Supporting Information

An environmentally friendly protocol for 2,3-difunctionlization of indole derivatives

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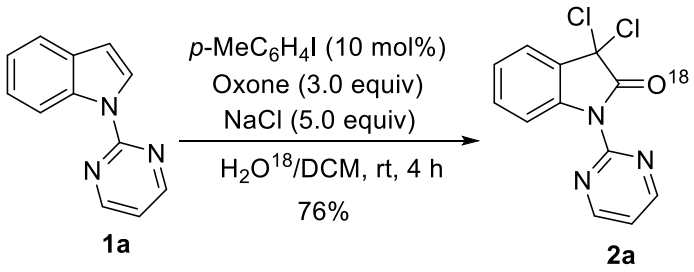
2015084@mail.scuec.edu.cn (Bin Wu)

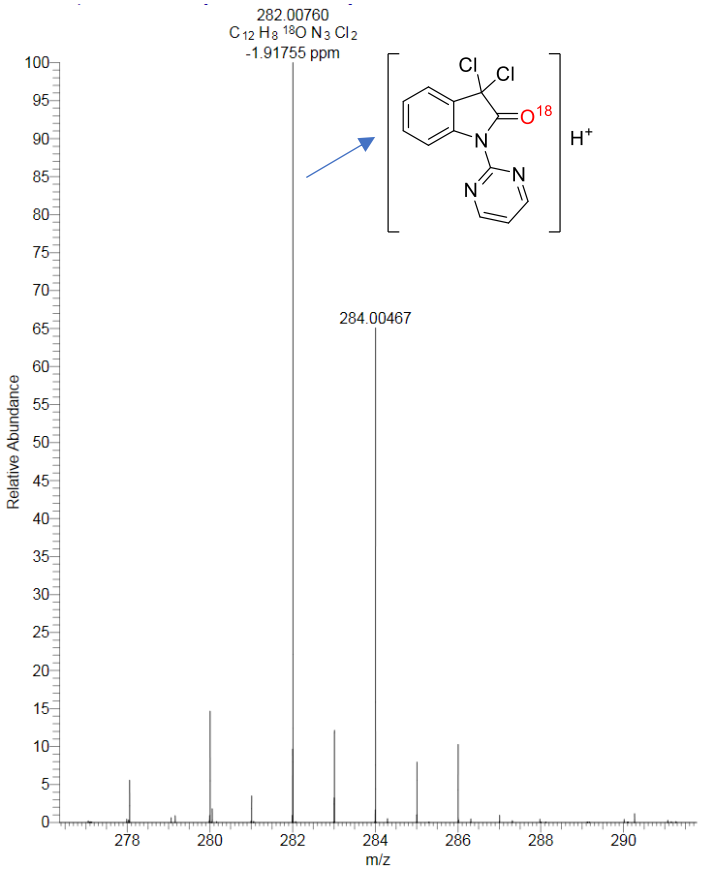
Contents of Supporting Information

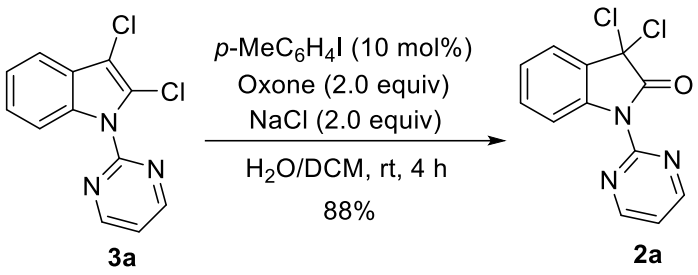
Mechanism studies



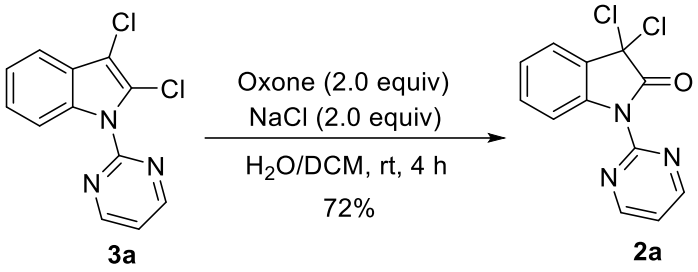
To a 10 mL of round-bottom flask equipped with a stirrer was charged with substrate **1a** (19.5 mg, 0.1 mmol), *p*-MePhI (2.2 mg, 0.1 mmol), Oxone (182.2 mg, 0.3 mmol) and NaCl (29.2 mg, 0.5 mmol). Then, H_2O^{18} (0.2 mL) and DCM (1.0 mL) were added to the reaction flask. The reaction mixture was stirred at room temperature for 4 h and monitored by TLC. Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by flash chromatography (Silica gel, eluent: petroleum ether: ethyl acetate = 10:1) to afford the product **2a** (21.5 mg, 76% yield).

The ESI$^+$ spectrum Characterization of **2a-^{18}O**



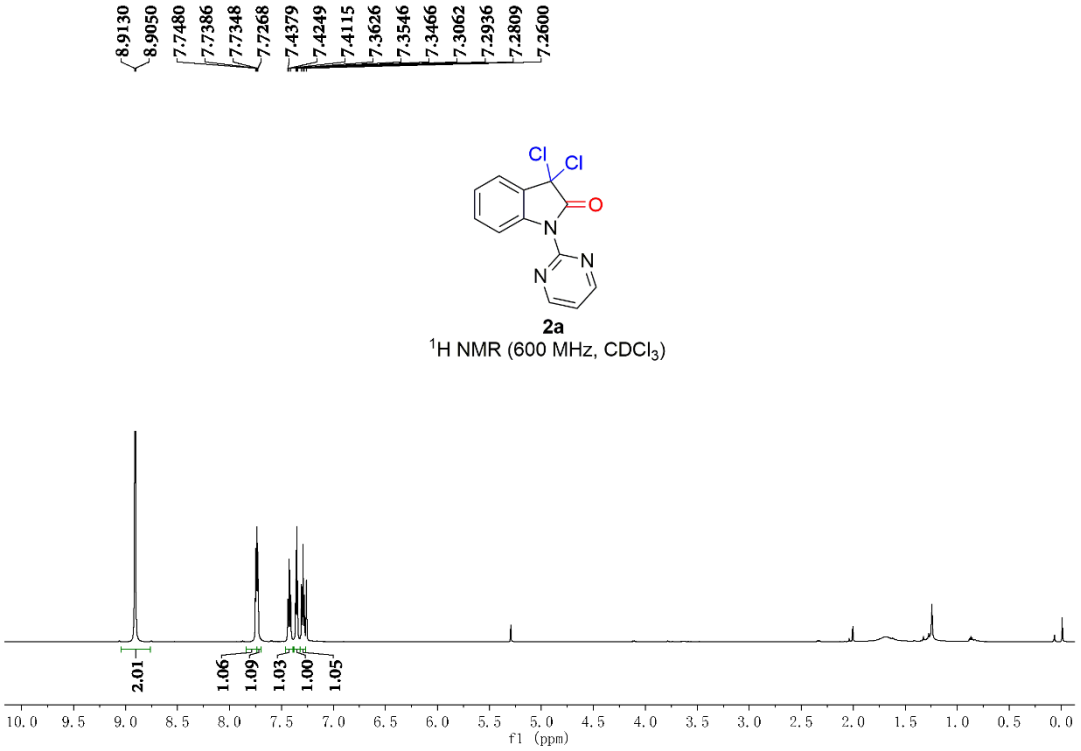


To a 10 mL of round-bottom flask equipped with a stirrer was charged with substrate **3a** (26.4 mg, 0.1 mmol), *p*-MePhI (2.2 mg, 0.01 mmol), Oxone (122.9 mg, 0.2 mmol) and NaCl (11.7 mg, 0.2 mmol). Then, H_2O (1.0 mL) and DCM (0.2 mL) were added to the reaction flask. The reaction mixture was stirred at room temperature for 4 h and monitored by TLC. Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by flash chromatography (Silica gel, eluent: petroleum ether: ethyl acetate = 10:1) to afford the product **2a** (24.6 mg, 88% yield).



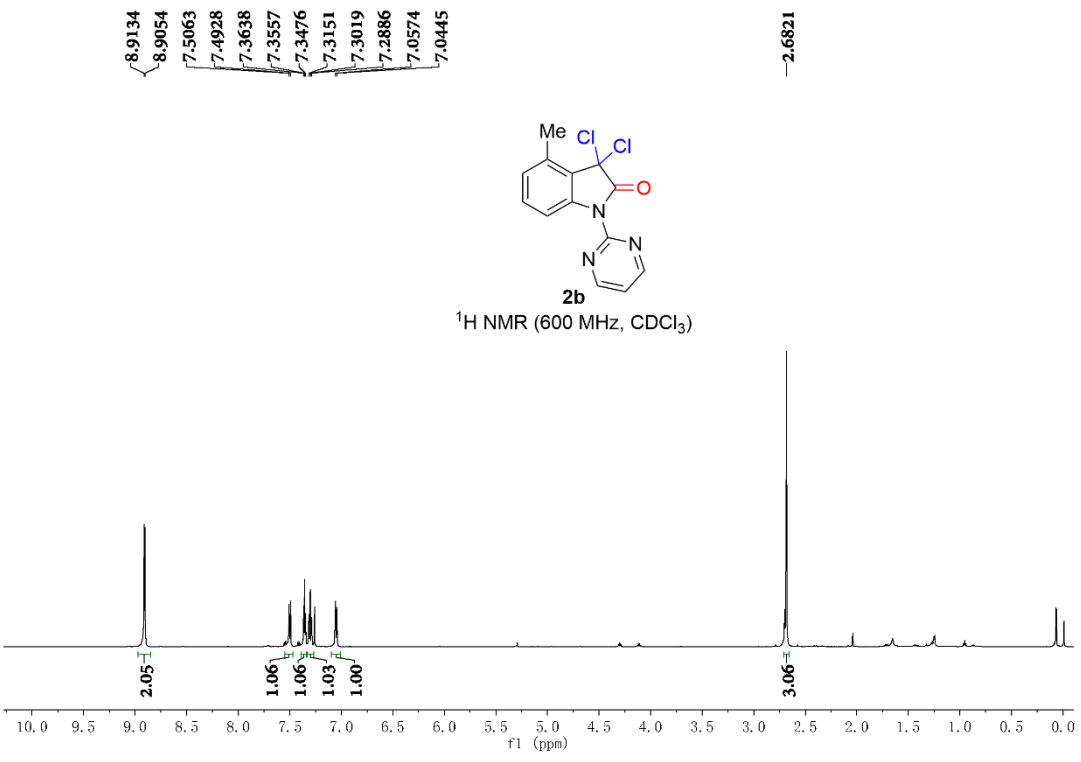
To a 10 mL of round-bottom flask equipped with a stirrer was charged with substrate **3a** (26.4 mg, 0.1 mmol), Oxone (122.9 mg, 0.2 mmol) and NaCl (11.7 mg, 0.2 mmol). Then, H_2O (1.0 mL) and DCM (0.2 mL) were added to the reaction flask. The reaction mixture was stirred at room temperature for 4 h and monitored by TLC. Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by flash chromatography (Silica gel, eluent: petroleum ether: ethyl acetate = 10:1) to afford the product **2a** (20.1 mg, 72% yield).

^{1}H NMR and ^{13}C NMR spectra of compounds



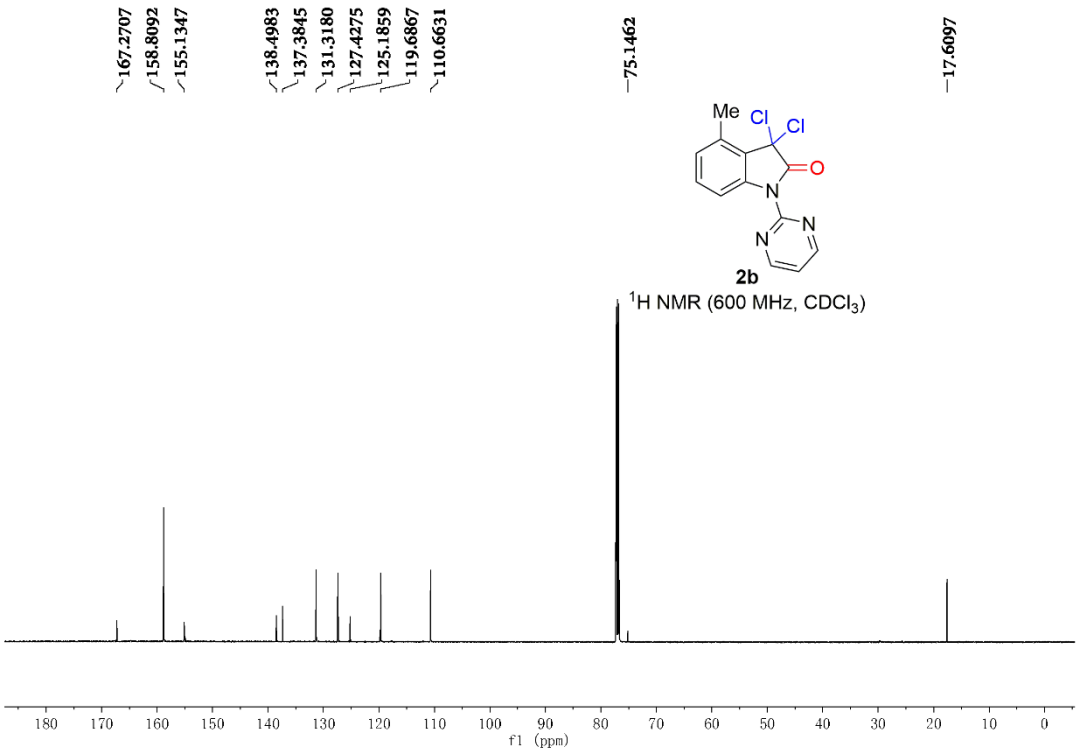
2a

^{1}H NMR (600 MHz, $CDCl_3$)



2b

^{1}H NMR (600 MHz, $CDCl_3$)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155.1347
138.4983
137.3845
131.3180
127.4275
125.1859
119.6867
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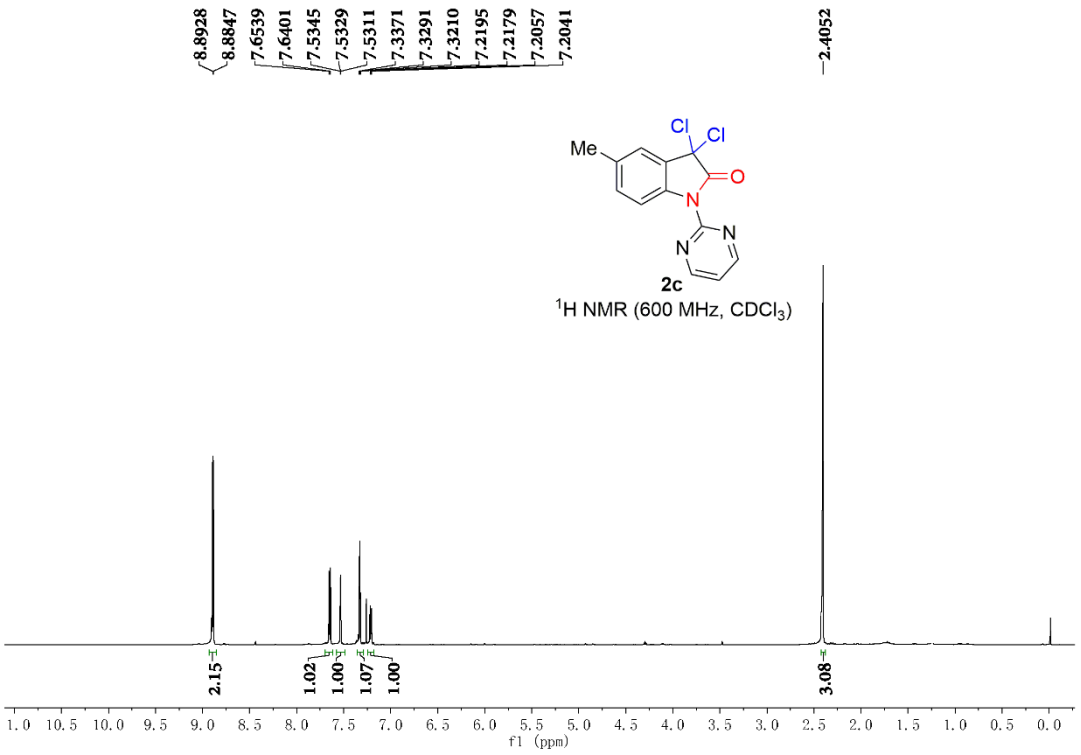
75.1462
17.6097
Me
Cl
Cl
O
N
N
N
2b
1H NMR (600 MHz, CDCl3)
f1 (ppm)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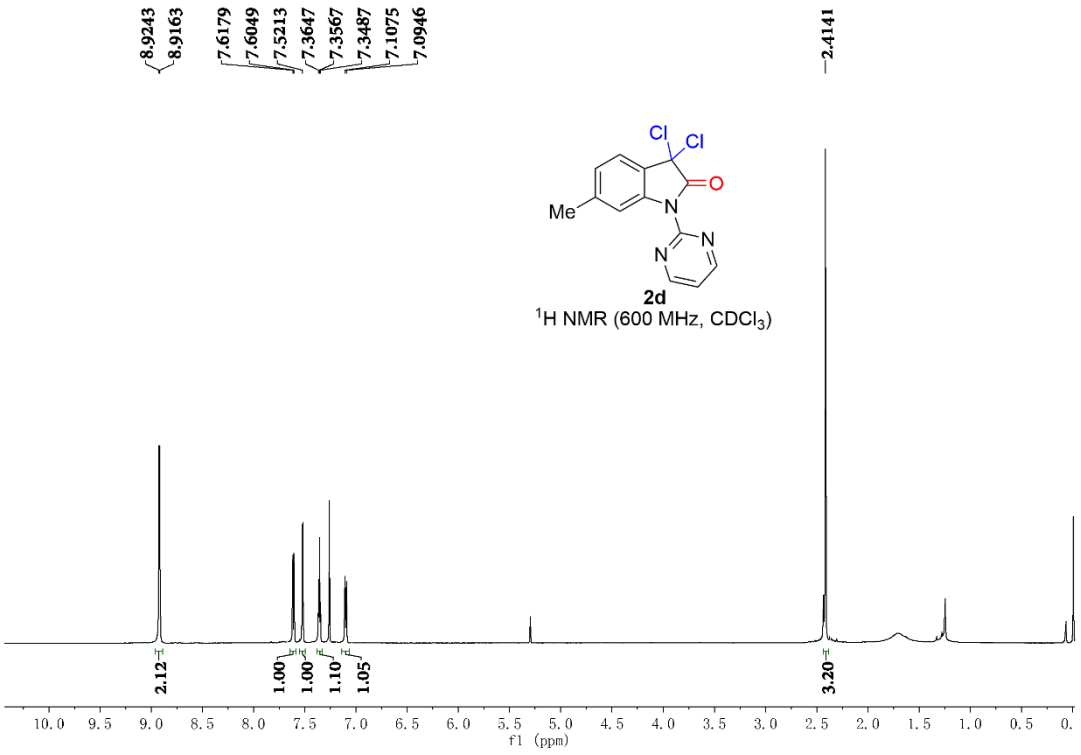
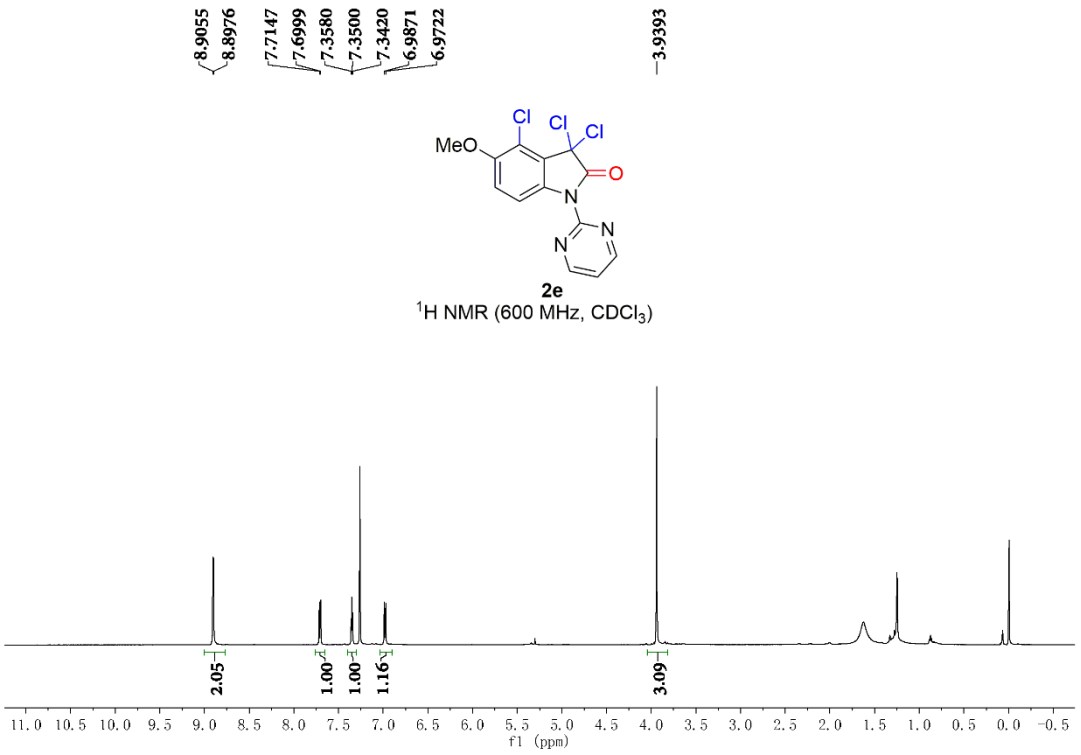
7.6539
7.6401
7.5345
7.5329
7.5311
7.3371
7.3291
7.3210
7.2195
7.2179
7.2057
7.2041
2.4052
Cl
Cl
Me
O
N
N
N
2c
1H NMR (600 MHz, CDCl3)
2.15
1.02
1.00
1.07
1.00
3.08
f1 (ppm)



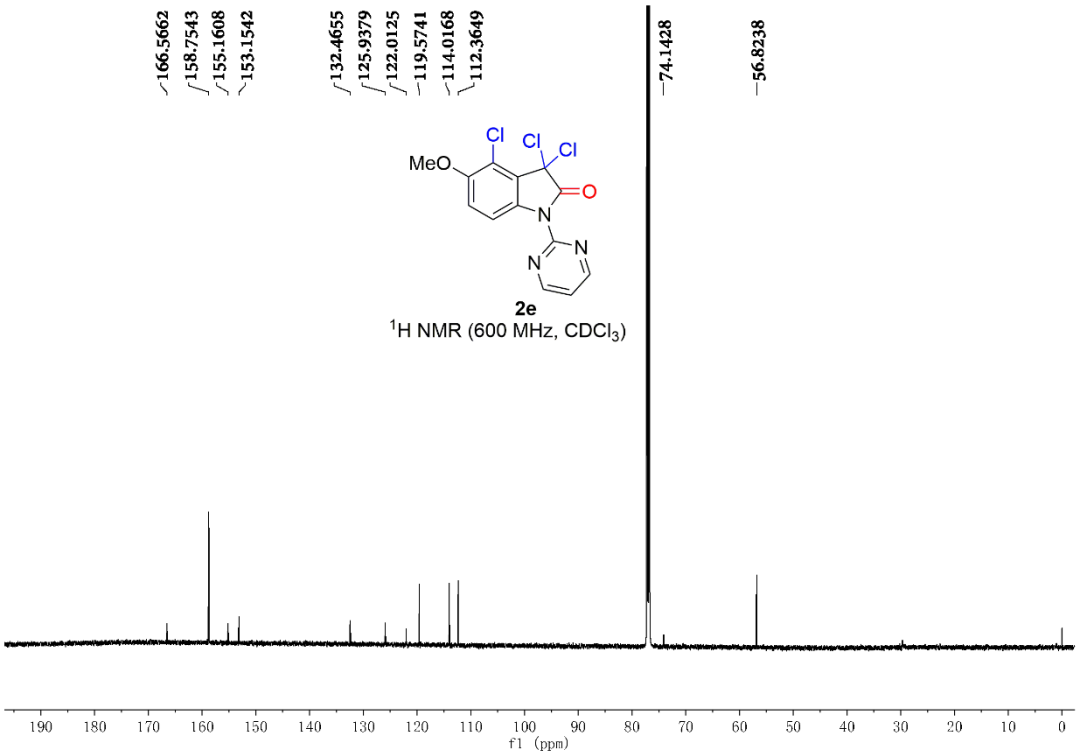
2d

^{1}H NMR (600 MHz, $CDCl_3$)



2e

^{1}H NMR (600 MHz, $CDCl_3$)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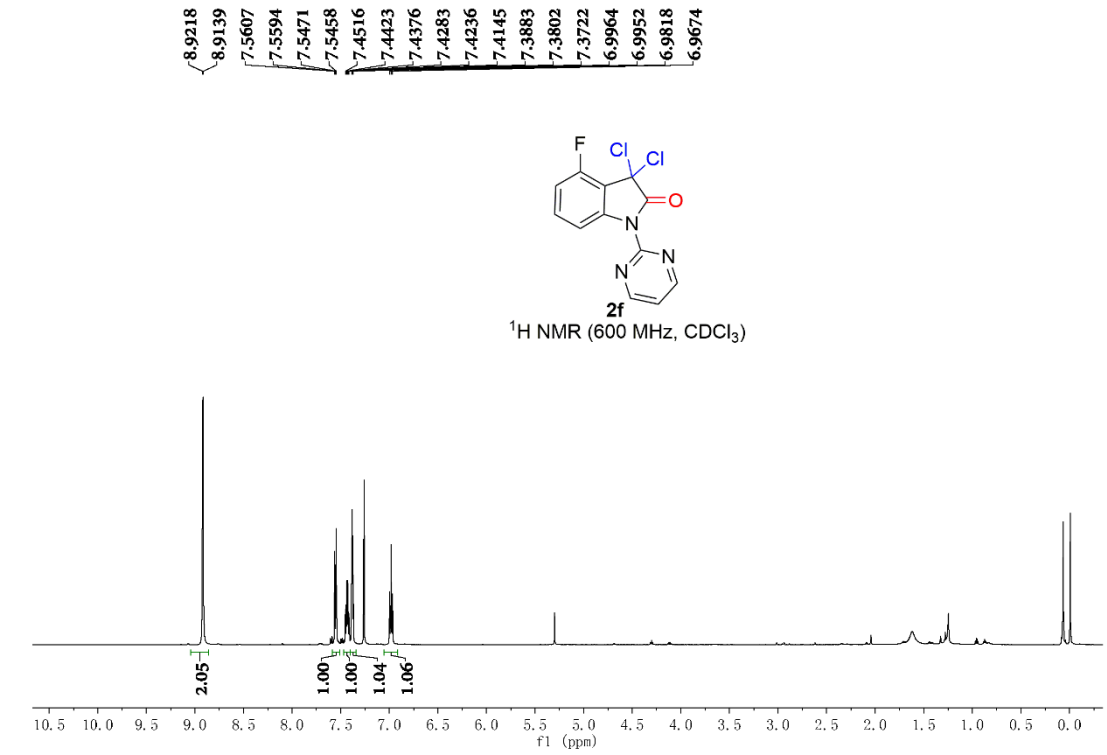
155.1608
153.1542
132.4655
125.9379
122.0125
119.5741
114.0168
112.3649
74.1428
56.8238
Cl
Cl
Cl
MeO
O
N
N
N
2e
1H NMR (600 MHz, CDCl3)
f1 (ppm)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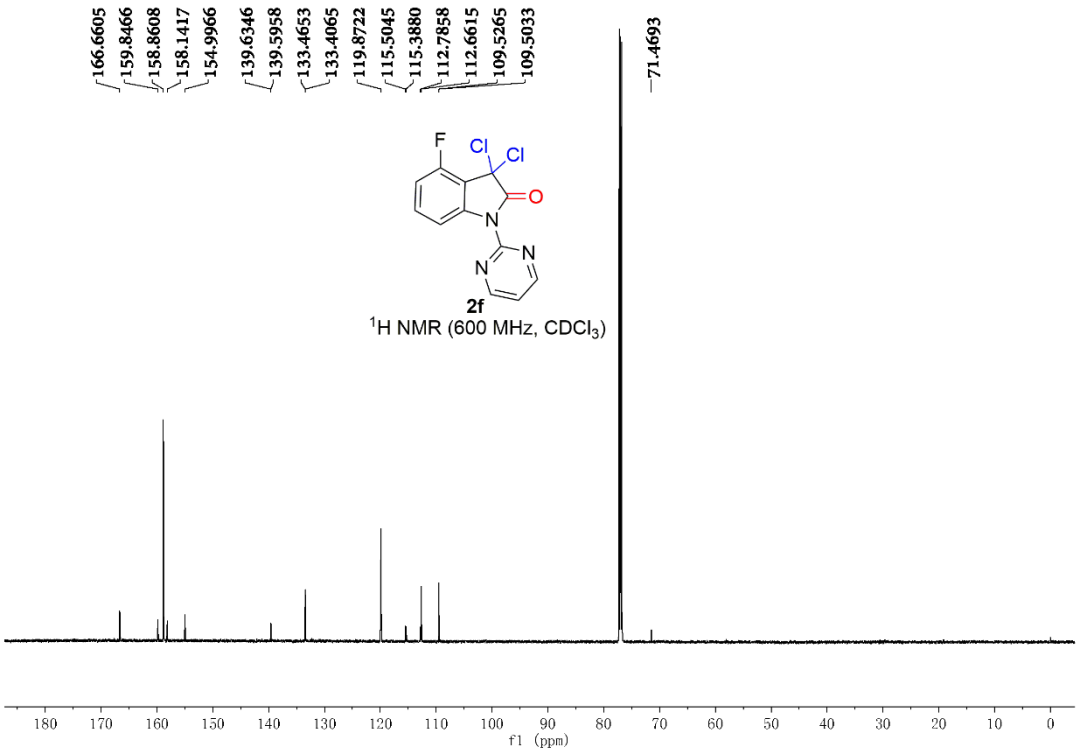
7.5607
7.5594
7.5471
7.5458
7.4516
7.4423
7.4376
7.4283
7.4236
7.4145
7.3883
7.3802
7.3722
6.9964
6.9952
6.9818
6.9674
F
Cl
Cl
O
N
N
N
2f
1H NMR (600 MHz, CDCl3)
2.05
1.00
1.00
1.04
1.06
f1 (ppm)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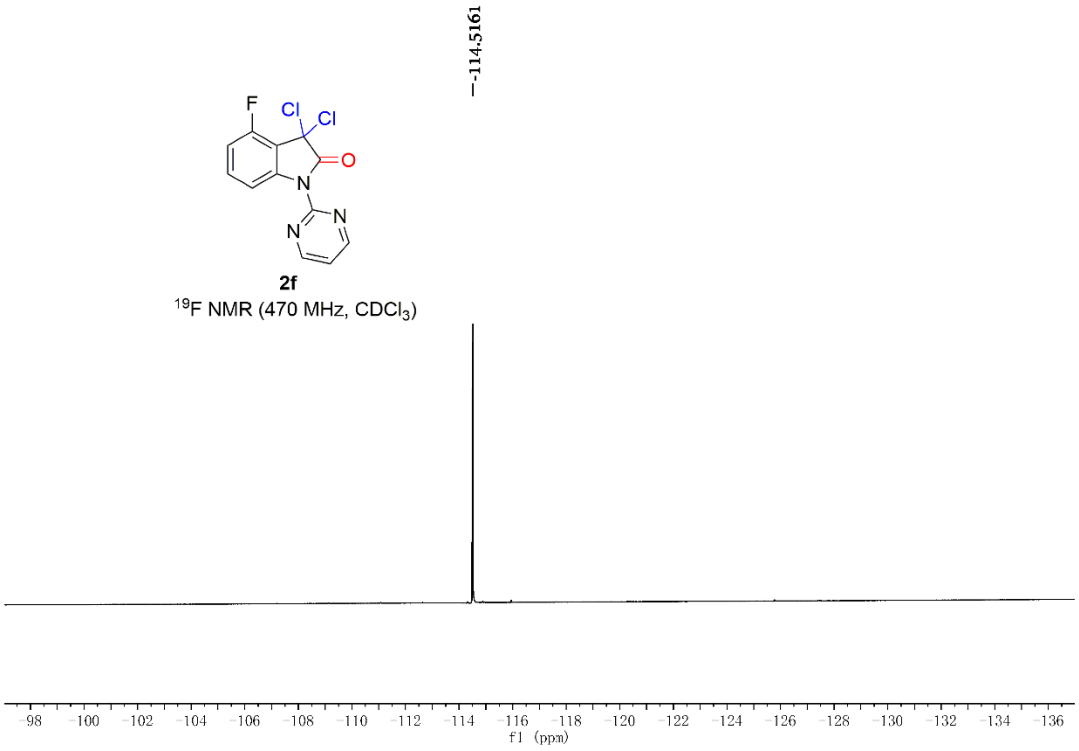
158.1417
154.9966
139.6346
139.5958
133.4653
133.4065
119.8722
115.5045
115.3880
112.7858
112.6615
109.5265
109.5033
71.4693
F
Cl
Cl
O
N
N
N
2f
1H NMR (600 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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F
Cl
Cl
O
N
N
N
2f
19F NMR (470 MHz, CDCl3)
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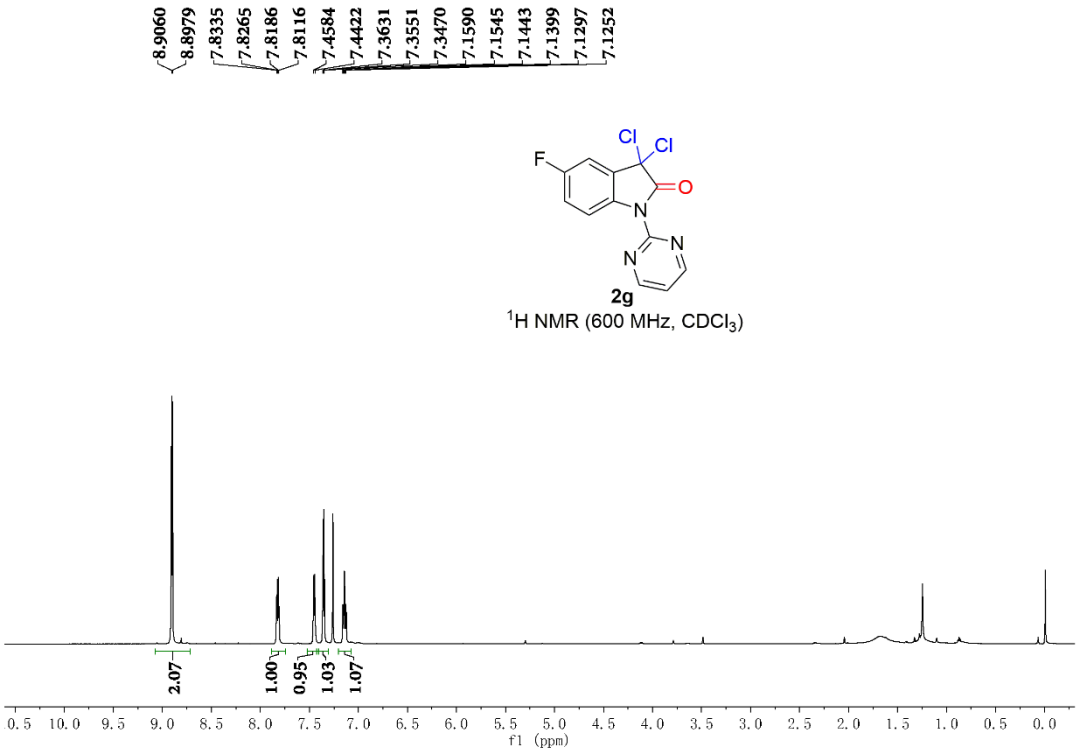
-100
-102
-104
-106
-108
-110
-112
-114
-116
-118
-120
-122
-124
-126
-128
-130
-132
-134
-136
f1 (ppm)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7.8116
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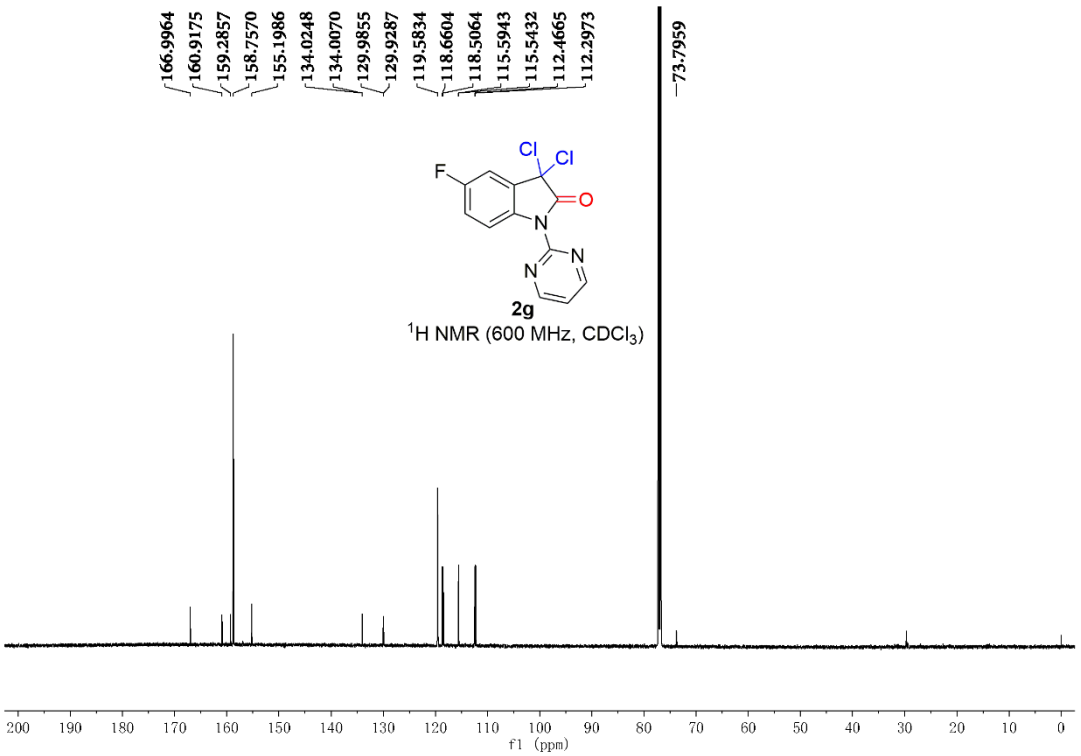
7.1590
7.1545
7.1443
7.1399
7.1297
7.1252
Cl
Cl
F
O
N
N
N
2g
1H NMR (600 MHz, CDCl3)
2.07
1.00
0.95
1.03
1.07
f1 (ppm)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158.7570
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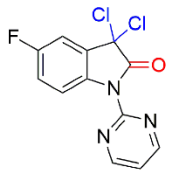
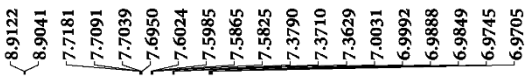
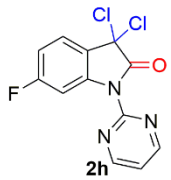
134.0070
129.9855
129.9287
119.5834
118.6604
118.5064
115.5943
115.5432
112.4665
112.2973
73.7959
Cl
Cl
F
O
N
N
N
2g
1H NMR (600 MHz, CDCl3)
f1 (ppm)



2g

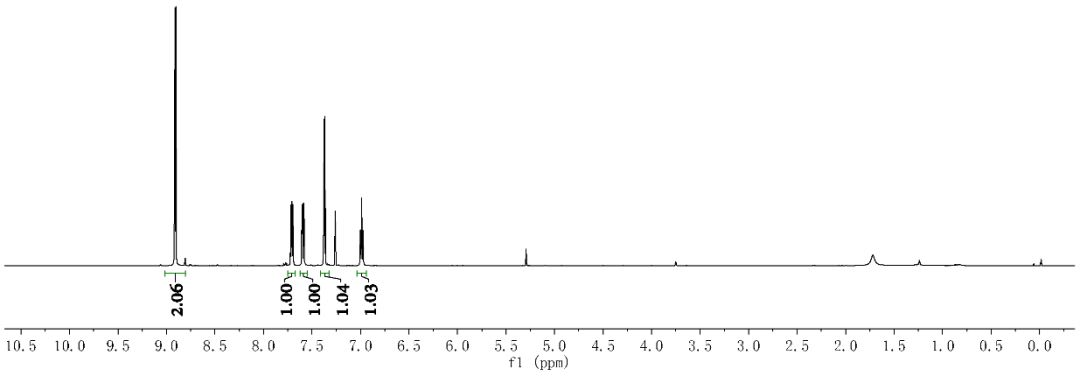
^{19}F NMR (470 MHz, $CDCl_3$)

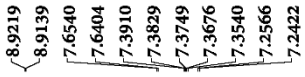


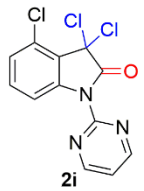


2h

^{1}H NMR (600 MHz, $CDCl_3$)

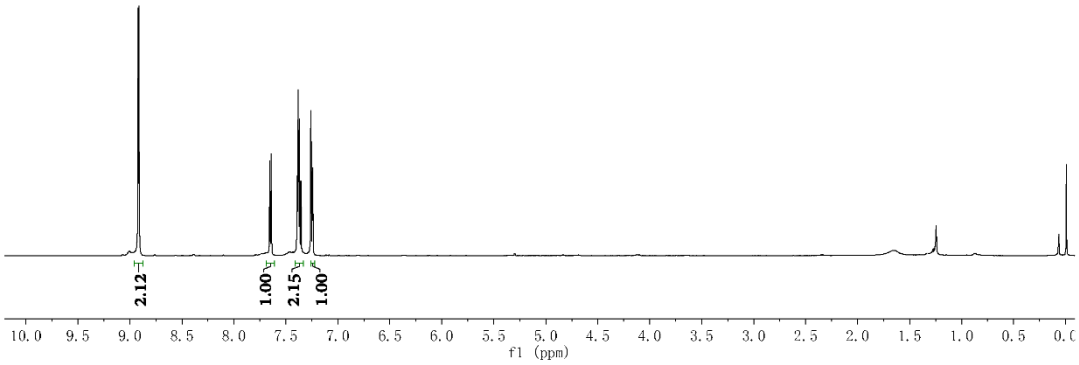


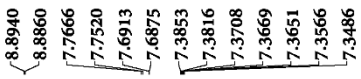


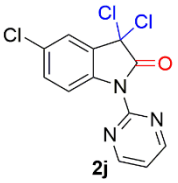


2i

^{1}H NMR (600 MHz, $CDCl_3$)







2j

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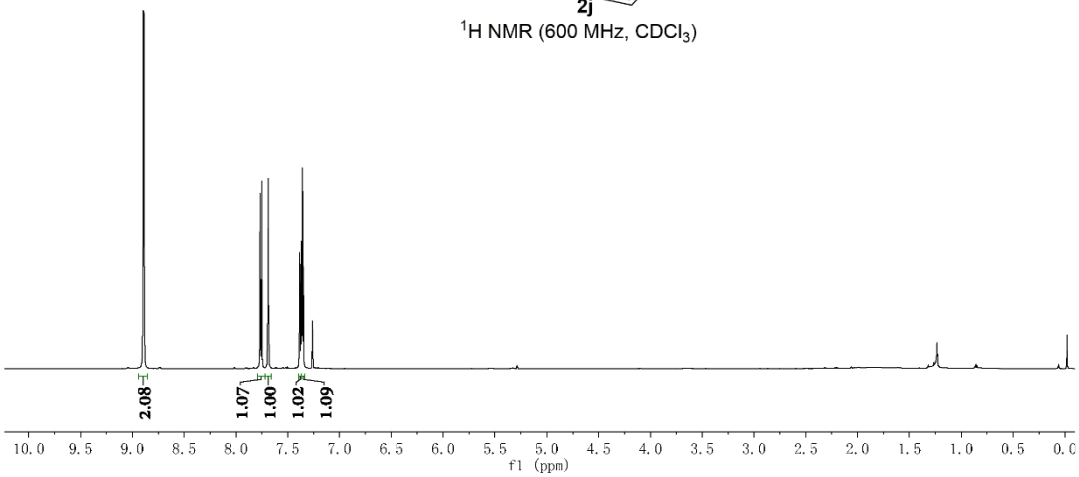
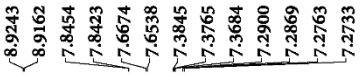
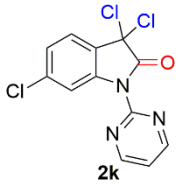
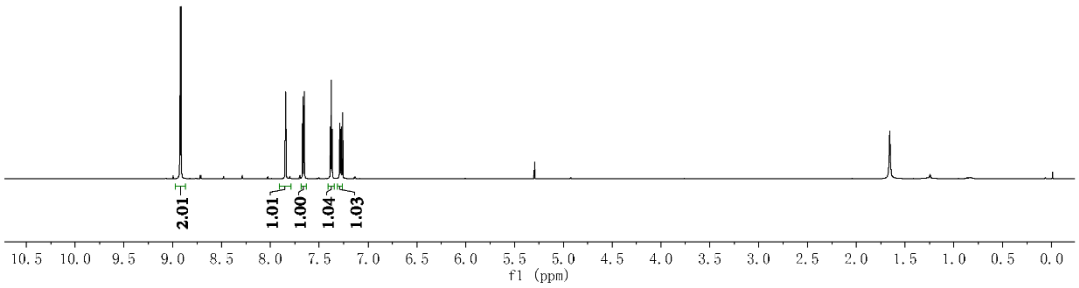


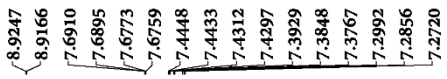


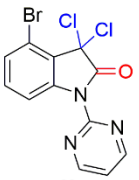


2k

^{1}H NMR (600 MHz, $CDCl_3$)

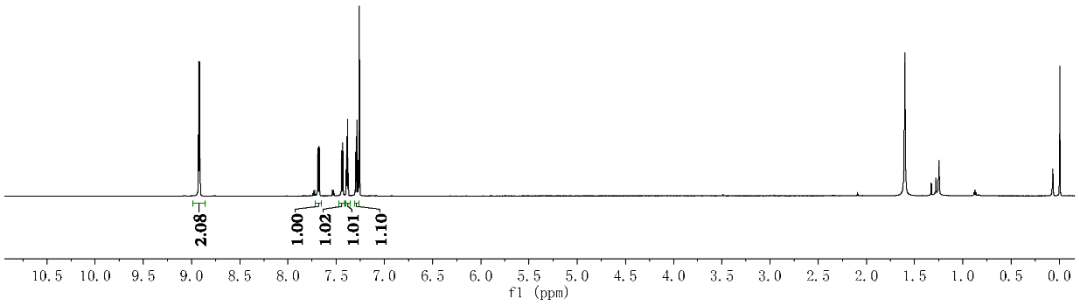


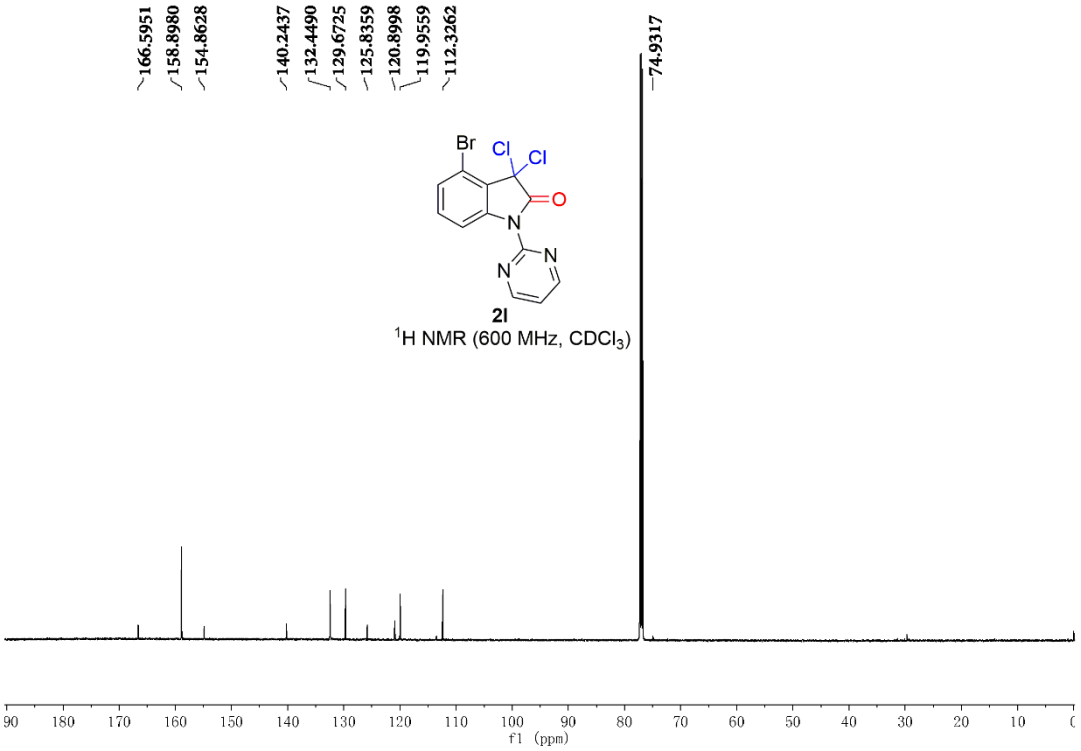




2l

^{1}H NMR (600 MHz, $CDCl_3$)

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140.2437
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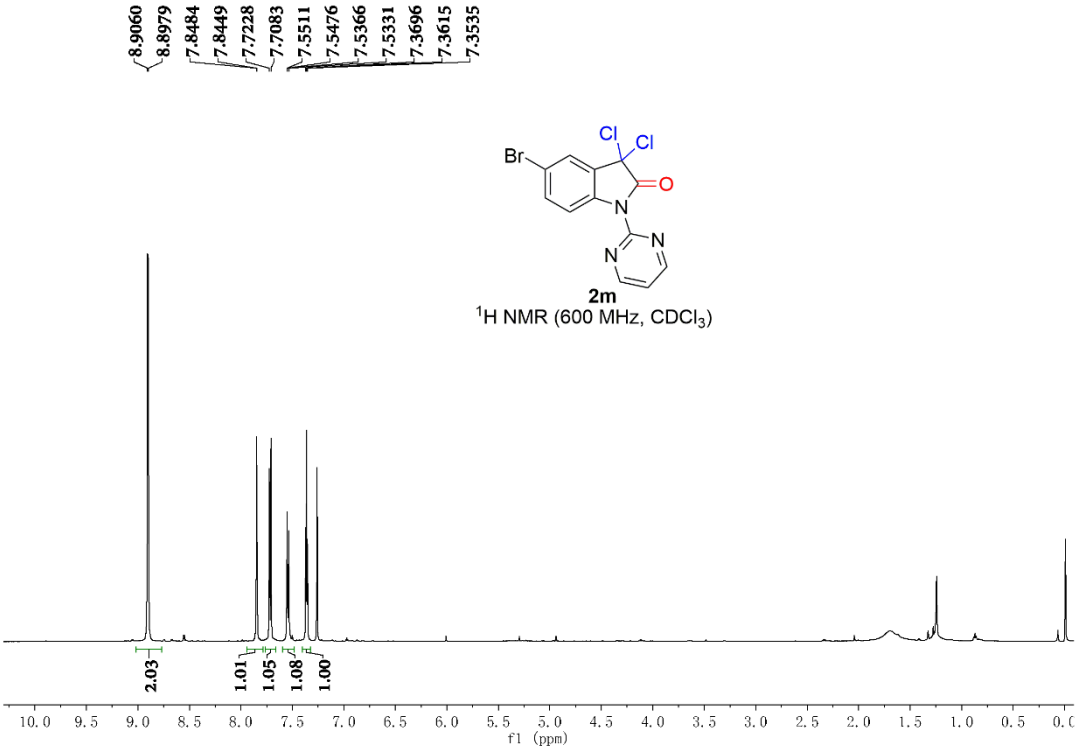
Br
Cl
Cl
O
N
N
N
2l
1H NMR (600 MHz, CDCl3)
f1 (ppm)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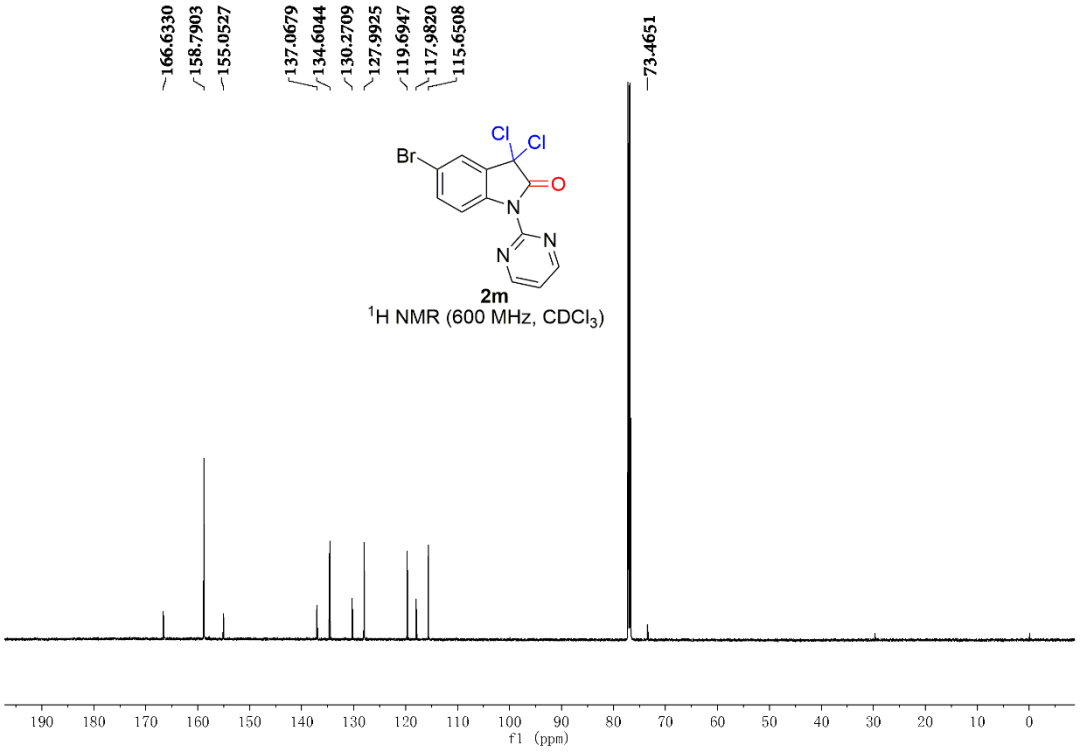
7.5331
7.3696
7.3615
7.3535
Br
Cl
Cl
O
N
N
N
2m
1H NMR (600 MHz, CDCl3)
2.03
1.01
1.05
1.08
1.00
f1 (ppm)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Cl
Cl
Br
O
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N
2m
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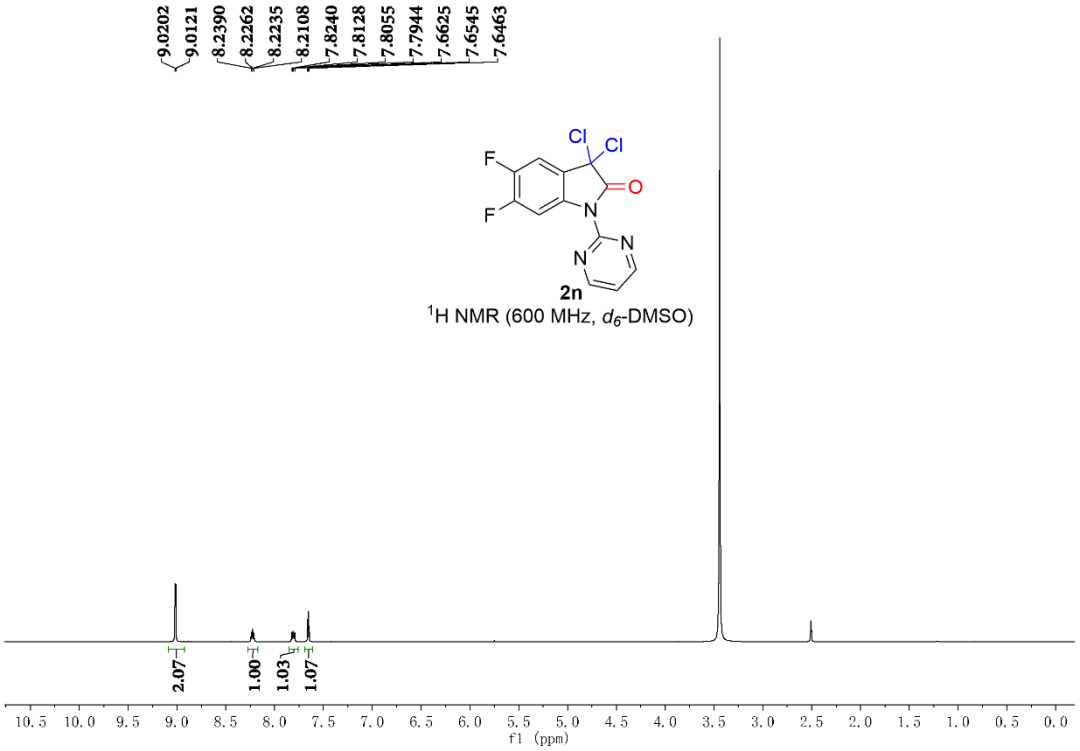
f1 (ppm)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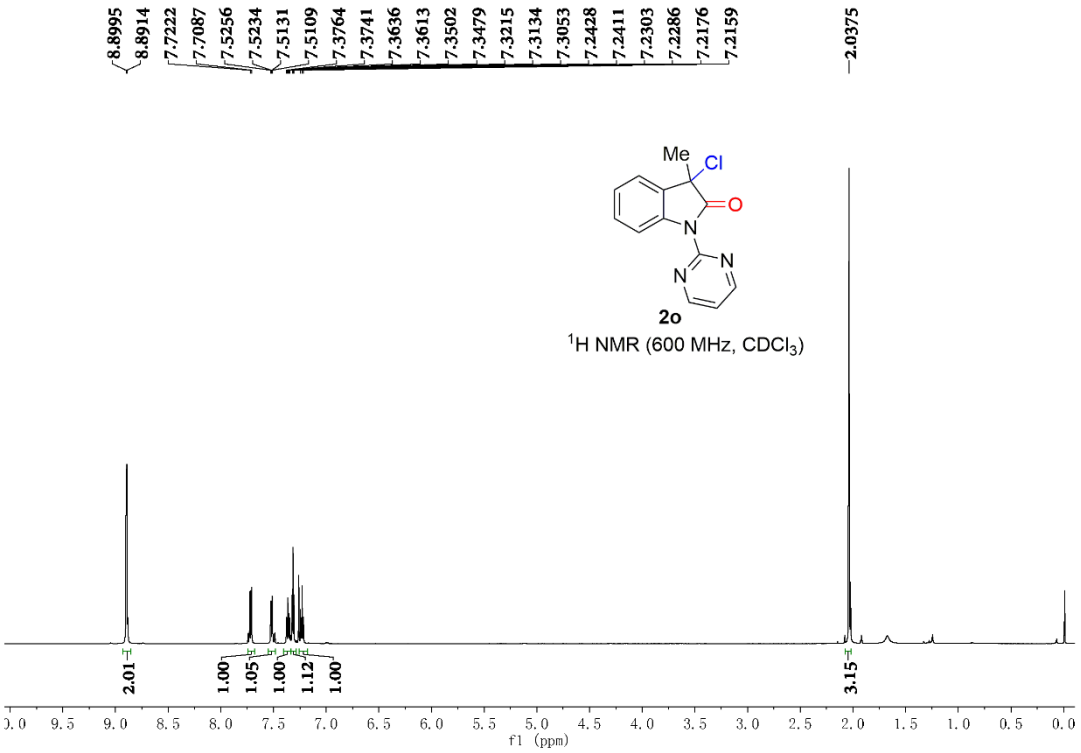
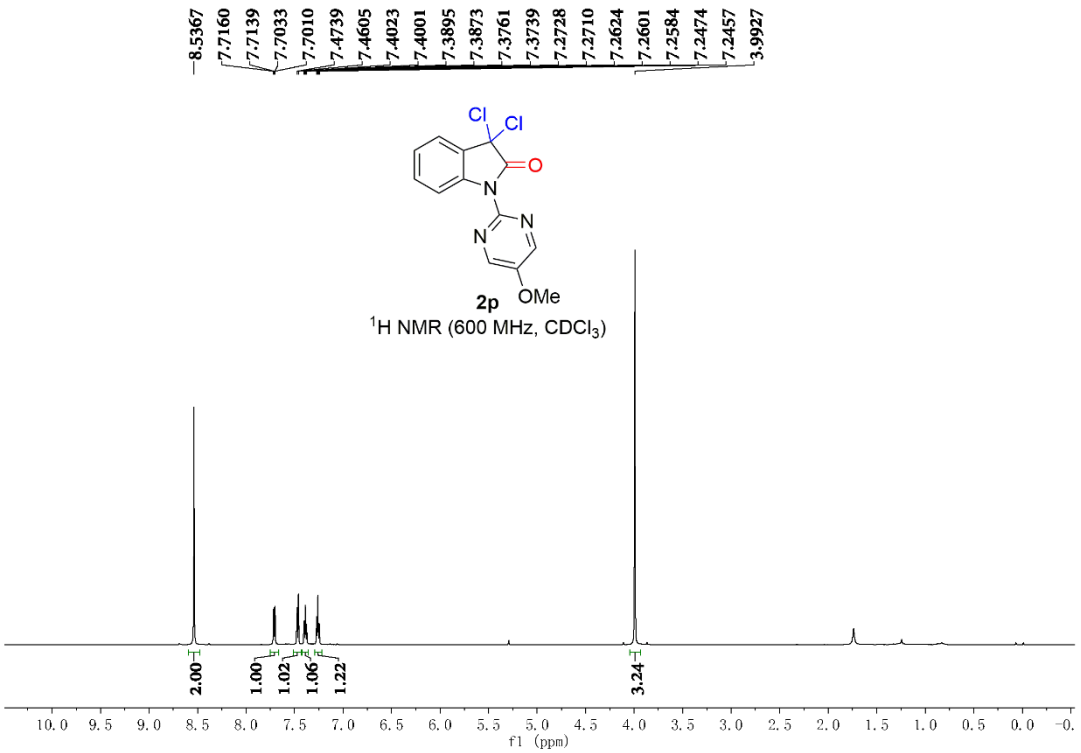
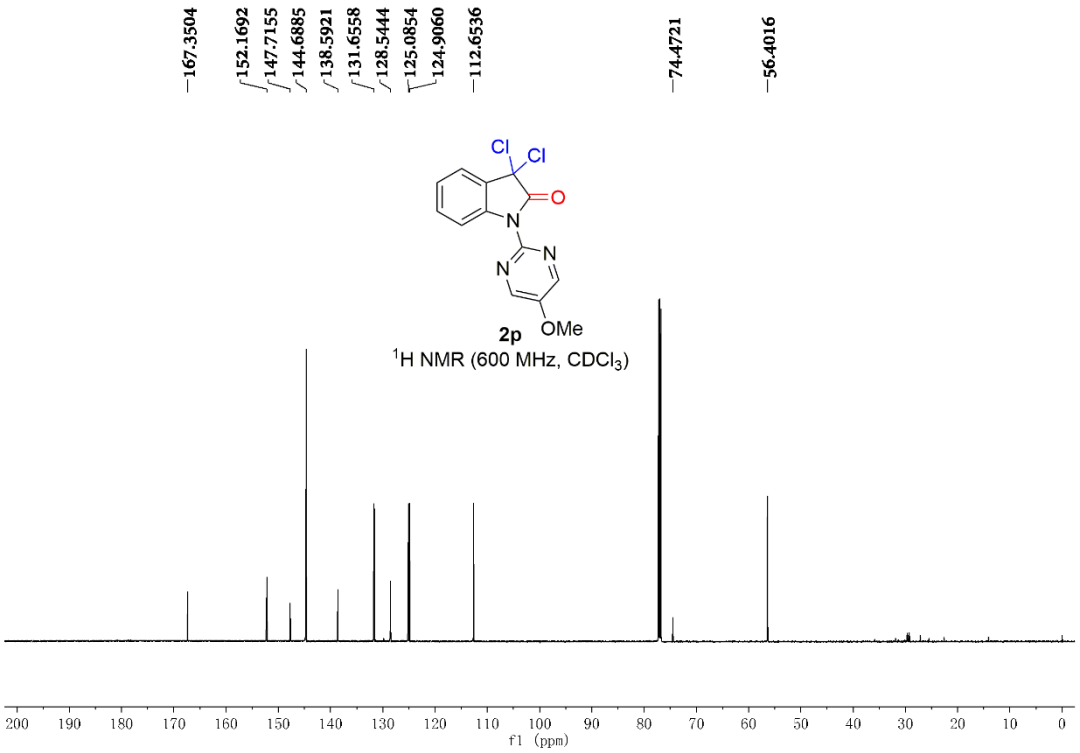
7.6545
7.6463
Cl
Cl
F
F
O
N
N
N
2n
1H NMR (600 MHz, d6-DMSO)
2.07
1.00
1.03
1.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

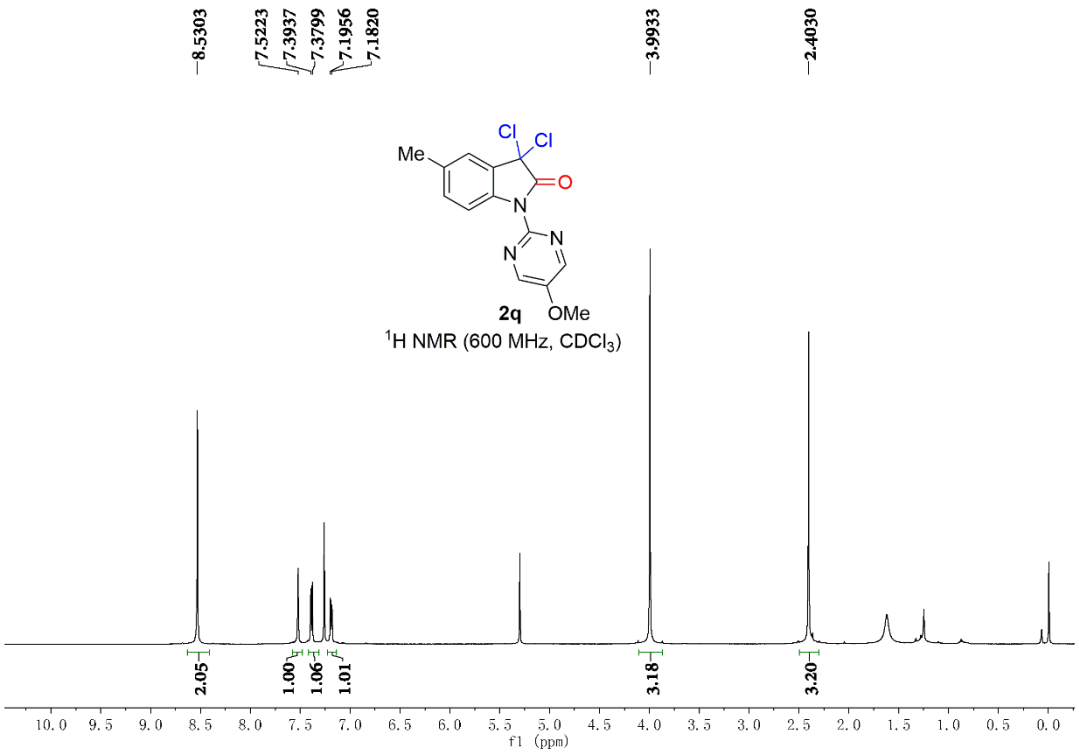


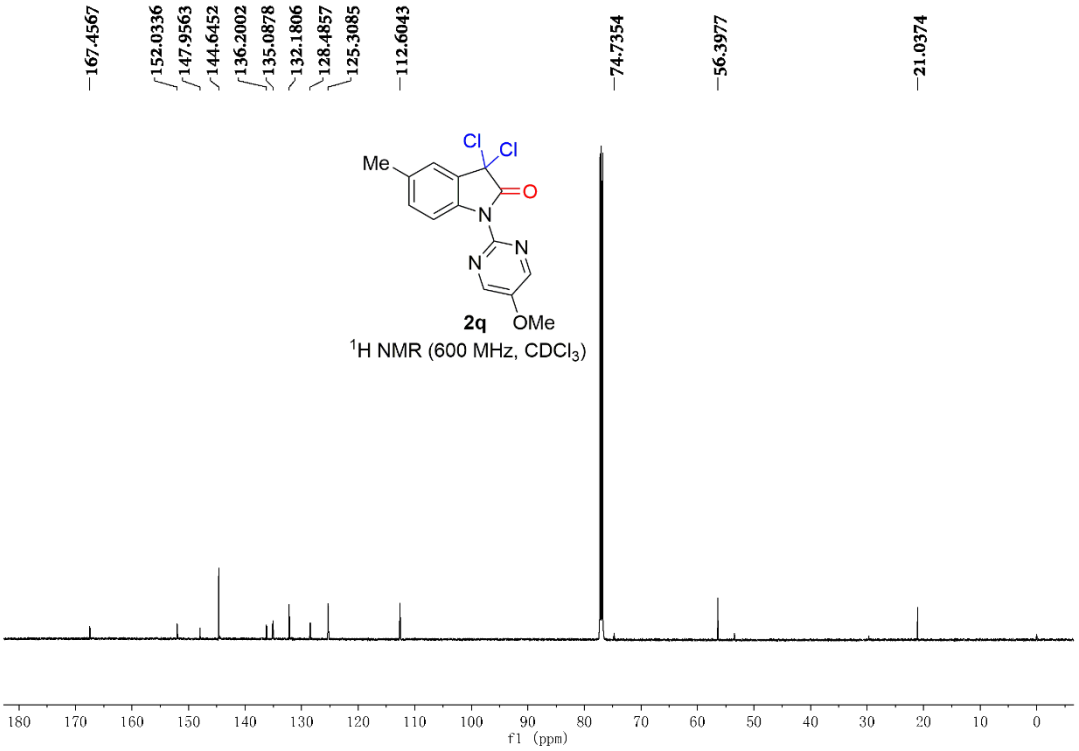
^{1}H NMR (600 MHz, $CDCl_3$)

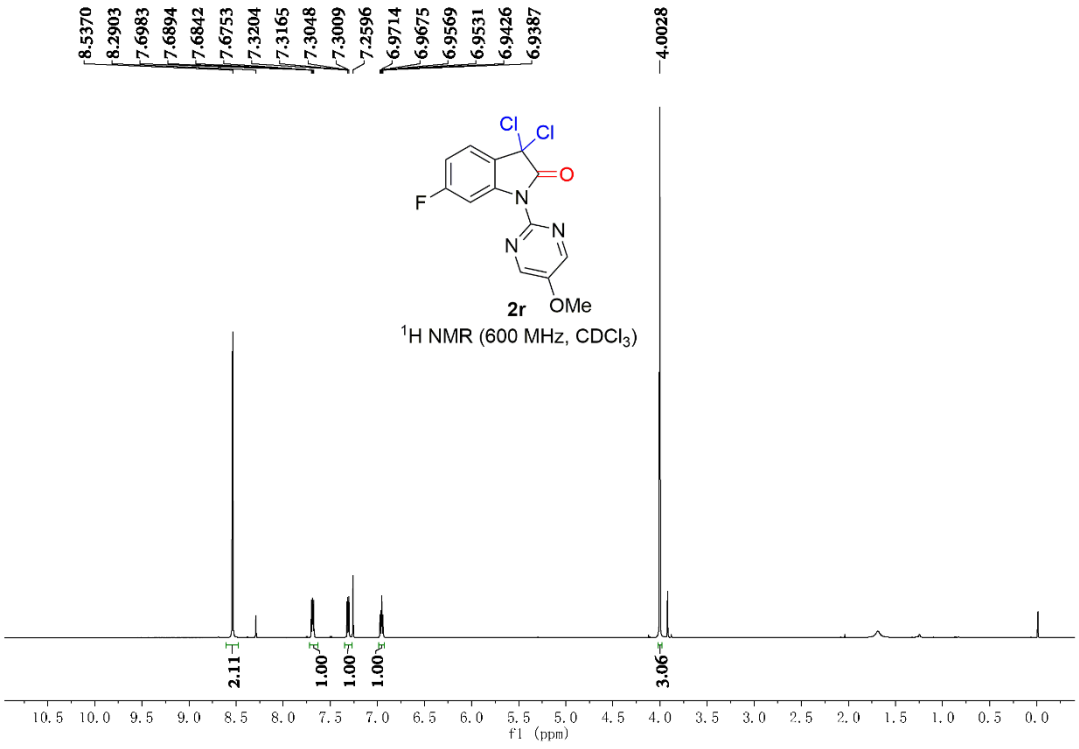


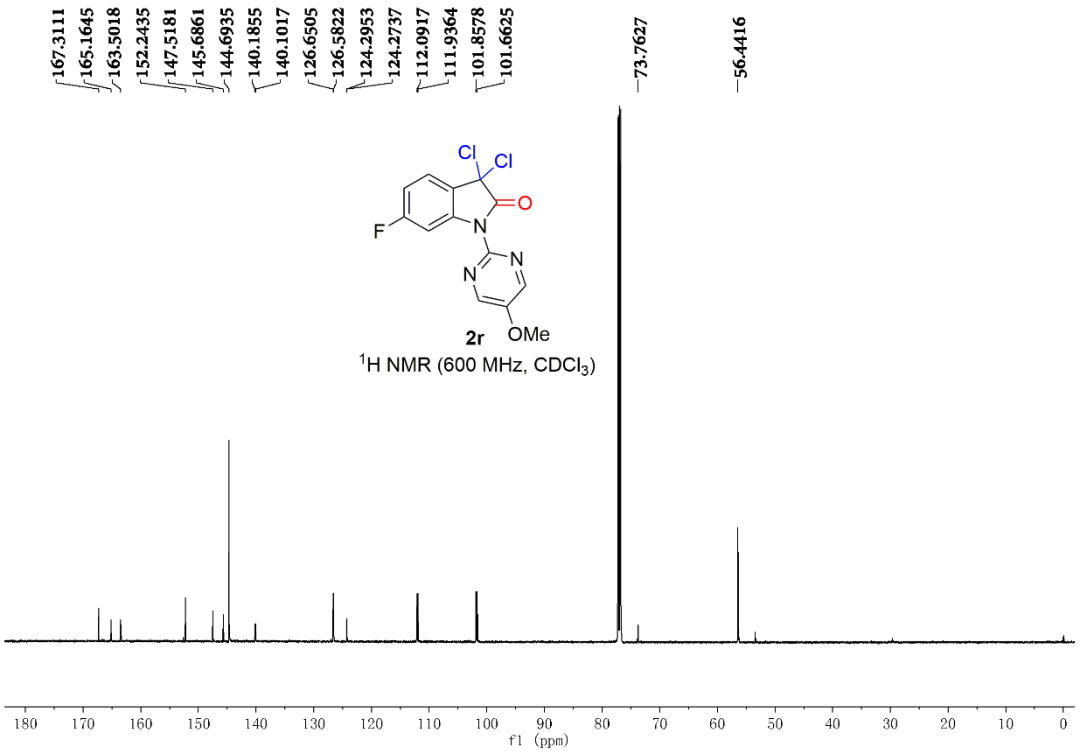
^{1}H NMR (600 MHz, $CDCl_3$)


167.3504
152.1692
147.7155
144.6885
138.5921
131.6558
128.5444
125.0854
124.9060
112.6536
74.4721
56.4016
Cl
Cl
O
N
N
N
OMe
2p
1H NMR (600 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.5303
7.5223
7.3937
7.3799
7.1956
7.1820
3.9933
2.4030
Me
Cl
Cl
O
N
N
N
OMe
2q
1H NMR (600 MHz, CDCl3)
2.05
1.00
1.06
1.01
3.18
3.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

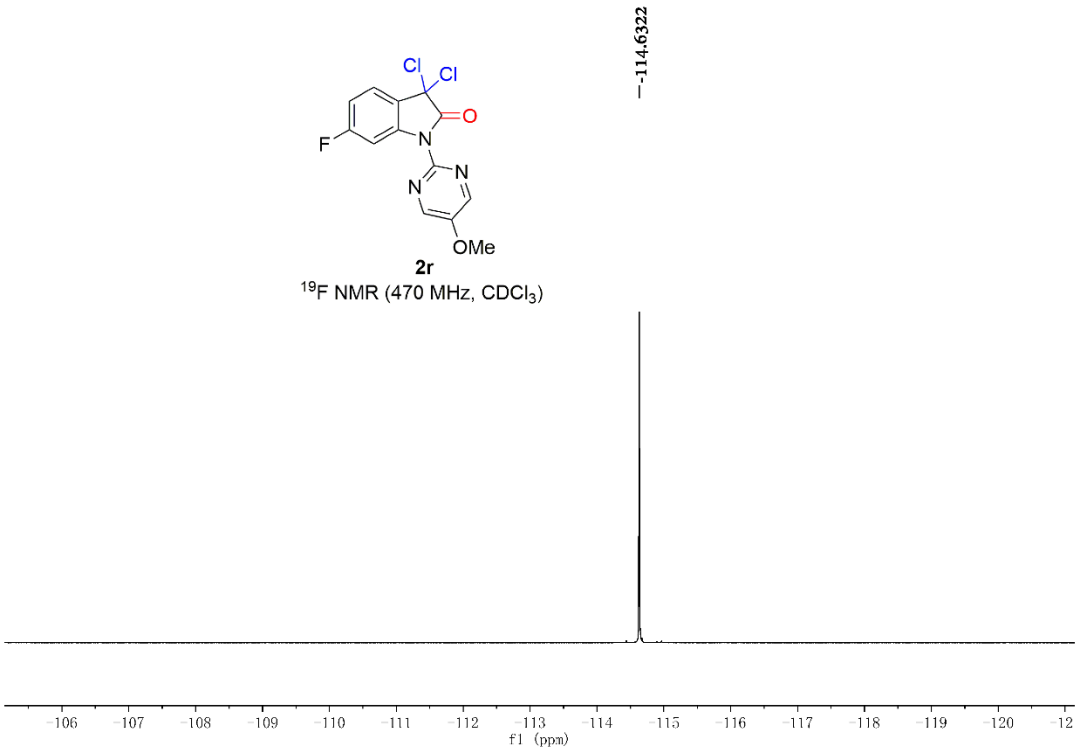

167.4567
152.0336
147.9563
144.6452
136.2002
135.0878
132.1806
128.4857
125.3085
112.6043
74.7354
56.3977
21.0374
Cl
Cl
Me
O
N
N
N
OMe
2q
1H NMR (600 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.5370
8.2903
7.6983
7.6894
7.6842
7.6753
7.3204
7.3165
7.3048
7.3009
7.2596
6.9714
6.9675
6.9569
6.9531
6.9426
6.9387
4.0028
Cl
Cl
F
O
N
N
N
OMe
2r
1H NMR (600 MHz, CDCl3)
2.11
1.00
1.00
1.00
3.06
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
f1 (ppm)



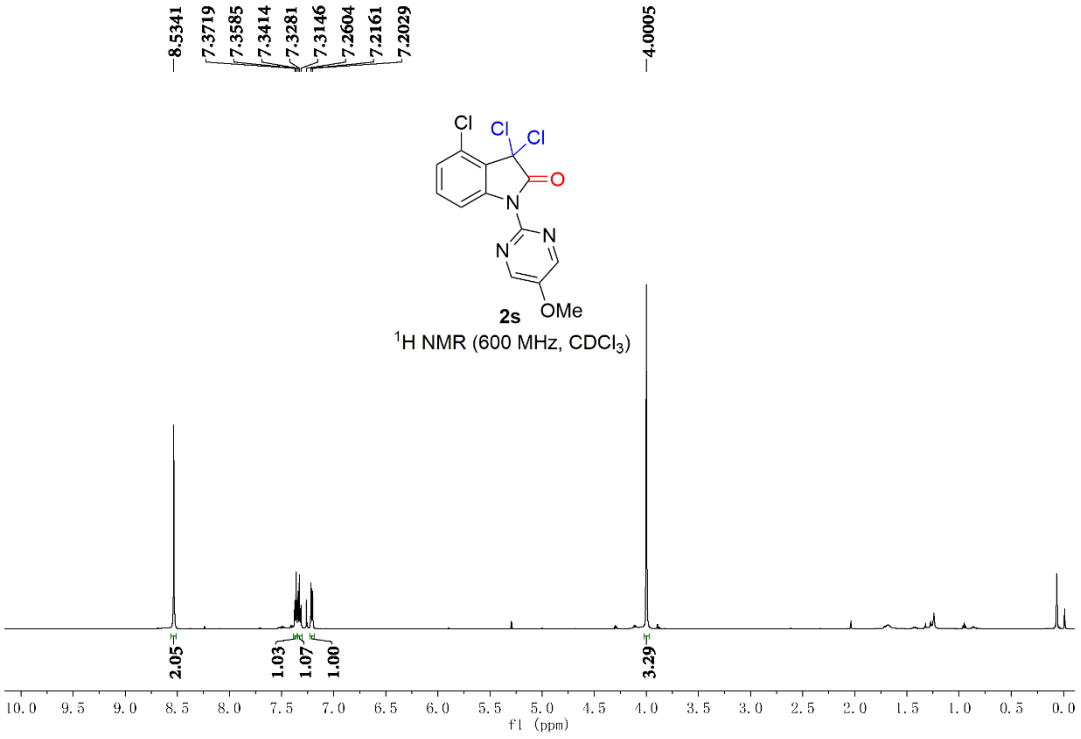
2r

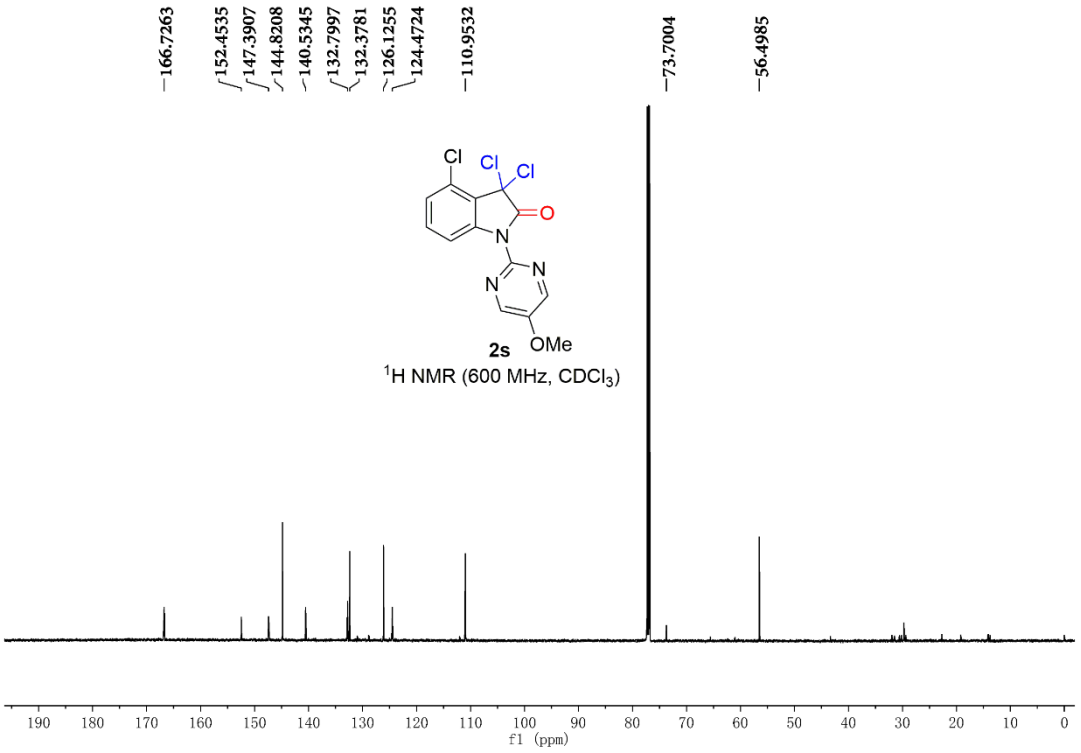
^{1}H NMR (600 MHz, $CDCl_3$)

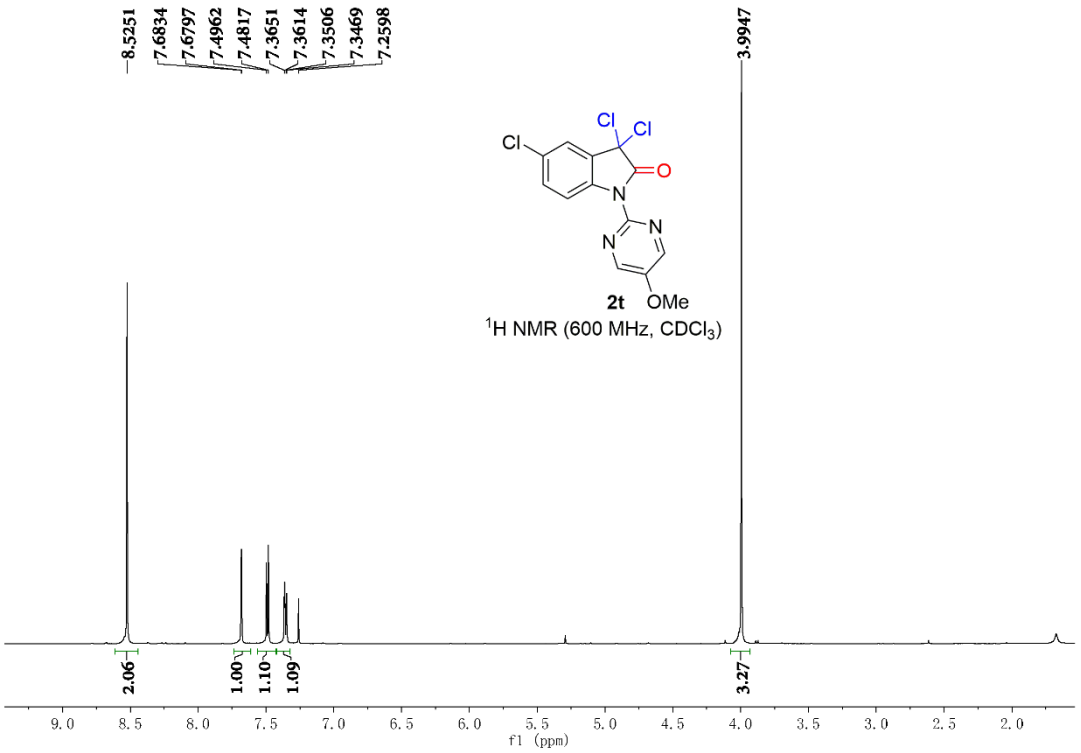


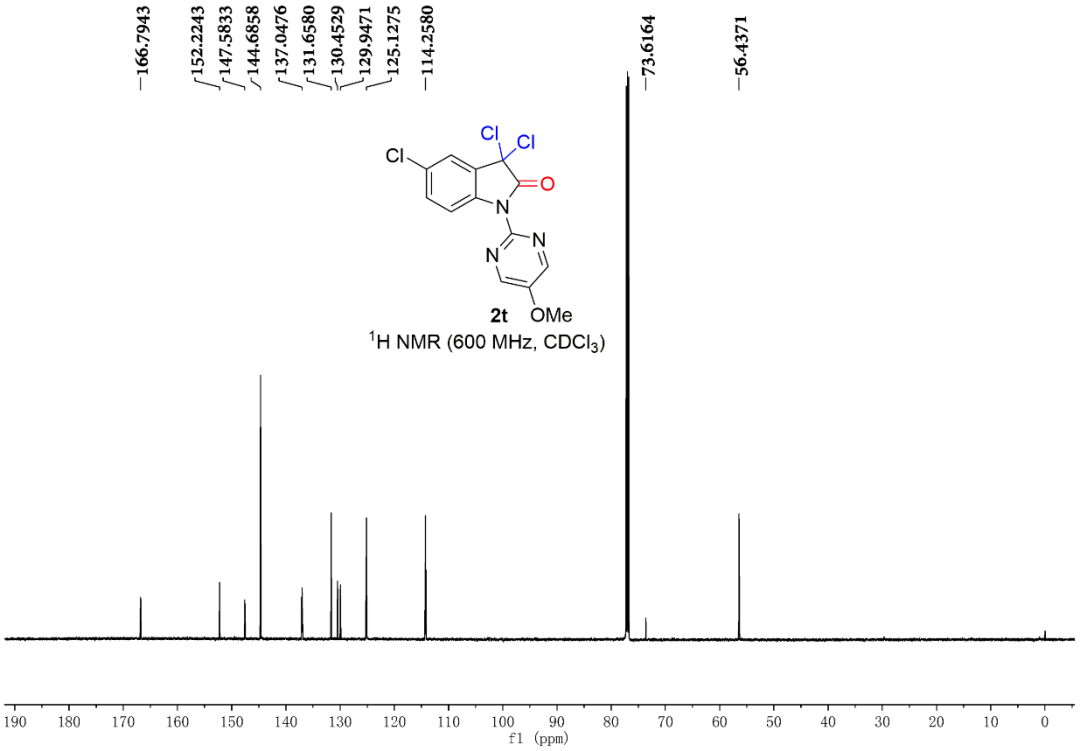
2r

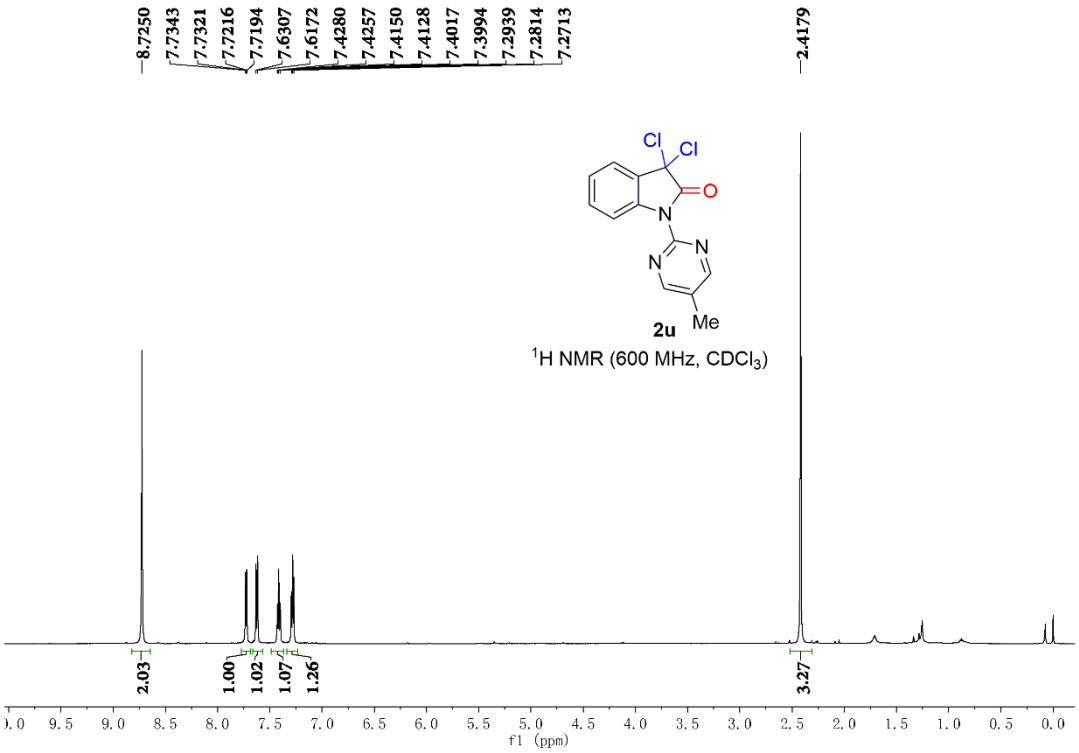
^{19}F NMR (470 MHz, $CDCl_3$)

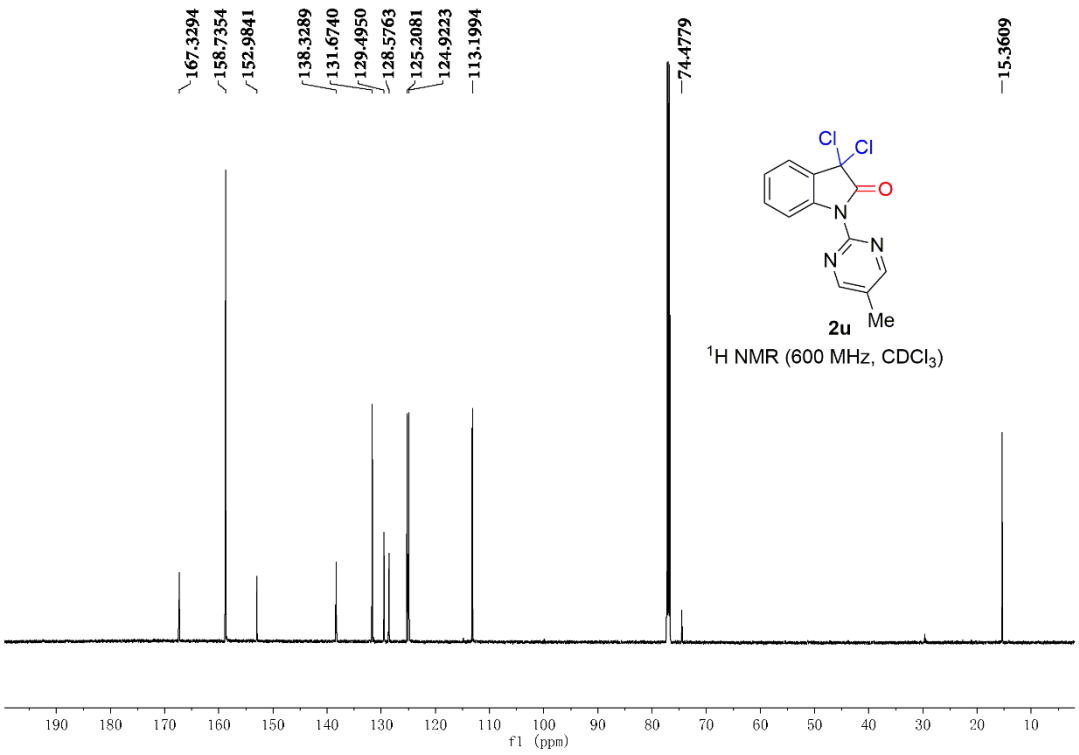

8.5341
7.3719
7.3585
7.3414
7.3281
7.3146
7.2604
7.2161
7.2029
4.0005
Cl
Cl
Cl
O
N
N
N
OMe
2s
1H NMR (600 MHz, CDCl3)
2.05
1.03
1.07
1.00
3.29
f1 (ppm)

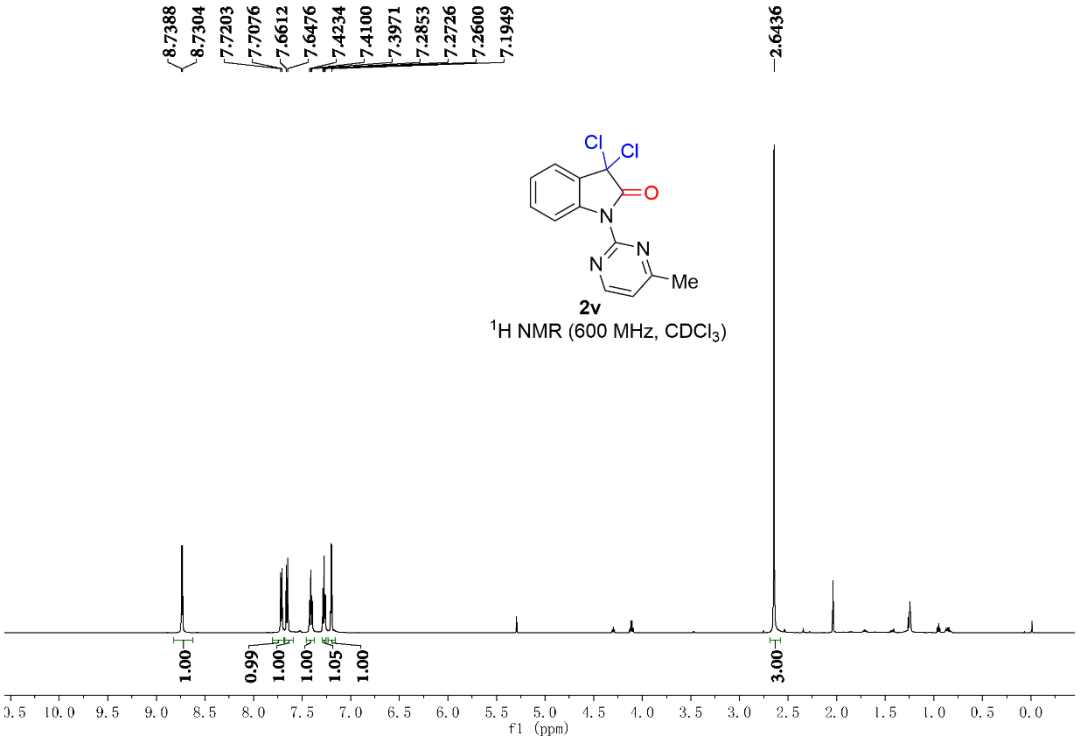

166.7263
152.4535
147.3907
144.8208
140.5345
132.7997
132.3781
126.1255
124.4724
110.9532
73.7004
56.4985
Cl
Cl
Cl
O
N
N
N
OMe
2s
1H NMR (600 MHz, CDCl3)
f1 (ppm)


8.5251
7.6834
7.6797
7.4962
7.4817
7.3651
7.3614
7.3506
7.3469
7.2598
3.9947
Cl
Cl
Cl
O
N
N
N
OMe
2t
1H NMR (600 MHz, CDCl3)
2.06
1.00
1.10
1.09
3.27
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
f1 (ppm)


166.7943
152.2243
147.5833
144.6858
137.0476
131.6580
130.4529
129.9471
125.1275
114.2580
73.6164
56.4371
Cl
Cl
Cl
O
N
N
N
OMe
2t
1H NMR (600 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

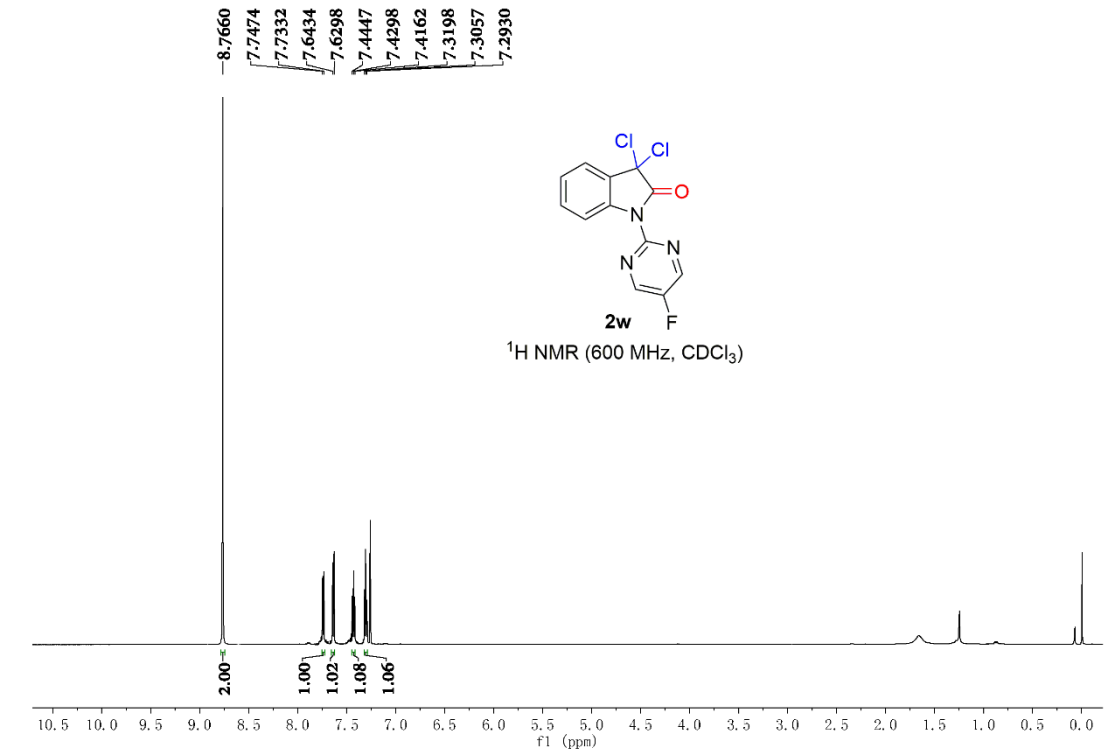

8.7250
7.7343
7.7321
7.7216
7.7194
7.6307
7.6172
7.4280
7.4257
7.4150
7.4128
7.4017
7.3994
7.2939
7.2814
7.2713
2.4179
Cl
Cl
O
N
N
N
Me
2u
1H NMR (600 MHz, CDCl3)
2.03
1.00
1.02
1.07
1.26
3.27
f1 (ppm)


167.3294
158.7354
152.9841
138.3289
131.6740
129.4950
128.5763
125.2081
124.9223
113.1994
74.4779
15.3609
Cl
Cl
O
N
N
N
Me
2u
1H NMR (600 MHz, CDCl3)
f1 (ppm)



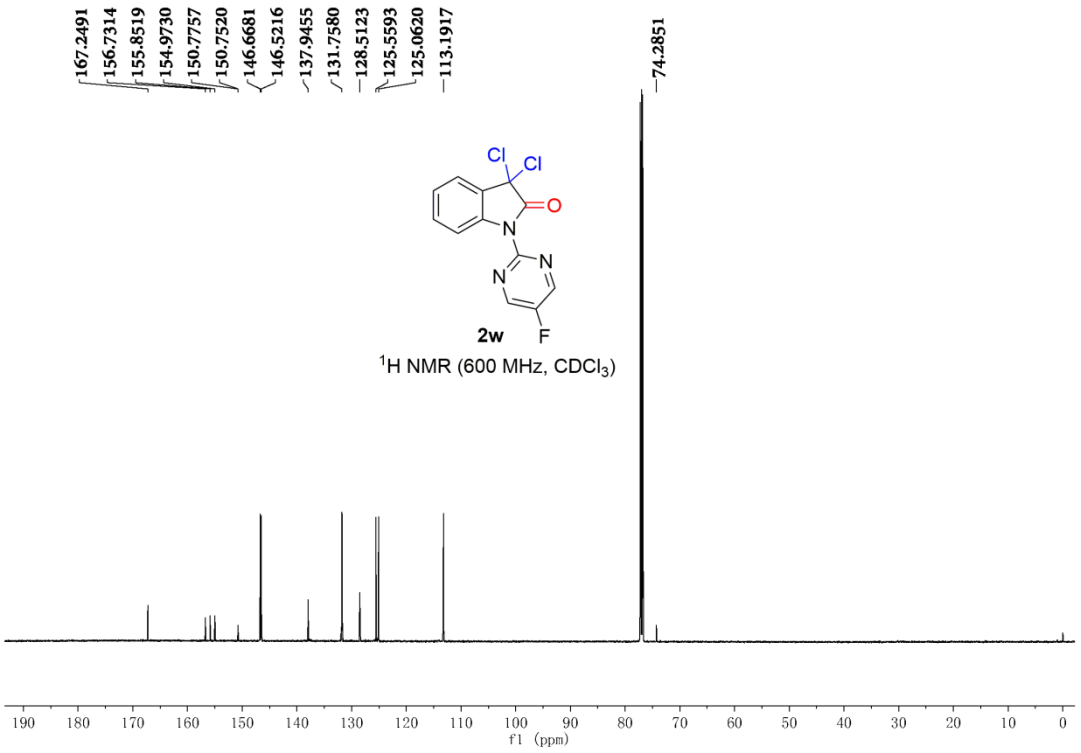
2v

^{1}H NMR (600 MHz, $CDCl_3$)

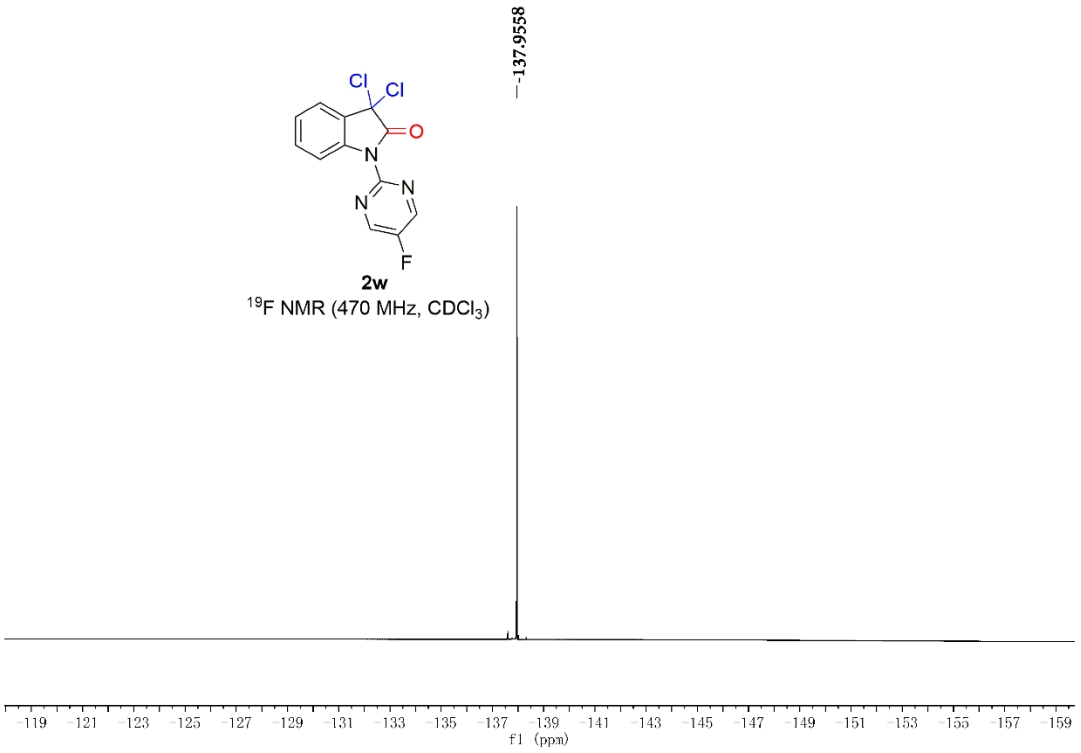


2w

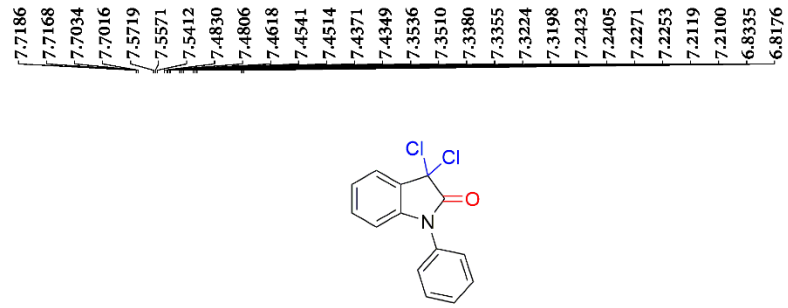
^{1}H NMR (600 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)

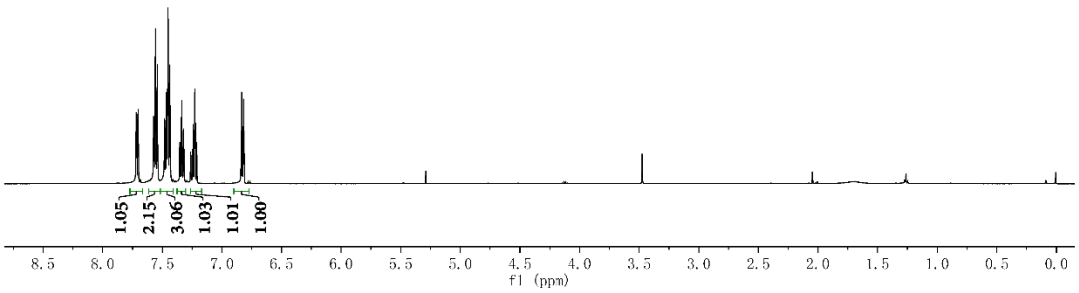


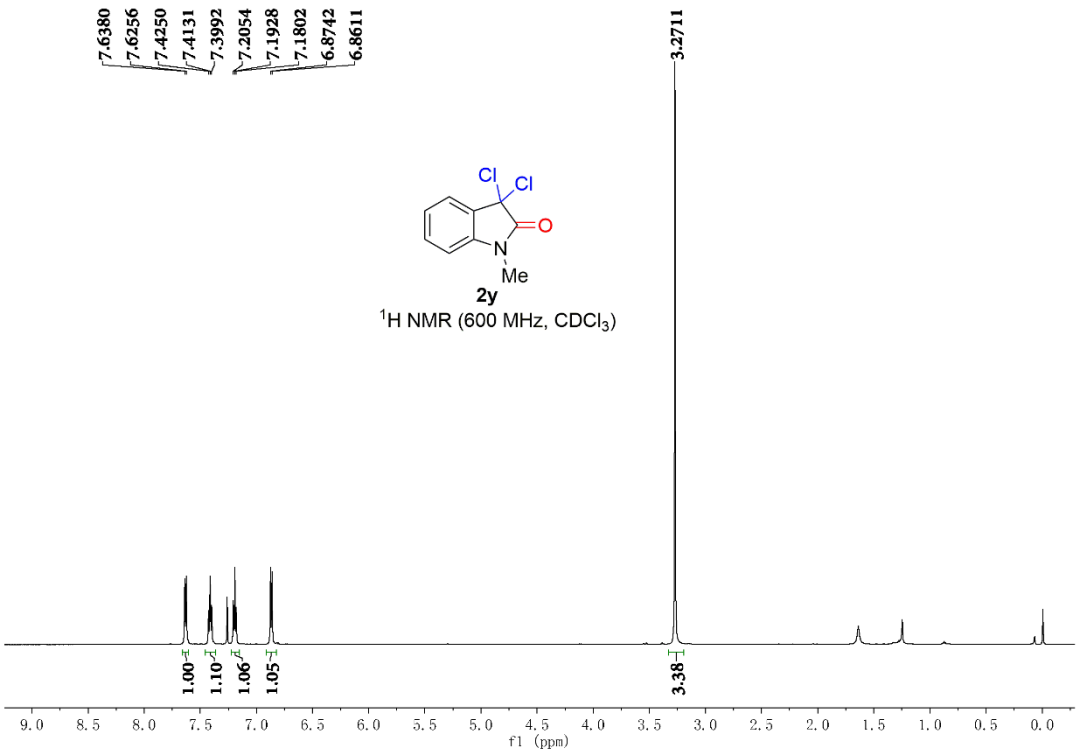
^{19}F NMR (470 MHz, $CDCl_3$)



2x

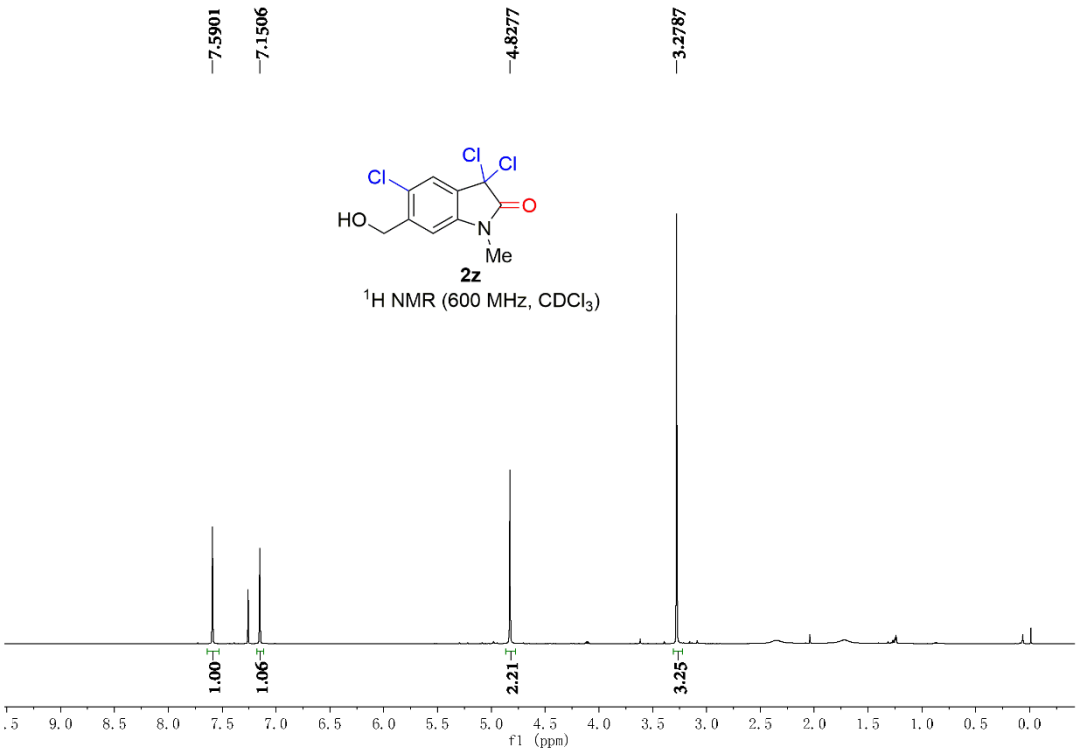
^{1}H NMR (500 MHz, $CDCl_3$)

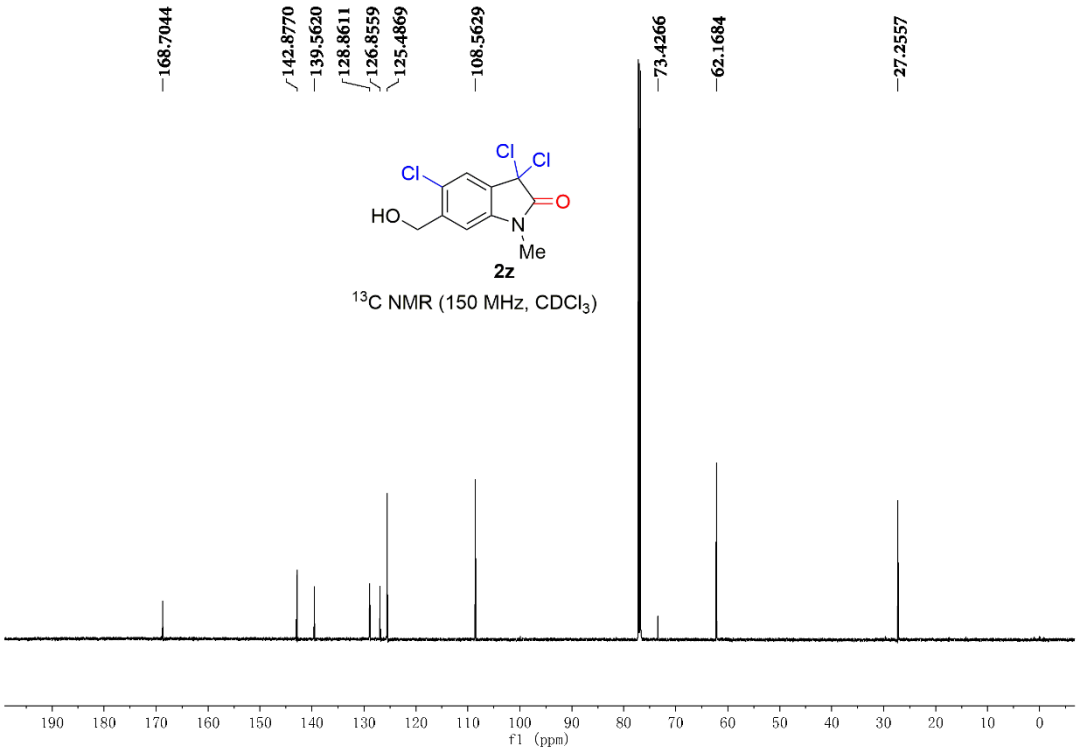


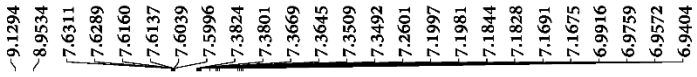


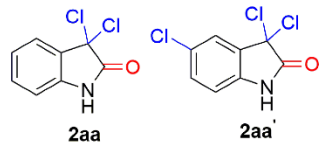
2y

^{1}H NMR (600 MHz, $CDCl_3$)

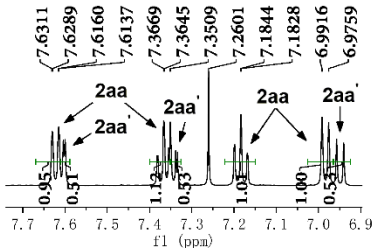

7.5901
7.1506
4.8277
3.2787
Cl
Cl
Cl
HO
O
N
Me
2z
1H NMR (600 MHz, CDCl3)
1.00
1.06
2.21
3.25
f1 (ppm)

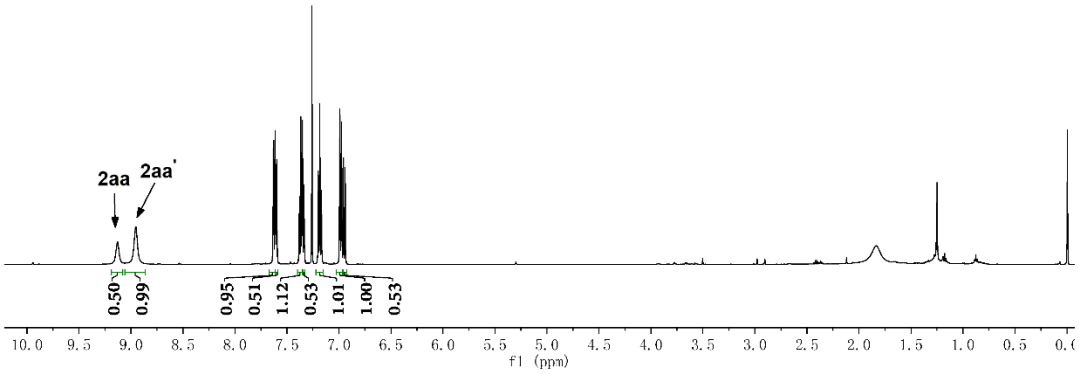

168.7044
142.8770
139.5620
128.8611
126.8559
125.4869
108.5629
73.4266
62.1684
27.2557
Cl
Cl
Cl
HO
O
N
Me
2z
13C NMR (150 MHz, CDCl3)
f1 (ppm)

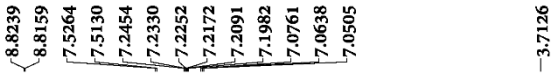


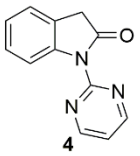


^{1}H NMR (500 MHz, $CDCl_3$)

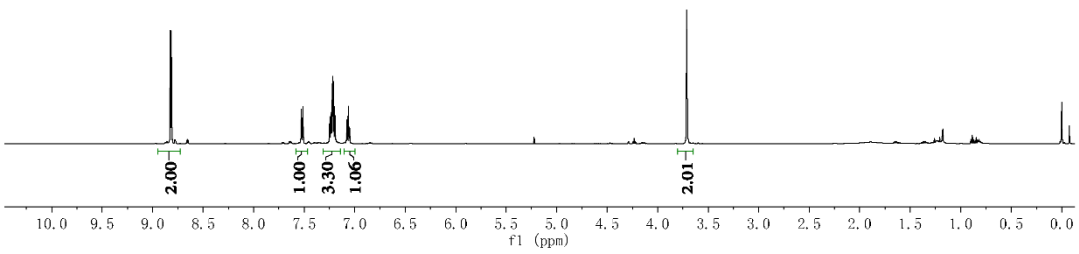


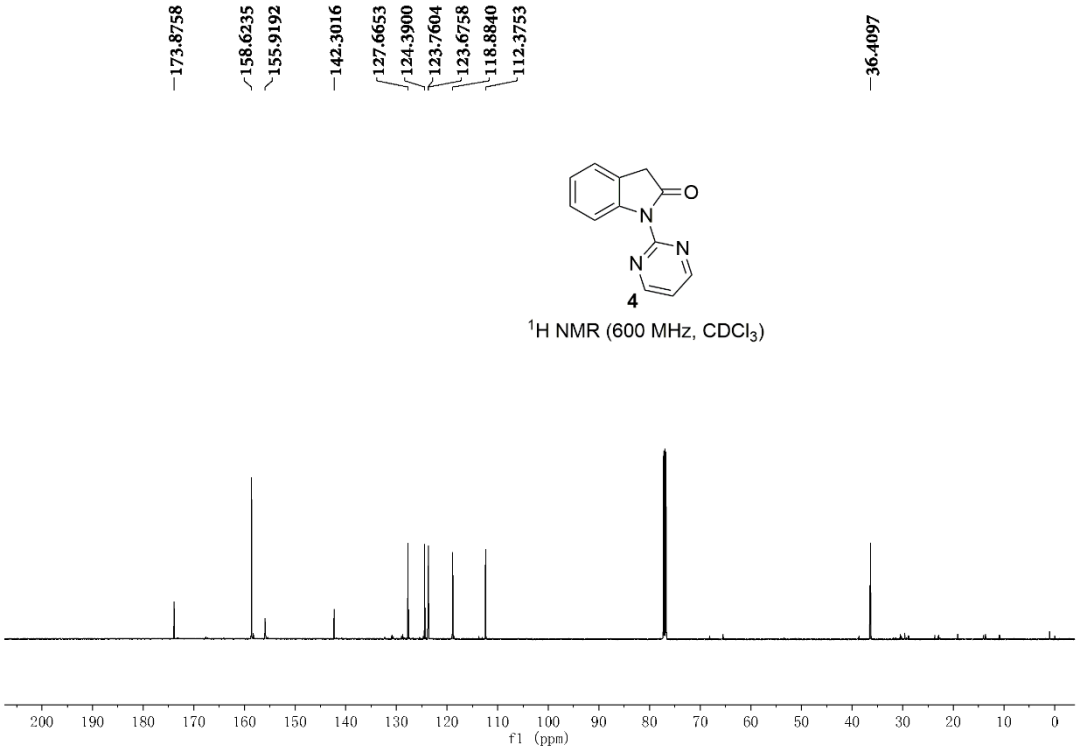






^{1}H NMR (600 MHz, $CDCl_3$)




173.8758
158.6235
155.9192
142.3016
127.6653
124.3900
123.7604
123.6758
118.8840
112.3753
36.4097
O
N
N
N
4
^{1}H NMR (600 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)