Visible-light-promoted synthesis of phenanthridines via intermolecular isocyanide insertion reaction

Hui Zhou,[a] Xinzhao Deng,[a] Ai Hua Zhang,[a,*] and Ren Xiang Tan*,[a]

[a] *Institute of Functional Biomolecules, State Key Laboratory of Pharmaceutical Biotechnology, Nanjing University, Nanjing, 210023, China.*
E-mail: rxtan@nju.edu.cn.

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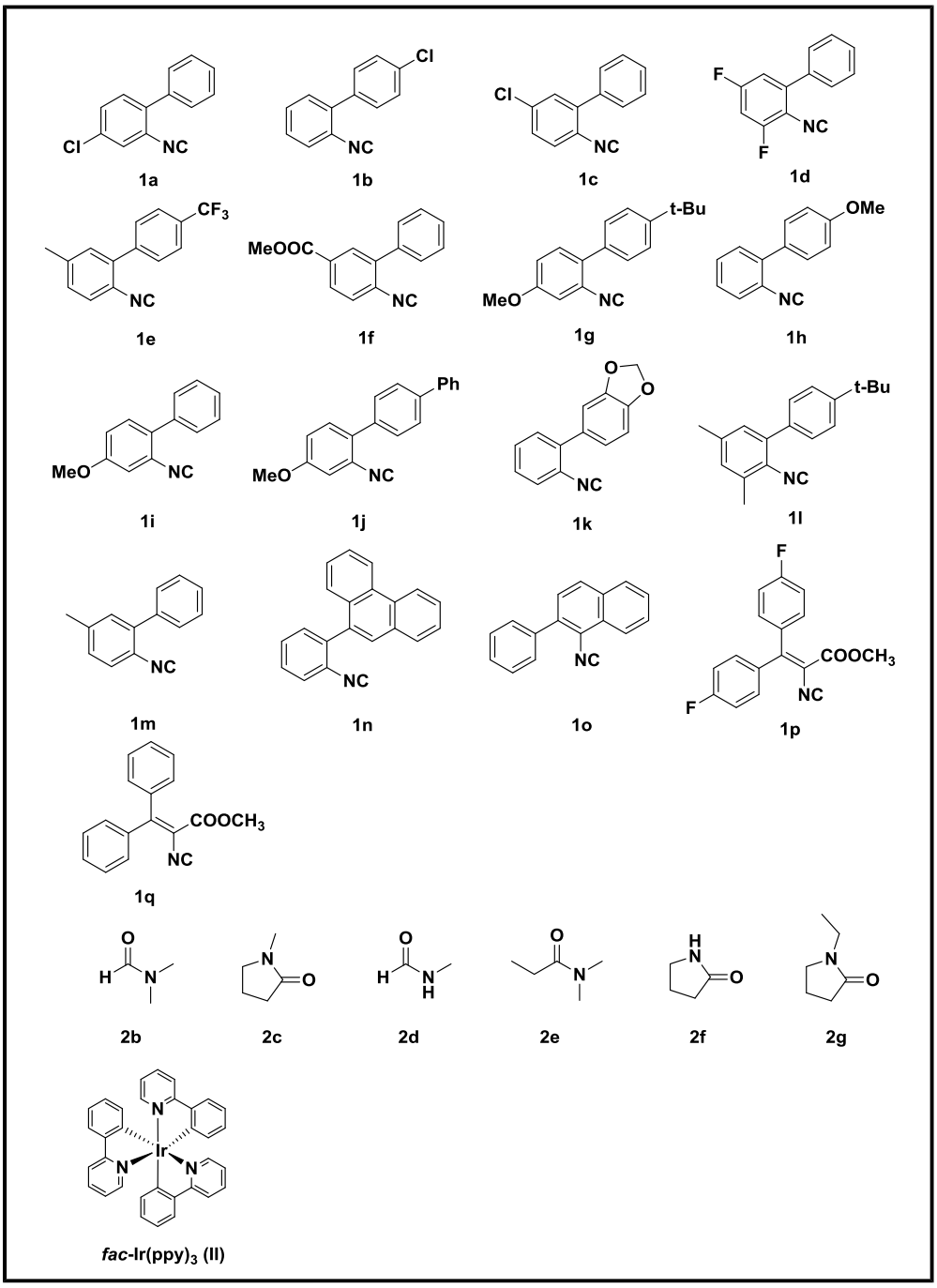
1. List of the substrates

Isocyanides could be generated according to the previously reported procedures.[1] All amides and *fac*-Ir(ppy)$_3$ were obtained from commercial suppliers and used without further purification.



2. Crystal data

3s: Diffraction measurements were performed at 296 K on a Bruker APEX-II diffractometer equipped with Mo–K_α radiation (λ = 0.71073 Å). $C_{16}H_{13}ClN_2O$, M_r =

284.73, orthorhombic, space group *P* 21 21 21, *a* = 4.7439(8) Å, *b* = 16.180(3) Å, *c* = 18.262(3) Å, *V* = 1401.7(4) $Å^3$, *Z* = 4, D_x = 1.349 g/cm^3, μ = 0.269 mm^{-1} and *F*(000) = 592.0; crystal dimensions: 0.18 ×0.03 × 0.02 mm^3; 1714 unique reflections with 3171 obeying the $I \geq 2\sigma(I)$; *R*1 = 0.0445, *wR*2 = 0.1182, *S* = 1.002; supplementary publication no.CCDC-1499099.

3t: Diffraction measurements were performed at 100 K on a Bruker APEX II diffractometer equipped with Cu–K_α radiation (λ = 1.54178 Å). $C_{18}H_{15}ClN_2O$, M_r = 310.77, orthorhombic, space group *P* b c a, *a* = 8.2579(5) Å, *b* = 16.2062(10) Å, *c* = 21.6169(13) Å, *V* = 2893.0(3) $Å^3$, *Z* = 8, D_x = 1.427 g/cm^3, μ = 2.355 mm^{-1} and *F*(000) = 1296.0; crystal dimensions: 0.26 × 0.21 × 0.10 mm^3; 2234 unique reflections with 2509 obeying the $I \geq 2\sigma(I)$; *R*1 = 0.0384, *wR*2 = 0.1207, *S* = 1.050; supplementary publication no.CCDC-1499100.

3. Biological evaluation

(1) Reagents

DMEM (Dulbecco's modified Eagle's medium, WISENT)； FBS (Fetal bovine serum, Gibco); Doxorubicin HCl (Sigma-Aldrich); Penicillin (Sangon Biotech, Shanghai, China); Streptomycin (Sangon Biotech, Shanghai, China); MTT (Sangon Biotech , Shanghai, China)

(2) Cell Culture

Cells (A375, HepG-2, HT-29, MCF-7, CaoV-3) were maintained in cell culture dishes in complete growth medium (DMEM), supplemented with 10% FBS, 100U/mL penicillin, and 100μg/mL streptomycin. The cells were grown in a carbon dioxide incubator (37 ℃, 5% CO_2). All cell lines were obtained from the Cell Bank of the Chinese Academic of Science (Shanghai, China)

(3) Cytotoxicity

The cytotoxicity was tested on the five cell lines (human melanoma A375, human hepatoma HepG-2, human colon carcinoma HT-29, human breast cancer MCF-7 and human ovarian cancer Caov-3) by MTT [3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyl-2-H-tetrazolium bromide] assay as

described.[2] Briefly, the test cell at the exponential growth phase were collected and transferred into 96-well plates. After incubated for 24 h, compound dilutions were dispensed to the established culture plates. Two days (48 h) later, the MTT solution (0.1 mg per well) was then added to each well. After further incubation for 4 h, the supernatant was removed, the crystals were fully dissolved in DMSO (150 mL), and the absorbance of each well was read at 570 nm (Safire, Tecan). The IC_{50} value was determined as the concentration, at which a half of the test cell growth was inhibited and calculated using GraphPad Prism 5.0 (GraphPad Software Inc., San Diego, CA, USA). The experiment was performed in triplicate, and the data expressed as means ±SEM.[3]

(4) Neuraminidase Inhibitory Assay

The fluorimetric assay was used to measure NA activity performed as previously reported with a slight modification.[4,5] The NA activity was measured using the substrate 4-methylumbelliferyl-R-D-N-acetylneuraminic acid sodium salt hydrate (4-MU-NANA) in the MES buffer [32.5 mM 2-(*N*-morpholino) ethanesulfonic acid, 4 mM $CaCl_2$, pH 6.5]. All compounds were dissolved in DMSO and diluted to the corresponding concentrations in MES buffer. An enzyme inhibitory assay was carried out in 96-well plates containing 50μl MES buffer, 10 μl of NA (0.035 U/ml) and 10 μl of test compound incorporated in the MES buffer at different concentrations to assess their inhibitory activity. The mixture was incubated for 30 min at 37°C, and 30 μl of 4-MU-NANA substrate per well in MES buffer was added. The enzymatic reactions were carried out for 1 h at 37 °C and quenched by adding 100 μL of the stop solution (83% EtOH, 14mM NaOH). The fluorescence intensity of the product (4-MU) was acquired with excitation and emission wavelengths of 360 and 450 nm, respectively. The IC_{50} for reducing the NA activity was then determined.

4. Reference

1. M. Suzuki, K.-I. Nunami, K. Matsumoto, N. Yoneda, O. Kasuga, H. Yoshida and T. Yamaguchi, *Chem. Pharm. Bull.* 1980, **28**, 2374.

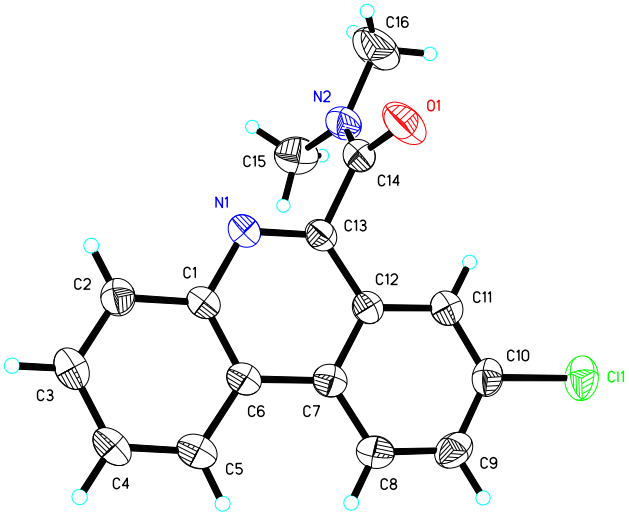
2. R. Menicagli, S. Samaritani, G. Signore, F. Vaglini and L. D. Via, *J. Med. Chem.* 2004, **47**, 4649–4652.
3. H. M. Ge, Z. G. Yu, J. Zhang, J. H. Wu and R. X. Tan, *J. Nat. Prod.* 2009, **72**, 753−755.
4. W. Irith, H. Kai and E. W. H. Robert, *Nat. Protoc.* 2008, **3**, 163-175.
5. R. H. Jiao, H. Xu, J. T. Cui, H. M. Ge and R. X. Tan, *J. Appl. Microbiol.* 2013, **114**, 1046—1053.
6. T. T. Dao, B. T. Tung, P. H. Nguyen, P. T. Thuong, S. S. Yoo, E. H. Kim, S. K. Kim and W. K. Oh, *J. Nat. Prod.* 2010, **73**, 1636-1642.

5. Table S1 The inhibitory effect of compounds on neuraminidase

Compounds	3d	3k	3r	Oseltamivir [b]
IC_{50} (μM)	7.19±0.26[a]	10.71±0.36	8.34±0.31	0.23±0.02

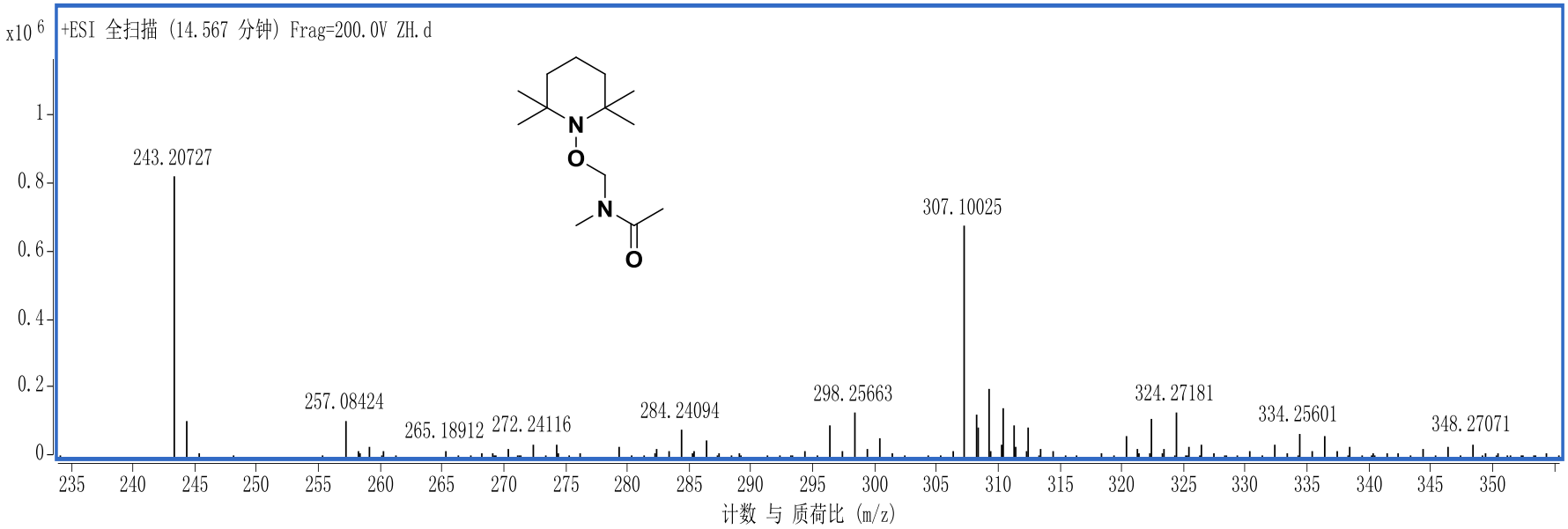
[a] IC_{50} values (μM) are the mean ± SEM of three independent assays.
[b] Oseltamivir is the reference standard used in the present study.

6. The X-ray structure of 3s, 3t (see for main article)

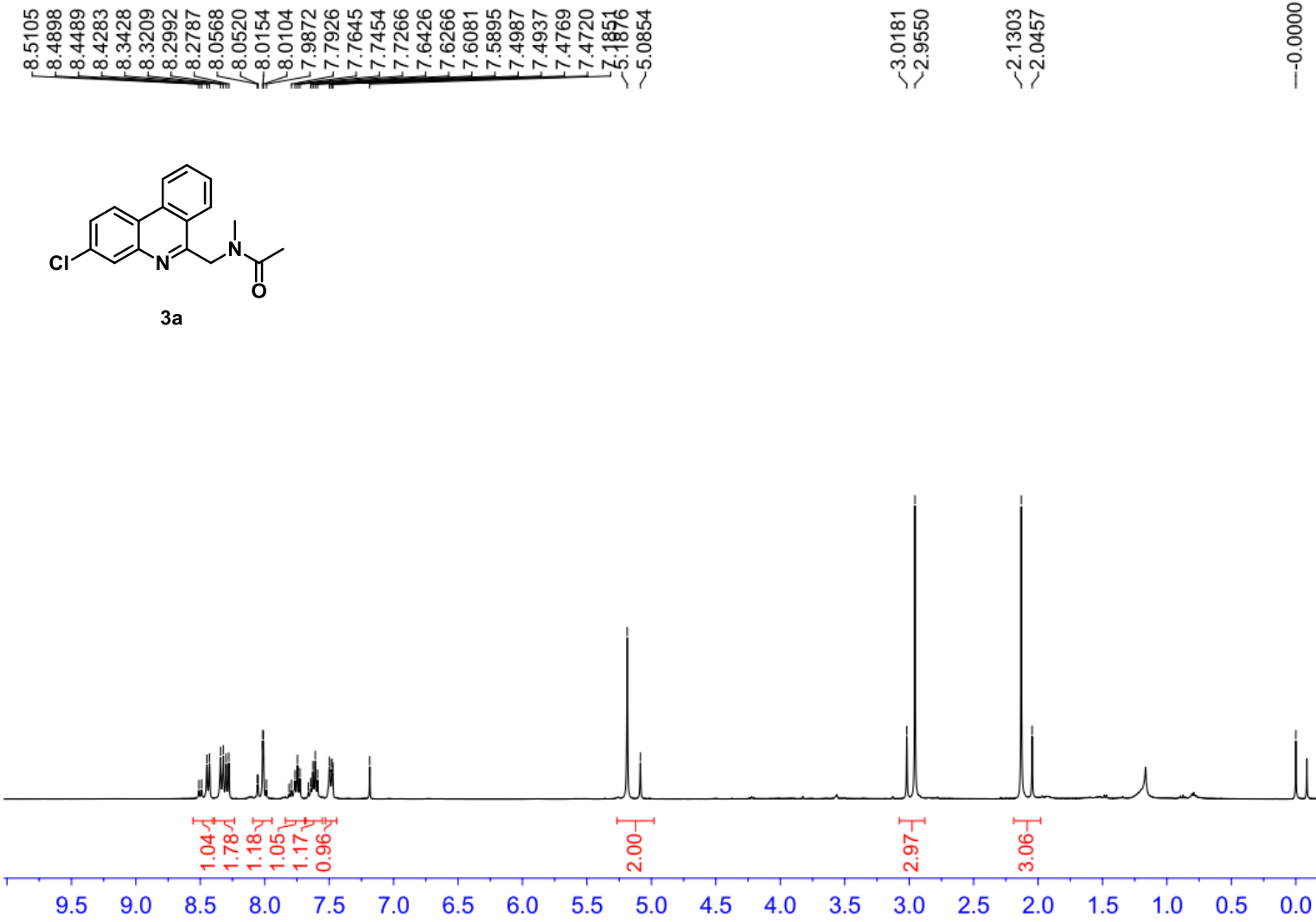


7. Figure S1 LC-UV-MS for detection of TEMPO-DMAc adduct

ESI-MS calcd for $C_{13}H_{27}N_2O_2$ $[M + H]^+$: 243.2073, found: 243.2073.



8. NMR and ESI-MS Spectra for All Compounds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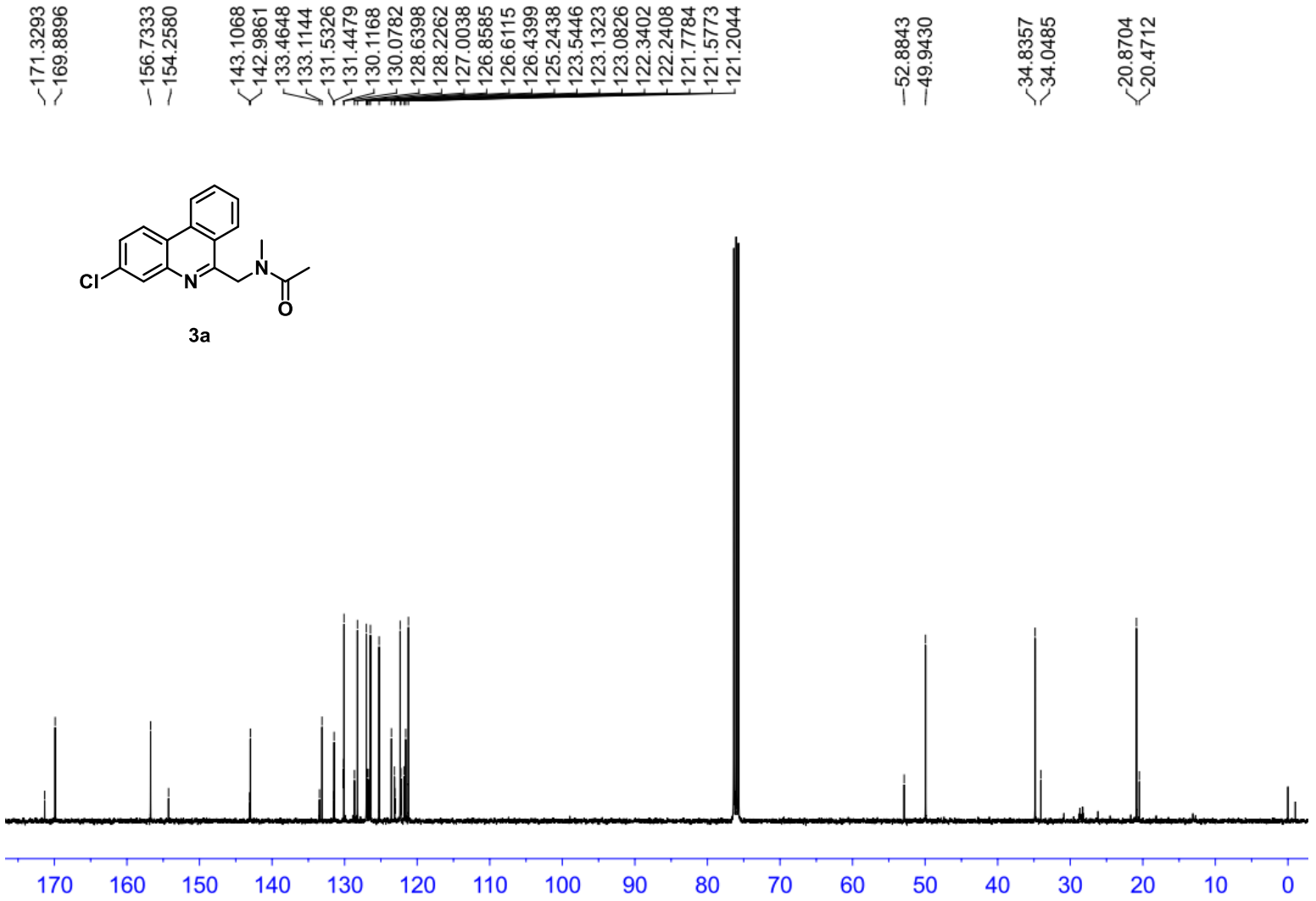
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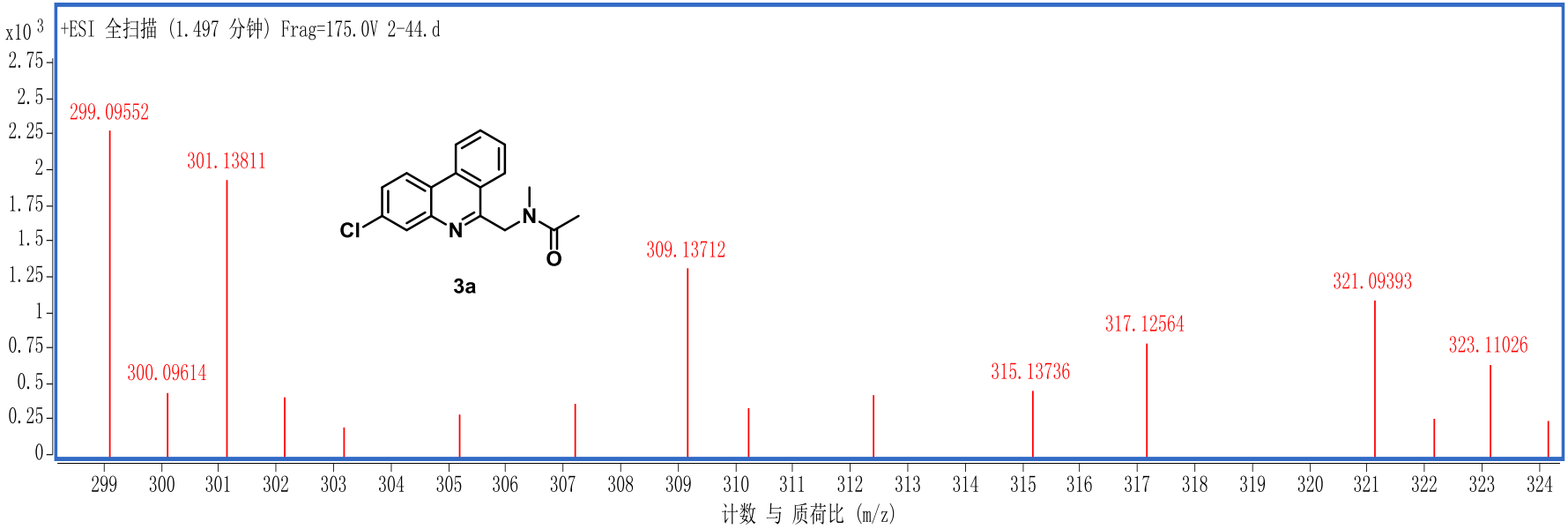
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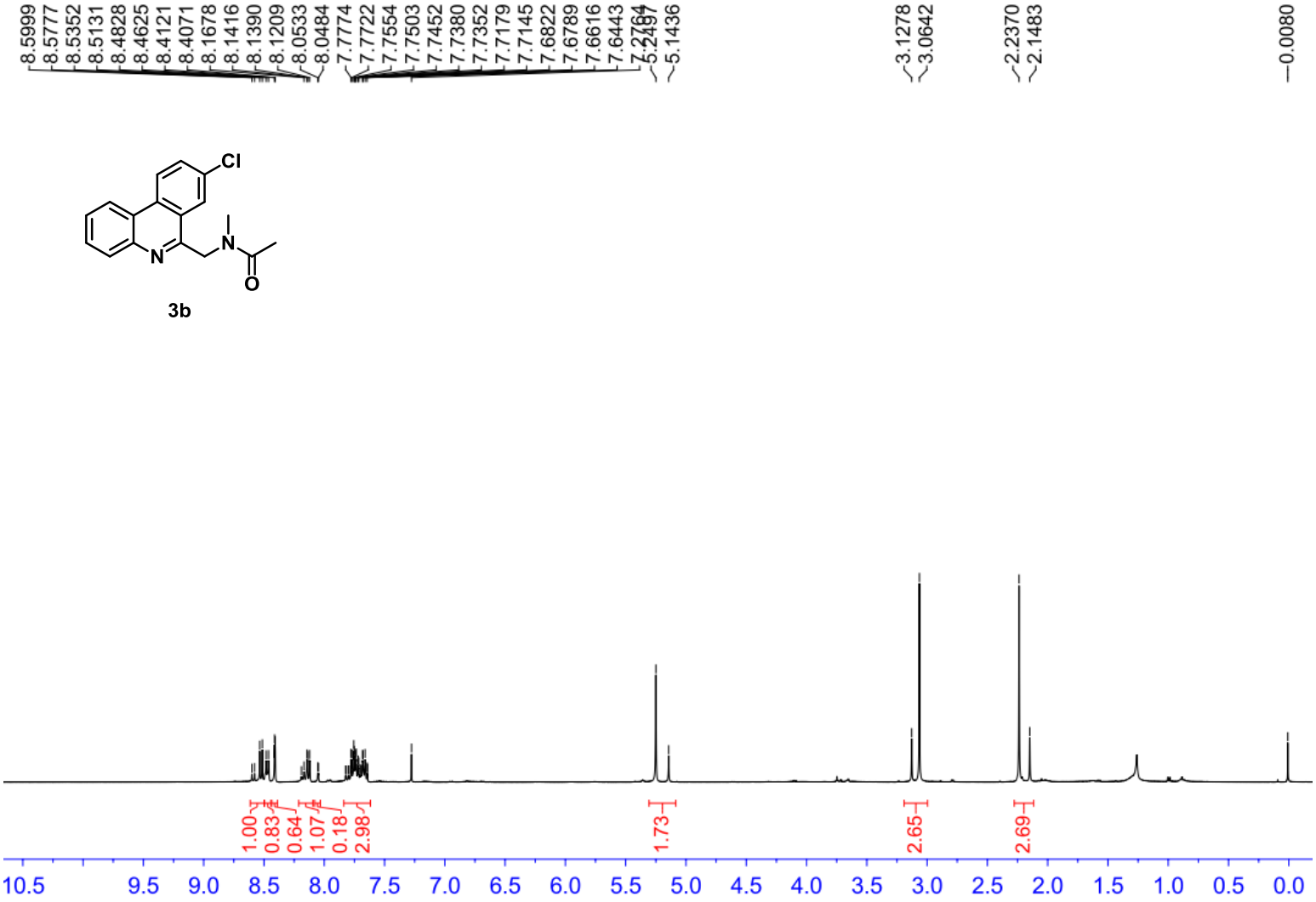
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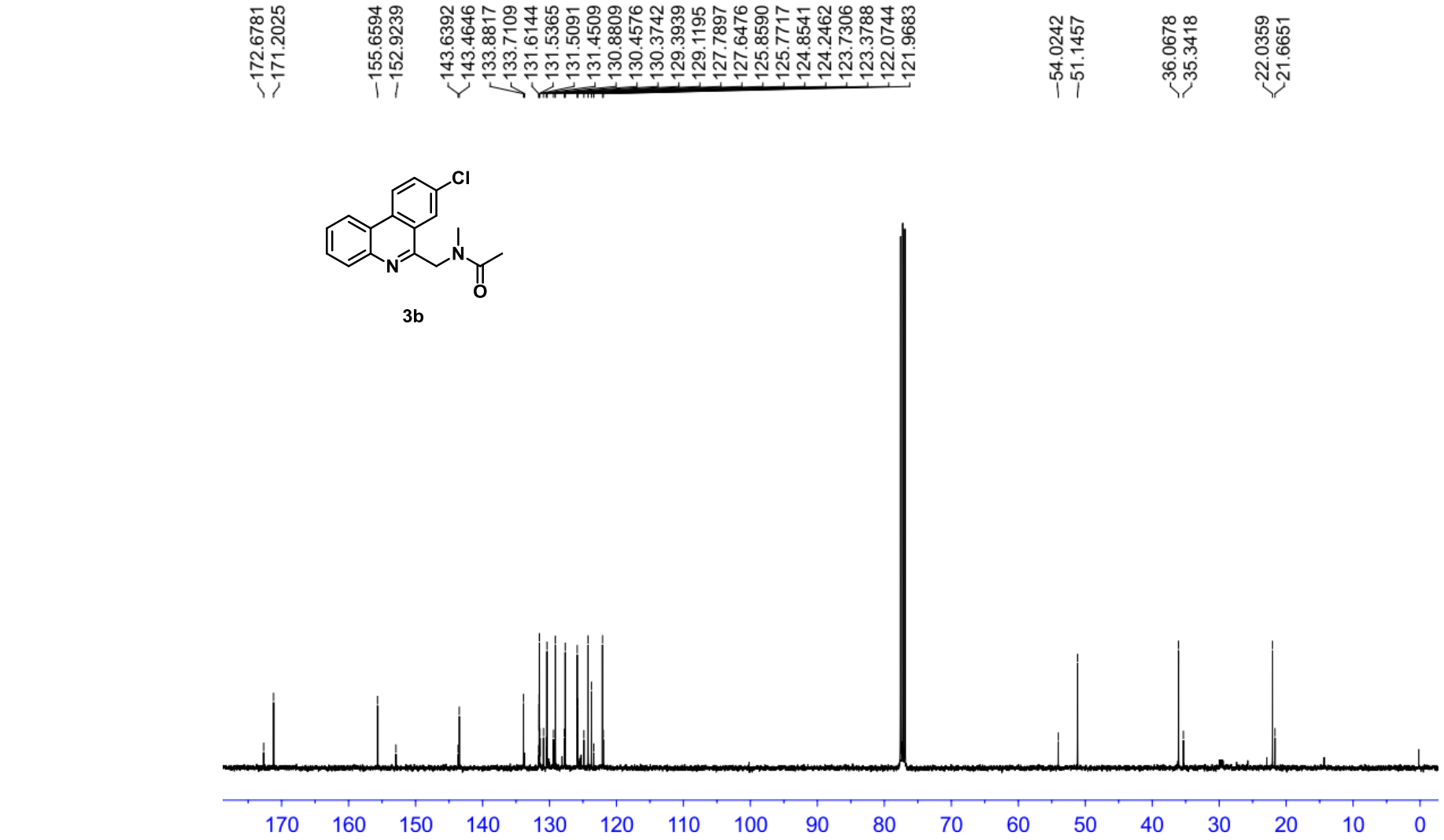
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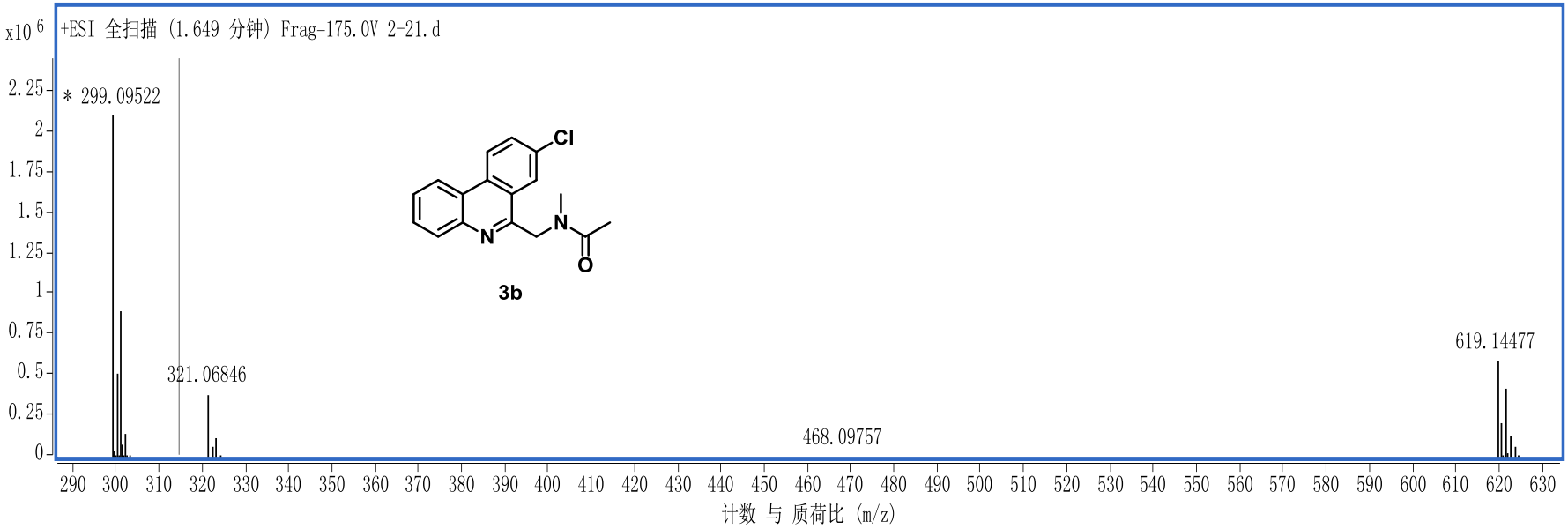
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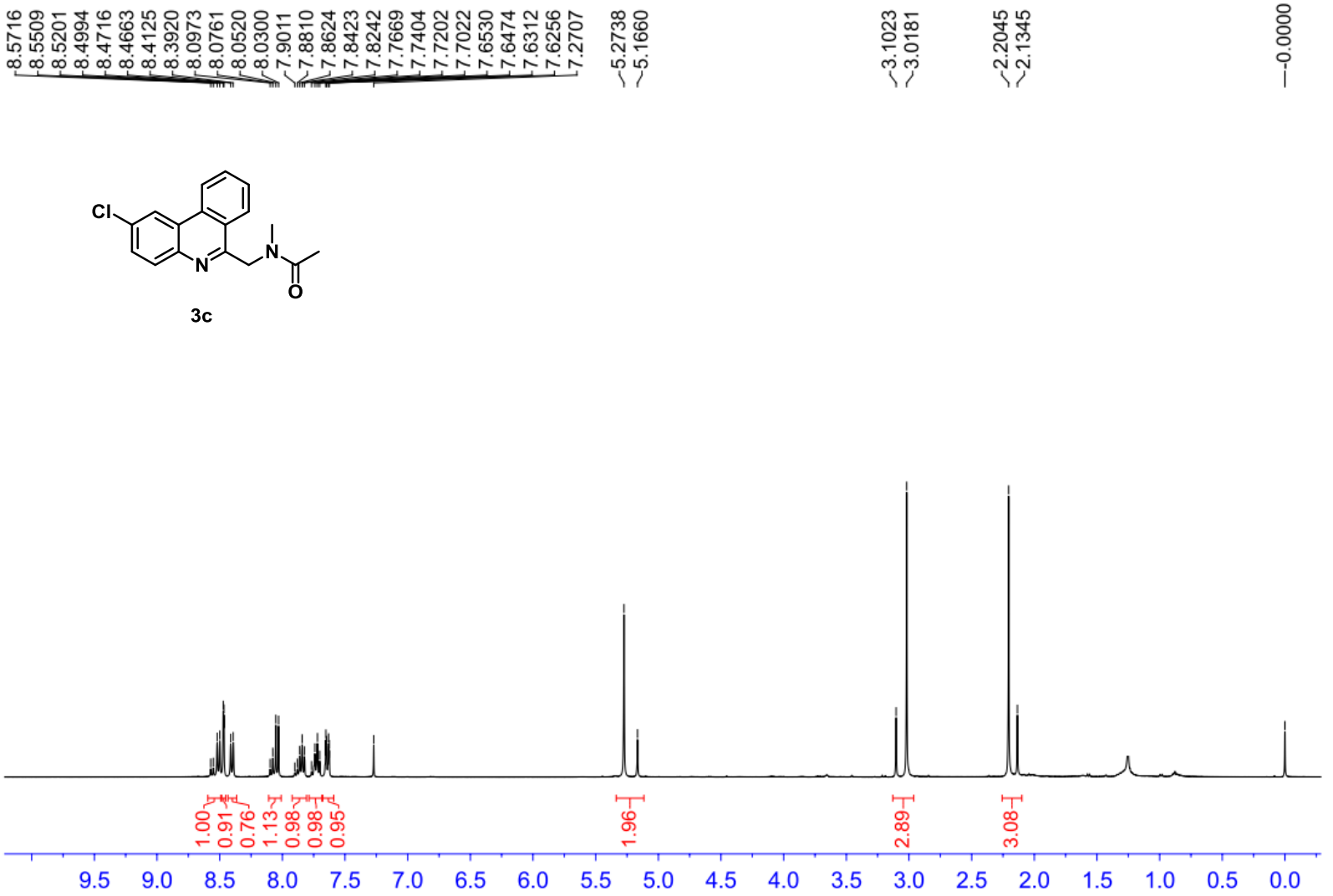
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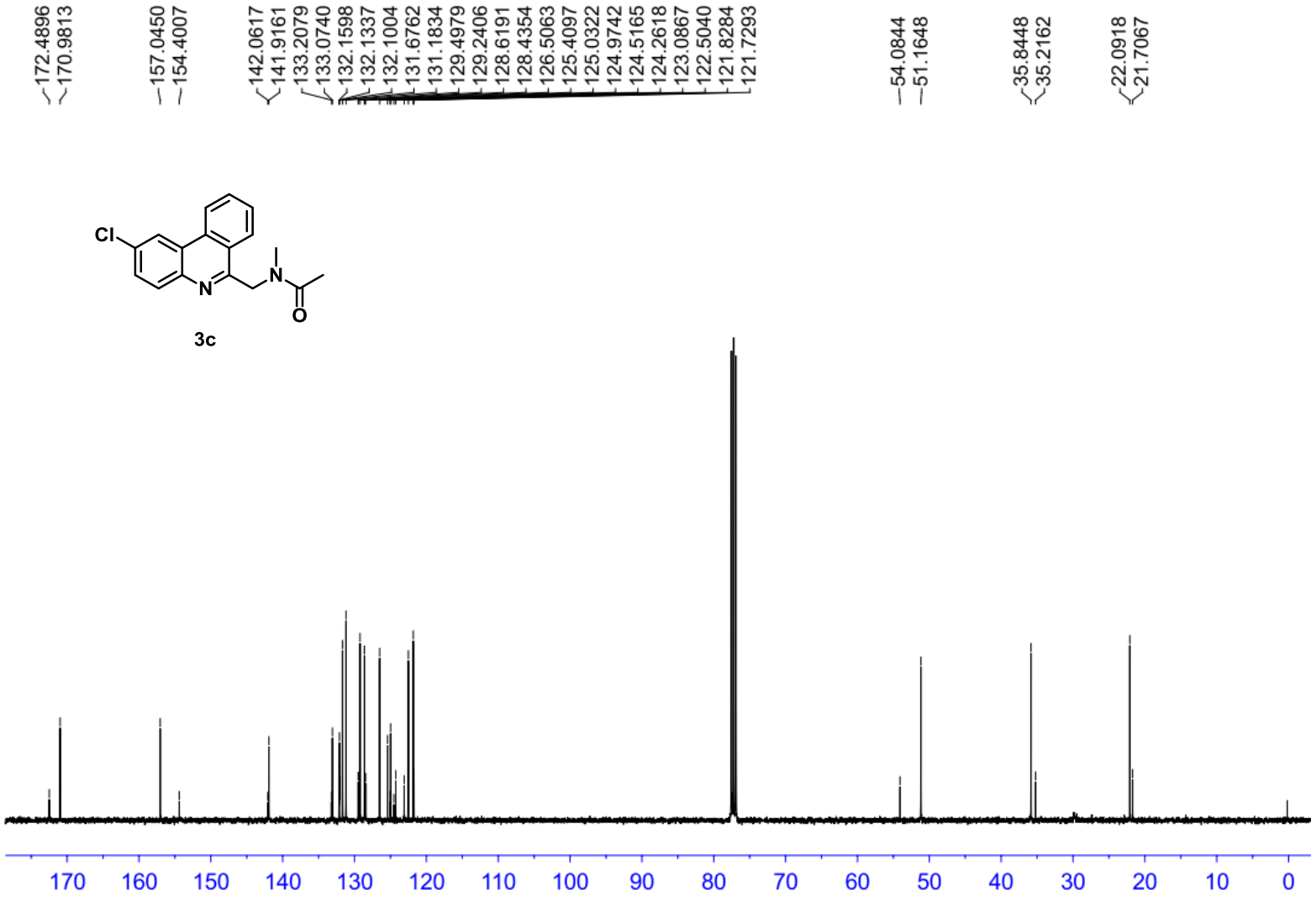
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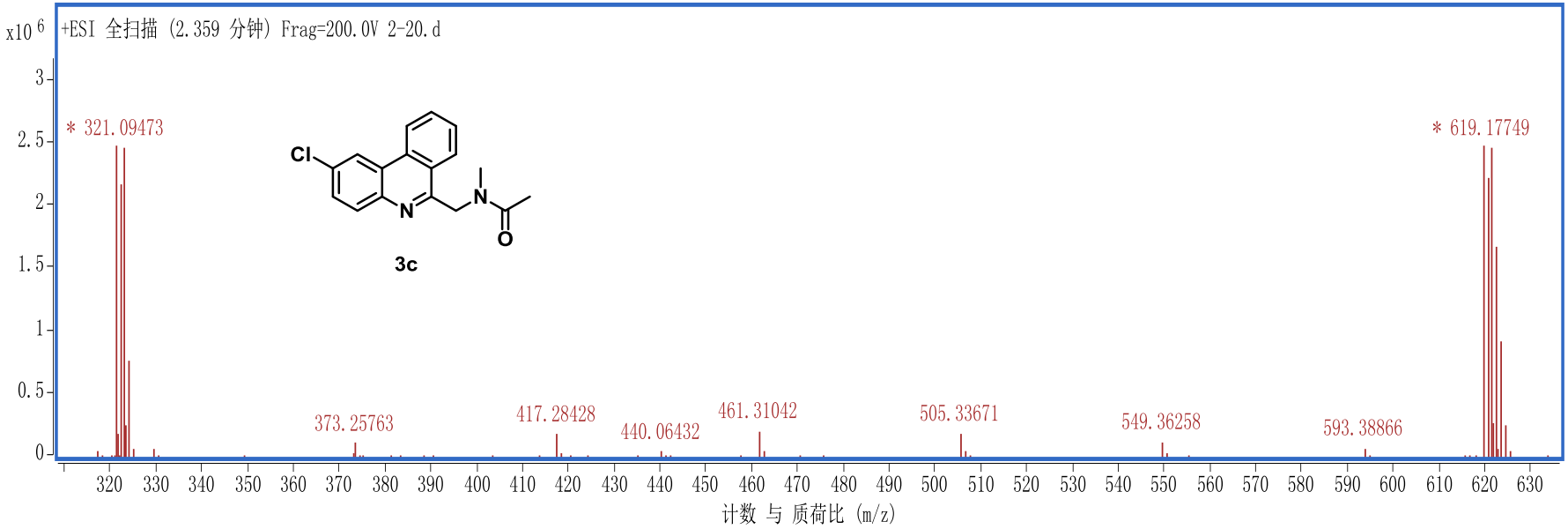
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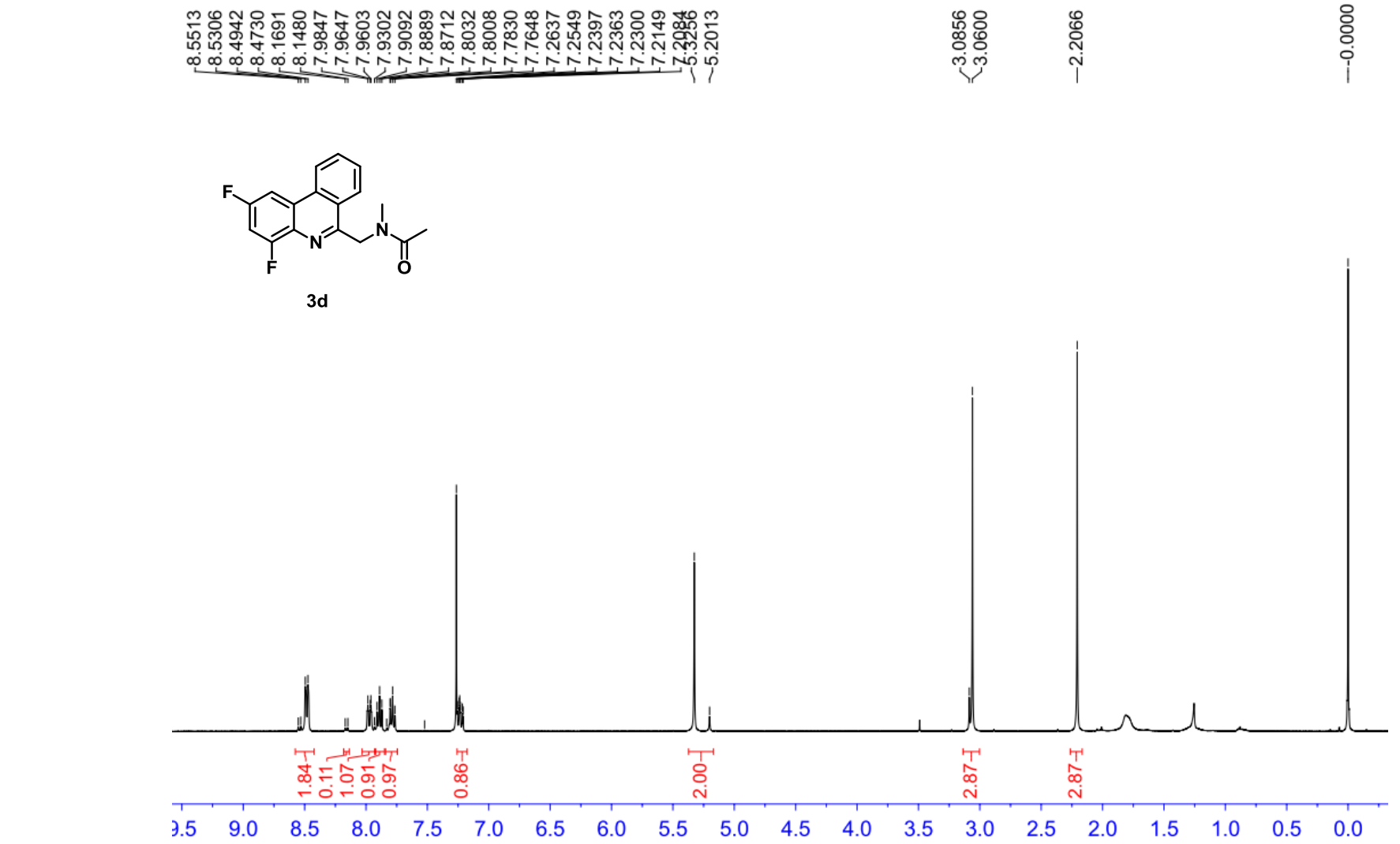
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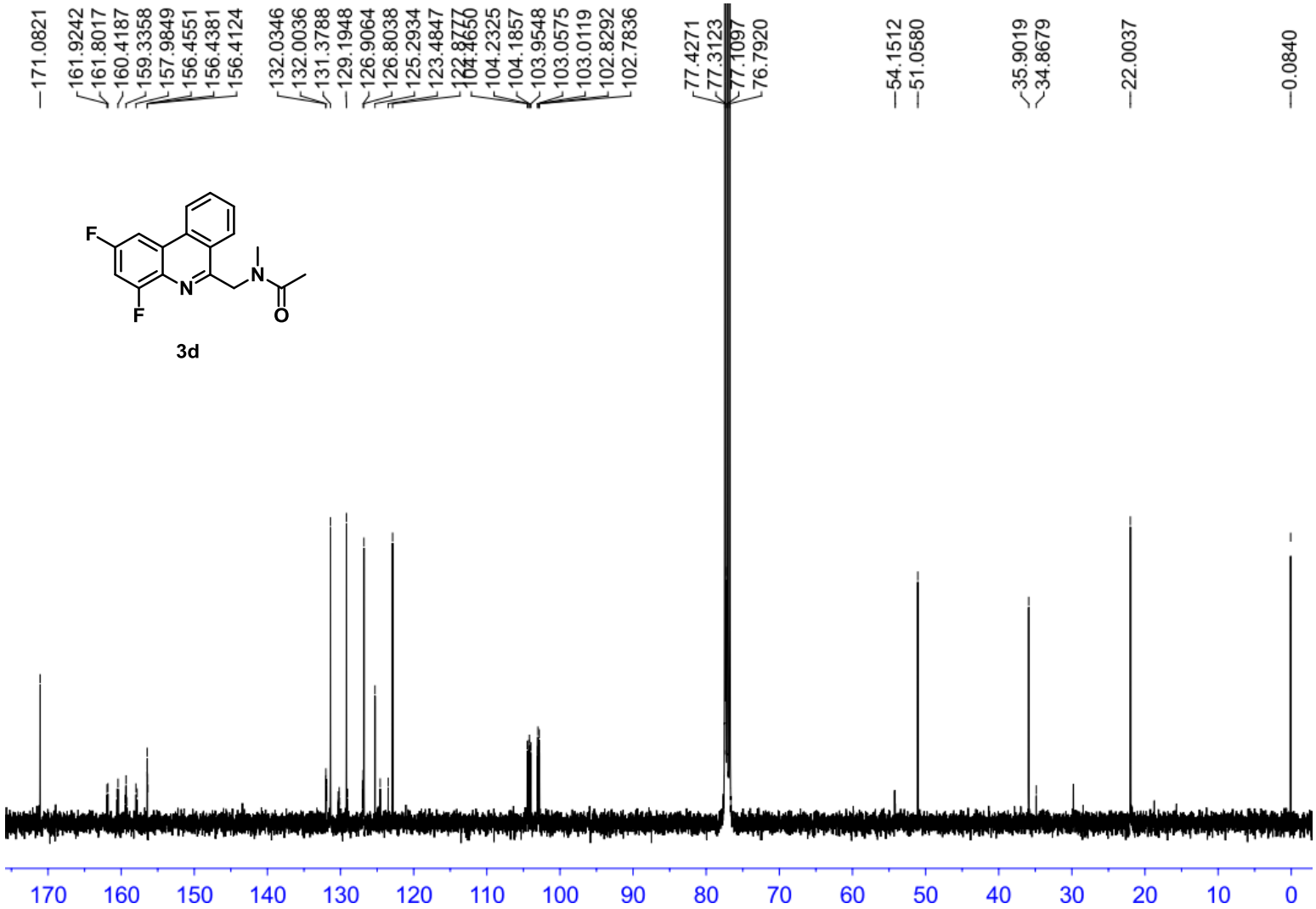
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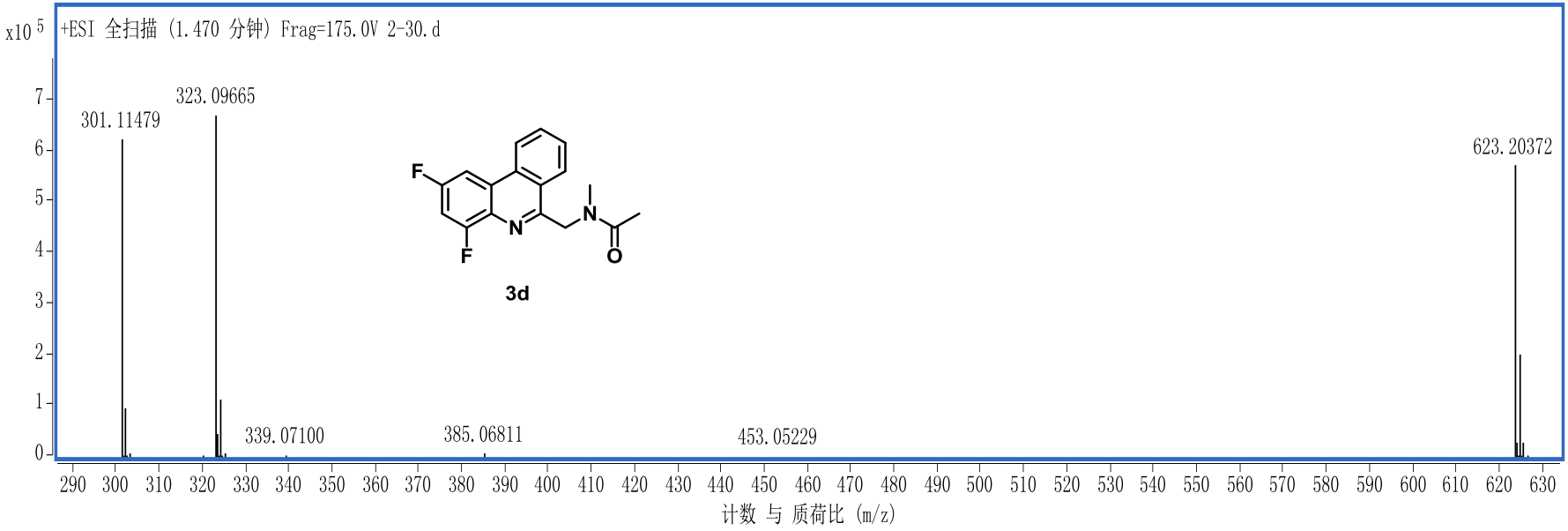
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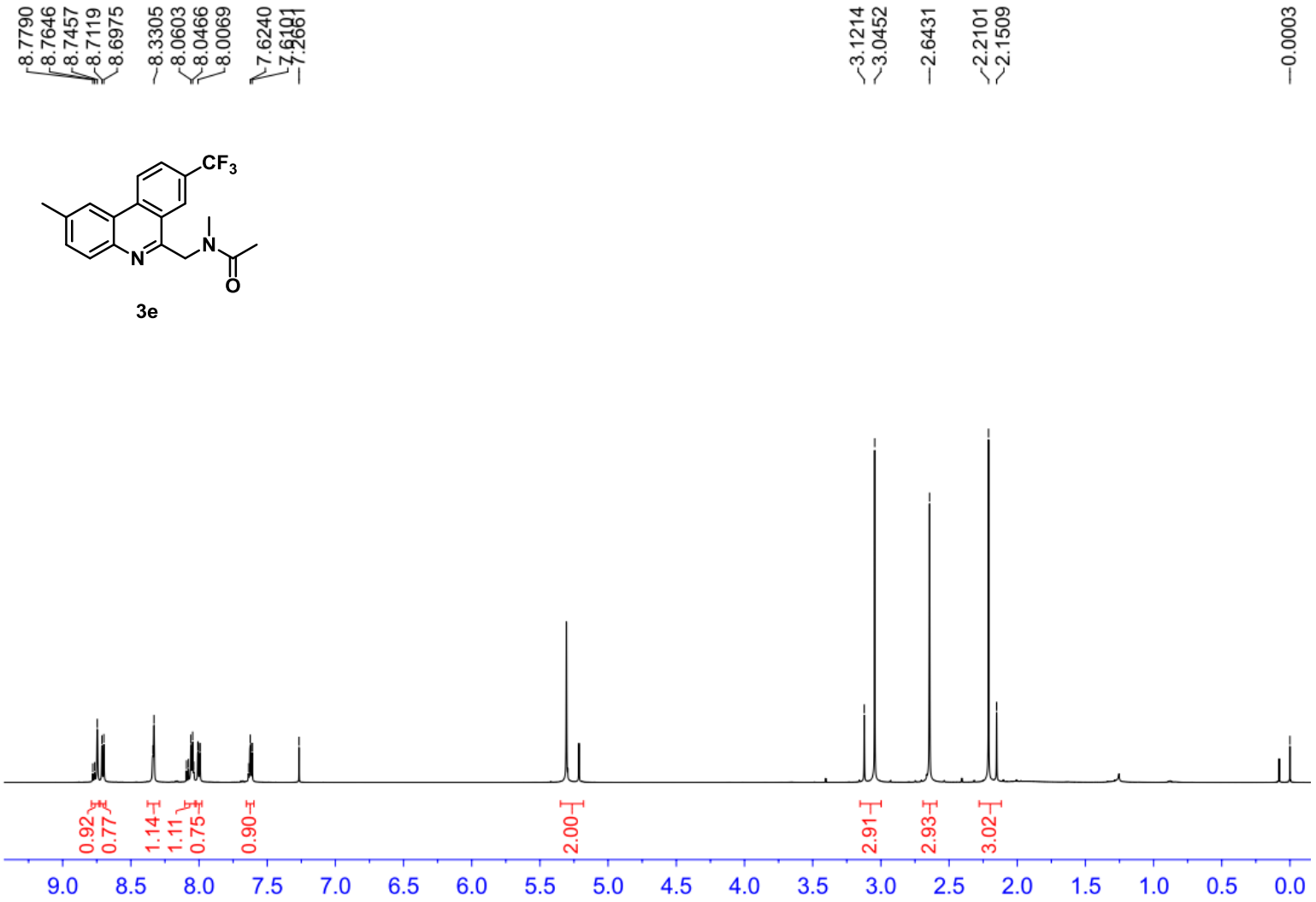
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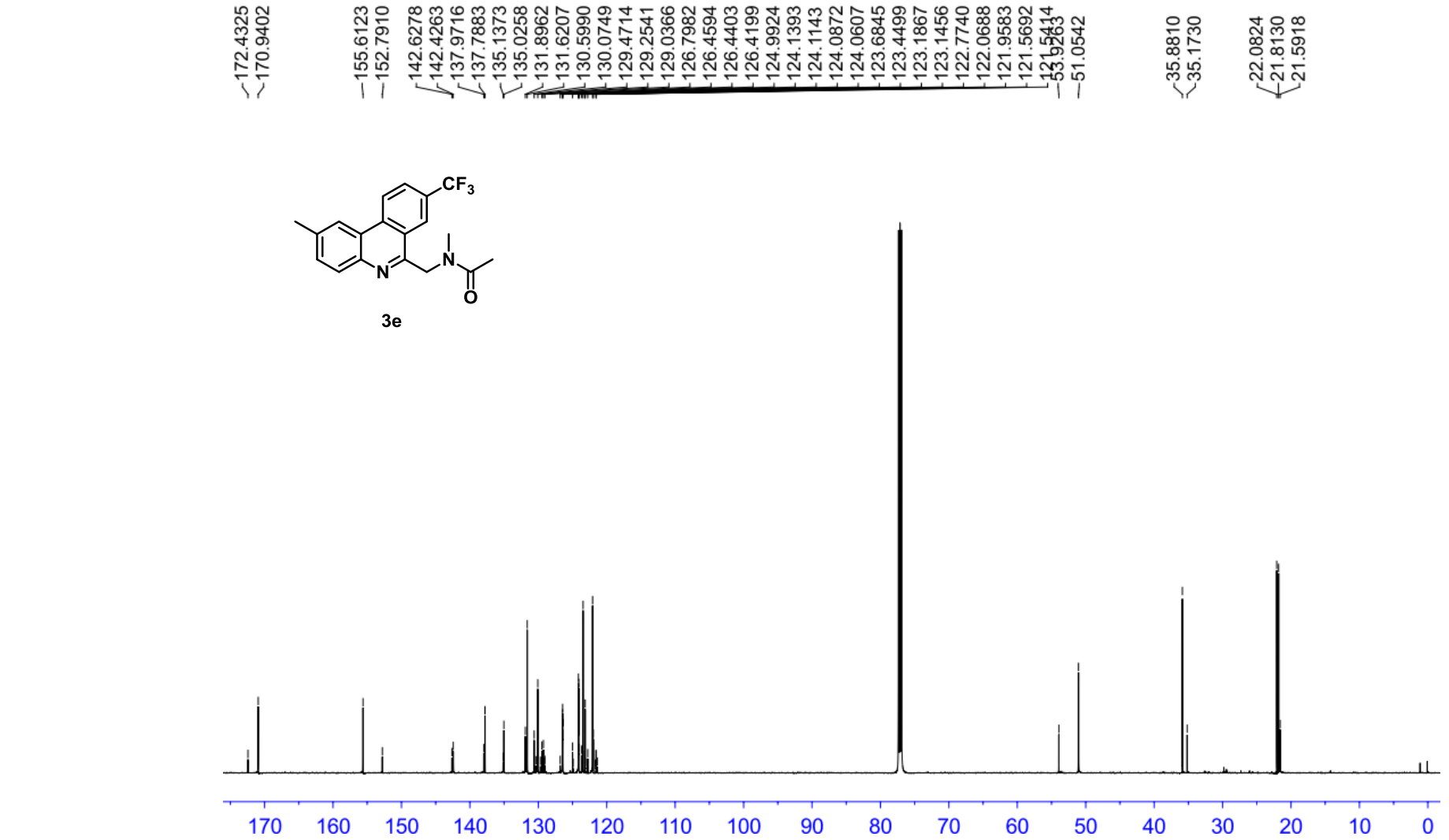
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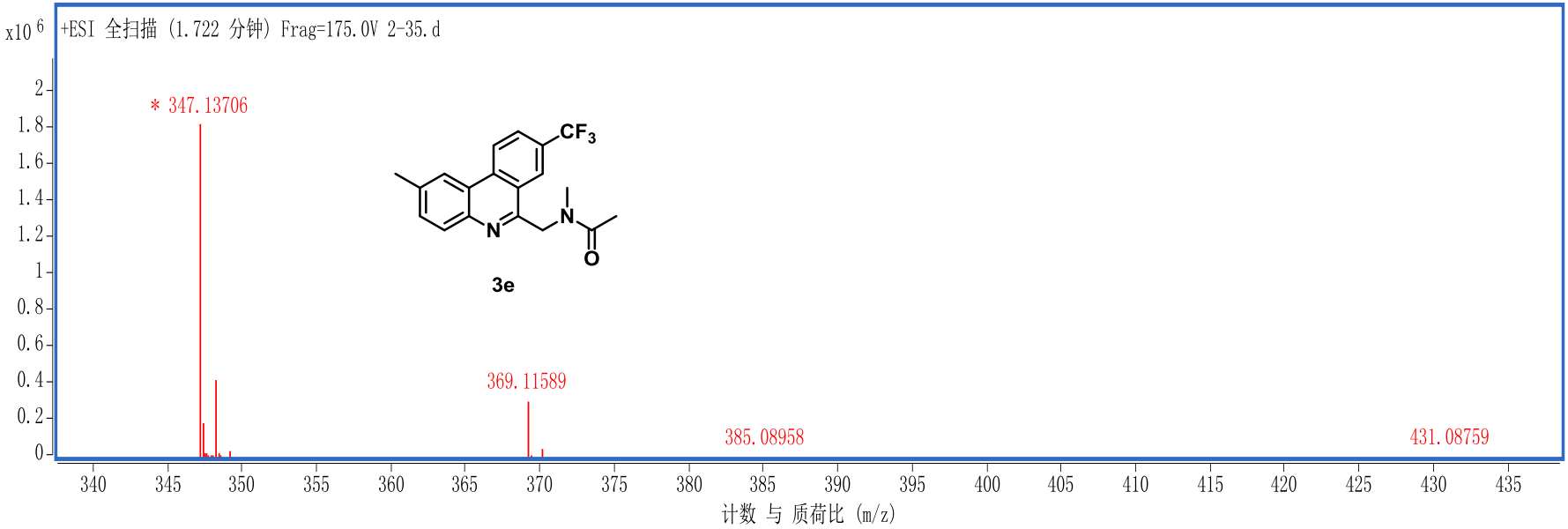
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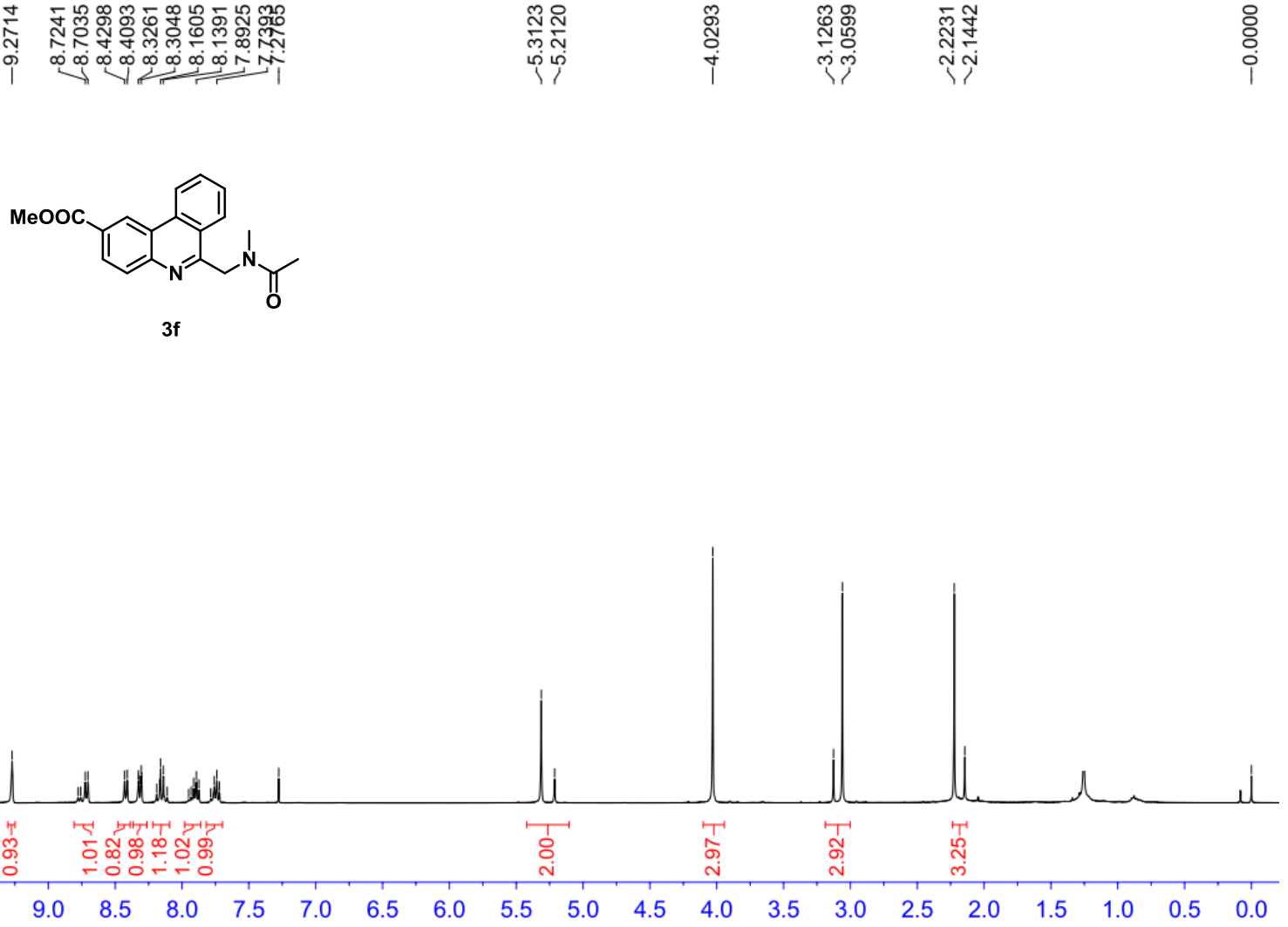
计数 与 质荷比 (m/z)


9.2714
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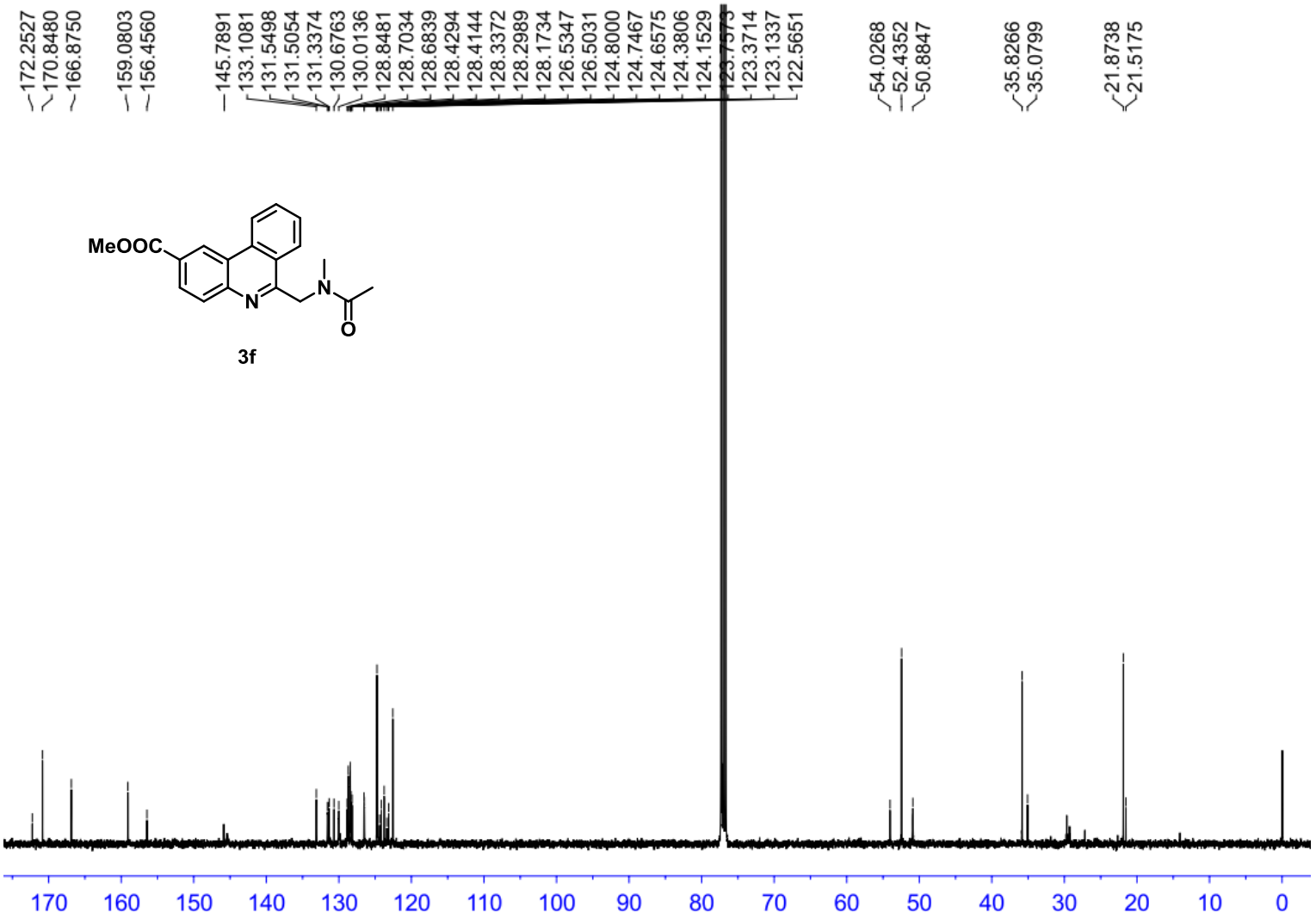
8.7035
8.4298
8.4093
8.3261
8.3048
8.1605
8.1391
7.8925
7.7393
7.7265
7.2765
5.3123
5.2120
4.0293
3.1263
3.0599
2.2231
2.1442
0.0000
MeOOC
N
N
O
3f
0.93
1.01
0.82
0.98
1.18
1.02
0.99
2.00
2.97
2.92
3.25
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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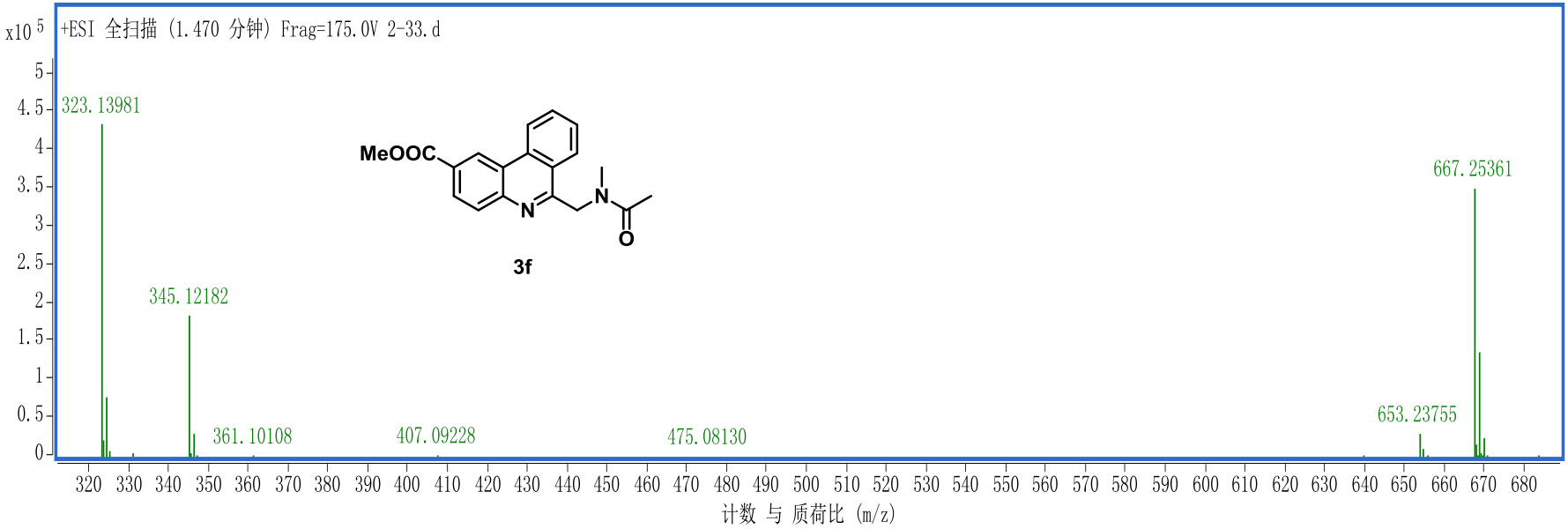
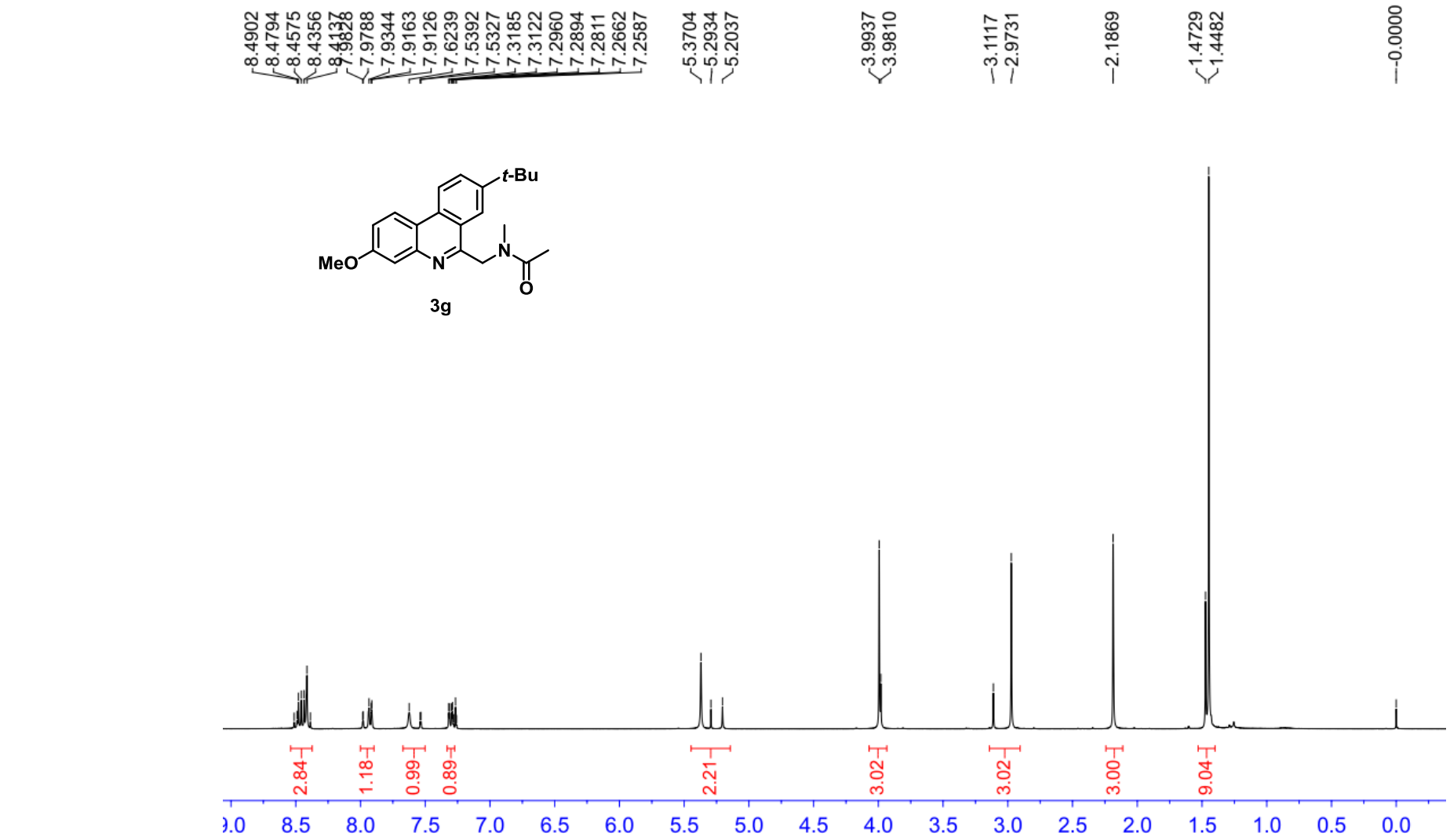
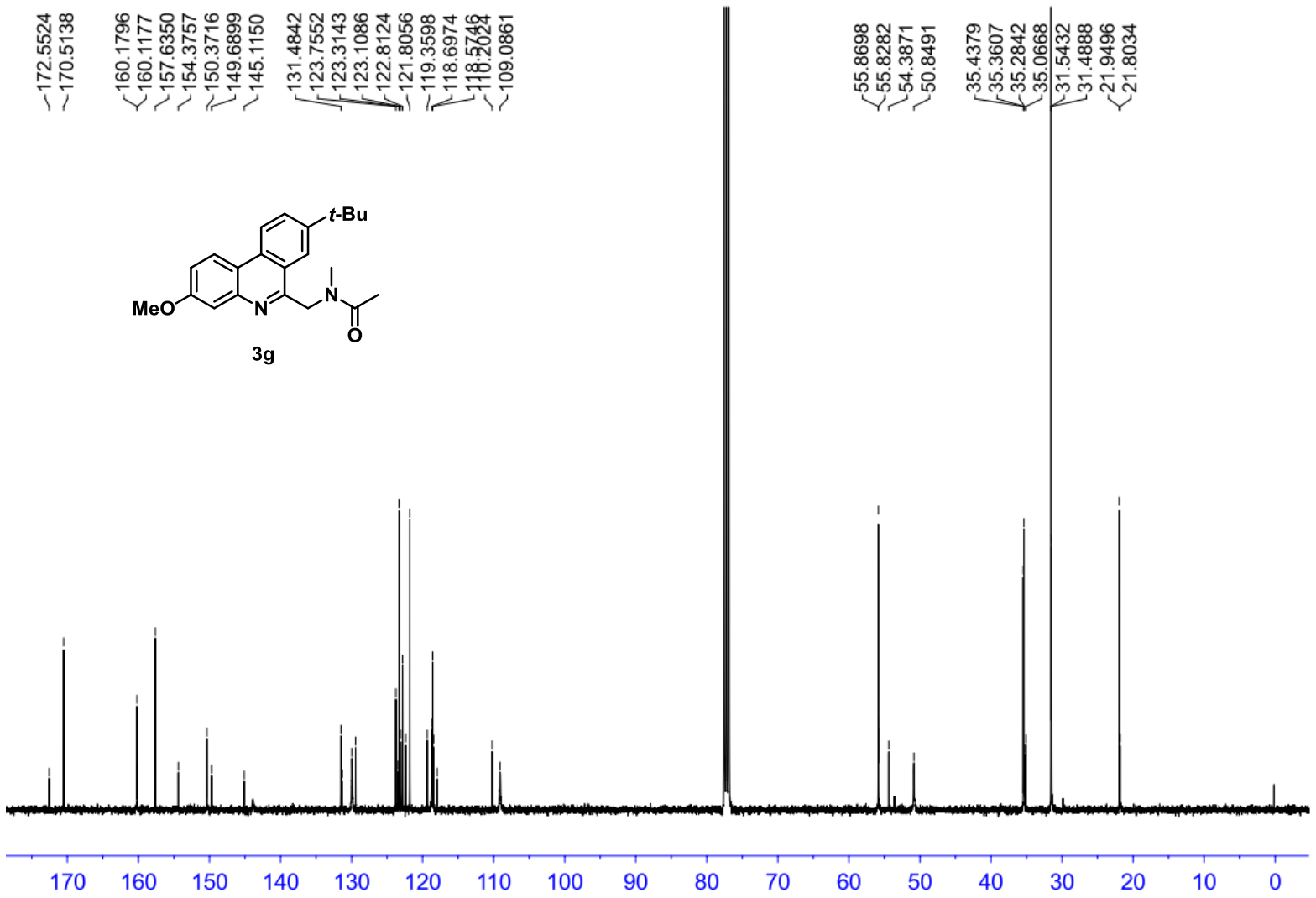
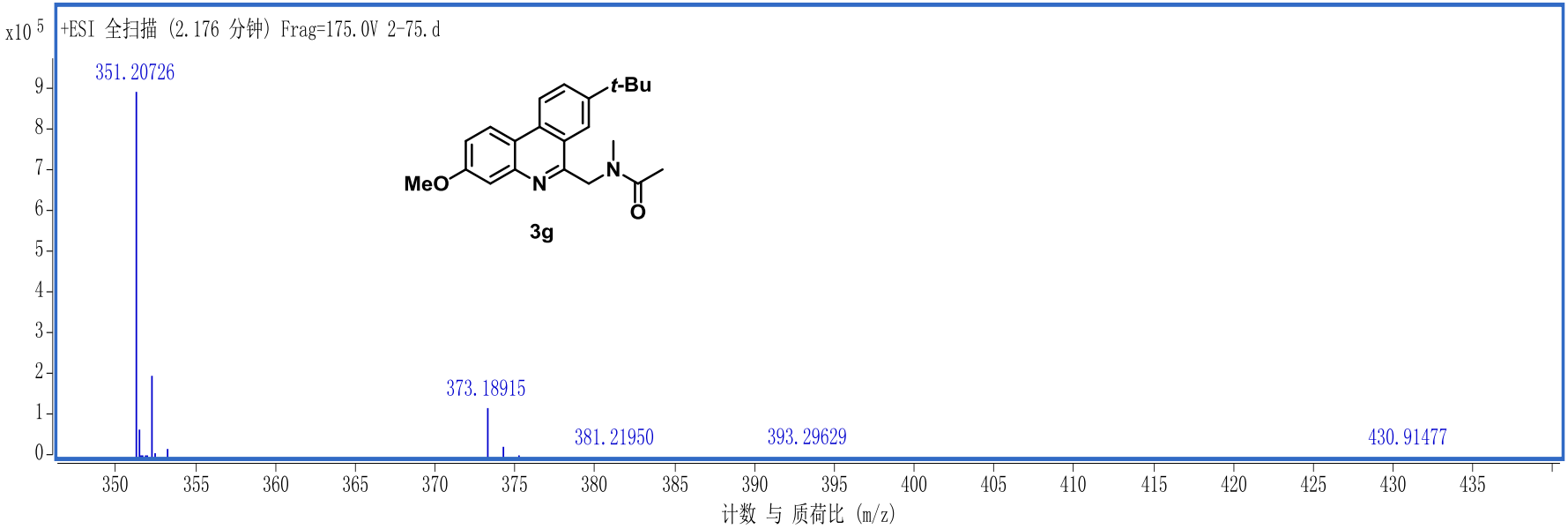
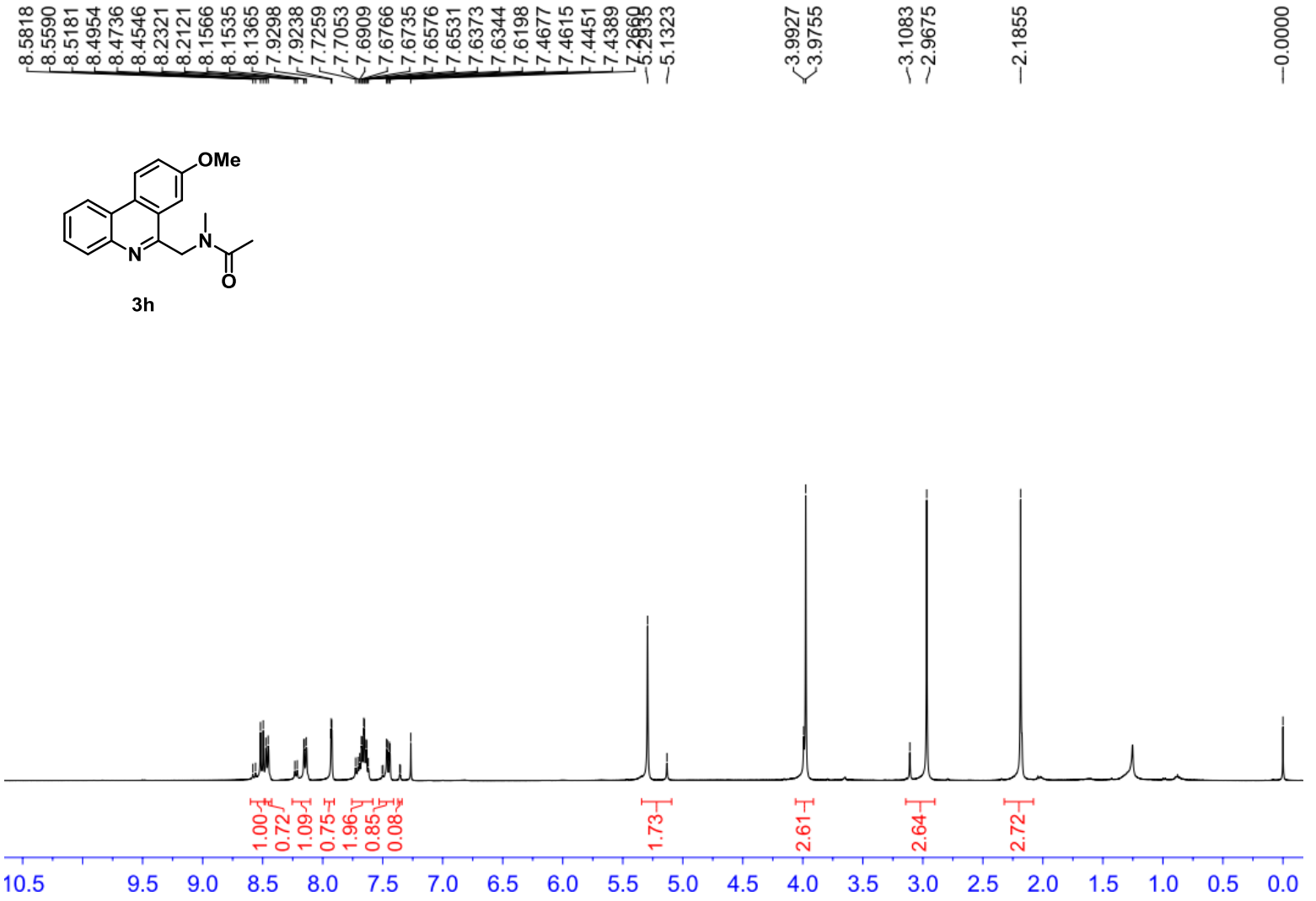
166.8750
159.0803
156.4560
145.7891
133.1081
131.5498
131.5054
131.3374
130.6763
130.0136
128.8481
128.7034
128.6839
128.4294
128.4144
128.3372
128.2989
128.1734
126.5347
126.5031
124.8000
124.7467
124.6575
124.3806
124.1529
123.7573
123.3714
123.1337
122.5651
54.0268
52.4352
50.8847
35.8266
35.0799
21.8738
21.5175
MeOOC
N
N
O
3f
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

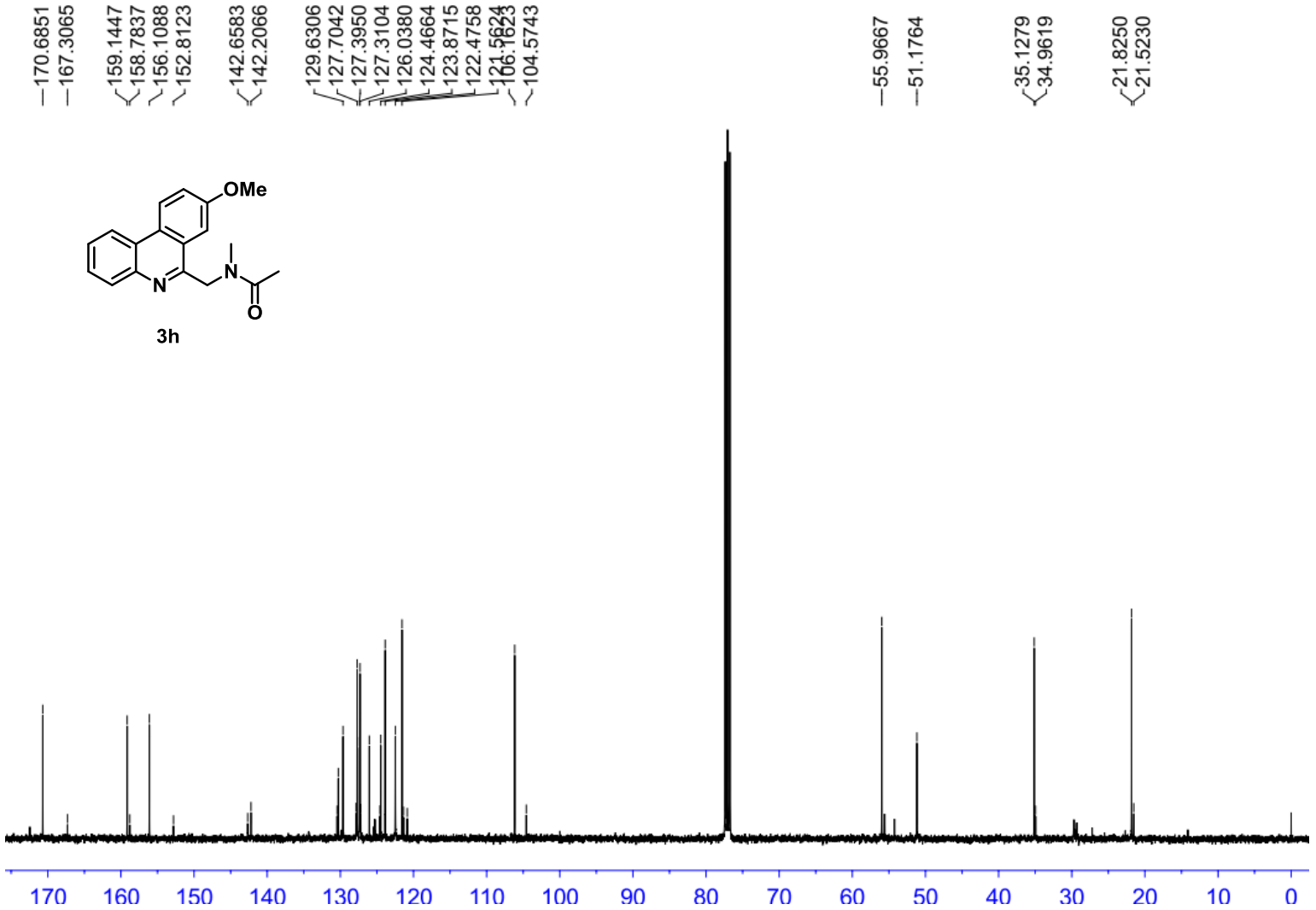

x10 5
+ESI 全扫描 (1.470 分钟) Frag=175.0V 2-33.d
323.13981
345.12182
361.10108
407.09228
475.08130
653.23755
667.25361
MeOOC
N
N
O
3f
计数 与 质荷比 (m/z)

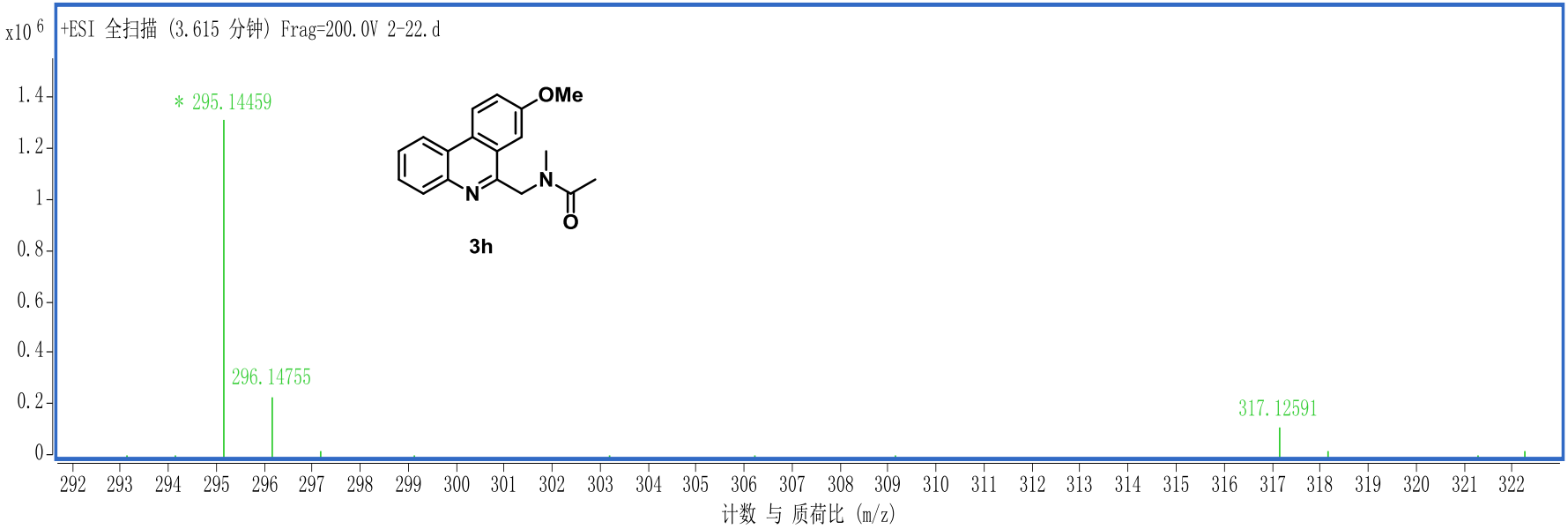

8.4902
8.4794
8.4575
8.4356
8.4137
7.9828
7.9788
7.9344
7.9163
7.9126
7.6239
7.5392
7.5327
7.3185
7.3122
7.2960
7.2894
7.2811
7.2662
7.2587
5.3704
5.2934
5.2037
3.9937
3.9810
3.1117
2.9731
2.1869
1.4729
1.4482
0.0000
t-Bu
MeO
N
N
O
3g
2.84
1.18
0.99
0.89
2.21
3.02
3.02
3.00
9.04
9.0
8.5
8.0
7.5
7.0
6.5
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

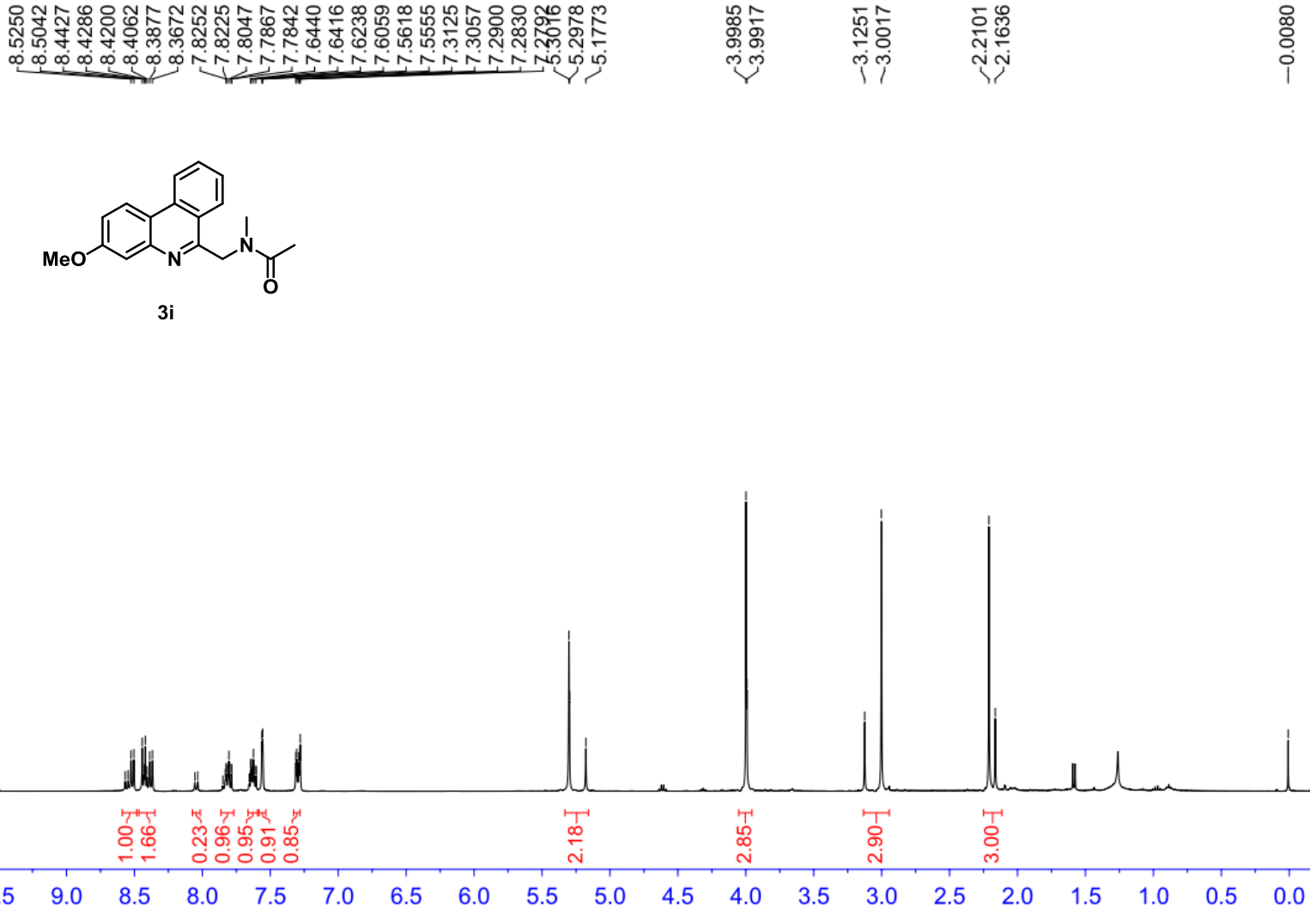

172.5524
170.5138
160.1796
160.1177
157.6350
154.3757
150.3716
149.6899
145.1150
131.4842
123.7552
123.3143
123.1086
122.8124
121.8056
119.3598
118.6974
118.5746
110.2024
109.0861
55.8698
55.8282
54.3871
50.8491
35.4379
35.3607
35.2842
35.0668
31.5432
31.4888
21.9496
21.8034
t-Bu
MeO
N
N
O
3g
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


x10 5
+ESI 全扫描 (2.176 分钟) Frag=175.0V 2-75.d
351.20726
373.18915
381.21950
393.29629
430.91477
t-Bu
MeO
N
N
O
3g
计数 与 质荷比 (m/z)

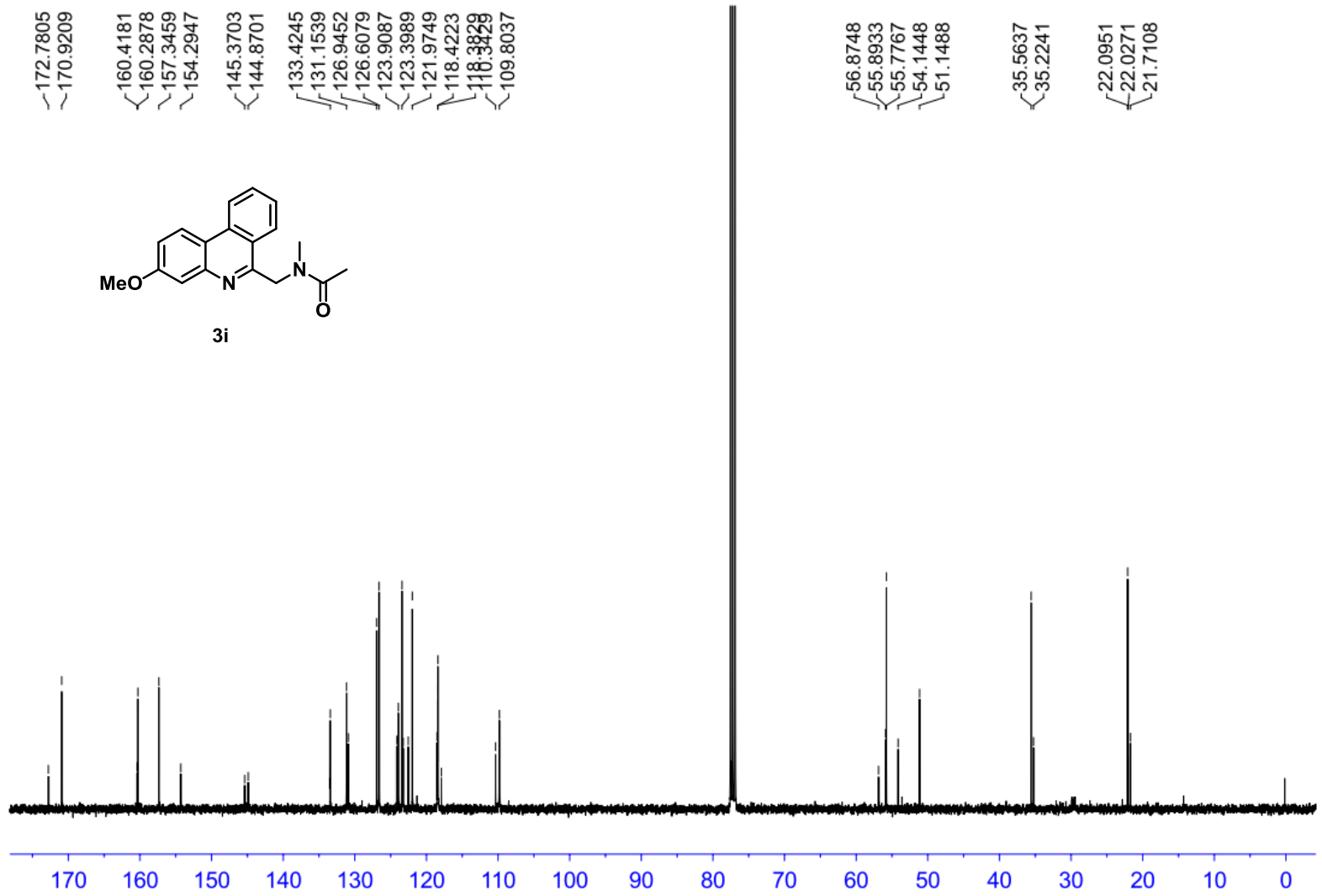

8.5818
8.5590
8.5181
8.4954
8.4736
8.4546
8.2321
8.2121
8.1566
8.1535
8.1365
7.9298
7.9238
7.7259
7.7053
7.6909
7.6766
7.6735
7.6576
7.6531
7.6373
7.6344
7.6198
7.4677
7.4615
7.4451
7.4389
5.2935
5.1323
3.9927
3.9755
3.1083
2.9675
2.1855
0.0000
OMe
N
N
O
3h
1.00
0.72
1.09
0.75
1.96
0.85
0.08
1.73
2.61
2.64
2.72
10.5
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

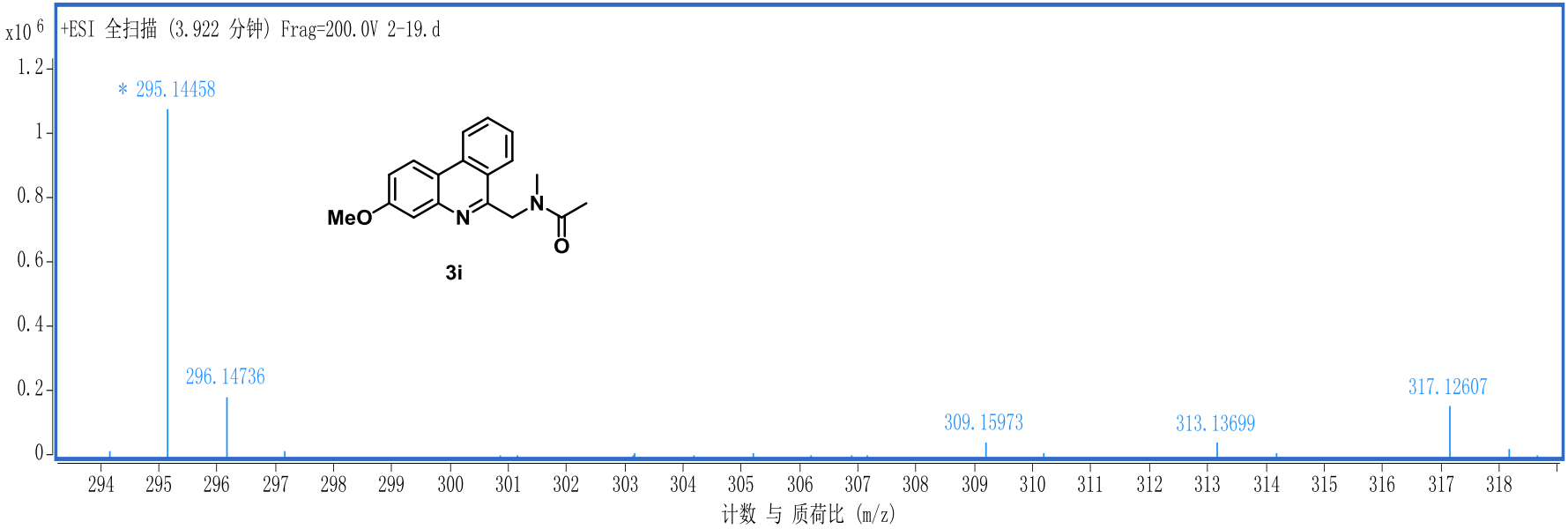

170.6851
167.3065
159.1447
158.7837
156.1088
152.8123
142.6583
142.2066
129.6306
127.7042
127.3950
127.3104
126.0380
124.4664
123.8715
122.4758
121.5624
106.1623
104.5743
55.9667
51.1764
35.1279
34.9619
21.8250
21.5230
OMe
N
N
O
3h
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

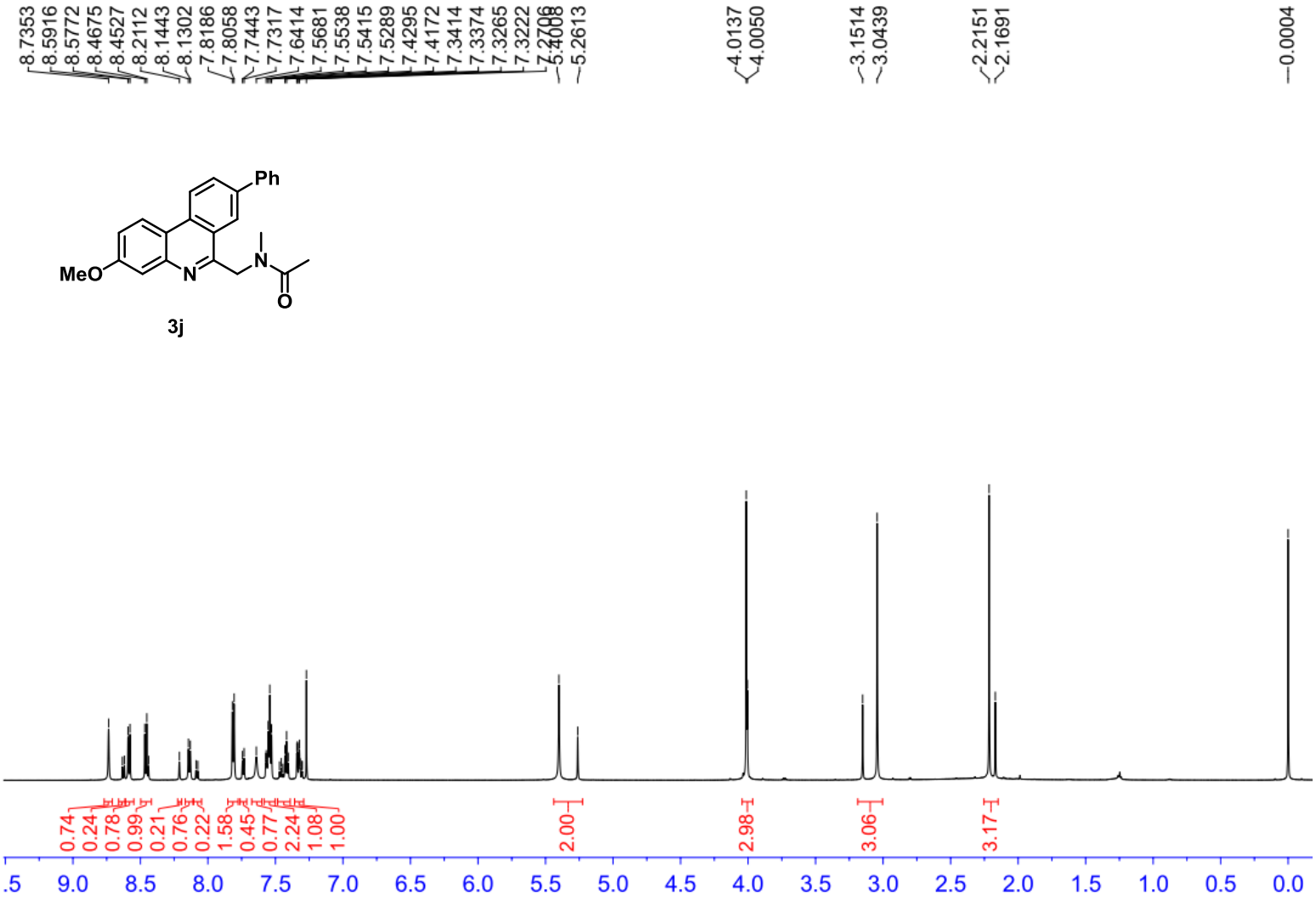

x10 6
+ESI 全扫描 (3.615 分钟) Frag=200.0V 2-22.d
* 295.14459
296.14755
317.12591
OMe
N
N
O
3h
1.4
1.2
1
0.8
0.6
0.4
0.2
0
292 293 294 295 296 297 298 299 300 301 302 303 304 305 306 307 308 309 310 311 312 313 314 315 316 317 318 319 320 321 322
计数 与 质荷比 (m/z)

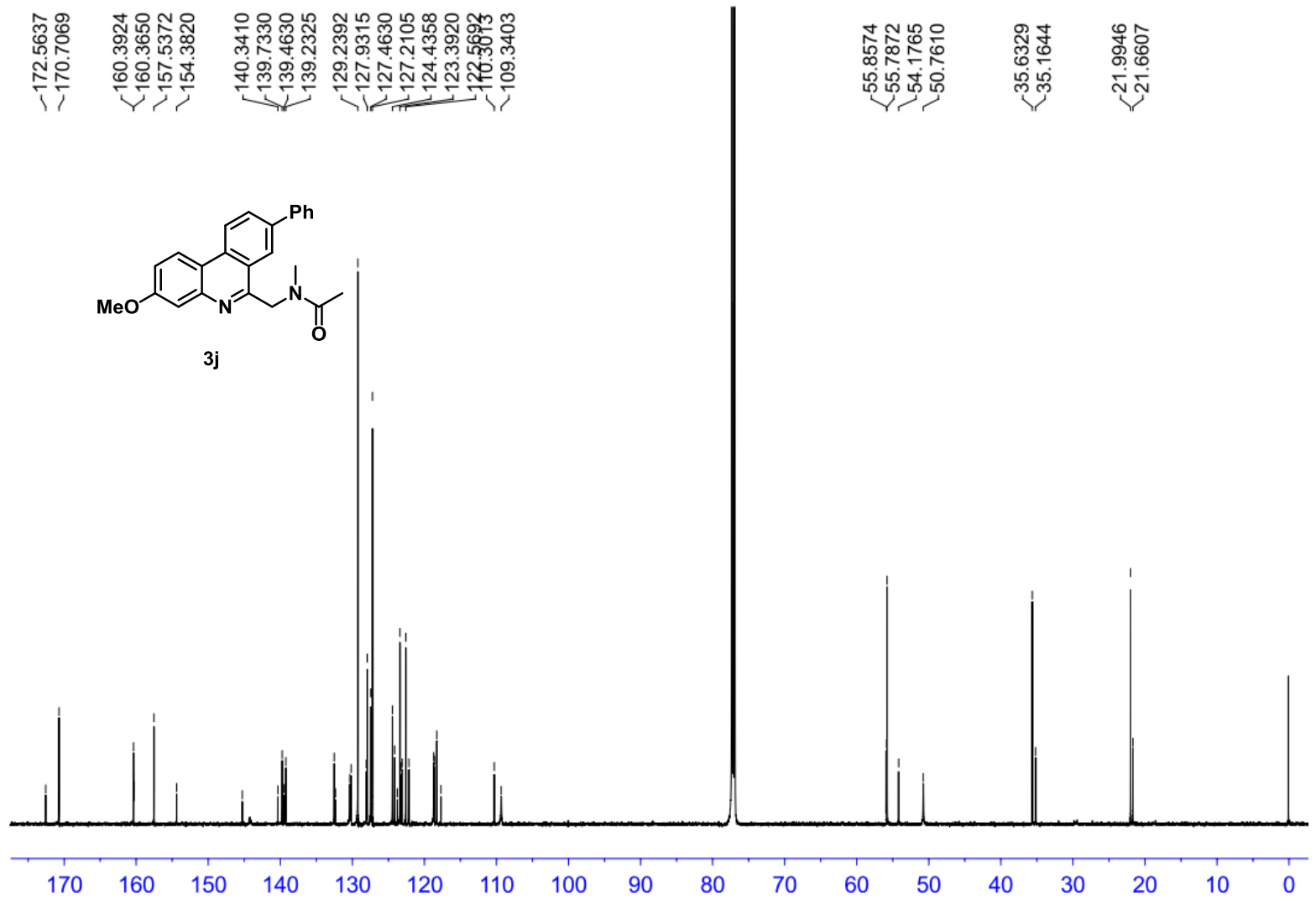

8.5250
8.5042
8.4427
8.4286
8.4200
8.4062
8.3877
8.3672
7.8252
7.8225
7.8047
7.7867
7.7842
7.6440
7.6416
7.6238
7.6059
7.5618
7.5555
7.3125
7.3057
7.2900
7.2830
7.2792
7.2676
7.3016
5.2978
5.1773
3.9985
3.9917
3.1251
3.0017
2.2101
2.1636
0.0080
MeO
N
N
O
1.00
1.66
0.23
0.96
0.95
0.91
0.85
2.18
2.85
2.90
3.00
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

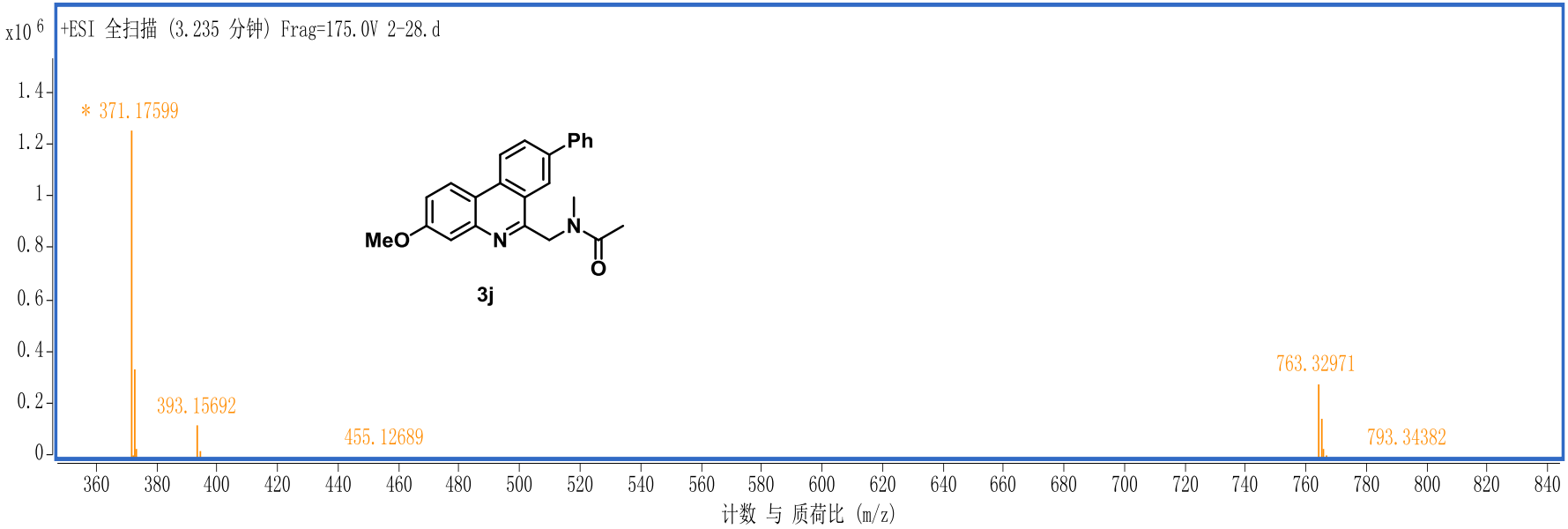
3i

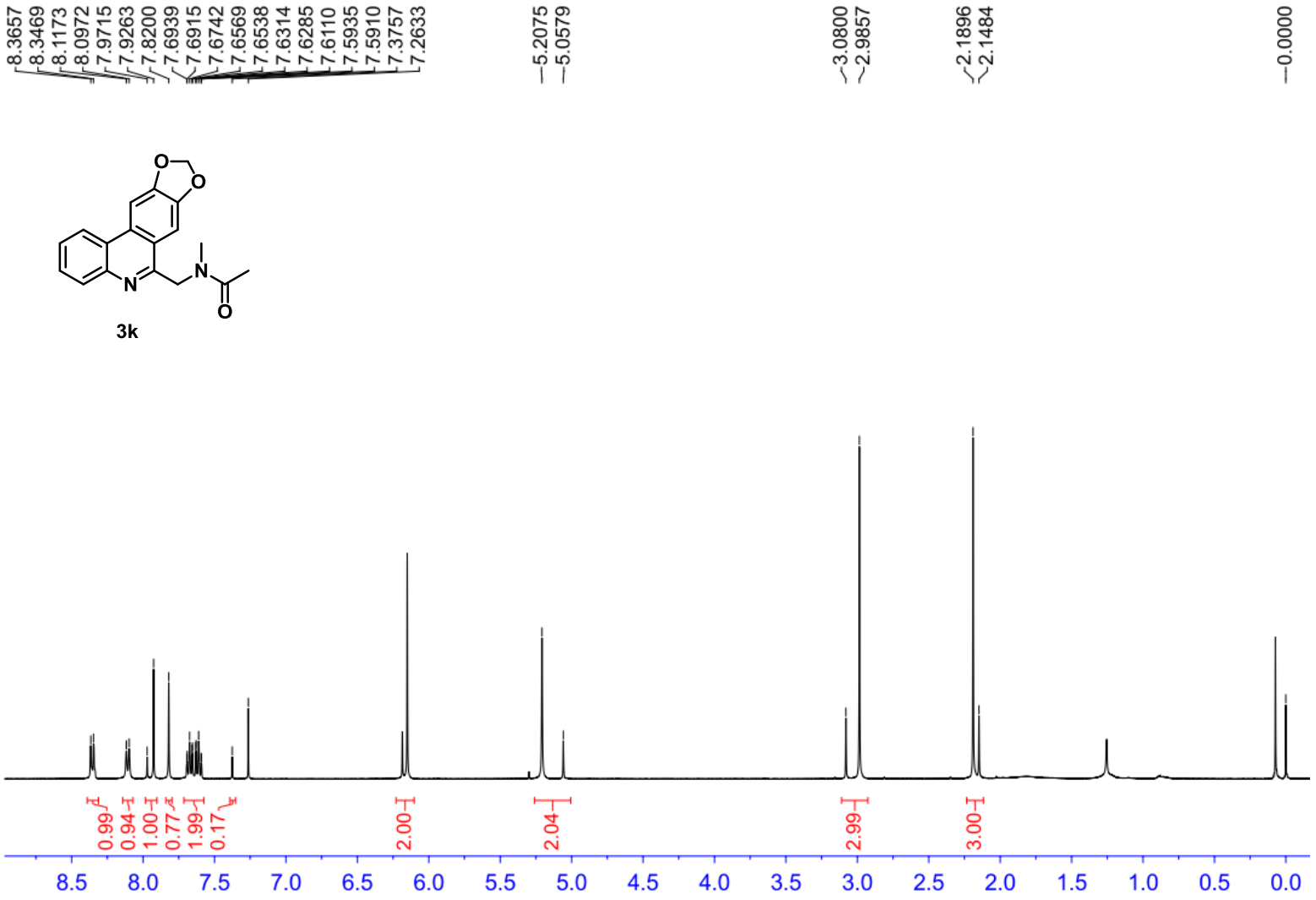

172.7805
170.9209
160.4181
160.2878
157.3459
154.2947
145.3703
144.8701
133.4245
131.1539
126.9452
126.6079
123.9087
123.3989
121.9749
118.4223
118.3829
110.3429
109.8037
56.8748
55.8933
55.7767
54.1448
51.1488
35.5637
35.2241
22.0951
22.0271
21.7108
MeO
N
N
O
3i
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

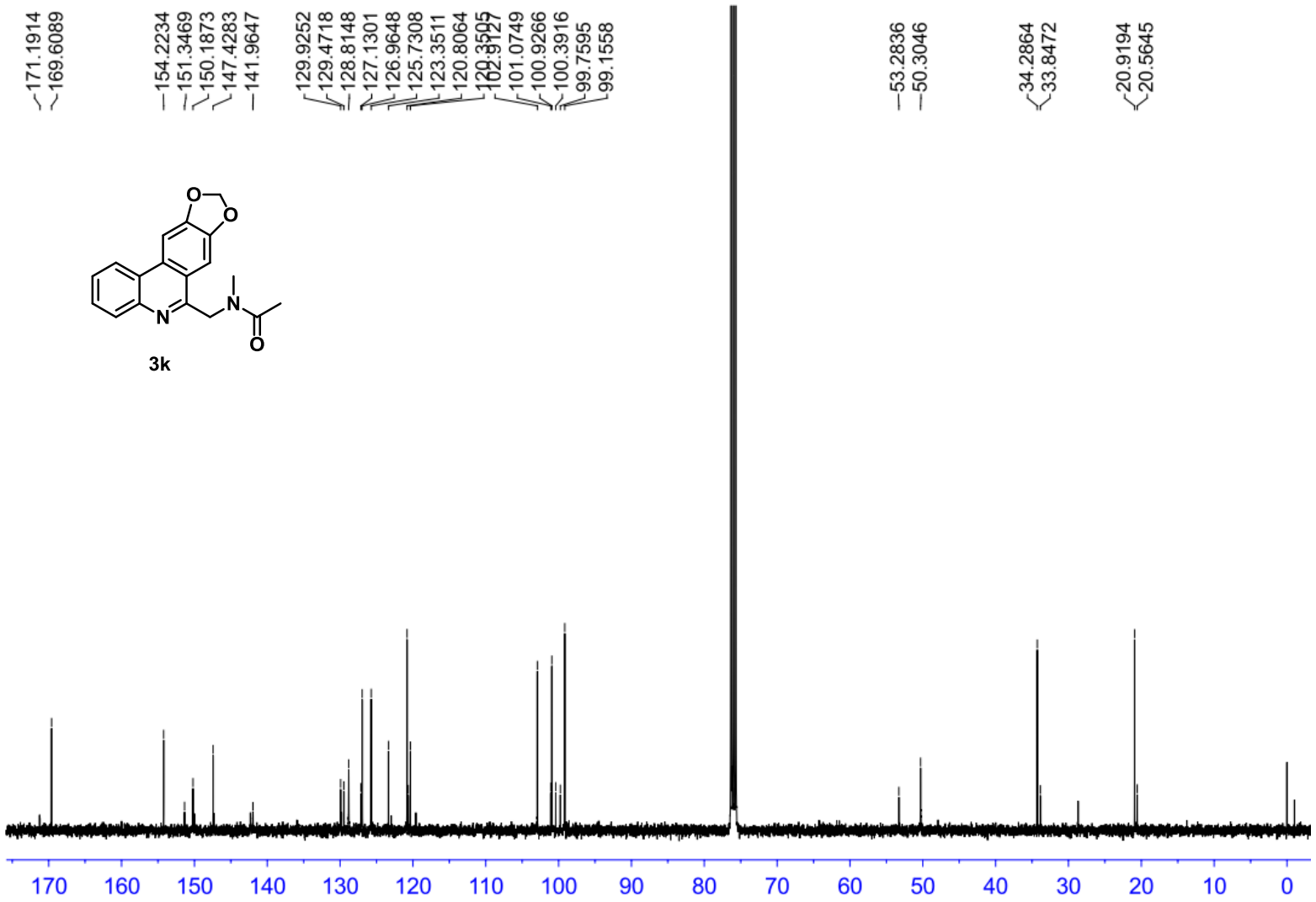

x10 6
+ESI 全扫描 (3.922 分钟) Frag=200.0V 2-19.d
1.2
1
0.8
0.6
0.4
0.2
0
* 295.14458
296.14736
309.15973
313.13699
317.12607
MeO
N
N
O
3i
294 295 296 297 298 299 300 301 302 303 304 305 306 307 308 309 310 311 312 313 314 315 316 317 318
计数 与 质荷比 (m/z)

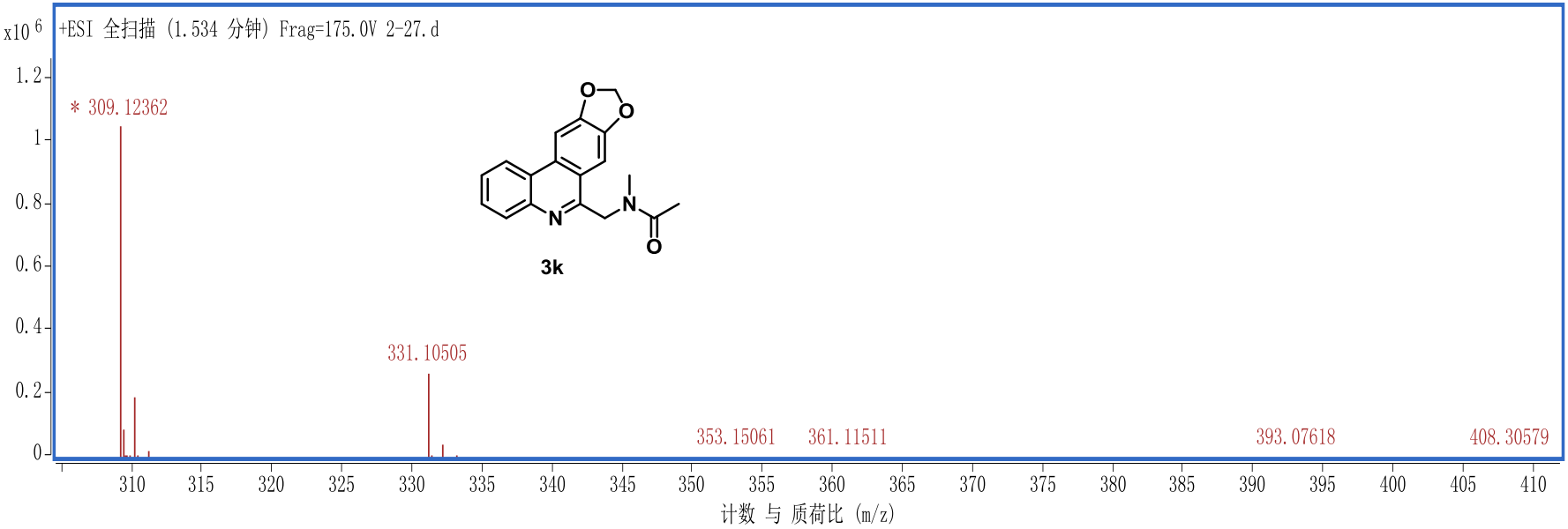

8.7353
8.5916
8.5772
8.4675
8.4527
8.2112
8.1443
8.1302
7.8186
7.8058
7.7443
7.7317
7.6414
7.5681
7.5538
7.5415
7.5289
7.4295
7.4172
7.3414
7.3374
7.3265
7.3222
5.4008
5.2613
4.0137
4.0050
3.1514
3.0439
2.2151
2.1691
0.0004
Ph
MeO
N
N
O
3j
0.74
0.24
0.78
0.99
0.21
0.76
0.22
1.58
0.45
0.77
2.24
1.08
1.00
2.00
2.98
3.06
3.17
.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

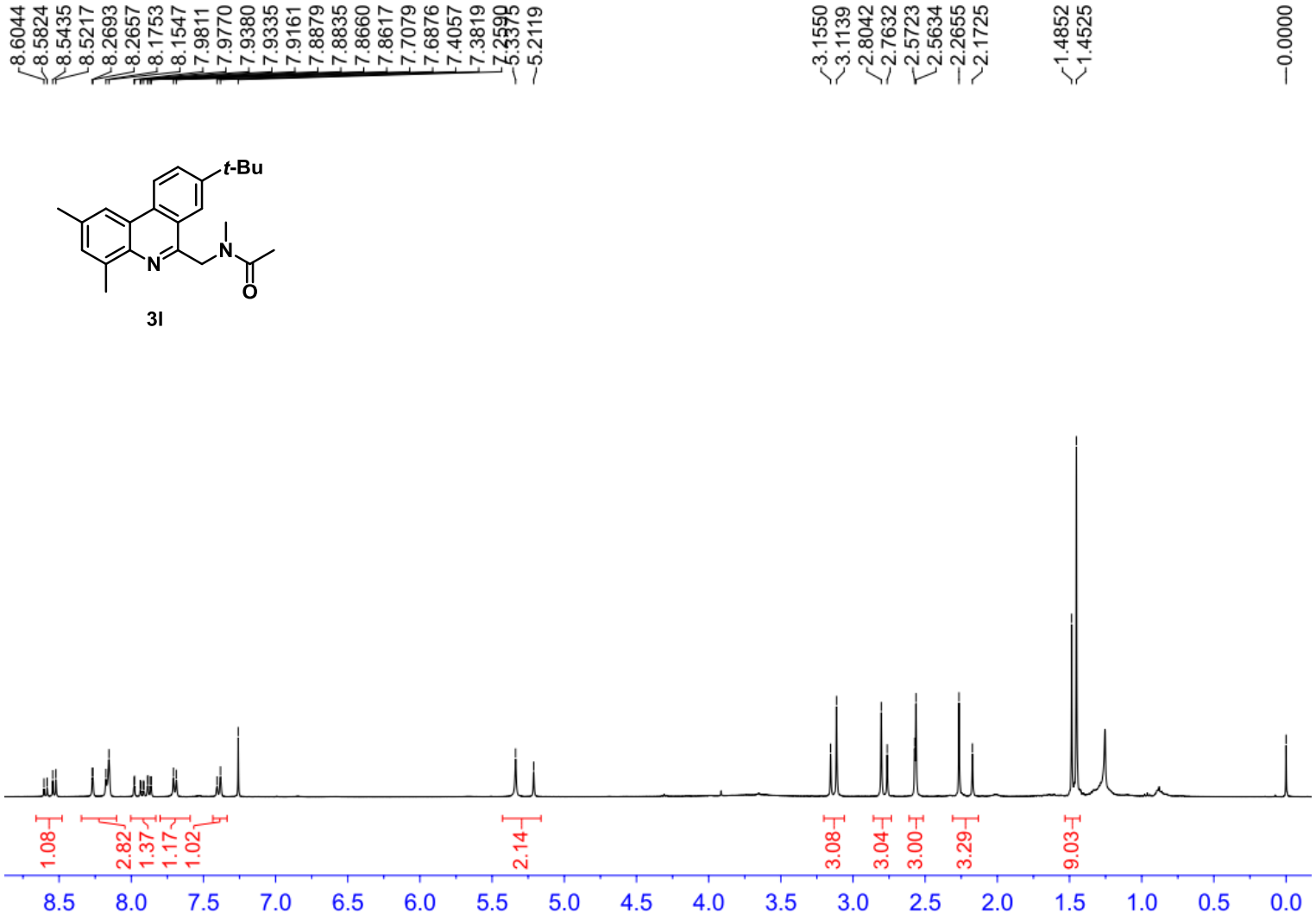

172.5637
170.7069
160.3924
160.3650
157.5372
154.3820
140.3410
139.7330
139.4630
139.2325
129.2392
127.9315
127.4630
127.2105
124.4358
123.3920
122.5692
110.3013
109.3403
55.8574
55.7872
54.1765
50.7610
35.6329
35.1644
21.9946
21.6607
Ph
MeO
N
N
O
3j
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

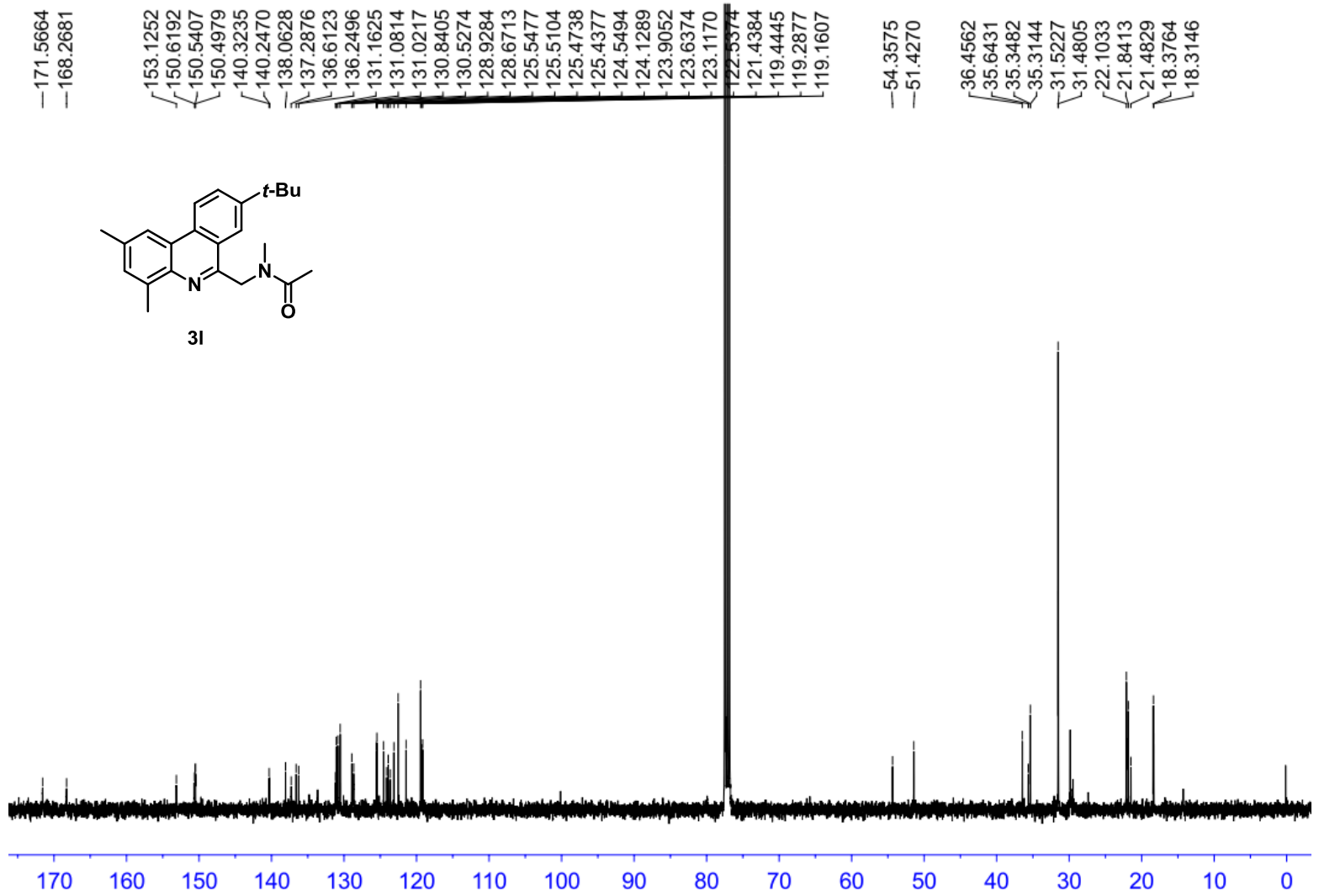

x10 6
+ESI 全扫描 (3.235 分钟) Frag=175.0V 2-28.d
1.4
1.2
1
0.8
0.6
0.4
0.2
0
* 371.17599
393.15692
455.12689
763.32971
793.34382
Ph
MeO
N
N
O
3j
360 380 400 420 440 460 480 500 520 540 560 580 600 620 640 660 680 700 720 740 760 780 800 820 840
计数 与 质荷比 (m/z)

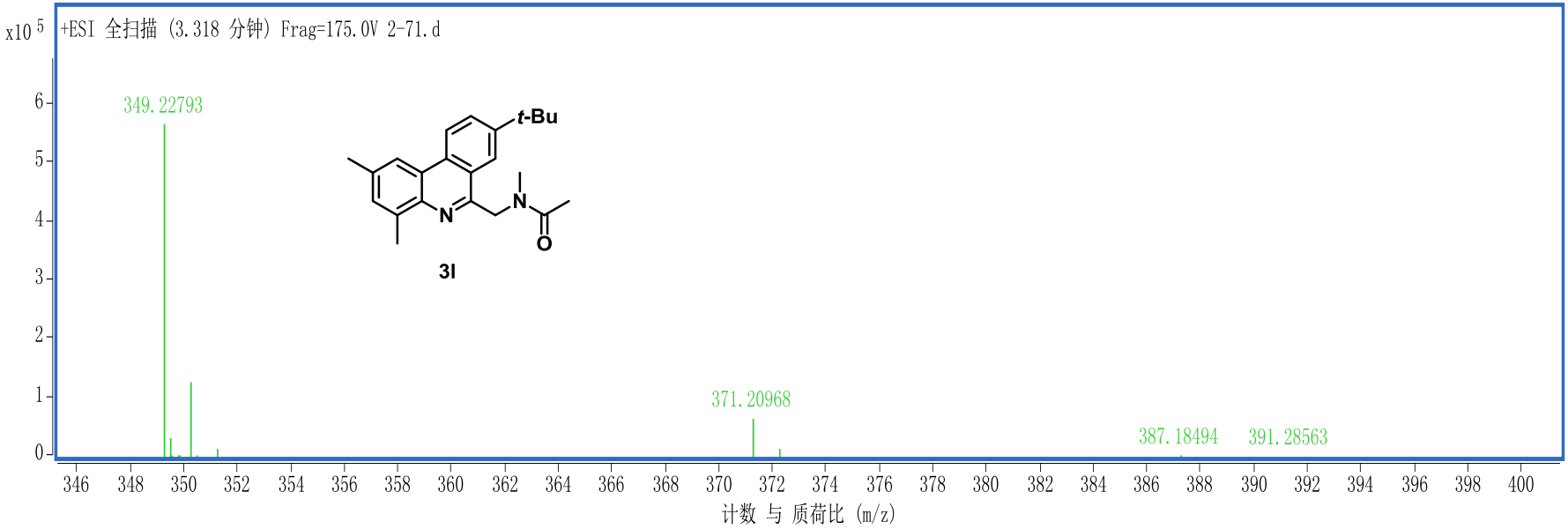

8.3657
8.3469
8.1173
8.0972
7.9715
7.9263
7.8200
7.6939
7.6915
7.6742
7.6569
7.6538
7.6314
7.6285
7.6110
7.5935
7.5910
7.3757
7.2633
5.2075
5.0579
3.0800
2.9857
2.1896
2.1484
0.0000
O
O
N
N
O
3k
0.99
0.94
1.00
0.77
1.99
0.17
2.00
2.04
2.99
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

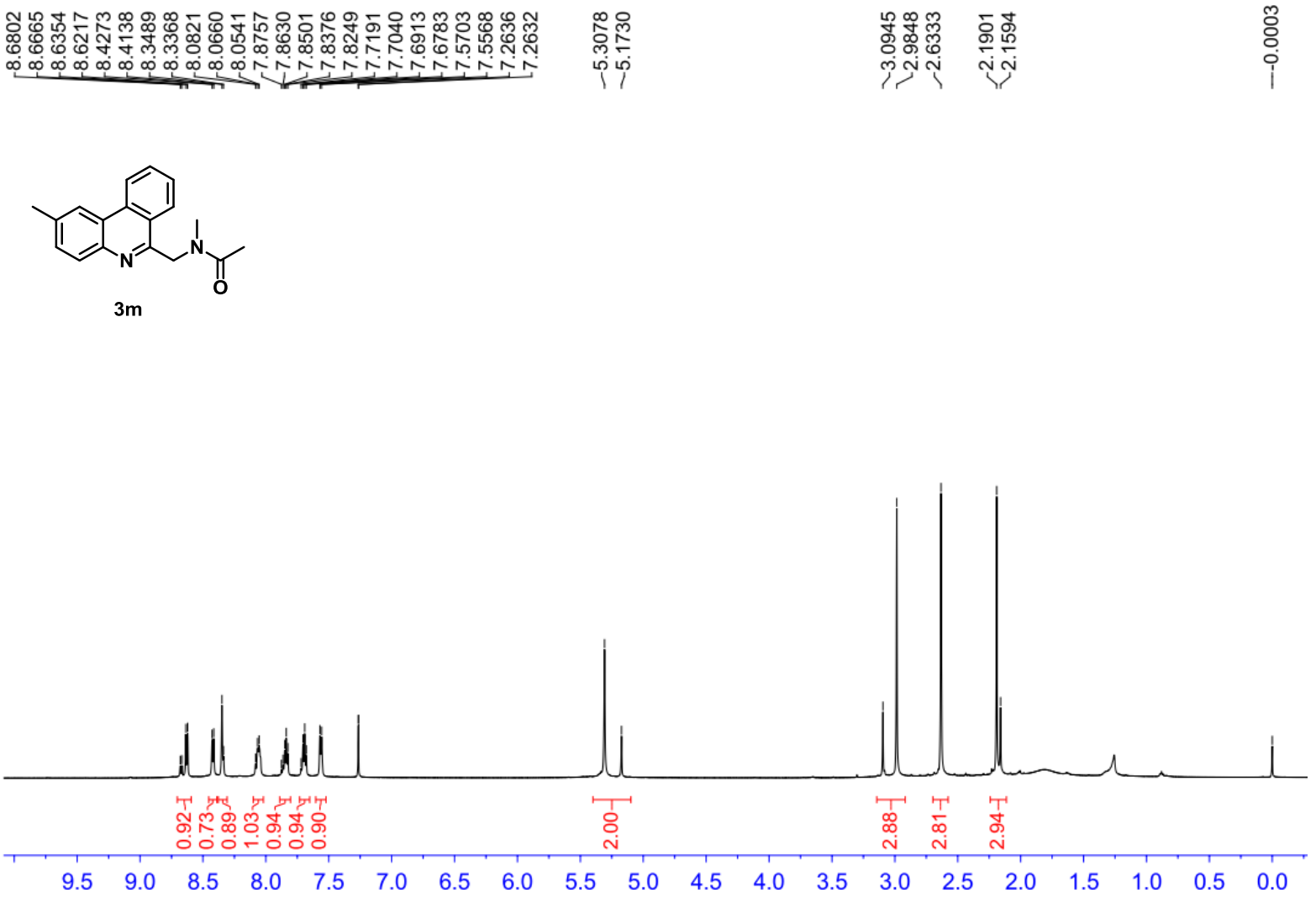

171.1914
169.6089
154.2234
151.3469
150.1873
147.4283
141.9647
129.9252
129.4718
128.8148
127.1301
126.9648
125.7308
123.3511
120.8064
101.0749
100.9266
100.3916
99.7595
99.1558
53.2836
50.3046
34.2864
33.8472
20.9194
20.5645
O
O
N
N
O
3k
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

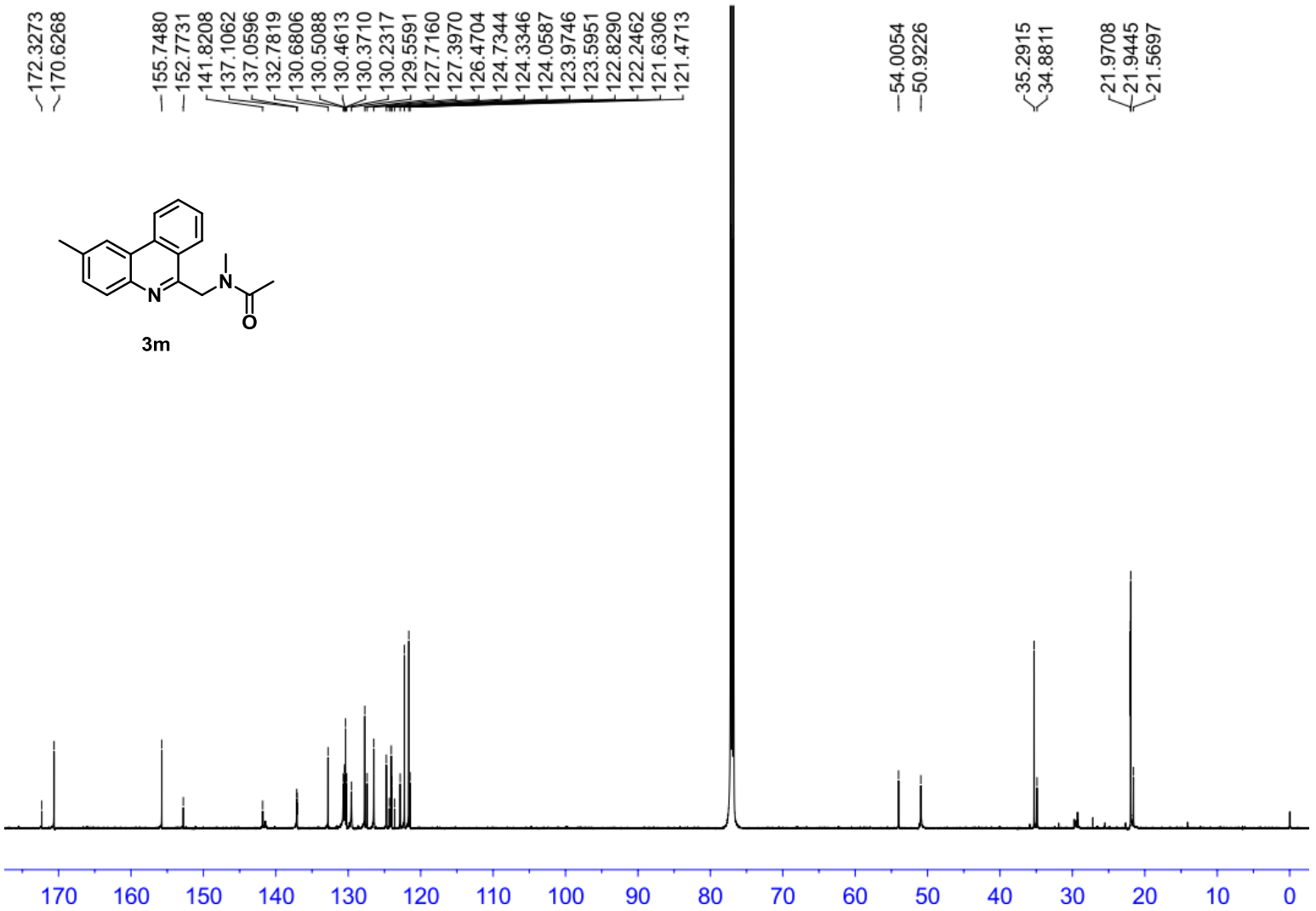

x10 6
+ESI 全扫描 (1.534 分钟) Frag=175.0V 2-27.d
1.2
1
0.8
0.6
0.4
0.2
0
* 309.12362
331.10505
353.15061
361.11511
393.07618
408.30579
O
O
N
N
O
3k
310
315
320
325
330
335
340
345
350
355
360
365
370
375
380
385
390
395
400
405
410
计数 与 质荷比 (m/z)

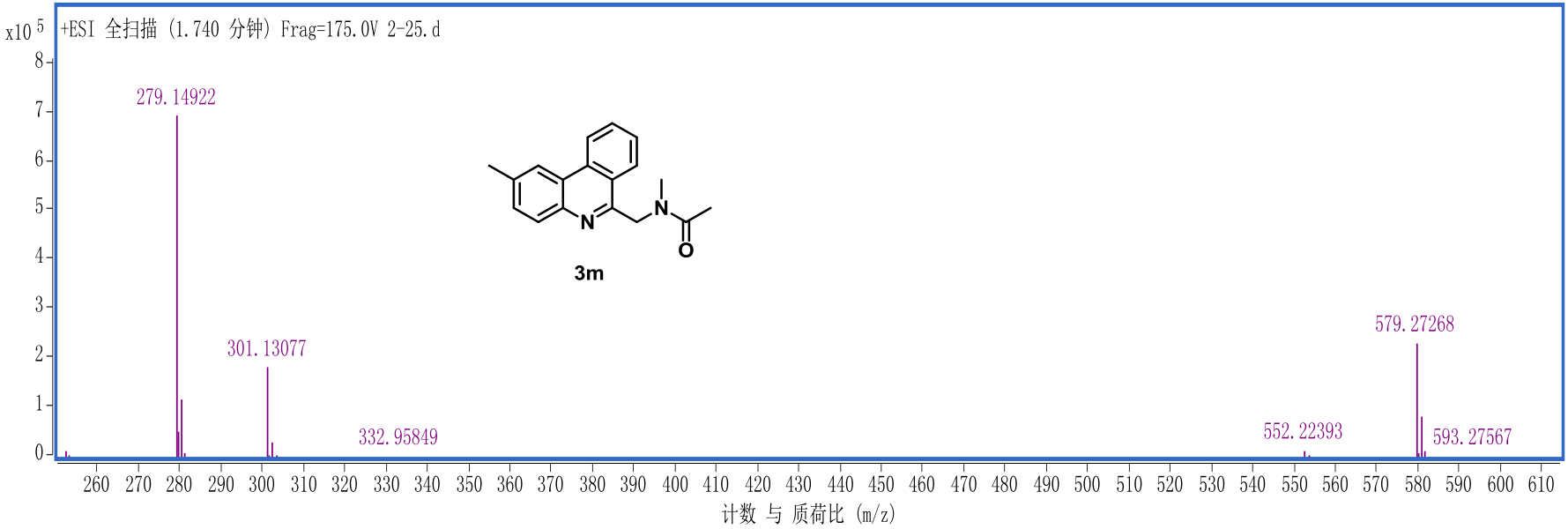

8.6044
8.5824
8.5435
8.5217
8.2693
8.2657
8.1753
8.1547
7.9811
7.9770
7.9380
7.9335
7.9161
7.8879
7.8835
7.8660
7.8617
7.7079
7.6876
7.4057
7.3819
5.3375
5.2119
3.1550
3.1139
2.8042
2.7632
2.5723
2.5634
2.2655
2.1725
1.4852
1.4525
0.0000
t-Bu
N
N
O
3l
1.08
2.82
1.37
1.17
1.02
2.14
3.08
3.04
3.00
3.29
9.03
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

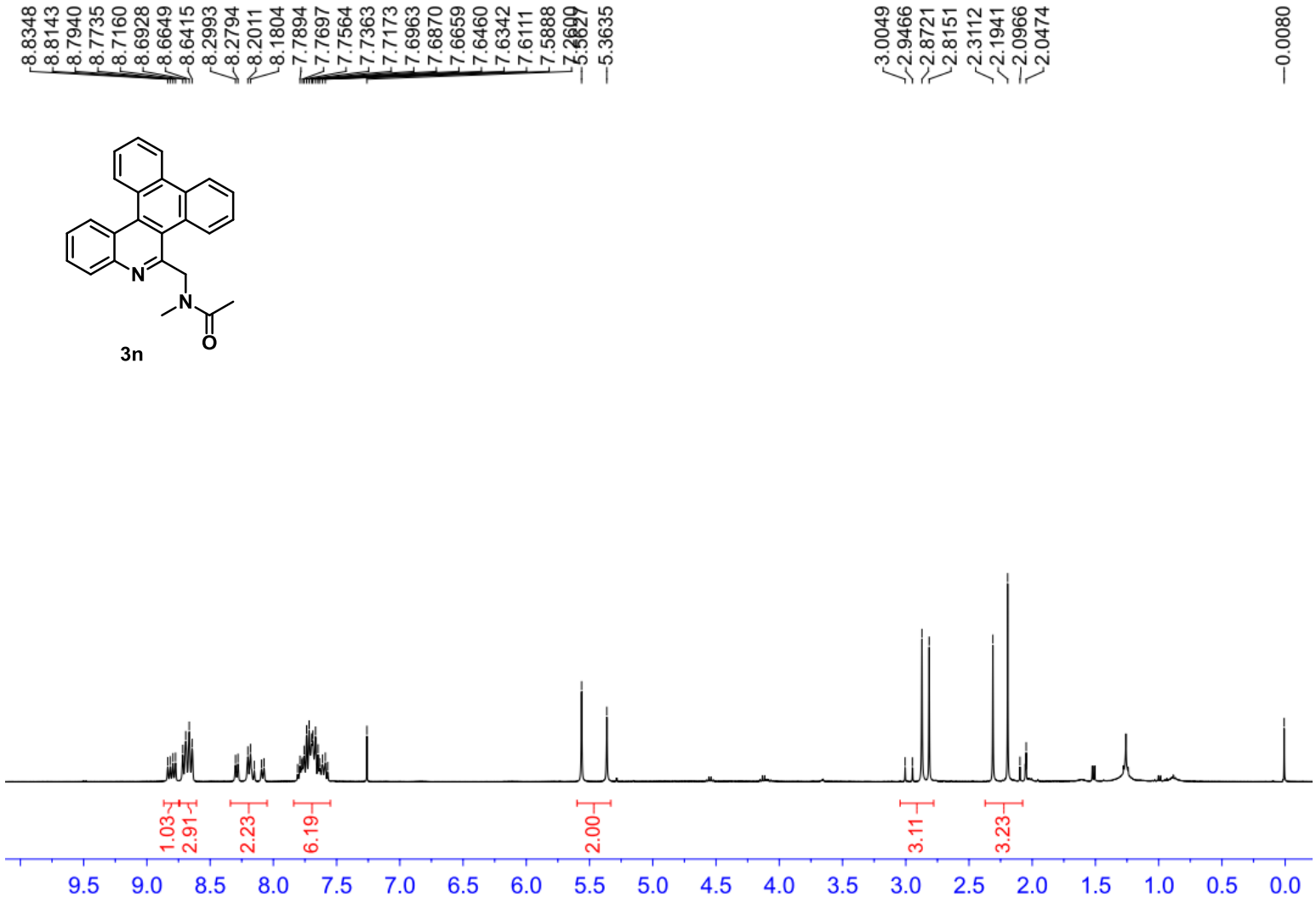

171.5664
168.2681
153.1252
150.6192
150.5407
150.4979
140.3235
140.2470
138.0628
137.2876
136.6123
136.2496
131.1625
131.0814
131.0217
130.8405
130.5274
128.9284
128.6713
125.5477
125.5104
125.4738
125.4377
124.5494
124.1289
123.9052
123.6374
123.1170
121.4384
119.4445
119.2877
119.1607
54.3575
51.4270
36.4562
35.6431
35.3482
35.3144
31.5227
31.4805
22.1033
21.8413
21.4829
18.3764
18.3146
t-Bu
N
N
O
3l
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

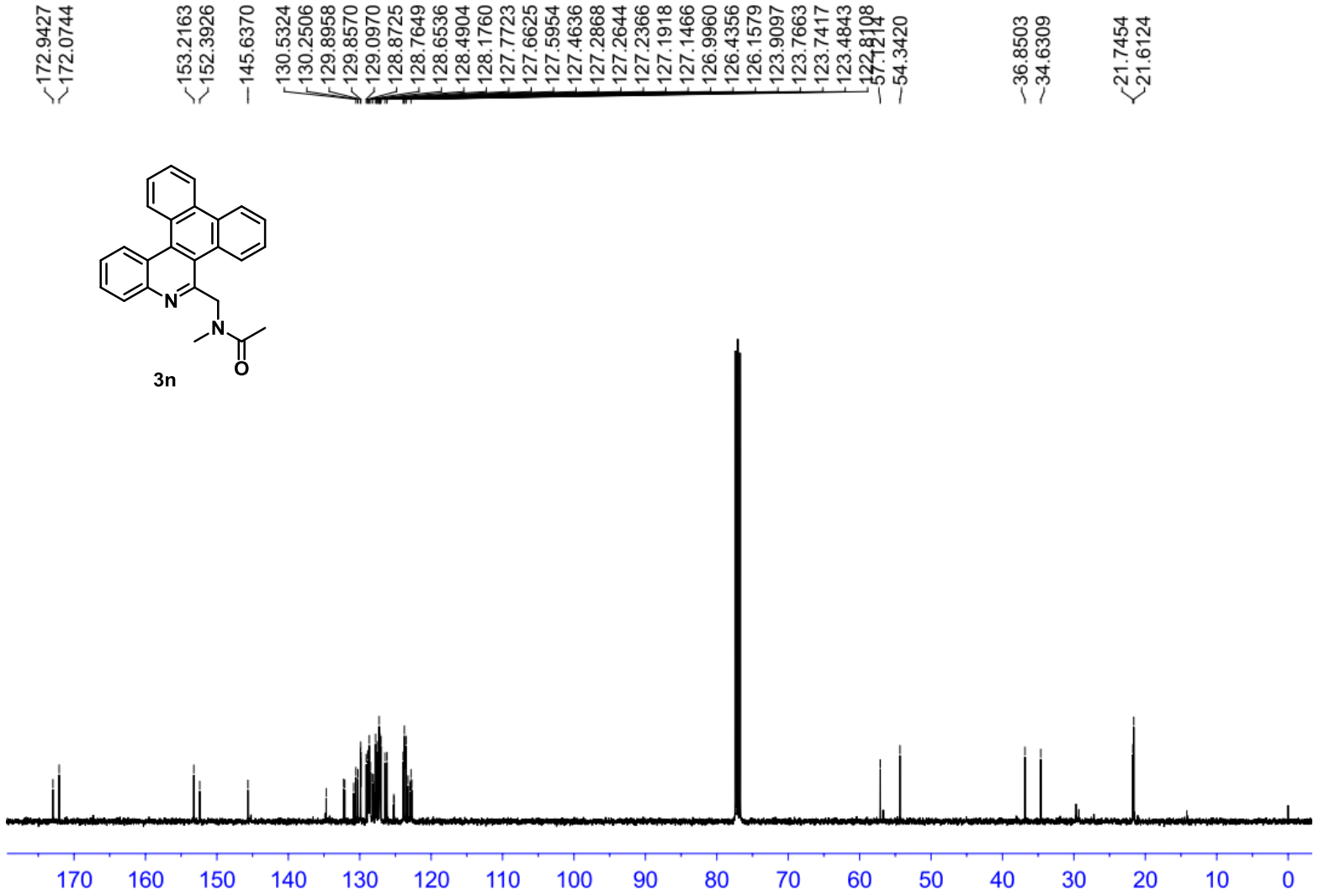

x10 5
+ESI 全扫描 (3.318 分钟) Frag=175.0V 2-71.d
349.22793
371.20968
387.18494
391.28563
t-Bu
N
N
O
3l
计数 与 质荷比 (m/z)

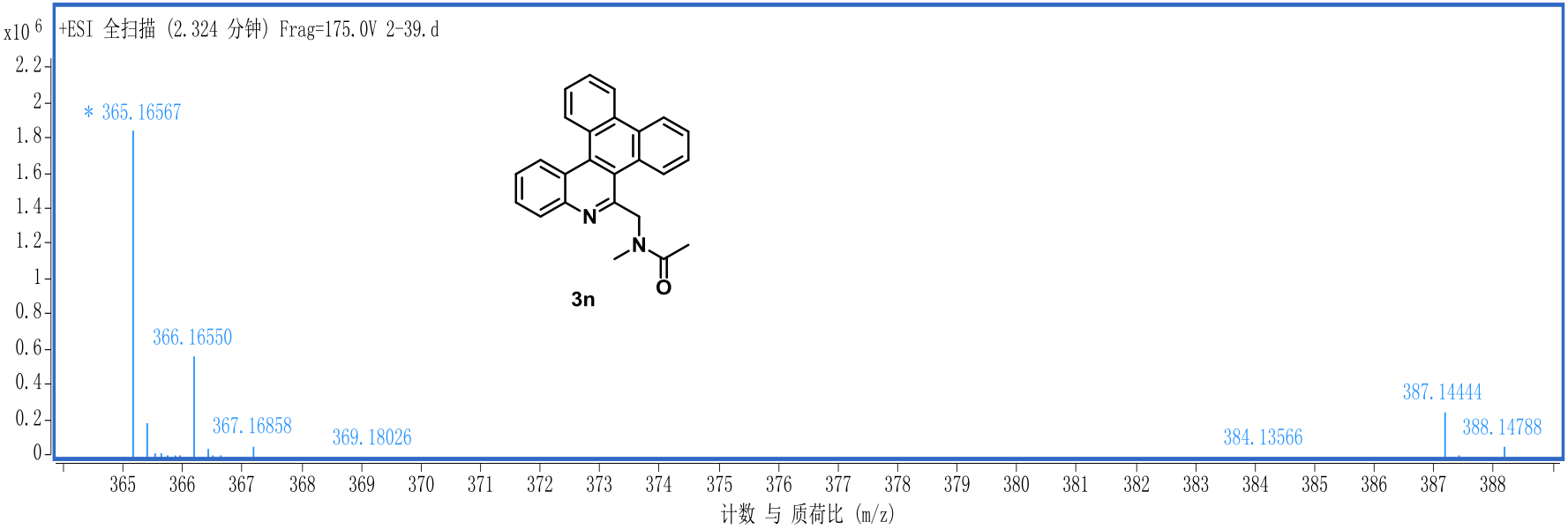

8.6802
8.6665
8.6354
8.6217
8.4273
8.4138
8.3489
8.3368
8.0821
8.0660
8.0541
7.8757
7.8630
7.8501
7.8376
7.8249
7.7191
7.7040
7.6913
7.6783
7.5703
7.5568
7.2636
7.2632
5.3078
5.1730
3.0945
2.9848
2.6333
2.1901
2.1594
0.0003
N
N
O
3m
0.92
0.73
0.89
1.03
0.94
0.94
0.90
2.00
2.88
2.81
2.94
9.5
9.0
8.5
8.0
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

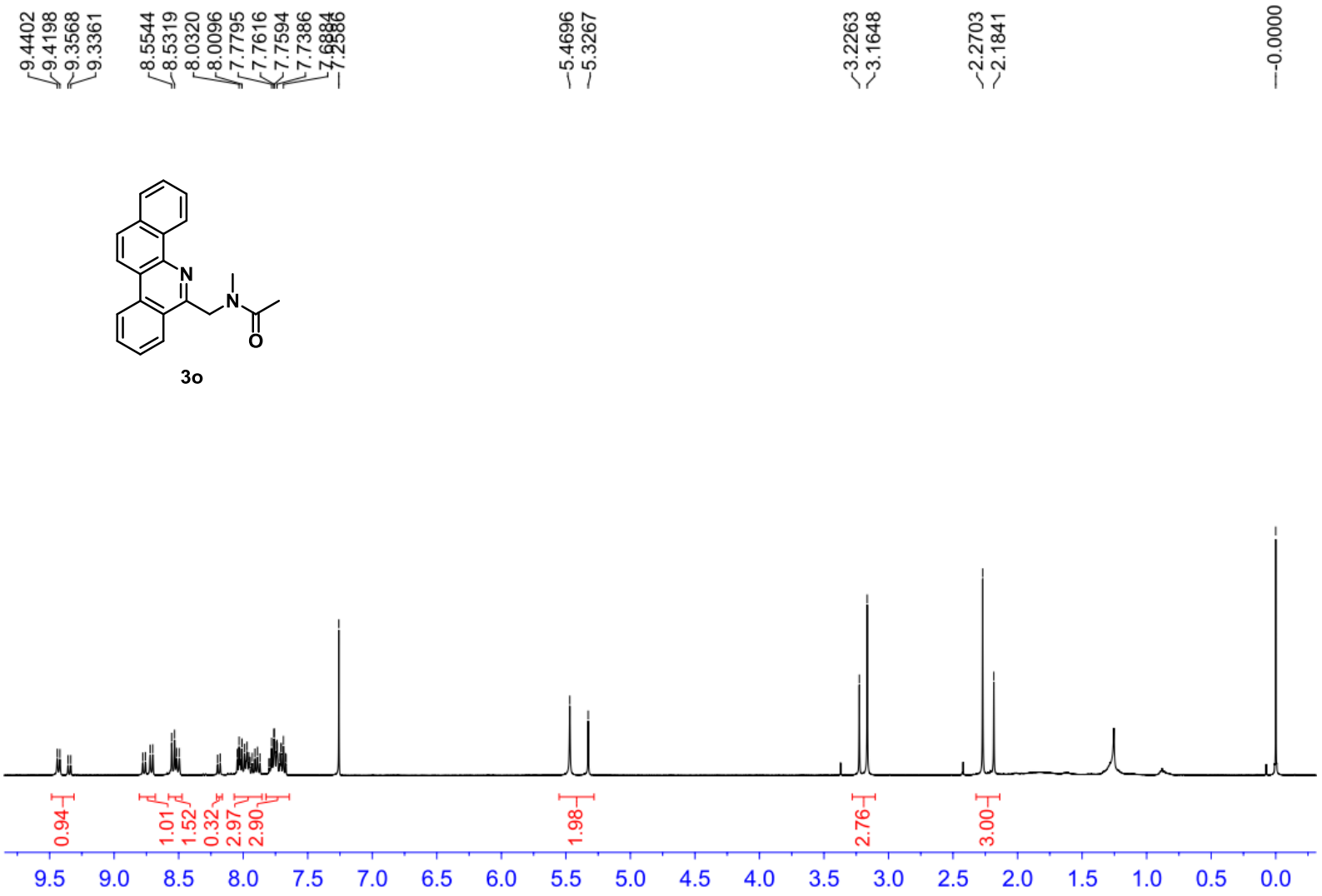

172.3273
170.6268
155.7480
152.7731
141.8208
137.1062
137.0596
132.7819
130.6806
130.5088
130.4613
130.3710
130.2317
129.5591
127.7160
127.3970
126.4704
124.7344
124.3346
124.0587
123.9746
123.5951
122.8290
122.2462
121.6306
121.4713
54.0054
50.9226
35.2915
34.8811
21.9708
21.9445
21.5697
N
N
O
3m
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

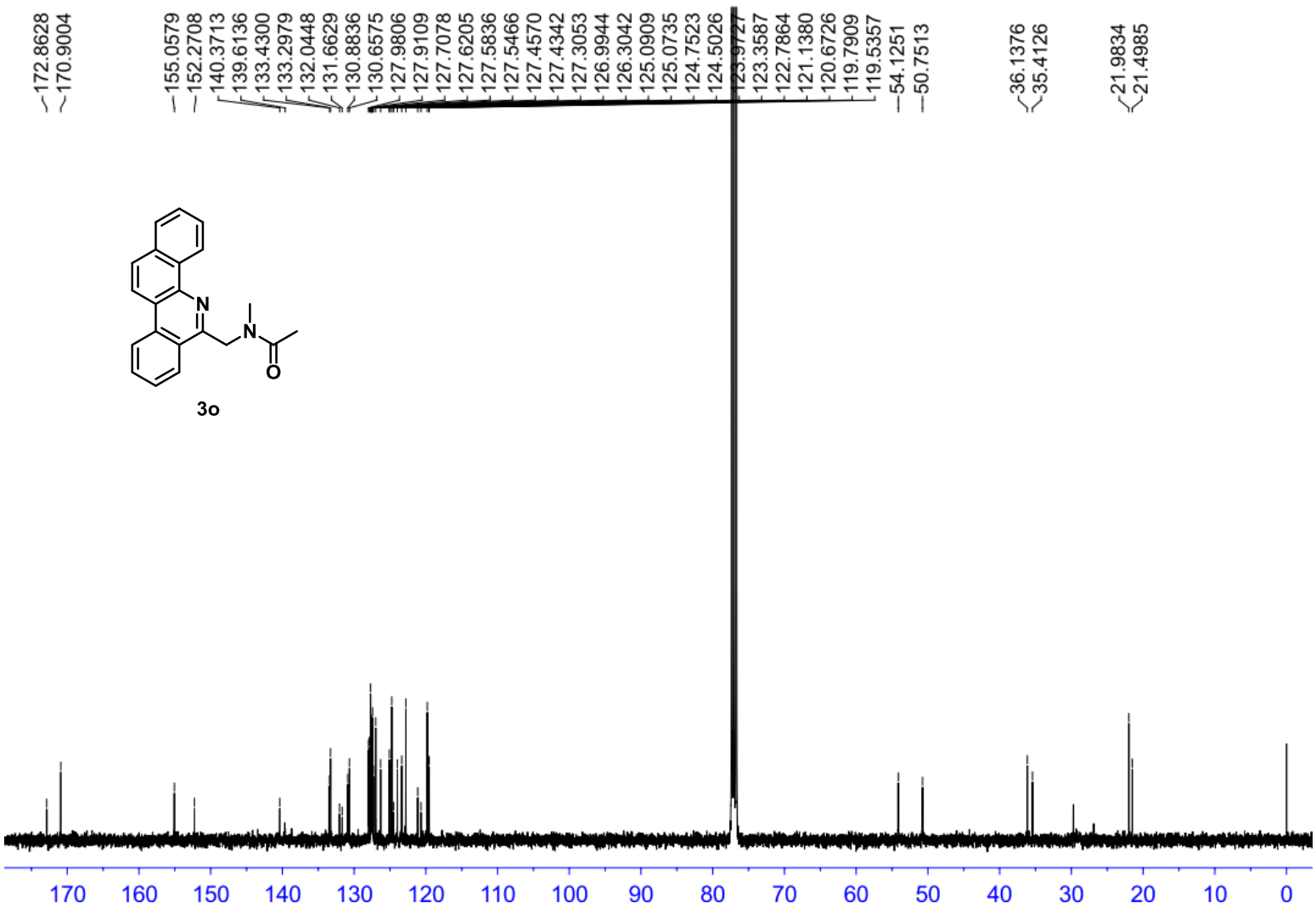

x10 5
+ESI 全扫描 (1.740 分钟) Frag=175.0V 2-25.d
279.14922
301.13077
332.95849
552.22393
579.27268
593.27567
3m
计数 与 质荷比 (m/z)

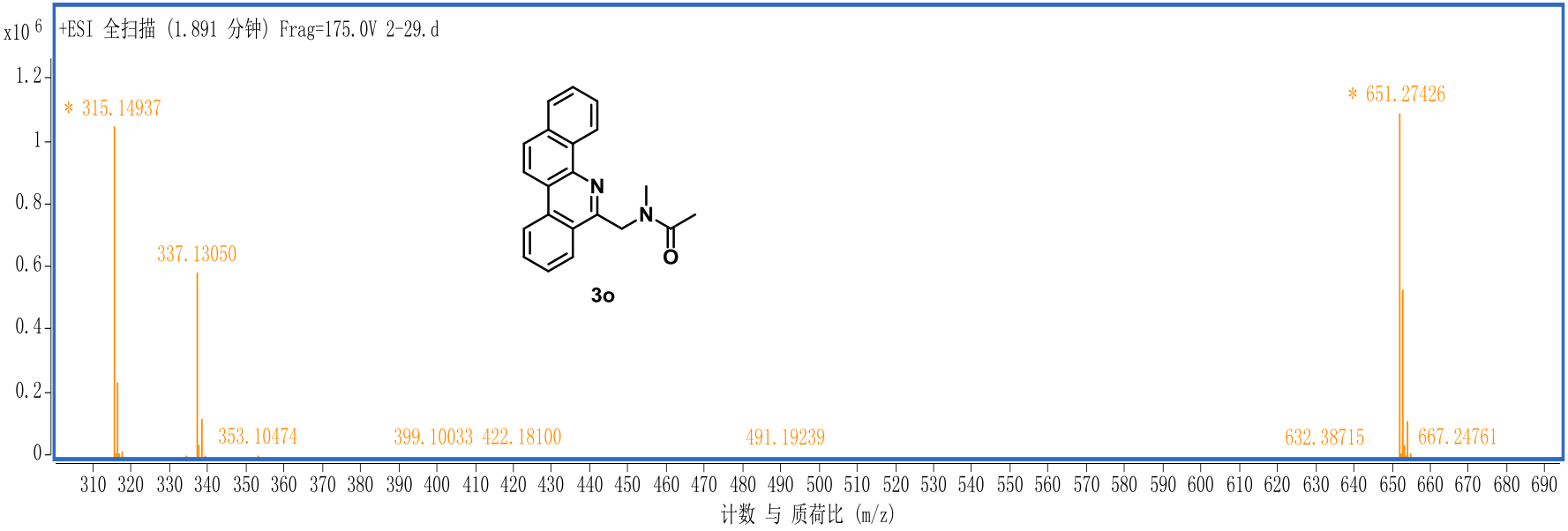

8.8348
8.8143
8.7940
8.7735
8.7160
8.6928
8.6649
8.6415
8.2993
8.2794
8.2011
8.1804
7.7894
7.7697
7.7564
7.7363
7.7173
7.6963
7.6870
7.6659
7.6460
7.6342
7.6111
7.5888
5.3635
3.0049
2.9466
2.8721
2.8151
2.3112
2.1941
2.0966
2.0474
0.0080
N
N
O
3n
1.03
2.91
2.23
6.19
2.00
3.11
3.23
9.5
9.0
8.5
8.0
7.5
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

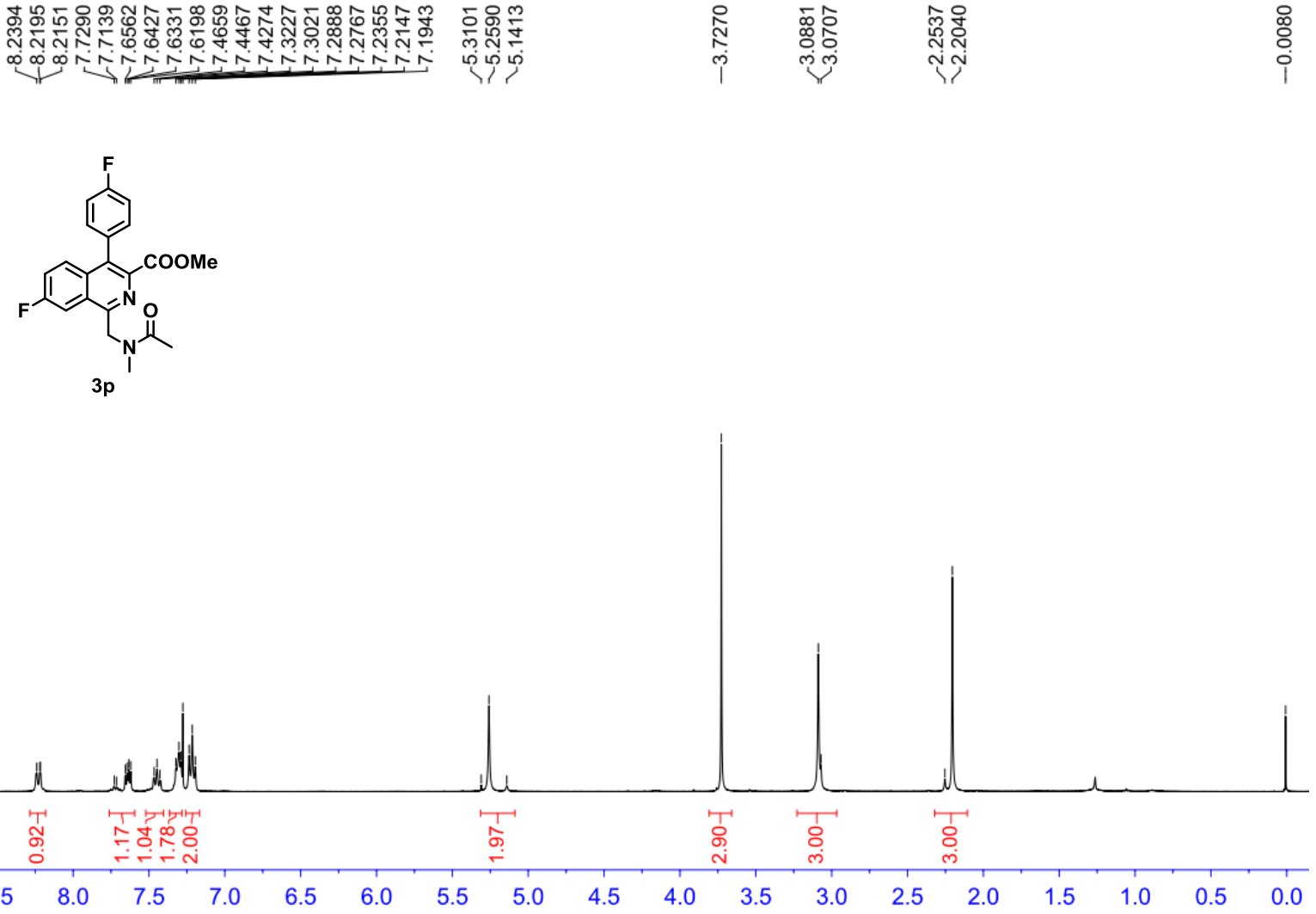

172.9427
172.0744
153.2163
152.3926
145.6370
130.5324
130.2506
129.8958
129.8570
129.0970
128.8725
128.7649
128.6536
128.4904
128.1760
127.7723
127.6625
127.5954
127.4636
127.2868
127.2644
127.2366
127.1918
127.1466
126.9960
126.4356
126.1579
123.9097
123.7663
123.7417
123.4843
122.8108
77.1214
54.3420
36.8503
34.6309
21.7454
21.6124
N
N
O
3n
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

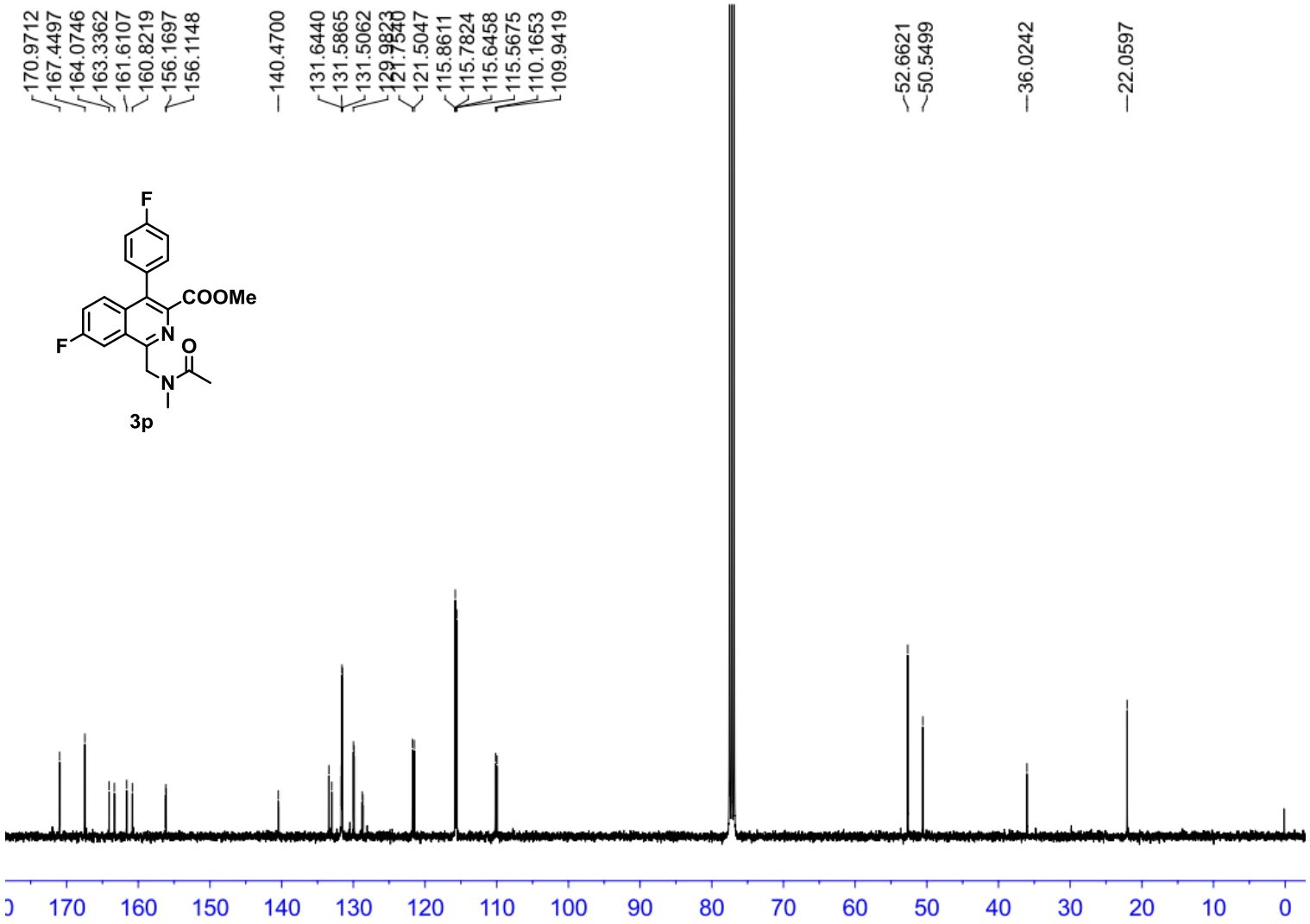

x10 6
+ESI 全扫描 (2.324 分钟) Frag=175.0V 2-39.d
* 365.16567
366.16550
367.16858
369.18026
384.13566
387.14444
388.14788
3n
计数 与 质荷比 (m/z)

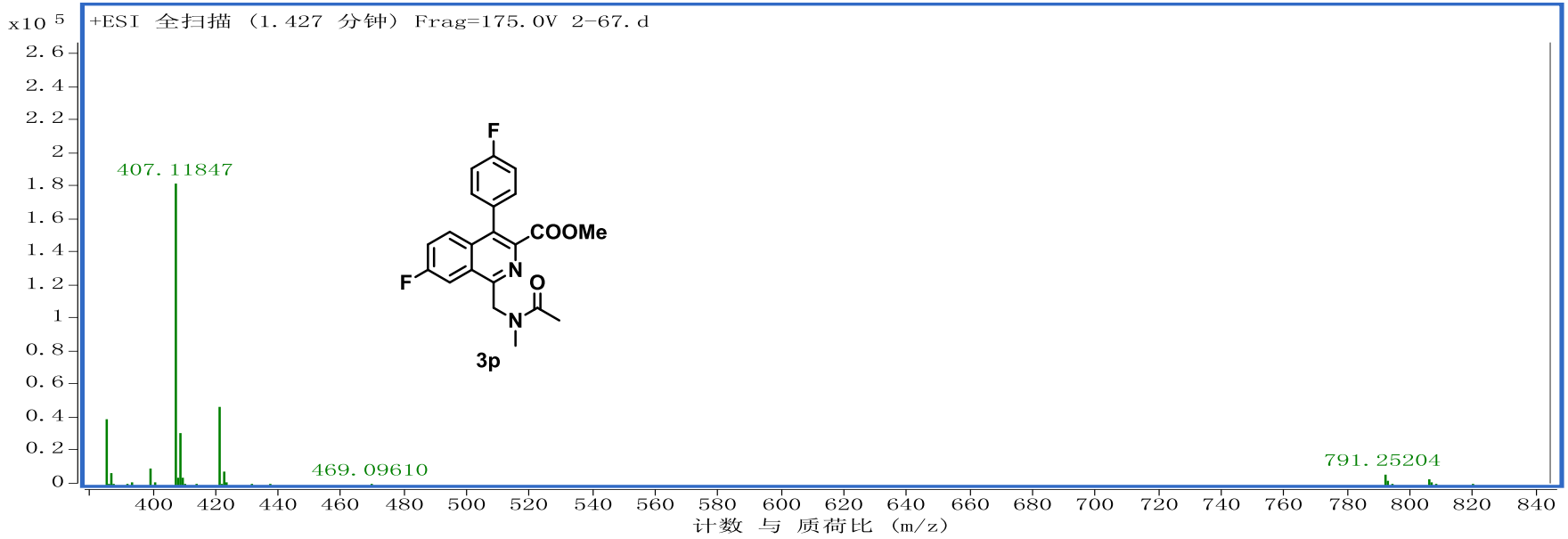

9.4402
9.4198
9.3568
9.3361
8.5544
8.5319
8.0320
8.0096
7.7795
7.7616
7.7594
7.7386
5.4696
5.3267
3.2263
3.1648
2.2703
2.1841
0.0000
N
N
O
3o
0.94
1.01
1.52
0.32
2.97
2.90
1.98
2.76
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

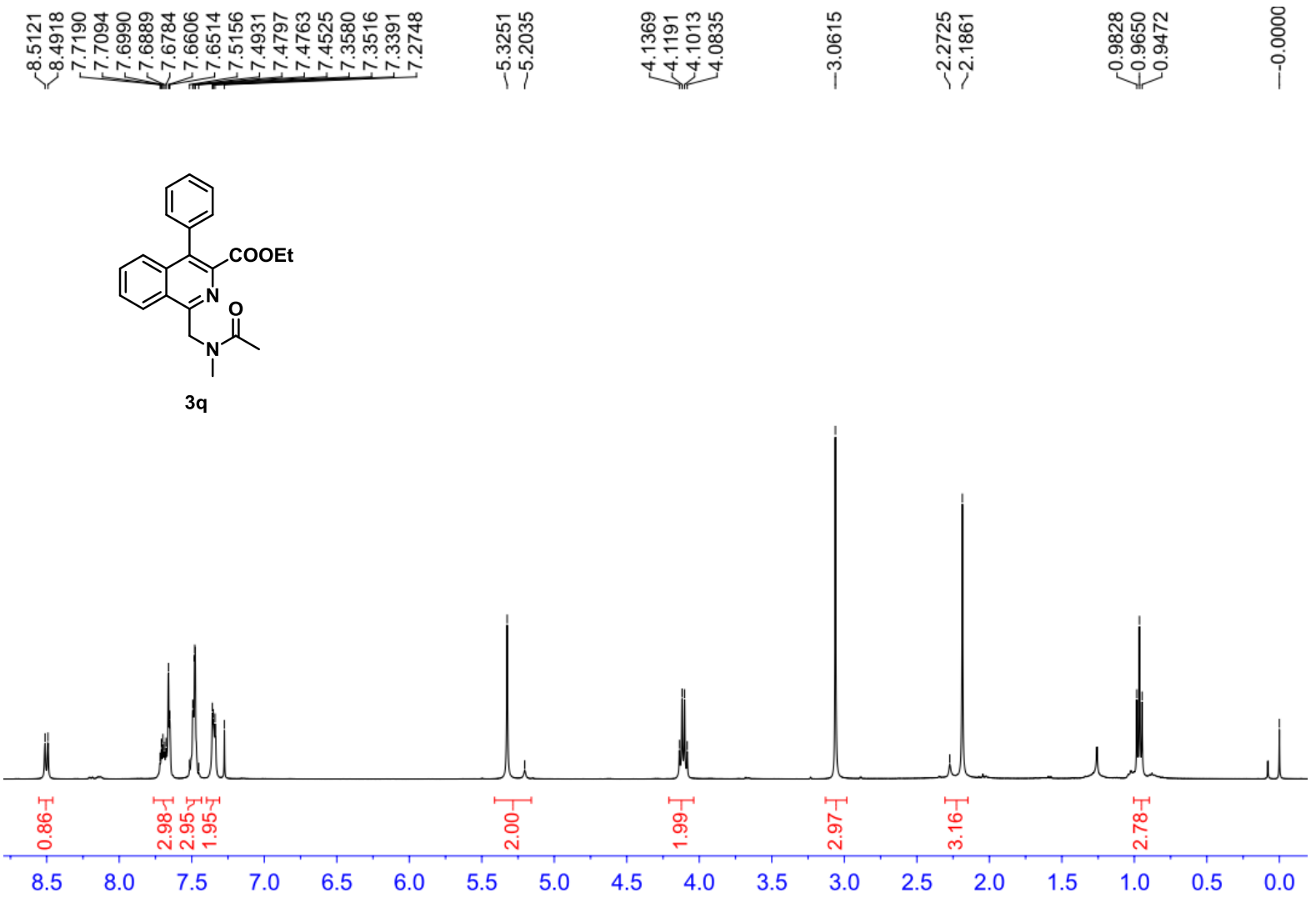

172.8628
170.9004
155.0579
152.2708
140.3713
139.6136
133.4300
133.2979
132.0448
131.6629
130.8836
130.6575
127.9806
127.9109
127.7078
127.6205
127.5836
127.5466
127.4570
127.4342
127.3053
126.9944
126.3042
125.0909
125.0735
124.7523
124.5026
123.9727
123.3587
122.7864
121.1380
120.6726
119.7909
119.5357
54.1251
50.7513
36.1376
35.4126
21.9834
21.4985
N
N
O
3o
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

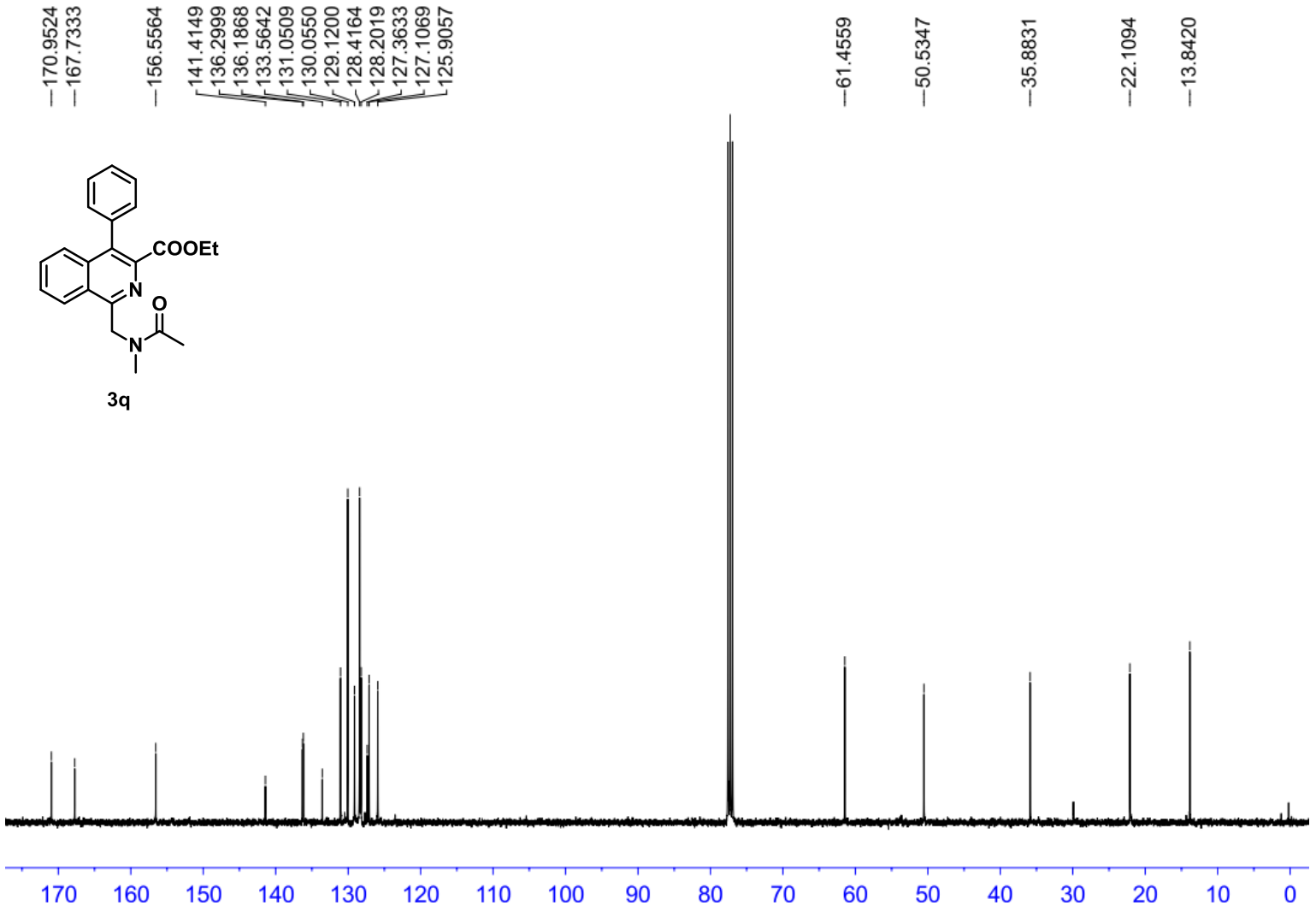

x10 6
+ESI 全扫描 (1.891 分钟) Frag=175.0V 2-29.d
1.2
1
0.8
0.6
0.4
0.2
0
* 315.14937
337.13050
353.10474
399.10033
422.18100
491.19239
632.38715
* 651.27426
667.24761
N
N
O
3o
310 320 330 340 350 360 370 380 390 400 410 420 430 440 450 460 470 480 490 500 510 520 530 540 550 560 570 580 590 600 610 620 630 640 650 660 670 680 690
计数 与 质荷比 (m/z)

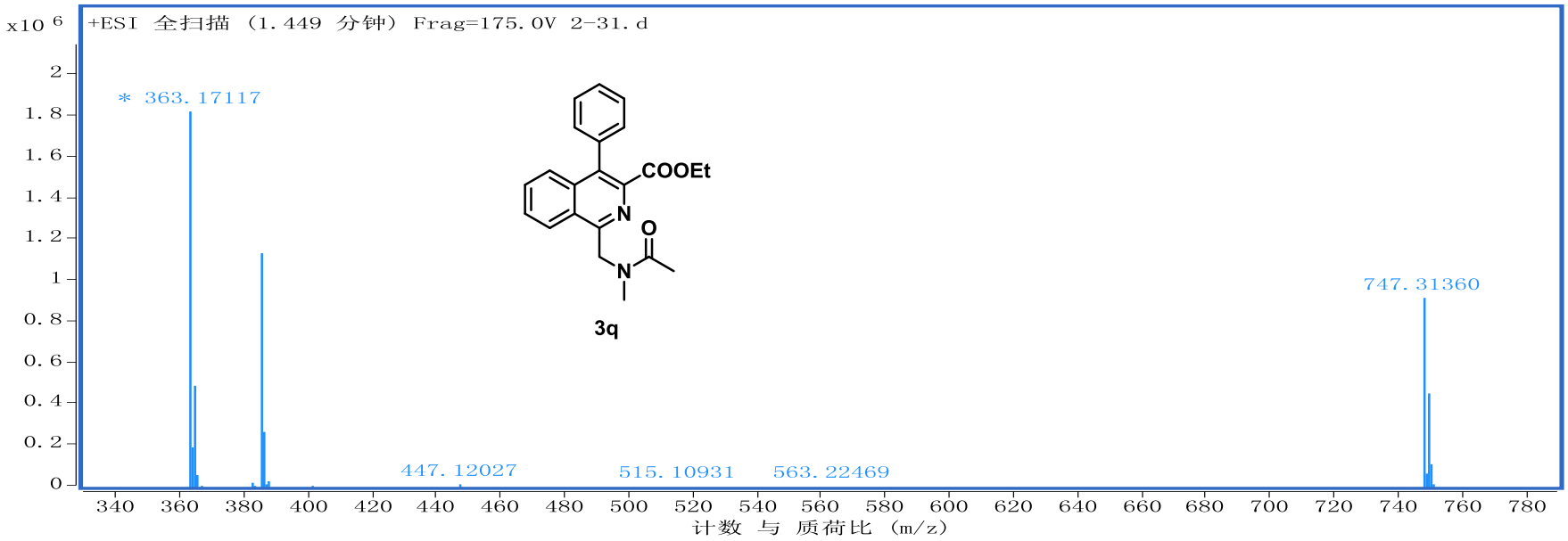

8.2394
8.2195
8.2151
7.7290
7.7139
7.6562
7.6427
7.6331
7.6198
7.4659
7.4467
7.4274
7.3227
7.3021
7.2888
7.2767
7.2355
7.2147
7.1943
5.3101
5.2590
5.1413
3.7270
3.0881
3.0707
2.2537
2.2040
0.0080
F
COOMe
F
N
O
N
3p
0.92
1.17
1.04
1.78
2.00
1.97
2.90
3.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


170.9712
167.4497
164.0746
163.3362
161.6107
160.8219
156.1697
156.1148
140.4700
131.6440
131.5865
131.5062
129.9823
121.7540
121.5047
115.8611
115.7824
115.6458
115.5675
110.1653
109.9419
52.6621
50.5499
36.0242
22.0597
F
COOMe
F
N
O
N
3p
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

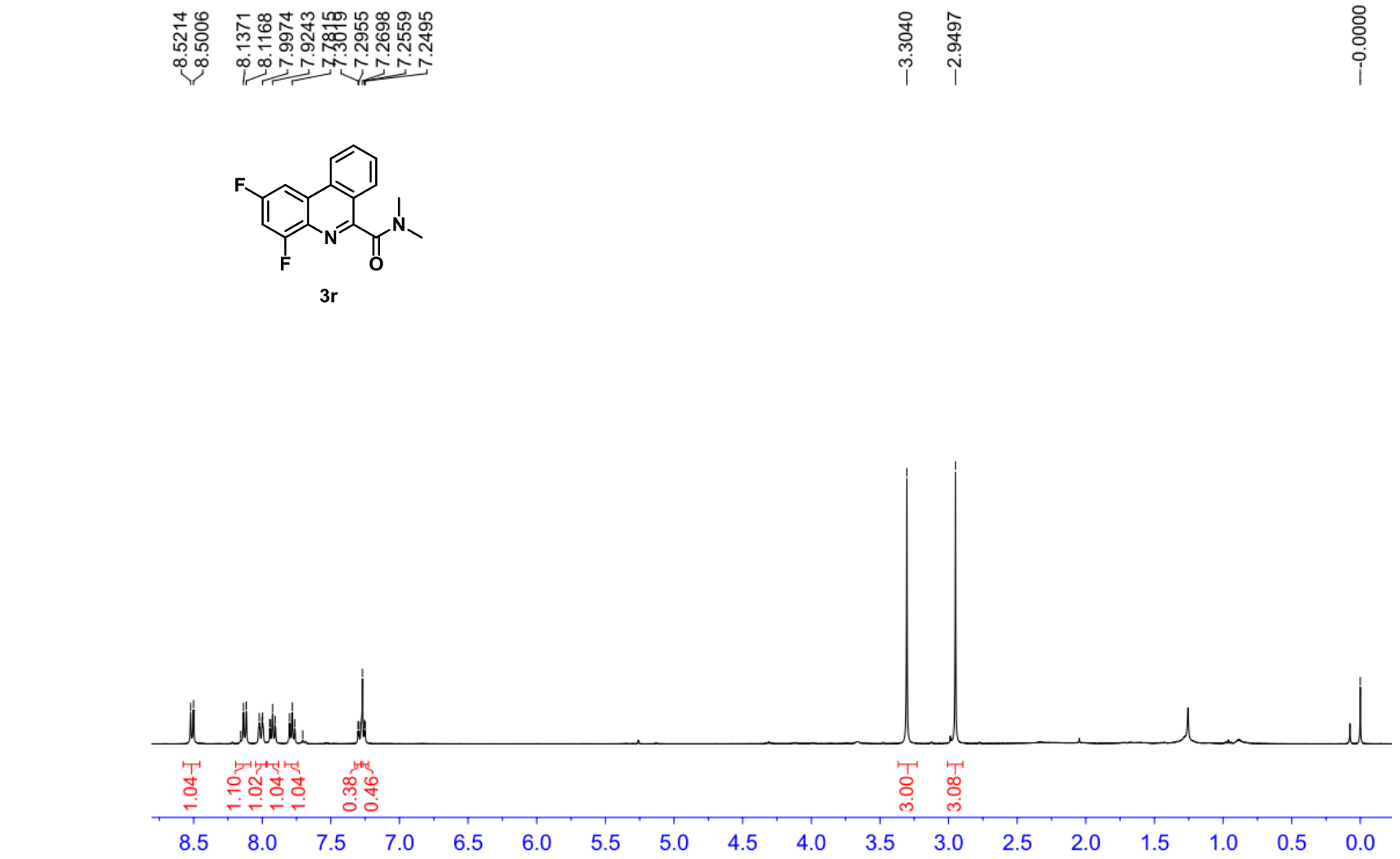

x10 5
+ESI 全扫描 (1.427 分钟) Frag=175.0V 2-67.d
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
407.11847
469.09610
791.25204
F
COOMe
N
O
F
N
3p
400 420 440 460 480 500 520 540 560 580 600 620 640 660 680 700 720 740 760 780 800 820 840
计数 与 质荷比 (m/z)

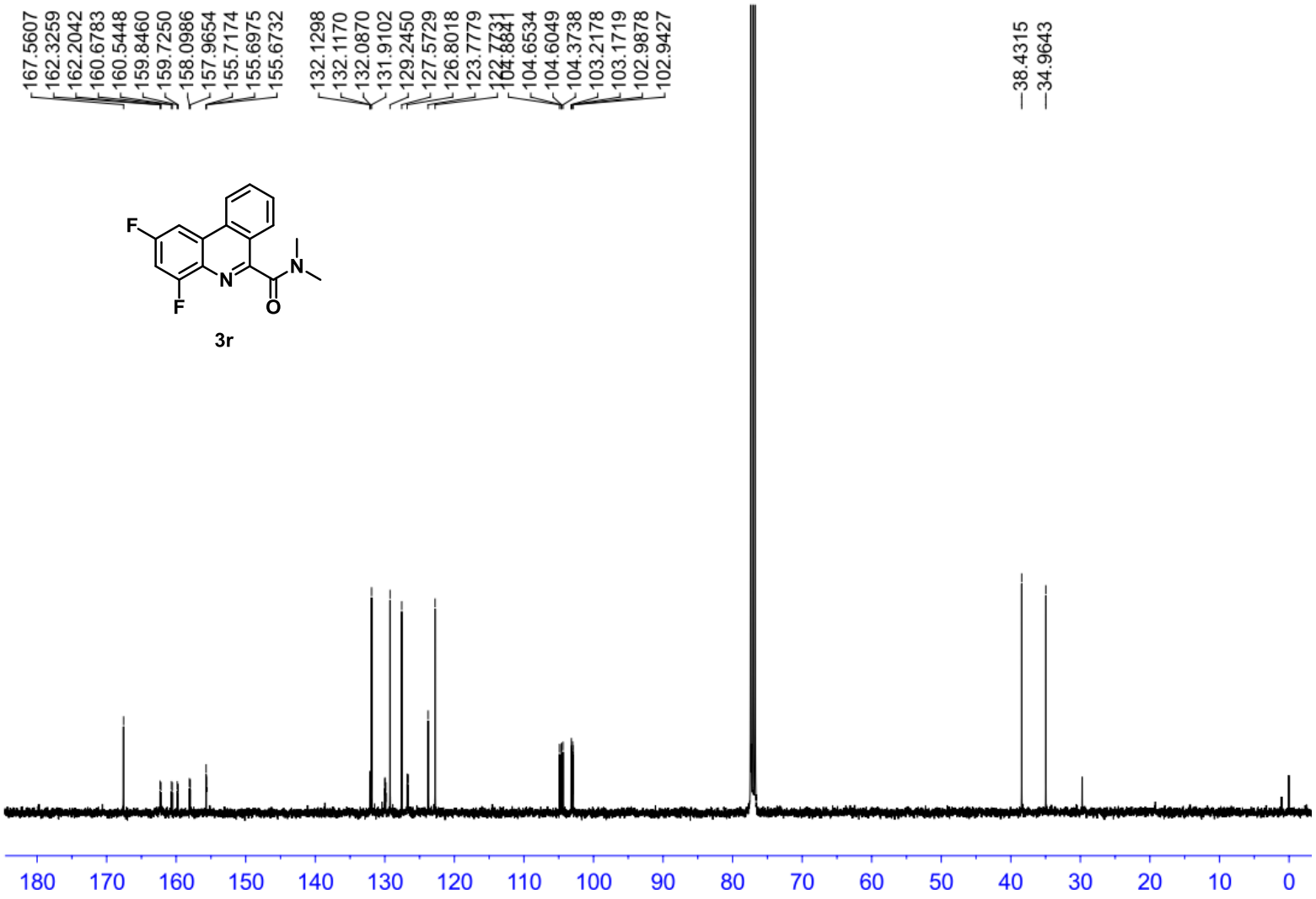

8.5121
8.4918
7.7190
7.7094
7.6990
7.6889
7.6784
7.6606
7.6514
7.5156
7.4931
7.4797
7.4763
7.4525
7.3580
7.3516
7.3391
7.2748
5.3251
5.2035
4.1369
4.1191
4.1013
4.0835
3.0615
2.2725
2.1861
0.9828
0.9650
0.9472
0.0000
COOEt
N
O
N
3q
0.86
2.98
2.95
1.95
2.00
1.99
2.97
3.16
2.78
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

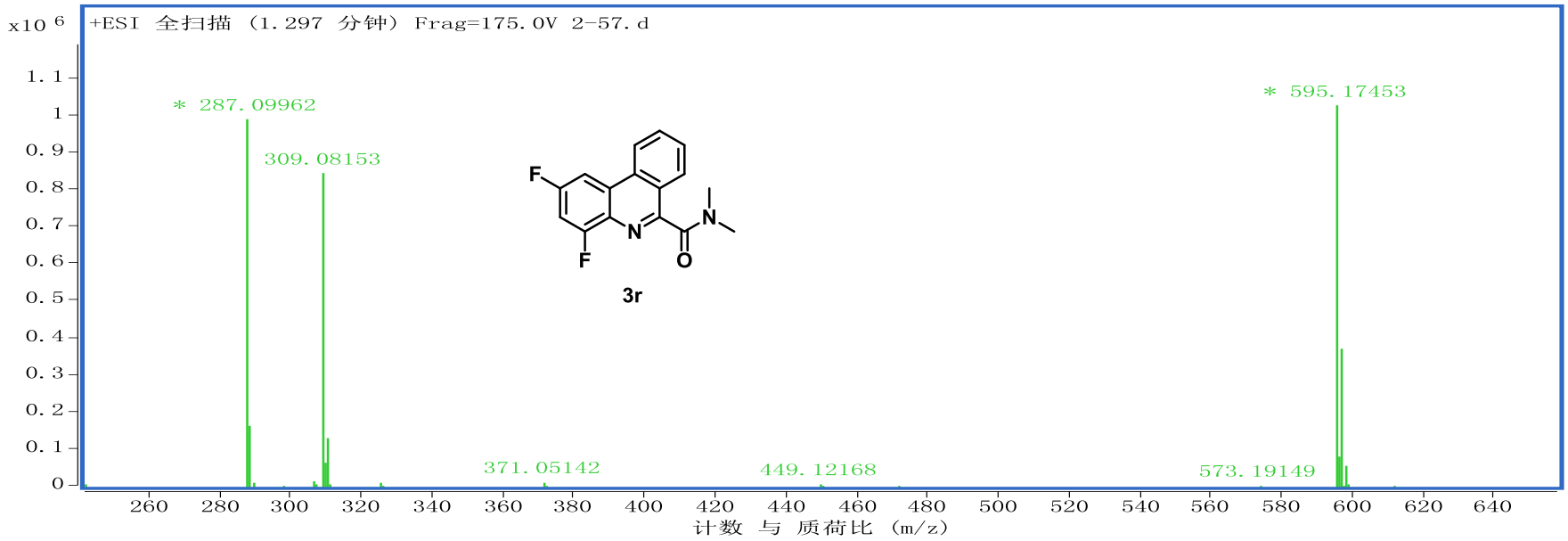

170.9524
167.7333
156.5564
141.4149
136.2999
136.1868
133.5642
131.0509
130.0550
129.1200
128.4164
128.2019
127.3633
127.1069
125.9057
61.4559
50.5347
35.8831
22.1094
13.8420
COOEt
N
O
N
3q
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

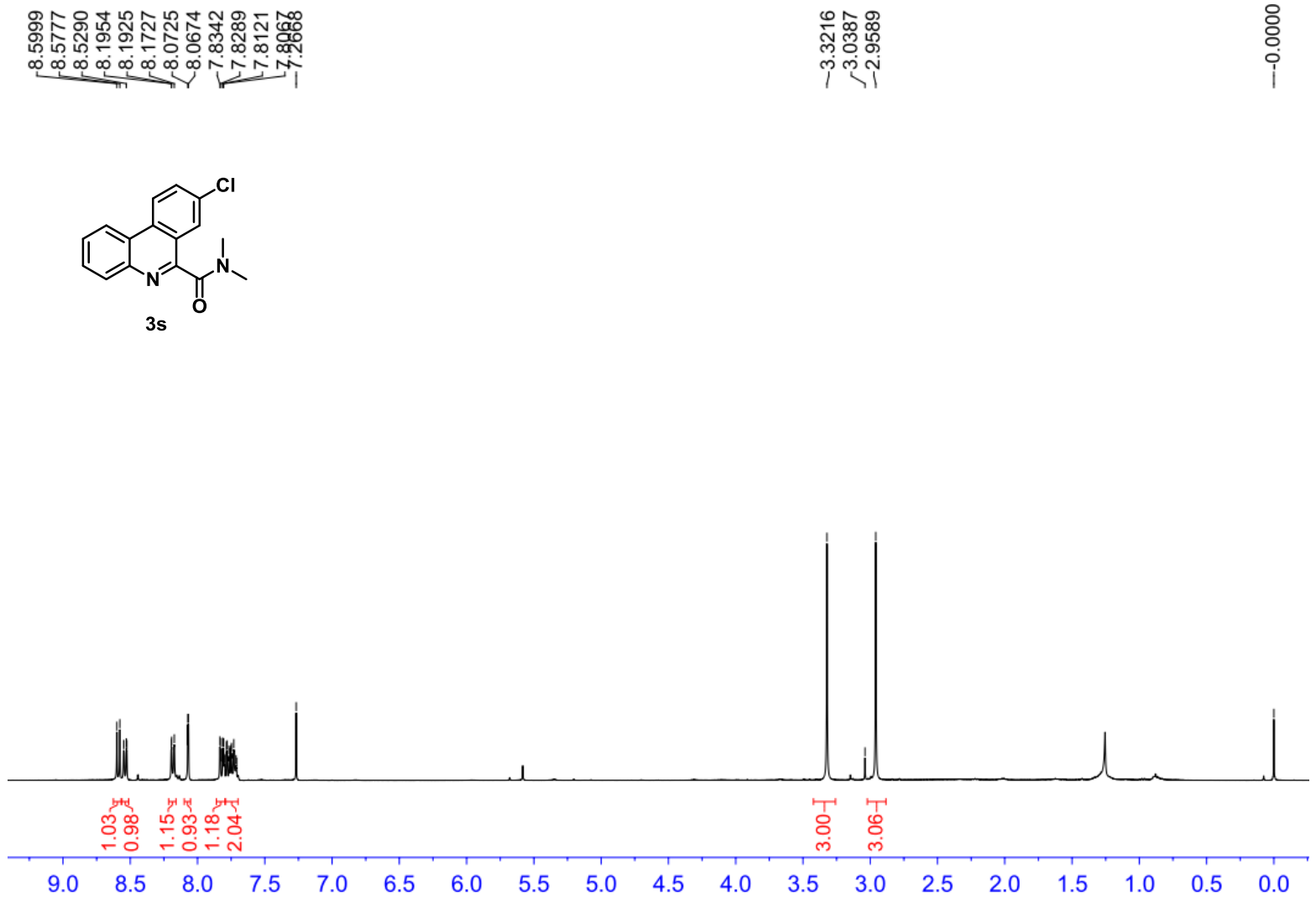

+ESI 全扫描 (1.449 分钟) Frag=175.0V 2-31.d
x10 6
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
* 363.17117
447.12027
515.10931
563.22469
747.31360
COOEt
N
O
N
340 360 380 400 420 440 460 480 500 520 540 560 580 600 620 640 660 680 700 720 740 760 780
计数 与 质荷比 (m/z)

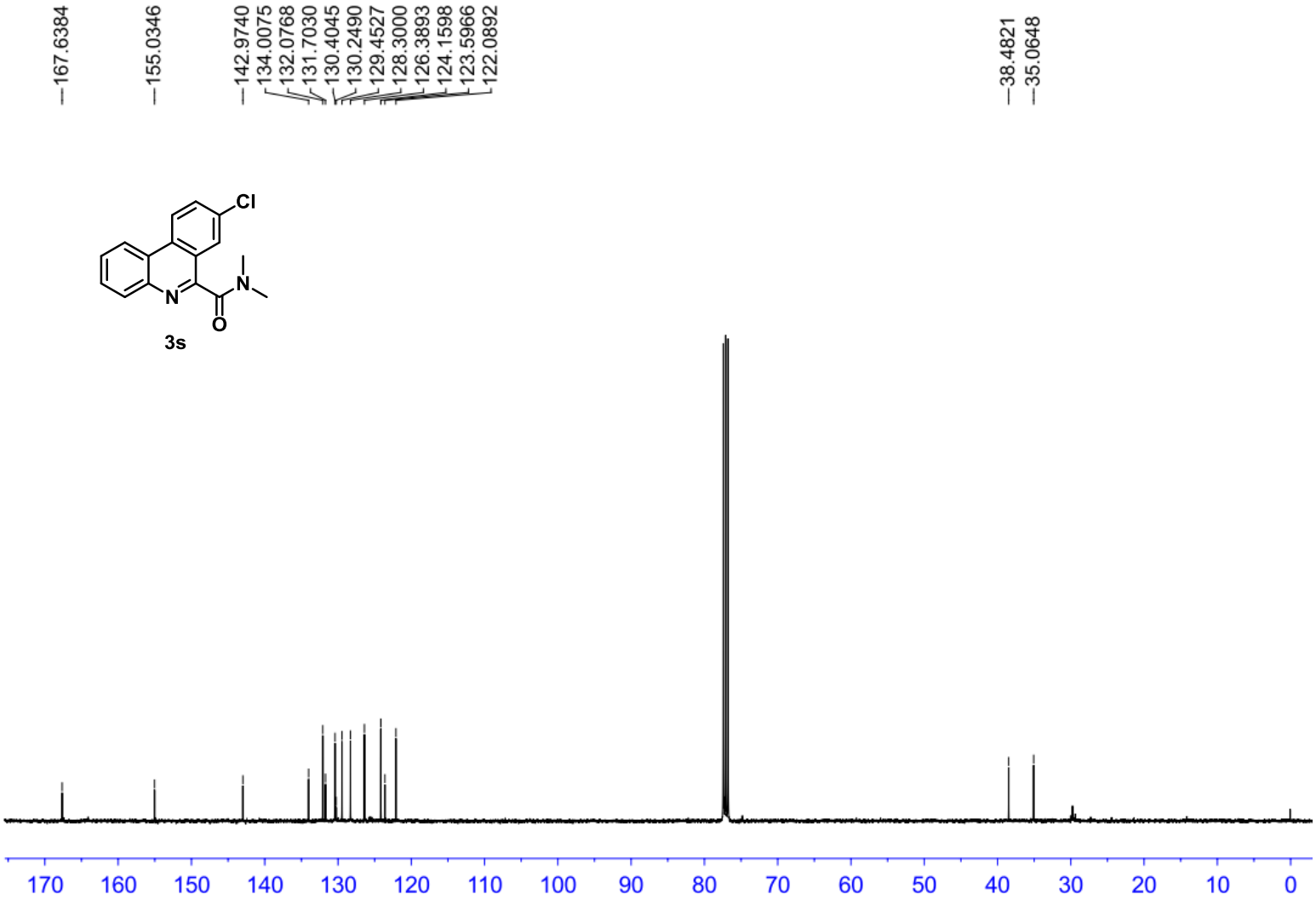
3q

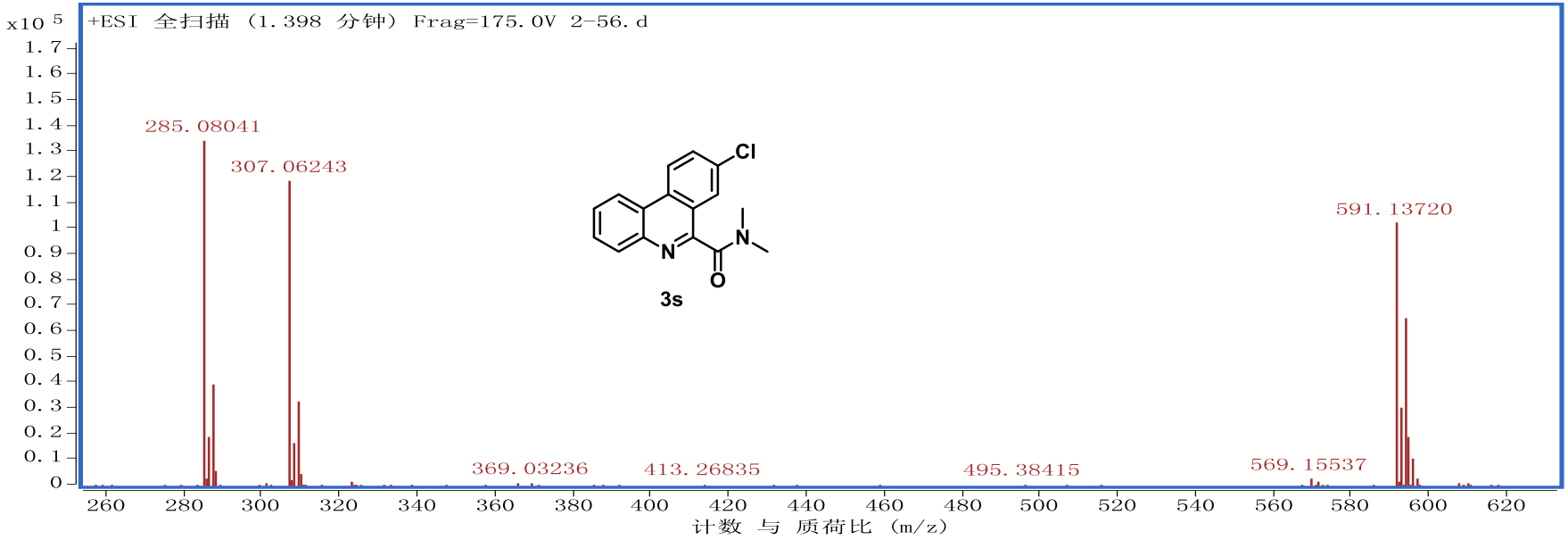

8.5214
8.5006
8.1371
8.1168
7.9974
7.9243
7.7815
7.3019
7.2955
7.2698
7.2559
7.2495
3.3040
2.9497
0.0000
F
F
N
N
O
3r
1.04
1.10
1.02
1.04
1.04
0.38
0.46
3.00
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

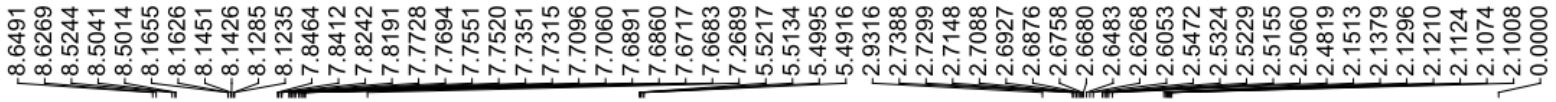

167.5607
162.3259
162.2042
160.6783
160.5448
159.8460
159.7250
158.0986
157.9654
155.7174
155.6975
155.6732
132.1298
132.1170
132.0870
131.9102
129.2450
127.5729
126.8018
123.7779
122.7731
104.8841
104.6534
104.6049
104.3738
103.2178
103.1719
102.9878
102.9427
38.4315
34.9643
F
F
N
N
O
3r
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

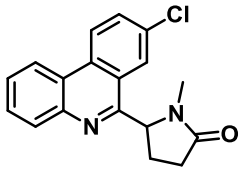

x10 6
+ESI 全扫描 (1.297 分钟) Frag=175.0V 2-57.d
* 287.09962
309.08153
371.05142
449.12168
573.19149
* 595.17453
F
F
N
N
O
3r
计数 与 质荷比 (m/z)


8.5999
8.5777
8.5290
8.1954
8.1925
8.1727
8.0725
8.0674
7.8342
7.8289
7.8121
3.3216
3.0387
2.9589
0.0000
Cl
N
N
O
3s
1.03
0.98
1.15
0.93
1.18
2.04
3.00
3.06
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

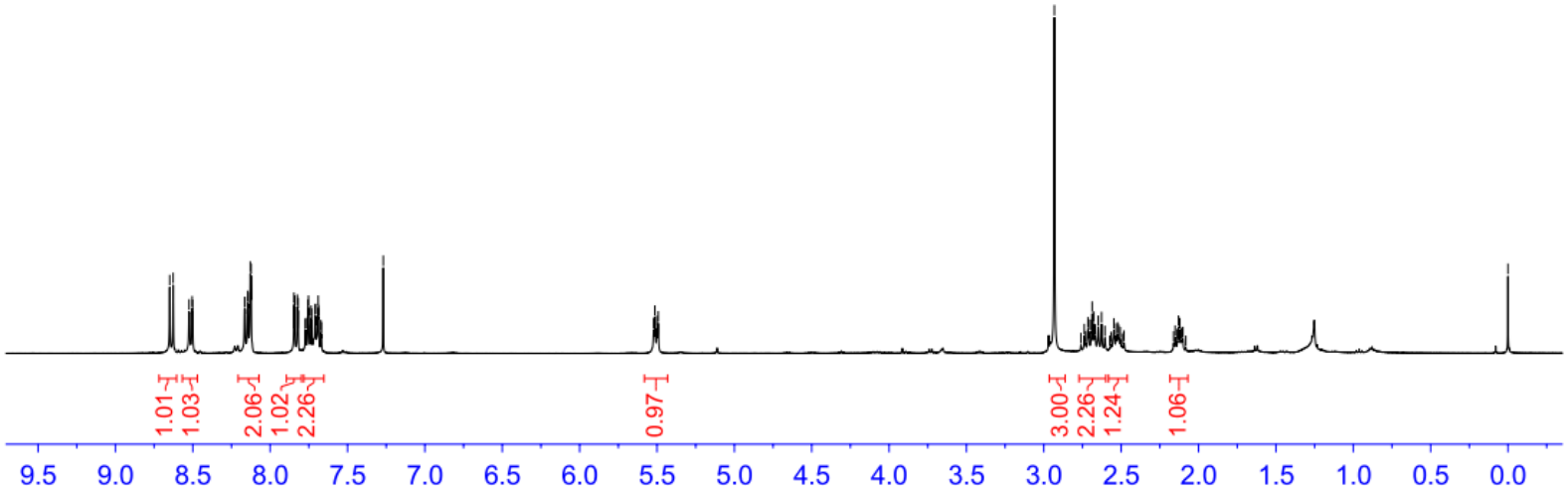

167.6384
155.0346
142.9740
134.0075
132.0768
131.7030
130.4045
130.2490
129.4527
128.3000
126.3893
124.1598
123.5966
122.0892
38.4821
35.0648
Cl
N
N
O
3s
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

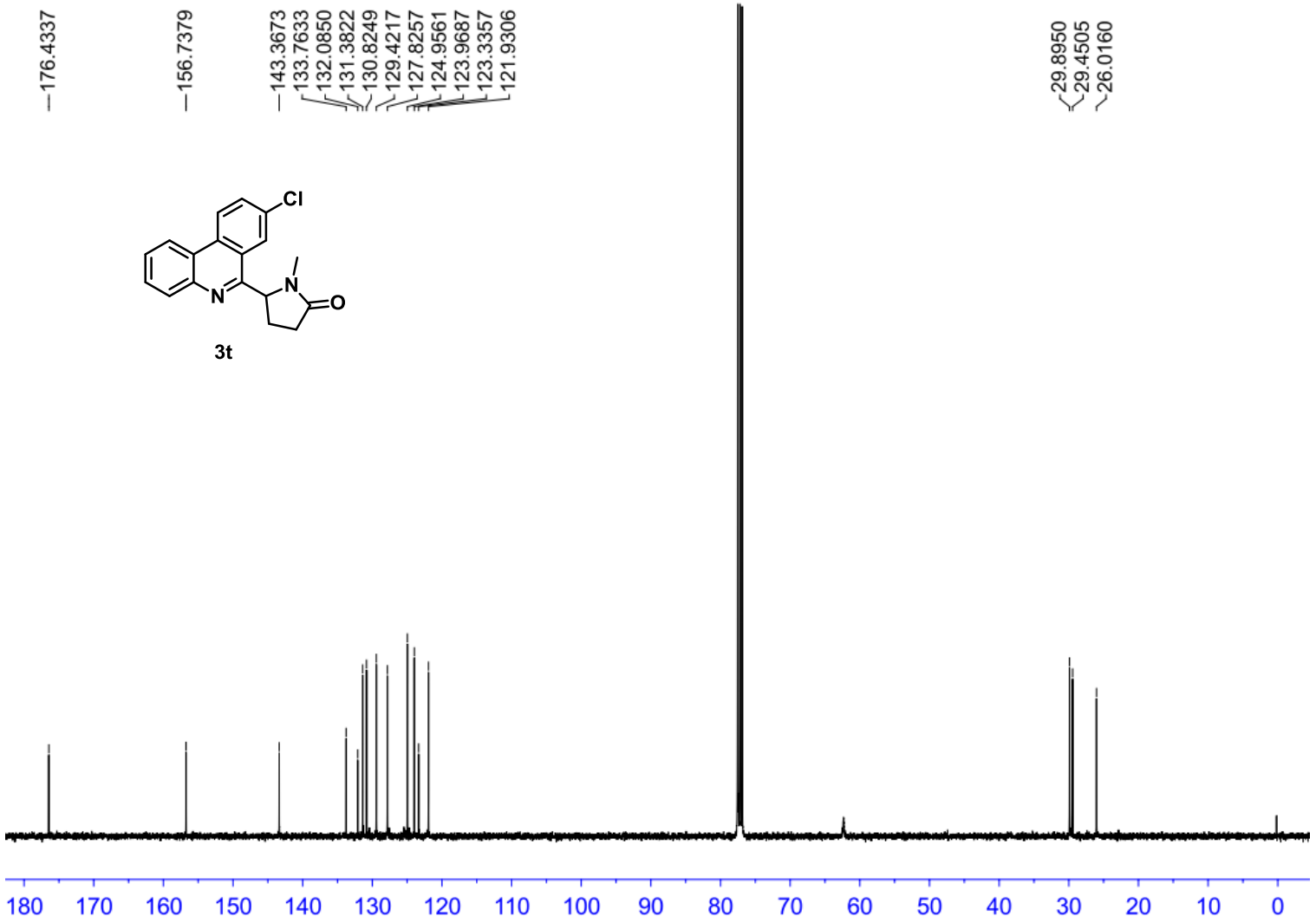

x10 5
+ESI 全扫描 (1.398 分钟) Frag=175.0V 2-56.d
285.08041
307.06243
369.03236
413.26835
495.38415
569.15537
591.13720
Cl
N
N
O
3s
计数 与 质荷比 (m/z)

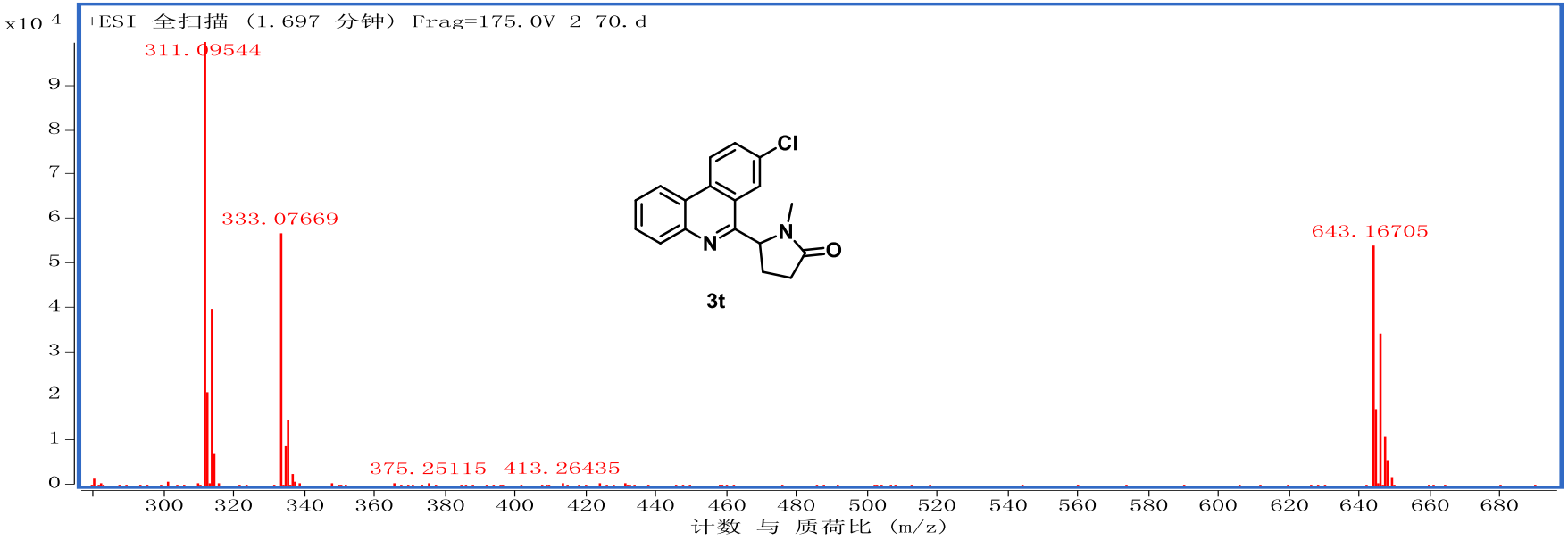

8.6491
8.6269
8.5244
8.5041
8.5014
8.1655
8.1626
8.1451
8.1426
8.1285
8.1235
7.8464
7.8412
7.8242
7.8191
7.7728
7.7694
7.7551
7.7520
7.7351
7.7315
7.7096
7.7060
7.6891
7.6860
7.6717
7.6683
7.2689
5.5217
5.5134
5.4995
5.4916
2.9316
2.7388
2.7299
2.7148
2.7088
2.6927
2.6876
2.6758
2.6680
2.6483
2.6268
2.6053
2.5472
2.5324
2.5229
2.5155
2.5060
2.4819
2.1513
2.1379
2.1296
2.1210
2.1124
2.1074
2.1008
0.0000


Cl
N
N
O

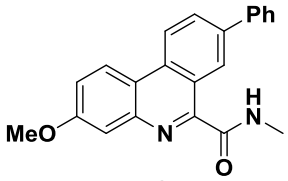
3t


1.01
1.03
2.06
1.02
2.26
0.97
3.00
2.26
1.24
1.06
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

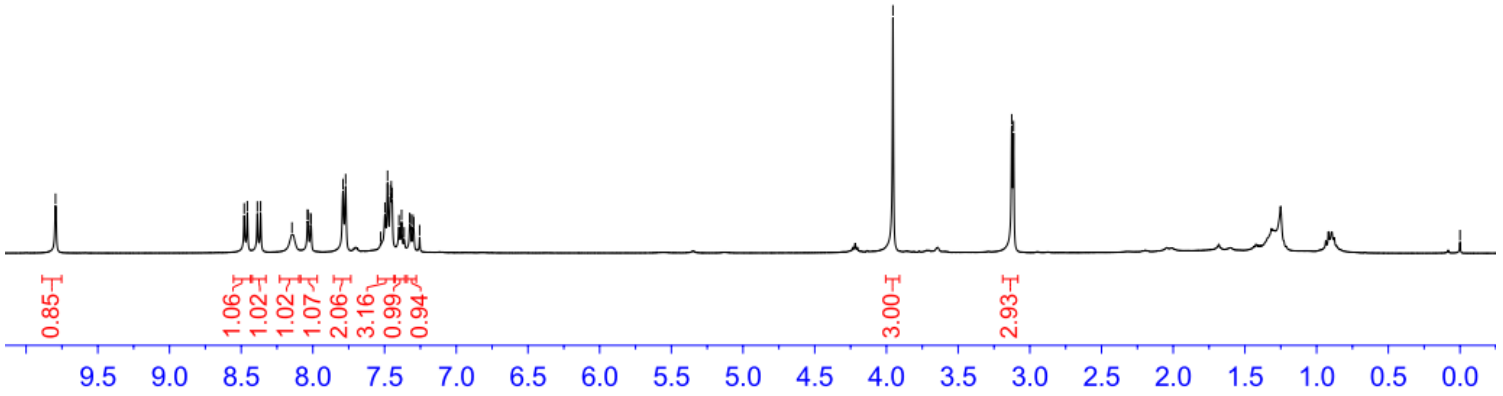

176.4337
156.7379
143.3673
133.7633
132.0850
131.3822
130.8249
129.4217
127.8257
124.9561
123.9687
123.3357
121.9306
29.8950
29.4505
26.0160
Cl
N
N
O
3t
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

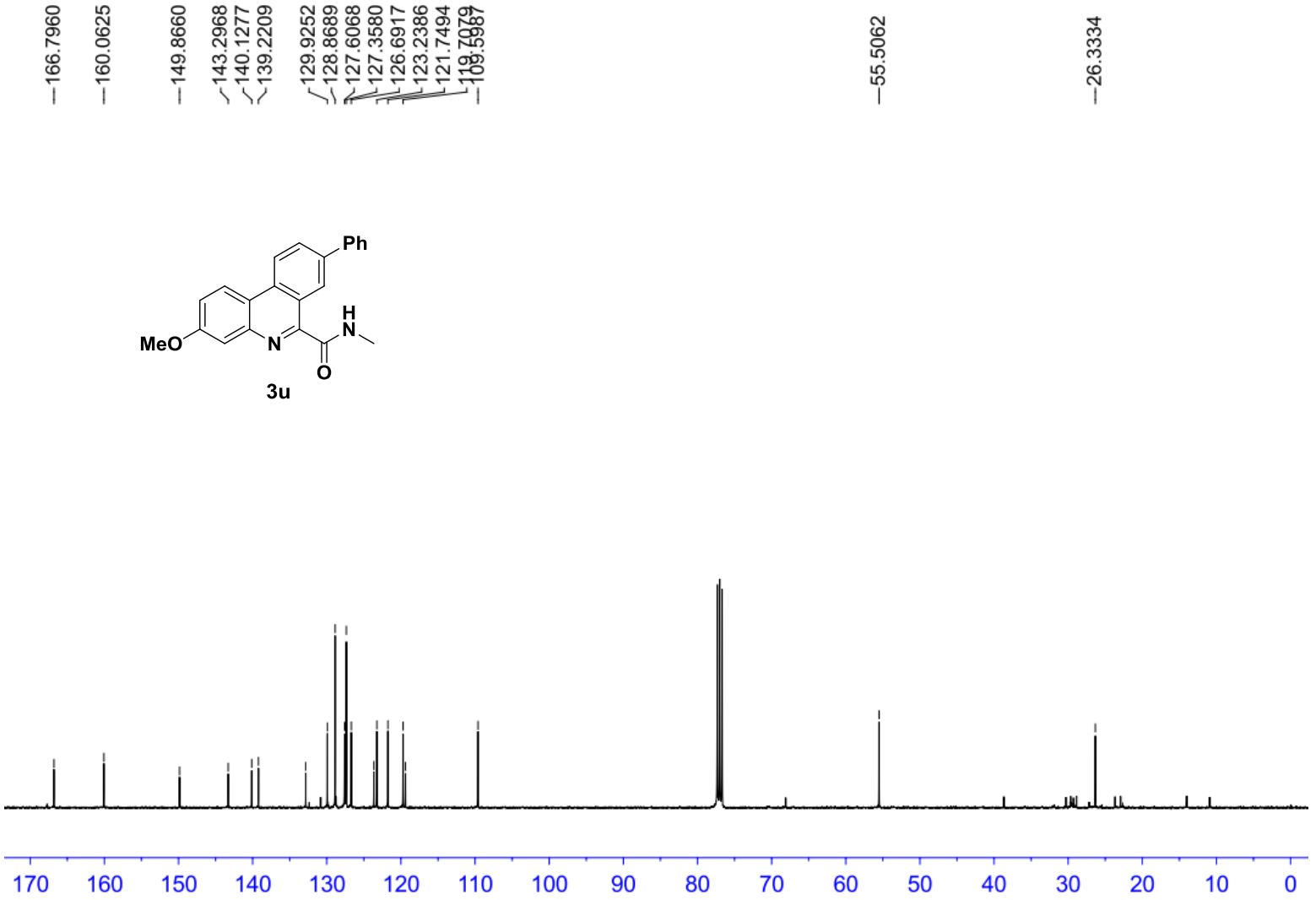

x10 4
+ESI 全扫描 (1.697 分钟) Frag=175.0V 2-70.d
311.09544
333.07669
375.25115
413.26435
643.16705
Cl
N
N
O
3t
计数 与 质荷比 (m/z)

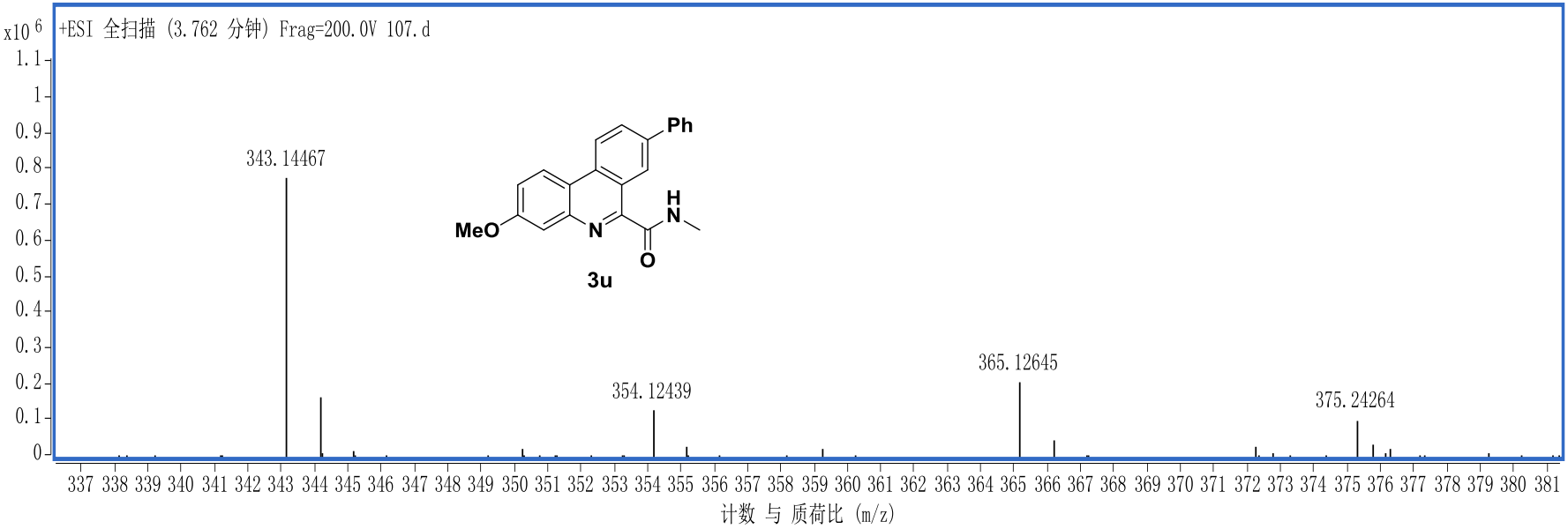

9.7950
8.4790
8.4574
8.3872
8.3645
8.1457
8.0373
8.0342
8.0159
8.0129
7.7901
7.7715
7.5272
7.4977
7.4792
7.4593
7.4536
7.4475
7.3996
7.3814
7.3632
7.3246
7.3187
7.3022
7.2963
7.2556
3.9546
3.1261
3.1138
0.0000

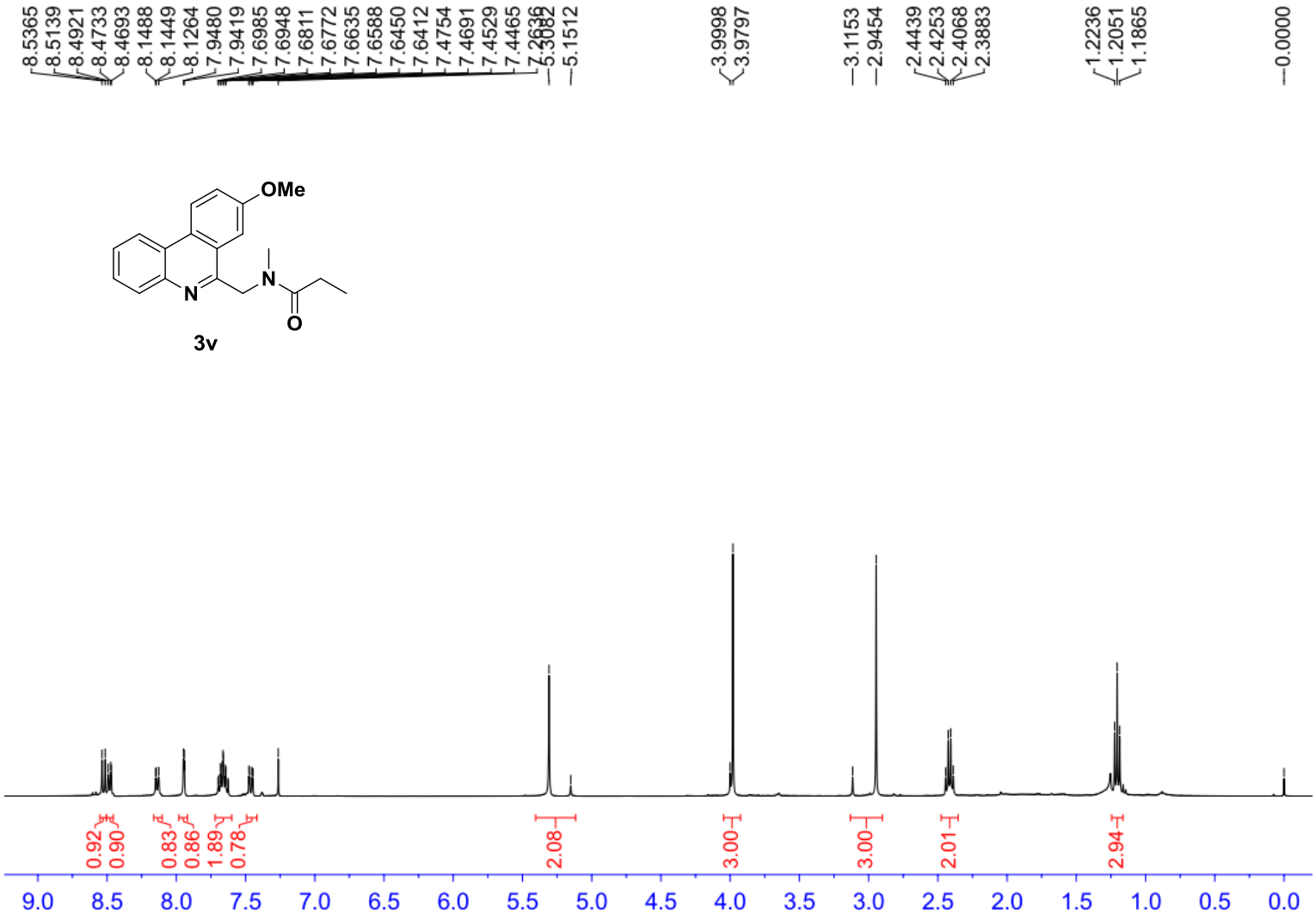

Ph
H
N
MeO
N
O

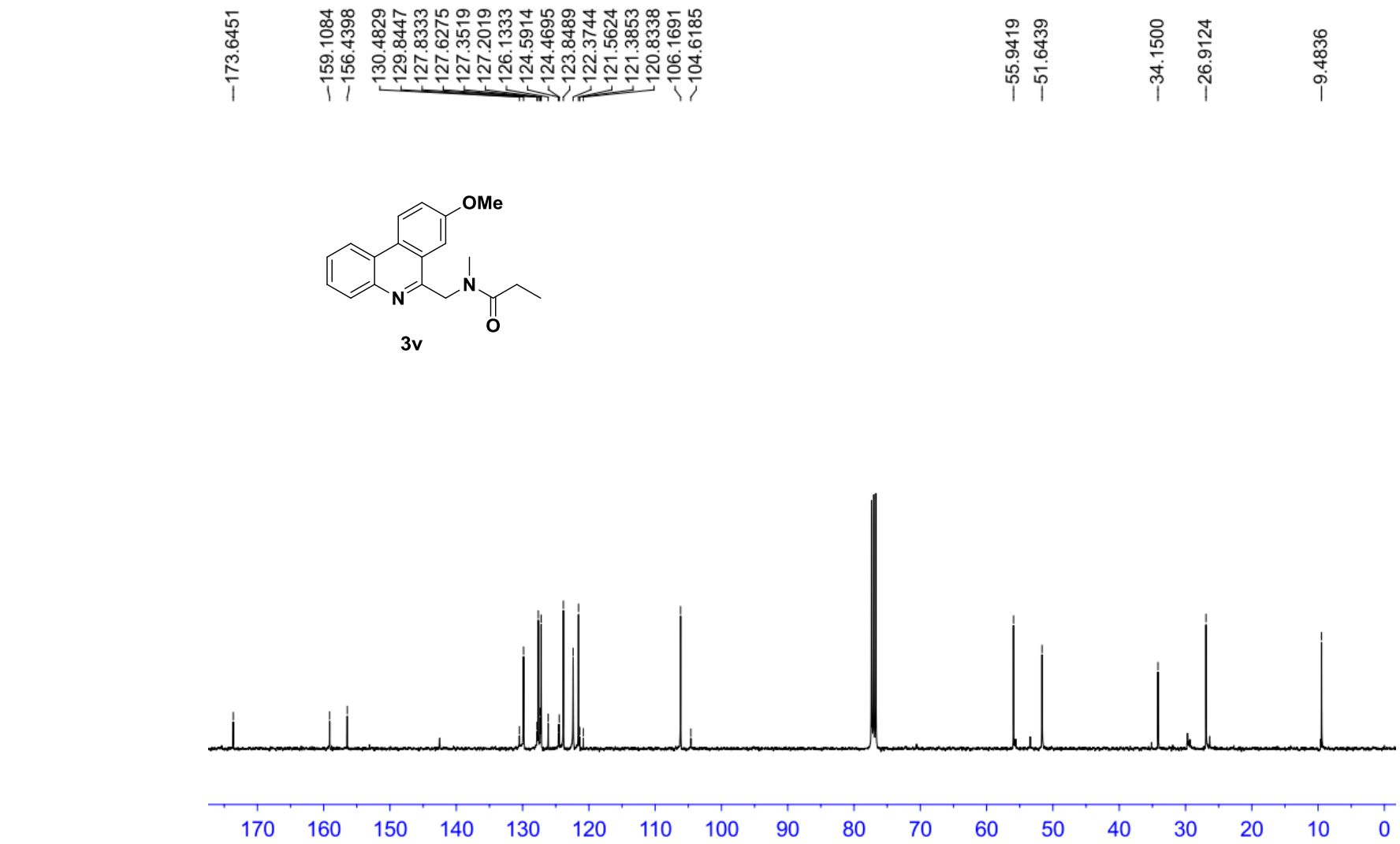
3u

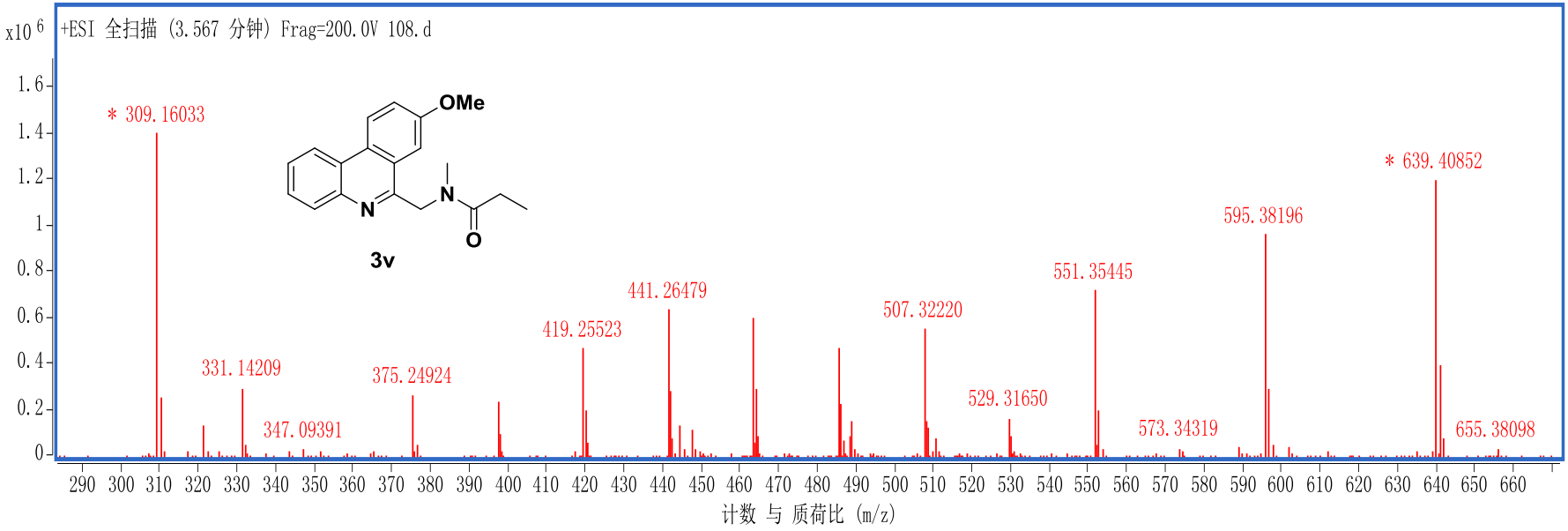

0.85
1.06
1.02
1.02
1.07
2.06
3.16
0.99
0.94
3.00
2.93
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

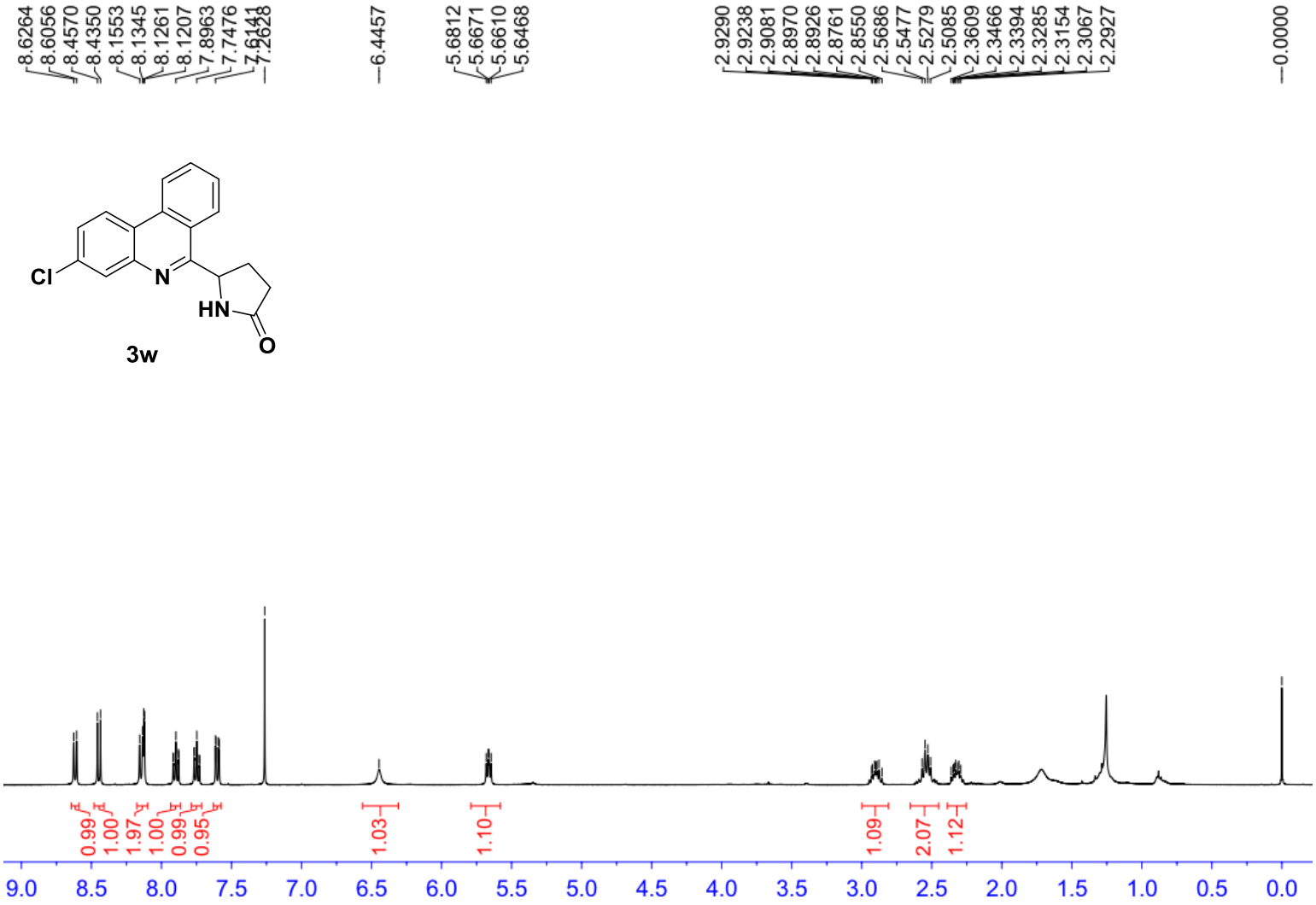

166.7960
160.0625
149.8660
143.2968
140.1277
139.2209
129.9252
128.8689
127.6068
127.3580
126.6917
123.2386
121.7494
55.5062
26.3334
Ph
MeO
N
H
N
O
3u
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

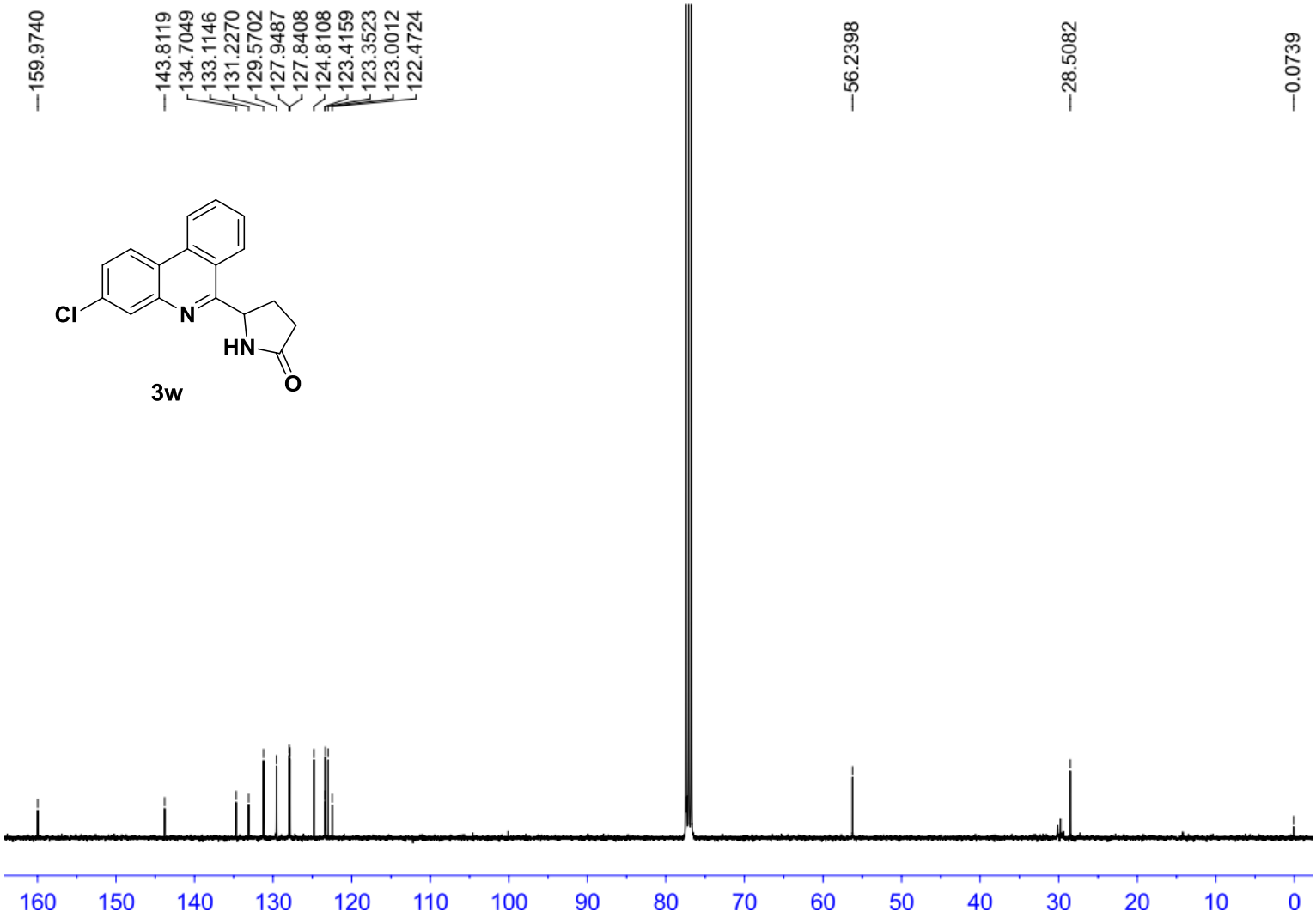

x10 6
+ESI 全扫描 (3.762 分钟) Frag=200.0V 107.d
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
343.14467
354.12439
365.12645
375.24264
Ph
MeO
N
H
N
O
3u
337 338 339 340 341 342 343 344 345 346 347 348 349 350 351 352 353 354 355 356 357 358 359 360 361 362 363 364 365 366 367 368 369 370 371 372 373 374 375 376 377 378 379 380 381
计数 与 质荷比 (m/z)

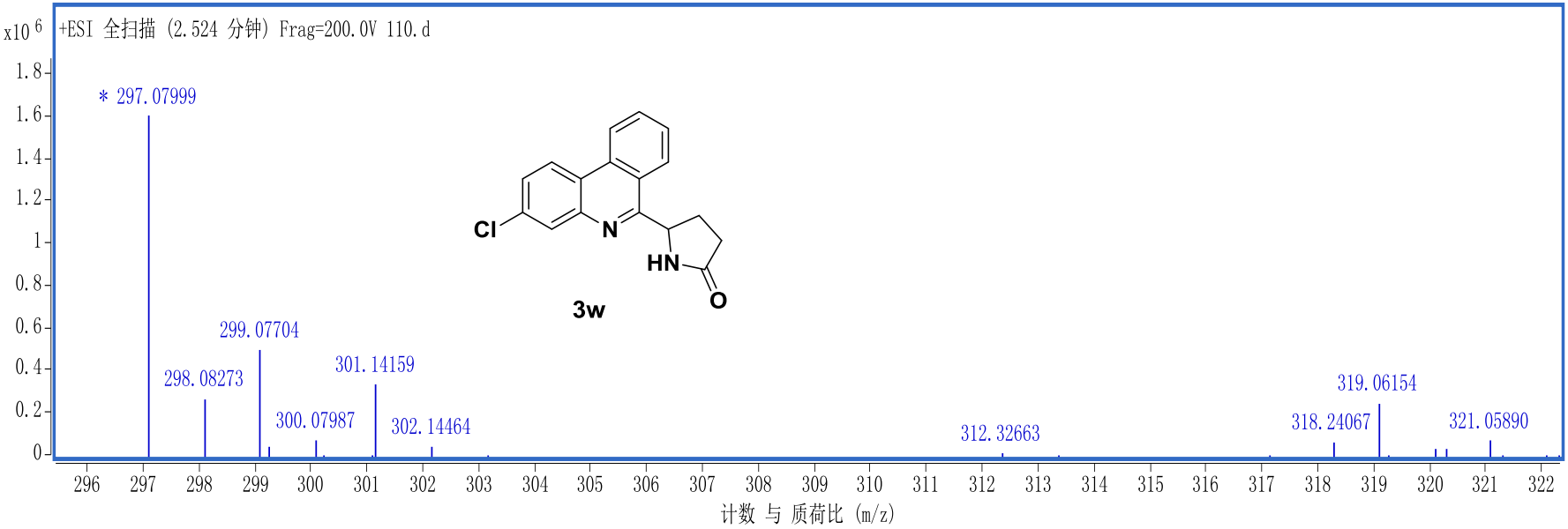

8.5365
8.5139
8.4921
8.4733
8.4693
8.1488
8.1449
8.1264
7.9480
7.9419
7.6985
7.6948
7.6811
7.6772
7.6635
7.6588
7.6450
7.6412
7.4754
7.4691
7.4529
7.4465
7.3082
5.1512
3.9998
3.9797
3.1153
2.9454
2.4439
2.4253
2.4068
2.3883
1.2236
1.2051
1.1865
0.0000
OMe
N
N
O
3v
0.92
0.90
0.83
0.86
1.89
0.78
2.08
3.00
3.00
2.01
2.94
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

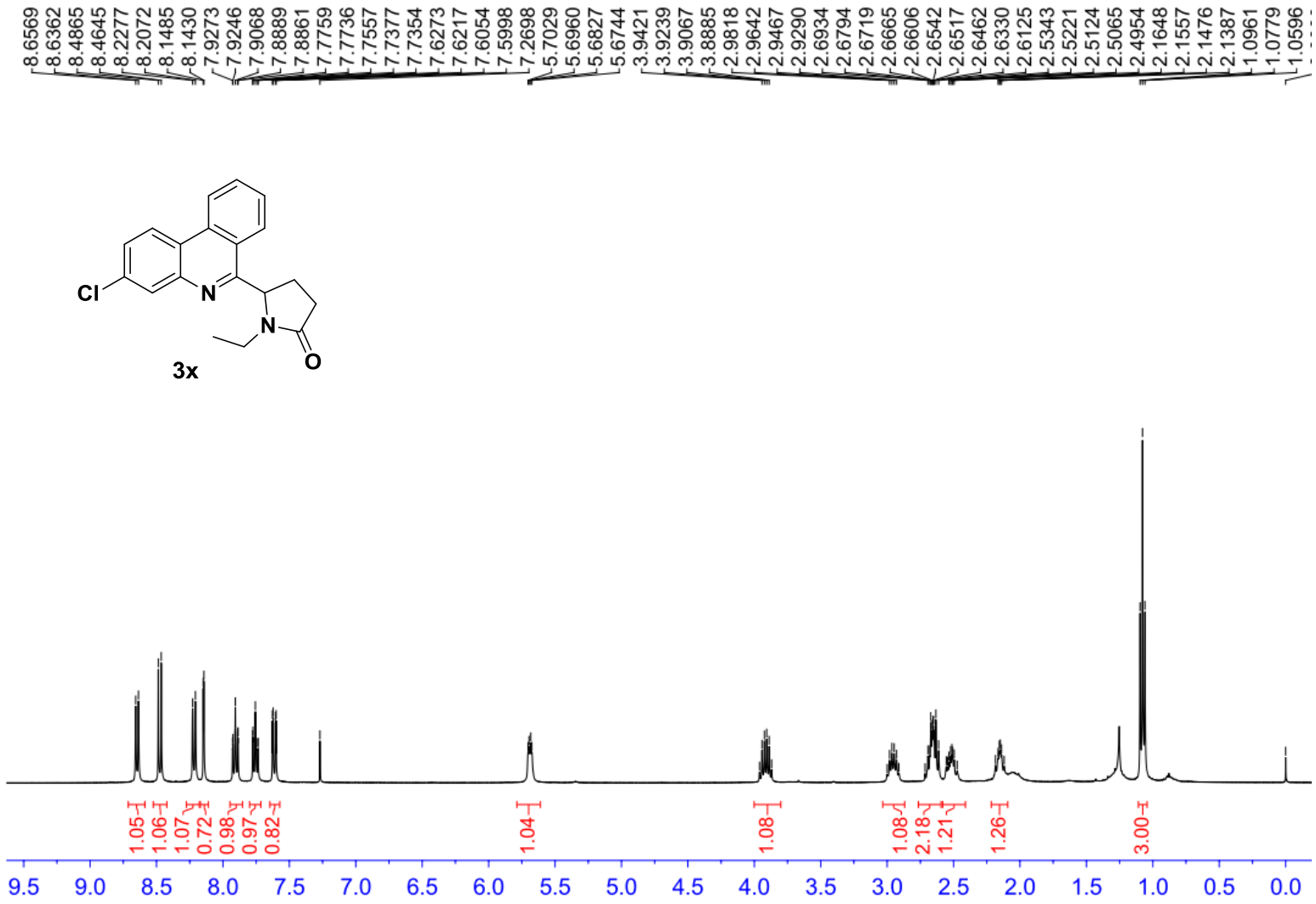

173.6451
159.1084
156.4398
130.4829
129.8447
127.8333
127.6275
127.3519
127.2019
126.1333
124.5914
124.4695
123.8489
122.3744
121.5624
121.3853
120.8338
106.1691
104.6185
55.9419
51.6439
34.1500
26.9124
9.4836
OMe
N
N
O
3v
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


x10 6
+ESI 全扫描 (3.567 分钟) Frag=200.0V 108.d
* 309.16033
OMe
N
N
O
3v
331.14209
347.09391
375.24924
419.25523
441.26479
507.32220
529.31650
551.35445
573.34319
595.38196
* 639.40852
655.38098
计数 与 质荷比 (m/z)


8.6264
8.6056
8.4570
8.4350
8.1553
8.1345
8.1261
8.1207
7.8963
7.7476
7.6141
7.2628
6.4457
5.6812
5.6671
5.6610
5.6468
2.9290
2.9238
2.9081
2.8970
2.8926
2.8761
2.8550
2.5686
2.5477
2.5279
2.5085
2.3609
2.3466
2.3394
2.3285
2.3154
2.3067
2.2927
0.0000
Cl
N
HN
O
3w
0.99
1.00
1.97
1.00
0.99
0.95
1.03
1.10
1.09
2.07
1.12
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


159.9740
143.8119
134.7049
133.1146
131.2270
129.5702
127.9487
127.8408
124.8108
123.4159
123.3523
123.0012
122.4724
56.2398
28.5082
0.0739
Cl
N
HN
O
3w
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


x10 6
+ESI 全扫描 (2.524 分钟) Frag=200.0V 110.d
* 297.07999
299.07704
298.08273
301.14159
300.07987
302.14464
312.32663
319.06154
318.24067
321.05890
Cl
N
HN
O
3w
计数 与 质荷比 (m/z)


8.6569
8.6362
8.4865
8.4645
8.2277
8.2072
8.1485
8.1430
7.9273
7.9246
7.9068
7.8889
7.8861
7.7759
7.7736
7.7557
7.7377
7.7354
7.6273
7.6217
7.6054
7.5998
7.2698
5.7029
5.6960
5.6827
5.6744
3.9421
3.9239
3.9067
3.8885
2.9818
2.9642
2.9467
2.9290
2.6934
2.6794
2.6719
2.6665
2.6606
2.6542
2.6517
2.6462
2.6330
2.6125
2.5343
2.5221
2.5124
2.5065
2.4954
2.1648
2.1557
2.1476
2.1387
1.0961
1.0779
1.0596
Cl
N
N
O
3x
1.05
1.06
1.07
0.72
0.98
0.97
0.82
1.04
1.08
1.08
2.18
1.21
1.26
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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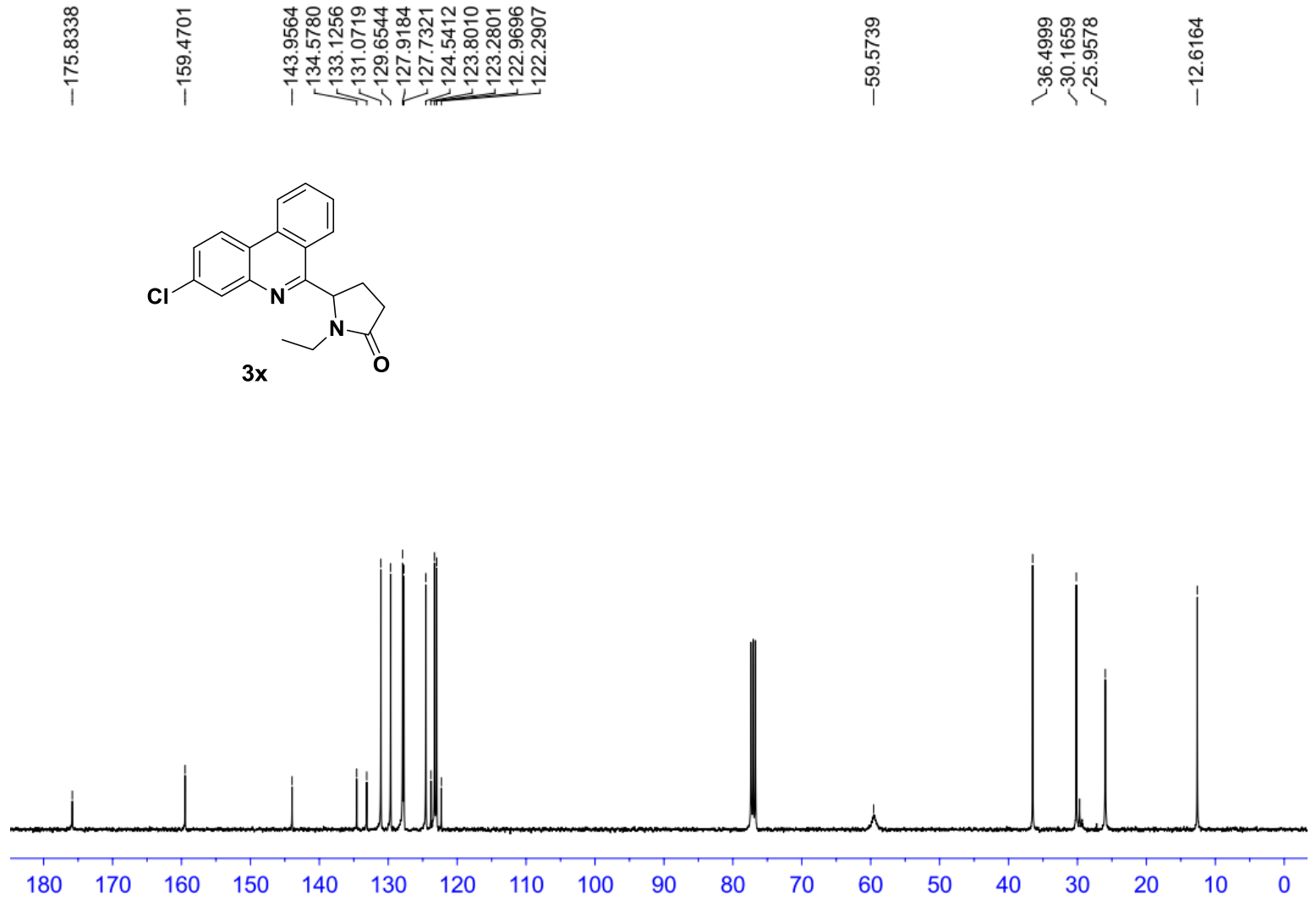
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


175.8338
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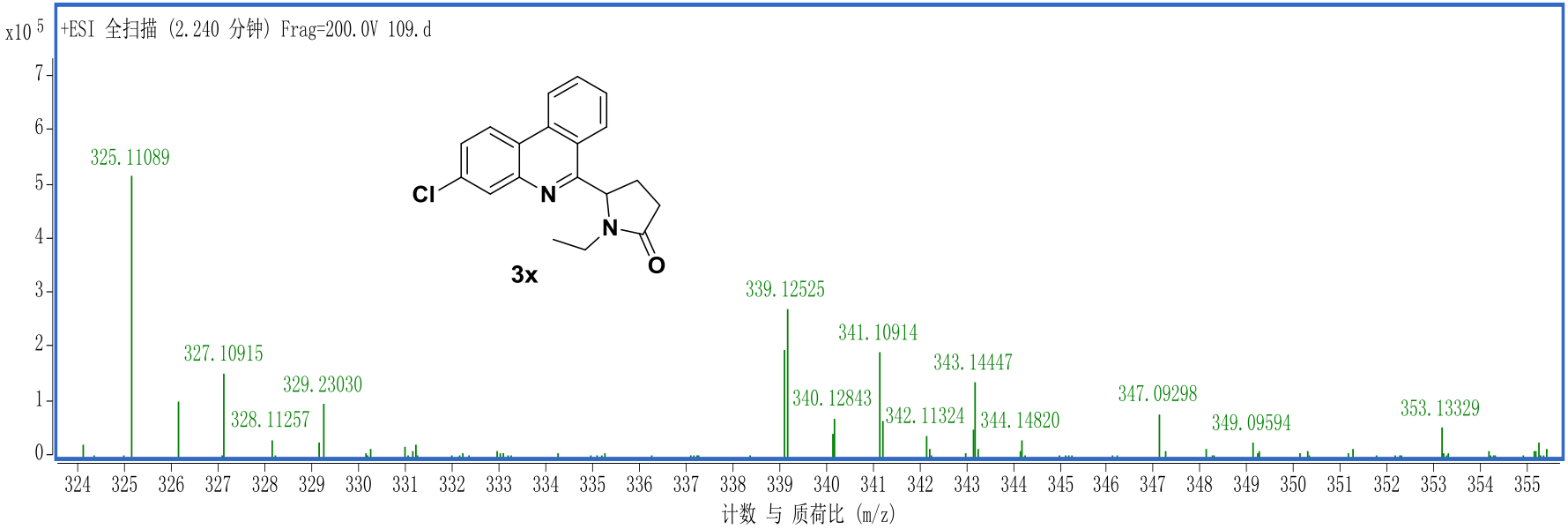
143.9564
134.5780
133.1256
131.0719
129.6544
127.9184
127.7321
124.5412
123.8010
123.2801
122.9696
122.2907
59.5739
36.4999
30.1659
25.9578
12.6164
Cl
N
N
O
3x
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


x10 5
+ESI 全扫描 (2.240 分钟) Frag=200.0V 109.d
325.11089
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329.23030
328.11257
339.12525
341.10914
343.14447
340.12843
342.11324
344.14820
347.09298
349.09594
353.13329
Cl
N
N
O
3x
计数 与 质荷比 (m/z)