Copper(II)- Catalyzed Electrophilic Amination of Quinoline *N*-Oxides with *O*-Benzoyl hydroxylamines

Gang Li[a]*, Chunqi Jia[b], Kai Sun[a], Yunhe Lv[a], Feng Zhao[a], Kexiao Zhou[a], and Hankui Wu[a]*

[a] College of Chemistry and Chemical Engineering, Anyang Normal University, Anyang, 455000 P. R. China Fax: (+86)-372-2900040; E-mail: ligang@aynu.edu.cn; hkwu@aynu.edu.cn

[b] School of Biomedical Sciences, Engineering Research Center of Molecular Medicine of Chinese Education Ministry, Xiamen Key Laboratory of Ocean and Gene Drugs, Institute of Molecular Medicine of Huaqiao University, Xiamen, 361021 P. R. China

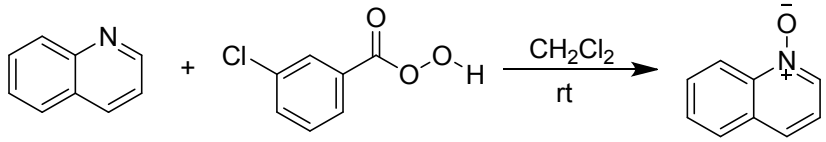
Table of contents

1. General Information

All commercial reagents and solvents were used directly without additional purification. Column chromatography was performed on silica gel 200-300 mesh. ^{1}H NMR and ^{13}C NMR spectra were registered on a Bruker Ascend^{TM} 400 spectrometer (Germany). Chemical shifts were reported in units (ppm) referenced to 0.0 ppm of TMS in the ^{1}H spectrum and 77.0 ppm of $CDCl_3$ in the ^{13}C spectrum. All coupling constants were reported in Hertz (Hz). HRMS data were obtained on a Waters LCT Premierxe^{TM} (USA).

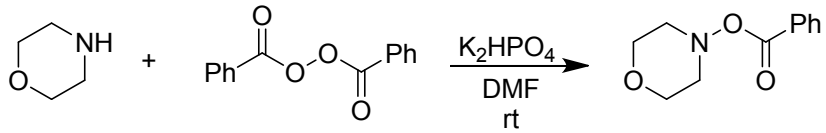
2. Experimental Section

2.1. General Procedure to Prepare Quinoline *N*-Oxide Derivatives



Under vigorous magnetic stirring, 3-Chloroperbenzoicacid (*m*CPBA) (345 mg, 2 mmol) in CH_2Cl_2 (5 mL) was dropped into solution of quinoline derivatives (2 mmol) in CH_2Cl_2 (5 mL) cooled to 0°C. After the completion of this course, the reaction mixture was allowed up to room temperature and stirred overnight. An aqueous solution of saturated $NaHCO_3$ was added to the mixture to neutralize residual *m*CPBA. The resulting mixture was extracted with CH_2Cl_2 (3x 10 mL). The organic phase were combined and washed with a saturated NaCl solution (3x 5 mL). The organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure to give crude product, which was purified by column chromatography (silica gel 200-300 mesh, EtOAc: methanol (8:1) as eluent). The product was identified by ^{1}H NMR and MS spectra and compared to the previous literature.

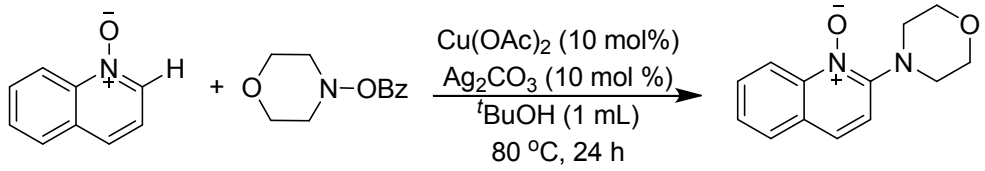
2.2 **General Procedure to Prepare *O*-Benzoyl hydroxylamine**



Benzoyl peroxide (12.11 g, 50 mmol), dipotassium hydrogen phosphate (13.06 g, 75 mmol), and *N,N*-dimethyl formamide (125 mL) were added into a 500 mL, one-necked, round-bottomed flask equipped with a Teflon-coated magnetic stirbar.

Under vigorous magnetic stirring, the amine (60-125 mmol) was dropped into the system at ambient temperature. After 24h, deionized water (200 mL) was added to dissolve all solids. Then, the reaction mixture was transferred to a separatory funnel and extracted with 150 mL of ethyl acetate. The organic phase was collected and washed with saturated aq. $NaHCO_3$ solution. The organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporation to give crude product, which was purified by column chromatography to obtain desired product, which identified by ^{1}H NMR.

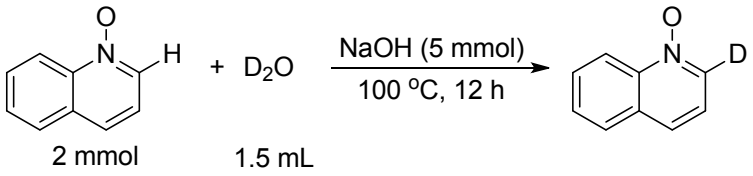
2.3. Typical Experimental Procedures of the Electrophilic Amination



Quinoline *N*-oxide (0.2 mmol), *O*-Benzoyl hydroxylamine (0.6 mmol, 3.0 equiv.), $Cu(OAc)_2$ (0.02 mmol, 10 mol%), Ag_2CO_3 (0.02 mmol, 10 mol%), ^{t}BuOH (1 mL) were charged into a 30 mL pressure tube sealed with rubber plugs under air atmosphere. The reaction mixture was stirred at 80 °C for 24 h. After the starting material was completely consumed (based on thin layer chromatography (TLC) monitoring, EtOAc: methanol as eluent), the reaction was cooled down to room temperature. The mixture was passed through a short pad of celite, washing with a mixture of methanol/Ethyl acetate in a 1 : 1 ratio repeatedly. The organic layer was concentrated under reduced pressure to give a crude oil, which was purified by column chromatography on silica gel (200-300 mesh) to afford desired products.[2]

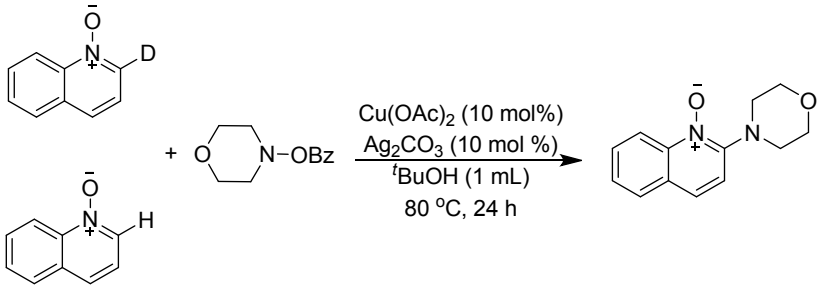
3. Kinetic Isotope Effect Studies in the Amidation of Quinoline *N*-Oxides

3.1. Synthesis of 2-d1-Quinoline *N*-Oxide.



D_2O (1.5 mL), NaOH (200 mg, 5 mmol), quinoline *N*-oxide (258 mg, 2.0 mmol) were weighed into 30-mL pressure tube sealed with rubber plugs. The reaction mixture was stirred at 100 °C for overnight. After cooling to room temperature, the mixture was then extracted with Chloroform (3 x 10 mL). The combined organic phases were washed with saturated NaCl solution (3 x 5 mL), dried over $MgSO_4$, and filtered. Chloroform was removed under reduced pressure to obtain the product. Deuterium incorporation was detected to be 91% by ^{1}H NMR in $DCCl_3$. Peak areas at 8.76 ppm and 8.53 ppm were compared to obtain the deuterium incorporation (see ^{1}H spectrum). Spectral data were consistent with related reports.[3]

3.2. KIE Experiment



2-d1-quinoline *N*-oxide(0.1 mmol) and quinoline *N*-oxide (0.1 mmol), *O*-Benzoyl hydroxylamine (0.6 mmol), $Cu(OAc)_2$ (0.02 mmol), and Ag_2CO_3 (0.02 mmol),

^{t}BuOH (1 mL) were added into tube sealed with rubber plugs under air atmosphere. The system was stirred at 80 °C for 5 minutes. After cold quenching rapidly in a cold pool, the mixture was passed through a short pad of celite and washed with methanol/ethyl acetate (1:1 volume ratio) to remove metal salt. The organic phase was concentrated under reduced pressure to obtain a crude mixture. Residual reactant was recovered by column chromatography on silica gel. The ratio (0.51:0.49) of 2-d_1-quinoline *N*-oxide to quinoline *N*-oxide in residual material was obtained by ^{1}H NMR spectroscopy. K_H/K_D was calculated by the following expression:

$$K_H/K_D = \frac{M/2 - 0.49m}{M/2 - 0.51m}$$

M, m represent the amount of 2- d_1-quinoline *N*-oxide and quinoline *N*-oxide in staring material and residual material, respectively. Here, M = 29, m = 20, which corresponds to K_H/K_D = 1.1.

References：

(1) Liu, C.; Han, N.; Song, X.-X.; Qiu, J.-S. *Eur. J. Org. Chem.* **2010**, *29*, 5548.

(2) (a) Qiu, Y.-T; Liu, Y.-H.; Yang, K.; Hong, W.-K.; Li, Z.; Wang, Z.-Y.; Yao, Z.-Y.; Jiang, S. *Org. Lett.*, **2011**, *13*, 3556, (b) Berg, M.; Bal, G.; Goeminne, A.; Veken, P. V.; Versées, W.; Steyaert, J.; Haemers, A.; Augustyns, K. *ChemMedChem*. **2009**, *4*, 249.

(3) Sylvester, K. T.; Wu, K.; Doyle, A. G.; *J. Am. Chem. Soc.*, **2012**, *134*, 16967.

4. Data and Spectra of ^{1}H NMR and ^{13}C NMR

2-morpholinoquinoline 1-oxide (3a): obtained as pale yellow solid (77% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 8.8 Hz, 1H), 7.80–7.68 (m, 3H), 7.51 (t, 1H), 7.06 (d, 1H), 4.02–3.96 (m, 4H), 3.66–3.60 (m, 4H).^{13}C NMR (101 MHz, $CDCl_3$) δ 130.78, 127.75, 127.02, 126.23, 118.69, 113.28, 77.34, 66.80, 47.91. HRMS (ESI) Calcd. For $C_{13}H_{15}N_2O_2$: $[M+H]^+$, 231.1134. Found: m/z 243.1128.

6-methyl-2-morpholinoquinoline 1-oxide (3b): obtained as white solid (90% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 9.0 Hz, 1H), 7.60–7.39 (m, 3H), 6.93 (d, *J* = 9.0 Hz, 1H), 3.89 (t, *J* = 4.6 Hz, 4H), 3.51 (d, *J* = 4.6 Hz, 4H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.84, 140.70, 136.20, 132.86, 126.77, 126.60, 125.83, 118.52, 113.23, 66.81, 47.96, 21.14. HRMS (ESI) Calcd. For $C_{14}H_{17}N_2O_2$: $[M+H]^+$, 245.1290. Found: m/z 245.1289.

3-methyl-2-morpholinoquinoline 1-oxide (3c): obtained as white solid (83% yield), ^{1}H NMR (400 MHz, CDCl3) δ 8.63 (d, *J* = 8.8, 1H), 7.76–7.61 (m, 2H), 7.59–7.47 (m, 2H), 3.91 (d, *J* = 4.7 Hz, 4H), 3.49 (s, 4H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 150.03, 141.13, 130.44, 129.39, 127.41, 127.36, 127.14, 126.95, 119.14, 67.66,

48.21, 19.09. HRMS (ESI) Calcd. For $C_{14}H_{17}N_2O_2$: $[M+H]^+$, 245.1290. Found: m/z 245.1291.

5-methoxy-2-morpholinoquinoline 1-oxide (3d): obtained as white solid (60% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.9 Hz, 1H), 8.10 (d, *J* = 9.3 Hz, 1H), 7.65 (t, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 9.3 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 4.01 (s, 3H), 4.01–3.96 (m, 4H), 3.65 (d, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.67, 150.80, 143.21, 131.05, 121.96, 118.02, 111.80, 110.67, 104.66, 66.78, 55.95, 47.93. HRMS (ESI) Calcd. For $C_{14}H_{17}N_2O_3$: $[M+H]^+$, 261.1239. Found: m/z 261.1240.

2-morpholino-5-nitroquinoline 1-oxide (3e): obtained as red solid (51% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (d, *J* = 8.8 Hz, 1H), 8.47 (d, *J* = 9.7 Hz, 1H), 8.29 (d, *J* = 7.7 Hz, 1H), 7.82 (t, *J* = 8.3 Hz, 1H), 7.27 (s, 1H), 4.00 (t, *J* = 4.7 Hz, 4H), 3.71 (d, *J* = 4.7 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.49, 145.91, 143.21, 128.88, 125.18, 123.73, 122.32, 118.70, 116.32, 66.68, 47.86. HRMS (ESI) Calcd. For $C_{13}H_{14}N_3O_4$: $[M+H]^+$, 276.0984. Found: m/z 243.0981.

4-chloro-2-morpholinoquinoline 1-oxide(3f): obtained as pale yellow solid (71% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.8 Hz, 1H), 8.21–8.08 (d, 1H), 7.84–7.80 (t, 1H), 7.62 (t, 1H), 7.16 (s, 1H), 4.11–3.93 (m, 4H), 3.64 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.98, 142.62, 131.65, 131.34, 126.96, 124.89, 123.46, 119.14, 113.44, 66.68, 47.94. HRMS (ESI) Calcd. For $C_{13}H_{14}ClN_2O_2$: $[M+H]^+$, 265.0744. Found: m/z 265.0749.

6-chloro-2-morpholinoquinoline 1-oxide(3g): obtained as yellow solid (73% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, 1H), 7.75 (d, 1H), 7.71–7.52 (d, 2H), 7.08 (d, 1H), 3.98 (s, 4H), 3.63 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.38, 140.82, 132.17, 131.36, 126.44, 126.31, 125.80, 120.63, 114.51, 66.75, 47.88. HRMS (ESI) Calcd. For $C_{13}H_{14}ClN_2O_2$: $[M+H]^+$, 265.0744. Found: m/z 265.0752.

4-bromo-2-morpholinoquinoline 1-oxide (3h): obtained as pale yellow solid (55% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, 1H), 8.07 (t, 1H), 7.88–7.71 (m, 1H), 7.71–7.51 (m, 1H), 7.34 (d, 1H), 3.98 (s, 4H), 3.62 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.05, 142.63, 131.61, 127.54, 127.19, 124.77, 121.47, 119.12, 116.99, 66.68, 47.94. HRMS (ESI) Calcd. For $C_{13}H_{14}BrN_2O_2$: $[M+H]^+$, 309.0239. Found: m/z 309.0231.

1-morpholinoisoquinoline 2-oxide (3i): obtained as white solid (80% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.3 Hz, 1H), 8.06 (d, *J* = 7.2 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.62 (t, 2H), 7.45 (d, J = 7.1 Hz, 1H), 3.98 (s, 4H), 3.60 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.28, 137.58, 131.00, 128.89, 128.79, 127.45, 127.12, 124.10, 120.41, 67.55, 48.63. HRMS (ESI) Calcd. For $C_{13}H_{15}N_2O_2$: $[M+H]^+$, 231.1134. Found: m/z 243.1130.

2-morpholinoquinoxaline 1-oxide (3j): obtained as pale yellow solid (59% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 9.8 Hz, 2H), 8.05 (d, *J* = 8.2, 1H), 7.71 (d, 2H), 4.08–3.95 (m, 4H), 3.75–3.60 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.95, 140.71, 138.85, 137.15, 130.72, 129.70, 128.80, 117.92, 66.65, 47.63. HRMS (ESI) Calcd. For $C_{12}H_{14}N_3O_2$: $[M+H]^+$, 232.1086. Found: m/z 232.1082.

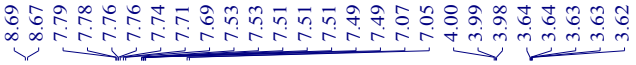
2-(piperidin-1-yl)quinoline 1-oxide (3k): obtained as pale yellow solid (65% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.7 Hz, 1H), 7.84–7.57 (m, 3H), 7.47 (t, *J*

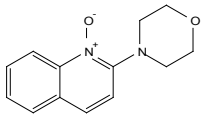
= 7.5 Hz, 1H), 7.09 (d, *J* = 9.1 Hz, 1H), 3.56 (t, *J* = 5.3 Hz, 4H), 1.85 (t, *J* = 5.3 Hz, 4H), 1.72 (d, *J* = 5.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.38, 142.35, 130.49, 127.60, 126.86, 125.68, 125.36, 118.66, 114.15, 48.92, 25.86, 24.51. HRMS (ESI) Calcd. For $C_{14}H_{17}N_2O$: $[M+H]^+$, 229.1341. Found: m/z 229.1337.

2-(4-methylpiperidin-1-yl)quinoline 1-oxide (3l): obtained as pale yellow solid (58% yield), 1H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 8.7 Hz, 1H), 7.80–7.61 (m, 3H), 7.53–7.43 (m, 1H), 7.09 (d, *J* = 9.1 Hz, 1H), 4.24 (d, *J* = 11.3 Hz, 2H), 2.94 (t, *J* = 11.5 Hz, 2H), 1.89–1.75 (m, 2H), 1.67 (s, 1H), 1.58 (m, 2H), 1.04 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.25, 142.34, 130.51, 127.58, 126.74, 125.70, 125.40, 118.72, 114.29, 48.24, 34.09, 31.01, 21.91. HRMS (ESI) Calcd. For $C_{15}H_{19}N_2O$: $[M+H]^+$, 243.1497. Found: m/z 243.1500.

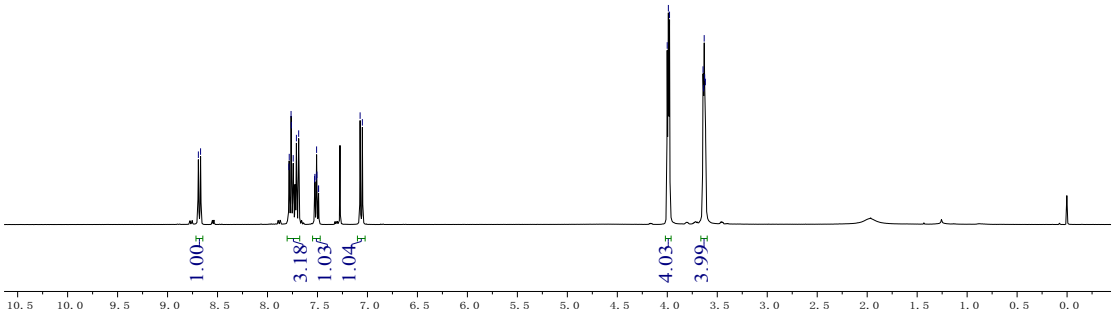
2-(pyrrolidin-1-yl)quinoline 1-oxide (3m): obtained as pale yellow solid (52% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.6 Hz, 1H), 7.83–7.55 (m, 3H), 7.39 (d, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 9.2 Hz, 1H), 3.94 (s, 4H), 2.00 (s, 4H). 13C NMR (101 MHz, $CDCl_3$) δ 148.41, 142.03, 130.72, 128.17, 127.43, 124.58, 123.86, 117.82, 112.45, 50.63, 25.47. HRMS (ESI) Calcd. For $C_{13}H_{15}N_2O$: $[M+H]^+$, 215.1184. Found: m/z 215.1181.

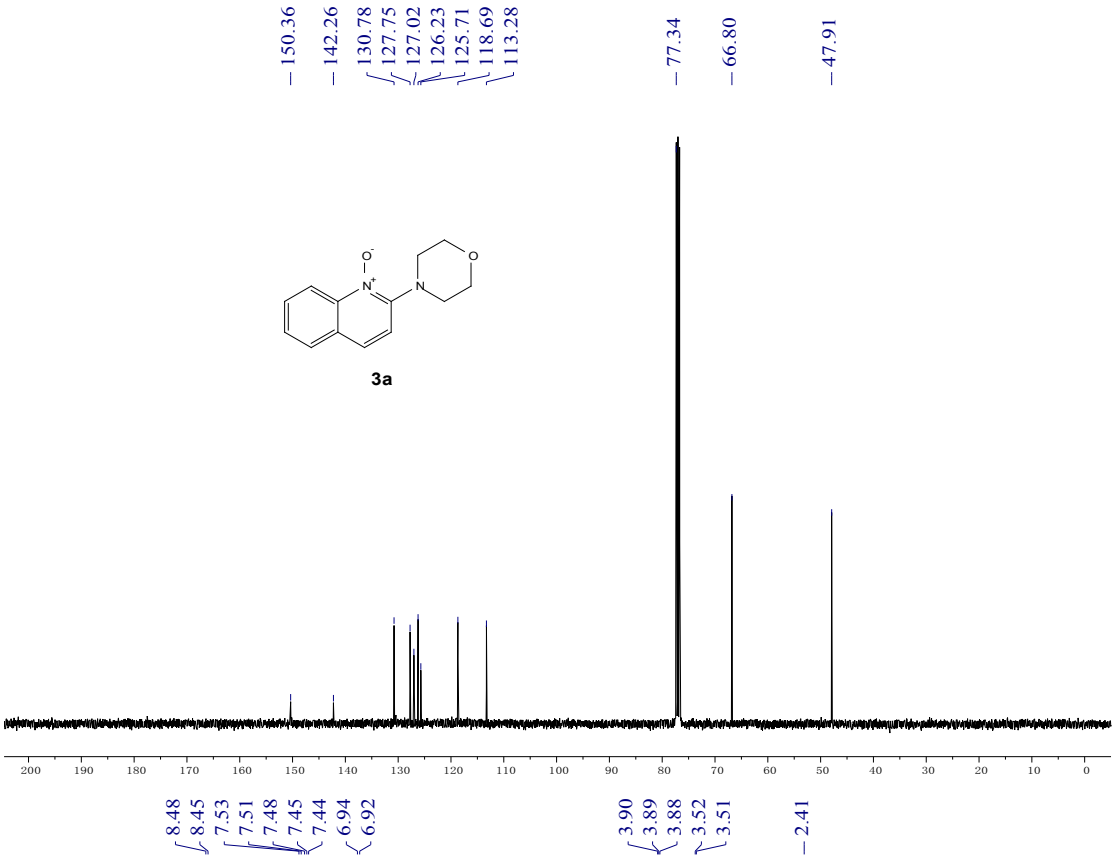
4-(quinolin-2-yl)morpholine (4a): obtained as white solid (92%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 9.1 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 9.1 Hz, 1H), 3.85 (d, *J* = 4.8 Hz, 4H), 3.72 (d, *J* = 5.0 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.55, 147.75, 137.58, 129.61, 127.24, 126.75, 123.32, 122.67, 109.27, 66.90, 45.61. HRMS (ESI) Calcd. For $C_{13}H_{15}N_2$: $[M+H]^+$, 215.1184 Found: m/z 215.1181.



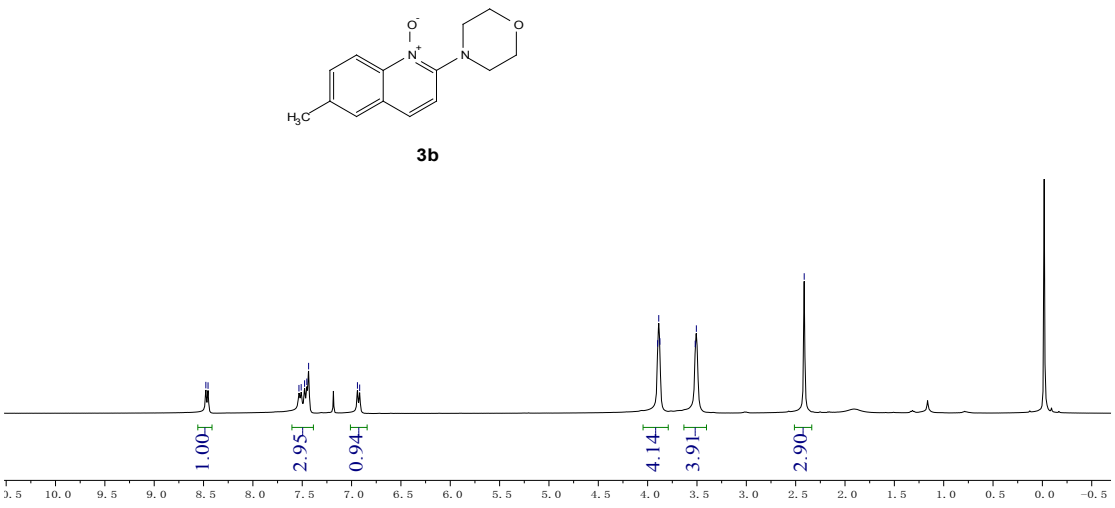


3a

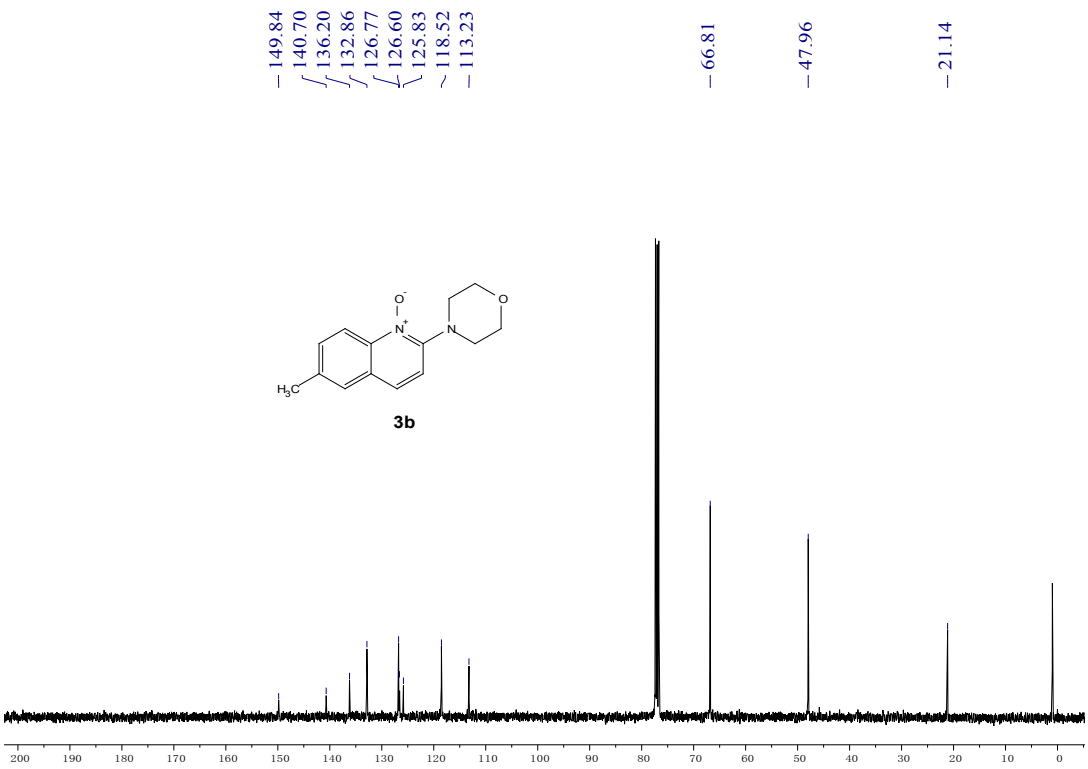


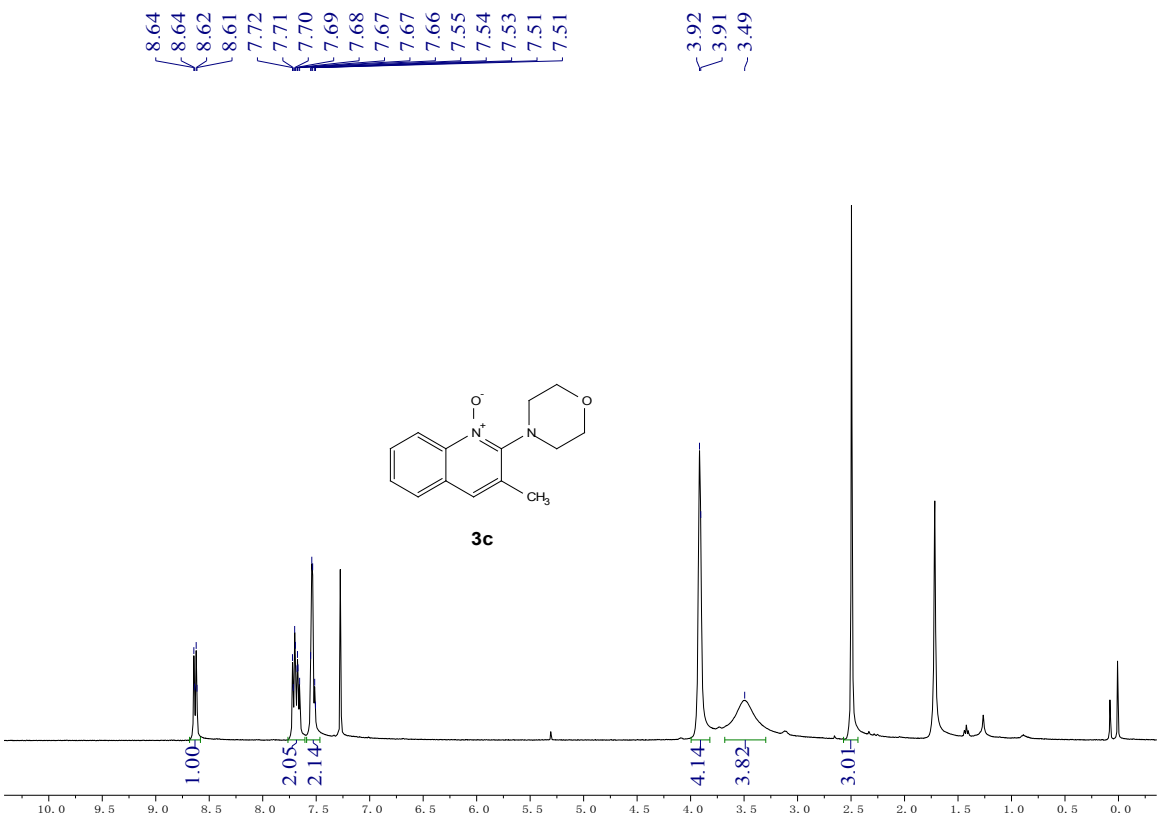

150.36
142.26
130.78
127.75
127.02
126.23
125.71
118.69
113.28
77.34
66.80
47.91
8.48
8.45
7.53
7.51
7.48
7.45
7.44
6.94
6.92
3.90
3.89
3.88
3.52
3.51
2.41

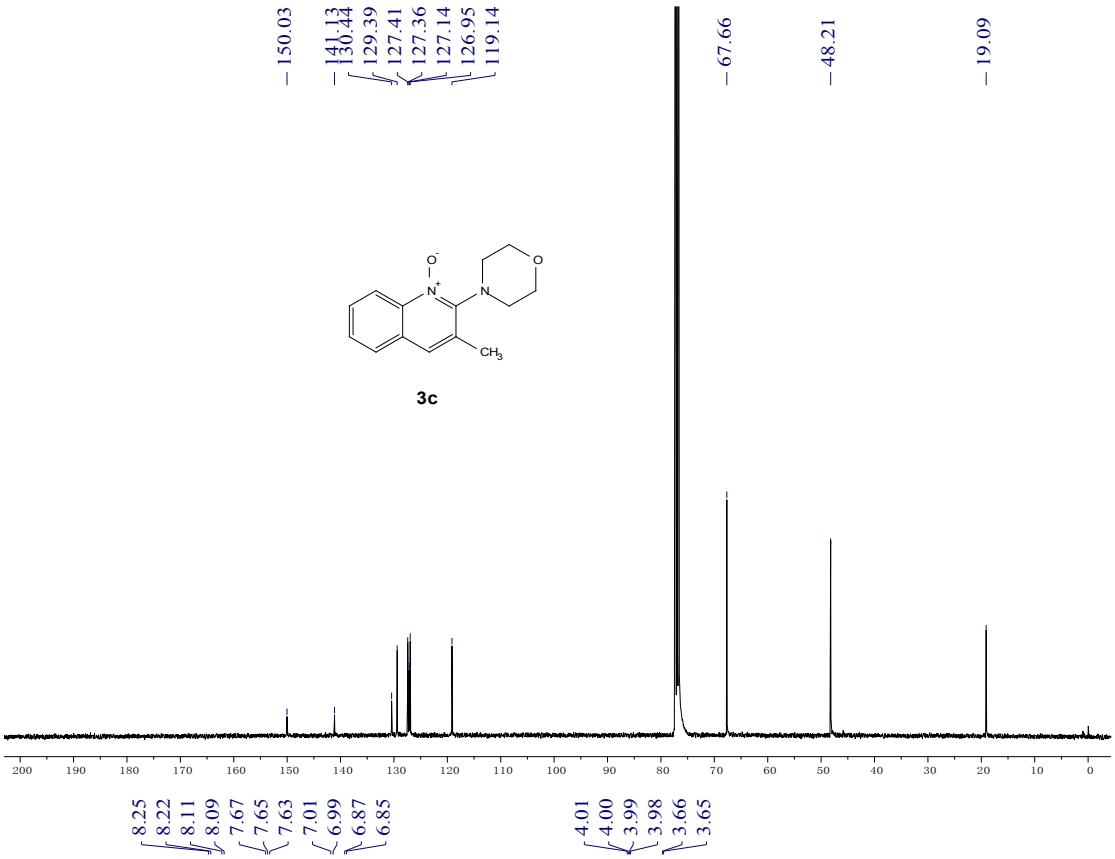
3a


1.00
2.95
0.94
4.14
3.91
2.90

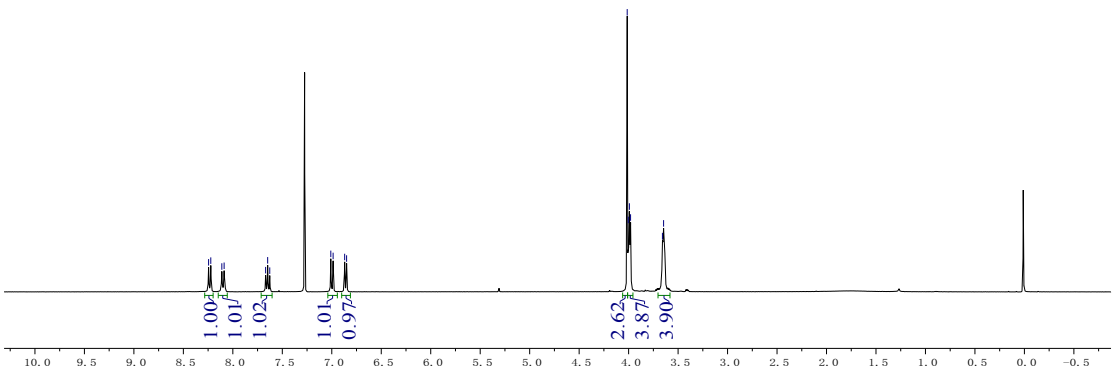
3b


149.84
140.70
136.20
132.86
126.77
126.60
125.83
118.52
113.23
66.81
47.96
21.14
3b

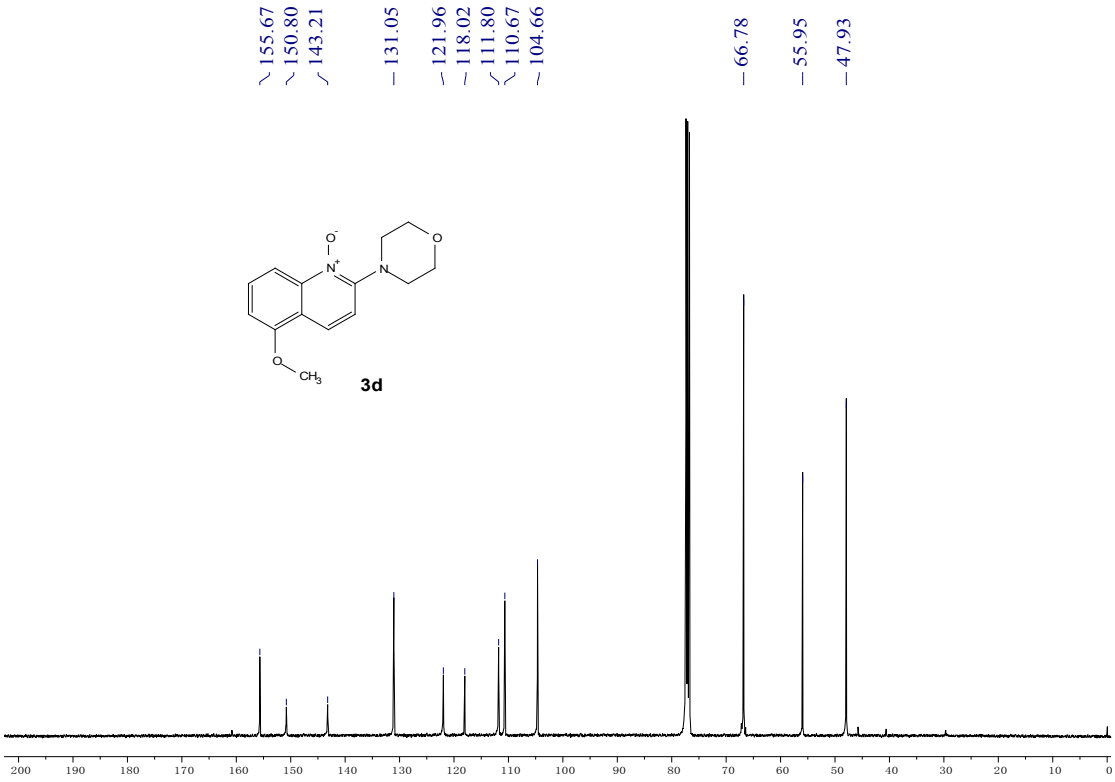

8.64
8.64
8.62
8.61
7.72
7.71
7.70
7.69
7.68
7.67
7.67
7.66
7.55
7.54
7.53
7.51
7.51
3.92
3.91
3.49
1.00
2.05
2.14
4.14
3.82
3.01
3c

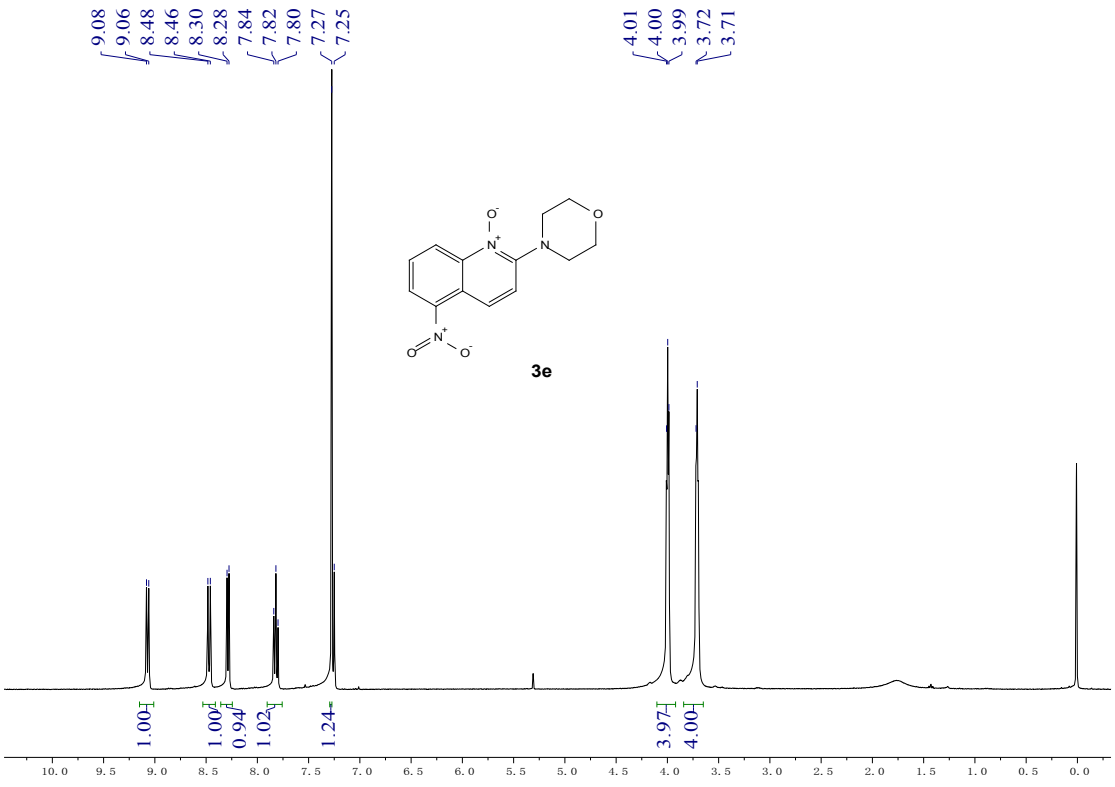

150.03
141.13
130.44
129.39
127.41
127.36
127.14
126.95
119.14
67.66
48.21
19.09
8.25
8.22
8.11
8.09
7.67
7.65
7.63
7.01
6.99
6.87
6.85
4.01
4.00
3.99
3.98
3.66
3.65

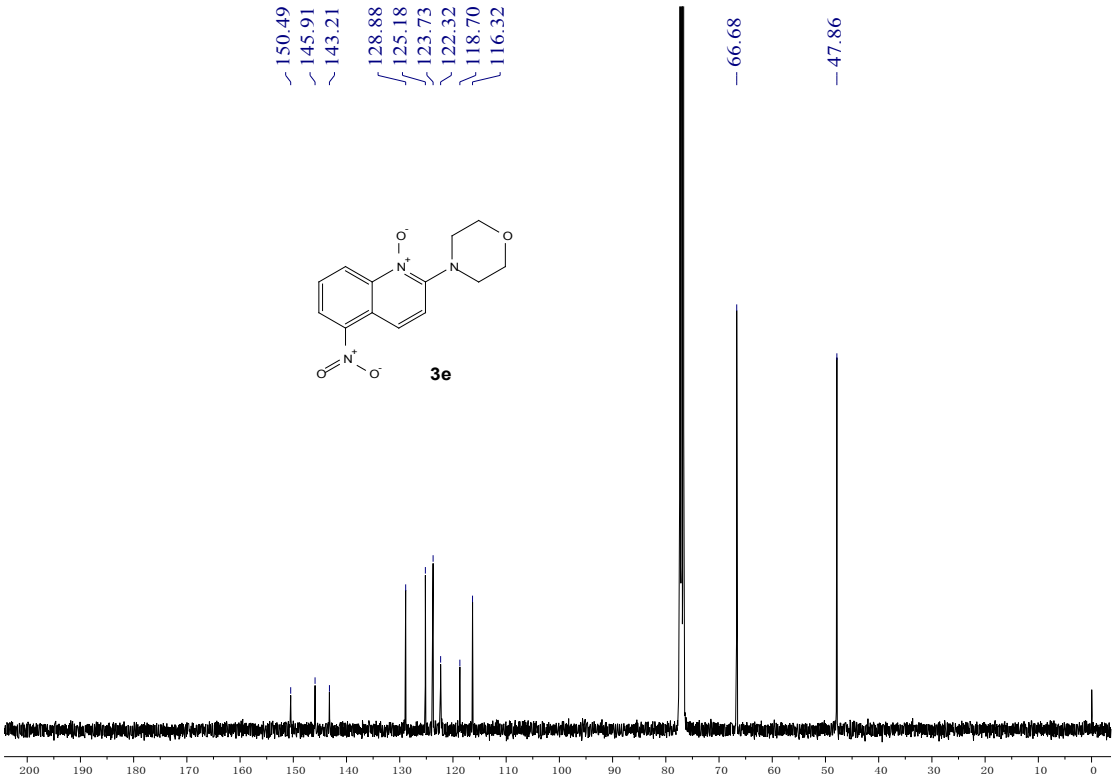
3c

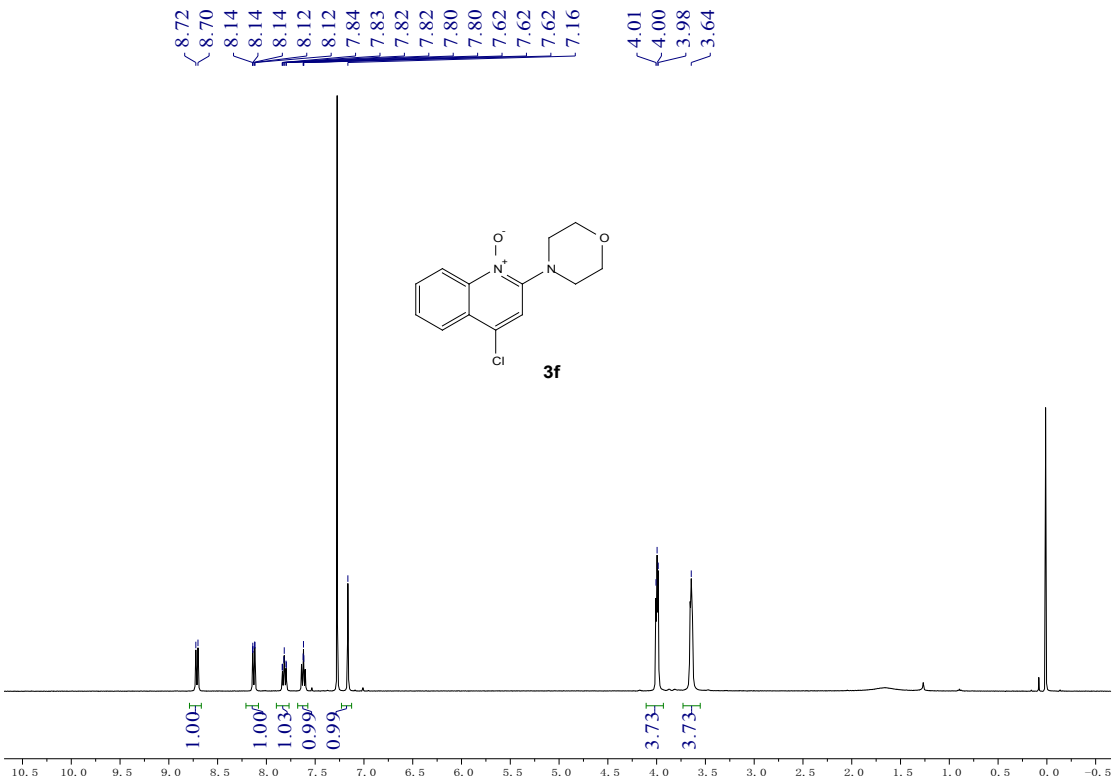

1.00
1.01
1.02
1.01
0.97
2.62
3.87
3.90

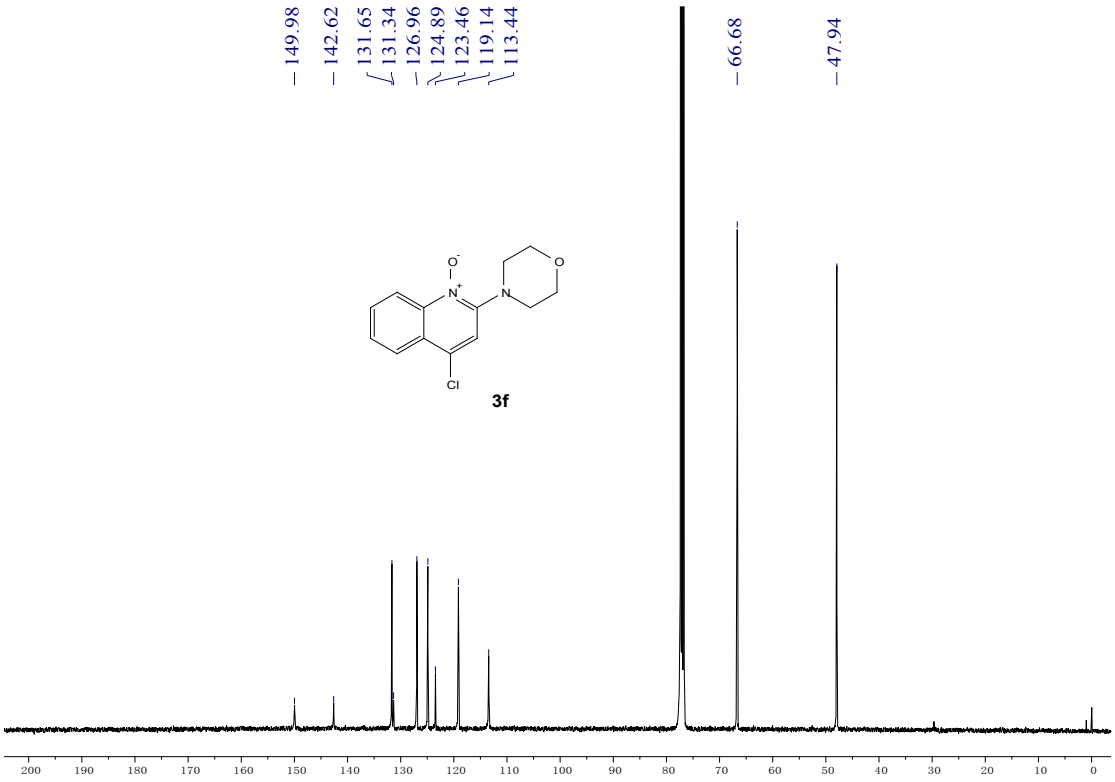
3d


155.67
150.80
143.21
131.05
121.96
118.02
111.80
110.67
104.66
66.78
55.95
47.93
3d

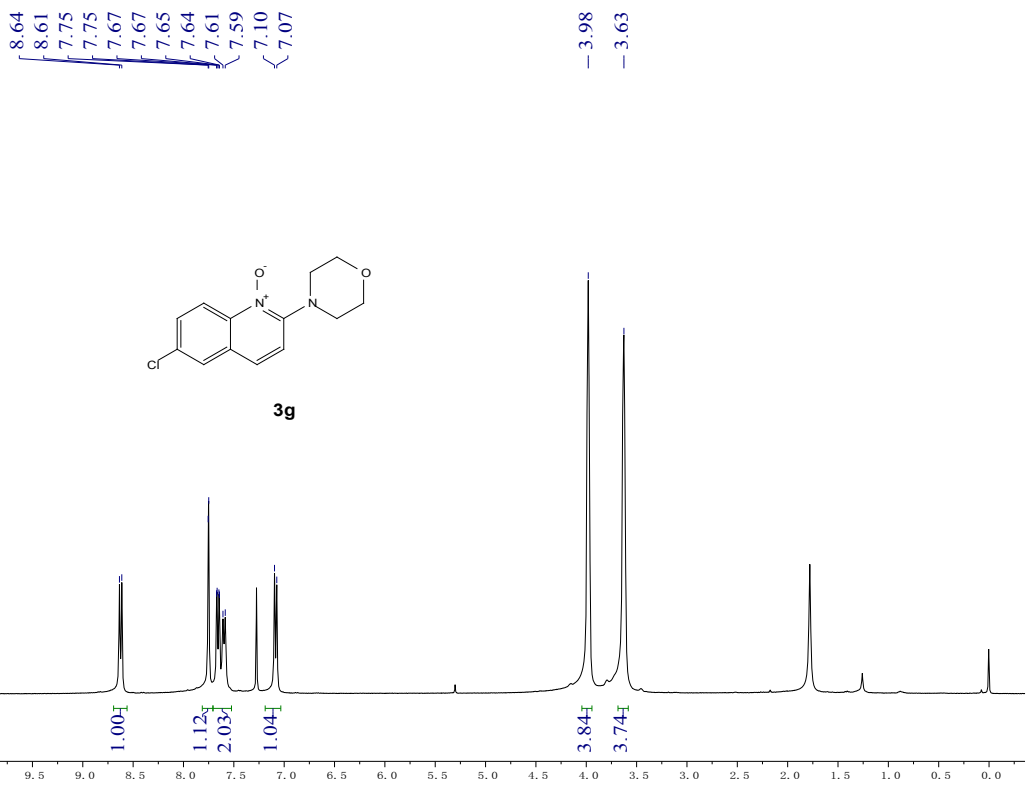

9.08
9.06
8.48
8.46
8.30
8.28
7.84
7.82
7.80
7.27
7.25
4.01
4.00
3.99
3.72
3.71
3e
1.00
1.00
0.94
1.02
1.24
3.97
4.00


150.49
145.91
143.21
128.88
125.18
123.73
122.32
118.70
116.32
66.68
47.86
3e

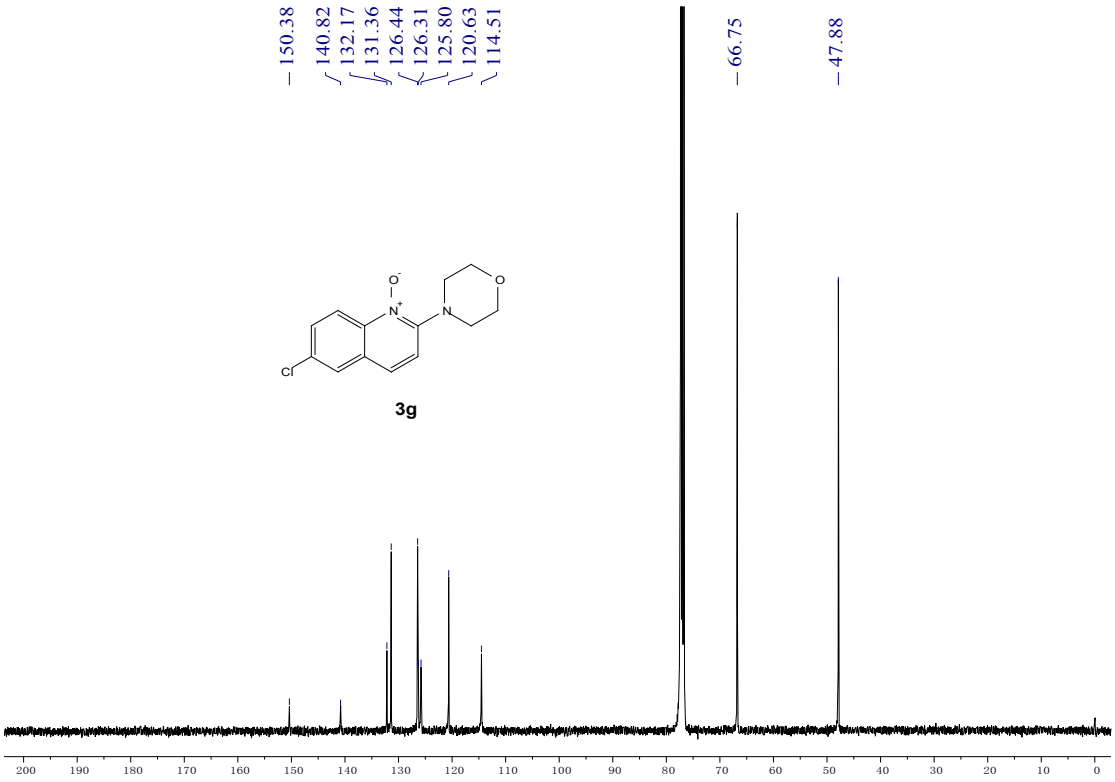

8.72
8.70
8.14
8.14
8.14
8.12
8.12
7.84
7.83
7.82
7.82
7.80
7.80
7.62
7.62
7.62
7.16
4.01
4.00
3.98
3.64
3f
1.00
1.00
1.03
0.99
0.99
3.73
3.73

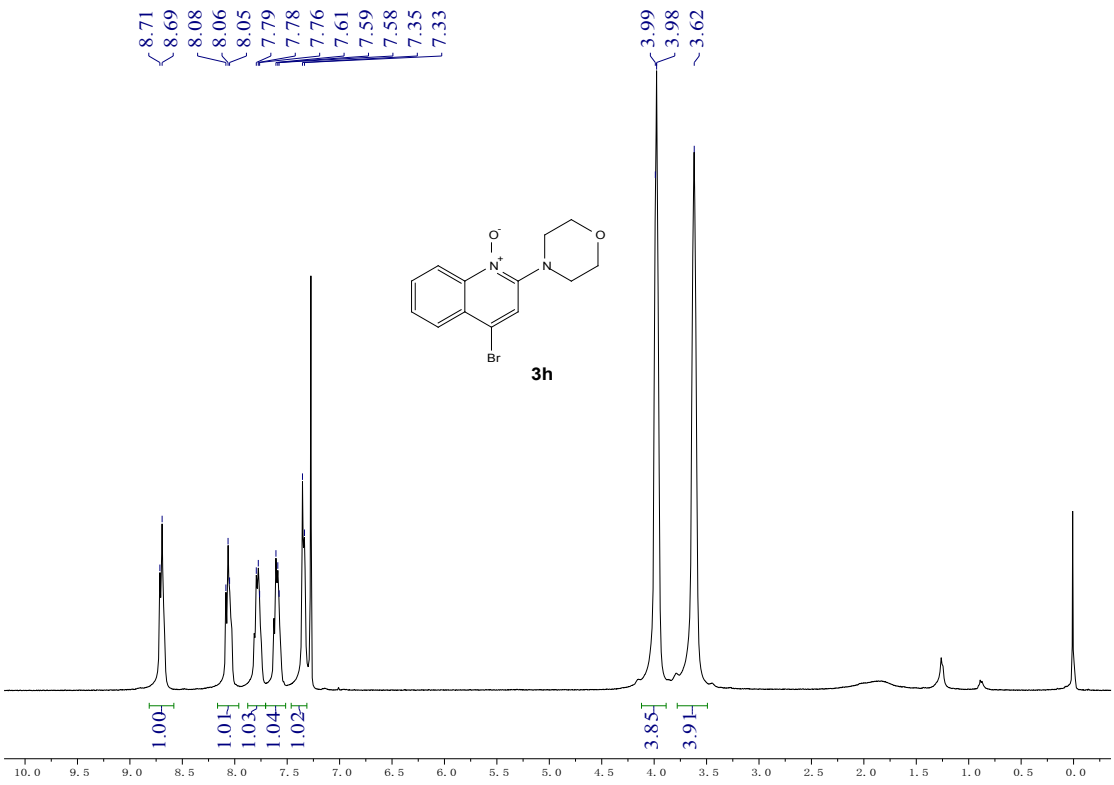

149.98
142.62
131.65
131.34
126.96
124.89
123.46
119.14
113.44
66.68
47.94
O
N
N
O
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

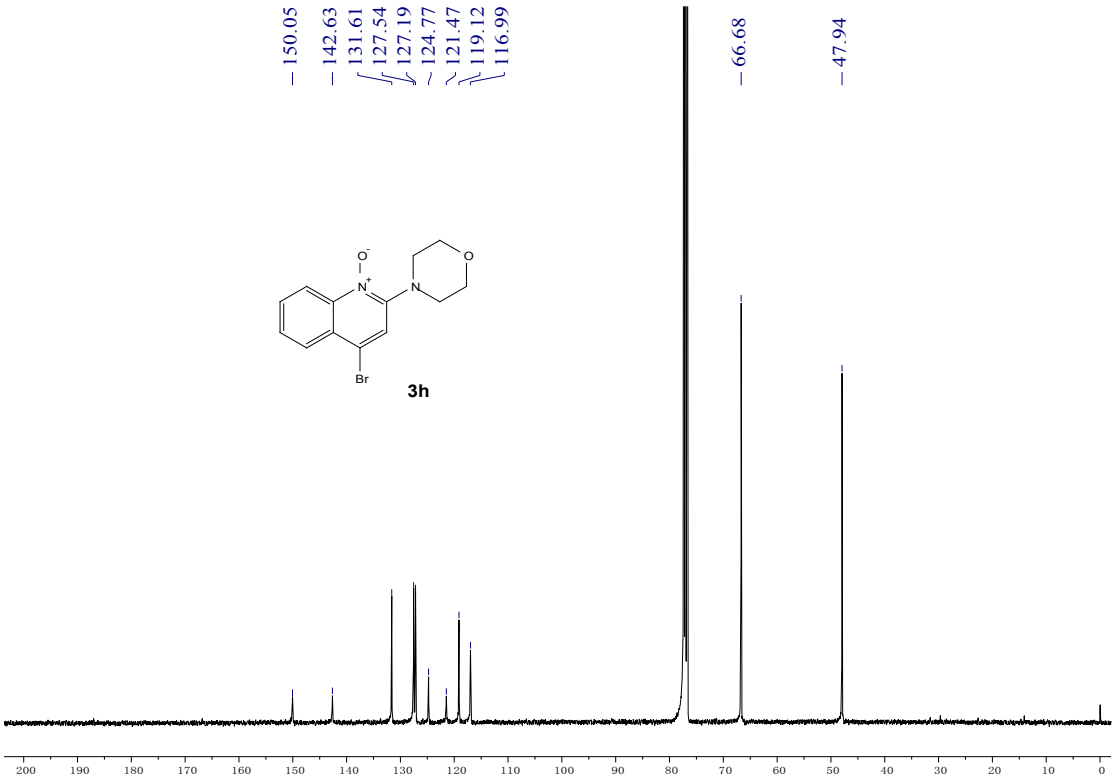
3f

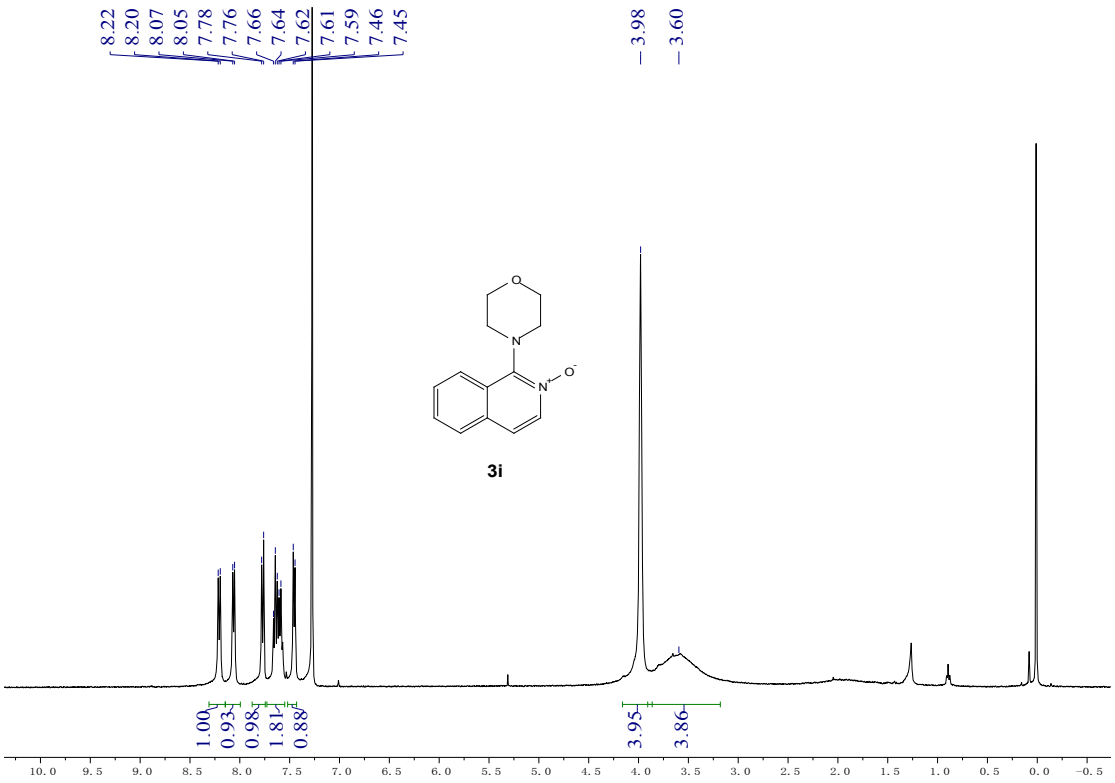

8.64
8.61
7.75
7.75
7.67
7.67
7.65
7.64
7.61
7.59
7.10
7.07
3.98
3.63
O
N
N
O
Cl
1.00
1.12
2.03
1.04
3.84
3.74
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

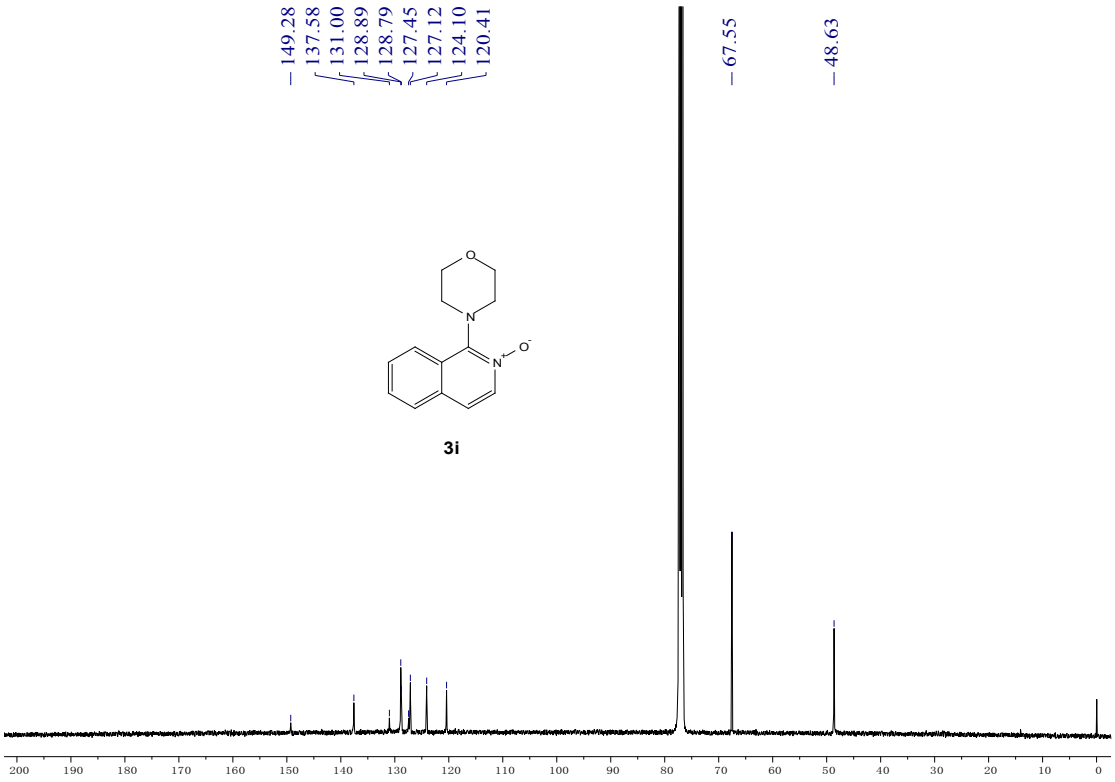
3g


150.38
140.82
132.17
131.36
126.44
126.31
125.80
120.63
114.51
66.75
47.88
O
N
O
N
Cl
3g

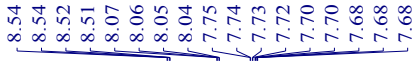

8.71
8.69
8.08
8.06
8.05
7.79
7.78
7.76
7.61
7.59
7.58
7.35
7.33
3.99
3.98
3.62
O
N
O
N
Br
3h
1.00
1.01
1.03
1.04
1.02
3.85
3.91

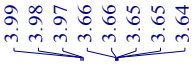

150.05
142.63
131.61
127.54
127.19
124.77
121.47
119.12
116.99
66.68
47.94
O
N
N
O
Br
3h

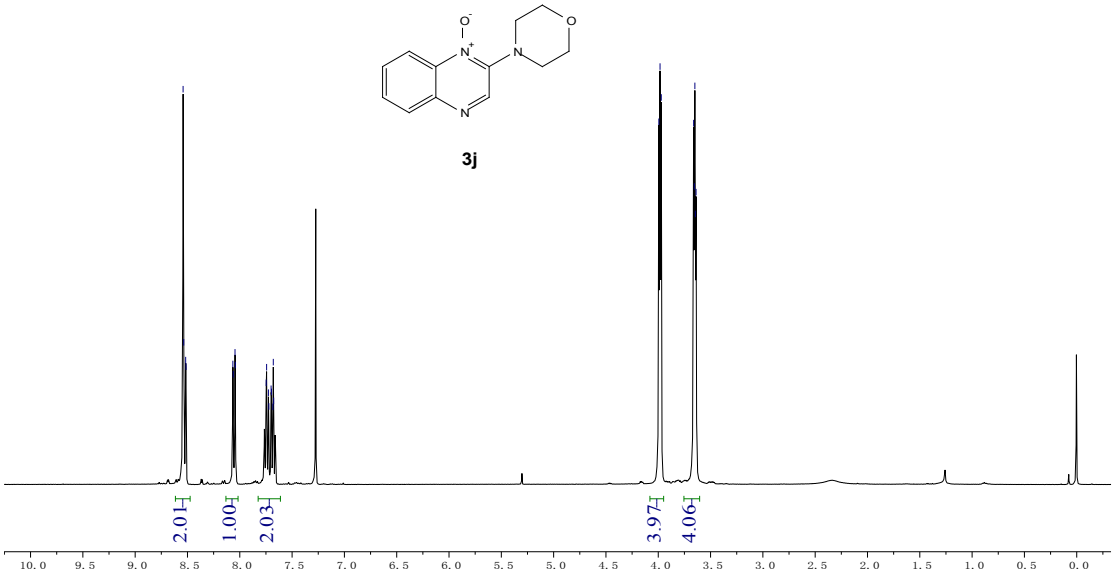

8.22
8.20
8.07
8.05
7.78
7.76
7.66
7.64
7.62
7.61
7.59
7.46
7.45
3.98
3.60
O
N
N
O
3i
1.00
0.93
0.98
1.81
0.88
3.95
3.86


149.28
137.58
131.00
128.89
128.79
127.45
127.12
124.10
120.41
67.55
48.63
O
N
N+
O-
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

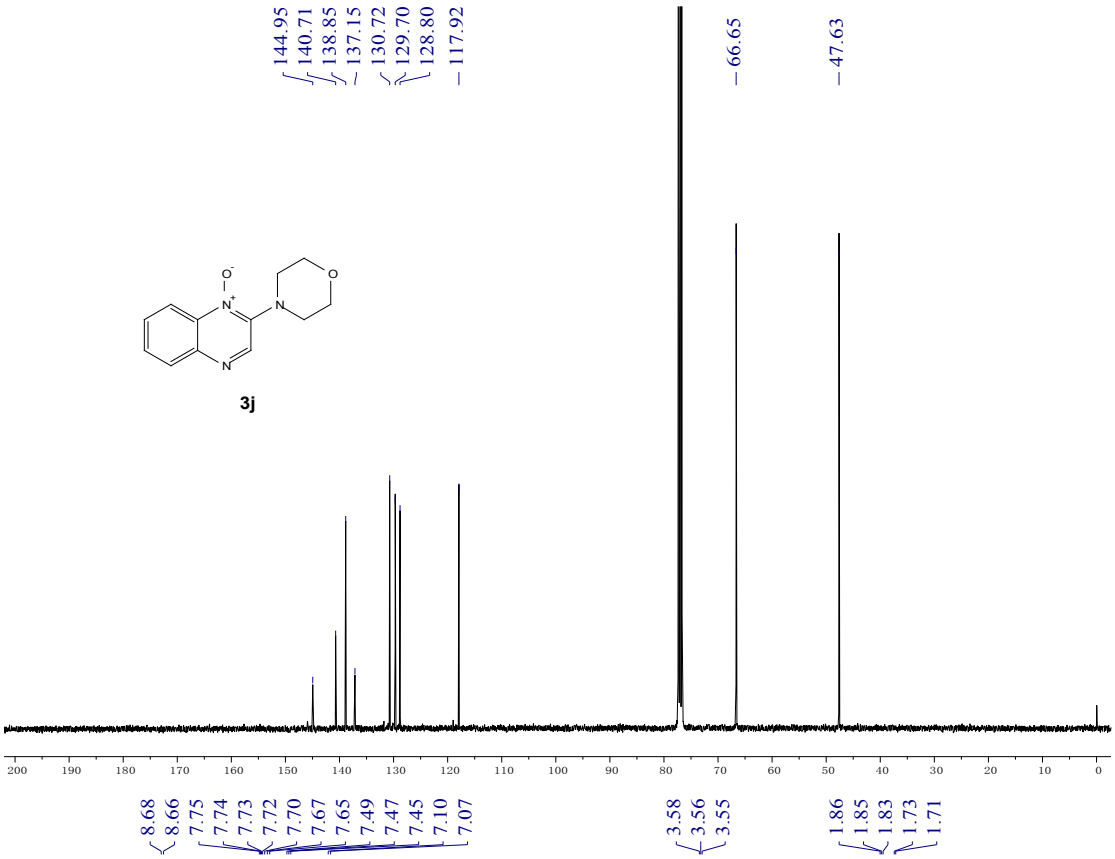
3i


8.54
8.54
8.52
8.51
8.07
8.06
8.05
8.04
7.75
7.74
7.73
7.72
7.70
7.70
7.68
7.68
7.68

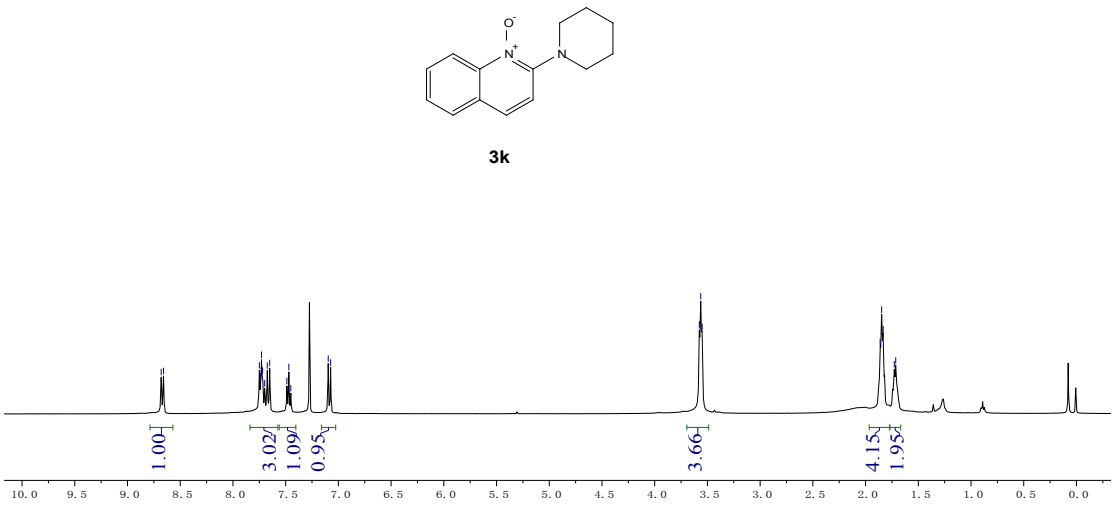

3.99
3.98
3.97
3.66
3.66
3.65
3.65
3.64


O-
N+
N
O
N
2.01
1.00
2.03
3.97
4.06
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

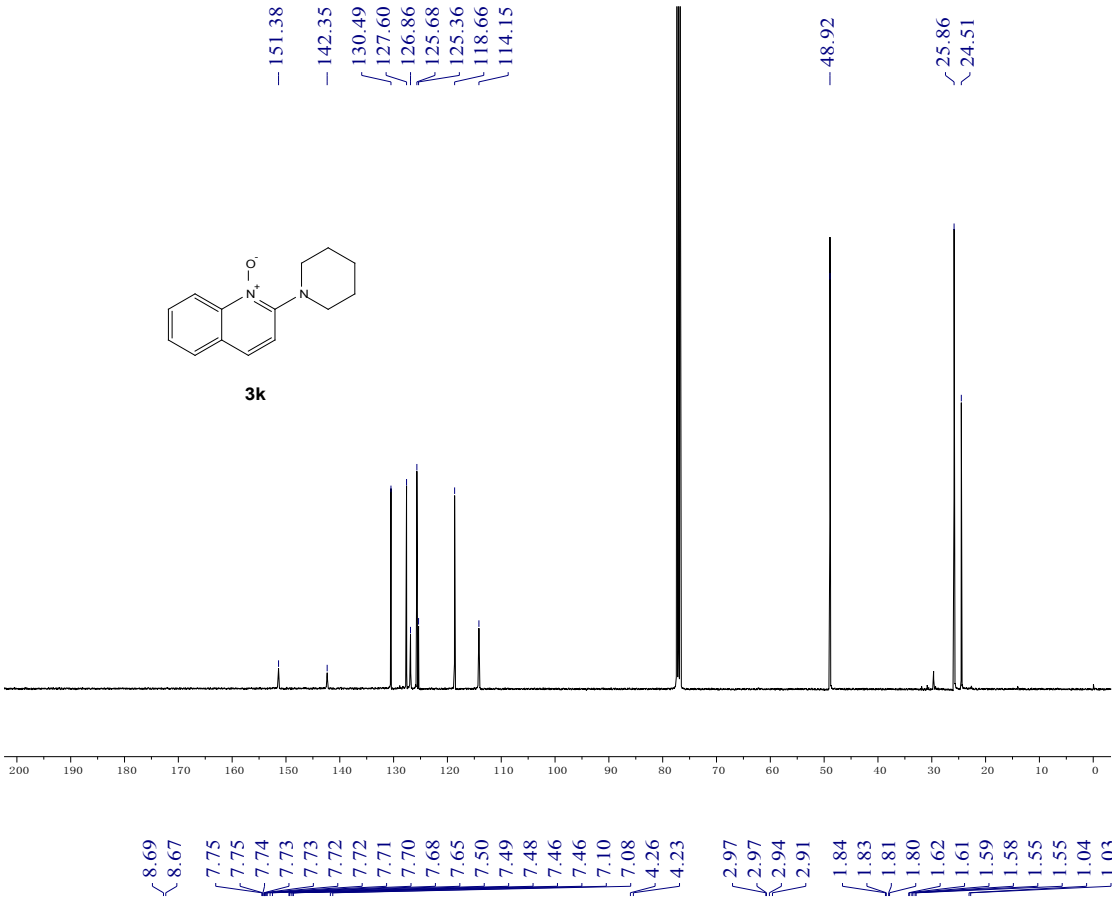
3j

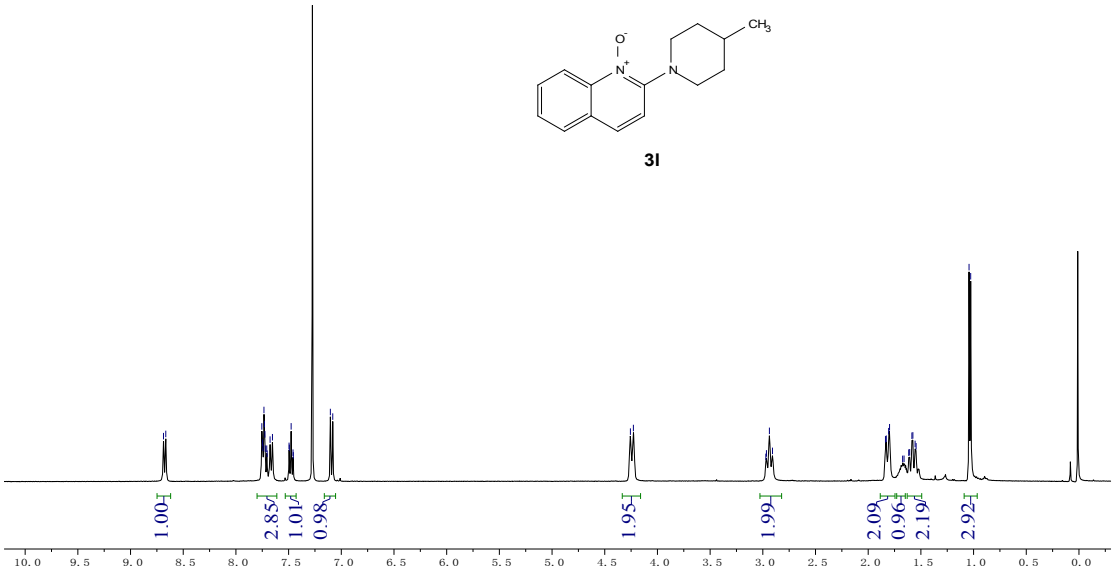

144.95
140.71
138.85
137.15
130.72
129.70
128.80
117.92
66.65
47.63
8.68
8.66
7.75
7.74
7.73
7.72
7.70
7.67
7.65
7.49
7.47
7.45
7.10
7.07
3.58
3.56
3.55
1.86
1.85
1.83
1.73
1.71

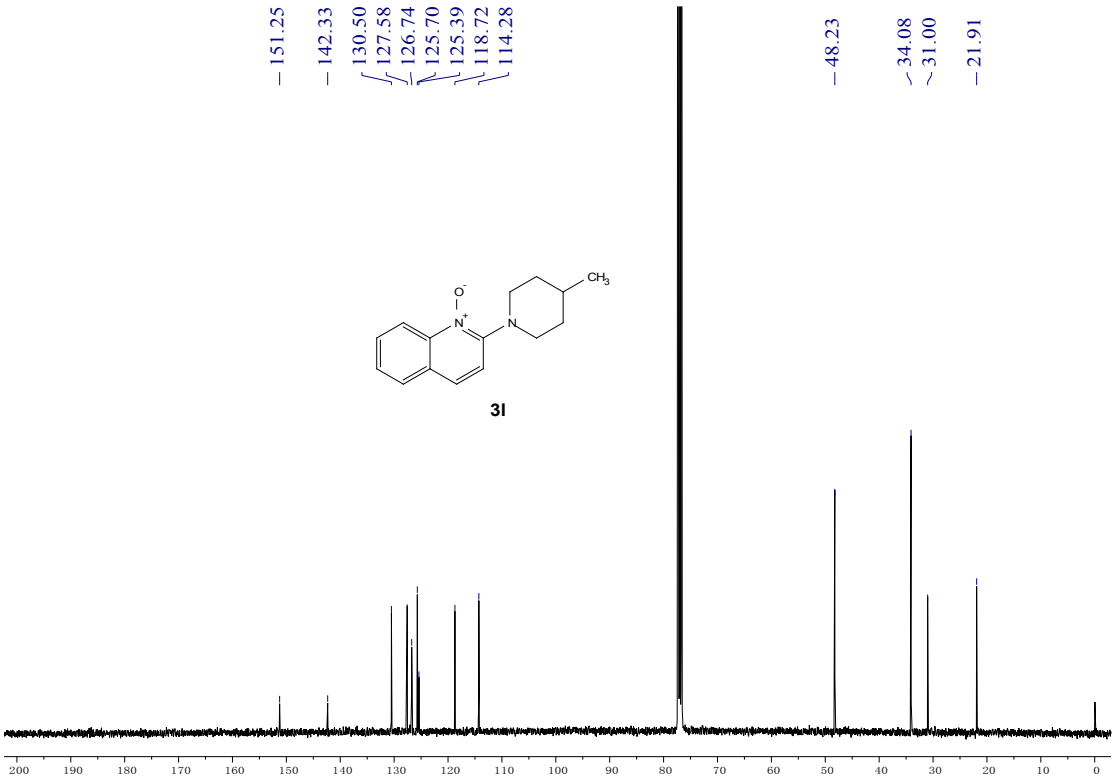
3j


1.00
3.02
1.09
0.95
3.66
4.15
1.95

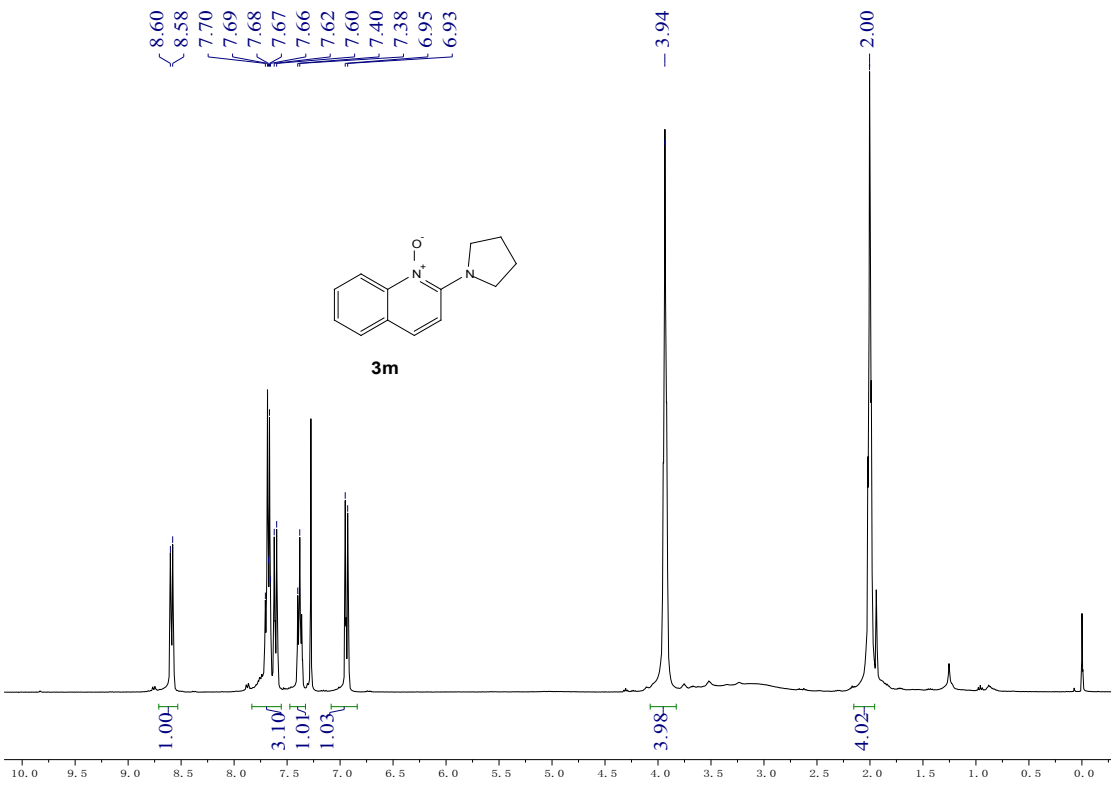
3k


151.38
142.35
130.49
127.60
126.86
125.68
125.36
118.66
114.15
48.92
25.86
24.51
3k
8.69
8.67
7.75
7.75
7.74
7.73
7.73
7.72
7.72
7.71
7.70
7.68
7.65
7.50
7.49
7.48
7.46
7.46
7.10
7.08
4.26
4.23
2.97
2.97
2.94
2.91
1.84
1.83
1.81
1.80
1.62
1.61
1.59
1.58
1.55
1.55
1.04

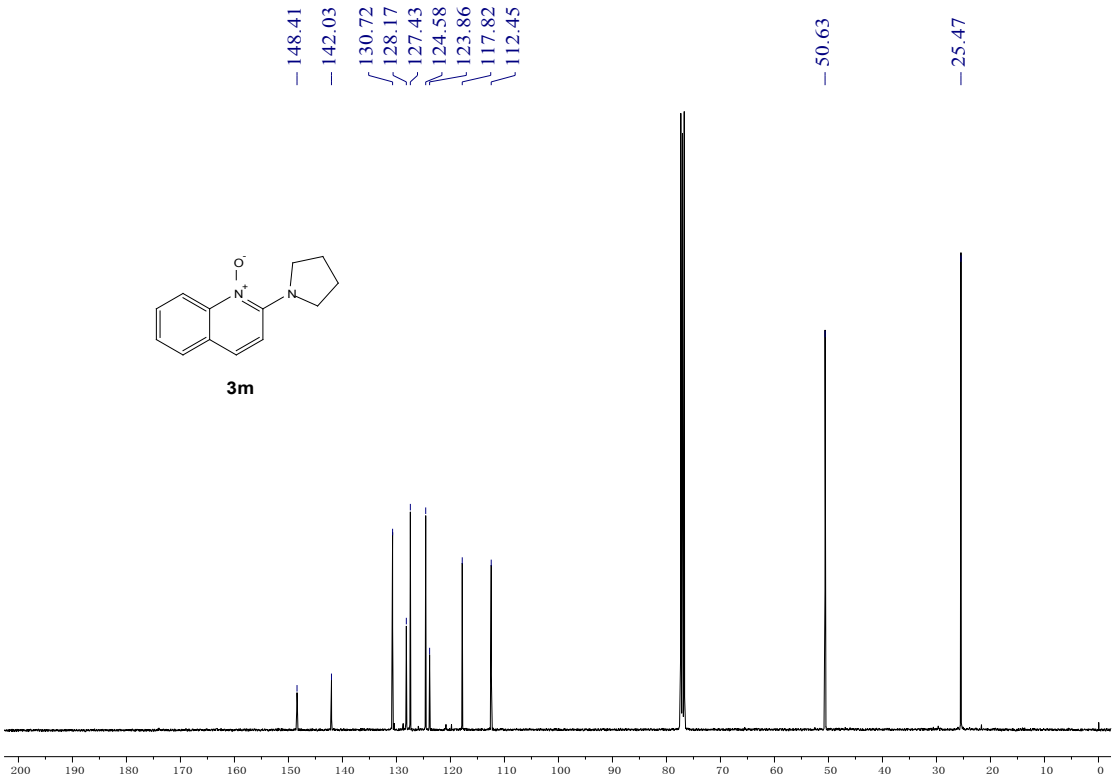

CH3
3l
1.00
2.85
1.01
0.98
1.95
1.99
2.09
0.96
2.19
2.92


151.25
142.33
130.50
127.58
126.74
125.70
125.39
118.72
114.28
48.23
34.08
31.00
21.91
CH3
O
N+
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

3l

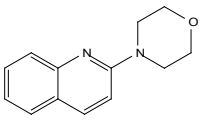

8.60
8.58
7.70
7.69
7.68
7.67
7.66
7.62
7.60
7.40
7.38
6.95
6.93
3.94
2.00
O
N+
N
1.00
3.10
1.01
1.03
3.98
4.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

3m

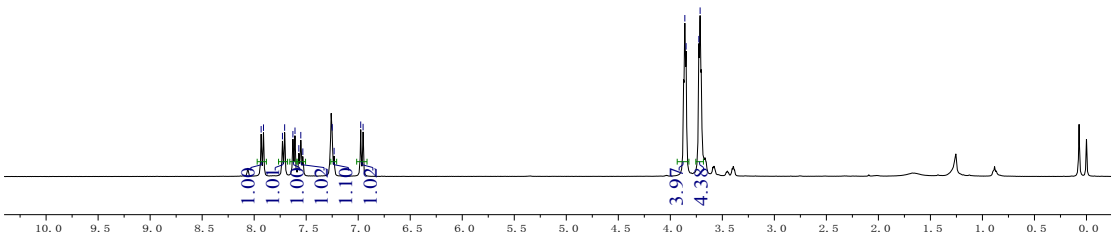

148.41
142.03
130.72
128.17
127.43
124.58
123.86
117.82
112.45
50.63
25.47
O
N
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

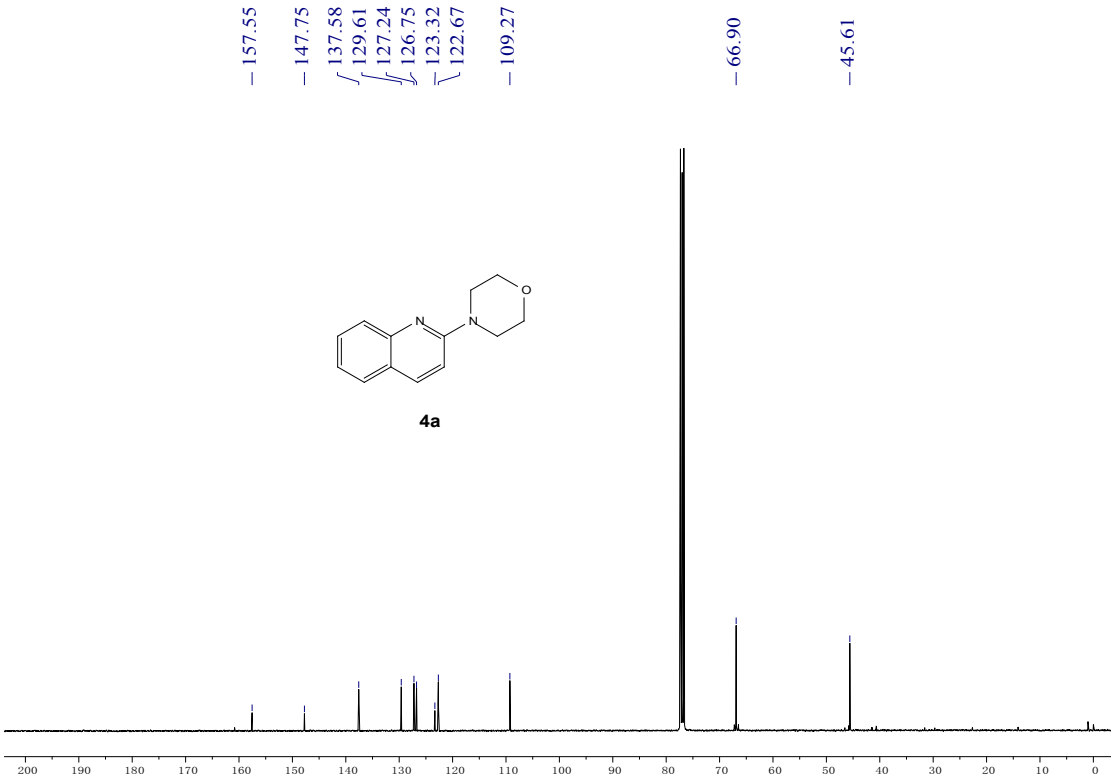
3m


7.93
7.91
7.73
7.71
7.63
7.61
7.57
7.55
7.53
7.25
7.23
6.98
6.95
3.86
3.85
3.73
3.71

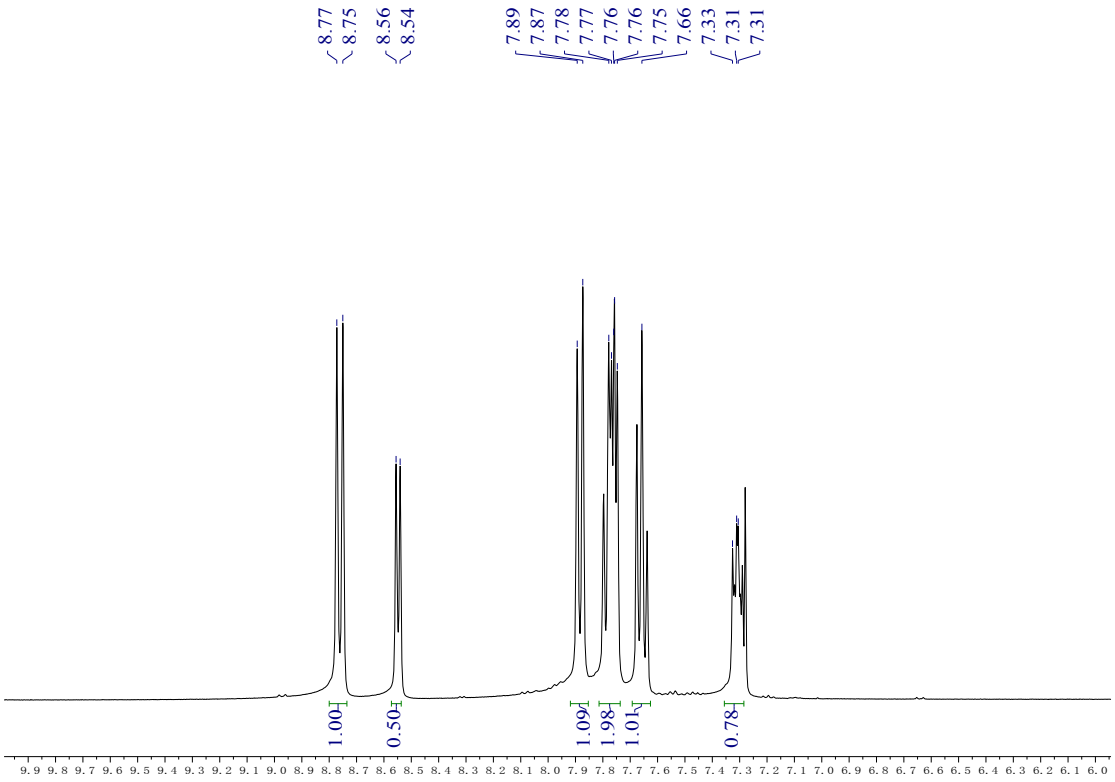

N
O
N

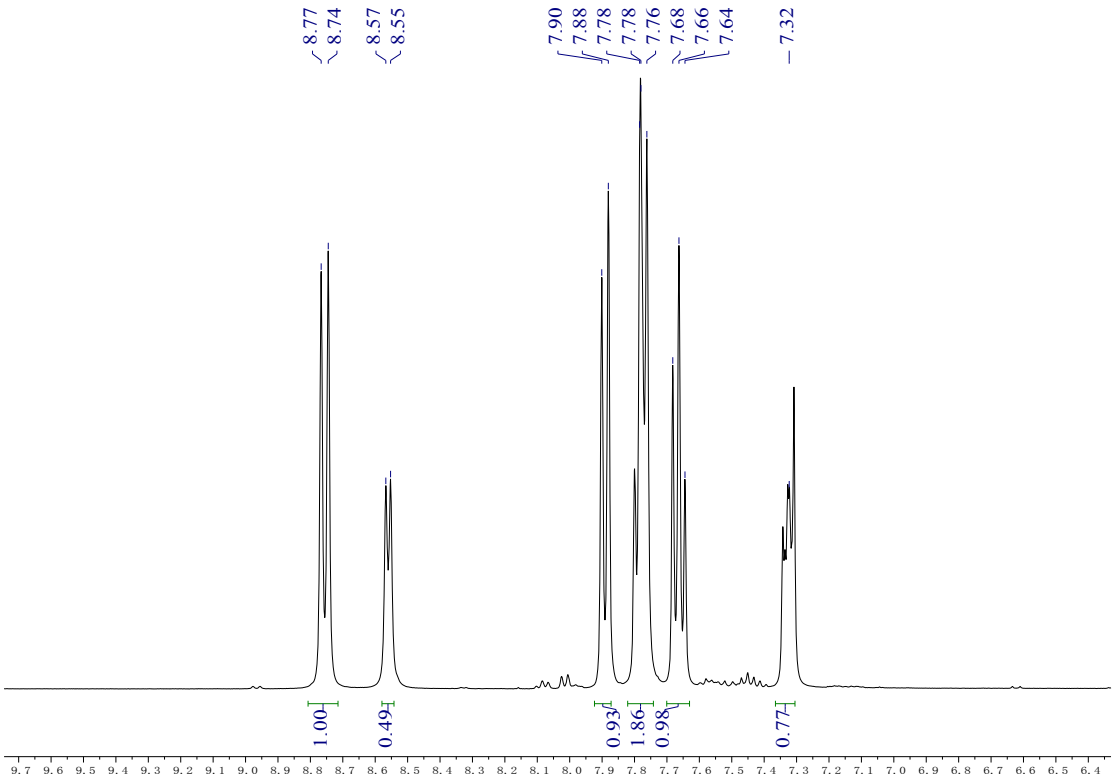
4a


1.09
1.05
1.06
1.02
1.10
1.02
3.97
4.32
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


157.55
147.75
137.58
129.61
127.24
126.75
123.32
122.67
109.27
66.90
45.61
N
N
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

4a


8.77
8.75
8.56
8.54
7.89
7.87
7.78
7.77
7.76
7.76
7.75
7.66
7.33
7.31
7.31
1.00
0.50
1.09
1.98
1.01
0.78
9.9 9.8 9.7 9.6 9.5 9.4 9.3 9.2 9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0


8.77
8.74
8.57
8.55
7.90
7.88
7.78
7.78
7.76
7.68
7.66
7.64
7.32
1.00
0.49
0.93
1.86
0.98
0.77
9.7 9.6 9.5 9.4 9.3 9.2 9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4