Supporting Information

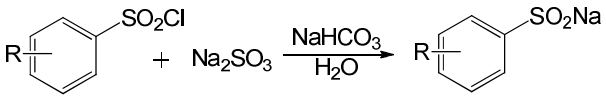
Cu-Catalyzed Deoxygenative C2-Sulfonylation Reaction of Quinoline N-Oxides with Sodium Sulfinate

Bingnan Du, Ping Qian, Yang Wang, Haibo Mei, Jianlin Han* and Yi Pan*

1. General information

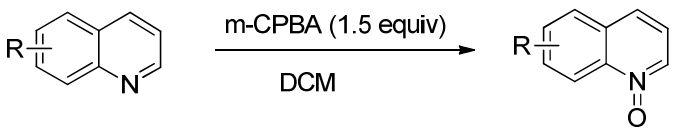
Unless otherwise noted, all of the reagents were purchased from commercial suppliers and used without purification. Melting points were measured on a microscopic apparatus and were uncorrected. High-resolution mass spectrometry (HRMS) was performed on a Q-TOF spectrometer with micromass MS software using electrospray ionization (ESI).^{1}H NMR spectra were recorded on a 400 MHz spectrometer in deuterated chloroform. The chemical shifts (δ) are reported in parts per million relative to tetramethylsilane. The multiplicities of signals are designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants (J) are reported in hertz. ^{13}C NMR spectra were recorded using a 400 MHz spectrometer. The chemical shifts are reported relative to residual $CHCl_3$ (δ C= 77.00 ppm). Sodium sulfinates were prepared according to literature report[1]. Quinoline *N*-oxide derivatives were prepared according to literature report[2].

2. The synthesis of sodium sulfinates



Add sodium sulfite (2.50 g, 20 mmol), sodium bicarbonate (1.68 g, 20 mmol) and 4-methoxybenzenesulphonyl chloride (2.06 g, 10 mmol) to 10 mL H_2O. After stirred at 80 °C for 4 h. Water was removed by rotary evaporator. Then the remaining solid was extracted and recrystallized by ethanol to get a white solid - the required compound. Other sodium sulfinate was prepared through similar method from their corresponding sulphonyl chlorides.

3. The synthesis of quinoline *N*-oxide derivatives



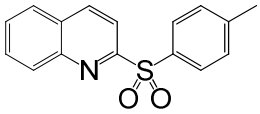
A solution of quinolone (2.0 mmol) in DCM (10 mL) was stirred at 0 °C for 10 min. Then m-CPBA (3-chloroperbenzoic acid, 3.0 mmol） was added to the solution through several times.

The mixture was stirred at 25 °C for 6 h and a saturated aqueous $NaHCO_3$ solution (15 mL) was added. The resulting solution was extracted with DCM (20 mL × 3). Then it was dried by Na_2SO_4 and concentrated under reduced pressure. Next the crude product was purified by column chromatography on silica gel (eluent: petroleum ether/ethylacetate) to afford desired product *N*-oxides.

4. Typical procedure for the Cu-catalyzed sulfonylation reaction

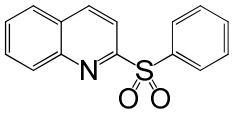
N-oxide **1** (0.25 mmol, 36.2 mg), sodium sulfonate **2** (0.5 mmol, 89 mg), $CuBr_2$ (0.05 mmol, 11.1 mg) and $K_2S_2O_8$ (0.125 mmol, 33.8 mg) were added to a 25 mL schlenk tube under Ar, followed by addition of DCE (1 mL), CH_3NO_2 (3 mL) and H_2O (0.1 mL). The mixture was stirred at 40 ºC for 15 h, then filtered and the solid was washed with ethylacetate. The organic solution was concentrated by rotary evaporator. Next, crude product was purified over a column of silica gel (eluent: petroleum ether/ethylacetate) to afford the desired product **3**.

2-tosylquinoline (3aa)[3]



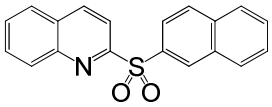
White solid. m.p. 143-144 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.5 Hz, 1H), 8.21 – 8.14 (m, 2H), 8.02 (d, *J* = 8.3 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.77 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.64 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 147.4, 144.8, 138.7, 136.1, 130.9, 130.3, 129.8, 129.1, 129.0, 128.8, 127.7, 117.6, 21.6. IR (neat, cm^{-1}) 1596, 1498, 1322, 1167, 816.

2-(phenylsulfonyl)quinolone (3ab)[3]



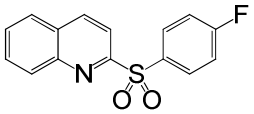
White solid, m.p.164-165 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.5 Hz, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 8.15 (dd, *J* = 11.3, 4.3 Hz, 3H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.78 (ddd, *J* = 8.4, 7.0, 1.3 Hz, 1H), 7.69 – 7.62 (m, 1H), 7.62 – 7.56 (m, 1H), 7.56 – 7.50 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 147.4, 139.1, 138.7, 133.7, 131.0, 130.4, 129.2, 129.1, 129.0, 128.8, 127.7, 117.7. IR (neat, cm^{-1}) 2103, 1576, 1447, 1320, 1162, 1072, 824.

2-(naphthalen-2-ylsulfonyl)quinoline (3ac)[3]



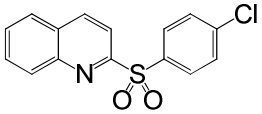
White solid. m.p. 134-136 °C:^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.37 (d, *J* = 8.6 Hz, 1H), 8.26 (d, *J* = 8.6 Hz, 1H), 8.15 (d, *J* = 8.6 Hz, 1H), 8.09 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.94 (d, *J* = 8.7 Hz, 1H), 7.89 – 7.81 (m, 2H), 7.78 – 7.71 (m, 1H), 7.66 – 7.54 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 147.4, 138.7, 136.0, 135.3, 132.1, 131.0, 130.8, 130.3, 129.5, 129.3, 129.2, 128.8, 127.9, 127.7, 127.5, 123.7, 117.8. IR (neat, cm^{-1}) 1578, 1497, 1322, 1168, 1097, 1067, 818.

2-((4-fluorophenyl)sulfonyl)quinoline (3ad)



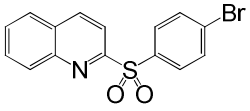
White solid. m.p. 120-122 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.5 Hz, 1H), 8.23 – 8.12 (m, 4H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.80 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.67 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.22 (t, *J* = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 147.4, 138.8, 132.0, 131.9, 131.1, 130.3, 129.3, 128.8, 127.7, 117.4, 116.5, 116.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -103.44. IR (neat, cm^{-1}) 1977, 1584, 1490, 1327, 1245, 1162, 1075, 819. HRMS Calcd for $C_{15}H_{10}FNO_2S$ [M + Na]$^{+}$: m/z 310.0314, found 310.0310.

2-((4-chlorophenyl)sulfonyl)quinoline (3ae)[3]



White solid. m.p. 136-137 °C: ^{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 – 8.05 (m, 2H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.82 – 7.76 (m, 1H), 7.70 – 7.63 (m, 1H), 7.53 – 7.48 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 147.4, 140.5, 138.9, 137.5, 131.1, 130.5, 130.3, 129.4, 129.3, 128.9, 127.7, 117.5. IR (neat, cm^{-1}) 1492, 1323, 1137.

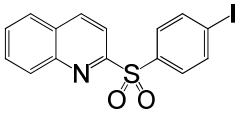
2-((4-bromophenyl)sulfonyl)quinoline (3af)



White solid. m.p. 143-145 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.5 Hz, 1H), 8.20 (d, *J* =

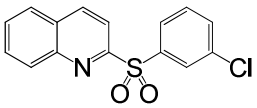
8.5 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.03 – 7.98 (m, 2H), 7.89 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.80 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.67 (tdd, *J* = 5.3, 3.6, 1.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 147.4, 138.9, 138.0, 132.4, 131.1, 130.6, 130.3, 129.3, 129.2, 128.9, 127.7, 117.5. IR (neat, cm^{-1}) 1571, 1496, 1390, 1323, 1162, 1134, 1066,1008, 823. HRMS Calcd for $C_{15}H_{10}BrNO_2S$ [M + Na]$^+$: m/z 369.9513, found 369.9508.

2-((4-iodophenyl)sulfonyl)quinoline (3ag)



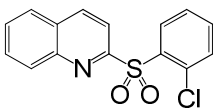
Pale yellow solid. m.p. 148-149 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.5 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.90 (dt, *J* = 6.5, 1.9 Hz, 3H), 7.86 – 7.81 (m, 2H), 7.79 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.71 – 7.64 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 147.4, 138.9, 138.7, 138.3, 131.1, 130.4, 130.3, 129.3, 128.9, 127.7, 117.5, 101.9. IR (neat, cm^{-1}) 2920, 2849, 1646, 1565, 1497, 1380, 1311, 1163, 1070, 1006, 830. HRMS Calcd for $C_{15}H_{10}INO_2S$ [M + Na]$^+$: m/z 417.9375, found 417.9366.

2-((3-chlorophenyl)sulfonyl)quinoline (3ah)



White solid. m.p. 110-112 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.5 Hz, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 8.18 (d, *J* = 8.6 Hz, 1H), 8.13 (t, *J* = 1.8 Hz, 1H), 8.06 – 8.01 (m, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.81 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.68 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.57 (ddd, *J* = 8.0, 2.0, 1.1 Hz, 1H), 7.49 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 147.4, 140.8, 138.9, 135.3, 133.9, 131.2, 130.4, 129.4, 129.0, 128.9, 127.8, 127.2, 117.6. IR (neat, cm^{-1}) 1576, 1497, 1320, 1166, 1072, 837, 791. HRMS Calcd for $C_{15}H_{10}ClNO_2S$ [M + Na]$^+$: m/z 326.0018, found 326.0014.

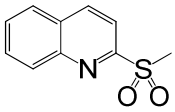
2-((2-chlorophenyl)sulfonyl)quinoline (3ai)



White solid. m.p. 166-167 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 – 8.47 (m, 1H), 8.44 (d, *J* = 8.6 Hz, 1H), 8.33 (d, *J* = 8.6 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.78 – 7.71 (m, 1H), 7.70 – 7.62 (m, 1H), 7.59 – 7.52 (m, 2H), 7.44 – 7.37 (m, 1H). ^{13}C NMR (101 MHz,

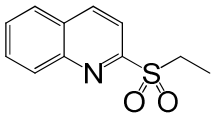
$CDCl_3$) δ 157.3, 147.2, 138.4, 136.7, 134.9, 133.0, 132.1, 131.5, 130.9, 130.2, 129.2, 129.0, 127.8, 127.2, 118.4. IR (neat, cm^{-1}) 1576, 1317, 1138, 1038, 828. HRMS Calcd for $C_{15}H_{10}ClNO_2S$ [M + Na]$^+$: m/z 326.0018, found 326.0022.

2-(methylsulfonyl)quinoline (3aj)[4]



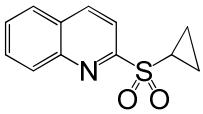
White solid. m.p.100-101 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.4 Hz, 1H), 8.22 (d, *J* = 8.6 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.86 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.72 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 3.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 147.0, 138.9, 131.2, 130.1, 129.2, 129.2, 127.9, 116.2, 39.8.

2-(ethylsulfonyl)quinoline (3ak)[3]



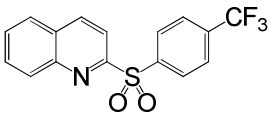
White solid. m.p. 106-107 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.5 Hz, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.86 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.72 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 3.59 (q, *J* = 7.5 Hz, 2H), 1.37 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.42, 147.23, 138.83, 131.22, 130.16, 129.29, 129.16, 127.93, 117.41, 46.39, 6.96. IR (neat, cm^{-1}) 1579, 1497, 1308, 1120, 1098, 833, 769.

2-(cyclopropylsulfonyl)quinoline (3al)



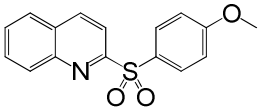
White solid. m.p. 59-61°C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.5 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.77 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.63 (ddd, *J* = 8.1, 7.0, 1.0 Hz, 1H), 2.91 (tt, *J* = 8.0, 4.8 Hz, 1H), 1.38 – 1.31 (m, 2H), 1.07 – 0.99 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 146.3, 137.6, 130.0, 129.2, 128.1, 126.8, 116.2, 28.7, 4.6. IR (neat, cm^{-1}) 1501, 1314, 1164, 1125, 1097, 889, 829. HRMS Calcd for $C_{12}H_{11}NO_2S$ [M + Na]$^+$: m/z 256.0408, found 256.0407.

2-((4-(trifluoromethyl)phenyl)sulfonyl)quinoline (3am)



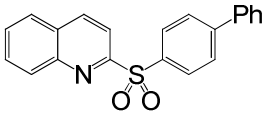
White solid. m.p. 128-129 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.5 Hz, 1H), 8.30 (d, *J* = 8.2 Hz, 2H), 8.25 (d, *J* = 8.5 Hz, 1H), 8.15 (d, *J* = 8.6 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.84 – 7.78 (m, 3H), 7.69 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 147.4, 142.6, 139.0, 131.3, 130.3, 129.7, 129.5, 129.0, 127.8, 126.2, 126.2, 126.1, 126.1, 124.5, 121.8, 117.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.24. IR (neat, cm^{-1}) 1973, 1575, 1495, 1404, 1319, 1166, 1061, 1014, 830. HRMS Calcd for $C_{16}H_{10}F_3NO_2S$ $[M + Na]^+$: m/z 360.0282, found 360.0277.

2-((4-methoxyphenyl)sulfonyl)quinoline (3an)



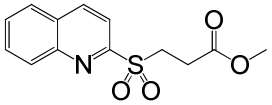
White solid. m.p.129-131 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.5 Hz, 1H), 8.17 (dd, *J* = 8.5, 4.8 Hz, 2H), 8.10 – 8.04 (m, 2H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.78 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.64 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.03 – 6.96 (m, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 158.6, 147.4, 138.7, 131.2, 130.9, 130.4, 130.3, 129.0, 128.7, 127.7, 117.5, 114.4, 55.6. IR (neat, cm^{-1}) 2919, 1577, 1497, 1318, 1255, 1137, 1076, 1022, 832. HRMS Calcd for $C_{16}H_{13}NO_3S$ $[M + Na]^+$: m/z 322.0514, found 322.0516.

2-([1,1'-biphenyl]-4-ylsulfonyl)quinoline (3ao)



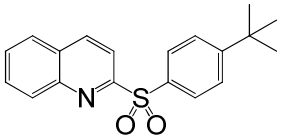
White solid. m.p.176-177 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.5 Hz, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 8.23 – 8.17 (m, 3H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.79 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.76 – 7.71 (m, 2H), 7.66 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.56 (dt, *J* = 3.4, 2.0 Hz, 2H), 7.48 – 7.42 (m, 2H), 7.40 (dt, *J* = 9.8, 4.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 147.5, 146.7, 139.1, 138.8, 137.6, 131.0, 130.4, 129.6, 129.2, 129.0, 128.8, 128.6, 127.7, 127.4, 117.7. IR (neat, cm^{-1}) 1591, 1497, 1325, 1167, 1134, 1077, 828. HRMS Calcd for $C_{21}H_{15}NO_2S$ $[M + Na]^+$: m/z 368.0721, found 368.0722.

methyl 3-(quinolin-2-ylsulfonyl)propanoate (3ap)



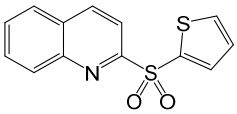
Pale yellow solid. m.p. 63-65 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.5 Hz, 1H), 8.22 (d, *J* = 8.6 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.87 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.73 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 3.93 – 3.86 (m, 2H), 3.67 (s, 3H), 2.96 – 2.90 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 156.4, 147.1, 139.0, 131.3, 130.1, 129.4, 129.2, 127.9, 117.0, 52.3, 47.5, 27.5. IR (neat, cm^{-1}) 3372, 2976, 1653, 1315, 1086, 1044, 878. HRMS Calcd for $C_{13}H_{13}NO_4S$ $[M + Na]^+$: m/z 302.0463, found 302.0463.

2-((4-(tert-butyl)phenyl)sulfonyl)quinoline (3aq)[3]



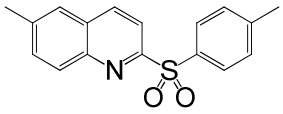
White solid. m.p.197-198 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.5 Hz, 1H), 8.21 (d, *J* = 8.5 Hz, 2H), 8.09 – 8.03 (m, 2H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.79 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.65 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.57 – 7.51 (m, 2H), 1.30 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 157.6, 147.4, 138.7, 136.1, 130.9, 130.4, 129.1, 128.8, 128.8, 127.7, 126.2, 117.8, 35.2, 31.0. IR (neat, cm^{-1}) 1578, 1322, 1168, 1077, 828.

2-(thiophen-2-ylsulfonyl)quinolone (3ar)



White solid. m.p 150 –151 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.6 Hz, 1H), 8.22 (dd, *J* = 8.5, 1.9 Hz, 2H), 7.95 – 7.88 (m, 2H), 7.85 – 7.79 (m, 1H), 7.73 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.17 – 7.10 (m, 1H). ^{13}C NMR (101 MHz, CDCl3) δ 157.9, 147.4, 139.7, 138.9,135.3, 135.2, 131.1, 130.4, 129.3, 128.9, 127.8, 127.7, 117.3. IR (neat, cm^{-1}) 1575, 1399, 1322, 1128, 876, 679.

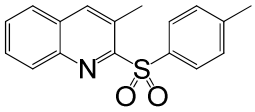
6-methyl-2-tosylquinoline (3ba)[3]



White solid. m.p. 129-130 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.5 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 8.03 – 7.99 (m, 2H), 7.61 – 7.56 (m, 2H), 7.31 (d, *J* = 8.0

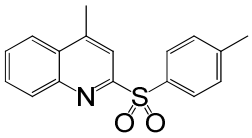
Hz, 2H), 2.53 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 146.1, 144.7, 139.6, 137.8, 136.3, 133.3, 129.9, 129.7, 128.9, 128.9, 126.4, 117.7, 21.8, 21.6. IR (neat, cm^{-1}) 1594, 1497, 1318, 1161, 1134, 1076, 795.

3-methyl-2-tosylquinoline (3ca)



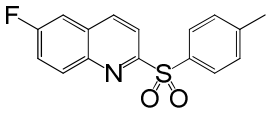
White solid. m.p. 113-114 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.93 (t, *J* = 9.2 Hz, 3H), 7.77 – 7.72 (m, 1H), 7.66 – 7.60 (m, 1H), 7.60 – 7.54 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.85 (d, *J* = 0.6 Hz, 3H), 2.45 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 144.7, 144.5, 139.8, 135.8, 129.9, 129.7, 129.4, 129.3, 129.1, 128.9, 128.5, 126.7, 21.7, 18.8. IR (neat, cm^{-1}) 2918, 2828, 1597, 1491, 1312, 1146, 1088, 1040, 906, 810. HRMS Calcd for $C_{17}H_{15}NO_2S$ $[M + Na]^+$: m/z 320.0721, found 320.0730.

4-methyl-2-tosylquinoline (3da)[3]



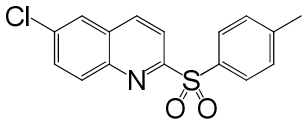
White solid. m.p.152-153 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.4 Hz, 1H), 8.05 – 7.96 (m, 4H), 7.74 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.64 (ddd, *J* = 8.2, 6.9, 1.1 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 2.76 (d, *J* = 0.5 Hz, 3H), 2.38 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 147.9, 147.2, 144.7, 136.3, 131.0, 130.5, 129.7, 129.0, 128.8, 128.7, 123.8, 118.0, 21.6, 19.1. IR (neat, cm^{-1}) 1577, 1318, 1139, 1080, 861.

6-fluoro-2-tosylquinoline (3ea)



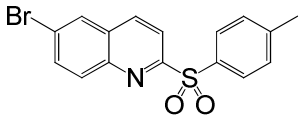
White solid. m.p. 123-125 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.6 Hz, 1H), 8.23 – 8.14 (m, 2H), 8.01 (d, *J* = 8.3 Hz, 2H), 7.58 – 7.51 (m, 1H), 7.49 (dd, *J* = 8.5, 2.7 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 160.6, 157.9, 157.8, 144.9, 144.5, 138.1, 138.0, 135.9, 133.1, 133.0, 129.8, 129.7, 129.0, 121.7, 121.4, 118.5, 110.9, 110.7, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.36. IR (neat, cm^{-1}) 1627, 1498, 1315, 1228, 1161, 1161, 1075, 925, 870, 802. HRMS Calcd for $C_{16}H_{12}FNO_2S$ $[M + Na]^+$: m/z 324.0470, found 324.0471.

6-chloro-2-tosylquinoline (3fa)



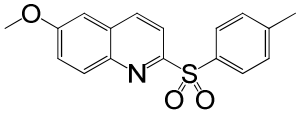
White solid. m.p. 165-166 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.6 Hz, 1H), 8.21 (d, *J* = 8.6 Hz, 1H), 8.09 (d, *J* = 9.1 Hz, 1H), 8.05 – 7.98 (m, 2H), 7.85 (d, *J* = 2.2 Hz, 1H), 7.69 (dd, *J* = 9.1, 2.3 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 145.7, 145.0, 137.8, 135.8, 135.2, 132.0, 131.8, 129.8, 129.3, 129.1, 126.3, 118.6, 21.6. IR (neat, cm^{-1}) 1596, 1486, 1321, 1165, 1134, 876. HRMS Calcd for $C_{16}H_{12}ClNO_2S$ $[M + Na]^+$: m/z 340.0175, found 340.0171.

6-bromo-2-tosylquinoline (3ga)



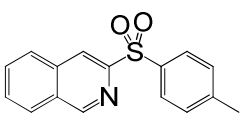
White solid. m.p. 179-180 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.5 Hz, 1H), 8.21 (d, *J* = 8.6 Hz, 1H), 8.06 – 7.98 (m, 4H), 7.84 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 145.9, 145.0, 137.6, 135.8, 134.5, 131.9, 129.8, 129.7, 129.1, 123.5, 118.6, 21.7. IR (neat, cm^{-1}) 1481, 1314, 1162, 1104, 879, 826. HRMS Calcd for $C_{16}H_{12}BrNO_2S$ $[M + Na]^+$: m/z 383.9670, found 383.9665.

6-methoxy-2-tosylquinoline (3ha)



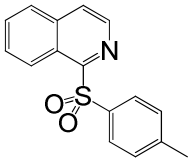
Pale yellow solid. m.p. 162-164 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.5 Hz, 1H), 8.12 (d, *J* = 8.6 Hz, 1H), 8.04 (d, *J* = 9.3 Hz, 1H), 8.02 – 7.97 (m, 2H), 7.40 (dd, *J* = 9.3, 2.8 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 2.7 Hz, 1H), 3.93 (s, 3H), 2.38 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 155.6, 144.6, 143.6, 136.8, 136.5, 131.7, 130.4, 129.7, 128.8, 124.2, 118.2, 104.6, 55.7, 21.6. IR (neat, cm^{-1}) 1617, 1497, 1318, 1161, 1075, 803. HRMS Calcd for $C_{17}H_{15}NO_3S$ $[M + Na]^+$: m/z 336.0670, found 336.0675.

3-tosylisoquinoline (3ia-1)[3]



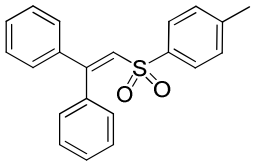
White solid. m.p.179-180 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (ddd, *J* = 4.9, 2.5, 1.4 Hz, 1H), 8.36 (d, *J* = 5.4 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.85 – 7.80 (m, 1H), 7.73 – 7.65 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 144.7, 140.5, 137.7, 136.0, 131.1, 129.6, 129.2, 129.2, 127.5, 125.4, 125.0, 124.3, 21.7. IR (neat, cm^{-1}) 1593, 1495, 1388, 1288, 1144, 1093, 1057, 904, 813.

1-tosylisoquinoline (3ia-2)[3]



White solid. m.p. 183-184 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 8.57 (s, 1H), 7.97 – 7.90 (m, 4H), 7.76 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1H), 7.69 (ddd, *J* = 8.0, 7.0, 1.2 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.31 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 152.4, 144.6, 136.4, 135.3, 131.96, 130.2, 129.7, 129.4, 128.8, 128.2, 127.8, 120.9, 21.6. IR (neat, cm^{-1}) 2848, 1629, 1548, 1475, 1343, 1227, 1033, 896, 787.

(2-tosylethene-1,1-diyl)dibenzene (4)[5]



Pale yellow solid. m.p 92−94 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 2H), 7.40 – 7.33 (m, 2H), 7.33 – 7.27 (m, 4H), 7.23 – 7.18 (m, 2H), 7.17 – 7.12 (m, 2H), 7.12 – 7.07 (m, 2H), 6.99 (s, 1H), 2.38 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 143.7, 139.2, 138.6, 135.5, 130.2, 129.7, 129.3, 128.9, 128.8, 128.5, 128.2, 127.8, 127.7, 21.5. IR (neat, cm^{-1}) 3036, 1592, 1491, 1300, 1134, 758.

[1] L. K. Liu, Y. Chi, K. Y. Jen, *J. Org. Chem.* **1980**, 45,406−410.

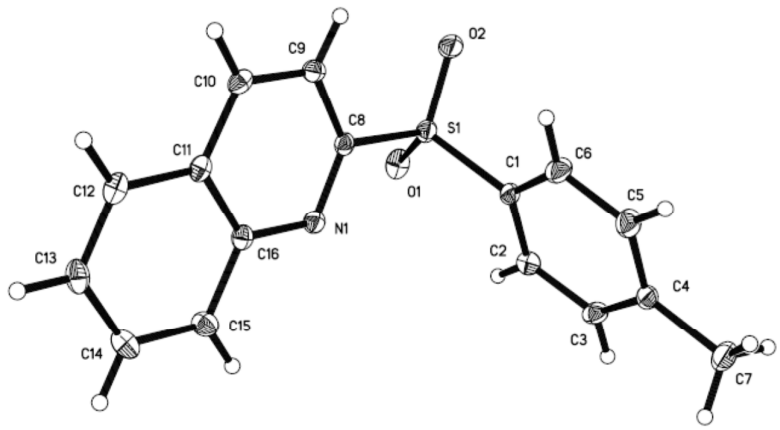
[2] G. Li, C. Q. Jia, K. Sun, *Org. Lett.***2013**, 15, 5198−5201.

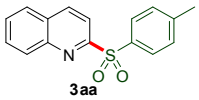
[3] K. Sun, X. L. Chen, X. Li, L. B. Qu, W. Z. Bi, X. Chen, H. Li. Ma, S. T. Zhang, B. W. Han, Y. F. Zhao, C. J. Li, *Chem. Commun.***2015**, 51, 12111−12114.

[4] C. Venkatesh, G. S. M. Sundaram, H. Ila, H. Junjappa, *J. Org. Chem.* **2006**, 71. 1280–1283.

[5] S Mao, Y. R. Gao, X. Q. Zhu, D. D. Guo, Y. Q. Wang, *Org. Lett.* **2015**, 17, 1692–1695.

5. X-ray analysis of 3aa



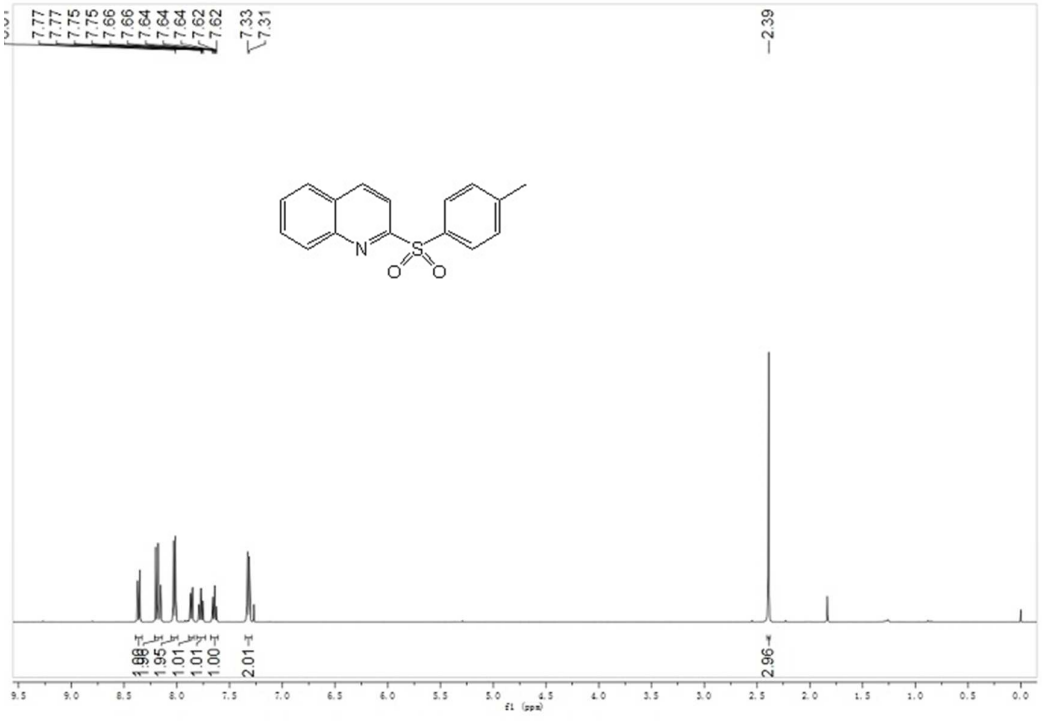


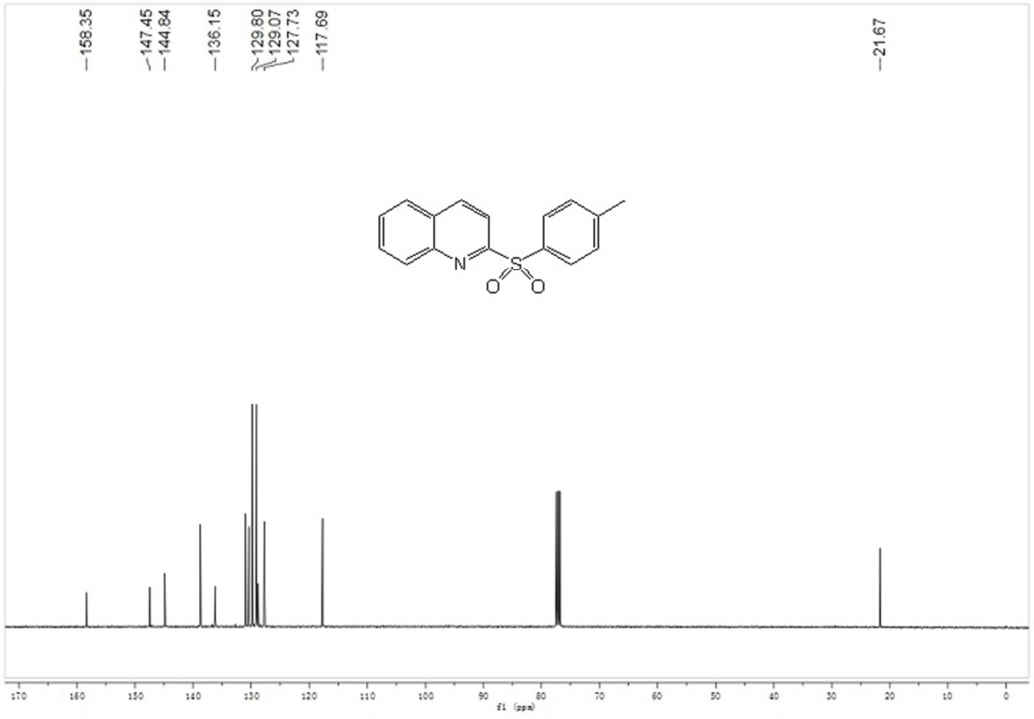
3aa

(CCDC 1480646)

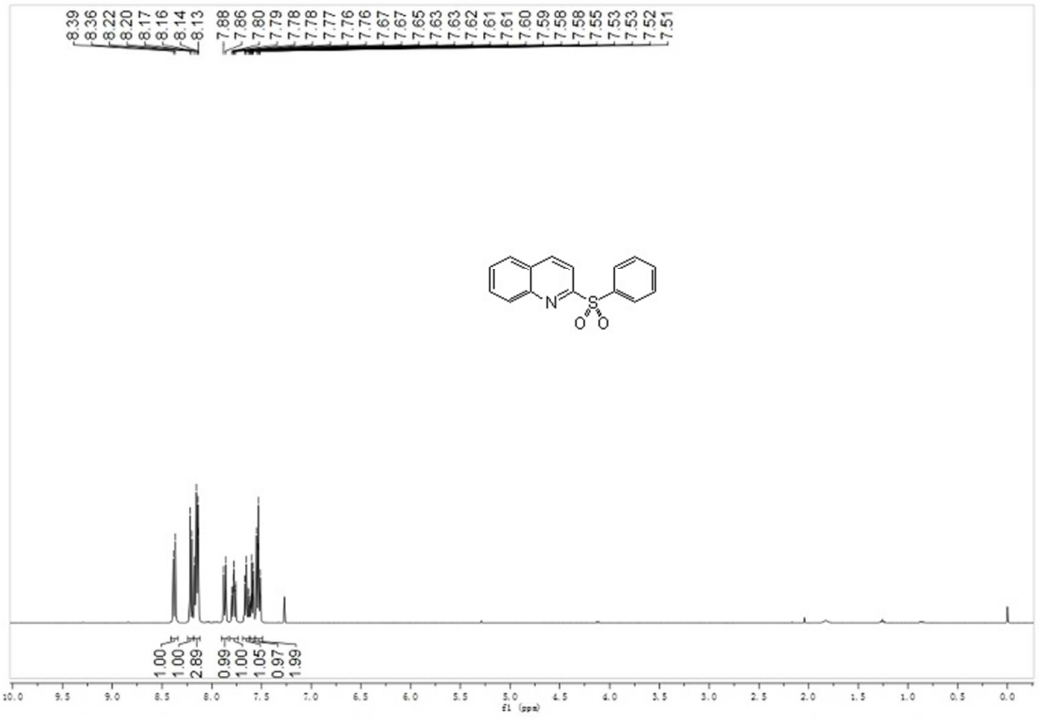
6. ^{1}H NMR and ^{13}C NMR spectra of 3 and 4

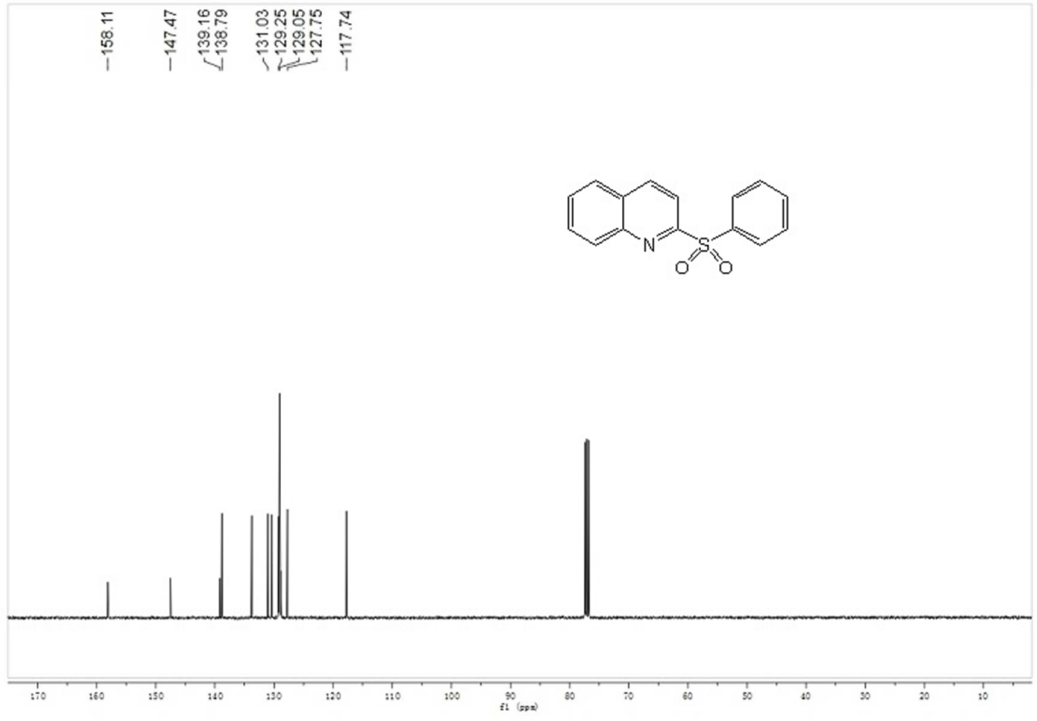
2-tosylquinoline (3aa)



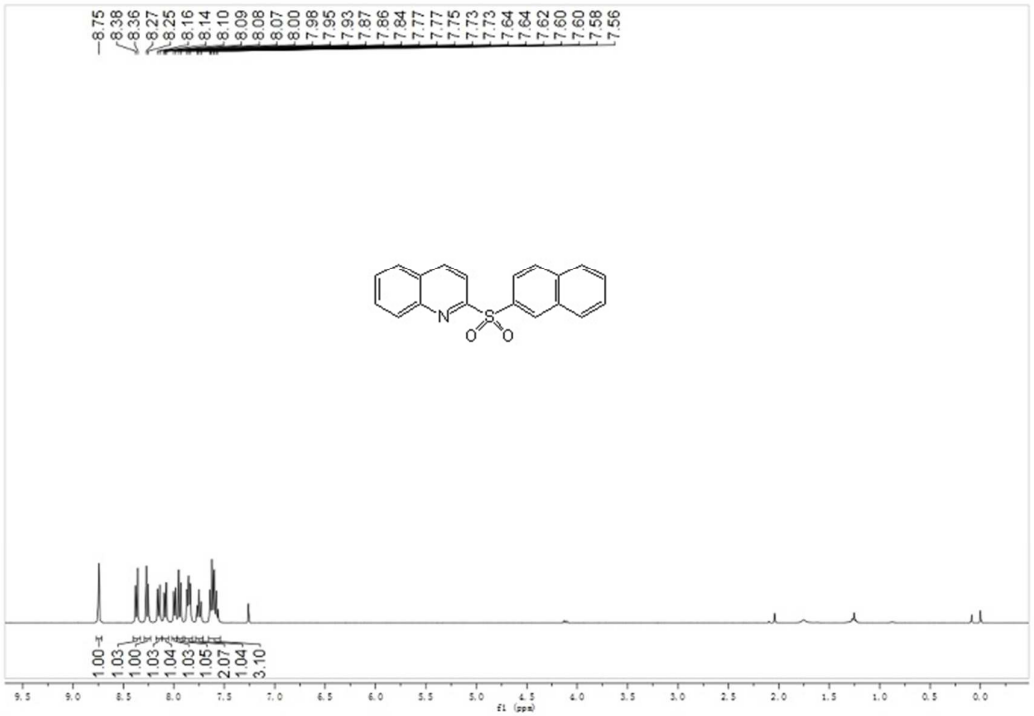


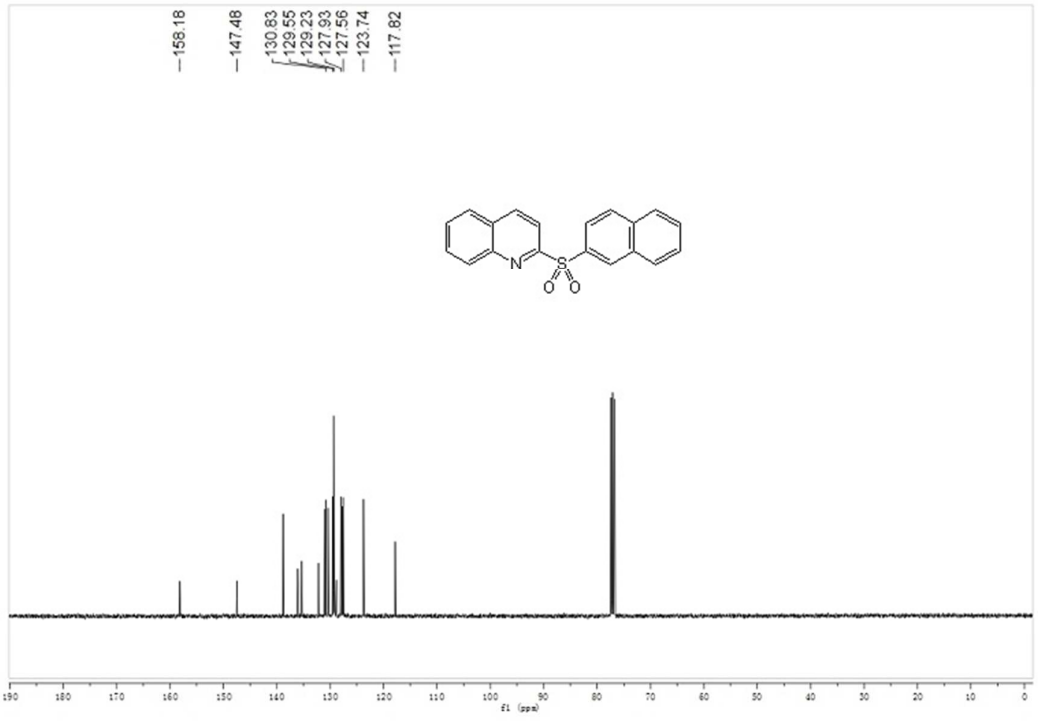
2-(phenylsulfonyl)quinolone (3ab)



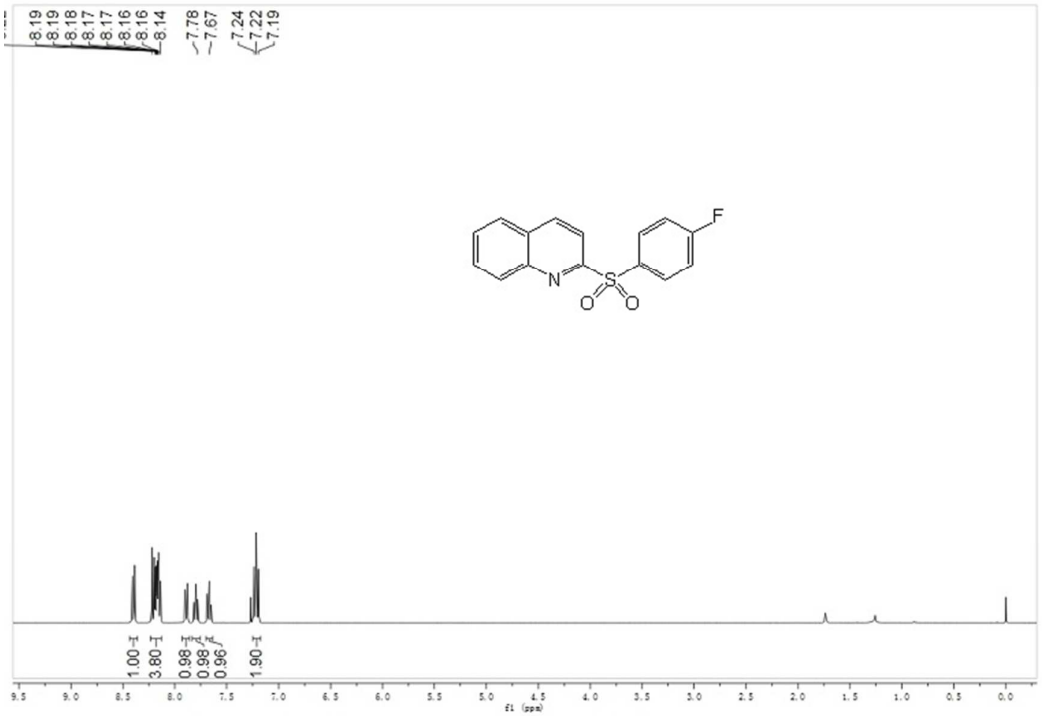


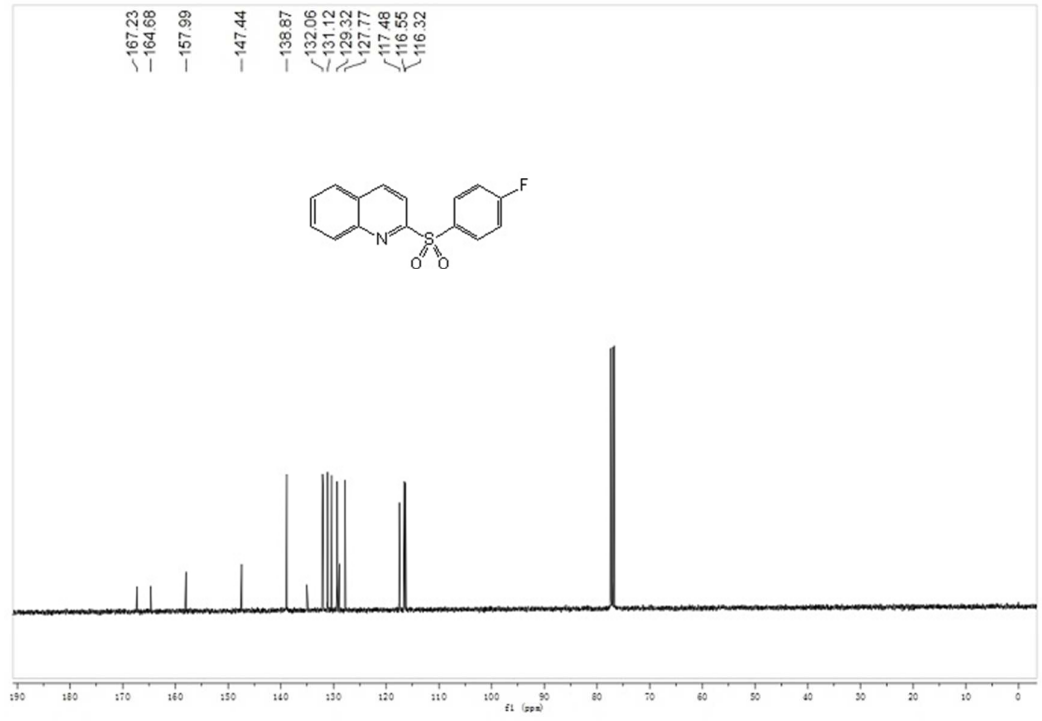
2-(naphthalen-2-ylsulfonyl)quinoline (3ac)



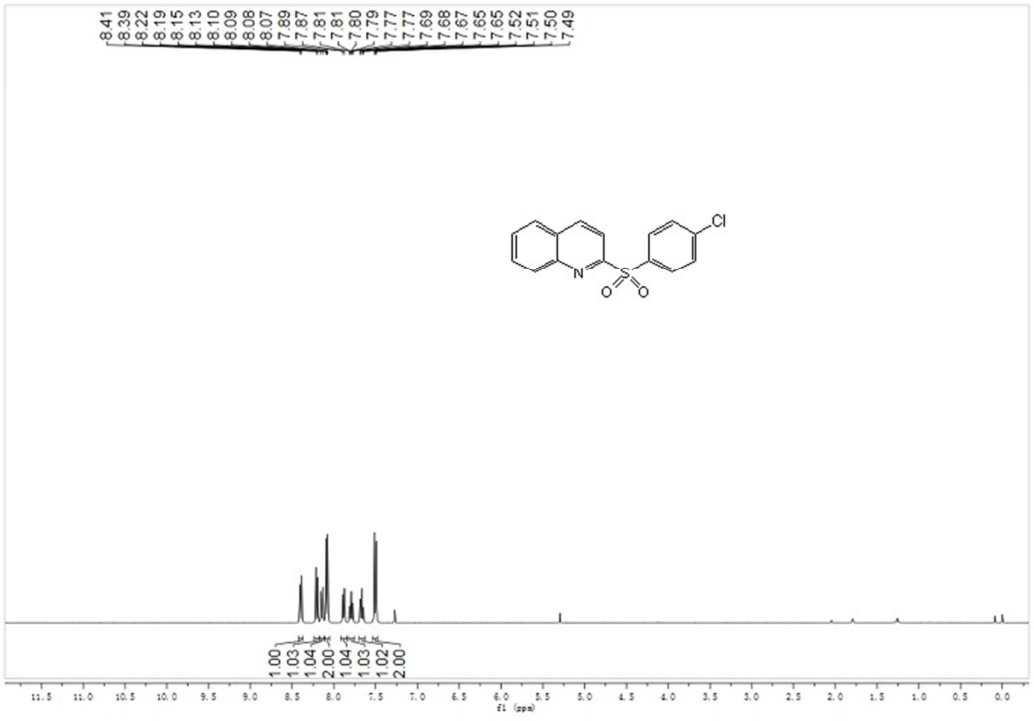


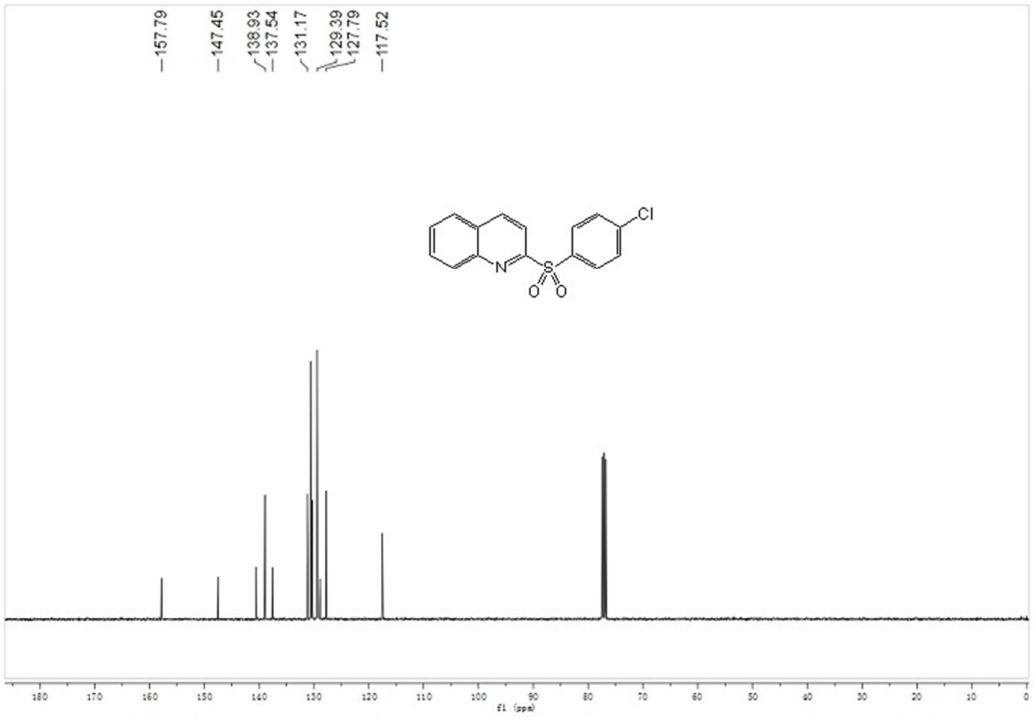
2-((4-fluorophenyl)sulfonyl)quinoline (3ad)



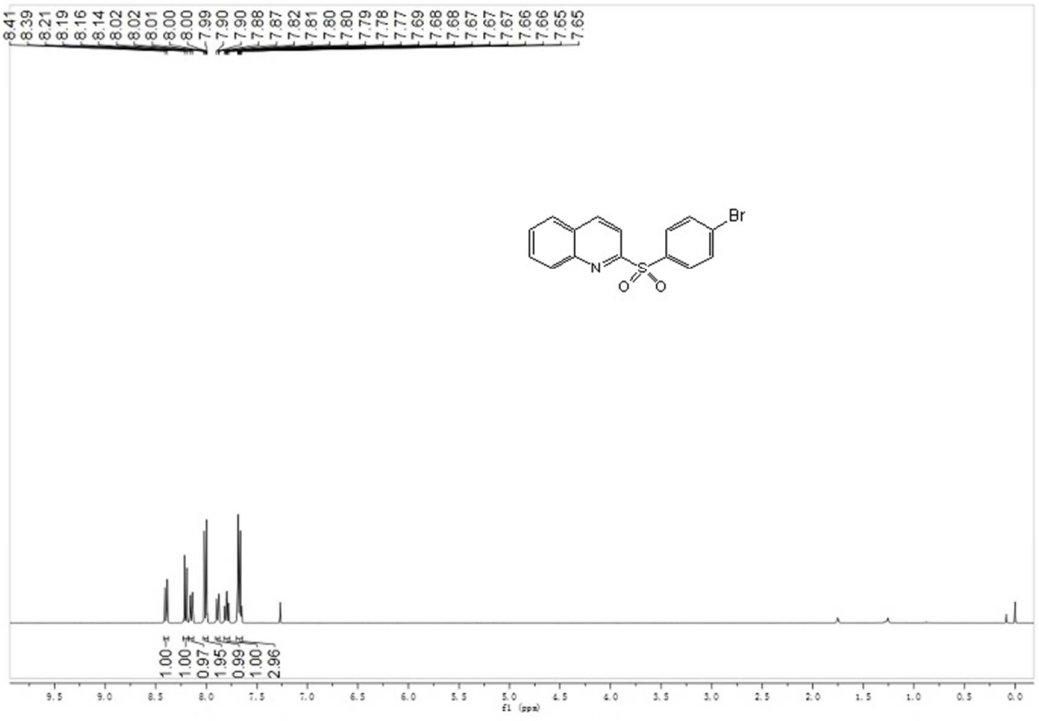


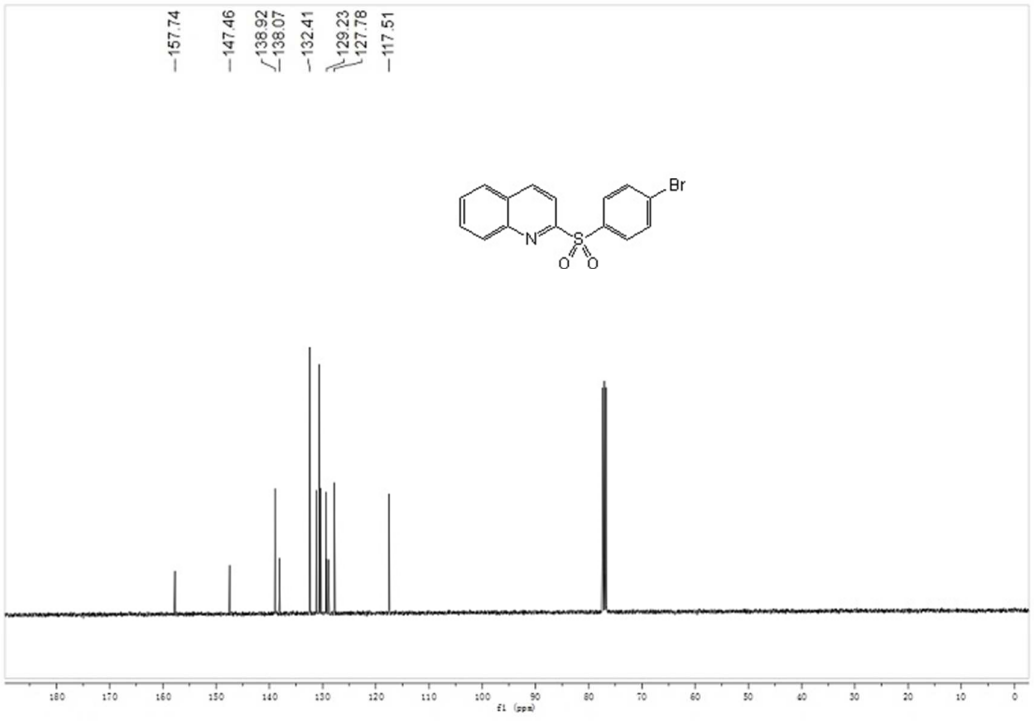
2-((4-chlorophenyl)sulfonyl)quinoline (3ae)



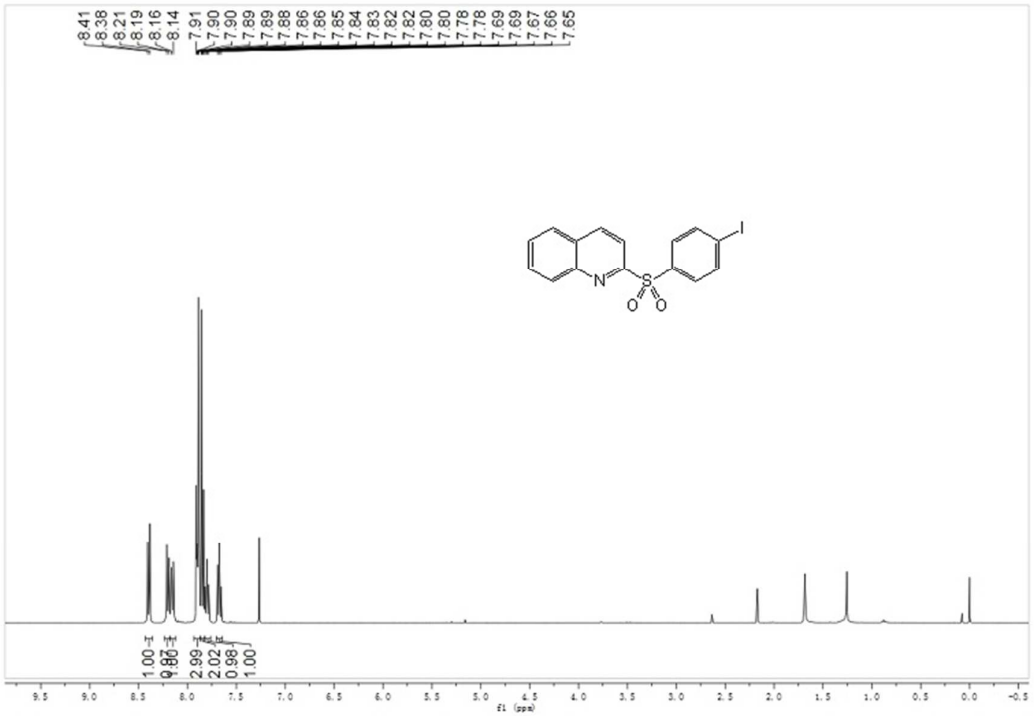


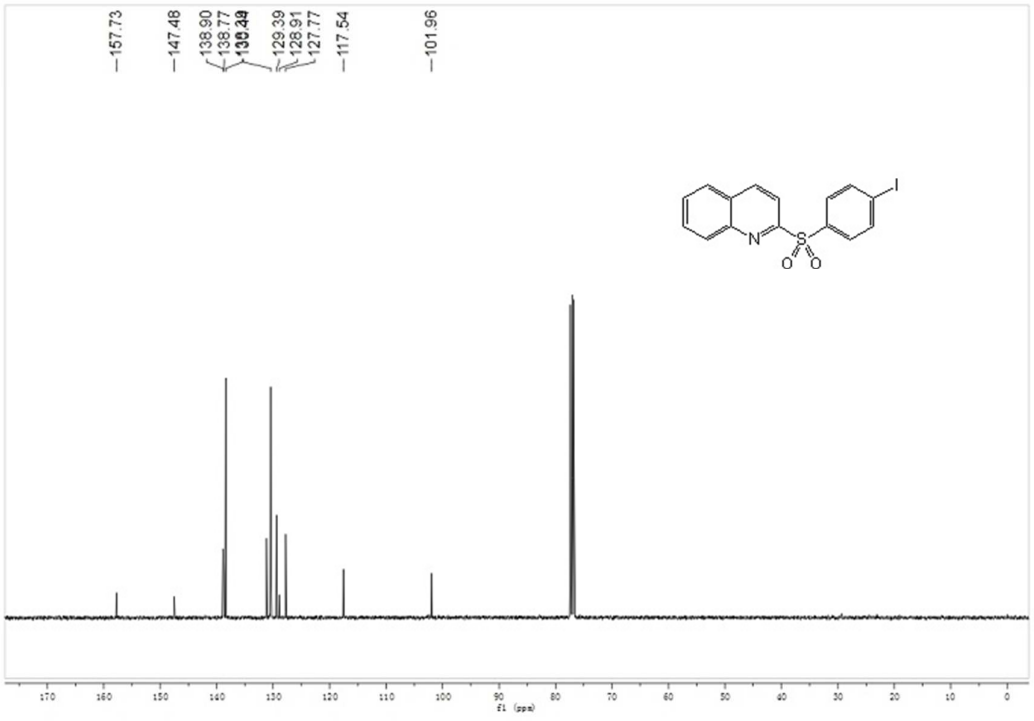
2-((4-bromophenyl)sulfonyl)quinoline (3af)



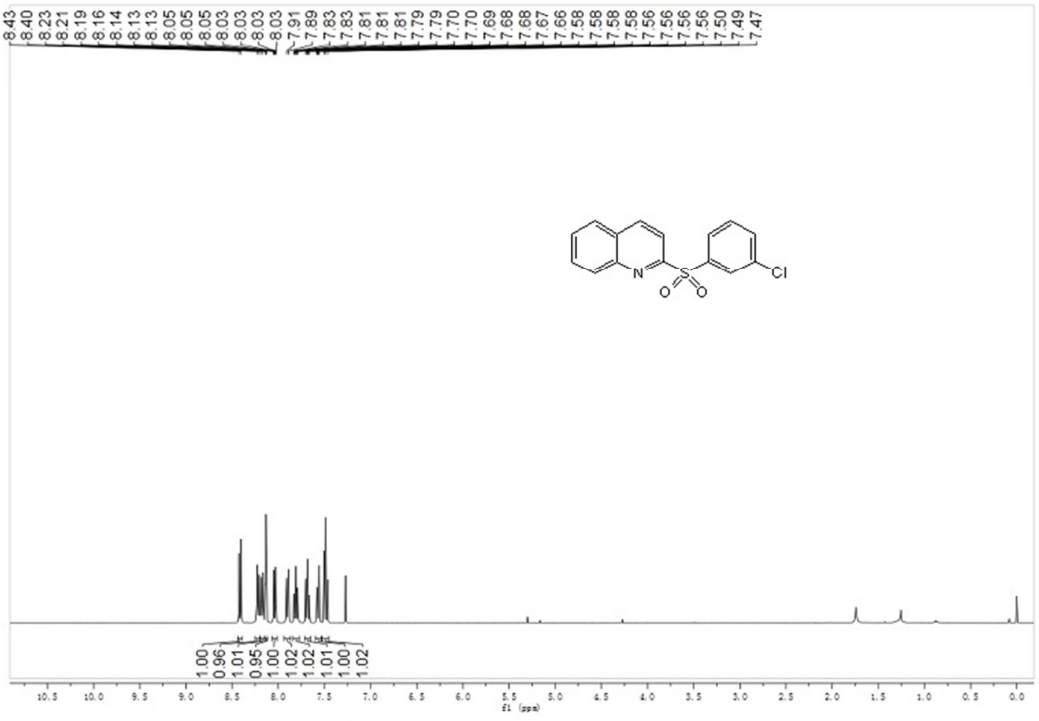


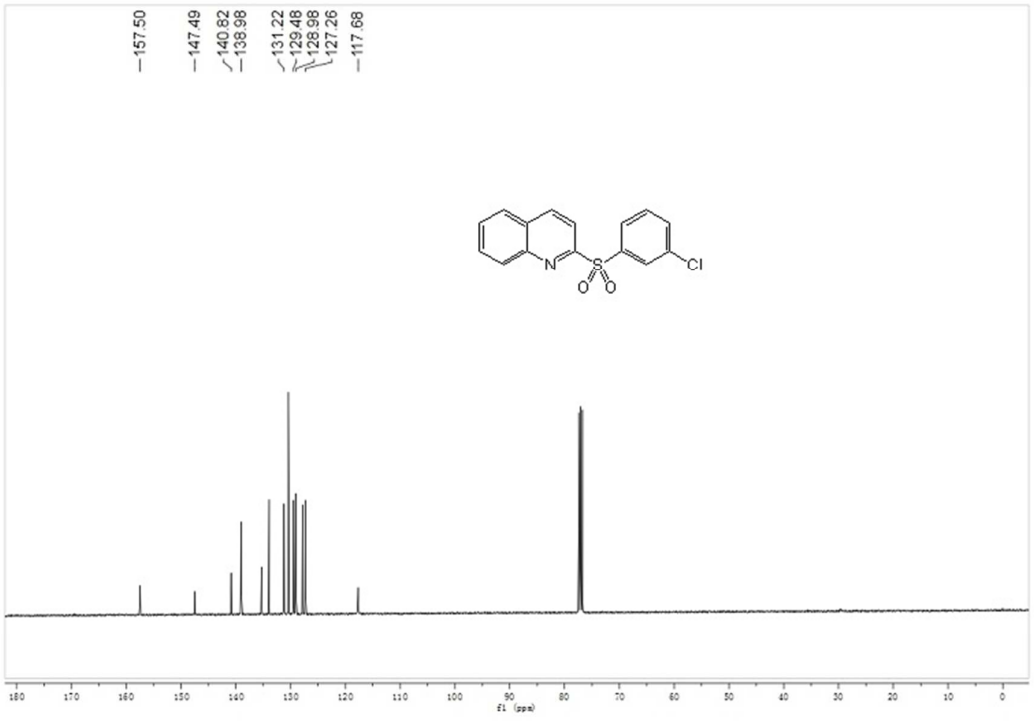
2-((4-iodophenyl)sulfonyl)quinoline (3ag)



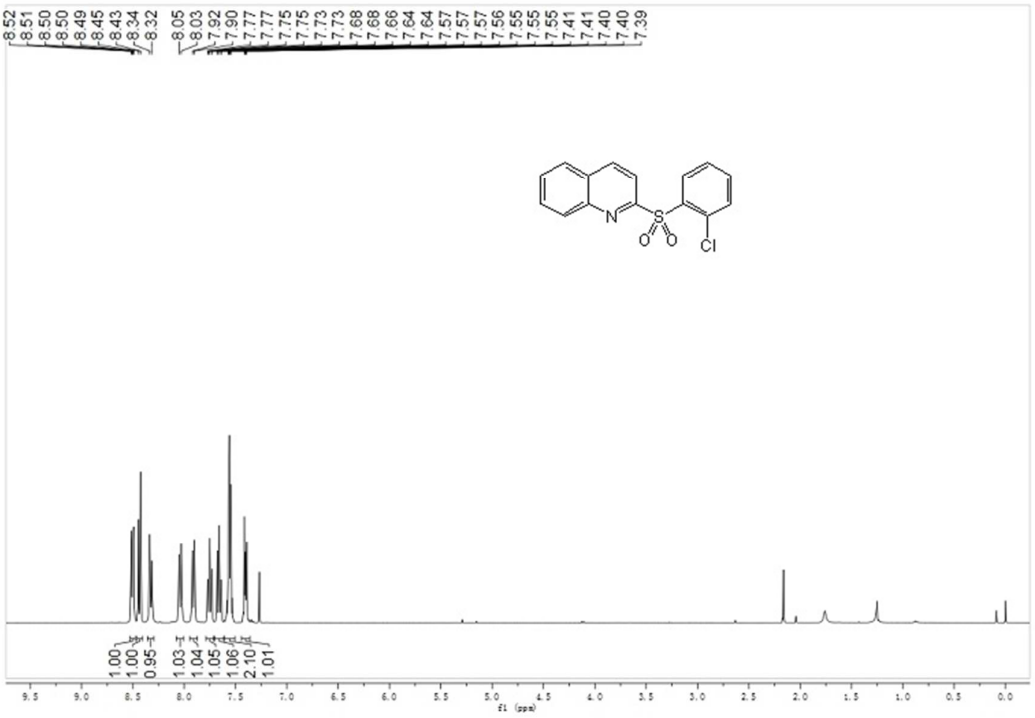


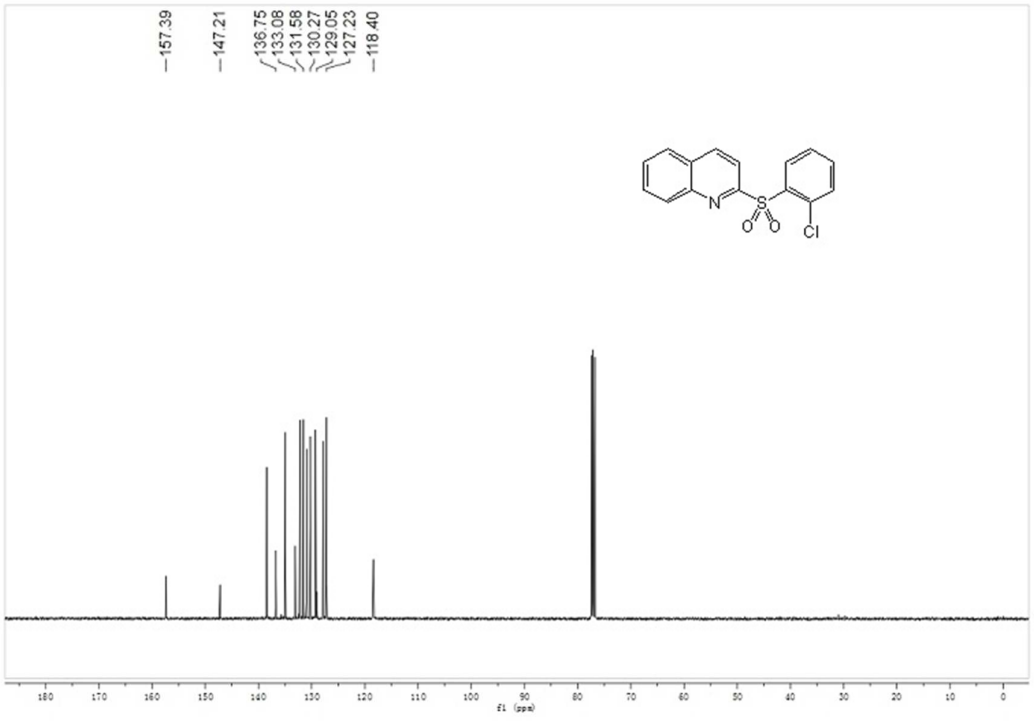
2-((3-chlorophenyl)sulfonyl)quinoline (3ah)



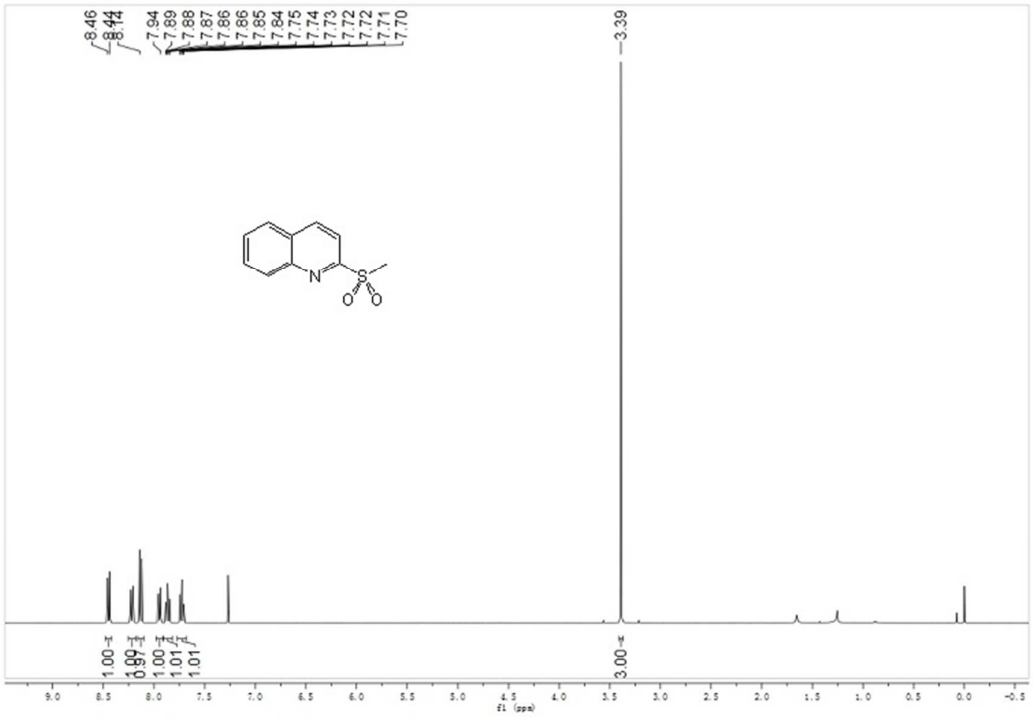


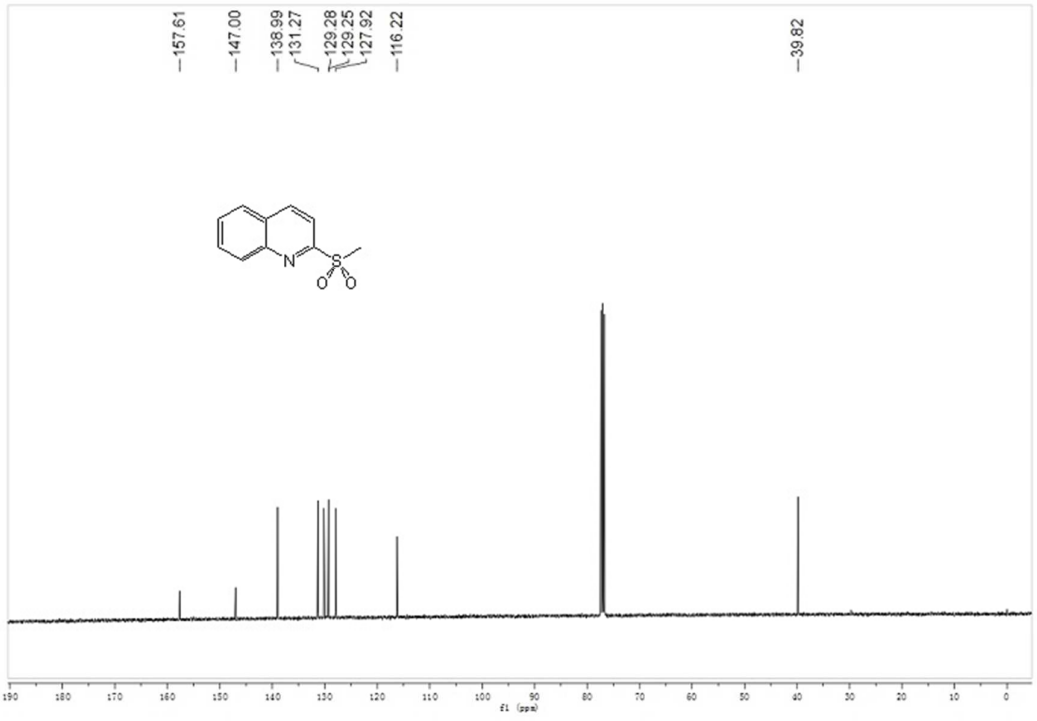
2-((2-chlorophenyl)sulfonyl)quinoline (3ai)



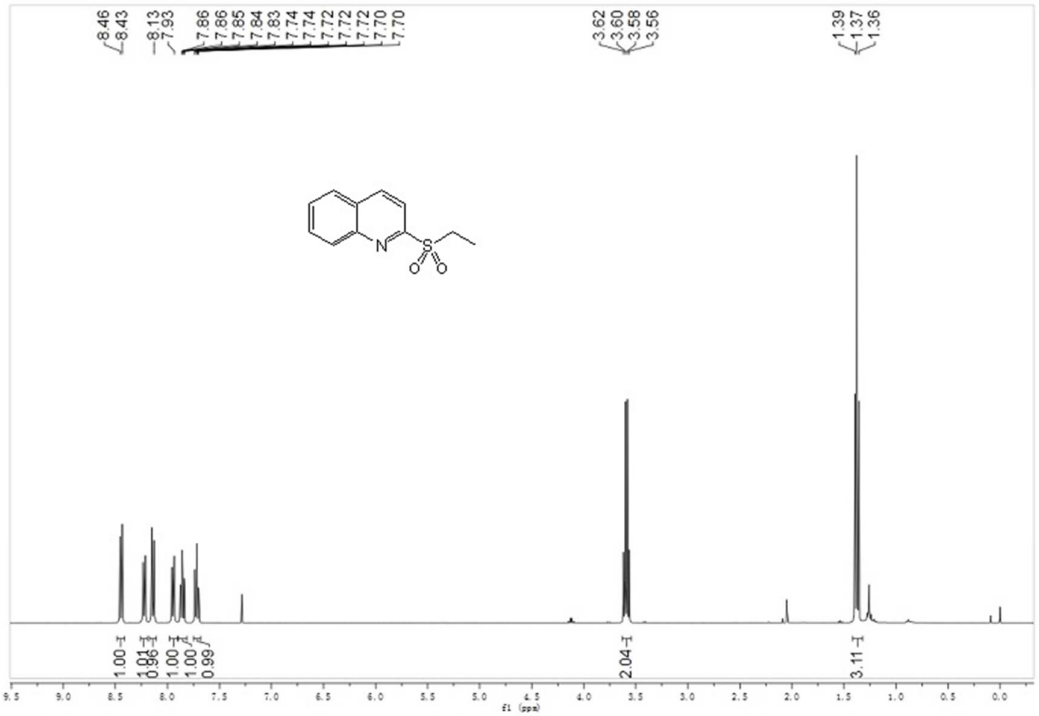


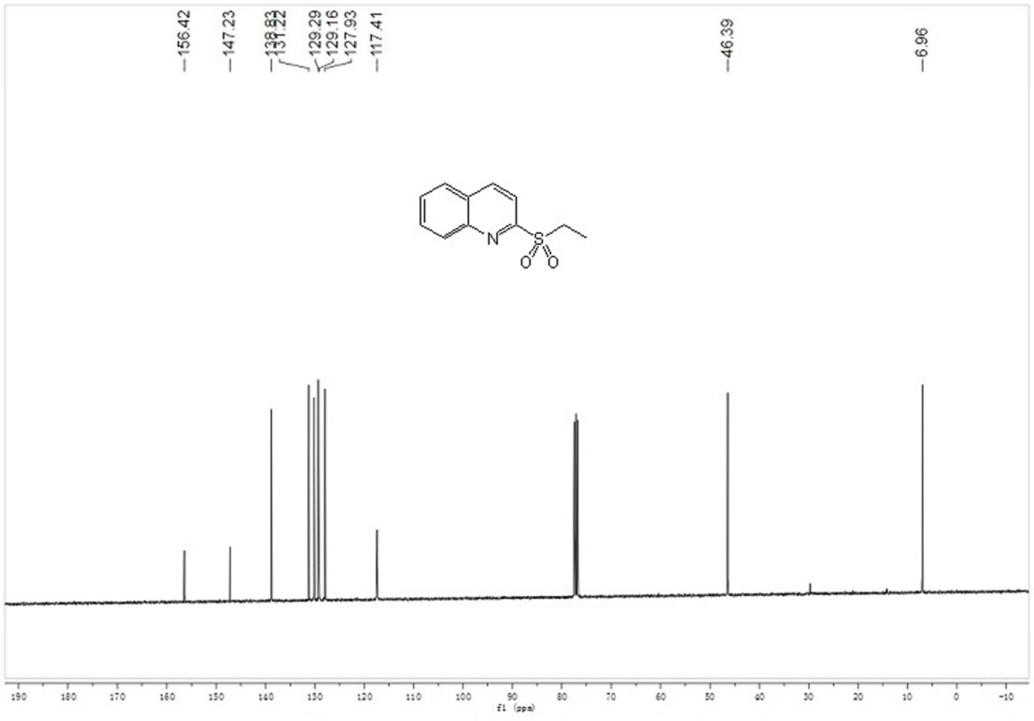
2-(methylsulfonyl)quinoline (3aj)



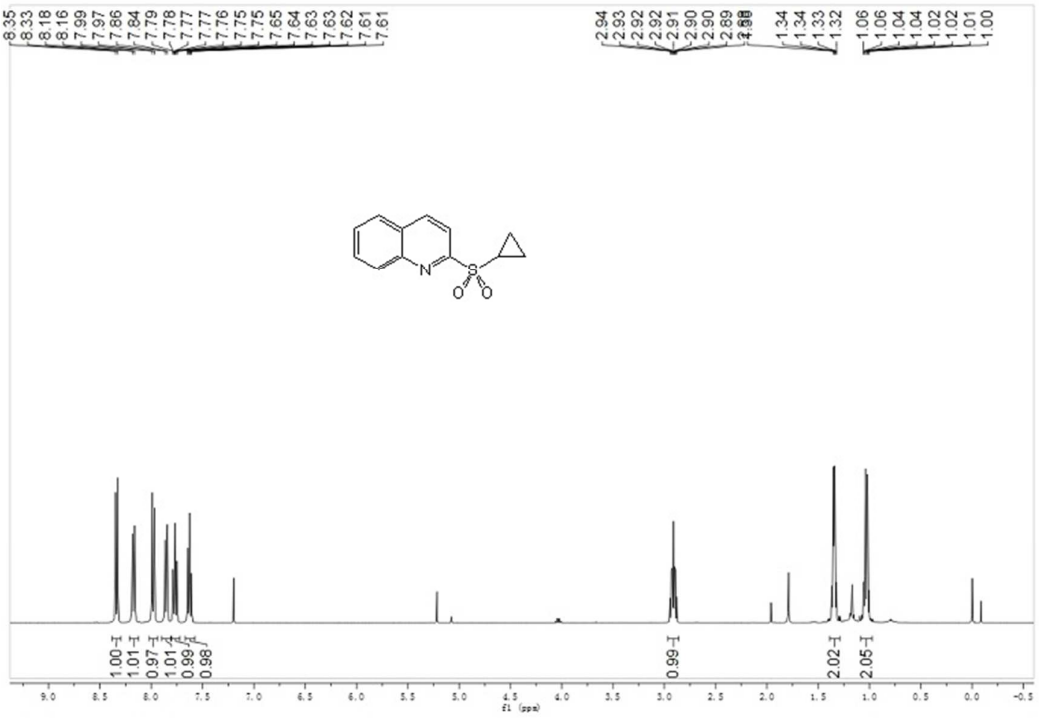


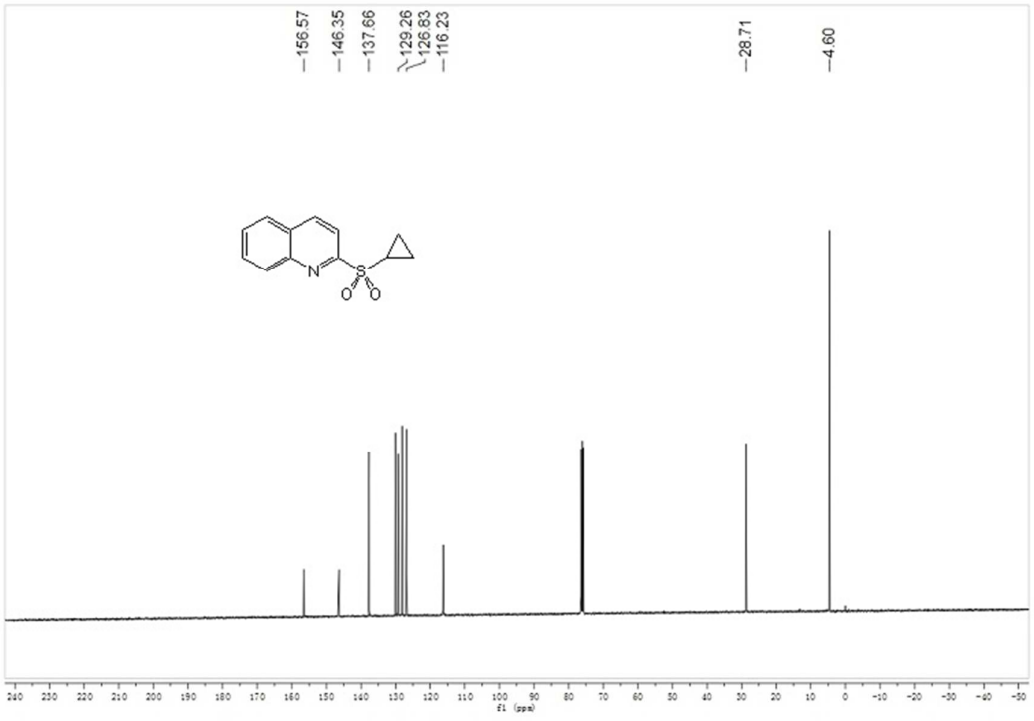
2-(ethylsulfonyl)quinoline (3ak)



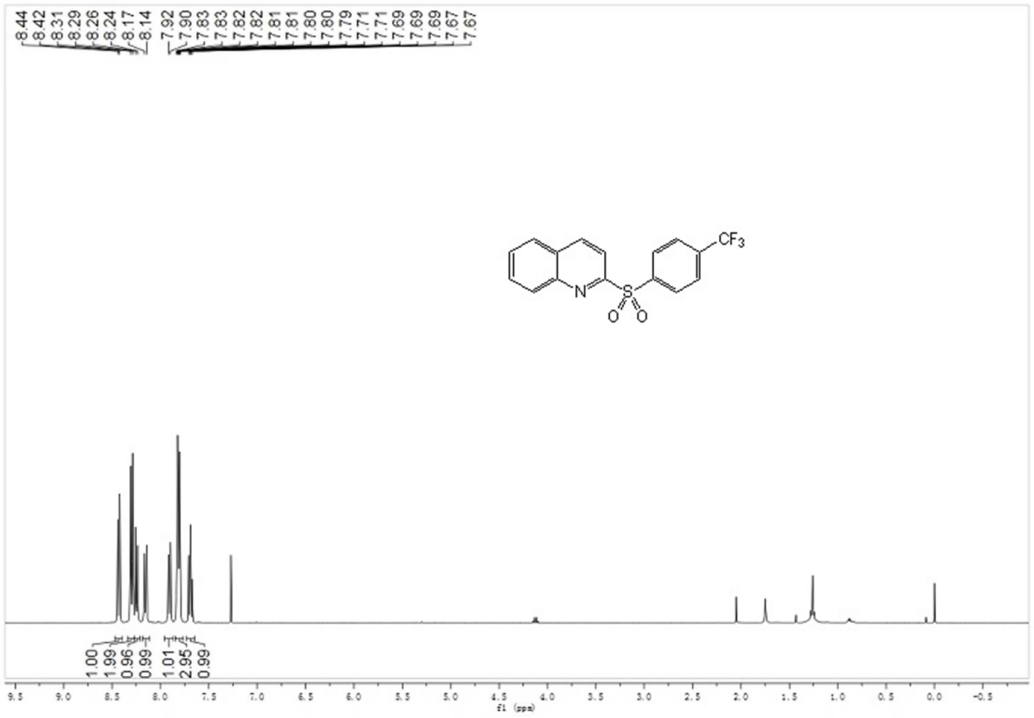


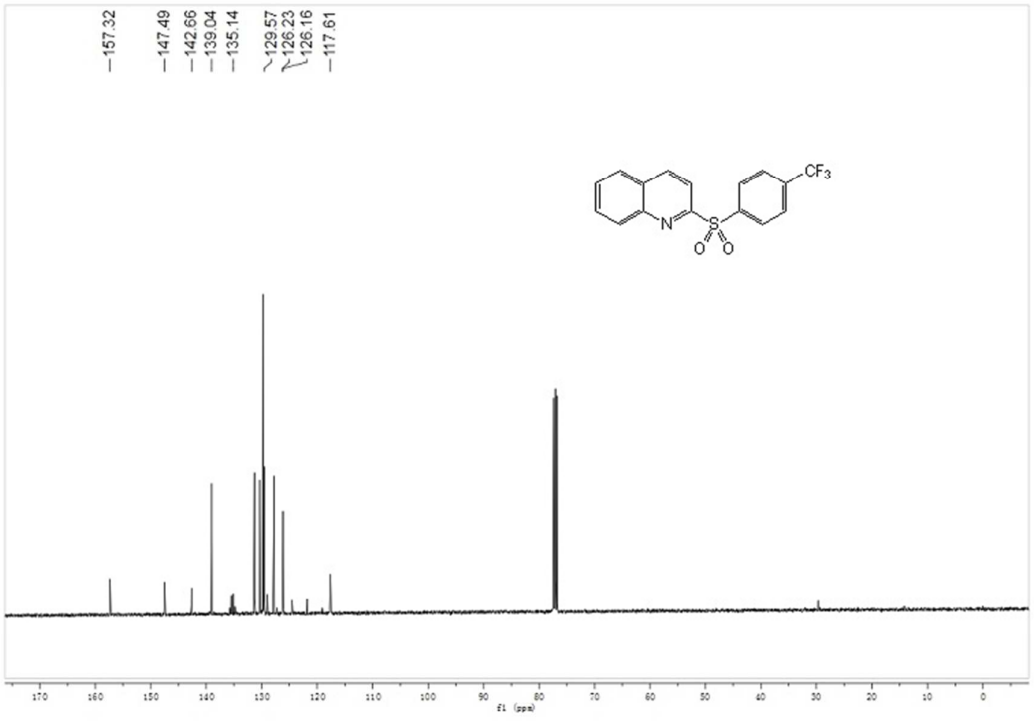
2-(cyclopropylsulfonyl)quinoline (3al)



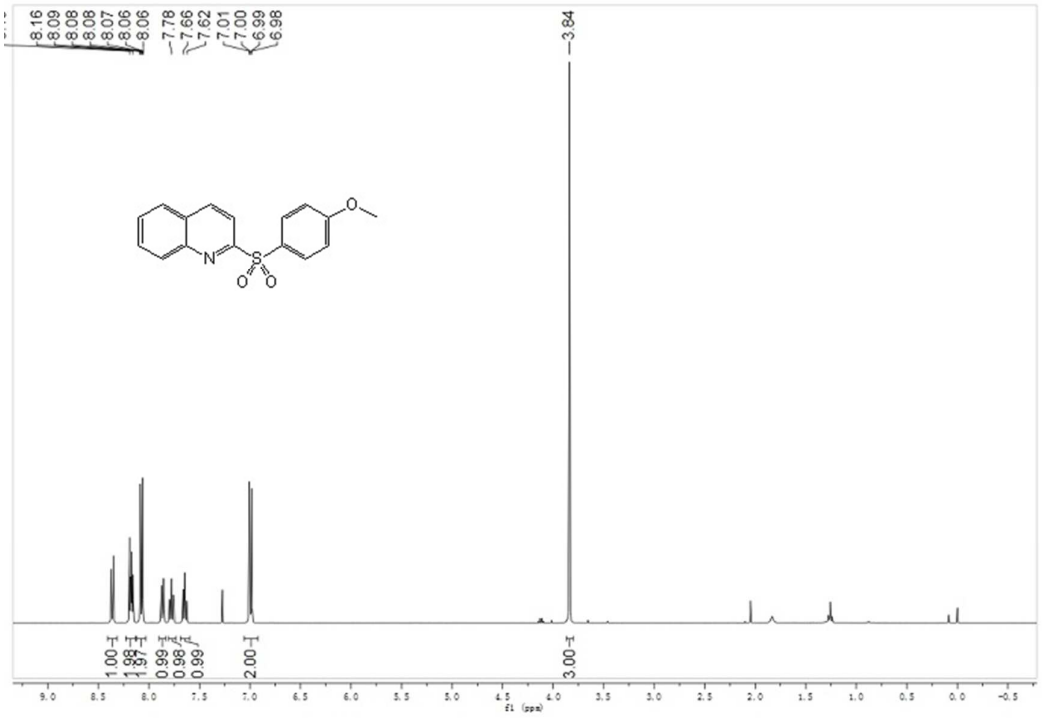


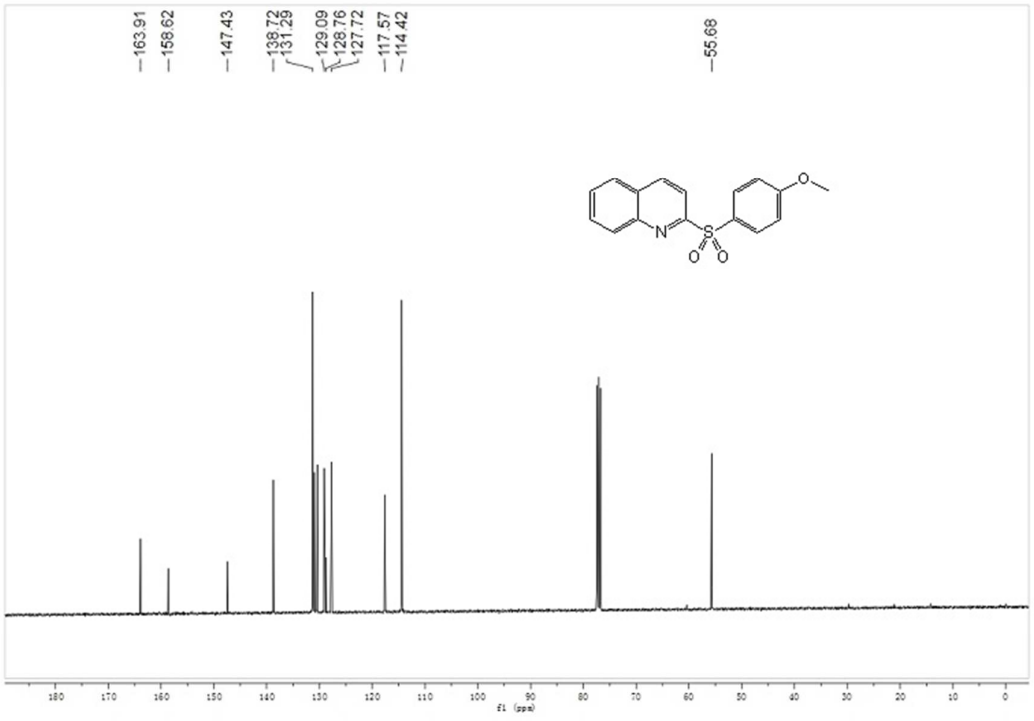
2-((4-(trifluoromethyl)phenyl)sulfonyl)quinoline (3am)



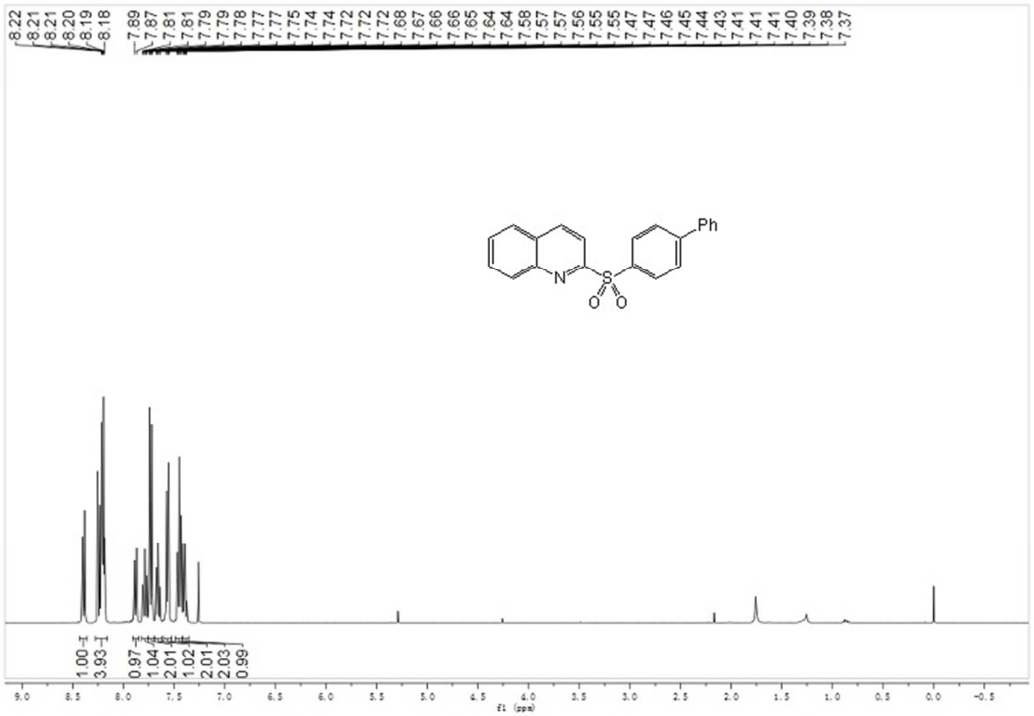


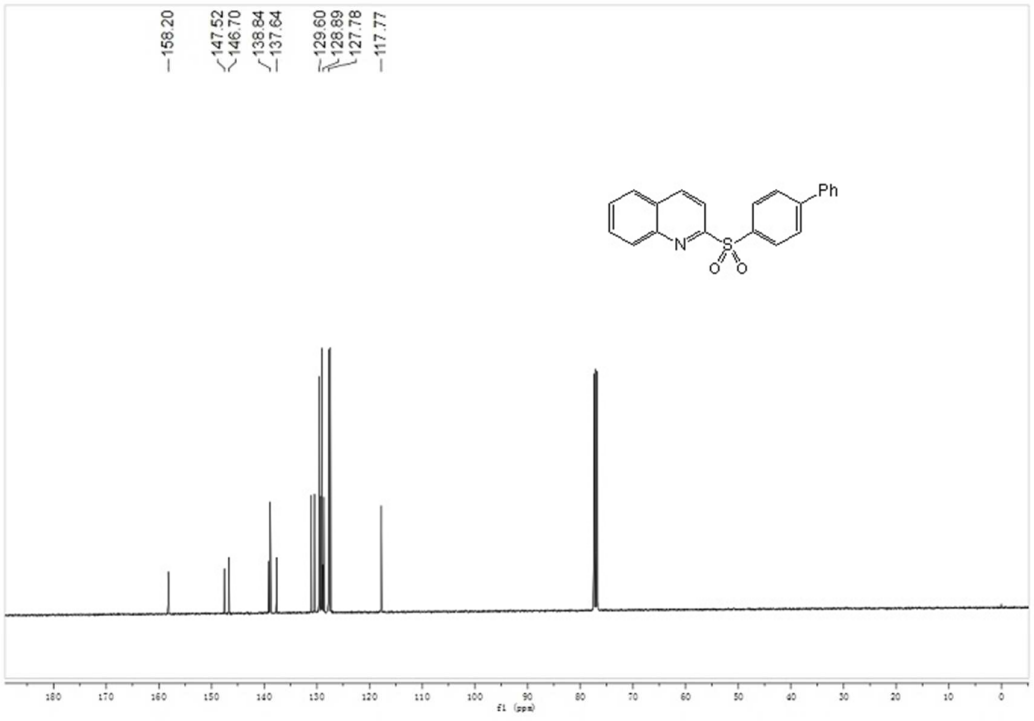
2-((4-methoxyphenyl)sulfonyl)quinoline (3an)



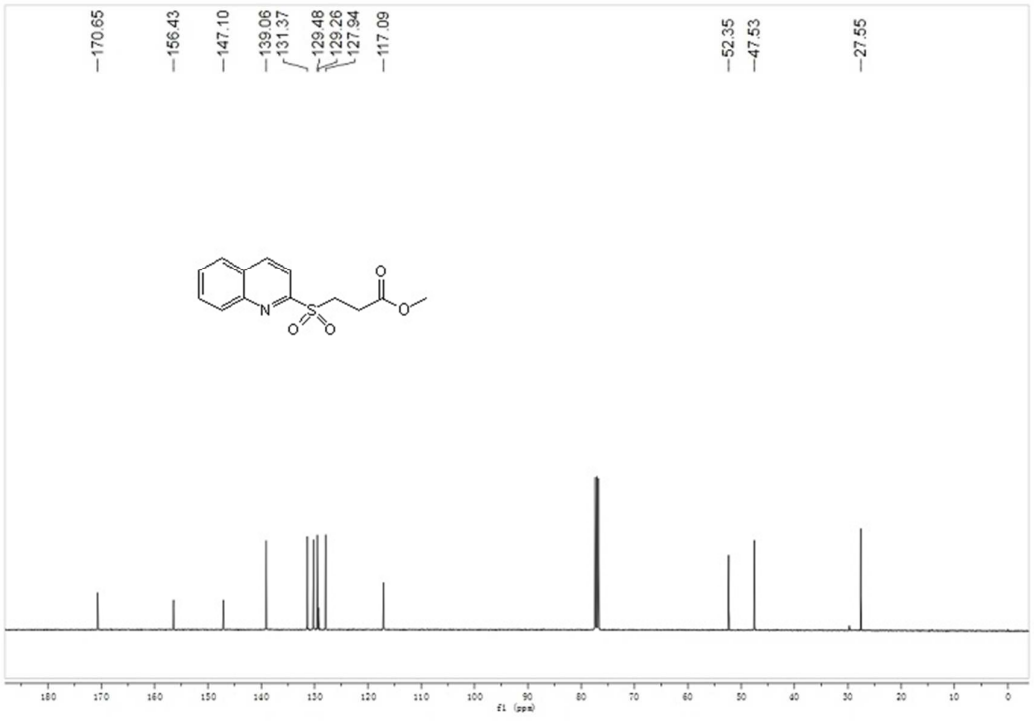


2-([1,1'-biphenyl]-4-ylsulfonyl)quinoline (3ao)

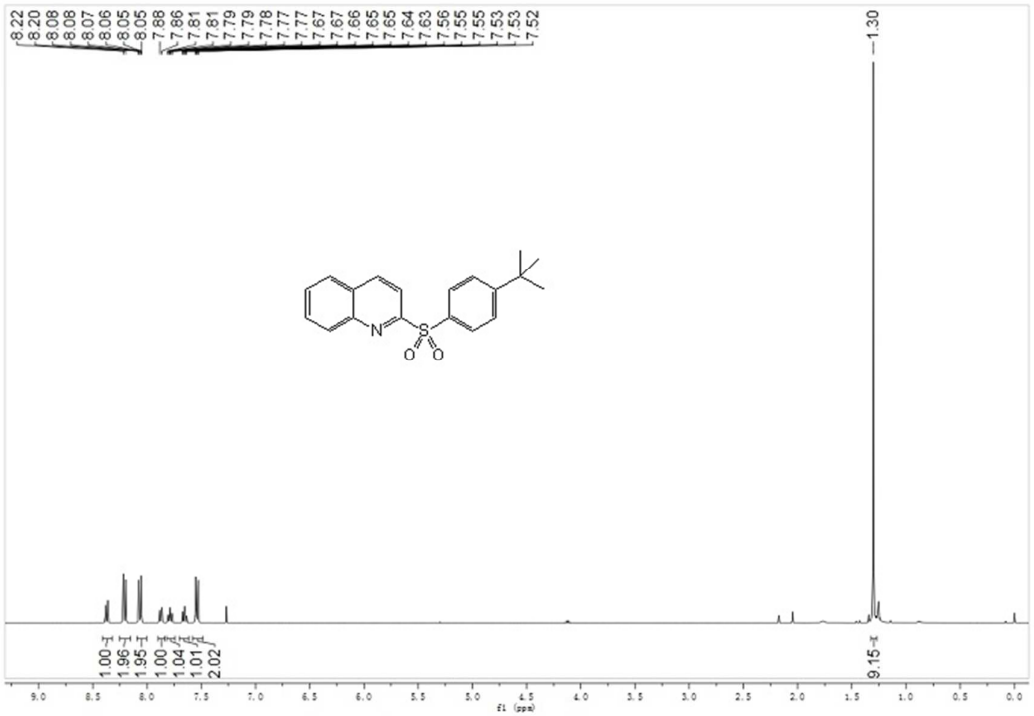


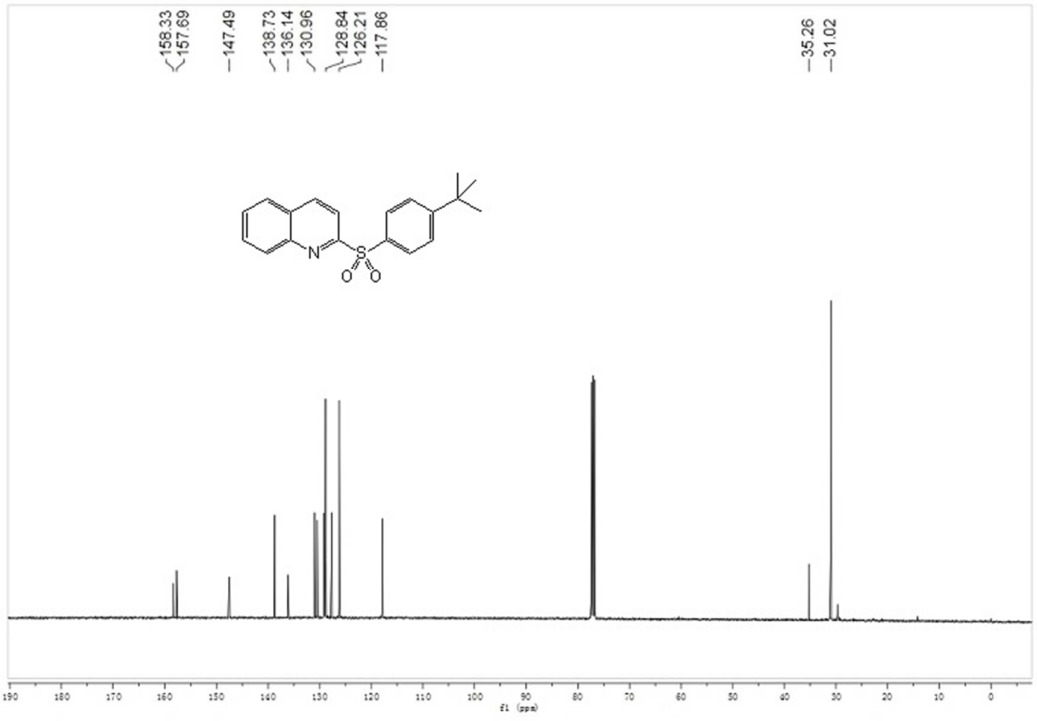


methyl 3-(quinolin-2-ylsulfonyl)propanoate (3ap)

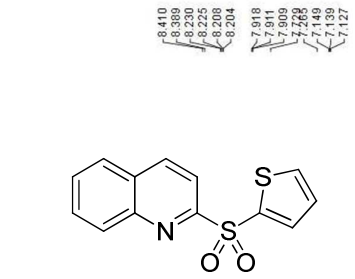


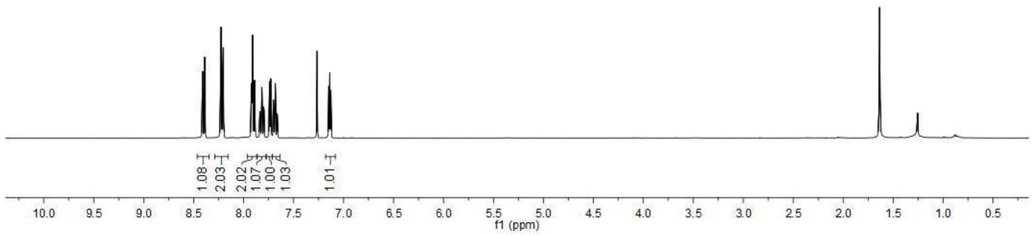
2-((4-(tert-butyl)phenyl)sulfonyl)quinolone (3aq)

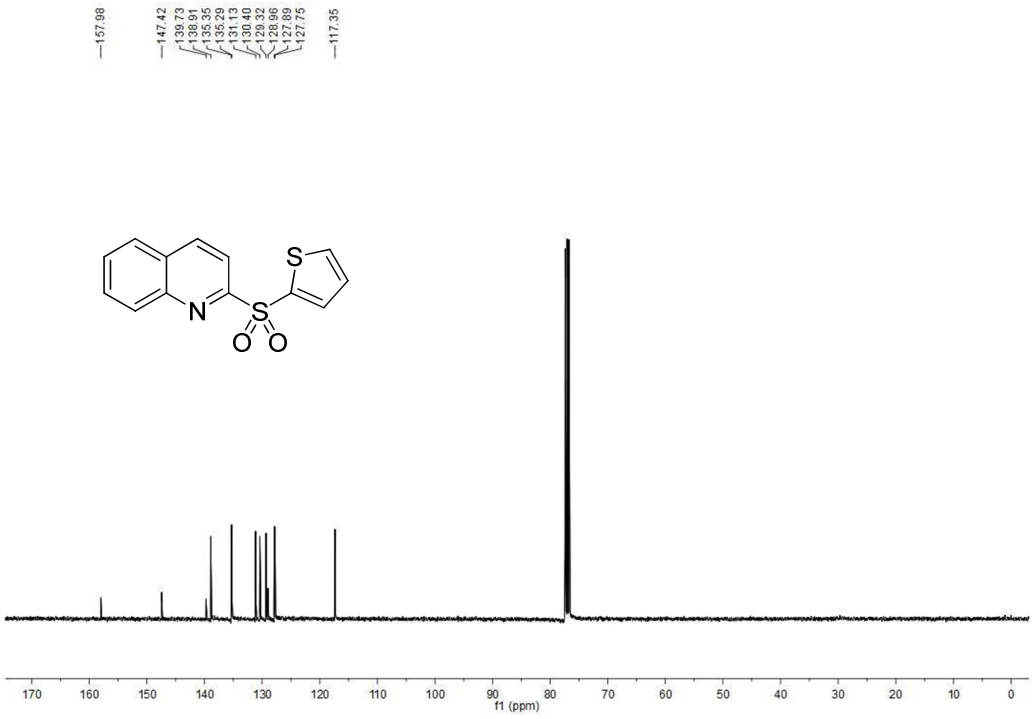




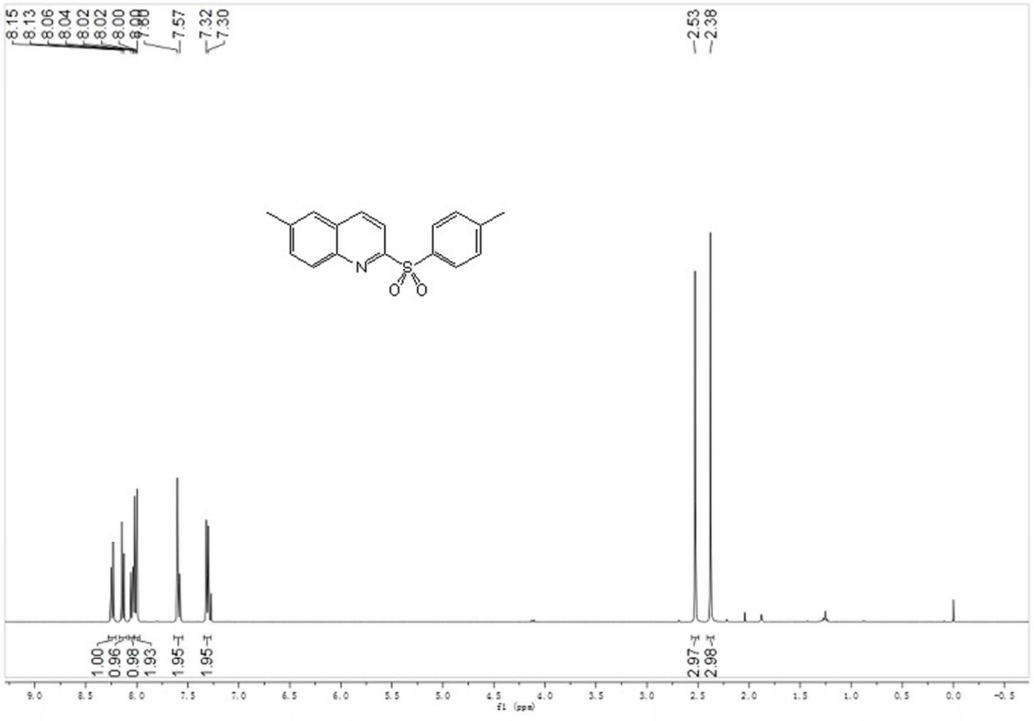
2-(thiophen-2-ylsulfonyl)quinoline (3ar)

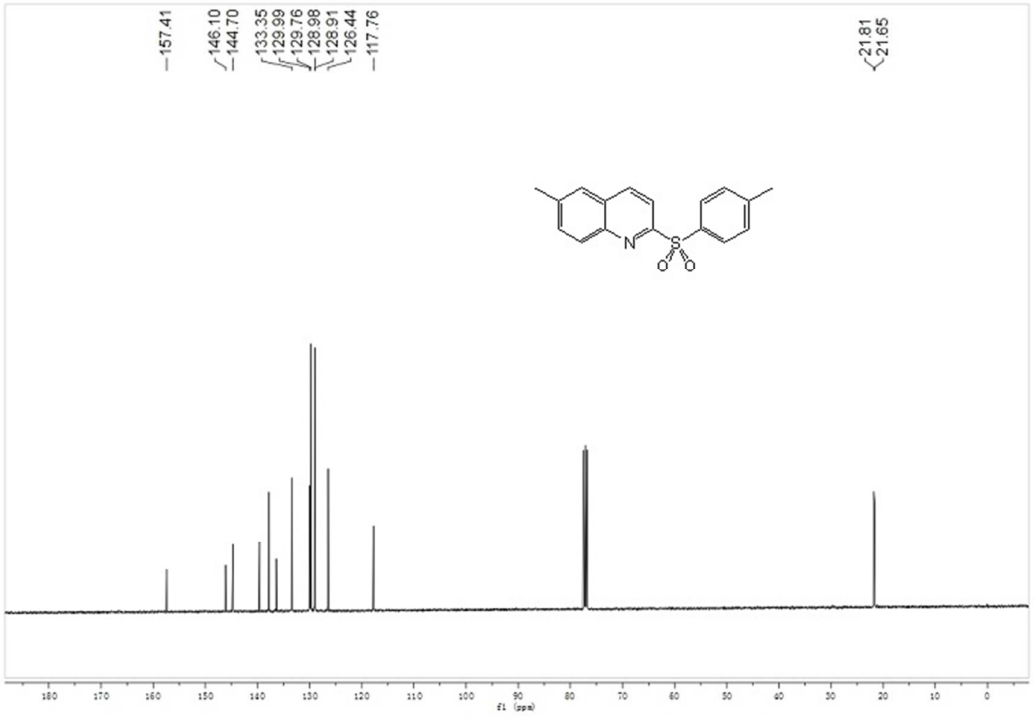




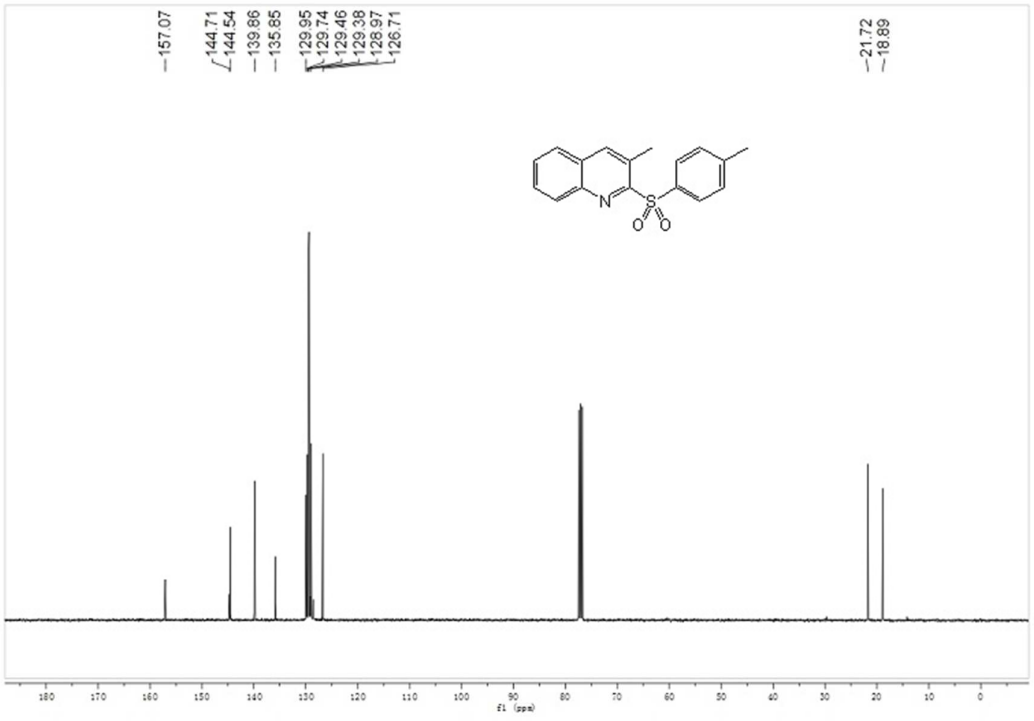


6-methyl-2-tosylquinoline (3ba)

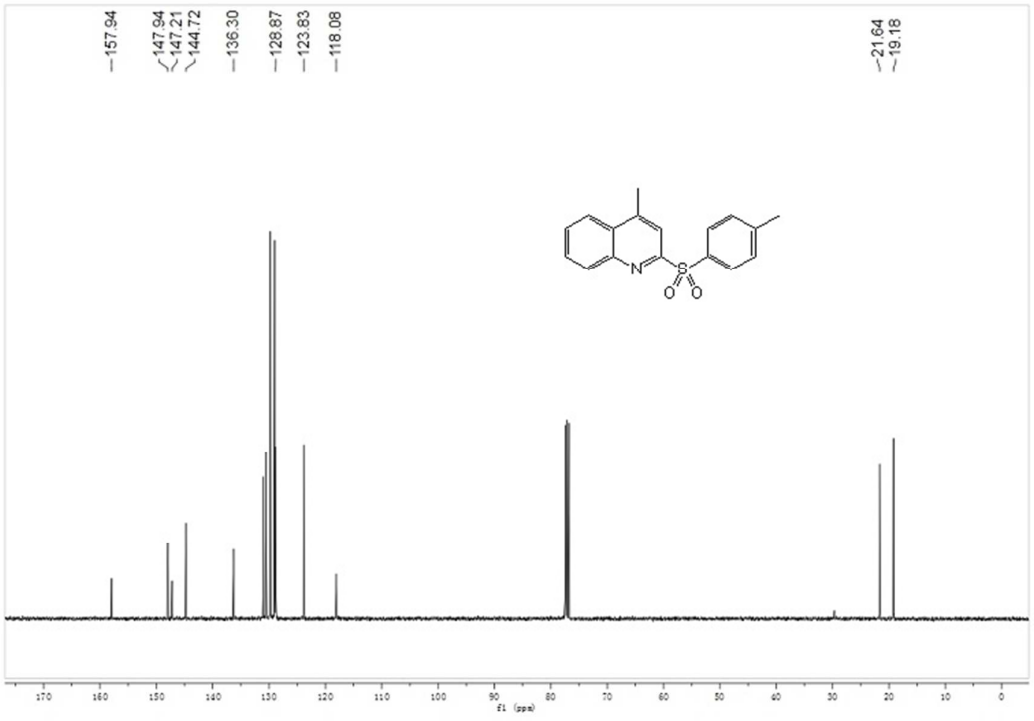




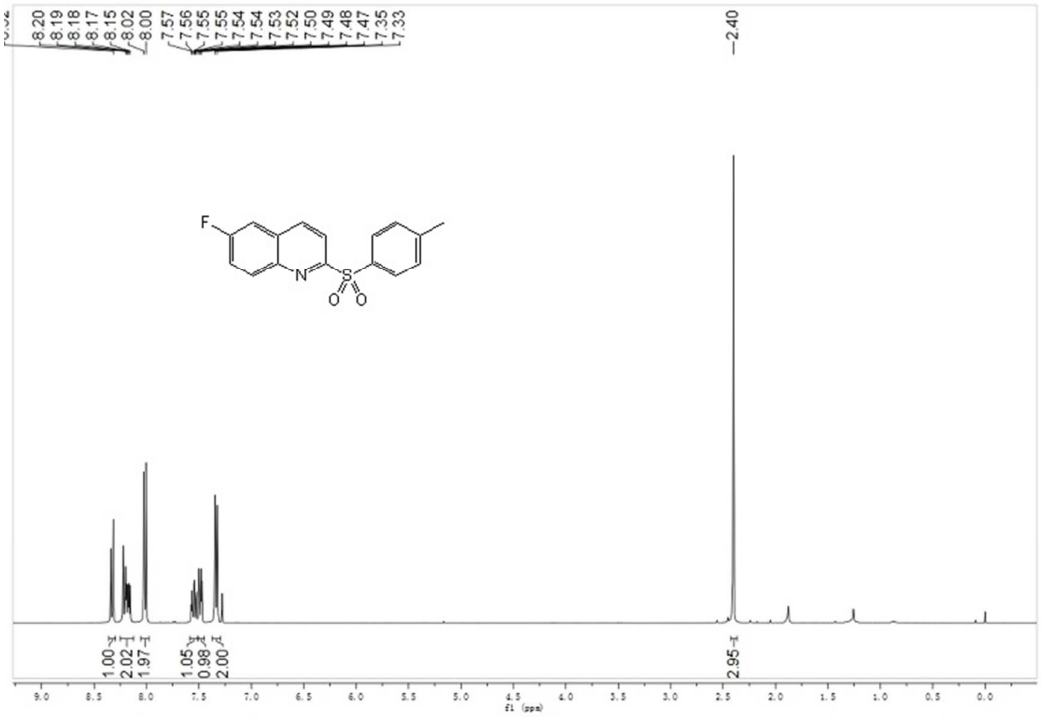
3-methyl-2-tosylquinoline (3ca)

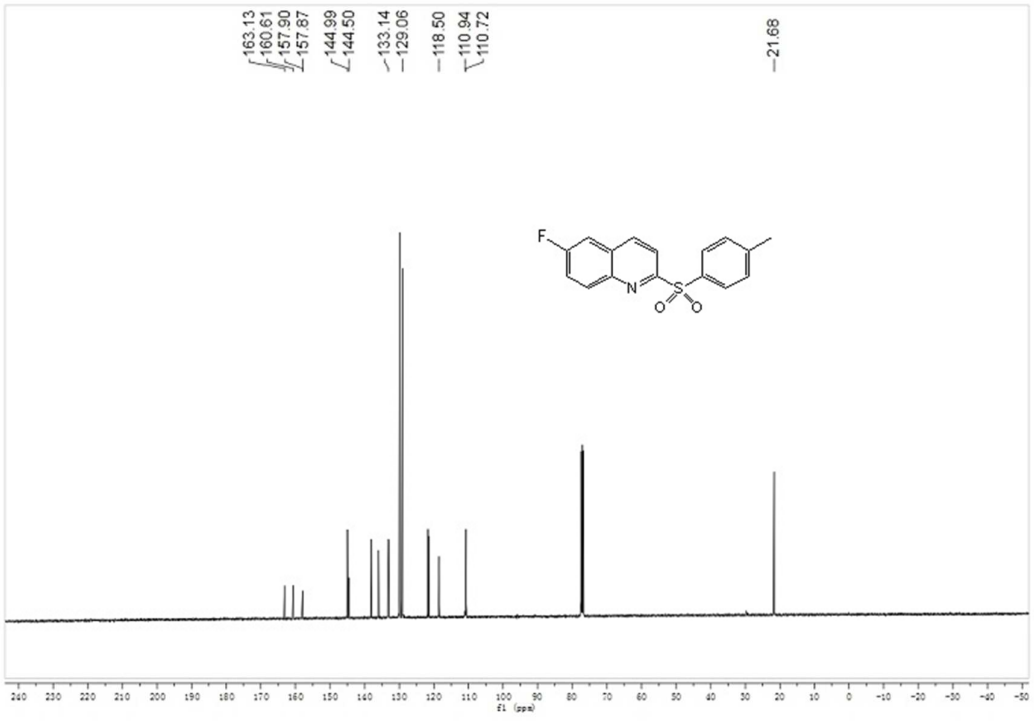


4-methyl-2-tosylquinoline (3da)

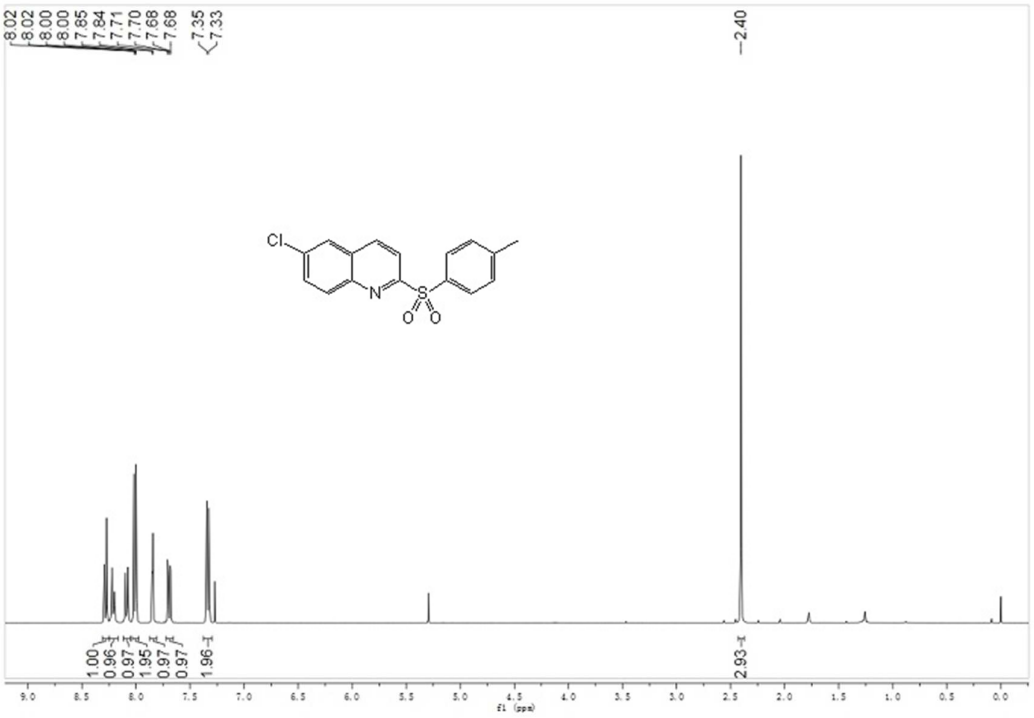


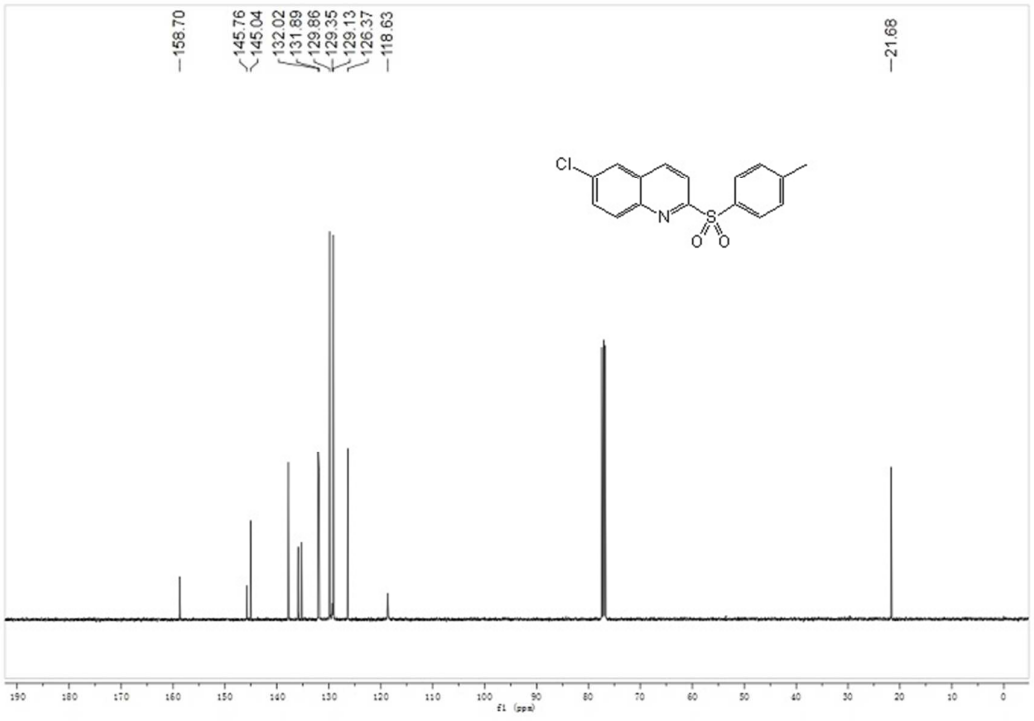
6-fluoro-2-tosylquinoline (3ea)



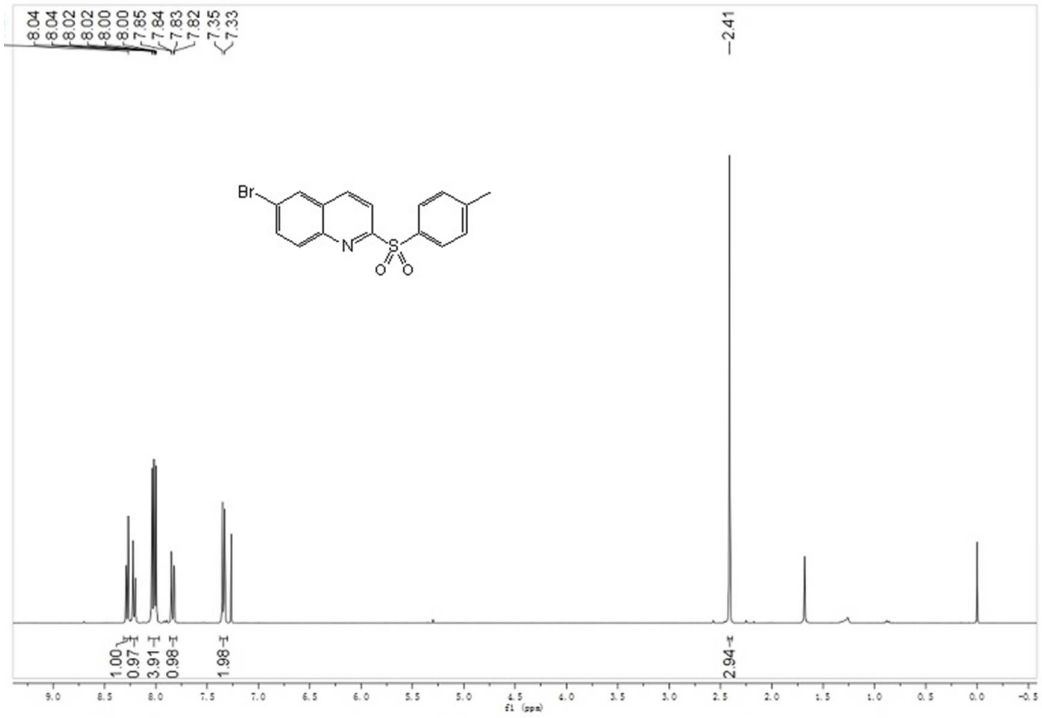


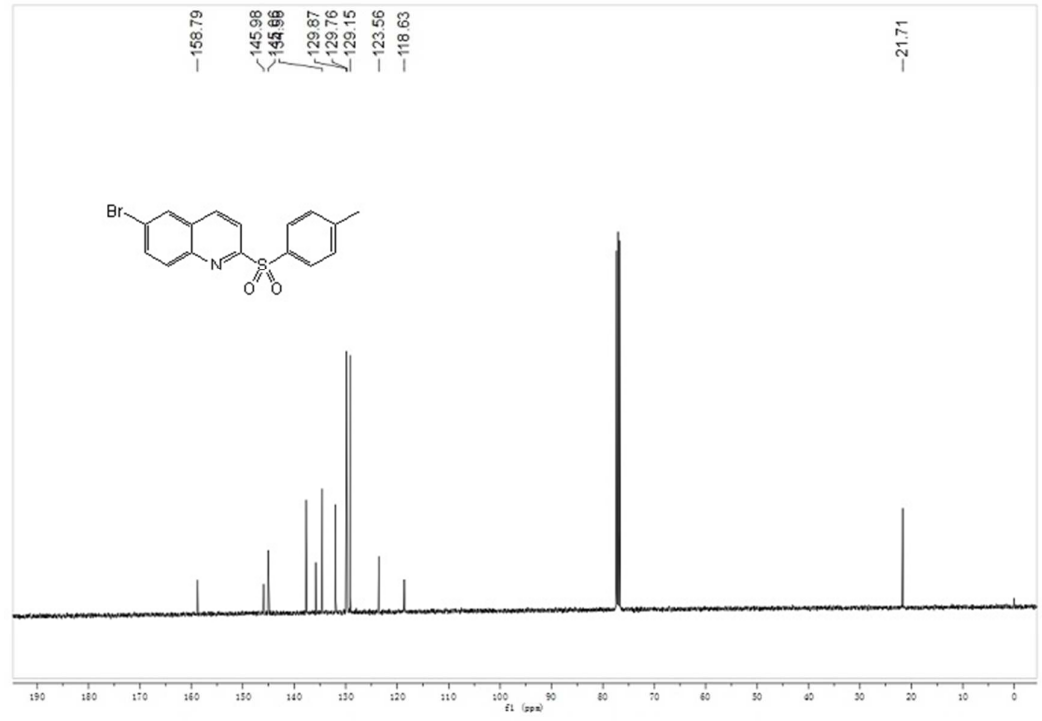
6-chloro-2-tosylquinoline (3fa)



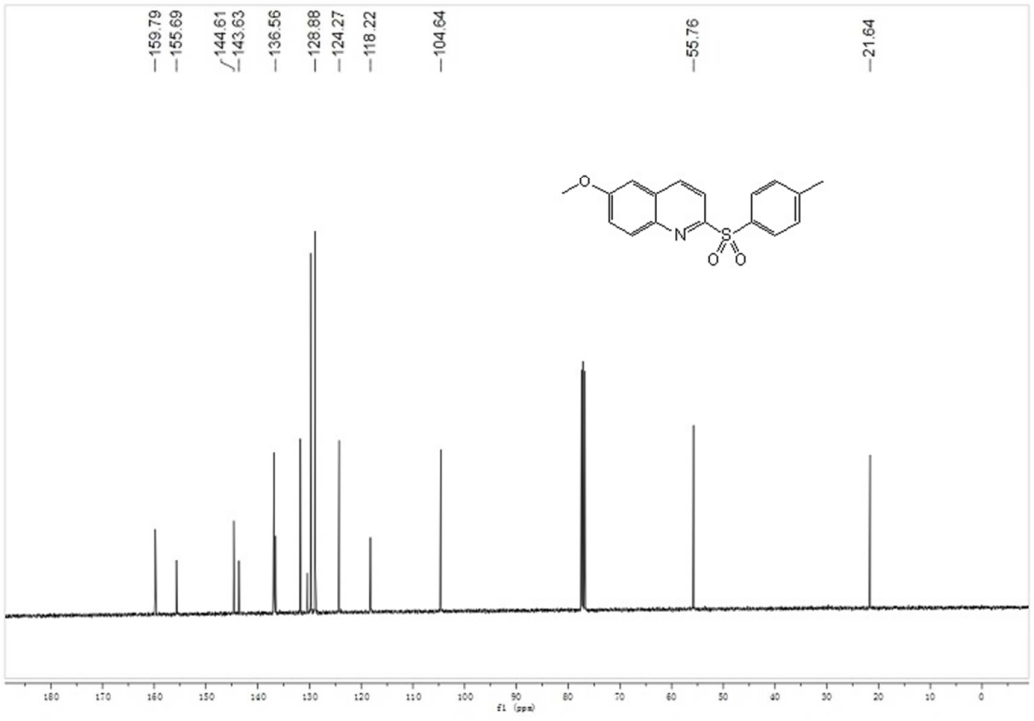


6-bromo-2-tosylquinoline (3ga)

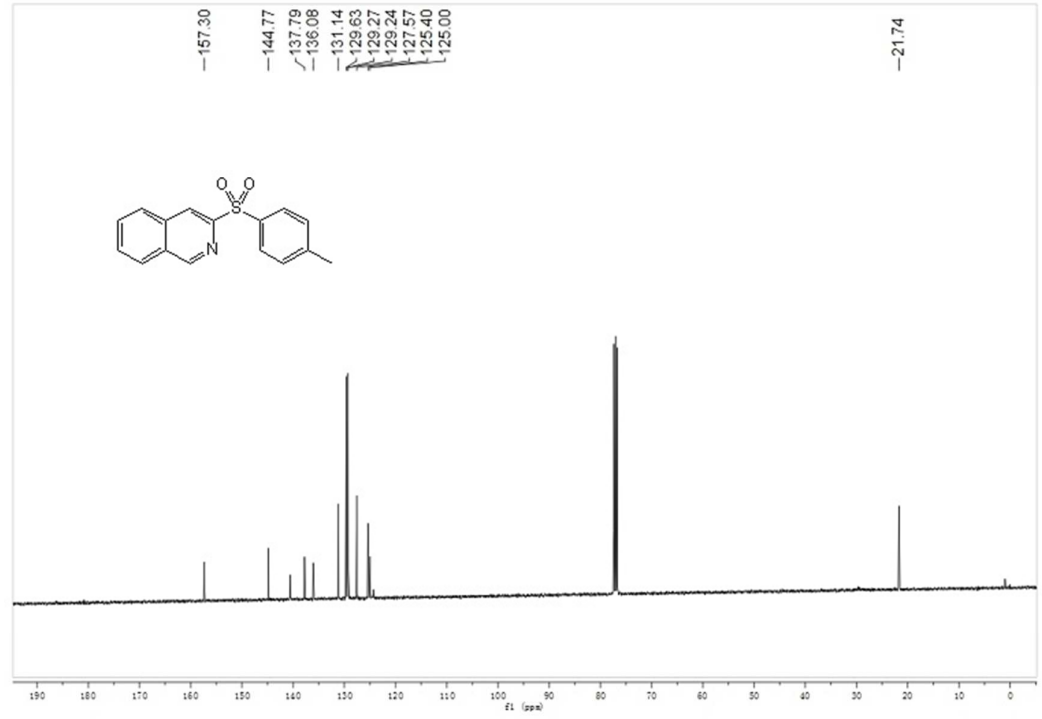




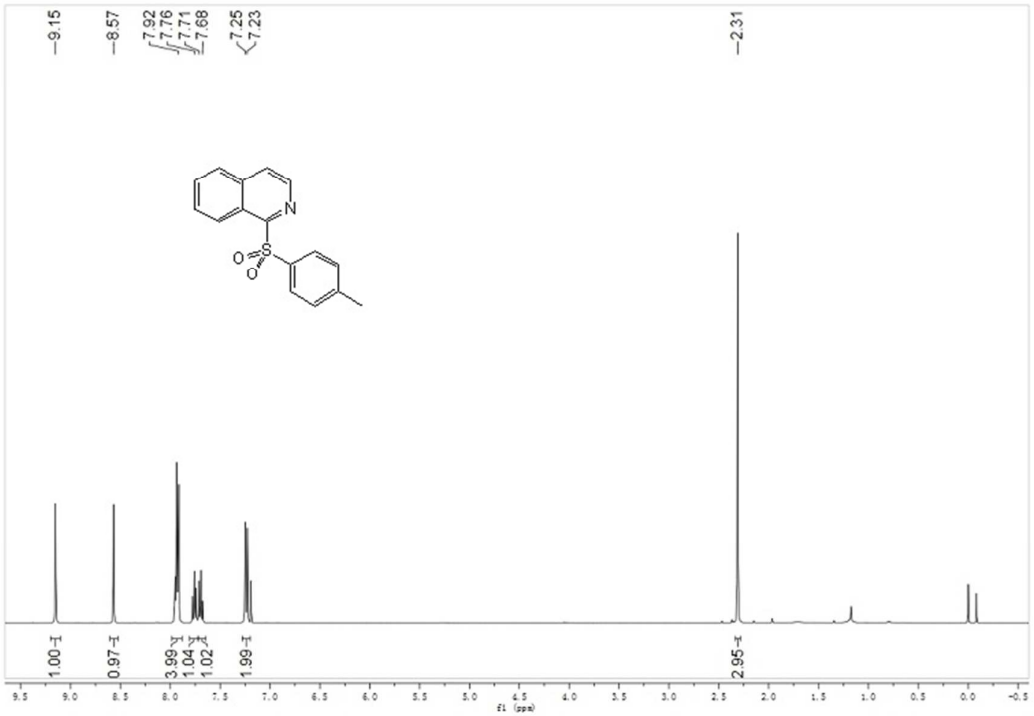
6-methoxy-2-tosylquinoline (3ha)

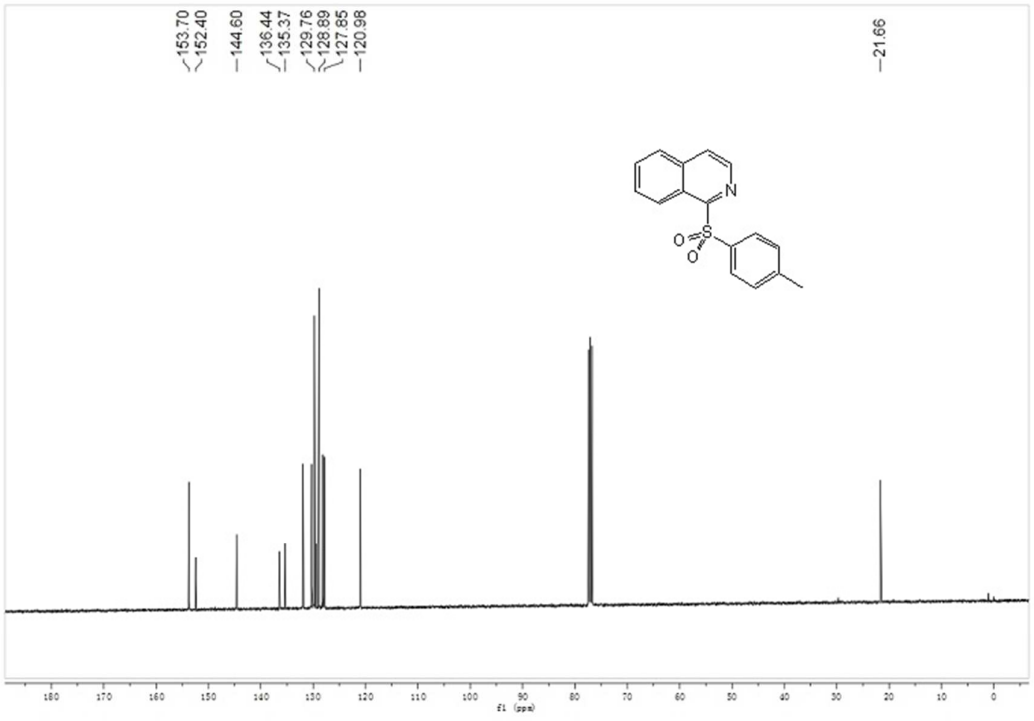


3-tosylisoquinoline (3ia-1)



1-tosylisoquinoline (3ia-2)





(2-tosylethene-1,1-diyl)dibenzene (4)