

Supporting Information

Cu-catalysed synthesis of benzo[f]indole-2,4,9(3H)-triones by reaction of 2-amino-1,4-naphthoquinones with α -bromocarboxylates

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^a Department of Applied Chemistry, China Agricultural University, 2 Yuanmingyuan West Road, Beijing 100193, China.

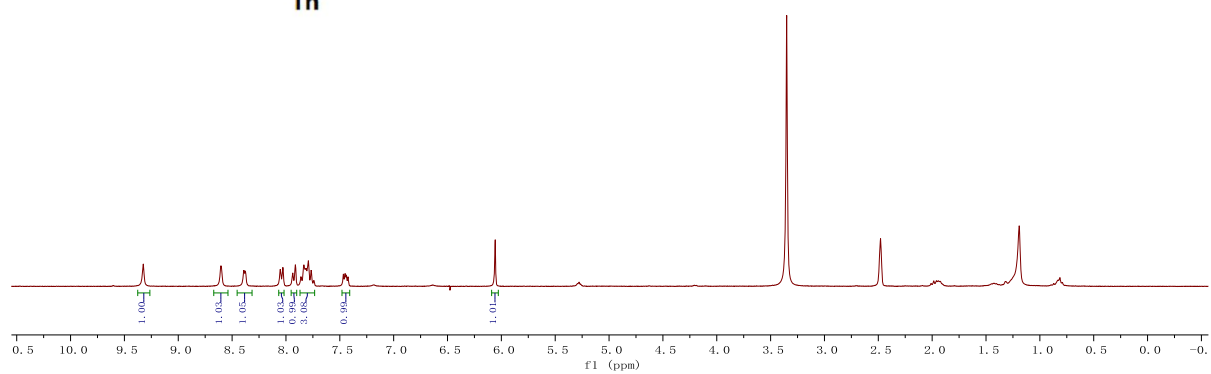
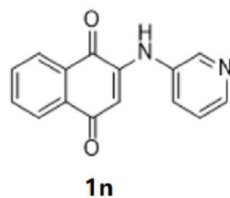
^b College of public health, Zhengzhou University, Zhengzhou 450001, China

Table of Contents

Copies of ¹H NMR and ¹³C NMR spectra.....	S1
Single crystallographic data for compound 3aa.....	S44

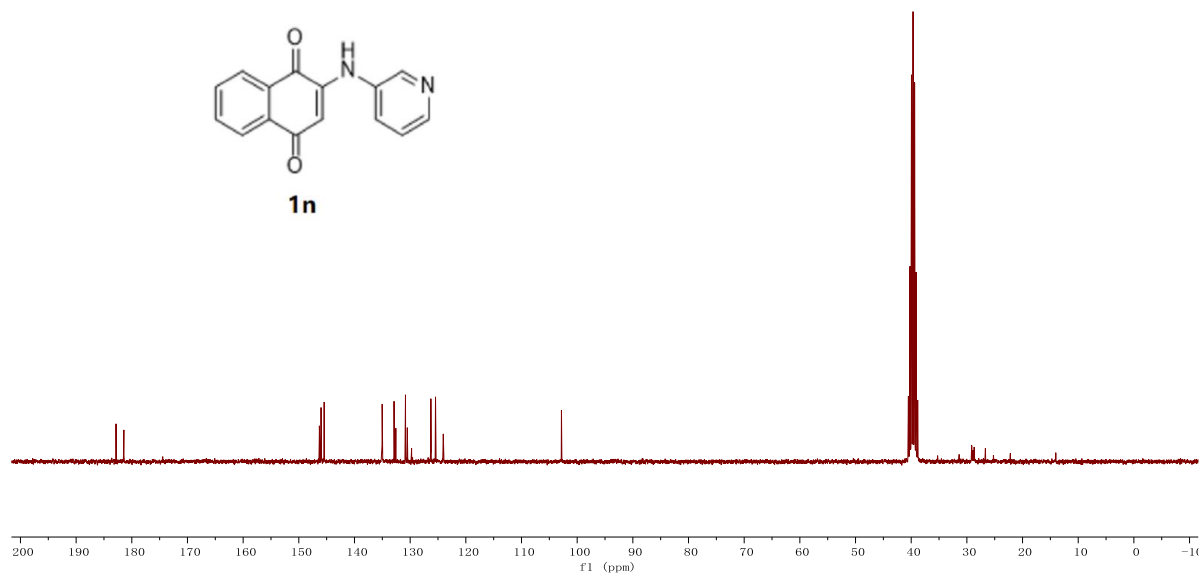
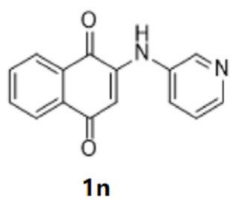
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7.857
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7.819
7.798
7.794
7.786
7.786
7.761
7.467
7.451
7.423
6.058

^1H NMR in $\text{DMSO-}d_6$ for **1n**



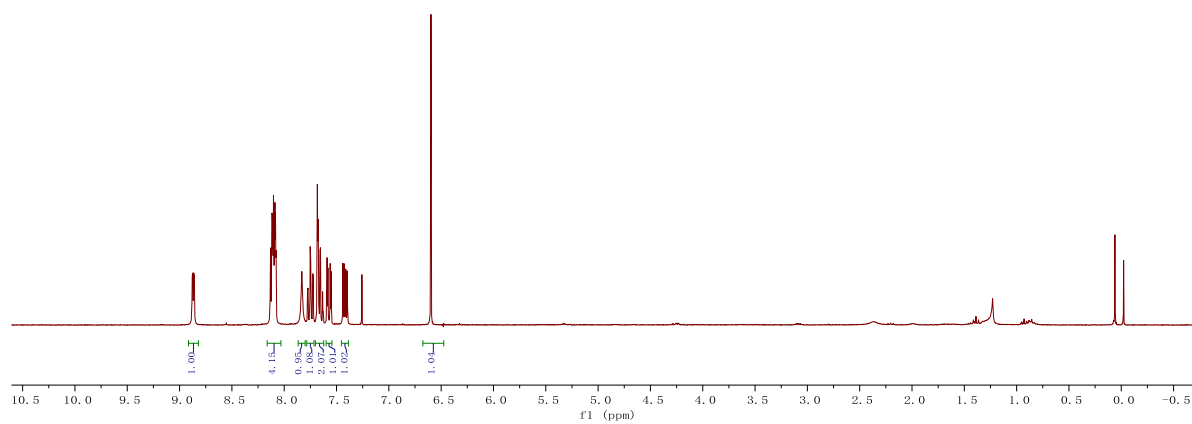
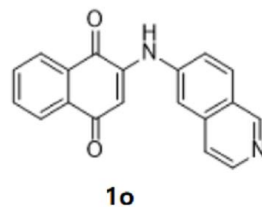
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146.305
146.004
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126.278
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102.823

^{13}C NMR in $\text{DMSO-}d_6$ for **1n**



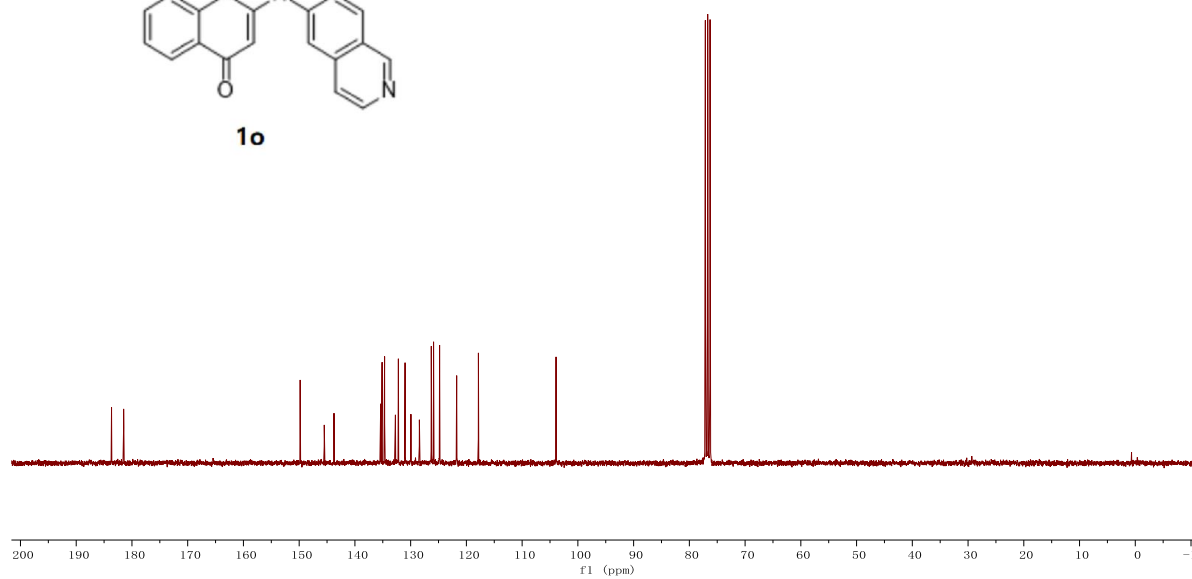
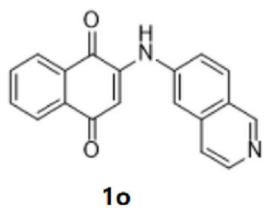
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8.873
8.865
8.858
8.850
8.820
8.818
8.813
8.809
8.807
8.806
8.805
8.800
8.888
8.884
8.879
8.877
8.851
8.831
7.777
7.772
7.772
7.767
7.747
7.727
7.722
7.722
7.675
7.679
7.658
7.654
7.653
7.659
7.652
7.582
7.561
7.552
7.552
7.425
7.411
7.411
7.397
1.0397

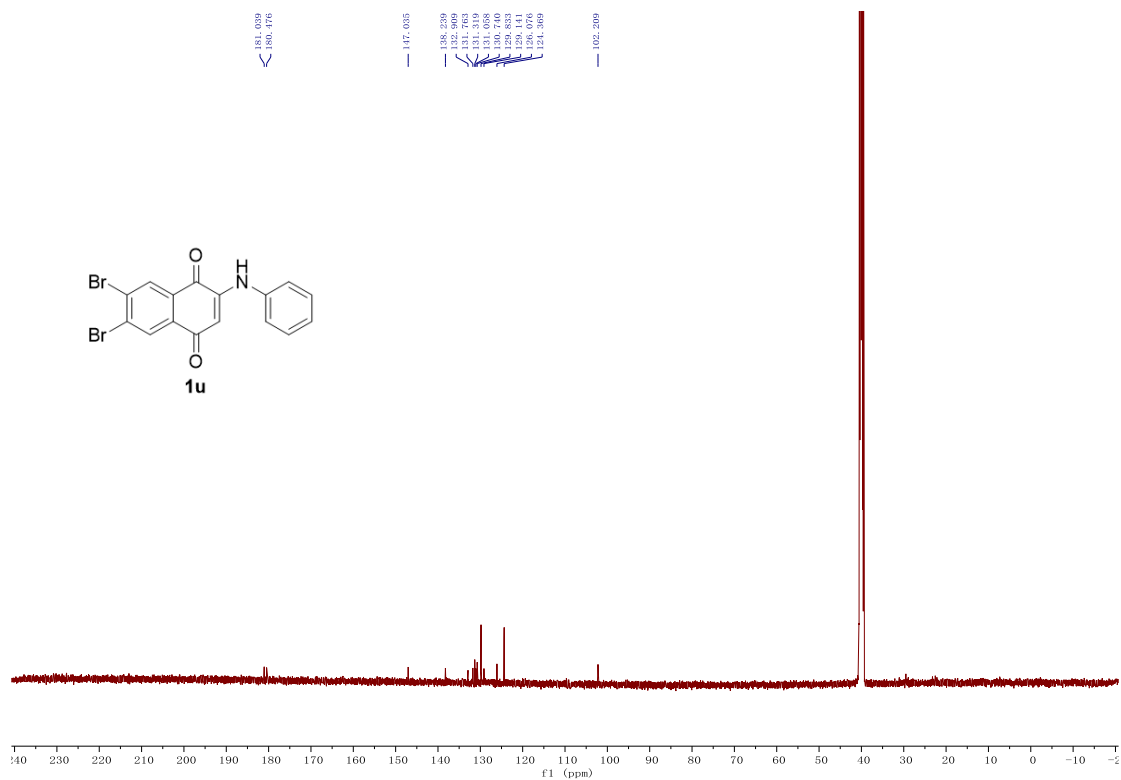
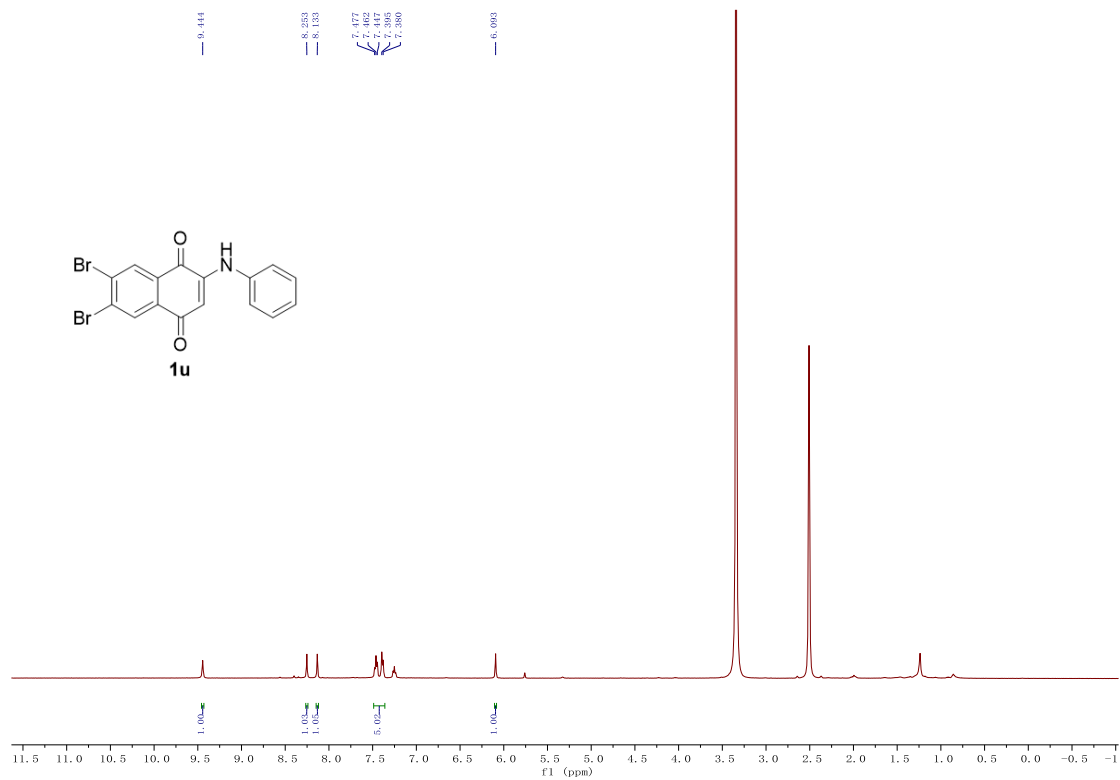
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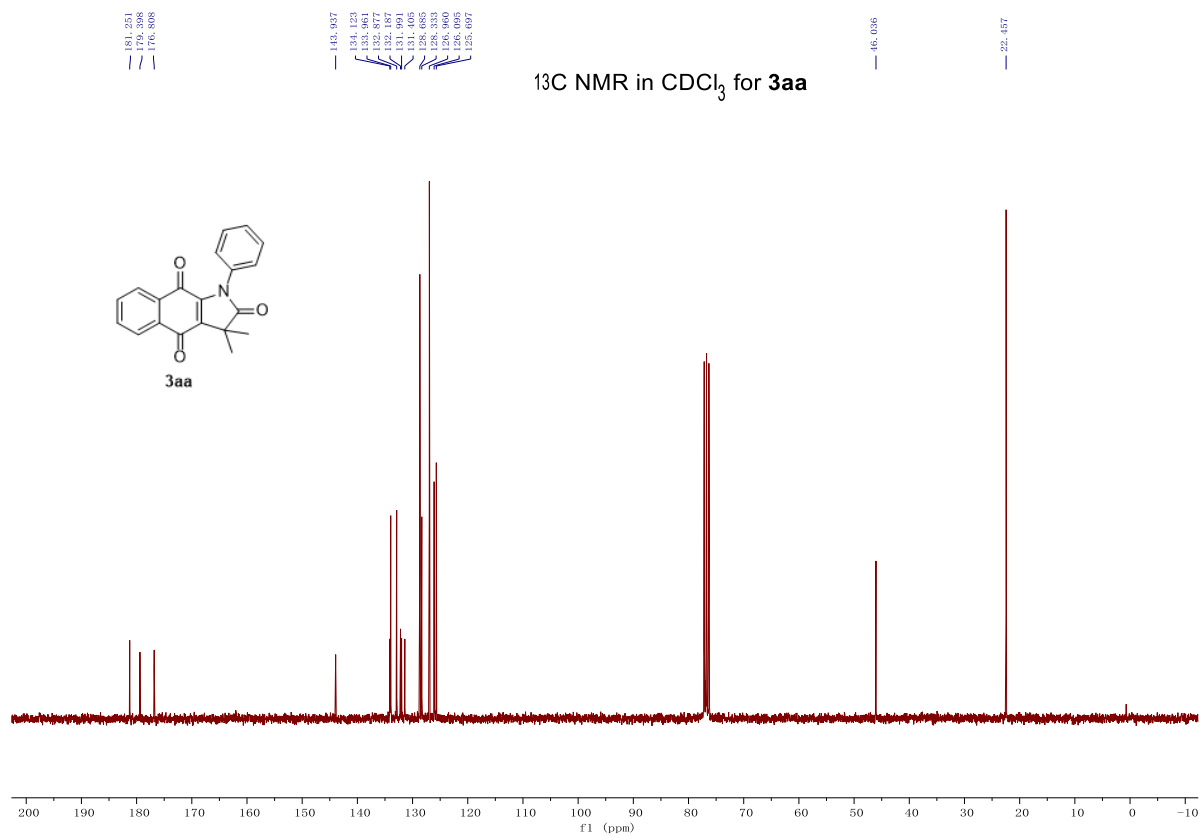
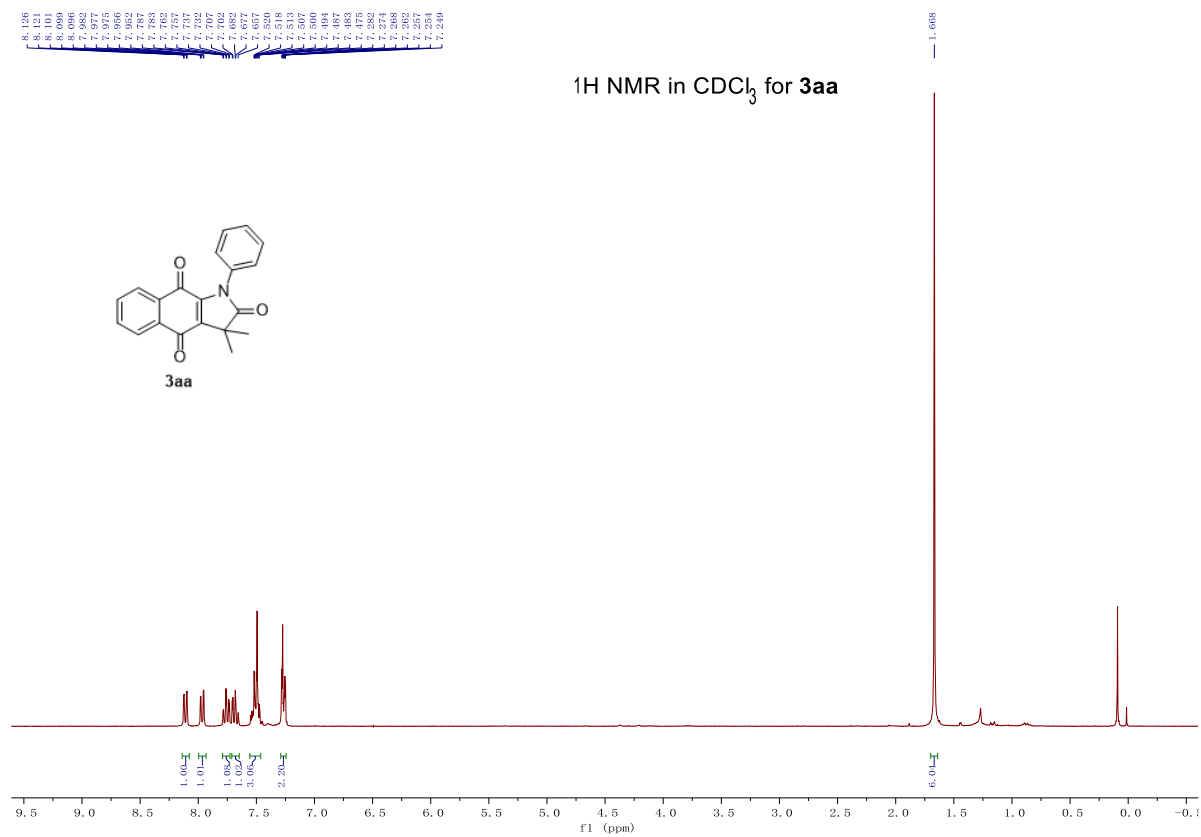


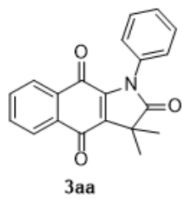
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151.492
149.821
145.099
143.752
135.375
135.125
134.674
132.535
132.235
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125.891
124.897
117.842
103.915

¹³C NMR in CDCl₃ for **1o**

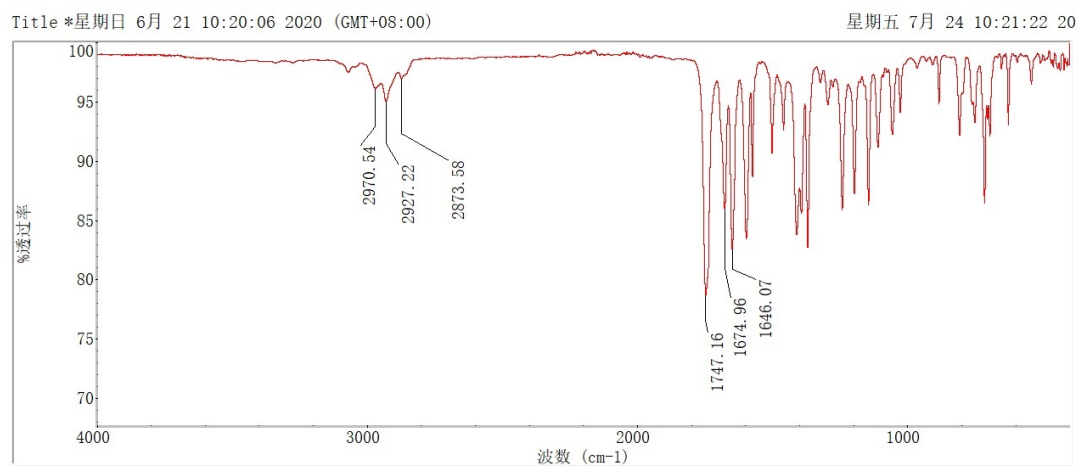




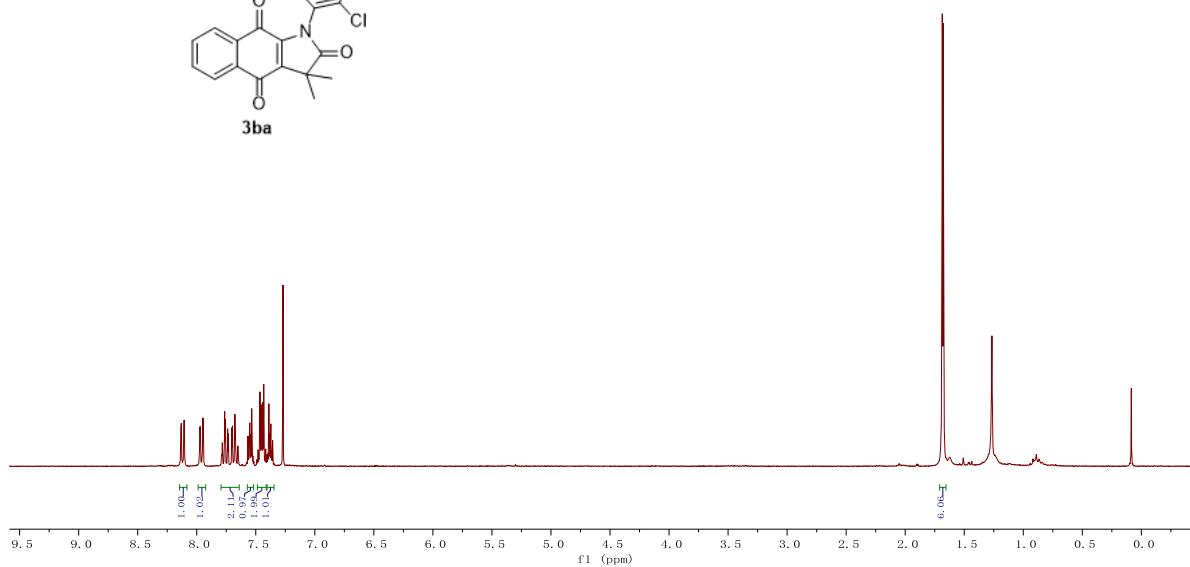
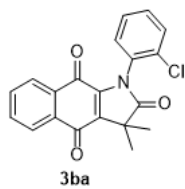


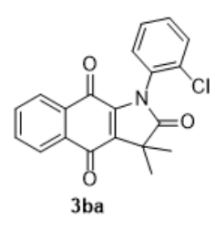
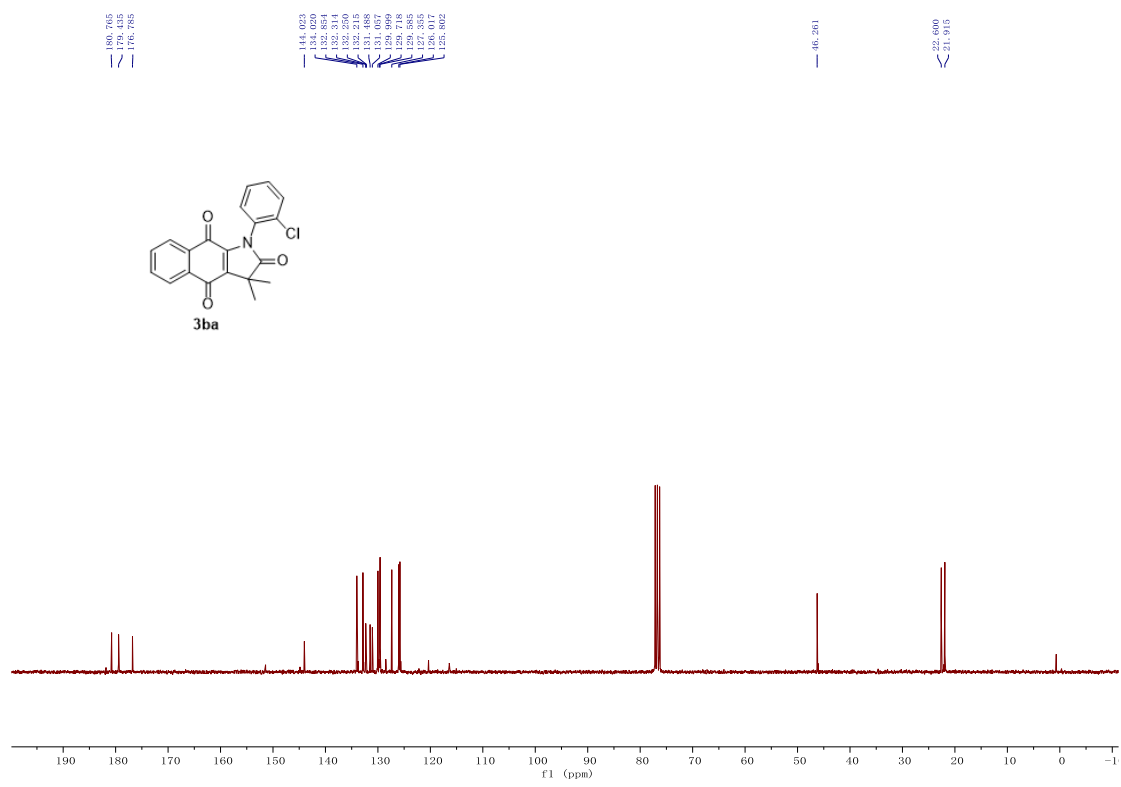


IR (KBr) spectrum of compound **3aa**

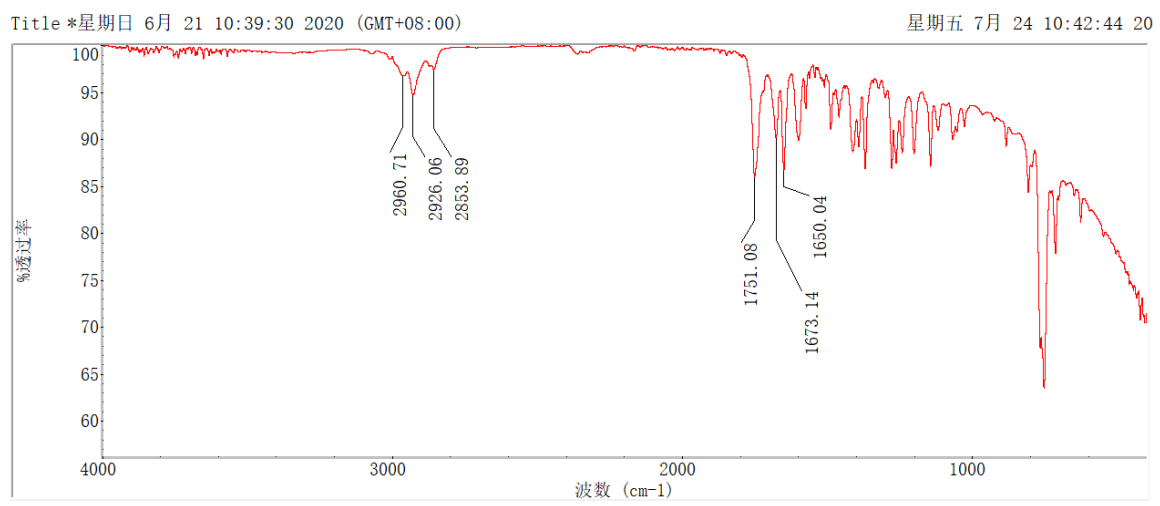


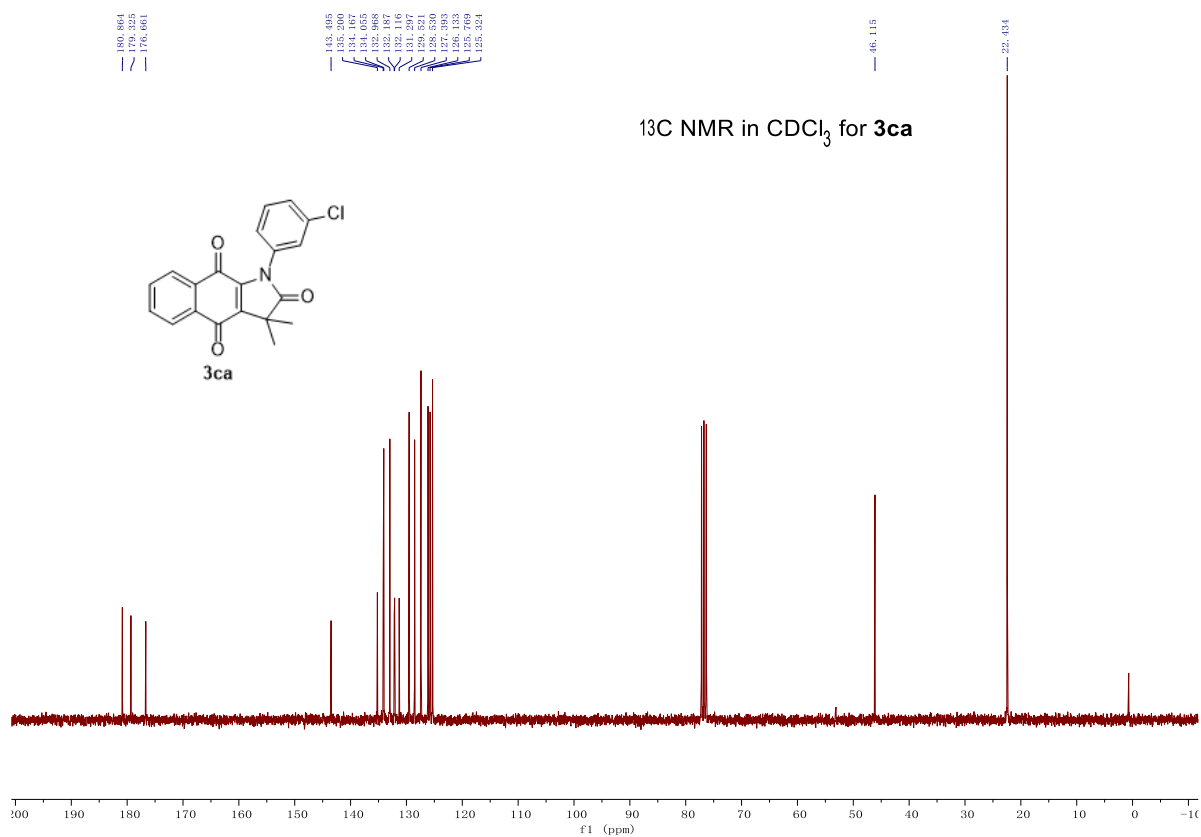
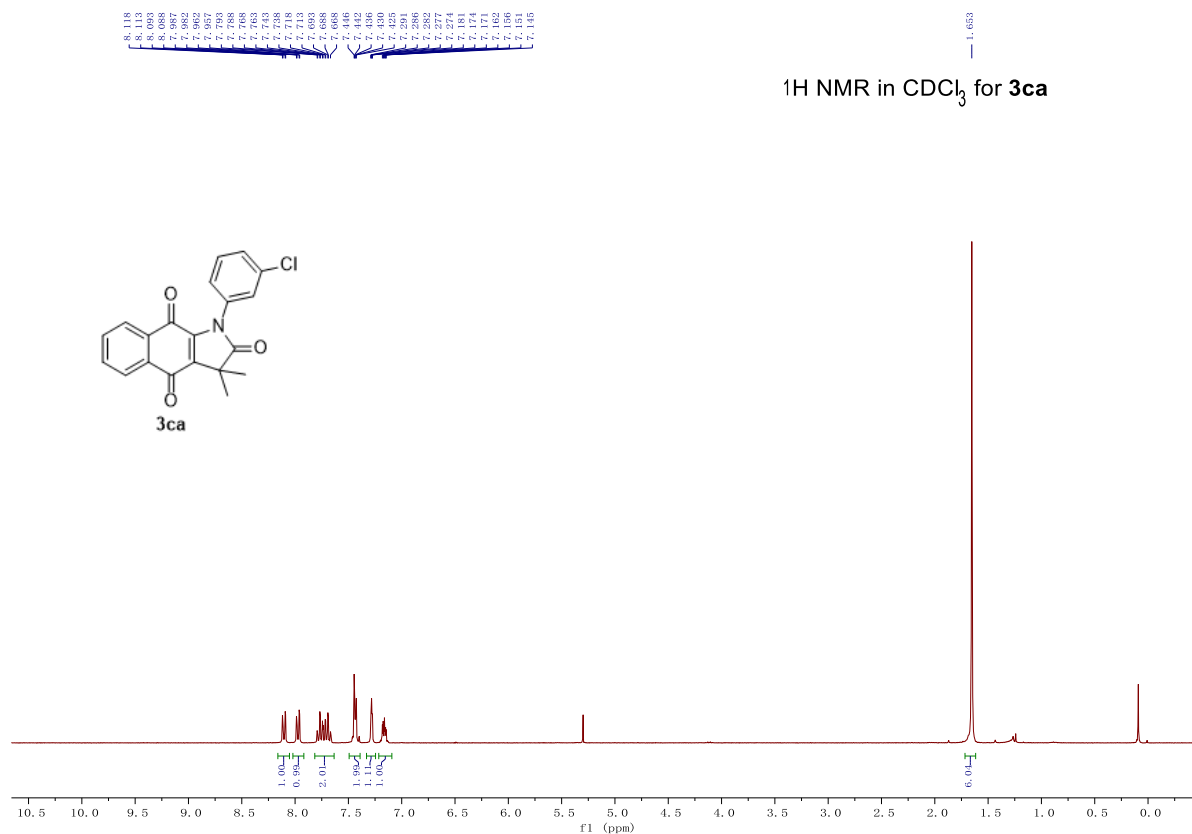
¹H NMR in CDCl₃ for **3ba**

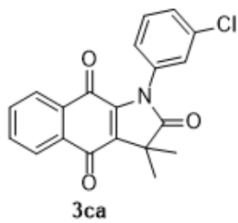




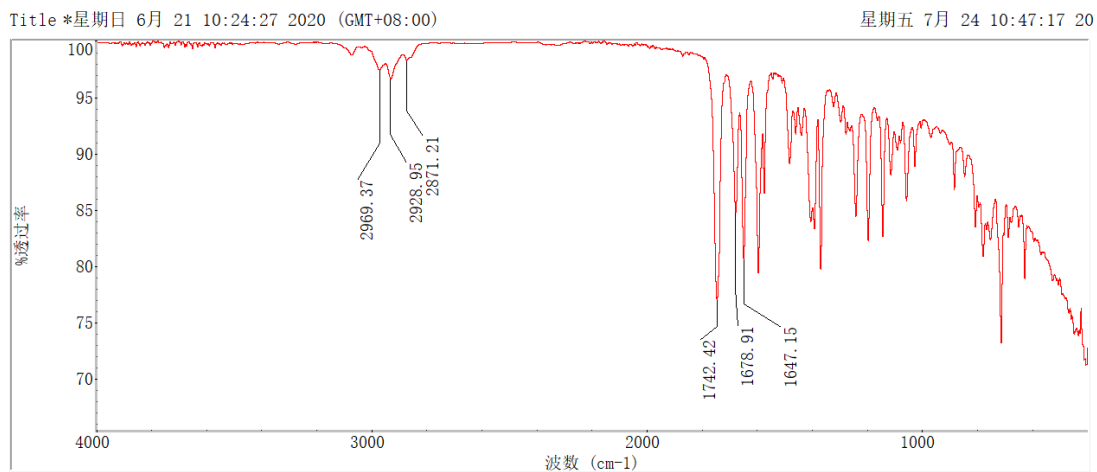
IR (KBr) spectrum of compound **3ba**



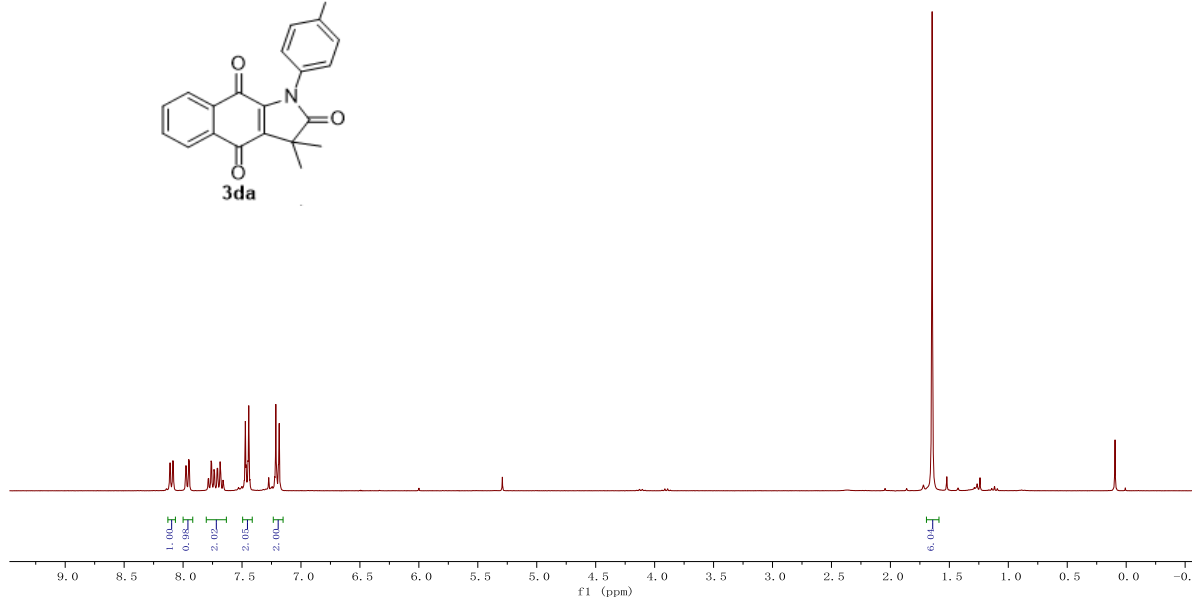
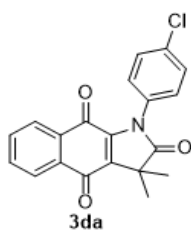




IR (KBr) spectrum for compound **3ca**



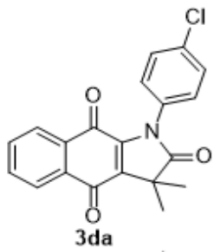
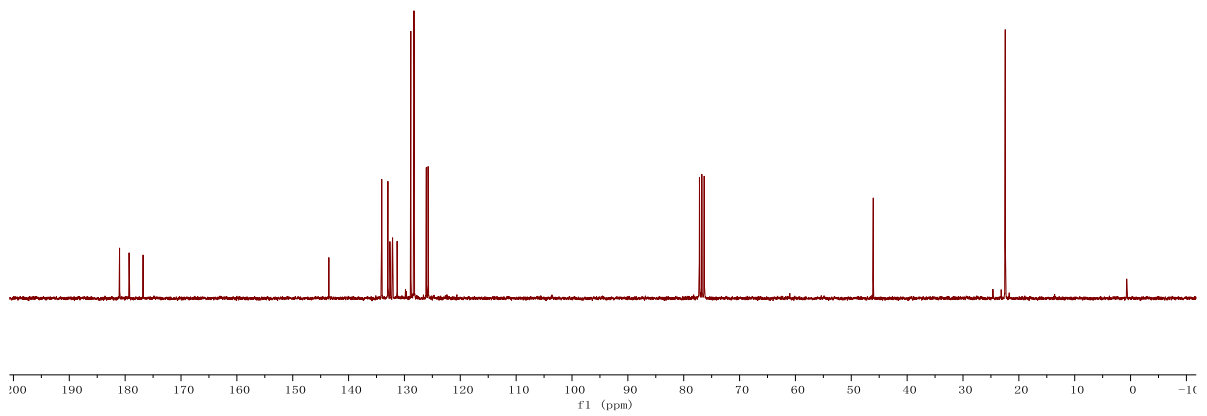
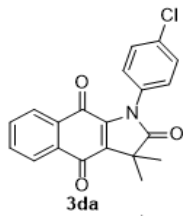
¹H NMR in CDCl₃ for **3da**



181.006
179.299
176.792

145.532
134.102
133.972
132.959
132.601
132.195
131.309
128.860
126.964
125.763

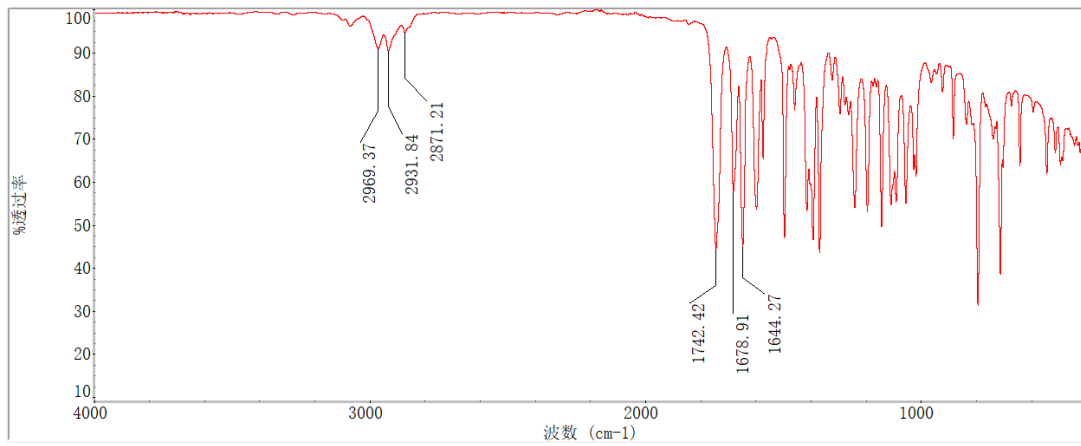
46.063
22.431
¹³C NMR in CDCl₃ for 3da

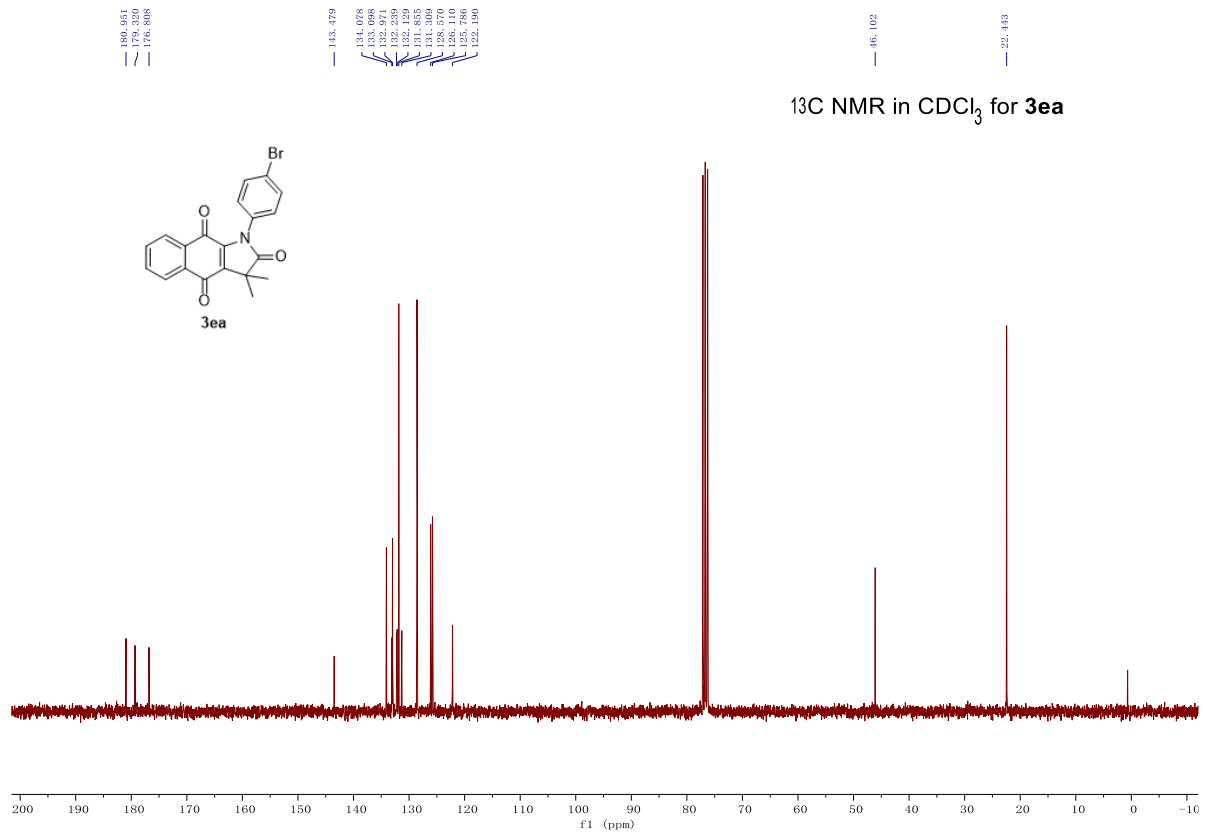
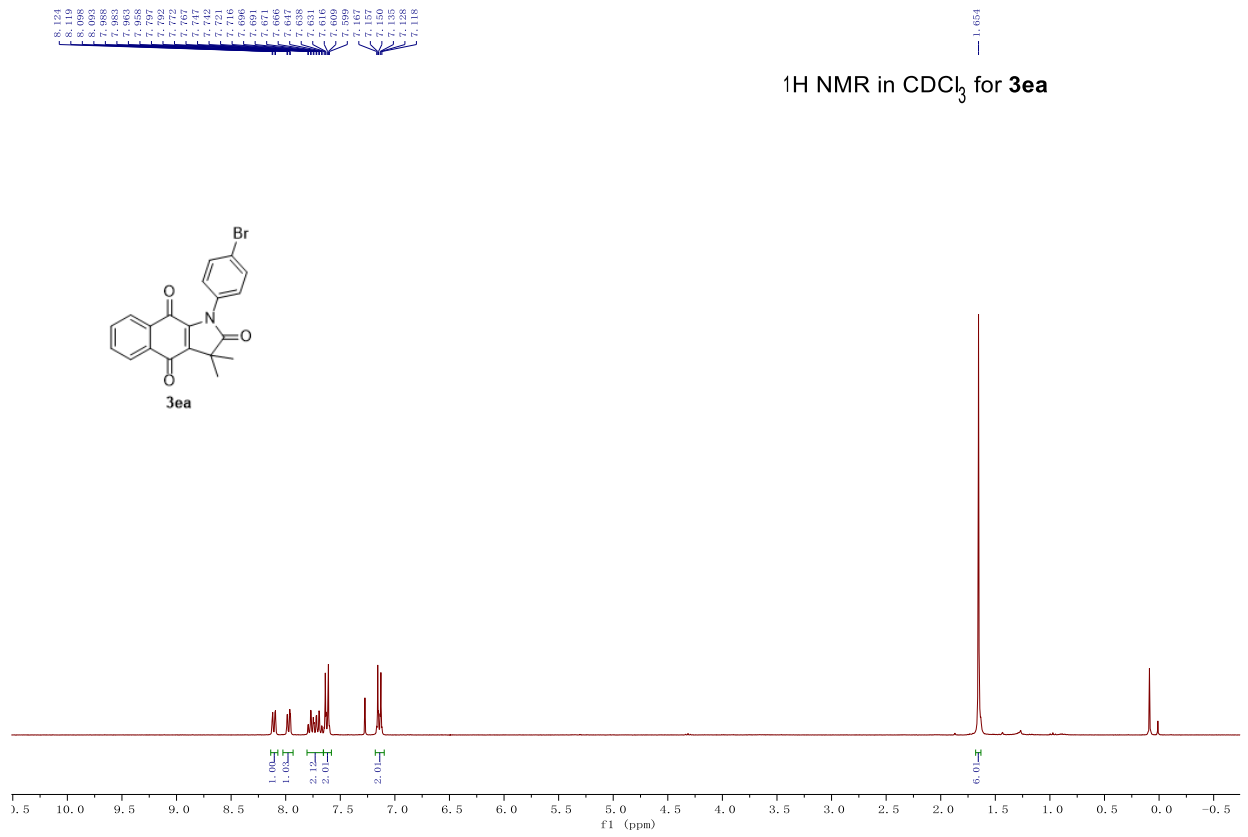


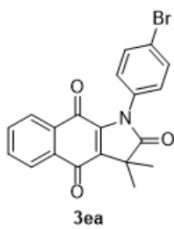
IR (KBr) spectrum for compound
3da

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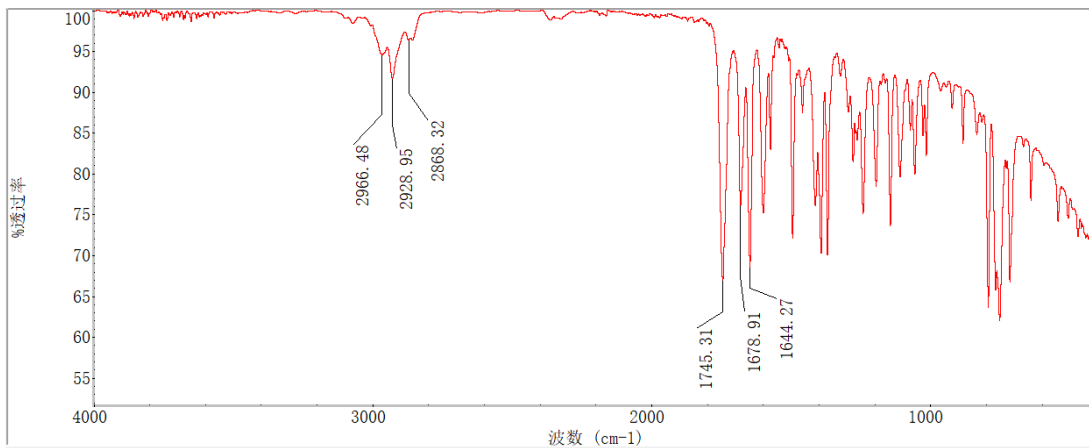




IR (KBr) spectrum for compound **3ea**

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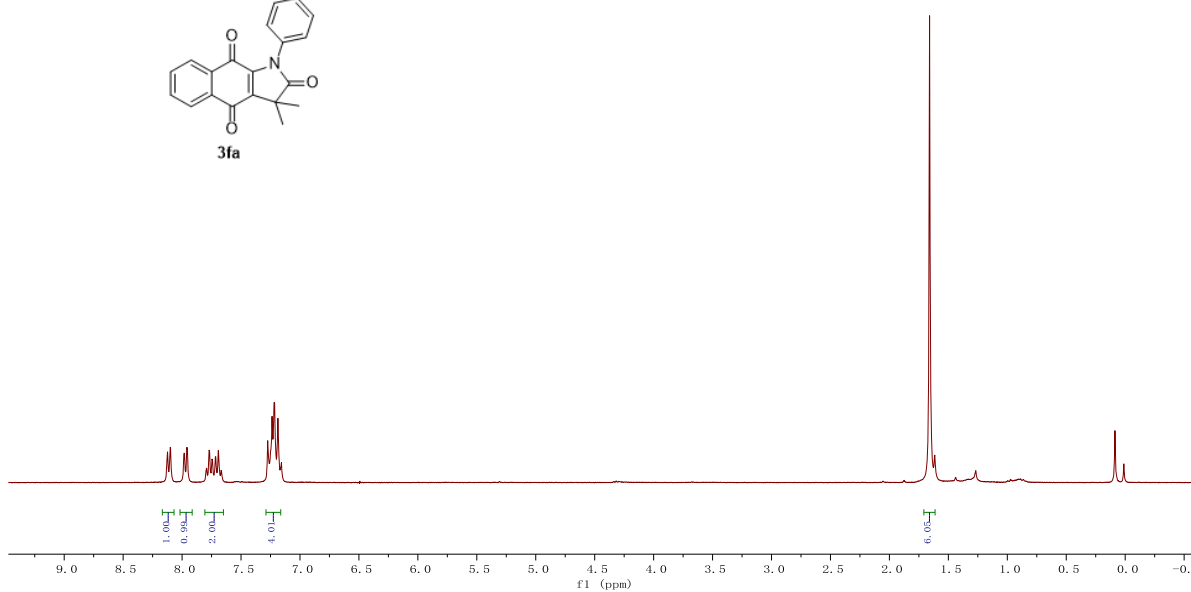
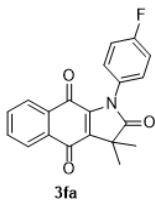
星期五 7月 24 10:54:15 20



8.137
8.122
8.107
7.985
7.980
7.965
7.796
7.791
7.766
7.746
7.718
7.713
7.693
7.688
7.664
7.574
7.559
7.537
7.514
7.487

1.659

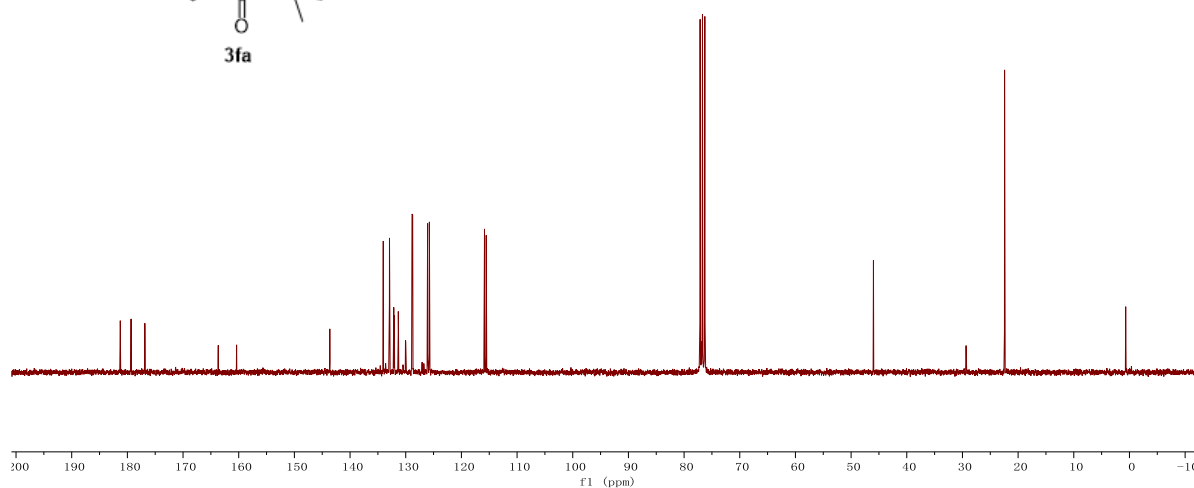
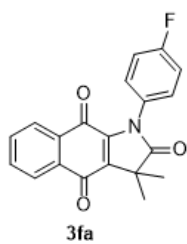
¹H NMR in CDCl₃ for **3fa**



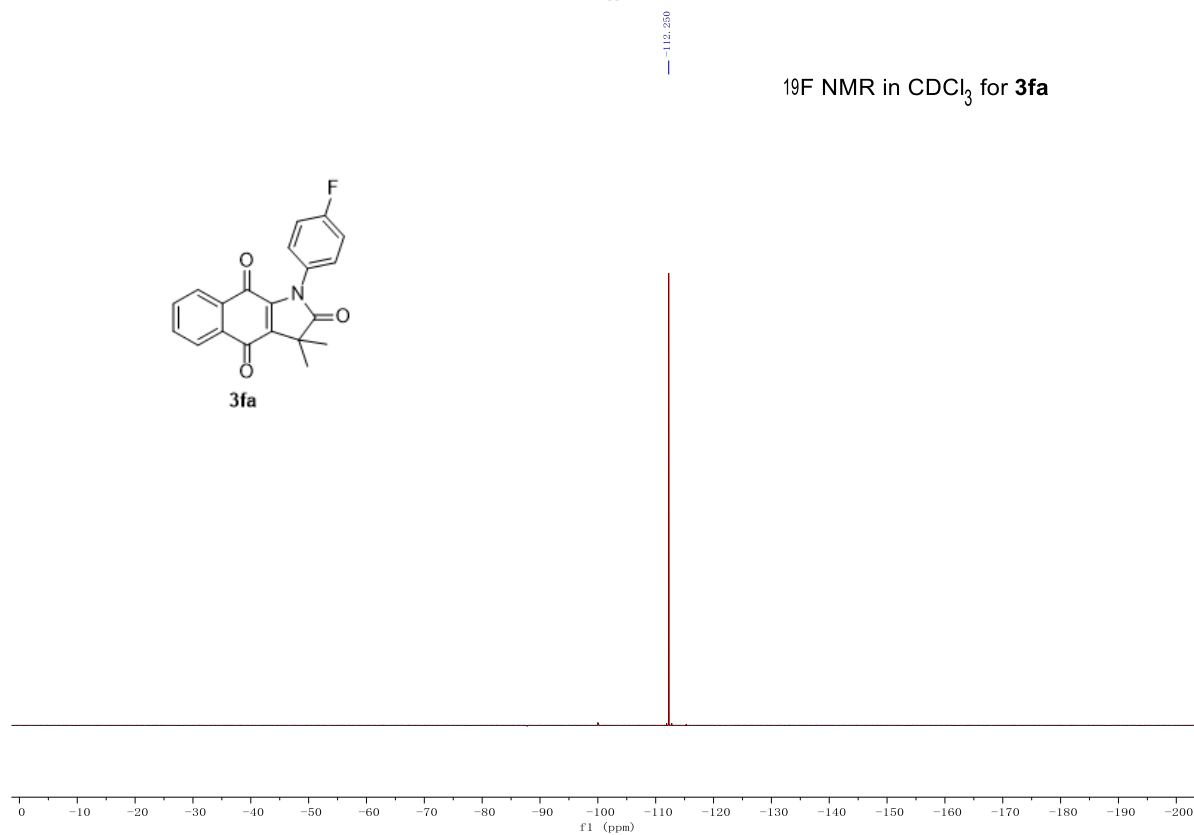
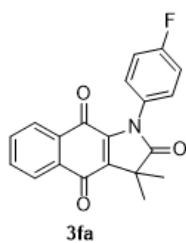
181.274
179.335
176.866
165.673
160.381
145.639
134.037
133.726
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131.822
130.023
129.998
128.869
128.672
126.068
125.751
115.850
115.544

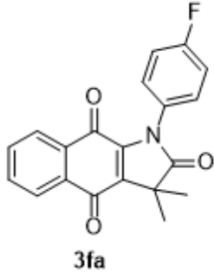
45.985
22.430

^{13}C NMR in CDCl_3 for **3fa**



^{19}F NMR in CDCl_3 for **3fa**

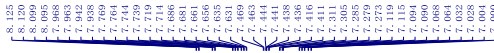
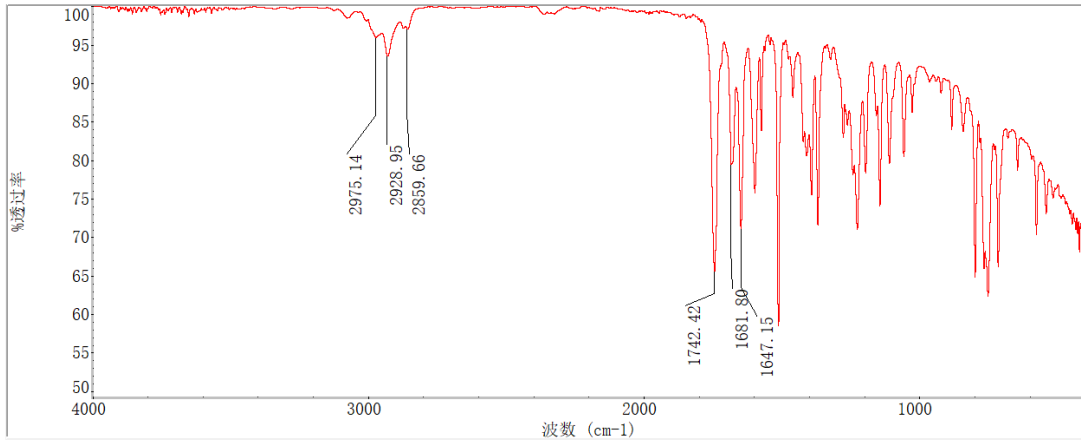




IR (KBr) spectrum for compound **3fa**

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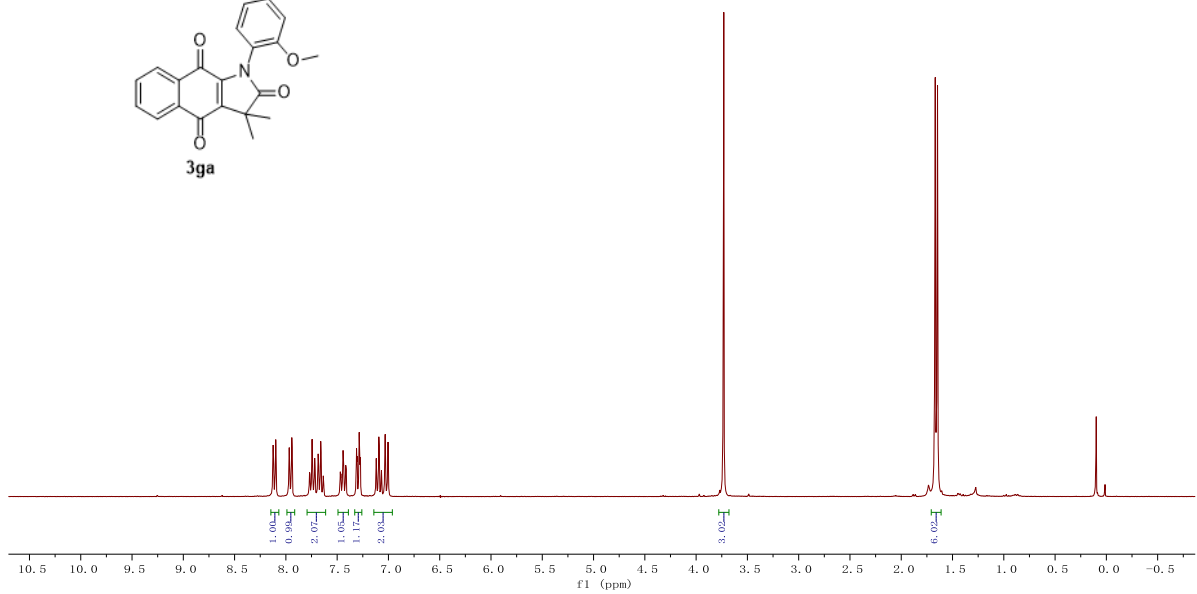
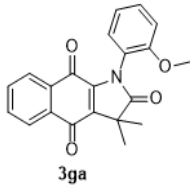
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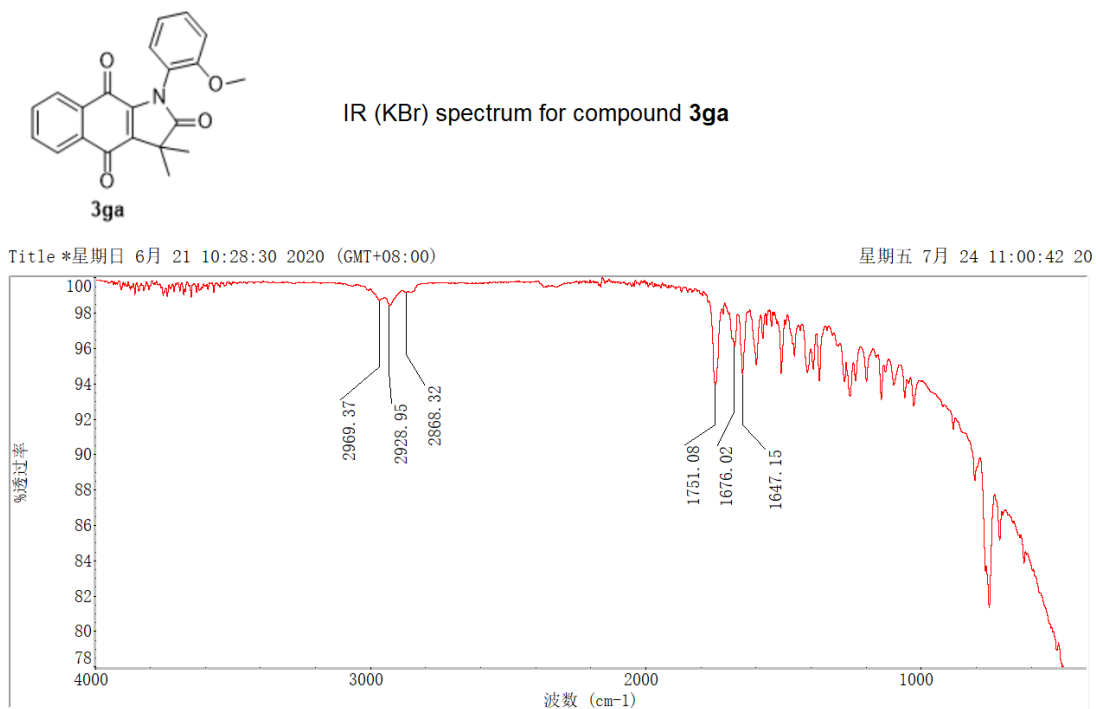
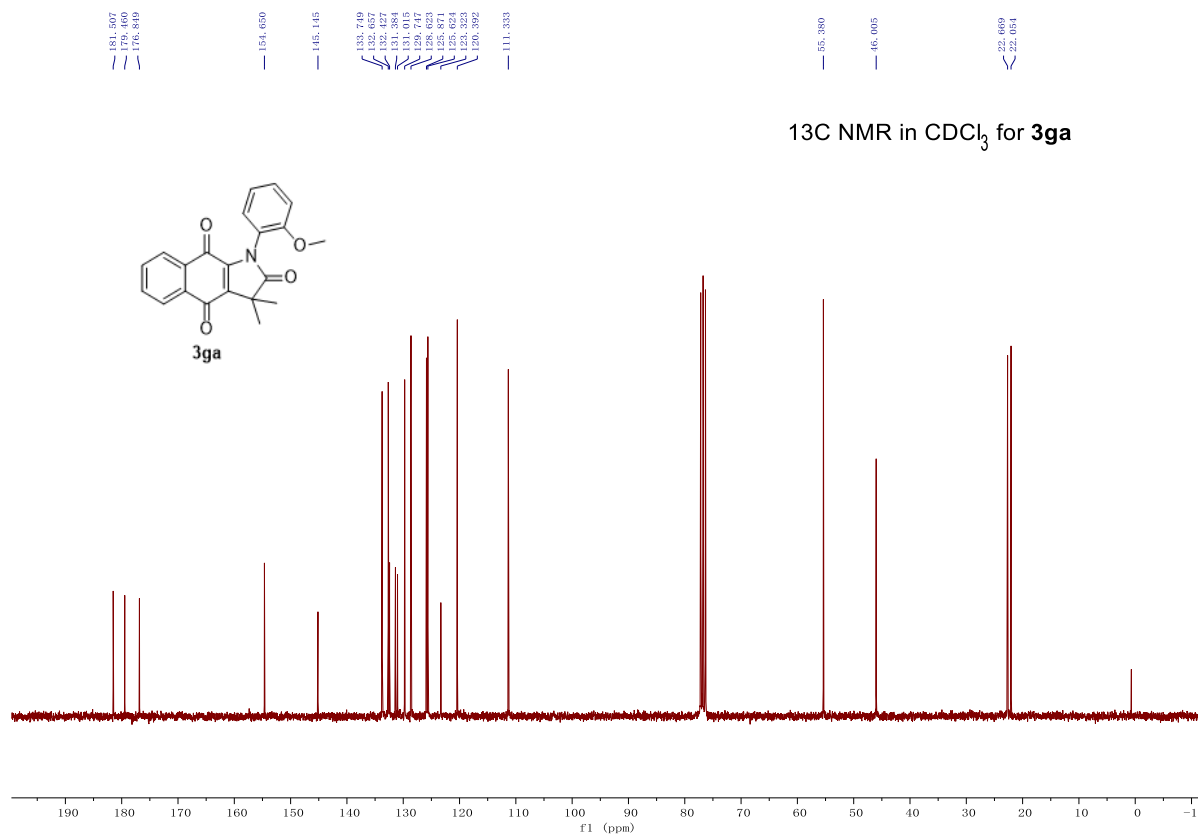


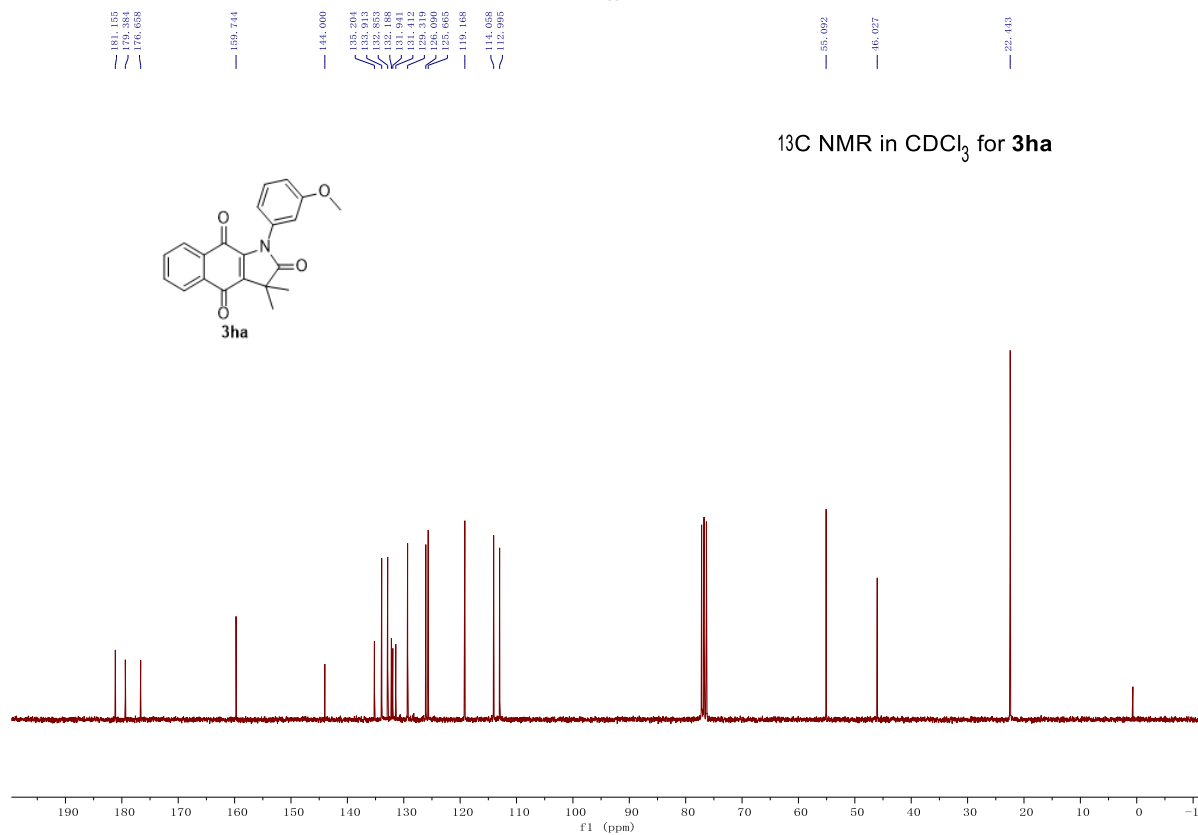
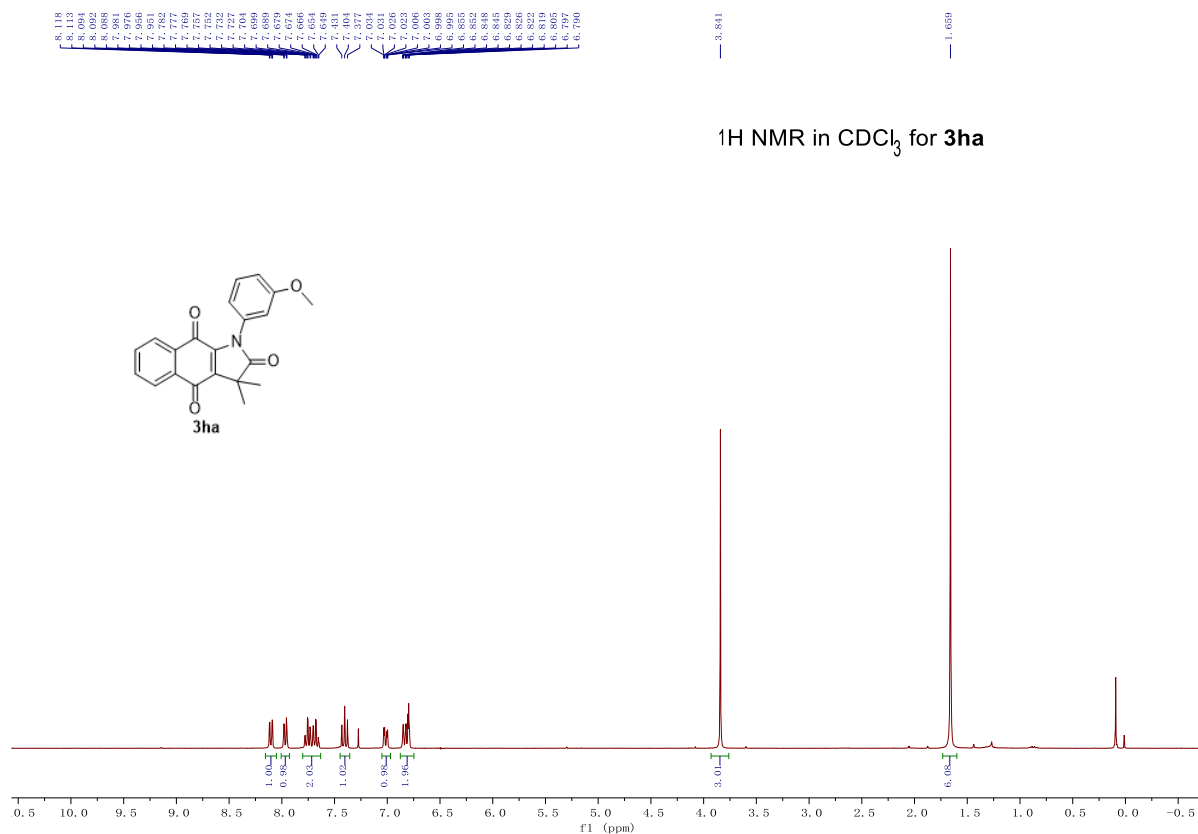
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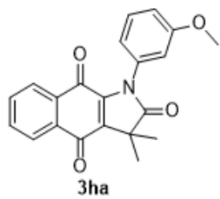
1.669
1.646

^1H NMR in CDCl_3 for **3ga**

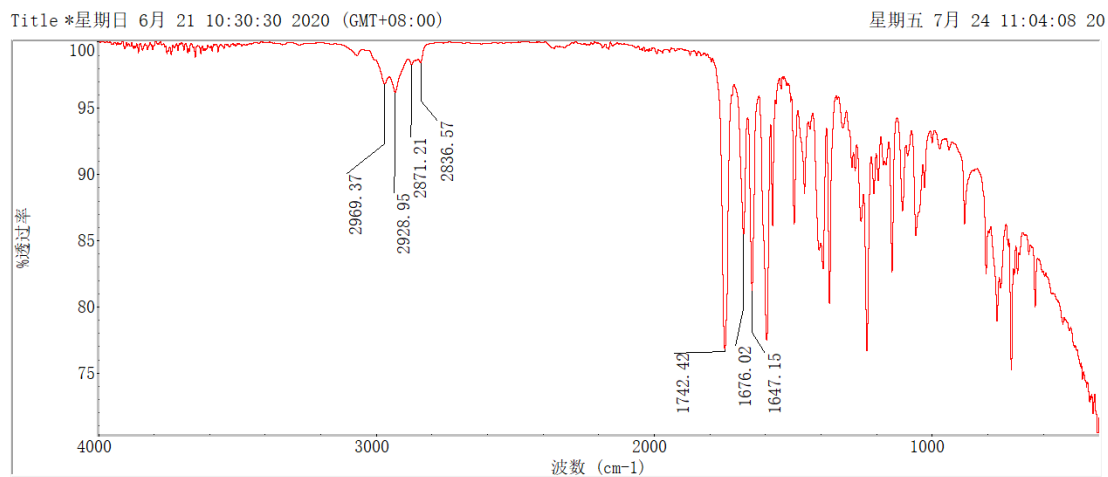








IR (KBr) spectrum for compound **3ha**

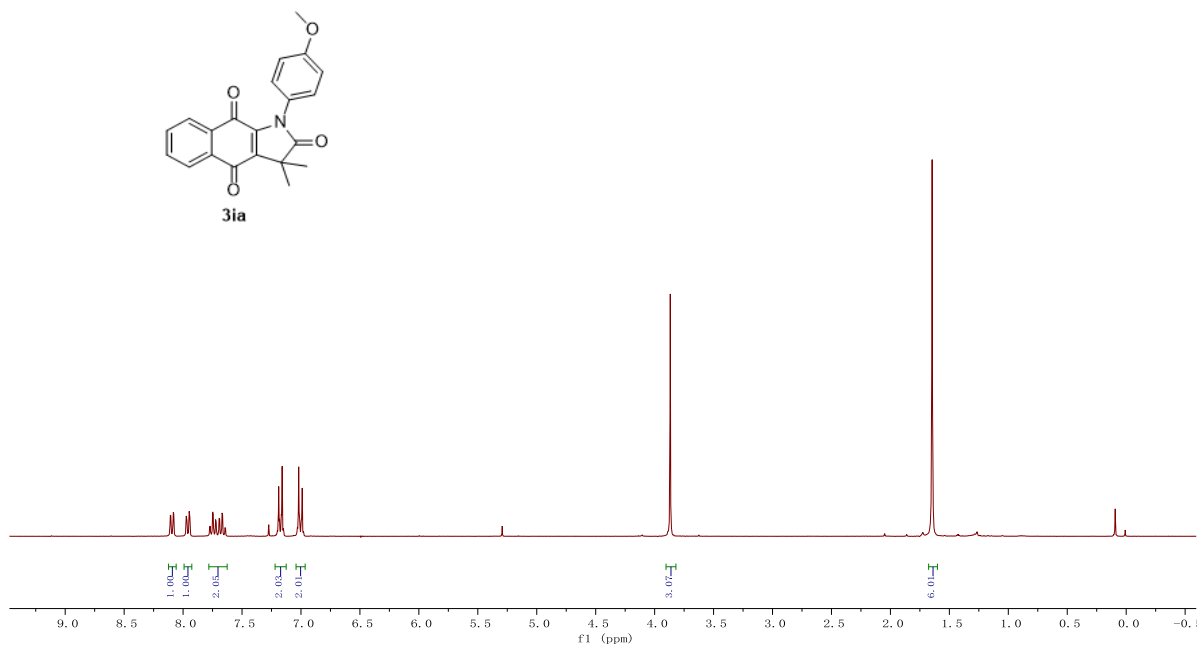


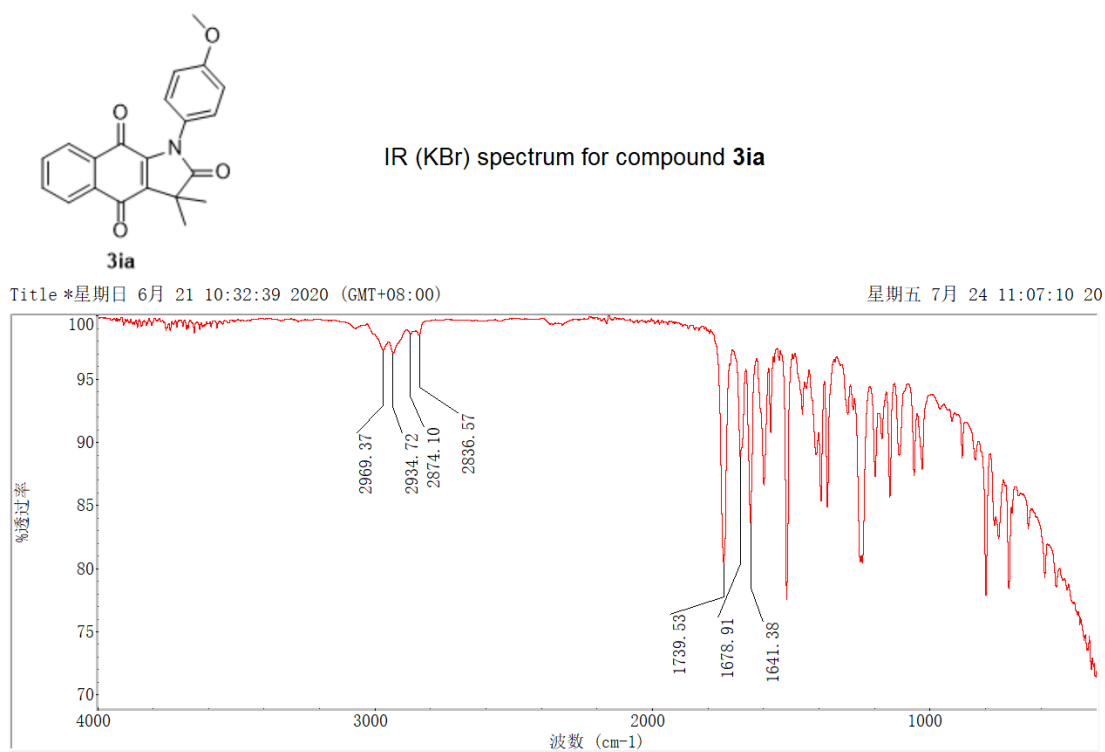
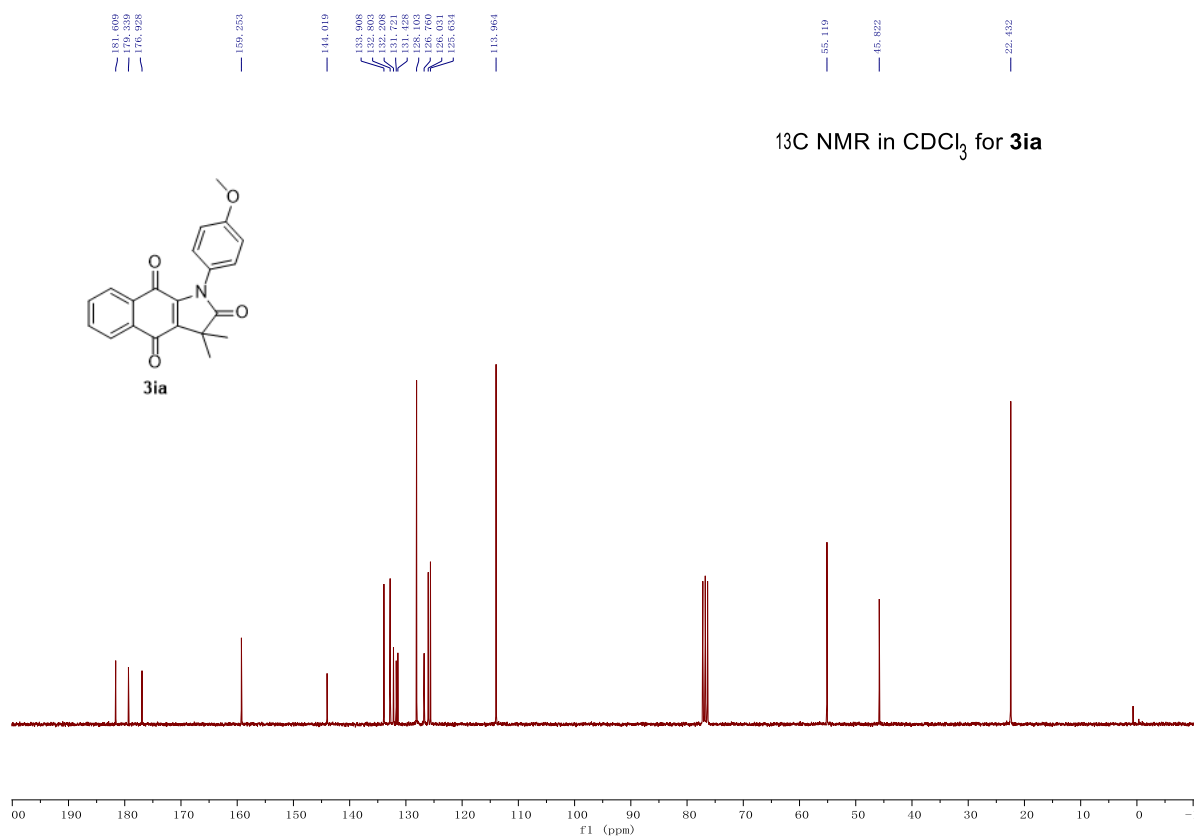
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8.106
8.083
8.078
7.968
7.968
7.948
7.943
7.749
7.749
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7.694
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7.664
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7.182
7.057
7.019
7.011
6.989

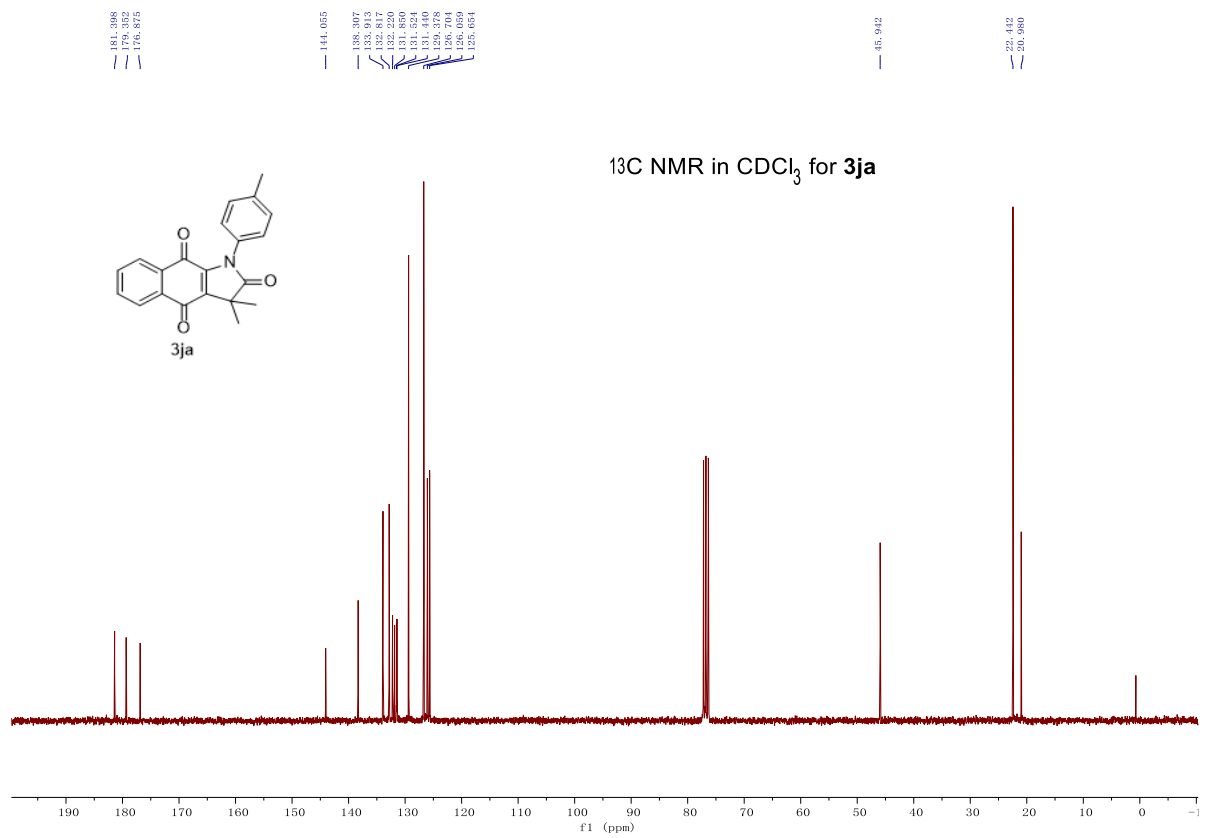
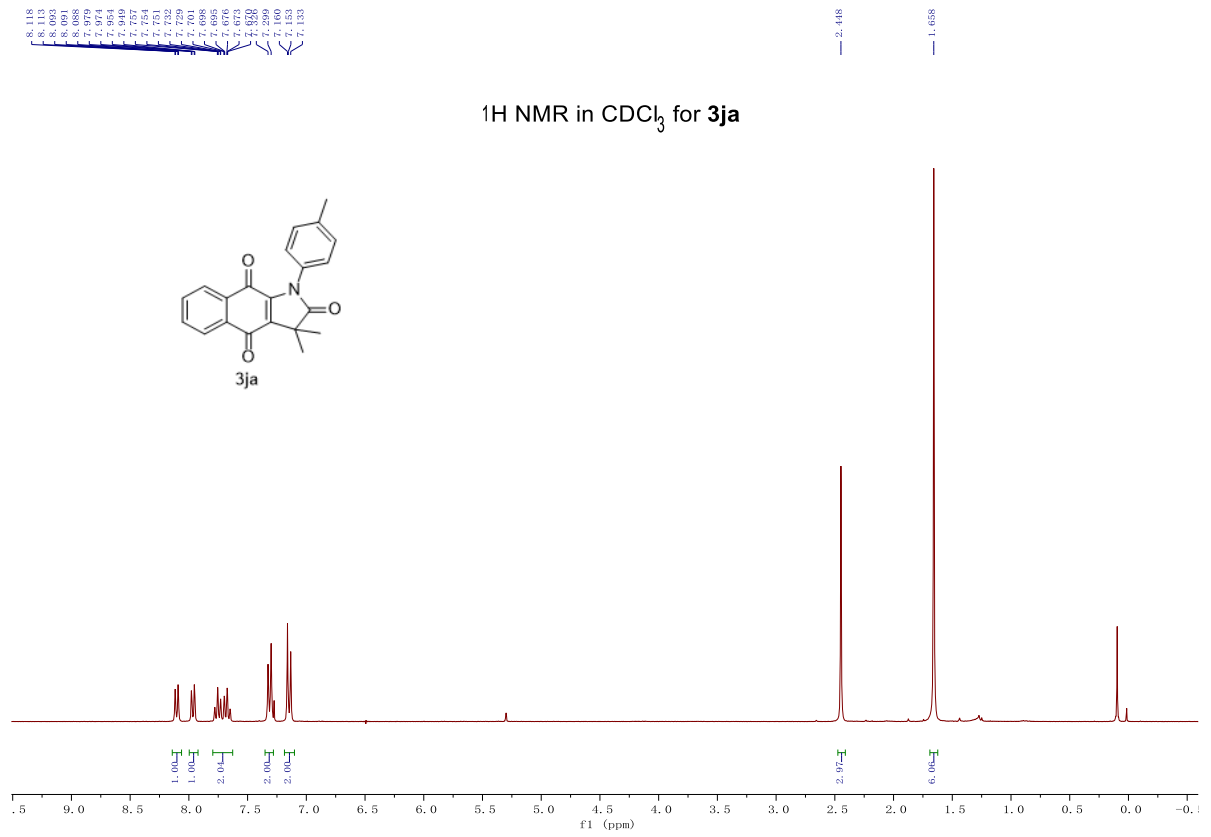
3.867

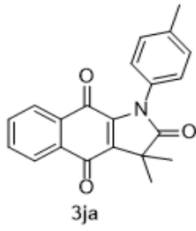
1.646

¹H NMR in CDCl₃ for **3ia**





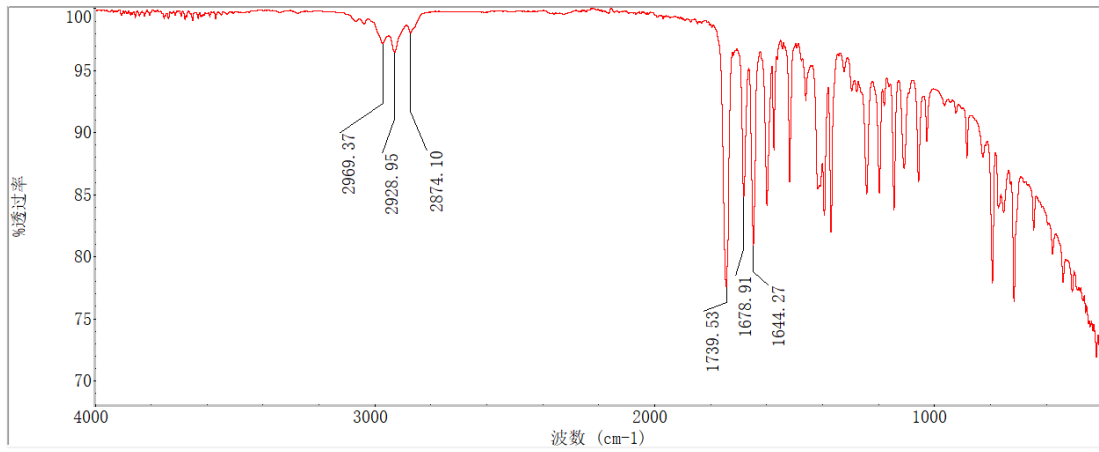




IR (KBr) spectrum for compound **3ja**

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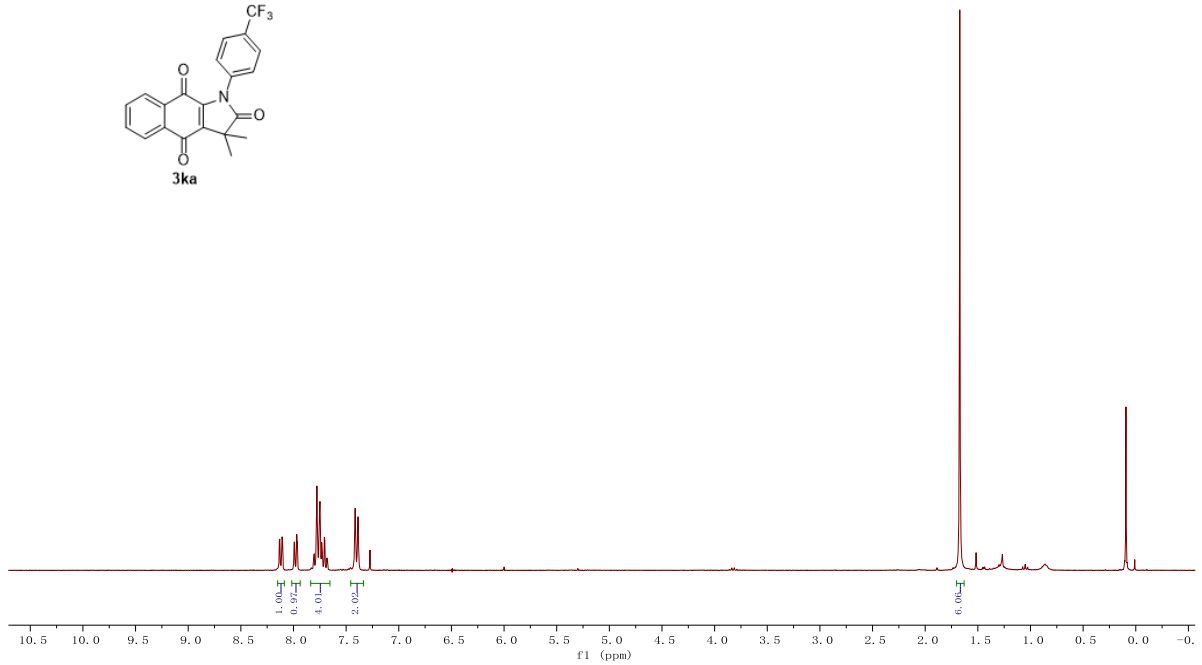
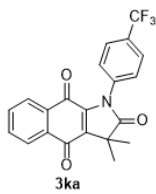
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8.131
8.129
8.101
7.994
7.989
7.964
7.868
7.863
7.778
7.772
7.753
7.748
7.732
7.722
7.707
7.702
7.687
7.677
7.614
7.387

1.672

¹H NMR in CDCl₃ for **3ka**



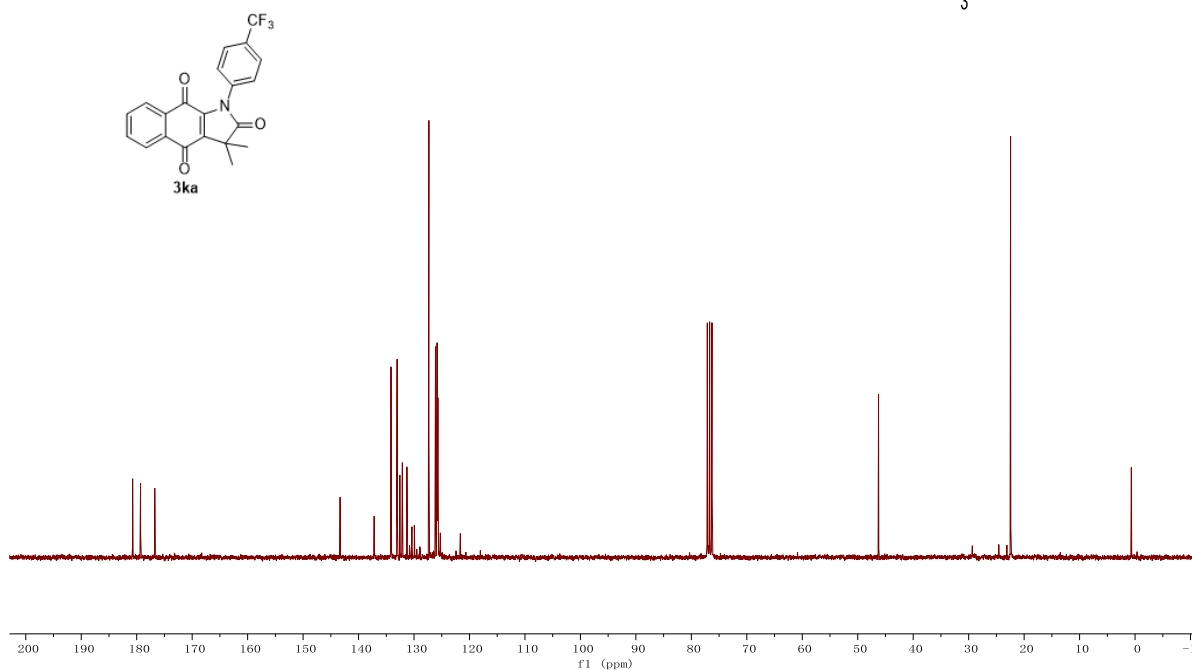
186.733
178.306
176.744

145.324
137.193
134.142
133.142
132.595
132.100
131.890
130.378
129.941
129.909
127.322
126.128
125.791
125.742
125.692
125.257
124.688
118.039

46.247

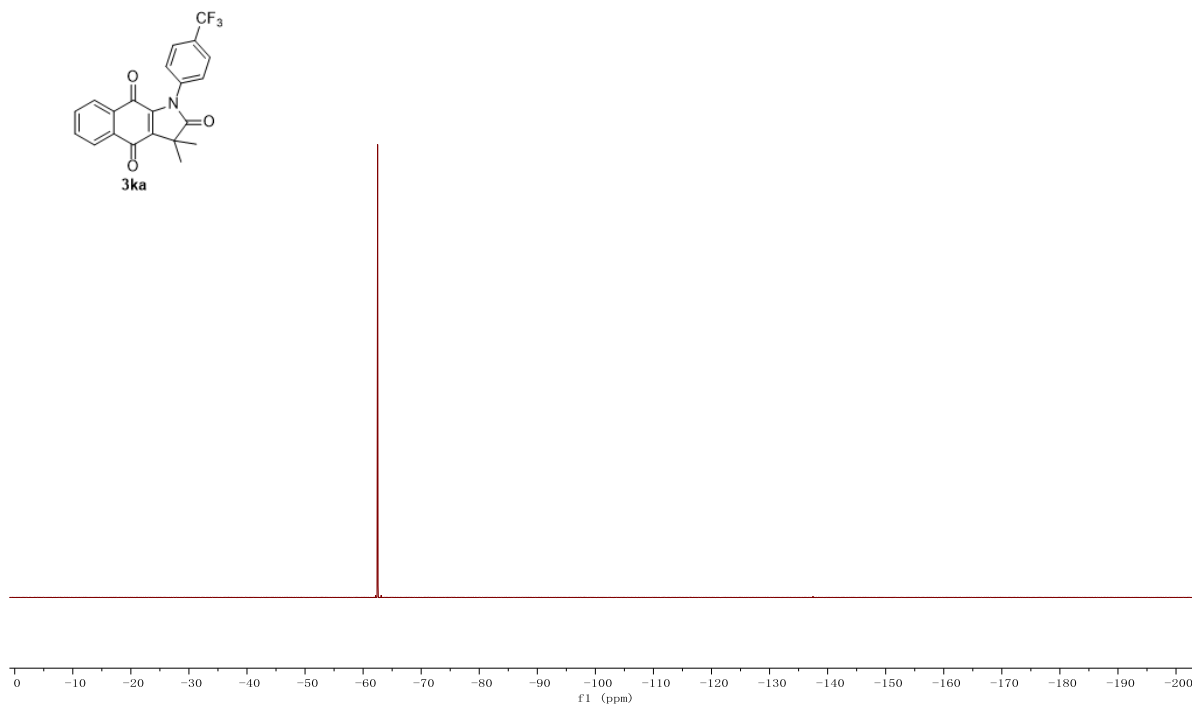
22.444

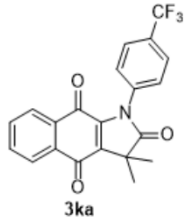
^{13}C NMR in CDCl_3 for **3ka**



-62.503

^{19}F NMR in CDCl_3 for **3ka**

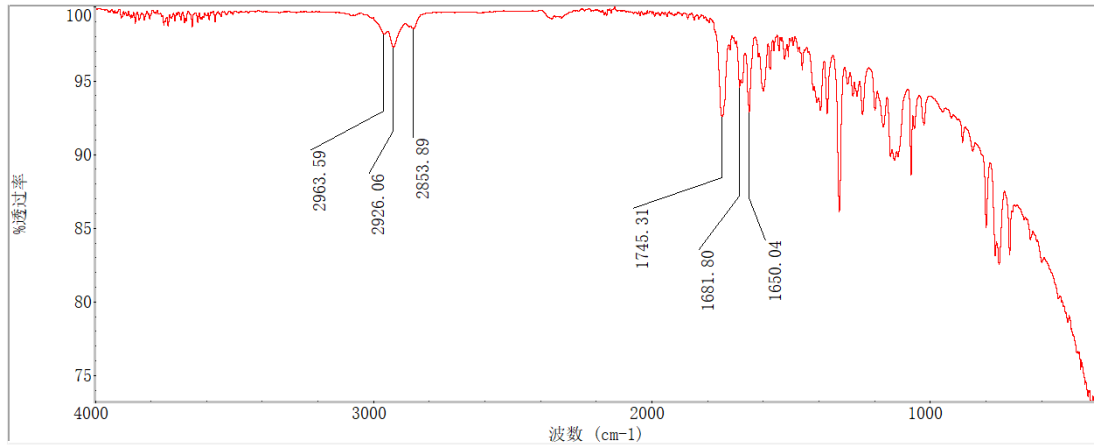




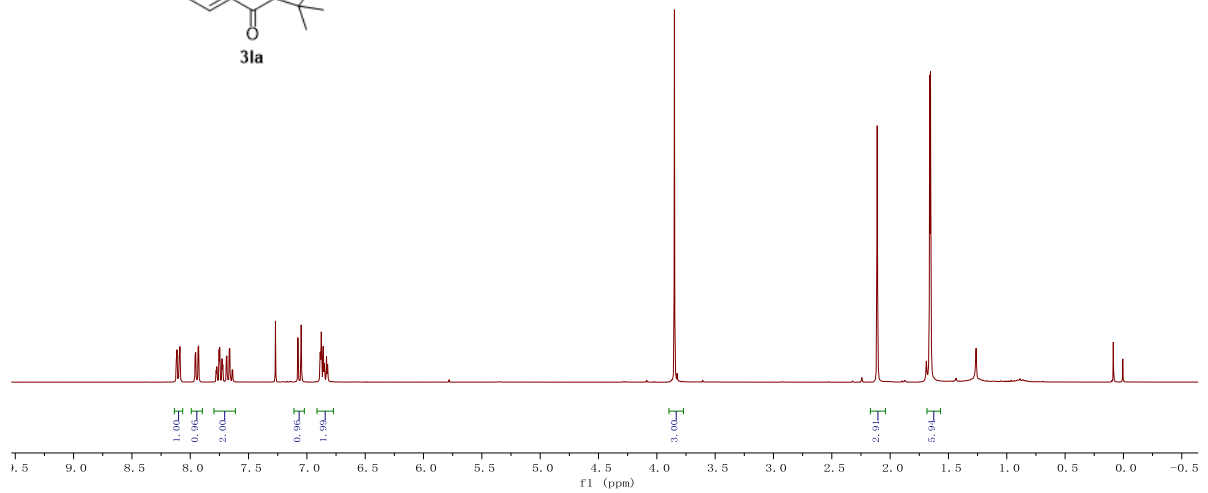
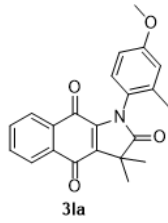
IR (KBr) spectrum for compound **3ka**

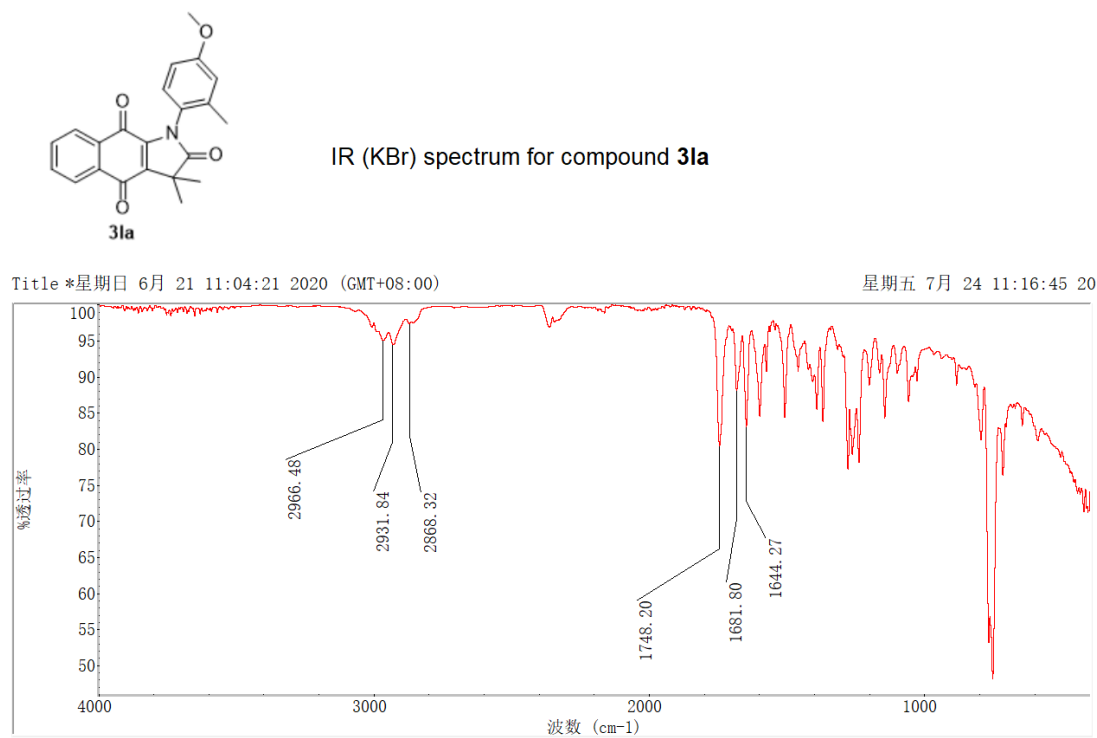
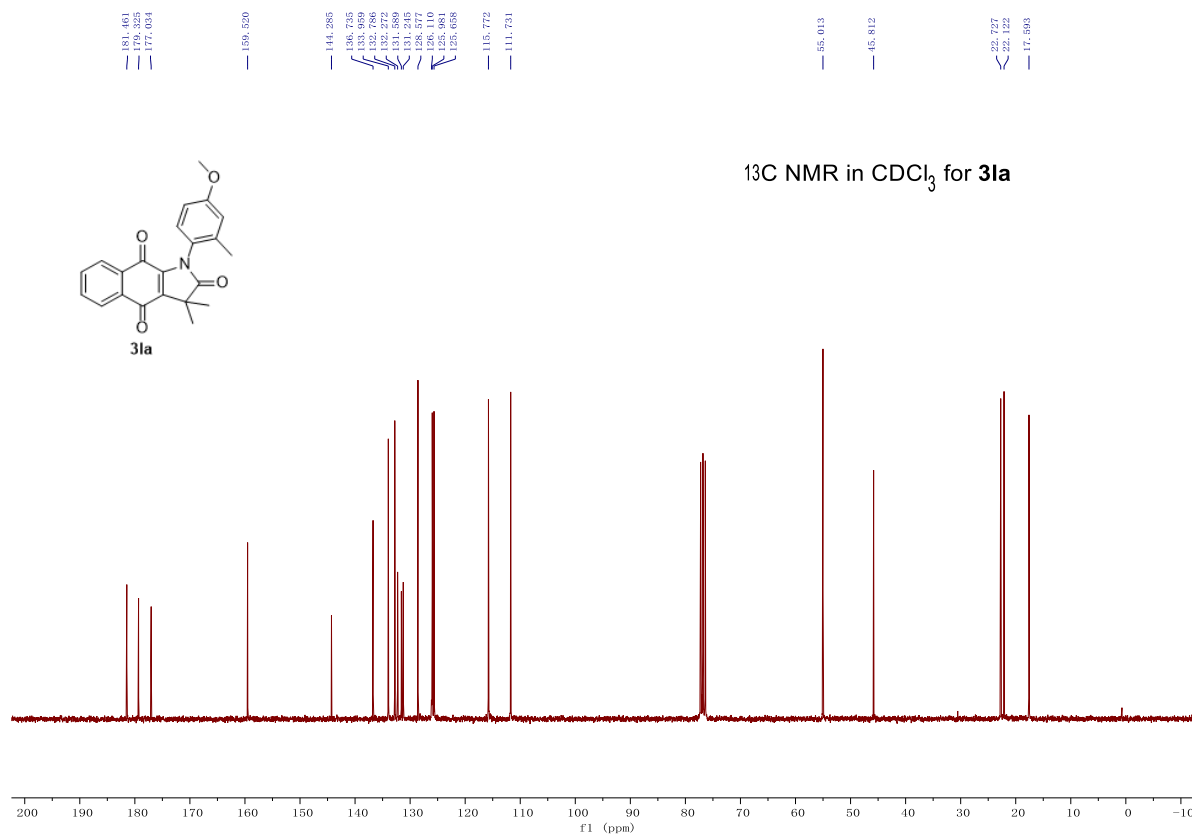
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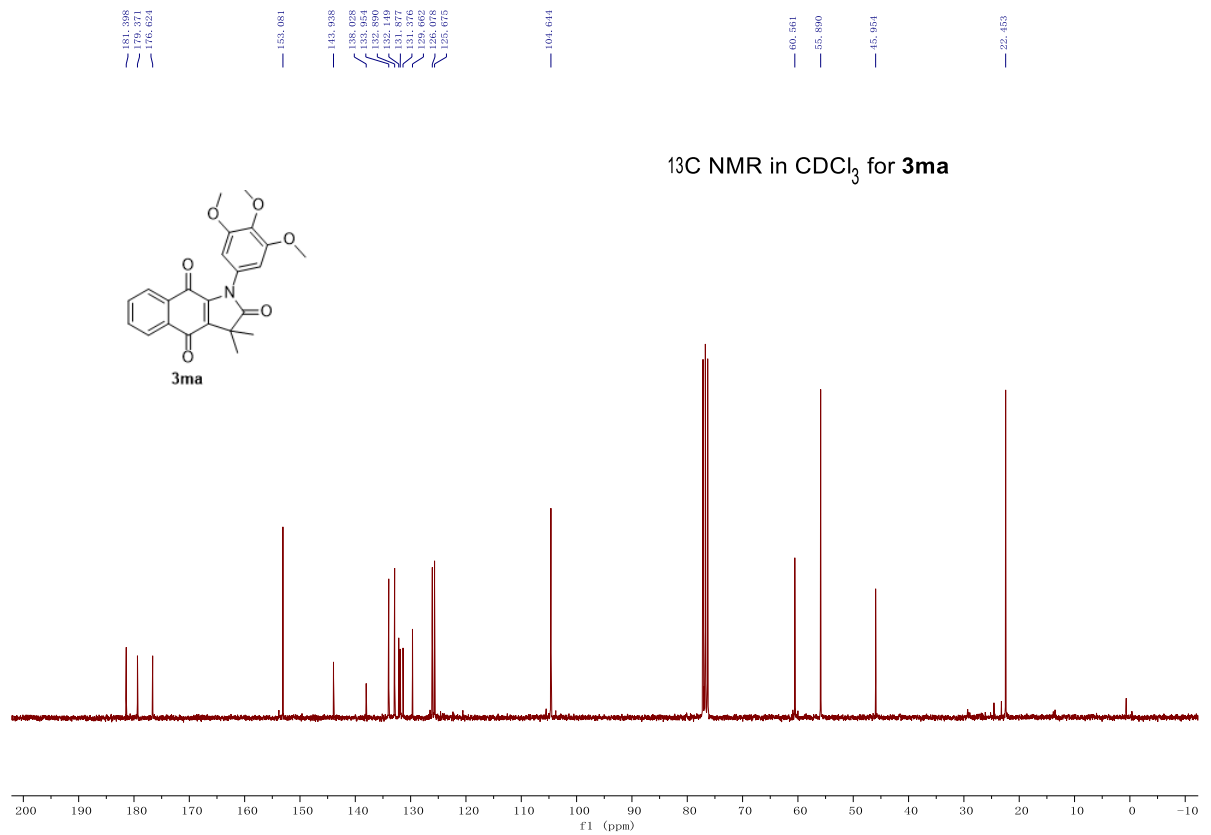
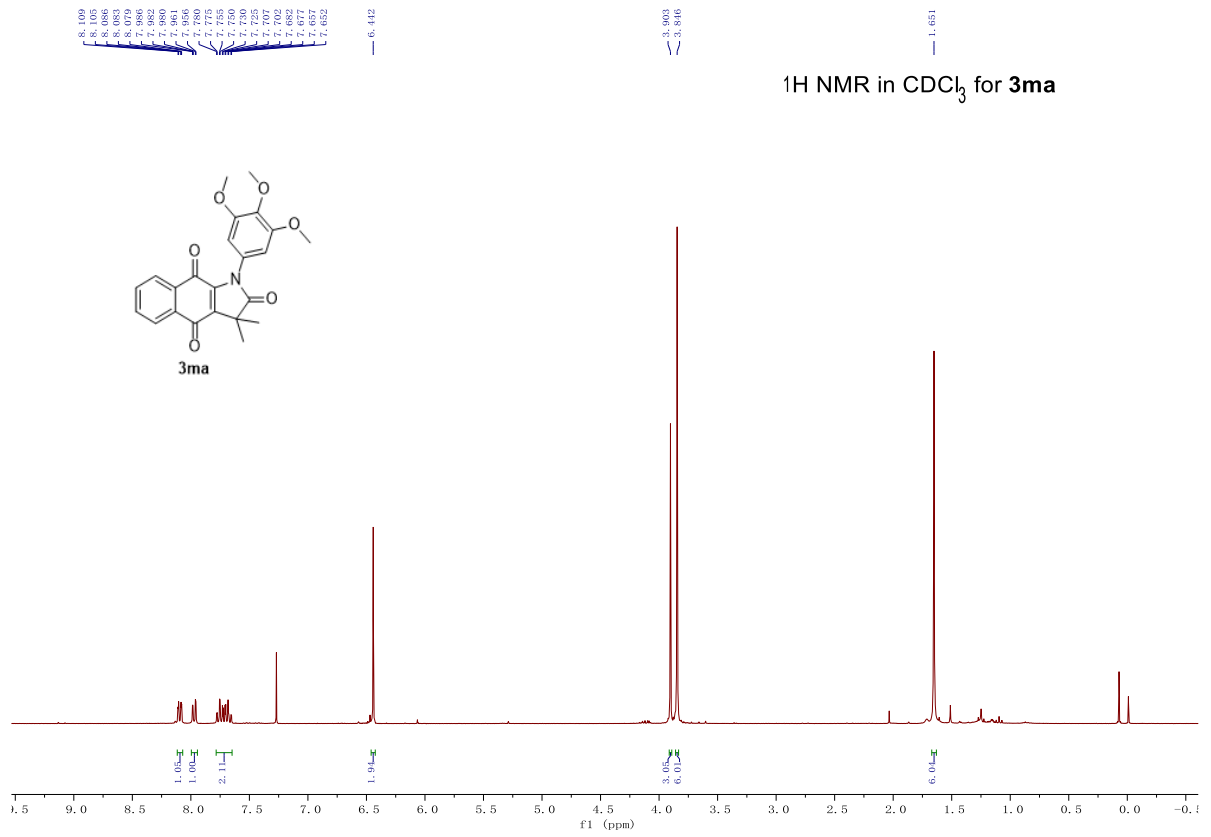
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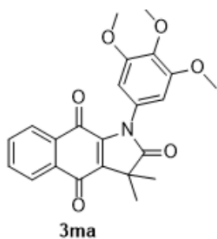


^1H NMR in CDCl_3 for **3la**





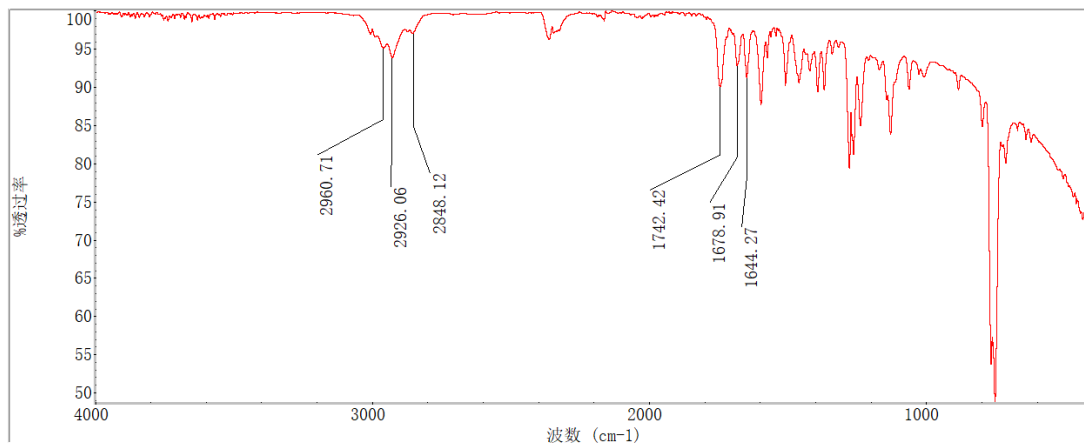




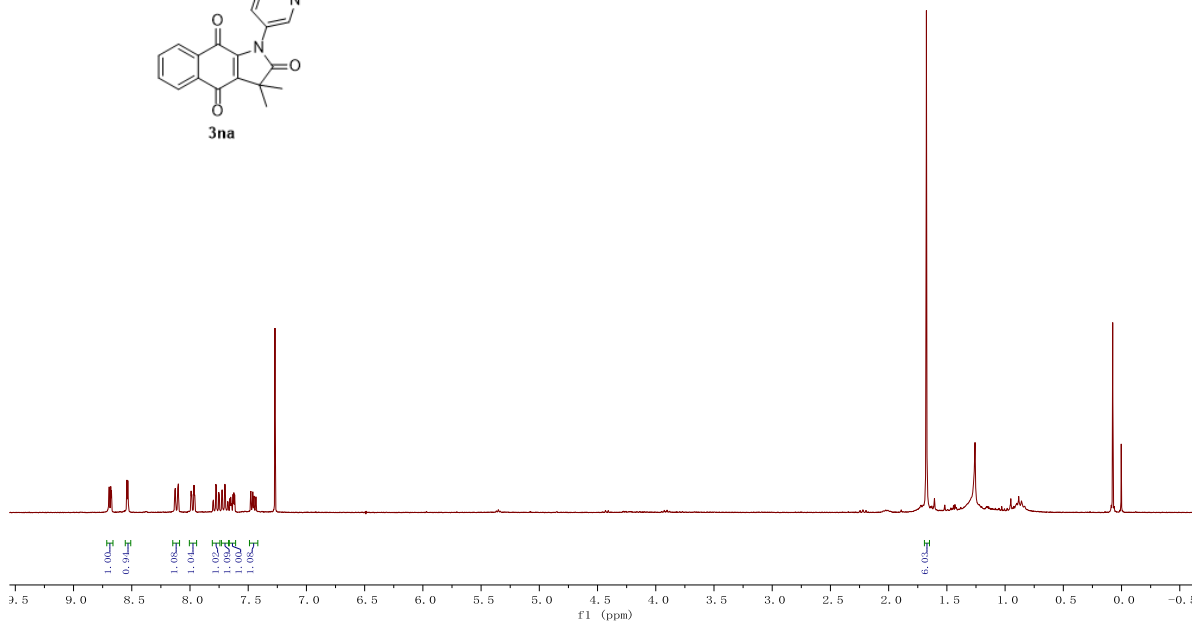
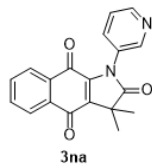
IR (KBr) spectrum for compound **3ma**

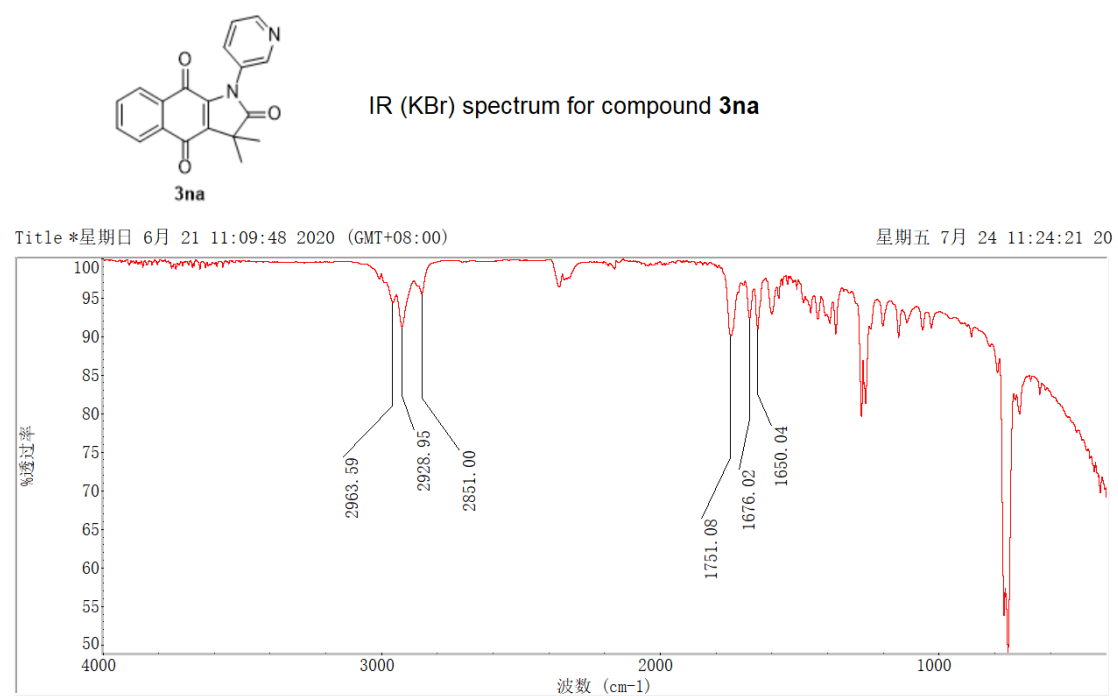
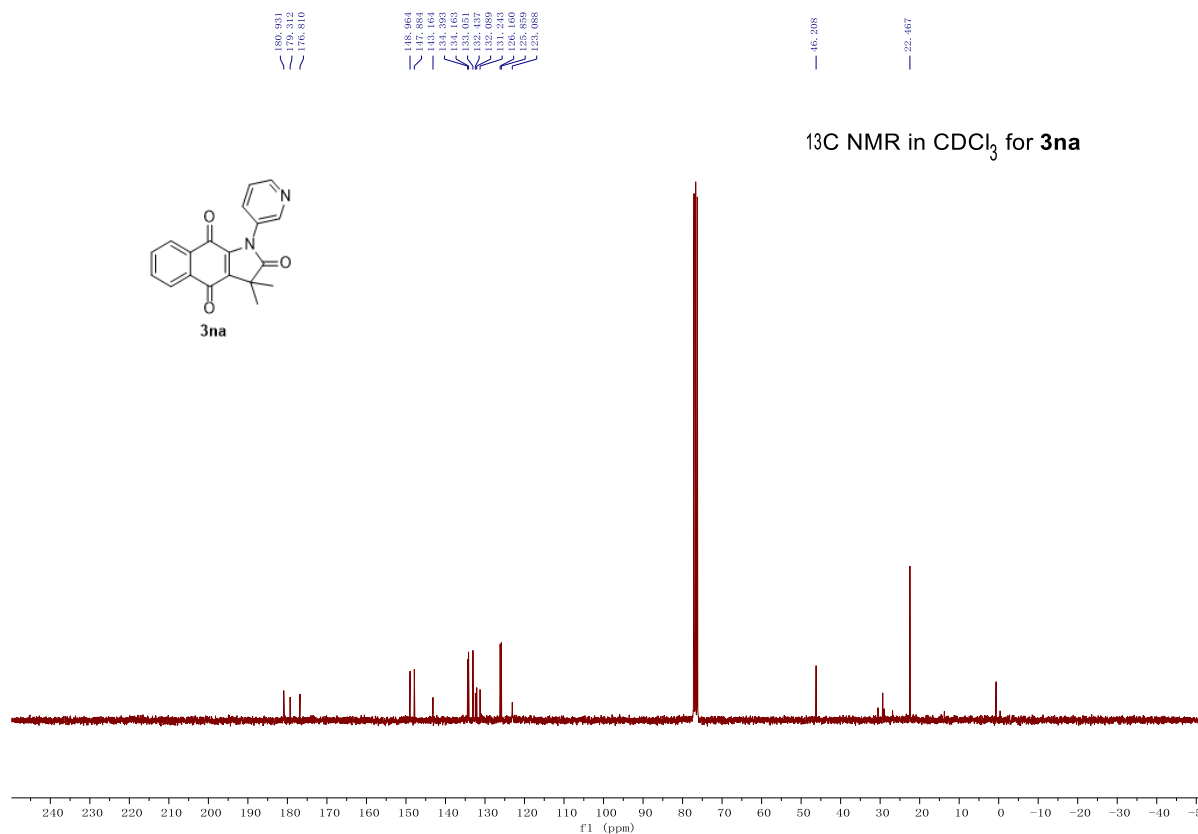
Title *星期日 6月 21 11:11:21 2020 (GMT+08:00)

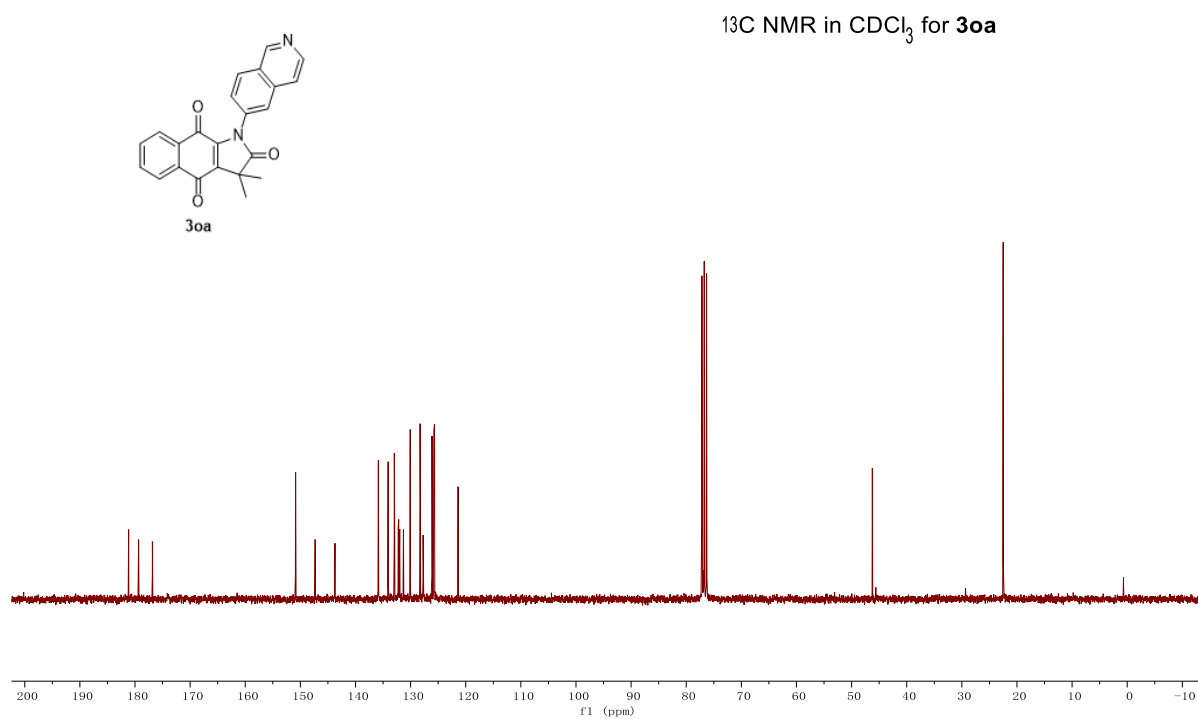
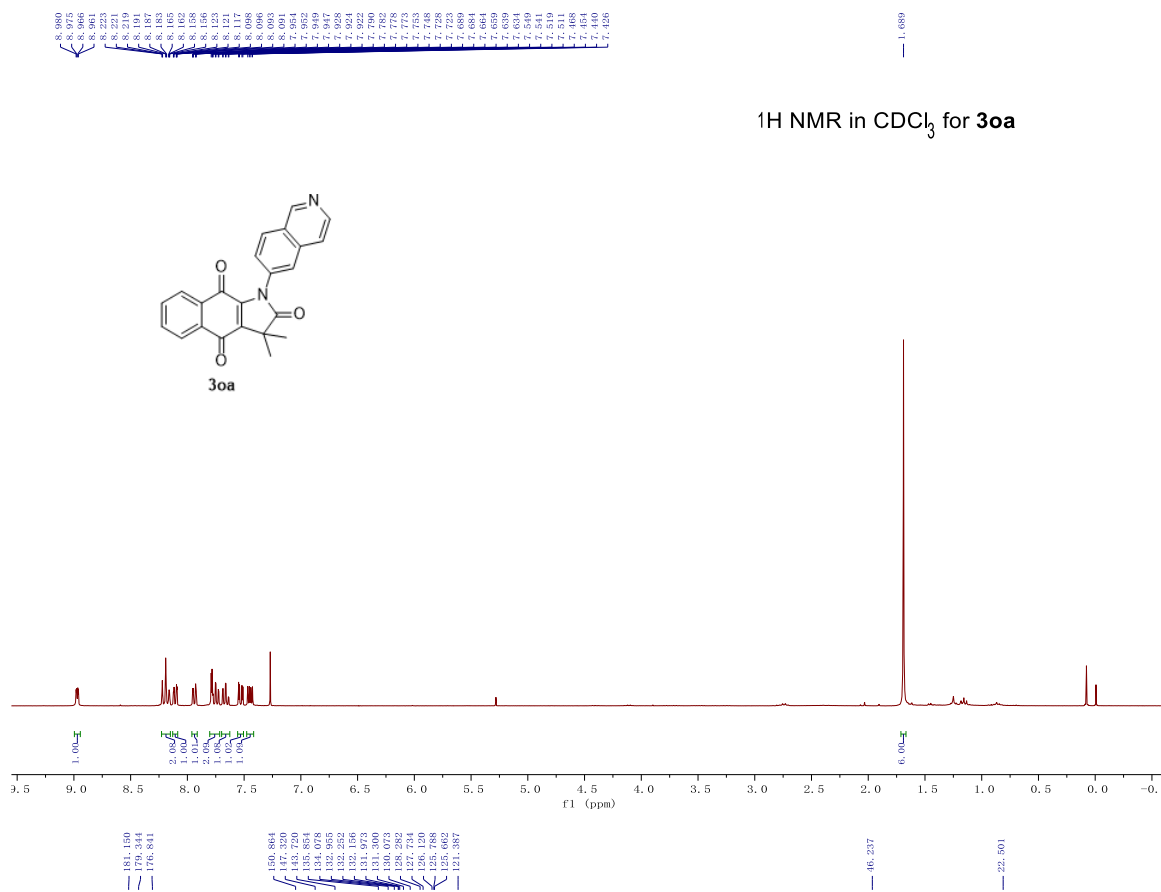
星期五 7月 24 11:21:28 20

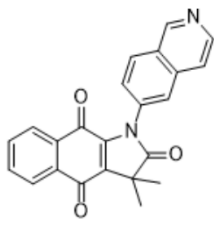


¹H NMR in CDCl₃ for **3na**







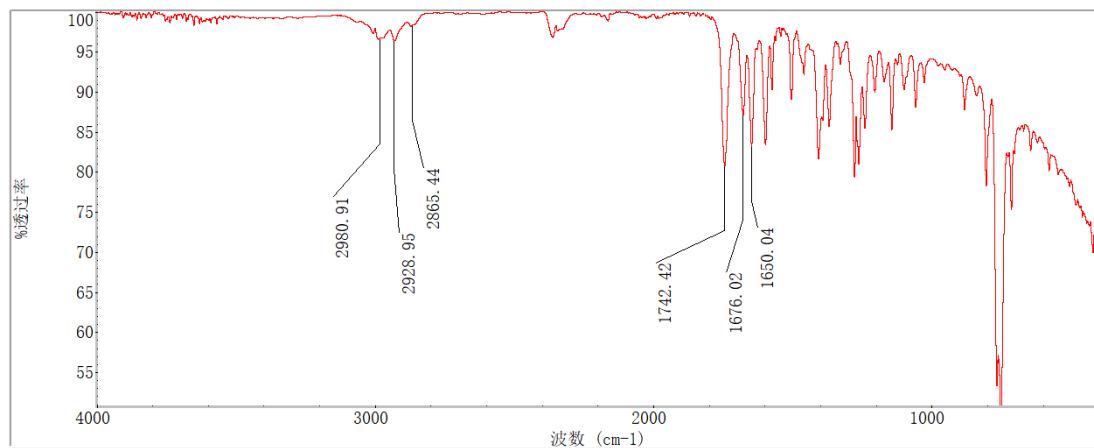


3oa

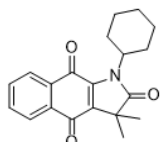
IR (KBr) spectrum for compound 3oa

Title *星期日 6月 21 11:07:02 2020 (GMT+08:00)

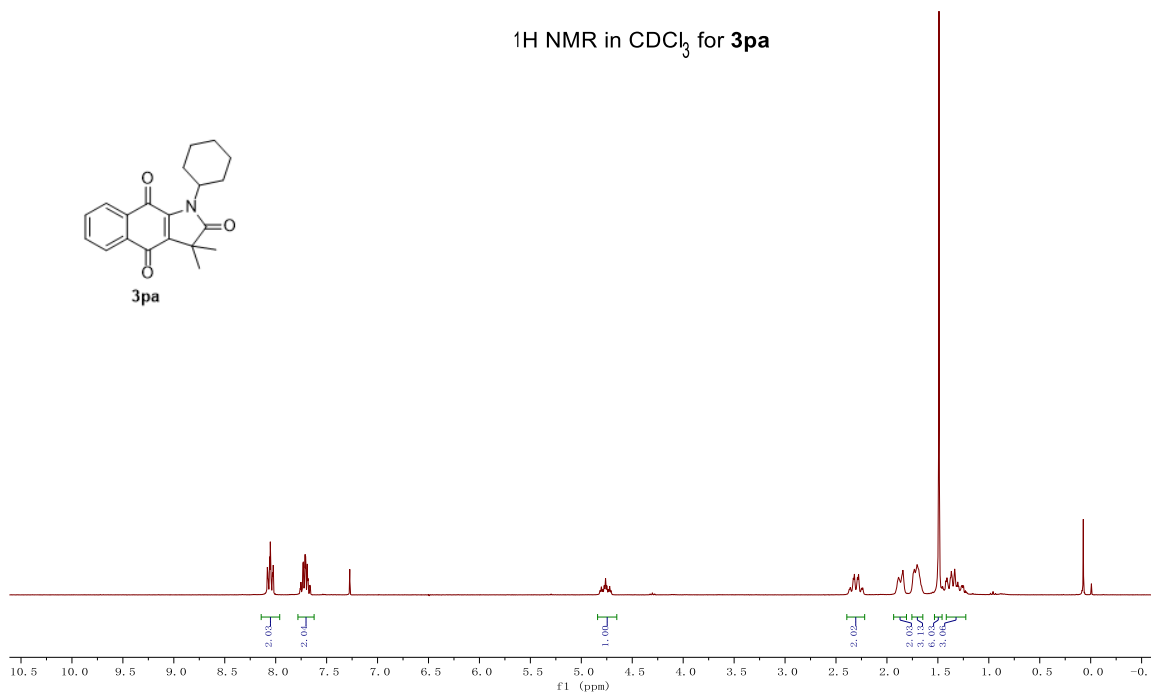
星期五 7月 24 11:26:41 20



1H NMR in CDCl₃ for 3pa



3pa

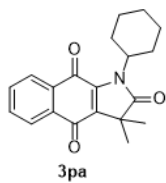


182.495
178.978
176.361

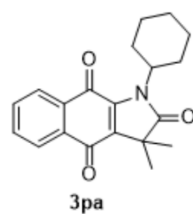
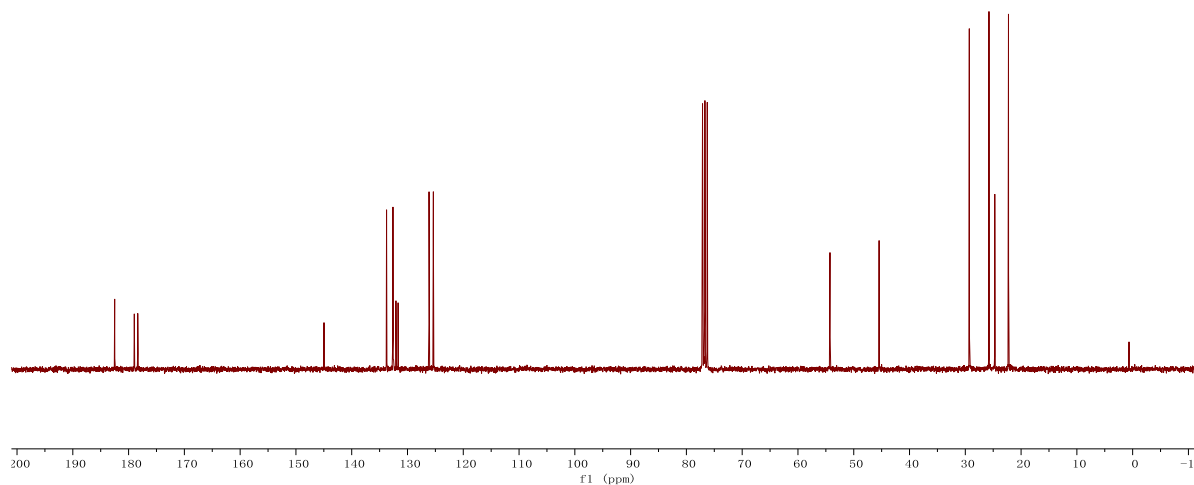
144.968
138.752
136.677
135.920
132.668
131.684
128.385
125.384

54.261
45.454

29.283
28.778
22.559



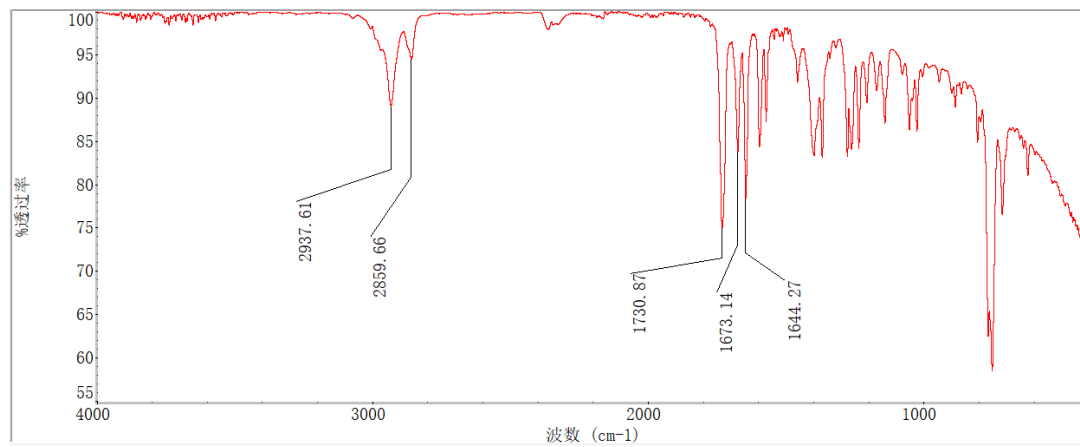
¹³C NMR in CDCl₃ for **3pa**



IR (KBr) spectrum for compound **3pa**

Title *星期日 6月 21 10:54:21 2020 (GMT+08:00)

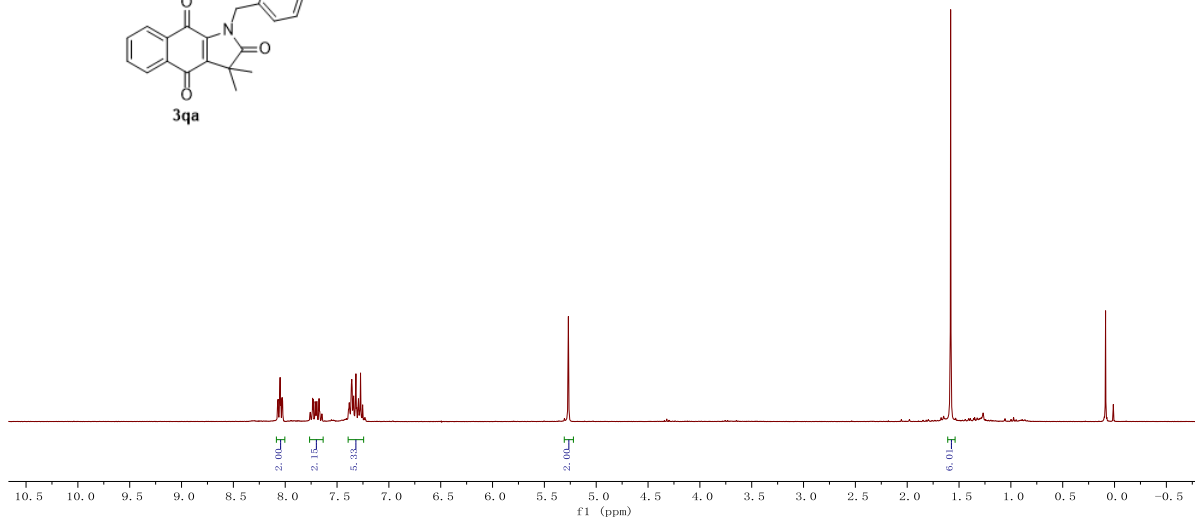
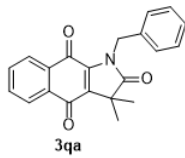
星期五 7月 24 11:30:54 20



8.0473
8.0452
8.0455
8.0449
8.0441
8.0433
8.0255
7.7914
7.7396
7.7331
7.7242
7.7209
7.6999
7.6993
7.6988
7.6688
7.6483
7.6483
7.3952
7.3775
7.3765
7.3762
7.3588
7.3535
7.3535
7.3490
7.3333
7.3223
7.3118
7.3118
7.3111
7.2926
7.2926
7.2776
7.2563
7.2563
7.2558

1.1894

¹H NMR in CDCl₃ for 3qa



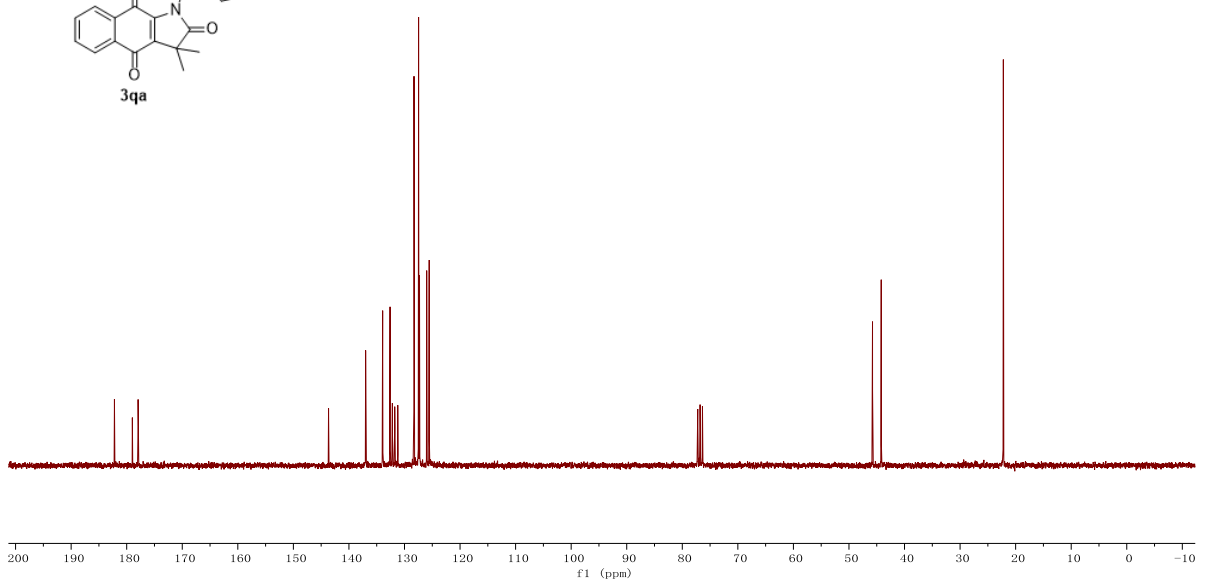
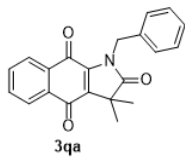
182.205
178.982
177.986

135.659
135.999
132.931
132.597
132.577
131.757
131.214
128.289
127.299
126.005
125.552

45.762
44.192

22.214

¹³C NMR in CDCl₃ for 3qa



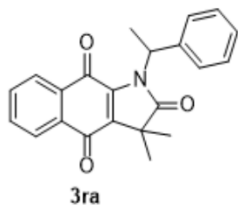
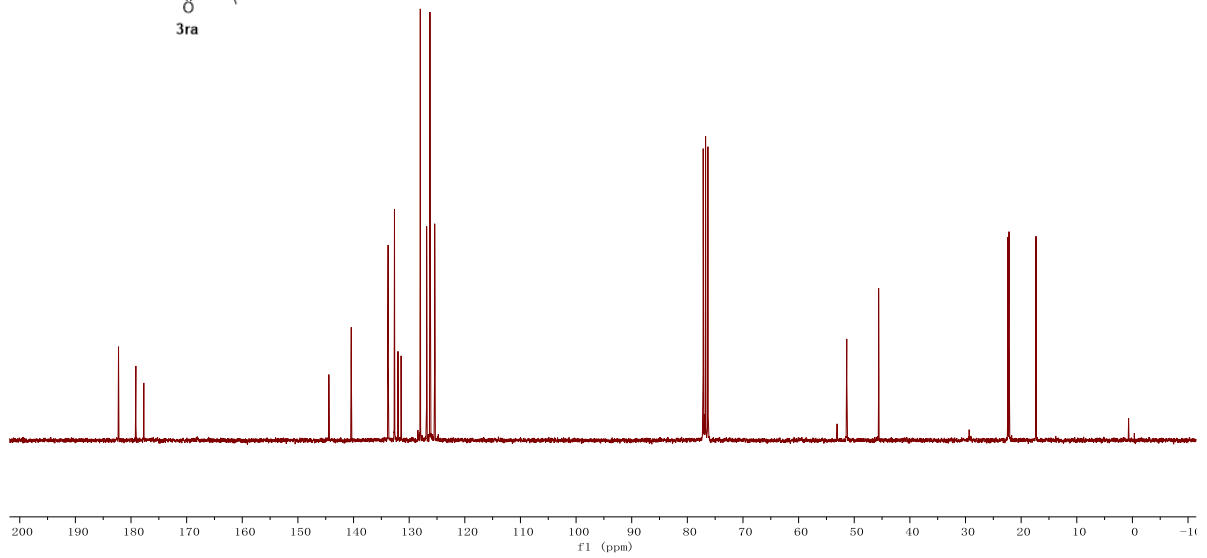
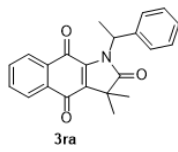
182.215
179.130
177.702

144.140
140.408
133.789
132.675
132.015
131.452
128.908
128.882
128.206
128.216
125.413

51.346
45.016

22.401
22.176
17.332

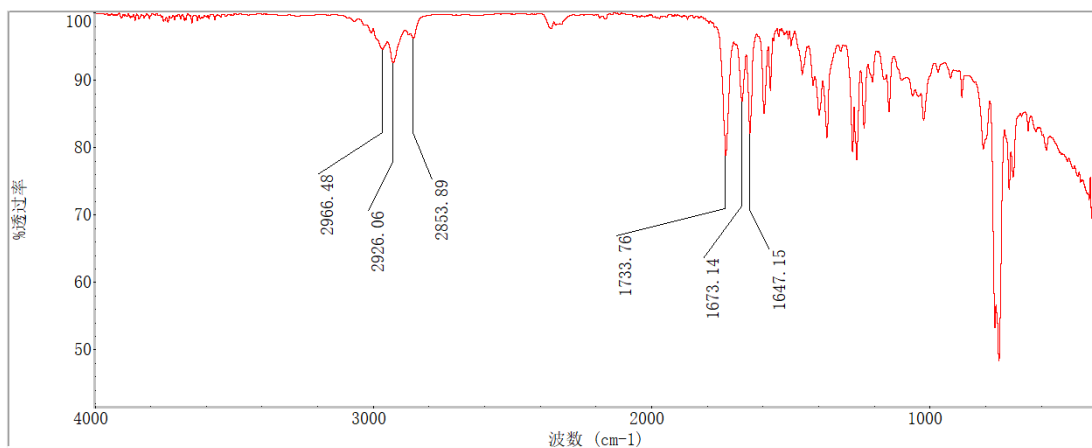
^{13}C NMR in CDCl_3 for **3ra**



IR (KBr) spectrum for compound **3ra**

Title *星期日 6月 21 10:56:48 2020 (GMT+08:00)

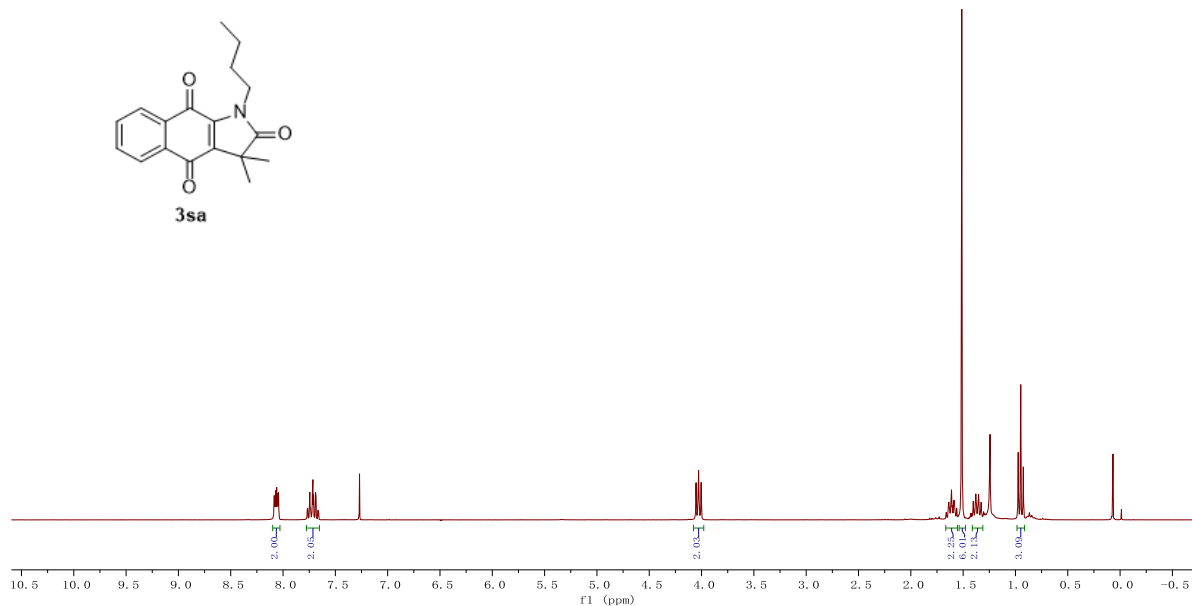
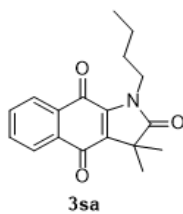
星期五 7月 24 11:35:49 20



8.086
8.084
8.081
8.078
8.073
8.071
8.067
8.056
8.054
8.049
8.043
8.041
7.781
7.744
7.739
7.736
7.714
7.709
7.685
7.685
7.685
7.680

4.053
4.035
4.029
4.029
4.014
4.011
4.001
4.000
1.627
1.627
1.611
1.602
1.590
1.589
1.580
1.574
1.573
1.499
1.403
1.388
1.379
1.374
1.374
1.353
1.328
1.328
1.324
1.324
0.974
0.950
0.925

¹H NMR in CDCl₃ for **3sa**

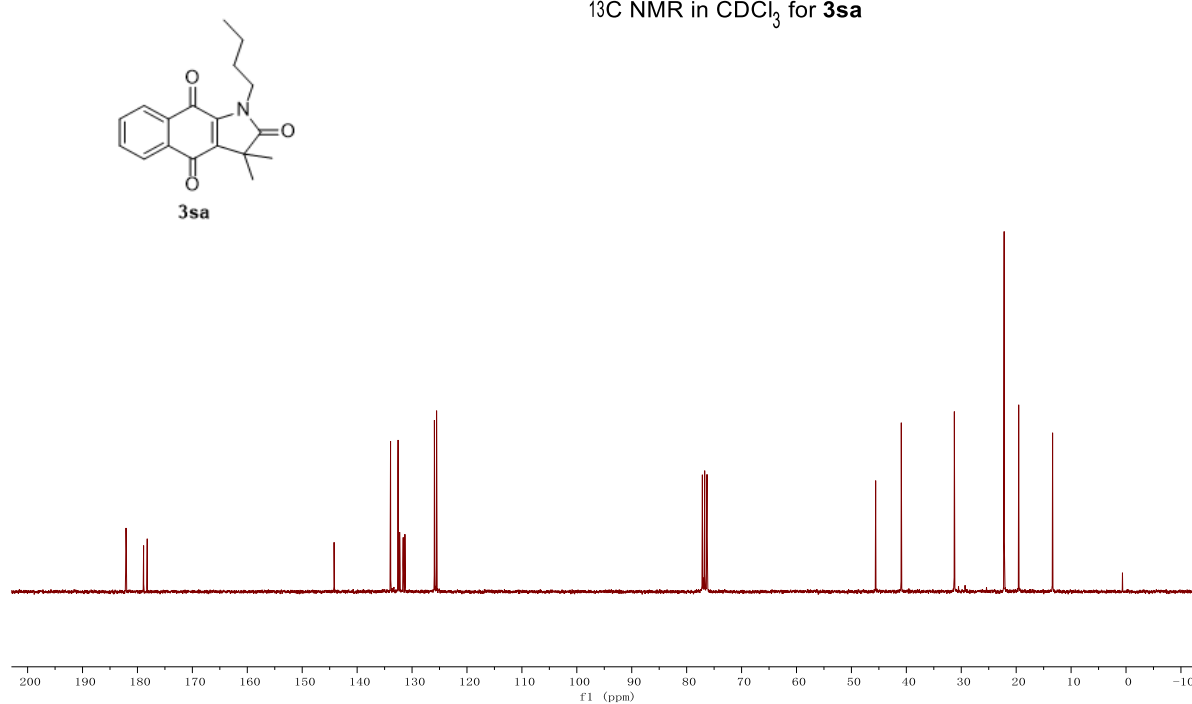
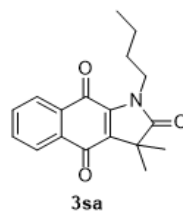


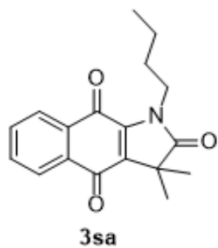
185.853
185.883
178.222

144.196
133.917
132.514
132.497
131.299
125.930
125.533

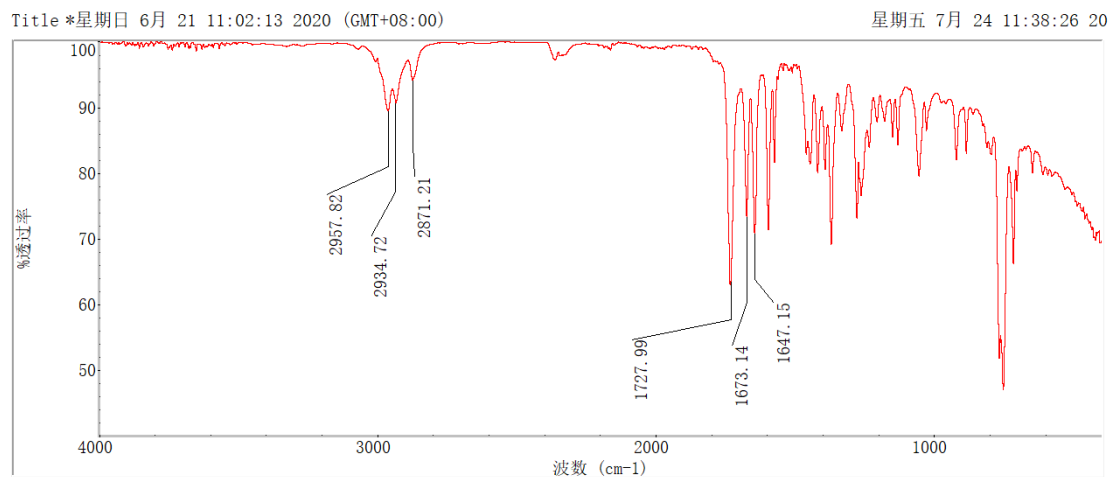
45.588
40.921
31.261
22.191
19.541
13.307

¹³C NMR in CDCl₃ for **3sa**





IR (KBr) spectrum for compound **3sa**

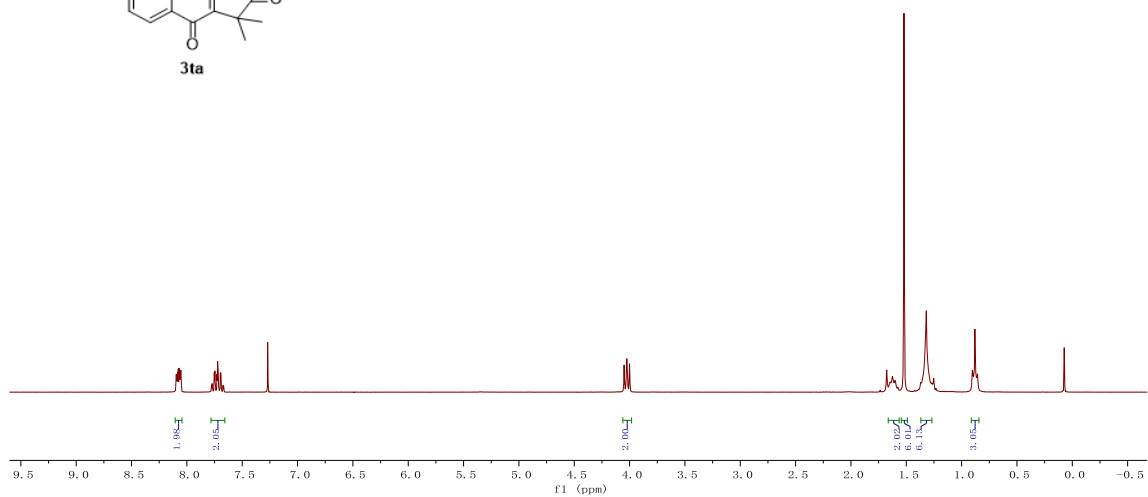
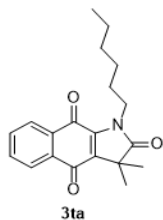


8.086
8.089
8.083
8.072
8.066
8.058
8.054
7.732
7.728
7.722
7.698
7.693

4.049
4.020
4.020
4.000

1.649
1.632
1.625
1.576
1.521
1.326
1.319
1.310
0.903
0.897
0.884
0.856

¹H NMR in CDCl₃ for **3ta**



188.085
178.210

144.223

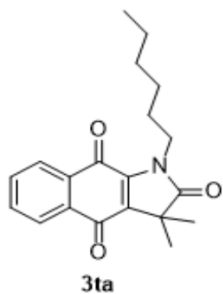
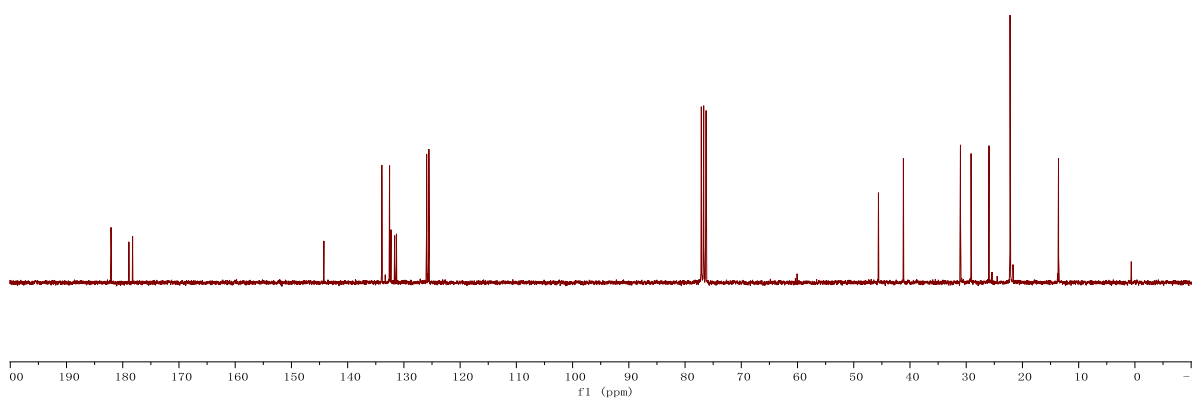
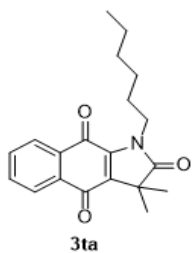
138.922
138.291
133.639
131.350
126.555

45.007
41.166

31.023
29.136
25.948
22.204
22.165

13.591

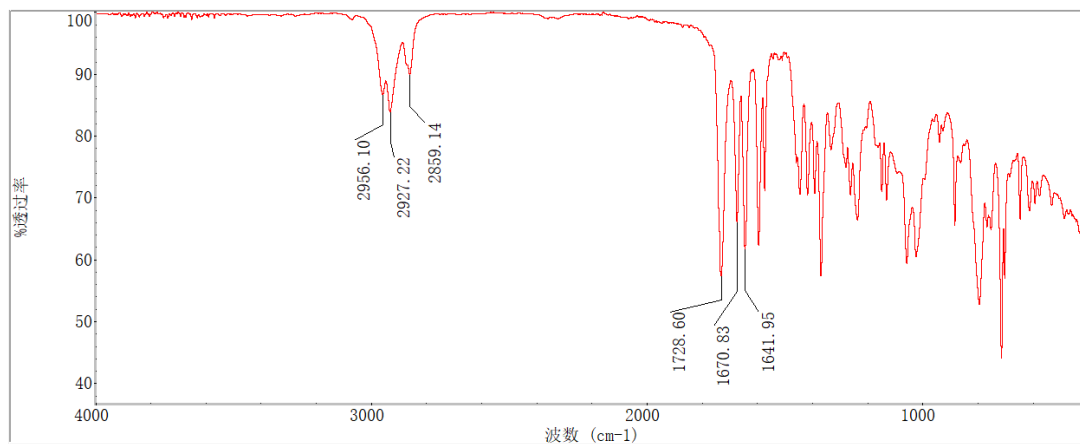
^{13}C NMR in CDCl_3 for **3ta**



IR (KBr) spectrum for compound **3ta**

Title *星期日 6月 21 10:37:07 2020 (GMT+08:00)

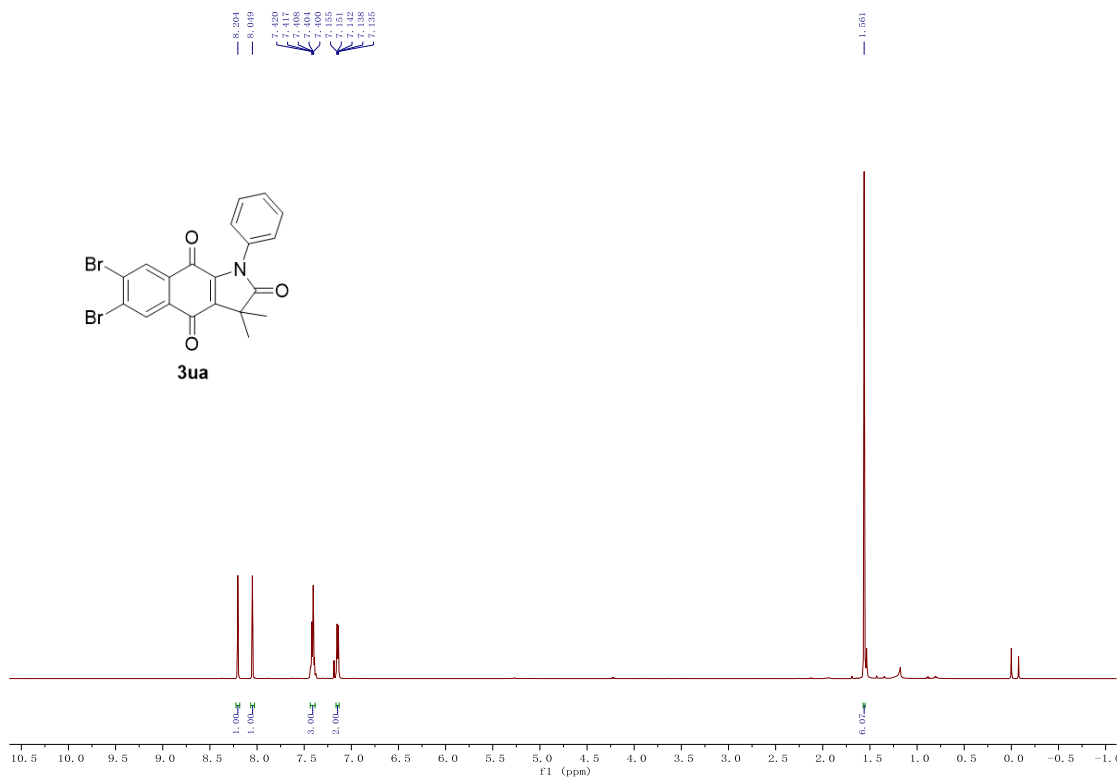
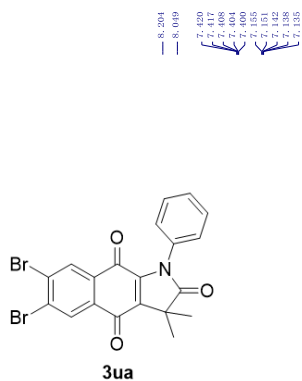
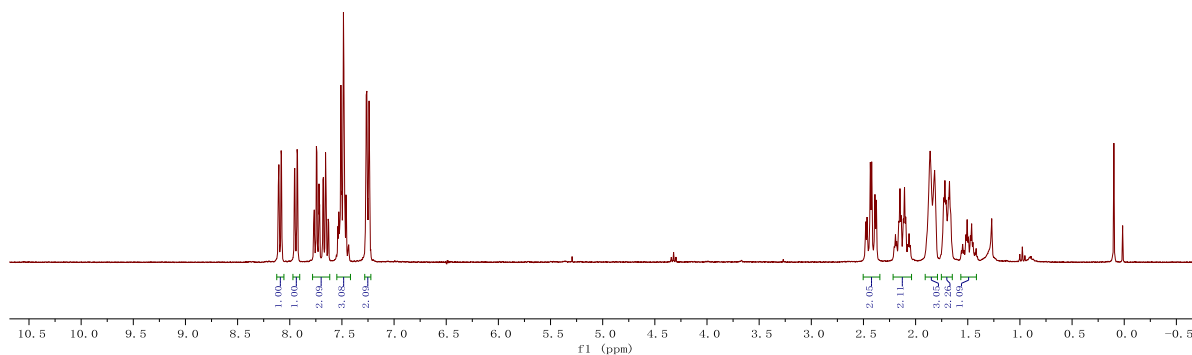
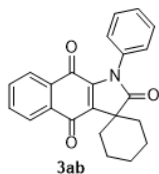
星期五 7月 24 12:43:48 20

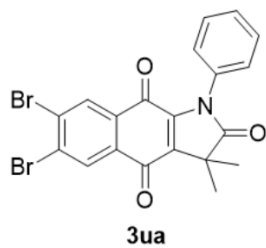
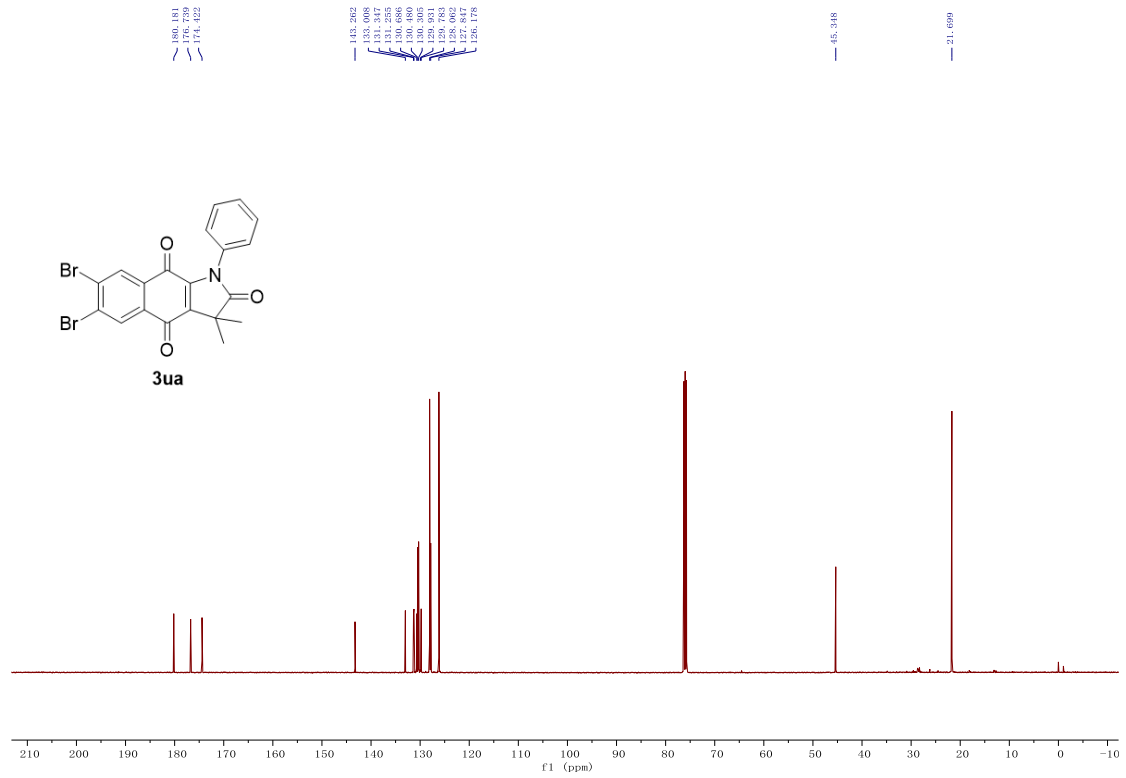


8.1109
8.083
8.079
8.056
7.950
7.930
7.925
7.765
7.745
7.730
7.715
7.682
7.657
7.652
7.632
7.575
7.540
7.533
7.520
7.520
7.510
7.510
7.500
7.491
7.480
7.480
7.481
7.475
7.465
7.462
7.458
7.272
7.262
7.261
7.253
7.246
7.240
7.240
7.235

2.470
2.465
2.434
2.434
2.390
2.376
2.290
2.282
2.182
2.162
2.150
2.148
2.118
2.106
2.056
2.025
2.063
2.050
1.828
1.817
1.805
2.362
1.719
1.708
1.686
1.675
1.662
1.650
1.518
1.500
1.475
1.463
1.420

¹H NMR in CDCl₃ for **3ab**

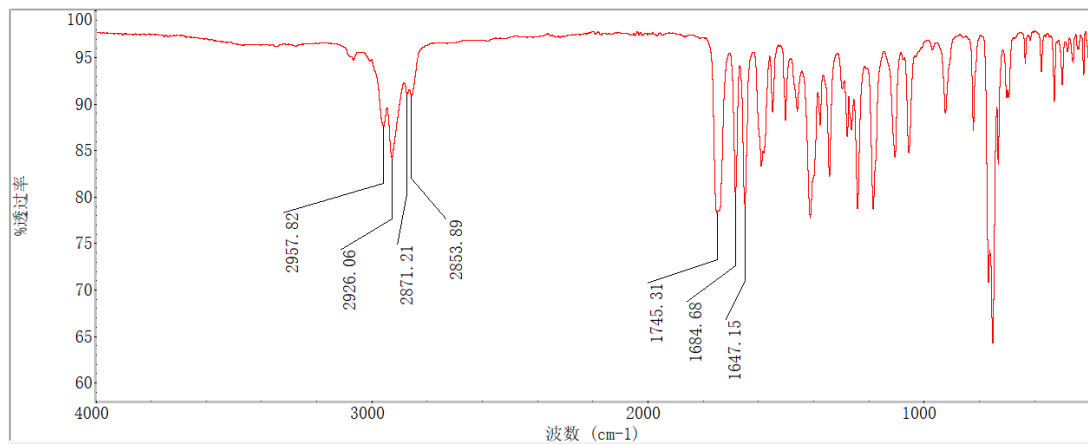


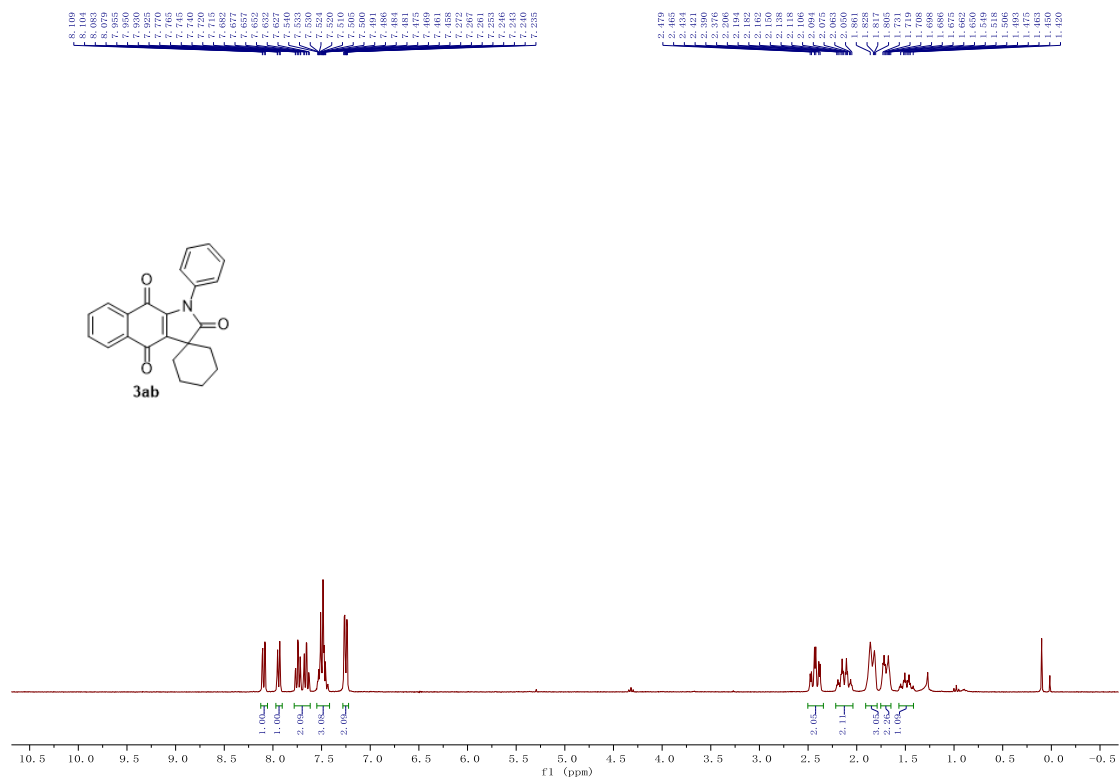


IR (KBr) spectrum for compound **3ua**

Title *星期四 7月 16 19:40:00 2020 (GMT+08:00)

星期五 7月 24 11:44:36 20





179.866
179.289
176.527

144.296
134.229
133.909
133.588
132.880
131.405
130.884
129.884
128.191
127.063
125.933
125.178

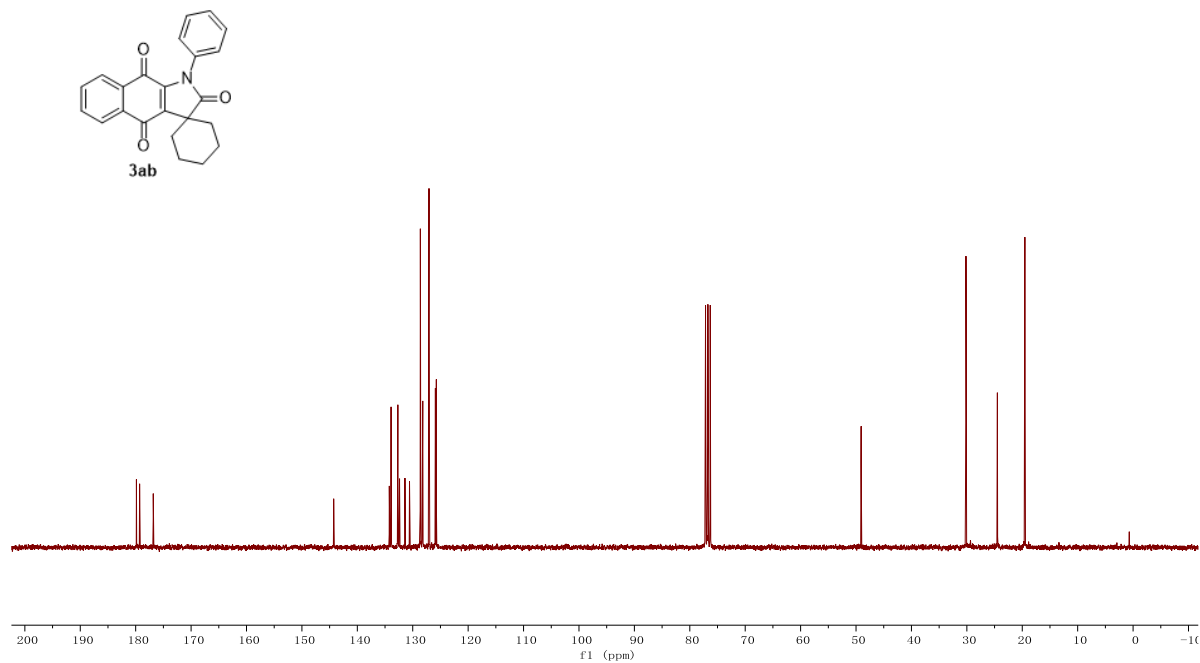
49.075

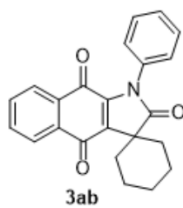
30.158

24.492

19.527

¹³C NMR in CDCl₃ for 3ab

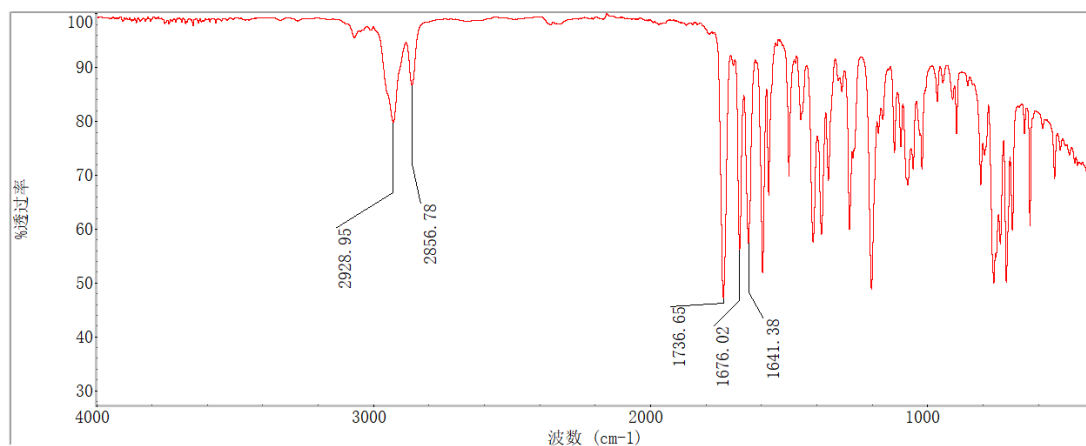




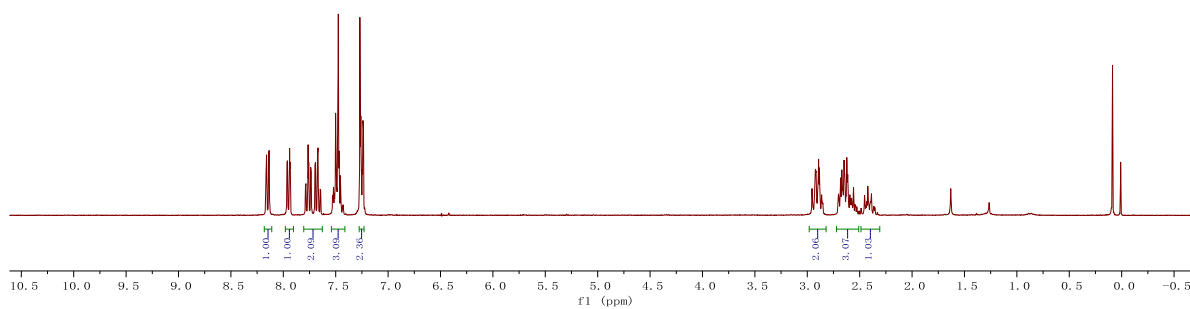
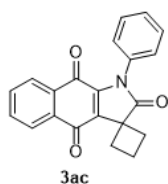
IR (KBr) spectrum for compound **3ab**

Title *星期日 6月 21 10:47:53 2020 (GMT+08:00)

星期五 7月 24 11:50:28 20



¹H NMR in CDCl₃ for **3ac**



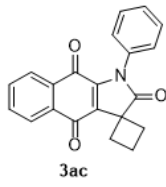
180.658
179.619
176.552

145.948
134.179
133.842
132.845
132.247
131.988
128.604
128.205
127.605
126.054
125.712

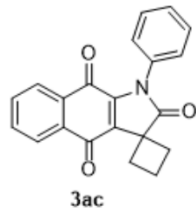
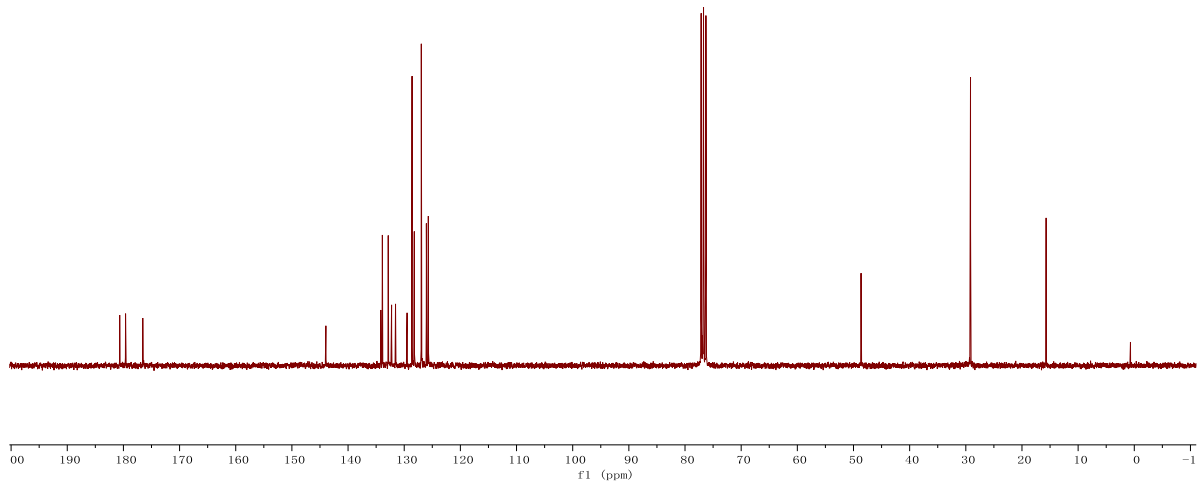
48.657

29.166

15.699



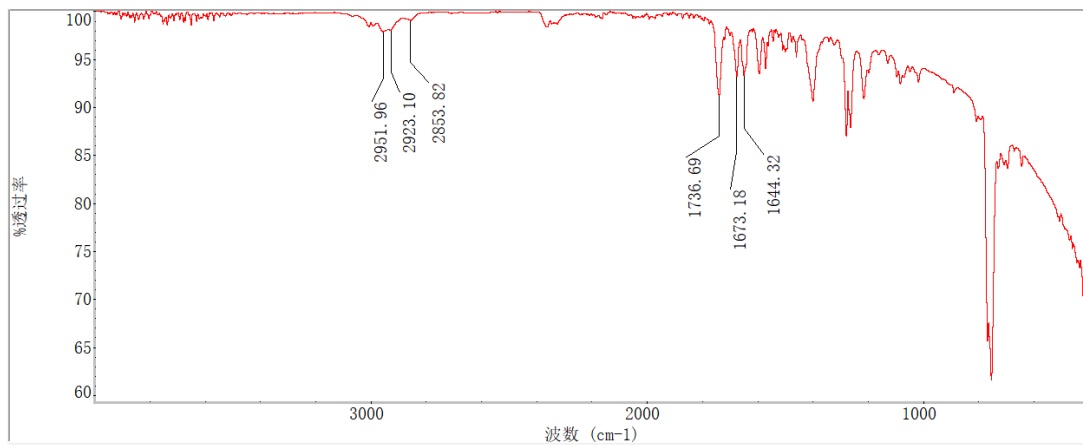
^{13}C NMR in CDCl_3 for **3ac**



IR (KBr) spectrum for compound **3ac**

Title *星期日 6月 21 10:50:04 2020 (GMT+08:00)

星期五 7月 24 11:53:37 20

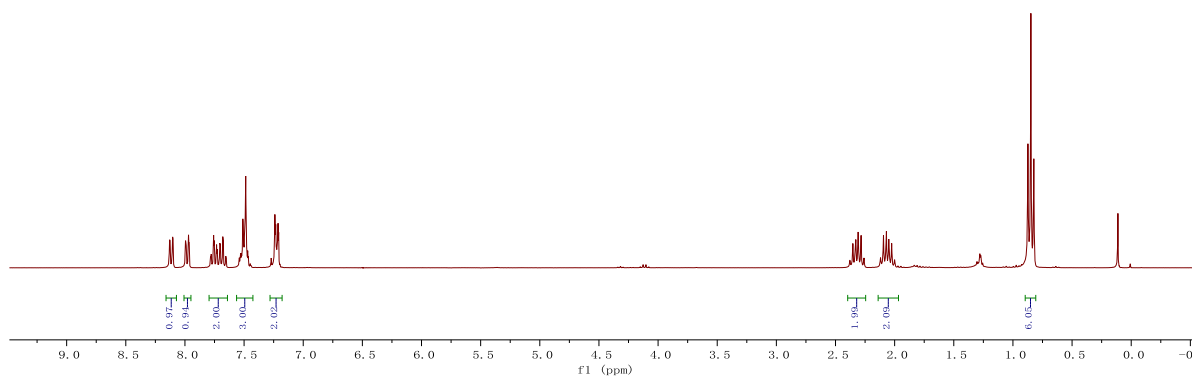
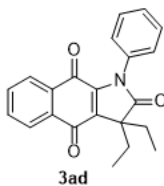


8.130
8.127
8.105
8.100
7.995
7.970
7.965
7.753
7.733
7.728
7.700
7.680
7.675
7.594
7.487
7.482
7.238
7.232
7.220
7.215
7.213
7.207

2.328
2.323
2.328
2.328
2.284
2.259
2.119
2.074
2.069
2.050
2.045
2.025
2.000

0.873
0.848
0.824

¹H NMR in CDCl₃ for **3ad**



180.316
176.323

146.394

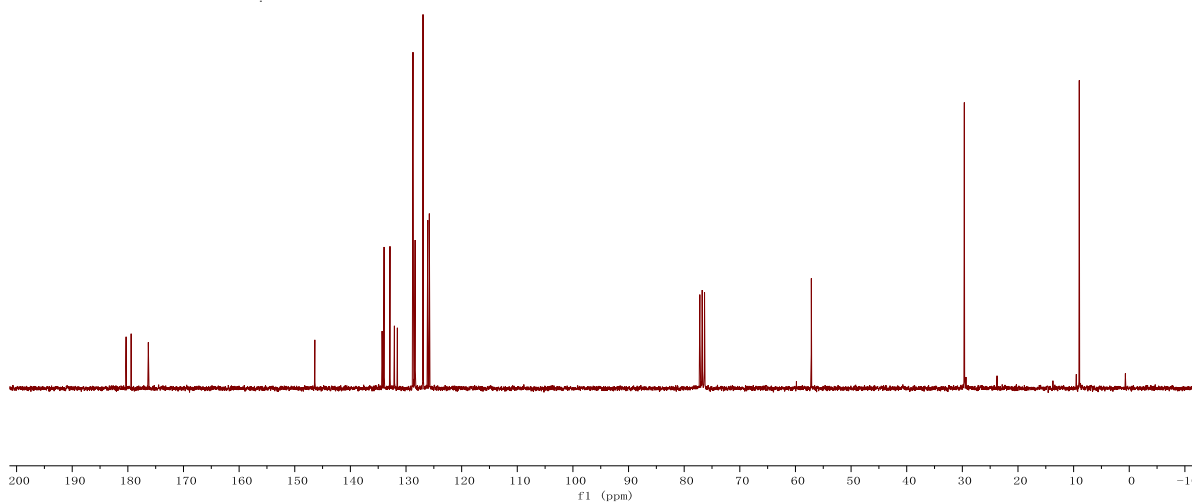
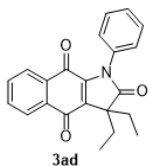
134.302
133.919
132.688
131.557
128.746
126.916
126.096
125.813

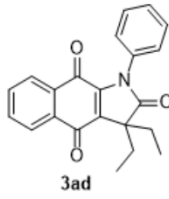
57.146

29.615

8.984

¹³C NMR in CDCl₃ for **3ad**

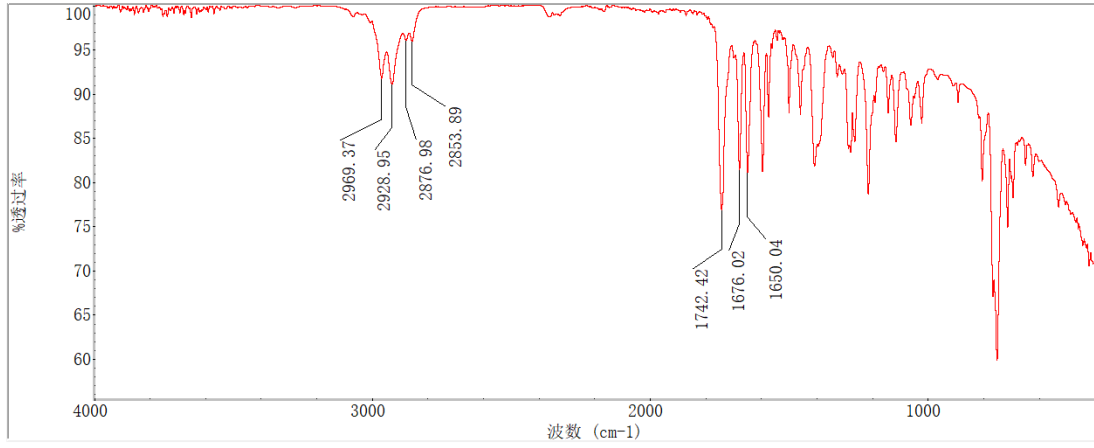




IR (KBr) spectrum for compound **3ad**

Title *星期日 6月 21 10:45:35 2020 (GMT+08:00)

星期五 7月 24 11:56:07 20

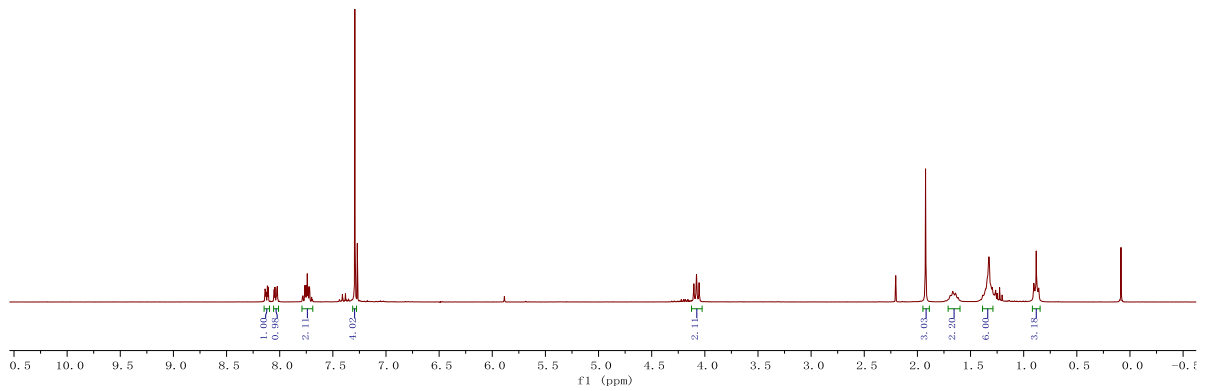
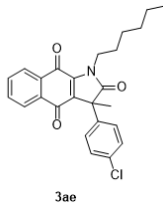


8.135
8.118
8.109
8.107
8.053
8.051
8.045
8.027
8.021
7.763
7.752
7.740
7.738
7.718
7.293
7.270

4.103
4.078
4.054

1.923
1.693
1.682
1.640
1.361
1.342
1.338
1.328
1.313
1.309
1.296
1.264
1.227
1.227
0.887
0.882
0.868
0.858

¹H NMR in CDCl₃ for **3ae**



179.974
178.362
176.229

146.237
136.138
135.142
133.445
132.794
131.656
131.909
130.625
129.908
129.612
127.174
126.097
125.935

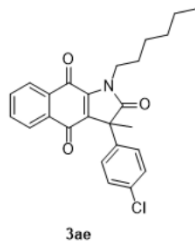
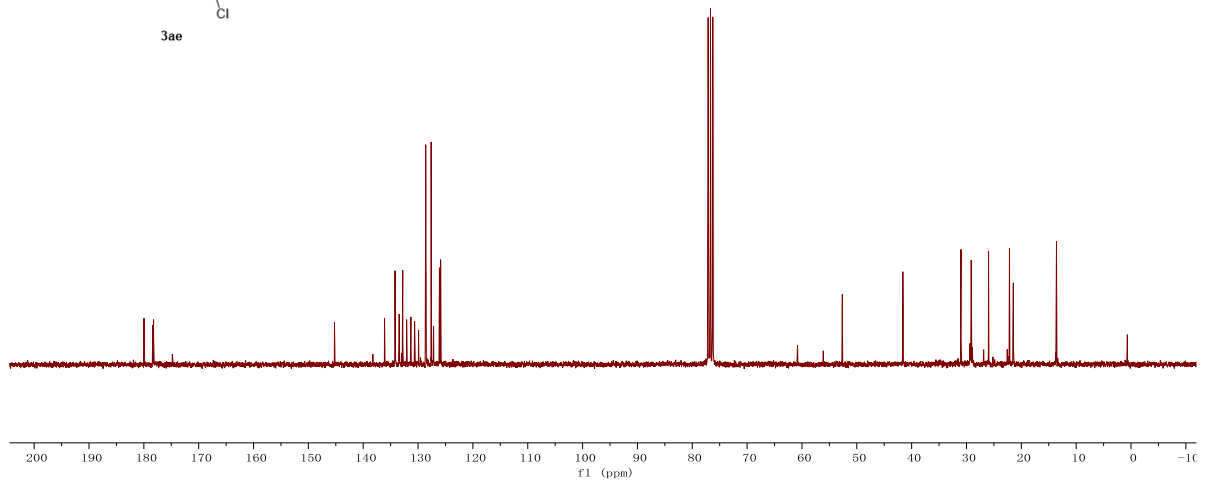
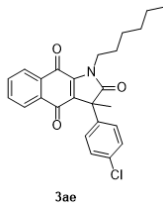
52.639

41.602

35.689
30.138
25.978
22.163
21.498

13.589

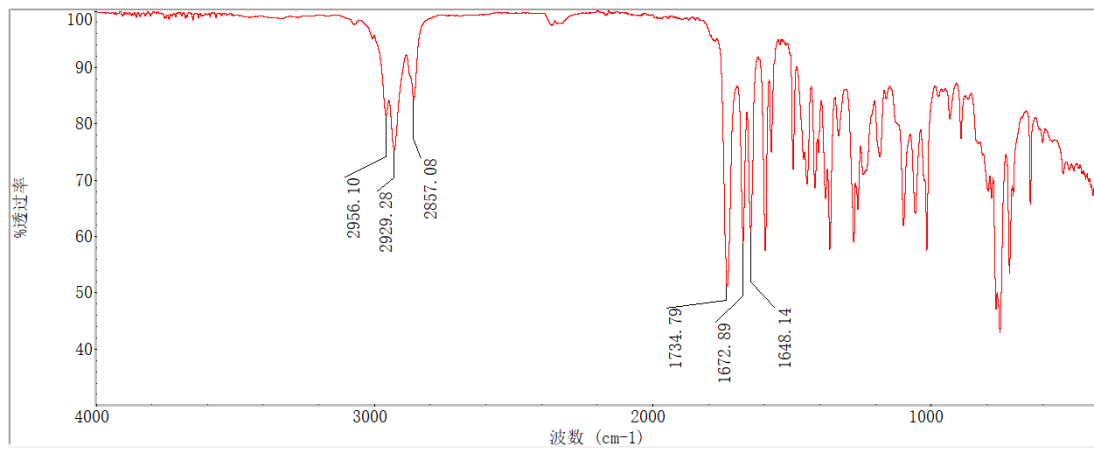
^{13}C NMR in CDCl_3 for **3ae**



IR (KBr) sepctrum for compound **3ae**

Title *星期日 6月 21 10:59:05 2020 (GMT+08:00)

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Single crystallographic data for compound **3aa**.

Single crystals of $C_{20}H_{15}NO_3$ (**3aa**) were obtained by slow evaporation of a solution containing **3aa** in the mixture of EtOH and DCM. A suitable crystal was selected and the crystal data and structure refinement results for compound **3aa** are listed in the Table S1.

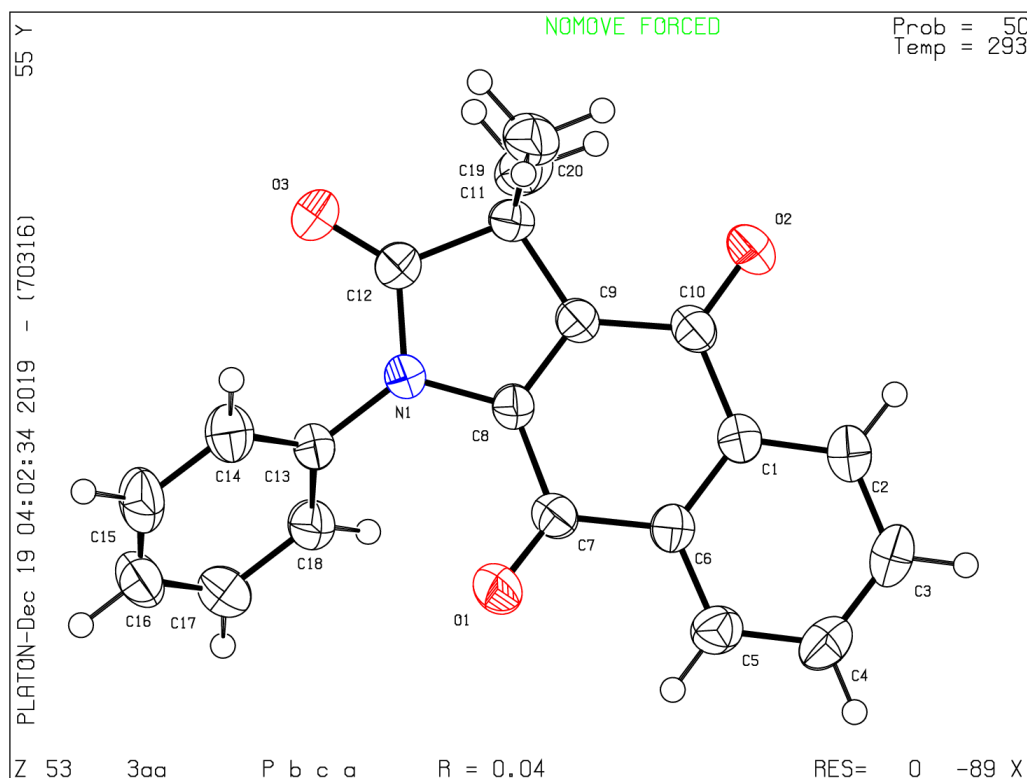


Figure S1. ORTEP view of the compound **3aa with thermal ellipsoids drawn at the 50% probability level**

Table 1 Crystal data and structure refinement for **3aa.**

Identification code	3AA
Empirical formula	$C_{20}H_{15}NO_3$
Formula weight	317.33
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Pbca
a/Å	13.5094(16)
b/Å	11.0920(9)

$c/\text{\AA}$	21.2668(18)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/ \AA^3	3186.8(5)
Z	8
$\rho_{\text{calc}}/\text{g/cm}^3$	1.323
μ/mm^{-1}	0.089
F(000)	1328.0
Crystal size/ mm^3	$0.14 \times 0.13 \times 0.12$
Radiation	Mo K α ($\lambda = 0.71073$)
2Θ range for data collection/ $^\circ$	4.876 to 49.99
Index ranges	$-16 \leq h \leq 10, -13 \leq k \leq 13, -25 \leq l \leq 24$
Reflections collected	8730
Independent reflections	2800 [$R_{\text{int}} = 0.0298, R_{\text{sigma}} = 0.0335$]
Data/restraints/parameters	2800/0/219
Goodness-of-fit on F^2	1.075
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0446, wR_2 = 0.1005$
Final R indexes [all data]	$R_1 = 0.0607, wR_2 = 0.1093$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.14/-0.20