Supporting Information

TFA-Mediated DMSO-Participant Sequential Oxidation/1,3-Dipolar Cycloaddition Cascade of Pyridinium Ylides for Assembly of Indolizines

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Supporting Information

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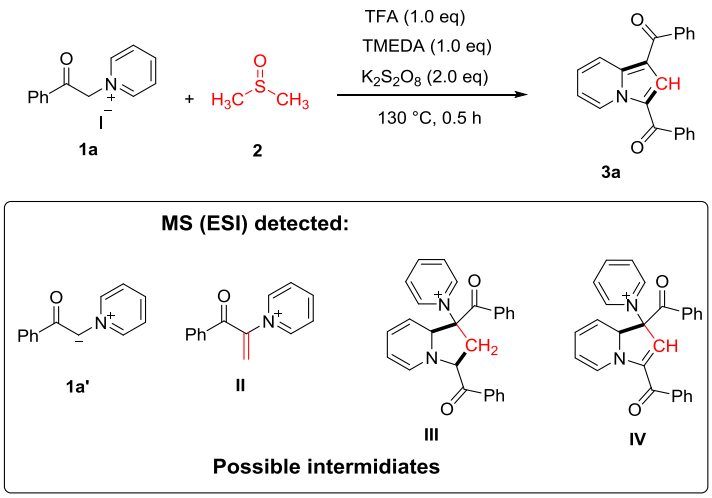
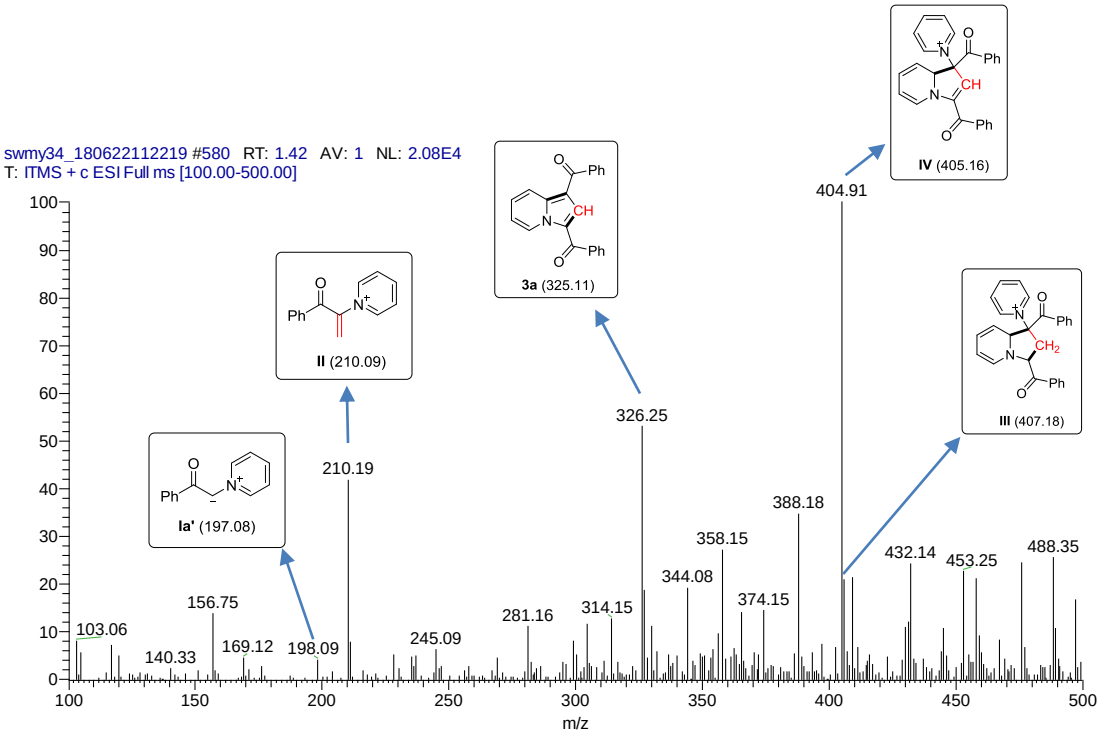
Experimental Section

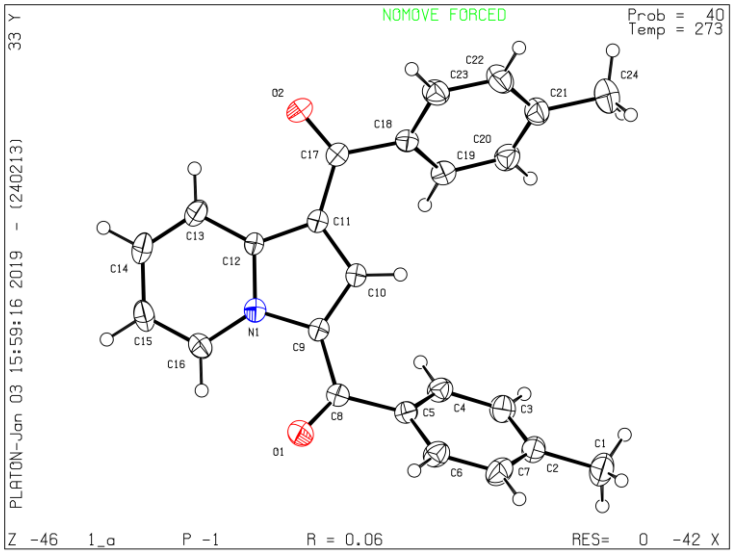
1. The MS Spectra of intermediates

A mixture of N-phenacylpyridinium iodide **1a** (325.2 mg, 1.0 mmol), TFA (57.0 mg, 0.5 mmol), TMEDA (58.1 mg, 0.5 mmol), and $K_2S_2O_8$ (540.5 mg, 2.0 mmol) was soluted in DMSO (5 mL) at 130 ℃ for 0.5 h. Then the mixture detected by ITMS (ESI). The following intermediates were detected.





2. The Crystallographic Data



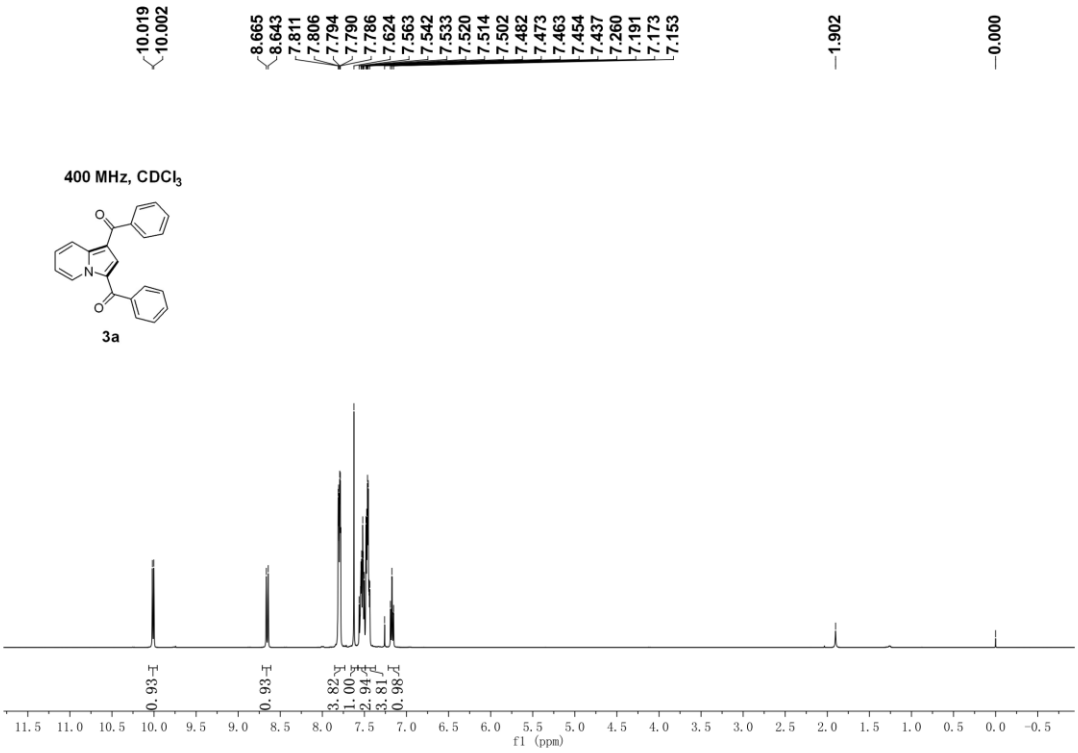
The purified compound **3b** is dissolved in a mixed solvent of acetonitrile and n-hexane, and placed in a dark cabinet to slowly evaporate. After several days, a yellow bulk crystal is obtained. The X-ray crystal-structure determinations were obtained on a Bruker APEX DUO CCD system.

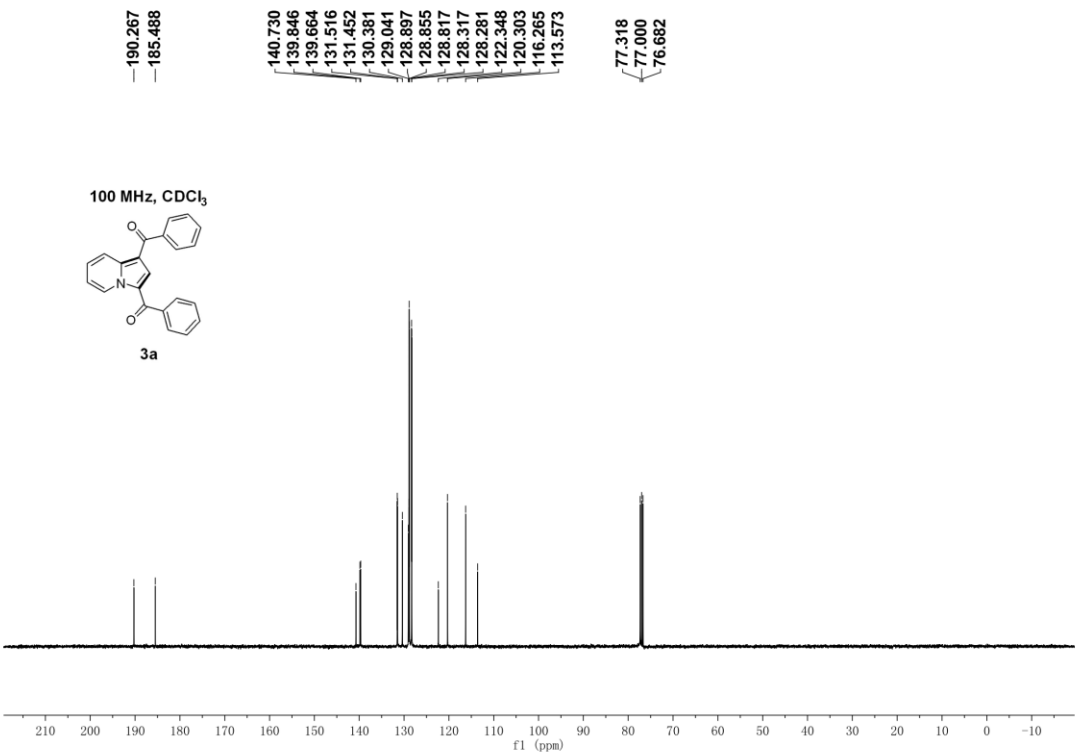
Figure S1. X-ray structural details of **3b**

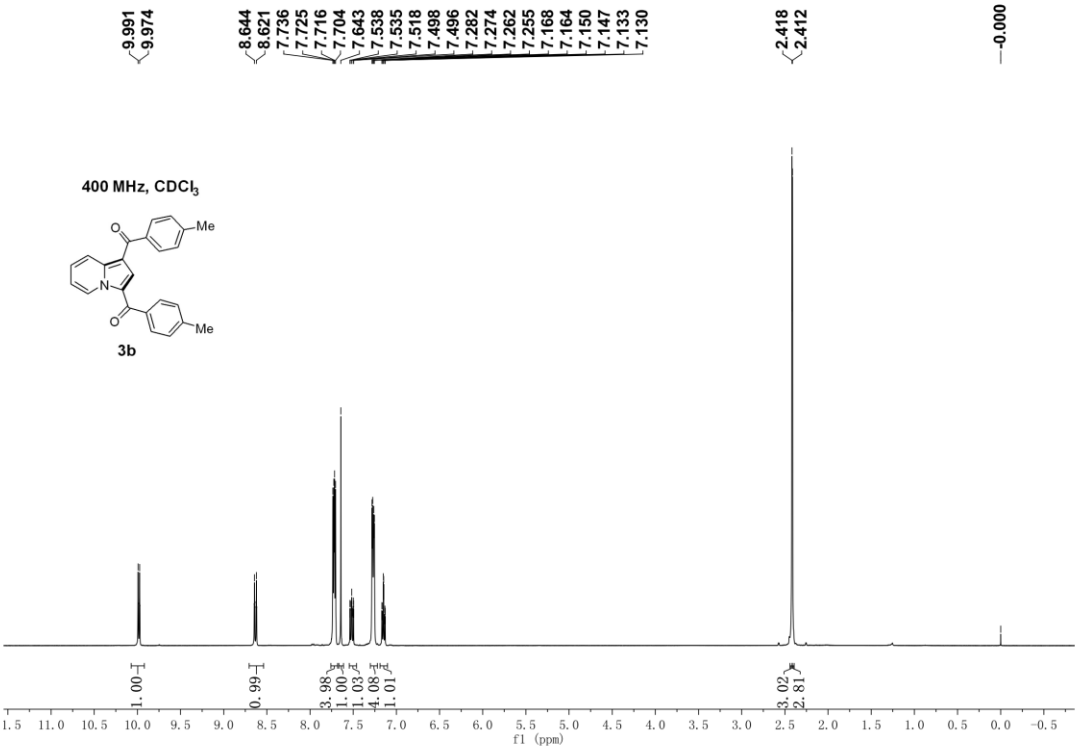
Table S1. The crystallographic data of **3b** (CCDC: 1848089).

Empirical formula	$C_{24}H_{19}NO_2$		Absorption coefficient	0.083 mm^{-1}
Formula weight	353.40		F(000)	372
Temperature	273(2) K		Crystal size	0.22 x 0.20 x 0.18 mm^3
Wavelength	0.71073 Å		Reflections collected	45310
Crystal system	Triclinic		Independent reflections	7453 [R(int) = 0.0305]
Space group	P-1		Max. and min. transmission	0.9920 and 0.9920
Unit cell dimensions	a = 7.326(2) Å	α = 106.563 °	Refinement method Full	Full-matrix least-squares on F^2
	b = 9.882(3) Å	β = 92.469 °	Data / restraints / parameters	5172 / 0 / 246
	c = 13.685(4) Å	γ = 107.893 °	Goodness-of-fit on F^2	1.033
Volume	894.4(4) $Å^3$		Final R indices [I>2sigma(I)]	R1 = 0.0562, wR2 = 0.1168
Z	2		R indices (all data)	R1 = 0.1051, wR2 = 0.2207
Density (calculated)	1.312 Mg/m^3		Largest diff. peak and hole	0.386 and -0.274 e.$Å^{-3}$

3. Appendix: spectral copies of ^{1}HNMR, and ^{13}CNMR



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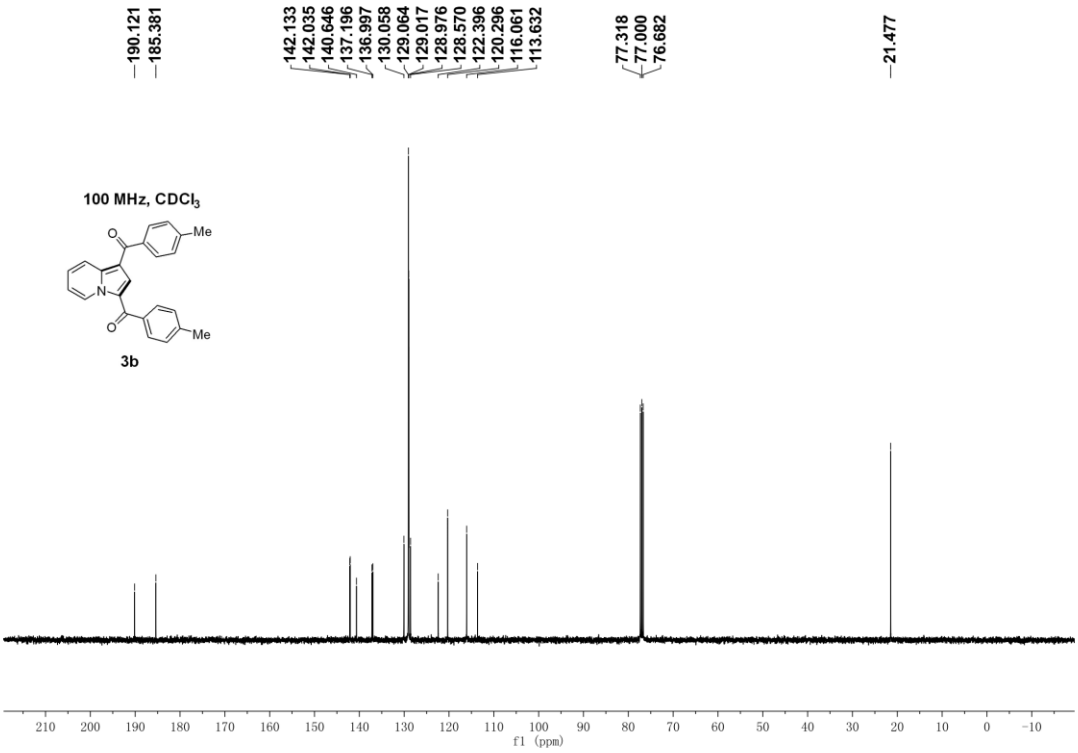
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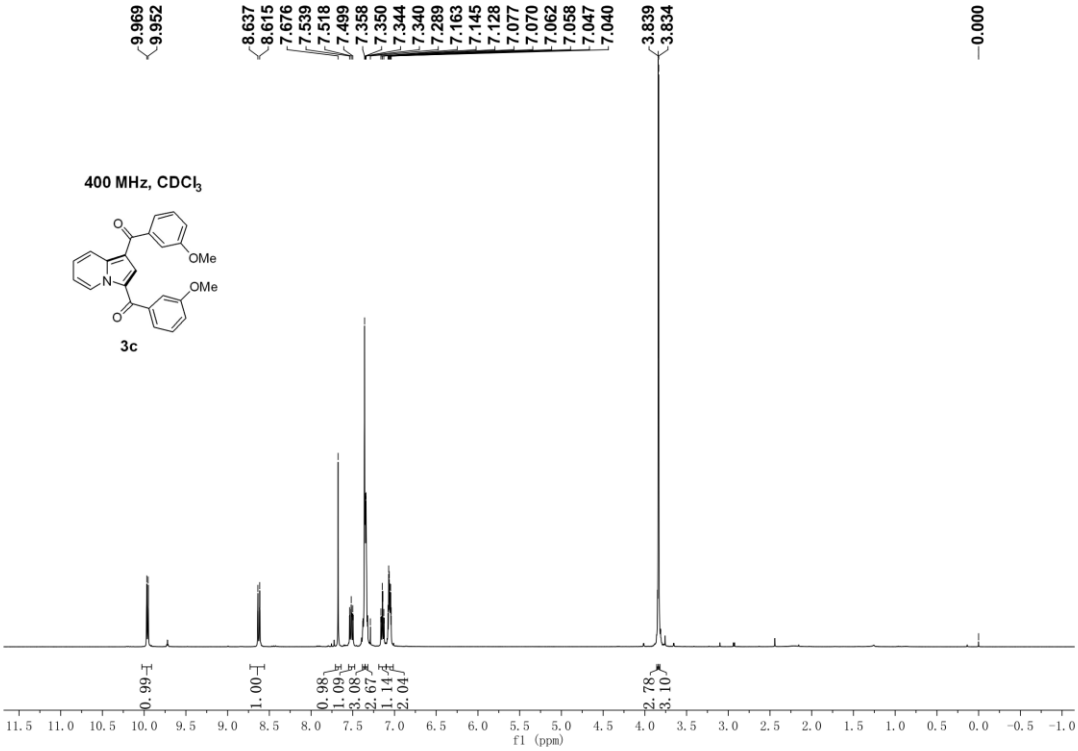
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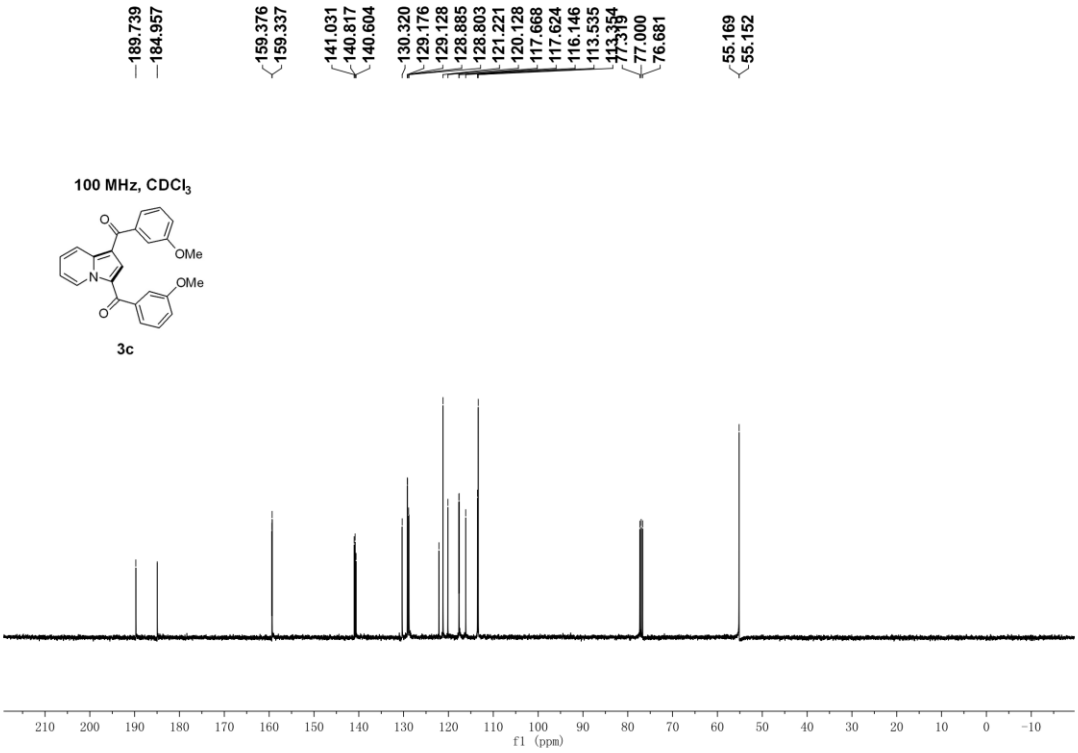
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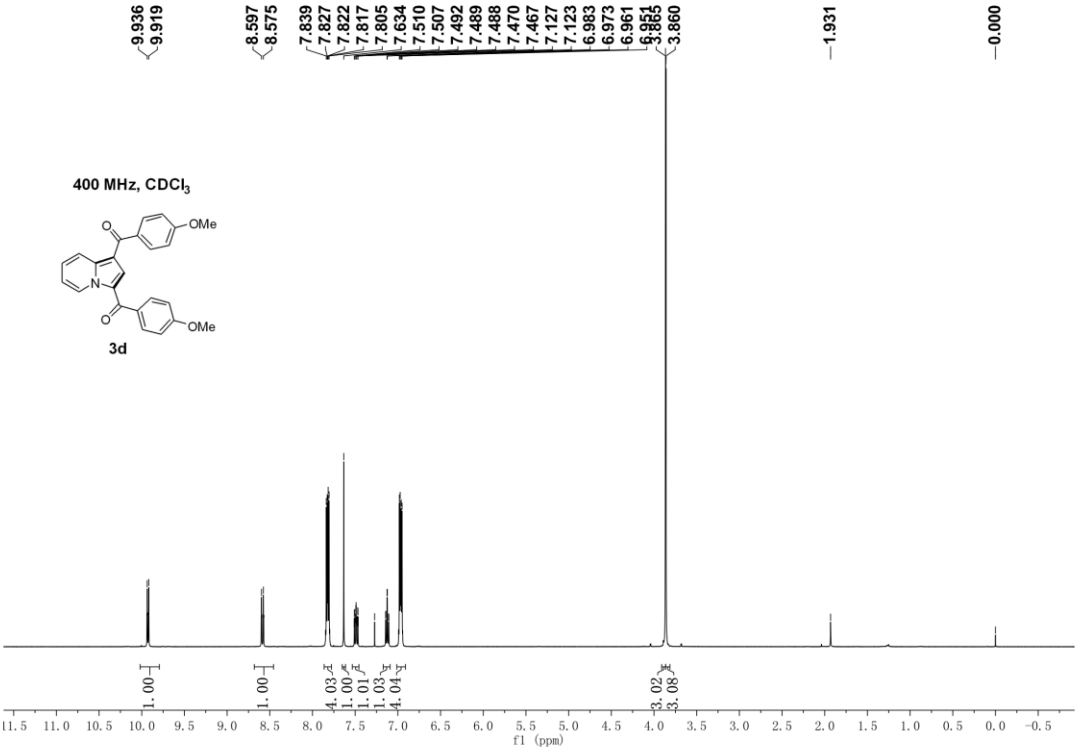
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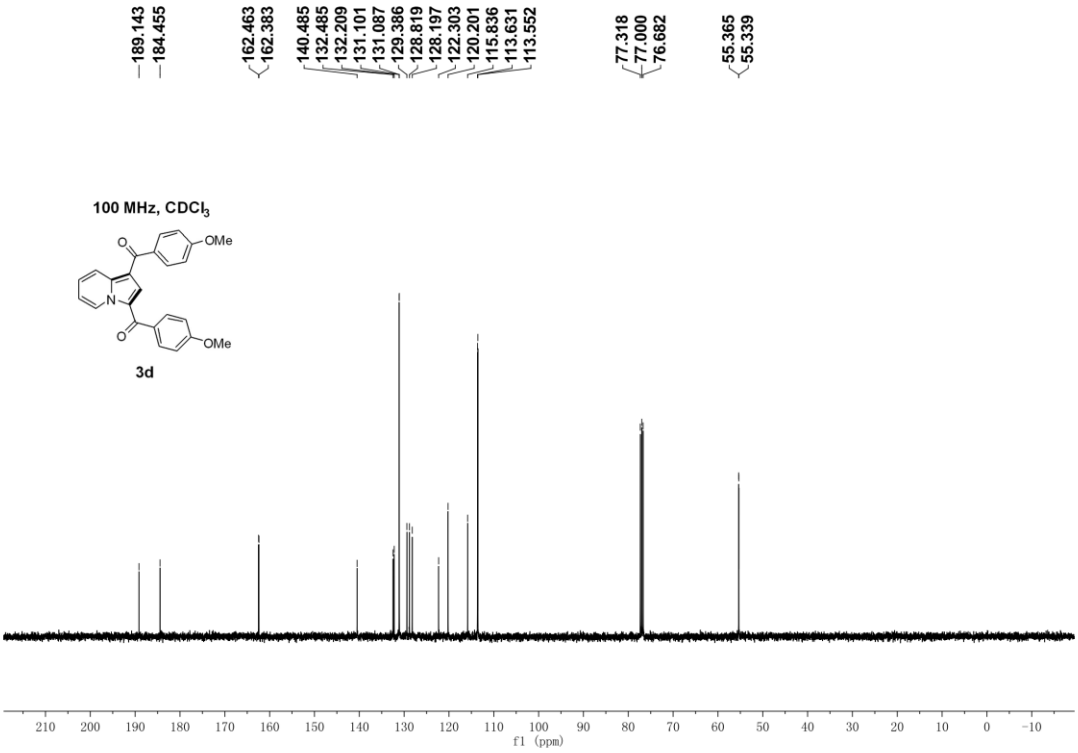
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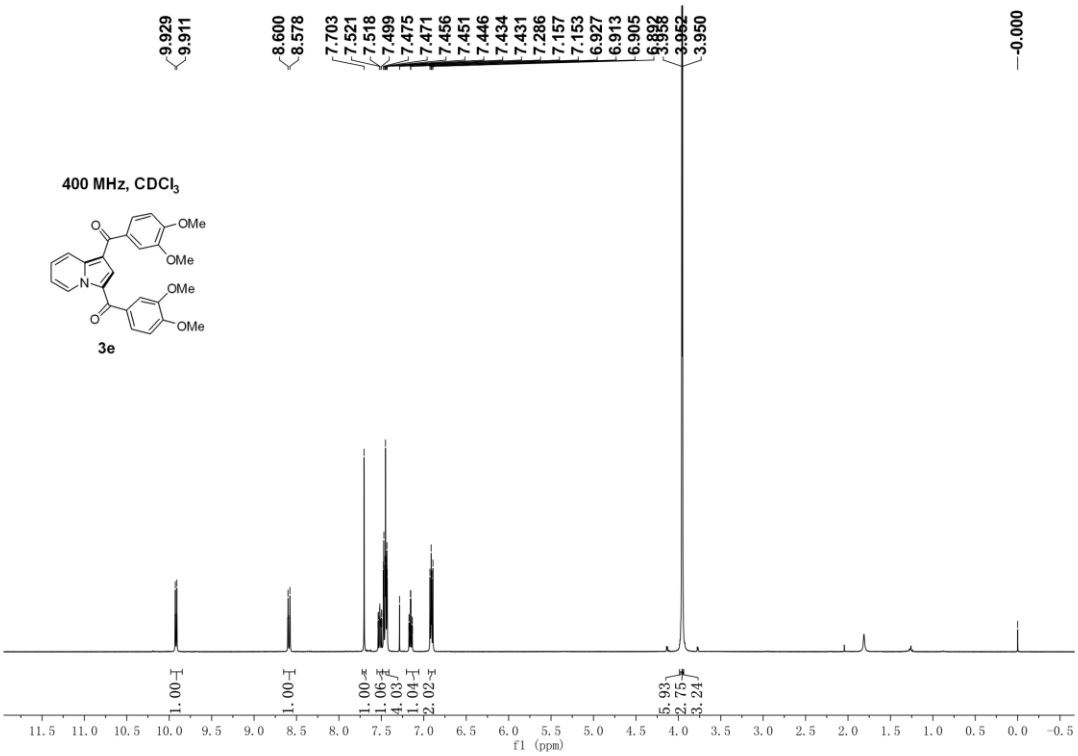
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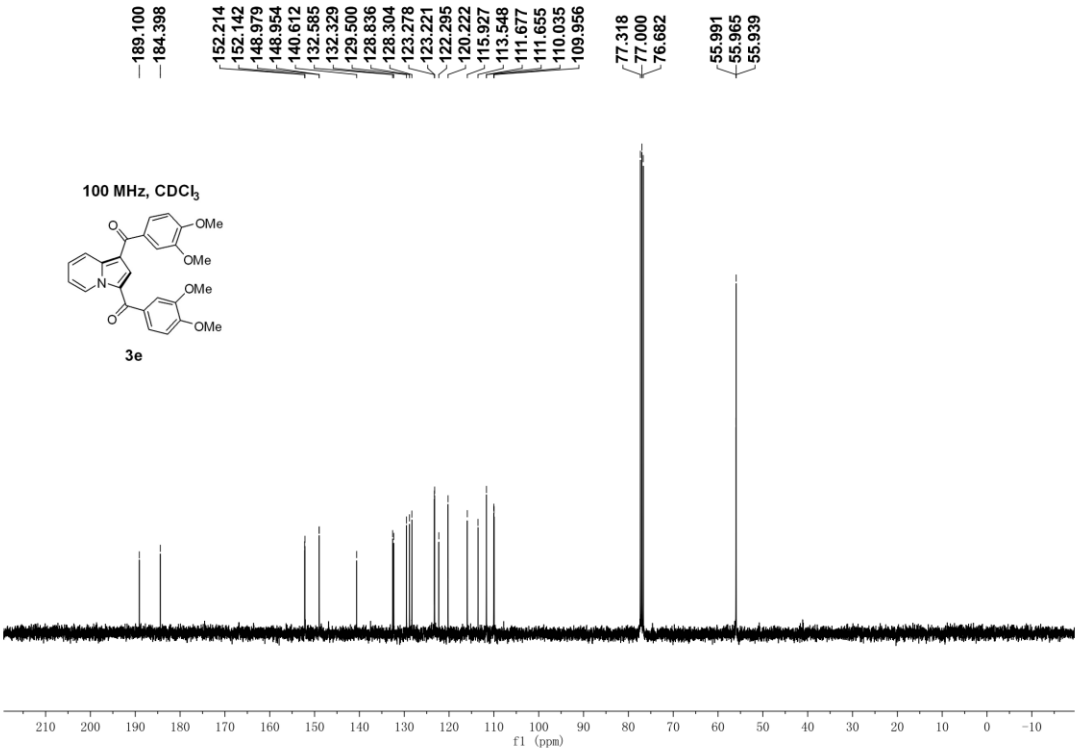
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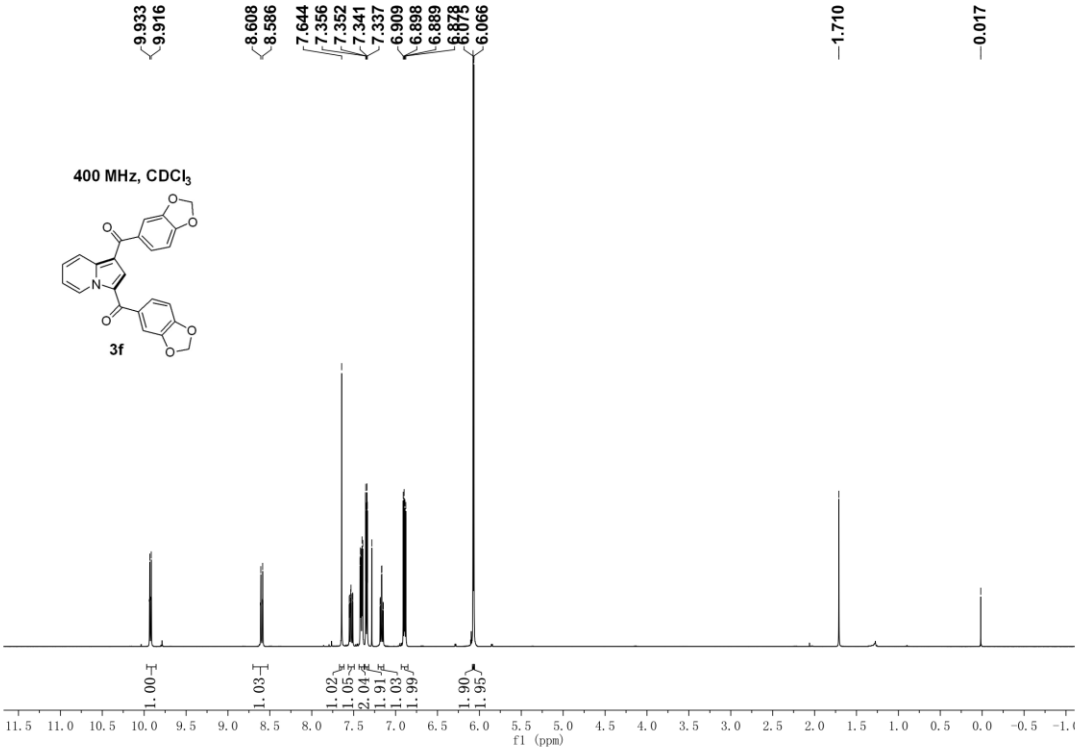
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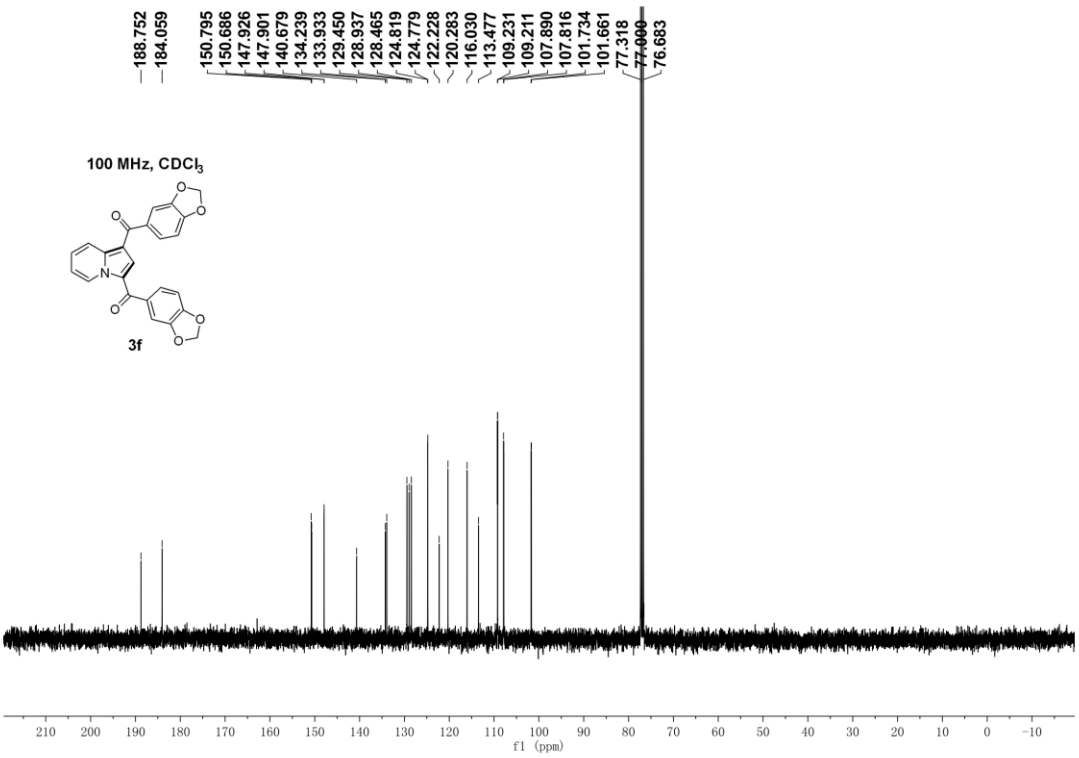
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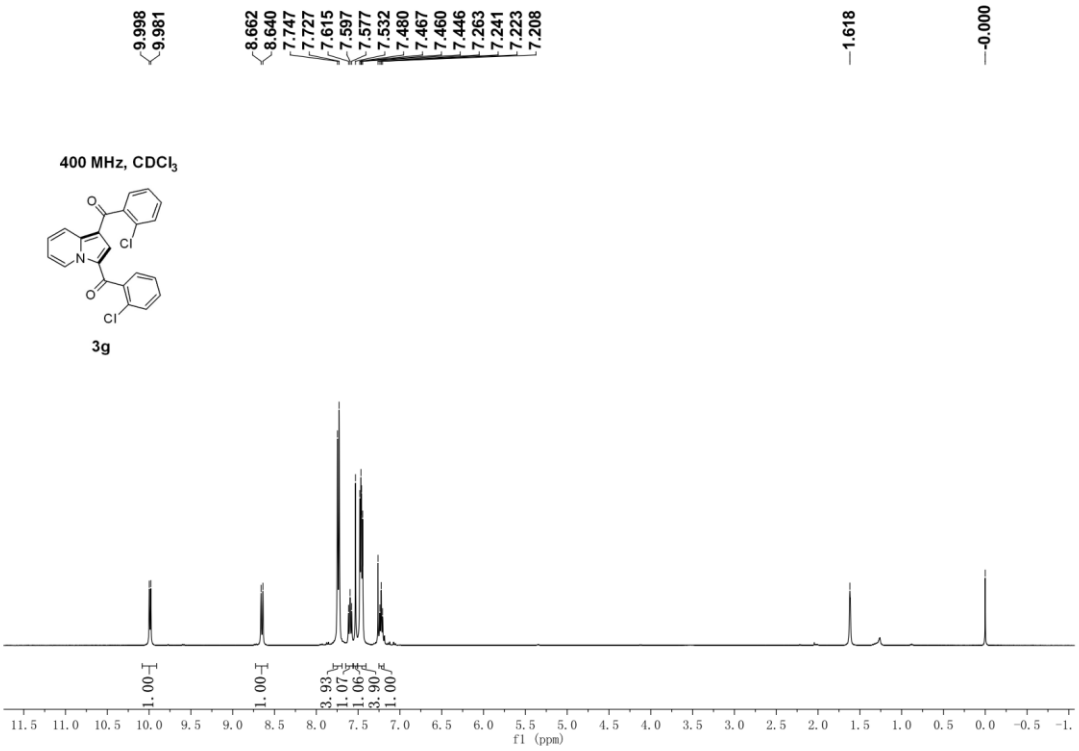
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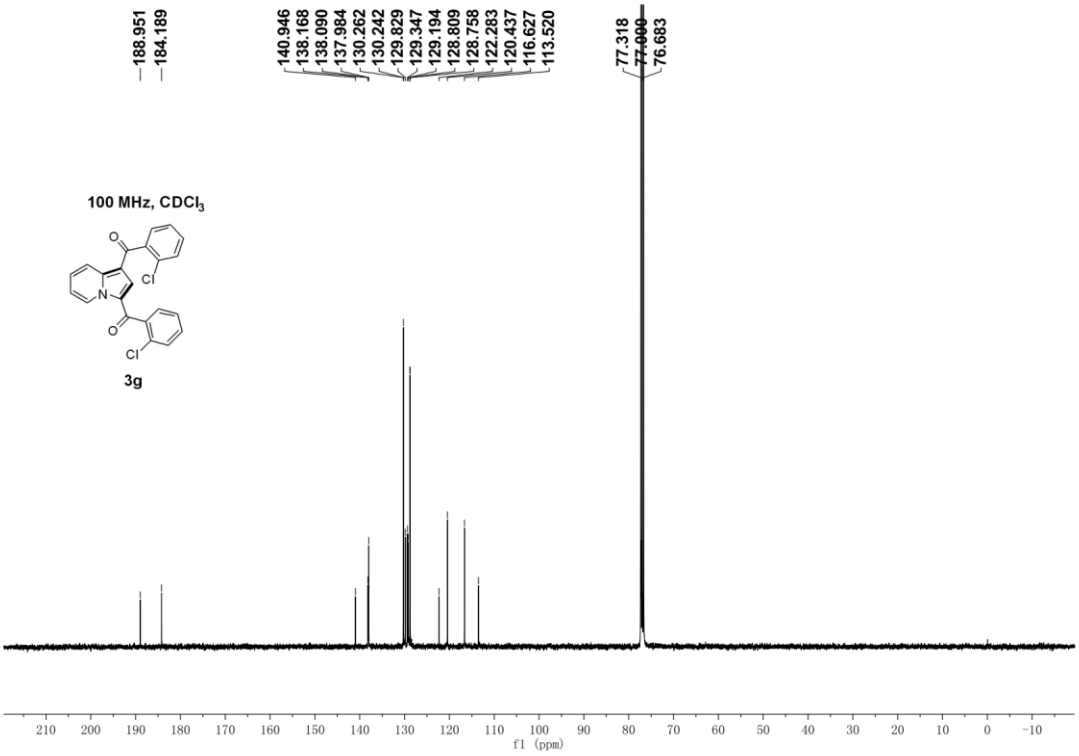
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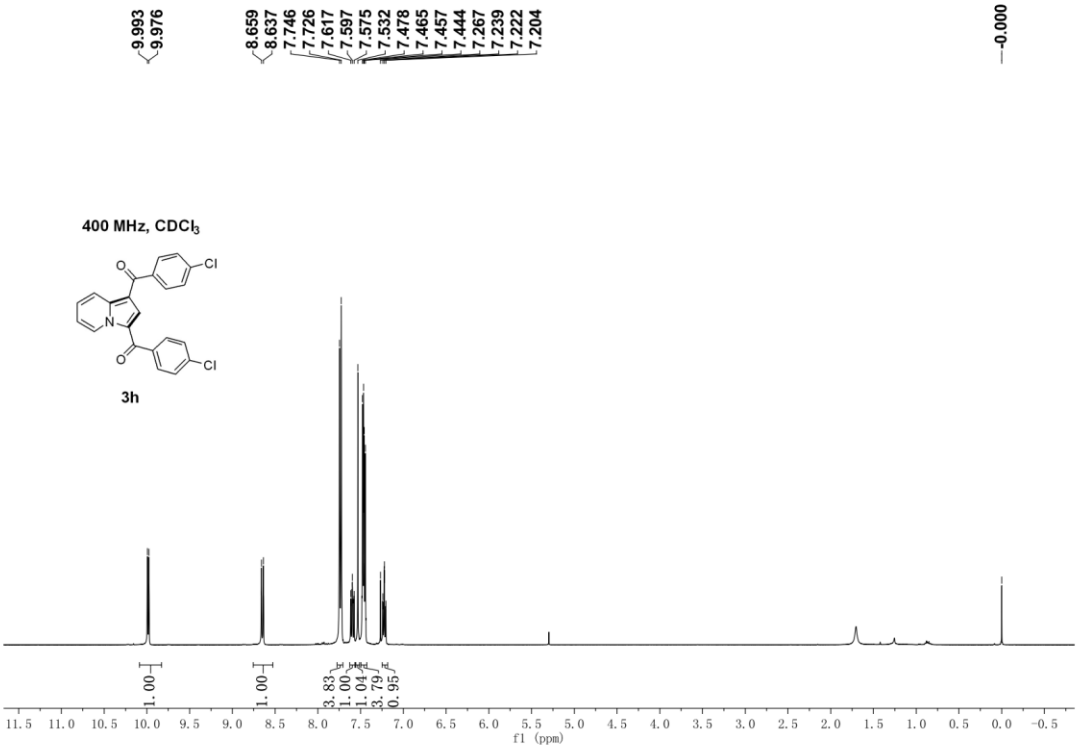
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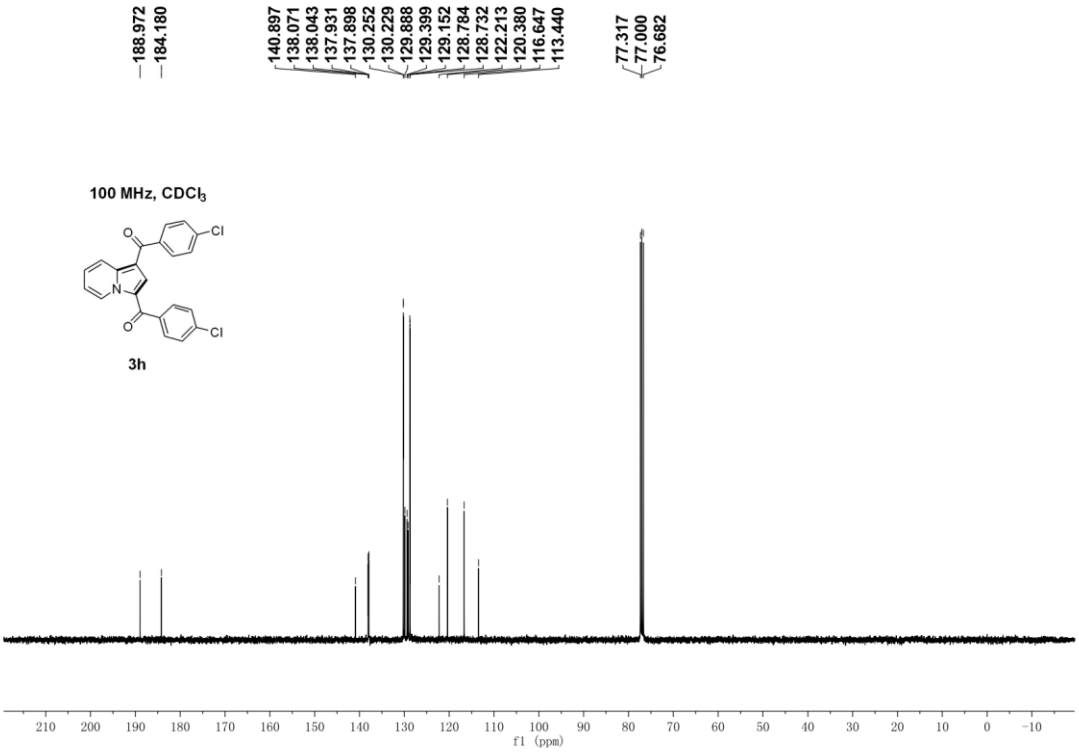
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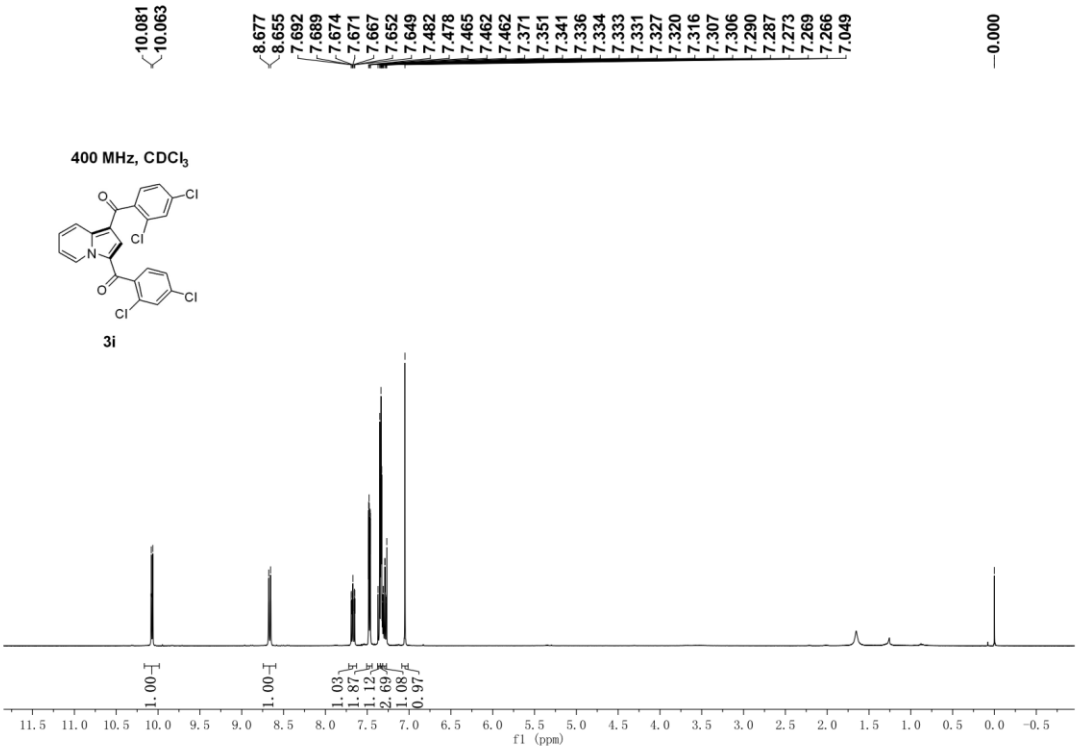
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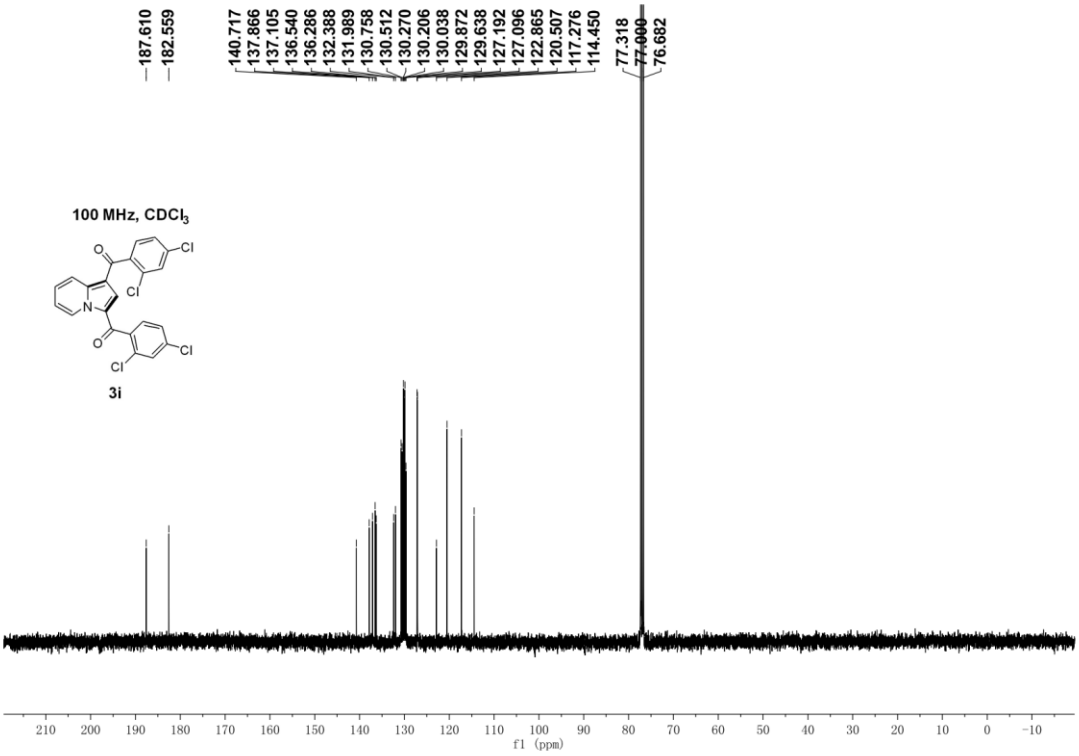
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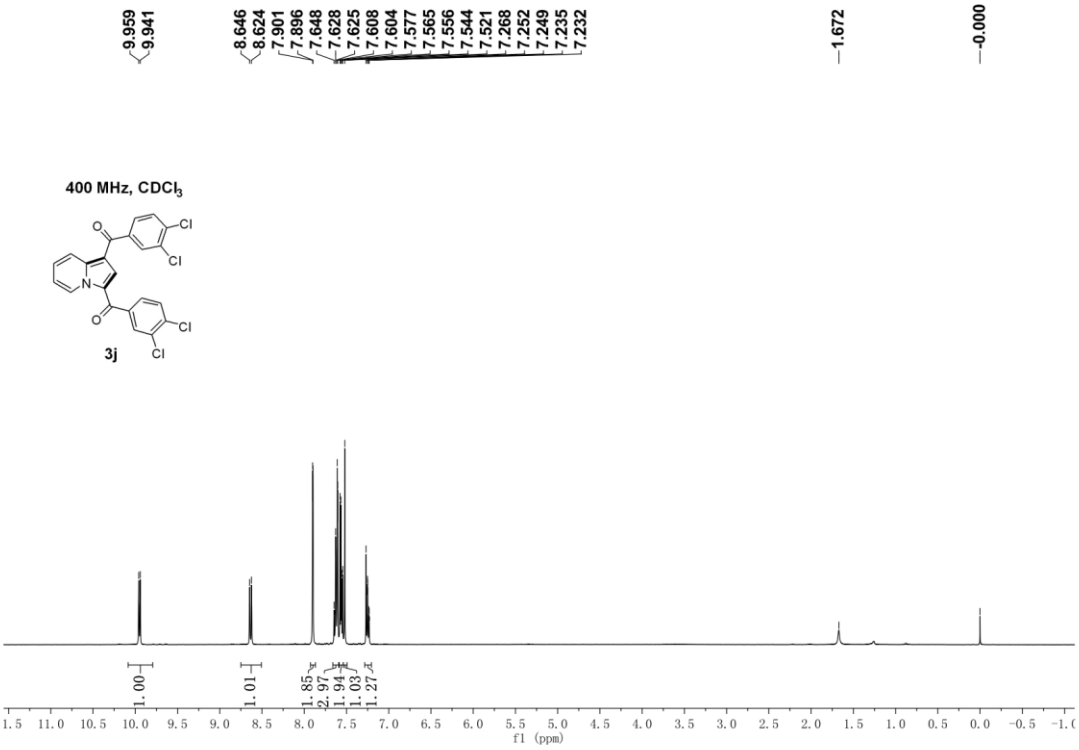
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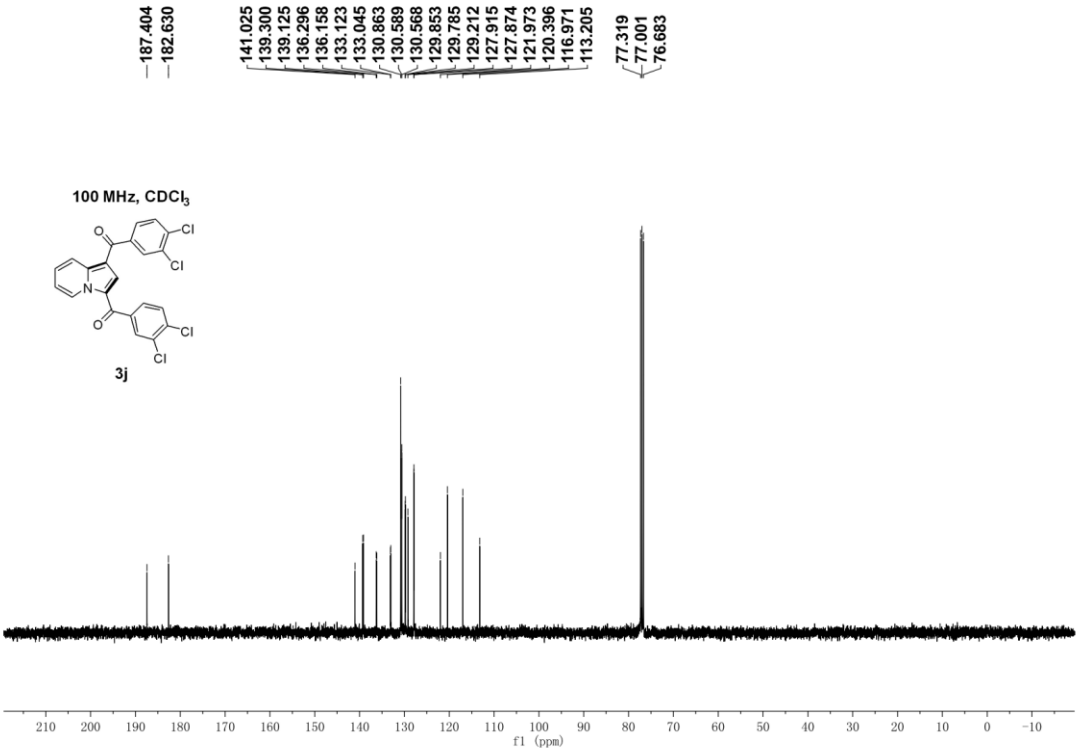
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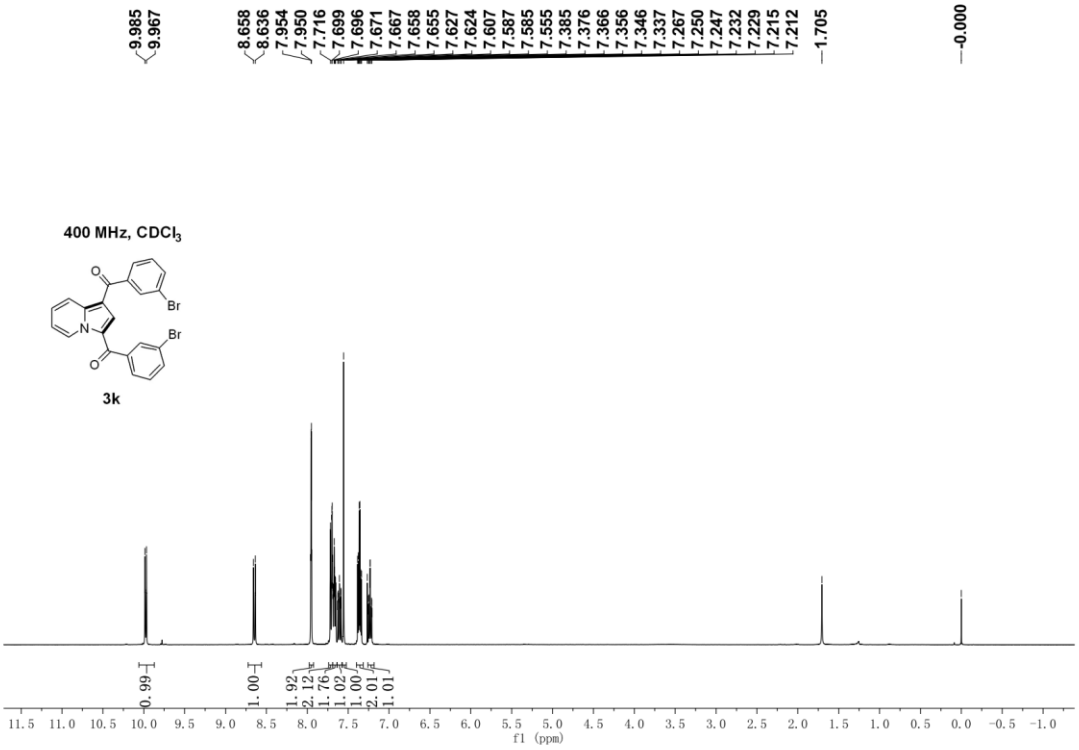
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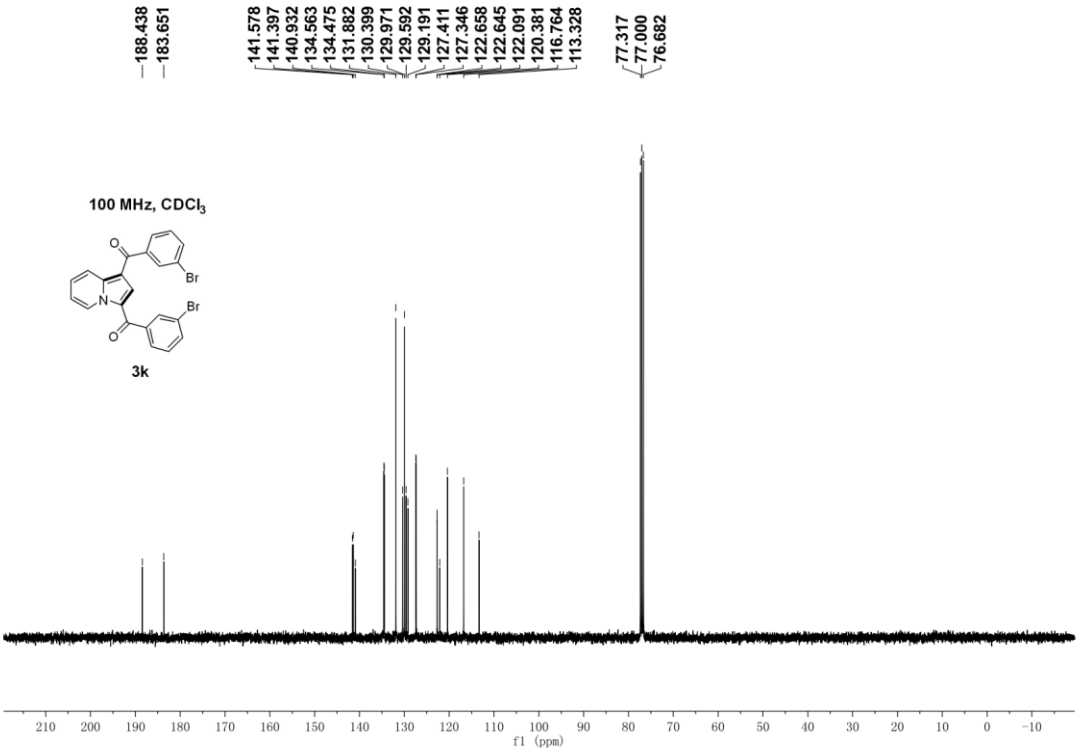
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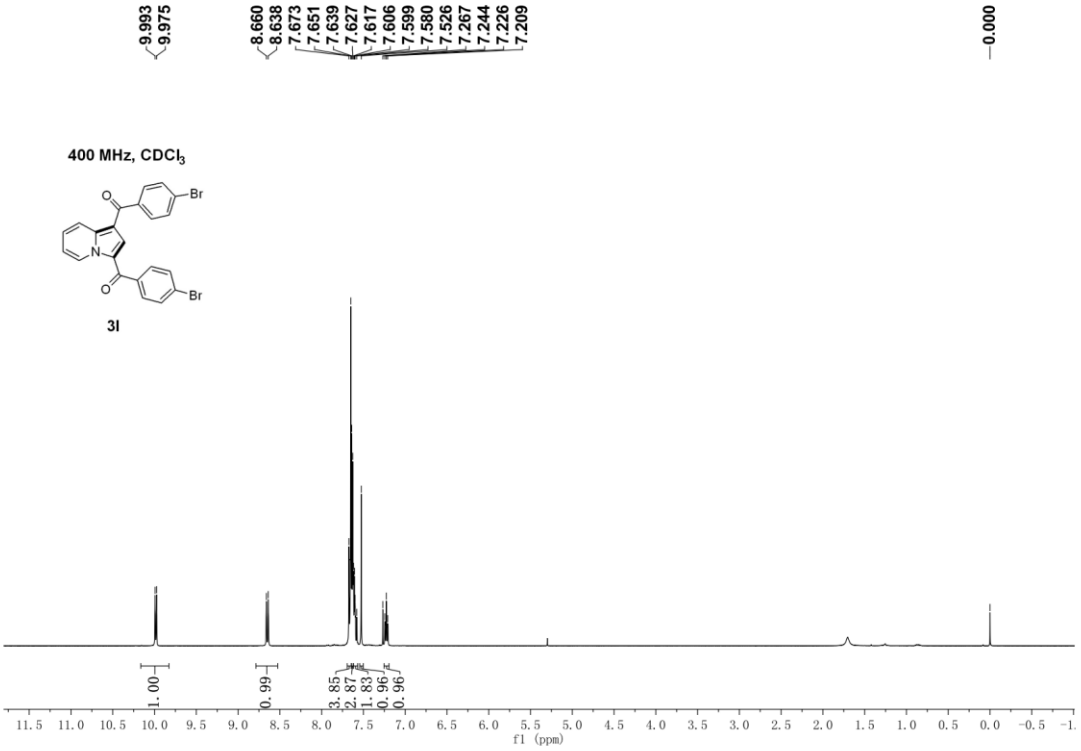
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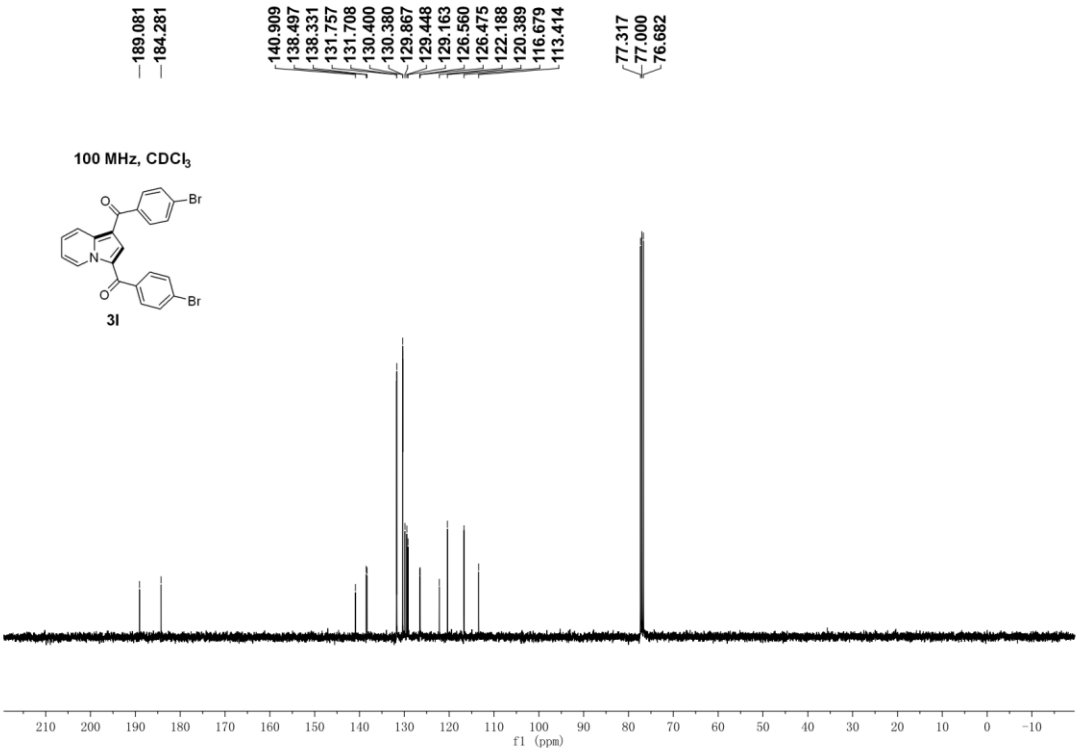
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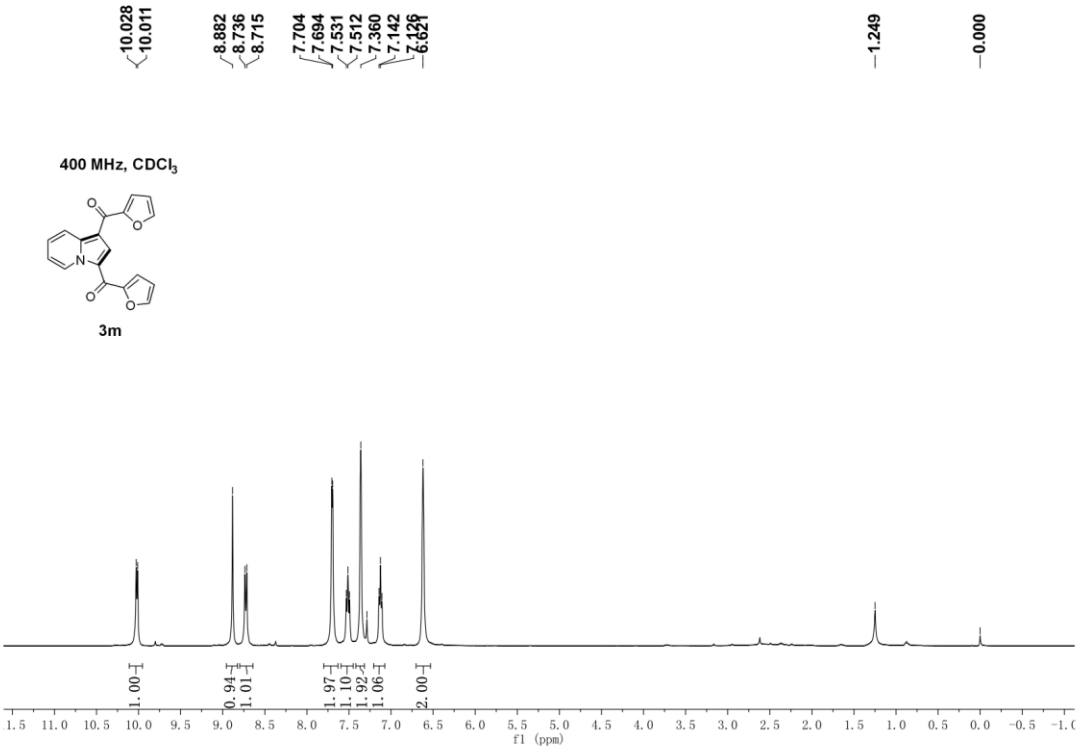
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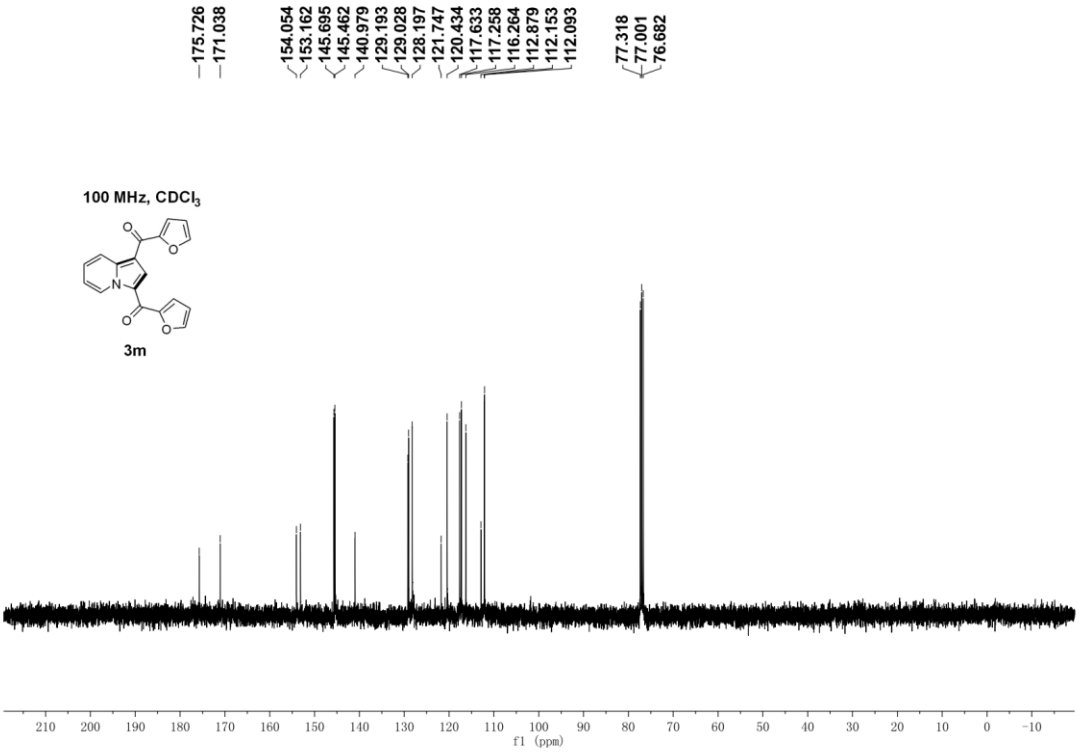
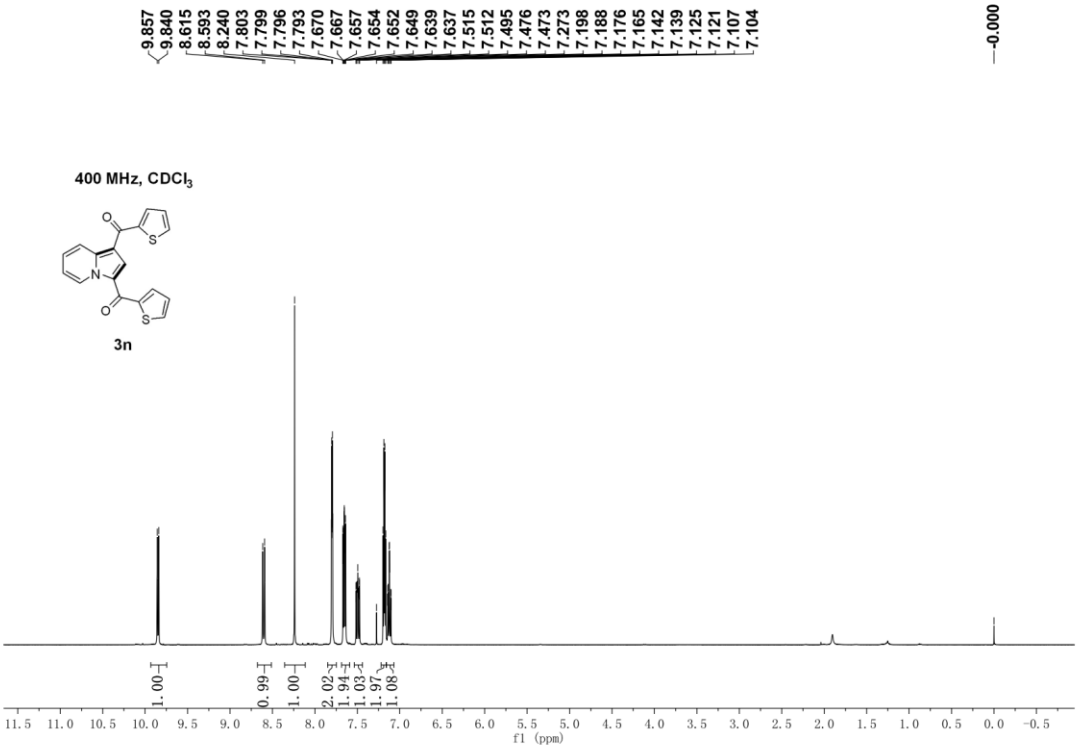
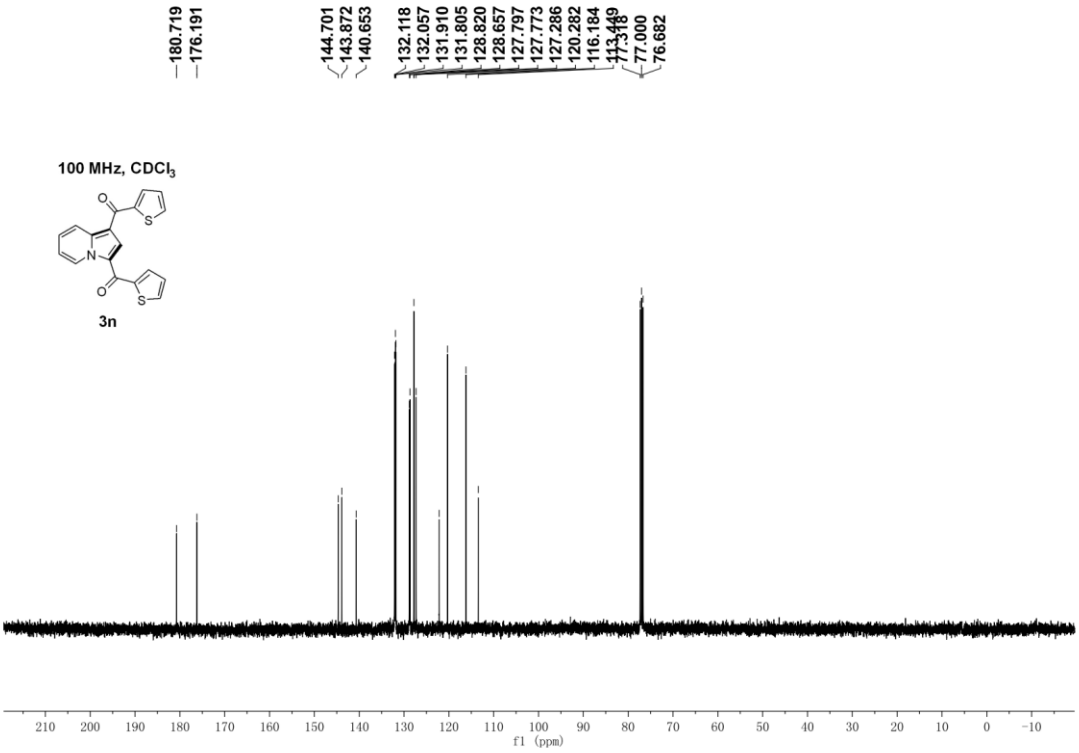
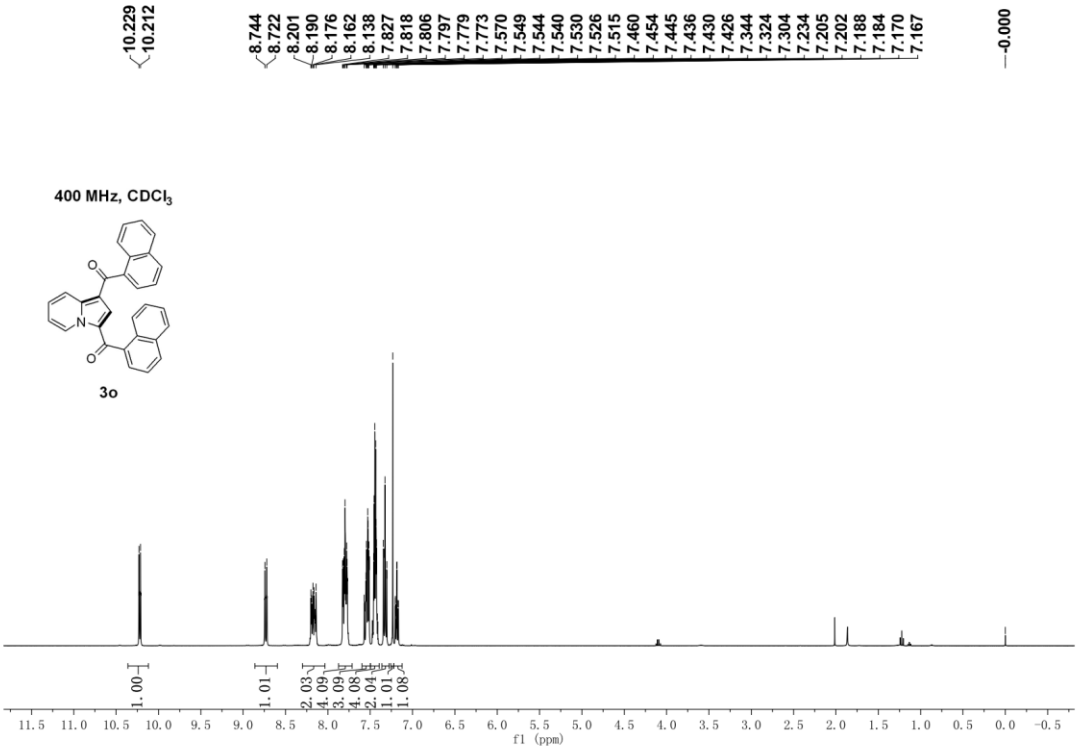
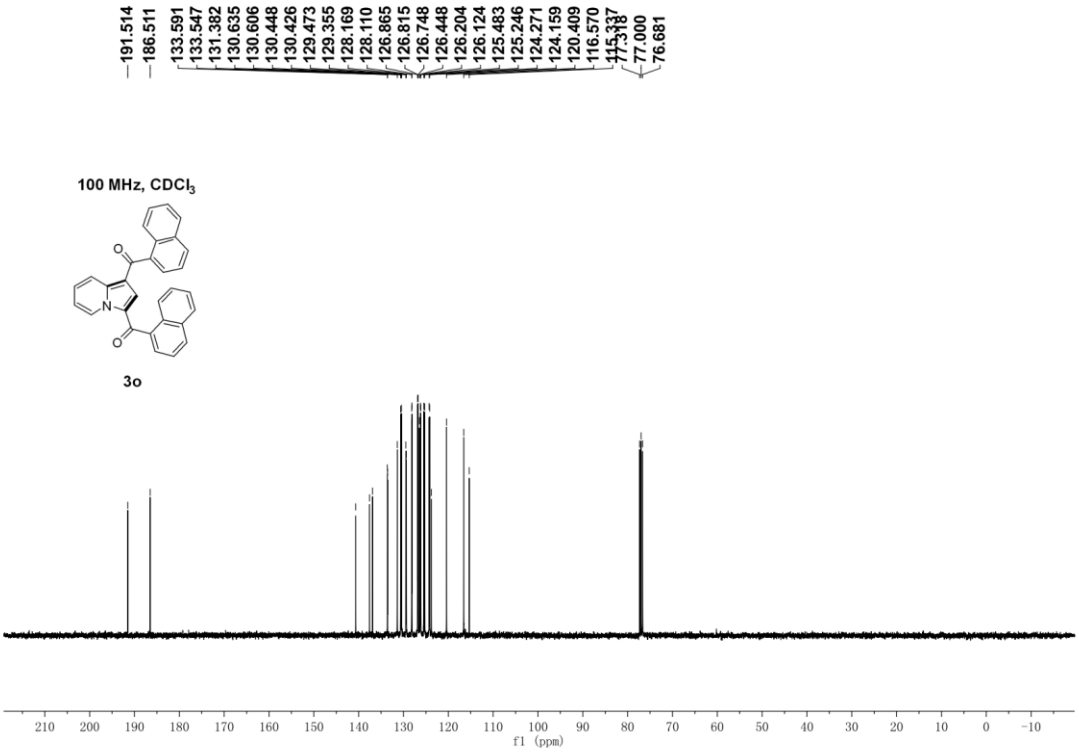
1.10
1.92
1.06
2.00
f1 (ppm)

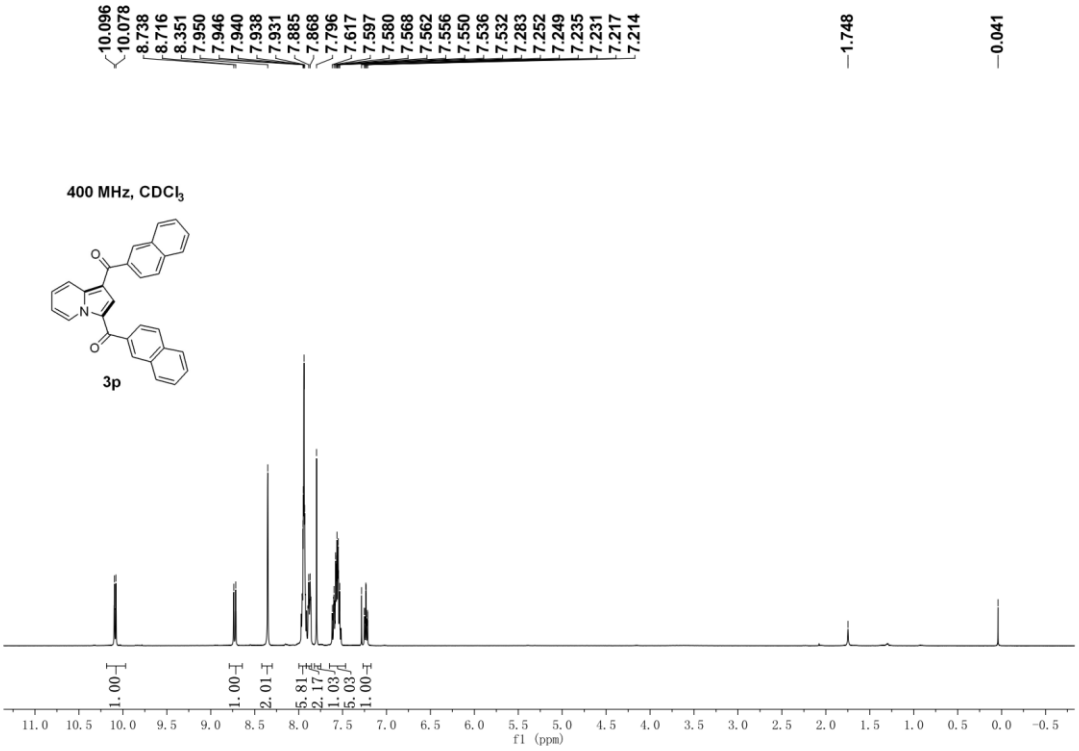

175.726
171.038
154.054
153.162
145.695
145.462
140.979
129.193
129.028
128.197
121.747
120.434
117.633
117.258
116.264
112.879
112.153
112.093
77.318
77.001
76.682
100 MHz, CDCl3
3m
f1 (ppm)

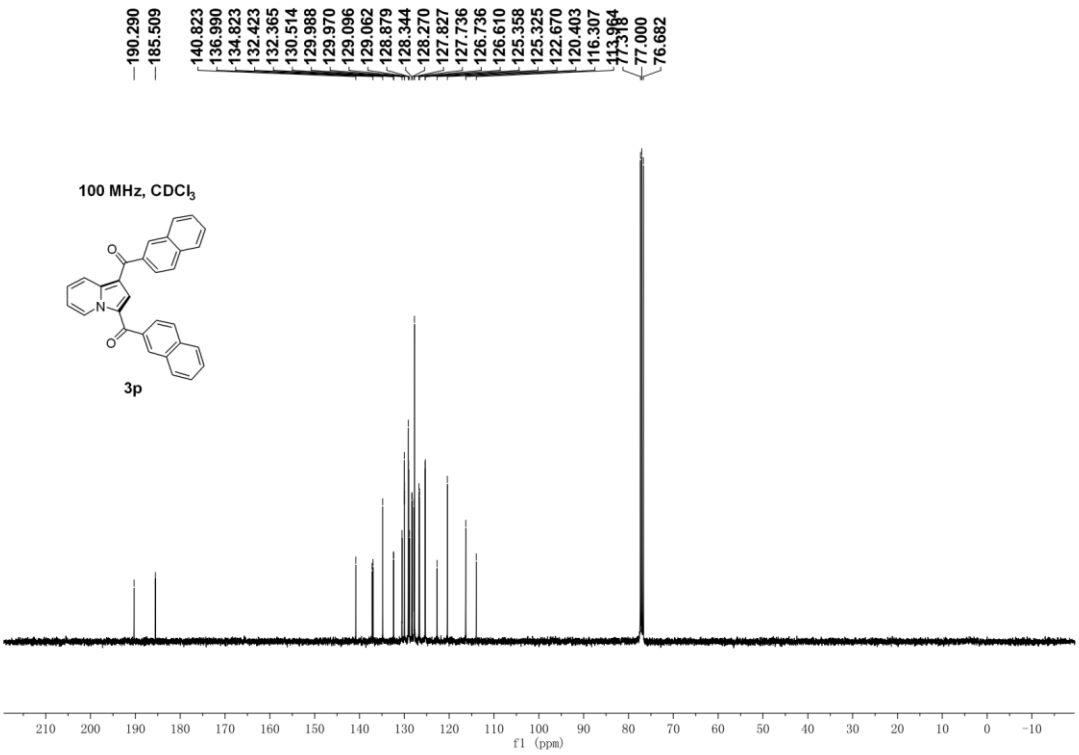

9.857
9.840
8.615
8.593
8.240
7.803
7.799
7.796
7.793
7.670
7.667
7.657
7.654
7.652
7.649
7.639
7.637
7.515
7.512
7.495
7.476
7.473
7.273
7.198
7.188
7.176
7.165
7.142
7.139
7.125
7.121
7.107
7.104
0.000
400 MHz, CDCl3
3n
1.00
0.99
1.00
2.02
1.94
1.03
1.97
1.08
f1 (ppm)

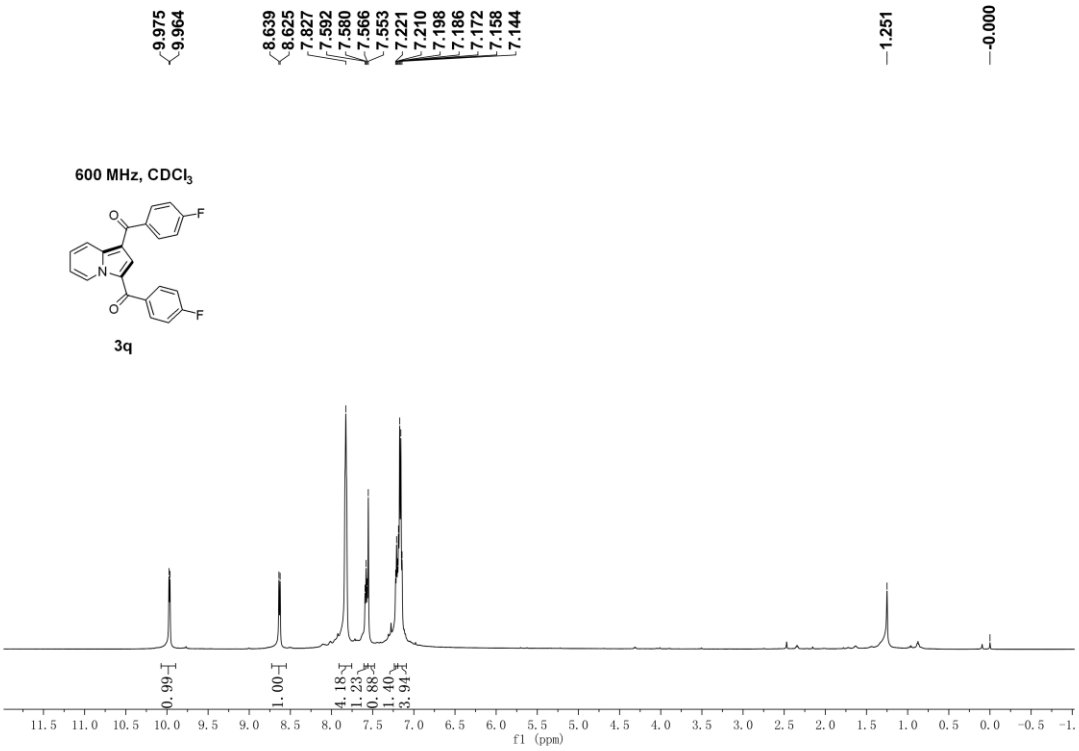

180.719
176.191
144.701
143.872
140.653
132.118
132.057
131.910
131.805
128.820
128.657
127.797
127.773
127.286
120.282
116.184
113.449
77.318
77.000
76.682
100 MHz, CDCl3
3n
f1 (ppm)

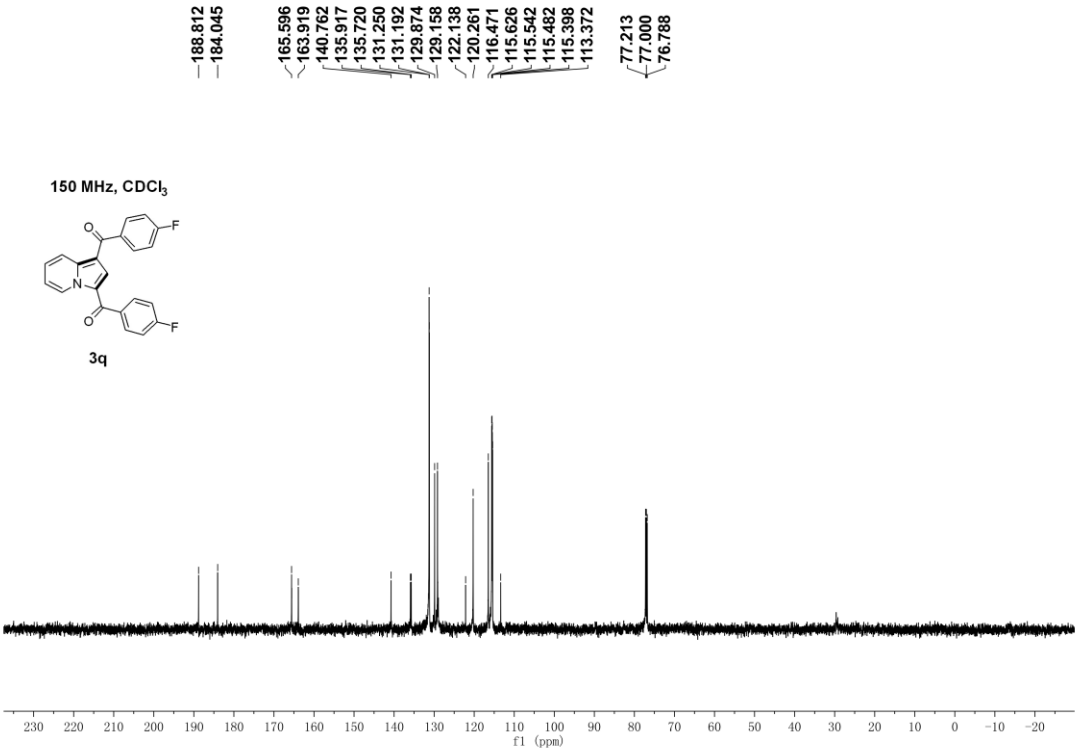

10.229
10.212
8.744
8.722
8.201
8.190
8.176
8.162
8.138
7.827
7.818
7.806
7.797
7.779
7.773
7.570
7.549
7.544
7.540
7.530
7.526
7.515
7.460
7.454
7.445
7.436
7.430
7.426
7.344
7.324
7.304
7.234
7.205
7.202
7.188
7.184
7.170
7.167
0.000
400 MHz, CDCl3
3o
1.00
1.01
2.03
4.09
3.09
4.08
2.04
1.01
1.08
f1 (ppm)

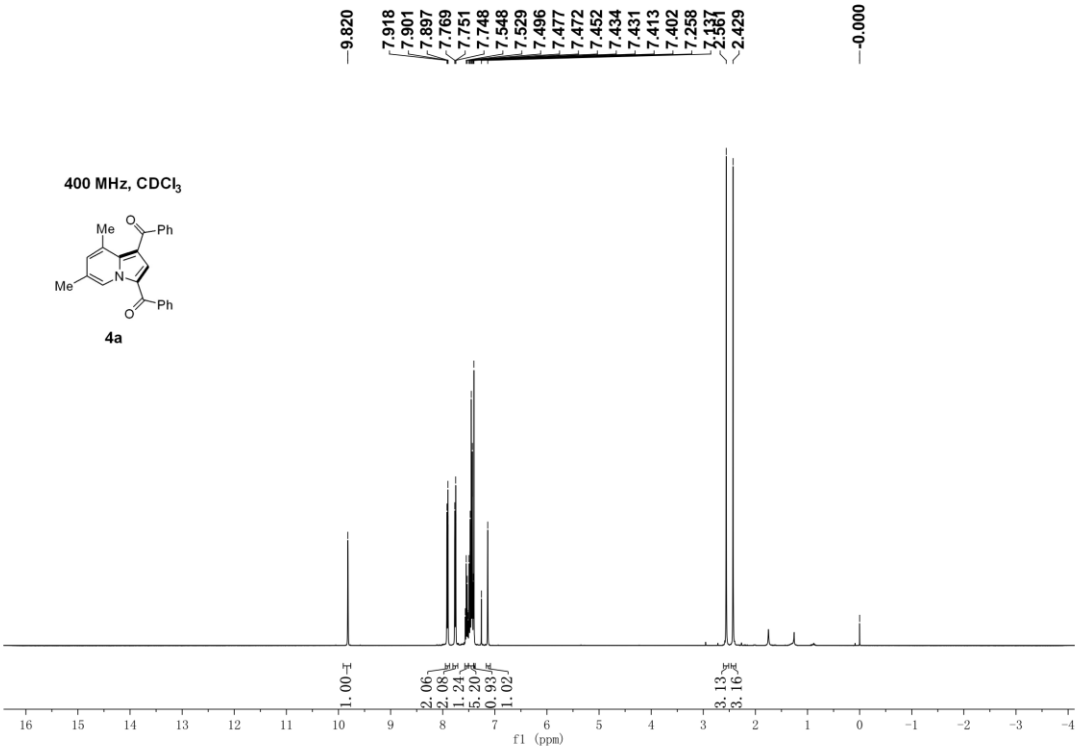

191.514
186.511
133.591
133.547
131.382
130.635
130.606
130.448
130.426
129.473
129.355
128.169
128.110
126.865
126.815
126.748
126.448
126.204
126.124
125.483
125.246
124.271
124.159
120.409
116.570
115.337
77.318
77.000
76.681
100 MHz, CDCl3
3o
f1 (ppm)

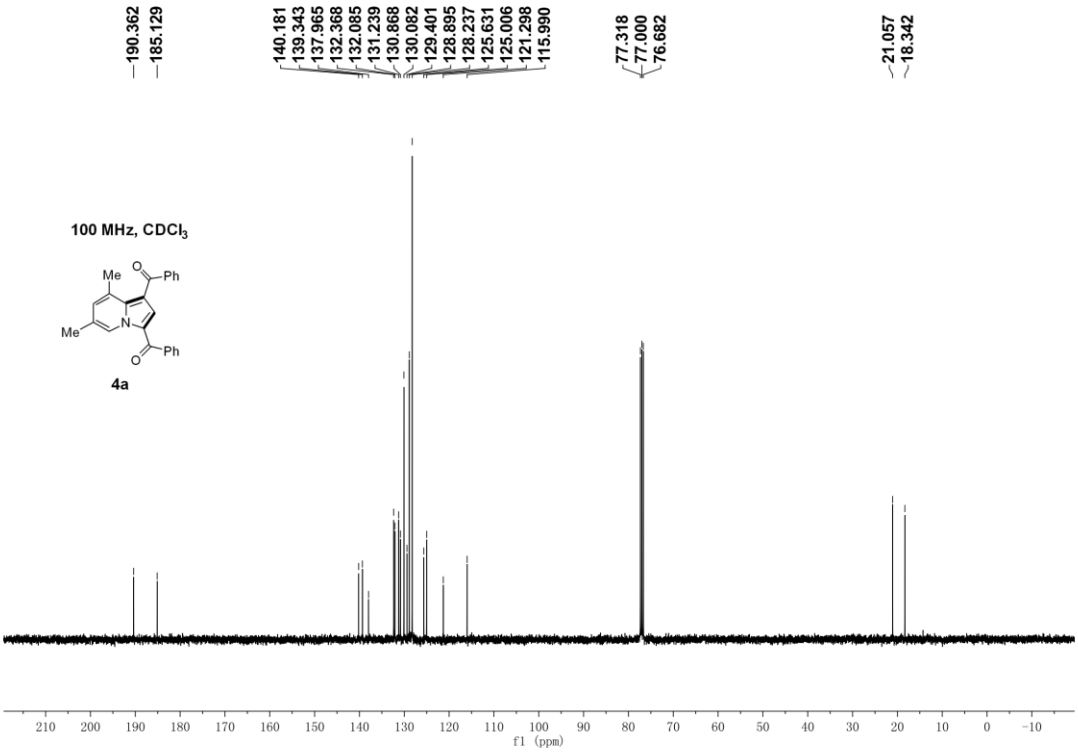

10.096
10.078
8.738
8.716
8.351
7.950
7.946
7.940
7.938
7.931
7.885
7.868
7.796
7.617
7.597
7.580
7.568
7.562
7.556
7.550
7.536
7.532
7.283
7.252
7.249
7.235
7.231
7.217
7.214
1.748
0.041
400 MHz, CDCl3
3p
1.00
1.00
2.01
5.81
2.17
1.03
5.03
1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

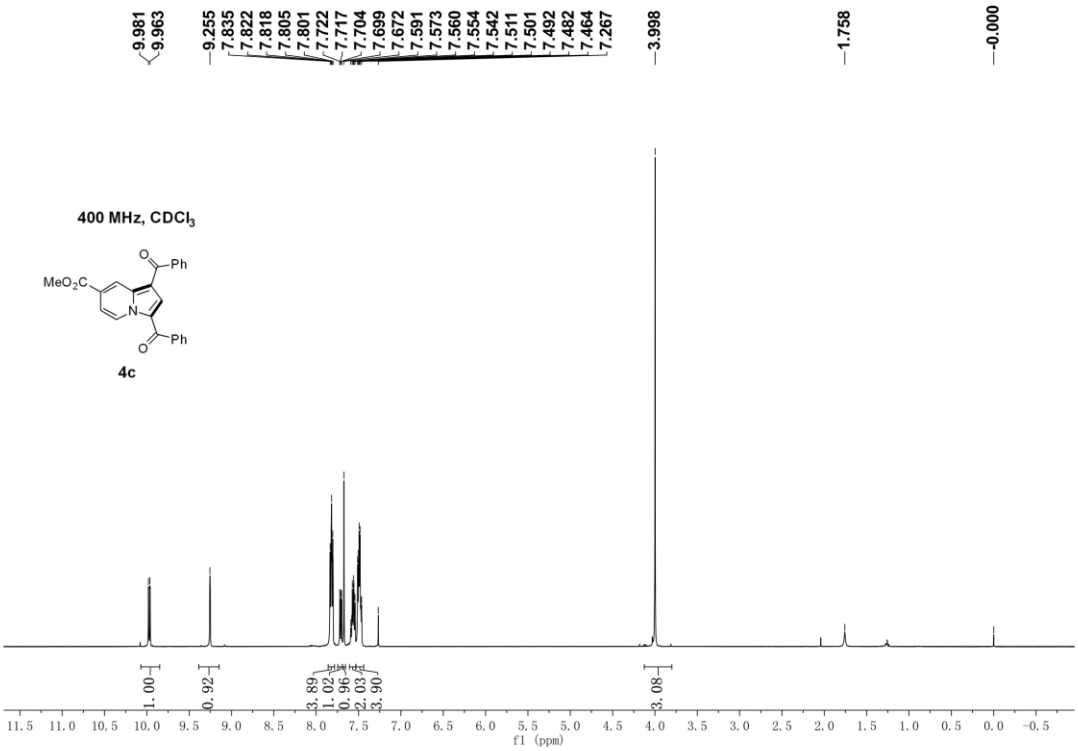

190.290
185.509
140.823
136.990
134.823
132.423
132.365
130.514
129.988
129.970
129.096
129.062
128.879
128.344
128.270
127.827
127.736
126.736
126.610
125.358
125.325
122.670
120.403
116.307
113.964
77.318
77.000
76.682
100 MHz, CDCl3
3p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

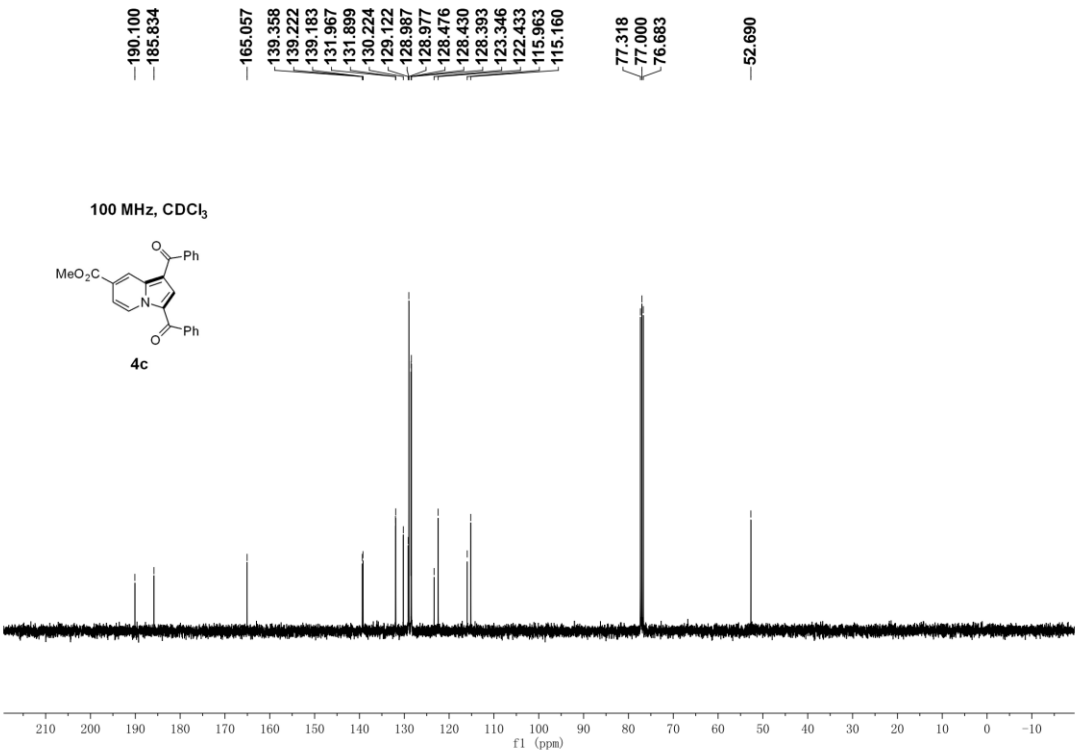

9.975
9.964
8.639
8.625
7.827
7.592
7.580
7.566
7.553
7.221
7.210
7.198
7.186
7.172
7.158
7.144
1.251
-0.000
600 MHz, CDCl3
3q
0.99
1.00
4.18
1.23
0.88
1.40
3.94
f1 (ppm)

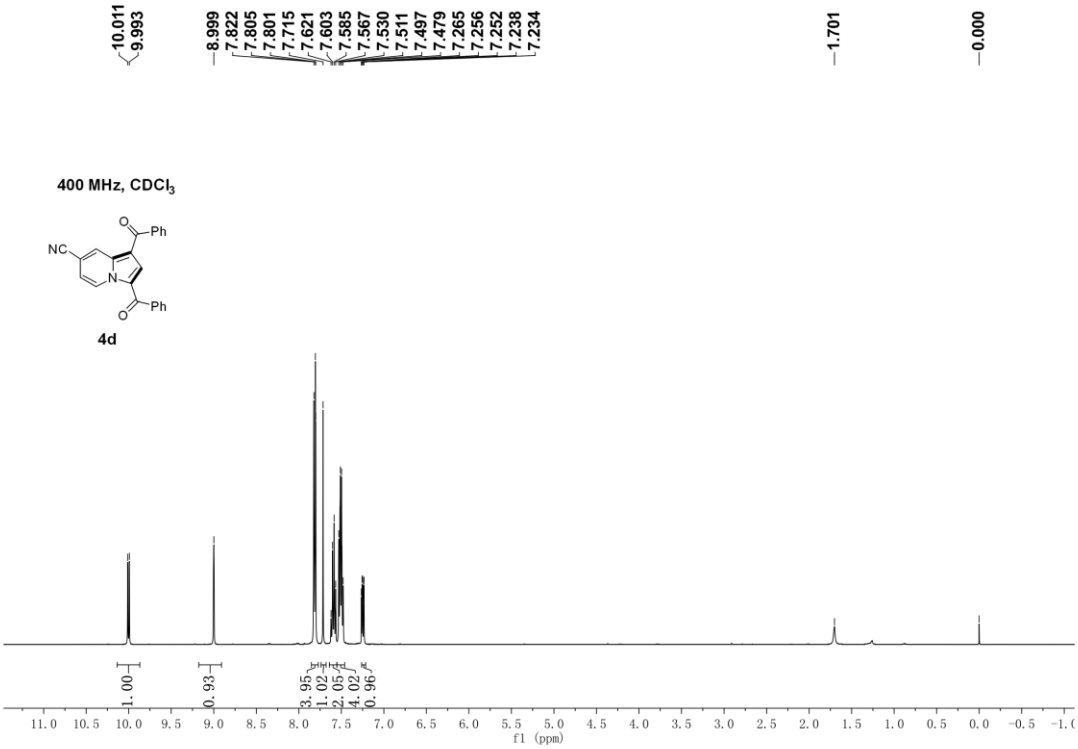

188.812
184.045
165.596
163.919
140.762
135.917
135.720
131.250
131.192
129.874
129.158
122.138
120.261
116.471
115.626
115.542
115.482
115.398
113.372
77.213
77.000
76.788
150 MHz, CDCl3
3q
f1 (ppm)

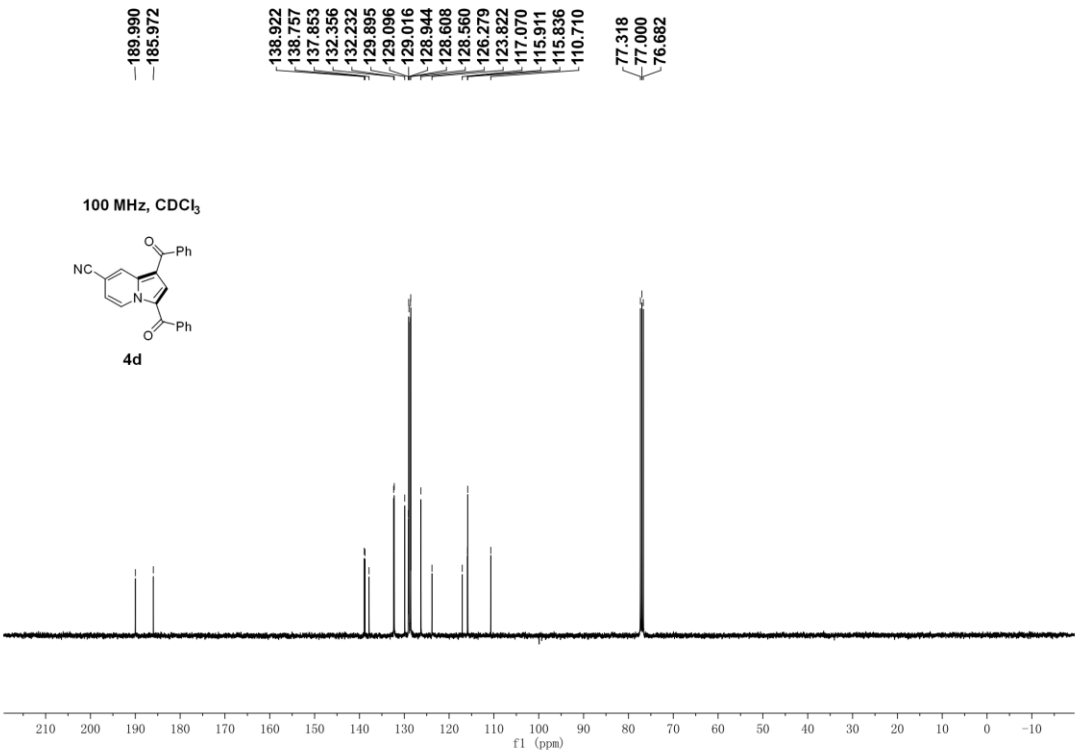

9.820
7.918
7.901
7.897
7.769
7.751
7.748
7.548
7.529
7.496
7.477
7.472
7.452
7.434
7.431
7.413
7.402
7.258
7.137
2.581
2.429
0.000
400 MHz, CDCl3
Me
Ph
Me
Ph
4a
1.00
2.06
2.08
1.24
5.20
0.93
1.02
3.13
3.16
f1 (ppm)

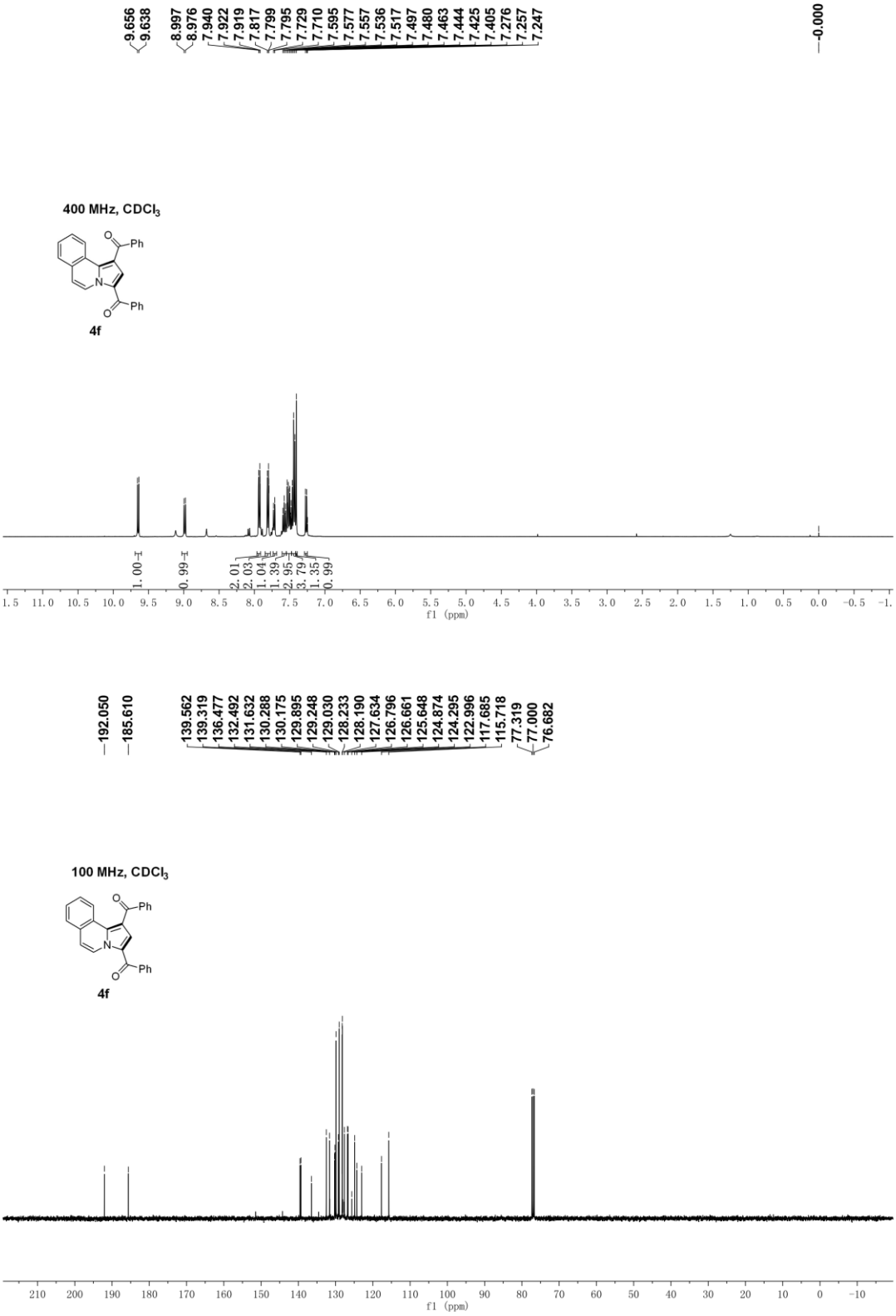

190.362
185.129
140.181
139.343
137.965
132.368
132.085
131.239
130.868
130.082
129.401
128.895
128.237
125.631
125.006
121.298
115.990
77.318
77.000
76.682
21.057
18.342
100 MHz, CDCl3
Me
Ph
Me
Ph
4a
f1 (ppm)


9.981
9.963
9.255
7.835
7.822
7.818
7.805
7.801
7.722
7.717
7.704
7.699
7.672
7.591
7.573
7.560
7.554
7.542
7.511
7.501
7.492
7.482
7.464
7.267
3.998
1.758
0.000
400 MHz, CDCl3
MeO2C
Ph
Ph
4c
1.00
0.92
3.89
1.02
0.96
2.03
3.90
3.08
f1 (ppm)


190.100
185.834
165.057
139.358
139.222
139.183
131.967
131.899
130.224
129.122
128.987
128.977
128.476
128.430
128.393
123.346
122.433
115.963
115.160
77.318
77.000
76.683
52.690
100 MHz, CDCl3
MeO2C
Ph
Ph
4c
f1 (ppm)


10.011
9.993
8.999
7.822
7.805
7.801
7.715
7.621
7.603
7.585
7.567
7.530
7.511
7.497
7.479
7.265
7.256
7.252
7.238
7.234
1.701
0.000
400 MHz, CDCl3
NC
Ph
Ph
4d
1.00
0.93
3.95
1.02
2.05
4.02
0.96
f1 (ppm)


189.990
185.972
138.922
138.757
137.853
132.356
132.232
129.895
129.096
129.016
128.944
128.608
128.560
126.279
123.822
117.070
115.911
115.836
110.710
77.318
77.000
76.682
100 MHz, CDCl3
NC
Ph
Ph
4d
f1 (ppm)


9.656
9.638
8.997
8.976
7.940
7.922
7.919
7.817
7.799
7.795
7.729
7.710
7.595
7.577
7.557
7.536
7.517
7.497
7.480
7.463
7.444
7.425
7.405
7.276
7.257
7.247
0.000
400 MHz, CDCl3
Ph
Ph
4f
1.00
0.99
2.01
2.03
1.04
1.39
2.95
3.79
1.35
0.99
f1 (ppm)
192.050
185.610
139.562
139.319
136.477
132.492
131.632
130.288
130.175
129.895
129.248
129.030
128.233
128.190
127.634
126.796
126.661
125.648
124.874
124.295
122.996
117.685
115.718
77.319
77.000
76.682
100 MHz, CDCl3
Ph
Ph
4f
f1 (ppm)