Supplementary Material

Synthesis of 3-sulfonylquinolines by visible-light promoted metal-free cascade cycloaddition involving *N*-propargylanilines and sodium sulfinates

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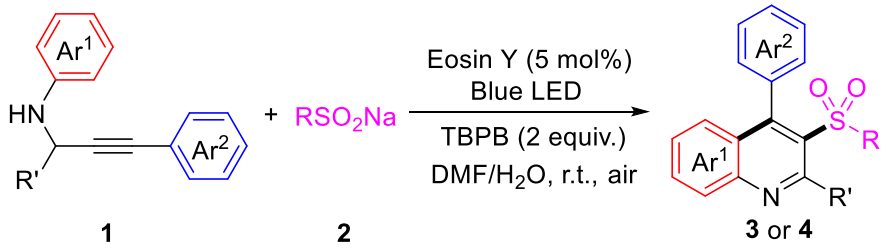
General: All reactions were performed in a 10 mL tube. Solvents were dried over 4 Å molecular sieves before using. For chromatography, 200-300 mesh silica gel (Qingdao, China) was used. Melting points (mp) were taken on a MEL-TEMP® apparatus and were uncorrected. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectras were measured recorded on 300 M or 400 M spectrometer in $CDCl_3$ solution. HRMS was measured in ESI mode and the mass analyzer of the HRMS was TOF. Chemical shifts (δ) were given in ppm, referenced to the residual proton resonance of $CDCl_3$ (7.26), to the carbon resonance of $CDCl_3$ (77.16). Coupling constants (J) were given in Hertz (Hz). The term m, q, t, d, s referred to multiplet, quartet, triplet, doublet, singlet. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. *N*-propargylanilines[1] and sodium sulfinates[2] were prepared according to previously reported procedures.

Typical procedure for the visible-light promoted cascade cycloaddition of N-propargylanilines with sodium sulfinates:

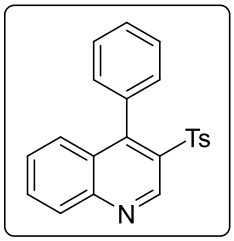


1 **2** **3** or **4**

A 10 mL tube in air was charged with *N*-propargylaniline **1** (0.2 mmol), sodium sulfinate **2** (2 equiv.), Eosin Y (5 mol%) and TBPB (2 equiv.). Then 2 mL of DMF/H_2O (2 mL, V/V = 3:1) was added via syringe. The resulting solution was stirred at room temperature with the irradiation of a 5 W blue LED for over night. After the reaction was completed, it was quenched with 10 mL of H_2O. The reaction mixture was extracted with ethyl acetate (10 mL × 3), washed with Saturated ammonium chloride solution, and then dried over anhydrous Na_2SO_4. The volatile compounds were removed in *vacuo* and the residue was purified by column chromatography to give the desired 3-sulfonylquinolines **3** or **4**.

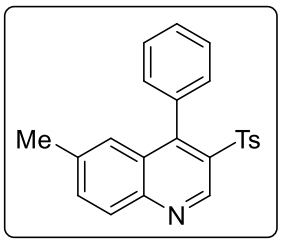
Characterization datas

4-phenyl-3-tosylquinoline (3a)[1b]



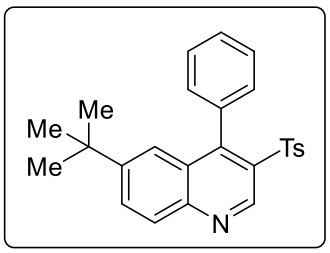
Light yellow solid (88%, 63.3 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 168 – 169 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.78 (s, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.85 – 7.72 (m, 1H), 7.49 – 7.38 (m, 2H), 7.36 – 7.27 (m, 3H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 7.4 Hz, 2H), 2.33 (s, 3H); HRMS (ESI) calcd. for $C_{22}H_{18}NO_2S^+$ [(M + H)$^+$] 360.1053, found: 360.1036.

6-methyl-4-phenyl-3-tosylquinoline (3b)[1b]



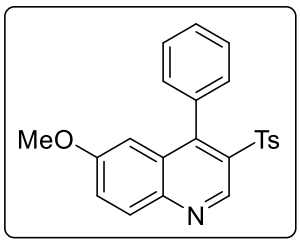
Light yellow solid (60%, 44.8 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 203 – 204 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.70 (s, 1H), 8.08 (d, *J* = 8.6 Hz, 1H), 7.63 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.36 – 7.29 (m, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 3H), 6.96 – 6.90 (m, 2H), 2.34 (s, 3H), 2.34 (s, 3H); HRMS (ESI) calcd. for $C_{23}H_{20}NO_2S^+$ [(M + H)$^+$] 374.1209, found: 374.1194.

6-(tert-butyl)-4-phenyl-3-tosylquinoline (3c)



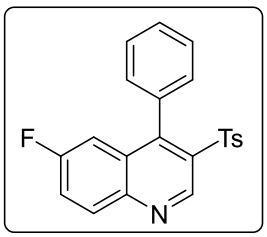
Light yellow solid (70%, 58.2 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 196 – 198 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.73 (s, 1H), 8.15 (d, *J* = 8.9 Hz, 1H), 7.91 (dd, *J* = 8.9, 1.9 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.24 – 7.15 (m, 3H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 7.4 Hz, 2H), 2.34 (s, 3H), 1.18 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.9, 149.7, 148.4, 147.2, 144.0, 138.2, 132.8, 132.6, 131.3, 130.1, 129.3, 129.2, 128.7, 127.9, 127.6, 127.2, 122.2, 35.1, 30.9, 21.6; HRMS (ESI) calcd. for $C_{26}H_{26}NO_2S^+$ [(M + H)$^+$] 416.1679, found: 416.1677.

6-methoxy-4-phenyl-3-tosylquinoline (3d)[1b]



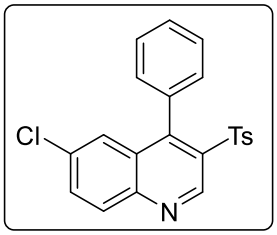
Light yellow solid (45%, 35.1 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 217 – 219 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.62 (s, 1H), 8.09 (d, *J* = 9.2 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 7.1 Hz, 2H), 6.50 (d, *J* = 2.5 Hz, 1H), 3.59 (s, 3H), 2.34 (s, 3H); HRMS (ESI) calcd. for $C_{23}H_{20}NO_3S^+$ [(M + H)$^+$] 390.1158, found: 390.1138.

6-fluoro-4-phenyl-3-tosylquinoline (3e)[1b]



Light yellow solid (85%, 64.2 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 169 – 171 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.74 (s, 1H), 8.22 (dd, *J* = 9.0, 5.3 Hz, 1H), 7.63 – 7.52 (m, 1H), 7.51 – 7.41 (m, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.93 (d, *J* = 6.8 Hz, 3H), 2.34 (s, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -109.54 (s); HRMS (ESI) calcd. for $C_{22}H_{17}FNO_2S^+$ [(M + H)$^+$] 378.0959, found: 378.0941.

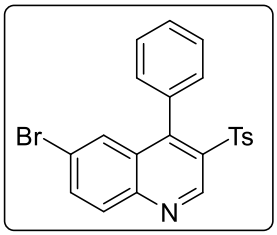
6-chloro-4-phenyl-3-tosylquinoline (3f)[1b]



Light yellow solid (64%, 50.4 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 164 – 165 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.78 (s, 1H), 8.17 (d, *J* = 8.9 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.29 (s, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 7.9

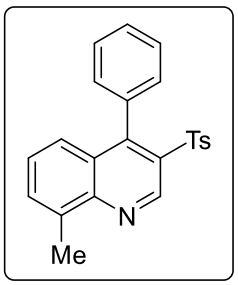
Hz, 2H), 6.95 (d, *J* = 7.5 Hz, 2H), 2.37 (s, 3H); HRMS (ESI) calcd. for $C_{22}H_{17}ClNO_2S^+$ [(M + H)$^+$] 394.0663, found: 394.0643.

6-bromo-4-phenyl-3-tosylquinoline (3g)[1b]



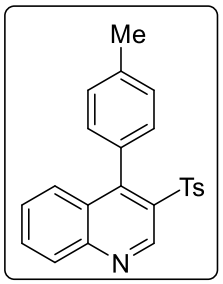
Light yellow solid (72%, 63.1 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 178– 179 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.76 (s, 1H), 8.06 (d, *J* = 8.9 Hz, 1H), 7.85 (d, *J* = 8.9 Hz, 1H), 7.51 – 7.40 (m, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.93 (d, *J* = 7.5 Hz, 2H), 2.34 (s, 3H); HRMS (ESI) calcd. for $C_{22}H_{17}BrNO_2S^+$ [(M + H)$^+$] 438.0158, found: 438.0135.

8-methyl-4-phenyl-3-tosylquinoline (3h)[1b]



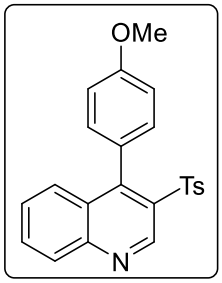
Light yellow solid (76%, 56.8 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 162 – 164 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.64 (d, *J* = 6.6 Hz, 1H), 7.50 – 7.39 (m, 1H), 7.32 (t, *J* = 7.6 Hz, 3H), 7.25 – 7.11 (m, 3H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.94 (d, *J* = 7.5 Hz, 2H), 2.86 (s, 3H), 2.34 (s, 3H); HRMS (ESI) calcd. for $C_{23}H_{20}NO_2S^+$ [(M + H)$^+$] 374.1209, found: 374.1207.

4-(p-tolyl)-3-tosylquinoline (3i)[1b]



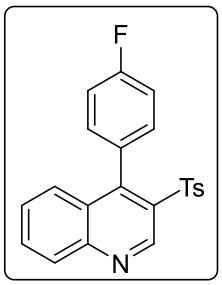
Light yellow solid (65%, 48.6 mg, eluent: petroleum ether/ethyl acetate =10/1), mp 174 – 176 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.76 (s, 1H), 8.20 (d, *J* = 8.3 Hz, 1H), 7.80 (t, *J* = 7.3 Hz, 1H), 7.48 – 7.34 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.84 (d, *J* = 7.7 Hz, 2H), 2.46 (s, 3H), 2.34 (s, 3H); HRMS (ESI) calcd. for $C_{23}H_{20}NO_2S^+$ [(M + H)$^+$] 374.1209, found: 374.1189.

4-(4-methoxyphenyl)-3-tosylquinoline (3j)[1b]



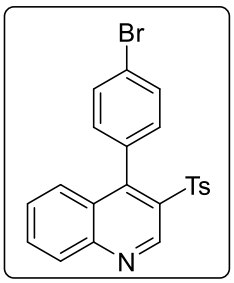
Light yellow solid (79%, 61.5 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 154 – 157 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.77 (s, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.81 (t, *J* = 7.4 Hz, 1H), 7.50 – 7.35 (m, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.87 (s, 4H), 3.90 (s, 3H), 2.34 (s, 3H); HRMS (ESI) calcd. for $C_{23}H_{20}NO_3S^+$ [(M + H)$^+$] 390.1158, found: 390.1136.

4-(4-fluorophenyl)-3-tosylquinoline (3k)[3]



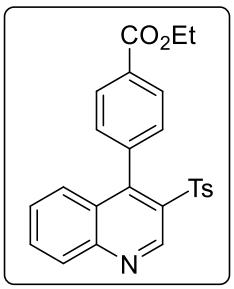
Light yellow solid (87%, 65.7 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 139 – 141 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.78 (s, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 6.6 Hz, 1H), 7.54 – 7.45 (m, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 6.7 Hz, 2H), 7.16 – 6.90 (m, 6H), 2.37 (s, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.14 (s). HRMS (ESI) calcd. for $C_{22}H_{17}FNO_2S^+$ [(M + H)$^+$] 378.0959, found: 378.0937.

4-(4-bromophenyl)-3-tosylquinoline (3l)[3]



Light yellow solid (76%, 66.6 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 203 – 205 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.76 (s, 1H), 8.16 (d, *J* = 8.9 Hz, 1H), 7.74 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.24 (m, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.94 (d, *J* = 7.3 Hz, 2H), 2.35 (s, 3H); HRMS (ESI) calcd. for $C_{22}H_{17}BrNO_2S^+$ [(M + H)$^+$] 438.0158, found: 438.0136.

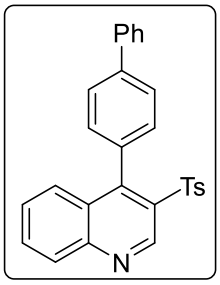
ethyl 4-(3-tosylquinolin-4-yl)benzoate (3m)



Light yellow solid (93%, 80.3 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 138 - 140 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.77 (s, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 7.5 Hz, 2H), 7.84 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 3H), 7.17 – 6.96 (m, 4H), 4.48 (dd, *J* = 13.7, 6.7 Hz, 2H), 2.38 (s, 3H), 1.48 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 149.6, 148.5, 147.6, 144.4, 137.8, 137.4, 132.4, 132.3, 130.8, 130.0,

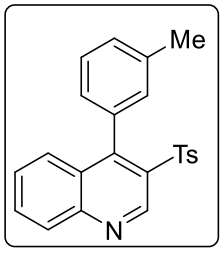
129.7, 129.4, 128.7, 128.1, 127.8, 127.0, 126.8, 61.3, 21.5, 14.4; HRMS (ESI) calcd. for $C_{25}H_{22}NO_4S^+$ [(M + H)$^+$] 432.1264, found: 432.1249.

4-([1,1'-biphenyl]-4-yl)-3-tosylquinoline (3n)



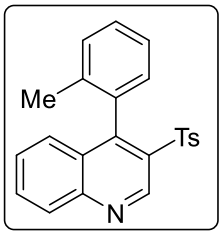
Light yellow solid (67%, 56.4 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 168 – 170 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.82 (s, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 7.86 – 7.77 (m, 1H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.60 – 7.37 (m, 7H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.03 (dd, *J* = 8.0, 2.2 Hz, 4H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.7, 149.6, 147.7, 144.1, 141.5, 140.2, 137.9, 132.9, 132.3, 131.5, 130.5, 129.6, 129.2, 129.0, 127.9, 127.4, 127.1, 126.2, 21.6; HRMS (ESI) calcd. for $C_{28}H_{22}NO_2S^+$ [(M + H)$^+$] 436.1366, found: 436.1365.

4-(m-tolyl)-3-tosylquinoline (3o)



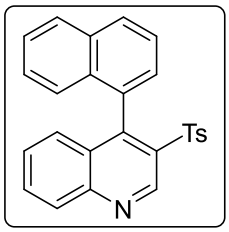
Light yellow solid (80%, 59.8 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 137 – 138 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.80 (s, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.86 – 7.76 (m, 1H), 7.48 – 7.34 (m, 2H), 7.30 – 7.14 (m, 4H), 7.06 (d, *J* = 7.5 Hz, 2H), 6.89 (d, *J* = 3.3 Hz, 1H), 6.53 (s, 1H), 2.36 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.3, 149.7, 147.8, 144.0, 138.1, 137.3, 132.8, 132.6, 132.3, 130.4, 129.7, 129.4, 129.3, 128.1, 127.9, 127.7, 127.4, 21.6, 21.4; HRMS (ESI) calcd. for $C_{23}H_{19}NO_2SNa^+$ [(M + Na)$^+$] 396.1029, found: 396.1019.

4-(o-tolyl)-3-tosylquinoline (3p)



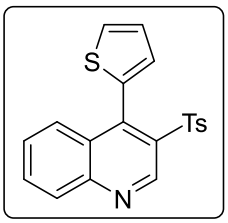
Light yellow solid (78%, 58.3 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 157 – 159 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.79 (s, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.45 – 7.32 (m, 2H), 7.17 (dd, *J* = 18.7, 8.1 Hz, 5H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.81 (d, *J* = 7.5 Hz, 1H), 2.33 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.8, 149.6, 148.1, 144.3, 137.6, 137.0, 132.4, 132.3, 132.2, 130.2, 129.8, 129.8, 129.3, 129.2, 128.3, 128.1 127.0, 126.9, 125.2, 21.6, 19.6; HRMS (ESI) calcd. for $C_{23}H_{19}NO_2SNa^+$ [(M + Na)$^+$] 396.1029, found: 396.1031.

4-(naphthalen-1-yl)-3-tosylquinoline (3q)



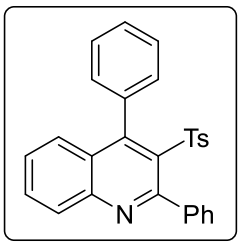
Light yellow solid (70%, 57.3 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 150 - 152 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.93 (s, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.79 (t, *J* = 7.0 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 7.0 Hz, 1H), 7.29 (dd, *J* = 14.4, 7.2 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.97 – 6.79 (m, 3H), 6.60 (d, *J* = 7.9 Hz, 2H), 6.30 (d, *J* = 8.4 Hz, 1H), 2.07 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.7, 148.6, 148.1, 143.8, 136.6, 134.1, 132.9, 132.4, 131.6, 129.9, 129.8, 128.9, 128.1, 127.9, 127.8, 127.7, 126.3, 125.6, 125.5, 125.1, 21.4; HRMS (ESI) calcd. for $C_{26}H_{20}NO_2S^+$ [(M + H)$^+$] 410.1209, found: 410.1185.

4-(thiophen-2-yl)-3-tosylquinoline (3r)[3]



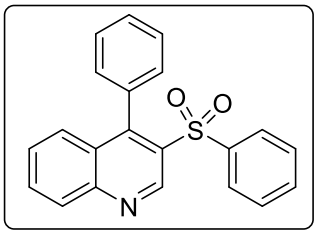
Light yellow solid (68%, 49.7 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 155 – 157 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.81 (s, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 7.83 (t, *J* = 7.4 Hz, 1H), 7.63 – 7.46 (m, 3H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.2 Hz, 3H), 7.04 – 6.95 (m, 1H), 2.36 (s, 3H); HRMS (ESI) calcd. for $C_{20}H_{16}NO_2S_2^+$ [(M + H)$^+$] 366.0617, found: 366.0598.

2,4-diphenyl-3-tosylquinoline (3s)



Light yellow solid (80%, 69.7 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 181 – 186 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.5 Hz, 1H), 7.88 – 7.76 (m, 1H), 7.55 (d, *J* = 6.4 Hz, 2H), 7.50 – 7.35 (m, 7H), 7.27 (d, *J* = 6.6 Hz, 3H), 6.95 (d, *J* = 8.1 Hz, 2H), 6.87 (d, *J* = 7.9 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.8, 151.3, 147.6, 143.0, 141.0, 139.2, 135.0, 133.4, 132.1, 130.2, 129.6, 129.5, 128.9, 128.5, 127.8, 127.7, 127.6, 127.4, 127.2, 126.6, 21.5; HRMS (ESI) calcd. for $C_{28}H_{21}NNaO_2S^+$ [(M + Na)$^+$] 458.1185, found: 458.1184.

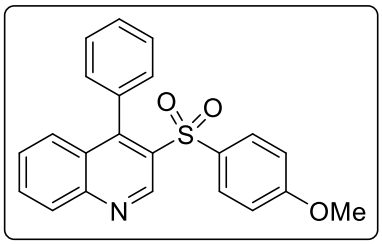
4-phenyl-3-(phenylsulfonyl)quinoline (4a)[1b]



Light yellow solid (75%, 51.8 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 188 – 190 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.81 (s, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.83 (t, *J* = 7.6 Hz, 1H), 7.53 – 7.39 (m, 3H), 7.38 – 7.15 (m, 7H), 6.93 (d, *J* = 7.6 Hz, 2H); HRMS (ESI)

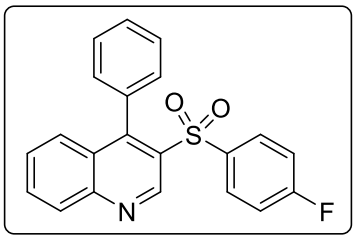
calcd. for $C_{21}H_{16}NO_2S^+$ [(M + H)$^+$] 346.0896, found: 346.0878.

3-((4-methoxyphenyl)sulfonyl)-4-phenylquinoline (4b)[1b]



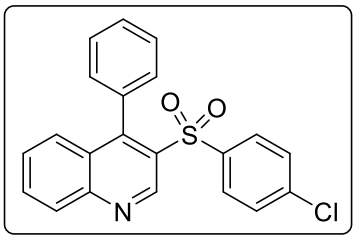
Light yellow solid (92%, 69.1 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 169 – 170 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.78 (s, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.81 (t, *J* = 7.6 Hz, 1H), 7.51 – 7.40 (m, 2H), 7.39 – 7.29 (m, 3H), 7.22 (d, *J* = 8.9 Hz, 2H), 6.98 (d, *J* = 7.2 Hz, 2H), 6.70 (d, *J* = 8.9 Hz, 2H), 3.80 (s, 3H); HRMS (ESI) calcd. for $C_{22}H_{18}NO_3S^+$ [(M + H)$^+$] 376.1002, found: 376.0981.

3-((4-fluorophenyl)sulfonyl)-4-phenylquinoline (4c)[1b]



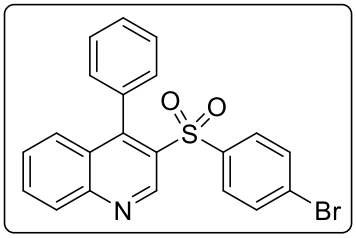
Light yellow solid (63%, 45.8 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 181 – 182 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.79 (s, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.82 (t, *J* = 7.4 Hz, 1H), 7.51 – 7.41 (m, 2H), 7.39 – 7.22 (m, 5H), 7.03 – 6.82 (m, 4H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -103.92 (s); HRMS (ESI) calcd. for $C_{21}H_{15}FNO_2S^+$ [(M + H)$^+$] 364.0802, found: 364.0779.

3-((4-chlorophenyl)sulfonyl)-4-phenylquinoline (4d)[1b]



Light yellow solid (59%, 44.8 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 167 – 169 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.78 (s, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 7.89 – 7.77 (m, 1H), 7.55 – 7.42 (m, 2H), 7.41 – 7.28 (m, 5H), 7.18 – 7.07 (m, 2H), 6.95 (d, *J* = 7.5 Hz, 2H); HRMS (ESI) calcd. for $C_{21}H_{15}ClNO_2S^+$ [(M + H)$^+$] 380.0507, found: 380.0505.

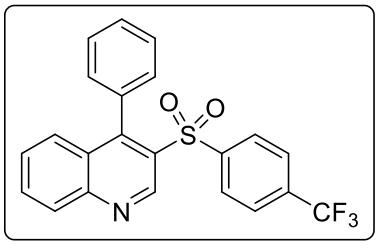
3-((4-bromophenyl)sulfonyl)-4-phenylquinoline (4e)[1b]



Light yellow solid (62%, 52.6 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 253 – 255 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.80 (s, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 7.90 – 7.80 (m, 1H), 7.54 – 7.44 (m, 2H), 7.43 – 7.31 (m, 5H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.97 (d,

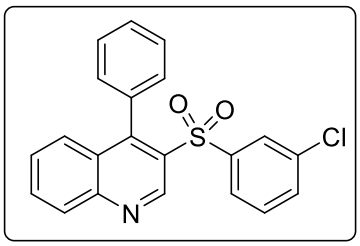
J = 7.2 Hz, 2H); HRMS (ESI) calcd. for $C_{21}H_{15}BrNO_2S^+$ [(M + H)$^+$] 424.0001, found: 424.0002.

4-phenyl-3-((4-(trifluoromethyl)phenyl)sulfonyl)quinoline (4f)[1b]



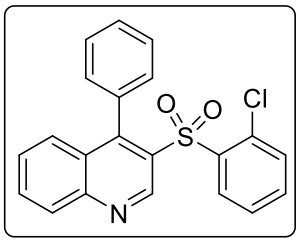
Light yellow solid (55%, 45.5 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 217 – 219 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.82 (s, 1H), 8.24 (d, J = 8.4 Hz, 1H), 7.86 (t, J = 7.6 Hz, 1H), 7.56 – 7.40 (m, 6H), 7.38 – 7.27 (m, 3H), 6.94 (d, J = 7.5 Hz, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.27 (s); HRMS (ESI) calcd. for $C_{22}H_{15}F_3NO_2S^+$ [(M + H)$^+$] 414.0770, found: 414.0770.

3-((3-chlorophenyl)sulfonyl)-4-phenylquinoline (4g)[3]



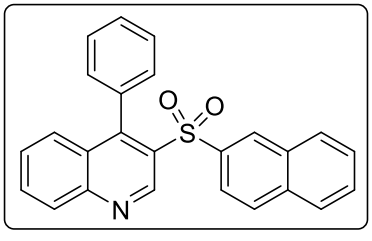
Light yellow solid (62%, 47.1 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 145 – 148 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.78 (s, 1H), 8.22 (d, J = 8.5 Hz, 1H), 7.83 (t, J = 7.6 Hz, 1H), 7.53 – 7.32 (m, 6H), 7.28 – 7.12 (m, 3H), 6.95 (d, J = 7.2 Hz, 2H); HRMS (ESI) calcd. for $C_{21}H_{15}ClNO_2S^+$ [(M + H)$^+$] 380.0507, found: 380.0505.

3-((2-chlorophenyl)sulfonyl)-4-phenylquinoline (4h)[3]



Light yellow solid (48%, 36.5 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 135 – 137 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.84 (s, 1H), 8.24 (d, J = 8.5 Hz, 1H), 7.84 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.39 – 7.23 (m, 5H), 7.17 (t, J = 7.4 Hz, 2H), 7.00 (t, J = 7.6 Hz, 1H), 6.90 (d, J = 7.6 Hz, 2H); HRMS (ESI) calcd. for $C_{21}H_{15}ClNO_2S^+$ [(M + H)$^+$] 380.0507, found: 380.0506.

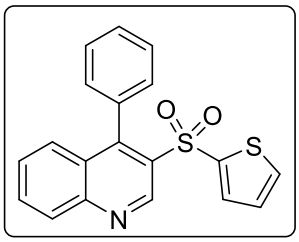
3-(naphthalen-2-ylsulfonyl)-4-phenylquinoline (4i)[1b]



Light yellow solid (63%, 49.8 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 99 – 101 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.21 (d, J = 8.5 Hz, 1H), 7.84 – 7.50 (m, 7H), 7.45 – 7.25 (m, 4H), 7.16 (t, J = 7.7 Hz, 2H), 6.86 (d, J = 7.3 Hz, 2H);

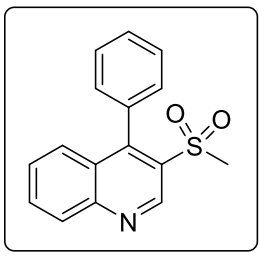
HRMS (ESI) calcd. for $C_{25}H_{18}NO_2S^+$ [(M + H)$^+$] 396.1053, found: 396.1055.

4-phenyl-3-(thiophen-2-ylsulfonyl)quinoline (4j)[3]



Light yellow solid (60%, 42.2 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 138 – 140 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.73 (s, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.83 (t, *J* = 7.6 Hz, 1H), 7.57 – 7.34 (m, 6H), 7.08 (d, *J* = 7.2 Hz, 2H), 7.00 – 6.91 (m, 1H), 6.89 – 6.79 (m, 1H); HRMS (ESI) calcd. for $C_{19}H_{14}NO_2S_2^+$ [(M + H)$^+$] 352.0460, found: 352.0459.

3-(methylsulfonyl)-4-phenylquinoline (4k)



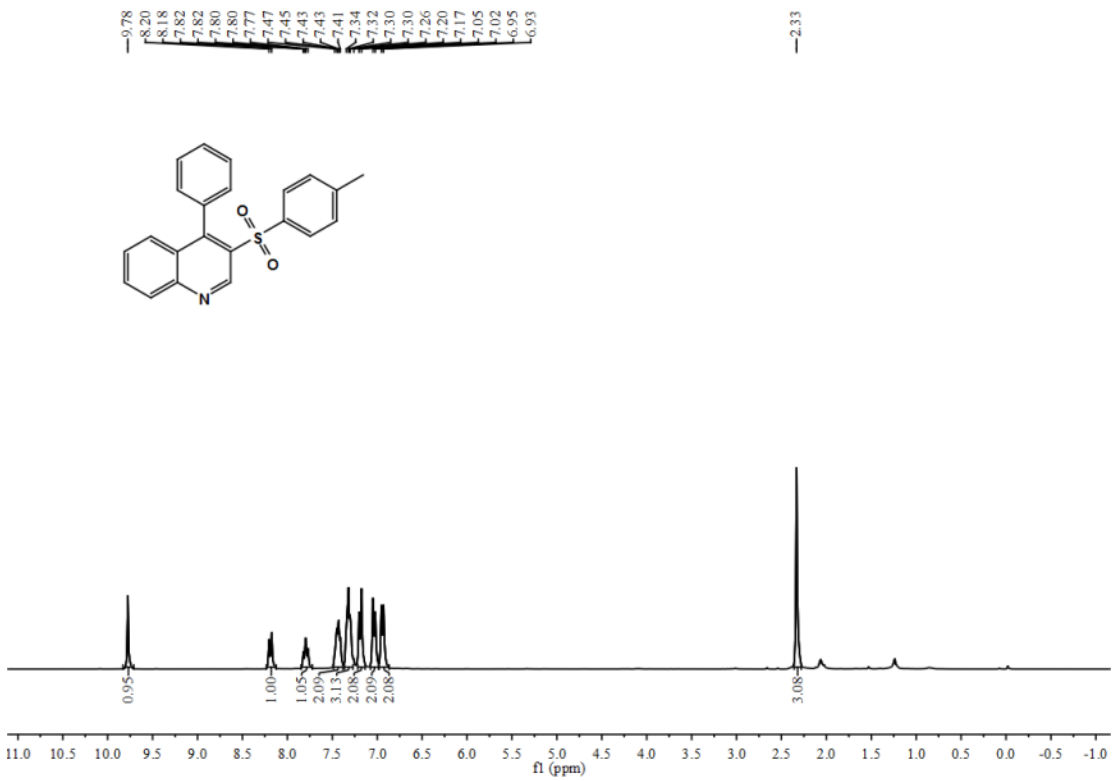
Light yellow solid (82%, 46.5 mg, eluent: petroleum ether/ethyl acetate = 10/1), mp 133 – 135 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.56 (s, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 7.85 (t, *J* = 7.6 Hz, 1H), 7.60 – 7.49 (m,, 4H), 7.49 – 7.39 (m, 3H), 2.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 149.7, 147.6, 133.1, 132.5, 131.8, 130.2, 129.9, 129.6, 128.4, 128.2, 127.8, 127.3, 44.6; HRMS (ESI) calcd. for $C_{16}H_{14}NO_2S^+$ [(M + H)$^+$] 284.0740, found: 284.0740.

References:

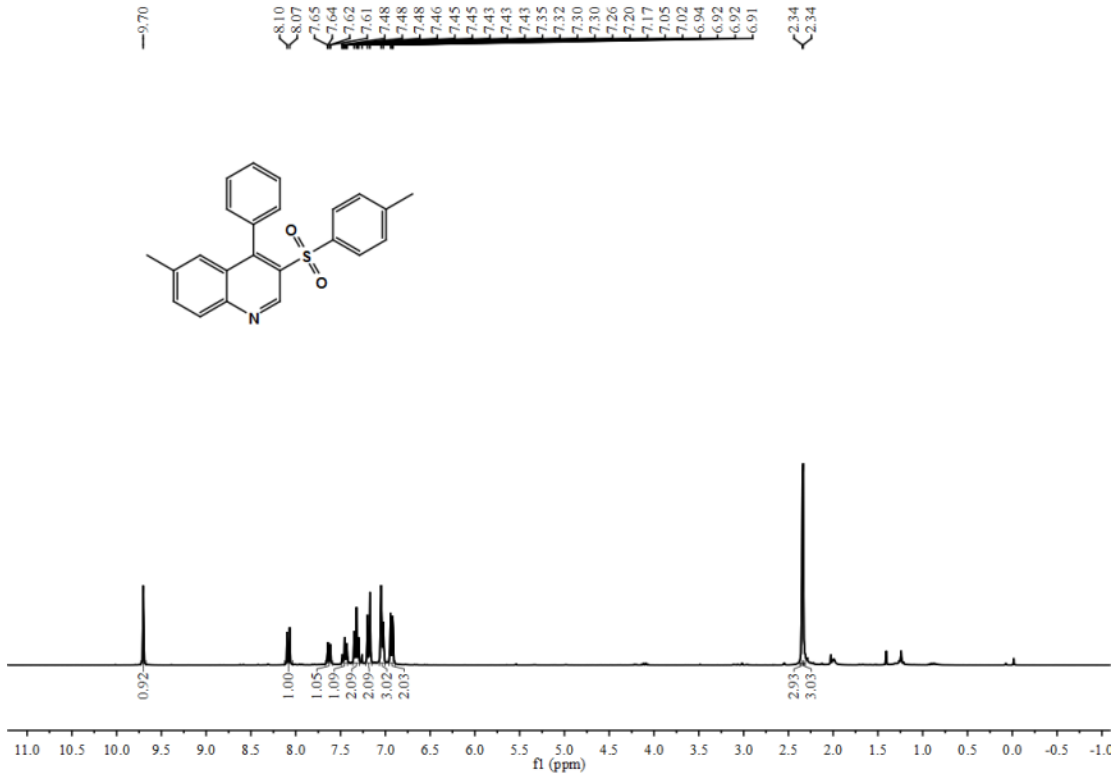
1 (a) L.-C. Hong, Y.-L. Shao, L.-X. Zhang and X.-G. Zhou, *Chem. Eur. J.*, 2014, **20**, 8551; (b) L.-L. Zhang, S. Chen, Y.-Z. Gao, P.-B. Zhang, Y.-L. Wu, G. Tang, and Y.-F. Zhao, *Org. Lett.*, 2016, **18**, 1286.

2 (a) L. Liu, Y. Chi and K. Jen, *J. Org. Chem.*, 1980, **45**, 406; (b) X. Zhou, J. Luo, J. Liu, S. Peng and G.-J. Deng, *Org. Lett.*, 2011, **13**, 1432.

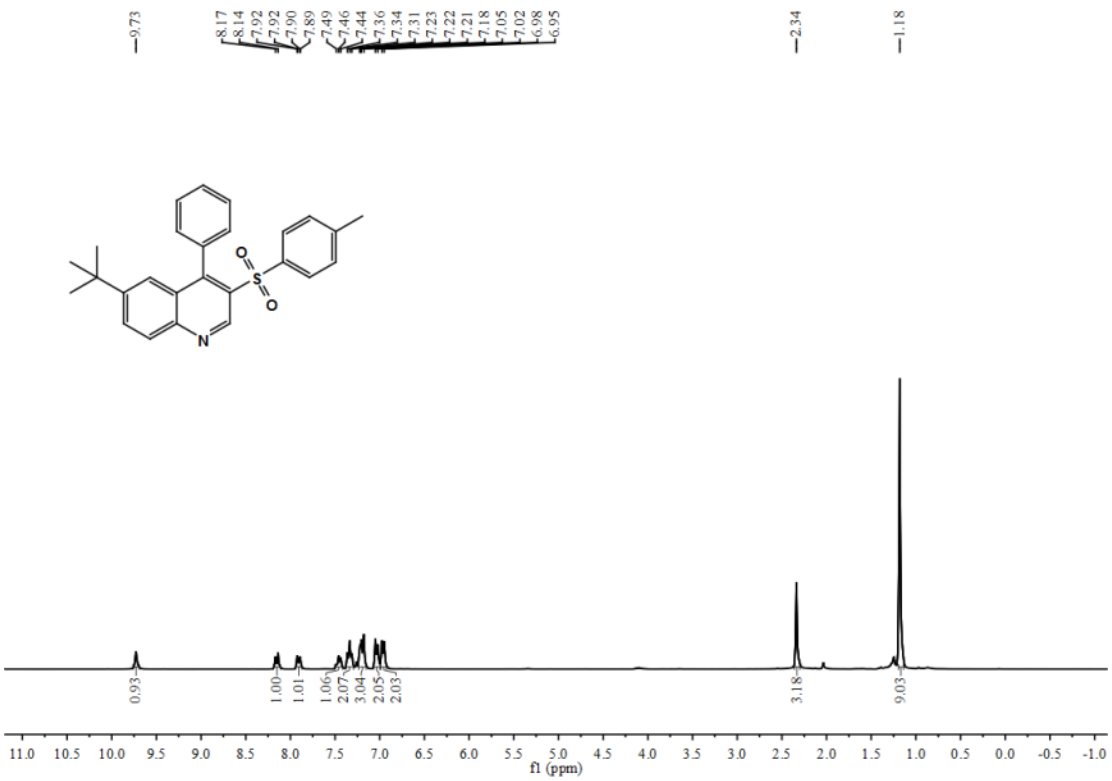
3 Y. Zhang, W. Chen, X. Jia, L. Wang and P. Li, *Chem. Commun.*, 2019, **55**, 2785.



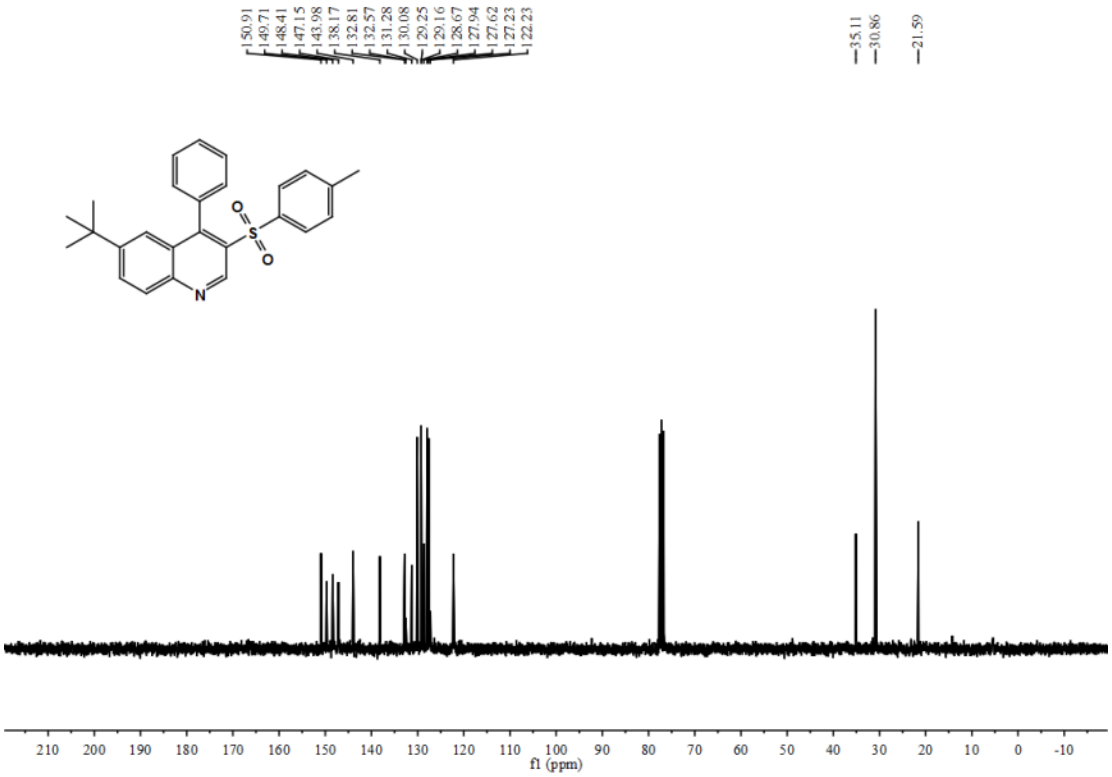
H[1] NMR of **3a**



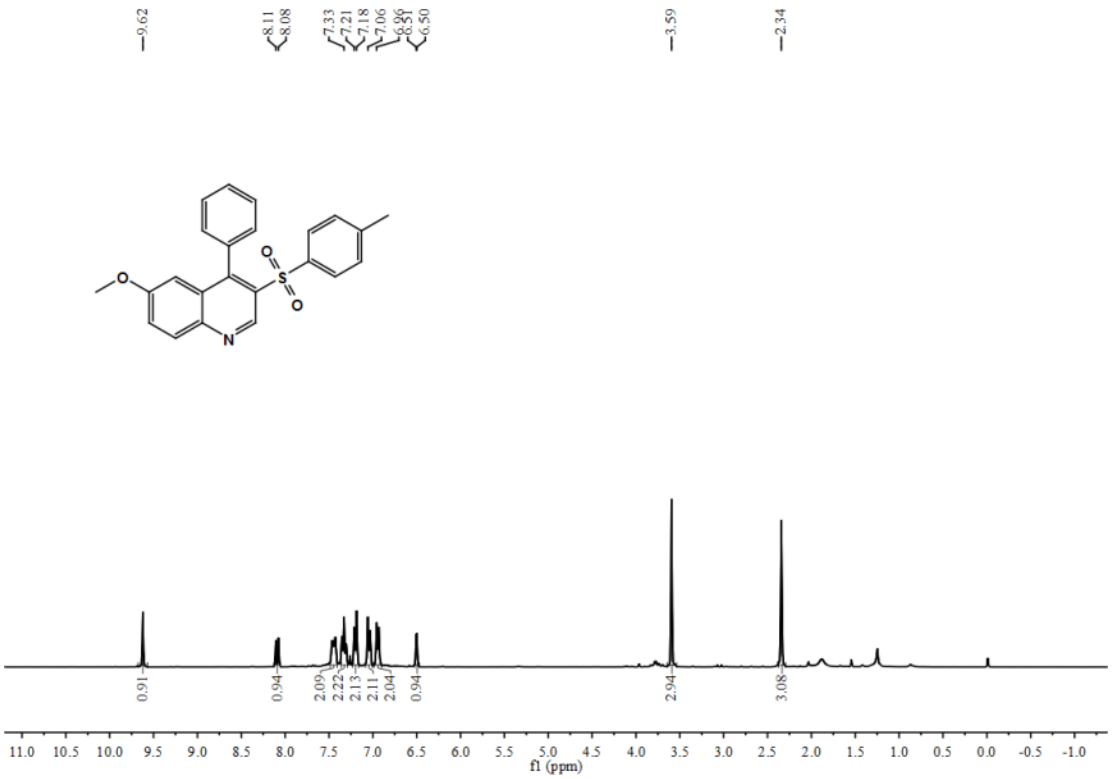
H[1] NMR of **3b**



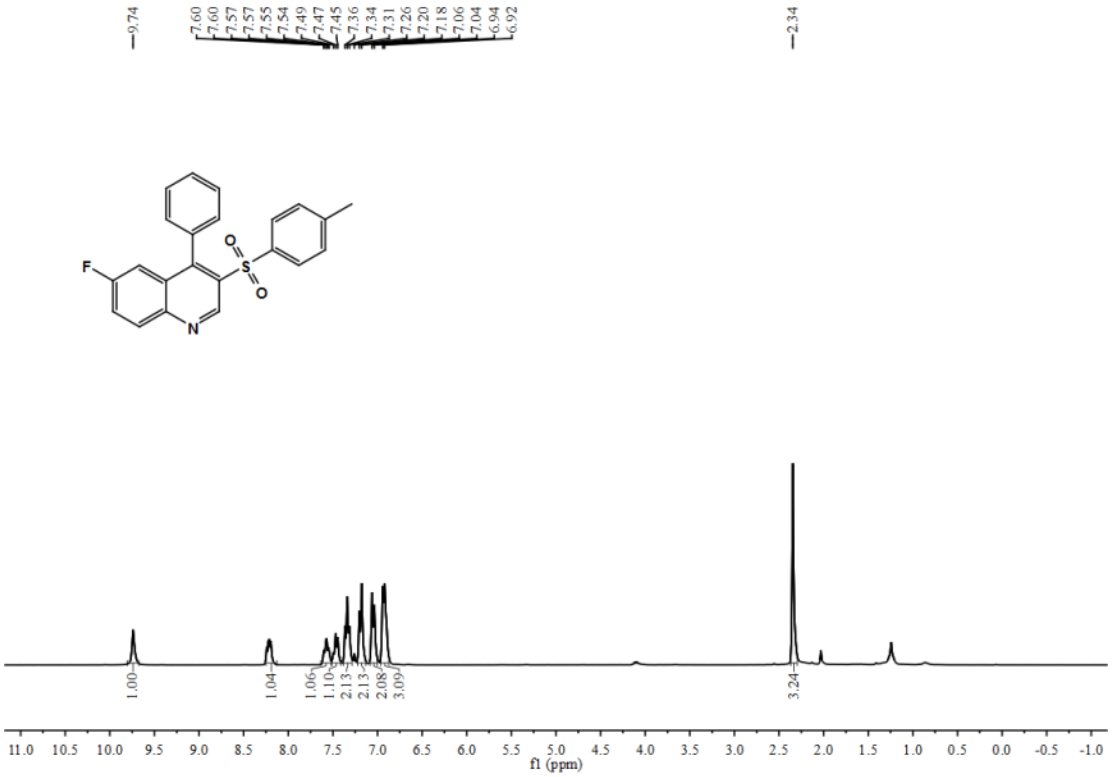
H^1 NMR of **3c**



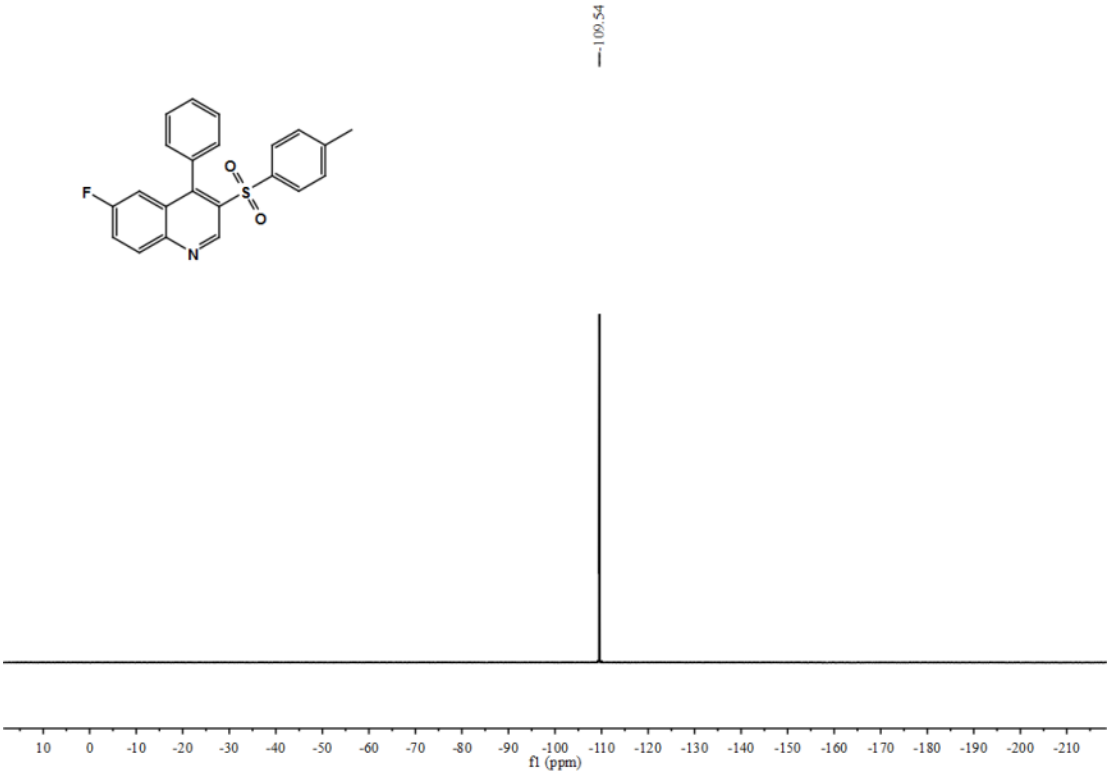
C^{13} NMR of **3c**



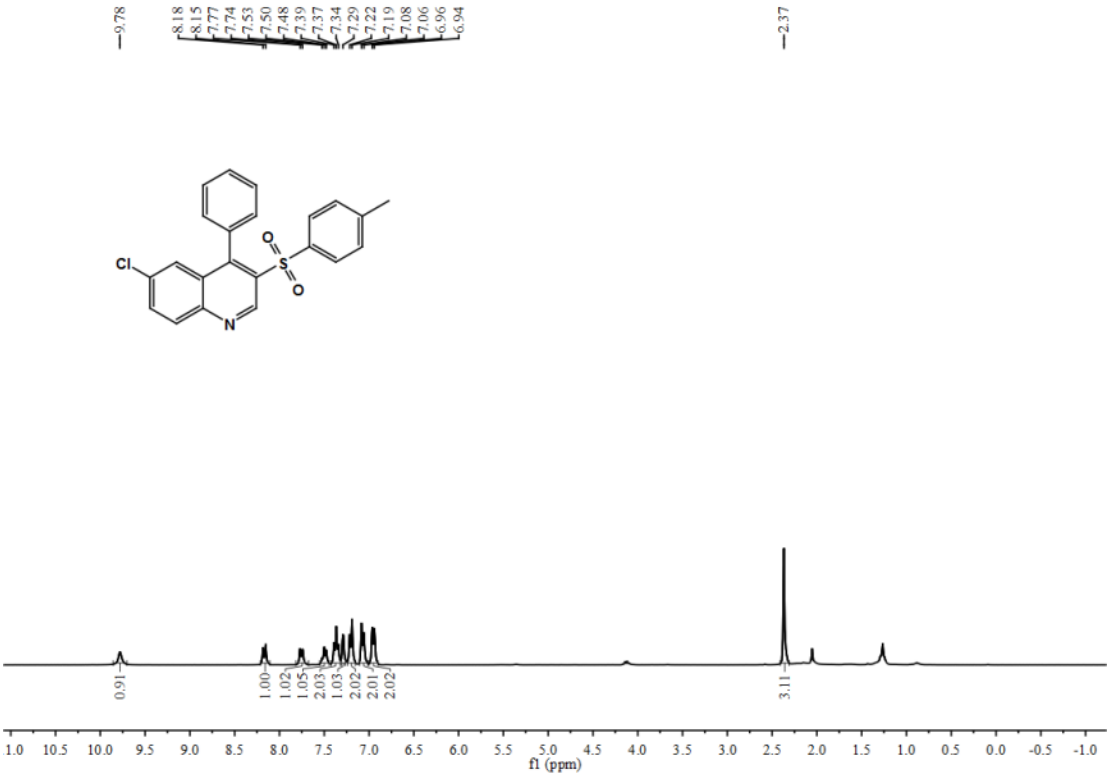
H[1] NMR of **3d**



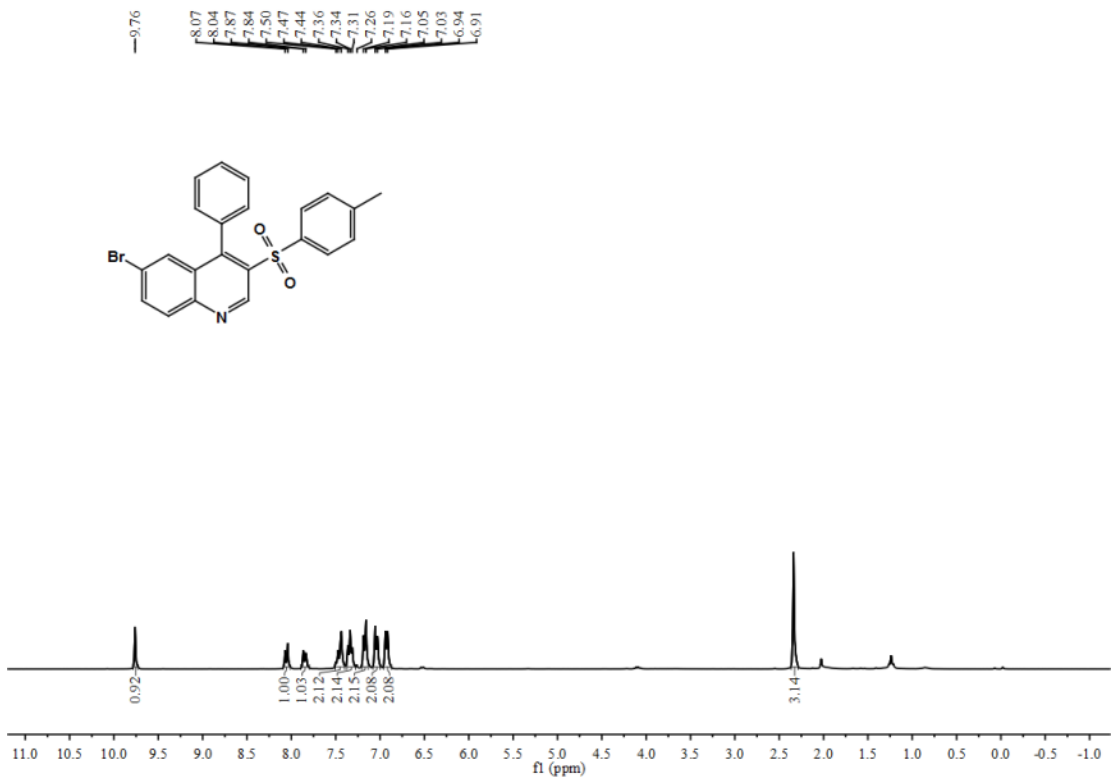
H[1] NMR of **3e**



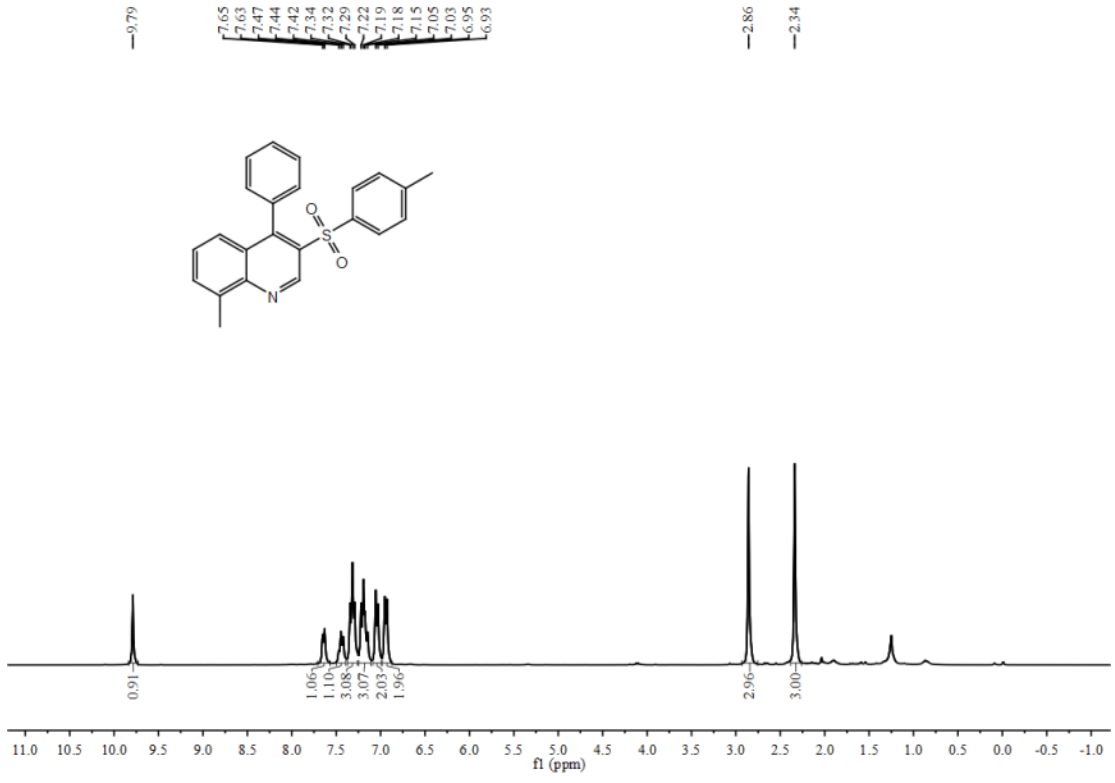
F^{19} NMR of **3e**



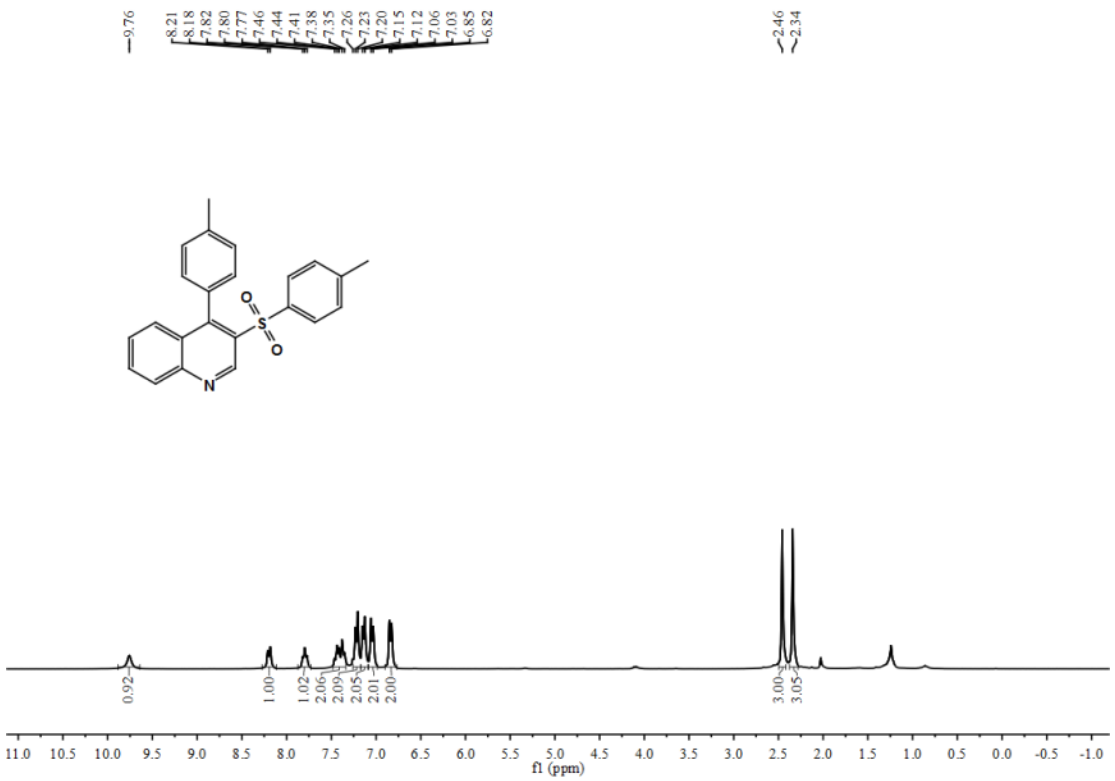
H^{1} NMR of **3f**



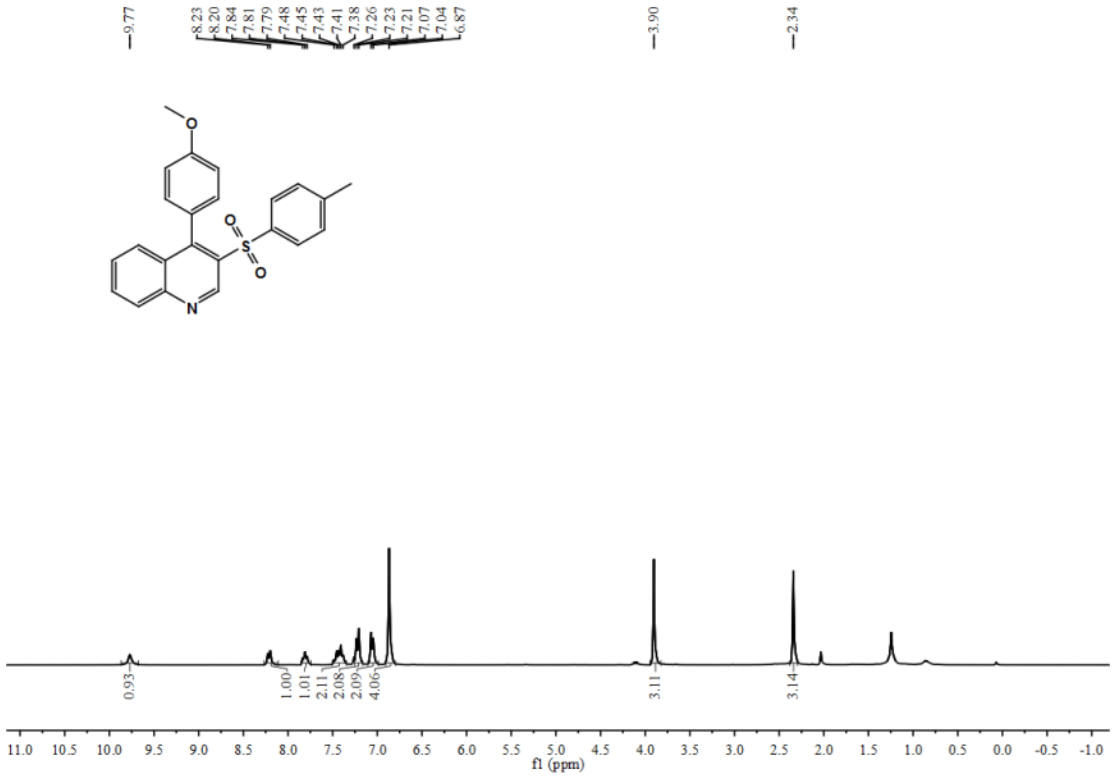
H[1] NMR of **3g**



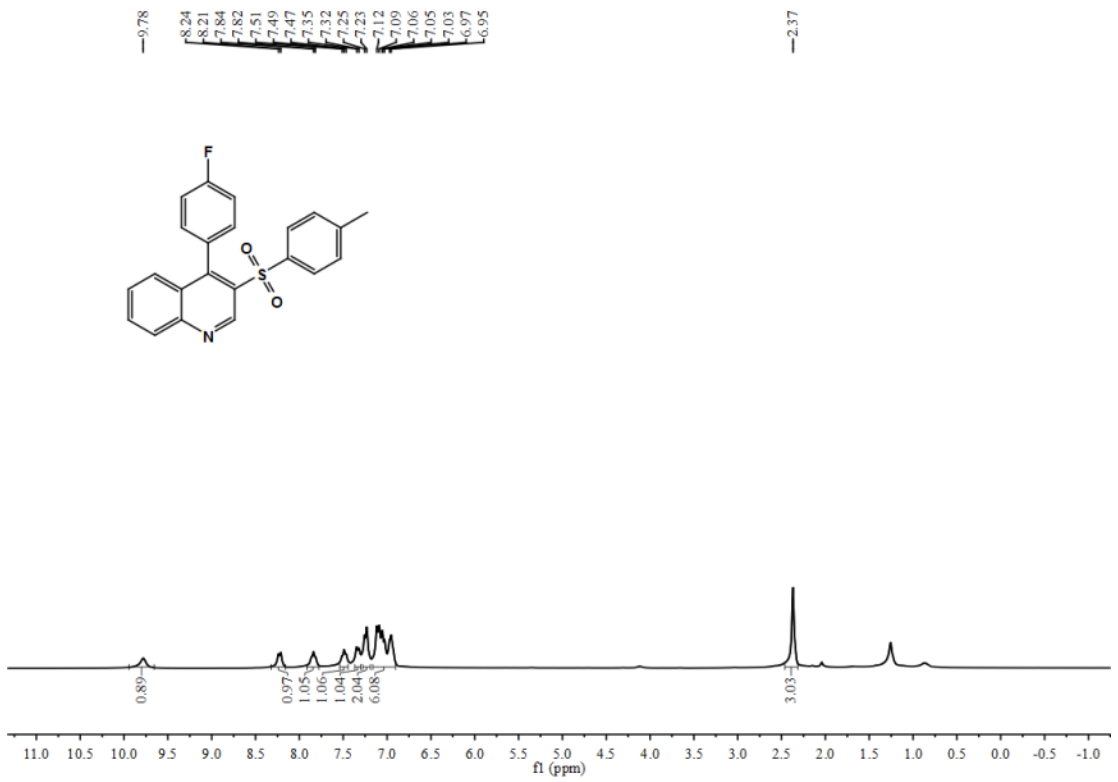
H[1] NMR of **3h**



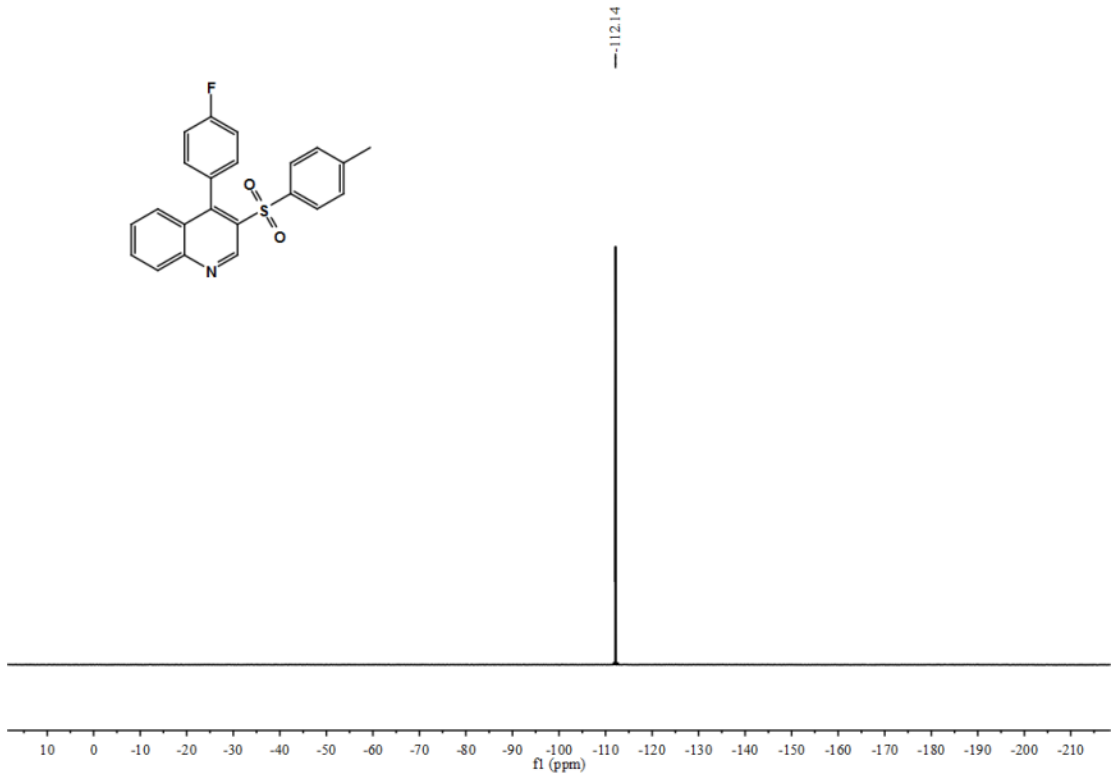
H^1 NMR of **3i**



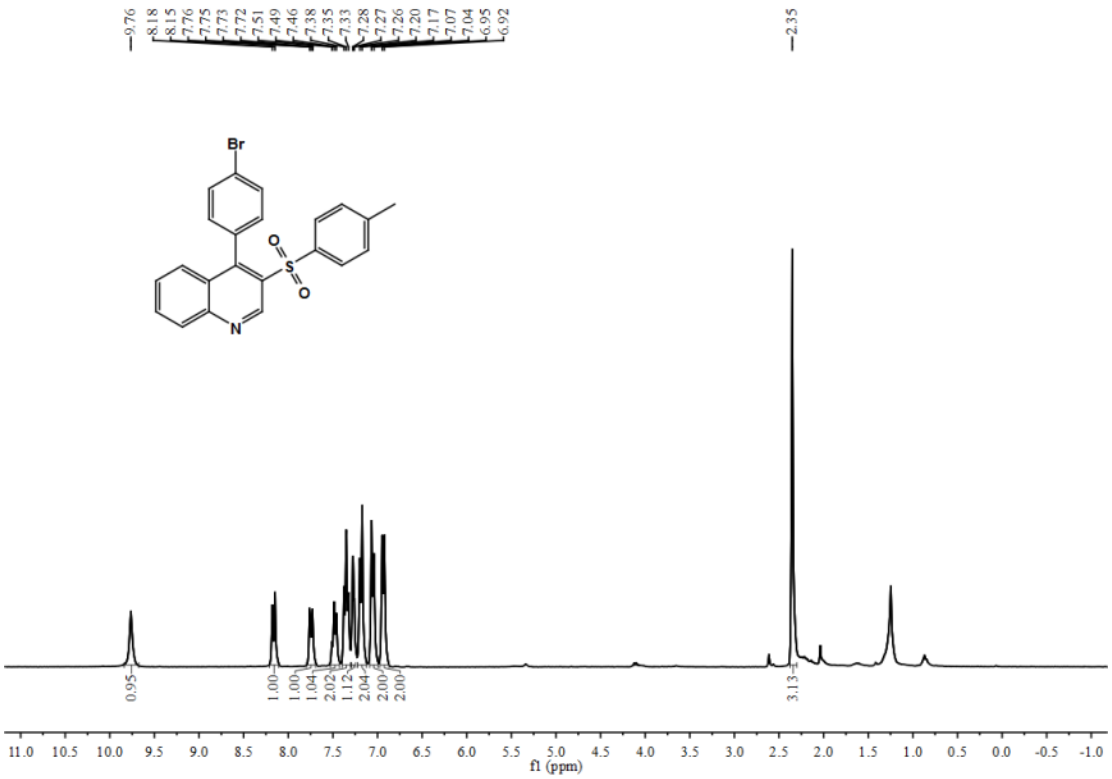
H^1 NMR of **3j**



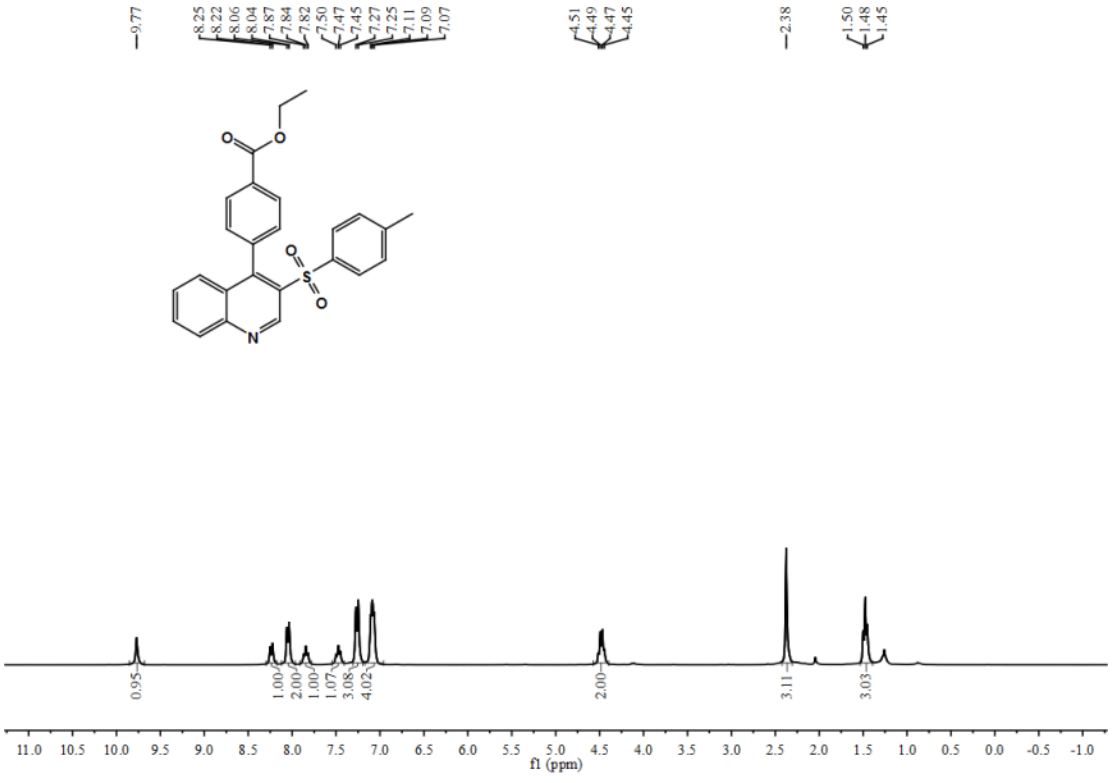
H^1 NMR of **3k**



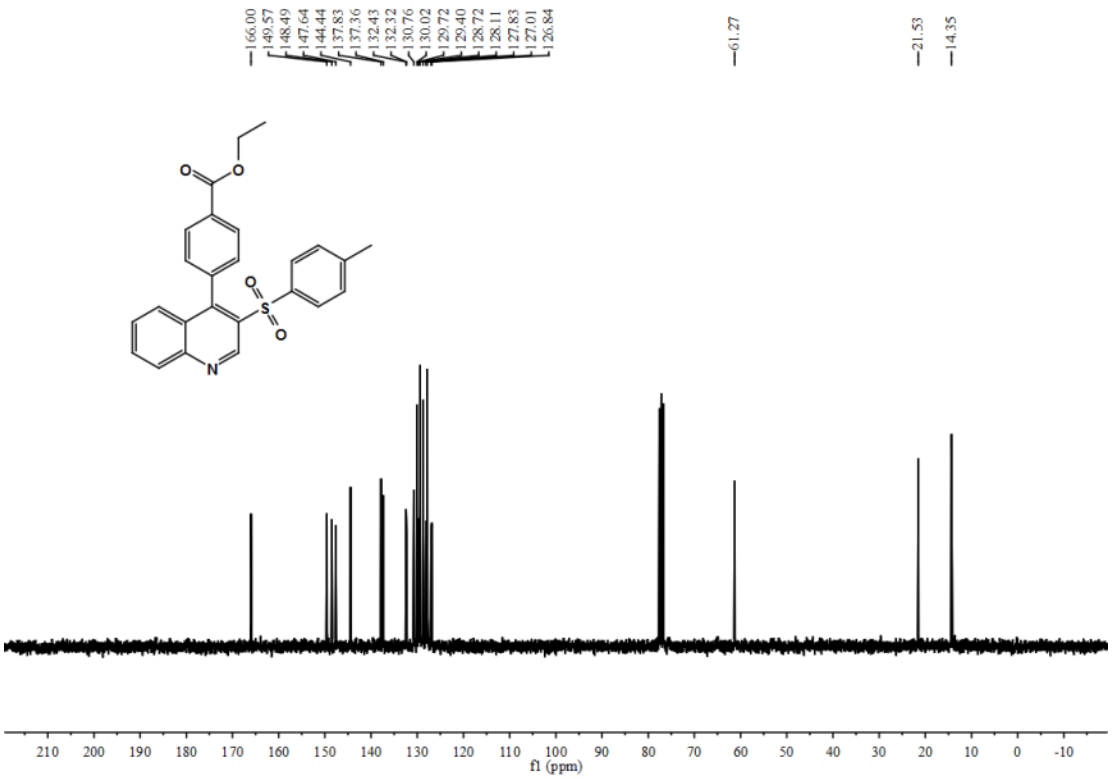
F^{19} NMR of **3k**



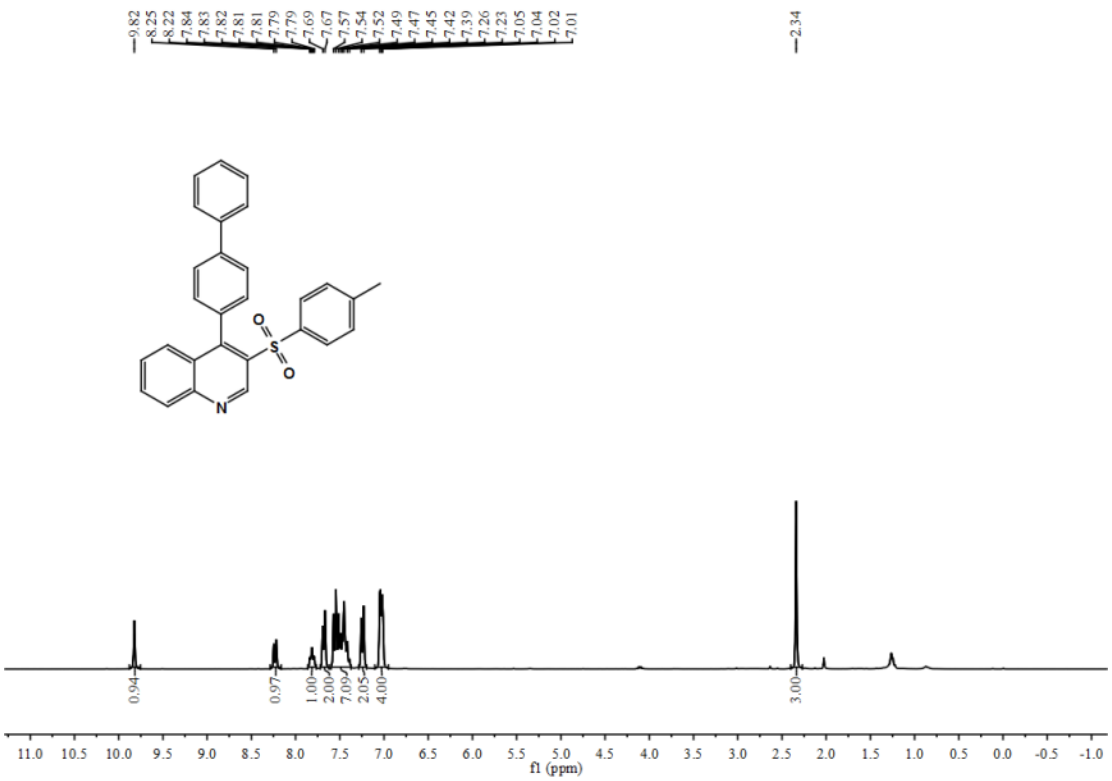
H^1 NMR of **3l**



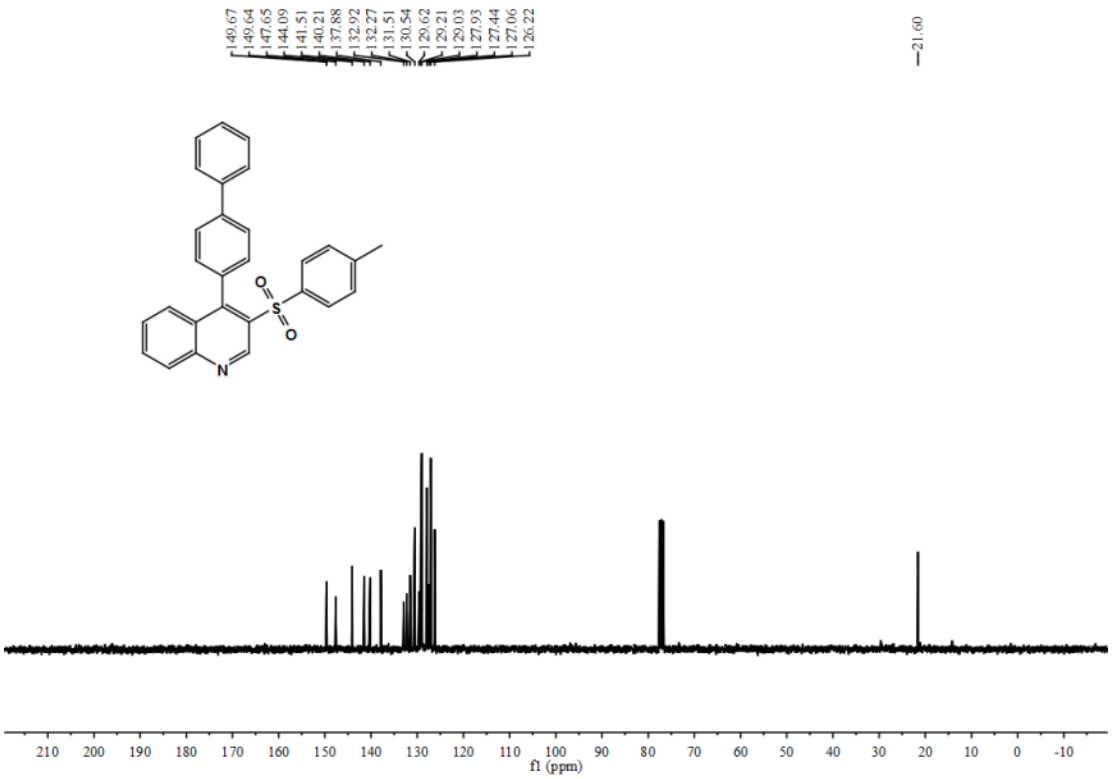
H^1 NMR of **3m**



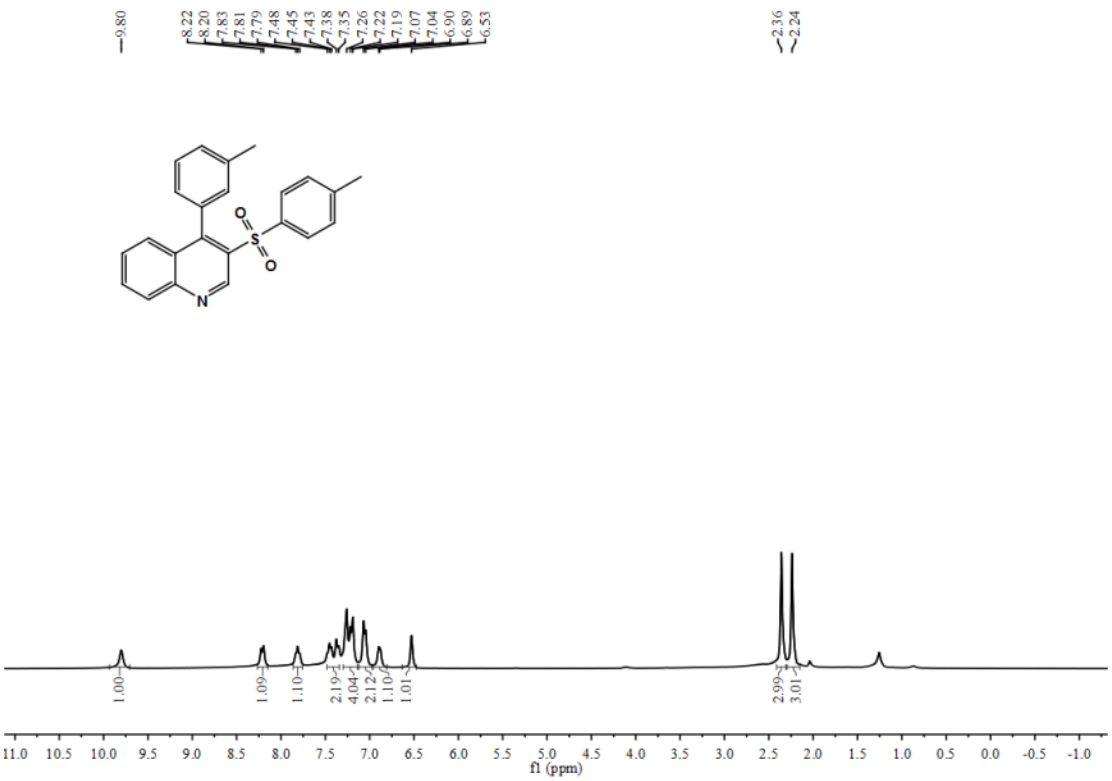
C^{13} NMR of **3m**



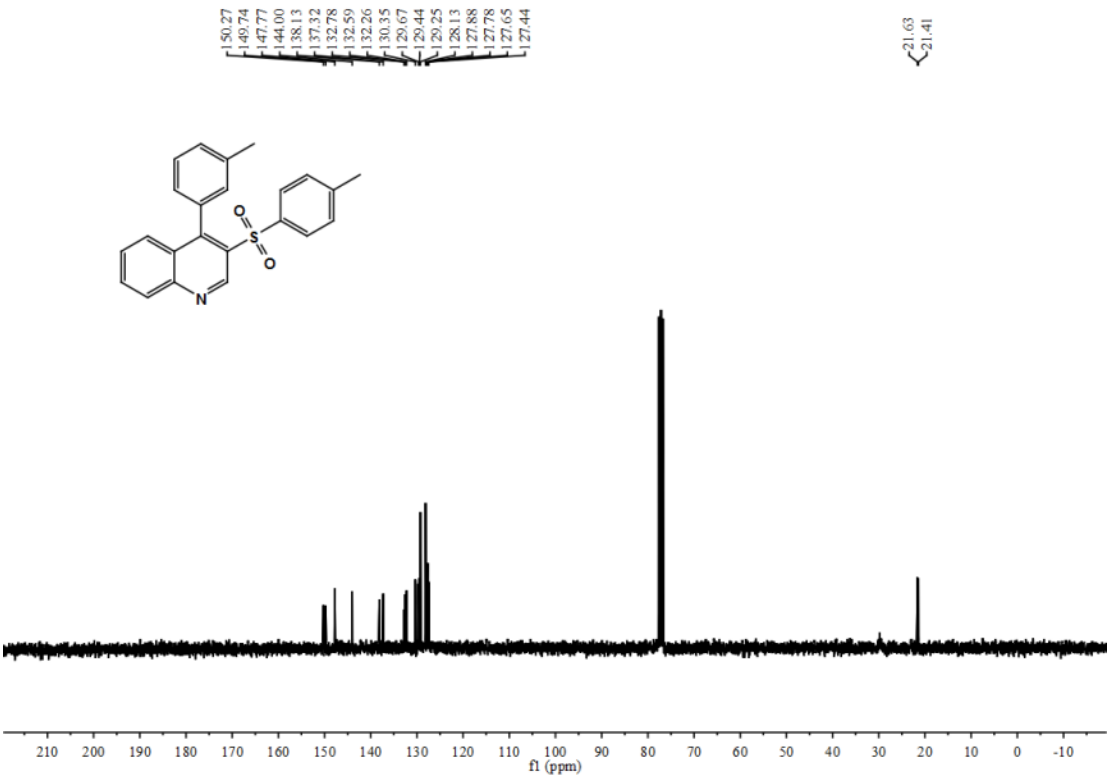
H^{1} NMR of **3n**



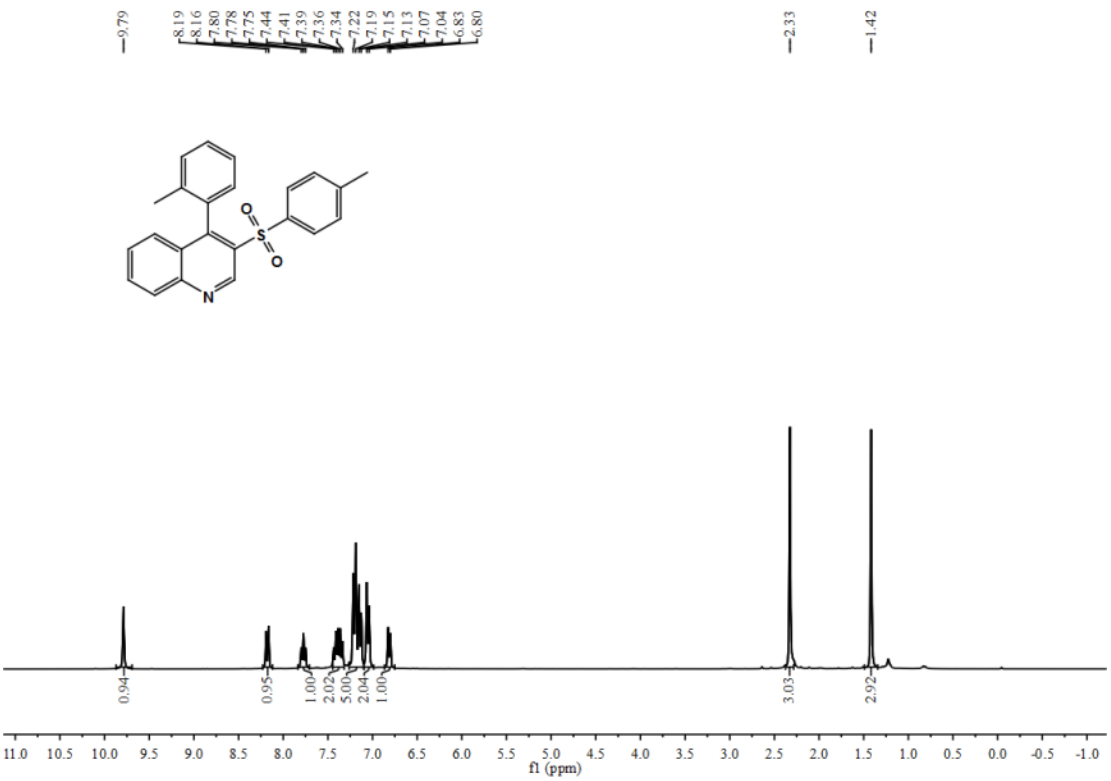
C^{13} NMR of **3n**



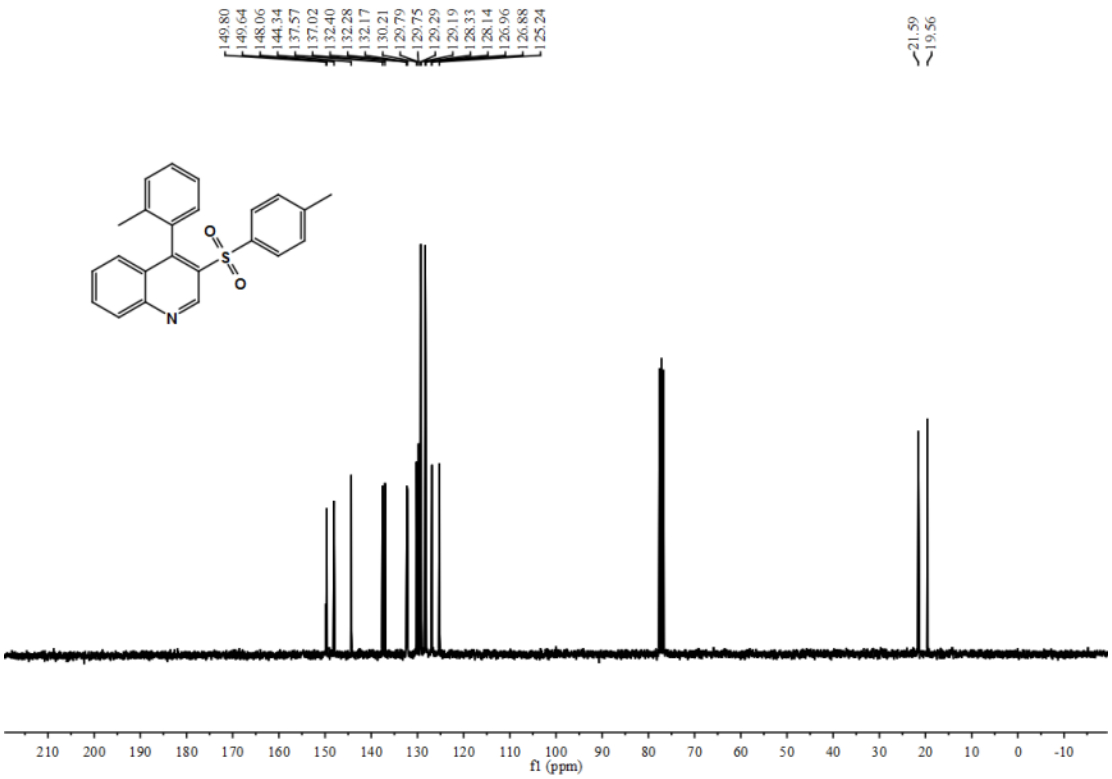
H^{1} NMR of **3o**



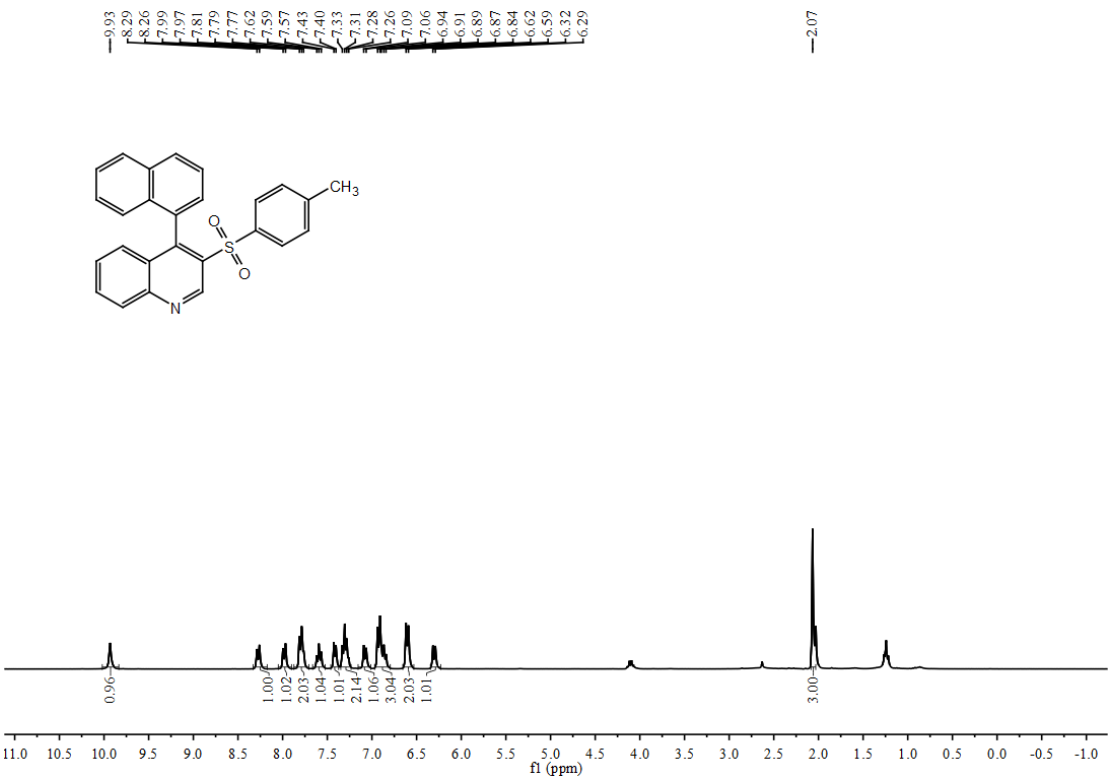
C^{13} NMR of **3o**



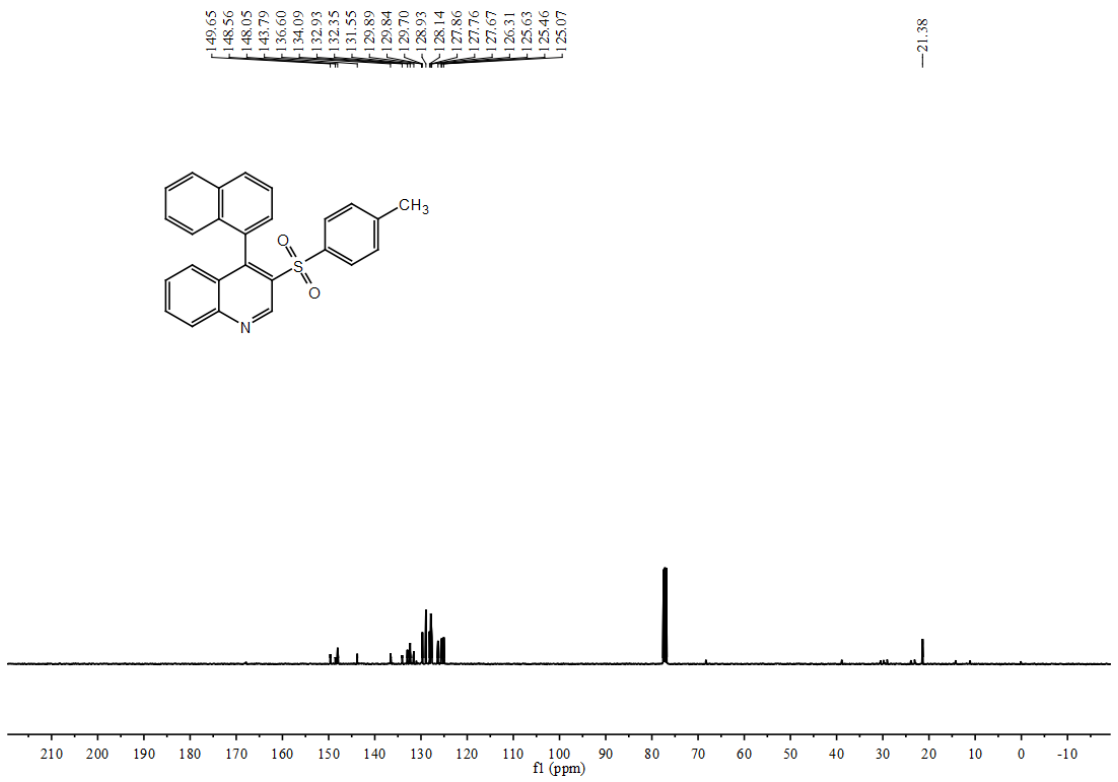
H^{1} NMR of **3p**



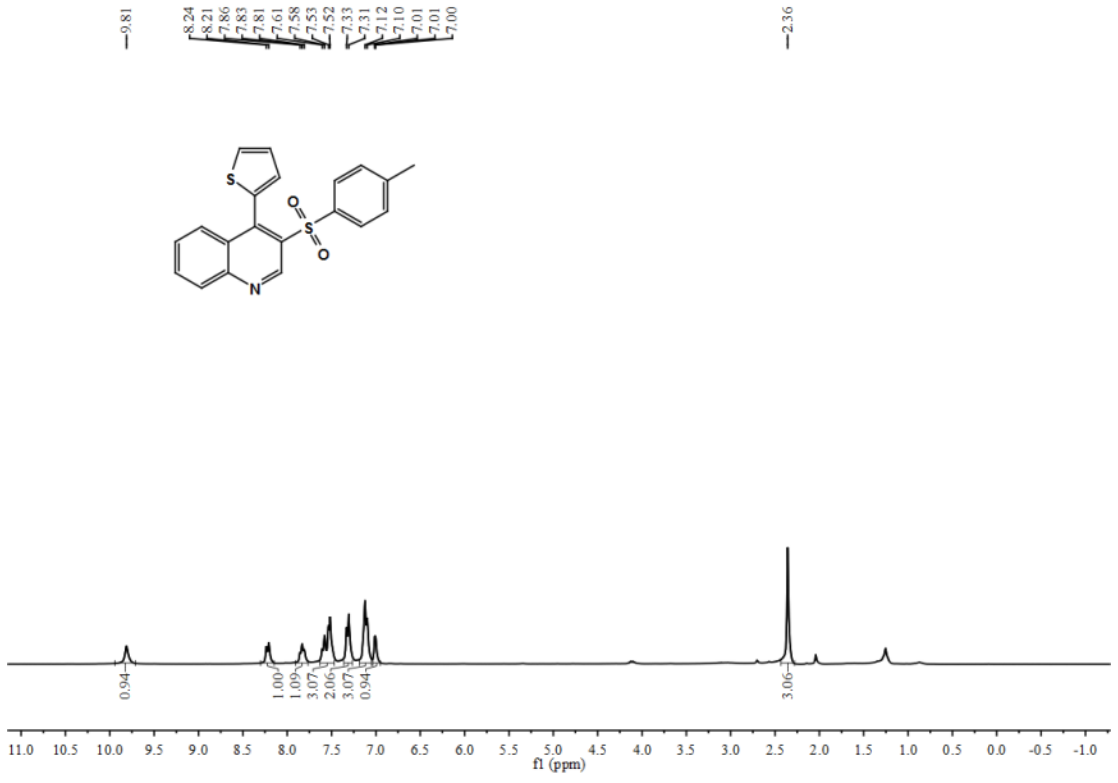
C^{13} NMR of **3p**



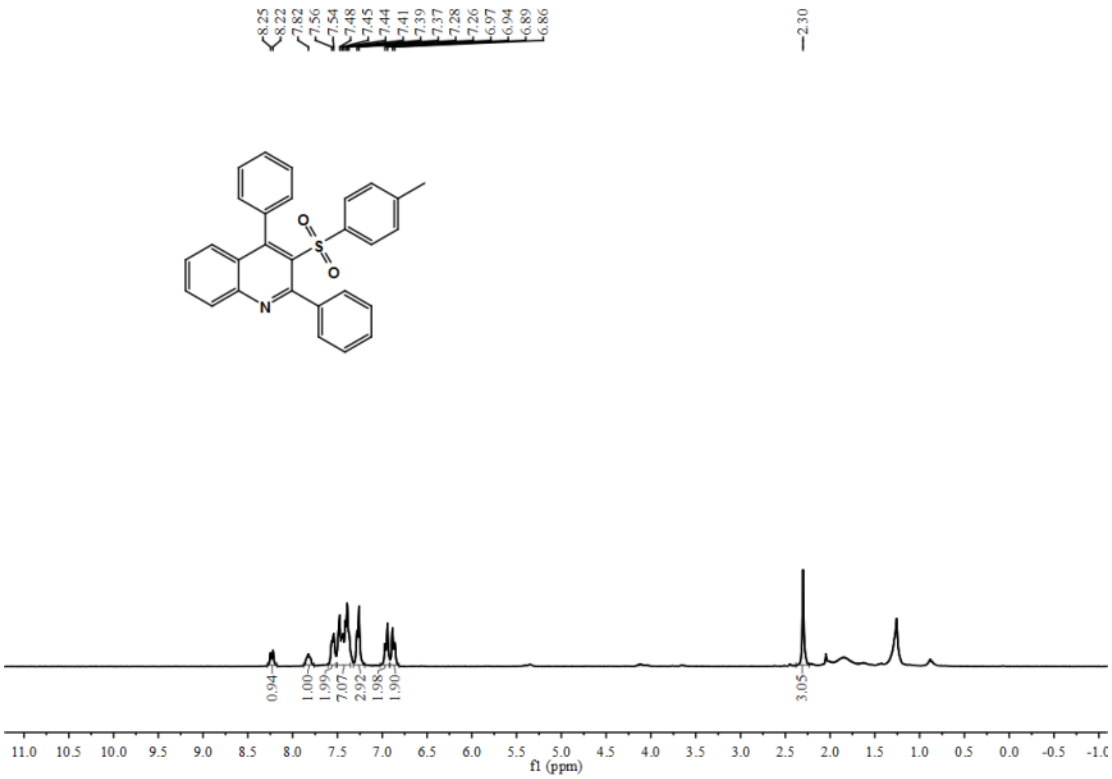
H^{1} NMR of **3q**



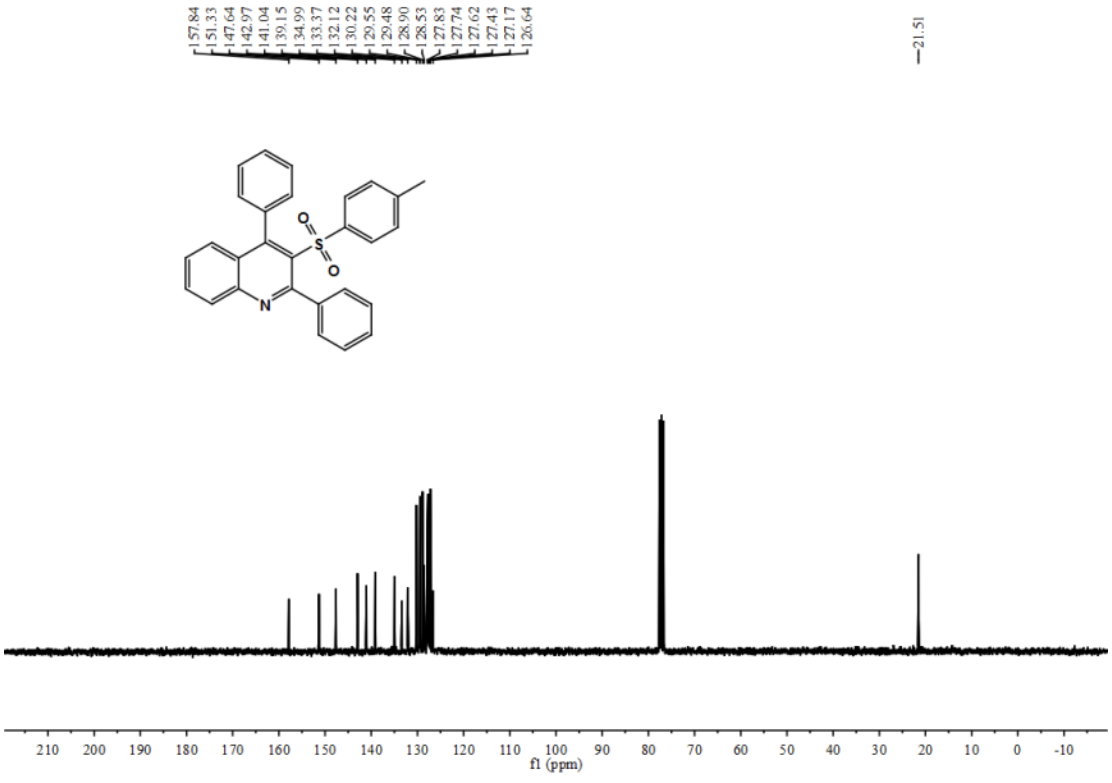
C[13] NMR of **3q**



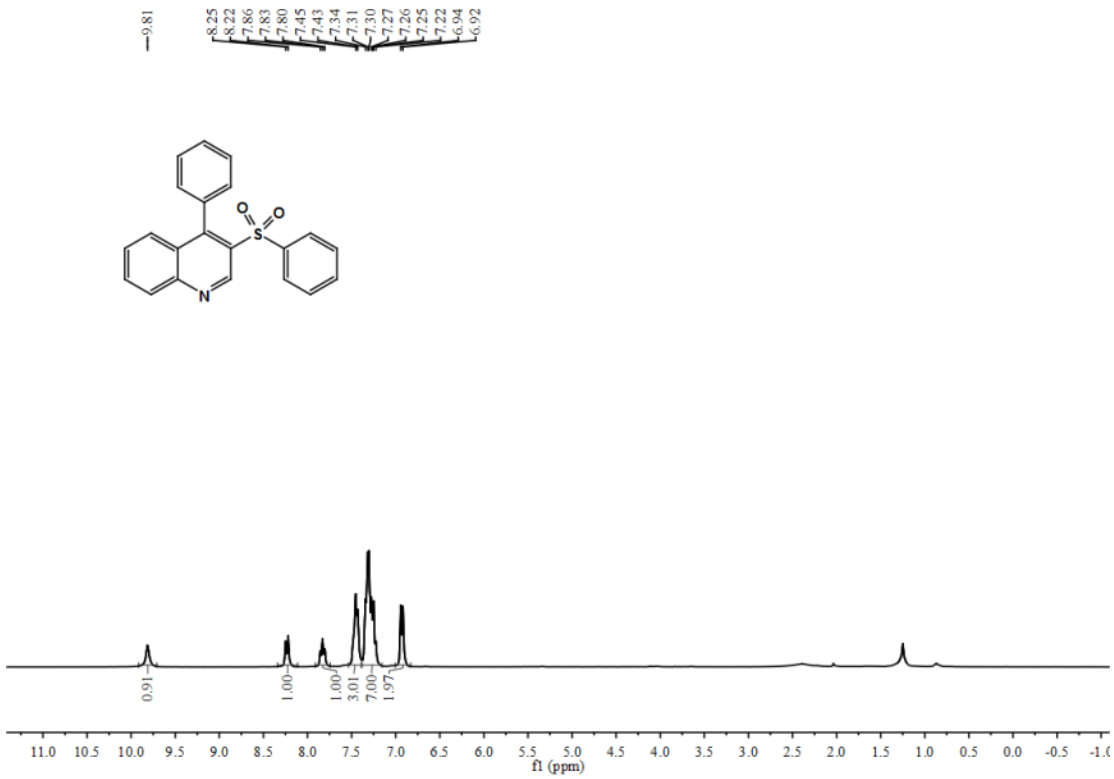
H[1] NMR of **3r**



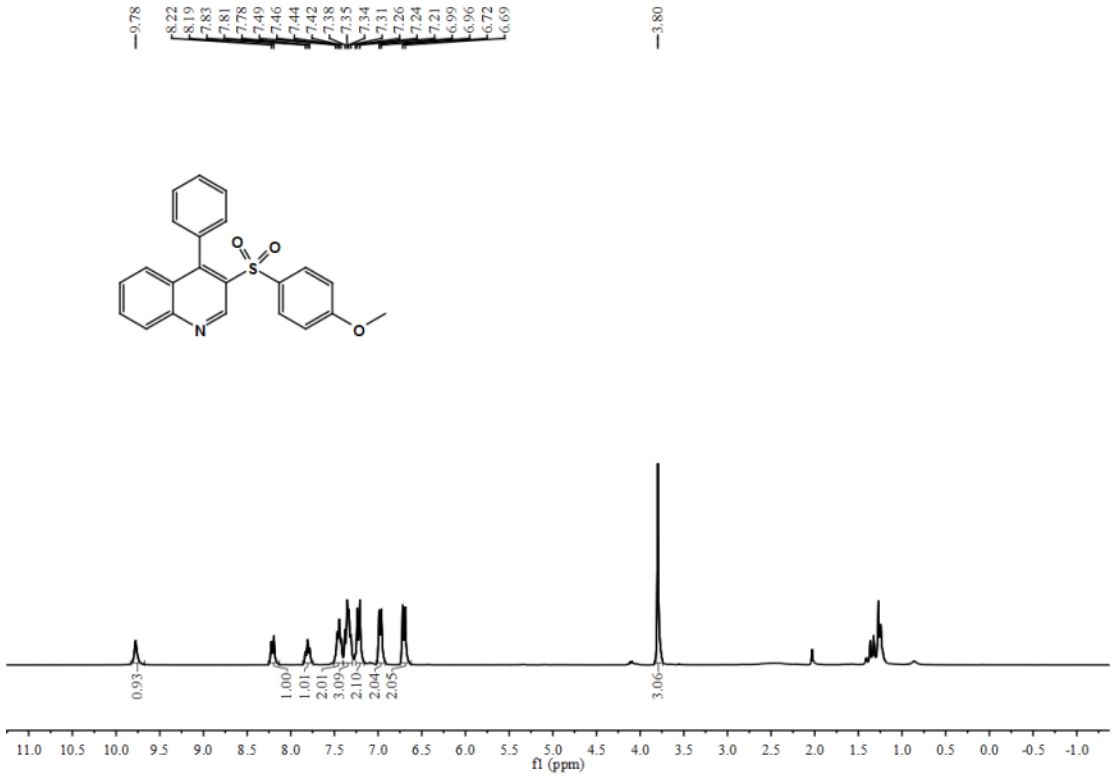
H[1] NMR of **3s**



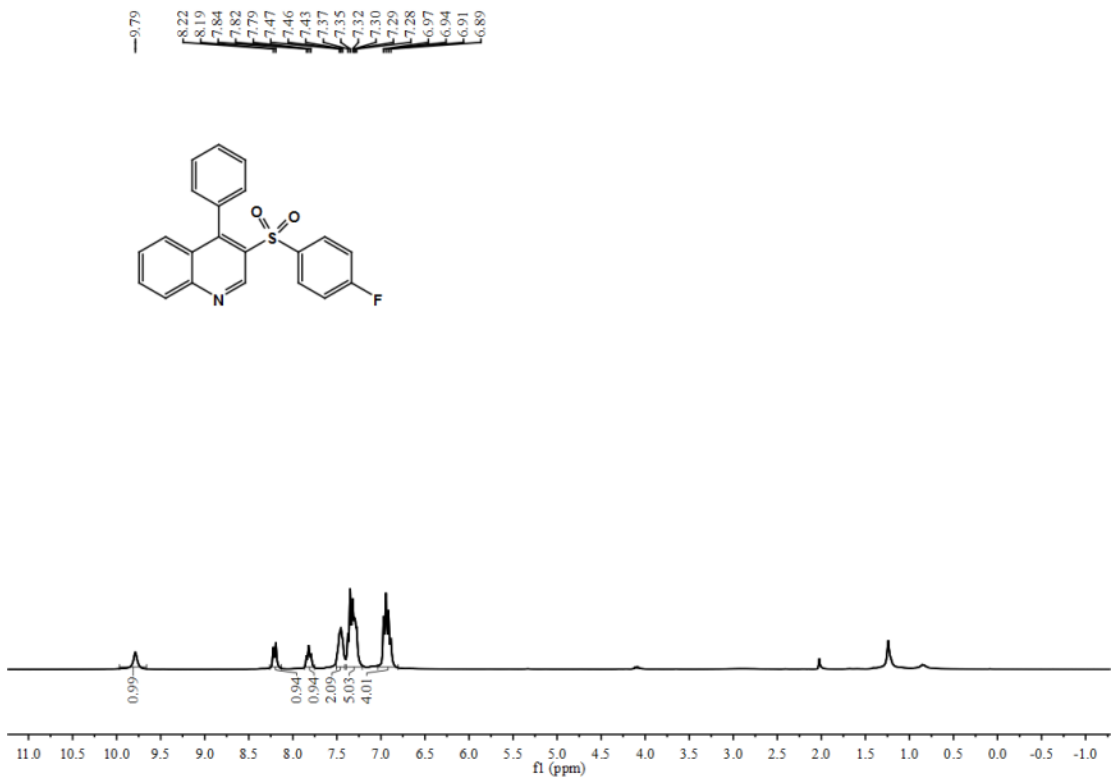
C[13] NMR of **3s**



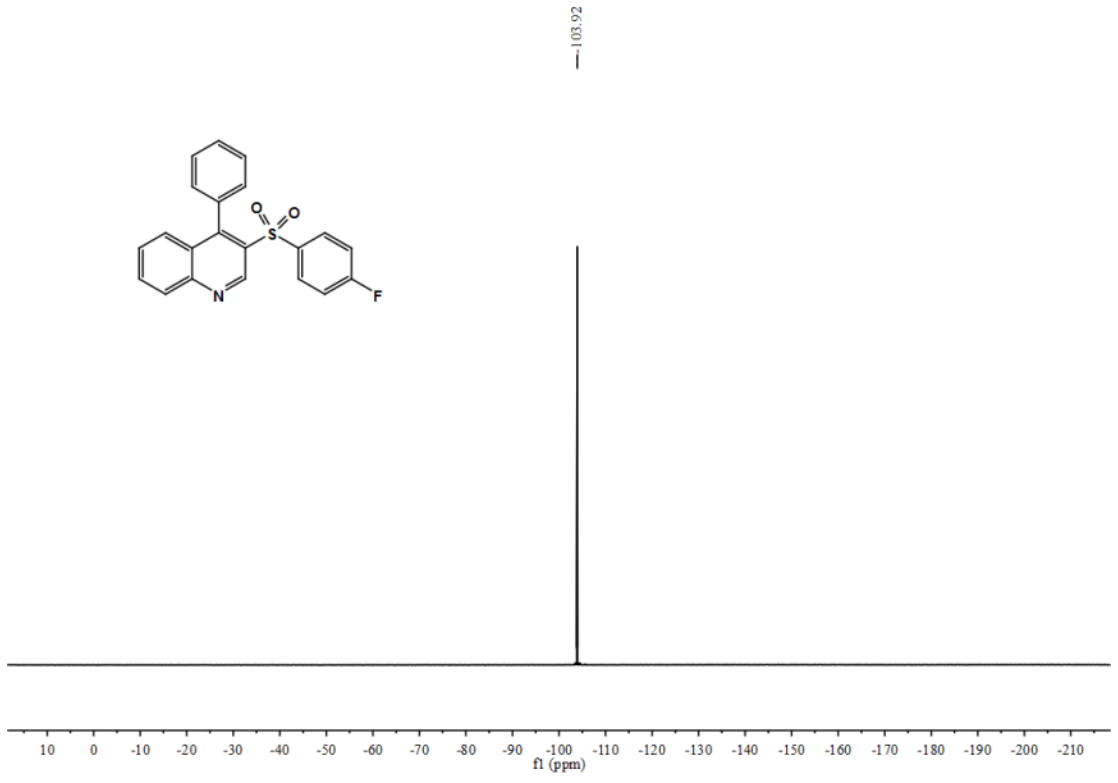
H[1] NMR of **4a**



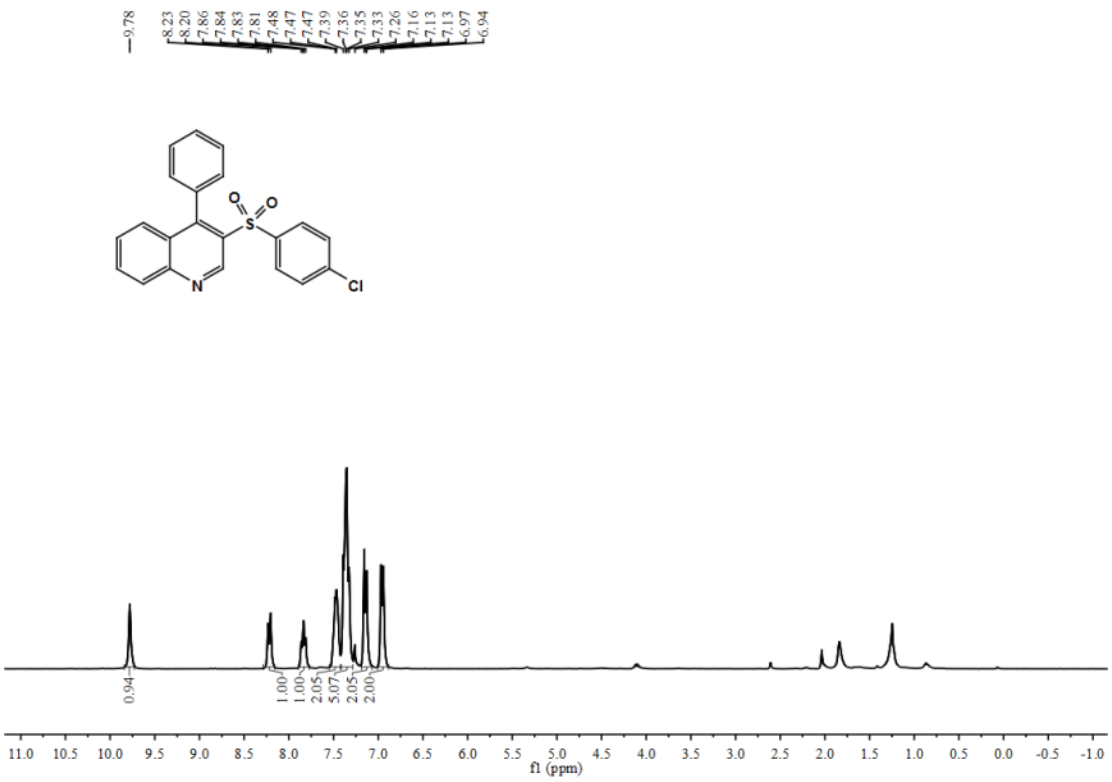
H[1] NMR of **4b**



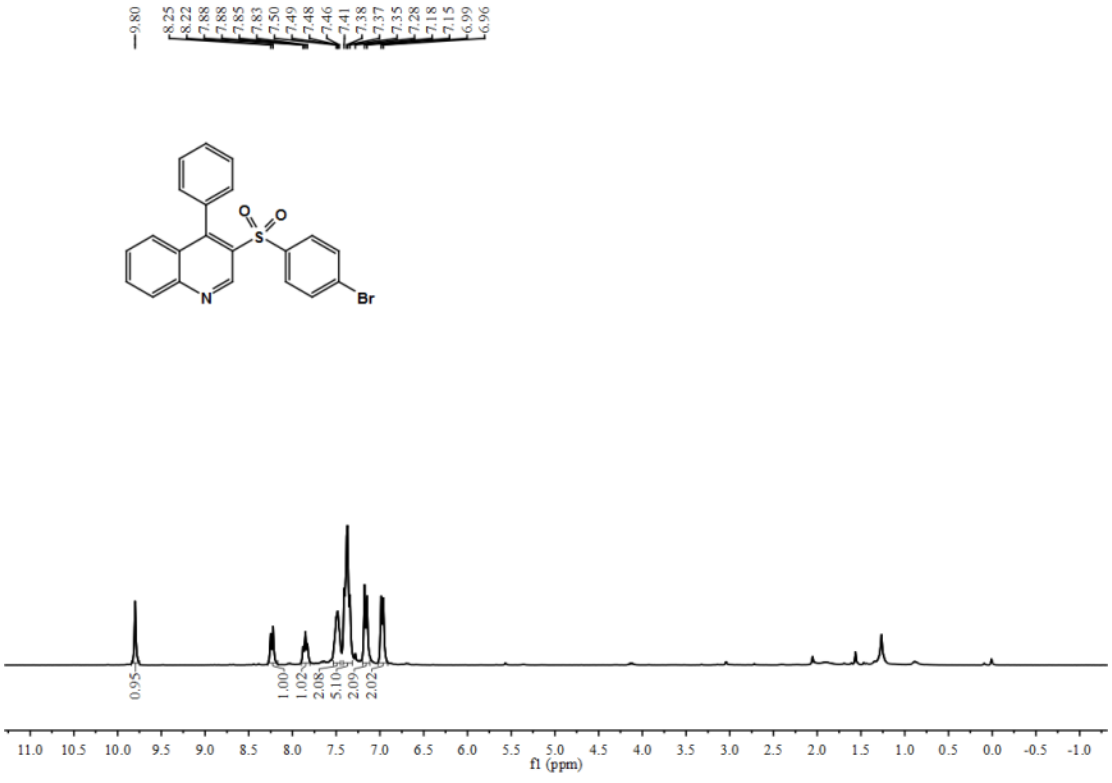
H^1 NMR of **4c**



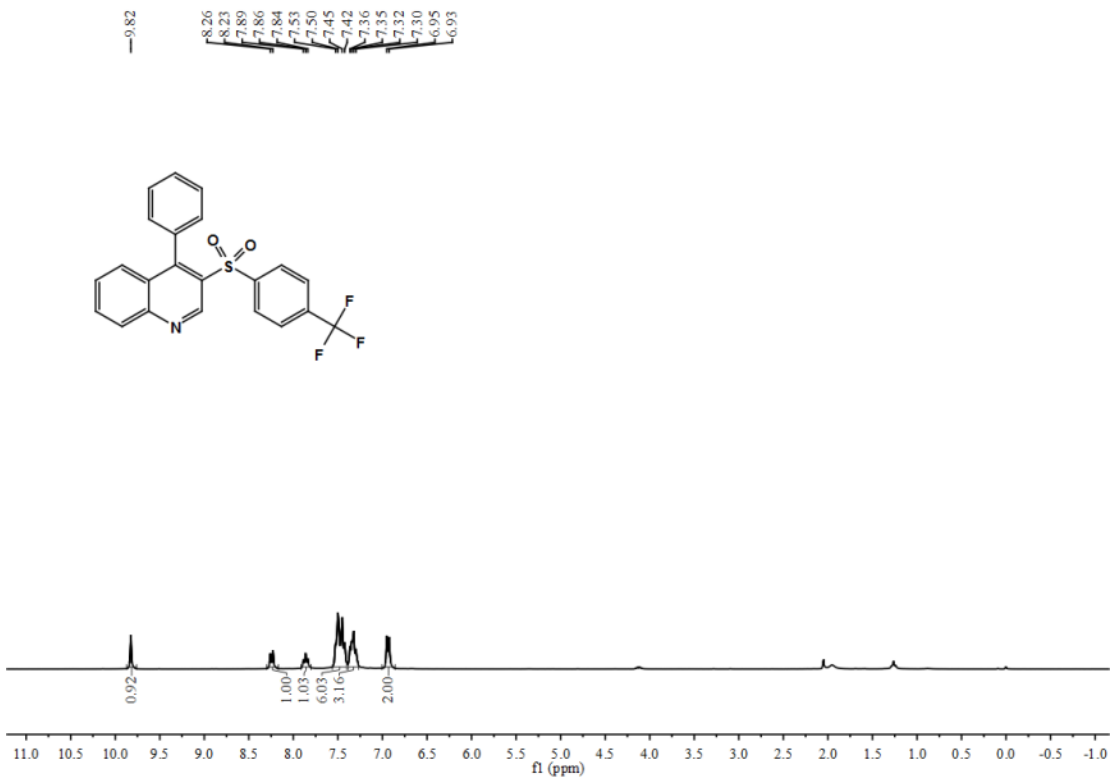
F^{19} NMR of **4c**



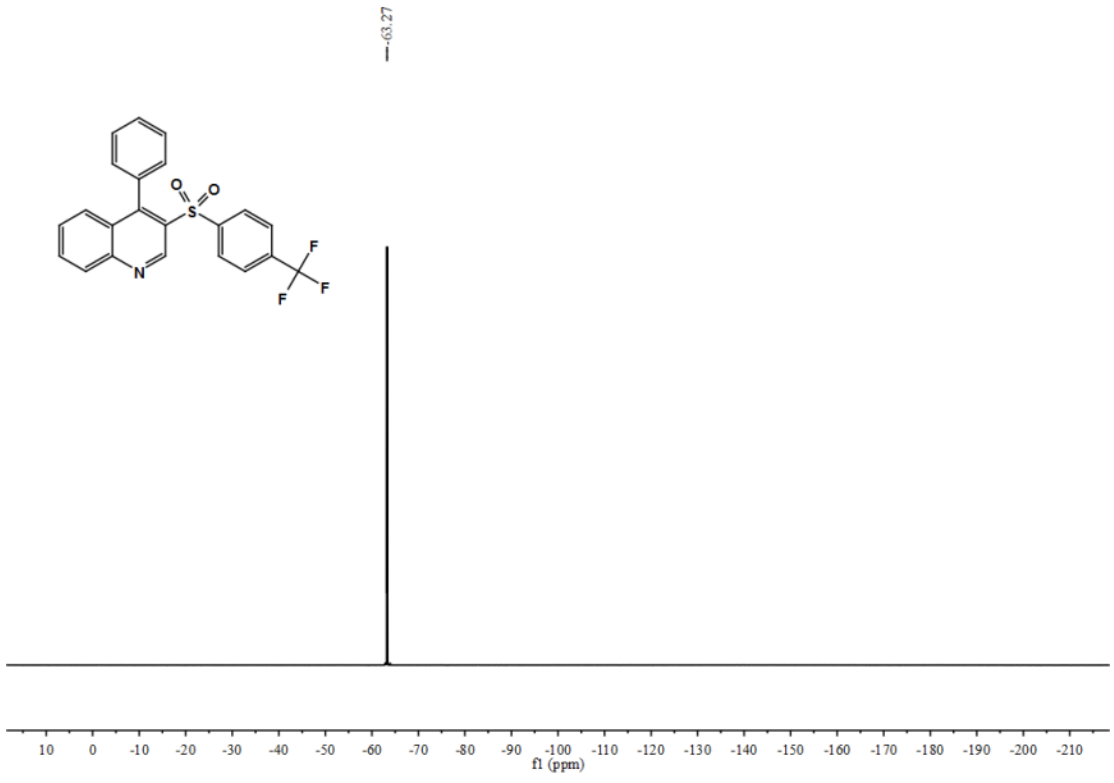
H^1 NMR of **4d**



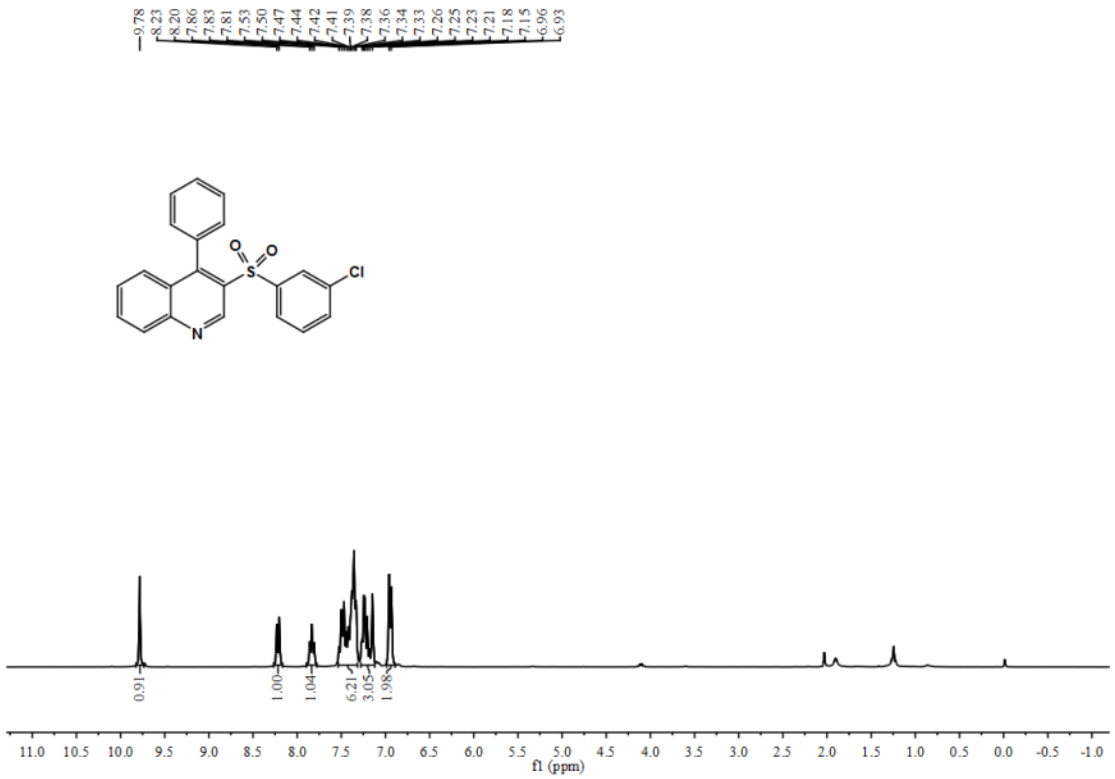
H^1 NMR of **4e**



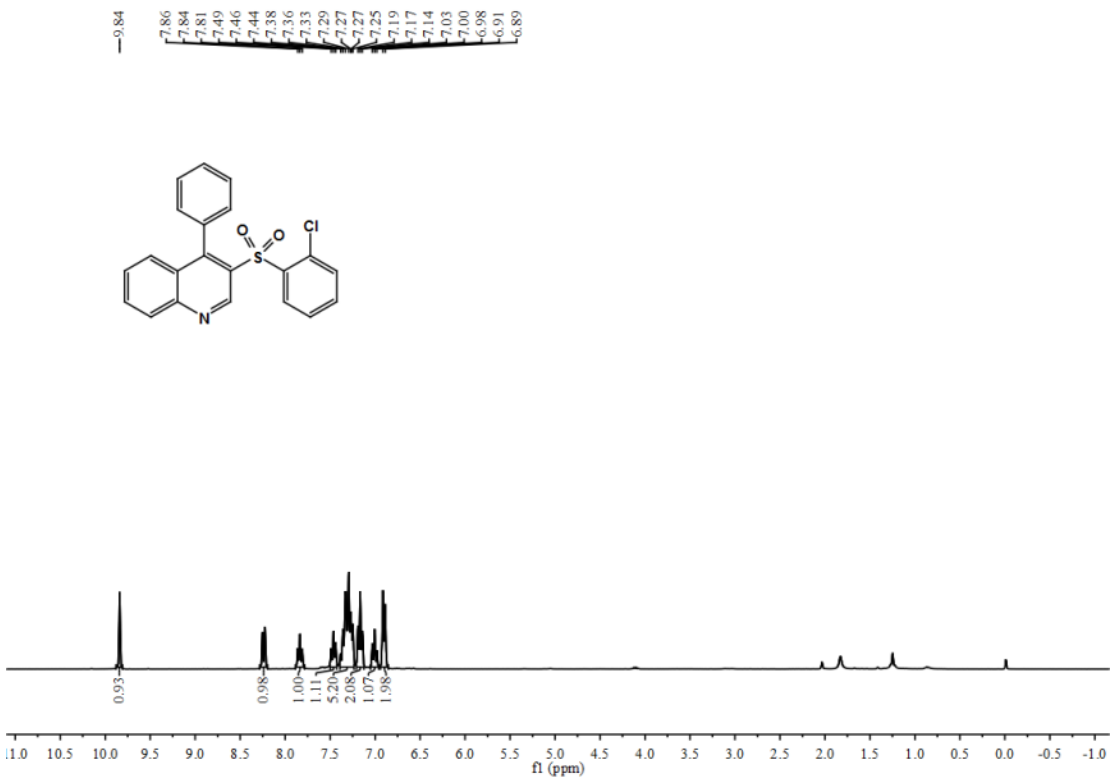
H[1] NMR of **4f**



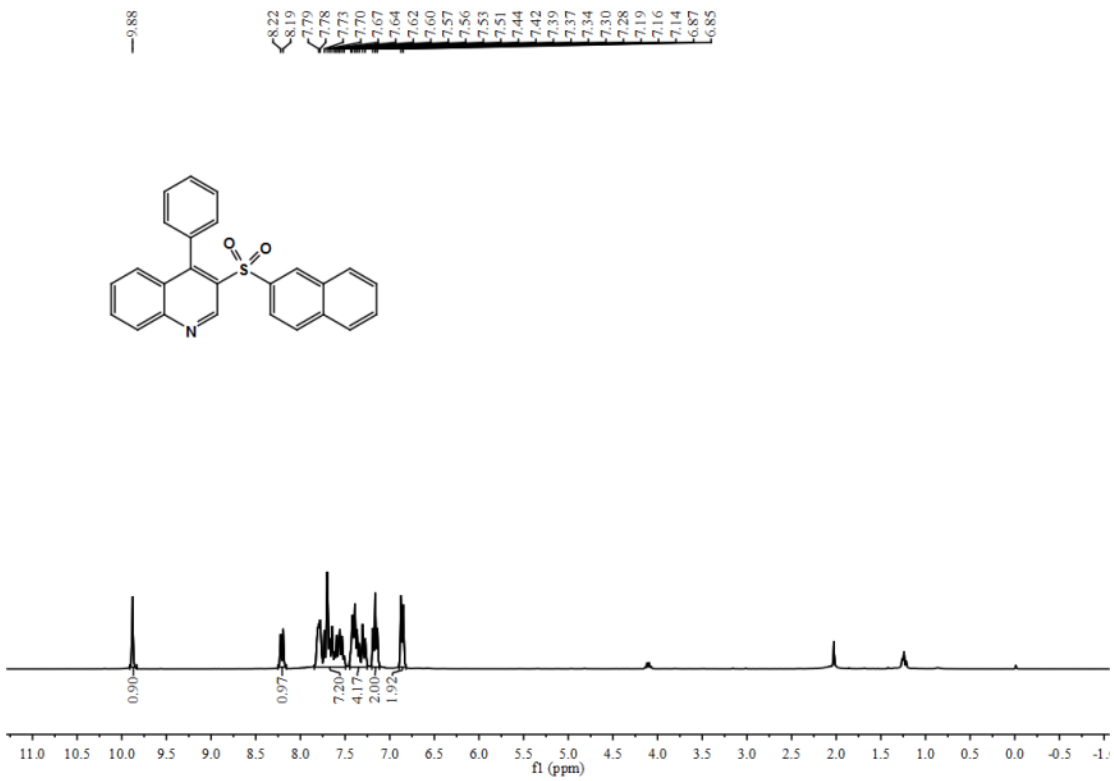
F[19] NMR of **4f**



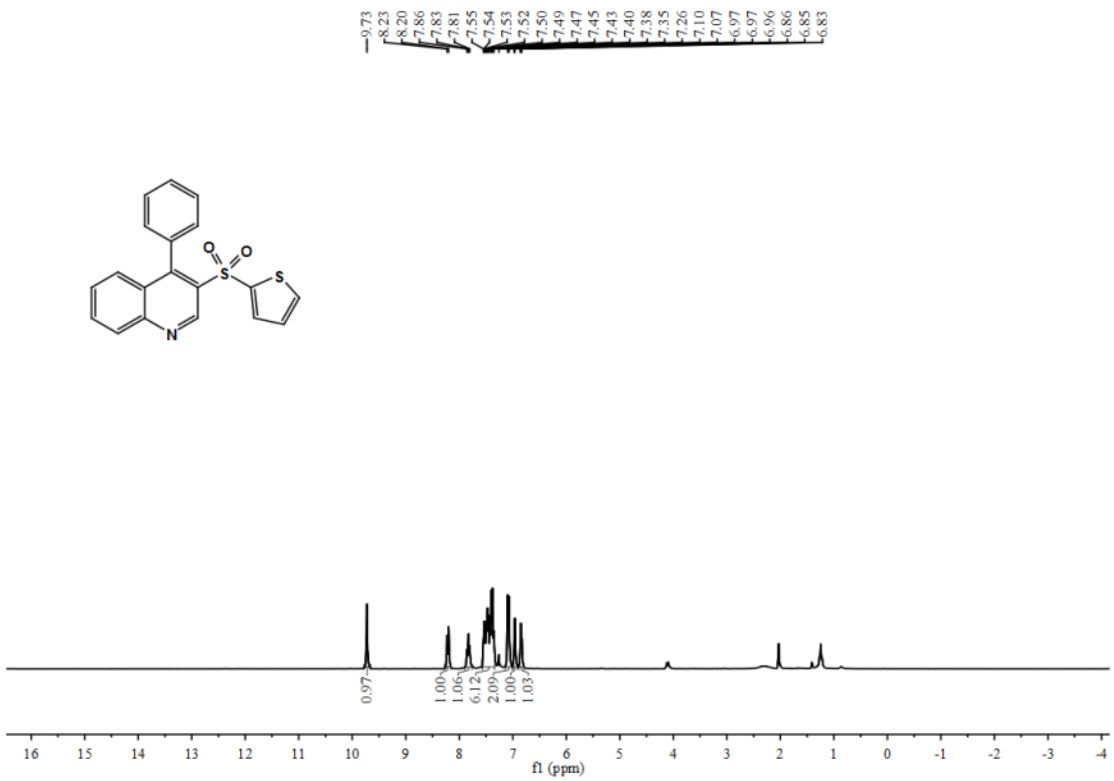
H[1] NMR of **4g**



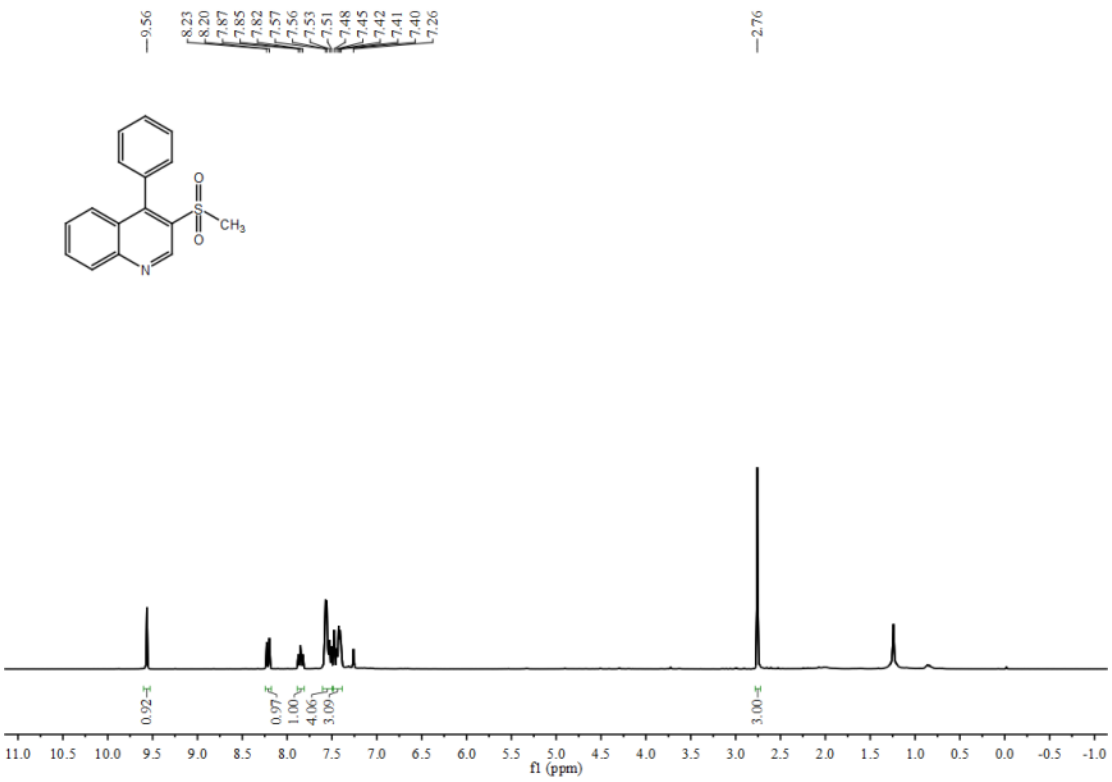
H[1] NMR of **4h**



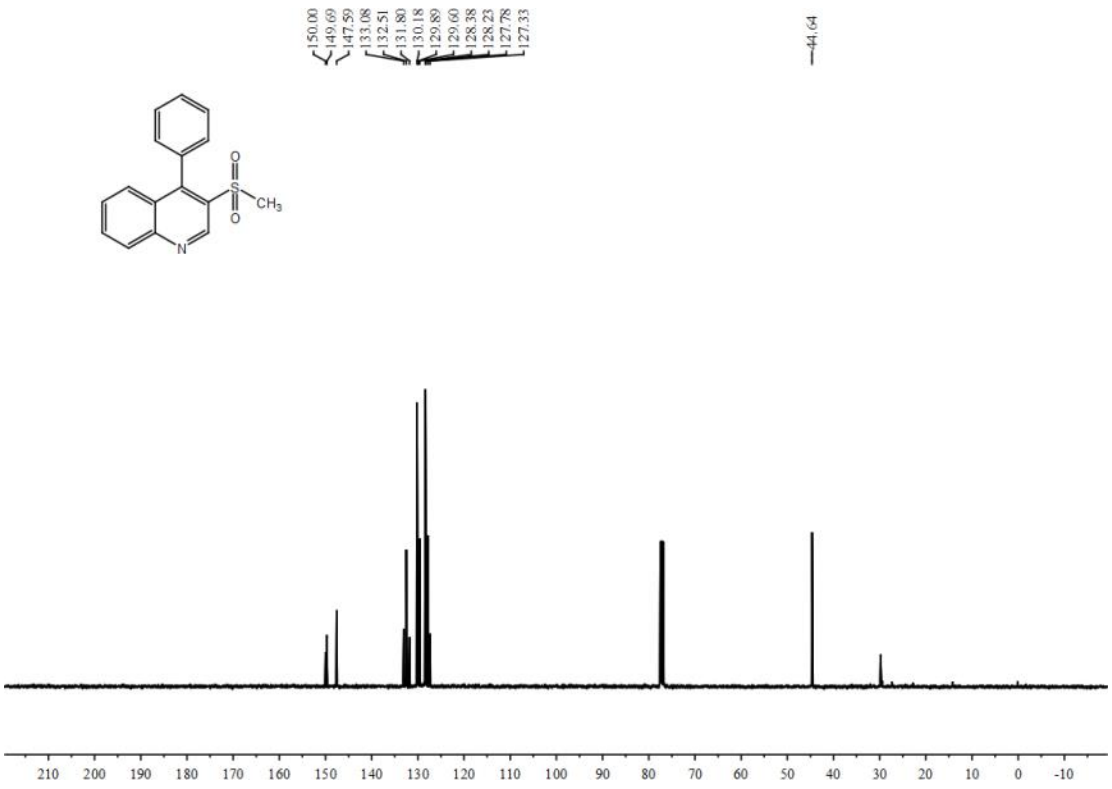
H^1 NMR of **4i**



H^1 NMR of **4j**



H[1] NMR of **4k**



C[13] NMR of **4k**