Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Copper-catalyzed oxygen atom transfer of *N*-oxides leading to a facile deoxygenation procedure applicable to both heterocyclic and amine *N*-oxides

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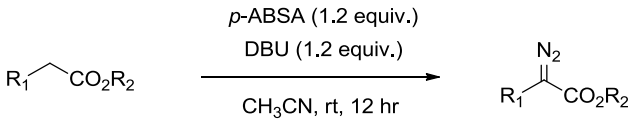
I. General Methods

Unless otherwise stated, all commercial reagents and solvents were used without additional purification. Analytical thin layer chromatography (TLC) was performed on Merck pre-coated silica gel 60 F_{254} plates or Merck pre-coated aluminium oxide (basic) 60 F_{254} plates. Visualization on TLC was achieved by the use of UV light (254 nm) or treatment with acidic anisaldehyde, phosphomolybdic acid, ninhydrin or ceric ammonium molydate stain followed by heating. Column chromatography was undertaken on Merck silica gel 60 (230 – 400 mesh) or Merck aluminum oxide 90 active basic (70 – 230 mesh) using a proper eluent system. ^{1}H NMR was recorded on Agilent Technologies DD2 (600 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br (broad), s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), td (triplet of doublet), ddd (doublet of doublet of doublet), and m (multiplet). Coupling constants, *J*, were reported in hertz unit (Hz). ^{13}C NMR was recorded on Agilent Technologies DD2 (150 MHz) and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center of a triplet at 77.0 ppm of chloroform-*d*. Infrared (IR) spectra were recorded on Bruker Alpha FT-IR Spectrometer. Frequencies are given in reciprocal centimeters (cm^{-1}) and only selected absorbance is reported. High resolution mass spectra were obtained from the Korea Basic Science Institute (Daegu) by using EI and FAB method.

II. Experimental Procedure for the Preparation of Starting Materials

1. Preparation of Diazo Compounds

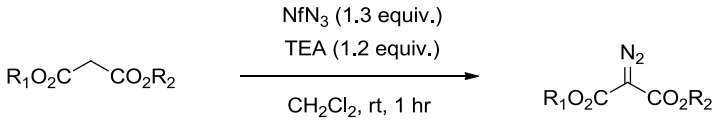
1.1. General Procedure I[S1]



To a solution of the corresponding carbonyl compound (3.0 mmol) and *p*-acetamidobenzene sulfonyl azide (*p*-ABSA, 0.86 g, 3.6 mmol) in anhydrous CH_3CN (9 mL) was added dropwise 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.54 ml, 3.6 mmol) at 0 ^{o}C. The reaction mixture was allowed to stir at room temperature for 12 h, and then quenched by adding diethyl ether (20 mL) and a saturated aqueous NH_4Cl solution (20 mL). The organic layer was separated and extracted with saturated aqueous NH_4Cl solution (20 mL x 2). The organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was washed with *n*-hexene/diethyl ether (1/1, *v*/*v*) to remove *p*-acetamidobenzene sulfonyl amide. The filtrate was concentrated under reduced

pressure and then purified by column chromatography on silica gel with EtOAc/*n*-hexane to afford the desired diazo compounds.

1.2. General Procedure II[S2a]

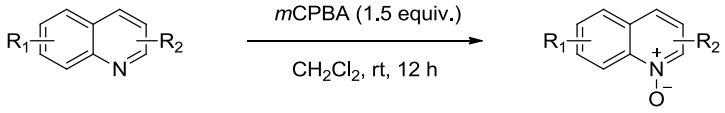


To a solution of the corresponding carbonyl compound (3.0 mmol) in anhydrous CH_2Cl_2 (6 mL) were added dropwise Et_3N (0.50 mL, 3.6 mmol) and perfluorobutanesulfonyl azide[S2b] (NfN_3, 0.71 mL, 3.9 mmol) at 0 °C. The reaction mixture was allowed to stir at room temperature for 1 h, and a saturated aqueous $NaHCO_3$ solution (20 mL) was added. The organic layer was separated and extracted with saturated aqueous $NaHCO_3$ solution (20 mL x 3). The organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with EtOAc/*n*-hexane to afford the desired diazo compounds.

2. Preparation of Heterocyclic *N*-Oxides

6-Methyl-8-[(triisopropylsilyl)ethynyl]quinoline *N*-oxide[S3a], 8-(1,3-dimethoxy-1,3-dioxopropan-2-yl)-6-methylquinoline *N*-oxide[S3a], and 6-methyl-8-(4-methylphenylsulfonamido)quinoline *N*-oxide[S3b] were prepared according to the previously reported procedures.

2.1. General Procedure for the Preparation of Heterocyclic *N*-Oxides[S3]



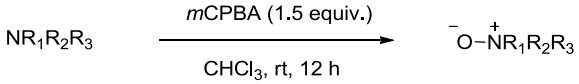
To a solution of the corresponding quinoline (3.0 mmol) in CH_2Cl_2 (9 mL) was added *m*-chloroperoxybenzoic acid (*m*CPBA, 0.67 g, 4.5 mmol) at 0 ℃. The reaction mixture was allowed to stir at room temperature for 12 h and a saturated aqueous $NaHCO_3$ solution (20 mL) was added. The reaction mixture was extracted with $CHCl_3$ (10 mL x 3) and the organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with CH_2Cl_2/acetone or EtOAc/*n*-hexane to afford the desired *N*-oxides.

3. Preparation of Alkyl(aryl)amine *N*-Oxides

3.1. Preparation of Alkyl(aryl)amine[S4]

1-Benzylmorpholine[S4a], 1-phenethylpiperidine[S4b], 1-(3-phenylpropyl)piperidine[S4b], *N*,*N*-diethyl-3-phenylpropylamine[S4c], 1-(4-methoxyphenyl)piperidine[S4d], and 1-(4-nitrophenyl)piperidine[S4e] were prepared according to the previously reported procedures.

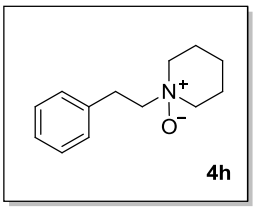
3.2. General Procedure for the Preparation of Alkyl(aryl)amine *N*-Oxides[S5]



To a solution of the corresponding amine (3.0 mmol) in CH_3Cl (9 mL) was added *m*-chloroperoxybenzoic acid (*m*CPBA, 0.67 g, 4.5 mmol) at 0 ℃. The reaction mixture was allowed to stir at room temperature for 12 h and dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on basic alumina with CH_2Cl_2/methanol to afford the desired *N*-oxides.

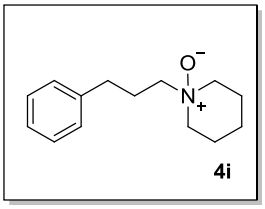
3.3. Spectroscopic Data of Prepared Alkyl(aryl)amine *N*-Oxides

1-Phenethylpiperidine *N*-oxide (Table 3, **4h**)



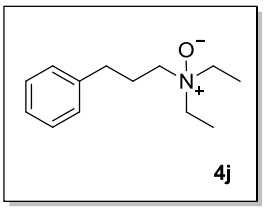
White solid; m.p. 110 – 112 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.5 Hz, 2H), 7.24 – 7.17 (m, 3H), 3.36 – 3.31 (m, 2H), 3.28 – 3.19 (m, 4H), 3.08 (td, *J* = 11.2, 3.0 Hz, 2H), 2.40 – 2.28 (m, 2H), 1.75 – 1.67 (m, 1H), 1.61 – 1.53 (m, 2H), 1.41 – 1.31 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 137.9, 128.9, 128.6, 126.5, 71.5, 65.8, 28.7, 22.4, 21.0; **IR** (cm^{-1}) 3392, 3316, 2936, 2874, 1729, 1665, 1602, 1454, 962; **HRMS** (FAB) m/z calculated for $C_{13}H_{20}NO$ $[M+H]^+$: 206.1545, found: 206.1544.

1-(3-Phenylpropyl)piperidine *N*-oxide (Table 3, **4i**)



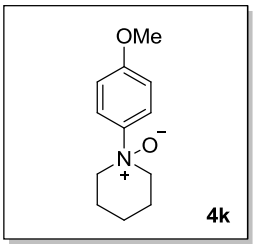
White solid; m.p. 152 – 154 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.6 Hz, 2H), 7.12 – 7.05 (m, 3H), 3.09 – 3.03 (m, 4H), 2.92 (td, *J* = 11.3, 3.1 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.28 – 2.14 (m, 4H), 1.64 – 1.56 (m, 1H), 1.48 – 1.39 (m, 2H), 1.29 – 1.17 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 140.4, 128.2, 128.0, 125.9, 69.6, 65.3, 32.8, 23.3, 22.1, 20.8; **IR** (cm^{-1}) 3062, 3029, 2994, 2934, 2851, 1728, 1603, 1494, 959; **HRMS** (FAB) m/z calculated for $C_{14}H_{22}NO$ $[M+H]^+$: 220.1701, found: 220.1702.

***N*,*N*-Diethyl-3-phenylpropylamine *N*-oxide** (Table 3, **4j**)



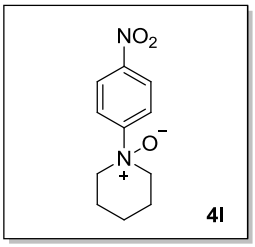
White solid; m.p. 81 – 83 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.5 Hz, 2H), 7.17 – 7.11 (m, 3H), 3.09 (q, *J* = 7.2 Hz, 4H), 3.05 – 3.00 (m, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.12 – 2.01 (m, 2H), 1.19 (t, *J* = 7.3 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 140.5, 128.5, 128.2, 126.3, 64.4, 60.2, 33.0, 24.6, 8.5; **IR** (cm^{-1}) 3419, 3217, 3020, 2974, 2928, 2869, 1717, 1602, 1455, 1379, 940; **HRMS** (FAB) m/z calculated for $C_{13}H_{22}NO$ $[M+H]^+$: 208.1701, found: 208.1699.

1-(4-Methoxyphenyl)piperidine (Table 3, **4k**)



White solid; m.p. 136 – 138 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 9.2 Hz, 2H), 6.92 (d, *J* = 9.2 Hz, 2H), 3.81 (s, 3H), 3.64 – 3.56 (m, 2H), 3.22 – 3.14 (m, 2H), 2.67 (qt, *J* = 13.3, 3.9 Hz, 2H), 1.92 – 1.83 (m, 1H), 1.67 – 1.61 (m, 2H), 1.39 (qt, *J* = 13.3, 4.0 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.3, 148.8, 121.7, 113.7, 69.0, 55.5, 22.0, 21.3; **IR** (cm^{-1}) 2976, 2943, 2930, 1609, 1593, 1506, 1251, 833; **HRMS** (FAB) m/z calculated for $C_{12}H_{18}NO_2$ $[M+H]^+$: 208.1338, found: 208.1340.

1-(4-Nitrophenyl)piperidine *N*-oxide (Table 3, **4l**)



Light yellow solid; m.p. 119 – 121 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 9.2 Hz, 2H), 8.24 (d, *J* = 9.2 Hz, 2H), 3.71 – 3.59 (m, 2H), 3.22 – 3.16 (m, 2H), 2.66 (qt, *J* = 13.3, 3.9 Hz, 2H), 1.94 – 1.83 (m, 1H), 1.72 – 1.64 (m, 2H), 1.41 (qt, *J* = 13.4, 4.1 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.6, 147.6, 124.3, 122.1, 69.0, 21.7, 21.0; **IR** (cm^{-1}) 3111, 3010, 2958, 2927, 1614, 1591, 1513, 1351, 964; **HRMS** (FAB) m/z calculated for $C_{11}H_{15}N_2O_3$ $[M+H]^+$: 223.1083, found: 223.1085.

III. Experimental Procedure for the Cu-Catalyzed Deoxygenation

1. Optimization Table for the Cu-Catalyzed Deoxygenation (Table 1)

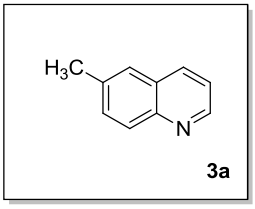
To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added 6-methylquinoline *N*-oxide (0.20 mmol), catalyst, and 4 Å molecular sieves powder (50 mg) under argon atmosphere. 1,2-Dichloroethane (0.5 mL) was added followed by diazo compound (0.22 mmol, 1.1 equiv.), and the reaction mixture was stirred at the indicated temperature for 12 h. The reaction mixture was cooled to room temperature, filtered through a pad of celite, and then washed with CH_2Cl_2 (10 mL x 3). Organic solvents were removed under reduced pressure and then diluted to measure the crude yield using HPLC, calibration of which was performed using 1,3,5-trimethylbenzene as an internal standard.

2. General Procedure for the Cu-Catalyzed Deoxygenation of *N*-Oxides (Table 2–3)

To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added *N*-oxide (0.20 mmol), catalyst and 4 Å molecular sieves powder (50 mg) under argon atmosphere. 1,2-dichloroethane (0.5 mL) was added followed by methyl phenyldiazoacetate (0.22 mmol, 1.1 equiv.) and the reaction mixture was stirred at 60 ^{o}C for 12 h. The reaction mixture was cooled to room temperature, filtered through a pad of celite, and then washed with CH_2Cl_2 (10 mL x 3). Organic solvents were removed under reduced pressure and the crude reaction mixture was purified by column chromatography on silica gel with EtOAc/*n*-hexane or CH_2Cl_2/methanol as an eluent. In some cases, the crude reaction mixture was purified by preparative thin-layer chromatography on basic alumina with EtOAc/*n*-hexane as an eluent followed by column chromatography on silica gel with EtOAc/*n*-hexane/triethylamine to give the desired product.

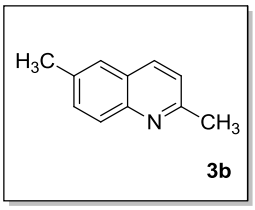
3. Spectroscopic Data of Deoxygenated Products Obtained in This Study

6-Methylquinoline (Table 2, **3a**)[S6]



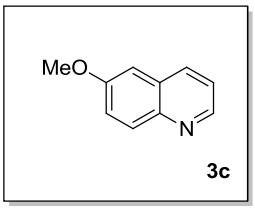
Colorless liquid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.84 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.56 (m, 1H), 7.54 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.34 (dd, *J* = 8.3, 4.2 Hz, 1H), 2.53 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.5, 146.9, 136.3, 135.3, 131.7, 129.1, 128.3, 126.5, 121.0, 21.5.

2,6-Dimethylquinoline (Table 2, **3b**)[S7]



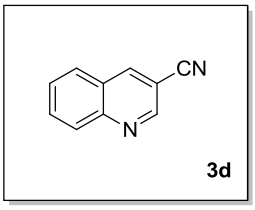
Light yellow solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.7, 8.7 Hz, 2H), 7.50 – 7.48 (m, 2H), 7.21 (d, *J* = 8.4 Hz, 1H), 2.71 (s, 3H), 2.50 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.9, 146.4, 135.4, 135.3, 131.5, 128.2, 126.4, 126.3, 121.9, 25.2, 21.4.

6-Methoxyquinoline (Table 2, **3c**)[S8]



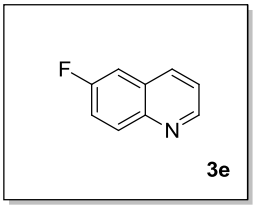
Light yellow solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.76 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.03 – 8.01 (m, 1H), 8.00 (d, *J* = 9.2 Hz, 1H), 7.36 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.33 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.04 (d, *J* = 2.8 Hz, 1H), 3.91 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.6, 147.9, 144.4, 134.7, 130.8, 129.2, 122.2, 121.3, 105.1, 55.4.

3-Cyanoquinoline (Table 2, **3d**)[S9]



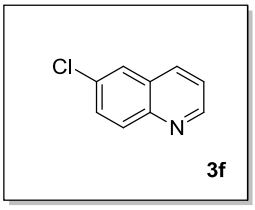
White solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.04 (d, *J* = 2.2 Hz, 1H), 8.54 (d, *J* = 2.1 Hz, 1H), 8.18 (d, *J* = 8.8 Hz, 1H), 7.92 – 7.89 (m, 2H), 7.70 (dd, *J* = 7.6, 7.6 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.7, 148.7, 141.4, 132.7, 129.8, 128.4, 128.2, 126.1, 117.0, 106.5.

6-Fluoroquinoline (Table 2, **3e**)[S10]



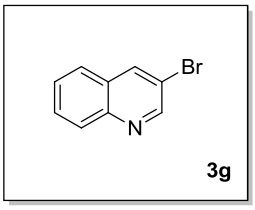
Light yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.88 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.12 – 8.09 (m, 2H), 7.49 (ddd, *J* = 9.2, 8.4, 2.8 Hz, 1H), 7.43 – 7.40 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.3 (d, *J* = 247.5 Hz), 149.6 (d, *J* = 3.0 Hz), 145.4, 135.3 (d, *J* = 4.5 Hz), 132.0 (d, *J* = 9.0 Hz), 128.8 (d, *J* = 9.0 Hz), 121.7, 119.7 (d, *J* = 25.5 Hz), 110.6 (d, *J* = 22.5 Hz).

6-Chloroquinoline (Table 2, **3f**)[S11]



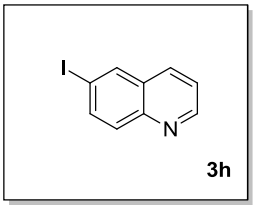
Light yellow solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.90 (dd, *J* = 4.4, 1.7 Hz, 1H), 8.06 – 8.03 (m, 2H), 7.78 (d, *J* = 2.3 Hz, 1H), 7.64 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.41 (dd, *J* = 8.3, 4.2 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.5, 146.6, 135.0, 132.2, 131.1, 130.3, 128.8, 126.4, 121.8.

3-Bromoquinoline (Table 2, **3g**)[S12]



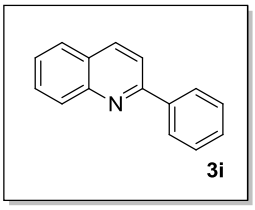
White solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.90 (d, *J* = 2.3 Hz, 1H), 8.29 (d, *J* = 2.3 Hz, 1H), 8.08 (d, *J* = 8.7 Hz, 1H), 7.73 – 7.71 (m, 2H), 7.56 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.3, 146.3, 137.1, 129.7, 129.5, 129.1, 127.6, 126.9, 117.1. (CAS Registry Number: 5332-24-1)

6-Iodoquinoline (Table 2, **3h**)[S12]



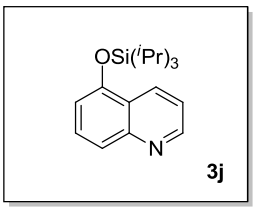
Light yellow solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.91 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.19 (d, *J* = 2.0 Hz, 1H), 8.02 (d, *J* = 8.3 Hz, 1H), 7.93 (dd, *J* = 8.9, 1.9 Hz, 1H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.39 (dd, *J* = 8.3, 4.2 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.8, 147.1, 138.1, 136.5, 134.7, 131.1, 129.8, 121.7, 92.1. (CAS Registry Number: 13327-31-6)

2-Phenylquinoline (Table 2, **3i**)[S13]



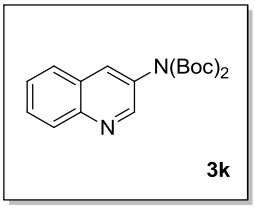
White solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.19 – 8.15 (m, 4H), 7.85 (d, *J* = 8.6 Hz, 1H), 7.80 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.71 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H), 7.53 – 7.49 (m, 3H), 7.47 – 7.44 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.3, 148.3, 139.7, 136.7, 129.7, 129.6, 129.3, 128.8, 127.5, 127.4, 127.2, 126.2, 118.9.

5-(Triisopropylsilyloxy)quinoline (Table 2, **3j**)[S3b]



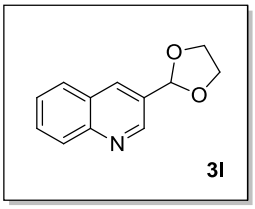
Colorless liquid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.89 (dd, *J* = 4.1, 1.8 Hz, 1H), 8.58 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.54 (dd, *J* = 8.1, 8.1 Hz, 1H), 7.37 (dd, *J* = 8.4, 4.2 Hz, 1H), 6.93 (d, *J* = 7.7 Hz, 1H), 1.41 (hept, *J* = 7.5 Hz, 3H), 1.15 (d, *J* = 7.8 Hz, 18H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.7, 150.4, 149.5, 131.2, 129.3, 122.8, 122.0, 120.1, 112.2, 18.0, 12.9.

3-[Bis(*tert*-butoxycarbonyl)amino]quinoline (Table 2, **3k**)[S3a]



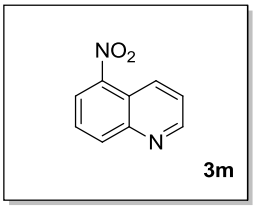
White solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.71 (d, *J* = 2.4 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 2.5 Hz, 1H), 7.83 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.74 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H), 7.57 (dd, *J* = 7.5, 7.5 Hz, 1H), 1.42 (s, 18H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.2, 150.4, 146.6, 133.4, 132.7, 129.6, 129.2, 127.8, 127.6, 126.9, 83.5, 27.8.

3-(1,3-Dioxolan-2-yl)quinoline (Table 2, **3l**)[S14]



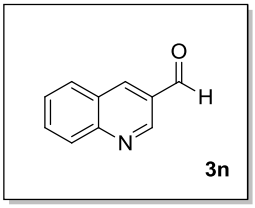
Light yellow solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.01 (d, *J* = 2.1 Hz, 1H), 8.23 (d, *J* = 2.2 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.73 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.55 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 6.03 (s, 1H), 4.20 – 4.14 (m, 2H), 4.12 – 4.07 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.1, 148.5, 133.9, 130.8, 129.8, 129.3, 128.0, 127.3, 126.8, 102.2, 65.4.

5-Nitroquinoline (Table 2, **3m**)[S12]



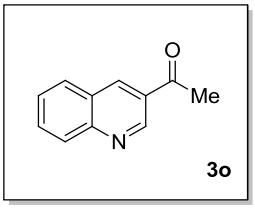
Light yellow solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.04 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.99 (dd, *J* = 8.7, 1.6 Hz, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 8.38 (d, *J* = 7.7 Hz, 1H), 7.81 (t, *J* = 8.1 Hz, 1H), 7.65 (dd, *J* = 8.8, 4.1 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.6, 148.2, 145.5, 136.5, 131.8, 127.4, 124.6, 123.9, 121.1. (CAS Registry Number: 607-34-1)

3-Formylquinoline (Table 2, **3n**)[S15]



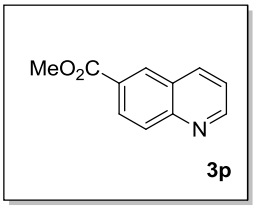
Light yellow solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.26 (s, 1H), 9.37 (d, *J* = 2.0 Hz, 1H), 8.63 (d, *J* = 2.1 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.99 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.89 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.67 (ddd, *J* = 7.9, 7.0, 1.2 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 190.7, 150.6, 149.1, 140.0, 132.6, 129.7, 129.4, 128.6, 127.8, 127.0.

3-Acetylquinoline (Table 2, **3o**)[S16]



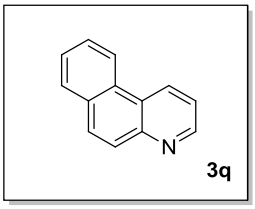
Light orange solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.43 (d, *J* = 2.2 Hz, 1H), 8.70 – 8.69 (m, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.94 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.84 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.63 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 2.74 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 196.6, 149.8, 149.1, 137.2, 131.9, 129.4, 129.3, 129.2, 127.5, 126.7, 26.7.

6-(Methoxycarbonyl)quinoline (Table 2, **3p**)[S17]



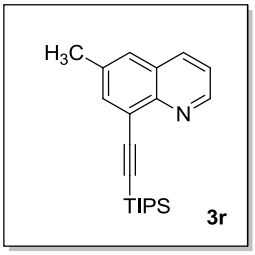
Light yellow solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.00 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.58 (m, 1H), 8.30 (dd, *J* = 8.8, 1.9 Hz, 1H), 8.26 – 8.24 (m, 1H), 8.14 (d, *J* = 8.8 Hz, 1H), 7.46 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.00 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.5, 152.4, 150.0, 137.2, 130.9, 129.7, 128.9, 128.1, 127.3, 121.8, 52.3.

Benzo[*f*]quinoline (Table 2, **3q**)[S18]



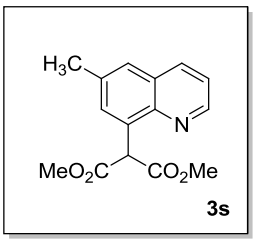
White solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.94 – 8.93 (m, 1H), 8.87 (d, *J* = 8.3 Hz, 1H), 8.55 (d, *J* = 8.1 Hz, 1H), 7.99 – 7.93 (m, 2H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.63 (dt, *J* = 22.5, 7.2 Hz, 2H), 7.51 – 7.49 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.6, 148.1, 131.6, 130.8, 130.6, 129.5, 128.6, 128.1, 127.2, 127.0, 125.3, 122.5, 121.2.

6-Methyl-8-[(triisopropylsilyl)ethynyl]quinoline (Table 2, **3r**)[S3a]



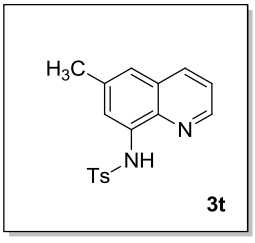
Light yellow solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.91 (d, *J* = 4.8 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.77 (s, 1H), 7.50 (s, 1H), 7.34 (dd, *J* = 8.1, 4.1 Hz, 1H), 2.48 (s, 3H), 1.22 (s, 21H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.2, 147.2, 136.5, 135.6, 135.3, 128.2, 127.4, 123.4, 121.4, 104.8, 96.7, 21.3, 18.8, 11.5.

8-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-6-methylquinoline (Table 2, **3s**)[S3a]



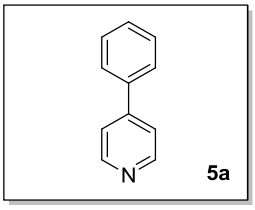
Light yellow solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.83 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.04 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.66 (d, *J* = 1.9 Hz, 1H), 7.56 (s, 1H), 7.35 (dd, *J* = 8.2, 4.2 Hz, 1H), 6.33 (s, 1H), 3.77 (s, 6H), 2.53 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.5, 149.0, 144.4, 136.0, 135.5, 131.5, 131.3, 128.3, 127.1, 121.3, 52.7, 51.1, 21.6.

6-Methyl-8-(4-methylphenylsulfonamido)quinoline (Table 2, **3t**)[S3b]



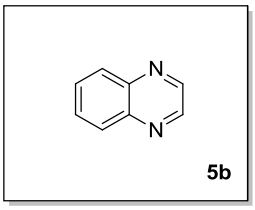
White solid; m.p. 121 – 123; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.65 (dd, *J* = 4.2, 1.7 Hz, 1H), 7.95 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 1.8 Hz, 1H), 7.33 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.18 (s, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H), 2.26 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.7, 143.6, 137.1, 136.9, 136.4, 135.4, 133.4, 129.4, 128.1, 127.1, 121.9, 120.9, 116.9, 22.1, 21.4; **IR** (diamond) 3219, 3060, 3028, 2916, 2856, 1742, 1595, 1497, 1360, 1318, 1169, 1081 cm^{-1}; **HRMS** (EI) m/z calculated for $C_{17}H_{16}N_2O_2S$ $[M]^+$: 312.0931, found: 312.0930.

4-Phenylpyridine (Table 3, **5a**)[S19]



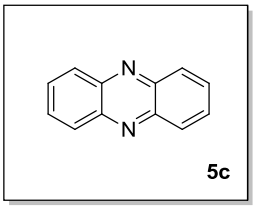
White solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.66 (d, *J* = 5.6 Hz, 2H), 7.63 (dd, *J* = 7.4, 1.7 Hz, 2H), 7.50 – 7.47 (m, 4H), 7.45 – 7.42 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.2, 148.3, 138.1, 129.1, 129.0, 126.9, 121.6.

Quinoxaline (Table 3, **5b**)[S20]



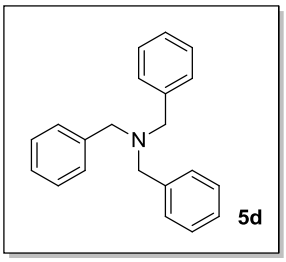
Light yellow solid; **^{1}H NMR** (600 MHz, $CDCl_3$)) δ 8.86 (s, 2H), 8.12 (dd, *J* = 6.4, 3.5 Hz, 2H), 7.79 (dd, *J* = 6.5, 3.4 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.9, 143.0, 130.0, 129.5.

Phenazine (Table 3, **5c**)[S21]



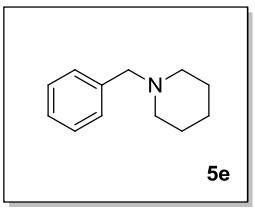
Yellow solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 6.7, 3.4 Hz, 4H), 7.82 (dd, *J* = 6.8, 3.4 Hz, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.4, 130.3, 129.6.

Tribenzylamine (Table 3, **5d**)[S22]



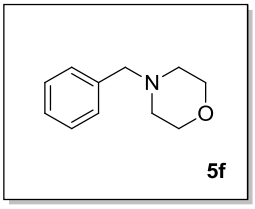
White solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 6.8 Hz, 6H), 7.30 (dd, *J* = 7.6, 7.6 Hz, 6H), 7.21 (dd, *J* = 7.3, 7.3 Hz, 3H), 3.54 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 139.6, 128.7, 128.2, 126.8, 57.9.

1-Benzylpiperidine (Table 3, **5e**)[S22]



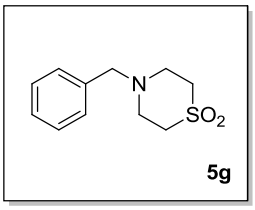
Light yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.32 – 7.29 (m, 4H), 7.24 – 7.22 (m, 1H), 3.48 (s, 2H), 2.38 (br, 4H), 1.57 (p, *J* = 5.6 Hz, 4H), 1.45 – 1.40 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 138.4, 129.2, 128.1, 126.8, 63.8, 54.4, 25.9, 24.3.

1-Benzylmorpholine (Table 3, **5f**)[S4a]



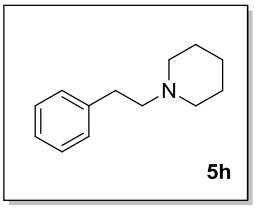
Colorless liquid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 4H), 7.26 – 7.24 (m, 1H), 3.70 (t, *J* = 4.7 Hz, 4H), 3.49 (s, 2H), 2.44 – 2.43 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 137.7, 129.1, 128.2, 127.1, 67.0, 63.4, 53.6.

4-Benzylthiomorpholine 1,1-dioxide (Table 3, **5g**)[S23]



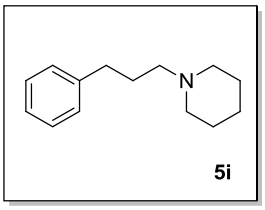
Colorless liquid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 5H), 3.65 (s, 2H), 3.06 – 3.04 (m, 4H), 2.98 – 2.97 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 137.2, 128.7, 128.5, 127.6, 61.4, 51.4, 50.5.

1-Phenethylpiperidine (Table 3, **5h**)[S24]



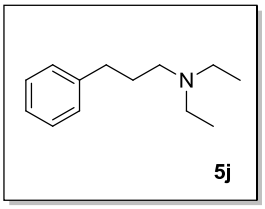
Colorless liquid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 7.20 – 7.17 (m, 3H), 2.82 – 2.79 (m, 2H), 2.57 – 2.46 (m, 6H), 1.62 (p, *J* = 5.7 Hz, 4H), 1.47 – 1.43 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 140.7, 128.7, 128.3, 125.9, 61.4, 54.5, 33.7, 26.0, 24.4.

1-(3-Phenylpropyl)piperidine (Table 3, **5i**)[S25]



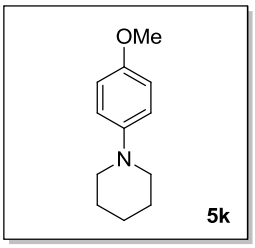
Colorless liquid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.19 – 7.15 (m, 3H), 2.61 (t, *J* = 7.8 Hz, 2H), 2.36 – 2.31 (m, 6H), 1.82 (p, *J* = 7.9 Hz, 2H), 1.58 (p, *J* = 5.7 Hz, 4H), 1.44 – 1.41 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 142.3, 128.3, 128.2, 125.6, 58.9, 54.6, 33.9, 28.7, 26.0, 24.5.

***N*,*N*-Diethyl-3-phenylpropylamine** (Table 3, **5j**)[S26]



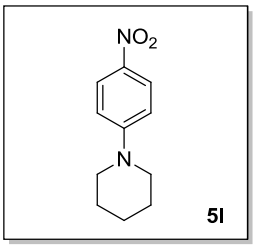
Colorless liquid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 2H), 7.20 – 7.16 (m, 3H), 2.61 (t, *J* = 7.9 Hz, 2H), 2.52 (q, *J* = 7.2 Hz, 4H), 2.46 (t, *J* = 7.6 Hz, 2H), 1.78 (p, *J* = 7.8 Hz, 2H), 1.00 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 142.4, 128.3, 128.2, 125.6, 52.5, 46.9, 33.9, 28.7, 11.7.

1-(4-Methoxyphenyl)piperidine (Table 3, **5k**)[S27]



Light yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.91 (d, *J* = 9.0 Hz, 2H), 6.82 (d, *J* = 9.0 Hz, 2H), 3.76 (s, 3H), 3.02 (t, *J* = 5.5 Hz, 4H), 1.72 (p, *J* = 5.7 Hz, 4H), 1.54 (p, *J* = 6.1 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 153.5, 146.9, 118.7, 114.3, 55.5, 52.3, 26.1, 24.2.

1-(4-Nitrophenyl)piperidine (Table 3, **5l**)[S4e]



Yellow solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 9.5 Hz, 2H), 6.78 (d, *J* = 9.3 Hz, 2H), 3.44 (t, *J* = 4.6 Hz, 4H), 1.69 – 1.68 (m, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.9, 137.4, 126.1, 112.3, 48.3, 25.3, 24.2.

IV. Experimental Procedure for the One-Pot Synthesis

To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added *m*-chloroperbenzoic acid (*m*CPBA, 45 mg, 0.20 mmol) and 1,2-dichloroethane (0.5 mL) under atmospheric conditions. 6-Methylquinoline (27 μL, 0.20 mmol) was then added dropwise and the reaction mixture was stirred at 50 ^{o}C for 12 h. After being cooled to room temperature, 4 Å molecular sieves powder (50 mg), $[IrCp^*Cl_2]_2$ (3.2 mg, 0.0040 mmol, 2.0 mol%), $AgNTf_2$ (6.2 mg, 0.016 mmol, 8.0 mol%), and *p*-toluenesulfonyl azide (TsN_3, 31 μL, 0.20 mmol) were added. The resulting reaction mixture was stirred at 50 ^{o}C for additional 6 h. Upon cooling, $Cu(OTf)_2$ (2.9 mg, 0.0080 mmol, 4.0 mol%) and methyl phenyldiazoacetate (32 μL, 0.22 mmol) were added. The reaction mixture was stirred at 60 ^{o}C for 12 h, cooled to room temperature, filtered through a pad of celite, and then washed with CH_2Cl_2 (10 mL x 3). Saturated aqueous $NaHCO_3$ solution (20 mL) was added and the reaction mixture was extracted with $CHCl_3$ (10 mL x 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/methanol to obtain 6-methyl-8-(4-methylphenylsulfonamido)quinoline **3t**[S3b] (white solid, 54 mg, 86%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.65 (dd, *J* = 4.2, 1.7 Hz, 1H), 7.95 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 1.8 Hz, 1H), 7.33 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.18 (s, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H), 2.26 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.7, 143.6, 137.1, 136.9, 136.4, 135.4, 133.4, 129.4, 128.1, 127.1, 121.9, 120.9, 116.9, 22.1, 21.4.

V. References

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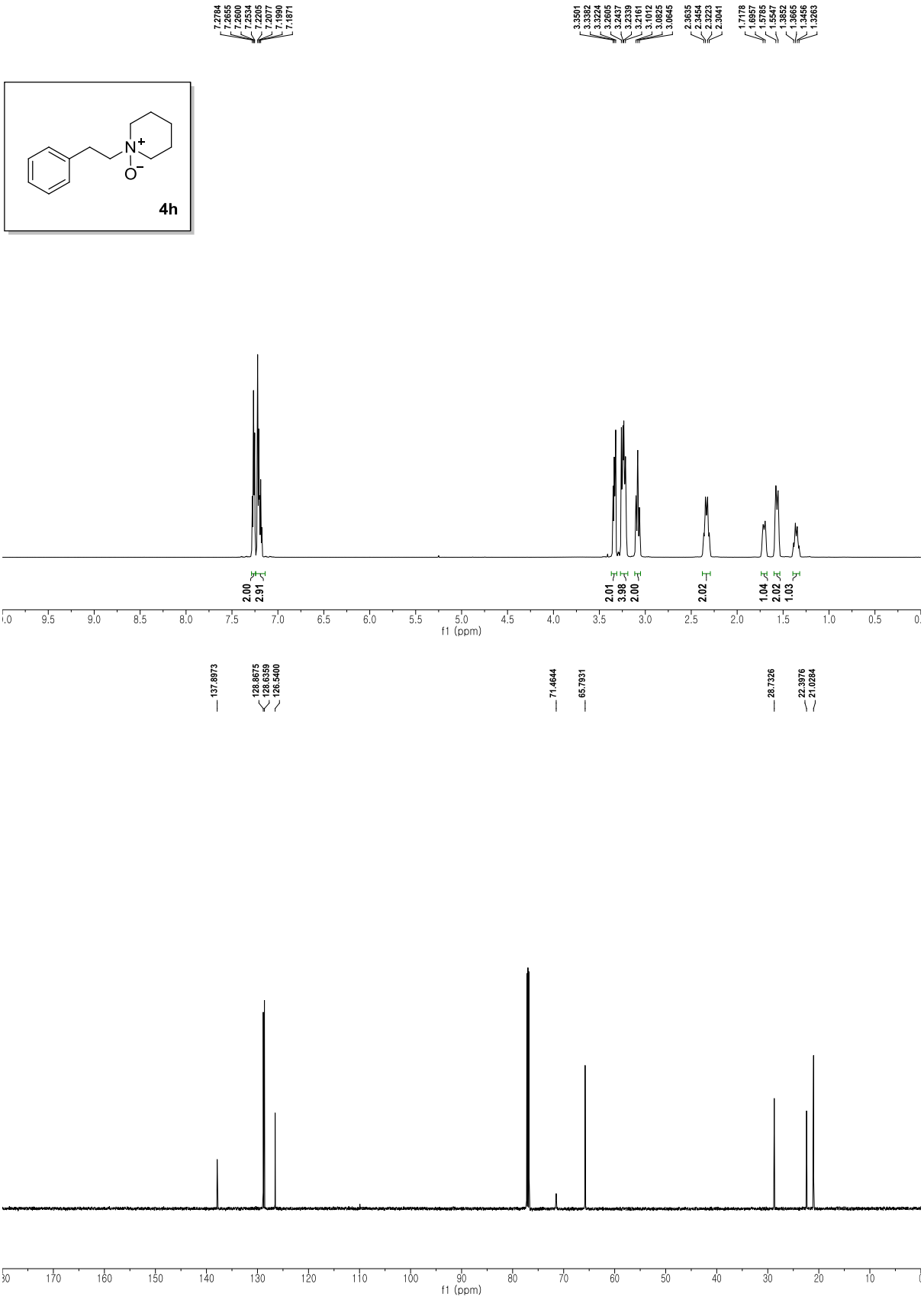
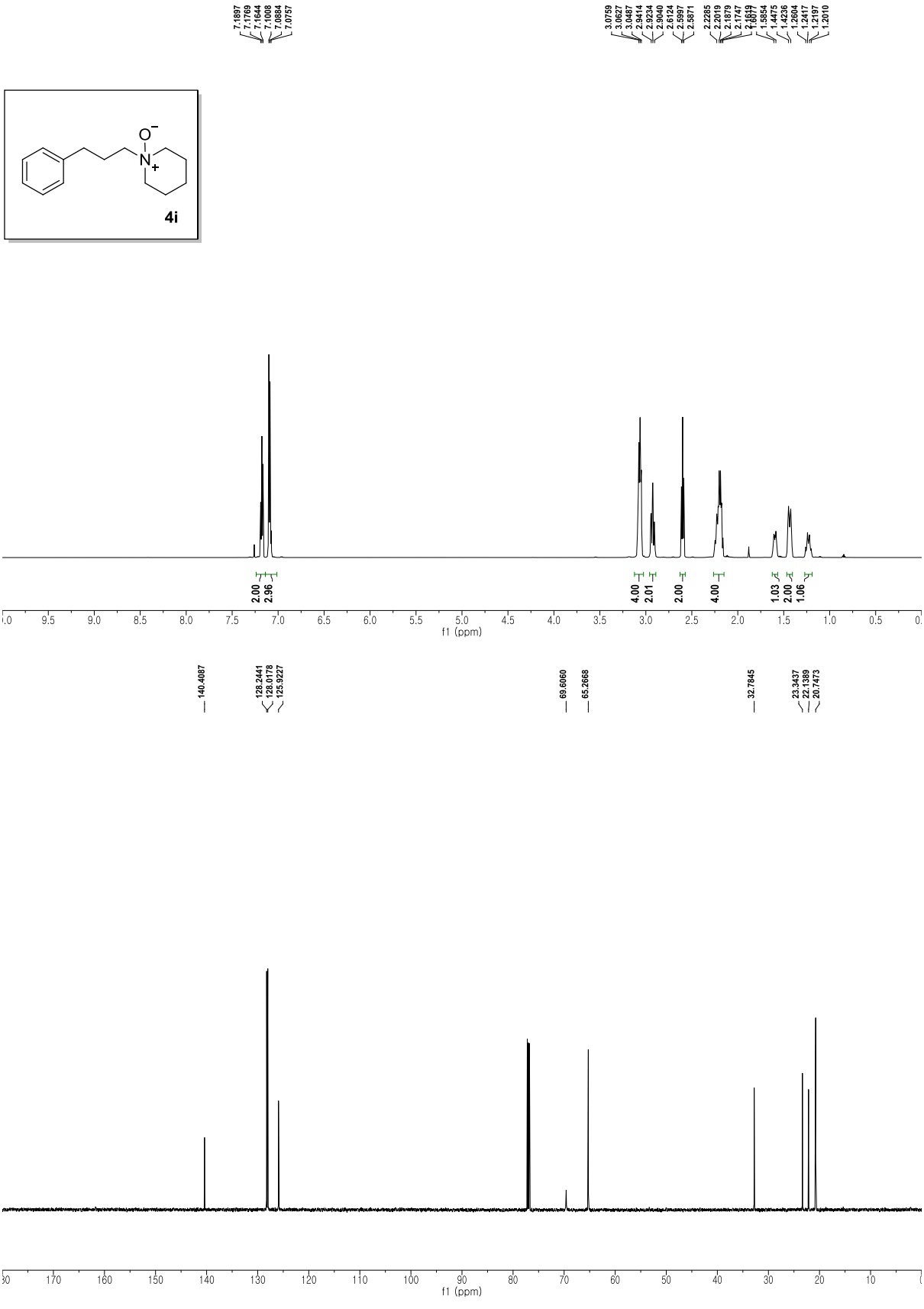
Appendix I

Copies of Spectroscopic Data of Compounds Obtained in This Study

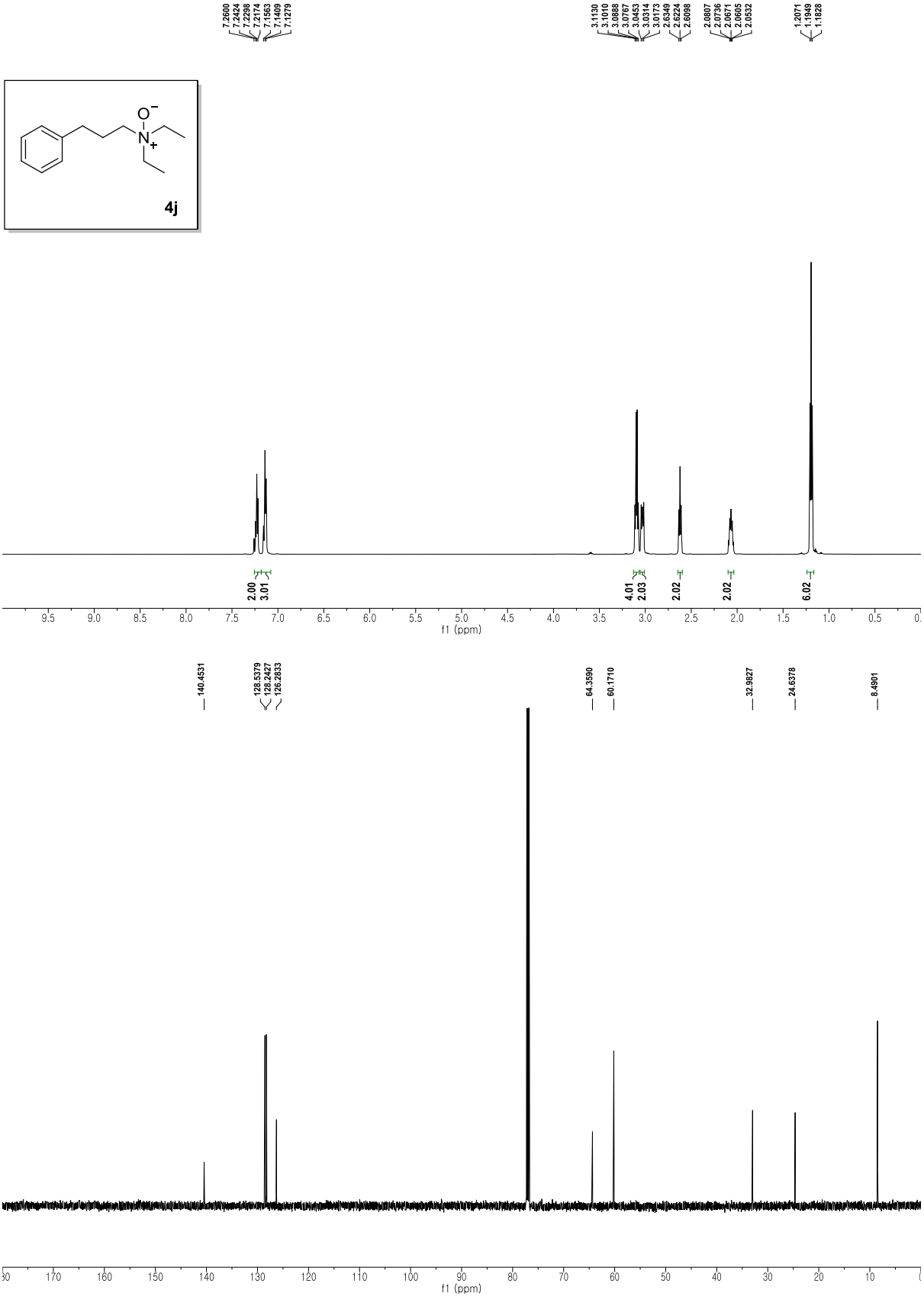
1-Phenethylpiperidine *N*-oxide (Table 3, **4h**)



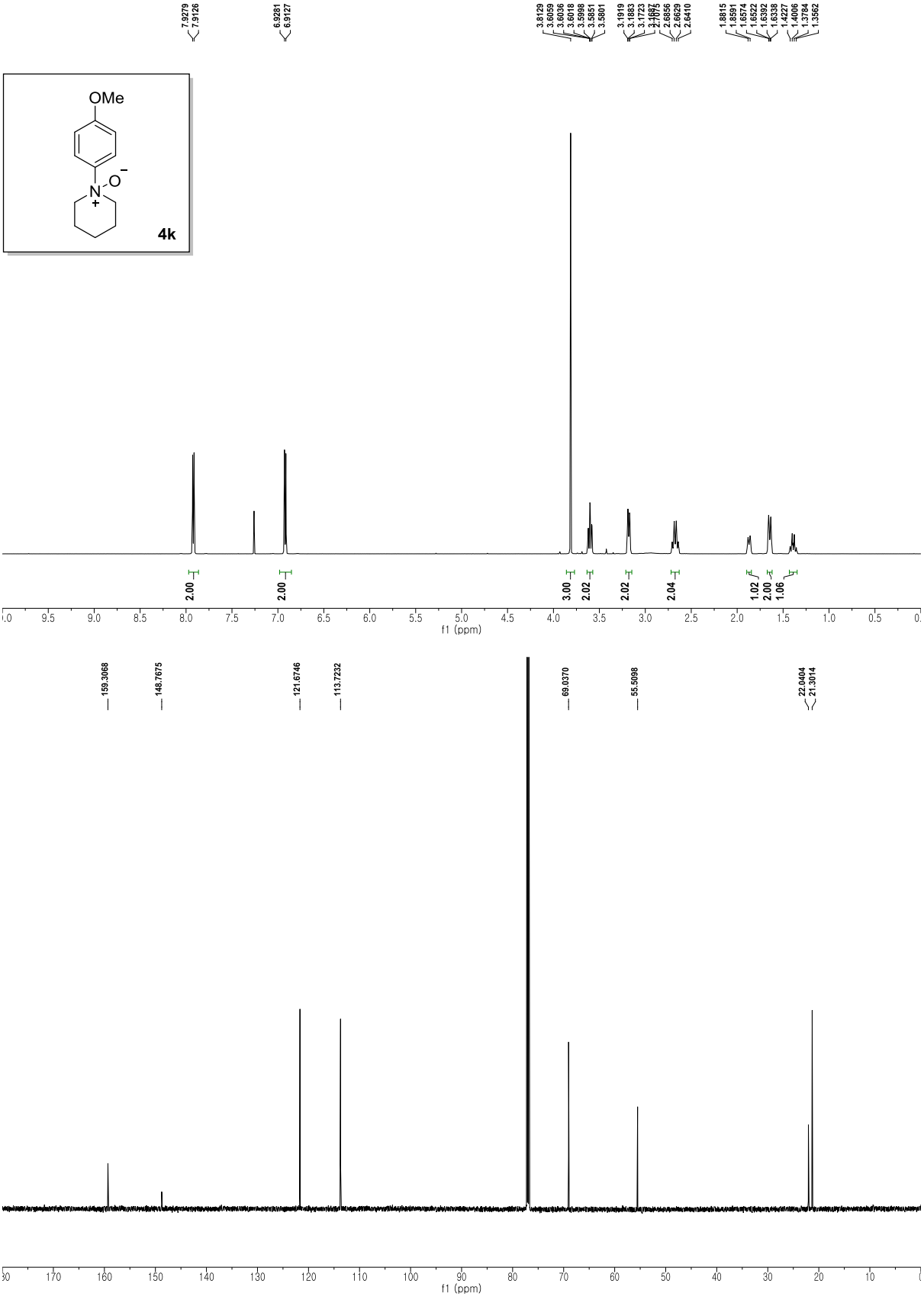
1-(3-Phenylpropyl)piperidine *N*-oxide (Table 3, **4i**)



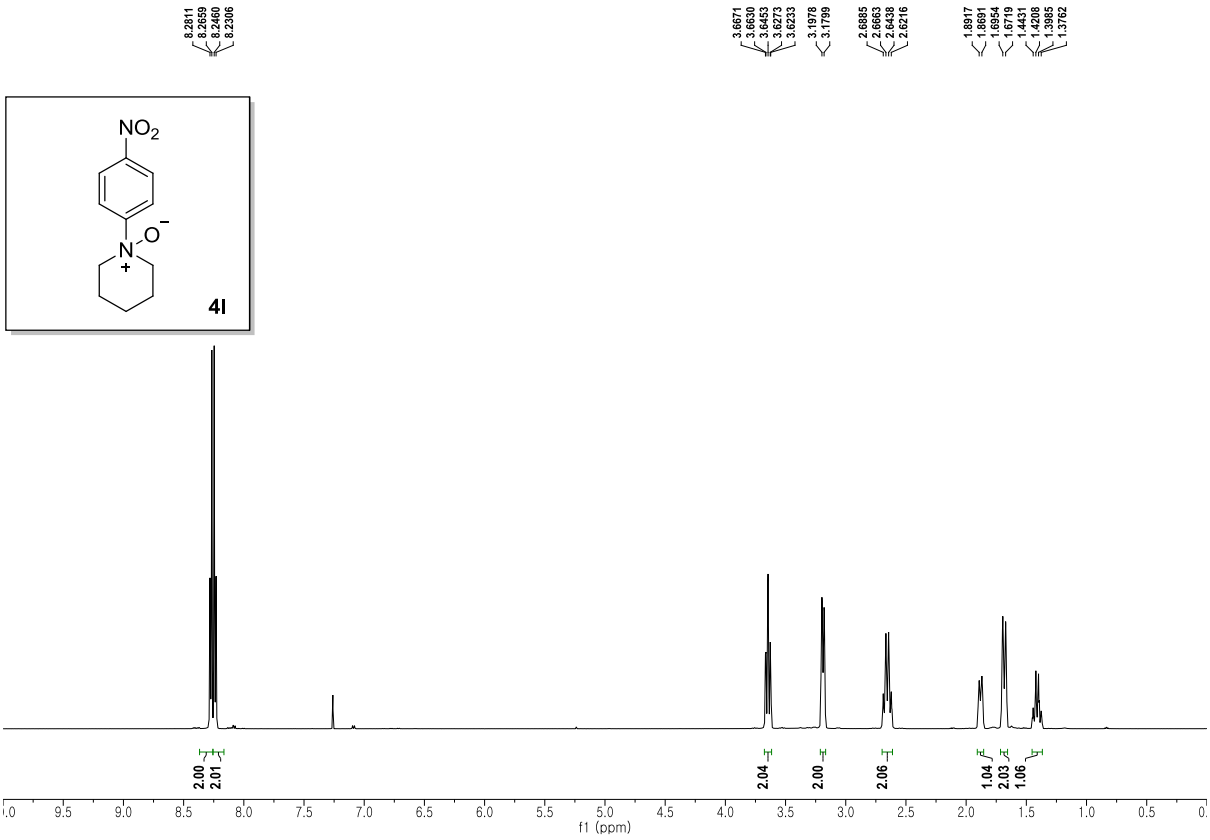
***N*,*N*-Diethyl-3-phenylpropylamine *N*-oxide** (Table 3, **4j**)

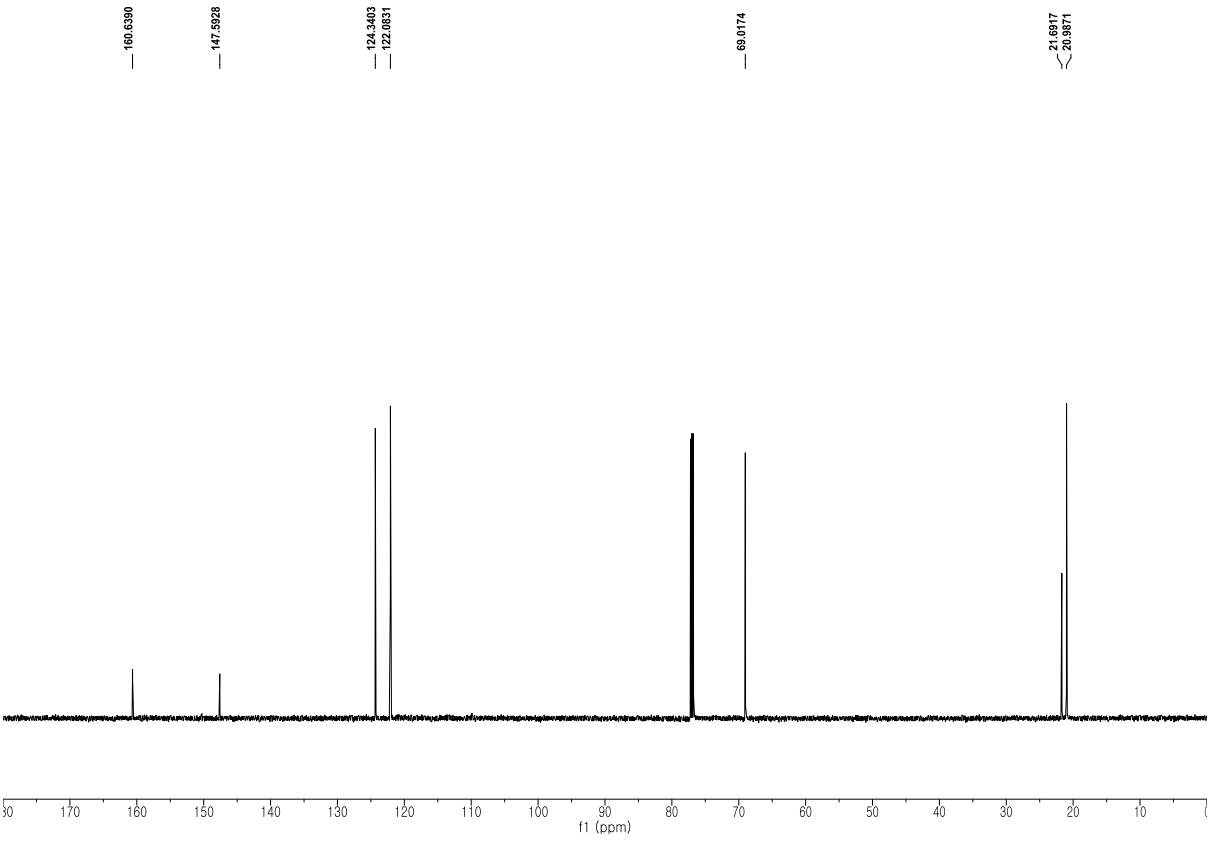


1-(4-Methoxyphenyl)piperidine *N*-oxide (Table 3, **4k**)

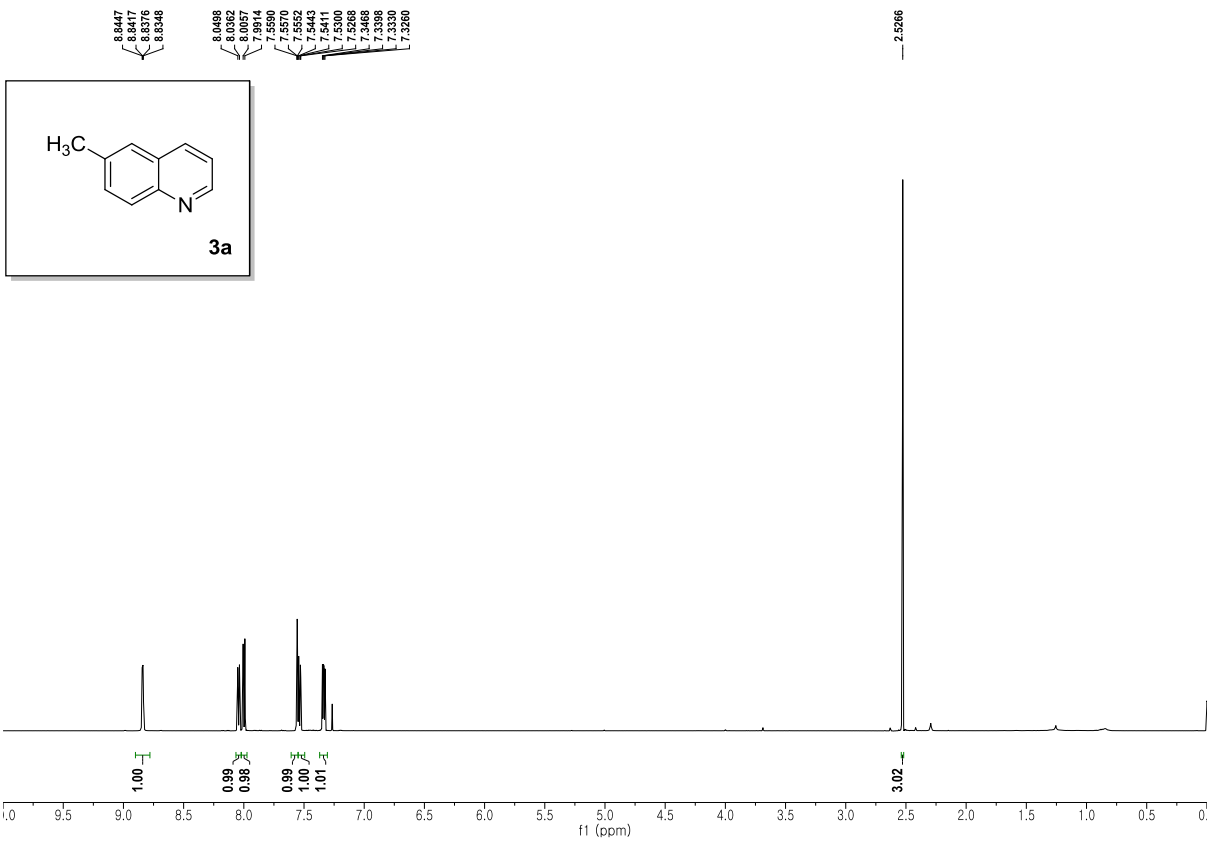


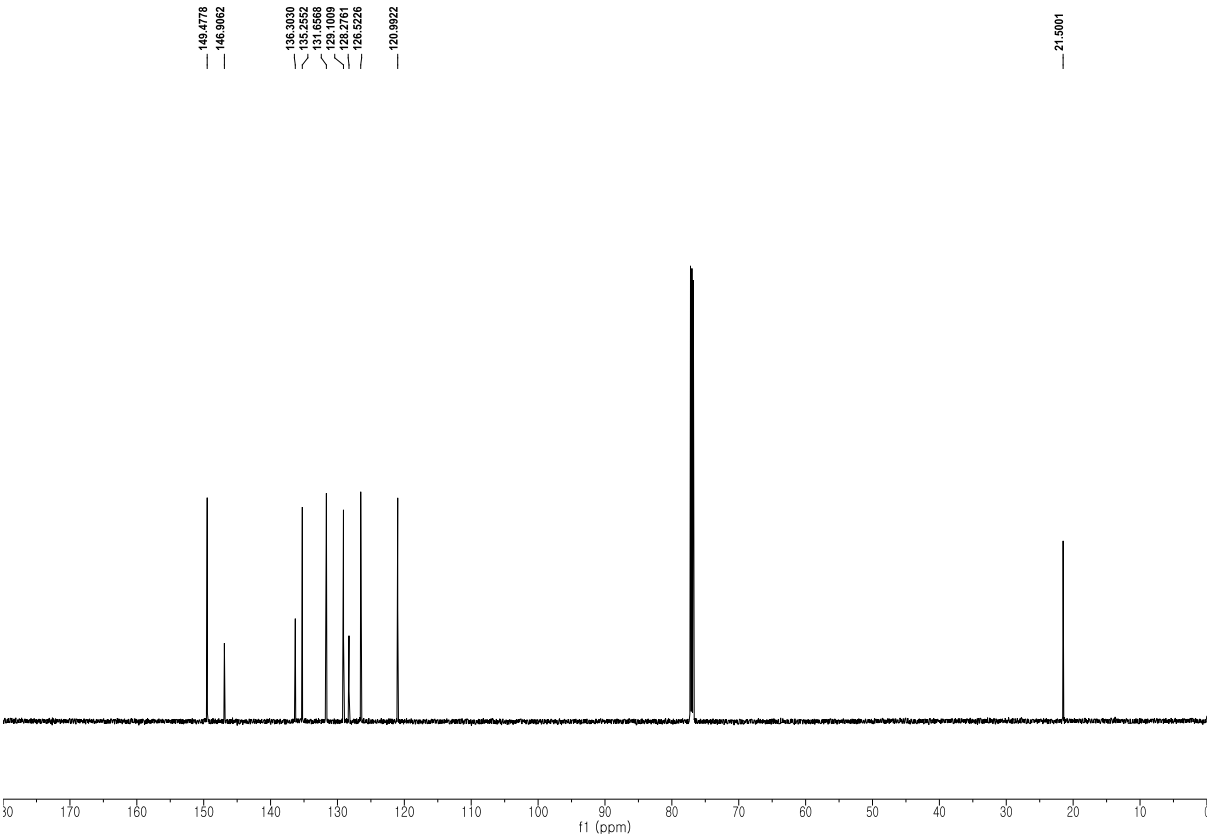
1-(4-Nitrophenyl)piperidine *N*-oxide (Table 3, **4l**)



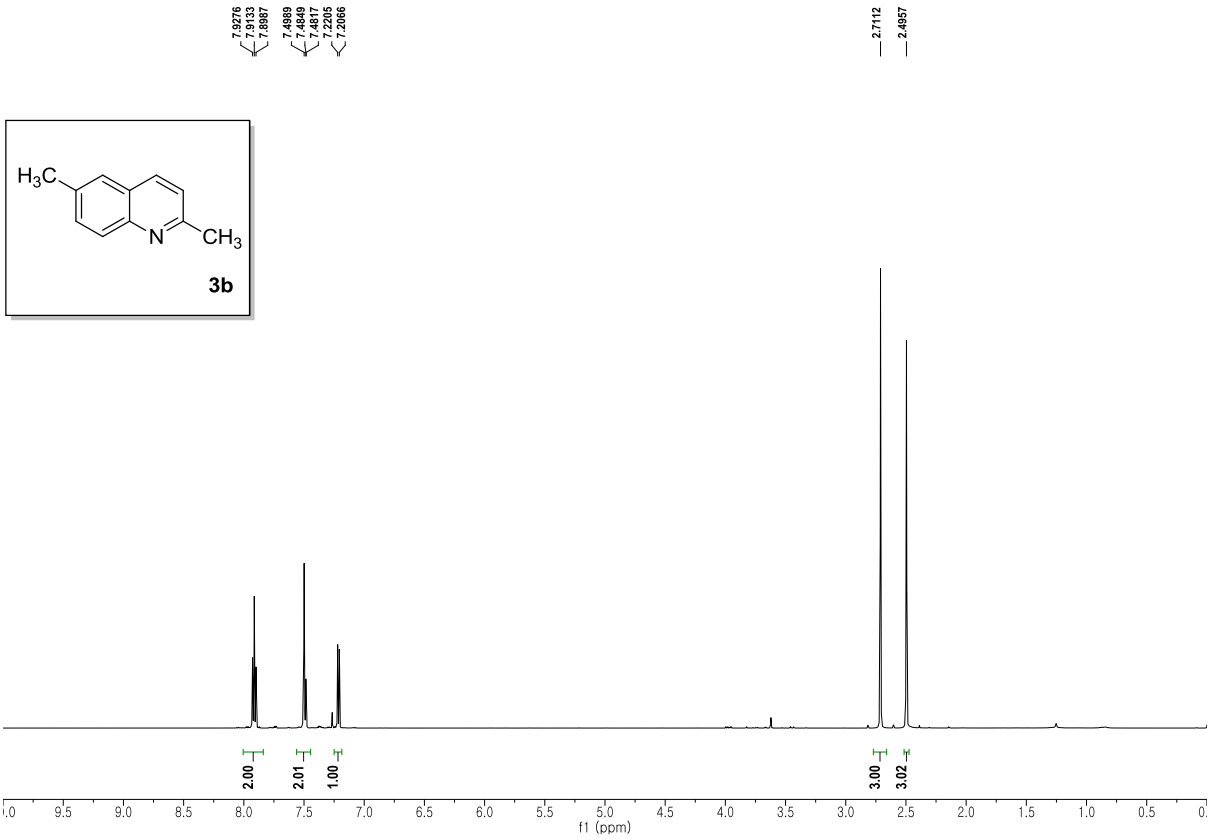


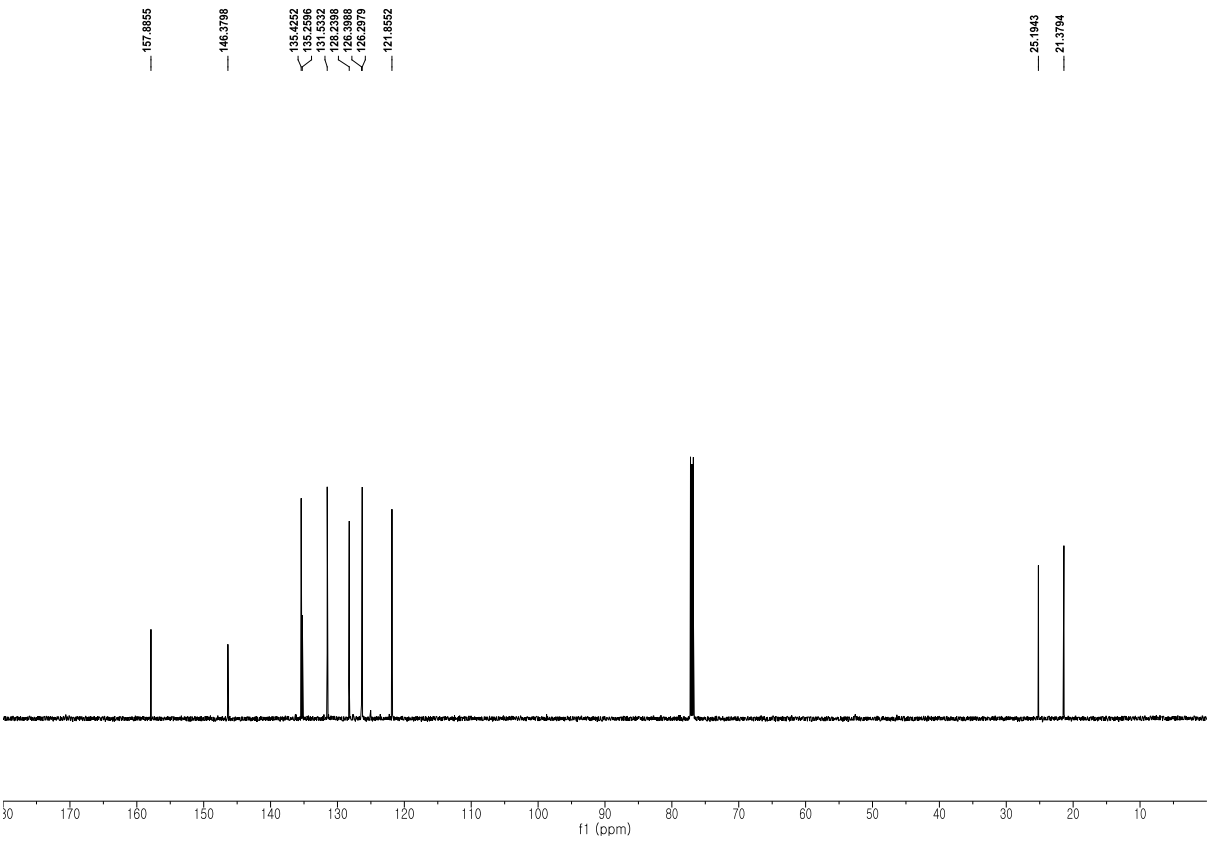
6-Methylquinoline (Scheme 2, **3a**)



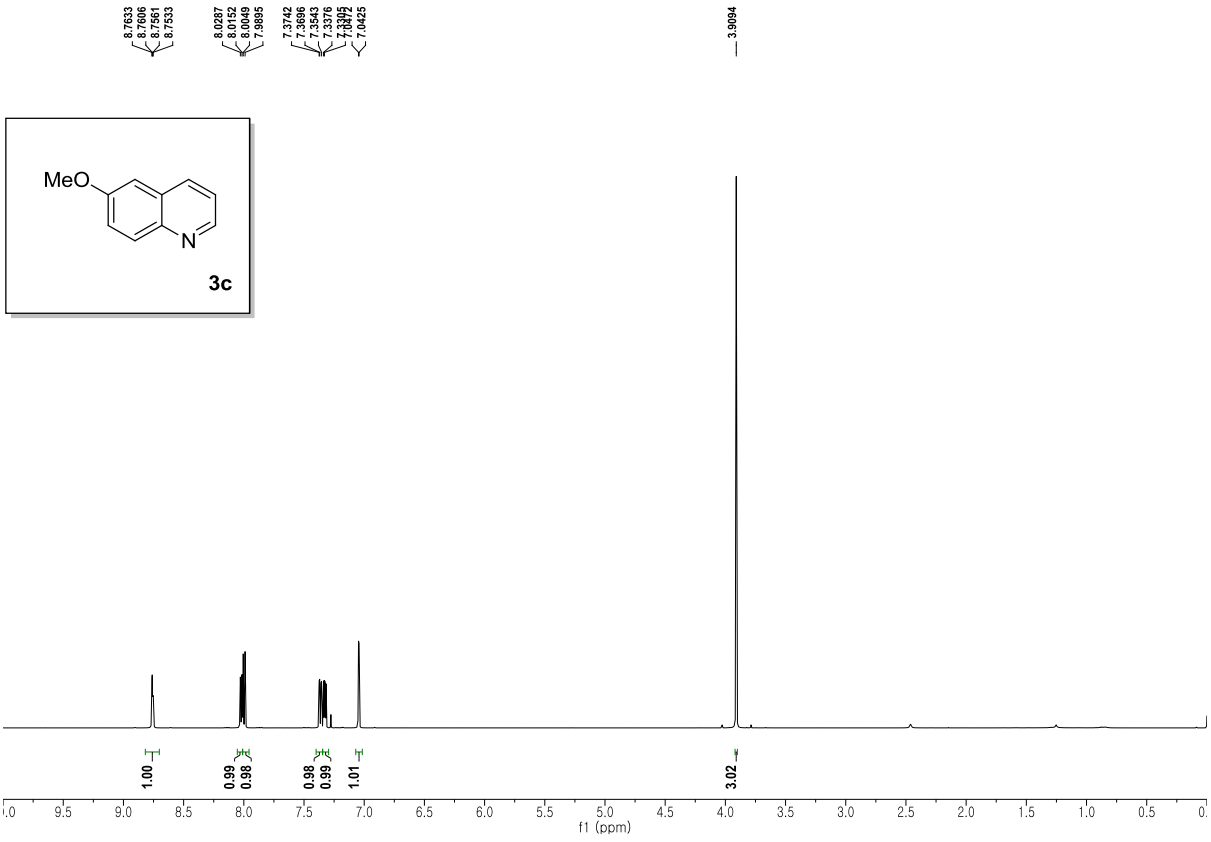


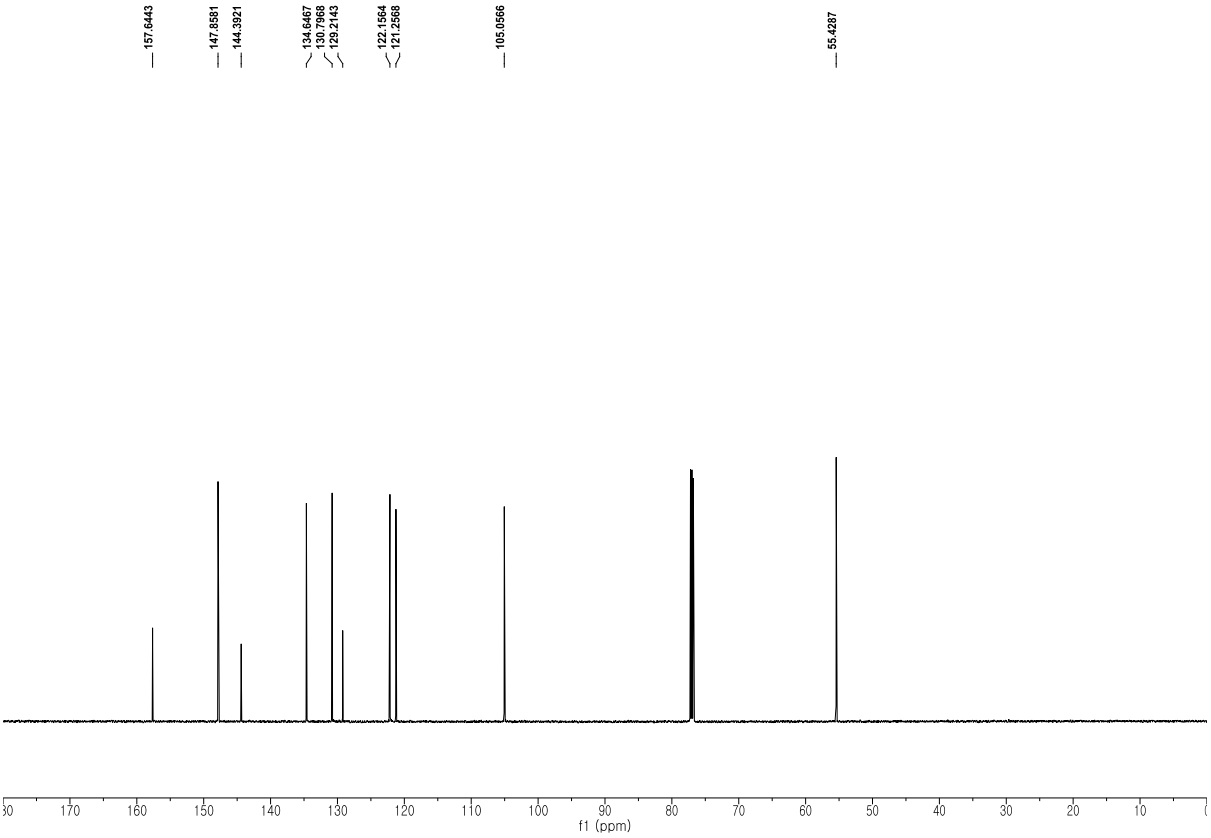
2,6-Dimethylquinoline (Table 2, **3b**)



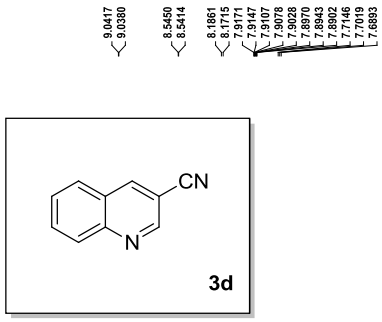


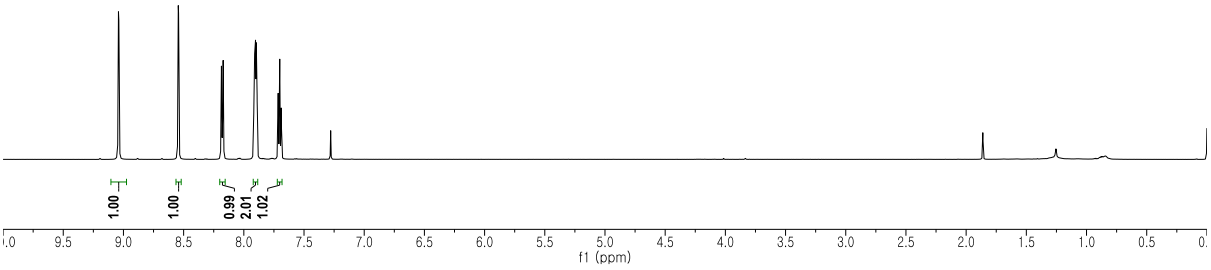
6-Methoxyquinoline (Table 2, **3c**)

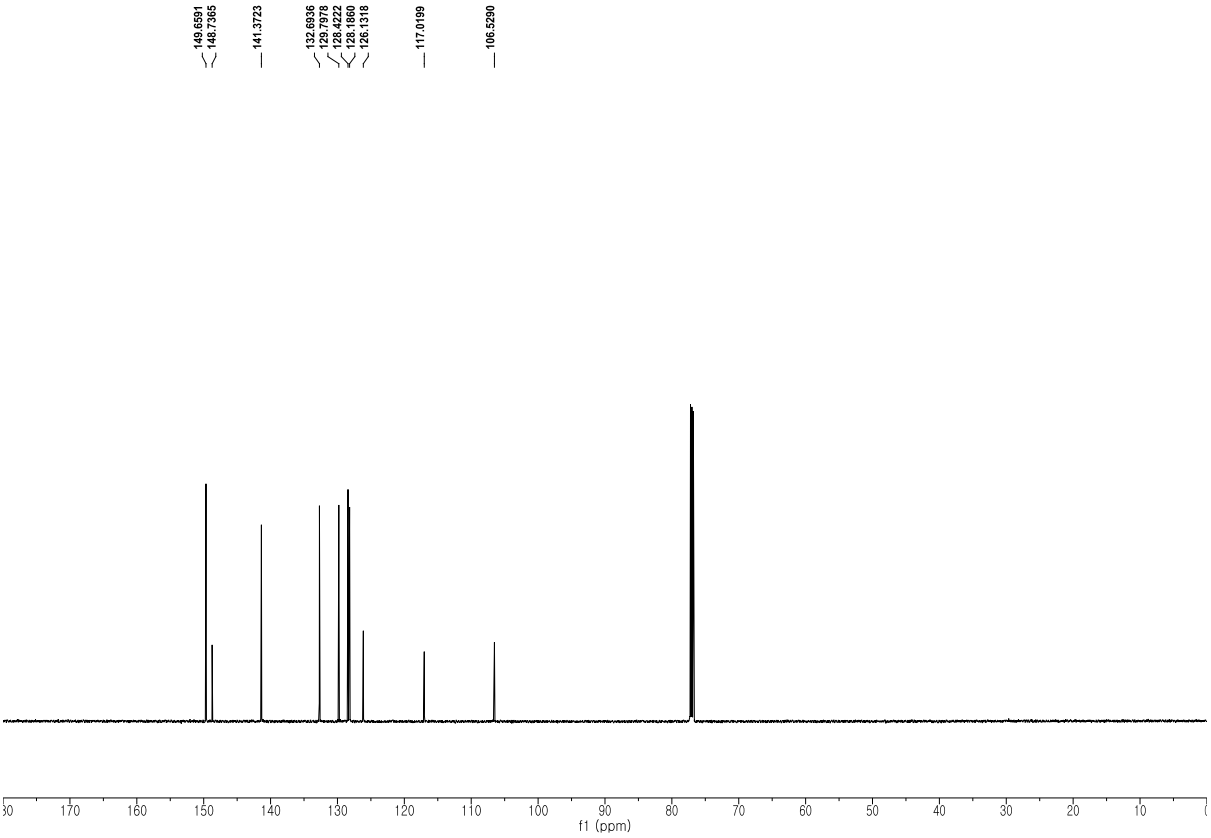




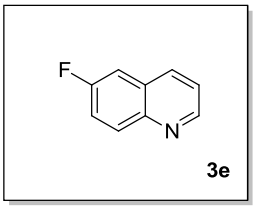
3-Cyanoquinoline (Table 2, **3d**)

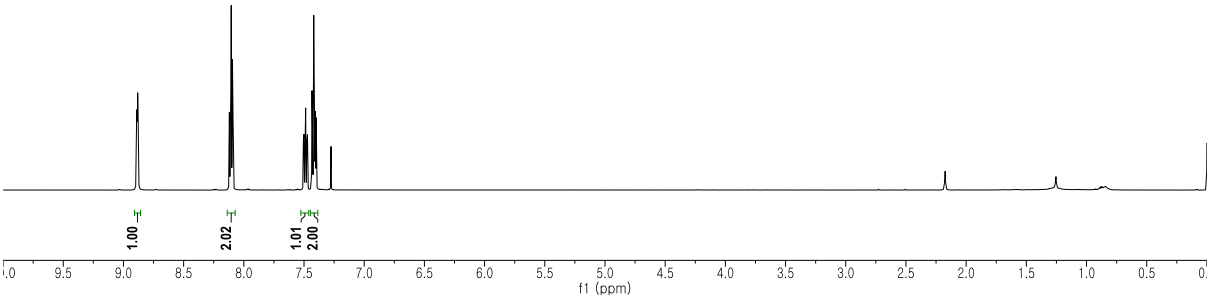


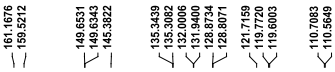


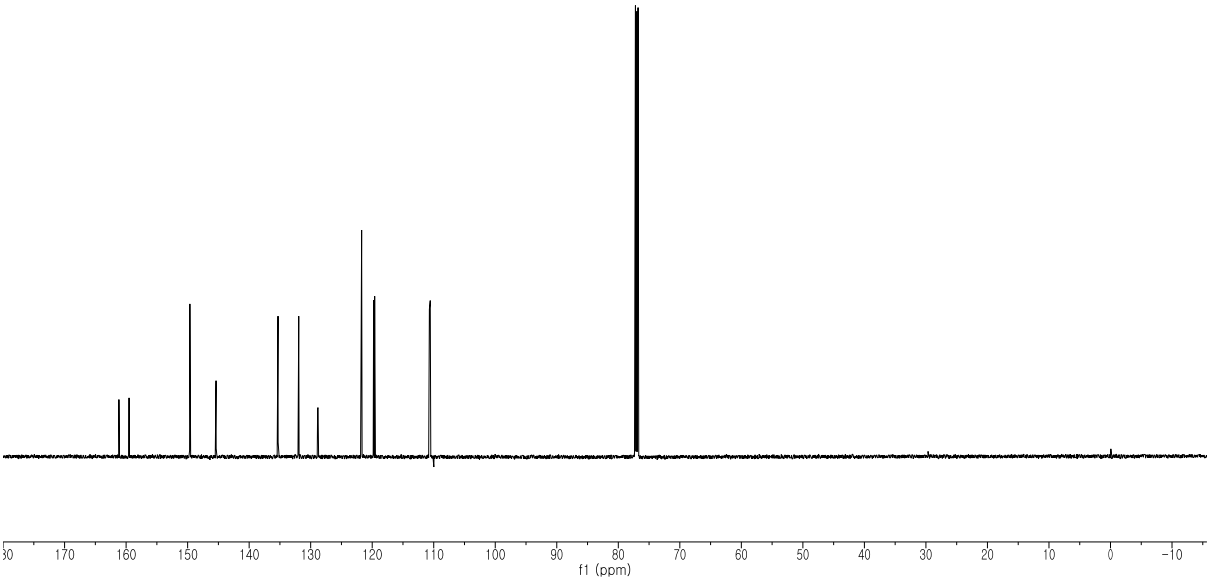


6-Fluoroquinoline (Table 2, **3e**)

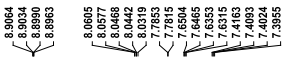


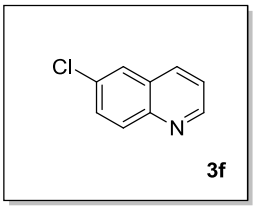


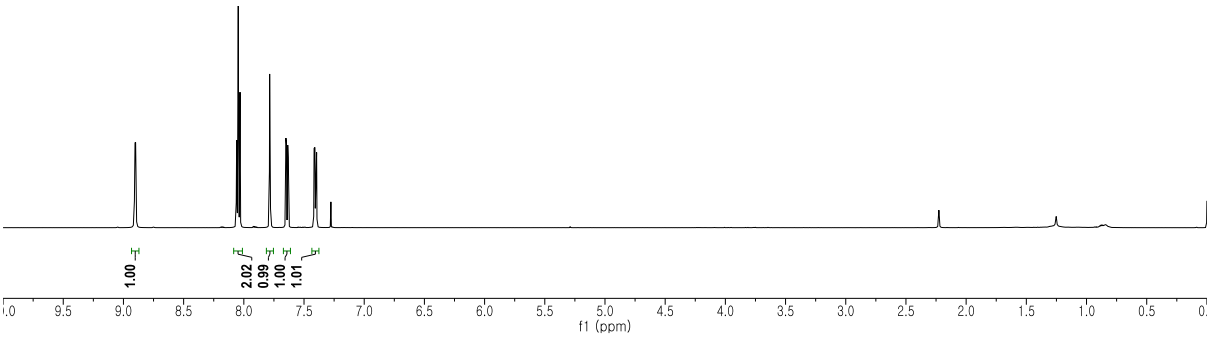


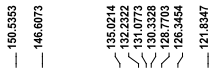


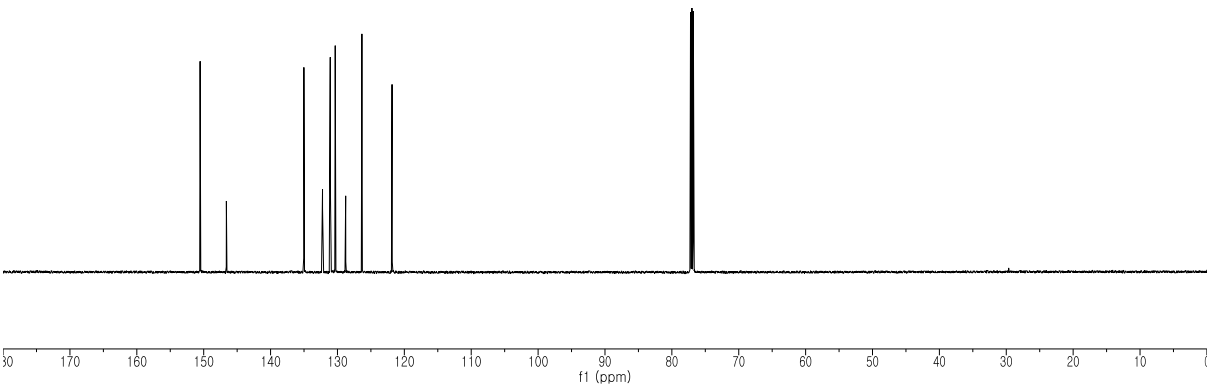
6-Chloroquinoline (Table 2, **3f**)



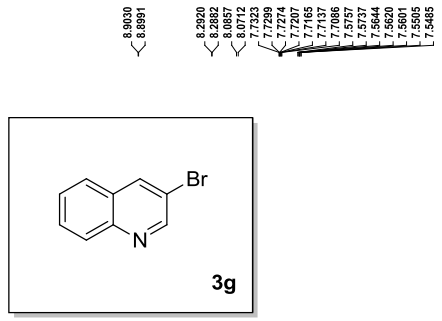


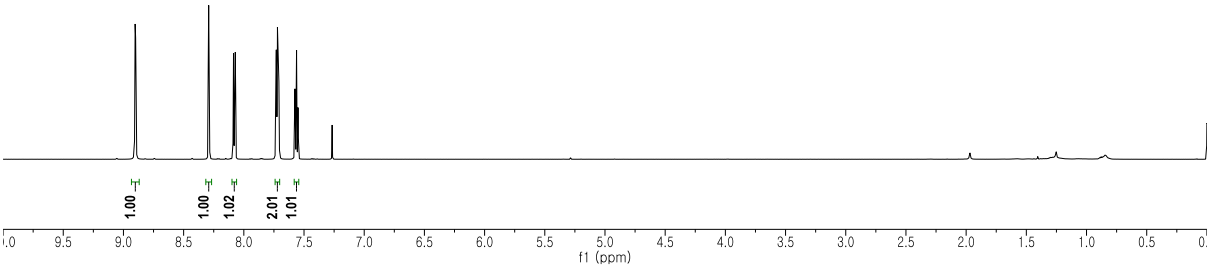


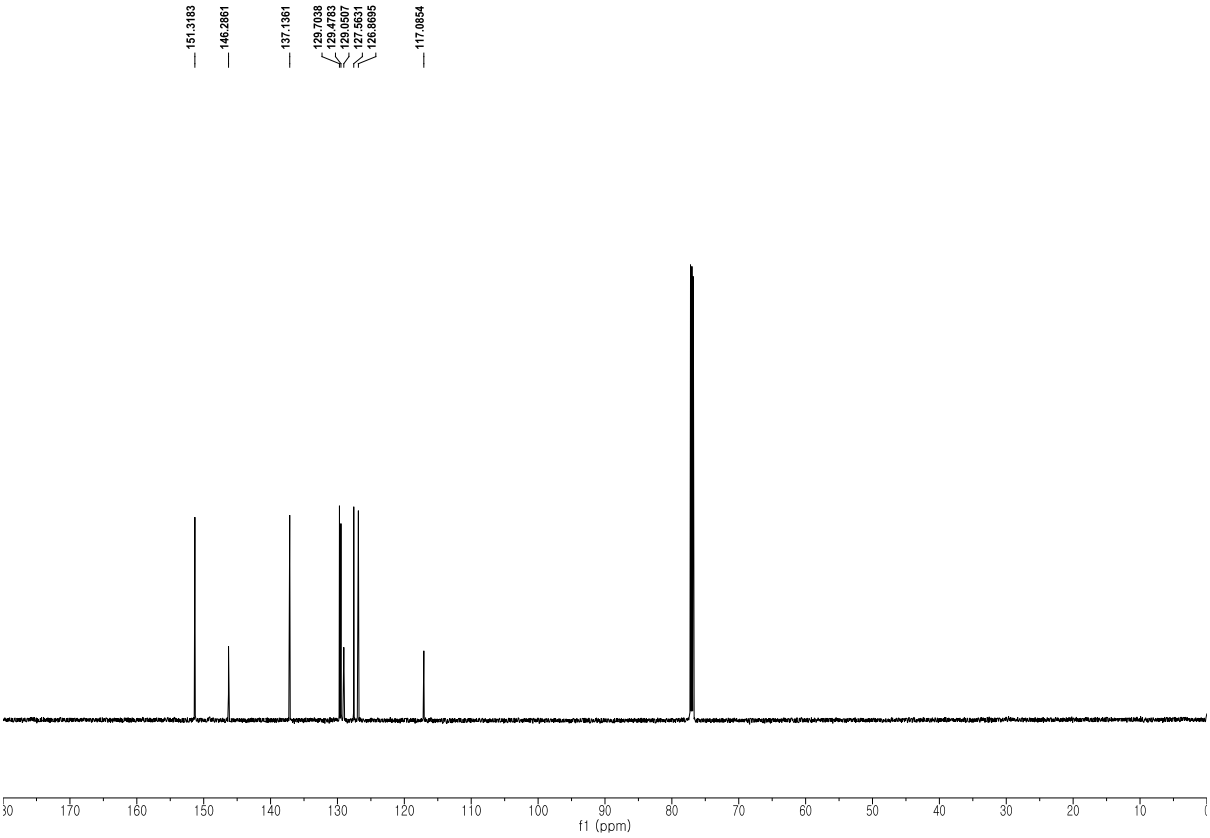




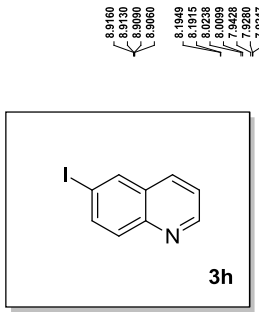
3-Bromoquinoline (Table 2, **3g**)



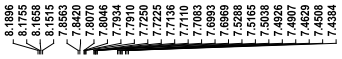


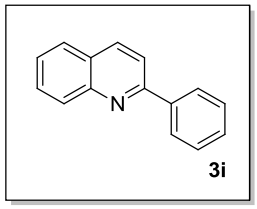


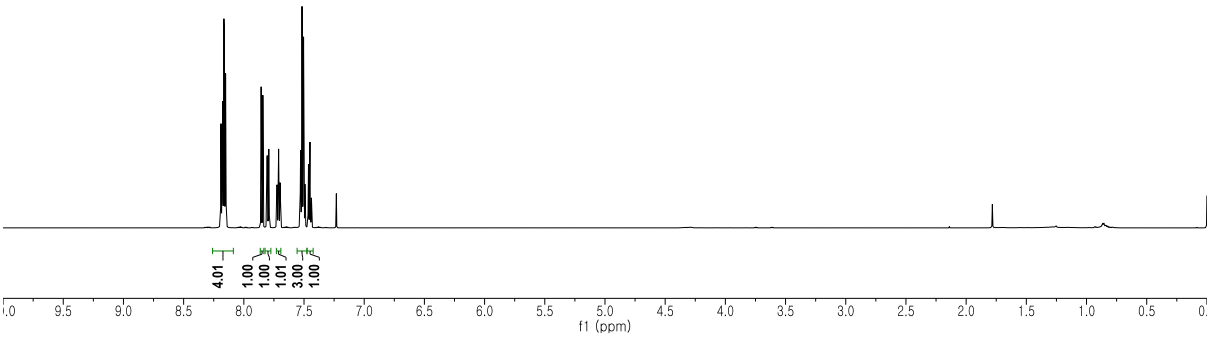
6-Iodoquinoline (Table 2, **3h**)

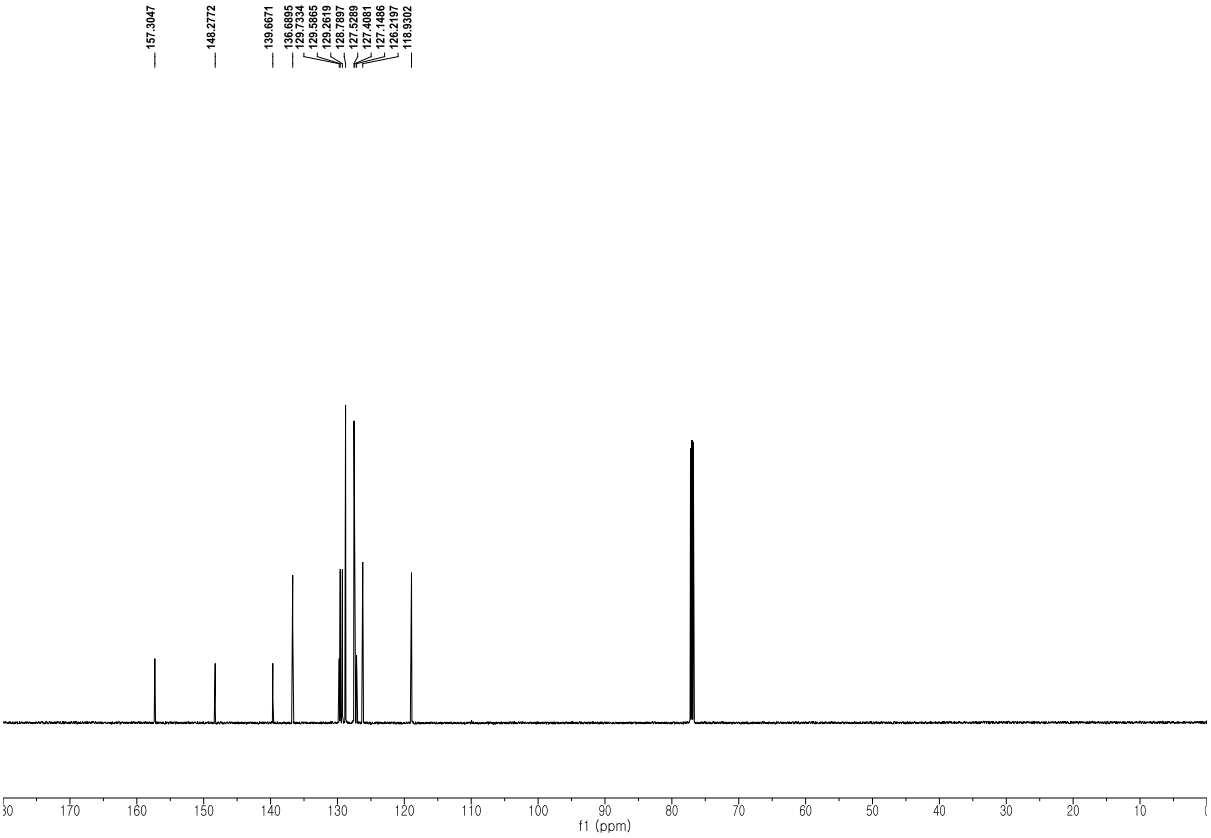


2-Phenylquinoline (Table 2, **3i**)

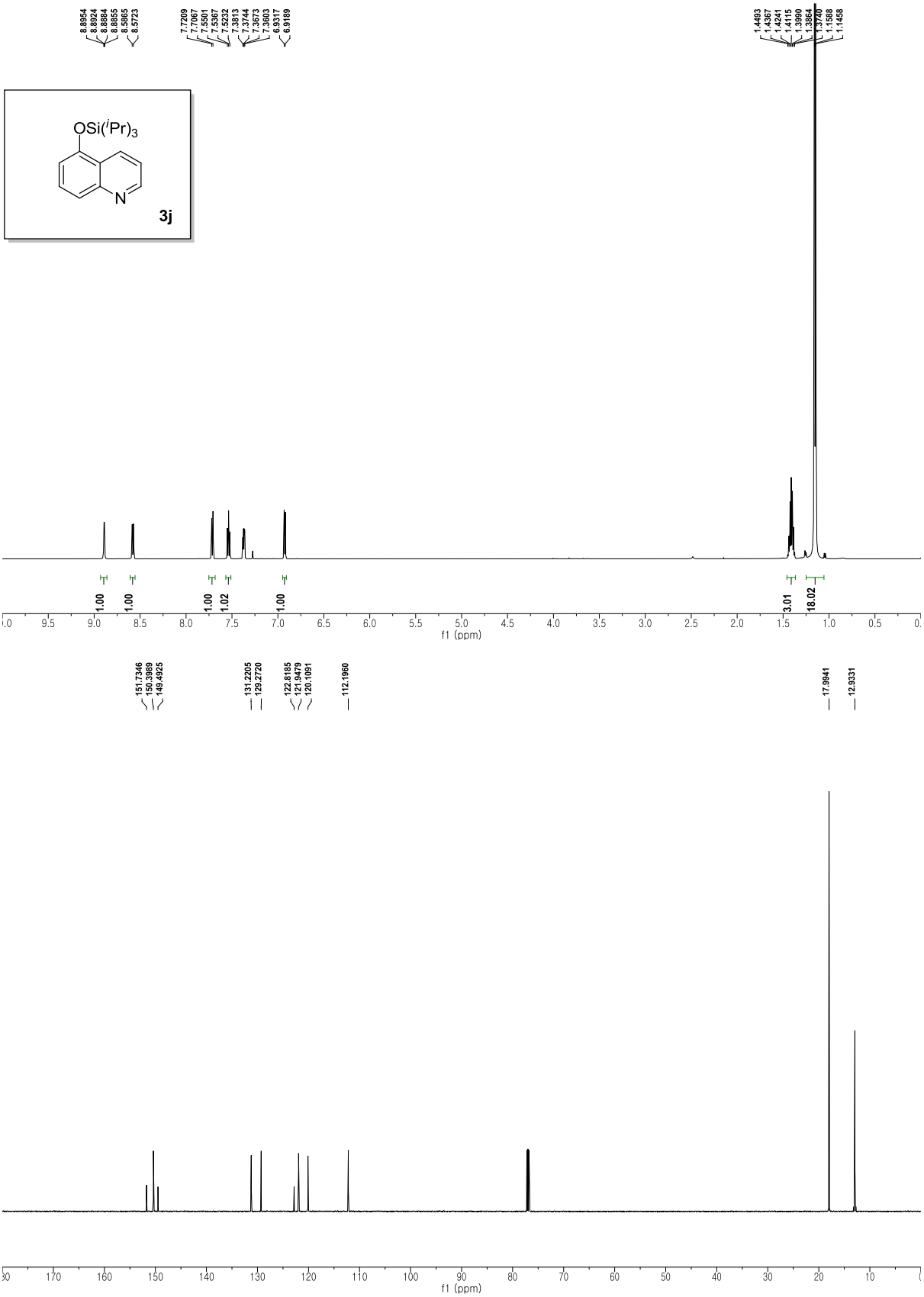




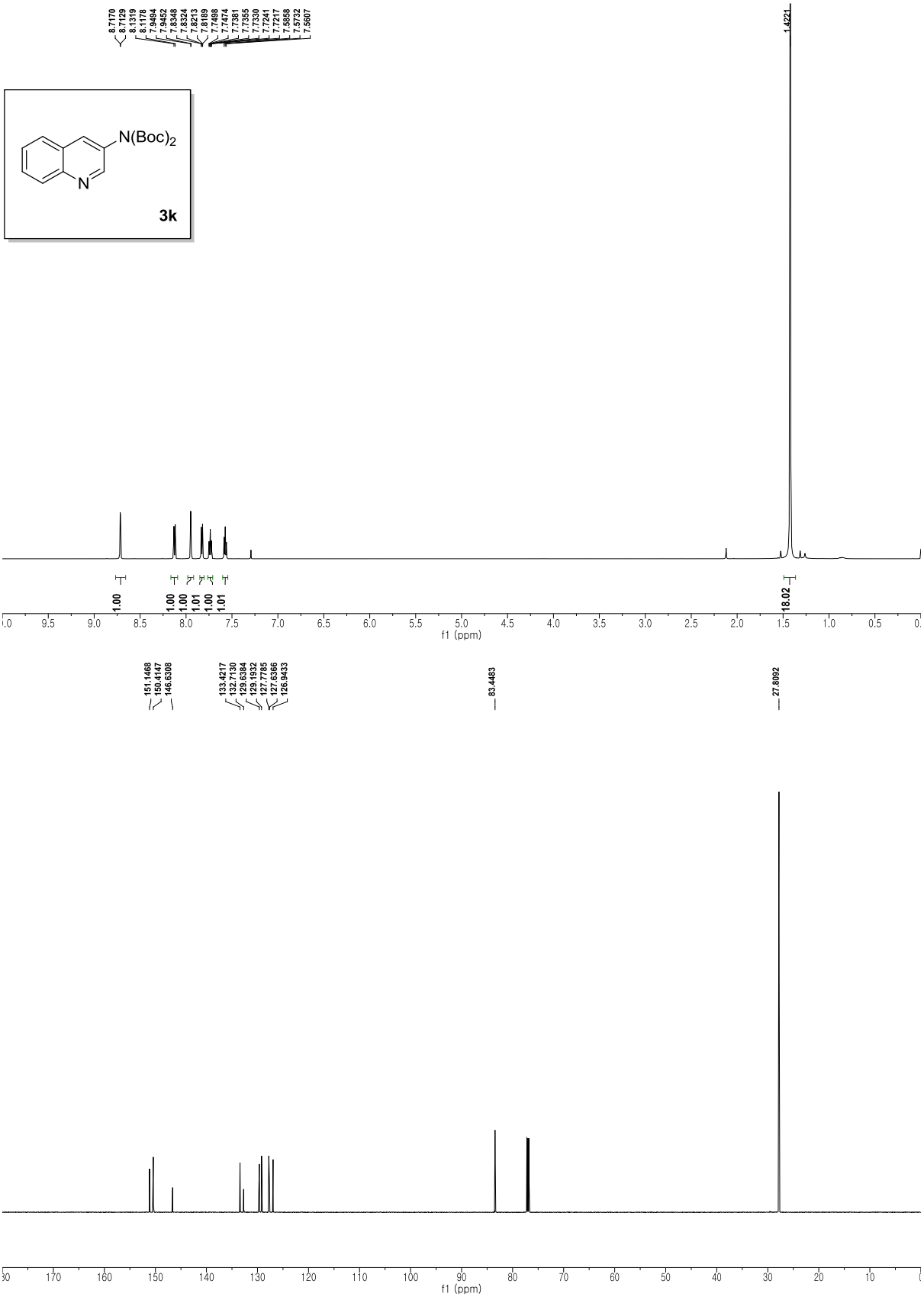




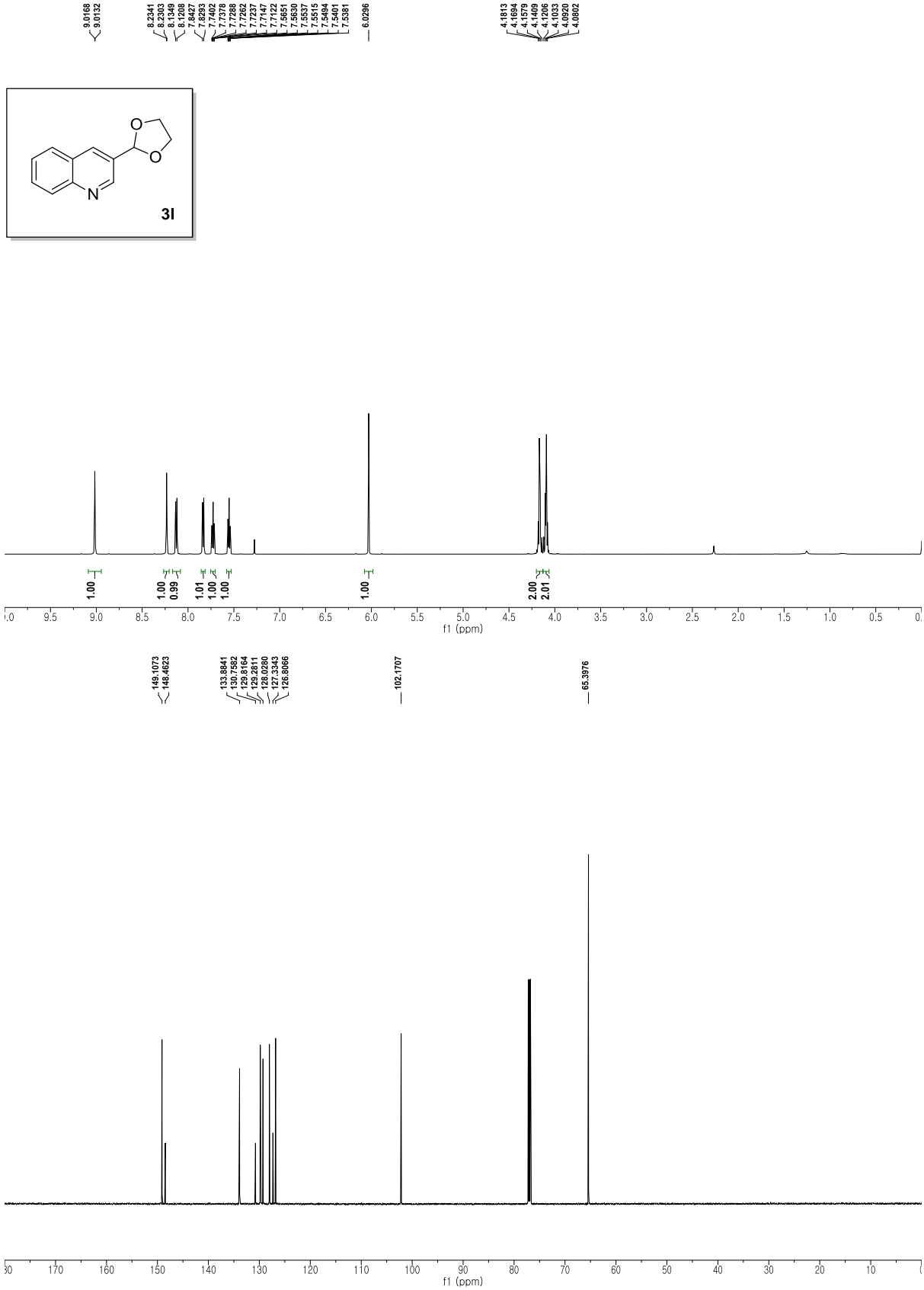
5-(Triisopropylsilyloxy)quinoline (Table 2, **3j**)



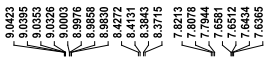
3-[Bis(*tert*-butoxycarbonyl)amino]quinoline (Table 2, **3k**)

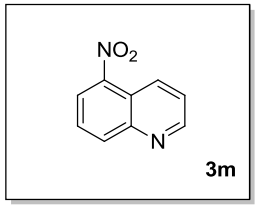


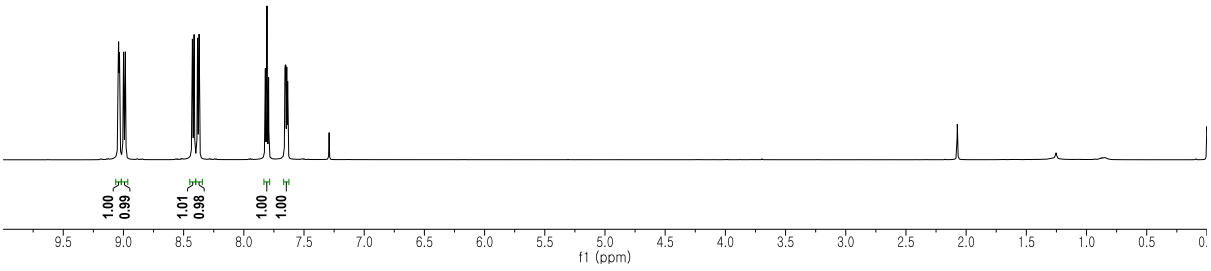
3-(1,3-Dioxolan-2-yl)quinoline (Table 2, **3l**)

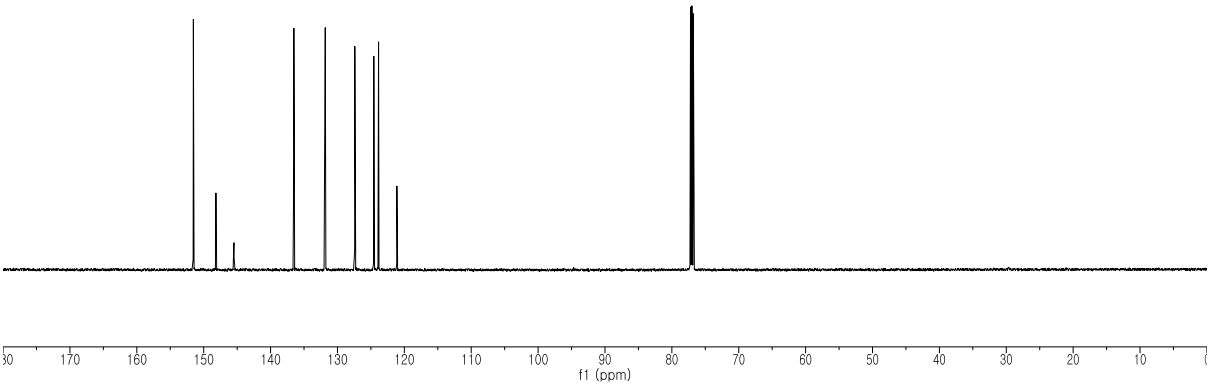


5-Nitroquinoline (Table 2, **3m**)

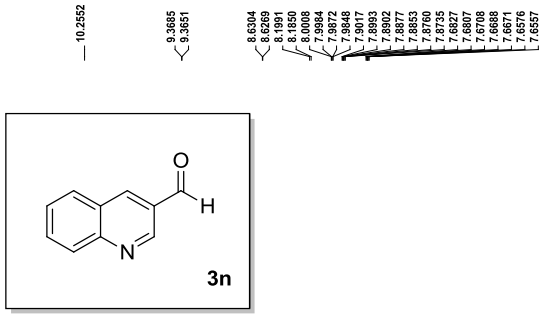


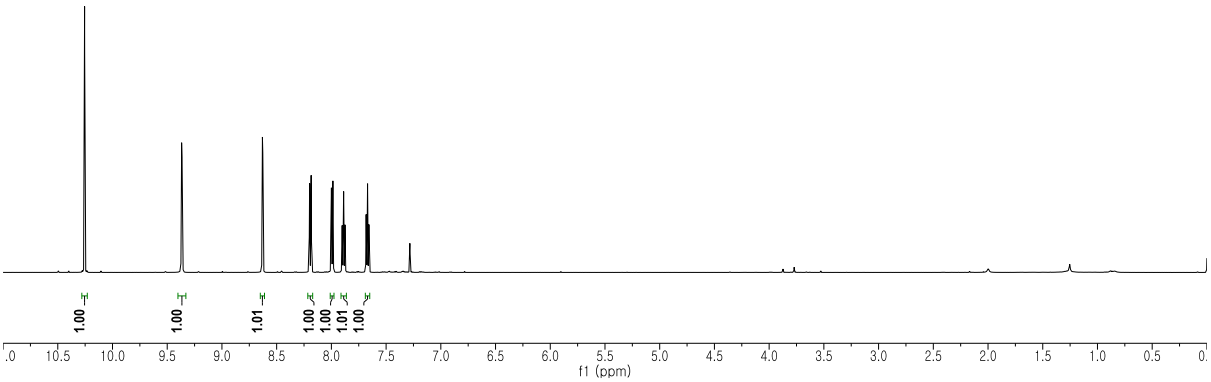


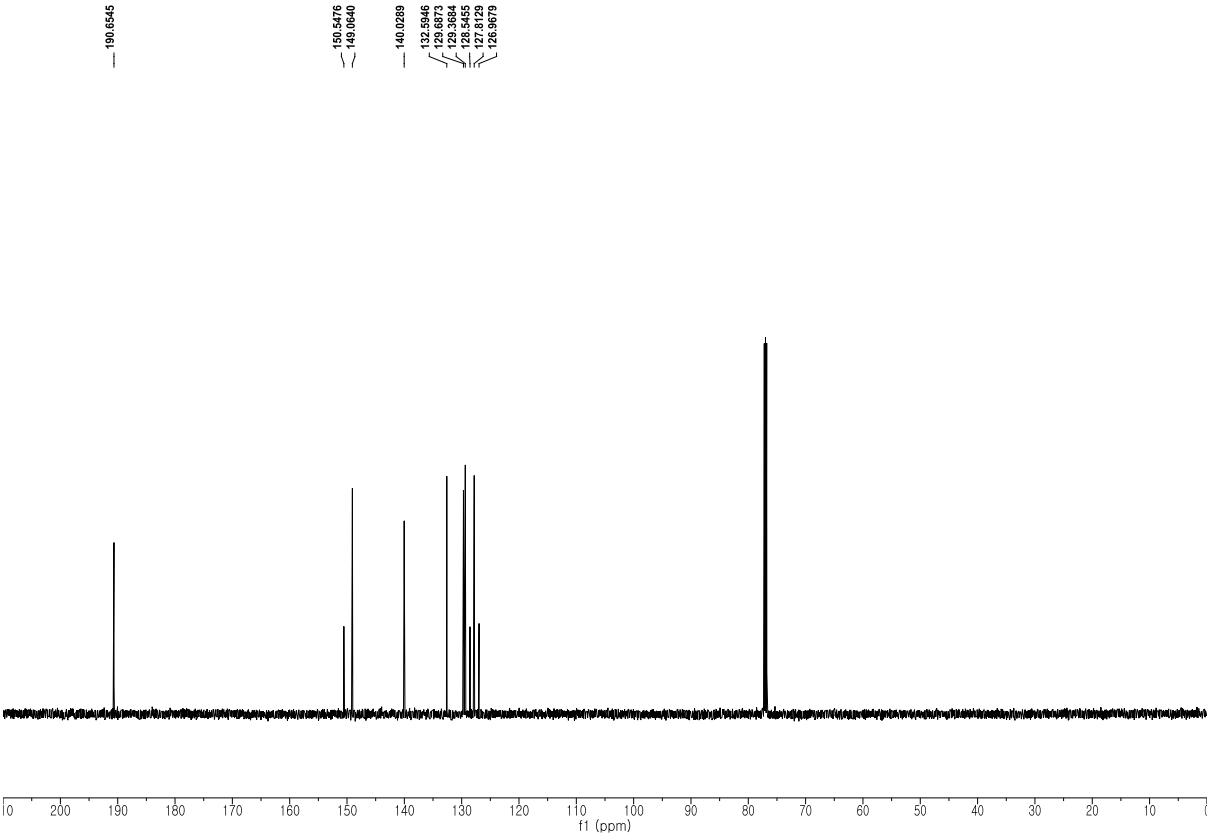




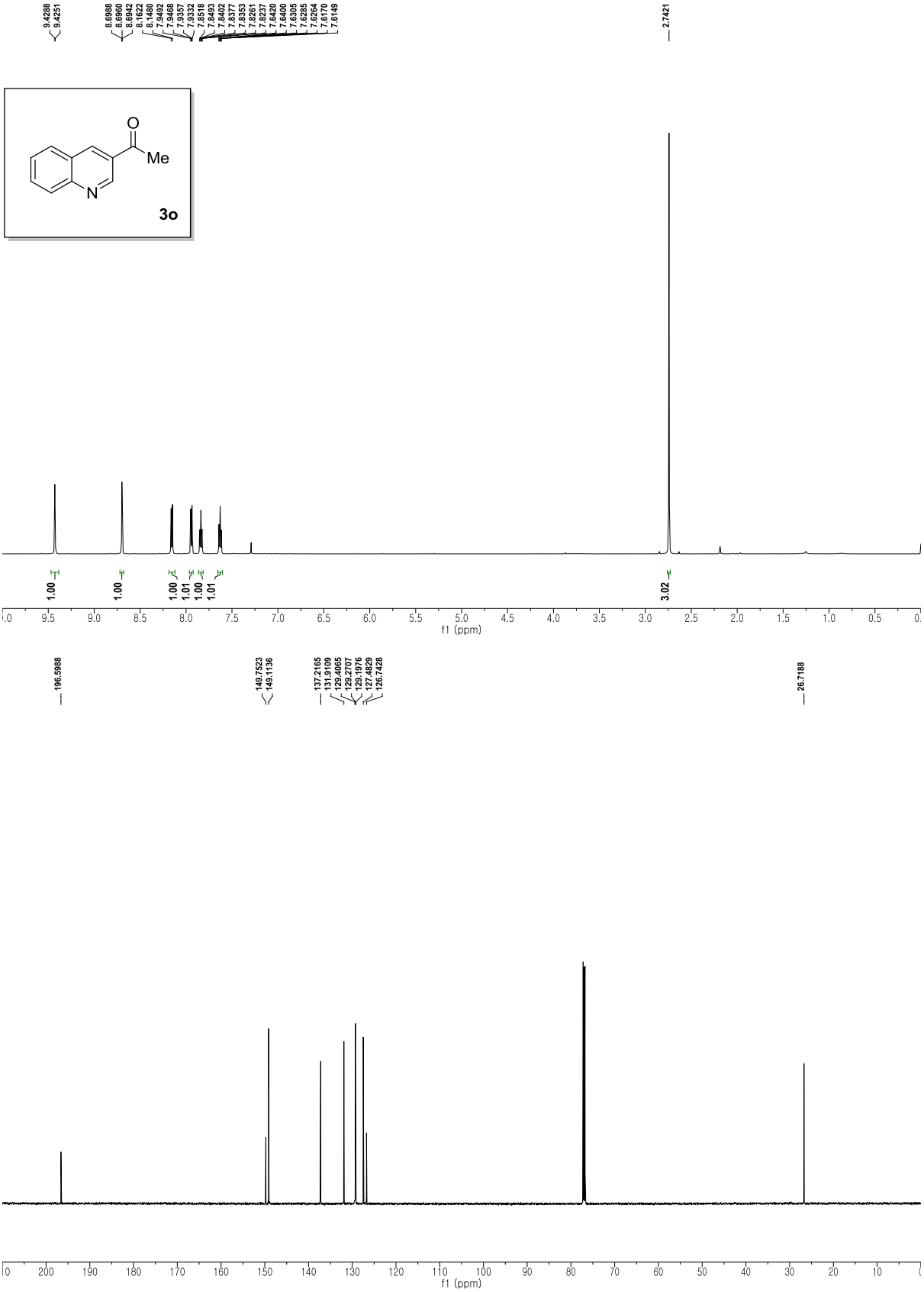
3-Formylquinoline (Table 2, **3n**)



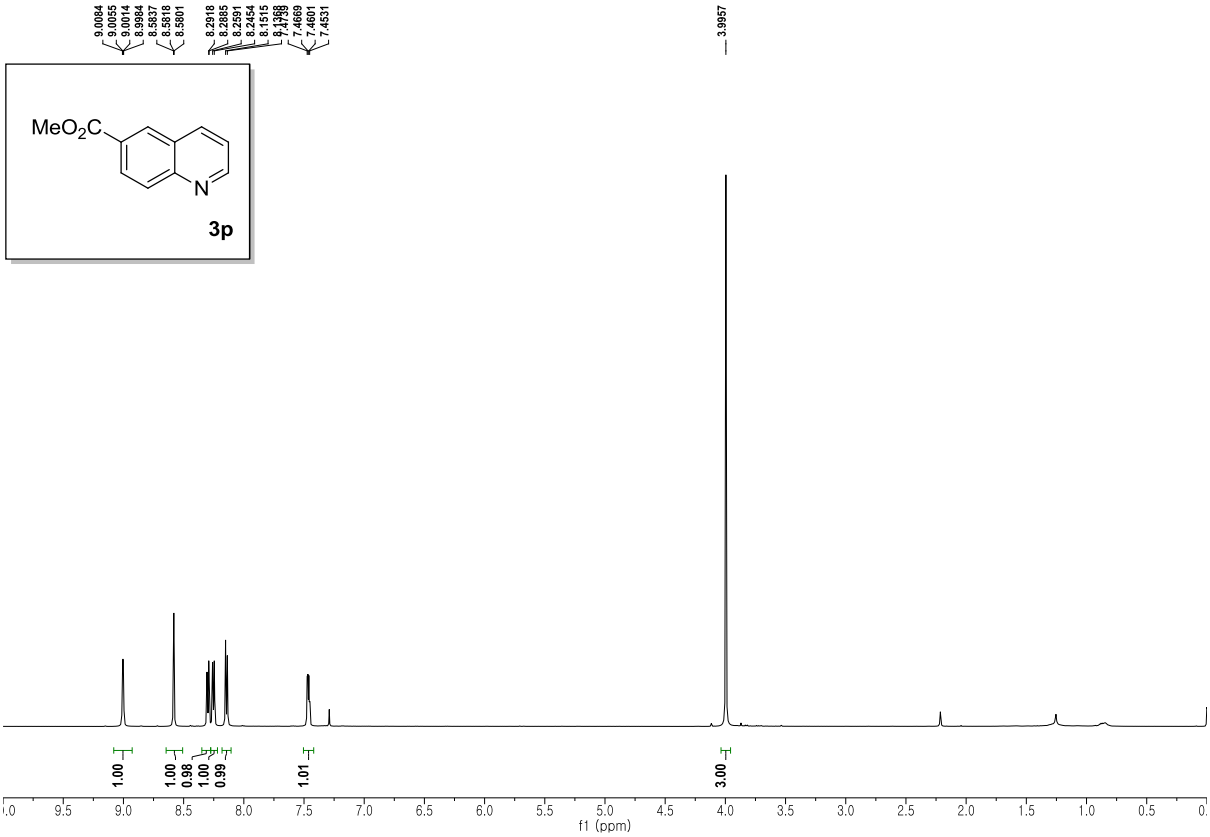


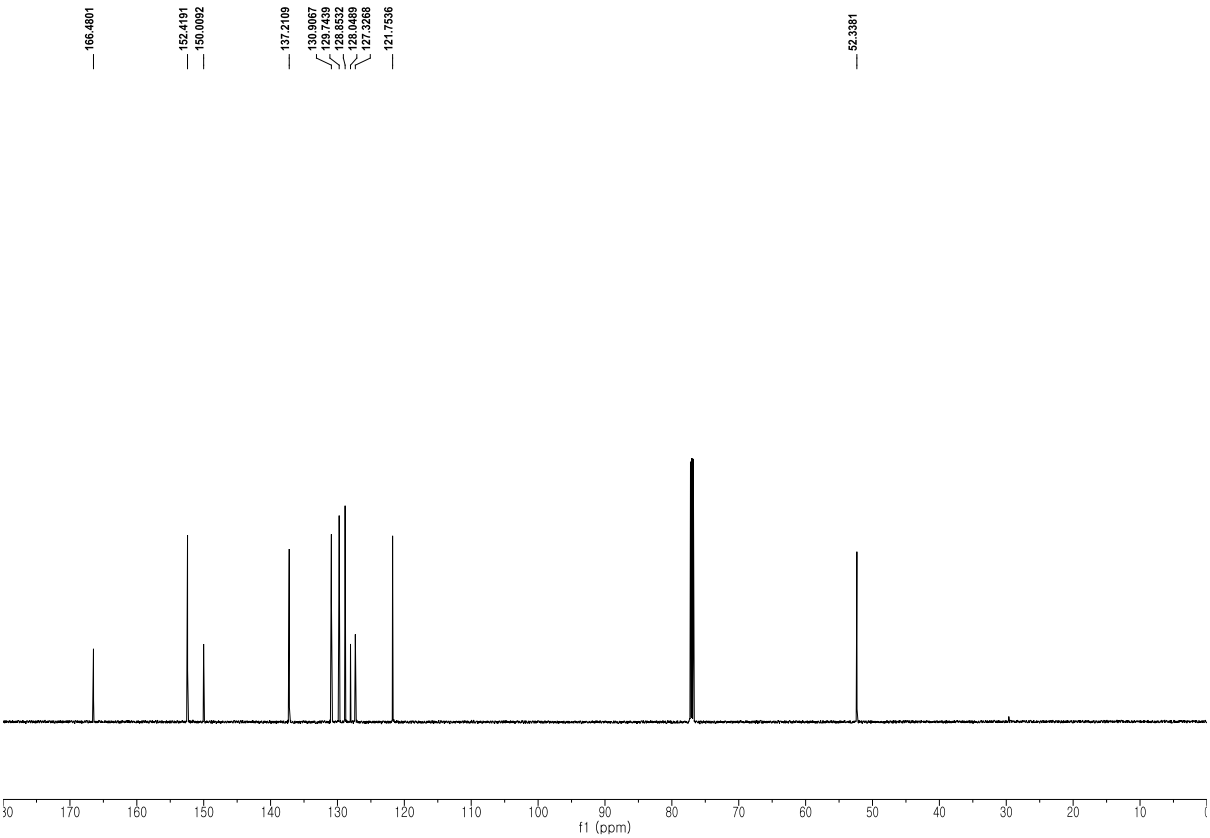


3-Acetylquinoline (Table 2, **3o**)

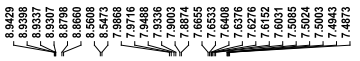


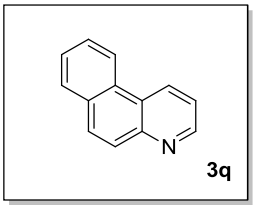
6-(Methoxycarbonyl)quinoline (Table 2, **3p**)

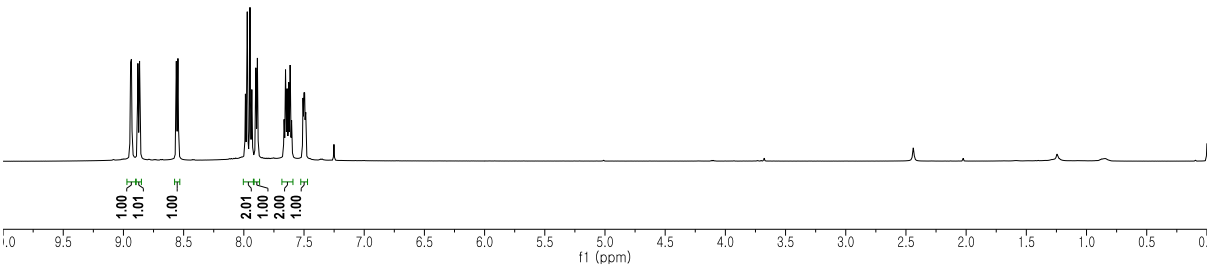


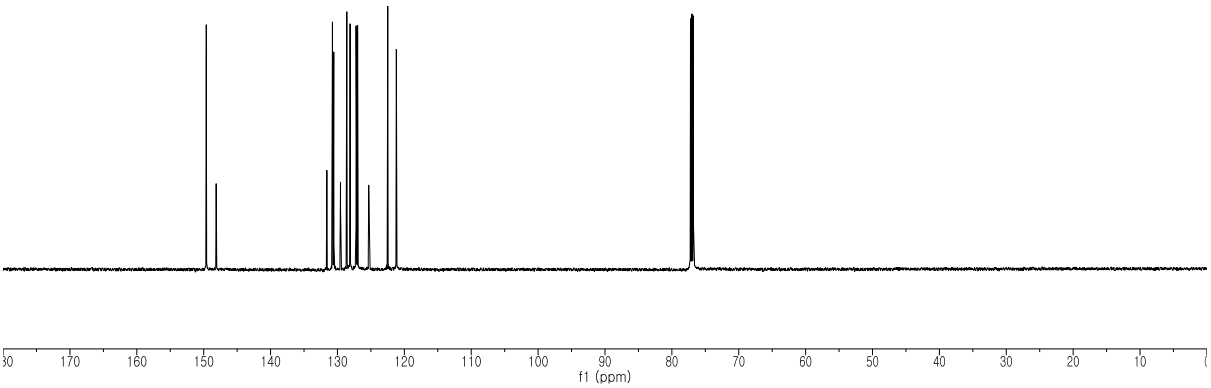


Benzo[*f*]quinoline (Table 2, **3q**)

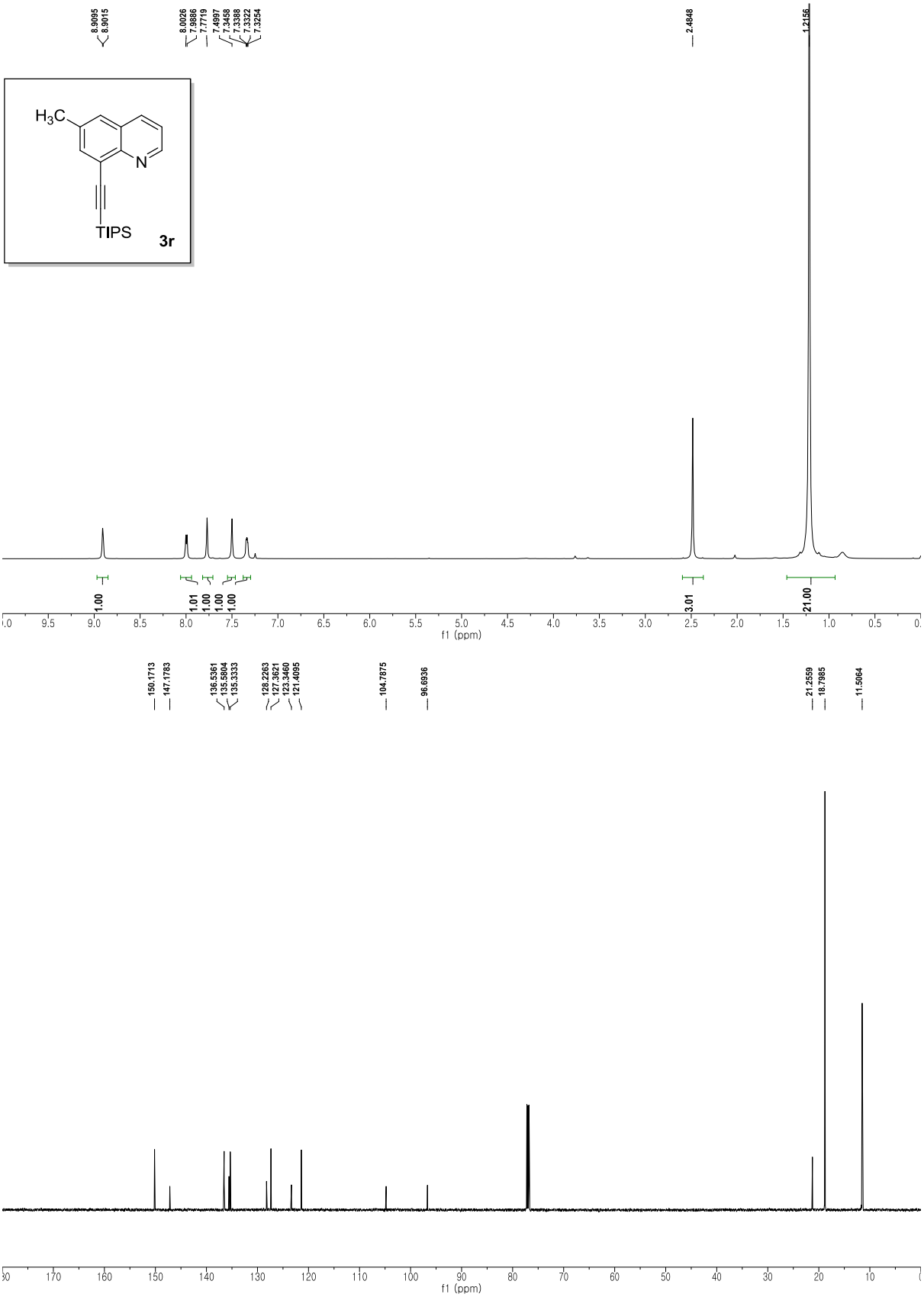




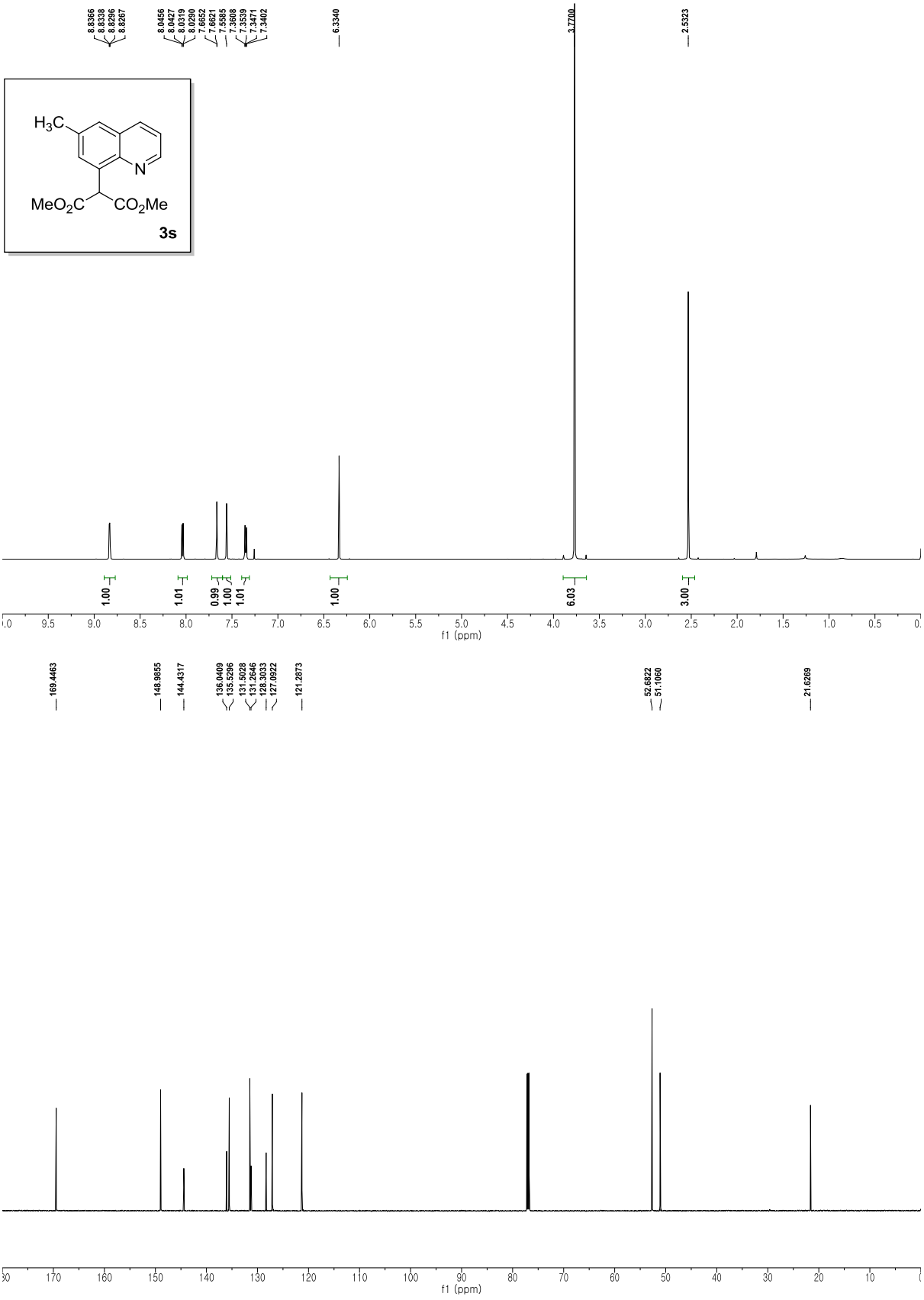




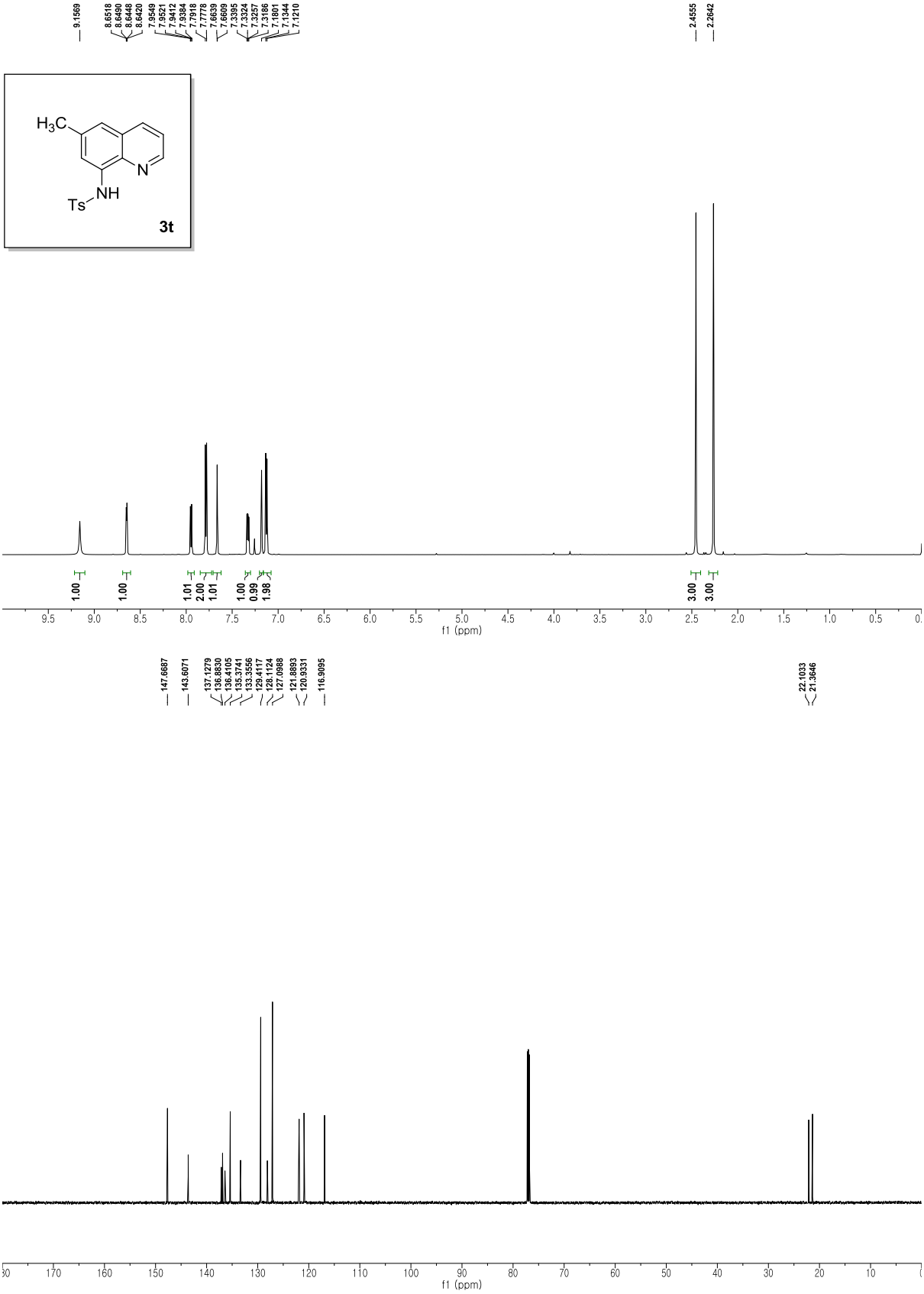
6-Methyl-8-[(triisopropylsilyl)ethynyl]quinoline (Table 2, **3r**)



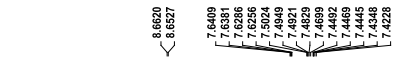
8-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-6-methylquinoline (Table 2, **3s**)

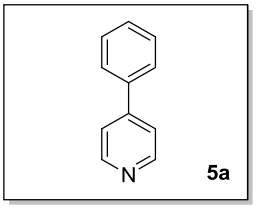


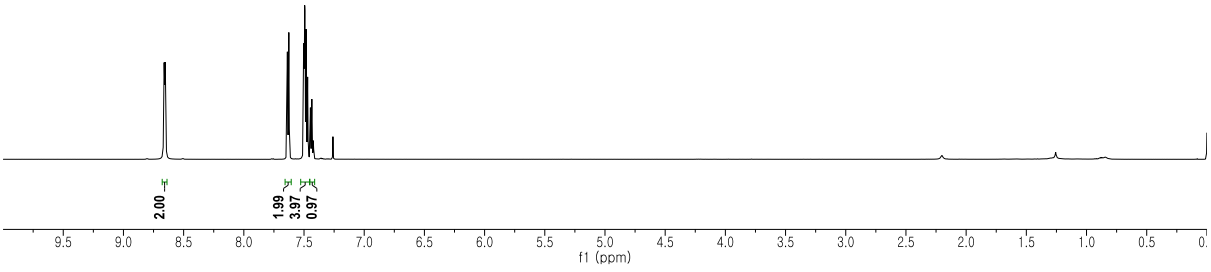
6-Methyl-8-(4-methylphenylsulfonamido)quinoline (Table 2, **3t**)

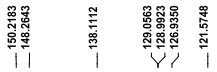


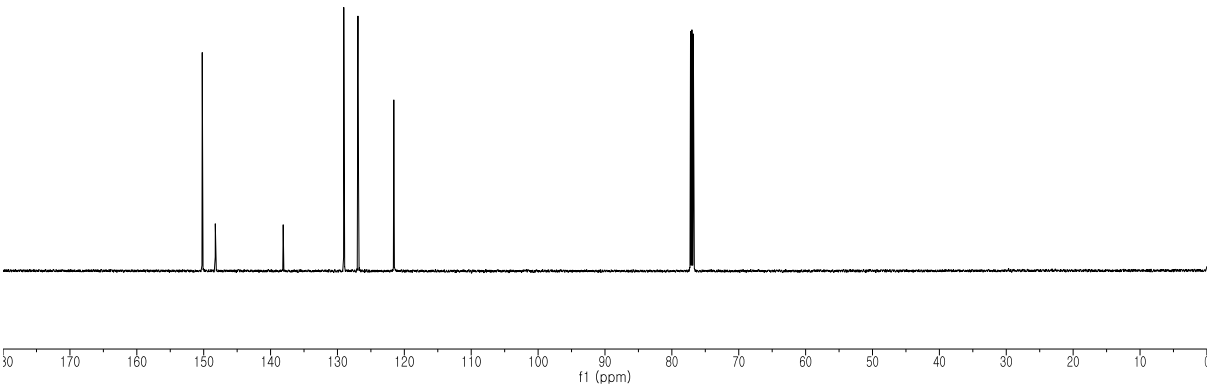
4-Phenylpyridine (Table 3, **5a**)



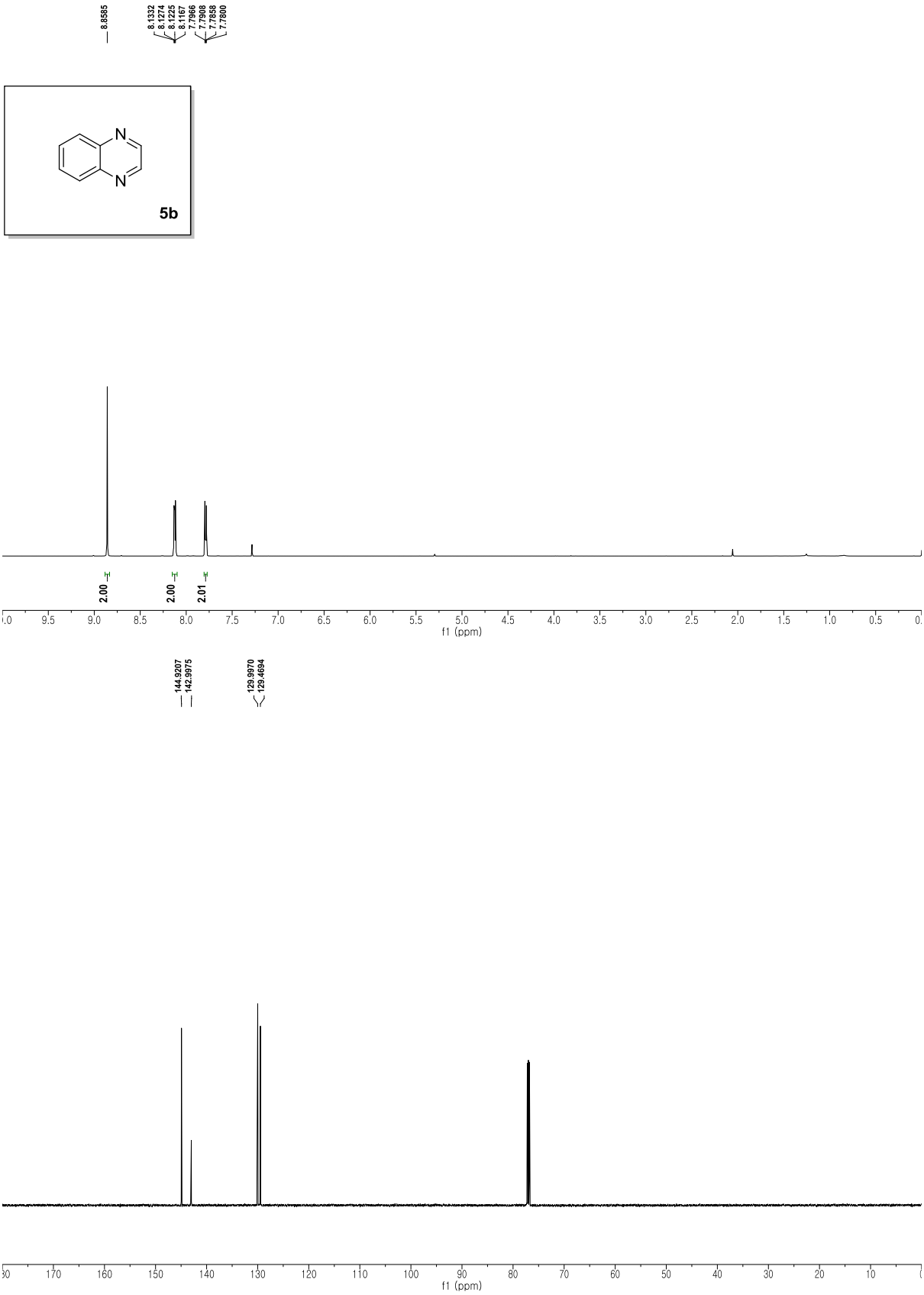




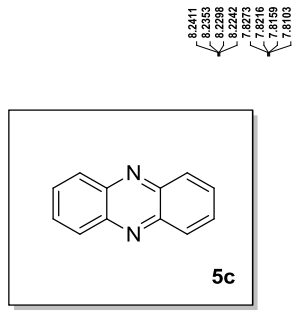


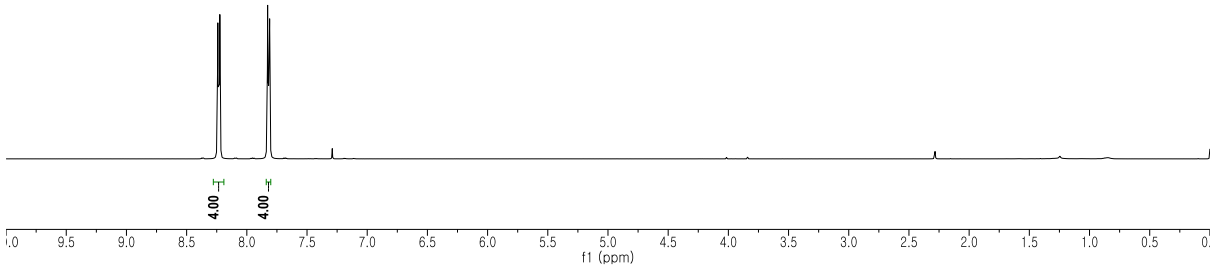


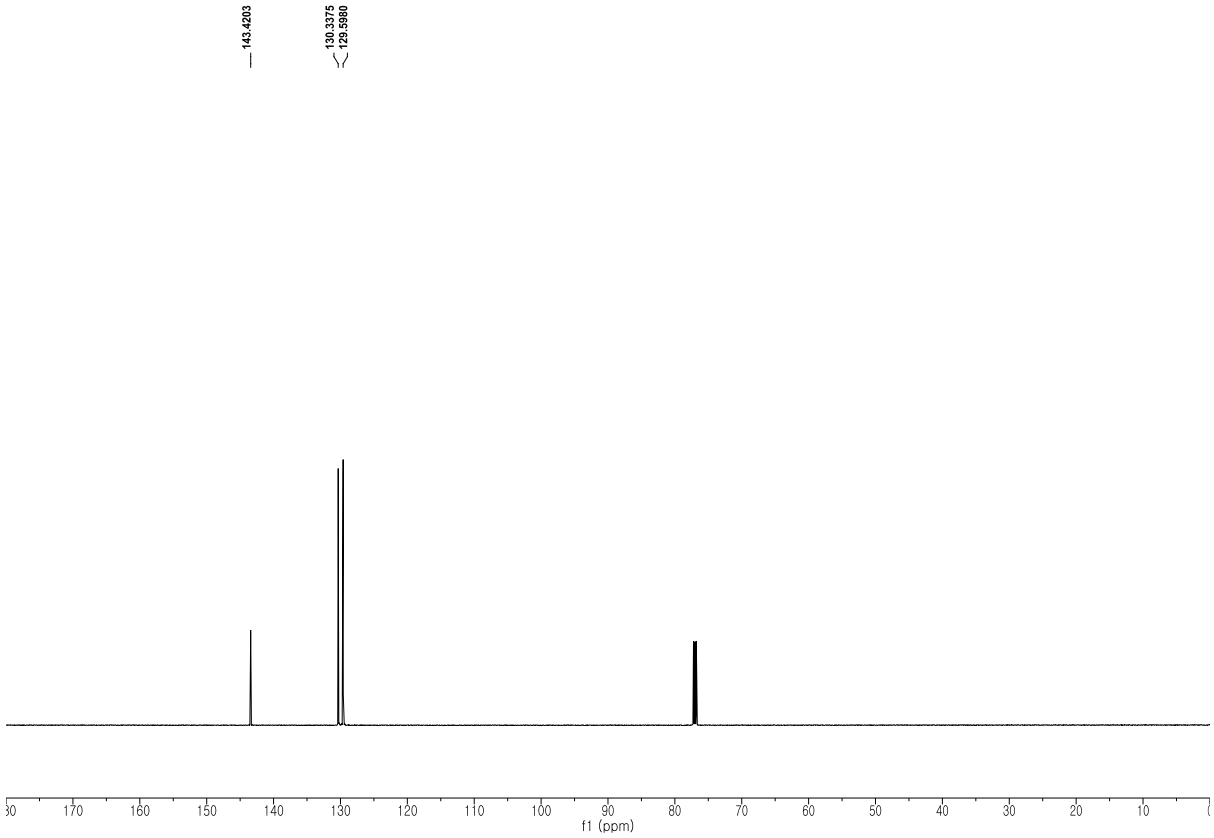
Quinoxaline (Table 3, **5b**)



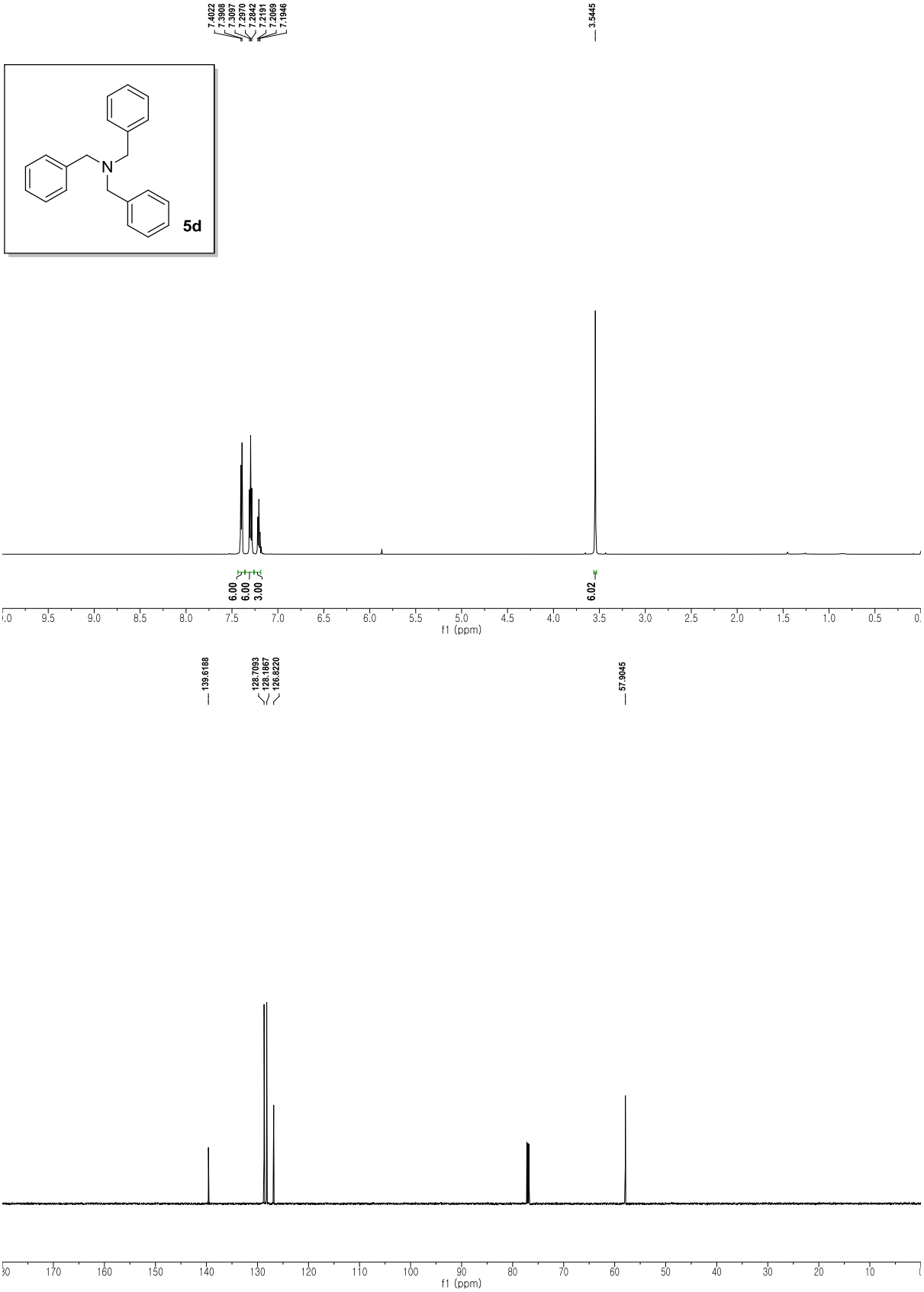
Phenazine (Table 3, **5c**)



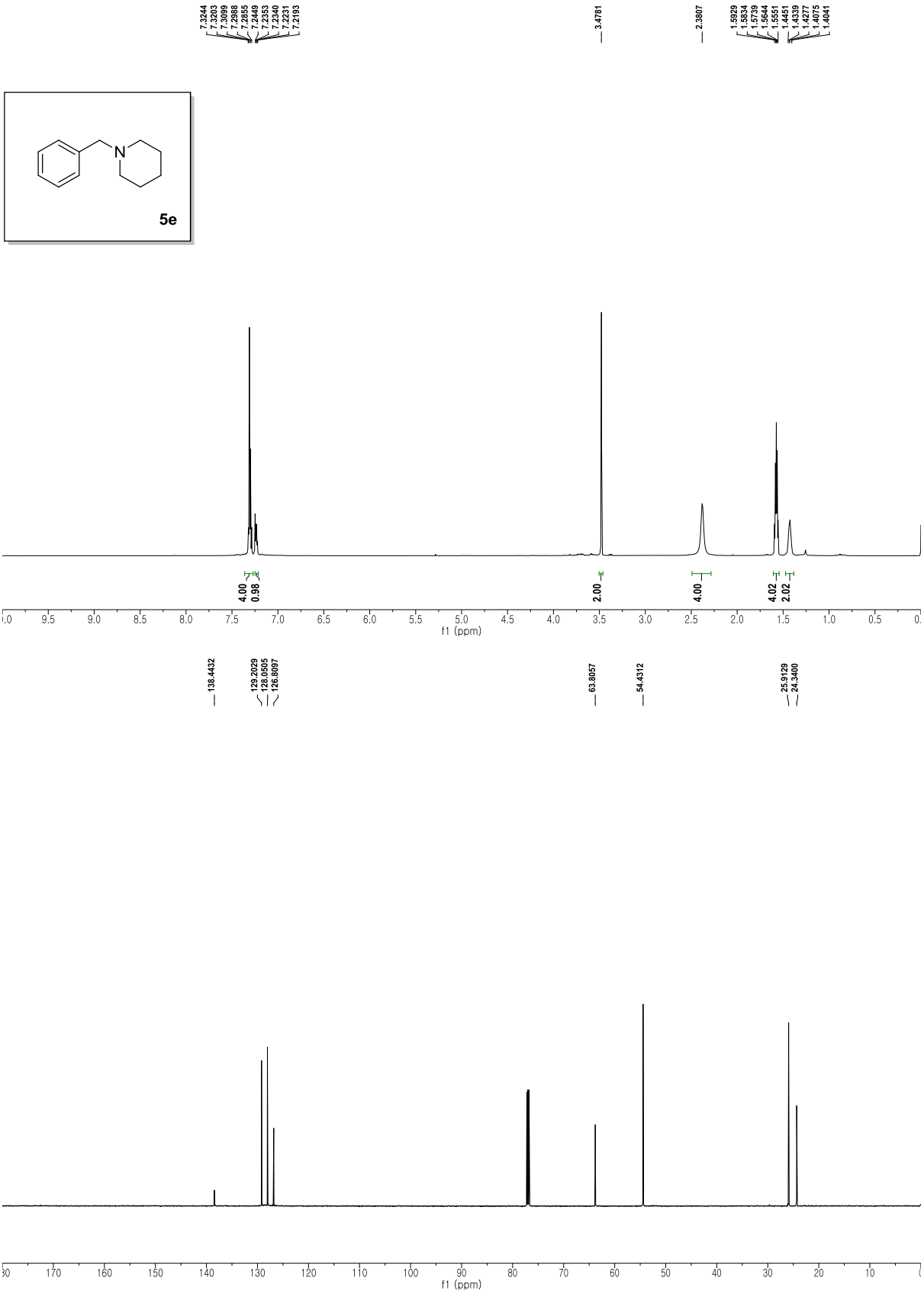




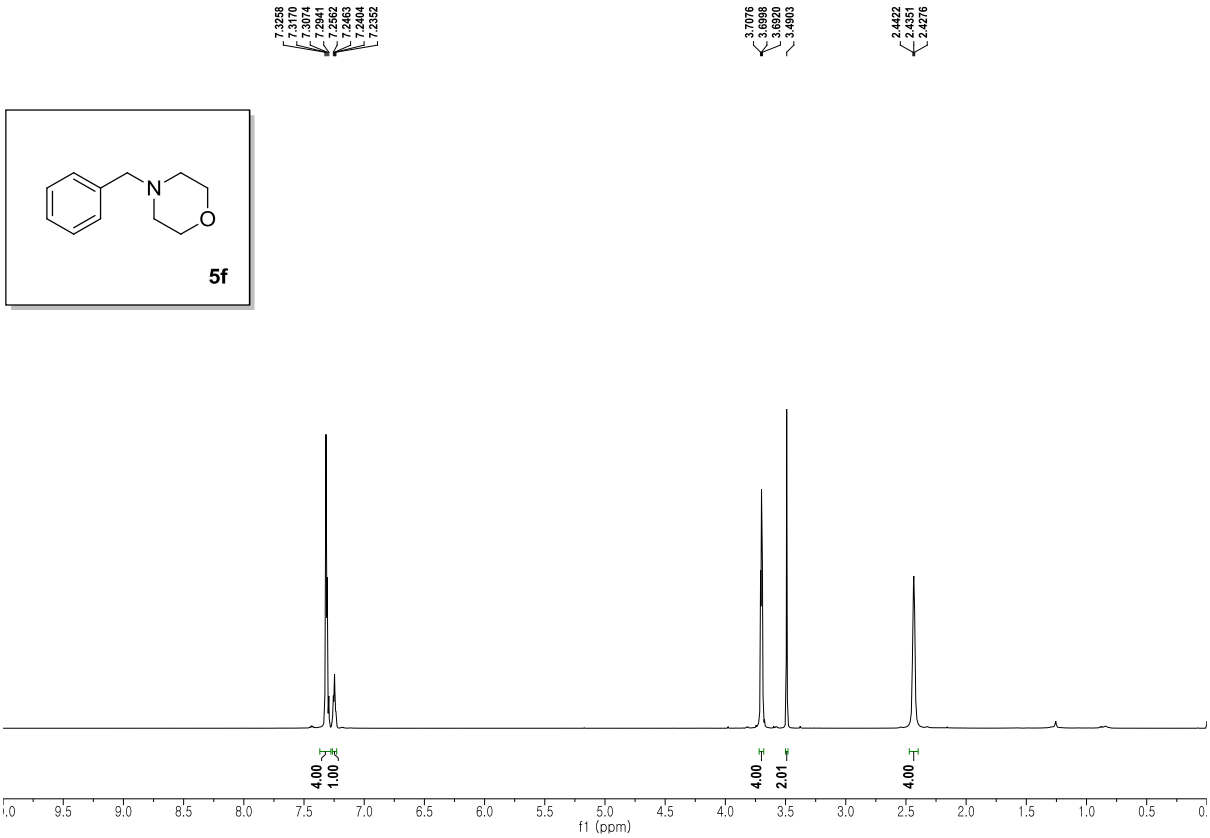
Tribenzylamine (Table 3, **5d**)

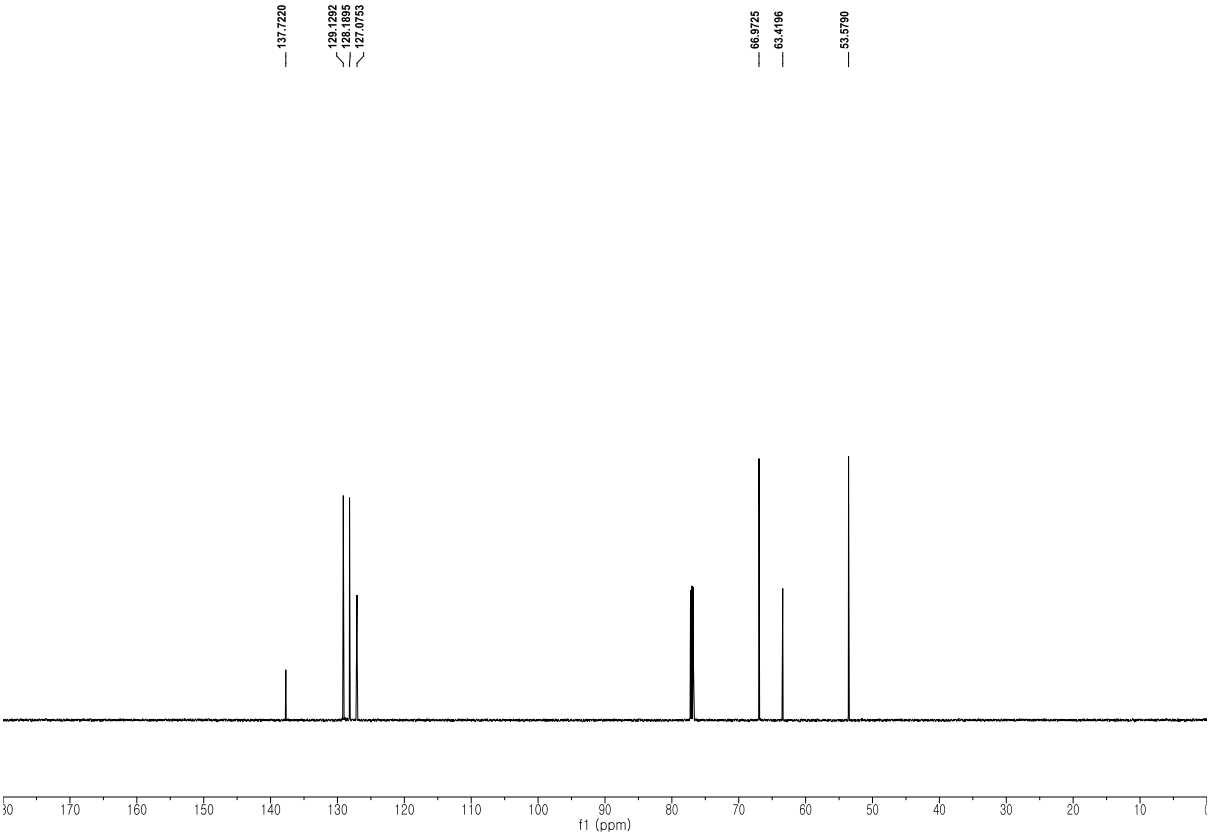


1-Benzylpiperidine (Table 3, **5e**)

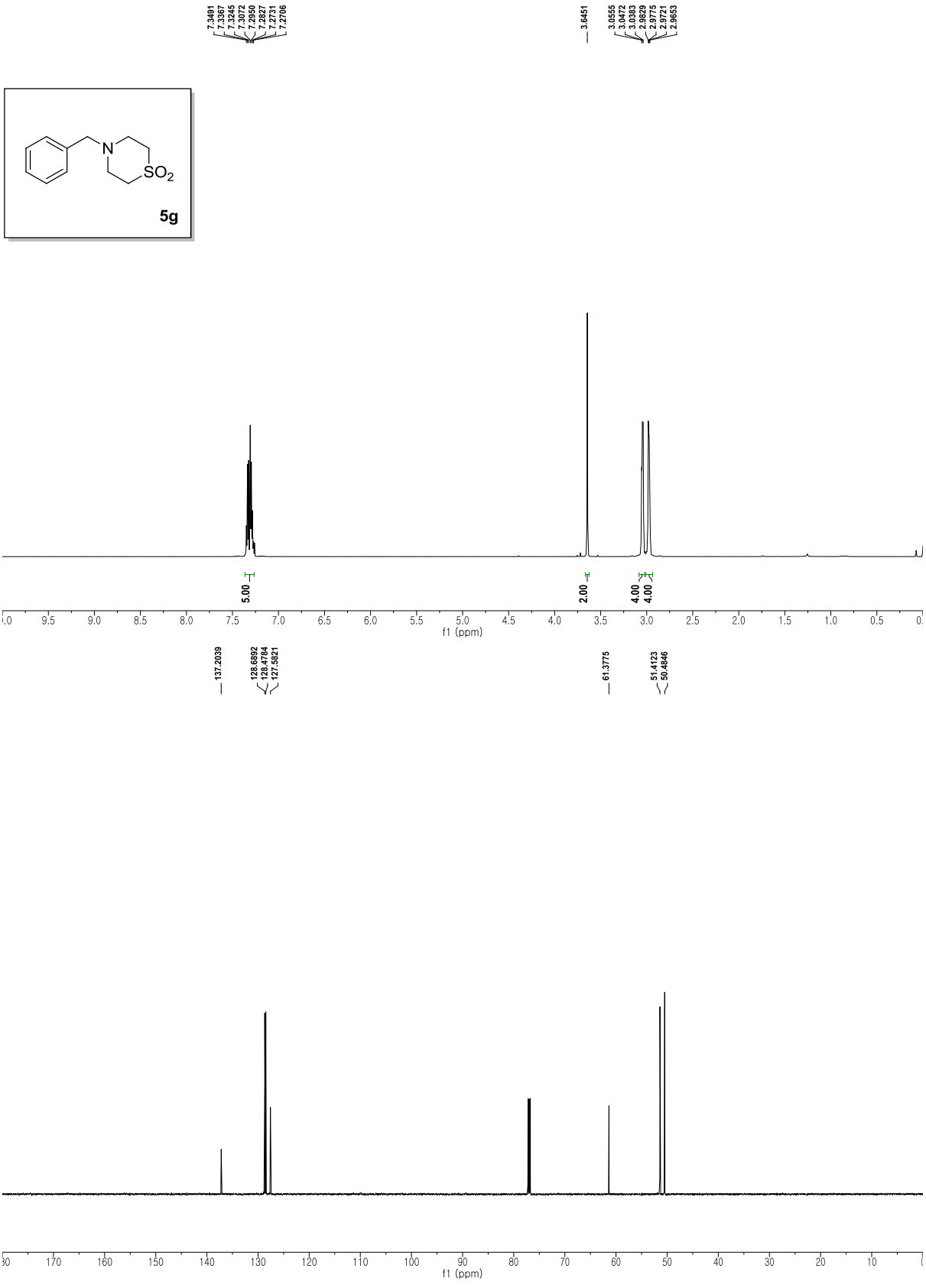


1-Benzylmorpholine (Table 3, **5f**)

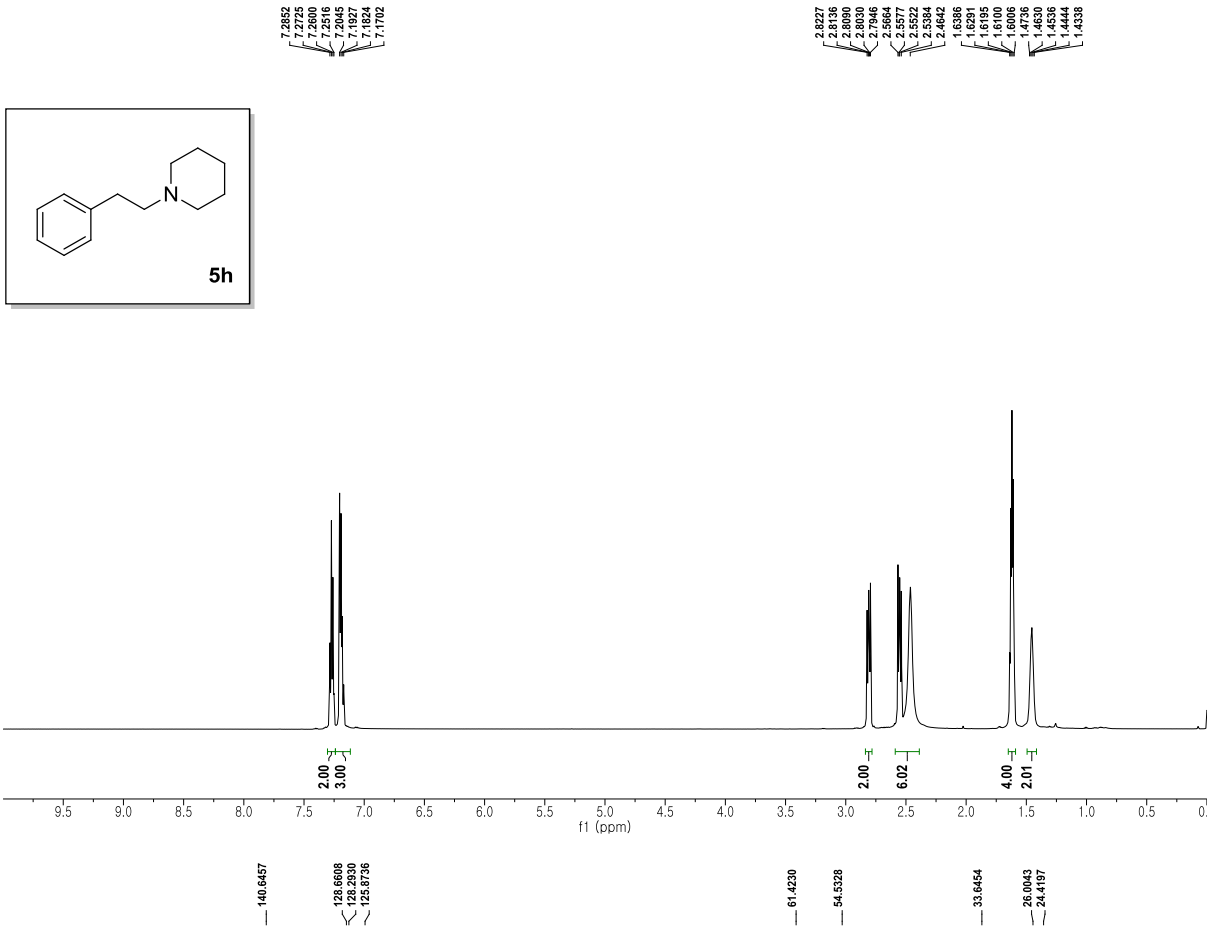


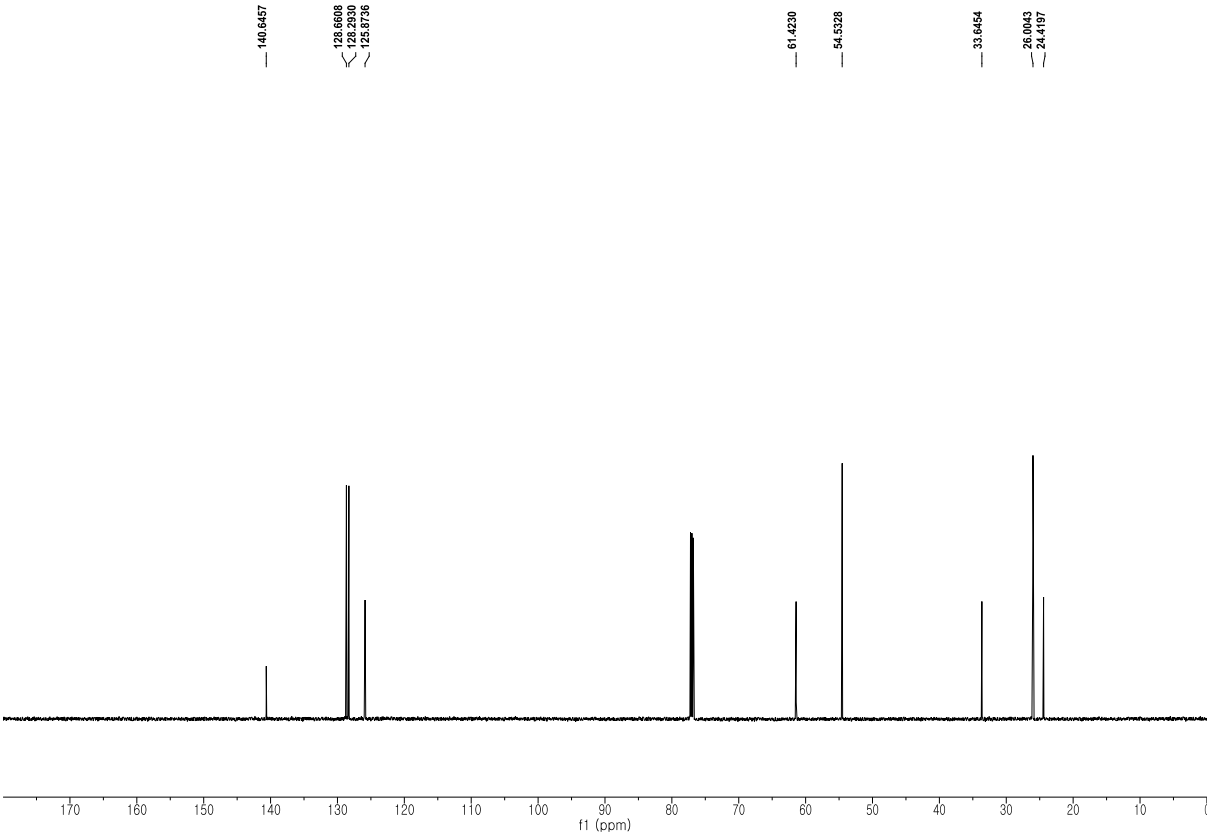


4-Benzylthiomorpholine 1,1-dioxide (Table 3, **5g**)

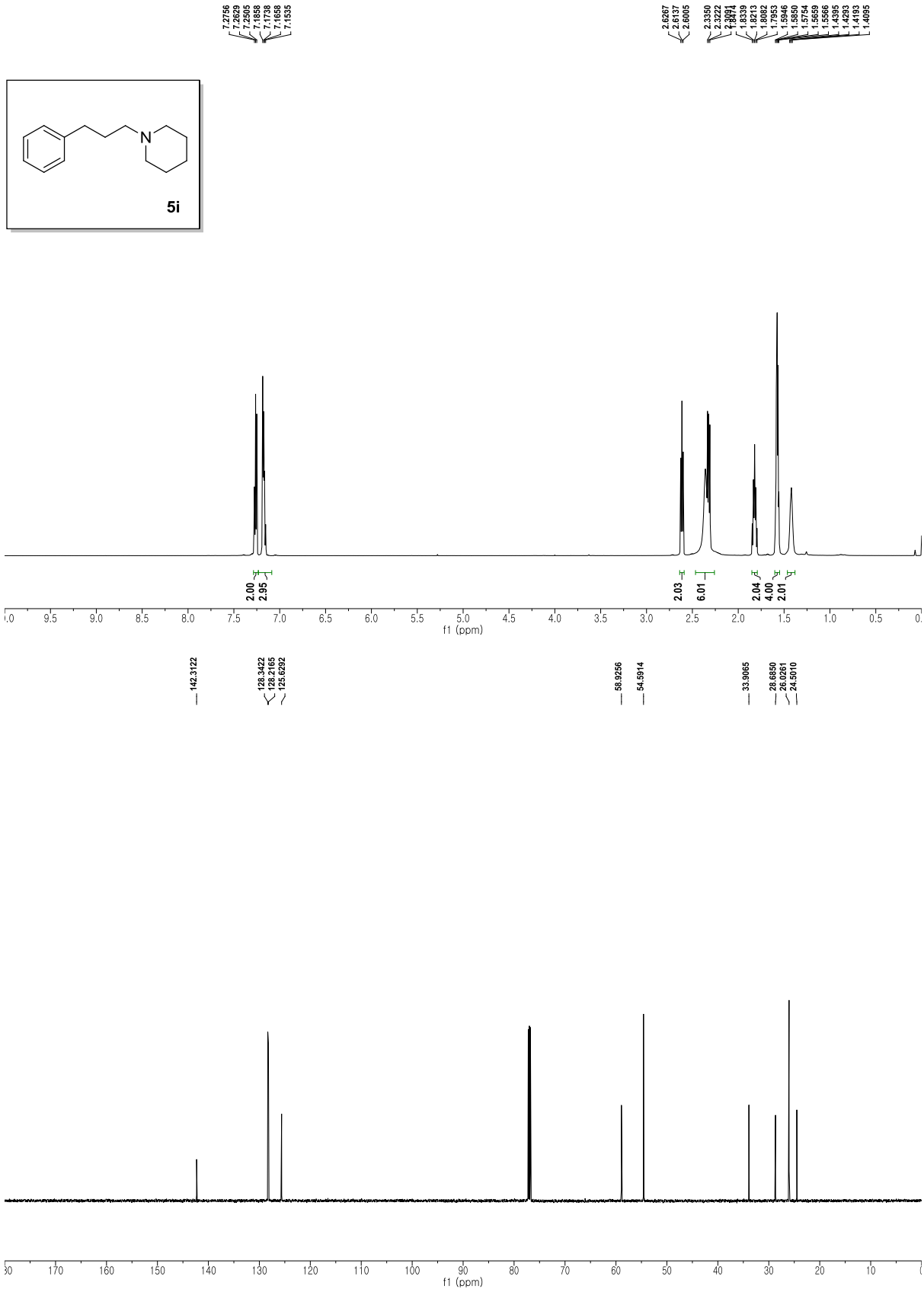


1-Phenethylpiperidine (Table 3, **5h**)

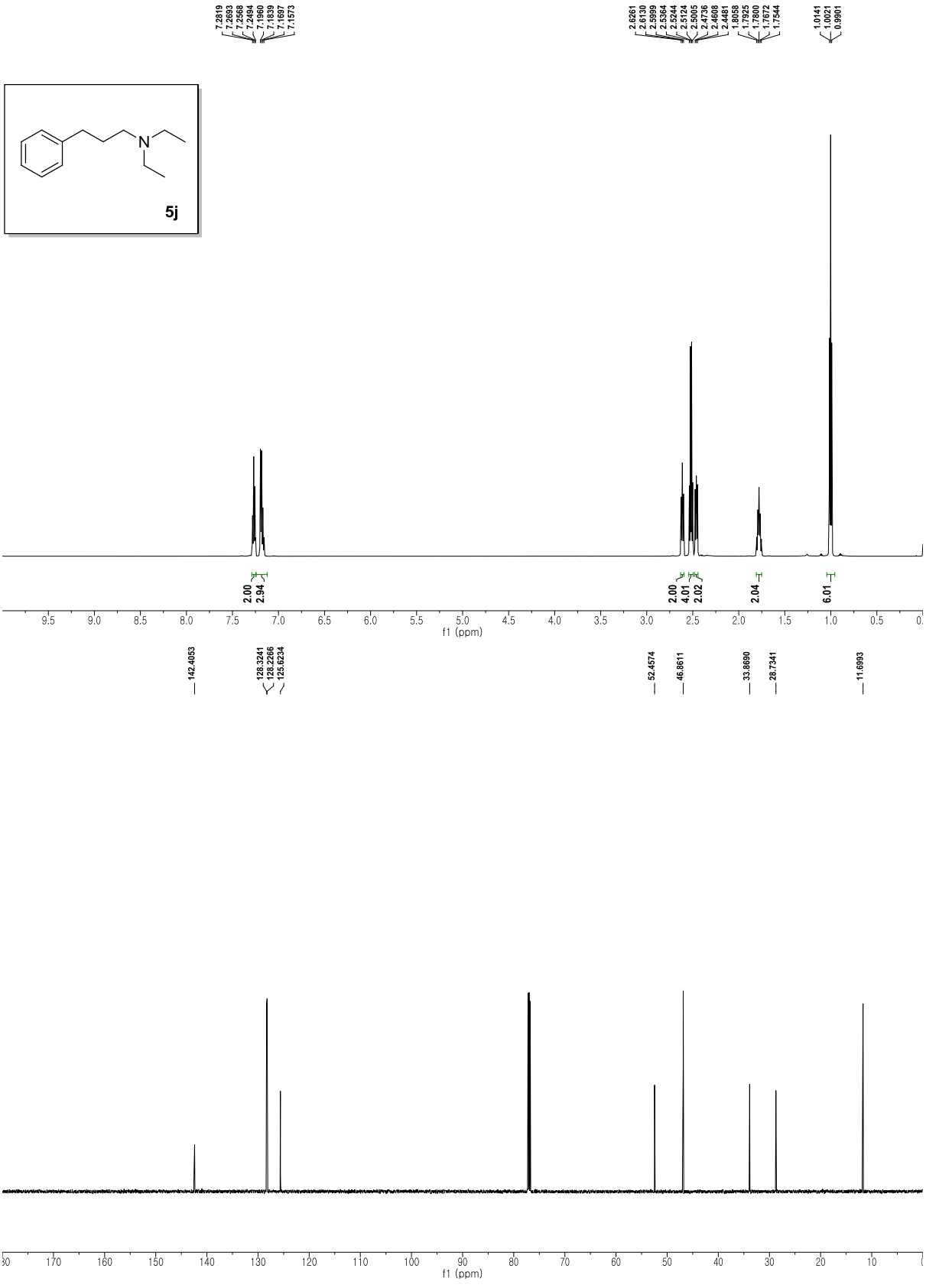




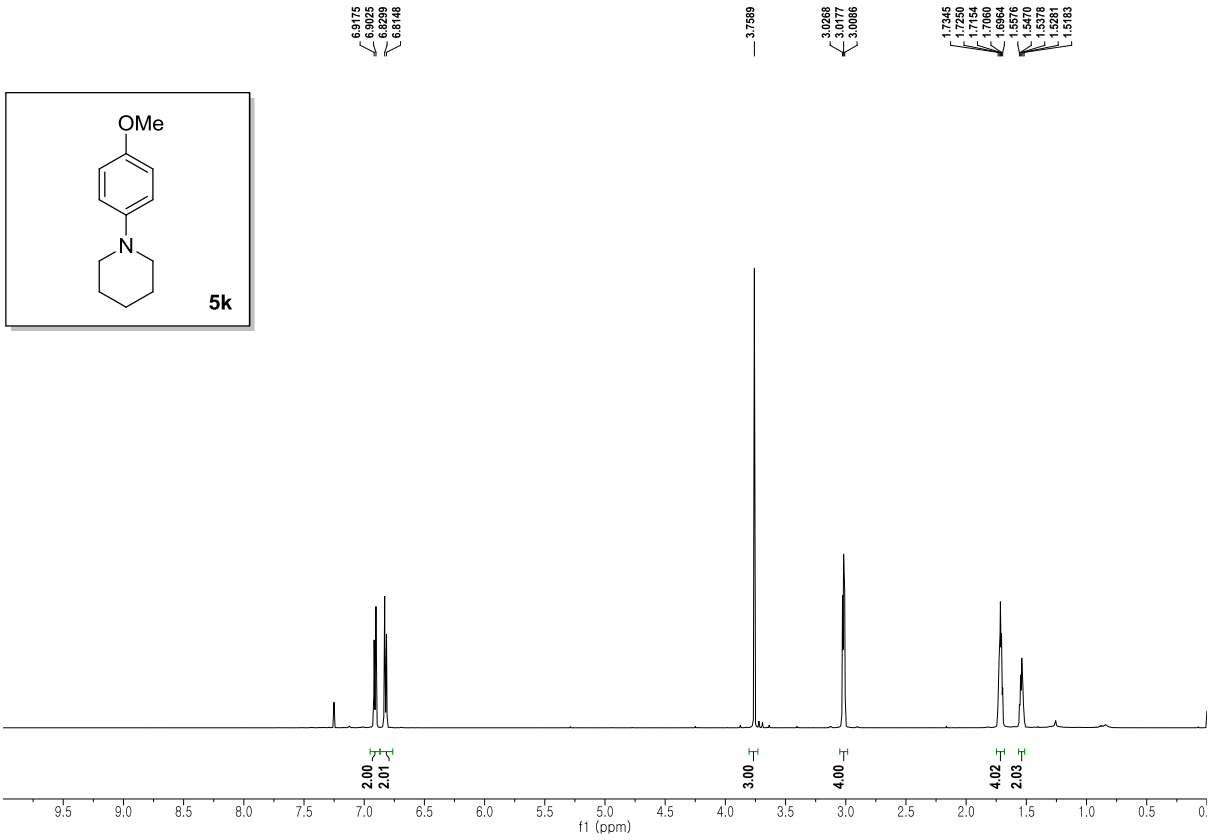
1-(3-Phenylpropyl)piperidine (Table 3, **5i**)

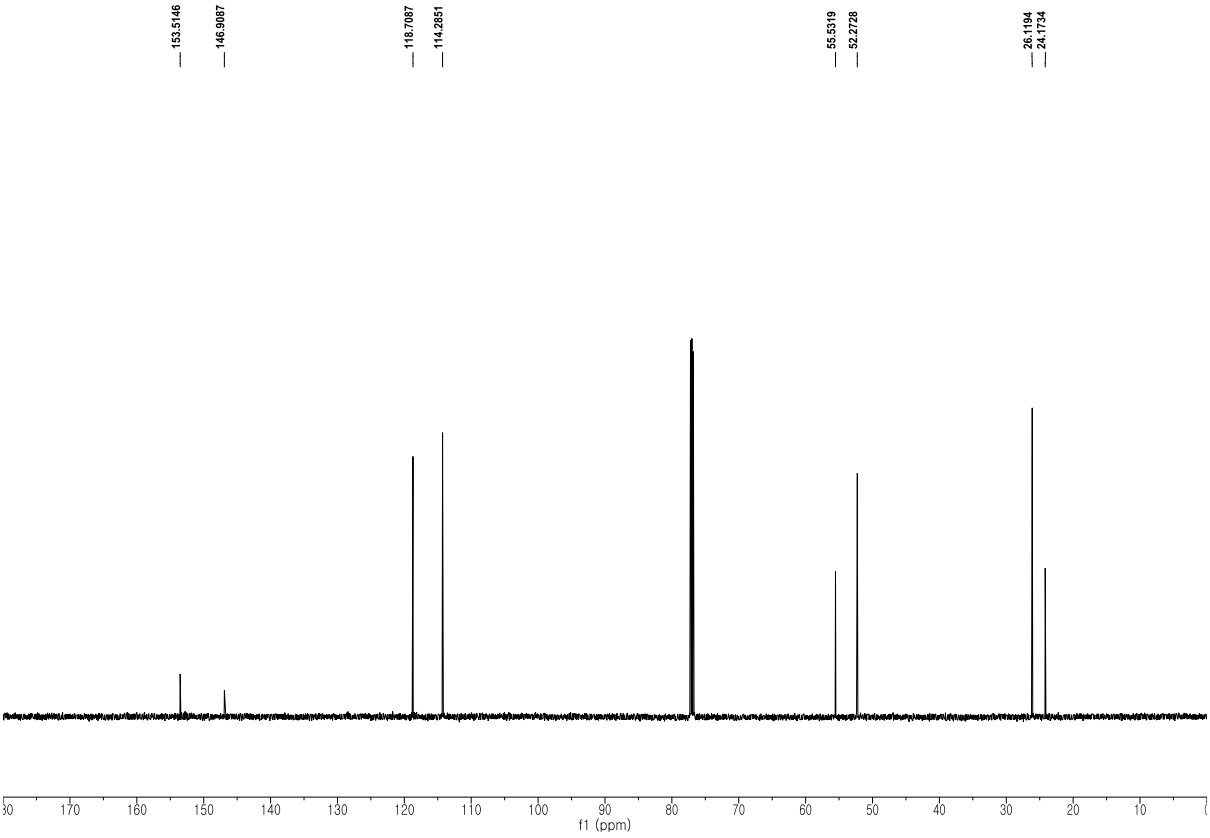


***N*,*N*-Diethyl-3-phenylpropylamine** (Table 3, **5j**)

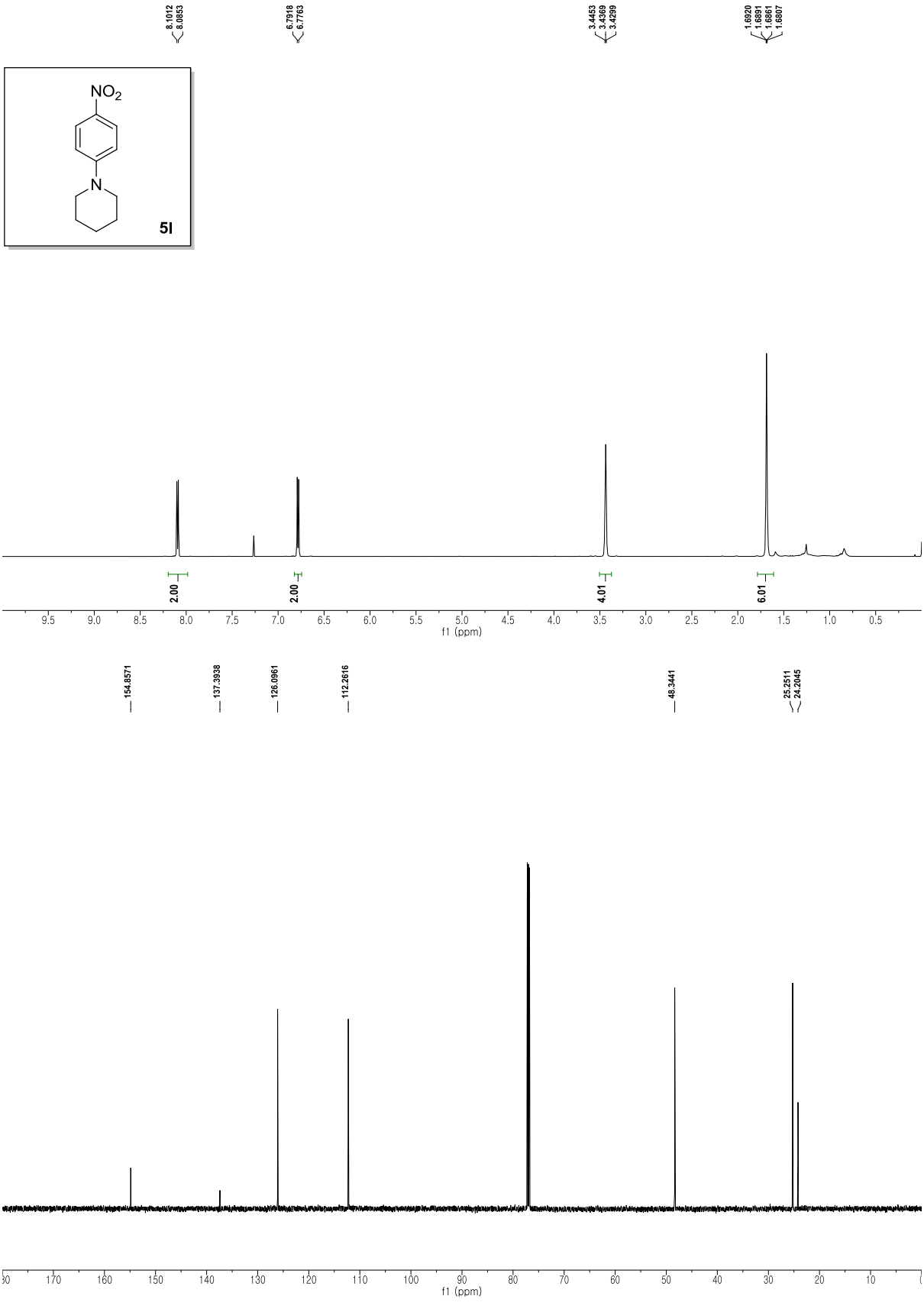


1-(4-Methoxyphenyl)piperidine (Table 3, **5k**)





1-(4-Nitrophenyl)piperidine (Table 3, **5l**)



Appendix II

Crystallographic Data

Crystallographic data of 1t (Figure 1)

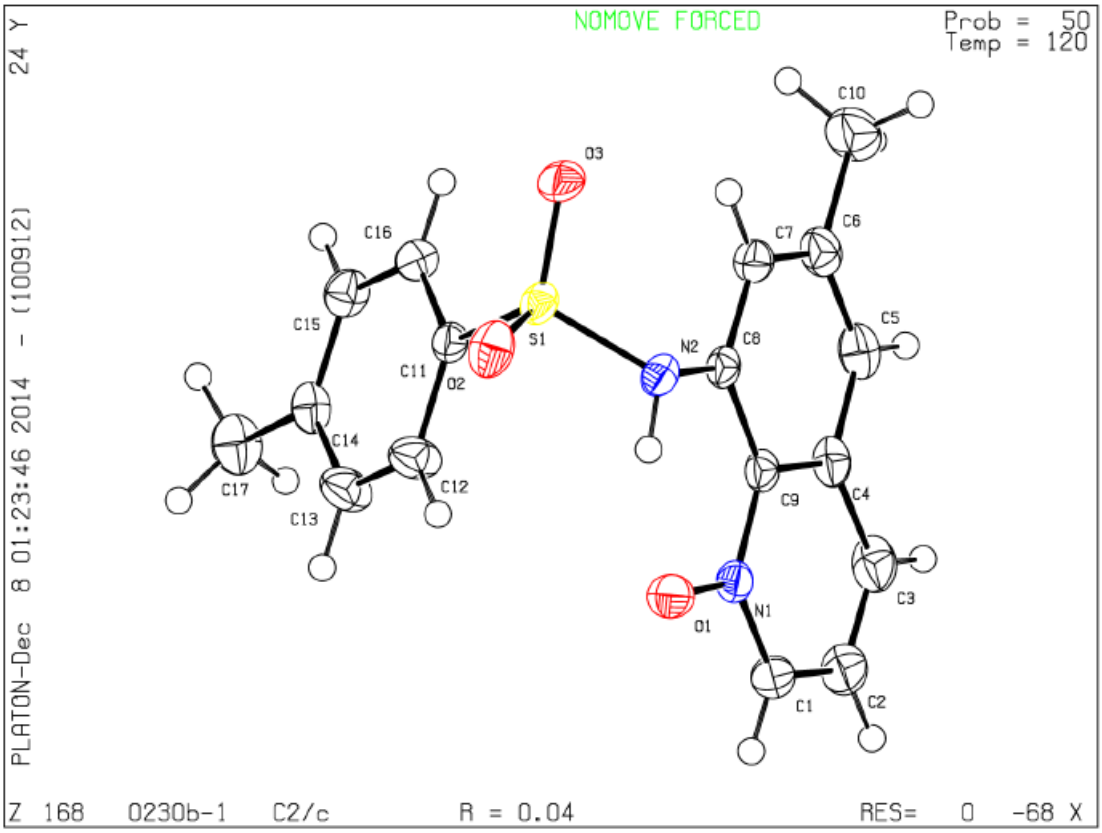


Table S1. Crystal data and structure refinement of **1t**

Identification code	0230b-1	
Empirical formula	C17 H16 N2 O3 S	
Formula weight	328.38	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 26.8782(11) Å	α= 90°.
	b = 8.2244(3) Å	β= 132.6436(12)°.
	c = 19.4674(8) Å	γ = 90°.
Volume	3165.5(2) $Å^3$	
Z	8	
Density (calculated)	1.378 Mg/m^3	
Absorption coefficient	0.221 mm^{-1}	
F(000)	1376	
Crystal size	0.37 x 0.28 x 0.26 mm^3	
Theta range for data collection	2.06 to 28.28°.	
Index ranges	-35<=h<=35, -10<=k<=10, -25<=l<=25	
Reflections collected	33667	
Independent reflections	3921 [R(int) = 0.0239]	
Completeness to theta = 28.28°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9448 and 0.9227	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3921 / 0 / 213	
Goodness-of-fit on F^2	1.060	
Final R indices [I>2sigma(I)]	R1 = 0.0350, wR2 = 0.0992	
R indices (all data)	R1 = 0.0386, wR2 = 0.1031	
Largest diff. peak and hole	0.480 and -0.430 e.$Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å ^{2}x 10^3) for 1t. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	2047(1)	8710(1)	1231(1)	24(1)
C(11)	1933(1)	6917(2)	647(1)	22(1)
C(14)	1733(1)	4101(2)	-304(1)	27(1)
C(15)	1960(1)	4016(2)	584(1)	29(1)
C(16)	2056(1)	5423(2)	1060(1)	26(1)
C(13)	1610(1)	5625(2)	-706(1)	34(1)
C(17)	1615(1)	2581(2)	-832(1)	37(1)
C(12)	1709(1)	7039(2)	-241(1)	33(1)
O(2)	2430(1)	9855(1)	1192(1)	34(1)
O(3)	2284(1)	8260(1)	2122(1)	33(1)
N(2)	1294(1)	9528(1)	591(1)	23(1)
O(1)	532(1)	10168(1)	-1158(1)	30(1)
N(1)	26(1)	9385(1)	-1330(1)	24(1)
C(9)	111(1)	8624(1)	-614(1)	22(1)
C(8)	738(1)	8637(1)	339(1)	21(1)
C(7)	777(1)	7840(2)	998(1)	27(1)
C(1)	-571(1)	9360(2)	-2214(1)	32(1)
C(6)	220(1)	7008(2)	763(1)	30(1)
C(2)	-1136(1)	8613(2)	-2453(1)	38(1)
C(4)	-455(1)	7821(2)	-851(1)	27(1)
C(5)	-384(1)	7017(2)	-147(1)	31(1)
C(3)	-1086(1)	7855(2)	-1788(1)	35(1)
C(10)	286(1)	6185(2)	1513(1)	44(1)

Table S3. Bond lengths [Å] and angles [°] of **1t**.

S(1)-O(3)	1.4330(10)
S(1)-O(2)	1.4357(11)
S(1)-N(2)	1.6388(10)
S(1)-C(11)	1.7581(12)
C(11)-C(16)	1.3806(18)
C(11)-C(12)	1.3958(17)
C(14)-C(15)	1.3922(19)
C(14)-C(13)	1.393(2)
C(14)-C(17)	1.5094(18)
C(15)-C(16)	1.3926(18)
C(13)-C(12)	1.3847(19)
N(2)-C(8)	1.4205(15)
O(1)-N(1)	1.3247(14)
N(1)-C(1)	1.3398(16)
N(1)-C(9)	1.3986(16)
C(9)-C(4)	1.4193(17)
C(9)-C(8)	1.4304(16)
C(8)-C(7)	1.3809(17)
C(7)-C(6)	1.4116(19)
C(1)-C(2)	1.395(2)
C(6)-C(5)	1.370(2)
C(6)-C(10)	1.506(2)
C(2)-C(3)	1.360(2)
C(4)-C(5)	1.4124(19)
C(4)-C(3)	1.4186(19)

O(3)-S(1)-O(2)	119.15(6)
O(3)-S(1)-N(2)	109.58(6)
O(2)-S(1)-N(2)	104.56(6)
O(3)-S(1)-C(11)	107.81(6)
O(2)-S(1)-C(11)	109.39(6)
N(2)-S(1)-C(11)	105.55(5)
C(16)-C(11)-C(12)	121.10(12)
C(16)-C(11)-S(1)	120.14(9)
C(12)-C(11)-S(1)	118.75(10)
C(15)-C(14)-C(13)	118.68(12)

C(15)-C(14)-C(17)	121.15(13)
C(13)-C(14)-C(17)	120.17(13)
C(14)-C(15)-C(16)	120.85(12)
C(11)-C(16)-C(15)	119.26(12)
C(12)-C(13)-C(14)	121.38(12)
C(13)-C(12)-C(11)	118.73(12)
C(8)-N(2)-S(1)	121.28(9)
O(1)-N(1)-C(1)	117.61(11)
O(1)-N(1)-C(9)	121.22(10)
C(1)-N(1)-C(9)	121.17(11)
N(1)-C(9)-C(4)	118.04(11)
N(1)-C(9)-C(8)	122.85(11)
C(4)-C(9)-C(8)	119.10(11)
C(7)-C(8)-N(2)	121.62(11)
C(7)-C(8)-C(9)	118.90(11)
N(2)-C(8)-C(9)	119.42(11)
C(8)-C(7)-C(6)	122.18(12)
N(1)-C(1)-C(2)	121.42(13)
C(5)-C(6)-C(7)	118.95(12)
C(5)-C(6)-C(10)	121.02(14)
C(7)-C(6)-C(10)	119.98(14)
C(3)-C(2)-C(1)	120.17(13)
C(5)-C(4)-C(3)	120.94(12)
C(5)-C(4)-C(9)	119.49(12)
C(3)-C(4)-C(9)	119.56(12)
C(6)-C(5)-C(4)	121.35(12)
C(2)-C(3)-C(4)	119.58(13)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters (Å ^{2}x 10^3) of **1t**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	17(1)	26(1)	19(1)	-3(1)	9(1)	2(1)
C(11)	20(1)	23(1)	22(1)	-1(1)	14(1)	3(1)
C(14)	25(1)	26(1)	34(1)	-6(1)	21(1)	-3(1)
C(15)	31(1)	22(1)	35(1)	3(1)	23(1)	1(1)
C(16)	25(1)	28(1)	24(1)	3(1)	16(1)	2(1)
C(13)	49(1)	31(1)	30(1)	-2(1)	30(1)	2(1)
C(17)	41(1)	28(1)	46(1)	-12(1)	30(1)	-7(1)
C(12)	51(1)	23(1)	30(1)	3(1)	29(1)	5(1)
O(2)	23(1)	31(1)	39(1)	-6(1)	18(1)	-4(1)
O(3)	27(1)	42(1)	17(1)	-2(1)	10(1)	7(1)
N(2)	18(1)	23(1)	23(1)	0(1)	12(1)	2(1)
O(1)	24(1)	39(1)	27(1)	2(1)	17(1)	-2(1)
N(1)	19(1)	29(1)	22(1)	-2(1)	13(1)	2(1)
C(9)	20(1)	22(1)	23(1)	-3(1)	14(1)	2(1)
C(8)	20(1)	20(1)	23(1)	-2(1)	14(1)	3(1)
C(7)	29(1)	26(1)	26(1)	1(1)	18(1)	6(1)
C(1)	24(1)	46(1)	21(1)	-2(1)	13(1)	4(1)
C(6)	39(1)	24(1)	39(1)	2(1)	31(1)	5(1)
C(2)	20(1)	58(1)	25(1)	-10(1)	11(1)	-1(1)
C(4)	24(1)	28(1)	31(1)	-8(1)	19(1)	-2(1)
C(5)	33(1)	28(1)	43(1)	-4(1)	30(1)	-3(1)
C(3)	21(1)	47(1)	34(1)	-13(1)	17(1)	-7(1)
C(10)	58(1)	37(1)	51(1)	11(1)	44(1)	6(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å ^{2}x 10^3) of **1t**.

	x	y	z	U(eq)
H(15A)	2050	2986	869	35
H(16A)	2205	5354	1662	31
H(13A)	1455	5696	-1312	41
H(17A)	1131	2322	-1287	56
H(17B)	1867	1675	-393	56
H(17C)	1769	2758	-1160	56
H(12A)	1626	8071	-520	40
H(7A)	1193	7852	1632	32
H(1A)	-610	9862	-2689	39
H(2A)	-1557	8634	-3082	46
H(5A)	-763	6471	-309	38
H(3A)	-1472	7352	-1949	42
H(10A)	234	6992	1830	65
H(10B)	733	5677	1967	65
H(10C)	-64	5350	1231	65
H(1)	1174(11)	9940(30)	76(15)	52

Table S6. Torsion angles [°] of **1t**.

O(3)-S(1)-C(11)-C(16)	1.51(12)
O(2)-S(1)-C(11)-C(16)	132.46(10)
N(2)-S(1)-C(11)-C(16)	-115.54(10)
O(3)-S(1)-C(11)-C(12)	-179.35(11)
O(2)-S(1)-C(11)-C(12)	-48.40(12)
N(2)-S(1)-C(11)-C(12)	63.60(12)
C(13)-C(14)-C(15)-C(16)	0.5(2)
C(17)-C(14)-C(15)-C(16)	-178.79(12)
C(12)-C(11)-C(16)-C(15)	0.56(19)
S(1)-C(11)-C(16)-C(15)	179.68(10)
C(14)-C(15)-C(16)-C(11)	-0.87(19)
C(15)-C(14)-C(13)-C(12)	0.1(2)
C(17)-C(14)-C(13)-C(12)	179.44(14)
C(14)-C(13)-C(12)-C(11)	-0.4(2)
C(16)-C(11)-C(12)-C(13)	0.1(2)
S(1)-C(11)-C(12)-C(13)	-179.06(12)
O(3)-S(1)-N(2)-C(8)	-61.21(11)
O(2)-S(1)-N(2)-C(8)	170.00(9)
C(11)-S(1)-N(2)-C(8)	54.63(11)
O(1)-N(1)-C(9)-C(4)	179.46(11)
C(1)-N(1)-C(9)-C(4)	0.04(17)
O(1)-N(1)-C(9)-C(8)	0.04(17)
C(1)-N(1)-C(9)-C(8)	-179.38(12)
S(1)-N(2)-C(8)-C(7)	51.64(15)
S(1)-N(2)-C(8)-C(9)	-131.35(10)
N(1)-C(9)-C(8)-C(7)	-179.37(11)
C(4)-C(9)-C(8)-C(7)	1.21(17)
N(1)-C(9)-C(8)-N(2)	3.53(17)
C(4)-C(9)-C(8)-N(2)	-175.89(10)
N(2)-C(8)-C(7)-C(6)	177.27(11)
C(9)-C(8)-C(7)-C(6)	0.24(18)
O(1)-N(1)-C(1)-C(2)	-177.74(13)
C(9)-N(1)-C(1)-C(2)	1.7(2)
C(8)-C(7)-C(6)-C(5)	-1.28(19)
C(8)-C(7)-C(6)-C(10)	-178.85(12)
N(1)-C(1)-C(2)-C(3)	-1.5(2)

N(1)-C(9)-C(4)-C(5)	178.94(11)
C(8)-C(9)-C(4)-C(5)	-1.62(17)
N(1)-C(9)-C(4)-C(3)	-1.91(18)
C(8)-C(9)-C(4)-C(3)	177.53(11)
C(7)-C(6)-C(5)-C(4)	0.9(2)
C(10)-C(6)-C(5)-C(4)	178.39(13)
C(3)-C(4)-C(5)-C(6)	-178.56(13)
C(9)-C(4)-C(5)-C(6)	0.59(19)
C(1)-C(2)-C(3)-C(4)	-0.4(2)
C(5)-C(4)-C(3)-C(2)	-178.78(14)
C(9)-C(4)-C(3)-C(2)	2.1(2)

Symmetry transformations used to generate equivalent atoms:

Table S7. Hydrogen bonds of **1t** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(1)...O(1)	0.89(2)	1.78(2)	2.5712(14)	148(2)

Symmetry transformations used to generate equivalent atoms: