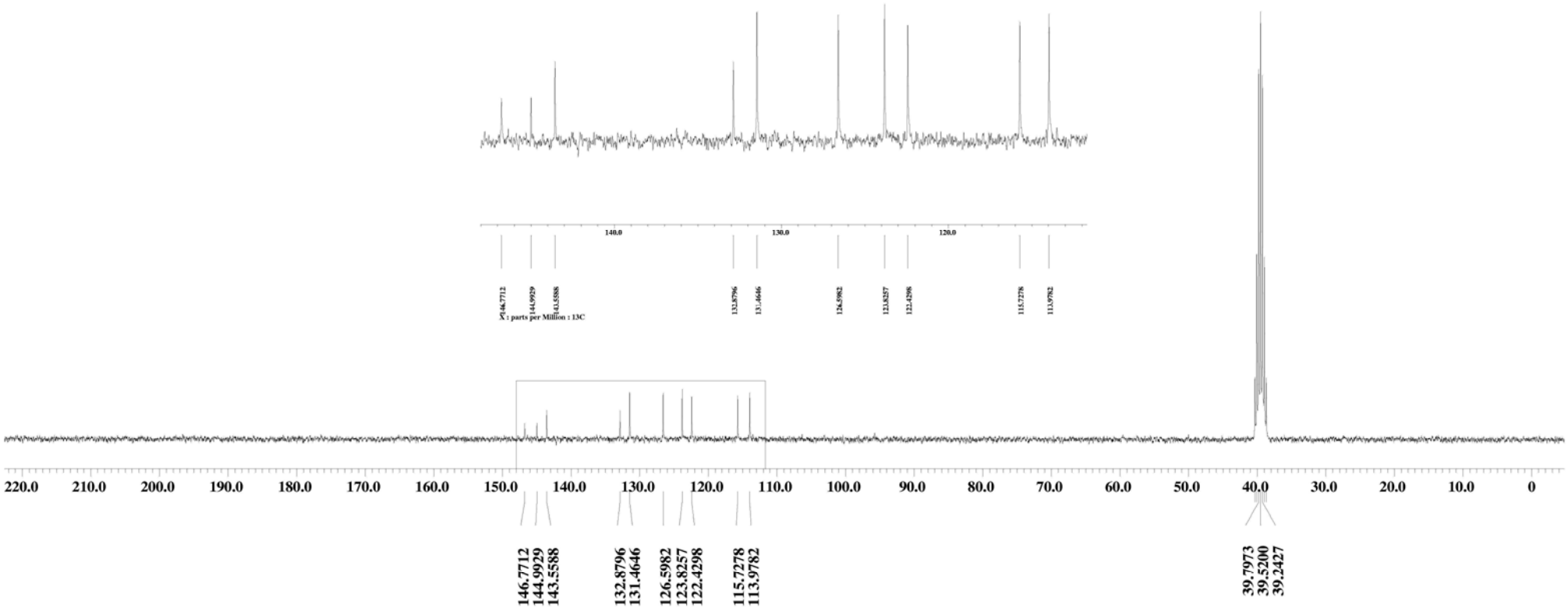
6.8026
6.7648
6.7374
6.0426
6.0174
6.0129
3.3300
2.4990


NO2
N
O

2k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123.8257
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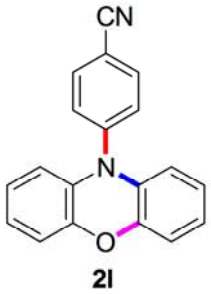
115.7278
113.9782
39.7973
39.5200
39.2427


CN
N
O

2l


2
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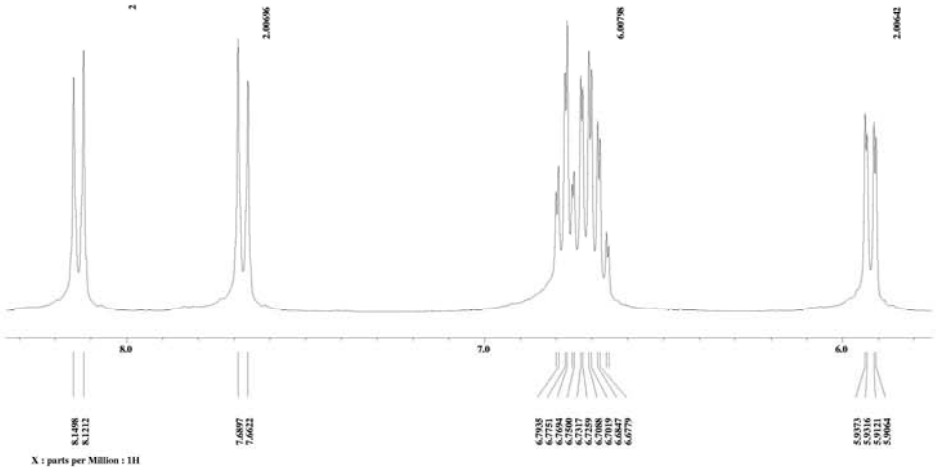
6.00798
2.00642


2
2.00696
6.00798
2.00642
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7.0
6.0
8.1498
8.1212
7.6897
7.6622
6.7751
6.7694
6.7588
6.7317
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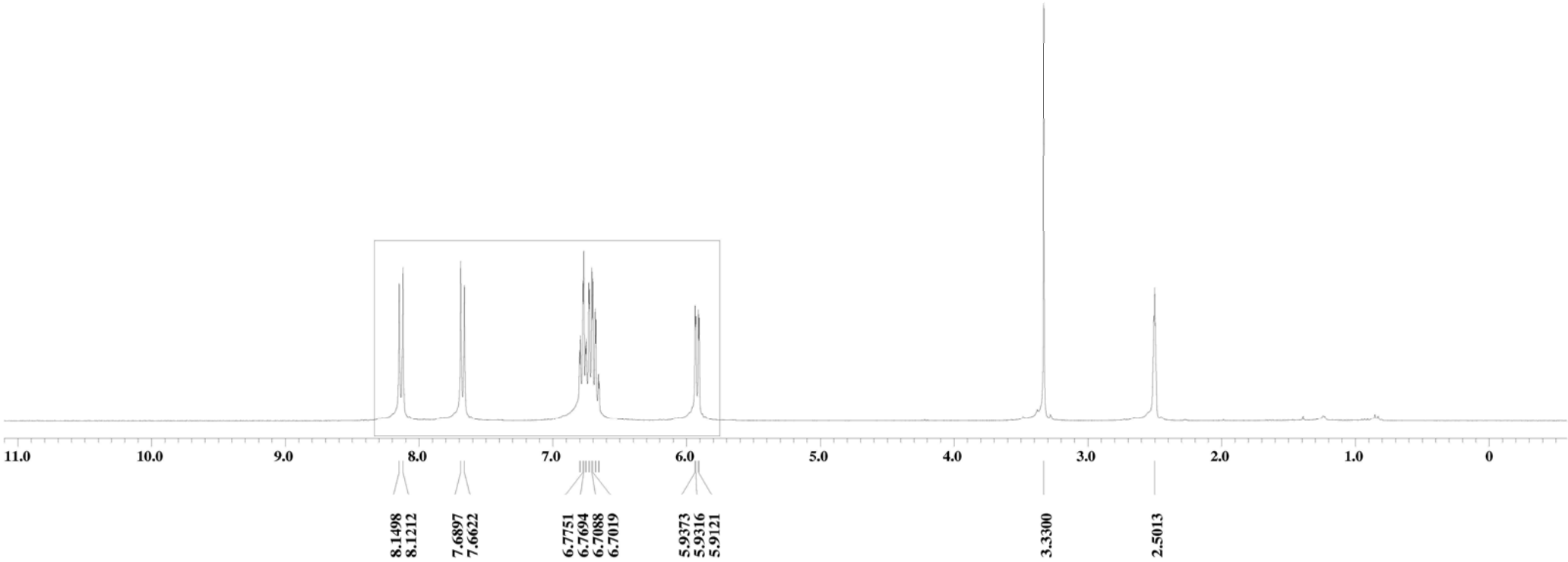
6.6647
6.6779
5.9373
5.9316
5.9121
5.9064
X : parts per Million : 1H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10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.1498
8.1212
7.6897
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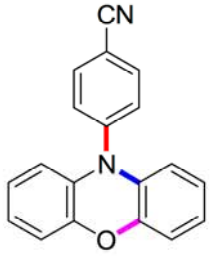
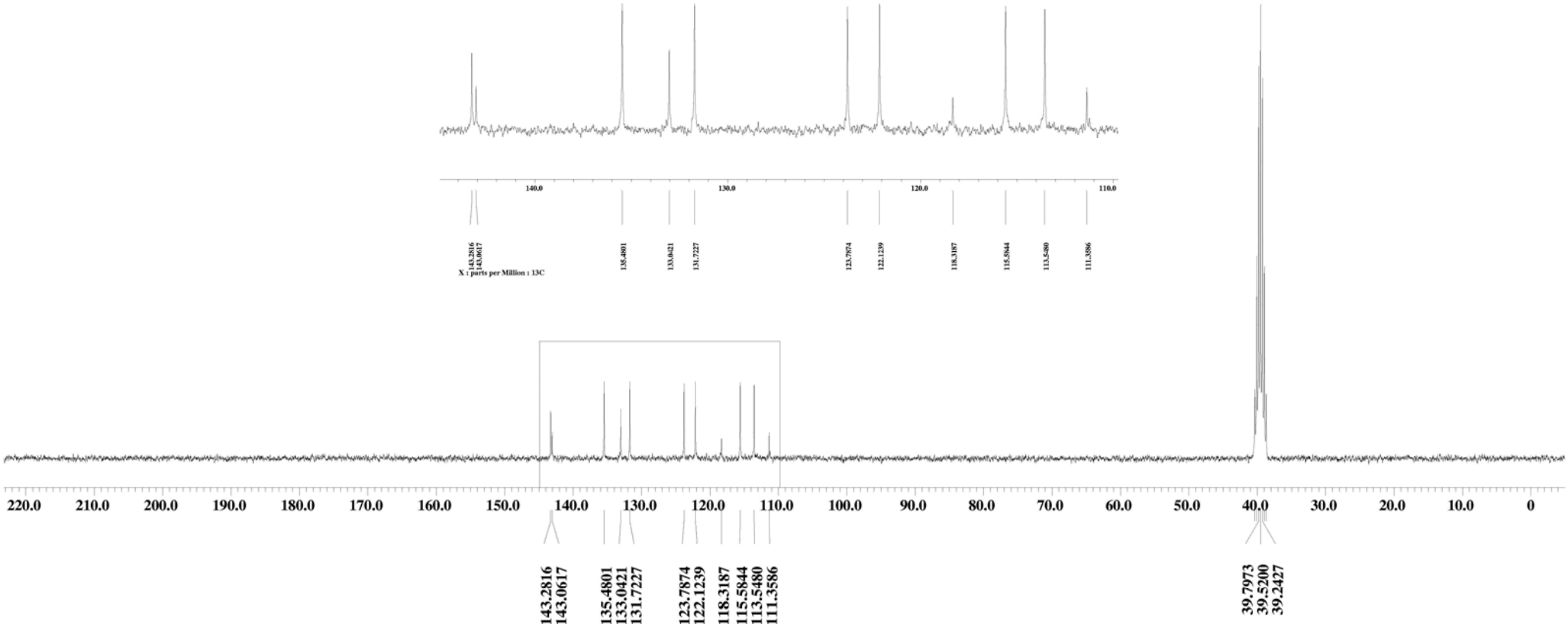
6.7694
6.7088
6.7019
5.9373
5.9316
5.9121
3.3300
2.5013


CN
N
O

2l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120.0
110.0
143.2816
143.0617
135.4801
133.0421
131.7227
123.7874
122.1239
118.3187
115.5844
113.5480
111.3586
X : parts per Million : 13C
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
143.2816
143.0617
135.4801
133.0421
131.7227
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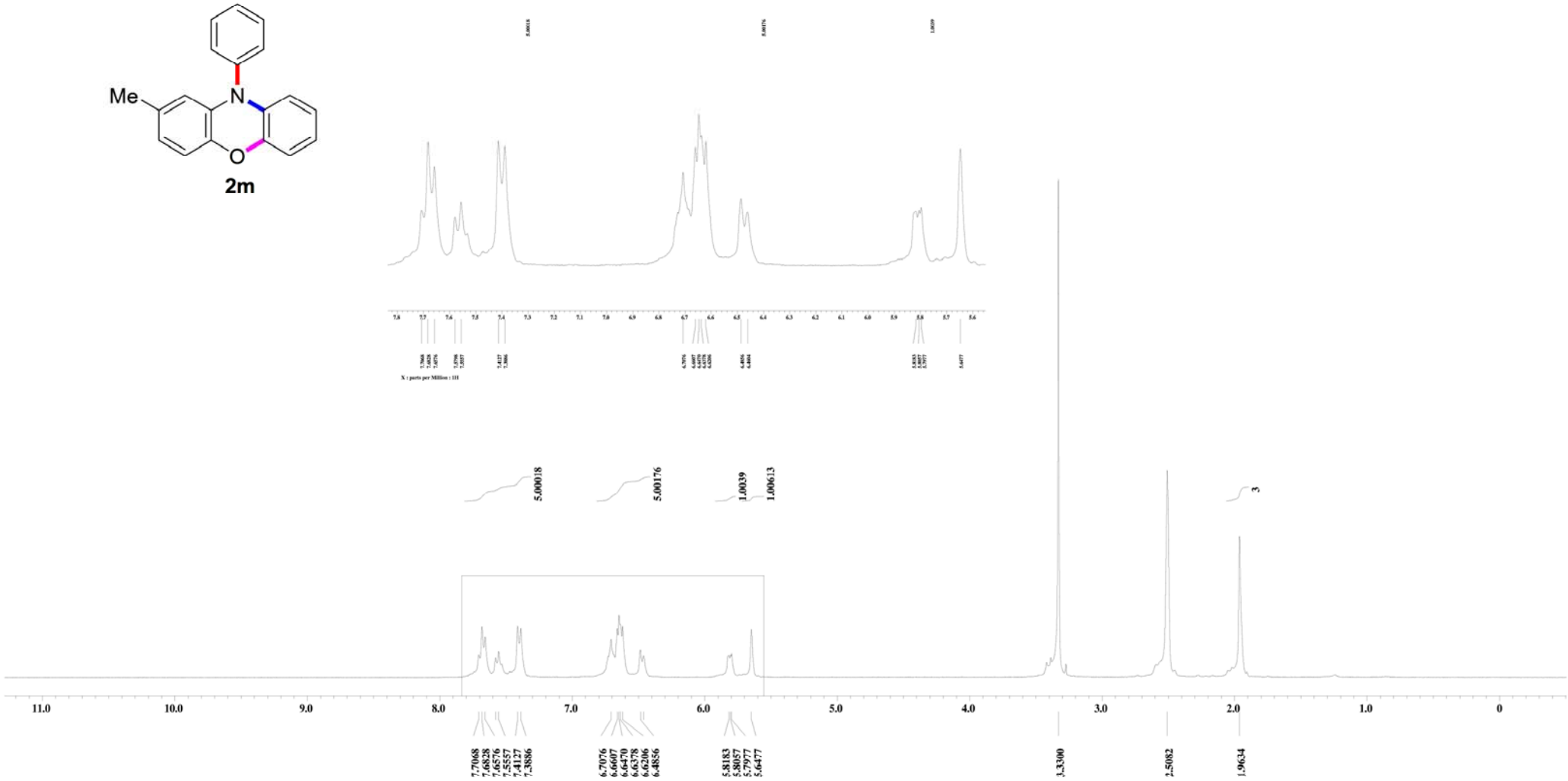
122.1239
118.3187
115.5844
113.5480
111.3586
39.7973
39.5200
39.2427


Me
N
O
2m
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1.00039
1.00613
3
11.0
10.0
9.0
8.0
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7.55574
7.41274
7.38864
6.70764
6.66074
6.64704
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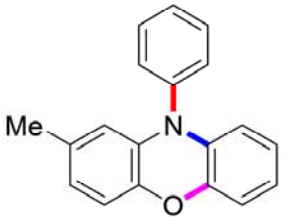
Me
N
O

2m

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
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138.9912
134.3734
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132.6525
130.9794
130.8168
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122.9675
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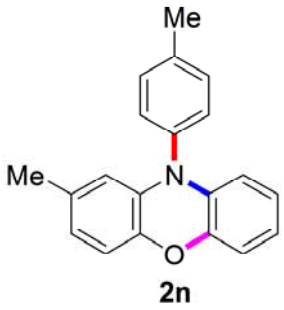
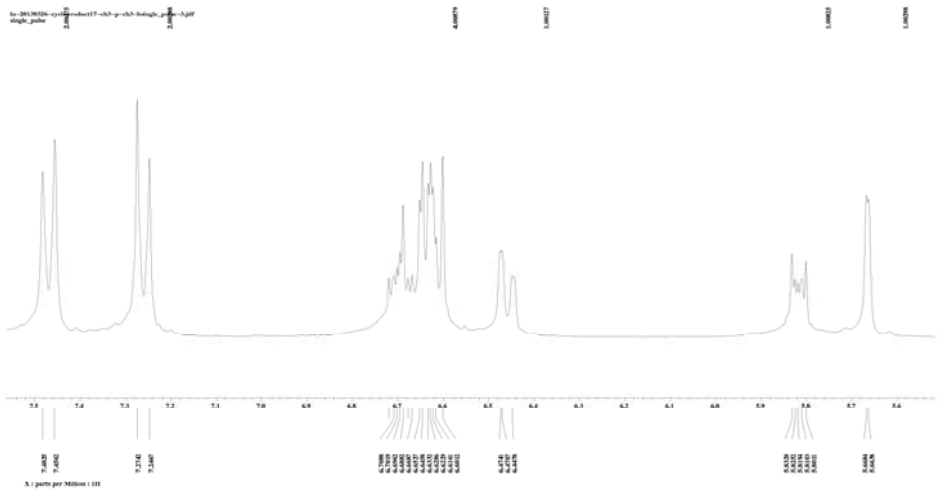
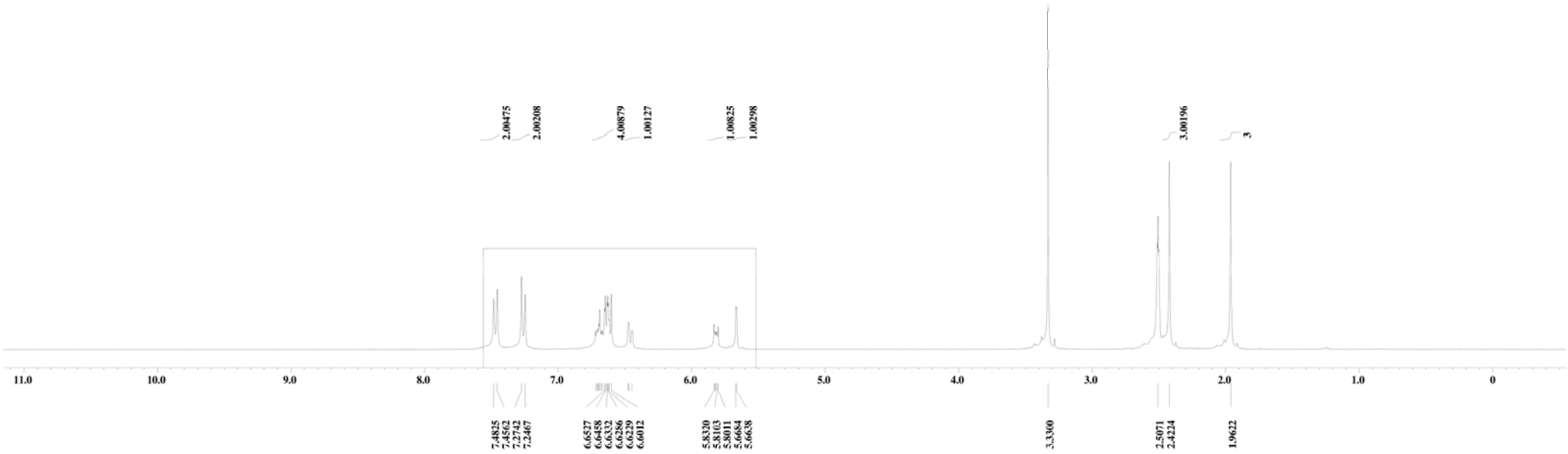
77.0000
76.5793
20.7930


Me
Me
N
O

2n

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3.00196
3
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9.0
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3.0
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1.0
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7.4562
7.2742
7.2467
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6.6458
6.6332
6.6286
6.6229
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5.6684
5.6638
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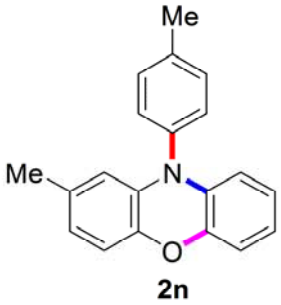
2.4224
1.9622


Me
Me
N
O

2n

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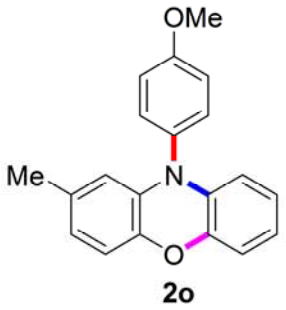
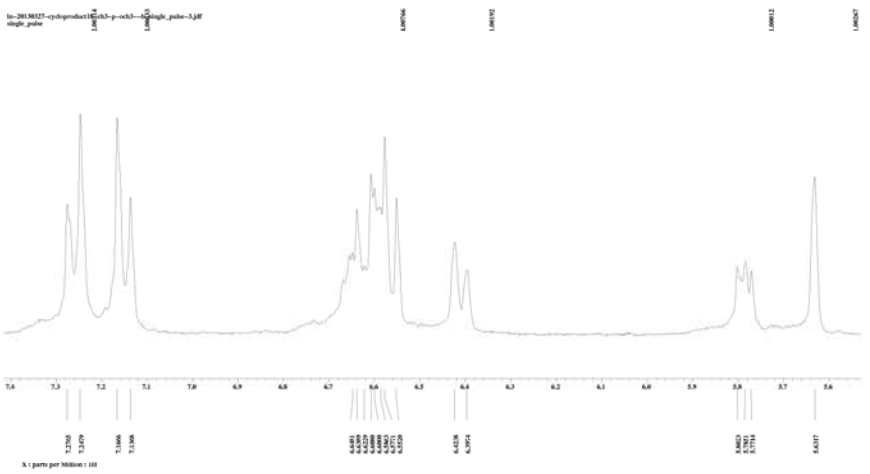
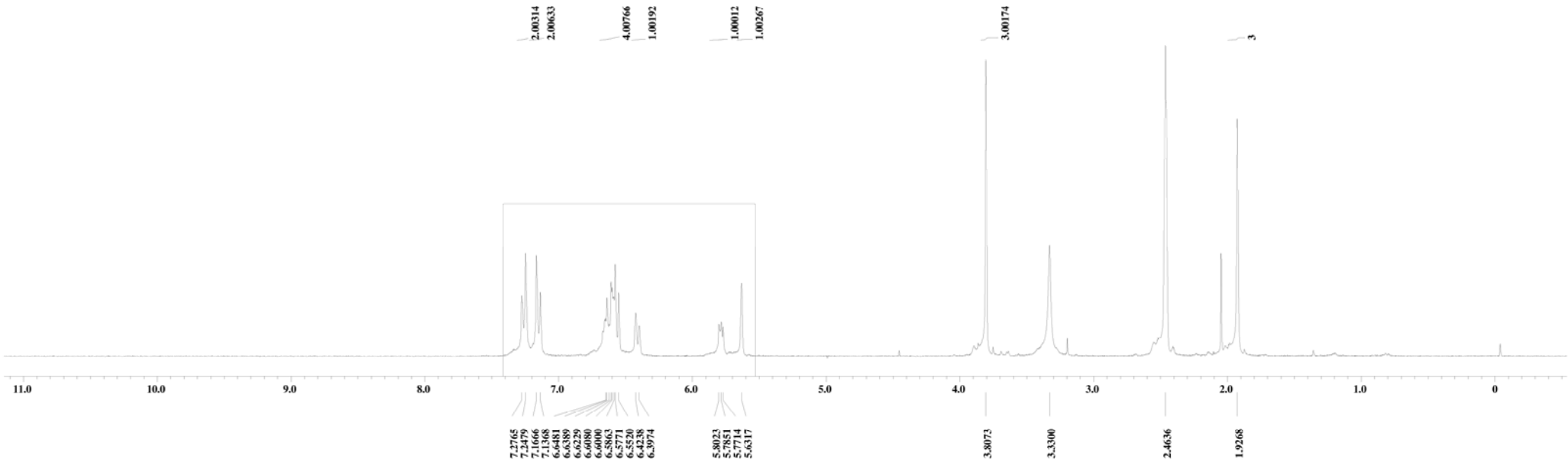
21.2519
20.7930


OMe
Me
N
O

2o

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6.0
5.0
4.0
3.0
2.0
1.0
0
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7.1666
7.1368
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6.6000
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6.5771
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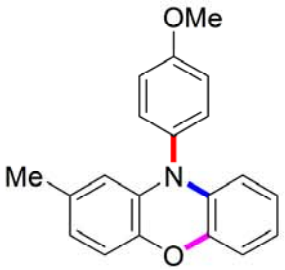
1.9268


OMe
Me
N
O

2o

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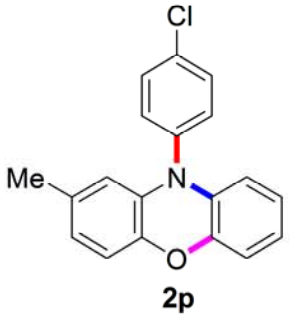
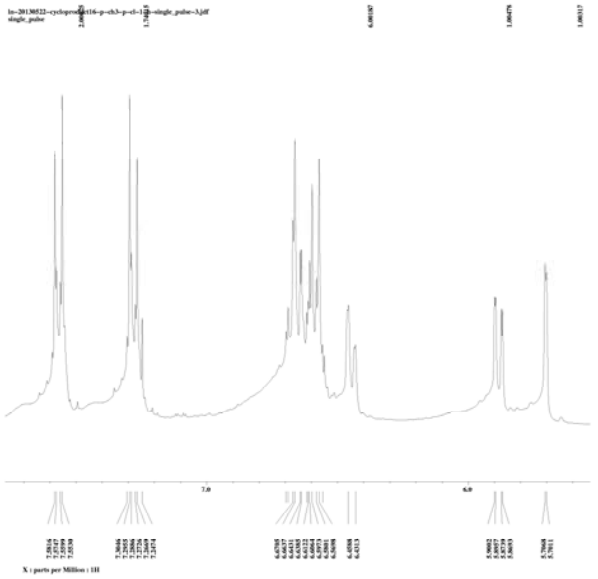
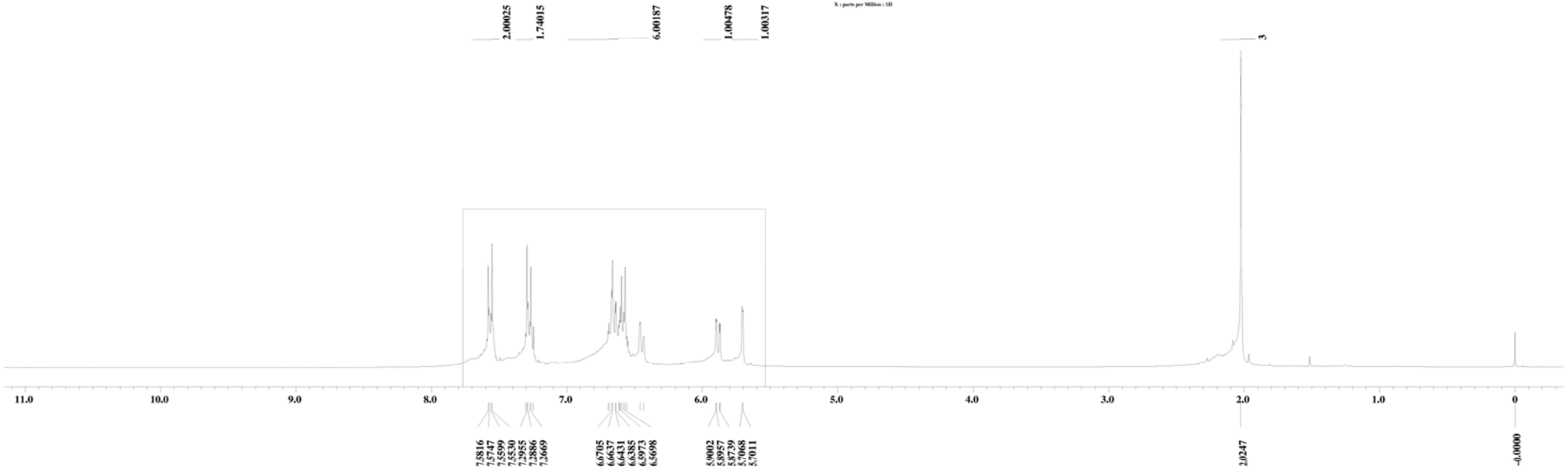
20.8217


Cl
Me
N
O

2p

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6.0
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4.0
3.0
2.0
1.0
0
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7.5530
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7.2886
7.2669
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6.6637
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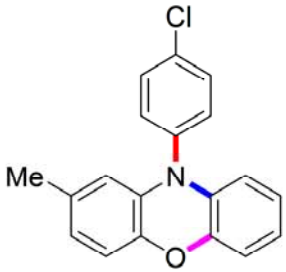
Cl
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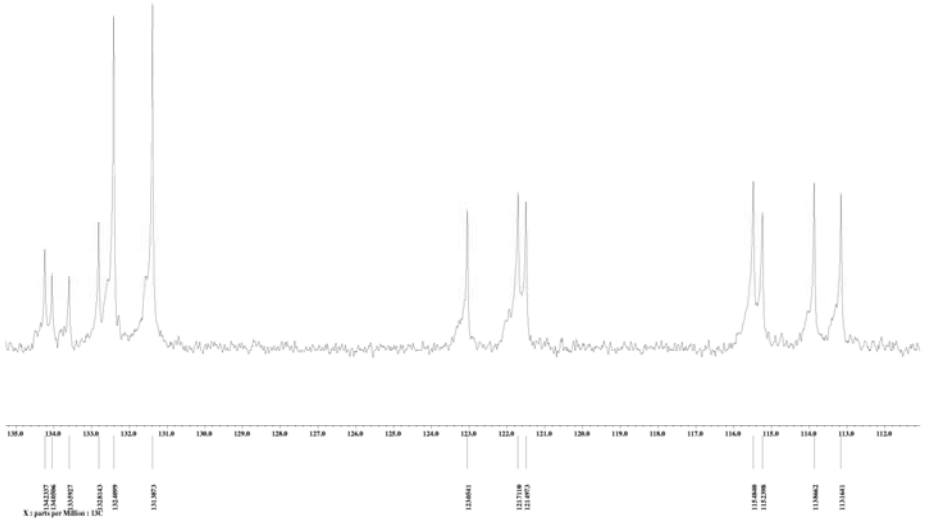
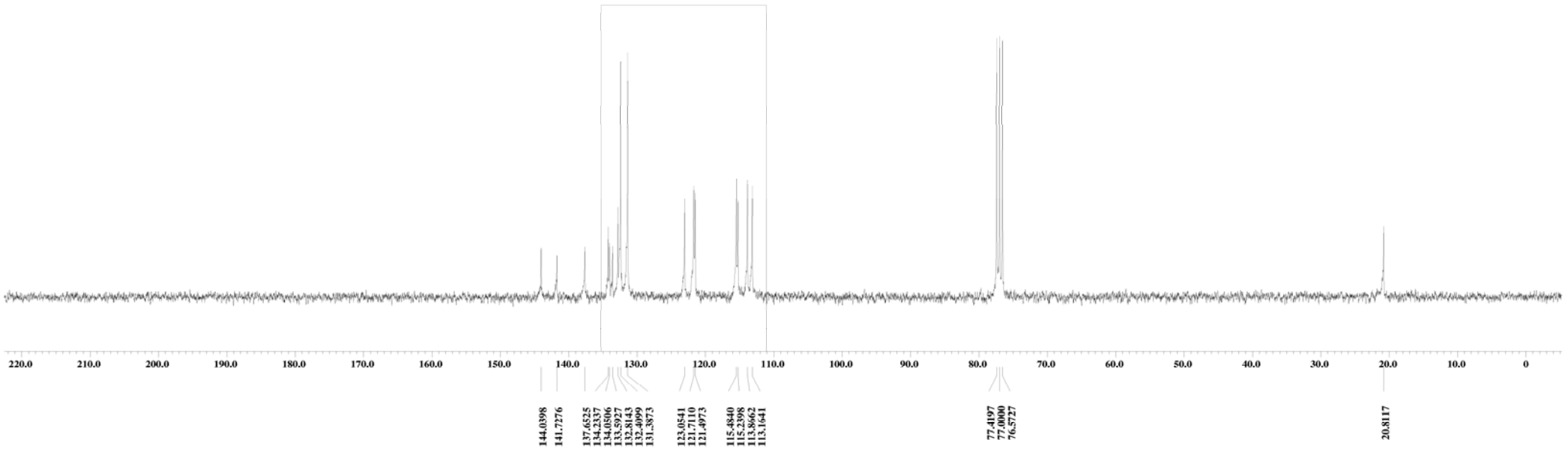
N
O

2p

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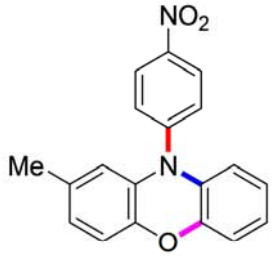
NO2
Me
N
O

2q

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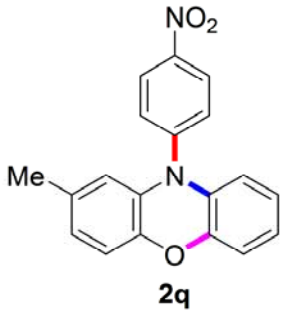
NO2
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N
O

2q

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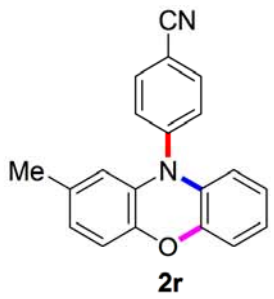
CN
Me
N
O

2r

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3.0
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6.7053
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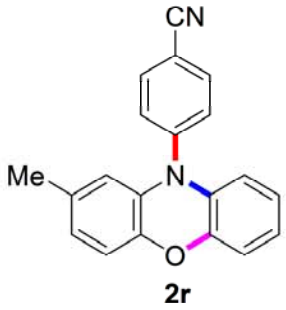
CN
Me
N
O

2r

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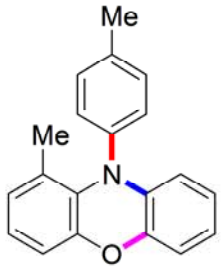
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Me
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O

2s

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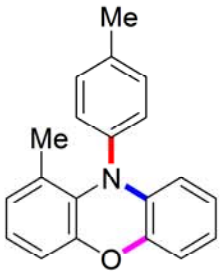
Me
Me
N
O

2s

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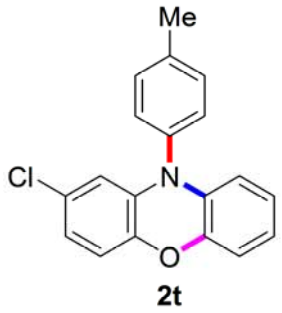
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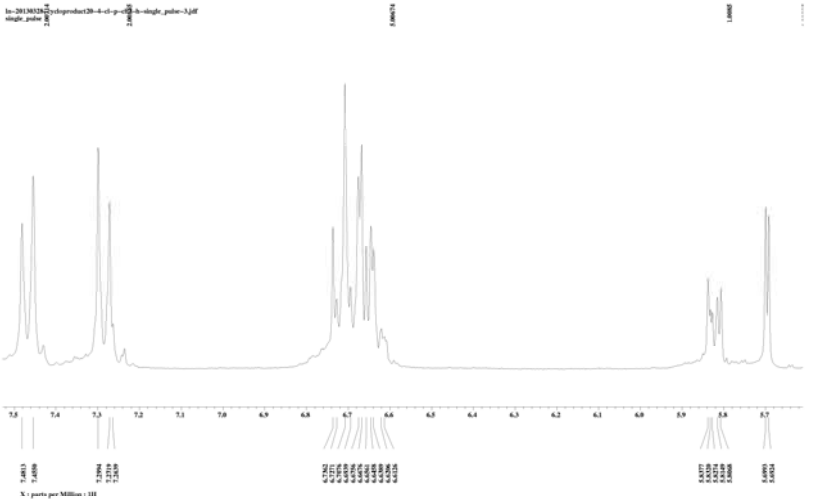
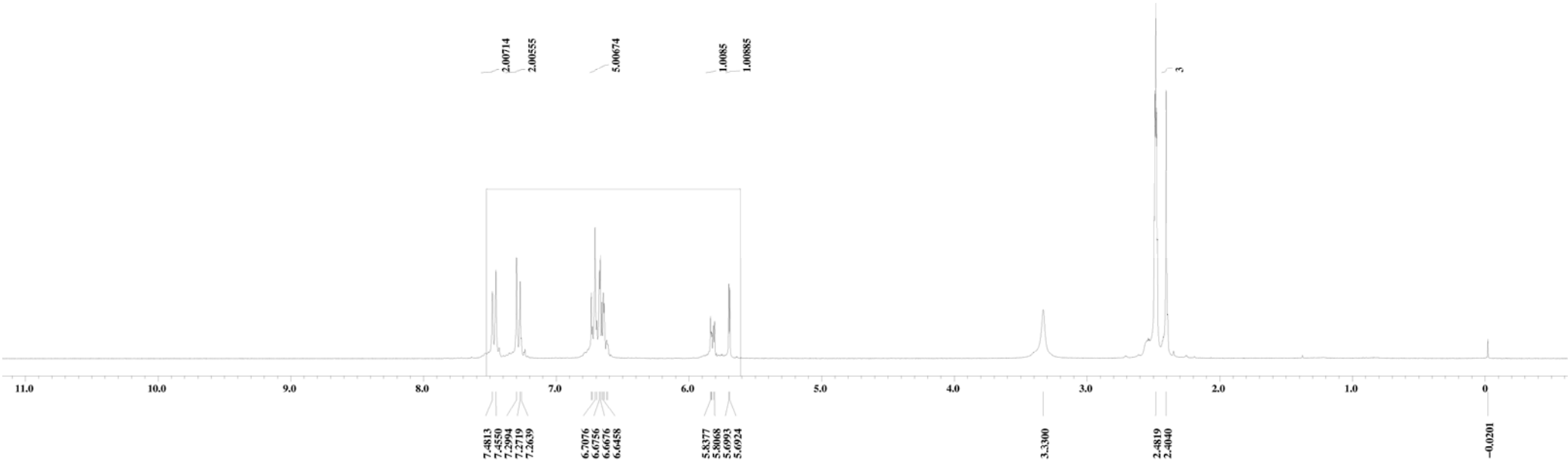
O

2t

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4.0
3.0
2.0
1.0
0
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7.2639
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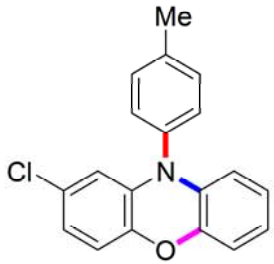
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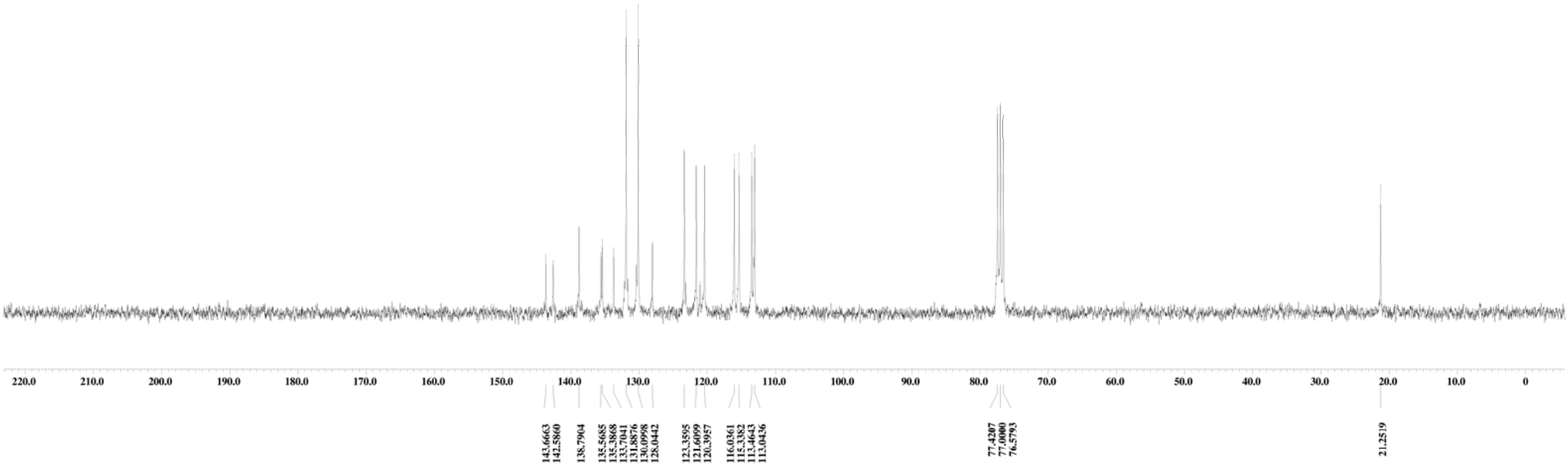
O

2t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121.6099
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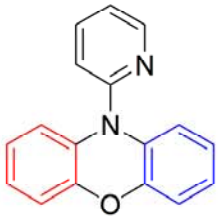
76.5793
21.2519
X : parts per Million : 13C


N
N
O

2u

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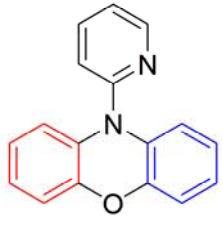
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N
O

2u

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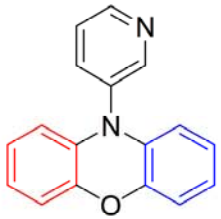
N
N
O

2v

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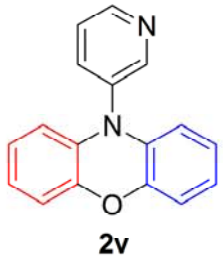
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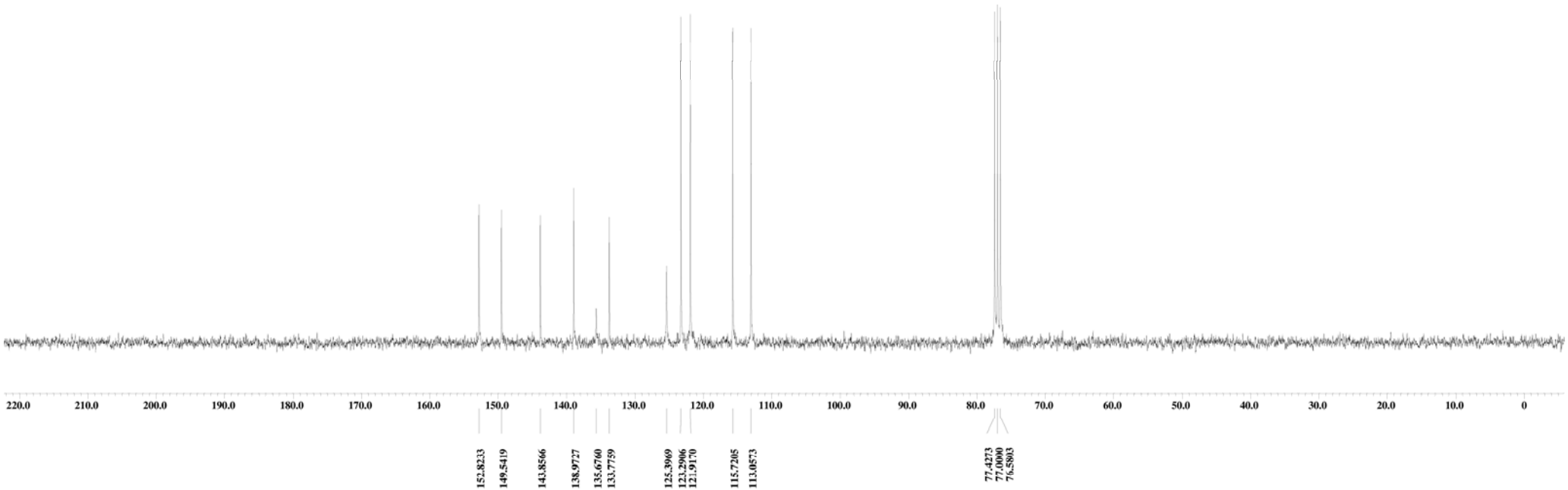
2v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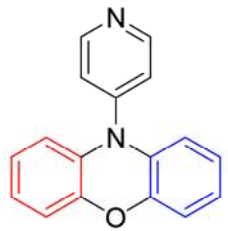
N
N
O

2w

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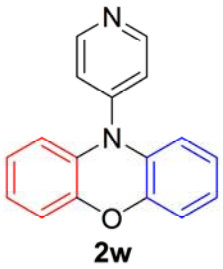
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2w

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S
N
O

2x

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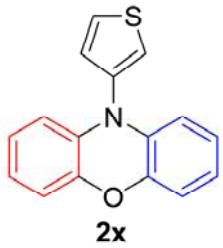
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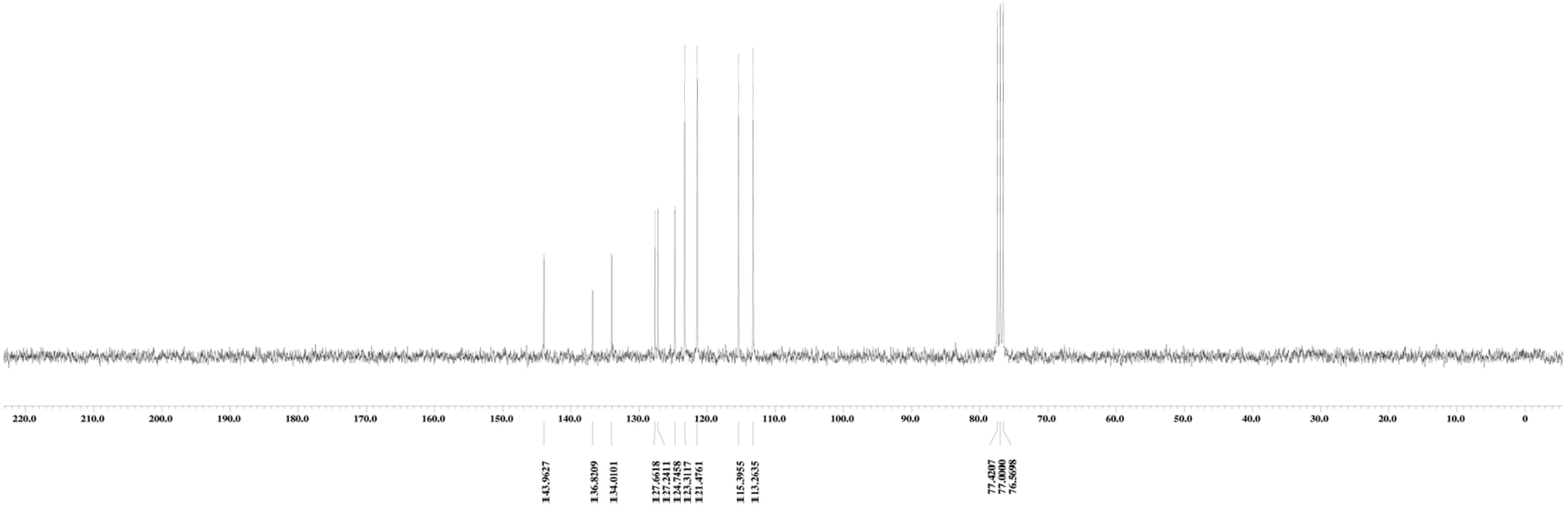
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