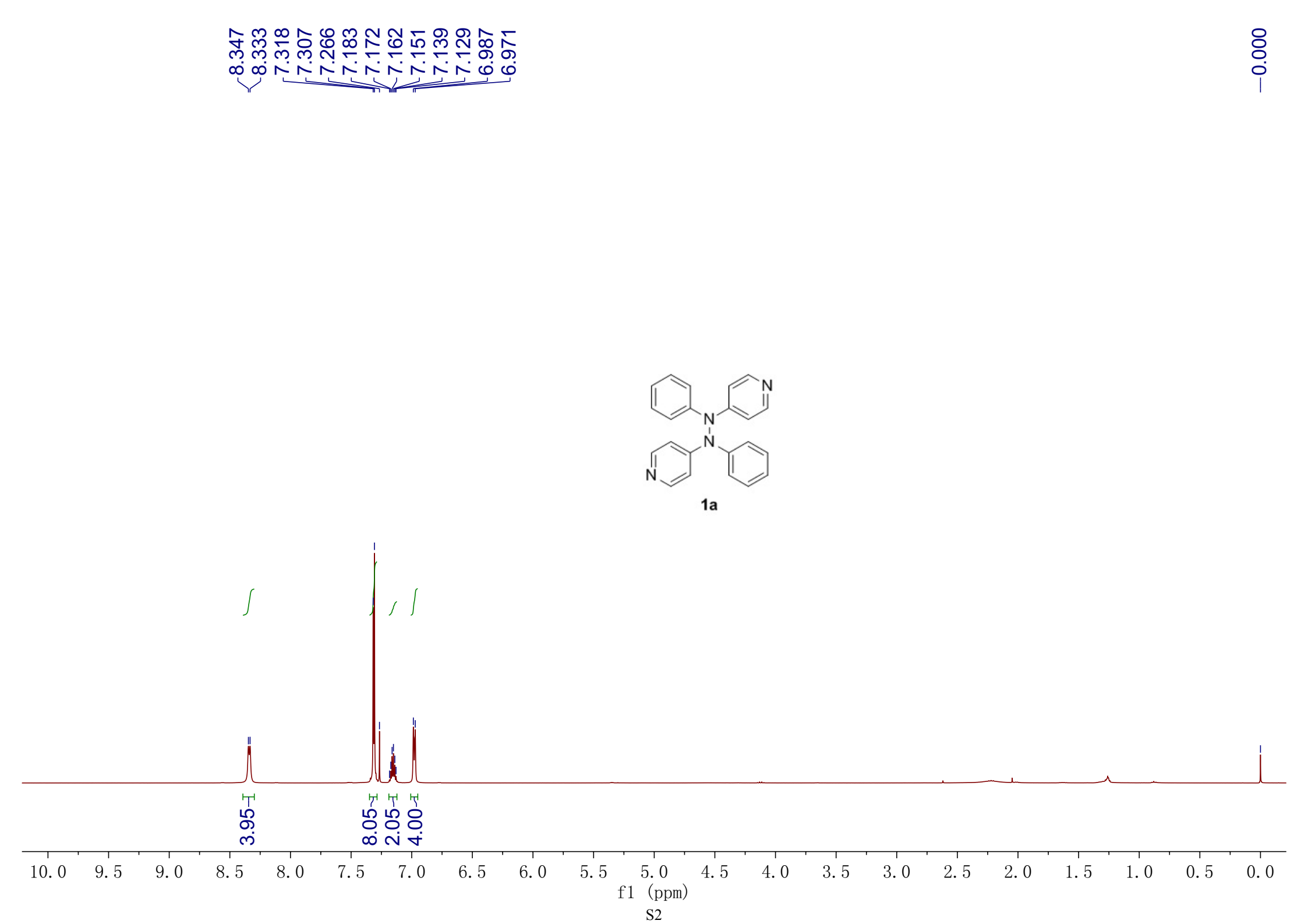
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Iodine-Mediated Oxidative N−N Coupling of Secondary Amines to Hydrazines

Linning Ren, Manman Wang, Benyao Fang, Wenquan Yu,* and Junbiao Chang*

College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou, Henan Province 450001, China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N
N
N
1a
3.95
8.05
2.05
4.00
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9.5
9.0
8.5
8.0
7.5
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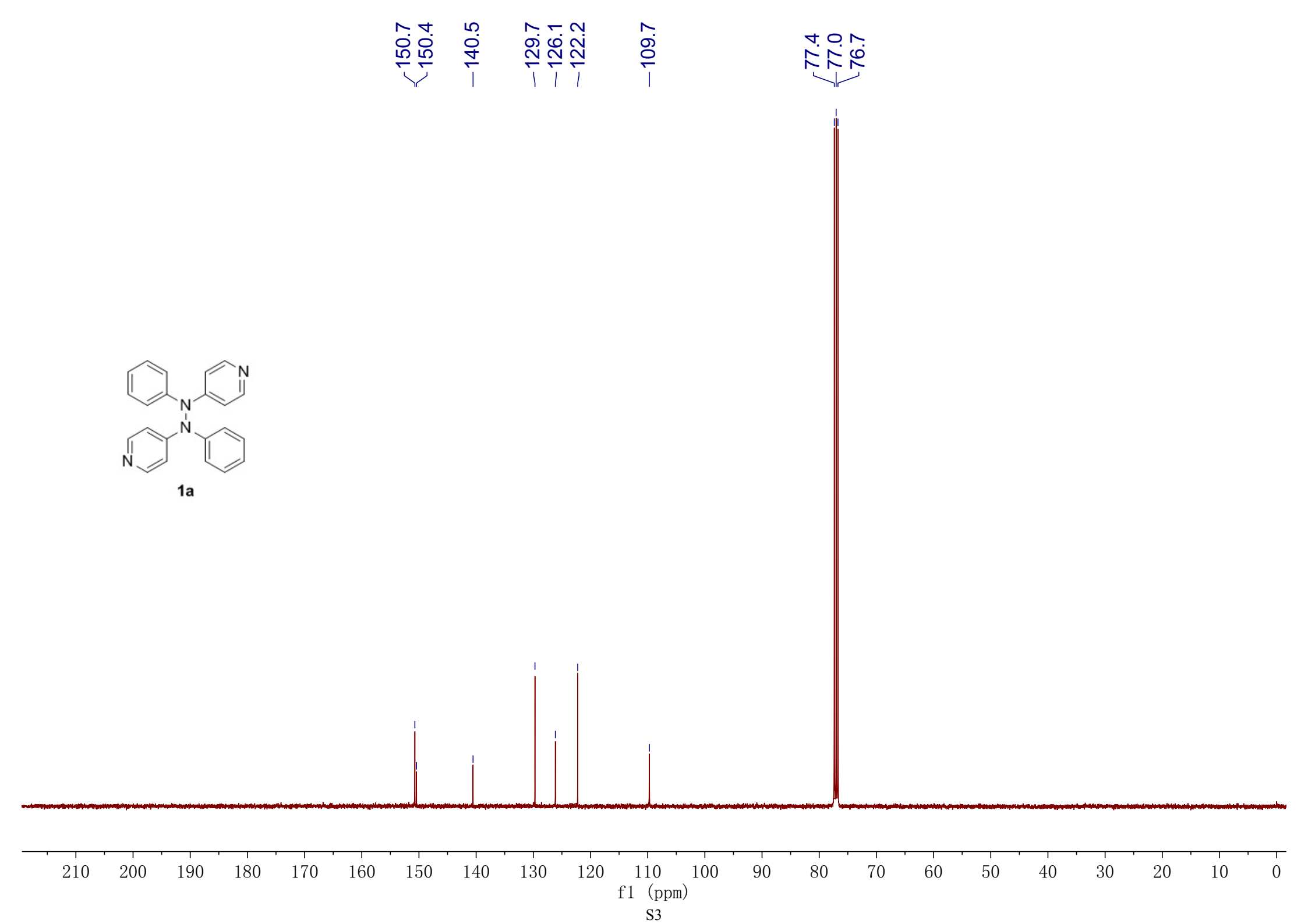
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109.7
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N
N
N
1a
210
200
190
180
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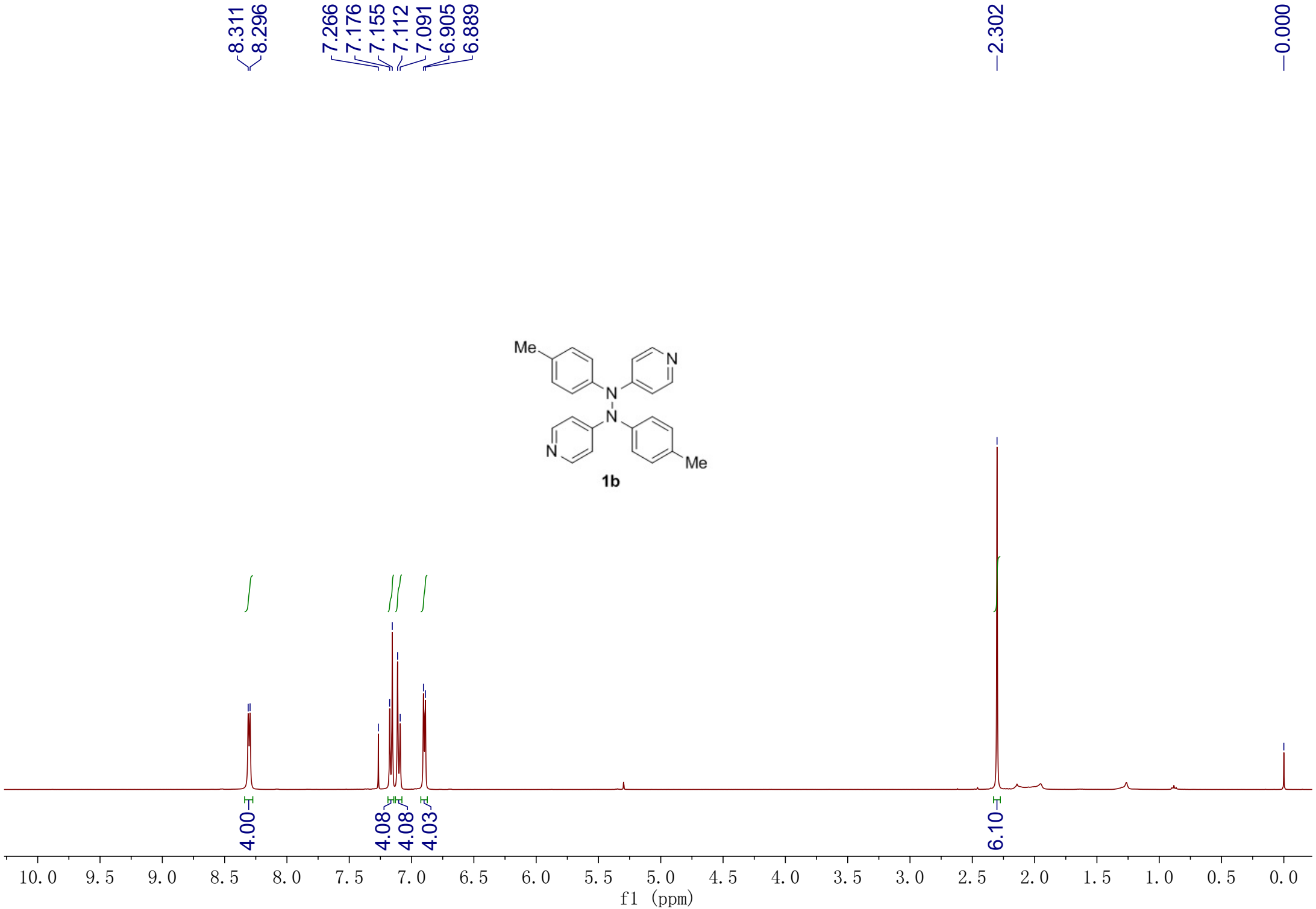
f1 (ppm)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N
Me
1b
4.00
4.08
4.08
4.03
6.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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1.0
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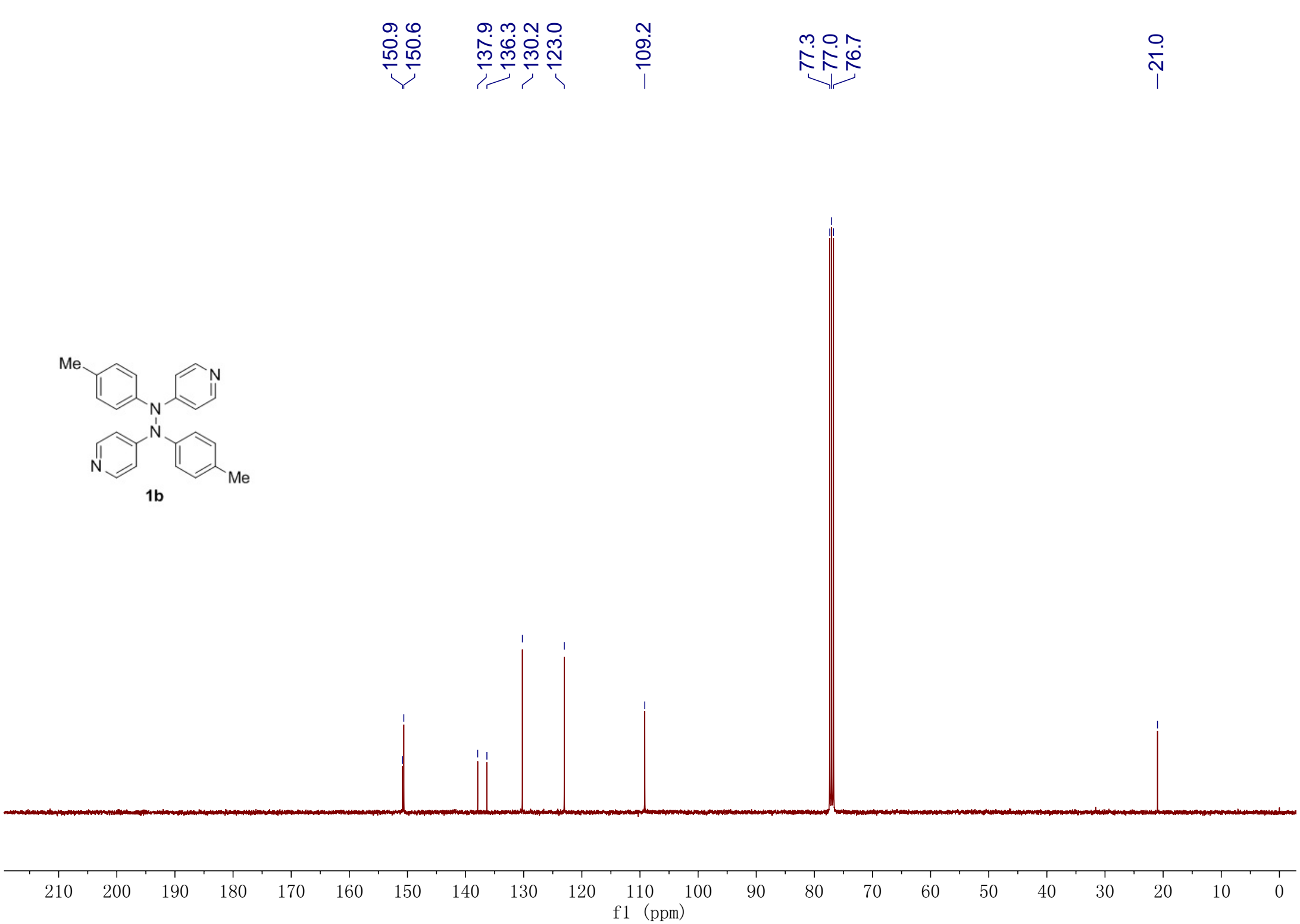
0.0
f1 (ppm)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77.3
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76.7
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N
N
Me
1b
210
200
190
180
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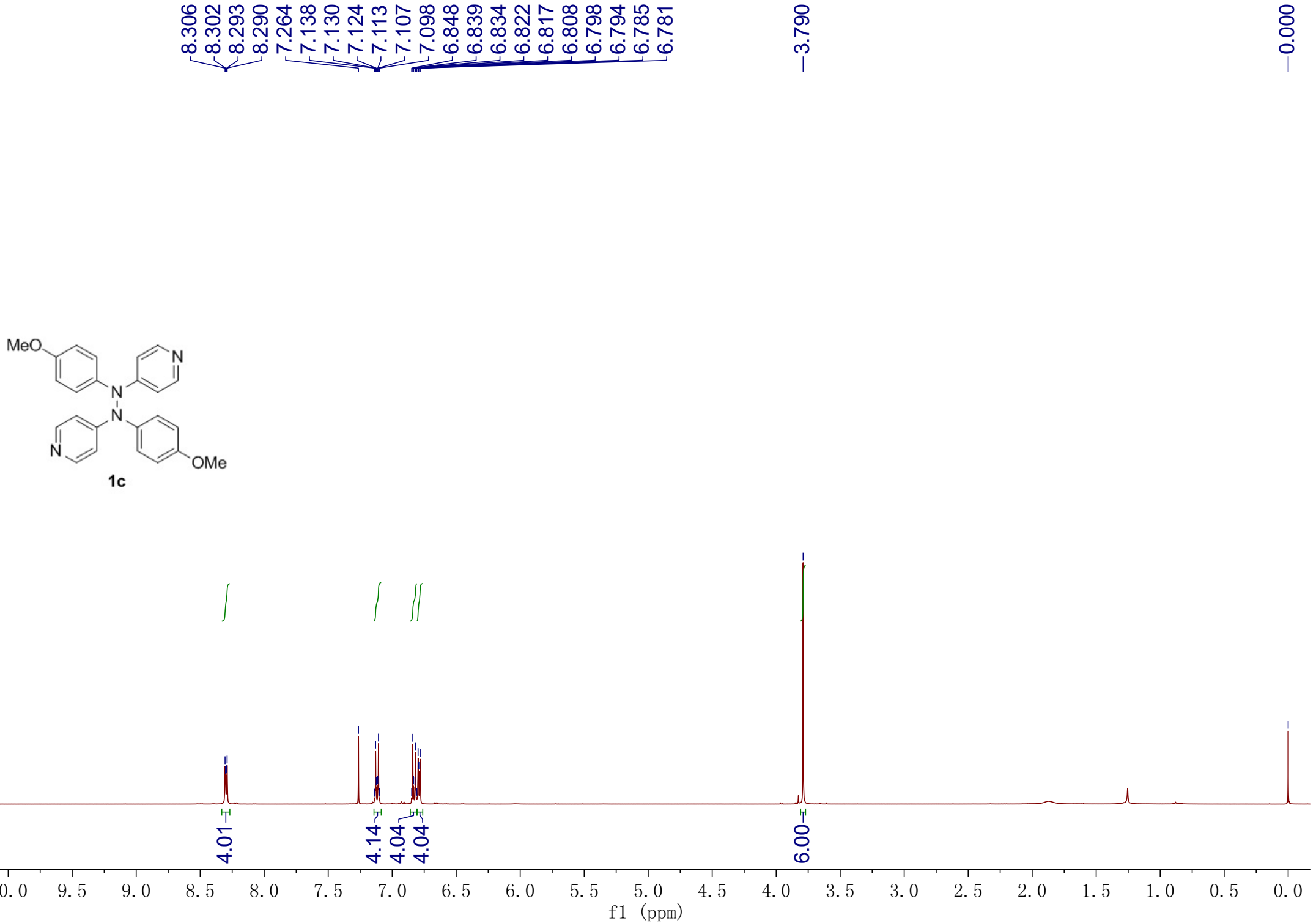
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7.107
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6.808
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6.794
6.785
6.781
3.790
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MeO
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N
N
OMe
1c
4.01
4.14
4.04
4.04
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.0
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1.0
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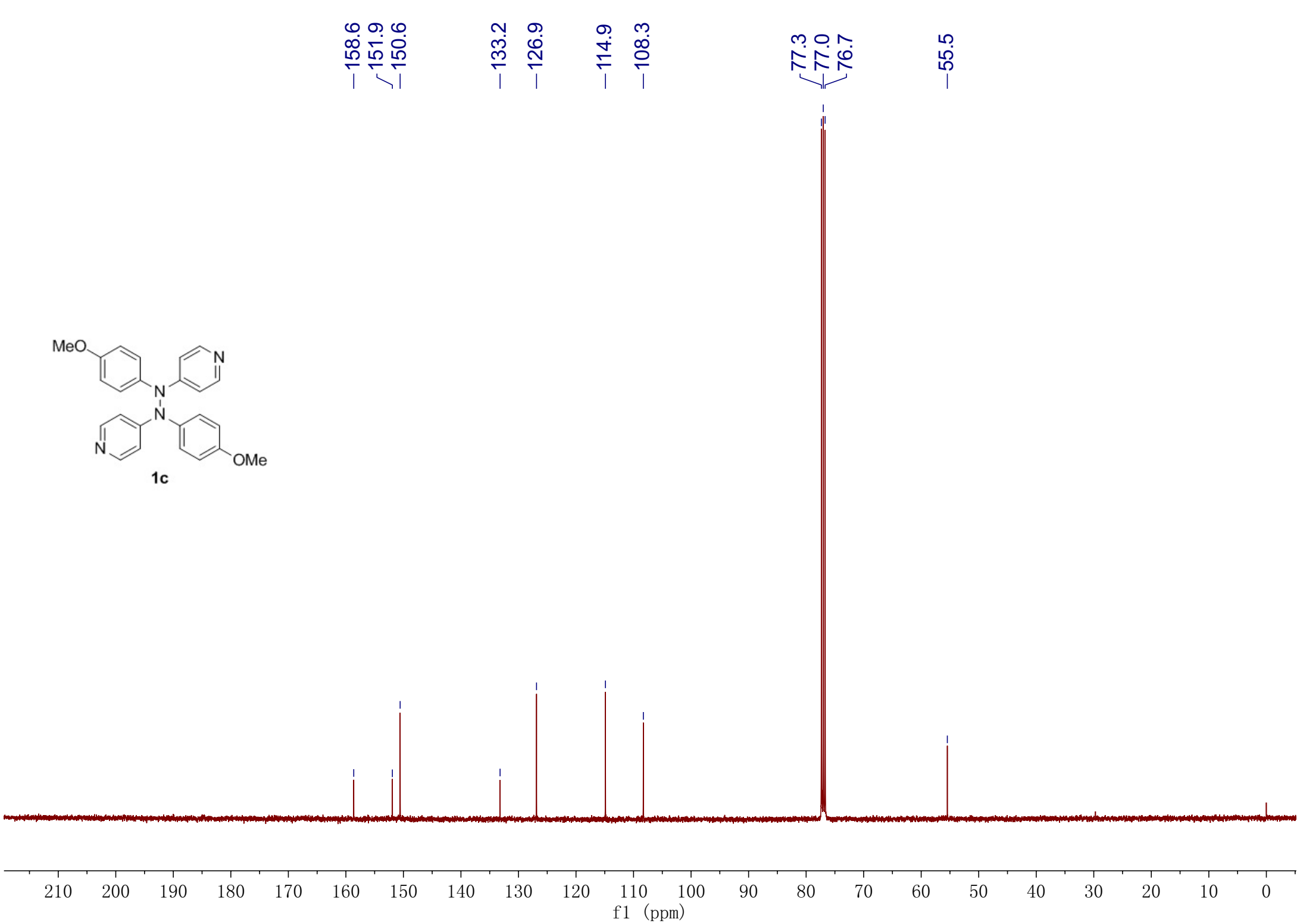
f1 (ppm)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76.7
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N
N
N
OMe
1c
210
200
190
180
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130
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90
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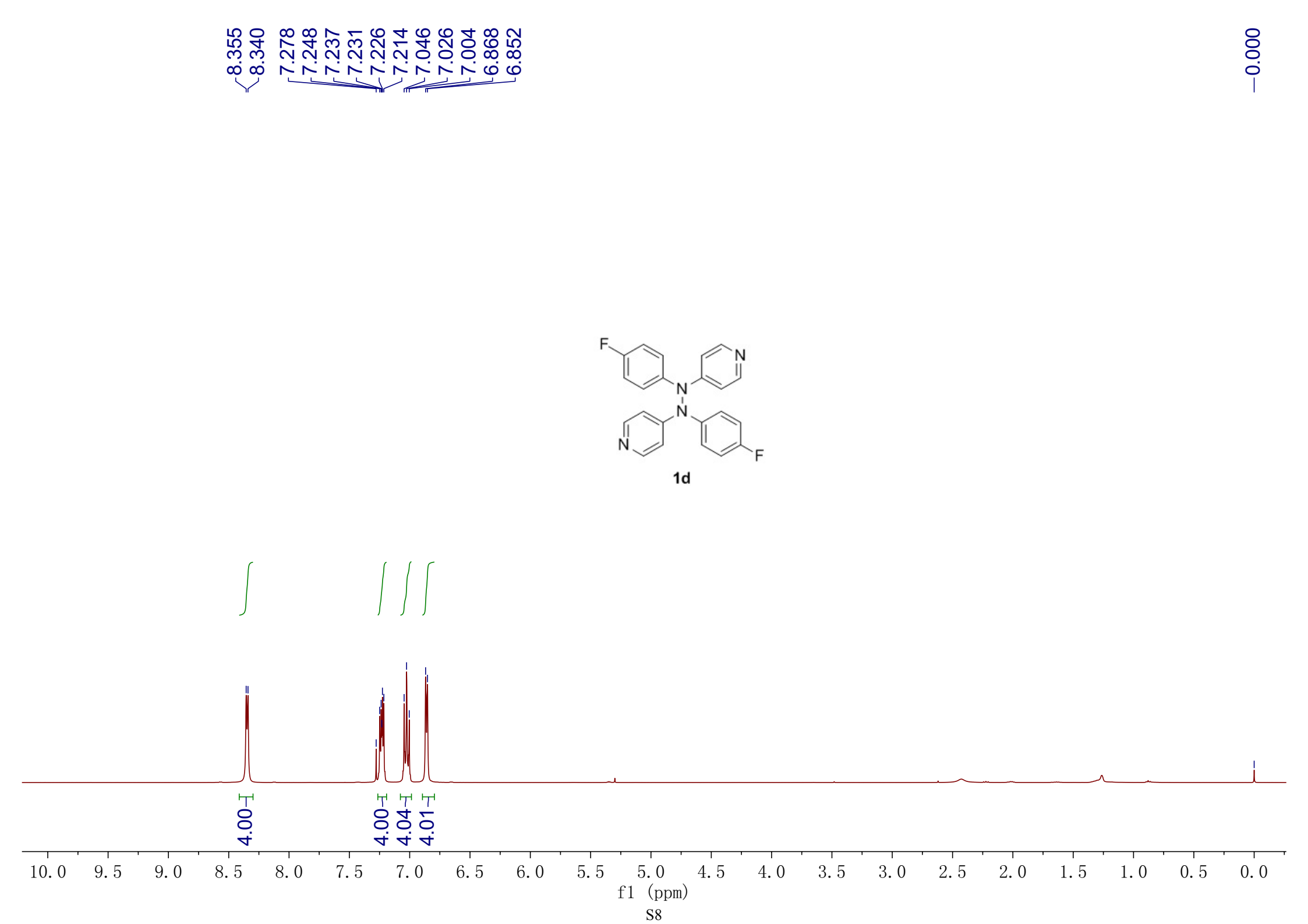
f1 (ppm)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6.852
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N
N
F
1d
4.00
4.00
4.04
4.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
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1.0
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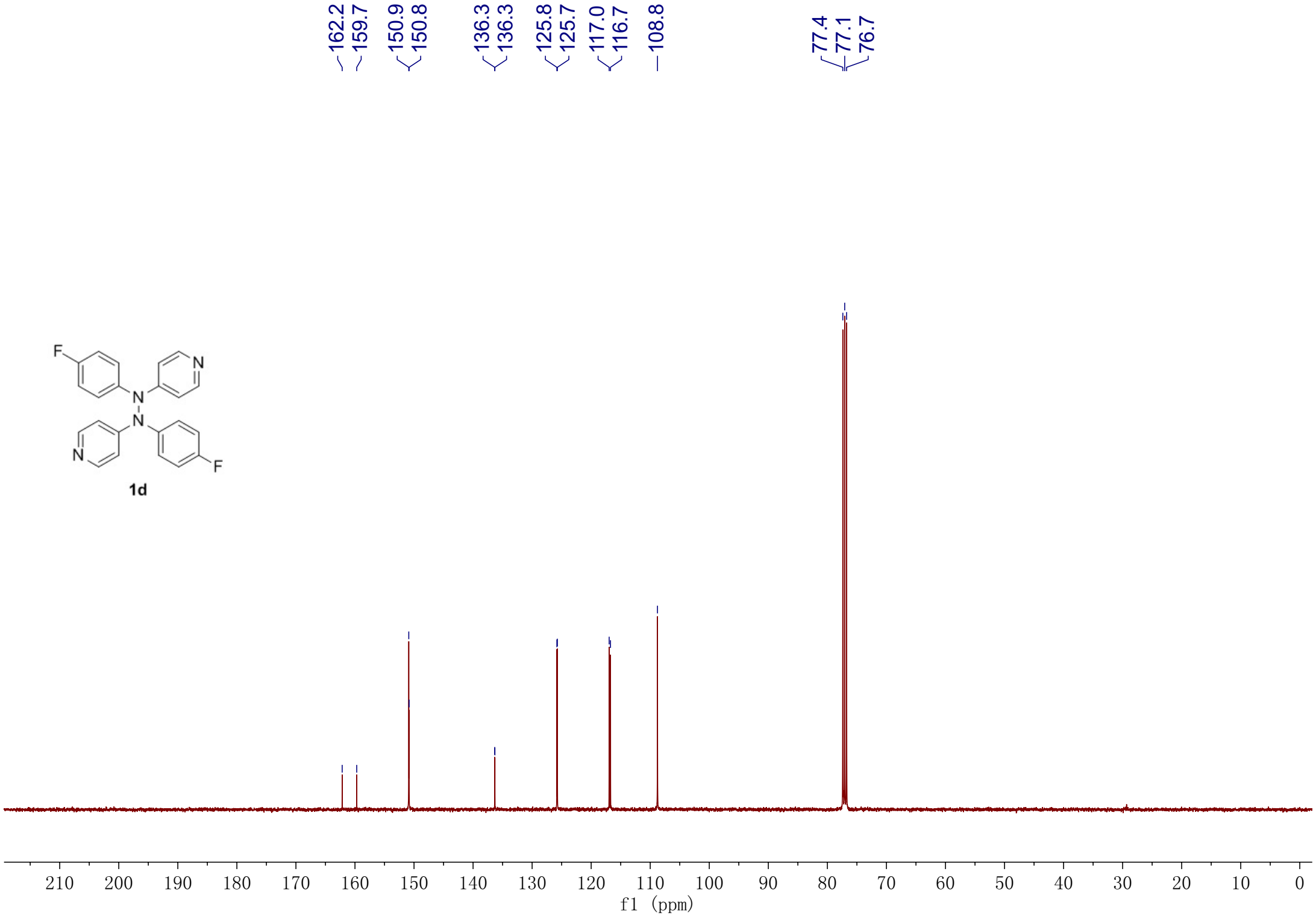
f1 (ppm)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136.3
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125.7
117.0
116.7
108.8
77.4
77.1
76.7
F
N
N
N
F
1d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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50
40
30
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10
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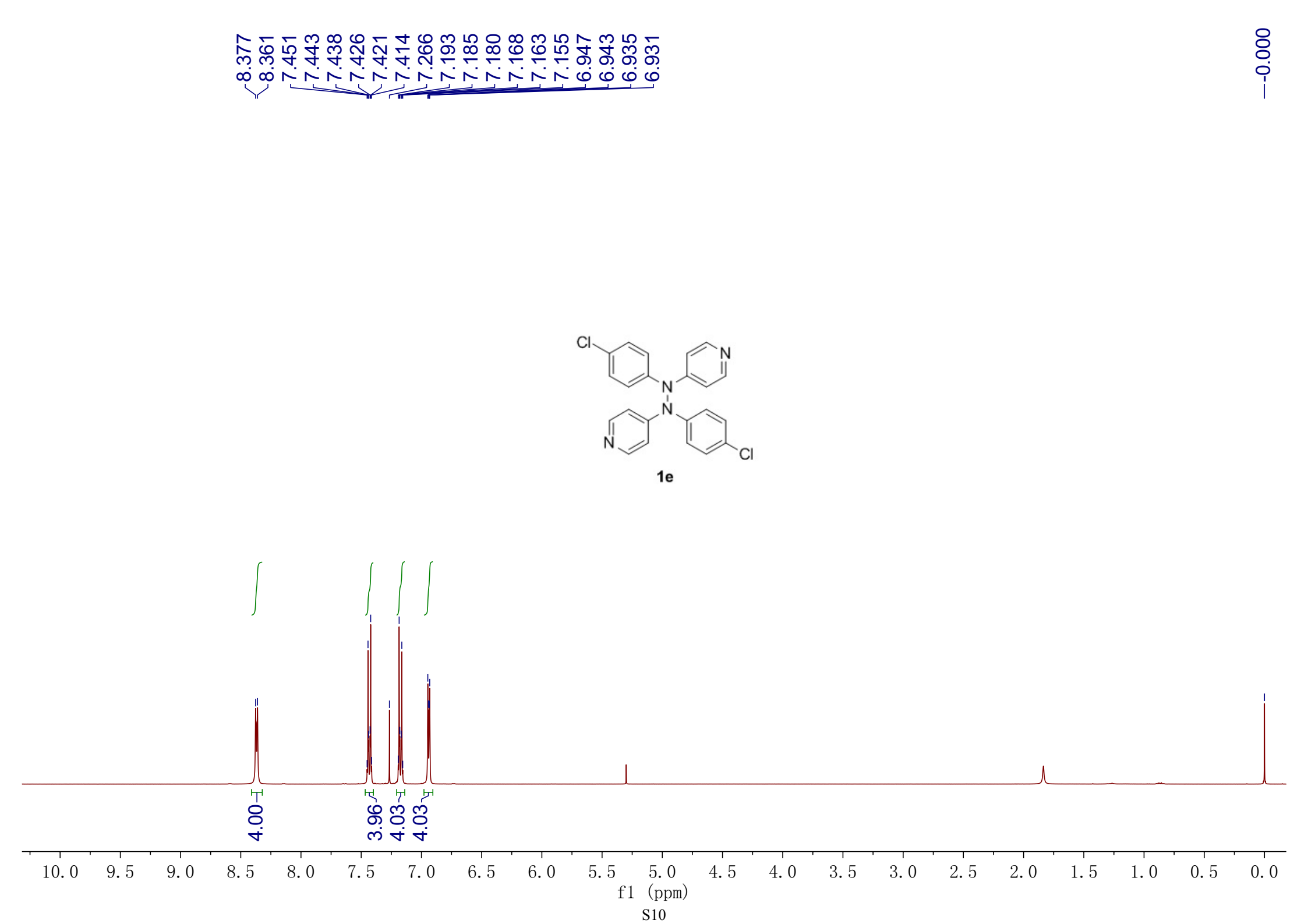
f1 (ppm)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7.421
7.414
7.266
7.193
7.185
7.180
7.168
7.163
7.155
6.947
6.943
6.935
6.931
-0.000
Cl
N
N
N
Cl
1e
4.00
3.96
4.03
4.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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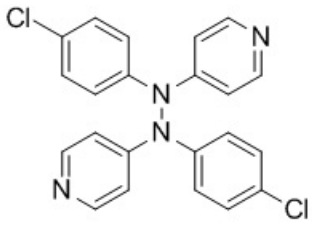
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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N
N
Cl

1e

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149.6
139.5
132.9
123.3
118.9
109.8
77.3
77.0
76.7
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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50
40
30
20
10
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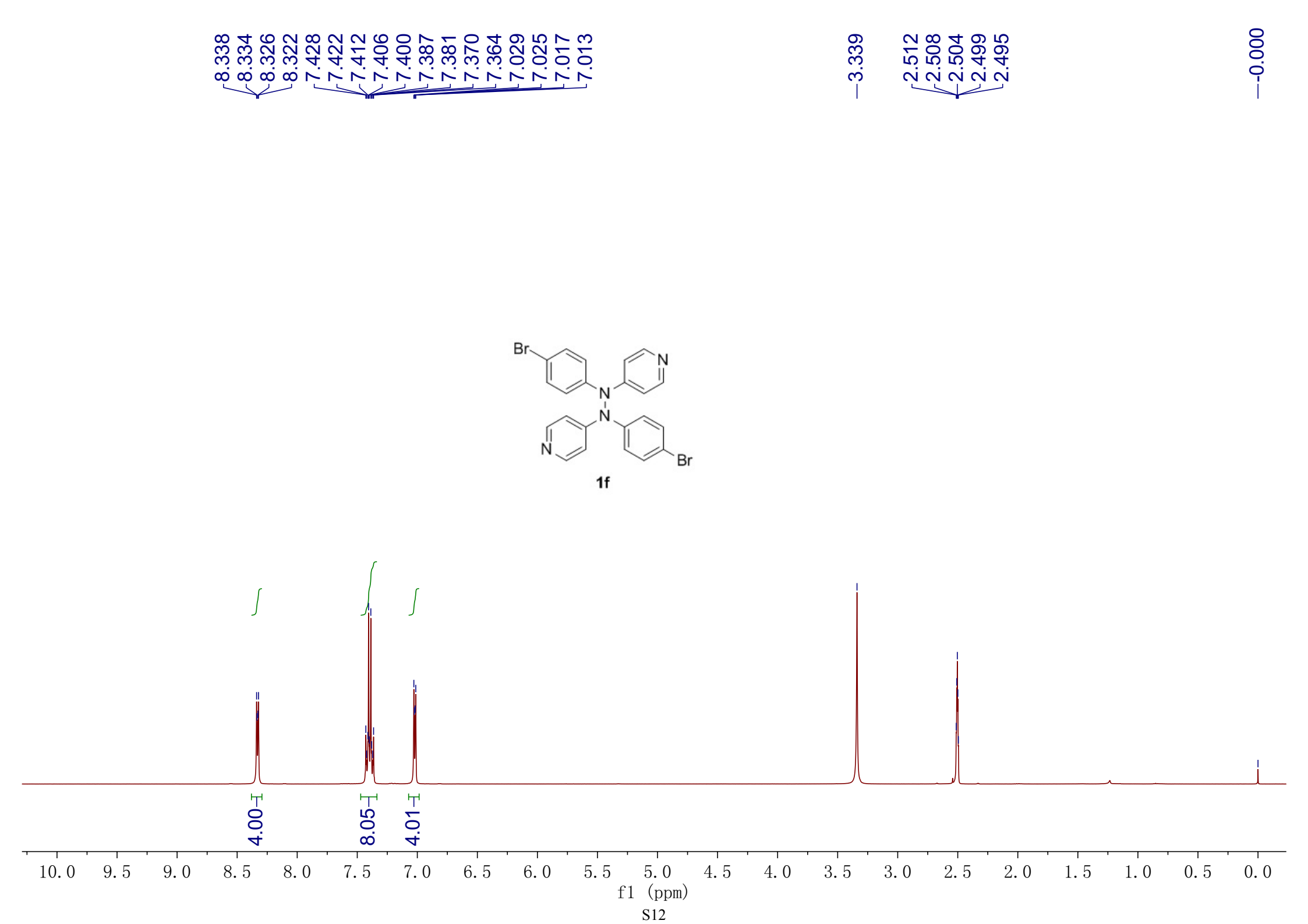
f1 (ppm)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7.406
7.400
7.387
7.381
7.370
7.364
7.029
7.025
7.017
7.013
3.339
2.512
2.508
2.504
2.499
2.495
0.000
Br
N
N
N
Br
1f
4.00
8.05
4.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.0
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1.0
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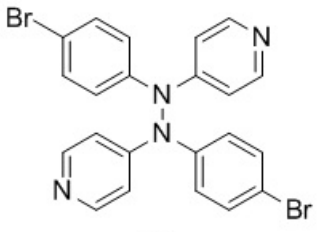
0.0
f1 (ppm)


Br
N
N
N
Br

1f

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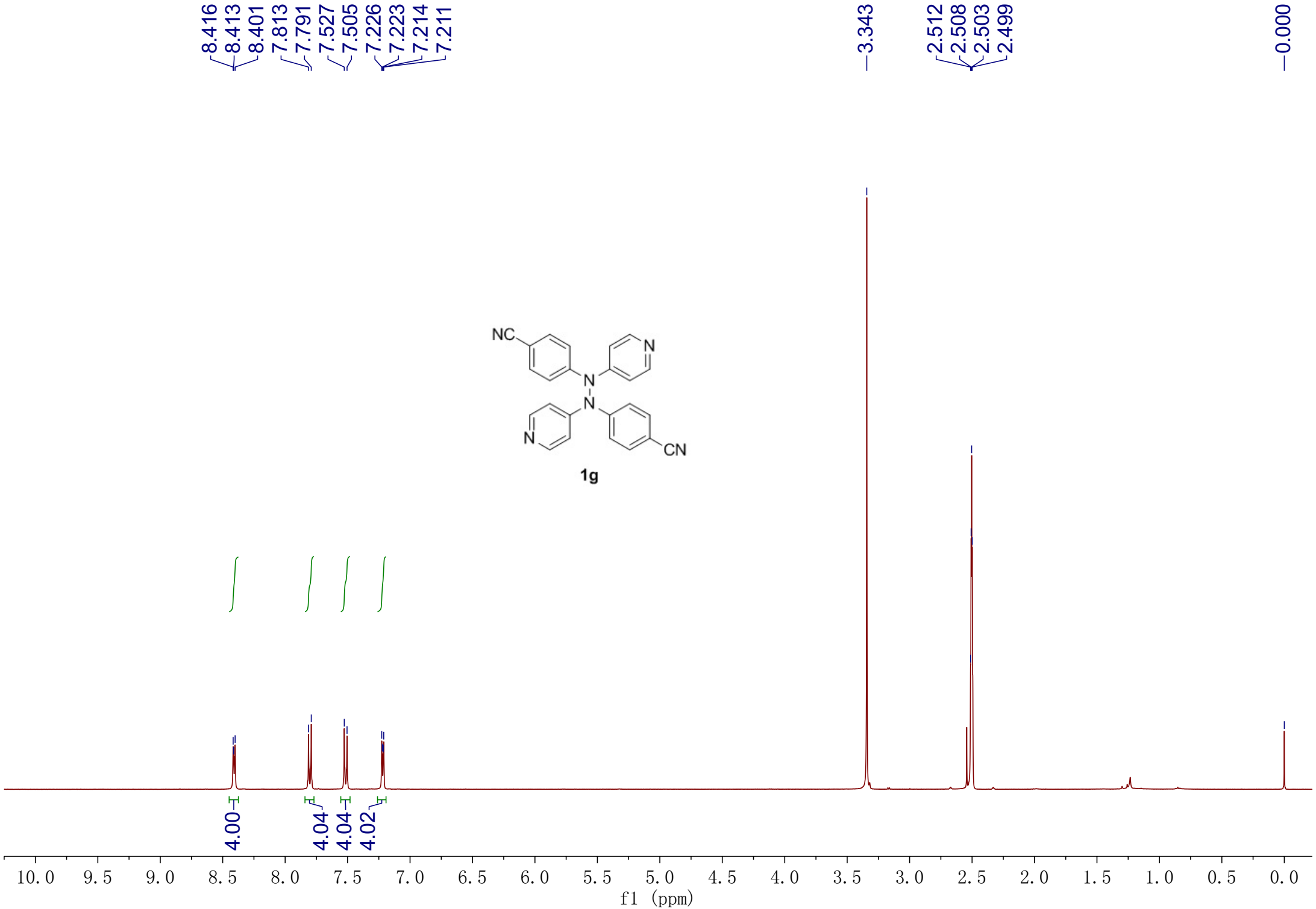
149.4
139.5
130.2
129.6
123.3
110.6
40.6
40.4
40.2
40.0
39.8
39.6
39.4
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.505
7.226
7.223
7.214
7.211
3.343
2.512
2.508
2.503
2.499
0.000
NC
N
N
N
CN
1g
4.00
4.04
4.04
4.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
2.0
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1.0
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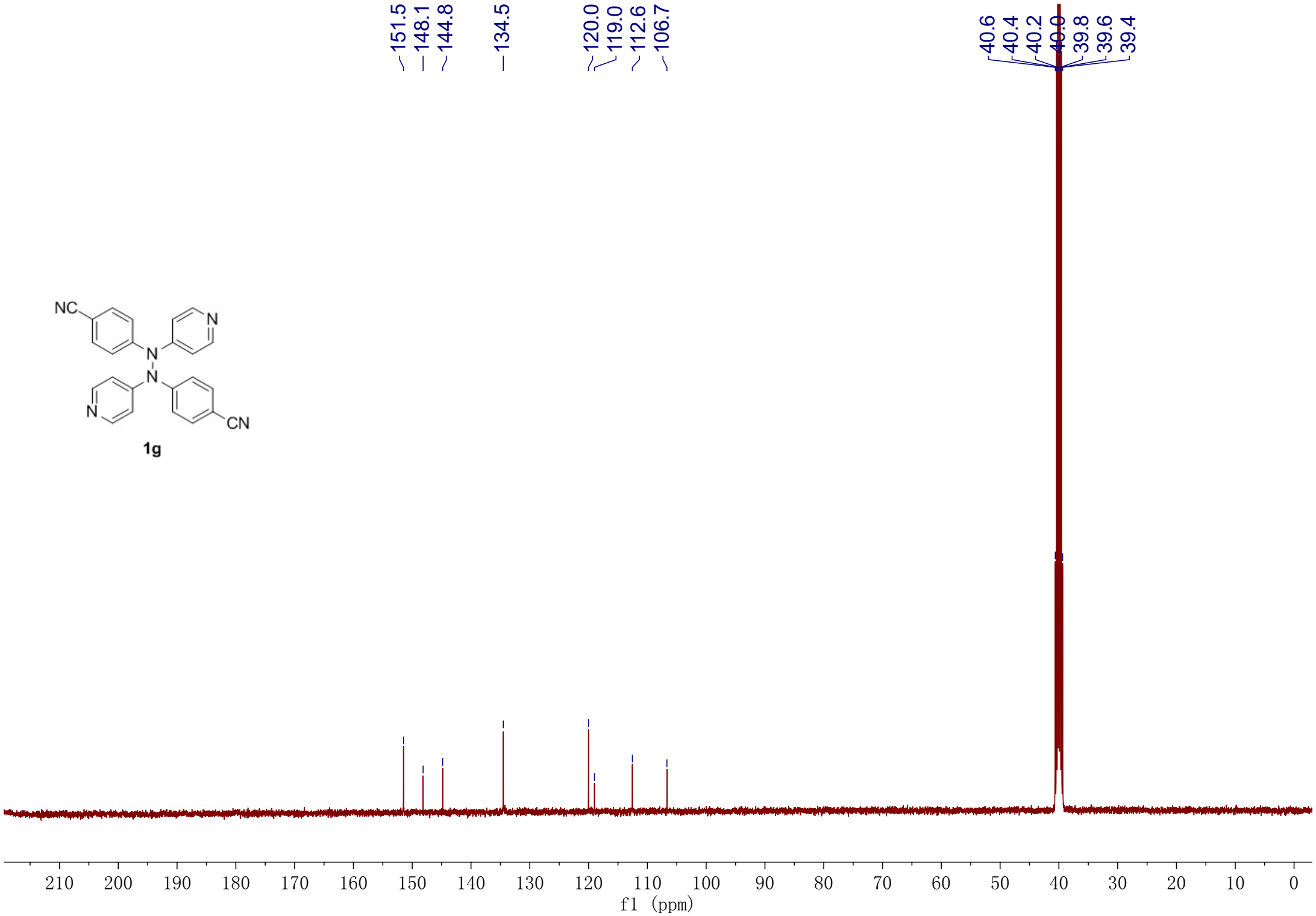
0.0
f1 (ppm)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144.8
134.5
120.0
119.0
112.6
106.7
40.6
40.4
40.2
40.0
39.8
39.6
39.4
NC
N
N
N
N
CN
1g
210
200
190
180
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150
140
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120
110
100
90
80
70
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50
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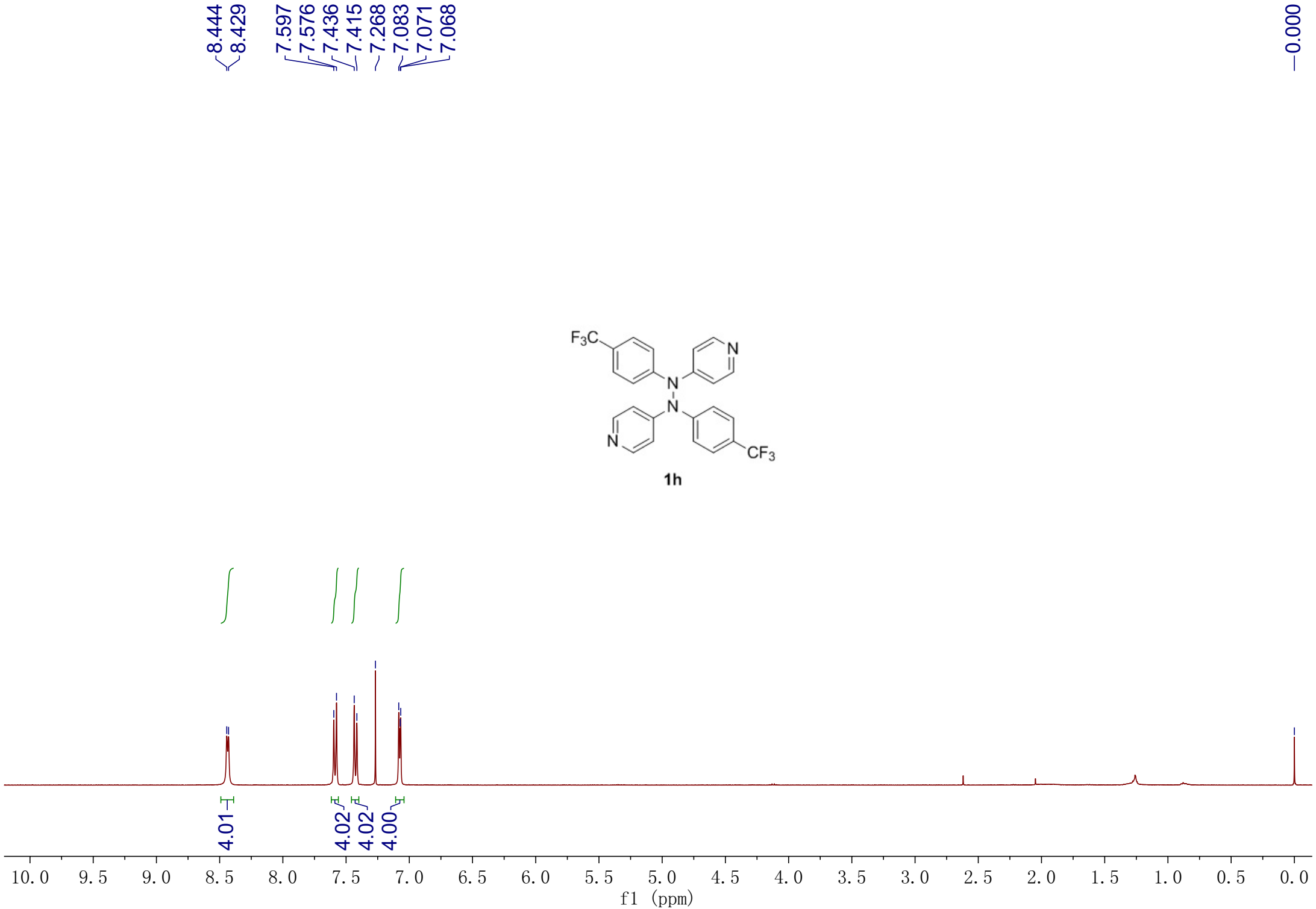
30
20
10
0
f1 (ppm)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N
N
CF3
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4.02
4.02
4.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
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6.0
5.5
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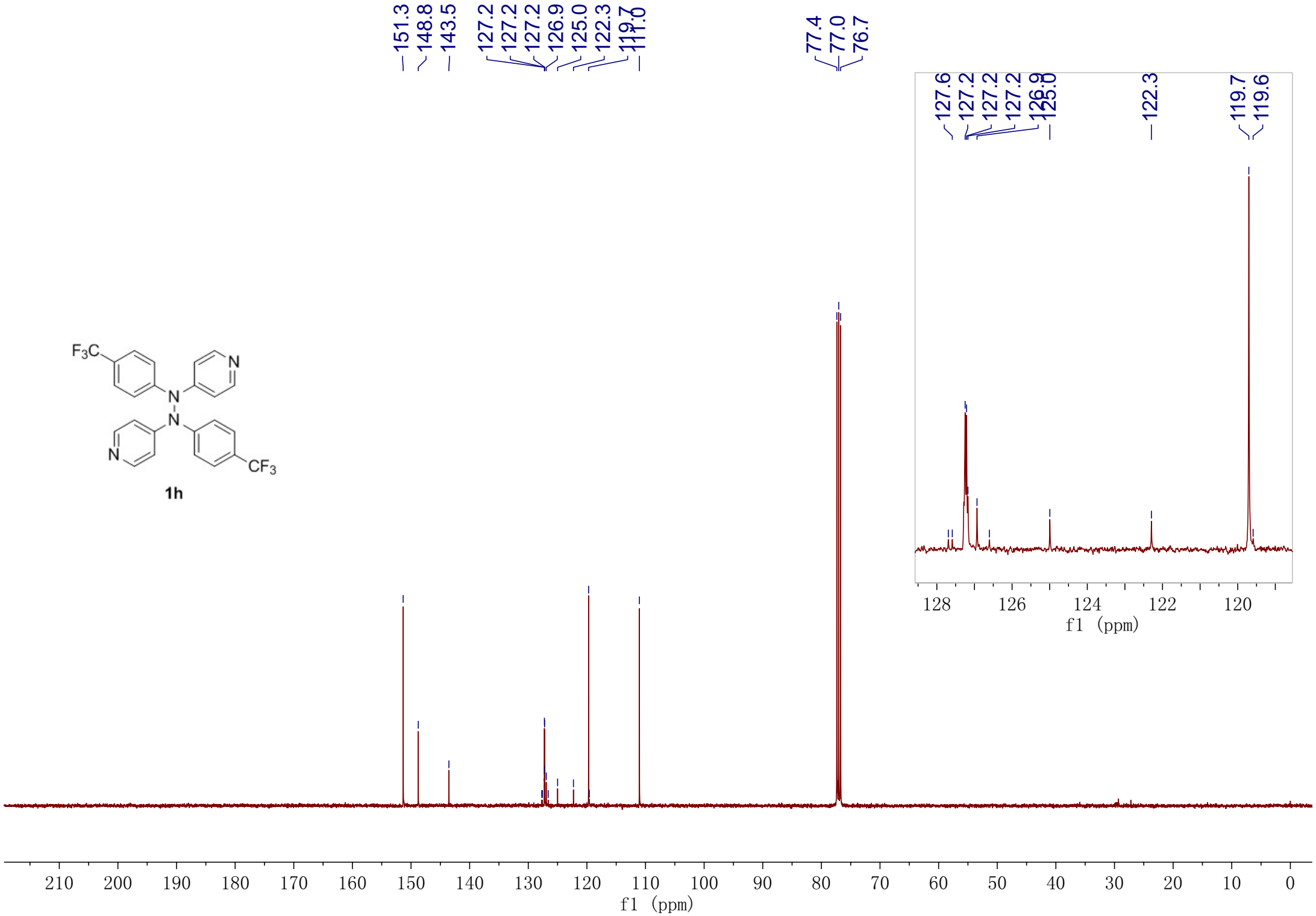
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127.2
127.2
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125.0
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111.0
77.4
77.0
76.7
127.6
127.2
127.2
127.2
126.9
125.0
122.3
119.7
119.6
128
126
124
122
120
f1 (ppm)
F3C
N
N
N
CF3
1h
210
200
190
180
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110
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90
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10
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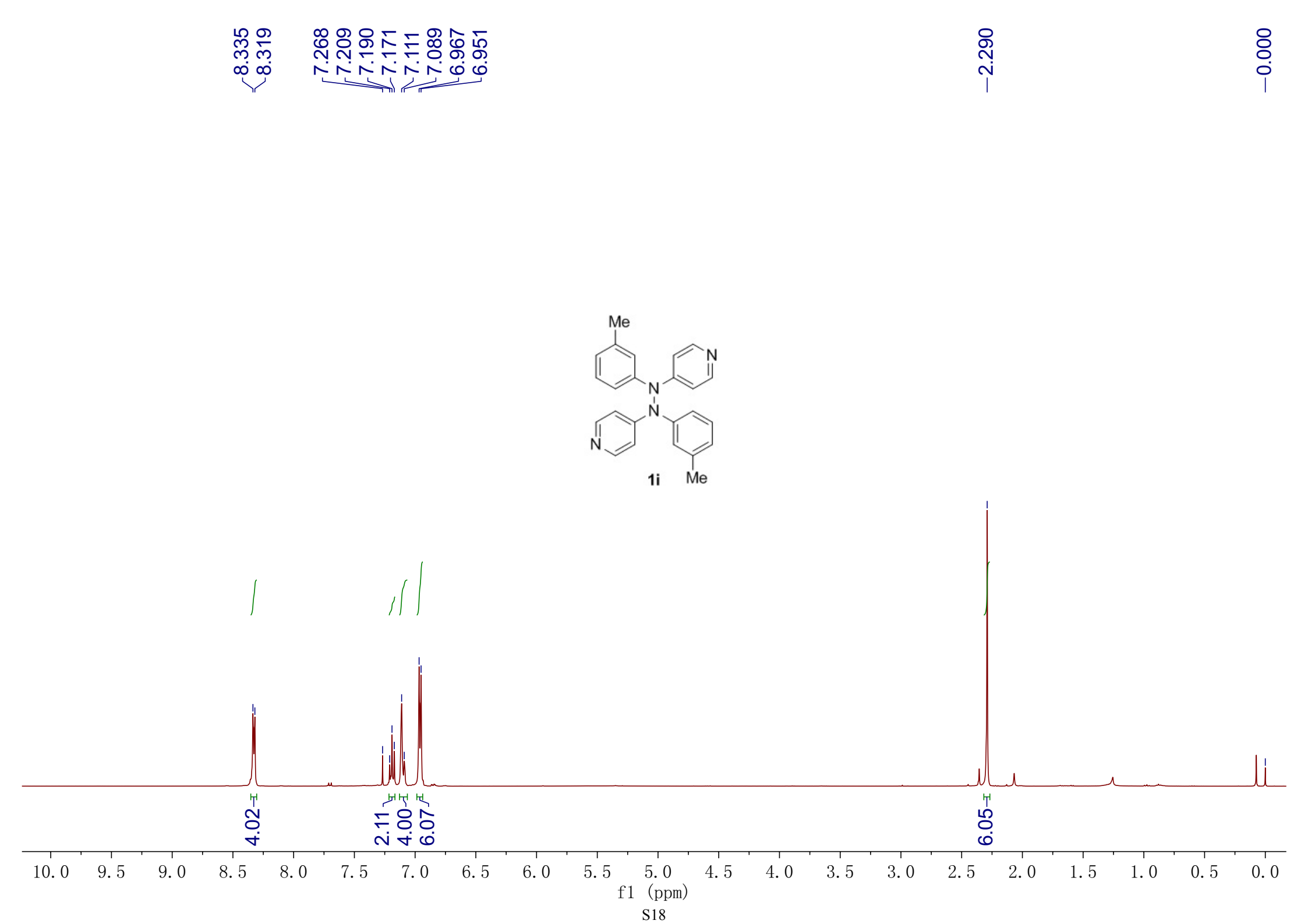
f1 (ppm)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7.089
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N
1i
Me
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2.11
4.00
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6.05
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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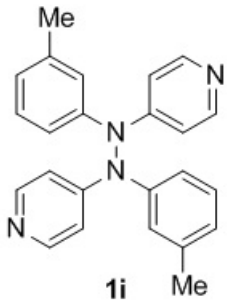
Me
N
N
N
N
Me

1i

150.6
150.5
140.5
139.7
129.4
126.9
122.7
119.3
109.8
77.4
77.1
76.7
21.5
210
200
190
180
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130
120
110
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90
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70
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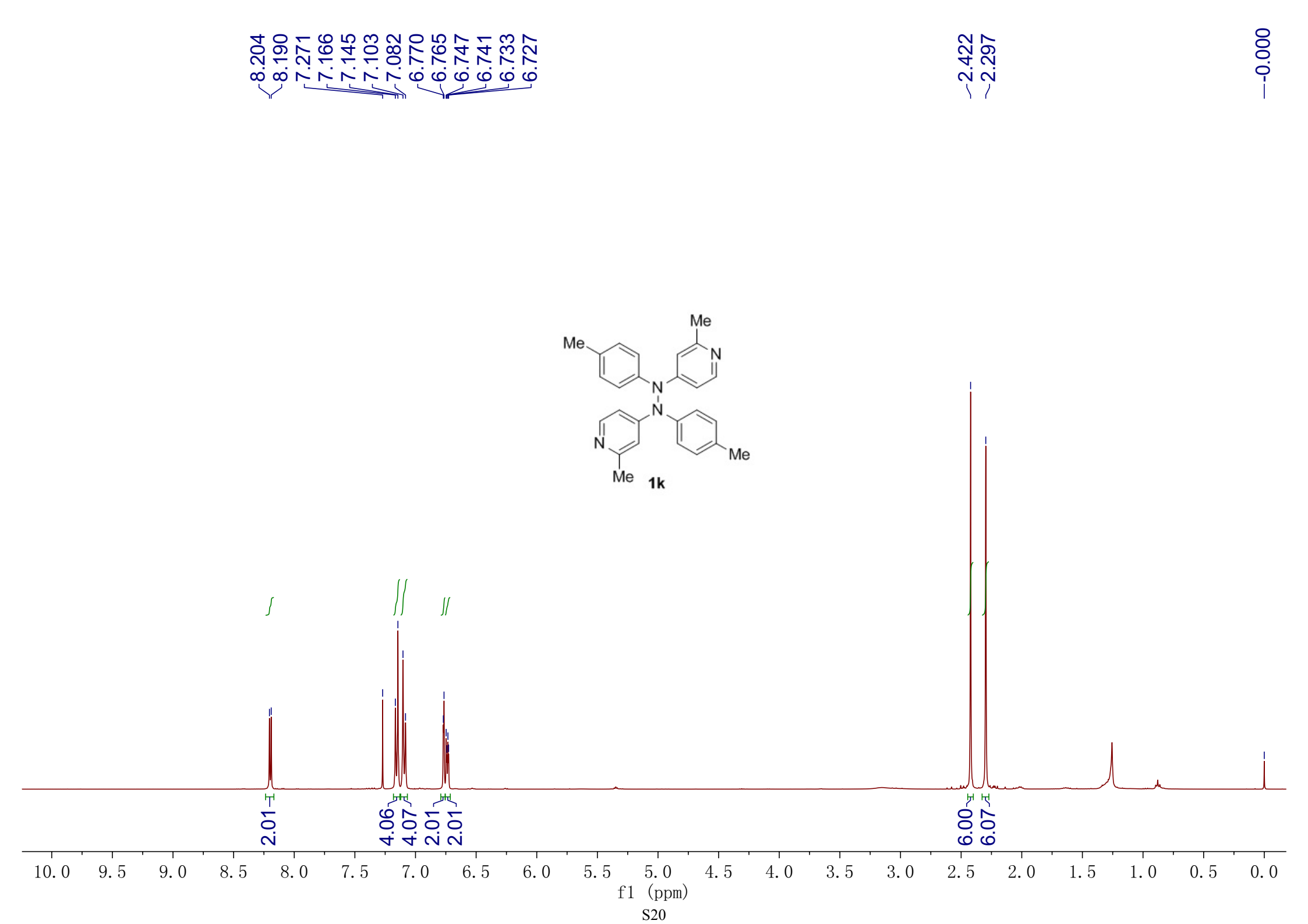
f1 (ppm)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N
Me
Me
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4.06
4.07
2.01
2.01
6.00
6.07
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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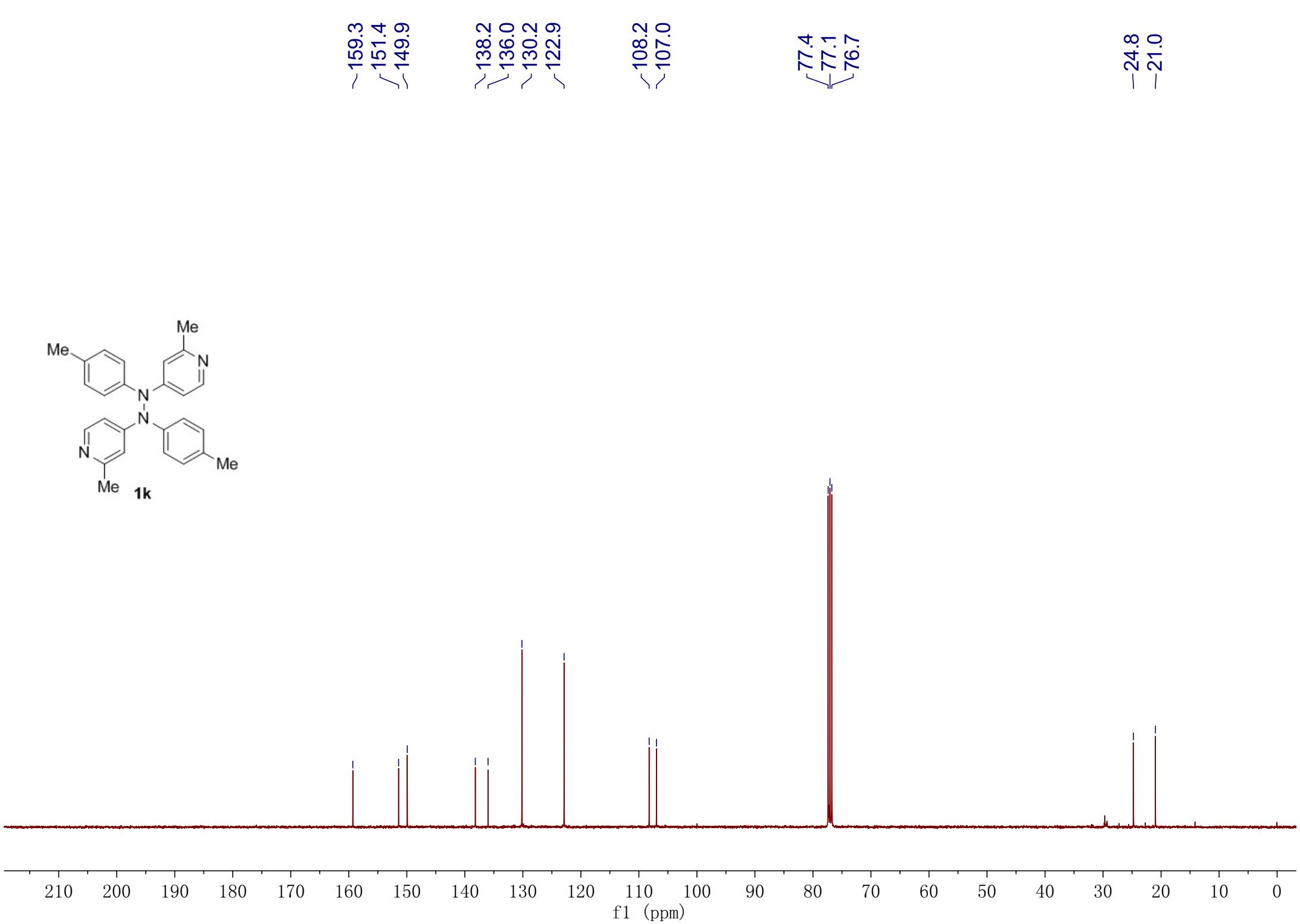
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21.0
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Me
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N
Me
Me
1k
210
200
190
180
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110
100
90
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50
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20
10
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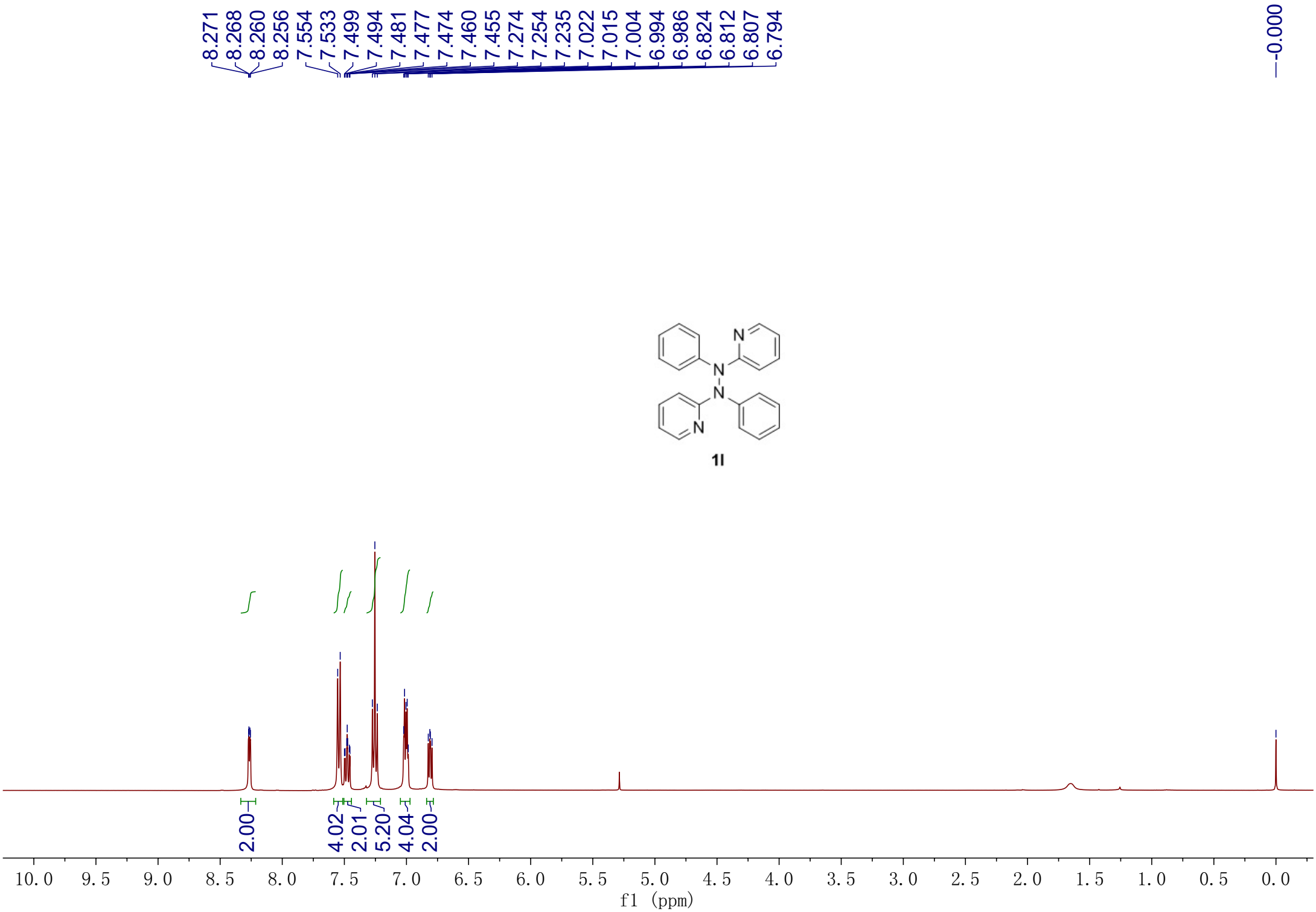
f1 (ppm)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7.274
7.254
7.235
7.022
7.015
7.004
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6.986
6.824
6.812
6.807
6.794
-0.000
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N
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4.02
2.01
5.20
4.04
2.00
10.0
9.5
9.0
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8.0
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6.5
6.0
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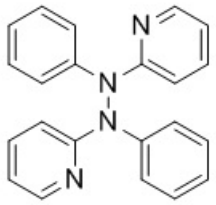

1l

156.2
147.9
141.8
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128.8
123.7
120.2
117.0
110.6
77.4
77.0
76.7
210
200
190
180
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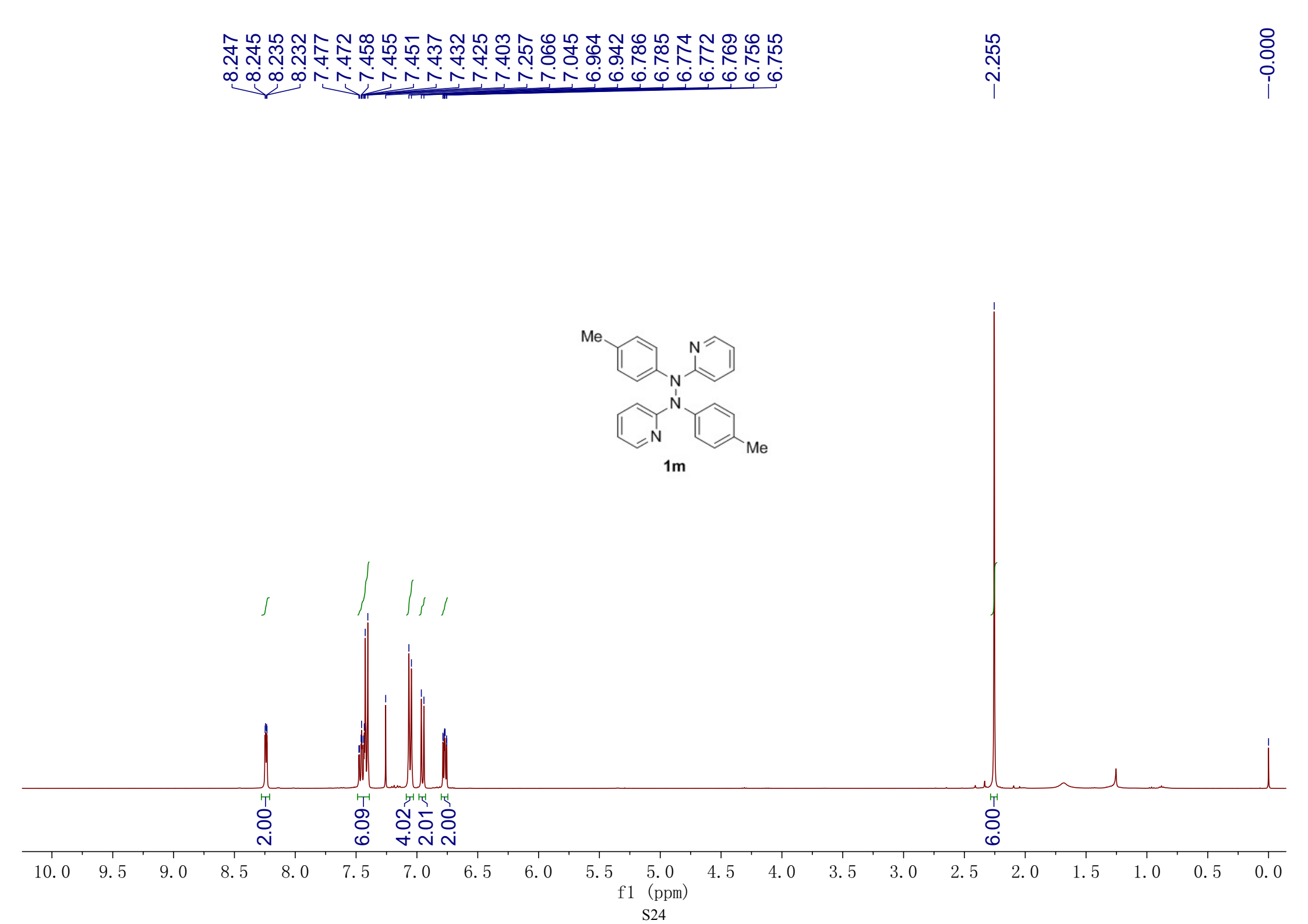
f1 (ppm)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Me
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2.00
6.00
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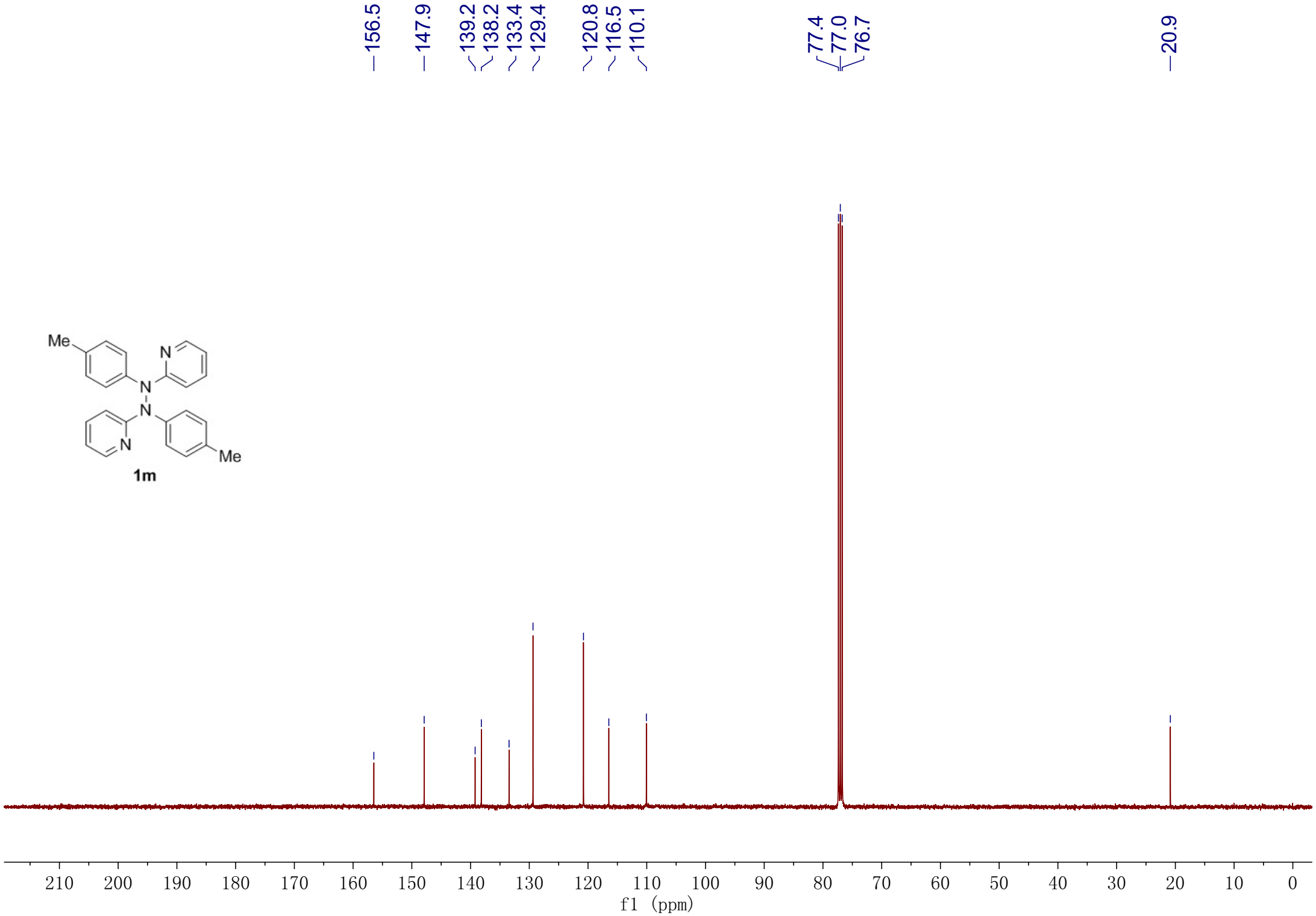
f1 (ppm)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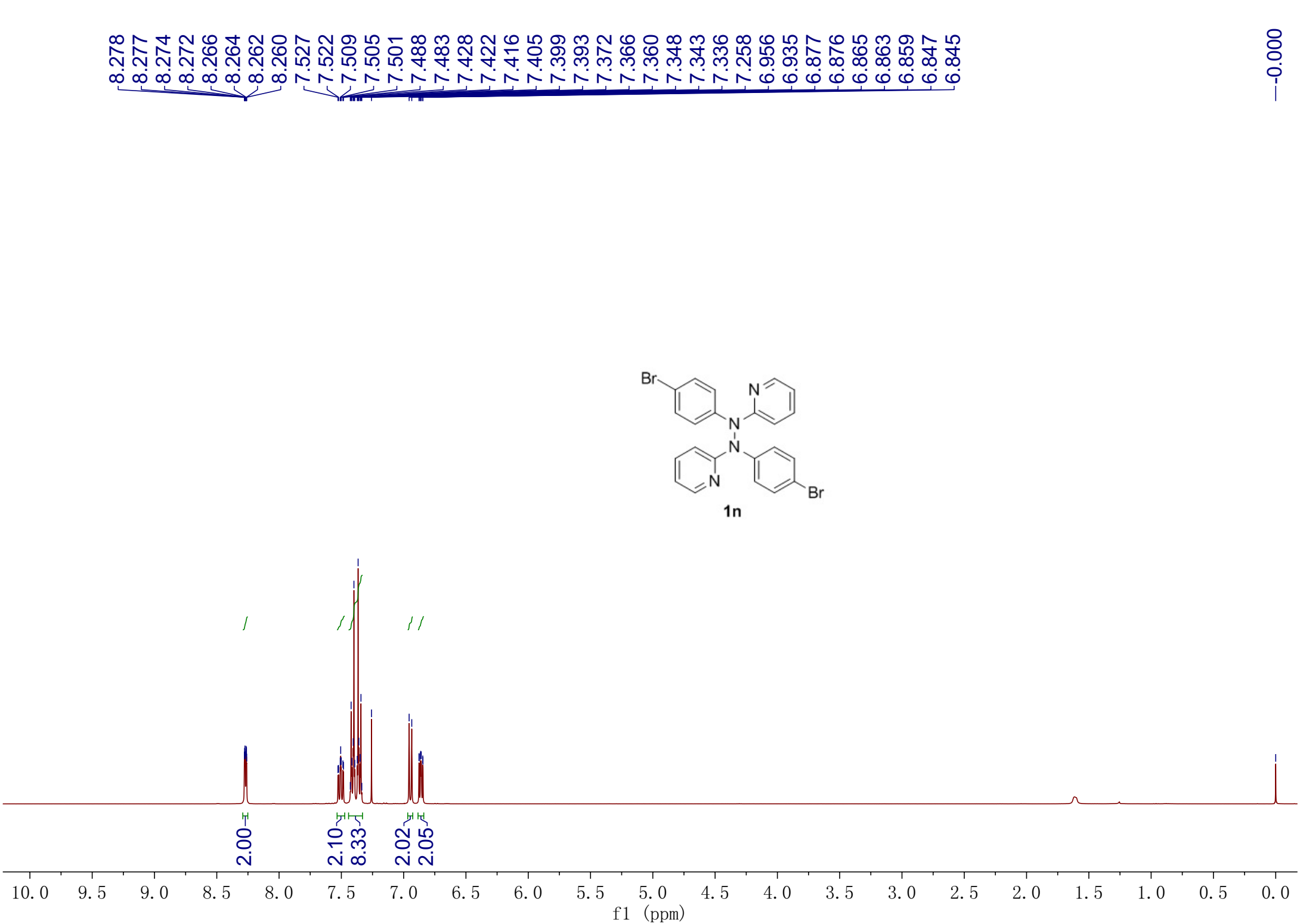
138.2
133.4
129.4
120.8
116.5
110.1
77.4
77.0
76.7
20.9
Me
N
N
N
Me
1m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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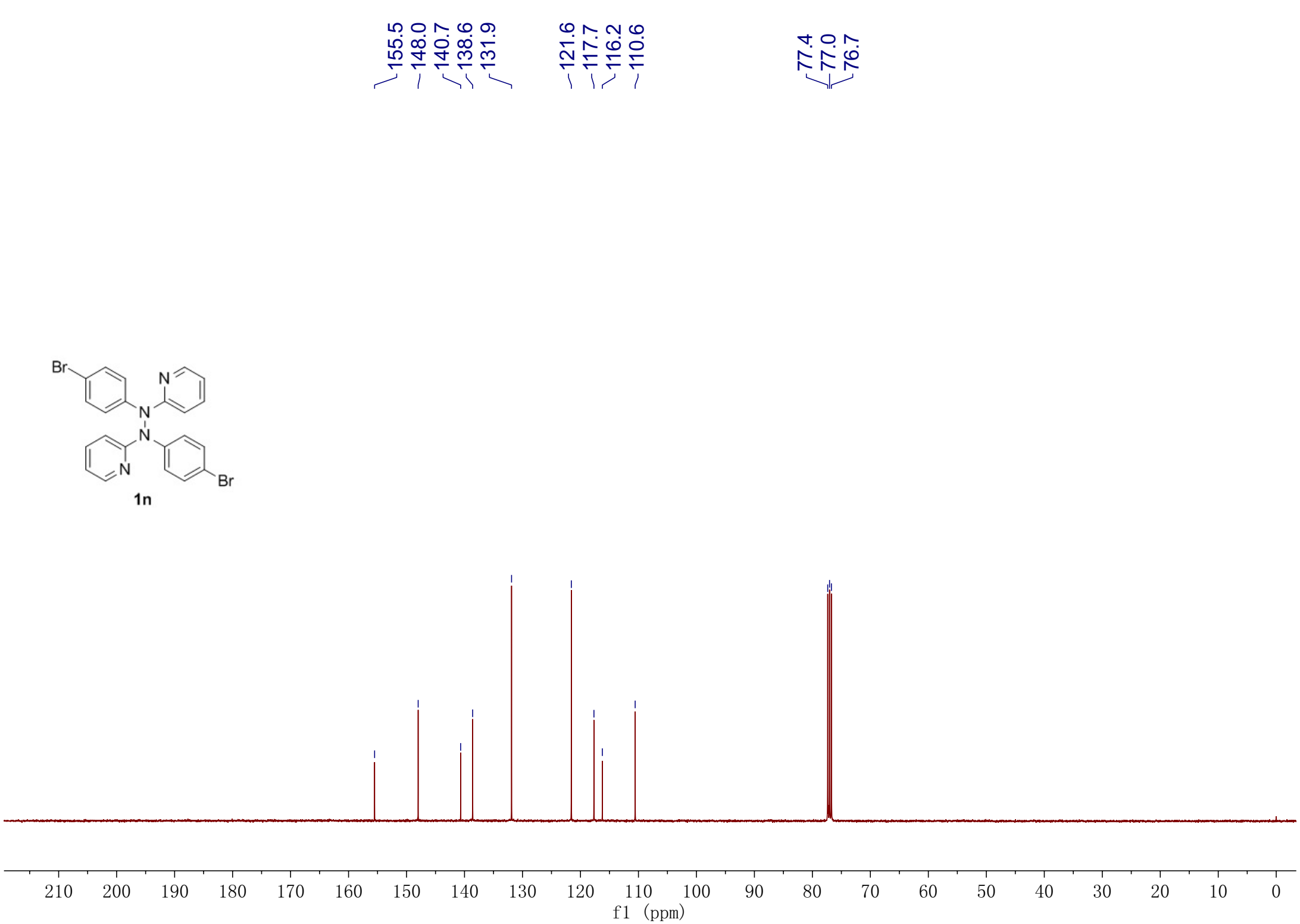
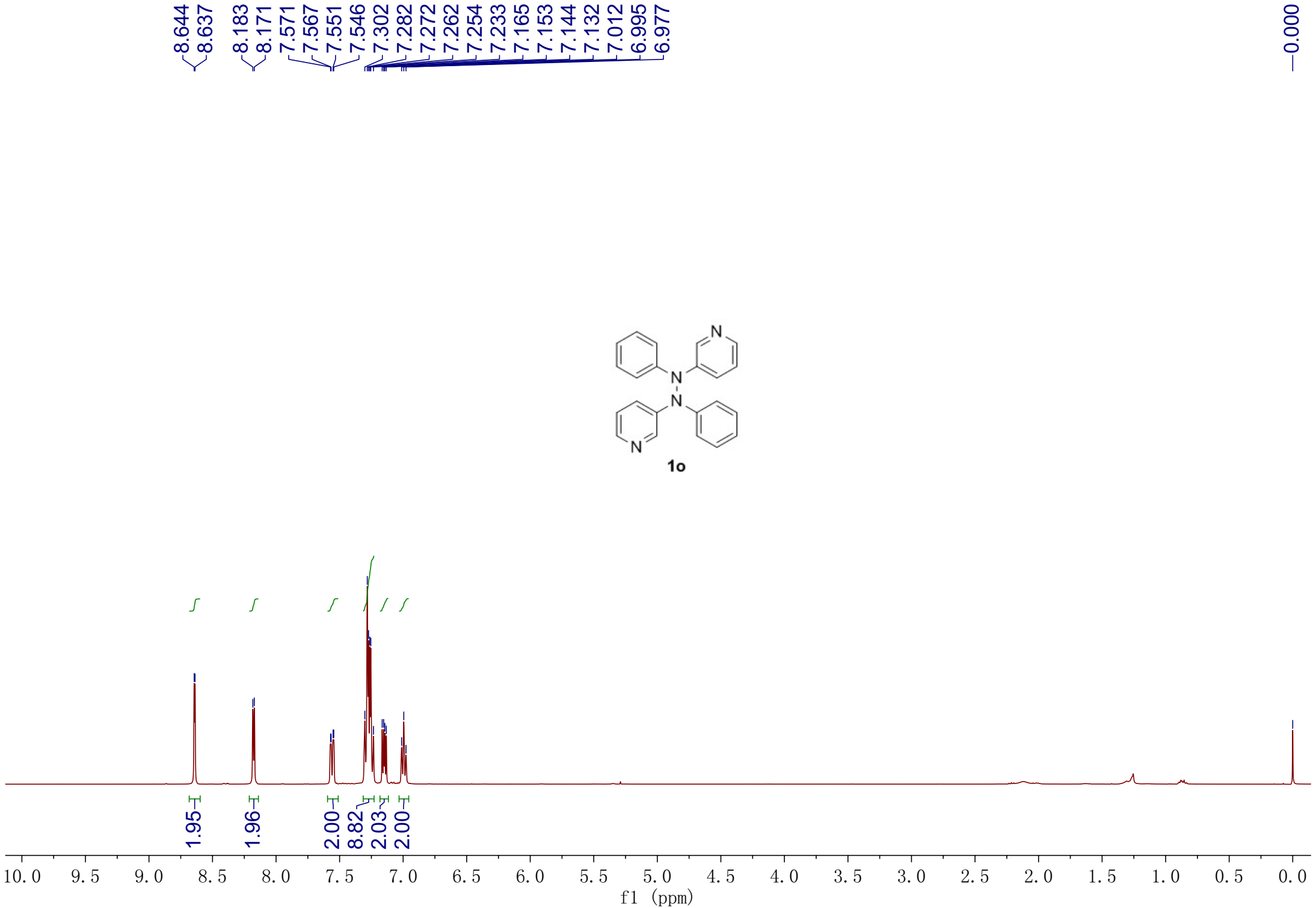
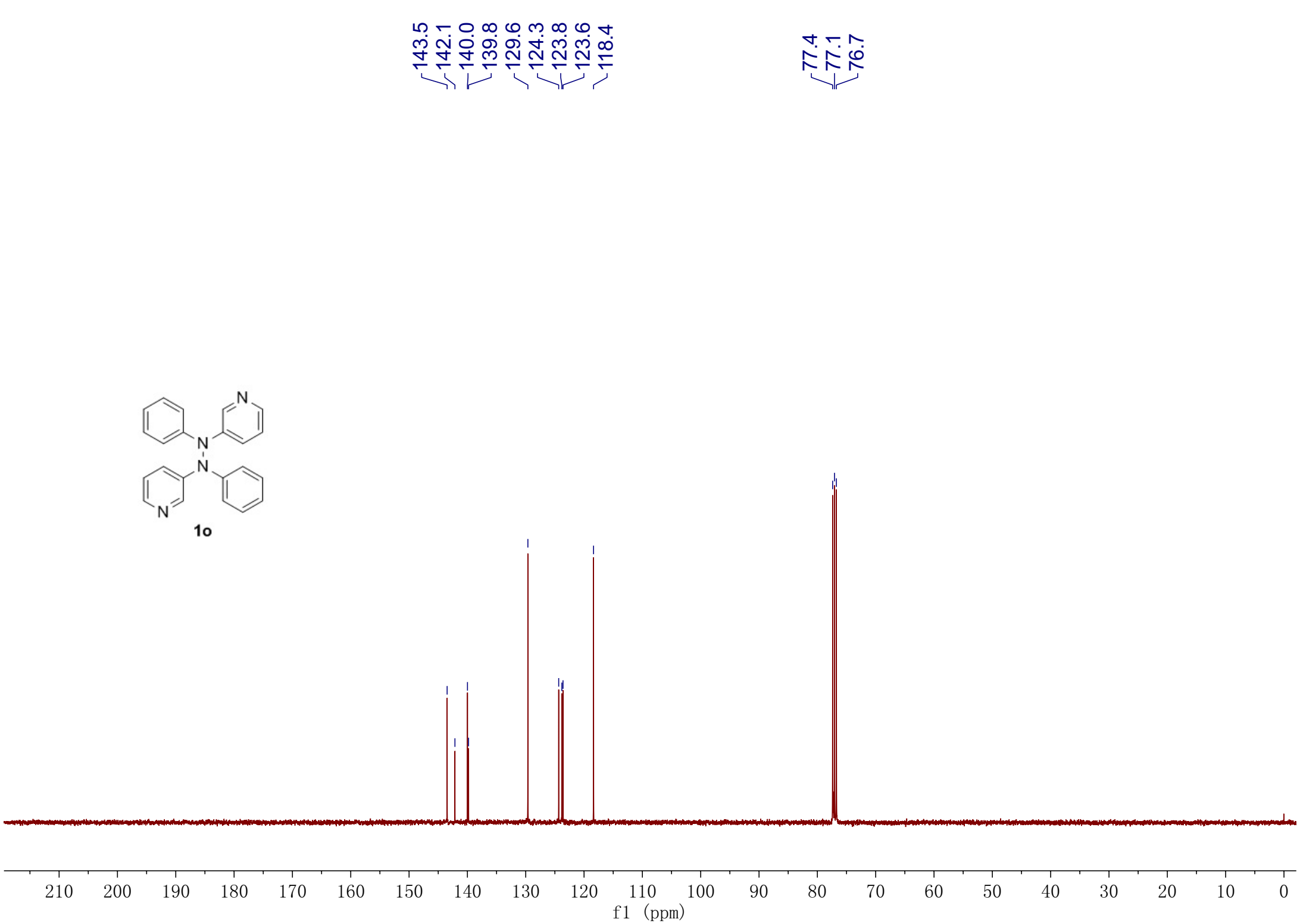
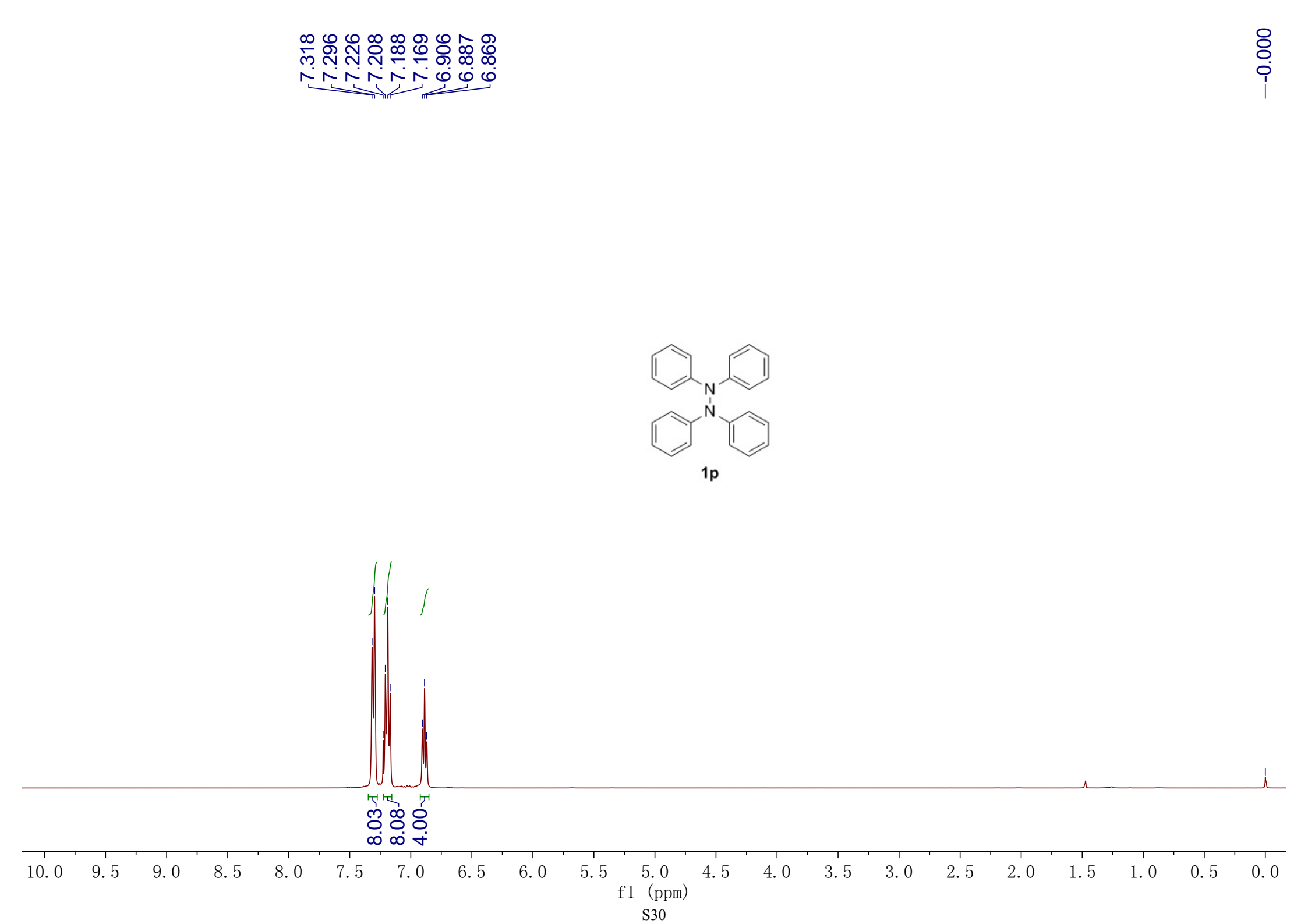
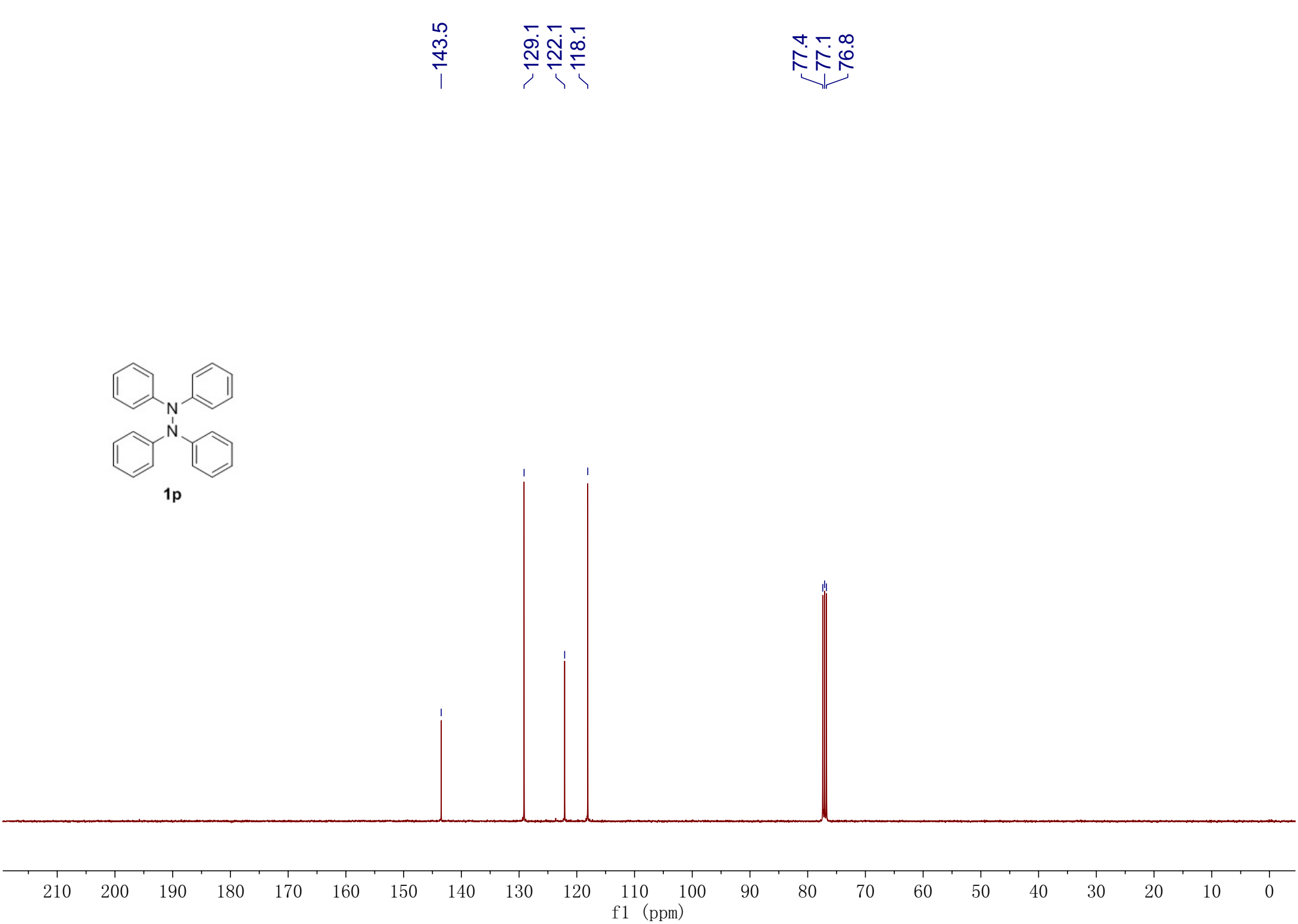
8.277
8.274
8.272
8.266
8.264
8.262
8.260
7.527
7.522
7.509
7.505
7.501
7.488
7.483
7.428
7.422
7.416
7.405
7.399
7.393
7.372
7.366
7.360
7.348
7.343
7.336
7.258
6.956
6.935
6.877
6.876
6.865
6.863
6.859
6.847
6.845
-0.000
Br
N
N
N
N
Br
1n
2.00
2.10
8.33
2.02
2.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

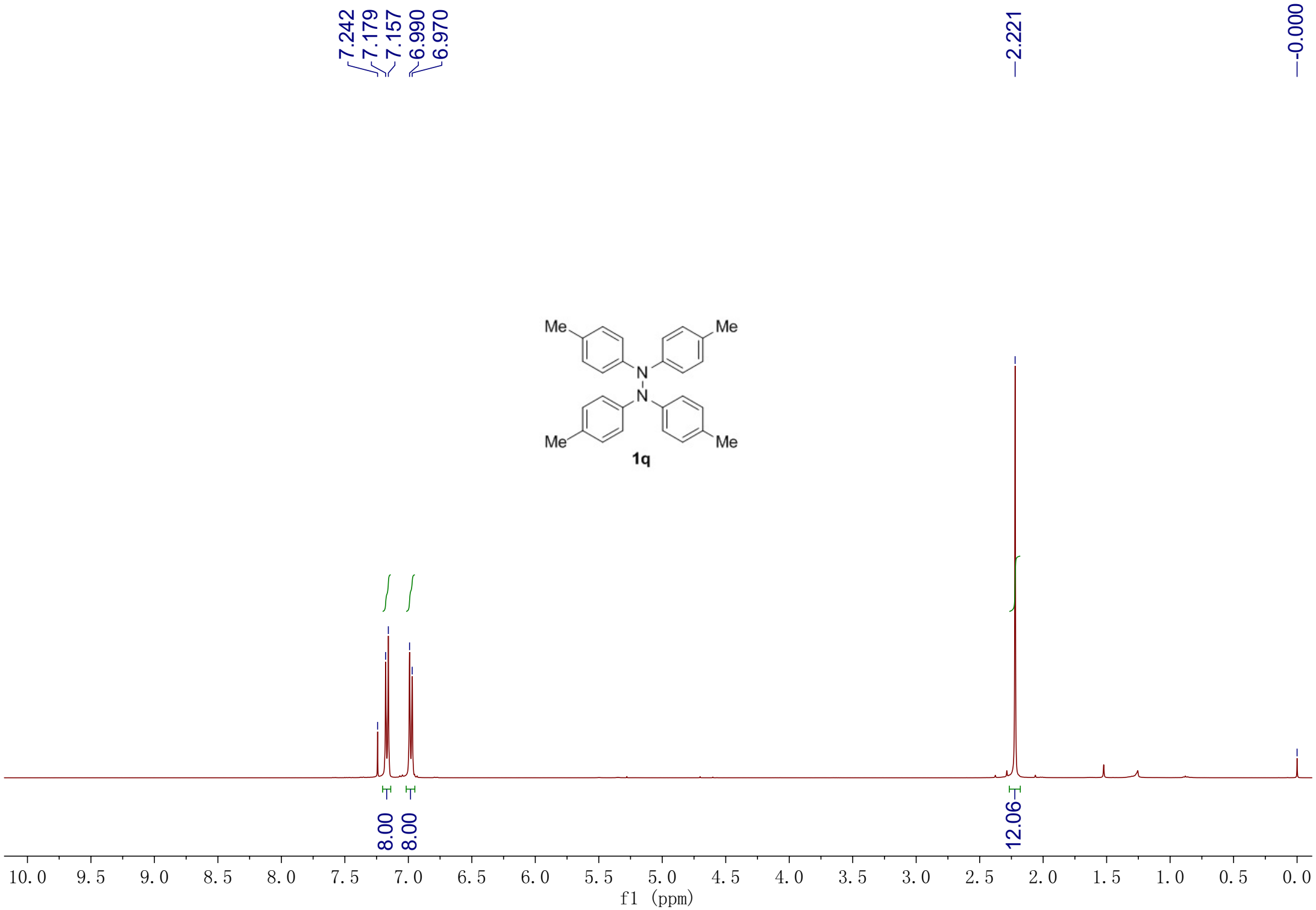

155.5
148.0
140.7
138.6
131.9
121.6
117.7
116.2
110.6
77.4
77.0
76.7
Br
N
N
N
N
Br
1n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

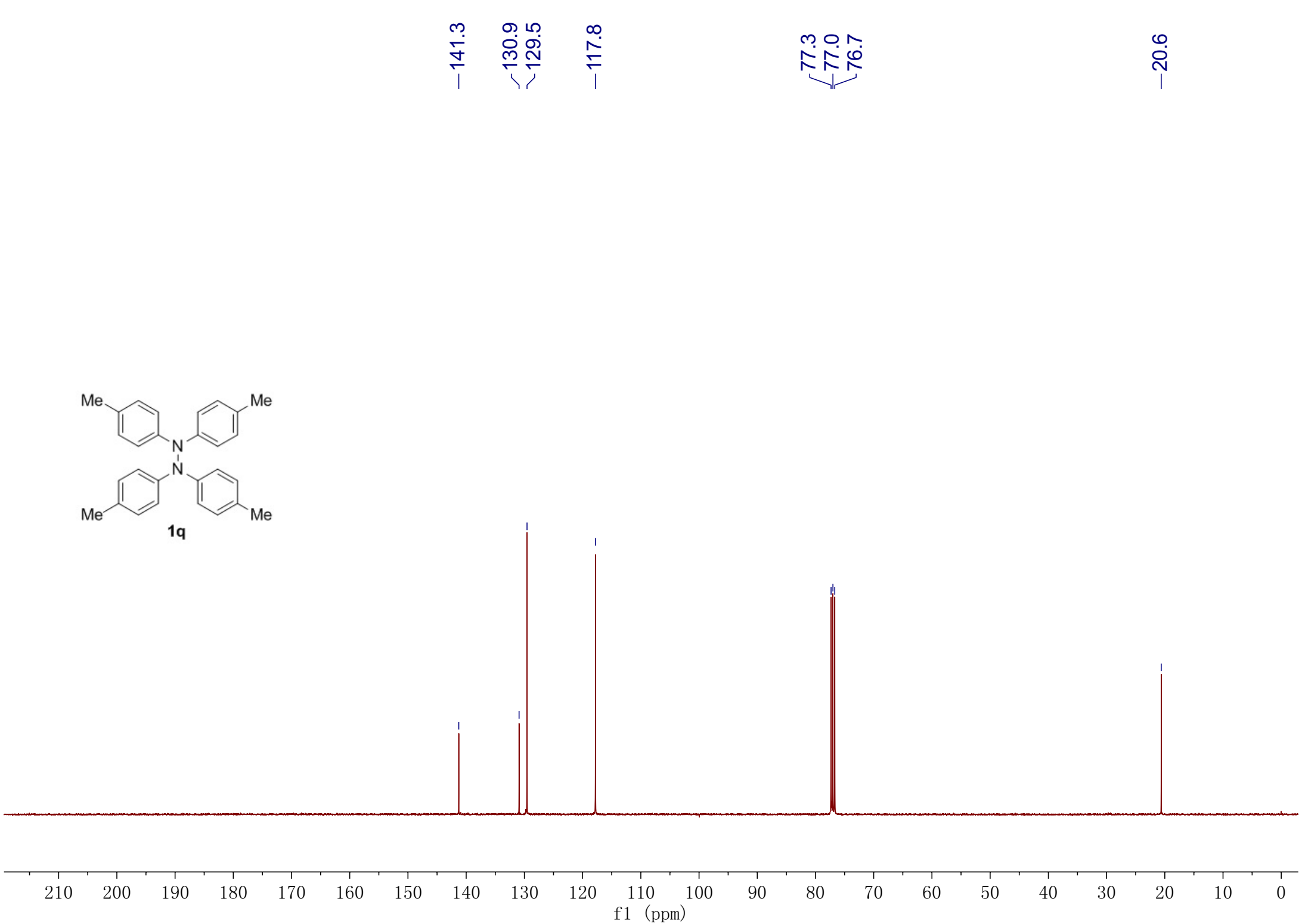

8.644
8.637
8.183
8.171
7.571
7.567
7.551
7.546
7.302
7.282
7.272
7.262
7.254
7.233
7.165
7.153
7.144
7.132
7.012
6.995
6.977
0.000
N
N
N
N
1o
1.95
1.96
2.00
8.82
2.03
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

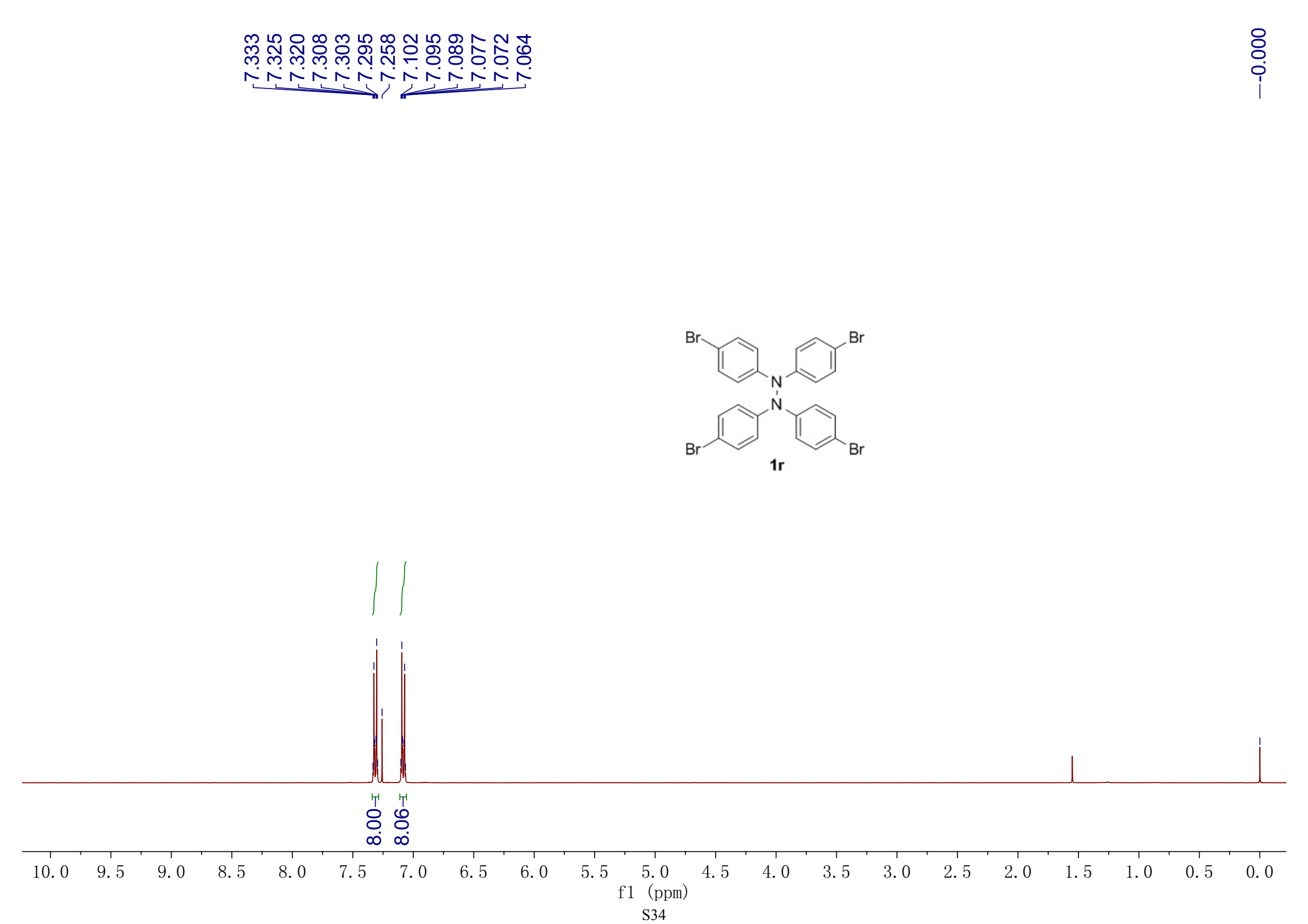

143.5
142.1
140.0
139.8
129.6
124.3
123.8
123.6
118.4
77.4
77.1
76.7
N
N
N
N
1o
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

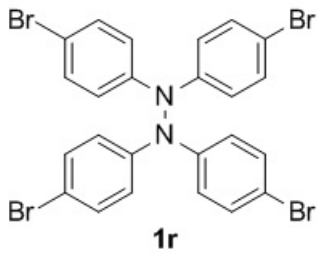

7.318
7.296
7.226
7.208
7.188
7.169
6.906
6.887
6.869
0.000
N
N
1p
8.03
8.08
4.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


143.5
129.1
122.1
118.1
77.4
77.1
76.8
N
N
1p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.242
7.179
7.157
6.990
6.970
2.221
0.000
Me
Me
N
N
Me
Me
1q
8.00
8.00
12.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


141.3
130.9
129.5
117.8
77.3
77.0
76.7
20.6
Me
Me
N
N
Me
Me
1q
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.333
7.325
7.320
7.308
7.303
7.295
7.258
7.102
7.095
7.089
7.077
7.072
7.064
-0.000
Br
Br
N
N
Br
Br
1r
8.00
8.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

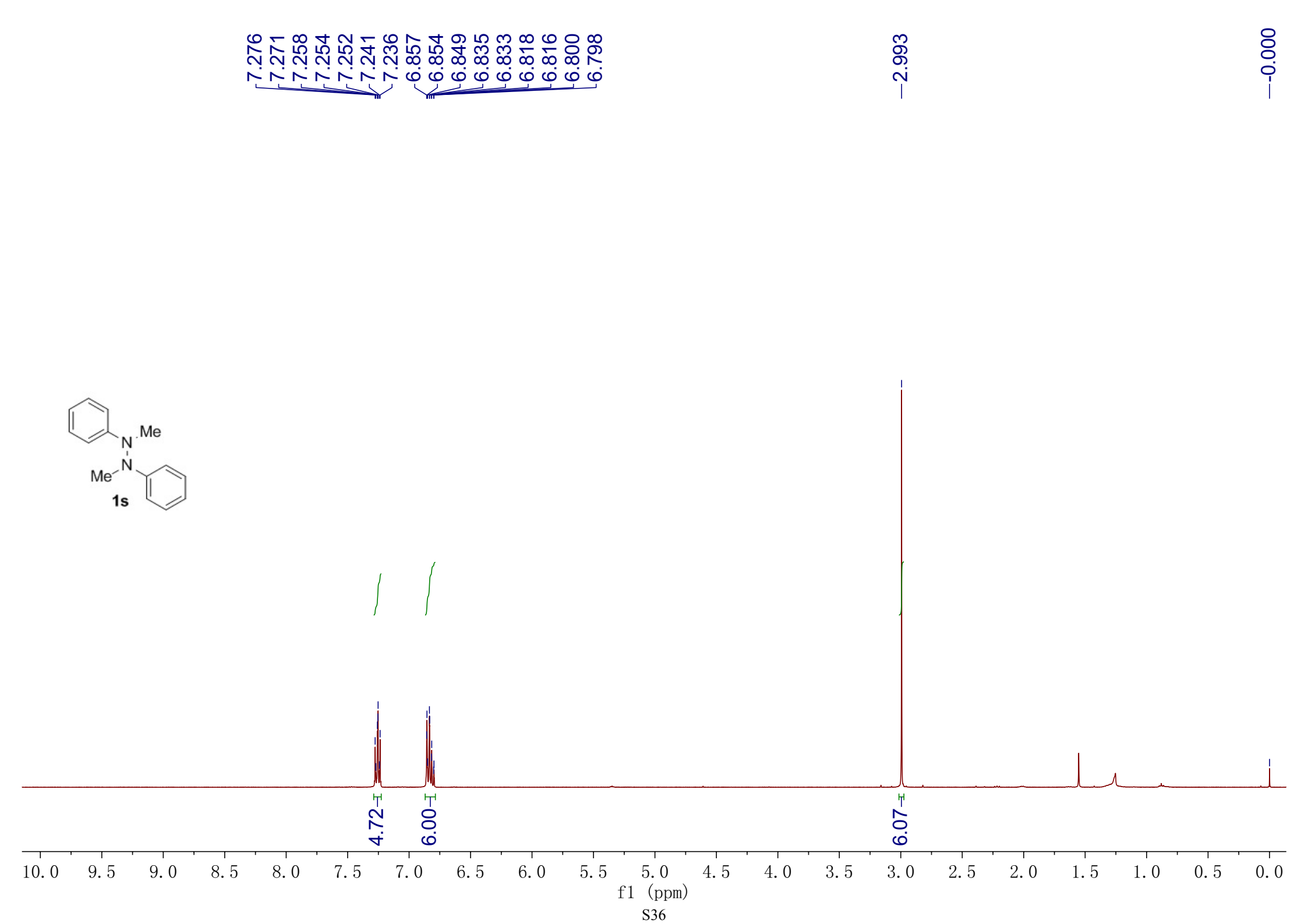


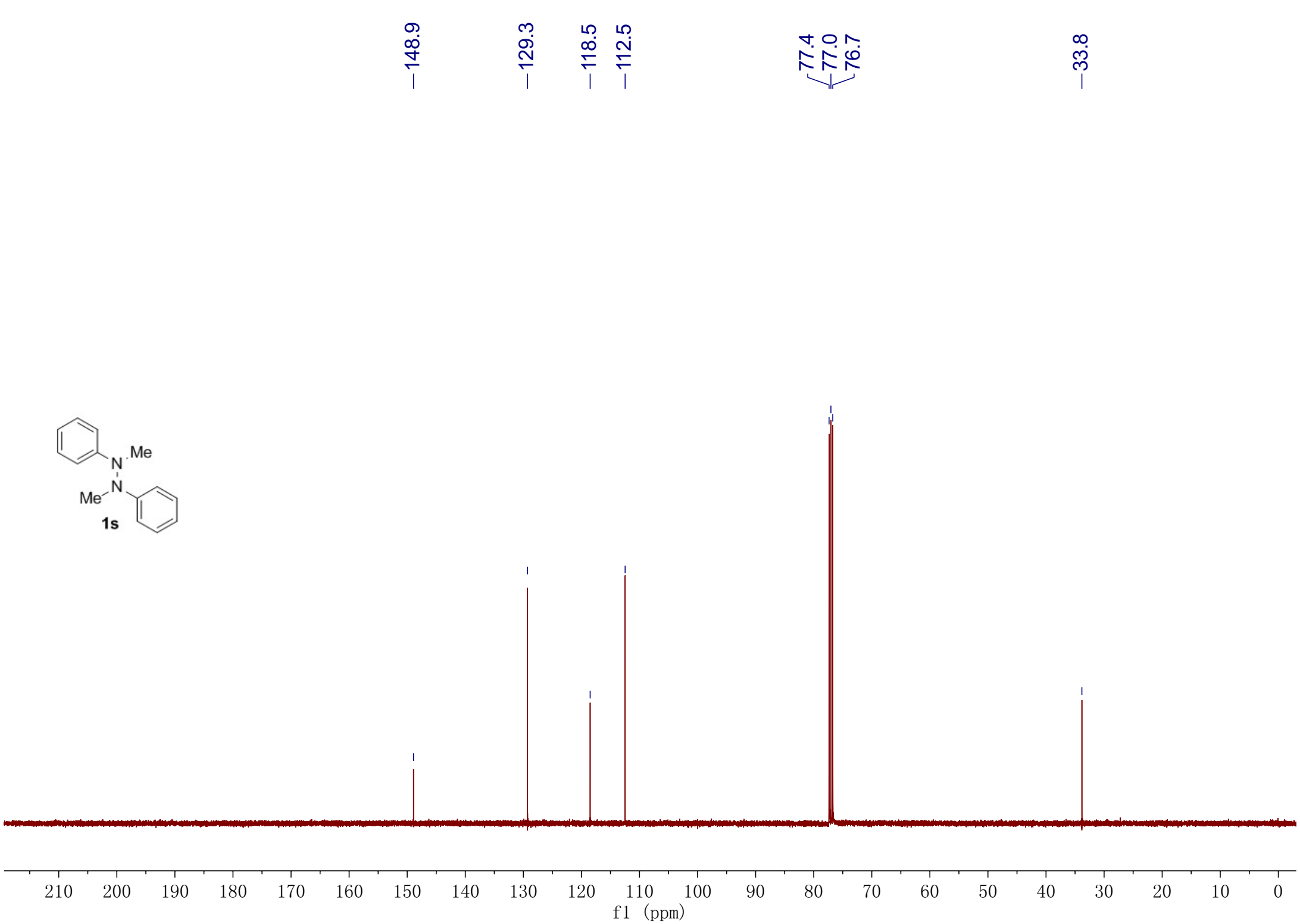
1r

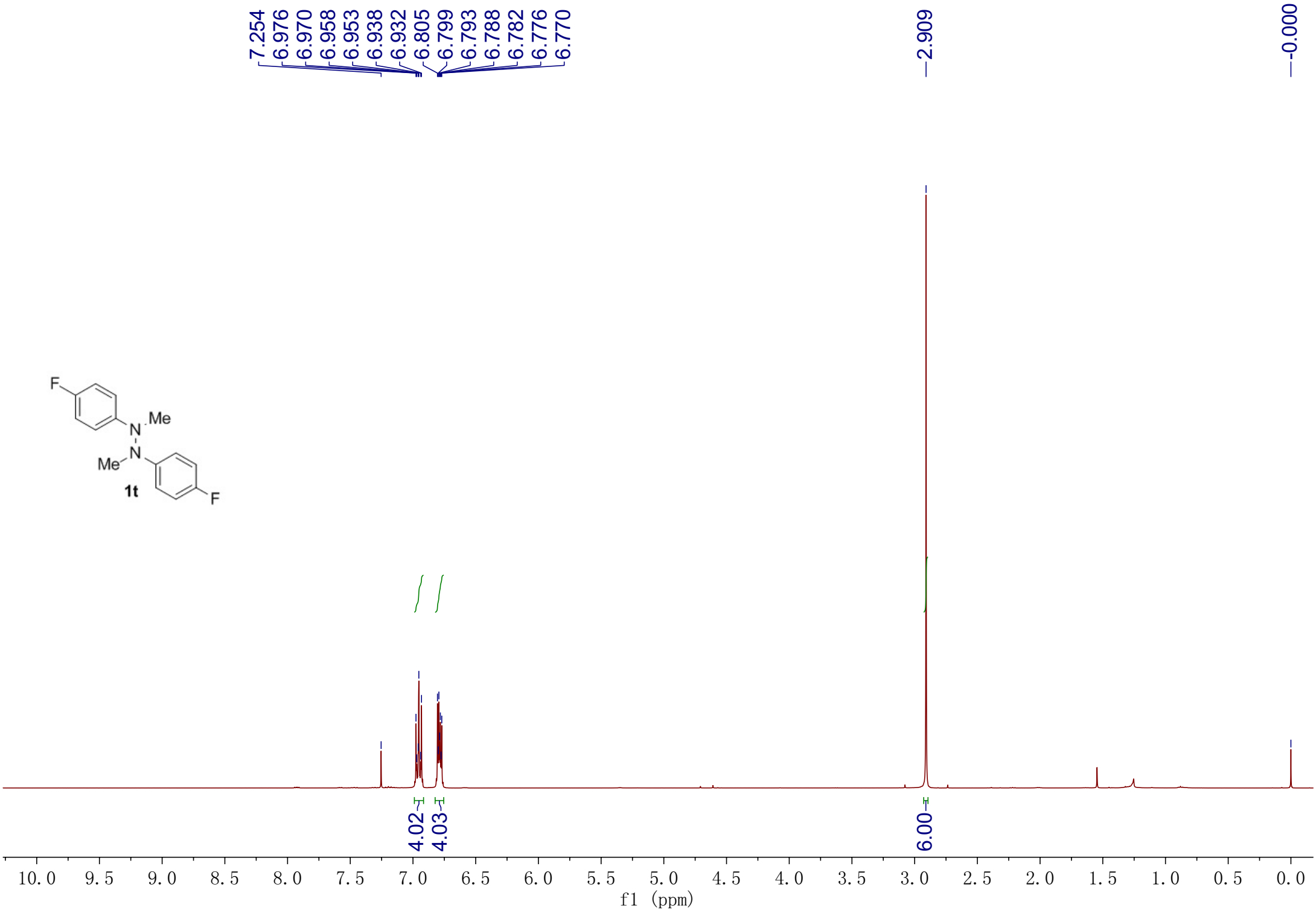
141.6
132.4
119.6
115.1
77.3
77.0
76.7

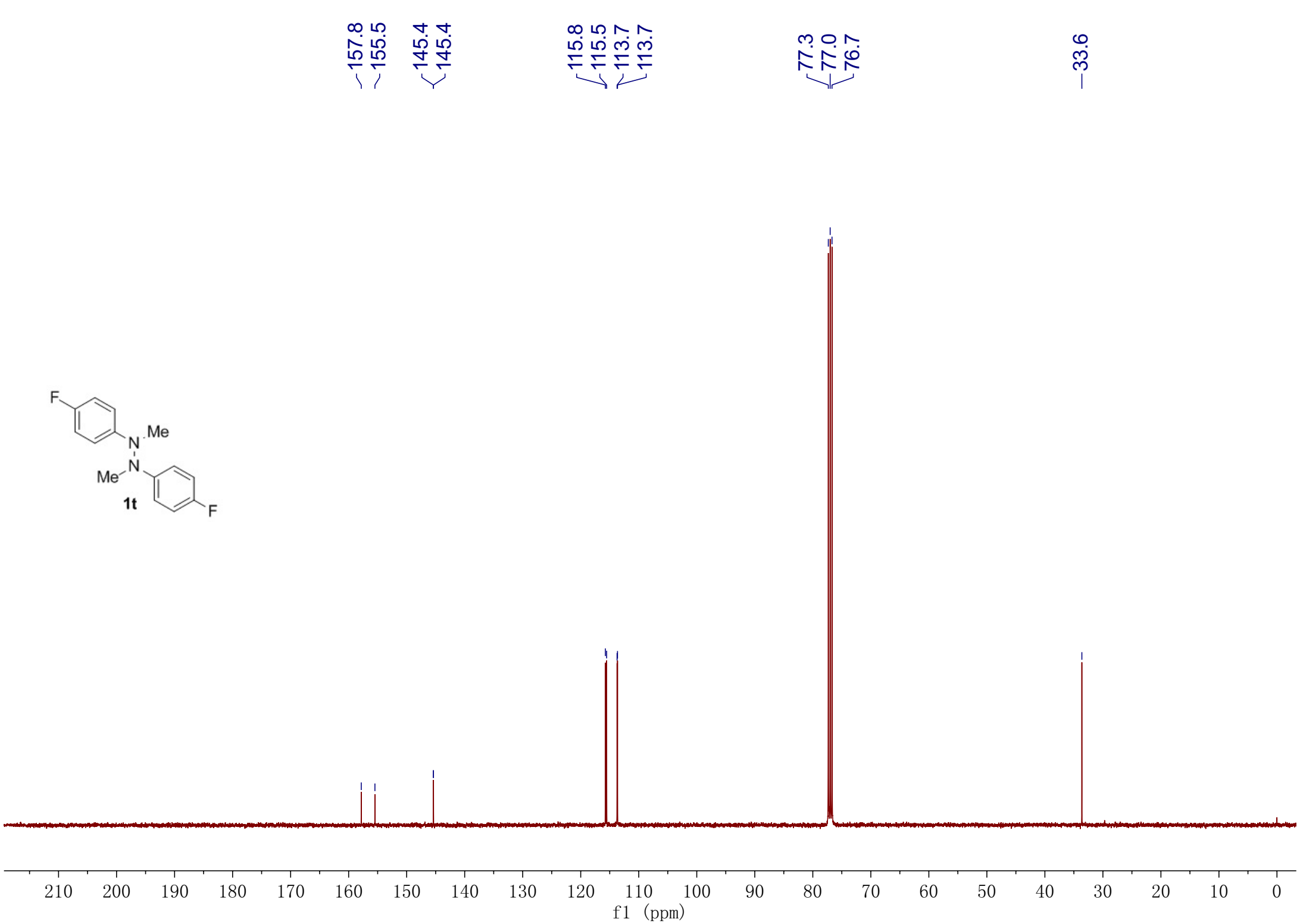
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

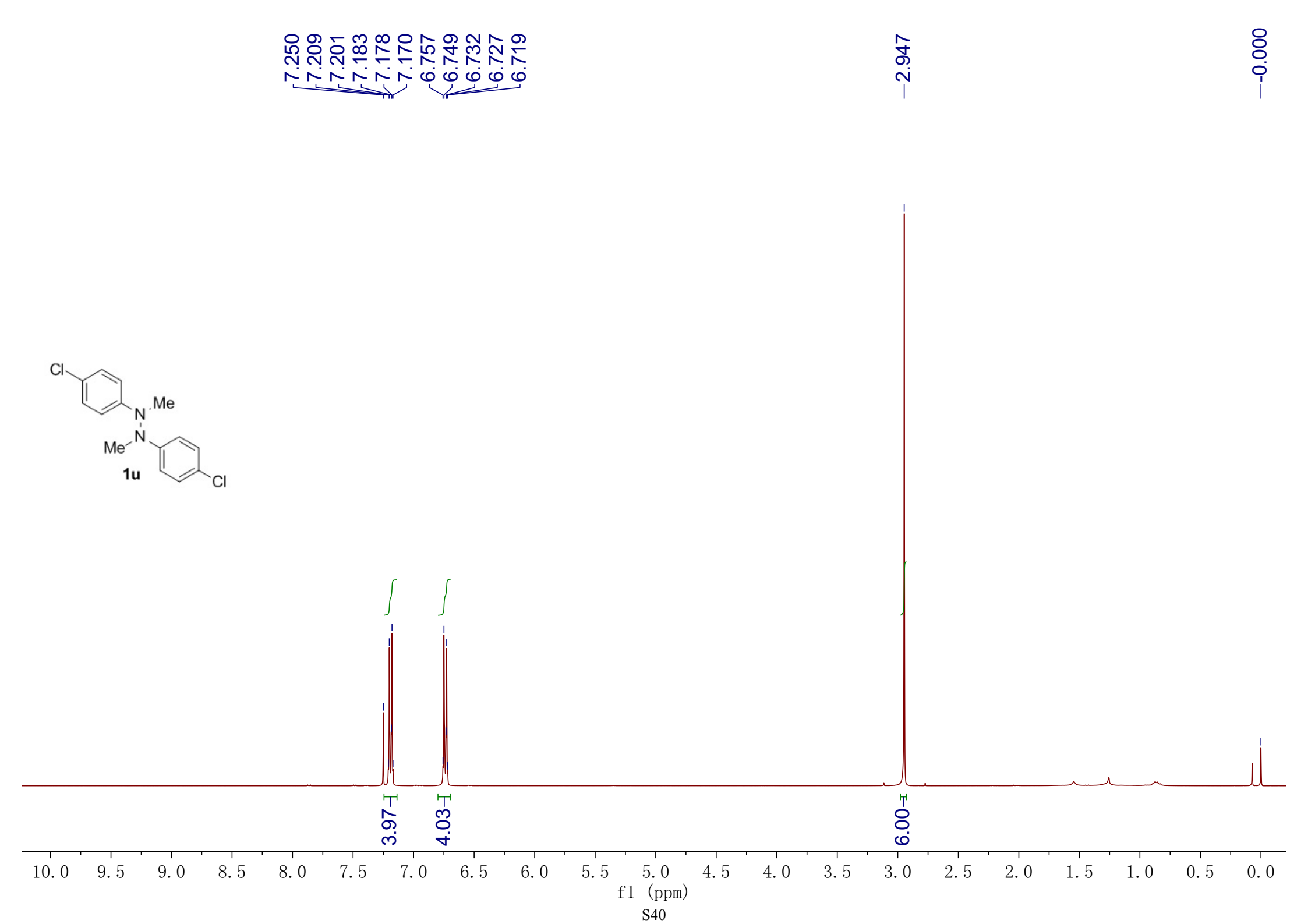
f1 (ppm)

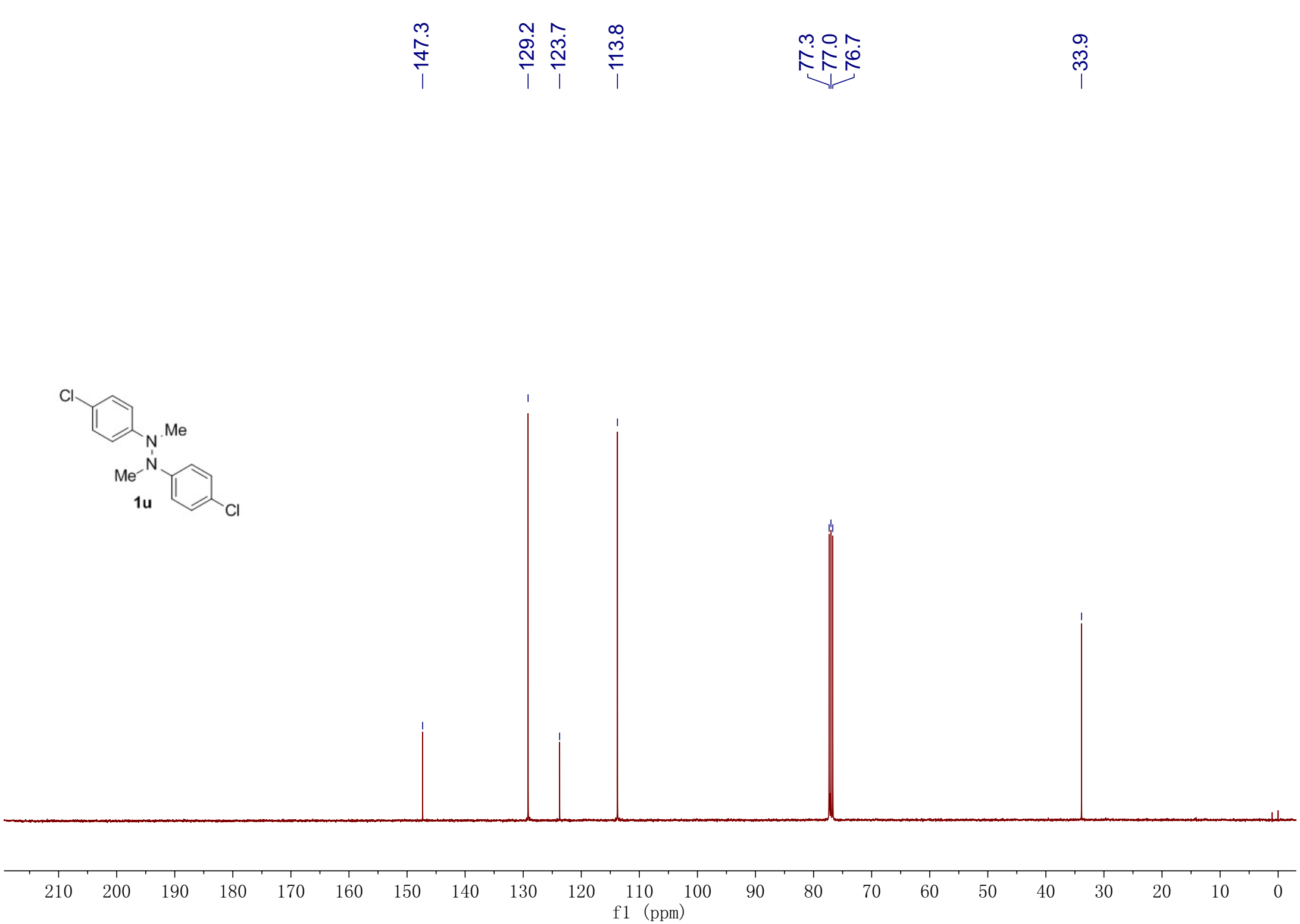

7.276
7.271
7.258
7.254
7.252
7.241
7.236
6.857
6.854
6.849
6.835
6.833
6.818
6.816
6.800
6.798
2.993
0.000
Me
N
N
Me
1s
4.72
6.00
6.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

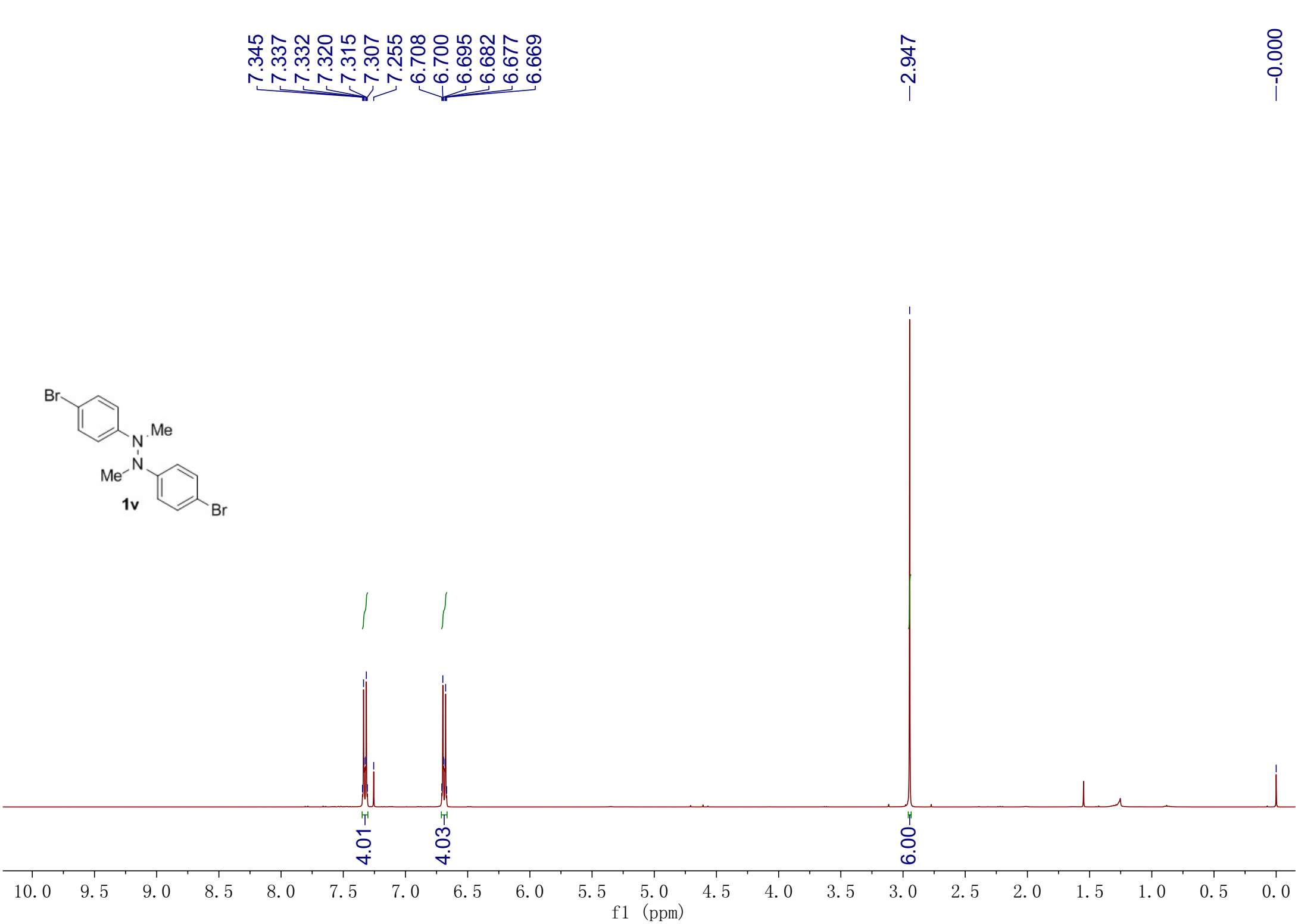

148.9
129.3
118.5
112.5
77.4
77.0
76.7
33.8
Me
N
N
Me
1s
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

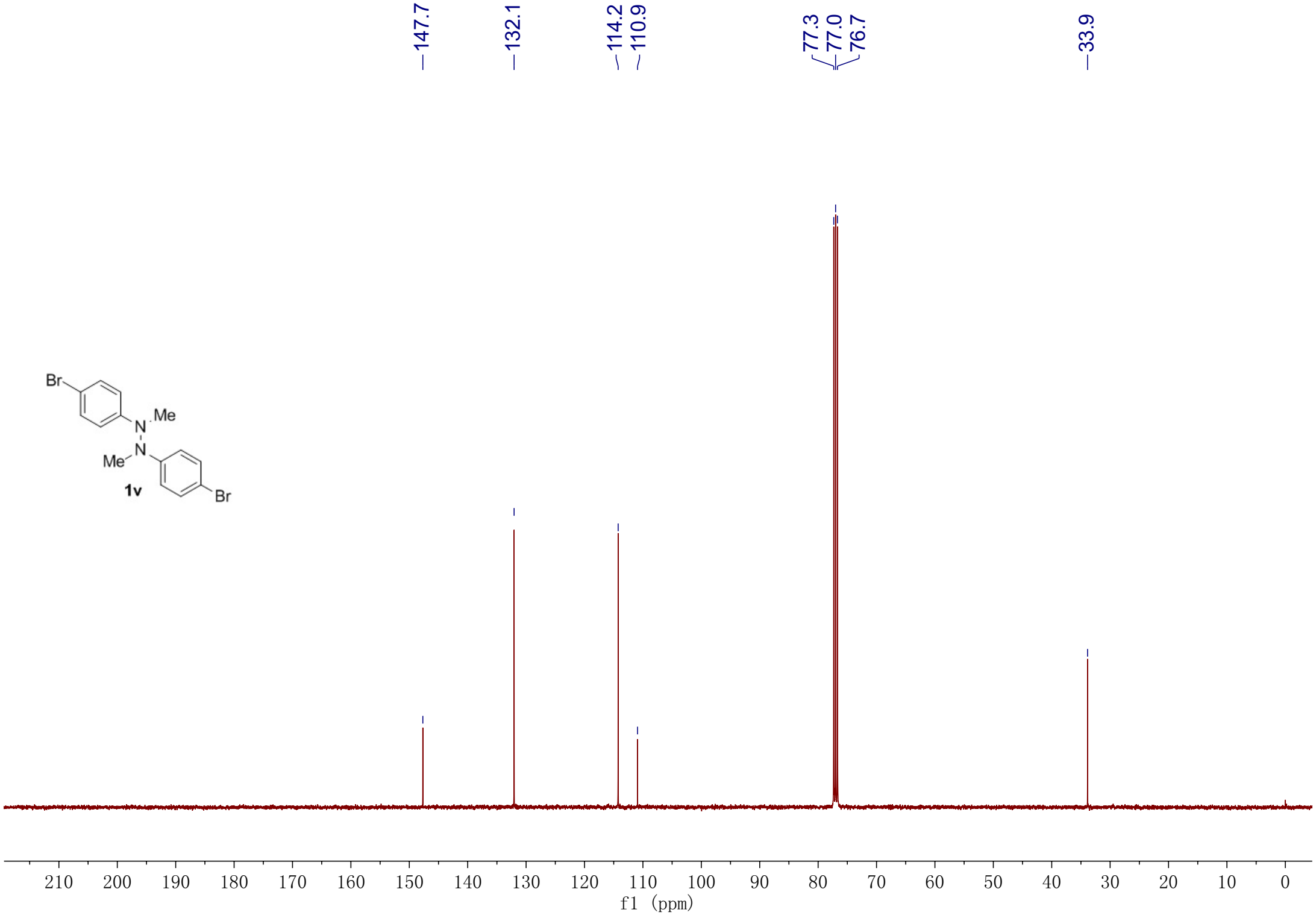

7.254
6.976
6.970
6.958
6.953
6.938
6.932
6.805
6.799
6.793
6.788
6.782
6.776
6.770
2.909
0.000
F
N
Me
N
Me
F
1t
4.02
4.03
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

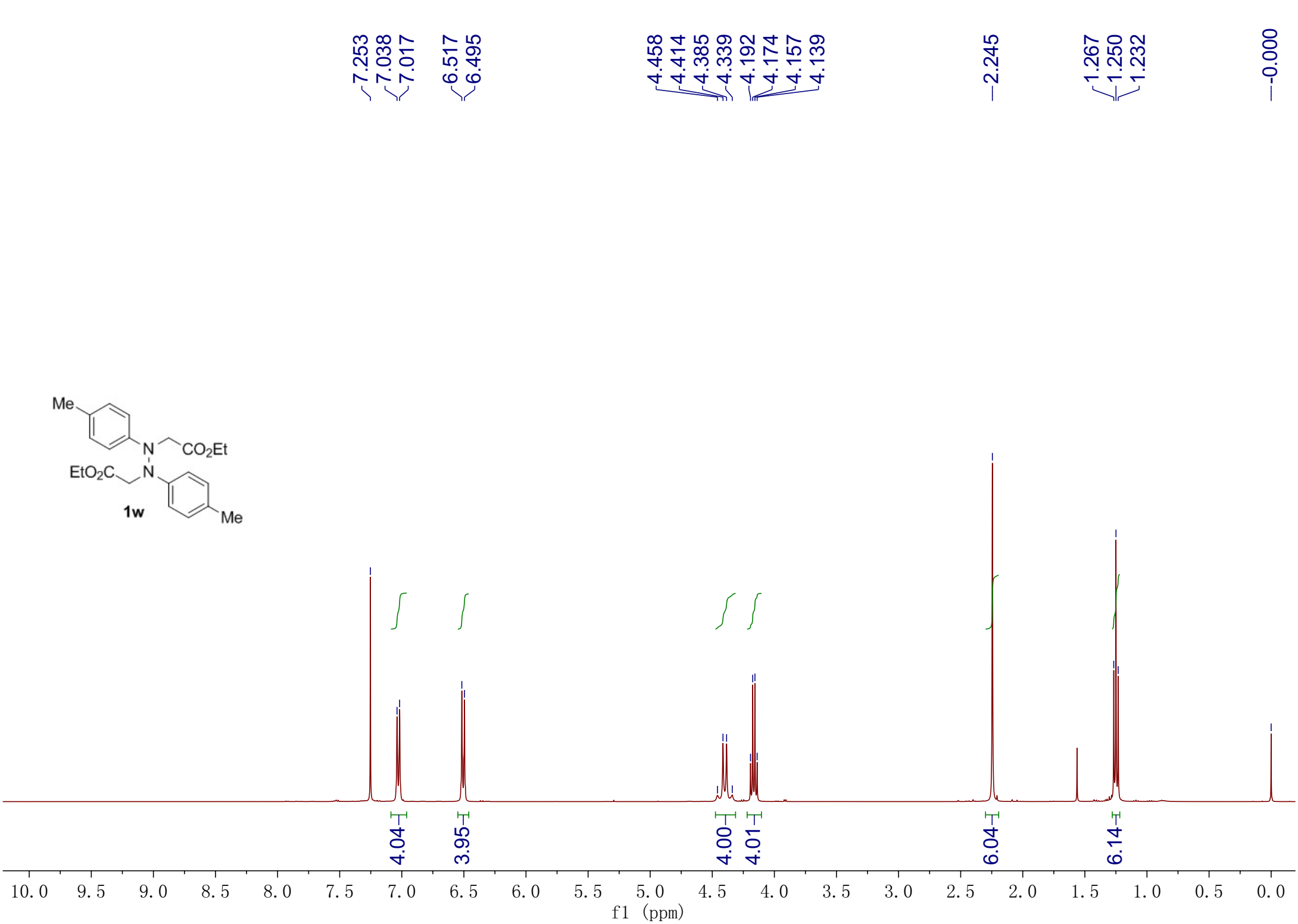

157.8
155.5
145.4
145.4
115.8
115.5
113.7
113.7
77.3
77.0
76.7
33.6
F
N
Me
N
Me
F
1t
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

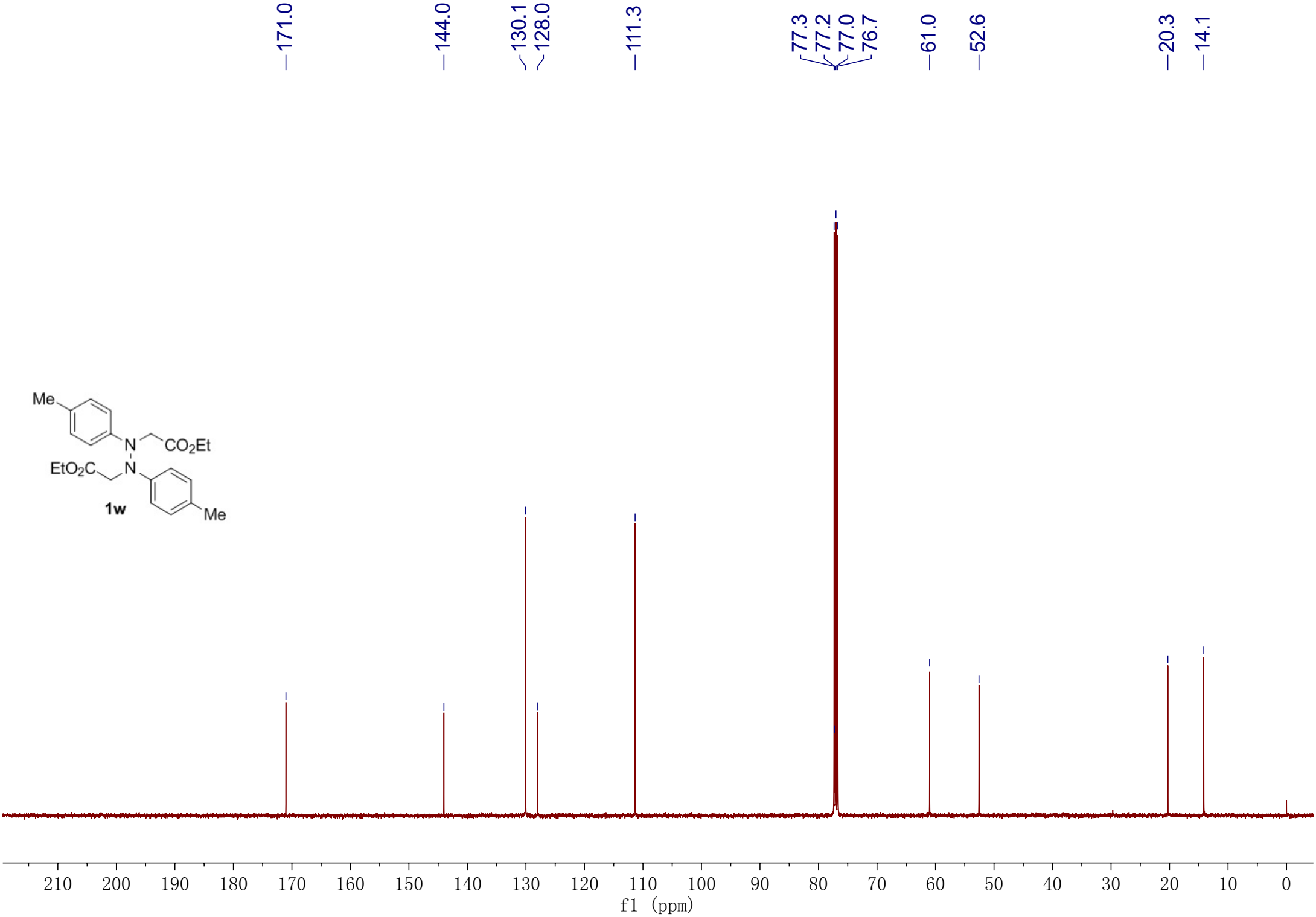

7.250
7.209
7.201
7.183
7.178
7.170
6.757
6.749
6.732
6.727
6.719
2.947
0.000
Cl
N
Me
N
Me
Cl
1u
3.97
4.03
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


147.3
129.2
123.7
113.8
77.3
77.0
76.7
33.9
Cl
N
Me
N
Me
Cl
1u
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.345
7.337
7.332
7.320
7.315
7.307
7.255
6.708
6.700
6.695
6.682
6.677
6.669
2.947
-0.000
Br
N
Me
N
Me
Br
1v
4.01
4.03
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


147.7
132.1
114.2
110.9
77.3
77.0
76.7
33.9
Br
N
Me
N
Me
Br
1v
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.253
7.038
7.017
6.517
6.495
4.458
4.414
4.385
4.339
4.192
4.174
4.157
4.139
2.245
1.267
1.250
1.232
-0.000
Me
N
CO2Et
EtO2C
N
Me
1w
4.04
3.95
4.00
4.01
6.04
6.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


171.0
144.0
130.1
128.0
111.3
77.3
77.2
77.0
76.7
61.0
52.6
20.3
14.1
Me
N
CO2Et
EtO2C
N
Me
1w
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)