N-Heterocyclic carbene (NHC)-modulated Pd/Cu cocatalyzed three-component synthesis of 2,6-diarylquinolines

Chen Xu,[*a,c] Hong-Mei Li,[b] Xiao-Er Yuan,[c] Zhi-Qiang Xiao,[c] Zhi-Qiang Wang,[a] Wei-Jun Fu,[a] Bao-Ming Ji,[a] Xin-Qi Hao,[*c] and Mao-Ping Song[c]

[a]College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang, Henan 471022, China
[b]Department of Life Science, Luoyang Normal University, Luoyang, Henan 471022, China
[c]College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou, Henan 450001, China

Table of Contents

To whom correspondence should be addressed. E-mail address: xubohan@163.com; xqhao@zzu.edu.cn

Single Crystal X-ray Structure Determination

Crystallographic data for **1**, **2**, **13**, **15**, **17** and **27** were collected on a Bruker SMART APEX-II CCD diffractometer equipped with a graphite monochromator at 296 K using Mo-Ka radiation (λ = 0.071073 Å). The data were corrected for Lorentz polarization factors as well as for absorption. Structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 with the SHELX-97 program (G. M. Sheldrick, *SHELXL-97*, *Program for refinement of crystal structure*, University of Göttingen, Germany, **1997**). All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in geometrically calculated positions. **CCDC** reference numbers **969892-969893**, **969896–969899** for **1**, **2**, **13**, **15**, **17** and **27** respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

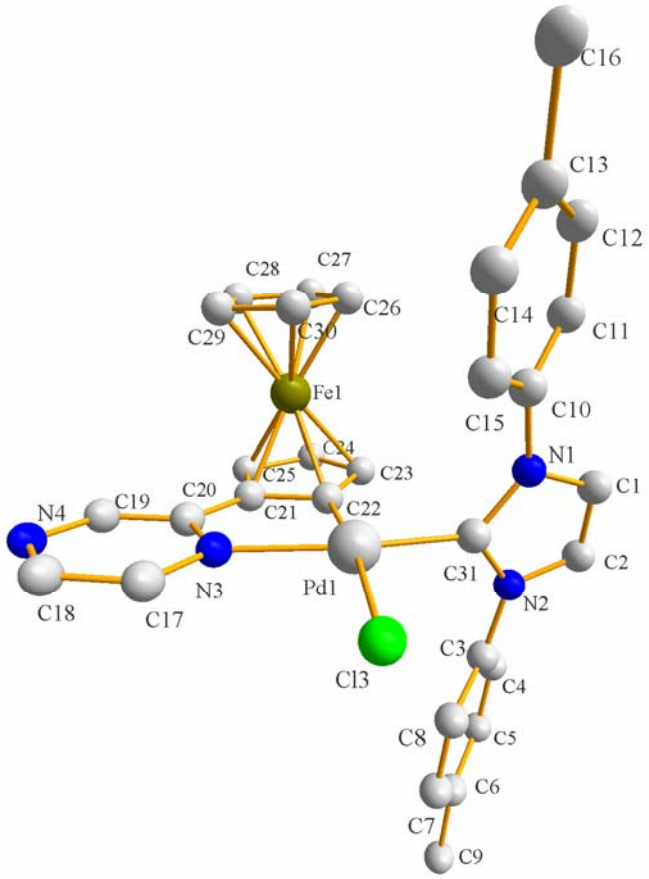


Fig S1 Molecular structure of **1**. H atoms are omitted for clarity.

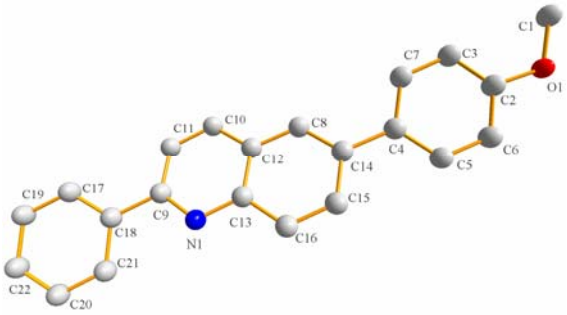


Fig S2 Molecular structure of **13**. H atoms are omitted for clarity.

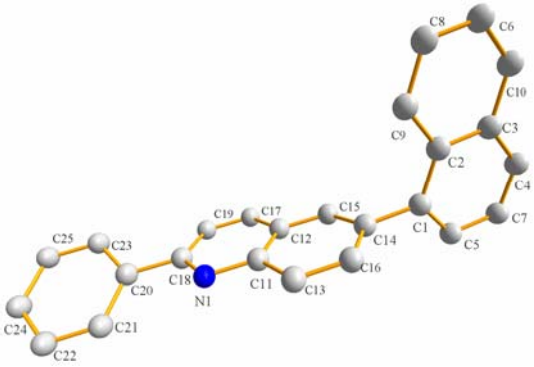


Fig S3 Molecular structure of **15**. H atoms are omitted for clarity.

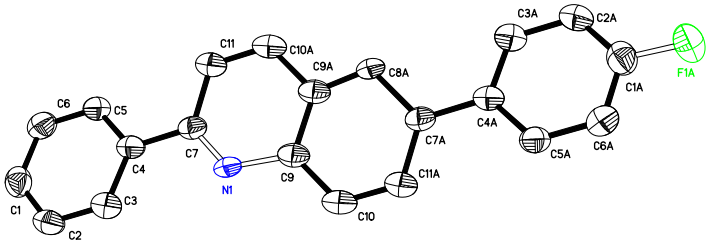
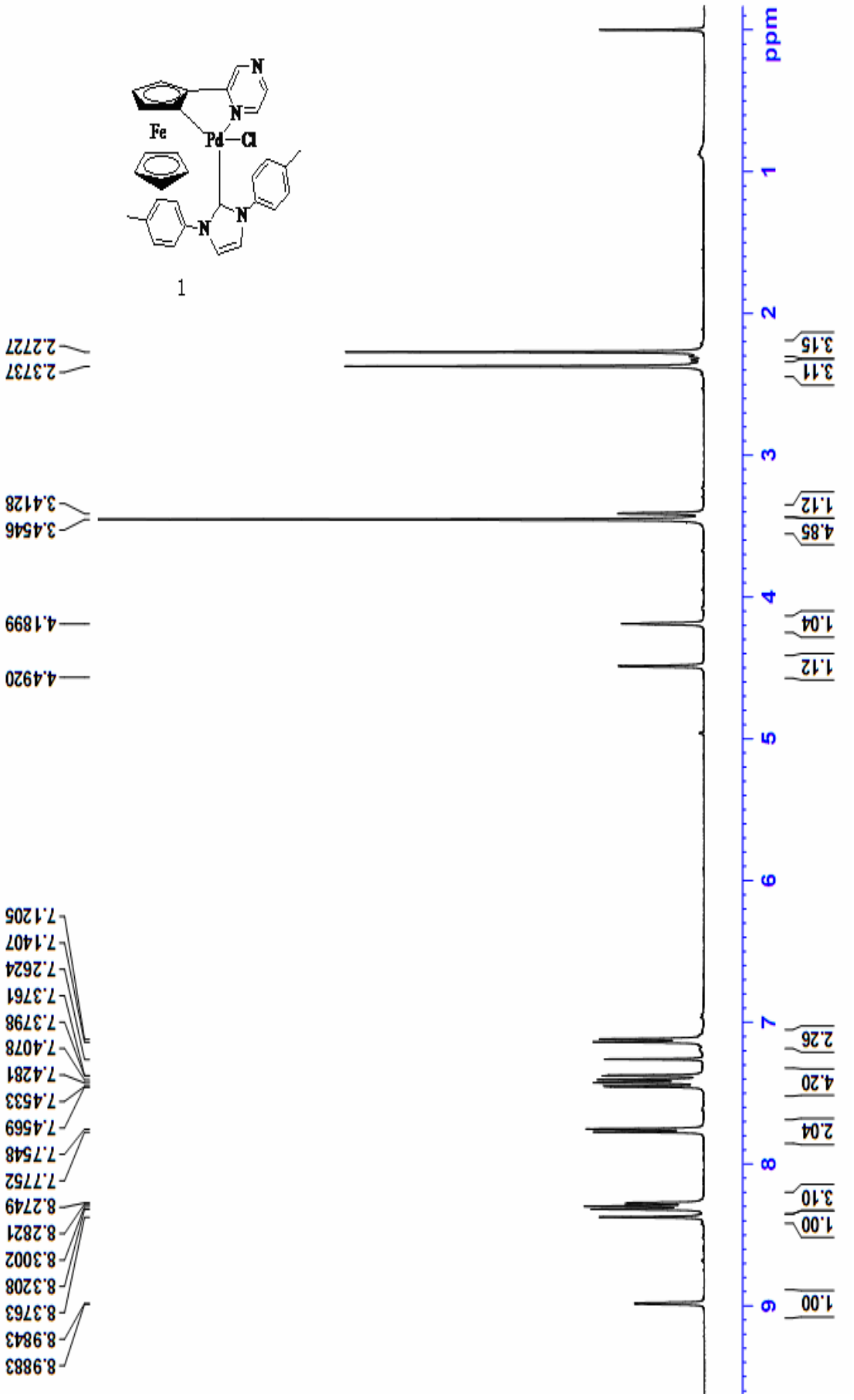


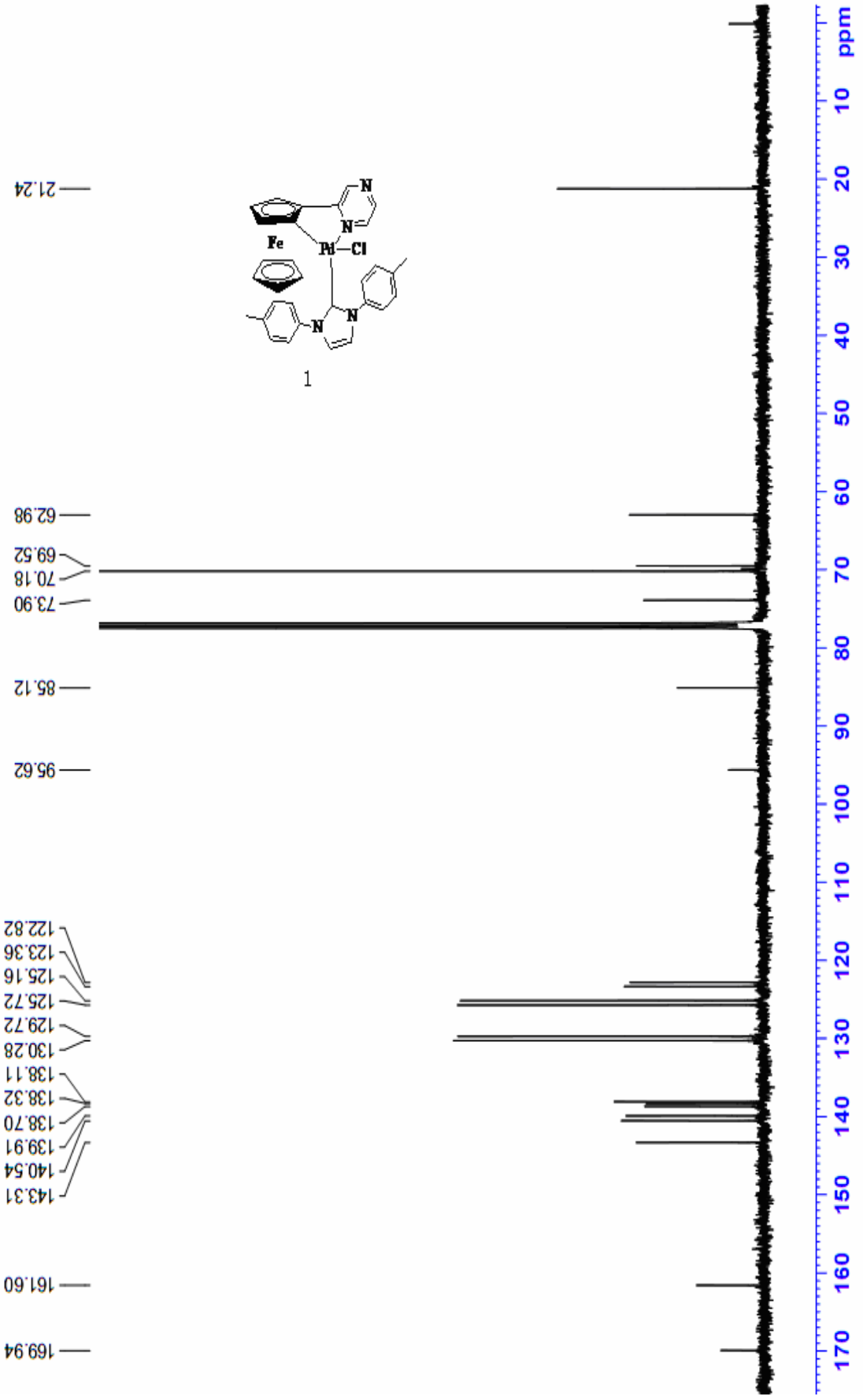
Fig S4 Molecular structure of **17**. H atoms are omitted for clarity.

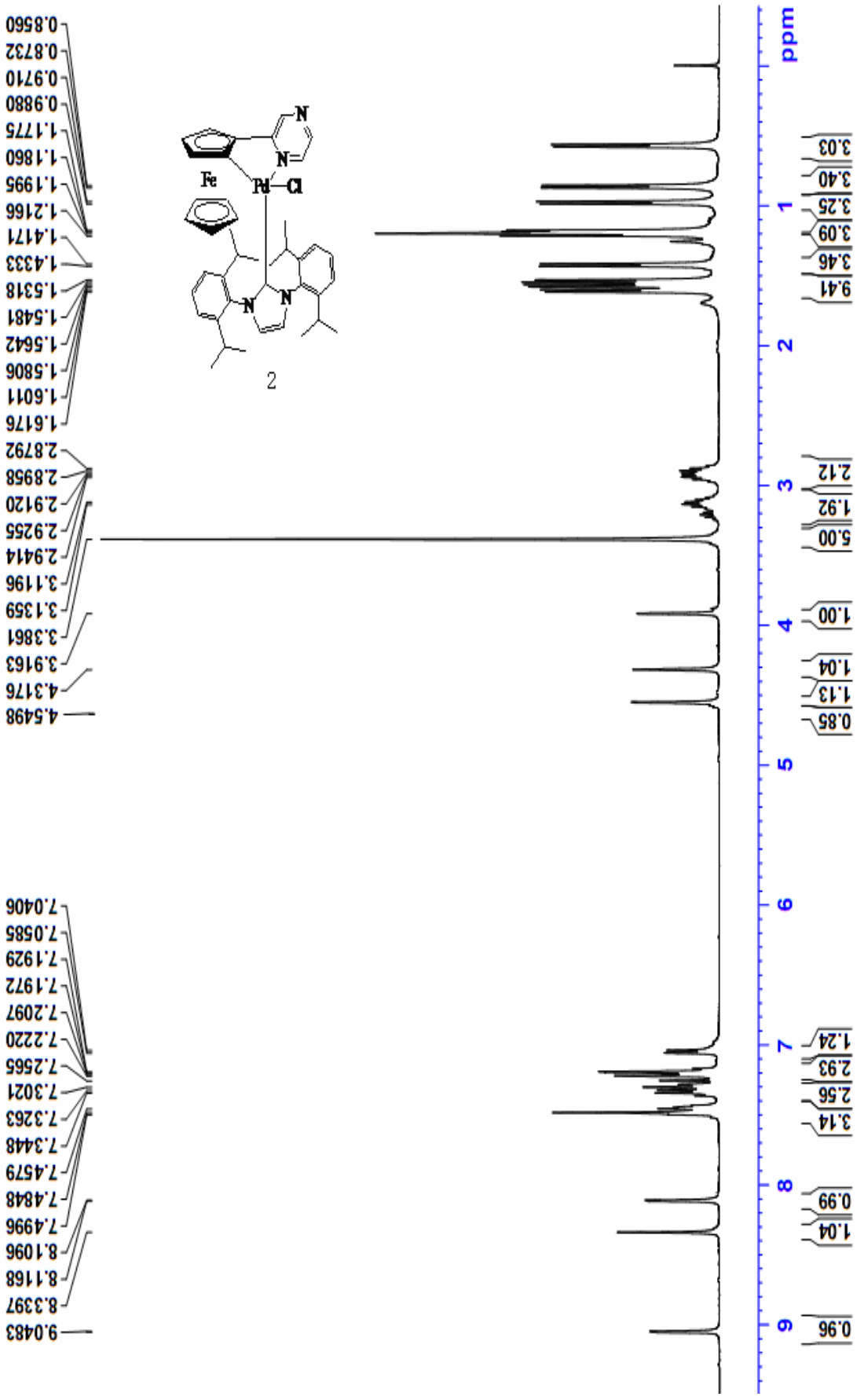
The ^{1}H and ^{13}C NMR Data of Compounds 3 and 11

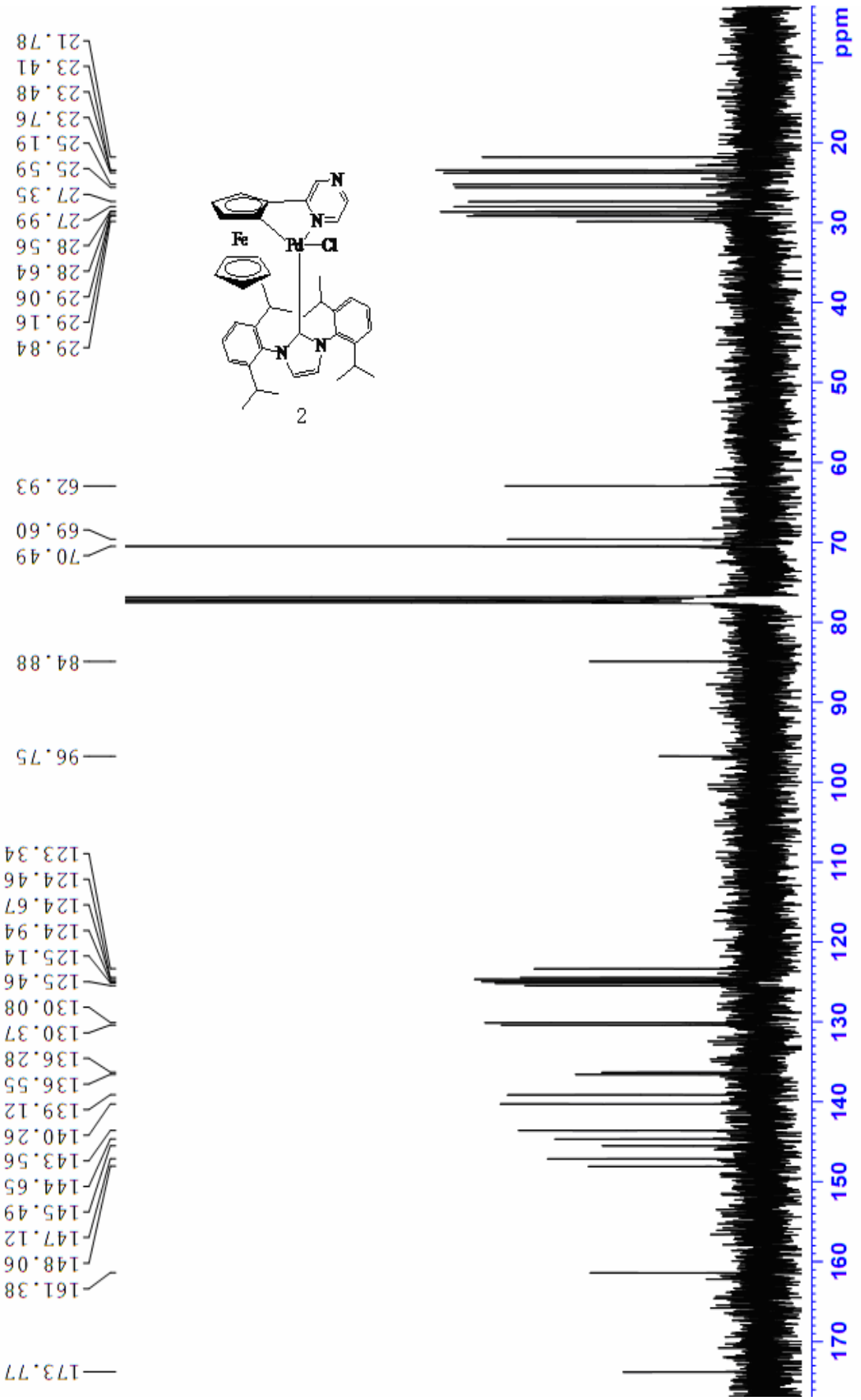
3: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18–8.23 (m, 4H), 7.92–7.94 (m, 1H), 7.81–7.83 (m, 1H), 7.67–7.77 (m, 5H), 7.45–7.54 (m, 3H), 7.36–7.39 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 148.4, 142.1, 140.6, 138.6, 136.8, 129.7, 128.9, 127.9, 127.7, 127.6, 127.5, 127.2, 126.3, 118.9.

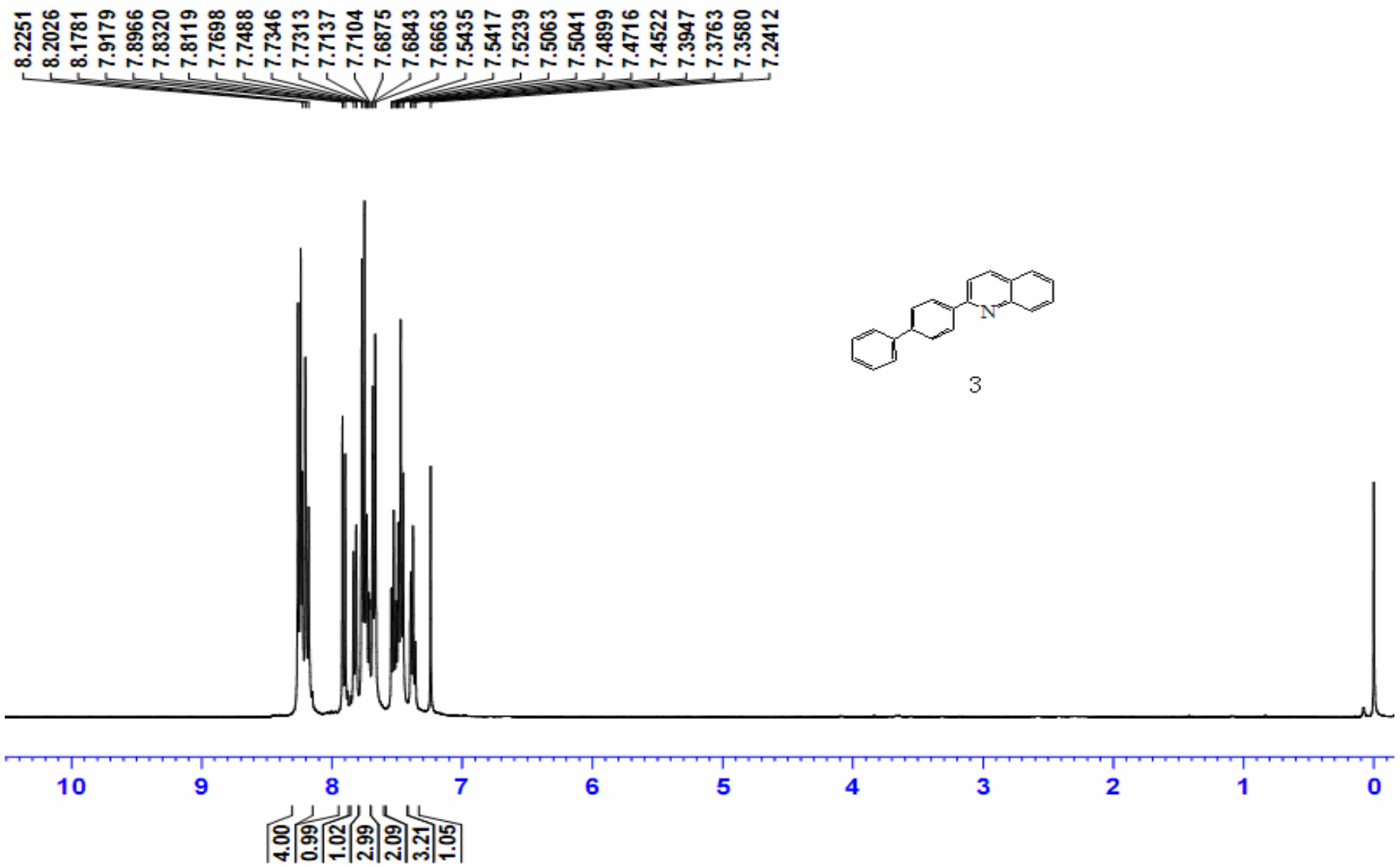
11: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22–8.25 (m, 2H), 8.18 (dd, 2H), 7.98–8.00 (m, 2H), 7.89 (d, 1H), 7.74 (dd, 2H), 7.38–7.56 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 147.7, 140.4, 139.6, 139.0, 136.9, 129.7, 129.4, 128.9, 128.7, 127.7, 127.6, 127.4, 126.3, 125.2, 119.4, 119.1.

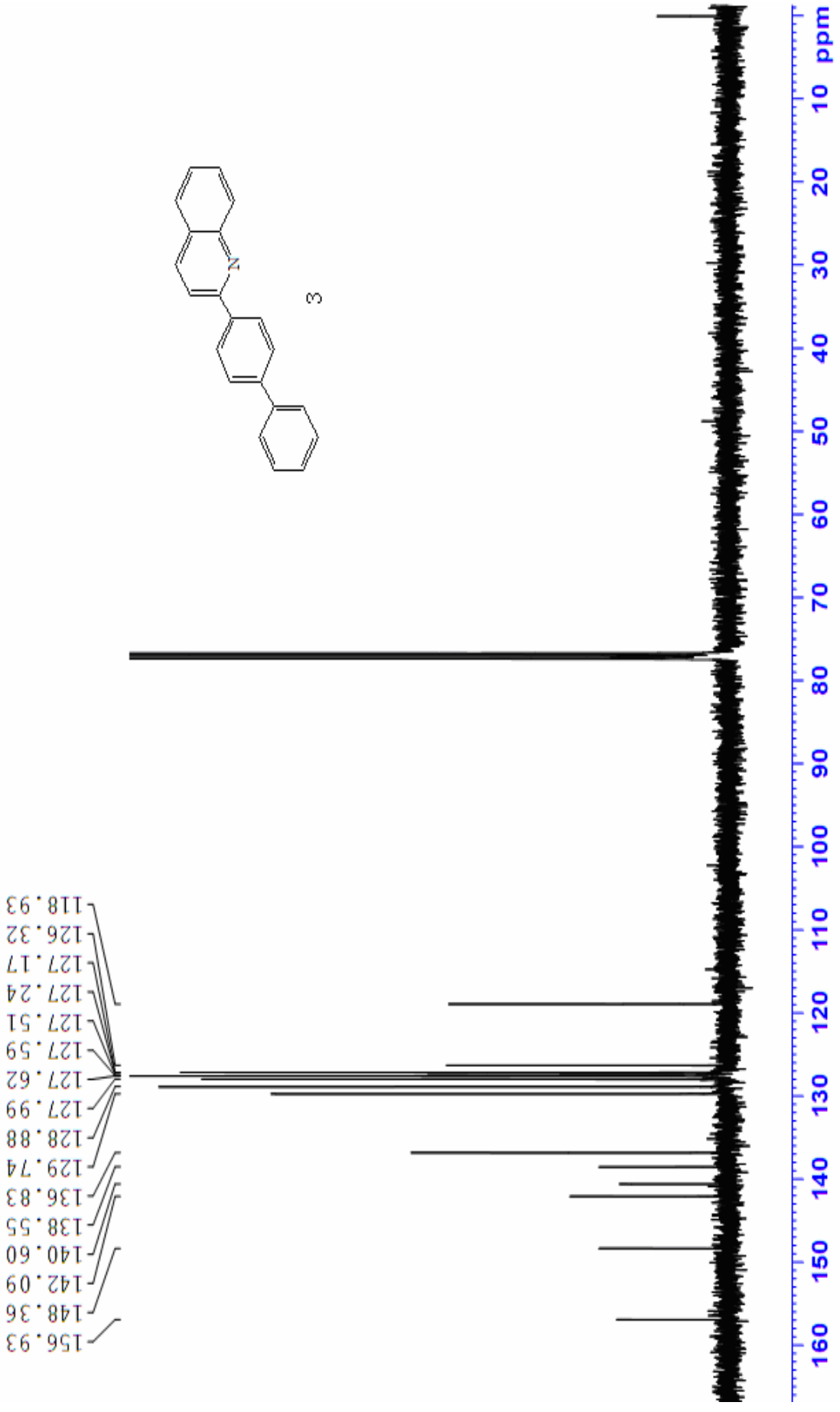

N
N
Fe
Pd
Cl
N
N
1
2.2727
2.3737
3.4128
3.4546
4.1899
4.4920
7.1205
7.1407
7.2624
7.3761
7.3798
7.4078
7.4281
7.4533
7.4569
7.7548
7.7752
8.2749
8.2821
8.3002
8.3208
8.3763
8.9843
8.9883
ppm
1
2
3
4
5
6
7
8
9
1.00
3.10
1.00
2.04
4.20
2.26
1.04
1.12
4.85
1.12
3.11
3.15


21.24
62.98
69.52
70.18
73.90
85.12
95.62
122.82
123.36
125.16
125.72
129.72
130.28
138.11
138.32
138.70
139.91
140.54
143.31
161.60
169.94
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
Fe
Pd
Cl
N
1


0.8560
0.8732
0.9710
0.9880
1.1775
1.1860
1.1995
1.2166
1.4171
1.4333
1.5318
1.5481
1.5642
1.5806
1.6011
1.6176
2.8792
2.8958
2.9120
2.9255
2.9414
3.1196
3.1359
3.3861
3.9163
4.3176
4.5498
9.0483
8.3397
8.1168
8.1096
7.4996
7.4848
7.4579
7.3448
7.3263
7.3021
7.2565
7.2220
7.2097
7.1972
7.1929
7.0585
7.0406
Fe
Pd
Cl
N
N
N
N
2
ppm
0.96
1.04
0.99
3.14
2.56
2.93
1.24
1.00
0.85
1.13
1.04
5.00
1.92
2.12
9.41
3.46
3.09
3.25
3.40
3.03

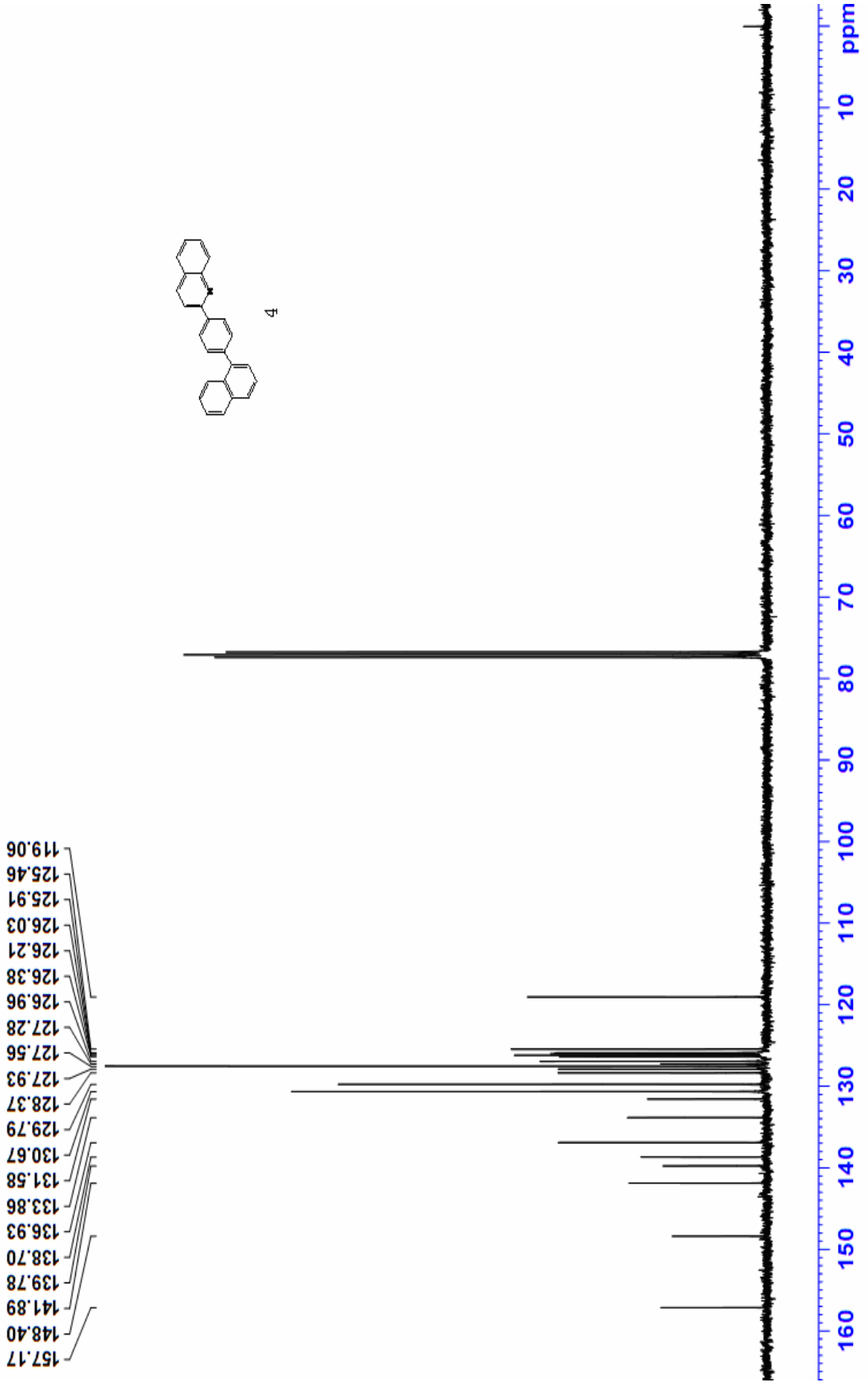

21.78
23.41
23.48
23.76
25.19
25.59
27.35
27.99
28.56
28.64
29.06
29.16
29.84
62.93
69.60
70.49
84.88
96.75
123.34
124.46
124.67
124.94
125.14
125.46
130.08
130.37
136.28
136.55
139.12
140.26
143.56
144.65
145.49
147.12
148.06
161.38
173.77
Fe
Pd
Cl
N
2
ppm
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170


8.2251
8.2026
8.1781
7.9179
7.8966
7.8320
7.8119
7.7698
7.7488
7.7346
7.7313
7.7137
7.7104
7.6875
7.6843
7.6663
7.5435
7.5417
7.5239
7.5063
7.5041
7.4899
7.4716
7.4522
7.3947
7.3763
7.3580
7.2412
N
3
10
9
8
7
6
5
4
3
2
1
0
4.00
0.99
1.02
2.99
2.09
3.21
1.05

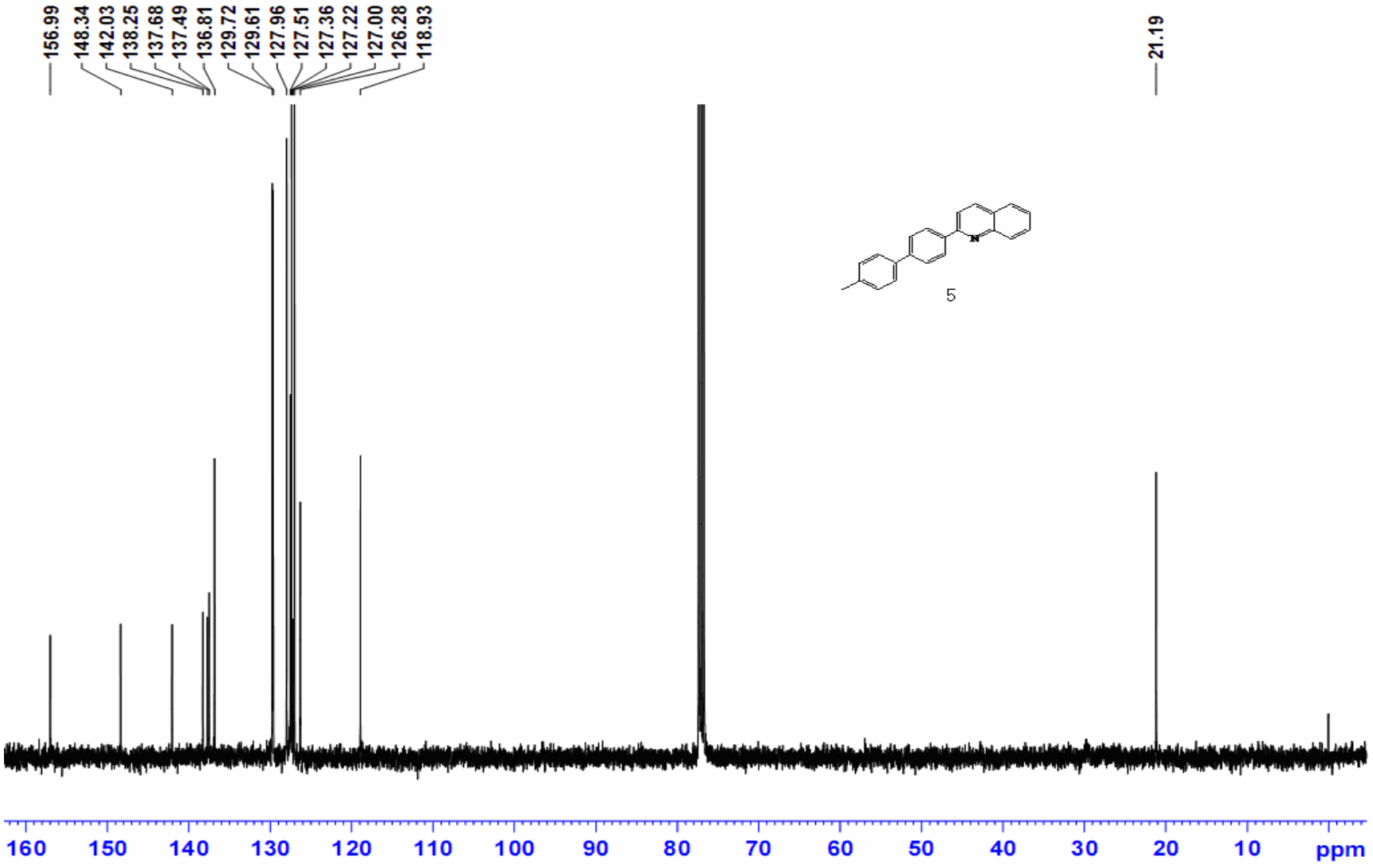

3
N
156.93
148.36
142.09
140.60
138.55
136.83
129.74
128.88
127.99
127.62
127.59
127.51
127.24
127.17
126.32
118.93
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

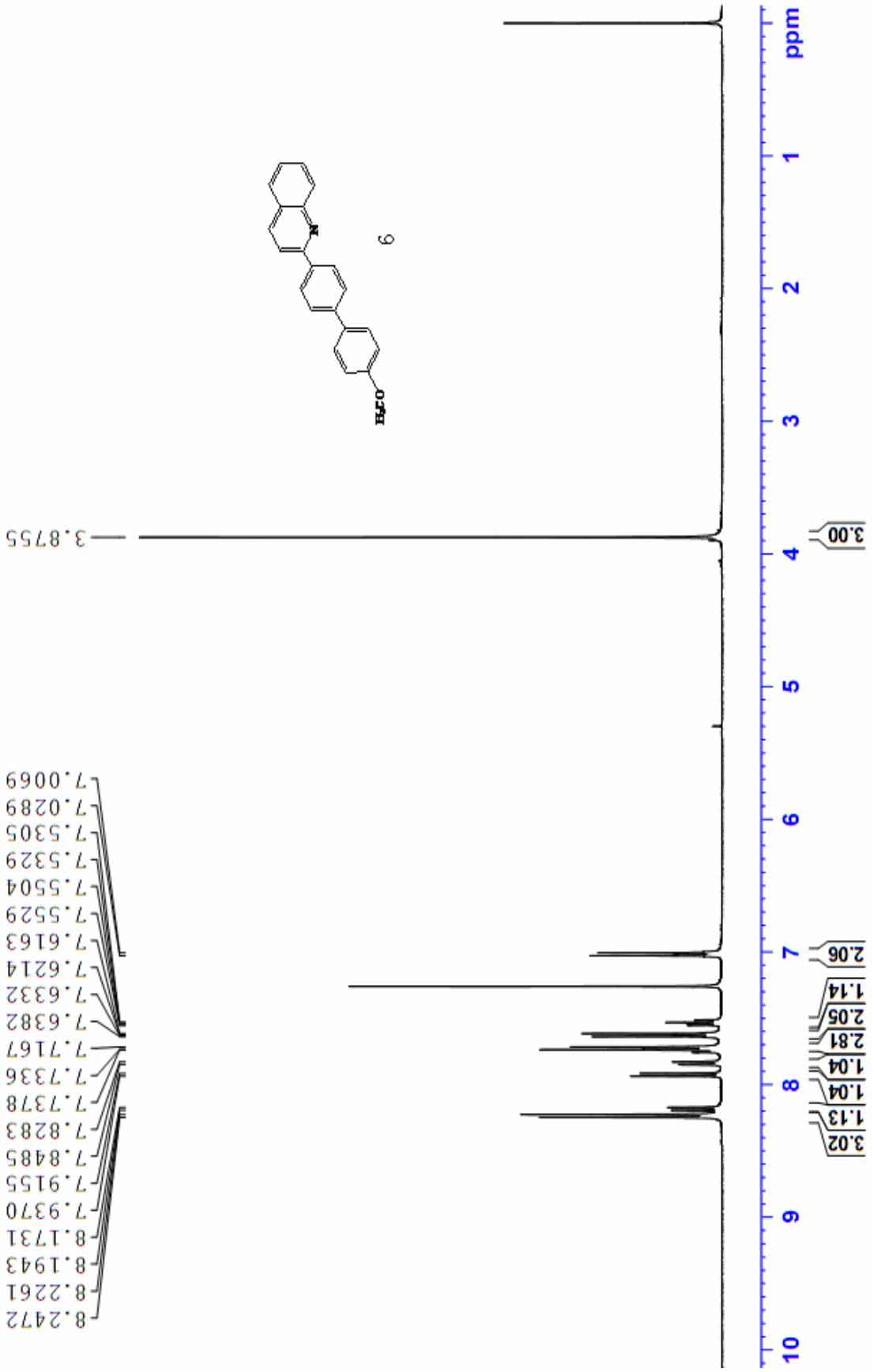
8.2959
8.2752
8.2514
8.2296
7.9560
7.9345
7.6774
7.6566
7.5483
7.5348
7.5282
7.4964
7.4932
7.2325
4.00
5.06
1.08
2.05
5.16
ppm
1
2
3
4
5
6
7
8
9

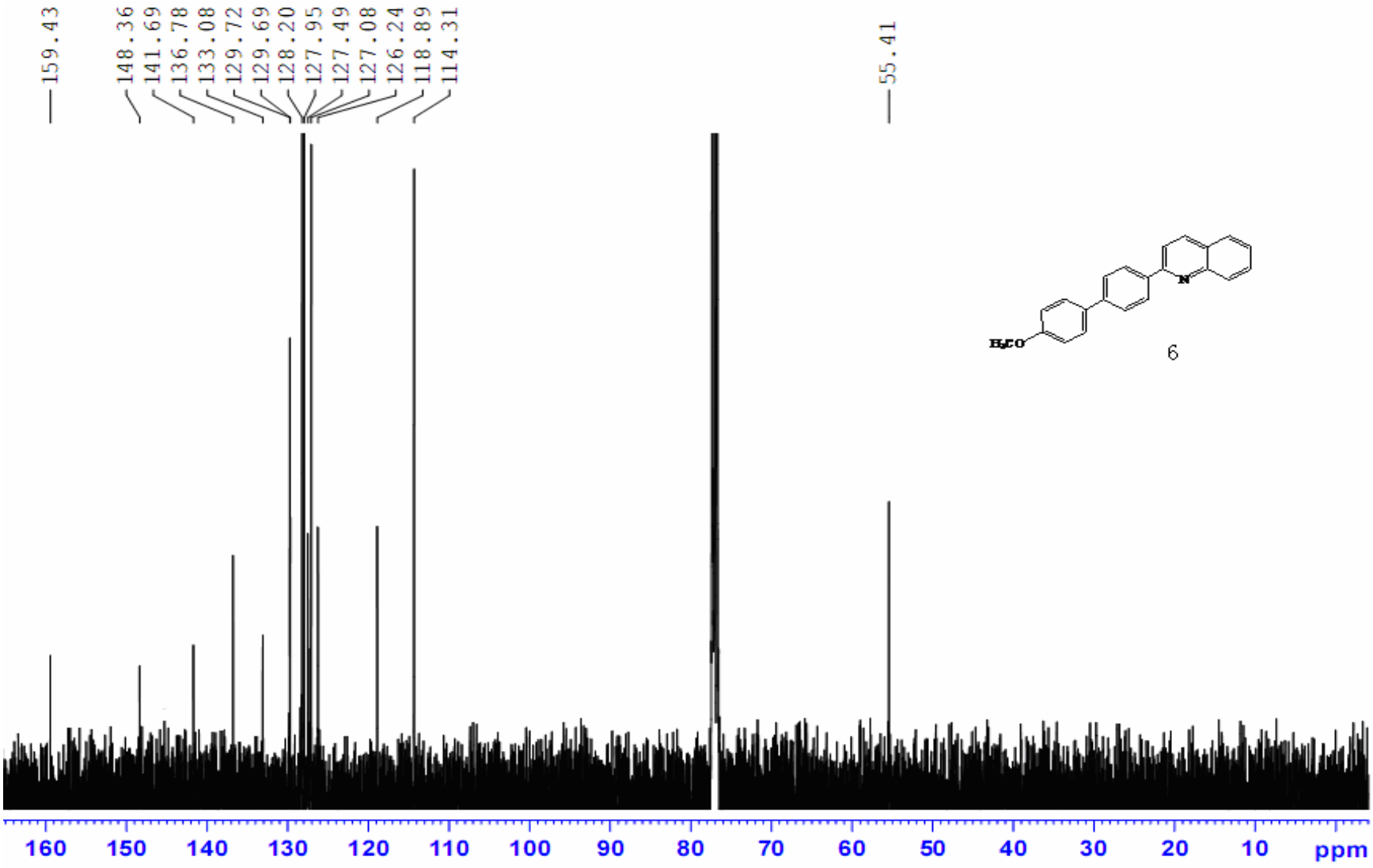
4

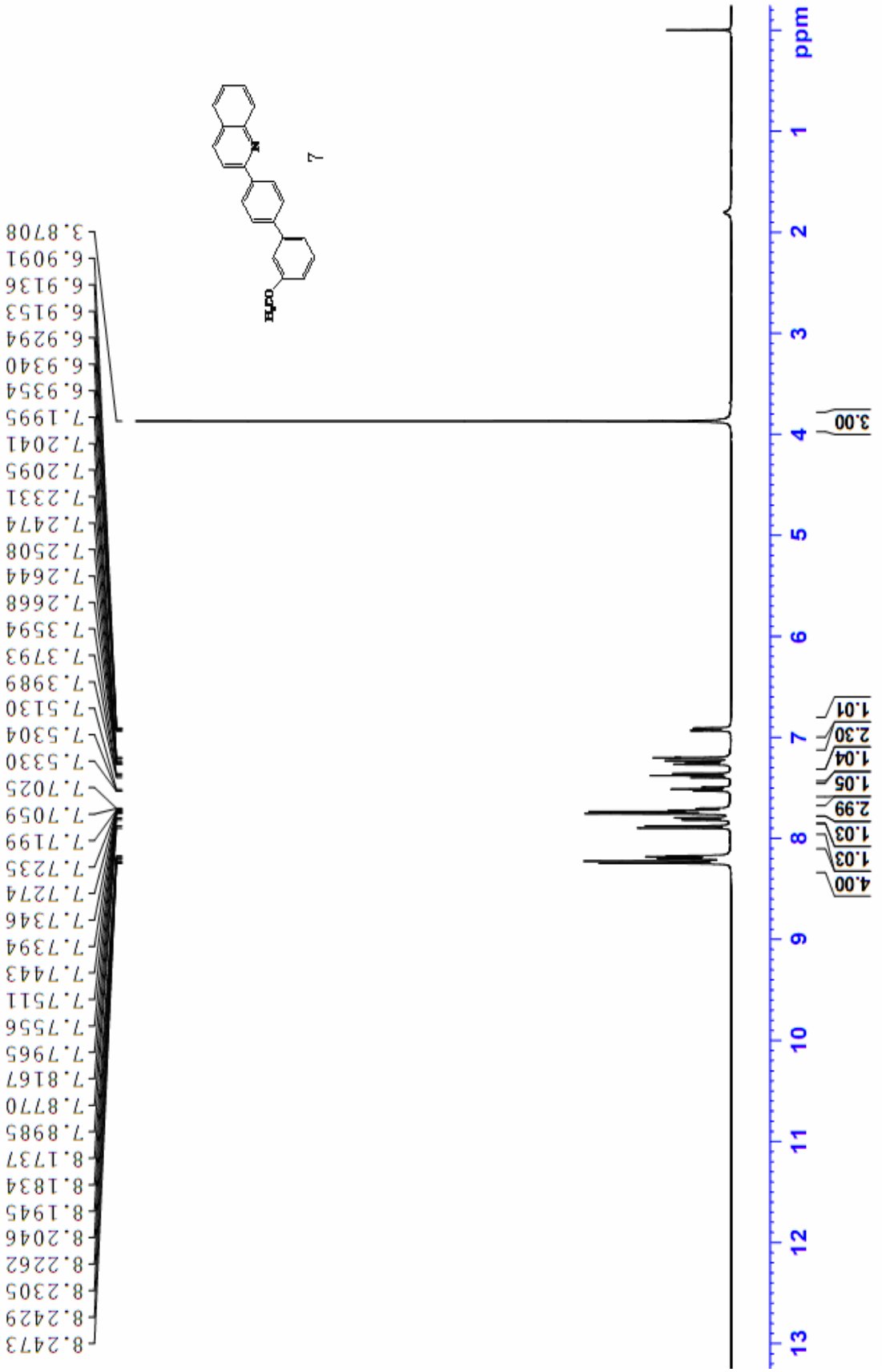

4
157.17
148.40
141.89
139.78
138.70
136.93
133.86
131.58
130.67
129.79
128.37
127.93
127.56
127.28
126.96
126.38
126.21
126.03
125.91
125.46
119.06
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

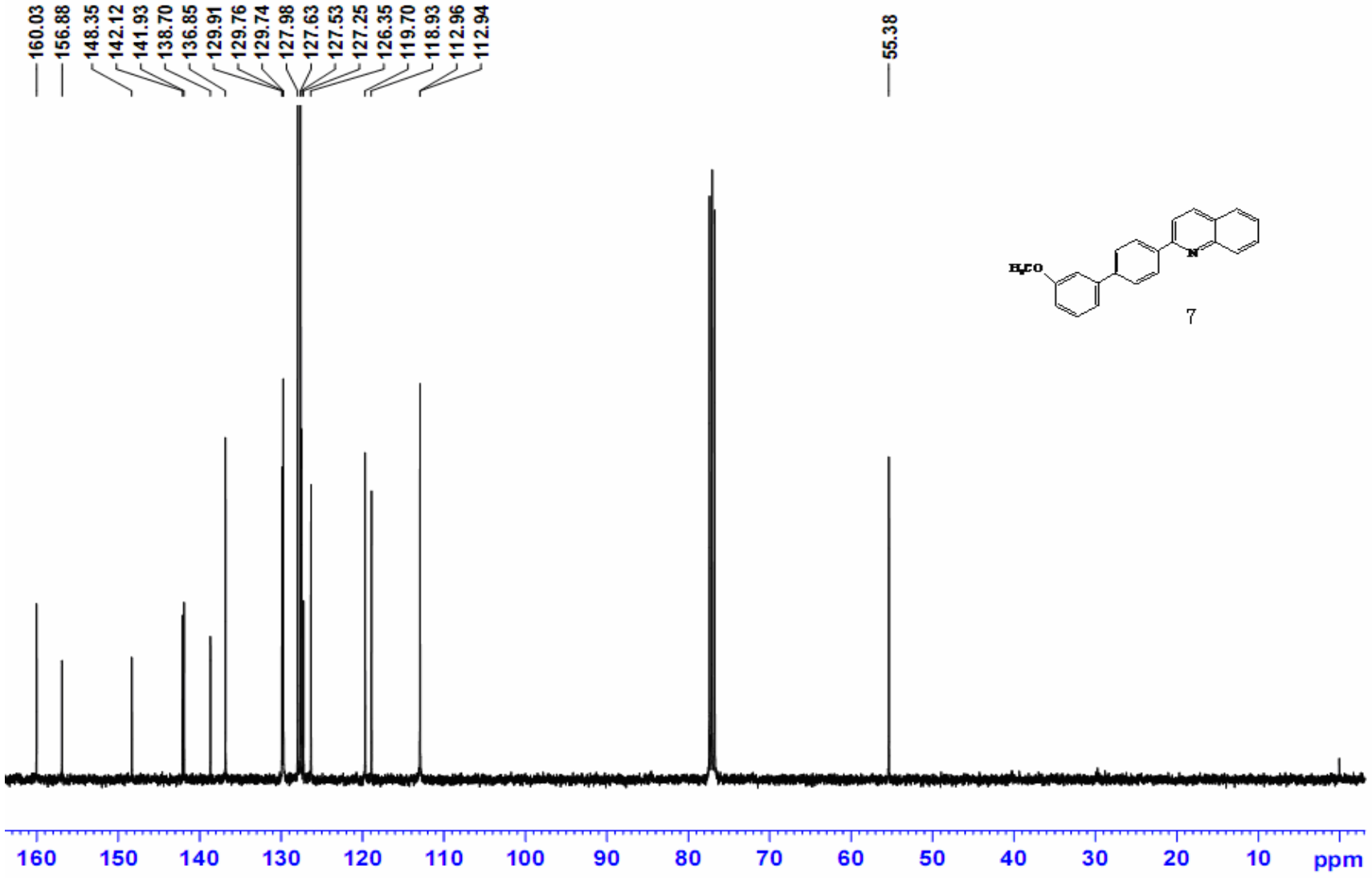
8.2441
8.2228
8.1987
7.9143
7.8929
7.7538
7.7492
7.7326
7.7283
7.5873
7.5671
7.2888
7.2691
7.2426
2.4116
5
3.94
1.01
1.02
2.91
1.89
1.19
1.90
3.00
ppm

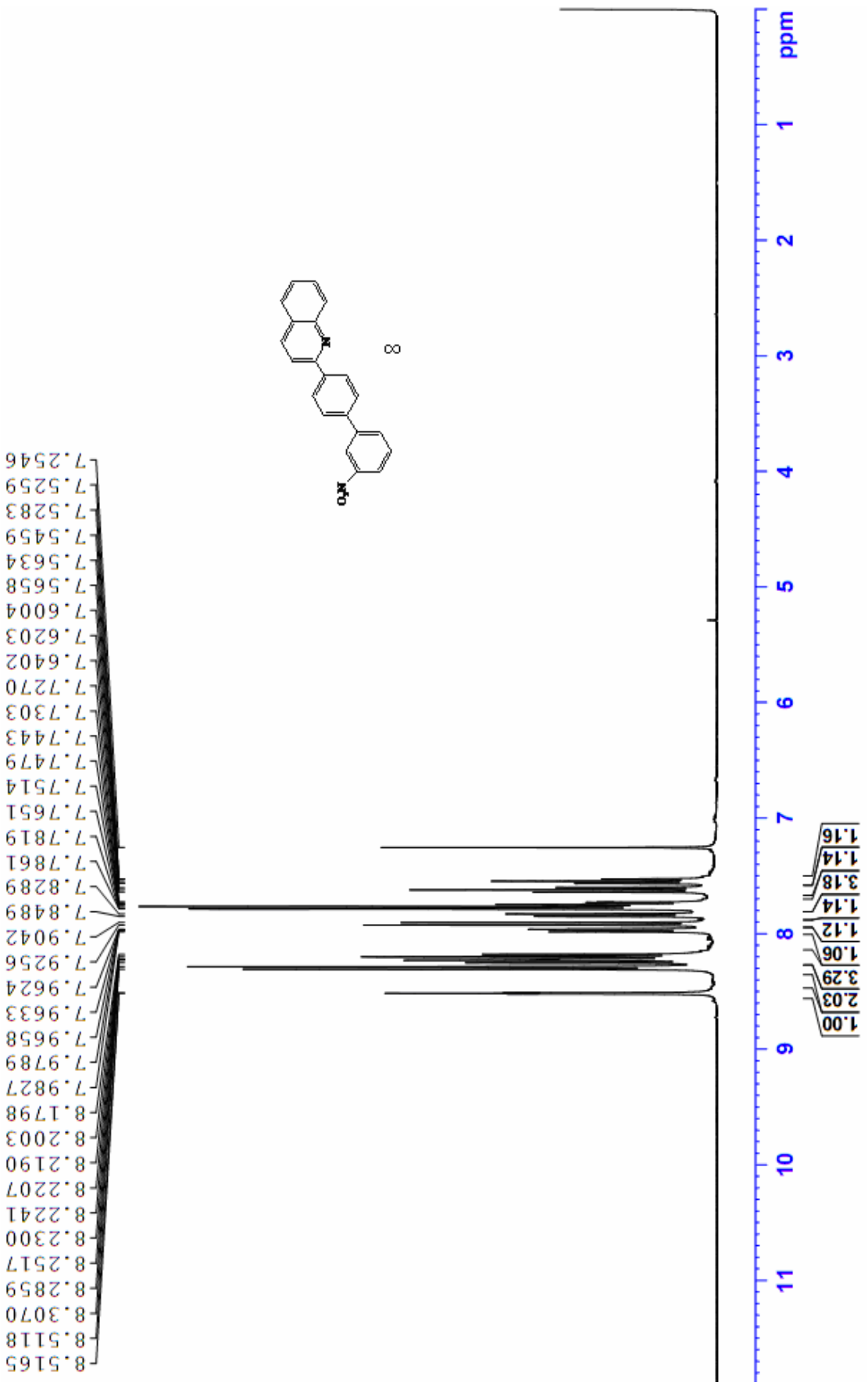

156.99
148.34
142.03
138.25
137.68
137.49
136.81
129.72
129.61
127.96
127.51
127.36
127.22
127.00
126.28
118.93
21.19
N
5
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

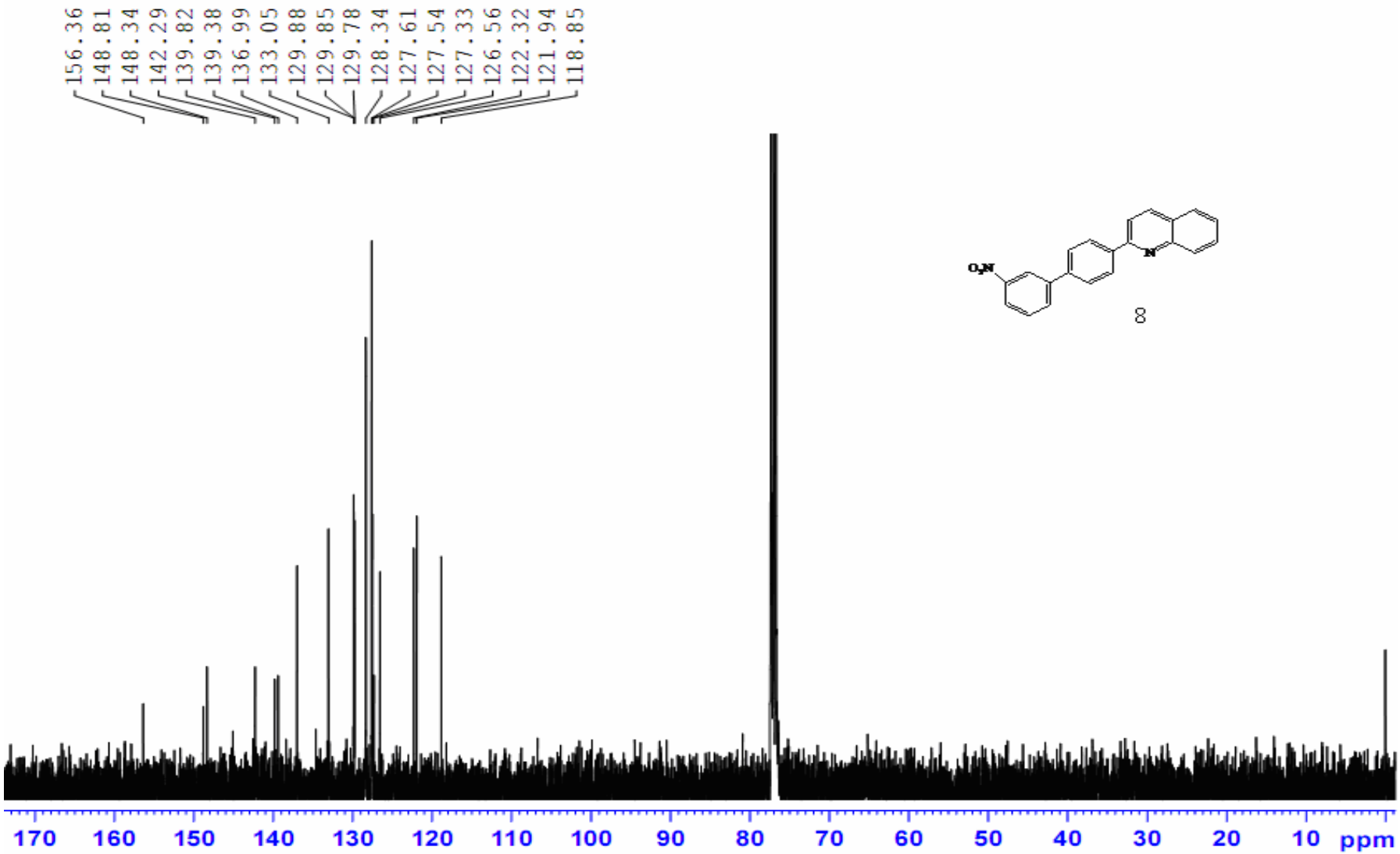

8.2472
8.2261
8.1943
8.1731
7.9370
7.9155
7.8485
7.8283
7.7378
7.7336
7.7167
7.6382
7.6332
7.6214
7.6163
7.5529
7.5504
7.5329
7.5305
7.0289
7.0069
3.8755
3.00
2.06
1.14
2.05
2.81
1.04
1.04
1.13
3.02
ppm
1
2
3
4
5
6
7
8
9
10
N
9

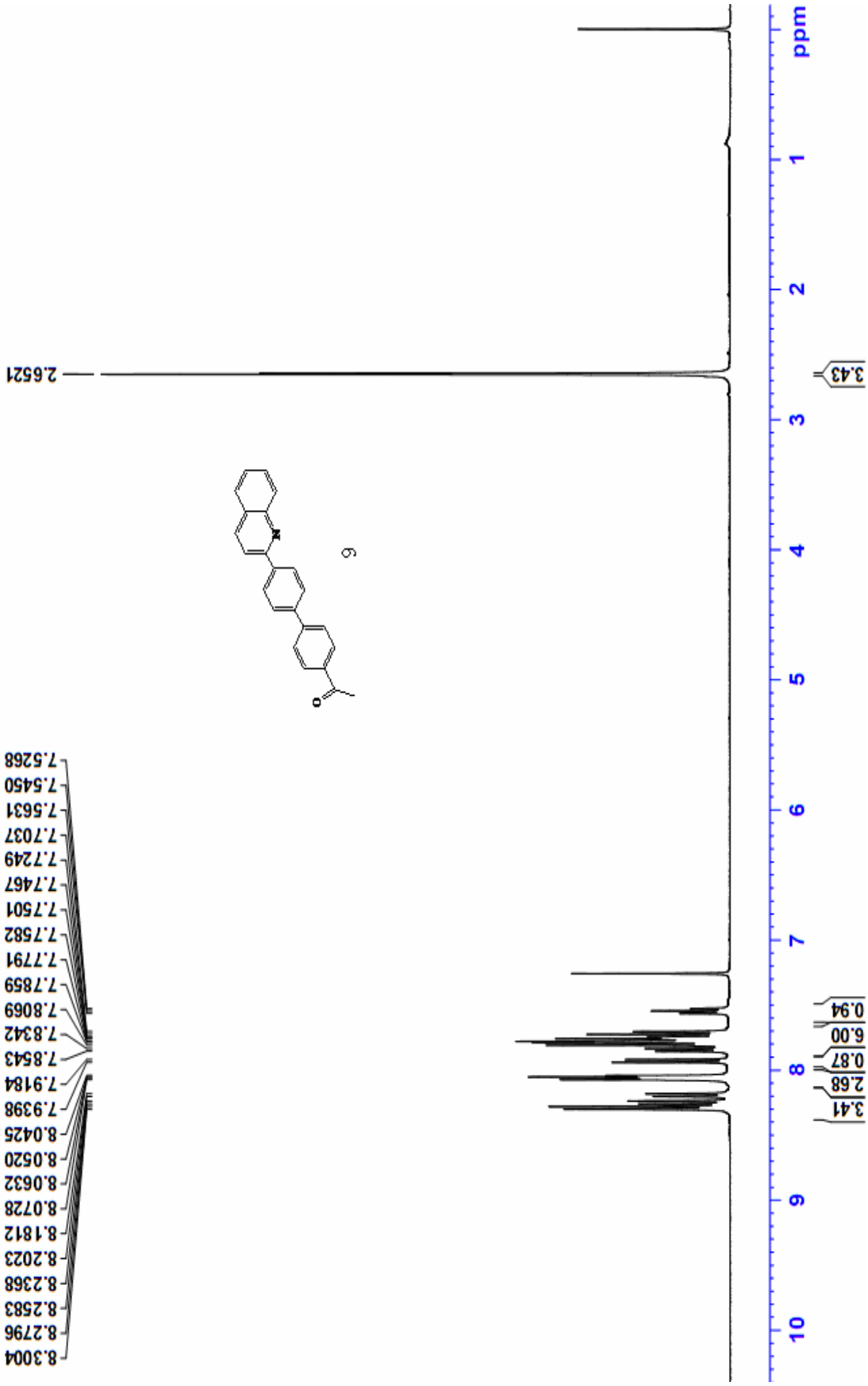

159.43
148.36
141.69
136.78
133.08
129.72
129.69
128.20
127.95
127.49
127.08
126.24
118.89
114.31
55.41
H3CO
N
6
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

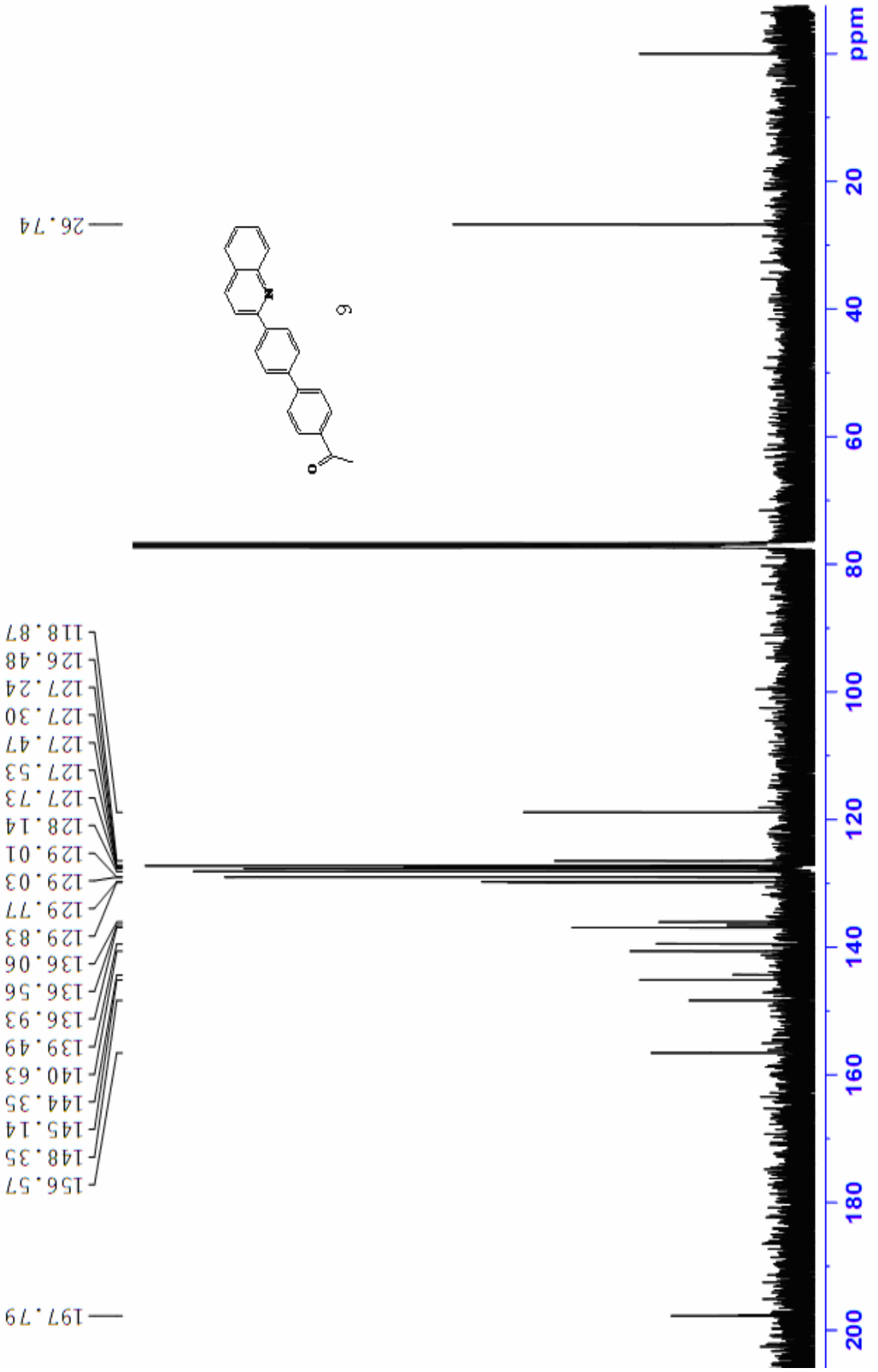

7
OEt
3.00
4.00
1.03
1.03
2.99
1.05
1.04
2.30
1.01
ppm
1
2
3
4
5
6
7
8
9
10
11
12
13
8.2473
8.2429
8.2305
8.2262
8.2046
8.1945
8.1834
8.1737
7.8985
7.8770
7.8167
7.7965
7.7556
7.7511
7.7443
7.7394
7.7346
7.7274
7.7235
7.7199
7.7059
7.7025
7.5330
7.5304
7.5130
7.3989
7.3793
7.3594
7.2668
7.2644
7.2508
7.2474
7.2331
7.2095
7.2041
7.1995
6.9354
6.9340
6.9294
6.9153
6.9136
6.9091
3.8708

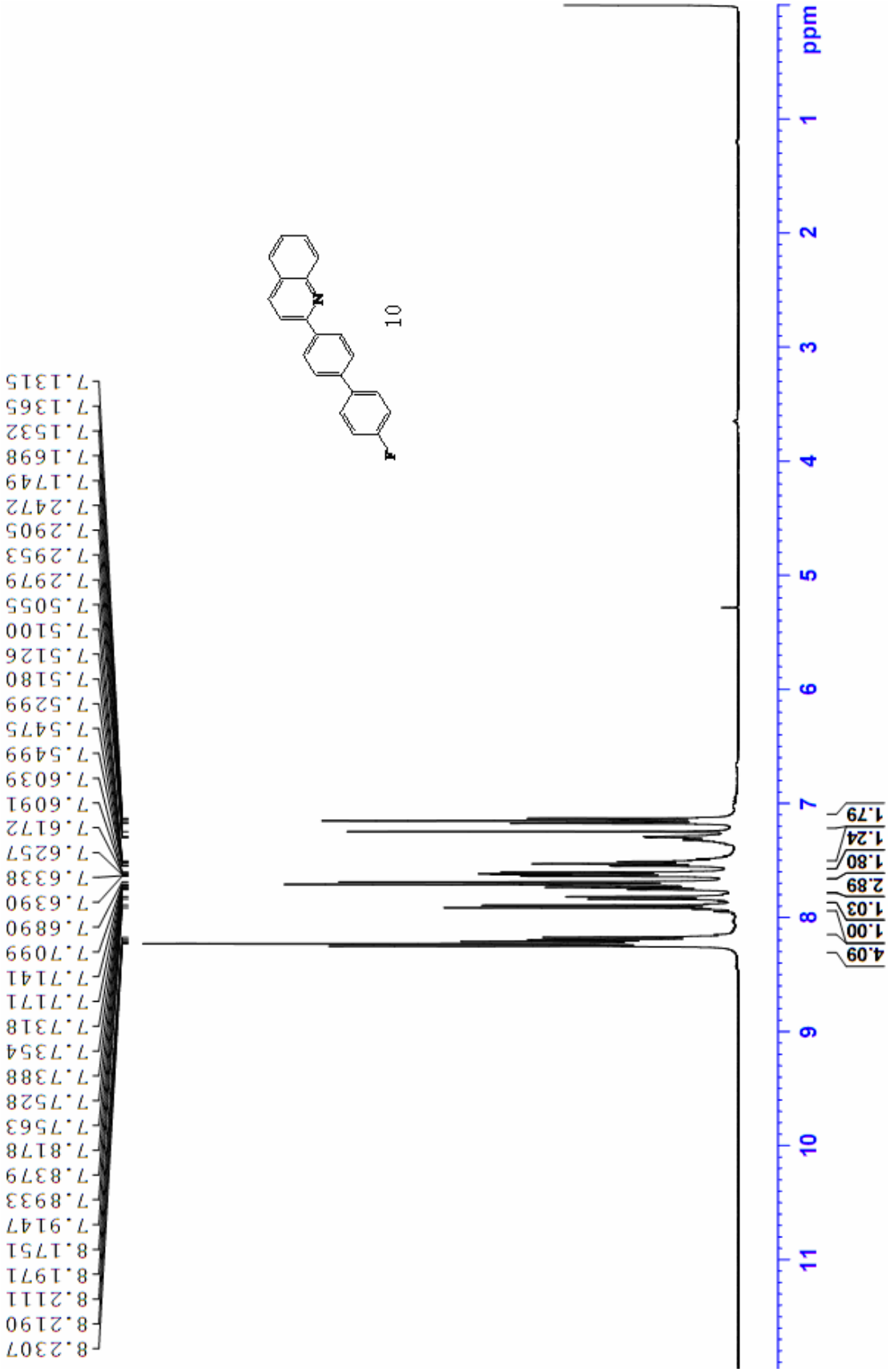

160.03
156.88
148.35
142.12
141.93
138.70
136.85
129.91
129.76
129.74
127.98
127.63
127.53
127.25
126.35
119.70
118.93
112.96
112.94
55.38
H3CO
N
7
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

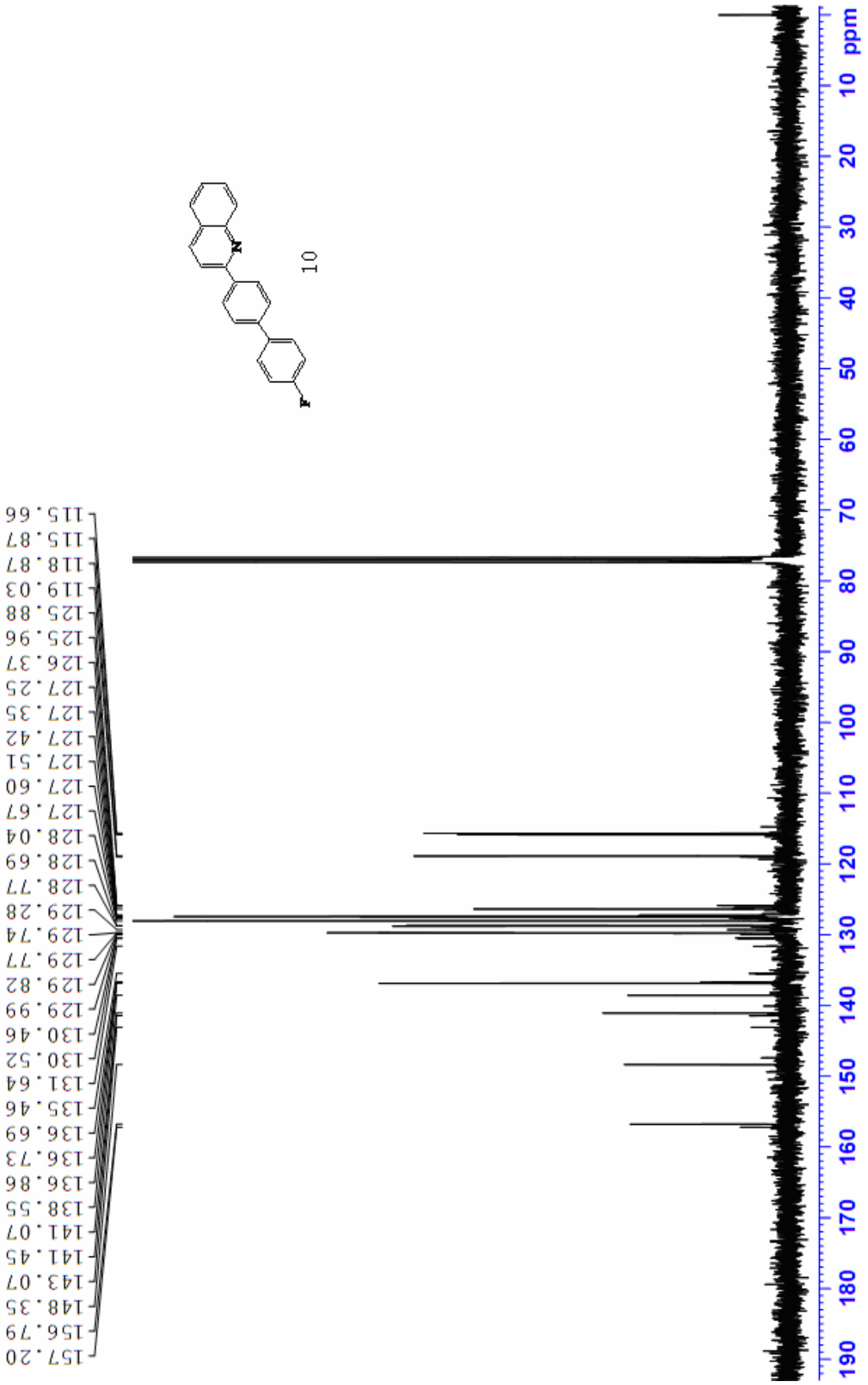

8.5165
8.5118
8.3070
8.2859
8.2517
8.2300
8.2241
8.2207
8.2190
8.2003
8.1798
7.9827
7.9789
7.9658
7.9633
7.9624
7.9256
7.9042
7.8489
7.8289
7.7861
7.7819
7.7651
7.7514
7.7479
7.7443
7.7303
7.7270
7.6402
7.6203
7.6004
7.5658
7.5634
7.5459
7.5283
7.5259
7.2546
O2N
8
ppm
1 2 3 4 5 6 7 8 9 10 11
1.00
2.03
3.29
1.06
1.12
1.14
3.18
1.14
1.16

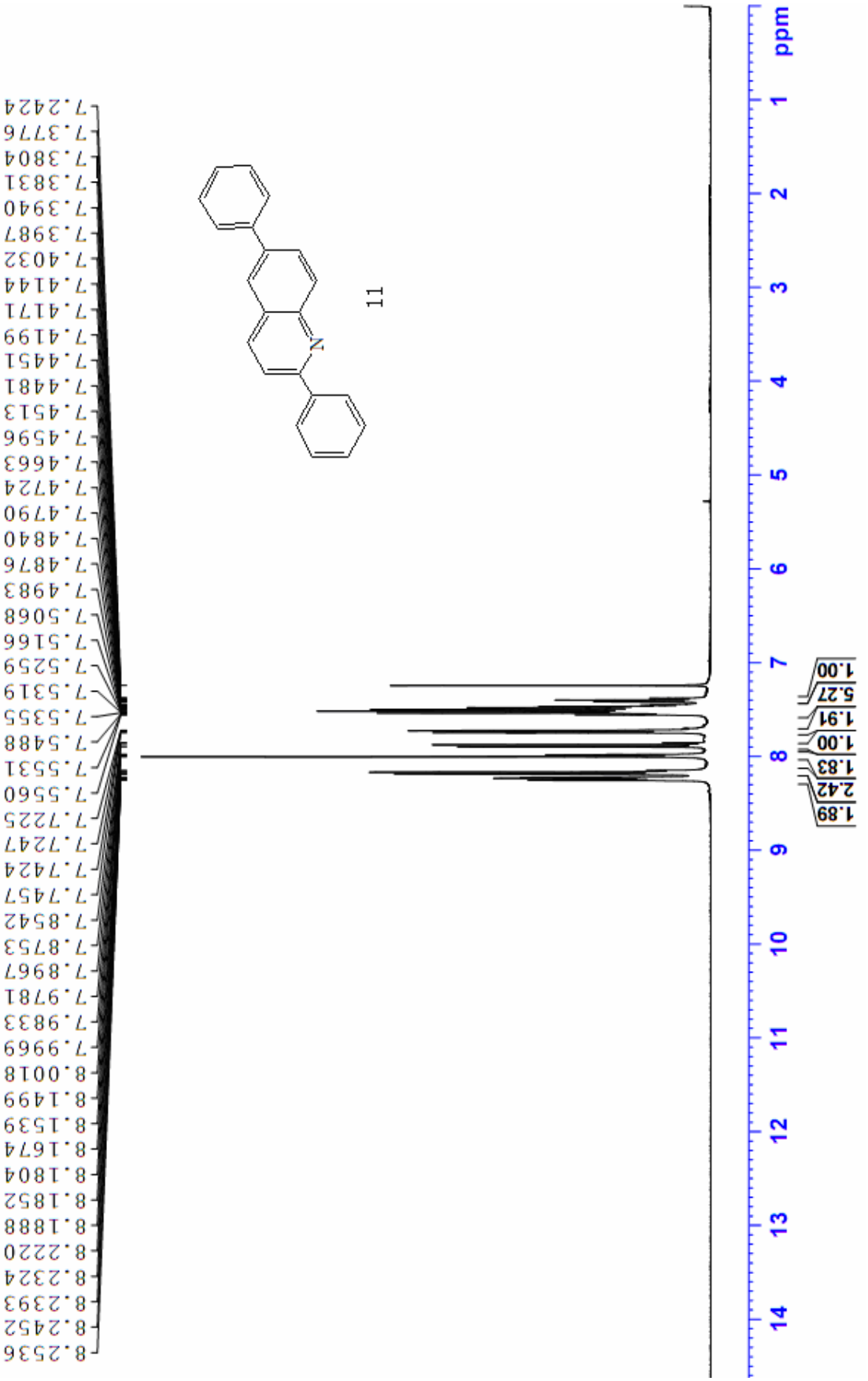

156.36
148.81
148.34
142.29
139.82
139.38
136.99
133.05
129.88
129.85
129.78
128.34
127.61
127.54
127.33
126.56
122.32
121.94
118.85
O2N
N
8
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

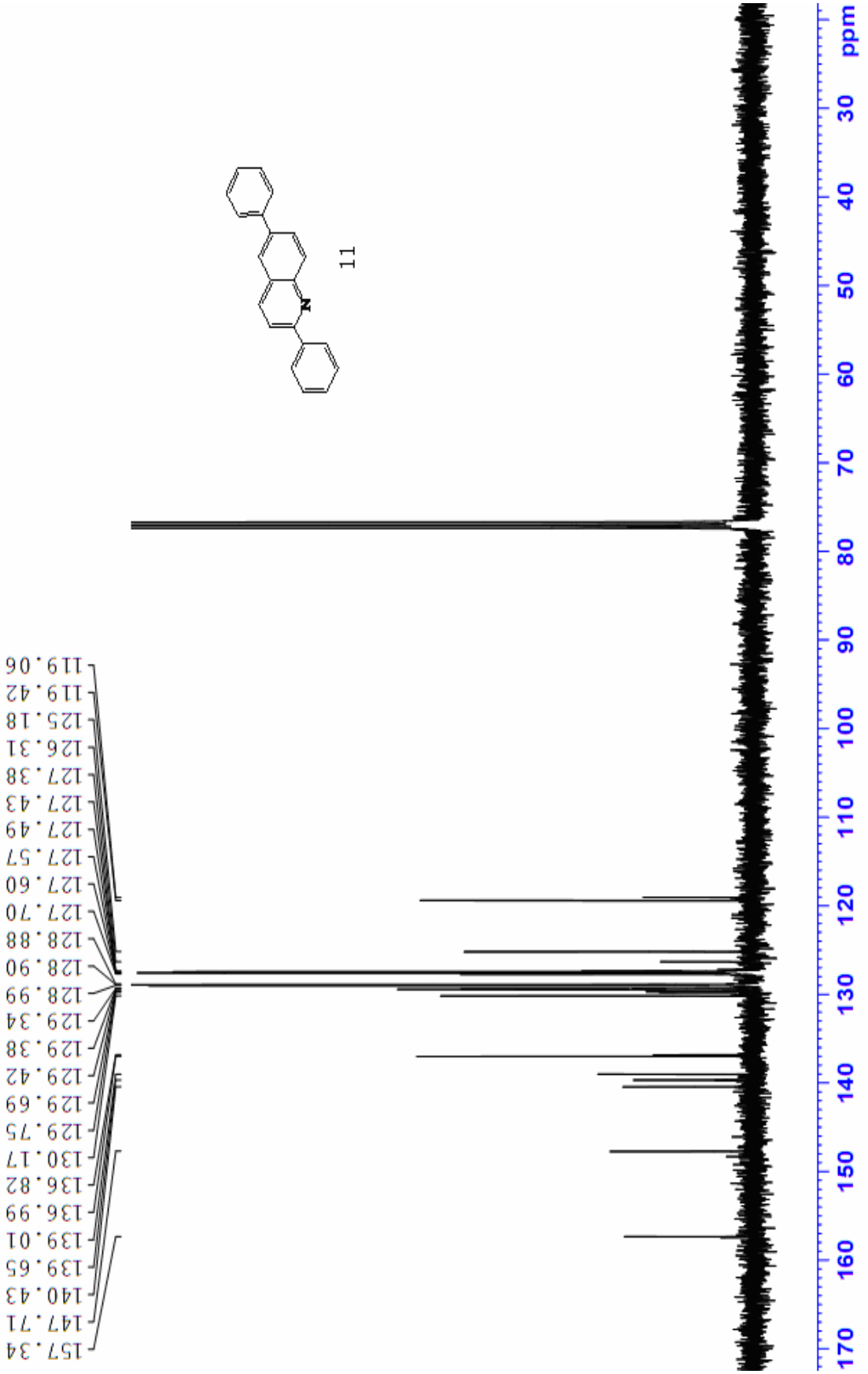

ppm
1
2
3
4
5
6
7
8
9
10
3.43
2.6521
3.41
2.68
0.87
6.00
0.94
8.3004
8.2796
8.2583
8.2368
8.2023
8.1812
8.0728
8.0632
8.0520
8.0425
7.9398
7.9184
7.8543
7.8342
7.8069
7.7859
7.7791
7.7582
7.7501
7.7467
7.7249
7.7037
7.5631
7.5450
7.5268
O
N
9

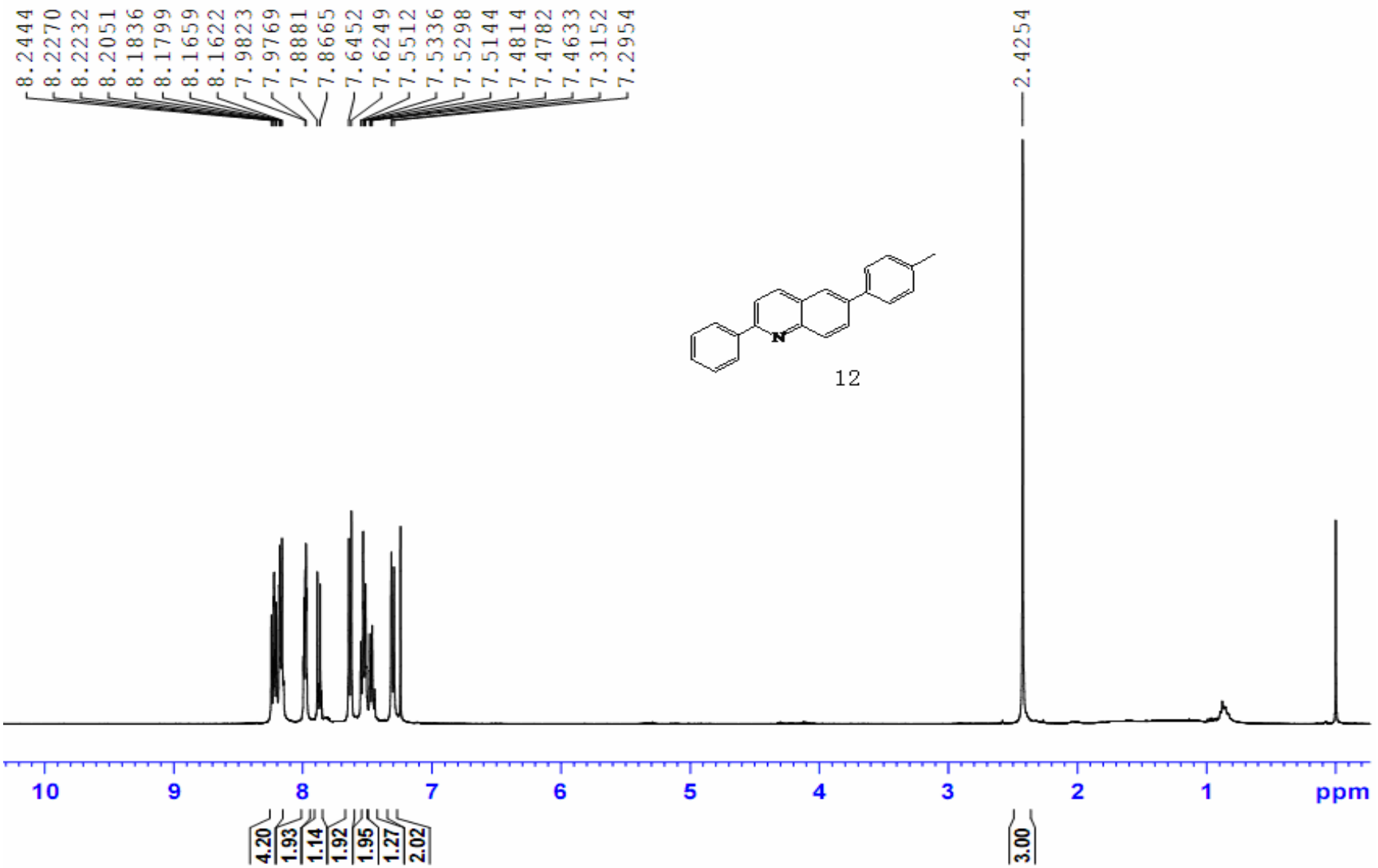

26.74
197.79
156.57
148.35
145.14
144.35
140.63
139.49
136.93
136.56
136.06
129.83
129.77
129.03
129.01
128.14
127.73
127.53
127.47
127.30
127.24
126.48
118.87
6
ppm
20
40
60
80
100
120
140
160
180
200

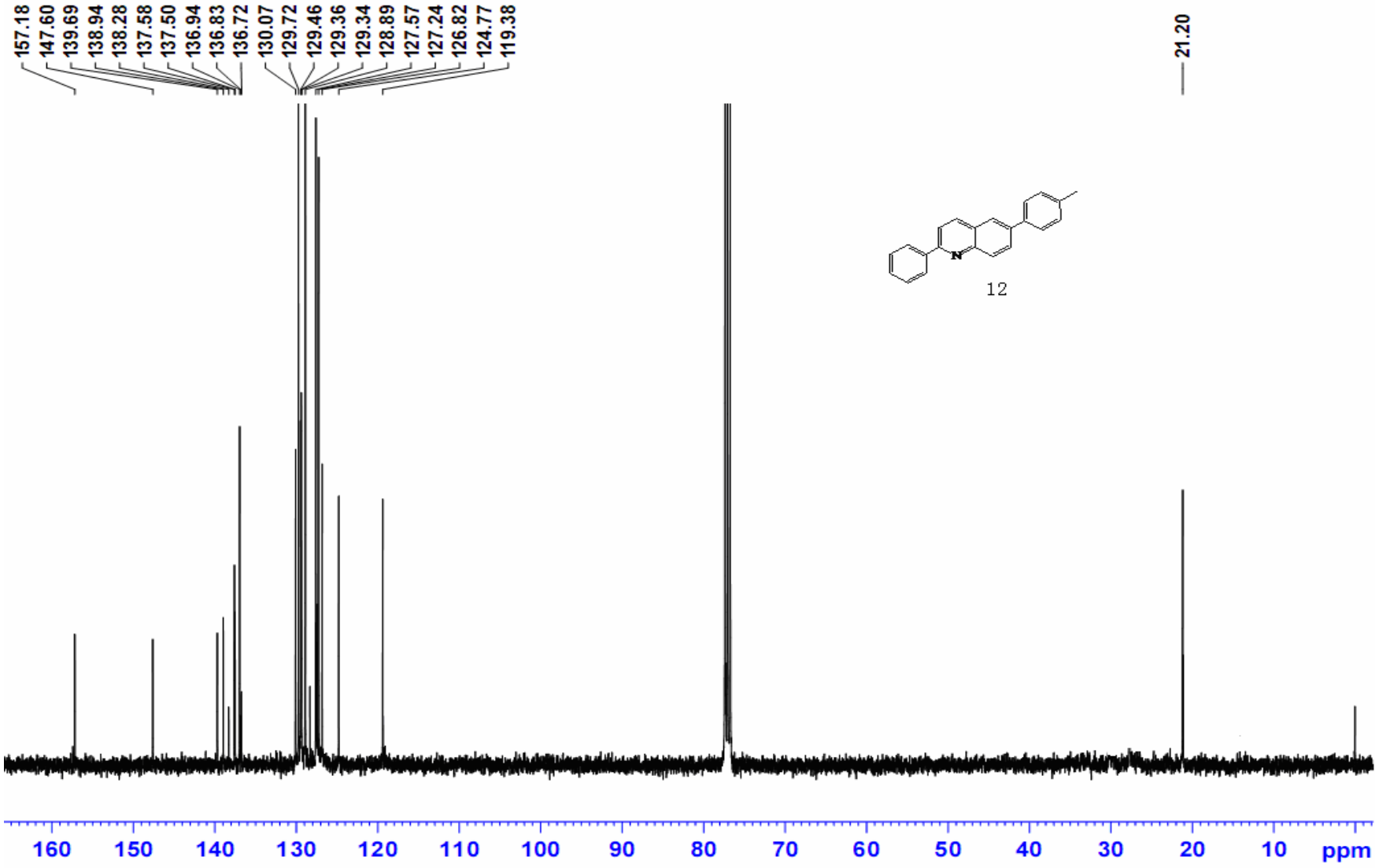

10
N
F
ppm
1
2
3
4
5
6
7
8
9
10
11
4.09
1.00
1.03
2.89
1.80
1.24
1.79
8.2307
8.2190
8.2111
8.1971
8.1751
7.9147
7.8933
7.8379
7.8178
7.7563
7.7528
7.7388
7.7354
7.7318
7.7171
7.7141
7.7099
7.6890
7.6390
7.6338
7.6257
7.6172
7.6091
7.6039
7.5499
7.5475
7.5299
7.5180
7.5126
7.5100
7.5055
7.2979
7.2953
7.2905
7.2472
7.1749
7.1698
7.1532
7.1365
7.1315

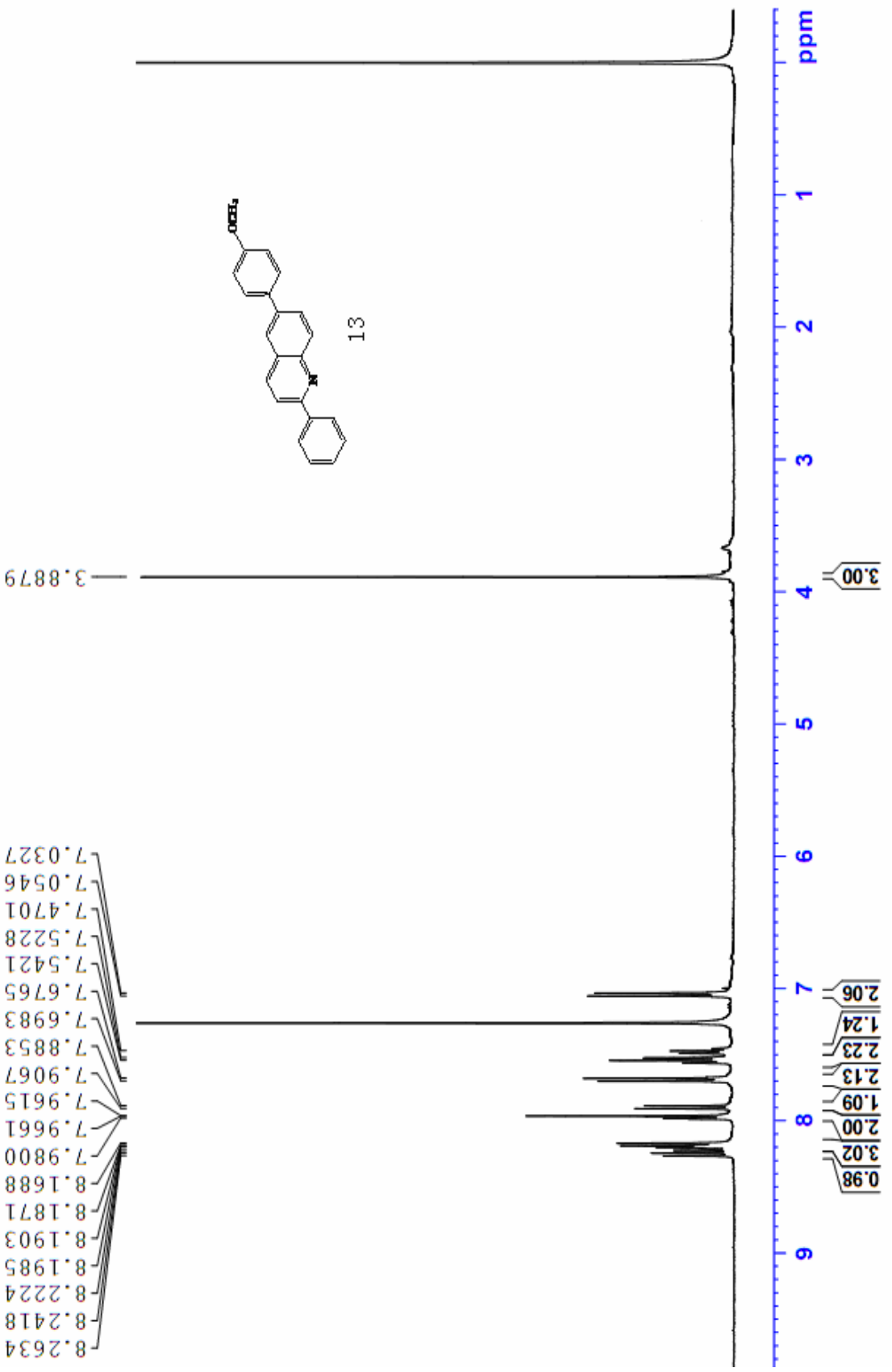

10
N
F
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
157.20
156.79
148.35
143.07
141.45
141.07
138.55
136.86
136.73
136.69
135.46
131.64
130.52
130.46
129.99
129.82
129.77
129.74
129.28
128.77
128.69
128.04
127.67
127.60
127.51
127.42
127.35
127.25
126.37
125.96
125.88
119.03
118.87
115.87
115.66

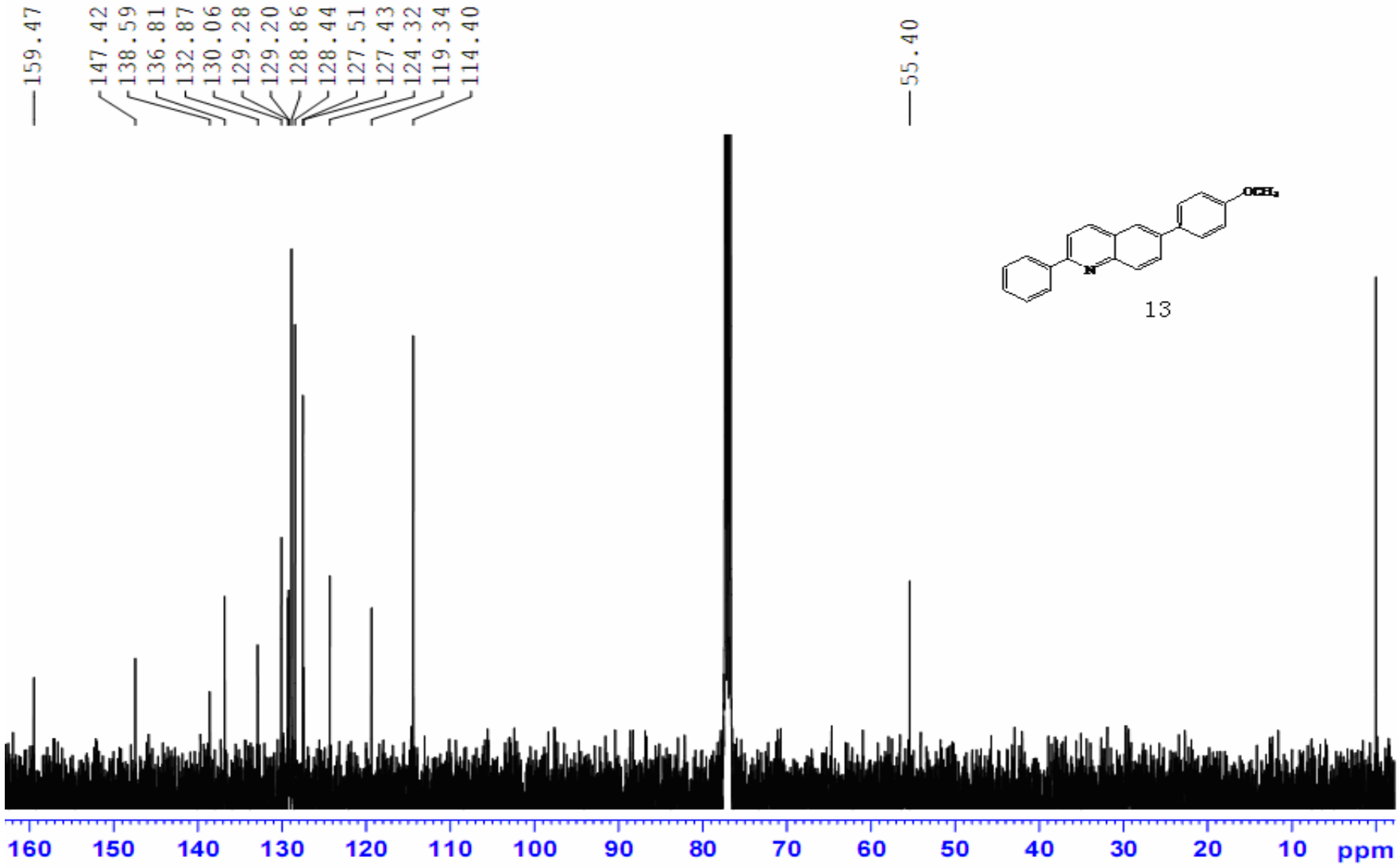

11
N
ppm
1 2 3 4 5 6 7 8 9 10 11 12 13 14
1.89
2.42
1.83
1.00
1.91
5.27
1.00
7.2424
7.3776
7.3804
7.3831
7.3940
7.3987
7.4032
7.4144
7.4171
7.4199
7.4451
7.4481
7.4513
7.4596
7.4663
7.4724
7.4790
7.4840
7.4876
7.4983
7.5068
7.5166
7.5259
7.5319
7.5355
7.5488
7.5531
7.5560
7.7225
7.7247
7.7424
7.7457
7.8542
7.8753
7.8967
7.9781
7.9833
7.9969
8.0018
8.1499
8.1539
8.1674
8.1804
8.1852
8.1888
8.2220
8.2324
8.2393
8.2452
8.2536

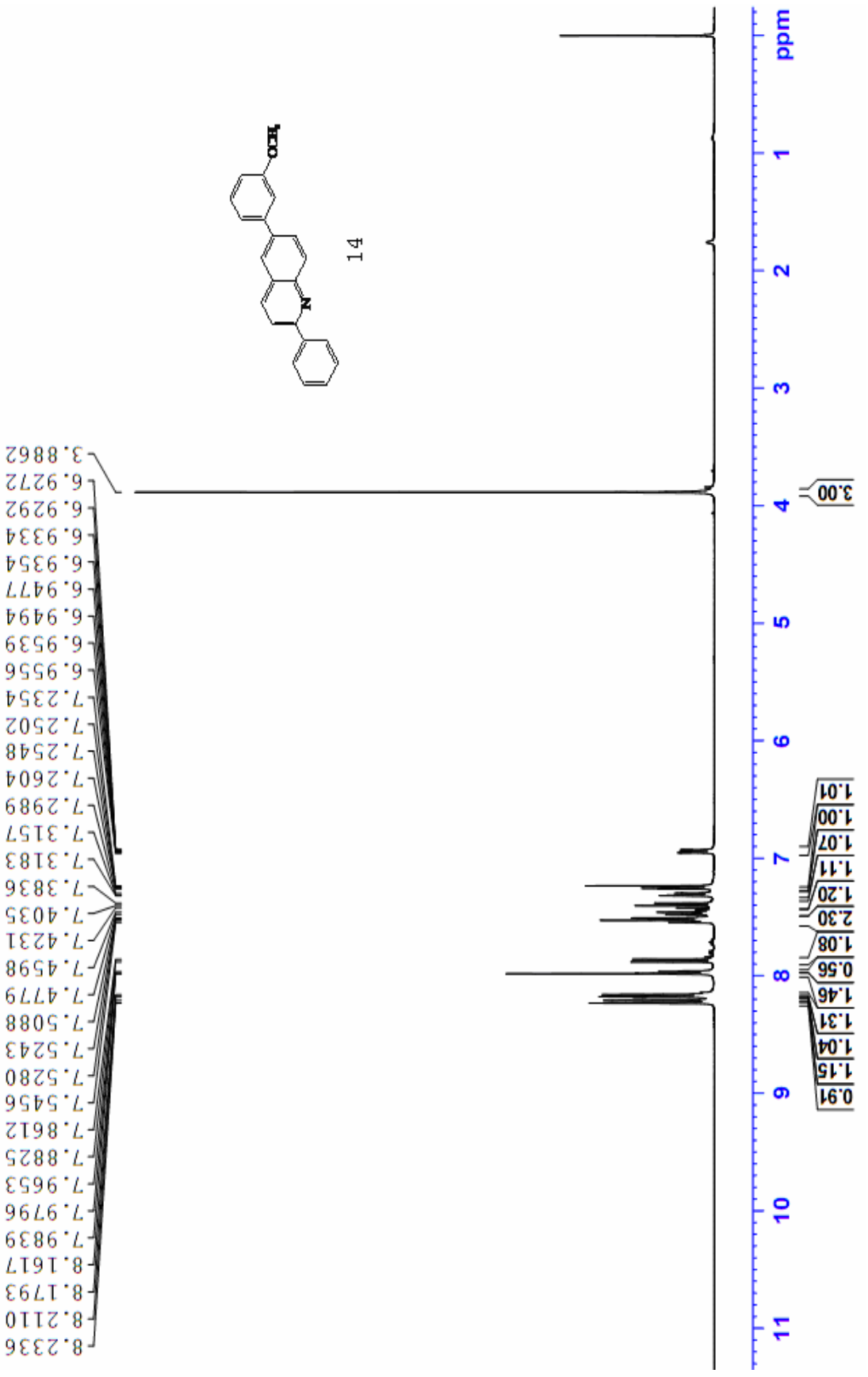

11
N
157.34
147.71
140.43
139.65
139.01
136.99
136.82
130.17
129.75
129.69
129.42
129.38
129.34
128.99
128.90
128.88
127.70
127.60
127.57
127.49
127.43
127.38
126.31
125.18
119.42
119.06
ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170

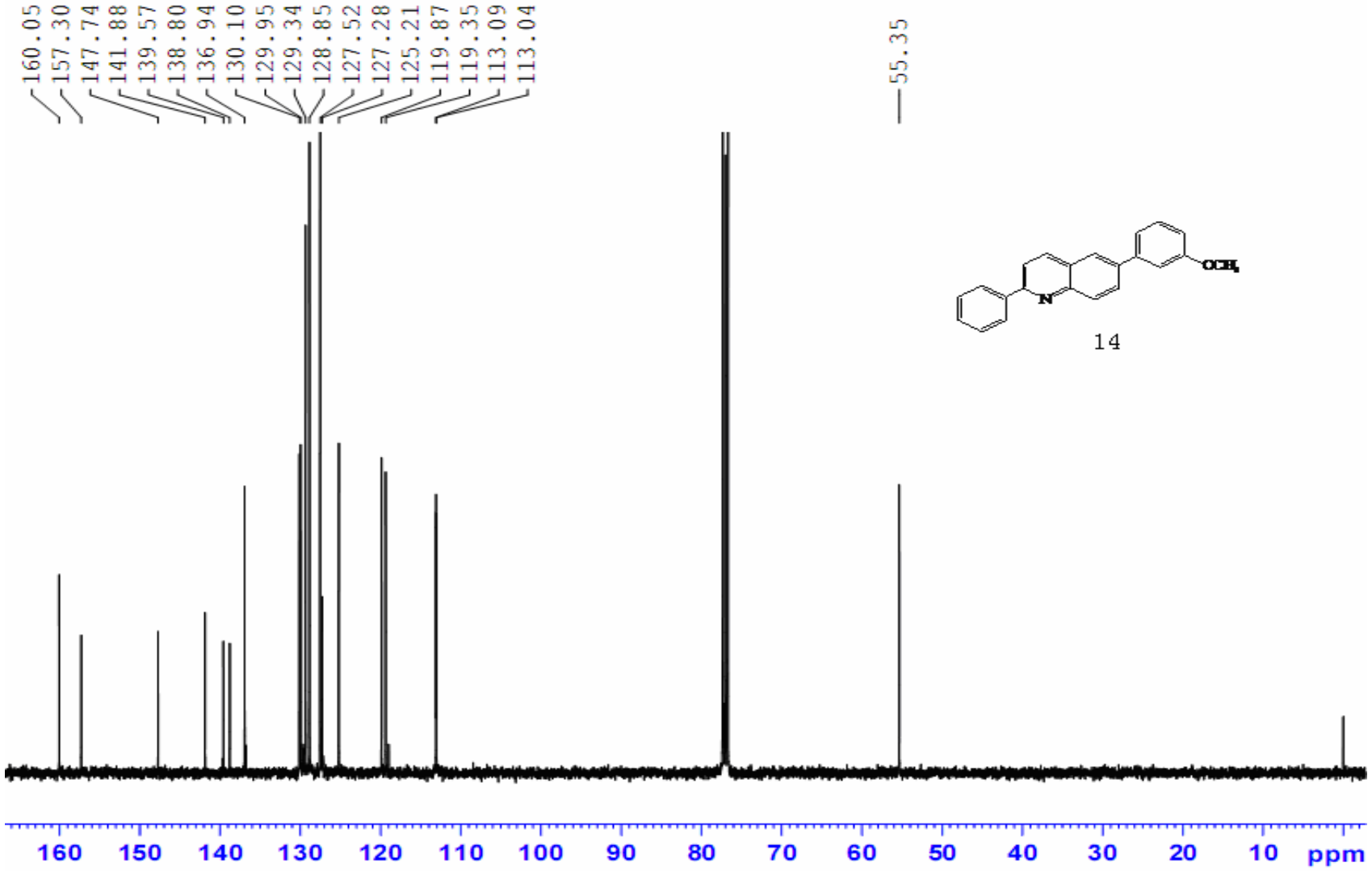

8.2444
8.2270
8.2232
8.2051
8.1836
8.1799
8.1659
8.1622
7.9823
7.9769
7.8881
7.8665
7.6452
7.6249
7.5512
7.5336
7.5298
7.5144
7.4814
7.4782
7.4633
7.3152
7.2954
2.4254
N
12
10
9
8
7
6
5
4
3
2
1
ppm
4.20
1.93
1.14
1.92
1.95
1.27
2.02
3.00

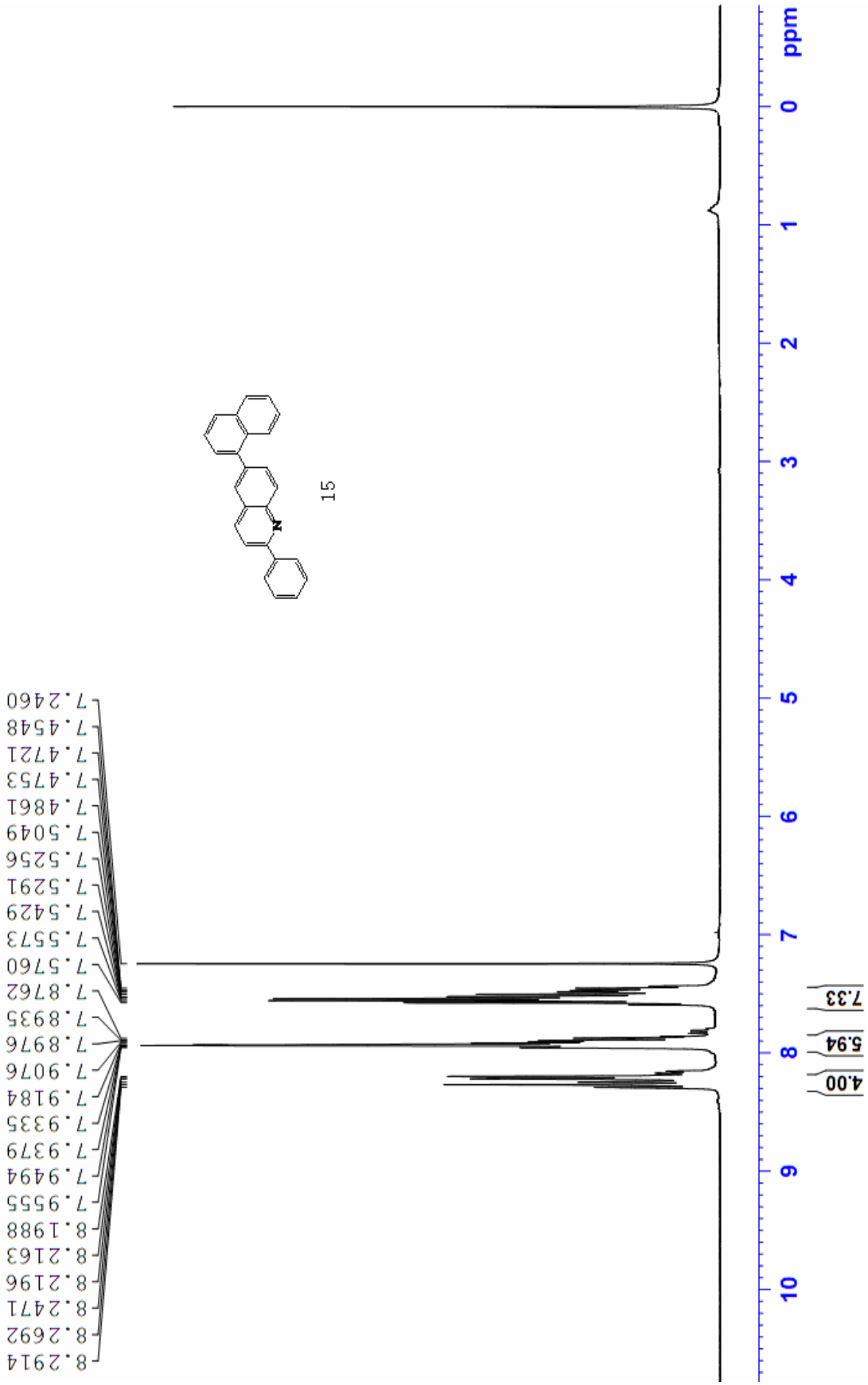

157.18
147.60
139.69
138.94
138.28
137.58
137.50
136.94
136.83
136.72
130.07
129.72
129.46
129.36
129.34
128.89
127.57
127.24
126.82
124.77
119.38
21.20
N
12
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

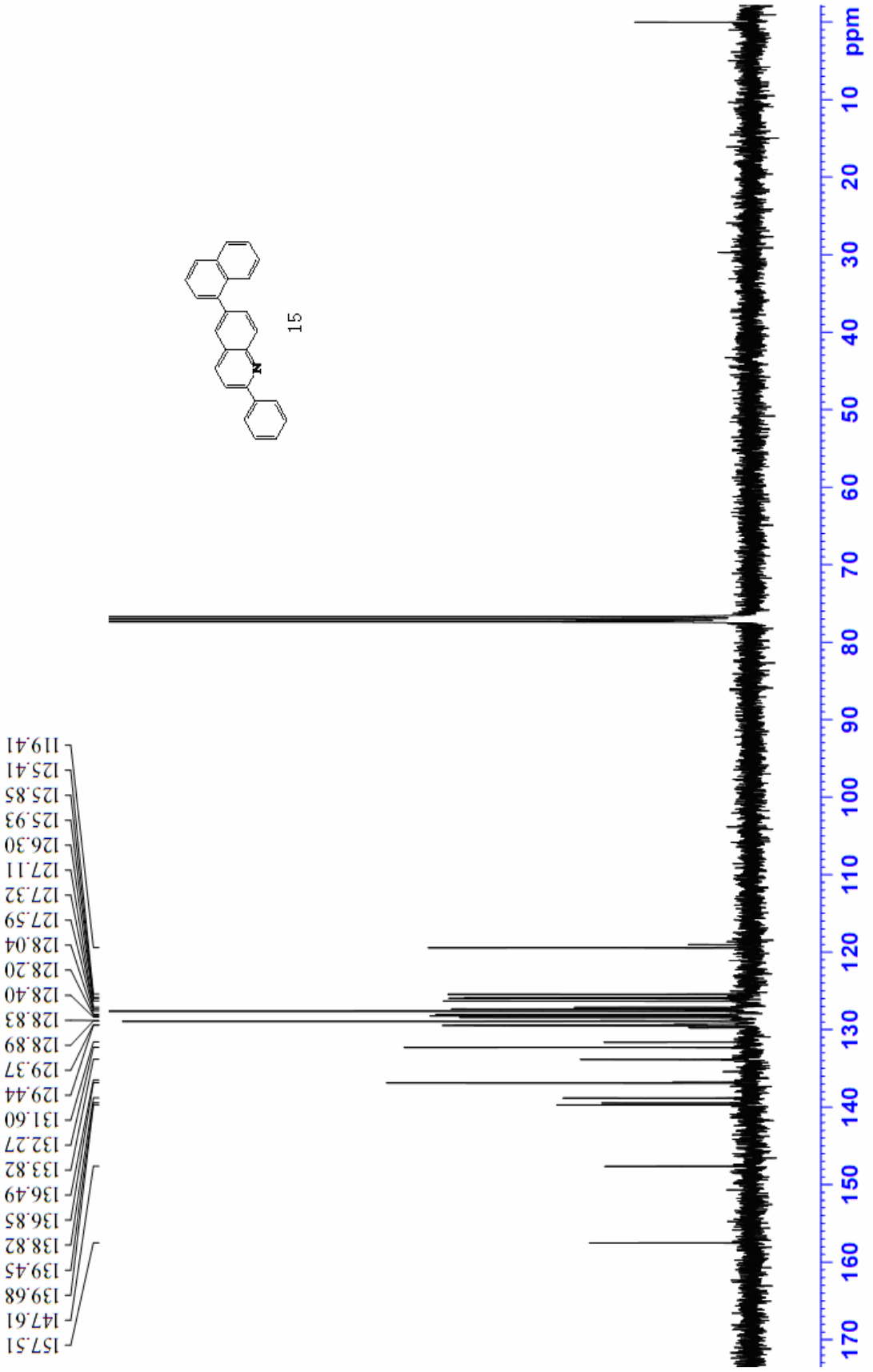

13
3.88
7.03
7.05
7.47
7.52
7.54
7.67
7.69
7.88
7.90
7.96
7.96
7.98
8.16
8.18
8.19
8.19
8.22
8.24
8.26
ppm
0.98
3.02
2.00
1.09
2.13
2.23
1.24
2.06
3.00


159.47
147.42
138.59
136.81
132.87
130.06
129.28
129.20
128.86
128.44
127.51
127.43
124.32
119.34
114.40
55.40
13
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

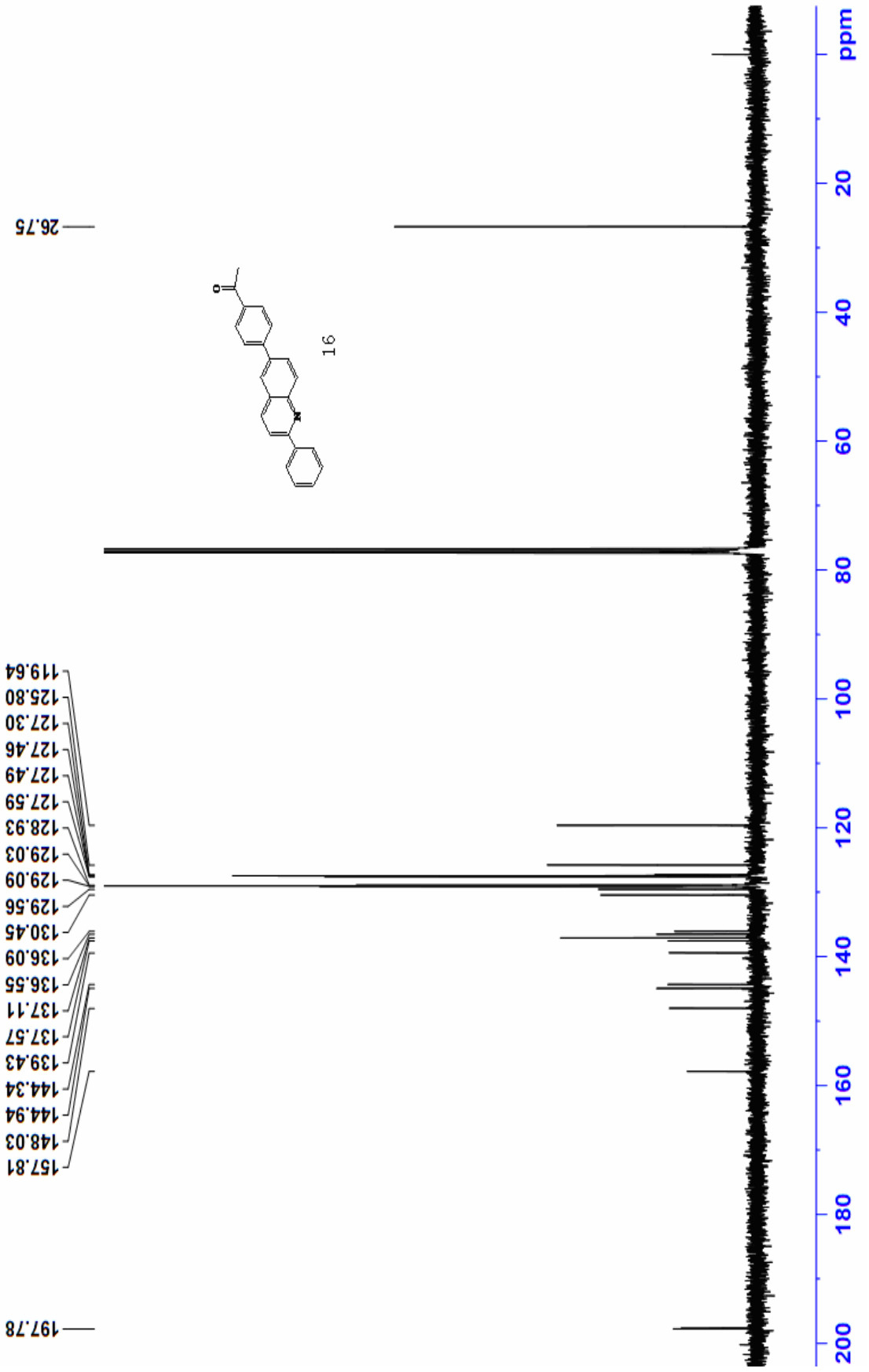

14
3.8862
6.9272
6.9292
6.9334
6.9354
6.9477
6.9494
6.9539
6.9556
7.2354
7.2502
7.2548
7.2604
7.2989
7.3157
7.3183
7.3836
7.4035
7.4231
7.4598
7.4779
7.5088
7.5243
7.5280
7.5456
7.8612
7.8825
7.9653
7.9796
7.9839
8.1617
8.1793
8.2110
8.2336
3.00
0.91
1.15
1.04
1.31
1.46
0.56
1.08
2.30
1.20
1.11
1.07
1.00
1.01
ppm

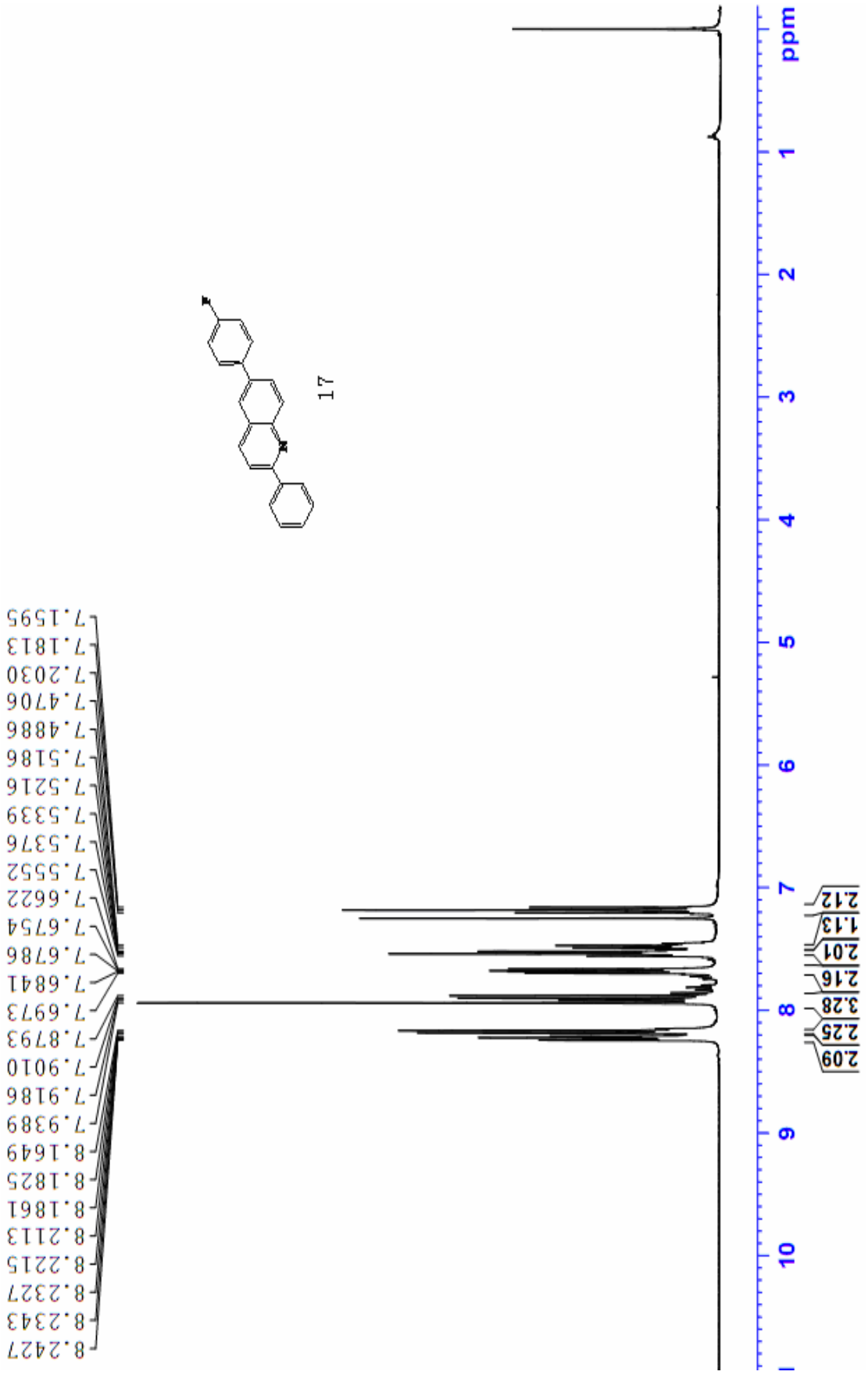

160.05
157.30
147.74
141.88
139.57
138.80
136.94
130.10
129.95
129.34
128.85
127.52
127.28
125.21
119.87
119.35
113.09
113.04
55.35
OCH3
N
14
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

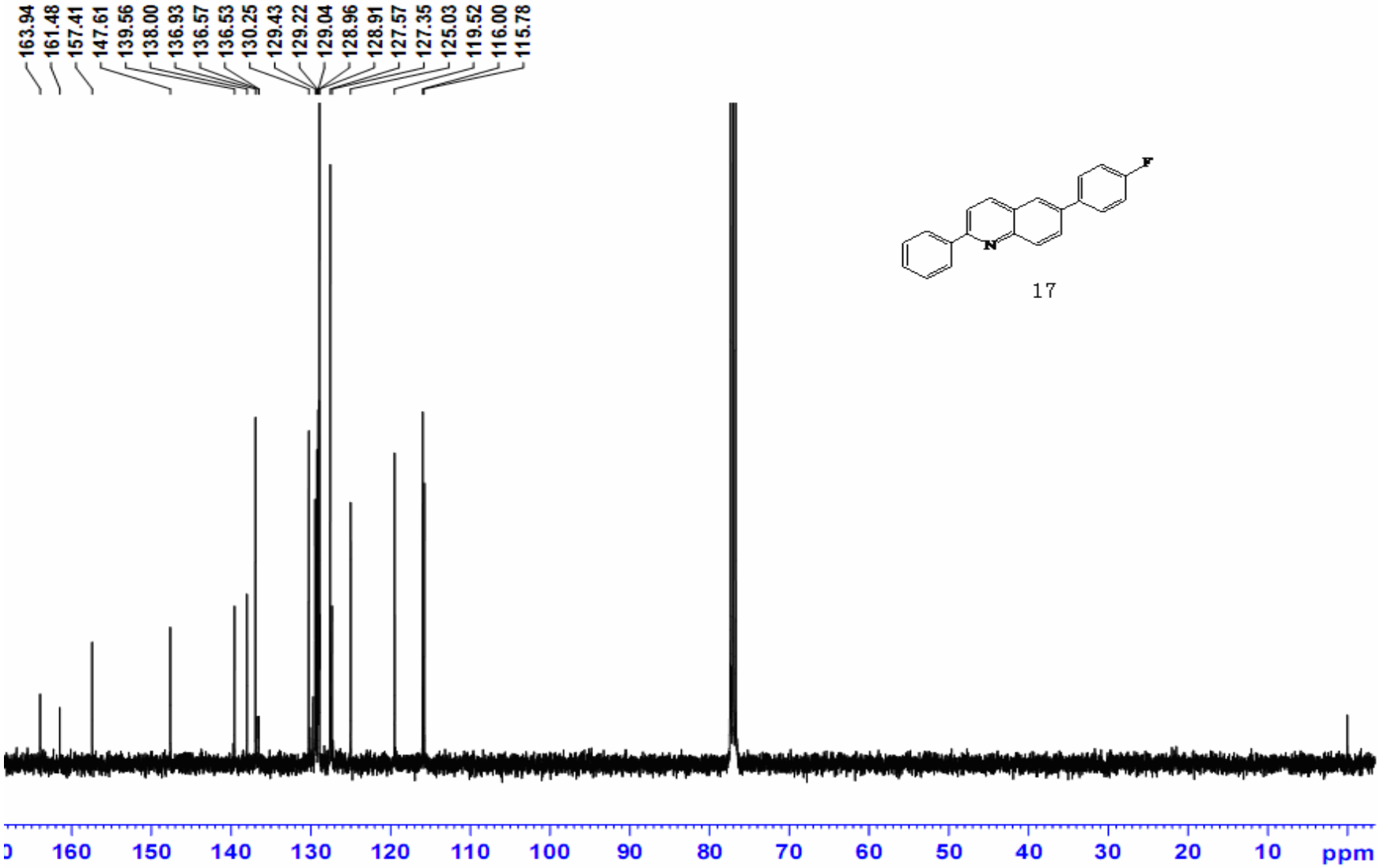

8.2914
8.2692
8.2471
8.2196
8.2163
8.1988
7.9555
7.9494
7.9379
7.9335
7.9184
7.9076
7.8976
7.8935
7.8762
7.5760
7.5573
7.5429
7.5291
7.5256
7.5049
7.4861
7.4753
7.4721
7.4548
7.2460
15
4.00
5.94
7.33
ppm
0
1
2
3
4
5
6
7
8
9
10

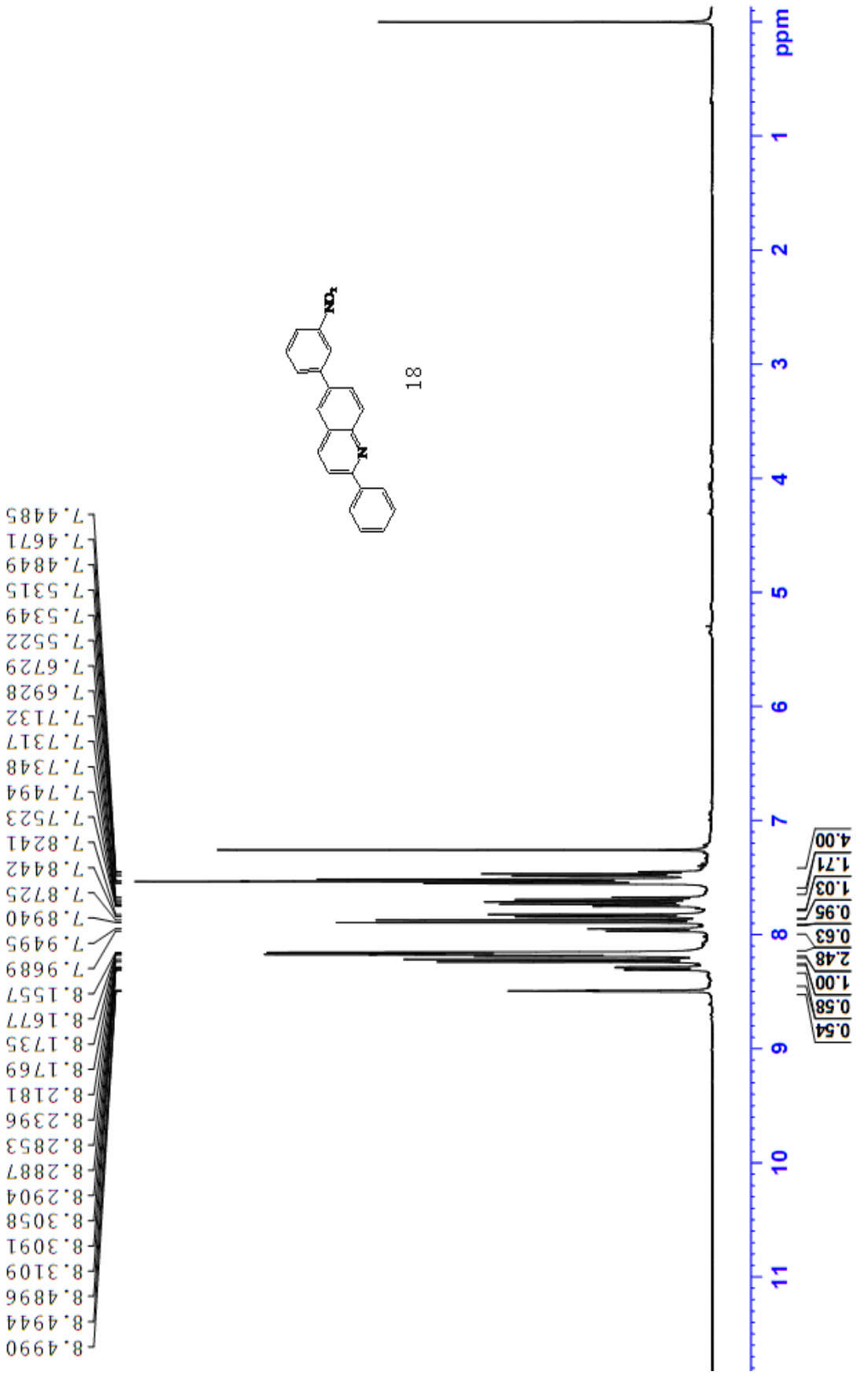

15
N
157.51
147.61
139.68
139.45
138.82
136.85
136.49
133.82
132.27
131.60
129.44
129.37
128.89
128.83
128.40
128.20
128.04
127.59
127.32
127.11
126.30
125.93
125.85
125.41
119.41
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

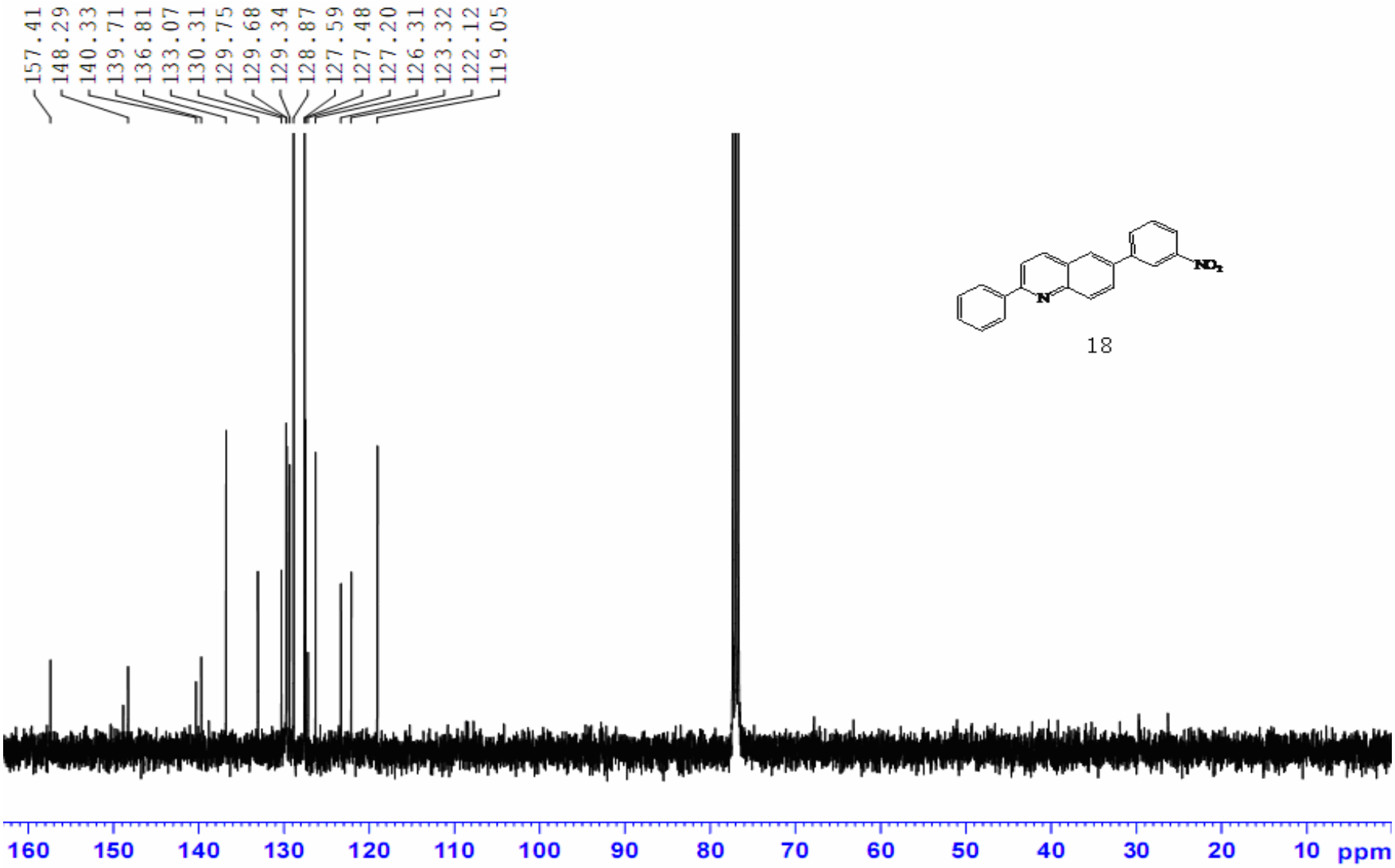
16
2.6474
3.00
1.86
1.89
4.61
1.07
1.02
1.92
1.93
8.2906
8.2692
8.2474
8.2018
8.1983
8.1805
8.1001
8.0791
8.0632
8.0584
8.0467
8.0426
8.0212
7.9372
7.9158
7.8418
7.8208
7.7240
7.7029
ppm


16
26.75
197.78
157.81
148.03
144.94
144.34
139.43
137.57
137.11
136.55
136.09
130.45
129.56
129.09
129.03
128.93
127.59
127.49
127.46
127.30
125.80
119.64
ppm
20
40
60
80
100
120
140
160
180
200

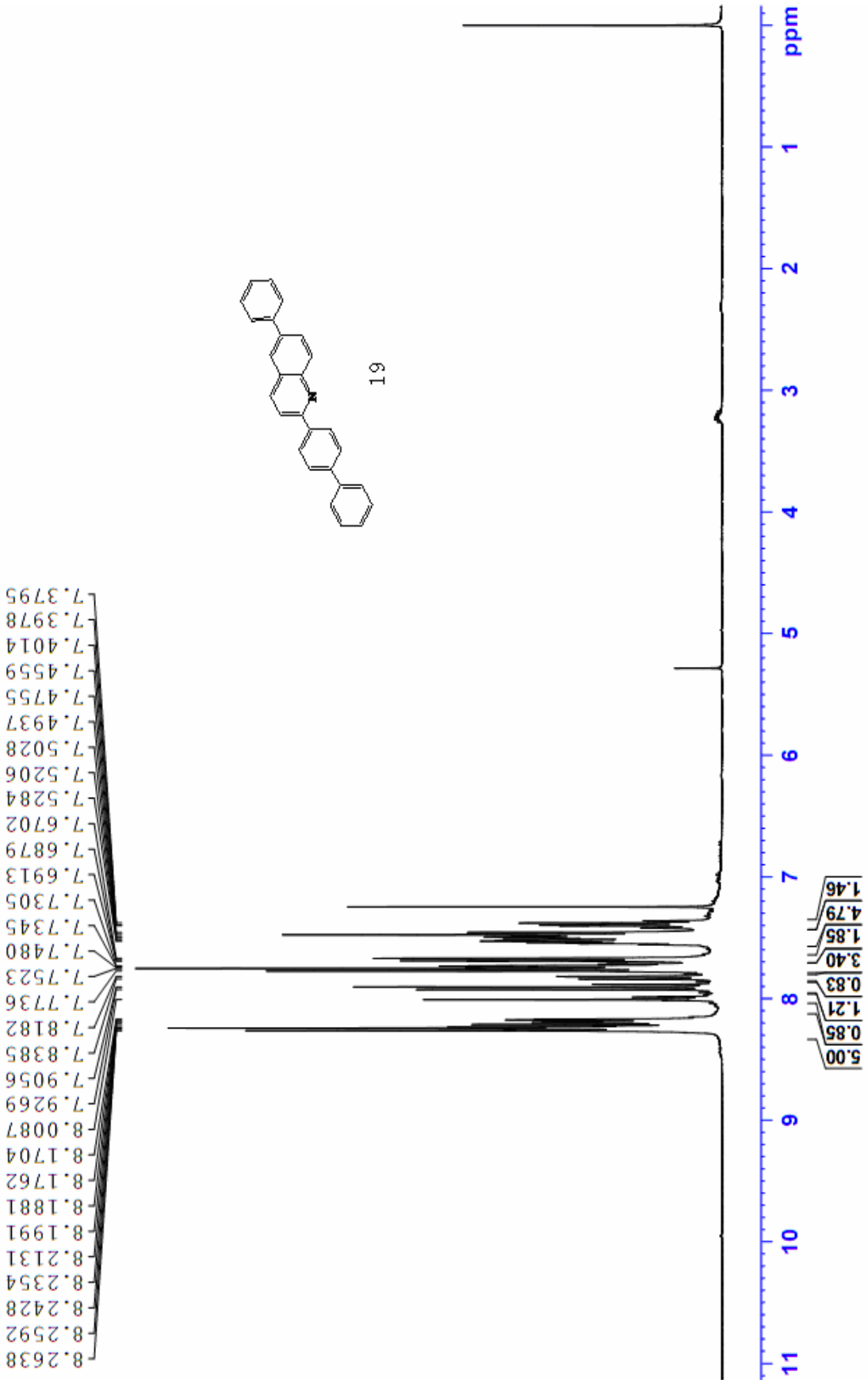

17
8.2427
8.2343
8.2327
8.2215
8.2113
8.1861
8.1825
8.1649
7.9389
7.9186
7.9010
7.8793
7.6973
7.6841
7.6786
7.6754
7.6622
7.5552
7.5376
7.5339
7.5216
7.5186
7.4886
7.4706
7.2030
7.1813
7.1595
2.09
2.25
3.28
2.16
2.01
1.13
2.12
ppm

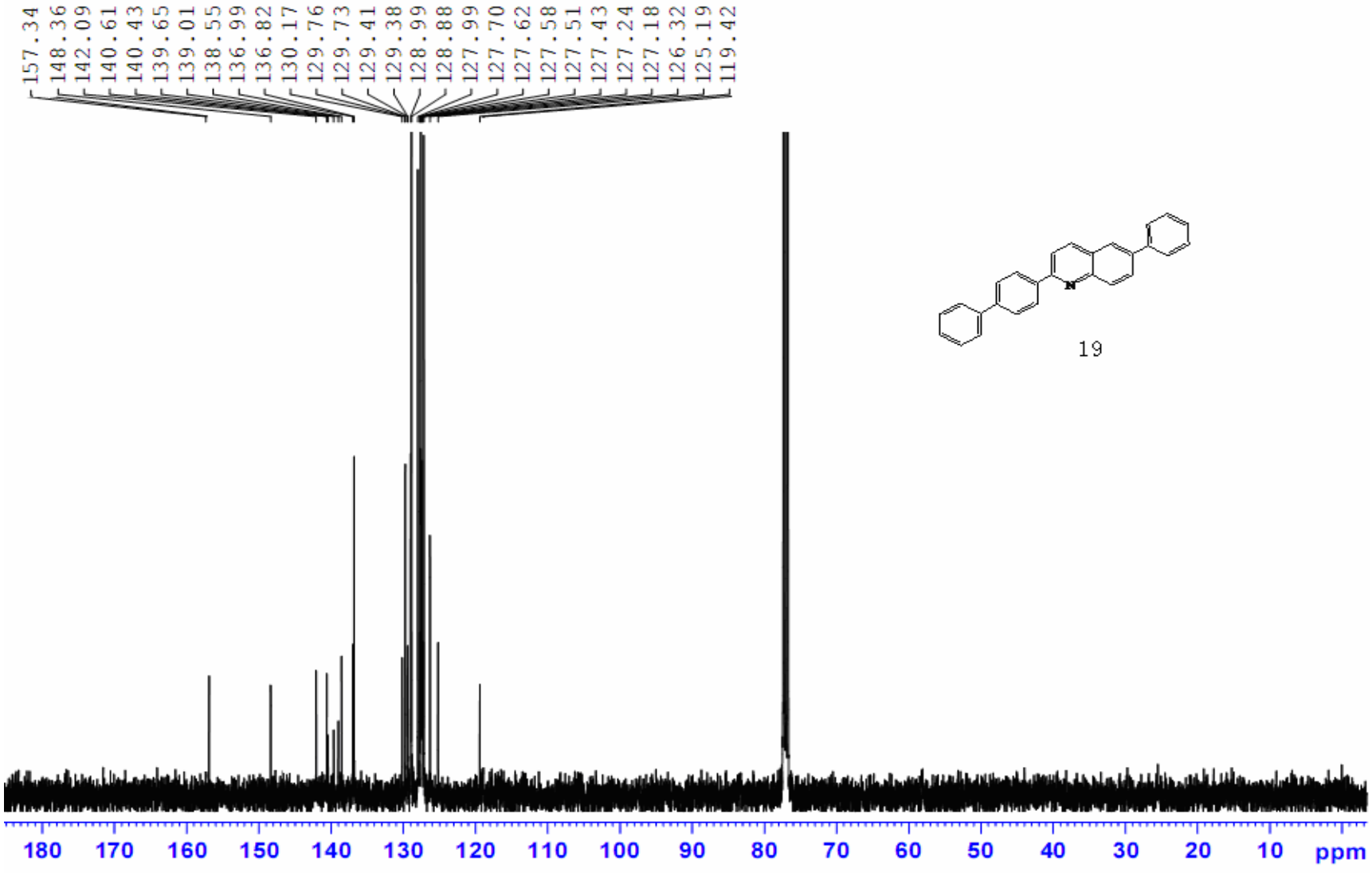

163.94
161.48
157.41
147.61
139.56
138.00
136.93
136.57
136.53
130.25
129.43
129.22
129.04
128.96
128.91
127.57
127.35
125.03
119.52
116.00
115.78
F
N
17
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

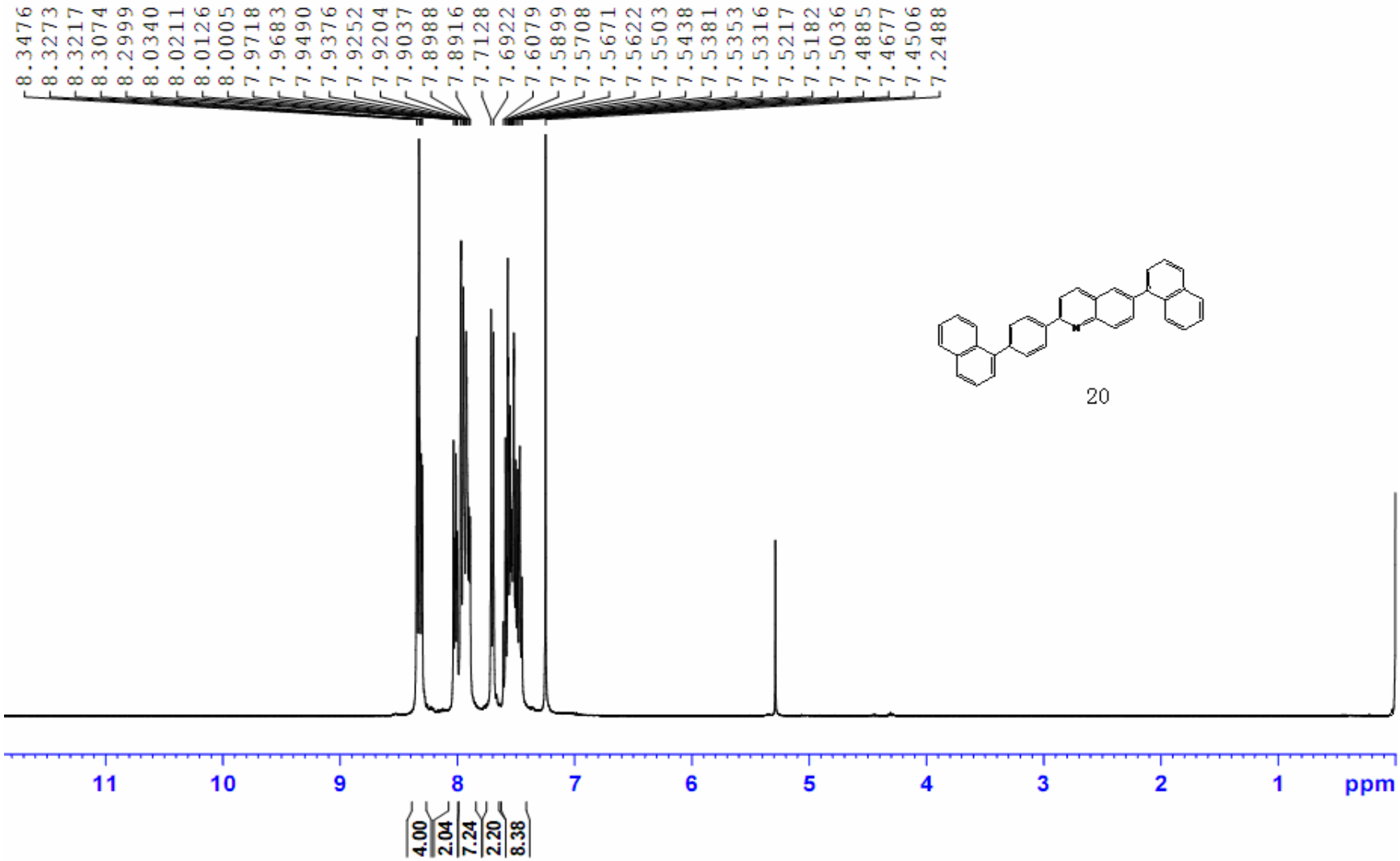

18
ppm
1
2
3
4
5
6
7
8
9
10
11
0.54
0.58
1.00
2.48
0.63
0.95
1.03
1.71
4.00
8.4990
8.4944
8.4896
8.3109
8.3091
8.3058
8.2904
8.2887
8.2853
8.2396
8.2181
8.1769
8.1735
8.1677
8.1557
7.9689
7.9495
7.8940
7.8725
7.8442
7.8241
7.7523
7.7494
7.7348
7.7317
7.7132
7.6928
7.6729
7.5522
7.5349
7.5315
7.4849
7.4671
7.4485

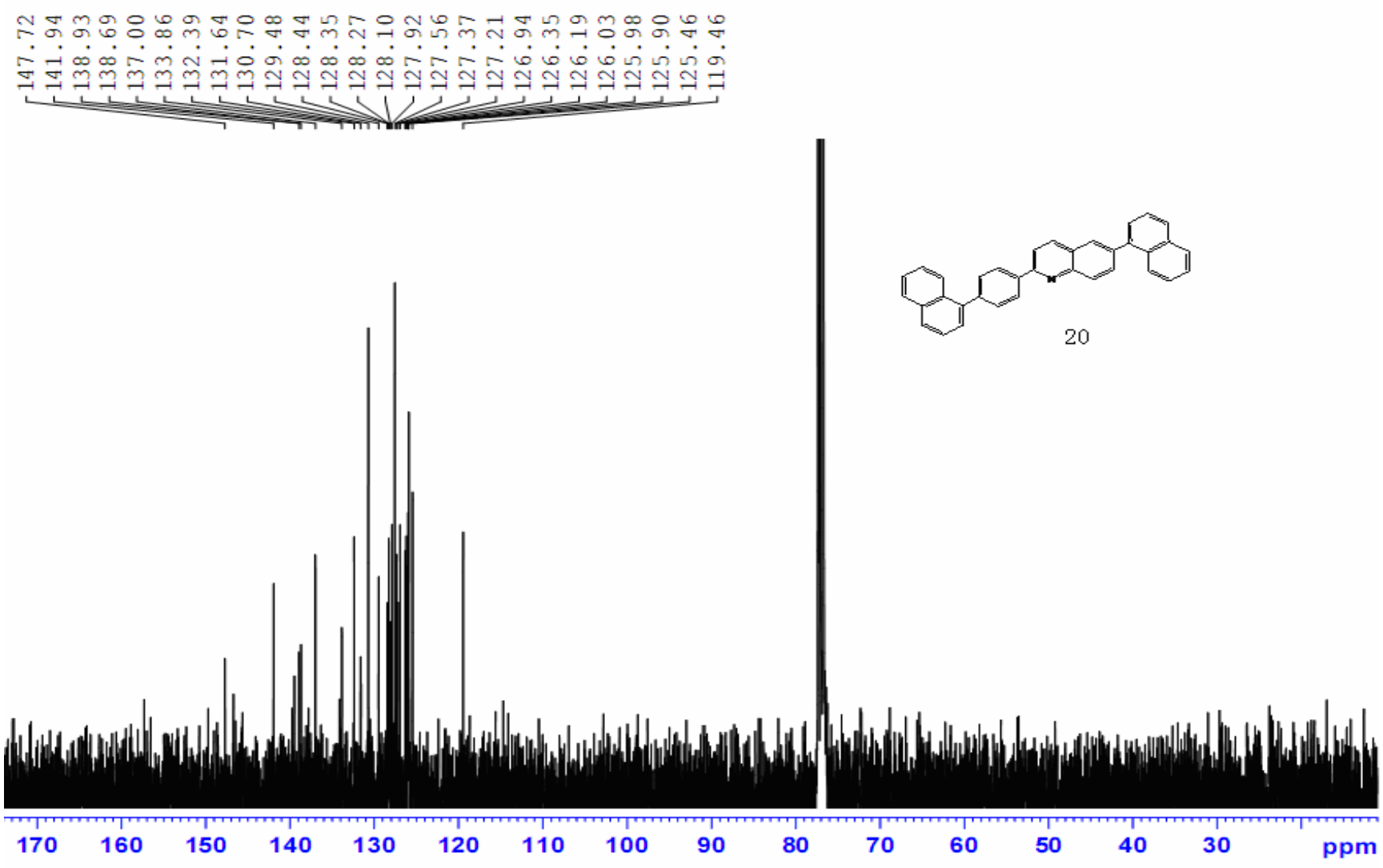

157.41
148.29
140.33
139.71
136.81
133.07
130.31
129.75
129.68
129.34
128.87
127.59
127.48
127.20
126.31
123.32
122.12
119.05
N
NO2
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

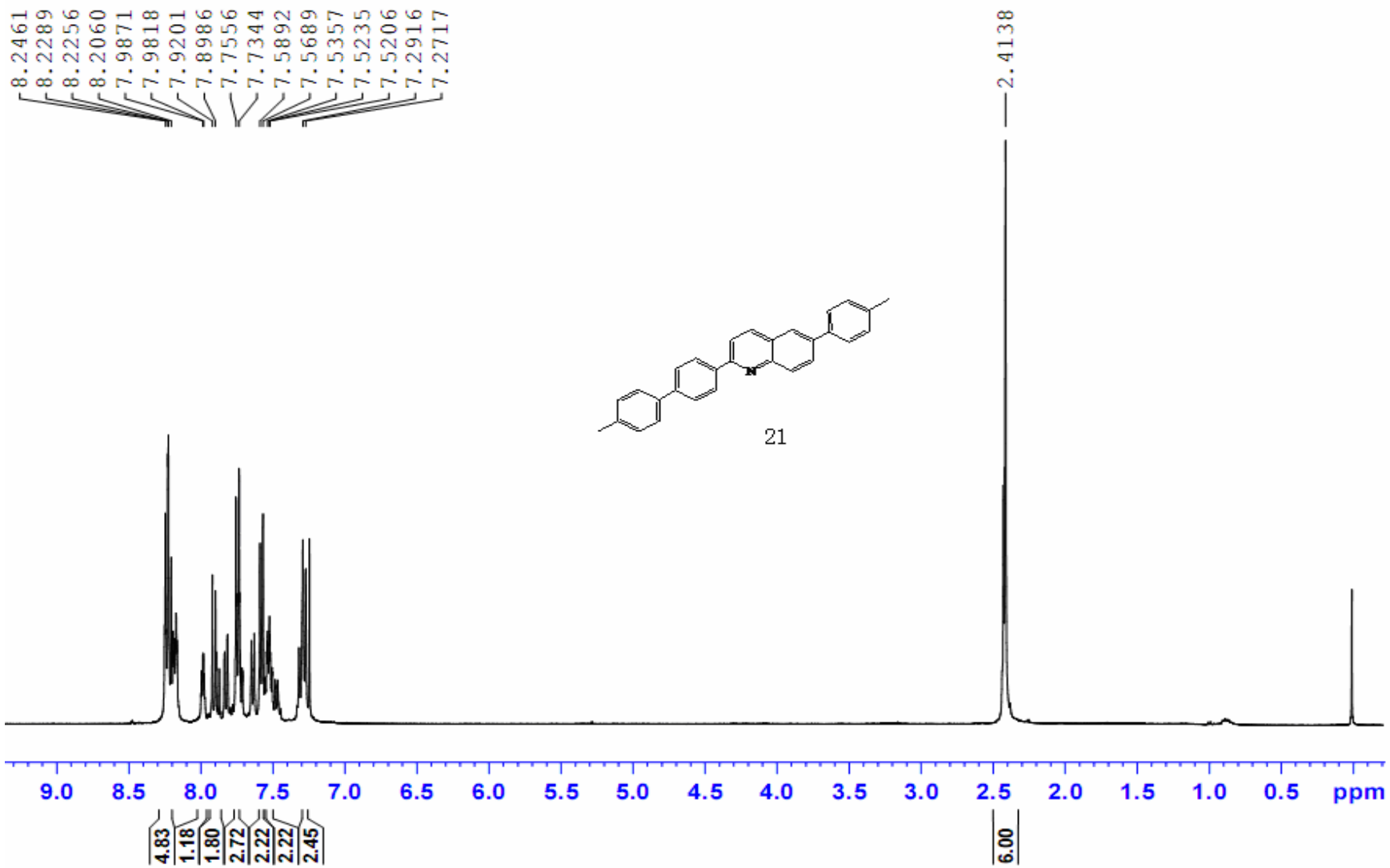
18

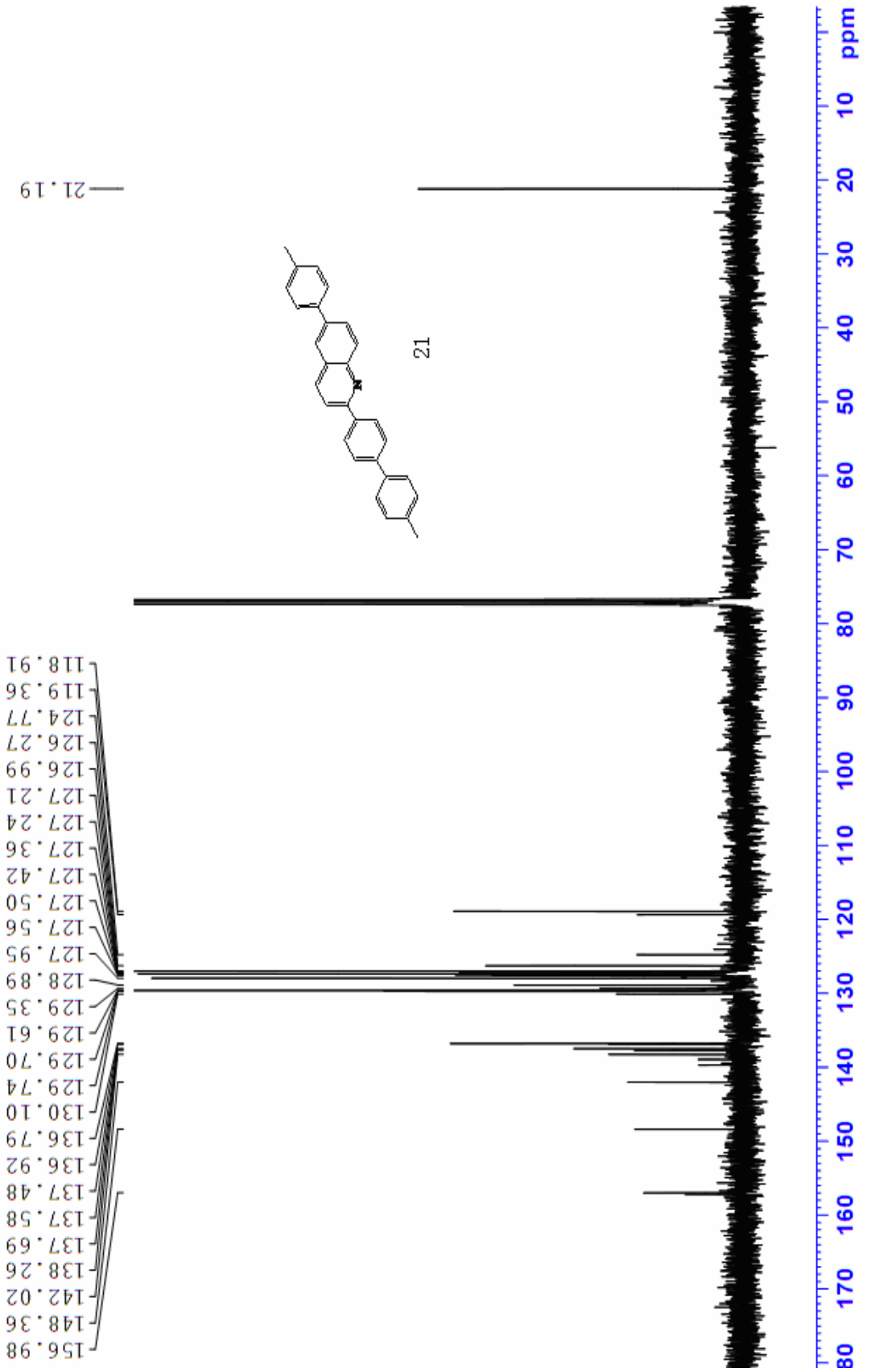

19
8.2638
8.2592
8.2428
8.2354
8.2131
8.1991
8.1881
8.1762
8.1704
8.0087
7.9269
7.9056
7.8385
7.8182
7.7736
7.7523
7.7480
7.7345
7.7305
7.6913
7.6879
7.6702
7.5284
7.5206
7.5028
7.4937
7.4755
7.4559
7.4014
7.3978
7.3795
5.00
0.85
1.21
0.83
3.40
1.85
4.79
1.46
ppm

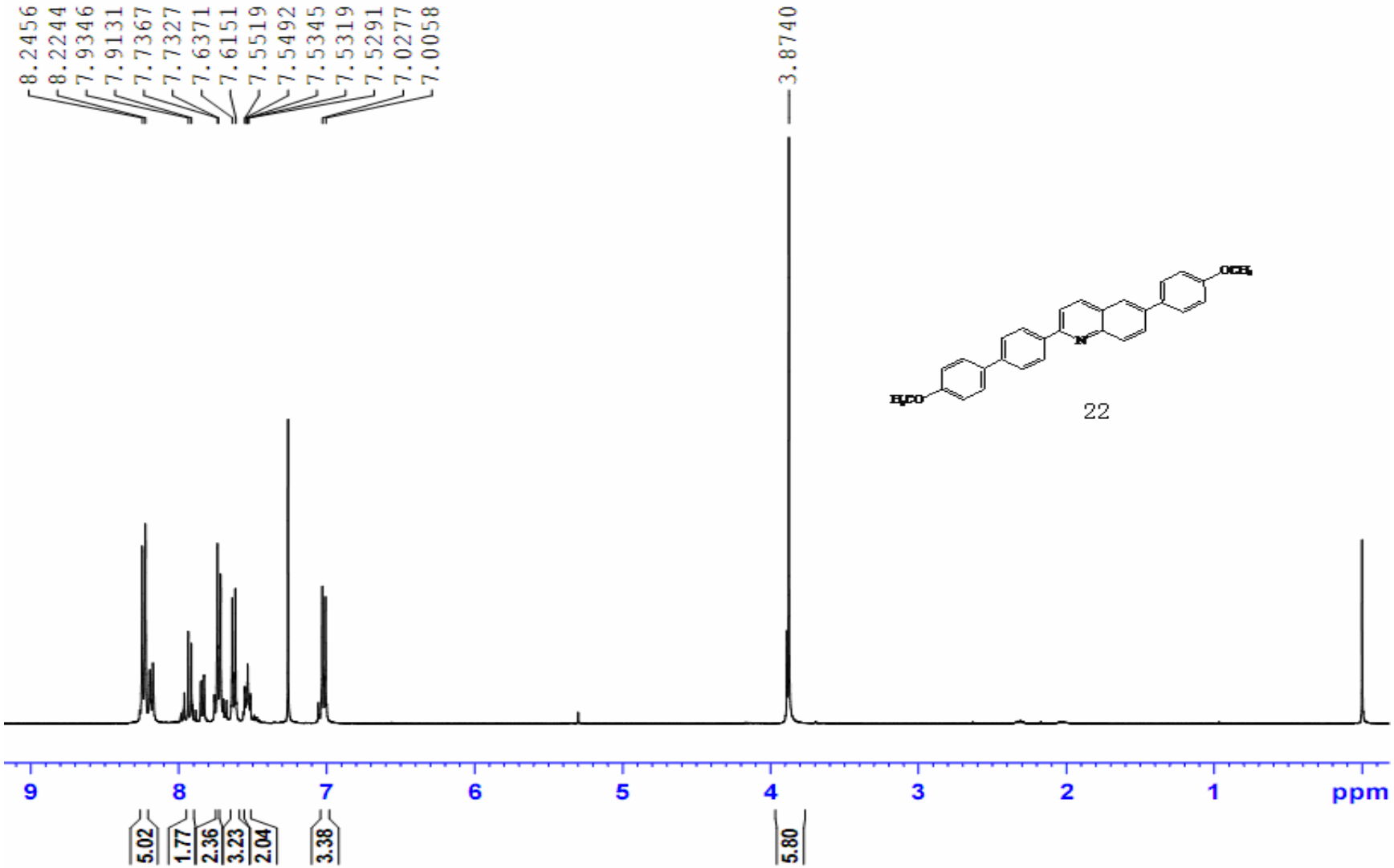

157.34
148.36
142.09
140.61
140.43
139.65
139.01
138.55
136.99
136.82
130.17
129.76
129.73
129.41
129.38
128.99
128.88
127.99
127.70
127.62
127.58
127.51
127.43
127.24
127.18
126.32
125.19
119.42
N
19
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

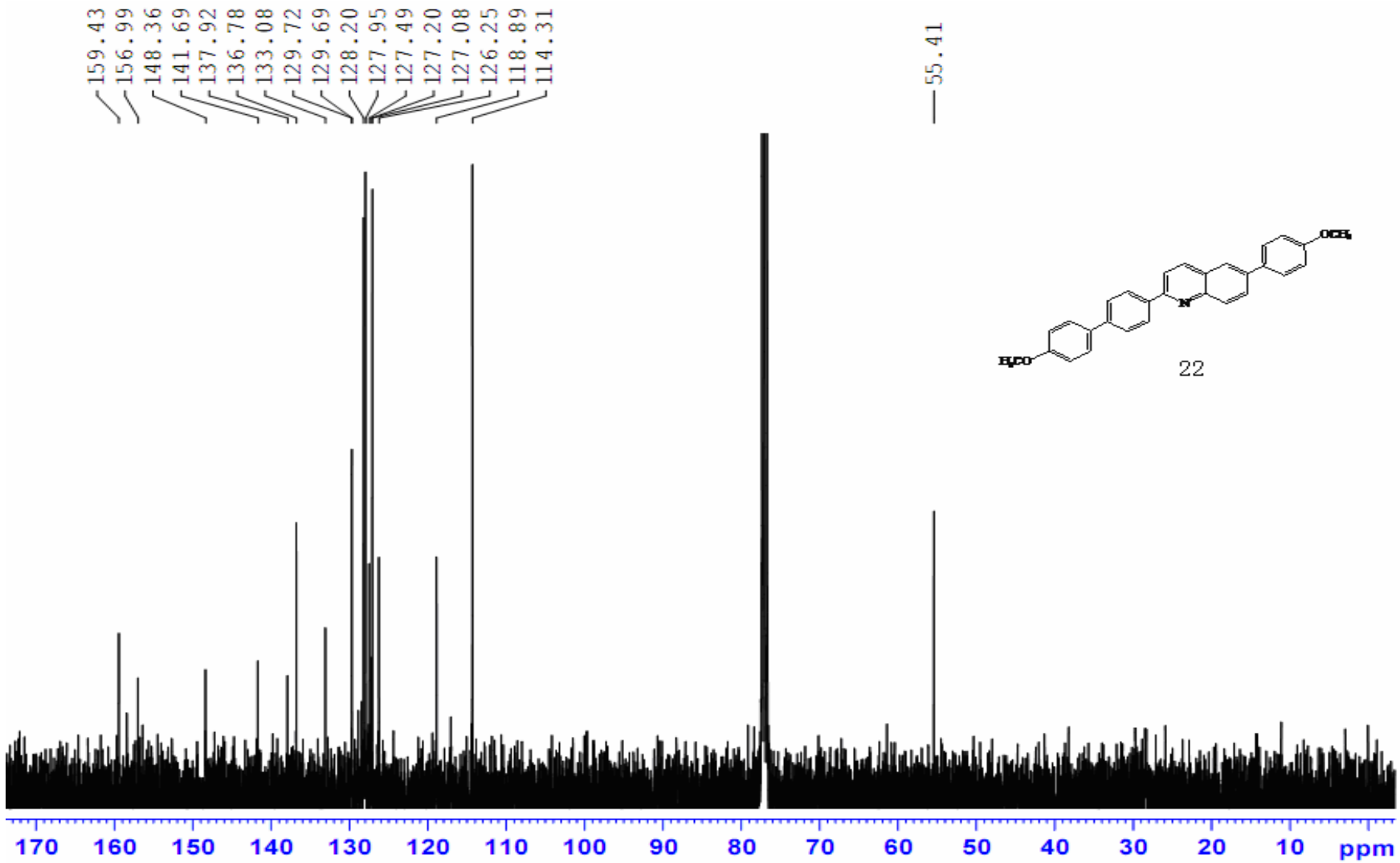

8.3476
8.3273
8.3217
8.3074
8.2999
8.0340
8.0211
8.0126
8.0005
7.9718
7.9683
7.9490
7.9376
7.9252
7.9204
7.9037
7.8988
7.8916
7.7128
7.6922
7.6079
7.5899
7.5708
7.5671
7.5622
7.5503
7.5438
7.5381
7.5353
7.5316
7.5217
7.5182
7.5036
7.4885
7.4677
7.4506
7.2488
20
11
10
9
8
7
6
5
4
3
2
1
ppm
4.00
2.04
7.24
2.20
8.38

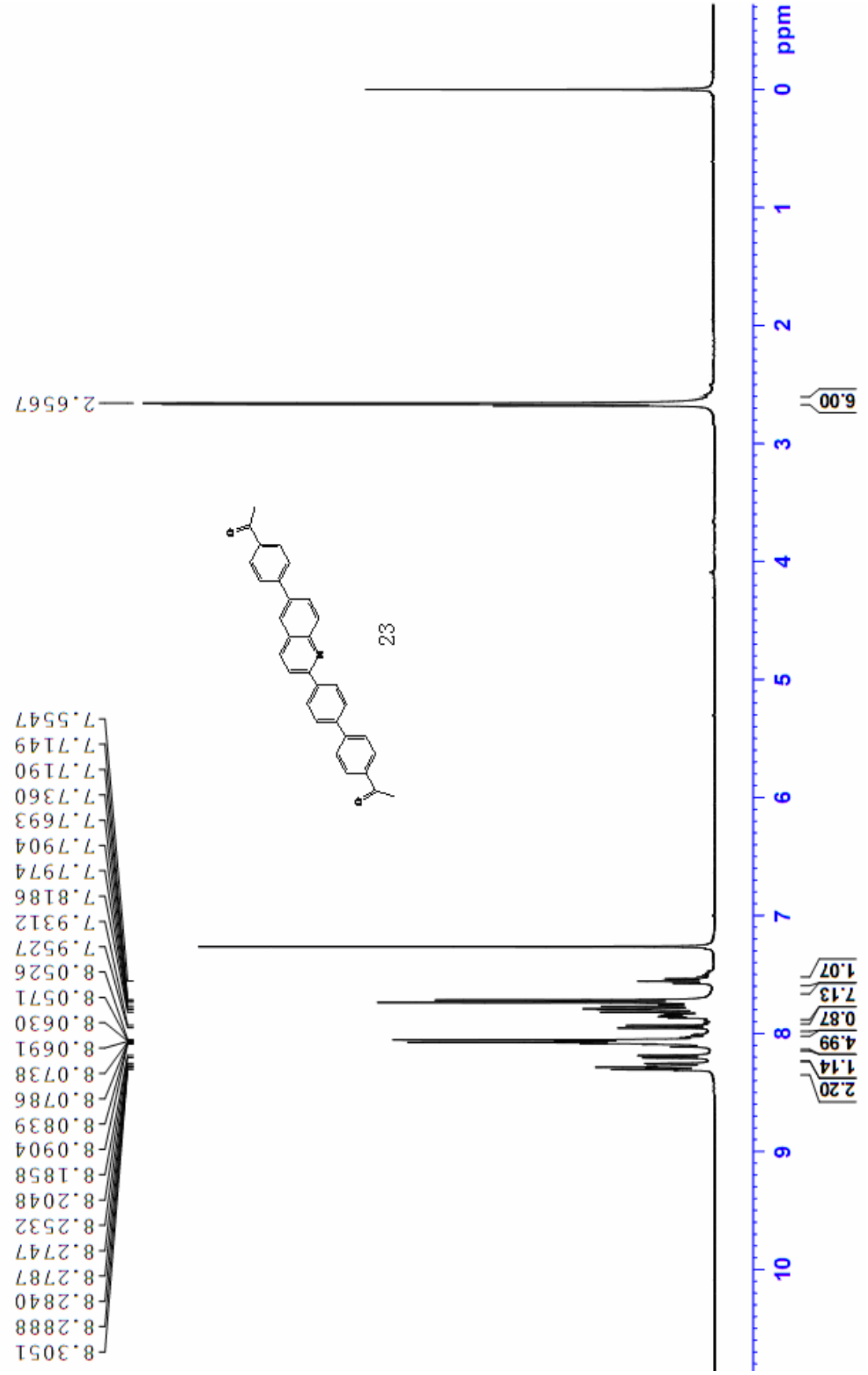

147.72
141.94
138.93
138.69
137.00
133.86
132.39
131.64
130.70
129.48
128.44
128.35
128.27
128.10
127.92
127.56
127.37
127.21
126.94
126.35
126.19
126.03
125.98
125.90
125.46
119.46
20
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

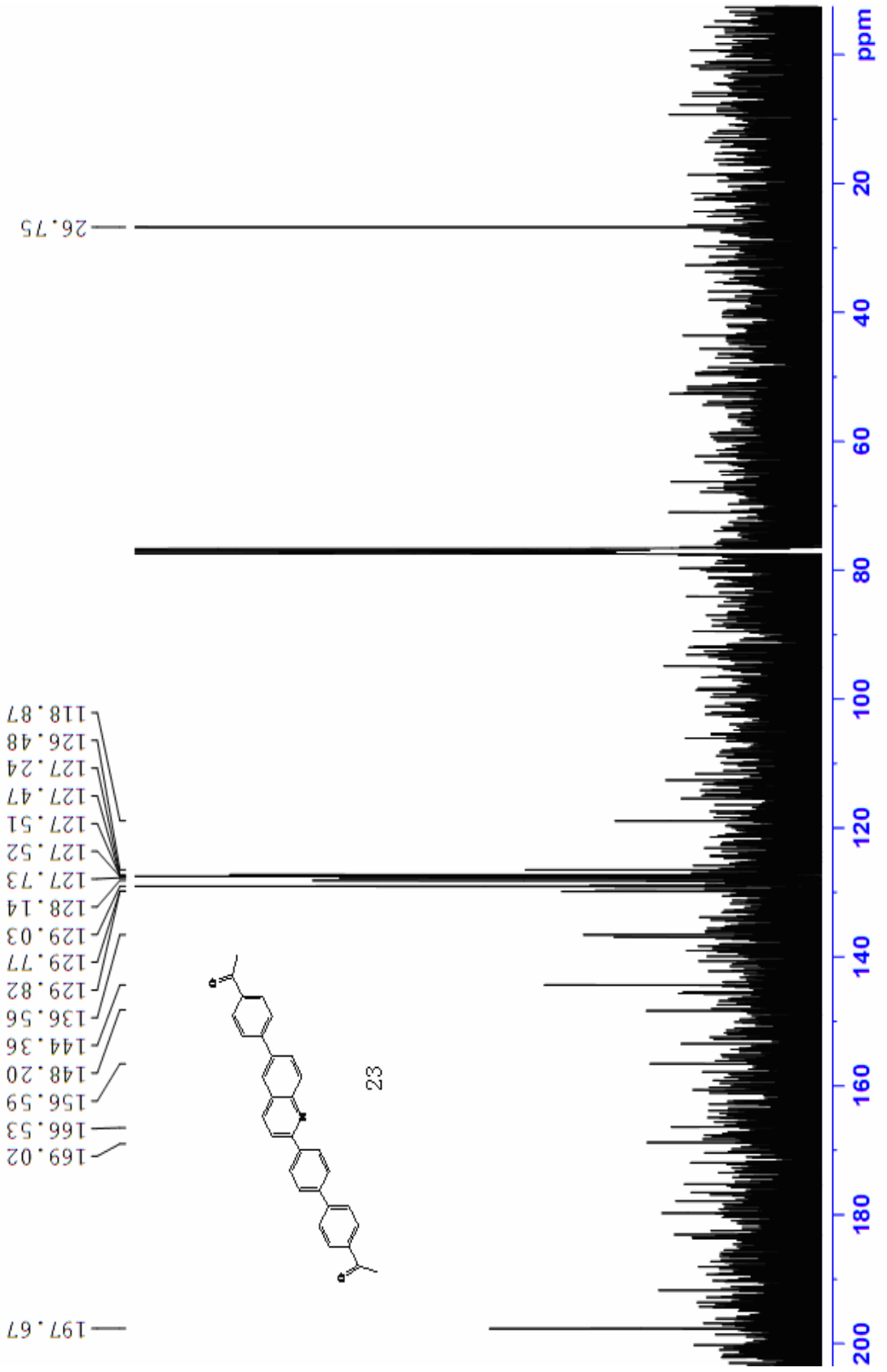

8.2461
8.2289
8.2256
8.2060
7.9871
7.9818
7.9201
7.8986
7.7556
7.7344
7.5892
7.5689
7.5357
7.5235
7.5206
7.2916
7.2717
2.4138
21
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.83
1.18
1.80
2.72
2.22
2.22
2.45
6.00

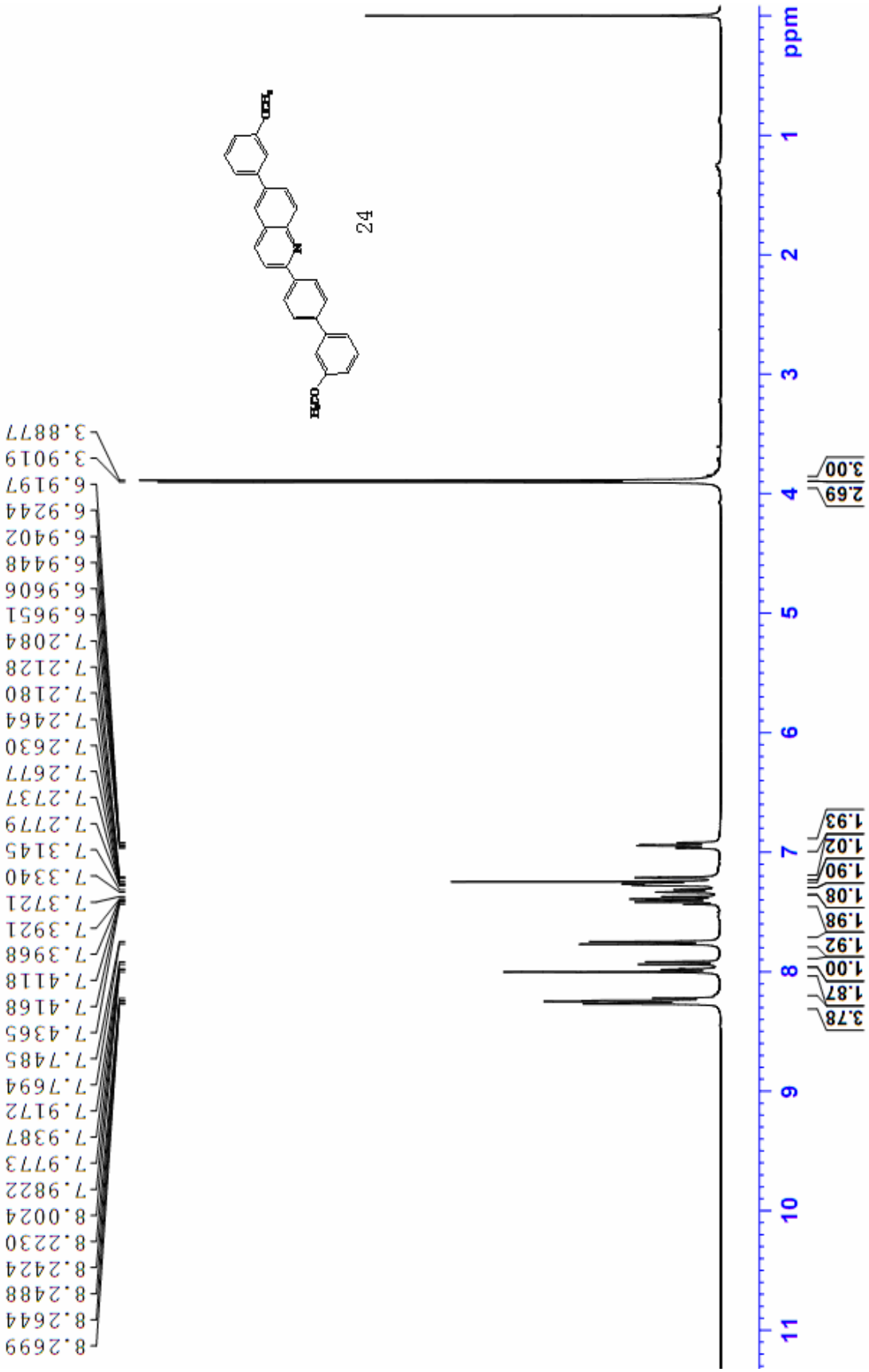

21.19
21
118.91
119.36
124.77
126.27
126.99
127.21
127.24
127.36
127.42
127.50
127.56
127.95
128.89
129.35
129.61
129.70
129.74
130.10
136.79
136.92
137.48
137.58
137.69
138.26
142.02
148.36
156.98
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180

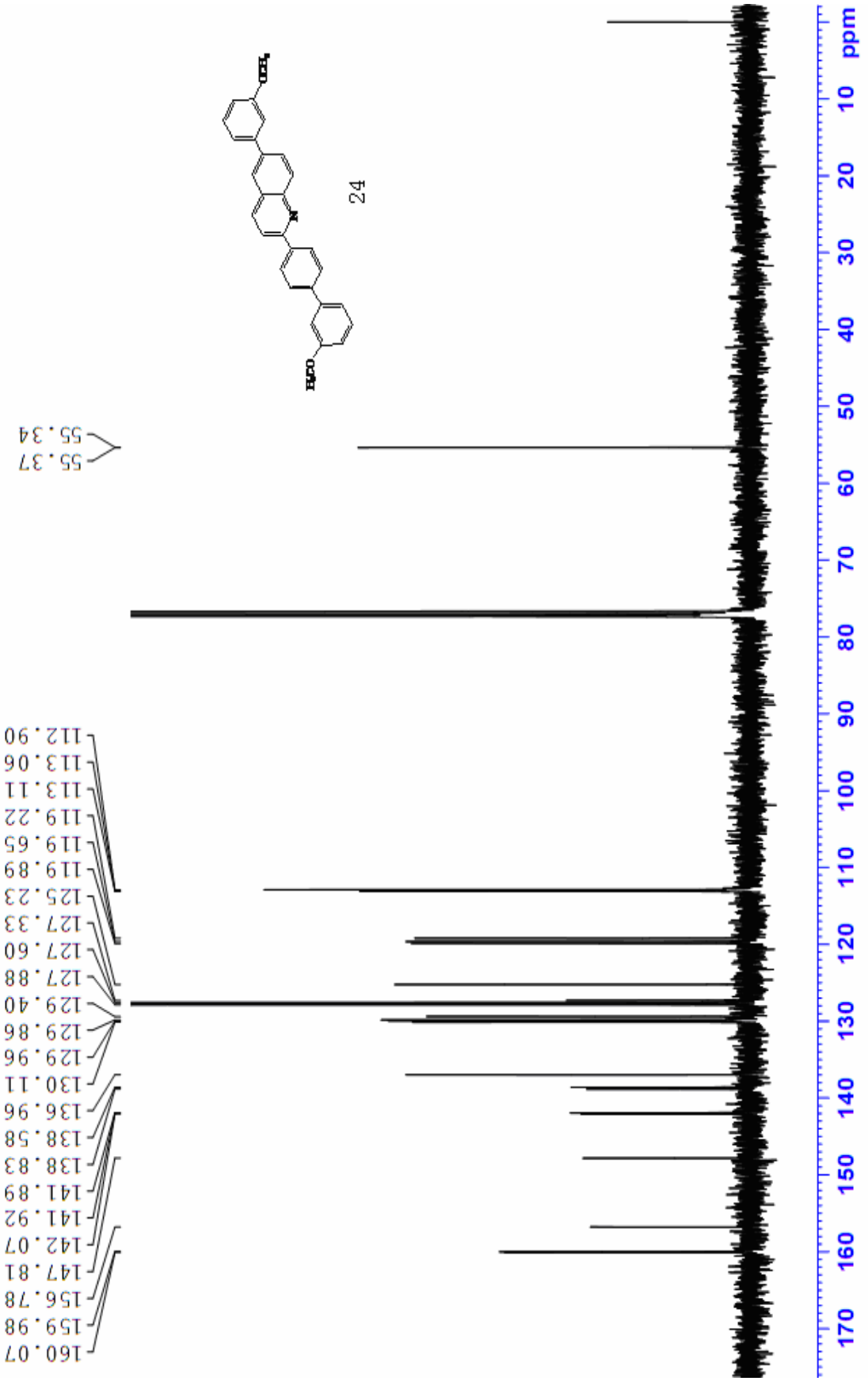

8.2456
8.2244
7.9346
7.9131
7.7367
7.7327
7.6371
7.6151
7.5519
7.5492
7.5345
7.5319
7.5291
7.0277
7.0058
3.8740
22
9
8
7
6
5
4
3
2
1
ppm
5.02
1.77
2.36
3.23
2.04
3.38
5.80

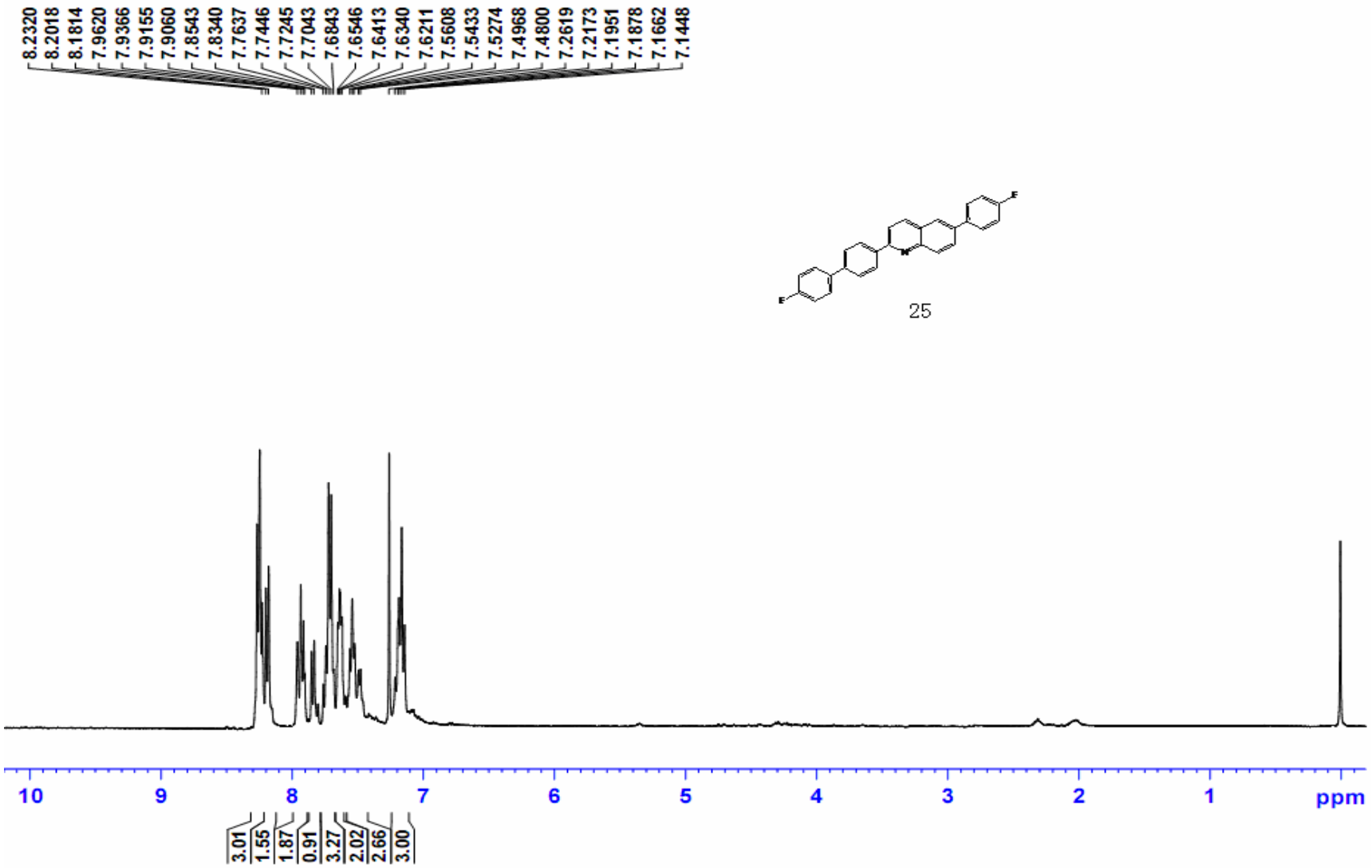

159.43
156.99
148.36
141.69
137.92
136.78
133.08
129.72
129.69
128.20
127.95
127.49
127.20
127.08
126.25
118.89
114.31
55.41
22
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

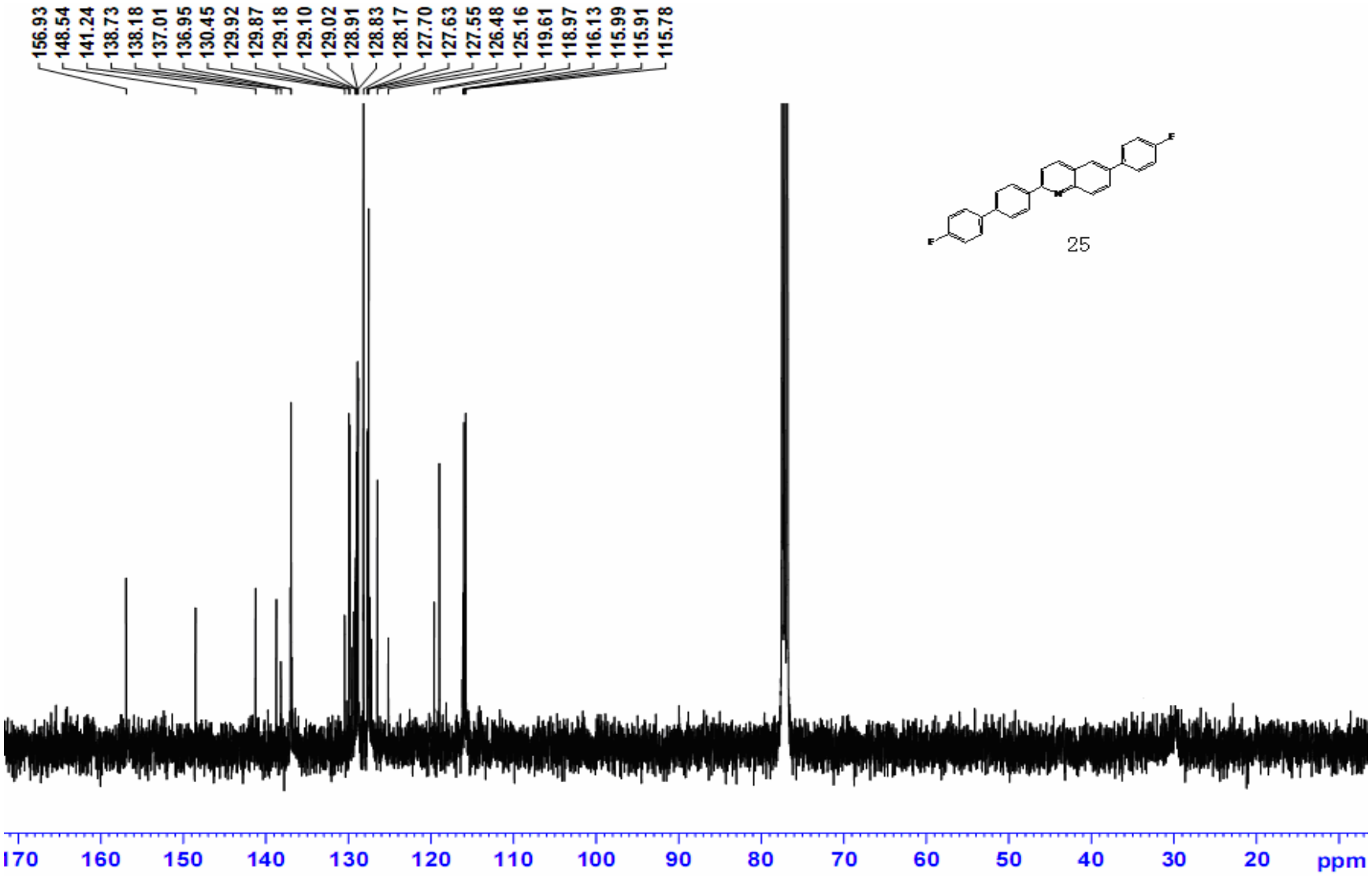

2.6567
8.3051
8.2888
8.2840
8.2787
8.2747
8.2532
8.2048
8.1858
8.0904
8.0839
8.0786
8.0738
8.0691
8.0630
8.0571
8.0526
7.9527
7.9312
7.8186
7.7974
7.7904
7.7693
7.7360
7.7190
7.7149
7.5547
23
6.00
2.20
1.14
4.99
0.87
7.13
1.07
ppm
0
1
2
3
4
5
6
7
8
9
10

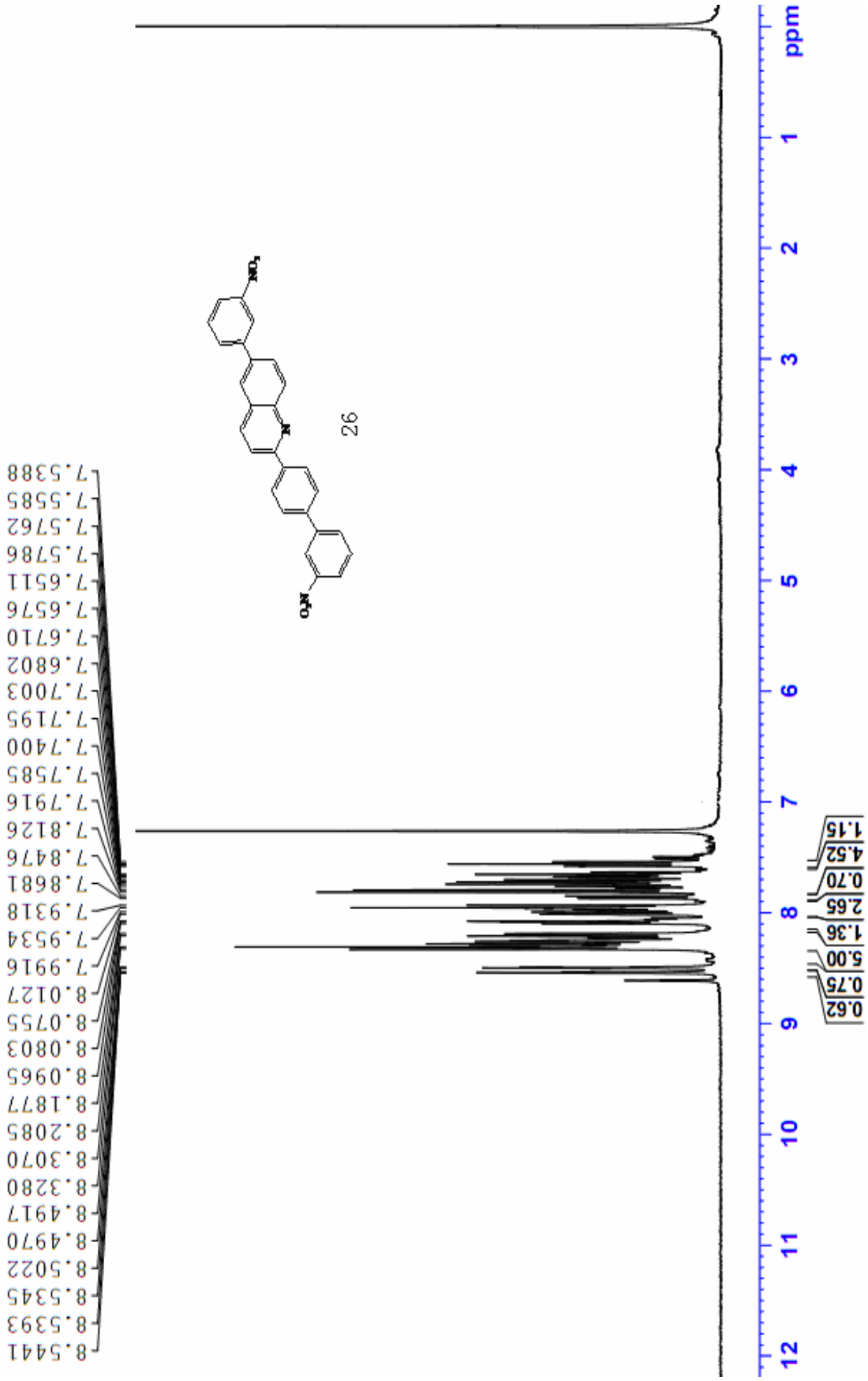

26.75
118.87
126.48
127.24
127.47
127.51
127.52
127.73
128.14
129.03
129.77
129.82
136.56
144.36
148.20
156.59
166.53
169.02
197.67
23
ppm
20
40
60
80
100
120
140
160
180
200

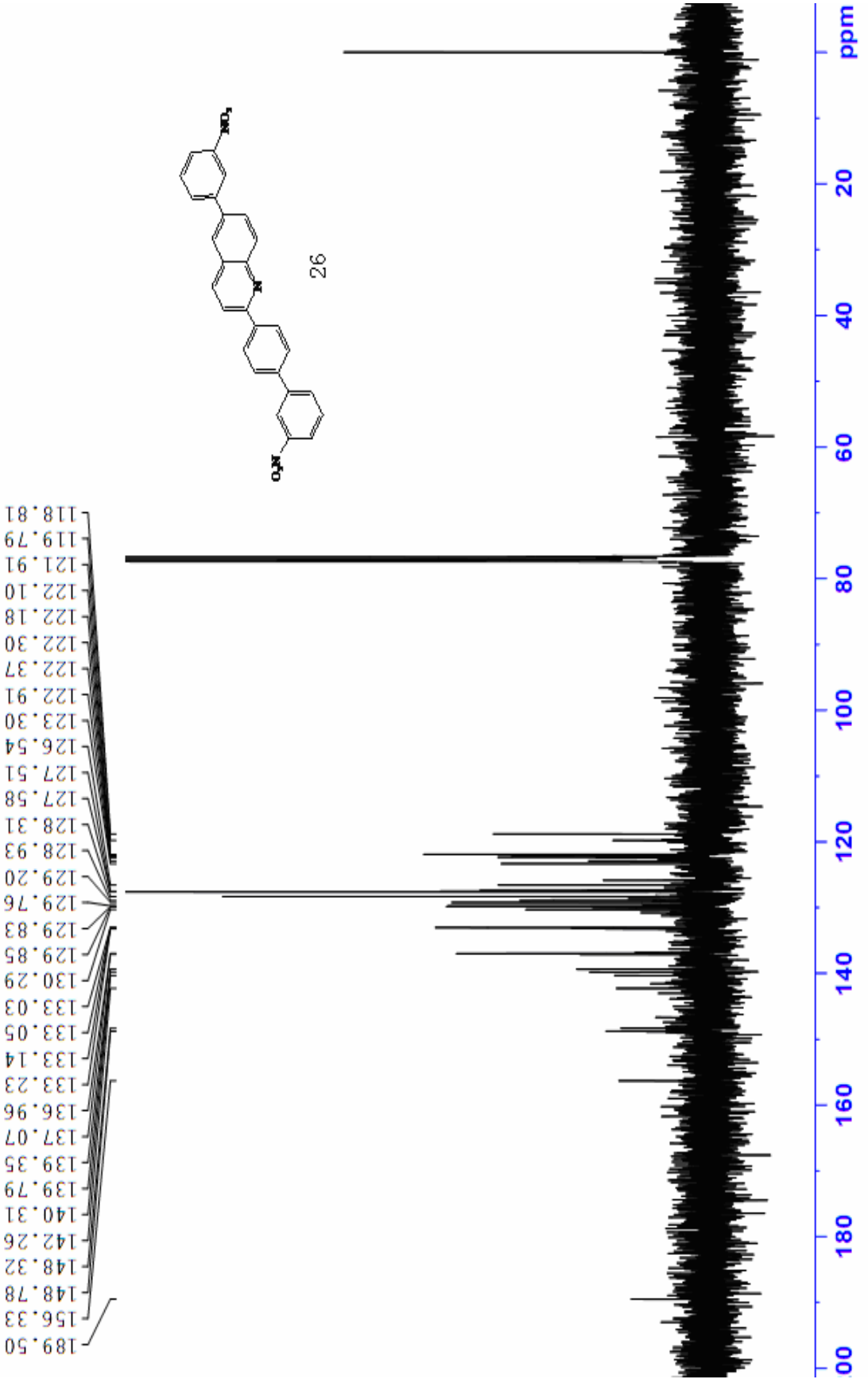

24
8.2699
8.2644
8.2488
8.2424
8.2230
8.0024
7.9822
7.9773
7.9387
7.9172
7.7694
7.7485
7.4365
7.4168
7.4118
7.3968
7.3921
7.3721
7.3340
7.3145
7.2779
7.2737
7.2677
7.2630
7.2464
7.2180
7.2128
7.2084
6.9651
6.9606
6.9448
6.9402
6.9244
6.9197
3.9019
3.8877
3.78
1.87
1.00
1.92
1.98
1.08
1.90
1.02
1.93
2.69
3.00
ppm


24
55.37
55.34
112.90
113.06
113.11
119.22
119.65
119.89
125.23
127.33
127.60
127.88
129.40
129.86
129.96
130.11
136.96
138.58
138.83
141.89
141.92
142.07
147.81
156.78
159.98
160.07
ppm

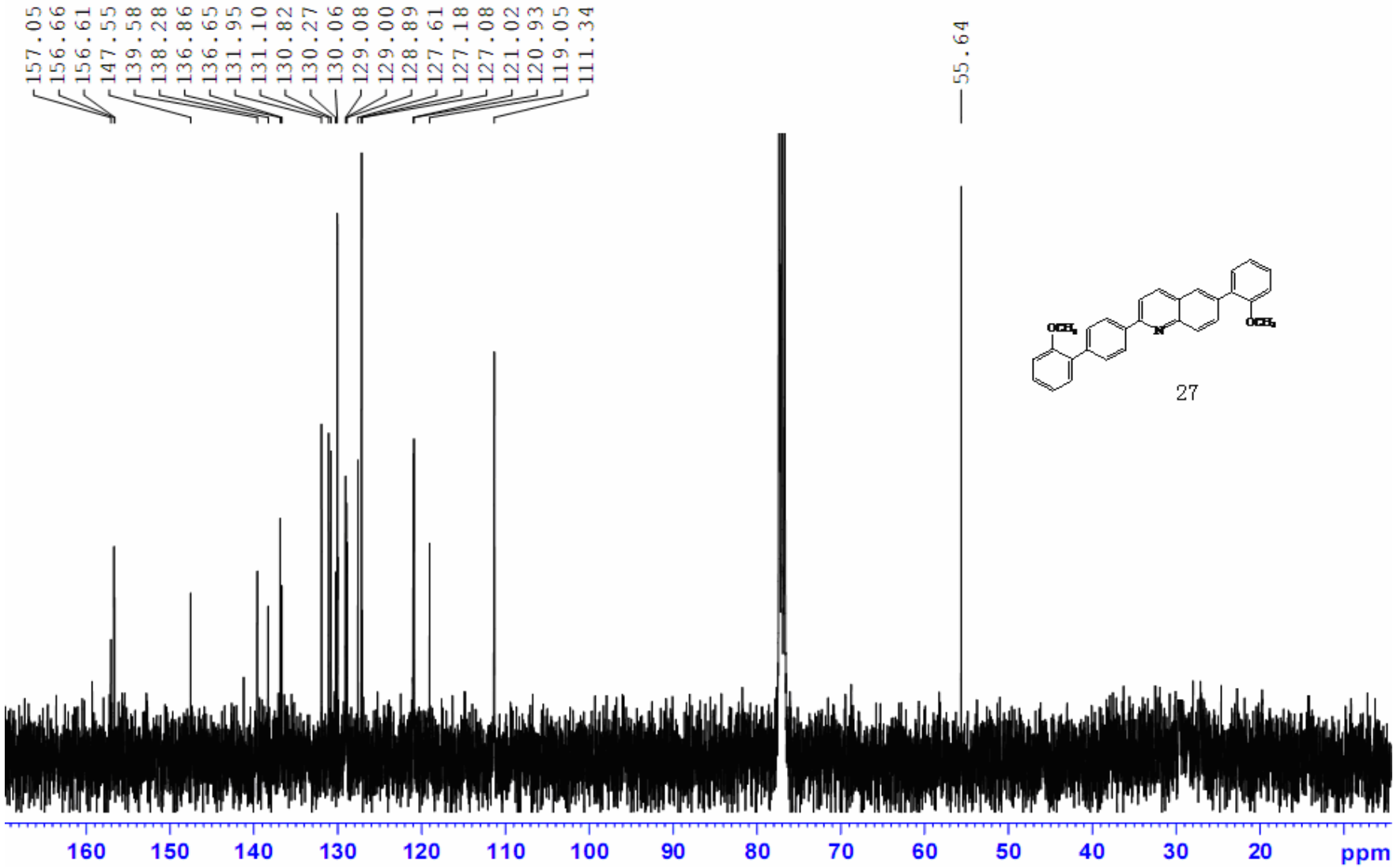

8.2320
8.2018
8.1814
7.9620
7.9366
7.9155
7.9060
7.8543
7.8340
7.7637
7.7446
7.7245
7.7043
7.6843
7.6546
7.6413
7.6340
7.6211
7.5608
7.5433
7.5274
7.4968
7.4800
7.2619
7.2173
7.1951
7.1878
7.1662
7.1448
25
10
9
8
7
6
5
4
3
2
1
ppm
3.01
1.55
1.87
0.91
3.27
2.02
2.66
3.00

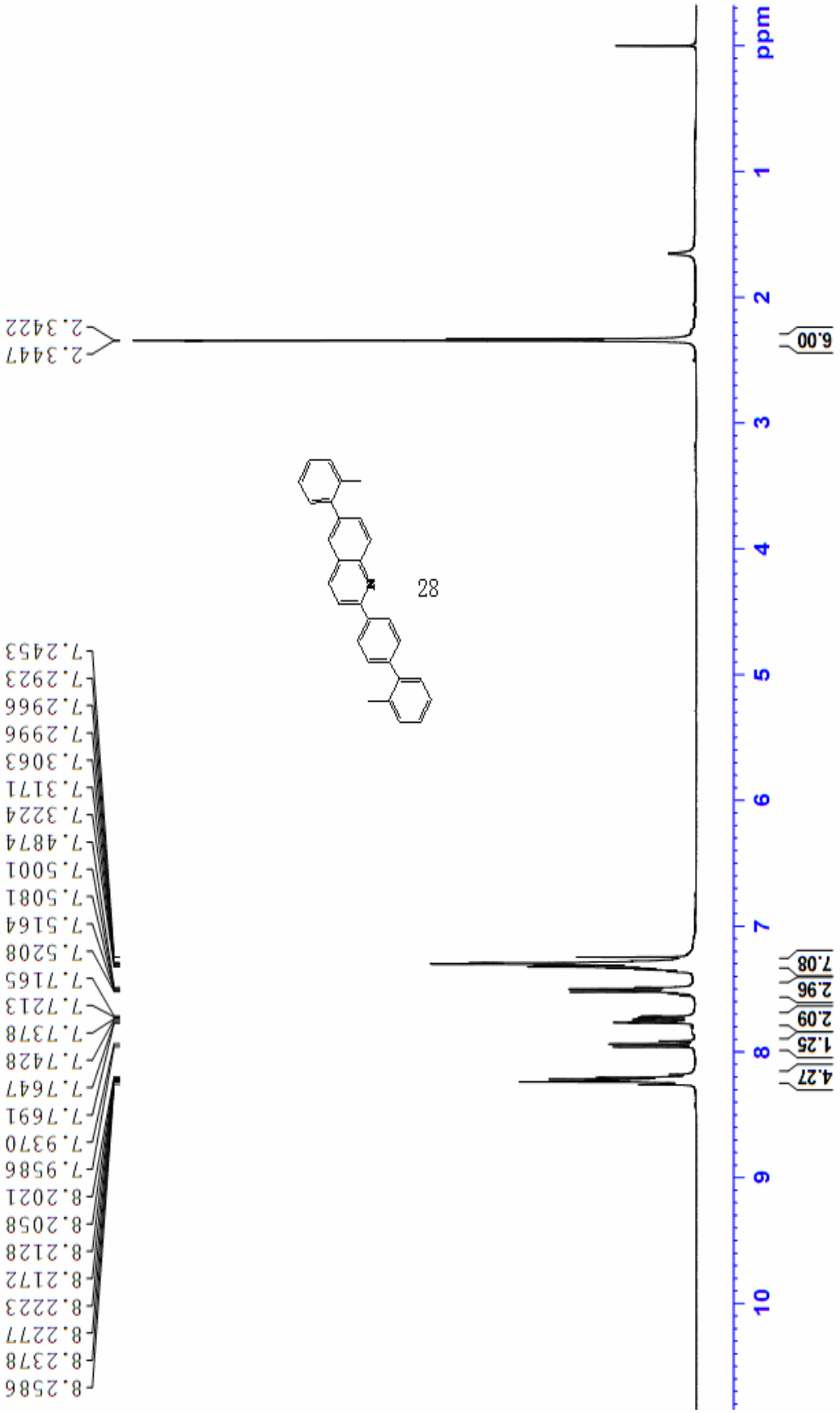

156.93
148.54
141.24
138.73
138.18
137.01
136.95
130.45
129.92
129.87
129.18
129.10
129.02
128.91
128.83
128.17
127.70
127.63
127.55
126.48
125.16
119.61
118.97
116.13
115.99
115.91
115.78
25
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

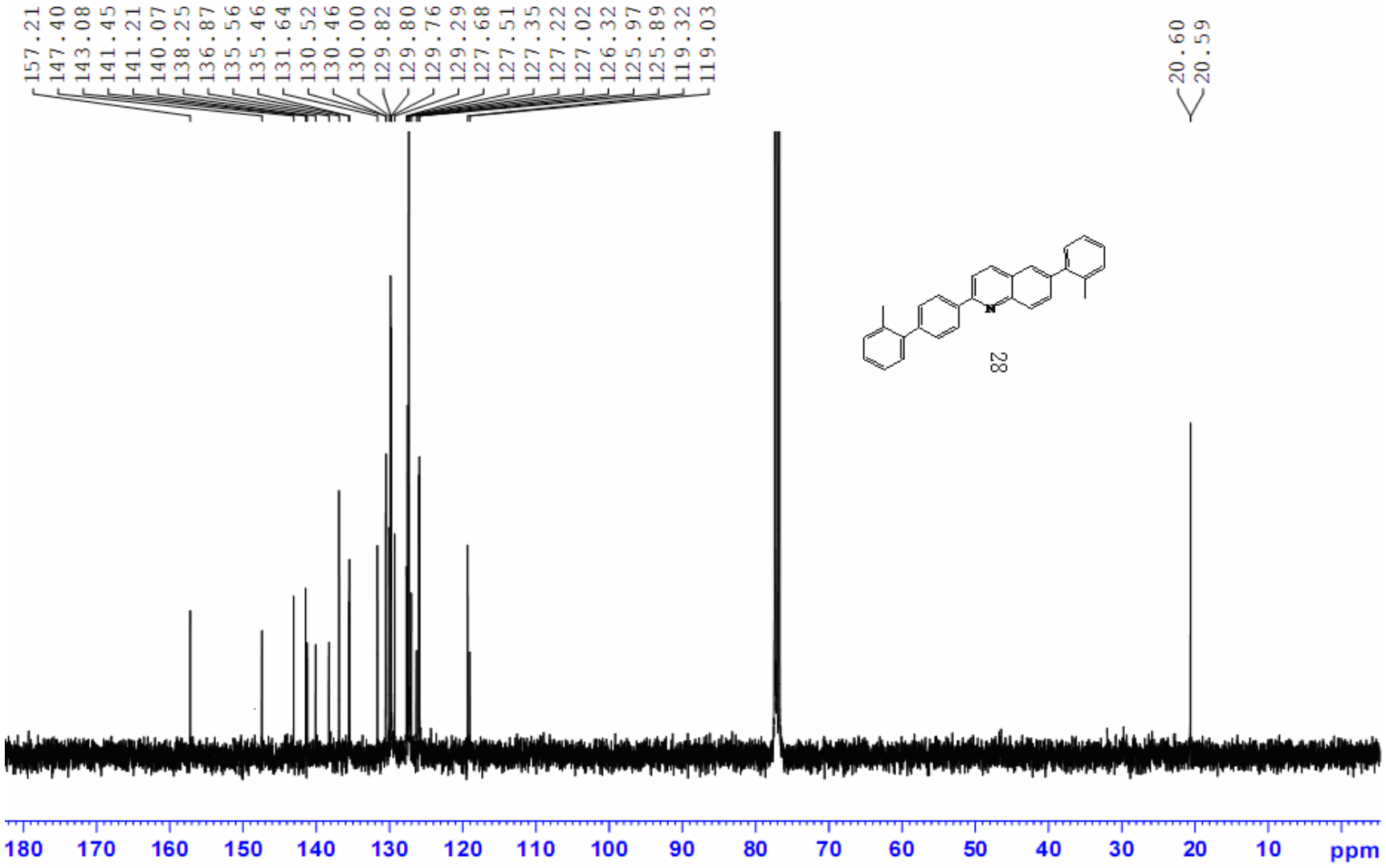

26
8.5441
8.5393
8.5345
8.5022
8.4970
8.4917
8.3280
8.3070
8.2085
8.1877
8.0965
8.0803
8.0755
8.0127
7.9916
7.9534
7.9318
7.8681
7.8476
7.8126
7.7916
7.7585
7.7400
7.7195
7.7003
7.6802
7.6710
7.6576
7.6511
7.5786
7.5762
7.5585
7.5388
0.62
0.75
5.00
1.36
2.65
0.70
4.52
1.15
ppm

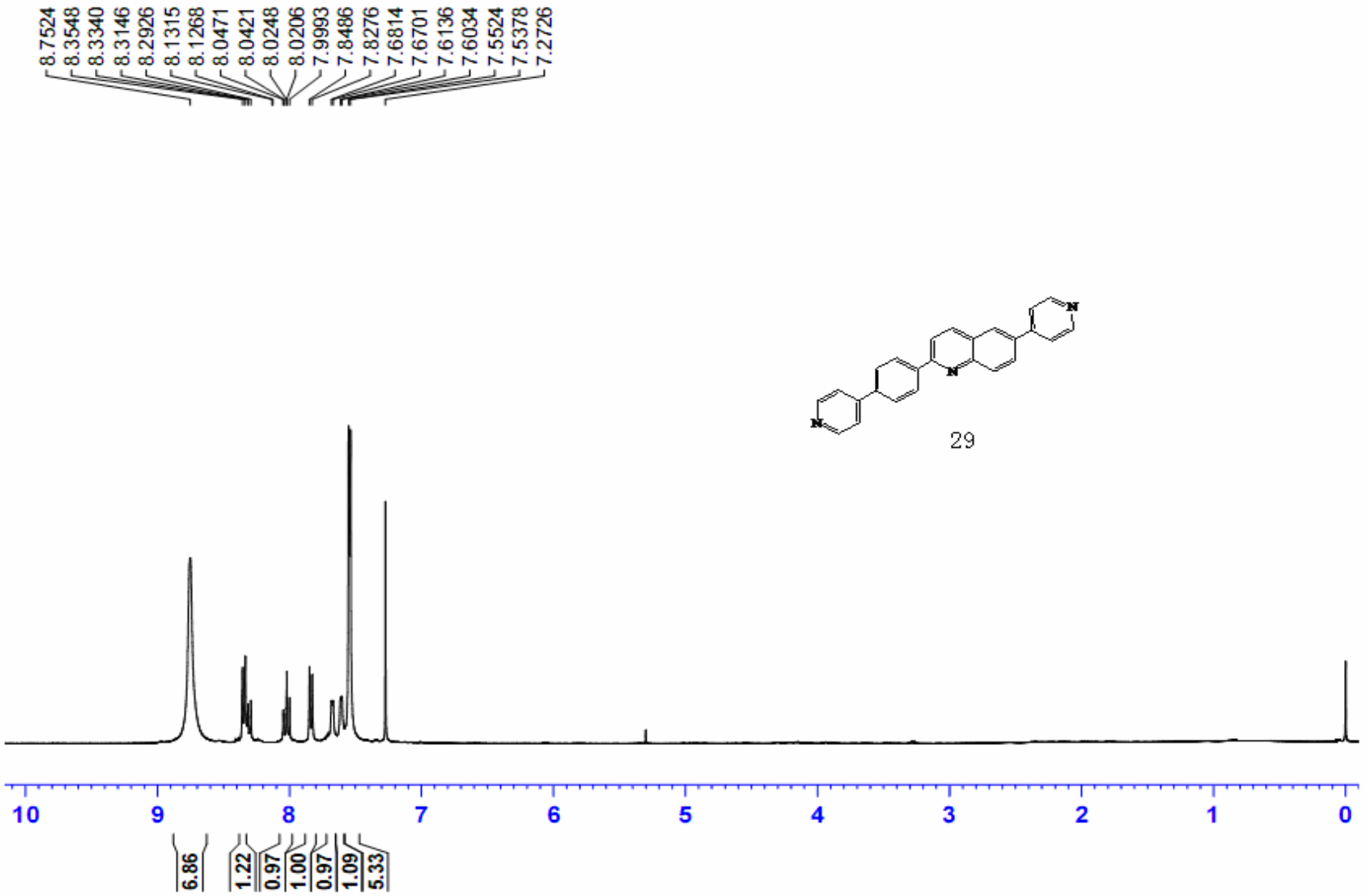

26
189.50
156.33
148.78
148.32
142.26
140.31
139.79
139.35
137.07
136.96
133.23
133.14
133.05
133.03
130.29
129.85
129.83
129.76
129.20
128.93
128.31
127.58
127.51
126.54
123.30
122.91
122.37
122.30
122.18
122.10
121.91
119.79
118.81
ppm

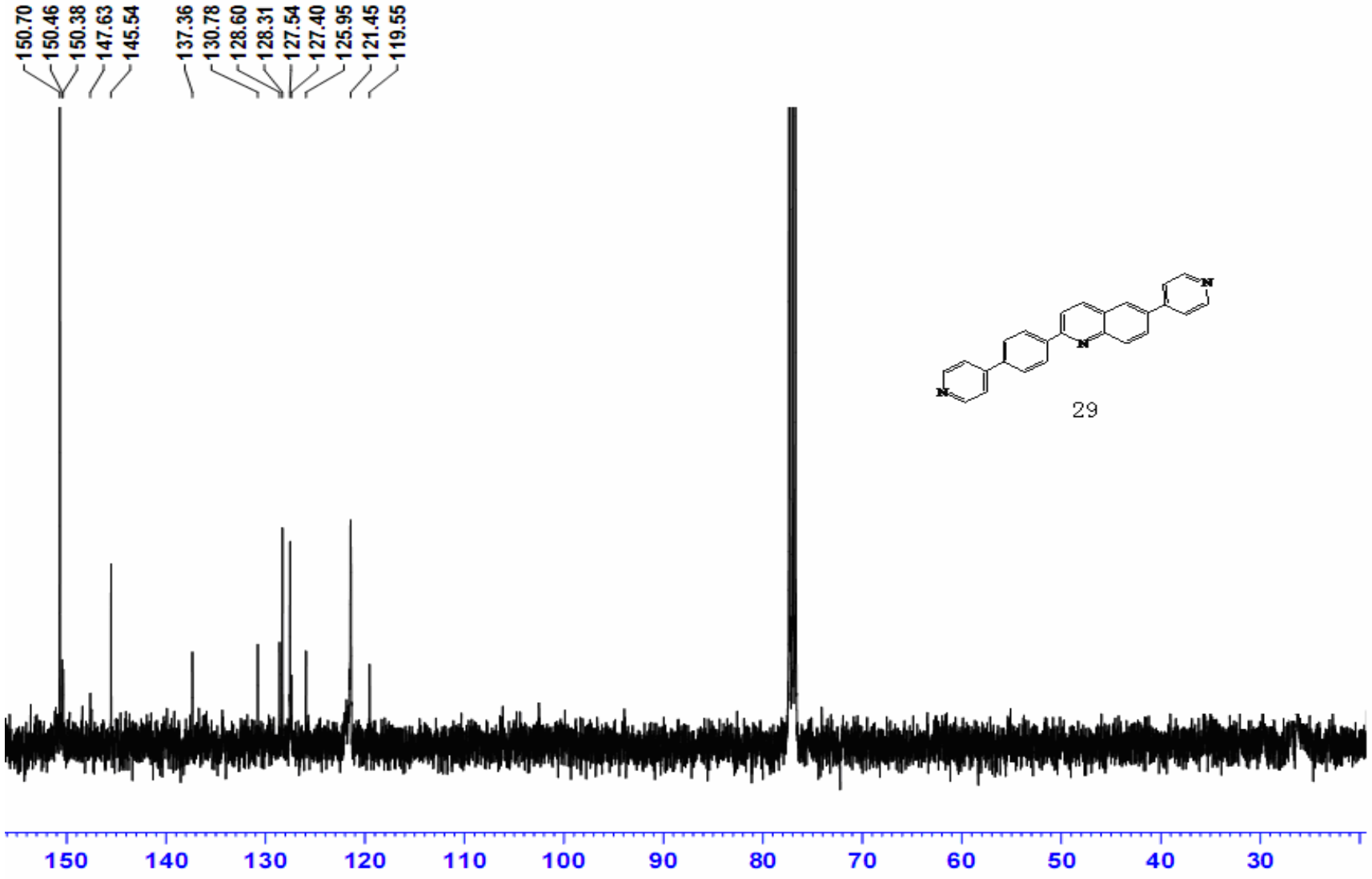
27
8.2570
8.2401
8.2360
8.2194
8.2054
8.1841
7.9538
7.9393
7.9179
7.7237
7.7029
7.4670
7.4629
7.4483
7.4443
7.4159
7.4116
7.3973
7.3928
7.3660
7.3611
7.1131
7.0943
7.0724
7.0704
7.0602
7.0543
7.0366
7.0146
3.8641
3.8492
4.00
2.99
2.08
4.39
4.45
3.00
3.08
ppm

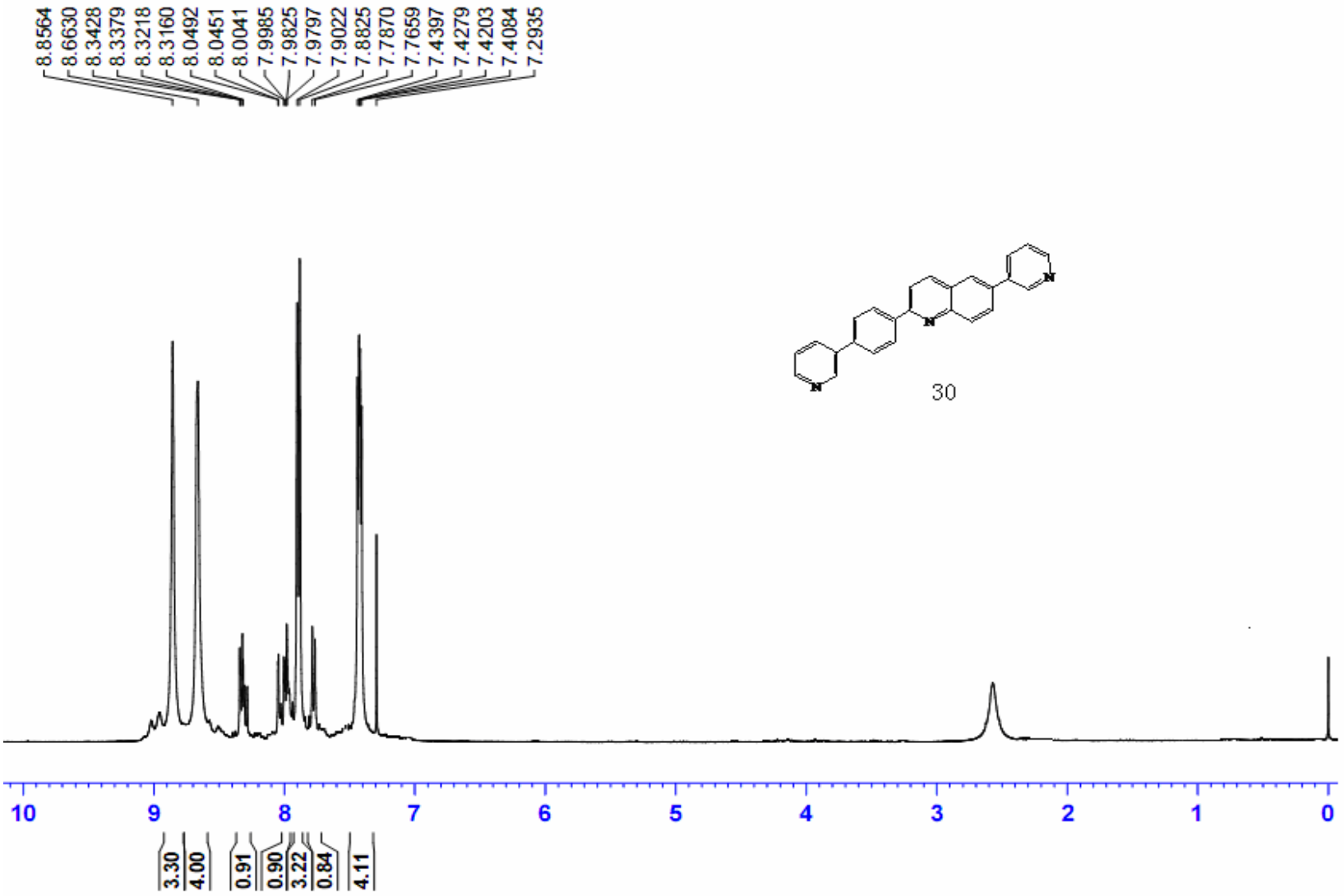

157.05
156.66
156.61
147.55
139.58
138.28
136.86
136.65
131.95
131.10
130.82
130.27
130.06
129.08
129.00
128.89
127.61
127.18
127.08
121.02
120.93
119.05
111.34
55.64
OCH3
N
OCH3
27
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

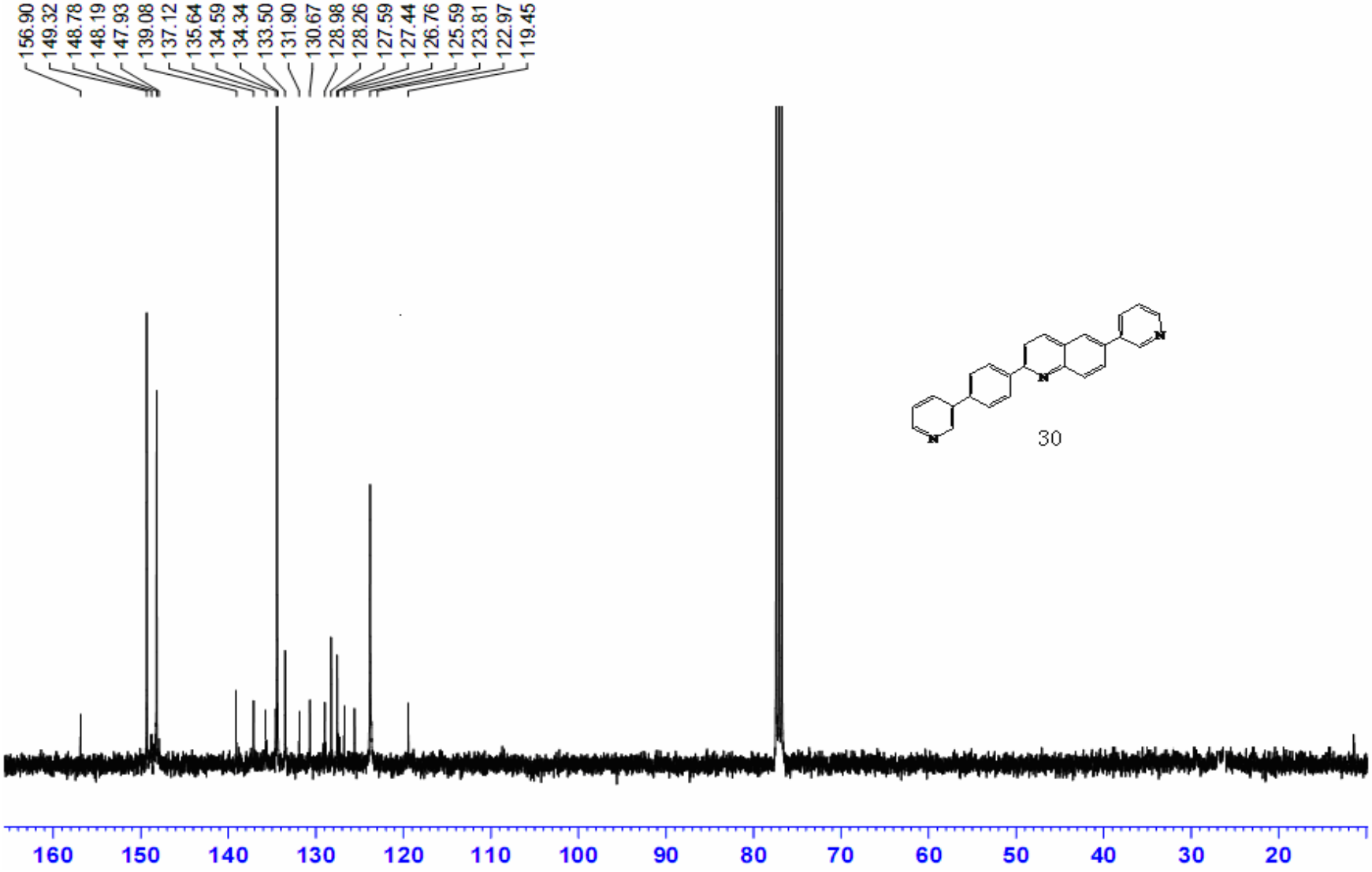

28
2.3422
2.3447
7.2453
7.2923
7.2966
7.2996
7.3063
7.3171
7.3224
7.4874
7.5001
7.5081
7.5164
7.5208
7.7165
7.7213
7.7378
7.7428
7.7647
7.7691
7.9370
7.9586
8.2021
8.2058
8.2128
8.2172
8.2223
8.2277
8.2378
8.2586
ppm
1
2
3
4
5
6
7
8
9
10
6.00
7.08
2.96
2.09
1.25
4.27


157.21
147.40
143.08
141.45
141.21
140.07
138.25
136.87
135.56
135.46
131.64
130.52
130.46
130.00
129.82
129.80
129.76
129.29
127.68
127.51
127.35
127.22
127.02
126.32
125.97
125.89
119.32
119.03
20.60
20.59
N
28
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

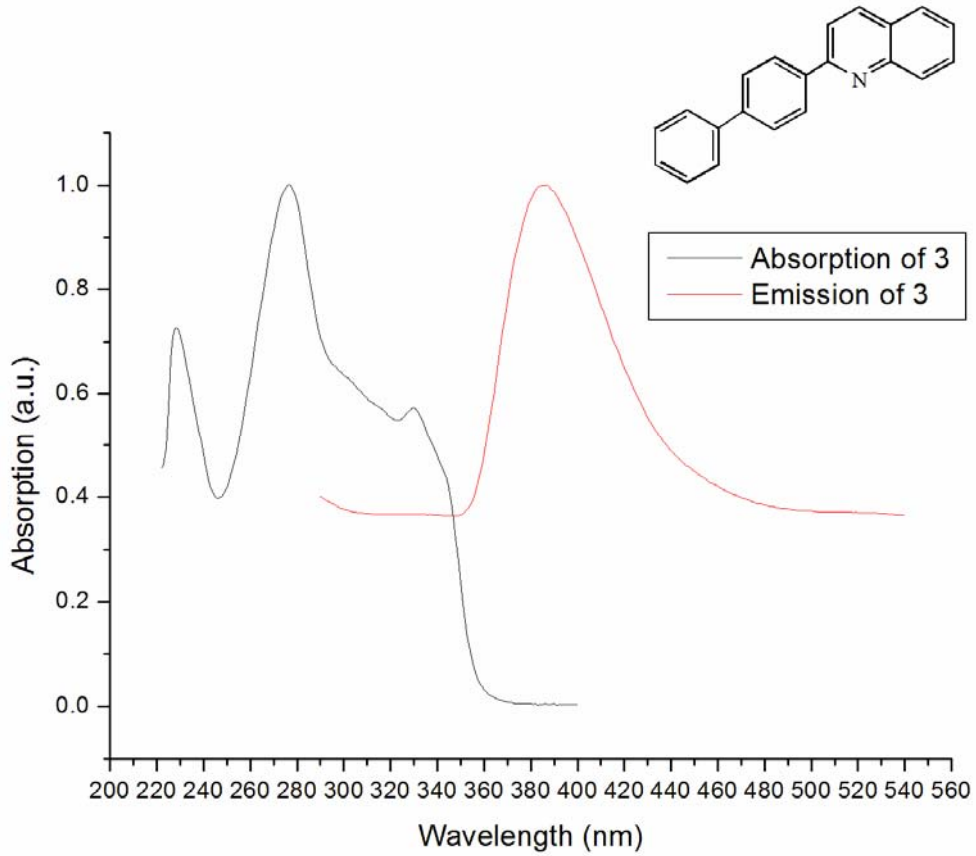

8.7524
8.3548
8.3340
8.3146
8.2926
8.1315
8.1268
8.0471
8.0421
8.0248
8.0206
7.9993
7.8486
7.8276
7.6814
7.6701
7.6136
7.6034
7.5524
7.5378
7.2726
29
10
9
8
7
6
5
4
3
2
1
0
6.86
1.22
0.97
1.00
0.97
1.09
5.33

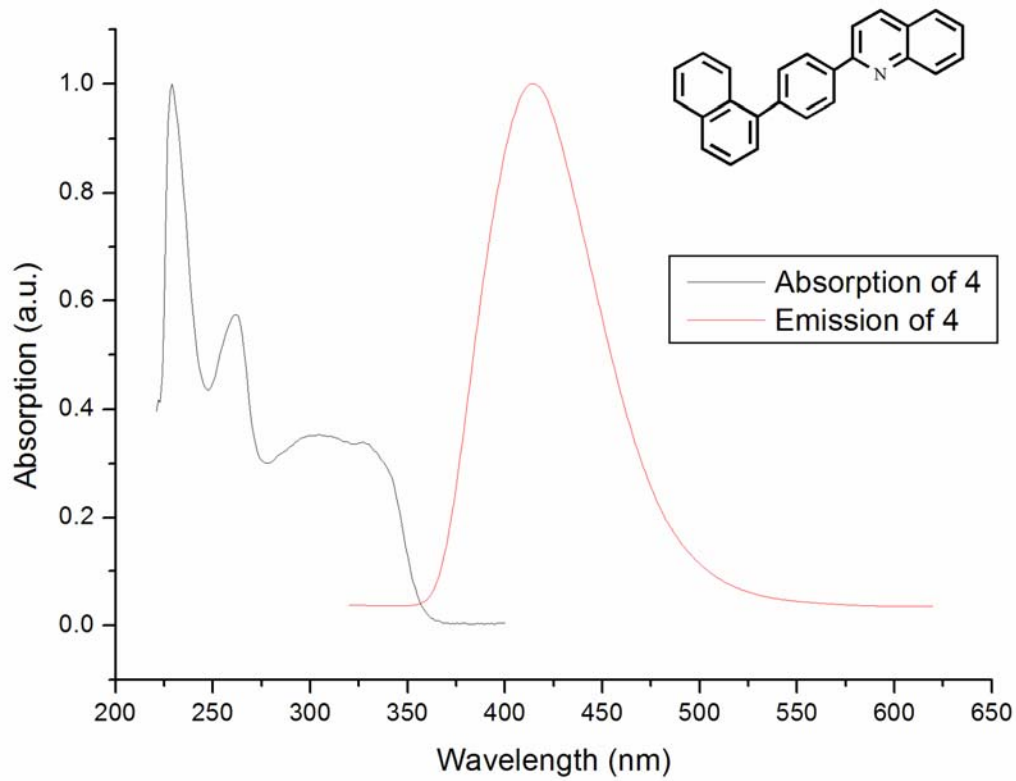

150.70
150.46
150.38
147.63
145.54
137.36
130.78
128.60
128.31
127.54
127.40
125.95
121.45
119.55
N
N
N
29
150
140
130
120
110
100
90
80
70
60
50
40
30

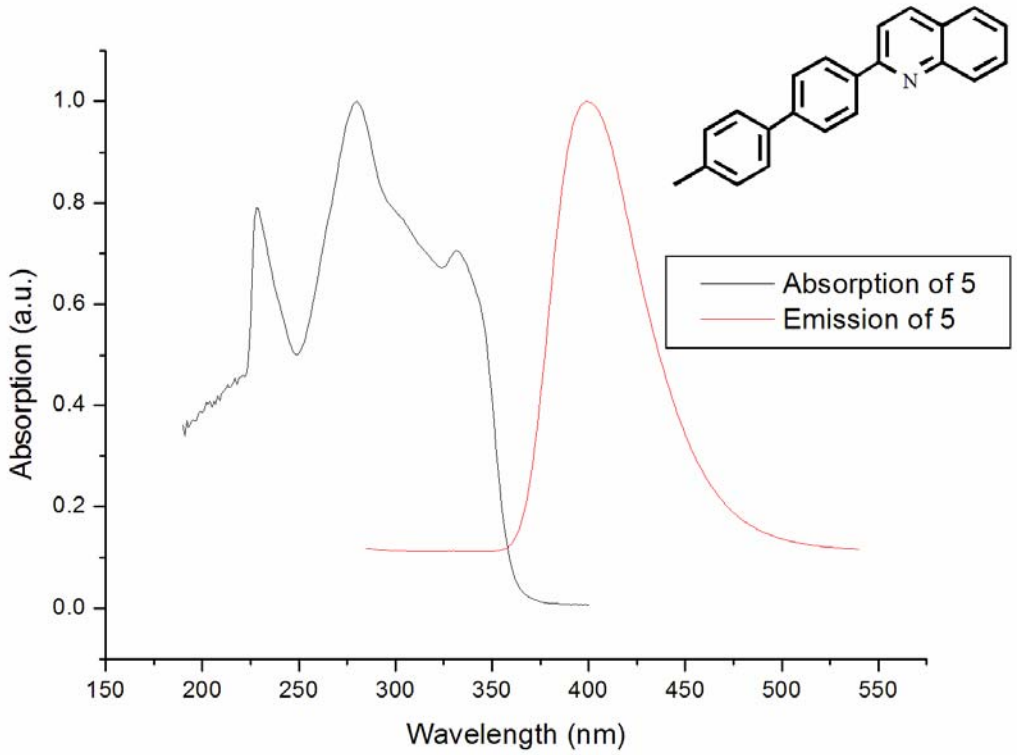

8.8564
8.6630
8.3428
8.3379
8.3218
8.3160
8.0492
8.0451
8.0041
7.9985
7.9825
7.9797
7.9022
7.8825
7.7870
7.7659
7.4397
7.4279
7.4203
7.4084
7.2935
30
10
9
8
7
6
5
4
3
2
1
0
3.30
4.00
0.91
0.90
3.22
0.84
4.11

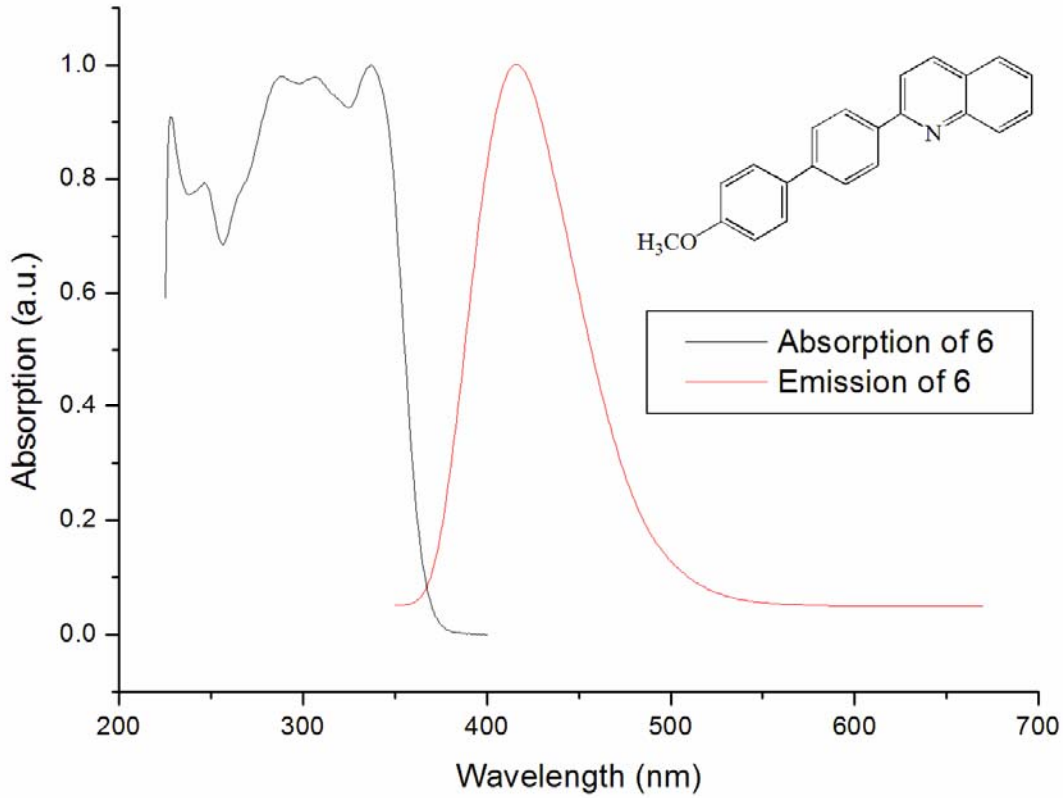

156.90
149.32
148.78
148.19
147.93
139.08
137.12
135.64
134.59
134.34
133.50
131.90
130.67
128.98
128.26
127.59
127.44
126.76
125.59
123.81
122.97
119.45
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

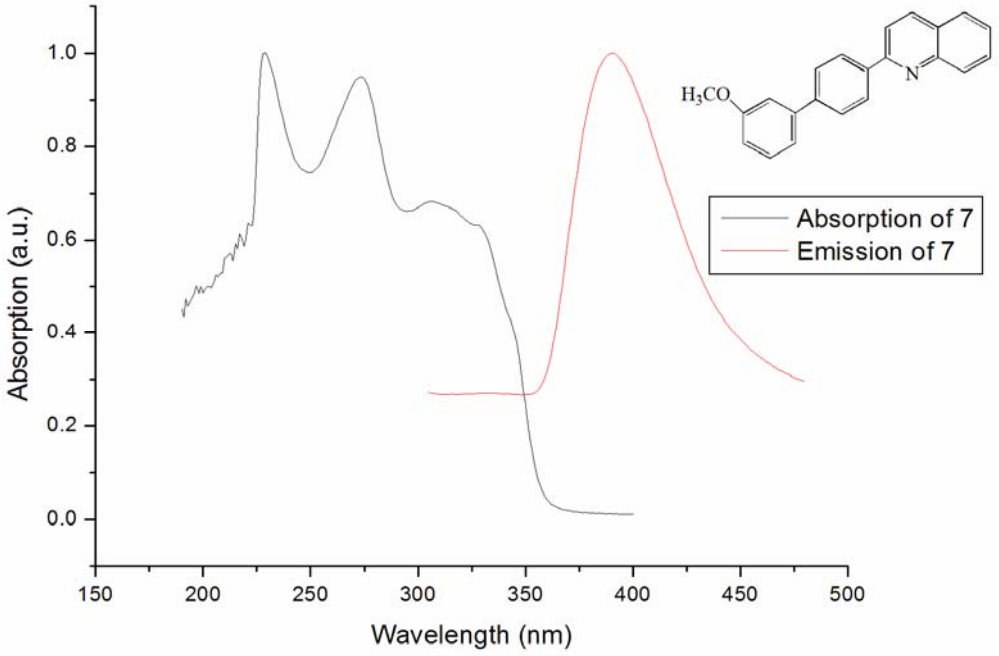
30

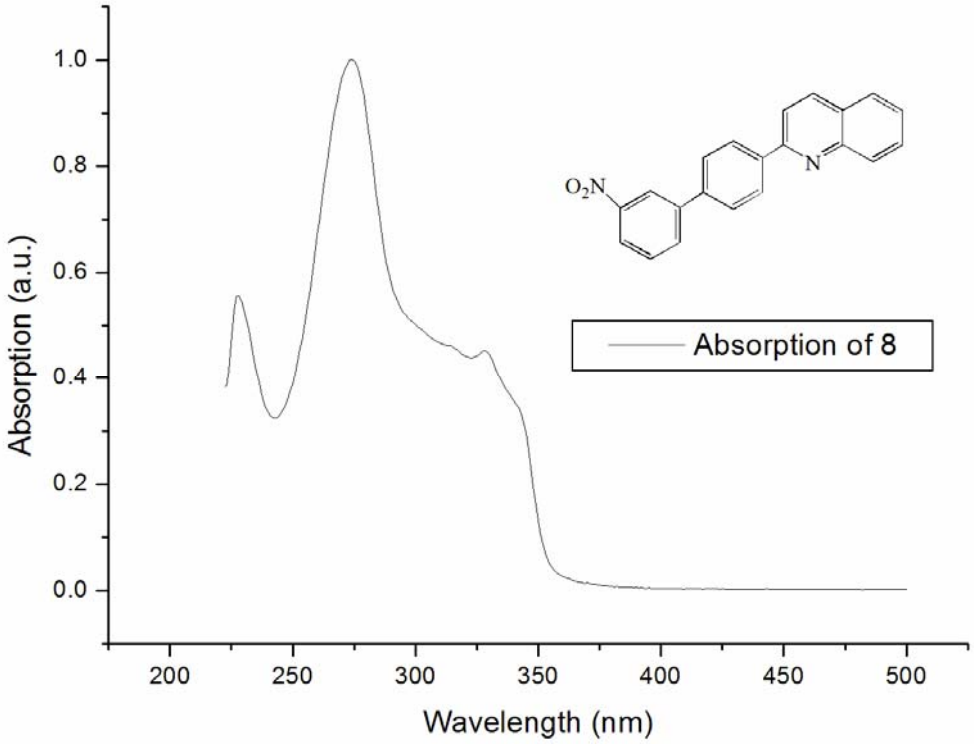

N
Absorption of 3
Emission of 3
Absorption (a.u.)
0.0
0.2
0.4
0.6
0.8
1.0
200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560
Wavelength (nm)

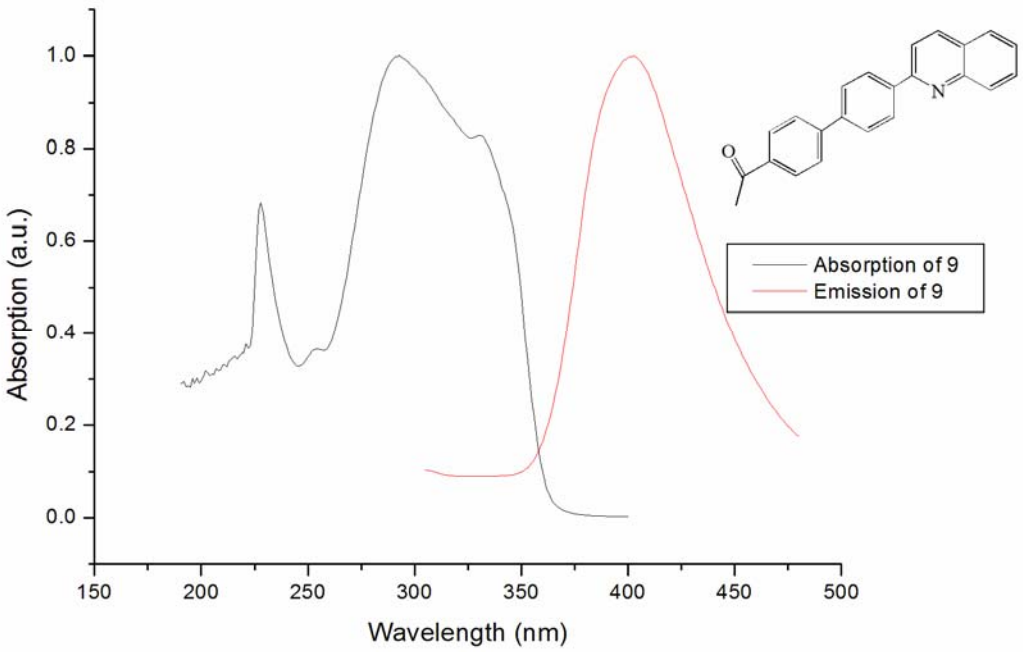

N
Absorption of 4
Emission of 4
Absorption (a.u.)
0.0
0.2
0.4
0.6
0.8
1.0
200 250 300 350 400 450 500 550 600 650
Wavelength (nm)

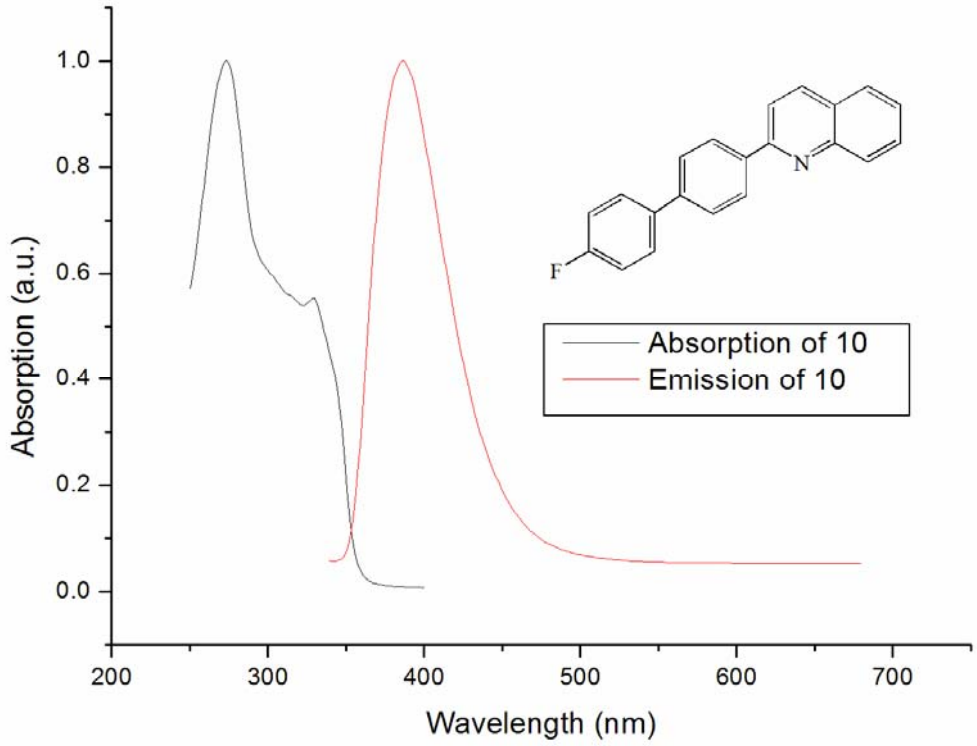

Absorption (a.u.)
Wavelength (nm)
Absorption of 5
Emission of 5
N

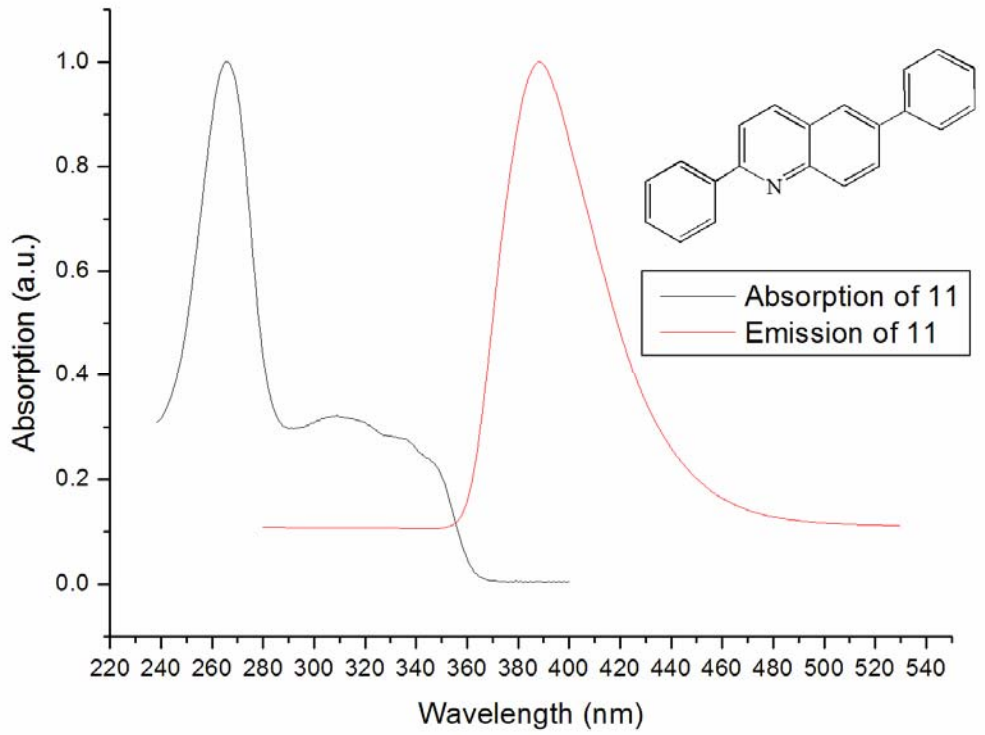

Absorption (a.u.)
Wavelength (nm)
Absorption of 6
Emission of 6
H3CO
N

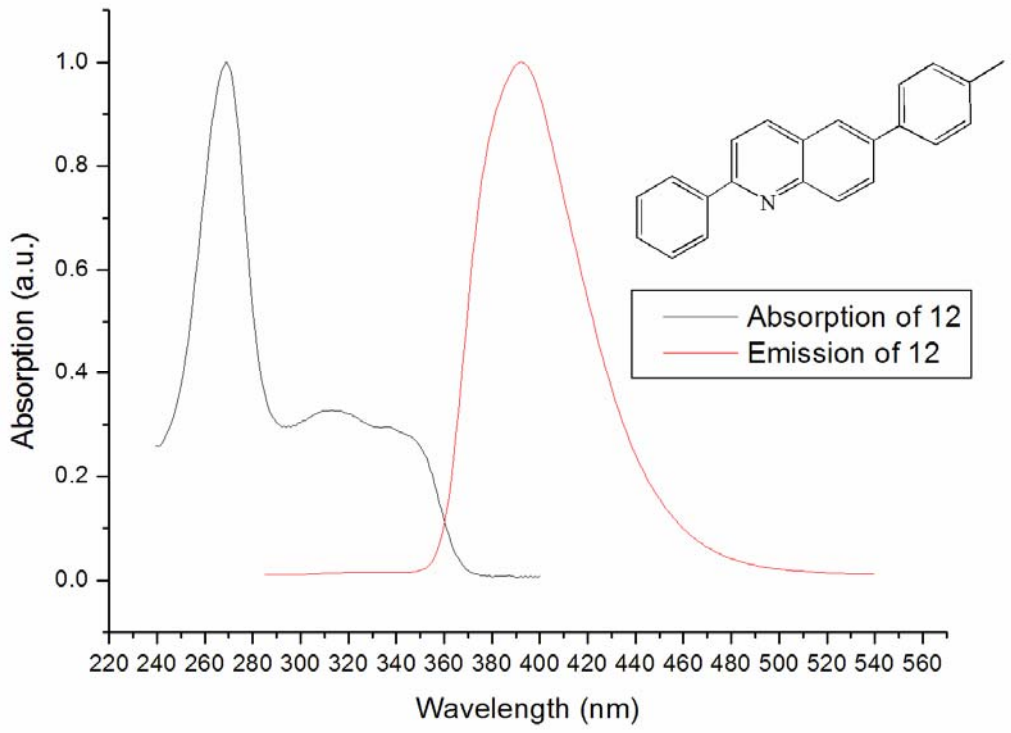

Absorption (a.u.)
Wavelength (nm)
H3CO
N
Absorption of 7
Emission of 7

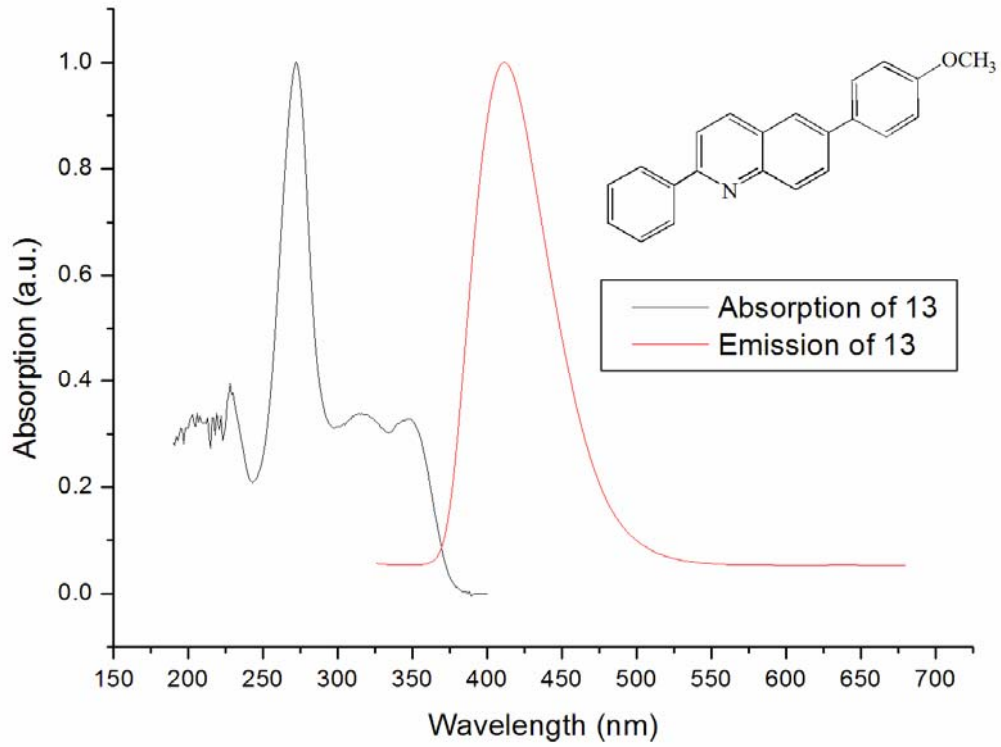

Absorption (a.u.)
Wavelength (nm)
O2N
N
Absorption of 8

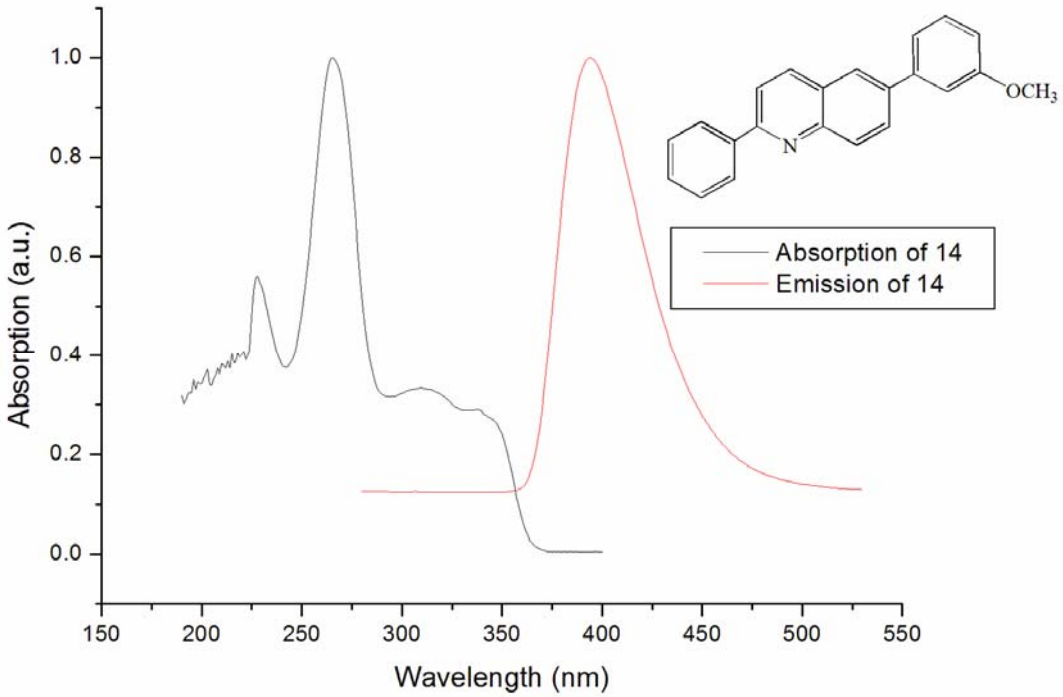

Absorption (a.u.)
Wavelength (nm)
Absorption of 9
Emission of 9
O
N

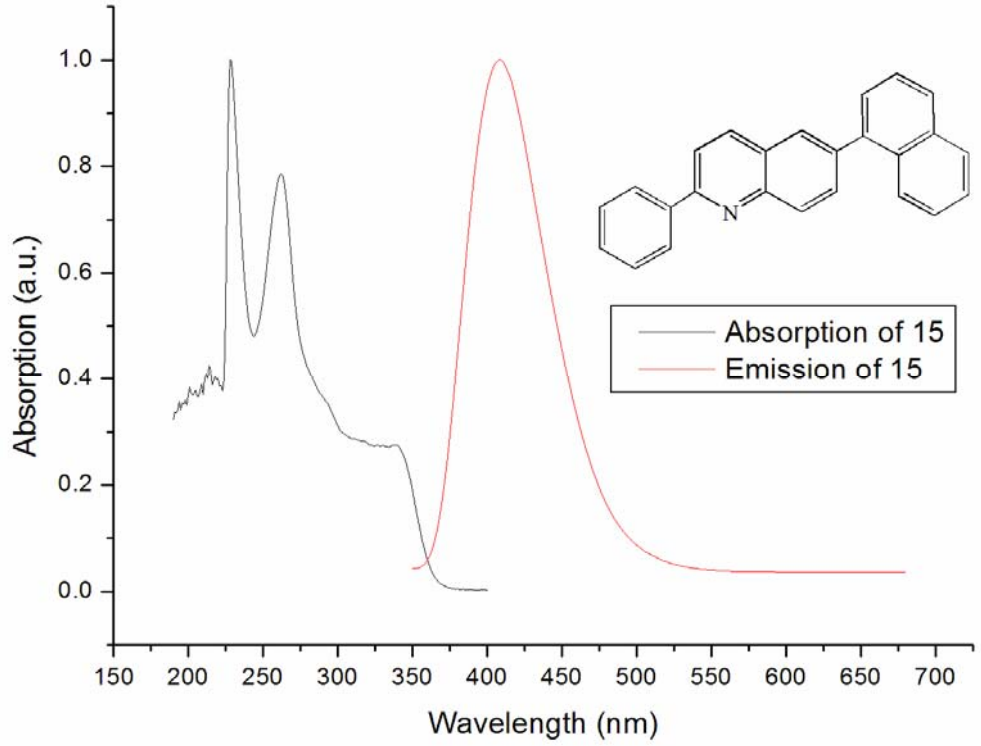

Absorption (a.u.)
Wavelength (nm)
Absorption of 10
Emission of 10
F
N

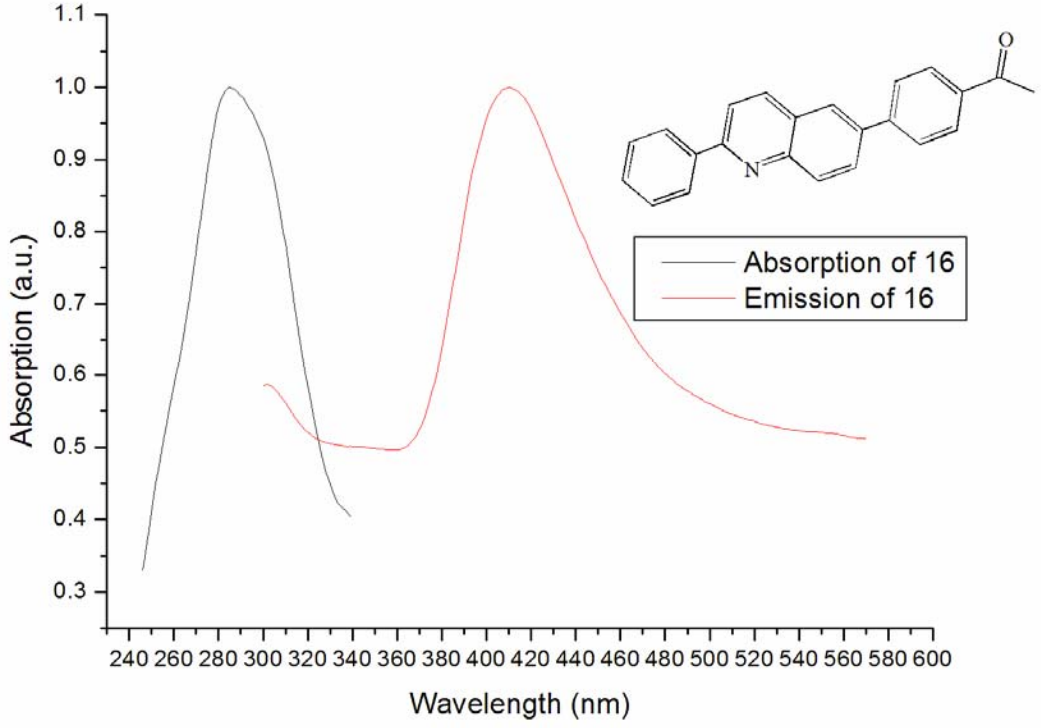

Absorption (a.u.)
1.0
0.8
0.6
0.4
0.2
0.0
220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540
Wavelength (nm)
N
Absorption of 11
Emission of 11

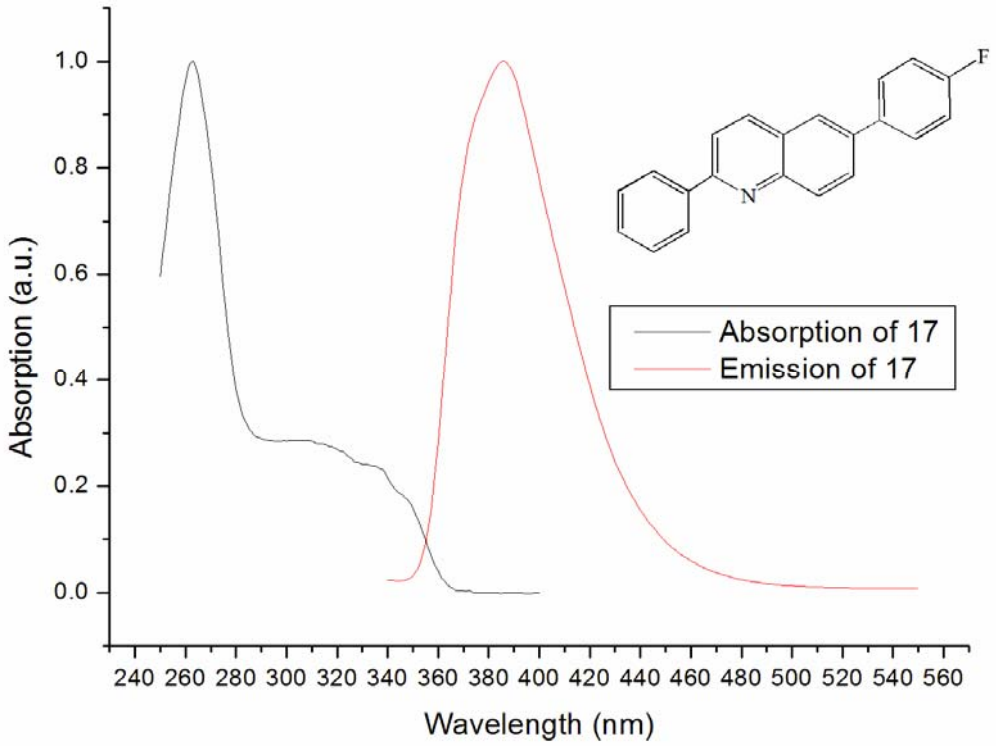

Absorption (a.u.)
1.0
0.8
0.6
0.4
0.2
0.0
220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560
Wavelength (nm)
N
Absorption of 12
Emission of 12

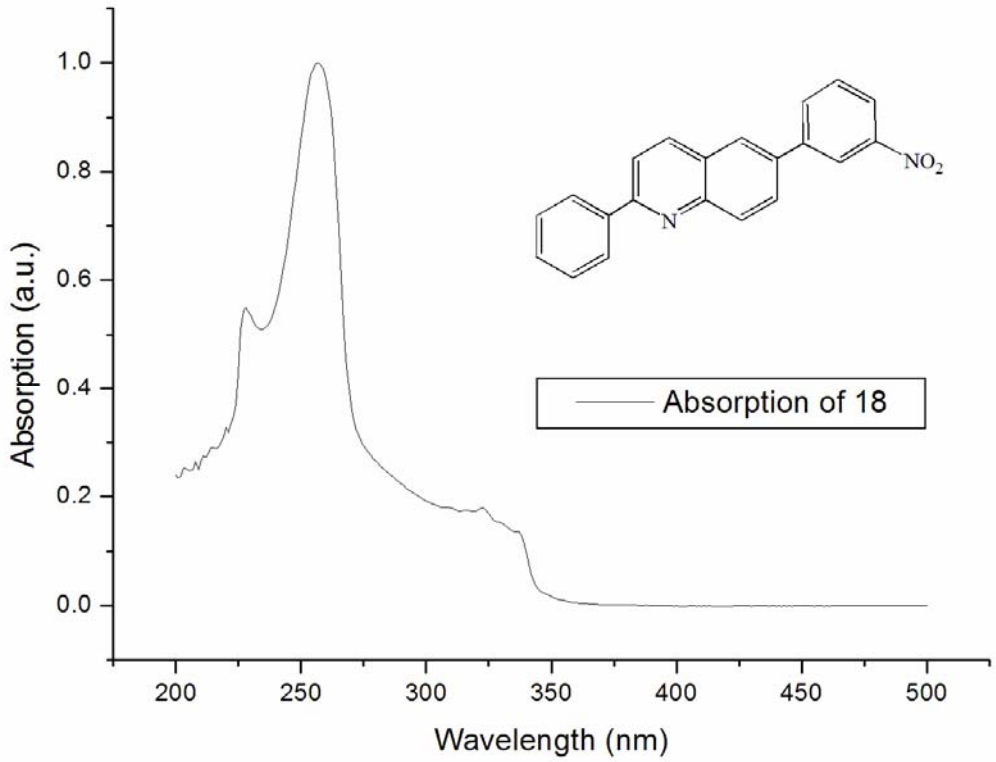

Absorption (a.u.)
Wavelength (nm)
Absorption of 13
Emission of 13
OCH3
N

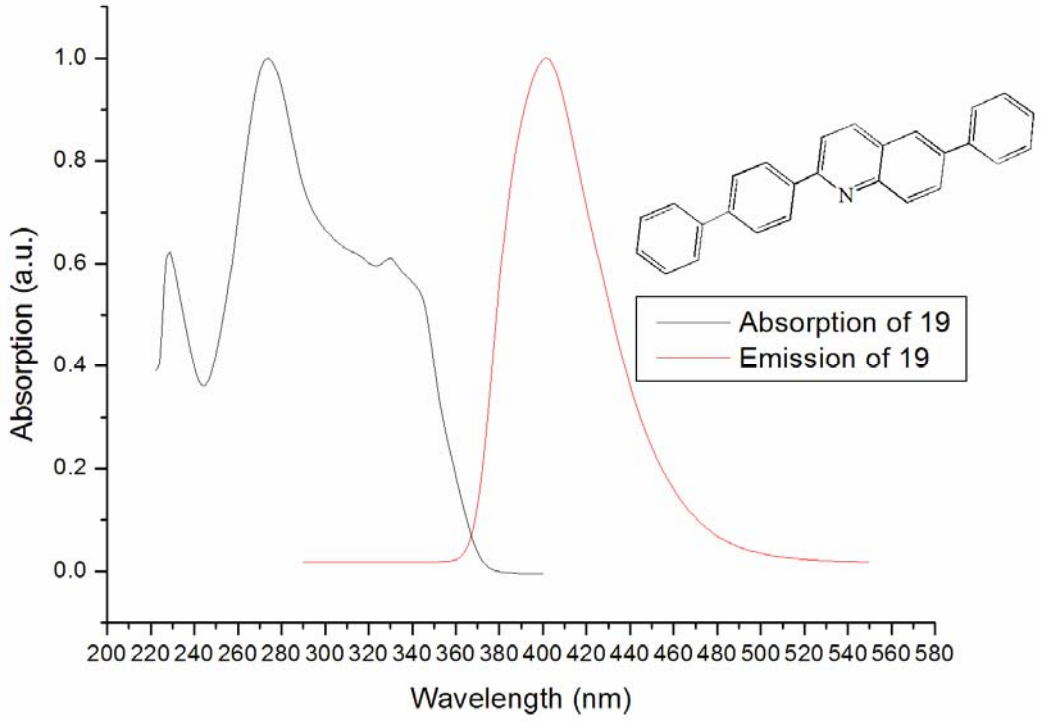

Absorption (a.u.)
Wavelength (nm)
Absorption of 14
Emission of 14
OCH3
N

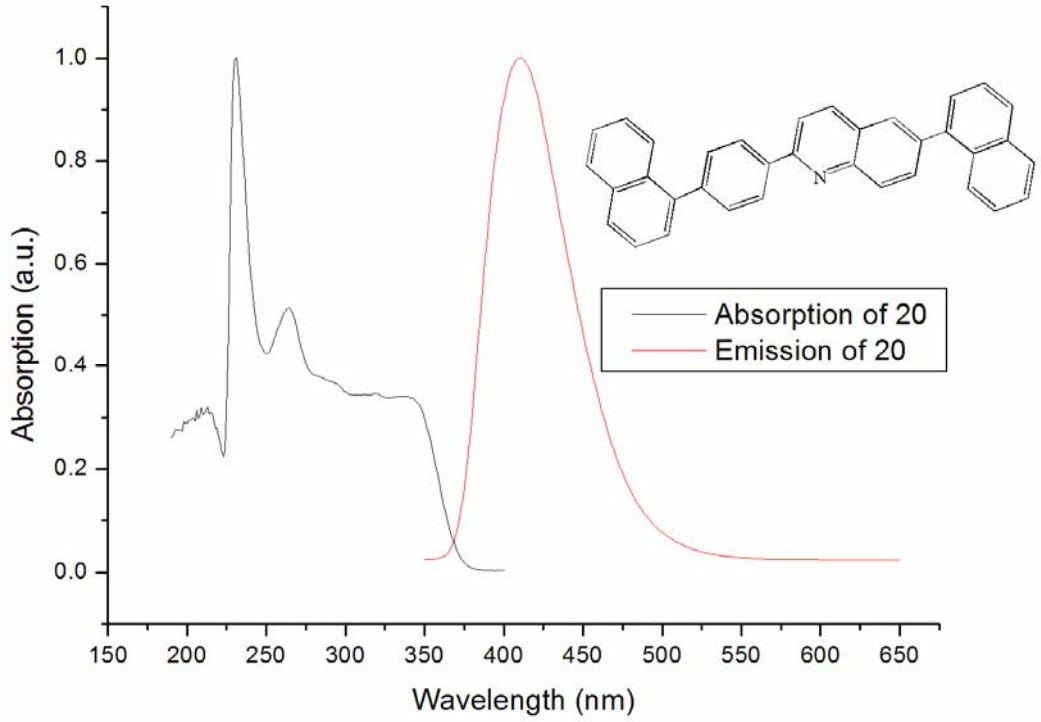

Absorption (a.u.)
Wavelength (nm)
Absorption of 15
Emission of 15
N

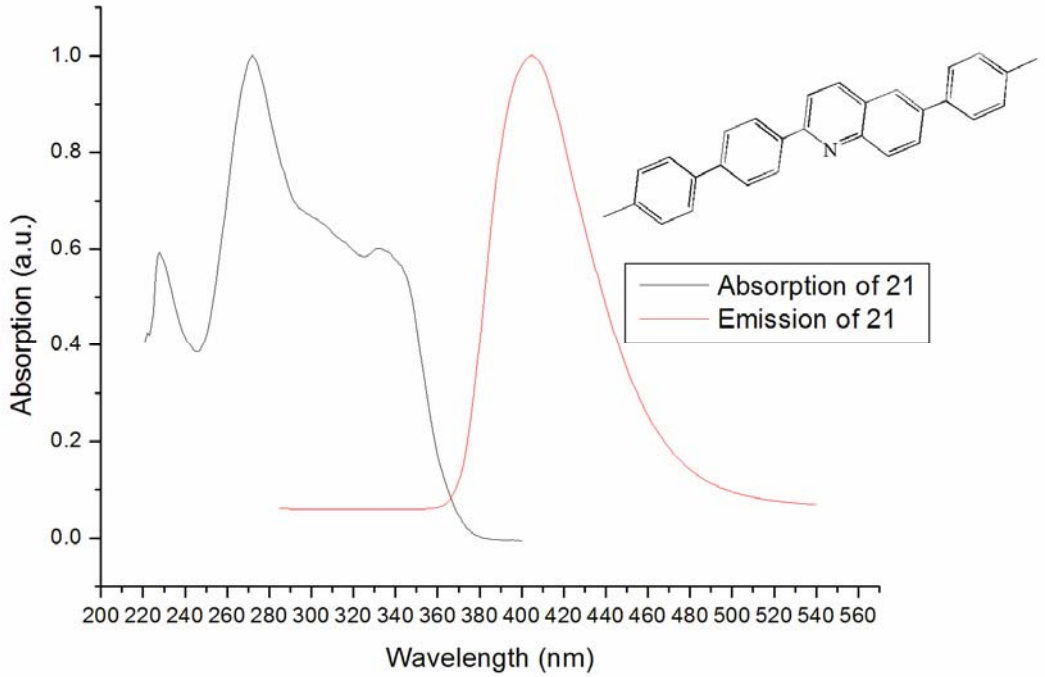

Absorption (a.u.)
Wavelength (nm)
Absorption of 16
Emission of 16
O
N

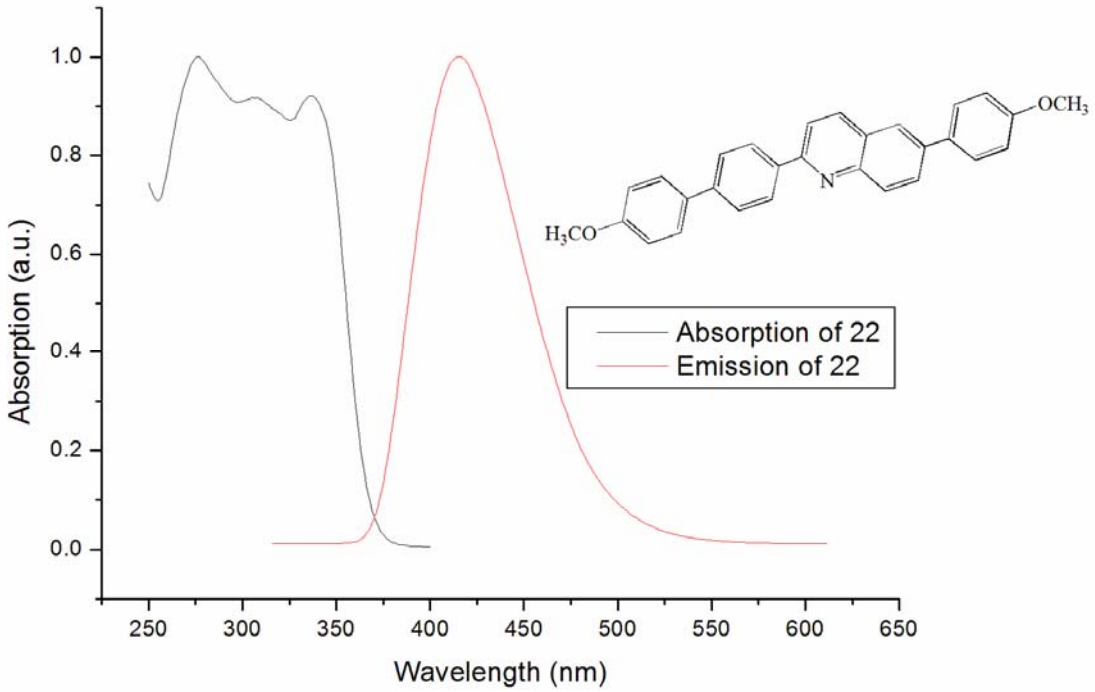

Absorption (a.u.)
1.0
0.8
0.6
0.4
0.2
0.0
240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560
Wavelength (nm)
F
N
Absorption of 17
Emission of 17

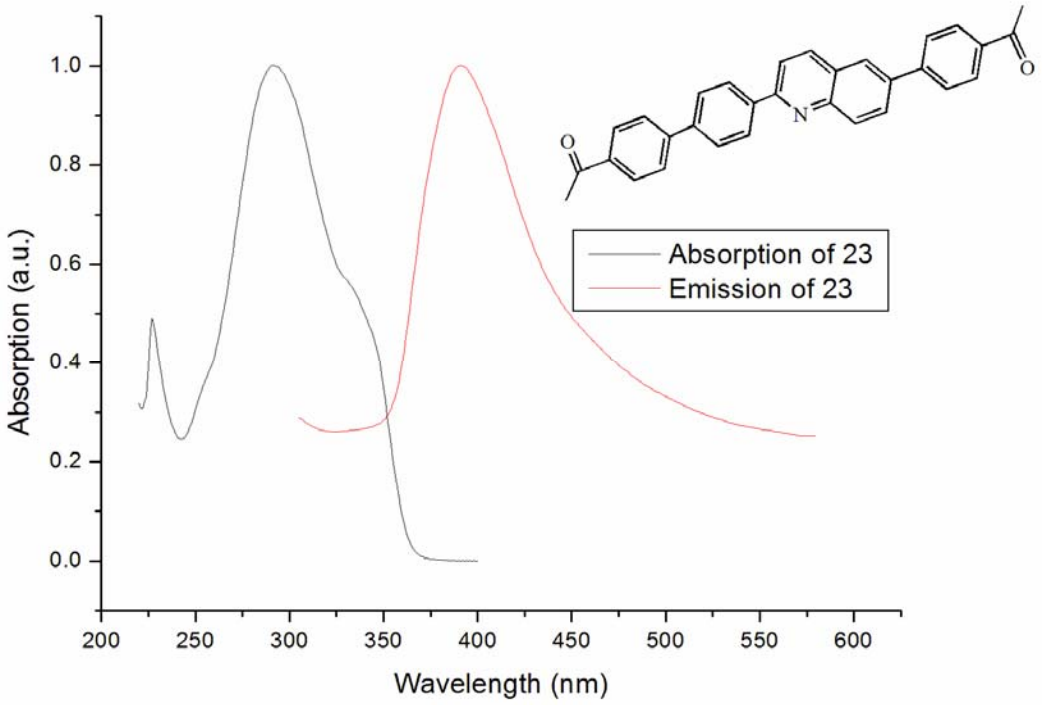

Absorption (a.u.)
1.0
0.8
0.6
0.4
0.2
0.0
200 250 300 350 400 450 500
Wavelength (nm)
NO2
N
Absorption of 18

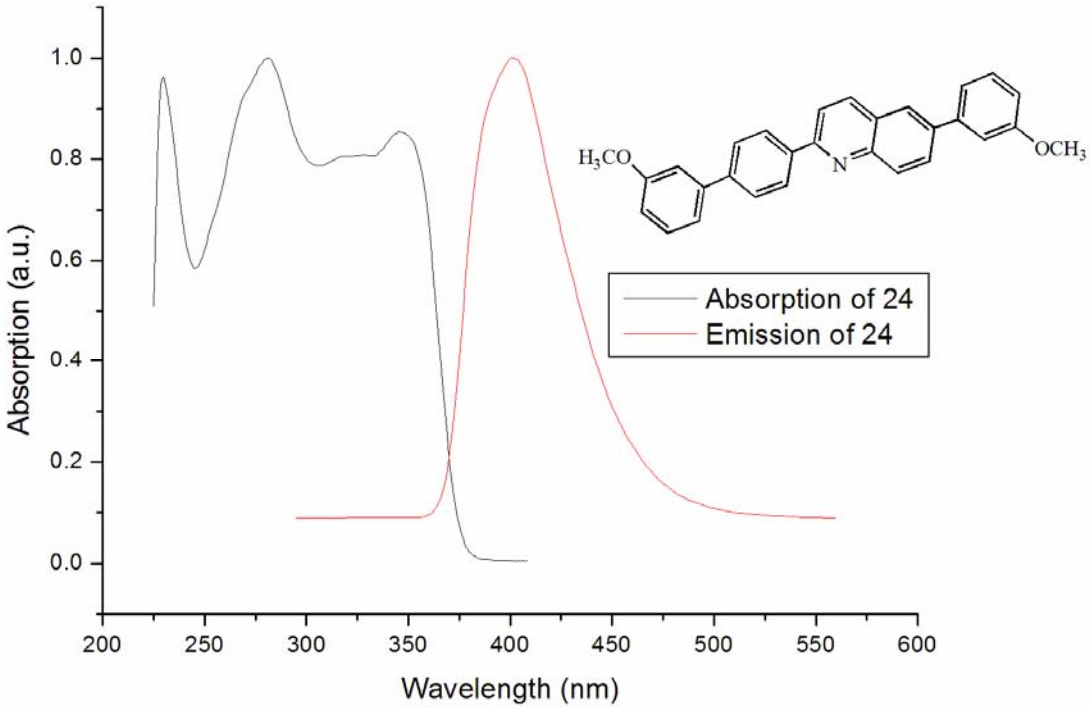

Absorption (a.u.)
1.0
0.8
0.6
0.4
0.2
0.0
200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560 580
Wavelength (nm)
N
Absorption of 19
Emission of 19

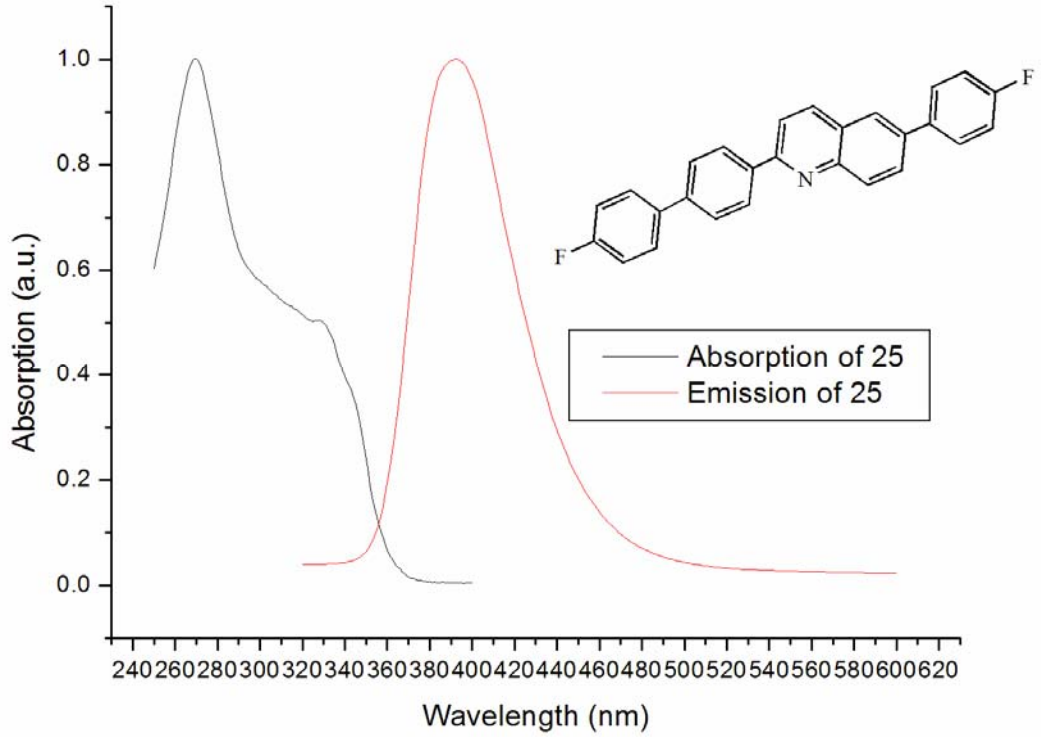

Absorption (a.u.)
1.0
0.8
0.6
0.4
0.2
0.0
150 200 250 300 350 400 450 500 550 600 650
Wavelength (nm)
N
Absorption of 20
Emission of 20

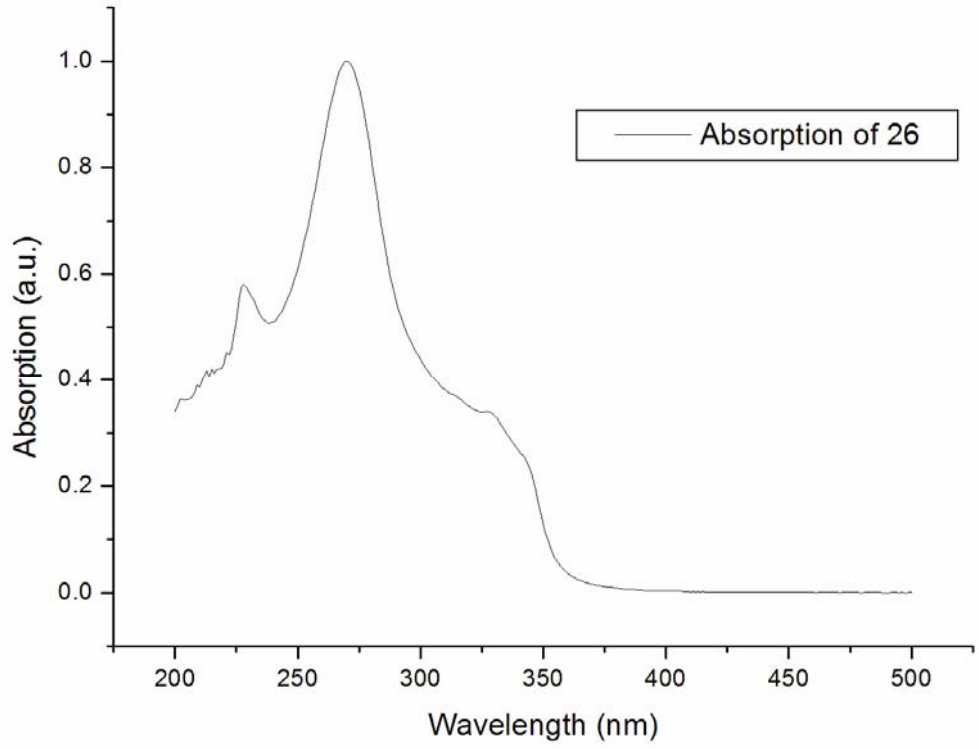

Absorption (a.u.)
1.0
0.8
0.6
0.4
0.2
0.0
200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560
Wavelength (nm)
N
Absorption of 21
Emission of 21

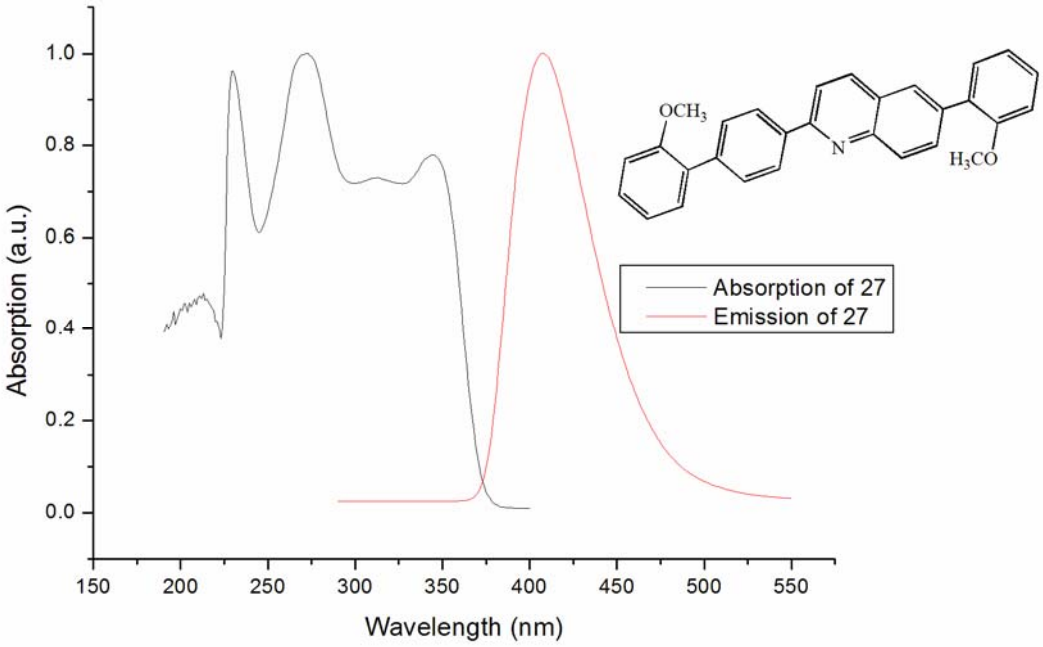

Absorption (a.u.)
1.0
0.8
0.6
0.4
0.2
0.0
250 300 350 400 450 500 550 600 650
Wavelength (nm)
N
OCH3
H3CO
Absorption of 22
Emission of 22

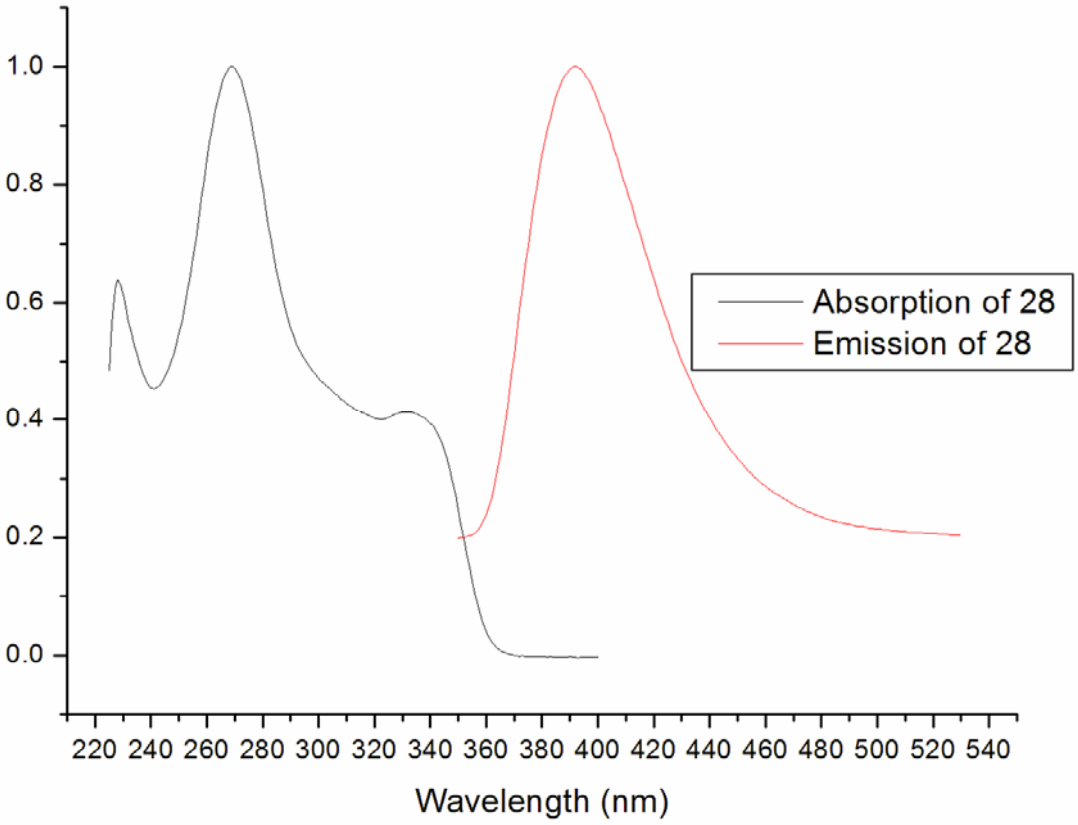

Absorption (a.u.)
Wavelength (nm)
Absorption of 23
Emission of 23
O
O
N

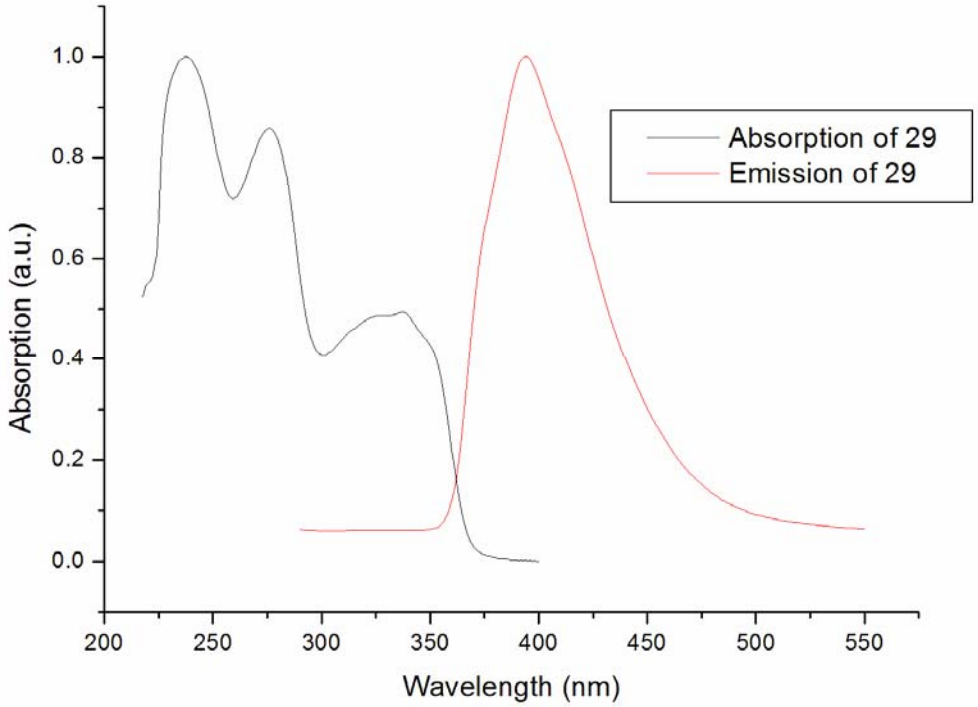

Absorption (a.u.)
Wavelength (nm)
Absorption of 24
Emission of 24
H3CO
OCH3
N


Absorption (a.u.)
1.0
0.8
0.6
0.4
0.2
0.0
240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560 580 600 620
Wavelength (nm)
Absorption of 25
Emission of 25
F
N
F


Absorption (a.u.)
1.0
0.8
0.6
0.4
0.2
0.0
200 250 300 350 400 450 500
Wavelength (nm)
Absorption of 26


Absorption (a.u.)
Wavelength (nm)
Absorption of 27
Emission of 27
OCH3
N
H3CO


Absorption of 28
Emission of 28
Wavelength (nm)


Absorption of 29
Emission of 29
Absorption (a.u.)
Wavelength (nm)
1.0
0.8
0.6
0.4
0.2
0.0
200
250
300
350
400
450
500
550

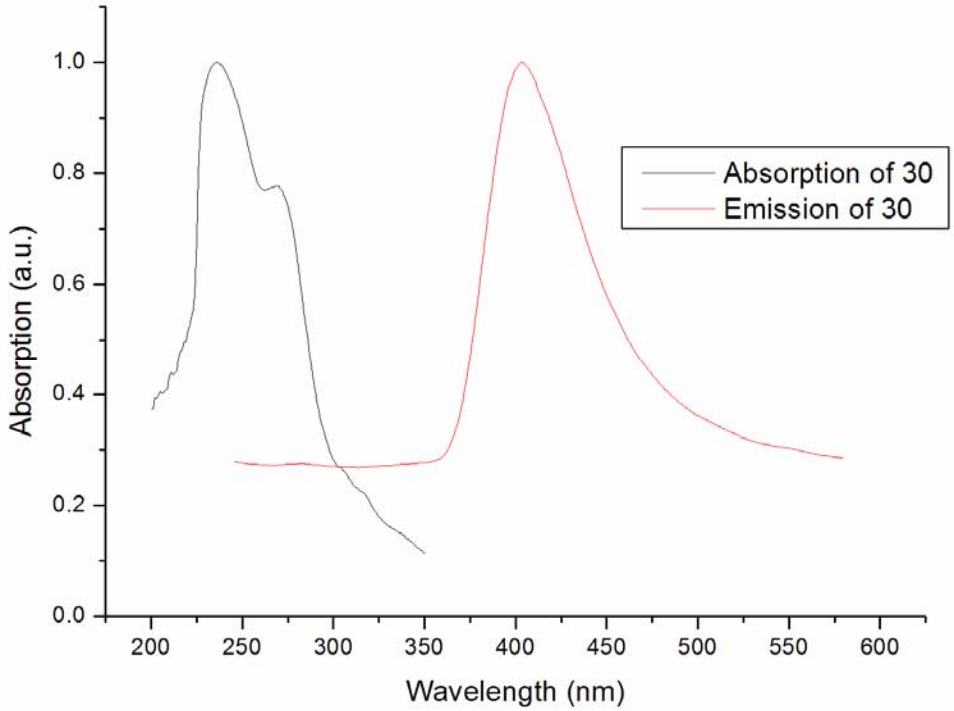

Absorption of 30
Emission of 30
Absorption (a.u.)
Wavelength (nm)
1.0
0.8
0.6
0.4
0.2
0.0
200
250
300
350
400
450
500
550
600

Table S1. Crystal data and structure refinement for 1.

Empirical formula	C31 H27 Cl Fe N Pd
Formula weight	611.24
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 13.9977(16) A alpha = 90 deg.
	b = 10.9009(12) A beta = 101.9790(10) deg.
	c = 18.025(2) A gamma = 90 deg.
Volume	2690.6(5) A^3
Z, Calculated density	4, 1.509 Mg/m^3
Absorption coefficient	1.326 mm^-1
F(000)	1236
Crystal size	0.40 x 0.30 x 0.20 mm
Theta range for data collection	2.31 to 25.50 deg.
Limiting indices	-16<=h<=16, -13<=k<=13, -21<=l<=21
Reflections collected / unique	19106 / 5007 [R(int) = 0.0521]
Completeness to theta = 25.50	99.9 %
Absorption correction	None
Max. and min. transmission	0.7773 and 0.6190
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5007 / 0 / 345
Goodness-of-fit on F^2	1.000
Final R indices [I>2sigma(I)]	R1 = 0.0362, wR2 = 0.0772
R indices (all data)	R1 = 0.0598, wR2 = 0.0888
Largest diff. peak and hole	0.484 and -0.352 e.A^-3

Table S2. Crystal data and structure refinement for 2.

Empirical formula	C82 H94 Cl2 Fe2 N8 Pd2
Formula weight	1587.05
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pca2(1)
Unit cell dimensions	a = 16.077(2) A alpha = 90 deg.
	b = 12.6076(17) A beta = 90 deg.
	c = 37.742(5) A gamma = 90 deg.
Volume	7650.3(18) A^3
Z, Calculated density	4, 1.378 Mg/m^3
Absorption coefficient	0.952 mm^-1
F(000)	3280
Crystal size	0.37 x 0.32 x 0.25 mm
Theta range for data collection	2.32 to 25.50 deg.
Limiting indices	-19<=h<=19, -15<=k<=15, -45<=l<=45
Reflections collected / unique	54077 / 14233 [R(int) = 0.0727]
Completeness to theta = 25.50	99.9 %
Absorption correction	None
Max. and min. transmission	0.7967 and 0.7195
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14233 / 244 / 881
Goodness-of-fit on F^2	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0525, wR2 = 0.1301
R indices (all data)	R1 = 0.0766, wR2 = 0.1462
Absolute structure parameter	0.12(3)
Largest diff. peak and hole	2.253 and -0.883 e.A^-3

Table S3. Crystal data and structure refinement for 13.

Empirical formula	C22 H17 N O
Formula weight	311.37
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pna2(1)
Unit cell dimensions	a = 6.3212(16) A alpha = 90 deg.
	b = 7.4318(19) A beta = 90 deg.
	c = 33.967(9) A gamma = 90 deg.
Volume	1595.7(7) A^3
Z, Calculated density	4, 1.296 Mg/m^3
Absorption coefficient	0.079 mm^-1
F(000)	656
Crystal size	0.41 x 0.32 x 0.26 mm
Theta range for data collection	2.81 to 25.50 deg.
Limiting indices	-6<=h<=7, -9<=k<=8, -13<=l<=41
Reflections collected / unique	4861 / 1796 [R(int) = 0.0584]
Completeness to theta = 25.50	99.5 %
Absorption correction	None
Max. and min. transmission	0.9797 and 0.9683
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1796 / 1 / 218
Goodness-of-fit on F^2	1.000
Final R indices [I>2sigma(I)]	R1 = 0.0478, wR2 = 0.0928
R indices (all data)	R1 = 0.0939, wR2 = 0.1132
Absolute structure parameter	0(3)
Largest diff. peak and hole	0.147 and -0.156 e.A^-3

Table S4. Crystal data and structure refinement for 15.

Empirical formula	C25 H17 N
Formula weight	331.40
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 14.2395(19) A alpha = 90 deg.
	b = 7.5461(10) A beta = 90 deg.
	c = 32.144(4) A gamma = 90 deg.
Volume	3454.0(8) A^3
Z, Calculated density	8, 1.275 Mg/m^3
Absorption coefficient	0.074 mm^-1
F(000)	1392
Crystal size	0.41 x 0.32 x 0.26 mm
Theta range for data collection	2.53 to 25.50 deg.
Limiting indices	-17<=h<=17, -9<=k<=9, -38<=l<=38
Reflections collected / unique	19334 / 3217 [R(int) = 0.0758]
Completeness to theta = 25.50	99.9 %
Absorption correction	None
Max. and min. transmission	0.9811 and 0.9705
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3217 / 0 / 235
Goodness-of-fit on F^2	0.993
Final R indices [I>2sigma(I)]	R1 = 0.0498, wR2 = 0.1021
R indices (all data)	R1 = 0.1219, wR2 = 0.1364
Largest diff. peak and hole	0.122 and -0.179 e.A^-3

Table S5. Crystal data and structure refinement for 17.

Empirical formula	C21 H14 F N
Formula weight	299.33
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 15.95(2) A alpha = 90 deg.
	b = 7.413(10) A beta = 94.011(18) deg.
	c = 6.299(9) A gamma = 90 deg.
Volume	742.9(17) A^3
Z, Calculated density	2, 1.338 Mg/m^3
Absorption coefficient	0.087 mm^-1
F(000)	312
Crystal size	0.34 x 0.25 x 0.21 mm
Theta range for data collection	2.56 to 25.49 deg.
Limiting indices	-19<=h<=19, -8<=k<=8, -7<=l<=5
Reflections collected / unique	3442 / 1369 [R(int) = 0.0512]
Completeness to theta = 25.49	99.5 %
Absorption correction	None
Max. and min. transmission	0.9821 and 0.9712
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1369 / 0 / 112
Goodness-of-fit on F^2	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0663, wR2 = 0.1535
R indices (all data)	R1 = 0.1626, wR2 = 0.1912
Largest diff. peak and hole	0.124 and -0.167 e.A^-3

Table S6. Crystal data and structure refinement for 27.

Empirical formula	C29 H23 N O2
Formula weight	417.48
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 12.397(5) A alpha = 90 deg.
	b = 13.109(5) A beta = 93.129(5) deg.
	c = 13.546(5) A gamma = 90 deg.
Volume	2198.2(14) A^3
Z, Calculated density	4, 1.261 Mg/m^3
Absorption coefficient	0.079 mm^-1
F(000)	880
Crystal size	0.49 x 0.33 x 0.30 mm
Theta range for data collection	2.67 to 25.50 deg.
Limiting indices	-14<=h<=15, -15<=k<=15, -13<=l<=16
Reflections collected / unique	11771 / 4014 [R(int) = 0.0292]
Completeness to theta = 25.50	98.3 %
Absorption correction	None
Max. and min. transmission	0.9768 and 0.9625
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4014 / 0 / 291
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0494, wR2 = 0.1221
R indices (all data)	R1 = 0.0860, wR2 = 0.1421
Largest diff. peak and hole	0.308 and -0.167 e.A^-3