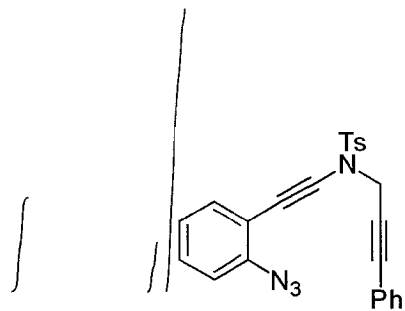


7.985
7.965
7.382
7.363
7.300
7.279
7.264
7.245
7.228
7.187
7.170
7.092
7.073
7.058
7.039

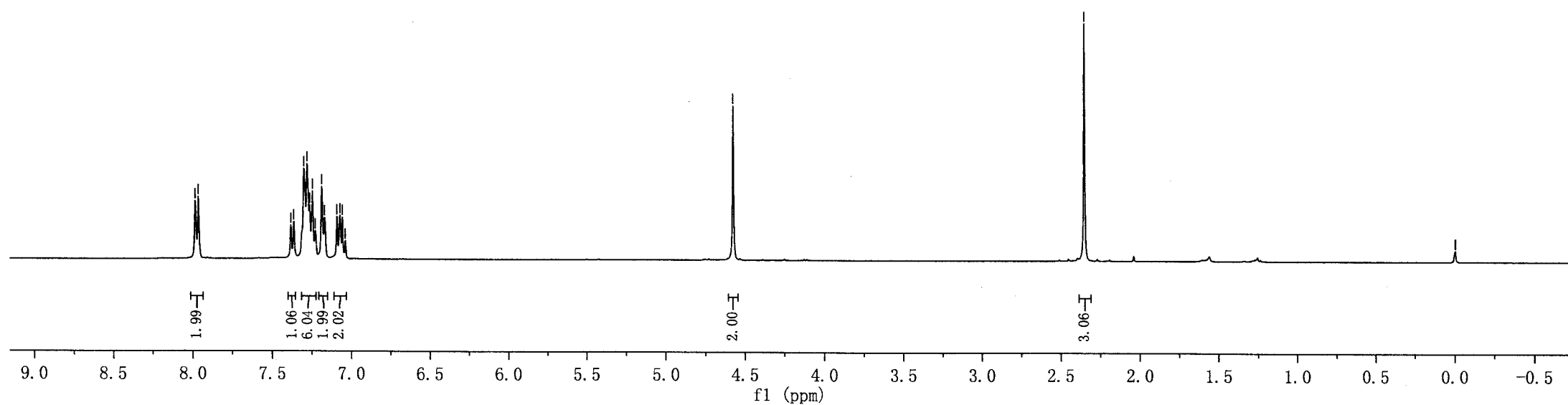
4.577

2.354

0.000



1a



144.94
140.98
134.34
133.52
131.63
129.54
129.16
128.55
128.40
128.11
124.55
122.06
118.63
114.93

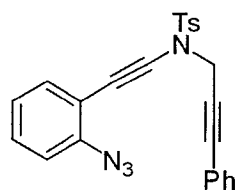
87.47
86.63

81.09
77.32
77.00
76.68

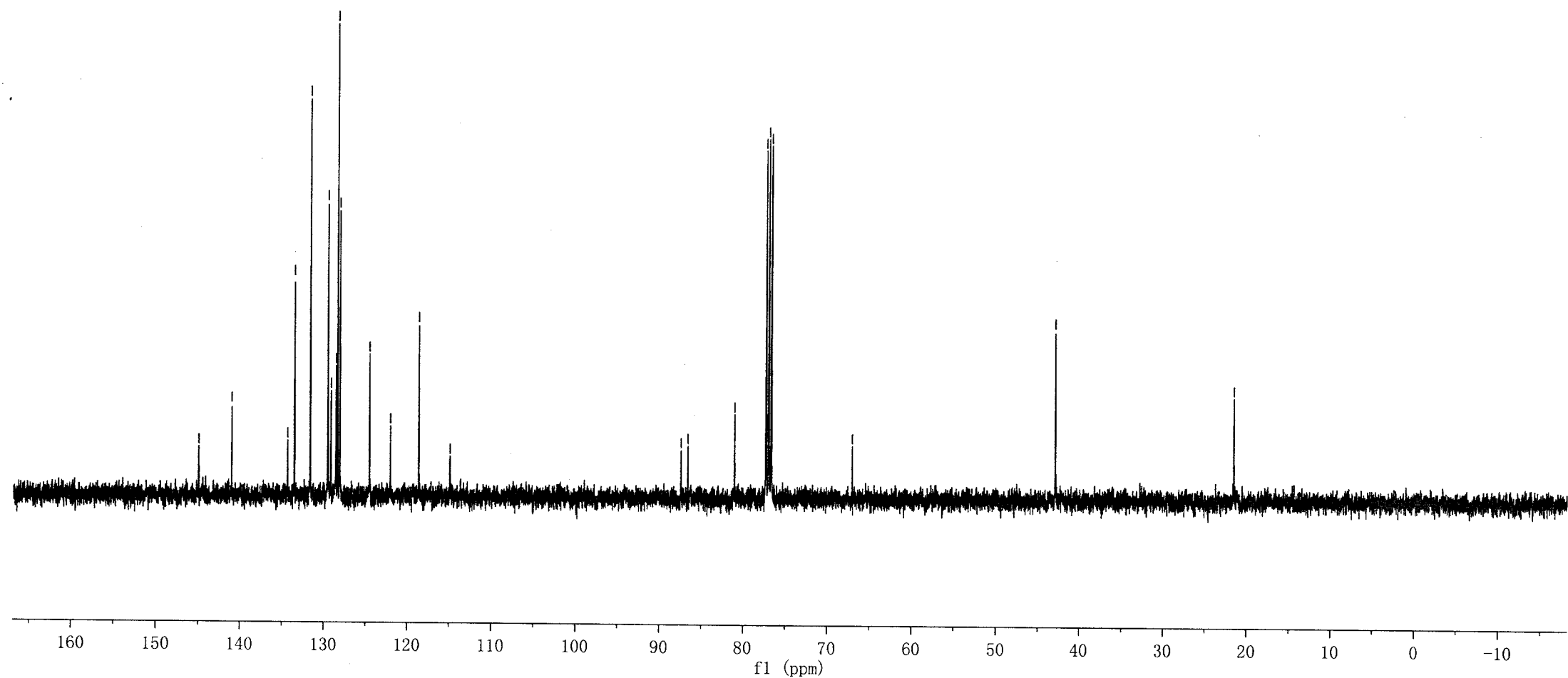
67.06

42.89

21.55



1a

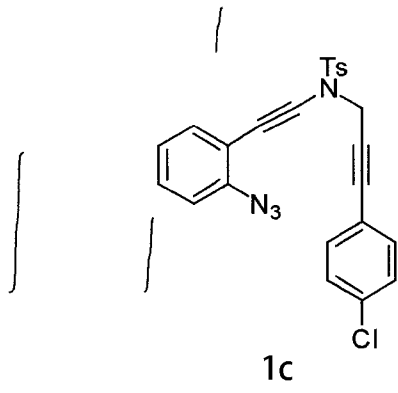


Supplementary Figure 1. ¹H and ¹³C NMR spectra for 1a

7.969
7.953
7.370
7.355
7.311
7.309
7.302
7.285
7.228
7.212
7.109
7.087
7.071
7.059
7.044

4.558

2.366



1.95-H

1.04-H
3.01-H
1.99-H
3.99-H

1.98-H

3.00-H

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

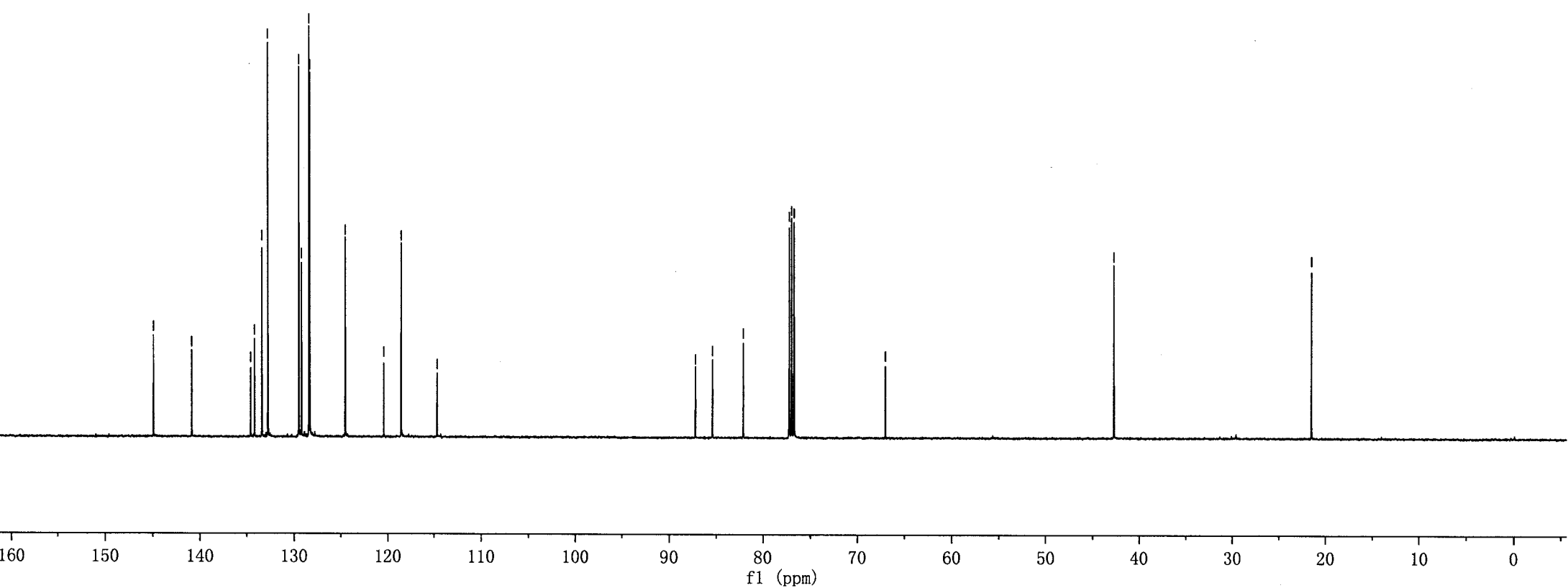
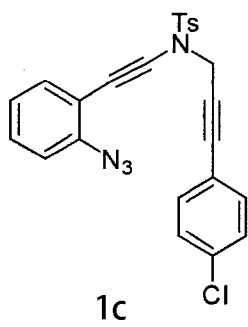
144.94
140.88
134.60
134.20
133.43
132.80
129.50
129.21
128.43
128.34
124.55
120.45
118.59
114.72

87.27
85.43
82.14
77.25
77.00
76.75

67.04

42.74

21.54



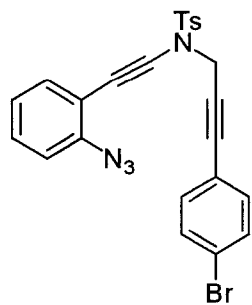
Supplementary Figure 3. ¹H and ¹³C NMR spectra for 1c

7.967
7.951
7.386
7.369
7.354
7.313
7.311
7.301
7.285
7.254
7.087
7.072
7.060
7.040
7.023

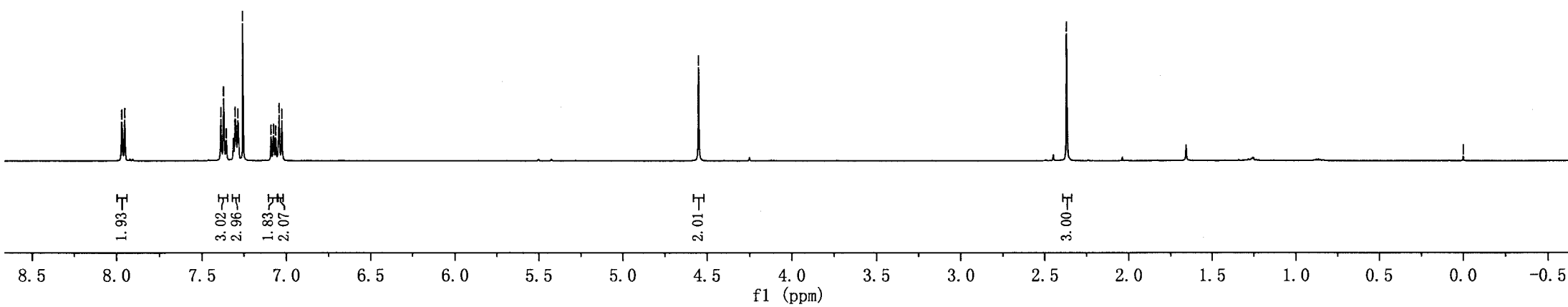
4.550

2.367

0.000



1d



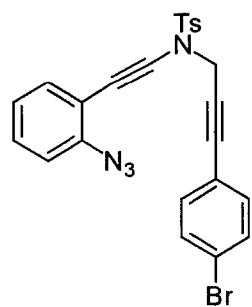
144.94
140.88
134.18
133.43
132.99
131.35
129.50
129.22
128.33
124.55
122.84
120.90
118.59
114.71

87.25
85.48
82.33
77.25
77.00
76.75

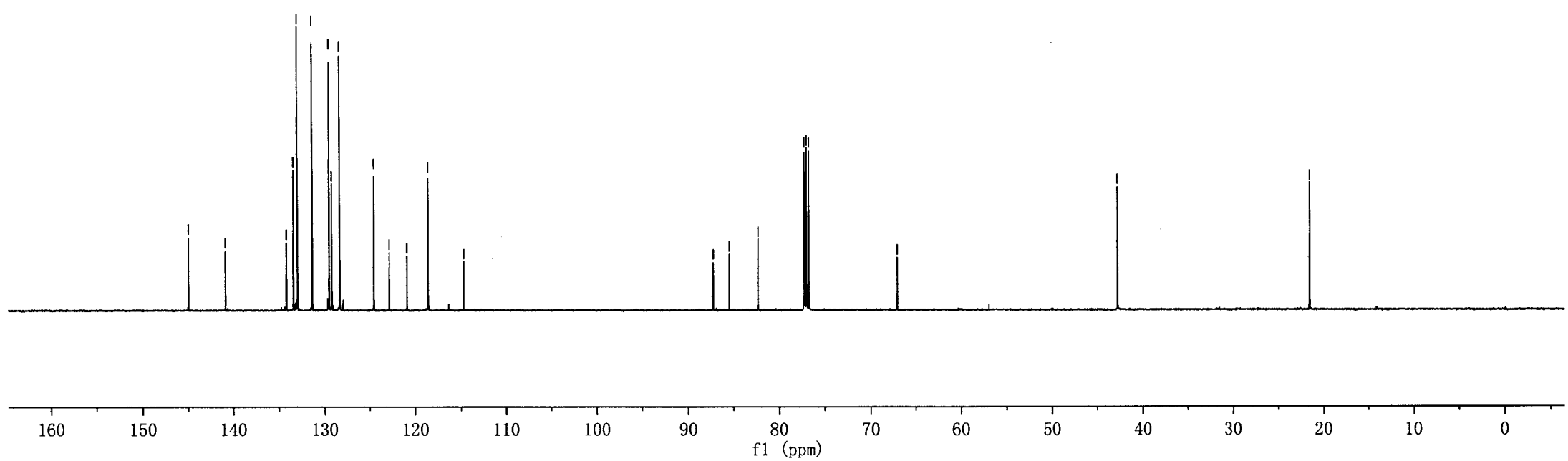
67.03

42.75

21.54



1d



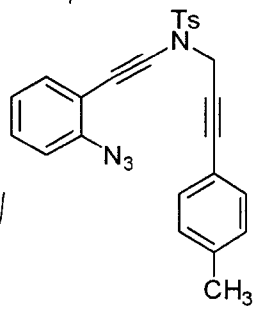
Supplementary Figure 4. ¹H and ¹³C NMR spectra for 1d

7.978
7.957
7.374
7.355
7.300
7.281
7.086
7.066
7.056
7.034

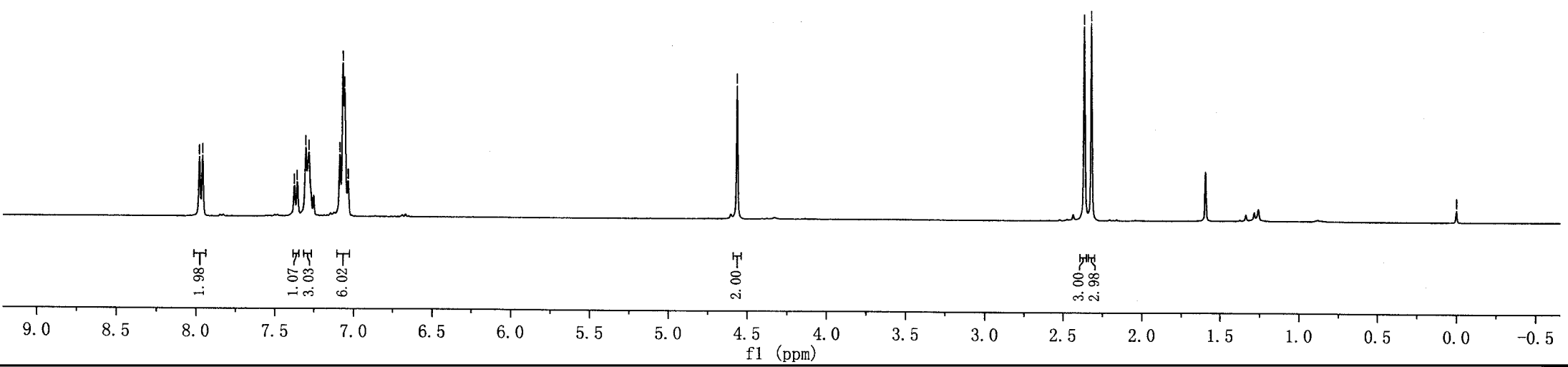
4.564

2.364
2.319

0.000



1e



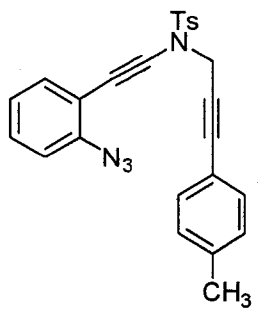
144.87
140.92
138.71
134.28
133.49
131.52
129.51
129.12
128.84
128.37
124.52
118.94
118.57
114.89

87.44
86.76
80.33
77.25
77.00
76.75

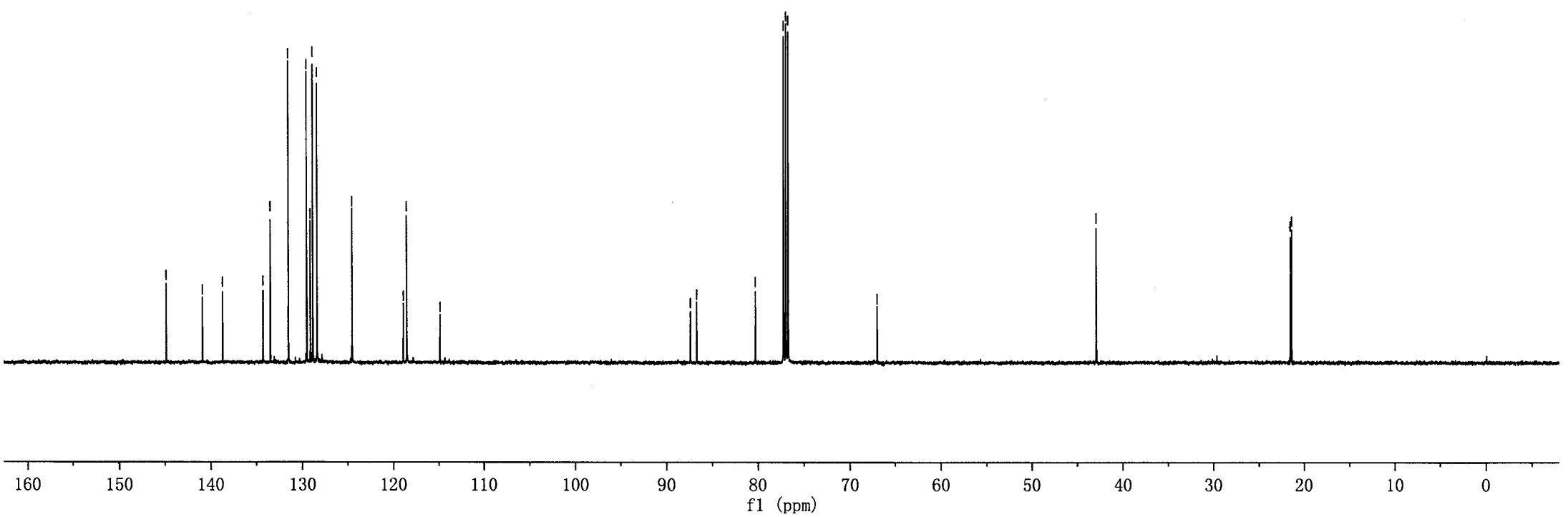
67.00

42.93

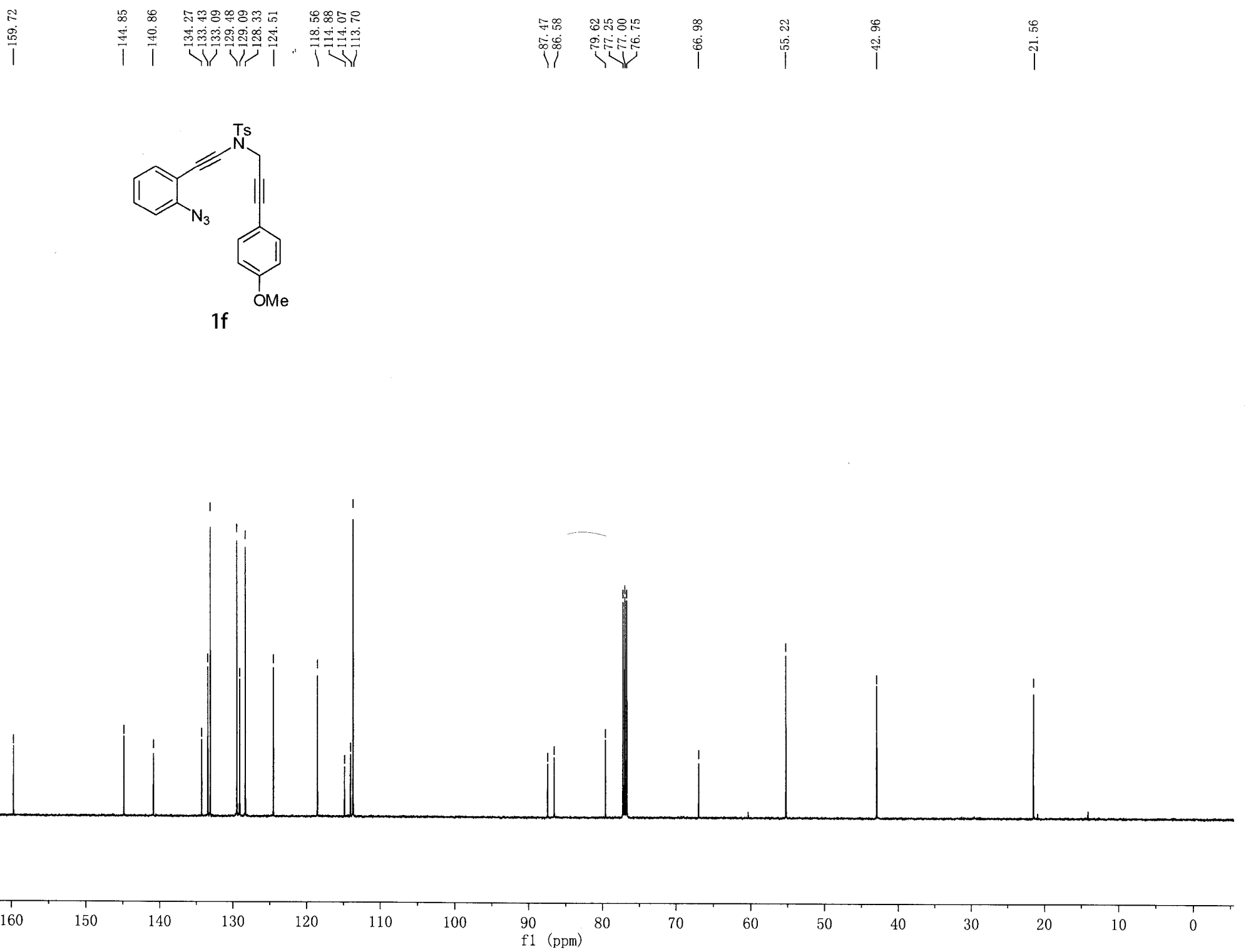
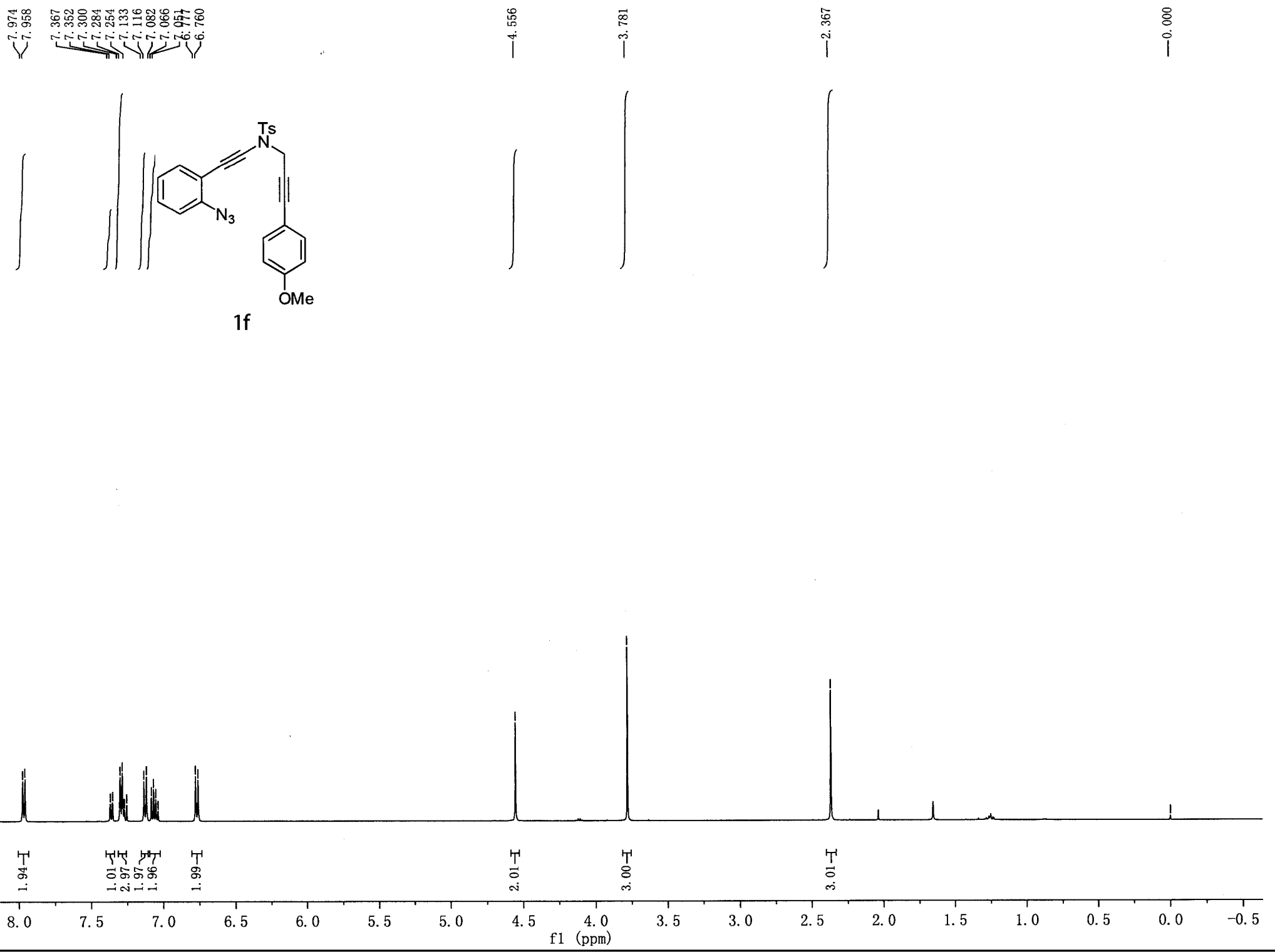
21.56
21.42



1e



Supplementary Figure 5. ¹H and ¹³C NMR spectra for 1e



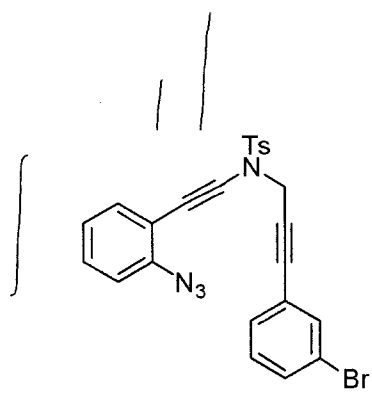
Supplementary Figure 6. ¹H and ¹³C NMR spectra for 1f

7.980
7.963
7.427
7.423
7.416
7.412
7.410
7.406
7.389
7.374
7.326
7.310
7.291
7.255
7.244
7.146
7.124
7.100
7.085
7.071
7.056

4.570

2.400

0.000



1g

1.97

0.95
0.99
3.05
1.05
4.00

2.00

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 -0.5

f1 (ppm)

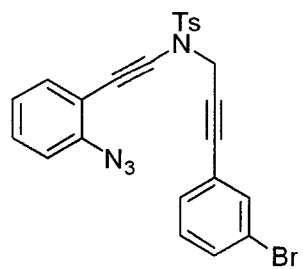
145.12
141.04
134.42
134.29
133.55
131.72
130.06
129.59
129.56
129.27
128.42
124.58
123.96
121.86
118.62
114.75

87.27
85.03
82.53
77.25
77.00
76.75

67.06

42.73

21.65

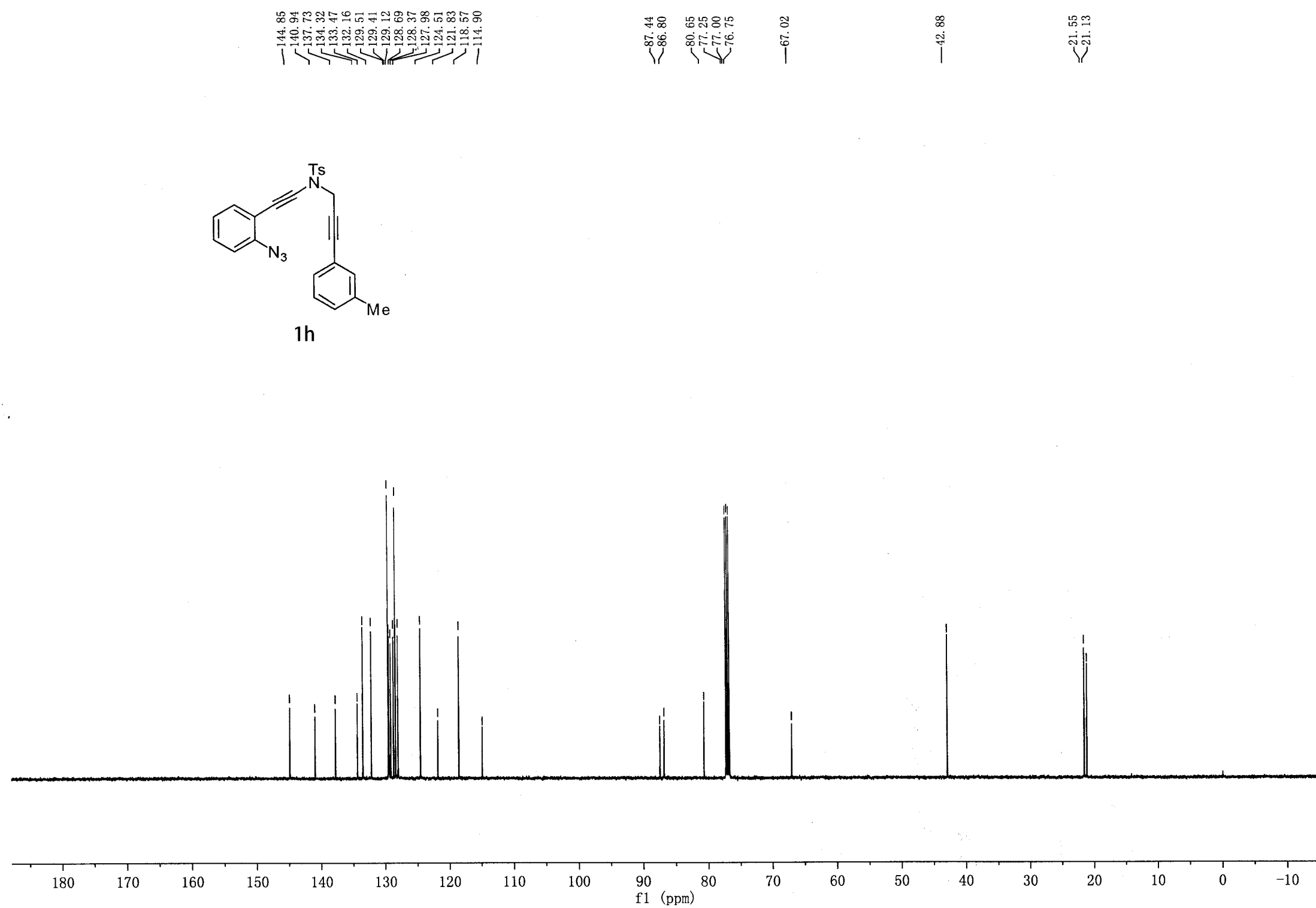
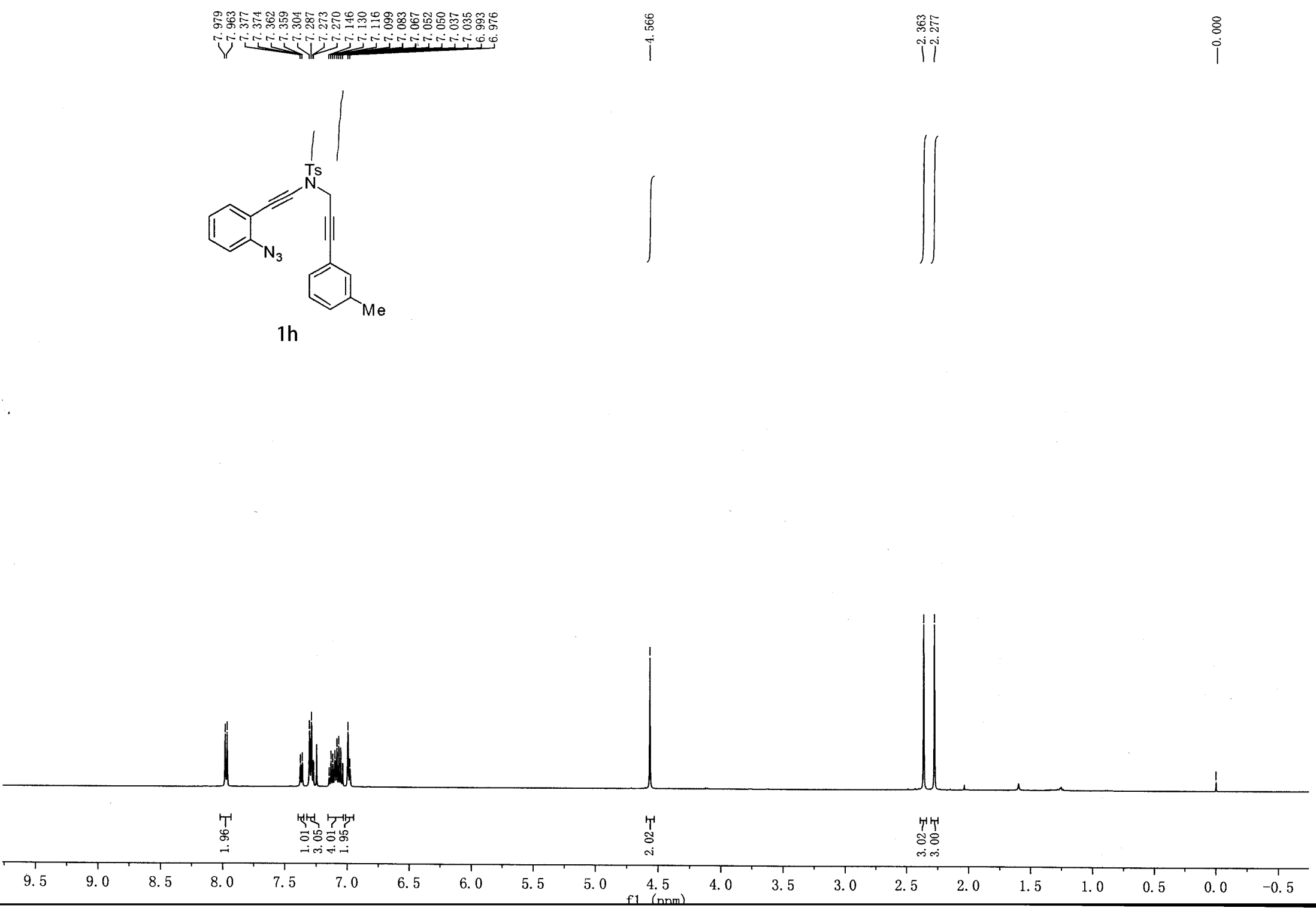


1g

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

f1 (ppm)

Supplementary Figure 7. ¹H and ¹³C NMR spectra for 1g



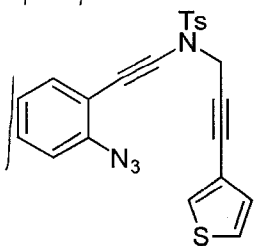
Supplementary Figure 8. ¹H and ¹³C NMR spectra for **1h**

7.971
7.955
7.366
7.364
7.351
7.349
7.306
7.290
7.273
7.270
7.250
7.240
7.236
7.206
7.200
7.196
7.190
7.082
7.067
7.054
7.039
6.884
6.882
6.874
6.873

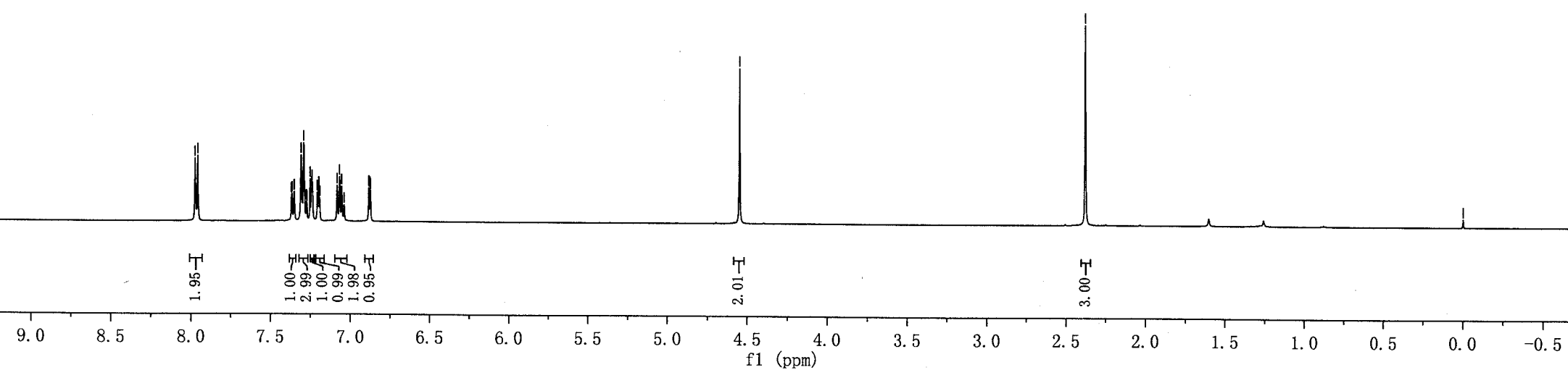
4.549

2.379

0.000



1i



144.91
140.86
134.28
133.42
129.64
129.48
129.28
129.13
128.34
125.16
124.54
121.10
118.62
114.88

87.44

81.78

80.71

77.25

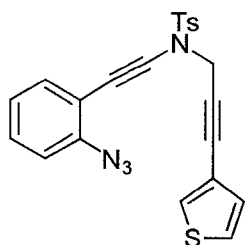
77.00

76.75

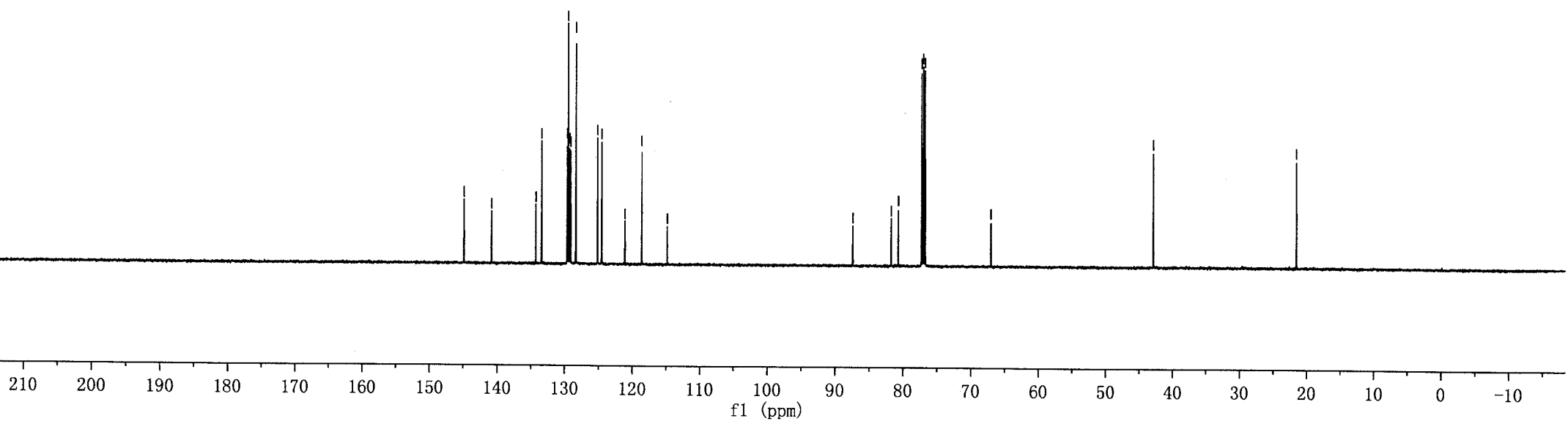
67.05

42.87

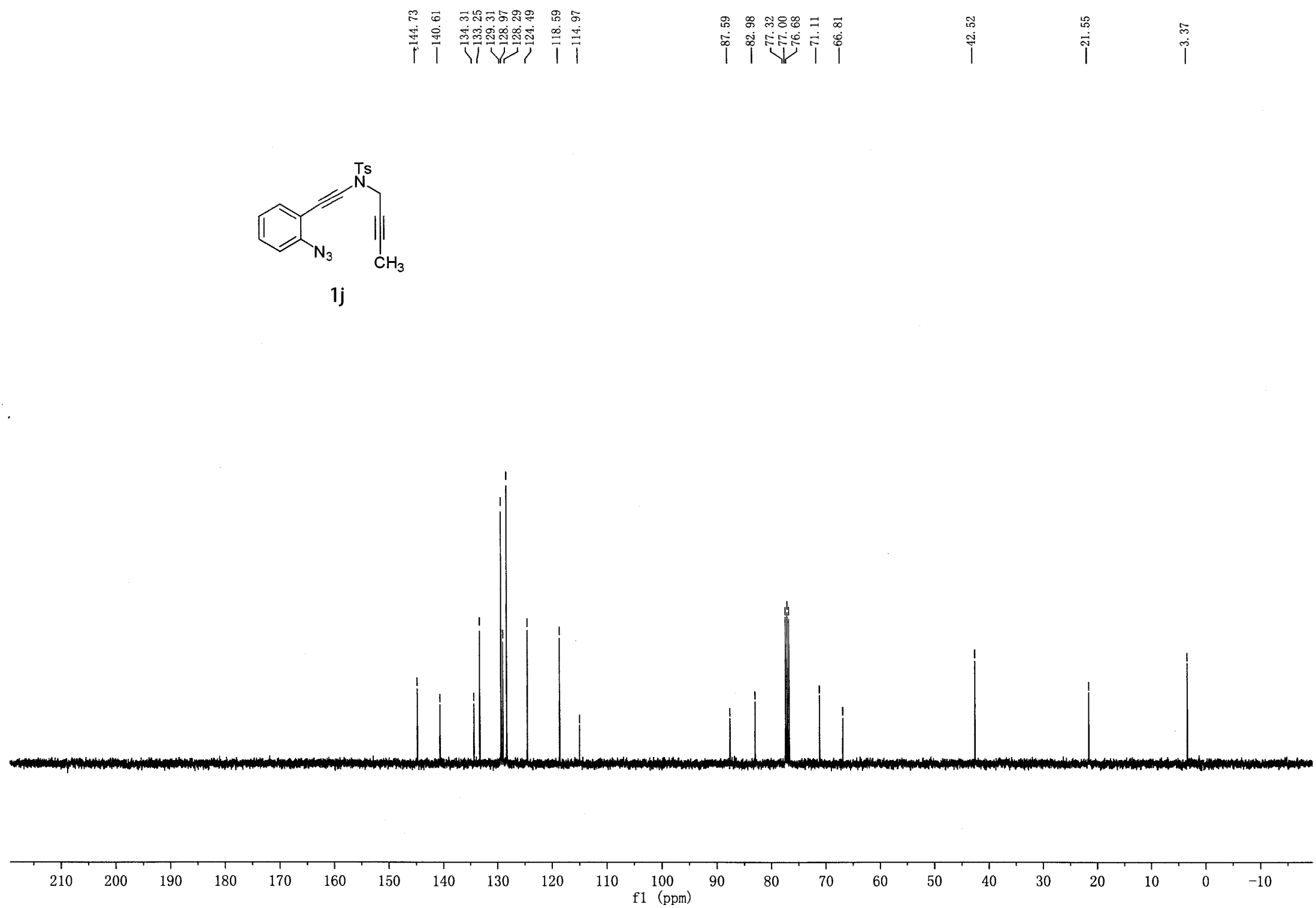
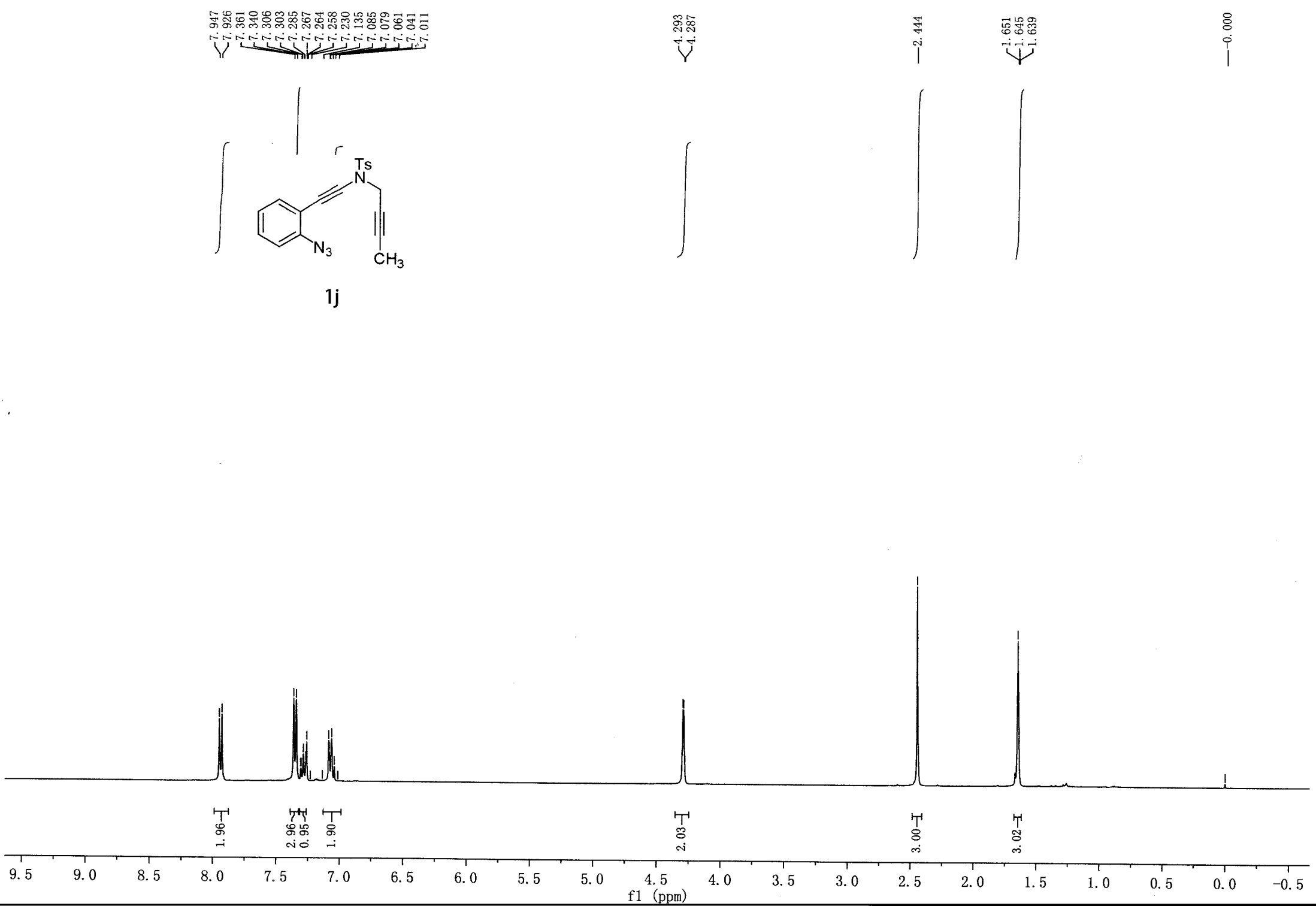
21.57



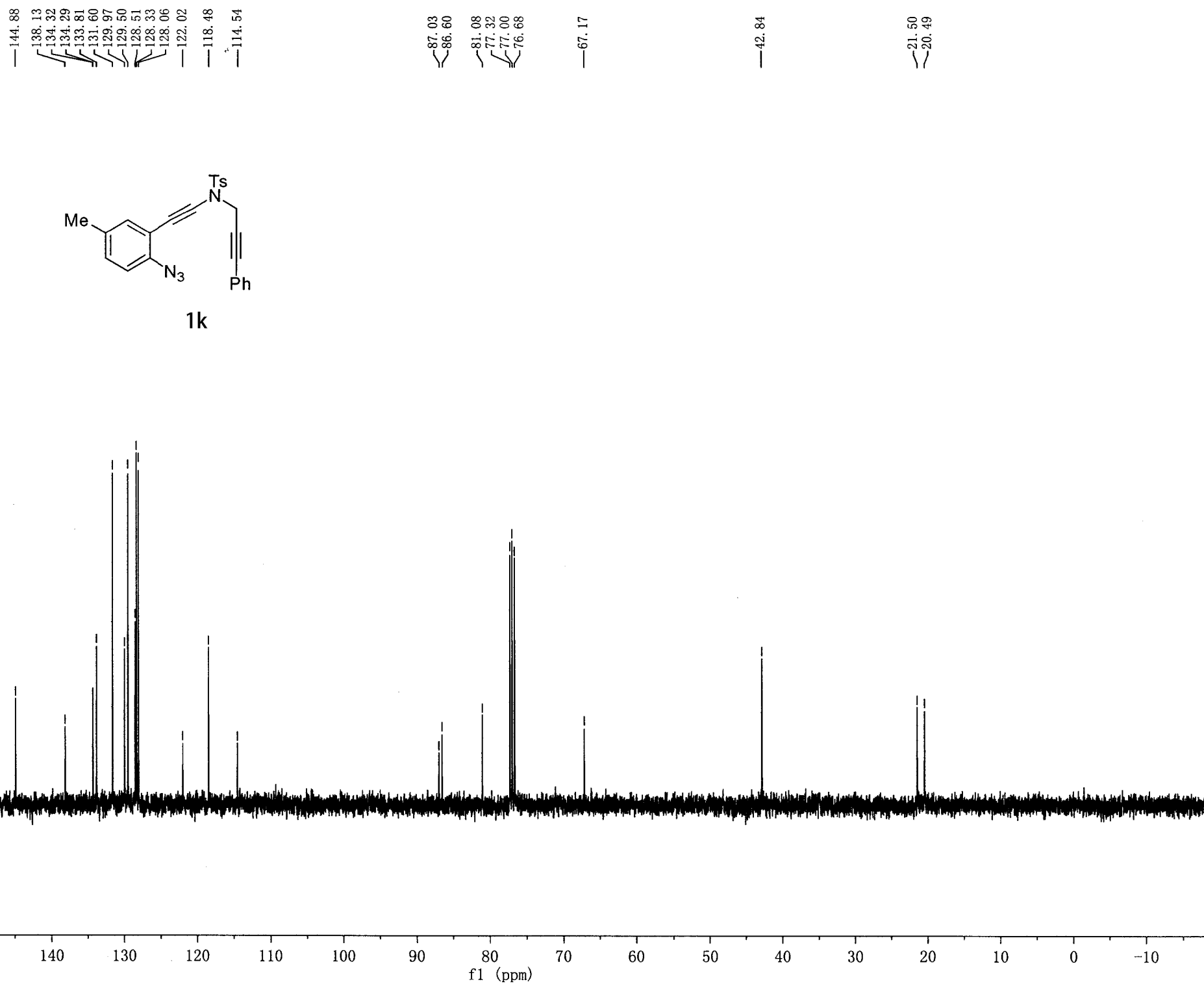
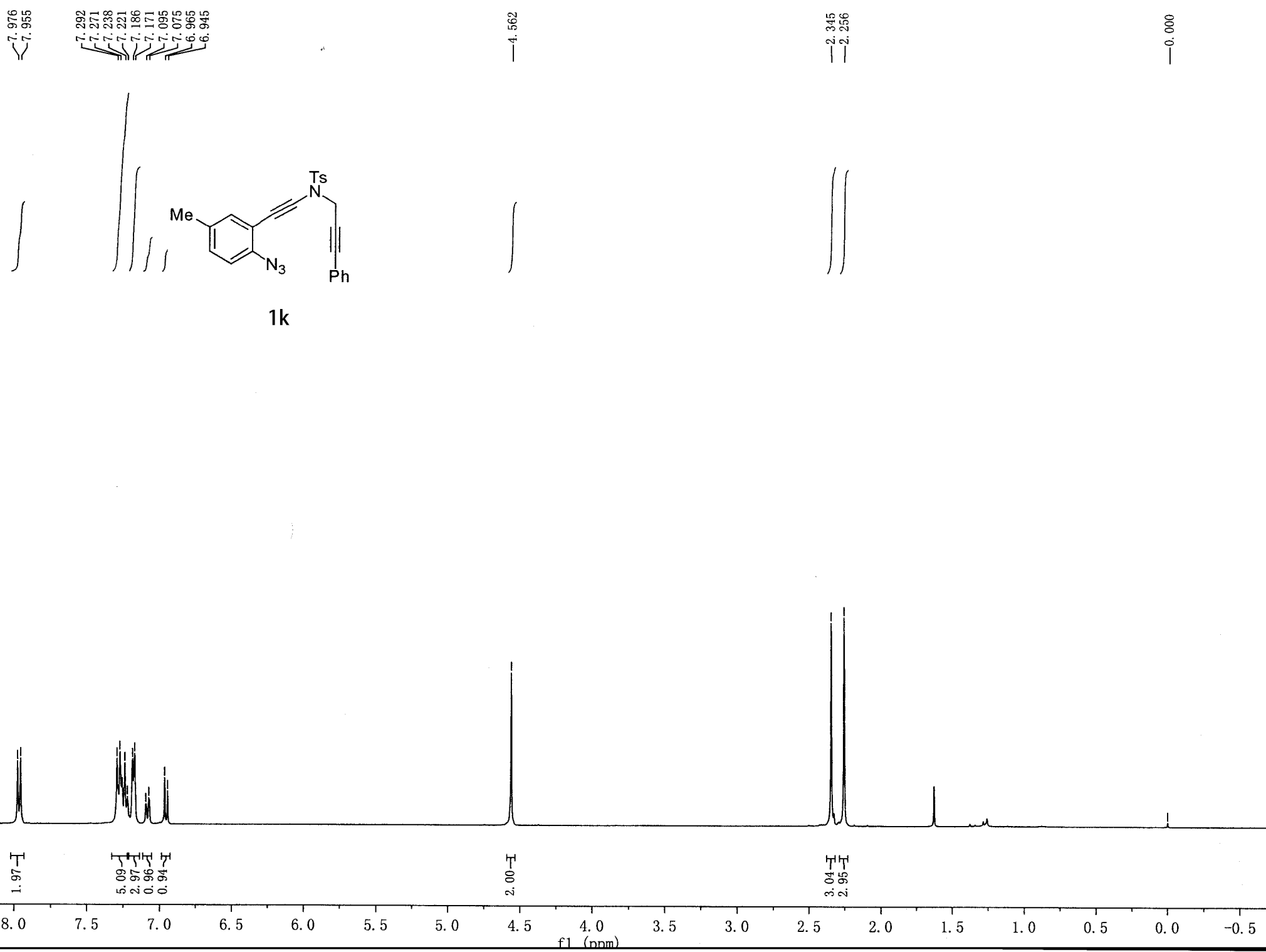
1i



Supplementary Figure 9. ^1H and ^{13}C NMR spectra for 1i



Supplementary Figure 10. ^1H and ^{13}C NMR spectra for **1j**

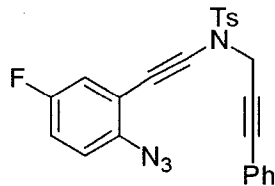


Supplementary Figure 11. ¹H and ¹³C NMR spectra for **1k**

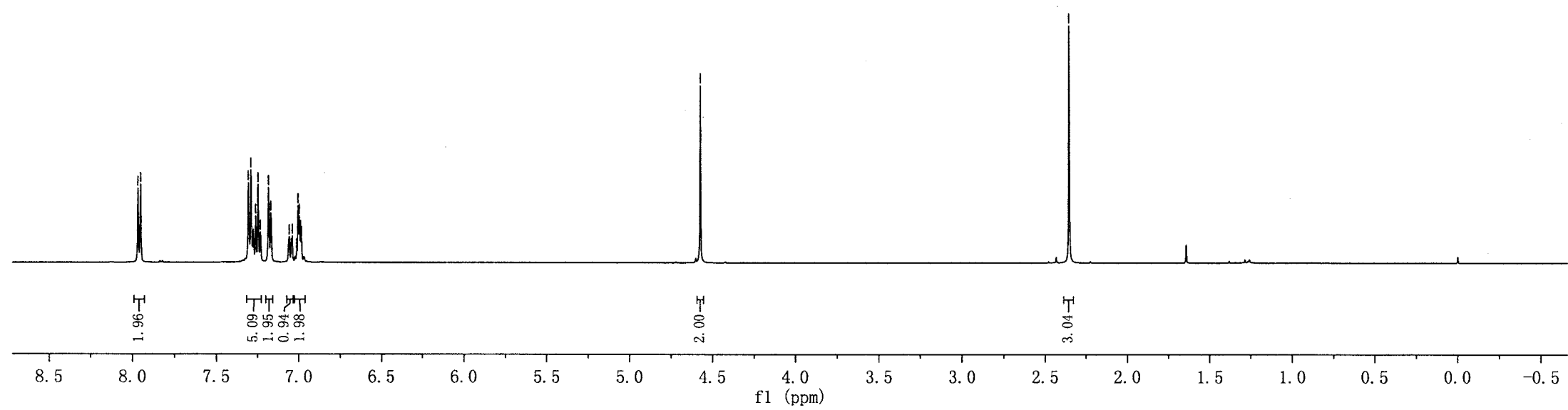
7.968
7.951
7.304
7.289
7.260
7.245
7.231
7.182
7.167
7.057
7.040
7.012
6.996
6.989
6.984

4.575

2.354



11



160.01
158.06

145.09
136.76
136.74
134.13
131.56
129.57
128.59
128.27
128.09
121.85
119.95
119.88
119.60
119.40
116.34
116.16

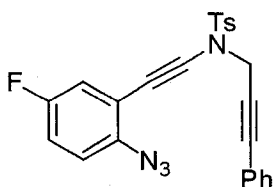
88.42
86.67

80.83
77.25
77.00
76.75

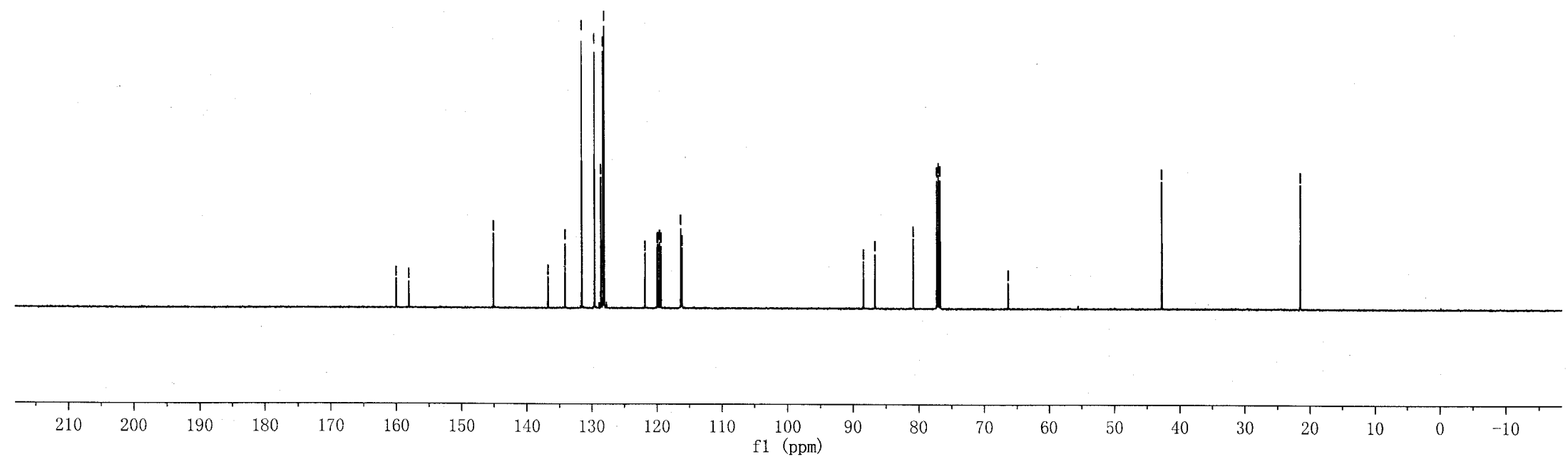
66.37
66.35

42.75

21.50



11



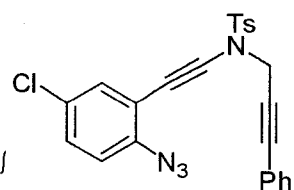
Supplementary Figure 12. ¹H and ¹³C NMR spectra for 11

7.962
7.946
7.324
7.320
7.312
7.296
7.268
7.254
7.242
7.188
7.173
7.003
6.986

4.574

2.364

0.000



1m

2.00

7.02
1.99
0.98

2.00

3.04

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

145.12

139.37

134.18

132.72

131.60

129.68

129.03

128.63

128.30

128.13

121.88

119.76

116.40

88.63

86.73

80.84

77.25

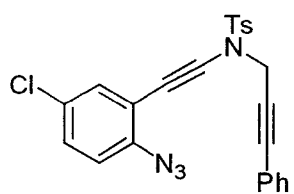
77.00

76.75

66.22

42.79

21.56



1m

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

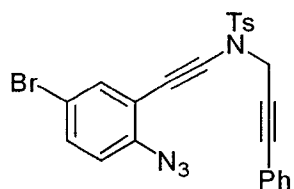
Supplementary Figure 13. ¹H and ¹³C NMR spectra for 1m

7.957
7.936
7.459
7.453
7.350
7.303
7.283
7.244
7.187
6.928
6.904

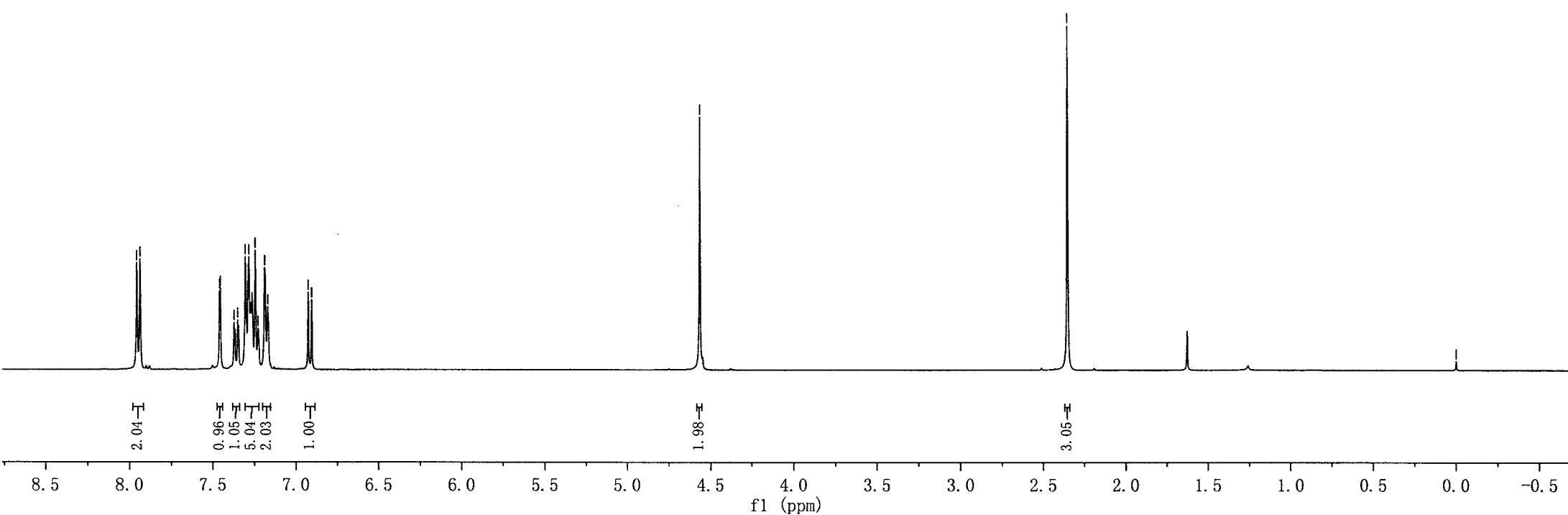
4.567

2.353

-0.000



1n



145.08
139.86
135.55
134.19
131.86
131.57
129.58
128.60
128.25
128.10
121.86
120.04
116.98
116.79

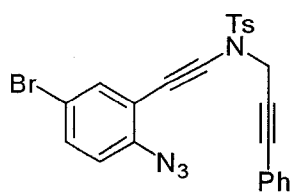
88.79
86.74

80.85
77.32
77.00
76.68

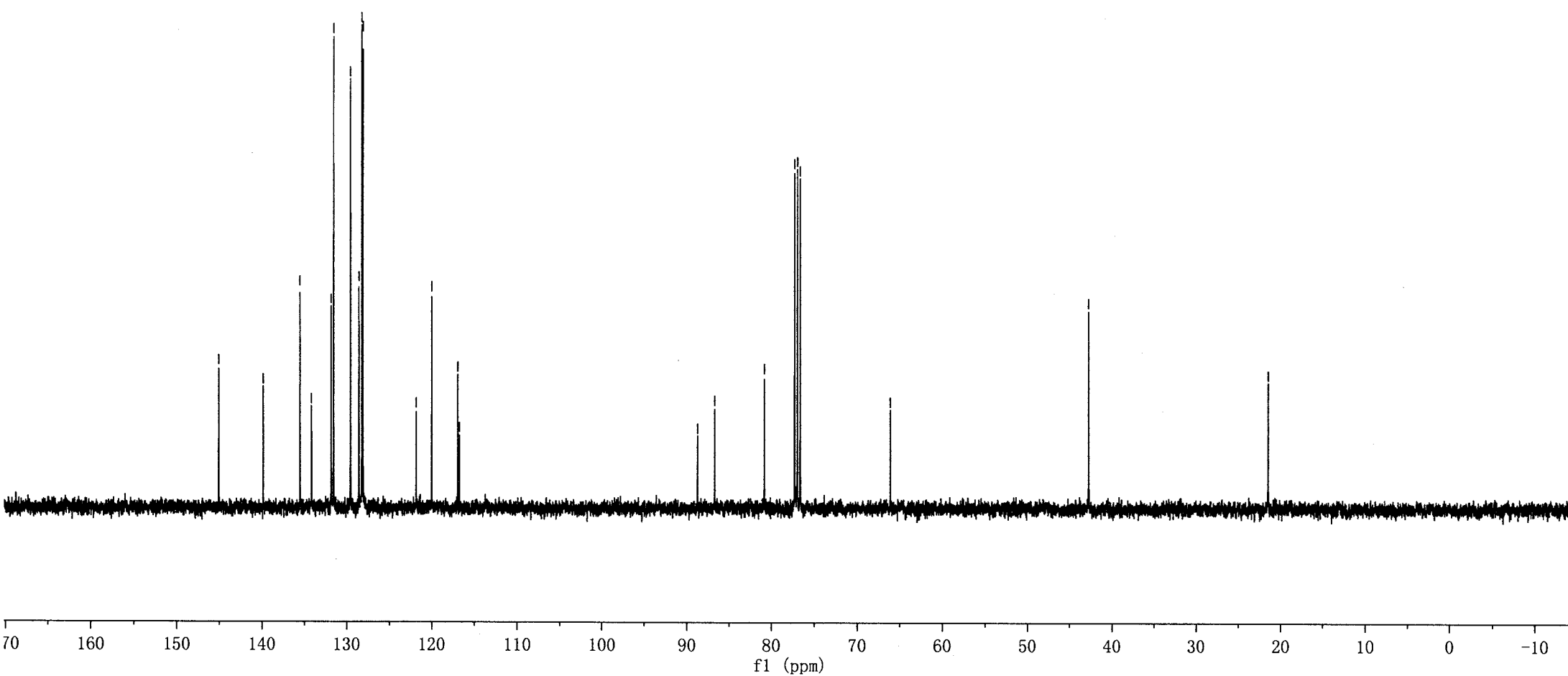
66.11

42.76

21.51



1n



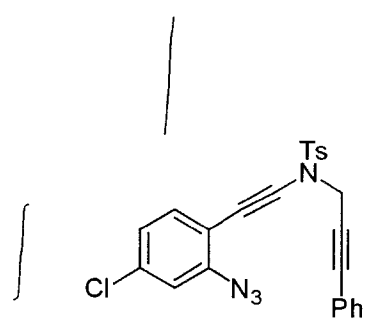
Supplementary Figure 14. ¹H and ¹³C NMR spectra for 1n

7.955
7.939
7.296
7.283
7.273
7.267
7.257
7.246
7.242
7.227
7.173
7.159
7.068
7.049
7.046
7.032
7.028
7.015
7.012
6.982

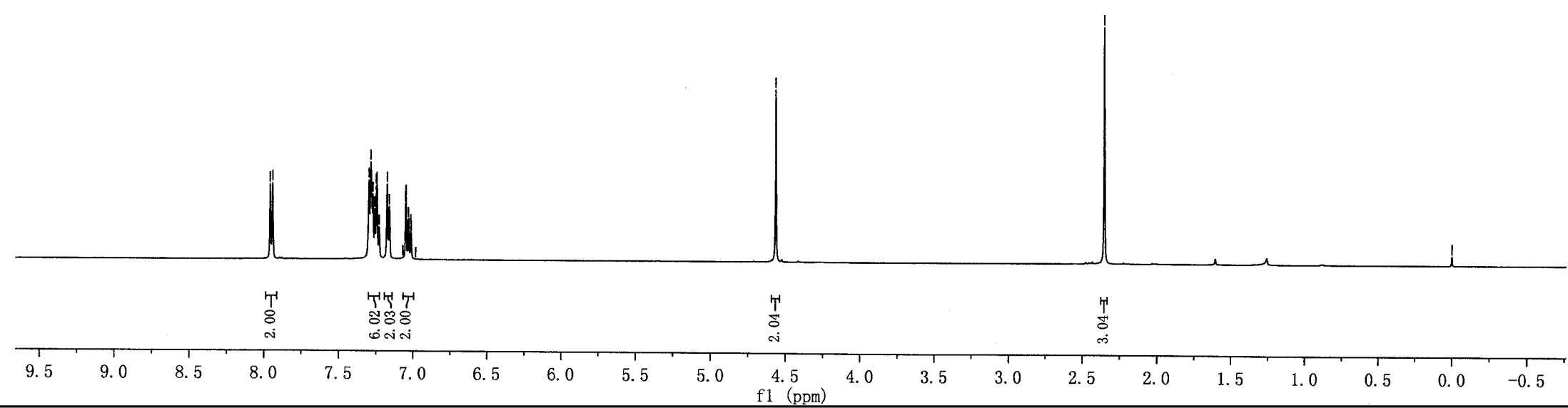
4.564

2.352

0.000



10



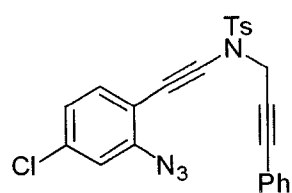
145.02
142.06
134.65
134.22
131.56
129.54
128.58
128.29
128.10
124.90
121.92
118.86
113.49

88.28
86.66
80.93
77.25
77.00
76.75

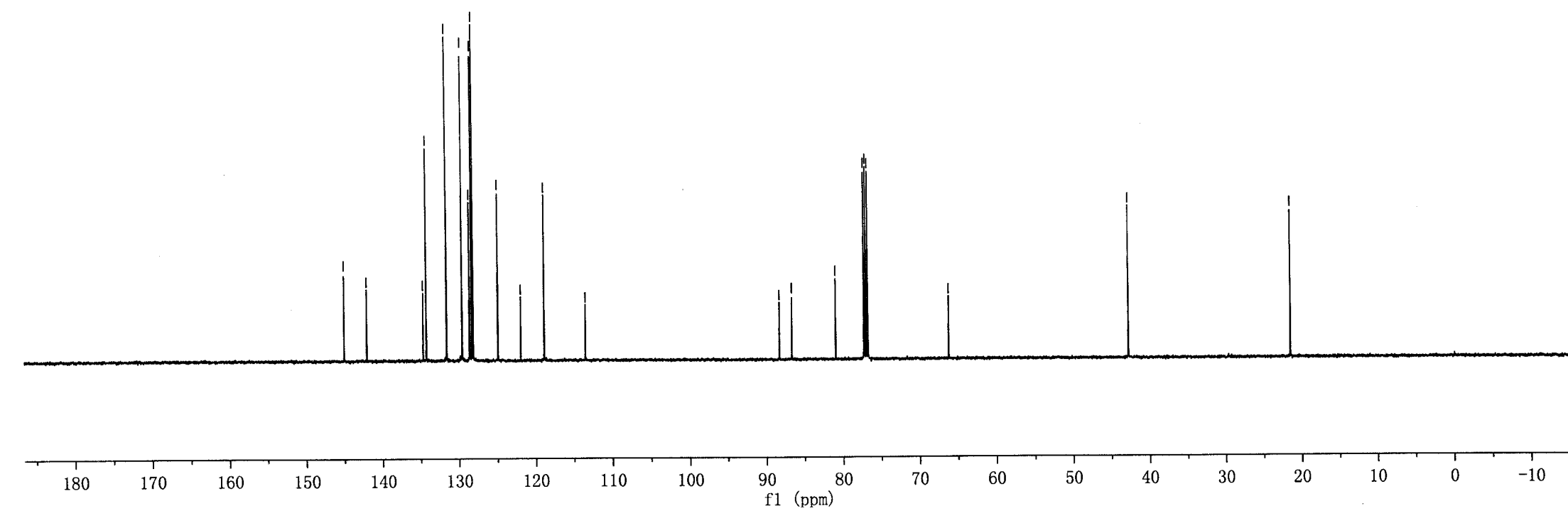
66.19

42.78

21.52



10

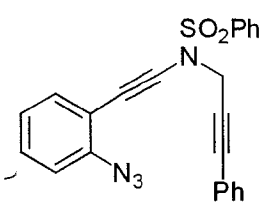


Supplementary Figure 15. ^1H and ^{13}C NMR spectra for 10

8.103
8.085
7.610
7.592
7.573
7.523
7.503
7.485
7.363
7.360
7.344
7.341
7.279
7.235
7.196
7.164
7.119
7.068
7.047
7.022
7.020
6.954

4.596

0.000



1p

2.00
1.02
2.00
1.00
6.09
1.90

2.11

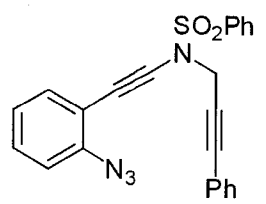
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

140.92
137.17
133.77
133.45
131.58
129.21
128.86
128.58
128.25
128.09
124.50
121.85
118.56
114.67

87.10
86.69
80.91
77.32
77.00
76.68

67.11

42.88



1p

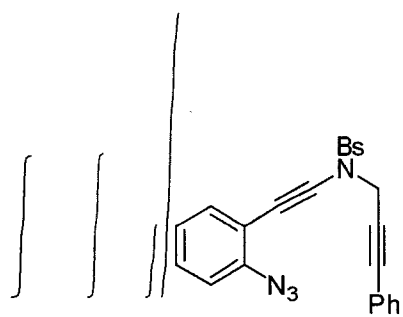
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Supplementary Figure 16. ¹H and ¹³C NMR spectra for 1p

7.963
7.947
7.631
7.614
7.374
7.359
7.319
7.304
7.285
7.269
7.255
7.244
7.157
7.142
7.093
7.076
7.059
7.044

4.596

0.000



1q

1.97
2.00
1.01
3.99
1.97
2.00

2.00

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

f1 (ppm)

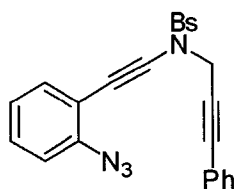
141.08
136.12
133.51
132.15
131.52
129.78
129.40
129.23
128.71
128.25
124.55
121.61
118.54
114.38

86.97
86.74

80.65
77.25
77.00
76.75

67.24

43.08



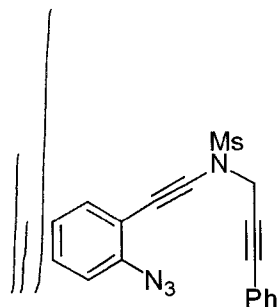
1q

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

Supplementary Figure 17. ¹H and ¹³C NMR spectra for 1q

7.475
7.460
7.436
7.421
7.376
7.362
7.344
7.328
7.309
7.253
7.131
7.108
7.097
7.082
7.067
7.041



4.619

3.317

0.000

1.95
1.00
4.00

1.95

2.03

3.00

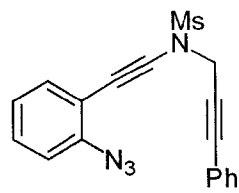
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

141.20
133.68
131.78
129.52
129.01
128.43
124.60
121.70
118.65
114.44

87.08
86.69
81.39
77.25
77.00
76.75

67.19

42.91
38.81



1r

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

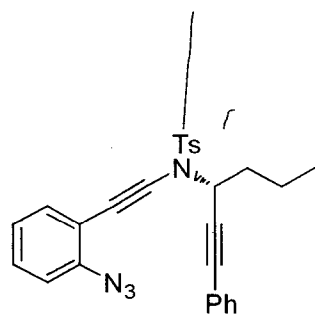
Supplementary Figure 18. ¹H and ¹³C NMR spectra for 1r

7.971
7.951
7.387
7.384
7.367
7.365
7.307
7.286
7.268
7.247
7.227
7.208
7.191
7.187
7.123
7.094
7.074
7.053
7.034
7.010

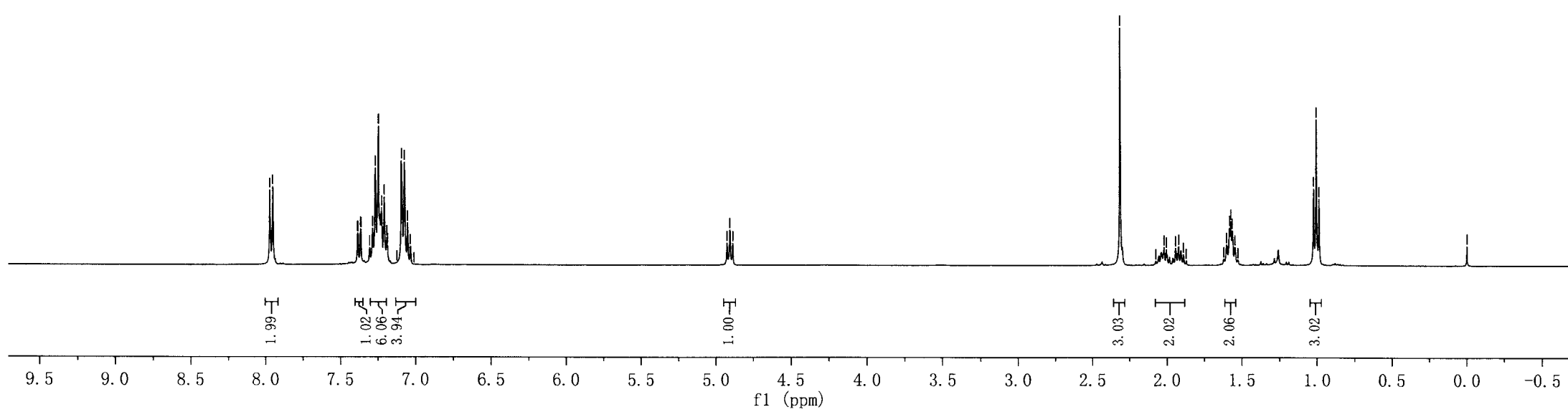
4.926
4.907
4.888

2.314
2.022
2.006
1.945
1.924
1.603
1.583
1.575
1.565
1.554
1.005
0.987

-0.000



1s



144.66
141.02
134.63
133.42
131.54
129.39
128.97
128.35
128.27
127.99
124.48
122.24
118.50
115.18

85.77
85.31
84.97
77.32
77.00
76.68

68.74

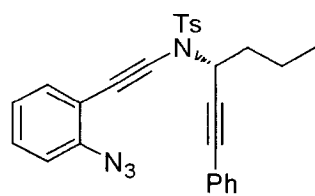
53.24

36.46

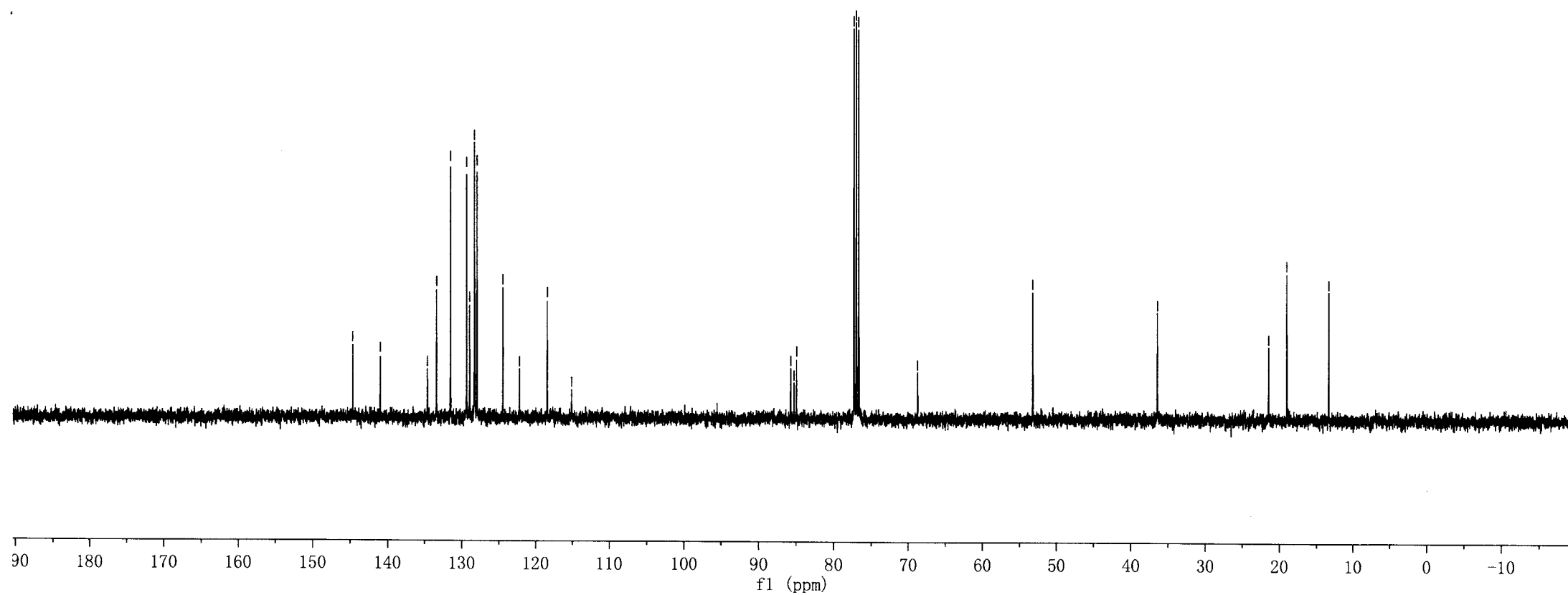
21.49

19.05

13.36



1s



Supplementary Figure 19. ¹H and ¹³C NMR spectra for 1s

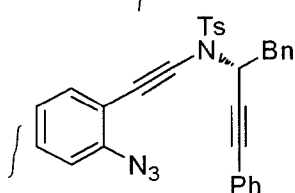
7.857
7.837
7.422
7.403
7.356
7.338
7.311
7.232
7.213
7.197
7.151
7.123
7.100
7.080
7.061
7.041

5.144
5.125
5.106

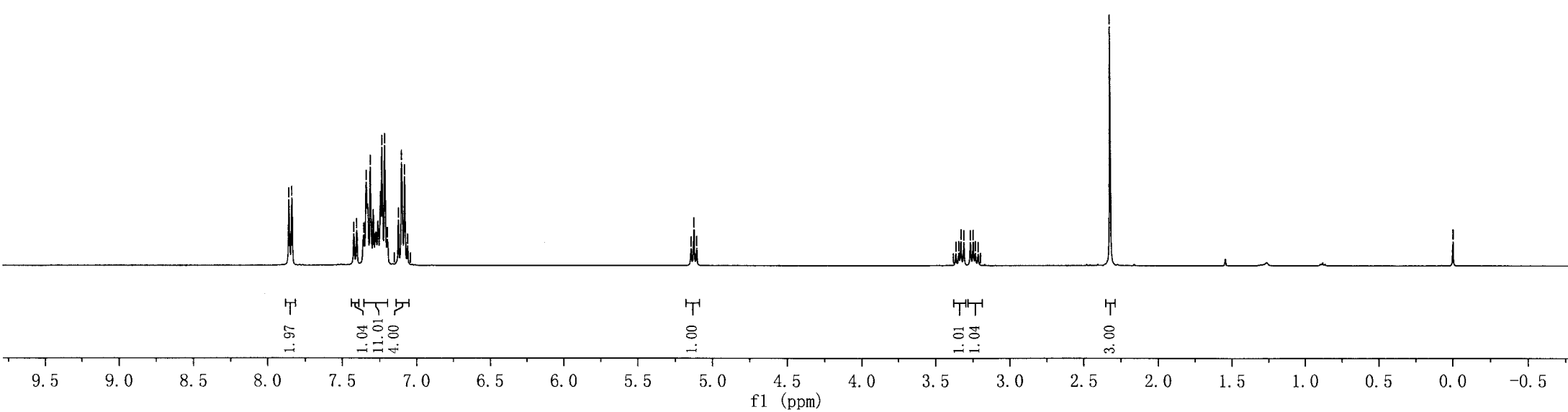
3.380
3.362
3.343
3.328
3.309
3.265
3.246
3.231
3.212
3.197

2.322

0.000



1t



144.64
141.08
136.02
134.55
133.40
131.54
129.58
129.40
129.05
128.47
128.39
128.29
128.03
127.09
124.54
122.13
118.49
115.11

86.70
85.24
84.54

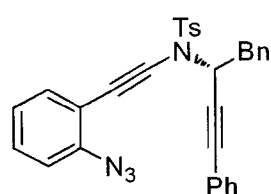
77.32
77.00
76.68

69.50

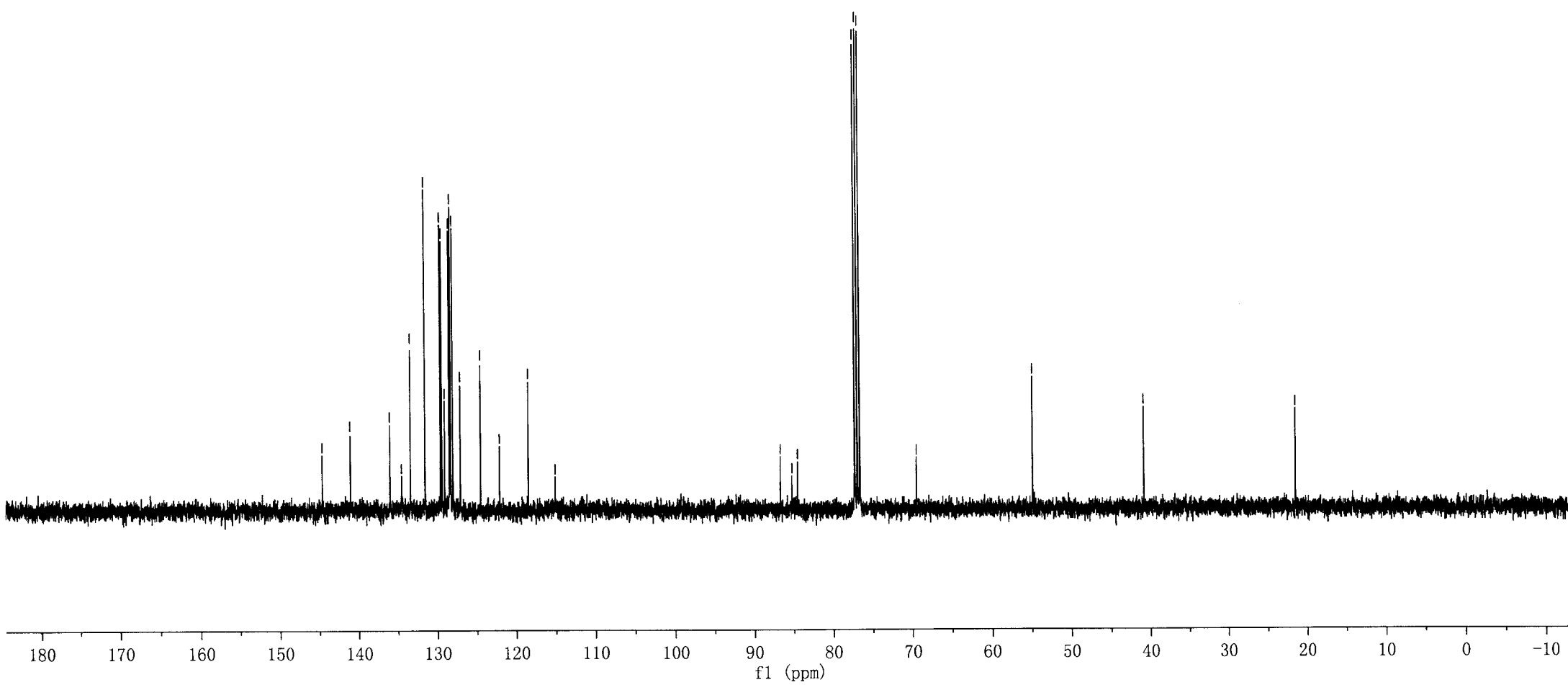
54.90

40.84

21.52



1t



Supplementary Figure 20. ¹H and ¹³C NMR spectra for 1t

7.972
7.956
7.714
7.710
7.693
7.673
7.317
7.305
7.291
7.276
7.262
7.247
7.244
7.222
7.205
7.201
7.199
7.185
7.182

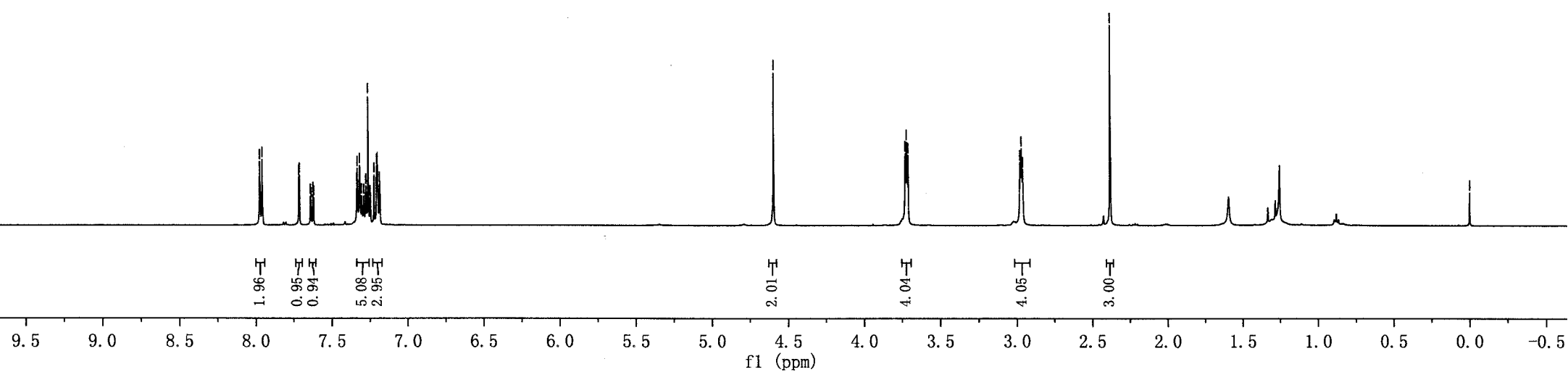
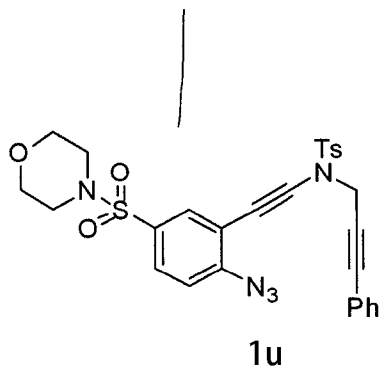
4.597

3.730
3.721
3.711

2.979
2.970
2.961

2.382

0.000



145.33
145.30
132.48
131.62
131.33
129.72
128.73
128.32
128.21
127.85
119.02
116.12

89.82

86.87

80.76

77.25

77.00

76.75

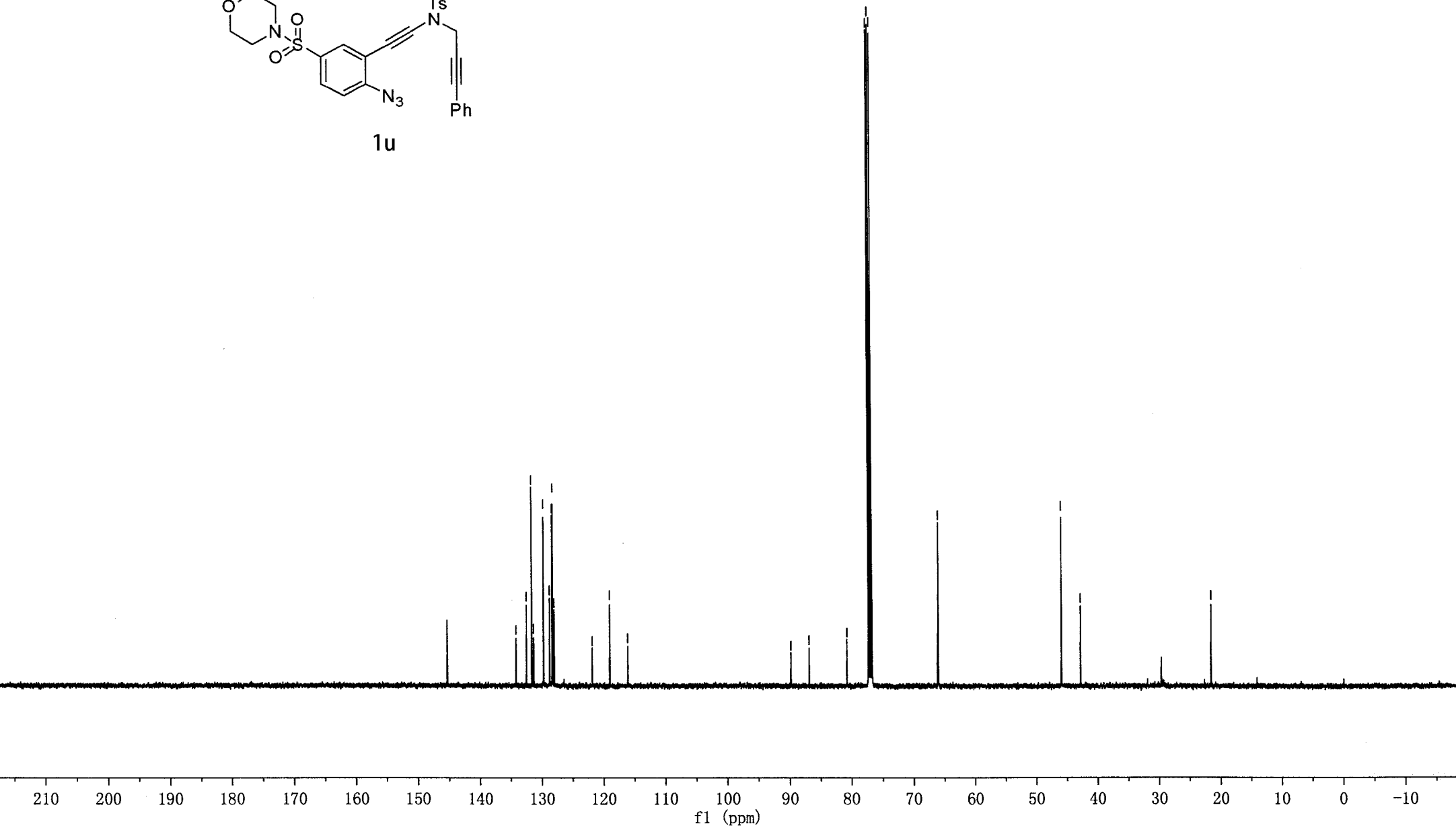
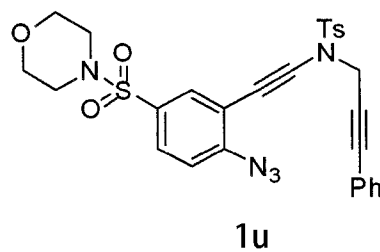
66.13

65.99

45.93

42.81

21.60



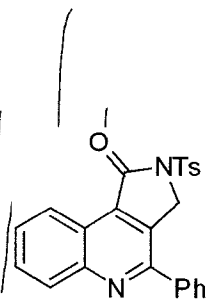
Supplementary Figure 21. ¹H and ¹³C NMR spectra for 1u

8.948
8.927
8.264
8.243
8.090
8.069
7.884
7.867
7.843
7.824
7.804
7.713
7.694
7.675
7.613
7.597
7.578
7.556
7.538
7.377
7.357
7.260

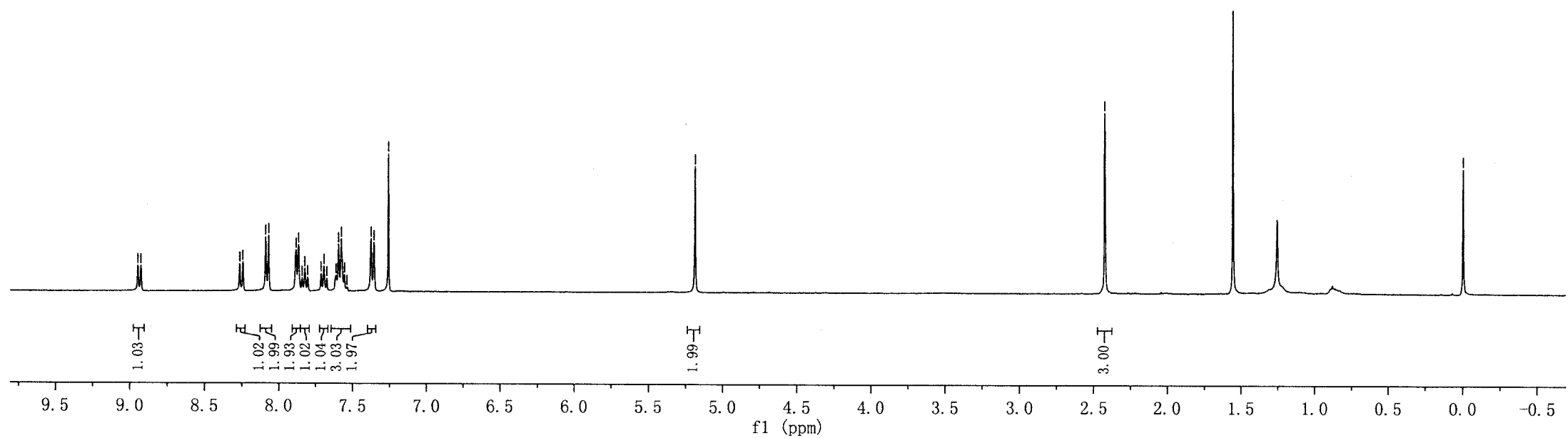
5.189

2.425

0.000



2a

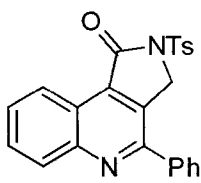


165.79
153.95
148.36
145.66
133.57
130.70
130.03
129.93
129.90
129.21
128.95
128.29
128.12
128.12
122.07

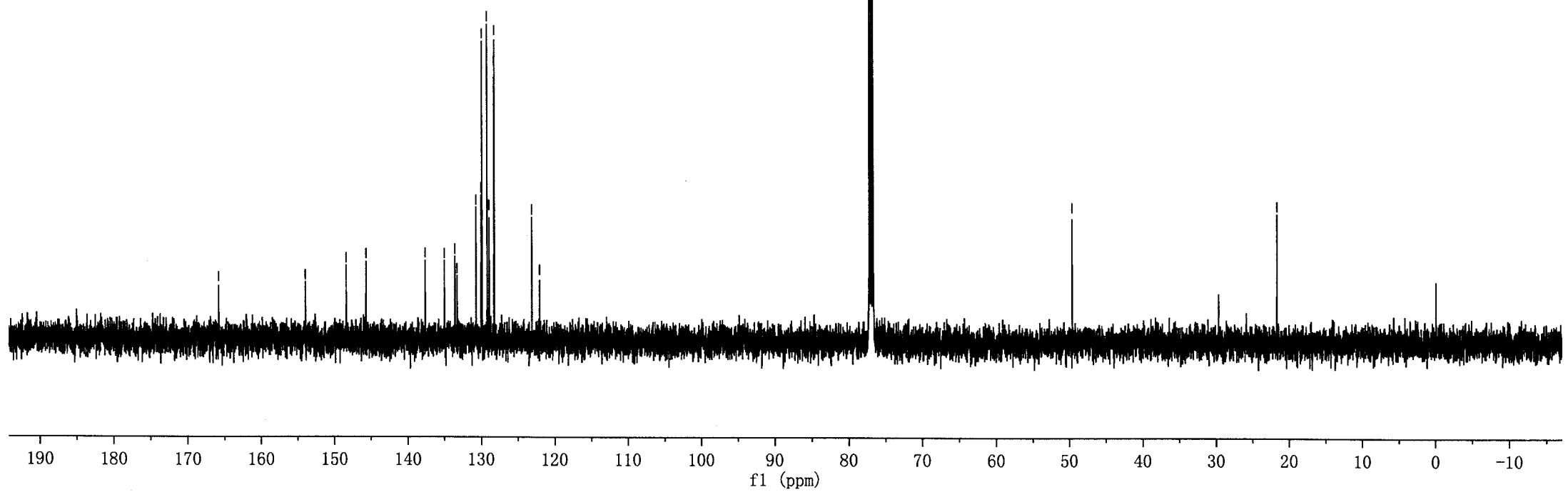
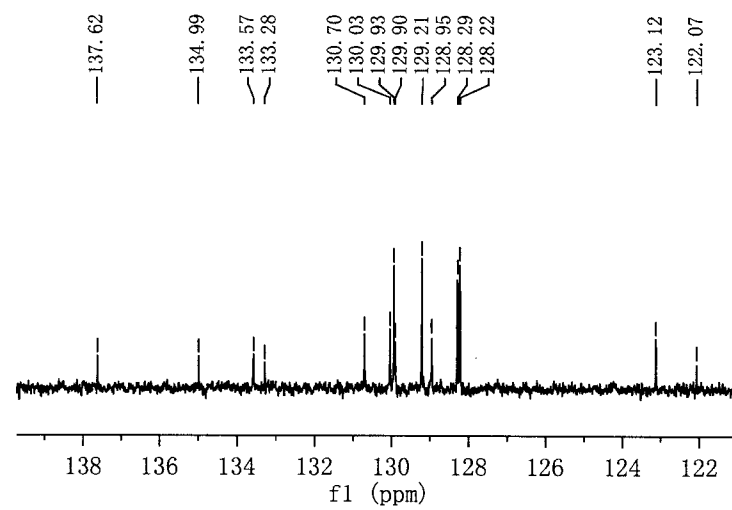
77.25
77.00
76.75

49.62

21.71



2a



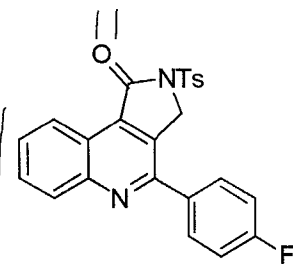
Supplementary Figure 22. ^1H and ^{13}C NMR spectra for 2a

8.936
8.920
8.234
8.217
8.089
8.073
7.911
7.900
7.894
7.883
7.822
7.806
7.706
7.692
7.378
7.361
7.315
7.298
7.281
7.264
7.260

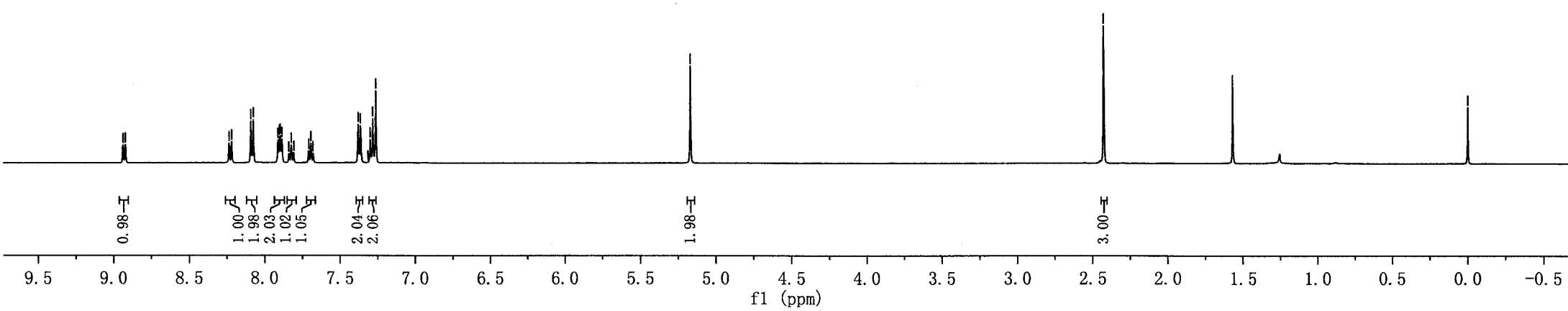
5.168

2.425

-0.000



2b

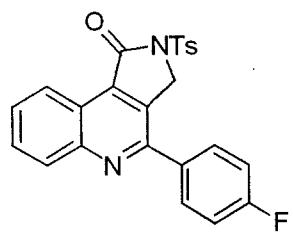


165.64
164.89
162.89
152.72
148.30
145.71
134.97
133.74
133.23
130.81
130.29
130.22
129.94
129.81
129.03
128.30
128.14
122.05
116.39
116.22

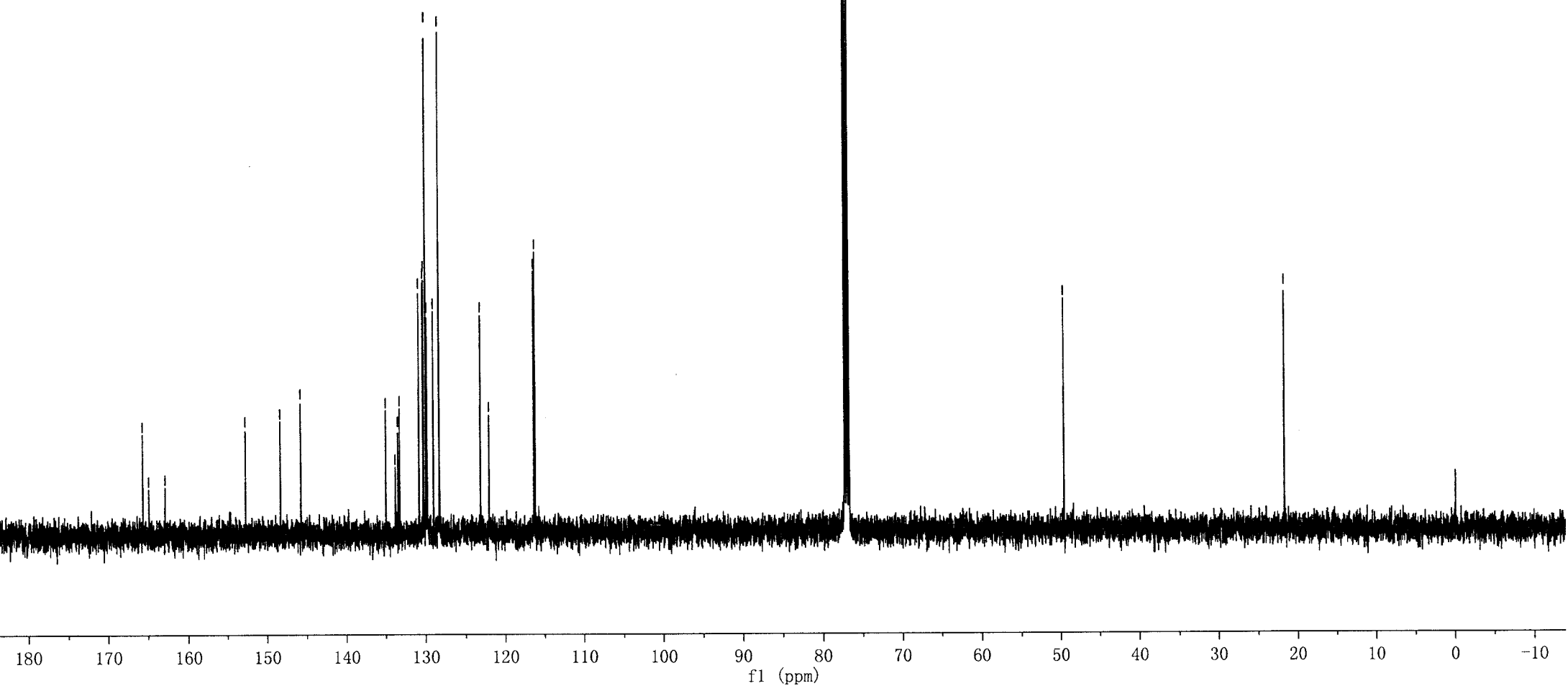
77.25
77.00
76.75

49.55

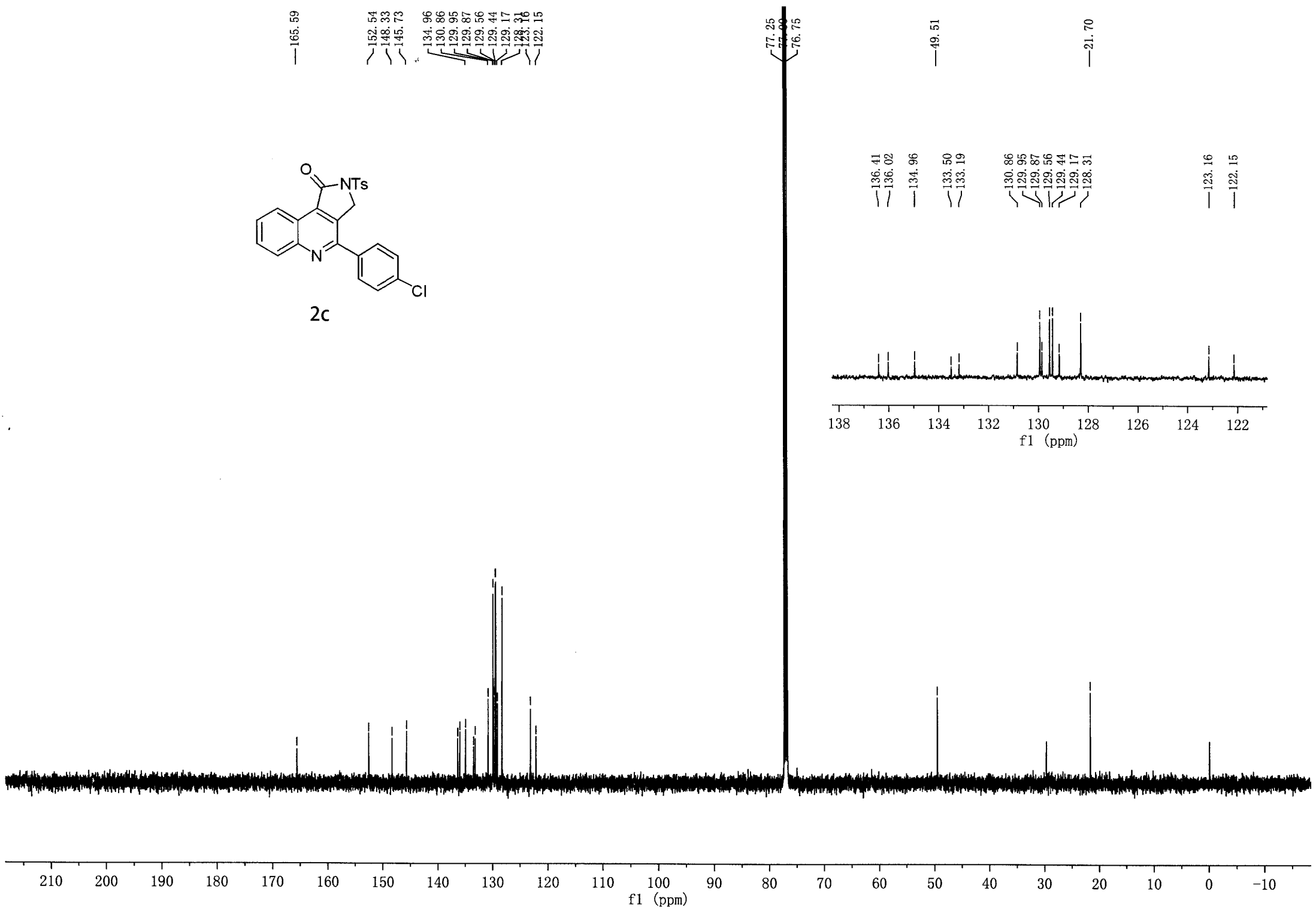
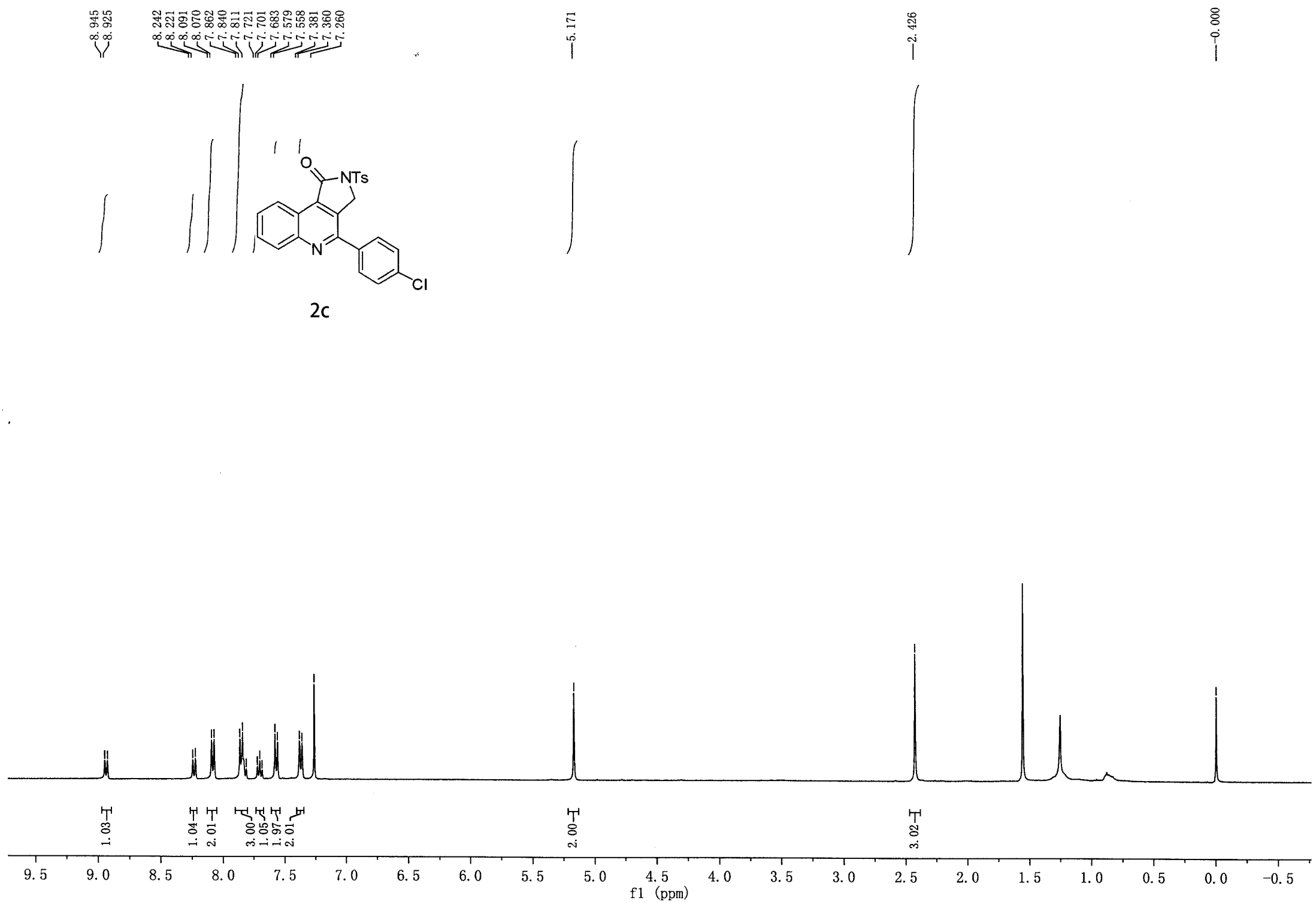
21.70



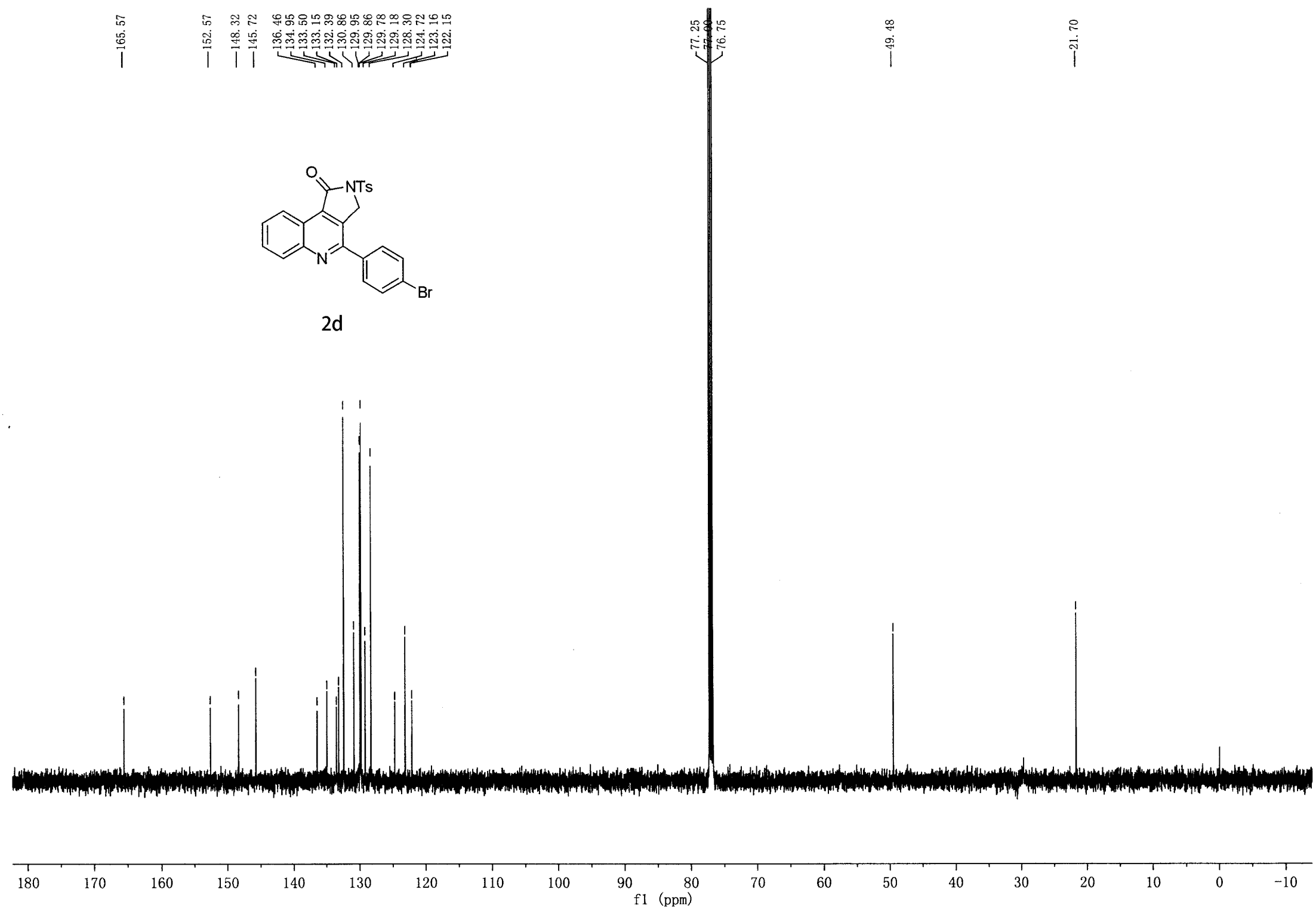
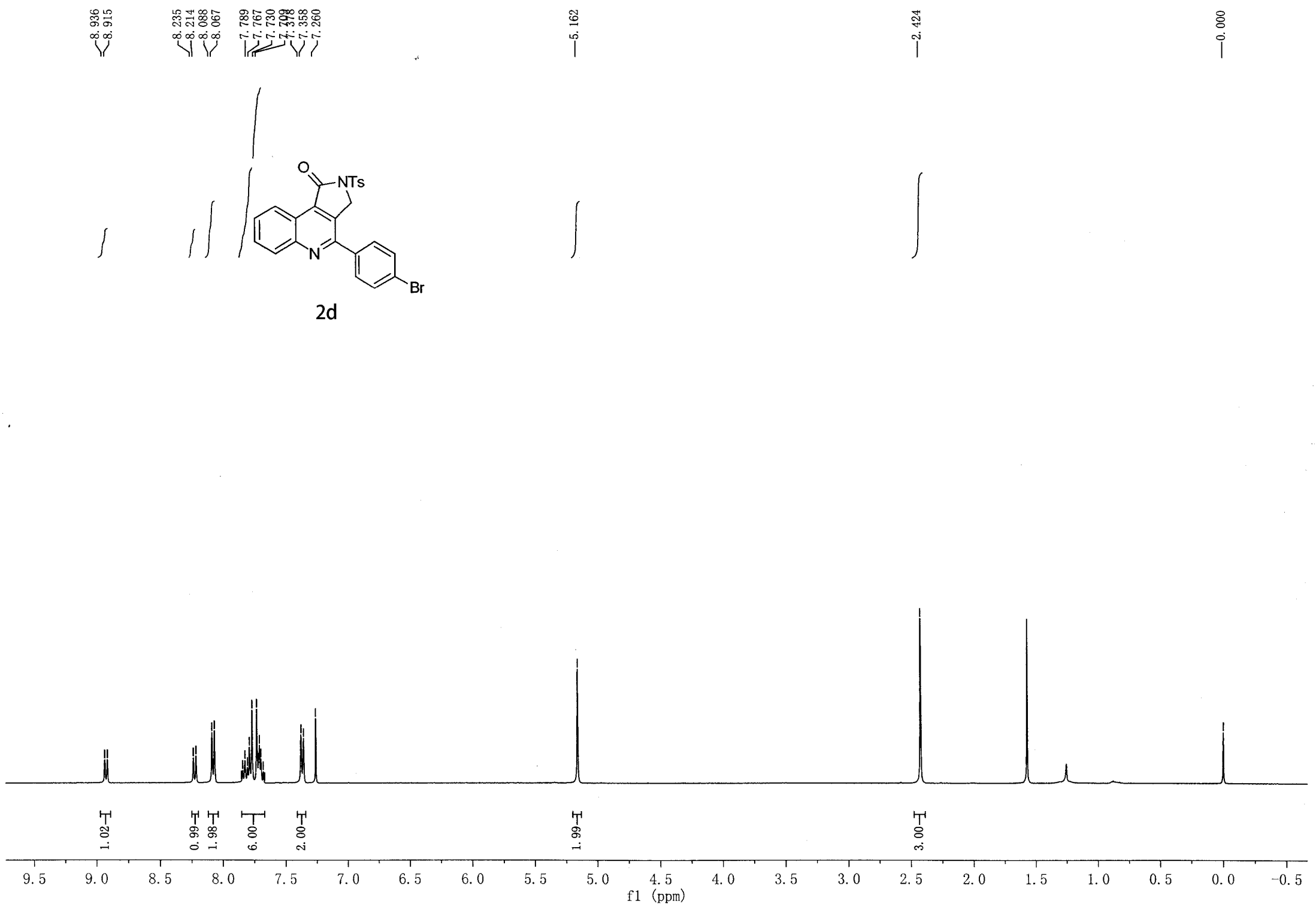
2b



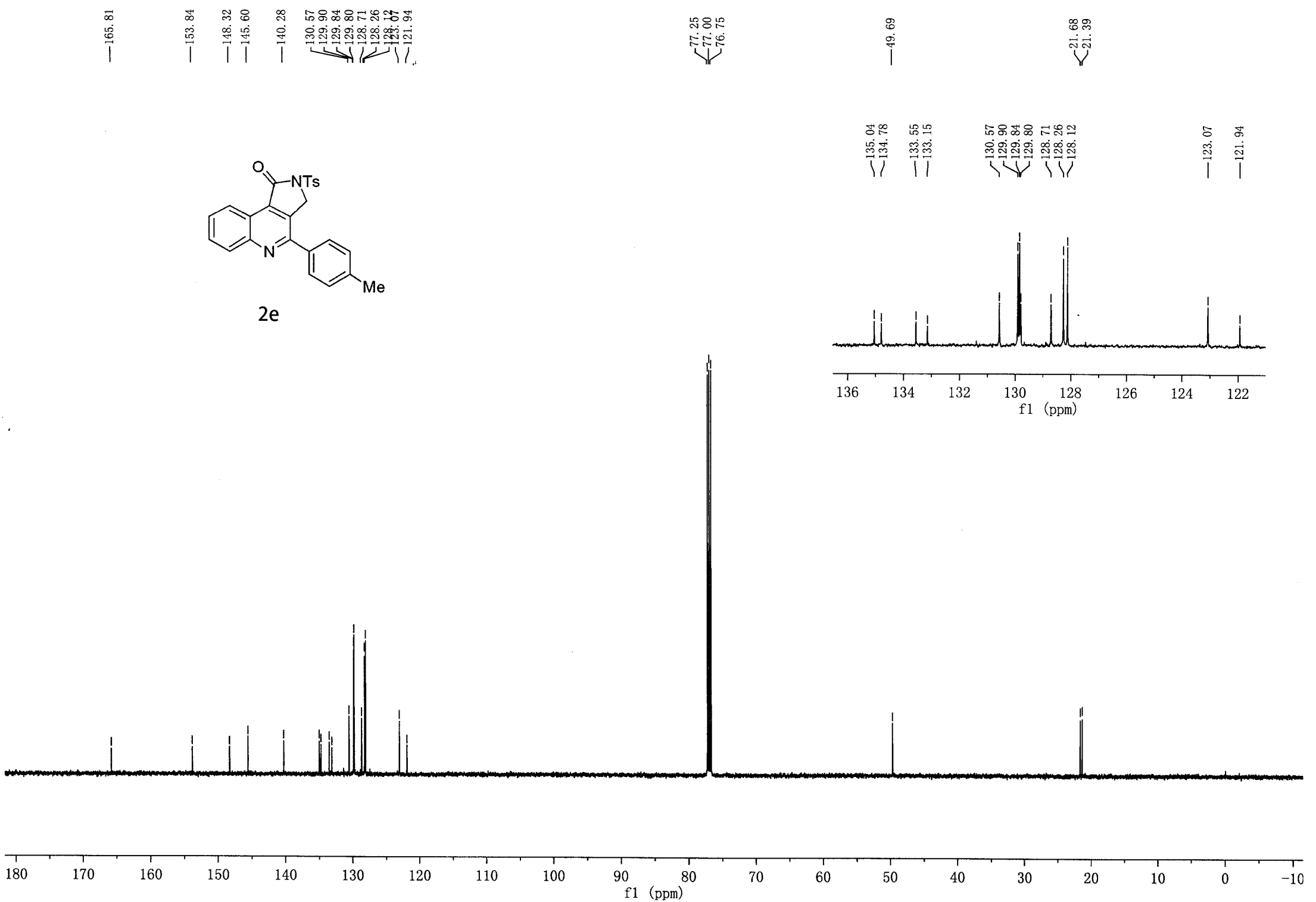
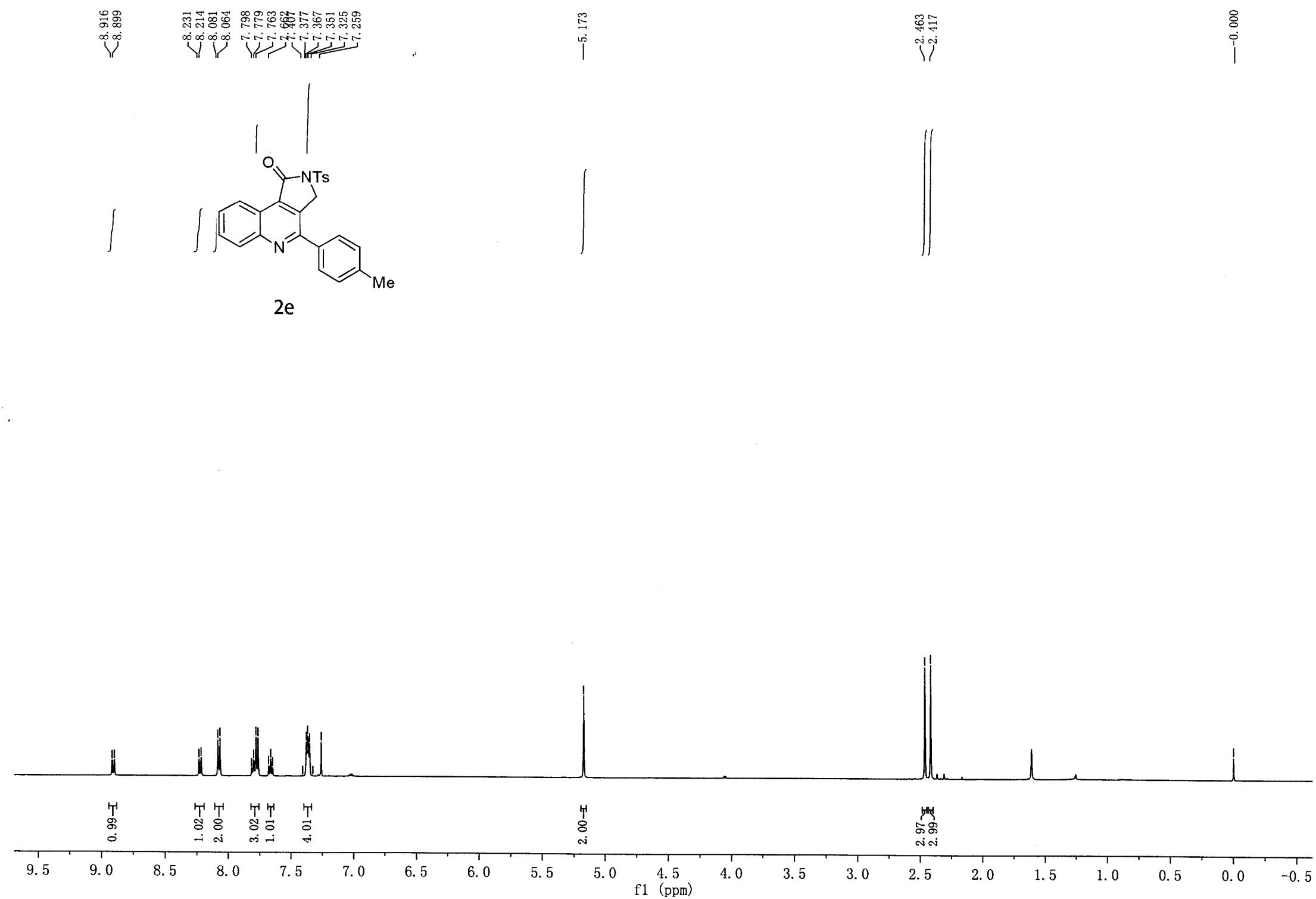
Supplementary Figure 23. ¹H and ¹³C NMR spectra for 2b



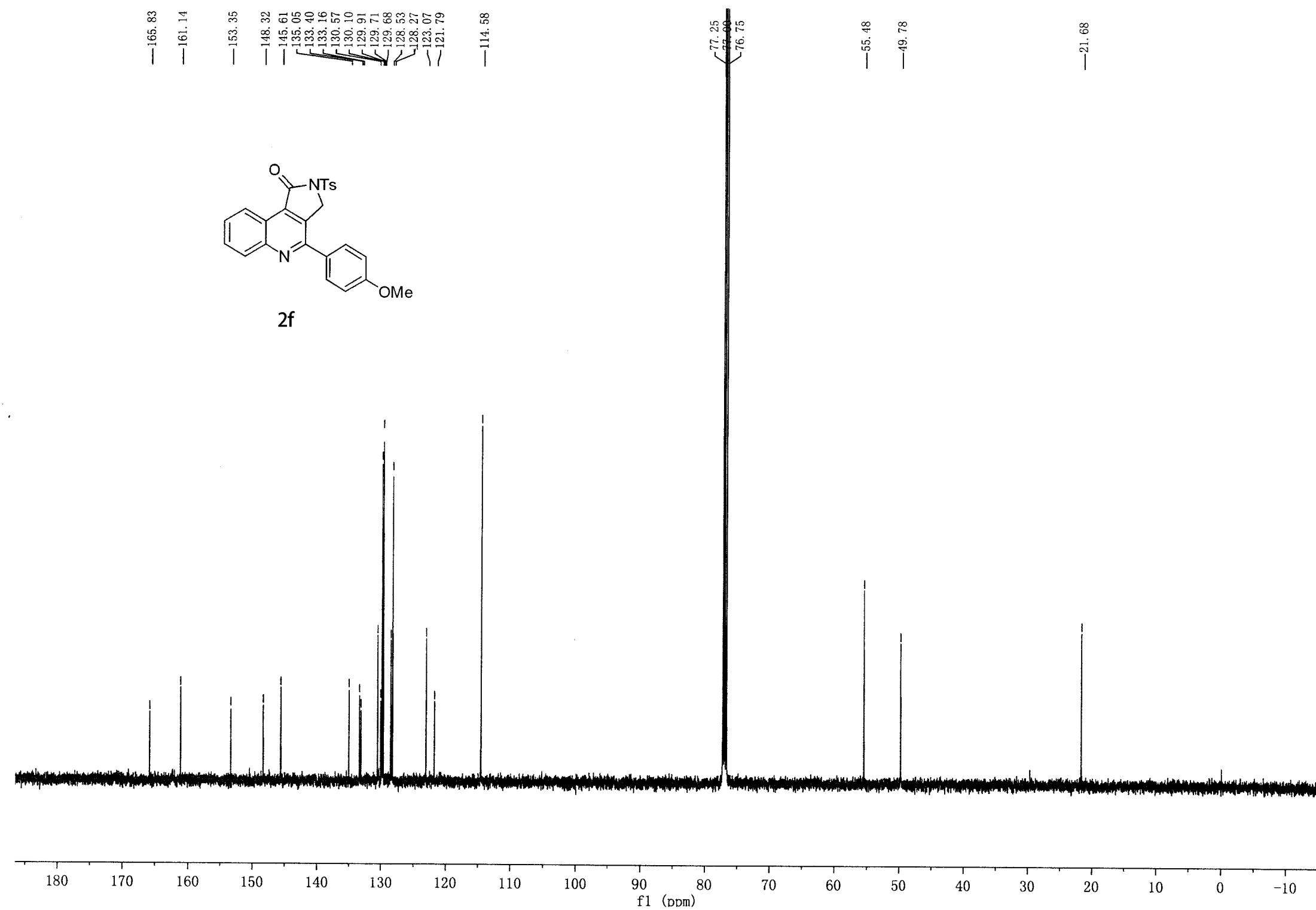
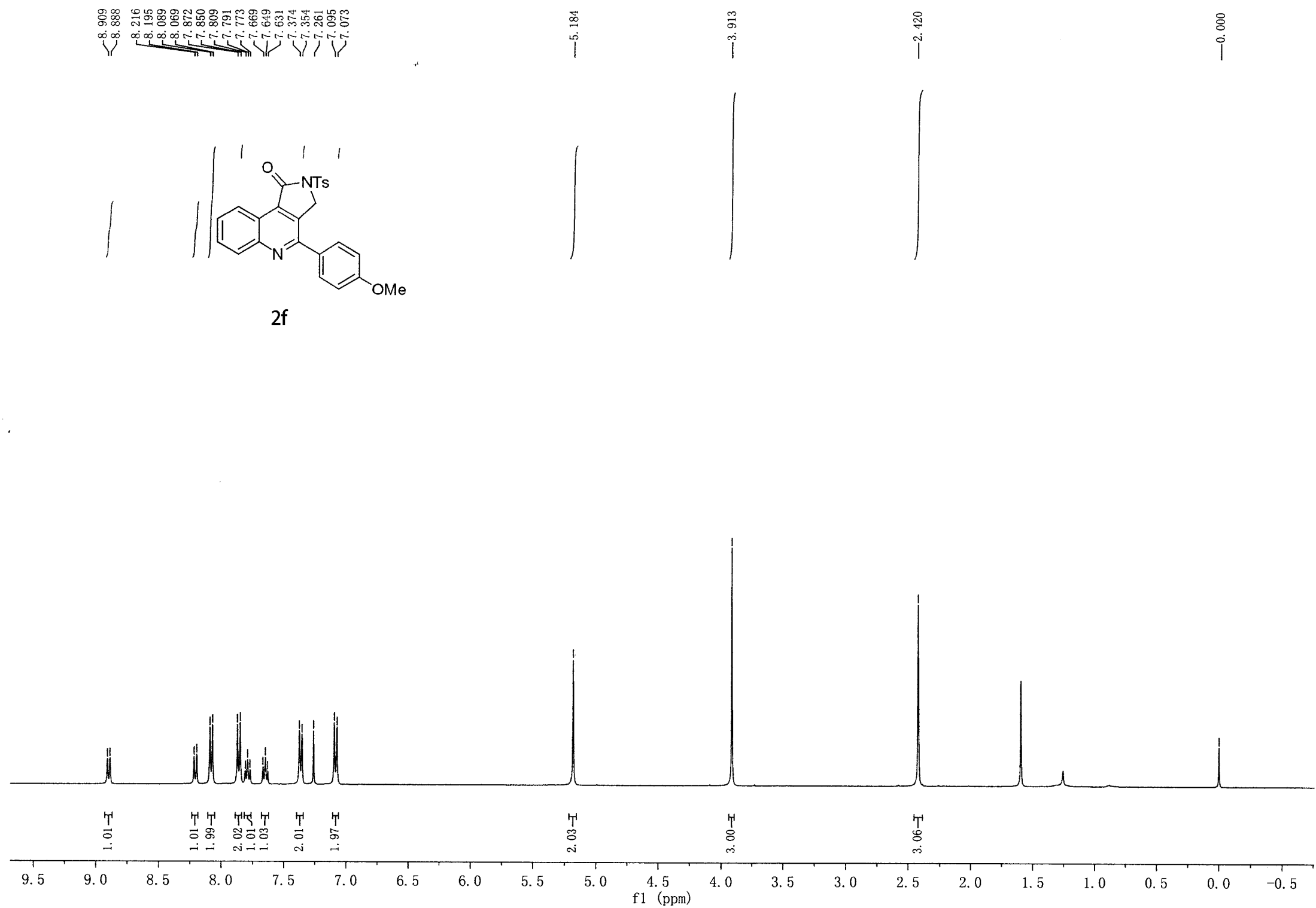
Supplementary Figure 24. ¹H and ¹³C NMR spectra for **2c**



Supplementary Figure 25. ^1H and ^{13}C NMR spectra for **2d**



Supplementary Figure 26. ¹H and ¹³C NMR spectra for 2e



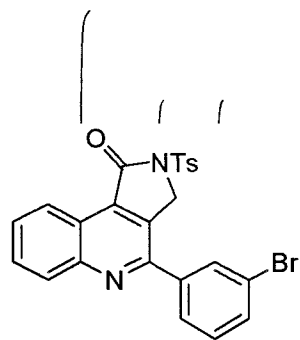
Supplementary Figure 27. ¹H and ¹³C NMR spectra for **2f**

8.932
8.916
8.240
8.224
8.087
8.074
7.843
7.829
7.813
7.760
7.745
7.717
7.702
7.686
7.669
7.468
7.453
7.437
7.377
7.361
7.261

5.160

2.423

0.000



2g

0.97

1.05

2.96

1.00

0.98

2.00

1.04

2.00

2.00

3.01

10.5 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 -0.5

f1 (ppm)

165.52

152.19

148.25

145.72

139.52

134.93

133.50

133.23

133.01

131.52

130.89

130.54

129.94

129.91

129.31

128.31

126.46

123.51

123.14

122.22

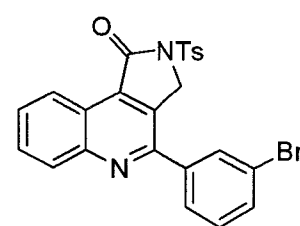
77.25

77.00

76.75

49.38

21.70

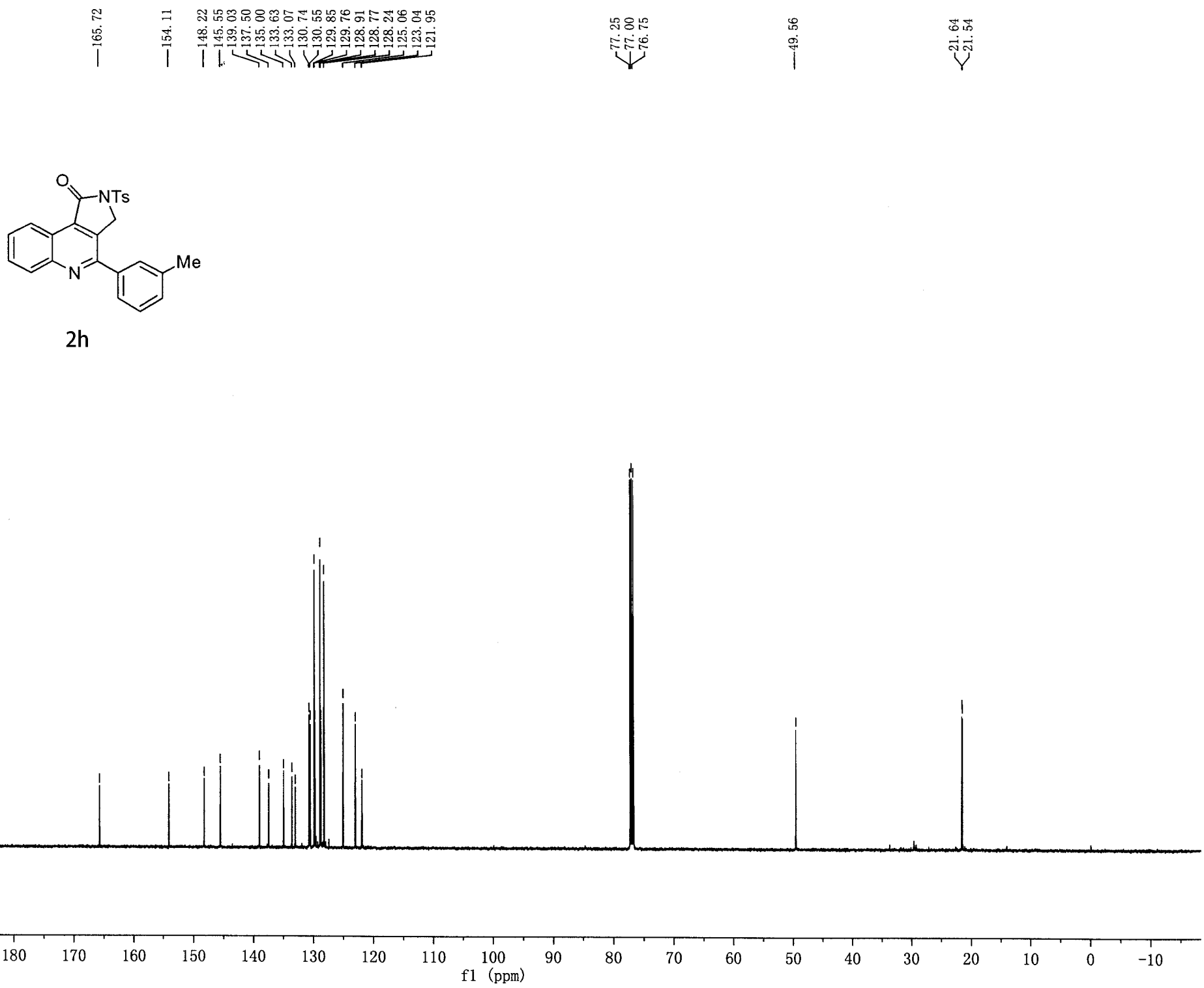
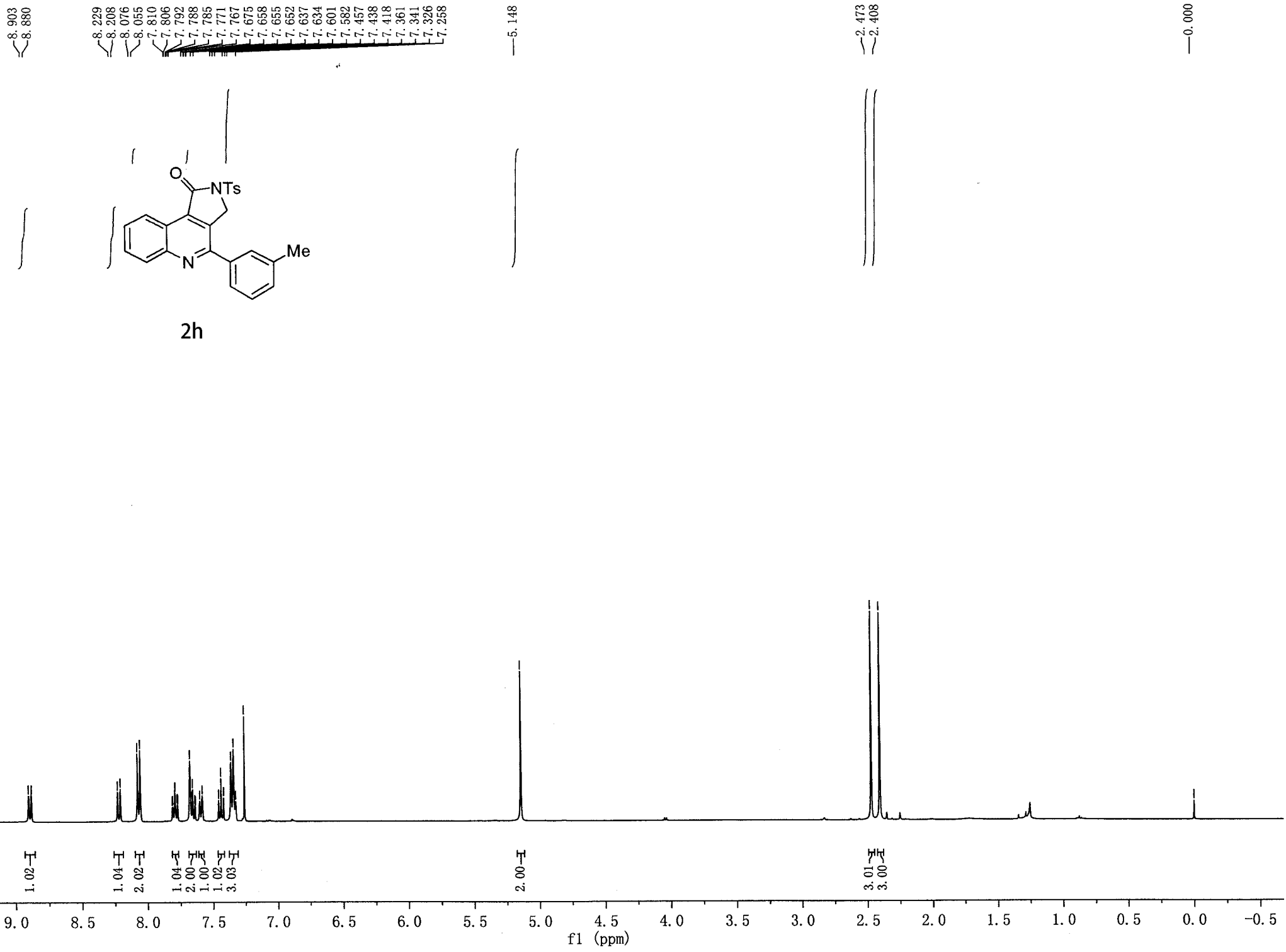


2g

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

f1 (ppm)

Supplementary Figure 28. ¹H and ¹³C NMR spectra for 2g



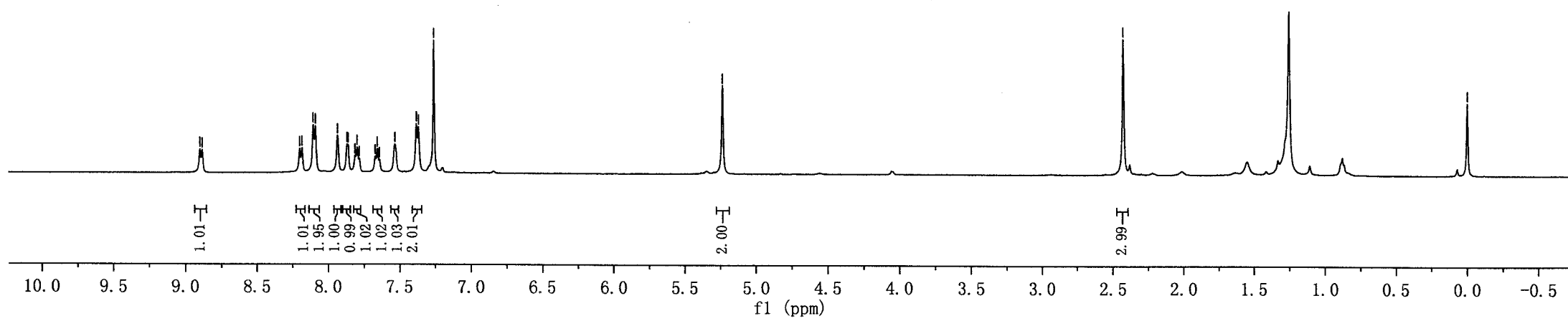
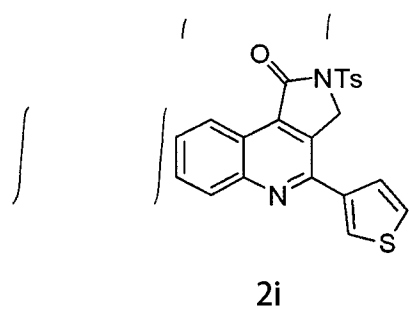
Supplementary Figure 29. ^1H and ^{13}C NMR spectra for **2h**

8.900
8.884
8.200
8.183
8.105
8.089
7.935
7.869
7.861
7.812
7.798
7.784
7.672
7.657
7.644
7.534
7.383
7.367
7.259

5.236

2.427

0.000



165.48

149.06

147.04

145.39

139.28

130.61

129.83

128.76

128.16

127.78

127.74

122.09

121.18

50.06

40.00

39.83

39.76

39.67

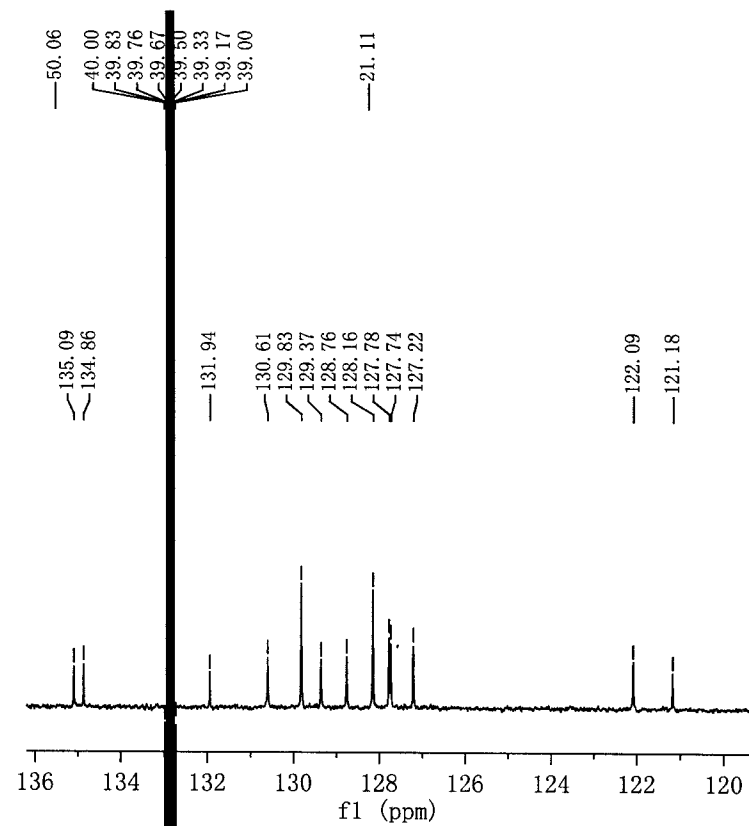
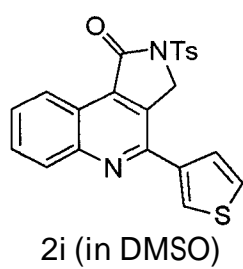
39.50

39.33

39.17

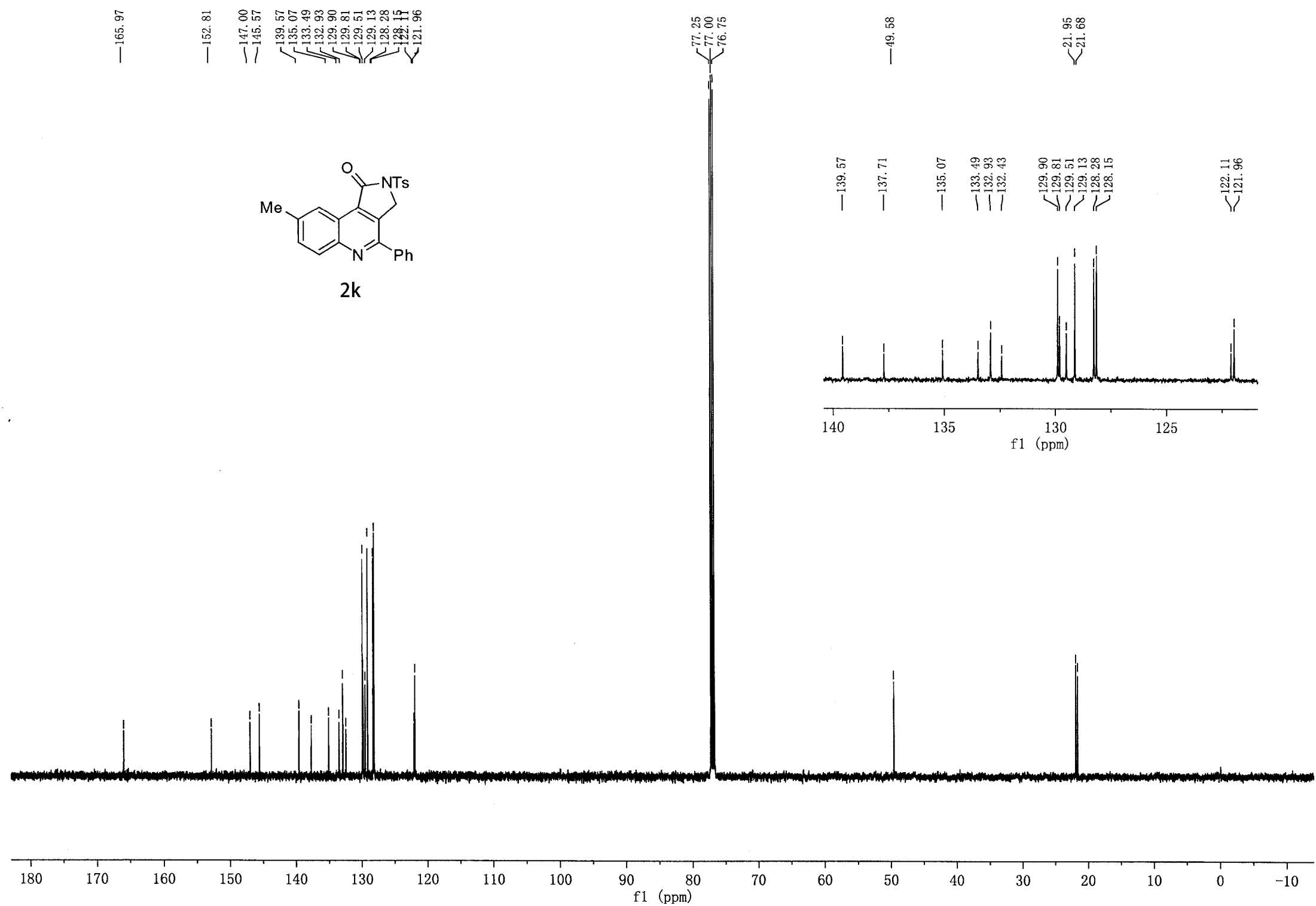
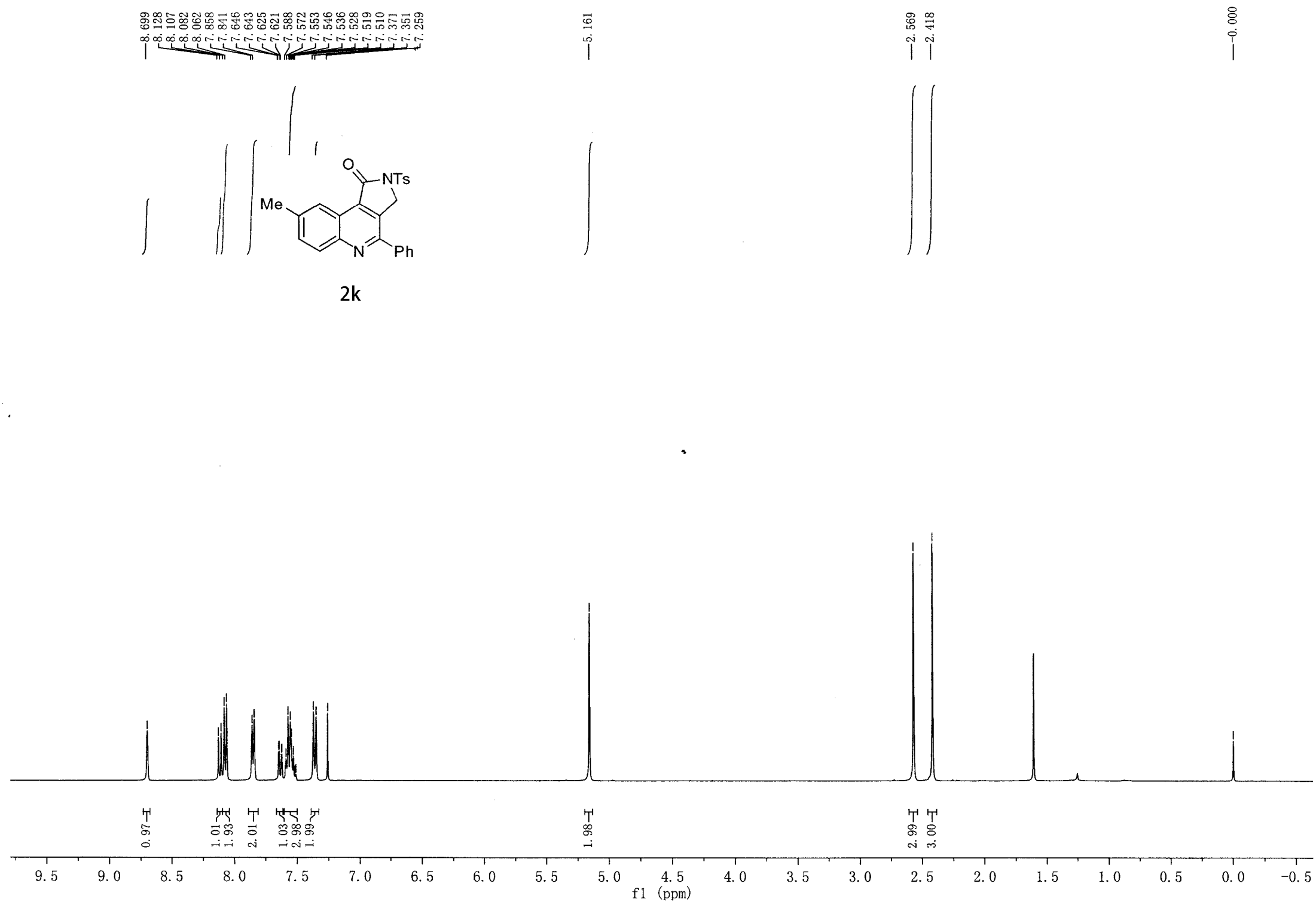
39.00

21.11

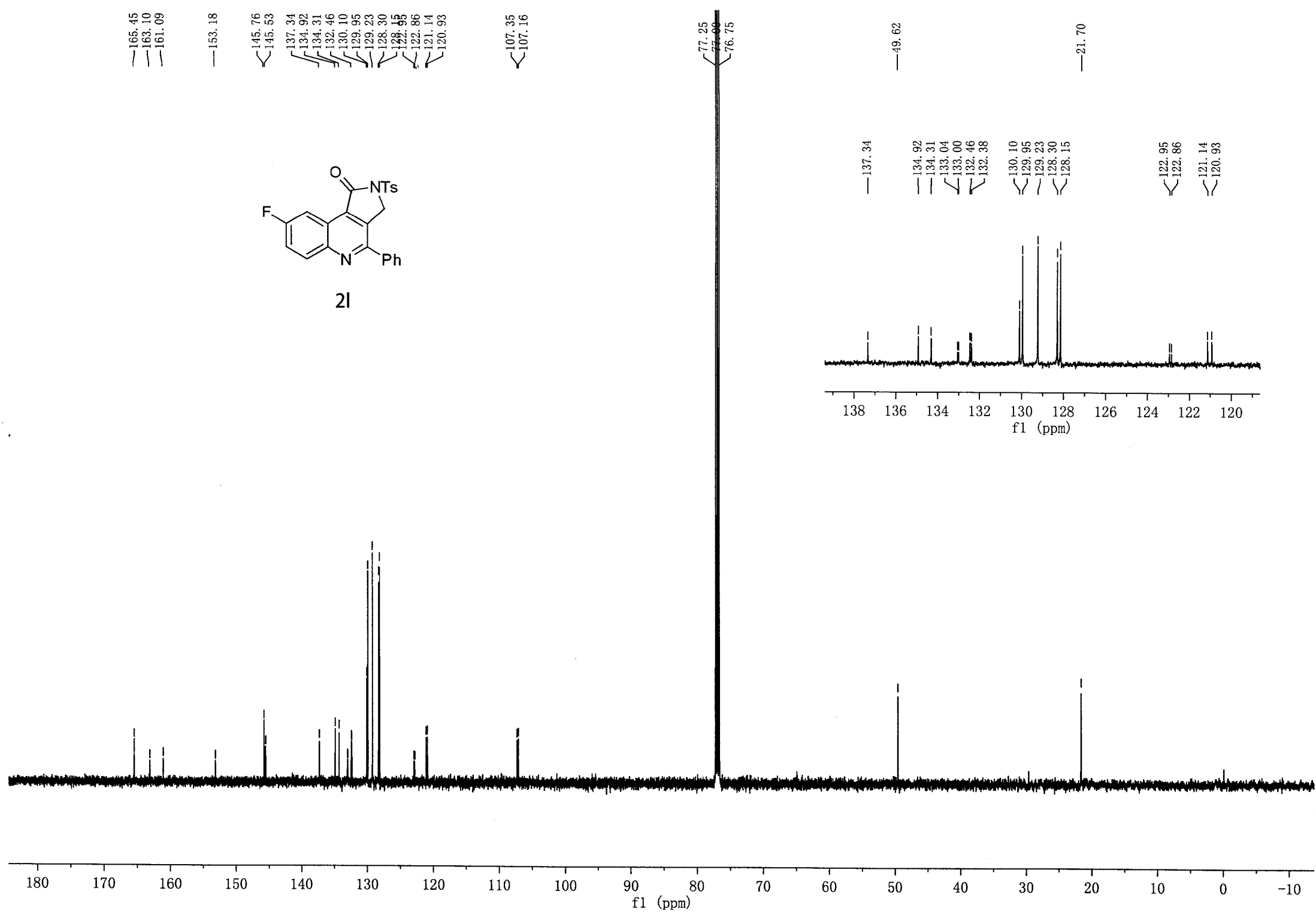
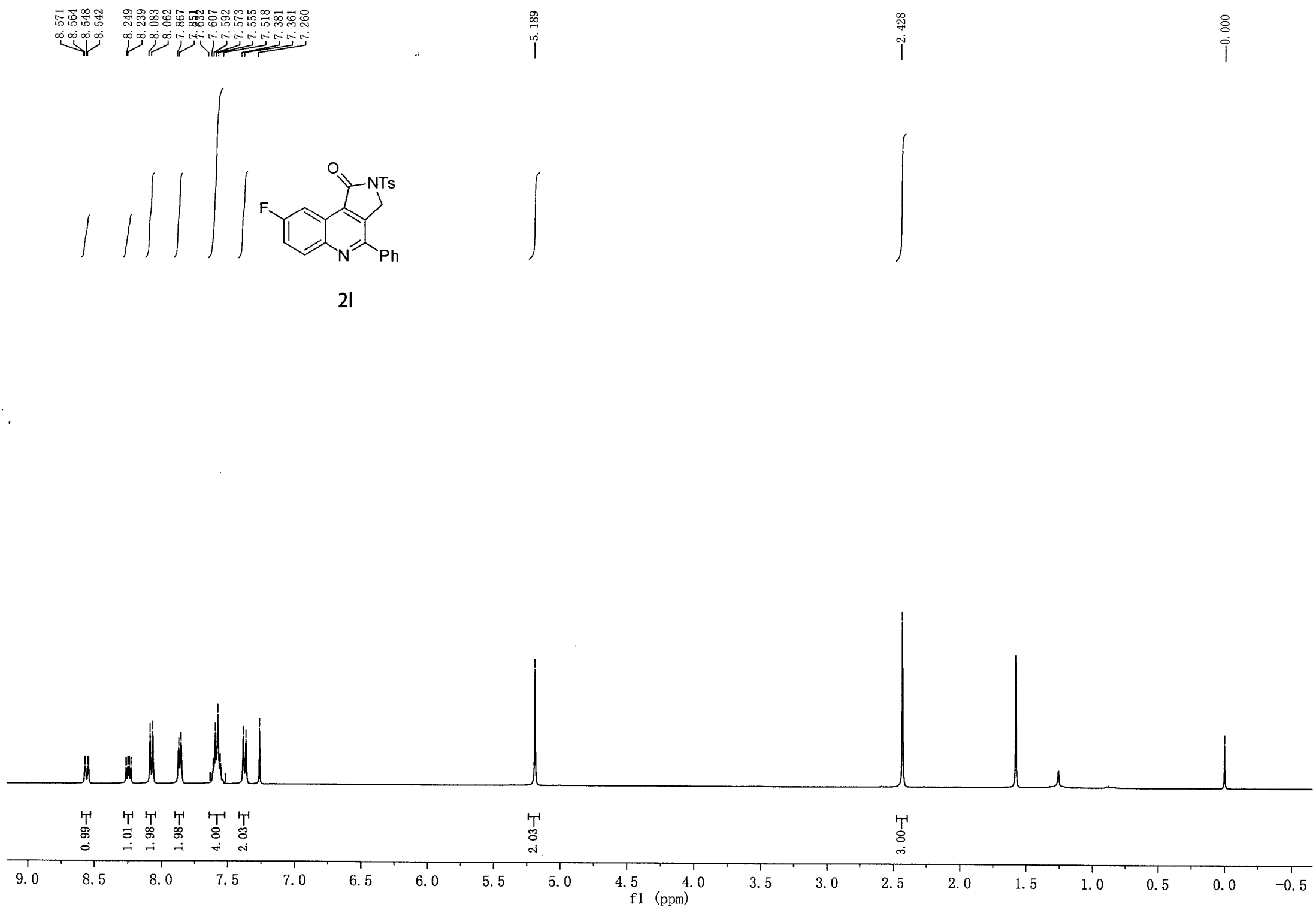


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

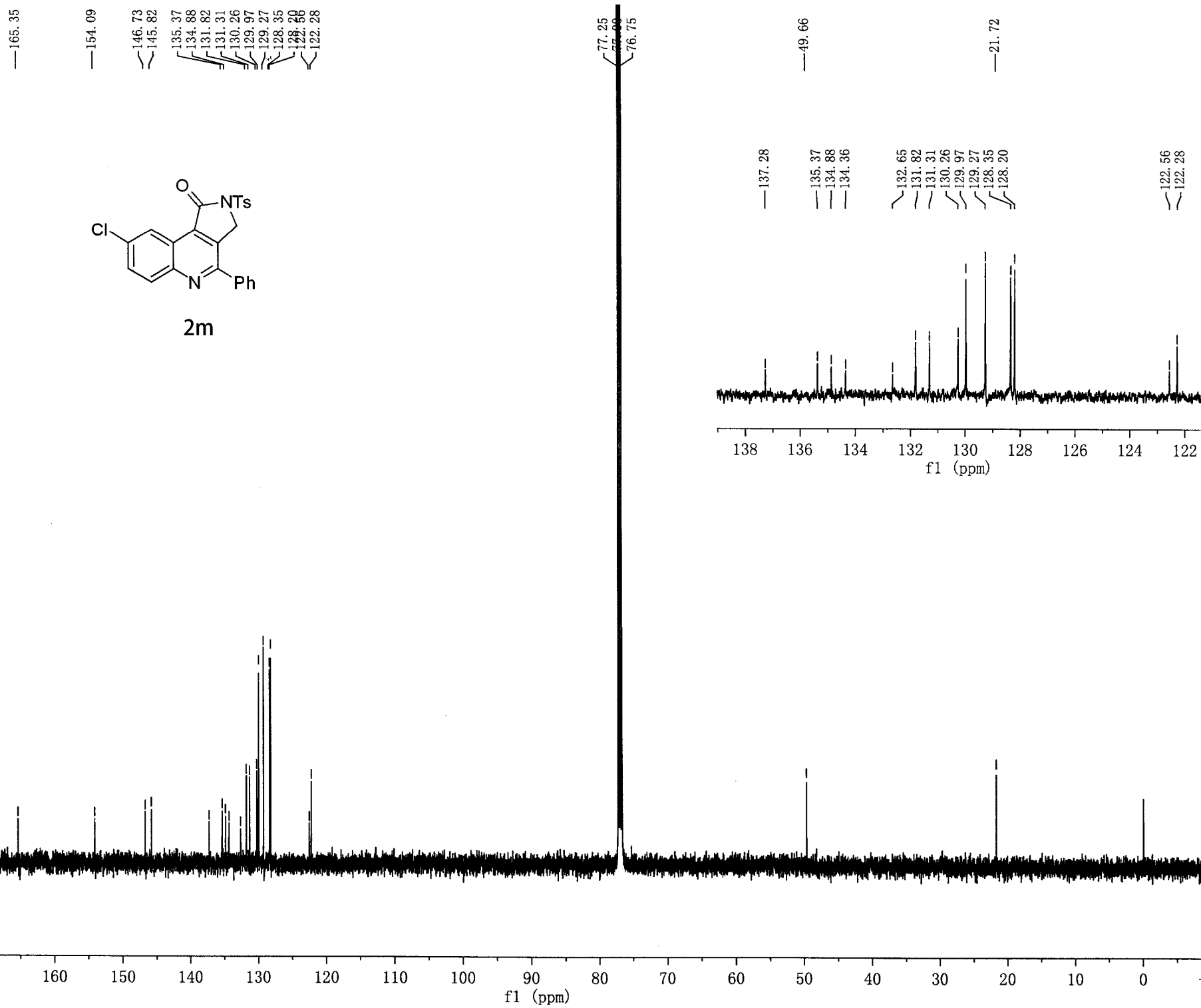
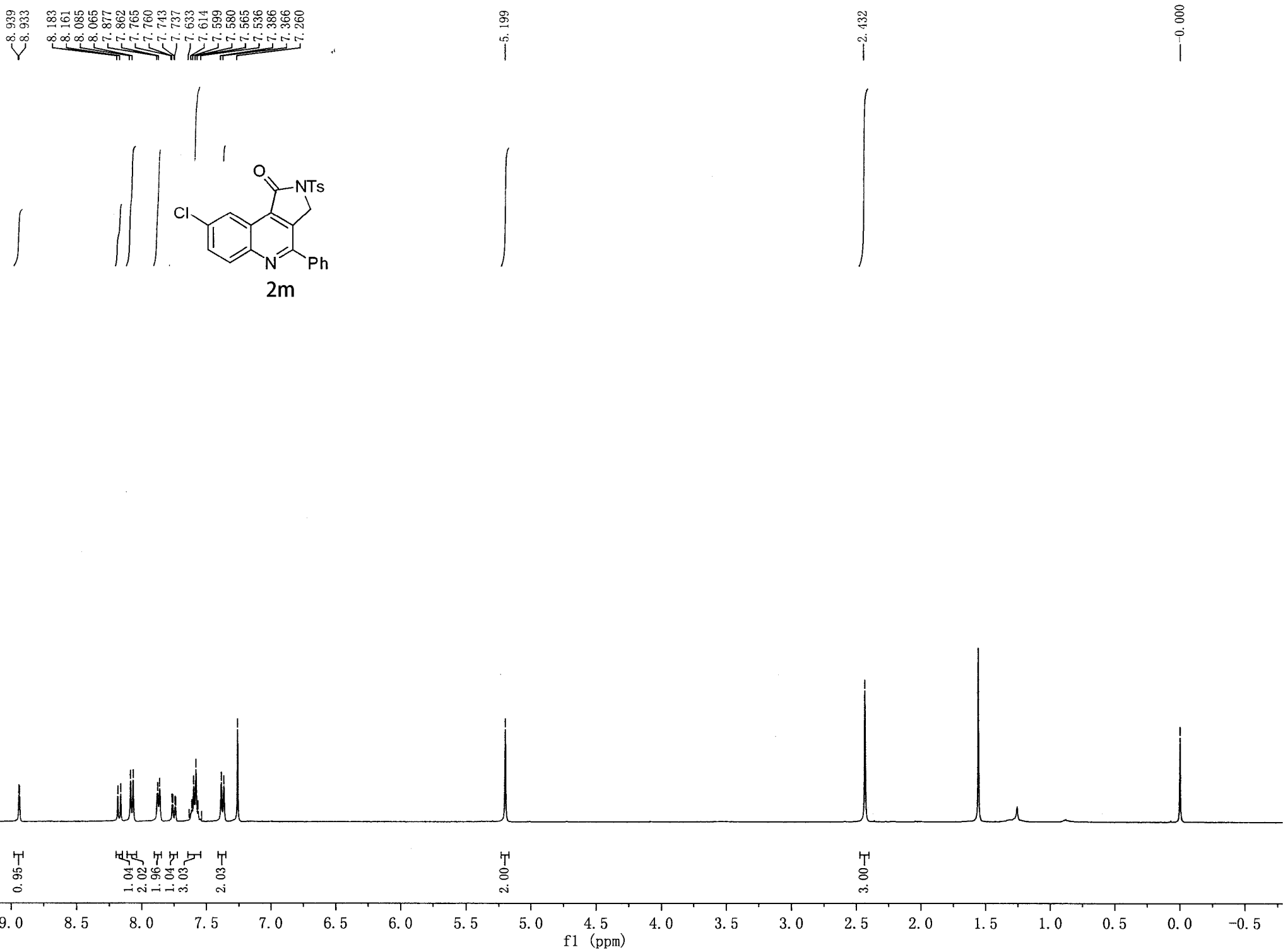
Supplementary Figure 30. ¹H and ¹³C NMR spectra for 2i



Supplementary Figure 31. ¹H and ¹³C NMR spectra for **2k**



Supplementary Figure 32. ¹H and ¹³C NMR spectra for 21



Supplementary Figure 33. ¹H and ¹³C NMR spectra for 2m

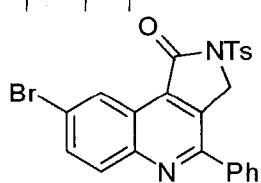
9.116
9.111

8.108
8.085
8.064
7.917
7.900
7.878
7.864
7.845
7.827
7.598
7.580
7.547
7.388
7.367
7.260

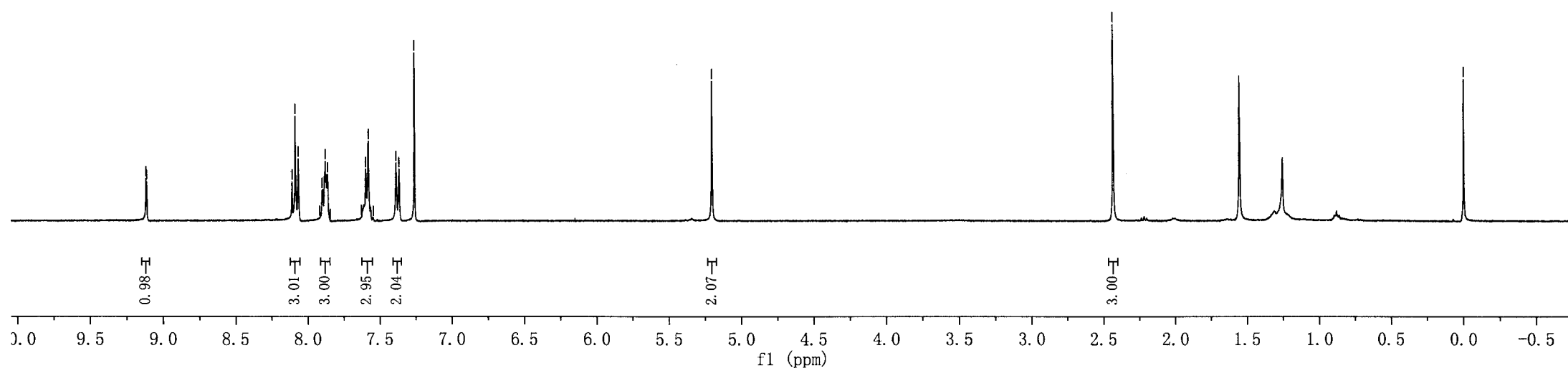
5.202

2.433

0.000



2n



165.32

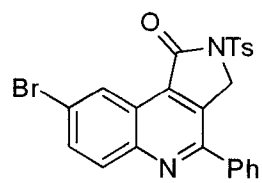
154.23

146.92
145.83
137.27
134.86
134.40
134.31
132.51
131.36
130.28
129.97
129.27
128.35
128.19
125.58
123.73
122.94

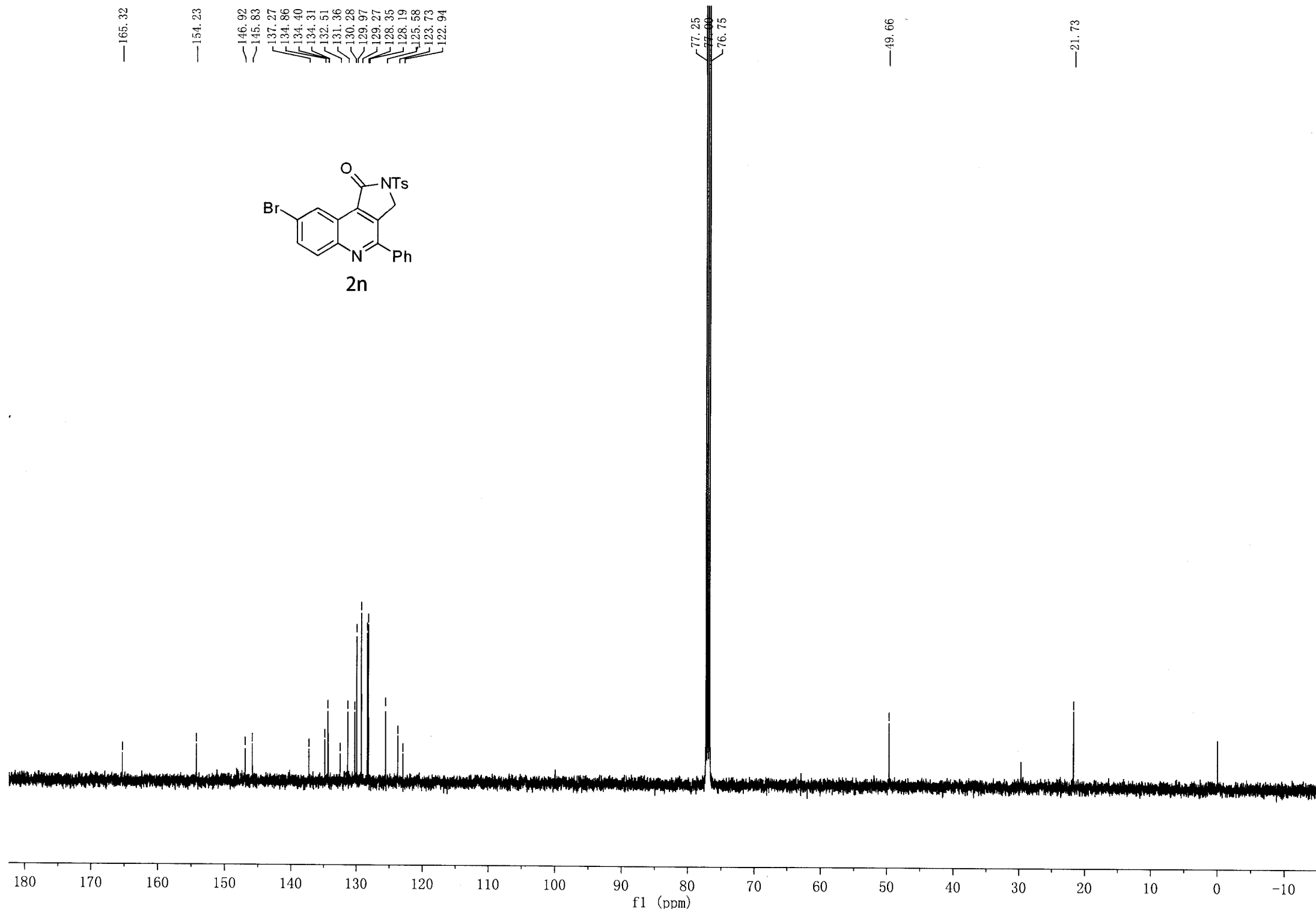
77.25
77.00
76.75

49.66

21.73



2n



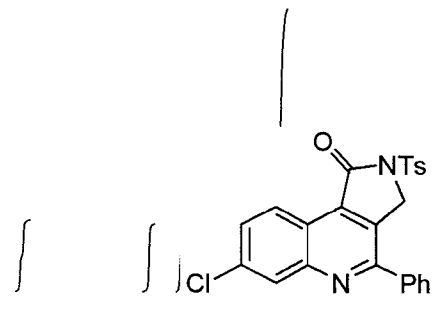
Supplementary Figure 34. ¹H and ¹³C NMR spectra for 2n

8.869
8.851
8.233
8.230
8.077
8.060
7.875
7.859
7.649
7.631
7.627
7.613
7.609
7.592
7.577
7.563
7.548
7.376
7.360
7.260

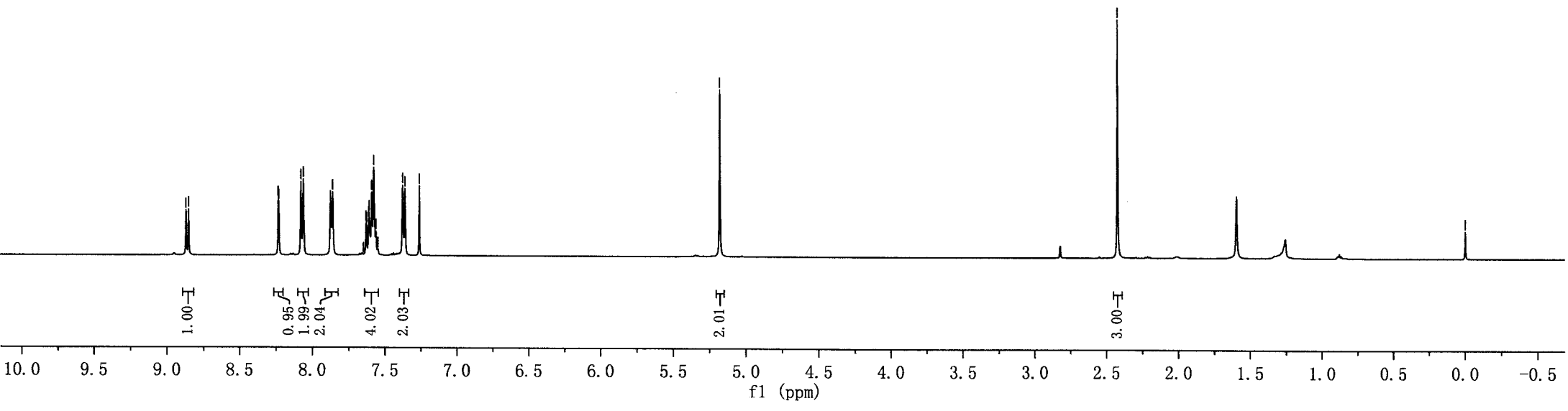
5.180

2.425

0.000



20

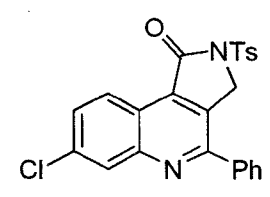


165.39
155.03
148.78
145.78
137.20
136.77
134.87
133.57
133.51
130.33
129.95
129.80
129.23
128.86
128.31
128.23
124.37
120.37

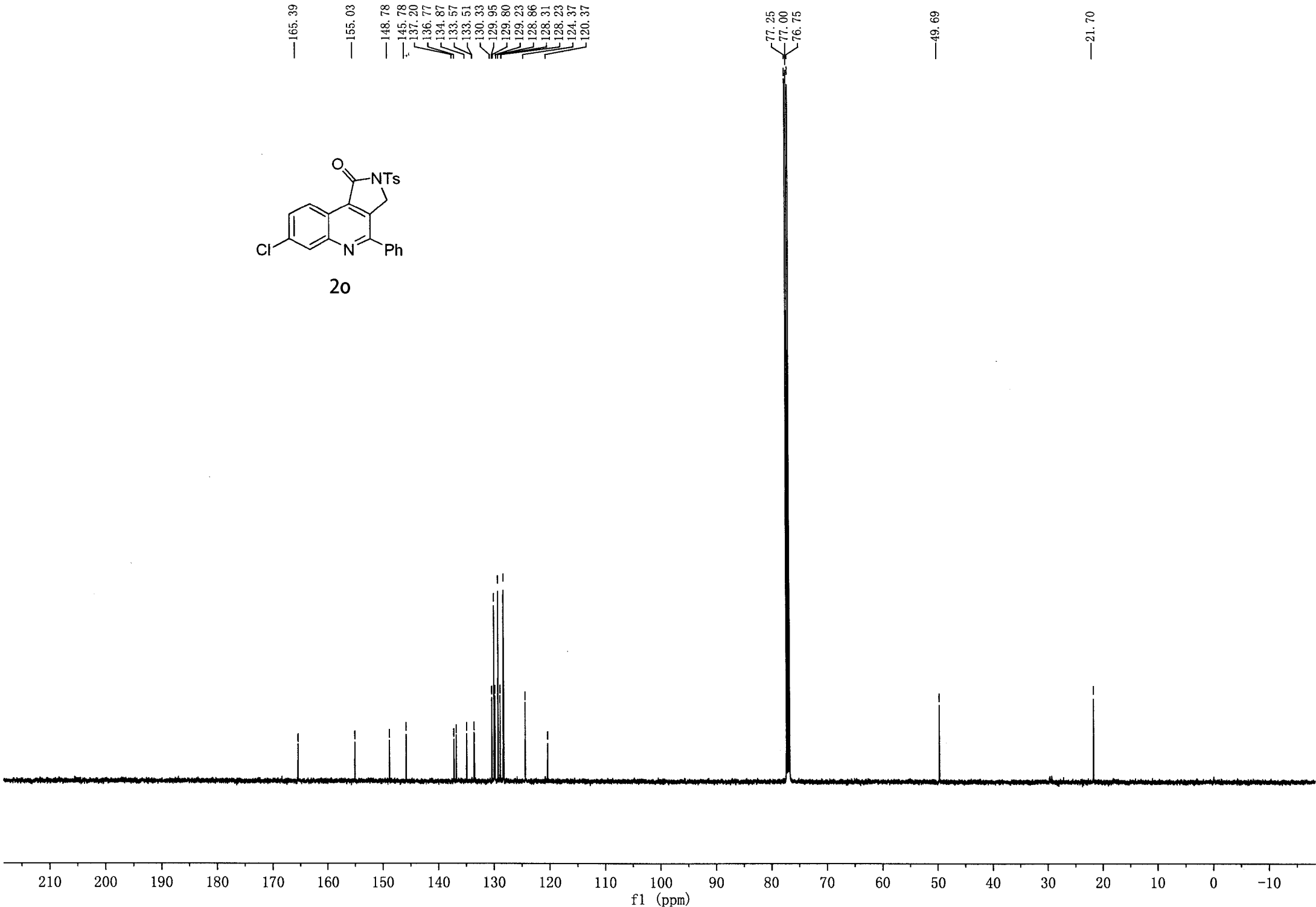
77.25
77.00
76.75

49.69

21.70



20

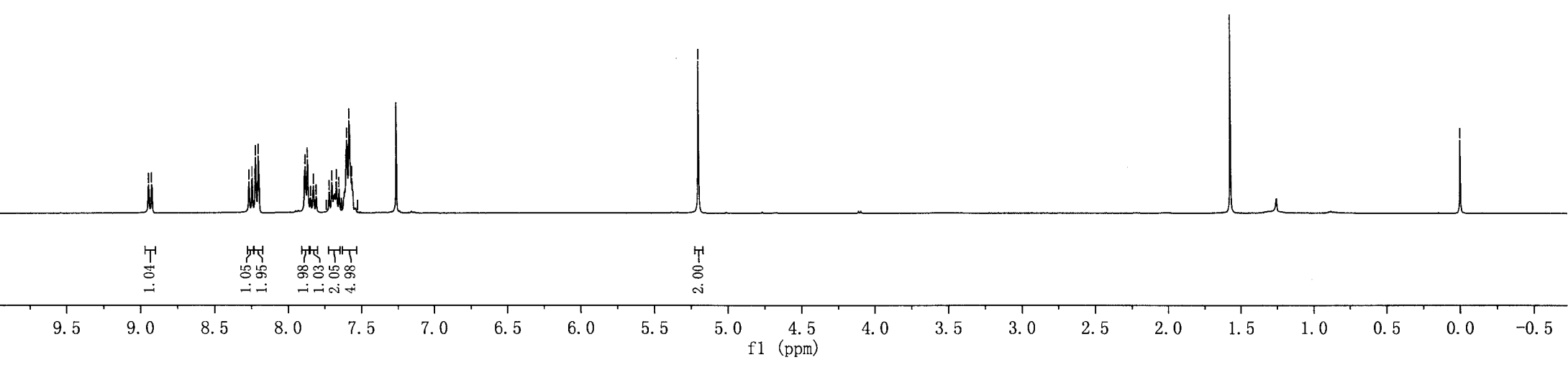
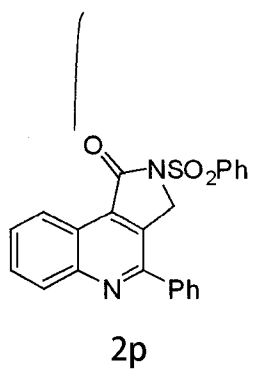


Supplementary Figure 35. ¹H and ¹³C NMR spectra for 20

8.941
8.921
8.263
8.241
8.217
8.198
7.881
7.865
7.843
7.825
7.807
7.738
7.716
7.698
7.667
7.649
7.633
7.596
7.581
7.563
7.524

5.199

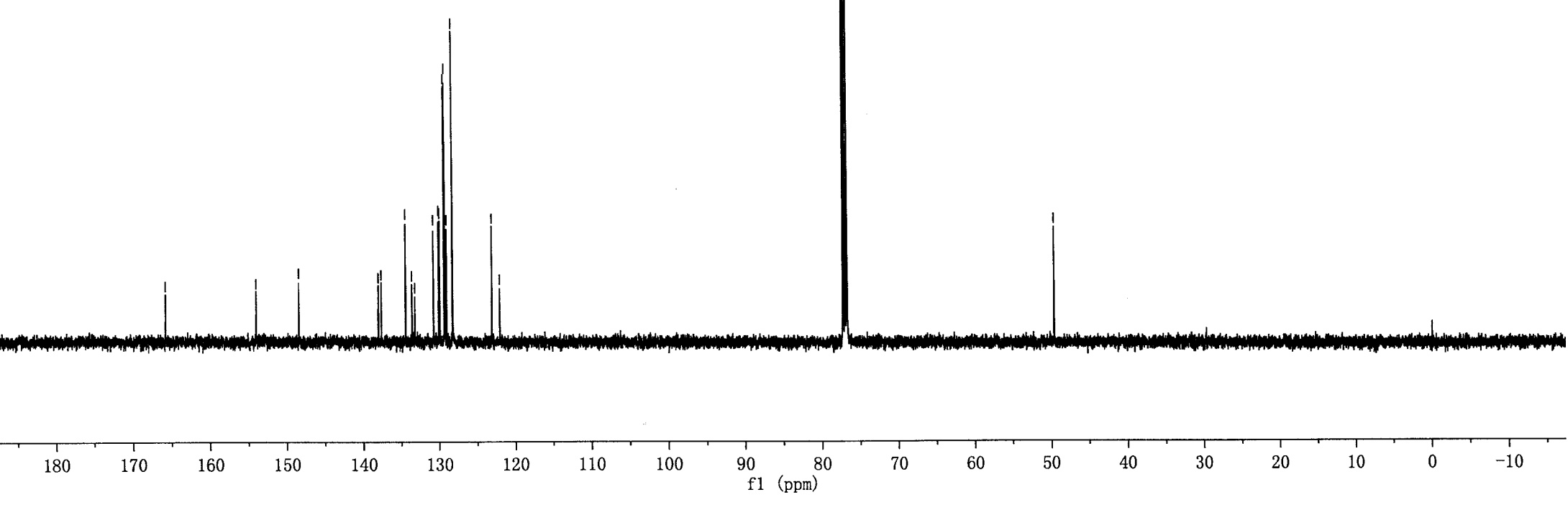
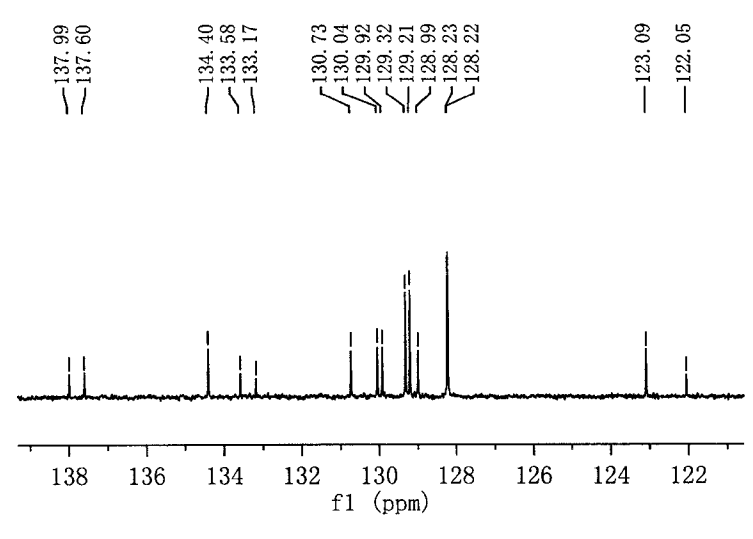
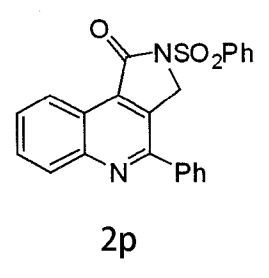
0.000



165.76
153.94
148.38
137.60
134.40
133.58
130.73
130.04
129.92
129.32
129.21
128.99
128.23
128.09
128.04
122.05

77.25
77.04
76.75

49.64

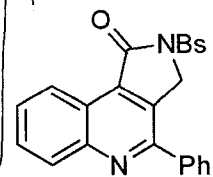


Supplementary Figure 36. ¹H and ¹³C NMR spectra for 2p

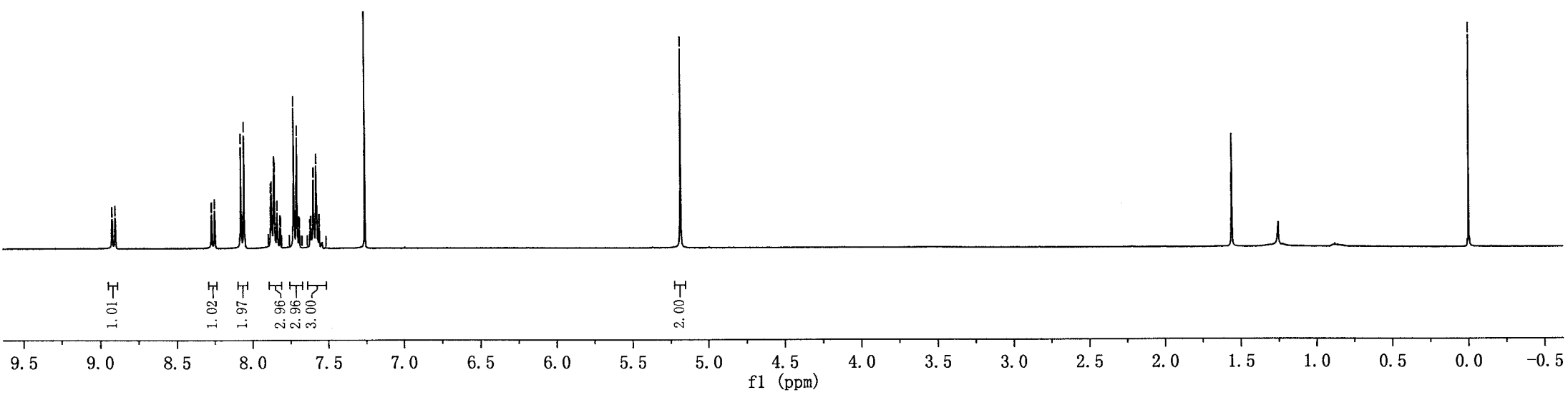
8.922
8.901
8.271
8.250
8.076
8.055
7.896
7.879
7.875
7.859
7.855
7.837
7.820
7.816
7.808
7.757
7.728
7.706
7.693
7.680
7.673
7.638
7.621
7.614
7.599
7.581
7.561
7.559
7.515

5.185

0.000



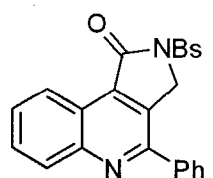
2q



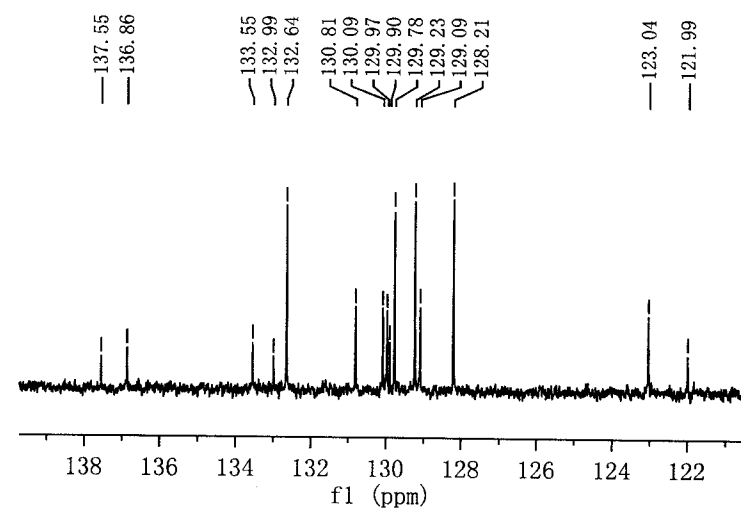
165.81
153.93
148.42
133.55
132.64
130.81
130.09
129.97
129.90
129.78
129.23
129.09
128.61
121.99

77.25
77.00
76.75

49.62



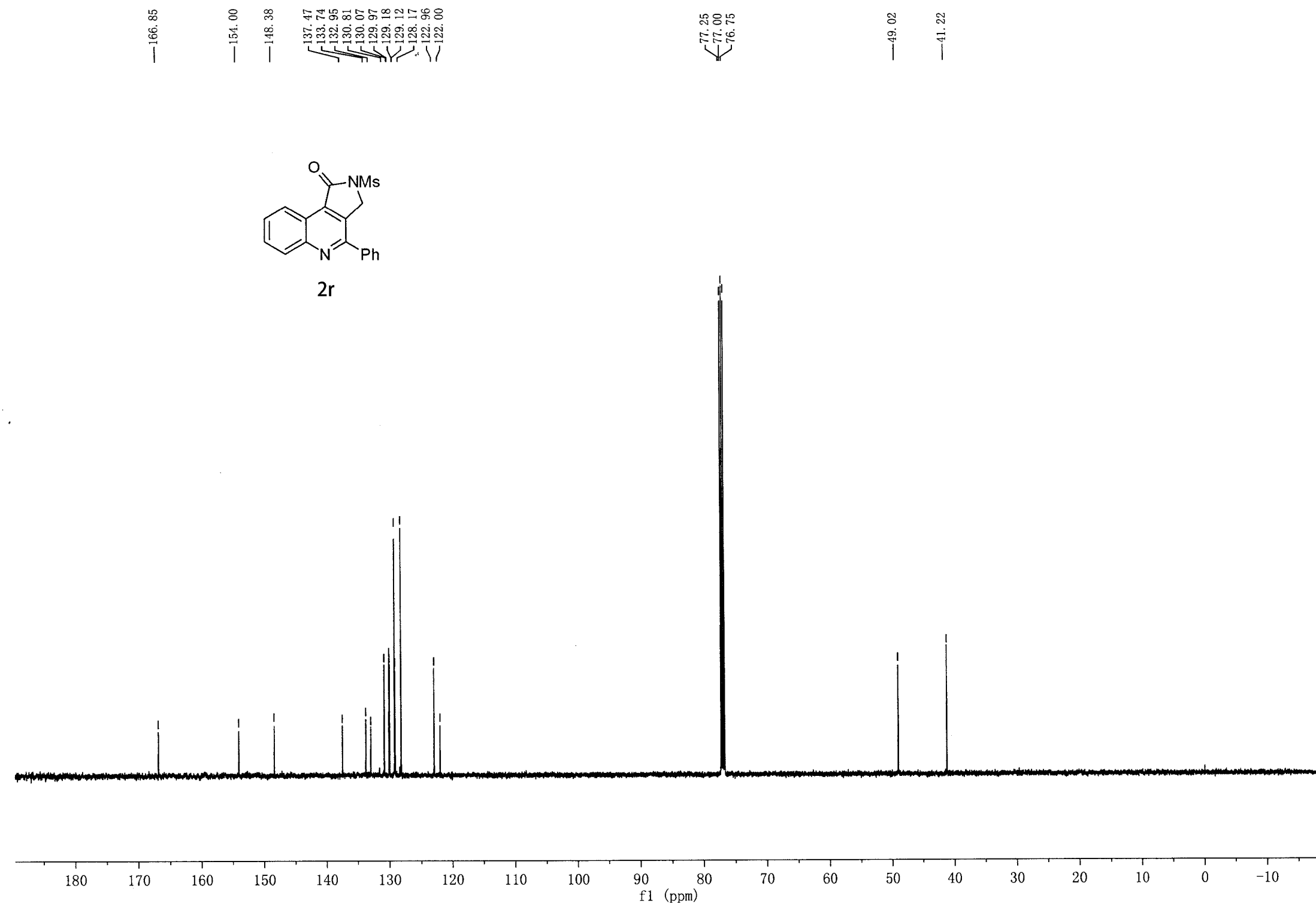
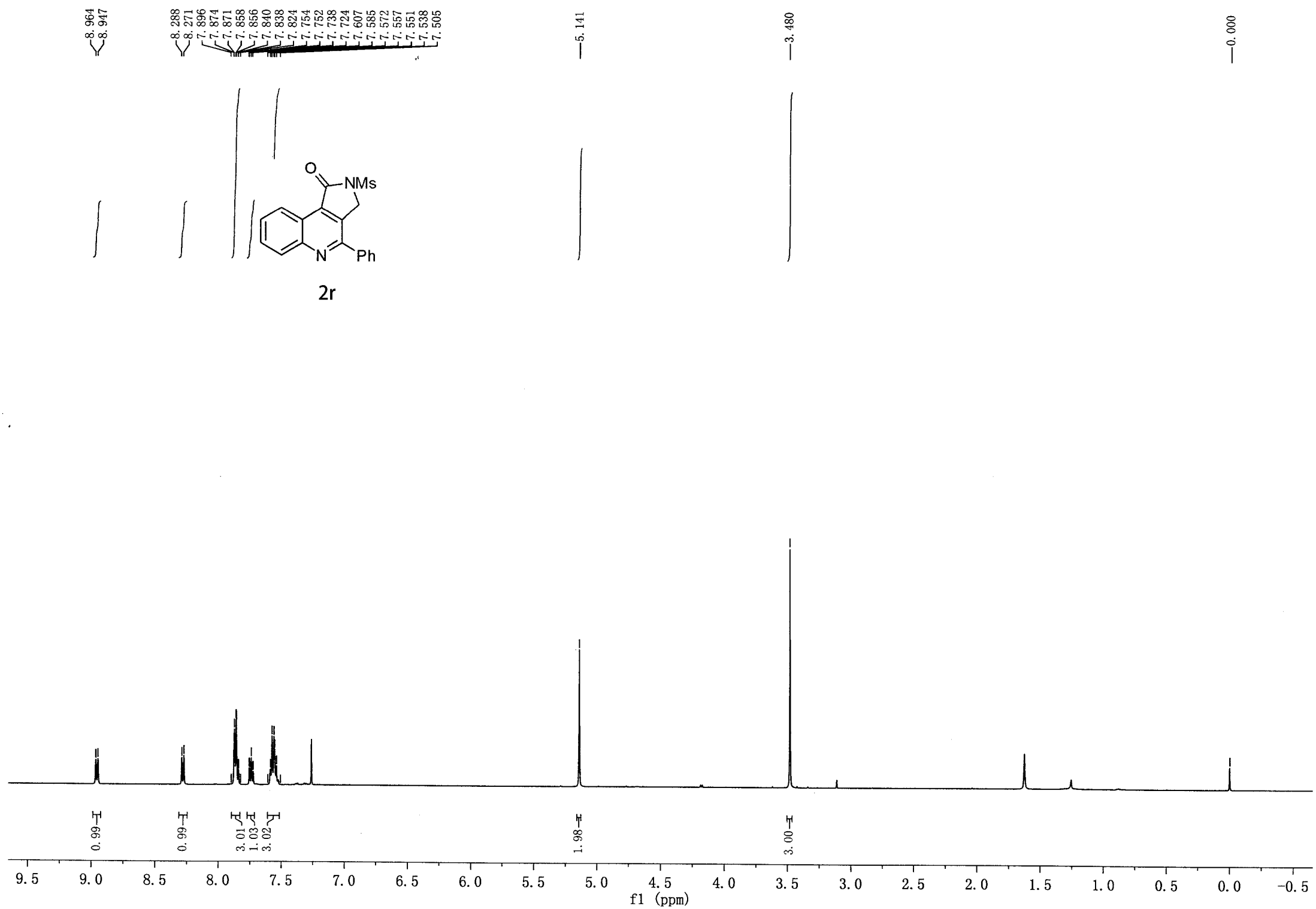
2q



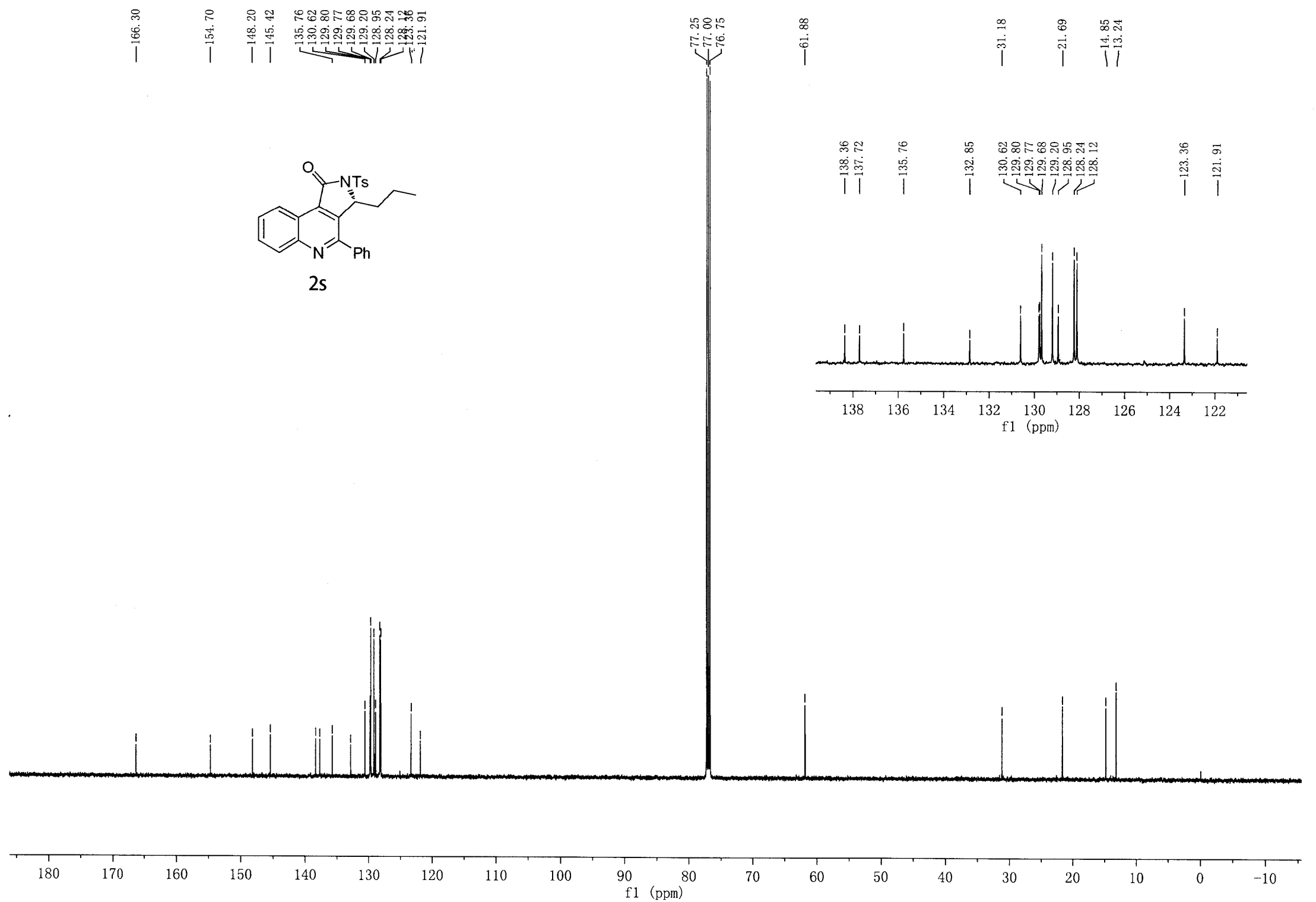
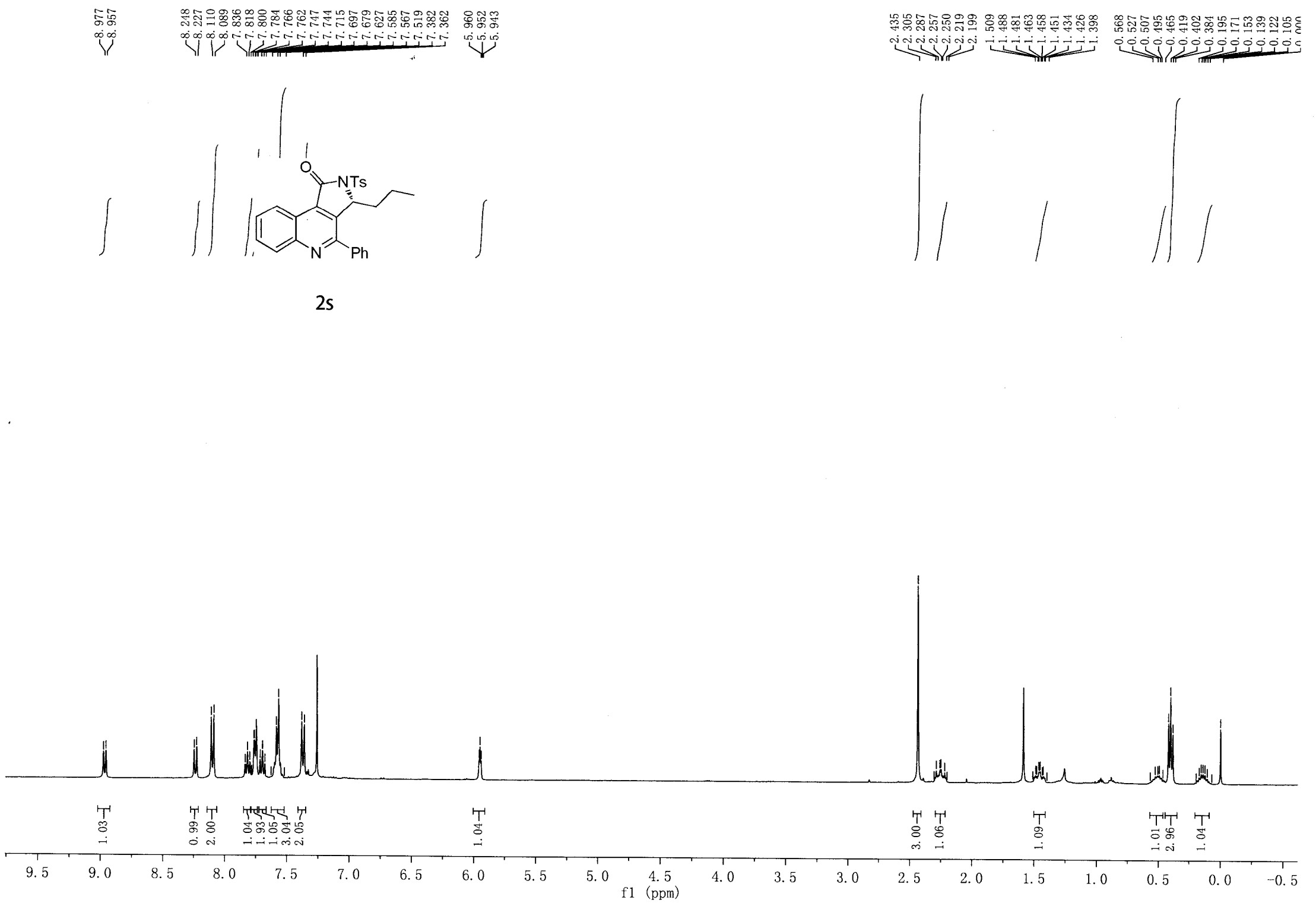
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

f1 (ppm)

Supplementary Figure 37. ¹H and ¹³C NMR spectra for 2q



Supplementary Figure 38. ^1H and ^{13}C NMR spectra for **2r**



Supplementary Figure 39. ¹H and ¹³C NMR spectra for 2s

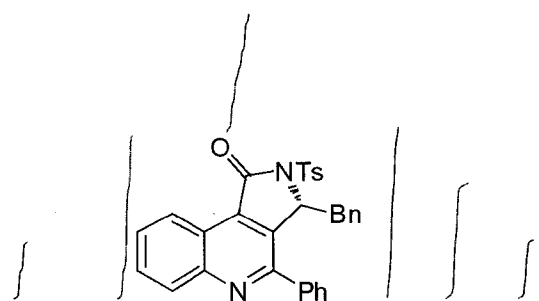
8.692
8.690
8.671
8.669
8.154
8.133
7.963
7.959
7.942
7.940
7.679
7.662
7.562
7.409
7.389
7.260
6.839
6.837
6.819
6.529
6.526
6.519
6.517
6.165
6.155

3.676
3.666
3.640
3.630

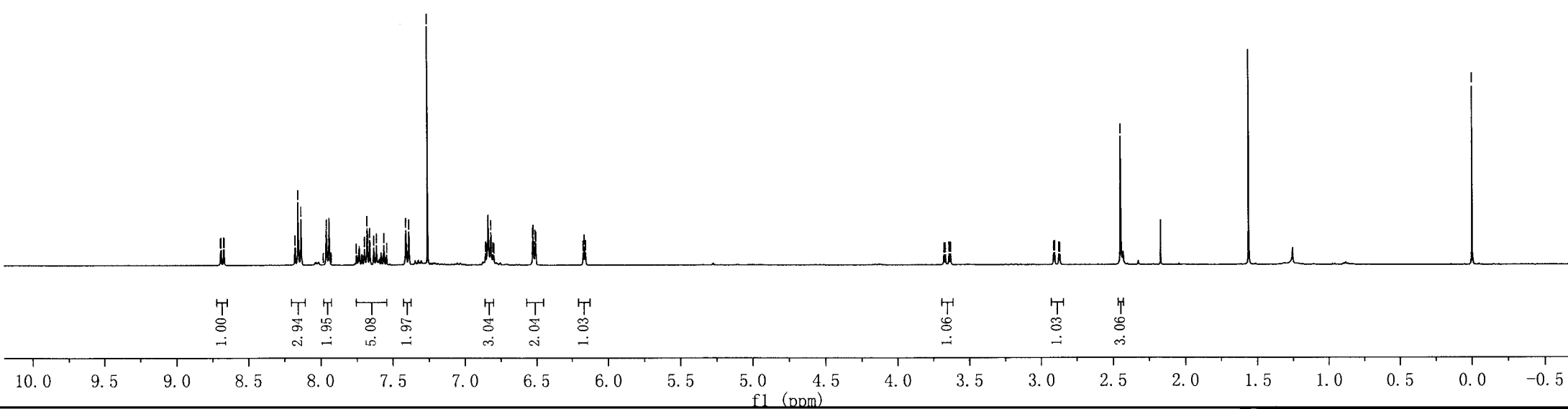
2.912
2.905
2.876
2.869

—2.446

—0.000



2t



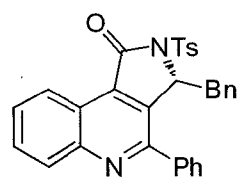
166.02
154.36
148.12
148.61
138.61
137.00
135.64
133.07
132.74
130.51
130.03
129.86
129.66
129.57
129.49
128.78
128.59
128.52
127.83
126.81
123.19
121.54

77.25
77.00
76.75

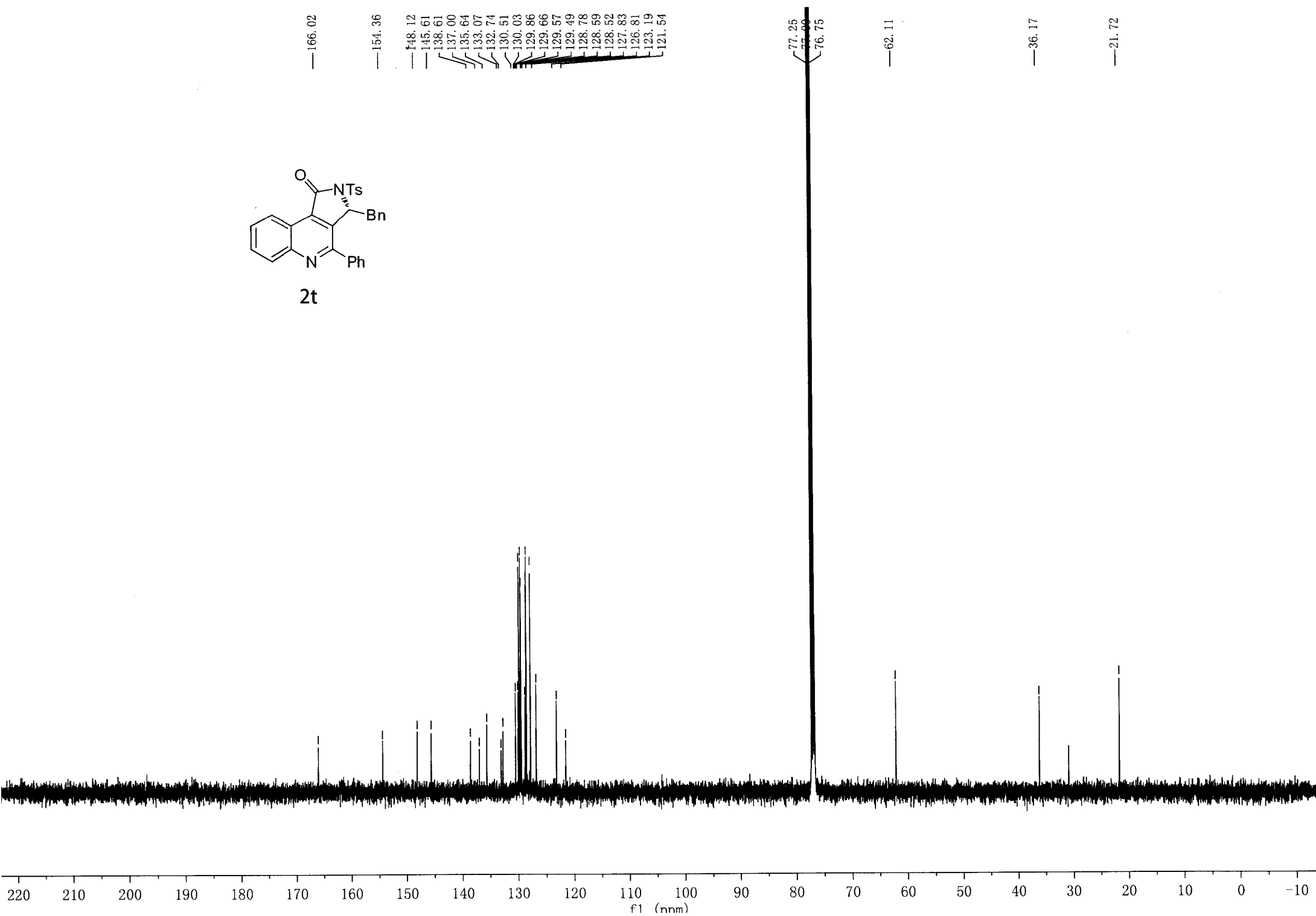
—62.11

—36.17

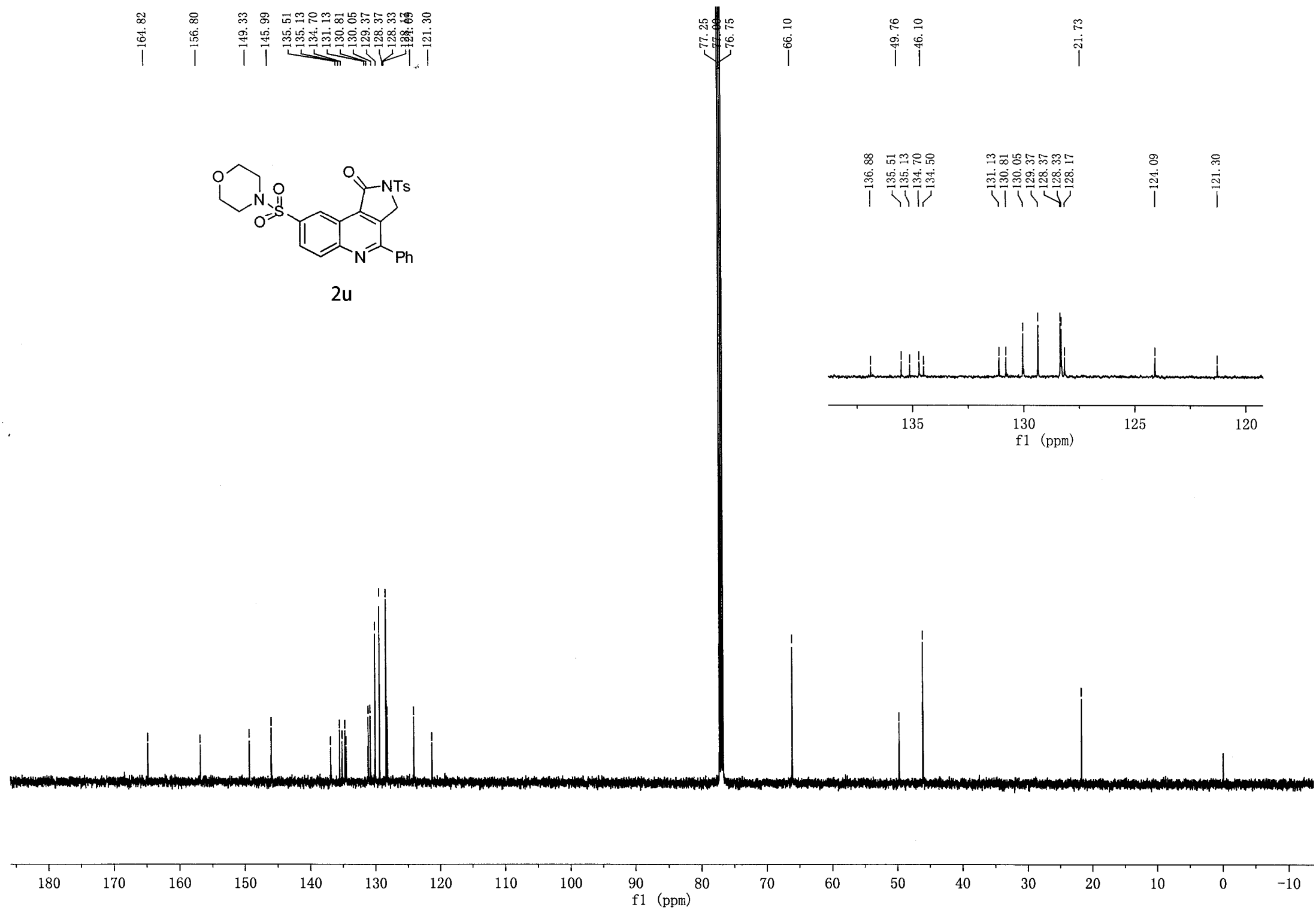
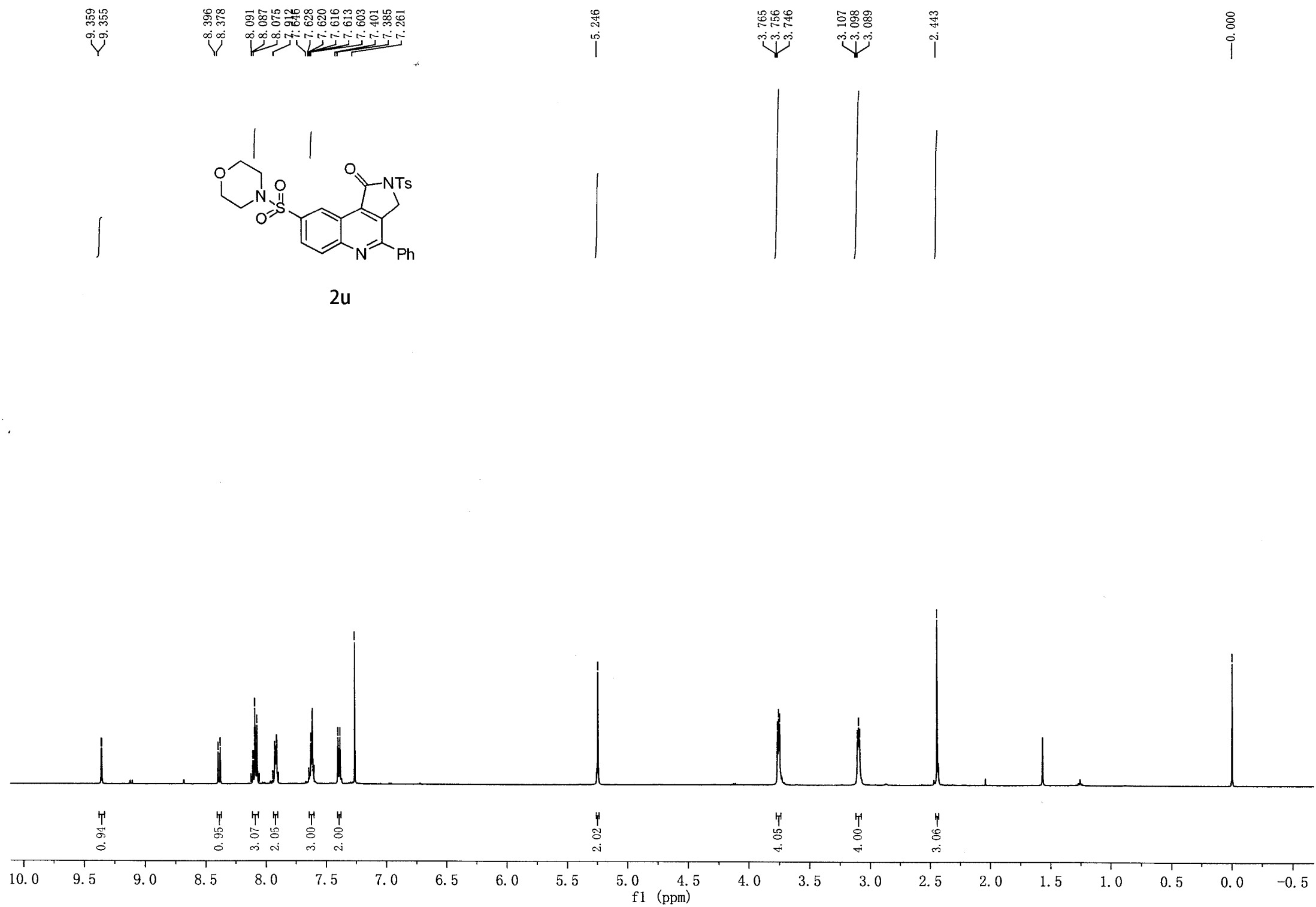
—21.72



2t

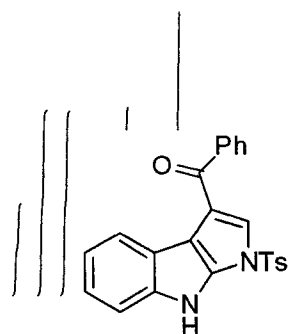


Supplementary Figure 40. ^1H and ^{13}C NMR spectra for 2t



Supplementary Figure 41. ¹H and ¹³C NMR spectra for 2u

8.816
8.025
7.904
7.889
7.795
7.778
7.628
7.613
7.598
7.526
7.511
7.496
7.463
7.447
7.293
7.263
7.255
7.247
7.220
7.204
7.189



3a

2.364

-0.000

1.01
0.99
2.00
1.99
1.05
2.03
1.05
1.02
3.06
1.05

3.00

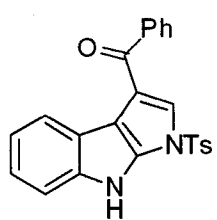
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

190.46

146.34
139.27
134.49
132.28
130.39
129.05
128.56
126.85
123.89
122.93
122.89
121.64
120.95
119.81
109.11

77.25
77.00
76.75

21.65



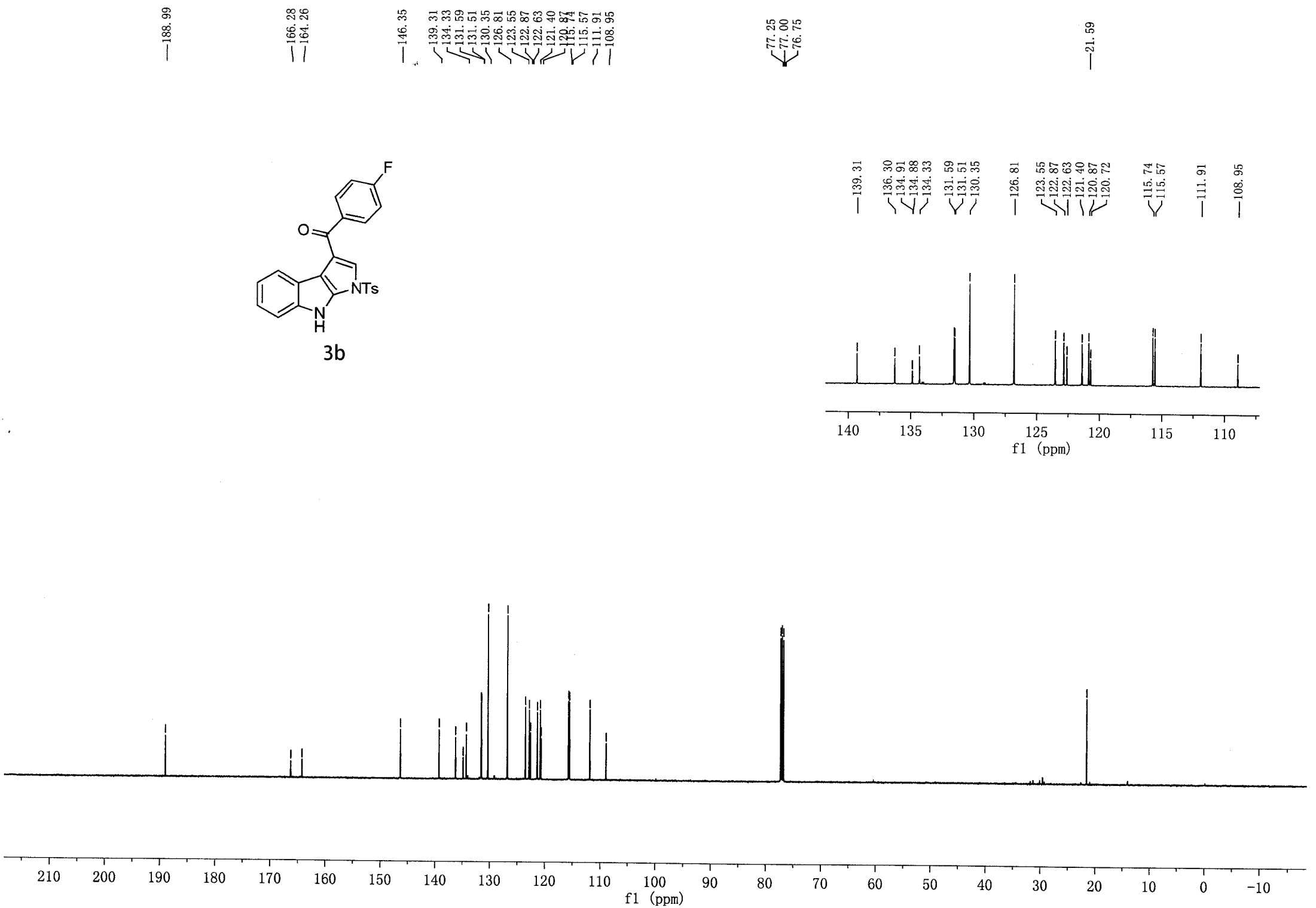
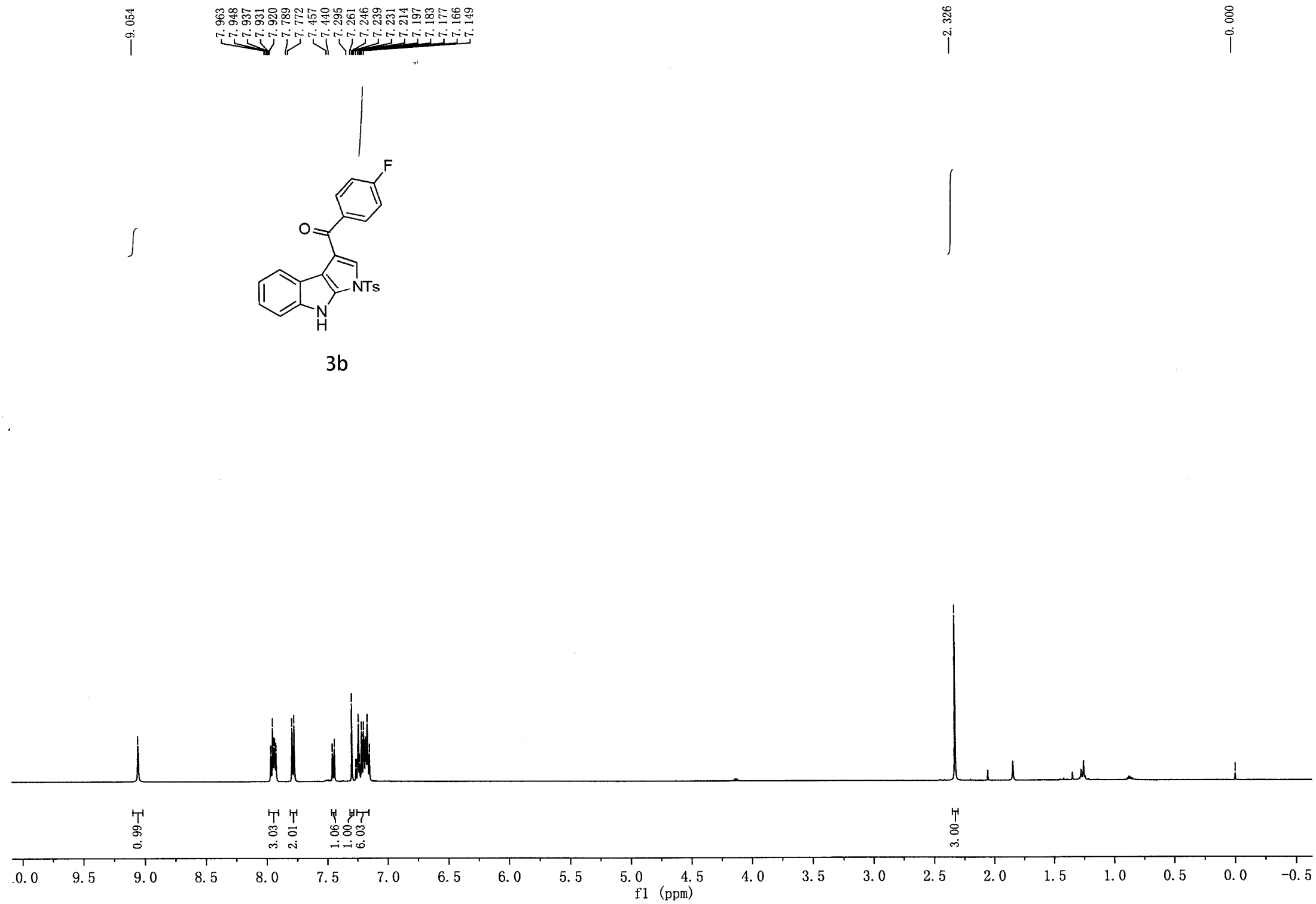
3a

139.27
138.75
136.33
134.49
132.28
130.39
129.05
128.56
126.85
123.89
122.93
122.89
121.64
120.95
111.81
109.11

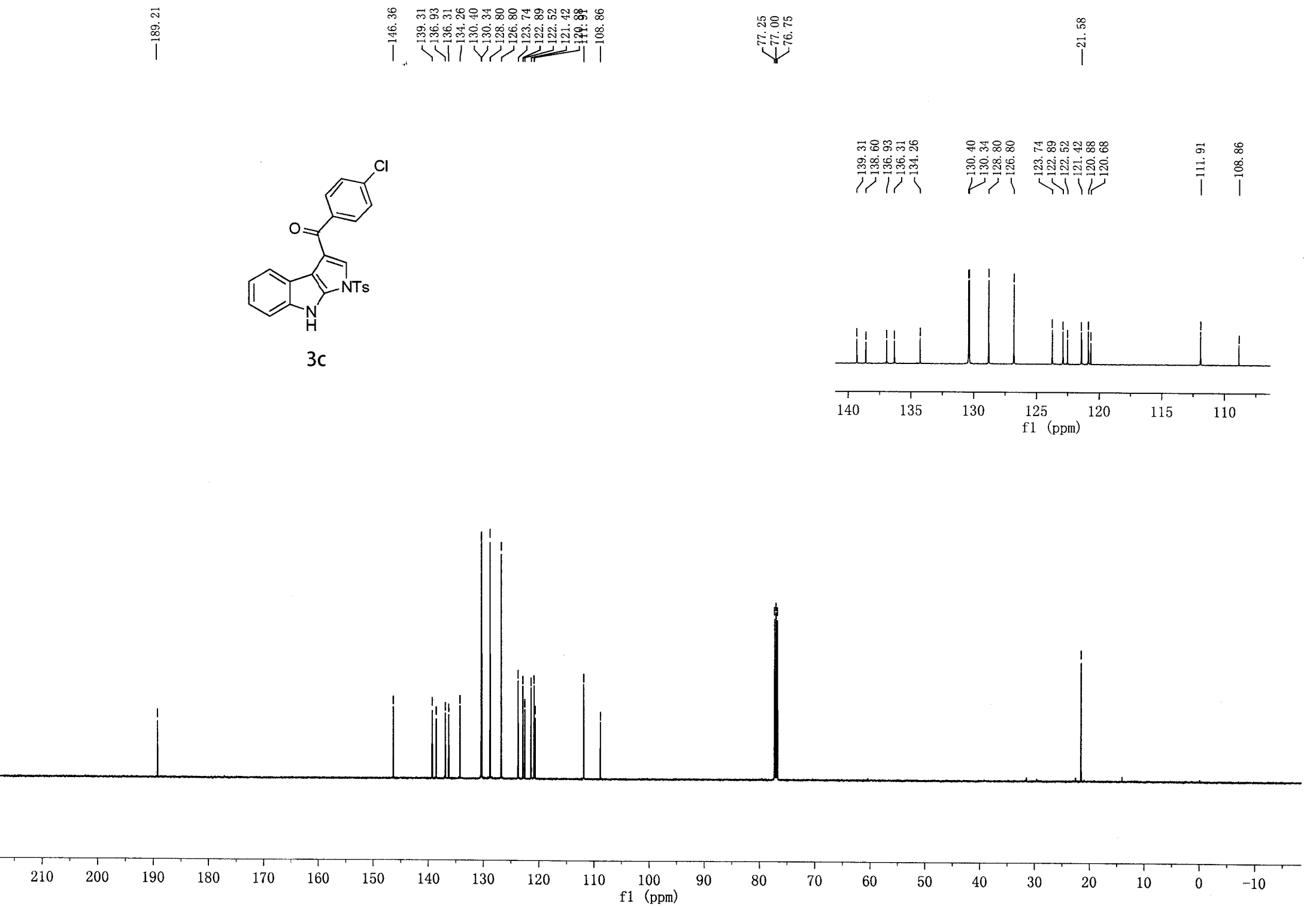
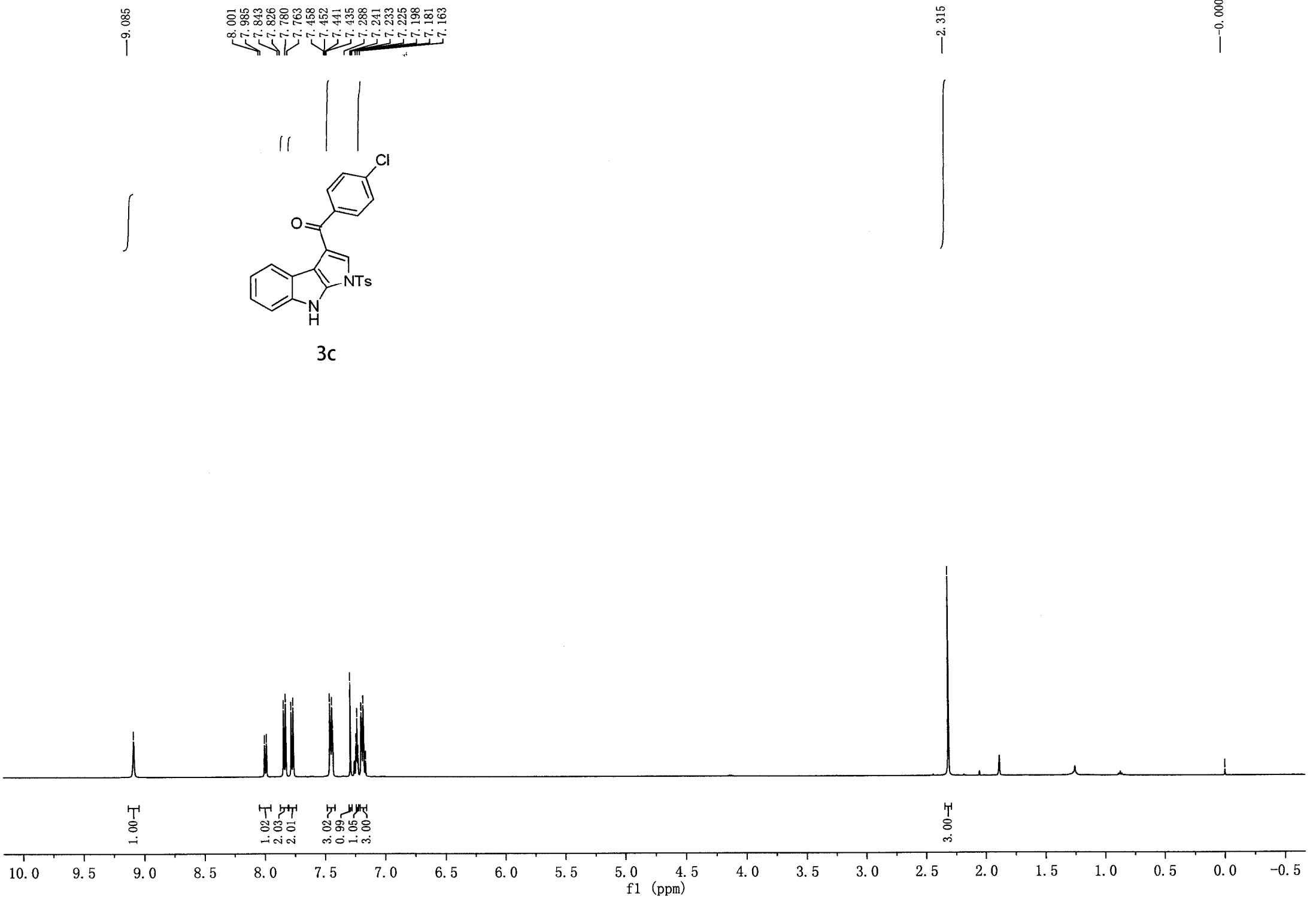
140 135 130 125 120 115 110
f1 (ppm)

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Supplementary Figure 42. ¹H and ¹³C NMR spectra for 3a



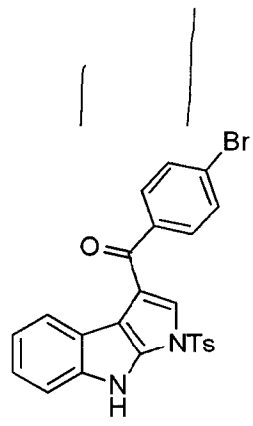
Supplementary Figure 43. ^1H and ^{13}C NMR spectra for **3b**



Supplementary Figure 44. ^1H and ^{13}C NMR spectra for 3c

9.002

8.009
7.993
7.786
7.769
7.767
7.750
7.633
7.616
7.455
7.439
7.270
7.255
7.242
7.225
7.208
7.192
7.177



3d

2.336

-0.000

0.98

1.00

4.02

2.02

1.05

5.05

3.00

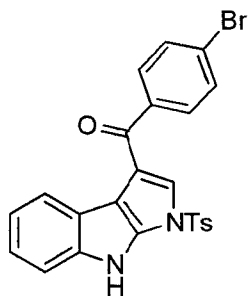
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

189.31

146.40
139.30
137.39
134.31
131.80
130.54
130.38
127.20
126.83
123.75
122.93
122.52
121.48
119.90
108.87

77.25
77.00
76.75

21.62



3d

139.30
137.39
136.33
134.31
131.80
130.54
130.38
127.20
126.83
123.75
122.93
122.52
121.48
120.93
120.72

111.90

108.87

140 135 130 125 120 115 110
f1 (ppm)

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

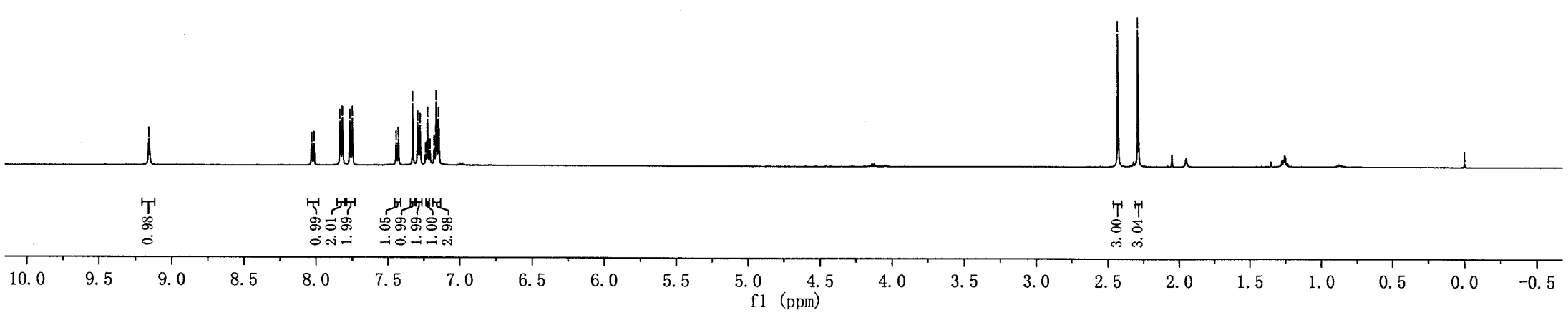
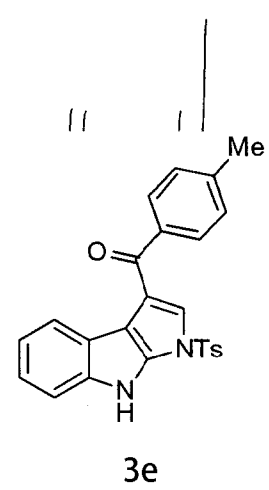
Supplementary Figure 45. ¹H and ¹³C NMR spectra for 3d

9.154

8.028
8.012
7.831
7.815
7.764
7.747
7.441
7.425
7.326
7.290
7.274
7.236
7.223
7.206
7.177
7.162
7.146

2.428
2.287

0.000

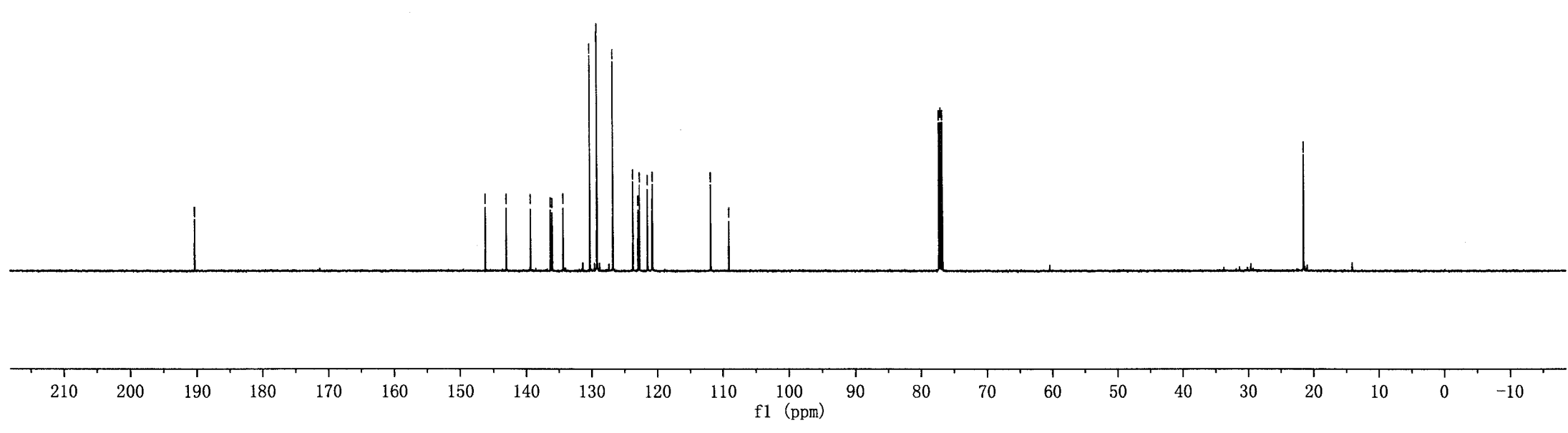
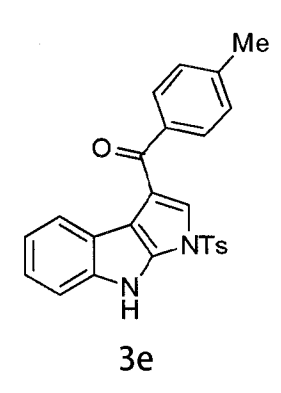


190.25

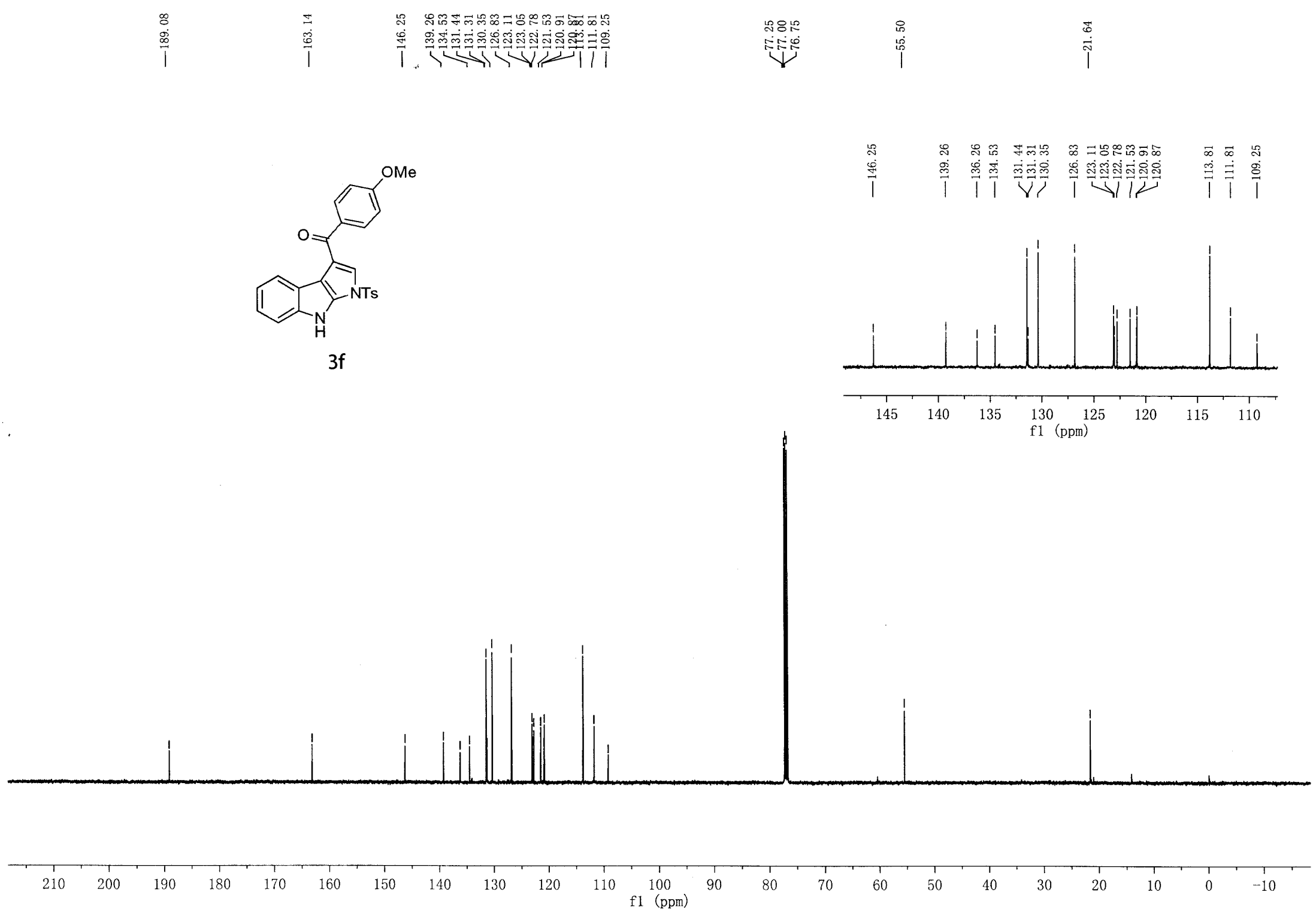
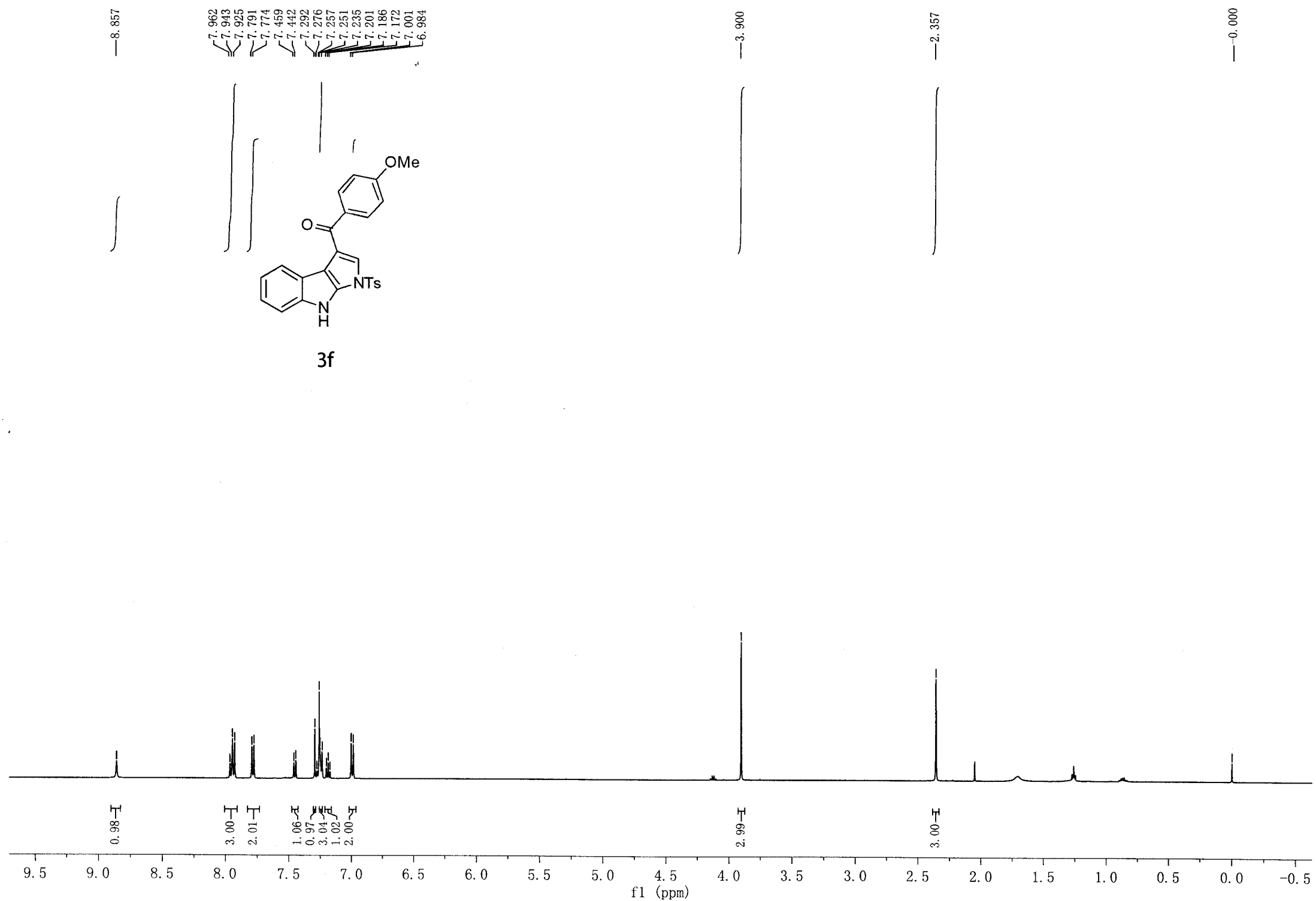
146.16
143.00
139.31
136.25
135.97
134.33
130.25
129.20
129.17
126.76
123.69
122.93
122.70
121.48
120.79
120.72
111.85
109.07

77.25
77.00
76.75

21.55
21.52

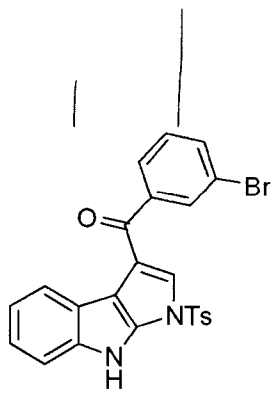


Supplementary Figure 46. ¹H and ¹³C NMR spectra for 3e



Supplementary Figure 47. ^1H and ^{13}C NMR spectra for **3f**

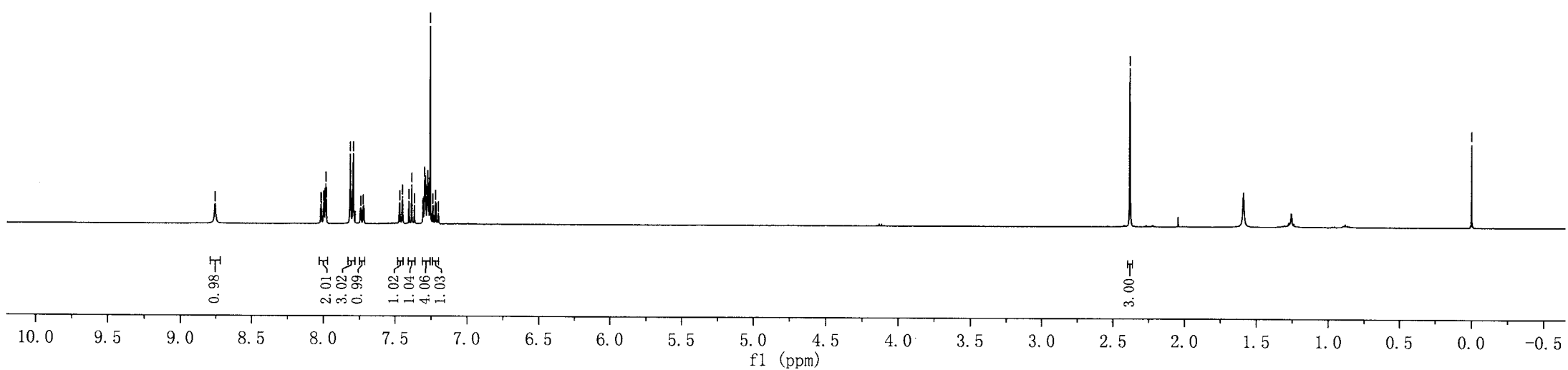
8.757
8.017
8.016
7.998
7.996
7.989
7.984
7.980
7.818
7.814
7.793
7.745
7.450
7.386
7.366
7.309
7.305
7.295
7.291
7.287
7.275
7.273
7.271
7.267
7.257
7.239
7.220
7.199



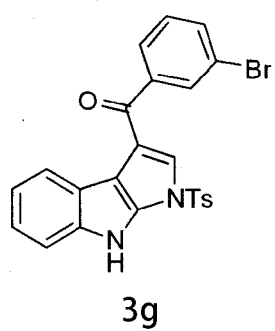
3g

2.381

-0.000



188.73

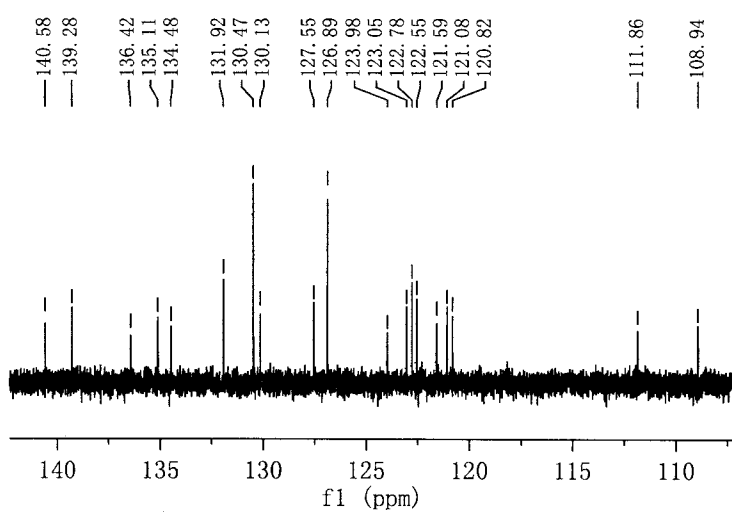


3g

146.47
140.58
139.28
135.11
131.92
130.47
130.13
127.55
126.89
123.05
122.78
122.55
121.08
119.86
108.94

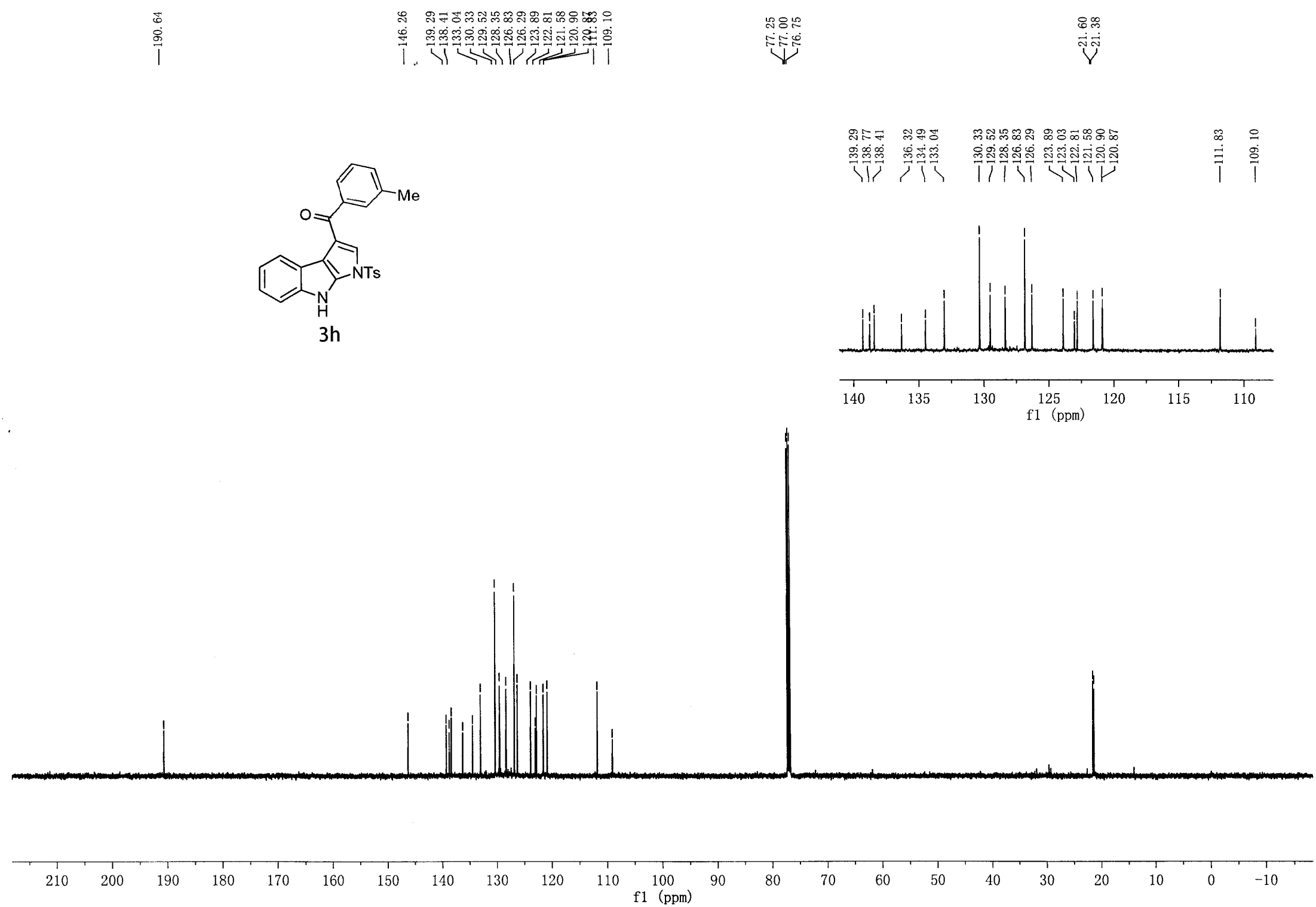
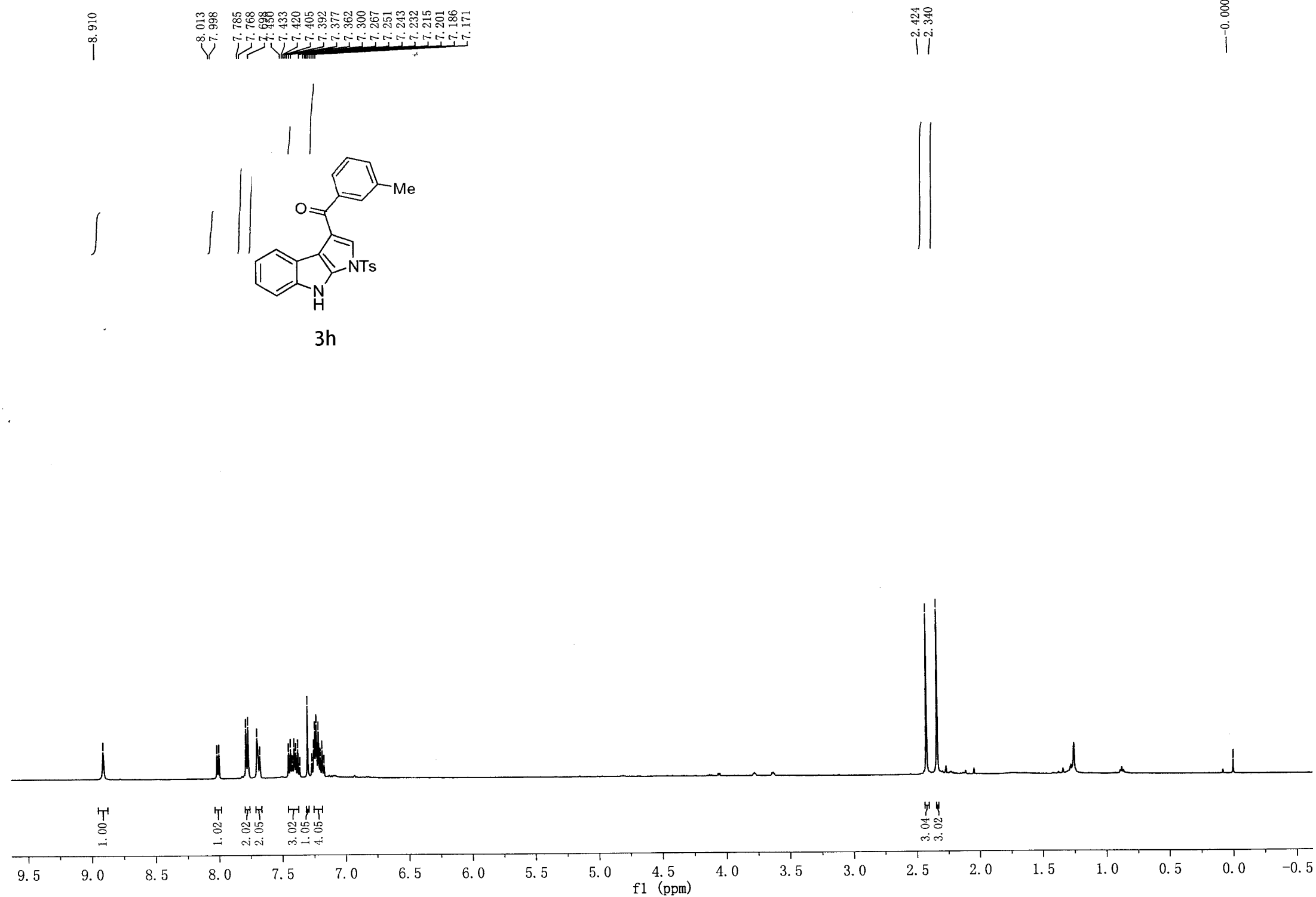
77.32
77.00
76.68

21.69

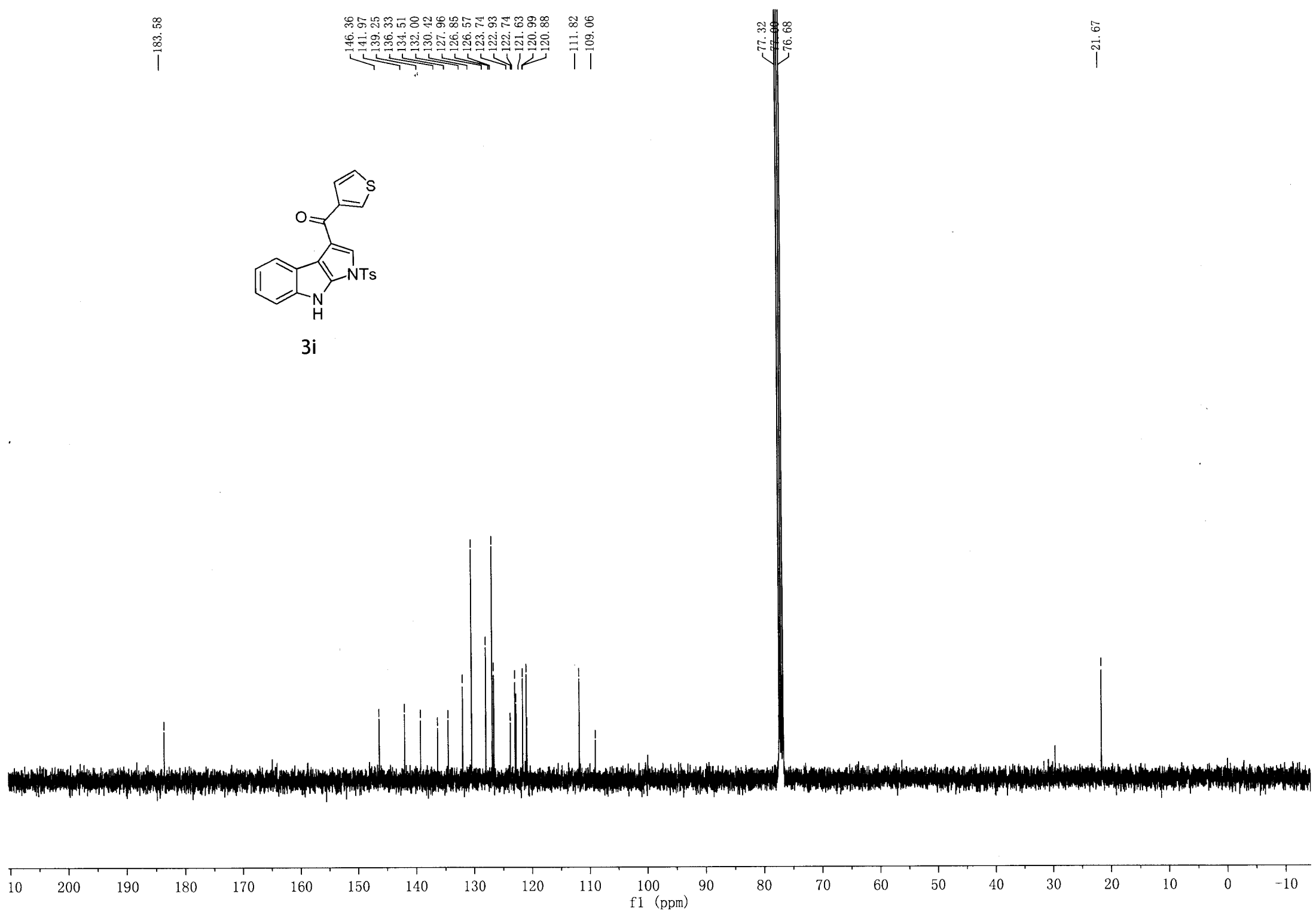
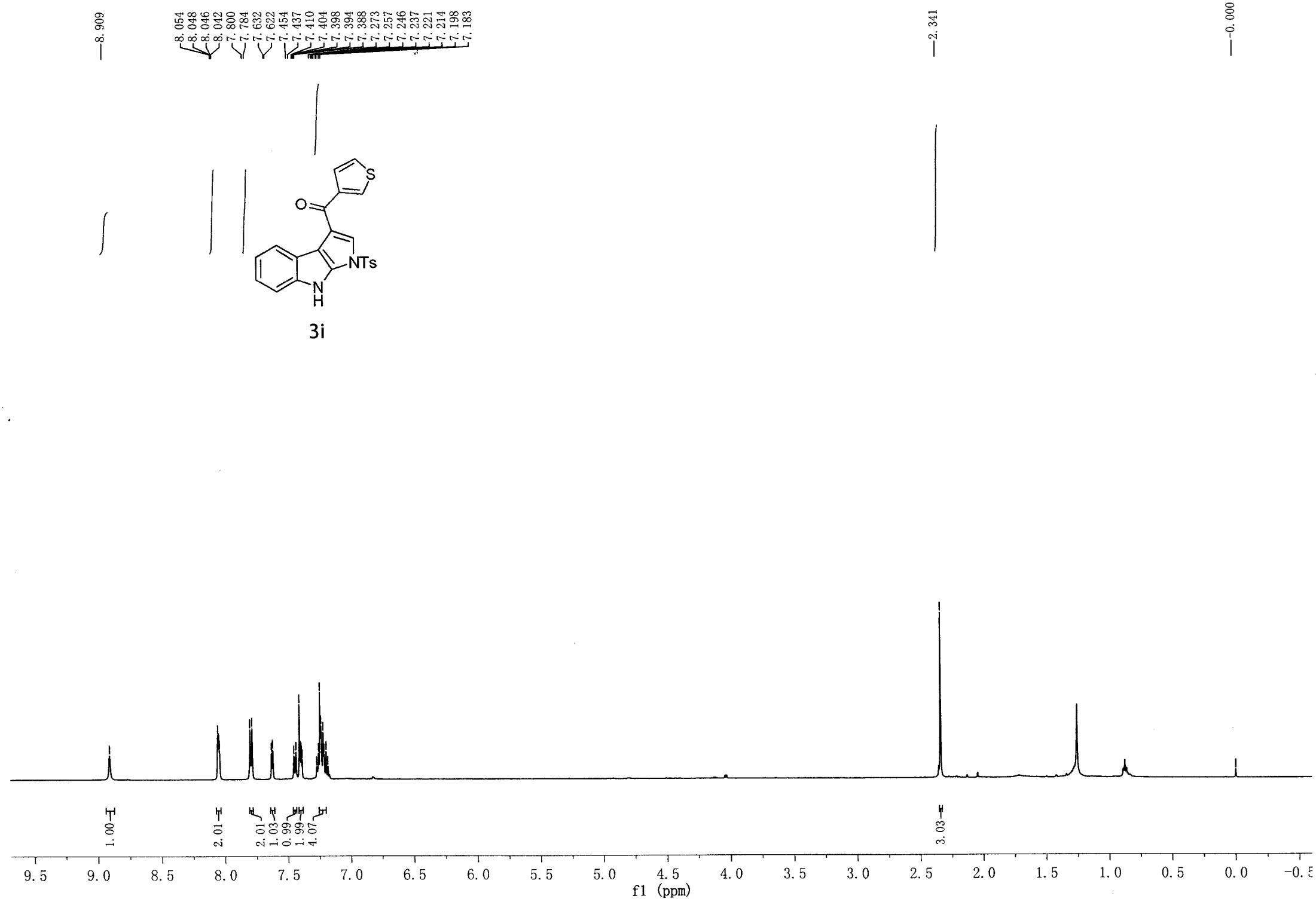


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

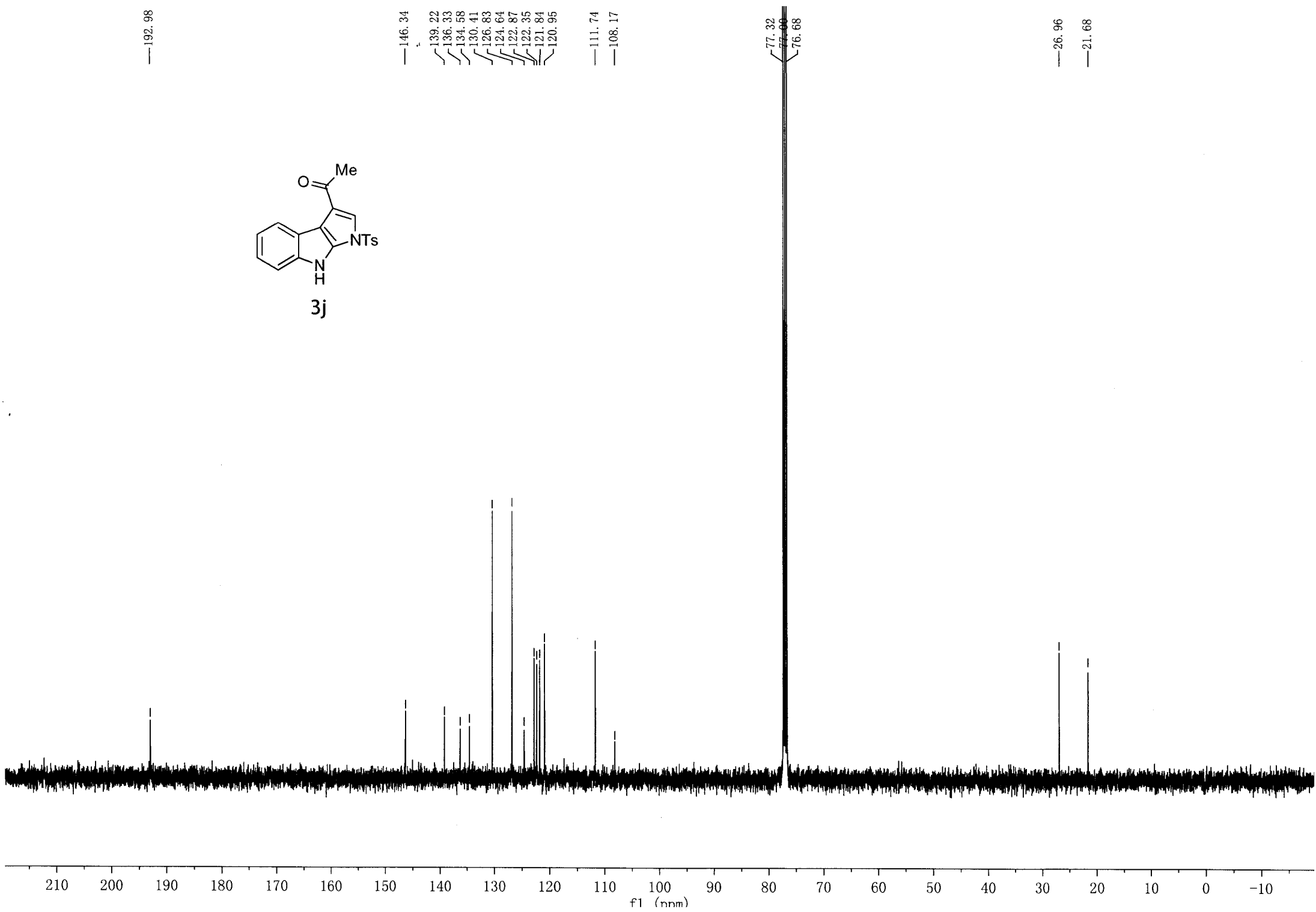
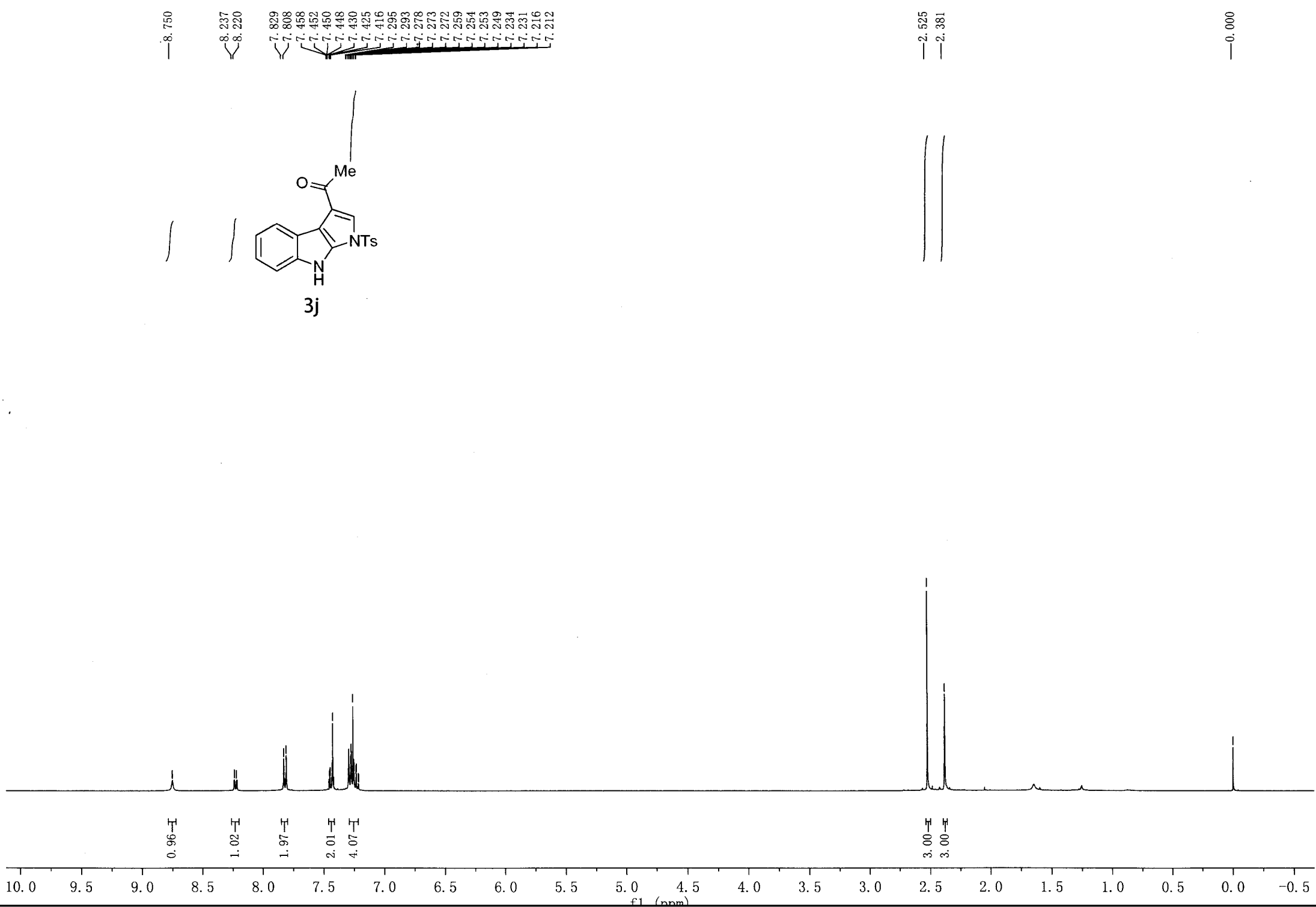
Supplementary Figure 48. ^1H and ^{13}C NMR spectra for 3g



Supplementary Figure 49. ¹H and ¹³C NMR spectra for **3h**

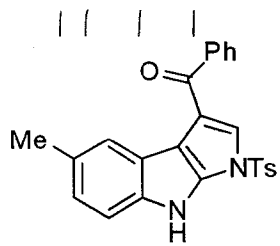


Supplementary Figure 50. ¹H and ¹³C NMR spectra for **3i**



Supplementary Figure 51. ¹H and ¹³C NMR spectra for 3j

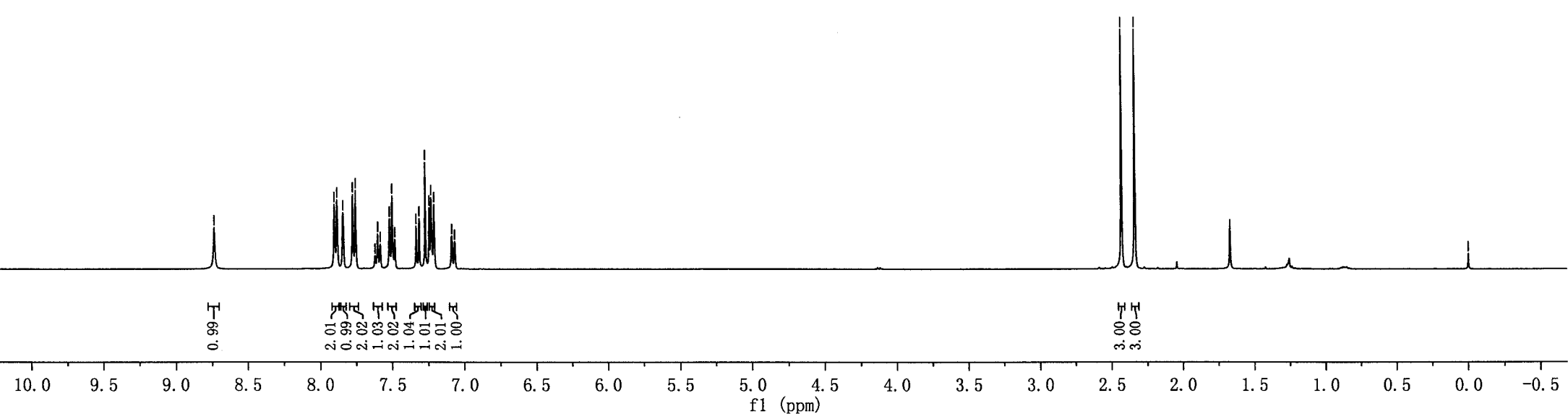
8.734
7.901
7.883
7.841
7.775
7.754
7.620
7.601
7.583
7.519
7.500
7.481
7.333
7.312
7.270
7.243
7.230
7.209
7.087
7.068



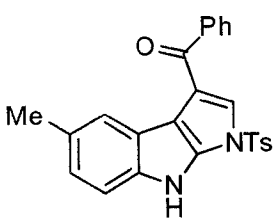
3k

2.431
2.338

0.000



190.53



3k

146.21
138.81
137.59
136.60
132.20
130.31
129.03
128.52
126.80
124.19
123.82
122.92
121.52
121.05
108.91

77.32
77.00
76.68

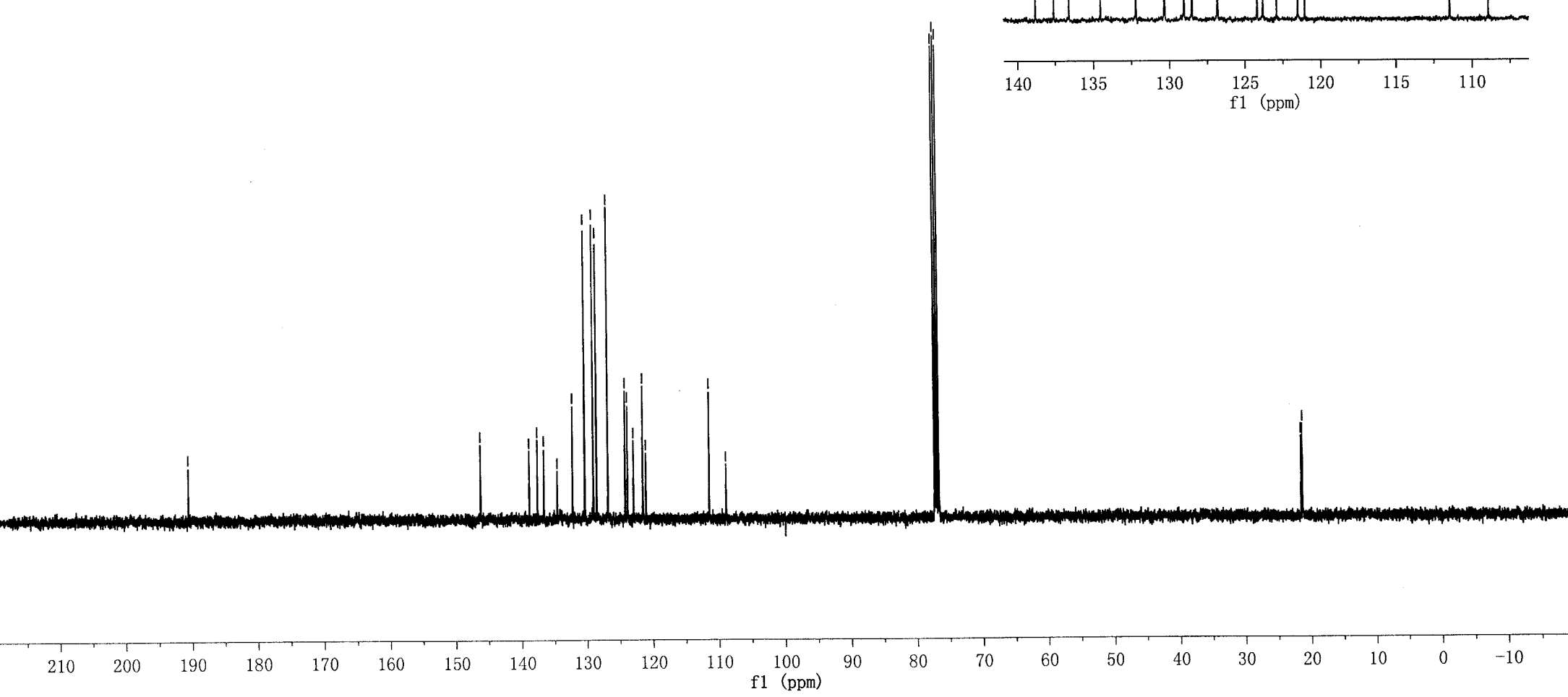
21.58
21.39

138.81
137.59
136.60
134.54

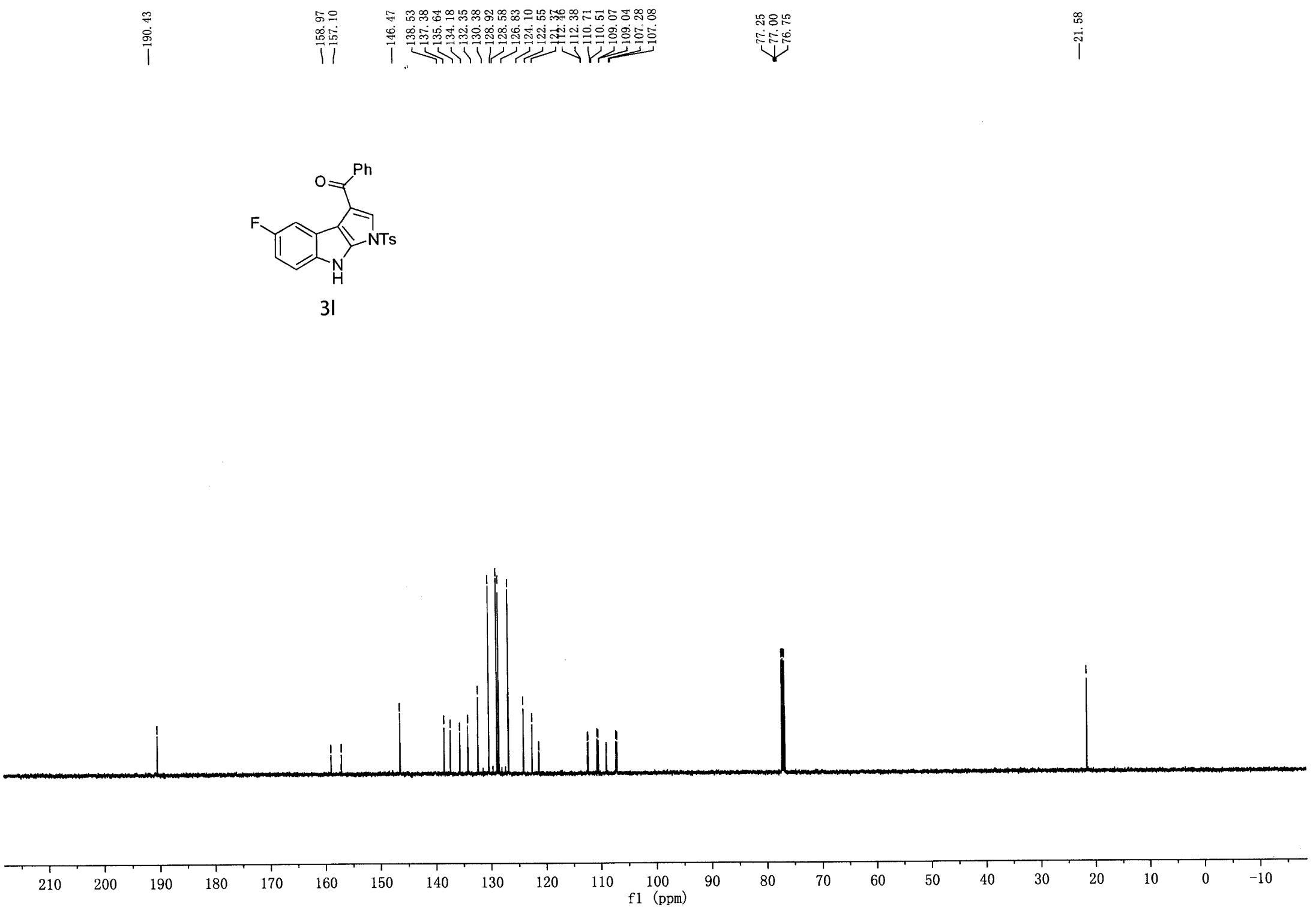
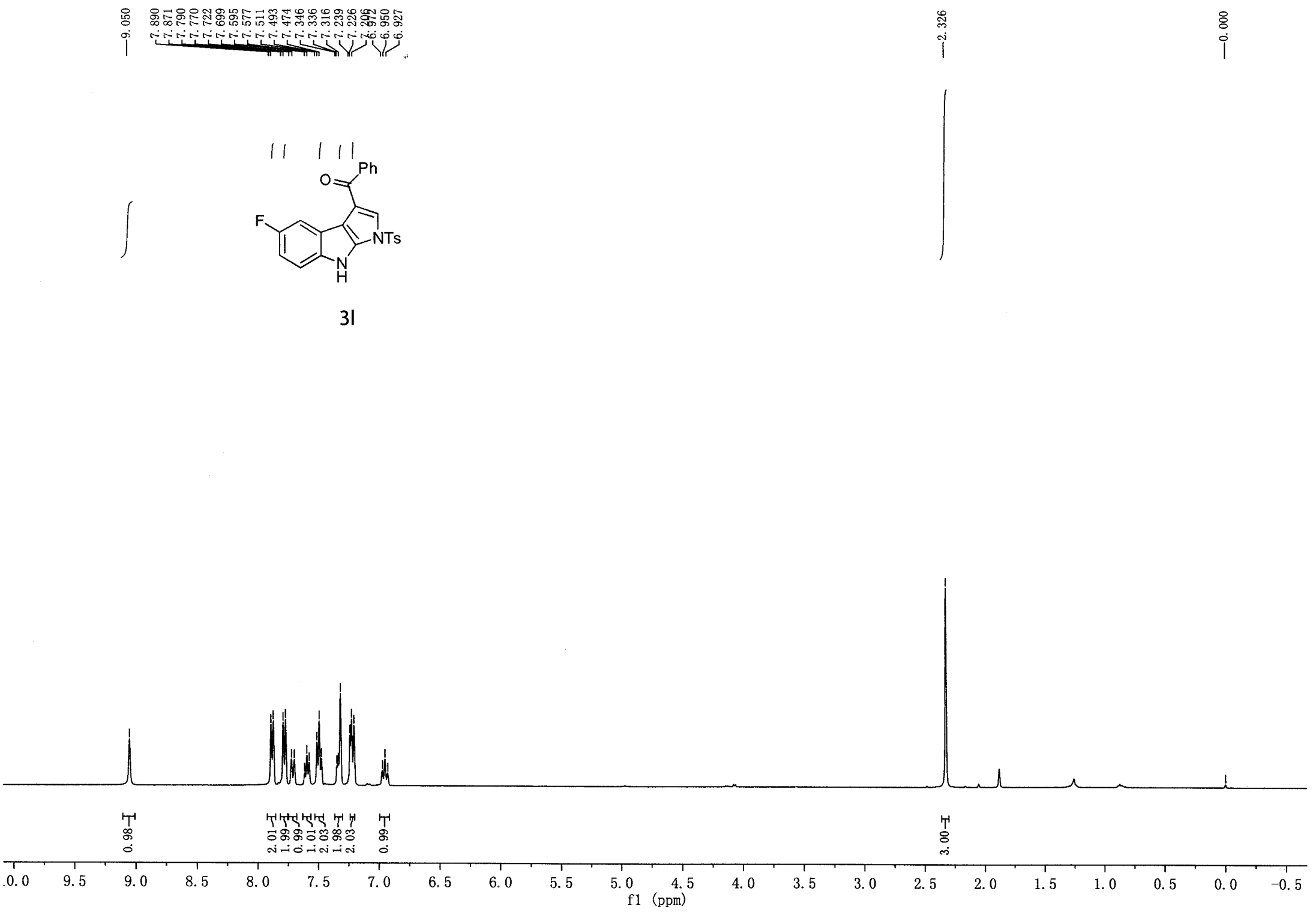
132.20
130.31
129.03
128.52
126.80

124.19
123.82
122.92
121.52
121.05

111.45
108.91

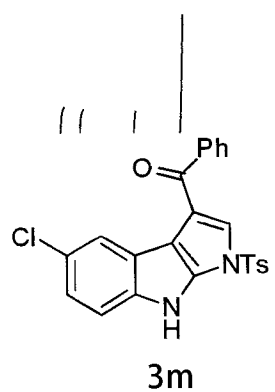


Supplementary Figure 52. ¹H and ¹³C NMR spectra for 3k

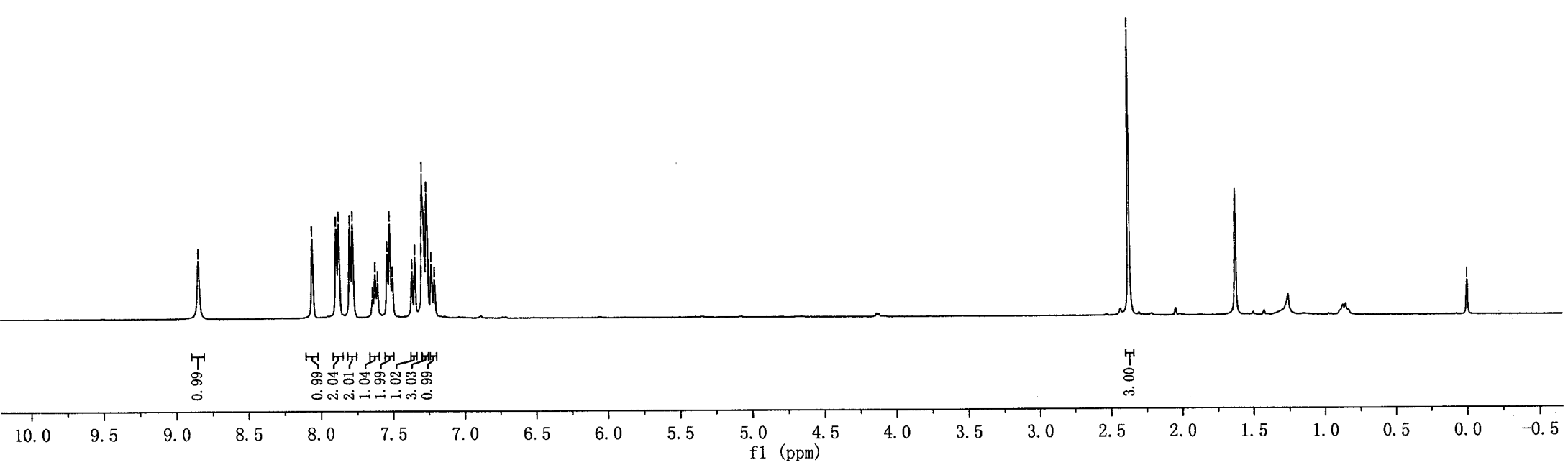


Supplementary Figure 53. ^1H and ^{13}C NMR spectra for 31

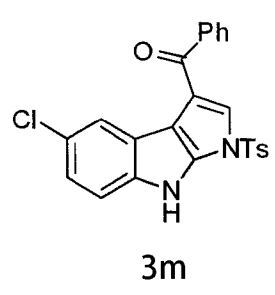
8.845
8.055
7.890
7.871
7.796
7.777
7.642
7.623
7.605
7.537
7.519
7.501
7.365
7.343
7.290
7.262
7.231
7.209



2.374
0.000



190.18

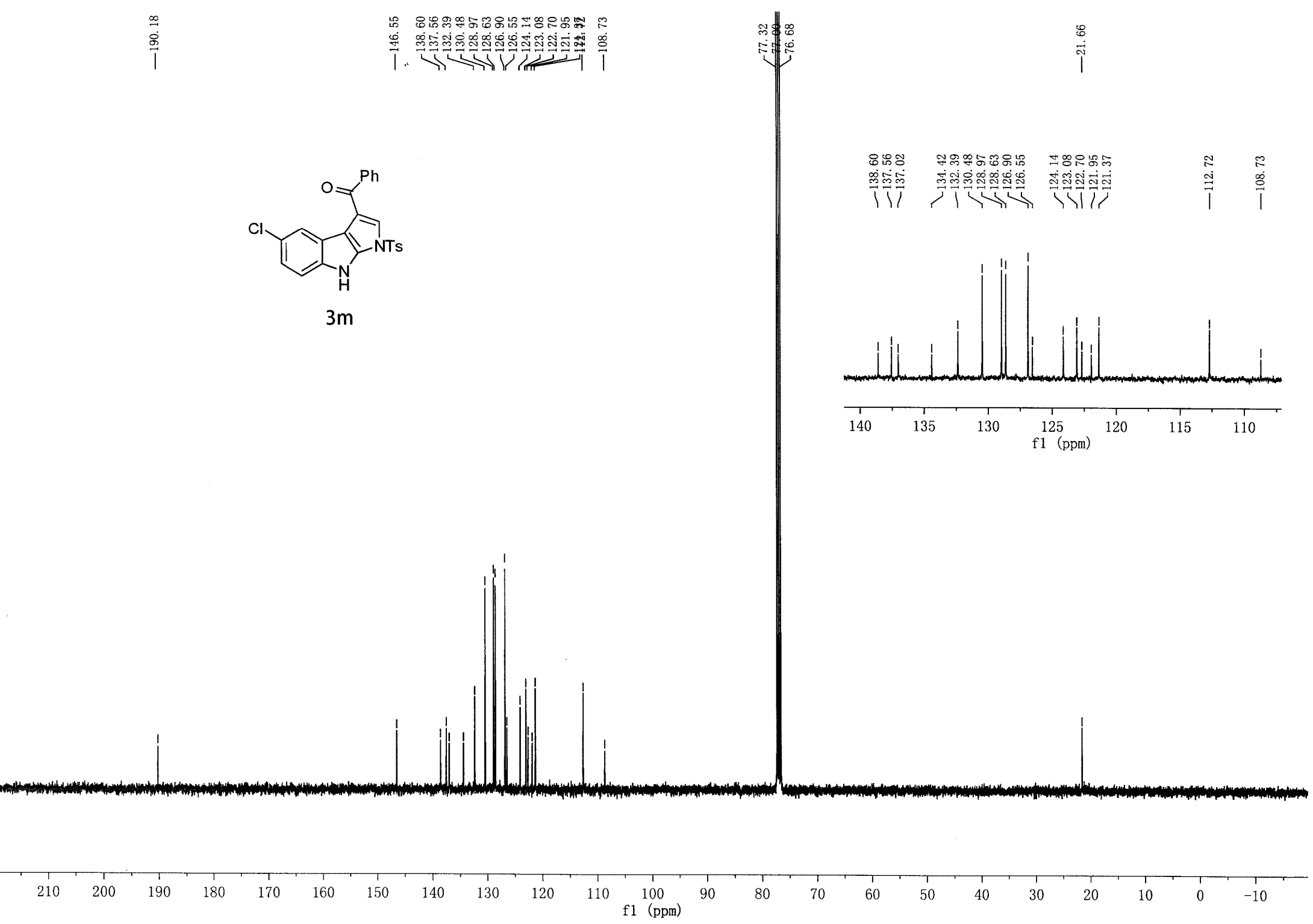


146.55
138.60
137.56
137.56
132.39
130.48
128.97
128.63
126.90
126.55
124.14
123.08
122.70
121.95
121.92
121.92
108.73

77.32
77.00
76.68

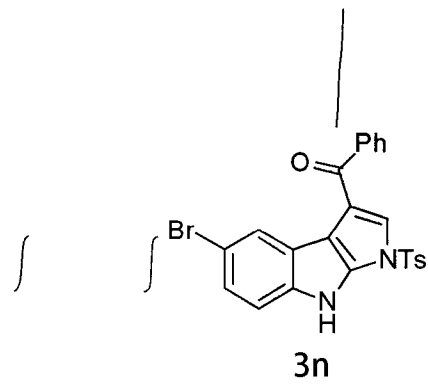
21.66

138.60
137.56
137.02
134.42
132.39
130.48
128.97
128.63
126.90
126.55
124.14
123.08
122.70
121.95
121.37
112.72
108.73



Supplementary Figure 54. ¹H and ¹³C NMR spectra for 3m

8.856
8.210
7.888
7.870
7.793
7.772
7.642
7.623
7.605
7.537
7.518
7.500
7.367
7.363
7.345
7.341
7.319
7.294
7.280
7.256



2.371

0.000

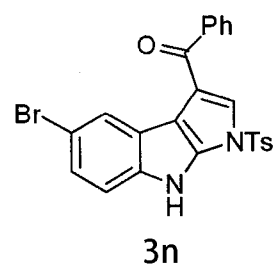
0.98
0.97
2.01
2.03
2.01
5.03

3.00

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 -0.5

f1 (ppm)

190.17



146.58
138.53
137.82
134.34
132.42
130.50
128.97
128.65
126.90
125.74
124.37
124.14
122.67
113.15
108.56

77.25
77.00
76.75

21.70

138.53
137.82
136.78
134.34
132.42
130.50
128.97
128.65
126.90
125.74
124.37
124.14
122.67
122.45
114.04
113.15
108.56

140 135 130 125 120 115 110

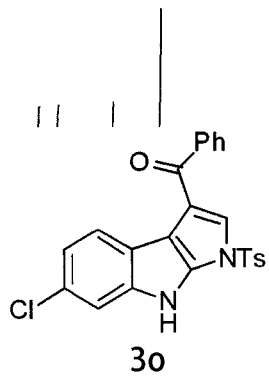
f1 (ppm)

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

f1 (ppm)

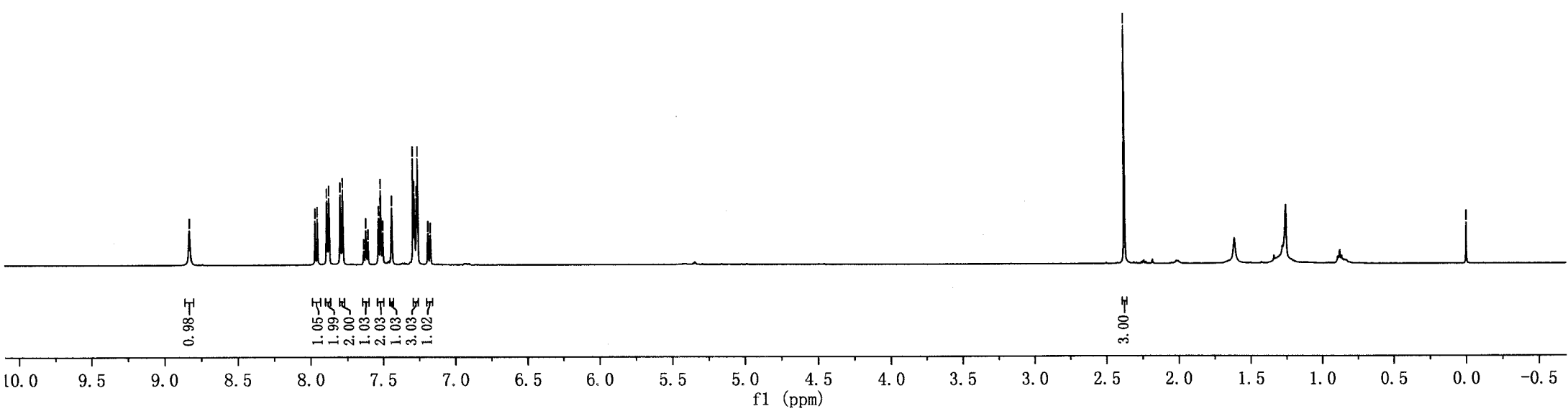
Supplementary Figure 55. ¹H and ¹³C NMR spectra for 3n

8.827
7.968
7.951
7.887
7.872
7.795
7.778
7.633
7.618
7.604
7.530
7.515
7.500
7.437
7.291
7.281
7.265
7.257
7.190
7.187
7.173
7.170



2.376

-0.000

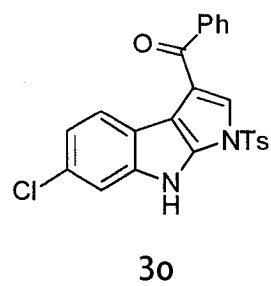


190.29

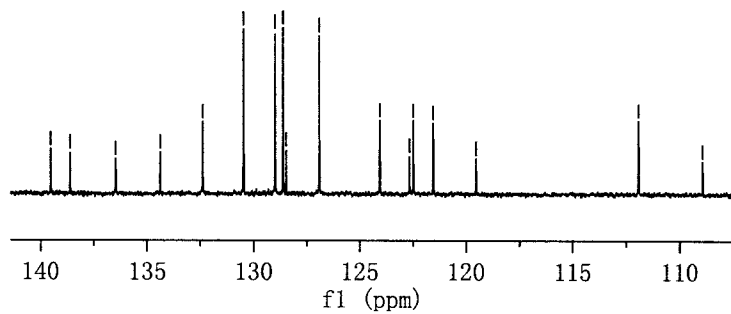
146.55
139.53
138.61
134.39
132.38
130.48
129.00
128.63
128.47
126.91
124.08
122.68
122.50
121.56
119.54
108.92

77.25
77.00
76.75

21.68



139.53
138.61
136.47
134.39
132.38
130.48
129.00
128.63
128.47
126.91
124.08
122.68
122.50
121.56
119.54
111.93
108.92



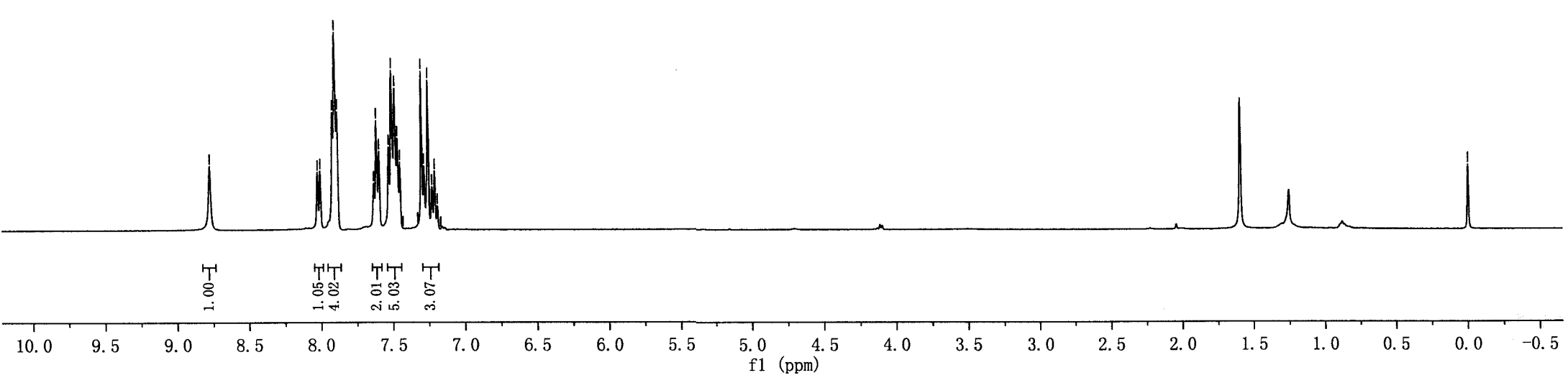
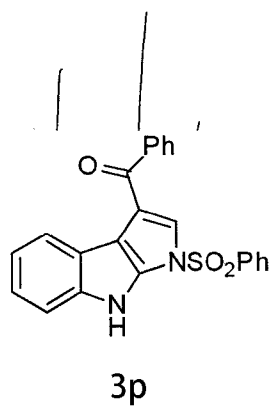
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Supplementary Figure 56. ¹H and ¹³C NMR spectra for 30

8.774

8.024
8.005
7.918
7.901
7.886
7.633
7.615
7.597
7.530
7.509
7.487
7.469
7.452
7.430
7.327
7.301
7.283
7.255
7.229
7.210
7.192
7.168

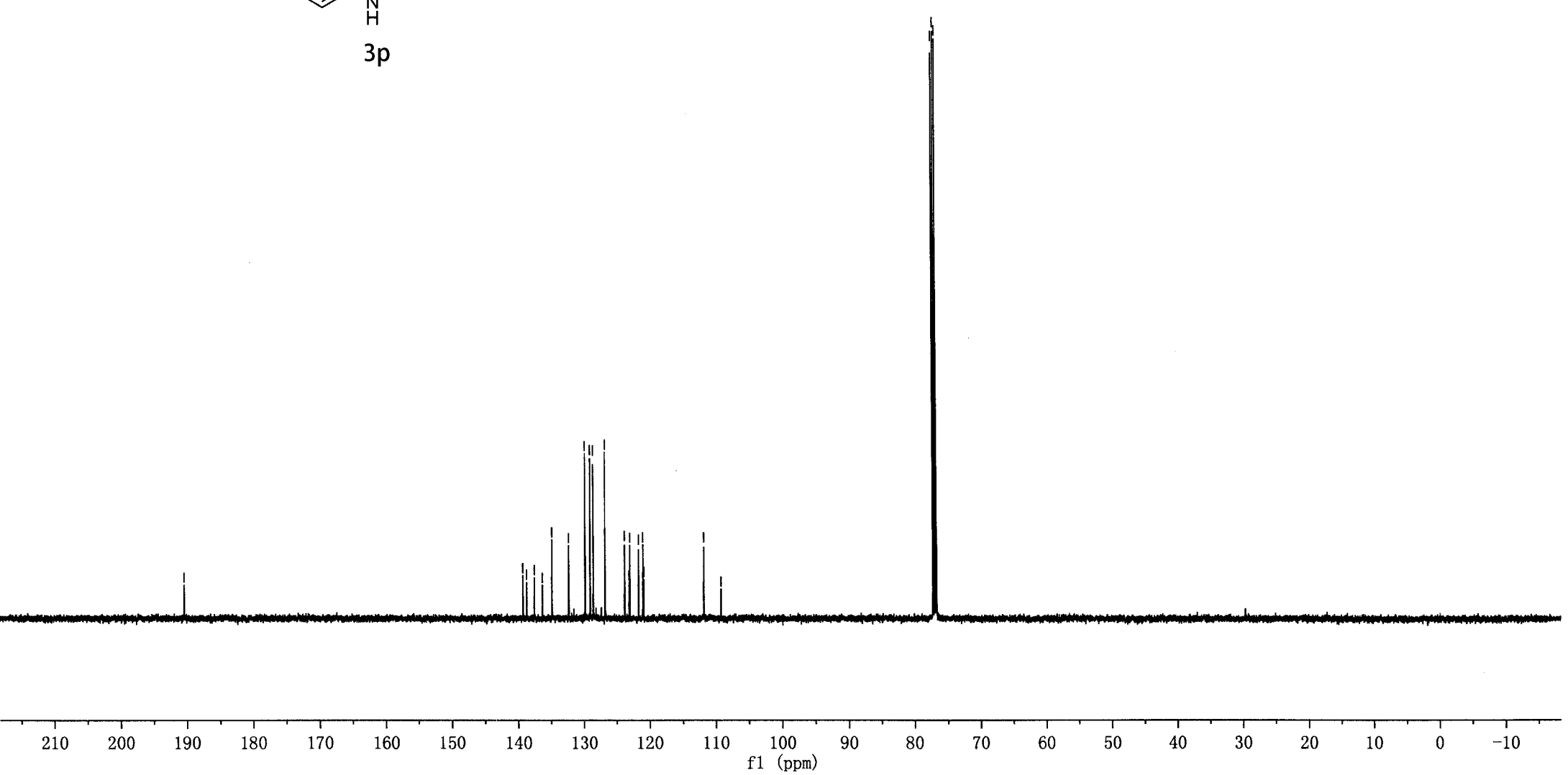
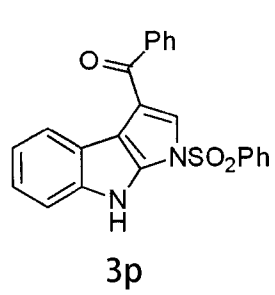
0.000



190.40

139.29
138.72
137.58
136.33
134.88
132.33
129.81
129.06
128.58
126.79
123.81
123.11
123.00
121.68
121.04
120.92
111.85
109.24

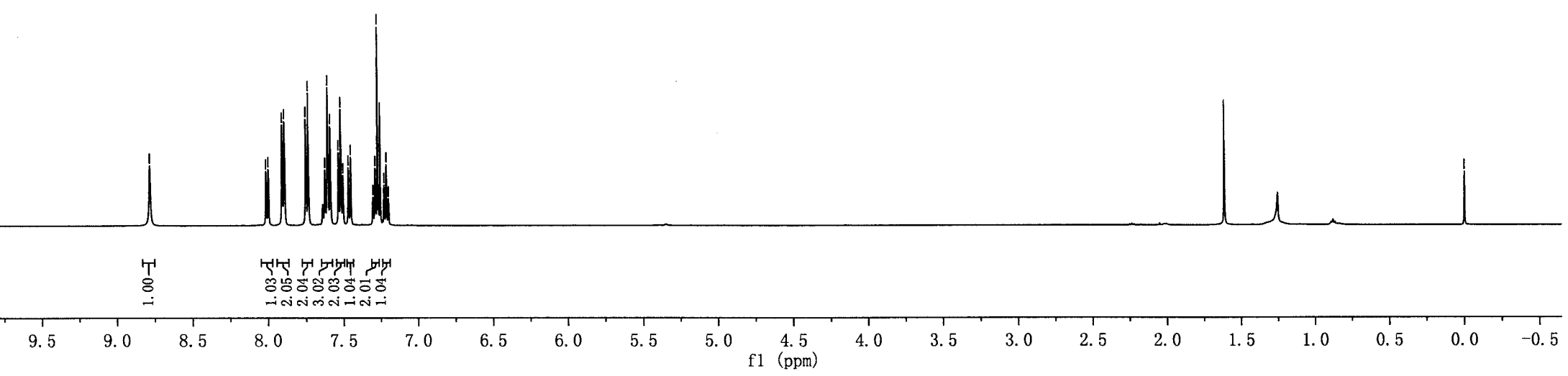
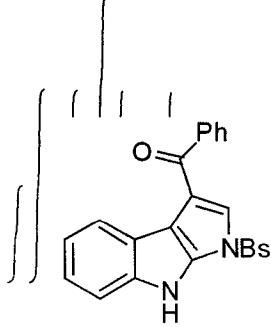
77.25
77.00
76.75



Supplementary Figure 57. ¹H and ¹³C NMR spectra for 3p

-0.000

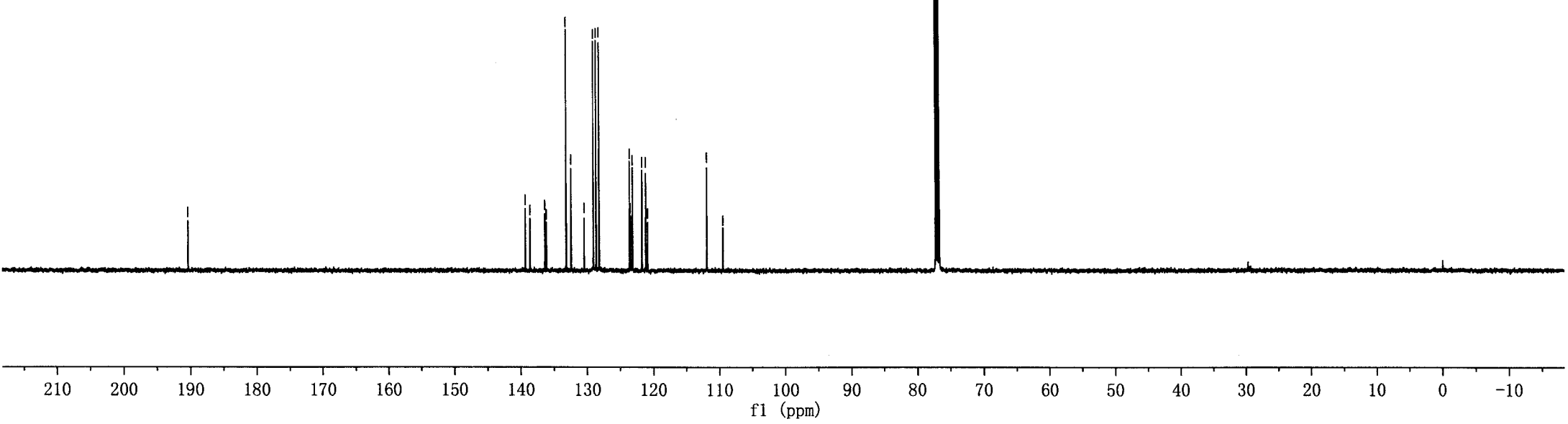
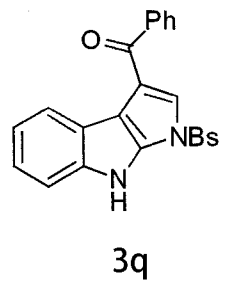
8.782
8.012
7.996
7.906
7.892
7.751
7.733
7.623
7.605
7.587
7.534
7.518
7.503
7.468
7.452
7.304
7.289
7.272
7.229
7.214
7.199



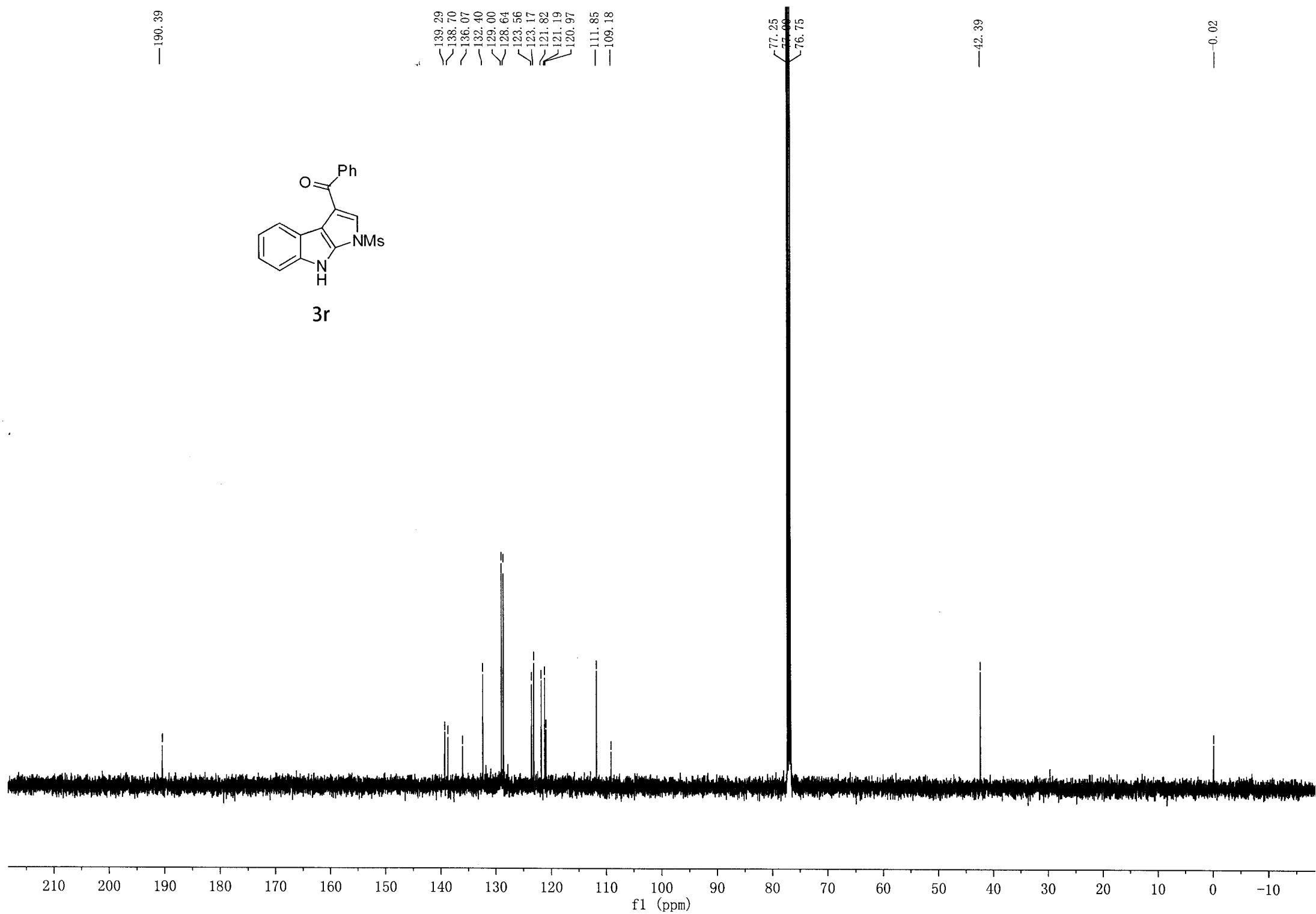
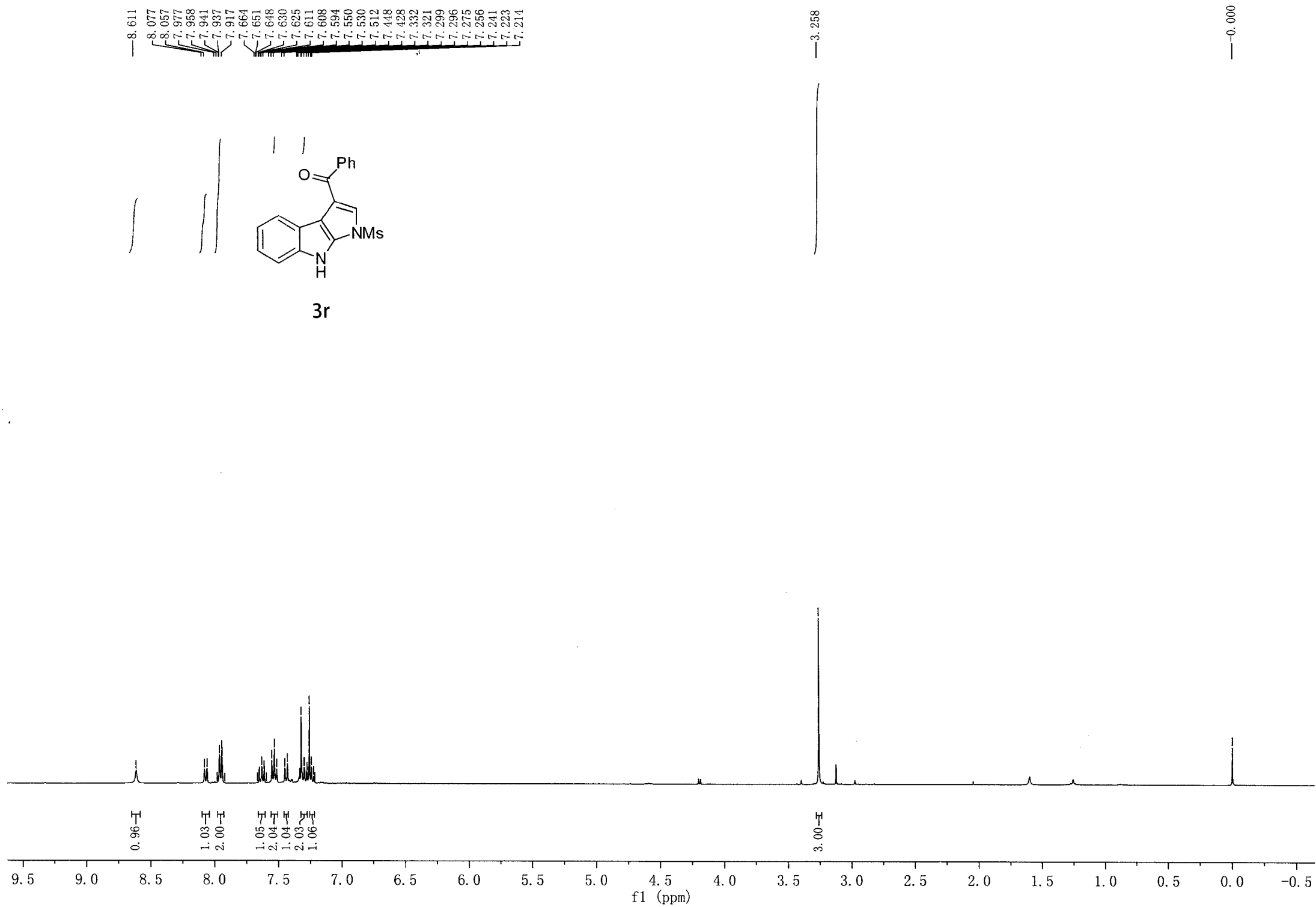
190.32

139.30
138.61
136.36
136.15
133.16
132.42
130.43
129.05
128.62
128.17
123.58
123.46
123.15
121.72
121.16
120.88
111.89
109.45

77.25
77.00
76.75



Supplementary Figure 58. ¹H and ¹³C NMR spectra for 3q



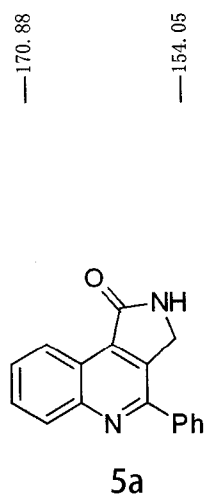
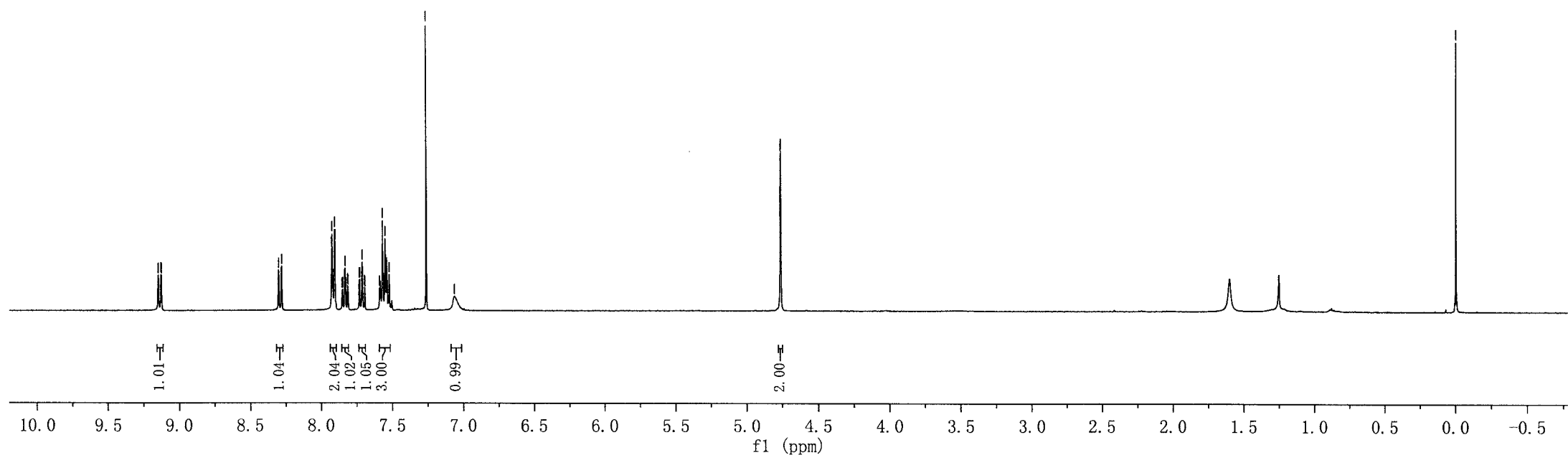
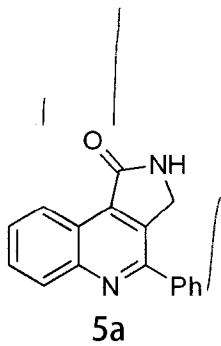
Supplementary Figure 59. ¹H and ¹³C NMR spectra for 3r

9.147
9.145
9.127
9.124

8.300
8.280
7.927
7.923
7.906
7.903
7.882
7.713
7.570
7.562
7.063

4.765
4.762

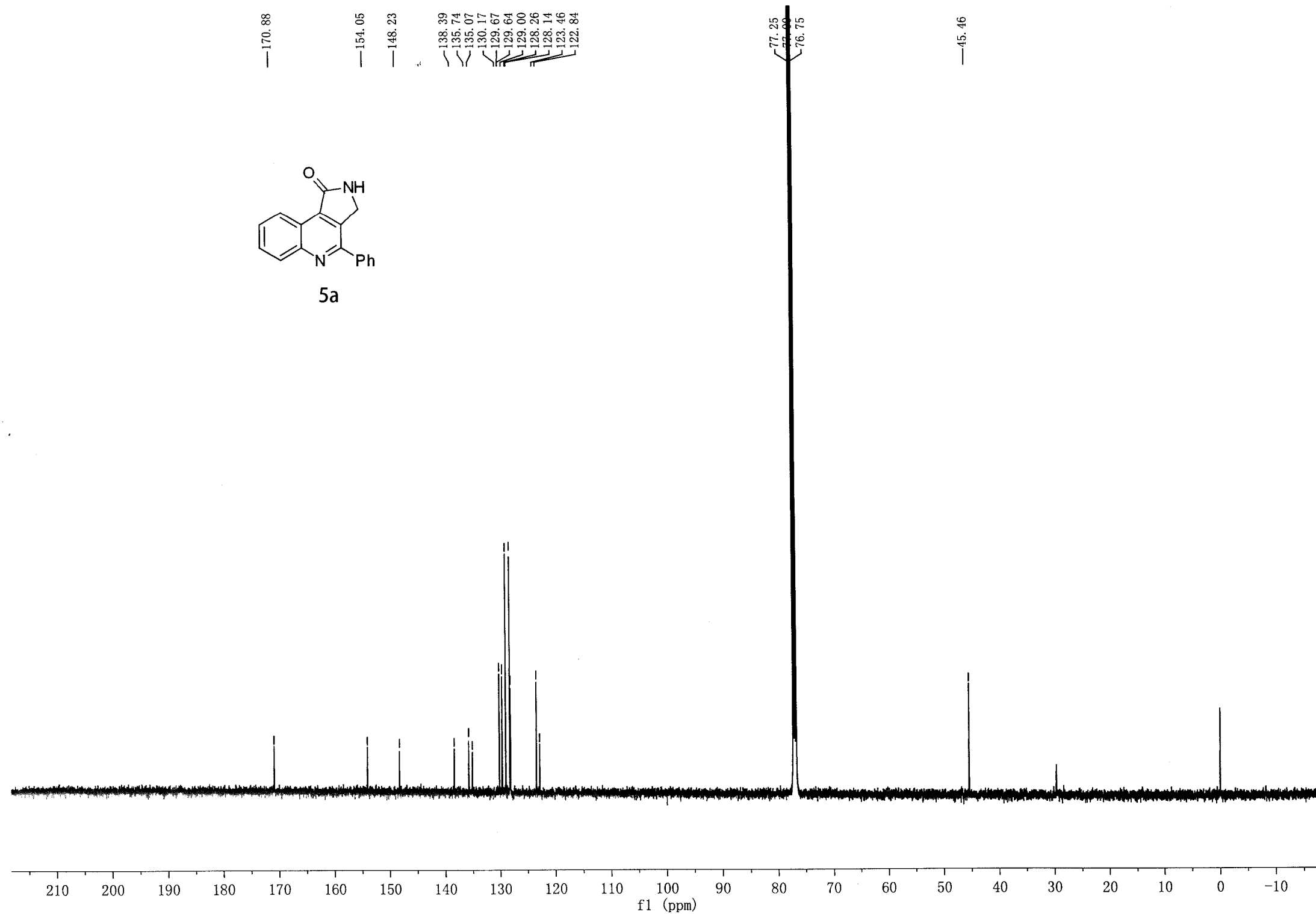
0.000



170.88
154.05
148.23
138.39
135.74
135.07
130.17
129.67
129.64
129.00
128.26
128.14
123.46
122.84

77.25
77.00
76.75

45.46



Supplementary Figure 60. ¹H and ¹³C NMR spectra for 5a

9.180
9.178
9.159
9.157

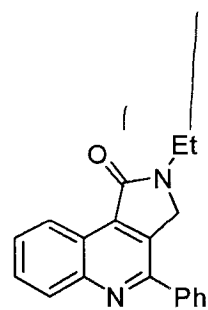
8.275
8.254
7.926
7.922
7.905
7.902
7.576
7.558
7.542

4.685

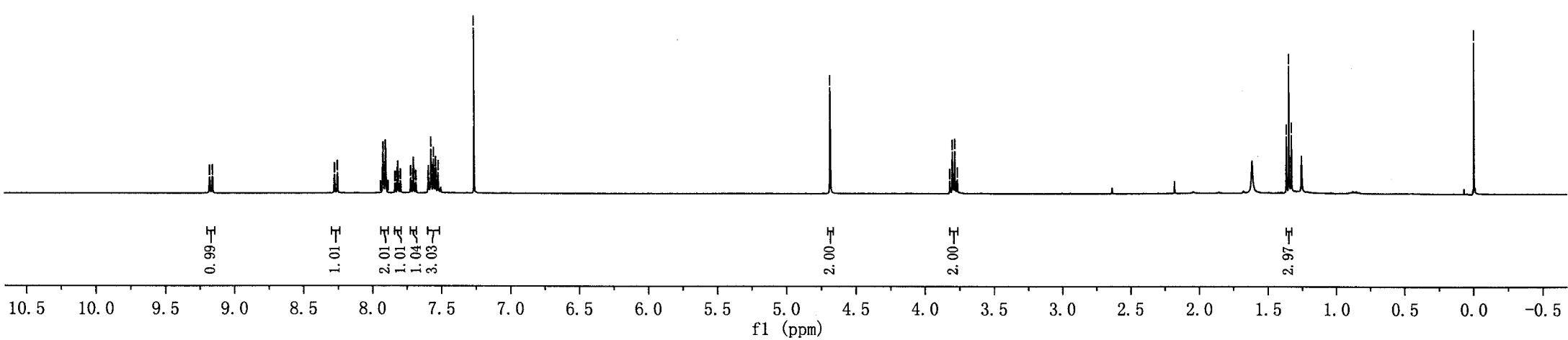
3.820
3.802
3.784
3.765

1.366
1.348
1.329

0.000



5b



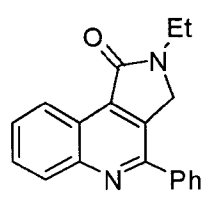
167.74
153.59
148.35
138.59
136.26
133.23
130.04
129.58
129.54
128.98
128.27
127.94
123.60
122.79

77.25
77.00
76.75

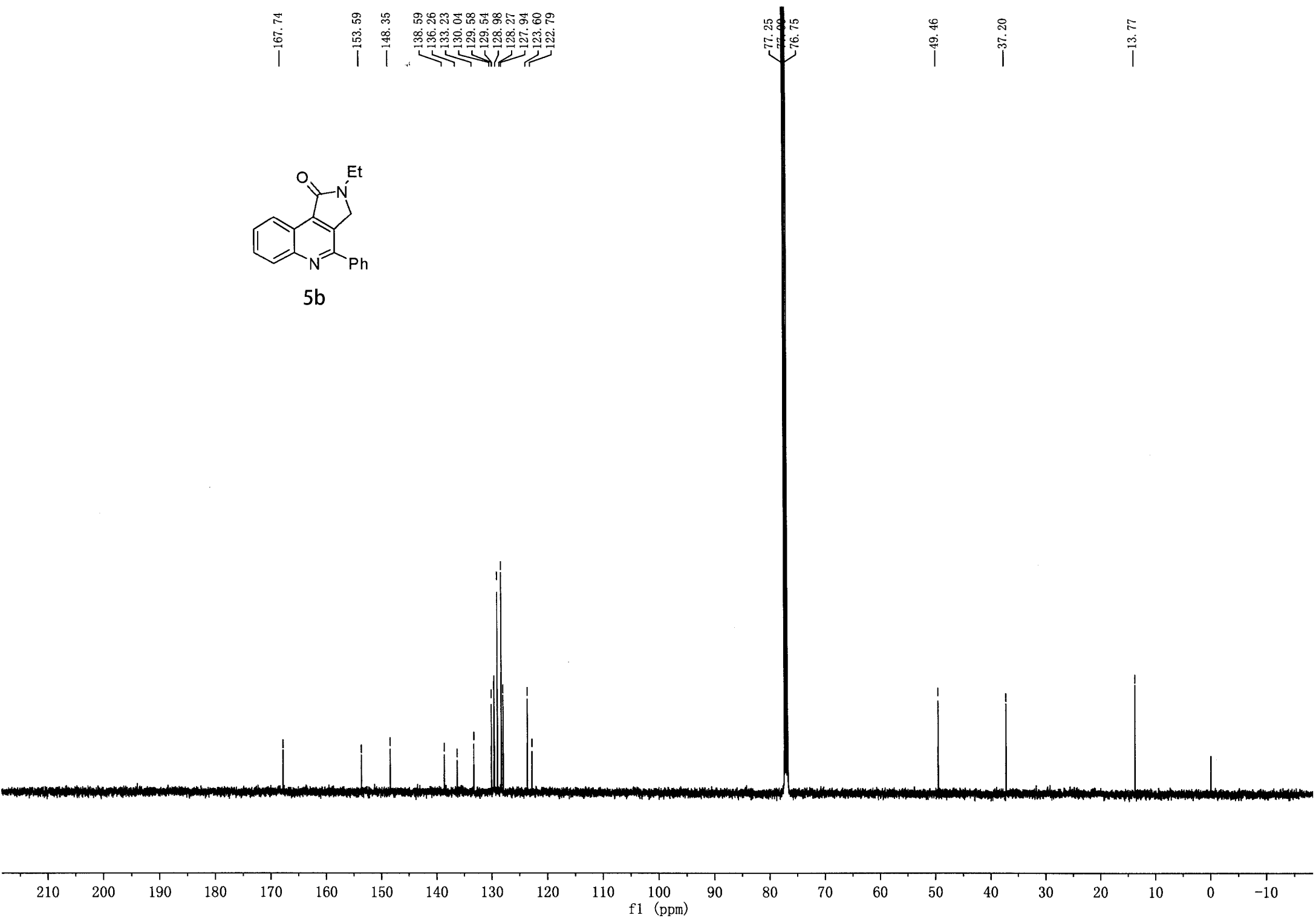
49.46

37.20

13.77

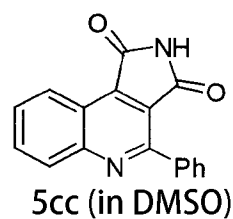


5b



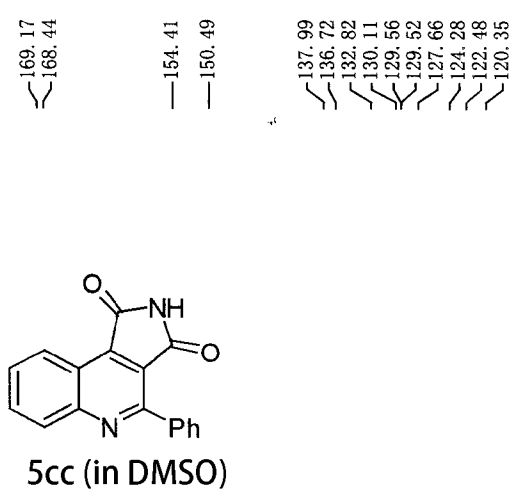
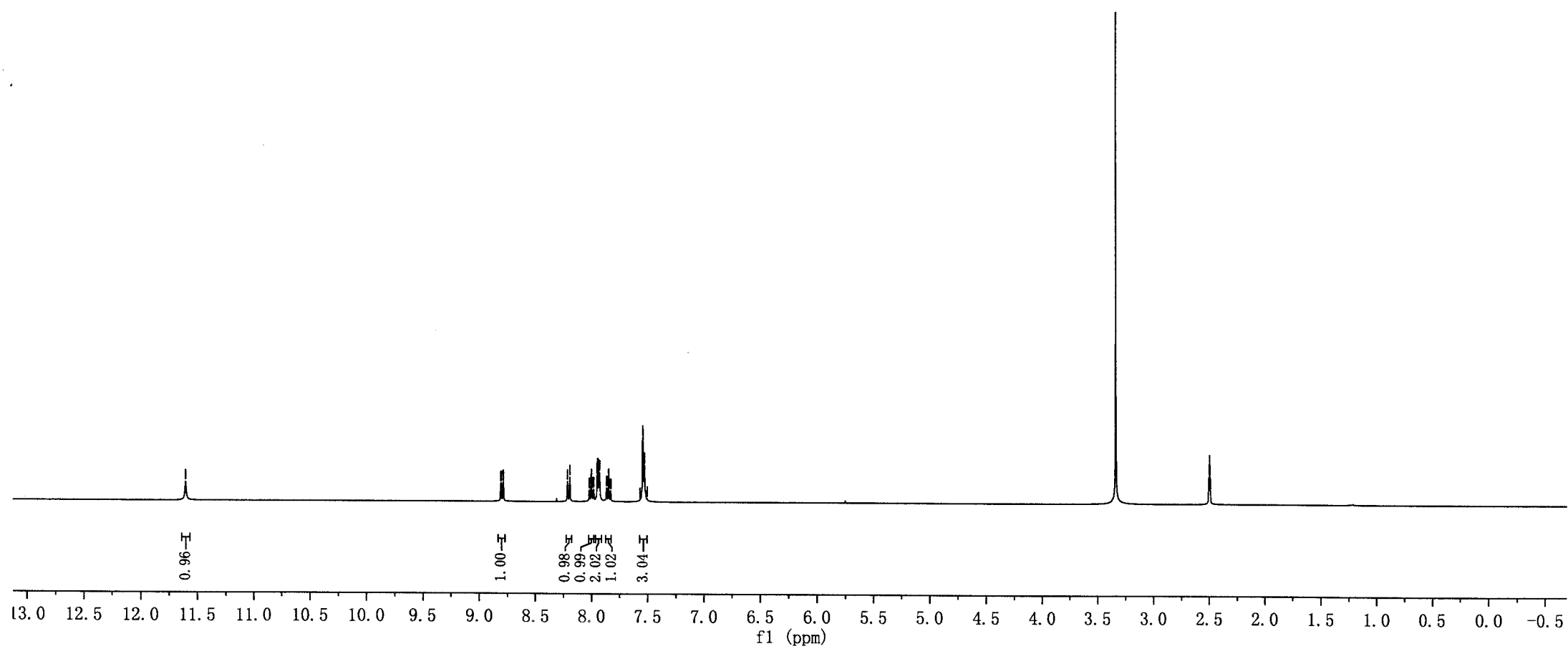
Supplementary Figure 61. ¹H and ¹³C NMR spectra for 5b

—11.604



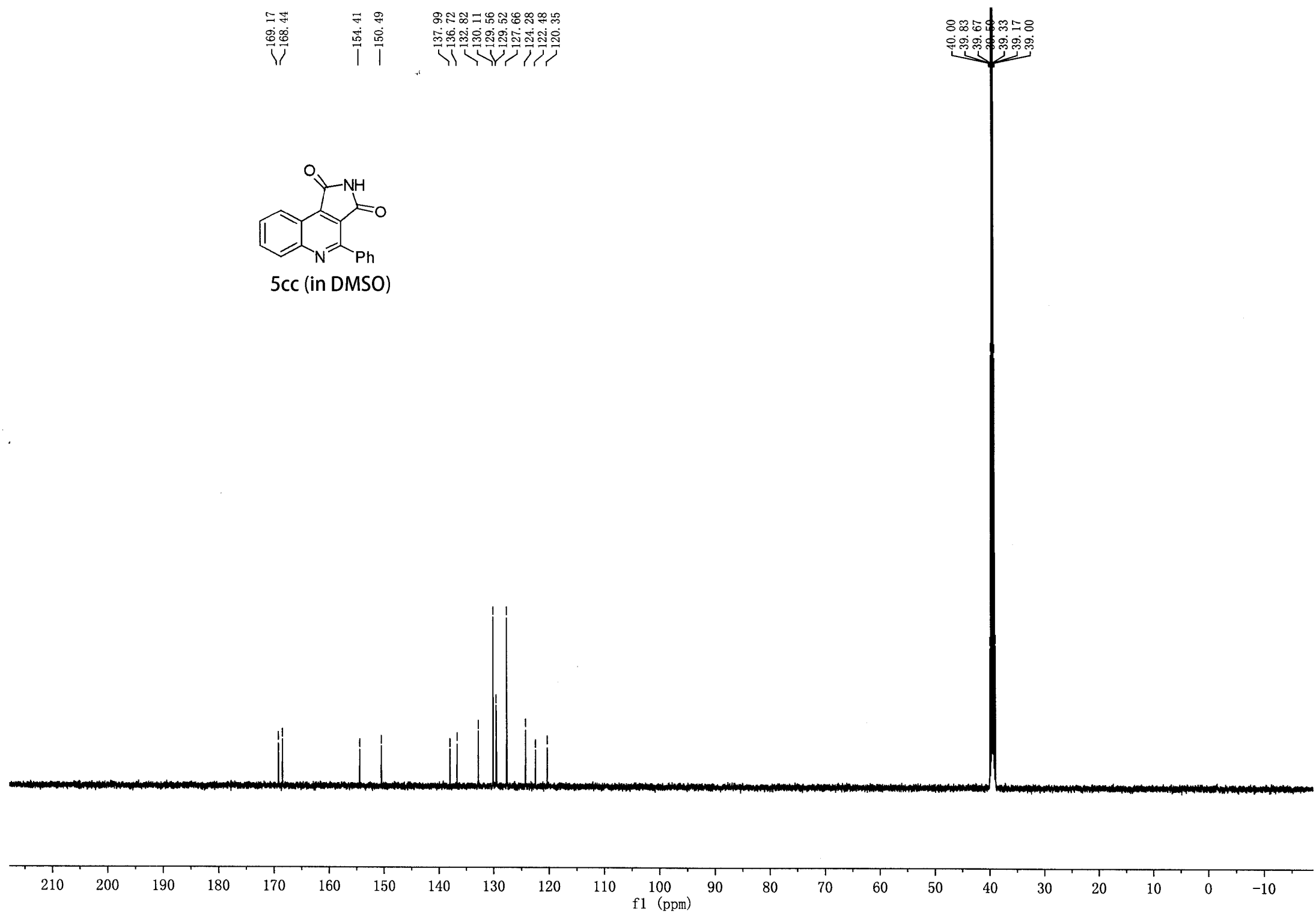
8.809
8.807
8.788
8.786
8.214
8.193
8.022
8.019
8.005
8.001
7.998
7.984
7.980
7.952
7.946
7.938
7.936
7.927
7.870
7.867
7.852
7.849
7.846
7.832
7.829
7.570
7.545
7.540
7.532
7.528
7.505

2.509
2.505
2.500
2.496
2.491



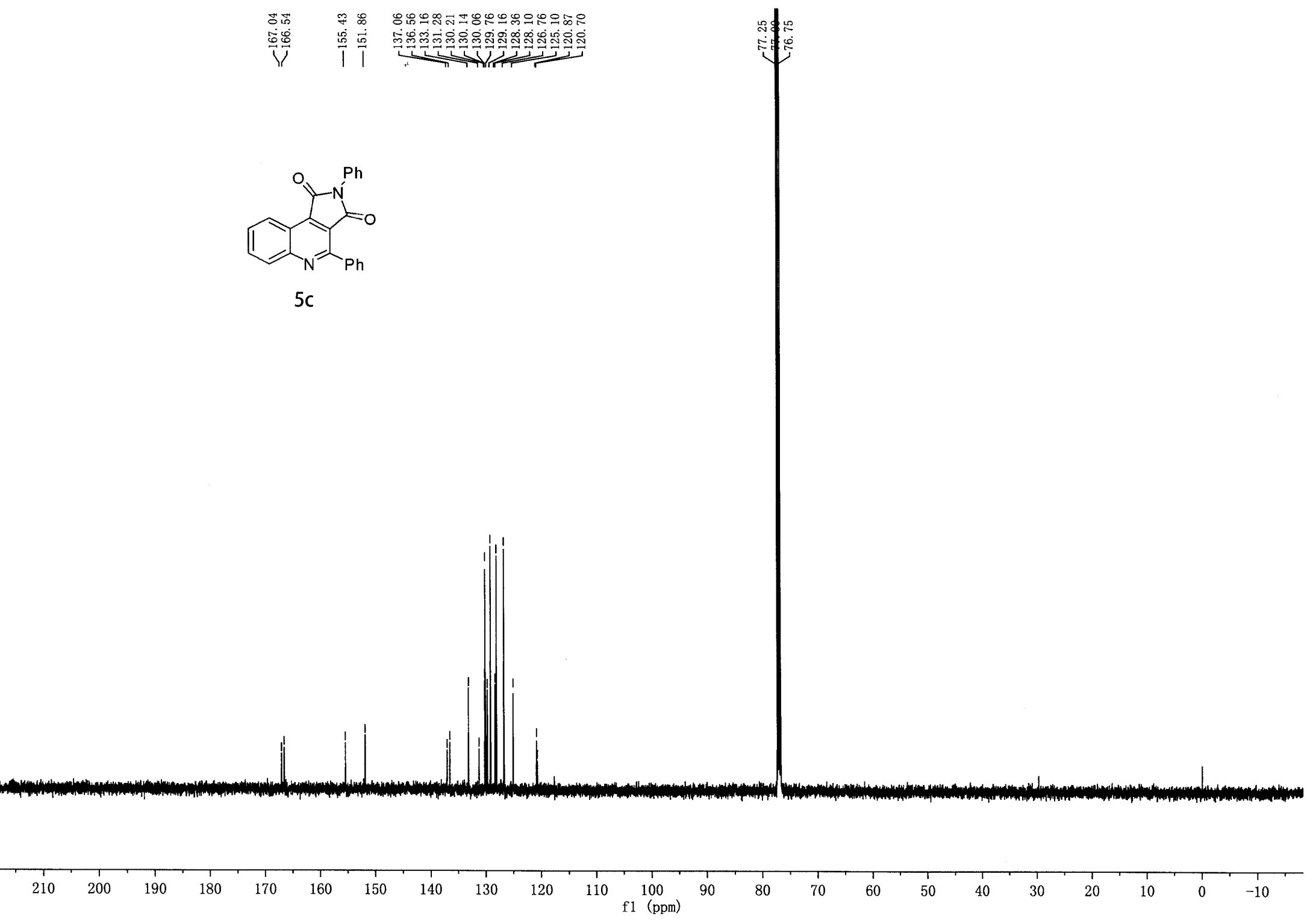
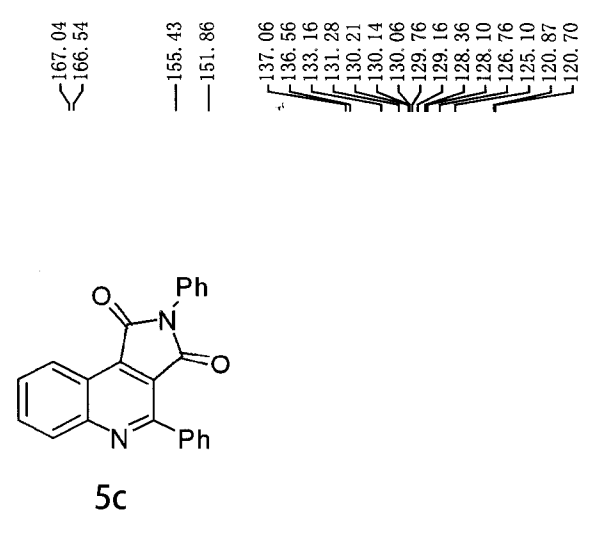
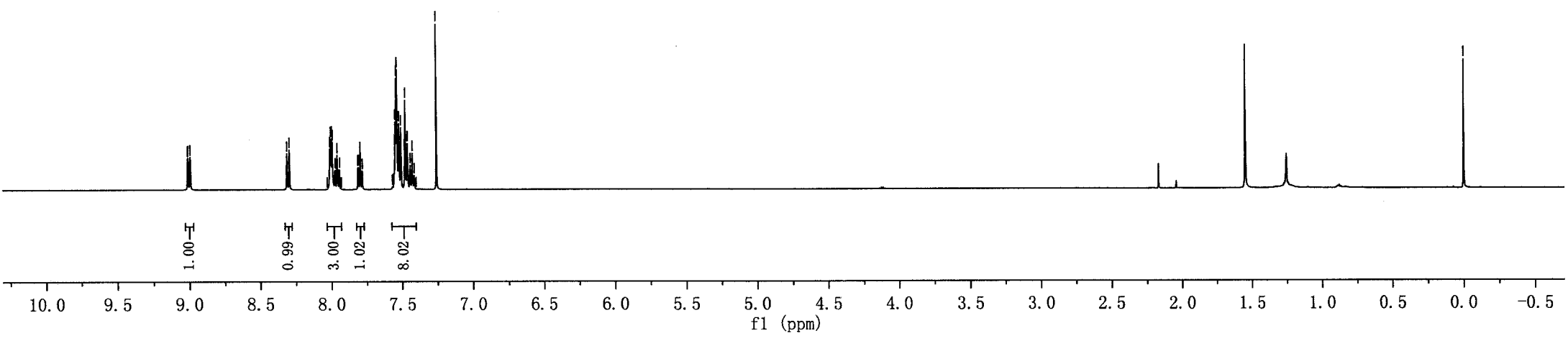
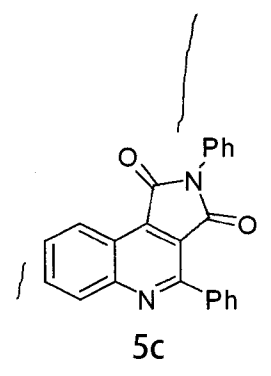
169.17
168.44
154.41
150.49
137.99
136.72
132.82
130.11
129.56
129.52
127.66
124.28
122.48
120.35

40.00
39.83
39.67
39.50
39.33
39.17
39.00



Supplementary Figure 62. ¹H and ¹³C NMR spectra for 5cc

9.010
9.009
8.994
8.992
8.312
8.295
8.032
8.012
8.004
7.997
7.992
7.973
7.959
7.942
7.930
7.814
7.812
7.800
7.797
7.795
7.783
7.781
7.568
7.549
7.545
7.540
7.535
7.522
7.507
7.477
7.463
7.443
7.428
7.414
7.400
7.257



Supplementary Figure 63. ¹H and ¹³C NMR spectra for 5c

9.471
9.467
9.447

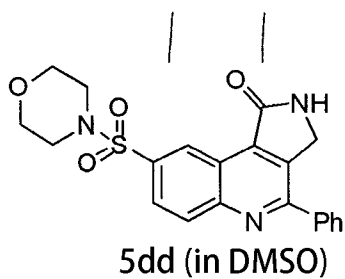
8.451
8.433
8.119
8.114
8.103
8.088
7.622
7.610
7.608
7.585

4.881

3.662
3.653
3.644

2.998
2.989
2.980

2.504
2.500
2.497



0.93
0.93

1.00

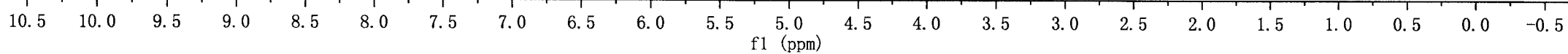
3.04

3.04

2.00

4.02

4.01



169.01

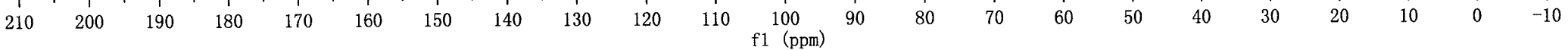
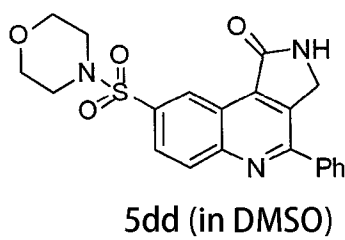
156.43

148.30

138.38
137.35
136.49
133.43
130.79
130.28
128.89
128.66
127.02
123.67
121.64

65.31

45.87
45.47
39.83
39.50
39.33
39.17



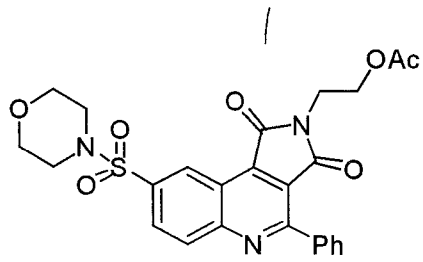
Supplementary Figure 64. ¹H and ¹³C NMR spectra for 5dd

9.351
9.347
8.420
8.398
8.207
8.202
8.185
8.179
8.032
8.024
8.019
8.007
8.000
7.976
7.597
7.592
7.584
7.579
7.561

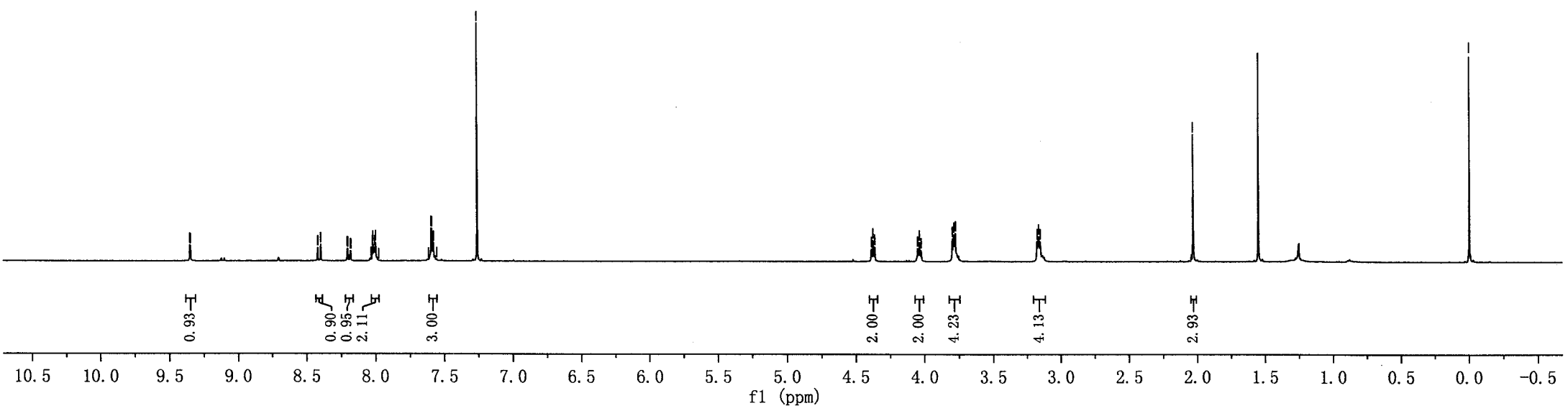
4.389
4.376
4.363
4.050
4.036
4.024
3.799
3.787
3.776
3.176
3.164
3.153

2.033

0.000

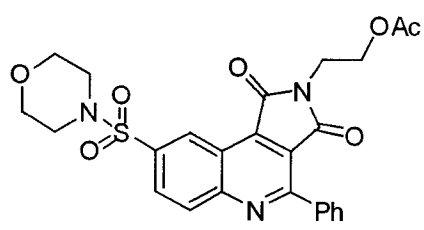


5d

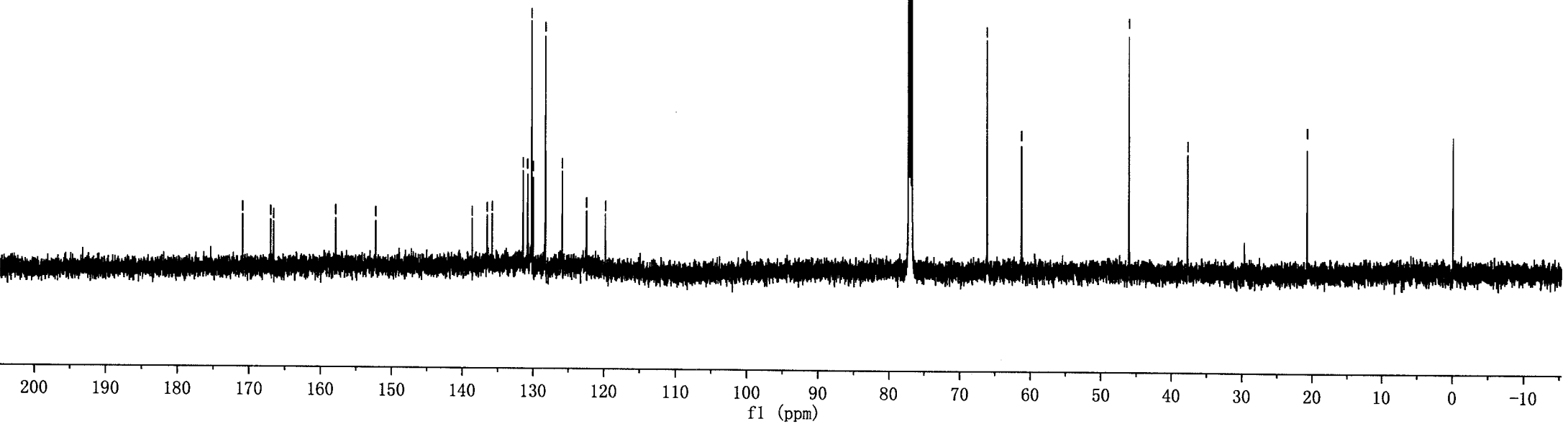


170.89
166.97
166.56
157.86
152.26
138.63
136.55
135.83
131.45
130.81
130.25
130.01
128.27
125.92
122.47
119.83

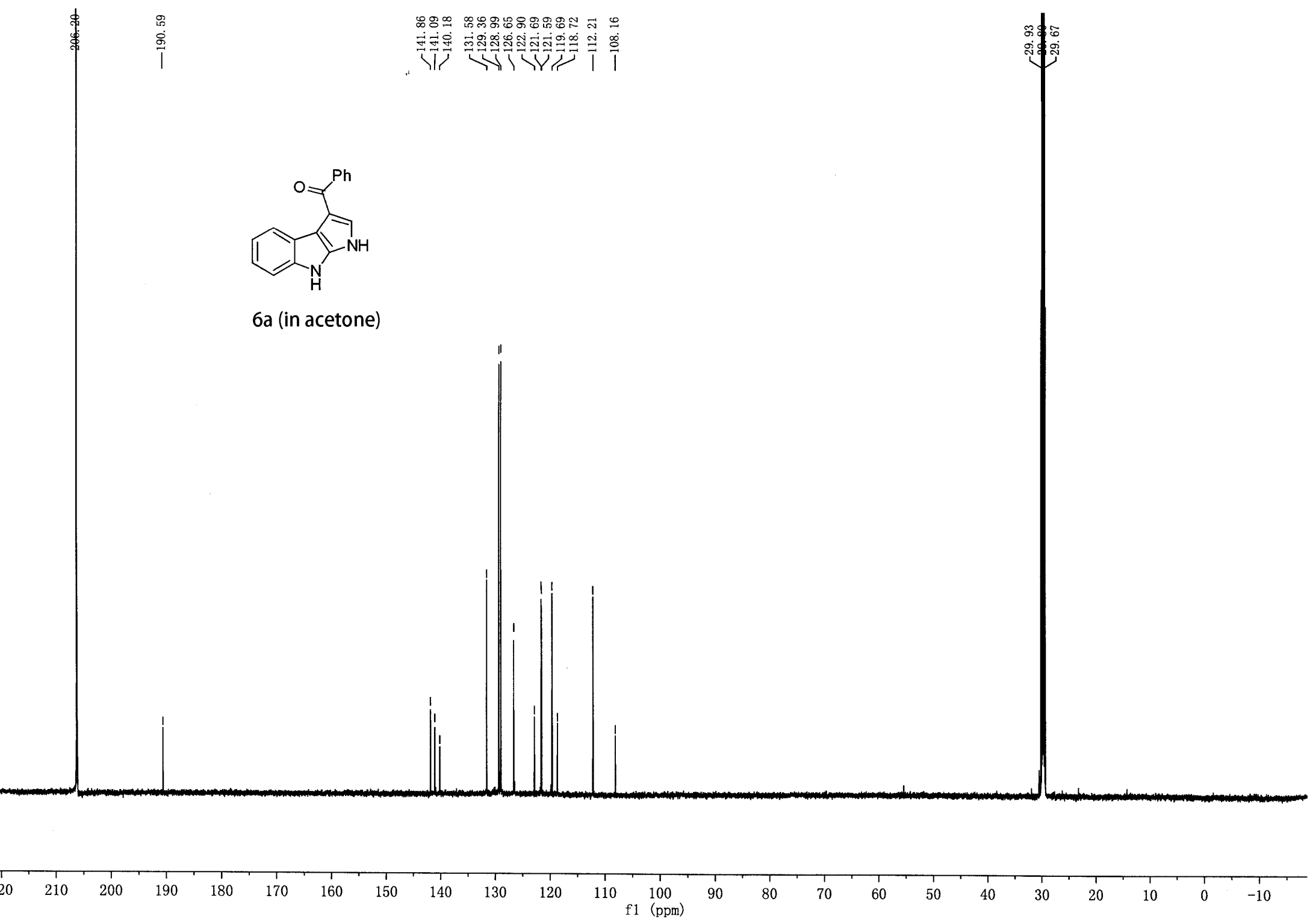
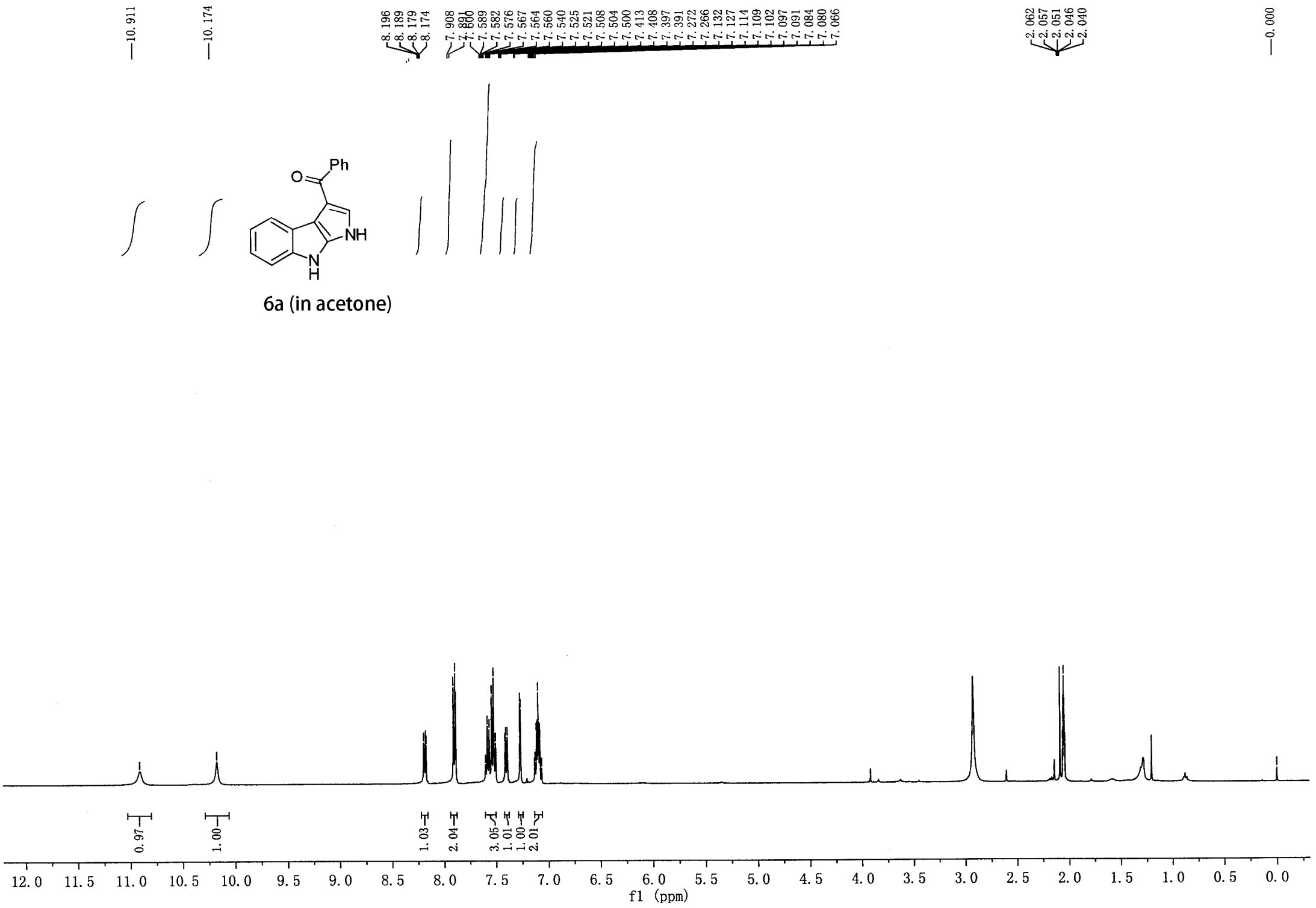
77.21
77.00
76.79
66.13
61.27
46.06
37.74
20.80



5d



Supplementary Figure 65. ¹H and ¹³C NMR spectra for 5d



Supplementary Figure 66. ¹H and ¹³C NMR spectra for 6a

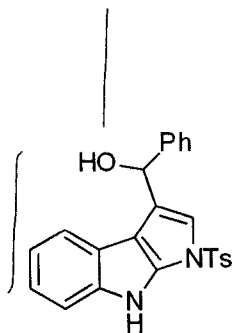
8.718

7.720
7.703
7.398
7.308
7.285
7.271
7.250
7.223
6.797
6.755

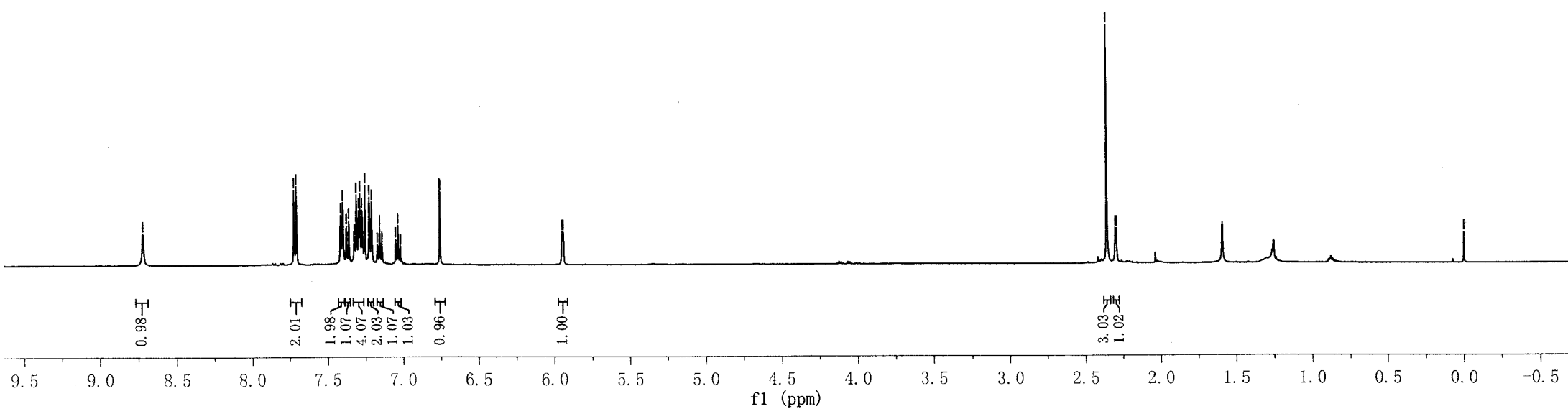
5.949
5.941

2.358
2.303
2.295

0.000



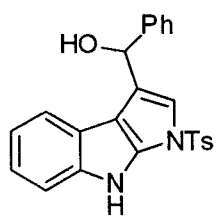
6b



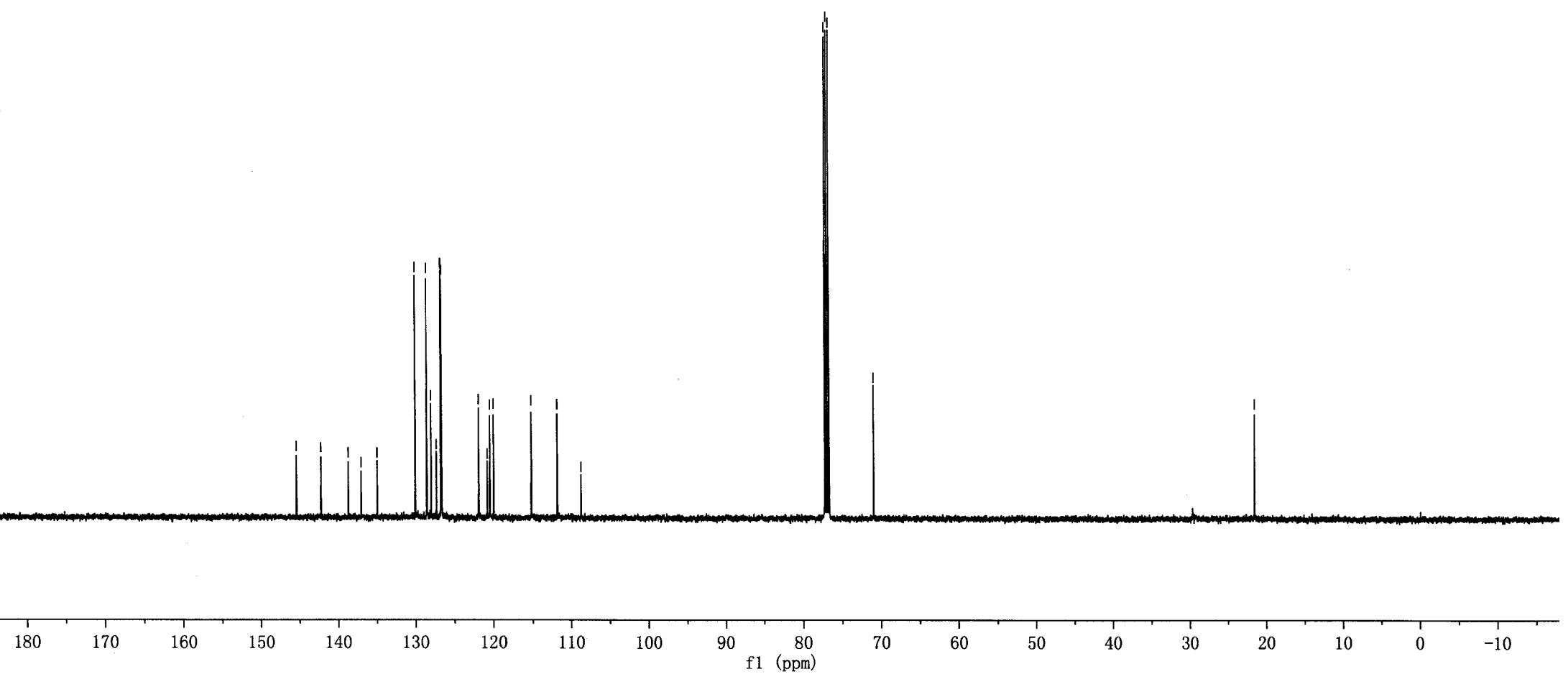
145.40
142.25
138.74
137.07
134.98
130.05
128.58
128.03
126.79
126.68
121.91
120.81
120.49
120.00
115.20
111.82
108.74

77.25
77.00
76.75
71.00

21.60

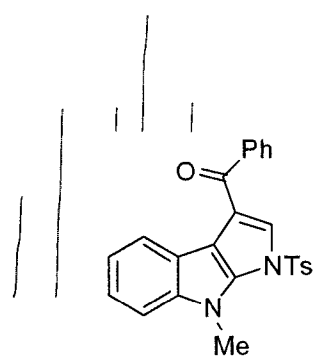


6b



Supplementary Figure 67. ¹H and ¹³C NMR spectra for 6b

8.136
8.116
7.940
7.923
7.686
7.665
7.648
7.645
7.630
7.625
7.614
7.611
7.608
7.553
7.535
7.517
7.348
7.325
7.309
7.306
7.268
7.258
7.248
7.225
7.220
7.209
7.205
7.201
7.189
7.185



3aa

4.049

2.368

-0.000

1.07
2.00
2.01
1.09
3.00
2.07
1.01
1.00
1.08

3.02

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 -0.5

f1 (ppm)

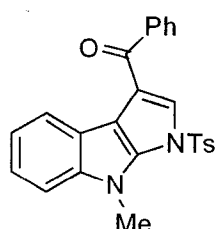
190.46

145.99
141.35
138.82
137.02
135.06
132.30
130.35
129.11
128.59
128.32
126.81
122.76
121.89
121.76
120.49
119.61
110.97
109.68

77.21
77.00
76.79

32.20

21.64



3aa

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

f1 (ppm)

Supplementary Figure 68. ¹H and ¹³C NMR spectra for 3aa

7.947
7.926
7.364
7.360
7.352
7.345
7.341
7.332
7.312
7.308
7.293
7.292
7.290
7.288
7.273
7.269
7.095
7.093
7.080
7.076
7.075
7.073
7.061
7.058
7.042
7.039

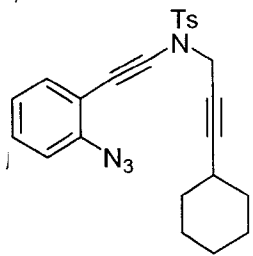
4.344
4.339

2.439

2.197

1.569
1.560
1.553
1.547
1.443
1.411
1.377
1.259
1.249
1.231
1.220
1.198
1.180

0.000



1v

1.98

3.00

0.98

1.95

2.02

3.00

0.98

4.00

1.06

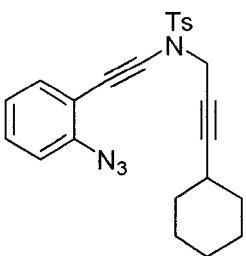
5.06

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 -0.5
f1 (ppm)

144.66
140.78
134.48
133.38
129.40
129.00
128.26
124.47
118.56
115.04

91.39
87.49
77.32
77.00
76.68
71.84
66.88

42.43
31.99
28.66
25.72
24.36
21.53



1v

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Supplementary Figure 69. ¹H and ¹³C NMR spectra for 1v

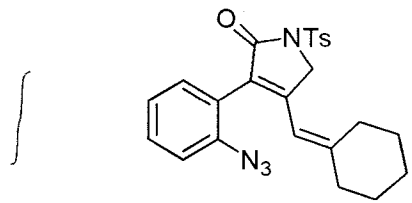
8.014
7.993
7.395
7.389
7.379
7.375
7.373
7.368
7.359
7.352
7.332
7.312
7.182
7.162
7.139
7.136
7.127
7.122
7.121

—5.792

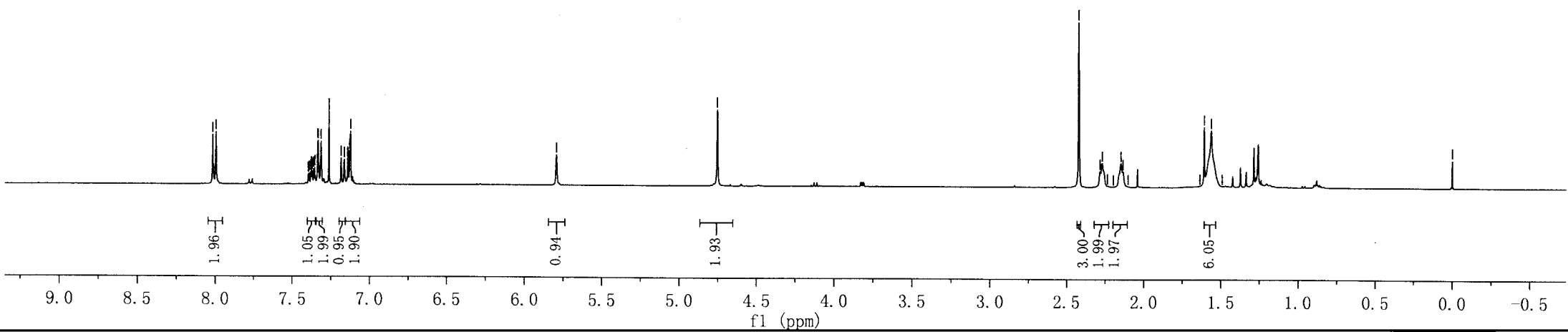
—4.752

2.419
2.282
2.269
2.234
2.197
2.148
2.134
2.101
1.636
1.607
1.561
1.490

—0.000



2va



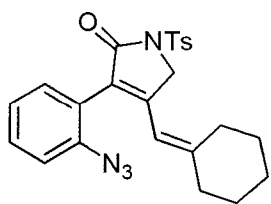
167.36
154.26
151.44
144.94
138.90
135.50
131.92
130.04
129.65
129.03
128.16
124.69
122.28
118.75
114.31

77.25
77.00
76.75

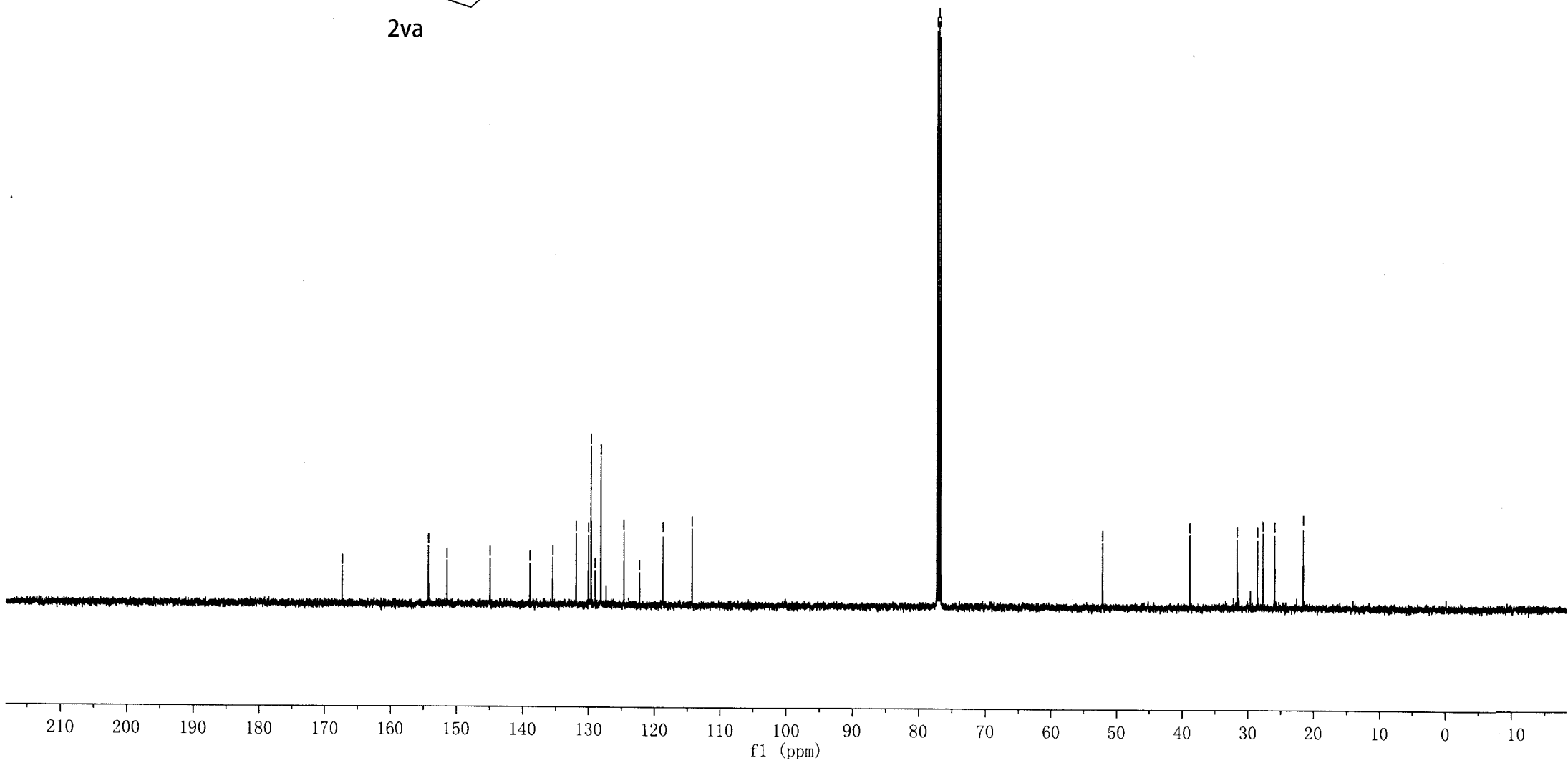
—52.16

—38.88

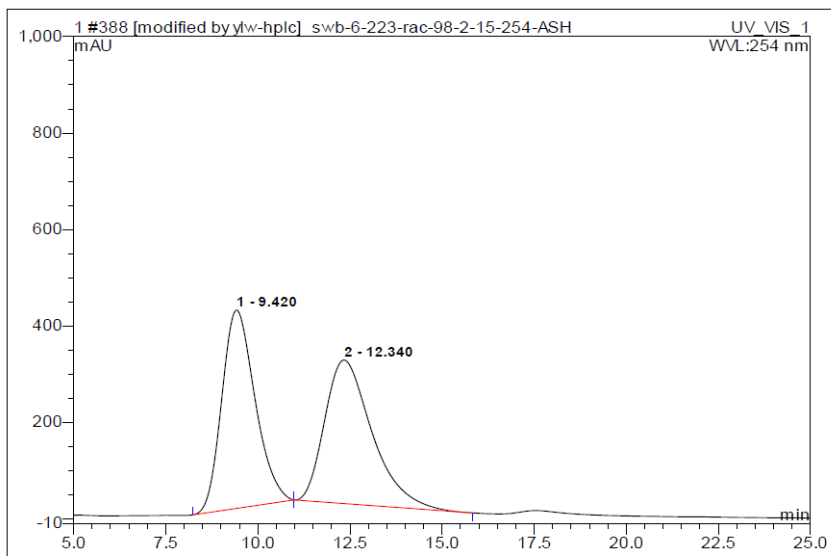
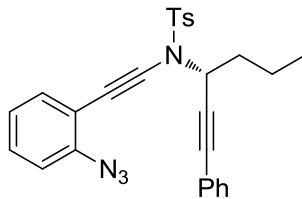
31.66
28.60
27.75
25.96
21.63



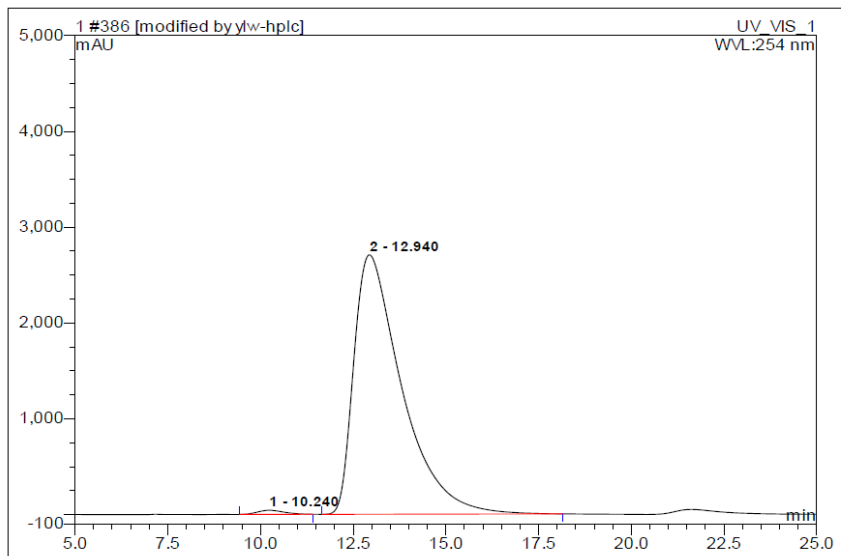
2va



Supplementary Figure 70. ¹H and ¹³C NMR spectra for 2va

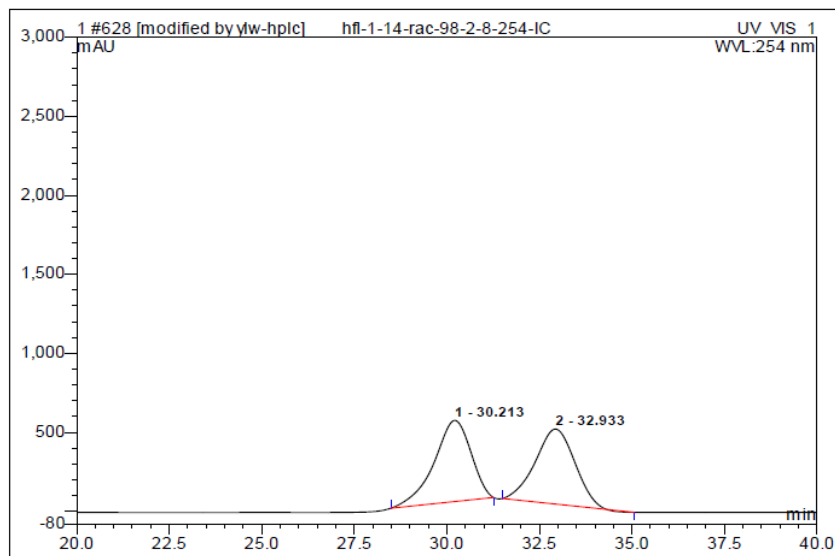
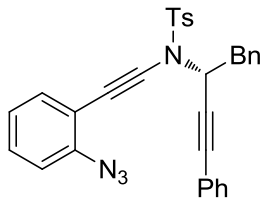


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	9.42	n.a.	411.085	429.936	49.25	n.a.	BMB*
2	12.34	n.a.	297.527	442.974	50.75	n.a.	bMB*
Total:			708.612	872.910	100.00	0.000	

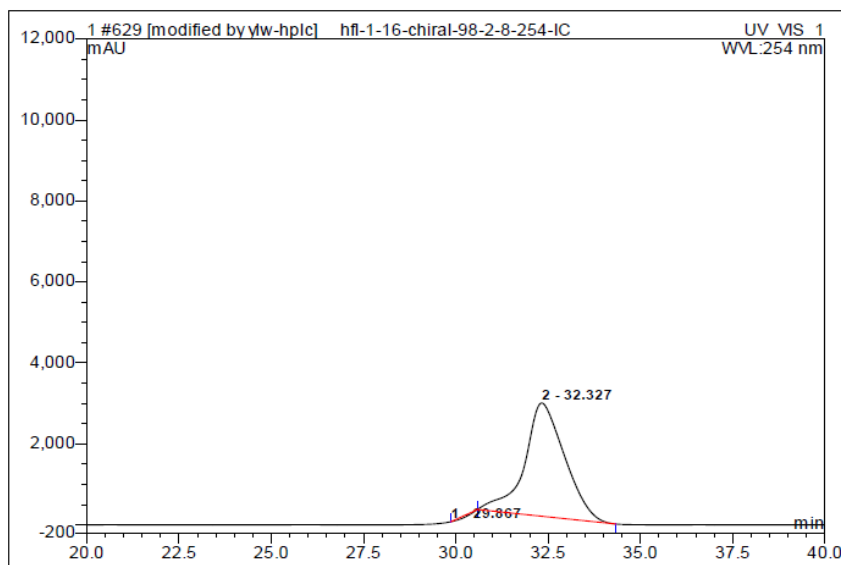


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	10.24	n.a.	42.491	35.252	0.86	n.a.	BMB*
2	12.94	n.a.	2707.758	4057.431	99.14	n.a.	BMB*
Total:			2750.249	4092.683	100.00	0.000	

Supplementary Figure 71. HPLC spectrum for compound 1s

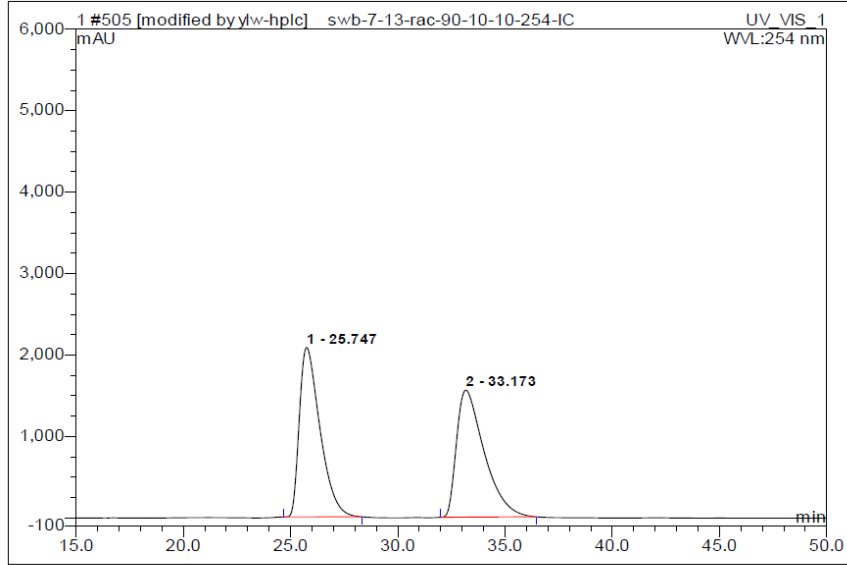
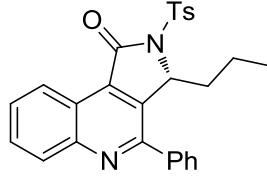


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	30.21	n.a.	512.906	592.461	50.24	n.a.	BMB*
2	32.93	n.a.	474.437	586.685	49.76	n.a.	BMB*
Total:			987.343	1179.146	100.00	0.000	

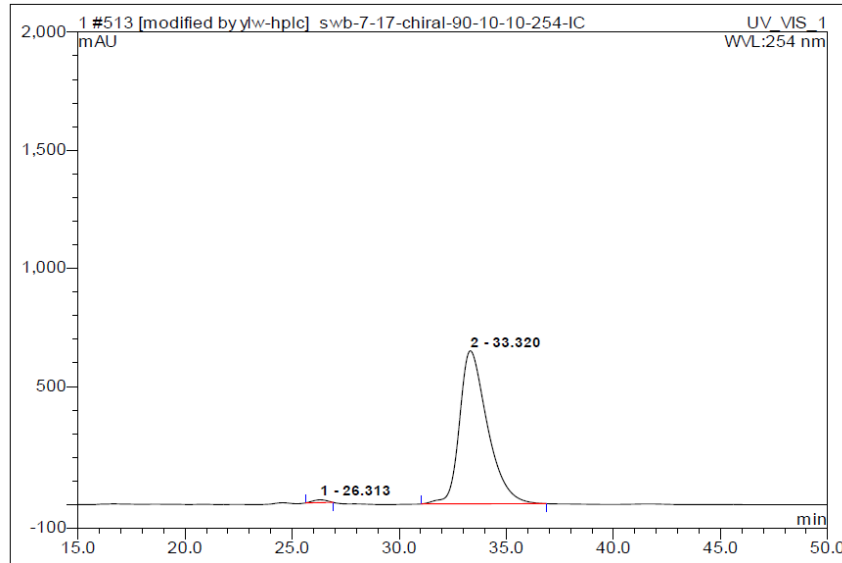


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	29.87	n.a.	1.513	21.214	0.59	n.a.	BMB*
2	32.33	n.a.	2796.109	3544.806	99.41	n.a.	bMB*
Total:			2797.622	3566.019	100.00	0.000	

Supplementary Figure 72. HPLC spectrum for compound 1t

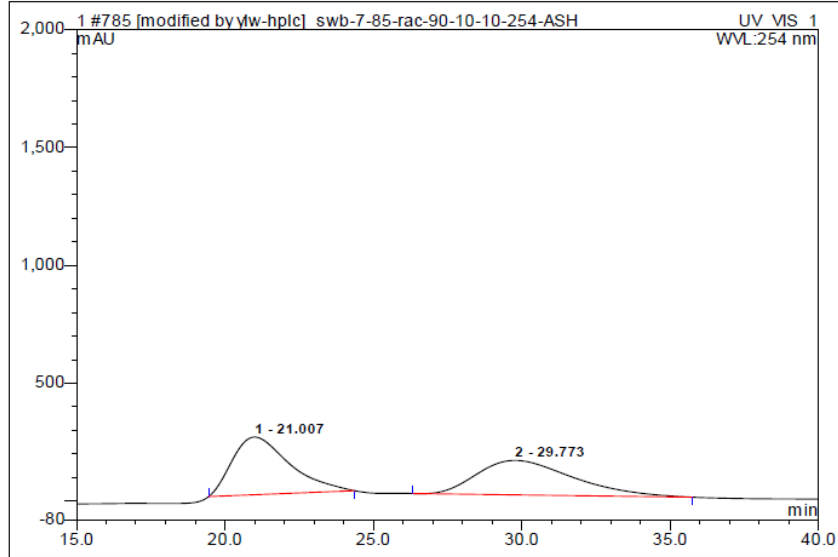
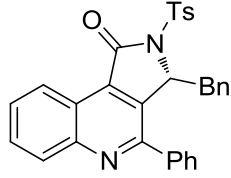


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	25.75	n.a.	2081.121	2320.170	49.88	n.a.	BMB*
2	33.17	n.a.	1558.788	2331.456	50.12	n.a.	BMB*
Total:			3639.909	4651.625	100.00	0.000	

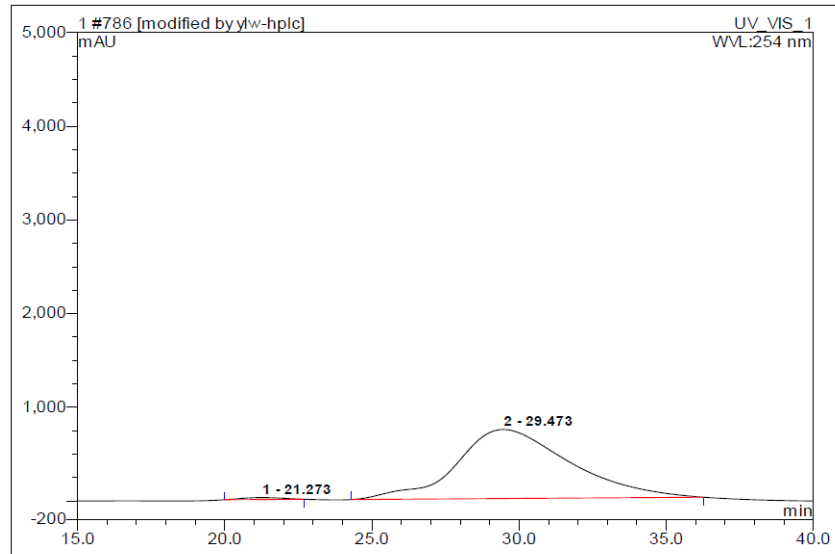


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	26.31	n.a.	12.011	9.058	0.91	n.a.	BMB*
2	33.32	n.a.	647.666	981.396	99.09	n.a.	BMB*
Total:			659.677	990.453	100.00	0.000	

Supplementary Figure 73. HPLC spectrum for compound 2s



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	21.01	n.a.	244.742	546.474	49.98	n.a.	BMB*
2	29.77	n.a.	146.210	546.925	50.02	n.a.	BMB*
Total:			390.952	1093.400	100.00	0.000	

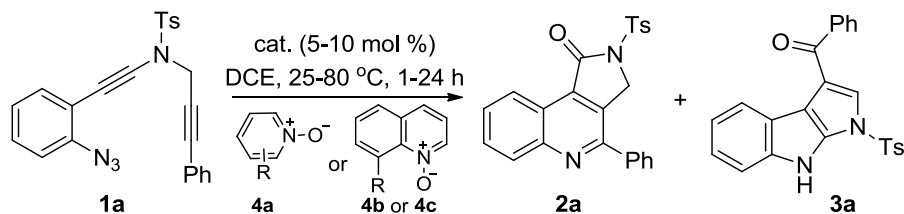


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	21.27	n.a.	20.743	32.808	0.99	n.a.	BMB*
2	29.47	n.a.	736.828	3296.182	99.01	n.a.	BMB*
Total:			757.571	3328.990	100.00	0.000	

Supplementary Figure 74. HPLC spectrum for compound 2t

Supplementary Tables

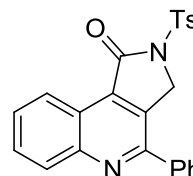
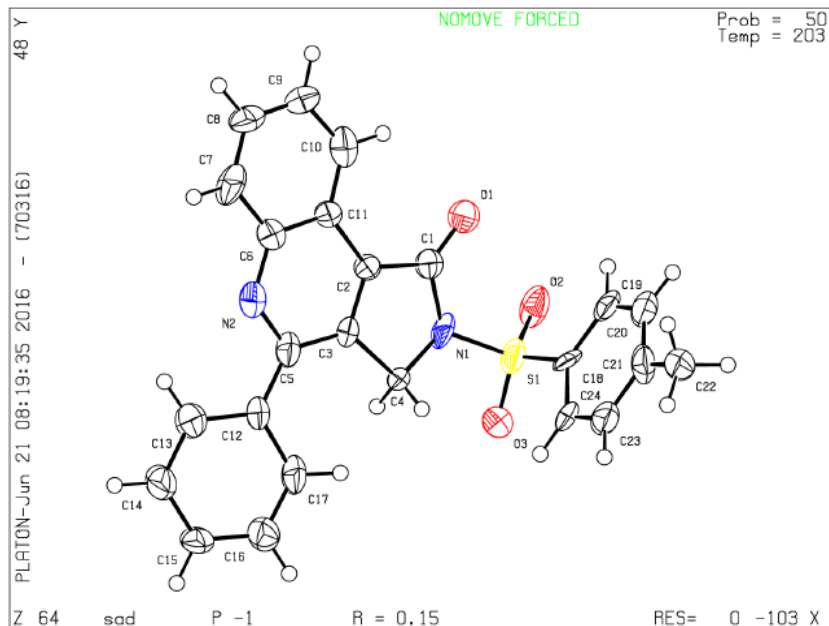
Supplementary Table 1. More reaction condition studies^a



entry	catalyst	oxidant (R)	reaction conditions	yield (%) ^b		
				2a	3a	1a
1	TfOH (10 mol %)	4a (2-Br)	DCE, 80 °C, 2 h	<1	<1	<1
2	MsOH (10 mol %)	4a (2-Br)	DCE, 80 °C, 2 h	<1	<1	<1
3	TsOH (10 mol %)	4a (2-Br)	DCE, 80 °C, 2 h	<1	<1	<1
4	CF ₃ CO ₂ H (10 mol %)	4a (2-Br)	DCE, 80 °C, 24 h	<1	<1	10
5	–	4a (2-Br)	DCE, 80 °C, 1 h	<1	<1	<1
6	CyJohnPhosAuNTf ₂ (5 mol %)	4a (2-Br)	DCE, 80 °C, 1 h	7	38	<1
7	XPhosAuNTf ₂ (5 mol %)	4a (2-Br)	DCE, 80 °C, 1 h	<5	23	<1
8	Cu(CH ₃ CN) ₄ PF ₆ (10 mol %)	4c (<i>i</i> -Pr)	DCE, 80 °C, 1 h	70	<1	<1
9	Cu(CH ₃ CN) ₄ PF ₆ (10 mol %)	4b (Me)	toluene, 80 °C, 10 h	15	<1	<1
10	Cu(CH ₃ CN) ₄ PF ₆ (10 mol %)	4b (Me)	PhCl, 80 °C, 10 h	61	<1	<1
11	Cu(CH ₃ CN) ₄ PF ₆ (10 mol %)	4b (Me)	DCE, 40 °C, 3 h	82	<1	<1
12	Cu(CH ₃ CN) ₄ BF ₄ (10 mol %)	4b (Me)	DCE, 60 °C, 2 h	74	<1	<1
13	Cu(hfacac) ₂ (10 mol %)	4b (Me)	DCE, 60 °C, 2 h	7	<1	6
14	CuI (10 mol %)	4b (Me)	DCE, 60 °C, 5 h	<1	<1	90
15	CyJohnPhosAuNTf ₂ (5 mol %)	–	DCE, rt, 1 h	<1	47	<1
16	XPhosAuNTf ₂ (5 mol %)	–	DCE, rt, 24 h	<1	27	44
17	(Ar O) ₃ PAuNTf ₂ (5 mol %)	–	DCE, rt, 1 h	<1	57	<1
18	IPrAuNTf ₂ (5 mol %)	–	DCE, 80 °C, 1 h	<1	44	<1
19	Cu(CH ₃ CN) ₄ PF ₆ (10 mol %)	–	DCE, 80 °C, 1 h	<1	<1	<1
20	Cu(OTf) ₂ (10 mol %)	–	DCE, 80 °C, 1 h	<1	<1	<1
21	Ph ₃ PAuNTf ₂ (5 mol %)	–	toluene, rt, 1 h	<1	<1	<1
22	Ph ₃ PAuNTf ₂ (5 mol %)	–	MeCN, rt, 1 h	<1	<1	<1
23 ^c	Ph ₃ PAuNTf ₂ (2 mol %)	–	CH ₃ NO ₂ , rt, 30 min	<1	86	<1

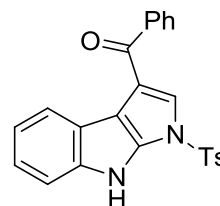
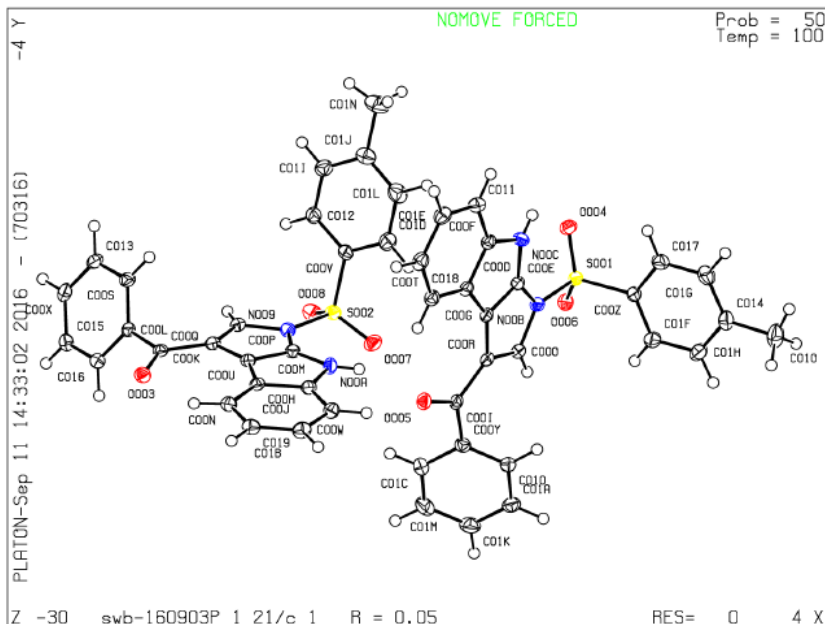
^a The reaction was performed with **1a** (0.1 mmol), **4** (0.15 mmol), and catalyst (2-10 mol %) in solvent (2 mL) at rt-80 °C. ^b Measured by ¹H NMR using diethyl phthalate as the internal standard. ^c The reaction was performed in a flame-dried vial with dry CH₃NO₂ as the solvent and H₂O (2 equiv) as an additive.

**Supplementary Table 2. Crystal data and structure refinement for 2a. CCDC
Number = 1535333**



Bond precision:	C-C = 0.0159 Å	Wavelength=0.71073	
Cell:	a=8.158 (5)	b=10.196 (7)	c=11.553 (7)
	alpha=88.931 (15)	beta=73.956 (11)	gamma=83.851 (13)
Temperature:	203 K		
	Calculated	Reported	
Volume	918.2 (10)	918.3 (10)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	C24 H18 N2 O3 S	C24 H18 N2 O3 S	
Sum formula	C24 H18 N2 O3 S	C24 H18 N2 O3 S	
Mr	414.46	414.46	
Dx, g cm ⁻³	1.499	1.499	
Z	2	2	
Mu (mm ⁻¹)	0.208	0.208	
F000	432.0	432.0	
F000'	432.43		
h, k, lmax	9, 12, 13	9, 12, 13	
Nref	3253	3193	
Tmin, Tmax	0.963, 0.969	0.116, 1.000	
Tmin'	0.959		
Correction method=	# Reported T Limits: Tmin=0.116 Tmax=1.000		
AbsCorr =	MULTI-SCAN		
Data completeness=	0.982	Theta(max) =	25.018
R(reflections) =	0.1455 (922)	wR2(reflections) =	0.3851 (3193)
S =	0.844	Npar =	272

Supplementary Table 3. Crystal data and structure refinement for 3a. CCDC
Number = 1535335



Bond precision:	C-C = 0.0023 Å	Wavelength=1.54184	
Cell:	a=12.6556(2)	b=18.6258(3)	c=16.9411(3)
	alpha=90	beta=94.8397(15)	gamma=90
Temperature:	100 K		
	Calculated	Reported	
Volume	3979.13(11)	3979.11(12)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C ₂₄ H ₁₈ N ₂ O ₃ S	4(C ₂₄ H ₁₈ N ₂ O ₃ S)	
Sum formula	C ₂₄ H ₁₈ N ₂ O ₃ S	C ₉₆ H ₇₂ N ₈ O ₁₂ S ₄	
Mr	414.46	1657.85	
Dx, g cm ⁻³	1.384	1.384	
Z	8	2	
Mu (mm ⁻¹)	1.688	1.688	
F ₀₀₀	1728.0	1728.0	
F ₀₀₀ '	1735.57		
h, k, lmax	15, 23, 21	15, 23, 20	
Nref	8193	7936	
Tmin, Tmax	0.817, 0.845	0.771, 1.000	
Tmin'	0.776		
Correction method= # Reported T Limits: Tmin=0.771 Tmax=1.000			
AbsCorr = MULTI-SCAN			
Data completeness=	0.969	Theta(max)=	74.887
R(reflections)=	0.0472(6891)	wR2(reflections)=	0.1381(7936)
S =	1.033	Npar=	685

Supplementary Notes

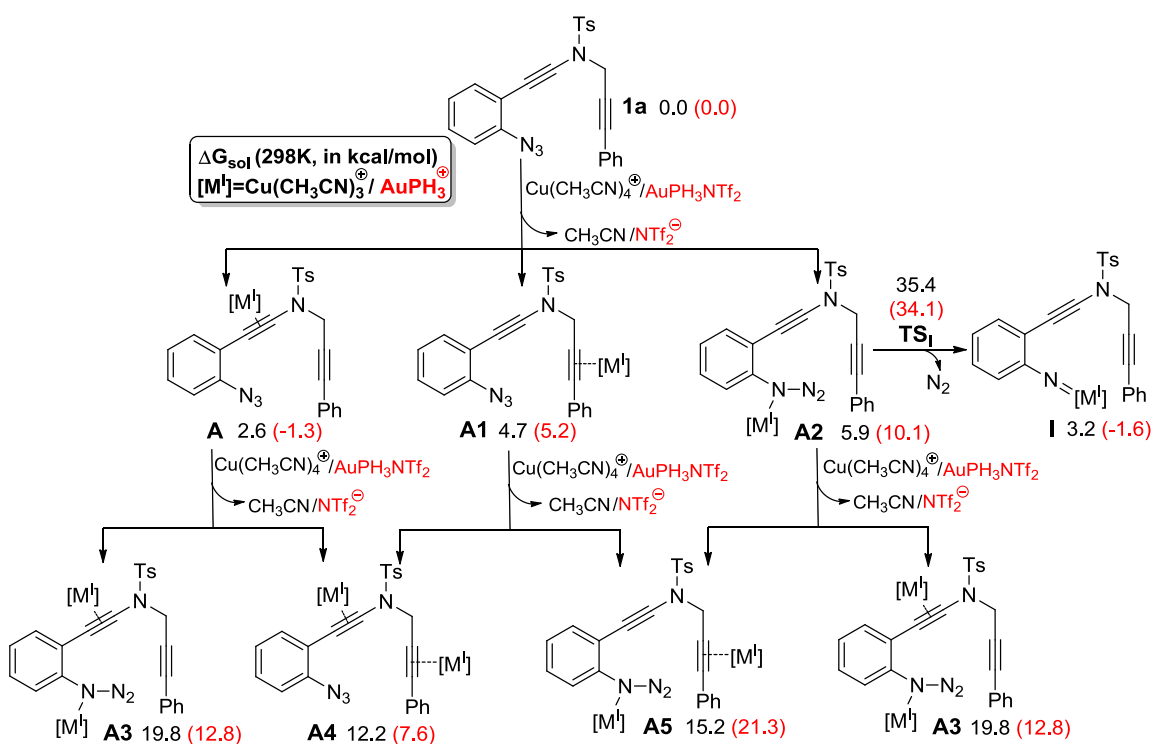
Computational methods.

All calculations were carried out with the Gaussian 09 programs¹. The geometries of all the species were fully optimized by using the density functional theory (DFT) method with the M06² functional. The 6-31G (d, p)³⁻⁷ basis set was used for C, H, N, O, F, S and P. For Au, we used the Stuttgart/Dresden small-core RECP (relativistic effective core potential) plus valence double- ζ basis set (SDD)⁸, which has been frequently used in the mechanistic investigations on Au-catalyzed organic transformations.⁹⁻¹² The Lanl (Los Alamos National Laboratory) basis sets, also known as LanL2DZ (Lanl-2-double zeta)¹³ was used for Br. These basis sets are denoted as DZP (double- ζ plus polarization). Frequency calculations at the same theoretical level (SMD-M06/DZP) were performed to confirm each stationary point to be either a local minimum or a transition state (TS). The transition states were verified by intrinsic reaction coordinate (IRC)¹⁴ calculations. The intermediates were characterized by all real frequencies. The solvent effects of DCE ($\epsilon = 10.125$) for Cu^I catalysis and nitromethane ($\epsilon = 36.562$) for Au^I catalysis were taken in account by using the SMD-flavor¹⁵ of self-consistent reaction field (SCRF) theory. For Au^I catalysis, the active catalytic species R₃PAu⁺ is simplified as H₃PAu⁺ in the computations^{16,17} in order to reduce the computational cost.

In addition, we should mention that both LanL2DZ and SDD basis sets for Cu have been proven to be appropriate for the mechanistic investigations of Cu-based systems¹⁸⁻²³, despite that we adopted LanL2DZ for Cu in the currently-concerned systems. Indeed, this is supported by the computational data given in Supplementary Table 4 that were obtained by using both LanL2DZ and SDD for Cu for a series of key structures (precursor **A**, transition states **TS_B**, **TS_C**, **TS_{B'}** and **TS_{C'}**) in the Cu^I-catalyzed reactions.

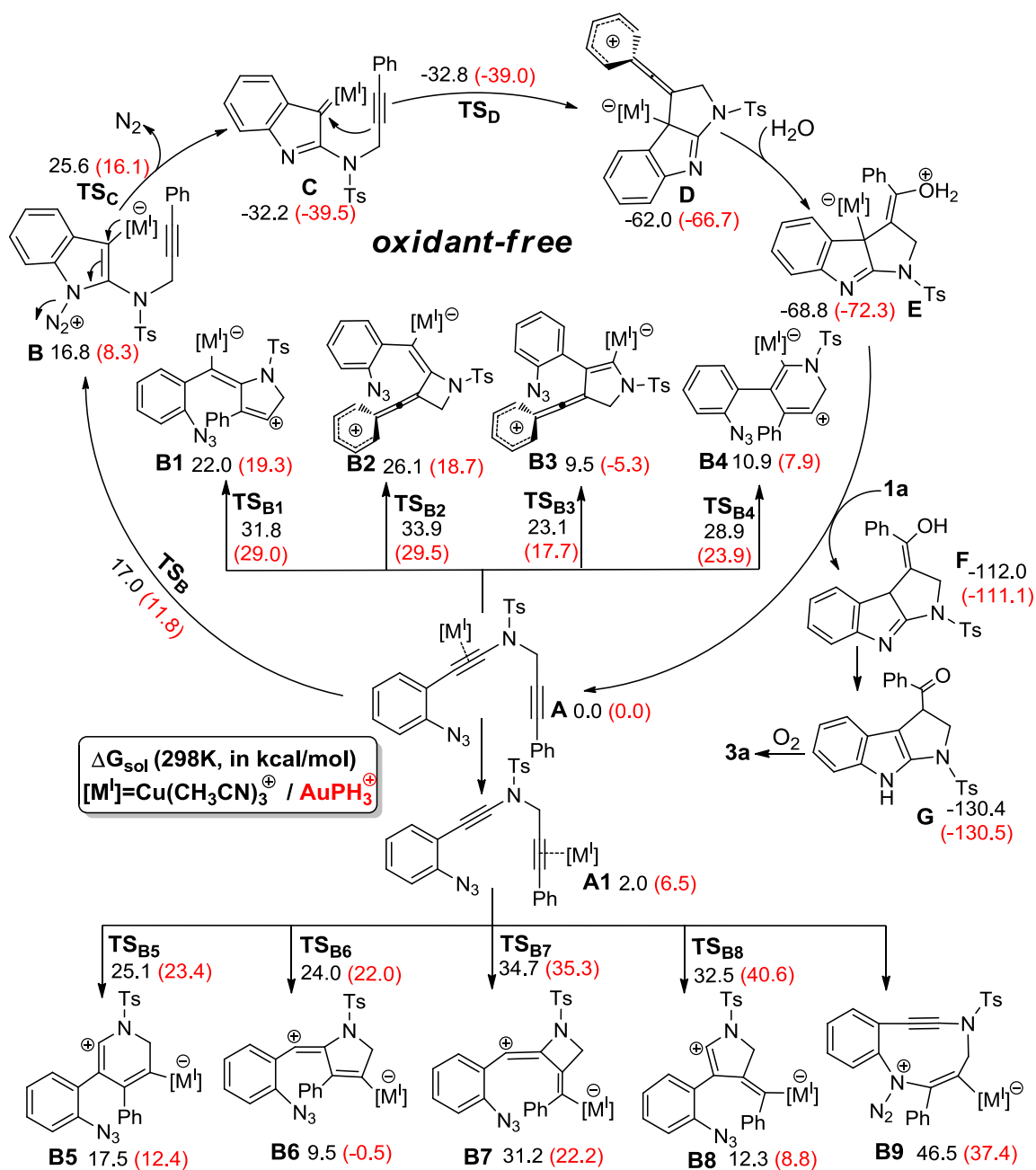
Supplementary Table 4. Relative free energies (in kcal/mol) of key structures (computed at the SMD-M06/DZP level of theory in DCE solvent for Cu^I catalysis at 298K).

Basis set for Cu	A	TS _B	TS _C	TS _{B'}	TS _{C'}
LanL2DZ	0.0	17.0	25.6	23.4	19.1
SDD	0.0	18.0	25.4	23.0	19.2



Supplementary Figure 75. The possible coordination of Cu^{I} and Au^{I} catalyst with substrate **1a** and energies for the formation of nitrene-like intermediates. Relative free energies of key intermediates and transition states were computed at the SMD-M06/DZP level of theory in solvent (DCE for Cu^{I} catalysis and CH_3NO_2 for Au^{I} catalysis) at 298K. Data for Au^{I} catalysis were given in parentheses.

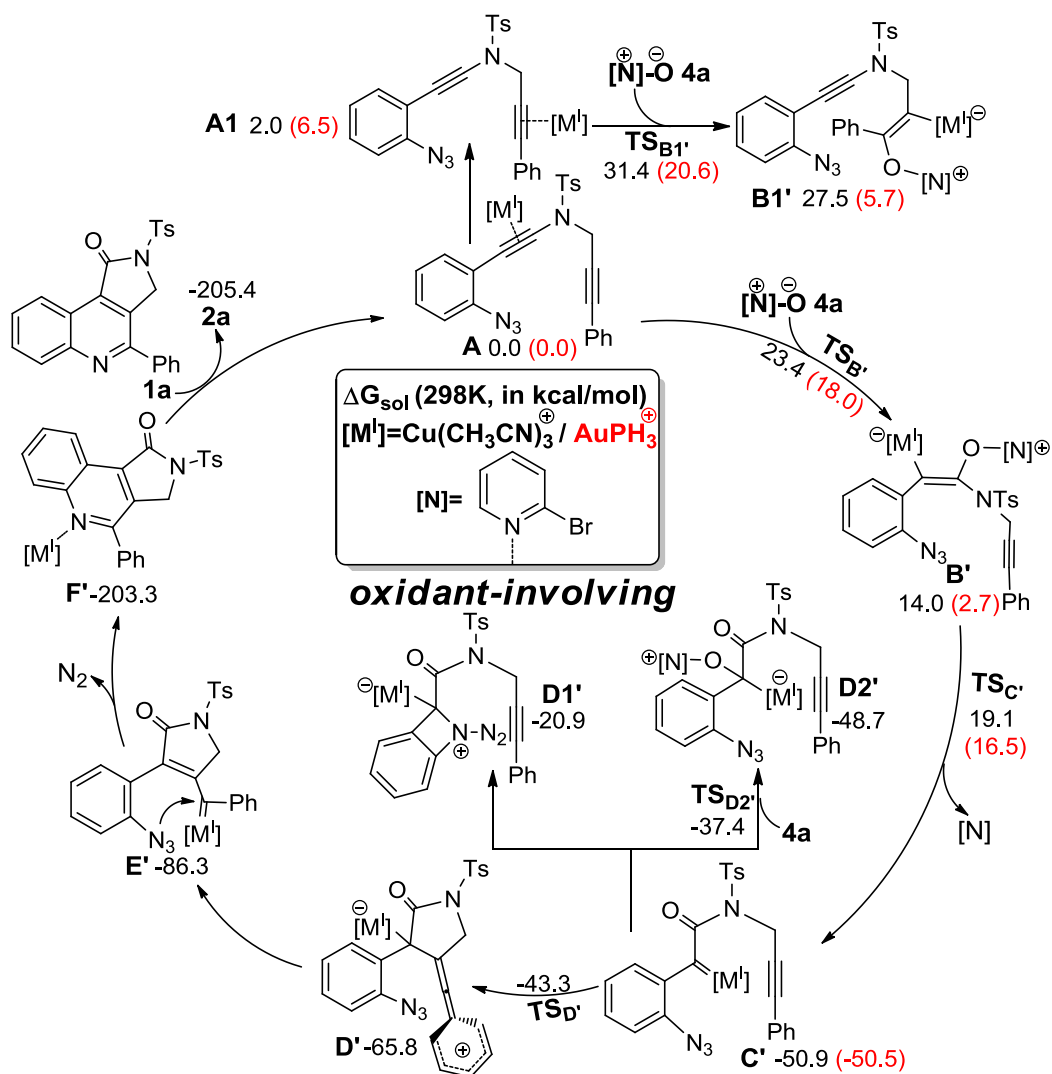
Supplementary Figure 75 shows the complexes formed by the $\text{Au}^{\text{I}}/\text{Cu}^{\text{I}}$ -catalytic species and the substrate **1a**, along with the DFT-computed relative free energies. Based on calculated energies, we can summarize our findings as follows. First, the $\text{Au}^{\text{I}}/\text{Cu}^{\text{I}}$ -catalytic species is preferentially coordinated to the electron-rich triple bond neighboring the electron-donative amide group to form precursor **A**. Second, simultaneous coordination of metal to both triple bonds or either one of them and the proximal N atom of azide group seem to be unfavorable. Third, direct generation of metal-nitrene intermediate upon metal coordinating to the azide group appears to be implausible in the currently-concerned systems, as the barrier height (at transition state **TS_I**) of such a process is too high (> 34 kcal/mol).



Supplementary Figure 76. Plausible mechanisms for the formation of pyrrolo[2,3-*b*]indoles **3a** in the oxidant-free cycle. Relative free energies of key intermediates and transition states were computed at the SMD-M06/DZP level of theory in solvent (DCE for Cu^I catalysis and CH₃NO₂ for Au^I catalysis) at 298K. Data for Au^I catalysis were given in parentheses.

Supplementary Figure 76 clearly shows that a series of reactions are carried out from precursor **A** in the oxidant-free cycle. Firstly, intramolecular cyclization of

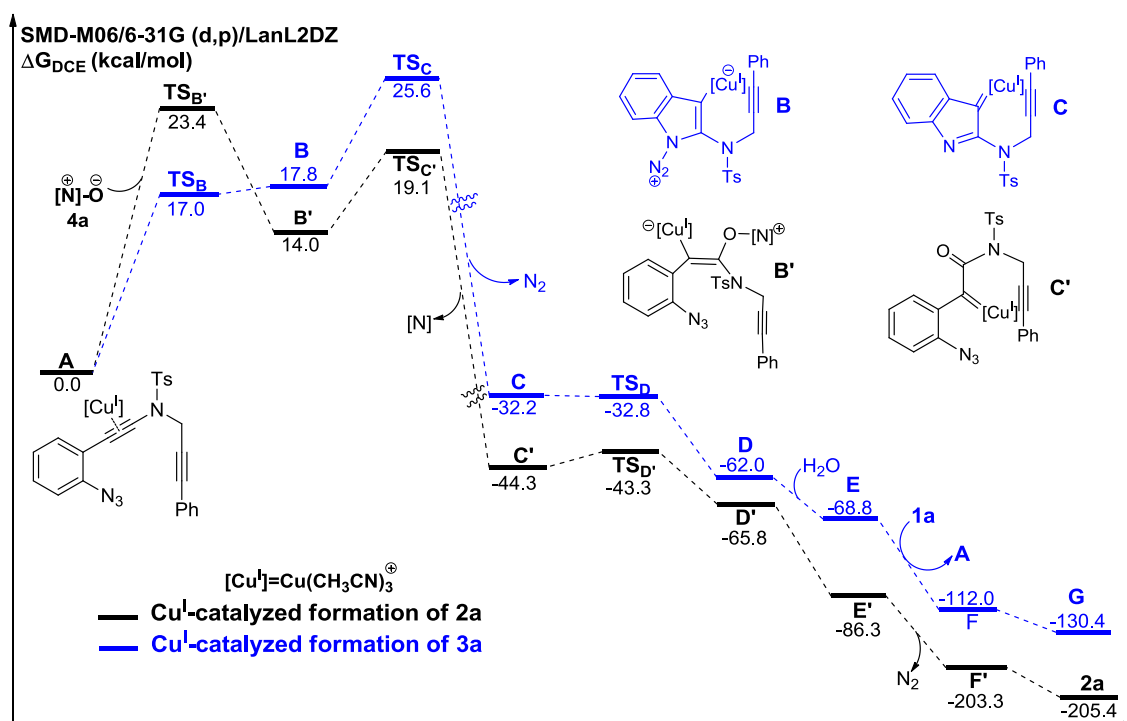
precursor **A** either it is initiated by nucleophilic attack of the proximal N atom of azide to form intermediate **B** or competitive attack of another triple bond to generate intermediate **B1**, **B2**, **B3** and **B4**, respectively. The latter are unfavorable because the barrier heights (at transition state **TS_{B3}**, **TS_{B4}**, **TS_{B5}** and **TS_{B6}**: > 23.0 kcal/mol for Cu^I catalysis; > 17.0 kcal/mol for Au^I catalysis) of these processes are much higher than the former (at transition state **TS_B**: 17.0 kcal/mol for Cu^I catalysis; 11.8 kcal/mol for Au^I catalysis). Moreover, precursor **A** can also transform into sub-stable intermediate **A1** and then competitive intramolecular cyclization would occur to generate intermediate **B5**, **B6**, **B7**, **B8** and **B9**, respectively. However, the current calculation results illustrate that these processes are also unfavorable. Then, elimination of **N₂** from **B** affords the metal-carbenoid intermediate **C**, and a second cyclization to the enylium-cationic intermediate **D**. The latter can readily react with ambient H₂O, leading eventually to product **3a** via the following successive steps: H₂O addition, proton demetallization, keto-enol tautomerization and dehydrogenative oxidation.



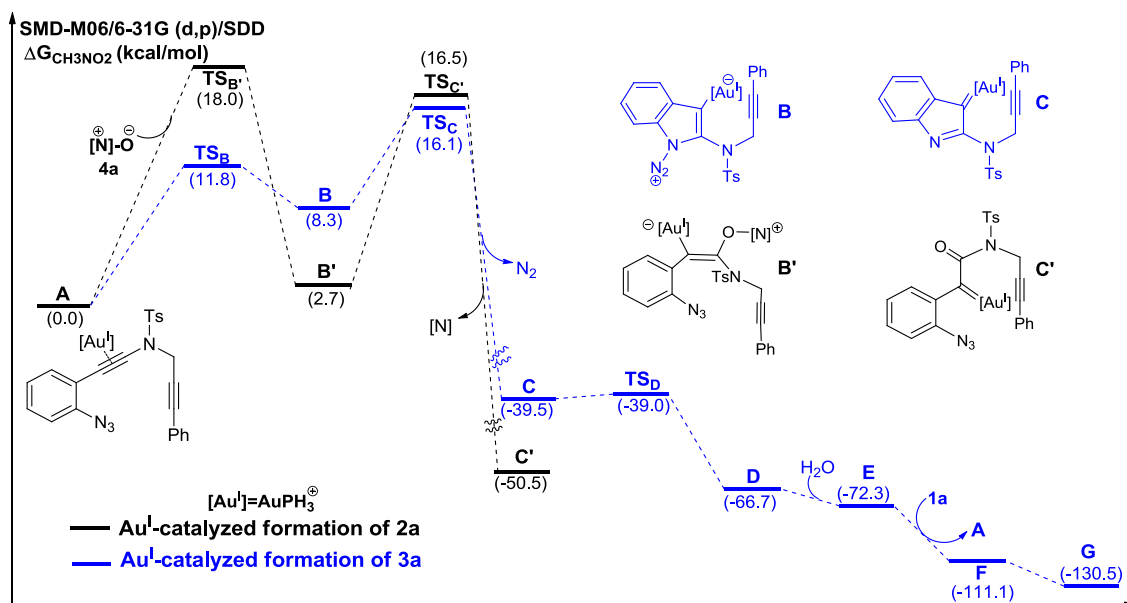
Supplementary Figure 77. Plausible mechanisms for the formation of pyrrolo[3,4-*c*]quinolin-1-ones **2a** in the oxidant-involving cycle. Relative free energies of key intermediates and transition states were computed at the SMD-M06/DZP level of theory in solvent (DCE for Cu^{I} catalysis and CH_3NO_2 for Au^{I} catalysis) at 298K. Data for Au^{I} catalysis were given in parentheses.

Plausible mechanisms for the formation of **2a** in the oxidant-involving cycle are illustrated in **Supplementary Figure 77**. Initially, nucleophilic attack of oxidant **4a** onto the precursor **A** forms vinyl-metal intermediate **B'** or onto the sub-stable intermediate **A1** generates intermediate **B1'**. However, based on calculated energies, the latter is thermodynamically and kinetically unfavorable. Subsequently, upon N–O bond cleavage, **B'** can transform into α -oxo metal-carbenoid intermediate **C'**. Then, penta and tetra-

cyclization as well as overoxidation of intermediate **C'** would occur to form intermediate **D'**, **D1'** and **D2'**, respectively. Note that generating more stable intermediate **D'** is favorable with a lower barrier than intermediate **D2'**. Furthermore, tetra-cyclization of intermediate **C'** to afford intermediate **D1'** is implausible since the process is highly endogenic. Ultimately, **D'** would furnish the product **2a** via catalyst migration, intramolecular nucleophilic cyclization, the loss of dinitrogen and substrate exchange.



Supplementary Figure 78. Reaction energy profiles for Cu^I-catalyzed formation of **2a** (black line) and **3a** (blue line).



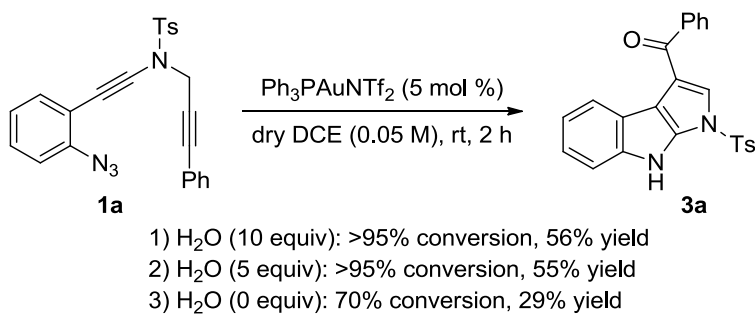
Supplementary Figure 79. Reaction energy profiles for Au^I-catalyzed formation of **2a** (black line) and **3a** (blue line).

Supplementary Discussion

More Mechanism Studies

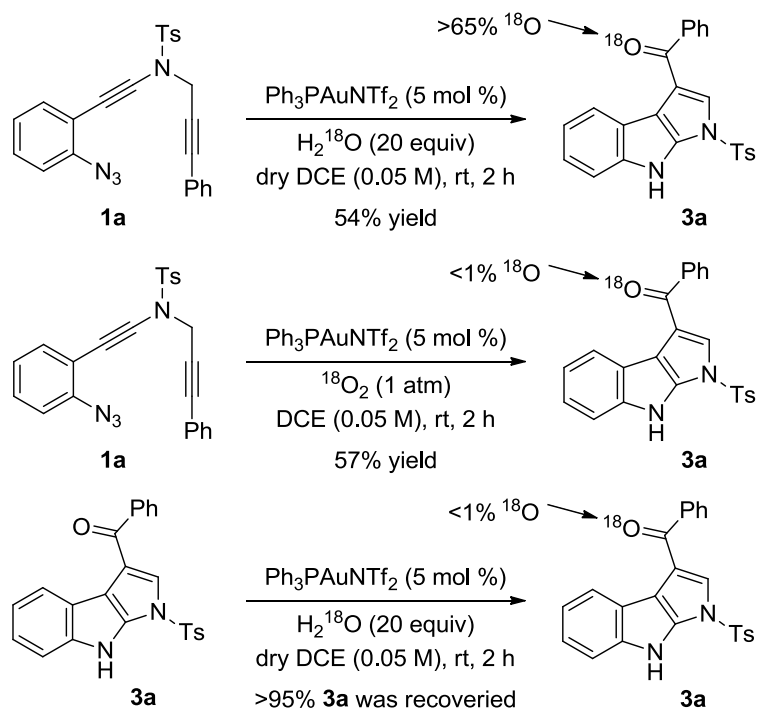
For more mechanism studies on the gold-catalyzed cascade cyclization reaction, please see as followed.

First, the addition of water significantly promoted the cascade reaction when the reaction ran in a flame-dried vial with dry DCE as the solvent (this acceleration is not obvious in CH_3NO_2 as the reaction is too fast). These results support that water presumably participates in this cascade cyclization.



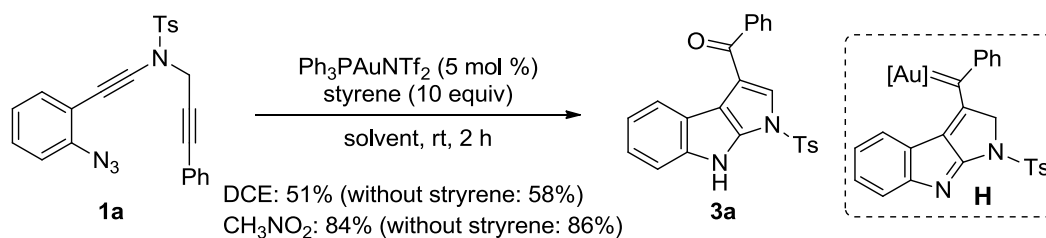
Supplementary Figure 80. The effect of water on the gold-catalyzed cascade reaction.

Second, control experiments with H_2^{18}O and $^{18}\text{O}_2$ isotopic labeling proved that the oxygen atom in the carbonyl group of **3a** originates from water but not molecular oxygen. Of note, no incorporation of ^{18}O into the **3a** was observed when **3a** was subjected to the reaction conditions with H_2^{18}O .



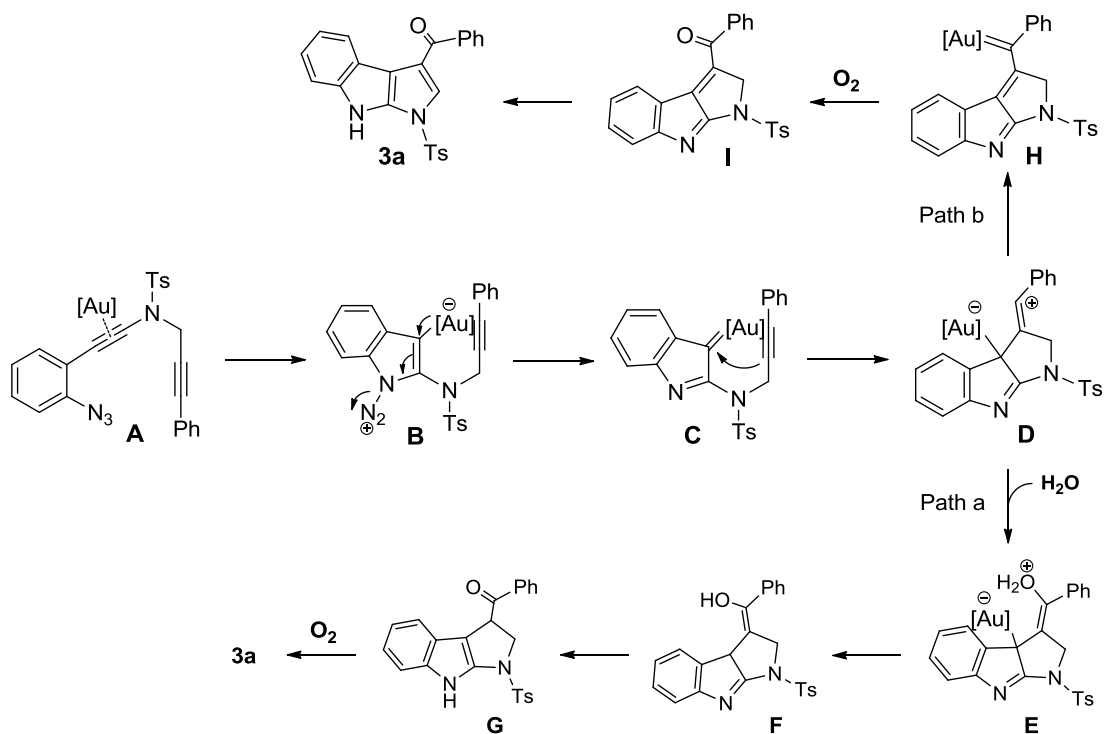
Supplementary Figure 81. Control experiments with H_2^{18}O and $^{18}\text{O}_2$ isotopic labeling.

Third, the addition of styrene did not significantly affect this cascade cyclization and no cyclopropane formation was observed under standard conditions, which further supports that the reaction presumably does not involve a gold-carbene intermediate **H**.



Supplementary Figure 82. Trying to trap the reaction intermediate with styrene.

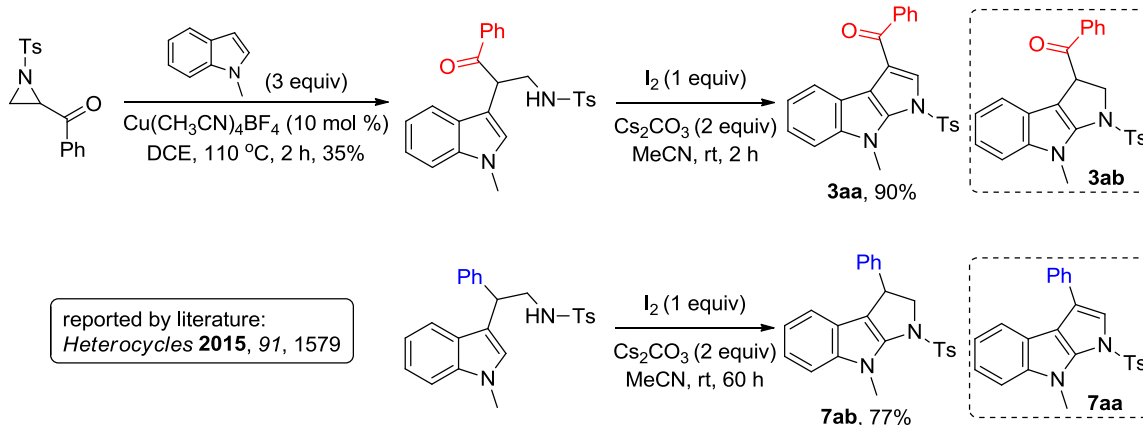
Thus, the above control experiments clearly indicate that the path b involving the direct oxidation of gold carbene into the corresponding carbonyl group is less likely.



Supplementary Figure 83. Two plausible reaction pathways.

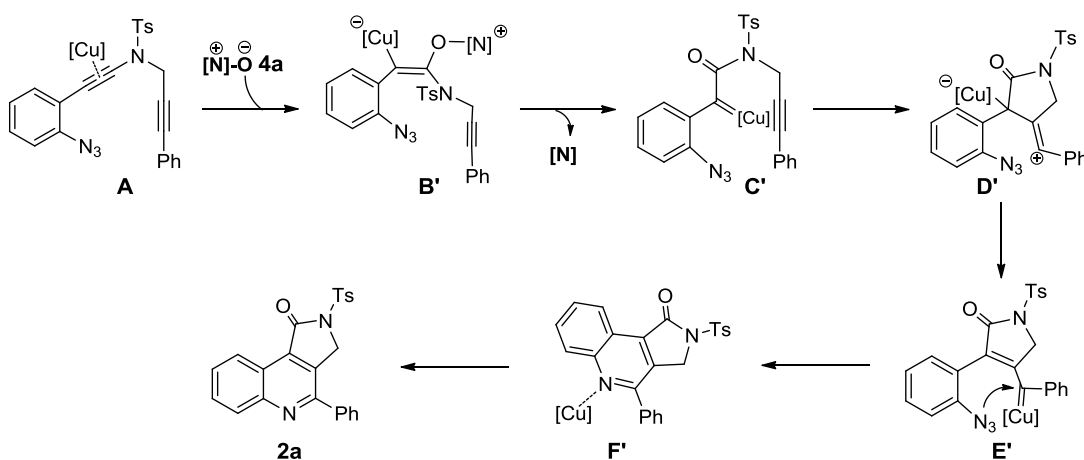
In addition, the reason that gold catalysts show much better reactivity than copper catalysts in this cascade cyclization can be explained by the fact that Au(I), as a cationic late-transition metal, has stronger π -backdonation effect than Cu(II) or Cu(I). As a result, the corresponding α -imino gold carbenes **C** can be readily generated while the generation of such a α -imino copper carbene is very difficult and has not been reported. This result is also well supported by DFT calculations, and please see the section of Computational Studies for details.

Of note, the dehydrogenative oxidation of intermediate **G** (or intermediate **F**) into the final **3a** by trace air in the reaction system is probably assisted by the carbonyl group of **G**²⁴ via a presumable radical process^{25,26}. This speculation is well supported by the following control experiment. When we tried to synthesize the key intermediate **3ab** according to the literature method²⁷, only the dehydrogenative oxidation product **3aa** was obtained.



Supplementary Figure 84. Synthesis of dehydrogenative oxidation product **3aa**.

For more mechanism studies on the copper-catalyzed oxidative cyclization reaction, please see as followed.



Supplementary Figure 85. Plausible reaction mechanism for the copper-catalyzed oxidative cyclization reaction.

First, as seen from the Supplementary Table 1, the copper catalysts especially the Cu(I) show much better reactivity than other non-noble metals such as In(OTf)₃ and Y(OTf)₃, which are difficult in the generation of the corresponding α -oxo metal carbene due to their weak π -backdonation effect. These results further support that α -oxo metal carbene intermediate **C'** is presumably involved in this oxidative cyclization.

In addition, the presumable copper carbene intermediates **C'** and **E'** have also been reported in the relevant copper-catalyzed cyclization of alkyne-tethered diazo compounds (R. Yao, G. Rong, B. Yan, L. Qiu, X. Xu, *ACS Catal.* **2016**, *6*, 1024).

Moreover, the above proposed mechanism is also well supported by DFT calculations, and please see the section of Computational Studies for details.

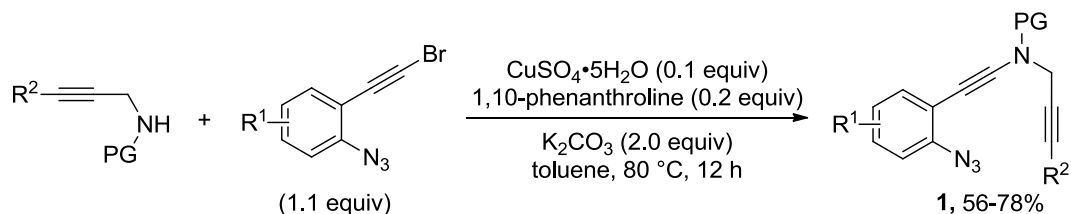
Supplementary Methods

General Information

Unless otherwise noted, materials were obtained commercially and used without further purification. All the solvents were treated according to general methods. Flash column chromatography was performed over silica gel (300-400 mesh). ¹H NMR spectra and ¹³C NMR spectra were recorded on a Bruker AV-400 spectrometer and a Bruker AV-500 spectrometer in chloroform-d₃. For ¹H NMR spectra, chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. For ¹³C NMR spectra, chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. Infrared spectra were recorded on a Nicolet AVATER FTIR330 spectrometer as thin film and are reported in reciprocal centimeter (cm⁻¹). Mass spectra were recorded with Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer using electron spray ionization.

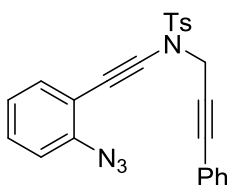
Experimental Section

Representative synthetic procedures for the preparation of ynamides **1** (**1a-1r**)²⁸:



Supplementary Figure 86. Representative synthetic procedures for the preparation of ynamides **1** (**1a-1r**).

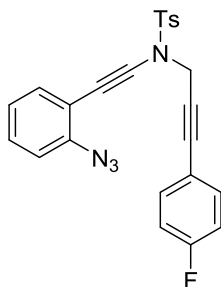
N-((2-azidophenyl)ethynyl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzene sulfonamide (**1a**)



1a

Yellow solid (mp 72-74 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.30 – 7.23 (m, 6H), 7.18 (d, *J* = 6.9 Hz, 2H), 7.07 (dd, *J* = 13.6, 7.5 Hz, 2H), 4.58 (s, 2H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 144.9, 141.0, 134.3, 133.5, 131.6, 129.5, 129.2, 128.6, 128.4, 128.1, 124.6, 122.1, 118.6, 114.9, 87.5, 86.6, 81.1, 67.1, 42.9, 21.6; IR (neat): 3443, 2234, 2128, 1490, 1368, 1301, 1170, 1088, 1037, 755, 659, 591; HRESIMS Calcd for [C₂₄H₁₈N₄NaO₂S]⁺ (M + Na⁺) 449.1043, found 449.1057.

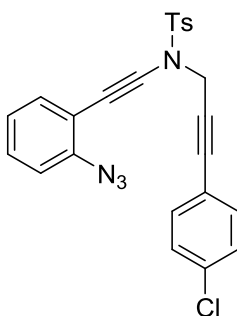
N-((2-azidophenyl)ethynyl)-*N*-(3-(4-fluorophenyl)prop-2-yn-1-yl)-4-methylbenzene sulfonamide (**1b**)



1b

Yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.97 (d, $J = 8.3$ Hz, 2H), 7.37 (d, $J = 7.7$ Hz, 1H), 7.30 (t, $J = 7.1$ Hz, 3H), 7.17 (dd, $J = 8.6, 5.5$ Hz, 2H), 7.07 (dd, $J = 14.8, 7.7$ Hz, 2H), 6.94 (t, $J = 8.7$ Hz, 2H), 4.56 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 162.6 (d, $J = 248.8$ Hz), 144.9, 140.9, 134.3, 133.6 (d, $J = 7.5$ Hz), 133.5, 129.5, 129.2, 128.4, 124.6, 118.6, 118.1 (d, $J = 3.8$ Hz), 115.4 (d, $J = 21.3$ Hz), 114.8, 87.3, 85.5, 80.8 (d, $J = 1.3$ Hz), 67.0, 42.8, 21.6; IR (neat): 3470, 2234, 2127, 1598, 1506, 1490, 1368, 1296, 1170, 837, 754, 586; HRESIMS Calcd for $[\text{C}_{24}\text{H}_{17}\text{FN}_4\text{NaO}_2\text{S}]^+$ ($\text{M} + \text{Na}^+$) 467.0948, found 467.0951.

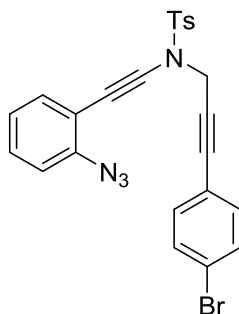
***N*-((2-azidophenyl)ethynyl)-*N*-(3-(4-chlorophenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1c)**



1c

Yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.96 (d, $J = 8.1$ Hz, 2H), 7.36 (d, $J = 7.7$ Hz, 1H), 7.32 – 7.26 (m, 3H), 7.22 (d, $J = 8.3$ Hz, 2H), 7.11 – 7.04 (m, 4H), 4.56 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 144.9, 140.9, 134.6, 134.2, 133.4, 132.8, 129.5, 129.2, 128.4, 128.3, 124.6, 120.5, 118.6, 114.7, 87.3, 85.4, 82.1, 67.0, 42.7, 21.5; IR (neat): 2920, 2234, 2128, 1489, 1369, 1303, 1170, 1089, 752, 662, 599; HRESIMS Calcd for $[\text{C}_{24}\text{H}_{17}\text{ClN}_4\text{NaO}_2\text{S}]^+$ ($\text{M} + \text{Na}^+$) 483.0653, found 483.0652.

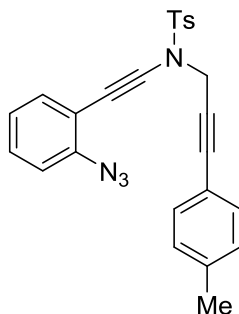
***N*-((2-azidophenyl)ethynyl)-*N*-(3-(4-bromophenyl)prop-2-yn-1-yl)-4-methylbenzene sulfonamide (**1d**)**



1d

Yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.96 (d, $J = 8.2$ Hz, 2H), 7.39 – 7.35 (m, 3H), 7.32 – 7.28 (m, 3H), 7.07 (t, $J = 8.0$ Hz, 2H), 7.03 (d, $J = 8.4$ Hz, 2H), 4.55 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 144.9, 140.9, 134.2, 133.4, 133.0, 131.4, 129.5, 129.2, 128.3, 124.6, 122.8, 120.9, 118.6, 114.7, 87.3, 85.5, 82.3, 67.0, 42.8, 21.5; IR (neat): 3460, 2919, 2127, 1645, 1486, 1368, 1170, 1089, 754, 594; HRESIMS Calcd for $[\text{C}_{24}\text{H}_{17}\text{BrN}_4\text{NaO}_2\text{S}]^+$ ($\text{M} + \text{Na}^+$) 527.0148, found 527.0156.

***N*-((2-azidophenyl)ethynyl)-4-methyl-*N*-(3-(*p*-tolyl)prop-2-yn-1-yl)benzene sulfonamide (**1e**)**

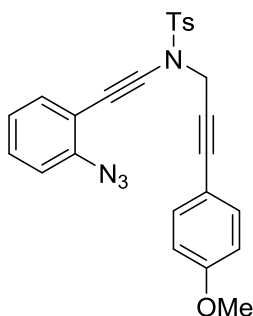


1e

Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 8.2$ Hz, 2H), 7.36 (d, $J = 7.6$ Hz, 1H), 7.32 – 7.28 (m, 3H), 7.09 – 7.03 (m, 6H), 4.56 (s, 2H), 2.36 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 144.9, 140.9, 138.7, 134.3, 133.5, 131.5, 129.5, 129.1, 128.8, 128.4, 124.5, 118.9, 118.6, 114.9, 87.4, 86.8, 80.3, 67.0, 42.9, 21.6, 21.4; IR (neat):

2234, 2128, 1596, 1491, 1445, 1368, 1304, 1170, 1089, 755, 587; HRESIMS Calcd for $[\text{C}_{25}\text{H}_{20}\text{N}_4\text{NaO}_2\text{S}]^+$ ($\text{M} + \text{Na}^+$) 463.1199, found 463.1197.

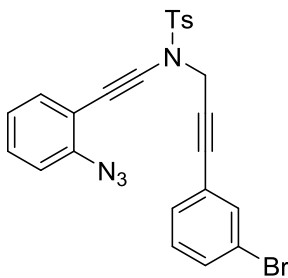
***N*-((2-azidophenyl)ethynyl)-*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1f)**



1f

Yellow solid (mp 56-58 °C). ^1H NMR (500 MHz, CDCl_3) δ 7.97 (d, $J = 8.3$ Hz, 2H), 7.36 (d, $J = 7.7$ Hz, 1H), 7.32 – 7.26 (m, 3H), 7.12 (d, $J = 8.7$ Hz, 2H), 7.06 (dd, $J = 15.3, 8.0$ Hz, 2H), 6.77 (d, $J = 8.8$ Hz, 2H), 4.56 (s, 2H), 3.78 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.7, 144.9, 140.9, 134.3, 133.4, 133.1, 129.5, 129.1, 128.3, 124.5, 118.6, 114.9, 114.1, 113.7, 87.5, 86.6, 79.6, 67.0, 55.2, 43.0, 21.6; IR (neat): 3396, 2918, 2234, 2128, 1606, 1509, 1367, 1293, 1249, 1169, 1034, 755, 588; HRESIMS Calcd for $[\text{C}_{25}\text{H}_{20}\text{N}_4\text{NaO}_3\text{S}]^+$ ($\text{M} + \text{Na}^+$) 479.1148, found 479.1160.

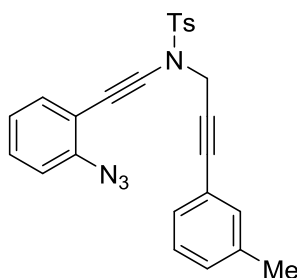
***N*-((2-azidophenyl)ethynyl)-*N*-(3-(3-bromophenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1g)**



1g

Yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.97 (d, $J = 8.2$ Hz, 2H), 7.43 – 7.41 (m, 1H), 7.38 (d, $J = 7.7$ Hz, 1H), 7.33 – 7.29 (m, 3H), 7.25 (d, $J = 5.6$ Hz, 1H), 7.15 – 7.06 (m, 4H), 4.57 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 145.1, 141.0, 134.4, 134.3, 133.6, 131.7, 130.1, 129.6, 129.5, 129.3, 128.4, 124.6, 124.0, 121.9, 118.6, 114.8, 87.3, 85.0, 82.5, 67.1, 42.7, 21.7; IR (neat): 3477, 2234, 2127, 1490, 1368, 1299, 1170, 1088, 753, 665, 592; HRESIMS Calcd for $[\text{C}_{24}\text{H}_{17}\text{BrN}_4\text{NaO}_2\text{S}]^+$ ($\text{M} + \text{Na}^+$) 527.0148, found 527.0158.

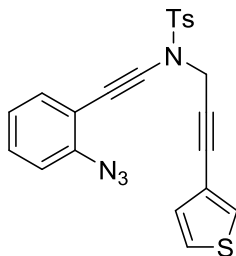
***N*-((2-azidophenyl)ethynyl)-4-methyl-*N*-(3-(*m*-tolyl)prop-2-yn-1-yl)benzene sulfonamide (**1h**)**



1h

Yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.97 (d, $J = 8.3$ Hz, 2H), 7.37 (dd, $J = 7.7, 1.3$ Hz, 1H), 7.29 – 7.26 (m, 3H), 7.15 – 7.04 (m, 4H), 6.98 (d, $J = 8.1$ Hz, 2H), 4.57 (s, 2H), 2.36 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 144.9, 140.9, 137.7, 134.3, 133.5, 132.2, 129.5, 129.4, 129.1, 128.7, 128.4, 128.0, 124.5, 121.8, 118.6, 114.9, 87.4, 86.8, 80.6, 67.0, 42.9, 21.5, 21.1; IR (neat): 2921, 2234, 2128, 1596, 1490, 1368, 1302, 1171, 1089, 1038, 921, 754, 592; HRESIMS Calcd for $[\text{C}_{25}\text{H}_{20}\text{N}_4\text{NaO}_2\text{S}]^+$ ($\text{M} + \text{Na}^+$) 463.1199, found 463.1195.

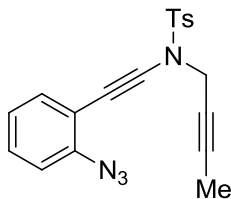
***N*-((2-azidophenyl)ethynyl)-4-methyl-*N*-(3-(thiophen-3-yl)prop-2-yn-1-yl)benzene sulfonamide (**1i**)**



1i

Yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.96 (d, $J = 8.3$ Hz, 2H), 7.36 (dd, $J = 7.7, 1.2$ Hz, 1H), 7.35 – 7.29 (m, 3H), 7.24 (d, $J = 2.0$ Hz, 1H), 7.20 (dd, $J = 4.9, 3.0$ Hz, 1H), 7.08 – 7.03 (m, 2H), 6.88 (dd, $J = 4.9, 0.9$ Hz, 1H), 4.55 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 144.9, 140.9, 134.3, 133.4, 129.6, 129.5, 129.3, 129.1, 128.3, 125.2, 124.5, 121.1, 118.6, 114.9, 87.4, 81.8, 80.7, 67.1, 42.9, 21.6; IR (neat): 3454, 2234, 2128, 1490, 1367, 1302, 1169, 1088, 1037, 922, 754, 664, 591; HRESIMS Calcd for $[\text{C}_{22}\text{H}_{16}\text{N}_4\text{NaO}_2\text{S}_2]^+$ ($\text{M} + \text{Na}^+$) 455.0607, found 455.0616.

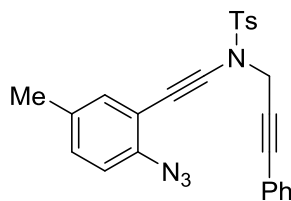
***N*-((2-azidophenyl)ethynyl)-*N*-(but-2-yn-1-yl)-4-methylbenzenesulfonamide (1j)**



1j

Yellow solid (mp 59-61 °C). ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 8.3$ Hz, 2H), 7.35 (d, $J = 8.3$ Hz, 3H), 7.31 – 7.23 (m, 1H), 7.14 – 7.01 (m, 2H), 4.29 (d, $J = 2.3$ Hz, 2H), 2.44 (s, 3H), 1.64 (t, $J = 2.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.7, 140.6, 134.3, 133.3, 129.3, 129.0, 128.3, 124.5, 118.6, 115.0, 87.6, 83.0, 71.1, 66.8, 42.5, 21.6, 3.4; IR (neat): 3440, 2920, 2234, 2128, 1596, 1490, 1366, 1302, 1169, 1089, 923, 754, 586; HRESIMS Calcd for $[\text{C}_{19}\text{H}_{16}\text{N}_4\text{NaO}_2\text{S}]^+$ ($\text{M} + \text{Na}^+$) 387.0886, found 387.0893.

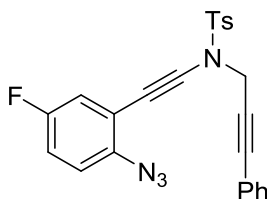
***N*-((2-azido-5-methylphenyl)ethynyl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzene sulfonamide (1k)**



1k

Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 8.3$ Hz, 2H), 7.30 – 7.23 (m, 5H), 7.22 – 7.17 (m, 3H), 7.08 (d, $J = 8.2$ Hz, 1H), 6.95 (d, $J = 8.2$ Hz, 1H), 4.56 (s, 2H), 2.35 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.9, 138.1, 134.3, 134.2, 133.8, 131.6, 130.0, 129.5, 128.5, 128.3, 128.1, 122.0, 118.5, 114.5, 87.0, 86.6, 81.1, 67.2, 42.8, 21.5, 20.5; IR (neat): 2920, 2849, 2239, 2120, 1492, 1368, 1305, 1170, 1089, 1039, 811, 757, 592; HRESIMS Calcd for $[\text{C}_{25}\text{H}_{20}\text{N}_4\text{NaO}_2\text{S}]^+$ ($\text{M} + \text{Na}^+$) 463.1199, found 463.1198.

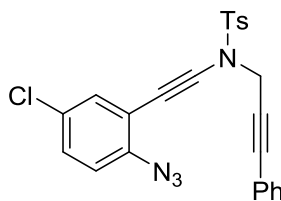
***N*-((2-azido-5-fluorophenyl)ethynyl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (1l)**



1l

Yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.96 (d, $J = 8.2$ Hz, 2H), 7.31 – 7.23 (m, 5H), 7.17 (d, $J = 7.1$ Hz, 2H), 7.05 (d, $J = 8.8$ Hz, 1H), 7.06 – 6.98 (m, 2H), 4.58 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.0 (d, $J = 243.8$ Hz), 145.1, 136.8 (d, $J = 2.5$ Hz), 134.1, 131.6, 129.6, 128.6, 128.3, 128.1, 121.9, 120.0 (d, $J = 8.8$ Hz), 119.5 (d, $J = 25.0$ Hz), 116.3 (d, $J = 22.5$ Hz), 88.4, 86.7, 80.8, 66.4 (d, $J = 2.5$ Hz), 42.8, 21.5; IR (neat): 3440, 2920, 2849, 2241, 2123, 1491, 1370, 1170, 1089, 1037, 876, 757, 591; HRESIMS Calcd for $[\text{C}_{24}\text{H}_{17}\text{FN}_4\text{NaO}_2\text{S}]^+$ ($\text{M} + \text{Na}^+$) 467.0948, found 467.0953.

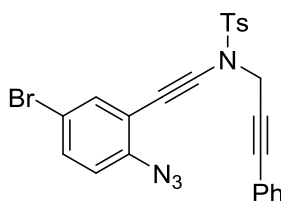
***N*-((2-azido-5-chlorophenyl)ethynyl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (1m)**



1m

Yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.95 (d, $J = 8.1$ Hz, 2H), 7.32 – 7.24 (m, 7H), 7.18 (d, $J = 7.3$ Hz, 2H), 6.99 (d, $J = 8.6$ Hz, 1H), 4.57 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 145.1, 139.4, 134.2, 132.7, 131.6, 129.7, 129.6, 129.0, 128.6, 128.3, 128.1, 121.9, 119.8, 116.4, 88.6, 86.7, 80.8, 66.2, 42.8, 21.6; IR (neat): 3445, 2919, 2115, 1645, 1488, 1370, 1301, 1169, 757, 591; HRESIMS Calcd for $[\text{C}_{24}\text{H}_{17}\text{ClN}_4\text{NaO}_2\text{S}]^+$ ($\text{M} + \text{Na}^+$) 483.0653, found 483.0659.

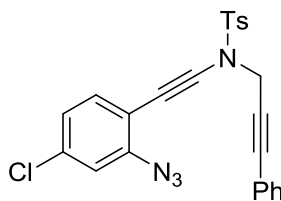
***N*-((2-azido-5-bromophenyl)ethynyl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzene sulfonamide (1n)**



1n

Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, $J = 8.3$ Hz, 2H), 7.46 (d, $J = 2.2$ Hz, 1H), 7.36 (d, $J = 8.6$ Hz, 1H), 7.30 – 7.24 (m, 5H), 7.18 (d, $J = 6.8$ Hz, 2H), 6.92 (d, $J = 8.6$ Hz, 1H), 4.57 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.1, 139.9, 135.6, 134.2, 131.9, 131.6, 129.6, 128.6, 128.3, 128.1, 121.9, 120.0, 117.0, 116.8, 88.8, 86.7, 80.9, 66.1, 42.8, 21.5; IR (neat): 3467, 2919, 2234, 2109, 1645, 1482, 1369, 1298, 1169, 1090, 1036, 928, 756, 590; HRESIMS Calcd for $[\text{C}_{24}\text{H}_{17}\text{BrN}_4\text{NaO}_2\text{S}]^+$ ($\text{M} + \text{Na}^+$) 527.0148, found 527.0158.

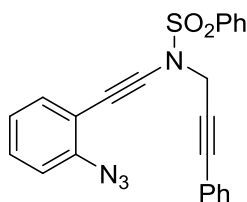
***N*-((2-azido-4-chlorophenyl)ethynyl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzene sulfonamide (1o)**



1o

Yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.95 (d, $J = 8.2$ Hz, 2H), 7.30 – 7.23 (m, 6H), 7.17 (d, $J = 7.2$ Hz, 2H), 7.07 – 6.98 (m, 2H), 4.56 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 145.0, 142.1, 134.7, 134.2, 131.6, 129.5, 128.6, 128.3, 128.1, 124.9, 121.9, 118.9, 113.5, 88.3, 86.7, 80.9, 66.2, 42.8, 21.5; IR (neat): 2236, 2109, 1589, 1489, 1401, 1369, 1291, 1171, 1102, 1089, 921, 758, 660, 578; HRESIMS Calcd for $[\text{C}_{24}\text{H}_{17}\text{ClN}_4\text{NaO}_2\text{S}]^+$ ($\text{M} + \text{Na}^+$) 483.0653, found 483.0660.

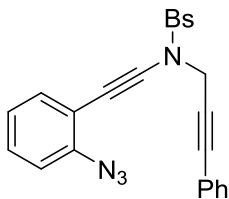
***N*-((2-azidophenyl)ethynyl)-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (1p)**



1p

Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 7.3$ Hz, 2H), 7.59 (t, $J = 7.4$ Hz, 1H), 7.50 (t, $J = 7.6$ Hz, 2H), 7.35 (dd, $J = 7.6, 1.3$ Hz, 1H), 7.28 – 7.16 (m, 6H), 7.12 – 6.95 (m, 2H), 4.60 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.9, 137.2, 133.8, 133.5, 131.6, 129.2, 128.9, 128.6, 128.3, 128.1, 124.5, 121.9, 118.6, 114.7, 87.1, 86.7, 80.9, 67.1, 42.9; IR (neat): 3062, 2925, 2235, 2128, 1569, 1490, 1447, 1369, 1302, 1173, 1089, 1038, 920, 754, 595; HRESIMS Calcd for $[\text{C}_{23}\text{H}_{16}\text{N}_4\text{NaO}_2\text{S}]^+$ ($\text{M} + \text{Na}^+$) 435.0886, found 435.0889.

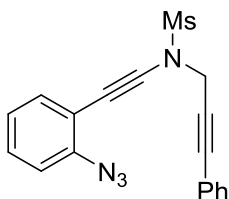
***N*-((2-azidophenyl)ethynyl)-4-bromo-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (1q)**



1q

Yellow solid (mp 104-106 °C). ¹H NMR (500 MHz, CDCl₃) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.32 – 7.24 (m, 4H), 7.15 (d, *J* = 7.5 Hz, 2H), 7.09 – 7.04 (m, 2H), 4.60 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 141.1, 136.1, 133.5, 132.2, 131.5, 129.8, 129.4, 129.2, 128.7, 128.3, 124.6, 121.6, 118.5, 114.4, 87.0, 86.7, 80.7, 67.2, 43.1; IR (neat): 3444, 2925, 2235, 2128, 1734, 1573, 1490, 1372, 1301, 1174, 1086, 1009, 919, 755, 614; HRESIMS Calcd for [C₂₃H₁₅BrN₄NaO₂S]⁺ (M + Na⁺) 512.9991, found 512.9999.

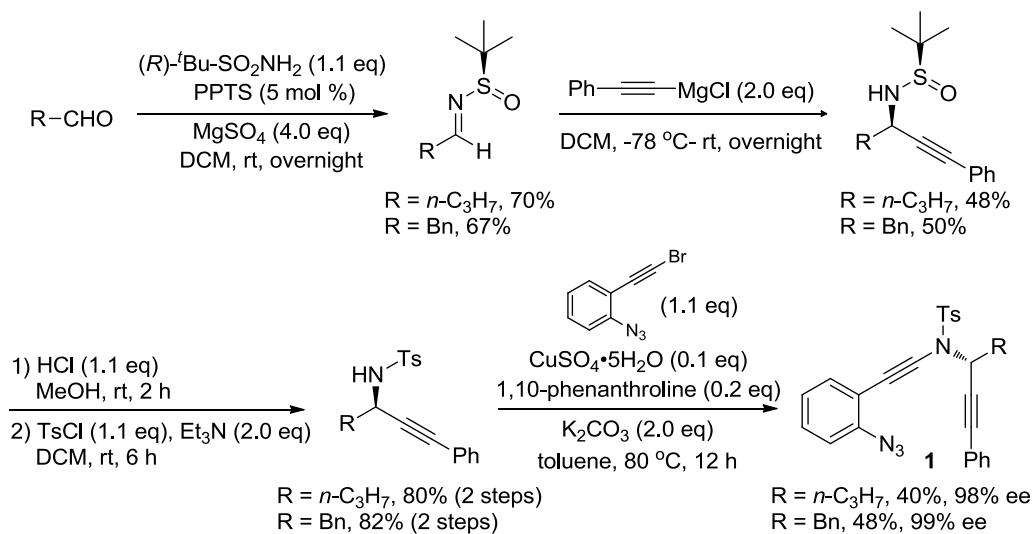
***N*-((2-azidophenyl)ethynyl)-*N*-(3-phenylprop-2-yn-1-yl)methanesulfonamide (1r)**



1r

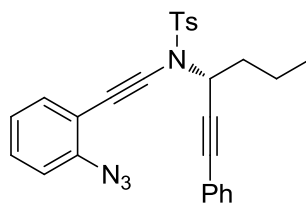
Yellow solid (mp 50-52 °C). ¹H NMR (500 MHz, CDCl₃) δ 7.47 (d, *J* = 7.8 Hz, 2H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.38 – 7.31 (m, 4H), 7.13 – 7.04 (m, 2H), 4.62 (s, 2H), 3.32 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 141.2, 133.7, 131.8, 129.5, 129.0, 128.4, 124.6, 121.7, 118.7, 114.4, 87.1, 86.7, 81.4, 67.2, 42.9, 38.8; IR (neat): 3459, 2922, 2236, 2127, 1644, 1490, 1361, 1299, 1166, 756, 692, 515; HRESIMS Calcd for [C₁₈H₁₄N₄NaO₂S]⁺ (M + Na⁺) 373.0730, found 373.0738.

Representative synthetic procedures for the preparation of ynamides 1 (1s-1t)²⁹:



Supplementary Figure 87. Representative synthetic procedures for the preparation of ynamides **1** (**1s-1t**).

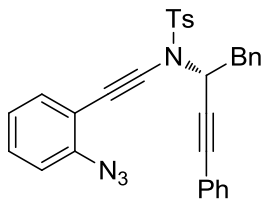
(*R*)-*N*-((2-azidophenyl)ethynyl)-4-methyl-*N*-(1-phenylhex-1-yn-3-yl)benzenesulfonamide (1s**)**



1s

Yellow solid (mp 85-87 °C). $[\alpha]_{\text{D}}^{20} = +97.5$ (c = 1.0, CHCl₃). 98% ee (determined by HPLC: Chiralcel AS-H Column, 2/98 *i*-PrOH/hexane, 1.5 mL/min, 254 nm; TR = 12.94 min (major), 10.24 min (minor)). ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.38 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.31 – 7.19 (m, 6H), 7.12 – 7.01 (m, 4H), 4.91 (t, *J* = 7.6 Hz, 1H), 2.31 (s, 3H), 2.08 – 1.87 (m, 2H), 1.62 – 1.53 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 144.7, 141.0, 134.6, 133.4, 131.5, 129.4, 129.0, 128.4, 128.3, 128.0, 124.5, 122.2, 118.5, 115.2, 85.8, 85.3, 85.0, 68.7, 53.2, 36.5, 21.5, 19.1, 13.4; IR (neat): 3443, 2921, 2234, 2128, 1506, 1489, 1369, 1249, 1170, 1089, 756, 669, 588; HRESIMS Calcd for [C₂₇H₂₄N₄NaO₂S]⁺ (M + Na⁺) 491.1512, found 491.1532.

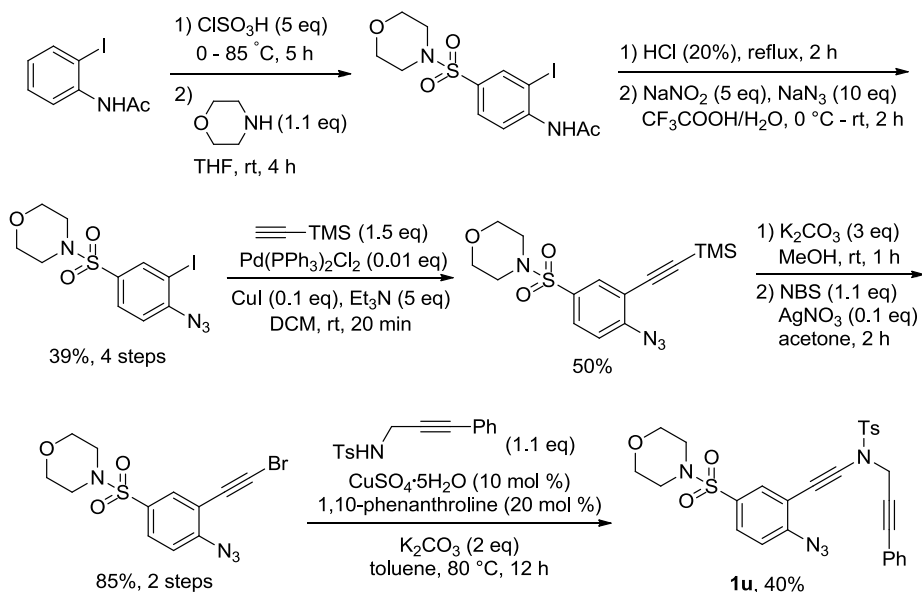
(*R*)-*N*-((2-azidophenyl)ethynyl)-*N*-(1,4-diphenylbut-3-yn-2-yl)-4-methylbenzenesulfonamide (1t**)**



1t

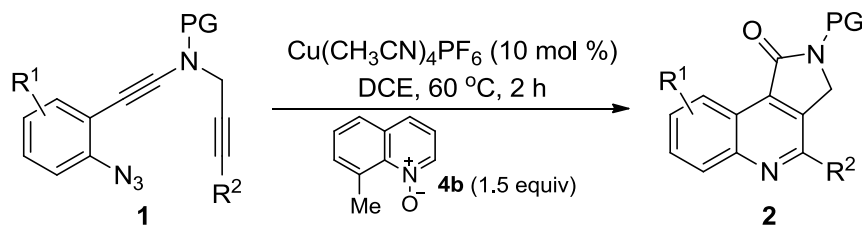
Yellow solid (mp 87-89 °C). $[\alpha]_D^{20} = -7.7^\circ$ ($c = 1.0$, CHCl_3). 99% ee (determined by HPLC: Chiralcel IC Column, 2/98 *i*-PrOH/hexane, 0.8 mL/min, 254 nm; TR = 32.33 min (major), 29.87 min (minor)). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.85 (d, $J = 8.2$ Hz, 2H), 7.41 (d, $J = 7.7$ Hz, 1H), 7.36 – 7.20 (m, 11H), 7.15 – 7.04 (m, 4H), 5.13 (t, $J = 7.6$ Hz, 1H), 3.38 – 3.30 (m, 1H), 3.27 – 3.19 (m, 1H), 2.32 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 144.6, 141.1, 136.0, 134.6, 133.4, 131.5, 129.6, 129.4, 129.1, 128.5, 128.4, 128.3, 128.0, 127.1, 124.5, 122.1, 118.5, 115.1, 86.7, 85.2, 84.5, 69.5, 54.9, 40.8, 21.5; IR (neat): 3444, 2921, 2236, 2127, 1596, 1490, 1368, 1301, 1169, 1089, 942, 724, 661, 598; HRESIMS Calcd for $[\text{C}_{31}\text{H}_{24}\text{N}_4\text{NaO}_2\text{S}]^+$ ($\text{M} + \text{Na}^+$) 539.1512, found 539.1521.

***N*-((2-azido-5-(morpholinosulfonyl)phenyl)ethynyl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (**1u**)**



Supplementary Figure 88. Synthesis of ynamide **1u**.

Compound **1u** was prepared according to the known procedures^{24-26,30}. Yellow solid (mp 71-73 °C). ¹H NMR (500 MHz, CDCl₃) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 2.1 Hz, 1H), 7.63 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.33 – 7.24 (m, 5H), 7.22 – 7.18 (m, 3H), 4.60 (s, 2H), 3.72 (t, 4H), 2.97 (t, 4H), 2.38 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 145.4, 145.3, 134.2, 132.5, 131.6, 131.3, 129.7, 128.7, 128.3, 128.2, 128.0, 121.9, 119.0, 116.1, 89.8, 86.9, 80.8, 66.1, 66.0, 45.9, 42.8, 21.6; IR (neat): 3440, 2920, 2234, 2128, 1596, 1491, 1369, 1268, 1170, 1088, 758, 664, 546; HRESIMS Calcd for [C₂₈H₂₅N₅NaO₅S₂]⁺ (M + Na⁺) 598.1189, found 598.1196.

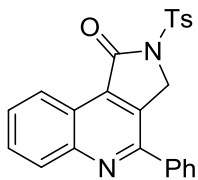


Supplementary Figure 89. Synthesis of pyrrolo[3,4-*c*]quinolin-1-ones **2**.

General procedure for the synthesis of pyrrolo[3,4-*c*]quinolin-1-ones **2**:

Methylquinoline *N*-oxide (0.3 mmol, 47.7 mg) and Cu(CH₃CN)₄PF₆ (0.02 mmol, 7.5 mg) were added in this order to the ynamide **1** (0.20 mmol) in DCE (4.0 mL) at room temperature. The reaction mixture was stirred at 60 °C and the progress of the reaction was monitored by TLC. The reaction typically took 2 h. Upon completion, the mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: hexanes/dichloromethane) to afford the desired product **2**.

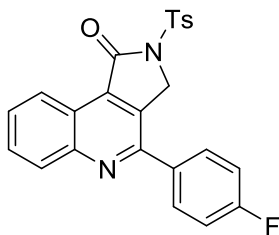
4-phenyl-2-tosyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (**2a**)



2a

Compound **2a** was prepared in 82% yield (67.9 mg) according to the general procedure (Table 2, entry 1). Yellow solid (mp 206-208 °C). ¹H NMR (400 MHz, CDCl₃) δ 8.94 (d, *J* = 8.2 Hz, 1H), 8.25 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 8.2 Hz, 2H), 7.88 (d, *J* = 6.9 Hz, 2H), 7.82 (t, *J* = 7.7 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.61 – 7.54 (m, 3H), 7.36 (d, *J* = 8.2 Hz, 2H), 5.19 (s, 2H), 2.43 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 165.8, 154.0, 148.4, 145.7, 137.6, 135.0, 133.6, 133.3, 130.7, 130.1, 130.0, 129.9, 129.2, 129.0, 128.3, 128.2, 123.1, 122.1, 49.6, 21.7; IR (neat): 2923, 1732, 1594, 1494, 1442, 1365, 1330, 1173, 1145, 1089, 1058, 985, 770, 662, 578; HRESIMS Calcd for [C₂₄H₁₈N₂NaO₃S]⁺ (M + Na⁺) 437.0930, found 437.0936.

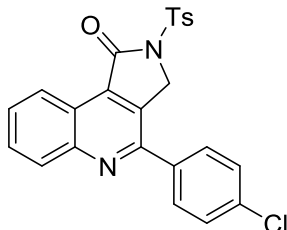
4-(4-fluorophenyl)-2-tosyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (2b)



2b

Compound **2b** was prepared in 62% yield (53.6 mg) according to the general procedure (Table 2, entry 2). Yellow solid (mp 229-231 °C). ¹H NMR (500 MHz, CDCl₃) δ 8.93 (d, *J* = 8.1 Hz, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 8.3 Hz, 2H), 7.90 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.82 (t, *J* = 8.3 Hz, 1H), 7.69 (t, *J* = 7.2 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.26 (m, 2H), 5.17 (s, 2H), 2.43 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 165.6, 163.9 (d, *J* = 250.0 Hz), 152.7, 148.3, 145.7, 135.0, 133.8 (d, *J* = 2.5 Hz), 133.4, 133.2, 130.8, 130.3 (d, *J* = 8.8 Hz), 129.9, 129.8, 129.0, 128.3, 123.1, 122.1, 116.3 (d, *J* = 21.3 Hz), 49.6, 21.7; IR (neat): 3476, 2920, 1729, 1586, 1498, 1459, 1364, 1295, 1171, 1145, 1089, 984, 769, 579; HRESIMS Calcd for [C₂₄H₁₇FN₂NaO₃S]⁺ (M + Na⁺) 455.0836, found 455.0841.

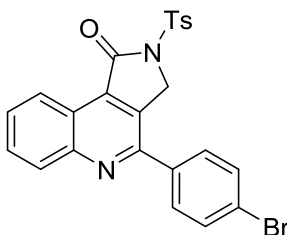
4-(4-chlorophenyl)-2-tosyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (2c)



2c

Compound **2c** was prepared in 69% yield (61.8 mg) according to the general procedure (Table 2, entry 3). Yellow solid (mp 221-223 °C). ¹H NMR (400 MHz, CDCl₃) δ 8.94 (d, *J* = 8.3 Hz, 1H), 8.23 (d, *J* = 8.6 Hz, 1H), 8.08 (d, *J* = 8.2 Hz, 2H), 7.87 – 7.81 (m, 3H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 5.17 (s, 2H), 2.43 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 165.6, 152.5, 148.3, 145.7, 136.4, 136.0, 135.0, 133.5, 133.2, 130.9, 130.0, 129.9, 129.6, 129.4, 129.2, 128.3, 123.2, 122.2, 49.5, 21.7; IR (neat): 3435, 2999, 2917, 1729, 1659, 1436, 1361, 1144, 1019, 952, 768, 658, 576; HRESIMS Calcd for [C₂₄H₁₇ClN₂NaO₃S]⁺ (M + Na⁺) 471.0541, found 471.0555.

4-(4-bromophenyl)-2-tosyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (2d)

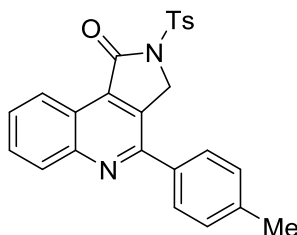


2d

Compound **2d** was prepared in 64% yield (63.0 mg) according to the general procedure (Table 2, entry 4). Yellow solid (mp 234-236 °C). ¹H NMR (400 MHz, CDCl₃) δ 8.93 (d, *J* = 8.3 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 8.3 Hz, 2H), 7.85 – 7.67 (m, 6H), 7.37 (d, *J* = 8.1 Hz, 2H), 5.16 (s, 2H), 2.42 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 165.6, 152.6, 148.3, 145.7, 136.5, 135.0, 133.5, 133.2, 132.4, 130.9, 130.0, 129.9, 129.8, 129.2, 128.3, 124.7, 123.2, 122.2, 49.5, 21.7; IR (neat): 3433, 1726, 1627, 1458, 1359, 1290,

1143, 1119, 1086, 767, 576; HRESIMS Calcd for $[\text{C}_{24}\text{H}_{17}\text{BrN}_2\text{NaO}_3\text{S}]^+$ ($\text{M} + \text{Na}^+$) 515.0035, found 515.0053.

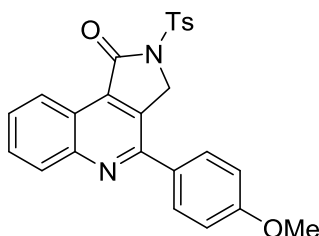
4-(*p*-tolyl)-2-tosyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (2e)



2e

Compound **2e** was prepared in 78% yield (66.8 mg) according to the general procedure (Table 2, entry 5). Yellow solid (mp 226-228 °C). ^1H NMR (500 MHz, CDCl_3) δ 8.91 (d, $J = 8.3$ Hz, 1H), 8.22 (d, $J = 8.4$ Hz, 1H), 8.07 (d, $J = 8.4$ Hz, 2H), 7.80 – 7.76 (m, 3H), 7.66 (t, $J = 7.6$ Hz, 1H), 7.41 – 7.33 (m, 4H), 5.17 (s, 2H), 2.46 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.8, 153.8, 148.3, 145.6, 140.3, 135.0, 134.8, 133.6, 133.2, 130.6, 129.9, 129.8, 129.7, 128.7, 128.3, 128.1, 123.1, 121.9, 49.7, 21.7, 21.4; IR (neat): 3460, 1731, 1631, 1365, 1336, 1172, 1146, 1123, 1091, 774, 661, 578; HRESIMS Calcd for $[\text{C}_{25}\text{H}_{20}\text{N}_2\text{NaO}_3\text{S}]^+$ ($\text{M} + \text{Na}^+$) 451.1087, found 451.1093.

4-(4-methoxyphenyl)-2-tosyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (2f)

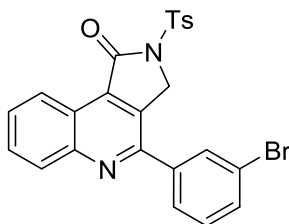


2f

Compound **2f** was prepared in 74% yield (65.7 mg) according to the general procedure (Table 2, entry 6). Yellow solid (mp 198-200 °C). ^1H NMR (400 MHz, CDCl_3) δ 8.90 (d, $J = 8.2$ Hz, 1H), 8.21 (d, $J = 8.4$ Hz, 1H), 8.08 (d, $J = 8.3$ Hz, 2H), 7.86 (d, $J = 8.7$ Hz, 2H), 7.79 (t, $J = 7.2$ Hz, 1H), 7.65 (t, $J = 7.6$ Hz, 1H), 7.36 (d, $J = 8.2$ Hz, 2H), 7.08 (d, $J = 8.2$ Hz, 2H), 3.80 (s, 3H); IR (neat): 3460, 1731, 1631, 1365, 1336, 1172, 1146, 1123, 1091, 774, 661, 578; HRESIMS Calcd for $[\text{C}_{25}\text{H}_{20}\text{N}_2\text{NaO}_4\text{S}]^+$ ($\text{M} + \text{Na}^+$) 467.1087, found 467.1093.

= 8.7 Hz, 2H), 5.18 (s, 2H), 3.91 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.8, 161.1, 153.4, 148.3, 145.6, 135.1, 133.4, 133.2, 130.6, 130.1, 129.9, 129.7, 129.6, 128.5, 128.3, 123.1, 121.8, 114.6, 55.5, 49.8, 21.7; IR (neat): 3477, 2923, 2852, 2128, 1725, 1596, 1502, 1452, 1366, 1254, 1170, 1146, 1089, 660, 578; HRESIMS Calcd for $[\text{C}_{25}\text{H}_{20}\text{N}_2\text{NaO}_4\text{S}]^+$ ($\text{M} + \text{Na}^+$) 467.1036, found 467.1047.

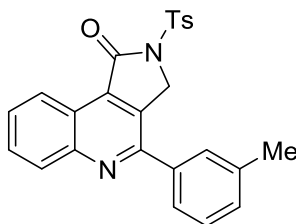
4-(3-bromophenyl)-2-tosyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (2g)



2g

Compound **2g** was prepared in 87% yield (85.6 mg) according to the general procedure (Table 2, entry 7). Yellow solid (mp 254-256 °C). ^1H NMR (500 MHz, CDCl_3) δ 8.92 (d, $J = 8.2$ Hz, 1H), 8.23 (d, $J = 8.3$ Hz, 1H), 8.09 – 8.07 (m, 3H), 7.83 (t, $J = 7.6$ Hz, 1H), 7.75 (d, $J = 7.3$ Hz, 1H), 7.69 (dd, $J = 15.8, 7.9$ Hz, 2H), 7.45 (t, $J = 7.7$ Hz, 1H), 7.37 (d, $J = 7.8$ Hz, 2H), 5.16 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.5, 152.2, 148.3, 145.7, 139.5, 134.9, 133.5, 133.2, 133.0, 131.5, 130.9, 130.5, 130.0, 129.9, 129.3, 128.3, 126.5, 123.5, 123.1, 122.2, 49.4, 21.7; IR (neat): 3473, 2919, 2359, 1720, 1589, 1466, 1356, 1329, 1173, 1150, 1093, 774, 585; HRESIMS Calcd for $[\text{C}_{24}\text{H}_{17}\text{BrN}_2\text{NaO}_3\text{S}]^+$ ($\text{M} + \text{Na}^+$) 515.0035, found 515.0050.

4-(*m*-tolyl)-2-tosyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (2h)

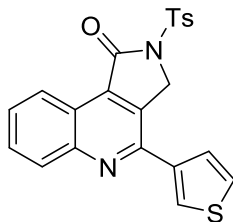


2h

Compound **2h** was prepared in 74% yield (63.4 mg) according to the general procedure (Table 2, entry 8). Yellow solid (mp 228-230 °C). ^1H NMR (400 MHz, CDCl_3) δ 8.89 (d,

$J = 9.1$ Hz, 1H), 8.22 (d, $J = 8.4$ Hz, 1H), 8.07 (d, $J = 8.4$ Hz, 2H), 7.81 – 7.77 (m, 1H), 7.68 – 7.63 (m, 2H), 7.59 (d, $J = 7.7$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 1H), 7.36 – 7.32 (m, 3H), 5.15 (s, 2H), 2.47 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.7, 154.1, 148.2, 145.6, 139.0, 137.5, 135.0, 133.6, 133.1, 130.7, 130.6, 129.9, 129.8, 128.9, 128.8, 128.2, 125.1, 123.0, 122.0, 49.6, 21.6, 21.5; IR (neat): 2921, 2850, 1730, 1644, 1594, 1505, 1460, 1366, 1336, 1172, 1090, 772, 580; HRESIMS Calcd for $[\text{C}_{25}\text{H}_{20}\text{N}_2\text{NaO}_3\text{S}]^+$ ($\text{M} + \text{Na}^+$) 451.1087, found 451.1094.

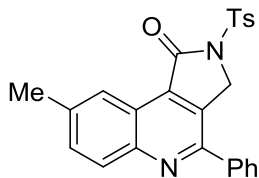
8-methyl-4-phenyl-2-tosyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (2i)



2i

Compound **2i** was prepared in 55% yield (46.2 mg) according to the general procedure (Table 2, entry 9). Yellow solid (mp 210-212 °C). ^1H NMR (500 MHz, CDCl_3) δ 8.89 (d, $J = 8.2$ Hz, 1H), 8.19 (d, $J = 8.3$ Hz, 1H), 8.10 (d, $J = 7.7$ Hz, 2H), 7.93 (s, 1H), 7.86 (d, $J = 4.0$ Hz, 1H), 7.80 (t, $J = 7.2$ Hz, 1H), 7.66 (t, $J = 7.2$ Hz, 1H), 7.53 (s, 1H), 7.38 (d, $J = 7.6$ Hz, 2H), 5.24 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, DMSO) δ 165.5, 149.1, 147.0, 145.4, 139.3, 135.1, 134.9, 132.0, 130.6, 129.8, 129.4, 128.8, 128.2, 127.8, 127.7, 127.2, 122.1, 121.2, 50.1, 21.1; IR (neat): 3423, 2254, 2127, 1650, 1366, 1232, 1166, 1015, 825, 763, 629; HRESIMS Calcd for $[\text{C}_{22}\text{H}_{16}\text{N}_2\text{NaO}_3\text{S}_2]^+$ ($\text{M} + \text{Na}^+$) 443.0495, found 443.0499.

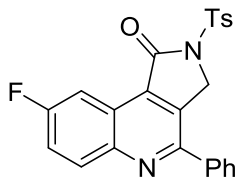
8-methyl-4-phenyl-2-tosyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (2k)



2k

Compound **2k** was prepared in 70% yield (59.9 mg) according to the general procedure (Table 2, entry 11). Yellow solid (mp 233-235 °C). ¹H NMR (400 MHz, CDCl₃) δ 8.70 (s, 1H), 8.12 (d, *J* = 8.6 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 2H), 7.85 (d, *J* = 6.7 Hz, 2H), 7.63 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.59 – 7.51 (m, 3H), 7.36 (d, *J* = 8.2 Hz, 2H), 5.16 (s, 2H), 2.57 (s, 3H), 2.42 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 166.0, 152.8, 147.0, 145.6, 139.6, 137.7, 135.1, 133.5, 132.9, 132.4, 129.9, 129.8, 129.5, 129.1, 128.3, 128.2, 122.1, 122.0, 49.6, 22.0, 21.7; IR (neat): 3463, 2921, 1729, 1594, 1446, 1365, 1290, 1202, 1170, 1141, 1088, 823, 666, 544; HRESIMS Calcd for [C₂₅H₂₀N₂NaO₃S]⁺ (M + Na⁺) 451.1087, found 451.1094.

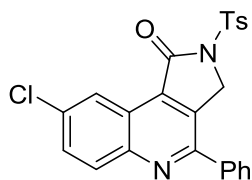
8-fluoro-4-phenyl-2-tosyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (2l)



2l

Compound **2l** was prepared in 72% yield (62.2 mg) according to the general procedure (Table 2, entry 12). Yellow solid (mp 265-267 °C). ¹H NMR (400 MHz, CDCl₃) δ 8.56 (dd, *J* = 9.1, 2.8 Hz, 1H), 8.24 (dd, *J* = 9.2, 5.3 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 2H), 7.86 (d, *J* = 6.5 Hz, 2H), 7.63 – 7.52 (m, 4H), 7.37 (d, *J* = 8.2 Hz, 2H), 5.19 (s, 2H), 2.43 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 165.5, 162.1 (d, *J* = 251.3 Hz), 153.2, 145.8, 145.5, 137.3, 134.9, 134.3, 133.0 (d, *J* = 5.0 Hz), 132.4 (d, *J* = 10.0 Hz), 130.1, 130.0, 129.2, 128.3, 128.2, 122.9 (d, *J* = 11.3 Hz), 121.0 (d, *J* = 26.3 Hz), 107.3 (d, *J* = 23.8 Hz), 49.6, 21.7; IR (neat): 3461, 2117, 1745, 1596, 1446, 1369, 1237, 1169, 1141, 1087, 1004, 836, 666, 578; HRESIMS Calcd for [C₂₄H₁₇FN₂NaO₃S]⁺ (M + Na⁺) 455.0836, found 455.0846.

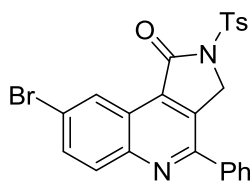
8-chloro-4-phenyl-2-tosyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (2m)



2m

Compound **2m** was prepared in 68% yield (60.9 mg) according to the general procedure (Table 2, entry 13). Yellow solid (mp 203-205 °C). ¹H NMR (400 MHz, CDCl₃) δ 8.94 (d, *J* = 2.1 Hz, 1H), 8.17 (d, *J* = 9.0 Hz, 1H), 8.08 (d, *J* = 8.3 Hz, 2H), 7.87 (d, *J* = 6.3 Hz, 2H), 7.75 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.63 – 7.54 (m, 3H), 7.38 (d, *J* = 8.1 Hz, 2H), 5.20 (s, 2H), 2.43 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 165.4, 154.1, 146.7, 145.8, 137.3, 135.4, 134.9, 134.4, 132.7, 131.8, 131.3, 130.3, 130.0, 129.3, 128.4, 128.2, 122.6, 122.3, 49.7, 21.7; IR (neat): 3471, 2920, 2125, 1721, 1658, 1620, 1484, 1449, 1365, 1142, 1075, 916, 659, 541; HRESIMS Calcd for [C₂₄H₁₇ClN₂NaO₃S]⁺ (M + Na⁺) 471.0541, found 471.0556.

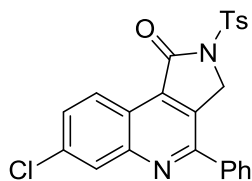
8-bromo-4-phenyl-2-tosyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (2n)



2n

Compound **2n** was prepared in 63% yield (62.0 mg) according to the general procedure (Table 2, entry 14). Yellow solid (mp 258-260 °C). ¹H NMR (400 MHz, CDCl₃) δ 9.11 (d, *J* = 2.2 Hz, 1H), 8.11 – 8.06 (m, 3H), 7.92 – 7.85 (m, 3H), 7.63 – 7.55 (m, 3H), 7.38 (d, *J* = 8.3 Hz, 2H), 5.20 (s, 2H), 2.43 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 165.3, 154.2, 146.9, 145.8, 137.3, 134.9, 134.4, 134.3, 132.5, 131.4, 130.3, 130.0, 129.3, 128.4, 128.2, 125.6, 123.7, 122.9, 49.7, 21.7; IR (neat): 3441, 2917, 1738, 1633, 1592, 1491, 1370, 1170, 1148, 1087, 996, 703, 543; HRESIMS Calcd for [C₂₄H₁₇BrN₂NaO₃S]⁺ (M + Na⁺) 515.0035, found 515.0053.

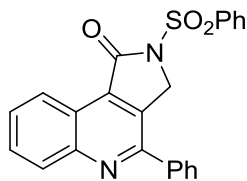
4-phenyl-2-(phenylsulfonyl)-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (2o)



2o

Compound **2o** was prepared in 94% yield (84.2 mg) according to the general procedure (Table 2, entry 15). Yellow solid (mp 278-280 °C). ^1H NMR (500 MHz, CDCl_3) δ 8.86 (d, $J = 8.9$ Hz, 1H), 8.23 (d, $J = 1.6$ Hz, 1H), 8.07 (d, $J = 8.3$ Hz, 2H), 7.87 (d, $J = 7.8$ Hz, 2H), 7.65 – 7.55 (m, 4H), 7.37 (d, $J = 8.2$ Hz, 2H), 5.18 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.4, 155.0, 148.8, 145.8, 137.2, 136.8, 134.9, 133.6, 133.5, 130.3, 130.0, 129.8, 129.2, 128.9, 128.3, 128.2, 124.4, 120.4, 49.7, 21.7; IR (neat): 3476, 3355, 2919, 2849, 1731, 1658, 1631, 1469, 1364, 1131, 1075, 666, 544; HRESIMS Calcd for $[\text{C}_{24}\text{H}_{17}\text{ClN}_2\text{NaO}_3\text{S}]^+$ ($\text{M} + \text{Na}^+$) 471.0541, found 471.0552.

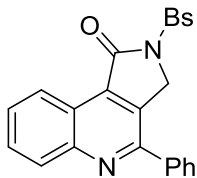
4-phenyl-2-(phenylsulfonyl)-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (2p)



2p

Compound **2p** was prepared in 77% yield (61.6 mg) according to the general procedure (Table 2, entry 16). Yellow solid (mp 247-249 °C). ^1H NMR (400 MHz, CDCl_3) δ 8.93 (d, $J = 8.2$ Hz, 1H), 8.25 (d, $J = 8.5$ Hz, 1H), 8.21 (d, $J = 7.6$ Hz, 2H), 7.87 (d, $J = 6.5$ Hz, 2H), 7.83 (t, $J = 7.3$ Hz, 1H), 7.74 – 7.65 (m, 2H), 7.63 – 7.52 (m, 5H), 5.20 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.8, 153.9, 148.4, 138.0, 137.6, 134.4, 133.6, 133.2, 130.7, 130.0, 129.9, 129.3, 129.2, 129.0, 128.2, 128.1, 123.1, 122.1, 49.6; IR (neat): 3458, 2920, 1721, 1511, 1445, 1357, 1170, 1122, 1087, 985, 771, 562; HRESIMS Calcd for $[\text{C}_{23}\text{H}_{16}\text{N}_2\text{NaO}_3\text{S}]^+$ ($\text{M} + \text{Na}^+$) 423.0774, found 423.0779.

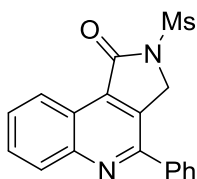
2-((4-bromophenyl)sulfonyl)-4-phenyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (2q)



2q

Compound **2q** was prepared in 68% yield (65.0 mg) according to the general procedure (Table 2, entry 17). Yellow solid (mp 280-282 °C). ¹H NMR (400 MHz, CDCl₃) δ 8.91 (d, *J* = 8.3 Hz, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.8 Hz, 2H), 7.90 – 7.81 (m, 3H), 7.76 – 7.67 (m, 3H), 7.64 – 7.52 (m, 3H), 5.19 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 165.8, 153.9, 148.4, 137.6, 136.9, 133.6, 133.0, 132.6, 130.8, 130.1, 130.0, 129.9, 129.8, 129.2, 129.1, 128.2, 123.0, 122.0, 49.6; IR (neat): 3092, 2922, 1753, 1573, 1372, 1333, 1287, 1167, 1143, 1085, 1008, 772, 562; HRESIMS Calcd for [C₂₃H₁₅BrN₂NaO₃S]⁺ (M + Na⁺) 500.9879, found 500.9891.

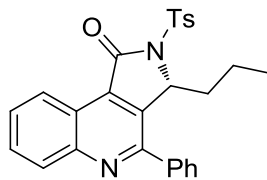
2-(methylsulfonyl)-4-phenyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (2r)



2r

Compound **2r** was prepared in 85% yield (73.1 mg) according to the general procedure (Table 2, entry 18). Pale yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 8.96 (d, *J* = 8.2 Hz, 1H), 8.28 (d, *J* = 8.5 Hz, 1H), 7.90 – 7.82 (m, 3H), 7.74 (t, *J* = 7.3 Hz, 1H), 7.61 – 7.51 (m, 3H), 5.14 (s, 2H), 3.48 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 166.9, 154.0, 148.4, 137.5, 133.7, 133.0, 130.8, 130.1, 130.0, 129.2, 129.1, 128.2, 123.0, 122.0, 49.0, 41.2; IR (neat): 3475, 2918, 2300, 1732, 1620, 1509, 1457, 1345, 1143, 1122, 1075, 973, 772, 522; HRESIMS Calcd for [C₁₈H₁₄N₂NaO₃S]⁺ (M + Na⁺) 361.0617, found 361.0622.

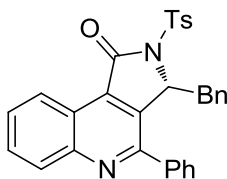
(S)-4-phenyl-3-propyl-2-tosyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (2s)



2s

Compound **2s** was prepared in 83% yield (75.2 mg) according to the general procedure (eq 1). Pale yellow oil. $[\alpha]_D^{20} = +84.6^\circ$ (c = 1.0, CHCl₃). 98% ee (determined by HPLC: Chiralcel IC Column, 10/90 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 33.32 min (major), 26.31 min (minor)). ¹H NMR (400 MHz, CDCl₃) δ 8.97 (d, *J* = 7.9 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.3 Hz, 2H), 7.82 (t, *J* = 7.1 Hz, 1H), 7.78 – 7.74 (m, 2H), 7.70 (t, *J* = 7.3 Hz, 1H), 7.63 – 7.52 (m, 3H), 7.37 (d, *J* = 8.2 Hz, 2H), 5.95 (t, *J* = 3.4 Hz, 1H), 2.44 (s, 3H), 2.31 – 2.20 (m, 1H), 1.51 – 1.40 (m, 1H), 0.57 – 0.47 (m, 1H), 0.40 (t, *J* = 7.1 Hz, 3H), 0.20 – 0.07 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 166.3, 154.7, 148.2, 145.4, 138.4, 137.7, 135.8, 132.9, 130.6, 129.9, 129.8, 129.7, 129.2, 129.0, 128.2, 128.1, 123.4, 121.9, 61.9, 31.2, 21.7, 14.9, 13.2; IR (neat): 3451, 2960, 2872, 1727, 1623, 1593, 1494, 1358, 1286, 1172, 1153, 1089, 1050, 777, 662; HRESIMS Calcd for [C₂₇H₂₄N₂NaO₃S]⁺ (M + Na⁺) 479.1400, found 479.1408.

(S)-3-benzyl-4-phenyl-2-tosyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (2t)

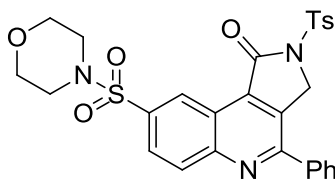


2t

Compound **2t** was prepared in 67% yield (67.2 mg) according to the general procedure (eq 1). Pale yellow oil. $[\alpha]_D^{20} = -164.8^\circ$ (c = 1.0, CHCl₃). 98% ee (determined by HPLC: Chiralcel AS-H Column, 10/90 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 29.47 min (major), 21.27 min (minor)). ¹H NMR (400 MHz, CDCl₃) δ 8.68 (dd, *J* = 8.4, 0.8 Hz, 1H), 8.15 (t, *J* = 8.3 Hz, 3H), 7.98 – 7.93 (m, 2H), 7.76 – 7.54 (m, 5H), 7.40 (d, *J* = 8.1 Hz,

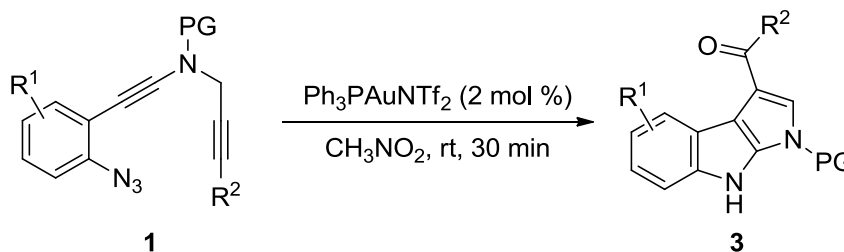
2H), 6.86 – 6.80 (m, 3H), 6.52 (dd, $J = 7.8, 1.6$ Hz, 2H), 6.16 (t, 1H), 3.65 (dd, $J = 14.5, 4.2$ Hz, 1H), 2.89 (dd, $J = 14.5, 3.1$ Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.0, 154.4, 148.1, 145.6, 138.6, 137.0, 135.6, 133.1, 132.7, 130.5, 130.0, 129.9, 129.7, 129.6, 129.5, 128.8, 128.6, 128.5, 127.8, 126.8, 123.2, 121.5, 62.1, 36.2, 21.7; IR (neat): 3444, 3062, 2923, 2125, 1729, 1596, 1493, 1454, 1359, 1299, 1241, 1171, 1089, 704, 662, 577; HRESIMS Calcd for $[\text{C}_{31}\text{H}_{24}\text{N}_2\text{NaO}_3\text{S}]^+$ ($\text{M} + \text{Na}^+$) 527.1400, found 527.1407.

8-(morpholinosulfonyl)-4-phenyl-2-tosyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (2u)



2u

Compound **2u** was prepared in 67% yield (75.6 mg) according to the general procedure (Scheme 2). Yellow solid (mp 275-277 °C). ^1H NMR (500 MHz, CDCl_3) δ 9.36 (d, $J = 1.9$ Hz, 1H), 8.39 (d, $J = 8.8$ Hz, 1H), 8.13 – 8.06 (m, 3H), 7.94 – 7.90 (m, 2H), 7.65 – 7.60 (m, 3H), 7.39 (d, $J = 8.2$ Hz, 2H), 5.25 (s, 2H), 3.76 (t, 4H), 3.10 (t, 4H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.8, 156.8, 149.3, 146.0, 136.9, 135.5, 135.1, 134.7, 134.5, 131.1, 130.8, 130.1, 129.4, 128.4, 128.3, 128.2, 124.1, 121.3, 66.1, 49.8, 46.1, 21.7; IR (neat): 3434, 2923, 2359, 1726, 1658, 1589, 1450, 1332, 1173, 1089, 952, 774, 544; HRESIMS Calcd for $[\text{C}_{28}\text{H}_{25}\text{N}_3\text{NaO}_6\text{S}_2]^+$ ($\text{M} + \text{Na}^+$) 586.1077, found 586.1085.

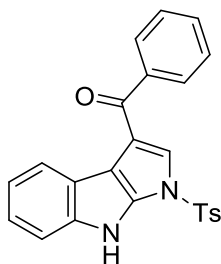


Supplementary Figure 90. Synthesis of pyrrolo[2,3-*b*]indoles **3**.

General procedure for the synthesis of pyrrolo[2,3-*b*]indoles **3**:

Ph₃PAuNTf₂ (0.004 mmol, 3.0 mg) were added in this order to the ynamide **1** (0.20 mmol) in CH₃NO₂ (4.0 mL) at room temperature. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. The reaction typically took 30 min. Upon completion, the mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: hexanes/ ethyl acetate) to afford the desired product **3**.

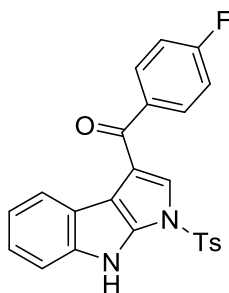
phenyl(1-tosyl-1,8-dihydropyrrolo[2,3-*b*]indol-3-yl)methanone (**3a**)



3a

Compound **3a** was prepared in 88% yield (72.8 mg) according to the general procedure (Table 3, entry 1). Yellow solid (mp 182-184 °C). ¹H NMR (500 MHz, CDCl₃) δ 8.82 (s, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.90 (d, *J* = 7.5 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.29 (s, 1H), 7.26 – 7.24 (m, 3H), 7.20 (t, *J* = 7.5 Hz, 1H), 2.36 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 190.5, 146.3, 139.3, 138.8, 136.3, 134.5, 132.3, 130.4, 129.1, 128.6, 126.9, 123.9, 122.9, 122.8, 121.6, 121.0, 120.9, 111.8, 109.1, 21.7; IR (neat): 3395 (br), 2359, 1731, 1638, 1500, 1483, 1378, 1292, 1176, 1142, 1006, 922, 670; HRESIMS Calcd for [C₂₄H₁₈N₂NaO₃S]⁺ (M + Na⁺) 437.0930, found 437.0937.

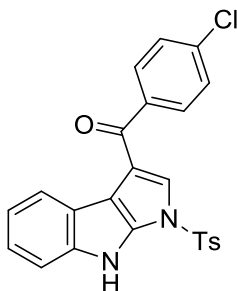
(4-fluorophenyl)(1-tosyl-1,8-dihydropyrrolo[2,3-*b*]indol-3-yl)methanone (**3b**)



3b

Compound **3b** was prepared in 80% yield (69.1 mg) according to the general procedure (Table 3, entry 2). Pale yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 9.05 (s, 1H), 7.96 – 7.92 (m, 3H), 7.78 (d, $J = 8.3$ Hz, 2H), 7.45 (d, $J = 8.1$ Hz, 1H), 7.30 (s, 1H), 7.26 – 7.15 (m, 6H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 189.0, 165.3 (d, $J = 252.5$ Hz), 146.4, 139.3, 136.3, 134.9 (d, $J = 3.8$ Hz), 134.3, 131.6 (d, $J = 10.0$ Hz), 130.4, 126.8, 123.6, 122.9, 122.6, 121.4, 120.9, 120.7, 115.7 (d, $J = 21.3$ Hz), 111.9, 109.0, 21.6; IR (neat): 3364 (br), 2924, 1731, 1639, 1598, 1451, 1378, 1230, 1175, 1110, 1007, 925, 671, 544; HRESIMS Calcd for $[\text{C}_{24}\text{H}_{17}\text{FN}_2\text{NaO}_3\text{S}]^+$ ($\text{M} + \text{H}^+$) 455.0836, found 455.0842.

(4-chlorophenyl)(1-tosyl-1,8-dihydropyrrolo[2,3-*b*]indol-3-yl)methanone (3c)

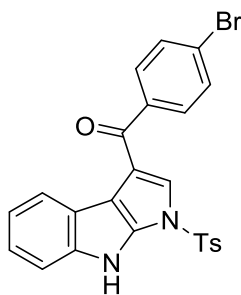


3c

Compound **3c** was prepared in 83% yield (74.4 mg) according to the general procedure (Table 3, entry 3). Pale yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 9.09 (s, 1H), 7.99 (d, $J = 7.8$ Hz, 1H), 7.83 (d, $J = 8.3$ Hz, 2H), 7.77 (d, $J = 8.3$ Hz, 2H), 7.45 (dd, $J = 8.4, 3.0$ Hz, 3H), 7.29 (s, 1H), 7.23 (t, $J = 3.9$ Hz, 1H), 7.18 (t, $J = 8.8$ Hz, 3H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 189.2, 146.4, 139.3, 138.6, 136.9, 136.3, 134.3, 130.4, 130.3, 128.8, 126.8, 123.7, 122.9, 122.5, 121.4, 120.9, 120.7, 111.9, 108.9, 21.6; IR (neat): 3324

(br), 3134, 2925, 1734, 1639, 1588, 1501, 1484, 1451, 1376, 1293, 1243, 1176, 1006, 924, 671; HRESIMS Calcd for $[C_{24}H_{17}ClN_2NaO_3S]^+$ ($M + Na^+$) 471.0541, found 471.0552.

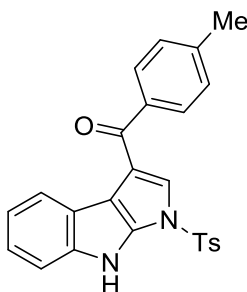
(4-bromophenyl)(1-tosyl-1,8-dihydropyrrolo[2,3-*b*]indol-3-yl)methanone (3d)



3d

Compound **3d** was prepared in 77% yield (75.8 mg) according to the general procedure (Table 3, entry 4). Yellow solid (mp 188-190 °C). 1H NMR (500 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.00 (d, $J = 7.8$ Hz, 1H), 7.79 – 7.75 (m, 4H), 7.62 (d, $J = 8.3$ Hz, 2H), 7.45 (d, $J = 8.1$ Hz, 1H), 7.27 – 7.18 (m, 5H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.3, 146.4, 139.3, 137.4, 136.3, 134.3, 131.8, 130.5, 130.4, 127.2, 126.8, 123.8, 122.9, 122.5, 121.5, 120.9, 120.7, 111.9, 108.9, 21.6; IR (neat): 3387 (br), 2923, 2852, 1723, 1637, 1585, 1500, 1451, 1378, 1293, 1176, 1144, 1006, 923, 670; HRESIMS Calcd for $[C_{24}H_{17}BrN_2NaO_3S]^+$ ($M + Na^+$) 515.0035, found 515.0056.

***p*-tolyl(1-tosyl-1,8-dihydropyrrolo[2,3-*b*]indol-3-yl)methanone (3e)**

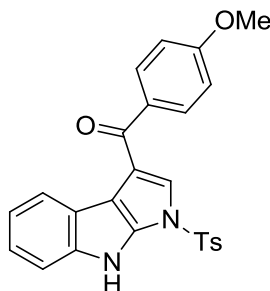


3e

Compound **3e** was prepared in 76% yield (65.1 mg) according to the general procedure (Table 3, entry 5). Pale yellow oil. 1H NMR (500 MHz, $CDCl_3$) δ 9.15 (s, 1H), 8.02 (d, J

= 7.8 Hz, 1H), 7.82 (d, $J = 8.0$ Hz, 2H), 7.76 (d, $J = 8.3$ Hz, 2H), 7.43 (d, $J = 8.1$ Hz, 1H), 7.33 (s, 1H), 7.28 (d, $J = 7.9$ Hz, 2H), 7.22 (t, $J = 7.5$ Hz, 1H), 7.18 – 7.14 (m, 3H), 2.43 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 190.3, 146.2, 143.0, 139.3, 136.3, 136.0, 134.3, 130.3, 129.2, 129.1, 126.8, 123.7, 122.9, 122.7, 121.5, 120.8, 120.7, 111.9, 109.1, 21.6, 21.5; IR (neat): 3305 (br), 3137, 2922, 1734, 1605, 1497, 1378, 1299, 1176, 1110, 1007, 925, 740, 671; HRESIMS Calcd for $[\text{C}_{25}\text{H}_{20}\text{N}_2\text{NaO}_3\text{S}]^+$ ($\text{M} + \text{Na}^+$) 451.1087, found 451.1099.

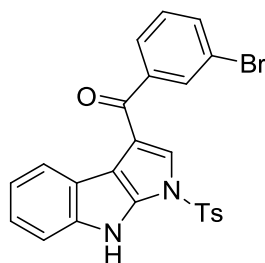
(4-methoxyphenyl)(1-tosyl-1,8-dihydropyrrolo[2,3-*b*]indol-3-yl)methanone (3f)



3f

Compound **3f** was prepared in 63% yield (55.9 mg) according to the general procedure (Table 3, entry 6). Pale yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 8.86 (s, 1H), 7.96 – 7.92 (m, 3H), 7.78 (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 8.1$ Hz, 1H), 7.29 (s, 1H), 7.28 – 7.24 (m, 3H), 7.19 (t, $J = 7.3$ Hz, 1H), 6.99 (d, $J = 8.8$ Hz, 2H), 3.90 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 189.1, 163.1, 146.3, 139.3, 136.3, 134.5, 131.4, 131.3, 130.4, 126.8, 123.1, 123.0, 122.8, 121.5, 120.9, 120.8, 113.8, 111.8, 109.3, 55.5, 21.6; IR (neat): 3394 (br), 2923, 2851, 1598, 1498, 1452, 1378, 1259, 1176, 1164, 1110, 1085, 925, 671; HRESIMS Calcd for $[\text{C}_{25}\text{H}_{20}\text{N}_2\text{NaO}_4\text{S}]^+$ ($\text{M} + \text{Na}^+$) 467.1036, found 467.1047.

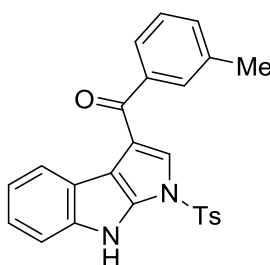
(3-bromophenyl)(1-tosyl-1,8-dihydropyrrolo[2,3-*b*]indol-3-yl)methanone (3g)



3g

Compound **3g** was prepared in 82% yield (80.7 mg) according to the general procedure (Table 3, entry 7). Pale yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 8.76 (s, 1H), 8.01 – 7.97 (m, 2H), 7.81 – 7.78 (m, 3H), 7.73 (d, $J = 8.0$ Hz, 1H), 7.46 (d, $J = 8.1$ Hz, 1H), 7.39 (t, $J = 7.8$ Hz, 1H), 7.31 – 7.26 (m, 4H), 7.22 (t, $J = 7.5$ Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 188.7, 146.5, 140.6, 139.3, 136.4, 135.1, 134.5, 131.9, 130.5, 130.1, 127.6, 126.9, 124.0, 123.1, 122.8, 122.6, 121.6, 121.1, 120.8, 111.9, 108.9, 21.7; IR (neat): 3409 (br), 2922, 1731, 1640, 1500, 1451, 1379, 1294, 1175, 1143, 1110, 1008, 934, 670; HRESIMS Calcd for $[\text{C}_{24}\text{H}_{17}\text{BrN}_2\text{NaO}_3\text{S}]^+$ ($\text{M} + \text{Na}^+$) 515.0035, found 515.0049.

***m*-tolyl(1-tosyl-1,8-dihydropyrrolo[2,3-*b*]indol-3-yl)methanone (3h)**

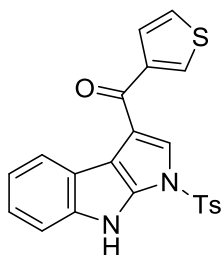


3h

Compound **3h** was prepared in 95% yield (81.3 mg) according to the general procedure (Table 3, entry 8). Pale yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 8.91 (s, 1H), 8.01 (d, $J = 7.8$ Hz, 1H), 7.78 (d, $J = 8.3$ Hz, 2H), 7.75 – 7.69 (m, 2H), 7.45 – 7.36 (m, 3H), 7.30 (s, 1H), 7.27 – 7.17 (m, 4H), 2.42 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 190.6, 146.3, 139.3, 138.8, 138.4, 136.3, 134.5, 133.0, 130.3, 129.5, 128.4, 126.8, 126.3, 123.9, 123.0, 122.8, 121.6, 120.9, 120.8, 111.8, 109.1, 21.6, 21.4; IR (neat): 3403 (br),

2924, 2854, 1633, 1598, 1499, 1451, 1378, 1298, 1234, 1177, 1159, 1109, 1085, 942, 734, 671; HRESIMS Calcd for $[C_{25}H_{20}N_2NaO_3S]^+$ ($M + Na^+$) 451.1087, found 451.1095.

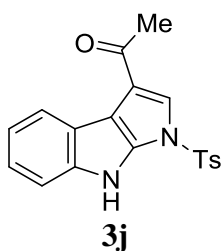
thiophen-3-yl(1-tosyl-1,8-dihydropyrrolo[2,3-*b*]indol-3-yl)methanone (3i)



3i

Compound **3i** was prepared in 73% yield (61.3 mg) according to the general procedure (Table 3, entry 9). Pale yellow oil. 1H NMR (500 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.05 (dd, $J = 3.6, 2.6$ Hz, 2H), 7.79 (d, $J = 8.3$ Hz, 2H), 7.63 (d, $J = 5.0$ Hz, 1H), 7.45 (d, $J = 8.0$ Hz, 1H), 7.41 – 7.39 (m, 2H), 7.27 – 7.18 (m, 4H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.6, 146.4, 142.0, 139.3, 136.3, 134.5, 132.0, 130.4, 127.9, 126.8, 126.6, 123.7, 122.9, 122.7, 121.6, 121.0, 120.9, 111.8, 109.1, 21.7; IR (neat): 3394 (br), 2922, 2851, 1620, 1509, 1451, 1378, 1287, 1176, 1109, 1009, 894, 670; HRESIMS Calcd for $[C_{22}H_{16}N_2NaO_3S_2]^+$ ($M + Na^+$) 443.0495, found 443.0498.

1-(1-tosyl-1,8-dihydropyrrolo[2,3-*b*]indol-3-yl)ethan-1-one (3j)

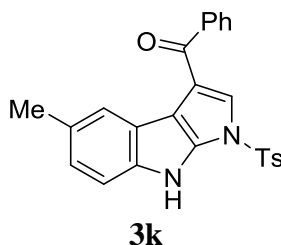


3j

Compound **3j** was prepared in 86% yield (60.6 mg) according to the general procedure (Table 3, entry 10). Pale yellow oil. 1H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.23 (d, $J = 6.9$ Hz, 1H), 7.82 (d, $J = 8.4$ Hz, 2H), 7.46 – 7.42 (m, 2H), 7.30 – 7.21 (m, 4H), 2.53 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 146.3, 139.2, 136.3, 134.6, 130.4, 126.8, 124.6, 122.9, 122.4, 121.8, 121.0, 111.7, 108.2, 27.0, 21.7; IR (neat): 3314

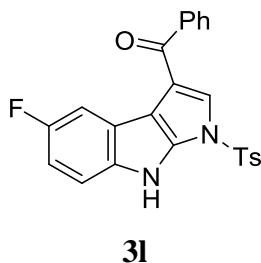
(br), 2924, 1731, 1658, 1503, 1451, 1376, 1288, 1176, 1090, 952, 672, 599; HRESIMS Calcd for $[C_{19}H_{16}N_2NaO_3S]^+$ ($M + Na^+$) 375.0774, found 375.0778.

(5-methyl-1-tosyl-1,8-dihydropyrrolo[2,3-*b*]indol-3-yl)(phenyl)methanone (3k)



Compound **3k** was prepared in 75% yield (64.2 mg) according to the general procedure (Table 3, entry 11). Pale yellow oil. 1H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.89 (d, $J = 7.3$ Hz, 2H), 7.84 (s, 1H), 7.76 (d, $J = 8.3$ Hz, 2H), 7.60 (t, $J = 7.4$ Hz, 1H), 7.50 (t, $J = 7.6$ Hz, 2H), 7.32 (d, $J = 8.3$ Hz, 1H), 7.27 (s, 1H), 7.26 – 7.21 (m, 2H), 7.08 (d, $J = 7.8$ Hz, 1H), 2.43 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 146.2, 138.8, 137.6, 136.6, 134.5, 132.2, 130.3, 129.0, 128.5, 126.8, 124.2, 123.8, 122.9, 121.5, 121.1, 111.5, 108.9, 21.6, 21.4; IR (neat): 3345 (br), 2922, 1732, 1639, 1596, 1538, 1498, 1455, 1375, 1292, 1176, 1157, 1111, 1086, 941, 800, 670; HRESIMS Calcd for $[C_{25}H_{20}N_2NaO_3S]^+$ ($M + Na^+$) 451.1087, found 451.1094.

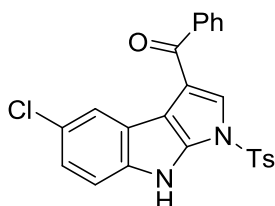
(5-fluoro-1-tosyl-1,8-dihydropyrrolo[2,3-*b*]indol-3-yl)(phenyl)methanone (3l)



Compound **3l** was prepared in 73% yield (63.1 mg) according to the general procedure (Table 3, entry 12). Pale yellow oil. 1H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 7.88 (d, $J = 7.6$ Hz, 2H), 7.78 (d, $J = 7.9$ Hz, 2H), 7.71 (d, $J = 9.3$ Hz, 1H), 7.59 (t, $J = 7.2$ Hz, 1H), 7.49 (t, $J = 7.5$ Hz, 2H), 7.35 – 7.32 (m, 2H), 7.24 – 7.21 (m, 2H), 6.95 (t, $J = 9.0$ Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.4, 158.0 (d, $J = 233.8$ Hz), 146.5,

138.5, 137.4, 135.6, 134.2, 132.4, 130.4, 128.9, 128.6, 126.8, 124.1, 122.6, 121.3 (d, $J = 11.3$ Hz), 112.4 (d, $J = 10.0$ Hz), 110.6 (d, $J = 25.0$ Hz), 109.1 (d, $J = 3.8$ Hz), 107.2 (d, $J = 25.0$ Hz), 21.6; IR (neat): 3332 (br), 2925, 1732, 1629, 1596, 1503, 1483, 1455, 1377, 1286, 1176, 1153, 1113, 1085, 945, 670, 543; HRESIMS Calcd for $[\text{C}_{24}\text{H}_{17}\text{FN}_2\text{NaO}_3\text{S}]^+$ ($\text{M} + \text{Na}^+$) 455.0836, found 455.0841.

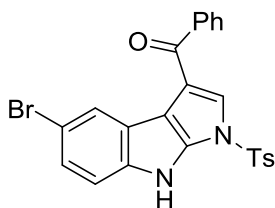
(5-chloro-1-tosyl-1,8-dihydropyrrolo[2,3-*b*]indol-3-yl)(phenyl)methanone (3m)



3m

Compound **3m** was prepared in 74% yield (66.3 mg) according to the general procedure (Table 3, entry 13). Pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.84 (s, 1H), 8.06 (s, 1H), 7.88 (d, $J = 7.5$ Hz, 2H), 7.79 (d, $J = 7.8$ Hz, 2H), 7.62 (t, $J = 7.3$ Hz, 1H), 7.52 (t, $J = 7.3$ Hz, 2H), 7.35 (d, $J = 8.7$ Hz, 1H), 7.30 – 7.21 (m, 4H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.2, 146.6, 138.6, 137.6, 137.0, 134.4, 132.4, 130.5, 129.0, 128.6, 126.9, 126.6, 124.1, 123.1, 122.7, 122.0, 121.4, 112.7, 108.7, 21.7; IR (neat): 3314 (br), 2924, 1712, 1638, 1596, 1500, 1442, 1377, 1284, 1255, 1176, 1113, 1086, 935, 666, 602; HRESIMS Calcd for $[\text{C}_{24}\text{H}_{17}\text{ClN}_2\text{NaO}_3\text{S}]^+$ ($\text{M} + \text{Na}^+$) 471.0541, found 471.0555.

(5-bromo-1-tosyl-1,8-dihydropyrrolo[2,3-*b*]indol-3-yl)(phenyl)methanone (3n)

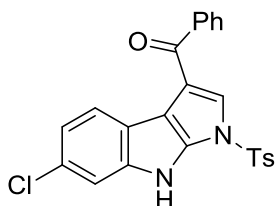


3n

Compound **3n** was prepared in 71% yield (69.9 mg) according to the general procedure (Table 3, entry 14). Pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.86 (s, 1H), 8.21 (d, J

= 1.3 Hz, 1H), 7.88 (d, $J = 7.2$ Hz, 2H), 7.78 (d, $J = 8.3$ Hz, 2H), 7.62 (t, $J = 7.4$ Hz, 1H), 7.52 (t, $J = 7.6$ Hz, 2H), 7.37 – 7.26 (m, 5H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 190.2, 146.6, 138.5, 137.8, 136.8, 134.3, 132.4, 130.5, 129.0, 128.7, 126.9, 125.7, 124.4, 124.1, 122.7, 122.5, 114.0, 113.2, 108.6, 21.7; IR (neat): 3376 (br), 2924, 2292, 1731, 1638, 1500, 1438, 1376, 1284, 1256, 1176, 1143, 1085, 927, 601; HRESIMS Calcd for $[\text{C}_{24}\text{H}_{17}\text{BrN}_2\text{NaO}_3\text{S}]^+$ ($\text{M} + \text{Na}^+$) 515.0035, found 515.0050.

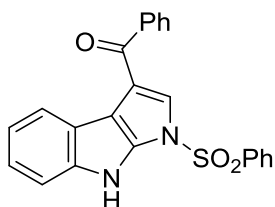
(6-chloro-1-tosyl-1,8-dihydropyrrolo[2,3-*b*]indol-3-yl)(phenyl)methanone (3o)



3o

Compound **3o** was prepared in 58% yield (52.0 mg) according to the general procedure (Table 3, entry 15). Pale yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 8.83 (s, 1H), 7.96 (d, $J = 8.5$ Hz, 1H), 7.88 (d, $J = 7.3$ Hz, 2H), 7.79 (d, $J = 8.3$ Hz, 2H), 7.62 (t, $J = 7.4$ Hz, 1H), 7.52 (t, $J = 7.6$ Hz, 2H), 7.44 (s, 1H), 7.29 – 7.19 (m, 4H), 7.17 (dd, $J = 8.4, 1.3$ Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 190.3, 146.6, 139.5, 138.6, 136.5, 134.4, 132.4, 130.5, 129.0, 128.6, 128.5, 126.9, 124.1, 122.7, 122.5, 121.6, 119.5, 111.9, 108.9, 21.7; IR (neat): 3489 (br), 2924, 1633, 1539, 1498, 1378, 1293, 1175, 1112, 1007, 923, 671; HRESIMS Calcd for $[\text{C}_{24}\text{H}_{17}\text{ClN}_2\text{NaO}_3\text{S}]^+$ ($\text{M} + \text{Na}^+$) 471.0541, found 471.0550.

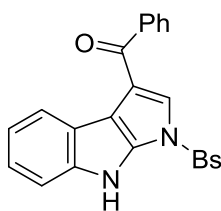
phenyl(1-(phenylsulfonyl)-1,8-dihydropyrrolo[2,3-*b*]indol-3-yl)methanone (3p)



3p

Compound **3p** was prepared in 84% yield (64.0 mg) according to the general procedure (Table 3, entry 16). Pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.77 (s, 1H), 8.01 (d, $J = 7.8$ Hz, 1H), 7.92 – 7.88 (m, 4H), 7.62 (t, $J = 7.4$ Hz, 2H), 7.53 – 7.43 (m, 5H), 7.33 – 7.17 (m, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 190.4, 139.3, 138.7, 137.6, 136.3, 134.9, 132.3, 129.8, 129.1, 128.6, 126.8, 123.8, 123.1, 123.0, 121.7, 121.0, 120.9, 111.9, 109.2; IR (neat): 3433 (br), 1727, 1632, 1500, 1483, 1448, 1380, 1291, 1178, 1142, 1110, 1007, 923, 725, 614; HRESIMS Calcd for $[\text{C}_{23}\text{H}_{16}\text{N}_2\text{NaO}_3\text{S}]^+$ ($\text{M} + \text{Na}^+$) 423.0774, found 423.0775.

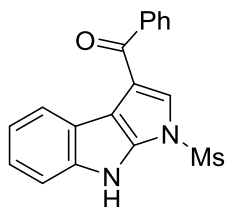
(1-((4-bromophenyl)sulfonyl)-1,8-dihydropyrrolo[2,3-*b*]indol-3-yl)(phenyl)methanone (3q)



3q

Compound **3q** was prepared in 86% yield (82.2 mg) according to the general procedure (Table 3, entry 17). Yellow solid (mp 194-196 °C). ^1H NMR (500 MHz, CDCl_3) δ 8.78 (s, 1H), 8.00 (d, $J = 7.9$ Hz, 1H), 7.90 (d, $J = 7.4$ Hz, 2H), 7.74 (d, $J = 8.6$ Hz, 2H), 7.63 – 7.58 (m, 3H), 7.52 (t, $J = 7.6$ Hz, 2H), 7.46 (d, $J = 8.1$ Hz, 1H), 7.30 – 7.27 (m, 2H), 7.21 (t, $J = 7.5$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 190.3, 139.3, 138.6, 136.4, 136.2, 133.2, 132.4, 130.4, 129.1, 128.6, 128.2, 123.6, 123.5, 123.2, 121.7, 121.2, 120.9, 111.9, 109.5; IR (neat): 3388 (br), 2923, 1731, 1639, 1573, 1501, 1484, 1391, 1292, 1186, 1143, 1007, 924, 744, 621; HRESIMS Calcd for $[\text{C}_{23}\text{H}_{15}\text{BrN}_2\text{NaO}_3\text{S}]^+$ ($\text{M} + \text{Na}^+$) 500.9879, found 500.9898.

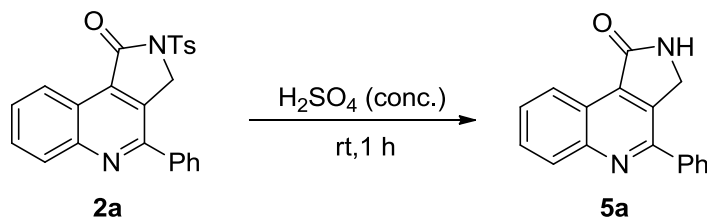
(1-(methylsulfonyl)-1,8-dihydropyrrolo[2,3-*b*]indol-3-yl)(phenyl)methanone (3r)



3r

Compound **3r** was prepared in 56% yield (37.9 mg) according to the general procedure (Table 3, entry 18). Pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.61 (s, 1H), 8.07 (d, $J = 7.7$ Hz, 1H), 7.98 – 7.92 (m, 2H), 7.66 – 7.60 (m, 1H), 7.53 (t, $J = 7.5$ Hz, 2H), 7.44 (d, $J = 7.9$ Hz, 1H), 7.33 – 7.28 (m, 2H), 7.26 – 7.21 (m, 1H), 3.26 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 190.4, 139.3, 138.7, 136.1, 132.4, 129.0, 128.6, 123.6, 123.2, 121.8, 121.2, 121.0, 111.9, 109.2, 42.4; IR (neat): 3395 (br), 2924, 1769, 1633, 1500, 1485, 1451, 1371, 1292, 1246, 1179, 1141, 1007, 964, 706; HRESIMS Calcd for $[\text{C}_{18}\text{H}_{14}\text{N}_2\text{NaO}_3\text{S}]^+$ ($\text{M} + \text{Na}^+$) 361.0617, found 361.0616.

4-phenyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (**5a**)

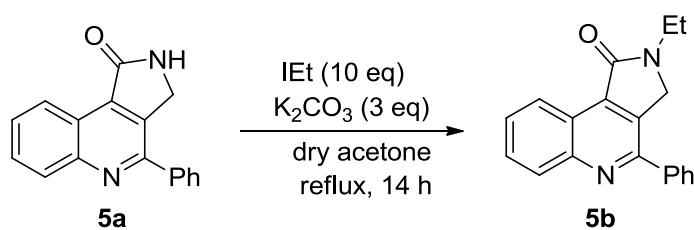


Supplementary Figure 91. Synthesis of compound **5a**.

H_2SO_4 (98%, 8.0 mL) was added to a flame dried *Schlenk*-flask containing **2a** (0.2 mmol, 82.8 mg) at room temperature. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. The reaction took 1 h. Upon completion, the solution was diluted with 20 mL EtOAc and neutralized with saturated Na_2CO_3 at 0 °C. The aqueous phase was extracted with EtOAc three times and the combined organic phase was dried with Mg_2SO_4 . The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired product **5a** (38.5 mg, 74% yield) White solid (mp 231-233 °C). ^1H NMR (400 MHz, CDCl_3) δ 9.14 (dd, $J = 8.3, 0.9$ Hz,

1H), 8.29 (d, $J = 8.2$ Hz, 1H), 7.91 (dd, $J = 8.1, 1.5$ Hz, 2H), 7.85 – 7.81 (m, 1H), 7.73 – 7.69 (m, 1H), 7.59 – 7.52 (m, 3H), 7.06 (s, 1H), 4.76 (d, $J = 0.9$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.9, 154.1, 148.2, 138.4, 135.7, 135.1, 130.2, 129.7, 129.6, 129.0, 128.3, 128.1, 123.5, 122.8, 45.5; IR (neat): 3442 (br), 2915, 2846, 2088, 1700, 1633, 1492, 1363, 1178, 1074, 906, 769; HRESIMS Calcd for $[\text{C}_{17}\text{H}_{12}\text{N}_2\text{NaO}]^+$ ($\text{M} + \text{Na}^+$) 283.0842, found 283.0846.

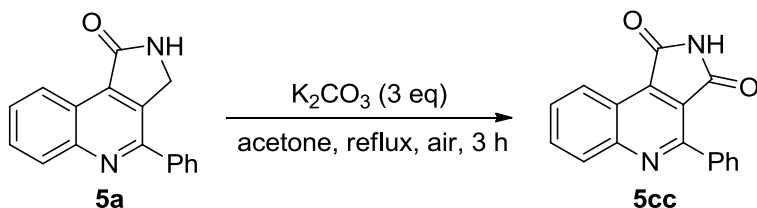
2-ethyl-4-phenyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (5b)



Supplementary Figure 92. Synthesis of compound **5b**.

Potassium carbonate (0.6 mmol, 82.8 mg) and ethyl iodide (2 mmol, 308 mg) were added in this order to the **5a** (0.20 mmol, 52 mg) in dry acetone (4.0 mL) at room temperature. The reaction mixture was refluxed for 14 h under the nitrogen. The reaction mixture was cooled and filtered. The filtrate was evaporated and the residue was purified by chromatography on silica gel (eluent: hexanes/ ethyl acetate) to afford the desired product **5b** (37.3 mg, 65% yield, white solid); This compound is known and the spectroscopic data match those reported³¹. ^1H NMR (400 MHz, CDCl_3) δ 9.17 (dd, $J = 8.3, 0.9$ Hz, 1H), 8.26 (d, $J = 8.1$ Hz, 1H), 7.94 – 7.88 (m, 2H), 7.84 – 7.80 (m, 1H), 7.72 – 7.68 (m, 1H), 7.60 – 7.53 (m, 3H), 4.69 (s, 2H), 3.79 (q, $J = 7.3$ Hz, 2H), 1.35 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 167.7, 153.6, 148.4, 138.6, 136.3, 133.2, 130.0, 129.6, 129.5, 129.0, 128.3, 127.9, 123.6, 122.8, 49.5, 37.2, 13.8; HRESIMS Calcd for $[\text{C}_{19}\text{H}_{16}\text{N}_2\text{NaO}]^+$ ($\text{M} + \text{Na}^+$) 311.1155, found 311.1173.

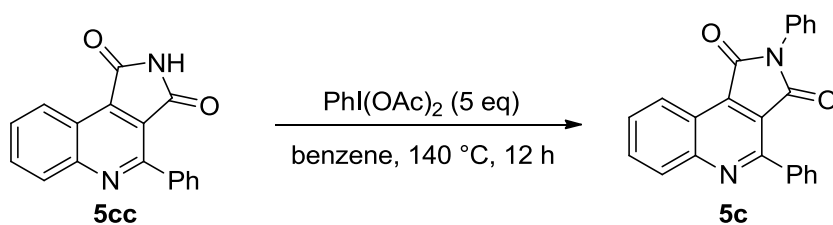
4-phenyl-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (5cc)



Supplementary Figure 93. Synthesis of compound **5cc**.

Potassium carbonate (0.6 mmol, 82.8 mg) were added in this order to the **5a** (0.2 mmol, 52.0 mg) in acetone (4.0 mL) at room temperature. The reaction mixture was refluxed in air for 3 h. The reaction mixture was cooled and filtered. The filtrate was evaporated and the residue was purified by chromatography on silica gel (eluent: hexanes/ ethyl acetate) to afford the desired product **5cc** (40.0 mg, 71% yield, yellow solid)^{32,33}. This compound is known and the spectroscopic data match those reported³⁴. ¹H NMR (400 MHz, DMSO) δ 11.60 (s, 1H), 8.80 (dd, $J = 8.3, 0.7$ Hz, 1H), 8.20 (d, $J = 8.5$ Hz, 1H), 8.02 – 7.98 (m, 1H), 7.95 – 7.93 (m, 2H), 7.87 – 7.83 (m, 1H), 7.57 – 7.51 (m, 3H); ¹³C NMR (125 MHz, DMSO) δ 169.2, 168.4, 154.4, 150.5, 138.0, 136.7, 132.8, 130.1, 129.6, 129.5, 127.7, 124.3, 122.5, 120.4; HRESIMS Calcd for $[\text{C}_{17}\text{H}_{10}\text{N}_2\text{NaO}_2]^+$ ($\text{M} + \text{Na}^+$) 297.0634, found 297.0639.

2,4-diphenyl-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (**5c**)

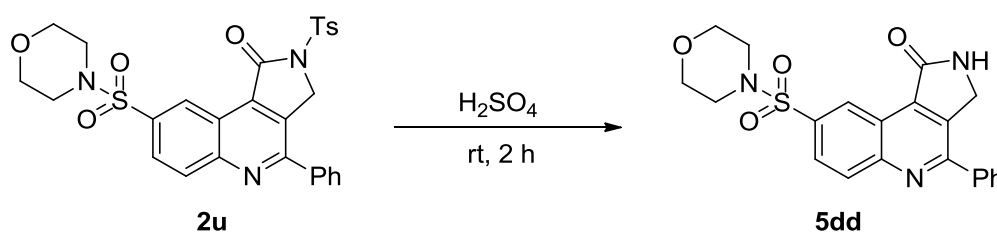


Supplementary Figure 94. Synthesis of compound **5c**.

$\text{PhI}(\text{OAc})_2$ (1.0 mmol, 322.0 mg) were added in this order to the **5cc** (0.2 mmol, 54.8 mg) in benzene (4.0 mL) at room temperature. The reaction mixture was stirred at 140 °C for 12 h. The mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: hexanes/ ethyl acetate) to afford the desired product **5c** (48.7 mg,

70% yield, yellow solid)³⁵. This compound is known and the spectroscopic data match those reported³⁶. ¹H NMR (500 MHz, CDCl₃) δ 9.00 (dd, *J* = 8.4, 0.6 Hz, 1H), 8.30 (d, *J* = 8.6 Hz, 1H), 8.03 – 7.93 (m, 3H), 7.81 – 7.78 (m, 1H), 7.57 – 7.40 (m, 8H); ¹³C NMR (125 MHz, CDCl₃) δ 167.0, 166.5, 155.4, 151.9, 137.1, 136.6, 133.2, 131.3, 130.2, 130.1, 130.0, 129.8, 129.2, 128.4, 128.1, 126.8, 125.1, 120.9, 120.7; HRESIMS Calcd for [C₂₃H₁₄N₂NaO₂]⁺ (*M* + Na⁺) 373.0947, found 373.0948.

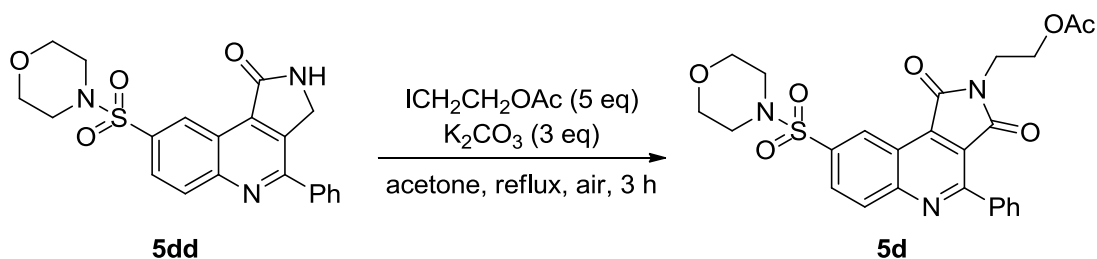
8-(morpholinosulfonyl)-4-phenyl-2,3-dihydro-1H-pyrrolo[3,4-*c*]quinolin-1-one (5dd)



Supplementary Figure 95. Synthesis of compound **5dd**.

H₂SO₄ (98%, 8.0 mL) was added to a flame dried *Schlenk*-flask containing **2u** (0.2 mmol, 112.6 mg) at room temperature. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. The reaction took 2 h. Upon completion, the solution was diluted with 20 mL EtOAc and neutralized with saturated Na₂CO₃ at 0 °C. The aqueous phase was extracted with EtOAc three times and the combined organic phase was dried with Mg₂SO₄. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired product **5dd** (45.6 mg, 56% yield). Yellow solid (mp 246-248 °C). ¹H NMR (500 MHz, DMSO) δ 9.47 (d, *J* = 2.0 Hz, 1H), 9.45 (s, 1H), 8.44 (d, *J* = 8.9 Hz, 1H), 8.14 – 8.07 (m, 3H), 7.64 – 7.59 (m, 3H), 4.88 (s, 2H), 3.65 (t, 4H), 2.99 (t, 4H); ¹³C NMR (125 MHz, DMSO) δ 169.0, 156.4, 148.3, 138.4, 137.4, 136.5, 133.4, 130.8, 130.3, 128.9, 128.7, 127.0, 123.7, 121.6, 65.3, 45.9, 45.5; IR (neat): 3445 (br), 2925, 2127, 1732, 1644, 1594, 1498, 1366, 1254, 1170, 1088, 985, 774, 663; HRESIMS Calcd for [C₂₁H₁₉N₃NaO₄S]⁺ (*M* + Na⁺) 432.0988, found 432.0994.

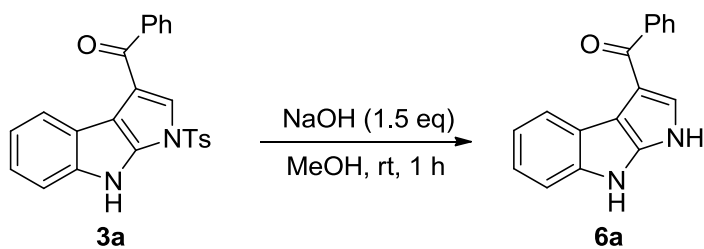
2-(8-(morpholinosulfonyl)-1,3-dioxo-4-phenyl-1*H*-pyrrolo[3,4-*c*]quinolin-2(3*H*)-yl)ethyl acetate (5d)



Supplementary Figure 96. Synthesis of compound **5d**.

Potassium carbonate (0.3 mmol, 41.4 mg) and $\text{ICH}_2\text{CH}_2\text{OAc}$ (0.5 mmol, 107 mg) were added in this order to the **5dd** (0.1 mmol, 40.9 mg) in acetone (2.0 mL) at room temperature. The reaction mixture was refluxed in air for 3 h. The reaction mixture was cooled and filtered. The filtrate was evaporated and the residue was purified by chromatography on silica gel (eluent: hexanes/ ethyl acetate) to afford the desired product **5d** (31.9 mg, 67% yield). This compound is known and the spectroscopic data match those reported³⁷. ^1H NMR (400 MHz, CDCl_3) δ 9.35 (d, $J = 1.6$ Hz, 1H), 8.41 (d, $J = 9.0$ Hz, 1H), 8.19 (dd, $J = 9.0, 2.1$ Hz, 1H), 8.03 – 7.98 (m, 2H), 7.61 – 7.56 (m, 3H), 4.38 (t, $J = 5.2$ Hz, 2H), 4.04 (t, $J = 5.2$ Hz, 2H), 3.79 (t, $J = 4.8$ Hz, 4H), 3.16 (t, $J = 4.8$ Hz, 4H), 2.03 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 170.9, 167.0, 166.6, 157.9, 152.3, 138.6, 136.6, 135.8, 131.5, 130.8, 130.3, 130.0, 128.3, 125.9, 122.5, 119.8, 66.1, 61.3, 46.1, 37.7, 20.8; HRESIMS Calcd for $[\text{C}_{25}\text{H}_{23}\text{N}_3\text{NaO}_7\text{S}]^+$ ($\text{M} + \text{Na}^+$) 532.1149, found 532.1160.

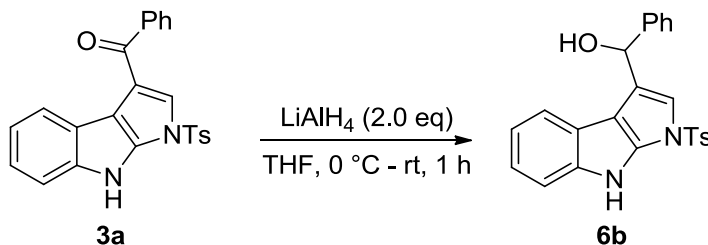
(1,8-dihydropyrrolo[2,3-*b*]indol-3-yl)(phenyl)methanone (6a)



Supplementary Figure 97. Synthesis of compound **6a**.

NaOH (0.3 mmol, 12.0 mg) was added in this order to the **3a** (0.2 mmol, 82.8 mg) in MeOH (4.0 mL) at room temperature. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. The reaction took 1 h. Upon completion, the mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: hexanes/ ethyl acetate) to afford the desired product **6a** (38.5 mg, 74% yield). Yellow solid (mp 135-137 °C). ¹H NMR (400 MHz, acetone) δ 10.91 (s, 1H), 10.17 (s, 1H), 8.18 (dd, *J* = 6.5, 2.4 Hz, 1H), 7.90 (dd, *J* = 8.1, 1.3 Hz, 2H), 7.60 – 7.50 (m, 3H), 7.40 (dd, *J* = 6.6, 2.1 Hz, 1H), 7.27 (d, *J* = 2.5 Hz, 1H), 7.13 – 7.07 (m, 2H); ¹³C NMR (150 MHz, acetone) δ 190.6, 141.9, 141.1, 140.2, 131.6, 129.4, 129.0, 126.7, 122.9, 121.7, 121.6, 119.7, 118.7, 112.2, 108.2; IR (neat): 3388 (br), 2923, 2852, 1606, 1573, 1483, 1456, 1357, 1294, 1175, 1096, 888, 732; HRESIMS Calcd for [C₁₇H₁₂N₂NaO]⁺ (M + Na⁺) 283.0842, found 283.0844.

phenyl(1-tosyl-1,8-dihydropyrrolo[2,3-*b*]indol-3-yl)methanol (6b)

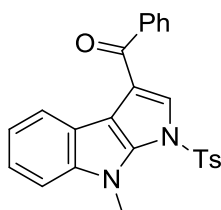


Supplementary Figure 98. Synthesis of compound **6b**.

LiAlH₄ (0.4 mmol, 15.2 mg) was added in this order to the **3a** (0.2 mmol, 82.8 mg) in dry THF (4.0 mL) at 0 °C. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. The reaction took 1 h. Upon completion, the mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: hexanes/ ethyl acetate) to afford the desired product **6b** (58.2 mg, 70% yield). Yellow solid (mp 97-99 °C). ¹H NMR (500 MHz, CDCl₃) δ 8.72 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 6.9 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.33 – 7.26 (m, 4H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.15 (t, *J* = 8.3 Hz, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 1.0

Hz, 1H), 5.94 (d, $J = 3.7$ Hz, 1H), 2.36 (s, 3H), 2.30 (d, $J = 4.2$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 145.4, 142.3, 138.7, 137.1, 135.0, 130.1, 128.6, 128.0, 127.4, 126.8, 126.7, 121.9, 120.8, 120.5, 120.0, 115.2, 111.8, 108.7, 71.0, 21.6; IR (neat): 3396 (br), 2923, 2853, 1725, 1596, 1535, 1452, 1370, 1235, 1118, 1085, 908, 671; HRESIMS Calcd for $[\text{C}_{24}\text{H}_{20}\text{N}_2\text{NaO}_3\text{S}]^+$ ($\text{M} + \text{Na}^+$) 439.1087, found 439.1103.

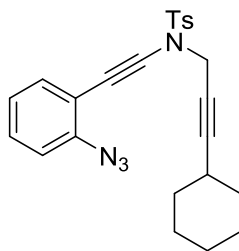
(8-methyl-1-tosyl-1,8-dihydropyrrolo[2,3-*b*]indol-3-yl)(phenyl)methanone (3aa)



3aa

Yellow solid (mp 97-99 °C). ^1H NMR (500 MHz, CDCl_3) δ 8.13 (d, $J = 7.8$ Hz, 1H), 7.93 (d, $J = 7.0$ Hz, 2H), 7.68 (d, $J = 8.4$ Hz, 2H), 7.65 – 7.61 (m, 1H), 7.56 – 7.52 (m, 3H), 7.35 – 7.31 (m, 2H), 7.27 – 7.19 (m, 3H), 4.05 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 190.5, 146.0, 141.4, 138.8, 137.0, 135.1, 132.3, 130.4, 129.1, 128.6, 128.3, 126.8, 122.8, 121.9, 121.8, 120.5, 119.6, 111.0, 109.7, 32.2, 21.6; IR (neat): 2922, 2851, 1640, 1513, 1459, 1375, 1319, 1174, 1087, 1008, 897, 720, 665; HRESIMS Calcd for $[\text{C}_{25}\text{H}_{20}\text{N}_2\text{NaO}_3\text{S}]^+$ ($\text{M} + \text{Na}^+$) 451.1087, found 451.1088.

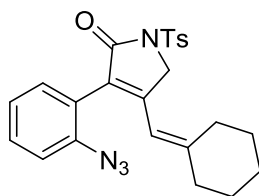
***N*-((2-azidophenyl)ethynyl)-*N*-(3-cyclohexylprop-2-yn-1-yl)-4-methylbenzenesulfonamide (1v)**



1v

Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 8.3$ Hz, 2H), 7.36 – 7.33 (m, 3H), 7.31 – 7.27 (m, 1H), 7.10 – 7.04 (m, 2H), 4.34 (d, $J = 2.1$ Hz, 2H), 2.44 (s, 3H), 2.20 (s, 1H), 1.57 – 1.55 (m, 4H), 1.44 – 1.38 (m, 1H), 1.26 – 1.18 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.7, 140.8, 134.5, 133.4, 129.4, 129.0, 128.3, 124.5, 118.6, 115.0, 91.4, 87.5, 71.8, 66.9, 42.4, 32.0, 28.7, 25.7, 24.4, 21.5; IR (neat): 2928, 2356, 2234, 2127, 1731, 1650, 1633, 1596, 1493, 1446, 1387, 1304, 1170, 1090, 754, 665; HRESIMS Calcd for $[\text{C}_{24}\text{H}_{24}\text{N}_4\text{NaO}_2\text{S}]^+$ ($\text{M} + \text{Na}^+$) 455.1512, found 455.1518.

3-(2-azidophenyl)-4-(cyclohexylidenemethyl)-1-tosyl-1,5-dihydro-2H-pyrrol-2-one (2va)



2va

Compound **2va** was prepared in 66% yield (59.1 mg) according to the general procedure. Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 8.4$ Hz, 2H), 7.40 – 7.35 (m, 1H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.17 (d, $J = 7.9$ Hz, 1H), 7.14 – 7.12 (m, 2H), 5.79 (s, 1H), 4.75 (s, 2H), 2.42 (s, 3H), 2.28 – 2.23 (m, 2H), 2.20 – 2.10 (m, 2H), 1.64 – 1.49 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 167.4, 154.3, 151.4, 144.9, 138.9, 135.5, 131.9, 130.0, 129.7, 129.0, 128.2, 124.7, 122.3, 118.8, 114.3, 52.2, 38.9, 31.7, 28.6, 27.8, 26.0, 21.6; IR (neat): 2928, 2854, 2125, 1714, 1633, 1465, 1446, 1360, 1159, 1092, 665, 583; HRESIMS Calcd for $[\text{C}_{24}\text{H}_{24}\text{N}_4\text{NaO}_3\text{S}]^+$ ($\text{M} + \text{Na}^+$) 471.1461, found 471.1466.

Supplementary References

1. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J.

Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2013**.

2. Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215.
3. R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.* **1971**, *54*, 724.
4. W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257.
5. P. C. Hariharan, J. A. Pople, *Theo. Chim. Acta.* **1973**, *28*, 213.
6. P. C. Hariharan, J. A. Pople, *Mol. Phys.* **1974**, *27*, 209.
7. M. S. Gordon, *Chem. Phys. Lett.* **1980**, *76*, 163.
8. D. Andrae, U. Häussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta.* **1990**, *77*, 123.
9. W.-B. Shen, X.-Y. Xiao, Q. Sun, B. Zhou, X.-Q. Zhu, J.-Z. Yan, X. Lu, L.-W. Ye, *Angew. Chem. Int. Ed.* **2017**, *56*, 605.
10. C. Shu, Y.-H. Wang, B. Zhou, X.-L. Li, Y.-F. Ping, X. Lu, L.-W. Ye, *J. Am. Chem. Soc.* **2015**, *137*, 9567.
11. A.-H. Zhou, Q. He, C. Shu, Y.-F. Yu, S. Liu, T. Zhao, W. Zhang, X. Lu, L.-W. Ye, *Chem. Sci.* **2015**, *6*, 1265.
12. C. Shu, R.-F. Liu, S. Liu, J.-Q. Li, Y.-F. Yu, Q. He, X. Lu, L.-W. Ye, *Chem. Asian J.* **2015**, *10*, 91.
13. P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270.
14. C. Gonzalez, H. B. Schlegel, *J. Phys. Chem.* **1990**, *94*, 5523.
15. A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378.
16. B. Lu, Y. Li, Y. Wang, D. H. Aue, Y. Luo, L. Zhang, *J. Am. Chem. Soc.*, **2013**, *135*, 8512.

17. Y. Wang, A. Yepremyan, S. Ghorai, R. Todd, D. H. Aue, L. Zhang, *Angew. Chem. Int. Ed.* **2013**, *52*, 7795.
18. A. T. Tran, P. Liu, K. N. Houk, K. M. Nicholas, *J. Org. Chem.* **2014**, *79*, 5617.
19. N. Yoshikai, K. Miura, E. Nakamura, *Adv. Synth. Catal.* **2009**, *351*, 1014.
20. J. Comas-Barceló, R. S. Foster, B. Fiser, E. Gomez-Bengoa, J. P. A. Harrity, *Chem. Eur. J.* **2014**, *20*, 1.
21. S. Özcubukcu, E. Ozkal, C. Jimeno, M. A. Perić, *Org. Lett.* **2009**, *11*, 4680.
22. C. Jarava-Barrera, A. Parra, A. López, F. Cruz-Acosta, D. Collado-Sanz, D. J. Cárdenas, M. Tortosa, *ACS Catal.* **2016**, *6*, 442.
23. D. Cantillo, M. Ávalos, R. Babiano, P. Cintas, J. L. Jiménez, J. C. Palacios, *Org. Biomol. Chem.* **2011**, *9*, 2952.
24. M. E. Bunnage, S. G. Davies, P. M. Roberts, A. D. Smith, J. M. Withey, *Org. Biomol. Chem.* **2004**, *2*, 2763.
25. M.-M. Wang, X.-S. Ning, J.-P. Qu, Y.-B. Kang, *ACS Catal.* **2017**, *7*, 4000.
26. X. Jie, Y. Shang, X. Zhang, W. Su, *J. Am. Chem. Soc.* **2016**, *138*, 5623.
27. T. Miura, Q. Zhao, Y. Funakoshi, M. Murakami, *Heterocycles* **2015**, *91*, 1579.
28. B. Prabagar, S. Nayak, R. Prasad, A. K. Sahoo, *Org. Lett.* **2016**, *18*, 3066.
29. C. Shu, M.-Q. Liu, S.-S. Wang, L. Li, L.-W. Ye, *J. Org. Chem.* **2013**, *78*, 3292.
30. M. A. Ilies, D. Vullo, J. Pastorek, A. Scozzafava, M. Ilies, M. T. Caproiu, S. Pastorekova, C. T. Supuran, *J. Med. Chem.* **2003**, *46*, 2187.
31. A. N. Boa, S. P. Canavan, P. R. Hirst, C. Ramsey, A. M. W. Stead, G. A. McConkey, *Bioorg. Med. Chem.* **2005**, *13*, 1945.
32. J. H. Lee, S. R. Byeon, Y. S. Kim, S. J. Lim, S. J. Oh, D. H. Moon, K. H. Yoo, B. Y. Chung, D. J. Kim, *Bioorg. Med. Chem. Lett.* **2008**, *18*, 5701.
33. J. H. Shah, B. P. Conner, G. M. Jr. Swartz, K. A. Hunsucker, J. Rougas, R. D'Amato, V. Pribluda, A. Treston, PCT Int. Appl. WO 2003014315A2, **2003**.
34. S. Mollin, S. Blanck, K. Harms, E. Meggers, *Inorg. Chim. Acta*, **2012**, *393*, 261.
35. H. J. Kim, J. Kim, S. H. Cho, S. Chang, *J. Am. Chem. Soc.* **2011**, *133*, 16382.
36. L. Xia, A. Idhayadhulla, Y. R. Lee, S. H. Kim, Y.-J. Wee, *ACS Comb. Sci.* **2014**, *16*, 333.

37. D. V. Kravchenko, Y. A. Kuzovkova, V. M. Kysil, S. E. Tkachenko, S. Maliarchouk, I. M. Okun, K. V. Balakin, A. V. Ivachtchenko, *J. Med. Chem.* **2005**, *48*, 3680.