Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Exogenous-oxidant- and catalyst-free electrochemical deoxygenative C2 sulfonylation of quinoline *N*-oxides

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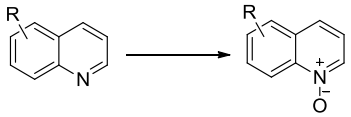
General information

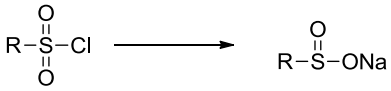
Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The instrument for electrolysis is dual display potentiostat (DJS-292B) (made in China). The anodic electrode was graphite rod (ϕ 6 mm) and cathodic electrode was platinum plate (15 mm×15 mm×0.3 mm). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 300-400 mesh silica gel in petroleum (boiling point is between 60-90 ^{o}C). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum to the indicated solvent, and they are listed as volume/volume ratios. NMR spectra were recorded on a Bruker spectrometer at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), 376 MHz (^{19}F NMR). All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks (77.00 ppm, chloroform), respectively. And all ^{1}H, ^{13}C and ^{19}F NMR data spectra were reported in delta (δ) units, parts per million (ppm) downfield from the internal standard. Coupling constants are reported in Hertz (Hz). GC-MS spectra were recorded on a Shimadzu GC-MS QP2010 Ultra.

General procedure for the preparation of quinoline-*N*-oxides [1]



To a mixture of quinolines (10.0 mmol) in AcOH (20 mL) was added H_2O_2 (30 wt%, 1.40 mL) at room temperature. The reaction mixture was stirred at 70 ℃ for 36 h, and then was cooled to room temperature. The product was extracted with DCM (3 × 10 mL), and the combined organic layers were dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue obtained was purified via silica gel chromatography (petroleum ether/ethyl acetate = 8/1) to afford quinoline *N*-oxide.

General procedure for the preparation of sodium sulfinates [2]



Sulfonyl chlorides (5.00 mmol) were added to a solution of sodium sulfites (10.0 mmol) and sodium bicarbonate (840 mg, 10.0 mmol) in water (5 mL, 1 M) and heated at 80 ℃ for 3 h, after cooling to room temperaturethe volatiles were removed in vacuo. The resultant solids were repeatedly washed with ethanol. The combined ethanol washes were evaporated under reduced pressure to yield the titled sulfinates as an amorphous solid.

General procedure for the preparation of 3a:

In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, quinoline-*N*-oxide derivatives **1a** (0.5 mmol), sodium sulfonate **2a** (1.25 mmol.), and $^{n}Bu_4NBF_4$ (0.1 mmol, 32.9 mg) were combined and added. The bottle was equipped with graphite rod (ϕ 6 mm, about 17 mm immersion depth in solution) as the anode and platinum plate (15 mm×15 mm×0.3 mm) as the cathode and was then charged with nitrogen. Under the protection of N_2, glacial acetic acid (1.0 mL), H_2O (1.0 mL) and MeCN (8.0 mL) were injected respectively into the tubes via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 30 mA at room temperature for 2.0 h. When the reaction was finished, the reaction was quenched with saturated aqueous solution of Na_2CO_3 and extracted with DCM (3 × 10 mL). The crude products were purified through silica gel column chromatography using petroleum ether/ethyl

acetate as eluent to give target product **3a** (petroleum ether/ethyl acetate = 10/1).

Procedure for gram scale synthesis of 3a:

In an oven-dried undivided three-necked bottle equipped with a stir bar, quinoline-*N*-oxide derivatives **1a** (5 mmol), sodium sulfonate **2a** (12.5 mmol), and $^{n}Bu_4NBF_4$ (1 mmol, 329 mg) were combined and added. The bottle was equipped with graphite rod (ϕ 6 mm, about 18 mm immersion depth in solution) as the anode and platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode and was then charged with nitrogen. Under the protection of N_2, glacial acetic acid (10 mL), H_2O (10 mL) and MeCN (80 mL) were injected respectively into the tubes via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 30 mA at room temperature for 20 h. When the reaction was finished, the reaction was quenched with saturated aqueous solution of Na_2CO_3 and extracted with DCM (3 × 30 mL). The crude products were purified through silica gel column chromatography using petroleum ether/ethyl acetate as eluent to give target product **3a** (petroleum ether/ethyl acetate = 10/1)

Procedure for cyclic voltammetry (CV):

Cyclic voltammetry was performed in a three-electrode cell connected to a Schlenk line under nitrogen at room temperature. The working electrode was a steady glassy carbon disk electrode while the counter electrode was a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. A mixed solvent (MeCN/HOAc/H_2O = 8.0/1.0/1.0, 10 mL) containing $^{n}Bu_4NBF_4$ (0.1 mmol) was poured into the electrochemical cell in cyclic voltammetry experiments. The scan rate was 0.10 V/s, ranging from 0 V to 2.5 V.

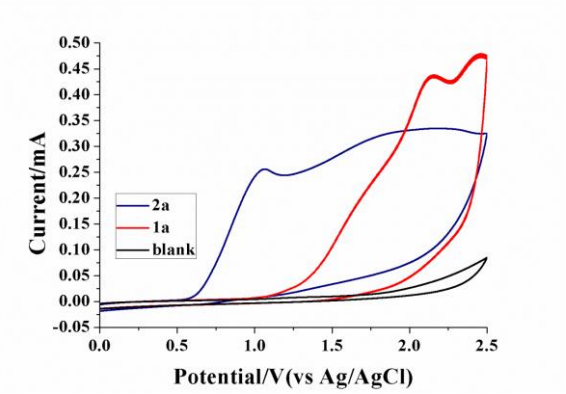
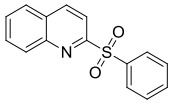
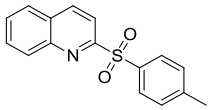


Figure S1. Cyclic voltammogram: **1a**, 0.1 mmol, **2a**, 0.1 mmol.

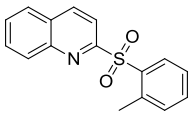
Detailed descriptions for products



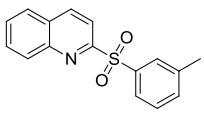
2-(Phenylsulfonyl)quinolone (3a)[3]. Yellowish solid (107.6 mg, 80%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.5 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 8.15 (d, *J* = 7.2 Hz, 3H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.77 (t, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 7.3 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.94, 147.30, 139.03, 138.69, 133.64, 130.91, 130.20, 129.12, 128.98, 128.89, 128.71, 127.63, 117.58.



2-Tosylquinoline (3b)[3]. Yellowish solid (89.2 mg, 63%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.5 Hz, 1H), 8.23 – 8.12 (m, 2H), 8.02 (d, *J* = 8.3 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.77 (t, *J* = 7.2 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 2.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.29, 147.35, 144.72, 138.62, 136.08, 130.85, 130.28, 129.69, 129.04, 128.98, 128.71, 127.62, 117.58, 21.57.

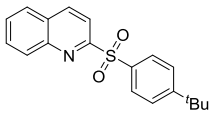


2-(*o*-Tolylsulfonyl)quinoline (3c)[4]. Yellowish solid (96.3 mg, 68%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.5 Hz, 1H), 8.31 (d, *J* = 7.9 Hz, 1H), 8.18 (d, *J* = 8.6 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.77 (t, *J* = 7.7 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 1H), 2.56 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.25, 147.16, 139.12, 138.56, 137.16, 133.85, 132.42, 130.91, 130.61, 130.37, 129.12, 128.87, 127.68, 126.35, 117.69, 20.67.

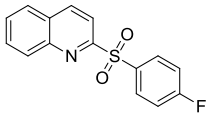


2-(*m*-Tolylsulfonyl)quinoline (3d)[4]. Yellowish solid (93.4 mg, 66%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.5 Hz, 1H), 8.14 – 8.02 (m, 2H), 7.84 (d, *J* = 6.4 Hz, 2H), 7.77 (d, *J* = 8.2

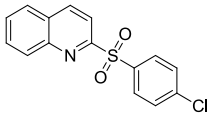
Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 2H), 2.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.09, 147.34, 139.26, 138.94, 138.64, 134.46, 130.87, 130.27, 129.12, 129.08, 128.87, 128.74, 127.62, 126.07, 117.67, 21.20.



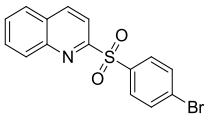
2-((4-(Tert-butyl)phenyl)sulfonyl)quinoline (3e)[4]. Yellowish solid (86.1 mg, 53%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.5 Hz, 1H), 8.20 (d, *J* = 8.6 Hz, 2H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.78 (t, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 1.30 (s, 9H). **^{13}C NMR** (100 MHz, CDCl3) δ 158.36, 157.63, 147.45, 138.62, 136.15, 130.87, 130.40, 129.07, 128.84, 128.79, 127.65, 126.12, 117.77, 35.19, 30.97.



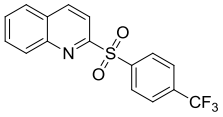
2-((4-Fluorophenyl)sulfonyl)quinolone (3f)[4]. Yellowish solid (103.3 mg, 72%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.5 Hz, 1H), 8.23 – 8.11 (m, 4H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.79 (t, *J* = 8.3 Hz, 1H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 8.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.83 (d, *J* = 256.5 Hz), 157.88, 147.31, 138.79, 134.96 (d, *J* = 3.0 Hz), 131.90 (d, *J* = 9.7 Hz), 131.02, 130.17, 129.21, 128.76, 127.68, 117.35, 116.32 (d, *J* = 22.7 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.34.



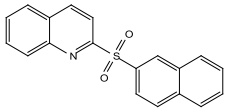
2-((4-Chlorophenyl)sulfonyl)quinolone (3g)[4]. Yellowish solid (106.1 mg, 70%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.5 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 8.12 – 8.06 (m, 2H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.82 – 7.76 (m, 1H), 7.67 (dd, *J* = 11.2, 3.9 Hz, 1H), 7.50 (d, *J* = 8.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.68, 147.34, 140.46, 138.82, 137.44, 131.07, 130.47, 130.19, 129.32, 129.28, 128.79, 127.68, 117.40.



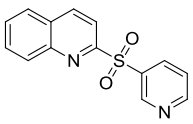
2-((4-Bromophenyl)sulfonyl)quinolone (3h)[4]. Yellowish solid (114 mg, 66%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.5 Hz, 1H), 8.20 (d, *J* = 8.6 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 8.01 (d, *J* = 8.6 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.78 (t, *J* = 7.2 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.56, 147.27, 138.81, 137.94, 132.25, 131.03, 130.47, 130.11, 129.24, 129.06, 128.74, 127.66, 117.36.



2-((4-(Trifluoromethyl)phenyl)sulfonyl)quinolone (3i)[4]. Yellowish solid (74.1 mg, 44%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.5 Hz, 1H), 8.30 (d, *J* = 8.3 Hz, 2H), 8.25 (d, *J* = 8.5 Hz, 1H), 8.14 (d, *J* = 8.6 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.80 (t, *J* = 7.2 Hz, 3H), 7.68 (t, *J* = 7.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.24, 147.37, 142.60, 138.96, 135.15 (q, *J* = 33.0 Hz), 131.18, 130.18, 129.62, 129.44, 128.88, 127.72, 126.05 (q, *J* = 3.6 Hz), 123.07 (q,*J* = 272.0 Hz), 117.47. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.21.

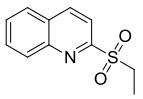


2-**(Naphthalen-2-ylsulfonyl)quinoline (3j)[4].** Yellowish solid (87.7 mg, 55%).**^{1}H NMR** (400 MHz,CDCl3) δ 8.75 (s, 1H), 8.37 (d, *J* = 8.6 Hz, 1H), 8.26 (d, *J* = 8.6 Hz, 1H), 8.15 (d, *J* = 8.6 Hz, 1H), 8.09 (d, *J* = 8.7 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.94 (d, *J* = 8.7 Hz, 1H), 7.89 – 7.81 (m, 2H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.61 (q, *J* = 9.3, 8.7 Hz, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.12, 147.41, 138.70, 136.02, 135.28, 132.10, 130.93, 130.75, 130.32, 129.47, 129.24, 129.14, 128.77, 127.85, 127.64, 127.47, 123.67, 117.73.

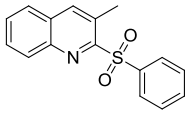


2-(Pyridin-3-ylsulfonyl)quinolone (3k). Yellowish solid (85.1 mg, 63%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.35 (s, 1H), 8.84 (d, *J* = 6.2 Hz, 1H), 8.45 (t, *J* = 8.1 Hz, 2H), 8.25 (d, *J* = 8.5 Hz, 1H),

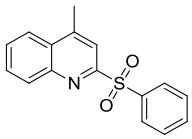
8.13 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.85 – 7.77 (m, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.51 (dd, *J* = 8.0, 4.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.37, 154.04, 149.93, 147.32, 138.98, 136.79, 135.54, 131.21, 130.18, 129.45, 128.89, 127.73, 123.59, 117.20 **HRMS (ESI)** Calcd. for $C_{14}H_{11}N_2O_2S$ **[M+H$^+$]**: 271.0536. Found: m/z 271.0542.



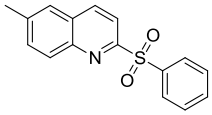
2-(Ethylsulfonyl)quinoline (3l). Yellowish solid (58.6 mg, 53%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.5 Hz, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.86 (t, *J* = 7.6 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 3.59 (q, *J* = 7.4 Hz, 2H), 1.37 (t, *J* = 7.4 Hz, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.38, 147.15, 138.73, 131.13, 130.09, 129.19, 129.08, 127.83, 117.32, 46.31, 6.86. **HRMS (ESI)** Calcd. for $C_{11}H_{11}NO_2SNa$ **[M+Na]$^+$**: 244.0403. Found: m/z 244.0404.



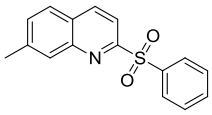
3-Methyl-2-(phenylsulfonyl)quinolone (4a). Yellowish solid (87.7 mg, 62%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.9 Hz, 3H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.69 – 7.61 (m, 2H), 7.56 (t, *J* = 7.6 Hz, 3H), 2.87 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ156.81, 144.55, 139.80, 138.71, 133.45, 129.81, 129.70, 129.35, 129.04, 128.93, 128.57, 128.44, 126.62, 18.68. **HRMS (ESI)** Calcd. for $C_{16}H_{13}NO_2SNa$ **[M+Na]$^+$**: 306.0559 Found: m/z 306.0552.



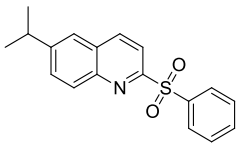
4-Methyl-2-(phenylsulfonyl)quinolone (4b)[4]. Yellowish solid (94.8 mg, 67%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 8.0, 3.3 Hz, 3H), 8.04 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.74 (t, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.3 Hz, 2H), 2.77 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$)δ 157.57, 147.91, 147.11, 139.18, 133.55, 130.90, 130.47, 128.95, 128.86, 128.68, 123.74, 118.01, 19.07.



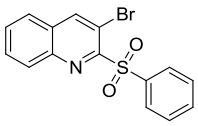
6-Methyl-2-(phenylsulfonyl)quinolone (4c)[4]. Yellowish solid (103.3 mg, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.5 Hz, 1H), 8.14 (dd, *J* = 10.8, 5.0 Hz, 3H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.58 (dd, *J* = 8.8, 6.7 Hz, 3H), 7.51 (t, *J* = 7.5 Hz, 2H), 2.52 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.99, 145.96, 139.60, 139.24, 137.75, 133.52, 133.29, 129.82, 128.94, 128.80, 126.33, 117.66, 21.66. **HRMS (ESI)** Calcd. for $C_{16}H_{13}NO_2SNa$ **[M+Na]$^+$**: 306.0559 Found: m/z 306.0549.



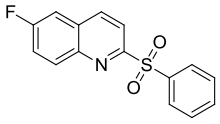
7-**Methyl-2-(phenylsulfonyl)quinoline (4d)[4].** Yellowish solid (101.9 mg, 72%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.5 Hz, 1H), 8.14 (d, *J* = 8.3 Hz, 3H), 7.94 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.57 – 7.45 (m, 3H), 2.55 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.03, 147.75, 141.72, 139.30, 138.30, 133.64, 131.60, 129.22, 129.05, 129.02, 127.30, 127.01, 116.91, 21.86. **HRMS (ESI)** Calcd. for $C_{16}H_{13}NO_2SNa$ **[M+Na]$^+$**: 306.0559 Found: m/z 306.0553.



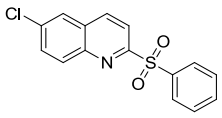
6-Isopropyl-2-(phenylsulfonyl)quinoline (4e). Yellowish solid (127.5 mg, 82%). **^{1}H NMR** (400 MHz, CDCl3) δ 8.31 (d, *J* = 8.5 Hz, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 8.16 – 8.04 (m, 3H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.66 (s, 1H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 3.12 – 3.08 (m, 1H), 1.33 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (100 MHz, CDCl3) δ 157.16, 150.26, 146.38, 139.37, 138.13, 133.52, 131.05, 130.15, 128.97, 128.84, 123.64, 117.71, 34.19, 23.57. **HRMS (ESI)** Calcd for $C_{18}H_{17}NO_2SNa$ **[M+Na]$^+$**: 334.0872 Found: m/z 334.0868.



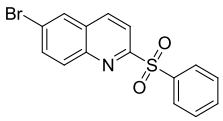
3-Bromo-2-(phenylsulfonyl)quinoline (4f)[4]. Yellowish solid (102.7 mg, 59%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.09 (d, *J* = 7.8 Hz, 2H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.76 (dd, *J* = 15.6, 8.3 Hz, 2H), 7.68 (q, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.7 Hz, 2H).**^{13}C NMR** (100 MHz, CDCl3) δ 154.42, 144.41, 142.90, 138.02, 133.82, 131.06, 130.20, 130.06, 129.78, 128.66, 126.49, 111.30.



6-Fluoro-2-(phenylsulfonyl)quinolone (4g). Yellowish solid (101.9 mg, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.6 Hz, 1H), 8.13 (d, *J* = 8.6 Hz, 1H), 8.06 (dd, *J* = 13.6, 6.4 Hz, 3H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 3H), 7.39 (d, *J* = 8.5 Hz, 1H).**^{13}C NMR** (100 MHz, CDCl3) δ 161.80 (d, *J* = 253.3 Hz), 157.52, 144.39, 138.89, 138.02 (d, *J* = 5.8 Hz), 133.75, 132.97 (d, *J* = 9.6 Hz), 129.70 (d, *J* = 10.6 Hz), 129.0, 128.91, 121.54 (d, *J* = 26.2 Hz), 118.41, 110.73 (d, *J* = 22.2 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -108.09. **HRMS (ESI)** Calcd for $C_{15}H_{10}FNO_2SNa$ **[M+Na]$^{+}$**: 310.0308 Found: m/z 310.0312.

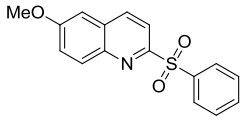


6-Chloro-2-(phenylsulfonyl)quinolone (4h)[4]. Yellowish solid (109.1 mg, 72%). **^{1}H NMR** (400 MHz, $CDCl_3$) 8.30 (d, *J* = 8.6 Hz, 1H), 8.23 (d, *J* = 8.6 Hz, 1H), 8.14 (d, *J* = 7.4 Hz, 2H), 8.08 (d, *J* = 9.1 Hz, 1H), 7.85 (d, *J* = 2.1 Hz, 1H), 7.69 (dd, *J* = 9.1, 2.2 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.31, 145.66, 138.75, 137.78, 135.20, 133.82, 132.00, 131.76, 129.27, 129.08, 128.98, 126.29, 118.55.

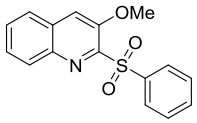


6-Bromo-2-(phenylsulfonyl)quinoline (4i). Yellowish solid (134.9 mg, 78%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.6 Hz, 1H), 8.22 (d, *J* = 8.6 Hz, 1H), 8.16 – 8.10 (m, 2H), 8.02 (dd, *J* = 12.0, 5.5 Hz, 2H), 7.82 (dd, *J* = 9.1, 2.1 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.42, 145.87, 138.73, 137.68, 134.54, 133.83, 131.79,

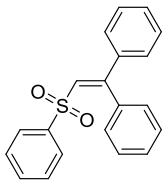
129.69, 129.08, 129.00, 123.55, 118.54. **HRMS (ESI)** Calcd. for $C_{15}H_{10}BrNO_2SNa$ **[M+Na]**$^+$: 347.9688 Found: m/z 347.9691.



6-Methoxy-2-(phenylsulfonyl)quinolone(4j)[4]. Yellowish solid (110.6 mg, 74%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.6 Hz, 1H), 8.16 – 8.10 (m, 3H), 8.02 (d, *J* = 9.3 Hz, 1H), 7.57 (dd, *J* = 8.5, 6.1 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.39 (dd, *J* = 9.3, 2.7 Hz, 1H), 7.08 (d, *J* = 2.7 Hz, 1H), 3.92 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.73, 155.23, 143.48, 139.43, 136.78, 133.44, 131.58, 130.32, 128.93, 128.67, 124.22, 118.11, 104.57, 55.64.



3-Methoxy-2-(phenylsulfonyl)quinoline (4k)[4]. Yellowish solid (59.8 mg, 40%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.8 Hz, 3H), 7.74 (d, *J* = 9.2 Hz, 1H), 7.66 – 7.57 (m, 3H), 7.54 (dd, *J* = 14.1, 6.3 Hz, 3H), 3.95 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.36, 148.55, 141.24, 139.38, 133.50, 130.91, 130.30, 129.50, 129.35, 128.52, 128.00, 126.24, 116.14, 56.11.



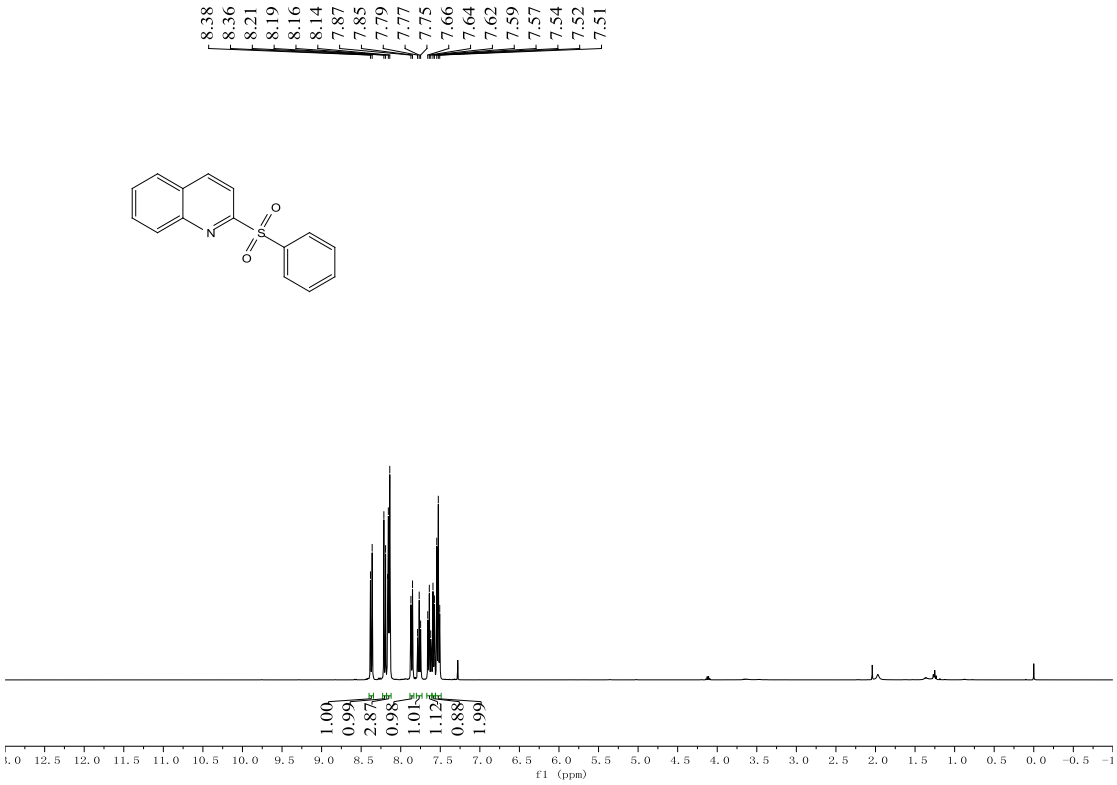
(2-(Phenylsulfonyl)ethene-1,1-diyl)dibenzene (5a). Yellowish oil (124.8 mg,39%) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 3H), 7.29 (q, *J* = 7.6 Hz, 5H), 7.21 (d, *J* = 7.6 Hz, 2H), 7.08 (d, *J* = 7.4 Hz, 2H), 7.03 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.16, 141.42, 139.04, 135.40, 132.79, 130.29, 129.71, 128.83, 128.71, 128.63, 128.55, 128.16, 127.81, 127.58. **HRMS (EI)** Calcd. for $C_{20}H_{16}O_2S$ **[M]**$^+$: 320.0871 Found: m/z 320.0873.

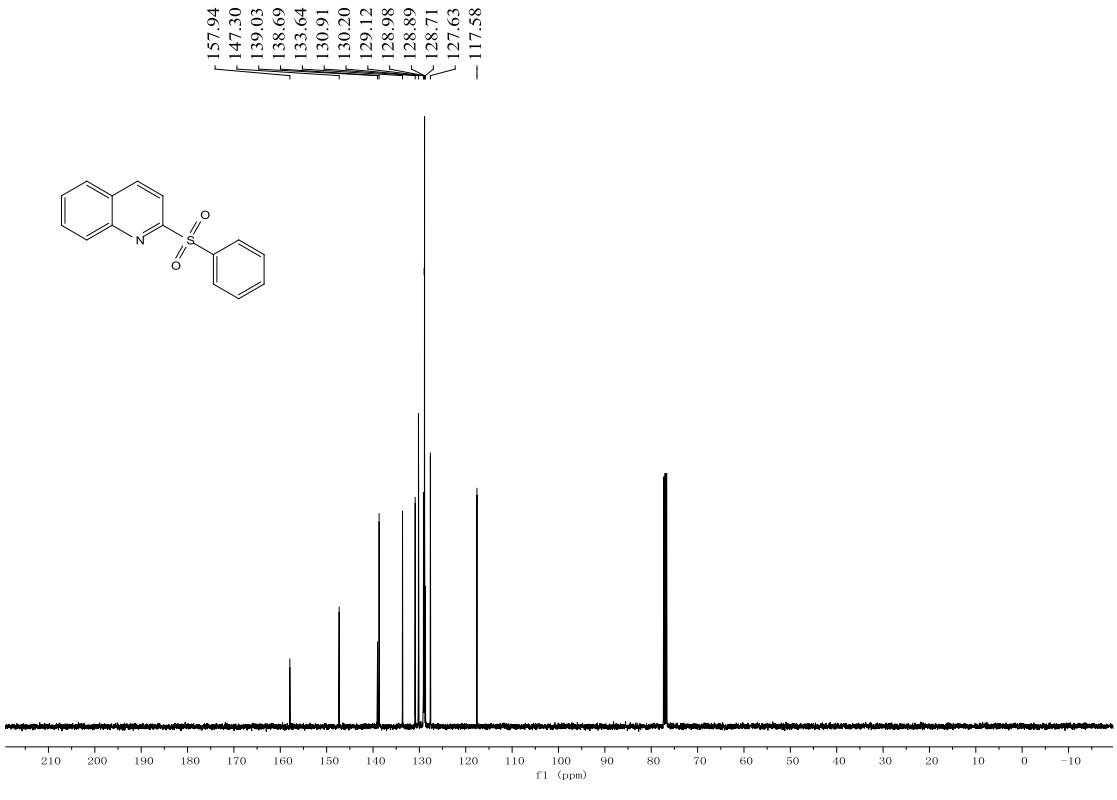
References:

1. X. Yu, S. Yang, Y. Zhang, M. Guo, Y. Yamamoto and M. Bao, *Org. Lett.*, 2017, **19**, 6088-6091.
2. T. C. Johnson, Bryony L. Elbert, A. J. M. Farley, T. W. Gorman, C. Genicot, B. Lallemand, P. Pasau, J. Flasz, J. L. Castro, M. MacCoss, D. J. Dixon, R. S. Paton, C. J. Schofield, M. D. Smith and M. C. Willis, *Chem. Sci.*, 2018, **9**, 629-633.
3. W.-K. Fu, K. Sun, C. Qu, X.-L. Chen, L.-B. Qu, W.-Z. Bi and Y.-F. Zhao, *Asian J. Org. Chem.*, 2017, **6**, 492-495.
4. L.-Y. Xie, T.-G. Fang, J.-X. Tan, B. Zhang, Z. Cao, L.-H. Yang and W.-M. He, *Green Chem.*, 2019, **21**, 3858-3863.

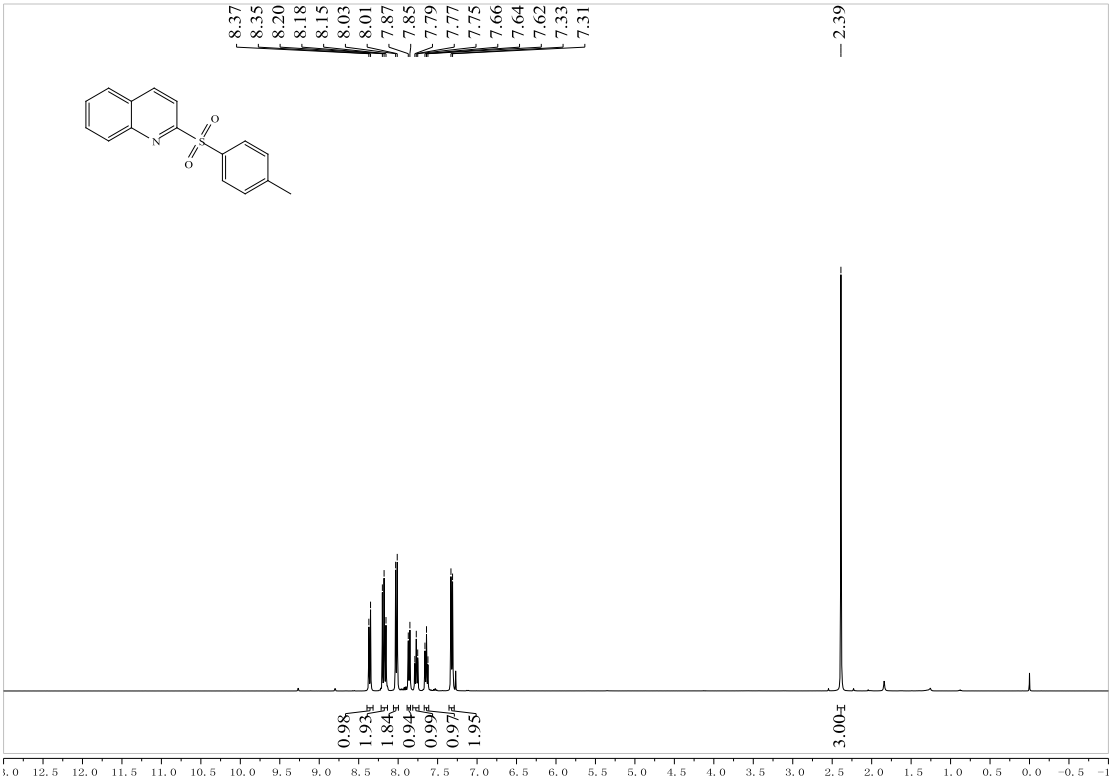
Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra

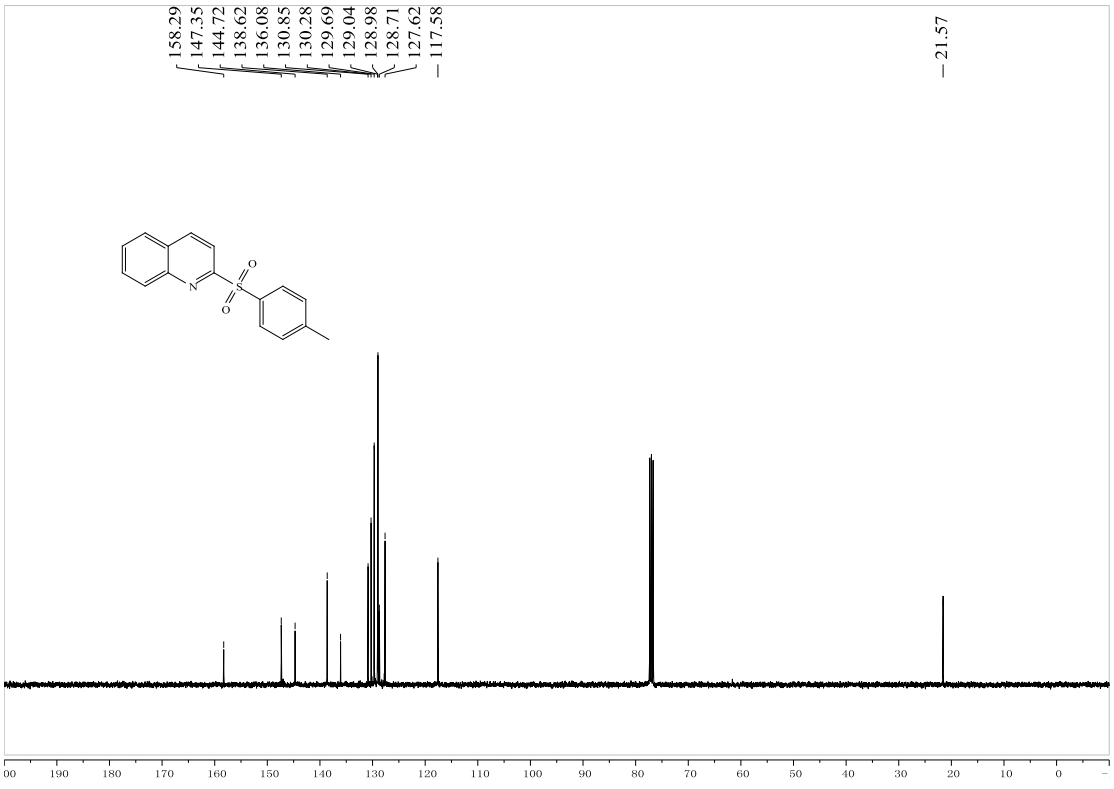
3-**(Phenylsulfonyl)quinoline (3a)**



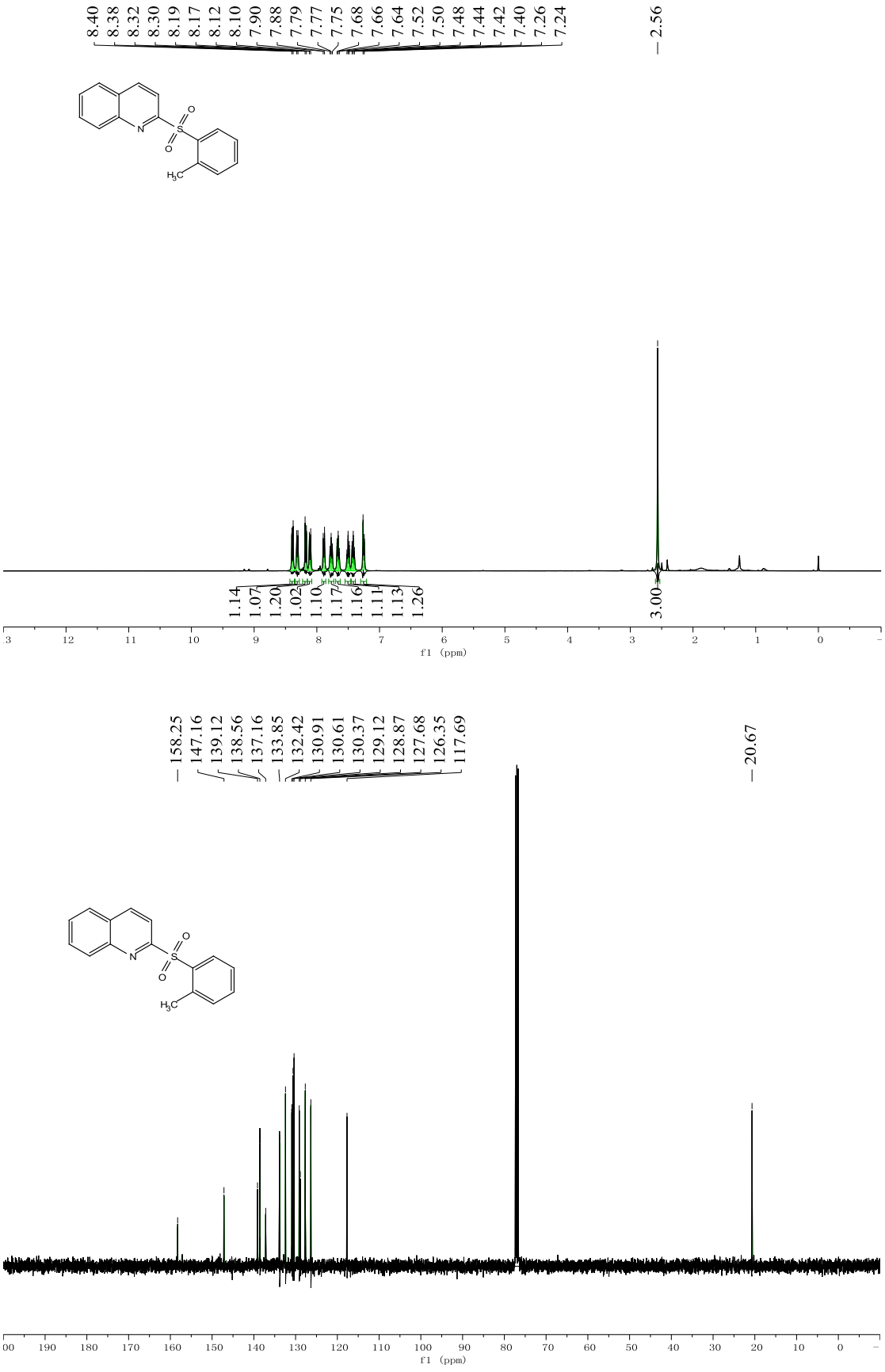


2-Tosylquinoline (3b)

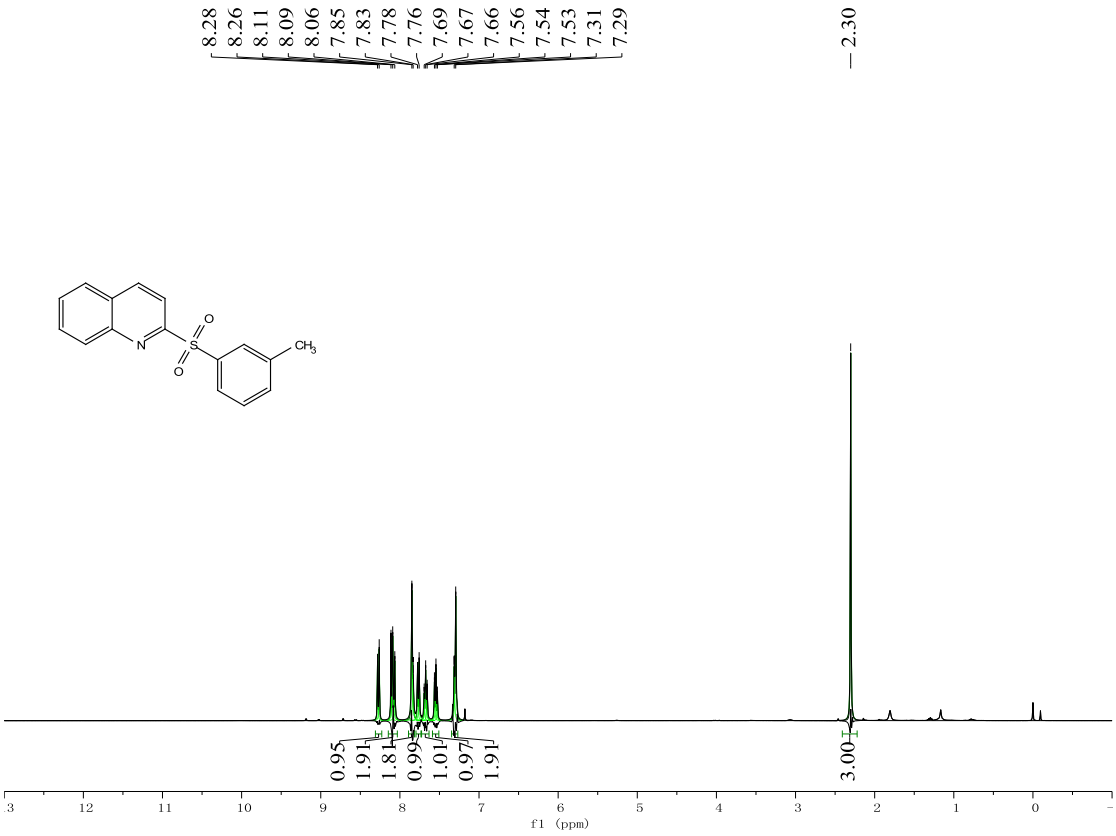


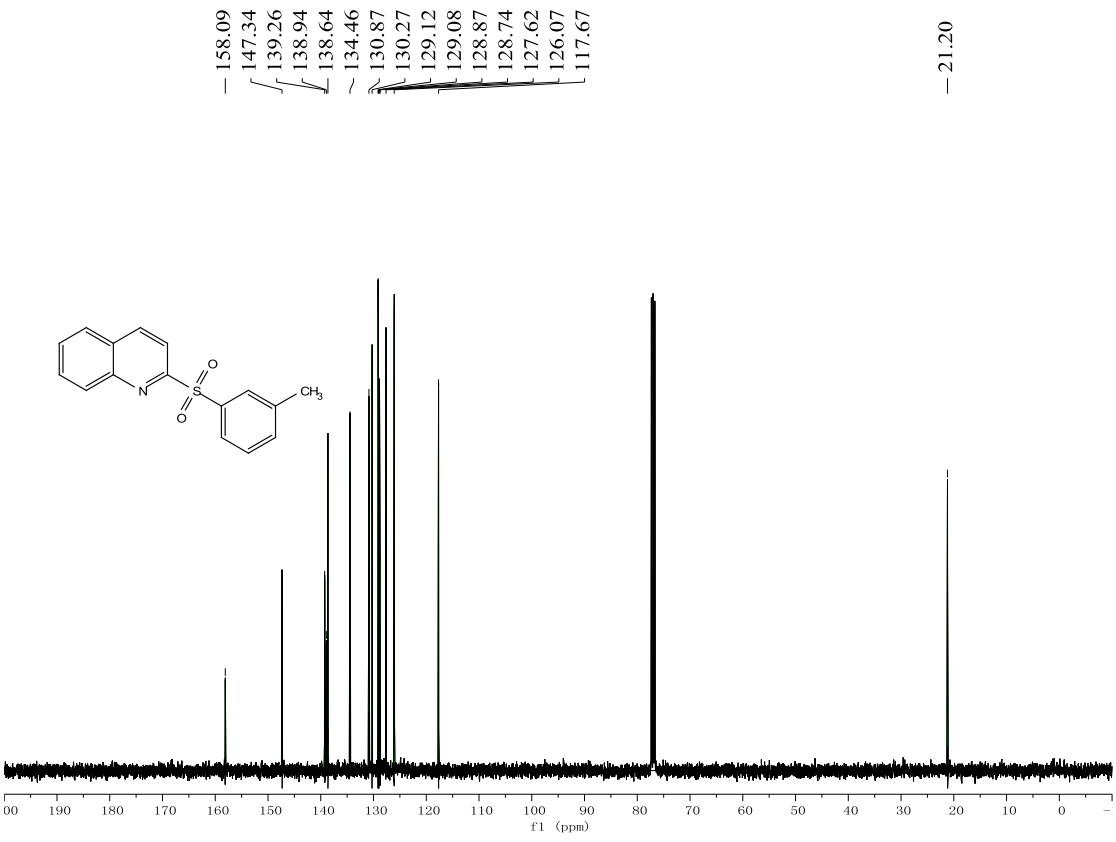


2-(*o*-Tolylsulfonyl)quinoline (3c)

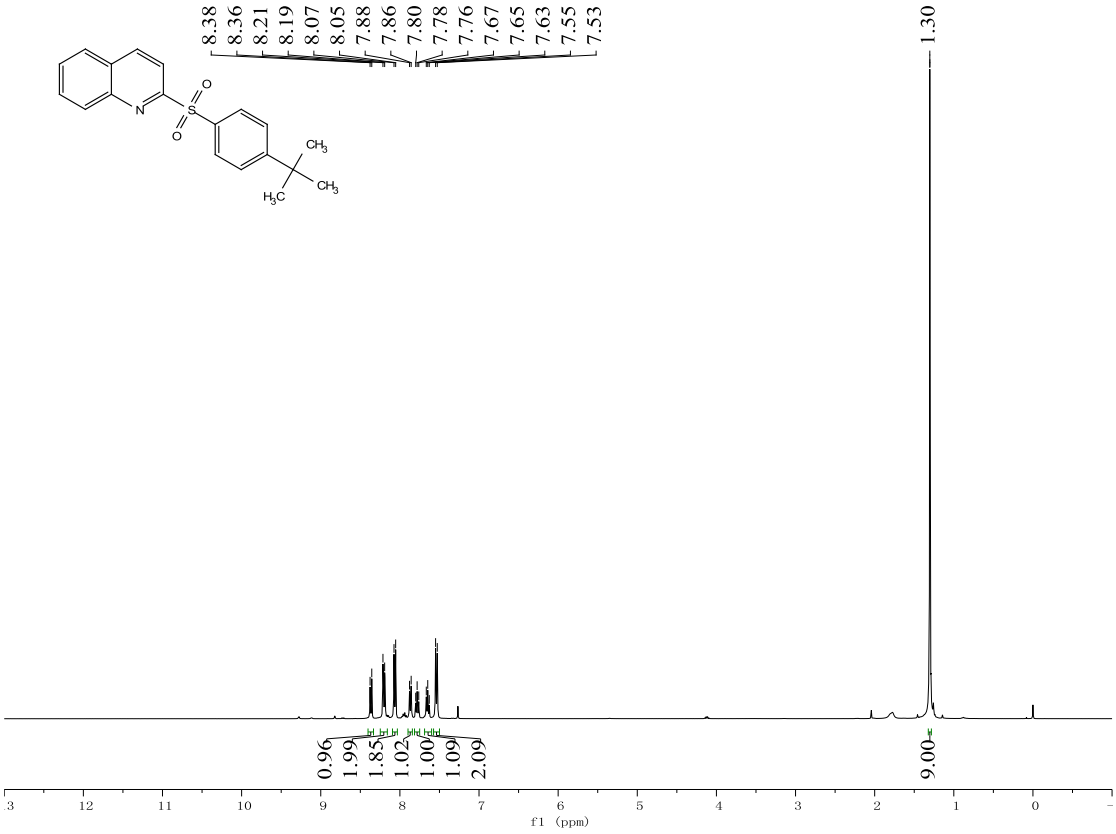


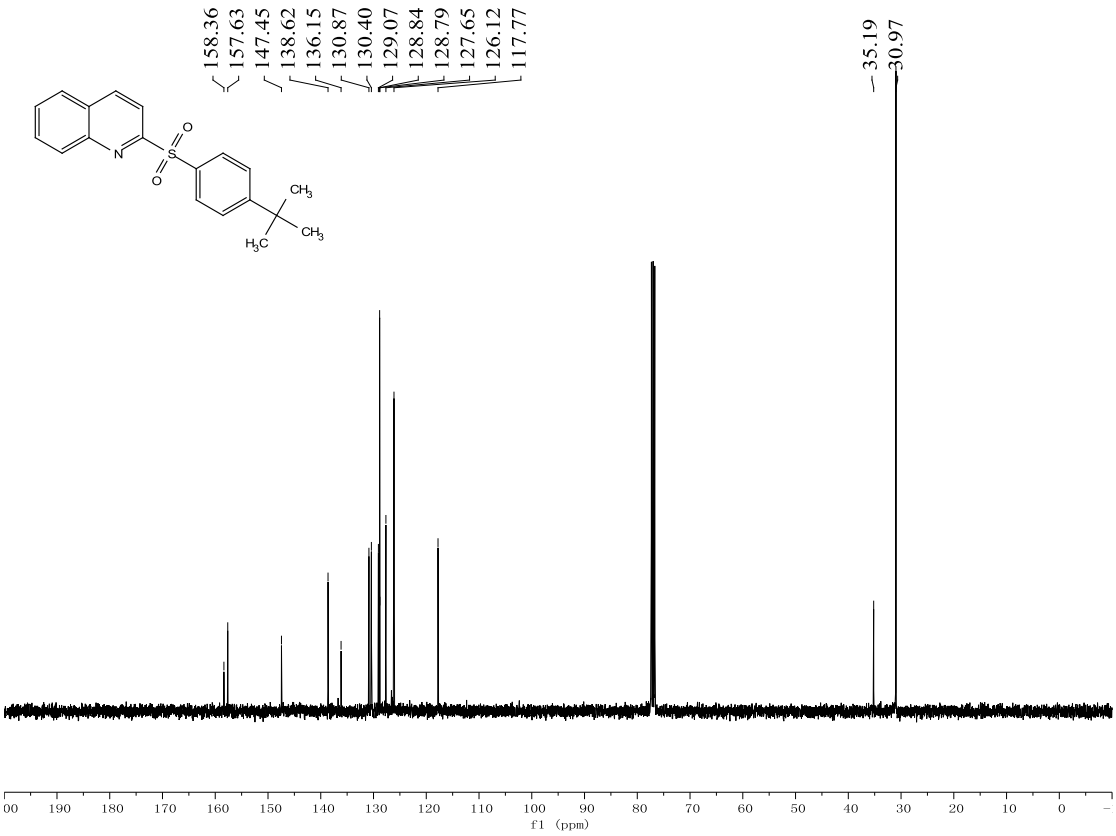
2-(*m*-Tolylsulfonyl)quinoline (3d)



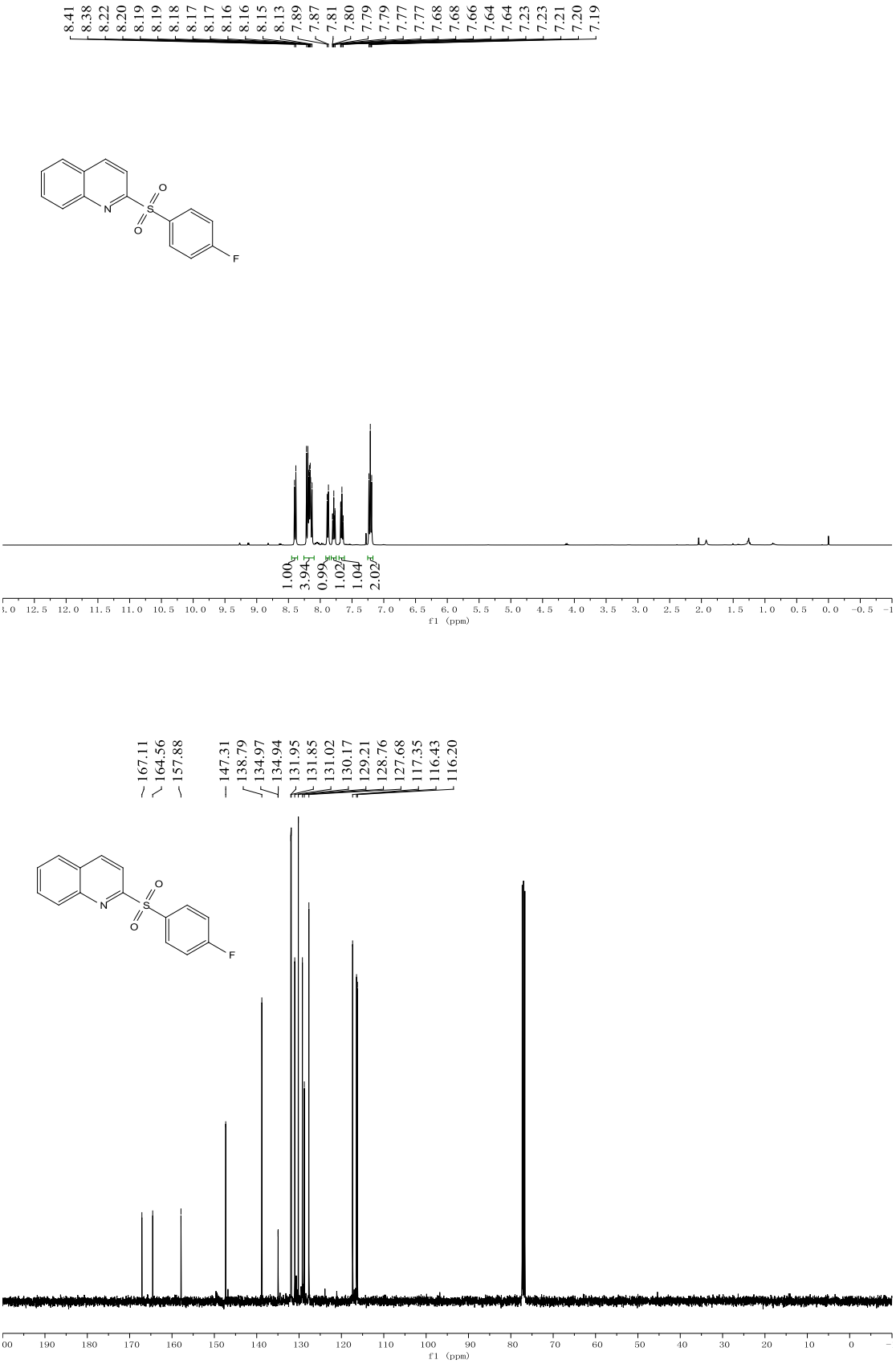


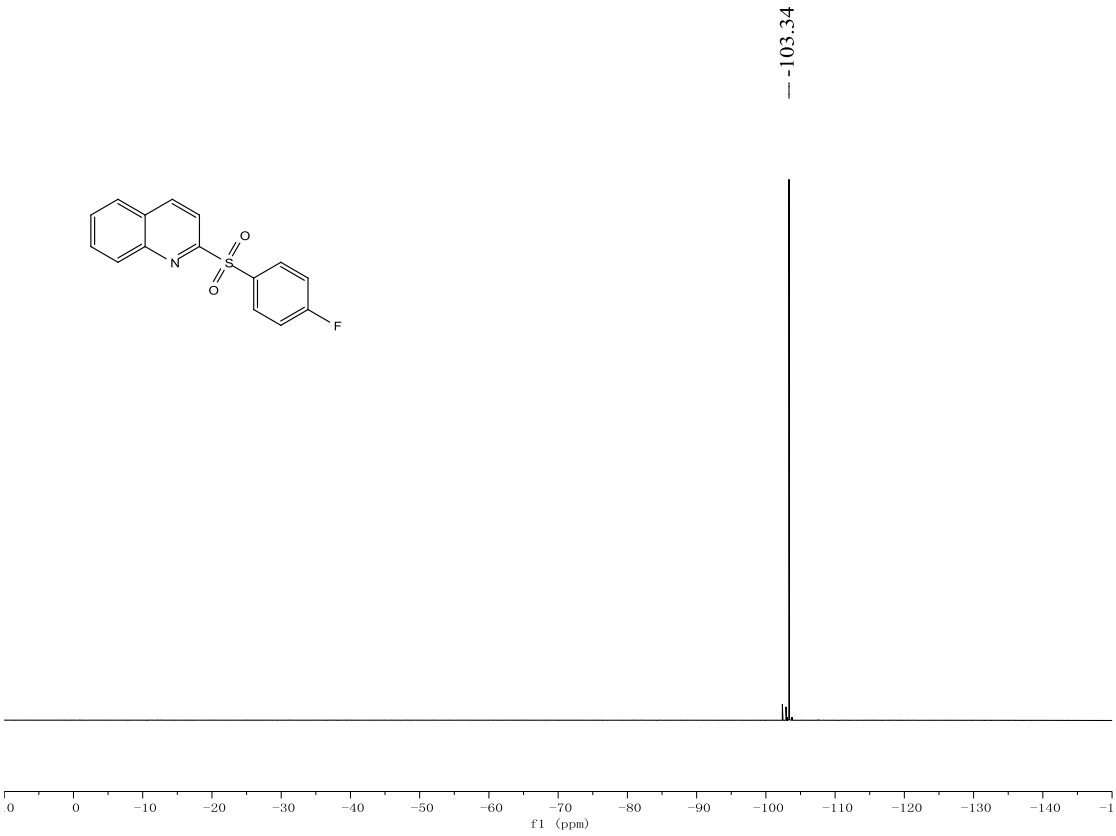
2-((4-(Tert-butyl)phenyl)sulfonyl)quinoline (3e)





2-((4-Fluorophenyl)sulfonyl)quinolone (3f)

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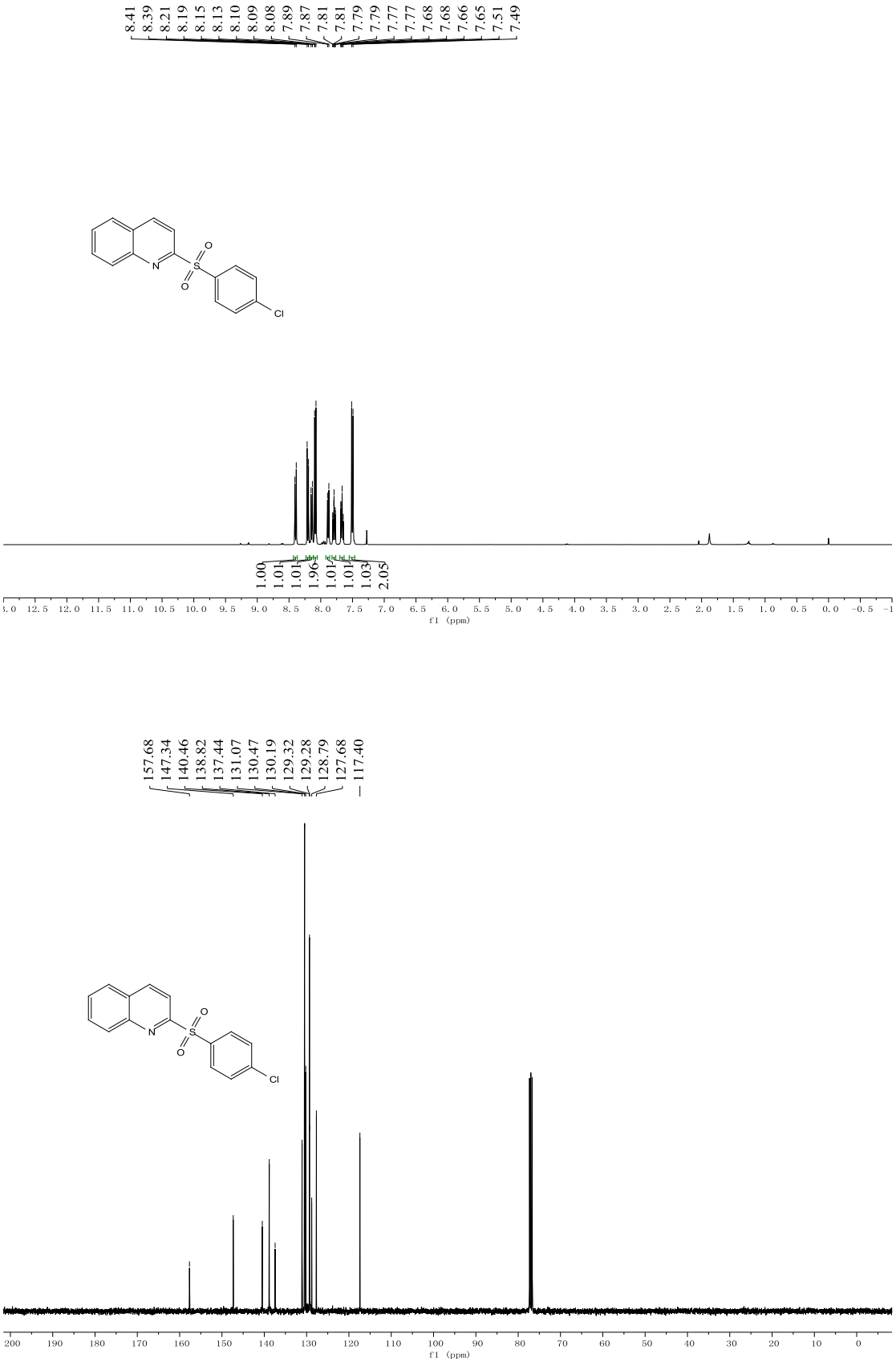
f1 (ppm)

2-((4-Chlorophenyl)sulfonyl)quinolone (3g)



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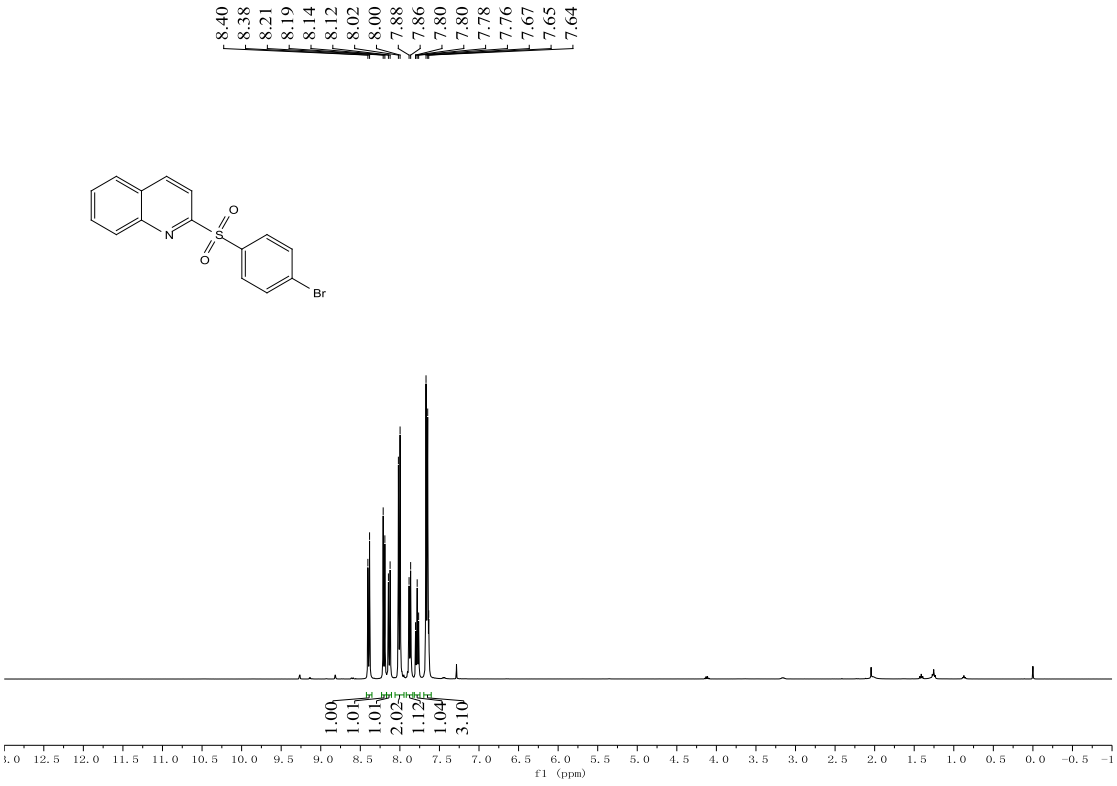
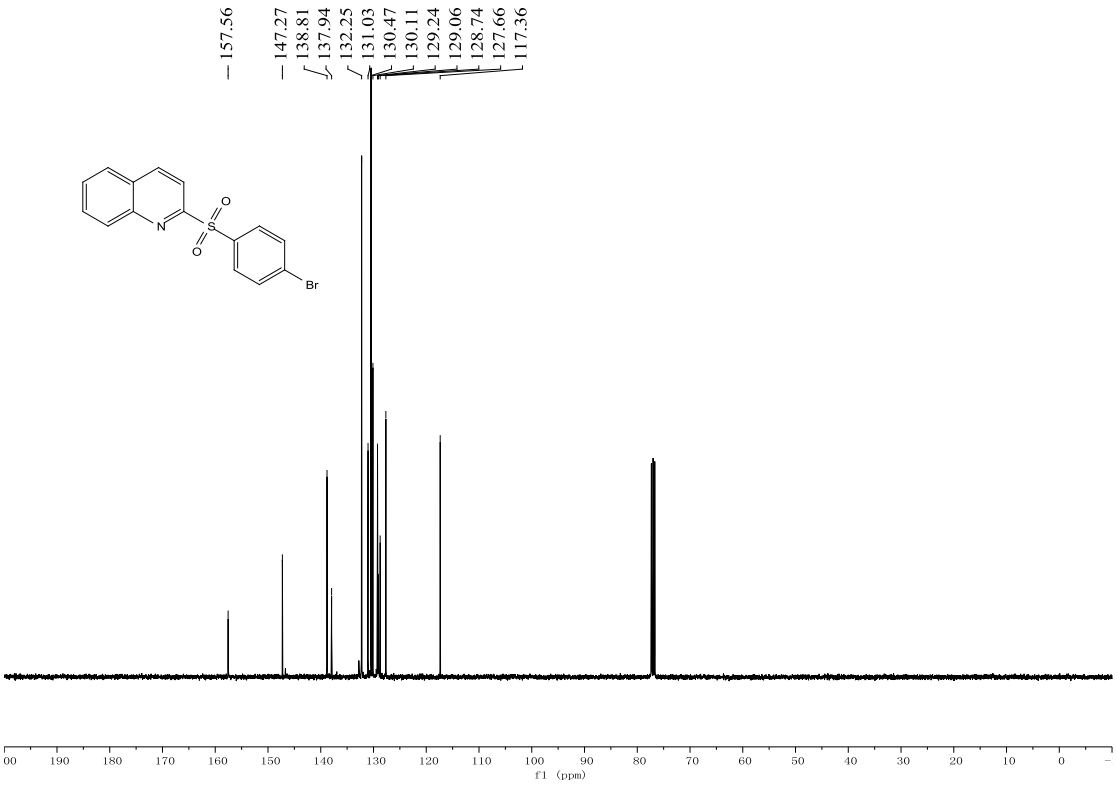
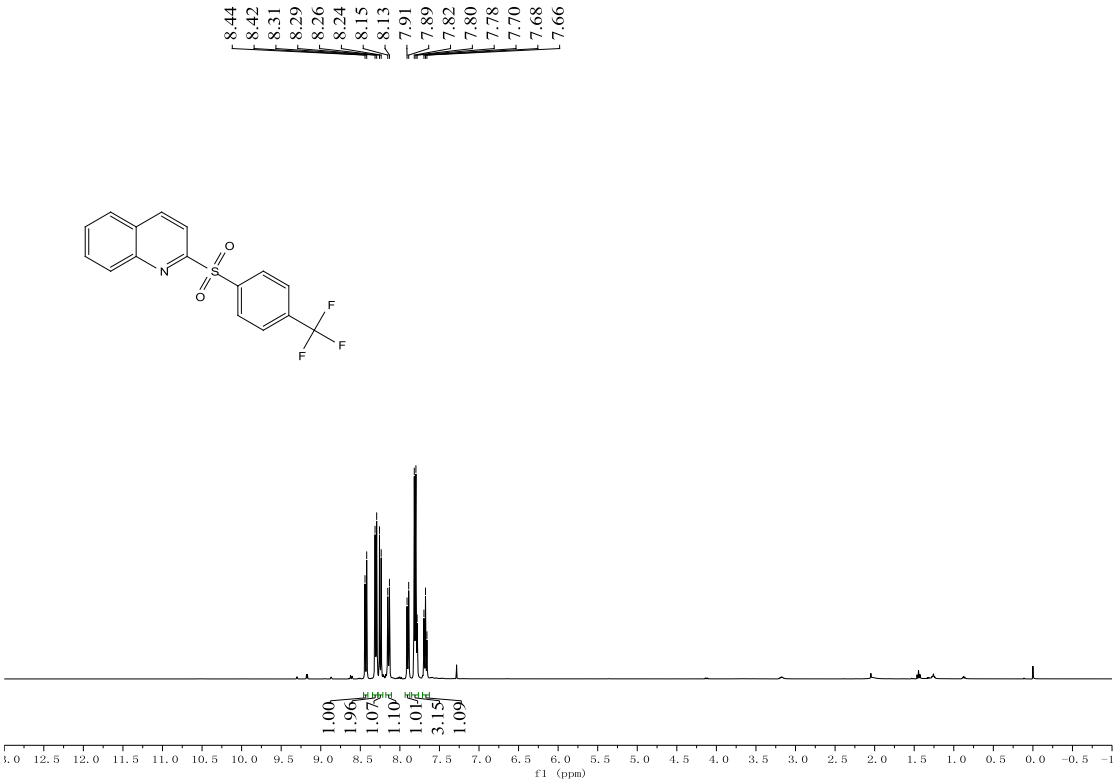
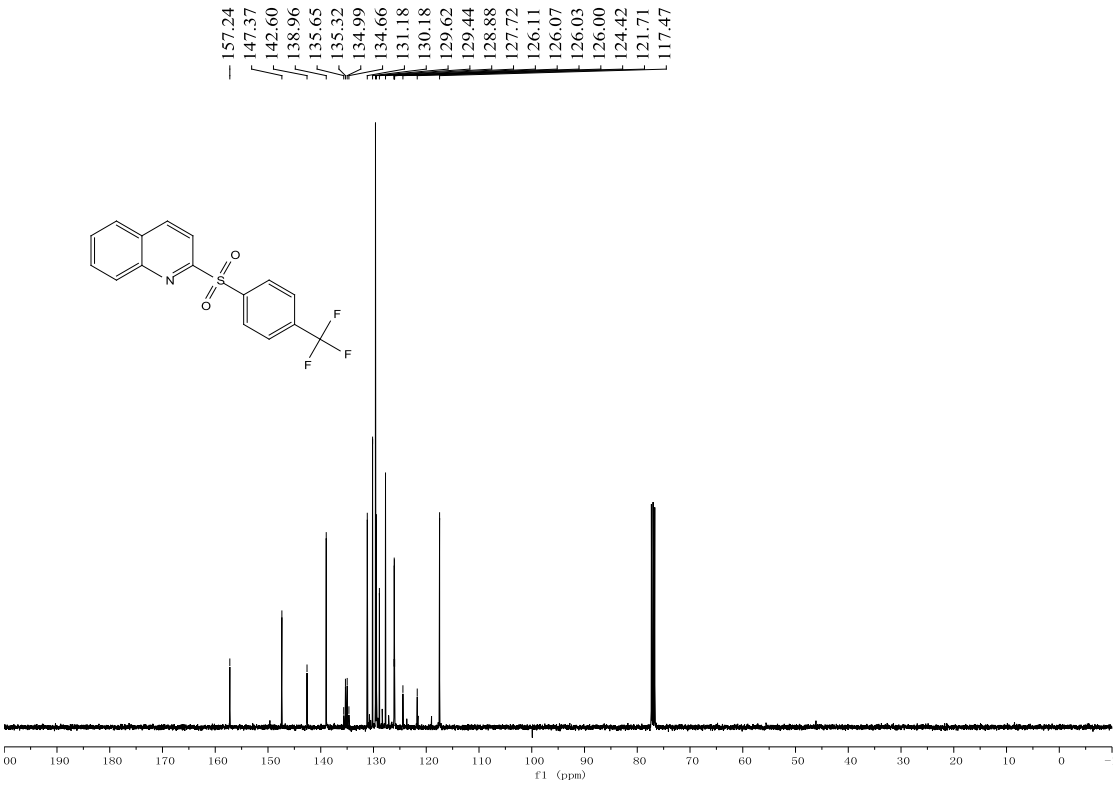
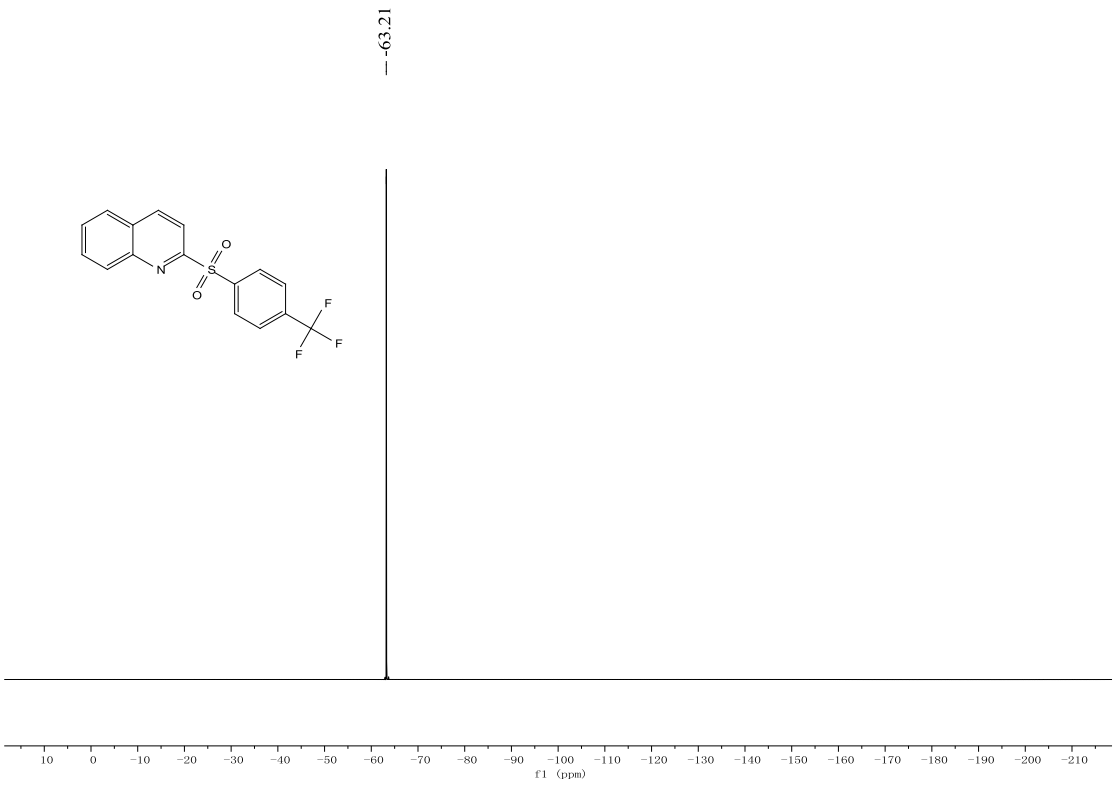




2-((4-(Trifluoromethyl)phenyl)sulfonyl)quinolone (3i)



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N
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F
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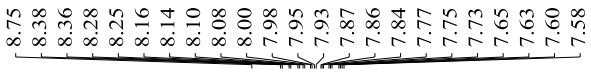
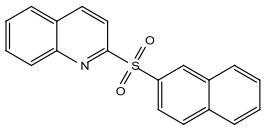
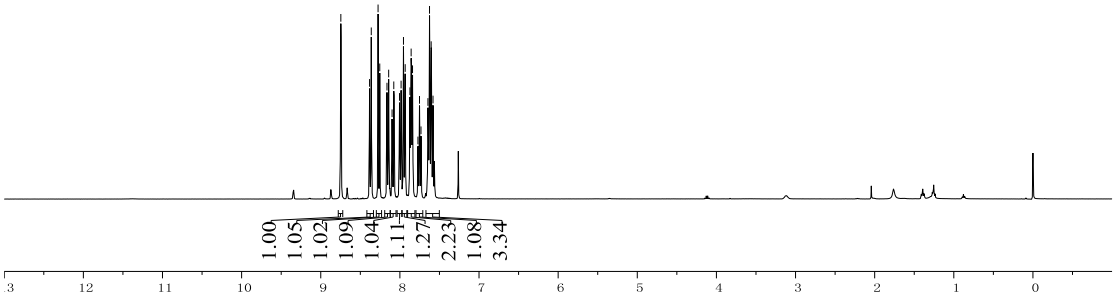
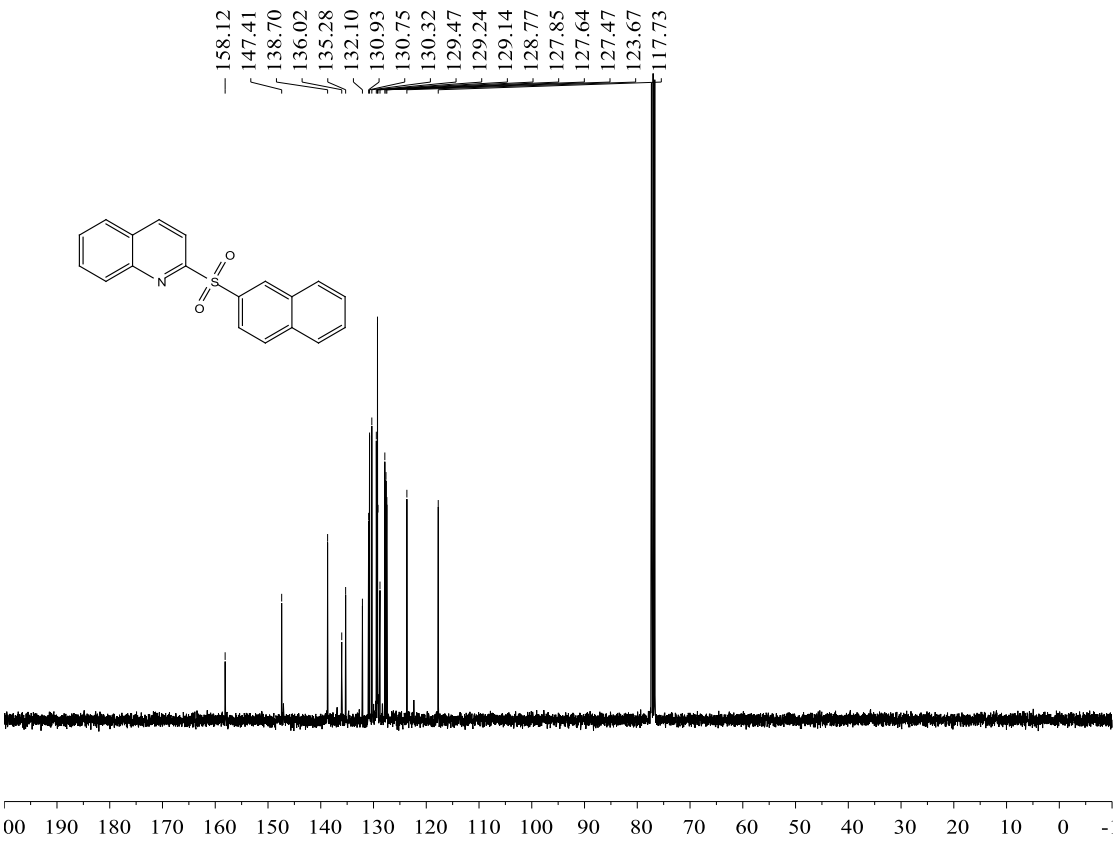
f1 (ppm)

2-(Naphthalen-2-ylsulfonyl)quinoline (3j)

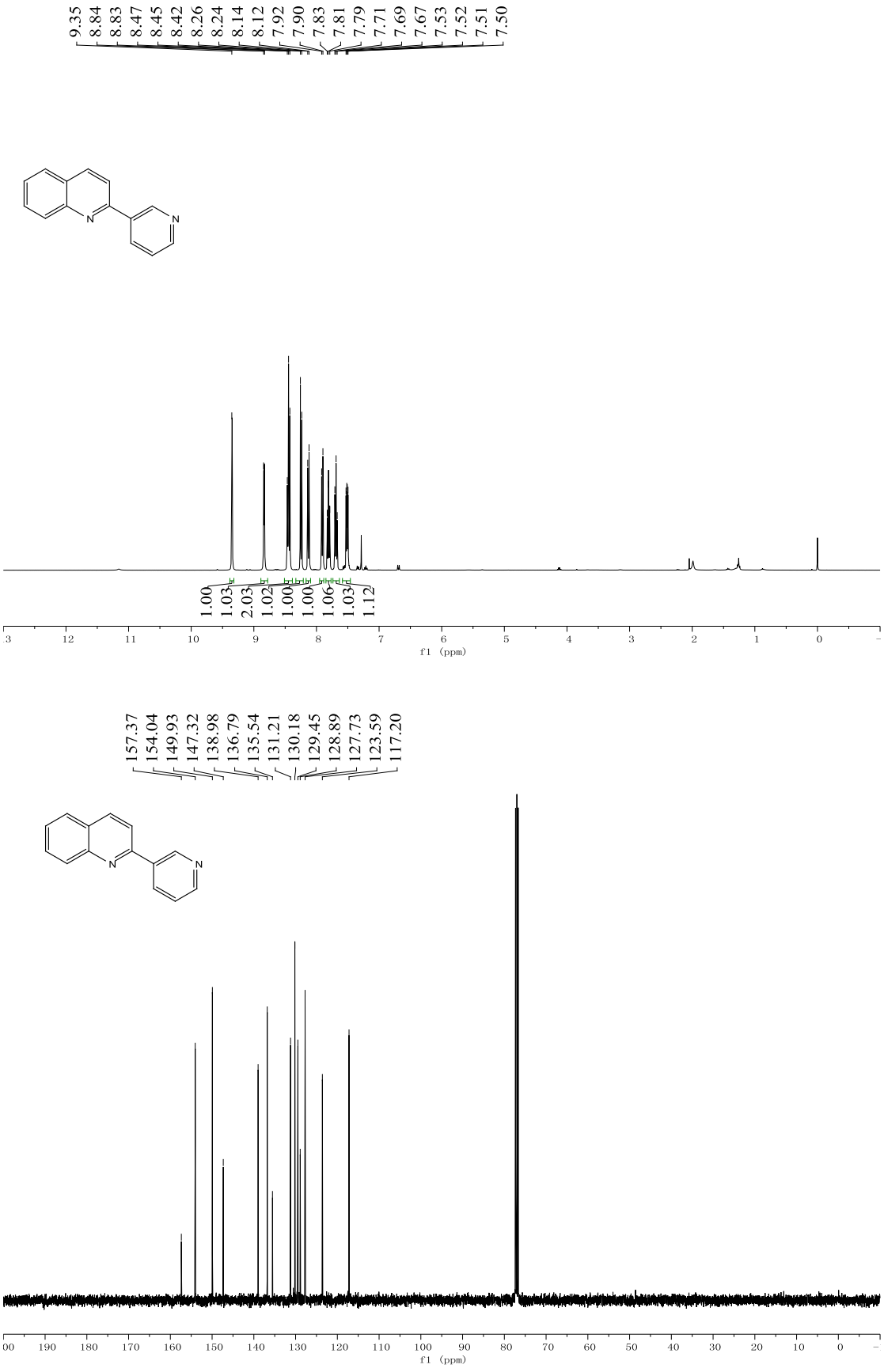




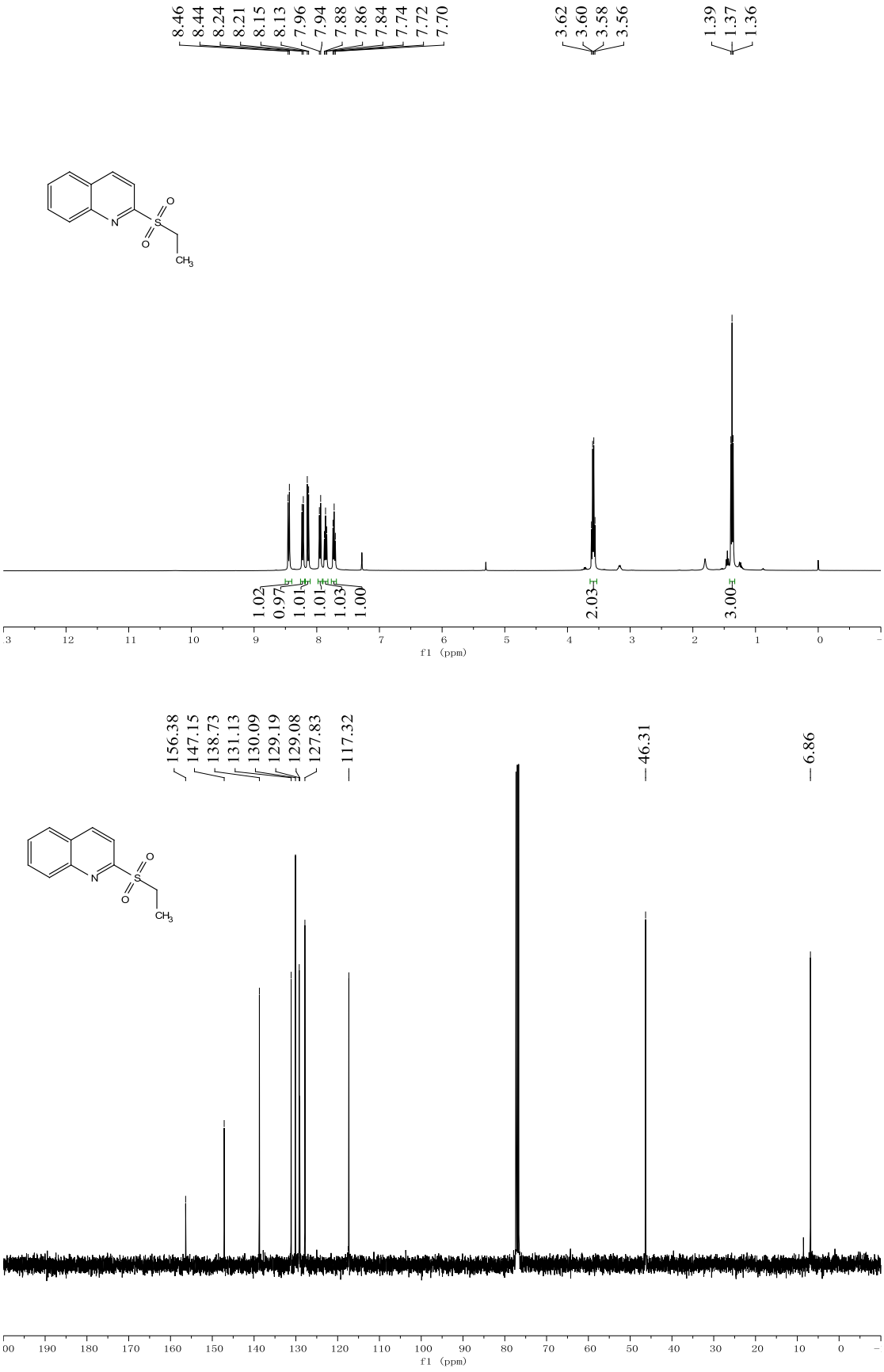




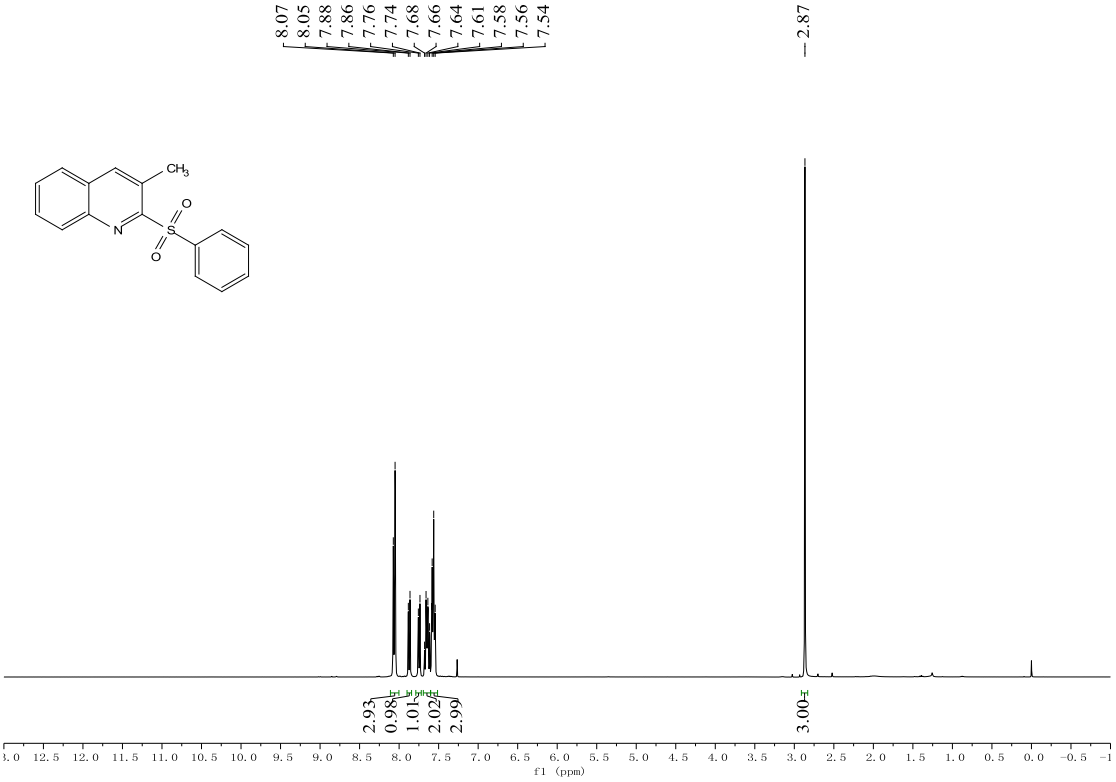
2-(Pyridin-3-ylsulfonyl)quinolone (3k)

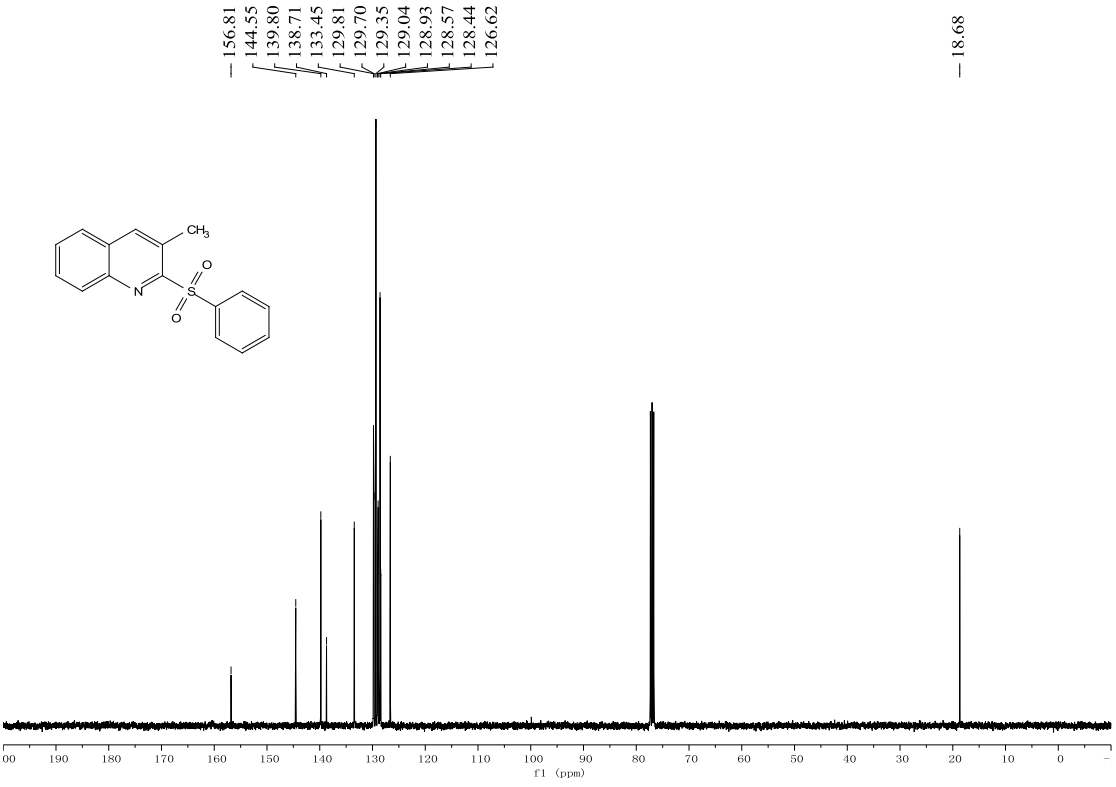


2-(Ethylsulfonyl)quinoline (3l)

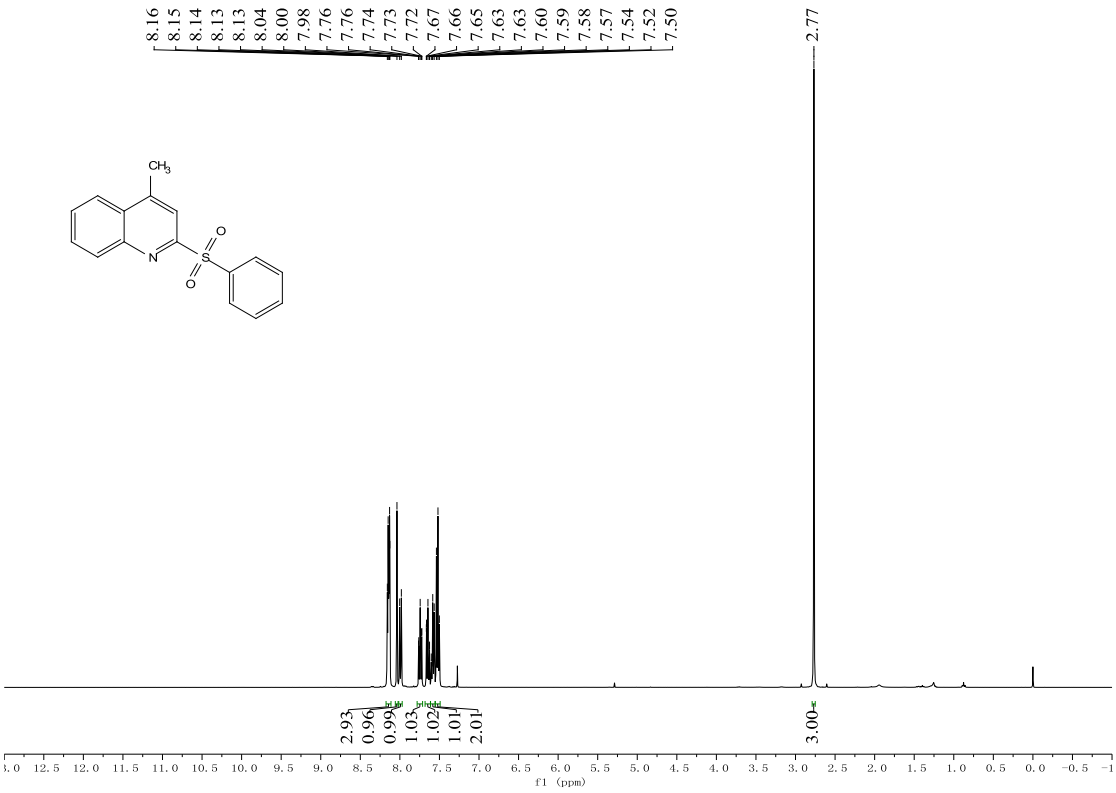


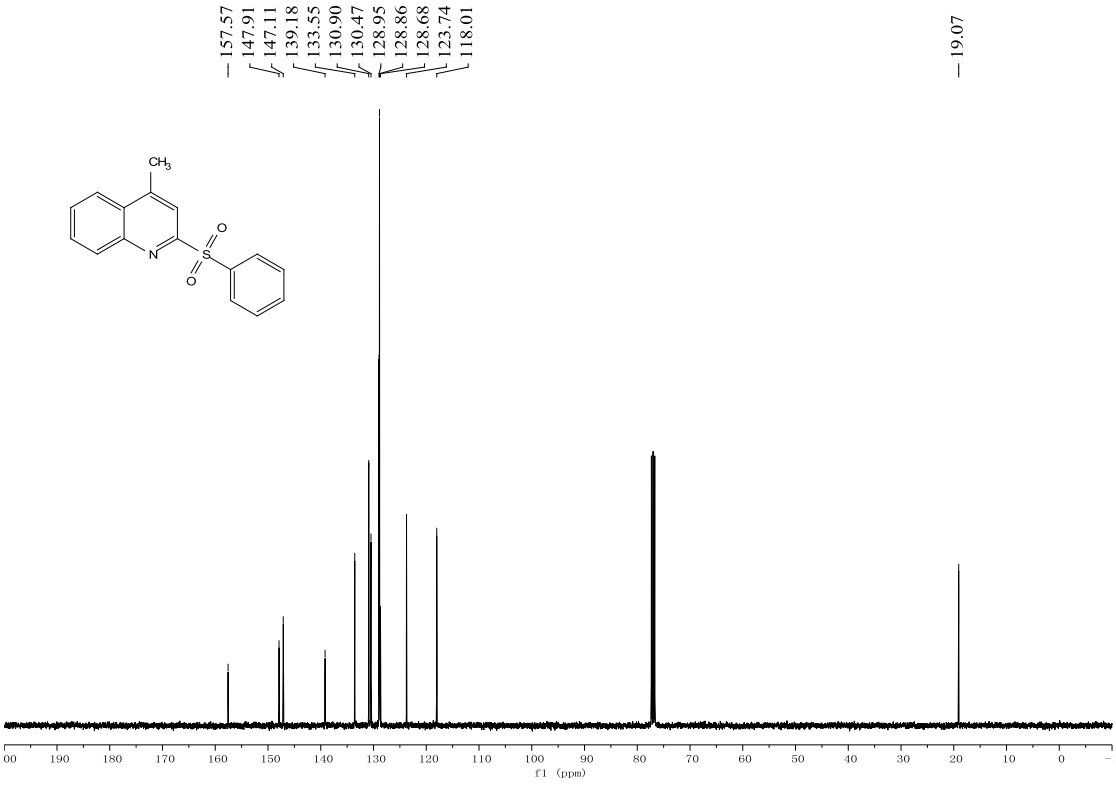
3-Methyl-2-(phenylsulfonyl)quinolone (4a)



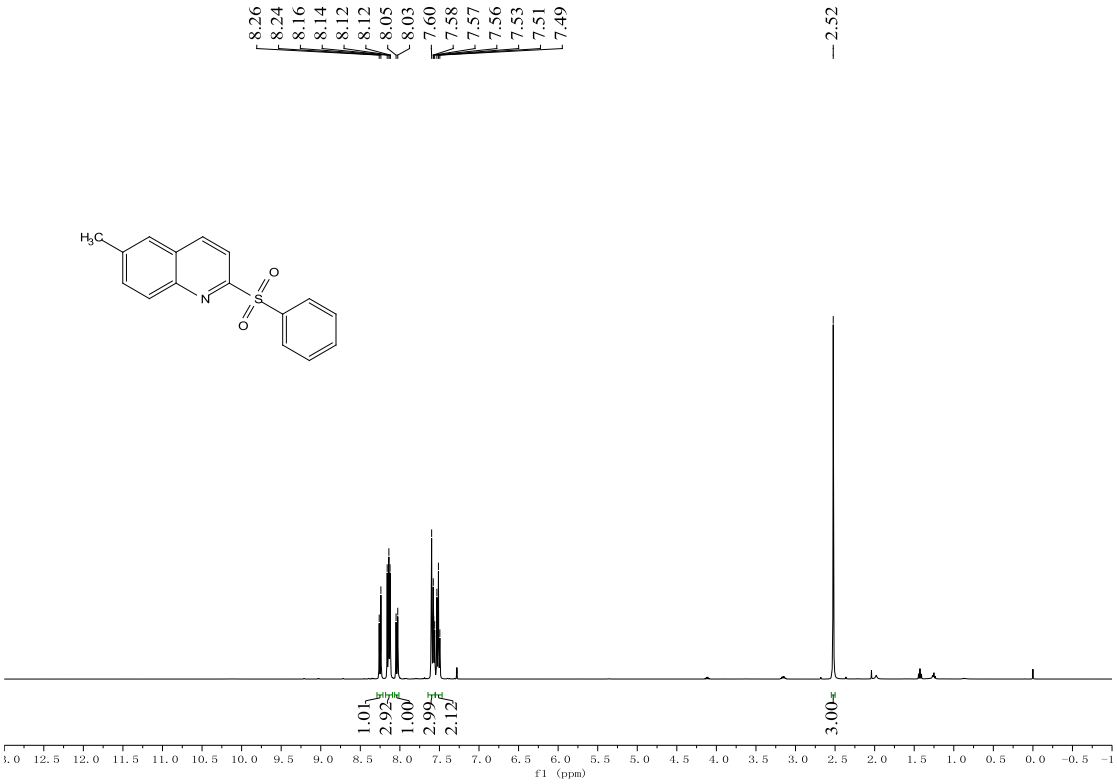


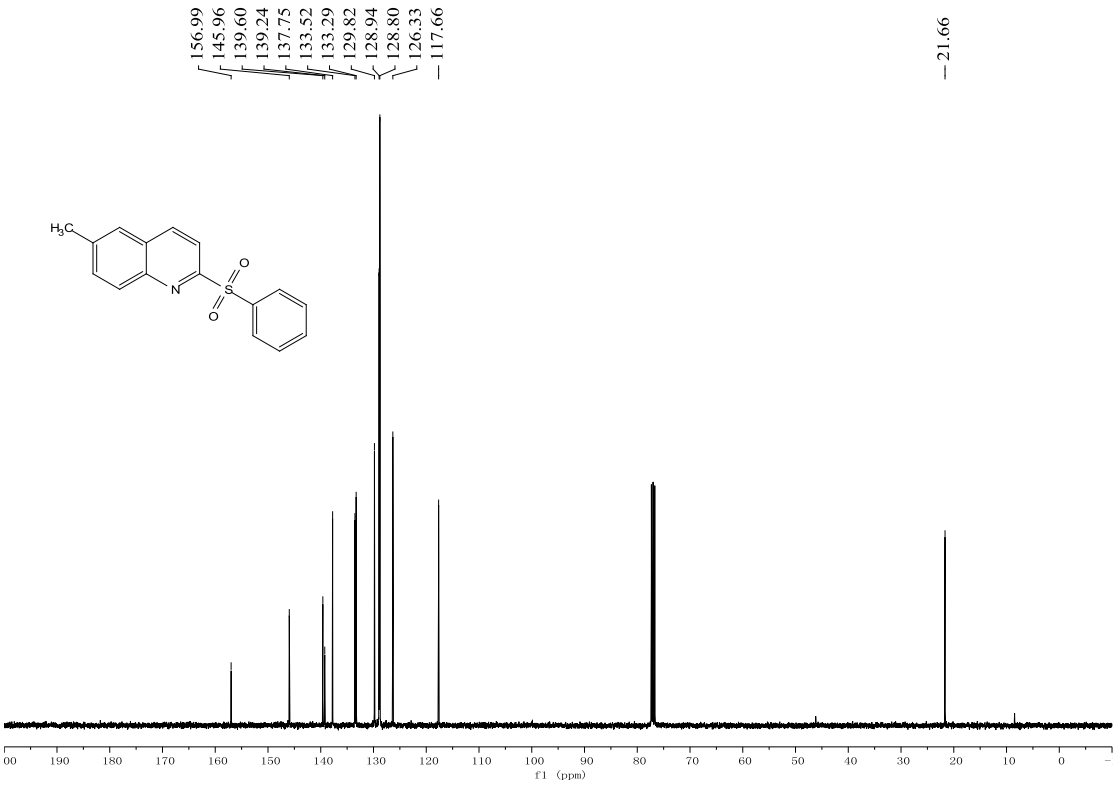
4-Methyl-2-(phenylsulfonyl)quinolone (4b)



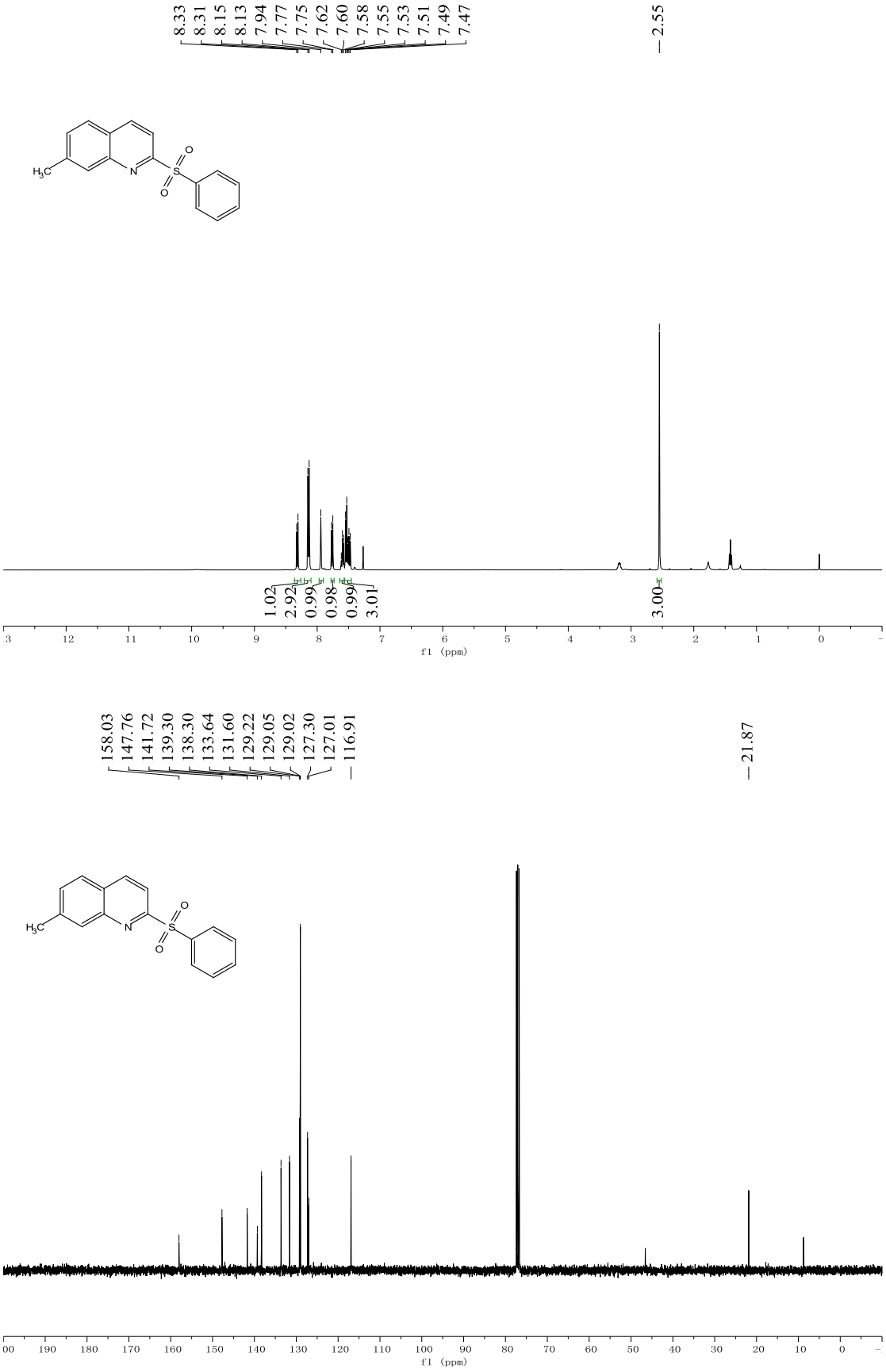


6-Methyl-2-(phenylsulfonyl)quinolone (4c)

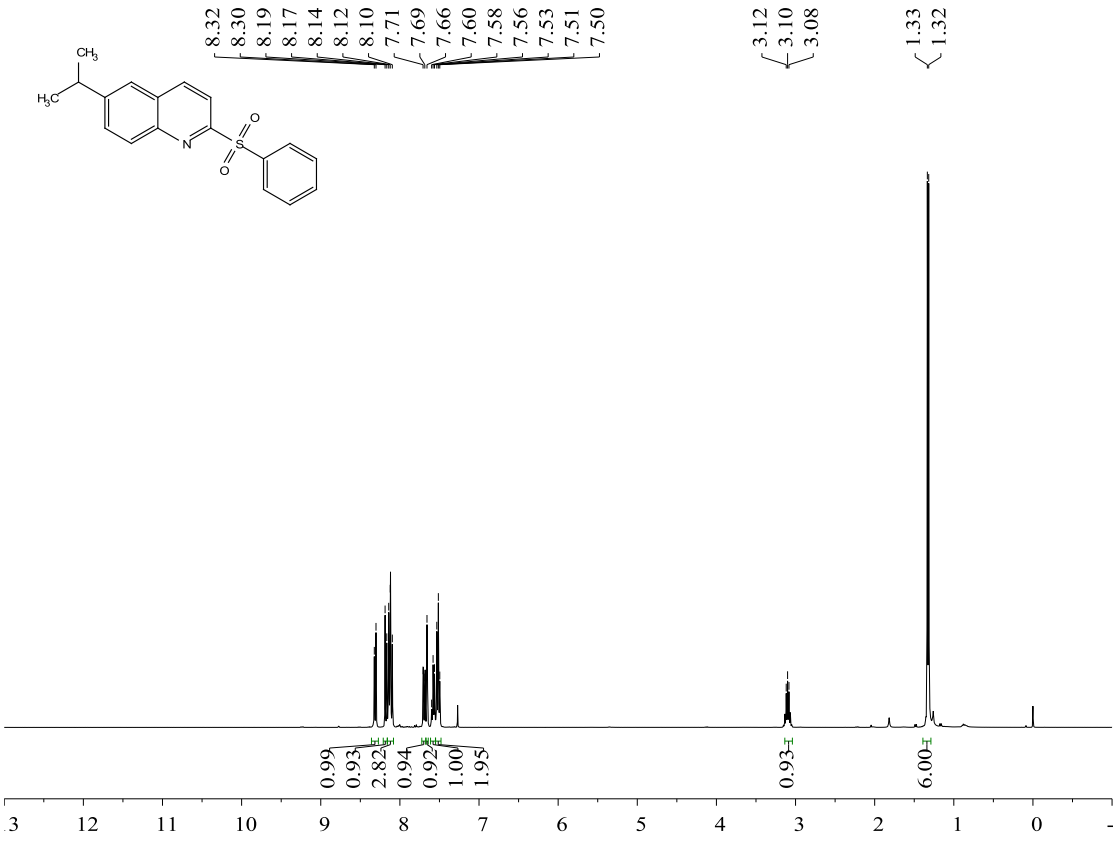


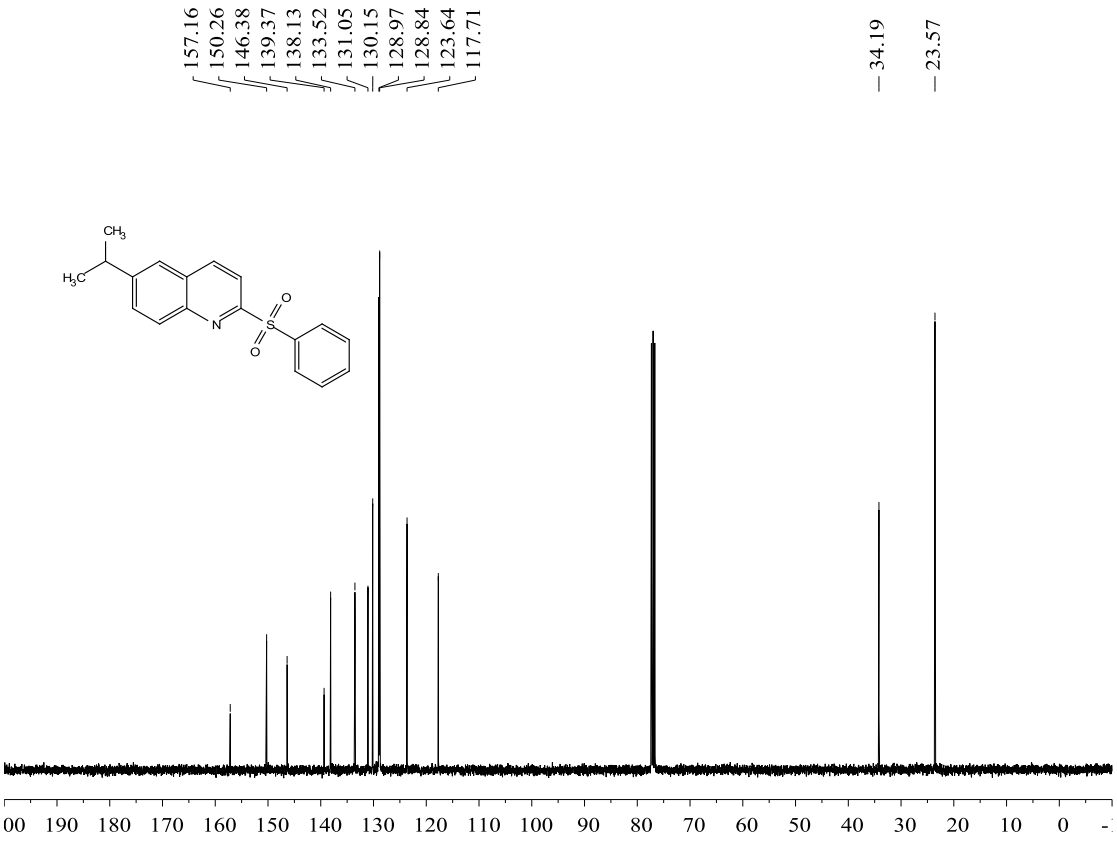


7-Methyl-2-(phenylsulfonyl)quinoline (4d)

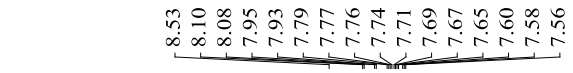


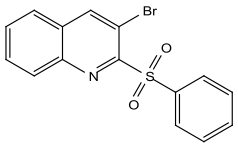
6-Isopropyl-2-(phenylsulfonyl)quinoline (4e)

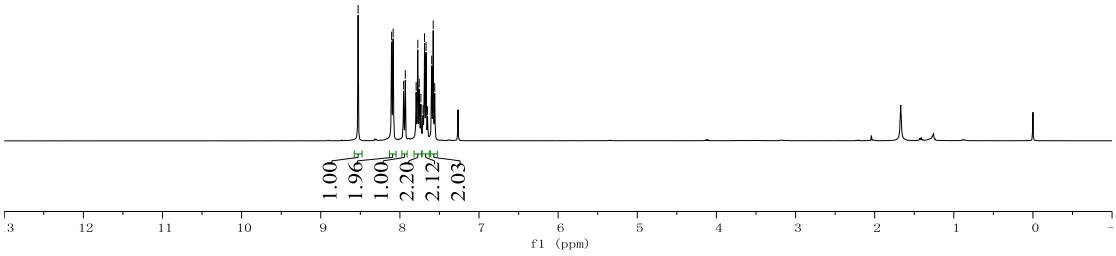


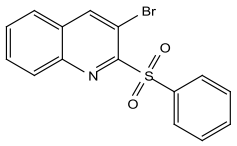


3-Bromo-2-(phenylsulfonyl)quinoline (4f)

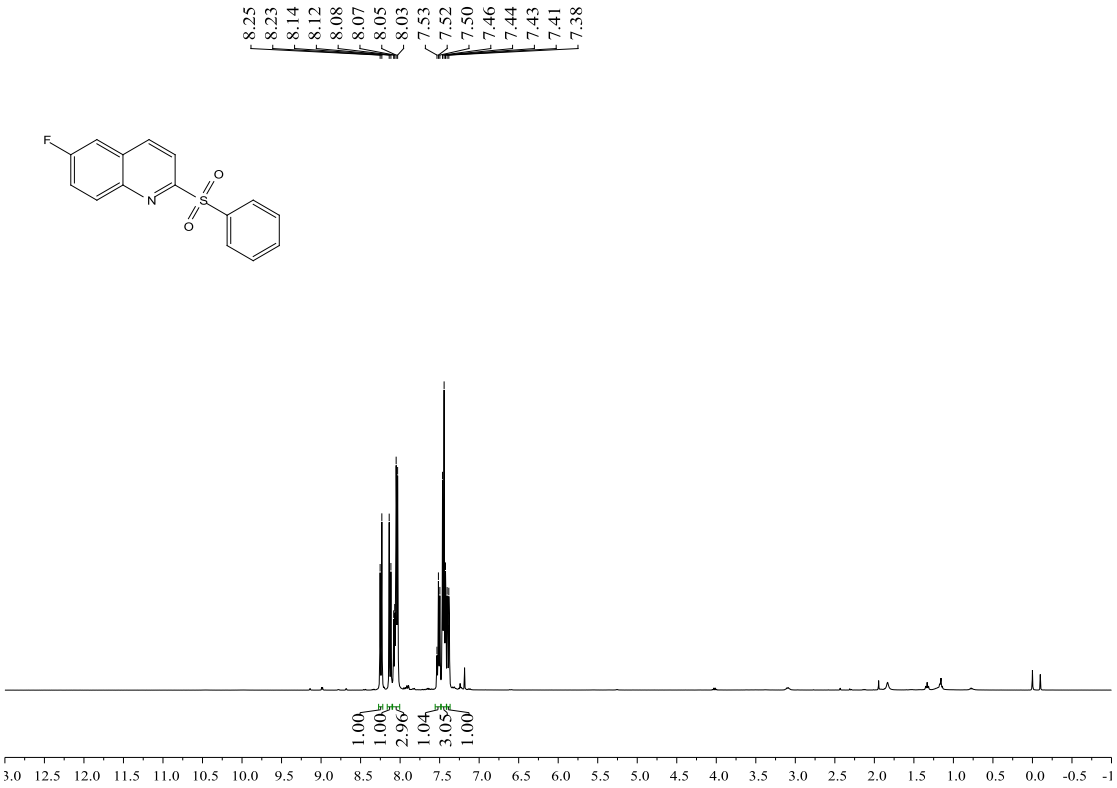


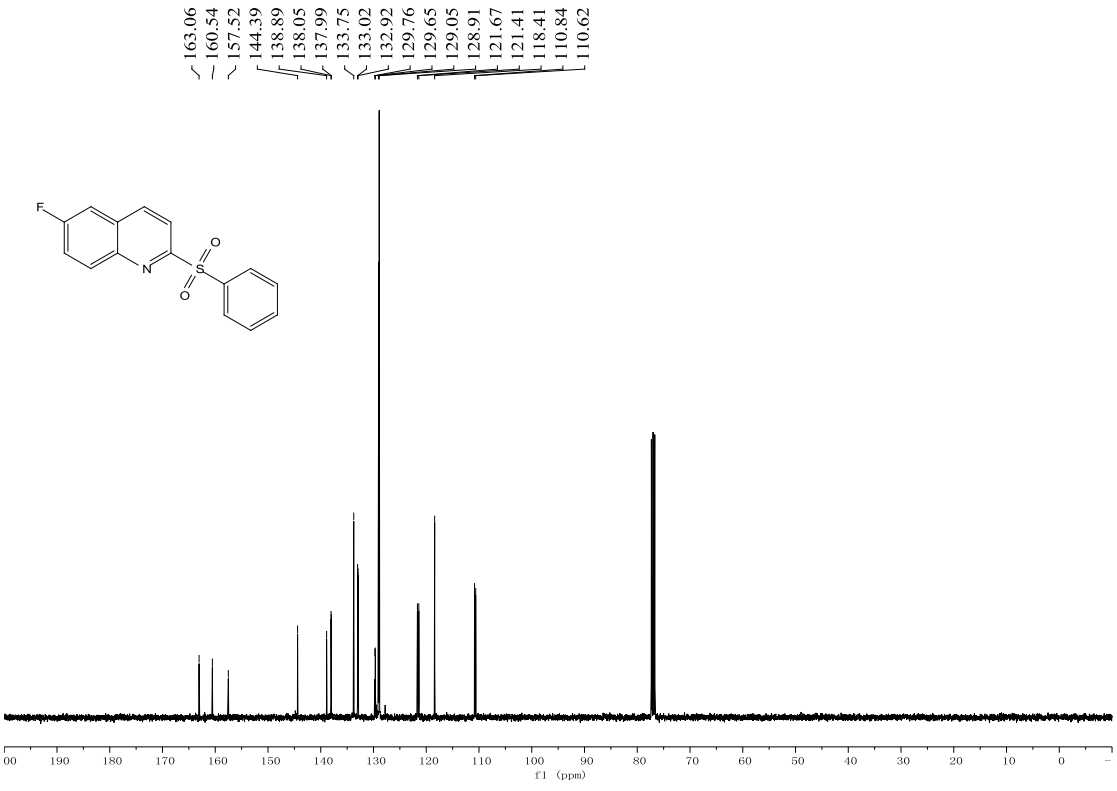


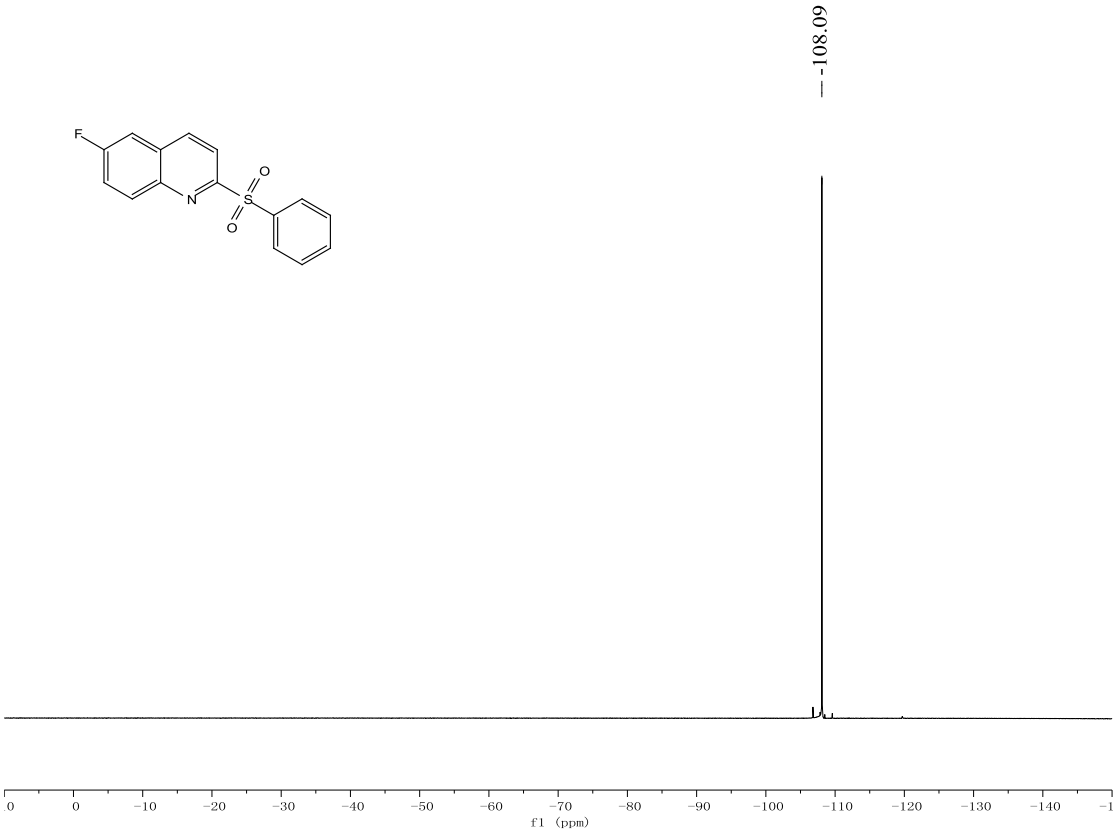




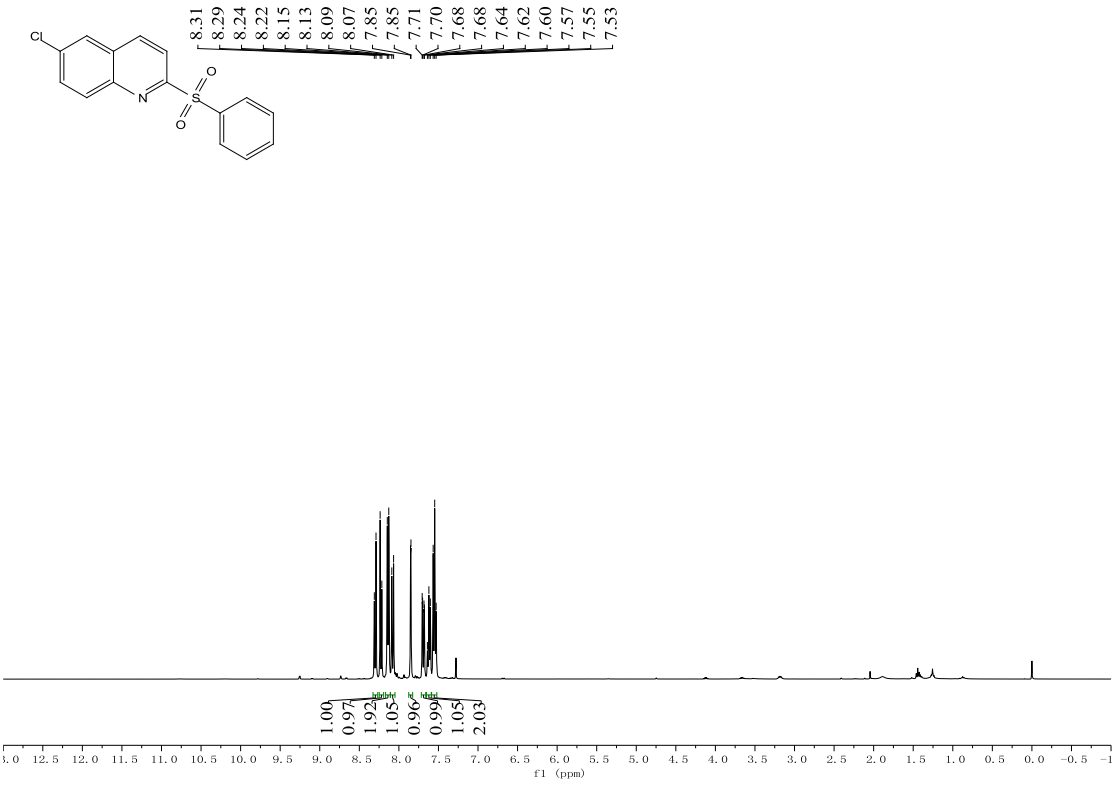
6-Fluoro-2-(phenylsulfonyl)quinolone (4g)

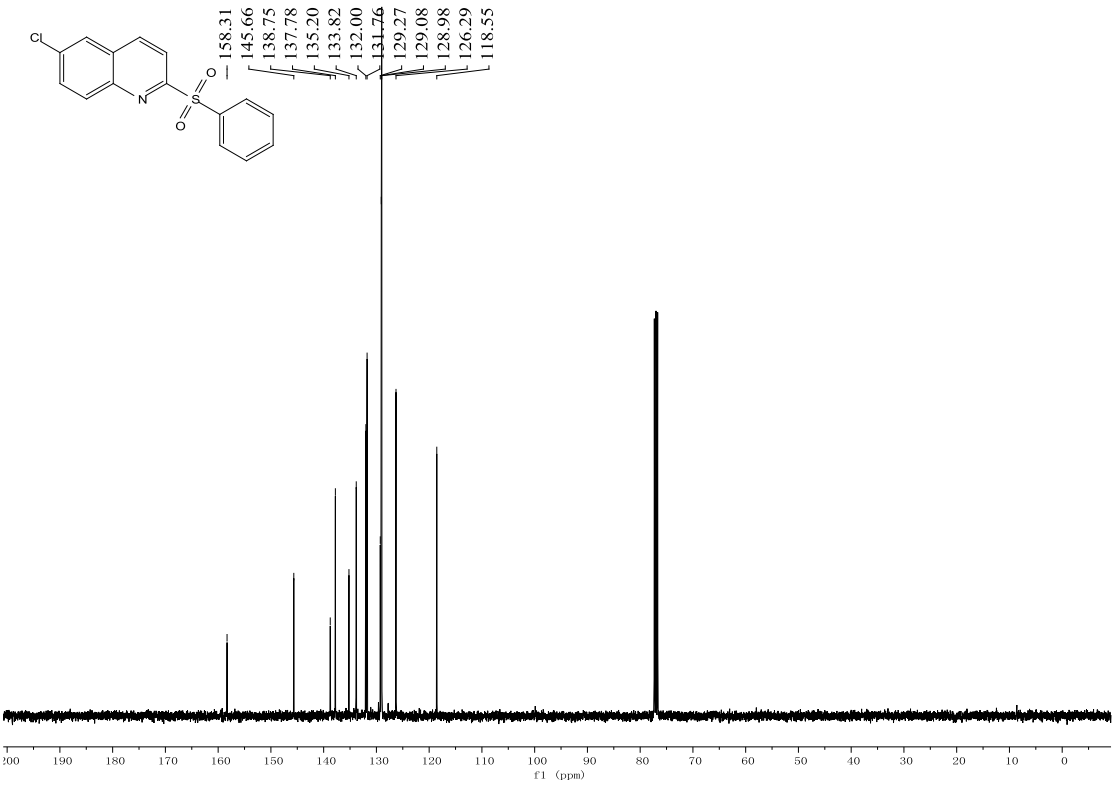




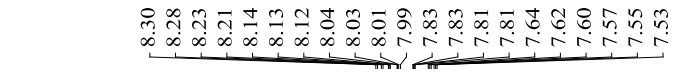

-108.09
F
N
S
O
O
0
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−1
f1 (ppm)

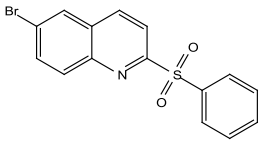
6-Chloro-2-(phenylsulfonyl)quinolone (4h)

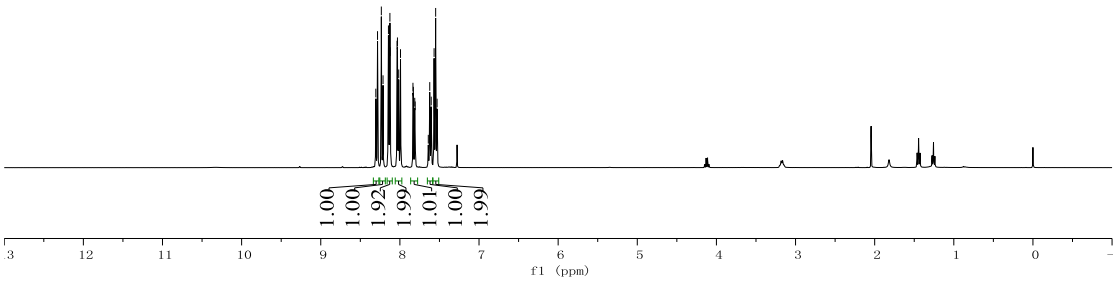


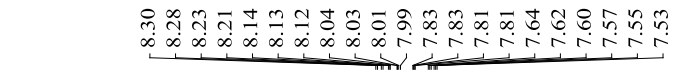


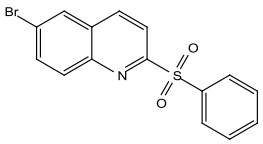
6-Bromo-2-(phenylsulfonyl)quinoline (4i)

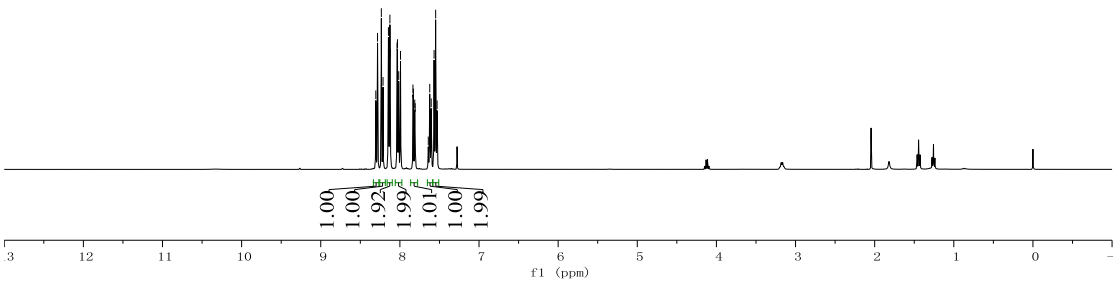




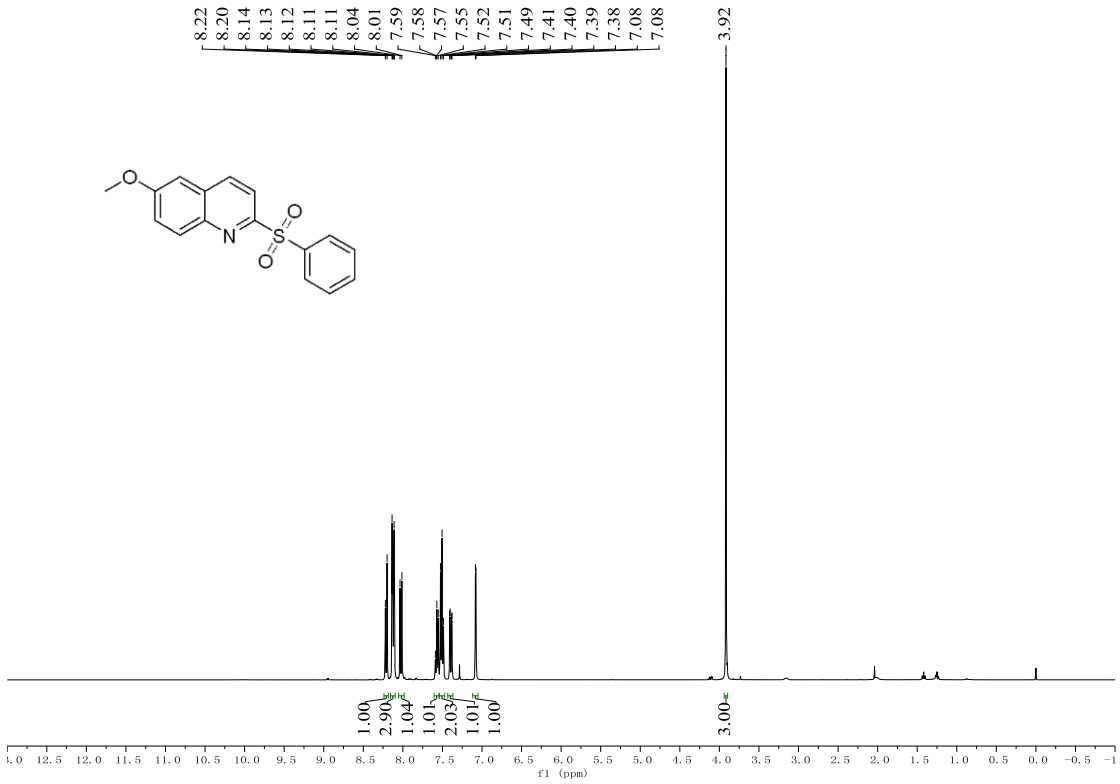


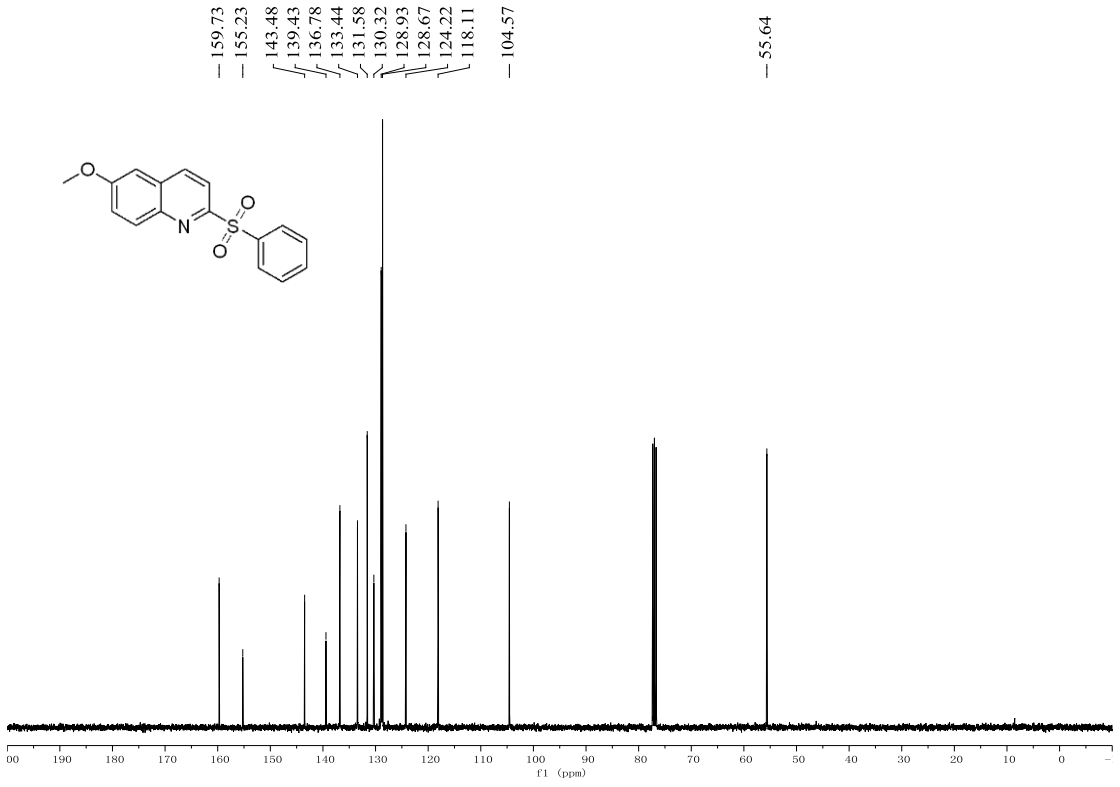




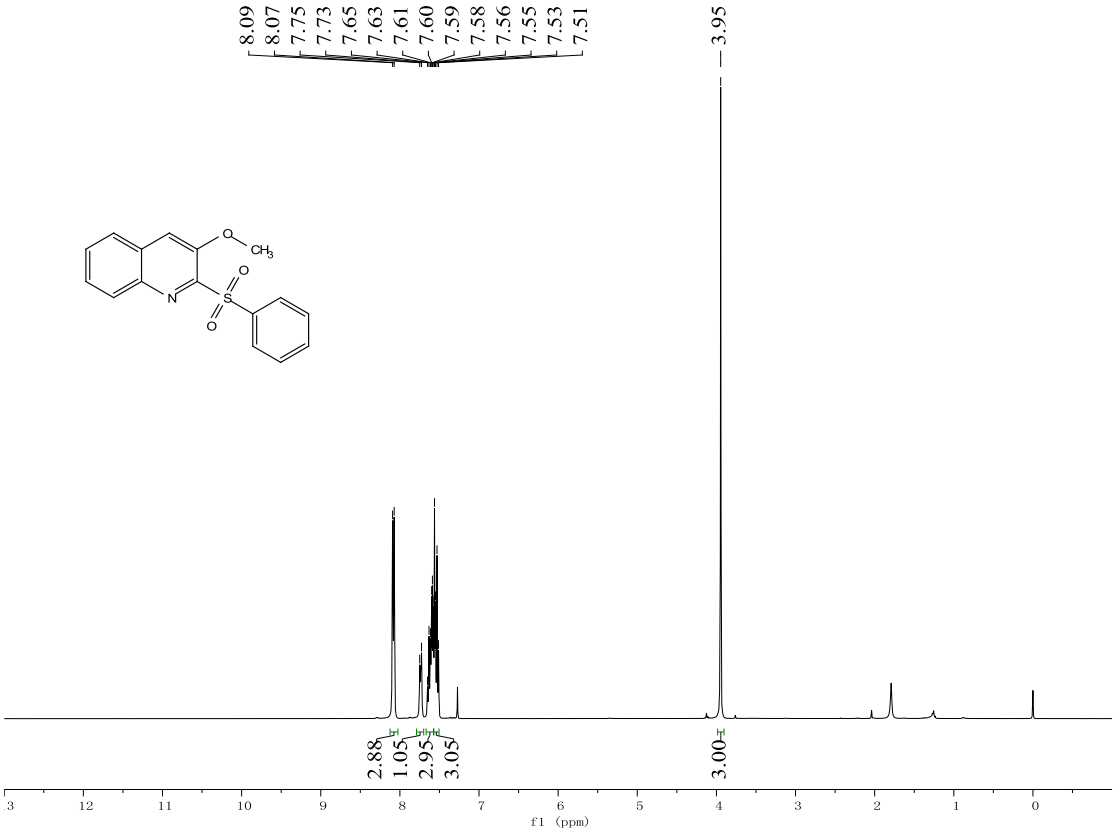


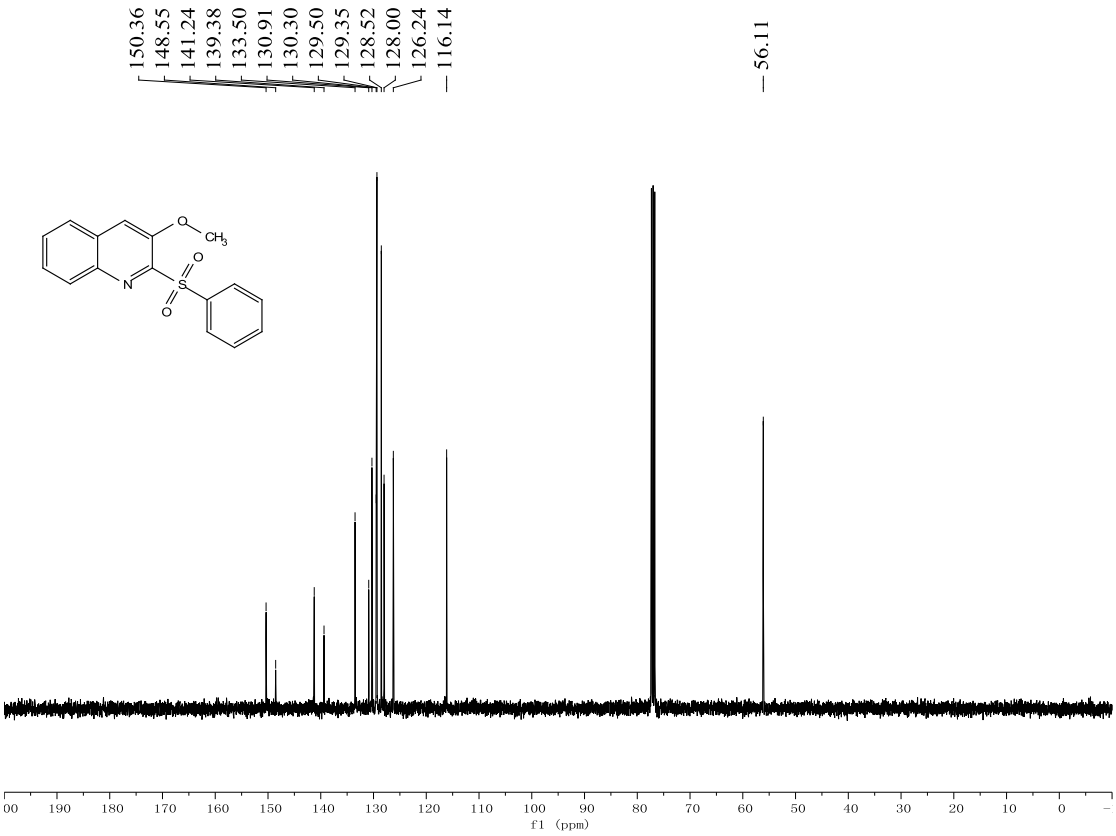
6-Methoxy-2-(phenylsulfonyl)quinolone (4j)





3-Methoxy-2-(phenylsulfonyl)quinoline (4k)





(2-(Phenylsulfonyl)ethene-1,1-diyl)dibenzene (5a)