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

Supporting Information

CONTENTS

1. General information

Except for the substituted quinoline N-oxides, all reagents were from commercial sources and used as received without further purification. All solvents were dried by standard techniques, and distilled prior to use. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (bp. 60~90 ^{o}C) and ethyl acetate as eluent. ^{1}H and ^{13}C NMR spectra were taken on 400 MHz instruments and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard and $CDCl_3$ or DMSO-d_6 as solvent. Mass spectra (MS) were measured on spectrometer by direct inlet at 70 eV.

The substituted quinoline N-oxides used here were synthesized according to the reported methods.[1]

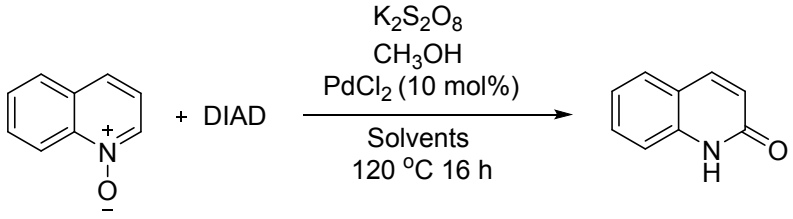
2.Optimization tables

Entry	DIAD (eq.)	Oxidant	Additives (10 eq.)	Temp. (^{o}C)	Yield[b] (%)
1	2.0	$K_2S_2O_8$	MeOH	120	44
2	2.0	$K_2S_2O_8$	^{i}PrOH	120	34
3	2.0	$K_2S_2O_8$	H_2O	120	47
4	2.0	DTBP	H_2O	120	62
5	2.0	BQ	H_2O	120	56
6	2.0	O_2	H_2O	120	50
7	2.0	N_2	H_2O	120	55
8[c]	2.0	–	H_2O	120	71
9[c,d]	2.0	–	H_2O	120	57
10[c,e]	2.0	–	–	120	trace
11[c]	2.0	–	H_2O	90	83
12[c]	2.0	–	H_2O	60	68
13[c,f]	2.0	–	H_2O	90	88
14[c]	**2.2**	–	**H_2O**	**90**	**90**

[a]Reaction condition: quinoline N-oxide (0.5 mmol), DIAD (1.0 mmol), oxidant (1.0 mmol), additives (5.0 mmol), PdCl2 (10 mol%), solvent (2 mL), 120 ^{o}C, 16 h.

[b]Isolated yield. [c]The reaction was performed in air condition. [d]2.5 mmol H_2O was added. [e]Without H_2O. [f]Solvent (1 mL).

Optimization of Reaction Conditions with the solvents

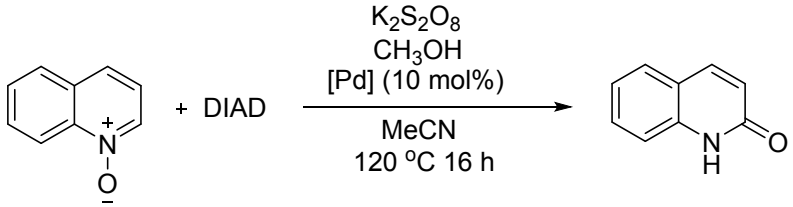


Entry[a]	Solvent	Yield[%][b]
1	DCE	22
2	Toluene	30
3	dioxane	35
4	AcOH	trace
5	MeCN	45
6	DMF	trace
7	DMSO	trace
8	THF	35

[a]Reaction conditions: quinoline N-oxide (0.5 mmol), DIAD (1 mmol), $K_2S_2O_8$ (1 mmol), MeOH (5 mmol), $PdCl_2$ (10 mol%), solvent 2 mL, 120 °C, 16 h.

[b]Isolated yield.

Optimization of Reaction Conditions with the palladium catalyst

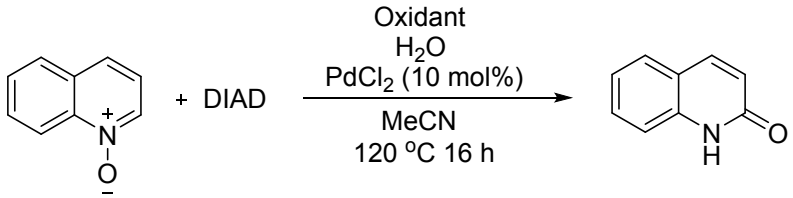


Entry[a]	[Pd]	Yield[%][b]
1	$Pd(OAc)_2$	43
2	Pd/C	25
3	$(PPh_3)_2PdCl_2$	43
4	$[PdCl_2(cinnamyl)]_2$	33
5	$Pd(TFA)_2$	19
6	Pd_2dba_3	10
7	$PdBr_2$	26
8	$Pd(PPh_3)_4$	27

[a]Reaction conditions: quinoline N-oxide (0.5 mmol), DIAD (1 mmol), $K_2S_2O_8$ (1 mmol), MeOH (5 mmol), [Pd] (10 mol%), MeCN 2 mL, 120 °C, 16 h.

[b]Isolated yield.

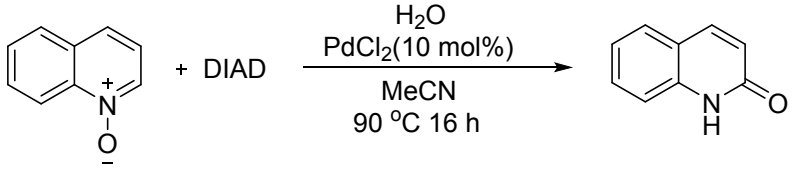
Optimization of Reaction Conditions with the metal-based oxidant



Entry[a]	Oxidant	Yield[%][b]
1	Ag_2CO_3	<5
2	$Cu(AcO)_2$	<5
3	$Mn(AcO)_3 \cdot 2H_2O$	trace

[a]Reaction conditions: quinoline N-oxide (0.5 mmol), DIAD (1 mmol), Oxidant (1 mmol), H_2O (5 mmol), $PdCl_2$ (10 mol%), MeCN 2 mL, 120 °C, 16 h.
[b]Isolated yield.

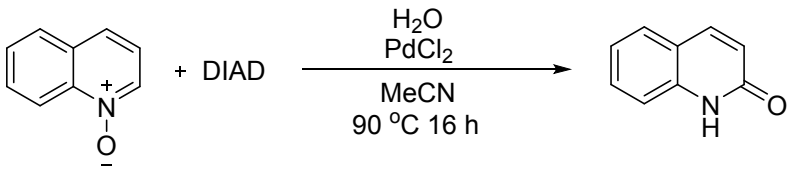
Optimization of Reaction Conditions with the amount of DIAD



Entry[a]	Amount of DIAD	Yield[%][b]
1	1.8 eq.	79
2	2.2 eq.	90
3	2.5 eq.	86
4	3.0 eq.	82
5	4.0 eq.	65
6	5.0 eq.	28
7[c,d]	2.0 eq.	68
8	0 eq.	0

[a]Reaction conditions: quinoline N-oxide (0.5 mmol), DIAD, H_2O (5 mmol), $PdCl_2$ (10 mol%), MeCN 2 mL, 90 °C, 16 h.
[b]Isolated yield. [c]Room temperature. [d]36 h.

Optimization of Reaction Conditions with the amount of $PdCl_2$



Entry[a]	Amount of $PdCl_2$	Yield[%][b]
1	0	0
2	3 mol%	45
3	5 mol%	67

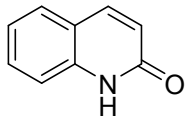
[a]Reaction conditions: quinoline N-oxide (0.5 mmol), DIAD (1.1 mmol), H_2O (5 mmol), $PdCl_2$,

MeCN 2 mL, 90 °C, 16 h.
[b]Isolated yield.

3. General Procedure

$PdCl_2$ (8.9 mg, 10 mol%), H_2O (90 mg, 5 mmol), substituted quinoline N-oxides (0.5 mmol), DIAD (216 μL, 1.1 mmol) were transferred into an oven-dried tube. MeCN (1.5 mL) was added to the reaction tube. Then sealed the tube and the mixture was stirred at 90 °C for 16 h. After the reaction finished, The crude product was filtered and concentrated under vacuum and was purified by column chromatography on silica gel column EtOAc/petroleum ether (1:4 to 1:2, v/v) to give the desired product.

4.Spectroscopic Data of Products

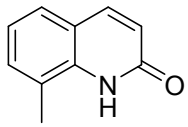


quinolin-2(*1H*)-one, **2a**, **90% yield**

Following General Procedure, using quinoline 1-oxide (72.6 mg, 0.5 mmol), compound **2a** (65 mg, 90% yield) was obtained. **2a** was an off-white powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.86 (s, 1H), 7.84 (d, *J* = 9.5 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.27 – 7.18 (t, 1H), 6.75 (d, *J* = 9.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.81, 141.11, 138.53, 130.68, 127.72, 122.70, 121.29, 119.92, 116.32.

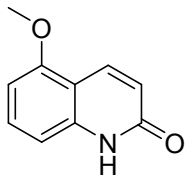


8-methylquinolin-2(*1H*)-one, 2b, 67% yield

Following General Procedure, using 8-methylquinoline 1-oxide (79.6 mg, 0.5 mmol), compound (53.5 mg, 67% yield) was obtained. **2b** was a light yellow powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 7.78 (dd, *J* = 9.5, 1.7 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.14 (td, *J* = 7.6, 1.7 Hz, 1H), 6.69 (dd, *J* = 9.5, 1.6 Hz, 1H), 2.55 (s, 3H).

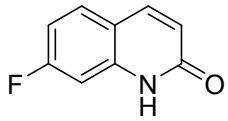
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.50, 141.30, 136.91, 131.82, 126.06, 123.29, 122.24, 121.40, 119.69, 16.89.



5-methoxyquinolin-2(*1H*)-one, 2c, 73% yield

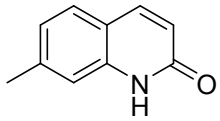
Following General Procedure, using 5-methoxyquinoline 1-oxide (87.6 mg, 0.5 mmol), compound **2c** (63.7 mg, 73% yield) was obtained. **2c** was a gray powder.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.75 (s, 1H), 8.01 (d, *J* = 9.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 7.7 Hz, 1H), 6.42 (d, *J* = 9.6 Hz, 1H), 3.89 (s, 3H).
^{13}C NMR (101 MHz, DMSO) δ 162.38, 155.98, 140.54, 134.54, 131.80, 120.89, 109.75, 108.23, 103.10, 56.25.



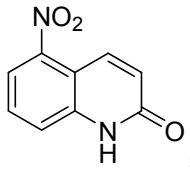
7-fluoroquinolin-2(*1H*)-one, 2d, 84% yield

Following General Procedure, using 7-fluoroquinoline 1-oxide (81.6 mg, 0.5 mmol), compound **2d** (68.2 mg, 84% yield) was obtained. **2d** was a brown powder.
^{1}H NMR (400 MHz, DMSO-d_6) δ 11.83 (s, 1H), 7.87 (t, *J* = 7.4 Hz, 1H), 7.53 (dt, *J* = 6.5, 3.0 Hz, 1H), 7.36 (ddd, *J* = 24.8, 8.9, 4.1 Hz, 2H), 6.56 (t, *J* = 7.2 Hz, 1H).
^{13}C NMR (101 MHz, DMSO) δ 162.08, 158.51, 156.14, 139.86, 136.05, 123.65, 120.23, 120.14, 118.91, 118.67, 117.38, 117.30, 113.18, 112.96.



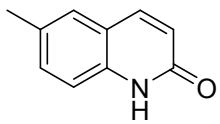
7-methylquinolin-2(*1H*)-one, 2e, 87% yield

Following General Procedure, using 7-methylquinoline 1-oxide (79.6 mg, 0.5 mmol), compound **2e** (69.4 mg, 87% yield) was obtained. **2e** was a light yellow powder.
^{1}H NMR (400 MHz, DMSO-d_6) δ 11.69 (s, 1H), 7.83 (d, *J* = 9.4 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.20 – 6.93 (m, 2H), 6.41 (d, *J* = 9.0 Hz, 1H), 2.36 (s, 3H).
^{13}C NMR (101 MHz, DMSO) δ 162.57, 140.87, 140.49, 139.46, 128.13, 123.62, 121.18, 117.46, 115.33, 21.82.



5-nitroquinolin-2(*1H*)-one, 2f, 65% yield

Following General Procedure, using 5-nitroquinoline 1-oxide (95 mg, 0.5 mmol), compound **2f** (61.2 mg, 65% yield) was obtained. **2f** was a khaki powder.
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.30 (s, 1H), 8.26 (d, *J* = 9.1 Hz, 1H), 7.89 (s, 1H), 7.70 (d, *J* = 19.1 Hz, 2H), 6.77 (d, *J* = 9.1 Hz, 1H).
^{13}C NMR (101 MHz, DMSO) δ 161.28, 146.72, 140.71, 134.67, 130.56, 125.81, 121.49, 118.96, 111.95.



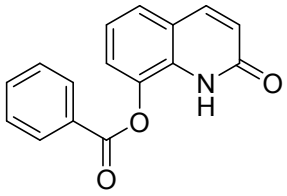
6-methylquinolin-2(*1H*)-one, 2g, 80% yield

Following General Procedure, using 6-methylquinoline 1-oxide (79.6 mg, 0.5 mmol), compound

2g (63.3 mg, 80% yield) was obtained. **2g** was a brown powder.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.68 (s, 1H), 7.82 (d, *J* = 8.9 Hz, 1H), 7.42 (s, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.21 (d, *J* = 7.4 Hz, 1H), 6.47 (d, *J* = 8.9 Hz, 1H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 162.30, 140.41, 137.31, 131.98, 131.11, 127.80, 122.31, 119.50, 115.48, 20.80.

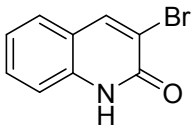


2-oxo-1,2-dihydroquinolin-8-yl benzoate, 2h, 36% yield

Following General Procedure, using 8-(benzoyloxy)quinoline 1-oxide (133 mg, 0.5 mmol), compound **2h** (48 mg, 36% yield) was obtained. **2h** was a white powder.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.29 (s, 1H), 8.34 – 8.29 (m, 2H), 7.80 – 7.73 (m, 2H), 7.61 (t, *J* = 7.7 Hz, 2H), 7.50 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.46 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 6.41 (d, *J* = 9.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.58, 162.56, 140.41, 136.84, 134.11, 131.13, 130.58, 128.76, 128.72, 125.36, 123.62, 122.48, 122.18, 121.22.

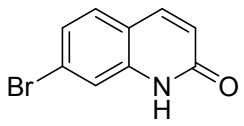


3-bromoquinolin-2(*1H*)-one, 2i, 61% yield

Following General Procedure, using 3-bromoquinoline 1-oxide (112 mg, 0.5 mmol), compound **2i** (69 mg, 61% yield) was obtained. **2i** was a khaki powder.

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.27 (s, 1H), 8.48 (s, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H).

^{13}C NMR (101 MHz, DMSO) δ 158.13, 142.13, 138.60, 131.16, 127.75, 122.74, 119.83, 117.54, 115.67.

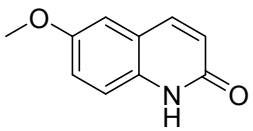


7-bromoquinolin-2(*1H*)-one, 2j, 71% yield

Following General Procedure, using 7-bromoquinoline 1-oxide (112 mg, 0.5 mmol), compound **2j** (80 mg, 71% yield) was obtained. **2j** was a brown powder.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.64 (s, 1H), 6.73 (d, *J* = 8.7 Hz, 1H), 6.44 (d, *J* = 7.0 Hz, 1H), 6.30 (s, 1H), 6.16 (d, *J* = 6.4 Hz, 1H), 5.36 (d, *J* = 8.1 Hz, 1H).

^{13}C NMR (101 MHz, DMSO) δ 166.90, 145.17, 145.00, 135.01, 129.87, 128.63, 127.62, 123.40, 122.59.



6-methoxyquinolin-2(*1H*)-one, 2k, 58% yield

Following General Procedure, using 6-methoxyquinoline 1-oxide (87.5 mg, 0.5 mmol), compound **2k** (50.7 mg, 58% yield) was obtained. **2k** was a khaki powder.

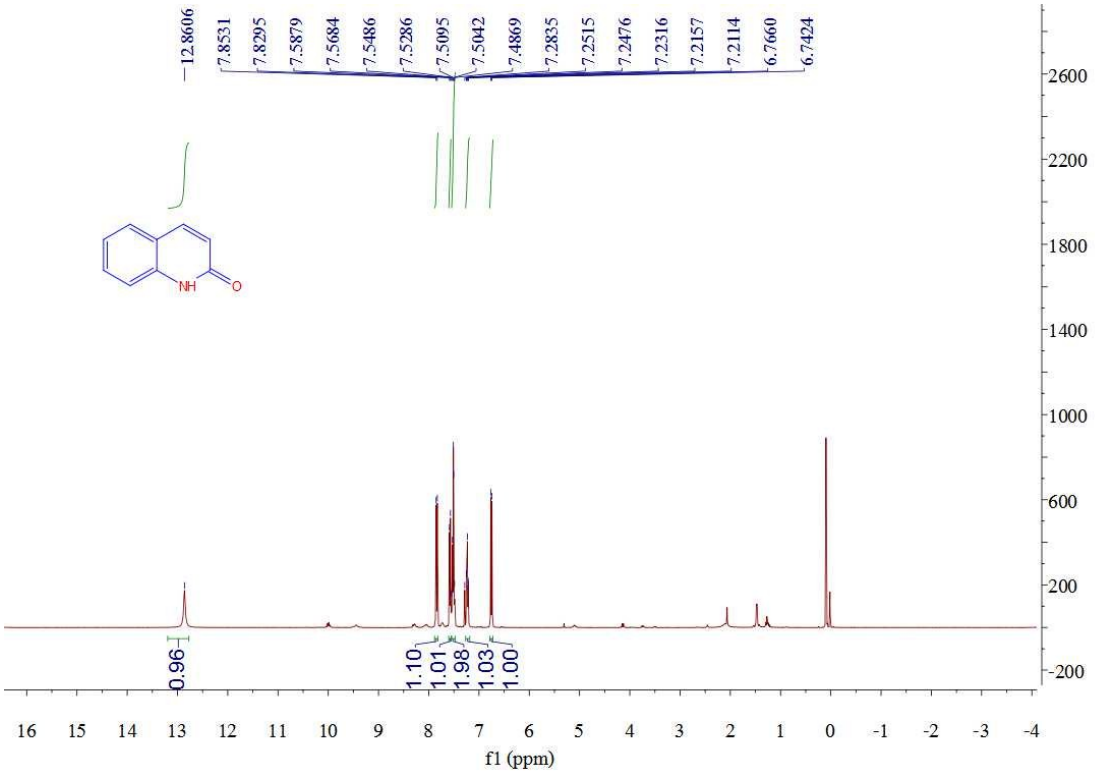
^{1}H NMR (400 MHz, DMSO-d_6) δ 11.64 (s, 1H), 7.85 (d, J = 9.5 Hz, 1H), 7.28 – 7.19 (m, 2H), 7.16 (d, J = 2.8 Hz, 1H), 6.49 (d, J = 9.5 Hz, 1H), 3.78 (s, 3H).

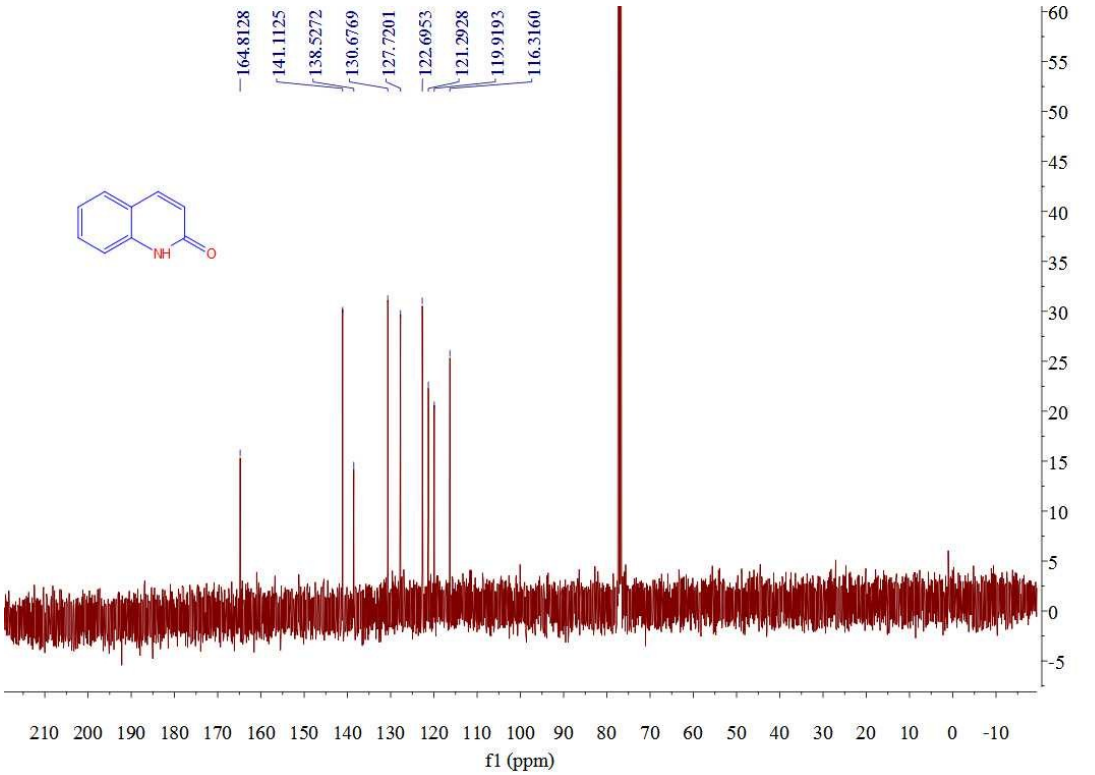
^{13}C NMR (101 MHz, DMSO) δ 166.71, 159.30, 144.99, 138.56, 127.53, 124.88, 124.70, 121.58, 114.53, 60.65.

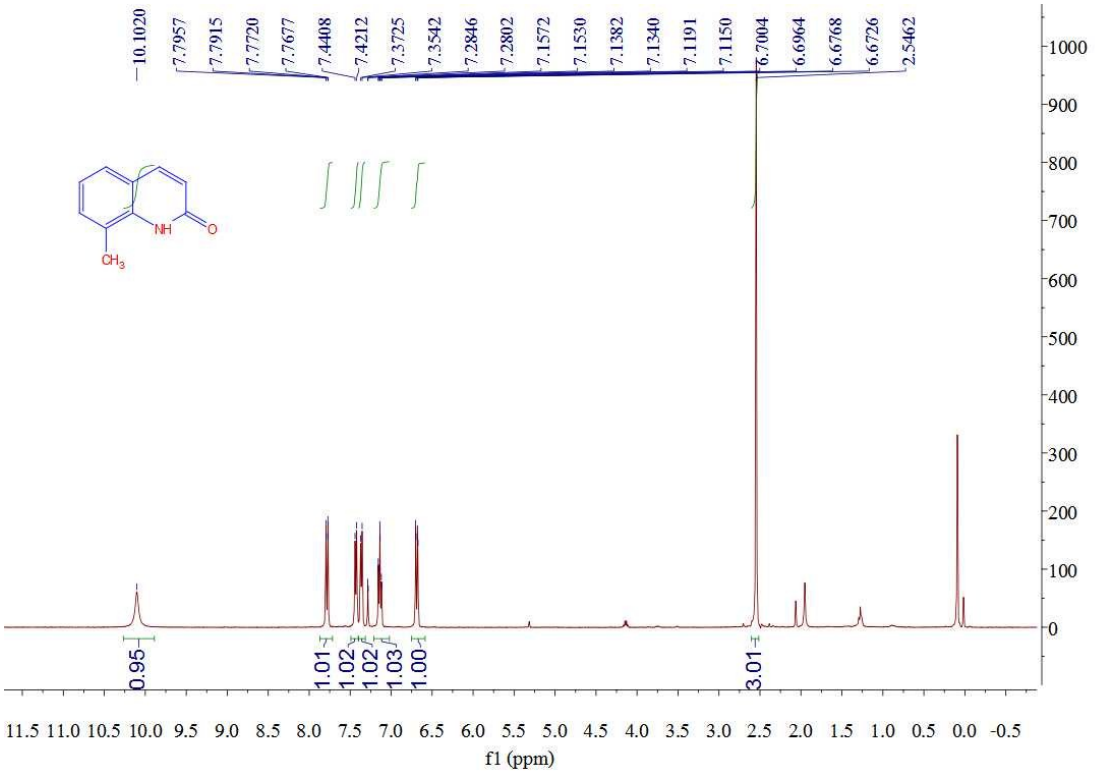
5.References

[1]. Allyn T. Londregan, Kristen Burford, Edward L. Conn, and Kevin D. Hesp, *Org. Lett.* **2014**, 16, 3336.

6.Copy of ^{1}H and ^{13}C NMR Spectra of Products



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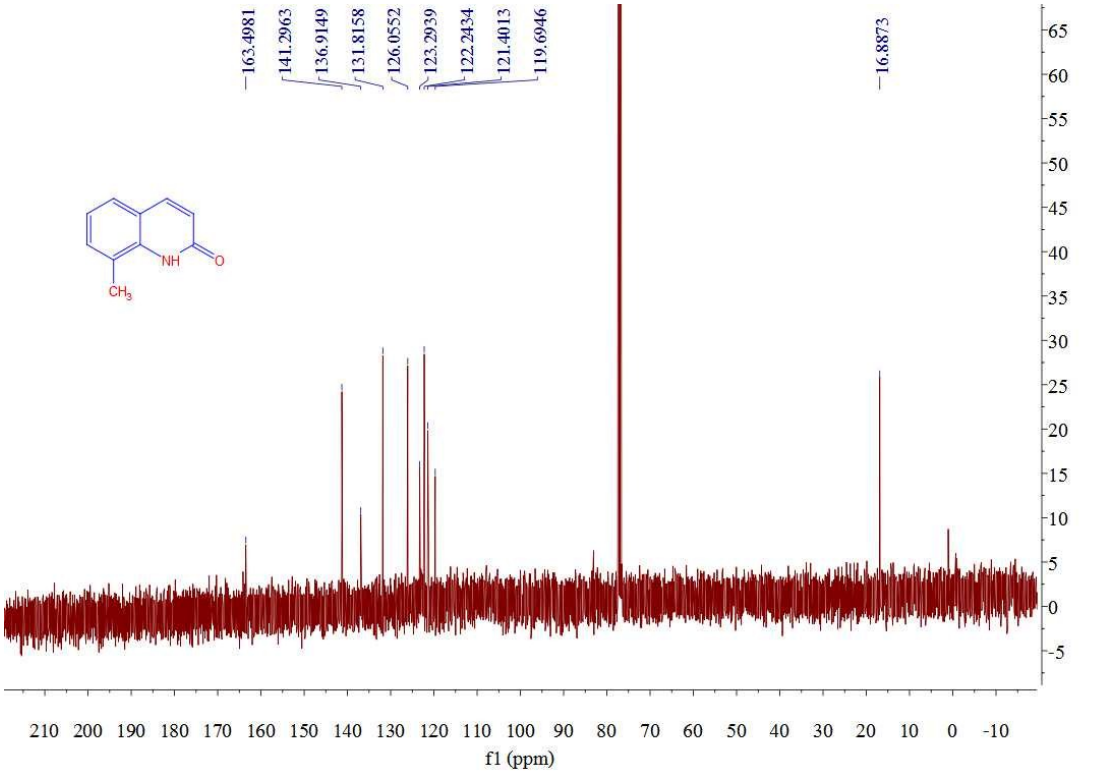
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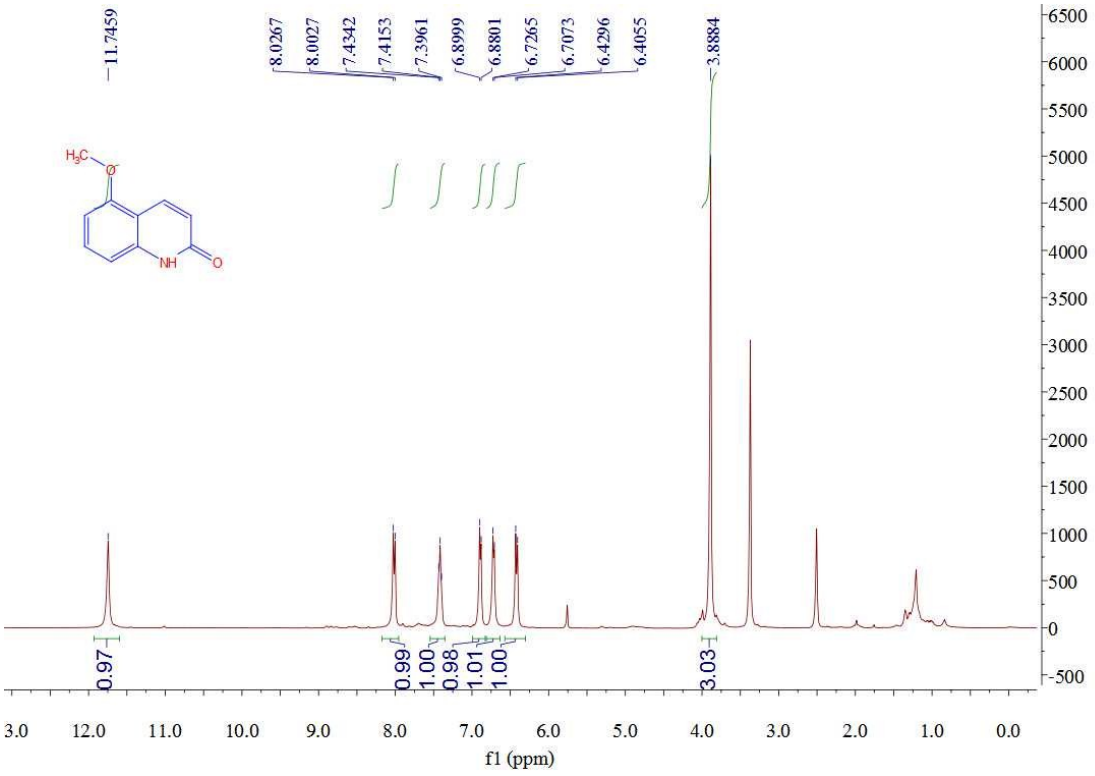
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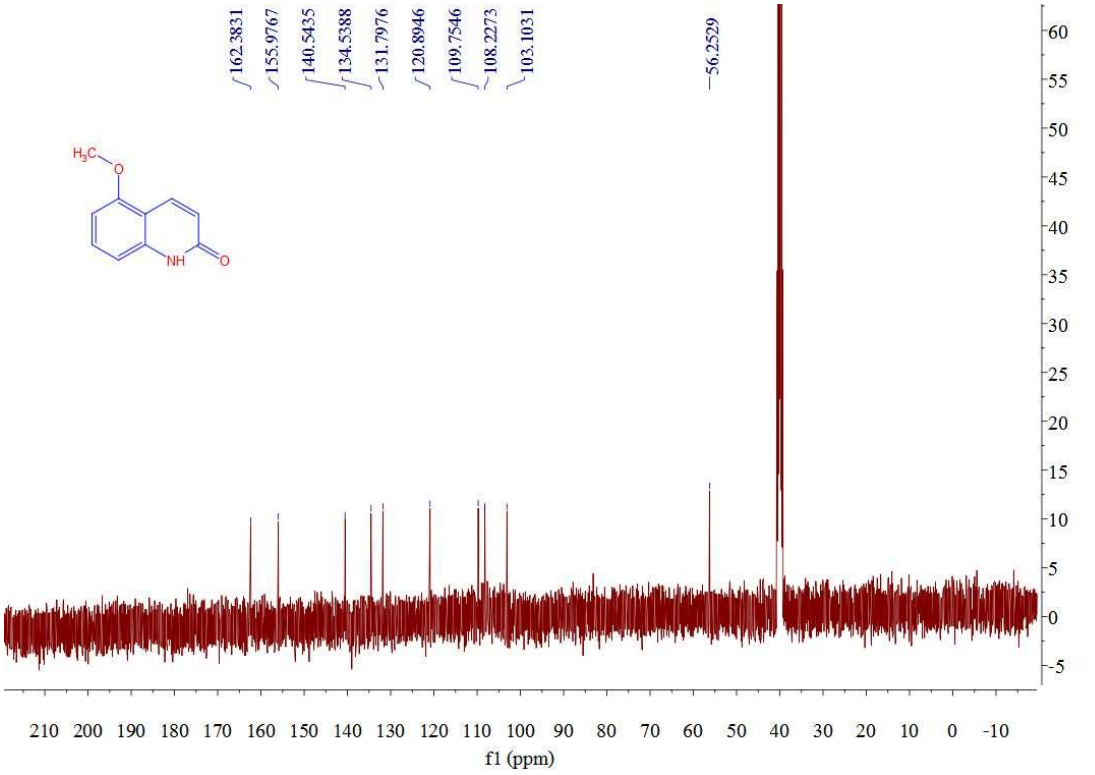
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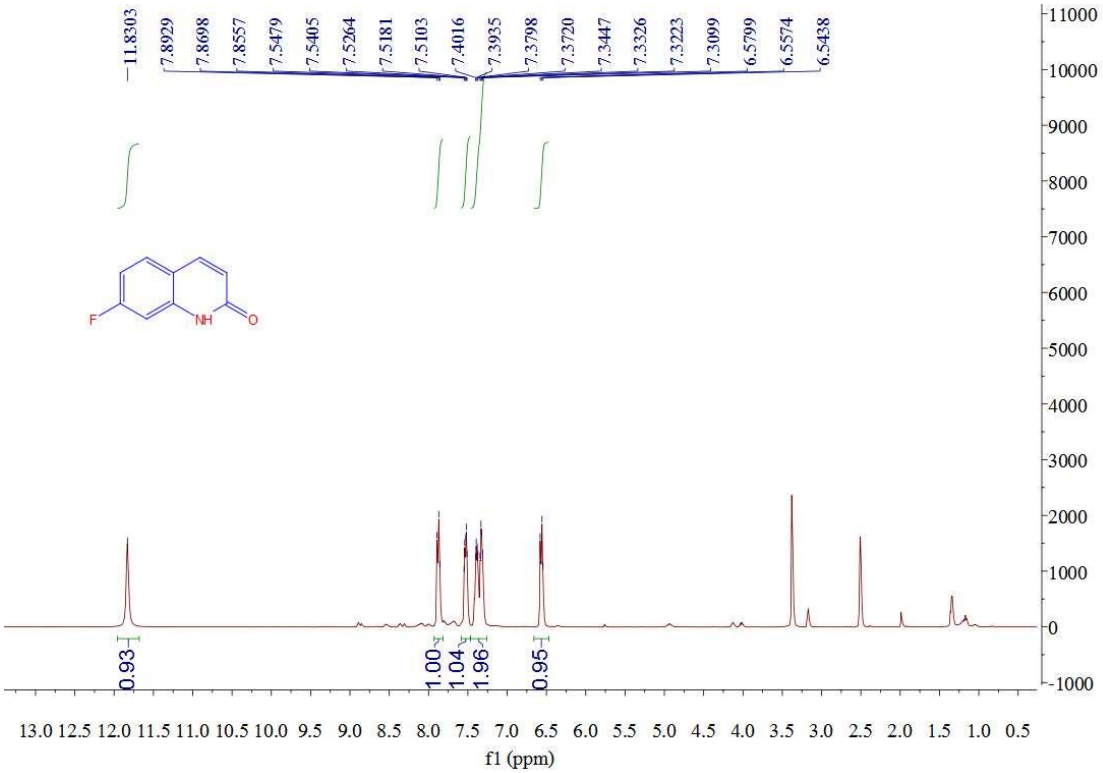
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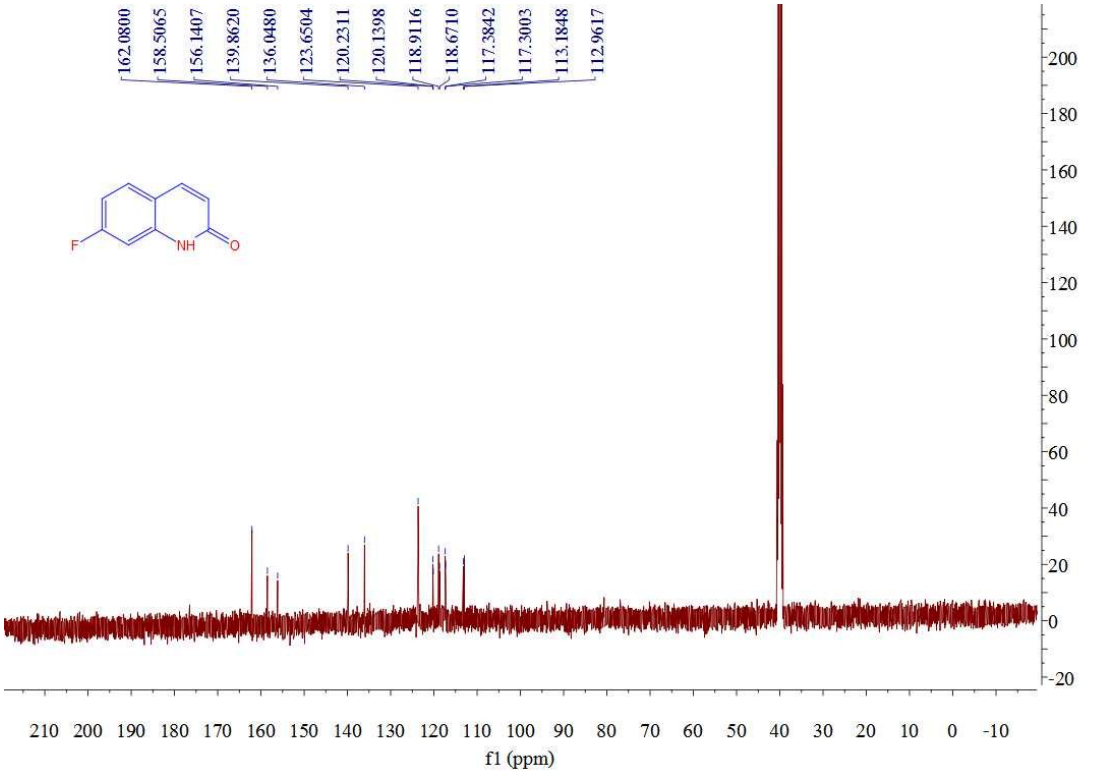
f1 (ppm)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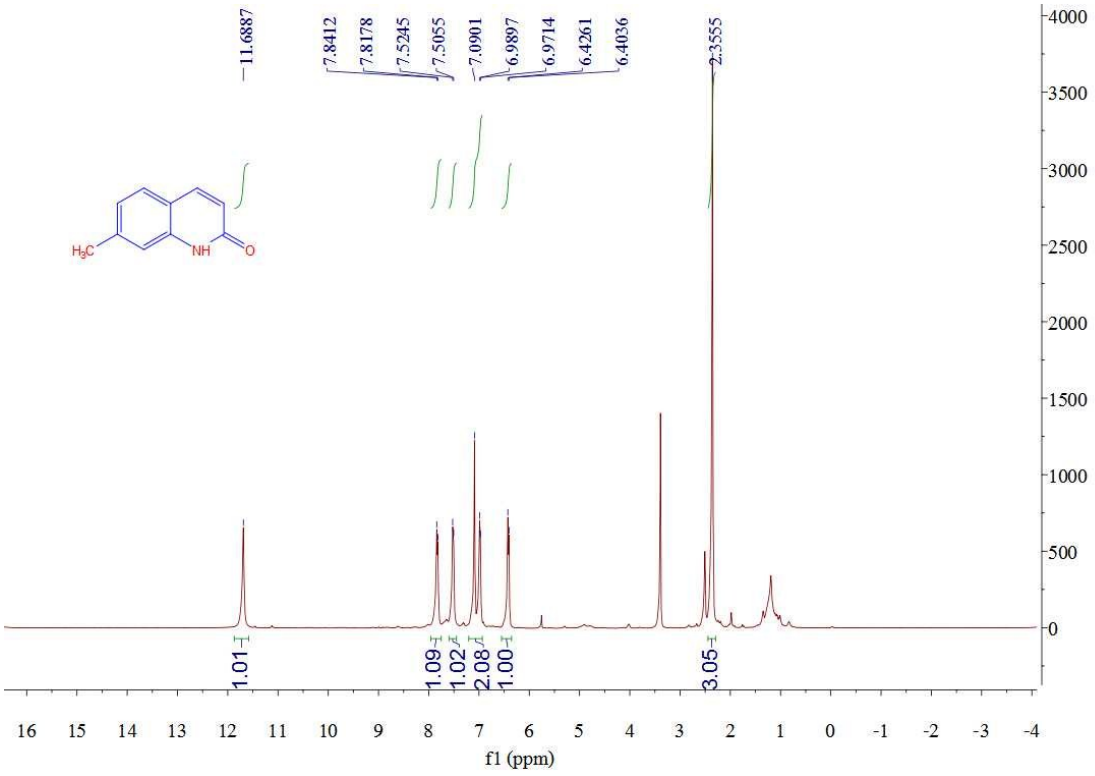
158.5065
156.1407
139.8620
136.0480
123.6504
120.2311
120.1398
118.9116
118.6710
117.3842
117.3003
113.1848
112.9617
F
NH
O
f1 (ppm)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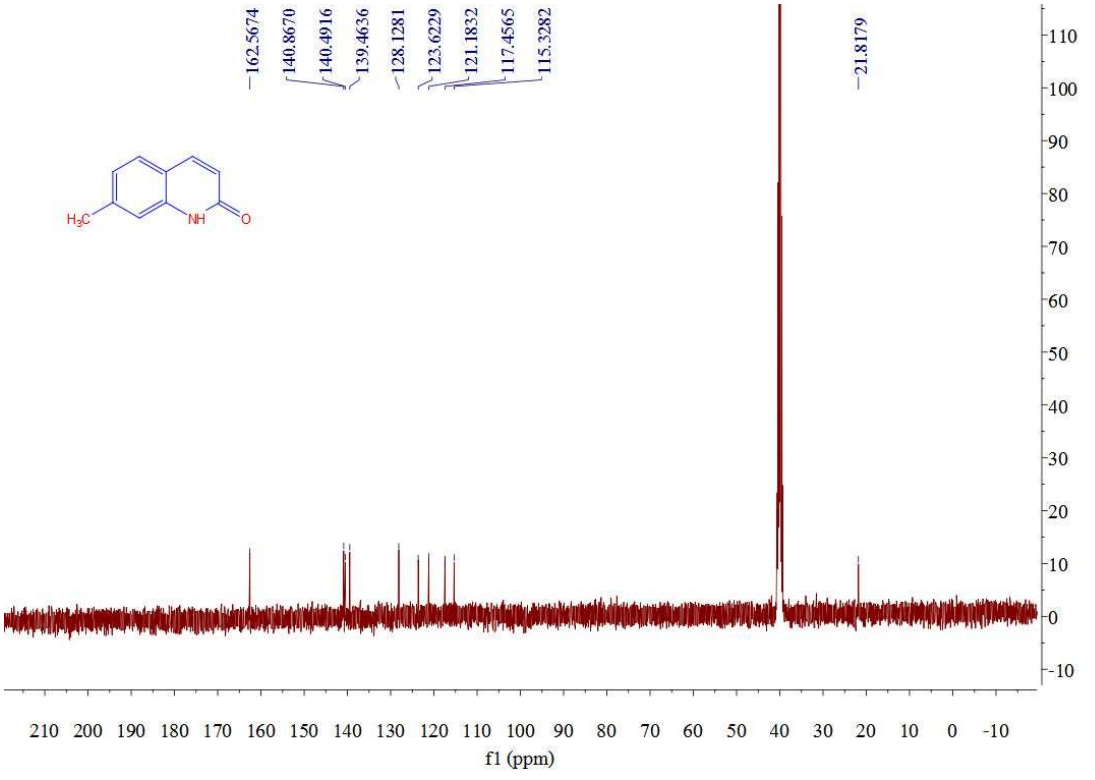
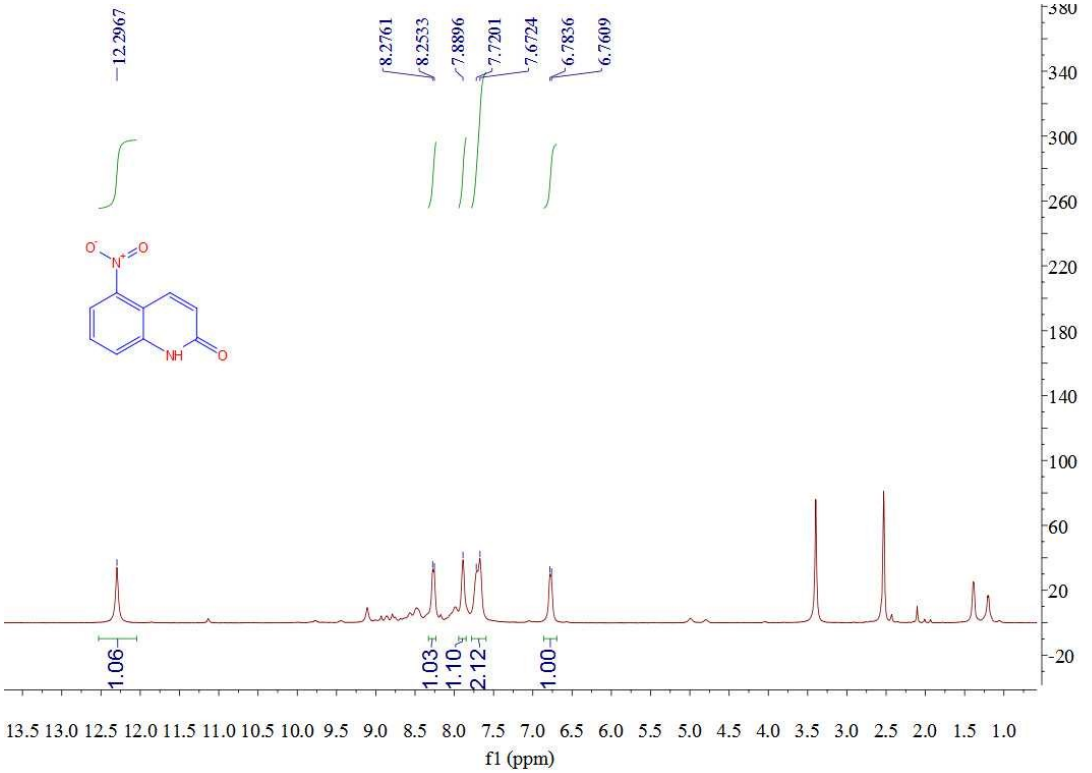
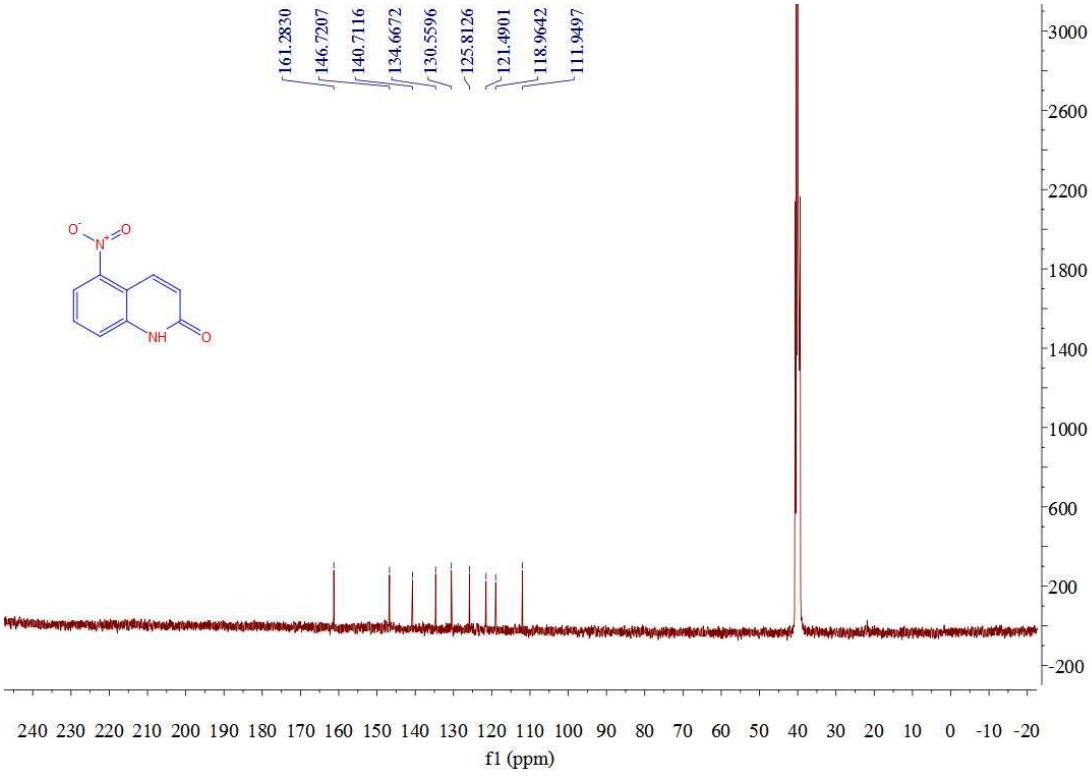
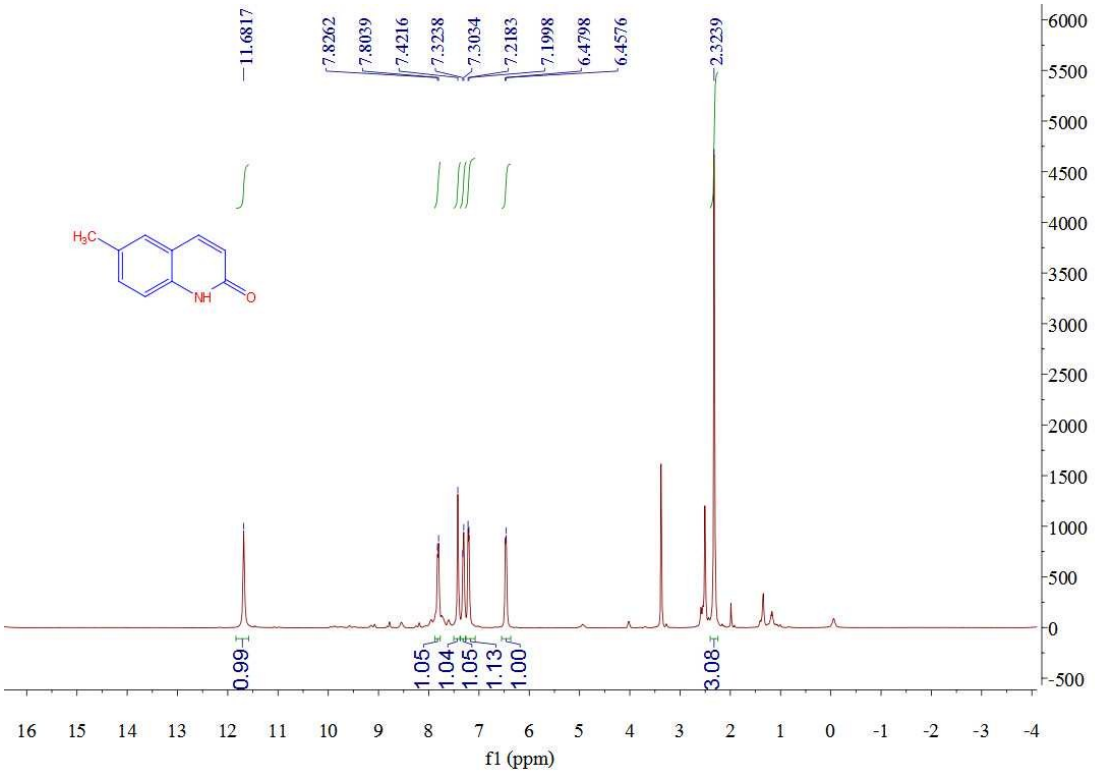
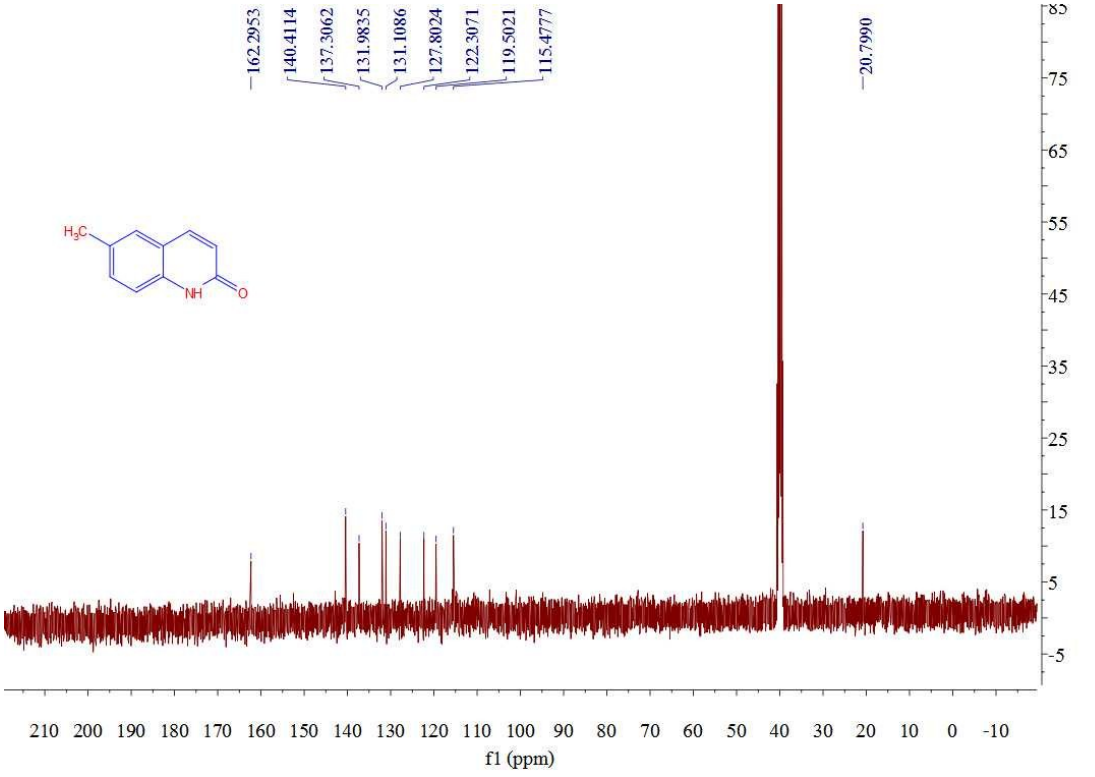
7.8412
7.8178
7.5245
7.5055
7.0901
6.9897
6.9714
6.4261
6.4036
2.3555
H3C
NH
O
1.01
1.09
1.02
2.08
1.00
3.05
f1 (ppm)

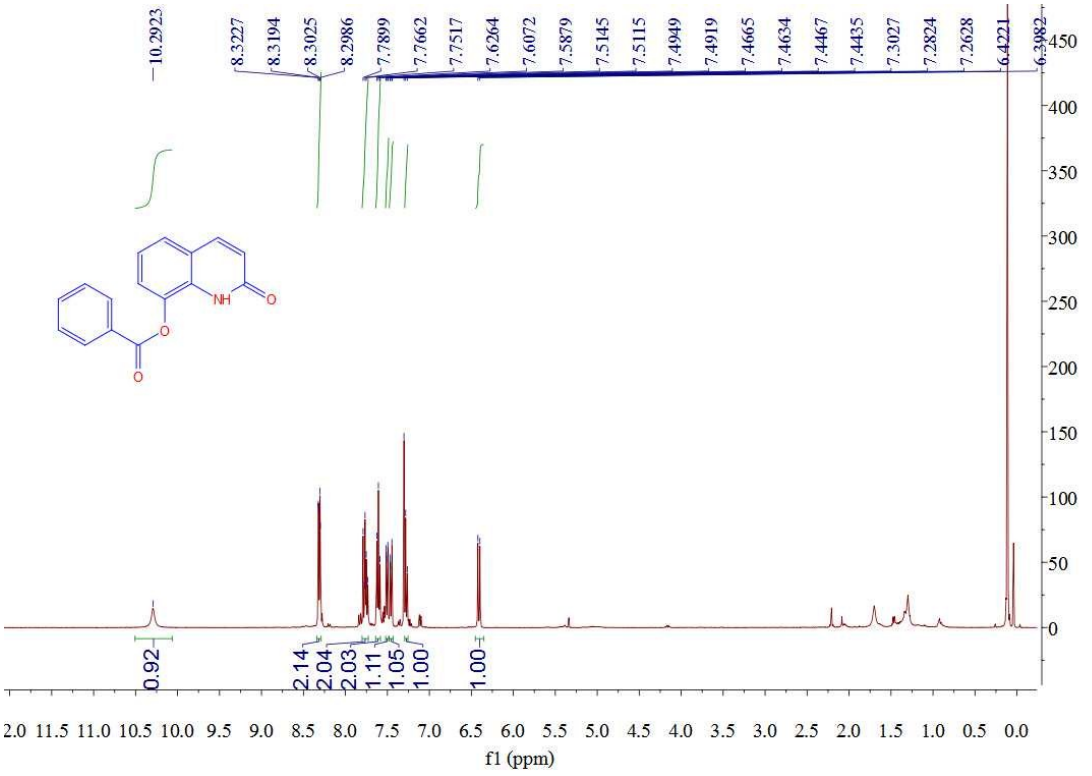

162.5674
140.8670
140.4916
139.4636
128.1281
123.6229
121.1832
117.4565
115.3282
21.8179
H3C
NH
O
f1 (ppm)


12.2967
8.2761
8.2533
7.8896
7.7201
7.6724
6.7836
6.7609
1.06
1.03
1.10
2.12
1.00
f1 (ppm)


161.2830
146.7207
140.7116
134.6672
130.5596
125.8126
121.4901
118.9642
111.9497
f1 (ppm)


11.6817
7.8262
7.8039
7.4216
7.3238
7.3034
7.2183
7.1998
6.4798
6.4576
2.3239
0.99
1.05
1.04
1.05
1.13
1.00
3.08
f1 (ppm)


162.2953
140.4114
137.3062
131.9835
131.1086
127.8024
122.3071
119.5021
115.4777
20.7990
f1 (ppm)


10.2923
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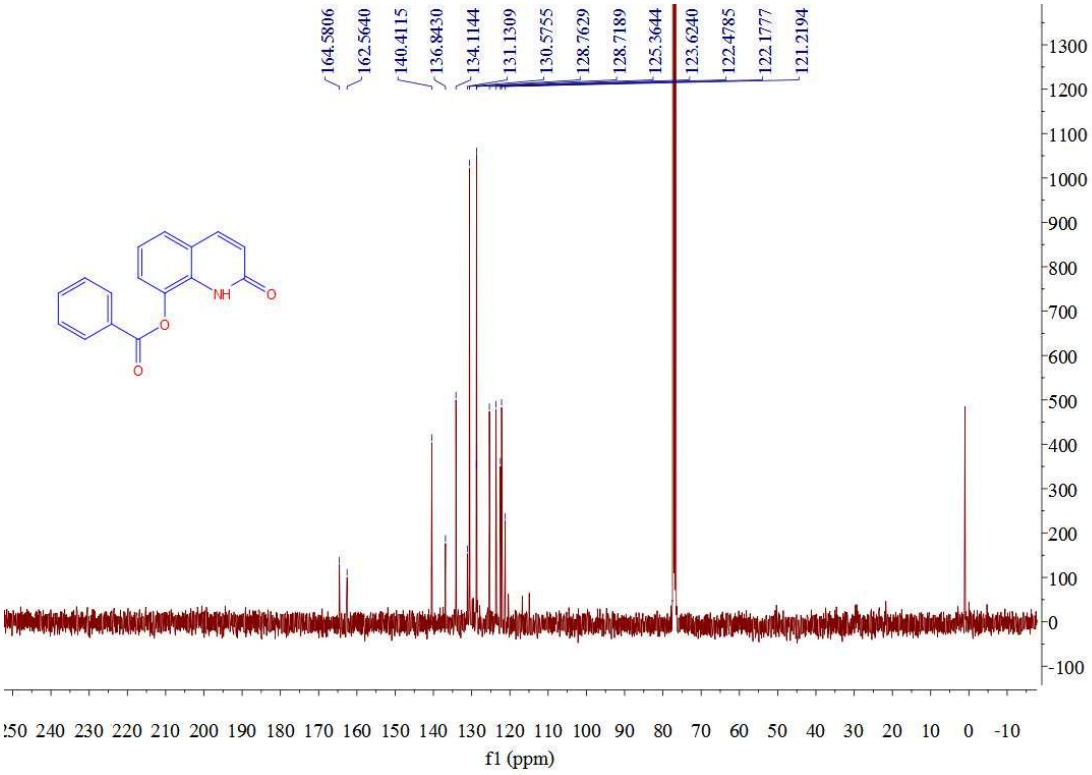
8.3194
8.3025
8.2986
7.7899
7.7662
7.7517
7.6264
7.6072
7.5879
7.5145
7.5115
7.4949
7.4919
7.4665
7.4634
7.4467
7.4435
7.3027
7.2824
7.2628
6.4221
6.3982
NH
O
O
O
0.92
2.14
2.04
2.03
1.11
1.05
1.00
1.00
f1 (ppm)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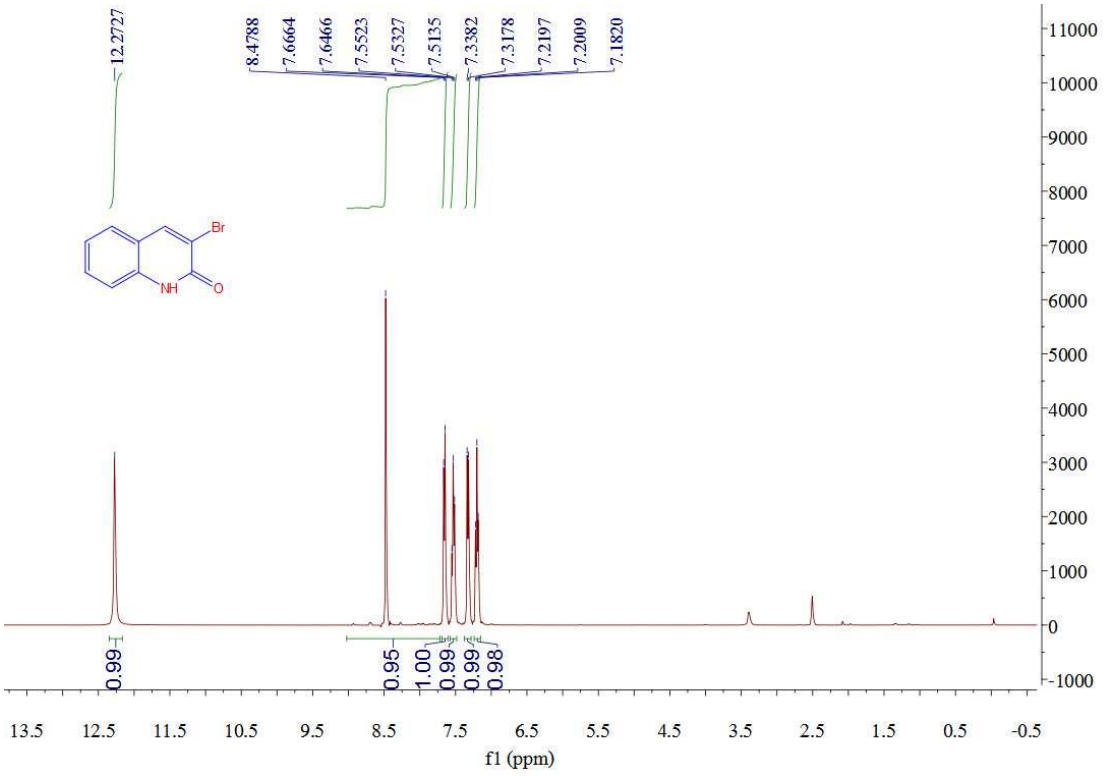
162.5640
140.4115
136.8430
134.1144
131.1309
130.5755
128.7629
128.7189
125.3644
123.6240
122.4785
122.1777
121.2194
NH
O
O
O
f1 (ppm)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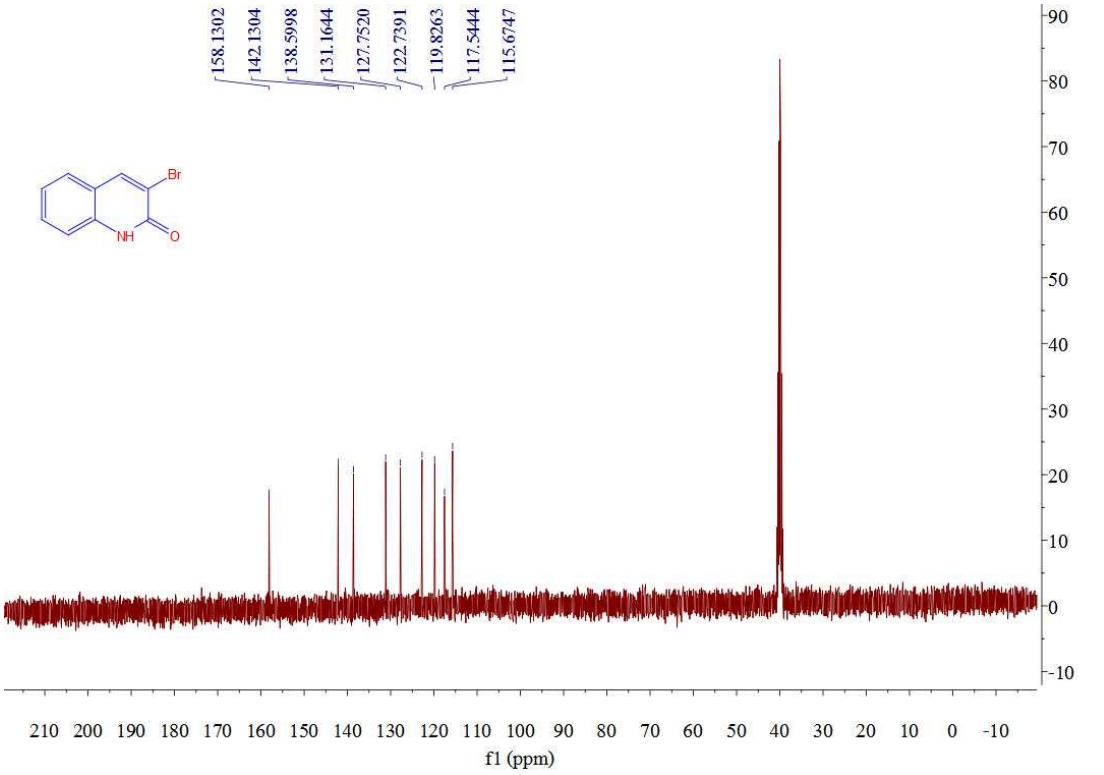
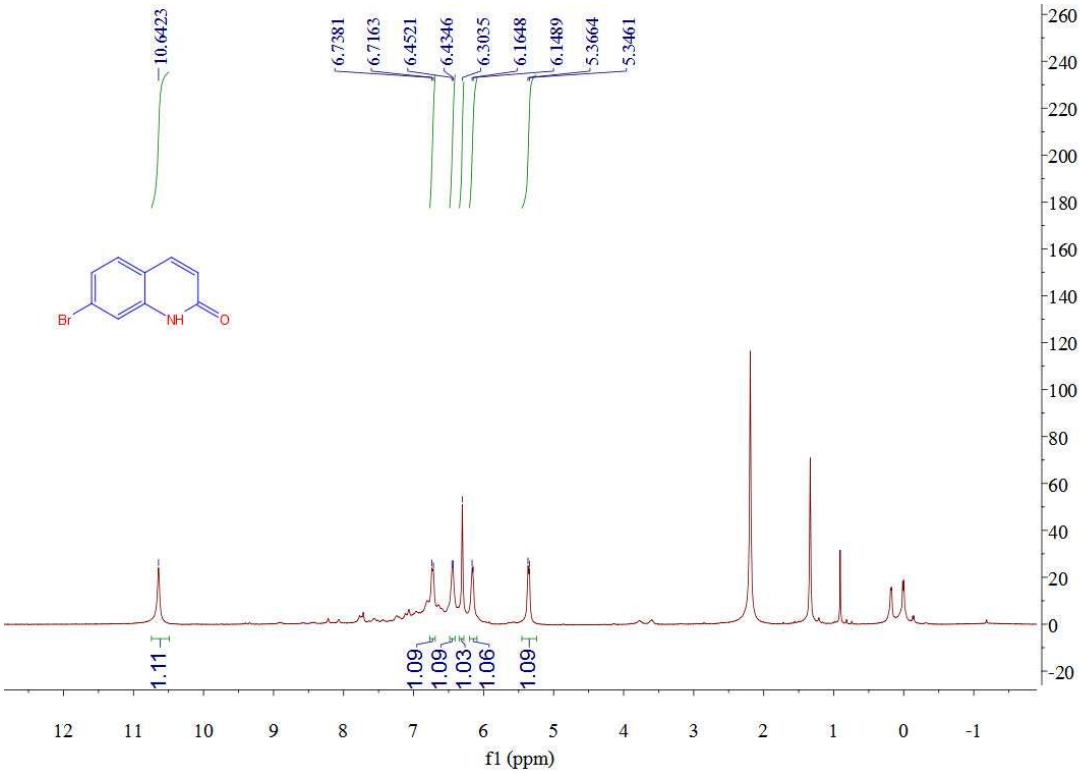
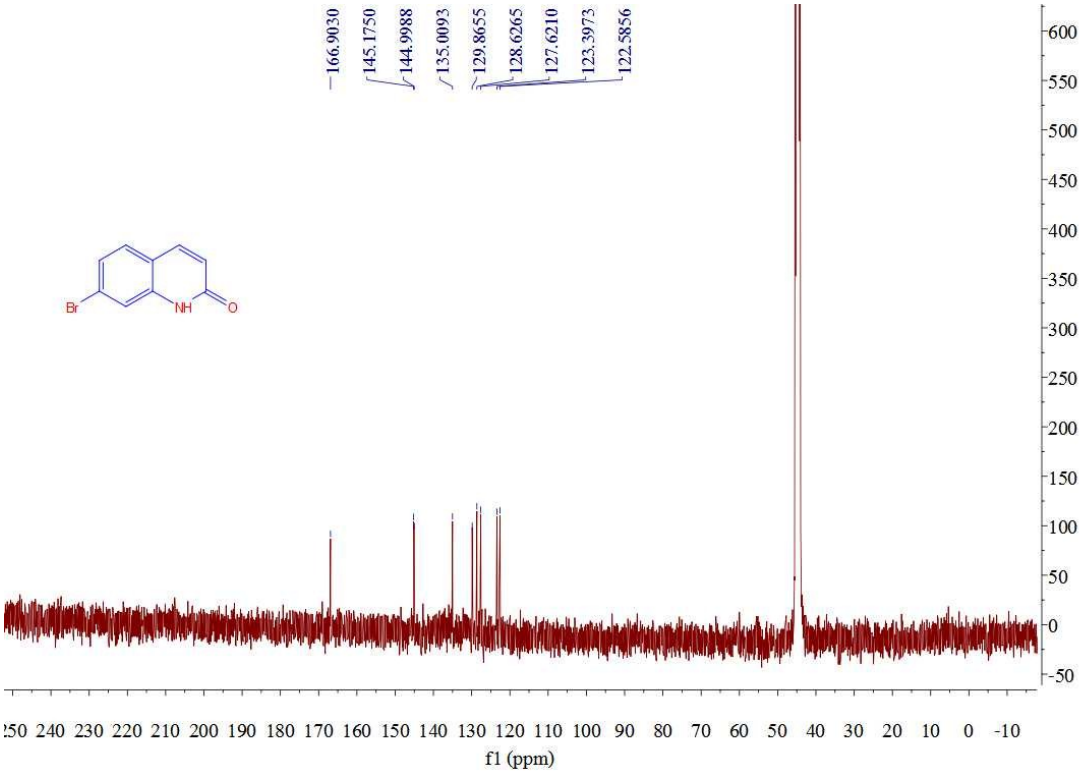
8.4788
7.6664
7.6466
7.5523
7.5327
7.5135
7.3382
7.3178
7.2197
7.2009
7.1820
Br
NH
O
0.99
0.95
1.00
0.99
0.99
0.98
f1 (ppm)


158.1302
142.1304
138.5998
131.1644
127.7520
122.7391
119.8263
117.5444
115.6747
Br
NH
O
f1 (ppm)


10.6423
6.7381
6.7163
6.4521
6.4346
6.3035
6.1648
6.1489
5.3664
5.3461
Br
NH
O
1.11
1.09
1.09
1.03
1.06
1.09
f1 (ppm)


166.9030
145.1750
144.9988
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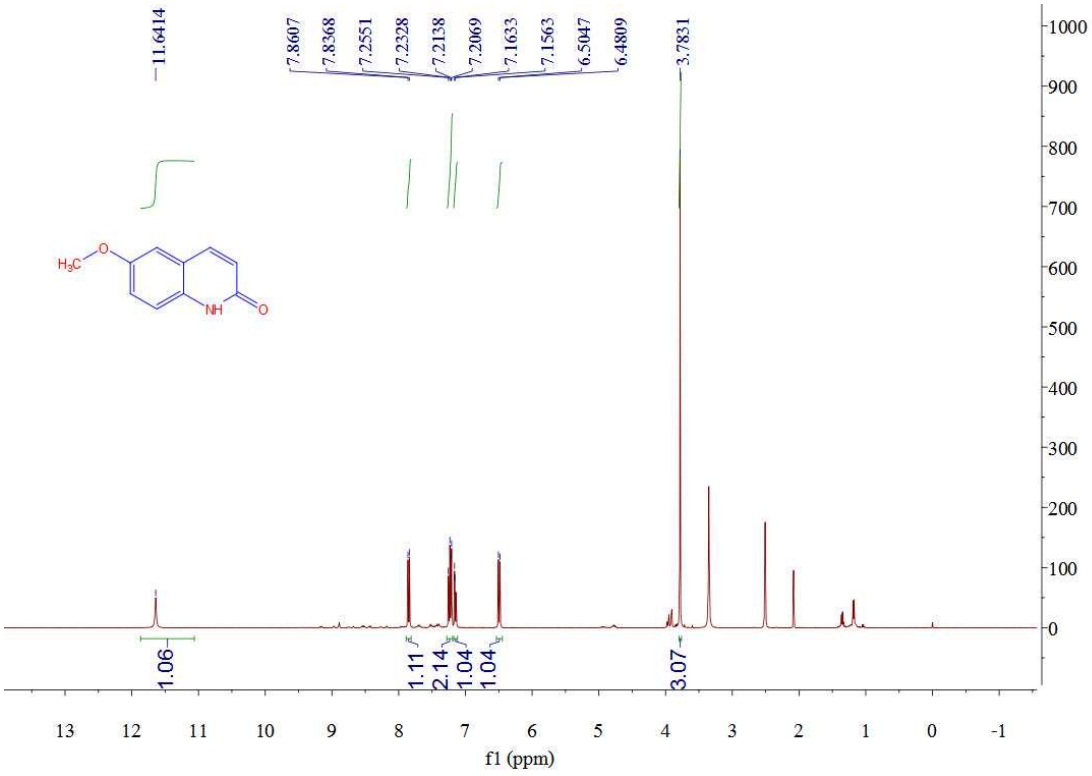
128.6265
127.6210
123.3973
122.5856
Br
NH
O
f1 (ppm)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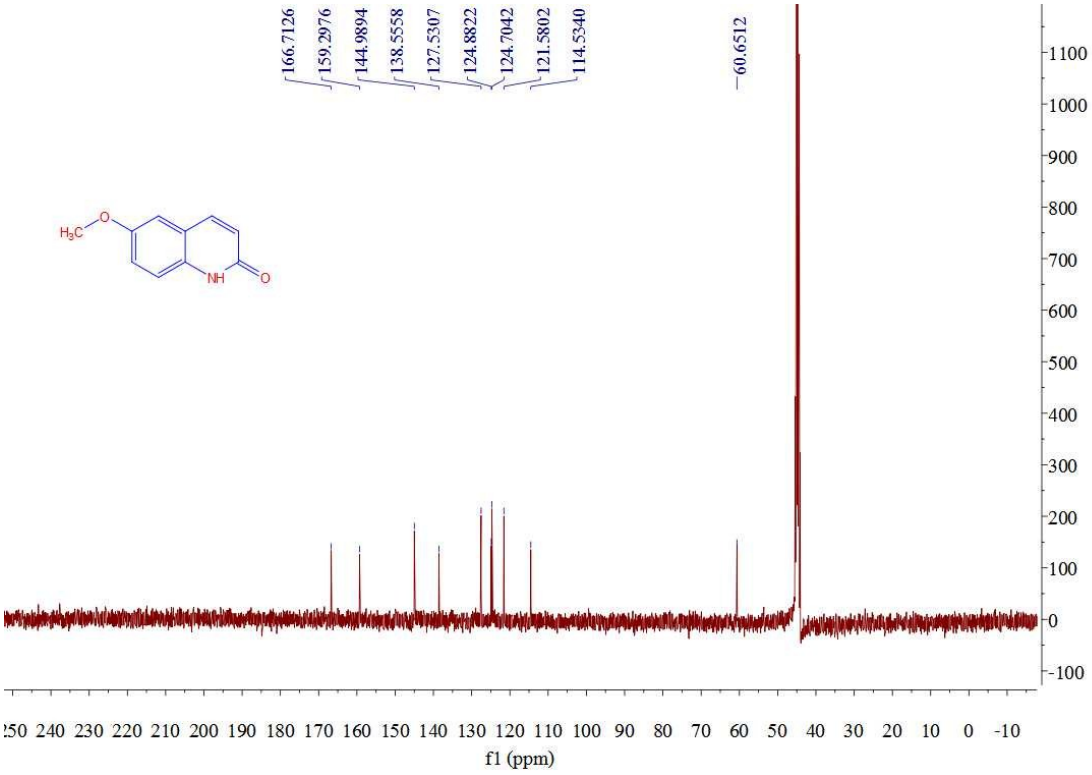
7.8607
7.8368
7.2551
7.2328
7.2138
7.2069
7.1633
7.1563
6.5047
6.4809
3.7831
1.06
1.11
2.14
1.04
1.04
3.07
f1 (ppm)


166.7126
159.2976
144.9894
138.5558
127.5307
124.8822
124.7042
121.5802
114.5340
60.6512
f1 (ppm)