

# *Supporting Information*

## **Regioselective Introduction of Heteroatoms at the C-8 Position of Quinoline *N*-Oxides: Remote C–H Activation Using *N*-Oxide as a Stepping Stone**

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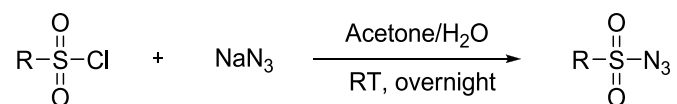
## I. General Methods

Unless otherwise stated, all commercial reagents and solvents were used without additional purification. Analytical thin layer chromatography (TLC) was performed on Merck pre-coated silica gel 60 F<sub>254</sub> plates. Visualization on TLC was achieved by the use of UV light (254 nm), exposure to iodine vapor, or treatment with acidic anisaldehyde or phosphomolybdic acid, ninhydrin or ceric ammonium molybdate stain followed by heating. Column chromatography was undertaken on silica gel (400-630 mesh) using a proper eluent system. <sup>1</sup>H NMR was recorded on Agilent Technologies DD2 (600 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br (broad), s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), td (triplet of doublet), ddd (doublet of doublet of doublet), m (multiplet). Coupling constants, *J*, were reported in hertz unit (Hz). <sup>13</sup>C NMR was recorded on Agilent Technologies DD2 (150 MHz) and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center of a triplet at 77.0 ppm of chloroform-*d*. Infrared (IR) spectra were recorded on Bruker Alpha FT-IR Spectrometer. Frequencies are given in reciprocal centimeters (cm<sup>-1</sup>) and only selected absorbance is reported. High resolution mass spectra were obtained from the Korea Basic Science Institute (Daegu) by using EI or FAB method. Quinoline *N*-oxide hydrate was purchased from TCI and its water content was analyzed by Karl Fischer titration to calculate exact yield based on active quinoline *N*-oxide before use. Dichloro(η<sup>5</sup>-pentamethylcyclopentadienyl)iridium(III) dimer (98%) was purchased from Strem Chemicals Co., Ltd. All solvents, other reagents or catalysts were directly used from purchased without further purification unless otherwise specified.

## II. Experimental Procedures for the Preparation of Starting Materials

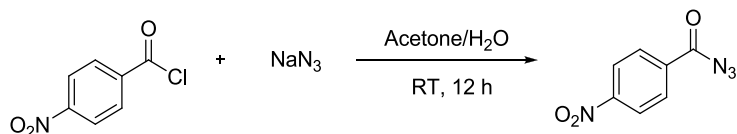
### 1. Preparation of Organic Azides

#### 1.1. General Procedure for the Preparation of Sulfonyl Azides<sup>1</sup>



To a solution of sodium azide (1.95 g, 30.0 mmol) in water (10 mL) was added dropwise a solution of sulfonyl chloride (20.0 mmol) in acetone (20 mL) at 0 °C. The reaction mixture was warmed up to room temperature and stirred for 11 h. Acetone was removed under reduced pressure and the reaction mixture was extracted with EtOAc (30 mL x 3). The combined organic layers were dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure. The crude product was used without further purification.

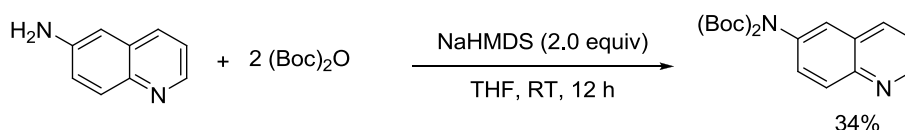
## 1.2. Preparation of 4-Nitrobenzoyl Azide<sup>2</sup>



A solution of 4-nitrobenzoyl chloride (928 mg, 5.0 mmol) in dry acetone (2.5 mL) was added dropwise over 1 h to a stirred solution of sodium azide (523 mg, 8.1 mmol) in water (2.5 mL) at 0 °C. A solid precipitated immediately. The suspension was stirred for additional 30 min before water (2.5 mL) was added and then stirring was continued for 30 min. The solid was collected, washed with water and air-dried to yield desired product as colourless crystal (859 mg, 90%)

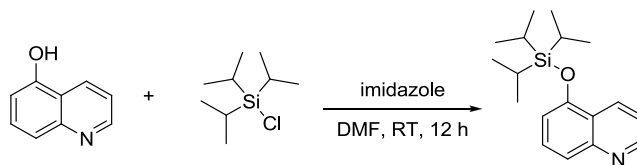
## 2. Preparation of Substituted Quinolines

### 2.1. 6-[Bis(*tert*-butoxycarbonyl)amino]quinoline



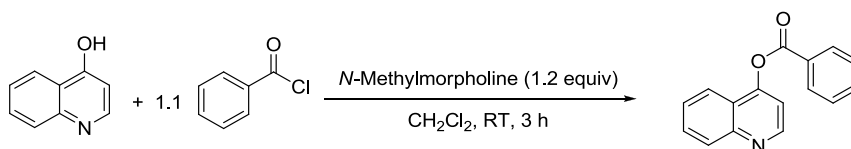
A solution of 6-aminoquinoline (360 mg, 2.5 mmol) in THF (3 mL) was added dropwise to a 1.9 M THF solution of NaHMDS (2.67 mL, 5.0 mmol) at room temperature. After 30 min, di-*tert*-butyl dicarbonate (1091 mg, 5.0 mmol) in THF (2 mL) was added at room temperature. The suspension was stirred for 12 h. The reaction mixture was quenched by water (10 mL) and poured into a saturated aqueous solution of NaHCO<sub>3</sub> (50 mL). The aqueous phase was extracted with ethyl acetate (30 mL x 3), dried over MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (EtOAc/*n*-hexane, 2:1) as a white solid of 6-[bis(*tert*-butoxycarbonyl)amino]quinoline (294 mg, 34%); m.p. 148~149 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.93 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.9 Hz, 1H), 7.61 (d, *J* = 2.3 Hz, 1H), 7.50 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.42 (dd, *J* = 8.3, 4.2 Hz, 1H), 1.42 (s, 18H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 151.7, 150.8, 147.2, 137.3, 136.0, 130.1, 130.0, 128.1, 126.0, 121.3, 83.1, 27.9; IR (diamond) 2979, 2934, 1748, 1712, 1367, 1273, 1249, 1151, 1097, 858 cm<sup>-1</sup>; HRMS (EI) *m/z* calcd. for C<sub>19</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub> [M]<sup>+</sup>: 344.1736, found: 344.1738.

## 2.2. 5-(Triisopropylsilyloxy)quinoline



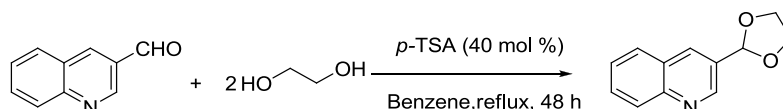
To a solution of 5-hydroxyquinoline (218 mg, 1.5 mmol) in DMF (10 mL) was added imidazole (129 mg, 3.75 equiv) followed by triisopropylsilyl chloride (434 mg, 1.5 equiv). After stirring the reaction mixture overnight at room temperature, water (20 mL) was added to the reaction solution, and the mixture was then extracted with dichloromethane (20 mL x 3). The solution was dried over  $\text{MgSO}_4$  and evaporated. The residue was purified by a silica gel column chromatography (EtOAc/*n*-hexane, 1:5) as colorless oil (409 mg, 90%);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.93 – 8.86 (m, 1H), 8.58 (d,  $J$  = 8.4 Hz, 1H), 7.71 (d,  $J$  = 8.5 Hz, 1H), 7.54 (t,  $J$  = 8.1 Hz, 1H), 7.42–7.33 (m, 1H), 6.92 (d,  $J$  = 7.6 Hz, 1H), 1.46–1.36 (m, 3H), 1.15 (d,  $J$  = 7.6 Hz, 18H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  151.8, 150.5, 149.5, 131.3, 129.3, 122.9, 122.0, 120.2, 112.2, 18.0, 13.0; IR (diamond) 2943, 2865, 1466, 1393, 1269, 1085, 915, 881, 795, 676  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{18}\text{H}_{27}\text{NOSi}$   $[\text{M}]^+$ : 301.1862, found: 301.1864

## 2.3. 4-(Benzoyloxy)quinoline



To a solution of 4-quinolinol (290 mg, 2.0 mmol) and 4-methylmorpholine (243 mg, 2.4 mmol) in dichloromethane (5 mL) was added benzoyl chloride (309 mg, 2.2 mmol) at room temperature. After stirring the reaction mixture for 3 h, the reaction mixture was quenched by water (5 mL) and poured into a saturated aqueous solution of  $\text{NaHCO}_3$  (30 mL). The aqueous phase was extracted with dichloromethane (30 mL x 3), dried over  $\text{MgSO}_4$ , filtered and concentrated under reduced pressure. The residue was used for preparation of the corresponding *N*-oxide without further purification.

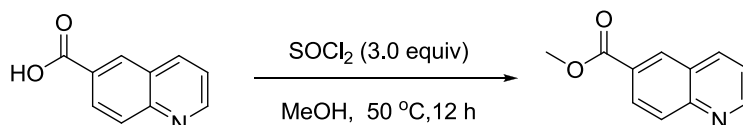
## 2.4. 3-(1,3-Dioxolan-2-yl)quinoline<sup>3</sup>



A two-neck round bottom flask equipped with Dean-Stark distillation apparatus was charged with 3-quinolinecarboxaldehyde (629 mg, 4.0 mmol) and *p*-toluenesulfonic acid monohydrate (304 mg, 0.4 equiv). Benzene (40 mL) and ethylene glycol (497 mg, 8.0 mmol) were added, and refluxed until the

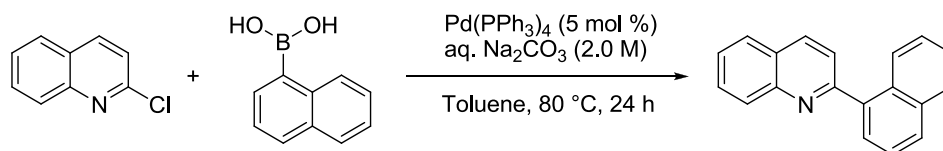
complete consumption of starting material as judged by TLC. The reaction mixture was then cooled to room temperature, evaporated under reduced pressure, and poured into saturated aqueous  $\text{NaHCO}_3$  solution. The water phase was extracted by  $\text{CH}_2\text{Cl}_2$  (20 mL x 3) and the organic phase was dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (EtOAc/*n*-hexane, 1:4) as a white solid (732 mg, 91%).

## 2.5. 6-(Methoxycarbonyl)quinoline<sup>4</sup>



Thionyl chloride (438 mg, 6.0 mmol) was added dropwise at 0 °C to a suspension of 6-quinolinecarboxylic acid (346 mg, 2.0 mmol) in MeOH (5 mL). After completion of the addition, the icebath was removed and the reaction mixture was stirred at 50 °C for 12 h. The reaction mixture was quenched by a saturated aqueous solution of  $\text{NaHCO}_3$  (30 mL). The aqueous phase was extracted with dichloromethane (30 mL x 3), dried over  $\text{MgSO}_4$ , filtered and concentrated under reduced pressure. The product was obtained as white solid (367 mg, 98%).

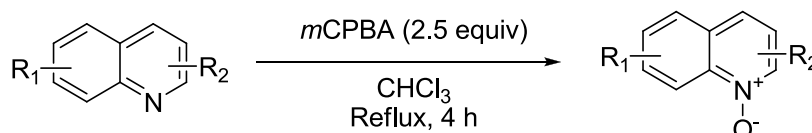
## 2.6. 2-(Naphthalen-1-yl)quinoline



To a solution of 2-chloroquinoline (818 mg, 5.0 mmol), naphthalen-1-ylboronic acid (1.29 g, 7.5 mmol), and tetrakis(triphenylphosphine)palladium (289 mg, 0.25 mmol) in toluene (25 mL) was added an aqueous solution of sodium carbonate (2.0 M, 5 mL) and stirred at 80 °C for 24 h. The reaction mixture was then cooled down, filtered through a pad of celite and silica gel, and extracted with ethyl acetate (20 mL x 3). The combined organic layer was dried over  $\text{MgSO}_4$  and the solvents were removed under reduced pressure. The crude mixture was purified by column chromatography on silica gel (*n*-hexane/EtOAc, 3:1,  $R_f = 0.5$ ) to yield the product (970 mg, 76%)

## 3. Preparation of Quinoline *N*-oxides

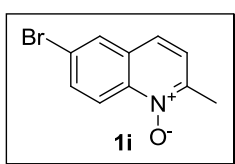
### 3.1. General Procedure for the Preparation of Quinoline *N*-oxides



*m*-Chloroperoxybenzoic acid (*m*CBPA, 2.5 equiv) was added to quinoline (3.0 mmol) in CHCl<sub>3</sub> (5 mL) and the mixture was refluxed for 4 h. After cooling down to room temperature, saturated aqueous NaHCO<sub>3</sub> solution (20 mL) were added. The aqueous layer was extracted with dichloromethane (10 mL x 3) and the combined organic extracts were dried over MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford desired *N*-oxides.

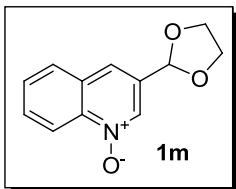
### 3.2. Spectroscopic Data of Prepared *N*-oxides

#### 6-Bromo-2-methylquinoline *N*-oxide (Table 3, 1i)



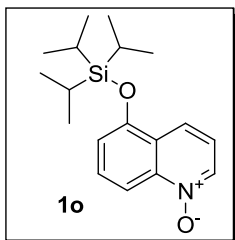
White solid; m.p. 151~152 °C: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.64 (d, *J* = 9.2 Hz, 1H), 7.97 (d, *J* = 2.0 Hz, 1H), 7.79 (dd, *J* = 9.2, 2.1 Hz, 1H), 7.53 (d, *J* = 8.6 Hz, 1H), 7.33 (d, *J* = 8.6 Hz, 1H), 2.69 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 146.0, 140.4, 133.4, 130.3, 129.9, 124.2, 123.5, 122.0, 121.6, 18.7; IR (diamond) 3034, 2981, 1557, 1326, 1243, 1186, 886, 806, 766, 644 cm<sup>-1</sup>; HRMS (EI) *m/z* calcd. for C<sub>10</sub>H<sub>8</sub>BrNO [M]<sup>+</sup>: 236.9789, found: 236.9792.

#### 3-(1,3-Dioxolan-2-yl)quinoline *N*-oxide (Table 3, 1m)



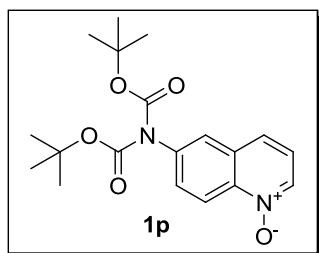
White solid; m.p. 79~80 °C: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.72 (d, *J* = 8.7 Hz, 1H), 8.66 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.81 (s, 1H), 7.76 (t, *J* = 8.8 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 5.95 (s, 1H), 4.11 (d, *J* = 20.8 Hz, 4H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 141.5, 134.2, 132.7, 130.7, 129.8, 129.0, 128.5, 123.7, 119.7, 101.0, 65.5; IR (diamond) 3059, 2957, 2886, 1579, 1364, 1212, 1079, 997, 852, 767 cm<sup>-1</sup>; HRMS (EI) *m/z* calcd. for C<sub>12</sub>H<sub>11</sub>NO<sub>3</sub> [M]<sup>+</sup>: 217.0739, found: 217.0738.

#### 5-(Triisopropylsilyloxy)quinoline *N*-oxide (Table 3, 1o)



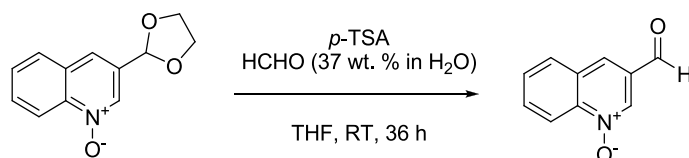
Yellow solid; m.p. 63~65 °C: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.52 (d, *J* = 5.9 Hz, 1H), 8.32 (d, *J* = 8.9 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 8.2 Hz, 1H), 7.29–7.21 (m, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 1.49–1.32 (m, 3H), 1.15 (d, *J* = 7.5 Hz, 18H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 152.5, 142.9, 135.8, 130.4, 125.5, 121.2, 119.6, 114.5, 112.0, 18.0, 12.9; IR (diamond) 3081, 2944, 2866, 1510, 1401, 1291, 980, 882, 786, 688 cm<sup>-1</sup>; HRMS (EI) *m/z* calcd. for C<sub>18</sub>H<sub>27</sub>NO<sub>2</sub>Si [M]<sup>+</sup>: 317.1811, Found: 317.1811.

### 6-[Bis(*tert*-butoxycarbonyl)amino]quinoline *N*-oxide (Table 3, 1p)



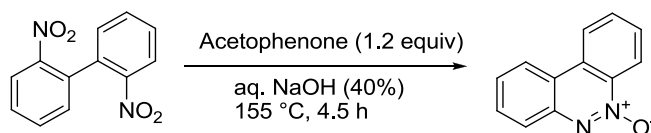
White solid; m.p. 188~189 °C:  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.76 (d,  $J = 9.2$  Hz, 1H), 8.54 (d,  $J = 6.0$  Hz, 1H), 7.73 (d,  $J = 8.5$  Hz, 1H), 7.69 (s, 1H), 7.55 (d,  $J = 9.5$  Hz, 1H), 7.41–7.25 (m, 1H), 1.43 (s, 18H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  151.2, 140.4, 139.6, 135.8, 130.8, 130.6, 126.4, 125.6, 121.6, 120.7, 83.5, 27.8; IR (diamond) 2979, 2935, 1750, 1571, 1369, 1275, 1153, 1115, 847, 749  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_5$   $[\text{M}]^+$ : 360.1685, found: 360.1683.

### 3.3. Preparation of 3-Formylquinoline *N*-oxide (Table 3, 1q)



To a solution of 3-(1,3-dioxolan-2-yl)quinoline *N*-oxide (152 mg, 0.7 mmol, **1m**) in THF (3 mL) was added formaldehyde (1.5 mL, 37 wt. % in water) and *p*-toluenesulfonic acid monohydrate (133 mg, 0.7 mmol). The resulting mixture was stirred at room temperature for 36 h. The solution was quenched with saturated  $\text{NaHCO}_3$  solution (20 mL) and then extracted with dichloromethane (20 mL x 3). The solution was dried over  $\text{MgSO}_4$  and evaporated. The residue was purified by a silica gel column chromatography (EtOAc/*n*-hexane, 3:1) as light yellow solid (96 mg, 80%); m.p. 205~206 °C:  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  10.09 (s, 1H), 8.92 (s, 1H), 8.80 (d,  $J = 8.7$  Hz, 1H), 8.20 (s, 1H), 8.07 (d,  $J = 8.1$  Hz, 1H), 7.93 (t,  $J = 7.9$  Hz, 1H), 7.78 (t,  $J = 7.6$  Hz, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  188.1, 143.9, 133.2, 132.9, 130.1, 129.9, 129.9, 129.3, 129.1, 120.3; IR (diamond) 3008, 2861, 1692, 1576, 1357, 1331, 1219, 993, 775, 573  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{10}\text{H}_7\text{NO}_2$   $[\text{M}]^+$ : 173.0477, found: 173.0476.

### 3.4. Preparation of benzo[*c*]cinnoline *N*-oxide (Table 5, 7e)<sup>5</sup>



To a suspension of 2,2'-dinitrobiphenyl (244 mg, 1.0 mmol) in 40% NaOH (25 mL) was added acetophenone (144 mg, 1.2 mmol) and refluxed at 155 °C for 4.5 h. The reaction mixture was then cooled down, slowly diluted with  $\text{H}_2\text{O}$  (100 mL) and EtOAc (50 mL), filtered through a celite cake to remove black tar, and extracted with EtOAc (20 mL x 3). The combined organic layer was dried over

Na<sub>2</sub>SO<sub>4</sub> and the solvents were removed under reduced pressure. The crude mixture was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/acetone, 30:1, R<sub>f</sub> = 0.5) to obtain the product (186 mg, 95%).

### III. Experimental Procedure for the Rh-Catalyzed Halogenation

#### 1. Optimization Table for the Rh-Catalyzed Iodination of Quinoline *N*-oxides

To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added 6-methyl quinoline *N*-oxide (0.1 mmol), halogen source (0.15 mmol), catalyst, additive, and 1,2-dichloroethane (0.5 mL) under atmospheric conditions. The reaction mixture was stirred at the indicated temperature for 12 h, filtered through a pad of celite and then washed with 1:1 mixture of acetone and methylene chloride (10 mL x 3). Organic solvents were removed under reduced pressure and the crude yield was measured by <sup>1</sup>H NMR spectrum using an internal standard (1,1,2,2-tetrachloroethane).

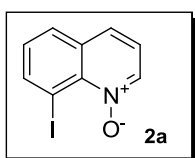
Entry	Catalyst (mol %)	Halogen Source (equiv)	Solvent	T (°C)	Yield (%)
1	-	NCS (1.1)	1,2-DCE	50	0
2	-	NBS (1.1)	1,2-DCE	50	0
3	-	NIS (1.1)	1,2-DCE	50	0
5	[RhCp*Cl <sub>2</sub> ] <sub>2</sub> (4) / AgNTf <sub>2</sub> (16)	NBS (1.1)	1,2-DCE	50	<10
6	[IrCp*Cl <sub>2</sub> ] <sub>2</sub> (4) / AgNTf <sub>2</sub> (16)	NBS (1.1)	1,2-DCE	50	0
7	Ru <sub>3</sub> (CO) <sub>12</sub> (33)	NBS (1.1)	1,2-DCE	50	0
4	[Ru(p-cymene)Cl <sub>2</sub> ] <sub>2</sub> (4) / AgNTf <sub>2</sub> (16)	NBS (1.1)	1,2-DCE	50	0
12	[RhCp*Cl <sub>2</sub> ] <sub>2</sub> (4) / AgNTf <sub>2</sub> (16)	NCS (1.1)	1,2-DCE	50	20
11	[RhCp*Cl <sub>2</sub> ] <sub>2</sub> (4) / AgNTf <sub>2</sub> (16)	NIS (1.1)	1,2-DCE	50	62
<b>16</b>	<b>[RhCp*Cl<sub>2</sub>]<sub>2</sub> (4) / AgNTf<sub>2</sub> (16)</b>	<b>NIS (1.5)</b>	<b>1,2-DCE</b>	<b>50</b>	<b>77</b>
17	[RhCp*Cl <sub>2</sub> ] <sub>2</sub> (4) / AgNTf <sub>2</sub> (16)	NIS (1.5)	1,2-DCE	rt	53
18	[RhCp*Cl <sub>2</sub> ] <sub>2</sub> (4) / AgNTf <sub>2</sub> (16)	I <sub>2</sub> (0.55) / PhI(OAc) <sub>2</sub> (0.55)	1,2-DCE	50	25
19	[RhCp*Cl <sub>2</sub> ] <sub>2</sub> (4) / AgNTf <sub>2</sub> (16)	I <sub>2</sub> (0.55)	1,2-DCE	50	0
20	[RhCp*Cl <sub>2</sub> ] <sub>2</sub> (4) / AgNTf <sub>2</sub> (16)	NIS (1.5)	DMF	50	0
21	[RhCp*Cl <sub>2</sub> ] <sub>2</sub> (4) / AgNTf <sub>2</sub> (16)	NIS (1.5)	NMP	50	0
22	[RhCp*Cl <sub>2</sub> ] <sub>2</sub> (4) / AgNTf <sub>2</sub> (16)	NIS (1.5)	1,4-dioxane	50	19
23	[RhCp*Cl <sub>2</sub> ] <sub>2</sub> (4) / AgNTf <sub>2</sub> (16)	NIS (1.5)	THF	50	0
24	[RhCp*Cl <sub>2</sub> ] <sub>2</sub> (4) / AgNTf <sub>2</sub> (16)	NIS (1.5)	Acetone	50	<10
25	[RhCp*Cl <sub>2</sub> ] <sub>2</sub> (4) / AgNTf <sub>2</sub> (16)	NIS (1.5)	CH <sub>3</sub> CN	50	0
26	[RhCp*Cl <sub>2</sub> ] <sub>2</sub> (4) / AgNTf <sub>2</sub> (16)	NIS (1.5)	DME	50	36
27	[RhCp*Cl <sub>2</sub> ] <sub>2</sub> (4) / AgNTf <sub>2</sub> (16)	NIS (1.5)	EtOAc	50	39
28	[RhCp*Cl <sub>2</sub> ] <sub>2</sub> (4) / AgNTf <sub>2</sub> (16)	NIS (1.5)	MeOH	50	15

## 2. General Procedure for the Rh-Catalyzed Iodination of Quinoline *N*-oxides

To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added quinoline *N*-oxide (0.1 mmol), *N*-iodosuccinimide (0.15 mmol), [RhCp\*Cl<sub>2</sub>]<sub>2</sub> (2.5 mg, 0.004 mmol, 4.0 mol %), AgNTf<sub>2</sub> (6.2 mg, 0.016 mmol, 8.0 mol %) and 1,2-dichloroethane (0.5 mL) under atmospheric conditions. The reaction mixture was stirred at 50 °C for 12 h, filtered through a pad of celite and then washed with 1:1 mixture of acetone and methylene chloride (10 mL x 3). Organic solvents were removed under reduced pressure and the residue was purified by chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/Acetone) to give the desired product.

## 3. Spectroscopic data of Iodinated products obtained in this study

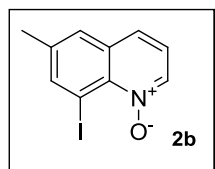
### 8-Iodoquinoline *N*-oxide (Table 1, 2a)



White solid; m.p. 158 – 160 °C; <sup>1</sup>H NMR (600 MHz, Acetone-*d*<sub>6</sub>) δ 8.45 (d, *J* = 6.1 Hz, 1H), 8.39 (dd, *J* = 7.4, 1.2 Hz, 1H), 8.01 (d, *J* = 8.9 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.44 (dd, *J* = 8.4, 6.1 Hz, 1H), 7.31 – 7.26 (m, 1H); <sup>13</sup>C NMR (150 MHz, Acetone-*d*<sub>6</sub>) δ 145.6, 139.2, 136.6, 132.5, 129.9, 129.4, 126.4, 122.0, 79.9;

IR (diamond) 3085, 3061, 1656, 1547, 1413, 1345, 1180, 568, 511 cm<sup>-1</sup>; HRMS (EI) *m/z* calcd. for C<sub>9</sub>H<sub>6</sub>INO [M]<sup>+</sup>: 270.9494, found: 270.9492.

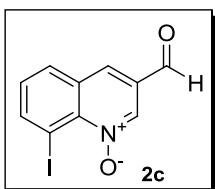
### 8-Iodo-6-methylquinoline *N*-oxide (Table 1, 2b)



White solid; m.p. 145 – 147 °C; <sup>1</sup>H NMR (600 MHz, Acetone-*d*<sub>6</sub>) δ 8.36 (dd, *J* = 6.1, 0.8 Hz, 1H), 8.24 (d, *J* = 1.8 Hz, 1H), 7.76 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.39 (dd, *J* = 8.4, 6.1 Hz, 1H), 2.44 (s, 3H); <sup>13</sup>C NMR (150 MHz, Acetone-*d*<sub>6</sub>) δ 146.88, 146.86, 139.6, 135.3, 132.3, 128.7, 124.5, 122.0, 80.0, 19.4; IR

(diamond) 3083, 1553, 1430, 1362, 731, 595, 500 cm<sup>-1</sup>; HRMS (EI) *m/z* calcd. for C<sub>10</sub>H<sub>8</sub>INO [M]<sup>+</sup>: 284.9651, found: 284.9650.

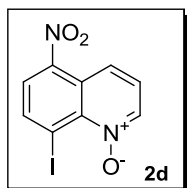
### 3-Formyl-8-iodoquinoline *N*-oxide (Table 1, 2c)



Yellow solid; m.p. 174 – 176 °C; <sup>1</sup>H NMR (600 MHz, Acetone-*d*<sub>6</sub>) δ 10.12 (s, 1H), 8.74 (s, 1H), 8.57 (d, *J* = 7.4 Hz, 1H), 8.43 (s, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 7.47 – 7.43 (m, 1H); <sup>13</sup>C NMR (150 MHz, Acetone-*d*<sub>6</sub>) δ 189.1, 147.8, 133.1, 131.7, 131.6, 130.5, 130.3, 128.1, 80.7; IR (diamond) 3062, 3043, 1693, 1360,

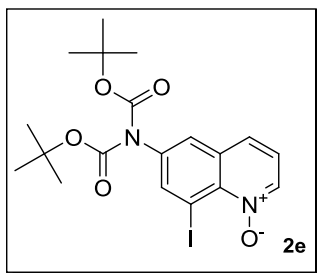
1240, 582, 553, 474 cm<sup>-1</sup>; HRMS (EI) *m/z* calcd. for C<sub>10</sub>H<sub>6</sub>INO<sub>2</sub> [M]<sup>+</sup>: 298.9443, found: 298.9447.

### 8-Iodo-5-nitroquinoline *N*-oxide (Table 1, 2d)



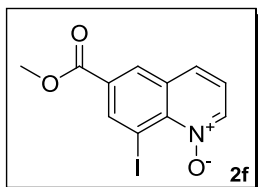
Red solid; m.p. 197 – 199 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.67 (d,  $J = 6.1$  Hz, 1H), 8.53 (d,  $J = 8.2$  Hz, 1H), 8.19 (d,  $J = 9.0$  Hz, 1H), 7.98 (d,  $J = 8.2$  Hz, 1H), 7.65 (dd,  $J = 8.9, 6.2$  Hz, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ )  $\delta$  147.0, 143.9, 140.0, 137.5, 126.3, 125.1, 124.5, 120.1, 91.8; IR (diamond) 1600, 1542, 1500, 1388, 1318, 1271, 1239, 1104, 898, 733, 623, 528  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_9\text{H}_5\text{IN}_2\text{O}_3$   $[\text{M}]^+$ : 315.9345, found: 315.9342.

### 6-[Bis(*tert*-butoxycarbonyl)amino]-8-iodoquinoline *N*-oxide (Table 1, 2e)



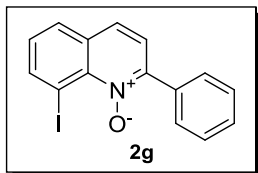
Yellow solid; m.p. 154 – 156 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.56 (d,  $J = 5.8$  Hz, 1H), 8.21 (d,  $J = 2.1$  Hz, 1H), 7.74 (d,  $J = 8.3$  Hz, 1H), 7.63 (d,  $J = 2.0$  Hz, 1H), 7.34 (dd,  $J = 8.2, 6.2$  Hz, 1H), 1.44 (s, 18H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  150.9, 146.1, 139.2, 138.1, 137.3, 131.6, 127.7, 127.3, 121.8, 84.0, 80.0, 27.9; IR (diamond) 3078, 2976, 2934, 1791, 1738, 1706, 1365, 1269, 615, 421  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{23}\text{IN}_2\text{O}_5$   $[\text{M}]^+$ : 486.0652, found: 486.0648.

### 8-Iodo-6-(methoxycarbonyl)quinoline *N*-oxide (Table 1, 2f)



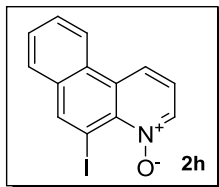
Yellow solid; m.p. 153 – 155 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.91 (d,  $J = 1.4$  Hz, 1H), 8.57 (d,  $J = 6.0$  Hz, 1H), 8.50 (d,  $J = 1.8$  Hz, 1H), 7.81 (d,  $J = 8.4$  Hz, 1H), 7.36 (dd,  $J = 8.3, 6.2$  Hz, 1H), 3.98 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  164.3, 144.9, 141.0, 138.3, 131.7, 131.4, 130.6, 127.8, 122.1, 81.0, 52.9; IR (diamond) 3037, 1720, 1439, 1279, 636, 502, 488  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{11}\text{H}_8\text{INO}_3$   $[\text{M}]^+$ : 328.9549, found: 328.9548.

### 8-Iodo-2-phenylquinoline *N*-oxide (Table 1, 2g)



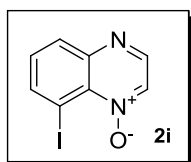
Yellow solid; m.p. 161 – 163 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.45 (dd,  $J = 7.5, 1.2$  Hz, 1H), 7.89 (d,  $J = 7.1$  Hz, 2H), 7.80 (d,  $J = 8.0$  Hz, 1H), 7.69 (d,  $J = 8.5$  Hz, 1H), 7.52 – 7.47 (m, 3H), 7.47 – 7.41 (m, 1H), 7.20 – 7.15 (m, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{Acetone-}d_6$ )  $\delta$  145.6, 144.7, 140.0, 134.0, 131.6, 129.7, 129.5, 129.2, 129.1, 127.9, 124.2, 123.9, 80.8; IR (diamond) 3010, 2959, 2921, 2852, 1608, 1406, 1216, 615, 448  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{15}\text{H}_{10}\text{INO}$   $[\text{M}]^+$ : 346.9807, found: 346.9805.

### 5-Iodobenzo[*f*]quinoline *N*-oxide (Table 1, 2h)



Yellow solid; m.p. 151 – 153 °C; <sup>1</sup>H NMR (600 MHz, Acetone-*d*<sub>6</sub>) δ 8.82 (s, 1H), 8.77 – 8.72 (m, 2H), 8.54 (d, *J* = 6.1 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.83 – 7.78 (m, 1H), 7.78 – 7.74 (m, 1H), 7.66 (dd, *J* = 8.5, 6.3 Hz, 1H); <sup>13</sup>C NMR (150 MHz, Acetone-*d*<sub>6</sub>) δ 146.0, 137.6, 137.0, 133.0, 129.8, 129.1, 129.0, 128.6, 127.9, 123.7, 122.5, 119.4, 76.3; IR (diamond) 3044, 1656, 1422, 1249, 482, 438 cm<sup>-1</sup>; HRMS (EI) *m/z* calcd. for C<sub>13</sub>H<sub>8</sub>INO [M]<sup>+</sup>: 320.9651, found: 320.9648.

### 8-Iodoquinoxaline *N*-oxide (Table 1, 2i)



Yellow solid; m.p. 169 – 171 °C; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ 8.76 (d, *J* = 3.6 Hz, 1H), 8.56 (d, *J* = 3.6 Hz, 1H), 8.37 (d, *J* = 7.5 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 7.54 – 7.45 (m, 1H); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>) δ 147.1, 146.9, 144.9, 135.9, 133.0, 131.4, 130.3, 81.2; IR (diamond) 2921, 2852, 1532, 1491, 1366, 1331, 1307, 833, 800, 753, 543, 495 cm<sup>-1</sup>; HRMS (EI) *m/z* calcd. for C<sub>10</sub>H<sub>8</sub>INO<sub>2</sub> [M]<sup>+</sup>: 271.9447, found: 271.9445.

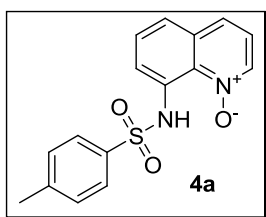
## IV. Experimental Procedure for the Ir-Catalyzed Amidation

### 1. General Procedure for the Ir-Catalyzed Amidation of Quinoline *N*-oxides with Azides

To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added quinoline *N*-oxide (0.2 mmol), azide (0.22 mmol), [IrCp\*Cl<sub>2</sub>]<sub>2</sub> (3.2 mg, 0.004 mmol, 2.0 mol %), AgNTf<sub>2</sub> (6.2 mg, 0.016 mmol, 8.0 mol %), AcOH (3.6 mg, 0.06 mmol, 30.0 mol %) and 1,2-dichloroethane (0.5 mL) under atmospheric conditions. The reaction mixture was stirred at 50 °C for 12 h, filtered through a pad of celite and then washed with dichloromethane (10 mL x 3). Organic solvents were removed under reduced pressure and the residue was purified by chromatography on silica gel (*n*-hexane/EtOAc) to give the desired product.

### 2. Spectroscopic data of amidated products obtained in this study

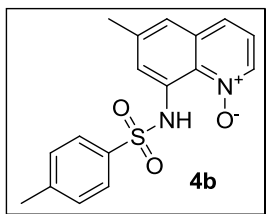
#### 8-(4-Methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4a)



Yellow solid; m.p. 171~173 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 14.40 (s, 1H), 8.28 (d, *J* = 4.9 Hz, 1H), 7.86 – 7.79 (m, 3H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.40 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.23 (dd, *J* = 8.4, 6.1 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 2.32 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 143.6, 137.0, 136.7, 133.8, 132.4, 131.1, 129.5, 129.1, 128.9, 127.3, 122.2, 120.9, 117.9, 21.5; IR (diamond) 3083, 2869, 1394, 1319, 1160, 1090, 817, 750, 654, 562 cm<sup>-1</sup>;

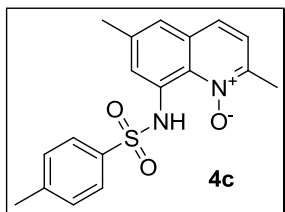
HRMS (EI)  $m/z$  calcd. for  $C_{16}H_{14}N_2O_3S$   $[M]^+$ : 314.0725, found: 314.0722.

### 6-Methyl-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4b)



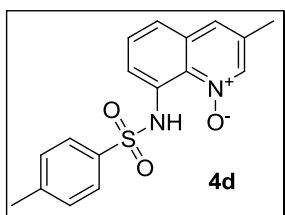
Pale brown solid; m.p 159~161 °C;  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  14.34 (s, 1H), 8.21 (dd,  $J = 6.1, 1.2$  Hz, 1H), 7.83 (d,  $J = 8.3$  Hz, 2H), 7.69 (d,  $J = 1.8$  Hz, 1H), 7.60 (d,  $J = 9.2$  Hz, 1H), 7.24–7.12 (m, 4H), 2.43 (s, 3H), 2.32 (s, 3H);  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  143.6, 139.7, 136.7, 136.2, 133.2, 132.4, 129.6, 129.5, 128.5, 127.3, 121.5, 120.9, 119.7, 21.7, 21.4; IR (diamond) 3067, 2920, 1584, 1394, 1329, 1160, 1091, 750, 668, 573  $cm^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $C_{17}H_{16}N_2O_3S$   $[M]^+$ : 328.0882, found: 328.0879.

### 2,6-Dimethyl-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4c)



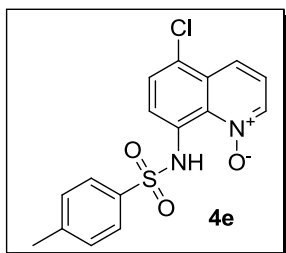
Light yellow solid; m.p 205~207 °C;  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  14.72 (s, 1H), 7.82 (d,  $J = 7.9$  Hz, 2H), 7.63 (s, 1H), 7.48 (d,  $J = 8.6$  Hz, 1H), 7.21–7.15 (m, 3H), 7.12 (s, 1H), 2.57 (s, 3H), 2.40 (s, 3H), 2.32 (s, 3H);  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  146.1, 143.3, 138.6, 137.0, 133.1, 131.1, 129.7, 129.4, 127.4, 127.3, 123.0, 121.4, 119.7, 21.5, 21.4, 18.6; IR (diamond) 3046, 2919, 1604, 1357, 1163, 1090, 764, 665, 573, 546  $cm^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $C_{18}H_{18}N_2O_3S$   $[M]^+$ : 342.1038, found: 342.1036.

### 3-Methyl-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4d)



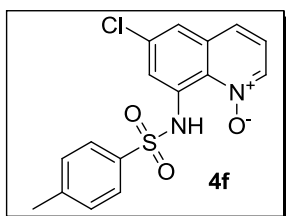
Light brown solid; m.p 181~183 °C;  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  14.36 (s, 1H), 8.18 (s, 1H), 7.82 (d,  $J = 8.4$  Hz, 2H), 7.76 (d,  $J = 7.9$  Hz, 1H), 7.48 (s, 1H), 7.40 (t,  $J = 8.0$  Hz, 1H), 7.30 (d,  $J = 8.2$  Hz, 1H), 7.19 (d,  $J = 8.0$  Hz, 2H), 2.39 (s, 3H), 2.32 (s, 3H);  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  143.5, 138.2, 136.7, 133.6, 132.1, 131.3, 129.5, 129.3, 129.1, 128.4, 127.3, 121.5, 116.8, 21.5, 18.3; IR (diamond) 3063, 2926, 1590, 1328, 1285, 1156, 1094, 749, 656, 551  $cm^{-1}$ ; HRMS (EI)  $m/z$  calcd.  $C_{17}H_{16}N_2O_3S$   $[M]^+$ : 328.0882, found: 328.0885.

#### 5-Chloro-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4e)



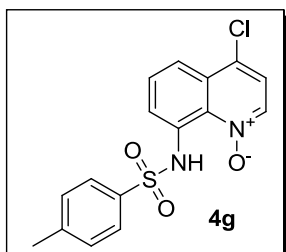
Yellow solid; m.p 186~188 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  14.29 (s, 1H), 8.35 (d,  $J = 6.0$  Hz, 1H), 8.14 (d,  $J = 8.8$  Hz, 1H), 7.88 – 7.76 (m, 3H), 7.55 (d,  $J = 8.6$  Hz, 1H), 7.35 (dd,  $J = 8.8, 6.1$  Hz, 1H), 7.21 (d,  $J = 8.0$  Hz, 2H), 2.33 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  143.8, 137.5, 136.5, 133.1, 132.0, 130.0, 129.7, 129.4, 127.3, 125.6, 125.1, 121.7, 117.4, 21.5; IR (diamond) 3083, 2733, 1576, 1455, 1386, 1346, 1159, 1090, 862, 805  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{13}\text{ClN}_2\text{O}_3\text{S}$   $[\text{M}]^+$ : 348.0335, found: 348.0333.

#### 6-Chloro-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4f)



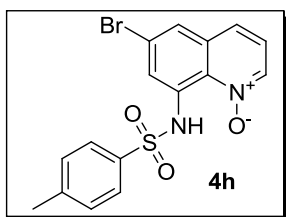
Pale yellow solid; m.p 174~176 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  14.52 (s, 1H), 8.26 (d,  $J = 6.0$  Hz, 1H), 7.84 (d,  $J = 7.9$  Hz, 2H), 7.78 (s, 1H), 7.61 (d,  $J = 8.5$  Hz, 1H), 7.35 (s, 1H), 7.29 – 7.21 (m, 3H), 2.35 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  144.1, 137.0, 136.4, 135.4, 135.2, 132.8, 129.8, 129.6, 127.9, 127.4, 122.0, 120.4, 117.3, 21.5; IR (diamond) 3077, 1575, 1383, 1321, 1160, 1091, 749, 657, 571, 544  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{13}\text{ClN}_2\text{O}_3\text{S}$   $[\text{M}]^+$ : 348.0335, found: 348.0337.

#### 4-Chloro-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4g)



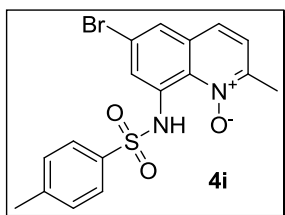
Yellow solid; m.p 189~190 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  14.39 (s, 1H), 8.21 (d,  $J = 6.6$  Hz, 1H), 7.94 (dd,  $J = 8.0, 1.2$  Hz, 1H), 7.83 (d,  $J = 8.3$  Hz, 2H), 7.78 (dd,  $J = 8.4, 1.3$  Hz, 1H), 7.57 (t,  $J = 8.2$  Hz, 1H), 7.34 (d,  $J = 6.6$  Hz, 1H), 7.21 (d,  $J = 8.1$  Hz, 2H), 2.33 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  143.8, 136.6, 136.2, 134.5, 133.1, 131.5, 130.2, 129.7, 129.7, 127.8, 121.1, 119.0, 118.7, 21.5; IR (diamond) 3087, 3005, 1382, 1315, 1161, 1090, 749, 655, 587, 561  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{13}\text{ClN}_2\text{O}_3\text{S}$   $[\text{M}]^+$ : 348.0335, found: 348.0337.

#### 6-Bromo-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4h)



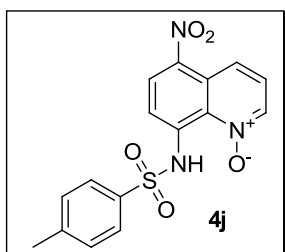
Pale yellow solid; m.p 190~192 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  14.46 (s, 1H), 8.28 (d,  $J = 6.0$  Hz, 1H), 7.93 (s, 1H), 7.85 (d,  $J = 7.9$  Hz, 2H), 7.59 (d,  $J = 8.4$  Hz, 1H), 7.53 (d,  $J = 2.1$  Hz, 1H), 7.29–7.18 (m, 3H), 2.35 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  144.0, 137.1, 136.3, 135.0, 133.1, 129.8, 129.7, 127.8, 127.4, 123.7, 123.4, 121.9, 119.9, 21.5; IR (diamond) 3070, 1574, 1379, 1320, 1160, 1090, 819, 656, 569, 545  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{13}\text{BrN}_2\text{O}_3\text{S}$   $[\text{M}]^+$ : 391.9830, found: 391.9832.

#### 6-Bromo-2-methyl-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4i)



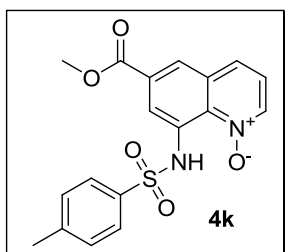
Light yellow solid; m.p 227~228 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  15.07 (s, 1H), 7.84 (d,  $J = 2.0$  Hz, 1H), 7.81 (d,  $J = 8.0$  Hz, 2H), 7.54–7.49 (m, 2H), 7.28 (d,  $J = 8.6$  Hz, 1H), 7.25 (d,  $J = 8.0$  Hz, 2H), 2.56 (s, 3H), 2.34 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  148.2, 144.5, 136.9, 135.3, 132.4, 130.4, 130.1, 127.7, 127.1, 124.7, 124.3, 122.2, 120.1, 21.6, 18.9; IR (diamond) 3065, 1594, 1355, 1325, 1163, 1089, 810, 657, 571, 544  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{17}\text{H}_{15}\text{BrN}_2\text{O}_3\text{S}$   $[\text{M}]^+$ : 405.9987, found: 405.9991.

#### 8-(4-Methylphenylsulfonamido)-5-nitroquinoline *N*-oxide (Table 3, 4j)



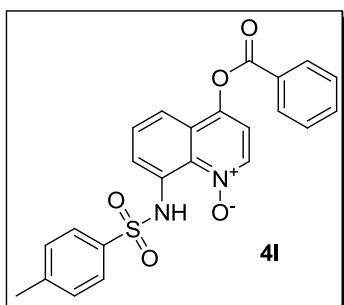
Orange solid; m.p 162~163 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  15.41 (s, 1H), 8.77 (d,  $J = 9.1$  Hz, 1H), 8.43 (d,  $J = 6.0$  Hz, 1H), 8.34 (d,  $J = 9.1$  Hz, 1H), 7.89 (d,  $J = 8.0$  Hz, 2H), 7.79 (d,  $J = 9.1$  Hz, 1H), 7.55–7.45 (m, 1H), 7.29 (d,  $J = 7.9$  Hz, 2H), 2.38 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  144.7, 140.5, 138.5, 137.8, 136.0, 130.2, 123.0, 128.7, 127.5, 126.5, 124.7, 123.9, 112.7, 21.6; IR (diamond) 3126, 3087, 1575, 1527, 1310, 1161, 1088, 808, 656, 546  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_5\text{S}$   $[\text{M}]^+$ : 359.0576, found: 359.0573.

#### 6-(Methoxycarbonyl)-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4k)



Pale yellow solid; m.p 240~242 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  14.45 (s, 1H), 8.36 (d,  $J = 6.1$  Hz, 1H), 8.30 (s, 1H), 8.12 (s, 1H), 7.85–7.79 (m, 3H), 7.32 (dd,  $J = 8.5, 6.2$  Hz, 1H), 7.23 (d,  $J = 8.0$  Hz, 2H), 3.97 (s, 3H), 2.32 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  165.6, 144.6, 139.0, 136.9, 134.8, 133.2, 132.5, 131.1, 130.2, 130.1, 127.8, 124.6, 122.4, 116.7, 53.2, 21.6; IR (diamond) 3126, 3087, 1575, 1527, 1310, 1161, 1088, 808, 656, 546  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_5\text{S}$   $[\text{M}]^+$ : 372.0780, found: 372.0782.

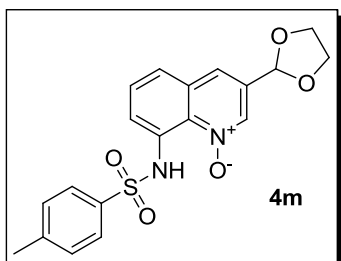
#### 4-(Benzoyloxy)-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4l)



Light yellow solid; m.p 205~207 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  13.73 (s, 1H), 8.21 (d,  $J = 7.7$  Hz, 2H), 7.82 (d,  $J = 7.9$  Hz, 2H), 7.79 (t,  $J = 7.4$  Hz, 1H), 7.67–7.54 (m, 3H), 7.47 (d,  $J = 8.1$  Hz, 1H), 7.41 (t,  $J = 8.3$  Hz, 1H), 7.22 (d,  $J = 7.9$  Hz, 2H), 6.83 (d,  $J = 8.4$  Hz, 1H), 6.20 (d,  $J = 8.1$  Hz, 1H), 2.35 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  180.8, 163.5, 143.7, 141.4, 139.8, 139.1, 136.7, 135.8, 133.9, 130.4, 129.7, 129.4, 127.3, 124.6, 113.1, 111.3, 109.1, 105.6, 21.5; IR (diamond) 3076, 2922, 2742, 1777, 1619, 1493, 1233, 1161, 992, 704  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for

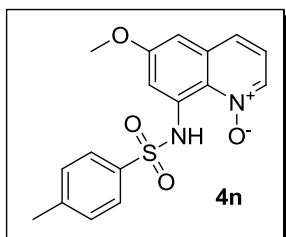
C<sub>23</sub>H<sub>18</sub>N<sub>2</sub>O<sub>5</sub>S [M]<sup>+</sup>: 434.0936, found: 434.0939.

### 3-(1,3-Dioxolan-2-yl)-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4m)



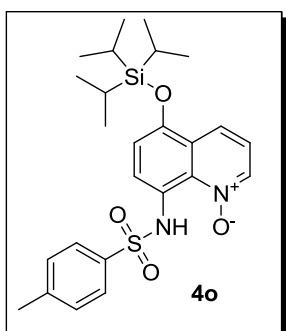
Yellow solid; m.p 159~161 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 14.33 (s, 1H), 8.40 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.75 (s, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.86 (s, 1H), 4.15–4.03 (m, 4H), 2.31 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 143.7, 136.6, 135.7, 133.8, 132.7, 131.7, 130.9, 129.6, 129.4, 127.3, 126.6, 122.7, 118.6, 100.4, 65.6, 21.5; IR (diamond) 3081, 2956, 2892, 1593, 1328, 1160, 1160, 1091, 655, 544 cm<sup>-1</sup>; HRMS (EI) *m/z* calcd. for C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>O<sub>5</sub>S [M]<sup>+</sup>: 386.0936, found: 386.0940.

### 6-Methoxy-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4n)



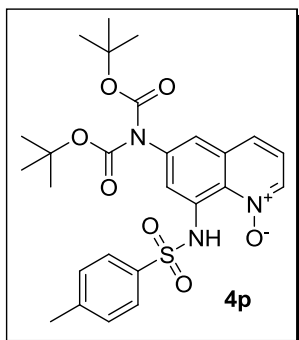
White solid; m.p 205~207 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 14.55 (s, 1H), 8.13 (d, *J* = 6.0 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 2.6 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.16 (dd, *J* = 8.5, 6.1 Hz, 1H), 6.67 (d, *J* = 2.6 Hz, 1H), 3.86 (s, 3H), 2.34 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 159.2, 143.6, 136.7, 135.2, 134.9, 133.7, 129.6, 127.9, 127.4, 127.1, 121.2, 108.7, 100.9, 55.7, 21.5; IR (diamond) 3087, 2837, 1616, 1333, 1159, 1089, 730, 669, 575, 546 cm<sup>-1</sup>; HRMS (EI) *m/z* calcd. for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>S [M]<sup>+</sup>: 344.0831, found: 344.0830

### 8-(4-Methylphenylsulfonamido)-5-(triisopropylsilyloxy)quinoline *N*-oxide (Table 3, 4o)



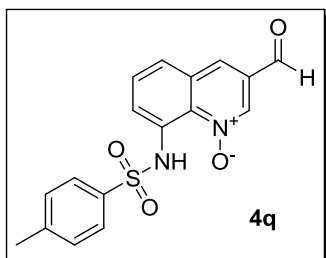
Yellow solid; m.p 136~137 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 13.53 (s, 1H), 8.25 (d, *J* = 5.5 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.18 (dd, *J* = 8.6, 6.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 1H), 2.28 (s, 3H), 1.35 (hept, *J* = 7.5 Hz, 3H), 1.10 (d, *J* = 7.5 Hz, 18H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 148.0, 143.2, 137.4, 136.7, 132.7, 129.3, 127.3, 126.4, 126.1, 123.8, 120.9, 119.8, 114.9, 21.4, 18.0, 12.9; IR (diamond) 2944, 2866, 1461, 1396, 1305, 1161, 970, 783, 654, 547 cm<sup>-1</sup>; HRMS (EI) *m/z* calcd. for C<sub>25</sub>H<sub>34</sub>N<sub>2</sub>O<sub>4</sub>SSi [M]<sup>+</sup>: 486.2009, found: 486.2011.

### 6-[Bis(*tert*-butoxycarbonyl)amino]-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4p)



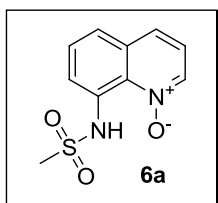
White solid; m.p 171~173 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  14.39 (s, 1H), 8.27 (d,  $J = 6.0$  Hz, 1H), 7.82 (d,  $J = 8.1$  Hz, 2H), 7.72 (d,  $J = 2.1$  Hz, 1H), 7.66 (d,  $J = 8.4$  Hz, 1H), 7.26–7.22 (m, 2H), 7.19 (d,  $J = 8.0$  Hz, 2H), 2.32 (s, 3H), 1.43 (s, 18H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  151.1, 143.7, 139.7, 137.2, 136.6, 134.5, 132.3, 130.0, 129.6, 128.8, 127.3, 121.3, 120.4, 118.0, 83.7, 27.8, 21.4; IR (diamond) 3080, 2980, 2933, 1751, 1338, 1272, 1157, 1092, 730, 537  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{26}\text{H}_{31}\text{N}_3\text{O}_7\text{S}$   $[\text{M}]^+$ : 529.1883, found: 529.1886.

### 3-Formyl-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4q)



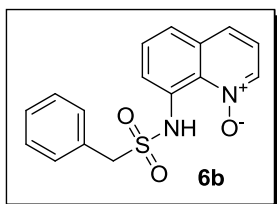
Yellow solid; m.p 188~189 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  14.15 (s, 1H), 10.00 (s, 1H), 8.65 (s, 1H), 8.16 (s, 1H), 7.97 (dd,  $J = 7.8, 1.5$  Hz, 1H), 7.79 (d,  $J = 8.5$  Hz, 2H), 7.68–7.54 (m, 2H), 7.23 (d,  $J = 7.9$  Hz, 2H), 2.32 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  187.5, 144.2, 136.4, 134.4, 134.3, 132.5, 132.0, 131.4, 130.2, 129.6, 129.6, 127.2, 124.1, 120.5, 21.2; IR (diamond) 3064, 2845, 1703, 1592, 1466, 1359, 1160, 1090, 655, 558  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_4\text{S}$   $[\text{M}]^+$ : 342.0674, found: 342.0678.

### 8-(Methylsulfonamido)quinoline *N*-oxide (Table 4, 6a)



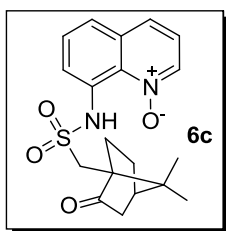
Light yellow solid; m.p 151~153 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  14.04 (s, 1H), 8.38 (d,  $J = 5.5$  Hz, 1H), 7.91 (dd,  $J = 7.8, 1.5$  Hz, 1H), 7.80 (d,  $J = 1.2$  Hz, 1H), 7.58 (t,  $J = 8.0$  Hz, 1H), 7.54 (d,  $J = 6.9$  Hz, 1H), 7.32 (dd,  $J = 8.4, 6.1$  Hz, 1H), 3.08 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  137.3, 133.9, 132.6, 131.0, 129.4, 129.2, 122.6, 121.2, 117.9, 39.5; IR (diamond) 3083, 2929, 1582, 1394, 1316, 1149, 1053, 967, 819, 749  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_3\text{S}$   $[\text{M}]^+$ : 238.0412, found: 238.0410.

### 8-(Phenylmethylsulfonamido)quinoline *N*-oxide (Table 4, 6b)



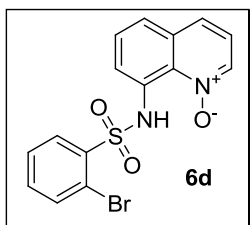
Yellow solid; m.p 123~125 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  14.09 (s, 1H), 8.26 (d,  $J = 6.0$  Hz, 1H), 7.73 (d,  $J = 8.4$  Hz, 1H), 7.65 (d,  $J = 7.4$  Hz, 1H), 7.45–7.35 (m, 2H), 7.29–7.24 (m, 1H), 7.22 (d,  $J = 7.2$  Hz, 2H), 7.17 (t,  $J = 7.1$  Hz, 1H), 7.11 (t,  $J = 7.8$  Hz, 2H), 4.42 (s, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  137.0, 134.2, 132.3, 130.9, 130.6, 129.1, 129.0, 128.6, 128.4, 128.3, 122.4, 121.0, 118.0, 58.8; IR (diamond) 3084, 3031, 1581, 1317, 1149, 1051, 818, 696, 537, 483  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_3\text{S}$   $[\text{M}]^+$ : 314.0725, found: 314.0727.

**8-[(7,7-Dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methylsulfonamido]quinoline *N*-oxide (Table 4, 6c)**



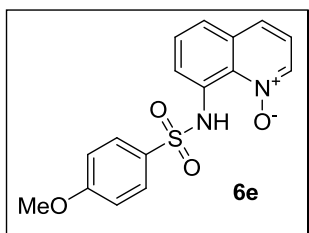
Light yellow solid; m.p 143~145 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  14.26 (s, 1H), 8.34 (d,  $J = 5.9$  Hz, 1H), 8.00 (d,  $J = 7.9$  Hz, 1H), 7.81 (d,  $J = 8.4$  Hz, 1H), 7.57 (t,  $J = 8.0$  Hz, 1H), 7.50 (d,  $J = 8.1$  Hz, 1H), 7.31 (dd,  $J = 8.4, 6.0$  Hz, 1H), 3.71 (d,  $J = 14.9$  Hz, 1H), 3.08 (d,  $J = 14.9$  Hz, 1H), 2.65 – 2.48 (m, 1H), 2.33 (dt,  $J = 18.6, 3.9$  Hz, 1H), 2.11 – 2.08 (m, 1H), 2.07 – 2.02 (m, 1H), 1.91 (d,  $J = 18.5$  Hz, 1H), 1.84 – 1.74 (m, 1H), 1.51 – 1.38 (m, 1H), 1.11 (s, 3H), 0.83 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  215.1, 137.1, 134.2, 132.5, 130.8, 129.4, 129.3, 122.0, 121.0, 116.8, 58.5, 48.6, 48.1, 42.7, 42.5, 26.9, 25.0, 19.8, 19.7; IR (diamond) 3080, 2957, 1741, 1317, 1144, 1049, 908, 817, 726, 482  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_4\text{S}$   $[\text{M}]^+$ : 374.1300, found: 374.1298.

**8-(2-Bromophenylsulfonamido)quinoline *N*-oxide (Table 4, 6d)**



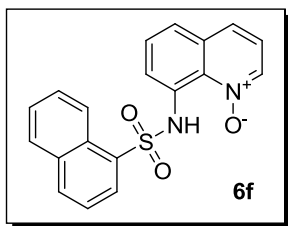
Light yellow solid; m.p 190~192 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  15.24 (s, 1H), 8.35 (d,  $J = 6.0$  Hz, 1H), 8.30 (d,  $J = 8.4$  Hz, 1H), 7.74 (t,  $J = 7.5$  Hz, 1H), 7.66 (d,  $J = 7.8$  Hz, 1H), 7.59–7.55 (m, 1H), 7.48 (t,  $J = 7.7$  Hz, 1H), 7.43–7.35 (m, 3H), 7.32–7.26 (m, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  138.7, 137.4, 135.9, 134.4, 133.7, 133.0, 132.8, 131.0, 129.4, 129.3, 127.9, 122.2, 121.6, 120.6, 115.9; IR (diamond) 3088, 3072, 1579, 1348, 1318, 1160, 1052, 816, 746, 572  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{15}\text{H}_{11}\text{BrN}_2\text{O}_3\text{S}$   $[\text{M}]^+$ : 377.9674, found: 377.9674.

**8-(4-Methoxyphenylsulfonamido)quinoline *N*-oxide (Table 4, 6e)**



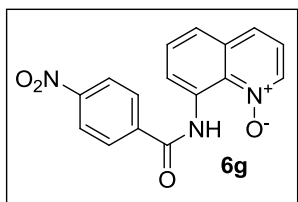
Yellow solid; m.p 179~181 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  14.31 (s, 1H), 8.28 (d,  $J = 6.1$  Hz, 1H), 7.87 (d,  $J = 8.5$  Hz, 2H), 7.84 (d,  $J = 7.8$  Hz, 1H), 7.70 (d,  $J = 8.4$  Hz, 1H), 7.46 (t,  $J = 8.1$  Hz, 1H), 7.41 (d,  $J = 8.1$  Hz, 1H), 7.26 – 7.19 (m, 1H), 6.85 (d,  $J = 8.5$  Hz, 2H), 3.78 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  162.9, 137.0, 133.8, 132.4, 131.3, 131.2, 129.5, 129.1, 128.9, 122.2, 120.9, 118.0, 114.1, 55.5; IR (diamond) 3078, 2969, 1594, 1318, 1260, 1155, 1092, 1052, 819, 564  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4\text{S}$   $[\text{M}]^+$ : 330.0674, found: 330.0675.

#### 8-(Naphthalene-1-sulfonamido)quinoline *N*-oxide (Table 4, 6f)



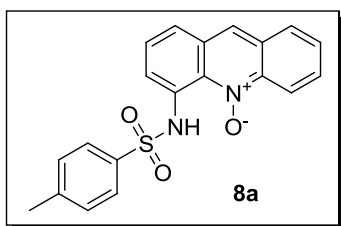
Light yellow solid; m.p 202~203 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  15.00 (s, 1H), 8.84 (d,  $J = 8.6$  Hz, 1H), 8.44 (d,  $J = 7.3$  Hz, 1H), 8.25 (d,  $J = 6.1$  Hz, 1H), 8.00 (d,  $J = 8.2$  Hz, 1H), 7.85 (d,  $J = 8.2$  Hz, 1H), 7.76–7.66 (m, 2H), 7.62 (d,  $J = 8.4$  Hz, 1H), 7.58–7.47 (m, 2H), 7.37 (t,  $J = 8.1$  Hz, 1H), 7.29 (d,  $J = 8.2$  Hz, 1H), 7.20–7.12 (m, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  136.7, 134.5, 134.4, 134.2, 133.8, 132.3, 130.6, 130.4, 129.0, 128.8, 128.7, 128.4, 128.2, 126.9, 124.7, 123.8, 121.5, 120.8, 116.3; IR (diamond) 3082, 2970, 1738, 1581, 1318, 1160, 1134, 1053, 770, 588  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_3\text{S}$   $[\text{M}]^+$ : 350.0725, found: 350.0729.

#### 8-(4-Nitrobenzamido)quinoline *N*-oxide (Table 4, 6g)



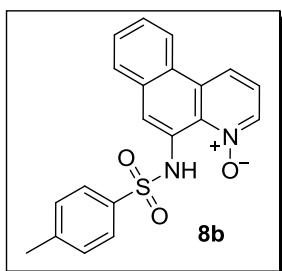
Yellow solid; m.p 260~265 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  15.78 (s, 1H), 9.22 (d,  $J = 7.8$  Hz, 1H), 8.43 (d,  $J = 6.0$  Hz, 1H), 8.35 (d,  $J = 8.8$  Hz, 2H), 8.24 (d,  $J = 8.7$  Hz, 2H), 7.88 (d,  $J = 8.4$  Hz, 1H), 7.67 (t,  $J = 8.0$  Hz, 1H), 7.62 (d,  $J = 8.0$  Hz, 1H), 7.36 (dd,  $J = 8.4, 5.9$  Hz, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  162.9, 149.7, 140.8, 137.6, 134.3, 132.4, 131.0, 129.5, 129.3, 128.4, 123.8, 122.8, 121.0, 119.2; IR (diamond) 3102, 2910, 1674, 1521, 1415, 1344, 1162, 815, 747, 712  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{11}\text{N}_3\text{O}_4$   $[\text{M}]^+$ : 309.0750, found: 309.0748.

#### 4-(4-Methylphenylsulfonamido)acridine 10-oxide (Table 5, 8a)



Orange solid; m.p. 196~198 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  14.70 (s, 1H), 8.69 (d,  $J = 9.1$  Hz, 1H), 8.20 (s, 1H), 7.89 (d,  $J = 8.4$  Hz, 1H), 7.84 (d,  $J = 8.3$  Hz, 2H), 7.81–7.74 (m, 2H), 7.58 (t,  $J = 7.5$  Hz, 1H), 7.50 (d,  $J = 8.4$  Hz, 1H), 7.35 (t,  $J = 8.0$  Hz, 1H), 7.13 (d,  $J = 8.1$  Hz, 2H), 2.25 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  143.4, 139.6, 136.8, 133.1, 131.9, 131.0, 129.4, 129.0, 128.2, 127.8, 127.4, 127.2, 127.1, 126.9, 122.6, 119.3, 117.2, 21.4; IR (diamond) 3046, 2698, 1620, 1573, 1540, 1452, 1328, 1219, 1156, 1090, 888, 755, 651  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_3\text{S}$   $[\text{M}]^+$ : 364.0882, found: 364.0879.

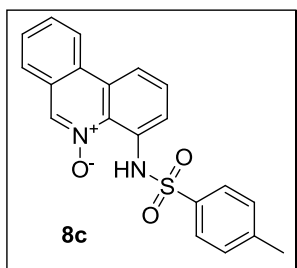
#### 5-(4-Methylphenylsulfonamido)benzo[*f*]quinoline 4-oxide (Table 5, 8b)



Yellow solid; m.p. 230~232 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$  15.10 (s, 1H), 8.97 (dd,  $J = 8.5, 1.0$  Hz, 1H), 8.69 (d,  $J = 8.4$  Hz, 1H), 8.67 (dd,  $J = 6.4, 0.9$  Hz, 1H), 7.98 (dd,  $J = 7.8, 1.4$  Hz, 1H), 7.97 (s, 1H), 7.73 (d,  $J = 8.3$  Hz, 2H), 7.70 (t,  $J = 7.4$  Hz, 2H), 7.64 (ddd,  $J = 8.3, 7.0, 1.4$  Hz, 1H),

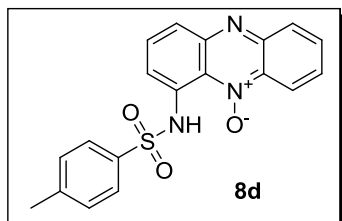
7.23 (d,  $J = 8.0$  Hz, 2H), 2.20 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ )  $\delta$  144.1, 139.3, 136.4, 131.74, 131.65, 130.6, 130.22, 130.19, 130.0, 128.4, 127.6, 127.4, 125.7, 125.5, 124.4, 123.5, 117.4, 21.3; IR (diamond) 3064, 2661, 1619, 1595, 1449, 1332, 1227, 1156, 1091, 897, 773, 754  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_3\text{S}$   $[\text{M}]^+$ : 364.0882, found: 364.0878.

#### 4-(4-Methylphenylsulfonamido)phenanthridine 5-oxide (Table 5, 8c)



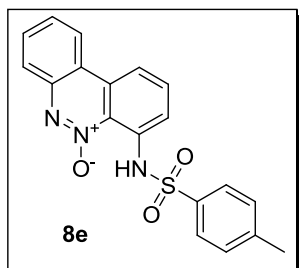
Yellow solid; m.p. 235~237  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$  15.42 (s, 1H), 9.19 (s, 1H), 8.67 (d,  $J = 8.3$  Hz, 1H), 8.46 (d,  $J = 7.8$  Hz, 1H), 8.02 (d,  $J = 7.9$  Hz, 1H), 7.84 (t,  $J = 7.4$  Hz, 1H), 7.80–7.64 (m, 5H), 7.27 (d,  $J = 8.2$  Hz, 2H), 2.22 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ )  $\delta$  144.2, 137.9, 136.5, 134.5, 131.8, 130.4, 130.3, 130.2, 128.9, 127.6, 127.4, 127.3, 126.6, 126.0, 123.5, 118.5, 118.3, 21.3; IR (diamond) 3076, 2649, 1596, 1534, 1465, 1334, 1307, 1153, 1093, 983, 954, 806, 750  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_3\text{S}$   $[\text{M}]^+$ : 364.0882, found: 364.0885.

#### 4-(4-Methylphenylsulfonamido)phenazine 5-oxide (Table 5, 8d)



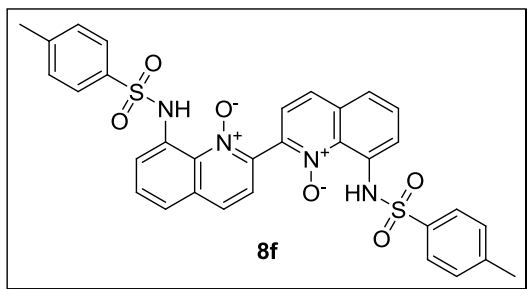
Orange solid; m.p. 189~191  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  12.94 (s, 1H), 8.51 (d,  $J = 8.9$  Hz, 1H), 8.05 (d,  $J = 8.6$  Hz, 1H), 7.87–7.69 (m, 6H), 7.61 (t,  $J = 8.2$  Hz, 1H), 7.14 (d,  $J = 8.0$  Hz, 2H), 2.24 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  146.4, 144.9, 144.0, 136.2, 134.1, 132.2, 131.9, 131.2, 131.1, 130.0, 129.6, 127.4, 126.0, 124.5, 118.7, 116.2, 21.4; IR (diamond) 3094, 2892, 1620, 1596, 1568, 1466, 1331, 1161, 1107, 1050, 828, 736  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{15}\text{N}_3\text{O}_3\text{S}$   $[\text{M}]^+$ : 365.0834, found: 364.0830.

#### 4-(4-Methylphenylsulfonamido)benzo[*c*]cinnoline 5-oxide (Table 5, 8e)



Yellow solid; m.p. 240~242  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  12.96 (s, 1H), 8.27 (d,  $J = 8.1$  Hz, 1H), 8.08 (d,  $J = 8.1$  Hz, 1H), 8.03 (d,  $J = 8.2$  Hz, 1H), 7.95 (d,  $J = 7.7$  Hz, 1H), 7.84 (d,  $J = 8.3$  Hz, 2H), 7.76 (t,  $J = 8.0$  Hz, 2H), 7.71 (t,  $J = 8.1$  Hz, 1H), 7.20 (d,  $J = 8.4$  Hz, 2H), 2.31 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  144.2, 141.6, 136.2, 134.7, 133.1, 131.2, 131.0, 130.2, 129.8, 127.4, 127.0, 126.7, 121.7, 118.7, 118.5, 116.1, 21.5; IR (diamond) 3088, 3046, 1595, 1562, 1470, 1440, 1334, 1293, 1218, 1159, 1088, 853, 739  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{15}\text{N}_3\text{O}_3\text{S}$   $[\text{M}]^+$ : 365.0834, found: 365.0833

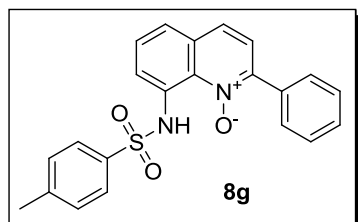
### 8,8'-Bis(4-methylphenylsulfonamido)-2,2'-biquinoline 1,1'-dioxide (Table 5, 8f)



Yellow solid; m.p. 187~189 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  13.90 (s, 2H), 7.86–7.79 (m, 6H), 7.70 (d,  $J$  = 8.6 Hz, 2H), 7.50–7.44 (m, 4H), 7.41 (d,  $J$  = 8.1 Hz, 2H), 7.22 (d,  $J$  = 8.0 Hz, 4H), 2.30 (s, 6H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  143.9, 139.6, 136.3, 133.9, 132.4, 131.3, 129.78, 129.75, 128.1, 127.3, 122.8, 122.6,

118.4, 21.5; IR (diamond) 2921, 2730, 1596, 1570, 1440, 1351, 1305, 1157, 1089, 1053, 826, 752  $\text{cm}^{-1}$ ; HRMS (FAB)  $m/z$  calcd. for  $\text{C}_{32}\text{H}_{26}\text{N}_4\text{O}_6\text{S}_2$   $[\text{M}+\text{H}]^+$ : 627.1372, found: 627.1375.

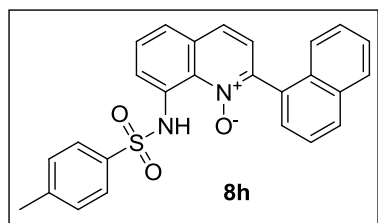
### 8-(4-Methylphenylsulfonamido)-2-phenylquinoline N-oxide (Table 5, 8g)



Yellow solid; m.p. 167~169 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  14.57 (s, 1H), 7.83 (dd,  $J$  = 7.8, 1.4 Hz, 1H), 7.81 (d,  $J$  = 8.3 Hz, 2H), 7.79–7.76 (m, 2H), 7.69 (d,  $J$  = 8.7 Hz, 1H), 7.54–7.46 (m, 3H), 7.43 (t,  $J$  = 8.0 Hz, 1H), 7.38 (dd,  $J$  = 8.1, 1.3 Hz, 1H), 7.36 (d,  $J$  = 8.7 Hz, 1H), 7.17 (d,  $J$  = 8.2 Hz, 2H), 2.30 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$

146.4, 143.4, 136.9, 134.2, 132.7, 131.53, 131.50, 130.0, 129.44, 129.42, 128.9, 128.4, 128.2, 127.4, 123.4, 122.2, 118.4, 21.5; IR (diamond) 3068, 3033, 2683, 1597, 1568, 1452, 1436, 1350, 1282, 1158, 1089, 1051, 842, 774  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_3\text{S}$   $[\text{M}]^+$ : 390.1038, found: 390.1036.

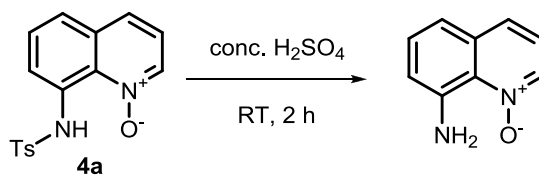
### 8-(4-Methylphenylsulfonamido)-2-(naphthalen-1-yl)quinoline N-oxide (Table 5, 8h)



Yellow solid; m.p. 203~205 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  14.37 (s, 1H), 8.00 (d,  $J$  = 8.3 Hz, 1H), 7.96–7.89 (m, 2H), 7.79 (d,  $J$  = 8.3 Hz, 2H), 7.75 (d,  $J$  = 8.5 Hz, 1H), 7.62–7.57 (m, 1H), 7.55 (d,  $J$  = 7.9 Hz, 1H), 7.52–7.43 (m, 4H), 7.36–7.31 (m, 2H), 7.18 (d,  $J$  = 8.1 Hz, 2H), 2.34 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  146.9,

143.4, 136.9, 134.1, 133.5, 132.0, 131.6, 131.2, 130.4, 130.3, 129.5, 129.1, 128.8, 127.9, 127.4, 126.9, 126.4, 125.4, 125.1, 124.5, 122.6, 118.7, 21.5; IR (diamond) 3053, 2667, 1596, 1568, 1442, 1351, 1305, 1157, 1089, 1050, 772, 655  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_3\text{S}$   $[\text{M}]^+$ : 440.1195, found: 440.1194.

### 3. Removal of *N*-Toluenesulfonyl Group<sup>6</sup>



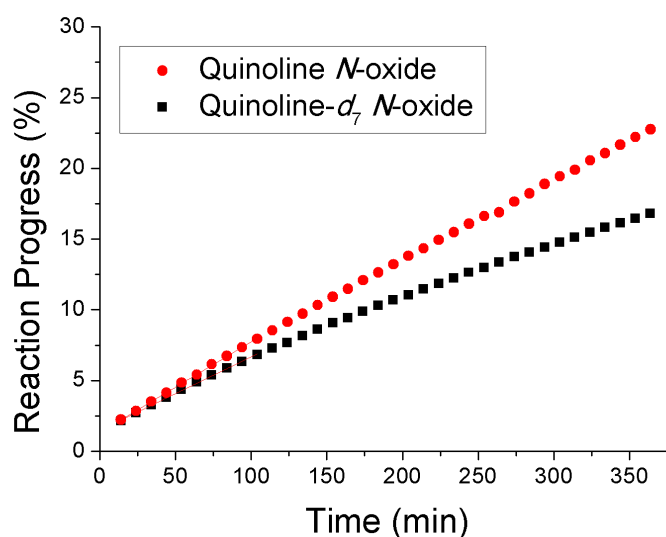
To 8-(*p*-toluenesulfonylamido)quinoline *N*-oxide (**4a**, 31.4 mg, 0.1 mmol) was added cold H<sub>2</sub>SO<sub>4</sub> (0.5 mL) slowly at 0 °C and stirred at room temperature for 2 hr. The reaction mixture was cooled to 0 °C and quenched by cold water (50 mL) and then saturated aqueous NaHCO<sub>3</sub> (10 mL) slowly, extracted with CHCl<sub>3</sub> (20 mL x 3), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified on silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/acetone, 1:1, R<sub>f</sub> = 0.5) to obtain 8-aminoquinoline *N*-oxide (13.4 mg, 84%); yellow solid; m.p. 104~106 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.18 (d, *J* = 6.0 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.07 (dd, *J* = 8.4, 6.1 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.81 (br, 2H), 6.70 (d, *J* = 7.8 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 143.4, 135.4, 133.5, 131.0, 129.4, 127.5, 120.3, 114.9, 113.2; IR (diamond) 3363, 3241, 3115, 3059, 1569, 1461, 1397, 1356, 1295, 1042 cm<sup>-1</sup>; HRMS (ESI) *m/z* calcd. for C<sub>9</sub>H<sub>8</sub>N<sub>2</sub>O [M+Na]<sup>+</sup>: 183.0534, found: 183.0502.

## V. Experimental Procedures of Mechanistic Studies

### 1. Kinetic isotope effect test in direct C–H amidation of *N*-oxide

#### 1.1. Kinetic isotope effects in the presence of AcOH additive (Figure 2 (a))

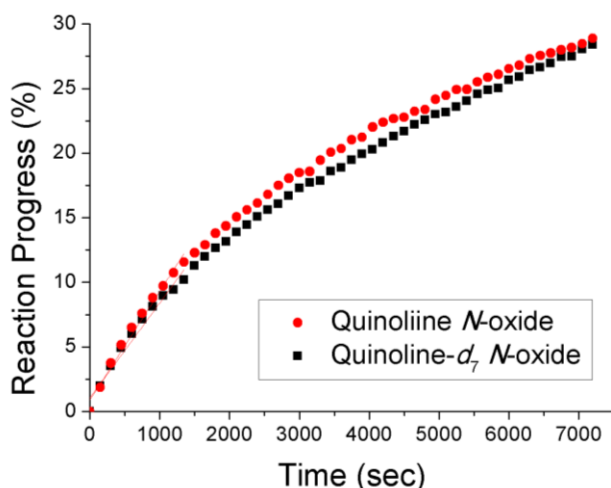
To a J. Young valve NMR tube were added quinoline *N*-oxide (**1a**, 29.0 mg, 0.2 mmol) or quinoline-*d*<sub>7</sub> *N*-oxide (**1a-d**<sub>7</sub>, 30.4 mg, 0.2 mmol), [IrCp\*Cl<sub>2</sub>]<sub>2</sub> (6.4 mg, 4 mol %), AgNTf<sub>2</sub> (12.4 mg, 16 mol %), AcOH (3.6 mg, 30 mol %), 1,1,2,2-tetrachloroethane (33.6 mg, 0.2 mmol) and 1,2-dichloroethane-*d*<sub>4</sub> (0.5 mL). *p*-Toluenesulfonyl azide (**3a**, 43.4 mg, 0.22 mmol) was added and crude yield was measured with 1,1,2,2-tetrachloroethane as an internal standard every 10 min for 6 h (except for the initial 10 min point) at room temperature. The initial rate was obtained by plotting initial 10 points to give a KIE value of 1.23.



**Figure S1.** Product yields over time in reactions of quinoline *N*-oxide (**1a**) and quinoline-*d*<sub>7</sub> *N*-oxide (**1a-d**<sub>7</sub>) in the presence of 30 mol % of AcOH.

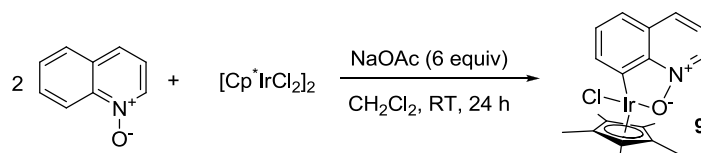
#### 1.2. Kinetic isotope effect in the absence of AcOH additive (Figure 2 (b))

To a J. Young valve NMR tube were added quinoline *N*-oxide (**1a**, 29.0 mg, 0.2 mmol) or quinoline-*d*<sub>7</sub> *N*-oxide (**1a-d**<sub>7</sub>, 30.4 mg, 0.2 mmol), [IrCp\*Cl<sub>2</sub>]<sub>2</sub> (6.4 mg, 4 mol %), AgNTf<sub>2</sub> (12.4 mg, 16 mol %), 1,1,2,2-tetrachloroethane (33.6 mg, 0.2 mmol) and 1,2-dichloroethane-*d*<sub>4</sub> (0.5 mL). *p*-Toluenesulfonyl azide (**3a**, 43.4 mg, 0.22 mmol) was added and crude yield was measured with 1,1,2,2-tetrachloroethane as an internal standard every 2.5 min for 2 h at 50 °C. The initial rate was obtained by plotting initial 10 points to afford a KIE value of 1.14.



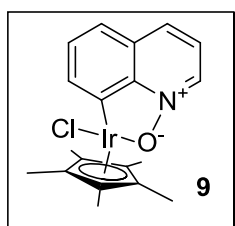
**Figure S2.** Product yields over time in reactions of quinoline *N*-oxide (**1a**) and quinoline-*d*<sub>7</sub> *N*-oxide (**1a-d**<sub>7</sub>) in the absence of AcOH.

## 2. Preparation of cyclometallated complex (Scheme 3 (a), **9**)<sup>7</sup>



A mixture of [IrCp\*Cl<sub>2</sub>]<sub>2</sub> (398.3 mg, 0.5 mmol), NaOAc (246.1 mg, 3.0 mmol), quinoline *N*-oxide dihydrate (181.2 mg, 1.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was stirred for 24 h at room temperature. The mixture was filtered through a plug of celite and washed with CH<sub>2</sub>Cl<sub>2</sub> (20 mL x 3). The solution was evaporated and recrystallized from CH<sub>2</sub>Cl<sub>2</sub> and diethyl ether to afford a cyclometalated compound **9** as a red-orange solid (51%).

### Complex **9** (Scheme 3 (a))



Red-orange solid; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) 8.44 (d, *J* = 5.9 Hz, 1H), 7.91 (d, *J* = 6.9 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.21 (dd, *J* = 8.2, 6.0 Hz, 1H), 1.77 (s, 15H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 154.1, 146.6, 135.9, 133.4, 132.1, 130.3, 120.7, 119.2, 87.0, 86.3, 9.1; IR (diamond) 3078, 3047, 2979, 2914, 1556, 1360, 1233, 924, 816, 767 cm<sup>-1</sup>; HRMS (EI) *m/z* calcd. for C<sub>19</sub>H<sub>21</sub>ClIrNO [M]<sup>+</sup>: 507.0941, found: 507.0941.

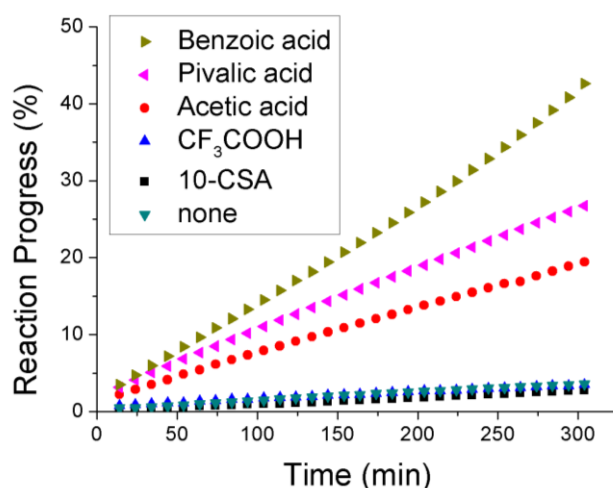
## 3. Catalytic amidation reaction using a cyclometalated complex **9** (Scheme 3 (b))

To a screw cap vial equipped with a spinnvane triangular-shaped Teflon stirbar were added quinoline *N*-oxide dihydrate (36.2 mg, 0.2 mmol, **1a**), *p*-toluenesulfonyl azide (**3a**, 43.4 mg, 0.22 mmol), complex **9** (4.1 mg, 4 mol %), AgNTf<sub>2</sub> (3.1 mg, 4 mol %), AcOH (3.6 mg, 30 mol %) and 1,2-dichloroethane (0.5 mL) under atmospheric conditions. The reaction mixture was stirred in a pre-

heated oil bath at 50 °C for 12 h in an oil bath with vigorous stirring. The reaction was cooled to room temperature, filtered through a plug of celite and then washed with dichloromethane (10 mL x 3). The solvents were removed under reduced pressure and the crude reaction mixture was purified by chromatography on silica gel (EtOAc/ *n*-hexane, 3:1) as an eluent to give the desired product. (62%, **4a**)

#### 4. Reaction profile in the presence of acid additives (Figure 4 (a))

To a J-Young NMR tube were added quinoline *N*-oxide (**1a**, 29.0 mg, 0.2 mmol), [IrCp\*Cl<sub>2</sub>]<sub>2</sub> (6.4 mg, 4 mol %), AgNTf<sub>2</sub> (12.4 mg, 16 mol %), acid additive (30 mol % in case), 1,1,2,2-tetrachloroethane (33.6 mg, 0.2 mmol) and 1,2-dichloroethane-*d*<sub>4</sub> (0.5 mL) under argon atmosphere. *p*-Toluenesulfonyl azide (**3a**, 43.4 mg, 0.22 mmol) was added, and a NMR tube was gently shaken to insure thorough mixing and immediately started to measure its conversion over time at room temperature using 1,1,2,2-tetrachloroethane as an internal standard.

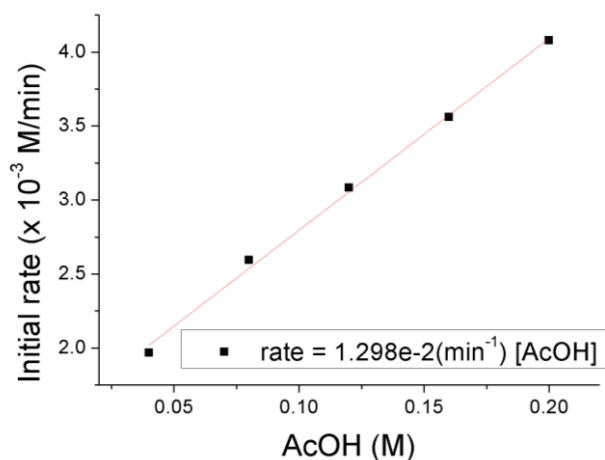


**Figure S3.** Reaction profile in the Ir-catalyzed amidation of quinoline *N*-oxide (**1a**) with TsN<sub>3</sub> at 25 °C in the presence of various acid additives (10-CSA: 10-camphorsulfonic acid)

#### 5. Kinetic Profile: Plot of initial rate vs AcOH (Figure 4 (b))

To a J-Young NMR tube were added quinoline *N*-oxide (**1a**, 29.0 mg, 0.2 mmol), [IrCp\*Cl<sub>2</sub>]<sub>2</sub> (6.4 mg, 4 mol %), AgNTf<sub>2</sub> (12.4 mg, 16 mol %), AcOH (1.2 mg, 10 mol %), 1,1,2,2-tetrachloroethane (33.6 mg, 0.2 mmol) and 1,2-dichloroethane-*d*<sub>4</sub> (0.5 mL) under argon atmosphere. *p*-Toluenesulfonyl azide (**3a**, 43.4 mg, 0.22 mmol) was added, and the NMR tube was gently shaken to insure thorough mixing and immediately started to measure its conversion at 40 °C using 1,1,2,2-tetrachloroethane as an internal standard. The same experimental procedure was repeated in the presence of 20, 30, 40, and 50 mol % of AcOH under otherwise identical conditions, and their corresponding conversions were measured over time every 1 min for the next 30 min (Figure S4). A plot of initial rate versus acetic

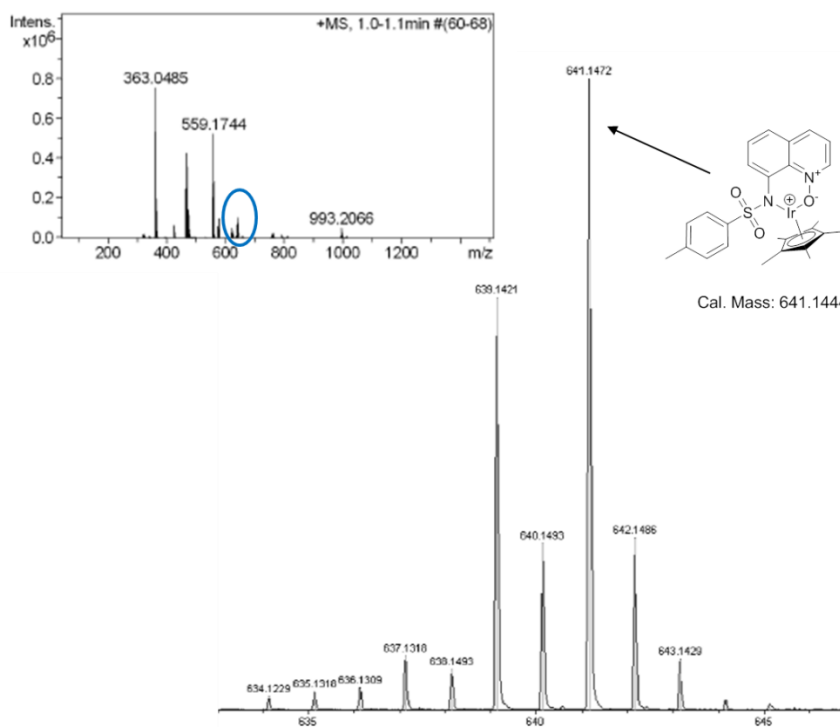
acid gave a straight line (slope =  $1.298 \times 10^{-2} \text{ min}^{-1}$ , y-intercept =  $1.499 \times 10^{-3} \text{ M/min}$ ,  $R^2 = 0.9966$ ), indicative of the first order dependence on acetic acid.



**Figure S4.** Plot of initial rates versus AcOH. Showing the first order

#### 6. Detecton of Amido-Inserted Iridium Intermediate III by ESI-Mass (Scheme 4)

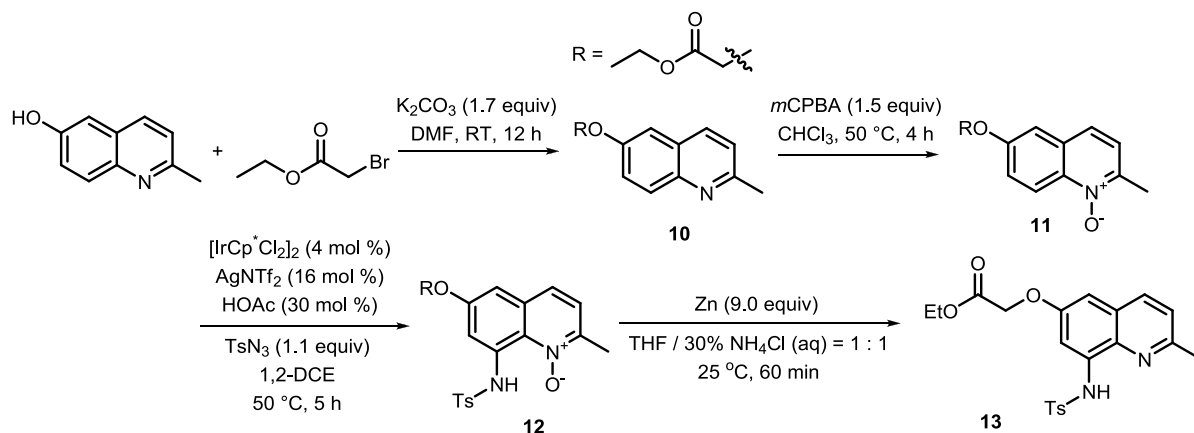
To a screw capped vial equipped with a spinvane triangular-shaped Teflon stirbar was added a cyclometalated cationic complex **9** (0.03 mmol),  $\text{AgNTf}_2$  (0.03 mmol), *p*-toluenesulfonyl azide (**3a**, 0.03 mmol) and 1,2-dichloroethane (0.5 mL) under atmospheric conditions. The reaction mixture was stirred at room temperature for 10 min and a small portion of aliquot (0.1 mL) was taken by a syringe, and then subject to an ESI spectroscopy (Figure S5)



**Figure S5.** ESI-Mass Spectroscopy of the Amidation Reaction

## VI. Experimental Procedure for the Synthetic Application

### 1. Synthesis of Zinquin ethyl ester (Scheme 5)



#### 1.1. Preparation of ethyl 2-(2-methylquinolin-6-yloxy)acetate (10)

To a suspension of  $K_2CO_3$  (460 mg, 3.3 mmol) and 2-methyl-6-hydroxyquinoline (318.4 mg, 2.0 mmol) in DMF (20 mL) was added ethyl bromoacetate (367 mg, 2.2 mmol) dropwise and stirred at room temperature for 12 h. The reaction was quenched with  $H_2O$  (20 mL), extracted with ethyl acetate (20 mL x 3), washed with brine, and dried over  $Na_2SO_4$ . The residue was purified with column chromatography on silica gel ( $CH_2Cl_2$ /acetone, 10:1,  $R_f = 0.3$ ) to obtain ethyl 2-(2-methylquinolin-6-yloxy)acetate (461 mg, 94%); yellow solid; m.p. 44~46 °C;  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  7.97 – 7.90 (m, 2H), 7.41 (dd,  $J = 9.2, 2.8$  Hz, 1H), 7.24 (d,  $J = 8.4$  Hz, 1H), 7.00 (d,  $J = 2.8$  Hz, 1H), 4.73 (s, 2H), 4.29 (q,  $J = 7.1$  Hz, 2H), 2.70 (s, 3H), 1.30 (t,  $J = 7.2$  Hz, 3H);  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  168.6, 157.0, 155.3, 144.3, 135.1, 130.4, 127.0, 122.4, 121.7, 106.8, 65.7, 61.5, 25.1, 14.2; IR (diamond) 3043, 2984, 2947, 2911, 2869, 1747, 1620, 1598, 1499, 1446, 1377, 1201, 1164, 1074, 1021, 832  $cm^{-1}$ ; HRMS (EI)  $m/z$  calcd. for  $C_{14}H_{15}NO_3$  [ $M+H^+$ ] $^+$ : 246.1125, found: 246.1129.

#### 1.2. Preparation of 6-(2-ethoxy-2-oxoethoxy)-2-methyl-8-(4-methylphenylsulfonamido)quinoline N-oxide (12)

To a solution of ethyl 2-(2-methylquinolin-6-yloxy)acetate (123 mg, 0.5 mmol) in  $CHCl_3$  (10 mL) was added *m*-chloroperbenzoic acid (168 mg, 0.75 mmol) in portions and stirred at 50 °C for 4 h. The reaction mixture was diluted with 50 mL of  $CHCl_3$ , washed with saturated aq.  $NaHCO_3$  (10 mL x 3), dried over  $MgSO_4$  and concentrated under reduced pressure to get ethyl 2-(2-methylquinolin-6-yloxy)acetate ethyl 2-(2-methylquinolin-6-yloxy)acetate (**11**) in 99% yield. The crude product was used for the next step without additional purification. To a solution of **11** (129.8 mg, 0.5 mmol),  $[IrCp^*Cl_2]_2$  (15.9 mg, 0.02 mmol),  $AgNTf_2$  (31.0 mg, 0.08 mmol) and acetic acid (9.0 mg, 0.15 mmol) in 1,2-dichloroethane (2.0 mL) was added *p*-toluenesulfonyl azide (108 mg, 0.55 mmol) and stirred at

50 °C for 5 h. The reaction mixture was filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/acetone, 10:1, *R<sub>f</sub>* = 0.5) to obtain 6-(2-ethoxy-2-oxoethoxy)-2-methyl-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (164 mg, 76%); **11** : <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.72 (d, *J* = 9.4 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.44 (dd, *J* = 9.5, 2.7 Hz, 1H), 7.27 (d, *J* = 8.6 Hz, 1H), 7.05 (d, *J* = 2.7 Hz, 1H), 4.74 (s, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.68 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 168.2, 156.9, 144.1, 137.8, 130.3, 124.0, 123.7, 122.0, 121.7, 107.5, 65.6, 61.6, 18.5, 14.1; **12** : yellow solid; m.p. 155~157 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 14.91 (s, 1H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 2.7 Hz, 1H), 7.44 (d, *J* = 8.6 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.6 Hz, 1H), 6.63 (d, *J* = 2.6 Hz, 1H), 4.65 (s, 2H), 4.28 (q, *J* = 7.2 Hz, 2H), 2.56 (s, 3H), 2.33 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 168.0, 156.6, 145.2, 143.5, 136.9, 135.1, 132.0, 129.5, 127.3, 127.1, 123.5, 107.9, 102.5, 65.4, 61.6, 21.4, 18.4, 14.1; IR (diamond) 3084, 2981, 2922, 2643, 1760, 1609, 1578, 1418, 1369, 1325, 1283, 1155, 1077, 841, 657 cm<sup>-1</sup>; HRMS (EI) *m/z* calcd. for C<sub>21</sub>H<sub>22</sub>N<sub>2</sub>O<sub>6</sub>S [M]<sup>+</sup>: 430.1199, found: 430.1199.

### 1.3. Preparation of zinquin ethyl ester (13)

To a solution of 6-(2-ethoxy-2-oxoethoxy)-2-methyl-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (43.1 mg, 0.1 mmol) in THF (1.5 mL) was added an 30% aqueous solution of NH<sub>4</sub>Cl (1.5 mL) and zinc dust (59 mg, 0.9 mmol) sequentially. The reaction mixture was stirred for 1 h at room temperature, diluted with H<sub>2</sub>O (20 mL), extracted with EtOAc (20 mL x 3), dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 20:1, *R<sub>f</sub>* = 0.3) to obtain zinquin ethyl ester (32 mg, 76%); white solid; m.p. 106~108 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 9.27 (s, 1H), 7.83 – 7.79 (m, 3H), 7.50 (d, *J* = 2.6 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.63 (d, *J* = 2.6 Hz, 1H), 4.66 (s, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.64 (s, 3H), 2.31 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 168.5, 155.6, 155.5, 143.7, 136.5, 135.2, 134.5, 134.4, 129.5, 127.2, 126.8, 123.3, 106.8, 101.2, 65.7, 61.5, 24.8, 21.4, 14.1; IR (diamond) 3271, 2980, 2916, 1765, 1627, 1605, 1577, 1501, 1424, 1378, 1340, 1203, 1157, 1089, 840 cm<sup>-1</sup>; HRMS (EI) *m/z* calcd. for C<sub>21</sub>H<sub>22</sub>N<sub>2</sub>O<sub>5</sub>S [M]<sup>+</sup>: 414.1249, found: 414.1248.

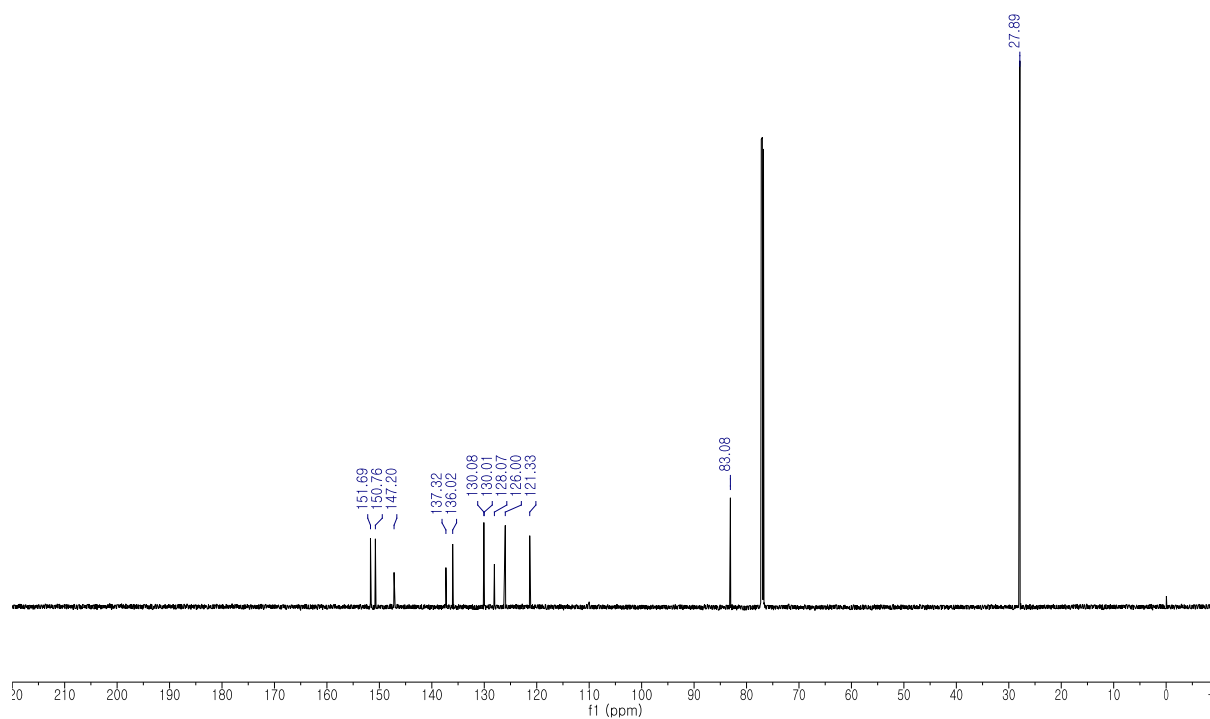
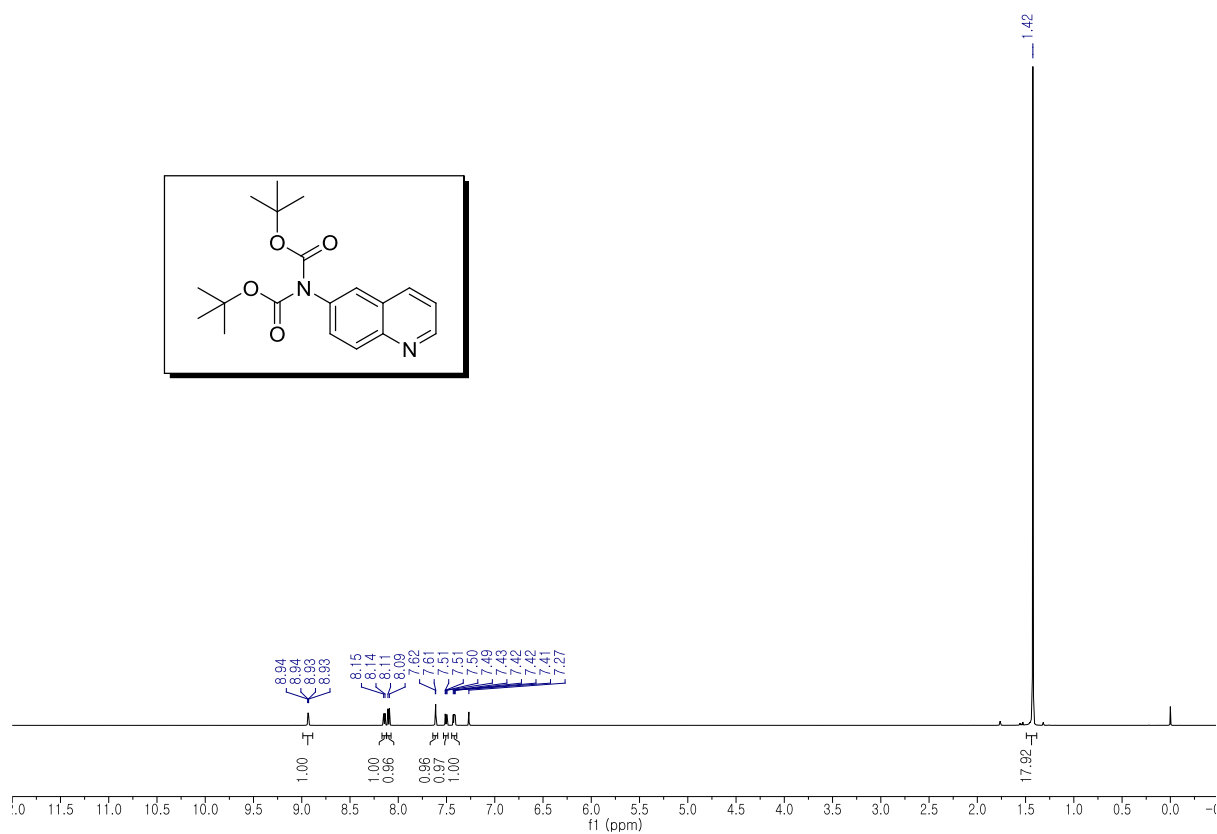
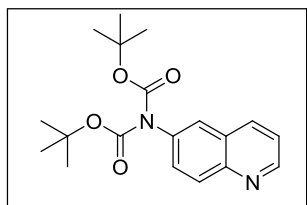
## VII. References

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- (7) Li, L.; Brennessel, W. W.; Jones, W. D. *J. Am. Chem. Soc.* **2008**, *130*, 12414.

## *Appendix I*

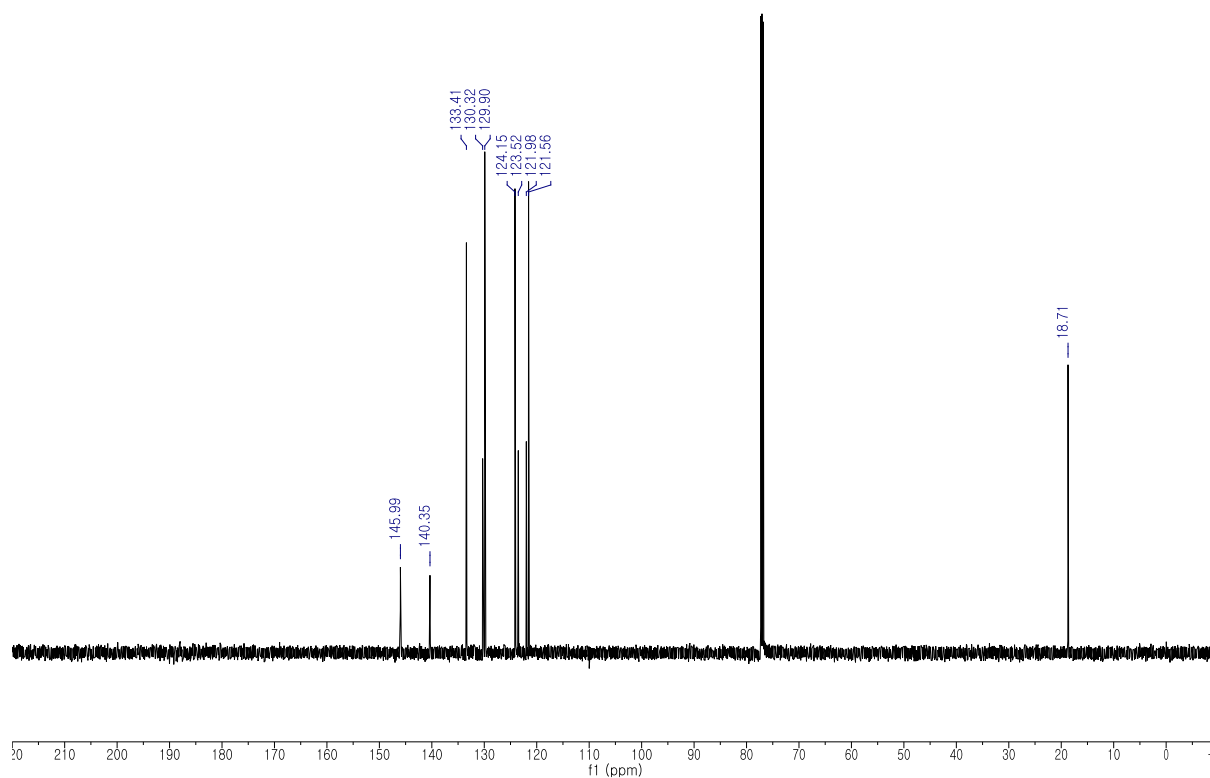
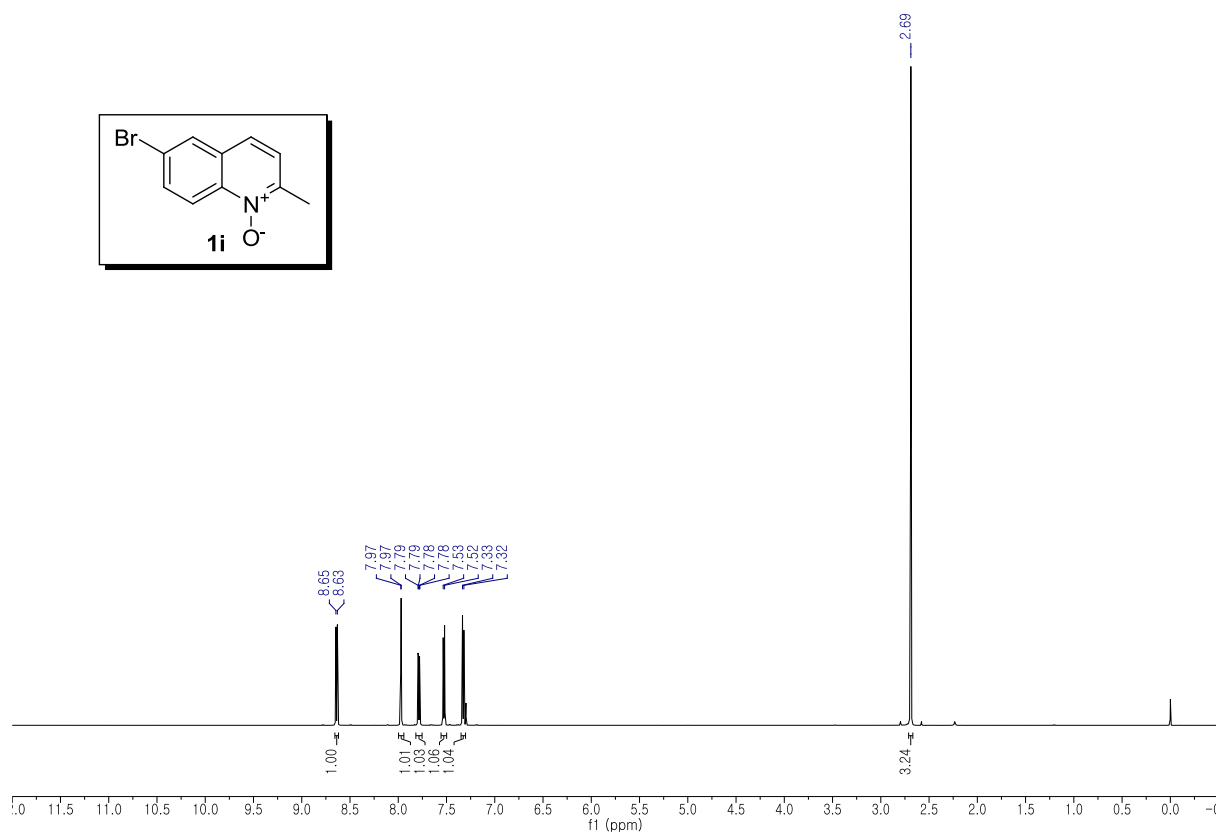
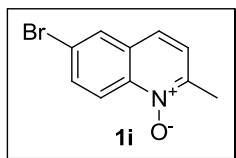
### **Spectral Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR of Compounds Obtained in this Study**

# 6-[Bis(*tert*-butoxycarbonyl)amino]quinoline

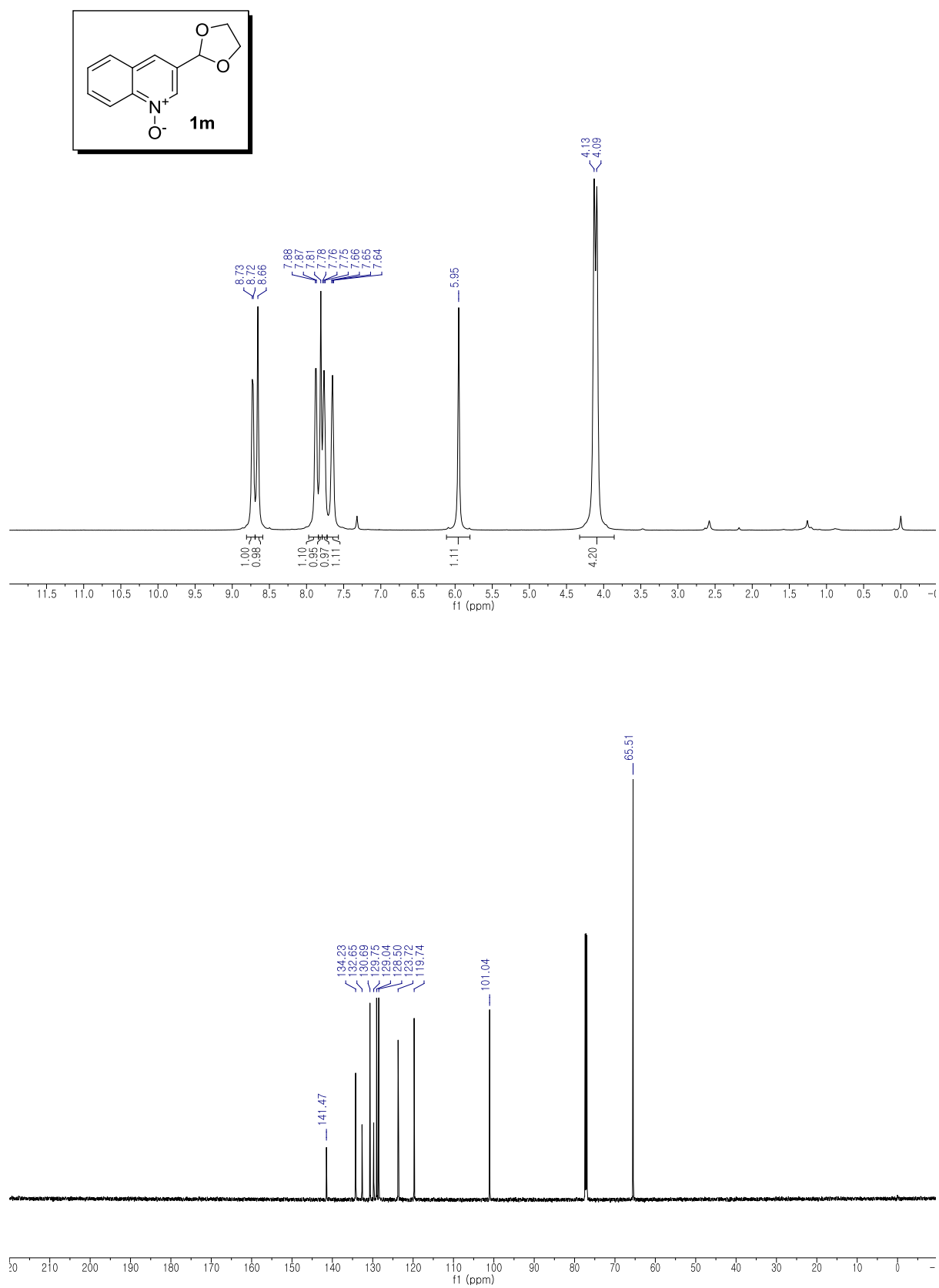




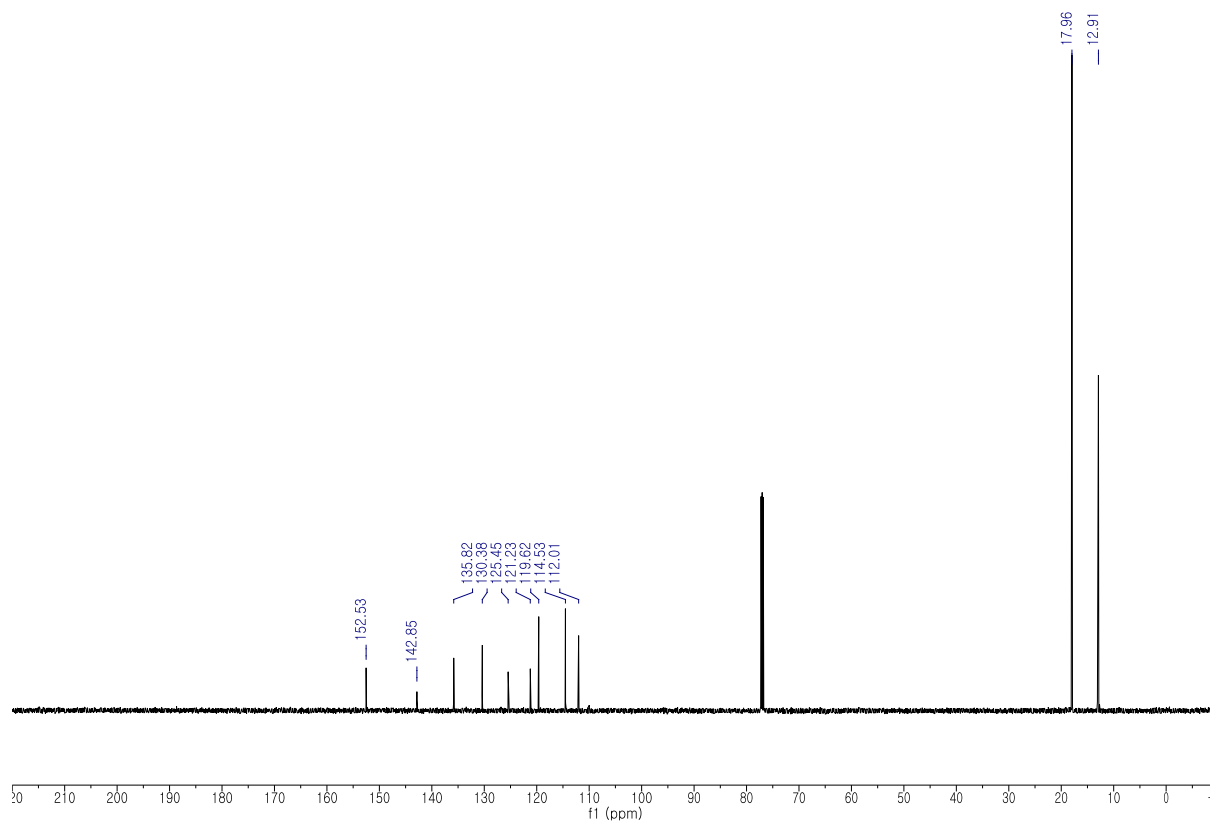
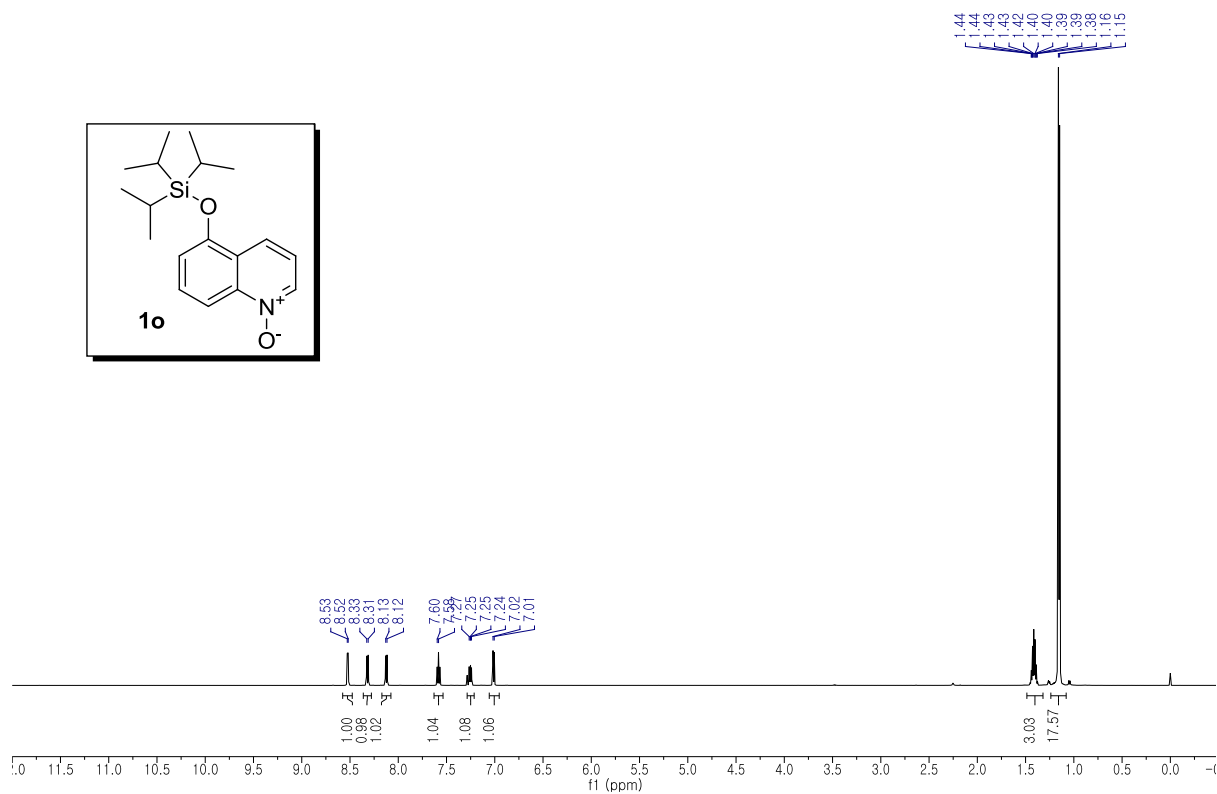
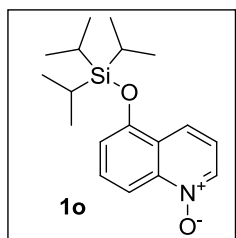
### 6-Bromo-2-methylquinoline *N*-oxide (Table 3, 1i)



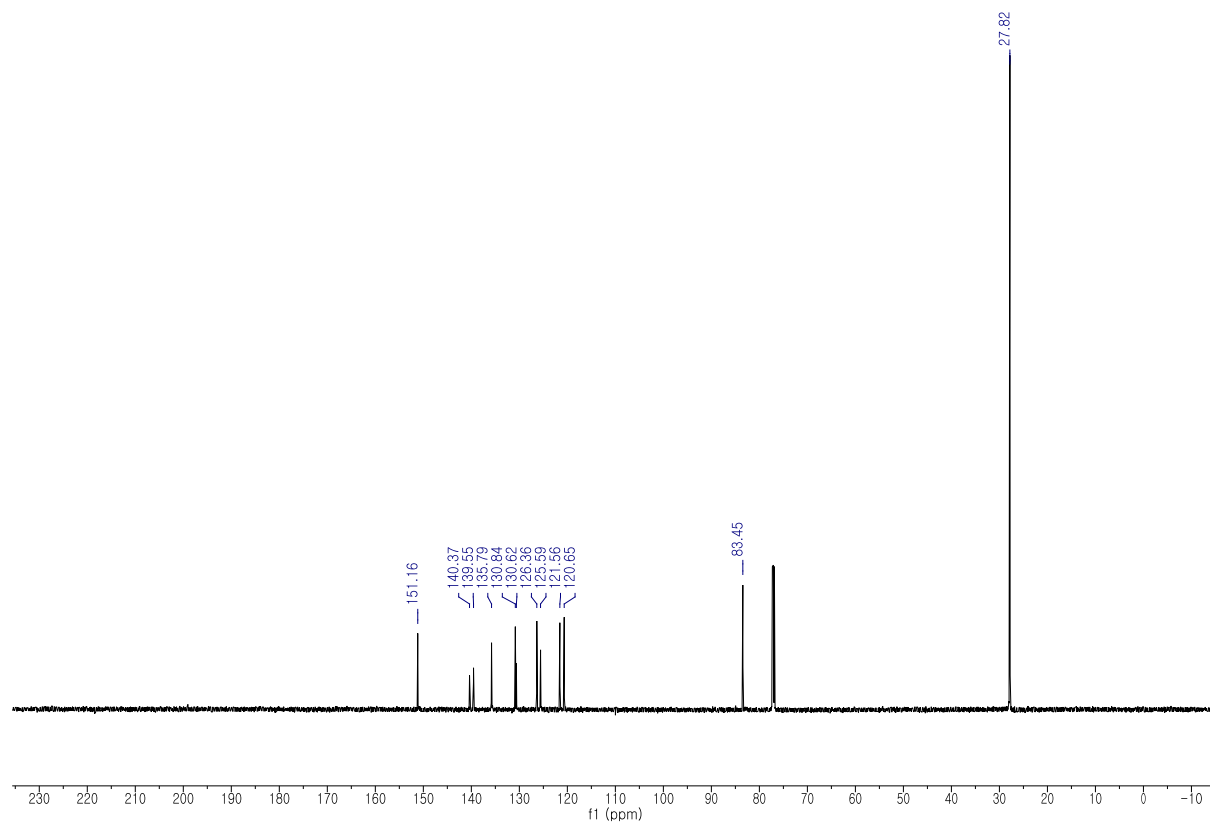
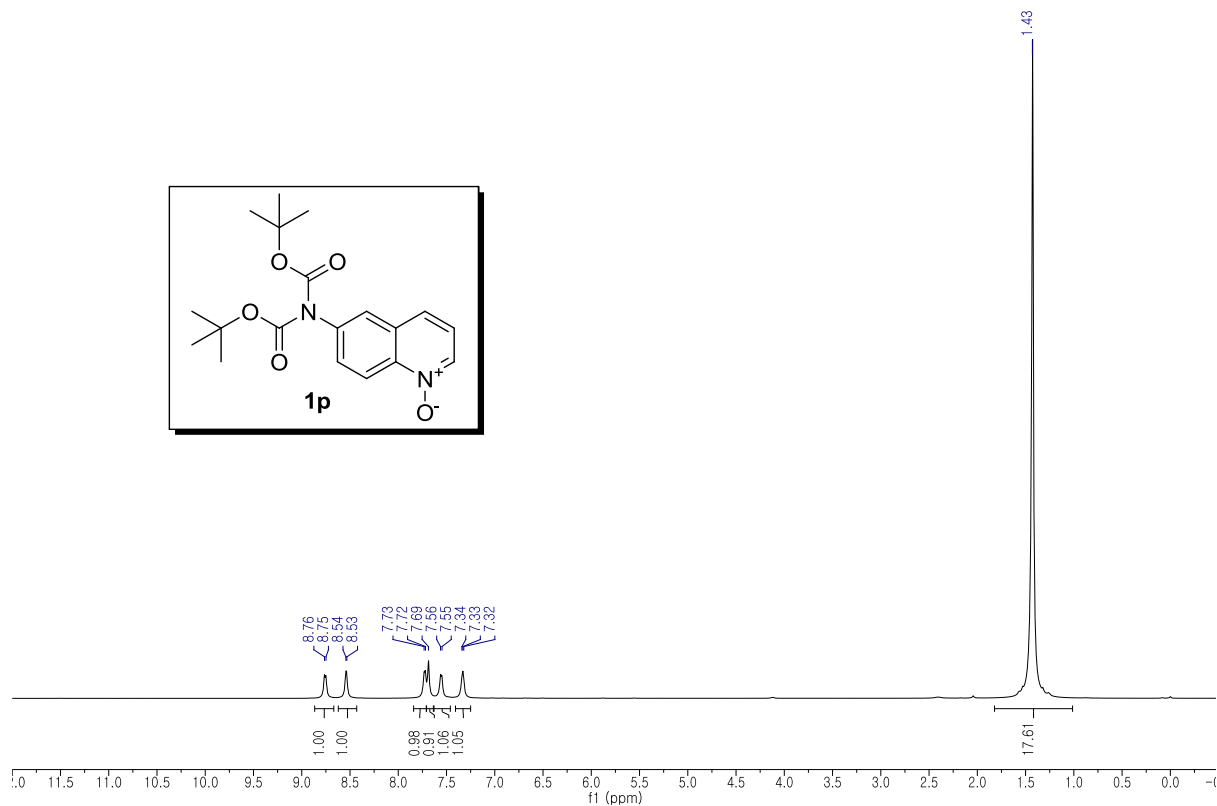
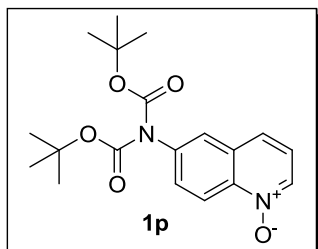
### 3-(1,3-Dioxolan-2-yl)quinoline *N*-oxide (Table 3, 1m)



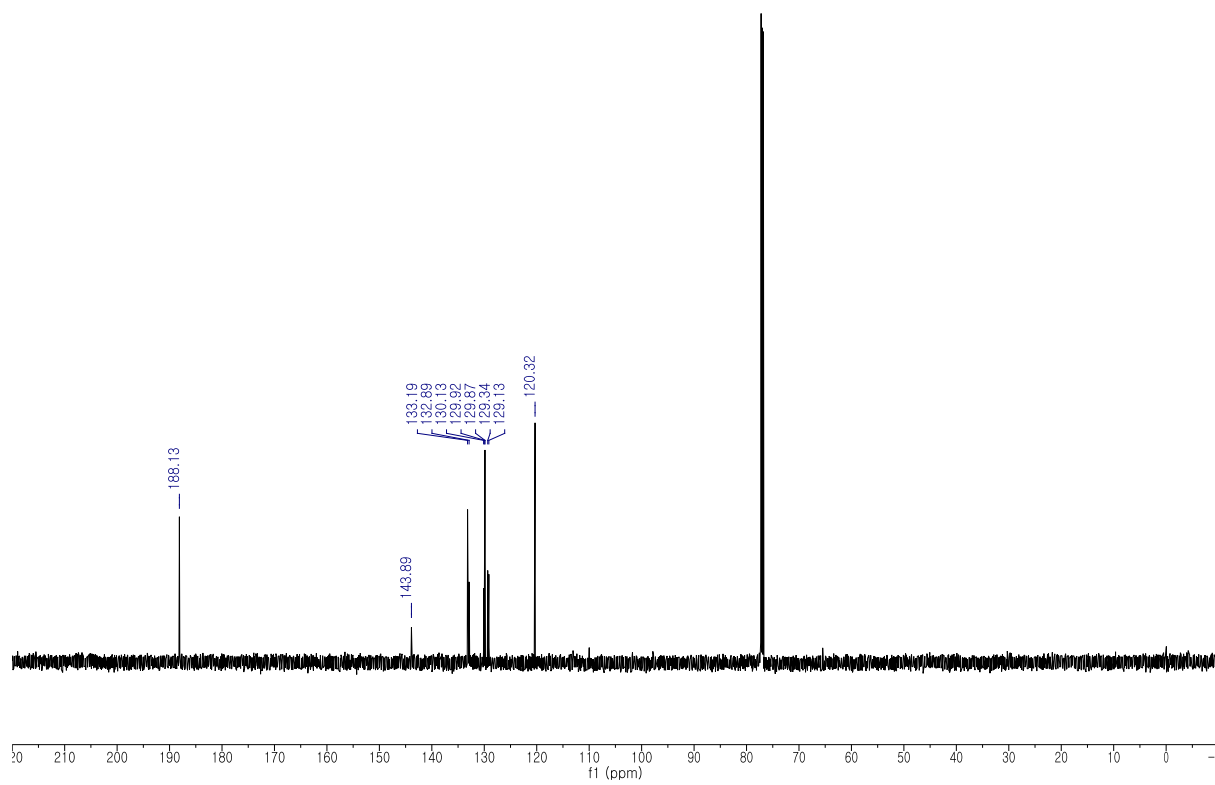
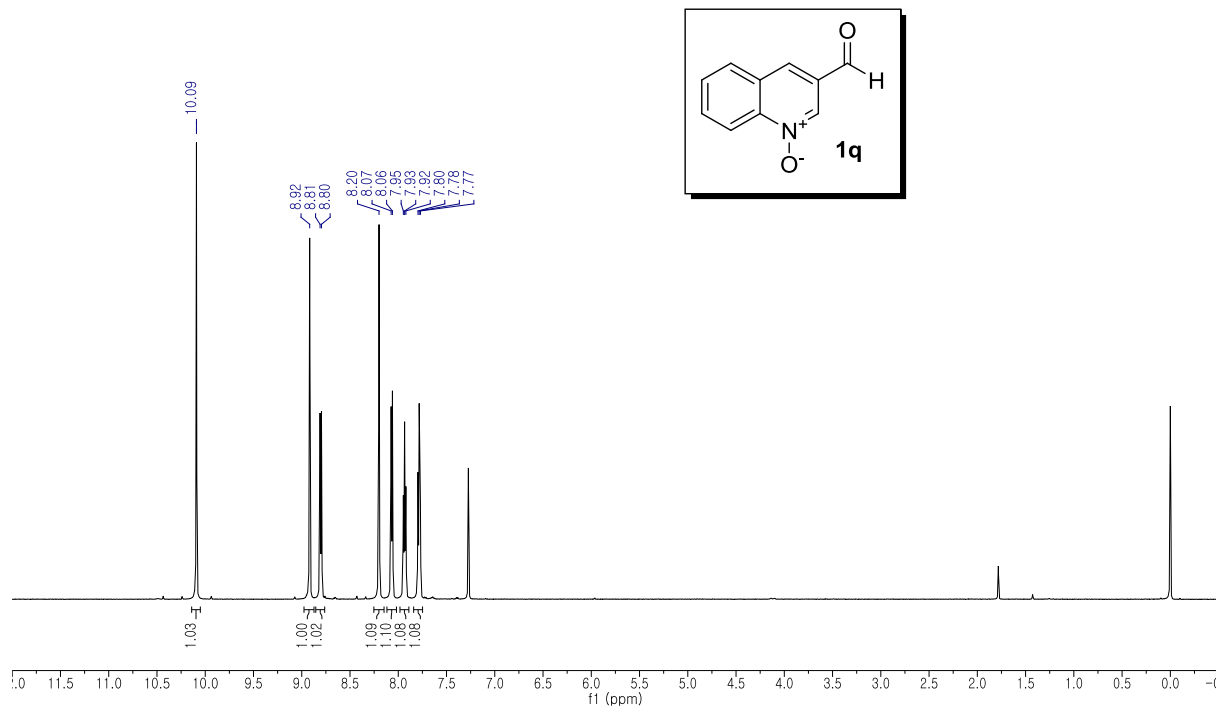
### 5-(Triisopropylsilyloxy)quinoline N-oxide (Table 3, 1o)



6-[Bis(*tert*-butoxycarbonyl)amino]quinoline *N*-oxide (Table 3, 1p)

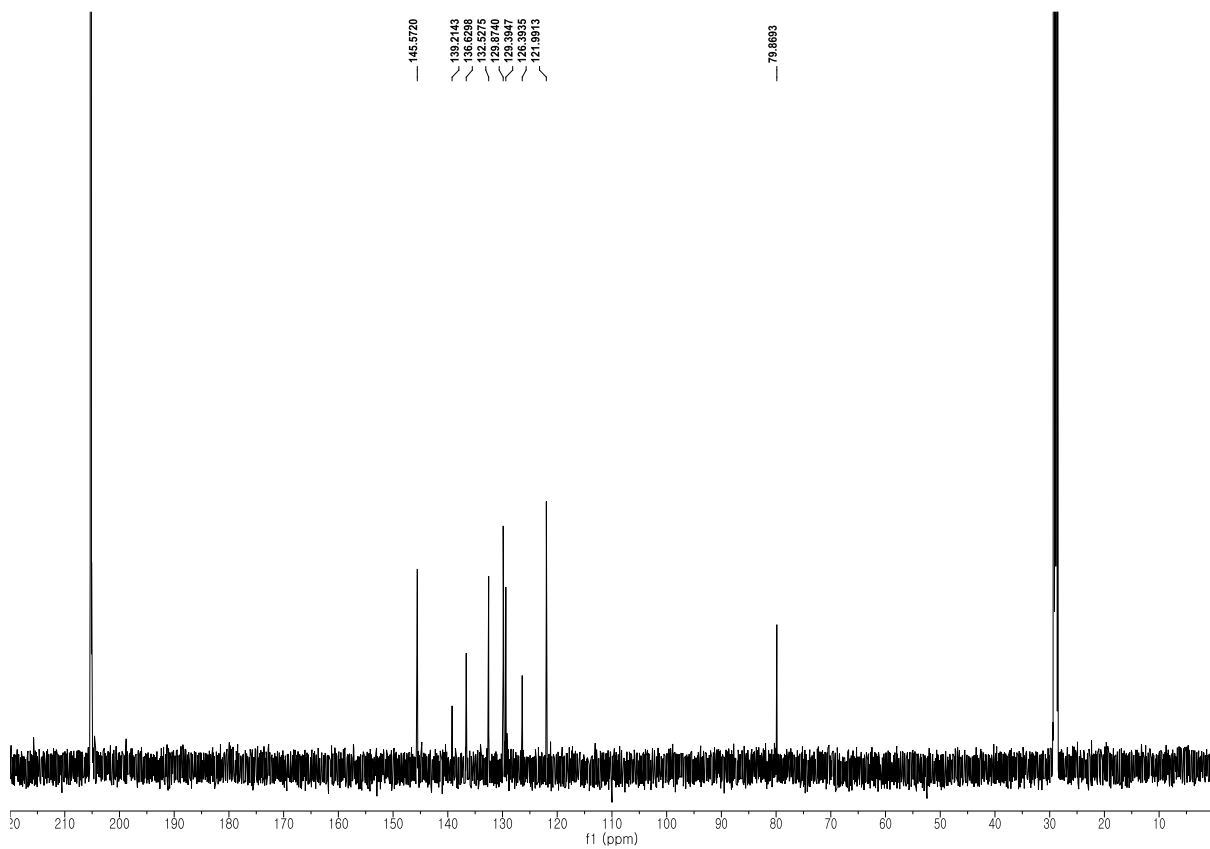
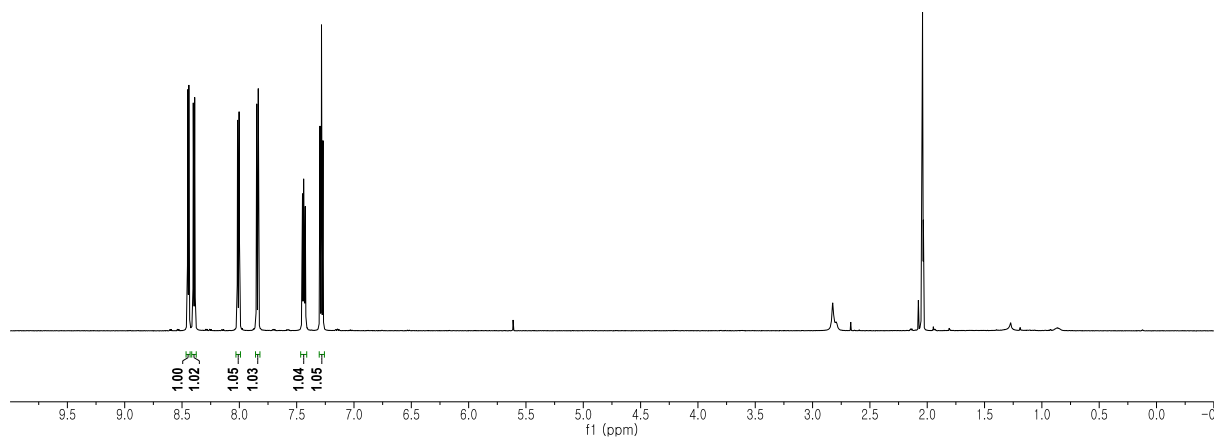
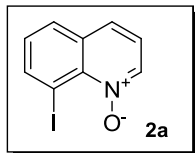


### 3-Formylquinoline N-oxide (Table 3, 1q)

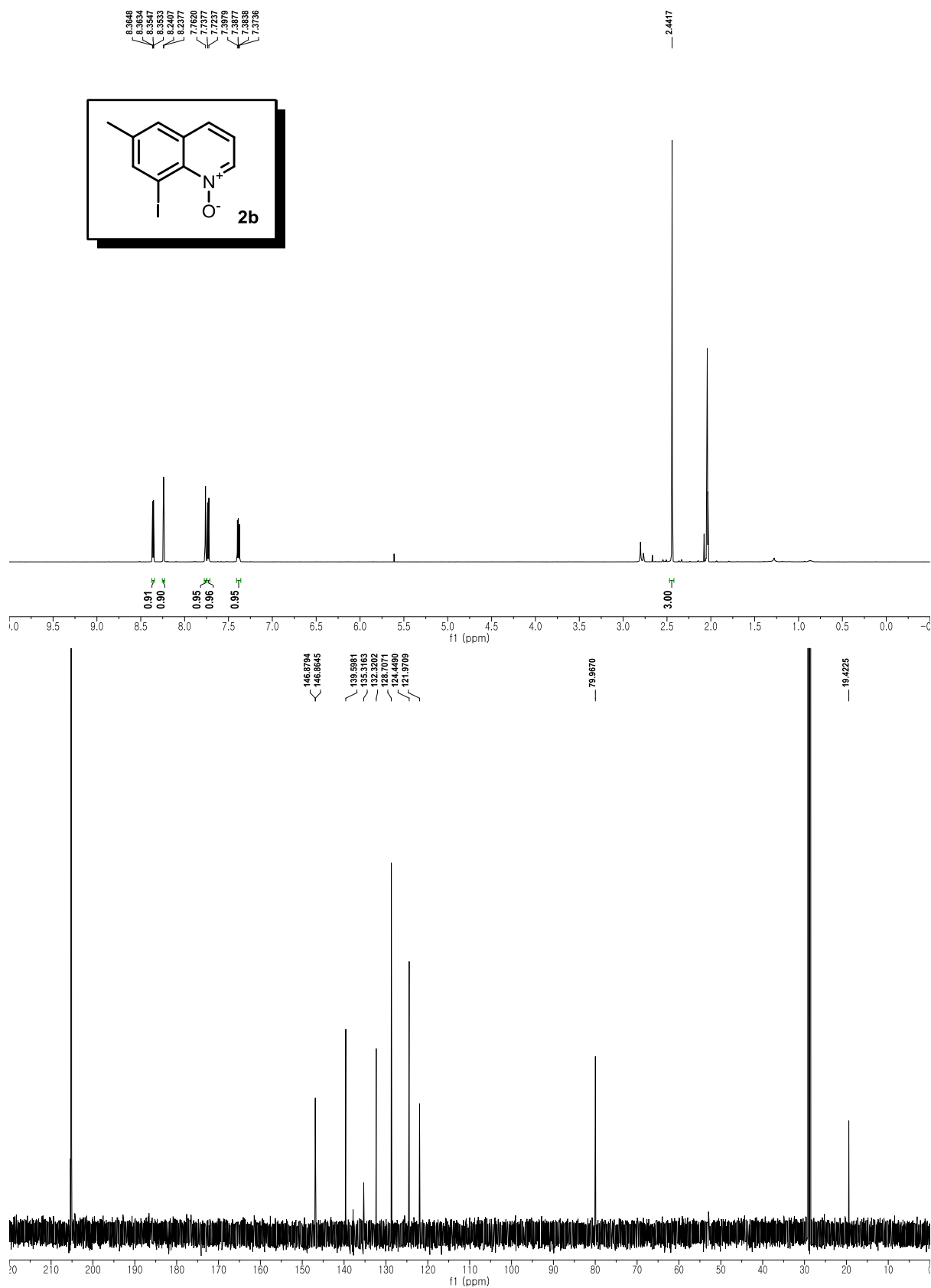


# 8-Iodoquinoline N-oxide (Table 1, 2a)

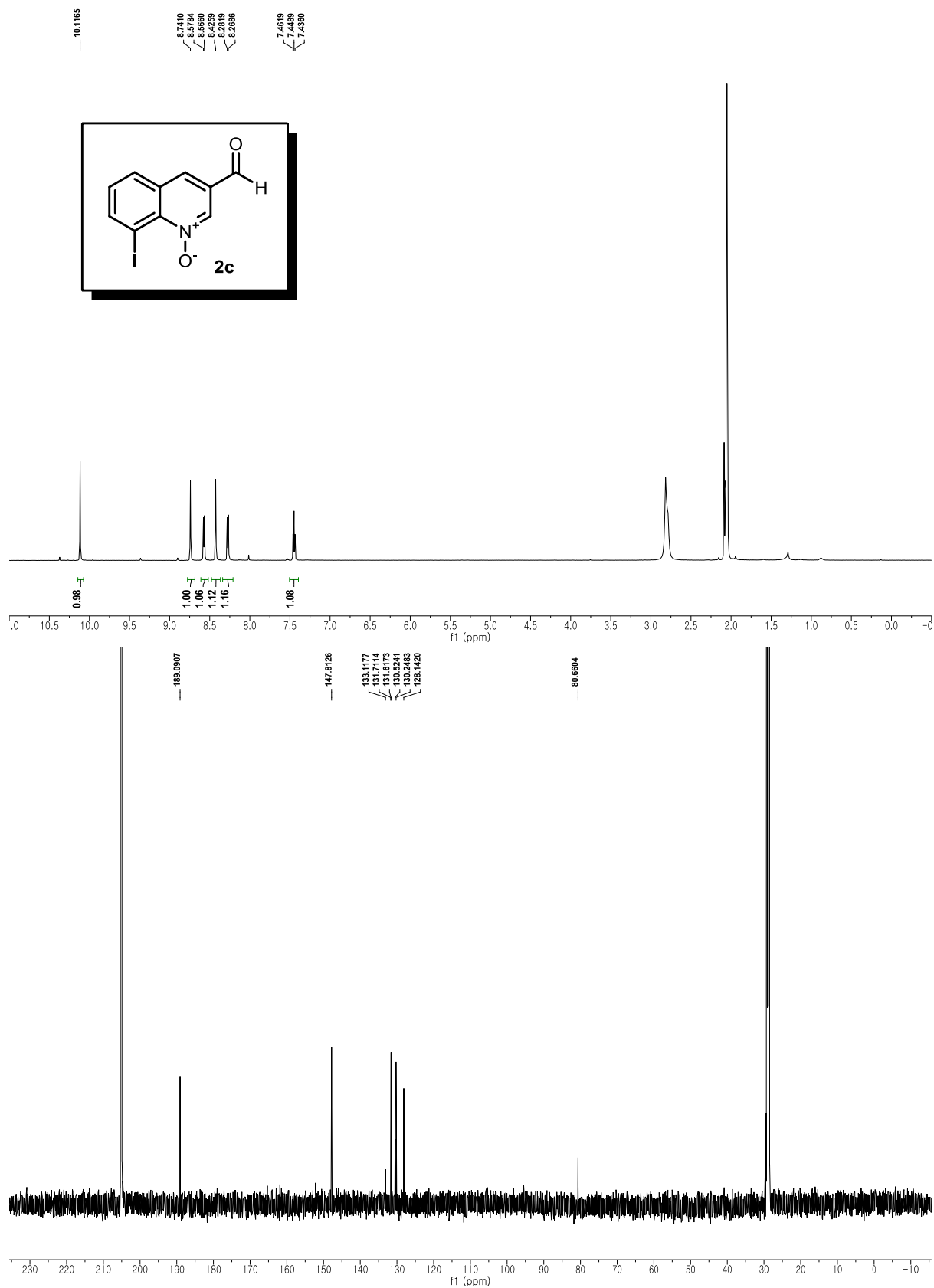
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# 8-Iodo-6-methylquinoline N-oxide (Table 1, 2b)

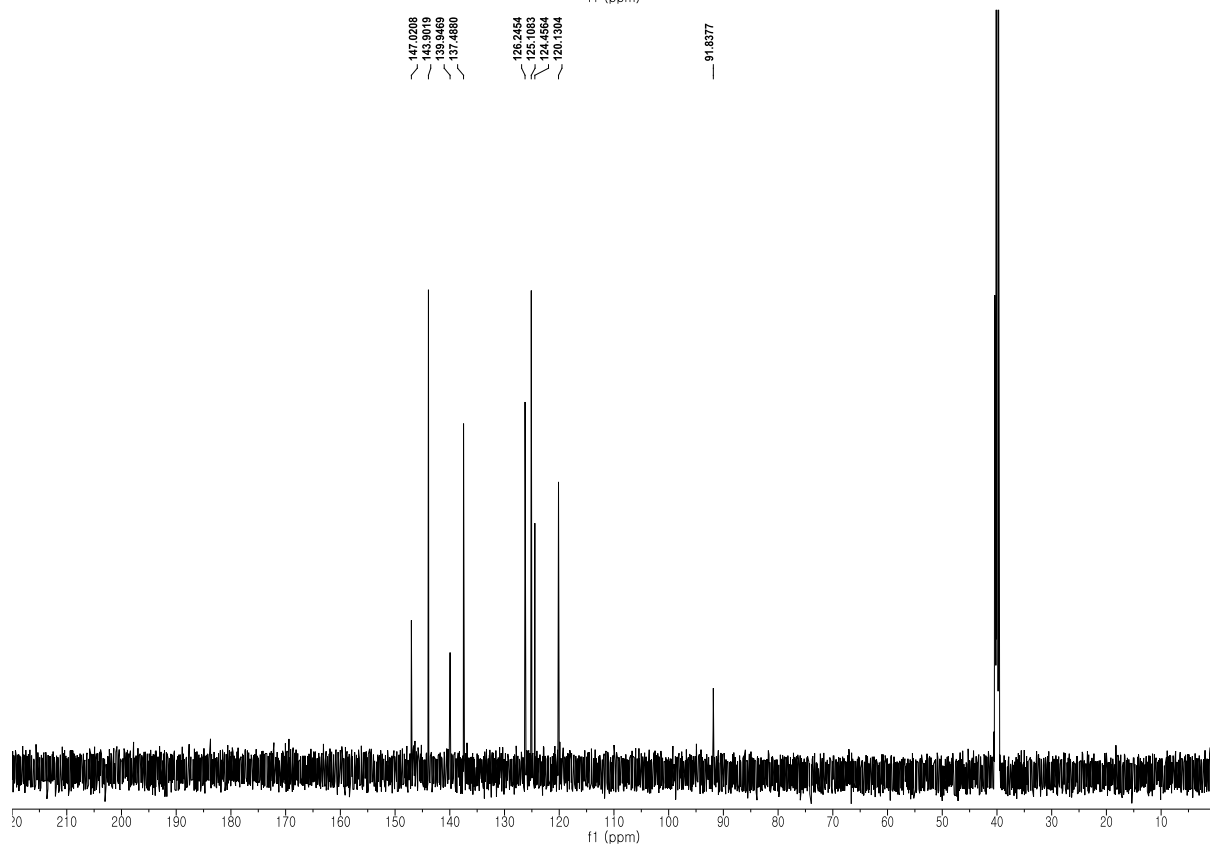
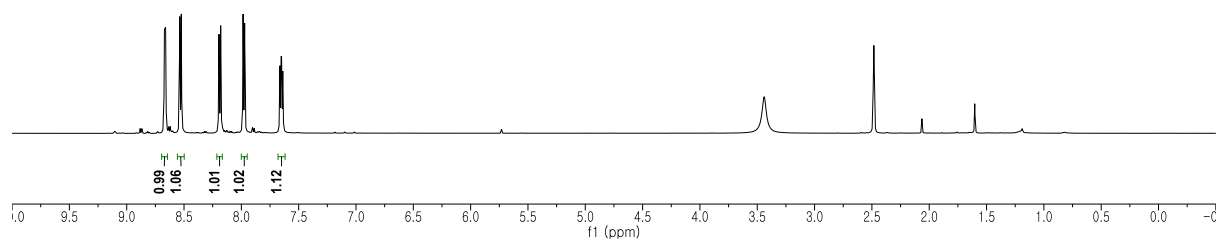
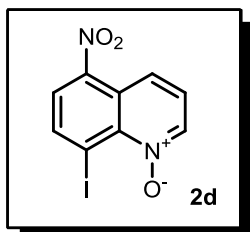


### 3-Formyl-8-iodoquinoline *N*-oxide (Table 1, 2c)

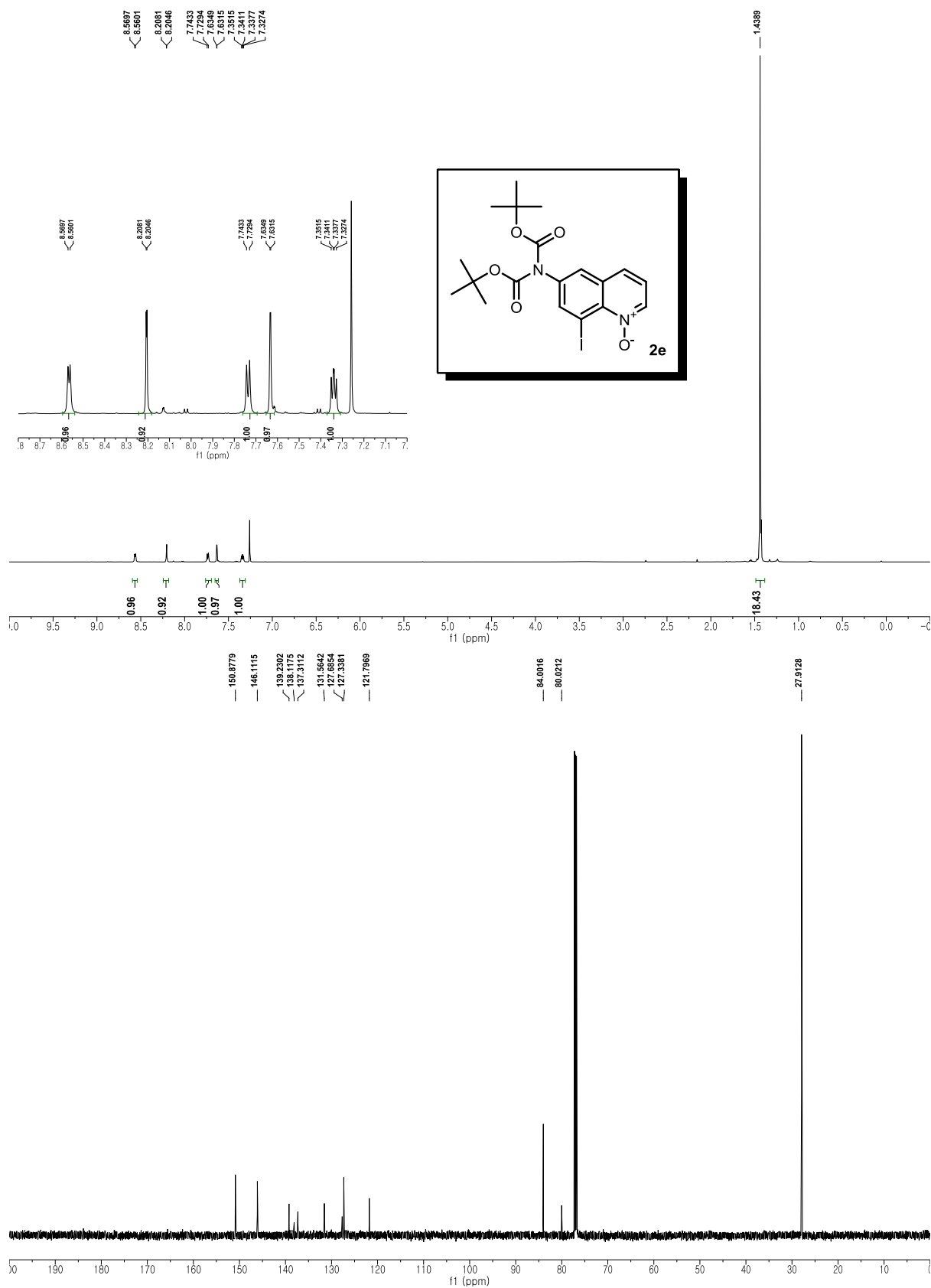


# 8-Iodo-5-nitroquinoline N-oxide (Table 1, 2d)

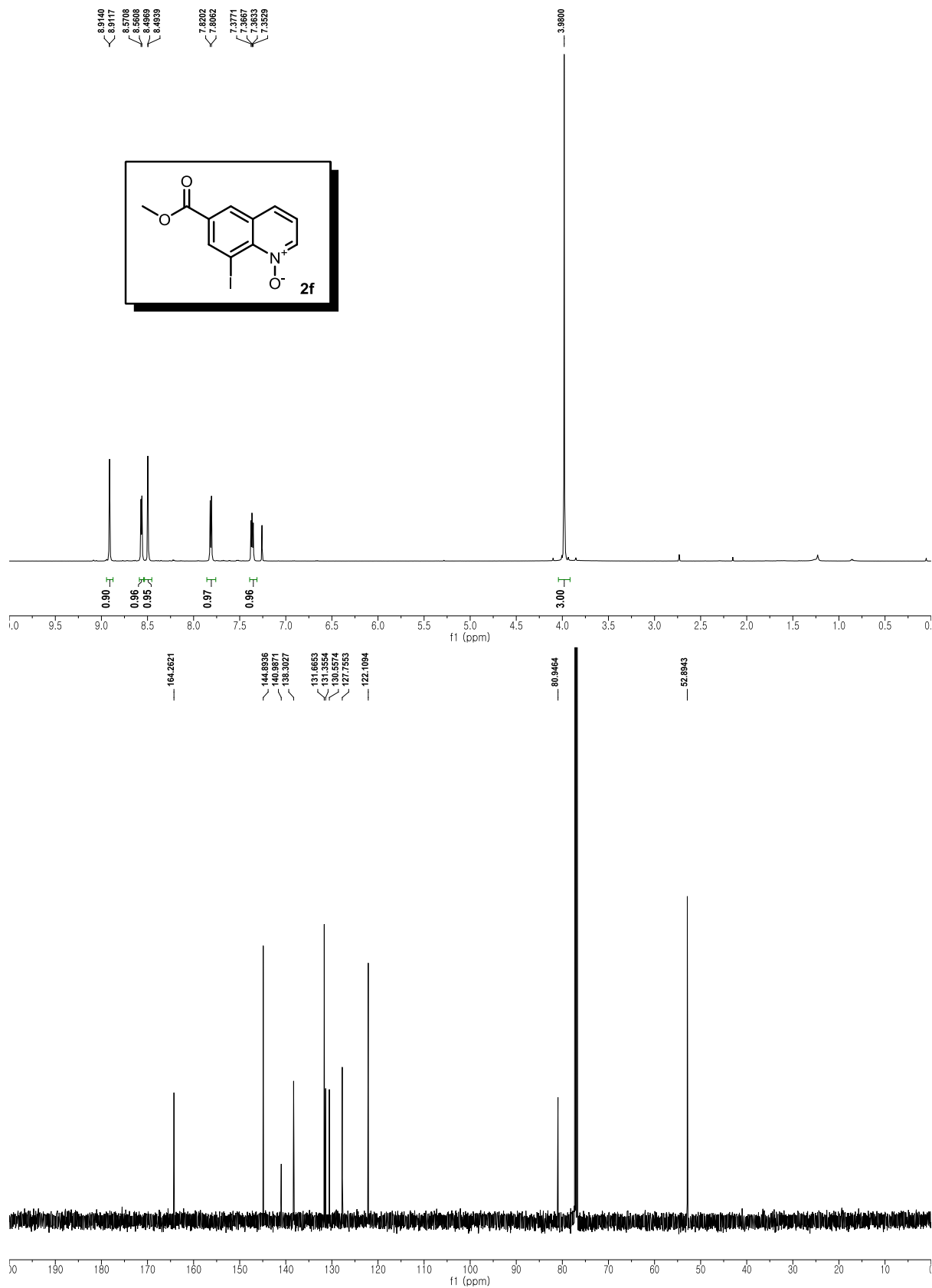
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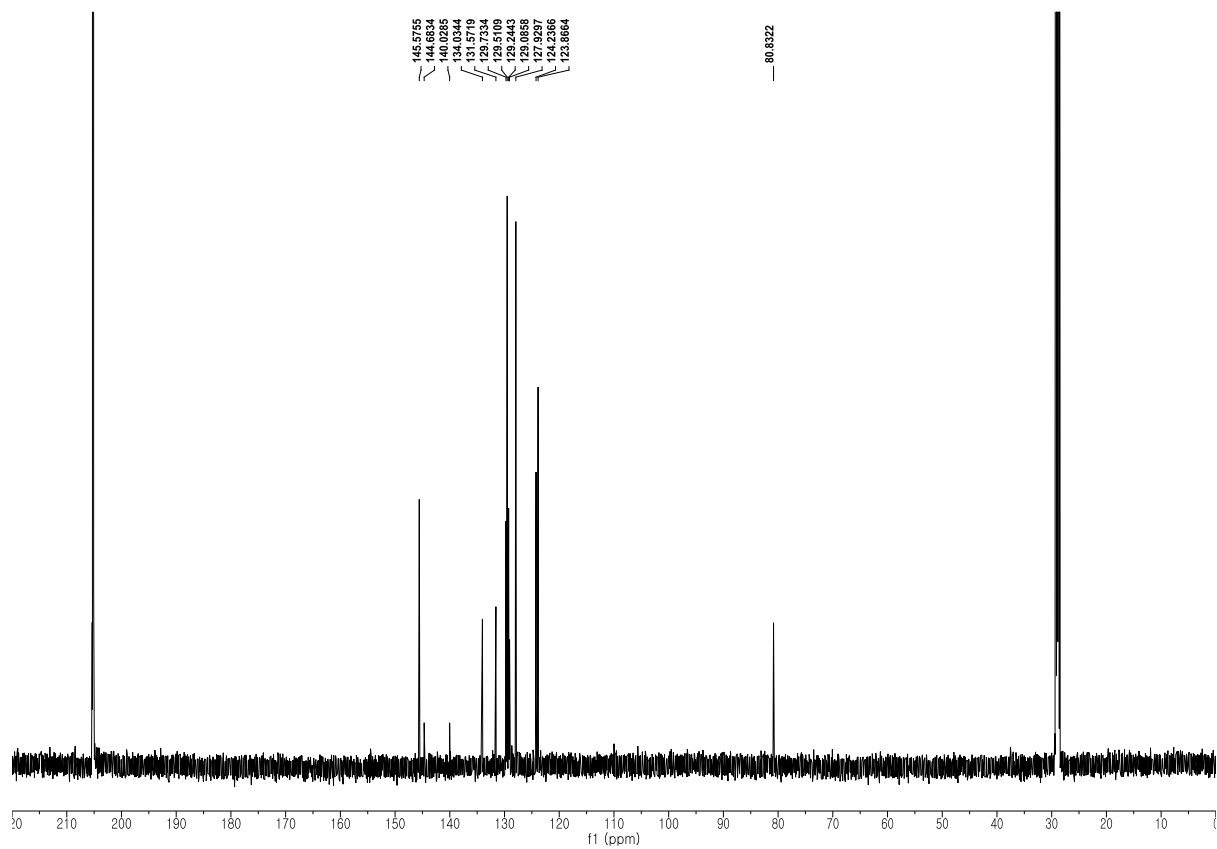
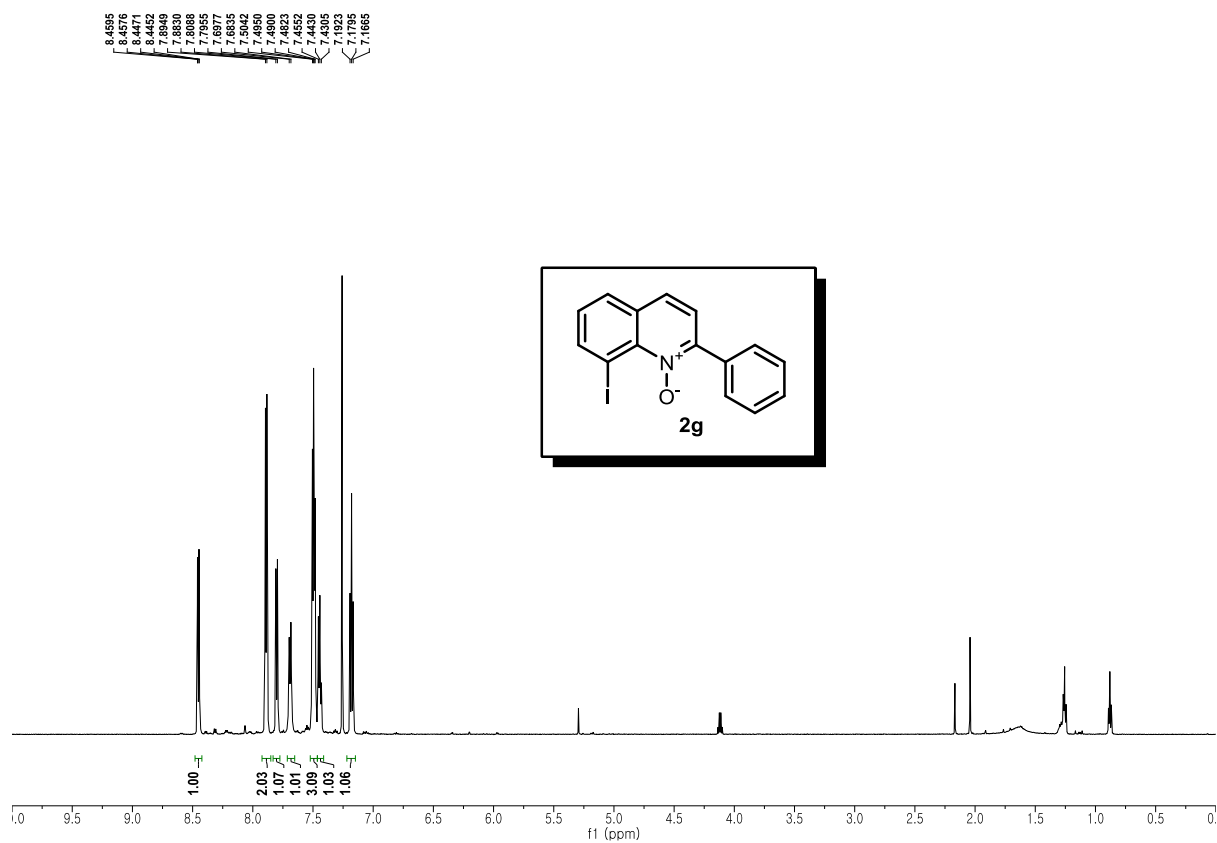
**6-[Bis(*tert*-butoxycarbonyl)amino]-8-iodoquinoline *N*-oxide (Table 1, 2e)**



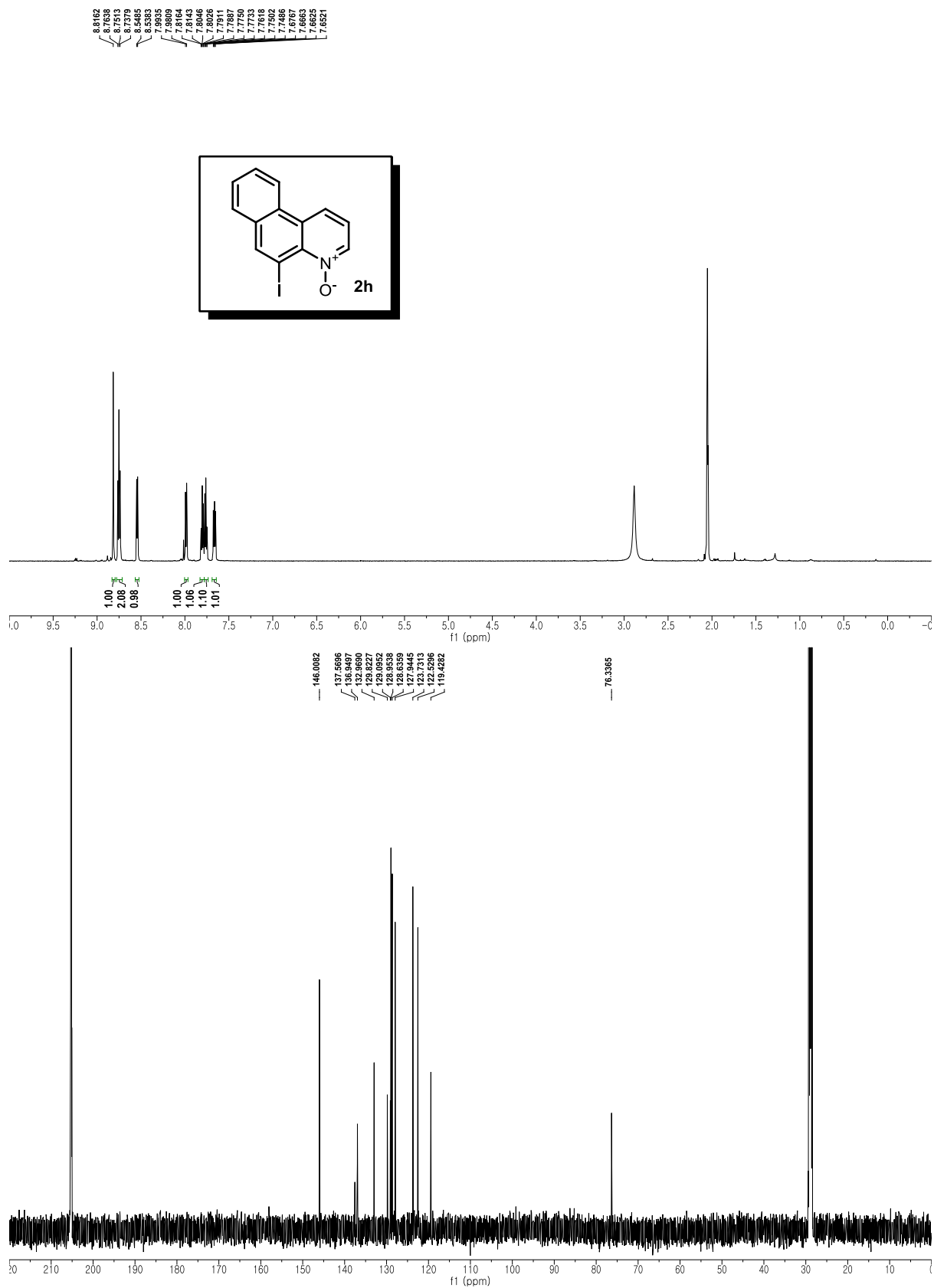
# 8-Iodo-6-(methoxycarbonyl)quinoline *N*-oxide (Table 1, 2f)



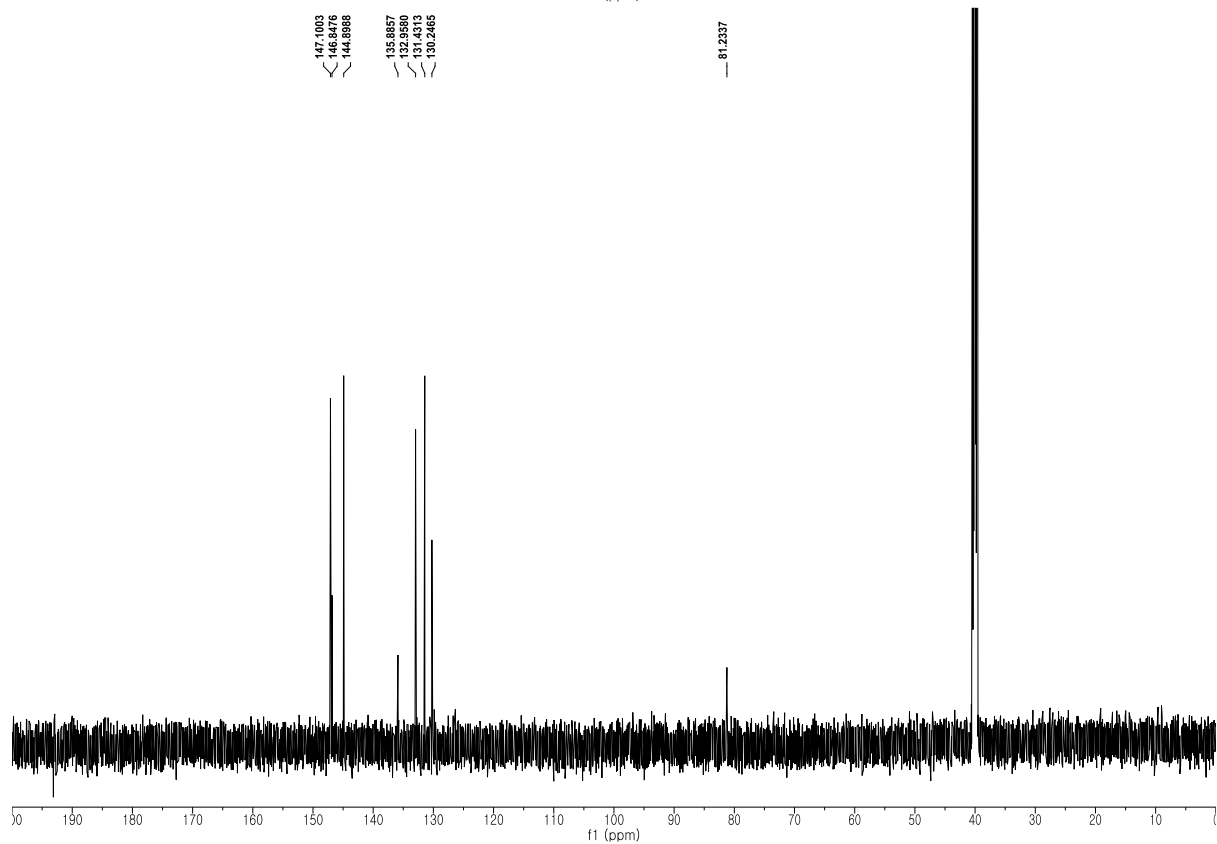
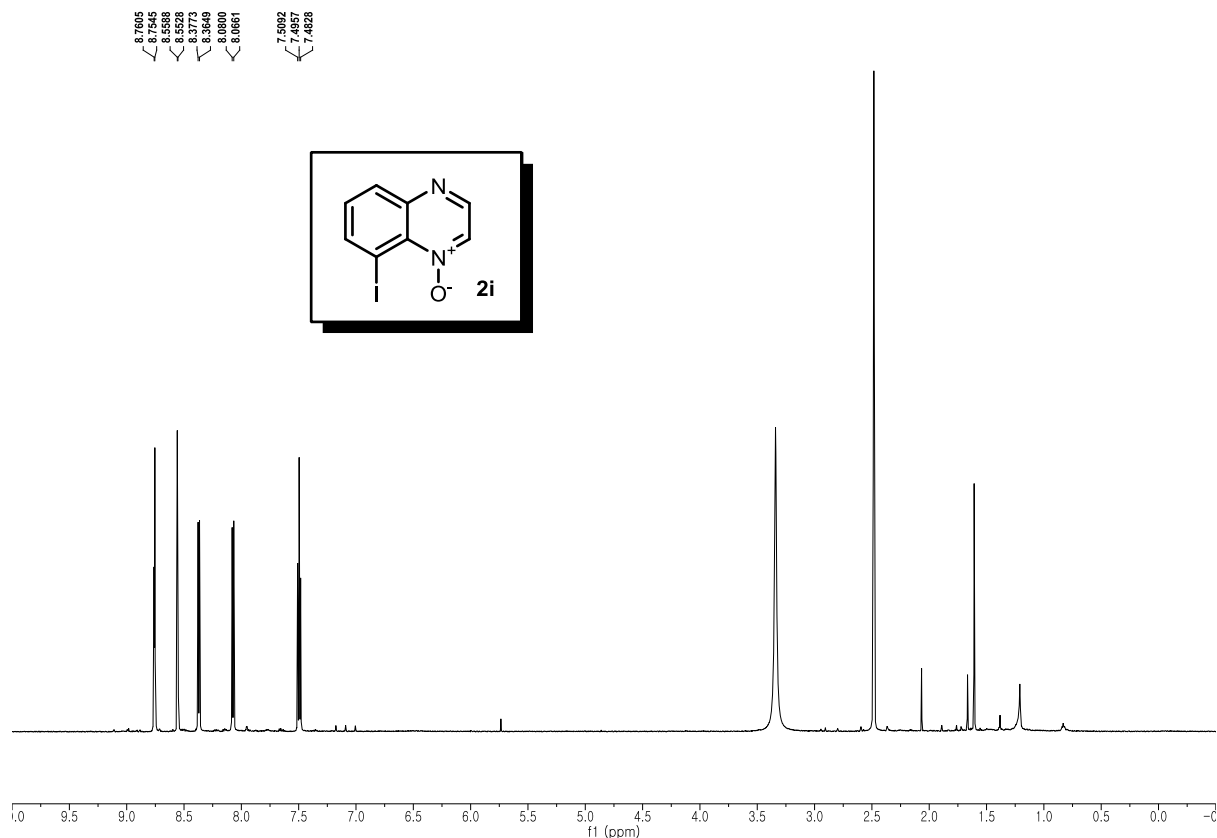
# 8-Iodo-2-phenylquinoline *N*-oxide (Table 1, 2g)



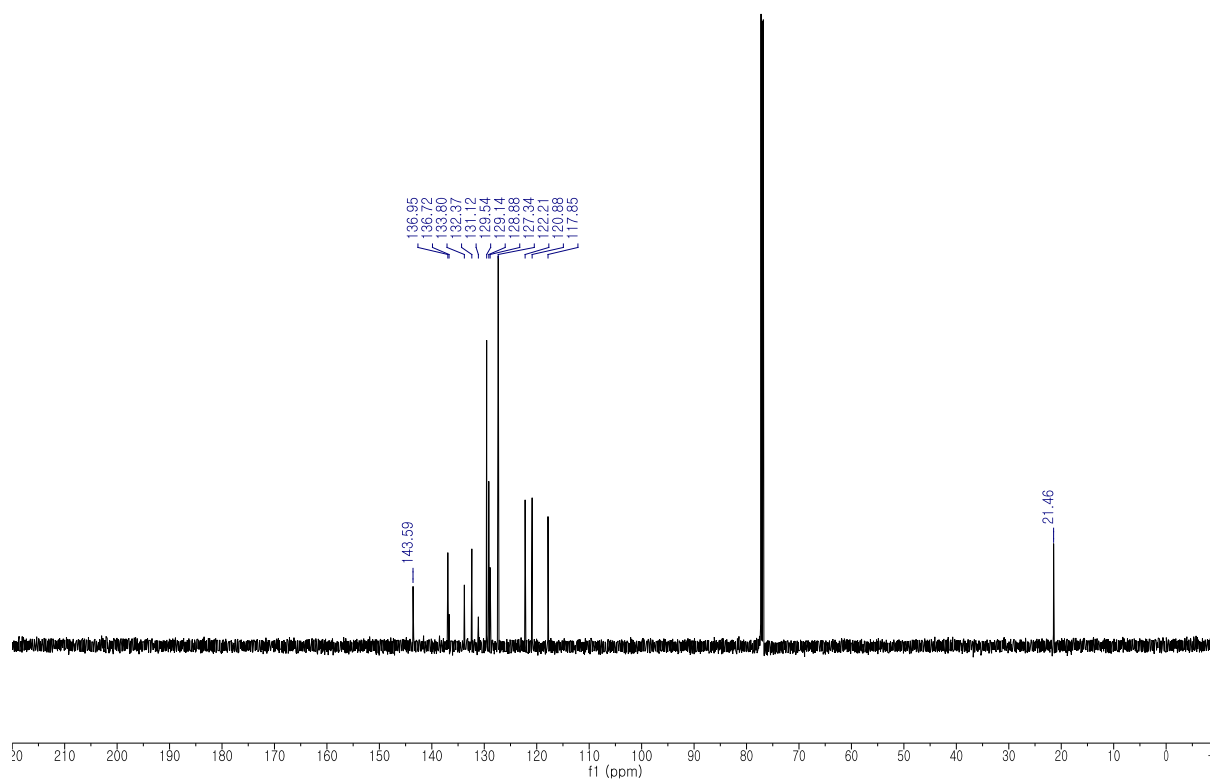
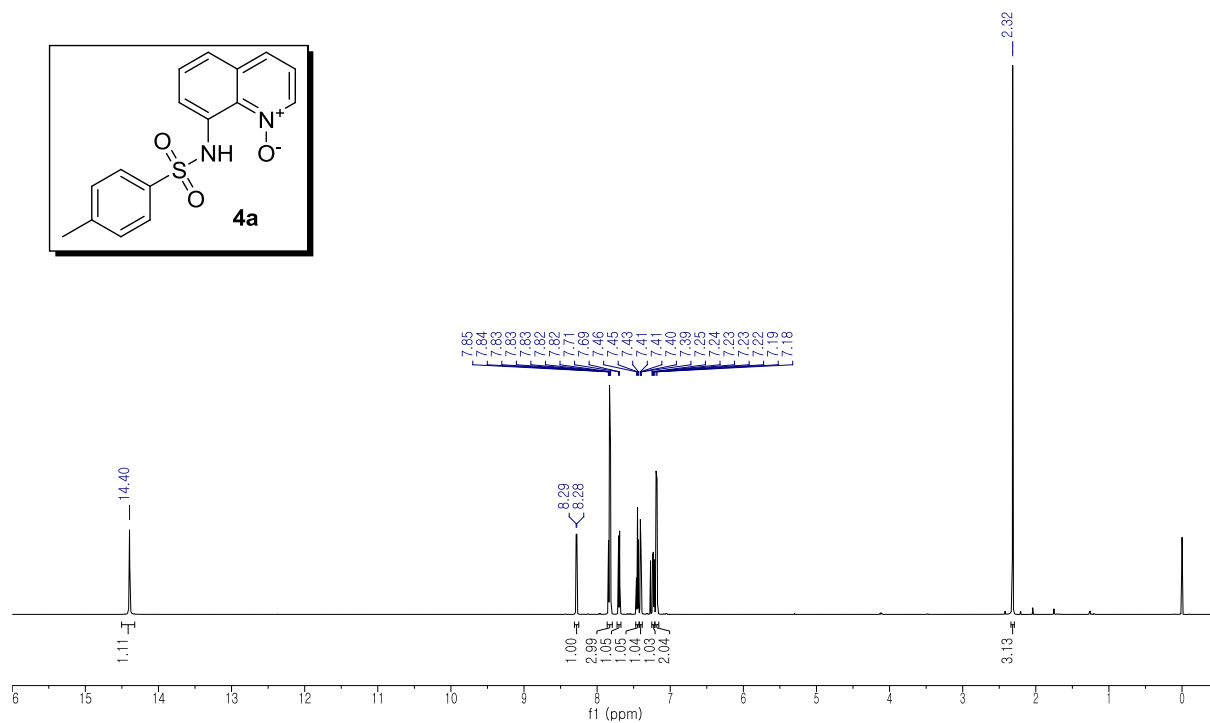
# 5-Iodobenzo[*f*]quinoline *N*-oxide (Table 1, 2h)



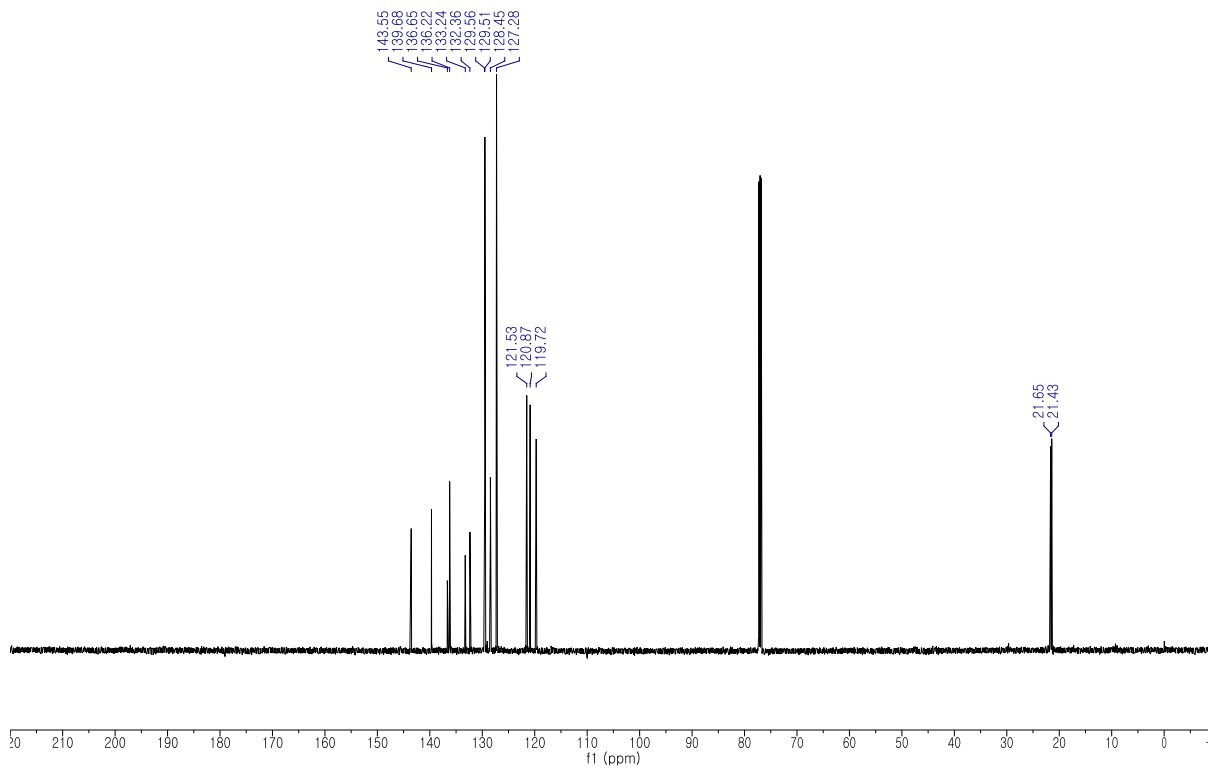
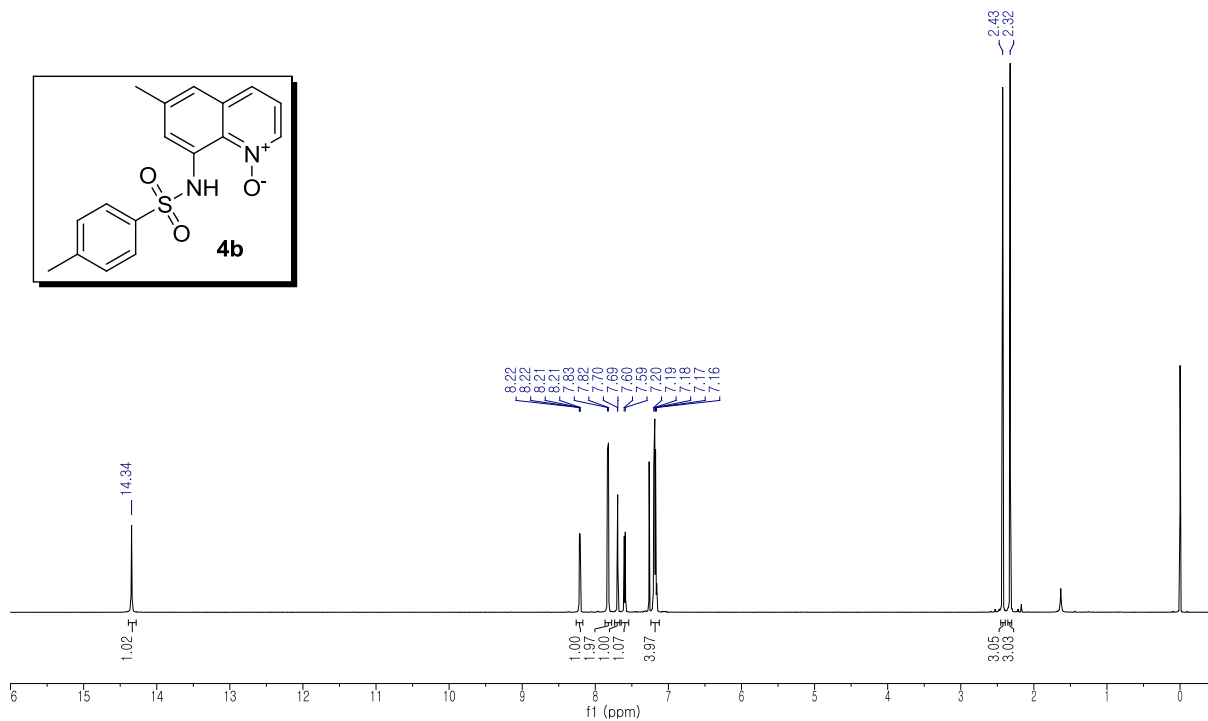
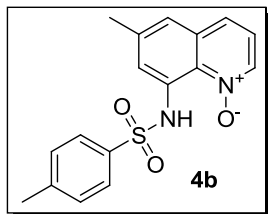
# 8-Iodoquinoxaline Noxide (Table 1, 2i)



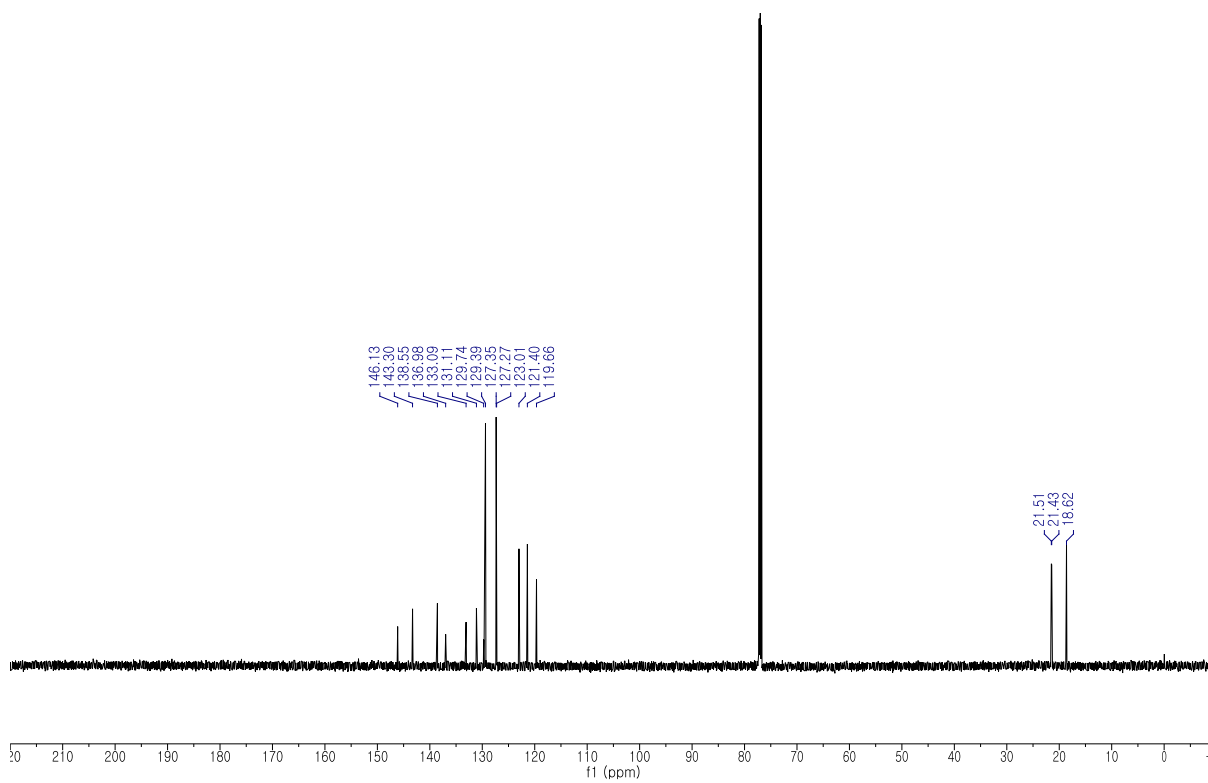
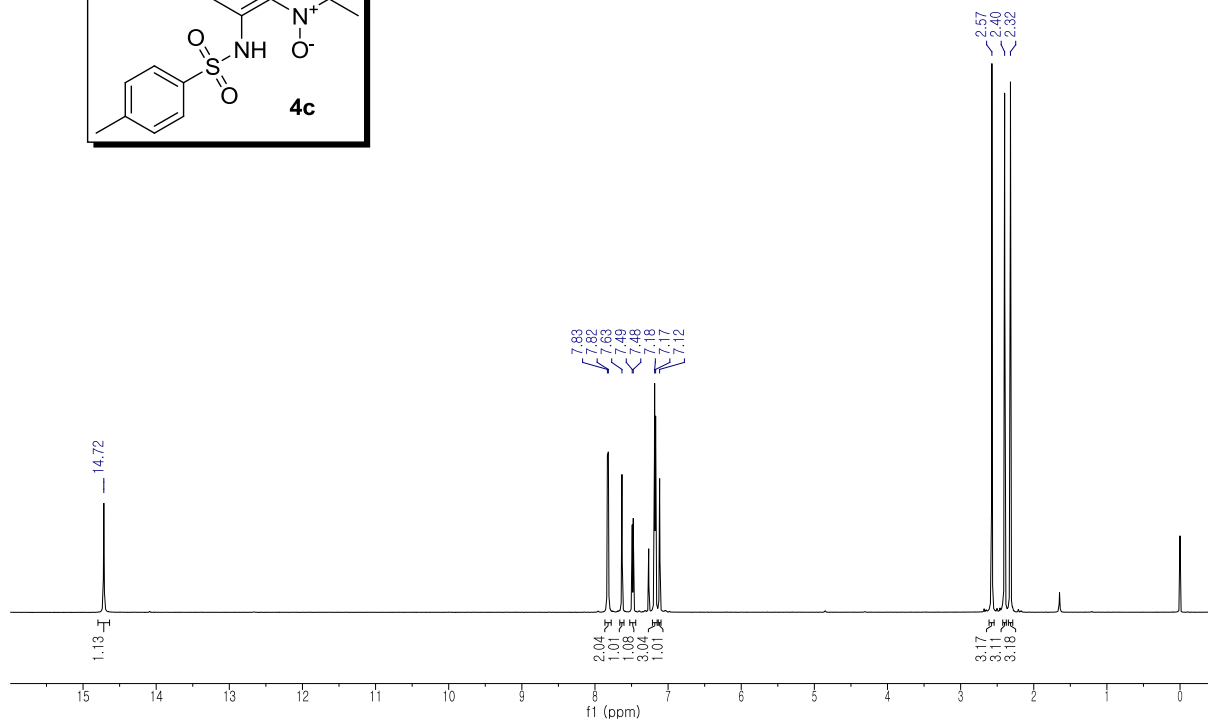
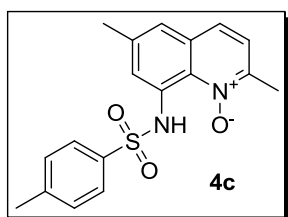
### 8-(4-Methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4a)



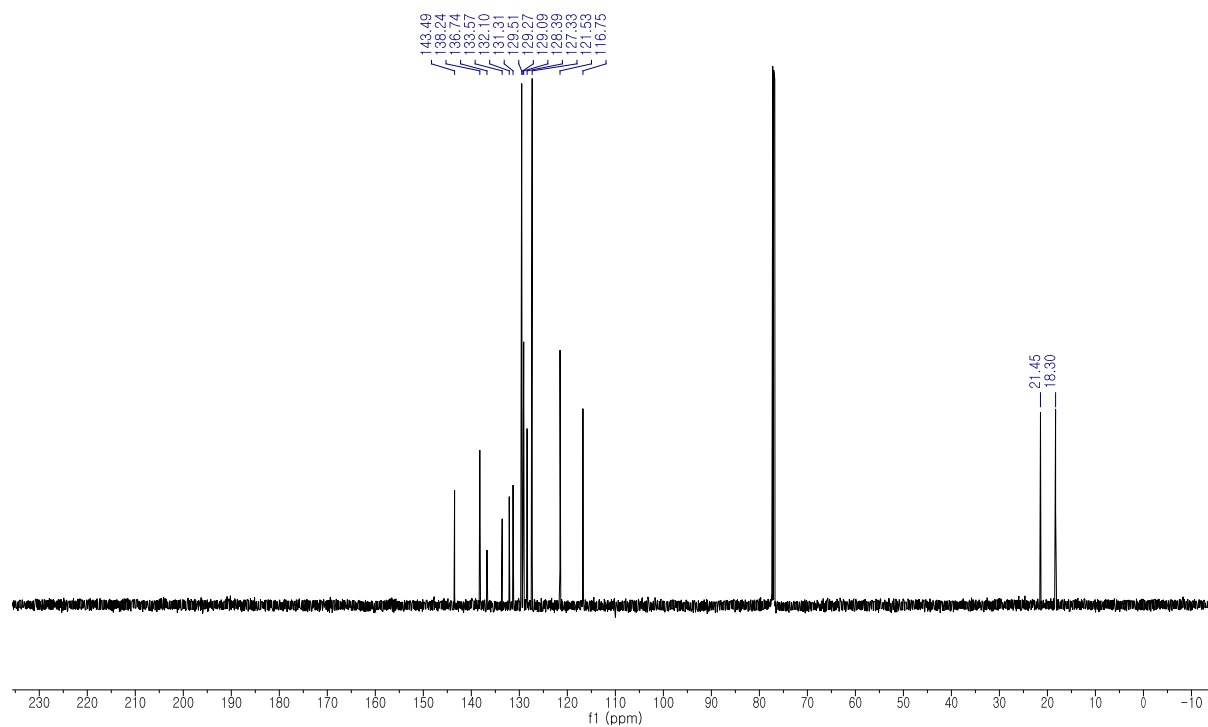
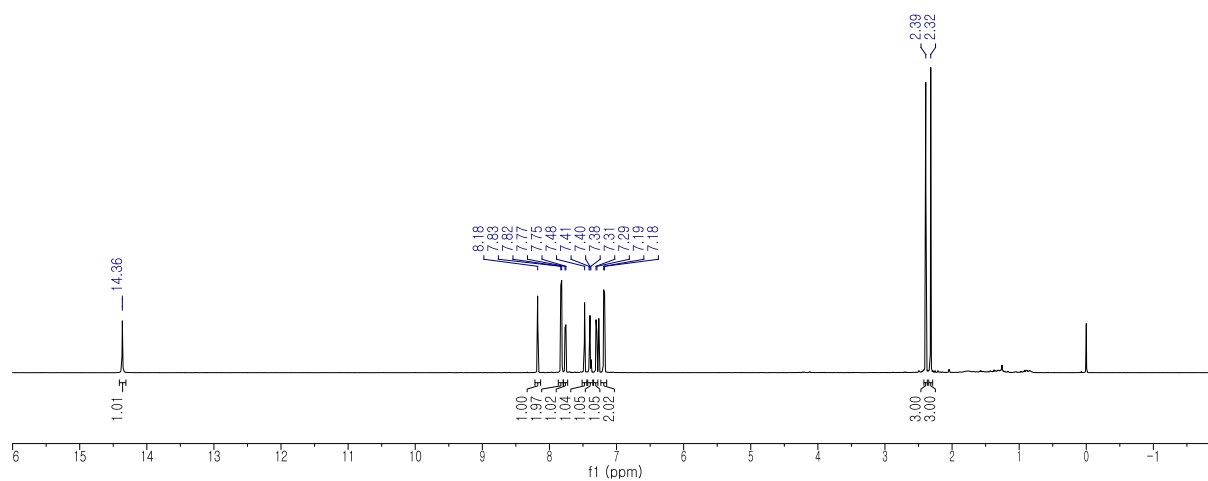
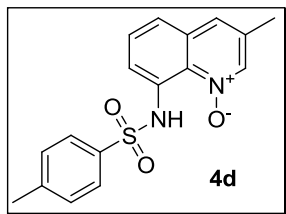
6-Methyl-8-(4-methylphenylsulfonamido)quinoline N-oxide (Table 3, 4b)



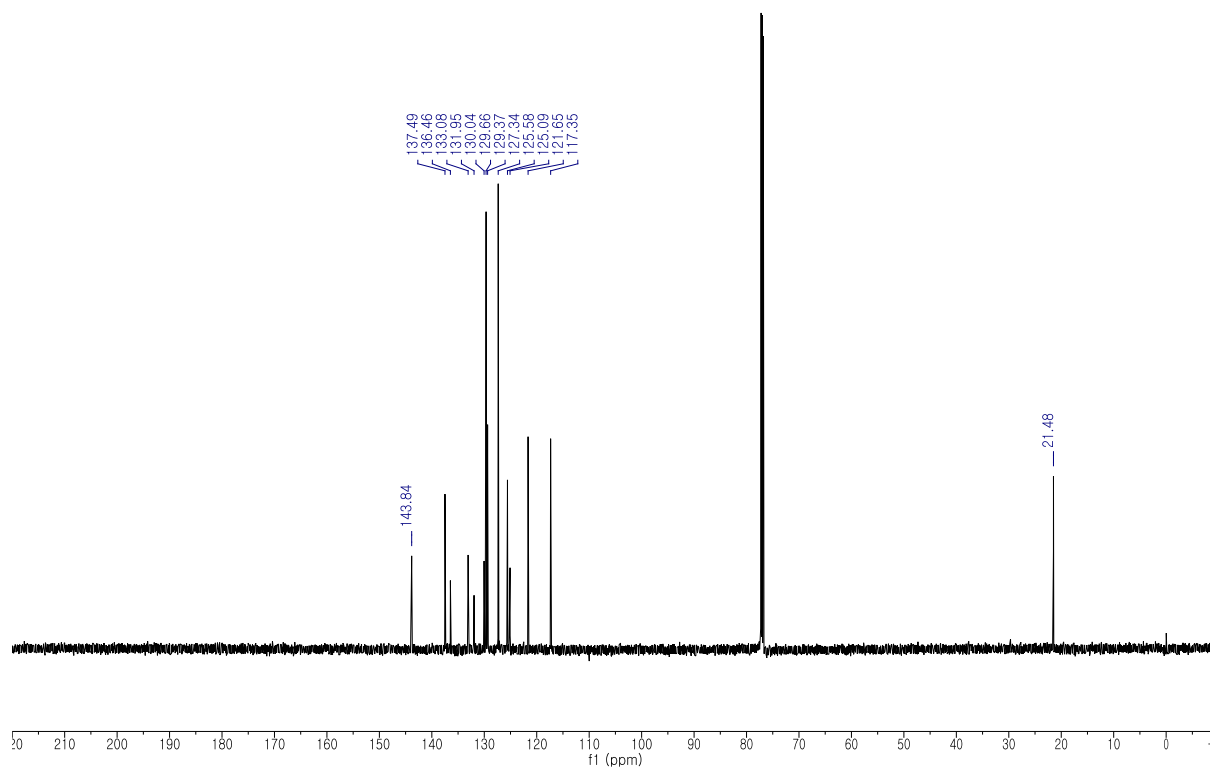
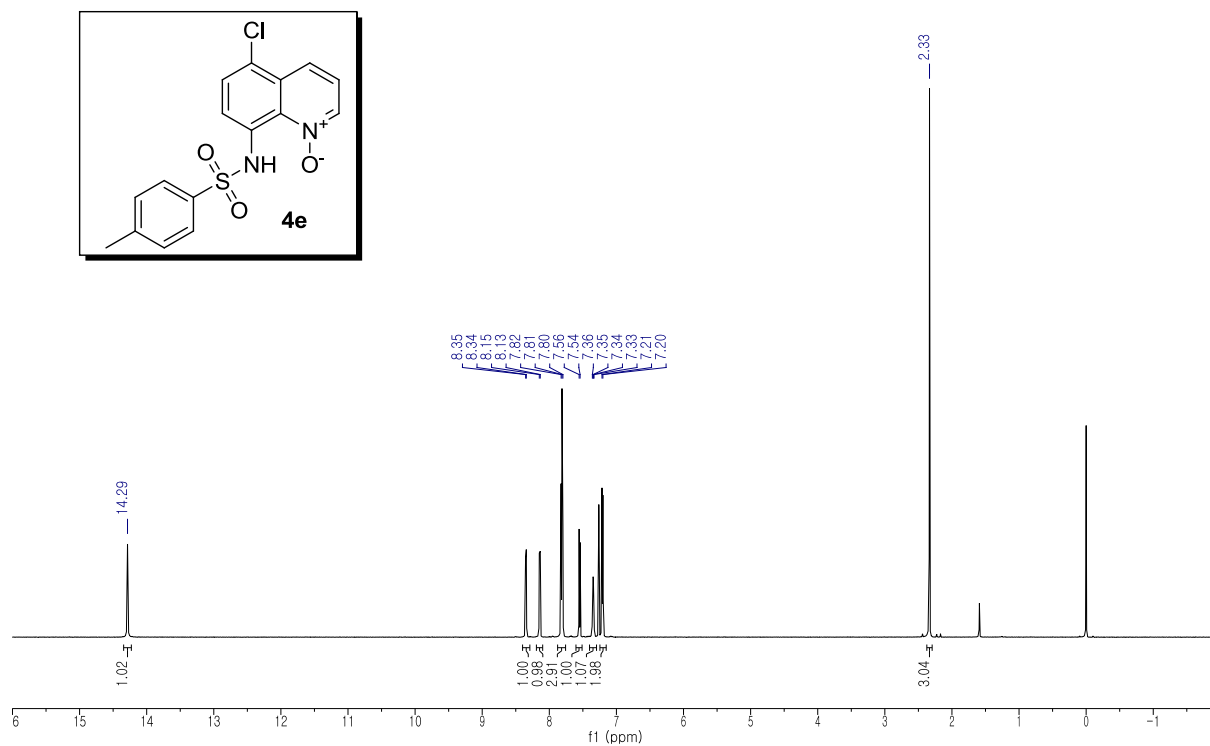
## 2,6-Dimethyl-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4c)



### 3-Methyl-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4d)

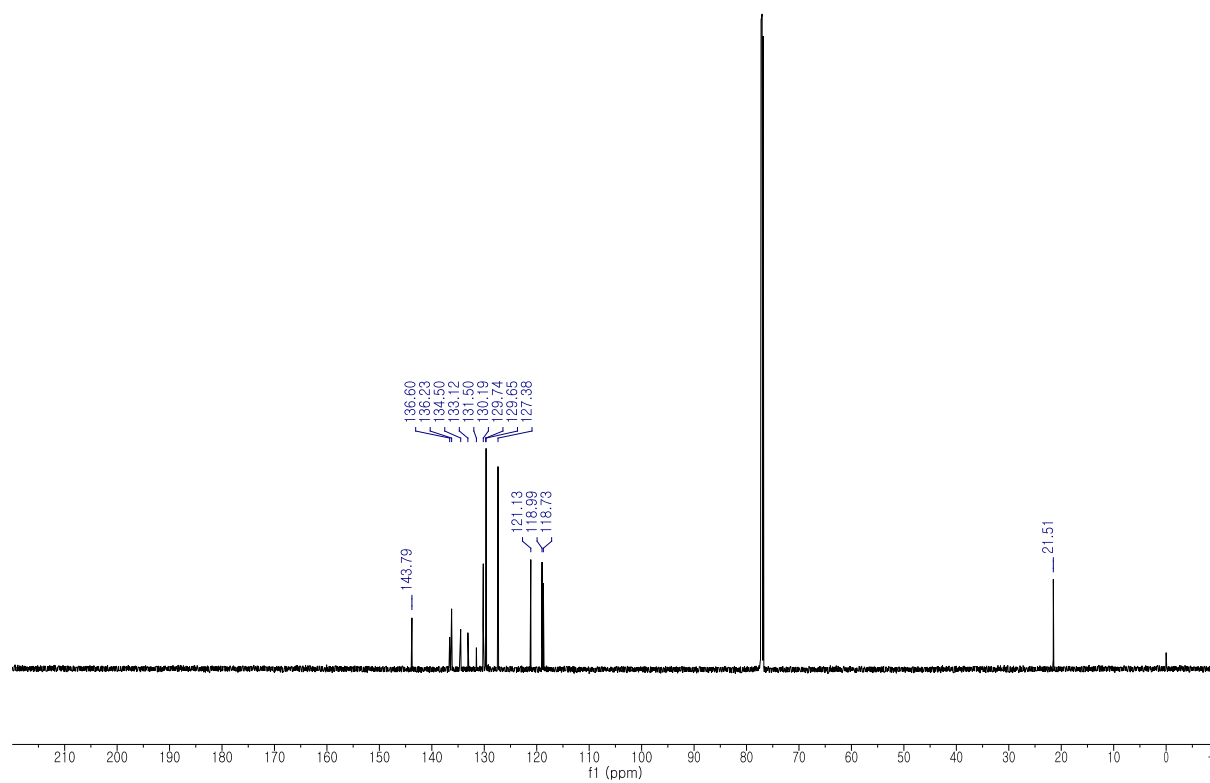
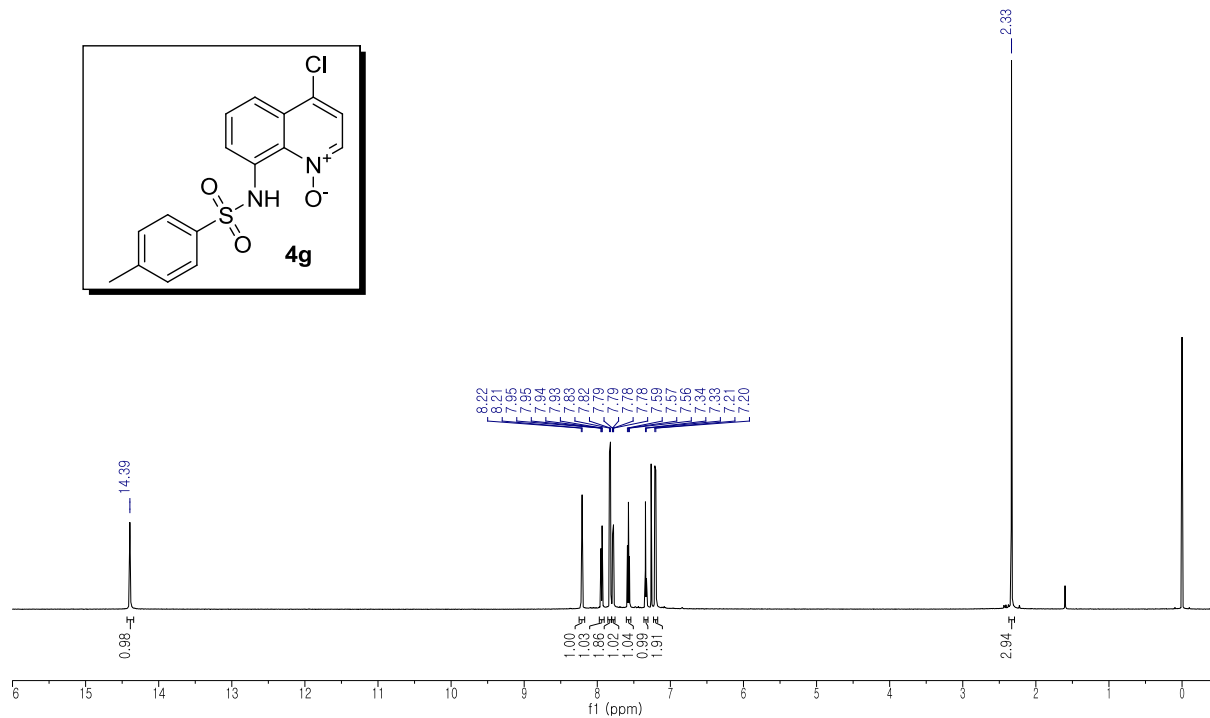
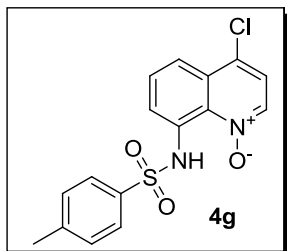


### 5-Chloro-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4e)

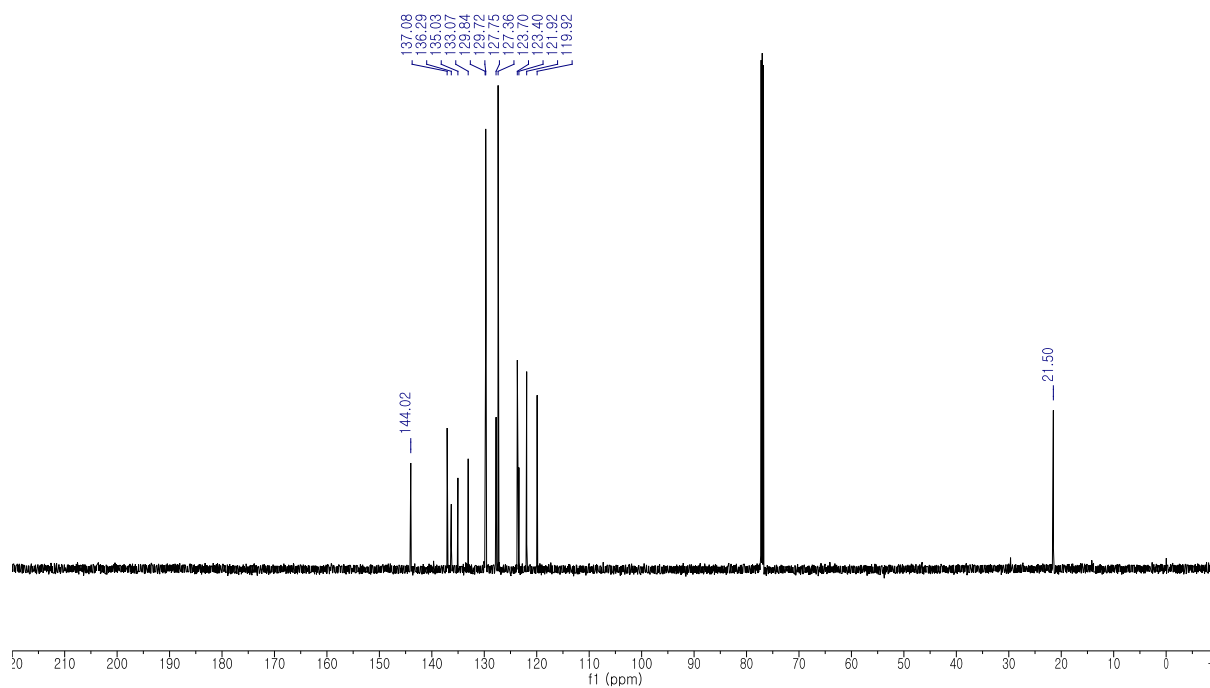
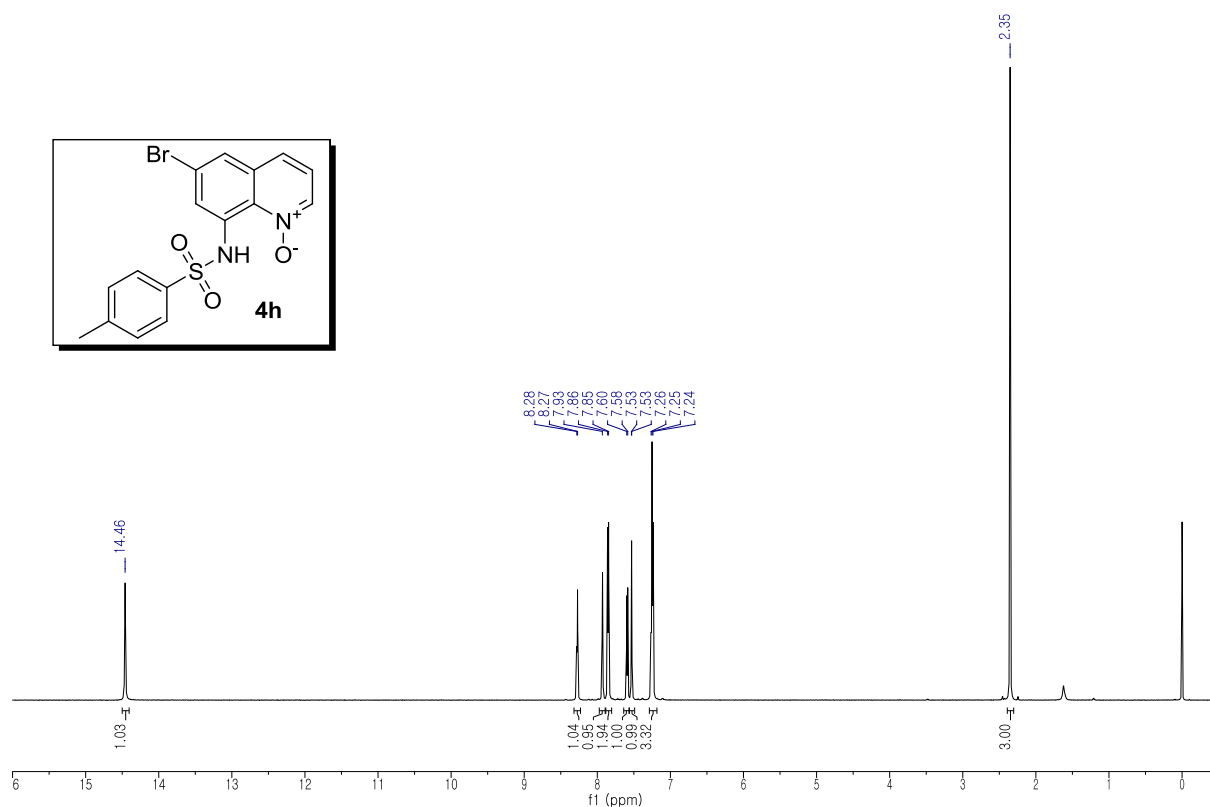




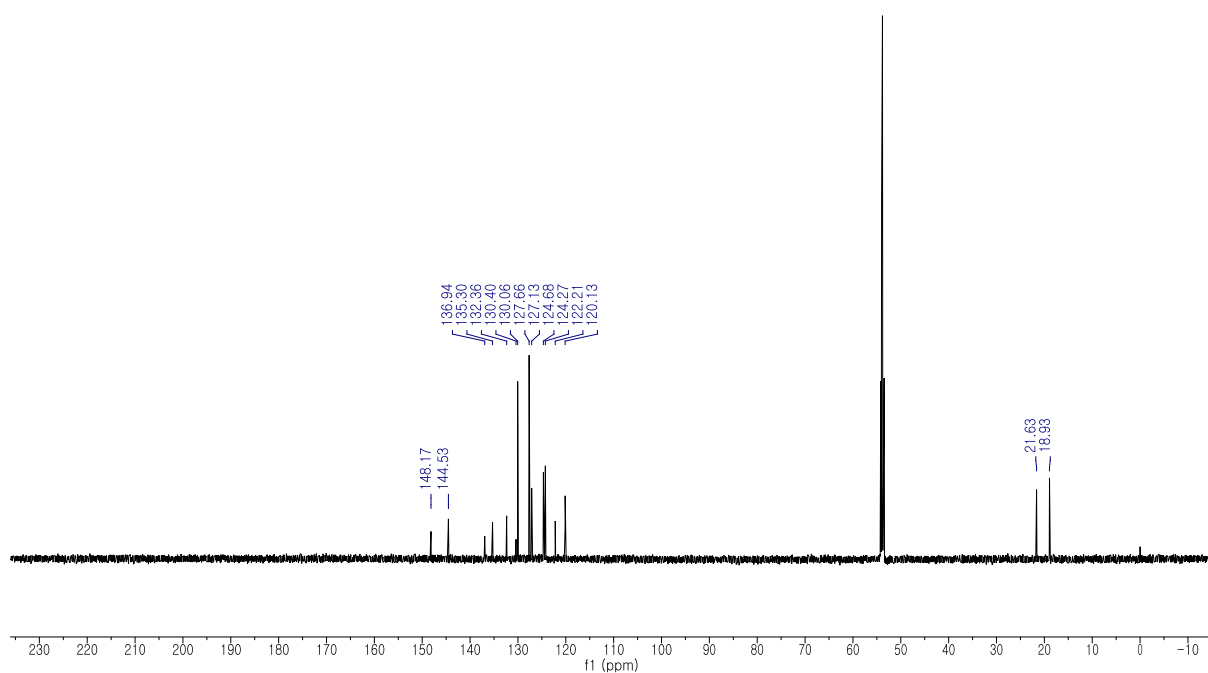
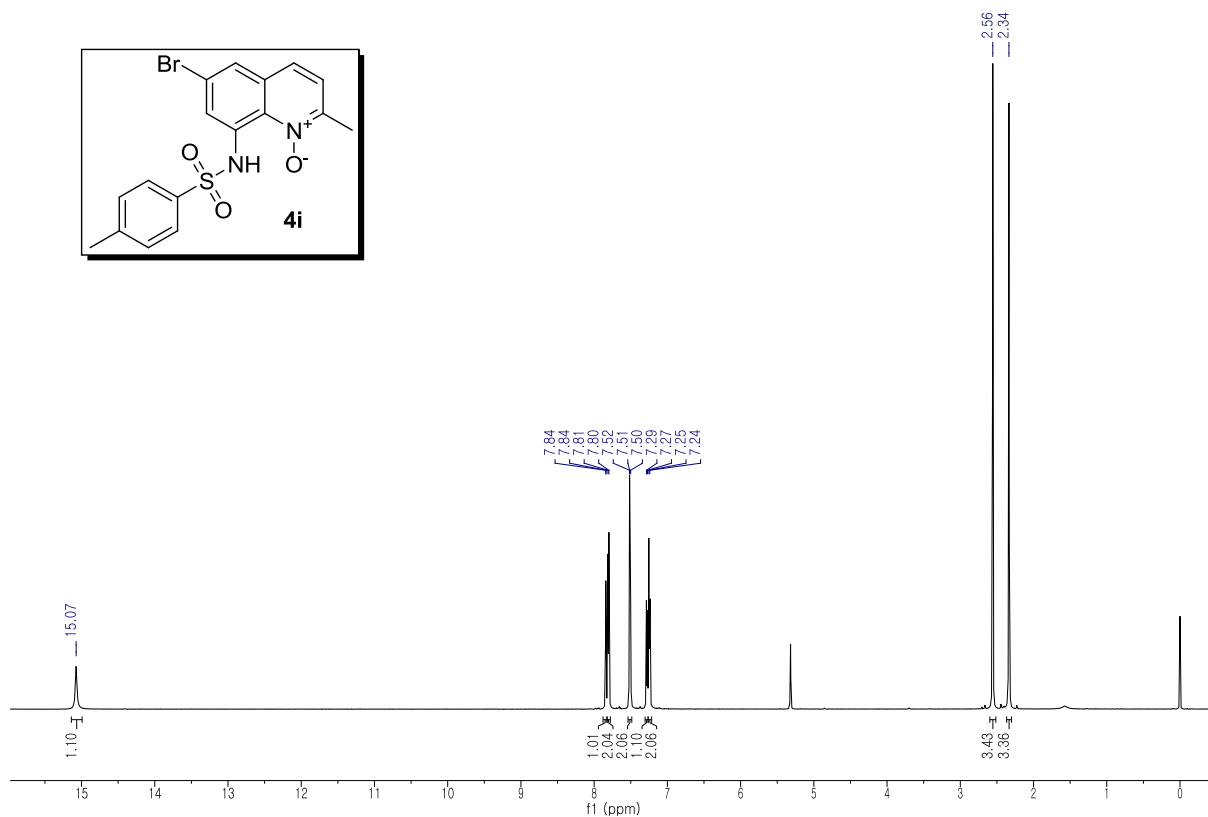
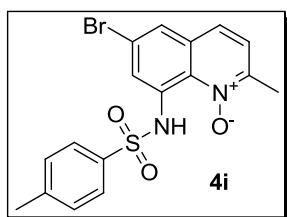
### 4-Chloro-8-(4-methylphenylsulfonamido)quinoline N-oxide (Table 3, 4g)



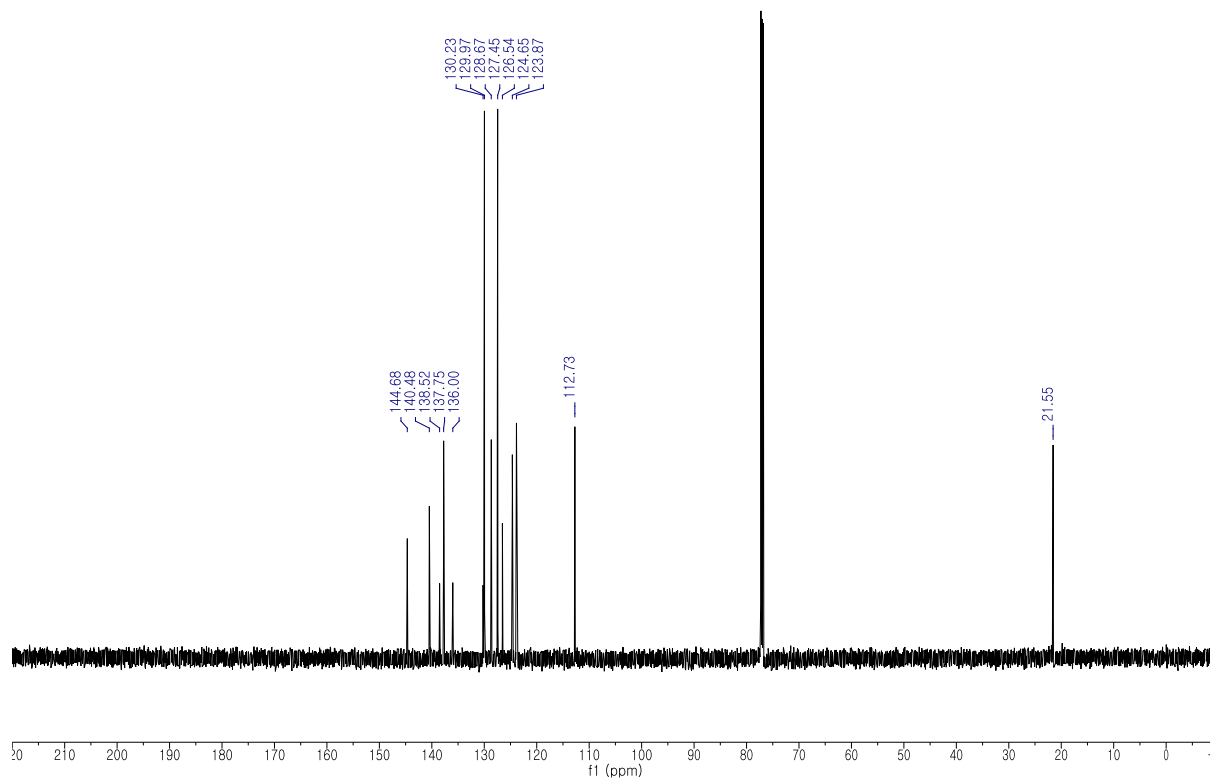
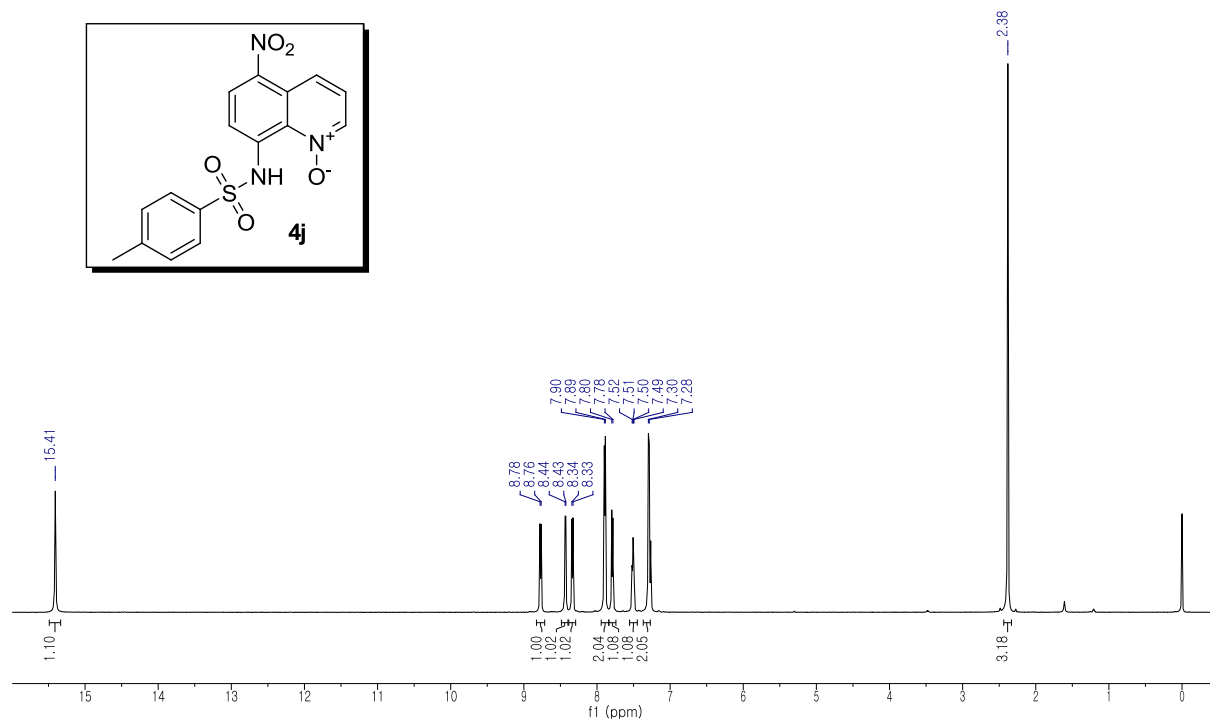
**6-Bromo-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4h)**



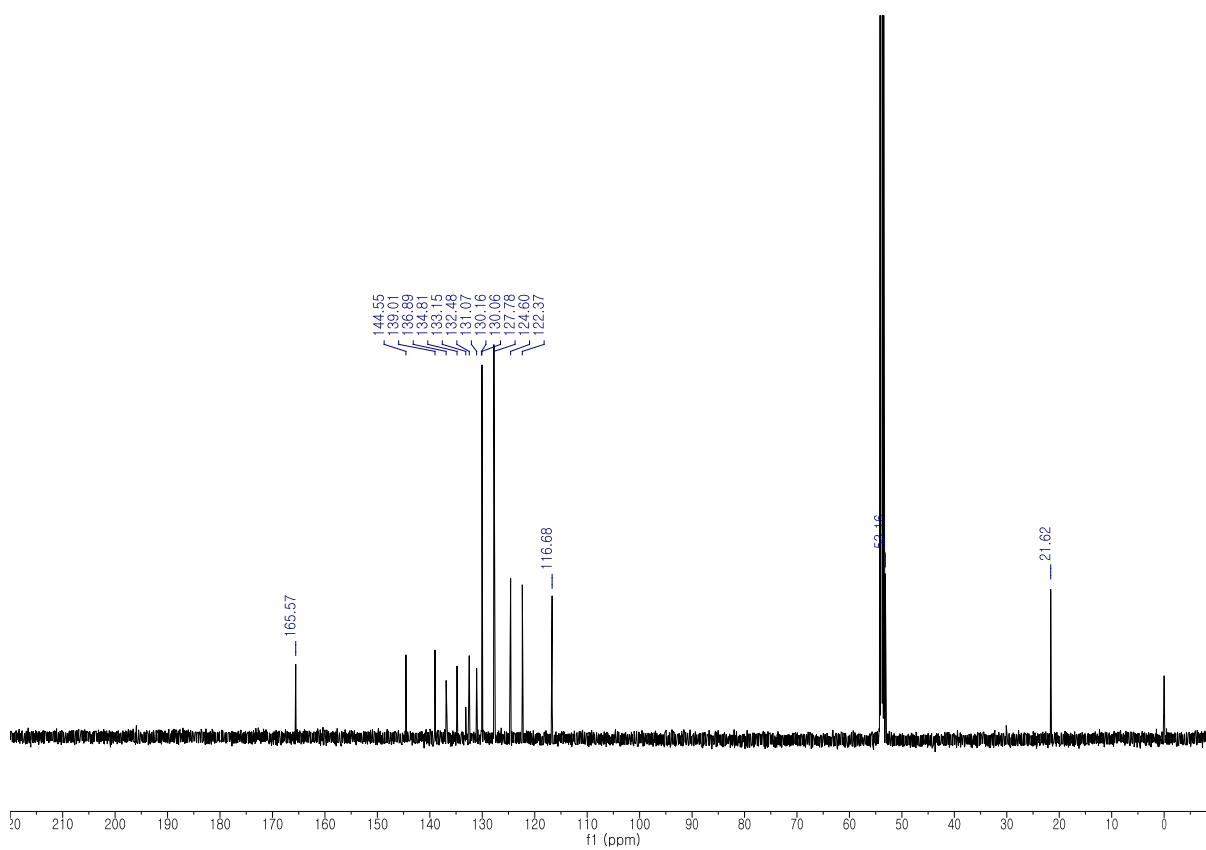
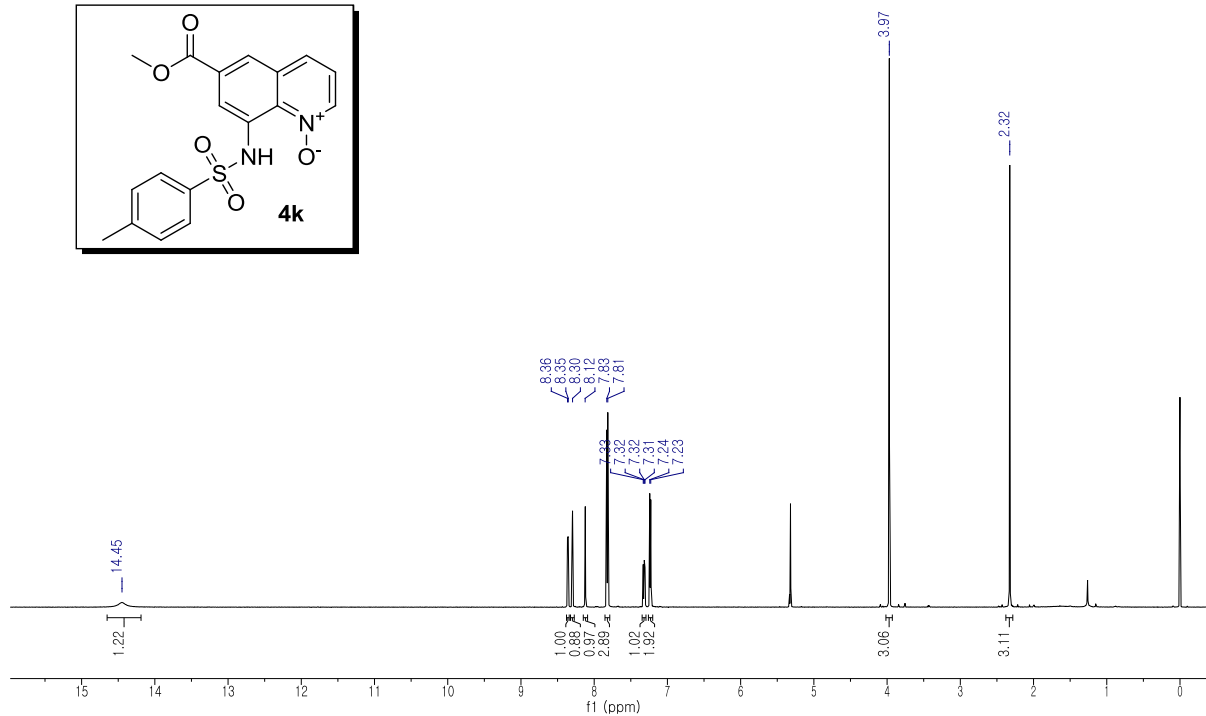
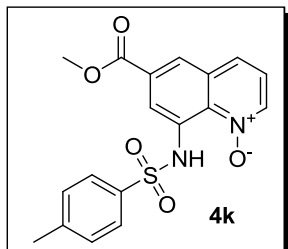
**6-Bromo-2-methyl-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4i)**



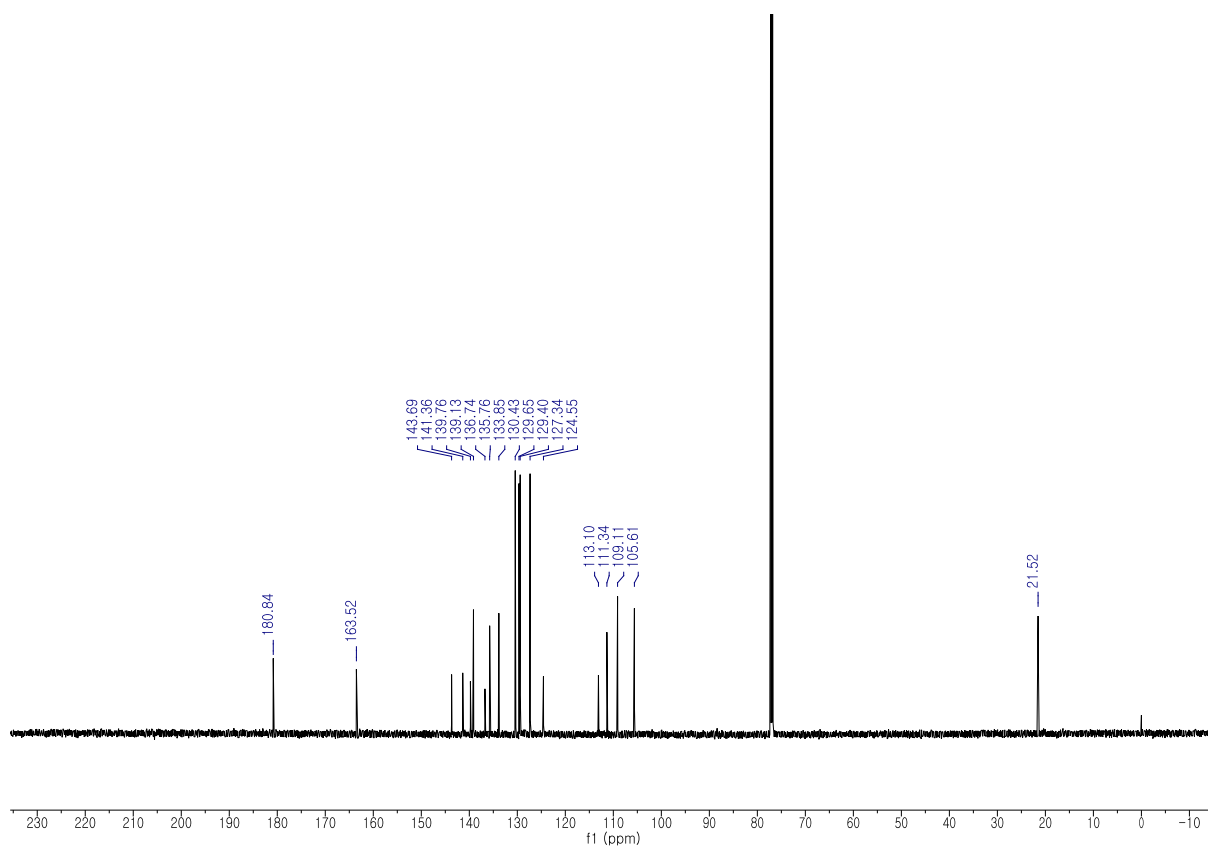
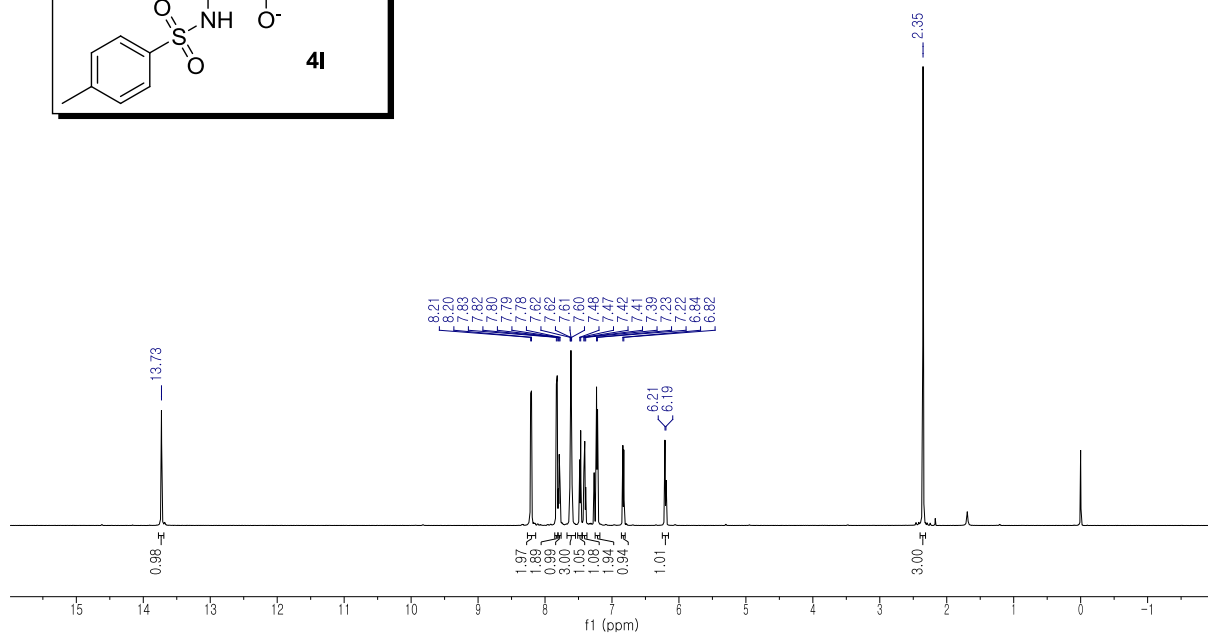
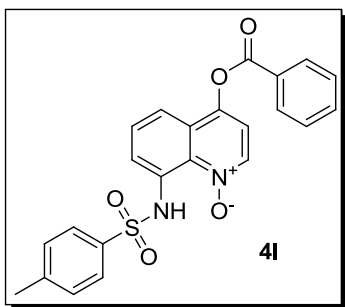
**8-(4-Methylphenylsulfonamido)-5-nitroquinoline *N*-oxide (Table 3, 4j)**



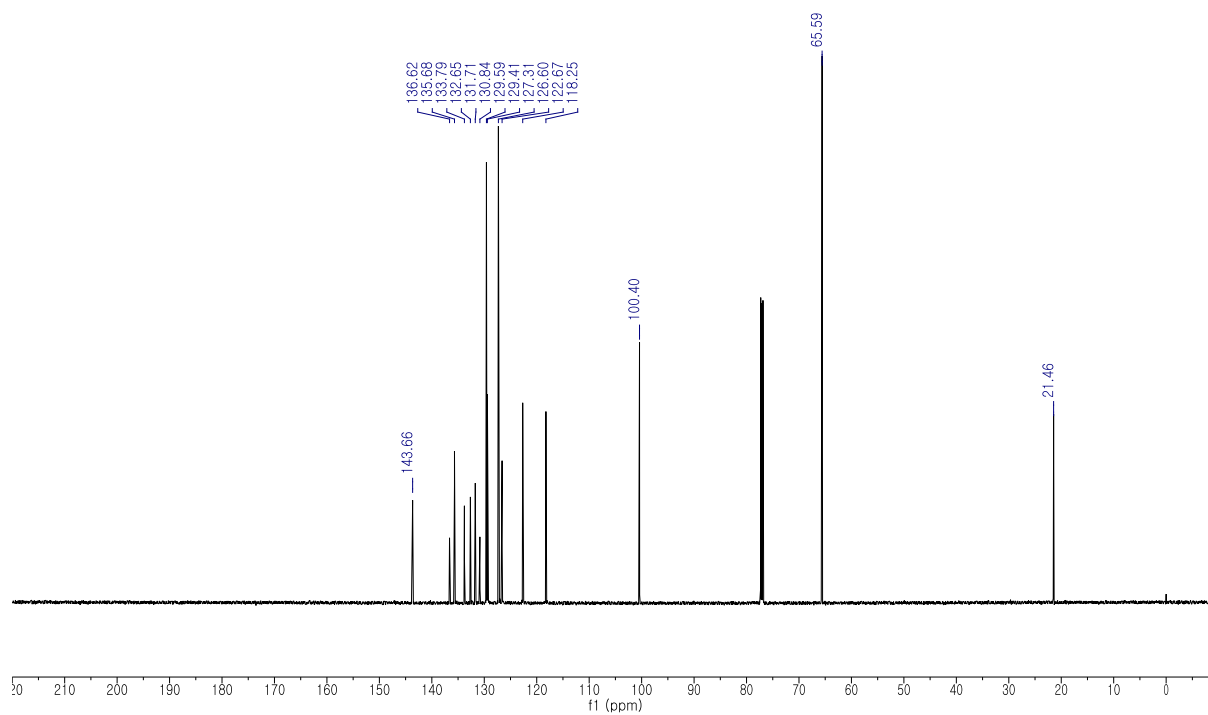
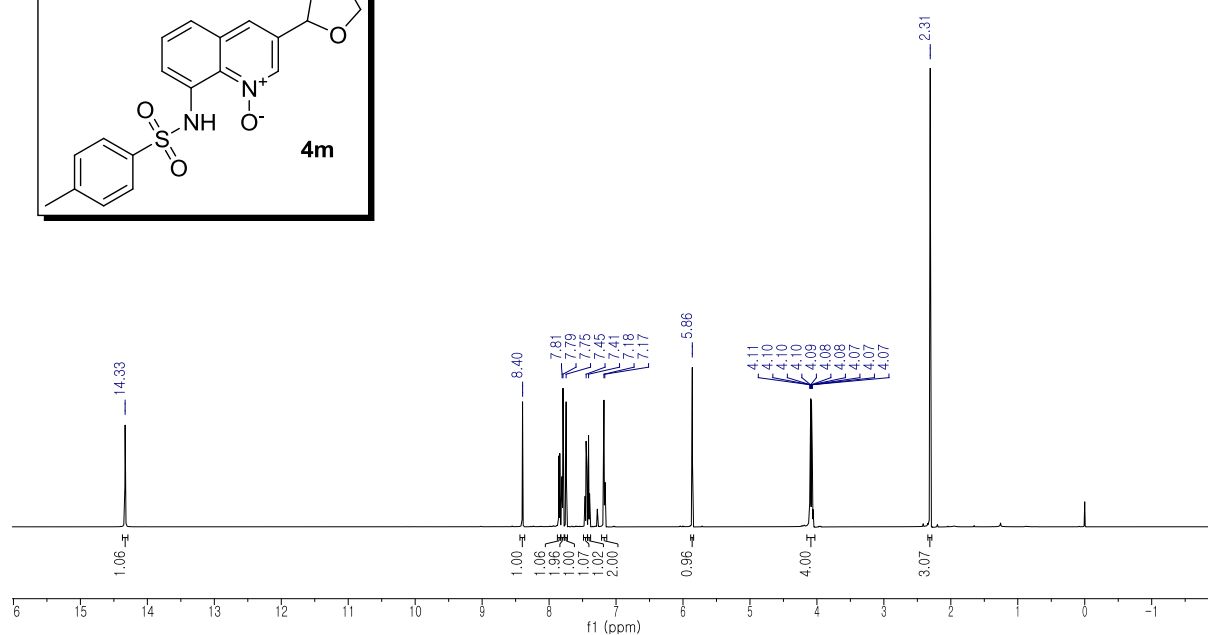
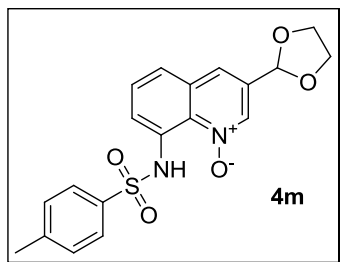
6-(Methoxycarbonyl)-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4k)



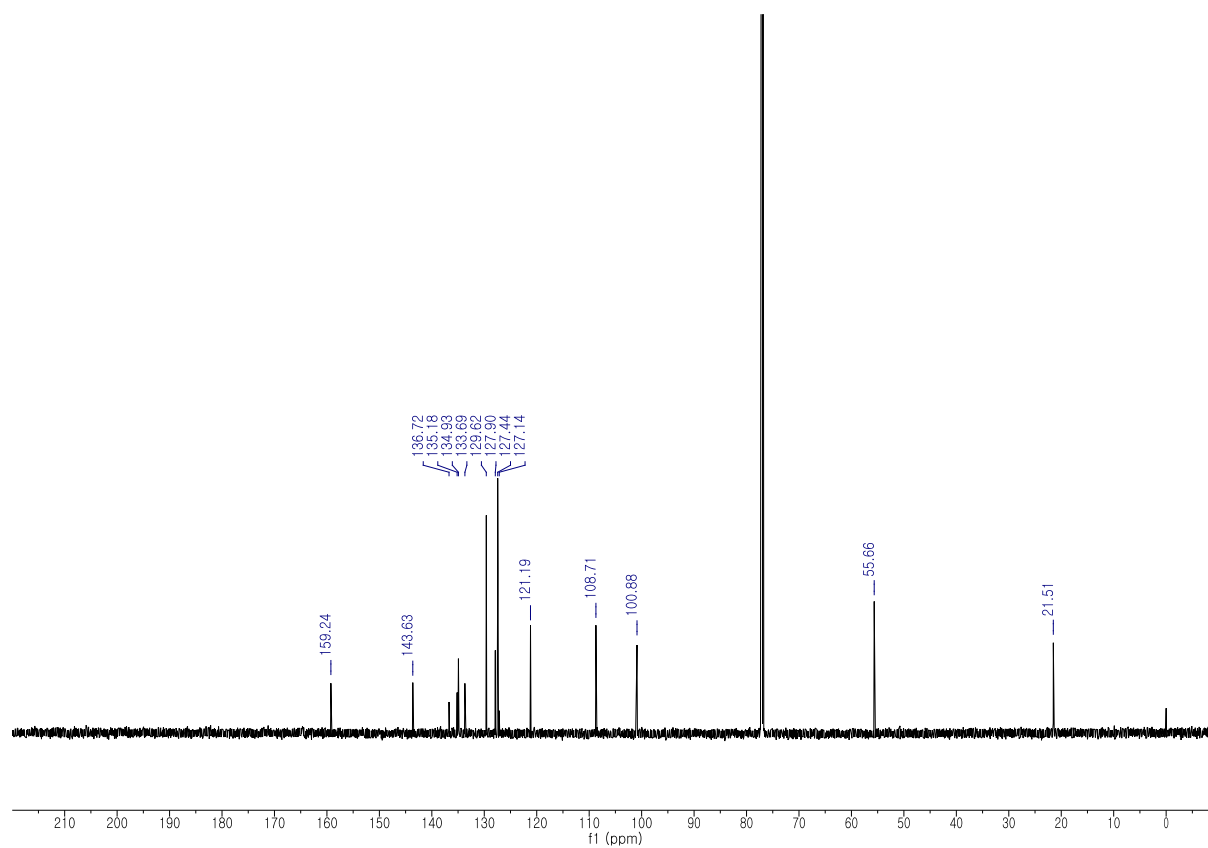
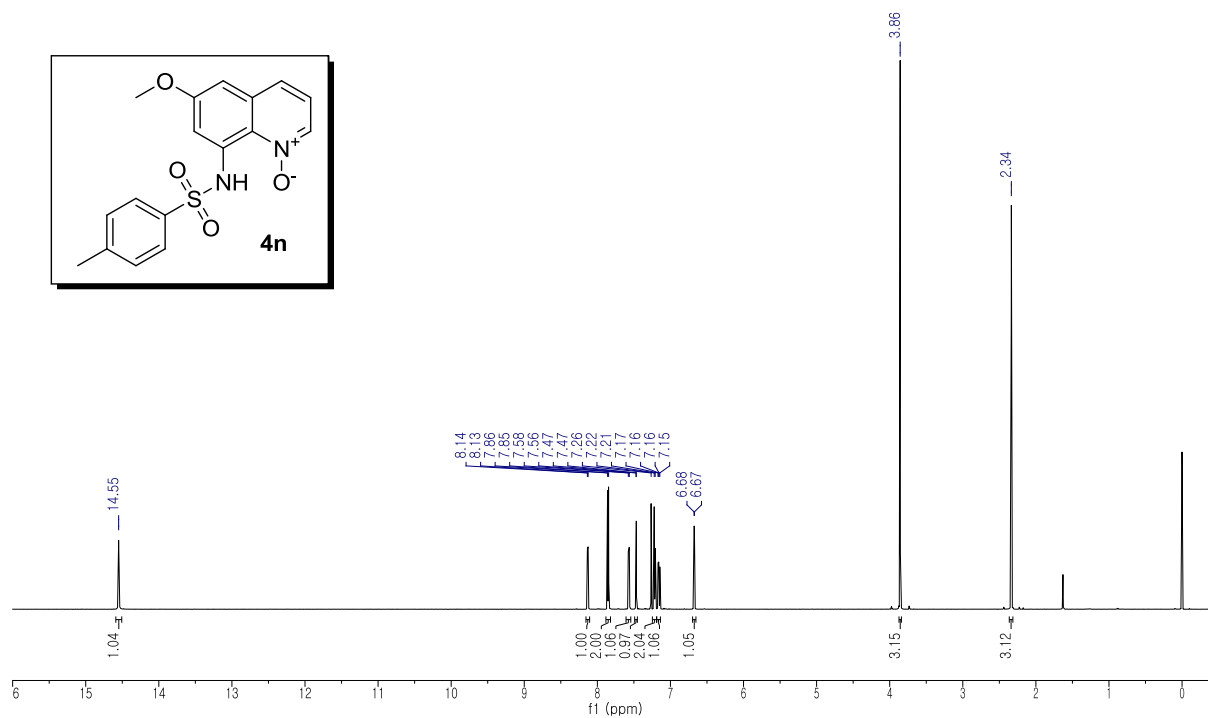
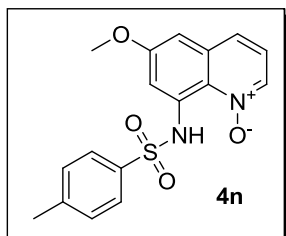
4-(Benzoyloxy)-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4I)



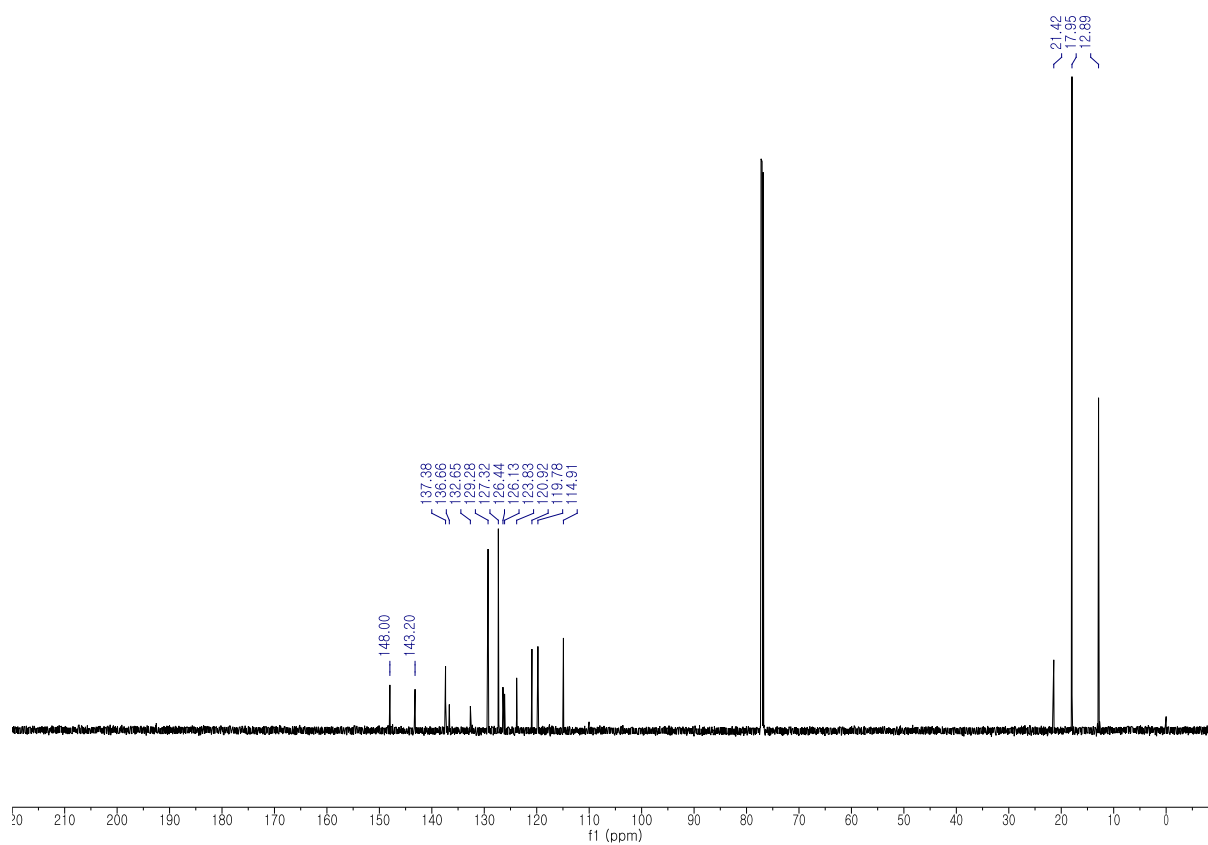
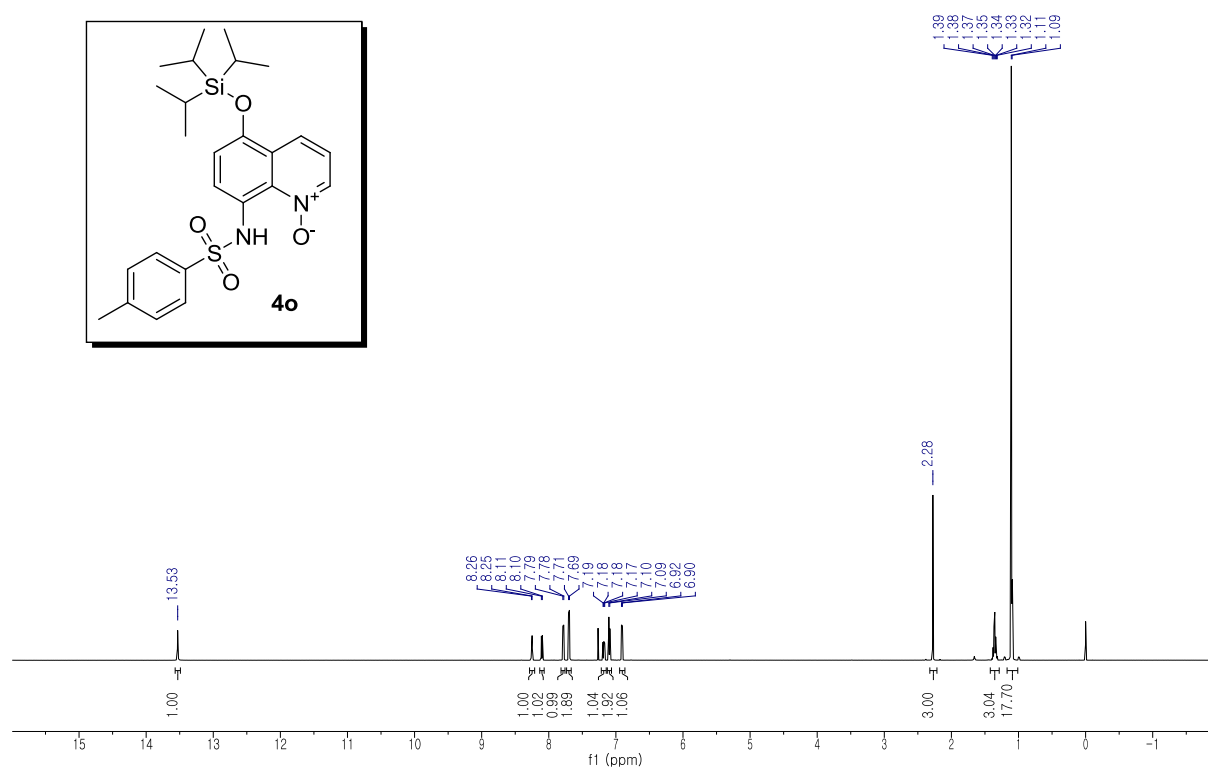
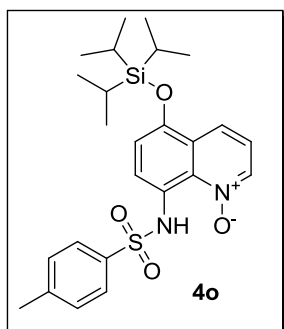
3-(1,3-Dioxolan-2-yl)-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4m)



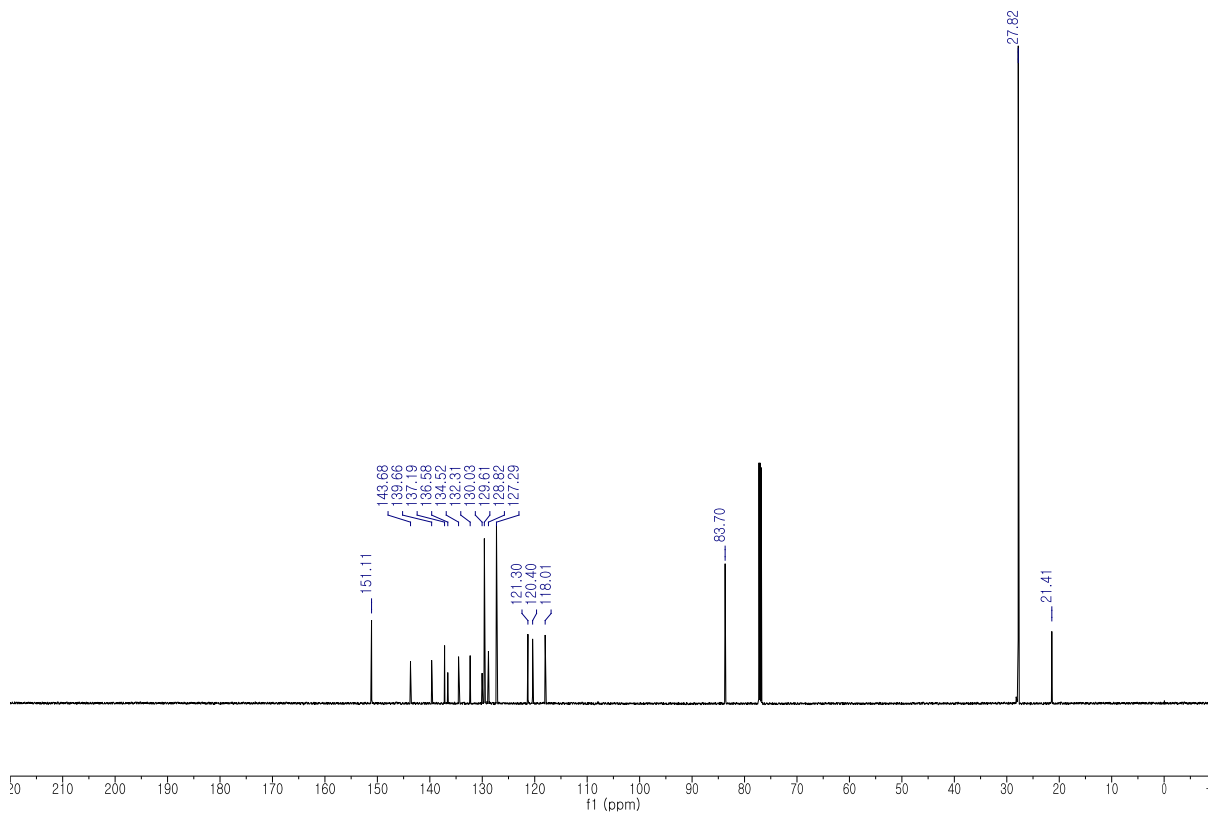
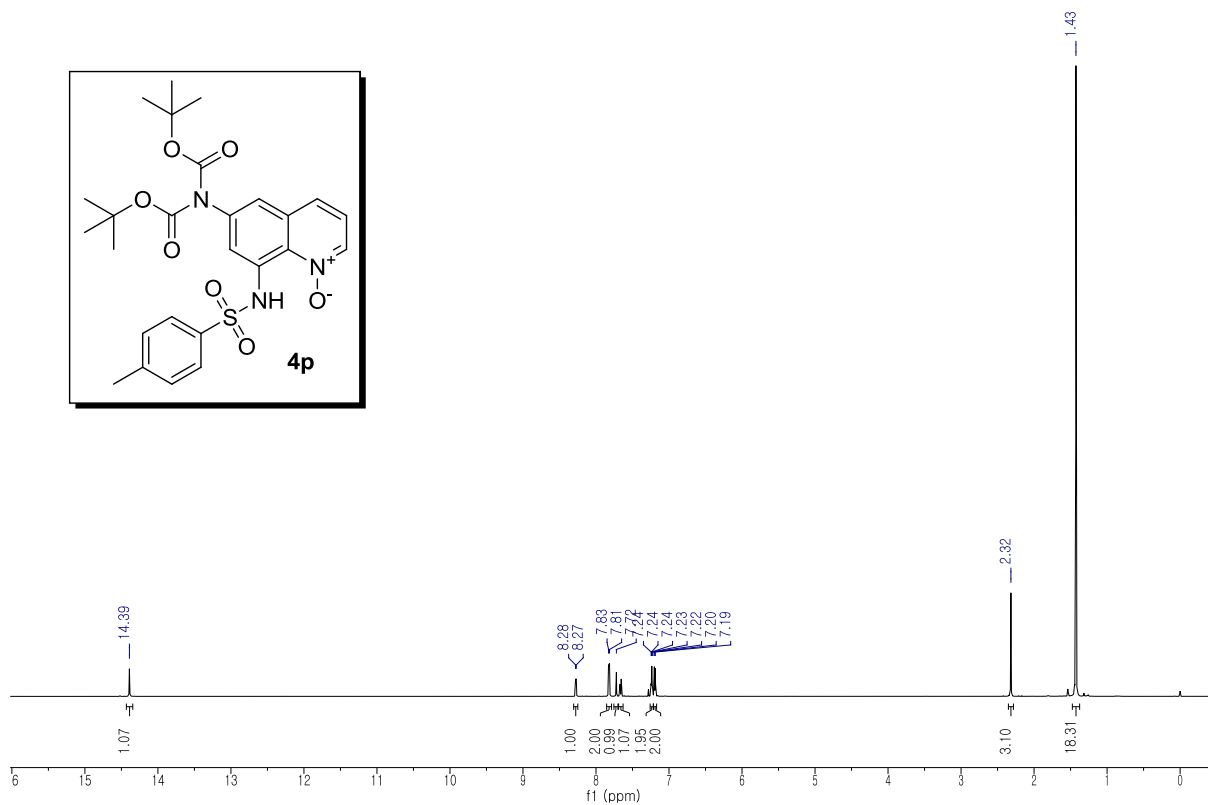
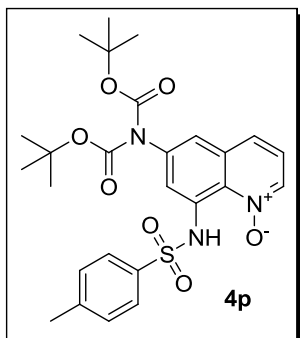
### 6-Methoxy-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4n)



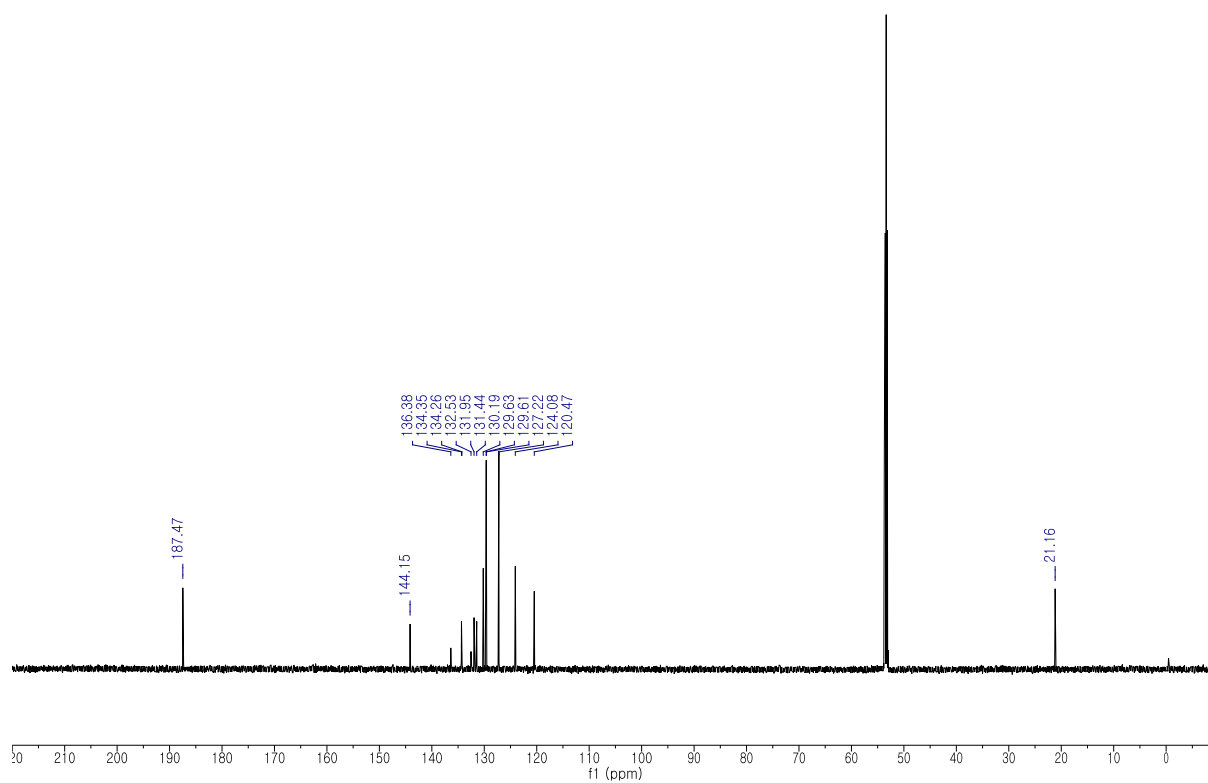
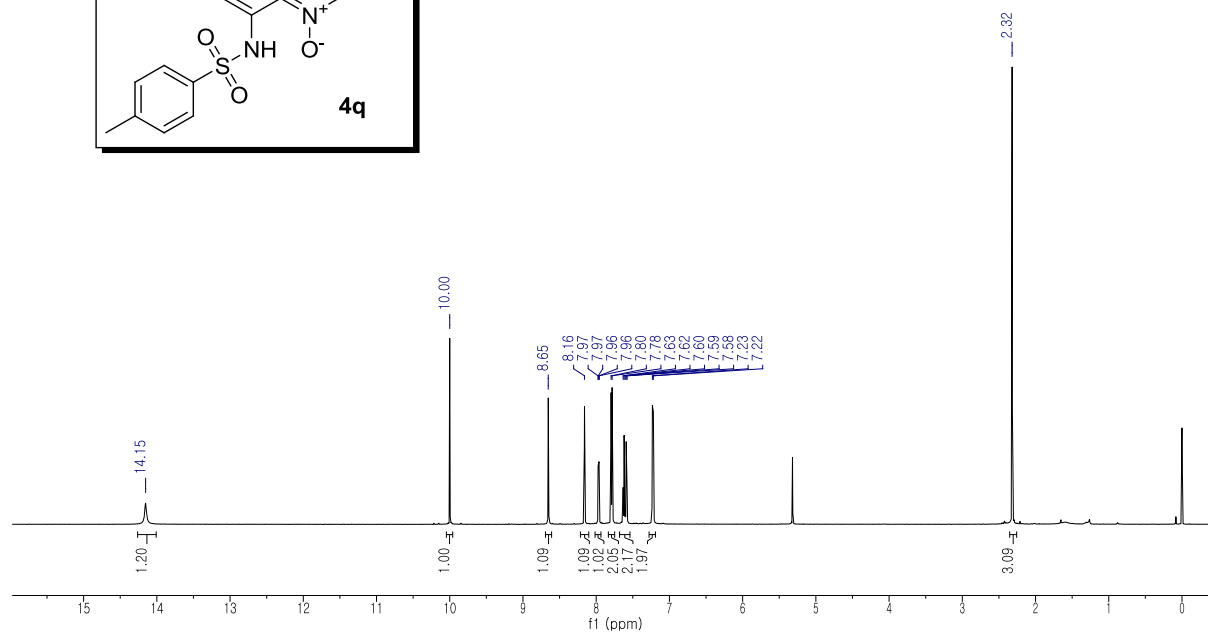
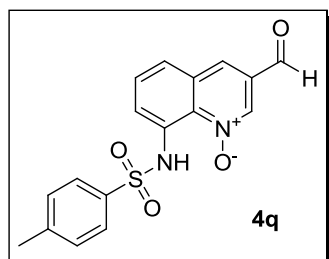
8-(4-Methylphenylsulfonamido)-5-(triisopropylsilyloxy)quinoline *N*-oxide (Table 3, 4o)



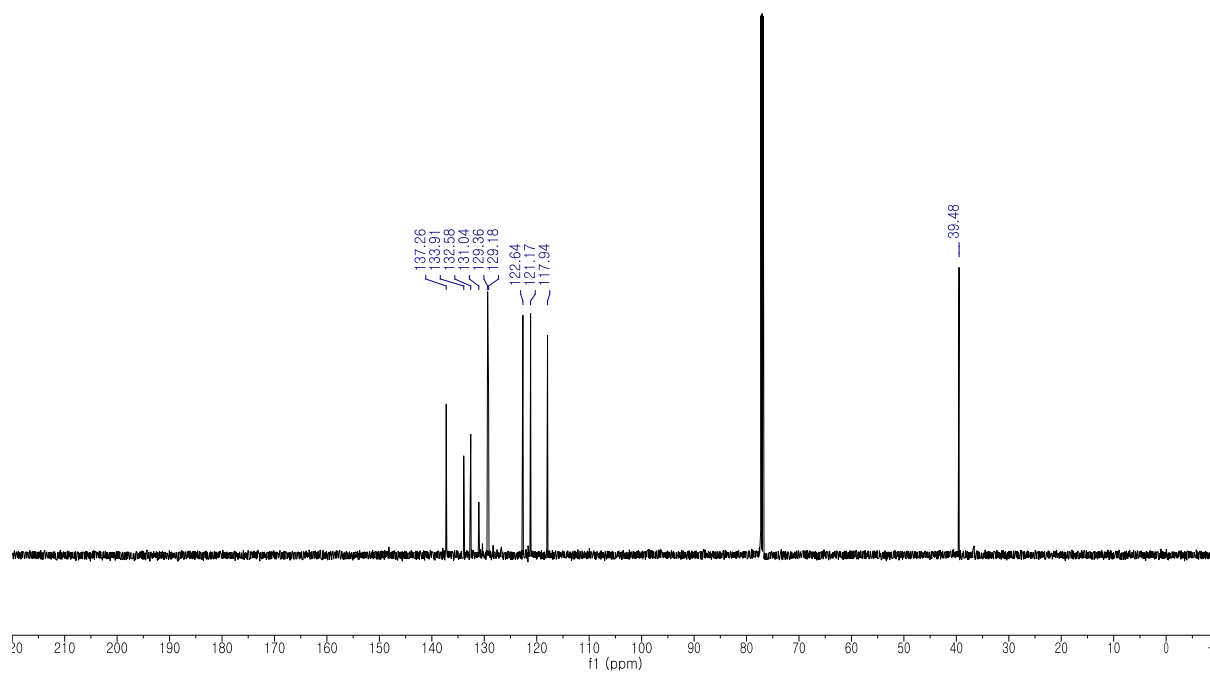
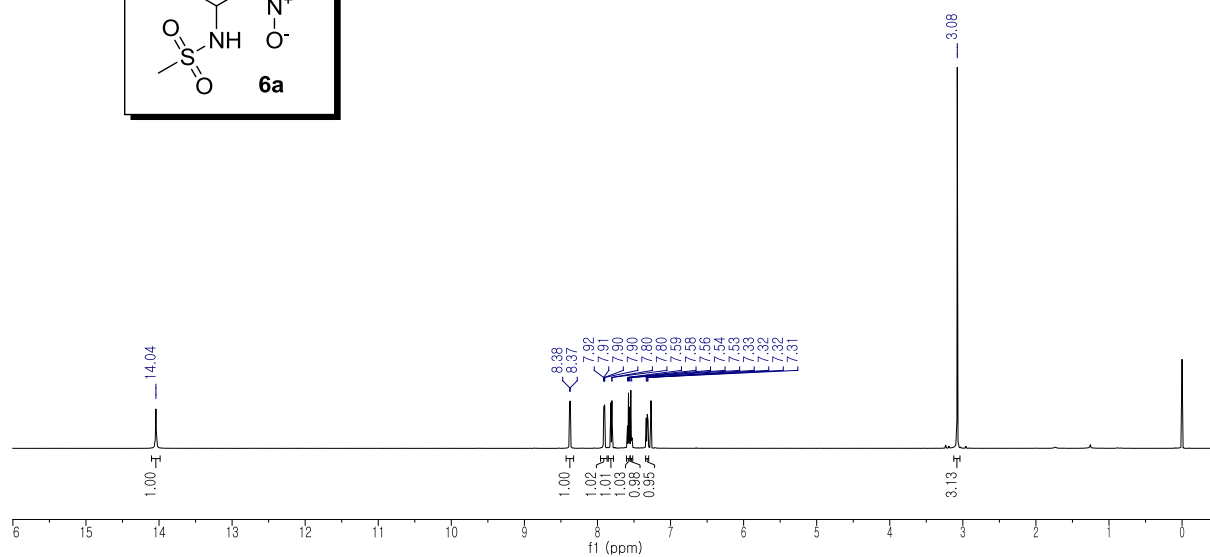
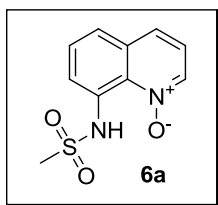
**6-(Bis(tert-butoxycarbonyl)amino)-8-(4-methylphenylsulfonamido)quinoline *N*-oxide** (Table 3, **4p**)



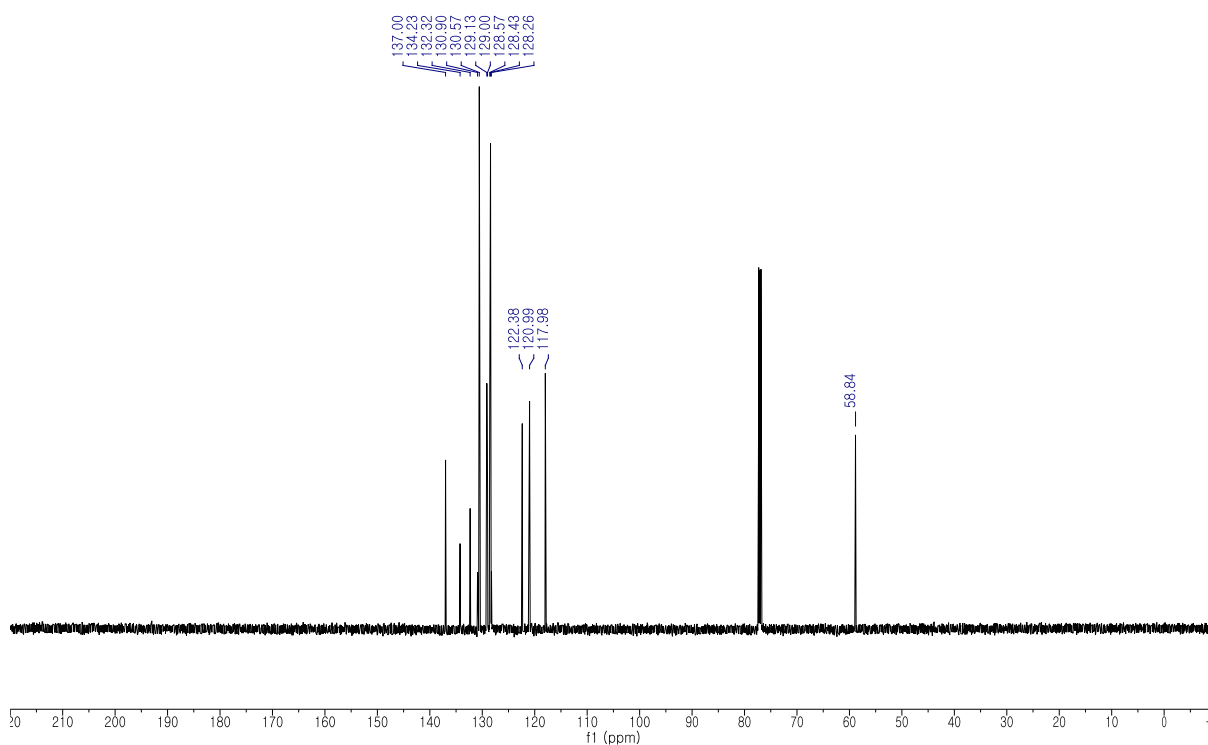
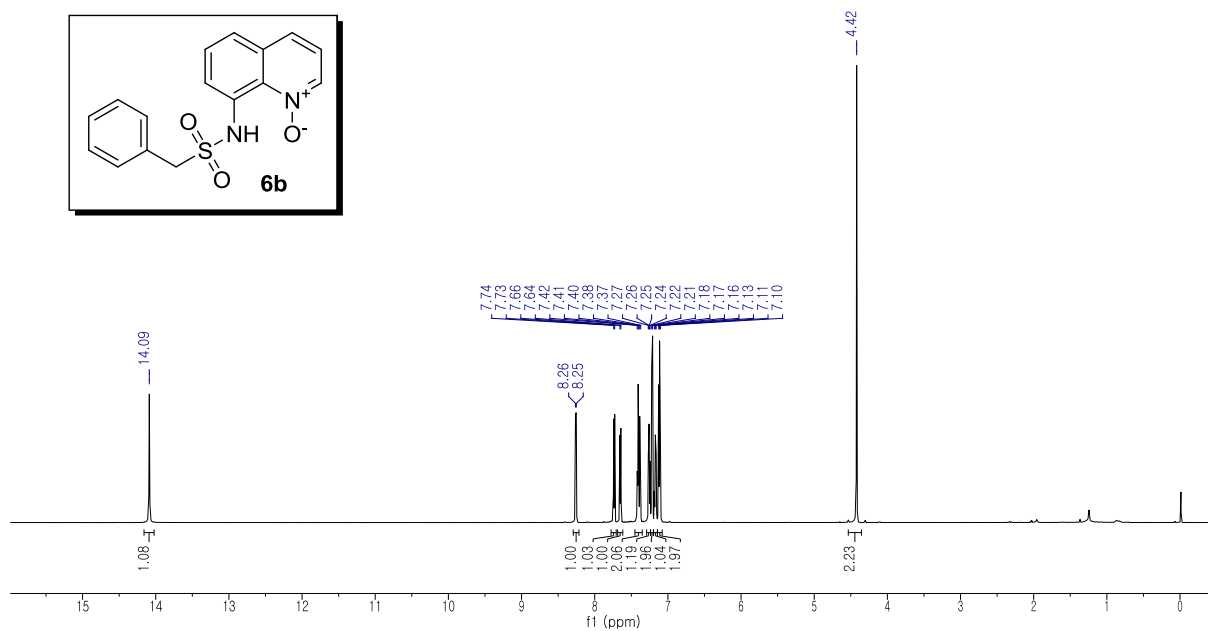
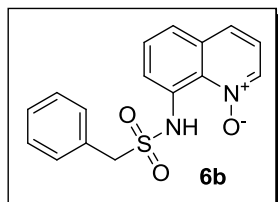
### 3-Formyl-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (Table 3, 4q)



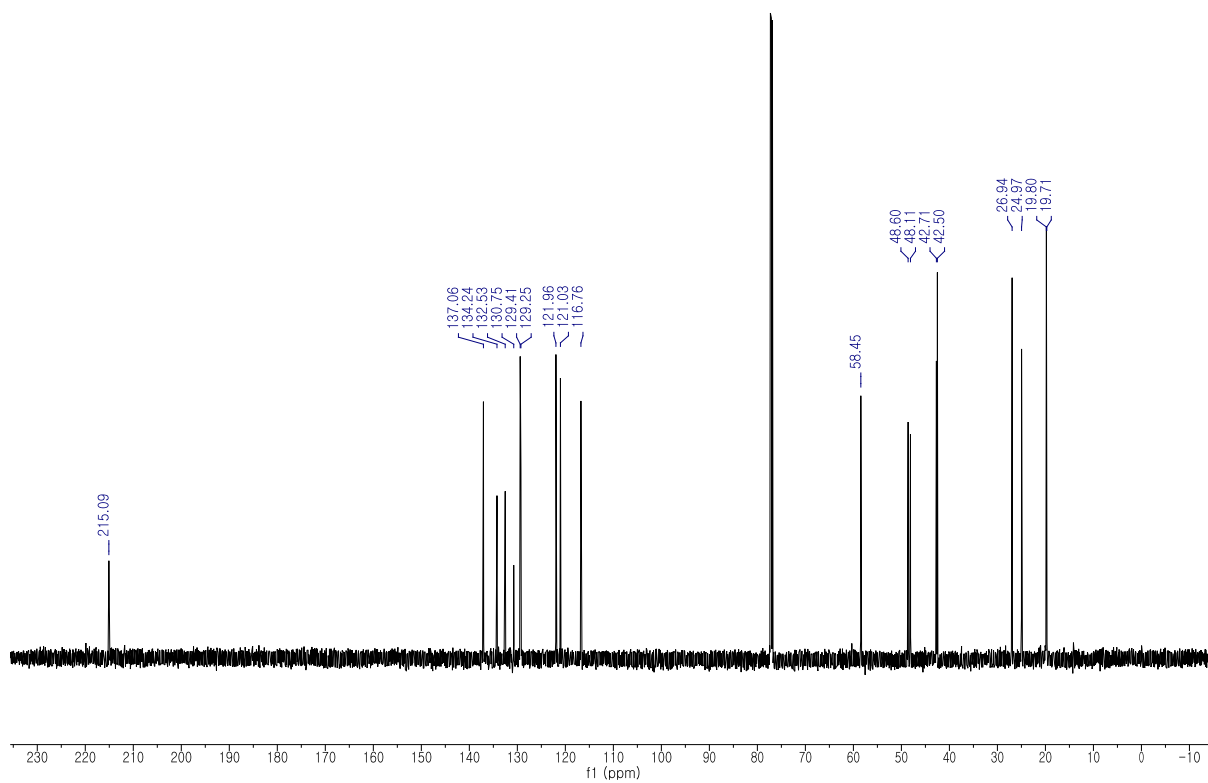
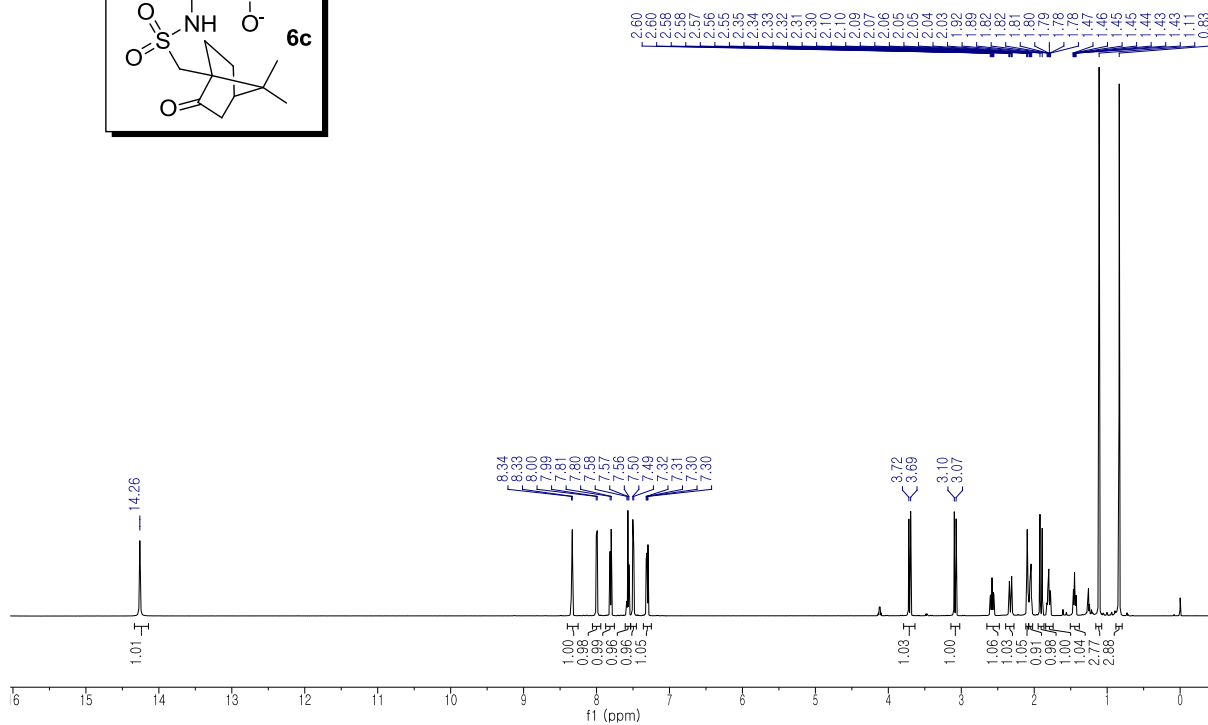
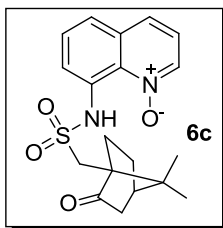
# 8-(Methylsulfonamido)quinoline *N*-oxide (Table 4, 6a)



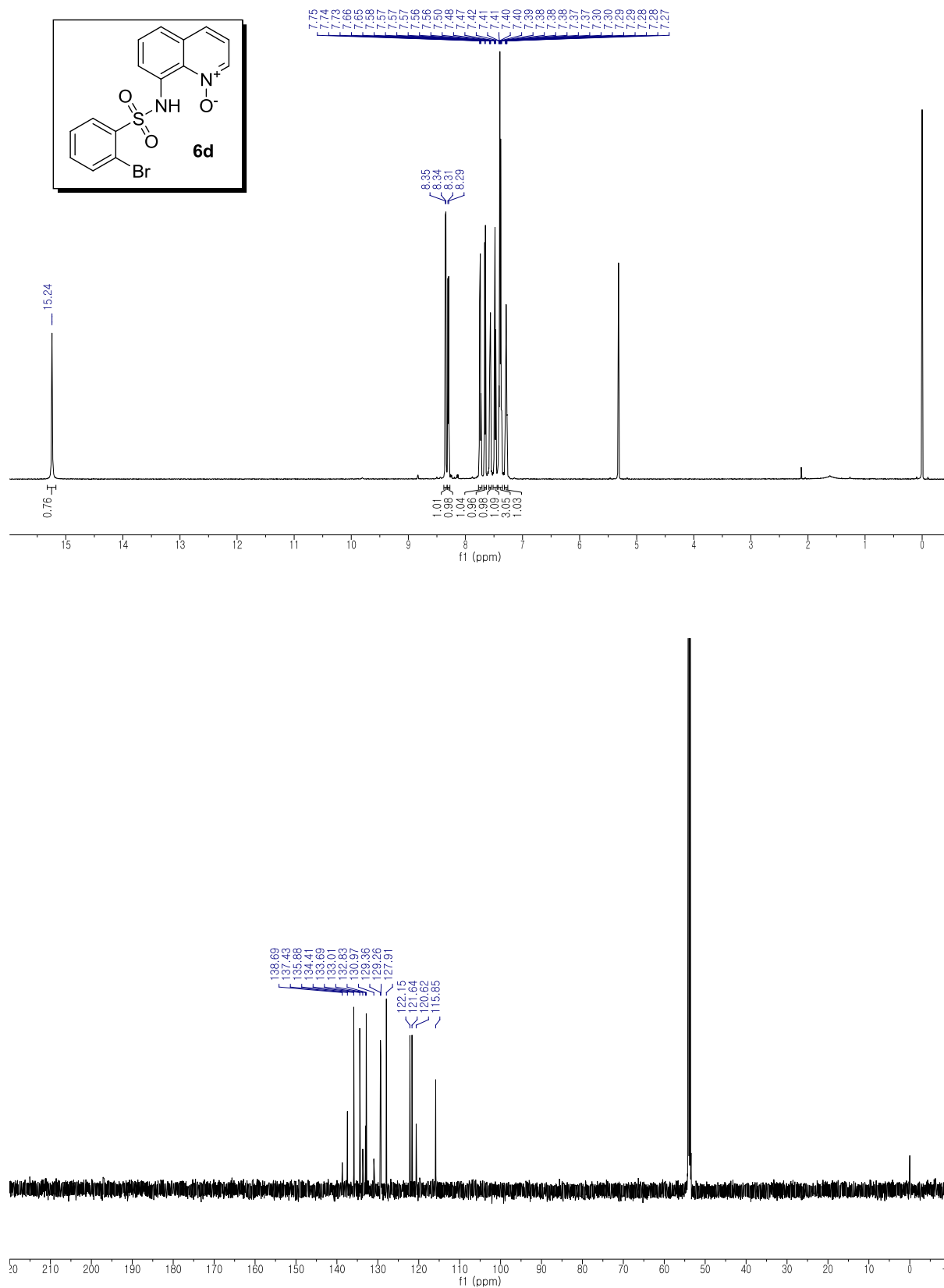
# 8-(Phenylmethylsulfonamido)quinoline *N*-oxide (Table 4, 6b)



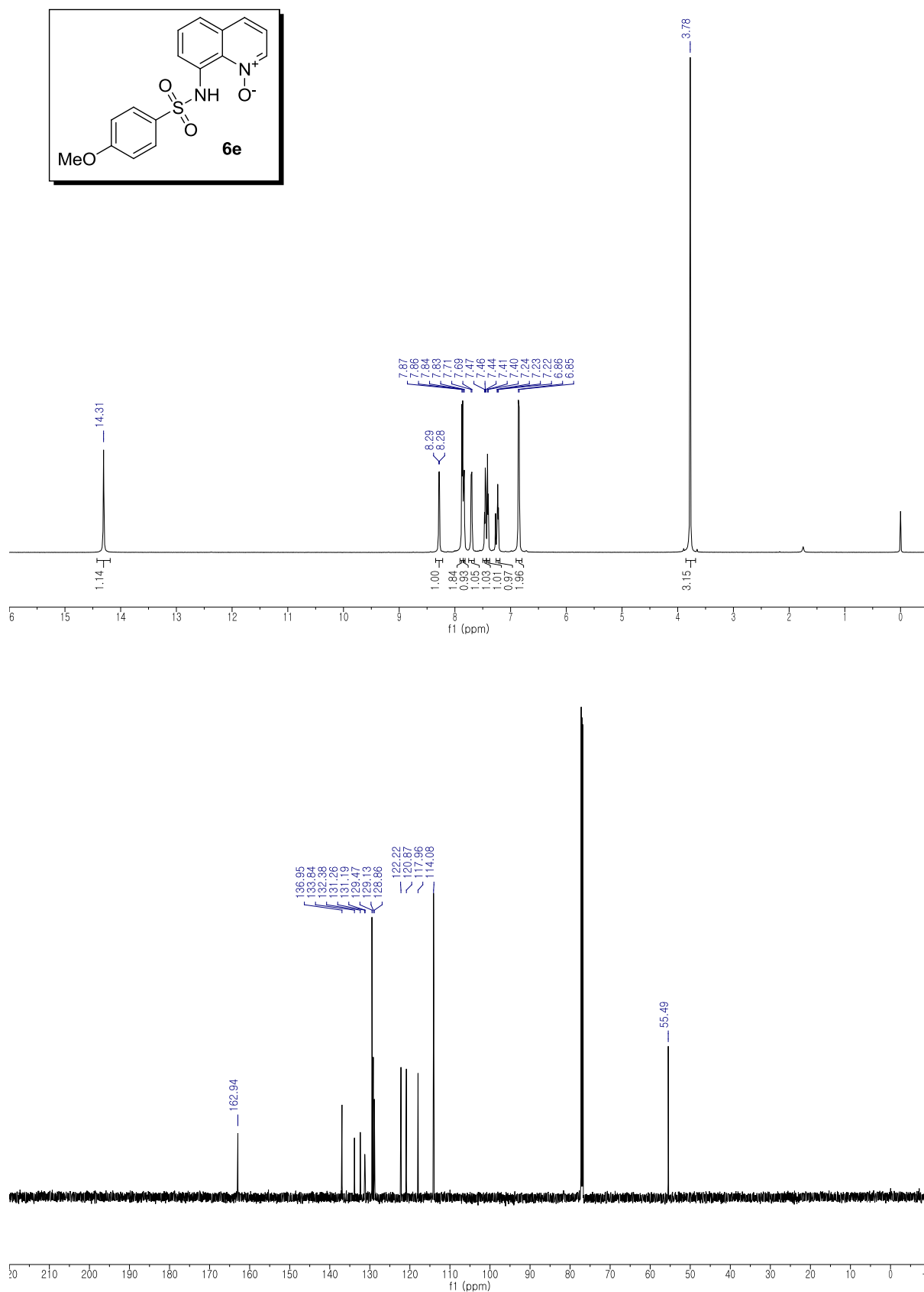
8-[(7,7-Dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methylsulfonamido]quinoline *N*-oxide (Table 4, 6c)



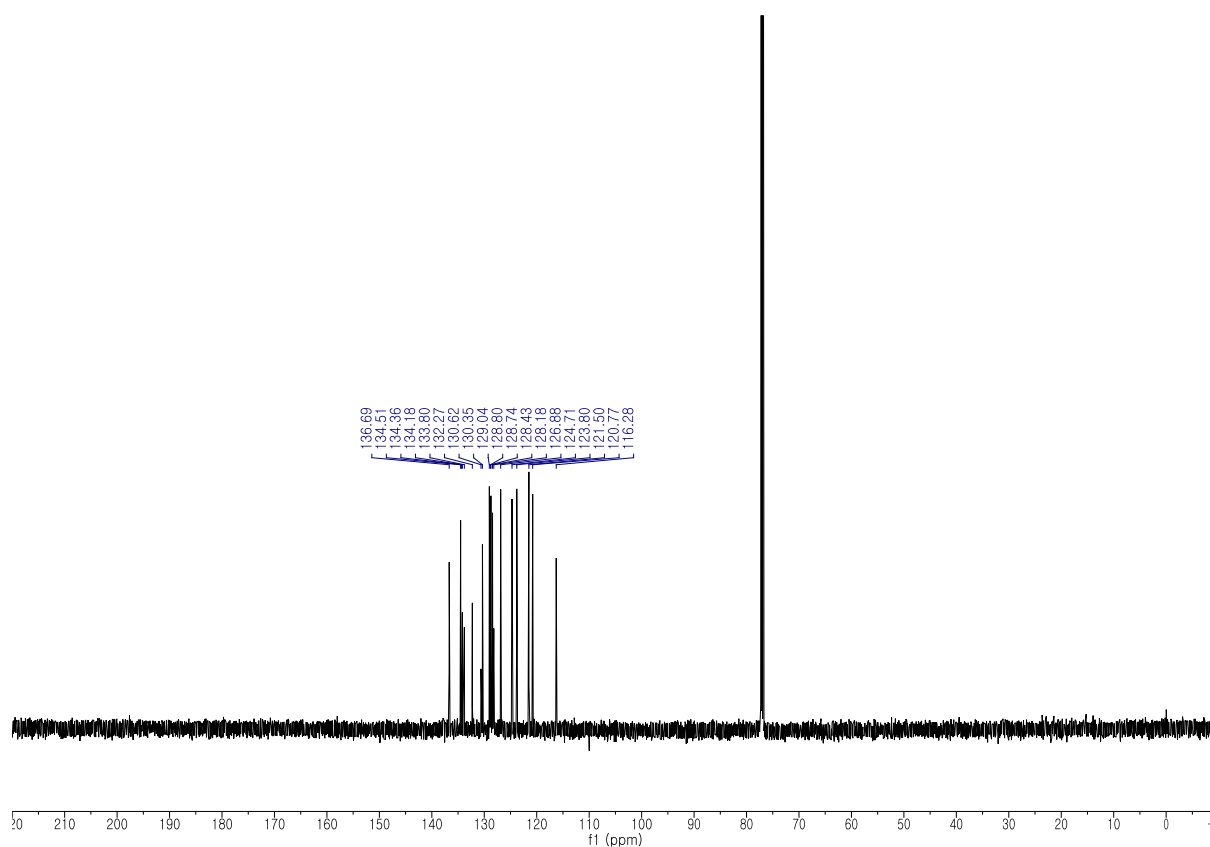
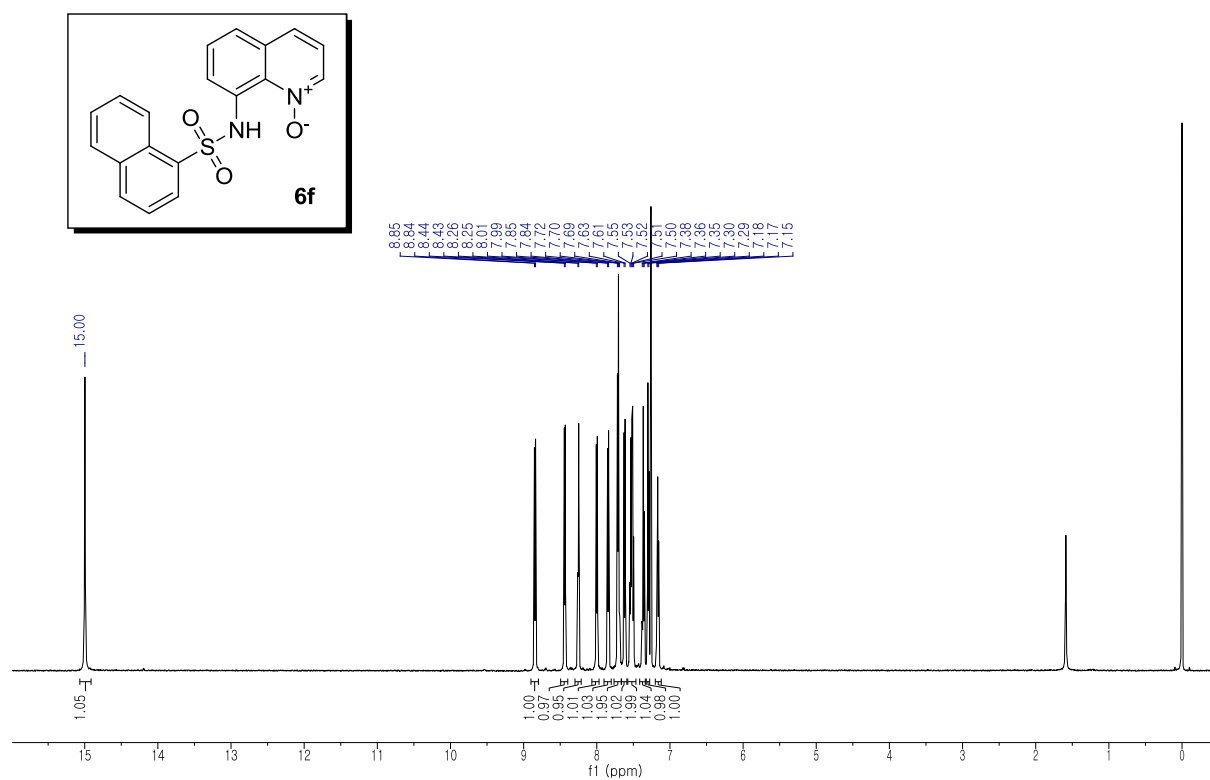
# 8-(2-Bromophenylsulfonamido)quinoline *N*-oxide (Table 4, 6d)



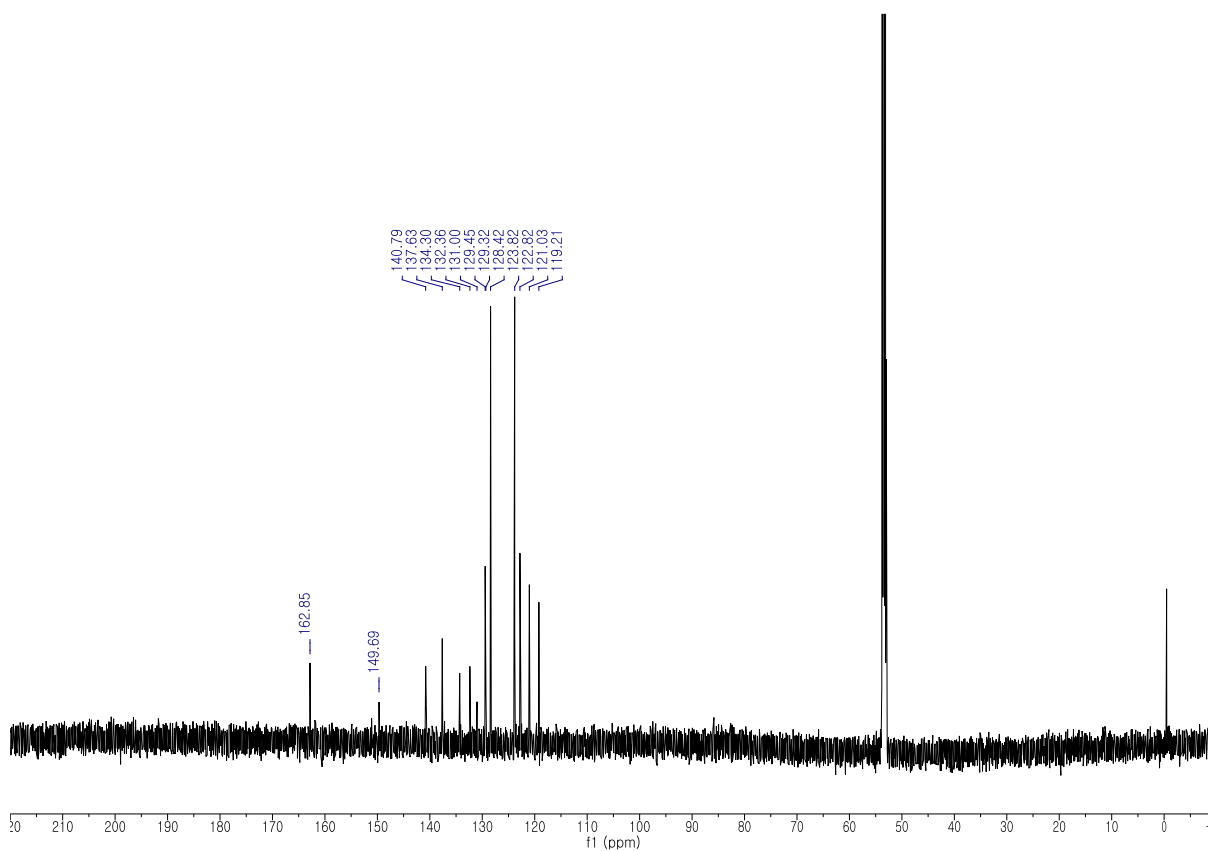
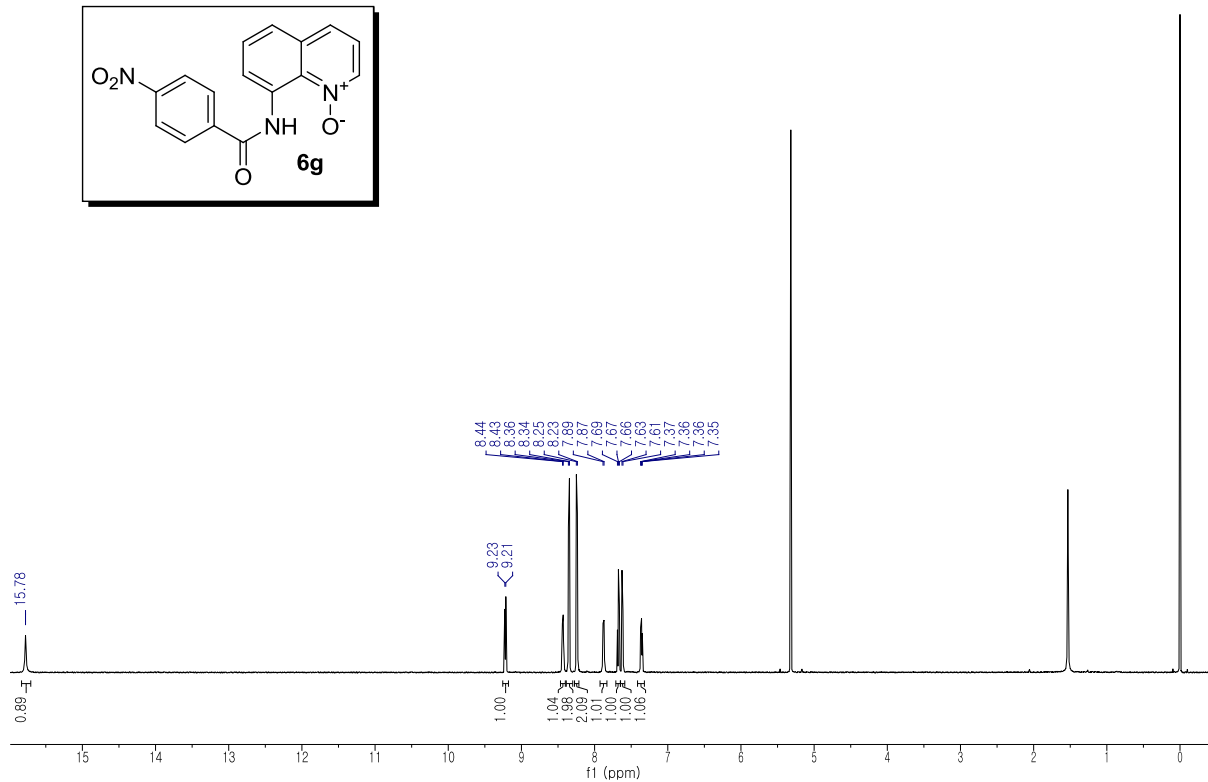
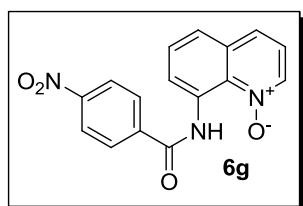
# 8-(4-Methoxyphenylsulfonamido)quinoline *N*-oxide (Table 4, 6e)



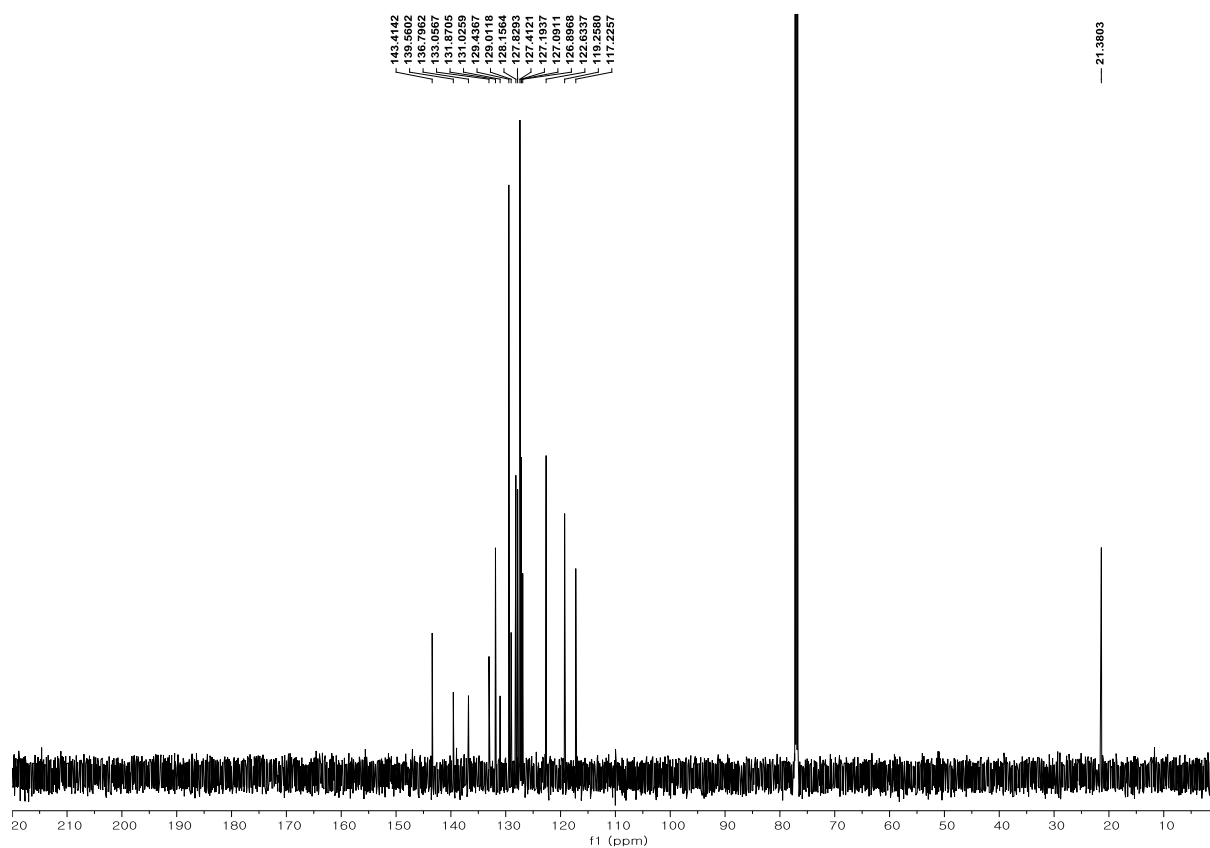
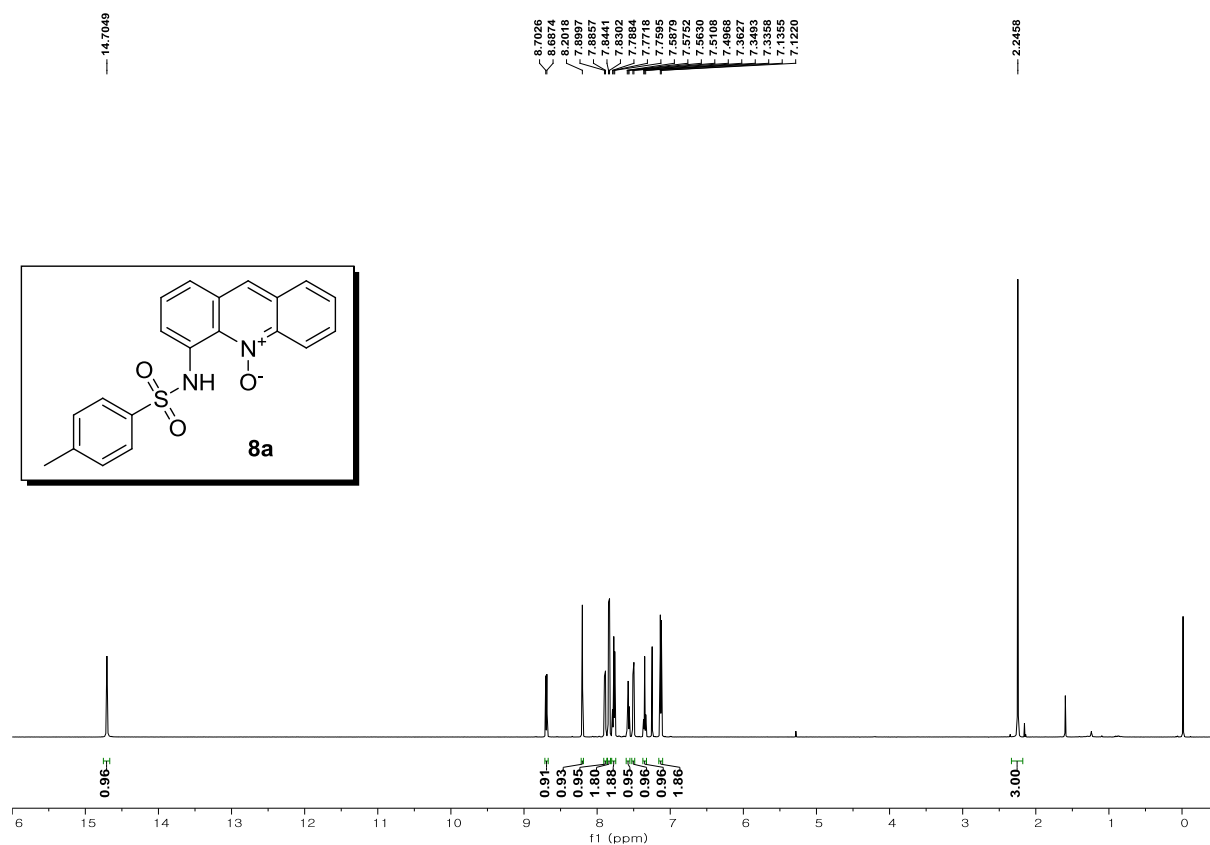
### 8-(Naphthalene-1-sulfonamido)quinoline *N*-oxide (Table 4, 6f)



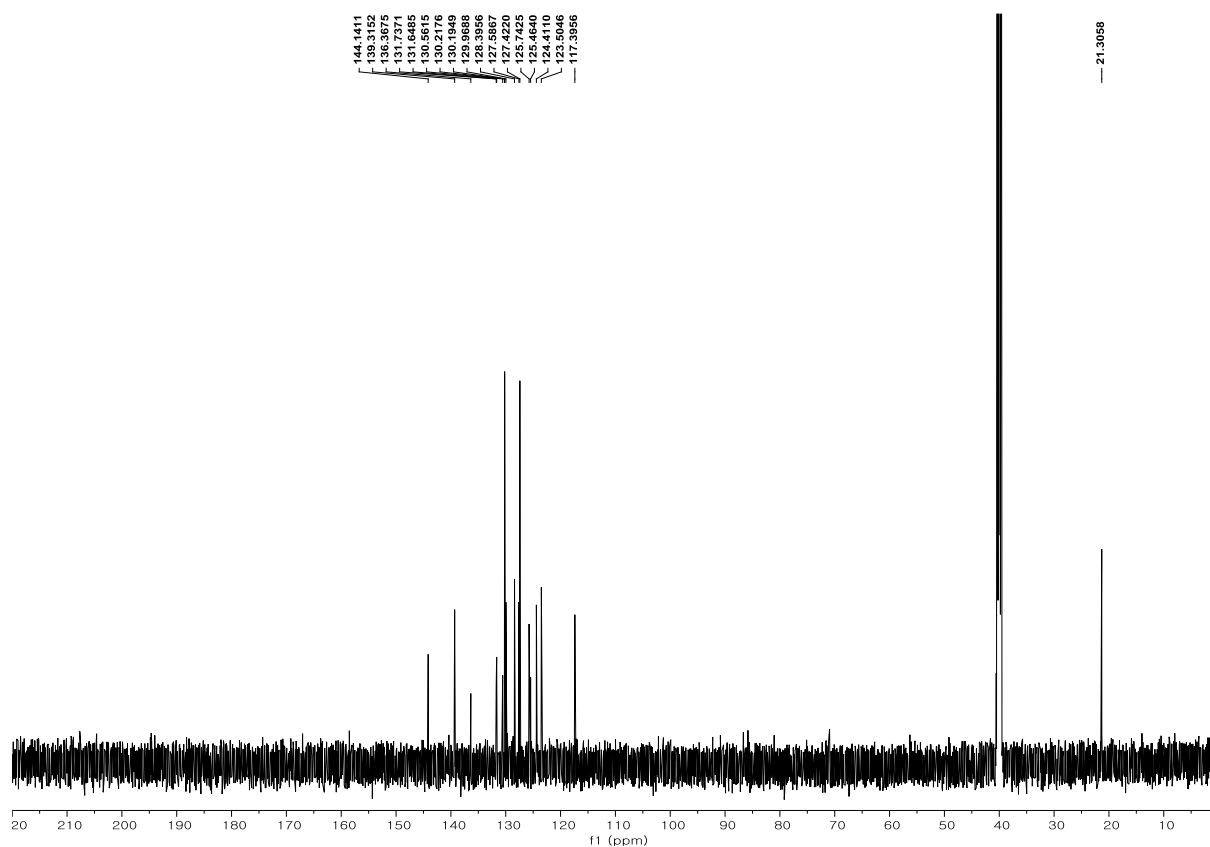
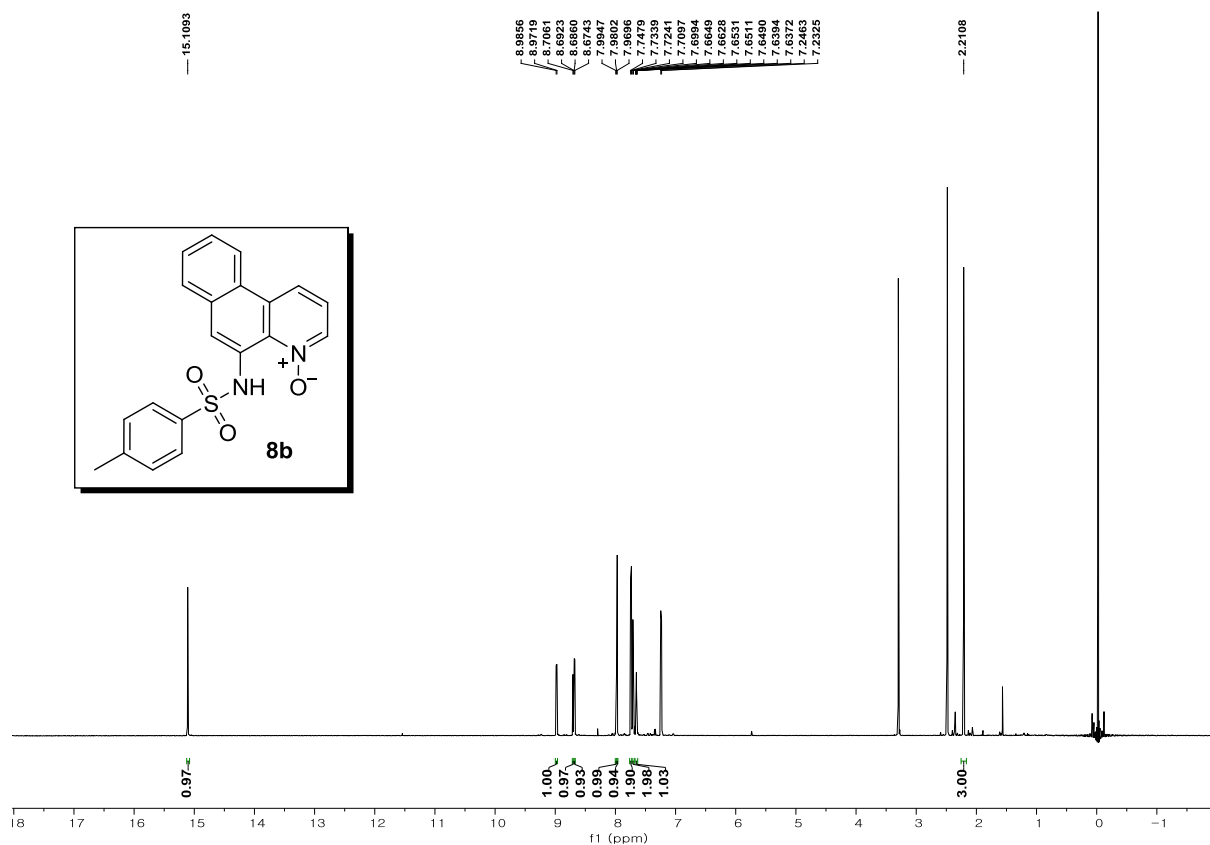
### 8-(4-Nitrobenzamido)quinoline *N*-oxide (Table 4, 6g)



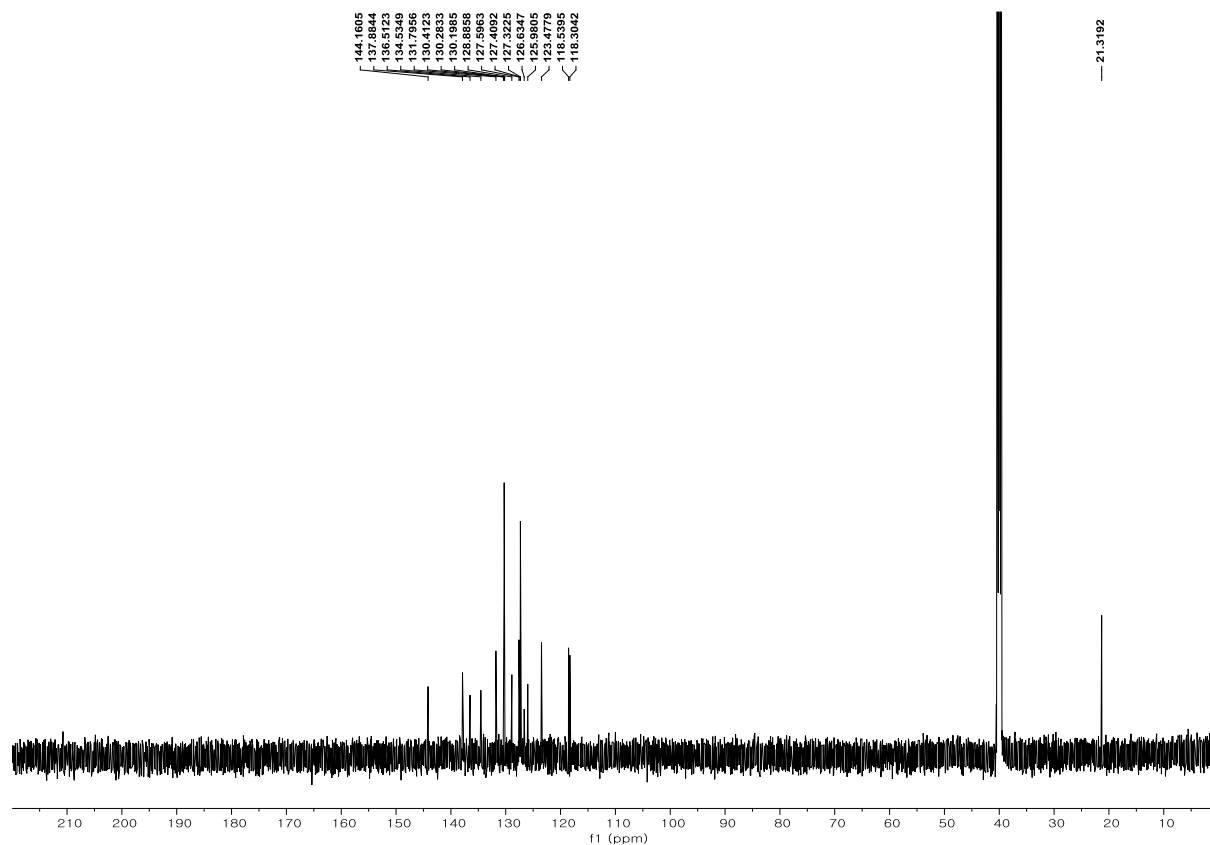
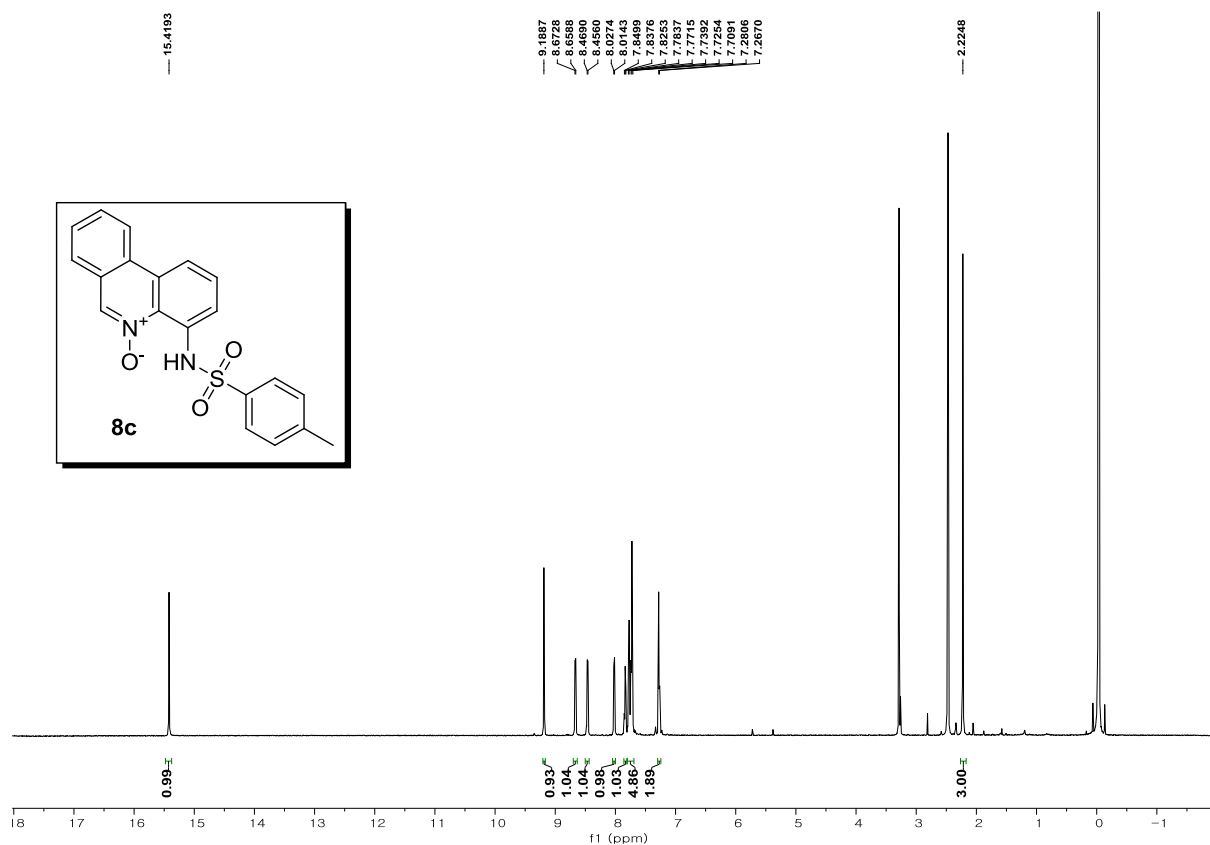
# 4-(4-Methylphenylsulfonamido)acridine 10-oxide (Table 5, 8a)



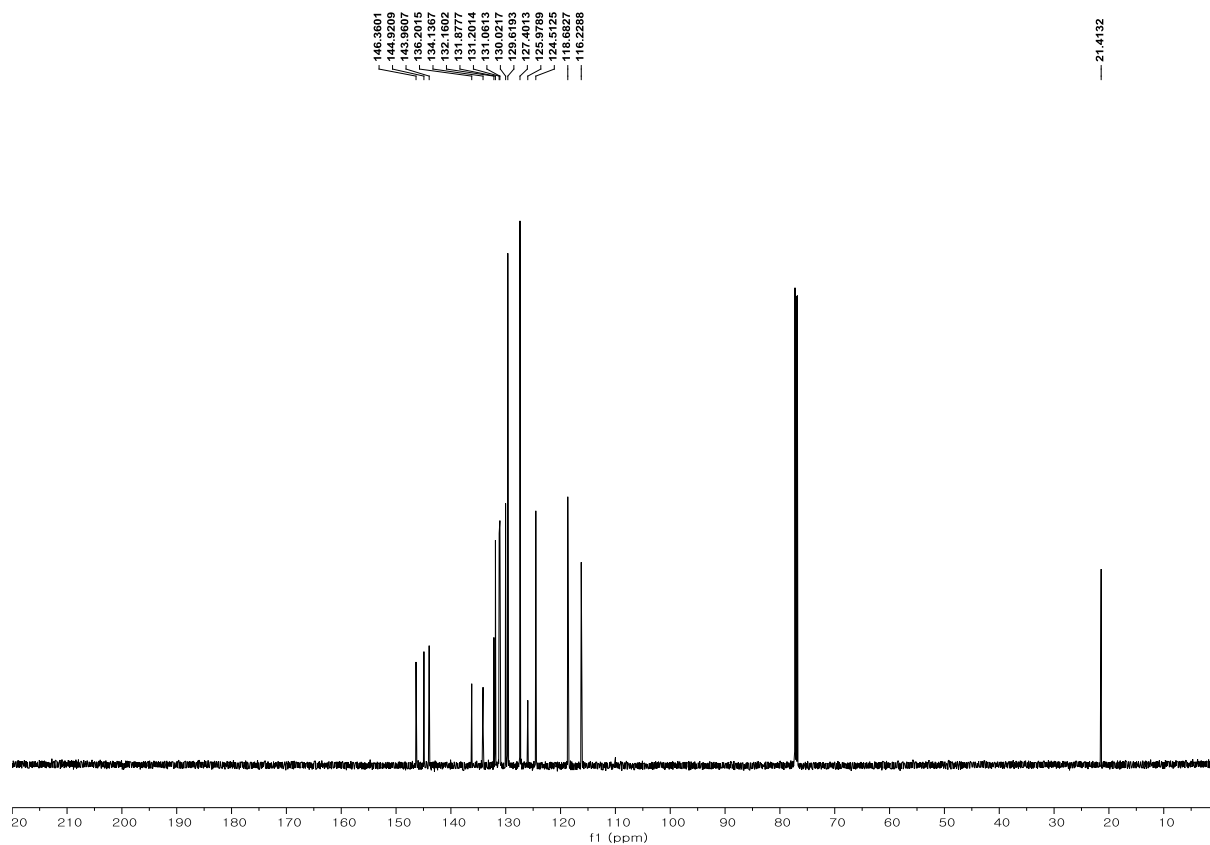
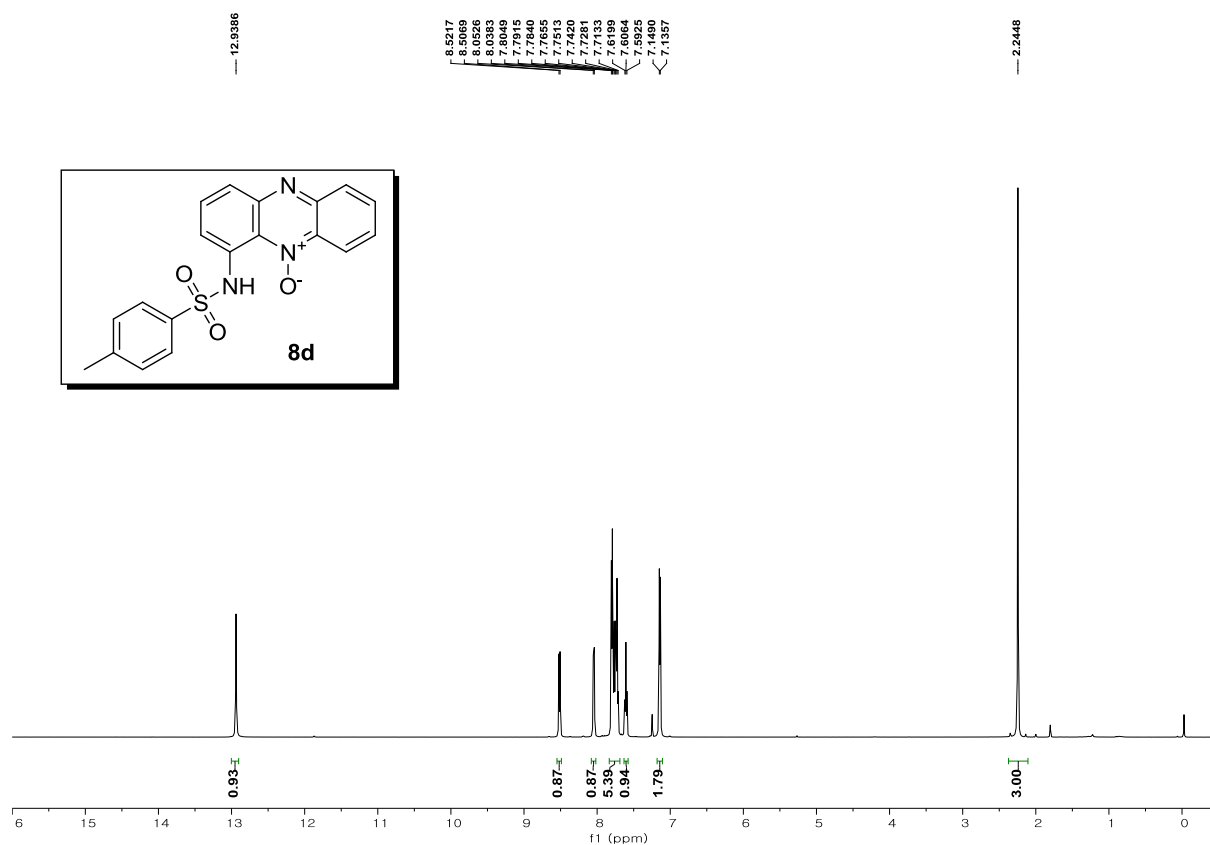
5-(4-Methylphenylsulfonamido)benzo[*f*]quinoline 4-oxide (Table 5, 8b)



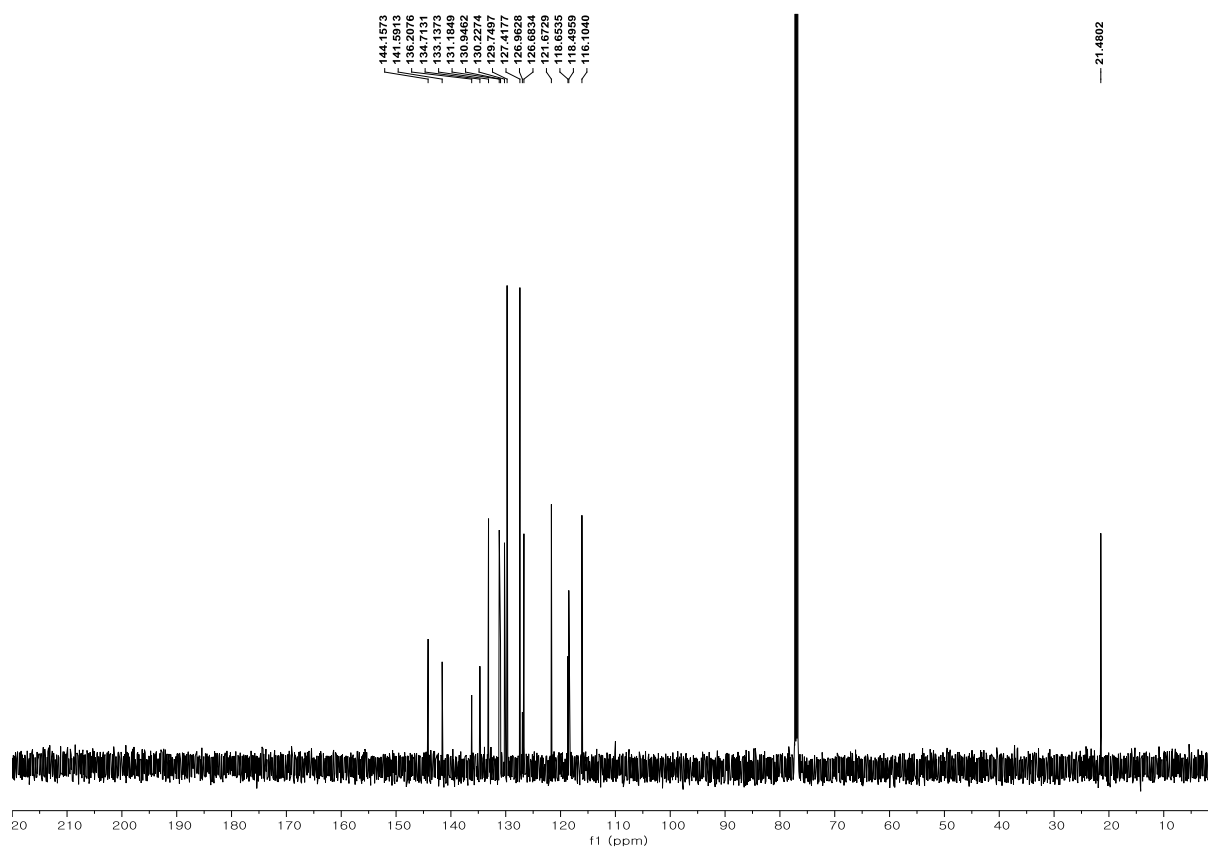
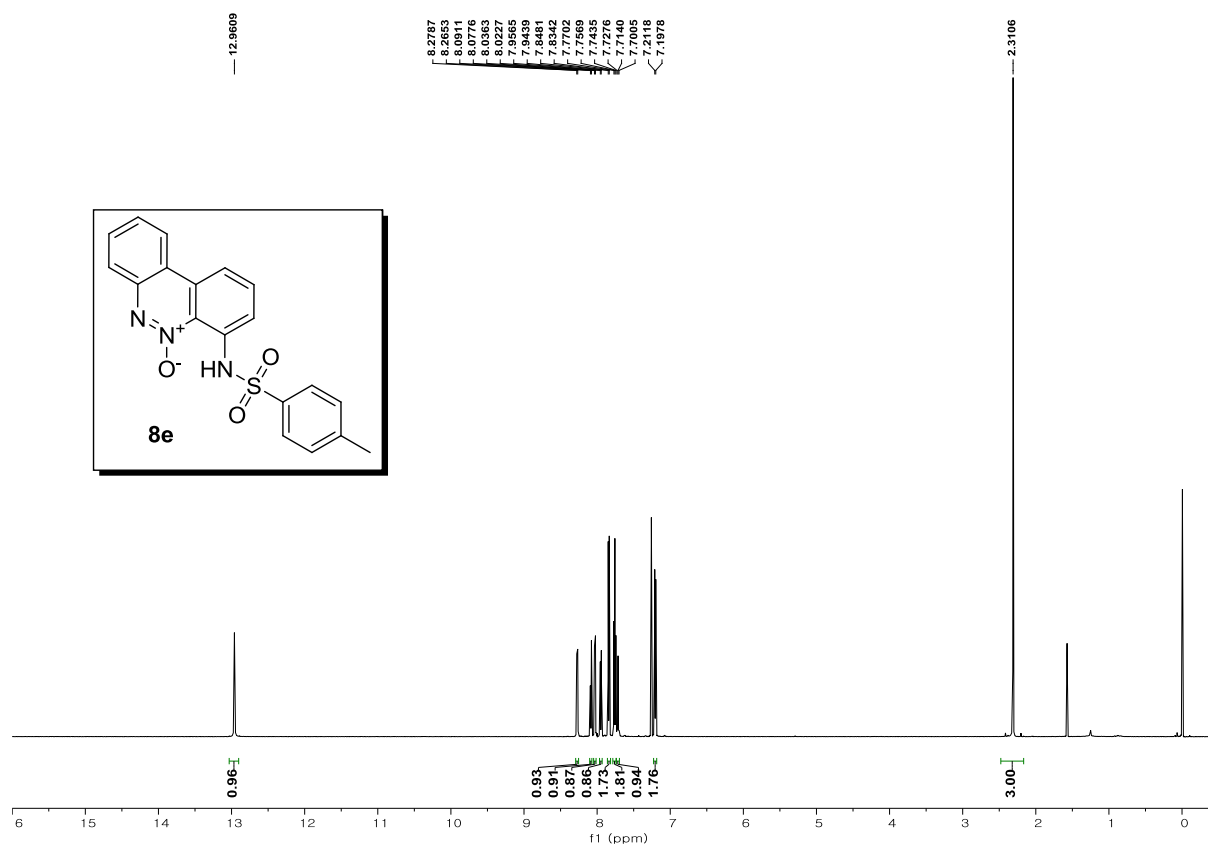
4-(4-Methylphenylsulfonamido)phenanthridine 5-oxide (Table 5, 8c)



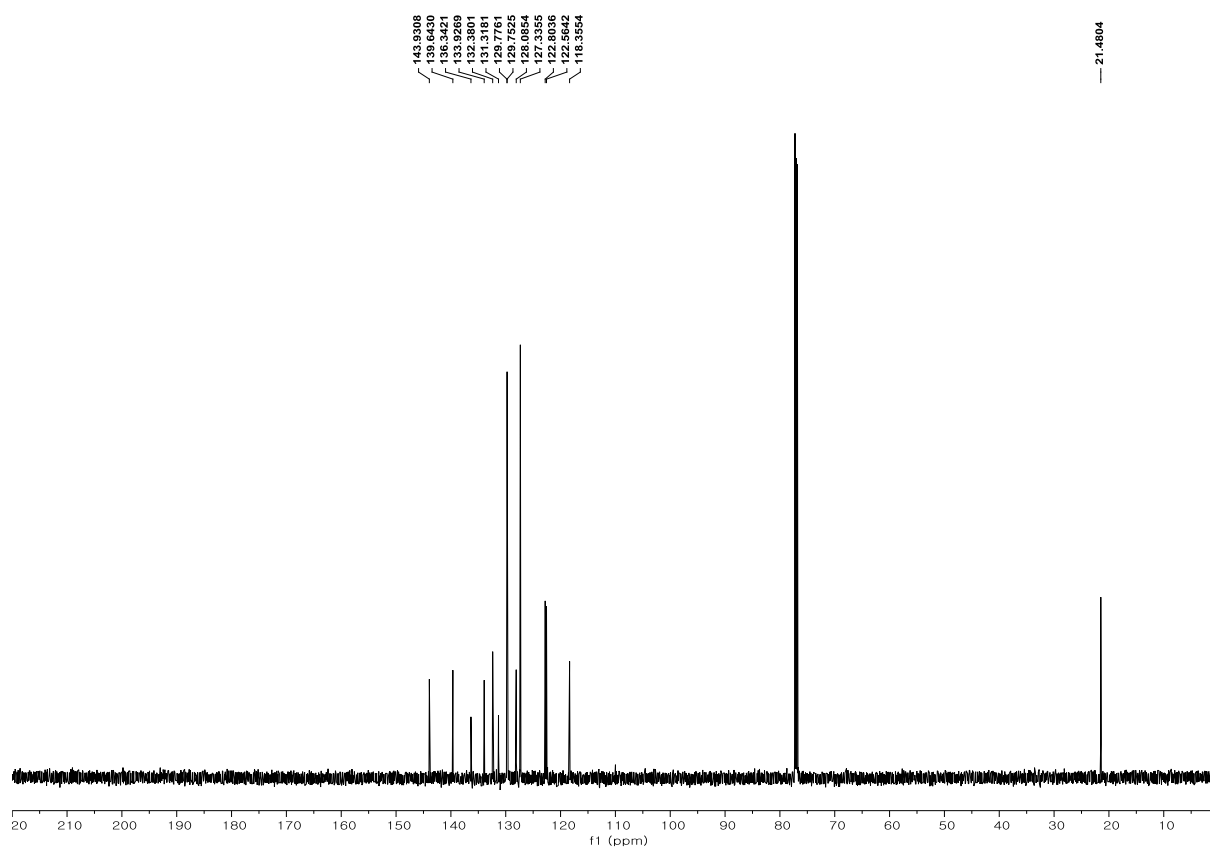
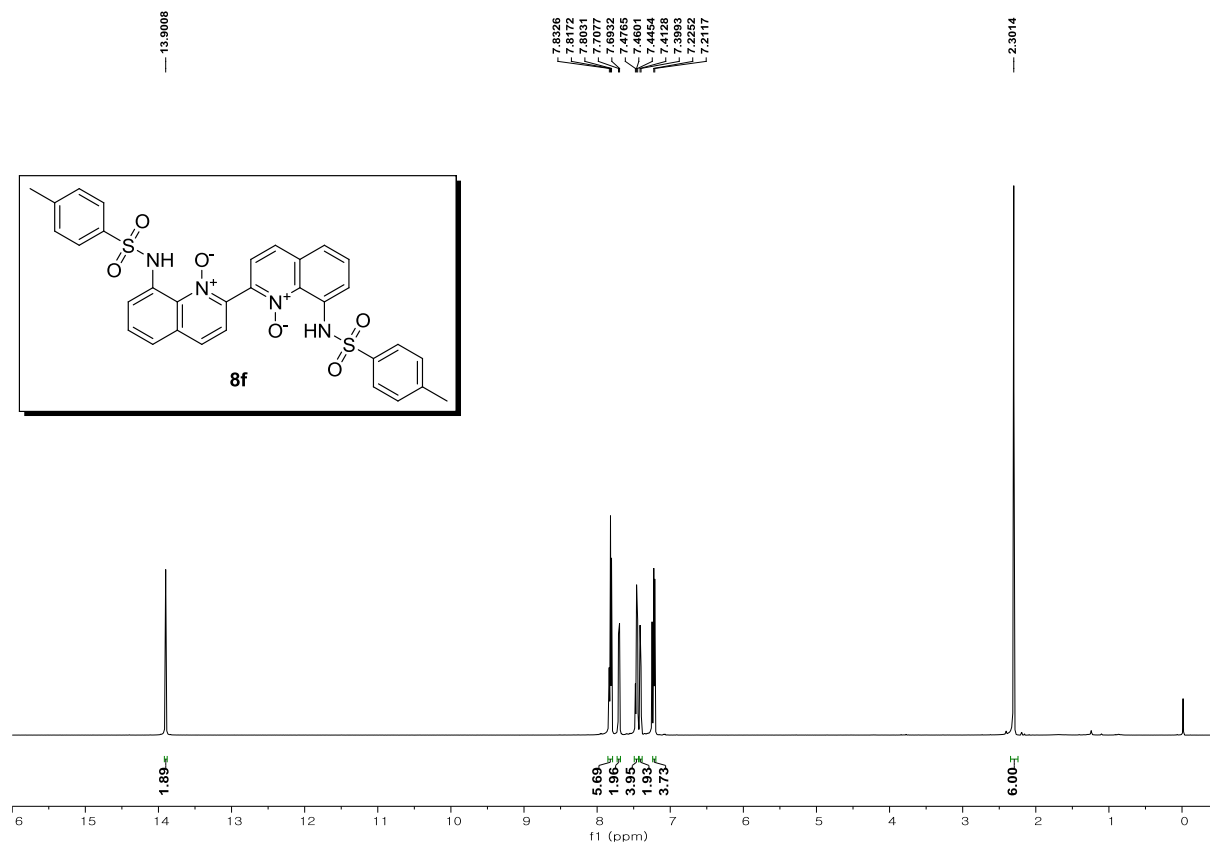
4-(4-Methylphenylsulfonamido)phenazine 5-oxide (Table 5, 8d)



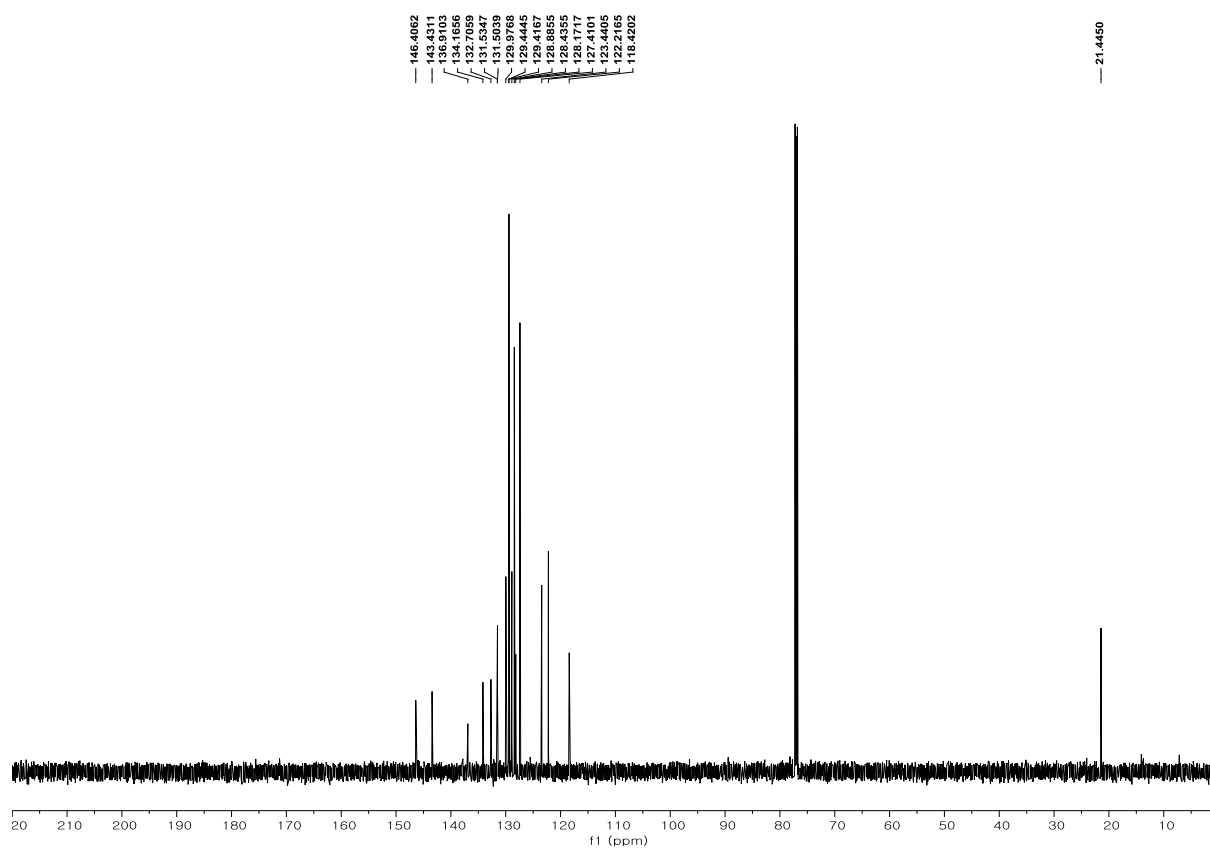
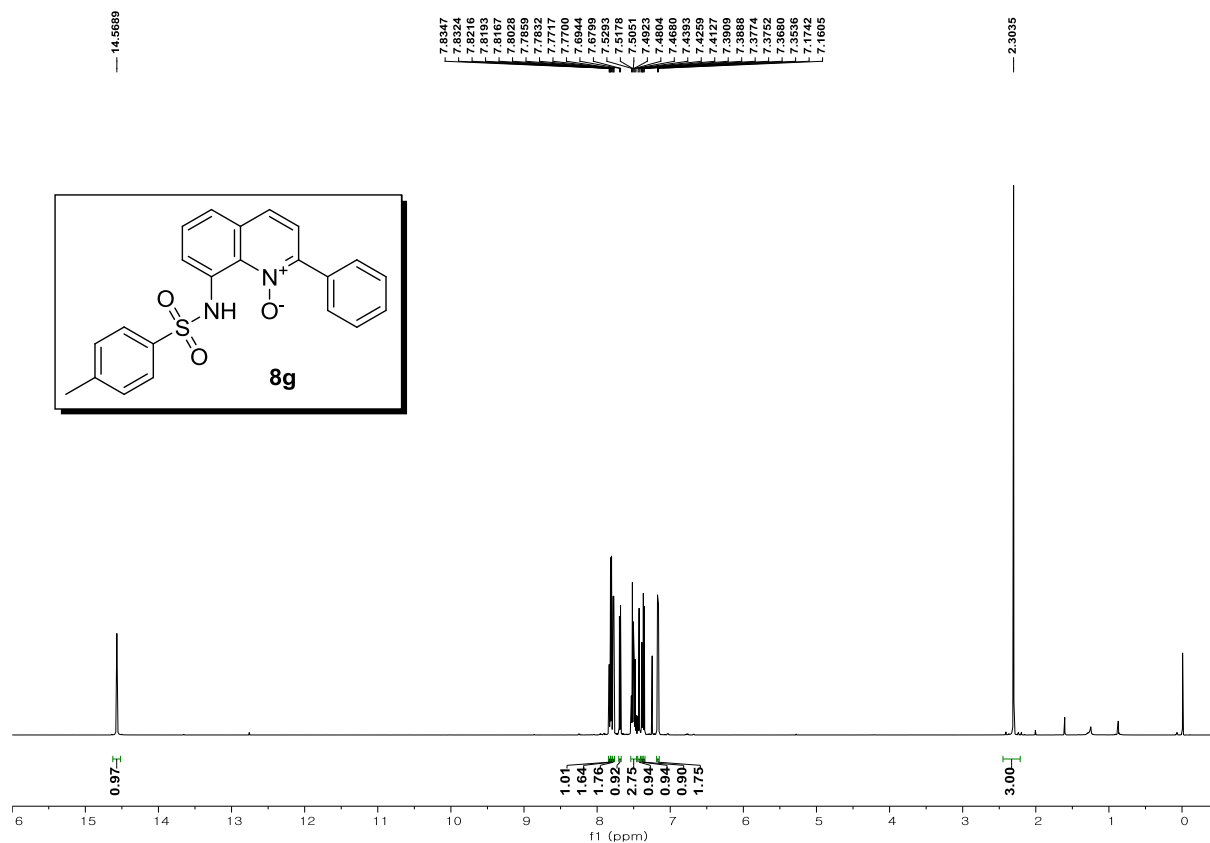
4-(4-Methylphenylsulfonamido)benzo[*c*]cinnoline 5-oxide (Table 5, 8e)



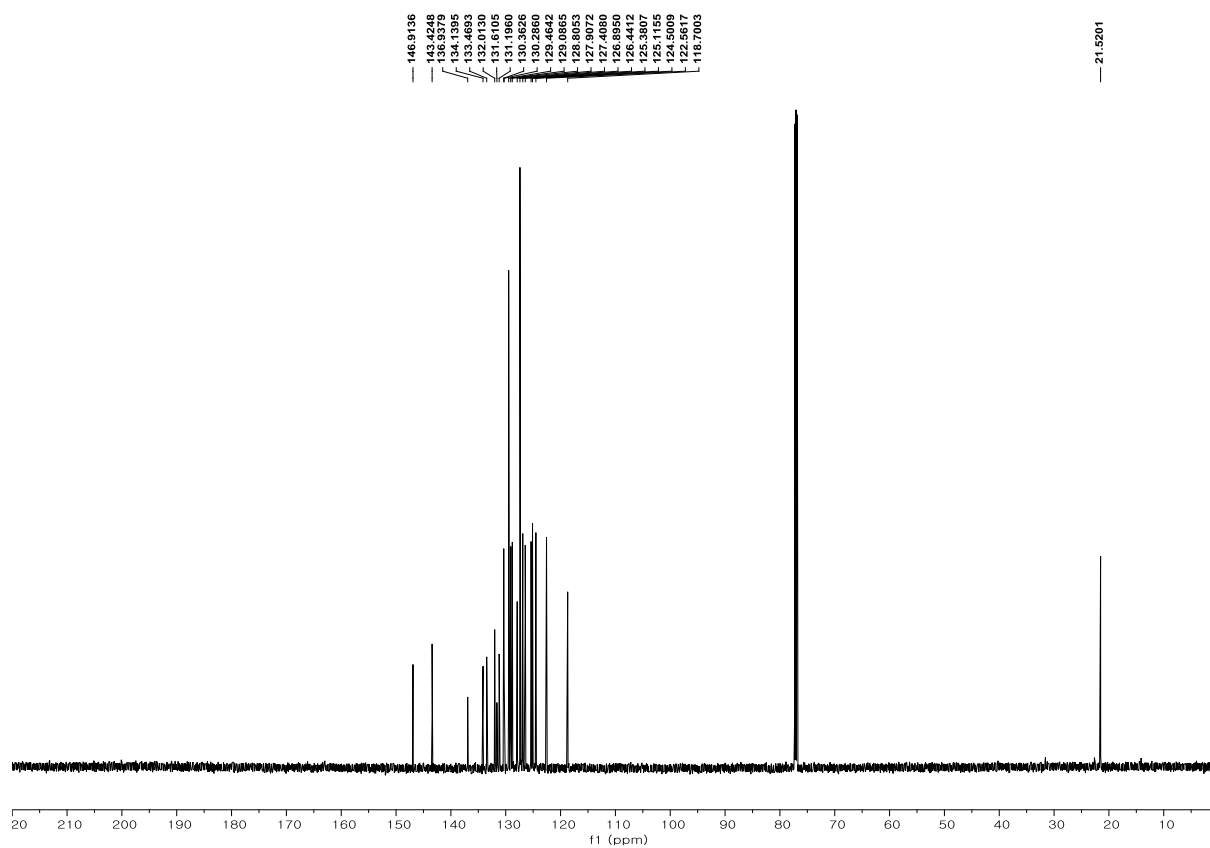
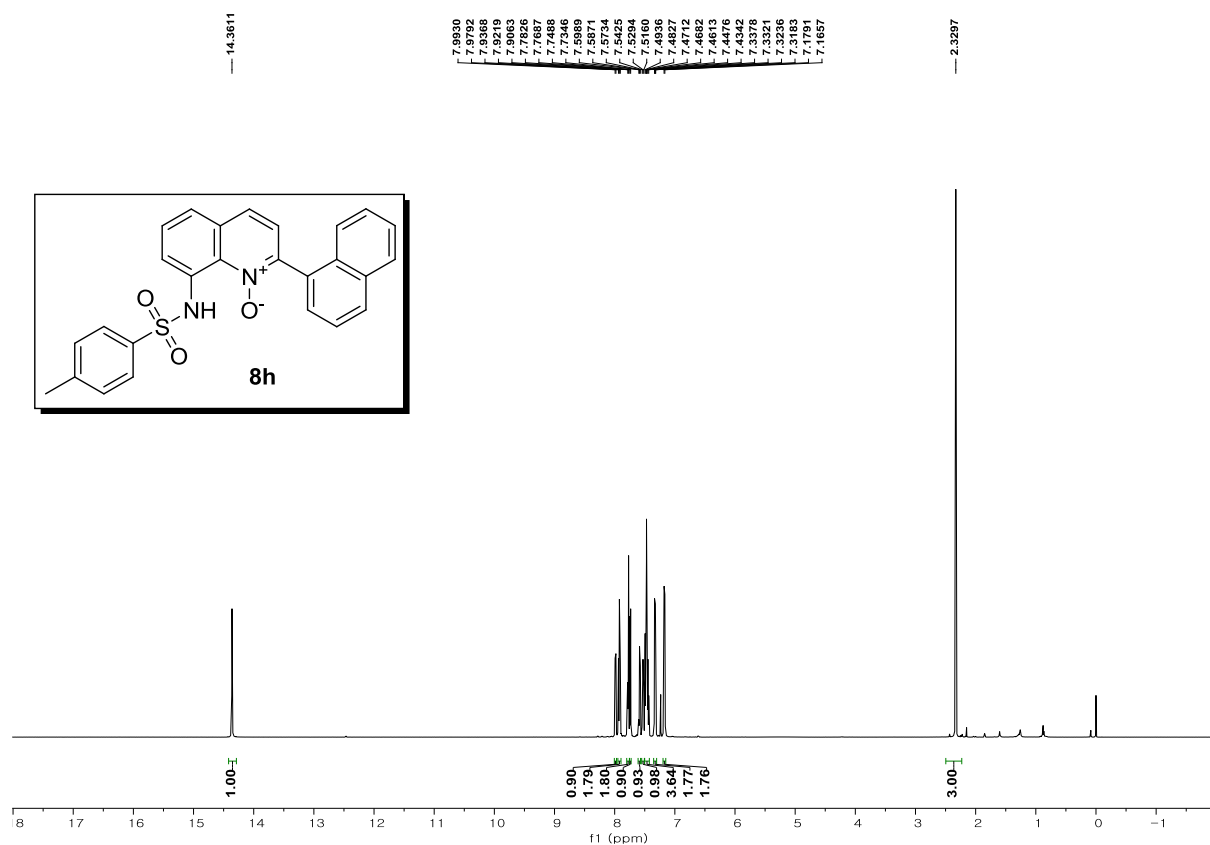
8,8'-Bis(4-methylphenylsulfonamido)-2,2'-biquinoline 1,1'-dioxide (Table 5, 8f)



# 8-(4-Methylphenylsulfonamido)-2-phenylquinoline 1-oxide (Table 5, 8g)

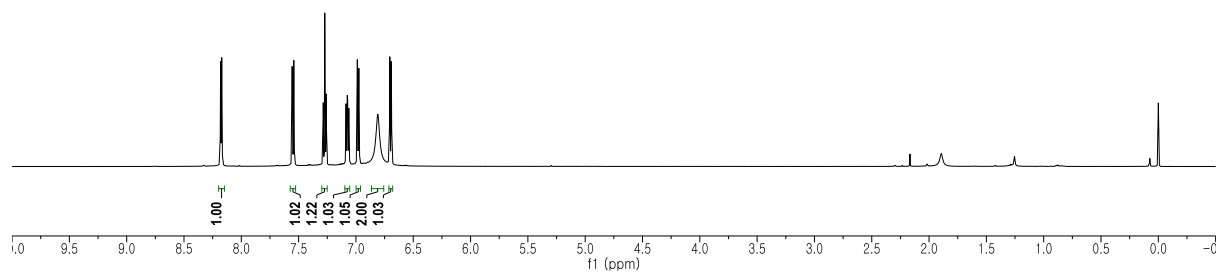
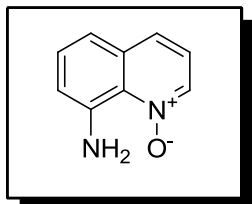


**8-(4-Methylphenylsulfonamido)-2-(naphthalen-1-yl)quinoline N-oxide (Table 5, 8h)**

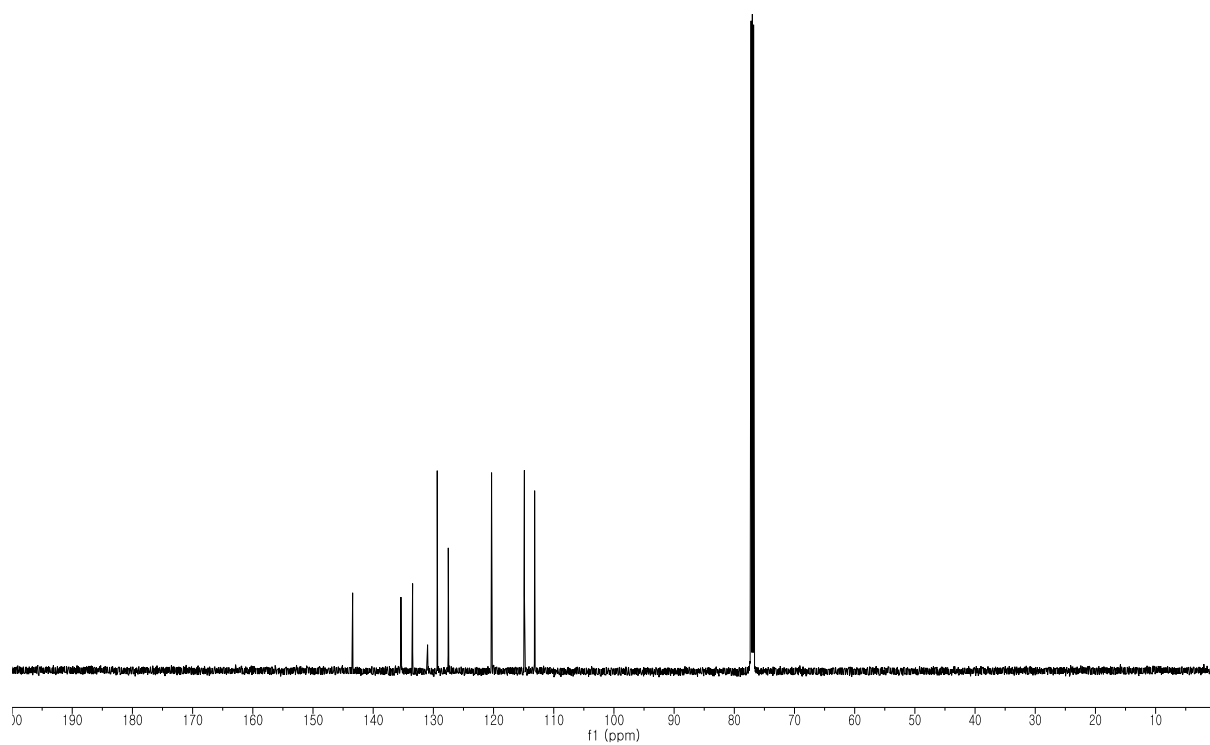


# 8-Aminoquinoline N-oxide

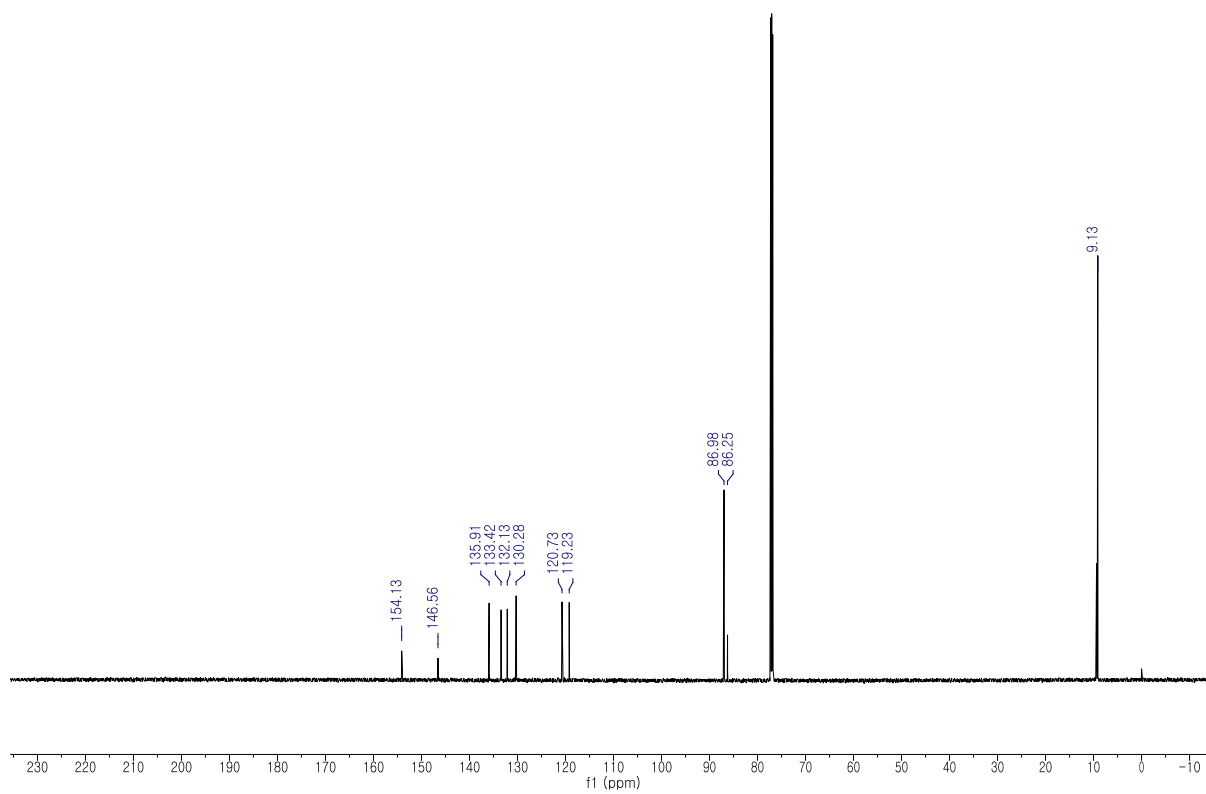
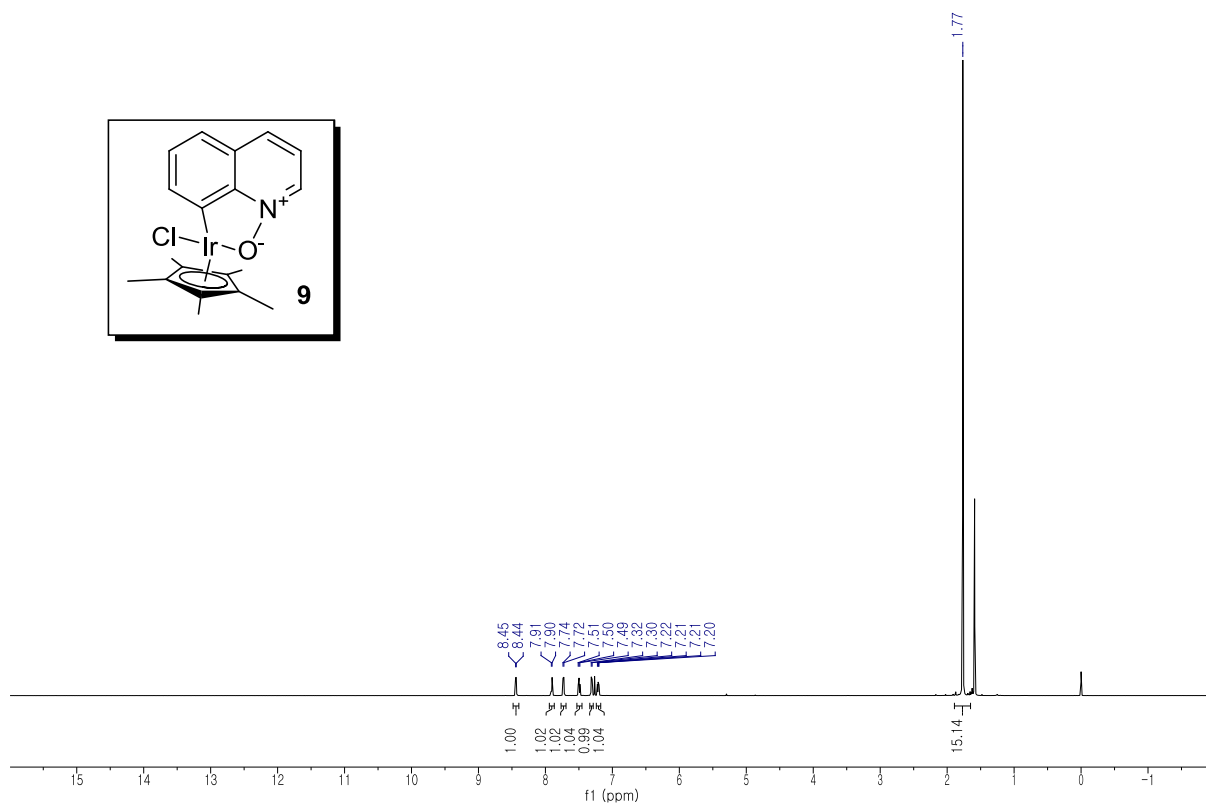
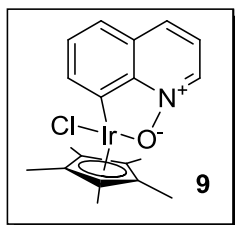
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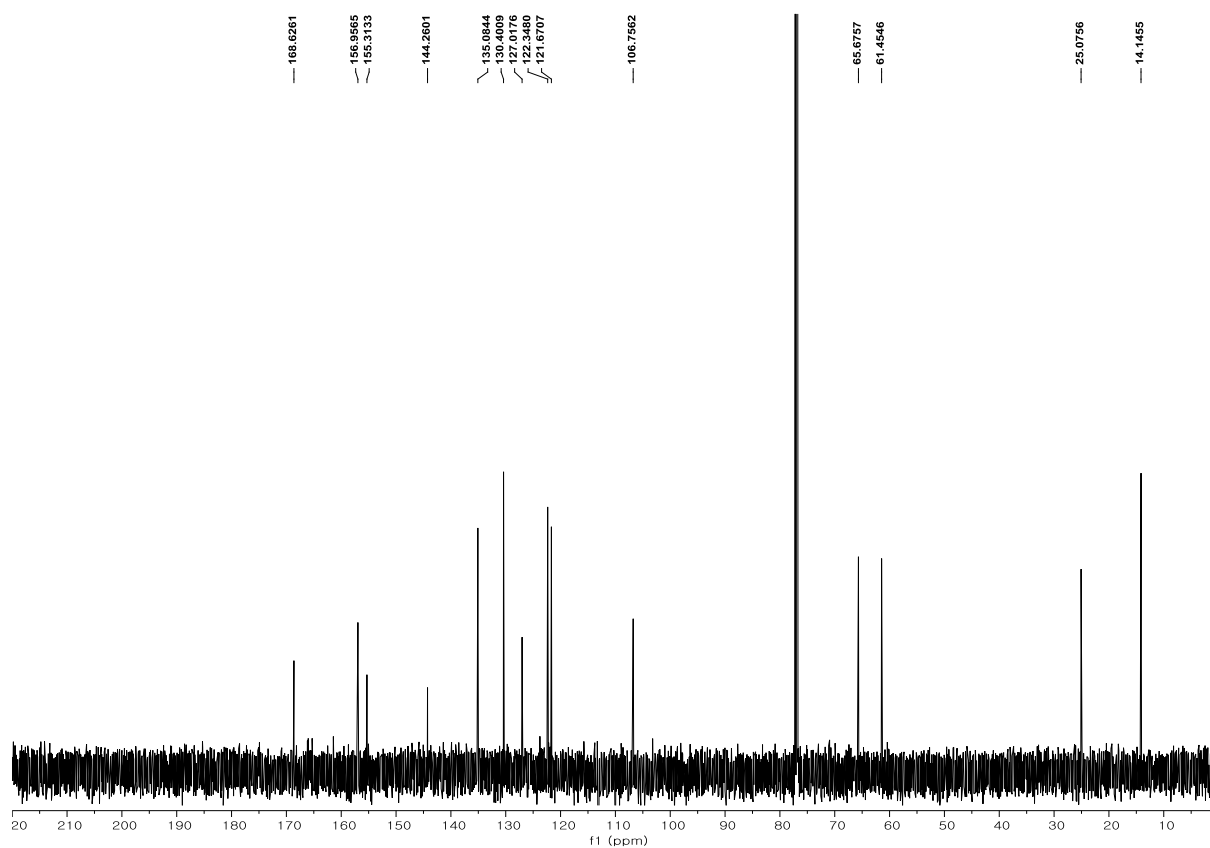
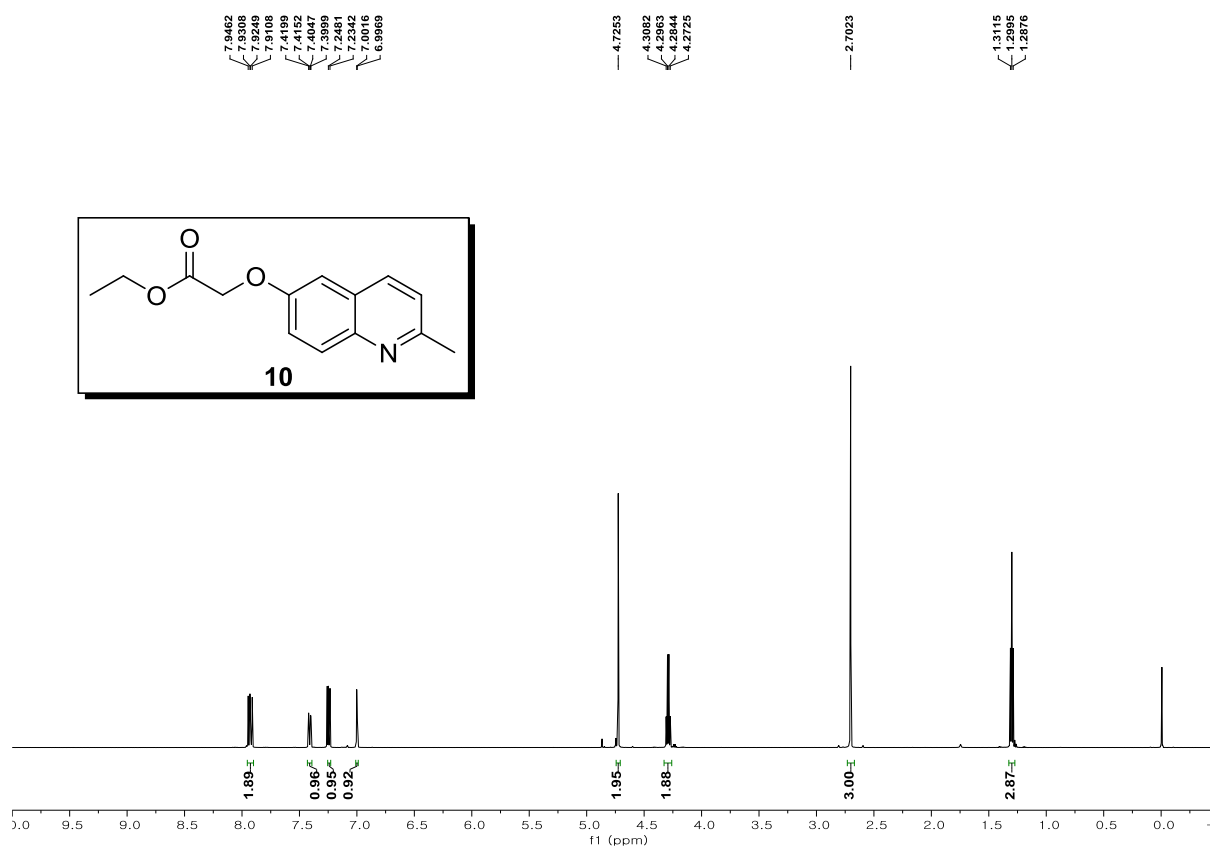
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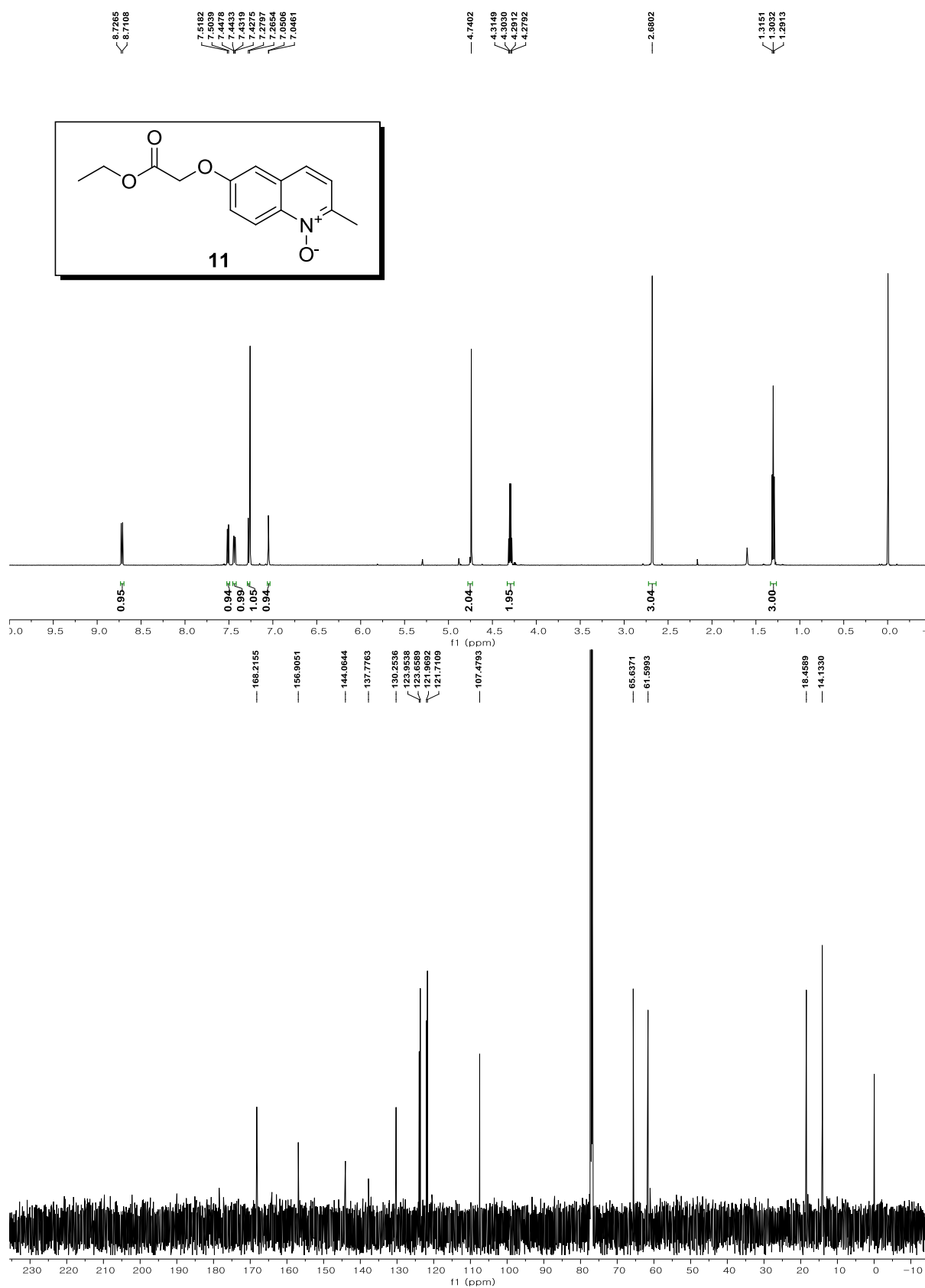
### Complex 9 (Scheme 3(a), 9)



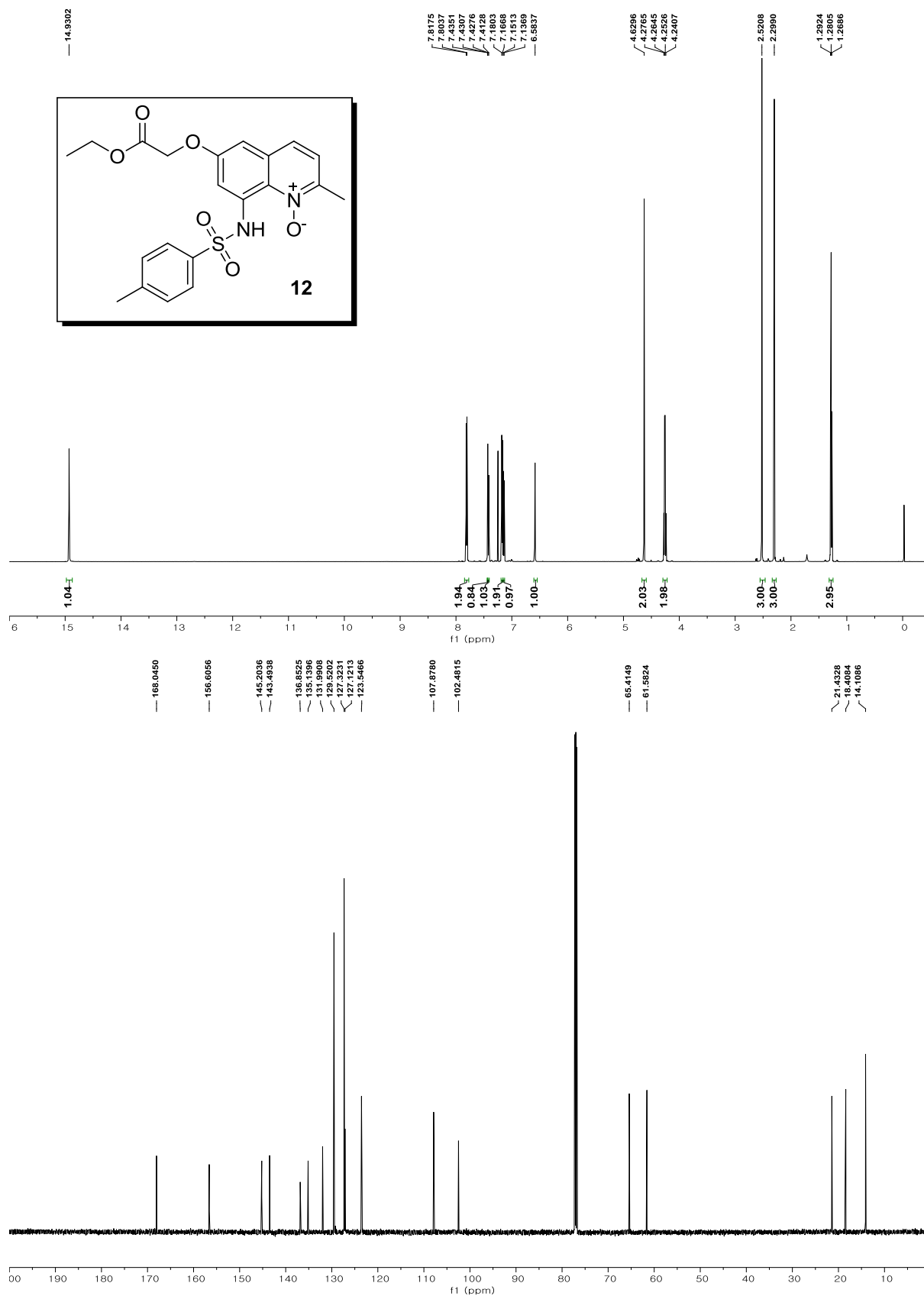
# Ethyl 2-(2-methylquinolin-6-yloxy)acetate (Scheme 5, 10)



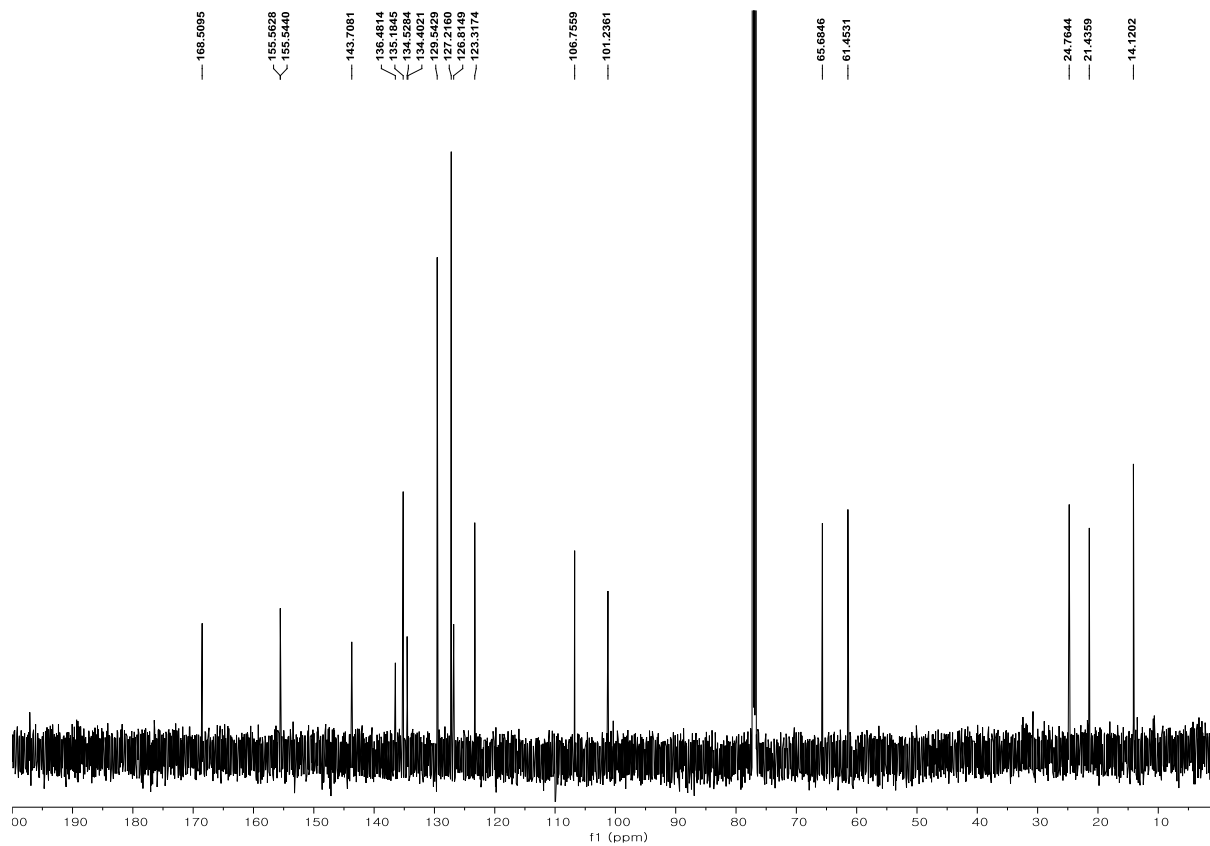
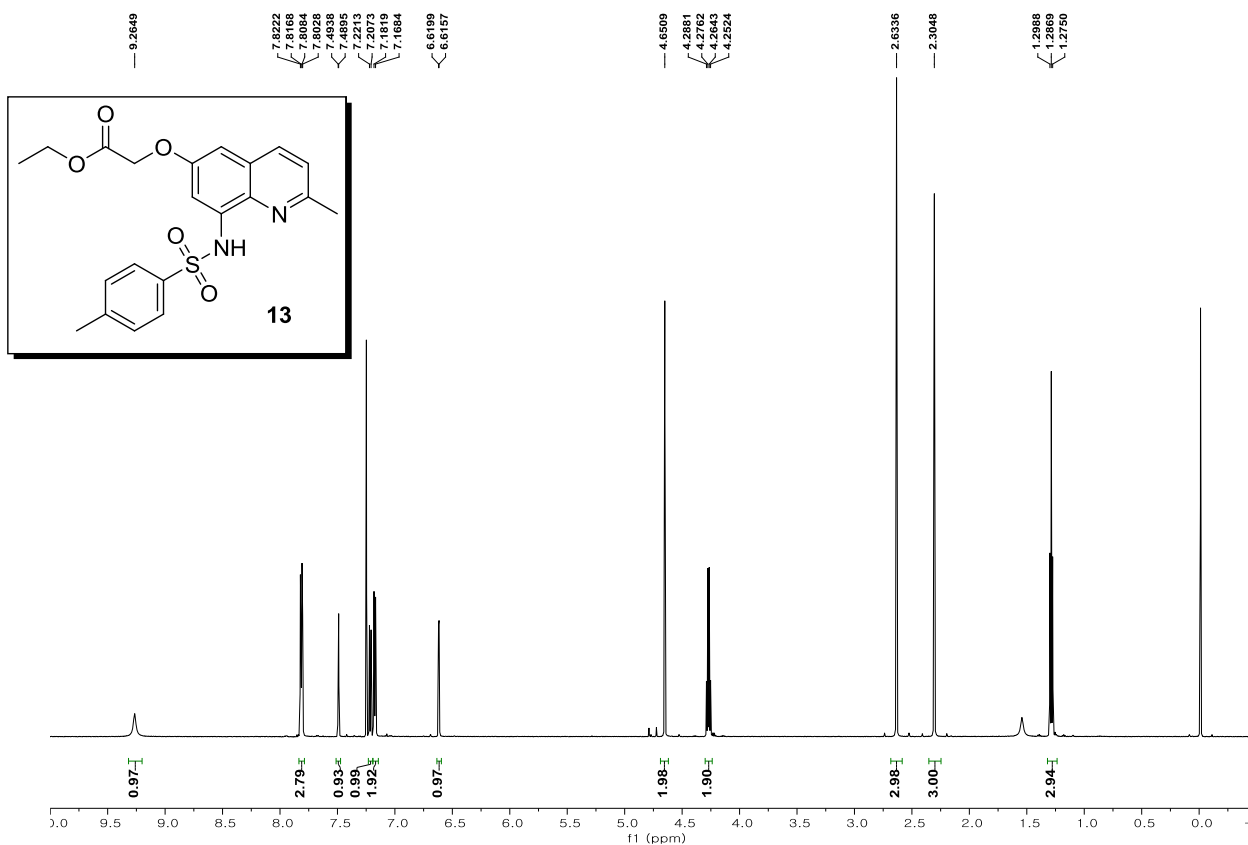
# Ethyl 2-(2-methylquinolin-6-yloxy)acetate *N*-oxide (Scheme 5, 11)



6-(2-Ethoxy-2-oxoethoxy)-2-methyl-8-(4-methylphenylsulfonamido)quinoline *N*-oxide (Scheme 5, 12)



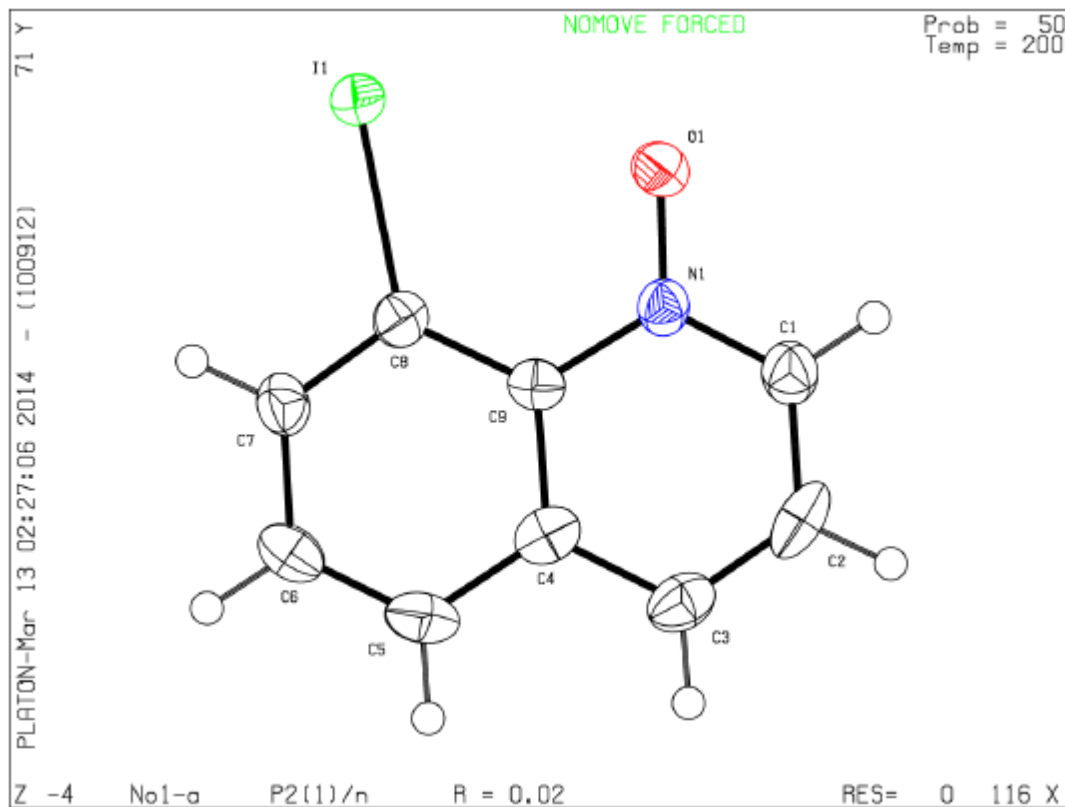
# Zinquin ethyl ester (Scheme 5, 13)



## *Appendix II*

### **Crystallographic Data for 2a, 8c, 8h, and 9**

### Crystallographic data for 2a (Table 1)



**Table S1.** Crystal data and structure refinement for **2a**.

Identification code	<b>2a</b>
Empirical formula	C <sub>9</sub> H <sub>6</sub> I N O
Formula weight	271.05
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 7.2476(6) Å = 90°. b = 8.2748(7) Å = 96.587(2)°. c = 14.1627(12) Å = 90°.
Volume	843.76(12) Å <sup>3</sup>
Z	4
Density (calculated)	2.134 Mg/m <sup>3</sup>
Absorption coefficient	3.740 mm <sup>-1</sup>
F(000)	512
Crystal size	0.21 x 0.11 x 0.04 mm <sup>3</sup>
Theta range for data collection	2.86 to 26.01°.
Index ranges	-5<=h<=8, -10<=k<=10, -17<=l<=17
Reflections collected	4876
Independent reflections	1608 [R(int) = 0.0177]
Completeness to theta = 26.01°	96.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8648 and 0.5072
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	1608 / 0 / 109
Goodness-of-fit on F <sup>2</sup>	1.361
Final R indices [I>2sigma(I)]	R1 = 0.0206, wR2 = 0.0427
R indices (all data)	R1 = 0.0279, wR2 = 0.0820
Largest diff. peak and hole	0.811 and -1.065 e.Å <sup>-3</sup>

**Table S2.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **2a**.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	U(eq)
N(1)	3318(7)	10469(6)	5969(3)	27(1)
O(1)	3674(7)	9801(5)	6806(3)	38(1)
C(1)	3722(9)	12040(8)	5869(5)	35(1)
C(2)	3483(9)	12791(8)	4987(5)	38(2)
C(3)	2842(9)	11945(8)	4191(5)	36(2)
C(4)	2324(8)	10313(8)	4289(4)	30(1)
C(5)	1600(10)	9415(9)	3481(4)	40(2)
C(6)	1089(9)	7824(9)	3572(4)	36(2)
C(7)	1306(8)	7099(8)	4471(4)	33(1)
C(8)	2002(8)	7908(7)	5277(4)	28(1)
C(9)	2554(8)	9544(7)	5193(4)	24(1)
I(1)	1964(1)	6580(1)	6551(1)	30(1)

**Table S3.** Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for **2a**.

---

N(1)-O(1)	1.307(6)
N(1)-C(1)	1.344(8)
N(1)-C(9)	1.399(7)
C(1)-C(2)	1.388(9)
C(1)-H(1A)	0.9500
C(2)-C(3)	1.362(10)
C(2)-H(2)	0.9500
C(3)-C(4)	1.413(9)
C(3)-H(3)	0.9500
C(4)-C(5)	1.414(9)
C(4)-C(9)	1.422(8)
C(5)-C(6)	1.378(10)
C(5)-H(5)	0.9500
C(6)-C(7)	1.399(9)
C(6)-H(6)	0.9500
C(7)-C(8)	1.369(8)
C(7)-H(7)	0.9500
C(8)-C(9)	1.421(8)
C(8)-I(1)	2.116(6)
O(1)-N(1)-C(1)	118.8(5)
O(1)-N(1)-C(9)	120.0(5)
C(1)-N(1)-C(9)	121.2(5)
N(1)-C(1)-C(2)	121.4(6)
N(1)-C(1)-H(1A)	119.3
C(2)-C(1)-H(1A)	119.3
C(3)-C(2)-C(1)	120.7(6)
C(3)-C(2)-H(2)	119.7
C(1)-C(2)-H(2)	119.7
C(2)-C(3)-C(4)	118.6(6)
C(2)-C(3)-H(3)	120.7
C(4)-C(3)-H(3)	120.7
C(3)-C(4)-C(5)	120.0(6)
C(3)-C(4)-C(9)	120.8(6)
C(5)-C(4)-C(9)	119.2(6)
C(6)-C(5)-C(4)	120.4(6)

C(6)-C(5)-H(5)	119.8
C(4)-C(5)-H(5)	119.8
C(5)-C(6)-C(7)	119.4(6)
C(5)-C(6)-H(6)	120.3
C(7)-C(6)-H(6)	120.3
C(8)-C(7)-C(6)	122.8(6)
C(8)-C(7)-H(7)	118.6
C(6)-C(7)-H(7)	118.6
C(7)-C(8)-C(9)	118.5(6)
C(7)-C(8)-I(1)	114.7(4)
C(9)-C(8)-I(1)	126.7(4)
N(1)-C(9)-C(8)	123.0(5)
N(1)-C(9)-C(4)	117.2(5)
C(8)-C(9)-C(4)	119.8(5)

---

Symmetry transformations used to generate equivalent atoms:

**Table S4.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **2a**. The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [ h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12} ]$

	U11	U22	U33	U23	U13	U12
N(1)	27(2)	27(3)	29(3)	-2(2)	6(2)	-4(2)
O(1)	55(3)	29(2)	27(2)	-1(2)	-2(2)	2(2)
C(1)	39(4)	33(3)	34(3)	-5(3)	10(3)	-5(3)
C(2)	28(3)	20(3)	68(5)	8(3)	14(3)	1(3)
C(3)	30(3)	38(4)	41(4)	11(3)	6(3)	-2(3)
C(4)	25(3)	32(3)	36(3)	6(3)	10(2)	7(3)
C(5)	42(4)	53(4)	24(3)	6(3)	4(3)	1(3)
C(6)	32(3)	47(4)	28(3)	-3(3)	-4(3)	2(3)
C(7)	30(3)	32(3)	34(3)	-4(3)	-1(3)	-5(3)
C(8)	21(3)	30(3)	32(3)	3(3)	0(2)	-2(2)
C(9)	21(3)	28(3)	23(3)	-1(2)	8(2)	6(2)
I(1)	35(1)	27(1)	27(1)	3(1)	-1(1)	-2(1)

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**Table S5.** Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **2a**.

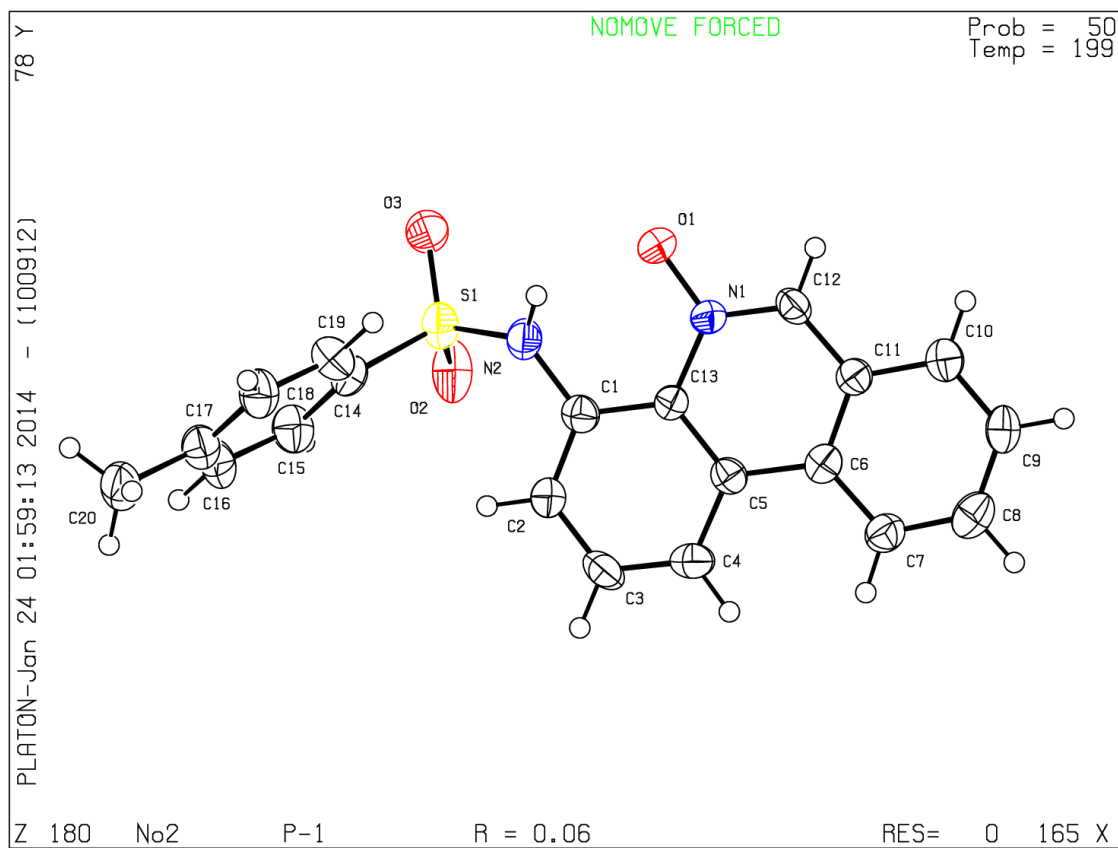
	x	y	z	U(eq)
H(1A)	4181	12650	6414	42
H(2)	3770	13906	4937	46
H(3)	2744	12442	3583	43
H(5)	1464	9912	2873	48
H(6)	594	7224	3030	43
H(7)	955	6000	4523	39

**Table S6.** Torsion angles [ $^\circ$ ] for **2a**.

O(1)-N(1)-C(1)-C(2)	176.0(6)
C(9)-N(1)-C(1)-C(2)	-3.1(9)
N(1)-C(1)-C(2)-C(3)	-0.5(10)
C(1)-C(2)-C(3)-C(4)	3.6(9)
C(2)-C(3)-C(4)-C(5)	178.1(6)
C(2)-C(3)-C(4)-C(9)	-3.1(9)
C(3)-C(4)-C(5)-C(6)	-179.9(6)
C(9)-C(4)-C(5)-C(6)	1.3(9)
C(4)-C(5)-C(6)-C(7)	-0.5(10)
C(5)-C(6)-C(7)-C(8)	0.4(10)
C(6)-C(7)-C(8)-C(9)	-1.1(9)
C(6)-C(7)-C(8)-I(1)	175.0(5)
O(1)-N(1)-C(9)-C(8)	4.9(8)
C(1)-N(1)-C(9)-C(8)	-176.1(6)
O(1)-N(1)-C(9)-C(4)	-175.6(5)
C(1)-N(1)-C(9)-C(4)	3.5(8)
C(7)-C(8)-C(9)-N(1)	-178.6(5)
I(1)-C(8)-C(9)-N(1)	5.8(8)
C(7)-C(8)-C(9)-C(4)	1.8(8)
I(1)-C(8)-C(9)-C(4)	-173.7(4)
C(3)-C(4)-C(9)-N(1)	-0.4(8)
C(5)-C(4)-C(9)-N(1)	178.5(5)
C(3)-C(4)-C(9)-C(8)	179.2(5)
C(5)-C(4)-C(9)-C(8)	-2.0(8)

Symmetry transformations used to generate equivalent atoms:

# Crystallographic data for 8c (Table 5)



**Table S7.** Crystal data and structure refinement for **8c**.

Identification code	<b>8c</b>
Empirical formula	C <sub>20</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> S
Formula weight	364.41
Temperature	199(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 6.9399(5) Å = 85.534(2)°. b = 7.6809(5) Å = 82.6980(10)°. c = 16.4129(11) Å = 73.5320(10)°.
Volume	831.39(10) Å <sup>3</sup>
Z	2
Density (calculated)	1.456 Mg/m <sup>3</sup>
Absorption coefficient	0.219 mm <sup>-1</sup>
F(000)	380
Crystal size	0.15 x 0.07 x 0.05 mm <sup>3</sup>
Theta range for data collection	1.25 to 25.98°.
Index ranges	-8<=h<=7, -9<=k<=7, -20<=l<=15
Reflections collected	5225
Independent reflections	3254 [R(int) = 0.0294]
Completeness to theta = 25.98°	99.4 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	3254 / 0 / 236
Goodness-of-fit on F <sup>2</sup>	1.115
Final R indices [I>2sigma(I)]	R1 = 0.0607, wR2 = 0.1591
R indices (all data)	R1 = 0.0970, wR2 = 0.2406
Largest diff. peak and hole	0.397 and -0.633 e.Å <sup>-3</sup>

**Table S8.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **8c**. U(eq) is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	U(eq)
C(1)	1728(6)	1320(5)	1965(2)	33(1)
C(2)	1918(6)	-196(5)	2483(3)	38(1)
C(3)	2389(7)	-1907(6)	2173(3)	43(1)
C(4)	2663(6)	-2143(5)	1343(3)	40(1)
C(5)	2482(5)	-621(5)	782(2)	31(1)
C(6)	2714(5)	-830(5)	-104(2)	31(1)
C(7)	3162(6)	-2503(5)	-475(3)	39(1)
C(8)	3342(6)	-2562(6)	-1318(3)	45(1)
C(9)	3138(6)	-997(6)	-1820(3)	41(1)
C(10)	2686(6)	658(6)	-1477(3)	37(1)
C(11)	2492(5)	755(5)	-616(2)	31(1)
C(12)	2045(6)	2452(5)	-255(2)	33(1)
N(1)	1845(5)	2636(4)	542(2)	32(1)
O(1)	1466(5)	4305(3)	813(2)	43(1)
C(13)	2014(5)	1112(5)	1110(2)	27(1)
N(2)	1262(5)	3077(4)	2274(2)	37(1)
S(1)	-221(2)	3795(2)	3095(1)	41(1)
O(2)	-1795(4)	2904(5)	3255(2)	54(1)
O(3)	-755(5)	5736(4)	2975(2)	51(1)
C(14)	1278(6)	3164(5)	3921(2)	36(1)
C(15)	540(6)	2402(6)	4636(3)	44(1)
C(16)	1693(7)	2009(6)	5303(3)	47(1)
C(17)	3551(6)	2342(6)	5253(3)	40(1)
C(18)	4236(6)	3104(6)	4525(3)	45(1)
C(19)	3143(6)	3502(6)	3859(3)	43(1)
C(20)	4783(7)	1890(6)	5971(3)	53(1)

**Table S9.** Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for **8c**.

---

C(1)-C(2)	1.373(5)
C(1)-C(13)	1.407(5)
C(1)-N(2)	1.414(5)
C(2)-C(3)	1.382(6)
C(2)-H(2)	0.9500
C(3)-C(4)	1.371(6)
C(3)-H(3)	0.9500
C(4)-C(5)	1.417(5)
C(4)-H(4)	0.9500
C(5)-C(13)	1.411(5)
C(5)-C(6)	1.458(5)
C(6)-C(7)	1.402(5)
C(6)-C(11)	1.407(5)
C(7)-C(8)	1.376(6)
C(7)-H(7)	0.9500
C(8)-C(9)	1.386(6)
C(8)-H(8)	0.9500
C(9)-C(10)	1.369(5)
C(9)-H(9)	0.9500
C(10)-C(11)	1.408(5)
C(10)-H(10)	0.9500
C(11)-C(12)	1.411(5)
C(12)-N(1)	1.311(5)
C(12)-H(12)	0.9500
N(1)-O(1)	1.334(4)
N(1)-C(13)	1.427(5)
N(2)-S(1)	1.620(3)
N(2)-H(2A)	0.8800
S(1)-O(2)	1.433(3)
S(1)-O(3)	1.435(3)
S(1)-C(14)	1.768(4)
C(14)-C(15)	1.376(6)
C(14)-C(19)	1.380(6)
C(15)-C(16)	1.401(6)
C(15)-H(15)	0.9500
C(16)-C(17)	1.375(6)

C(16)-H(16)	0.9500
C(17)-C(18)	1.378(6)
C(17)-C(20)	1.504(6)
C(18)-C(19)	1.376(6)
C(18)-H(18)	0.9500
C(19)-H(19)	0.9500
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800

C(2)-C(1)-C(13)	119.1(4)
C(2)-C(1)-N(2)	121.3(4)
C(13)-C(1)-N(2)	119.6(3)
C(1)-C(2)-C(3)	120.7(4)
C(1)-C(2)-H(2)	119.7
C(3)-C(2)-H(2)	119.7
C(4)-C(3)-C(2)	121.3(4)
C(4)-C(3)-H(3)	119.3
C(2)-C(3)-H(3)	119.3
C(3)-C(4)-C(5)	120.2(4)
C(3)-C(4)-H(4)	119.9
C(5)-C(4)-H(4)	119.9
C(13)-C(5)-C(4)	117.7(4)
C(13)-C(5)-C(6)	121.0(3)
C(4)-C(5)-C(6)	121.3(4)
C(7)-C(6)-C(11)	118.2(4)
C(7)-C(6)-C(5)	124.3(3)
C(11)-C(6)-C(5)	117.5(3)
C(8)-C(7)-C(6)	120.0(4)
C(8)-C(7)-H(7)	120.0
C(6)-C(7)-H(7)	120.0
C(7)-C(8)-C(9)	121.5(4)
C(7)-C(8)-H(8)	119.2
C(9)-C(8)-H(8)	119.2
C(10)-C(9)-C(8)	119.9(4)
C(10)-C(9)-H(9)	120.1
C(8)-C(9)-H(9)	120.1
C(9)-C(10)-C(11)	119.7(4)

C(9)-C(10)-H(10)	120.2
C(11)-C(10)-H(10)	120.2
C(6)-C(11)-C(10)	120.7(4)
C(6)-C(11)-C(12)	119.1(4)
C(10)-C(11)-C(12)	120.2(3)
N(1)-C(12)-C(11)	123.3(3)
N(1)-C(12)-H(12)	118.4
C(11)-C(12)-H(12)	118.4
C(12)-N(1)-O(1)	118.1(3)
C(12)-N(1)-C(13)	121.7(3)
O(1)-N(1)-C(13)	120.2(3)
C(1)-C(13)-C(5)	121.1(3)
C(1)-C(13)-N(1)	121.6(3)
C(5)-C(13)-N(1)	117.3(3)
C(1)-N(2)-S(1)	126.4(3)
C(1)-N(2)-H(2A)	116.8
S(1)-N(2)-H(2A)	116.8
O(2)-S(1)-O(3)	119.2(2)
O(2)-S(1)-N(2)	111.42(18)
O(3)-S(1)-N(2)	103.83(18)
O(2)-S(1)-C(14)	106.92(19)
O(3)-S(1)-C(14)	108.59(18)
N(2)-S(1)-C(14)	106.27(17)
C(15)-C(14)-C(19)	120.3(4)
C(15)-C(14)-S(1)	119.5(3)
C(19)-C(14)-S(1)	120.1(3)
C(14)-C(15)-C(16)	118.9(4)
C(14)-C(15)-H(15)	120.5
C(16)-C(15)-H(15)	120.5
C(17)-C(16)-C(15)	121.6(4)
C(17)-C(16)-H(16)	119.2
C(15)-C(16)-H(16)	119.2
C(16)-C(17)-C(18)	117.6(4)
C(16)-C(17)-C(20)	120.9(4)
C(18)-C(17)-C(20)	121.4(4)
C(19)-C(18)-C(17)	122.2(4)
C(19)-C(18)-H(18)	118.9
C(17)-C(18)-H(18)	118.9

C(18)-C(19)-C(14)	119.3(4)
C(18)-C(19)-H(19)	120.4
C(14)-C(19)-H(19)	120.4
C(17)-C(20)-H(20A)	109.5
C(17)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(17)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5

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Symmetry transformations used to generate equivalent atoms:

**Table S10.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **8c**. The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [ h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12} ]$

	U11	U22	U33	U23	U13	U12
C(1)	30(2)	35(2)	36(2)	1(2)	-10(2)	-10(2)
C(2)	45(2)	37(2)	32(2)	-4(2)	-8(2)	-11(2)
C(3)	53(3)	43(2)	35(2)	14(2)	-15(2)	-16(2)
C(4)	40(2)	30(2)	49(3)	4(2)	-11(2)	-11(2)
C(5)	26(2)	33(2)	32(2)	1(2)	-7(2)	-6(2)
C(6)	21(2)	35(2)	37(2)	-6(2)	-5(2)	-8(2)
C(7)	40(2)	34(2)	41(2)	-5(2)	-5(2)	-6(2)
C(8)	38(2)	46(3)	53(3)	-15(2)	-5(2)	-12(2)
C(9)	40(2)	53(3)	33(2)	-8(2)	-8(2)	-15(2)
C(10)	31(2)	44(2)	36(2)	-3(2)	-6(2)	-13(2)
C(11)	28(2)	32(2)	34(2)	-2(2)	-8(2)	-7(2)
C(12)	35(2)	34(2)	27(2)	4(2)	-8(2)	-7(2)
N(1)	36(2)	26(2)	33(2)	-2(1)	-7(1)	-5(1)
O(1)	60(2)	28(2)	40(2)	-5(1)	-11(1)	-8(1)
C(13)	23(2)	28(2)	29(2)	-3(2)	-4(2)	-5(1)
N(2)	44(2)	40(2)	30(2)	-5(2)	-3(2)	-14(2)
S(1)	36(1)	51(1)	33(1)	-7(1)	-4(1)	-8(1)
O(2)	37(2)	93(3)	40(2)	-16(2)	3(1)	-29(2)
O(3)	57(2)	42(2)	43(2)	-6(1)	-7(2)	7(1)
C(14)	36(2)	36(2)	35(2)	-10(2)	1(2)	-7(2)
C(15)	39(2)	56(3)	39(3)	-3(2)	2(2)	-19(2)
C(16)	52(3)	59(3)	28(2)	-3(2)	-3(2)	-12(2)
C(17)	34(2)	46(2)	35(2)	-5(2)	-4(2)	-2(2)
C(18)	39(2)	57(3)	40(3)	-7(2)	-6(2)	-12(2)
C(19)	41(2)	49(3)	39(3)	6(2)	-6(2)	-14(2)
C(20)	52(3)	55(3)	43(3)	-9(2)	-14(2)	6(2)

**Table S11.** Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **8c**.

	x	y	z	U(eq)
H(2)	1722	-68	3062	45
H(3)	2527	-2939	2543	52
H(4)	2974	-3330	1143	47
H(7)	3341	-3597	-144	47
H(8)	3612	-3701	-1561	54
H(9)	3312	-1074	-2401	49
H(10)	2505	1737	-1818	44
H(12)	1880	3515	-606	39
H(2A)	1833	3856	1992	44
H(15)	-731	2146	4677	52
H(16)	1180	1501	5800	56
H(18)	5506	3363	4482	54
H(19)	3666	4005	3361	52
H(20A)	4363	2903	6341	80
H(20B)	6218	1680	5771	80
H(20C)	4569	791	6268	80

**Table S12.** Torsion angles [°] for **8c**.

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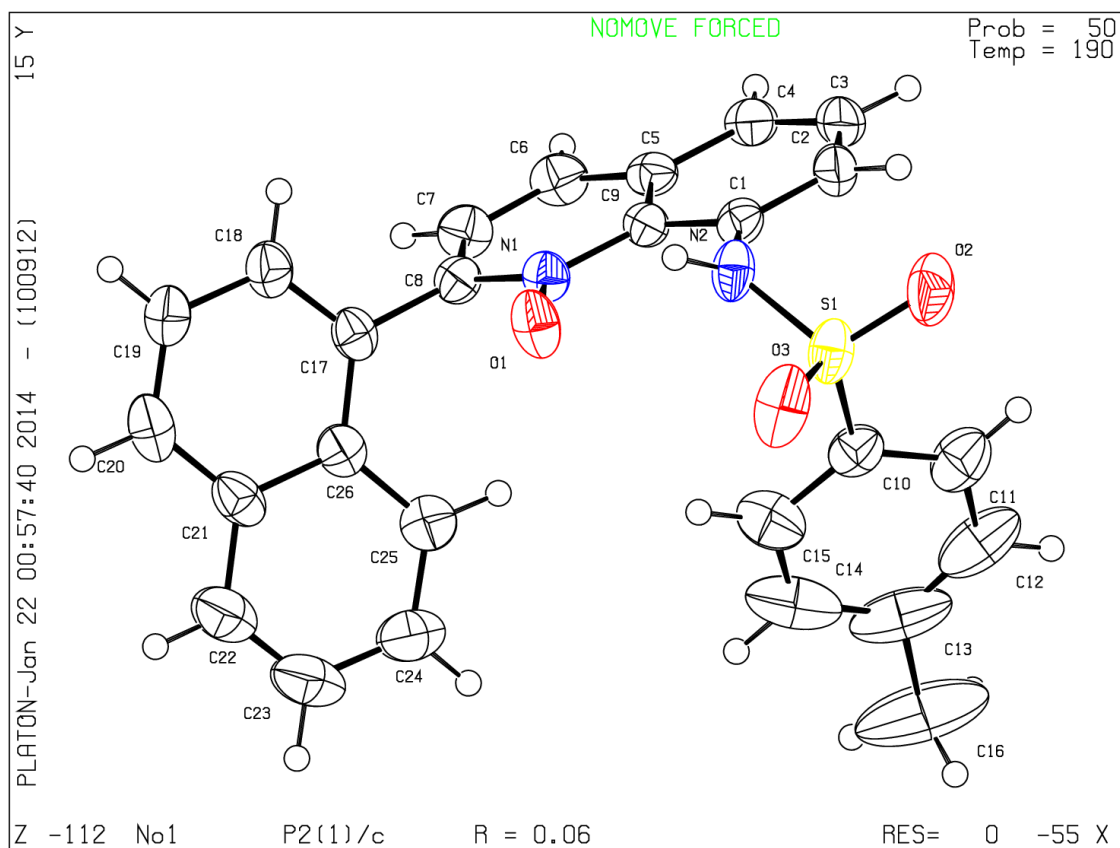
C(13)-C(1)-C(2)-C(3)	0.2(6)
N(2)-C(1)-C(2)-C(3)	-179.5(3)
C(1)-C(2)-C(3)-C(4)	-0.6(6)
C(2)-C(3)-C(4)-C(5)	0.6(6)
C(3)-C(4)-C(5)-C(13)	-0.1(6)
C(3)-C(4)-C(5)-C(6)	-178.4(4)
C(13)-C(5)-C(6)-C(7)	-179.5(3)
C(4)-C(5)-C(6)-C(7)	-1.3(6)
C(13)-C(5)-C(6)-C(11)	1.2(5)
C(4)-C(5)-C(6)-C(11)	179.4(3)
C(11)-C(6)-C(7)-C(8)	-1.0(6)
C(5)-C(6)-C(7)-C(8)	179.7(4)
C(6)-C(7)-C(8)-C(9)	1.6(6)
C(7)-C(8)-C(9)-C(10)	-2.0(6)
C(8)-C(9)-C(10)-C(11)	1.9(6)
C(7)-C(6)-C(11)-C(10)	0.9(5)
C(5)-C(6)-C(11)-C(10)	-179.7(3)
C(7)-C(6)-C(11)-C(12)	-179.9(3)
C(5)-C(6)-C(11)-C(12)	-0.5(5)
C(9)-C(10)-C(11)-C(6)	-1.4(5)
C(9)-C(10)-C(11)-C(12)	179.4(3)
C(6)-C(11)-C(12)-N(1)	0.8(5)
C(10)-C(11)-C(12)-N(1)	-180.0(4)
C(11)-C(12)-N(1)-O(1)	178.5(3)
C(11)-C(12)-N(1)-C(13)	-1.7(6)
C(2)-C(1)-C(13)-C(5)	0.2(5)
N(2)-C(1)-C(13)-C(5)	180.0(3)
C(2)-C(1)-C(13)-N(1)	-179.7(3)
N(2)-C(1)-C(13)-N(1)	0.0(5)
C(4)-C(5)-C(13)-C(1)	-0.3(5)
C(6)-C(5)-C(13)-C(1)	178.0(3)
C(4)-C(5)-C(13)-N(1)	179.7(3)
C(6)-C(5)-C(13)-N(1)	-2.0(5)
C(12)-N(1)-C(13)-C(1)	-177.7(3)
O(1)-N(1)-C(13)-C(1)	2.0(5)
C(12)-N(1)-C(13)-C(5)	2.3(5)

O(1)-N(1)-C(13)-C(5)	-178.0(3)
C(2)-C(1)-N(2)-S(1)	-35.8(5)
C(13)-C(1)-N(2)-S(1)	144.5(3)
C(1)-N(2)-S(1)-O(2)	-30.3(4)
C(1)-N(2)-S(1)-O(3)	-159.8(3)
C(1)-N(2)-S(1)-C(14)	85.8(3)
O(2)-S(1)-C(14)-C(15)	-16.0(4)
O(3)-S(1)-C(14)-C(15)	113.8(4)
N(2)-S(1)-C(14)-C(15)	-135.1(3)
O(2)-S(1)-C(14)-C(19)	166.6(3)
O(3)-S(1)-C(14)-C(19)	-63.7(4)
N(2)-S(1)-C(14)-C(19)	47.5(4)
C(19)-C(14)-C(15)-C(16)	1.2(6)
S(1)-C(14)-C(15)-C(16)	-176.2(3)
C(14)-C(15)-C(16)-C(17)	-1.0(7)
C(15)-C(16)-C(17)-C(18)	0.9(7)
C(15)-C(16)-C(17)-C(20)	-179.2(4)
C(16)-C(17)-C(18)-C(19)	-1.0(7)
C(20)-C(17)-C(18)-C(19)	179.0(4)
C(17)-C(18)-C(19)-C(14)	1.3(7)
C(15)-C(14)-C(19)-C(18)	-1.3(6)
S(1)-C(14)-C(19)-C(18)	176.1(3)

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Symmetry transformations used to generate equivalent atoms:

# Crystallographic data for 8h



**Table S13.** Crystal data and structure refinement for **8h**.

Identification code	<b>8h</b>
Empirical formula	C <sub>26</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub> S
Formula weight	440.50
Temperature	190(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 13.4902(9) Å = 90°. b = 7.8876(5) Å = 96.0890(10)°. c = 20.8018(14) Å = 90°.
Volume	2200.9(3) Å <sup>3</sup>
Z	4
Density (calculated)	1.329 Mg/m <sup>3</sup>
Absorption coefficient	0.178 mm <sup>-1</sup>
F(000)	920
Crystal size	0.29 x 0.14 x 0.07 mm <sup>3</sup>
Theta range for data collection	1.97 to 26.00°.
Index ranges	-16<=h<=16, -9<=k<=9, -25<=l<=16
Reflections collected	13253
Independent reflections	4329 [R(int) = 0.0803]
Completeness to theta = 26.00°	99.7 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	4329 / 0 / 290
Goodness-of-fit on F <sup>2</sup>	1.089
Final R indices [I>2sigma(I)]	R1 = 0.0562, wR2 = 0.1502
R indices (all data)	R1 = 0.0818, wR2 = 0.1870
Largest diff. peak and hole	0.488 and -0.464 e.Å <sup>-3</sup>

**Table S14.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **8h**. U(eq) is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	U(eq)
C(1)	3655(2)	6530(3)	10555(1)	35(1)
C(2)	3740(2)	5088(4)	10933(1)	44(1)
C(3)	3829(2)	3481(3)	10663(2)	47(1)
C(4)	3856(2)	3294(3)	10017(2)	41(1)
C(5)	3767(2)	4712(3)	9605(1)	35(1)
C(6)	3756(2)	4547(3)	8929(2)	42(1)
C(7)	3654(2)	5938(3)	8542(1)	42(1)
C(8)	3572(2)	7561(3)	8805(1)	34(1)
N(1)	3572(2)	7741(2)	9450(1)	34(1)
O(1)	3483(2)	9294(2)	9676(1)	47(1)
C(9)	3665(2)	6350(3)	9874(1)	31(1)
N(2)	3569(2)	8172(3)	10824(1)	39(1)
S(1)	2801(1)	8550(1)	11361(1)	42(1)
O(2)	3105(2)	7658(3)	11945(1)	60(1)
O(3)	2732(2)	10351(2)	11378(1)	61(1)
C(10)	1636(2)	7736(3)	11038(2)	42(1)
C(11)	1176(2)	6499(4)	11373(2)	57(1)
C(12)	242(3)	5964(5)	11131(2)	80(1)
C(13)	-243(3)	6600(6)	10586(3)	86(2)
C(14)	246(3)	7811(5)	10239(2)	85(1)
C(15)	1188(3)	8387(4)	10464(2)	60(1)
C(16)	-1313(3)	6117(7)	10333(3)	143(3)
C(17)	3499(2)	9116(3)	8398(1)	35(1)
C(18)	4340(2)	9758(3)	8180(1)	42(1)
C(19)	4304(2)	11161(4)	7763(1)	45(1)
C(20)	3407(2)	11889(3)	7553(1)	50(1)
C(21)	2504(2)	11251(3)	7768(1)	44(1)
C(22)	1577(2)	11997(4)	7564(2)	59(1)
C(23)	732(3)	11386(4)	7777(2)	66(1)
C(24)	759(2)	10009(4)	8206(2)	61(1)
C(25)	1651(2)	9255(4)	8420(2)	51(1)
C(26)	2561(2)	9862(3)	8204(1)	38(1)

**Table S15.** Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for **8h**.

---

C(1)-C(2)	1.381(4)
C(1)-N(2)	1.421(3)
C(1)-C(9)	1.424(4)
C(2)-C(3)	1.397(4)
C(2)-H(2)	0.9500
C(3)-C(4)	1.357(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.407(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.409(4)
C(5)-C(9)	1.421(3)
C(6)-C(7)	1.359(4)
C(6)-H(6)	0.9500
C(7)-C(8)	1.401(3)
C(7)-H(7)	0.9500
C(8)-N(1)	1.349(3)
C(8)-C(17)	1.487(3)
N(1)-O(1)	1.322(2)
N(1)-C(9)	1.405(3)
N(2)-S(1)	1.629(2)
N(2)-H(2A)	0.8800
S(1)-O(3)	1.425(2)
S(1)-O(2)	1.425(2)
S(1)-C(10)	1.763(3)
C(10)-C(15)	1.379(4)
C(10)-C(11)	1.383(4)
C(11)-C(12)	1.372(5)
C(11)-H(11)	0.9500
C(12)-C(13)	1.344(6)
C(12)-H(12)	0.9500
C(13)-C(14)	1.403(6)
C(13)-C(16)	1.532(5)
C(14)-C(15)	1.384(5)
C(14)-H(14)	0.9500
C(15)-H(15)	0.9500
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800

C(17)-C(18)	1.364(4)
C(17)-C(26)	1.415(4)
C(18)-C(19)	1.405(4)
C(18)-H(18)	0.9500
C(19)-C(20)	1.367(4)
C(19)-H(19)	0.9500
C(20)-C(21)	1.433(4)
C(20)-H(20)	0.9500
C(21)-C(22)	1.406(4)
C(21)-C(26)	1.419(4)
C(22)-C(23)	1.354(5)
C(22)-H(22)	0.9500
C(23)-C(24)	1.403(5)
C(23)-H(23)	0.9500
C(24)-C(25)	1.373(4)
C(24)-H(24)	0.9500
C(25)-C(26)	1.434(4)
C(25)-H(25)	0.9500

C(2)-C(1)-N(2)	122.1(2)
C(2)-C(1)-C(9)	118.4(2)
N(2)-C(1)-C(9)	119.5(2)
C(1)-C(2)-C(3)	121.5(3)
C(1)-C(2)-H(2)	119.2
C(3)-C(2)-H(2)	119.2
C(4)-C(3)-C(2)	120.7(3)
C(4)-C(3)-H(3)	119.7
C(2)-C(3)-H(3)	119.7
C(3)-C(4)-C(5)	120.5(3)
C(3)-C(4)-H(4)	119.7
C(5)-C(4)-H(4)	119.7
C(4)-C(5)-C(6)	121.7(2)
C(4)-C(5)-C(9)	119.2(3)
C(6)-C(5)-C(9)	119.1(2)
C(7)-C(6)-C(5)	120.4(2)
C(7)-C(6)-H(6)	119.8
C(5)-C(6)-H(6)	119.8
C(6)-C(7)-C(8)	120.9(3)
C(6)-C(7)-H(7)	119.5
C(8)-C(7)-H(7)	119.5

N(1)-C(8)-C(7)	119.5(2)
N(1)-C(8)-C(17)	118.2(2)
C(7)-C(8)-C(17)	122.3(2)
O(1)-N(1)-C(8)	117.4(2)
O(1)-N(1)-C(9)	120.3(2)
C(8)-N(1)-C(9)	122.2(2)
N(1)-C(9)-C(5)	117.9(2)
N(1)-C(9)-C(1)	122.5(2)
C(5)-C(9)-C(1)	119.6(2)
C(1)-N(2)-S(1)	121.39(16)
C(1)-N(2)-H(2A)	119.3
S(1)-N(2)-H(2A)	119.3
O(3)-S(1)-O(2)	118.97(14)
O(3)-S(1)-N(2)	104.30(12)
O(2)-S(1)-N(2)	110.35(12)
O(3)-S(1)-C(10)	108.34(14)
O(2)-S(1)-C(10)	107.98(13)
N(2)-S(1)-C(10)	106.19(12)
C(15)-C(10)-C(11)	121.3(3)
C(15)-C(10)-S(1)	119.0(2)
C(11)-C(10)-S(1)	119.6(3)
C(12)-C(11)-C(10)	118.4(4)
C(12)-C(11)-H(11)	120.8
C(10)-C(11)-H(11)	120.8
C(13)-C(12)-C(11)	122.7(4)
C(13)-C(12)-H(12)	118.7
C(11)-C(12)-H(12)	118.7
C(12)-C(13)-C(14)	118.3(3)
C(12)-C(13)-C(16)	123.7(5)
C(14)-C(13)-C(16)	118.0(5)
C(15)-C(14)-C(13)	121.0(4)
C(15)-C(14)-H(14)	119.5
C(13)-C(14)-H(14)	119.5
C(10)-C(15)-C(14)	118.2(3)
C(10)-C(15)-H(15)	120.9
C(14)-C(15)-H(15)	120.9
C(13)-C(16)-H(16A)	109.5
C(13)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(13)-C(16)-H(16C)	109.5

H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(18)-C(17)-C(26)	120.1(2)
C(18)-C(17)-C(8)	119.2(2)
C(26)-C(17)-C(8)	120.6(2)
C(17)-C(18)-C(19)	121.5(3)
C(17)-C(18)-H(18)	119.3
C(19)-C(18)-H(18)	119.3
C(20)-C(19)-C(18)	120.0(3)
C(20)-C(19)-H(19)	120.0
C(18)-C(19)-H(19)	120.0
C(19)-C(20)-C(21)	120.4(3)
C(19)-C(20)-H(20)	119.8
C(21)-C(20)-H(20)	119.8
C(22)-C(21)-C(26)	120.1(3)
C(22)-C(21)-C(20)	121.2(3)
C(26)-C(21)-C(20)	118.7(2)
C(23)-C(22)-C(21)	120.3(3)
C(23)-C(22)-H(22)	119.9
C(21)-C(22)-H(22)	119.9
C(22)-C(23)-C(24)	121.2(3)
C(22)-C(23)-H(23)	119.4
C(24)-C(23)-H(23)	119.4
C(25)-C(24)-C(23)	120.2(3)
C(25)-C(24)-H(24)	119.9
C(23)-C(24)-H(24)	119.9
C(24)-C(25)-C(26)	120.3(3)
C(24)-C(25)-H(25)	119.9
C(26)-C(25)-H(25)	119.9
C(17)-C(26)-C(21)	119.4(2)
C(17)-C(26)-C(25)	122.7(2)
C(21)-C(26)-C(25)	117.9(2)

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Symmetry transformations used to generate equivalent atoms:

**Table S16.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **8h**. The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [ h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12} ]$

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
C(1)	28(1)	38(1)	38(1)	2(1)	3(1)	-8(1)
C(2)	38(1)	54(2)	41(2)	17(1)	5(1)	-3(1)
C(3)	37(2)	38(2)	66(2)	23(1)	8(1)	-2(1)
C(4)	33(1)	30(1)	62(2)	9(1)	7(1)	-2(1)
C(5)	27(1)	29(1)	48(2)	1(1)	3(1)	-2(1)
C(6)	44(2)	29(1)	54(2)	-6(1)	7(1)	1(1)
C(7)	47(2)	38(1)	41(2)	-8(1)	6(1)	2(1)
C(8)	35(1)	35(1)	33(1)	-2(1)	5(1)	0(1)
N(1)	40(1)	25(1)	37(1)	-1(1)	5(1)	-2(1)
O(1)	82(2)	22(1)	37(1)	-2(1)	12(1)	1(1)
C(9)	27(1)	28(1)	38(1)	4(1)	1(1)	-4(1)
N(2)	45(1)	39(1)	32(1)	0(1)	6(1)	-18(1)
S(1)	54(1)	45(1)	30(1)	-6(1)	9(1)	-17(1)
O(2)	67(1)	85(2)	30(1)	6(1)	8(1)	-16(1)
O(3)	91(2)	42(1)	55(1)	-17(1)	29(1)	-25(1)
C(10)	42(2)	35(1)	51(2)	-6(1)	12(1)	0(1)
C(11)	55(2)	50(2)	69(2)	-6(2)	20(2)	-11(1)
C(12)	45(2)	90(3)	109(4)	-31(3)	26(2)	-26(2)
C(13)	34(2)	84(3)	138(4)	-53(3)	3(2)	-2(2)
C(14)	63(2)	79(3)	104(3)	-22(2)	-29(2)	25(2)
C(15)	61(2)	49(2)	67(2)	0(2)	-7(2)	4(1)
C(16)	38(2)	171(5)	215(7)	-97(5)	-5(3)	-4(3)
C(17)	46(2)	33(1)	27(1)	-2(1)	2(1)	1(1)
C(18)	51(2)	42(2)	34(2)	2(1)	8(1)	1(1)
C(19)	54(2)	45(2)	36(2)	3(1)	12(1)	-4(1)
C(20)	78(2)	37(1)	35(2)	4(1)	10(2)	0(1)
C(21)	60(2)	37(1)	33(2)	-1(1)	0(1)	13(1)
C(22)	65(2)	59(2)	53(2)	2(2)	-2(2)	21(2)
C(23)	62(2)	68(2)	64(2)	-5(2)	-7(2)	27(2)
C(24)	42(2)	73(2)	67(2)	-5(2)	6(2)	10(2)
C(25)	49(2)	54(2)	50(2)	3(2)	7(1)	4(1)
C(26)	47(2)	34(1)	33(1)	-3(1)	5(1)	4(1)

**Table S17.** Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **8h**.

	x	y	z	U(eq)
H(2)	3738	5191	11388	53
H(3)	3871	2509	10934	56
H(4)	3936	2196	9841	50
H(6)	3821	3458	8743	51
H(7)	3639	5808	8087	50
H(2A)	3939	9003	10698	47
H(11)	1499	6032	11761	68
H(12)	-74	5110	11358	96
H(14)	-75	8242	9844	102
H(15)	1518	9209	10229	72
H(16A)	-1414	4902	10401	214
H(16B)	-1429	6372	9870	214
H(16C)	-1781	6767	10565	214
H(18)	4965	9245	8314	50
H(19)	4901	11603	7625	54
H(20)	3384	12823	7264	59
H(22)	1543	12933	7276	71
H(23)	111	11898	7634	79
H(24)	158	9597	8349	73
H(25)	1665	8328	8712	61

**Table S18.** Torsion angles [°] for **8h**.

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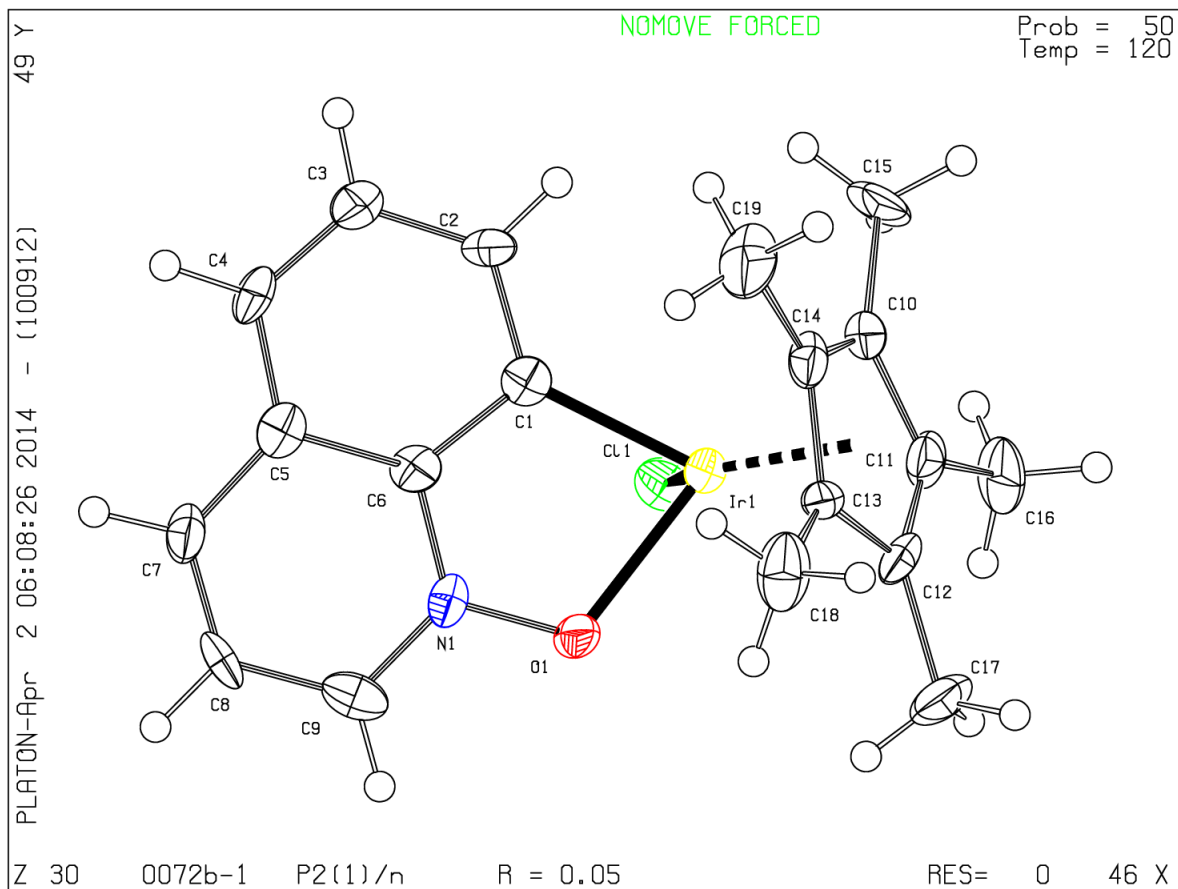
N(2)-C(1)-C(2)-C(3)	-179.7(2)
C(9)-C(1)-C(2)-C(3)	-0.3(4)
C(1)-C(2)-C(3)-C(4)	1.5(4)
C(2)-C(3)-C(4)-C(5)	-1.8(4)
C(3)-C(4)-C(5)-C(6)	-177.6(3)
C(3)-C(4)-C(5)-C(9)	1.0(4)
C(4)-C(5)-C(6)-C(7)	179.0(2)
C(9)-C(5)-C(6)-C(7)	0.3(4)
C(5)-C(6)-C(7)-C(8)	0.9(4)
C(6)-C(7)-C(8)-N(1)	-1.5(4)
C(6)-C(7)-C(8)-C(17)	177.6(2)
C(7)-C(8)-N(1)-O(1)	-179.4(2)
C(17)-C(8)-N(1)-O(1)	1.5(3)
C(7)-C(8)-N(1)-C(9)	0.8(4)
C(17)-C(8)-N(1)-C(9)	-178.3(2)
O(1)-N(1)-C(9)-C(5)	-179.4(2)
C(8)-N(1)-C(9)-C(5)	0.4(3)
O(1)-N(1)-C(9)-C(1)	0.8(3)
C(8)-N(1)-C(9)-C(1)	-179.3(2)
C(4)-C(5)-C(9)-N(1)	-179.7(2)
C(6)-C(5)-C(9)-N(1)	-1.0(3)
C(4)-C(5)-C(9)-C(1)	0.1(3)
C(6)-C(5)-C(9)-C(1)	178.8(2)
C(2)-C(1)-C(9)-N(1)	179.4(2)
N(2)-C(1)-C(9)-N(1)	-1.3(3)
C(2)-C(1)-C(9)-C(5)	-0.4(3)
N(2)-C(1)-C(9)-C(5)	178.9(2)
C(2)-C(1)-N(2)-S(1)	-46.6(3)
C(9)-C(1)-N(2)-S(1)	134.0(2)
C(1)-N(2)-S(1)-O(3)	-164.9(2)
C(1)-N(2)-S(1)-O(2)	66.2(2)
C(1)-N(2)-S(1)-C(10)	-50.6(2)
O(3)-S(1)-C(10)-C(15)	50.6(3)
O(2)-S(1)-C(10)-C(15)	-179.3(2)
N(2)-S(1)-C(10)-C(15)	-60.9(3)
O(3)-S(1)-C(10)-C(11)	-127.4(2)
O(2)-S(1)-C(10)-C(11)	2.7(3)
N(2)-S(1)-C(10)-C(11)	121.0(2)

C(15)-C(10)-C(11)-C(12)	-2.0(4)
S(1)-C(10)-C(11)-C(12)	176.0(2)
C(10)-C(11)-C(12)-C(13)	-0.4(5)
C(11)-C(12)-C(13)-C(14)	2.6(6)
C(11)-C(12)-C(13)-C(16)	-175.5(4)
C(12)-C(13)-C(14)-C(15)	-2.4(6)
C(16)-C(13)-C(14)-C(15)	175.7(3)
C(11)-C(10)-C(15)-C(14)	2.1(5)
S(1)-C(10)-C(15)-C(14)	-175.9(2)
C(13)-C(14)-C(15)-C(10)	0.1(5)
N(1)-C(8)-C(17)-C(18)	101.1(3)
C(7)-C(8)-C(17)-C(18)	-77.9(3)
N(1)-C(8)-C(17)-C(26)	-82.9(3)
C(7)-C(8)-C(17)-C(26)	98.0(3)
C(26)-C(17)-C(18)-C(19)	0.1(4)
C(8)-C(17)-C(18)-C(19)	176.0(2)
C(17)-C(18)-C(19)-C(20)	-1.5(4)
C(18)-C(19)-C(20)-C(21)	1.3(4)
C(19)-C(20)-C(21)-C(22)	179.3(3)
C(19)-C(20)-C(21)-C(26)	0.4(4)
C(26)-C(21)-C(22)-C(23)	-0.5(5)
C(20)-C(21)-C(22)-C(23)	-179.4(3)
C(21)-C(22)-C(23)-C(24)	0.3(5)
C(22)-C(23)-C(24)-C(25)	0.2(5)
C(23)-C(24)-C(25)-C(26)	-0.4(5)
C(18)-C(17)-C(26)-C(21)	1.6(4)
C(8)-C(17)-C(26)-C(21)	-174.3(2)
C(18)-C(17)-C(26)-C(25)	-179.5(3)
C(8)-C(17)-C(26)-C(25)	4.6(4)
C(22)-C(21)-C(26)-C(17)	179.3(3)
C(20)-C(21)-C(26)-C(17)	-1.8(4)
C(22)-C(21)-C(26)-C(25)	0.3(4)
C(20)-C(21)-C(26)-C(25)	179.2(3)
C(24)-C(25)-C(26)-C(17)	-178.8(3)
C(24)-C(25)-C(26)-C(21)	0.1(4)

---

Symmetry transformations used to generate equivalent atoms:

Crystallographic data for 9 (Scheme 3(a))



**Table S19.** Crystal data and structure refinement for **9**.

Identification code	<b>9</b>	
Empirical formula	C <sub>19</sub> H <sub>21</sub> Cl Ir N O	
Formula weight	507.02	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 8.2672(12) Å	= 90?
	b = 14.5253(19) Å	= 92.942(5)?
	c = 14.507(2) Å	= 90?
Volume	1739.7(4) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.936 Mg/m <sup>3</sup>	
Absorption coefficient	7.831 mm <sup>-1</sup>	
F(000)	976	
Crystal size	0.04 x 0.03 x 0.03 mm <sup>3</sup>	
Theta range for data collection	1.99 to 25.94°.	
Index ranges	-10<=h<=9, -17<=k<=17, -17<=l<=16	
Reflections collected	11076	
Independent reflections	3354 [R(int) = 0.0843]	
Completeness to theta = 25.94?	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7990 and 0.7447	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	3354 / 0 / 210	
Goodness-of-fit on F <sup>2</sup>	1.002	
Final R indices [I>2sigma(I)]	R1 = 0.0454, wR2 = 0.0670	
R indices (all data)	R1 = 0.0962, wR2 = 0.0879	
Largest diff. peak and hole	1.151 and -1.050 e.Å <sup>-3</sup>	

**Table S20.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **9**. U(eq) is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	U(eq)
Ir(1)	1477(1)	6482(1)	7047(1)	22(1)
N(1)	197(10)	4705(5)	6449(6)	24(2)
O(1)	1220(9)	5344(4)	6143(5)	27(2)
Cl(1)	-1004(3)	6976(2)	6244(2)	30(1)
C(1)	94(12)	5629(7)	7778(7)	23(3)
C(2)	-531(13)	5704(7)	8652(7)	29(3)
C(3)	-1496(15)	5024(7)	9041(8)	36(3)
C(4)	-1903(14)	4233(7)	8560(8)	34(3)
C(5)	-1366(13)	4107(7)	7673(7)	26(3)
C(6)	-387(13)	4801(6)	7314(7)	23(3)
C(7)	-1756(13)	3350(7)	7080(8)	30(3)
C(8)	-1208(13)	3300(6)	6231(8)	29(3)
C(9)	-214(13)	3984(7)	5900(8)	30(3)
C(10)	2333(14)	7636(7)	7832(8)	29(3)
C(11)	2704(14)	7845(7)	6867(8)	30(3)
C(12)	3749(13)	7162(7)	6575(7)	25(3)
C(13)	4054(12)	6507(7)	7339(7)	23(2)
C(14)	3235(13)	6839(7)	8129(7)	27(3)
C(15)	1329(15)	8243(7)	8413(8)	47(4)
C(16)	2072(14)	8645(7)	6313(8)	41(3)
C(17)	4448(14)	7082(8)	5657(8)	43(3)
C(18)	5201(14)	5717(7)	7319(9)	43(3)
C(19)	3402(16)	6420(9)	9087(7)	55(4)

**Table S21.** Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for **9**.

---

Ir(1)-C(1)	2.023(11)
Ir(1)-O(1)	2.113(6)
Ir(1)-C(10)	2.128(10)
Ir(1)-C(14)	2.147(10)
Ir(1)-C(13)	2.151(10)
Ir(1)-C(11)	2.246(10)
Ir(1)-C(12)	2.259(11)
Ir(1)-Cl(1)	2.416(3)
N(1)-O(1)	1.346(10)
N(1)-C(9)	1.350(12)
N(1)-C(6)	1.375(13)
C(1)-C(2)	1.398(14)
C(1)-C(6)	1.424(13)
C(2)-C(3)	1.405(14)
C(3)-C(4)	1.377(14)
C(4)-C(5)	1.394(15)
C(5)-C(6)	1.409(14)
C(5)-C(7)	1.424(13)
C(7)-C(8)	1.336(14)
C(8)-C(9)	1.390(14)
C(10)-C(14)	1.431(14)
C(10)-C(11)	1.481(15)
C(10)-C(15)	1.499(15)
C(11)-C(12)	1.395(15)
C(11)-C(16)	1.492(13)
C(12)-C(13)	1.472(13)
C(12)-C(17)	1.484(14)
C(13)-C(14)	1.444(14)
C(13)-C(18)	1.490(14)
C(14)-C(19)	1.517(13)
C(1)-Ir(1)-O(1)	78.7(3)
C(1)-Ir(1)-C(10)	112.5(4)
O(1)-Ir(1)-C(10)	165.6(4)
C(1)-Ir(1)-C(14)	98.3(4)
O(1)-Ir(1)-C(14)	133.3(3)

C(10)-Ir(1)-C(14)	39.1(4)
C(1)-Ir(1)-C(13)	119.2(4)
O(1)-Ir(1)-C(13)	101.7(3)
C(10)-Ir(1)-C(13)	65.3(4)
C(14)-Ir(1)-C(13)	39.3(4)
C(1)-Ir(1)-C(11)	150.7(4)
O(1)-Ir(1)-C(11)	130.5(4)
C(10)-Ir(1)-C(11)	39.5(4)
C(14)-Ir(1)-C(11)	65.1(4)
C(13)-Ir(1)-C(11)	63.8(4)
C(1)-Ir(1)-C(12)	158.1(4)
O(1)-Ir(1)-C(12)	102.3(3)
C(10)-Ir(1)-C(12)	63.8(4)
C(14)-Ir(1)-C(12)	64.8(4)
C(13)-Ir(1)-C(12)	38.9(3)
C(11)-Ir(1)-C(12)	36.1(4)
C(1)-Ir(1)-Cl(1)	86.9(3)
O(1)-Ir(1)-Cl(1)	83.0(2)
C(10)-Ir(1)-Cl(1)	105.9(3)
C(14)-Ir(1)-Cl(1)	143.8(3)
C(13)-Ir(1)-Cl(1)	153.9(3)
C(11)-Ir(1)-Cl(1)	93.4(3)
C(12)-Ir(1)-Cl(1)	115.0(3)
O(1)-N(1)-C(9)	119.0(9)
O(1)-N(1)-C(6)	119.1(8)
C(9)-N(1)-C(6)	121.9(10)
N(1)-O(1)-Ir(1)	112.3(6)
C(2)-C(1)-C(6)	112.7(10)
C(2)-C(1)-Ir(1)	132.3(8)
C(6)-C(1)-Ir(1)	114.9(8)
C(1)-C(2)-C(3)	123.6(10)
C(4)-C(3)-C(2)	120.7(11)
C(3)-C(4)-C(5)	119.8(11)
C(4)-C(5)-C(6)	117.6(10)
C(4)-C(5)-C(7)	125.9(10)
C(6)-C(5)-C(7)	116.5(10)
N(1)-C(6)-C(5)	120.0(9)
N(1)-C(6)-C(1)	114.5(10)

C(5)-C(6)-C(1)	125.5(10)
C(8)-C(7)-C(5)	121.5(10)
C(7)-C(8)-C(9)	121.0(10)
N(1)-C(9)-C(8)	119.1(10)
C(14)-C(10)-C(11)	108.6(10)
C(14)-C(10)-C(15)	127.0(10)
C(11)-C(10)-C(15)	124.0(10)
C(14)-C(10)-Ir(1)	71.2(6)
C(11)-C(10)-Ir(1)	74.5(6)
C(15)-C(10)-Ir(1)	125.9(8)
C(12)-C(11)-C(10)	107.6(9)
C(12)-C(11)-C(16)	126.6(11)
C(10)-C(11)-C(16)	125.8(11)
C(12)-C(11)-Ir(1)	72.5(6)
C(10)-C(11)-Ir(1)	66.0(5)
C(16)-C(11)-Ir(1)	127.0(8)
C(11)-C(12)-C(13)	108.5(9)
C(11)-C(12)-C(17)	127.1(10)
C(13)-C(12)-C(17)	124.4(10)
C(11)-C(12)-Ir(1)	71.5(6)
C(13)-C(12)-Ir(1)	66.6(6)
C(17)-C(12)-Ir(1)	127.3(7)
C(14)-C(13)-C(12)	108.2(9)
C(14)-C(13)-C(18)	126.7(9)
C(12)-C(13)-C(18)	124.6(10)
C(14)-C(13)-Ir(1)	70.2(6)
C(12)-C(13)-Ir(1)	74.5(6)
C(18)-C(13)-Ir(1)	127.4(7)
C(10)-C(14)-C(13)	106.9(9)
C(10)-C(14)-C(19)	128.4(11)
C(13)-C(14)-C(19)	124.6(10)
C(10)-C(14)-Ir(1)	69.7(6)
C(13)-C(14)-Ir(1)	70.5(6)
C(19)-C(14)-Ir(1)	126.8(7)

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Symmetry transformations used to generate equivalent atoms:

**Table S22.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **9**. The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [ h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12} ]$

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
Ir(1)	25(1)	20(1)	21(1)	1(1)	3(1)	-2(1)
N(1)	23(6)	23(5)	27(6)	6(4)	2(4)	-5(4)
O(1)	41(5)	16(4)	25(5)	3(3)	13(4)	1(4)
Cl(1)	28(2)	27(1)	33(2)	-3(1)	0(1)	7(1)
C(1)	18(7)	22(5)	28(7)	2(5)	1(5)	7(5)
C(2)	32(7)	34(6)	20(7)	-7(5)	8(5)	-1(6)
C(3)	49(9)	32(6)	27(7)	1(6)	13(6)	-6(6)
C(4)	46(9)	26(6)	30(8)	13(5)	12(6)	-9(6)
C(5)	19(7)	28(6)	30(7)	6(5)	0(5)	2(5)
C(6)	33(7)	22(5)	13(6)	8(5)	-5(5)	4(5)
C(7)	32(7)	24(6)	35(7)	6(5)	4(5)	-10(5)
C(8)	36(8)	13(6)	38(8)	-9(5)	-5(6)	-5(5)
C(9)	31(8)	30(6)	29(7)	-8(5)	-5(5)	15(6)
C(10)	30(7)	28(6)	30(7)	-7(5)	8(5)	-12(6)
C(11)	25(7)	31(6)	33(7)	2(5)	3(5)	-13(6)
C(12)	19(7)	34(6)	22(7)	8(5)	4(5)	-8(5)
C(13)	34(7)	17(5)	19(6)	-1(5)	9(4)	-2(6)
C(14)	32(8)	26(5)	23(7)	7(5)	-5(5)	-12(5)
C(15)	49(9)	40(7)	52(9)	-34(6)	19(7)	-5(6)
C(16)	45(8)	15(6)	64(9)	11(6)	3(6)	1(6)
C(17)	33(8)	71(9)	27(7)	-3(6)	14(6)	-17(7)
C(18)	26(8)	35(7)	69(10)	9(7)	2(6)	-1(6)
C(19)	73(10)	65(8)	24(7)	16(7)	-14(6)	-33(8)

**Table S23.** Hydrogen coordinates (  $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **9**

	x	y	z	U(eq)
H(2A)	-290	6243	9003	34
H(3A)	-1873	5111	9643	43
H(4A)	-2546	3775	8831	40
H(7A)	-2421	2869	7293	36
H(8A)	-1502	2790	5848	35
H(9A)	170	3943	5295	36
H(15A)	2020	8717	8710	70
H(15B)	834	7871	8887	70
H(15C)	477	8538	8022	70
H(16A)	2867	9146	6350	62
H(16B)	1054	8856	6558	62
H(16C)	1880	8458	5668	62
H(17A)	3853	7485	5216	65
H(17B)	4362	6443	5443	65
H(17C)	5590	7265	5705	65
H(18A)	6314	5942	7418	65
H(18B)	5082	5409	6718	65
H(18C)	4962	5279	7808	65
H(19A)	4321	6703	9434	82
H(19B)	3586	5755	9036	82
H(19C)	2407	6529	9410	82

**Table S24.** Torsion angles [°] for **9**.

---

C(9)-N(1)-O(1)-Ir(1)	173.4(7)
C(6)-N(1)-O(1)-Ir(1)	-7.2(10)
C(1)-Ir(1)-O(1)-N(1)	5.9(6)
C(10)-Ir(1)-O(1)-N(1)	148.5(13)
C(14)-Ir(1)-O(1)-N(1)	96.7(7)
C(13)-Ir(1)-O(1)-N(1)	123.7(6)
C(11)-Ir(1)-O(1)-N(1)	-170.8(6)
C(12)-Ir(1)-O(1)-N(1)	163.5(6)
Cl(1)-Ir(1)-O(1)-N(1)	-82.4(5)
O(1)-Ir(1)-C(1)-C(2)	178.2(10)
C(10)-Ir(1)-C(1)-C(2)	7.7(11)
C(14)-Ir(1)-C(1)-C(2)	45.6(10)
C(13)-Ir(1)-C(1)-C(2)	81.0(11)
C(11)-Ir(1)-C(1)-C(2)	-6.9(15)
C(12)-Ir(1)-C(1)-C(2)	83.2(15)
Cl(1)-Ir(1)-C(1)-C(2)	-98.3(10)
O(1)-Ir(1)-C(1)-C(6)	-3.8(7)
C(10)-Ir(1)-C(1)-C(6)	-174.4(7)
C(14)-Ir(1)-C(1)-C(6)	-136.4(7)
C(13)-Ir(1)-C(1)-C(6)	-101.0(8)
C(11)-Ir(1)-C(1)-C(6)	171.0(7)
C(12)-Ir(1)-C(1)-C(6)	-98.8(12)
Cl(1)-Ir(1)-C(1)-C(6)	79.6(7)
C(6)-C(1)-C(2)-C(3)	1.5(15)
Ir(1)-C(1)-C(2)-C(3)	179.5(8)
C(1)-C(2)-C(3)-C(4)	-0.9(17)
C(2)-C(3)-C(4)-C(5)	-0.7(17)
C(3)-C(4)-C(5)-C(6)	1.3(16)
C(3)-C(4)-C(5)-C(7)	-176.7(10)
O(1)-N(1)-C(6)-C(5)	-175.5(8)
C(9)-N(1)-C(6)-C(5)	3.9(14)
O(1)-N(1)-C(6)-C(1)	4.1(12)
C(9)-N(1)-C(6)-C(1)	-176.5(9)
C(4)-C(5)-C(6)-N(1)	179.0(9)
C(7)-C(5)-C(6)-N(1)	-2.8(14)

C(4)-C(5)-C(6)-C(1)	-0.6(15)
C(7)-C(5)-C(6)-C(1)	177.6(9)
C(2)-C(1)-C(6)-N(1)	179.6(8)
Ir(1)-C(1)-C(6)-N(1)	1.3(11)
C(2)-C(1)-C(6)-C(5)	-0.7(14)
Ir(1)-C(1)-C(6)-C(5)	-179.1(8)
C(4)-C(5)-C(7)-C(8)	178.6(10)
C(6)-C(5)-C(7)-C(8)	0.5(15)
C(5)-C(7)-C(8)-C(9)	0.9(16)
O(1)-N(1)-C(9)-C(8)	176.9(8)
C(6)-N(1)-C(9)-C(8)	-2.4(14)
C(7)-C(8)-C(9)-N(1)	0.0(15)
C(1)-Ir(1)-C(10)-C(14)	74.8(7)
O(1)-Ir(1)-C(10)-C(14)	-65.1(16)
C(13)-Ir(1)-C(10)-C(14)	-38.2(6)
C(11)-Ir(1)-C(10)-C(14)	-116.4(10)
C(12)-Ir(1)-C(10)-C(14)	-81.5(7)
Cl(1)-Ir(1)-C(10)-C(14)	168.1(6)
C(1)-Ir(1)-C(10)-C(11)	-168.8(6)
O(1)-Ir(1)-C(10)-C(11)	51.3(17)
C(14)-Ir(1)-C(10)-C(11)	116.4(10)
C(13)-Ir(1)-C(10)-C(11)	78.2(7)
C(12)-Ir(1)-C(10)-C(11)	34.9(6)
Cl(1)-Ir(1)-C(10)-C(11)	-75.5(6)
C(1)-Ir(1)-C(10)-C(15)	-47.7(11)
O(1)-Ir(1)-C(10)-C(15)	172.4(10)
C(14)-Ir(1)-C(10)-C(15)	-122.6(13)
C(13)-Ir(1)-C(10)-C(15)	-160.8(11)
C(11)-Ir(1)-C(10)-C(15)	121.1(13)
C(12)-Ir(1)-C(10)-C(15)	156.0(11)
Cl(1)-Ir(1)-C(10)-C(15)	45.5(10)
C(14)-C(10)-C(11)-C(12)	2.7(12)
C(15)-C(10)-C(11)-C(12)	176.0(10)
Ir(1)-C(10)-C(11)-C(12)	-60.8(7)
C(14)-C(10)-C(11)-C(16)	-177.1(10)
C(15)-C(10)-C(11)-C(16)	-3.8(17)
Ir(1)-C(10)-C(11)-C(16)	119.4(10)
C(14)-C(10)-C(11)-Ir(1)	63.5(7)

C(15)-C(10)-C(11)-Ir(1)	-123.2(11)
C(1)-Ir(1)-C(11)-C(12)	140.7(8)
O(1)-Ir(1)-C(11)-C(12)	-46.0(8)
C(10)-Ir(1)-C(11)-C(12)	119.2(9)
C(14)-Ir(1)-C(11)-C(12)	80.7(7)
C(13)-Ir(1)-C(11)-C(12)	37.0(6)
Cl(1)-Ir(1)-C(11)-C(12)	-129.6(6)
C(1)-Ir(1)-C(11)-C(10)	21.4(11)
O(1)-Ir(1)-C(11)-C(10)	-165.2(6)
C(14)-Ir(1)-C(11)-C(10)	-38.5(6)
C(13)-Ir(1)-C(11)-C(10)	-82.2(7)
C(12)-Ir(1)-C(11)-C(10)	-119.2(9)
Cl(1)-Ir(1)-C(11)-C(10)	111.1(6)
C(1)-Ir(1)-C(11)-C(16)	-96.3(12)
O(1)-Ir(1)-C(11)-C(16)	77.1(11)
C(10)-Ir(1)-C(11)-C(16)	-117.7(13)
C(14)-Ir(1)-C(11)-C(16)	-156.3(12)
C(13)-Ir(1)-C(11)-C(16)	160.0(12)
C(12)-Ir(1)-C(11)-C(16)	123.0(13)
Cl(1)-Ir(1)-C(11)-C(16)	-6.6(10)
C(10)-C(11)-C(12)-C(13)	0.4(11)
C(16)-C(11)-C(12)-C(13)	-179.8(10)
Ir(1)-C(11)-C(12)-C(13)	-56.4(7)
C(10)-C(11)-C(12)-C(17)	179.9(10)
C(16)-C(11)-C(12)-C(17)	-0.3(18)
Ir(1)-C(11)-C(12)-C(17)	123.2(11)
C(10)-C(11)-C(12)-Ir(1)	56.8(7)
C(16)-C(11)-C(12)-Ir(1)	-123.5(11)
C(1)-Ir(1)-C(12)-C(11)	-123.7(11)
O(1)-Ir(1)-C(12)-C(11)	145.9(6)
C(10)-Ir(1)-C(12)-C(11)	-38.2(6)
C(14)-Ir(1)-C(12)-C(11)	-81.8(7)
C(13)-Ir(1)-C(12)-C(11)	-120.6(9)
Cl(1)-Ir(1)-C(12)-C(11)	58.0(6)
C(1)-Ir(1)-C(12)-C(13)	-3.1(14)
O(1)-Ir(1)-C(12)-C(13)	-93.4(6)
C(10)-Ir(1)-C(12)-C(13)	82.4(6)
C(14)-Ir(1)-C(12)-C(13)	38.8(6)

C(11)-Ir(1)-C(12)-C(13)	120.6(9)
Cl(1)-Ir(1)-C(12)-C(13)	178.7(5)
C(1)-Ir(1)-C(12)-C(17)	113.4(12)
O(1)-Ir(1)-C(12)-C(17)	23.0(10)
C(10)-Ir(1)-C(12)-C(17)	-161.1(11)
C(14)-Ir(1)-C(12)-C(17)	155.2(11)
C(13)-Ir(1)-C(12)-C(17)	116.4(12)
C(11)-Ir(1)-C(12)-C(17)	-123.0(12)
Cl(1)-Ir(1)-C(12)-C(17)	-64.9(10)
C(11)-C(12)-C(13)-C(14)	-3.2(12)
C(17)-C(12)-C(13)-C(14)	177.2(10)
Ir(1)-C(12)-C(13)-C(14)	-62.6(7)
C(11)-C(12)-C(13)-C(18)	-175.5(10)
C(17)-C(12)-C(13)-C(18)	4.9(16)
Ir(1)-C(12)-C(13)-C(18)	125.1(10)
C(11)-C(12)-C(13)-Ir(1)	59.3(7)
C(17)-C(12)-C(13)-Ir(1)	-120.2(10)
C(1)-Ir(1)-C(13)-C(14)	-65.0(7)
O(1)-Ir(1)-C(13)-C(14)	-148.5(5)
C(10)-Ir(1)-C(13)-C(14)	38.1(6)
C(11)-Ir(1)-C(13)-C(14)	81.9(6)
C(12)-Ir(1)-C(13)-C(14)	116.3(8)
Cl(1)-Ir(1)-C(13)-C(14)	113.5(7)
C(1)-Ir(1)-C(13)-C(12)	178.7(6)
O(1)-Ir(1)-C(13)-C(12)	95.2(6)
C(10)-Ir(1)-C(13)-C(12)	-78.2(6)
C(14)-Ir(1)-C(13)-C(12)	-116.3(8)
C(11)-Ir(1)-C(13)-C(12)	-34.4(6)
Cl(1)-Ir(1)-C(13)-C(12)	-2.8(10)
C(1)-Ir(1)-C(13)-C(18)	56.7(10)
O(1)-Ir(1)-C(13)-C(18)	-26.9(10)
C(10)-Ir(1)-C(13)-C(18)	159.7(11)
C(14)-Ir(1)-C(13)-C(18)	121.7(12)
C(11)-Ir(1)-C(13)-C(18)	-156.4(11)
C(12)-Ir(1)-C(13)-C(18)	-122.0(12)
Cl(1)-Ir(1)-C(13)-C(18)	-124.8(9)
C(11)-C(10)-C(14)-C(13)	-4.6(12)
C(15)-C(10)-C(14)-C(13)	-177.7(10)

Ir(1)-C(10)-C(14)-C(13)	61.1(7)
C(11)-C(10)-C(14)-C(19)	172.9(10)
C(15)-C(10)-C(14)-C(19)	-0.2(18)
Ir(1)-C(10)-C(14)-C(19)	-121.5(11)
C(11)-C(10)-C(14)-Ir(1)	-65.7(7)
C(15)-C(10)-C(14)-Ir(1)	121.2(11)
C(12)-C(13)-C(14)-C(10)	4.8(11)
C(18)-C(13)-C(14)-C(10)	176.9(10)
Ir(1)-C(13)-C(14)-C(10)	-60.6(7)
C(12)-C(13)-C(14)-C(19)	-172.8(9)
C(18)-C(13)-C(14)-C(19)	-0.7(17)
Ir(1)-C(13)-C(14)-C(19)	121.8(10)
C(12)-C(13)-C(14)-Ir(1)	65.4(7)
C(18)-C(13)-C(14)-Ir(1)	-122.5(11)
C(1)-Ir(1)-C(14)-C(10)	-115.7(7)
O(1)-Ir(1)-C(14)-C(10)	162.0(6)
C(13)-Ir(1)-C(14)-C(10)	117.3(9)
C(11)-Ir(1)-C(14)-C(10)	38.9(6)
C(12)-Ir(1)-C(14)-C(10)	78.9(7)
Cl(1)-Ir(1)-C(14)-C(10)	-19.6(9)
C(1)-Ir(1)-C(14)-C(13)	126.9(6)
O(1)-Ir(1)-C(14)-C(13)	44.6(7)
C(10)-Ir(1)-C(14)-C(13)	-117.3(9)
C(11)-Ir(1)-C(14)-C(13)	-78.5(6)
C(12)-Ir(1)-C(14)-C(13)	-38.5(6)
Cl(1)-Ir(1)-C(14)-C(13)	-137.0(5)
C(1)-Ir(1)-C(14)-C(19)	7.7(11)
O(1)-Ir(1)-C(14)-C(19)	-74.6(12)
C(10)-Ir(1)-C(14)-C(19)	123.4(14)
C(13)-Ir(1)-C(14)-C(19)	-119.2(12)
C(11)-Ir(1)-C(14)-C(19)	162.3(12)
C(12)-Ir(1)-C(14)-C(19)	-157.7(12)
Cl(1)-Ir(1)-C(14)-C(19)	103.8(10)

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Symmetry transformations used to generate equivalent atoms: