SUPPORTING INFORMATION

FOR

Highly Chemoselective Deoxygenation of N-Heterocyclic *N*-Oxides Under Transition Metal-Free Conditions

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GENERAL INFORMATION

General Methods

Experiments involving moisture- and/or air-sensitive compounds were performed in oven- or flame-dried glassware with rubber septa under a positive pressure of nitrogen using standard Schlenk techniques. Non-aqueous reagents were transferred by hypodermic syringe. Heating was accomplished by silicon oil bath using a temperature controller. Brine is defined as a saturated aqueous solution of sodium chloride. Organic solutions were concentrated under reduced pressure at 30 °C (water bath temperature) using a Büchi rotary evaporator, unless otherwise noted. Reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) or GC. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous (>95%) materials, unless otherwise stated. Melting point were measured using a Stuart SMP50 apparatus and are uncorrected.

Chromatography

TLC was performed on E. Merck 60–F254 precoated plates (0.25 mm), and spots were visualized by UV fluorescence (254 nm) quenching, iodine vapor, and $KMnO_4$ staining. Flash chromatography was carried out with Merck silica gel 60 (200–400 mesh) according to the procedure of Still et al.[1]

NMR & IR Spectroscopy

^{1}H and ^{13}C NMR spectra were recorded with Bruker AVANCE III Ascend 500 (500 MHz and 126 MHz, respectively) and AVANCE III HD (400 MHz and 101 MHz, respectively) spectrometers. ^{19}F NMR spectra were obtained on a Bruker AVANCE III Ascend 500 spectrometer (471 MHz). Chemical shifts of the ^{1}H NMR ($CDCl_3$: 7.26 ppm, DMSO-d_6: 2.50 ppm, CD_3CN: 1.94 ppm) and ^{13}C NMR ($CDCl_3$: 77.00 ppm, DMSO-d_6: 39.50 ppm, CD_3CN: 118.26 ppm) spectra were referenced to residual solvent peaks or tetramethylsilane (0.00 ppm) as an internal standard. 2-Phenylquinoline *N*-oxide (**2u**) was dissolved in a minimum amount of $CDCl_3$, and the resulting homogeneous solution was diluted with CD_3CN. ^{1}H NMR spectra are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quarter, quin = quintet, sext = sextet, sept = septet, m = multiplet, br = broad), coupling constant (*J*) in Hz and integration. Infrared (IR) spectra were recorded on a Brucker AVATAR 370 DTGS spectrometer using thin film samples on KBr plates and are reported in terms of frequency of absorption (cm^{-1}).

Mass Spectrometry

Low-resolution mass spectra were acquired using a HP 6890 GC system coupled with a HP 5973 mass selective detector with electron impact (EI) mode or an Agilent 1260 infinity LC-MS system coupled with an Agilent 6120 quadrupole mass spectrometer with electrospray ionization (ESI) mode. High-resolution mass spectra (HRMS) were obtained from the Organic Chemistry Research Center (OCRC) at Sogang University (Seoul, Korea) using a Bruker Compact ESI-TOF mass spectrometer.

Starting Materials

Unless otherwise stated, all reagents and solvents were purchased at the highest commercial quality from commercial suppliers (Sigma-Aldrich, TCI, Alpha Aesar, Strem, or Acros) and used as received without further purification.

Visible Light-Mediated Deoxygenation Setup

For all deoxygenation reactions, irradiation of the stirred mixture in a borosilicate test tube or a borosilicate round-bottomed flask fitted with a rubber setup was accomplished using two MR16 3W green LED spotlight lamps (12 V, 530–535 nm). For mmol scale reactions, the two green LEDs were placed 3-cm-away from the reaction tube located in a customized reactor made from acrylic plates. A fan was employed for maintaining the reaction temperature between 20–30 °C during the irradiation.

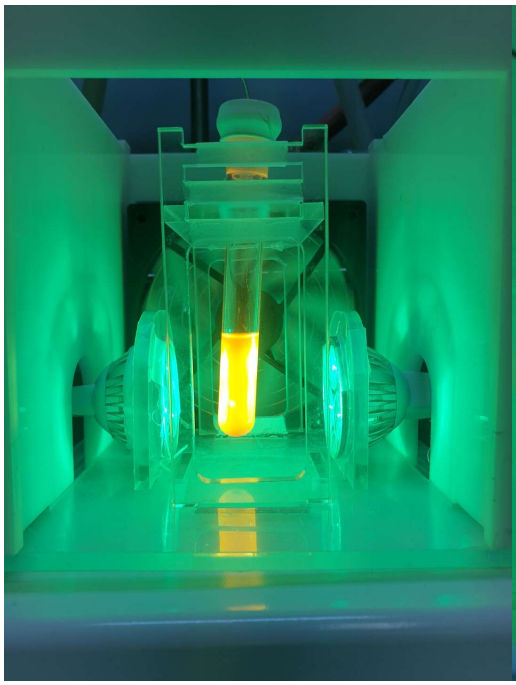


Figure S1. Deoxygenation setup (front view).

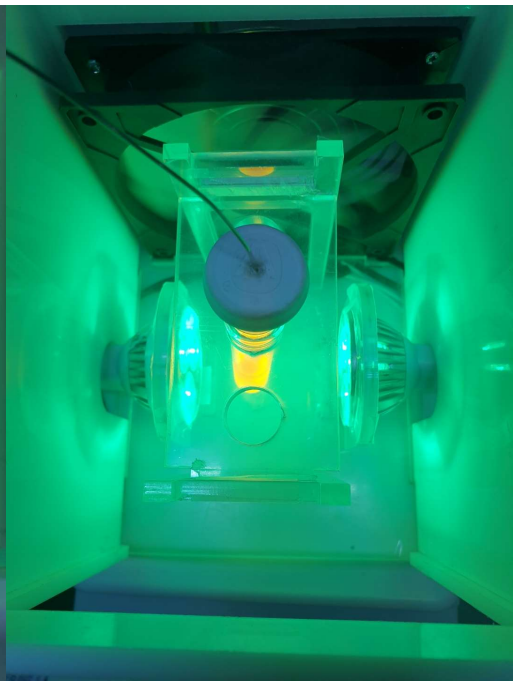


Figure S2. Deoxygenation setup (top view)

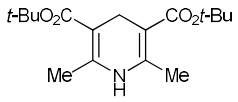
EXPERIMENTAL DATA

Experimental Procedures and Compounds Characterization Data

Preparation of Hantzsch esters (1)

Hantzsch esters were prepared according to the literature procedures, further purified by recrystallization from an appropriate mixture of solvents as indicated and stored in a refrigerator under an N_2 atmosphere.

Preparation of Di-*tert*-butyl 2,6-Dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2a)



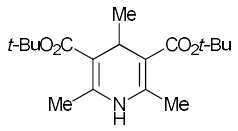
Prepared according to the literature procedure and further purified by recrystallization from a hot MeOH to afford the title compound as a light green solid.[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.09 (s, 1H), 3.16 (s, 2H), 2.13 (s, 6H), 1.47 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 143.7, 100.9, 79.4, 28.4, 25.4, 19.2.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{17}H_{17}NO_4$) 309.2, found 309.3.

Preparation of Di-*tert*-butyl 2,4,6-Trimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2b)



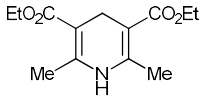
Prepared according to the literature procedure and further purified by recrystallization from a hot MeOH to afford the title compound as a white solid.[3]

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.39 (s, 1H), 3.74 (q, *J* = 6.5 Hz, 1H), 2.21 (s, 6H), 1.48 (s, 18H), 0.94 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 143.1, 106.0, 79.3, 29.2, 28.3, 22.1, 19.4.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{17}H_{17}NO_4$) 323.2, found 323.3.

Preparation of Diethyl 2,6-Dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2c)



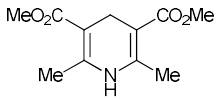
Prepared according to the literature procedure and further purified by recrystallization from a hot EtOH to afford the title compound as a light green solid.[4]

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.24 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 4H), 3.25 (s, 2H), 2.18 (s, 6H), 1.27 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 144.8, 99.5, 59.6, 24.8, 19.1, 14.4.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{13}H_{19}NO_4$) 253.1, found 253.1.

Preparation of Dimethyl 2,6-Dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2d)



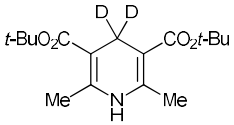
Prepared according to the literature procedure and further purified by recrystallization from a hot MeOH to afford the title compound as a light green solid.[2]

^{1}H NMR (500 MHz, DMSO) δ 8.32 (s, 1H), 3.58 (s, 6H), 3.13 (s, 2H), 2.11 (s, 6H).

^{13}C NMR (126 MHz, DMSO) δ 167.4, 146.7, 96.9, 50.6, 24.7, 17.8.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{11}H_{15}NO_4$) 225.1, found 225.1.

Preparation of Di-*tert*-butyl 4-Deuterio-2,6-dimethyl-1,4-dihydro-4-deuteriopyridine-3,5-dicarboxylate (2a-d_2)



Prepared according to the literature procedure and further purified by recrystallization from a hot MeOH to afford the title compound as a light green solid.[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.12 (s, 1H), 2.13 (s, 6H), 1.47 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 143.8, 100.7, 79.4, 28.4, 19.1.

IR (KBr) 3325, 3242, 2967, 2082, 1695, 1642, 1487, 1366, 1349, 1302, 1252, 1153, 1133, 1058, 1021, 831, 742 cm^{-1}.

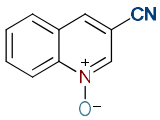
HRMS (ESI, TOF) *m*/*z* calculated for $[M + Na]^+$ ($C_{17}H_{25}D_2NNaO_4$) 334.1958, found 334.1958.

Melting point: 165.5-167.4 °C.

Preparation of N-Heterocyclic *N*-Oxides (1)

N-Heterocyclic *N*-oxides were prepared according to the literature procedures, further purified by recrystallization from an appropriate mixture of solvents as indicated and stored in a desiccator.

3-Quinolinecarbonitrile *N*-Oxide (1a)



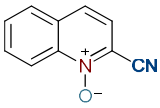
Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature.[5,6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 8.8 Hz, 1H), 8.60 (s, 1H), 8.05 (s, 1H), 7.99–7.88 (m, 2H), 7.79 (t, *J* = 7.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 134.8, 133.3, 130.5, 129.7, 129.0 (two carbons), 120.0, 114.9, 107.2.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ ($C_{10}H_7N_2O$) m/z 171.1, found m/z 171.1.

2-Quinolinecarbonitrile *N*-Oxide (1b)



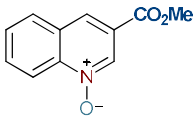
Prepared according to the literature procedure and further purified by recrystallization from a hot mixture of hexanes and EtOAc (1:1, *v*/*v*) to afford the title compound as a white solid.[6]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.7 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.83 (ddd, *J* = 8.6, 7.0, 1.3 Hz, 1H), 7.79–7.71 (m, 2H), 7.52 (d, *J* = 8.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.0, 131.5, 131.1, 130.9, 128.5, 124.6, 123.4, 121.3, 119.9, 112.9.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ ($C_{10}H_7N_2O$) m/z 171.1, found m/z 171.1.

Methyl 3-Quinolinecarboxylate *N*-Oxide (1c)



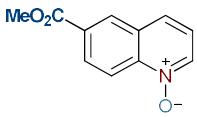
Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature.[5,7]

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.02 (d, *J* = 1.5 Hz, 1H), 8.75 (dd, *J* = 8.7, 0.9 Hz, 1H), 8.38 (s, 1H), 7.97 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.86 (ddd, *J* = 8.7, 7.0, 1.4 Hz, 1H), 7.71 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 3.99 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.8, 143.1, 135.0, 132.5, 129.6, 129.5, 129.1, 127.6, 124.4, 120.0, 52.9.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ ($C_{11}H_{10}NO_3$) 204.1, found 204.1.

Methyl 6-Quinolinecarboxylate *N*-Oxide (1d)



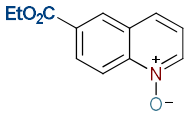
Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature.[5,7]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (d, *J* = 9.1 Hz, 1H), 8.60 (d, *J* = 1.8 Hz, 1H), 8.57 (dd, *J* = 6.1, 1.0 Hz, 1H), 8.31 (dd, *J* = 9.1, 1.8 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.35 (dd, *J* = 8.5, 6.1 Hz, 1H), 3.99 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 143.3, 137.0, 130.9, 130.5, 130.0, 129.8, 126.4, 121.9, 120.4, 52.6.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ ($C_{11}H_{10}NO_3$) 204.1, found 204.1.

Ethyl 6-Quinolinecarboxylate *N*-Oxide (1e)



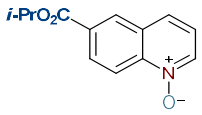
Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature. [5,8]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (d, *J* = 9.1 Hz, 1H), 8.59 (d, *J* = 1.8 Hz, 1H), 8.56 (dd, *J* = 6.0, 1.0 Hz, 1H), 8.31 (dd, *J* = 9.1, 1.8 Hz, 1H), 7.84–7.78 (m, 1H), 7.35 (dd, *J* = 8.4, 6.1 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.2, 143.2, 137.0, 130.8 (two carbons), 129.9, 129.8, 126.4, 121.8, 120.3, 61.7, 14.3.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ ($C_{12}H_{12}NO_3$) 218.1, found 218.1.

Isopropyl 6-Quinolinecarboxylate *N*-Oxide (1f)



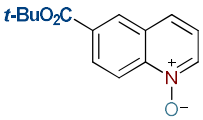
Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature.[5,9]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (d, *J* = 9.1 Hz, 1H), 8.62–8.55 (m, 2H), 8.31 (dd, *J* = 9.2, 1.8 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.35 (dd, *J* = 8.5, 6.0 Hz, 1H), 5.31 (sept, *J* = 6.3 Hz, 1H), 1.41 (d, *J* = 6.3 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 143.2, 137.0, 131.2, 130.7, 129.9 (two carbons), 126.4, 121.8, 120.3, 69.4, 21.9.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ ($C_{13}H_{13}NO_3$) 232.1, found 232.1.

***tert*-Butyl 6-Quinolinecarboxylate *N*-Oxide (1g)**



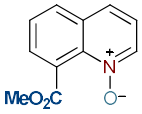
Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature.[5,7]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (d, *J* = 9.1 Hz, 1H), 8.56 (d, *J* = 6.1 Hz, 1H), 8.53 (d, *J* = 1.8 Hz, 1H), 8.26 (dd, *J* = 9.1, 1.8 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.34 (dd, *J* = 8.5, 6.0 Hz, 1H), 1.64 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.3, 143.2, 136.9, 132.3, 130.5, 130.0, 129.9, 126.5, 121.6, 120.1, 82.2, 28.1.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ ($C_{14}H_{16}NO_3$) 246.1, found 246.1.

Methyl 8-Quinolinecarboxylate *N*-Oxide (1h)



A 10 mL round-bottomed flask equipped with a magnetic stir bar and a reflux condenser was charged with 8-quinolinecarboxylic acid (173 mg, 1.0 mmol), MeOH (2.0 mL), and H_2SO_4 (0.4 mL). The resulting mixture was heated in an oil bath (bath temperature = 80 °C) under reflux overnight. The mixture was allowed to cool to room temperature, diluted with CH_2Cl_2, and neutralized with an aqueous solution of saturated $NaHCO_3$ (Caution! Evolution of CO_2). The mixture was then extracted with CH_2Cl_2 (5 mL × 3). The combined organic layer was washed successively with water and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (hexanes/EtOAc = 1:1) on silica gel to afford methyl 8-quinolinecarboxylate (**3h**, 146 mg, 78 %) as a yellow oil. One dram vial equipped with a small magnetic stir bar was charged with **3h** (187 mg, 1.76 mmol, 1.0 equiv), $MeReO_3$ (40 mg, 0.18 mmol), and CH_2Cl_2 (0.9 mL, ca. 2 M). The resulting mixture was cooled to 0 °C and treated with 30% H_2O_2 (0.36 mL, 2.0 equiv) via syringe. After stirring at the same temperature for 24 h, the mixture was extracted with CH_2Cl_2 (5 mL × 3). The combined organic layer was washed successively with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (EtOAc/MeOH = 9:1) on silica gel to afford the title compound (130 mg, 36%) as an off-white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.67–7.56 (m, 2H), 7.31 (dd, *J* = 8.4, 6.1 Hz, 1H), 4.01 (s, 2H).

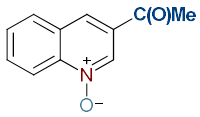
^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 137.8, 135.7, 130.8, 129.5, 129.4, 128.0, 127.6, 125.6, 121.7, 52.9.

HRMS (ESI, TOF) *m*/*z* calculated for $[M + Na]^+$ ($C_{11}H_9NNaO_3$) 226.0475, found 226.0475

IR (KBr) 3463, 3275, 1726, 1695, 1672, 1610, 1575, 1489, 1468, 1437, 1328, 1287, 1271, 1253, 1200, 1154, 1128, 1069 cm^{-1}.

Melting point: 170-185 °C.

3-Acetylquinoline *N*-Oxide (1i)



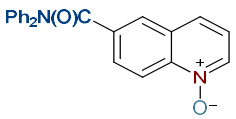
Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature. [5,6]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (d, *J* = 1.5 Hz, 1H), 8.77–8.71 (m, 1H), 8.24 (s, 1H), 8.00 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.86 (ddd, *J* = 8.5, 7.0, 1.4 Hz, 1H), 7.72 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 2.69 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 194.1, 143.0, 134.0, 132.6, 130.6, 129.8, 129.6, 129.2, 126.2, 120.0, 26.6.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ ($C_{11}H_{10}NO_2$) 188.1, found 188.1.

***N*,*N*-Diphenyl-6-quinolinecarboxamide *N*-Oxide (1j)**



A 25 mL round-bottomed flask equipped with a magnetic stir bar was charged whit 6-quinolinecarboxylic acid (693 mg, 4.00 mmol, 1.0 equiv), 1,1'-carbodiimidazole (685 mg, 4.00 mmol, 1.0 equiv), and dry DMF (5.8 mL, 0.69 M). After stirring in an oil bath (bath temperature = 40 °C) for 2 h, the mixture was treated with diphenylamine (2.03 g, 12.0 mmol, 3.0 equiv) followed by DBU (609 mg, 4.00 mmol, 1.0 equiv). After stirring at 80 °C for 16 h, the mixture was allowed to cool to room temperature and extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (hexanes/EtOAc = 1:2) on silica gel to afford *N*,*N*-diphenyl-6-quinolinecarboxamide (**3j**, 177 mg, 21 %) as a white solid. A 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with **3j** (277 mg, 0.850 mmol, 1.0 equiv) and CH_2Cl_2 (1.5 mL). The

resulting mixture was cooled in an ice-water bath. A separate pear-shaped flask was charged with *m*-CPBA (77%, 287 mg, 1.28 mmol, 1.5 equiv) in CH_2Cl_2 (1.3 mL), and the resulting *m*-CPBA solution was added dropwise to the flask containing **3j** at 0 °C via syringe. The pear-shaped flask was rinsed with CH_2Cl_2 (1.0 mL × 3), and the resulting solution was added via syringe. After stirring for 10 min, the cold reaction mixture was allowed to slowly warm to room temperature. After stirring for 4 h at that temperature, the reaction mixture was poured into water (20 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was washed successively with an aqueous solution of saturated $NaHCO_3$, water, and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (EtOAc/MeOH = 9:1) on silica gel to afford as an off-white solid, which was further purified by recrystallization from a hot mixture of EtOAc and hexanes (2:1, *v*/*v*) to yield the title compound (192 mg, 66%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53–8.47 (m, 1H), 8.11 (d, *J* = 1.6 Hz, 1H), 7.66 (dd, *J* = 9.1, 1.8 Hz, 1H), 7.35–7.27 (m, 4H), 7.20 (t, *J* = 7.0 Hz, 4H).

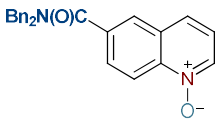
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.8, 143.1, 141.6, 136.8, 136.4, 129.9, 129.8, 129.7, 129.3, 127.4, 126.8, 126.0, 121.6, 119.5.

HRMS (ESI, TOF) *m*/*z* calculated for $[M + Na]^+$ ($C_{22}H_{16}N_2NaO_2$) 363.1104, found 363.1104

IR (KBr) 3059, 3035, 1653, 1621, 1590, 1494, 1457, 1422, 1366, 1300, 1271, 1236, 1211, 1173 cm^{-1}.

Melting point: 241.5-246.7 °C.

N,*N*-Dibenzyl-6-quinolinecarboxamide *N*-Oxide (1k)



A 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with 6-quinolinecarboxylic acid (693 mg, 4.00 mmol, 1.0 equiv), 1,1'-carbodiimidazole (685 mg, 4.00 mmol, 1.0 equiv), and dry DMF (5.8 mL, 0.69 M). After stirring in an oil bath (bath temperature = 40 °C) for 2 h, the mixture was treated with dibenzylamine (2.37 g, 12.0 mmol, 3.0 equiv) followed by DBU (609 mg, 4.00 mmol, 1.0 equiv). After stirring at 80 °C for 15 h, the mixture was allowed to cool to room temperature and extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was washed with brine, dried over anhydrous

Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (hexanes/EtOAc = 1:2) on silica gel to afford *N*,*N*-dibenzyl-6-quinolinecarboxamide (**3k**, 253 mg, 21 %) as an off-white solid. A 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with **3k** (352 mg, 0.500 mmol, 1.0 equiv) and CH_2Cl_2 (1.7 mL). The resulting mixture was cooled in an ice-water bath. A separate pear-shaped flask was charged with *m*-CPBA (77%, 168 mg, 0.750 mmol, 1.5 equiv) in CH_2Cl_2 (1.7 mL), and the resulting *m*-CPBA solution was added dropwise to the flask containing **3k** at 0 °C via syringe. The pear-shaped flask was rinsed with CH_2Cl_2 (1.0 mL × 3), and the resulting solution was added via syringe. After stirring for 10 min, the cold reaction mixture was allowed to slowly warm to room temperature. After stirring for 12 h at that temperature, the reaction mixture was poured into water (20 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was washed successively with an aqueous solution of saturated $NaHCO_3$, water, and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (EtOAc as a sole eluent) on silica gel to afford an off-white solid, which was further purified by recrystallization from a hot mixture of EtOAc and hexanes (3:1, *v*/*v*) to yield the title compound as a white solid (135 mg, 73%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, *J* = 9.0 Hz, 1H), 8.48 (d, *J* = 6.0 Hz, 1H), 7.96 (s, 1H), 7.79 (d, *J* = 8.9 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.43–7.27 (m, 13H), 7.10 (s, 2H), 4.75 (s, 2H), 4.38 (s, 2H).

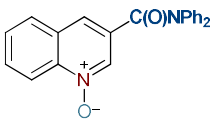
^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 141.5, 136.6, 136.4, 136.1, 135.8, 130.1, 128.8, 128.7, 128.4, 128.2, 127.7, 127.7, 126.7, 126.5, 125.5, 121.8, 120.4, 51.5, 47.3.

HRMS (ESI, TOF) *m*/*z* calculated for $[M + Na]^+$ ($C_{24}H_{20}N_2NaO_3$) 391.1417, found 391.1417

IR (KBr) 3075, 3056, 3019, 2997, 1636, 1620, 1578, 1492, 1474, 1450, 1426, 1362, 1271, 1177 cm^{-1}.

Melting point: 159-163 °C.

***N*,*N*-Diphenyl-3-quinolinecarboxamide *N*-Oxide (1l)**



A 25 mL round-bottomed flask equipped with a magnetic stir bar was charged whit 3-quinolinecarboxylic acid (520 mg, 3.00 mmol, 1.0 equiv), 1,1'-carbodiimidazole (535 mg, 3.30 mmol, 1.1 equiv), and dry

DMF (4.4 mL, 0.69 M). After stirring in an oil bath (bath temperature = 40 °C) for 24 h, the mixture was treated with diphenylamine (1.02 g, 6.00 mmol, 2.0 equiv) followed by DBU (457 mg, 3.00 mmol, 1.0 equiv). After stirring at 80 °C for 11 h, the mixture was allowed to cool to room temperature and extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (hexanes/EtOAc = 3:2) on silica gel to afford *N*,*N*-diphenyl-3-quinolinecarboxamide (**3l**, 407 mg, 42 %) as an off-white solid. A 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with **3l** (407 mg, 1.26 mmol, 1.0 equiv) and CH_2Cl_2 (2.1 mL). The resulting mixture was cooled in an ice-water bath. A separate pear-shaped flask was charged with *m*-CPBA (77%, 422 mg, 1.88 mmol, 1.5 equiv) in CH_2Cl_2 (2.1 mL), and the resulting *m*-CPBA solution was added dropwise to the flask containing **3l** at 0 °C via syringe. The pear-shaped flask was rinsed with CH_2Cl_2 (1.0 mL × 3), and the resulting solution was added via syringe. After stirring for 10 min, the cold reaction mixture was allowed to slowly warm to room temperature. After stirring for 12 h at that temperature, the reaction mixture was poured into water (20 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was washed successively with an aqueous solution of saturated $NaHCO_3$, water, and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (EtOAc as a sole eluent) on silica gel to afford an off-white solid, which was further purified by recrystallization from a hot mixture of EtOAc and hexanes (5:1, *v*/*v*) to yield the title compound as a white solid (305 mg, 71%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.7 Hz, 1H), 8.57 (s, 1H), 7.78–7.70 (m, 4H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 5H), 7.25–7.16 (m, 8H).

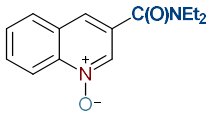
^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 142.8, 141.6, 135.2, 131.6, 130.2, 129.5, 129.2, 129.0, 128.9, 127.2, 126.5, 119.7.

HRMS (ESI, TOF) *m*/*z* calculated for $[M + Na]^+$ ($C_{22}H_{16}N_2NaO_2$) 363.1104, found 363.1104.

IR (KBr) 3106, 3051, 1651, 1585, 1495, 1460, 1384, 1219, 1195, 1138, 1084 cm^{-1}.

Melting point: 257.1-263.5 °C.

_N_,_N_-Diethyl-3-quinolinecarboxamide _N_-Oxide (1m)



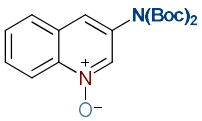
A 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with *N*,*N*-diethyl-3-quinolinecarboxamide[9] (**3m**, 114 mg, 0.500 mmol, 1.00 equiv) and CH_2Cl_2 (1.7 mL). The resulting mixture was cooled in an ice-water bath. A separate pear-shaped flask was charged with *m*-CPBA (77%, 168 mg, 0.750 mmol, 0.75 equiv) in CH_2Cl_2 (1.5 mL), and the resulting *m*-CPBA solution was added dropwise to the flask containing **3m** at 0 °C via syringe. The pear-shaped flask was rinsed with CH_2Cl_2 (0.5 mL × 2), and the resulting solution was added via syringe. After stirring for 10 min, the cold reaction mixture was allowed to slowly warm to room temperature. After stirring for 30 min at that temperature, the reaction mixture was poured into water (10 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was washed successively with aqueous solution of saturated $NaHCO_3$, water, and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (EtOAc/MeOH = 9:1) on silica gel to afford the title compound (64 mg, 53%) as a yellow dense oil. Spectroscopic data matched with those reported in the literature.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.7 Hz, 1H), 8.51 (d, *J* = 1.4 Hz, 1H), 7.87 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.78 (ddd, *J* = 8.6, 6.9, 1.4 Hz, 1H), 7.71 (s, 1H), 7.66 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 3.56 (br s, 2H), 3.33 (br s, 2H), 1.25 (br s, 3H), 1.17 (br s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 141.5, 133.5, 131.1, 130.9, 129.6, 129.4, 128.5, 123.0, 119.7, 43.5, 39.7, 14.3, 12.8.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ ($C_{14}H_{16}N_2O_2$) 245.1, found 245.1.

3-[Bis(*tert*-butoxycarbonyl)amino]quinoline _N_-Oxide (1n)



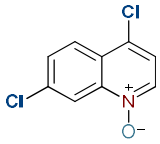
Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature.[5,10]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.8 Hz, 1H), 8.38 (d, *J* = 1.8 Hz, 1H), 7.84 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.75 (ddd, *J* = 8.7, 6.9, 1.4 Hz, 1H), 7.64 (ddd, *J* = 8.2, 7.0, 1.4 Hz, 1H), 7.55 (s, 1H), 1.41 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.6, 140.5, 136.2, 133.1, 130.5, 129.2 (two carbons), 128.3, 124.6, 119.7, 84.1, 27.8.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ ($C_{19}H_{25}N_2O_5$) 361.2, found 361.2.

4,7-Dichloroquinoline *N*-Oxide (1o)



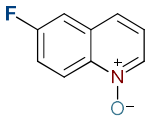
Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature.[5,11]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (d, *J* = 2.1 Hz, 1H), 8.41 (d, *J* = 6.6 Hz, 1H), 8.14 (d, *J* = 8.9 Hz, 1H), 7.68 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.36 (d, *J* = 6.6 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.4, 138.1, 135.8, 130.8, 129.5, 126.7, 126.5, 121.2, 120.0.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ ($C_9H_6Cl_2NO$) 214.0, found 214.0.

6-Fluoroquinoline *N*-Oxide (1p)



Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature.[5,12]

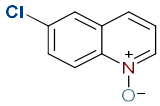
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (dd, *J* = 9.0, 5.2 Hz, 1H), 8.47 (d, *J* = 6.0 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.53–7.45 (m, 2H), 7.31 (dd, *J* = 8.5, 6.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.8 (d, $^{1}J_{C–F}$ = 251.8 Hz), 138.7, 135.0, 131.7 (d, $^{3}J_{C–F}$ = 10.0 Hz), 124.9 (d, $^{4}J_{C–F}$ = 5.8 Hz), 122.9 (d, $^{3}J_{C–F}$ = 9.3 Hz), 122.2, 120.3 (d, $^{2}J_{C–F}$ = 25.5 Hz), 111.5 (d, $^{2}J_{C–F}$ = 22.7 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ –109.4.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ (C_9H_7FNO) 164.1, found 164.1.

6-Chloroquinoline *N*-Oxide (1q)



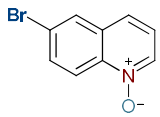
Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J_{HH} = 9.3 Hz, 1H), 8.49 (d, J_{HH} = 6.0 Hz, 1H), 7.85 (d, J_{HH} = 2.1 Hz, 1H), 7.68 (dd, J_{HH} = 9.3 , 2.1 Hz, 1H), 7.63 (d, J_{HH} = 8.5 Hz, 1H), 7.32 (dd, J_{HH} = 8.5, 6.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 135.7, 135.1, 131.2, 131.2, 126.8, 124.6, 122.2, 121.8.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ (C_9H_7ClNO) 180.0, found 180.0.

6-Bromoquinoline *N*-Oxide (1r)



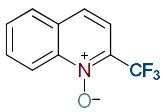
Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature.[5,13]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 9.2 Hz, 1H), 8.51 (d, *J* = 6.0 Hz, 1H), 8.04 (d, *J* = 2.0 Hz, 1H), 7.82 (dd, *J* = 9.2, 2.1 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.32 (dd, *J* = 8.5, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 135.8, 133.8, 131.6, 130.1, 124.6, 123.3, 122.2, 121.8.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ (C_9H_7BrNO) 224.0, found 224.0.

2-(Trifluoromethyl)quinoline *N*-Oxide (1s)



Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature.[5,14]

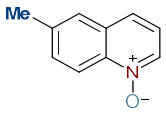
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (d, *J* = 8.8 Hz, 1H), 7.91 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.81 (ddd, *J* = 8.7, 6.9, 1.4 Hz, 1H), 7.78–7.70 (m, 2H), 7.63 (d, *J* = 8.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.8, 134.9 (q, $^{2}J_{C–F}$ = 34.2 Hz), 131.2, 131.1, 130.4, 128.3, 124.4, 120.5 (q, $^{1}J_{C–F}$ = 272.5 Hz), 119.9, 118.6 (q, $^{3}J_{C–F}$ = 4.1 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ –67.7.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ ($C_{10}H_7F_3NO$) 214.0, found 214.1.

6-Methylquinoline *N*-Oxide (1t)



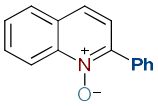
Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature.[5,13,15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.9 Hz, 1H), 8.47 (d, *J* = 5.9 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.62 (s, 1H), 7.59 (dd, *J* = 8.9, 1.7 Hz, 1H), 7.27–7.23 (m, 1H), 2.54 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 139.0, 135.0, 132.6, 130.7, 127.0, 125.5, 120.9, 119.6, 21.4.

LC-MS (ESI) calculated for $[M+1]^+$ ($C_{10}H_{10}NO$) *m*/*z* 160.1, found *m*/*z* 160.1.

2-Phenylquinoline *N*-Oxide (1u)



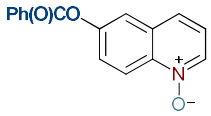
Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature.[5,15,16]

^{1}H NMR (500 MHz, CD_3CN) δ 8.69 (d, *J* = 8.8 Hz, 1H), 7.98–7.90 (m, 3H), 7.82 (dd, *J* = 8.7 Hz, 1H), 7.79 (ddd, *J* = 8.6, 6.9, 1.4 Hz, 1H), 7.67 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.57–7.43 (m, 4H).

^{13}C NMR (126 MHz, CD_3CN) δ 145.6, 143.2, 134.9, 131.5, 130.9, 130.6, 130.4, 129.5, 129.4, 129.2, 126.1, 124.6, 120.6.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ ($C_{15}H_{12}NO$) 222.1, found 222.1.

6-Benzoyloxyquinoline *N*-Oxide (1v)



A 100 ml round-bottomed flask equipped with a magnetic stir bar was charged with 6-hydroxyquinoline (155 mg, 1.07 mmol, 1.0 equiv), 4-(dimethylamino)pyridine (DMAP, 6.6 mg, 0.054 mmol, 5 mol%), triethylamine (Et_3N, 5 mL), and CH_2Cl_2 (25 mL). To this mixture was added dropwise benzoyl chloride (156 mg, 1.07 mmol, 1.0 equiv) via syringe at room temperature, and the resulting mixture was stirred for 1 h. The reaction was quenched by H_2O (1 mL), and the mixture was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried with Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (hexanes/EtOAc = 2:1) on silica gel to afford 6-benzoyloxyquinoline (**3v**, 188 mg, 71 %) as an off-white solid. A 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with **3v** (188 mg, 0.760 mmol, 1.0 equiv) and CH_2Cl_2 (1.2 mL). The resulting mixture was cooled in an ice-water bath. A separate pear-shaped flask was charged with *m*-CPBA (77%, 254 mg, 1.13 mmol, 1.5 equiv) in CH_2Cl_2 (1.3 mL), and the resulting *m*-CPBA solution was added dropwise to the flask containing **3v** at 0 °C via syringe. The pear-shaped flask was rinsed with CH_2Cl_2 (1 mL × 3), and the resulting solution was added via syringe. After stirring for 10 min, the cold reaction mixture was allowed to slowly warm to room temperature. After stirring for 1 hour at that temperature, the reaction mixture was poured into water (20 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was washed successively with an aqueous solution of saturated $NaHCO_3$, water, and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (EtOAc/MeOH = 9:1) on silica gel to afford the title compound as an off-white solid, which was further purified by recrystallization from a hot mixture of EtOAc and hexanes (5:1, *v*/*v*) to yield the title compound as a white solid (102 mg, 51 %).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80 (d, *J* = 9.4 Hz, 1H), 8.49 (d, *J* = 6.0 Hz, 1H), 8.21 (d, *J* = 7.3 Hz, 2H), 7.76 (d, *J* = 2.3 Hz, 1H), 7.71–7.57 (m, 4H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.29 (dd, *J* = 8.4, 6.1 Hz, 1H).

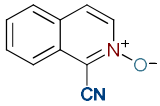
^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 150.6, 139.5, 135.3, 134.0, 131.2, 130.2, 128.8, 128.7, 125.5, 125.3, 121.8, 121.7, 119.1.

HRMS (ESI, TOF) *m*/*z* calculated for $[M + Na]^+$ ($C_{16}H_{11}NNaO_3$) 288.0631, found 288.0631.

IR (KBr) 3304, 3278, 3097, 3060, 1674, 1599, 1581, 1488, 1469, 1384, 1366, 1265, 1144, 906 cm^{-1}.

Melting point: 195-200.9 °C.

1-Isoquinolinecarbonitrile *N*-Oxide (1w)



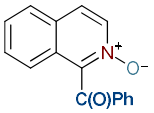
A 100 mL round-bottomed flask equipped with a magnetic stir bar was charged with 1-Isoquinolinecarbonitrile (**3w**) (308 mg, 2.00 mmol, 1.00 equiv) and CH_2Cl_2 (3.0 mL). The resulting mixture was cooled in an ice-water bath. A separate pear-shaped flask was charged with *m*-CPBA (77%, 672 mg, 3.00 mmol, 1.5 equiv) in CH_2Cl_2 (4 mL), and the resulting *m*-CPBA solution was added dropwise to the flask containing **3w** at 0 °C via syringe. The pear-shaped flask was rinsed with CH_2Cl_2 (1.0 mL × 3), and the resulting solution was added via syringe. After stirring for 10 min, the cold reaction mixture was allowed to slowly warm to room temperature. After stirring for 12 h at that temperature, the reaction mixture was poured into water (20 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (15 mL × 3). The combined organic layer was washed successively with aqueous solution of saturated $NaHCO_3$, water, and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (EtOAC/MeOH =12:1) on silica gel to afford the title compound as an white solid, which was further purified by recrystallization from a hot mixture of hexanes and EtOAc (1:1, *v*/*v*) to yield the title compound as a white solid (186 mg, 55%). Spectroscopic data matched with those reported in the literature.[17]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.2 Hz, 1H), 8.02–7.96 (m, 2H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 7.2 Hz, 1H), 7.82–7.77 (m, 2H), 7.71–7.64 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.0, 131.8, 130.1, 129.6, 127.5, 127.4, 127.0, 123.0, 121.7, 111.2.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ ($C_{10}H_7N_2O$) m/z 171.1, found m/z 171.1.

1-Benzoylisoquinoline *N*-Oxide (1x)



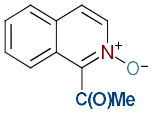
Prepared according to the literature procedure and further purified by recrystallization from a hot mixture of hexanes and EtOAc (1:1, *v*/*v*) to afford the title compound as a white solid. Spectroscopic data matched with those reported in the literature.[18]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.1 Hz, 1H), 7.88–7.82 (m, 6H), 7.77 (d, *J* = 7.1 Hz, 1H), 7.65–7.57 (m, 4H), 7.54 (td, *J* = 7.6, 6.9, 1.2 Hz, 1H), 7.52–7.41 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 189.6, 142.3, 136.6, 135.2, 134.4, 130.0, 129.2, 129.0, 129.0, 128.7, 127.4, 127.2, 124.8, 123.1.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ ($C_{16}H_{11}NO_2$) 250.1, found 250.1.

1-Acetylisoquinoline *N*-Oxide (1y)



A 100 mL round-bottomed flask equipped with a magnetic stir bar was charged with isoquinoline (517 mg, 4.00 mmol, 1.0 equiv), acetaldehyde (705 mg, 16.0 mmol, 4.0 equiv), tetra-*n*-butylammonium bromide (387 mg, 1.20 mmol, 0.3 equiv), $K_2S_2O_8$ (2.16 g, 8.00 mmol, 2.0 equiv), and 1,2-dichloroethane (33 mL). The resulting mixture was heated in an oil bath (bath temperature = 100 °C) under reflux for 3 h. The mixture was allowed to cool to room temperature, and the solvent was removed under vacuum. The crude mixture was diluted with CH_2Cl_2, washed successively with an aqueous solution of saturated $NaHCO_3$, water, and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography on silica gel (CH_2Cl_2 as a sole eluent) to afford 1-acetylisoquinoline (**3y**, 437 mg, 64 %) as a white solid. A 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with **3y** (437 mg, 2.55 mmol, 1.0 equiv) and CH_2Cl_2 (4.0 mL). The resulting mixture was cooled in an ice-water bath. A separate pear-shaped flask was charged with *m*-CPBA (77%, 1.14 g, 5.11 mmol, 2.0 equiv) in CH_2Cl_2 (4.5 mL), and the resulting *m*-CPBA solution was added dropwise to the flask containing **3y** at 0 °C via syringe. The

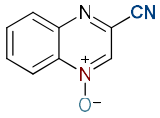
pear-shaped flask was rinsed with CH_2Cl_2 (1.0 mL × 3), and the resulting solution was added via syringe. After stirring for 10 min, the cold reaction mixture was allowed to slowly warm to room temperature. After stirring for 17 h at that temperature, the reaction mixture was poured into water (20 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (15 mL × 3). The combined organic layer was washed successively with an aqueous solution of saturated $NaHCO_3$, water, and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (EtOAc as a sole eluent) on silica gel to afford an off-white solid, which was further purified by recrystallization from a hot mixture of hexanes and EtOAc (3:1, *v*/*v*) to yield the title compound as a white solid (209 mg, 44%). Spectroscopic data matched with those reported in the literature.[19]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.1 Hz, 1H), 7.82–7.74 (m, 1H), 7.67 (dd, *J* = 17.3, 7.6 Hz, 2H), 7.58 (pd, *J* = 6.9, 1.3 Hz, 4H), 2.73 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.0, 143.2, 136.4, 130.2, 128.9, 127.1, 126.0, 124.9, 123.0, 29.7.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ ($C_{11}H_9NO_3$) 188.1, found 188.1.

3-Quinoxalinecarbonitrile *N*-Oxide (1z)



A 100 mL round-bottomed flask equipped with a magnetic stir bar was charged with quinoxaline (1.50 g, 11.9 mmol, 1.0 equiv) and CH_2Cl_2 (7.5 mL). The resulting mixture was cooled in an ice-water bath. A separate pear-shaped flask was charged with *m*-CPBA (77%, 2.60 g, 11.6 mmol, 1.0 equiv) in CH_2Cl_2 (7.5 mL), and the resulting *m*-CPBA solution was added dropwise to the flask containing the heterocycle at 0 °C via syringe. The pear-shaped flask was rinsed with CH_2Cl_2 (1.0 mL × 3), and the resulting solution was added via syringe. After stirring for 10 min, the cold reaction mixture was allowed to slowly warm to room temperature. After stirring for 4 h at that temperature, the reaction mixture was poured into water (20 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (15 mL × 3). The combined organic layer was washed successively with aqueous solution of saturated $NaHCO_3$, water, and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (EtOAc/MeOH =

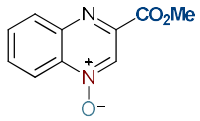
8:1) on silica gel to afford quinoxaline *N*-oxide as an off-white solid (1.56 g, 92%). A 250 mL round-bottomed flask equipped with a magnetic stir bar was charged with quinoxaline *N*-oxide (1.70 g,11.6 mmol, 1.0 equiv) dissolved in MeCN (51 mL) and KCN (1.51 g, 23.2 mmol, 2.0 equiv) dissolved in MeOH.(39 mL). To this mixture was added dropwise benzoyl chloride (3.3 g, 23.2 mmol, 2.0 equiv) at room temperature and the reaction mixture was stirred at that temperature for 9 h. After the completion of the reaction as judged by TLC, the solvent was evaporated under reduced pressure. The resulting residue was diluted with CH_2Cl_2, washed successively with water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (hexenes/EtOAc = 6:1) on silica gel to afford a yellow solid, which was further purified by recrystallization from a hot mixture of EtOAc and hexanes (9:1, *v*/*v*) to yield 2-quinoxalinecarbonitrile (**3z**) as a white solid (352 mg, 20 %). A 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with **3z** (135 mg, 0.870 mmol, 1.0 equiv) and CH_2Cl_2 (1.5 mL). The resulting mixture was cooled in an ice-water bath. A separate pear-shaped flask was charged with *m*-CPBA (77%, 291 mg, 1.30 mmol, 1.5 equiv) in CH_2Cl_2 (1.5 mL), and the resulting *m*-CPBA solution was added dropwise to the flask containing **3z** at 0 °C via syringe. The pear-shaped flask was rinsed with CH_2Cl_2 (1.0 mL × 3), and the resulting solution was added via syringe. After stirring for 10 min, the cold reaction mixture was allowed to slowly warm to room temperature. After stirring for 48 h at that temperature, the reaction mixture was poured into water (20 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (15 mL × 3). The combined organic layer was washed successively with an aqueous solution of saturated $NaHCO_3$, water, and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (EtOAc as a sole eluent) on silica gel to afford the title compound as an off-white solid (62 mg, 39%). Spectroscopic data matched with those reported in the literature.[20]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 7.2 Hz, 1H), 8.23–8.17 (m, 1H), 8.00–7.86 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.2, 138.4, 133.3, 133.0, 131.3, 131.0, 130.9, 118.9, 114.4.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ ($C_9H_5N_3O$) 172.0, found 172.0.

Methyl 3-Quinoxalinecarboxylate *N*-Oxide (1aa)



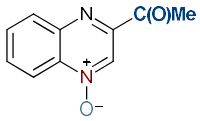
A 100 mL round-bottomed flask equipped with a magnetic stir bar and a reflux condenser was charged with 3-quinoxalinecarboxylic acid (522 mg, 3.00 mmol), MeOH (10 mL) and H_2SO_4 (0.3 mL). The resulting mixture was heated in an oil bath (bath temperature = 100 °C) under reflux for 3 h. The mixture was allowed to cool to room temperature, diluted with CH_2Cl_2, and neutralized with an aqueous solution of saturated $NaHCO_3$ (Caution! Evolution of CO_2). The mixture was then extracted with CH_2Cl_2 (5 mL × 3). The combined organic layer was washed successively with water and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (hexenes/EtOAc = 3:1) on silica gel to afford methyl 3-quinoxalinecarboxylate (**3aa**, 217 mg, 38 %) as an yellow solid. A 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with **3aa** (188 mg, 1.00 mmol, 1.0 equiv) and CH_2Cl_2 (1.5 mL). The resulting mixture was cooled in an ice-water bath. A separate pear-shaped flask was charged with *m*-CPBA (77%, 896 mg, 4.00 mmol, 4.0 equiv) in CH_2Cl_2 (1.5 mL), and the resulting *m*-CPBA solution was added dropwise to the flask containing **3aa** at 0 °C via syringe. The pear-shaped flask was rinsed with CH_2Cl_2 (1.0 mL × 3), and the resulting solution was added via syringe. After stirring for 10 min, the cold reaction mixture was allowed to slowly warm to room temperature. After stirring for 13 h at that temperature, the reaction mixture was poured into water (20 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (15 mL × 3). The combined organic layer was washed successively with an aqueous solution of saturated $NaHCO_3$, water, and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography on silica gel (EtOAc/MeOH = 9:1) to afford the title compound as an off-white solid (108 mg, 53%). Spectroscopic data matched with those reported in the literature.[21]

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.59 (dd, *J* = 8.5, 1.3 Hz, 1H), 8.31 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.87 (dddd, *J* = 23.8, 8.4, 7.0, 1.4 Hz, 3H), 4.10 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.4, 145.0, 144.7, 138.1, 132.5, 132.2, 131.3, 130.0, 118.9, 53.7.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ ($C_{10}H_8N_2O_3$) 205.1, found 205.1.

3-Acetylquinoxaline *N*-Oxide (1ab)



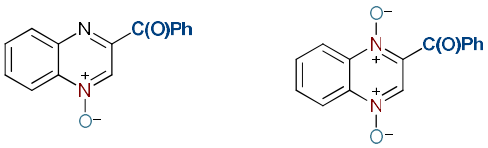
A 150 mL round-bottomed flask equipped with a magnetic stir bar and a reflux condenser was charged with quinoxaline (651 mg, 5.00 mmol, 1.0 equiv), acetaldehyde (1.10 g, 20.0 mmol, 4.0 equiv), tetra-*n*-butylammonium bromide (484 mg, 1.50 mmol, 0.3 equiv), $K_2S_2O_8$ (2.70 g, 10.0 mmol, 2.0 equiv), and 1,2-dichloroethane (42 mL). The resulting mixture was heated in an oil bath (bath temperature = 100 °C) under reflux for 2 h. The mixture was allowed to cool to room temperature, and the solvent was removed under vacuum. The crude mixture was diluted with CH_2Cl_2, washed successively with an aqueous solution of saturated $NaHCO_3$, water, and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography on silica gel (hexanes/EtOAc = 7:1) to afford 2-acetylquinoxaline (**3aa**) as a white solid (437 mg, 64 %). A 50 mL round-bottomed flask equipped with a magnetic stir bar was charged with **3aa** (528 mg, 3.08 mmol, 1.00 equiv) and CH_2Cl_2 (5.0 mL). The resulting mixture was cooled in an ice-water bath. A separate pear-shaped flask was charged with *m*-CPBA (77%, 1.38 g, 6.16 mmol, 2.0 equiv) in CH_2Cl_2 (5.3 mL), and the resulting *m*-CPBA solution was added dropwise to the flask containing **3aa** at 0 °C via syringe. The pear-shaped flask was rinsed with CH_2Cl_2 (1.0 mL × 3), and the resulting solution was added via syringe. After stirring for 10 min, the cold reaction mixture was allowed to slowly warm to room temperature. After stirring for 10 h at that temperature, the reaction mixture was poured into water (20 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (15 mL × 3). The combined organic layer was washed successively with aqueous solution of saturated $NaHCO_3$, water, and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (hexene/EtOAc = 4:1) on silica gel to afford a yellow solid, which was further purified by recrystallization from a hot mixture of hexanes and EtOAc (1:1, *v*/*v*) to yield the title compound as a white solid (209 mg, 44%). Spectroscopic data matched with those reported in the literature.[22]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.58–8.52 (m, 2H), 8.22–8.16 (m, 2H), 7.92–7.78 (m, 4H), 2.79 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.7, 149.6, 144.3, 137.9, 132.2, 132.0, 131.1, 127.2, 119.0, 25.2.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ ($C_{10}H_8N_2O_2$) 189.1, found 189.1.

3-Benzoylquinoxaline *N*-Oxide (1ac) and 2-Benzoylquinoxaline *N,N*-Oxide (1ac')



A 150 mL round-bottomed flask equipped with a magnetic stir bar and a reflux condenser was charged with quinoxaline (651 mg, 5.00 mmol, 1.0 equiv), benzaldehyde (2.12 g, 20.0 mmol, 4.0 equiv), tetra-*n*-butylammonium bromide (484 mg, 1.50 mmol, 0.30 equiv), $K_2S_2O_8$ (2.70 g, 10.0 mmol, 2.0 equiv), and 1,2-dichloroethane (42 mL). The resulting mixture was heated in an oil bath (bath temperature = 110 °C) under reflux for 2 h. The mixture was then cooled to room temperature, and the solvent was removed under vacuum. The crude mixture was diluted with CH_2Cl_2, washed successively with water and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (CH_2Cl_2 as a sole eluent) on silica gel to afford 2-benzoylquinoxaline (**3ac**) as a brown solid (615 mg, 53 %). A 50 mL round-bottomed flask was charged with **3ac** (234 mg, 1.00 mol, 1.0 equiv) and CH_2Cl_2 (1.5 mL), and the resulting mixture was cooled in an ice-water bath. A separate pear-shaped flask was charged with *m*-CPBA (77%, 448 mg, 2.00 mmol, 2.0 equiv) in CH_2Cl_2 (1.8 mL), and the resulting *m*-CPBA solution was added dropwise to the flask containing the heterocycle at 0 °C via syringe. The pear-shaped flask was rinsed with CH_2Cl_2 (1.0 mL × 3), and the resulting solution was added via syringe. After stirring for 10 min, the cold reaction mixture was allowed to slowly warm to room temperature. After stirring for 12 h at that temperature, the reaction mixture was poured into water (20 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (15 mL × 3). The combined organic layer was washed successively with an aqueous solution of saturated $NaHCO_3$, water, and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue thus obtained was loaded onto a column packed with silica gel. The column was eluted with a 25:1 mixture of CH_2Cl_2 and EtOAc to yield 3-benzoylquinoxaline *N*-oxide (**1ac**) along with 2-benzoylquinoxaline *N,N*-oxide (**1ac'**) as separable mixtures. 3-Benzoylquinoxaline *N*-oxide (**1ac**) was isolated as an off-white solid (52 mg, 21%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.48 (s, 1H), 8.27–8.16 (m, 7H), 7.92–7.81 (m, 3H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.2, 148.6, 145.2, 143.1, 140.4, 135.5, 133.6, 131.9, 131.2, 130.7, 130.4, 129.4, 128.3.

HRMS (ESI, TOF) *m*/*z* calculated for $[M + Na]^+$ ($C_{15}H_{10}N_2NaO_2$) 273.0634, found 273.0634.

IR (KBr) 3076, 3055, 1703, 1607, 1577, 1498, 1415, 1369, 1350, 1249, 1218, 1133, 922 cm^{-1}.

Melting point: 137.7-144.4 °C.

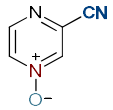
2-Benzoylquinoxaline *N,N*-Oxide (**1ac'**) was isolated as an off-white solid (68 mg, 27%) and spectroscopic data matched with those reported in the literature.[23]

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.15 (s, 1H), 8.67–8.61 (m, 2H), 8.38 (d, *J* = 8.2 Hz, 1H), 7.98–7.87 (m, 3H), 7.48 (t, *J* = 7.9 Hz, 2H), 7.38–7.27 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.6, 150.4, 144.8, 144.7, 138.3, 132.7, 132.5, 131.5, 130.3, 129.7, 126.7, 121.4, 119.0.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ ($C_{15}H_{10}N_2O_3$) 267.1, found 267.1.

3-Pyrazinecarbonitrile *N*-Oxide (1ad)



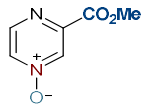
Prepared according to the literature procedure and further purified by recrystallization from a hot mixture of hexanes and EtOAc (4:1, *v*/*v*) to afford the title compound as an off-white solid. Spectroscopic data matched with those reported in the literature.[24]

^{1}H NMR (500 MHz, DMSO) δ 9.11–9.09 (m, 1H), 8.66 (d, *J* = 4.1 Hz, 1H), 8.60 (dd, *J* = 4.2, 1.6 Hz, 1H).

^{13}C NMR (126 MHz, DMSO) δ 148.91, 139.05, 137.20, 132.70, 114.59.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ ($C_5H_3N_3O$) 122.0, found 122.0.

Methyl Pyrazine-3-carboxylate *N*-Oxide (1ae)



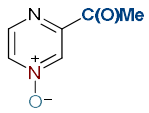
Prepared according to the literature procedure and further purified by recrystallization from a hot mixture of EtOAc to afford the title compound as an off-white solid. Spectroscopic data matched with those reported in the literature.[25]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (dd, *J* = 1.6, 0.7 Hz, 1H), 8.58–8.52 (m, 1H), 8.20 (dd, *J* = 4.0, 1.6 Hz, 1H), 4.03 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.6, 147.6, 147.3, 135.9, 135.9, 53.6.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ ($C_6H_6N_2O_3$) 155.0, found 155.0.

3-Acetylpyrazine *N*-Oxide (1af)



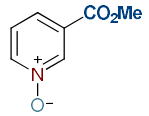
Prepared according to the literature procedure and further purified by recrystallization from a hot mixture of hexanes and EtOAc (1:3, *v*/*v*) to afford the title compound as a white solid. Spectroscopic data matched with those reported in the literature.[26]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (dd, *J* = 1.6, 0.7 Hz, 1H), 8.50 (d, *J* = 3.9 Hz, 1H), 8.18 (dd, *J* = 4.0, 1.7 Hz, 1H), 2.70 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 152.3, 146.6, 135.9, 132.7, 25.8.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ ($C_6H_6N_2O_2$) 139.0, found 139.0.

Methyl Nicotinate *N*-Oxide (1ag)



Prepared according to the literature procedure and further purified by recrystallization from a hot mixture of hexanes and EtOAc (1:1, *v*/*v*) to afford the title compound as a white solid. Spectroscopic data matched with those reported in the literature.[27]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (t, *J* = 1.5 Hz, 1H), 8.28 (ddd, *J* = 6.5, 1.5, 1.0 Hz, 1H), 7.79 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.33 (dd, *J* = 7.7, 6.7 Hz, 1H), 3.91 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.1, 142.3, 140.1, 129.8, 126.0, 125.7, 52.9.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ ($C_7H_8NO_3$) 154.0, found 154.1.

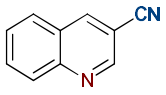
General Procedure for the Initial Optimization Studies (Table 1)

A 10 mL test tube equipped with a small magnetic stir bar was charged with 3-quinolinecarbonitrile *N*-oxide (**1a**, 34.0 mg, 0.200 mmol, 1.00 equiv), HEH (**1**, 0.300 mmol, 1.50 equiv), and a photocatalyst (2.0 μmol, 1.0 mol%). The tube was fitted with a rubber septum and CH_3CN (4.0 mL, 0.05 M) was added via syringe under an atmosphere of nitrogen. After degassing by N_2 bubbling at room temperature for 5–10 min, the reaction mixture was then irradiated at room temperature with two 3 W green LEDs for the indicated time (see Table 1). Upon the completion of the reaction as determined by TLC, the reaction mixture was concentrated on a rotary evaporator. The resulting residue was directly purified by flash column chromatography on silica gel (hexanes/EtOAc = 3:1) to afford 3-quinolinecarbonitrile (**3a**) as a white solid.

General Procedure for the Visible Light-Mediated Photoredox-Catalyzed Deoxygenation of N-Heterocyclic *N*-Oxides Using Na_2-eosin Y (4) as the Photocatalyst (Scheme 2)

A 10 mL test tube equipped with a small magnetic stir bar was charged with N-heterocyclic *N*-oxide (**1**, 0.200 mmol, 1.0 equiv), *tert*-Bu-HEH (**1c**, 92.8 mg, 0.300 mmol, 1.5 equiv), and Na_2-eosin Y (**4**, 1.4 mg, 2.0 μmol, 1.0 mol%). The tube was fitted with a rubber septum and CH_3CN (4.0 mL, 0.05 M) was added via syringe under an atmosphere of nitrogen. After degassing by N_2 bubbling at room temperature for 5–10 min, the reaction mixture was then irradiated at room temperature with two 3 W green LEDs for the indicated time (see Scheme 2). Upon the completion of the reaction as determined by TLC, the reaction mixture was concentrated on a rotary evaporator. The resulting residue was directly purified by flash column chromatography on silica gel (hexanes and EtOAc) to afford the corresponding deoxygenated N-heterocycle (**3**).

3-Quinolinecarbonitrile (3a)



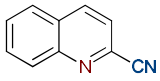
Prepared using 3-quinolinecarbonitrile *N*-oxide (**1a**, 34.0 mg, 0.200 mmol, 1.0 equiv), **2a** (92.8 mg, 0.300 mmol, 1.5 equiv), **4** (1.4 mg, 2.0 μmol, 1.0 mol%), and CH_3CN (4.0 mL, 0.05 M). 3-Quinolinecarbonitrile (**3a**, 29.3 mg, 95%) was isolated (hexanes/EtOAc = 3:1) as a white solid. Spectroscopic data matched with those reported in the literature.[28]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (d, *J* = 2.1 Hz, 1H), 8.49 (d, *J* = 2.0 Hz, 1H), 8.12 (d, *J* = 9.0 Hz, 1H), 7.89–7.82 (m, 2H), 7.69–7.62 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 148.6, 141.3, 132.6, 129.7, 128.3, 128.1, 126.0, 117.0, 106.4.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{10}H_6N_2$) 154.1, found 154.1.

2-Quinolinecarbonitrile (3b)



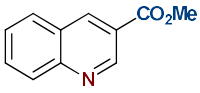
Prepared using 2-quinolinecarbonitrile *N*-oxide (**1b**, 34.0 mg, 0.200 mmol, 1.0 equiv), **2a** (92.8 mg, 0.300 mmol, 1.5 equiv), **4** (1.4 mg, 2.0 μmol, 1.0 mol%), and CH_3CN (4.0 mL, 0.05 M). 2-Quinolinecarbonitrile (**3b**, 27.5 mg, 89%) was isolated (hexanes/EtOAc = 6:1) as a white solid. Spectroscopic data matched with those reported in the literature.[28]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.84 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.75–7.67 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.2, 137.4, 133.6, 131.2, 130.0, 129.4, 128.6, 127.8, 123.3, 117.5.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{10}H_6N_2$) 154.1, found 154.1.

Methyl 3-Quinolinecarboxylate (3c)



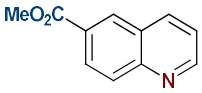
Prepared using methyl 3-quinolinecarboxylate *N*-oxide (**1c**, 40.6 mg, 0.200 mmol, 1.0 equiv), **2a** (92.8 mg, 0.300 mmol, 1.5 equiv), **4** (1.4 mg, 2.0 μmol, 1.0 mol%), and CH_3CN (4.0 mL, 0.05 M). Methyl 3-quinolinecarboxylate (**3c**, 36.5 mg, 98%) was isolated (hexanes/EtOAc = 3:2) as a white solid. Spectroscopic data matched with those reported in the literature.[7]

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.35 (d, *J* = 2.2 Hz, 1H), 8.71 (dd, *J* = 2.3, 0.9 Hz, 1H), 8.06 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.81 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.73 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.51 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 3.93 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 149.8, 149.6, 138.5, 131.6, 129.3, 128.9, 127.2, 126.6, 122.7, 52.2.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{11}H_9NO_2$) 187.1, found 187.1.

Methyl 6-Quinolinecarboxylate (3d)



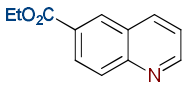
Prepared using methyl 6-quinolinecarboxylate *N*-oxide (**1d**, 40.6 mg, 0.200 mmol, 1.00 equiv), **2a** (92.8 mg, 0.300 mmol, 1.50 equiv), **4** (1.4 mg, 2.0 μmol, 1.0 mol%), and CH_3CN (4.00 mL, 0.05 M). Methyl quinoline-6-carboxylate (**3d**, 36.5 mg, 98%) was isolated (hexanes/EtOAc = 3:2) as a white solid. Spectroscopic data matched with those reported in the literature.[16]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.40 (d, *J* = 2.0 Hz, 1H), 8.15 (dd, *J* = 8.8, 2.0 Hz, 1H), 8.08 (dd, *J* = 8.4, 1.8 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.30 (dd, *J* = 8.3, 4.2 Hz, 1H), 3.86 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 152.2, 149.7, 137.0, 130.7, 129.5, 128.6, 127.8, 127.1, 121.5, 52.1.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{11}H_9NO_2$) 187.1, found 187.1.

Ethyl 6-Quinolinecarboxylate (3e)



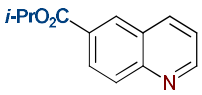
Prepared using ethyl 6-quinolinecarboxylate *N*-oxide (**1e**, 43.4 mg, 0.200 mmol, 1.0 equiv), **2a** (92.8 mg, 0.300 mmol, 1.5 equiv), **4** (1.4 mg, 2.0 μmol, 1.0 mol%), and CH_3CN (4.0 mL, 0.05 M). Ethyl 6-quinolinecarboxylate (**3e**, 37.8 mg, 94%) was isolated (hexanes/EtOAc = 2:1) as a white solid. Spectroscopic data matched with those reported in the literature.[29]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.57 (d, *J* = 2.0 Hz, 1H), 8.29 (dd, *J* = 8.8, 1.9 Hz, 1H), 8.24 (dd, *J* = 8.3, 2.0 Hz, 1H), 8.12 (d, *J* = 8.8 Hz, 1H), 7.44 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 152.4, 150.0, 137.2, 130.8, 129.7, 128.9, 128.4, 127.3, 121.7, 61.3, 14.3.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{12}H_{11}NO_2$) 201.1, found 201.1.

Isopropyl 6-Quinolinecarboxylate (3f)



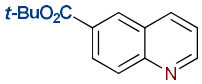
Prepared using isopropyl 6-quinolinecarboxylate *N*-oxide (**1f**, 46.3 mg, 0.200 mmol, 1.00 equiv), **2a** (92.8 mg, 0.300 mmol, 1.50 equiv), **4** (1.4 mg, 2.0 μmol, 1.0 mol%), and CH_3CN (4.00 mL, 0.05 M). Isopropyl 6-quinolinecarboxylate (**3f**, 42.3 mg, 98%) was isolated (hexanes/EtOAc = 3:1) as a white solid. Spectroscopic data matched with those reported in the literature.[30]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.53 (d, *J* = 2.0 Hz, 1H), 8.27 (dd, *J* = 8.8, 1.9 Hz, 1H), 8.22 (dd, *J* = 8.2, 2.0 Hz, 1H), 8.10 (d, *J* = 8.7 Hz, 1H), 7.41 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.29 (hept, *J* = 6.3 Hz, 1H), 1.39 (d, *J* = 6.3 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 152.3, 149.9, 137.2, 130.7, 129.6, 128.9, 128.8, 127.3, 121.7, 68.8, 21.9.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{13}H_{13}NO_2$) 215.1, found 215.2.

***tert*-Butyl 6-Quinolinecarboxylate (3g)**



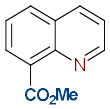
Prepared using *tert*-butyl 6-quinolinecarboxylate *N*-oxide (**1g**, 49.0 mg, 0.200 mmol, 1.0 equiv), **2a** (92.8 mg, 0.300 mmol, 1.5 equiv), **4** (1.4 mg, 2.0 μmol, 1.0 mol%), and CH_3CN (4.0 mL, 0.05 M). *tert*-Butyl 6-quinolinecarboxylate (**3g**, 42.2 mg, 98%) was isolated (hexanes/EtOAc = 3:1) as a white solid. Spectroscopic data matched with those reported in the literature.[31]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.50 (d, *J* = 1.9 Hz, 1H), 8.29–8.21 (m, 2H), 8.10 (d, *J* = 8.8 Hz, 1H), 7.43 (dd, *J* = 8.3, 4.2 Hz, 1H), 1.63 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.2, 152.2, 149.9, 137.2, 130.5, 129.9, 129.5, 129.0, 127.3, 121.6, 81.5, 28.2.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{14}H_{15}NO_2$) 229.1, found 229.1.

Methyl 8-Quinolinecarboxylate (3h)



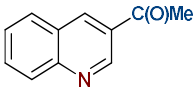
Prepared using methyl 8-quinolinecarboxylate *N*-oxide (**1h**, 40.6 mg, 0.200 mmol, 1.0 equiv), **2a** (123.8 mg, 0.400 mmol, 2.0 equiv), **4** (1.4 mg, 2.0 μmol, 1.0 mol%), and CH_3CN (4.0 mL, 0.05 M). Methyl 8-quinolinecarboxylate (**3h**, 26.6 mg, 98%) was isolated (hexanes/EtOAc = 3:2) as a white solid. Spectroscopic data matched with those reported in the literature.[32]

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.04 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.17 (dd, *J* = 8.3, 1.7 Hz, 1H), 8.02 (dd, *J* = 7.1, 1.3 Hz, 1H), 7.93 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.58–7.51 (m, 1H), 7.44 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.04 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 151.4, 145.4, 136.2, 131.5, 131.3, 130.4, 128.4, 125.5, 121.5, 52.6.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{11}H_9NO_2$) 187.1, found 187.1.

3-Acetylquinoline (3i)



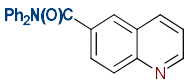
Prepared using 3-acetylquinoline *N*-oxide (**1i**, 37.4 mg, 0.200 mmol, 1.0 equiv), **2a** (92.8 mg, 0.300 mmol, 1.5 equiv), **4** (1.4 mg, 2.0 μmol, 1.0 mol%), and CH_3CN (4.0 mL, 0.05 M). 3-Acetylquinoline (**3i**, 33.0 mg, 97%) was isolated (hexanes/EtOAc = 1:1) as a white solid. Spectroscopic data matched with those reported in the literature.[6]

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.41 (d, *J* = 2.3 Hz, 1H), 8.68 (dd, *J* = 2.3, 0.9 Hz, 1H), 8.13 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.92 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.82 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.61 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 2.72 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.6, 149.8, 149.1, 137.2, 131.9, 129.4, 129.3, 129.2, 127.5, 126.8, 26.7.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{11}H_9NO$) 171.1, found 171.1.

***N*,*N*-Diphenyl-6-quinolinecarboxamide (3j)**



Prepared using *N*,*N*-diphenyl-6-quinolinecarboxamide *N*-oxide (**1j**, 68.1 mg, 0.200 mmol, 1.0 equiv), **2a** (92.8 mg, 0.300 mmol, 1.5 equiv), **4** (1.4 mg, 2.0 μmol, 1.0 mol%), and CH_3CN (4.0 mL, 0.05 M). *N*,*N*-Diphenyl-6-quinolinecarboxamide (**3j**, 59.0 mg, 91%) was isolated (hexanes/EtOAc = 1:3) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (dd, *J* = 4.1, 1.4 Hz, 1H), 8.07–8.01 (m, 2H), 7.69 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.34 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.29–7.14 (m, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.6, 151.6, 148.3, 143.5, 136.6, 134.2, 129.7, 129.1, 129.0, 128.9, 127.3, 127.2, 126.4, 121.5.

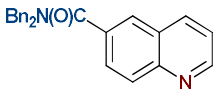
GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{22}H_{16}N_2O$) 324.1, found 324.1.

HRMS (ESI, TOF) *m/z* calculated for $[M + H]^+$ ($C_{22}H_{17}N_2O$) 325.1335, found 325.1335.

IR (KBr) 3062, 3037, 1657, 1623, 1589, 1490, 1461, 1450, 1355, 1335, 1304, 1291, 1122 cm^{-1}

Melting point: 175.4-179.7 °C.

***N*,*N*-Dibenzyl-6-quinolinecarboxamide (3k)**



Prepared using *N*,*N*-dibenzyl-6-quinolinecarboxamide *N*-oxide (**1k**, 73.7 mg, 0.200 mmol, 1.0 equiv), **2a** (123.8 mg, 0.400 mmol, 2.0 equiv), **4** (6.9 mg, 10.0 μmol, 5.0 mol%), and CH_3CN (4.0 mL, 0.05 M). *N*,*N*-Dibenzyl-6-quinolinecarboxamide (**3k**, 61.0 mg, 87%) was isolated (hexanes/EtOAc = 1:3) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.11 (td, *J* = 6.4, 5.8, 3.1 Hz, 2H), 7.97 (d, *J* = 1.7 Hz, 1H), 7.82 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.50–7.28 (m, 11H), 7.15 (s, 2H), 4.77 (s, 2H), 4.45 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.4, 151.4, 148.2, 136.7, 136.3, 136.1, 134.2, 129.9, 128.7, 128.4, 127.6, 127.5, 126.8, 126.4, 121.7, 51.5, 47.1.

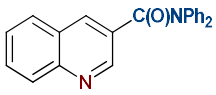
GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{24}H_{20}N_2O$) 352.2, found 352.2

HRMS (ESI, TOF) *m*/*z* calculated for $[M + H]^+$ ($C_{24}H_{21}N_2O$) 353.1648, found 353.1648.

IR (KBr) 3069, 3027, 3003, 2922, 2855, 1631, 1592, 1495, 1464, 1352, 1324, 1427, 1352, 1324, 1266, 1114 cm^{-1}

Melting point: 121.2-123.9 °C.

***N*,*N*-Diphenyl-3-quinolinecarboxamide (3l)**



Prepared using *N*,*N*-diphenyl-3-quinolinecarboxamide *N*-oxide (**1l**, 68.1 mg, 0.200 mmol, 1.0 equiv), **2a** (123.8 mg, 0.400 mmol, 2.0 equiv), **4** (6.9 mg, 10.0 µmol, 5.0 mol%), and CH_3CN (4.0 mL, 0.05 M). *N*,*N*-Diphenyl-3-quinolinecarboxamide (**3l**, 64.7 mg, 99%) was isolated (hexanes/EtOAc = 3:2) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 (d, *J* = 2.2 Hz, 1H), 8.34 (d, *J* = 1.8 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.76–7.68 (m, 3H), 7.55–7.49 (m, 1H), 7.30 (t, *J* = 7.6 Hz, 5H), 7.21 (dd, *J* = 14.3, 7.2 Hz, 8H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 149.5, 148.0, 143.2, 137.6, 130.9, 129.3, 129.2, 129.1, 128.4, 127.4, 127.1, 126.8, 126.7.

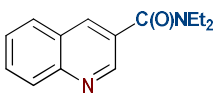
GC-MS (EI, 70 eV) *m*/*z* calculated for $[M]^+$ ($C_{22}H_{16}N_2O$) 324.1, found 324.1

HRMS (ESI, TOF) *m*/*z* calculated for $[M + H]^+$ ($C_{22}H_{17}N_2O$) 325.1335, found 325.1335.

IR (KBr) 3102, 3062, 3050, 1657, 1623, 1589, 1490, 1461, 1450, 1425, 1356, 1334, 1304, 1291, 1256, 1219 cm^{-1}

Melting point: 173.2-182.2 °C.

***N*,*N*-Diethyl-3-quinolinecarboxamide (3m)**



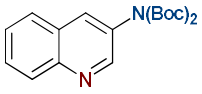
Prepared using *N*,*N*-diethyl-3-quinolinecarboxamide *N*-oxide (**1m**, 48.9 mg, 0.200 mmol, 1.0 equiv), **2a** (123.8 mg, 0.400 mmol, 2.0 equiv), **4** (6.9 mg, 10.0 µmol, 5.0 mol%), and CH_3CN (4.0 mL, 0.05 M). *N*,*N*-Diethyl-3-quinolinecarboxamide (**3m**, 41.0 mg, 85%) was isolated (hexenes/EtOAc = 1:3) as a yellow oil. Spectroscopic data matched with those reported in the literature.[33]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.93 (d, *J* = 2.2 Hz, 1H), 8.19 (d, *J* = 2.1 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.84 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.76 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.59 (ddd, *J* = 8.1, 6.7, 1.2 Hz, 1H), 3.61 (br s, 2H), 3.32 (br s, 2H), 1.29 (br s, 3H), 1.16 (br s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 148.1, 148.0, 134.0, 130.4, 130.1, 129.4, 128.1, 127.3, 127.1, 43.5, 39.6, 14.3, 12.9.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{14}H_{16}N_2O$) 228.1, found 228.1.

3-[Bis(*tert*-butoxycarbonyl)amino]quinoline (3n)



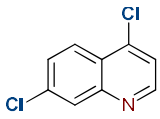
Prepared using 3-[bis(*tert*-butoxycarbonyl)amino]quinoline *N*-oxide (**1n**, 72.1 mg, 0.200 mmol, 1.0 equiv), **2a** (123.8 mg, 0.400 mmol, 2.0 equiv), **4** (6.9 mg, 10.0 μmol, 5.0 mol%), and CH_3CN (4.0 mL, 0.05 M). 3-[Bis(*tert*-butoxycarbonyl)amino]quinoline (**3n**, 66.0 mg, 96%) was isolated (hexanes/EtOAc = 4:1) as a yellow solid. Spectroscopic data matched with those reported in the literature.[10]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 2.5 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 2.5 Hz, 1H), 7.80 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.71 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.55 (ddd, *J* = 8.1, 6.8, 1.1 Hz, 1H), 1.39 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.2, 150.4, 146.6, 133.4, 132.7, 129.7, 129.2, 127.8, 127.6, 127.0, 83.5, 27.8.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{19}H_{24}N_2O_4$) 344.2, found 344.1.

4,7-Dichloroquinoline (3o)



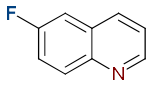
Prepared using 4,7-dichloroquinoline *N*-oxide (**1o**, 42.8 mg, 0.200 mmol, 1.0 equiv), **2a** (92.8 mg, 0.300 mmol, 1.5 equiv), **4** (2.8 mg, 4.0 μmol, 2.0 mol%), and CH_3CN (4.0 mL, 0.05 M). 4,7-Dichloroquinoline (**3o**, 30.8 mg, 78%) was isolated (hexanes/EtOAc = 1:1) as a white solid. Spectroscopic data matched with those reported in the literature.[34]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.7 Hz, 1H), 8.09–8.02 (m, 2H), 7.50 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.40 (d, *J* = 4.7 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.8, 149.3, 142.5, 136.3, 128.6, 128.5, 125.4, 124.8, 121.3.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_9H_5Cl_2N$) 197.0, found 197.1.

6-Fluoroquinoline (3p)



Prepared using 6-fluoroquinoline *N*-oxide (**1p**, 32.6 mg, 0.200 mmol, 1.0 equiv), **2a** (92.8 mg, 0.300 mmol, 1.5 equiv), **4** (2.8 mg, 4.0 μmol, 2.0 mol%), and CH_3CN (4.0 mL, 0.05 M). 6-Fluoroquinoline (**3p**, 22.8 mg, 78%) was isolated (hexanes/EtOAc = 2:1) as a yellow oil. Spectroscopic data matched with those reported in the literature.[15]

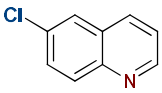
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.05 (dd, *J* = 9.3, 5.3 Hz, 1H), 8.01 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.46–7.38 (m, 1H), 7.37–7.30 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2 (d, $^{1}J_{C–F}$ = 248.3 Hz), 149.5 (d, $^{4}J_{C–F}$ = 2.9 Hz), 145.3, 135.2 (d, $^{4}J_{C–F}$ = 5.4 Hz), 131.9 (d, $^{3}J_{C–F}$ = 9.2 Hz), 128.7 (d, $^{3}J_{C–F}$ = 10.0 Hz), 121.6, 119.6 (d, $^{2}J_{C–F}$ = 25.8 Hz), 110.5 (d, $^{2}J_{C–F}$ = 21.8 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ –112.3.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ (C_9H_6FN) 147.0, found 147.1.

6-Chloroquinoline (3q)



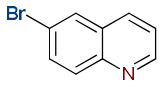
Prepared using 6-chloroquinoline *N*-oxide (**1q**, 35.9 mg, 0.200 mmol, 1.0 equiv), **2a** (92.8 mg, 0.300 mmol, 1.5 equiv), **4** (2.8 mg, 4.0 μmol, 2.0 mol%), and CH_3CN (4.0 mL, 0.05 M). 6-Chloroquinoline (**3q**, 28 mg, 86%) was isolated (hexanes/EtOAc = 3:1) as a yellow oil. Spectroscopic data matched with those reported in the literature.[15]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (dd, *J* = 4.1, 1.3 Hz, 1H), 8.05 (t, *J* = 9.7 Hz, 2H), 7.79 (d, *J* = 2.3 Hz, 1H), 7.64 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.41 (dd, *J* = 8.3, 4.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.51, 146.55, 135.14, 132.31, 131.03, 130.42, 128.81, 126.38, 121.87.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ (C_9H_6ClN) 163.0, found 163.0.

6-Bromoquinoline (3r)



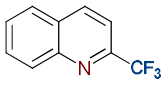
Prepared using 6-bromoquinoline *N*-oxide (**1r**, 44.8 mg, 0.200 mmol, 1.0 equiv), **2a** (92.8 mg, 0.300 mmol, 1.5 equiv), **4** (2.8 mg, 4.0 μmol, 2.0 mol%), and CH_3CN (4.0 mL, 0.05 M). 6-Bromoquinoline (**3r**, 40.4 mg, 97%) was isolated (hexanes/EtOAc = 3:1) as a yellow oil. Spectroscopic data matched with those reported in the literature.[15]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.03 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.98–7.93 (m, 2H), 7.75 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.39 (dd, *J* = 8.3, 4.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.7, 146.8, 134.9, 132.9, 131.2, 129.7, 129.3, 121.8, 120.4.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ (C_9H_6BrN) 207.0, found 207.1.

2-(Trifluoromethyl)quinoline (3s)



Prepared using 2-(trifluoromethyl)quinoline *N*-oxide (**1s**, 42.6 mg, 0.200 mmol, 1.0 equiv), **2a** (123.8 mg, 0.400 mmol, 2.0 equiv), **4** (6.9 mg, 10.0 μmol, 5.0 mol%), and CH_3CN (4.0 mL, 0.05 M). 2-(Trifluoromethyl)quinoline (**3s**, 34.8 mg, 88%) was isolated (hexanes/Et_2O = 15:1) as a white solid. Spectroscopic data matched with those reported in the literature.[15]

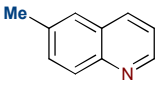
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.5 Hz, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 7.89 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.81 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.66 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9 (q, $^{2}J_{C–F}$ = 34.5 Hz), 147.1, 138.1, 130.8, 130.1, 128.8, 128.6, 127.6, 121.6 (q, $^{1}J_{C–F}$ = 275.2 Hz), 116.7 (q, $^{3}J_{C–F}$ = 2.3 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ –66.5.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{10}H_6F_3N$) 197.0, found 197.1.

6-Methylquinoline (3t)



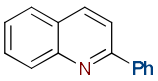
Prepared using 6-methylquinoline *N*-oxide (**1t**, 31.8 mg, 0.200 mmol, 1.0 equiv), **2a** (123.8 mg, 0.400 mmol, 2.0 equiv), **4** (6.9 mg, 10.0 μmol, 5.0 mol%), and CH_3CN (4.0 mL, 0.05 M). 6-Methylquinoline (**3t**, 22.5 mg, 79%) was isolated (hexanes/EtOAc = 2:1) as a white solid. Spectroscopic data matched with those reported in the literature.[15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.9 Hz, 1H), 8.47 (d, *J* = 5.9 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.62 (s, 1H), 7.59 (dd, *J* = 8.9, 1.7 Hz, 1H), 7.27–7.23 (m, 1H), 2.54 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 139.0, 135.0, 132.6, 130.7, 127.0, 125.5, 120.9, 119.6, 21.4.

LC-MS (ESI) calculated for $[M+1]^+$ ($C_{10}H_{10}NO$) *m*/*z* 144.1, found *m*/*z* 144.1.

2-Phenylquinoline (3u)



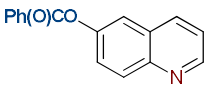
Prepared using 2-phenylquinoline *N*-oxide (**2u**, 44.3 mg, 0.200 mmol, 1.0 equiv), **2a** (123.8 mg, 0.400 mmol, 2.0 equiv), **4** (6.9 mg, 10.0 μmol, 5.0 mol%), and CH_3CN (4.0 mL, 0.05 M). 2-Phenylquinoline (**3u**, 21.3 mg, 52%) was isolated (hexanes/EtOAc = 2:1) as a pale yellow oil. Spectroscopic data matched with those reported in the literature.[15]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.6 Hz, 1H), 8.23–8.17 (m, 3H), 7.91 (d, *J* = 8.6 Hz, 1H), 7.86 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.76 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.61–7.53 (m, 3H), 7.53–7.46 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.3, 148.3, 139.7, 136.7, 129.8, 129.6, 129.3, 128.8, 127.6, 127.4, 127.2, 126.2, 119.0.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{15}H_{11}N$) 205.1, found 205.1.

6-Benzoyloxyquinoline (3v)



Prepared using 6-benzoyloxyquinoline *N*-oxide (**1v**, 53.0 mg, 0.200 mmol, 1.0 equiv), **2a** (92.8 mg, 0.300 mmol, 1.5 equiv), **4** (1.4 mg, 2.0 μmol, 1.0 mol%), and CH_3CN (4.0 mL, 0.05 M). 6-

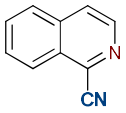
Benzoyloxyquinoline (**3v**, 32.4 mg, 65%) was isolated (hexanes/EtOAc = 3:2) as a white solid. Spectroscopic data matched with those reported in the literature.[35]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.91 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.27–8.21 (m, 2H), 8.17 (d, *J* = 9.1 Hz, 1H), 8.12 (d, *J* = 7.9 Hz, 1H), 7.69 (d, *J* = 2.5 Hz, 1H), 7.59 (dd, *J* = 9.1, 2.5 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.40 (dd, *J* = 8.3, 4.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.0, 150.2, 148.7, 146.3, 135.7, 133.8, 131.0, 130.2, 129.2, 128.6, 128.5, 124.8, 121.5, 118.5.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{16}H_{11}NO_2$) 249.1, found 249.1

1-Isoquinolinecarbonitrile (3w)



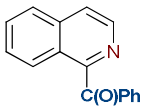
Prepared using 1-isoquinolinecarbonitrile *N*-oxide (**1w**, 34.3 mg, 0.200 mmol, 1.0 equiv), **2a** (92.8 mg, 0.300 mmol, 1.5 equiv), **4** (1.4 mg, 2.0 μmol, 1.0 mol%), and CH_3CN (4.0 mL, 0.05 M). 1-Isoquinolinecarbonitrile (**3w**, 30.3 mg, 97%) was isolated (hexanes/EtOAc = 1:1) as a white solid. Spectroscopic data matched with those reported in the literature.[36]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (d, *J* = 5.6 Hz, 1H), 8.32 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 7.7 Hz, 1H), 7.90 (d, *J* = 5.6 Hz, 1H), 7.86–7.76 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 135.8, 134.8, 131.7, 129.8, 129.3, 127.3, 125.2 (two carbons), 124.4, 115.8.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{10}H_6N_2$) 154.1, found 154.1.

1-Benzoylisoquinoline (3x)



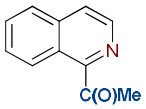
Prepared using 1-benzoylisoquinoline *N*-oxide (**1x**, 49.9 mg, 0.200 mmol, 1.0 equiv), **2a** (92.8 mg, 0.300 mmol, 1.5 equiv), **4** (1.4 mg, 2.0 μmol, 1.0 mol%), and CH_3CN (4.0 mL, 0.05 M). 1-Benzoylisoquinoline (**3x**, 40.1 mg, 86%) was isolated (hexanes/EtOAc = 6:1) as a white solid. Spectroscopic data matched with those reported in the literature.[37]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 5.6 Hz, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 8.02–7.93 (m, 3H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 5.6 Hz, 1H), 7.78–7.70 (m, 2H), 7.65–7.57 (m, 4H), 7.47 (t, *J* = 7.8 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 194.7, 156.4, 141.1, 136.6, 136.6, 133.6, 130.7, 130.6, 128.4, 128.3, 127.0, 126.4, 126.1, 122.5.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{16}H_{11}NO$) 233.1, found 233.1.

1-Acetylisoquinoline (3y)



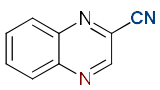
Prepared using 1-acetylisoquinoline *N*-oxide (**1y**, 37.4 mg, 0.200 mmol, 1.0 equiv), **2a** (92.8 mg, 0.300 mmol, 1.5 equiv), **4** (1.4 mg, 2.0 μmol, 1.0 mol%), and CH_3CN (4.0 mL, 0.05 M). 1-Acetylisoquinoline (**3y**, 23.1 mg, 68%) was isolated (CH_2Cl_2 as a sole eluent) as a white solid. Spectroscopic data matched with those reported in the literature.[38]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (d, *J* = 8.4 Hz, 1H), 8.58 (d, *J* = 5.5 Hz, 1H), 7.86 (d, *J* = 7.5 Hz, 1H), 7.82 (d, *J* = 5.5 Hz, 1H), 7.75–7.65 (m, 2H), 2.86 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 202.7, 152.8, 141.0, 137.0, 130.3, 129.1, 126.9, 126.9, 125.7, 124.6, 28.5.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{11}H_9NO_2$) 187.1, found 187.1.

2-Quinoxalinecarbonitrile (3z)



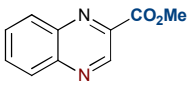
Prepared using 3-quinoxalinecarbonitrile *N*-oxide (**1z**, 34.2 mg, 0.200 mmol, 1.0 equiv), **2a** (92.8 mg, 0.300 mmol, 1.5 equiv), **4** (1.4 mg, 2.0 μmol, 1.0 mol%), and CH_3CN (4.0 mL, 0.05 M). 2-Quinoxalinecarbonitrile (**3z**, 27.9 mg, 90%) was isolated (hexanes/EtOAc = 9:1) as a white solid. Spectroscopic data matched with those reported in the literature.[39]

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.21–8.14 (m, 3H), 7.94 (dtt, *J* = 13.5, 6.8, 3.5 Hz, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.6, 142.9, 142.0, 133.3, 131.9, 129.9, 129.8, 129.6, 115.9.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_9H_5N_3$) 155.0, found 155.0.

Methyl 2-Quinoxalinecarboxylate (3aa)



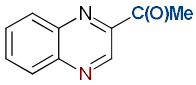
Prepared using methyl 3-quinoxalinecarboxylate *N*-oxide (**1aa**, 40.8 mg, 0.200 mmol, 1.0 equiv), **2a** (92.8 mg, 0.300 mmol, 1.5 equiv), **4** (1.4 mg, 2.0 µmol, 1.0 mol%), and CH_3CN (4.0 mL, 0.05 M). Methyl 2-quinoxalinecarboxylate (**3aa**, 37.3 mg, 99%) was isolated (hexanes/EtOAc = 3:1) as a white solid. Spectroscopic data matched with those reported in the literature.[40]

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.52 (s, 1H), 8.27 (dd, *J* = 8.3, 1.2 Hz, 2H), 8.15 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.92–7.80 (m, 4H), 4.09 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 145.0, 143.7, 142.3, 141.4, 132.3, 131., 130.5, 129.3, 53.3.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{10}H_8N_2O_2$) 188.1, found 188.1.

2-Acetylquinoxaline (3ab)



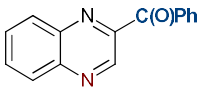
Prepared using 3-acetylquinoxaline *N*-oxide (**1ab**, 37.6 mg, 0.200 mmol, 1.0 equiv), **2a** (92.8 mg, 0.300 mmol, 1.5 equiv), **4** (1.4 mg, 2.0 µmol, 1.0 mol%), and CH_3CN (4.0 mL, 0.05 M). 2-Acetylquinoxaline (**3ab**, 34.1 mg, 94%) was isolated (hexanes/EtOAc = 7:1) as a white solid. Spectroscopic data matched with those reported in the literature.[41]

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.47 (s, 1H), 8.20–8.11 (m, 3H), 2.83 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.7, 146.5, 143.8, 143.0, 141.0, 132.1, 130.6, 130.4, 129.4, 25.4.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{10}H_8N_2O$) 172.1, found 172.1.

2-Benzoylquinoxaline (3ac)



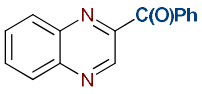
Prepared using 3-benzoylquinoxaline *N*-oxide (**1ac**, 48.9 mg, 0.200 mmol, 1.0 equiv), **2a** (92.8 mg, 0.300 mmol, 1.5 equiv), **4** (1.4 mg, 2.0 μmol, 1.0 mol%), and CH_3CN (4.00 mL, 0.05 M). 2-Benzoylquinoxaline (**3ac**, 44.0 mg, 94%) was isolated (hexenes/EtOAc = 4:1) as a white solid. Spectroscopic data matched with those reported in the literature.[42]

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.48 (s, 1H), 8.27–8.12 (m, 7H), 7.98–7.78 (m, 3H), 7.66 (s, 0H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.2, 148.6, 145.2, 143.1, 140.4, 135.5, 133.6, 131.9, 131.2, 130.7, 130.4, 129.4, 128.3.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{15}H_{10}N_2O$) 234.1, found 234.1.

2-Benzoylquinoxaline (3ac)



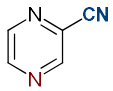
Prepared using 3-benzoylquinoxaline *N,N*-dioxide (**1ac'**, 53.3 mg, 0.200 mmol, 1.0 equiv), **2a** (185.6 mg, 0.600 mmol, 3.0 equiv), **4** (1.4 mg, 2.0 μmol, 1.0 mol%), and CH_3CN (4.00 mL, 0.05 M). 2-Benzoylquinoxaline (**3ac**, 43.2 mg, 94%) was isolated (CH_2Cl_2/EtOAc = 30:1) as a white solid. Spectroscopic data matched with those reported in the literature.[42]

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.48 (s, 1H), 8.27–8.14 (m, 7H), 7.91–7.81 (m, 3H), 7.66 (s, 0H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.2, 148.6, 145.2, 143.1, 140.4, 135.5, 133.6, 131.9, 131.2, 130.7, 130.4, 129.4, 128.3.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_{15}H_{10}N_2O$) 234.1, found 234.1.

3-Pyrazinecarbonitrile (3ad)



Prepared using 3-pyrazinecarbonitrile *N*-oxide (**1ad**, 24.2 mg, 0.200 mmol, 1.0 equiv), **2a** (92.8 mg, 0.300 mmol, 1.5 equiv), **4** (1.4 mg, 2.0 μmol, 1.0 mol%), and CH_3CN (4.0 mL, 0.05 M). The truth is that the deoxygenated product 2-pyrazinecarbonitrile (**3ad**) is volatile. Hence, an NMR yield (98%) was

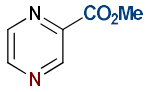
estimated using 1,3,5-trimethoxybenzene as an internal standard. An analytical sample was obtained by flash column chromatography of the crude mixture (hexanes/EtOAc = 4:1) on silica gel. Spectroscopic data matched with those reported in the literature.[43]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (d, *J* = 1.4 Hz, 1H), 8.79 (d, *J* = 2.4 Hz, 1H), 8.75–8.69 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.5, 138.2, 136.5, 134.0, 113.5.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_5H_3N_3$) 105.0, found 105.0.

Methyl 3-Pyrazinecarboxylate (3ae)



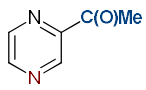
Prepared using methyl 3-pyrazinecarboxylate *N*-oxide (**1ae**, 30.8 mg, 0.200 mmol, 1.0 equiv), **2a** (92.8 mg, 0.300 mmol, 1.5 equiv), **4** (1.4 mg, 2.0 μmol, 1.0 mol%), and CH_3CN (4.0 mL, 0.05 M). Methyl 3-pyrazinecarboxylate (**3ae**, 24.3, 88%) was isolated (hexenes/EtOAc = 1:1) as a pale yellow oil. Spectroscopic data matched with those reported in the literature.[44]

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.32 (s, 1H), 8.77 (d, *J* = 2.2 Hz, 1H), 8.72 (s, 1H), 4.04 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.4, 147.7, 146.3, 144.4, 143.3, 53.1.

LC-MS (ESI) *m/z* calculated for $[M+1]^+$ ($C_6H_6N_2O_2$) 139.0, found 139.0.

3-Acetylpyrazine (3af)



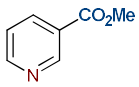
Prepared using 3-acetylpyrazine *N*-oxide (**1af**, 27.6 mg, 0.200 mmol, 1.0 equiv), **2a** (123.8 mg, 0.400 mmol, 2.0 equiv), **4** (1.4 mg, 2.0 μmol, 1.0 mol%), and CH_3CN (4.0 mL, 0.05 M). The truth is that the deoxygenated product 3-acetylpyrazine (**3af**) is volatile. Hence, an NMR yield (90%) was estimated using 1,3,5-trimethoxybenzene as an internal standard. An analytical sample was obtained by flash column chromatography of the crude mixture (hexanes/EtOAc = 1:1) on silica gel. Spectroscopic data matched with those reported in the literature.[45]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (d, *J* = 2.4 Hz, 1H), 8.67–8.61 (m, 1H), 2.71 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.3, 147.7, 143.5, 28.2, 25.7.

LC-MS (ESI) *m*/*z* calculated for $[M+1]^+$ ($C_6H_6N_2O$) 123.0, found 123.0.

Methyl Nicotinate (3ag)



Prepared using methyl nicotinate *N*-oxide (**1ag**, 30.6 mg, 0.2 mmol, 1.0 equiv), **2a** (92.8 mg, 0.3 mmol, 1.5 equiv), **4** (1.4 mg, 2.0 μmol, 1 0 mol%), and CH_3CN (4.0 mL, 0.05 M). Methyl nicotinate (**3ag,** 5.7 mg, 21%) was isolated (hexanes/EtOAc = 2:1) as a yellow oil. Spectroscopic data matched with those reported in the literature.[46]

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.12 (d, *J* = 2.4 Hz, 1H), 8.68 (dd, *J* = 4.9, 1.8 Hz, 1H), 8.19 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.30 (dd, *J* = 8.0, 4.9 Hz, 1H), 3.86 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 153.2, 150.7, 136.8, 125.8, 123.1, 52.2.

GC-MS (EI, 70 eV) *m/z* calculated for $[M]^+$ ($C_7H_7NO_2$) 137.0, found 137.2.

Experimental Procedure for Scheme 3a (In the Absence of Visible Light Irradiation)

A 10 mL test tube equipped with a small magnetic stir bar was charged with 3-quinolinecarbonitrile *N*-oxide (**1a**, 34.0 mg, 0.200 mmol, 1.0 equiv) and *tert*-Bu-HEH (**1c**, 92.8 mg, 0.300 mmol, 1.5 equiv). The tube was fitted with a rubber septum and wrapped with aluminum foil, and CH_3CN (4.0 mL, 0.05 M) was added via syringe under an atmosphere of nitrogen. After degassing by N_2 bubbling at room temperature for 10 min, the reaction mixture was stirred in the dark for 12 h. TLC analysis indicated that no conversion of **1a** into the deoxygenated product **3a** occurred.

Experimental Procedure for Scheme 3b (In the Absence of a Photocatalyst)

A 10 mL test tube equipped with a small magnetic stir bar was charged with 3-quinolinecarbonitrile *N*-oxide (**1a**, 34.0 mg, 0.200 mmol, 1.0 equiv) and *tert*-Bu-HEH (**1c**, 92.8 mg, 0.300 mmol, 1.5 equiv). The tube was fitted with a rubber septum and CH_3CN (4.0 mL, 0.05 M) was added via syringe under an atmosphere of nitrogen. After degassing by N_2 bubbling at room temperature for 10 min, the reaction mixture was then irradiated at room temperature with two 3 W green LEDs for 24 h. The reaction mixture was concentrated on a rotary evaporator. The resulting residue was directly purified by flash column

chromatography on silica gel (hexanes/EtOAc = 3:1) to afford 3-quinolinecarbonitrile (**3a**, 16.7 mg, 45%) as a white solid.

Experimental Procedure for Scheme 3c (Kinetic Deuterium Isotope Effect)

A 10 mL test tube equipped with a small magnetic stir bar was charged with methyl 3-quinolinecarboxylate *N*-oxide (**1a**, 40.6 mg, 0.200 mmol, 1.0 equiv), *tert*-Bu-HEH (**1c**, 46.4 mg, 0.150 mmol, 0.75 equiv), *t*-Bu-HEH-d_2 (**1c**-d_2, 46.7 mg, 0.150 mmol, 0.75 equiv), and Na_2-eosin Y (**4**, 1.4 mg, 2.0 μmol, 1.0 mol%). The tube was fitted with a rubber septum and CH_3CN (4.0 mL, 0.05 M) was added via syringe under an atmosphere of nitrogen. After degassing by N_2 bubbling at room temperature for 1 min, the reaction mixture was then irradiated at room temperature with two 3 W green LEDs for 1 h. Upon the completion of the reaction as determined by TLC, the reaction mixture was concentrated on a rotary evaporator. The resulting residue was purified by flash column chromatography on silica gel (hexanes/EtOAc = 7:1 → 1.2:1) to afford 3-quinolinecarbonitrile (**3a**, 36.7 mg, 97%) along with, as determined by 1H NMR analysis, a 1:1.3 mixture of di-*tert*-butyl 2,6-dimethylpyridine-3,5-dicarboxylate and di-*tert*-butyl 4-deuterio-2,6-dimethylpyridine-3,5-dicarboxylate.

Experimental Procedure for Scheme 3d (Using a Radical Inhibitor)

A 10 mL test tube equipped with a small magnetic stir bar was charged with isopropyl 6-quinolinecarboxylate *N*-oxide (**1a**, 48.3 mg, 0.200 mmol, 1.0 equiv), *tert*-Bu-HEH (**2a**, 92.8 mg, 0.300 mmol, 1.5 equiv), (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO, 187 mg, 1.20 mmol, 6.0 equiv), and Na_2-eosin Y (**4**, 1.4 mg, 2.0 μmol, 1.0 mol%). The tube was fitted with a rubber septum and CH_3CN (4.0 mL, 0.05 M) was added via syringe under an atmosphere of nitrogen. After degassing by N_2 bubbling at room temperature for 10 min, the reaction mixture was then irradiated at room temperature with two 3 W green LEDs. After irradiation of the reaction mixture for 6 h, the reaction mixture was concentrated on a rotary evaporator. The resulting residue was purified by flash column chromatography on silica gel (hexanes/EtOAc = 3:1) to afford 6-quinolinecarboxylate (**3a**, 2.8 mg, 7%) as a white solid.

Stern-Volmer Fluorescence Quenching Experiments

Emission Quenching of Na_2-eosin Y (4)

A 50 mL volumetric flask containing the photocatalyst Na_2-eosin Y (**4**, 4.3 mg, 6.25 μmol) was fitted with a rubber septum and charged with CH_3CN (slightly more than 100 mL) via syringe. The resulting solution was then degassed by sparging with nitrogen until its volume reached to 100 mL. Stern-Volmer luminescence quenching experiments were performed using a Varian Cary eclipse fluorescence spectrophotometer. In each experimentation, the solution of **4** and varying concentrations of quencher (**1e**, **1q**, **1t**, or **2a**) were combined in degassed CH_3CN in 1 cm screw-top quartz cuvettes. For the emission quenching of **4**, the photocatalyst concentration was 0.2 μM, the solution was excited at 530 nm, and the emission intensity was observed at 555 nm. Plots were constructed according to the Stern-Volmer equation $I_0/I = 1+k_q\tau_0[Q]$. I_0 and I represent the intensities of the emission in the absence and presence of a quencher at 555 nm, respectively.

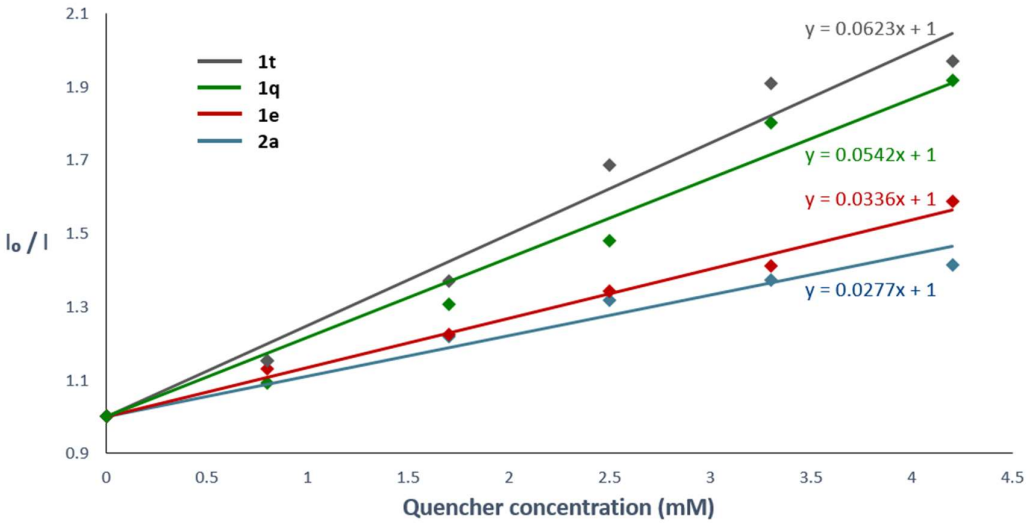


Figure S3. Emission Quenching of Na_2-eosin Y (**4**)

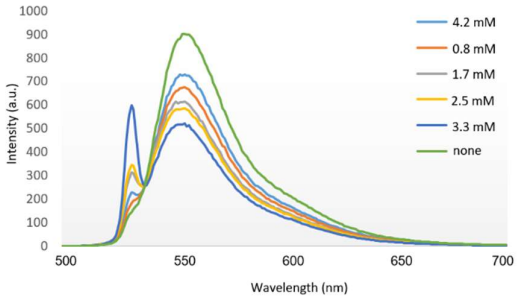


Figure S4. Emission Quenching of **4** by **1e**

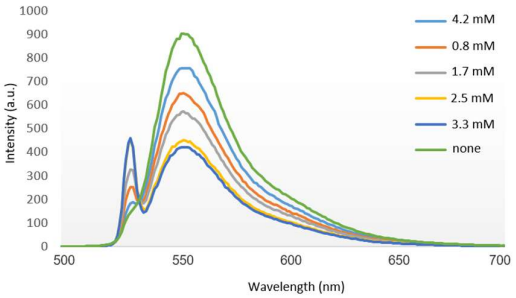


Figure S5. Emission Quenching of **4** by **1q**

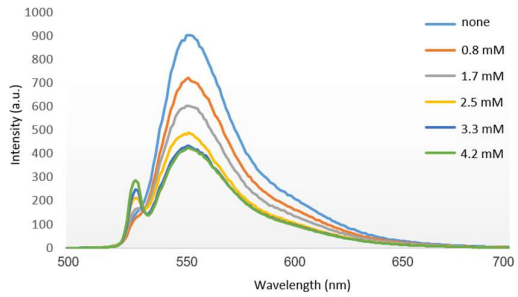


Figure S6. Emission Quenching of **4** by **1t**

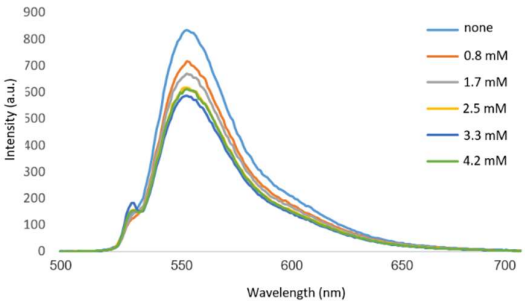


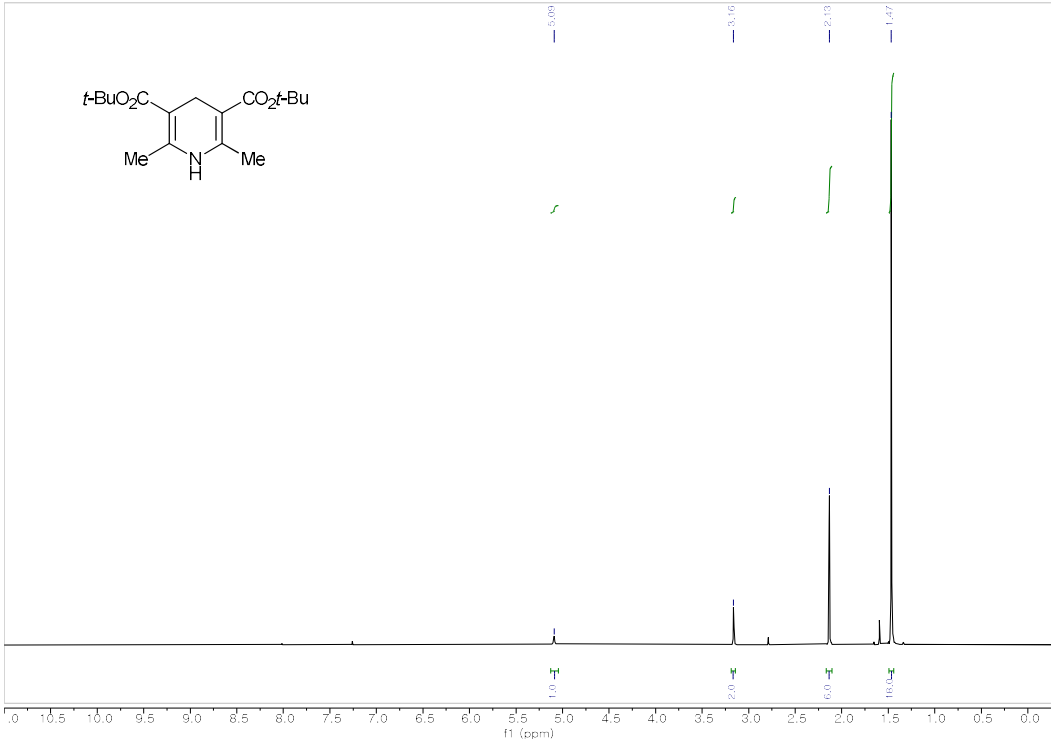
Figure S7. Emission Quenching of **4** by **2a**

Experimental Procedure for Multigram-Scale Reaction (Scheme 4)

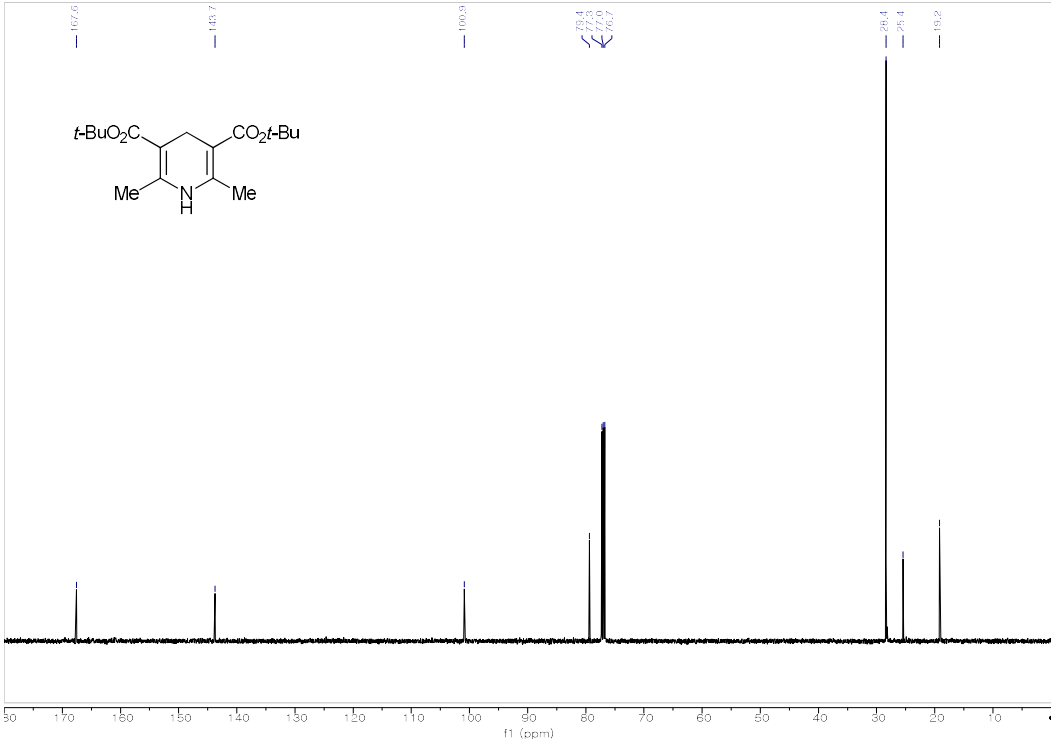
A 500 mL round-bottomed flask equipped with a magnetic stir bar was charged with methyl 6-quinolinecarboxylate *N*-oxide (**1c**, 3.00 g, 14.8 mmol, 1.0 equiv), *tert*-Bu-HEH (**2a**, 6.85 g, 22.2 mmol, 1.5 equiv), and Na_2-eosin Y (**4**, 103.8 mg, 0.148 mmol, 1.0 mol%). The flask was fitted with a rubber septum and CH_3CN (296 mL, 0.05 M) was added via syringe under an atmosphere of nitrogen. After degassing by N_2 bubbling at room temperature for 20 min, the reaction mixture was then irradiated at room temperature with two 3 W green LEDs for 6 h. Upon the completion of the reaction as determined by TLC, the reaction mixture was concentrated on a rotary evaporator. The resulting residue was directly purified by flash column chromatography on silica gel (hexanes/EtOAc = 3:1) to afford 6-quinolinecarboxylate (**3a**, 2.66 g, 96%) as a white solid.

Di-*tert*-butyl 2,6-Dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2a)

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

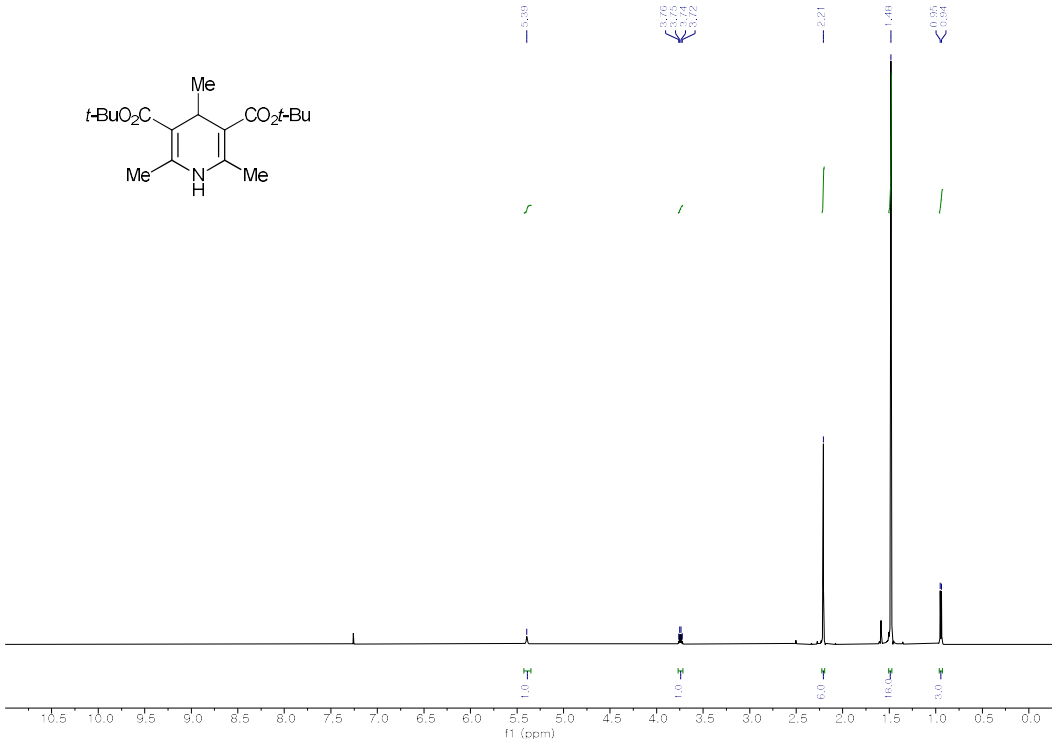


^{13}C NMR (126 MHz, $CDCl_3$)

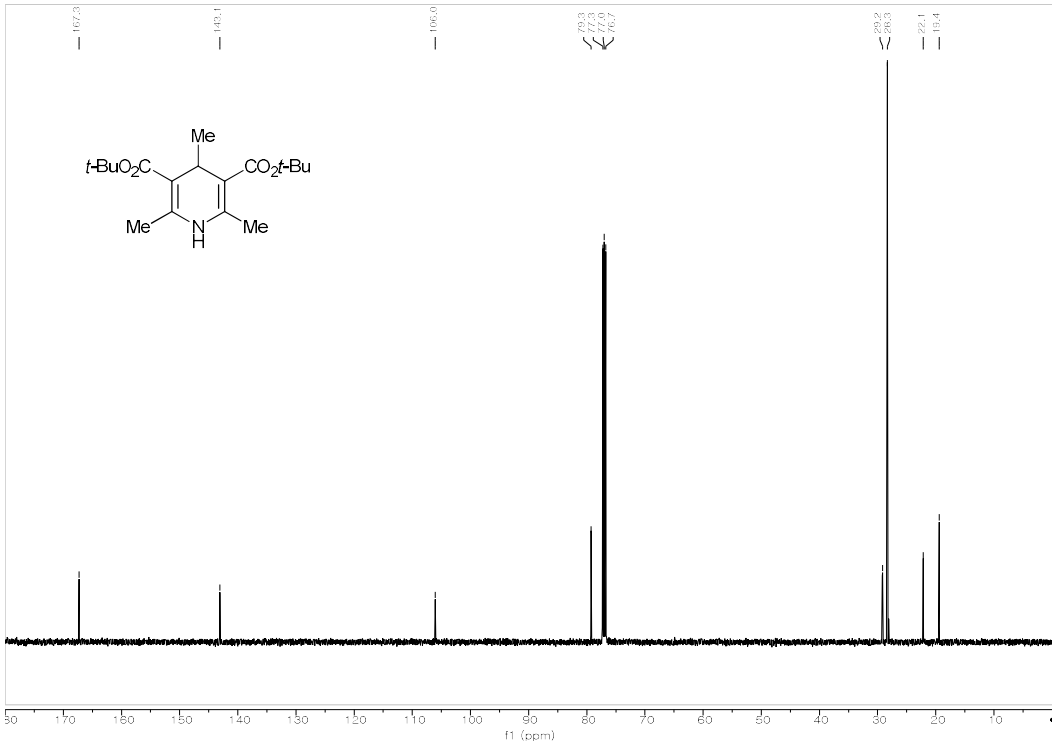


Di-*tert*-butyl 2,4,6-Trimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2b)

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

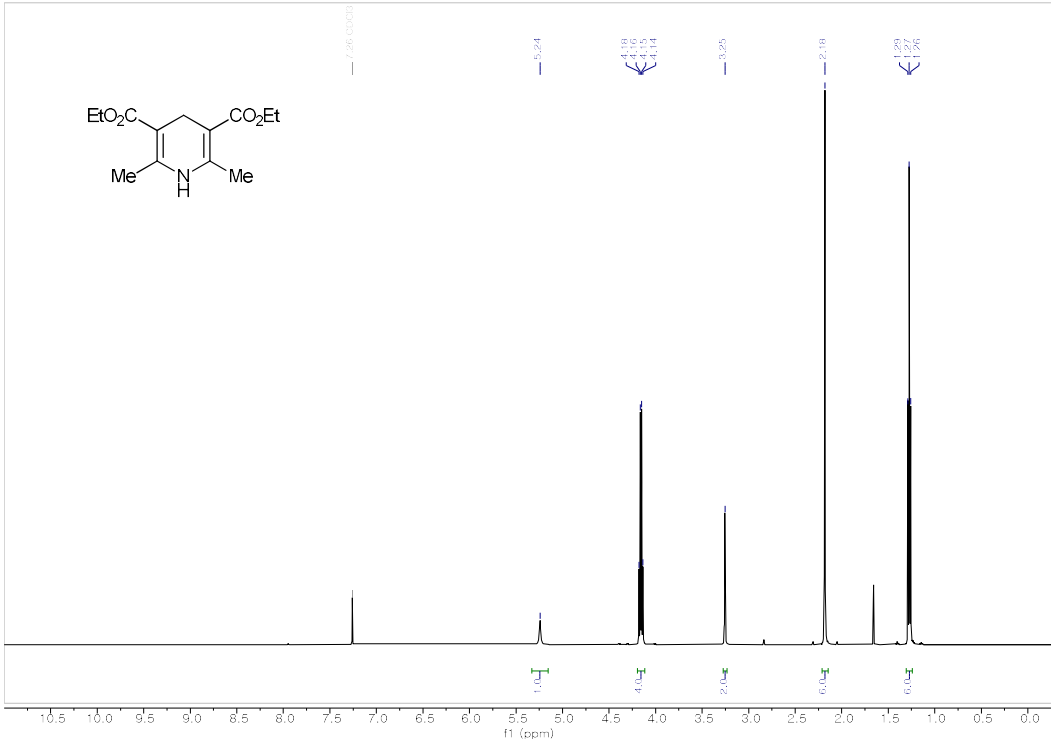


^{13}C NMR (126 MHz, $CDCl_3$)

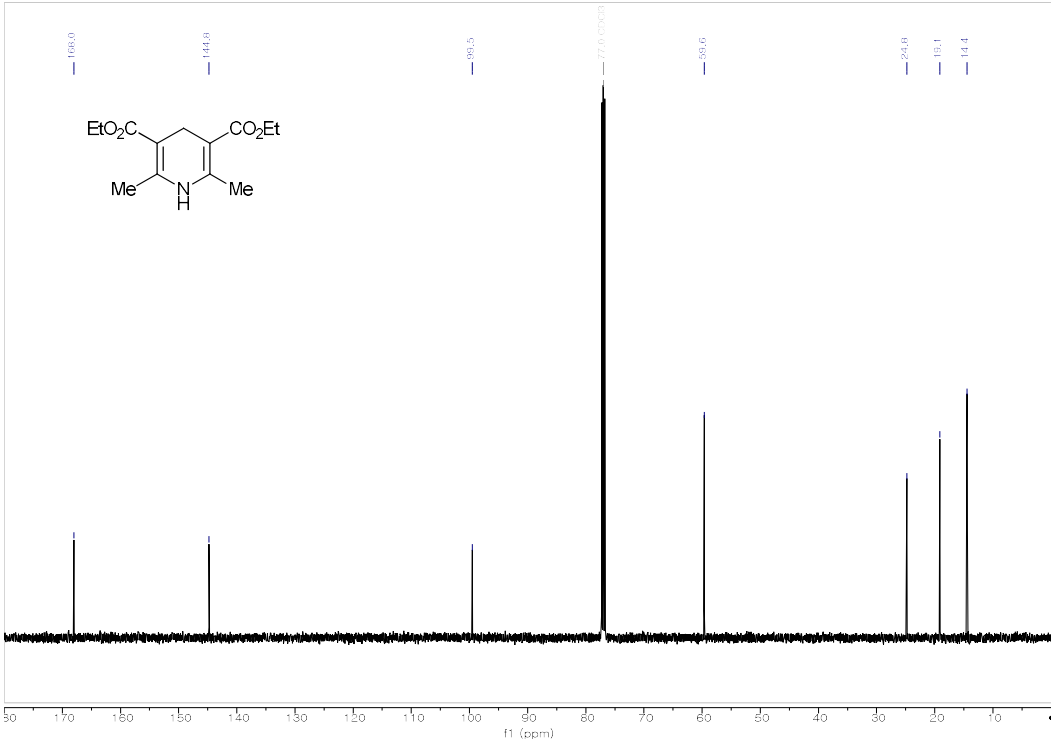


Diethyl 2,6-Dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2c)

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

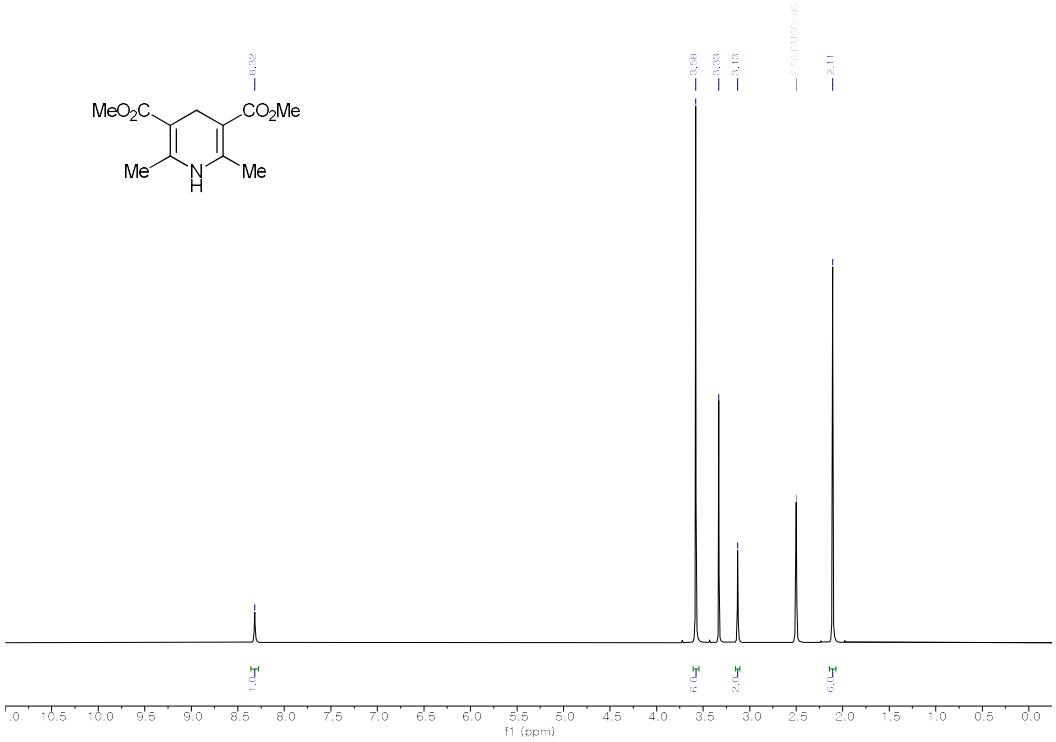


^{13}C NMR (126 MHz, $CDCl_3$)

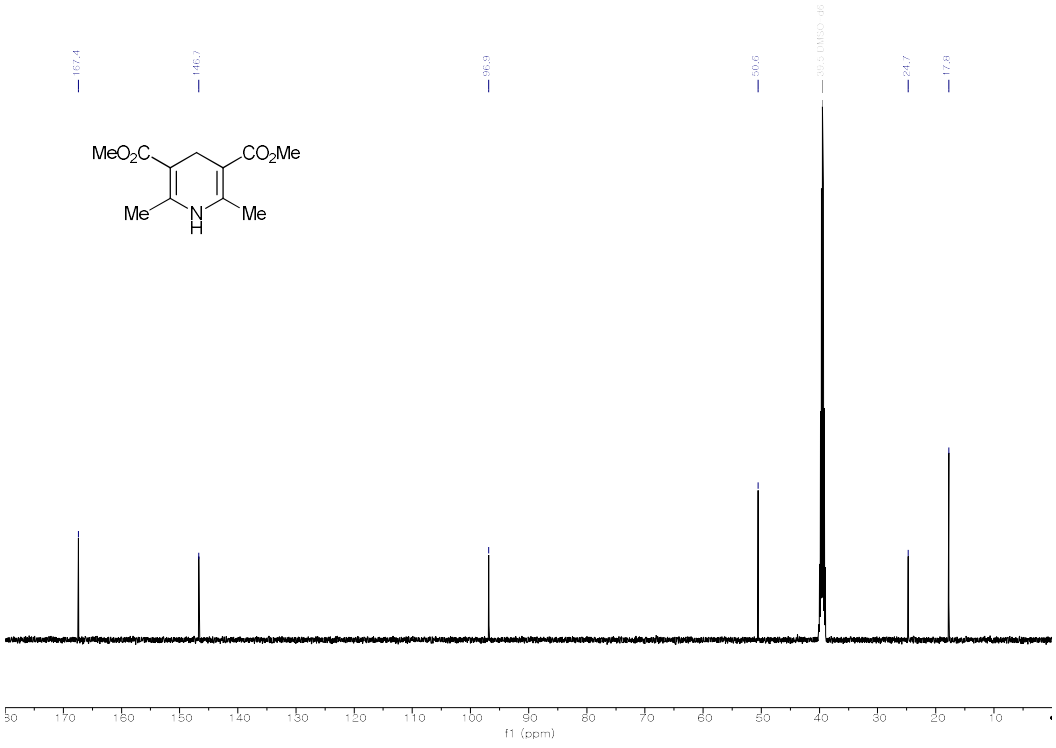


Dimethyl 2,6-Dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2d)

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

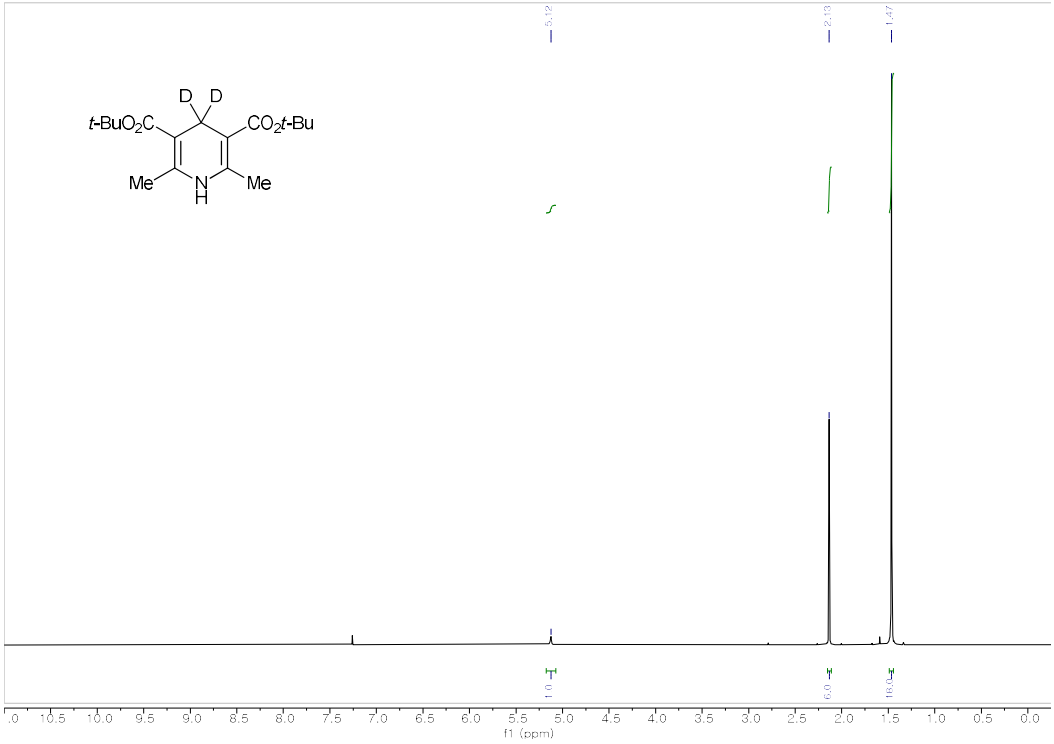


^{13}C NMR (126 MHz, $CDCl_3$)

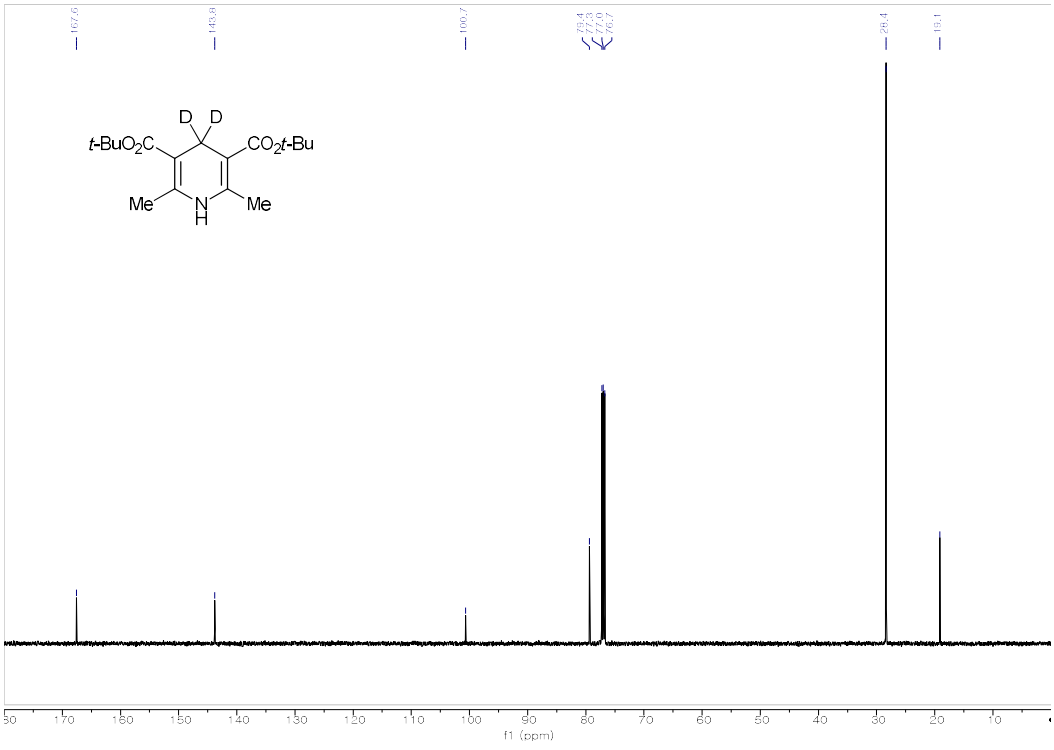


Di-*tert*-butyl 4-Deuterio-2,6-dimethyl-1,4-dihydro-4-deuteriopyridine-3,5-dicarboxylate (2a-d_2)

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

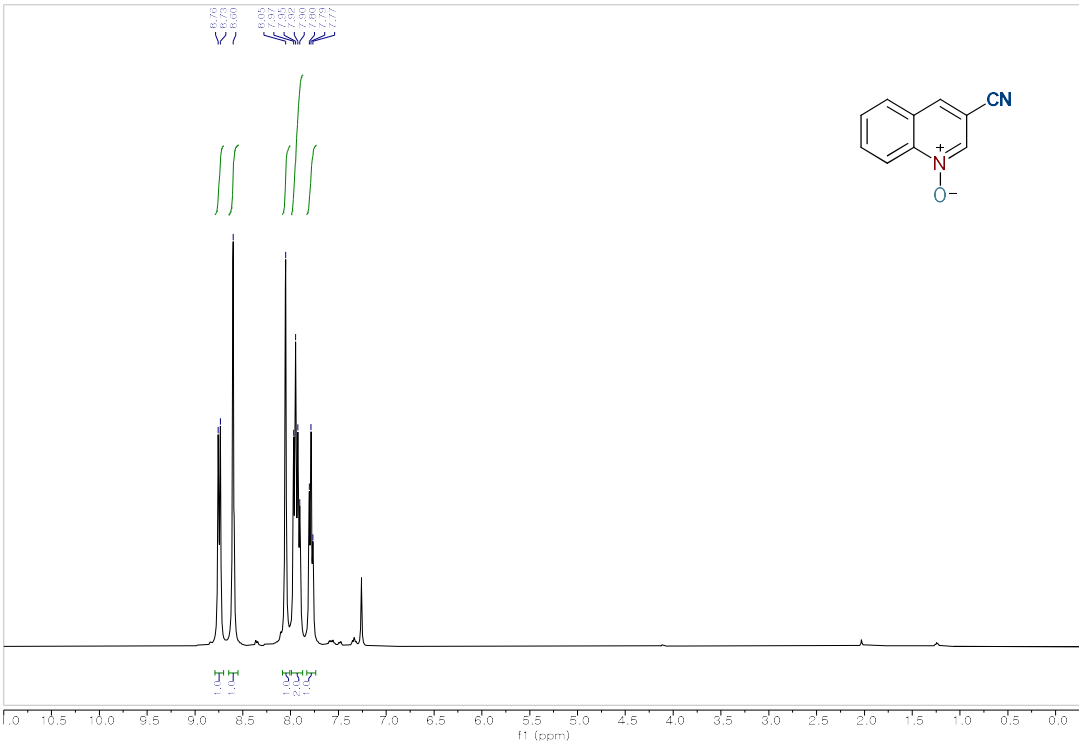


^{13}C NMR (126 MHz, $CDCl_3$)

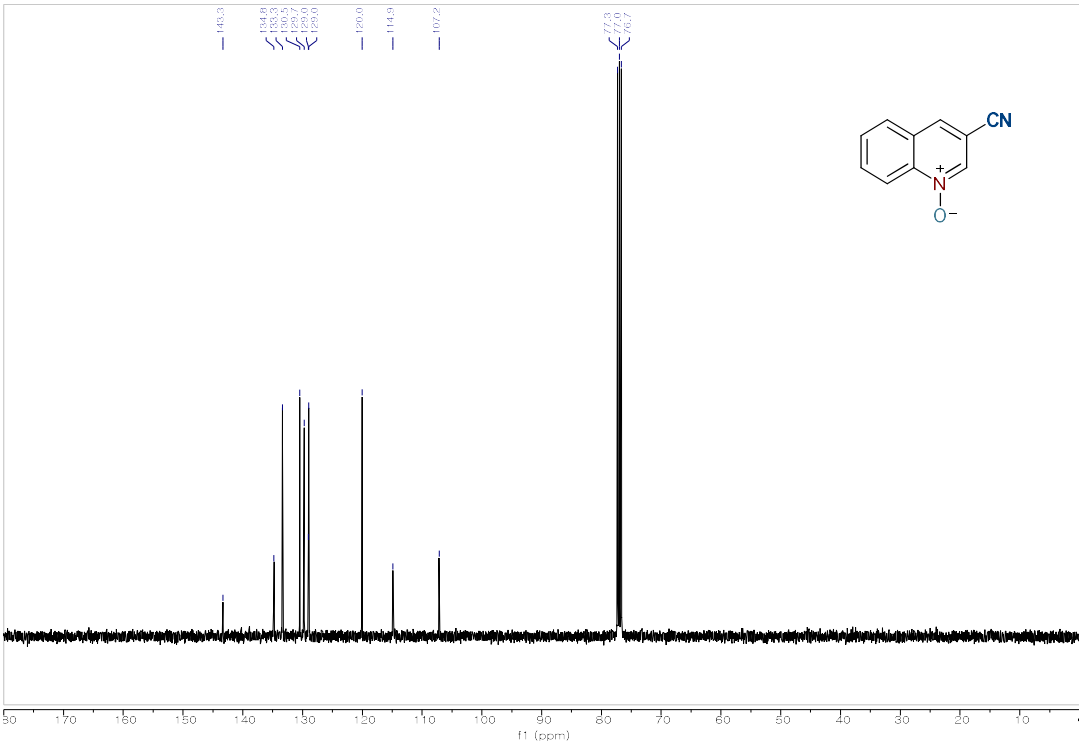


3-Quinolinecarbonitrile *N*-Oxide (1a)

^{1}H NMR (400 MHz, $CDCl_3$)

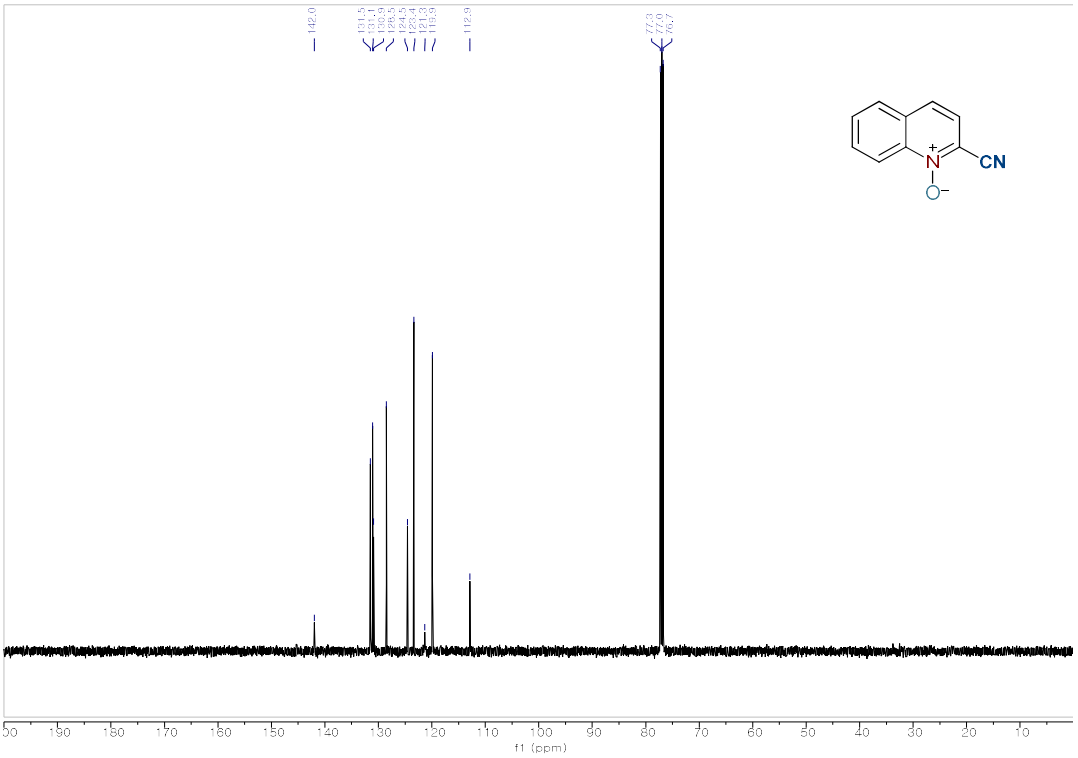


^{13}C NMR (101 MHz, $CDCl_3$)

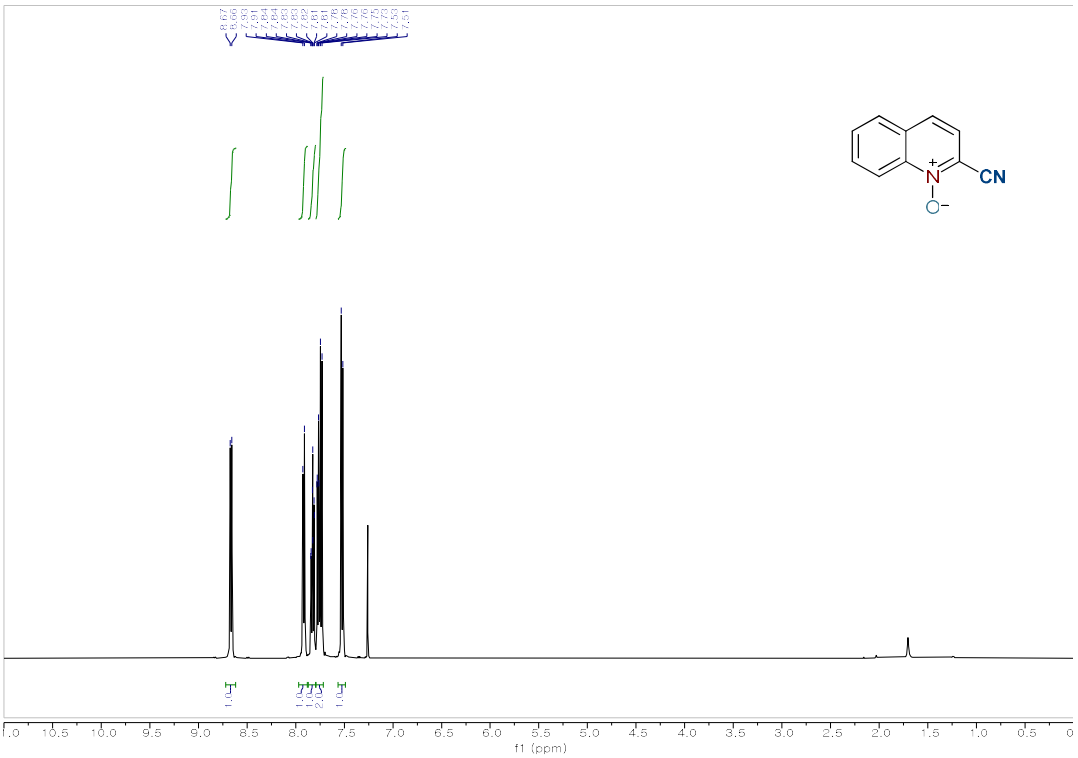


3-Quinolinecarbonitrile *N*-Oxide (1b)

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

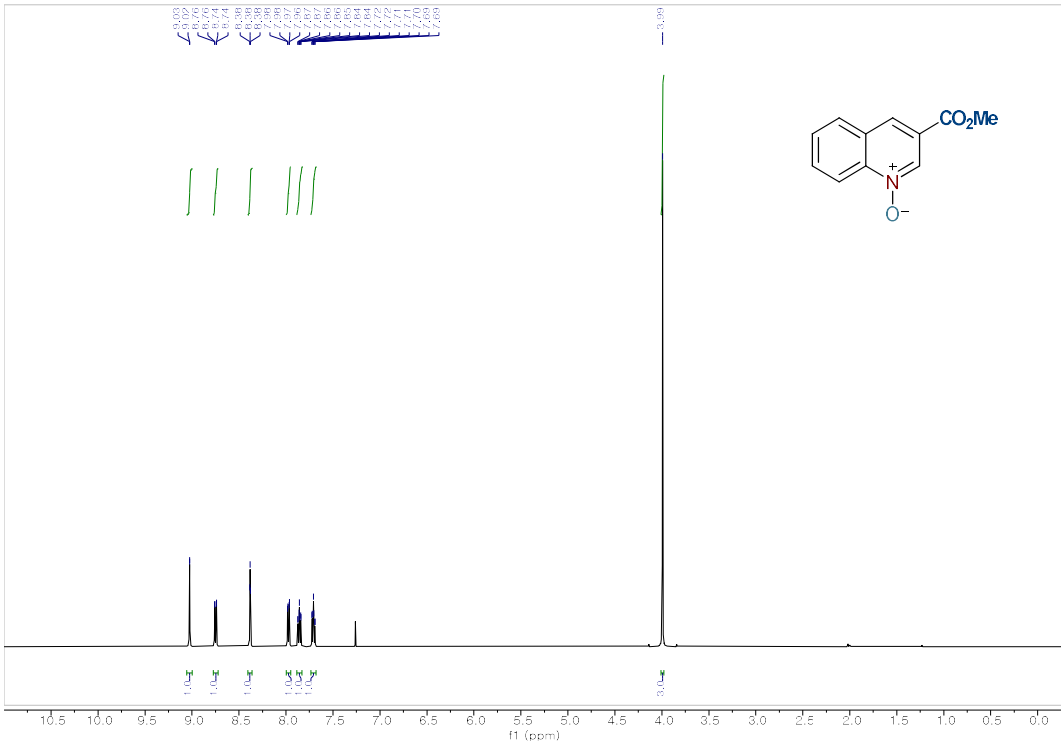


^{13}C NMR (126 MHz, $CDCl_3$)

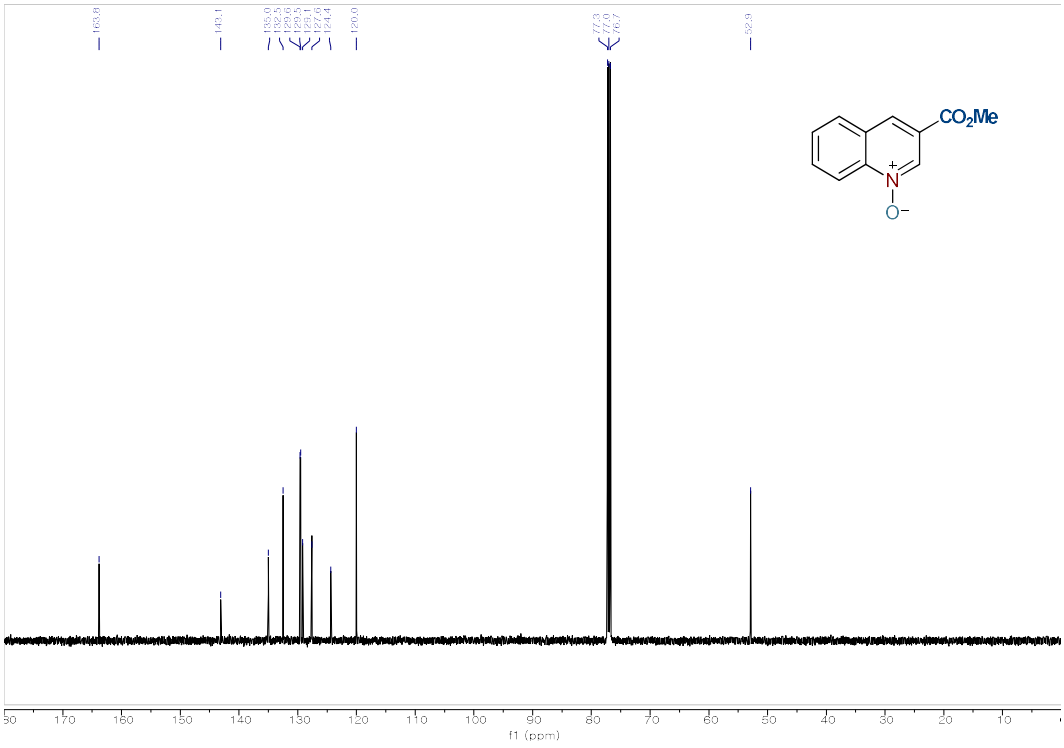


Methyl 3-Quinolinecarboxylate *N*-Oxide (1c)

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

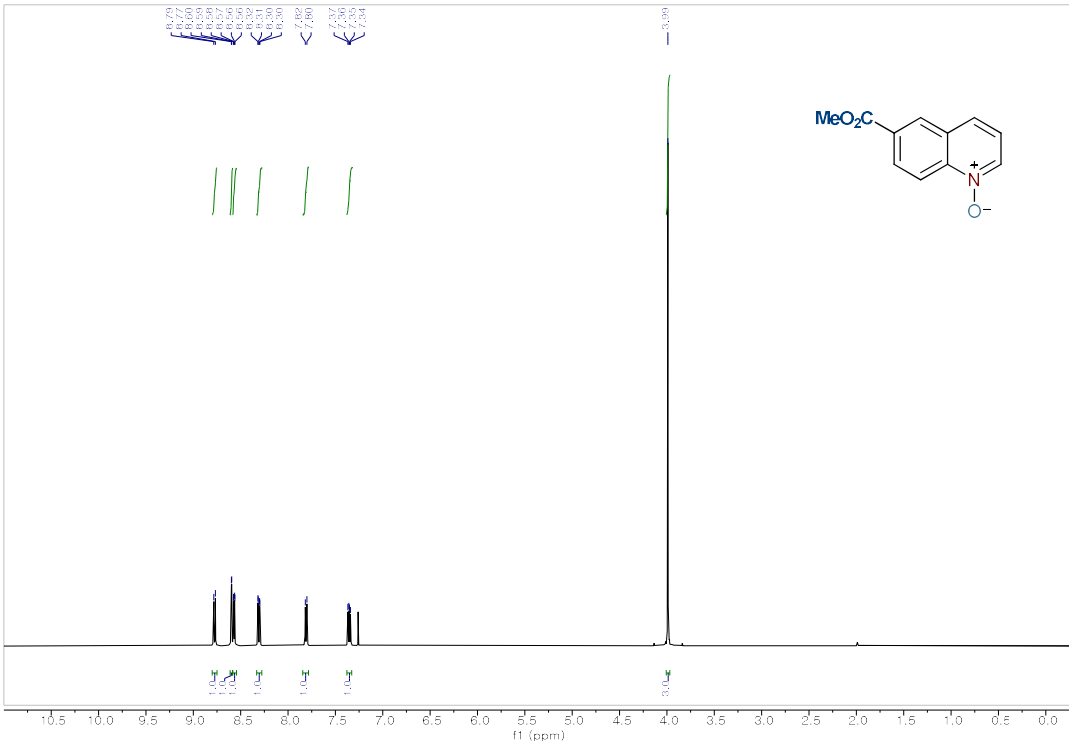


^{13}C NMR (126 MHz, $CDCl_3$)

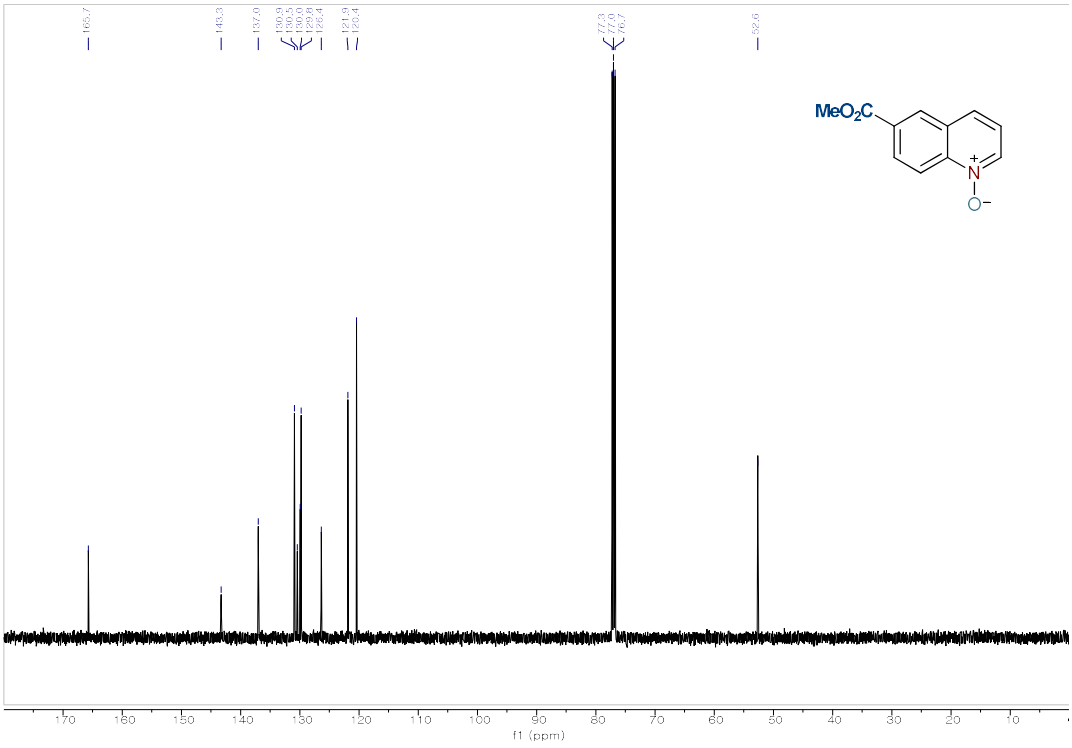


Methyl 6-Quinolinecarboxylate *N*-Oxide (1d)

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

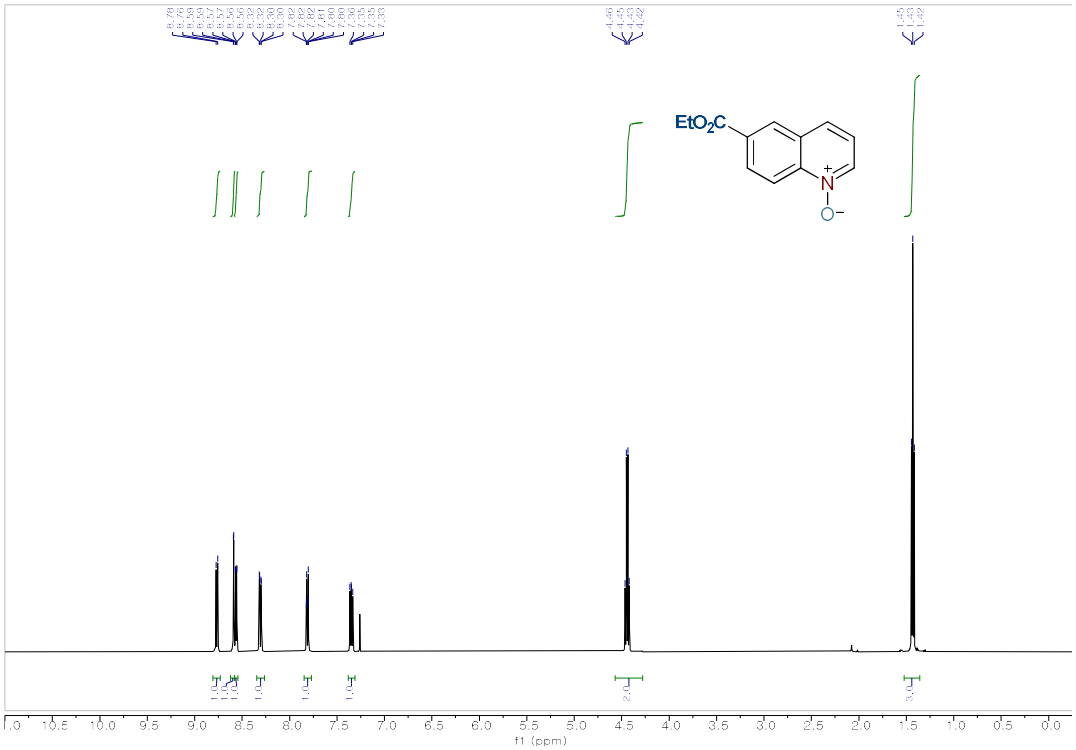


^{13}C NMR (126 MHz, $CDCl_3$)

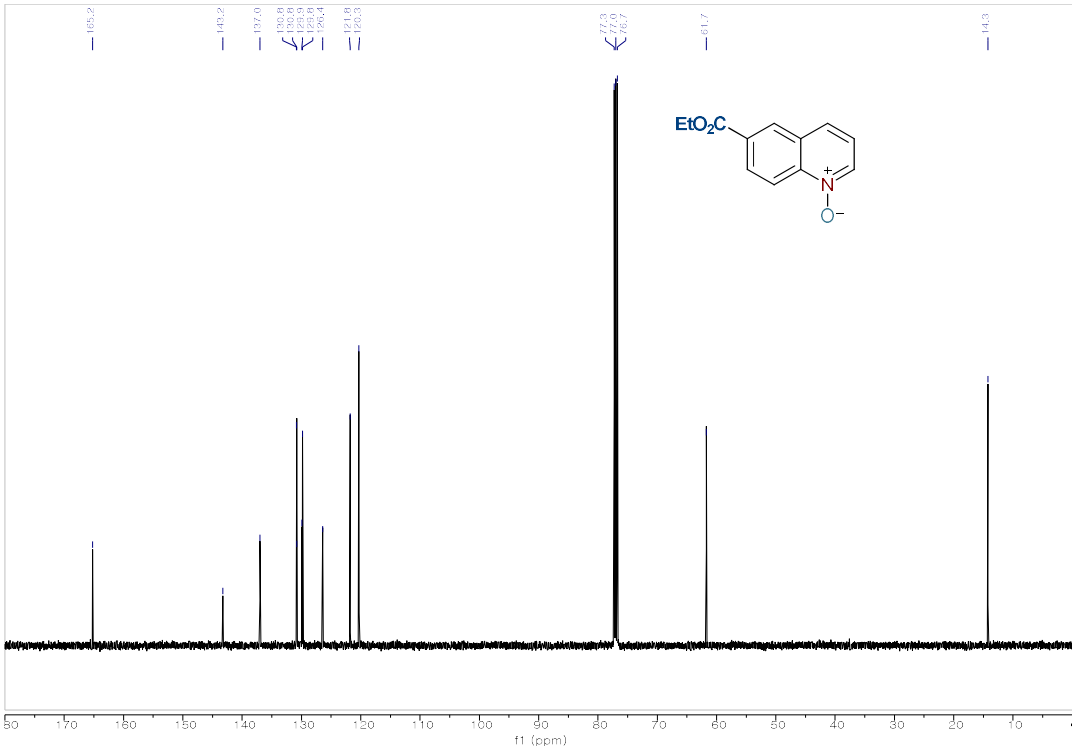


Ethyl 6-Quinolinecarboxylate *N*-Oxide (1e)

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

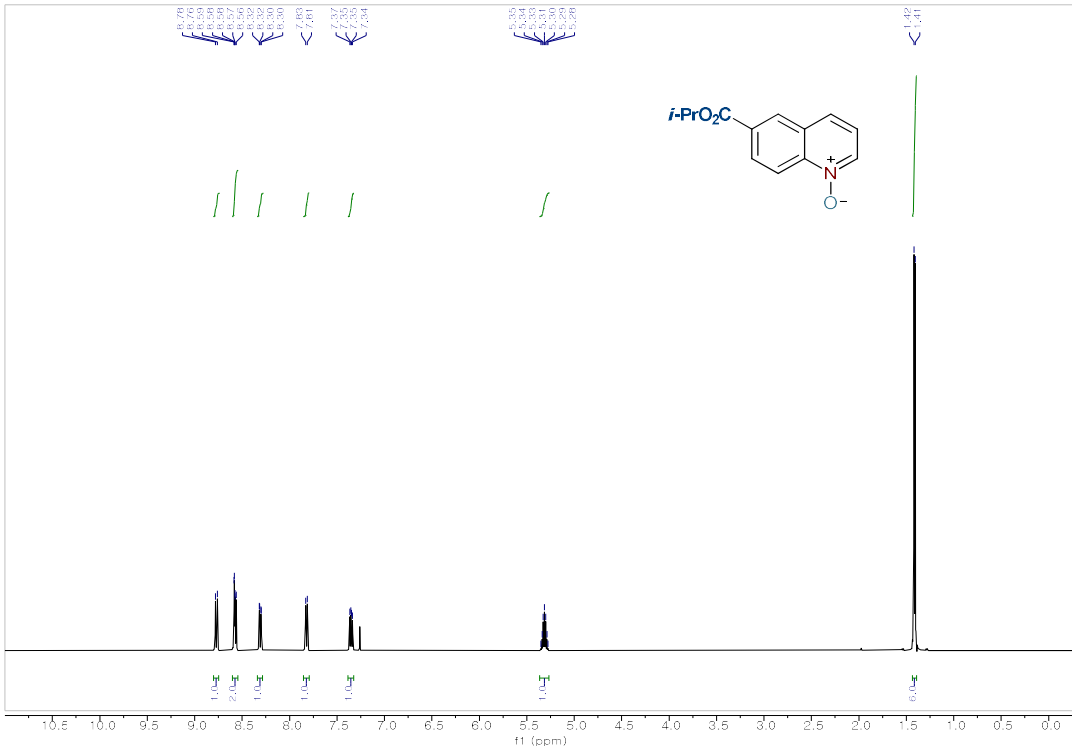


^{13}C NMR (126 MHz, $CDCl_3$)

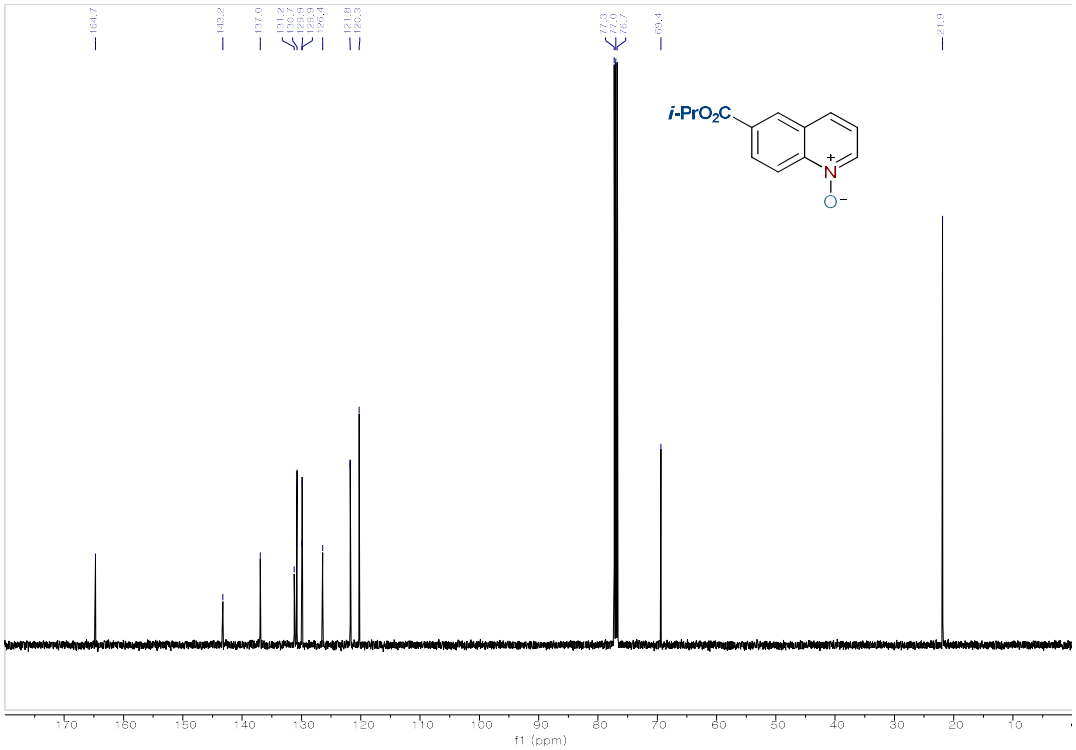


Isopropyl 6-Quinolinecarboxylate *N*-Oxide (1f)

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

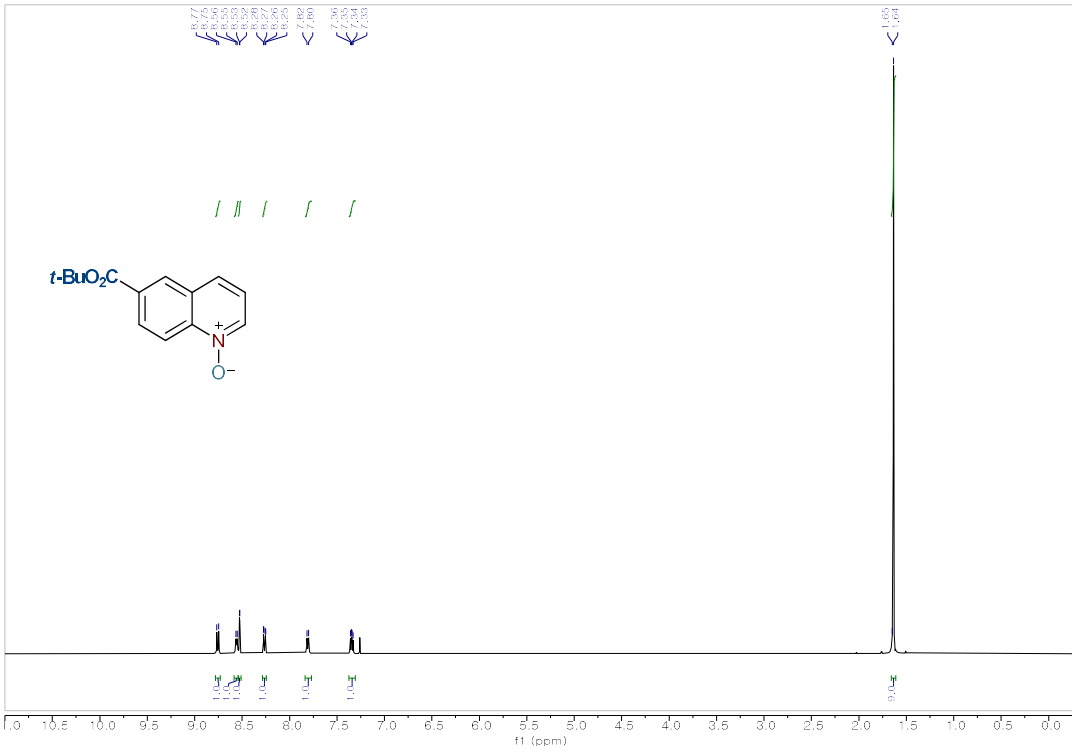


^{13}C NMR (126 MHz, $CDCl_3$)

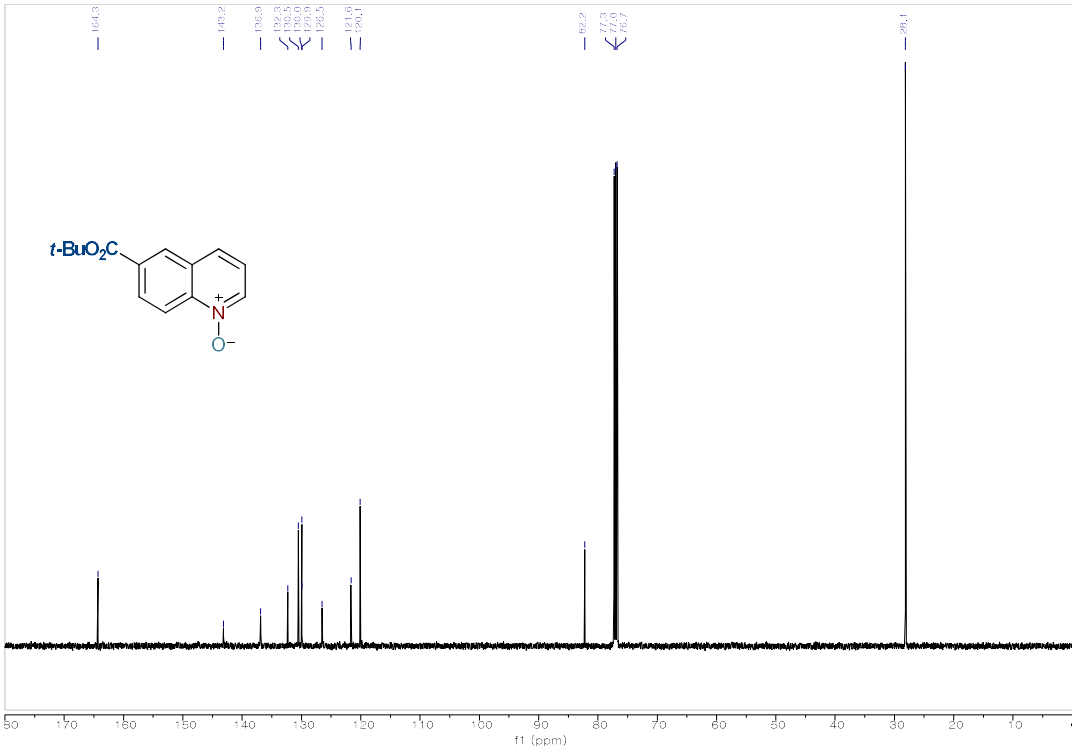


***tert*-Butyl 6-Quinolinecarboxylate *N*-Oxide (1g)**

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

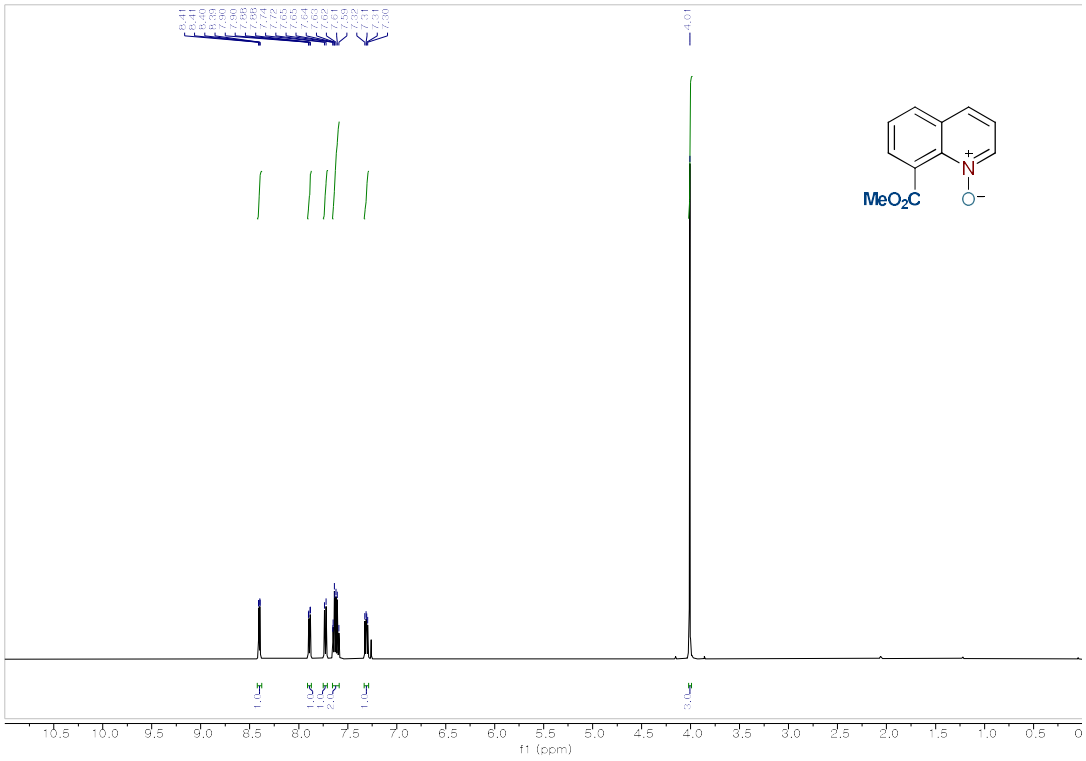


^{13}C NMR (126 MHz, $CDCl_3$)

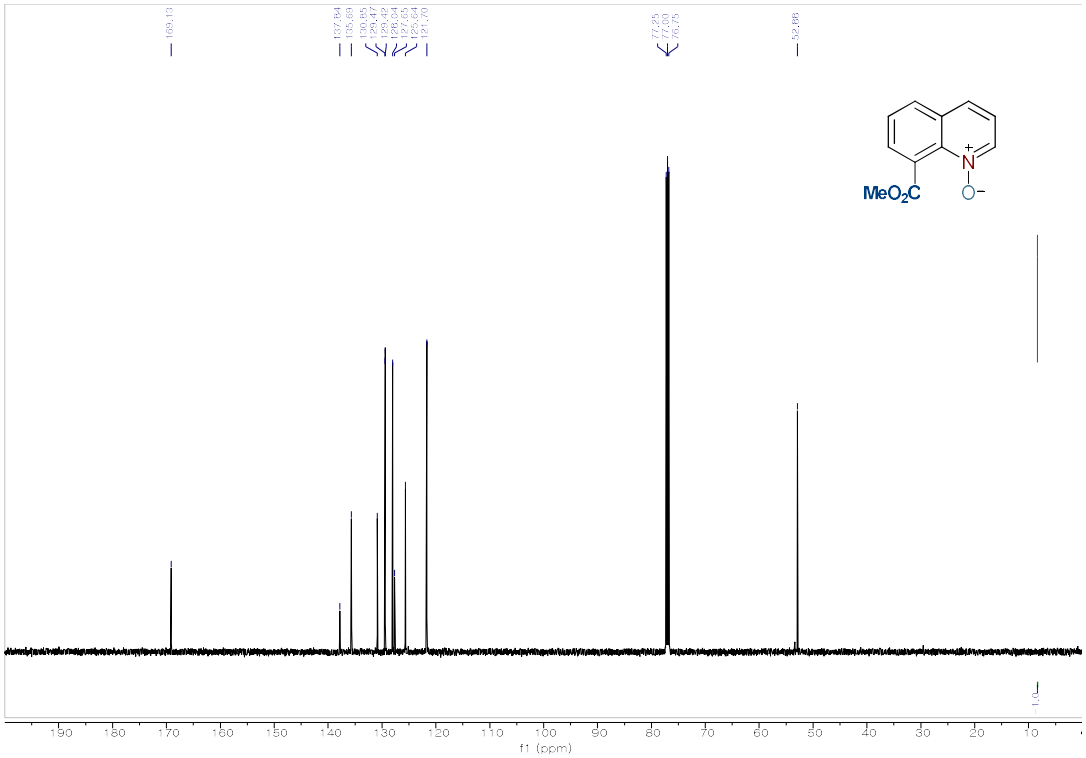


Methyl 8-Quinolinecarboxylate *N*-Oxide (1h)

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

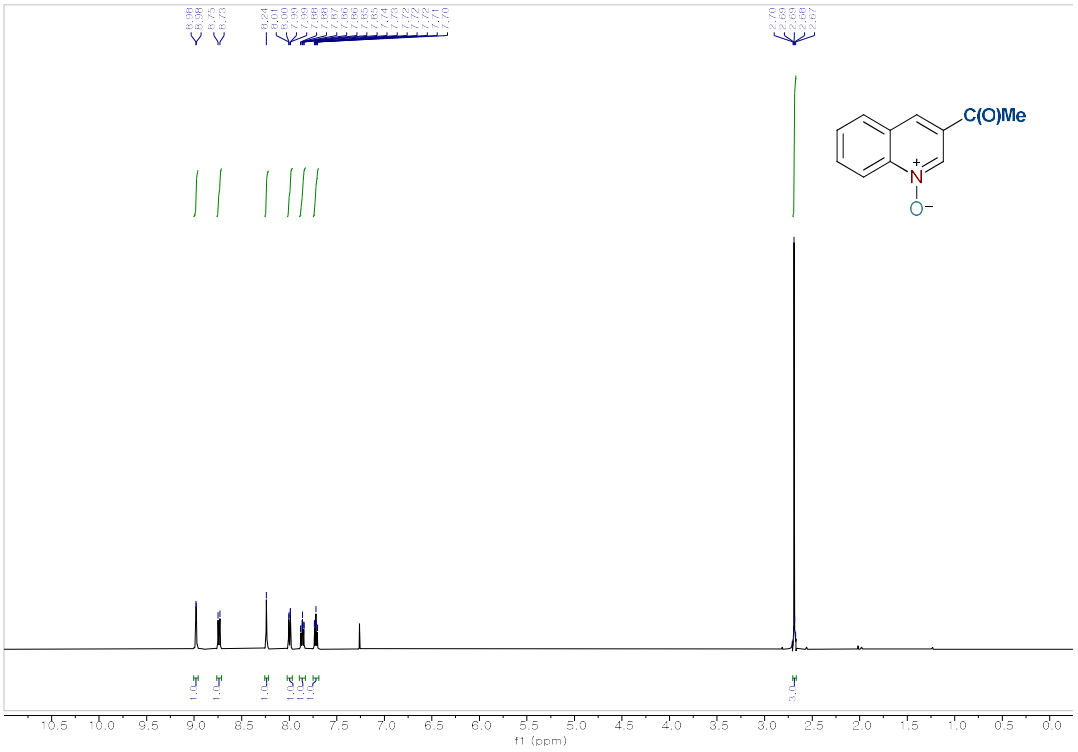


^{13}C NMR (126 MHz, $CDCl_3$)

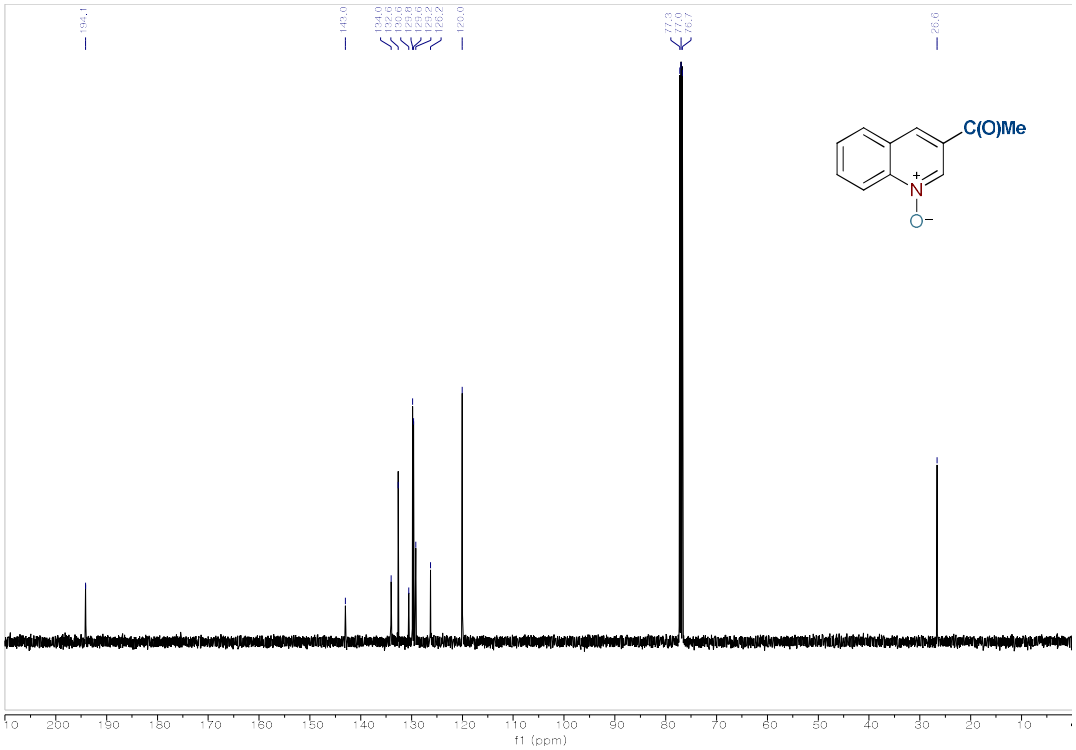


3-Acetylquinoline *N*-Oxide (1i)

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

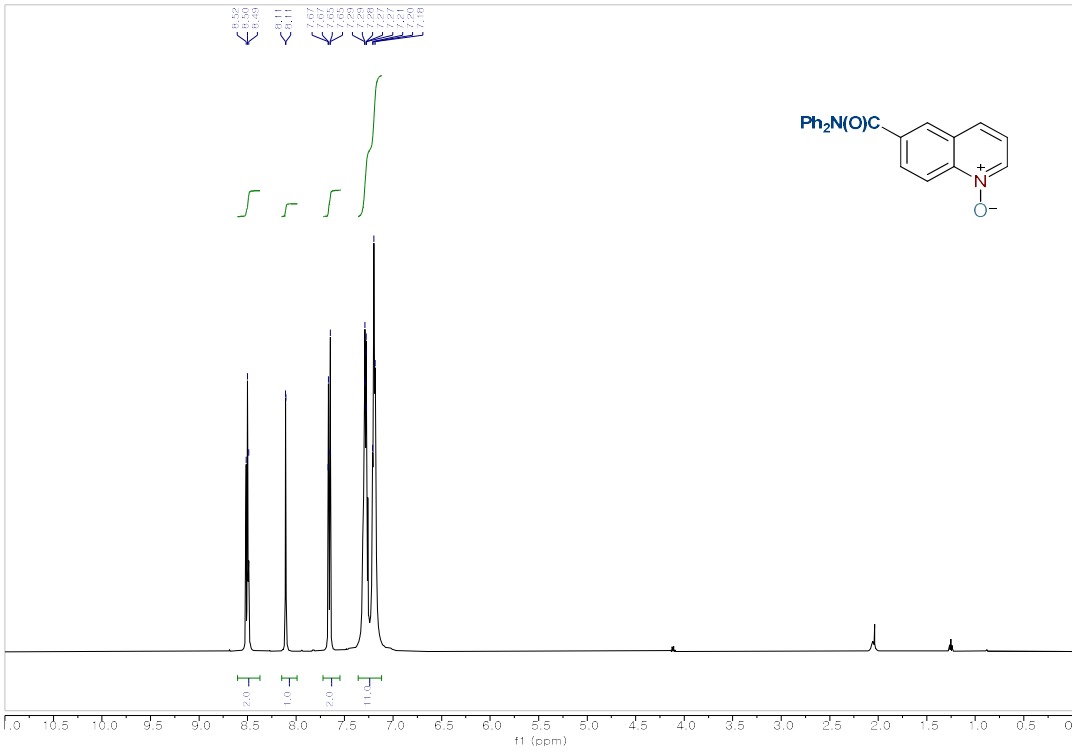


^{13}C NMR (126 MHz, $CDCl_3$)

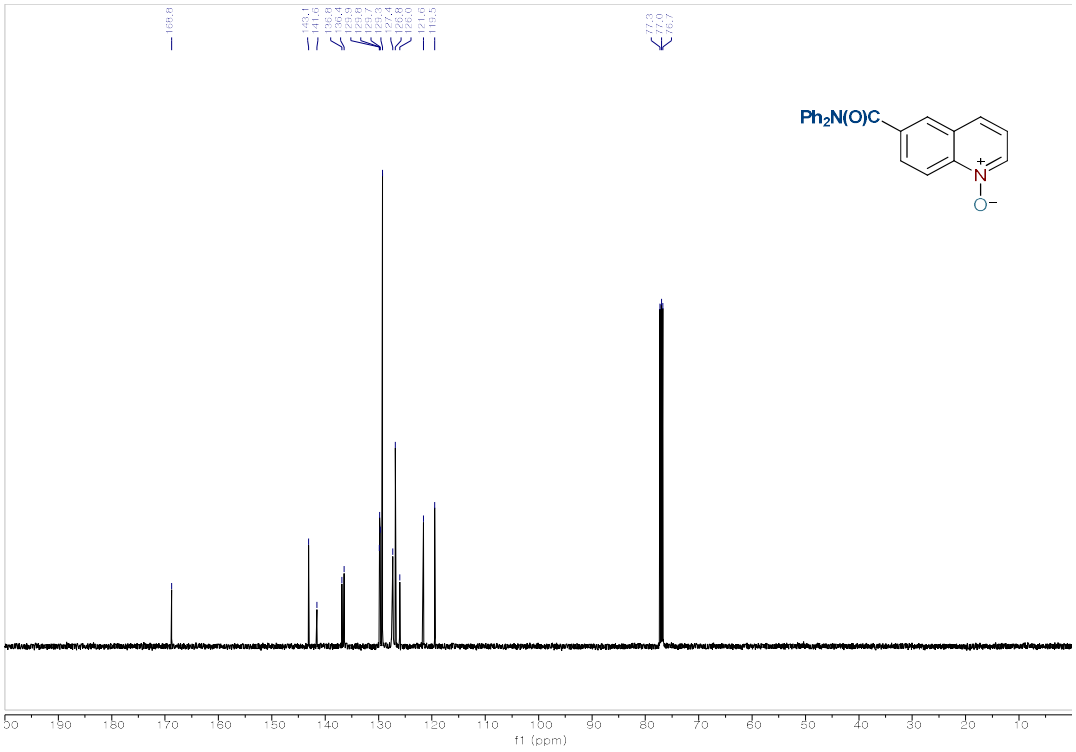


***N,N*-Diphenyl-6-quinolinecarboxamide *N*-Oxide (1j)**

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

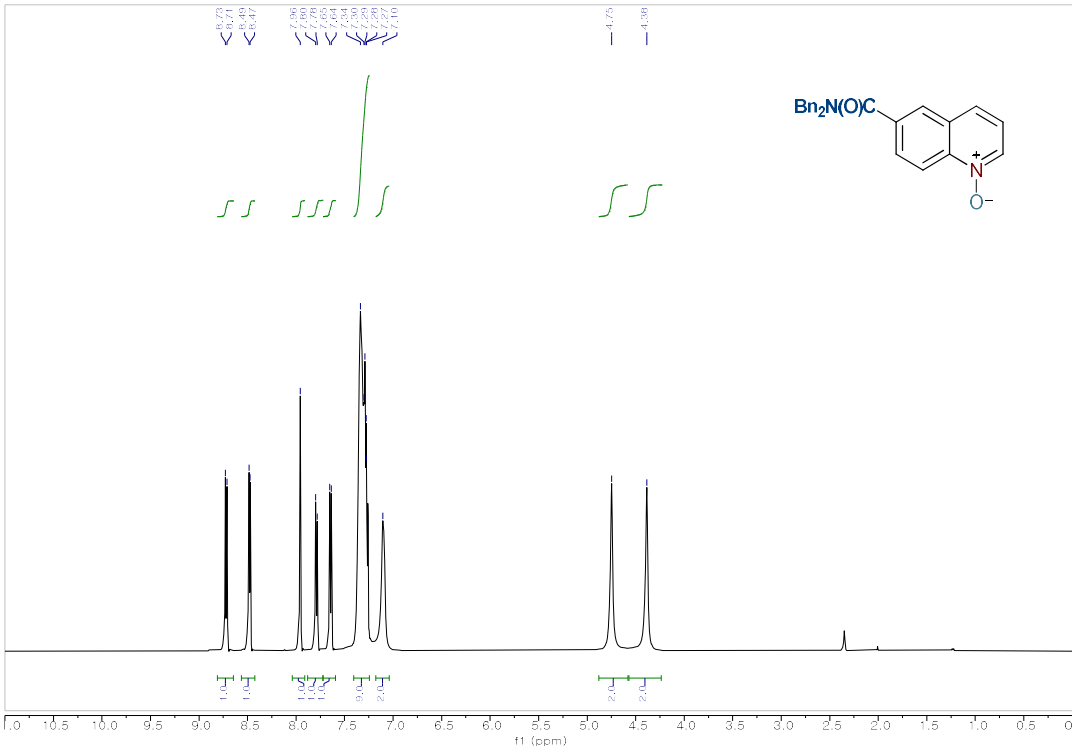


^{13}C NMR (126 MHz, $CDCl_3$)

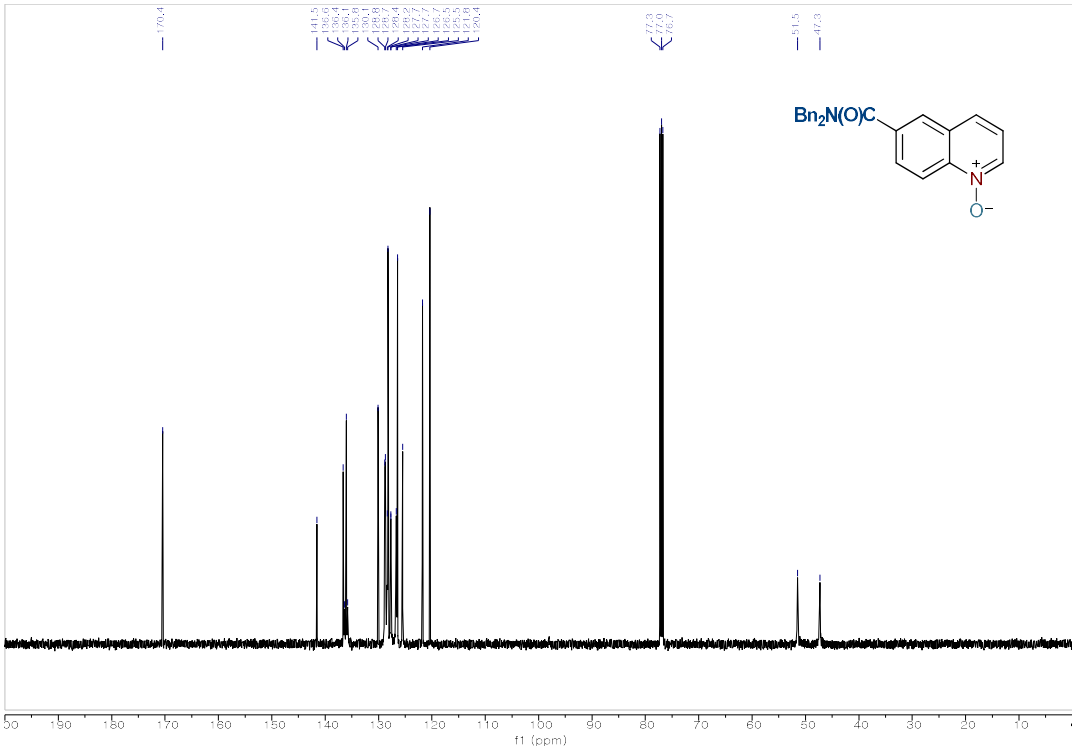


***N,N*-Dibenzyl-6-quinolinecarboxamide *N*-Oxide (1k)**

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

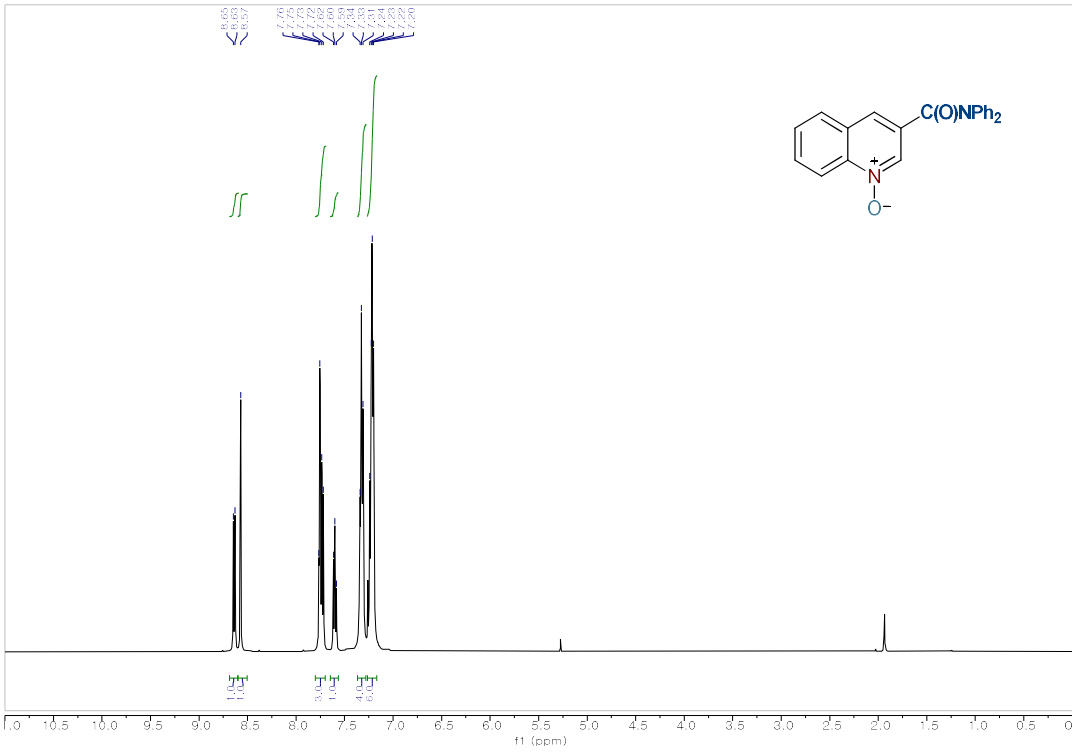


^{13}C NMR (126 MHz, $CDCl_3$)

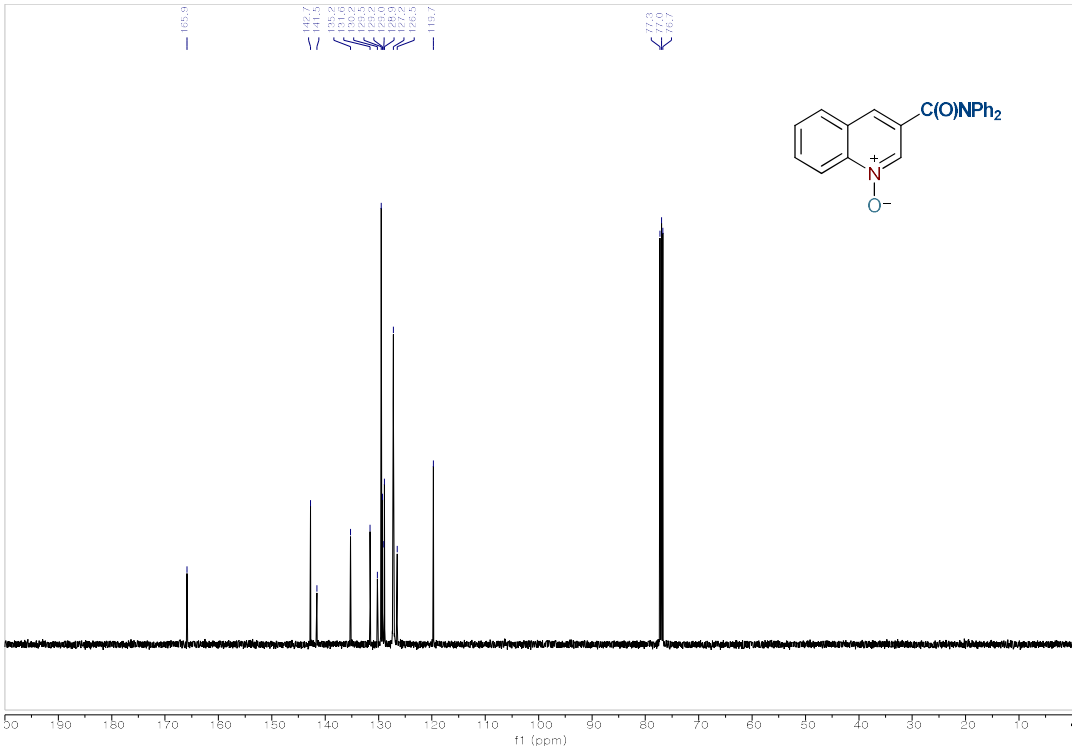


***N,N*-Diphenyl-3-quinolinecarboxamide *N*-Oxide (1l)**

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

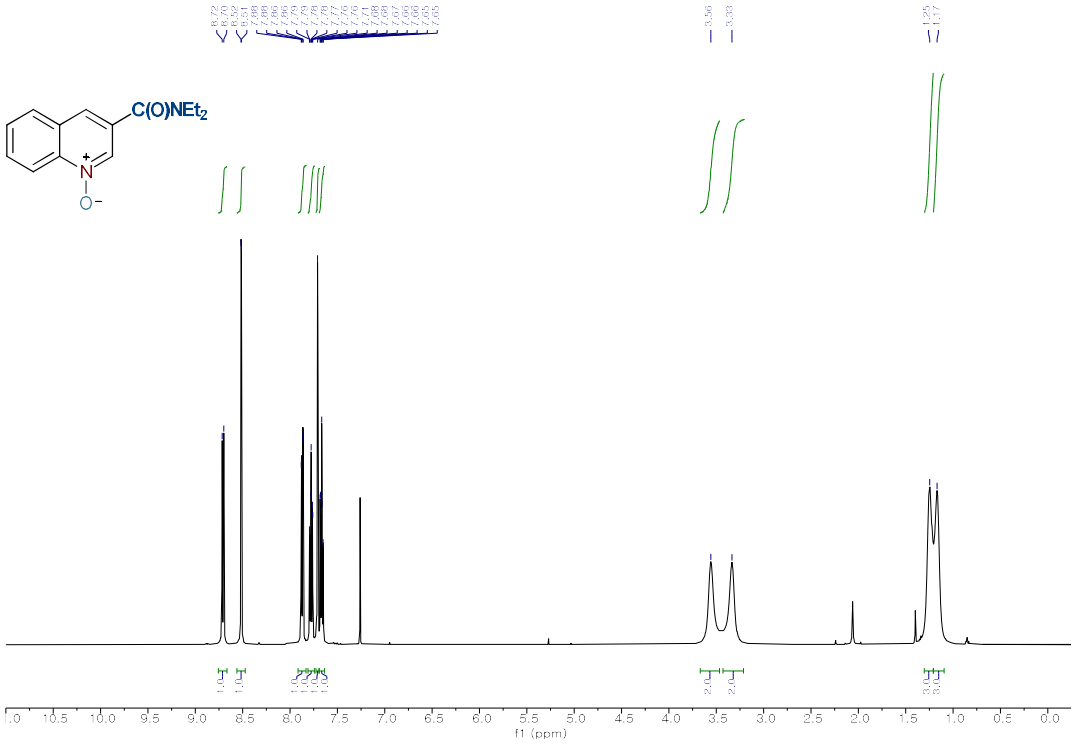


^{13}C NMR (126 MHz, $CDCl_3$)

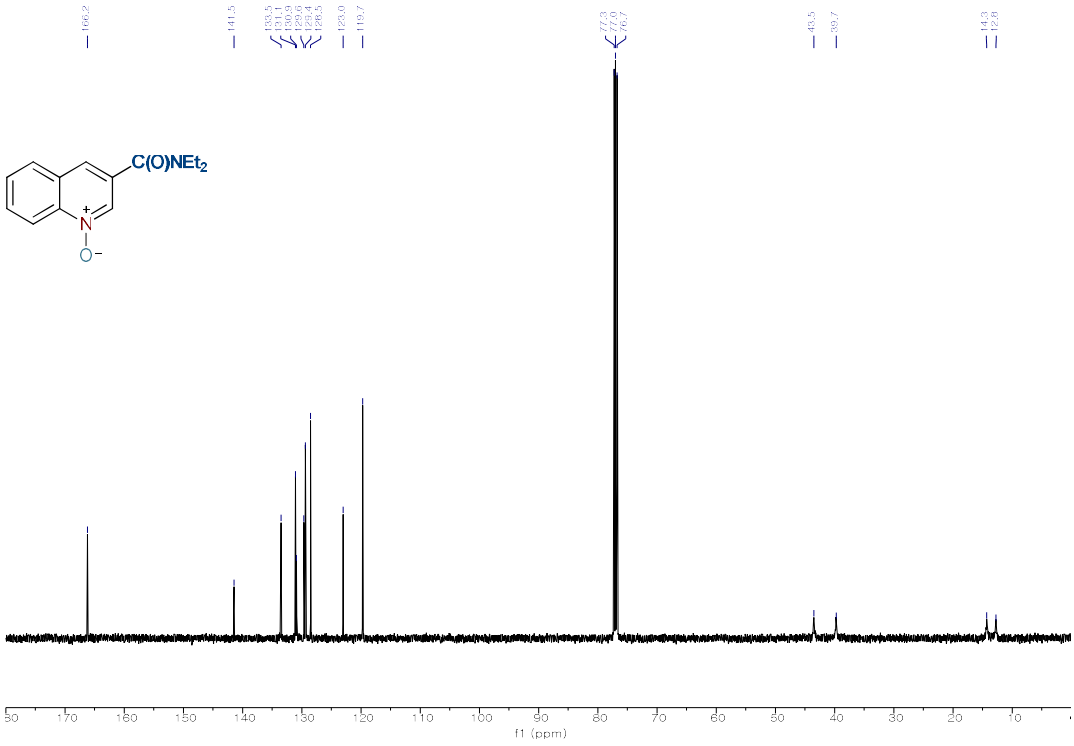


***N*,*N*-Diethyl-3-quinolinecarboxamide *N*-Oxide (1m)**

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

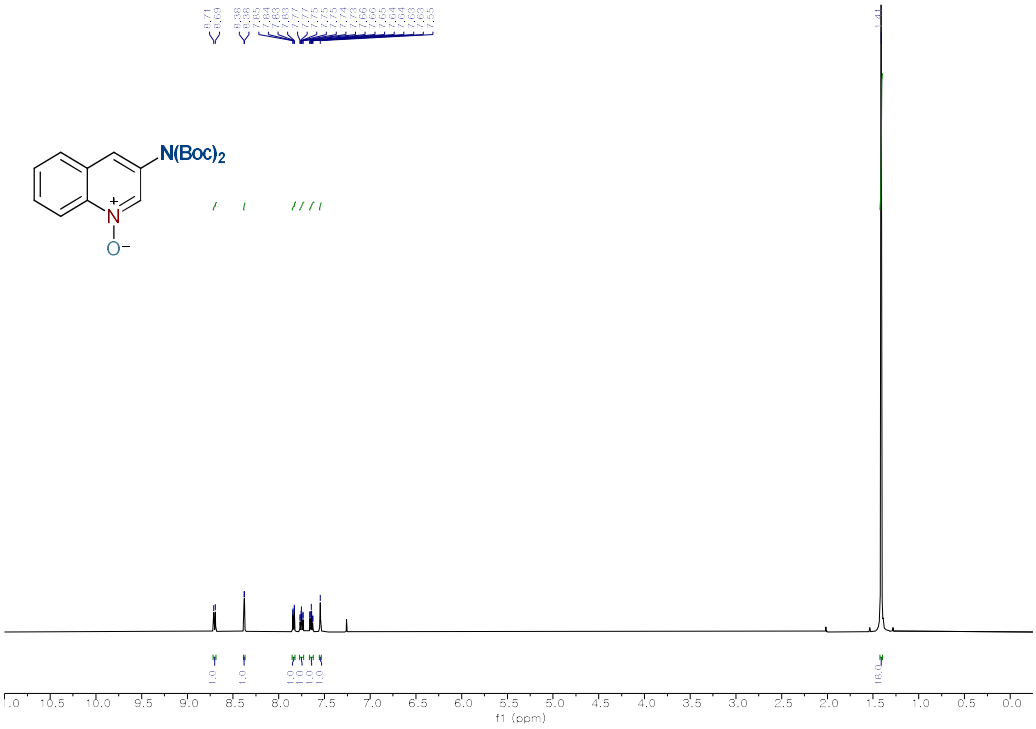


^{13}C NMR (126 MHz, $CDCl_3$)

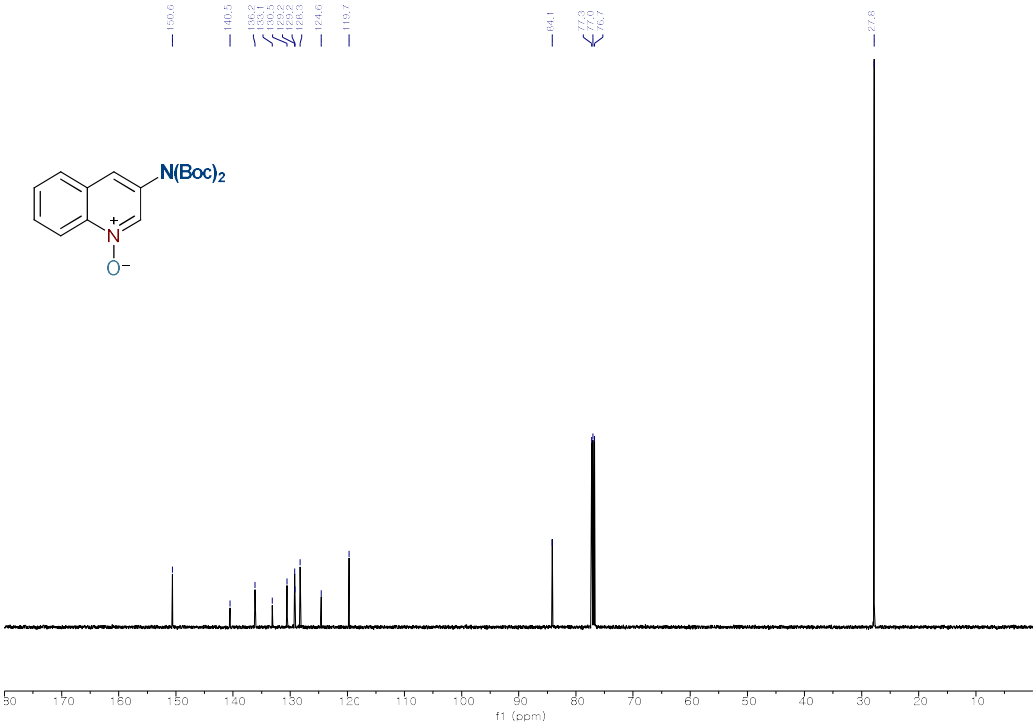


3-[Bis(*tert*-butoxycarbonyl)amino]quinoline *N*-Oxide (1n)

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

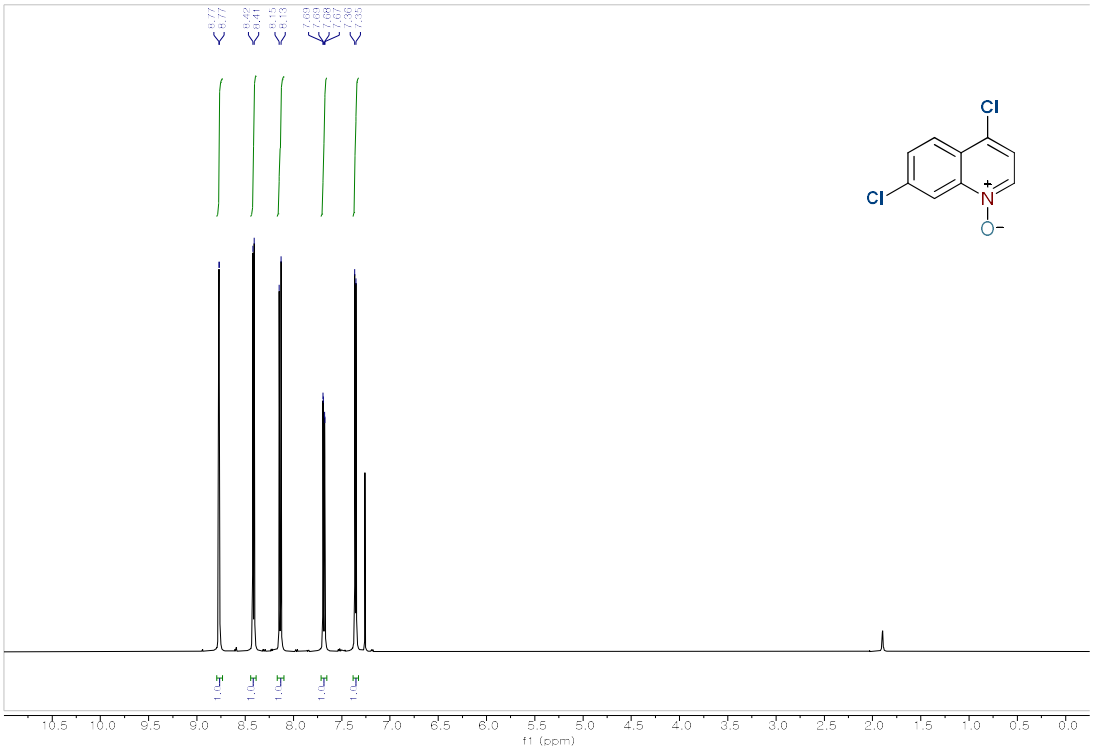


^{13}C NMR (126 MHz, $CDCl_3$)

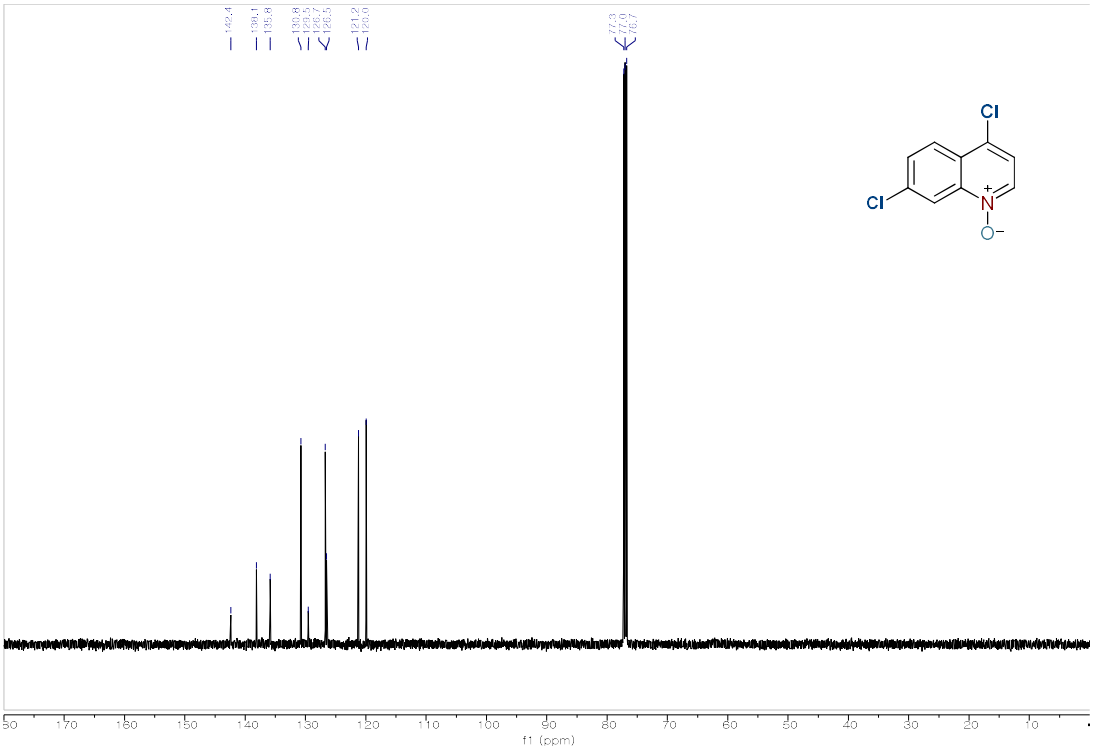


4,7-Dichloroquinoline *N*-Oxide (1o)

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

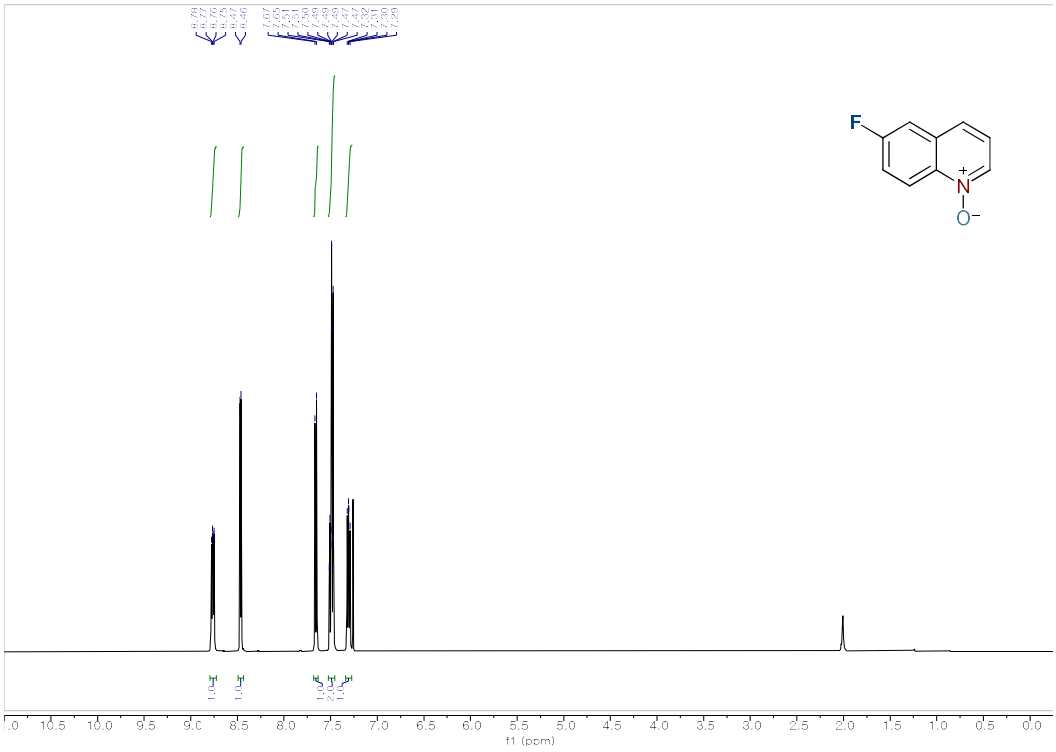


^{13}C NMR (126 MHz, $CDCl_3$)

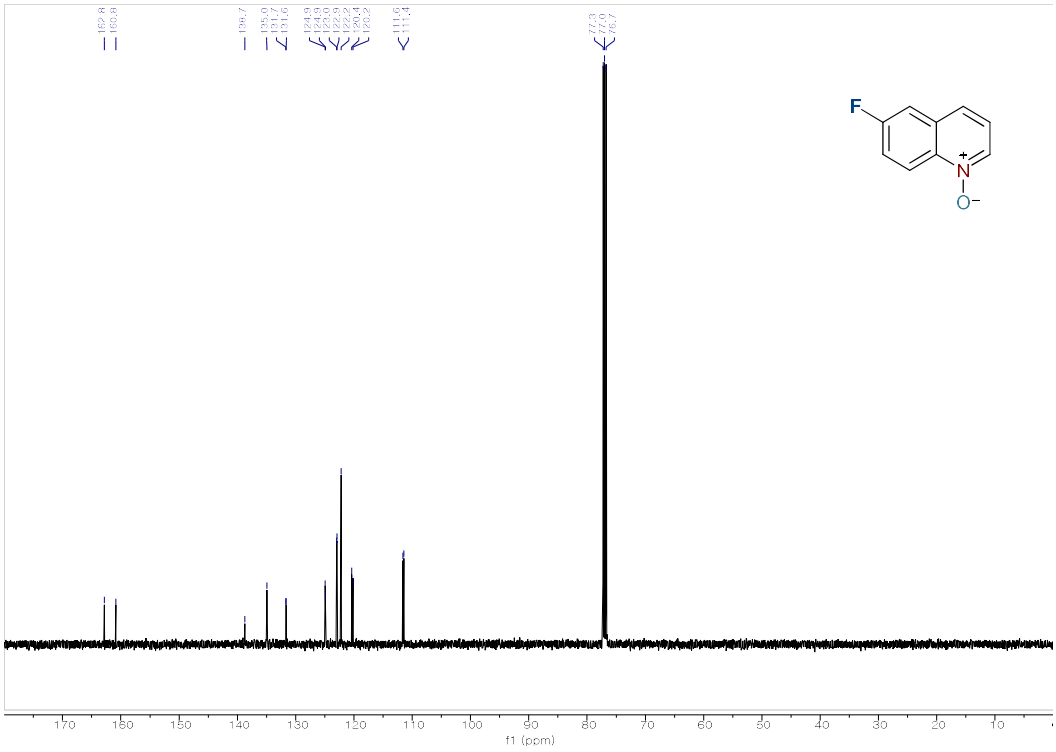


6-Fluoroquinoline *N*-Oxide (1p)

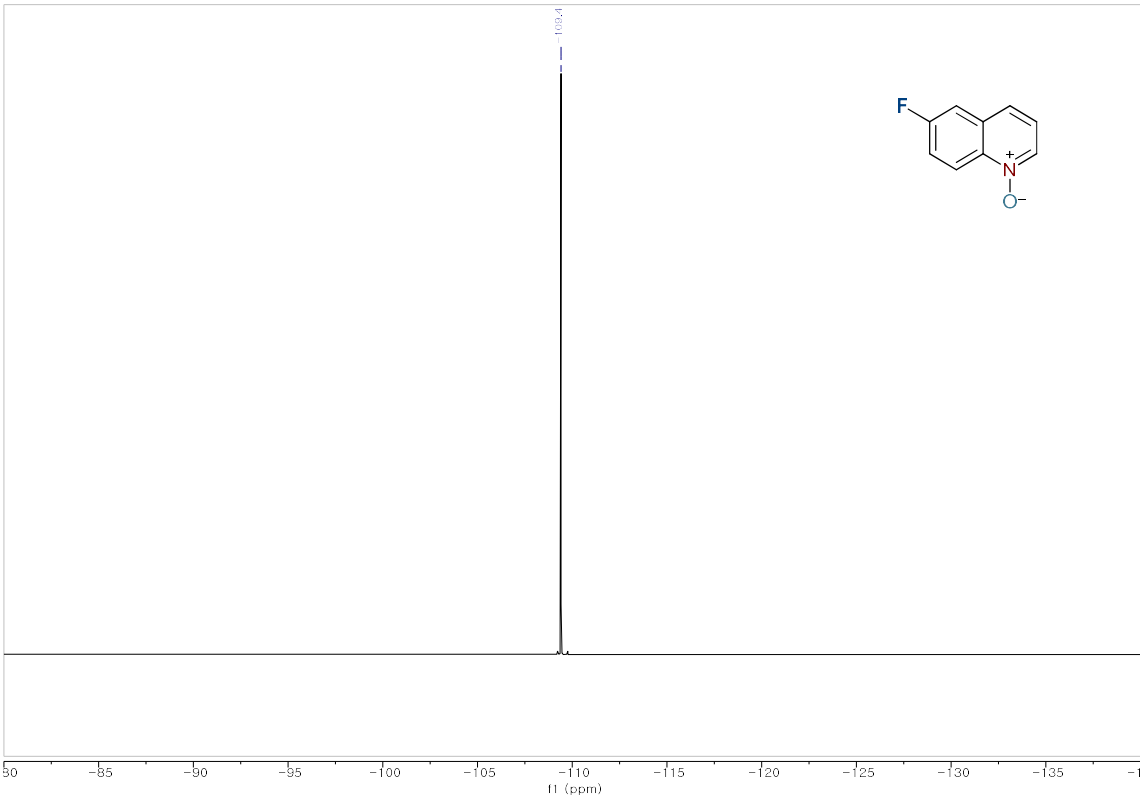
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

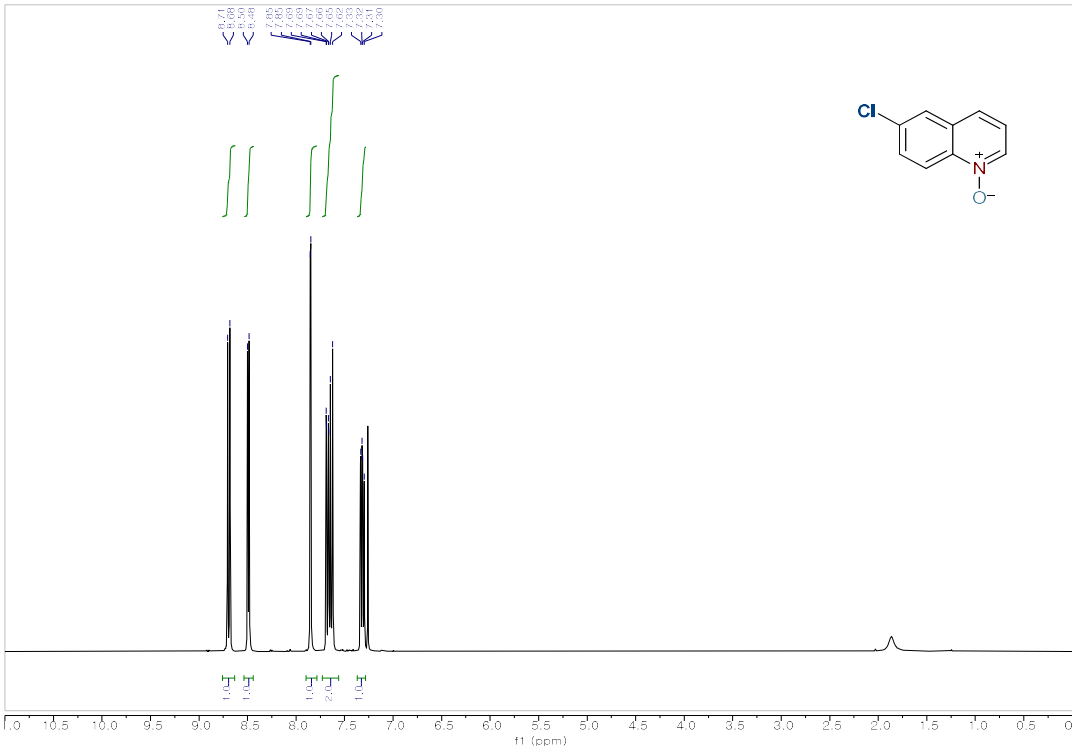


^{19}F NMR (471 MHz, $CDCl_3$)

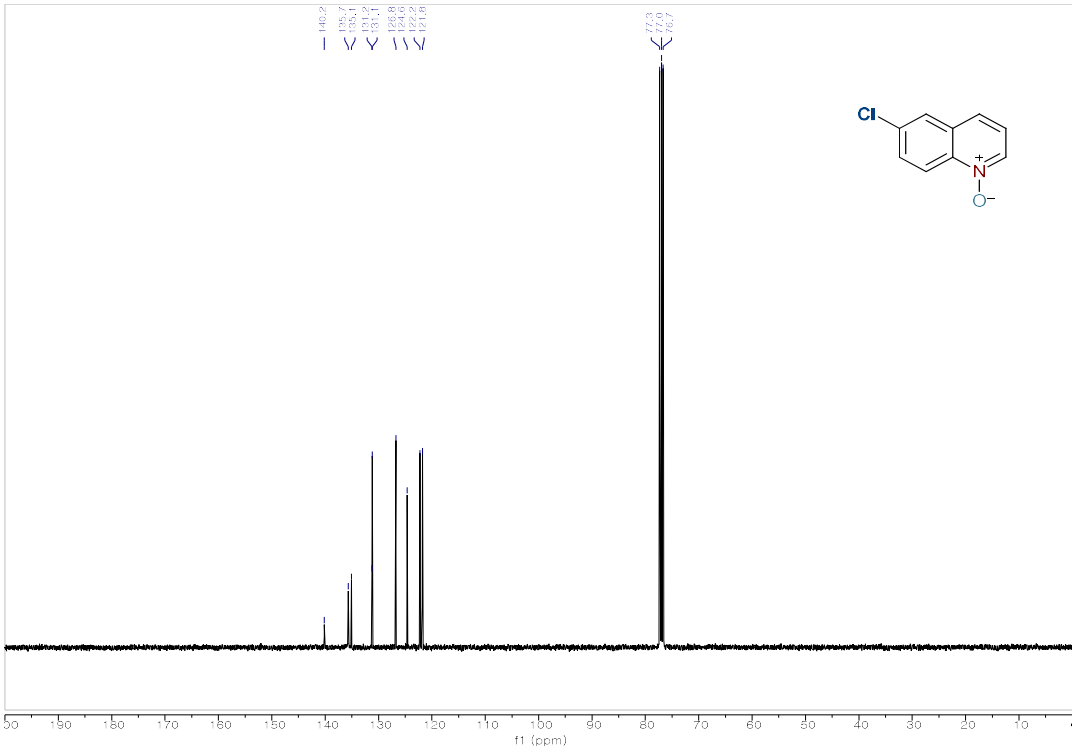


6-Chloroquinoline *N*-Oxide (1q)

^{1}H NMR (400 MHz, $CDCl_3$)

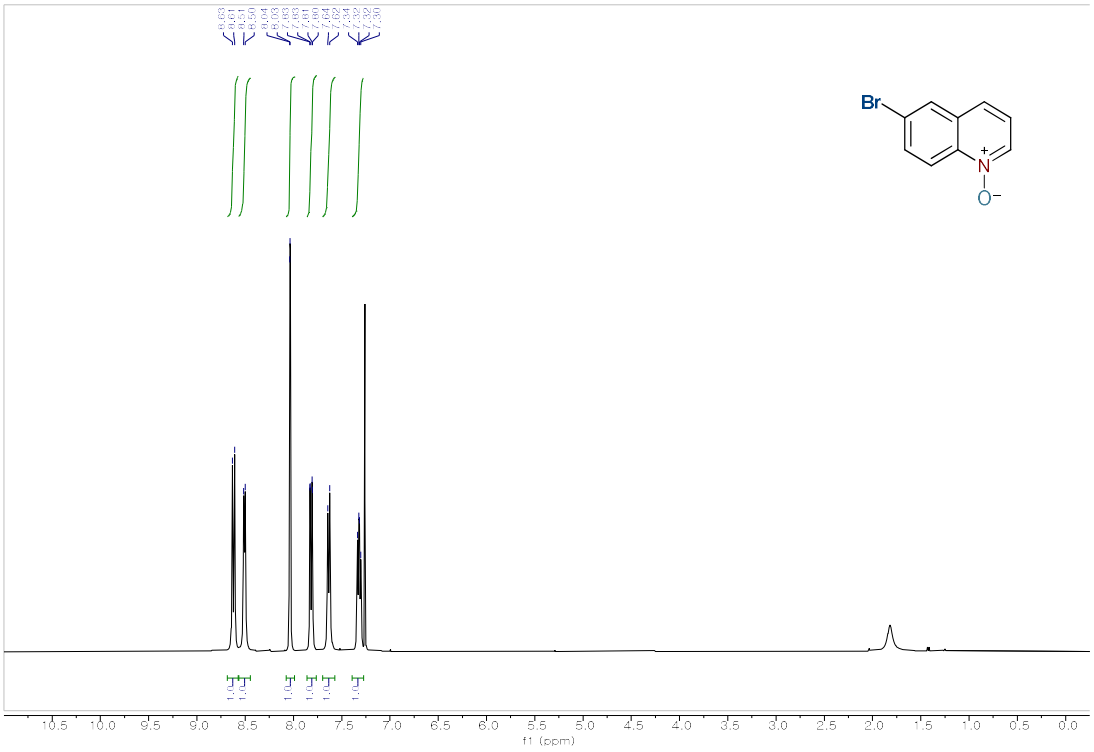


^{13}C NMR (101 MHz, $CDCl_3$)

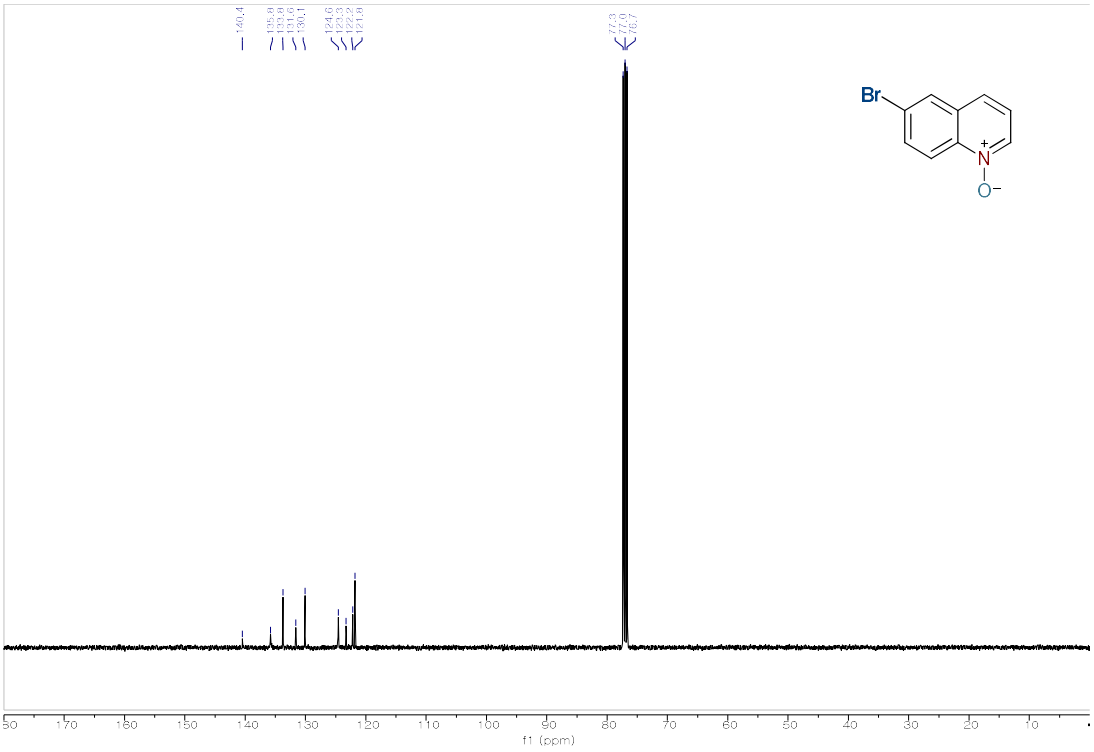


6-Bromoquinoline *N*-Oxide (1r)

^{1}H NMR (400 MHz, $CDCl_3$)

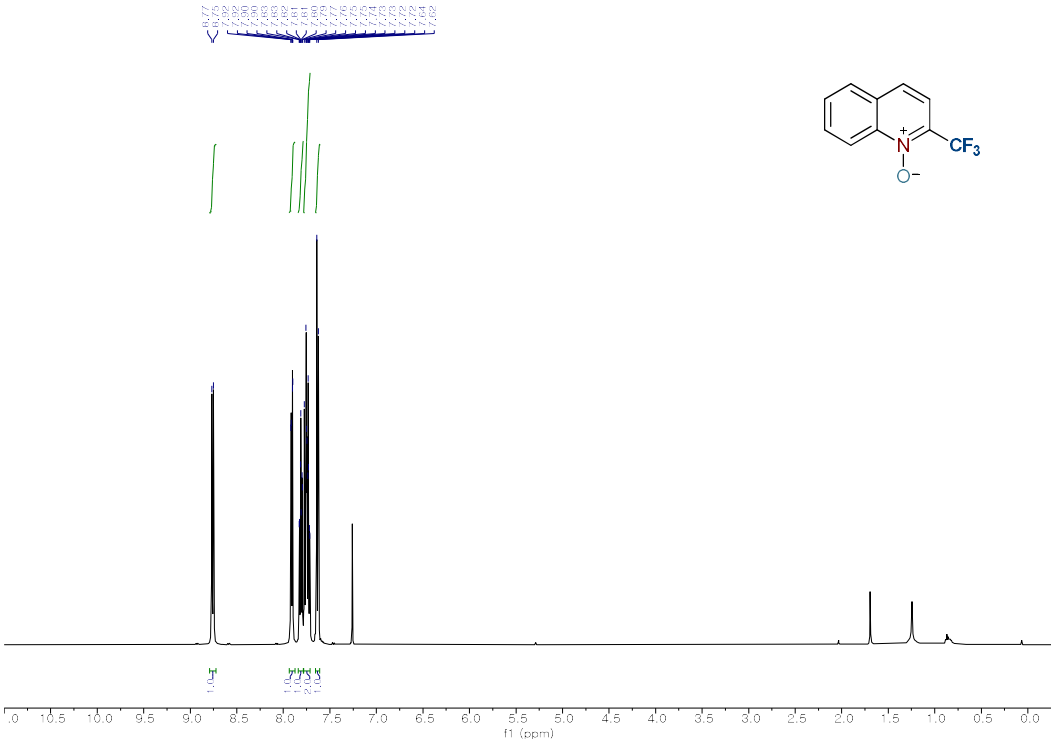


^{13}C NMR (101 MHz, $CDCl_3$)

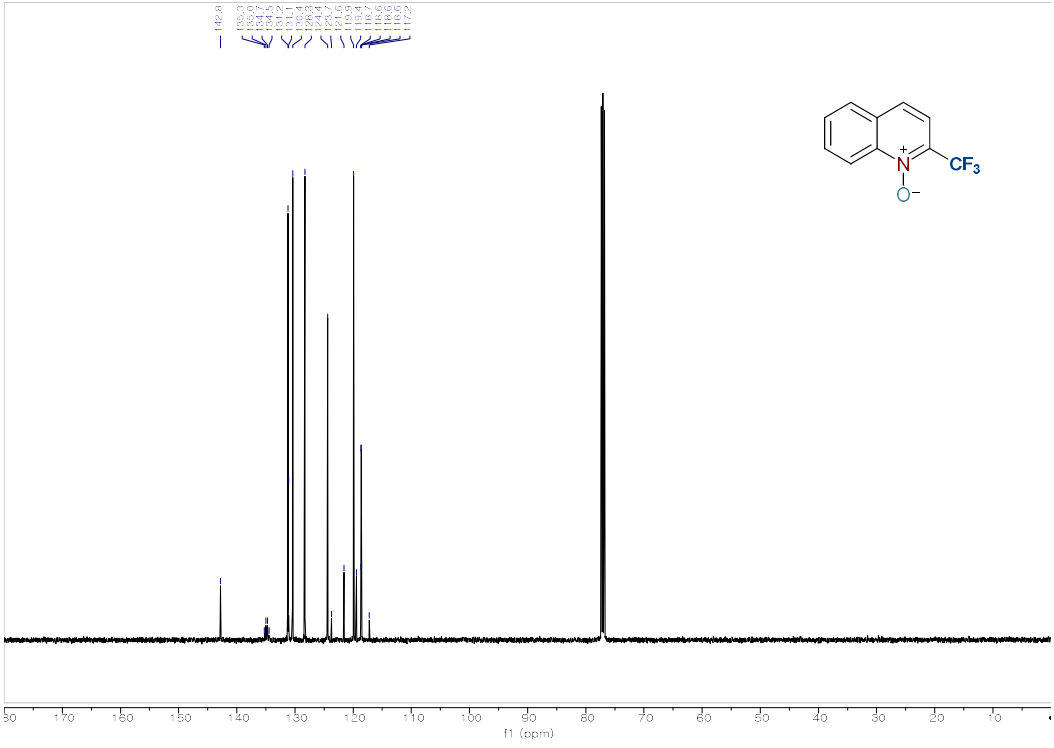


2-(Trifluoromethyl)quinoline *N*-Oxide (1s)

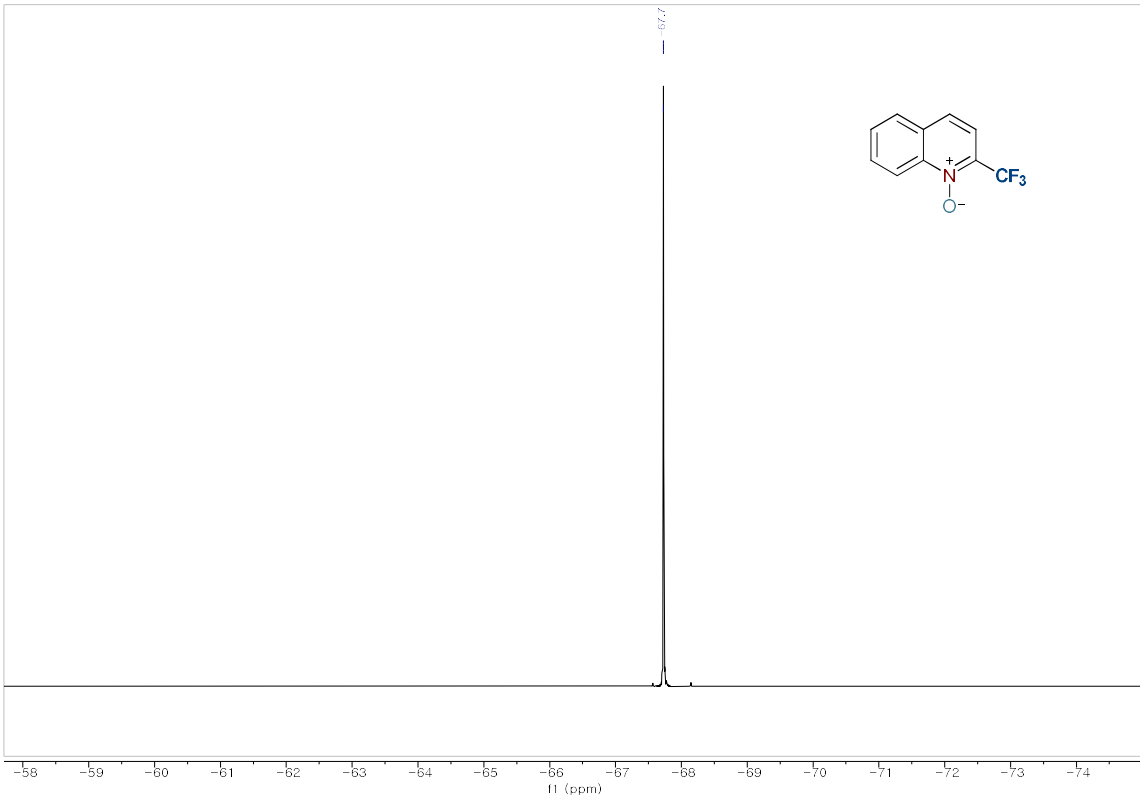
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

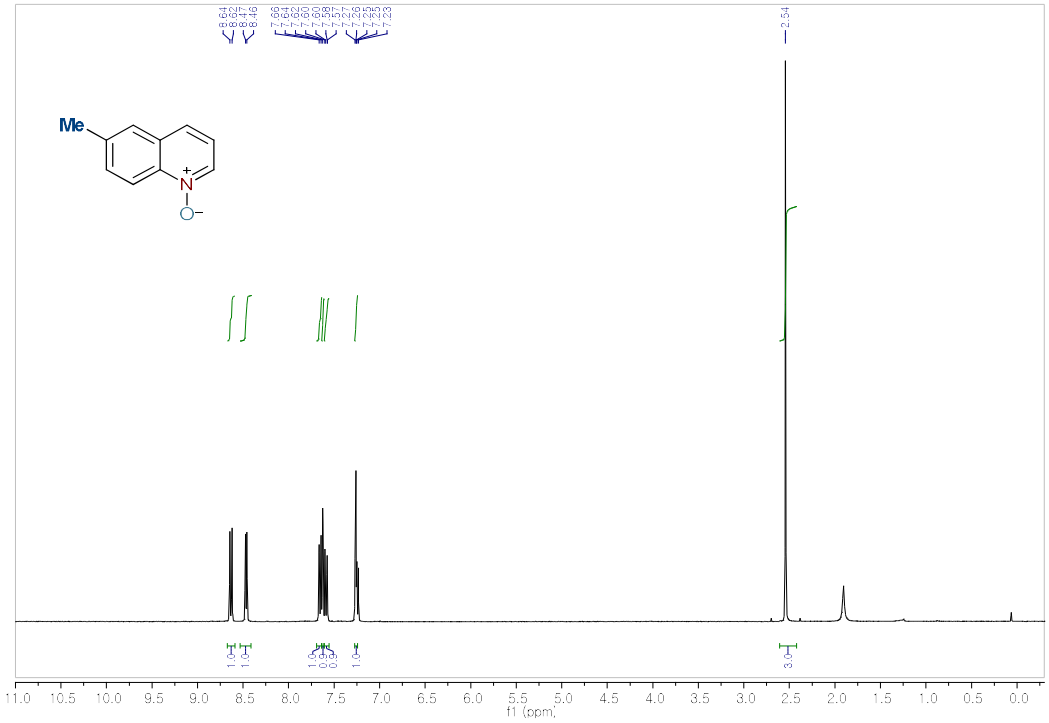


^{19}F NMR (471 MHz, $CDCl_3$)

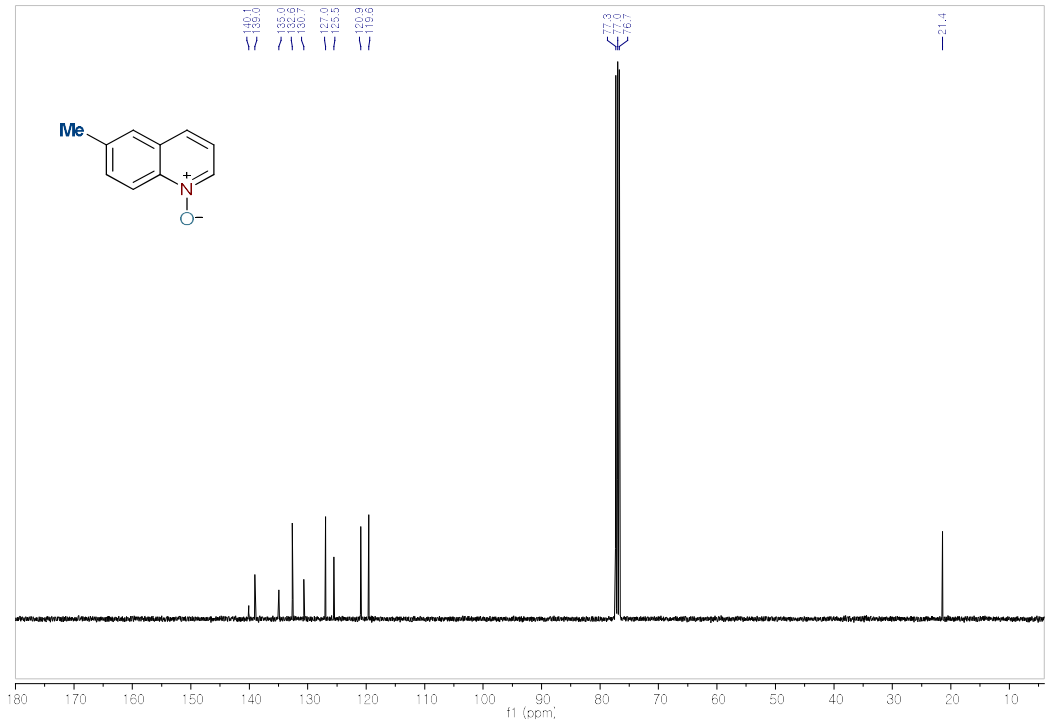


6-Methylquinoline *N*-Oxide (1t)

^{1}H NMR (400 MHz, $CDCl_3$)

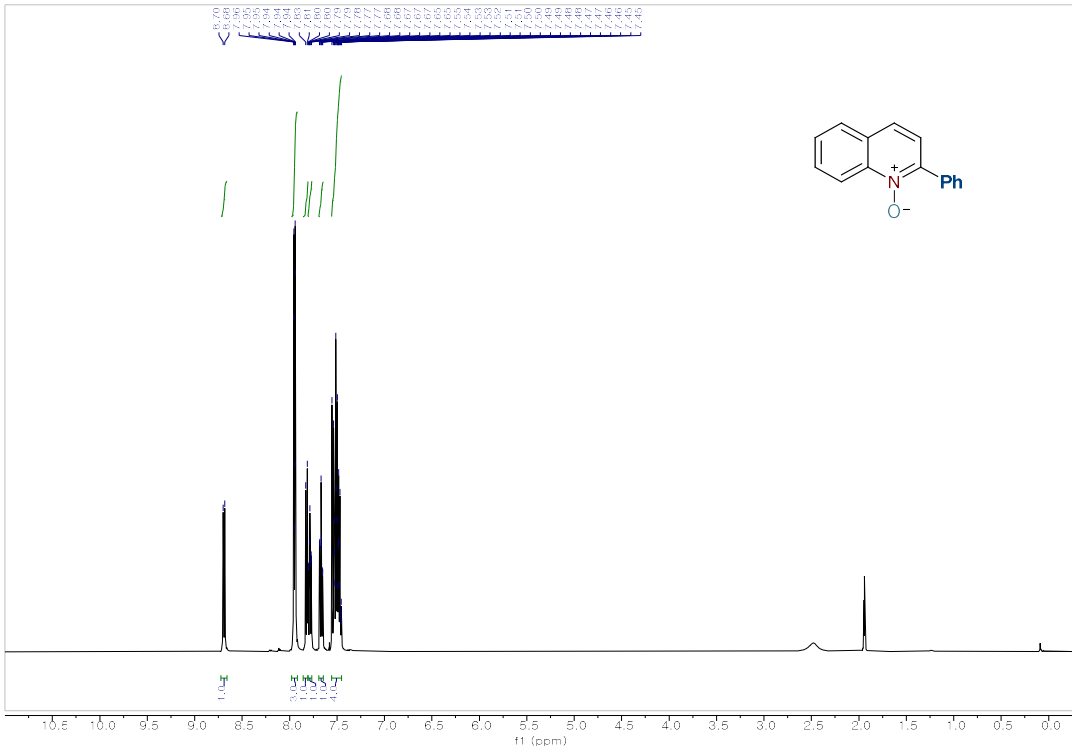


^{13}C NMR (101 MHz, $CDCl_3$)

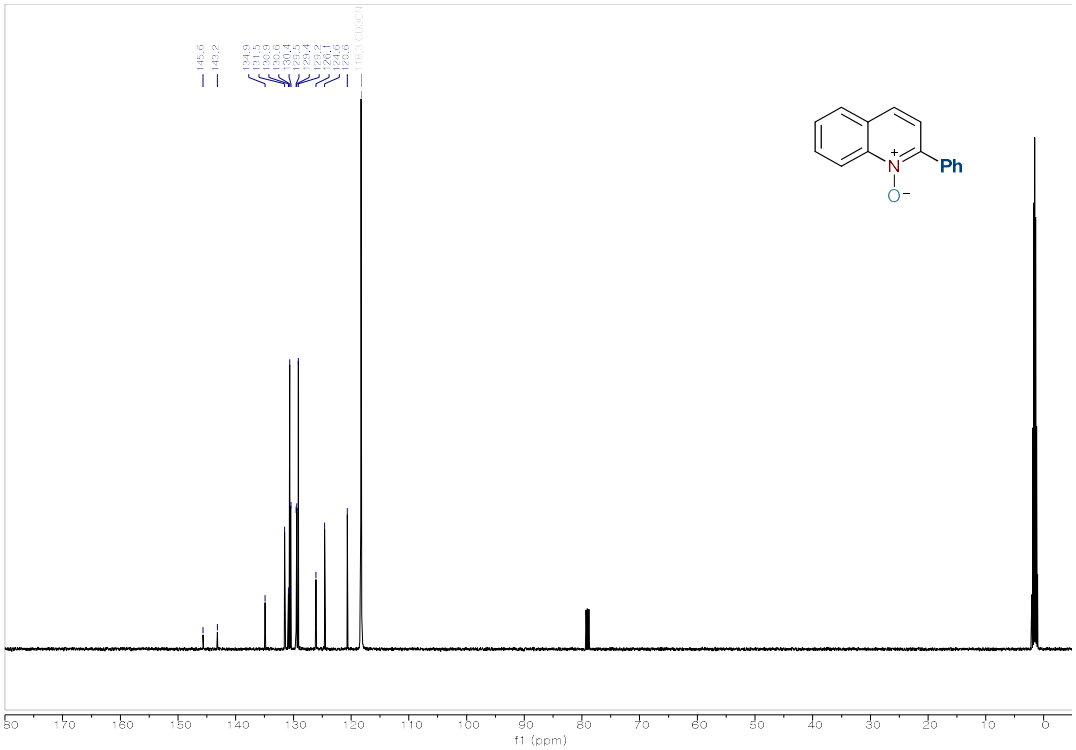


2-Phenylquinoline *N*-Oxide (1u)

^{1}H NMR (500 MHz, CD_3CN)

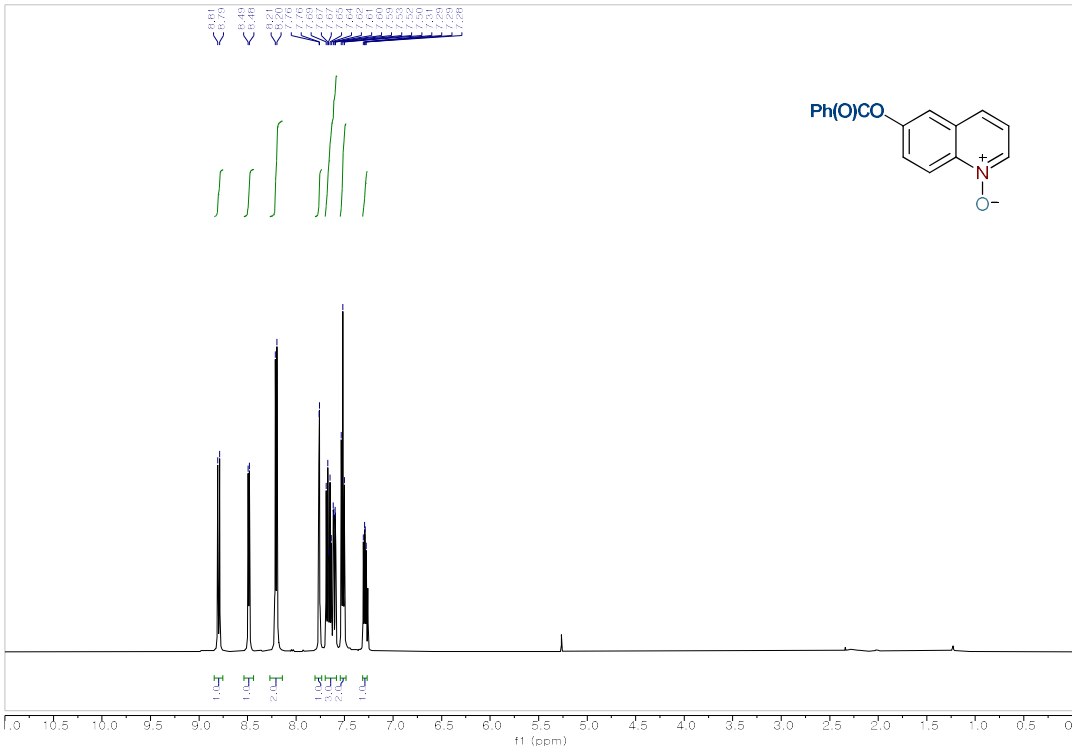


^{13}C NMR (126 MHz, CD_3CN)

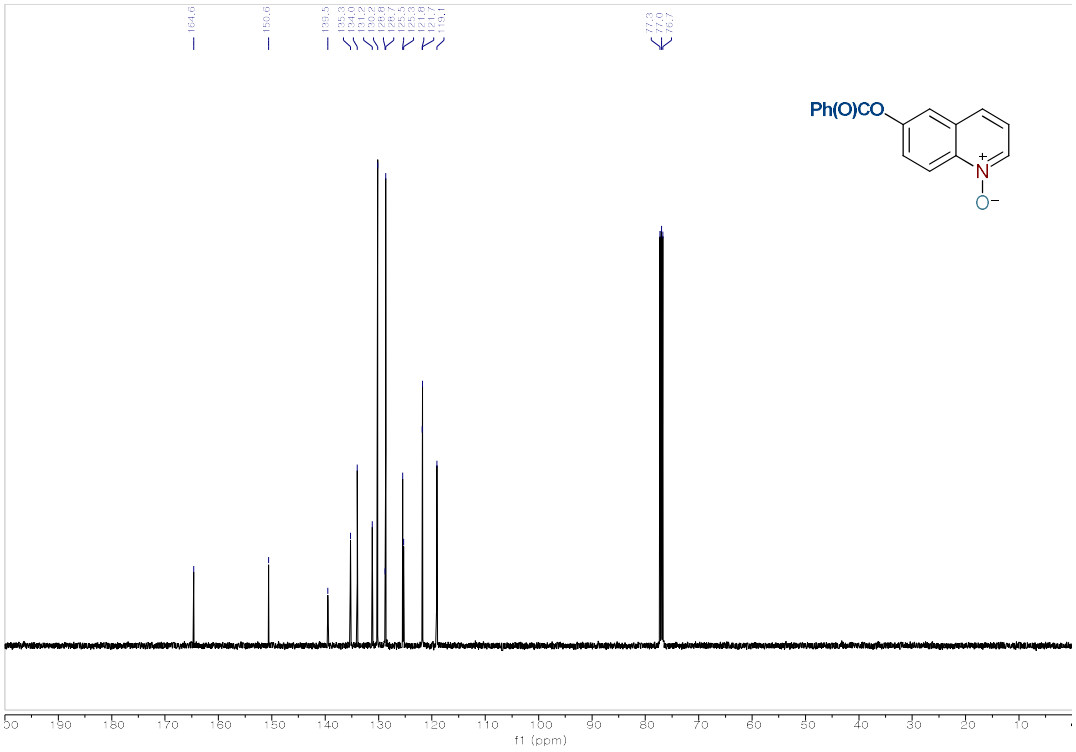


6-Benzoyloxyquinoline *N*-Oxide (1v)

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

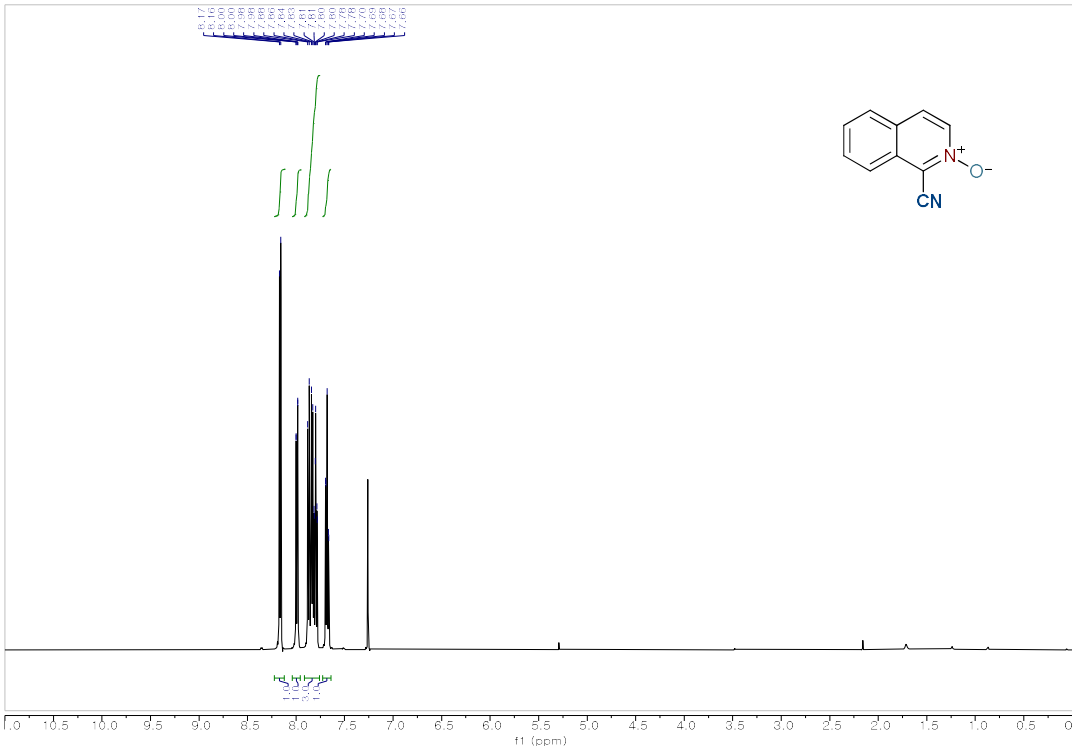


^{13}C NMR (126 MHz, $CDCl_3$)

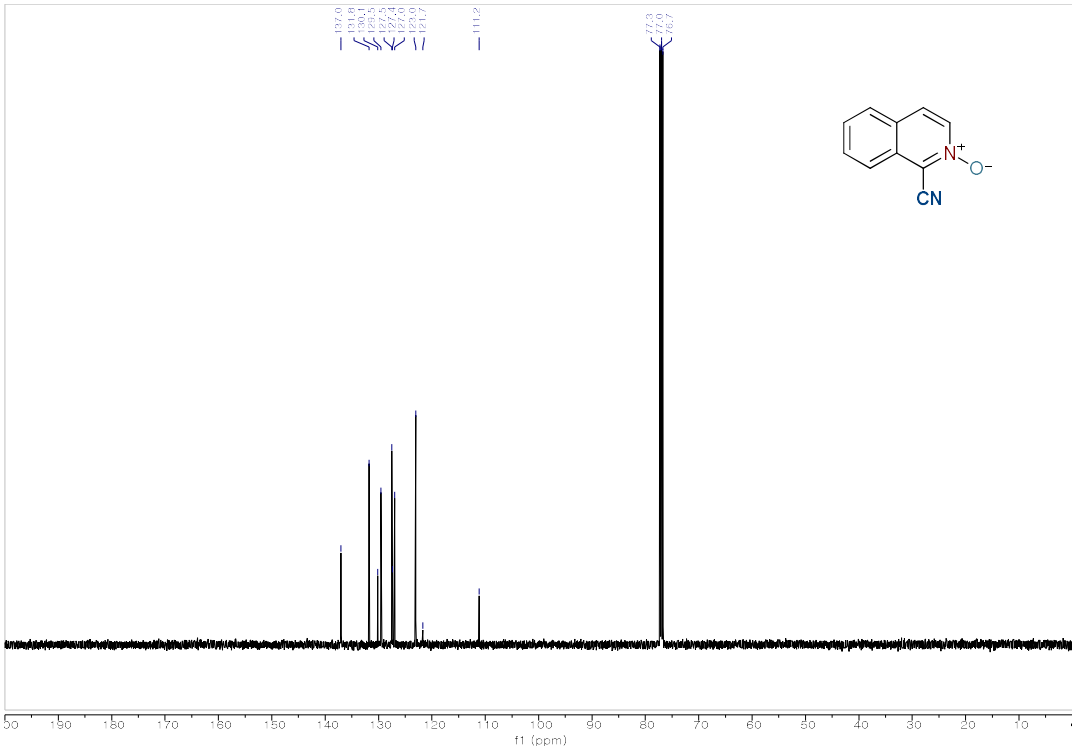


1-Isoquinolinecarbonitrile *N*-Oxide (1w)

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

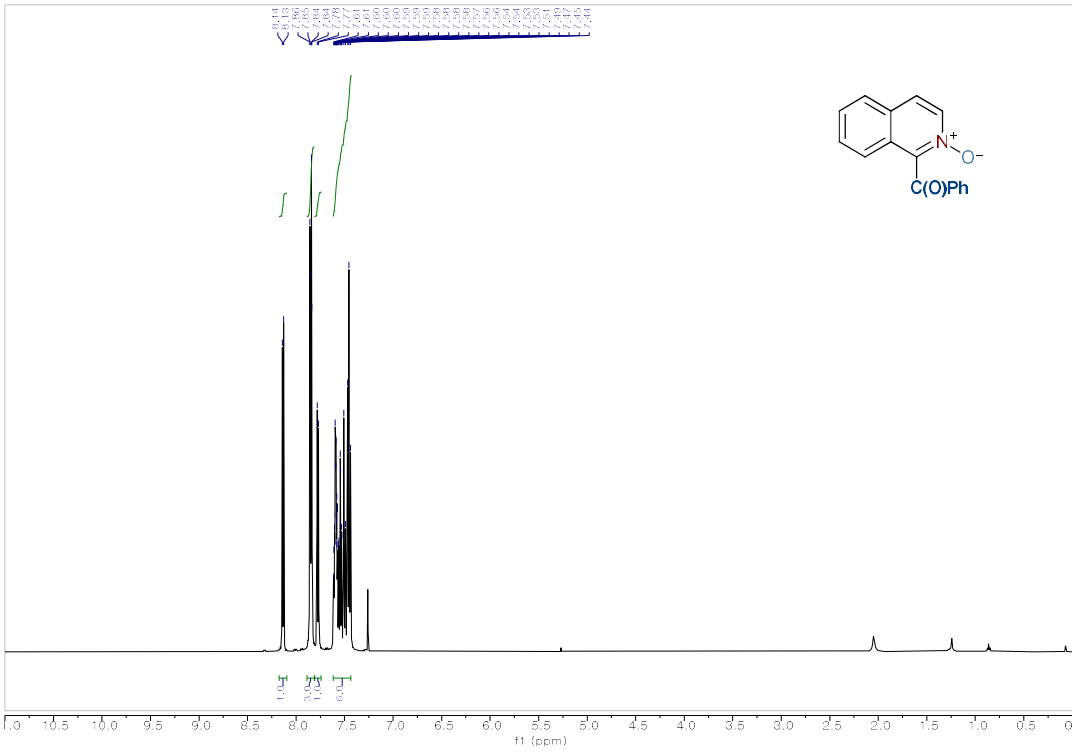


^{13}C NMR (126 MHz, $CDCl_3$)

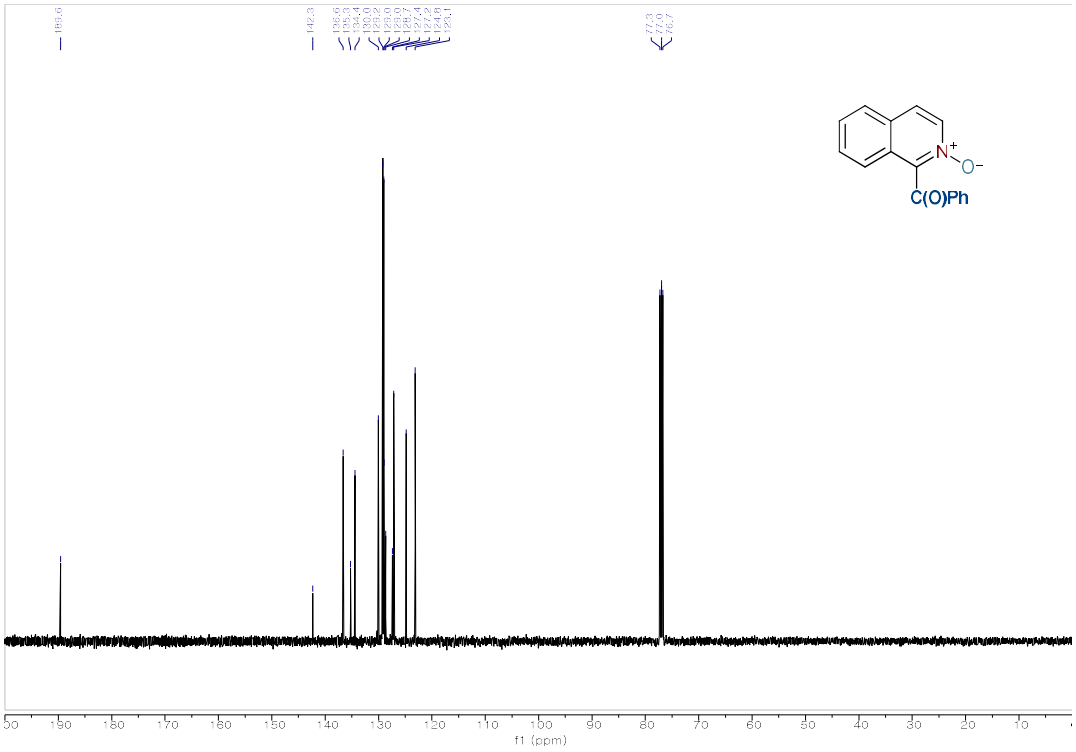


1-Benzoylisoquinoline *N*-Oxide (1x)

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

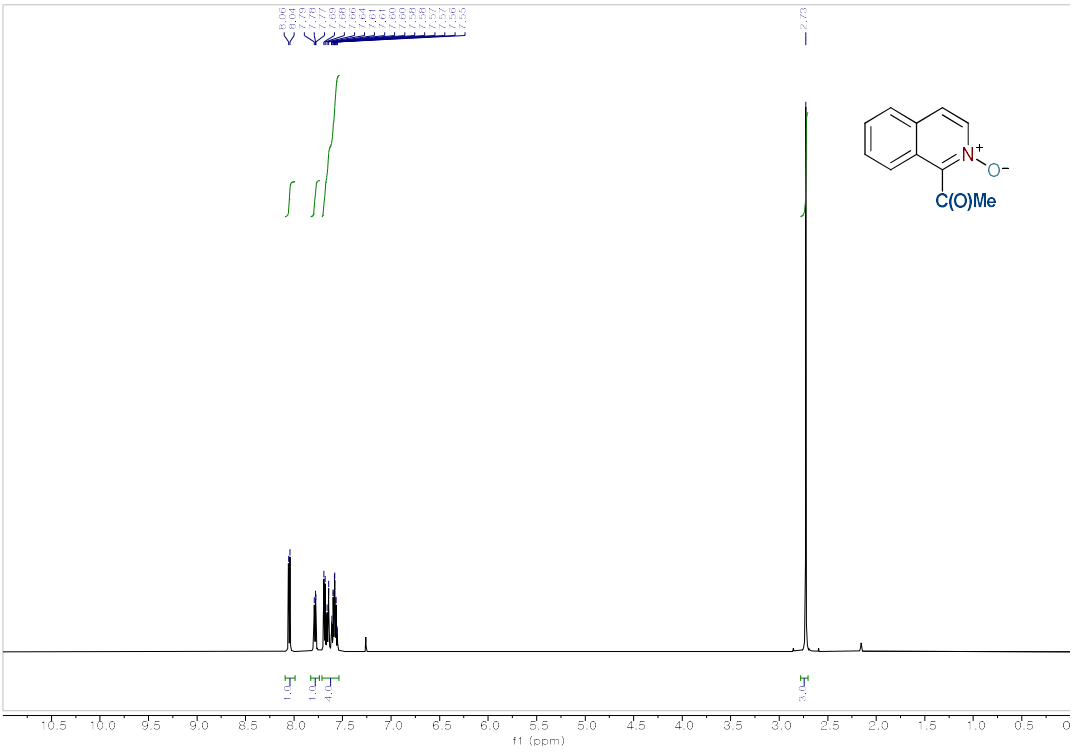


^{13}C NMR (126 MHz, $CDCl_3$)

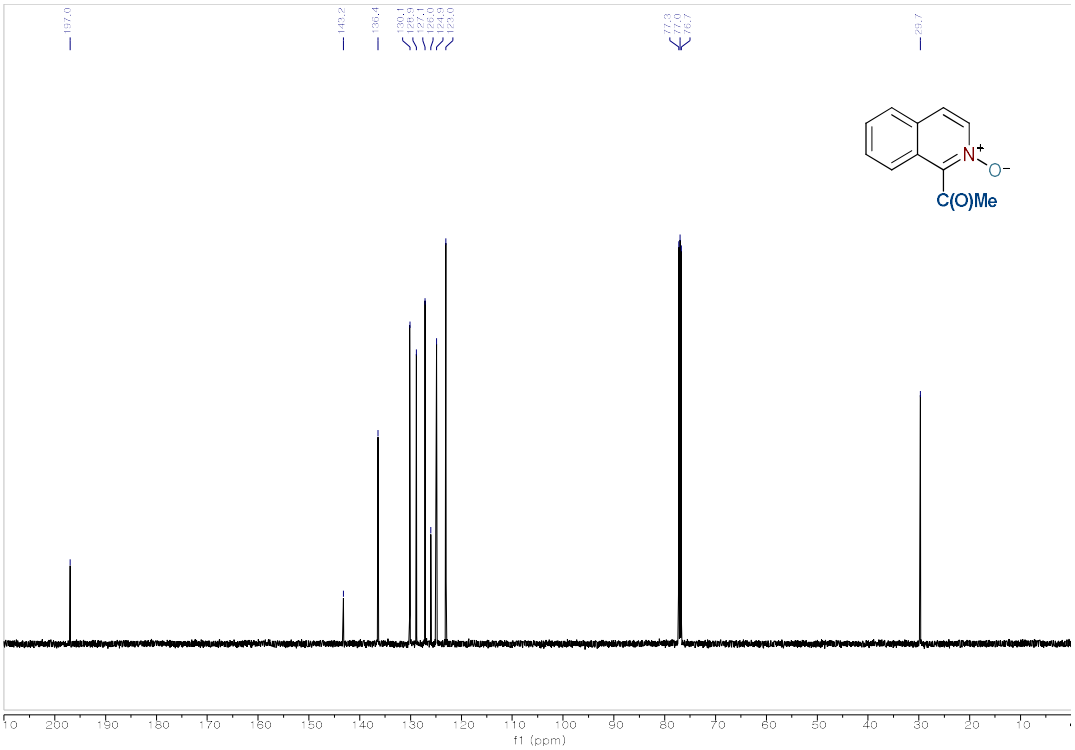


1-Acetylisoquinoline *N*-Oxide (1y)

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

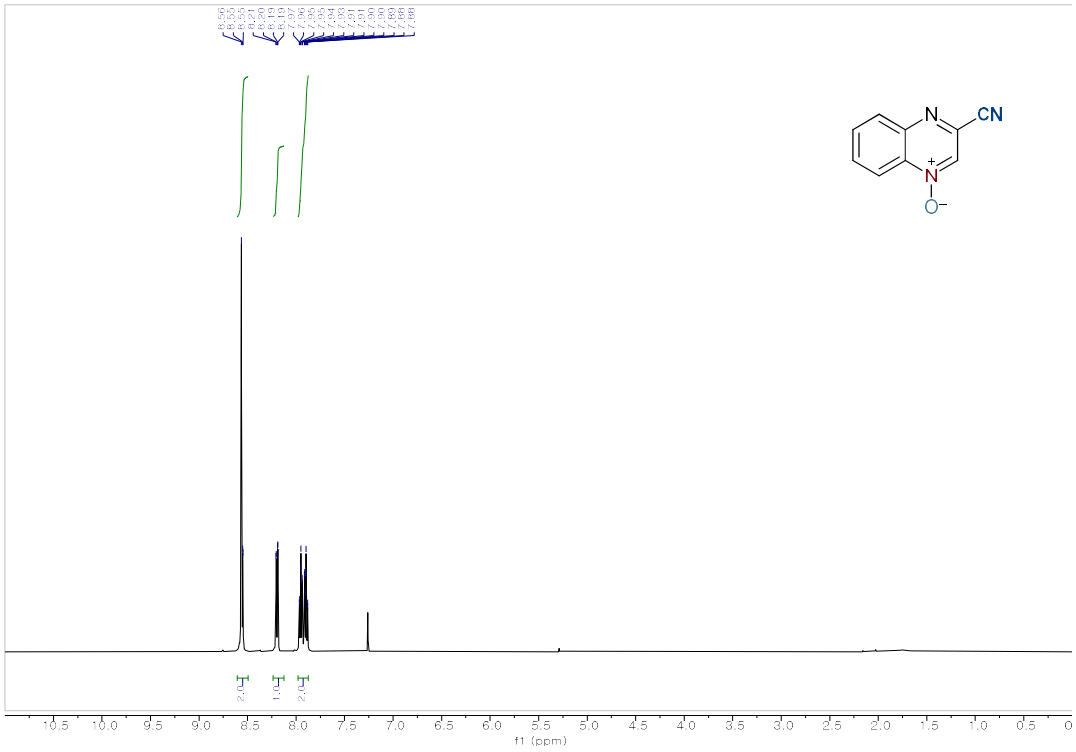


^{13}C NMR (126 MHz, $CDCl_3$)

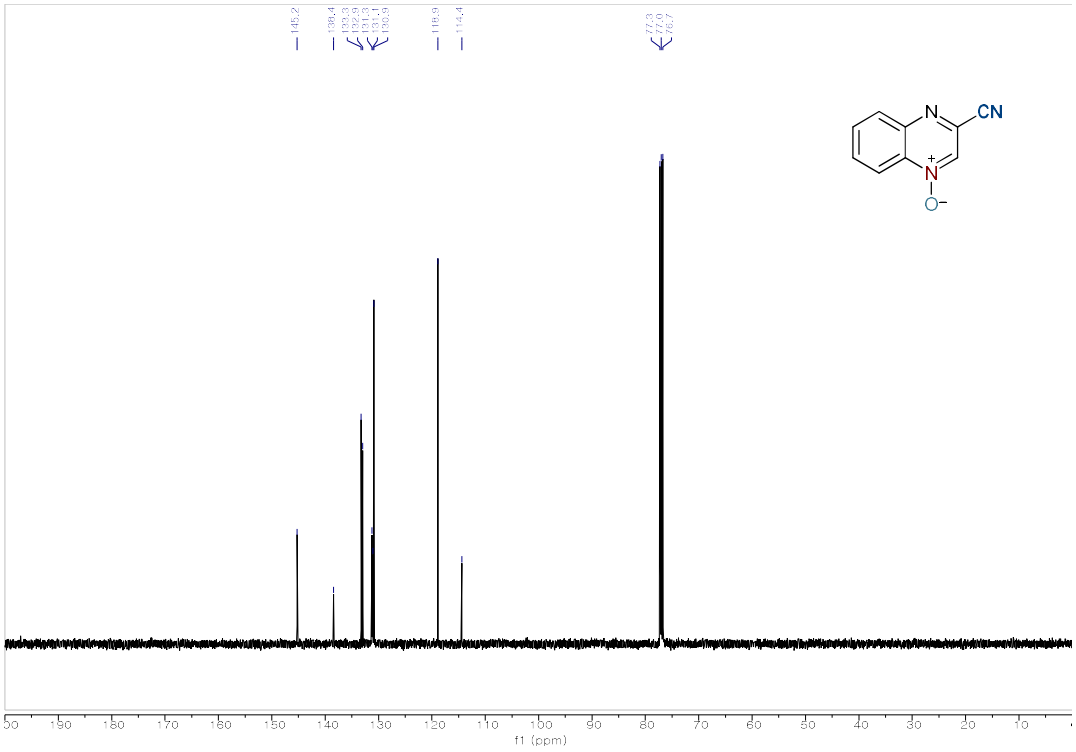


3-Quinoxalinecarbonitrile *N*-Oxide (1z)

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

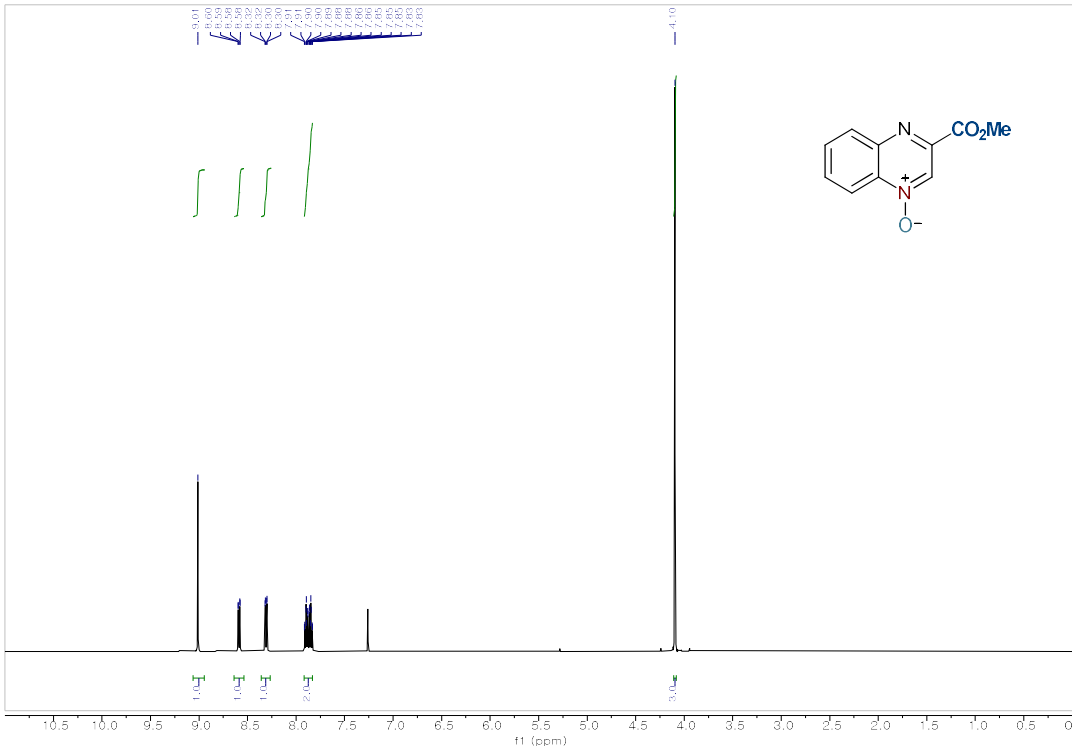


^{13}C NMR (126 MHz, $CDCl_3$)

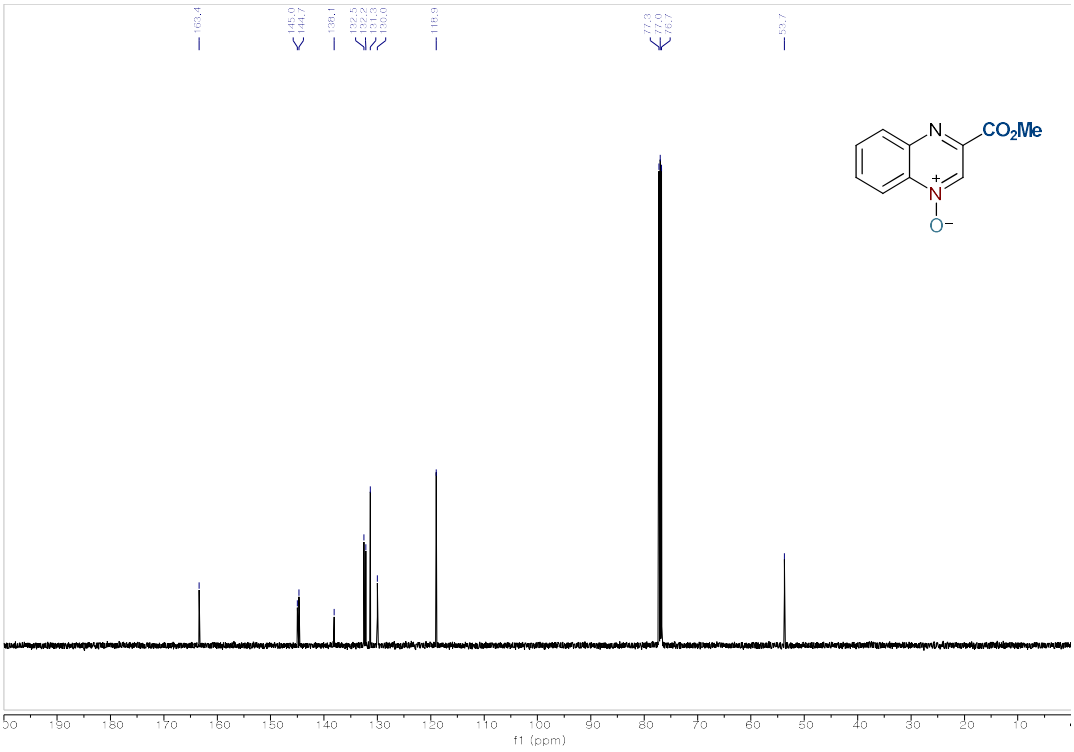


Methyl 3-Quinoxalinecarboxylate *N*-Oxide (1aa)

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

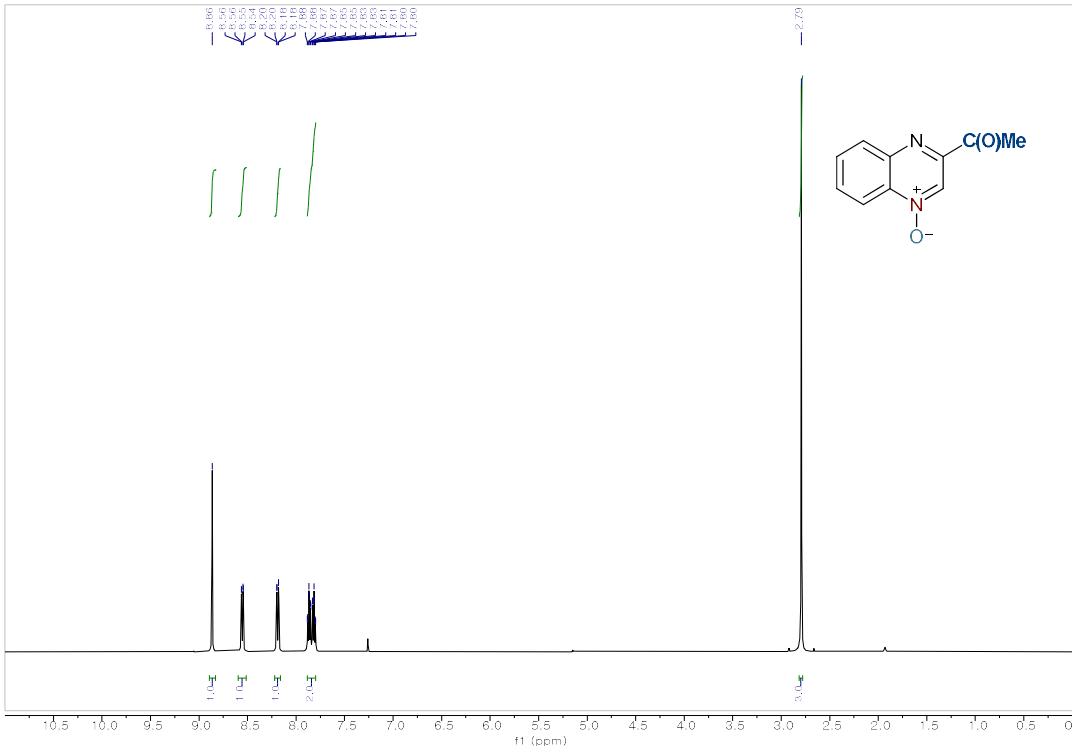


^{13}C NMR (126 MHz, $CDCl_3$)

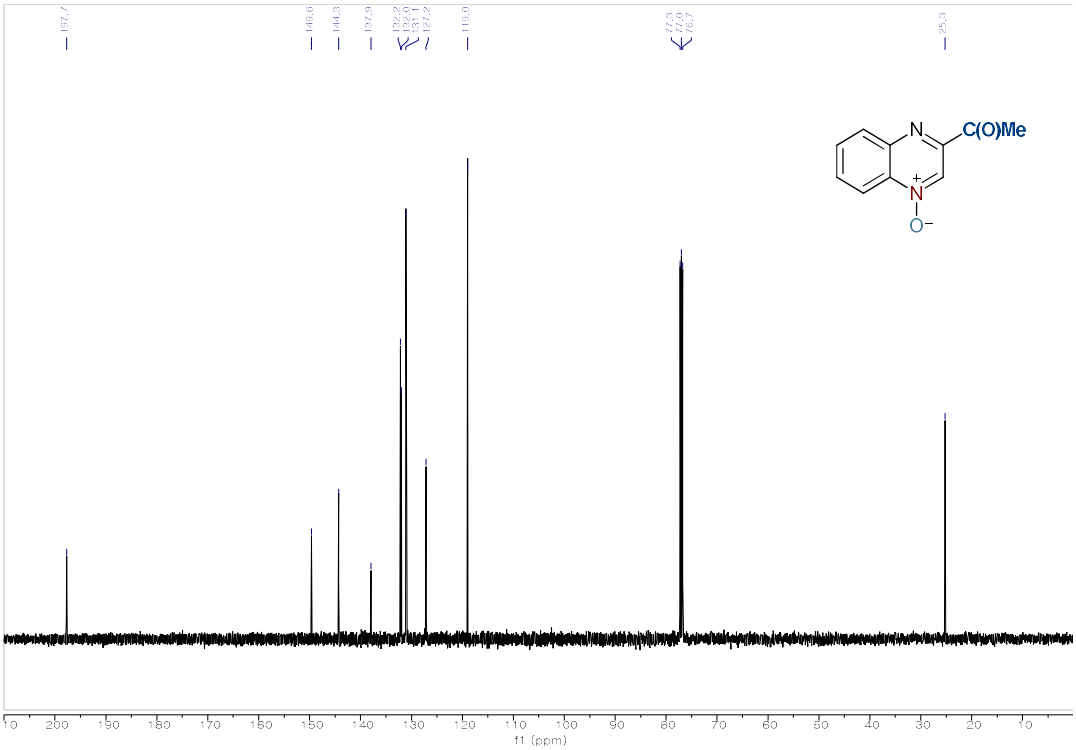


3-Acetylquinoxaline *N*-Oxide (1ab)

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

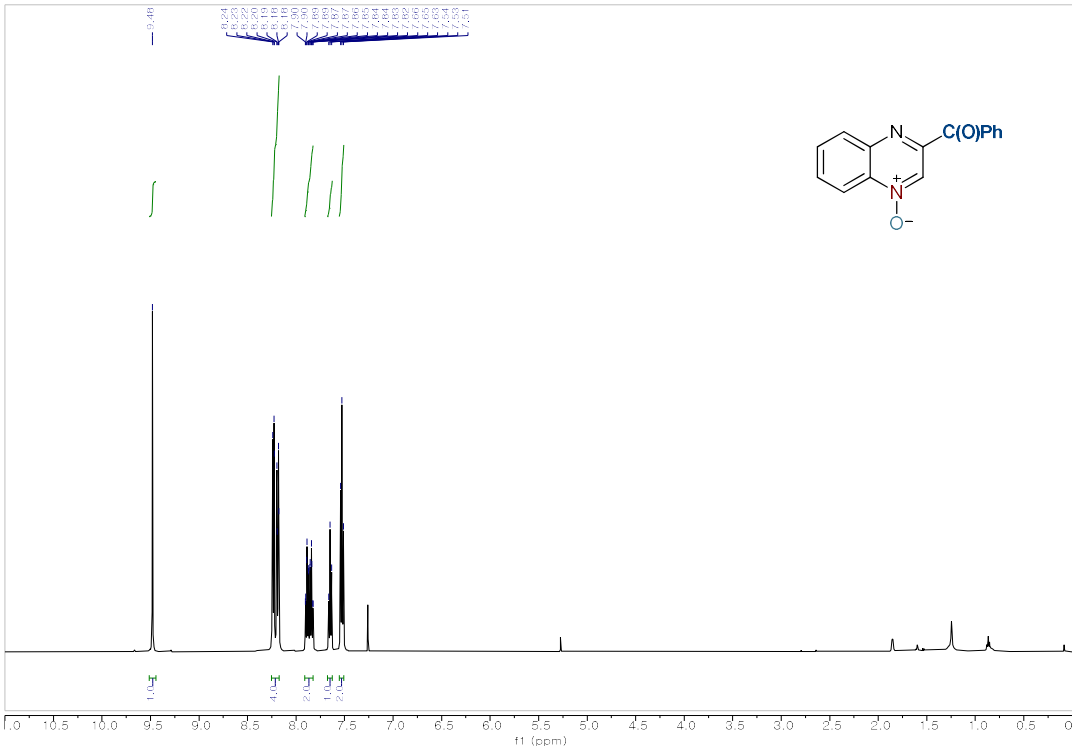


^{13}C NMR (126 MHz, $CDCl_3$)

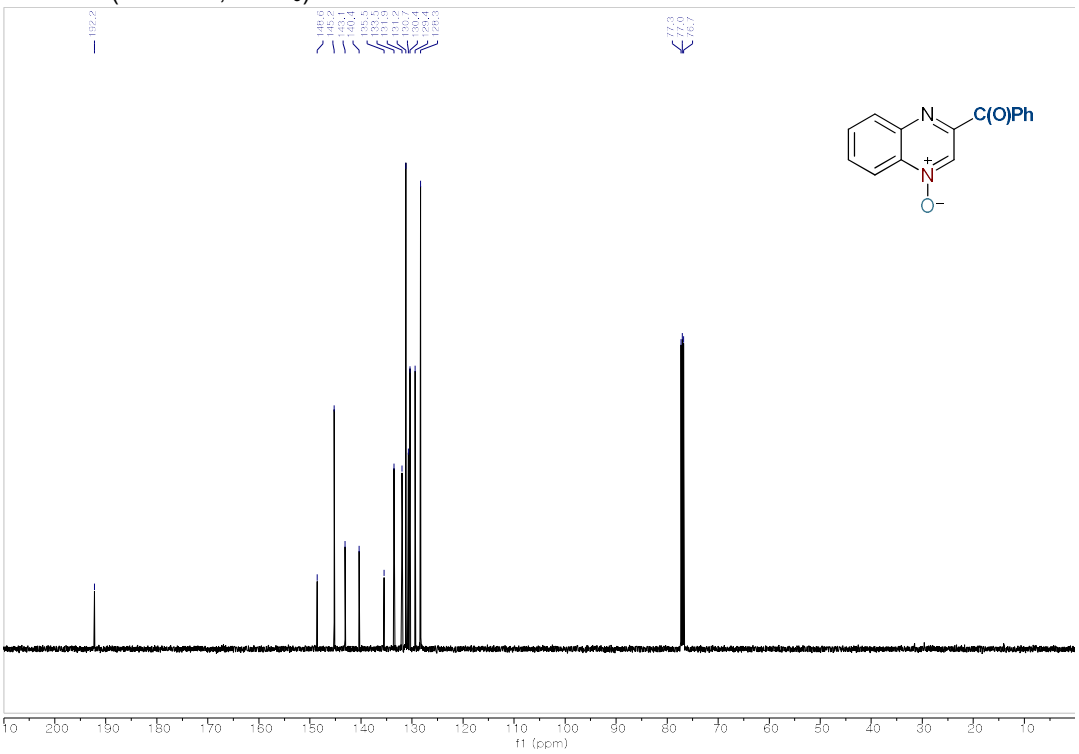


3-Benzoylquinoxaline *N*-Oxide (1ac)

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

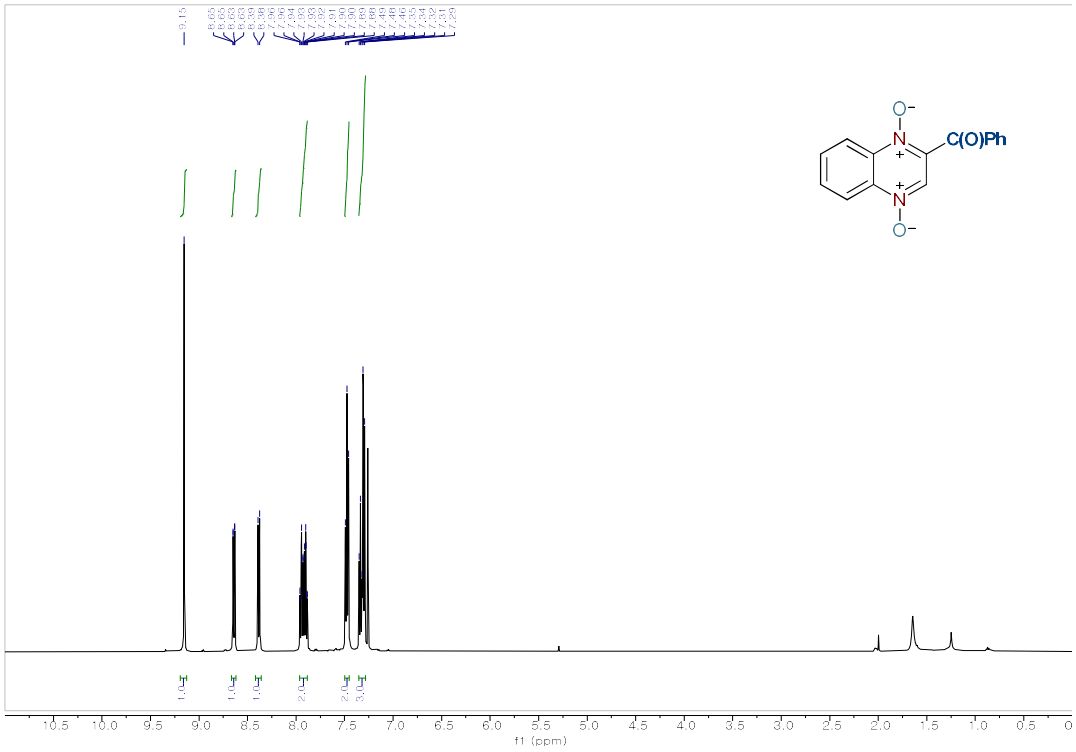


^{13}C NMR (126 MHz, $CDCl_3$)

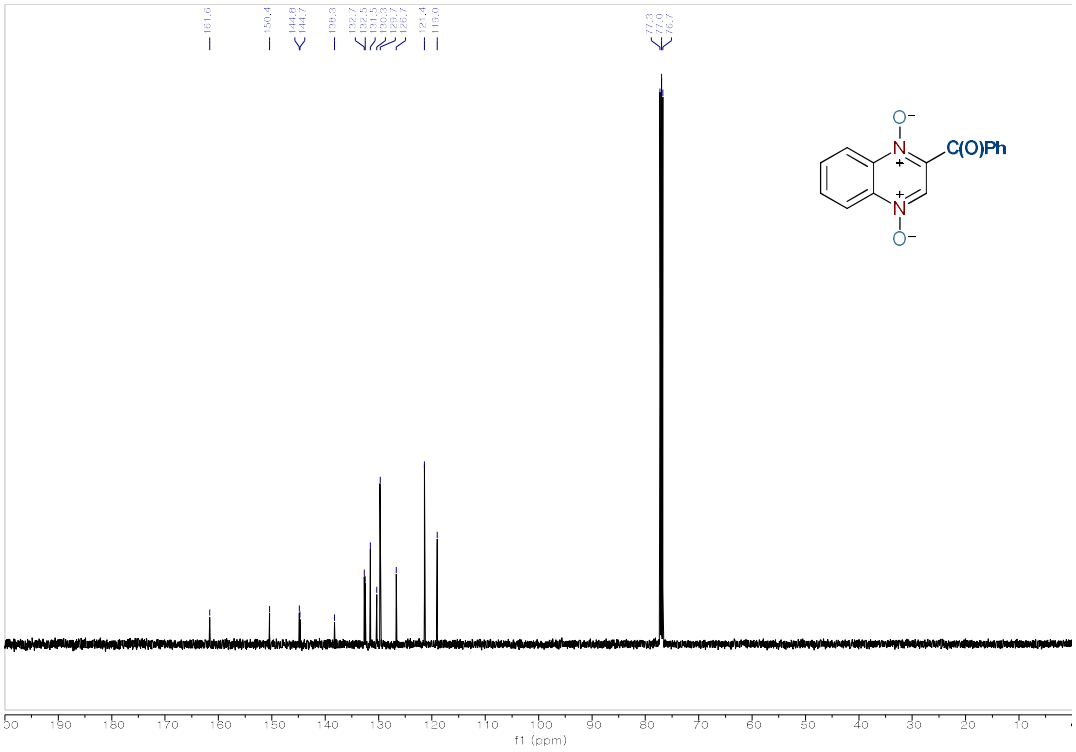


2-Benzoylquinoxaline *N,N*-Dioxide (1ad)

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

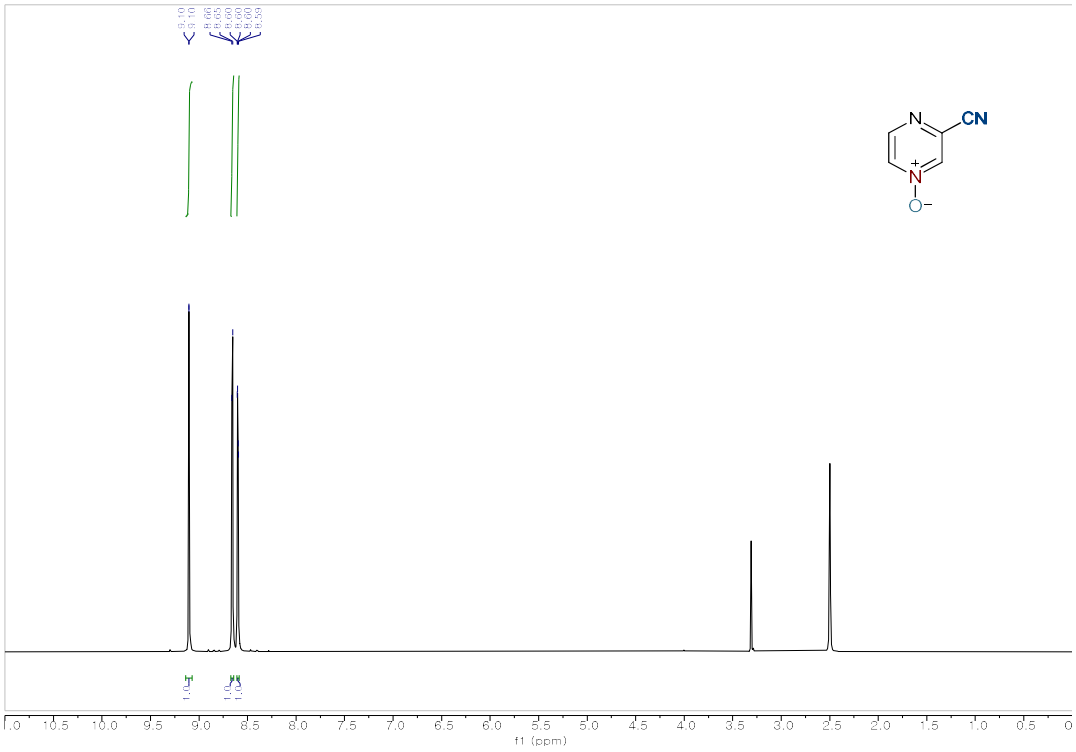


^{13}C NMR (126 MHz, $CDCl_3$)

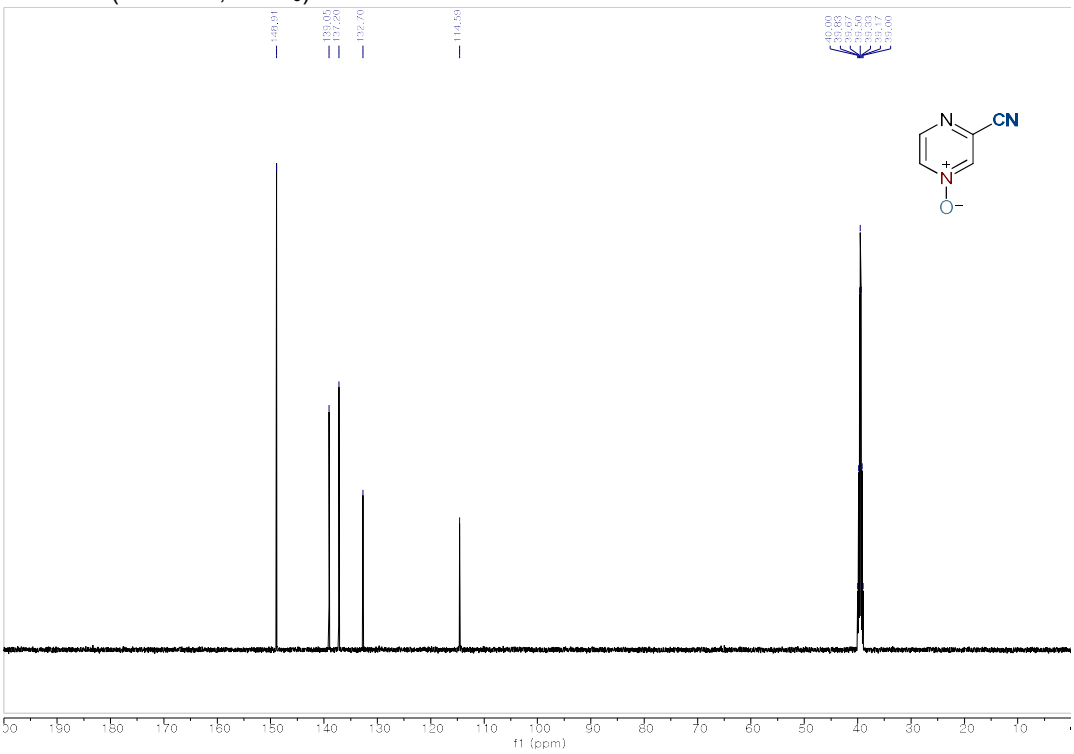


3-Pyrazinecarbonitrile *N*-Oxide (1ae)

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

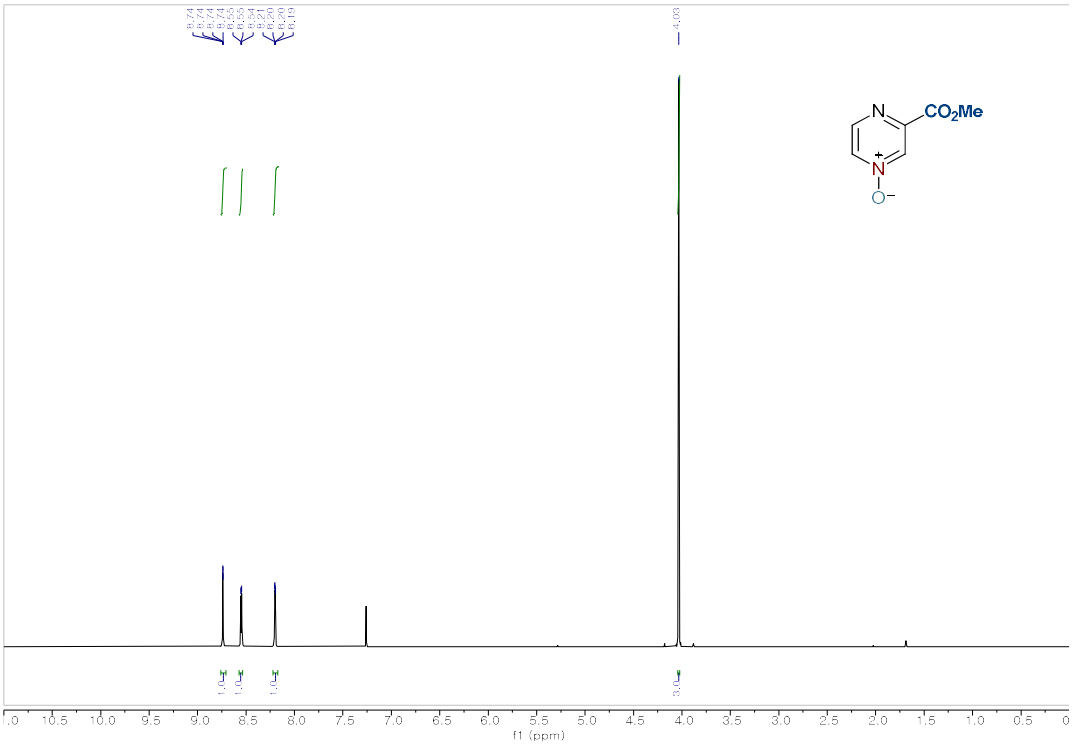


^{13}C NMR (126 MHz, $CDCl_3$)

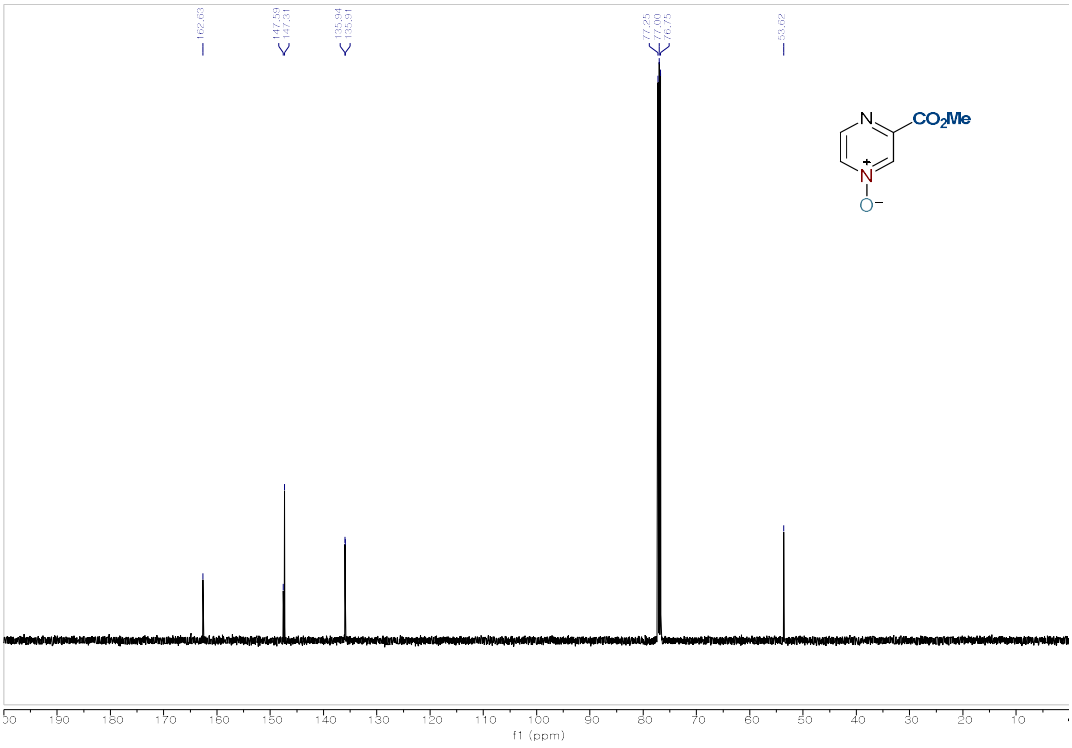


Methyl 3-Pyrazinecarboxylate *N*-Oxide (1af)

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

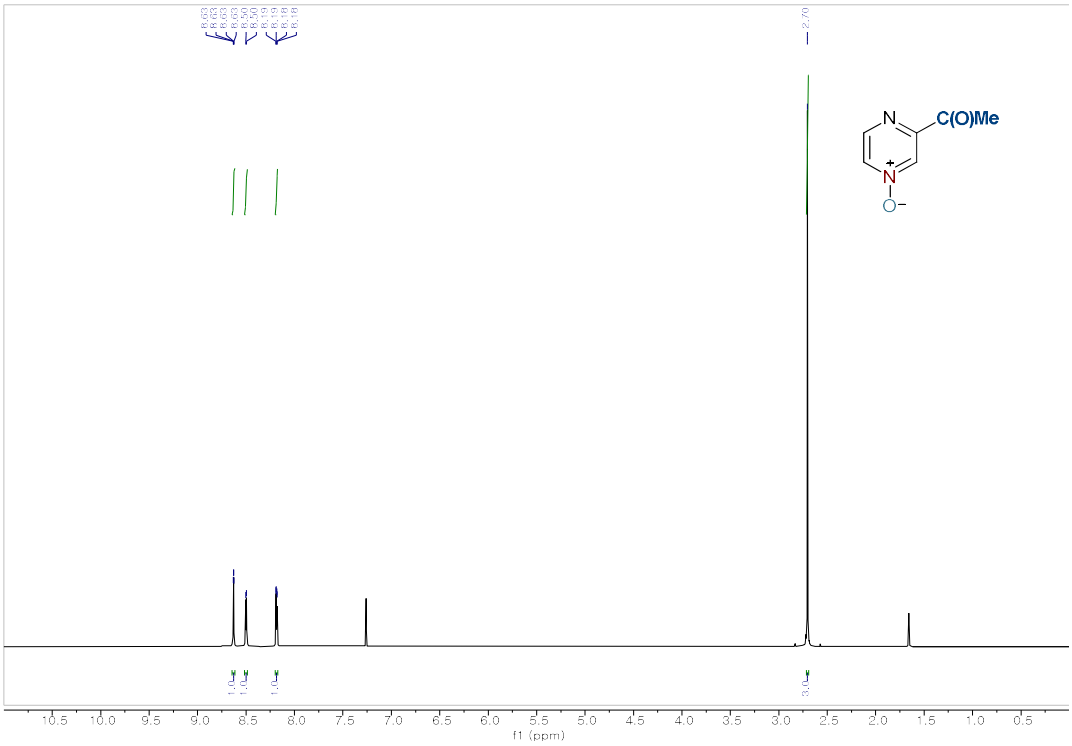


^{13}C NMR (126 MHz, $CDCl_3$)

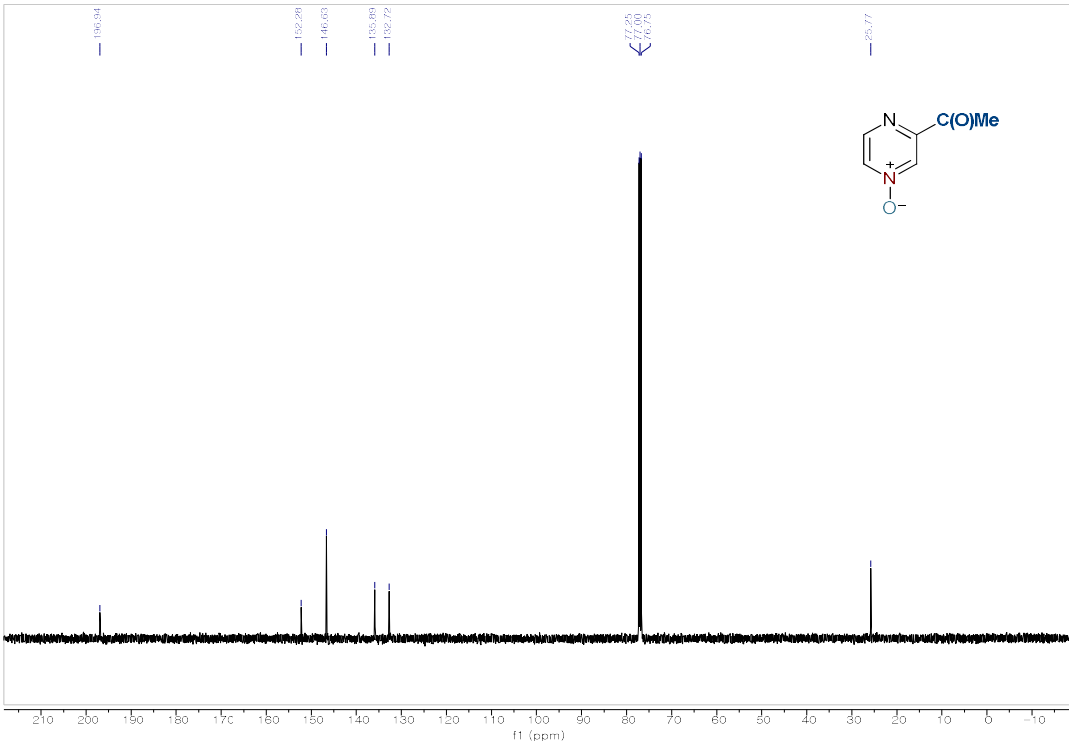


3-Acetylpyrazine *N*-Oxide (1ag)

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

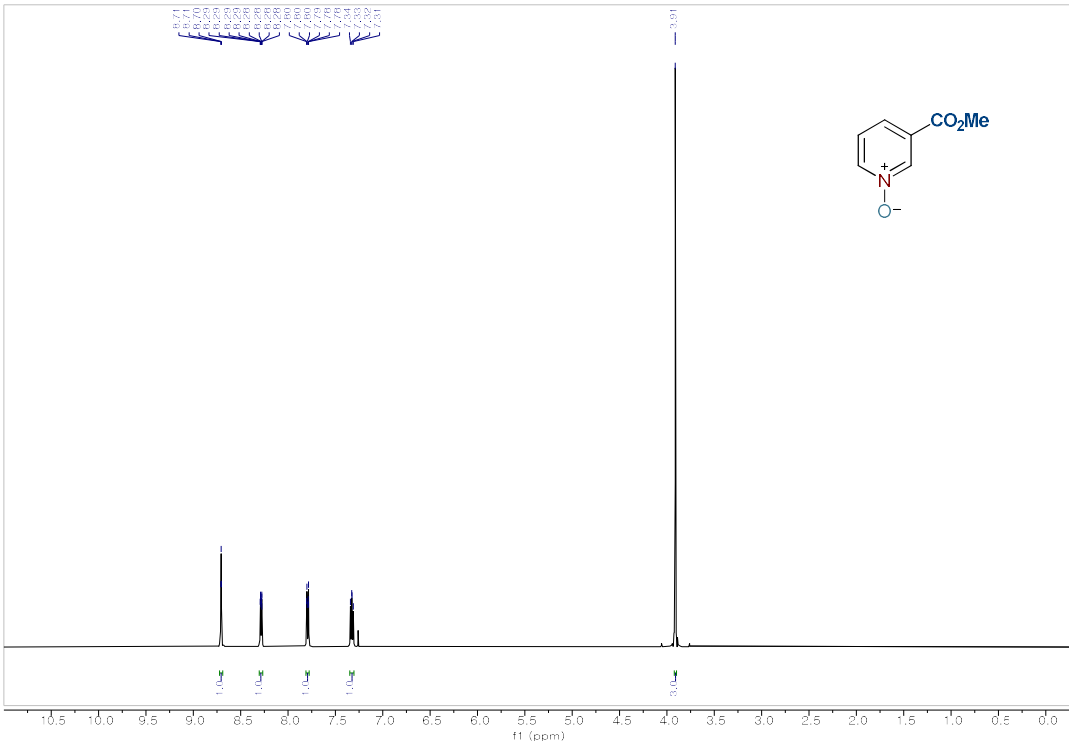


^{13}C NMR (126 MHz, $CDCl_3$)

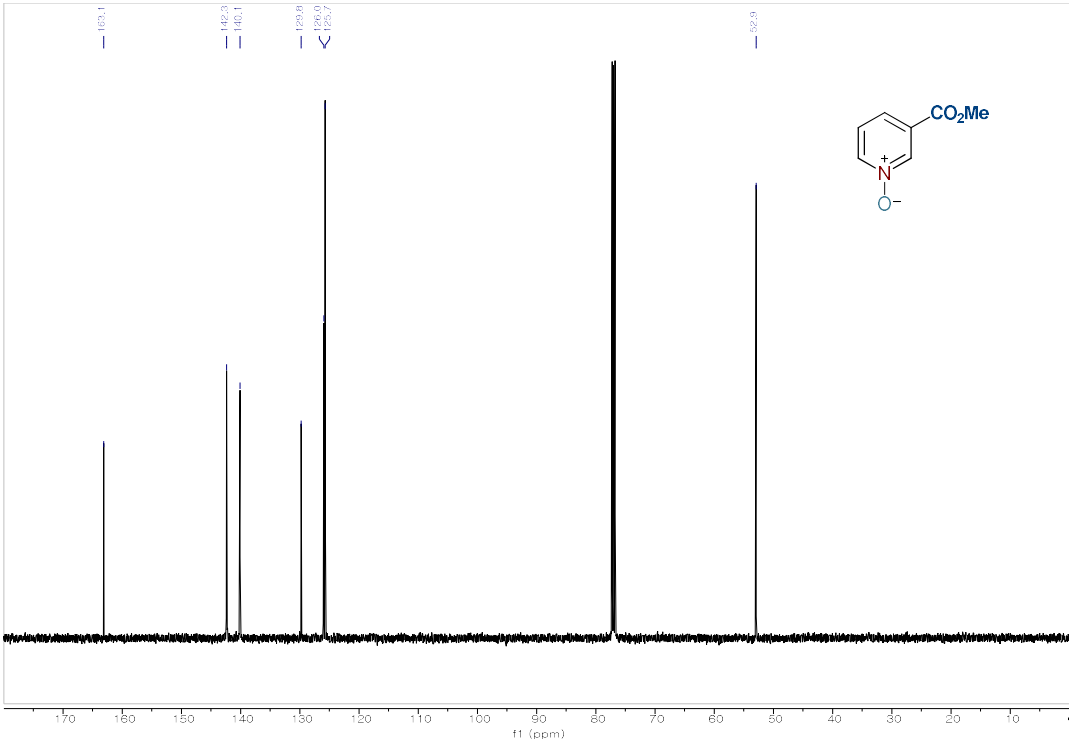


Methyl Nicotinate *N*-Oxide (1ah)

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

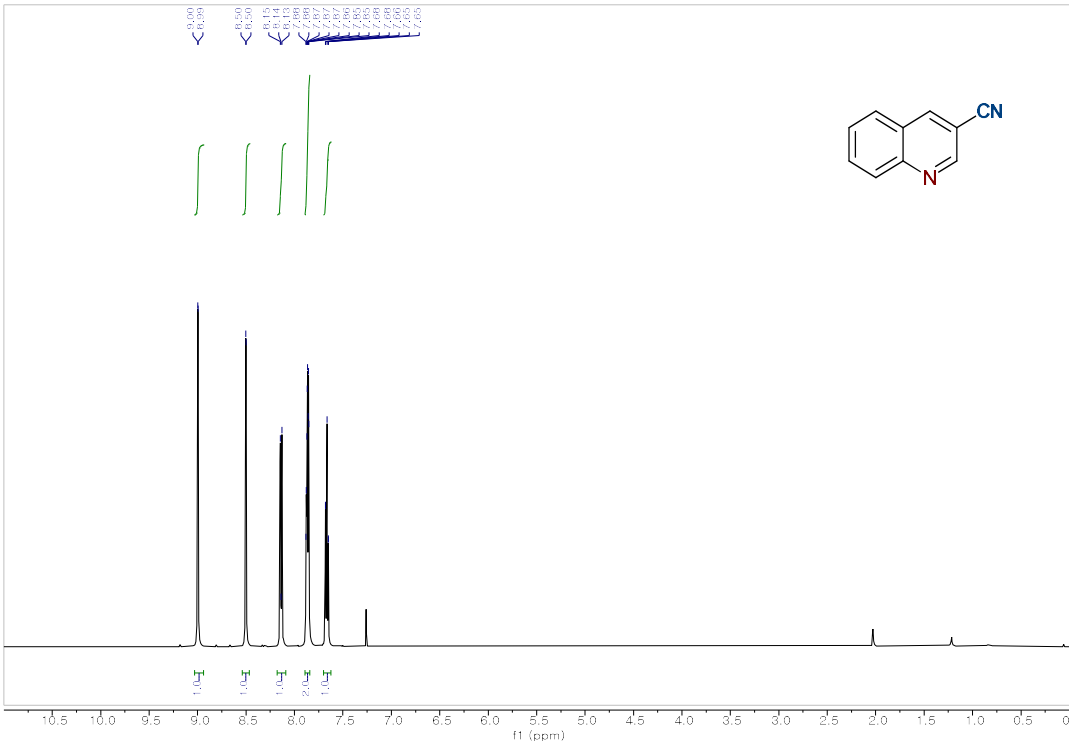


^{13}C NMR (126 MHz, $CDCl_3$)

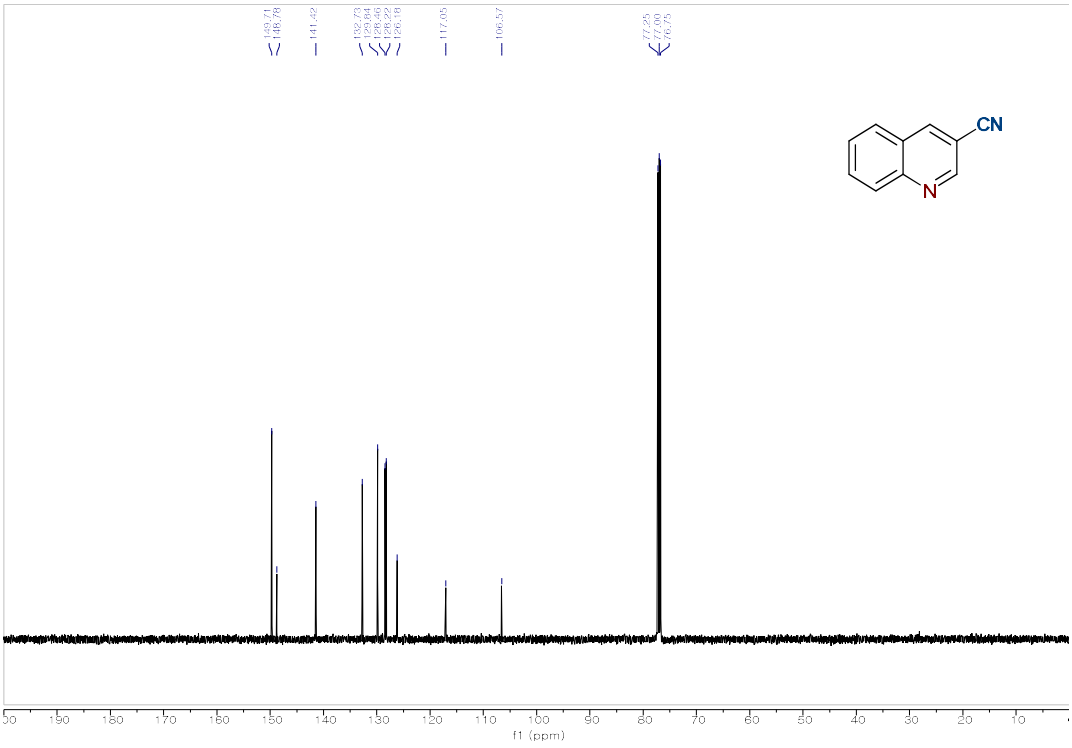


3-Quinolinecarbonitrile (3a)

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

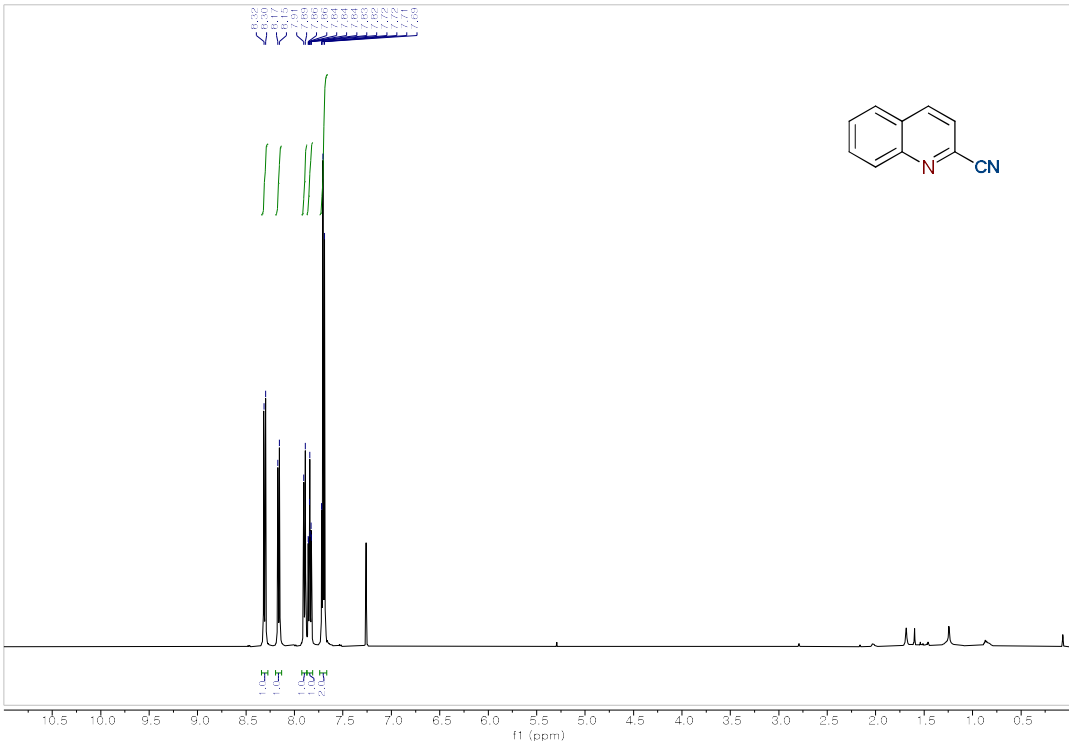


^{13}C NMR (126 MHz, $CDCl_3$)

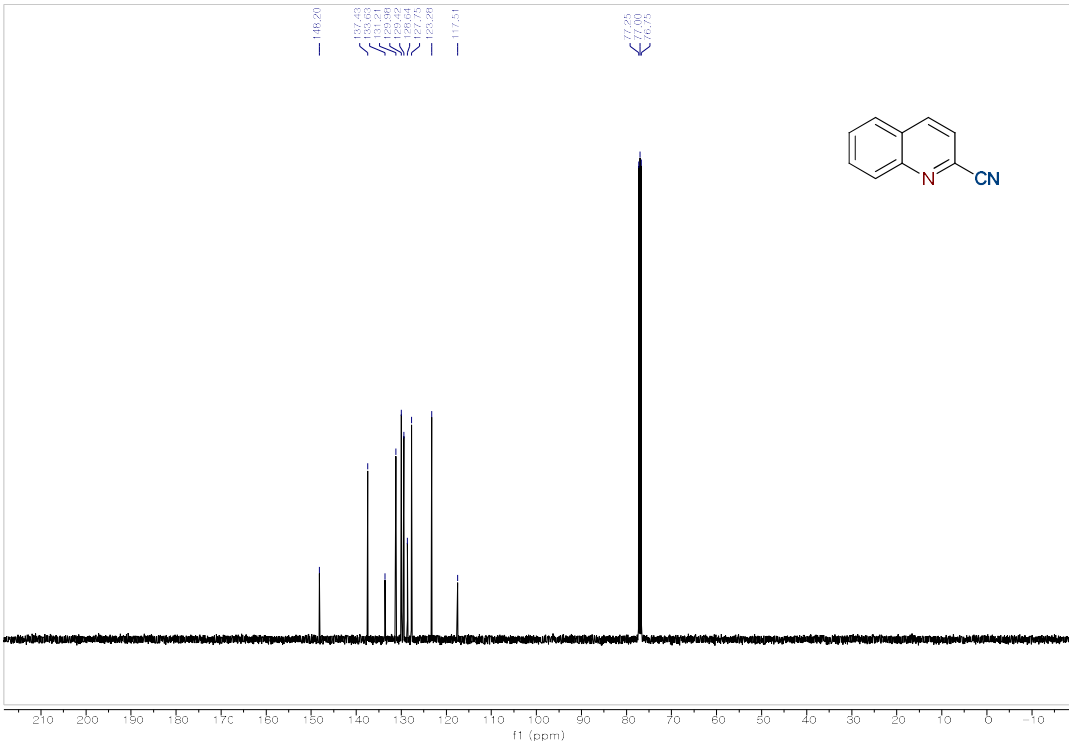


2-Quinolinecarbonitrile (3b)

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

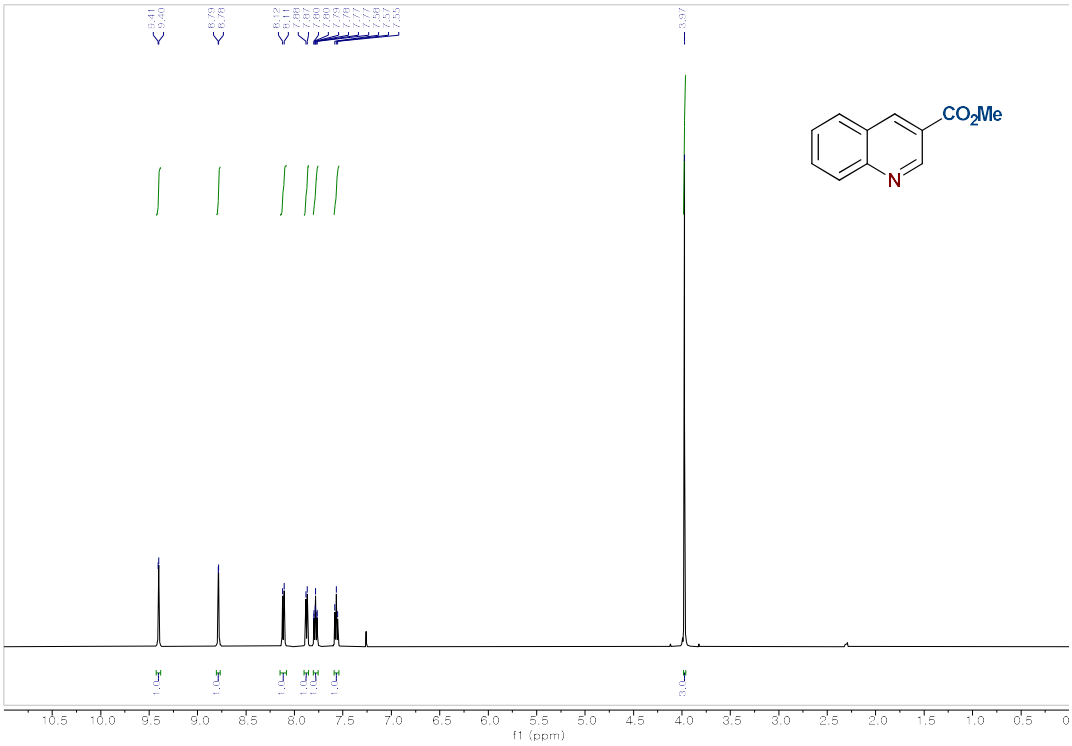


^{13}C NMR (126 MHz, $CDCl_3$)

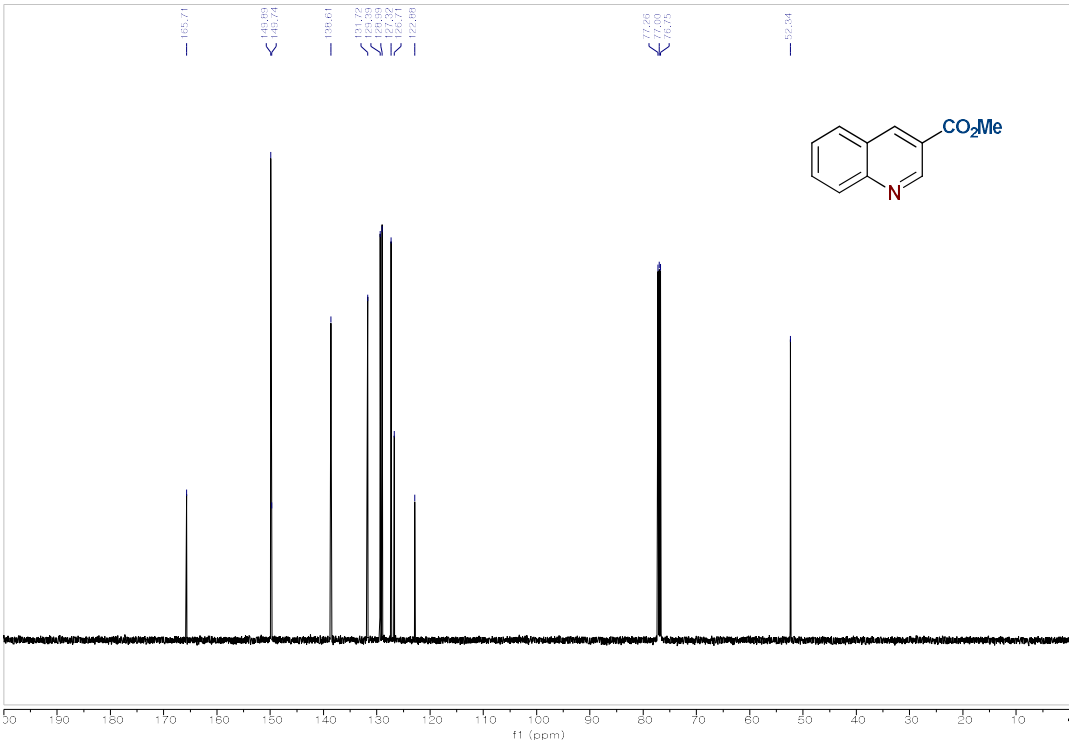


Methyl Quinoline-3-carboxylate (3c)

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

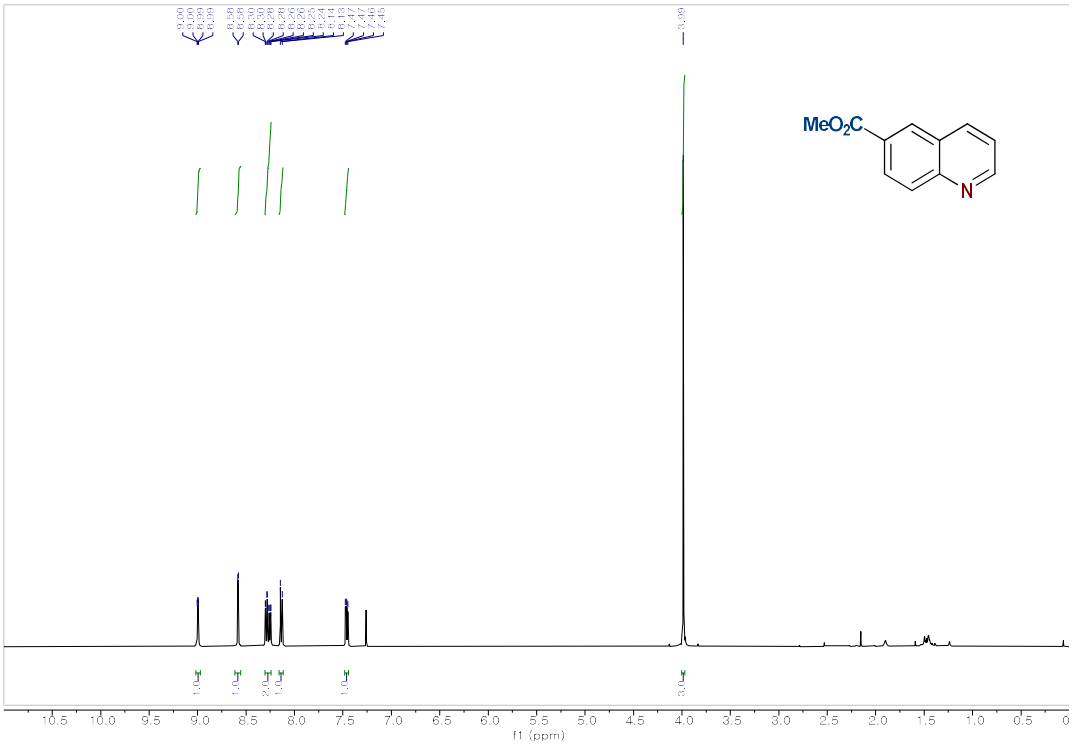


^{13}C NMR (126 MHz, $CDCl_3$)

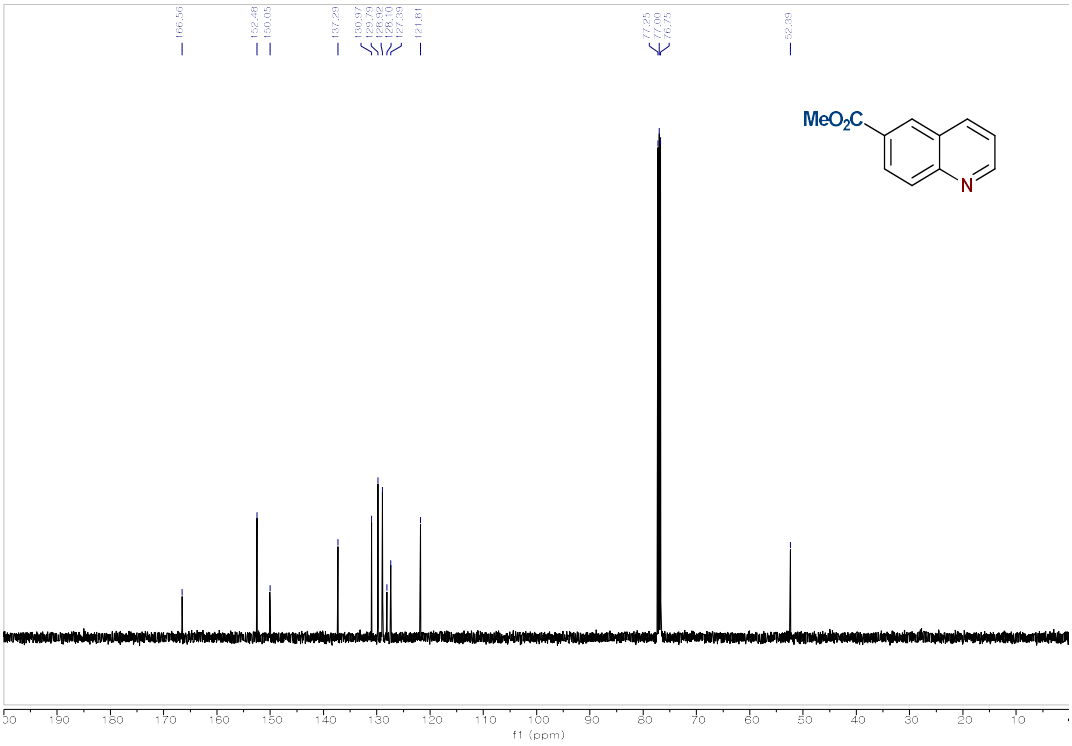


Methyl 6-Quinolinecarboxylate (3d)

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

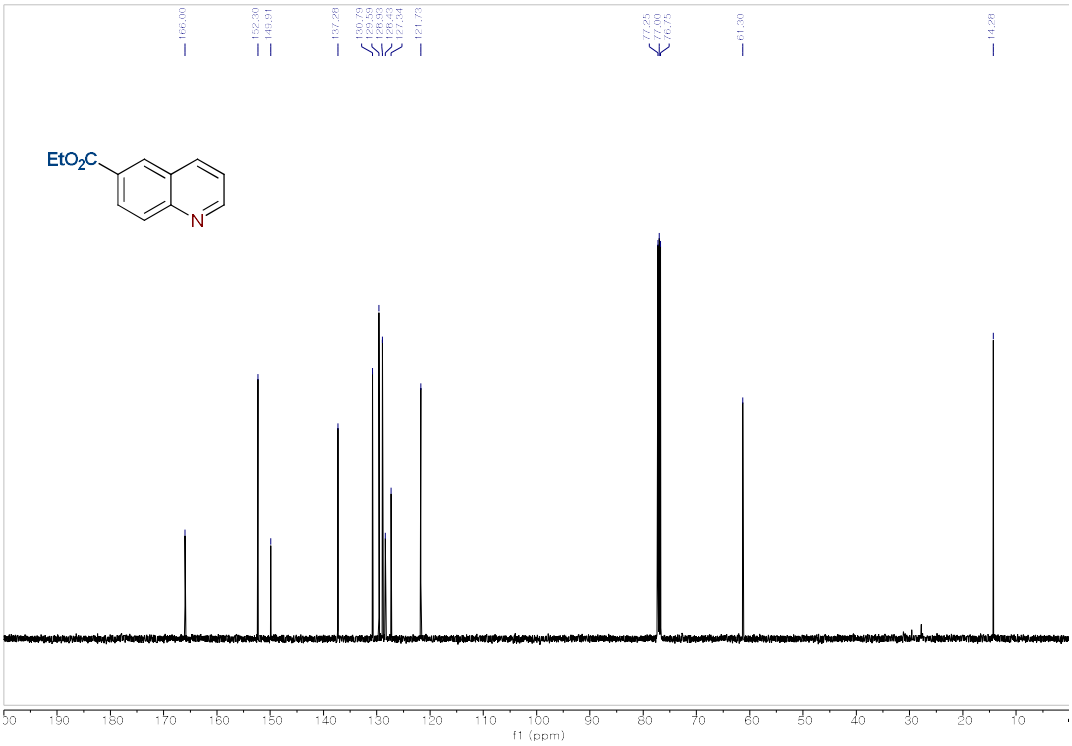


^{13}C NMR (126 MHz, $CDCl_3$)

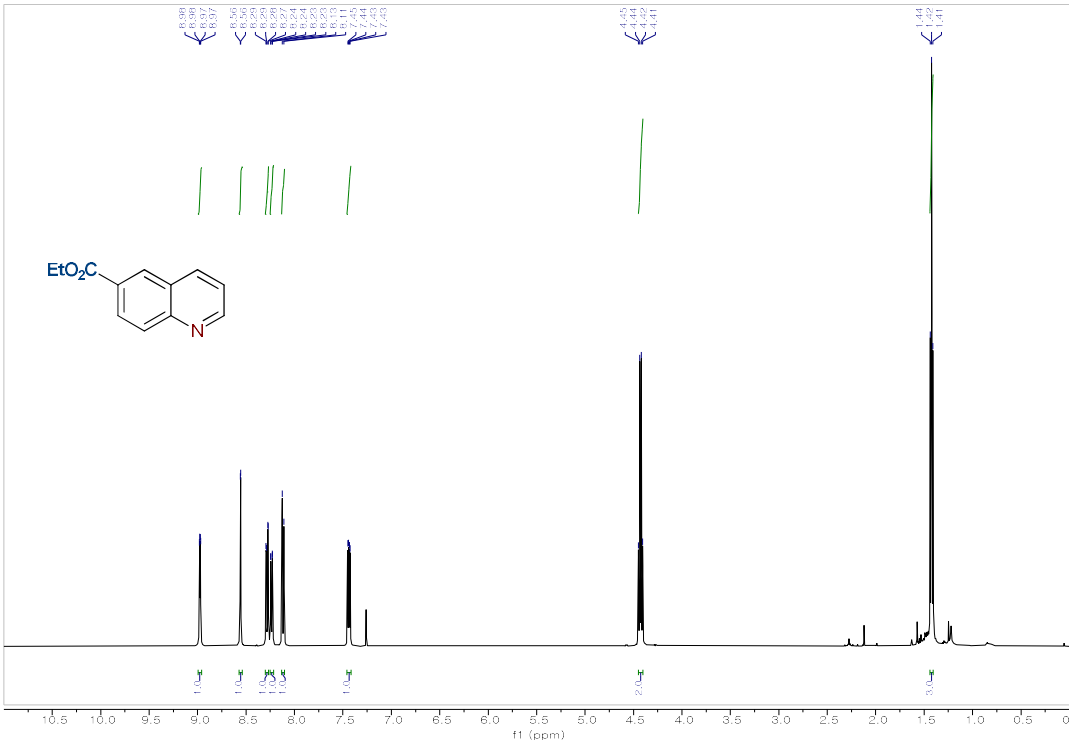


Ethyl 6-Quinolinecarboxylate (3e)

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

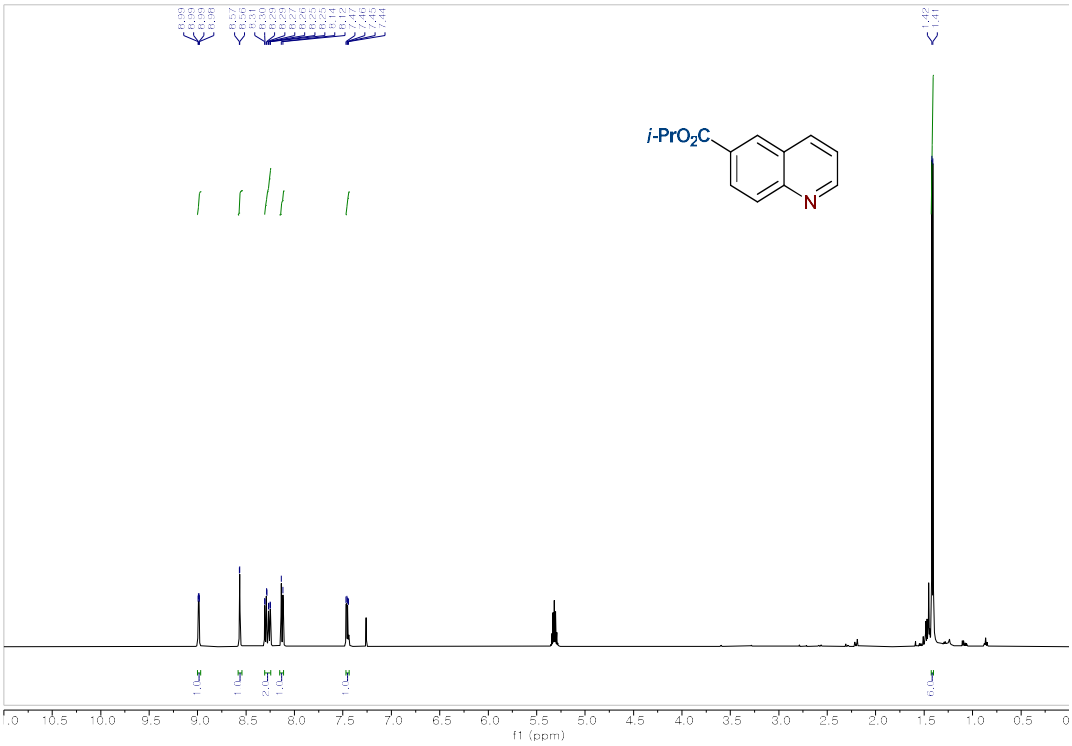


^{13}C NMR (126 MHz, $CDCl_3$)

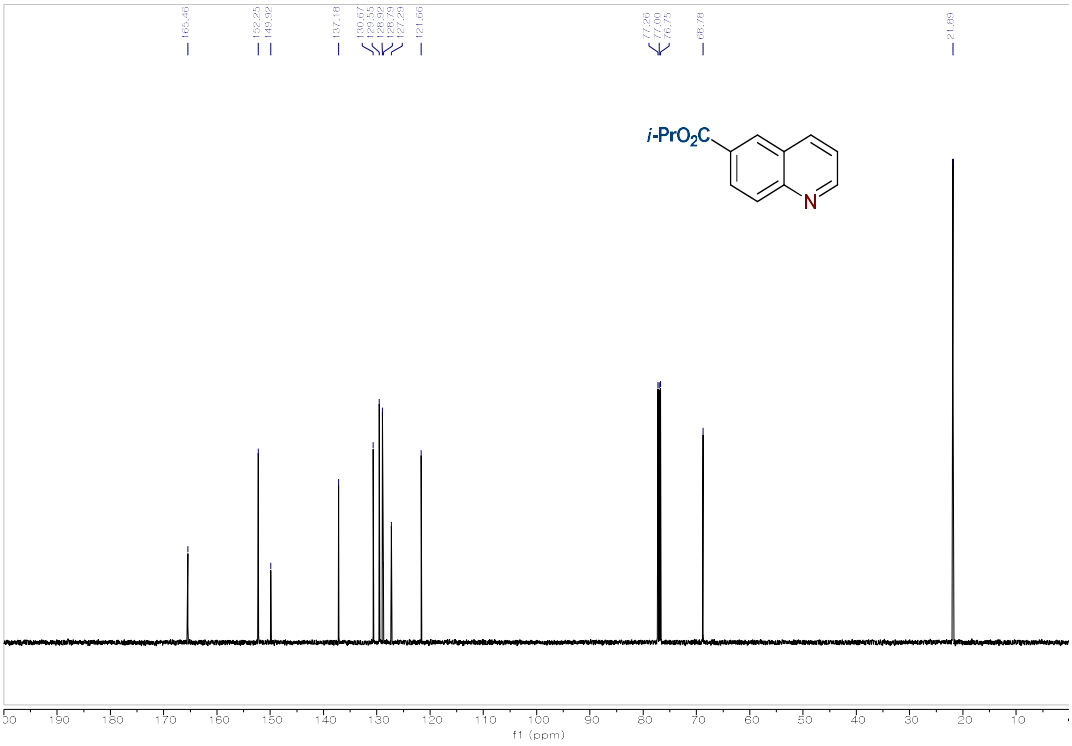


Isopropyl 6-Quinolinecarboxylate (3f)

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

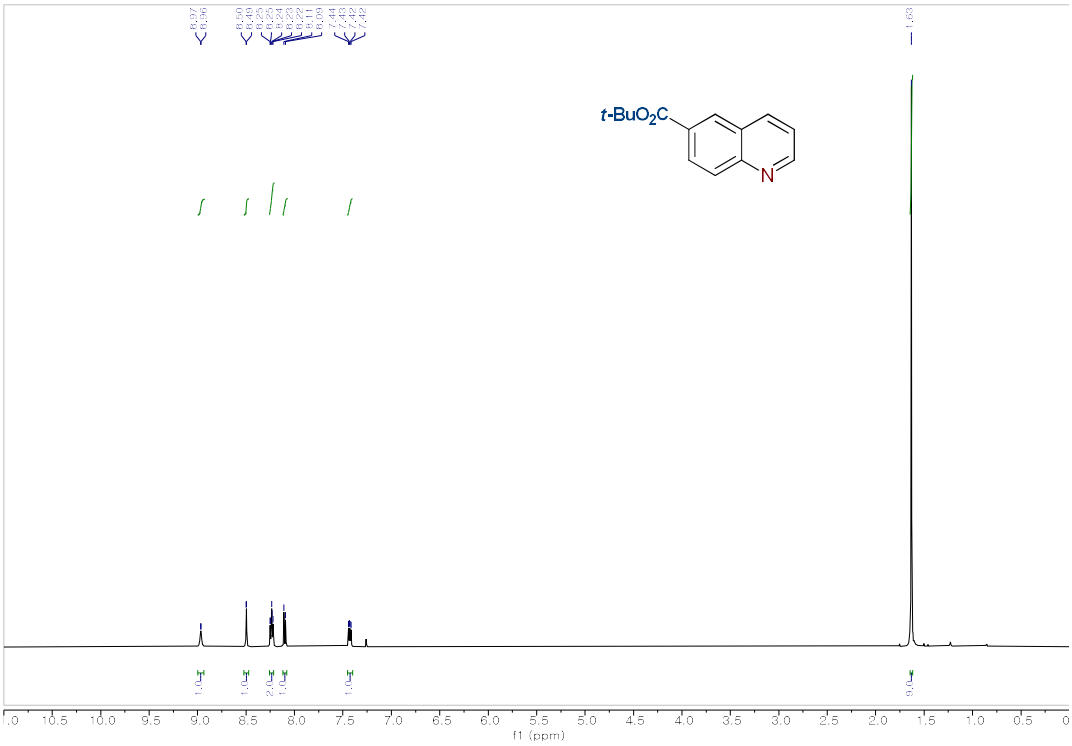


^{13}C NMR (126 MHz, $CDCl_3$)

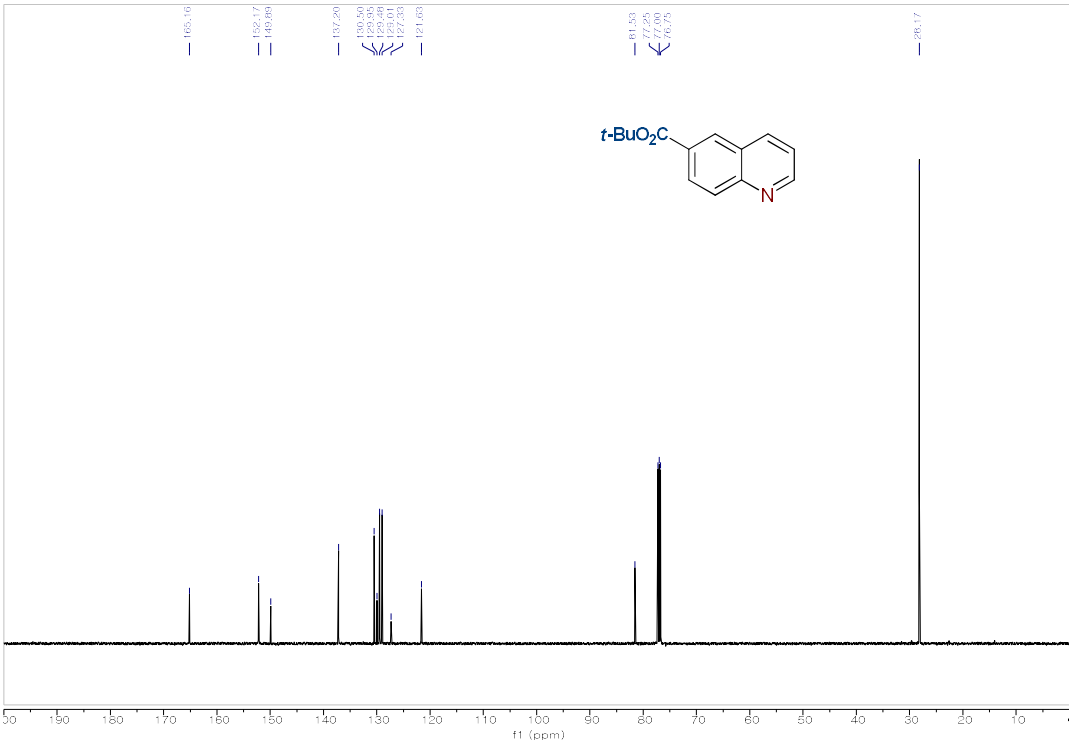


***tert*-Butyl 6-Quinolinecarboxylate (3g)**

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

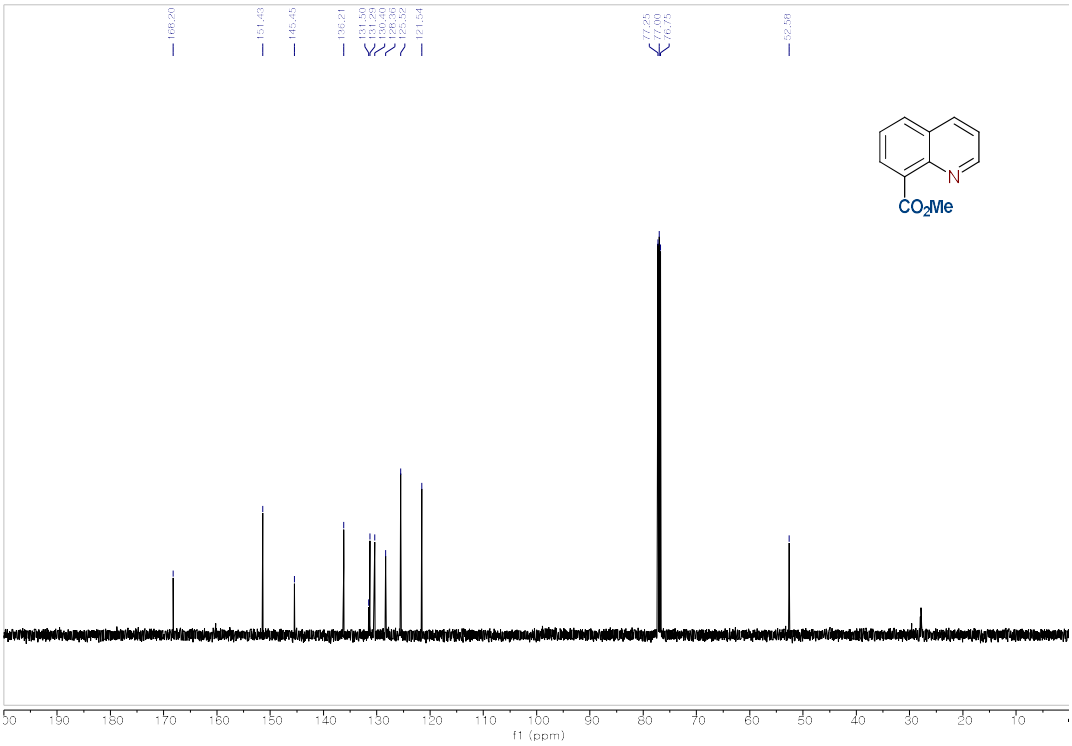


^{13}C NMR (126 MHz, $CDCl_3$)

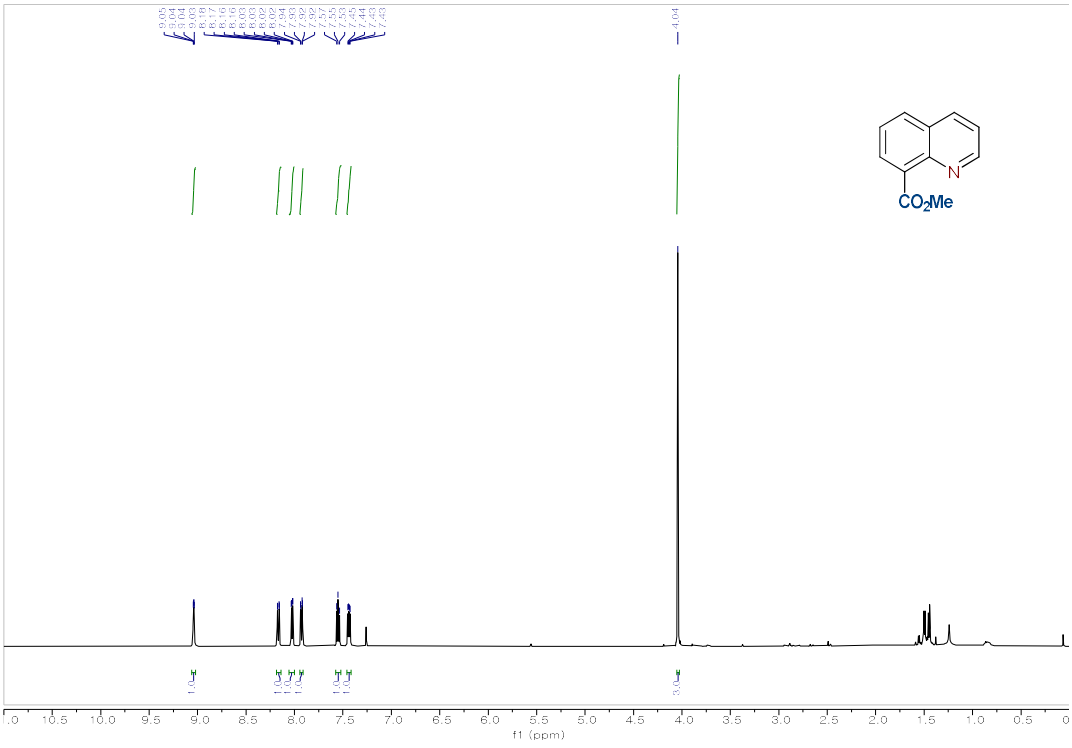


Methyl 8-Quinolinecarboxylate (3h)

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

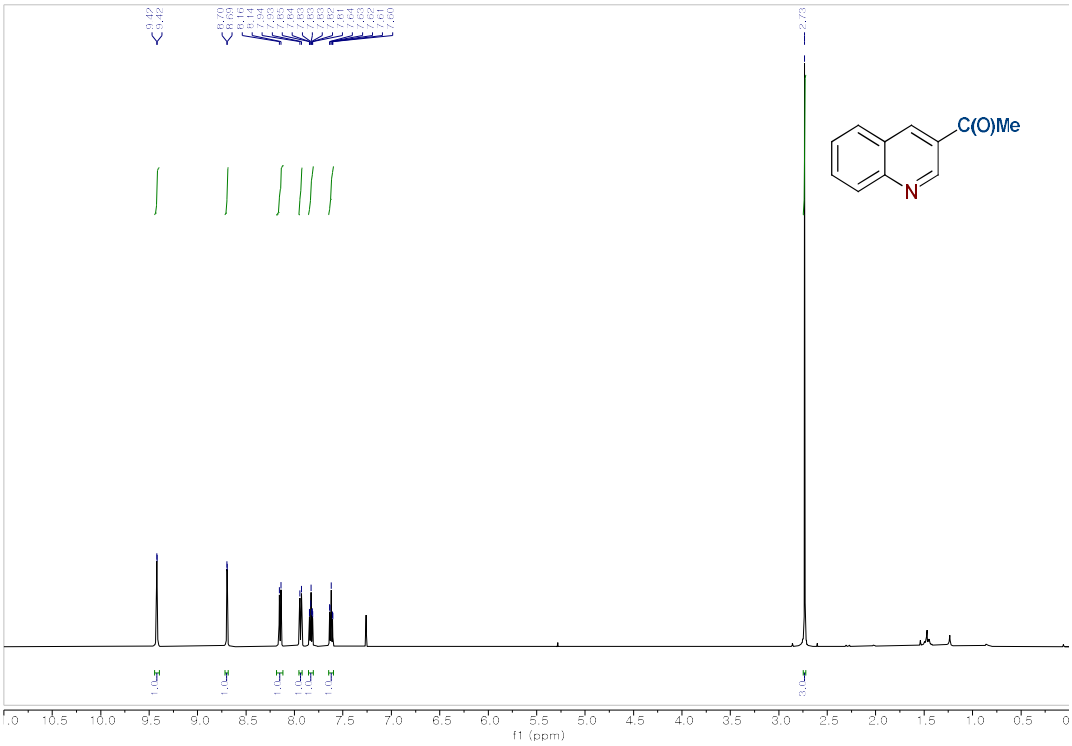


^{13}C NMR (126 MHz, $CDCl_3$)

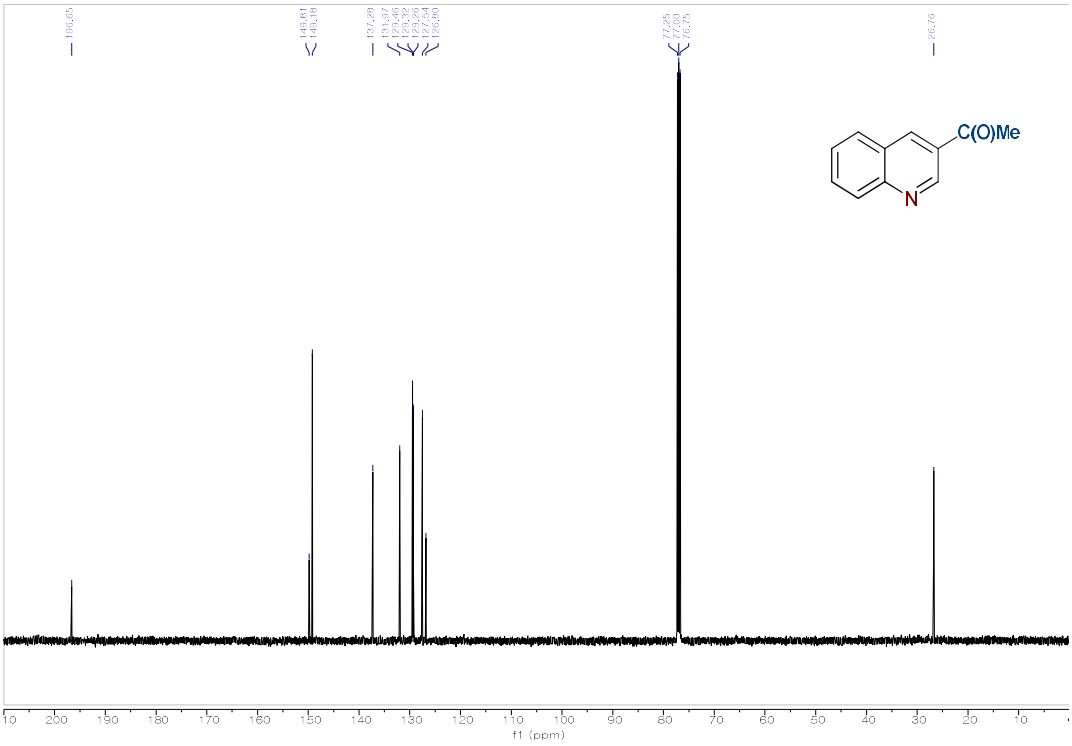


3-Acetylquinoline (3i)

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

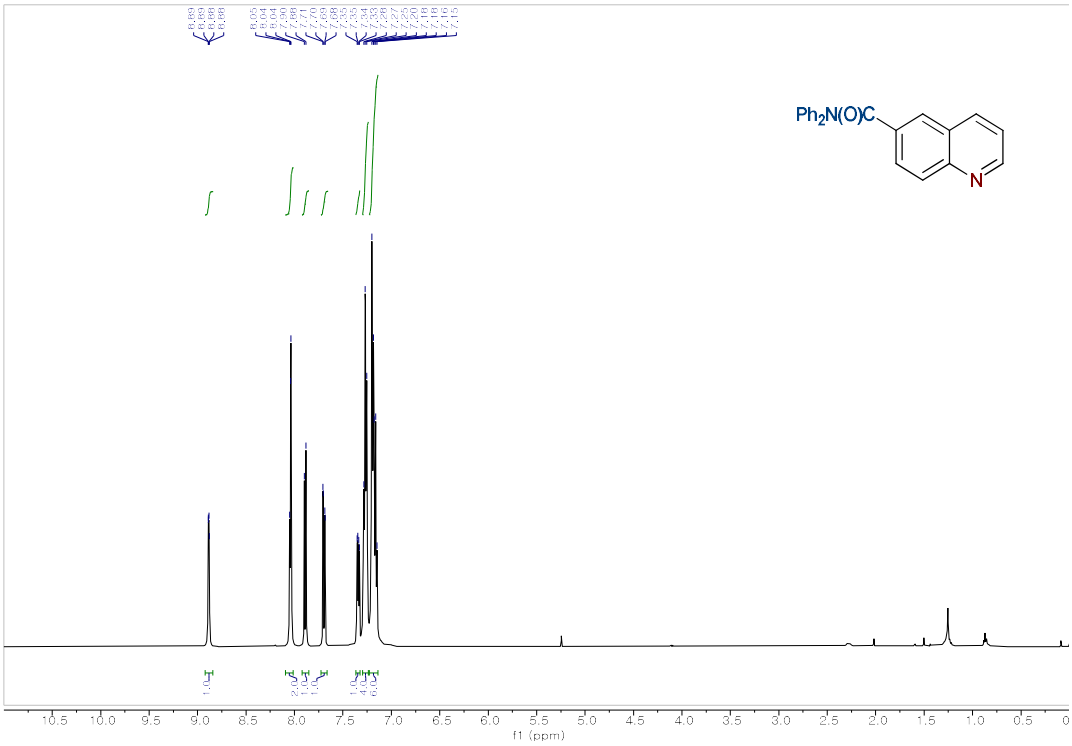


^{13}C NMR (126 MHz, $CDCl_3$)

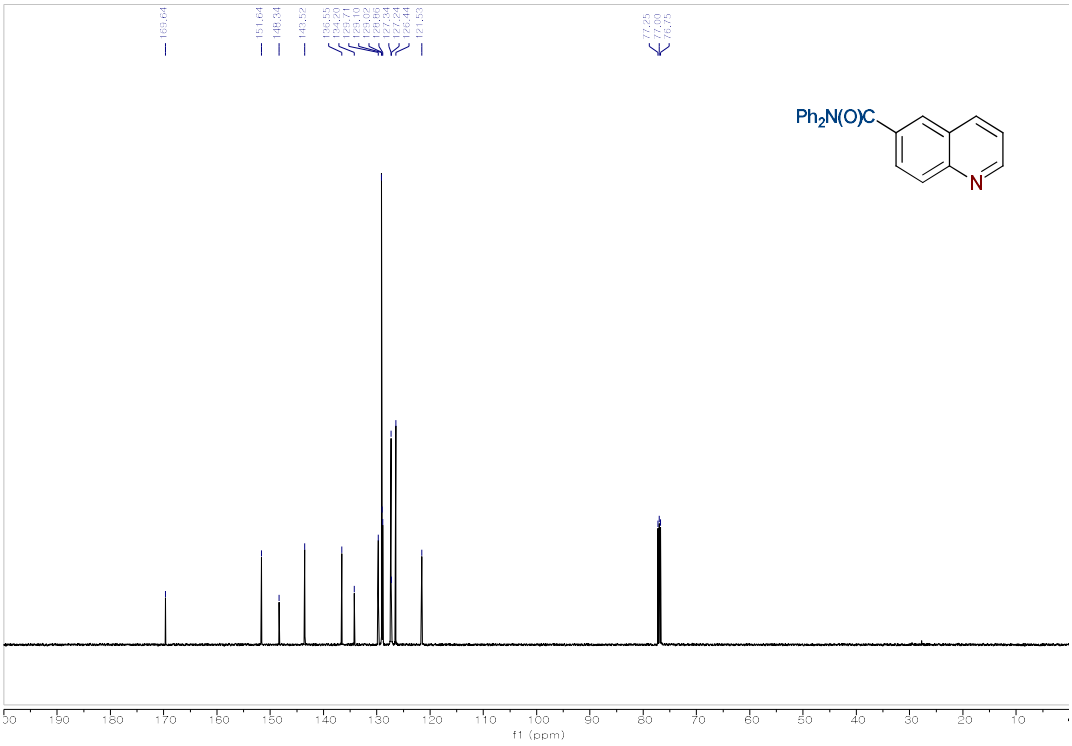


***N,N*-Dimethyl-6-quinolinecarboxamide (3j)**

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

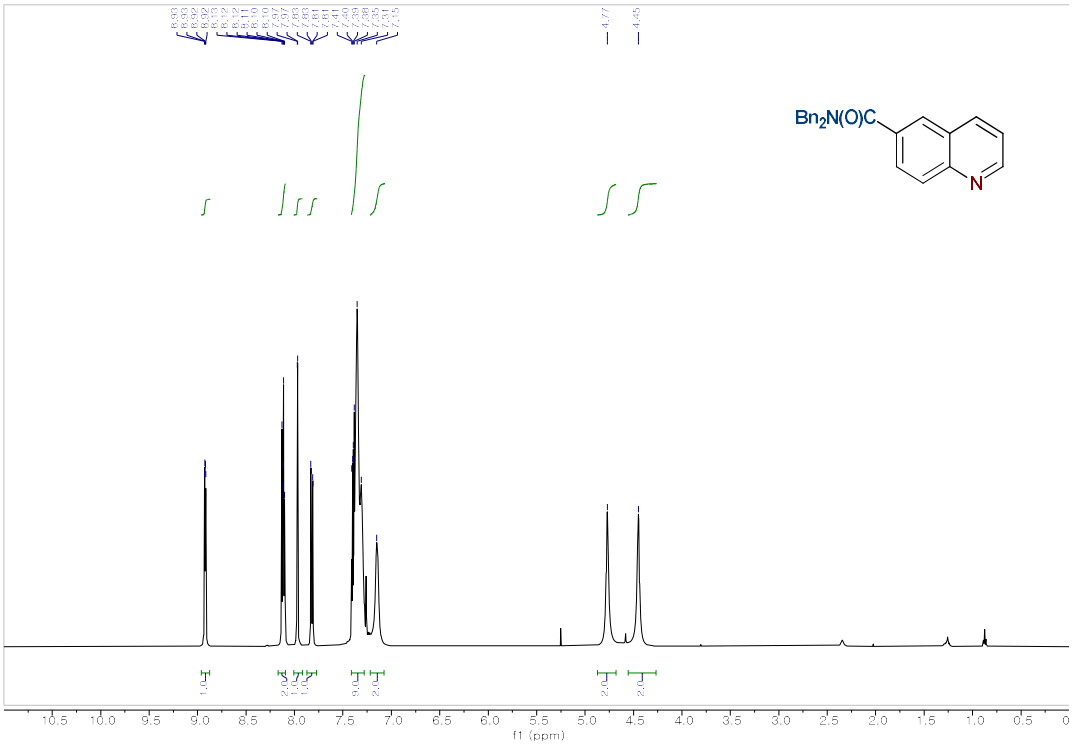


^{13}C NMR (126 MHz, $CDCl_3$)

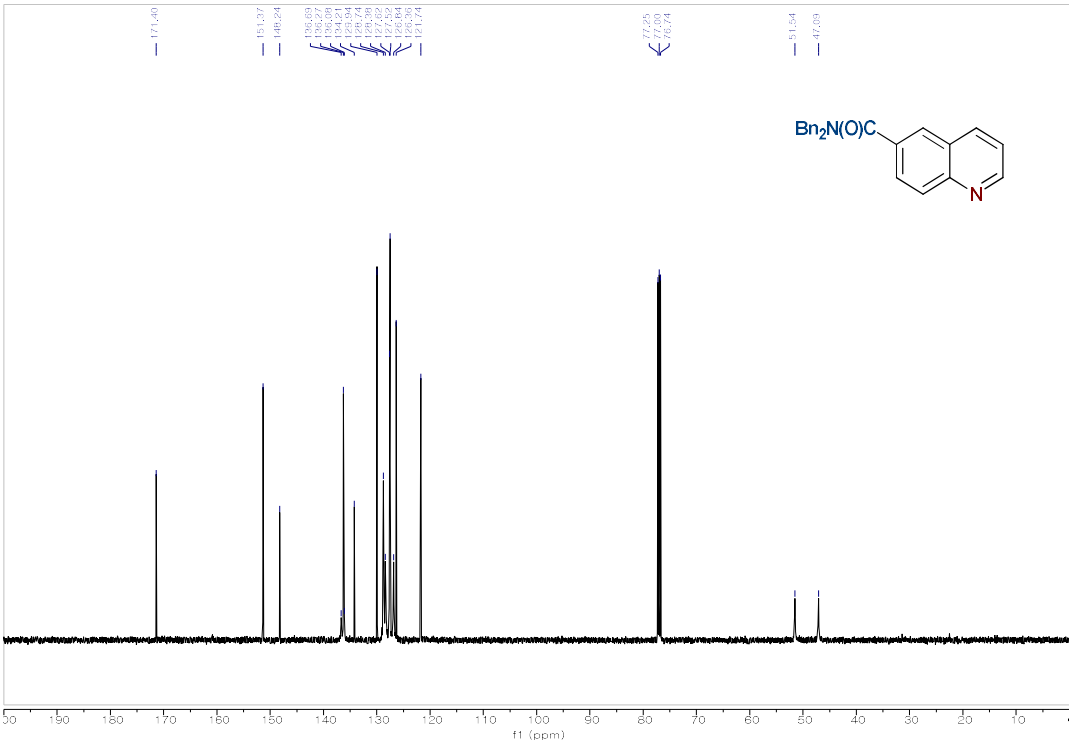


***N,N*-Dibenzyl-6-quinolinecarboxamide (3k)**

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

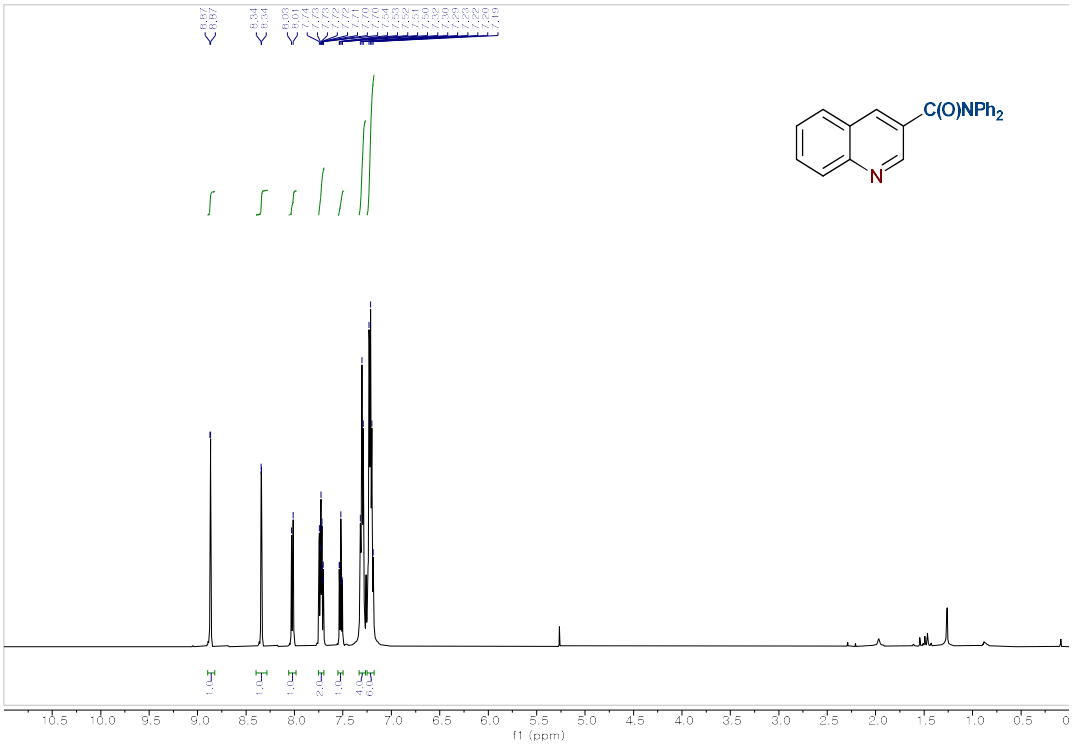


^{13}C NMR (126 MHz, $CDCl_3$)

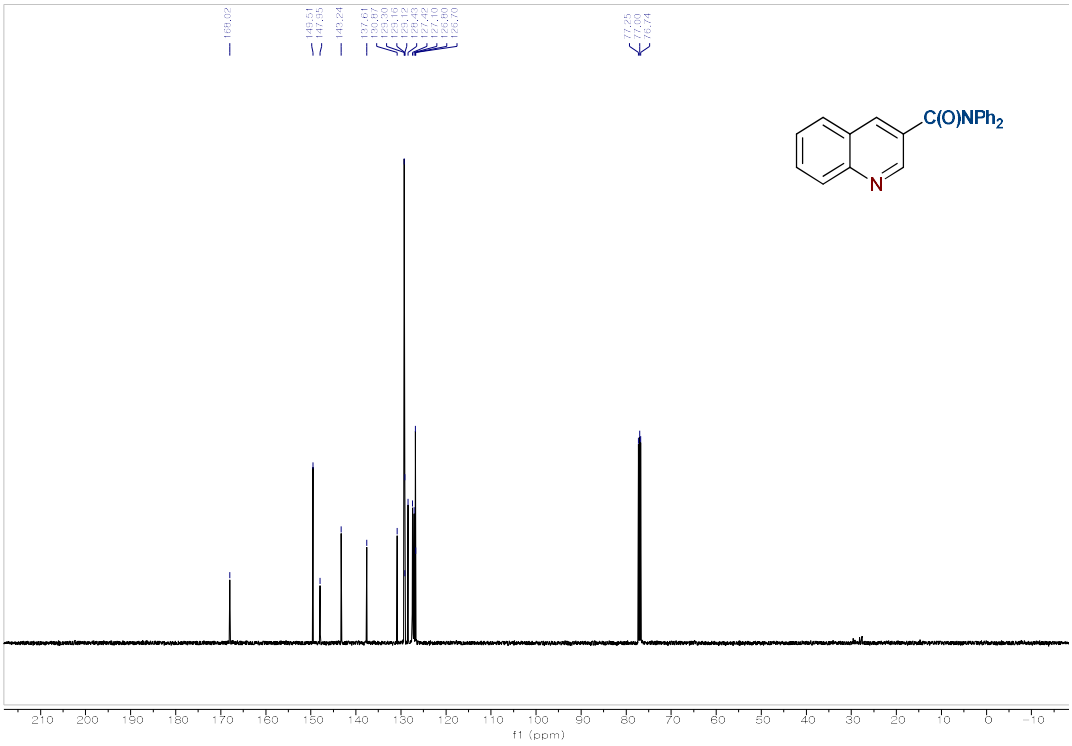


***N,N*-Diphenyl-3-quinolinecarboxamide (3l)**

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

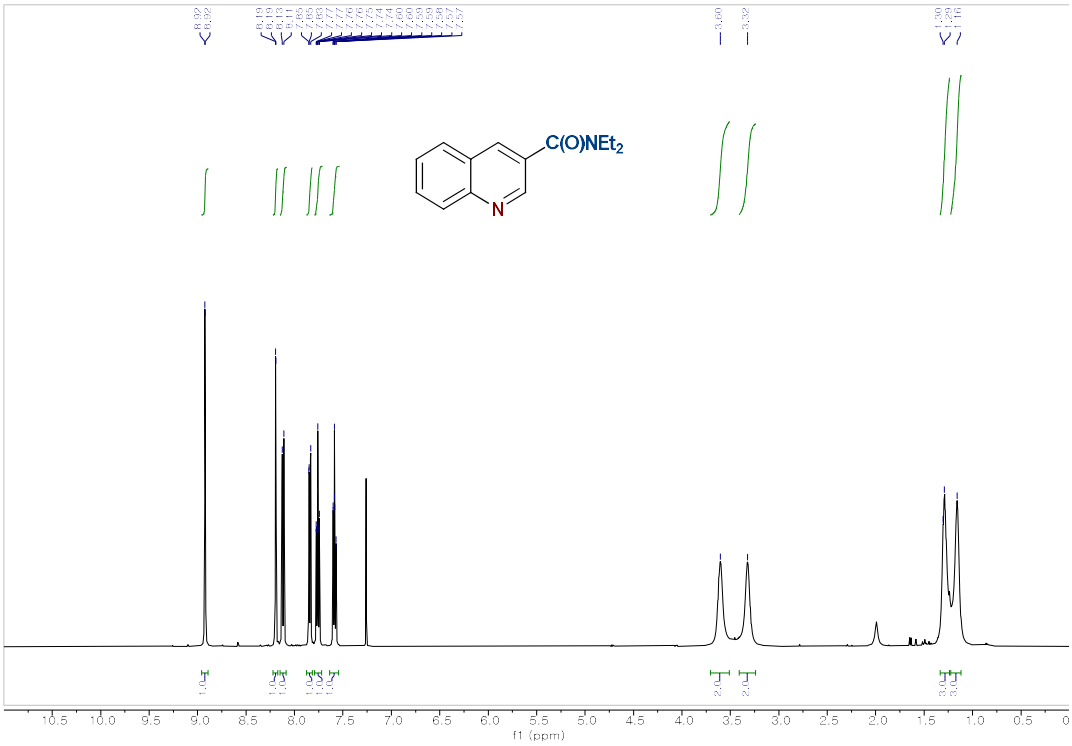


^{13}C NMR (126 MHz, $CDCl_3$)

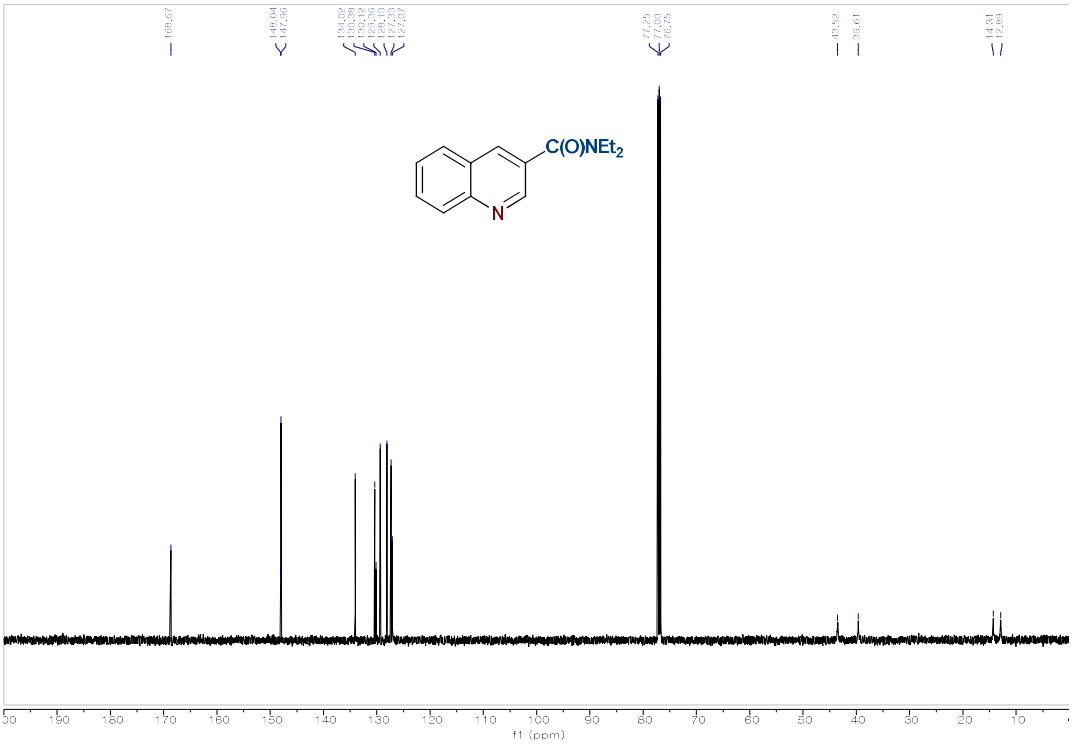


***N*,*N*-Diethyl-3-quinolinecarboxamide (3m)**

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

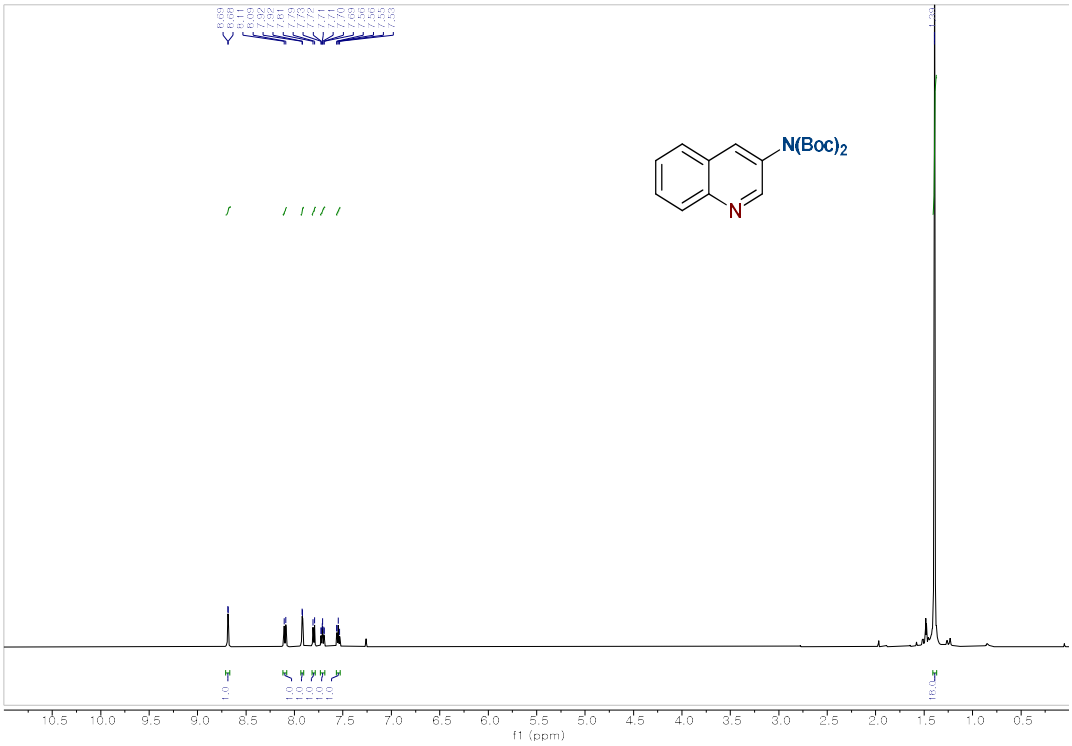


^{13}C NMR (126 MHz, $CDCl_3$)

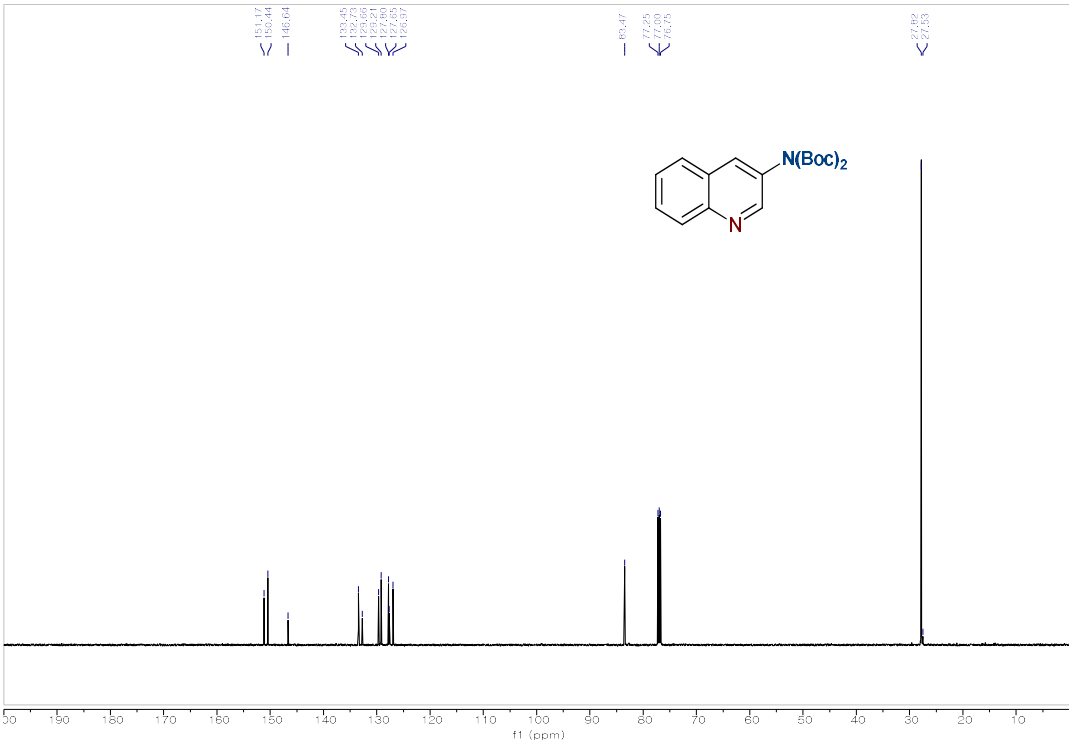


3-[Bis(*tert*-butoxycarbonyl)amino]quinoline (3n)

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

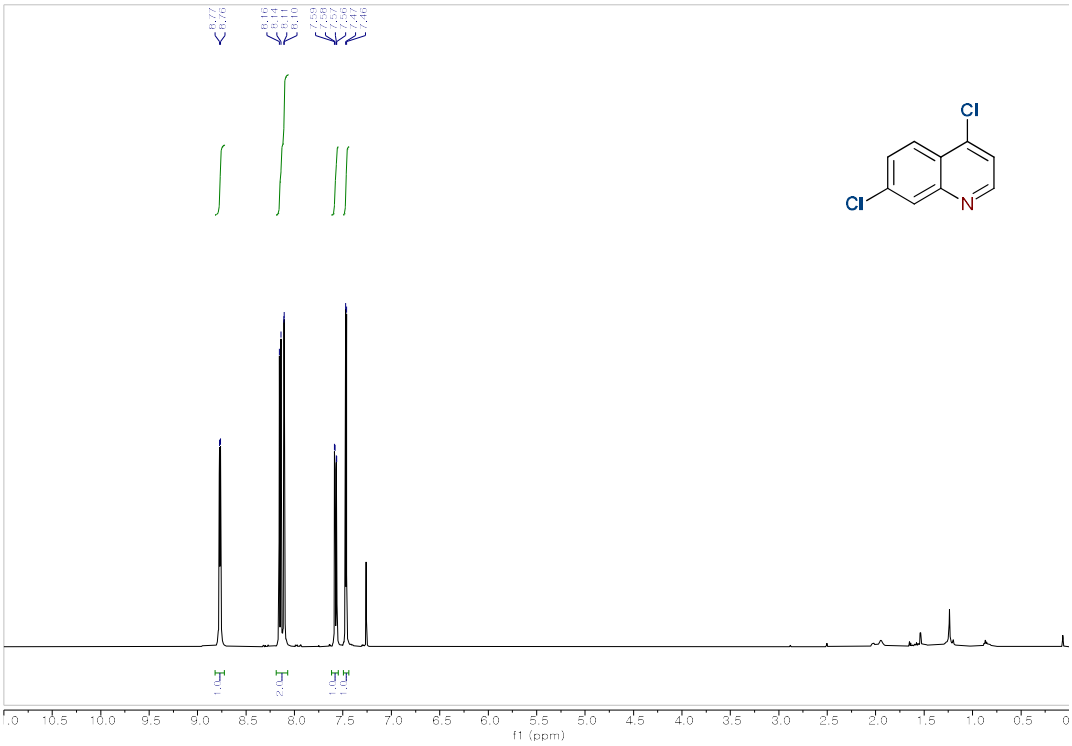


^{13}C NMR (126 MHz, $CDCl_3$)

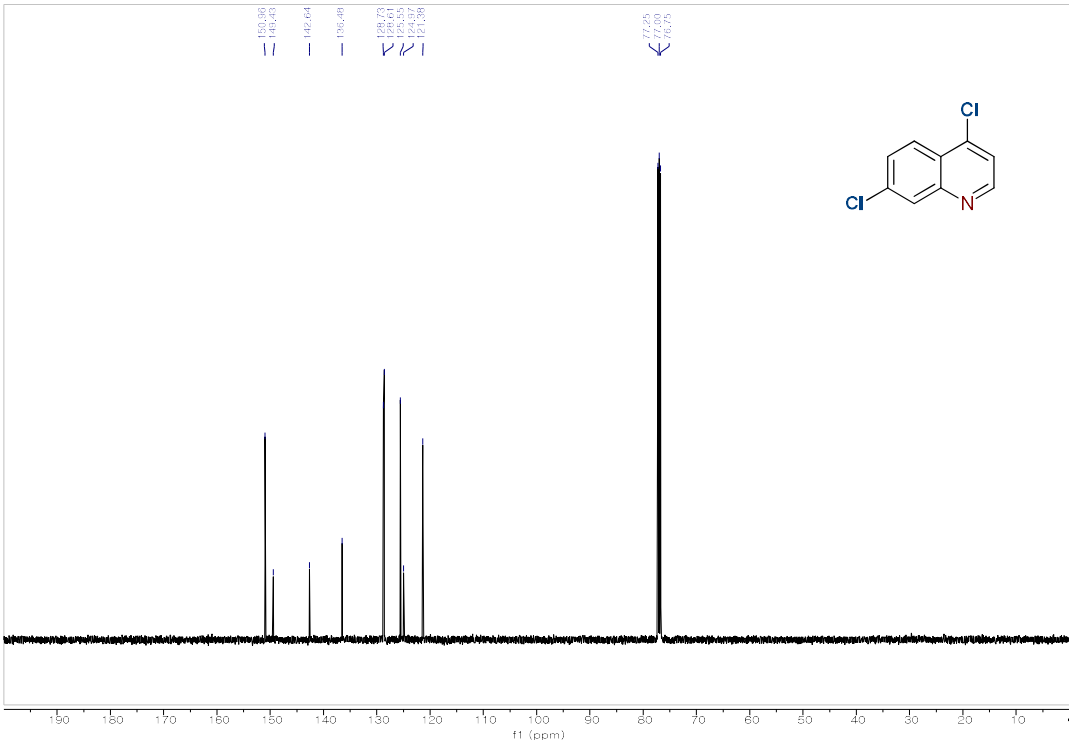


4,7-Dichloroquinoline (3o)

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

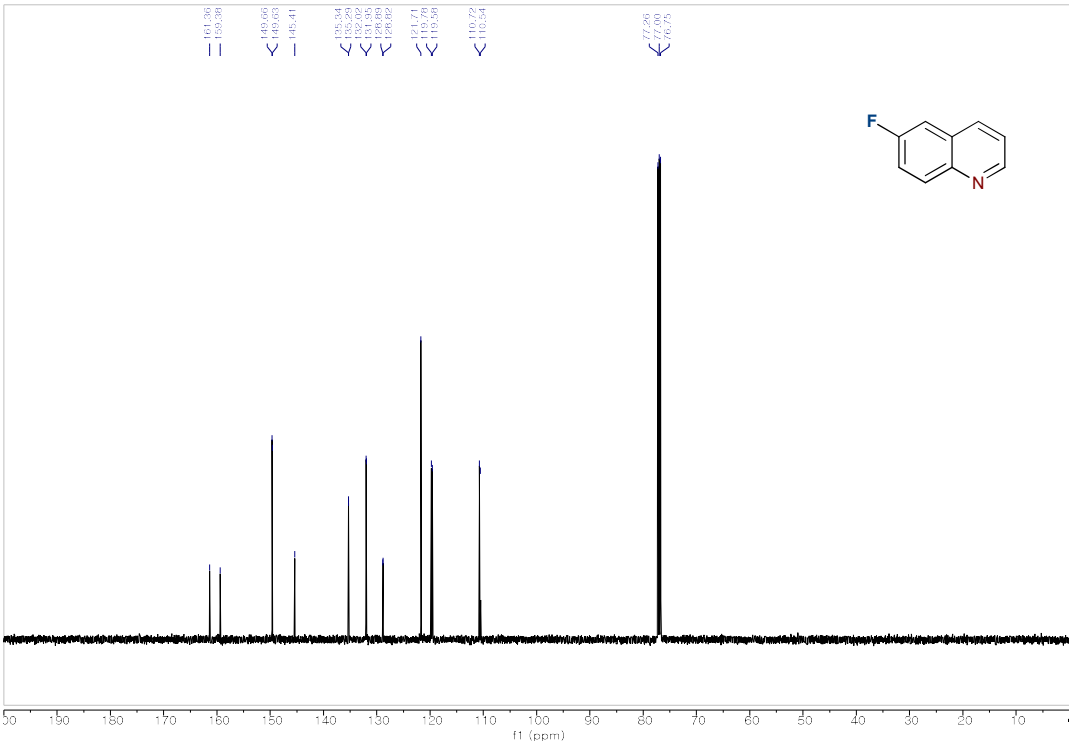


^{13}C NMR (126 MHz, $CDCl_3$)

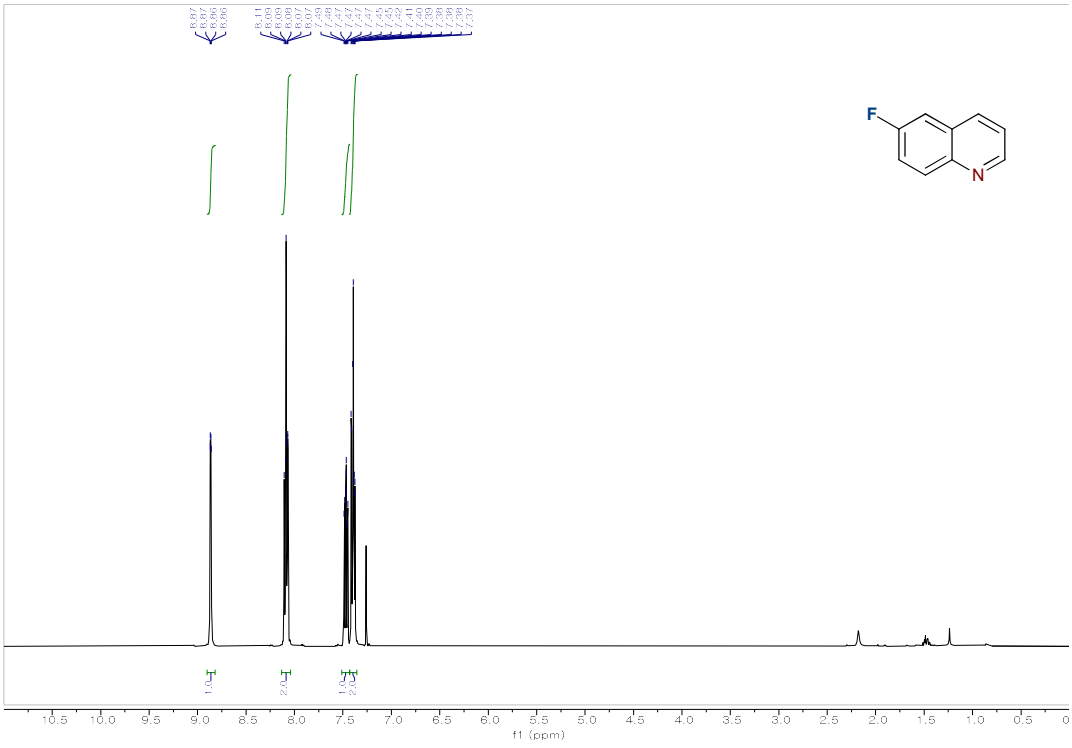


6-Fluoroquinoline(3p)

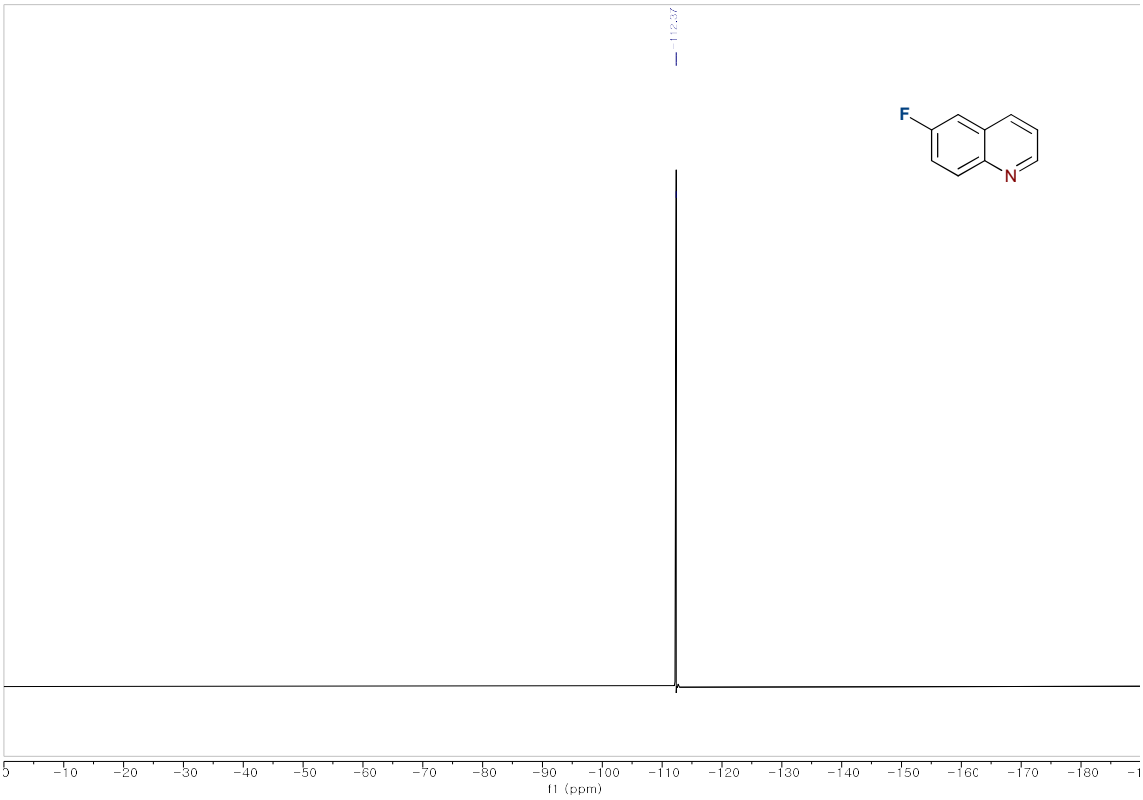
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

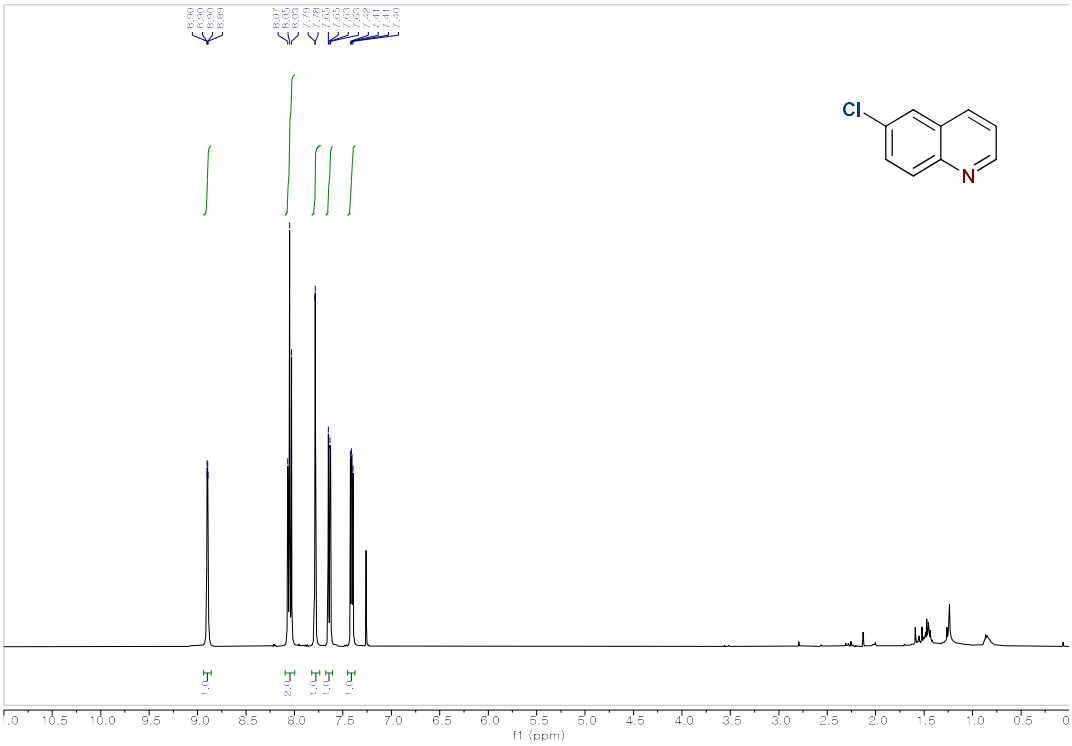


^{19}F NMR (471 MHz, $CDCl_3$)

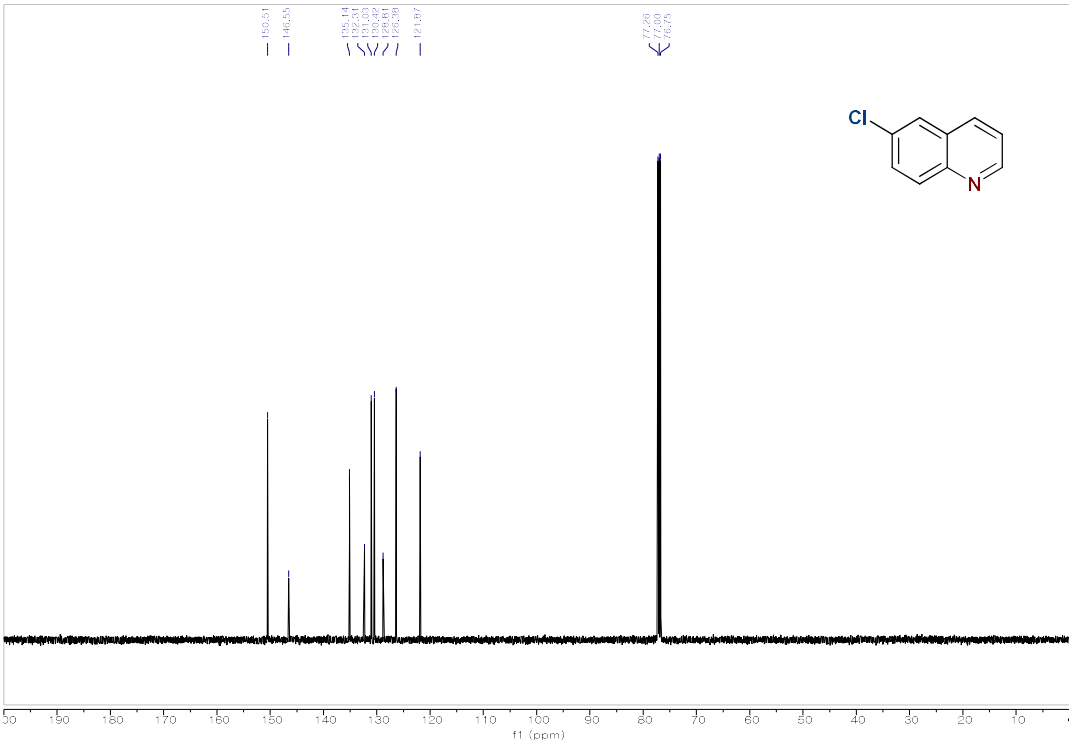


6-Chloroquinoline (3q)

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

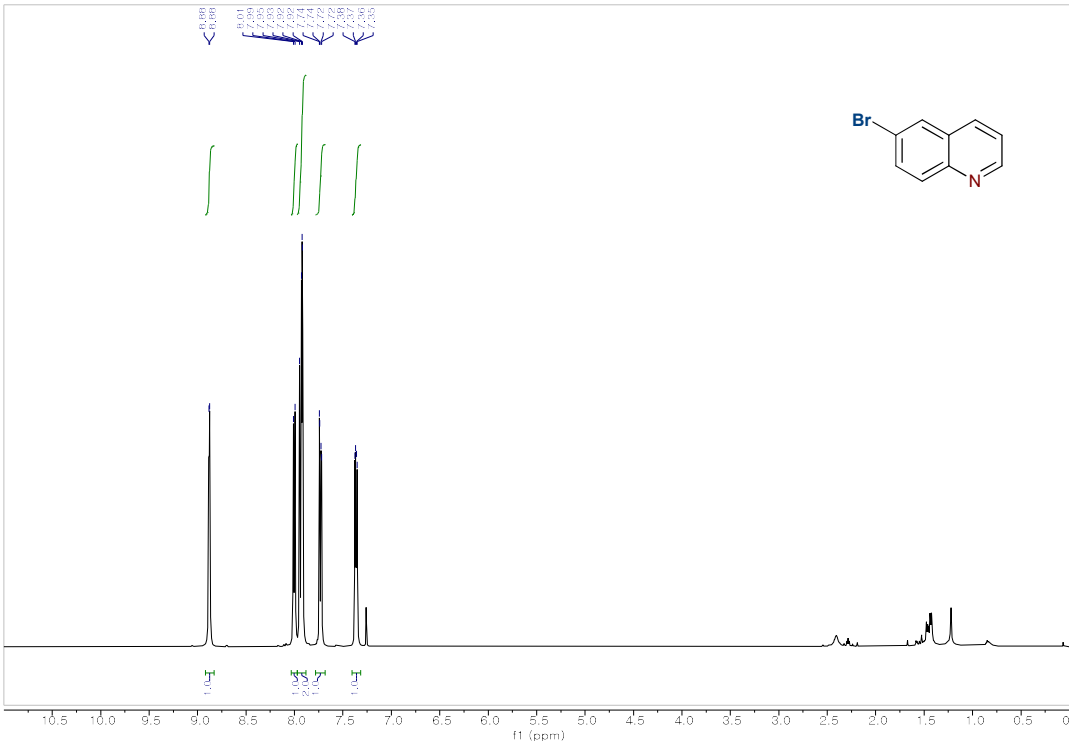


^{13}C NMR (126 MHz, $CDCl_3$)

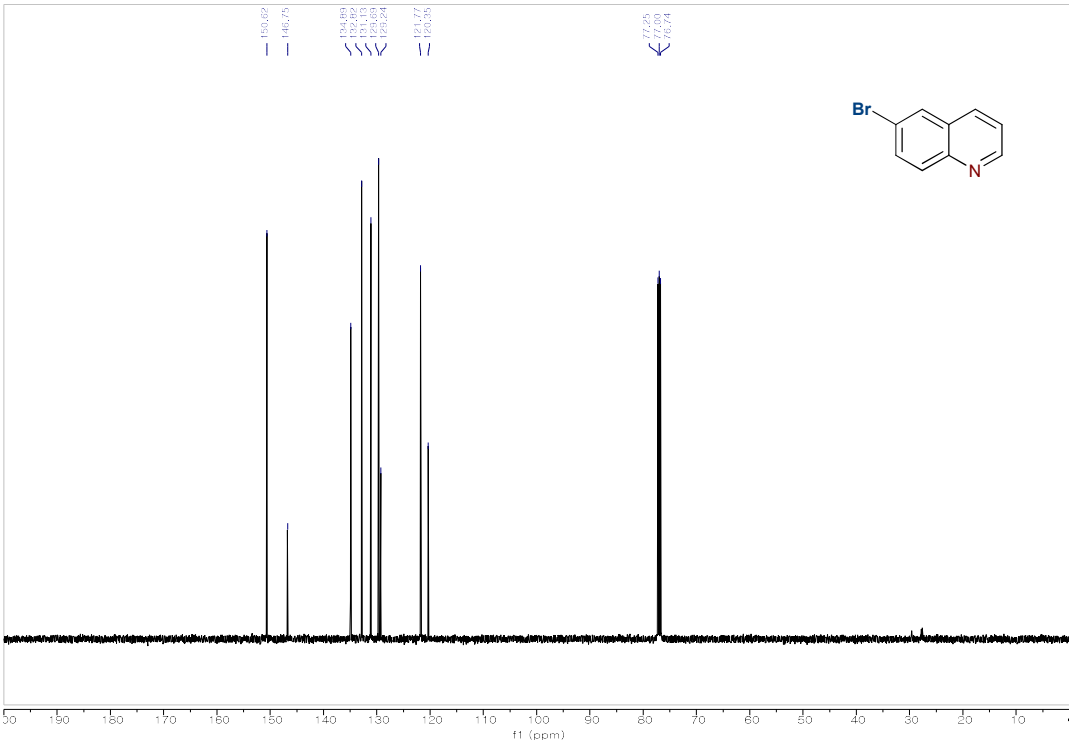


6-Bromoquinoline (3r)

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

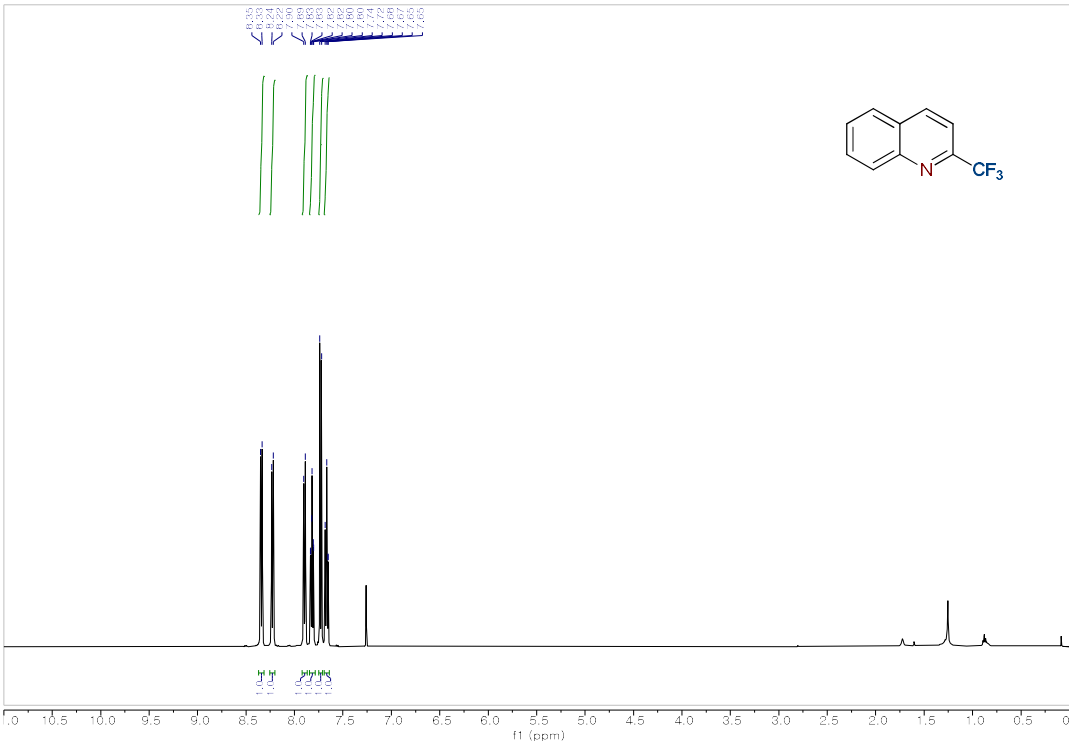


^{13}C NMR (126 MHz, $CDCl_3$)

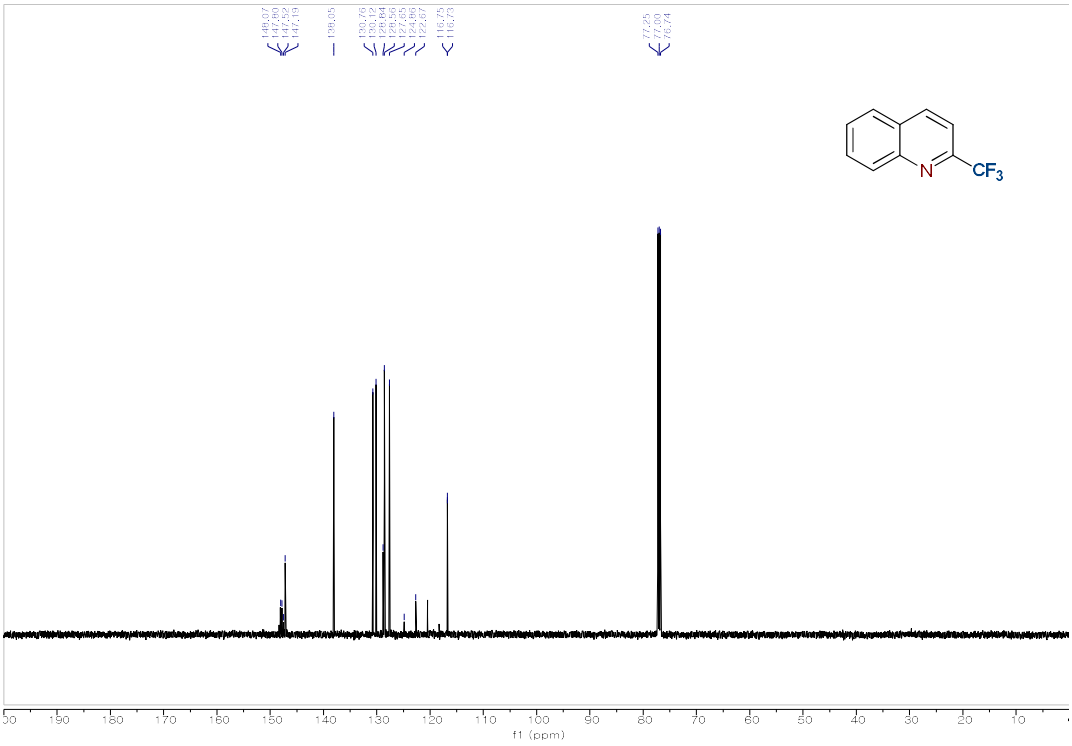


2-(Trifluoromethyl)quinoline(3s)

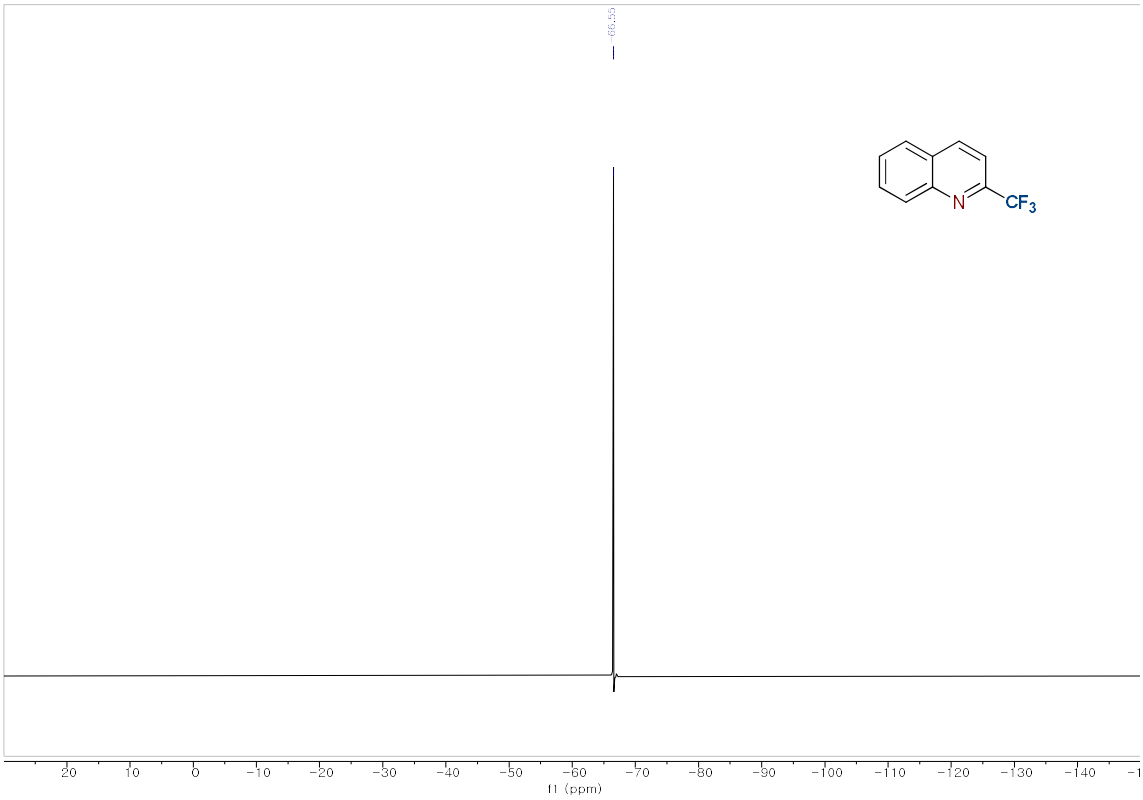
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

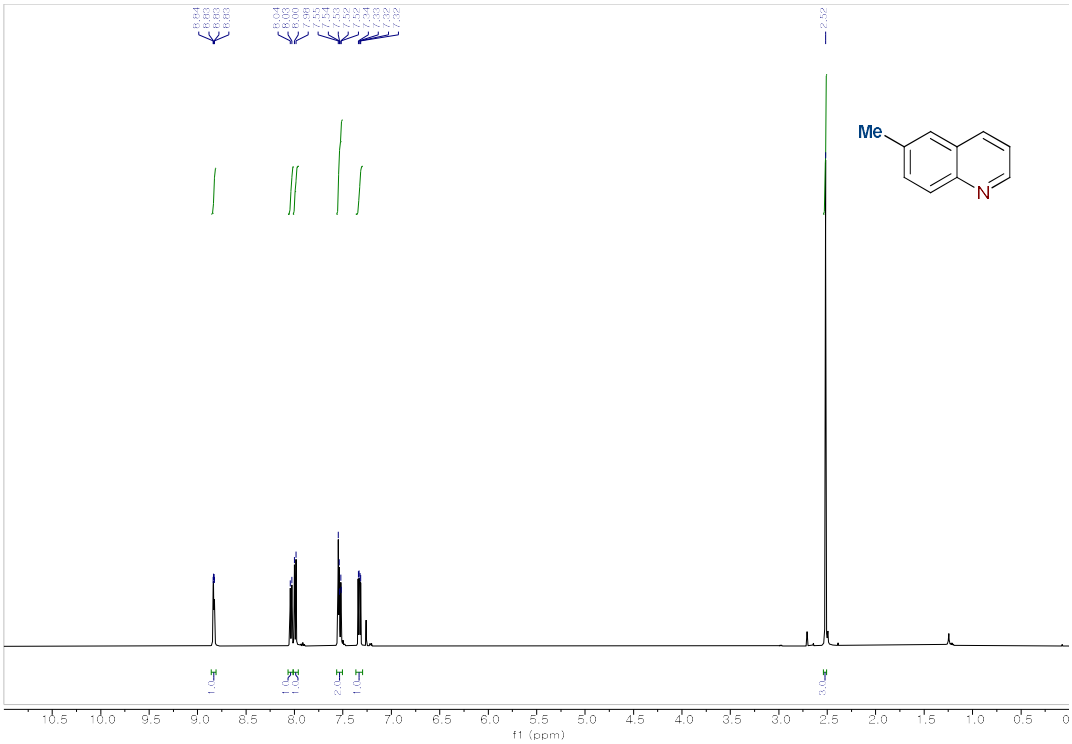


^{19}F NMR (471 MHz, $CDCl_3$)

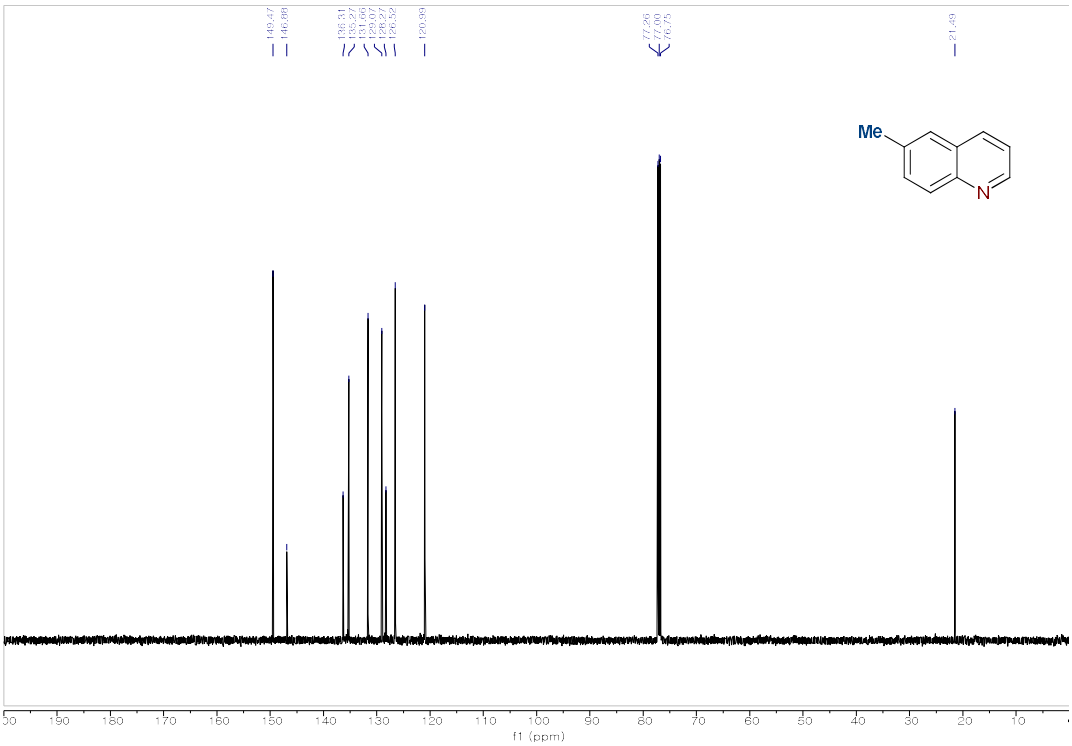


6-Methylquinoline (3t)

^{1}H NMR (400 MHz, $CDCl_3$)

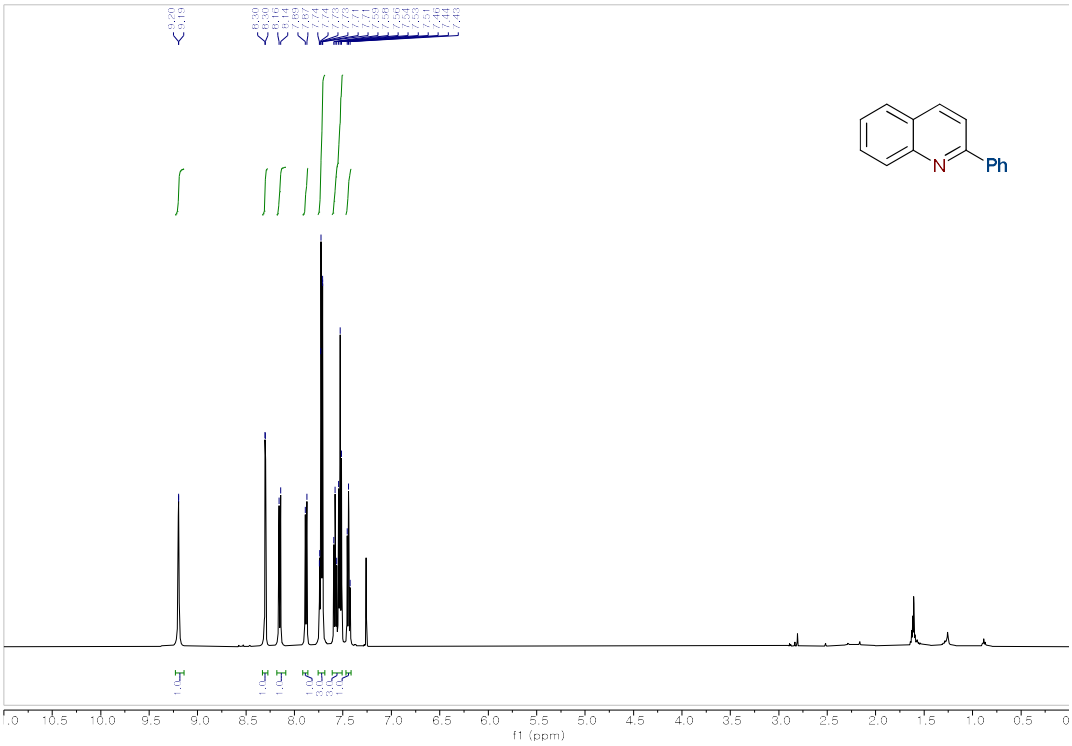


^{13}C NMR (101 MHz, $CDCl_3$)

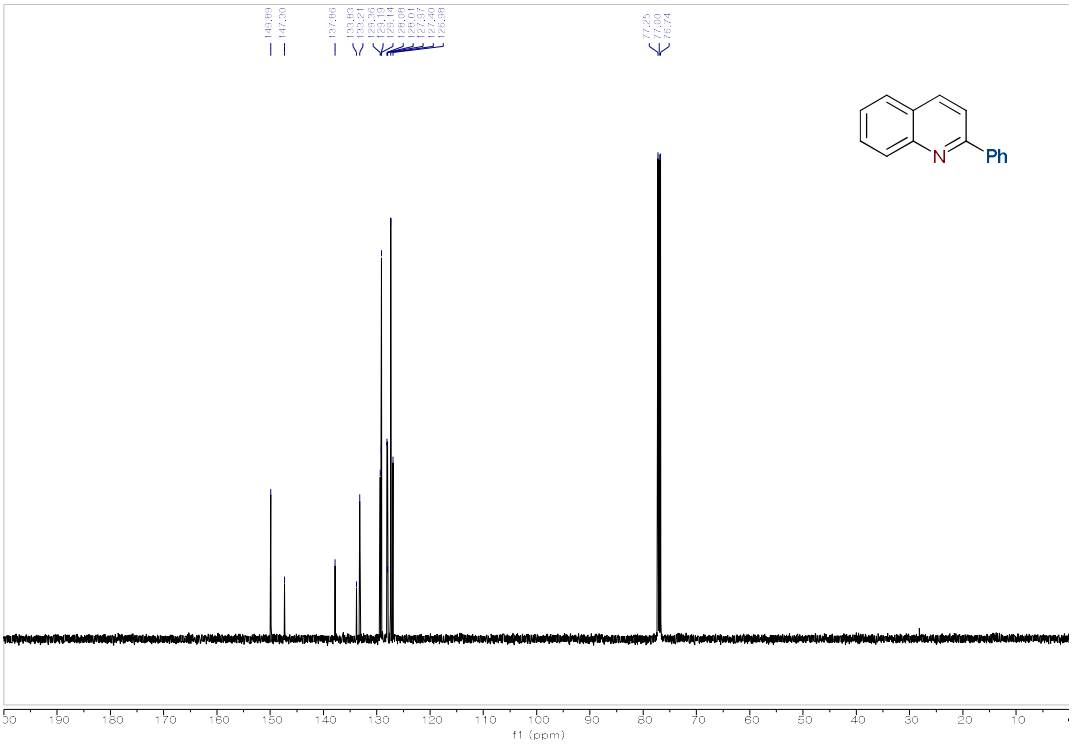


2-Phenylquinoline (3u)

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

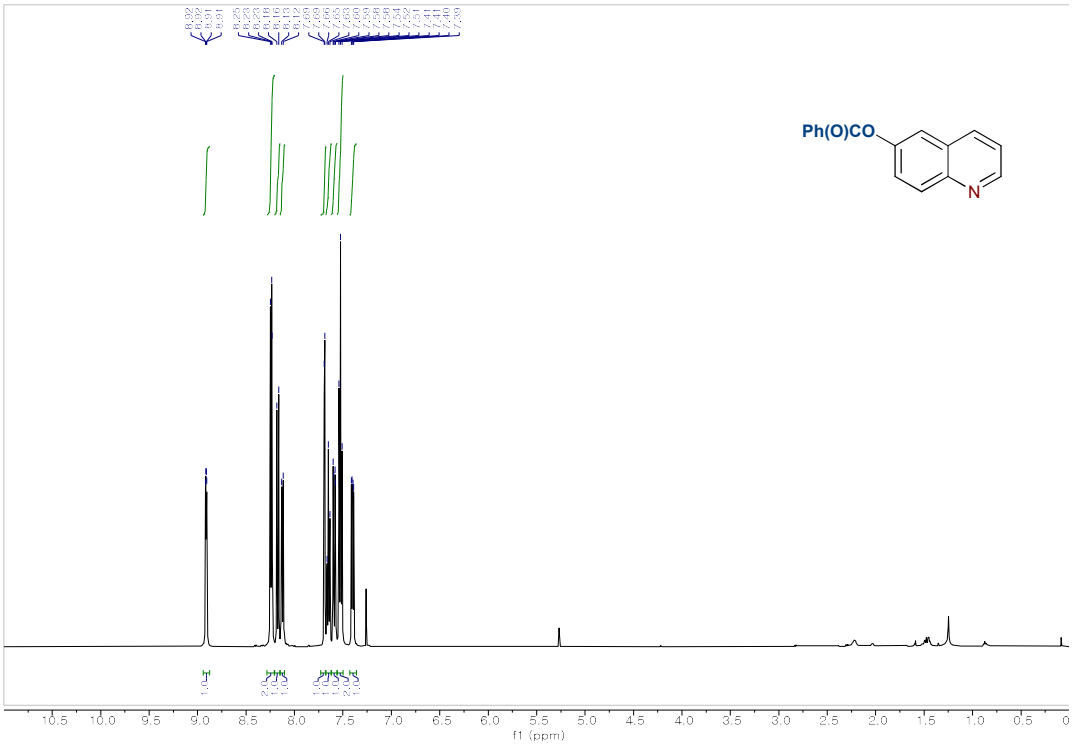


^{13}C NMR (126 MHz, $CDCl_3$)

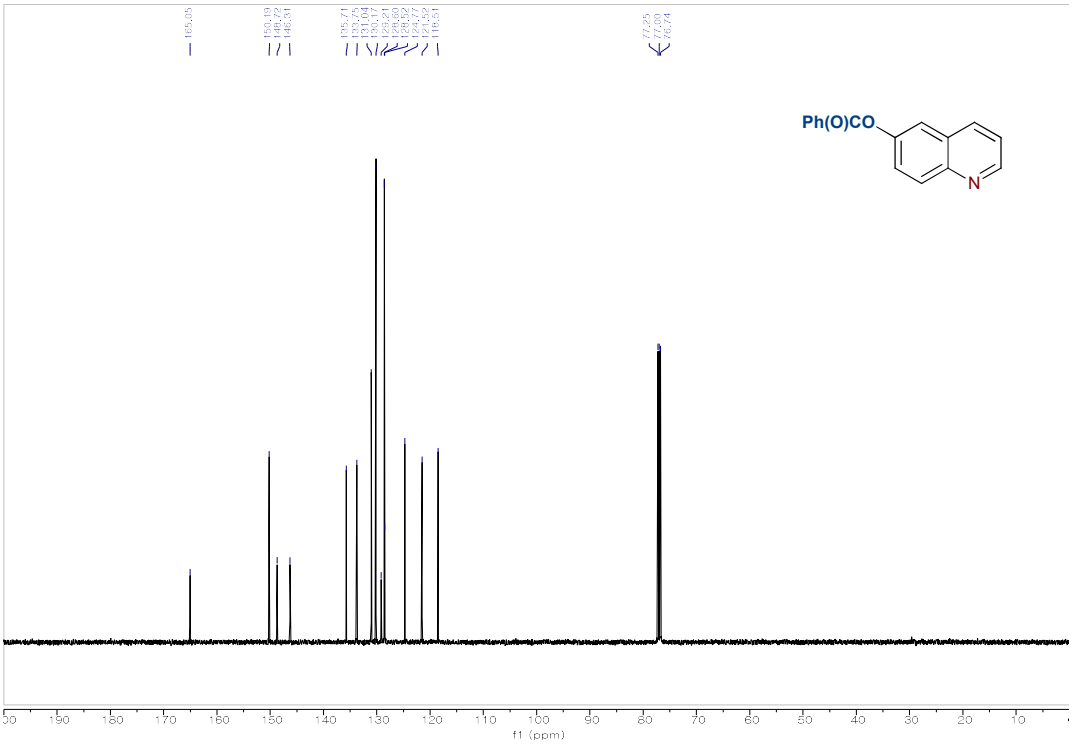


6-Benzoyloxyquinoline (3v)

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

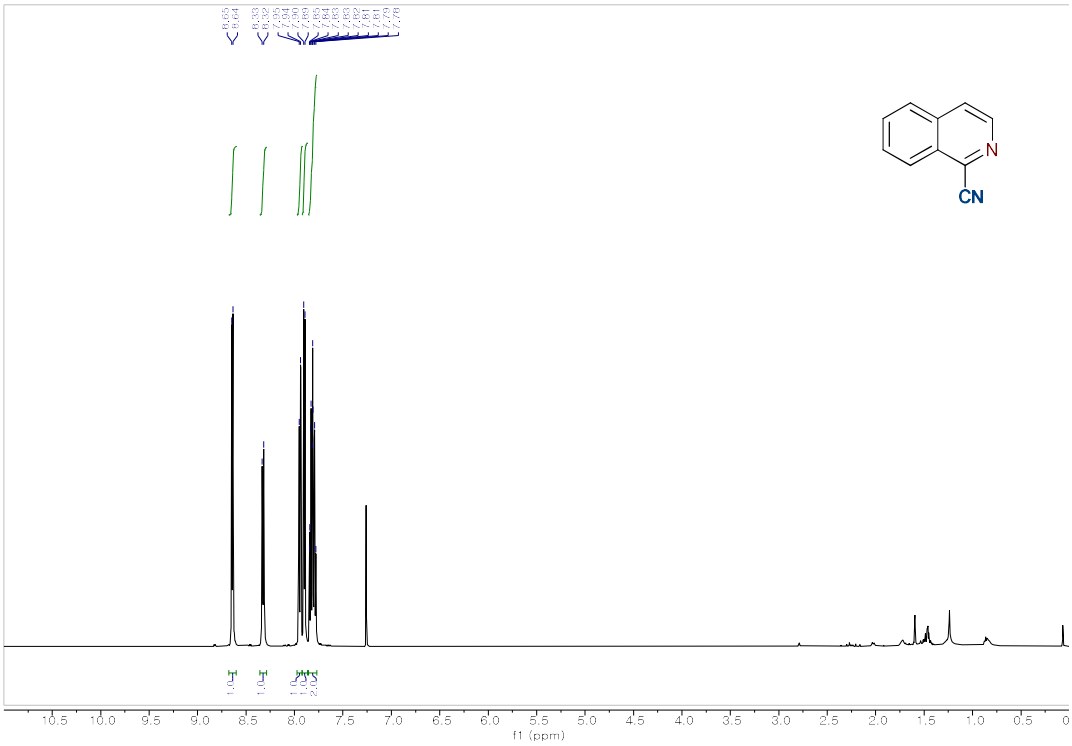


^{13}C NMR (126 MHz, $CDCl_3$)

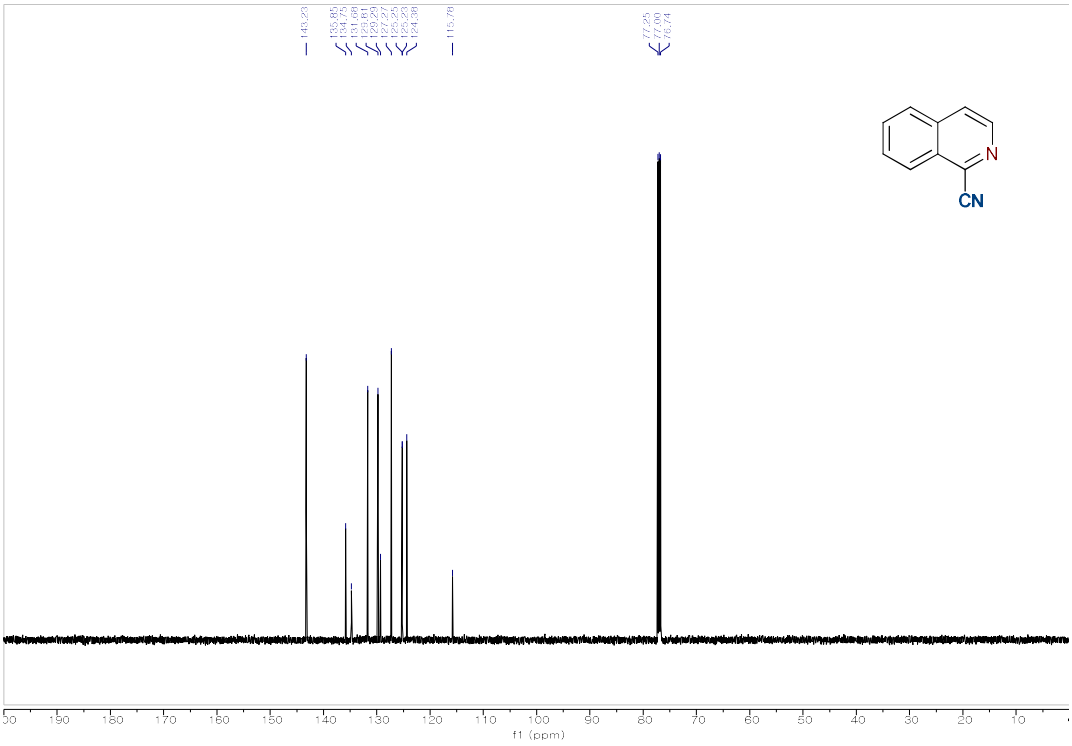


1-Isoquinolinecarbonitrile (3w)

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

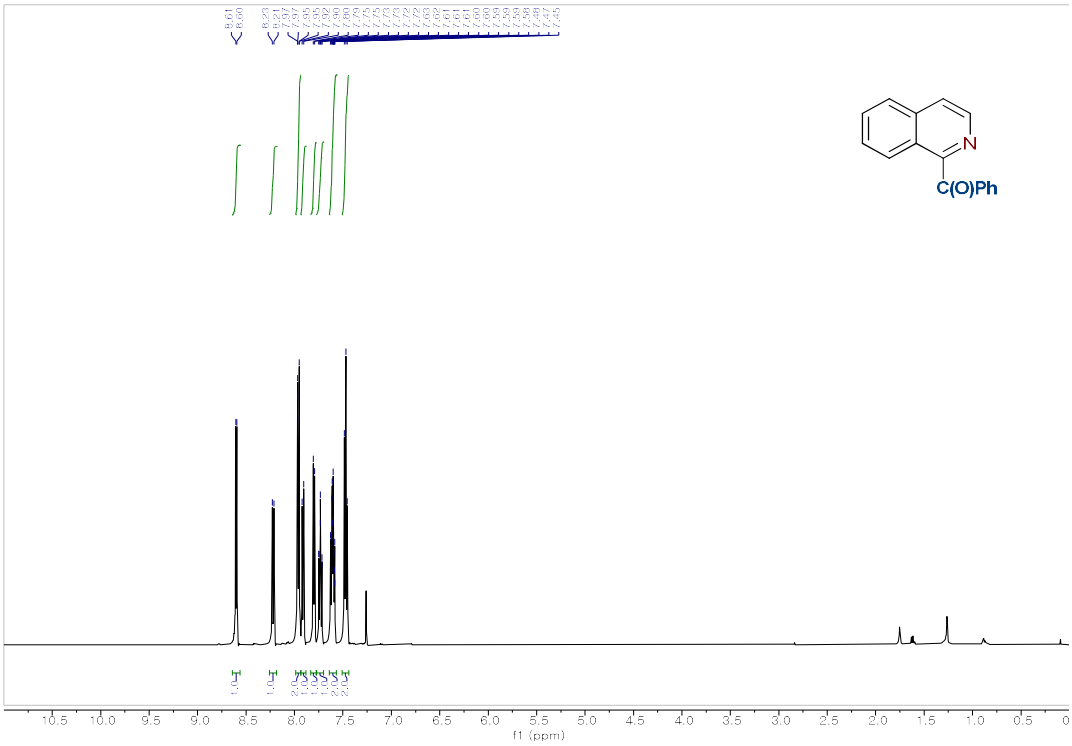


^{13}C NMR (126 MHz, $CDCl_3$)

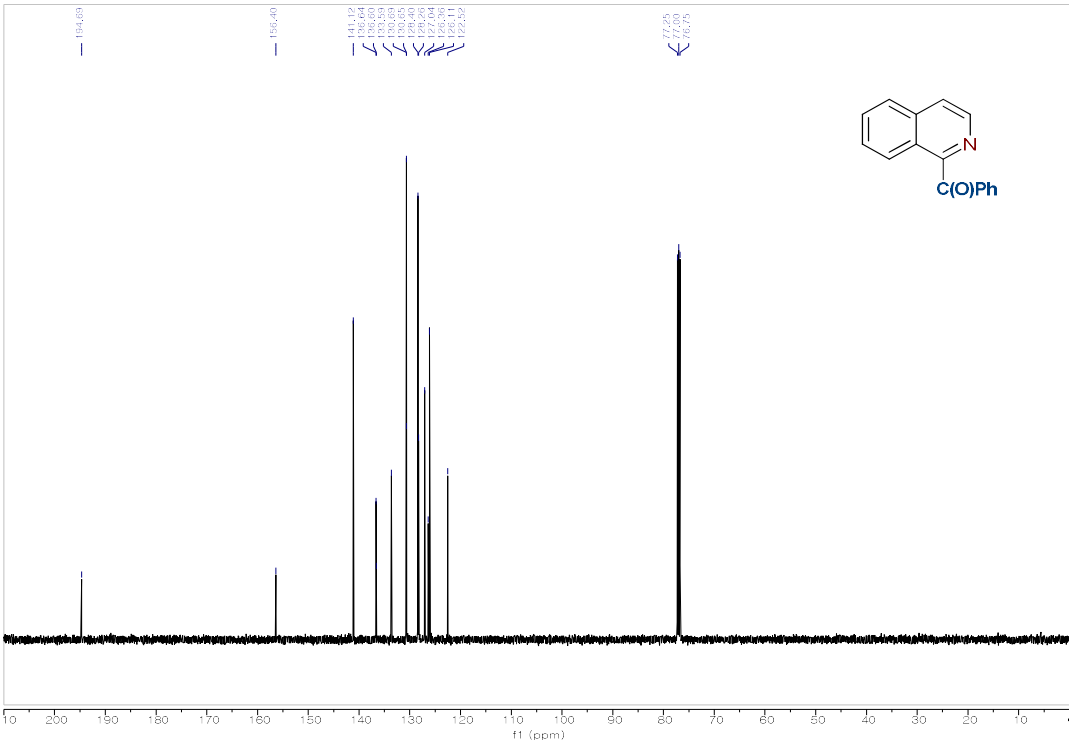


1-Benzoylisoquinoline (3x)

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

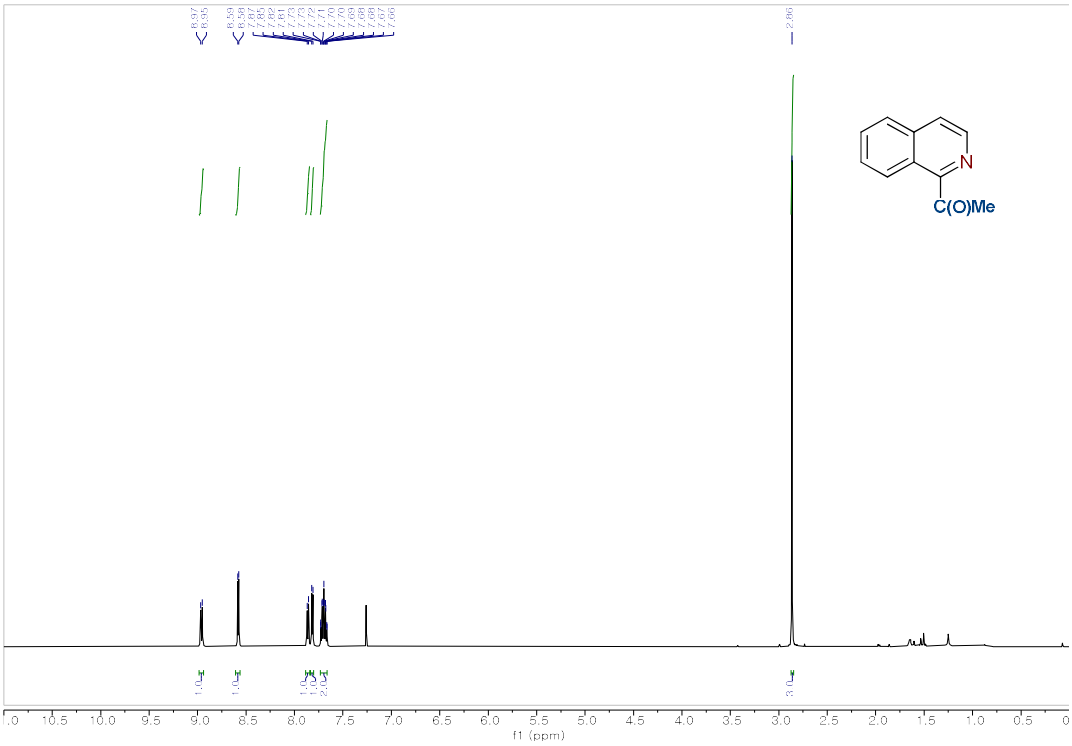


^{13}C NMR (126 MHz, $CDCl_3$)

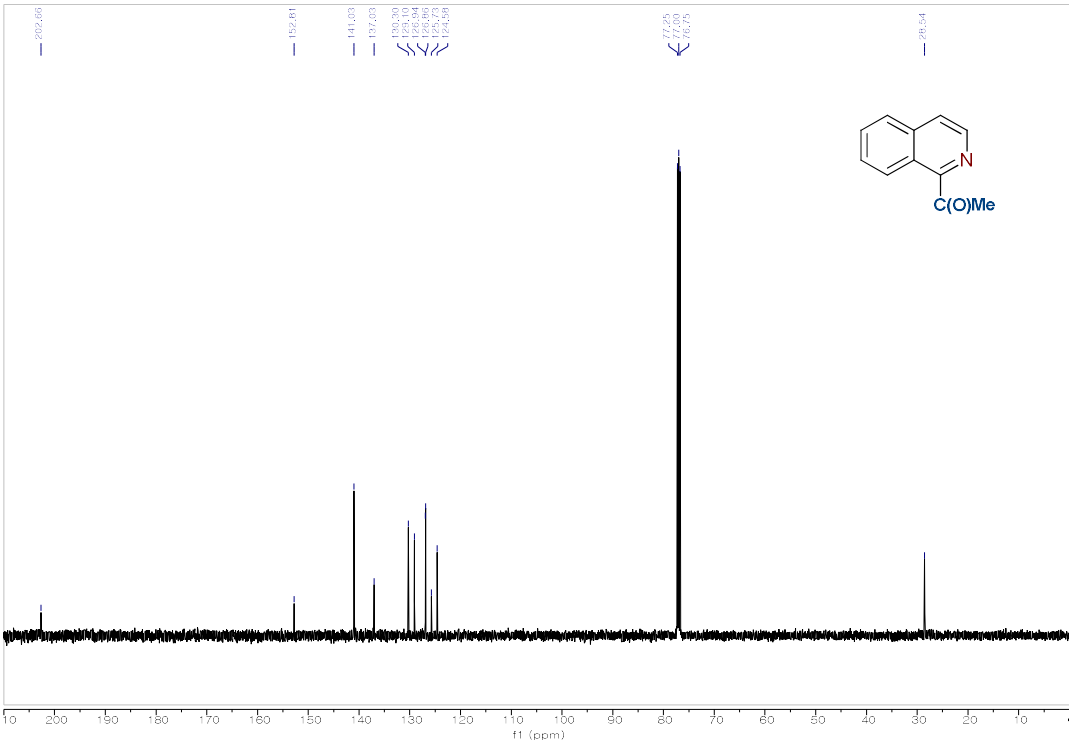


1-Acetylisoquinoline (3y)

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

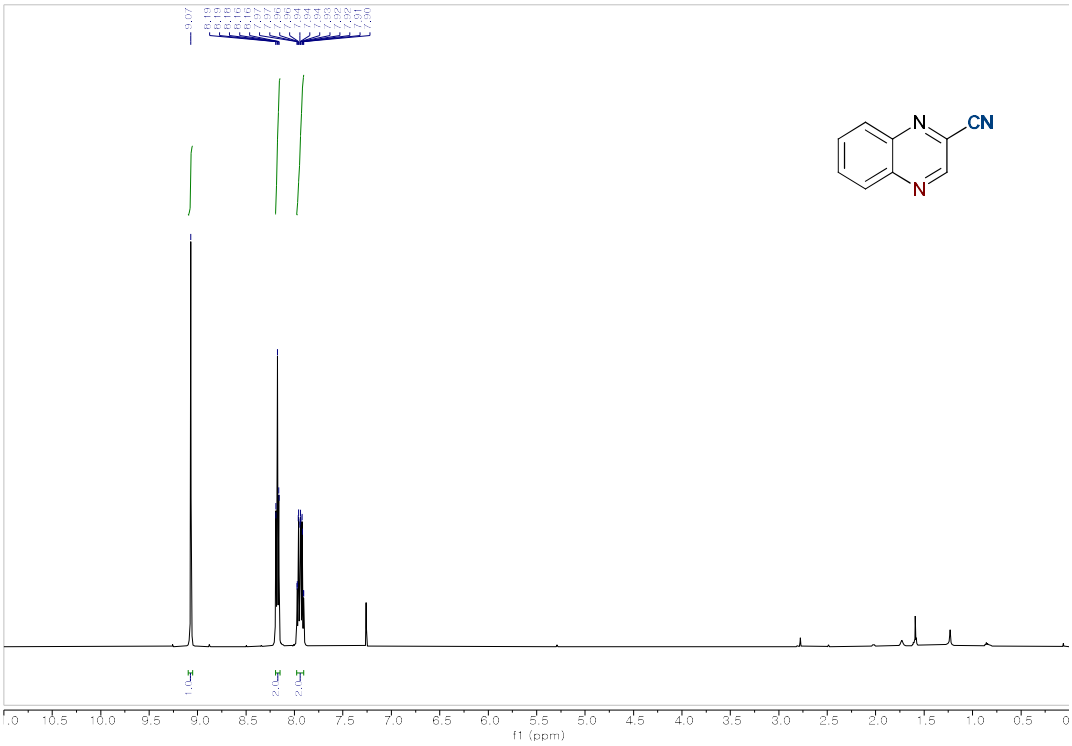


^{13}C NMR (126 MHz, $CDCl_3$)

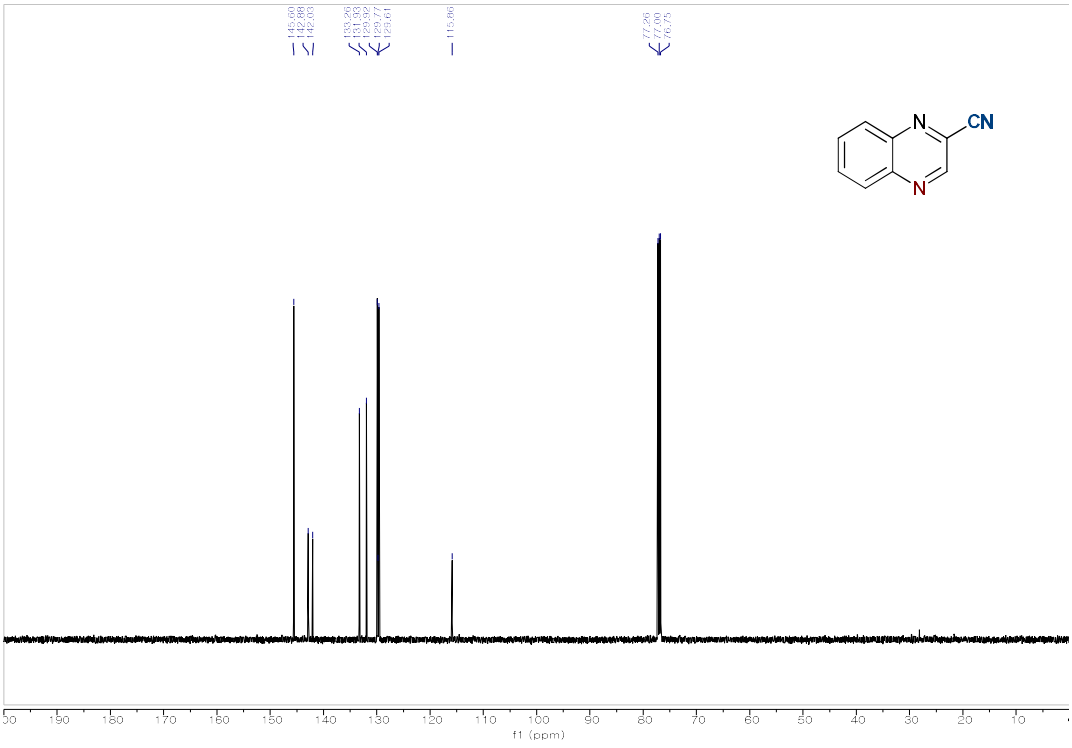


3-Quinoxalinecarbonitrile (3z)

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

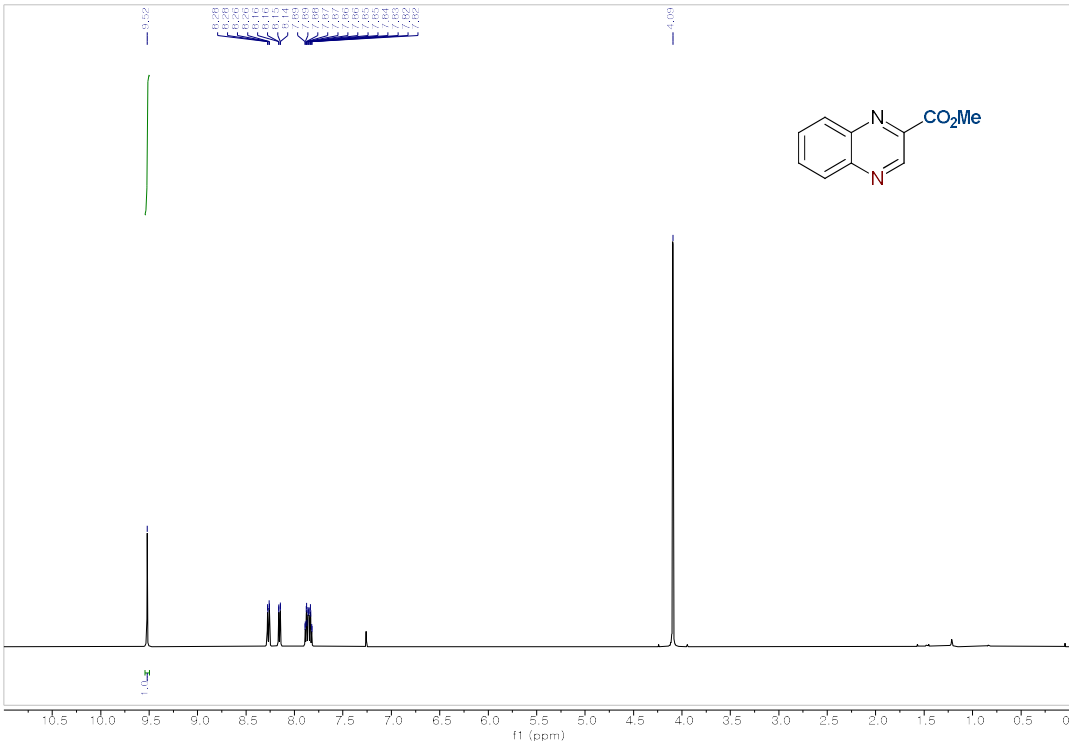


^{13}C NMR (126 MHz, $CDCl_3$)

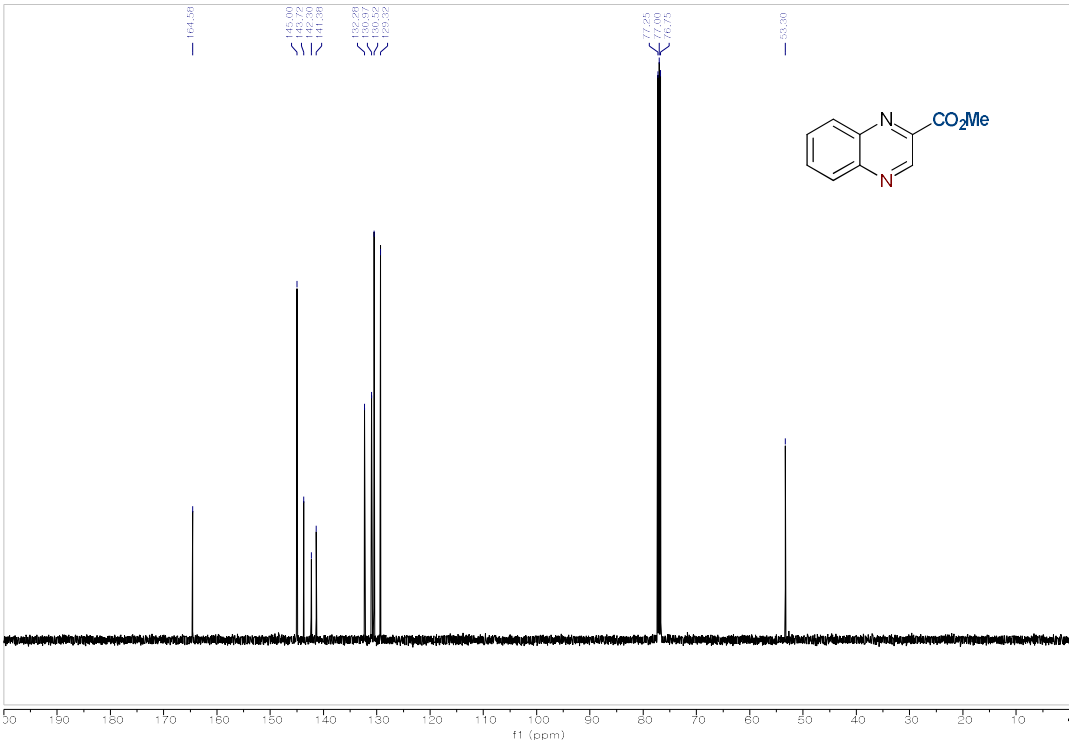


Methyl 3-Quinoxalinecarboxylate (3aa)

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

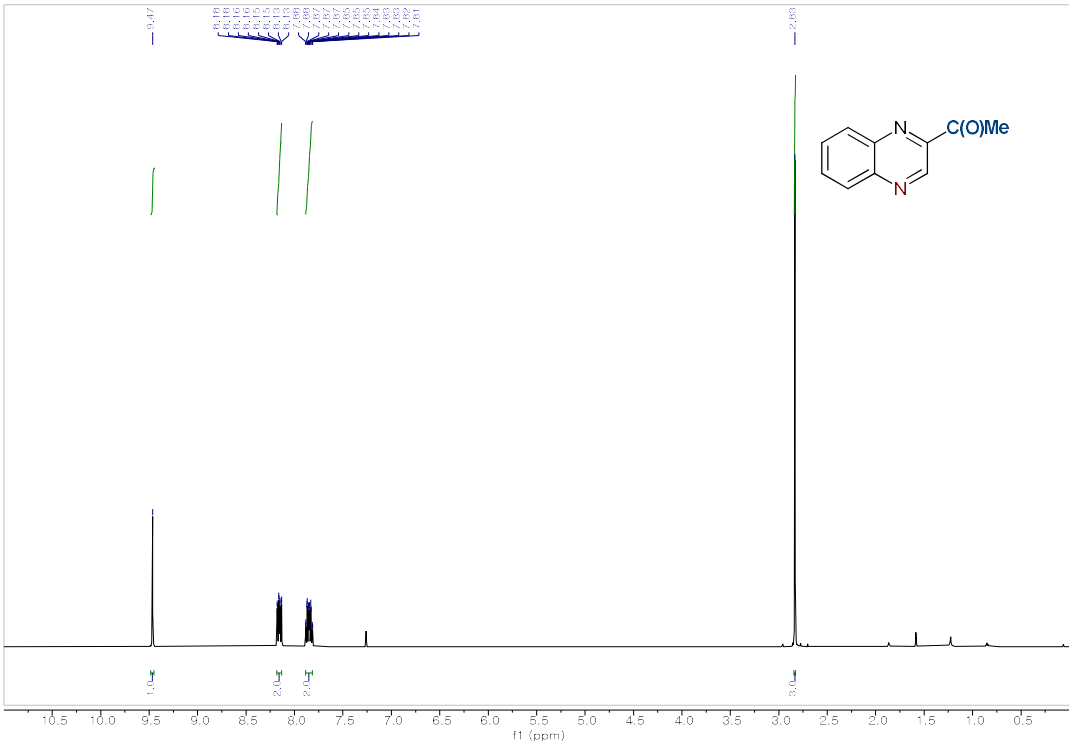


^{13}C NMR (126 MHz, $CDCl_3$)

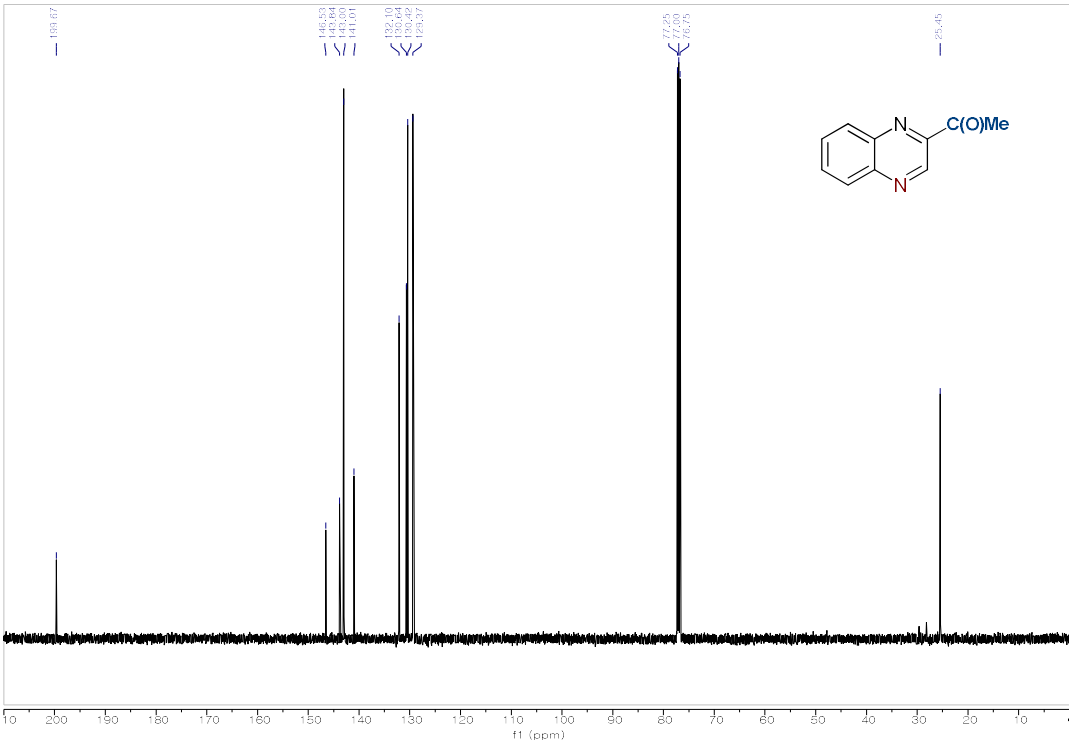


3-Acetylquinoxaline (3ab)

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

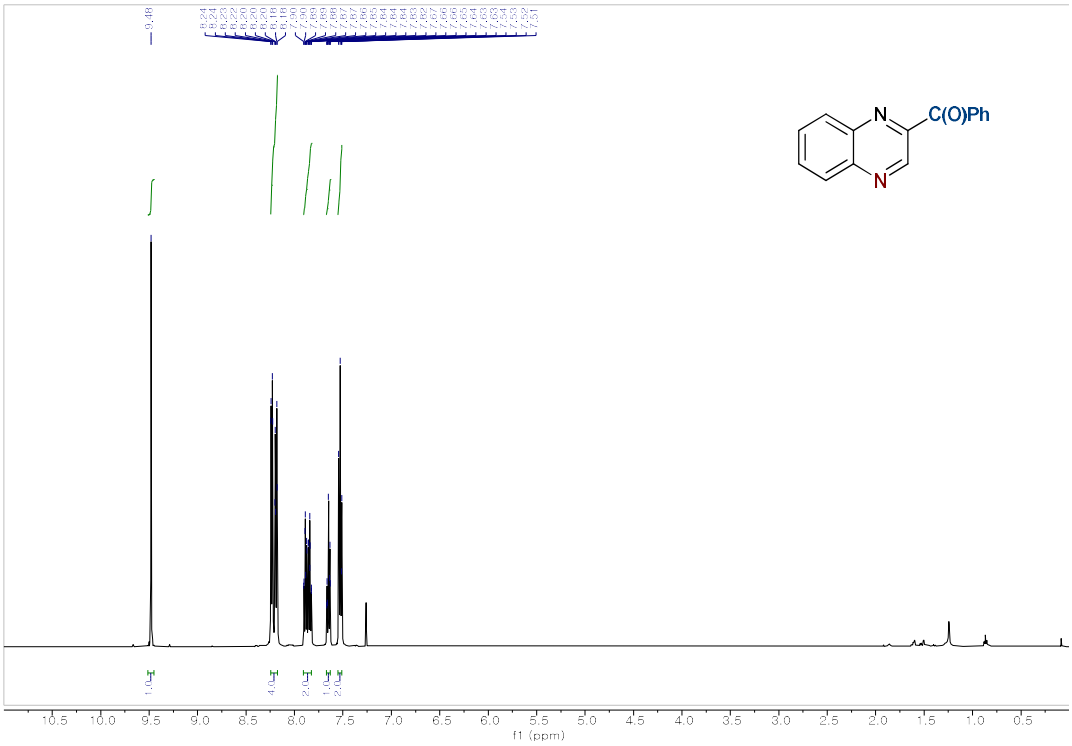


^{13}C NMR (126 MHz, $CDCl_3$)

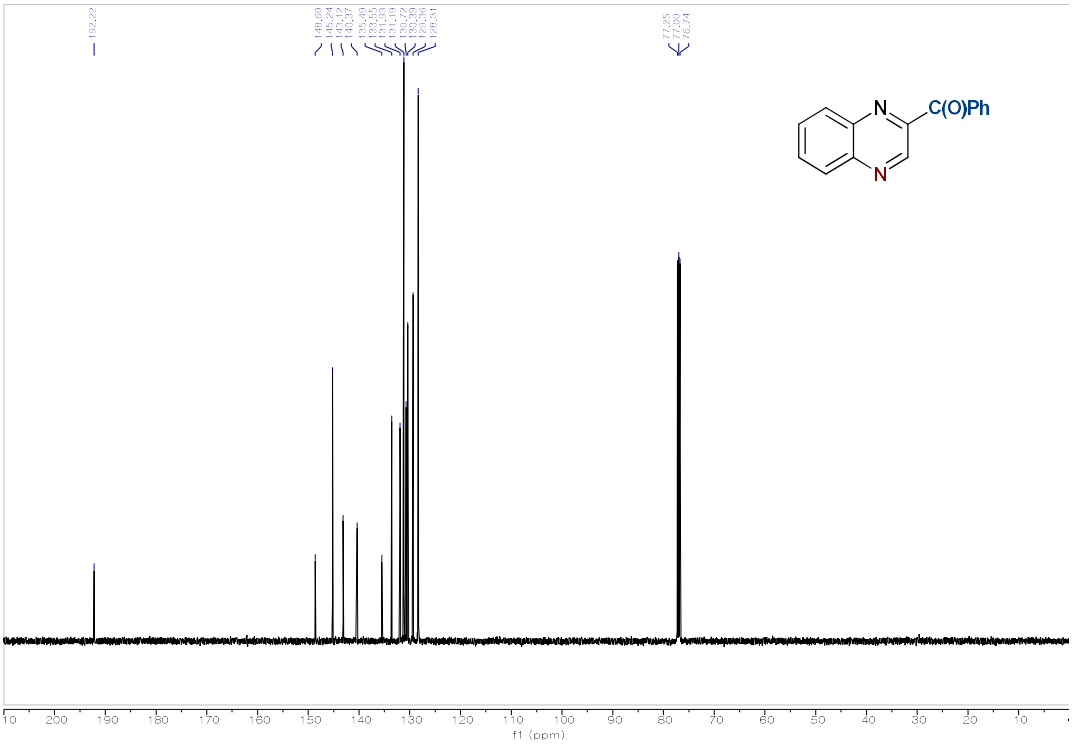


2-Benzoylquinoxaline (3ac)

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

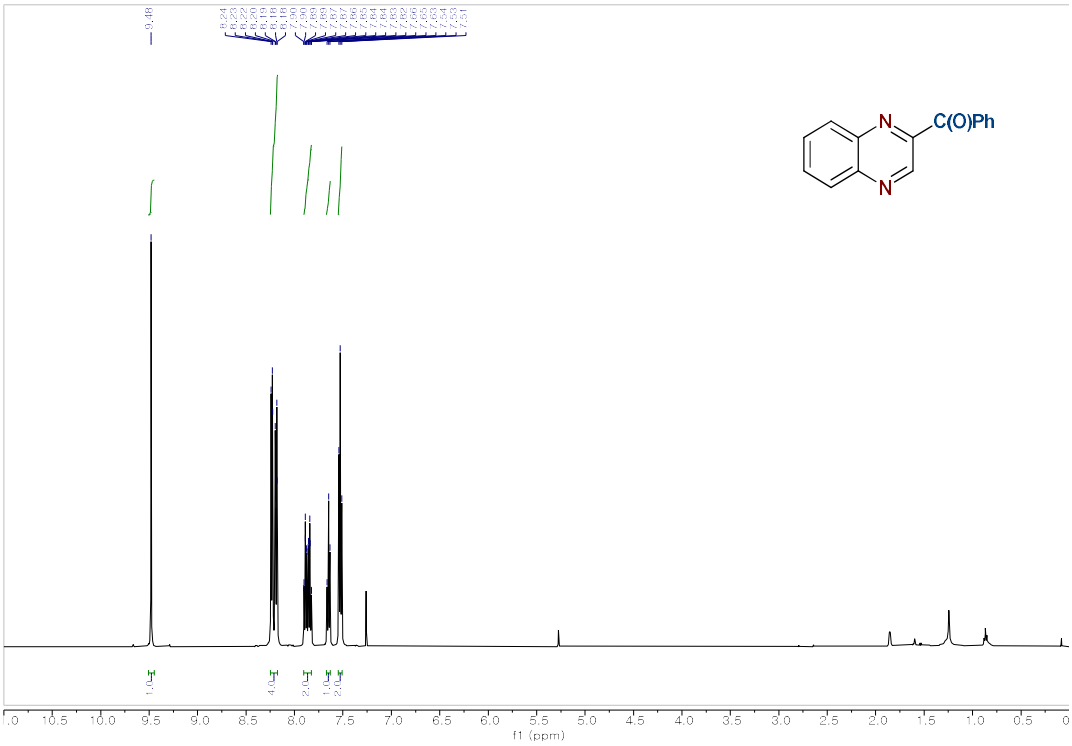


^{13}C NMR (126 MHz, $CDCl_3$)

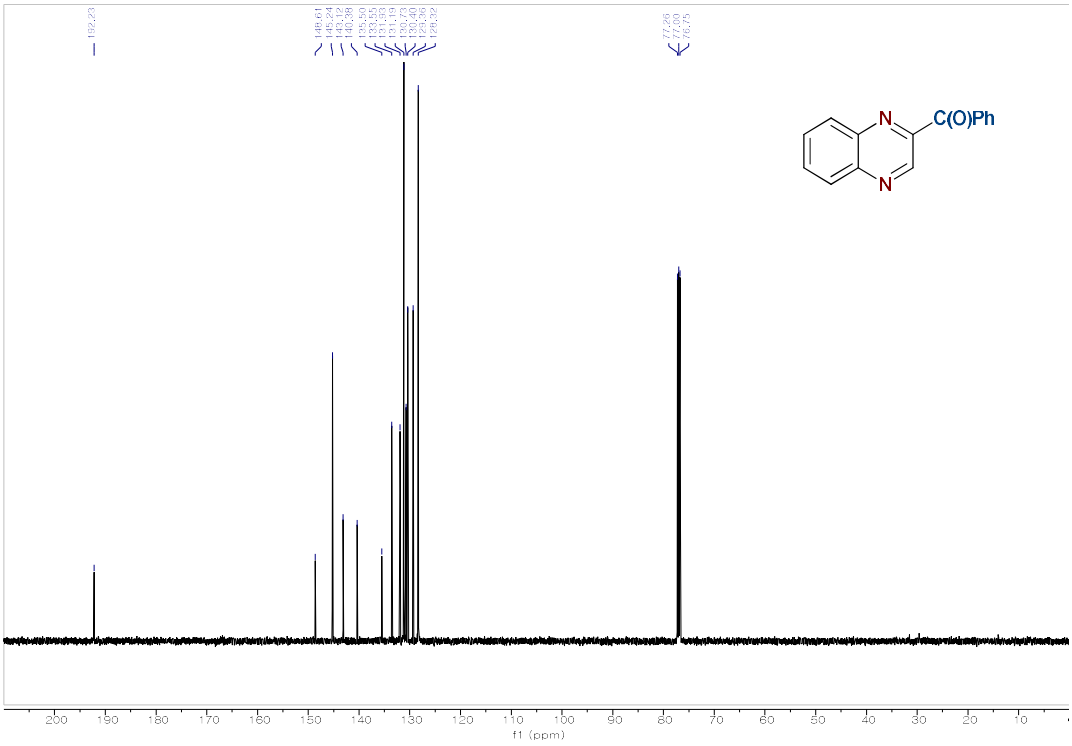


2-Benzoylquinoxaline (3ac)

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

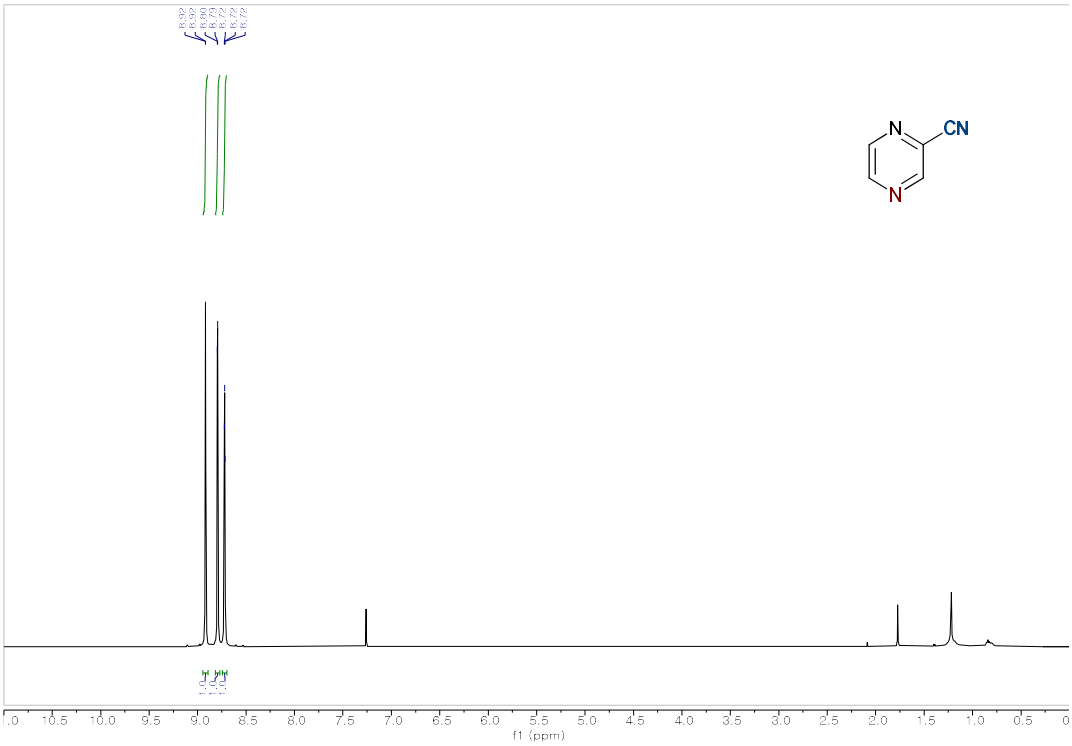


^{13}C NMR (126 MHz, $CDCl_3$)

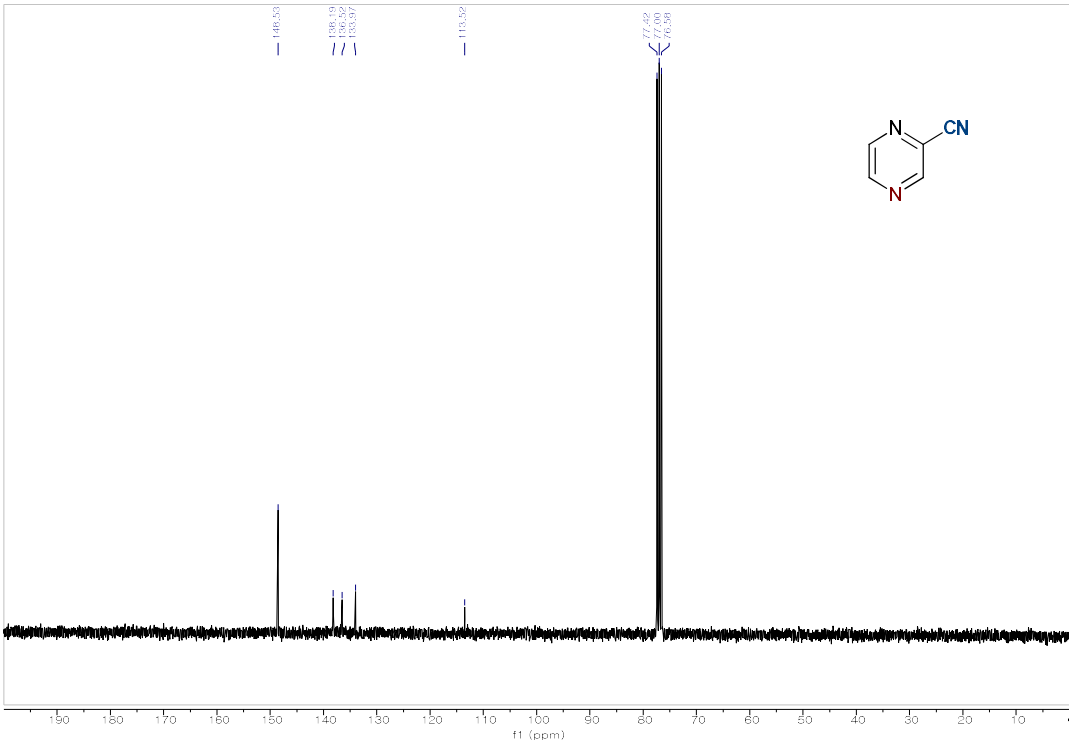


3-Pyrazinecarbonitrile (3ad)

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

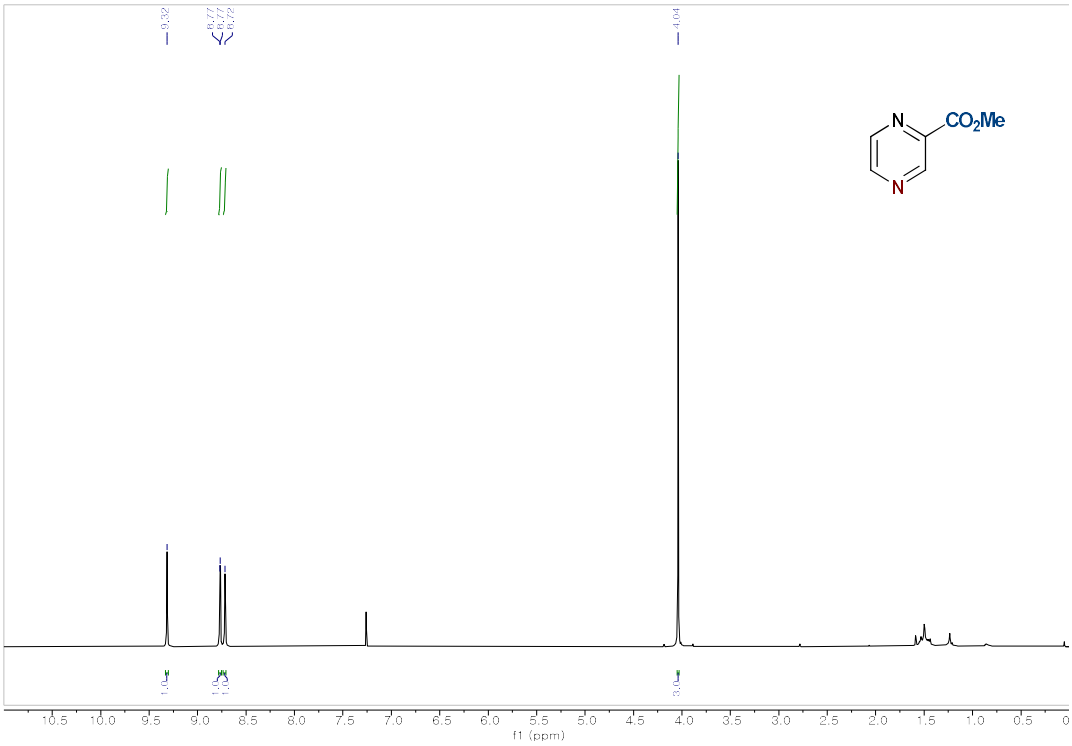


^{13}C NMR (126 MHz, $CDCl_3$)

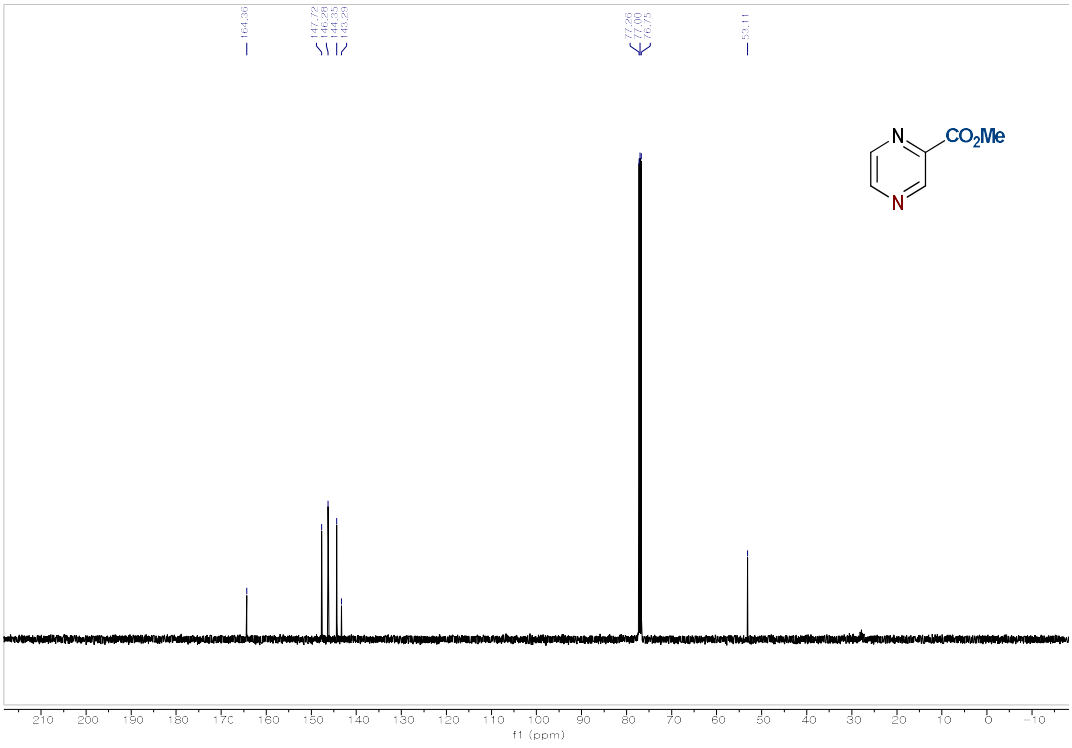


Methyl 3-Pyrazinecarboxylate (3ae)

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

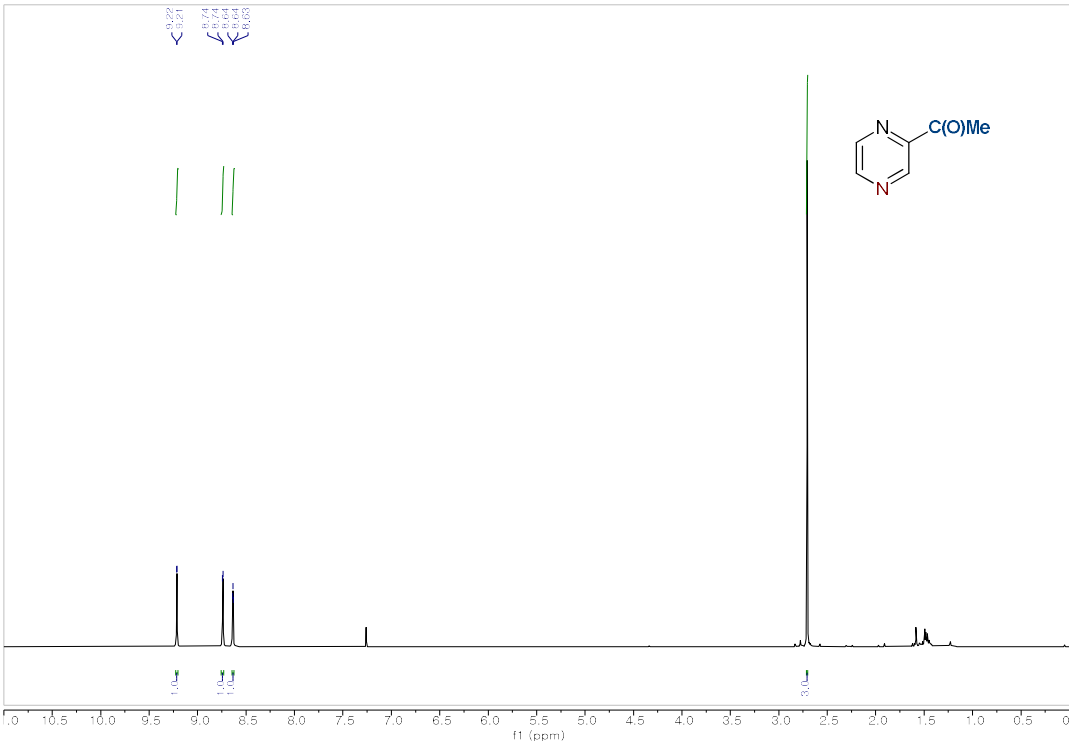


^{13}C NMR (126 MHz, $CDCl_3$)

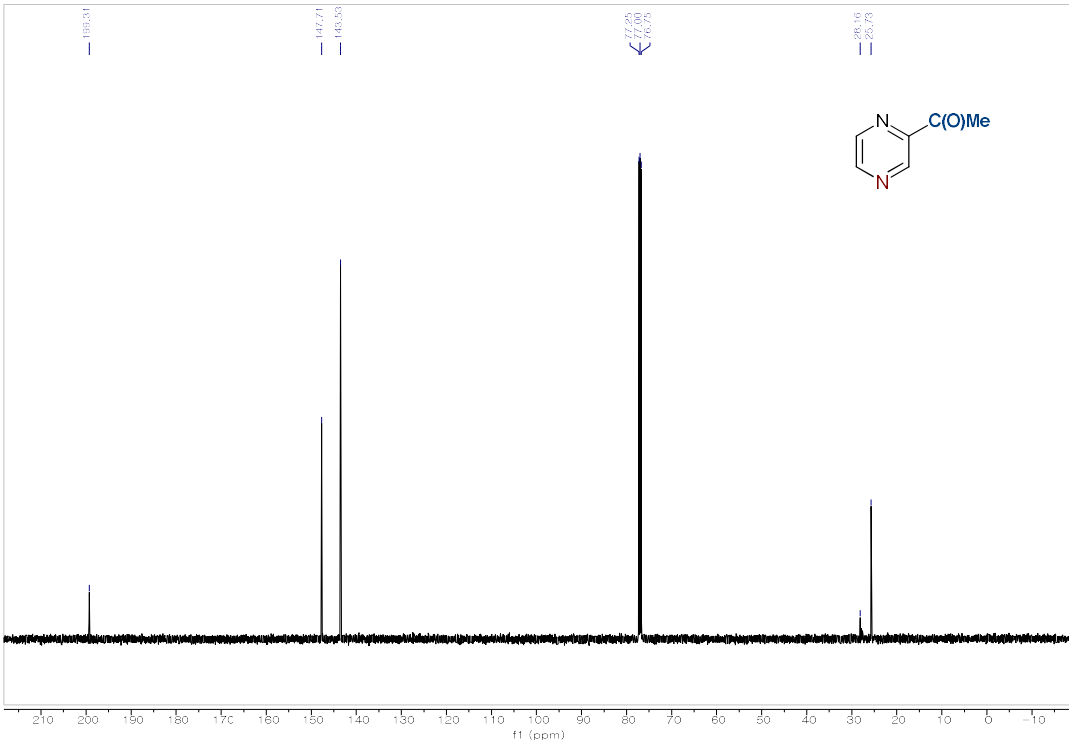


3-Acetylpyrazine (3af)

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

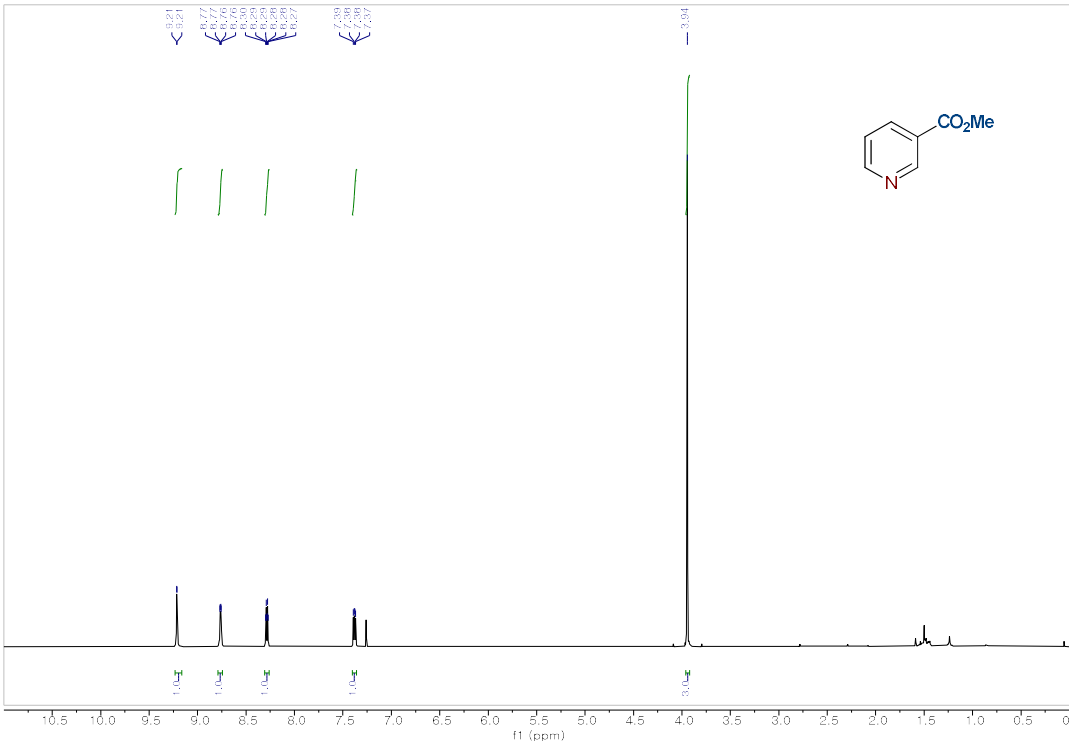


^{13}C NMR (126 MHz, $CDCl_3$)

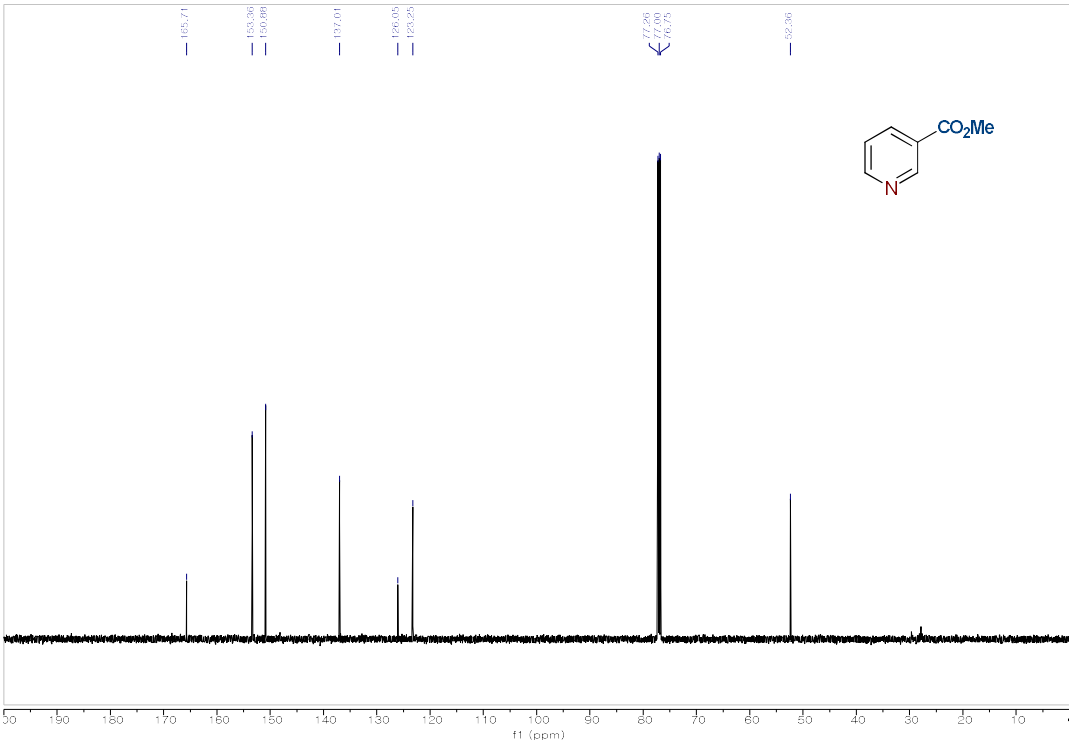


Methyl Nicotinate (3ag)

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

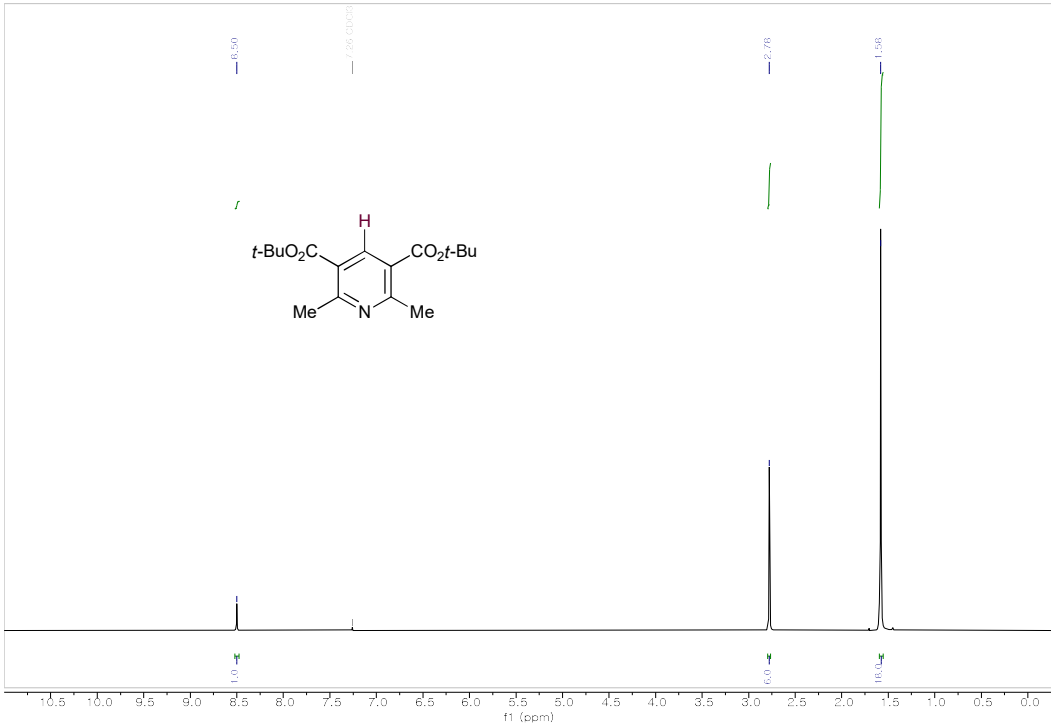


^{13}C NMR (126 MHz, $CDCl_3$)



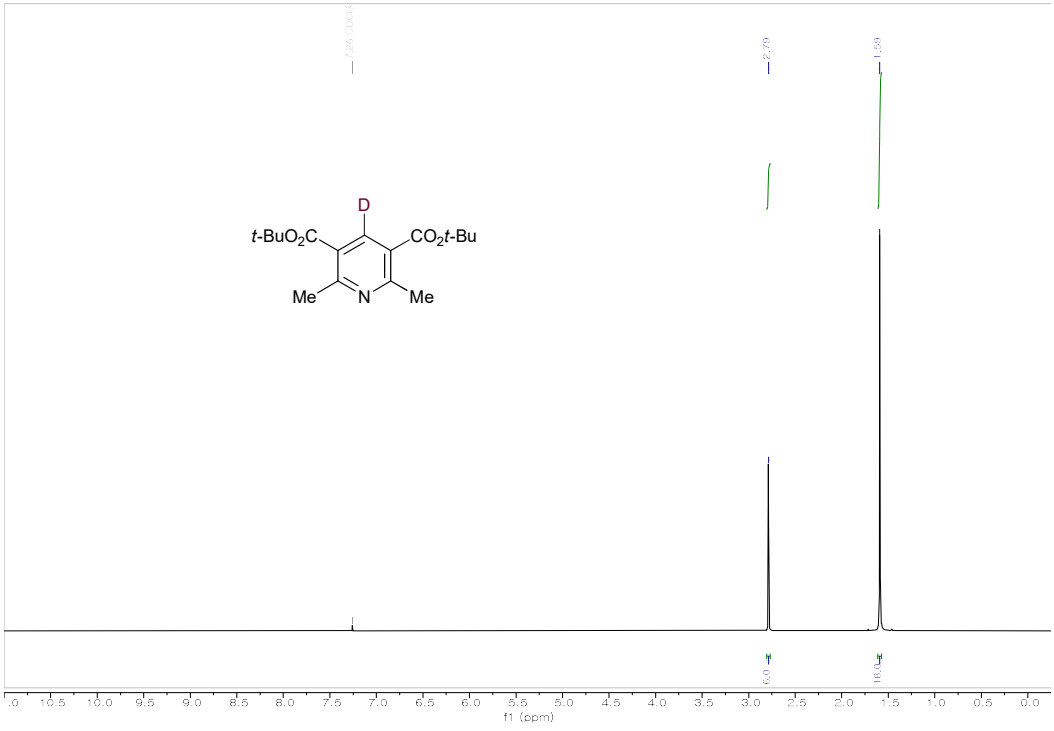
Pyridine-2a (Scheme 3c)

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



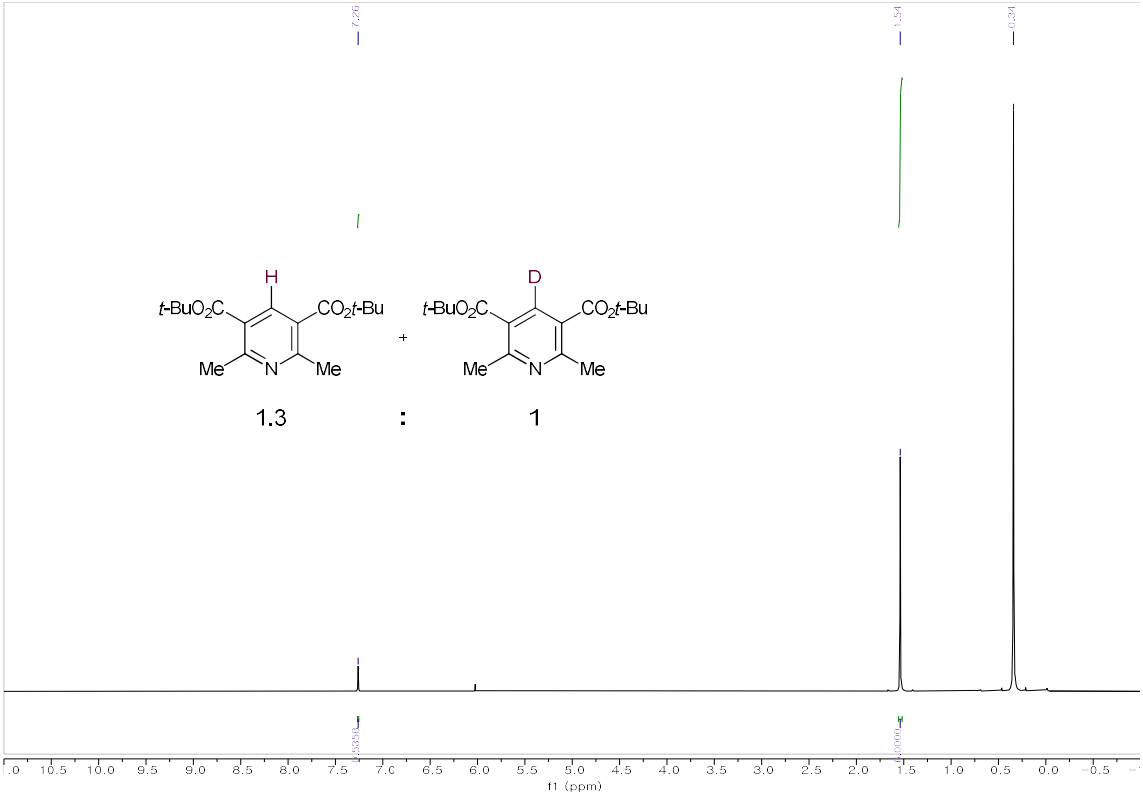
Pyridine-2a-*d* (Scheme 3c)

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



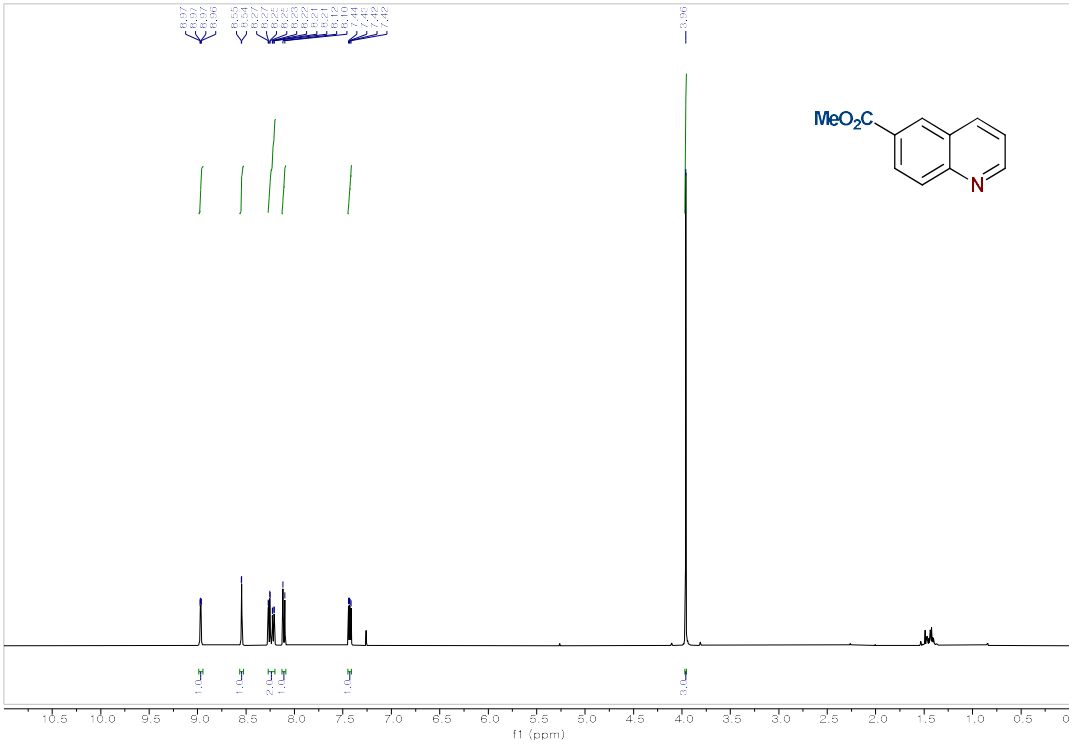
1.3:1 Mixture of Pyridine-2a and Pyridine-2a-*d* (Scheme 3c)

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

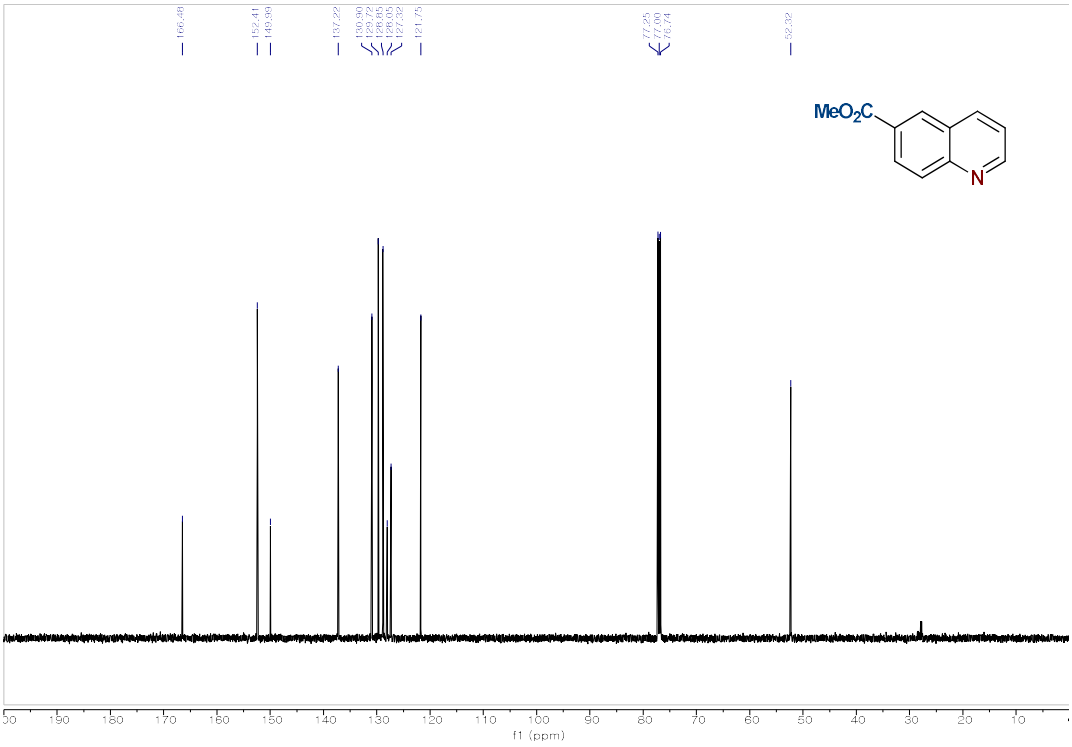


Multigram Scale Reaction (Scheme 4)

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



^{13}C NMR (126 MHz, $CDCl_3$)



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