# Supporting Information

# for

# Synthesis of 3-Aminoquinolines from α-Imino Rhodium Carbenes and 2-Aminobenzaldehydes

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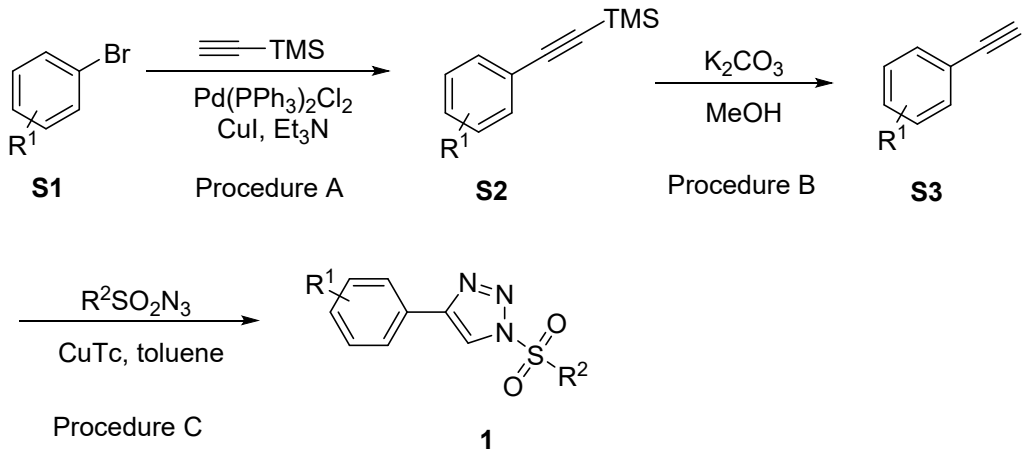
## 1 General information

All reactions were conducted in oven-dried glassware under an inert atmosphere of dry nitrogen unless otherwise noted. All commercial reagents were used without further purification unless otherwise noted. All solvents were freshly distilled prior to use in synthesis unless otherwise noted. Analytical thin layer chromatography (TLC) was performed using silica gel HSGF254 pre-coated plates. Flash column chromatography was performed using silica gel (200-300 mesh). $^{1}H$, $^{13}C$ NMR spectra were measured on Brucker Avance IIDMX 400MHz spectrometers (400 MHz for $^{1}H$ NMR, 101 MHz for $^{13}C$ NMR). Chemical shifts are reported as δ values relative to internal tetramethylsilane (TMS: 0.00 ppm) or deuterated solvent (chloroform-d: 7.26 ppm, 77.16 ppm; DMSO-$d_6$:2.50 ppm, 39.52 ppm. Abbreviations for signal couplings are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet and br, broad. Coupling constants (*J*) were taken from the spectra directly and are uncorrected. Melting points are uncorrected. High resolution mass spectra (HRMS) were recorded on a Waters TOFMS GCT Premier using ESI ionization.

## 2 Preparation of triazoles




**Procedure A:**

Under a nitrogen atmosphere, to a triethylamine solution (20 mL) of $Pd(PPh_3)_2Cl_2$ (213 mg, 0.3 mmol) and CuI (190 mg, 1.0 mmol) was added **S1** (10.0 mmol) and stirred for 10 min, then trimethylsilylacetylene (1.80 mL, 12.0 mmol) was added dropwise over 30 min. The resulting suspension was allowed to be stirred for 4 h at 50 ℃. After completion of the reaction, the mixture was filtered through a short celite bed and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE) to afford compound **S2**.

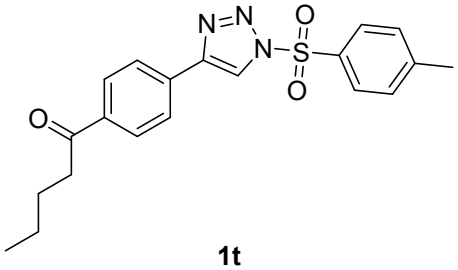
**Procedure B:**

To polysubstituted-trimethyl(phenylethynyl)silane **S2** (5 mmol) a solution of $K_2CO_3$ (0.276 g, 2 mmol) in 10 mL MeOH was added and the mixture was stirred at room temperature, until TLC analysis showed that **S2** was completely consumed. The reaction mixture was filtered through a short plug of silica gel. The filtration was concentrated and then purified by flash chromatography to give the corresponding product **S3**.

**Procedure C:**

Under a nitrogen atmosphere, dry toluene was added to a flask charged with copper (I) thiophene-2-carboxylate (CuTC, 0.1 equiv in regards to alkyne) and the alkyne (1 equiv, 0.33 M). The reaction mixture was cooled in an ice-water bath. Subsequently, the sulfonyl azide (1.2 equiv) was added slowly as the limiting reagent to avoid a run-away exotherm, and the reaction mixture was allowed to warm to room temperature and stirred until TLC analysis showed that alkyne was completely consumed. The reaction mixture filtered through a short plug of silica gel. The filtrate was concentrated and then purified by flash chromatography with PE/EtOAc (3:1) as eluent to give the corresponding product **1**.

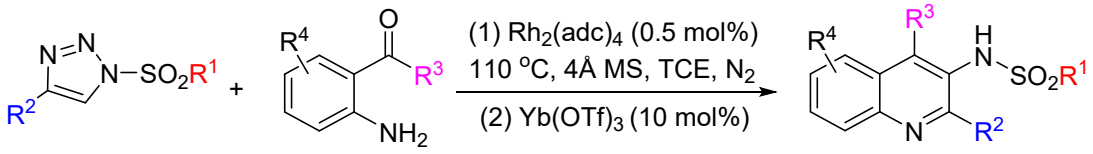
**1a**, **1c**, **1e**, **1f**, **1g**, **1i**, **1j**, **1k**, **1m**, **1n**, **1o** and **1u** were reported in ref. 1; **1b**, **1h** and **1v** were reported in ref. 2; **1d** was reported in ref. 3; **1l** and **1p** were reported in ref. 4; **1q** was reported in ref. 5. **1r** and **1s** were reported in ref. 6.



**1t**

**1-(4-(1-tosyl-1*H*-1,2,3-triazol-4-yl)phenyl)pentan-1-one (1t):** White solid, m.p.: 196.3-197.3 °C, 398.8 mg, yield: 52%, $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.42 (s, 1H), 8.03 (q, *J* = 8.4, 6.5 Hz, 4H), 7.93 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 2.98 (t, *J* = 7.4 Hz, 2H), 2.45 (s, 3H), 1.76 – 1.69 (m, 2H), 1.47 – 1.35 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 199.78, 147.56, 146.20, 137.18, 132.97, 132.81, 130.50, 128.76, 126.05, 119.83, 38.36, 26.37, 22.42, 21.83, 13.90. ESI-HRMS *m/z* calcd for $C_{20}H_{22}N_3O_3S^+$ $[M + H]^+$ 384.1376, found 384.1380.

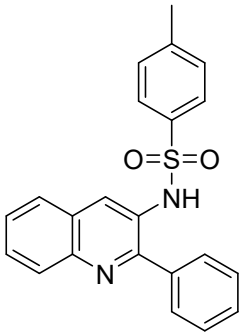
**3 Preparation of 3-aminoquinoline**



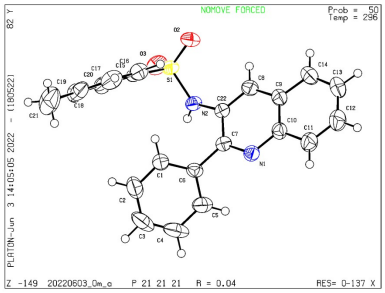

**1**, 0.2 mmol **2**, 1.2 equiv **3**

**General procedure:**

Triazole **1** (0.2 mmol), **2** (0.24 mmol, 1.2 equiv), $Rh_2(adc)_4$ (0.001 mmol, 0.5 mol%) and activated 4Å MS were successively added to the reaction tube containing a stirring bar under a nitrogen atmosphere. Then dried TCE (2 mL) was added as the solvent, and the mixture was heated at 110 °C. The reaction was monitored by TLC, and when triazole **1** was completely consumed, $Yb(OTf)_3$ (0.02 mmol, 10 mol%) was added as a Lewis acid to facilitate the conversion of the N-H inserted intermediate to the target product **3**. Upon completion, the mixture was filtered, the filtrate was concentrated, and the target product **3** was obtained by column chromatography.



**3a**



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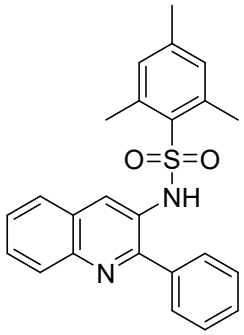
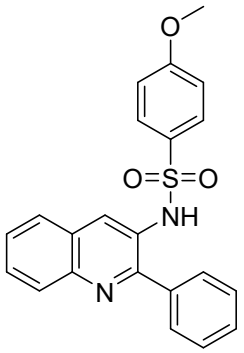
**4-methyl-*N*-(2-phenylquinolin-3-yl)benzenesulfonamide (3a)**: White solid, m.p.: 181.9-183.6 °C, 74.1 mg, 99% yield, $^1$H NMR (400 MHz, Chloroform-d) δ 8.46 (s, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.50 (d, J = 8.2 Hz, 2H), 7.47 – 7.40 (m, 3H), 7.18 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 6.7 Hz, 2H), 6.81 (s, 1H), 2.38 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 153.17, 145.06, 144.39, 136.56, 135.77, 129.80, 129.37, 129.28, 129.15, 129.12, 128.37, 127.67, 127.46, 127.33, 127.09, 126.23, 21.52. ESI-HRMS *m/z* calcd for $C_{22}H_{19}N_2O_2S^+$ $[M + H]^+$ 375.1162 , found 375.1170.



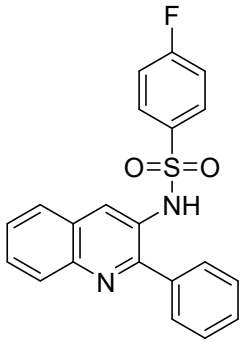
**3b**

**2,4,6-trimethyl-*N*-(2-phenylquinolin-3-yl)benzenesulfonamide (3b)**: White solid, m.p.: 177.3-179.6 °C, 57.0 mg, 72% yield, $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.24 (s, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.64 (t, *J* = 8.2 Hz, 1H), 7.54 (d, *J* = 7.1 Hz, 1H), 7.52 – 7.47 (m, 3H), 7.38 – 7.33 (m, 2H), 7.00 (s, 1H), 6.82 (s, 2H), 2.31 (s, 6H), 2.25 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 153.21, 144.92, 142.94, 139.26, 136.85, 133.18, 132.20, 129.45, 129.40, 129.16, 129.01, 128.48, 127.57, 127.31, 127.25, 125.93, 22.87, 20.91. ESI-HRMS *m/*z calcd for $C_{24}H_{23}N_2O_2S^+$ $[M + H]^+$ 403.1475, found 403.1478.



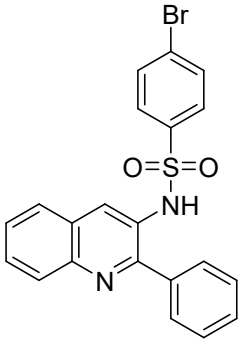
**3c**

**4-methoxy-*N*-(2-phenylquinolin-3-yl)benzenesulfonamide (3c)**: White solid, m.p.: 220.5-223.8 °C, 71.1 mg, 91% yield, $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.46 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.66 (t, *J* = 7.1 Hz, 1H), 7.59 – 7.51 (m, 3H), 7.49 – 7.42 (m, 3H), 7.19 – 7.13 (m, 2H), 6.84 (d, *J* = 7.9 Hz, 2H), 6.78 (s, 1H), 3.82 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 163.44, 153.21, 145.06, 136.62, 130.26, 129.39, 129.32, 129.25, 129.17, 129.10, 128.43, 128.38, 127.69, 127.45, 127.33, 126.24, 114.35, 55.62. ESI-HRMS *m/z* calcd for $C_{22}H_{19}N_2O_3S^+$ $[M + H]^+$ 391.1111, found 391.1118.



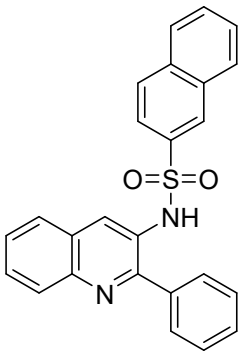
**3d**

**4-fluoro-*N*-(2-phenylquinolin-3-yl)benzenesulfonamide (3d)**: White solid, m.p.: 199.1-201.7 °C, 65.1 mg, 86% yield, $^{1}$H NMR (400 MHz, Chloroform-d) δ 8.47 (s, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.69 (t, J = 7.7 Hz, 1H), 7.63 – 7.53 (m, 3H), 7.50 – 7.40 (m, 3H), 7.14 (d, J = 6.4 Hz, 2H), 7.04 (t, J = 8.4 Hz, 2H), 6.85 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 165.43 (d, *J* = 256.5 Hz), 153.42, 145.37, 136.57, 134.78, 129.78 (d, *J* = 9.5 Hz), 129.46, 129.38, 129.27, 128.25, 127.83, 127.61, 127.50, 127.38, 116.49 (d, *J* = 22.7 Hz)..$^{19}$F NMR (376 MHz, Chloroform-*d*) δ -103.55. ESI-HRMS *m/z* calcd for $C_{21}H_{16}FN_2O_2S^+$ $[M + H]^+$ 379.0911, found 379.0917.



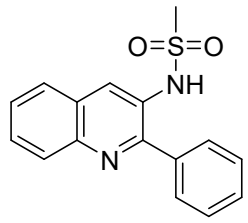

**3e**

**4-bromo-*N*-(2-phenylquinolin-3-yl)benzenesulfonamide (3e):** White solid, m.p.: 225.9-227.5 °C, 86.9 mg, 99% yield, $^{1}$H NMR (400 MHz, Chloroform-d) δ 8.45 (s, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.70 (t, J = 7.7 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.52 – 7.41 (m, 5H), 7.38 (d, J = 8.3 Hz, 2H), 7.13 (d, J = 6.3 Hz, 2H), 6.87 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 153.52, 145.47, 137.75, 136.58, 132.48, 129.54, 129.41, 129.35, 129.30, 128.49, 128.43, 128.24, 127.79, 127.68, 127.60, 127.51. ESI-HRMS *m/z* calcd for $C_{21}H_{16}BrN_2O_2S^+$ $[M + H]^+$ 439.0110, found 439.0114.



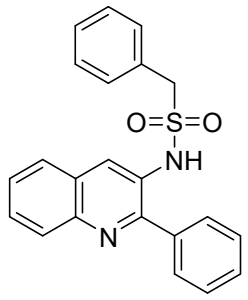

**3f**

***N*-(2-phenylquinolin-3-yl)naphthalene-2-sulfonamide (3f)**: White solid, m.p.: 180.3-181.0 °C, 78.0 mg, 95% yield, $^{1}$H NMR (400 MHz, Chloroform-d) δ 8.52 (s, 1H), 8.22 (s, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.88 – 7.79 (m, 4H), 7.68 – 7.61 (m, 2H), 7.60 – 7.54 (m, 2H), 7.49 (dd, J = 8.7, 1.9 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.29 (t, J = 7.6 Hz, 2H), 7.03 (d, J = 7.3 Hz, 2H), 6.92 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 153.33, 145.21, 136.55, 135.65, 135.02, 132.02, 129.53, 129.31, 129.26, 129.21, 129.18, 128.72, 128.28, 128.19, 127.88, 127.71, 127.67, 127.48, 127.36, 126.84, 121.89. ESI-HRMS *m/z* calcd for $C_{25}H_{19}N_2O_2S^+$ $[M + H]^+$ 411.1162 , found 411.1169.



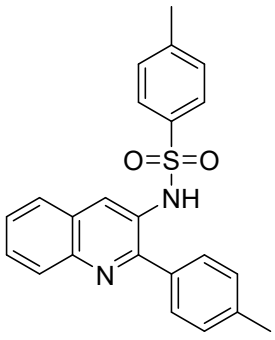
**3g**

***N*-(2-phenylquinolin-3-yl)methanesulfonamide (3g)**: White solid, m.p.: 151.4-152.6 °C, 57.9 mg, 97% yield, $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.38 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.62 – 7.43 (m, 6H), 6.78 (s, 1H), 2.94 (d, *J* = 2.3 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 152.43, 144.98, 136.70, 129.70, 129.61, 129.20, 129.16, 128.54, 128.50, 127.64, 127.56, 127.29, 124.49, 39.72. ESI-HRMS *m/z* calcd for $C_{16}H_{15}N_2O_2S^+$ [M + H]$^+$ 299.0849, found 299.0857.



**3h**

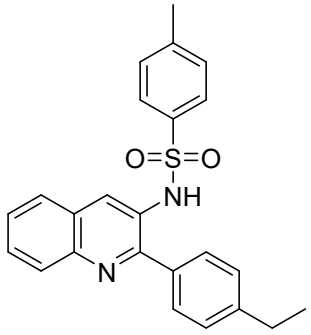
**1-phenyl-*N*-(2-phenylquinolin-3-yl)methanesulfonamide (3h)**: White solid, m.p.: 144.9-145.7 °C, 63.4 mg, 86% yield, $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.15 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 2.8 Hz, 3H), 7.40 (d, *J* = 3.6 Hz, 2H), 7.27 (t, 3H), 7.18 (d, *J* = 7.2 Hz, 2H), 6.56 (s, 1H), 4.40 (s, 2H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 151.27, 144.56, 136.39, 130.53, 129.61, 129.48, 129.20, 129.09, 129.01, 128.74, 128.51, 127.92, 127.61, 127.45, 127.20, 121.93, 57.97. ESI-HRMS *m/z* calcd for $C_{22}H_{19}N_2O_2S^+$ [M + H]$^+$ 375.1162, found 375.1167.



**3i**

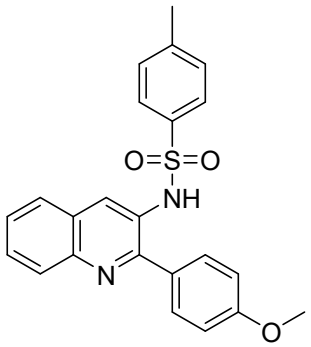
**4-methyl-*N*-(2-(*p*-tolyl)quinolin-3-yl)benzenesulfonamide (3i):** White solid m.p.: 230.8-231.5 °C, 76.1 mg, 98% yield, $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 9.1 Hz, 3H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 7.6 Hz, 2H), 6.83 (s, 1H), 2.42 (s, 3H), 2.37 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 153.16, 145.04, 144.38, 139.47, 135.82, 133.59, 129.96, 129.78,

129.15, 128.96, 128.50, 128.29, 127.61, 127.41, 127.21, 127.14, 125.60, 21.52, 21.31. ESI-HRMS *m/z* calcd for $C_{23}H_{21}N_2O_2S^+$ $[M + H]^+$ 389.1318, found 389.1322.



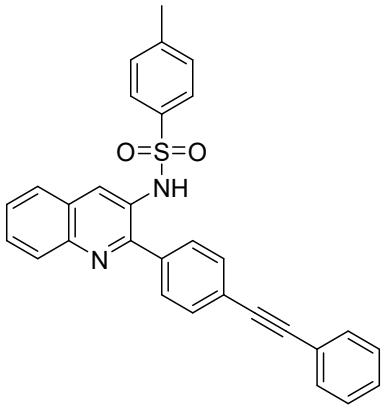
**3j**

***N*-(2-(4-ethylphenyl)quinolin-3-yl)-4-methylbenzenesulfonamide (3j)**: White solid, m.p.: 202.7-203.6 °C, 78.9 mg, 98% yield, $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.44 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.57 – 7.49 (m, 3H), 7.26 (s, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.84 (s, 1H), 2.72 (q, *J* = 7.6 Hz, 2H), 2.38 (s, 3H), 1.29 (t, *J* = 7.6 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 153.18, 145.78, 145.07, 144.37, 135.83, 133.84, 129.80, 129.18, 128.97, 128.86, 128.49, 128.37, 127.63, 127.42, 127.21, 127.14, 125.62, 28.74, 21.54, 15.54. ESI-HRMS *m/z* calcd for $C_{24}H_{23}N_2O_2S^+$ $[M + H]^+$ 403.1475, found 403.1481.



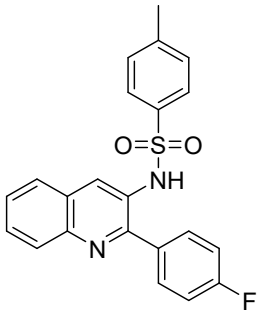
**3k**

***N*-(2-(4-methoxyphenyl)quinolin-3-yl)-4-methylbenzenesulfonamide (3k)**: White solid, m.p.: 220.1-221.5°C, 80.1 mg, 99% yield, $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.42 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.57 – 7.51 (m, 3H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.94 (d, *J* = 8.2 Hz, 2H), 6.90 (s, 1H), 3.87 (s, 3H), 2.37 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 160.52, 152.80, 144.85, 144.40, 135.88, 129.89, 129.80, 129.09, 128.91, 128.56, 127.55, 127.39, 127.22, 127.12, 125.95, 114.74, 55.45, 21.52. ESI-HRMS *m/z* calcd for $C_{23}H_{21}N_2O_3S^+$ $[M + H]^+$ 405.1267, found 405.1275.



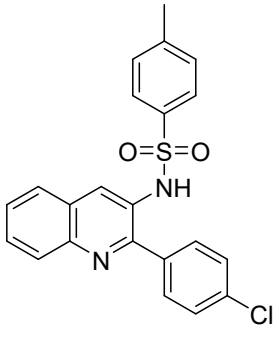
**3l**

**4-methyl-*N*-(2-(4-(phenylethynyl)phenyl)quinolin-3-yl)benzenesulfonamide (3l)**: White solid, m.p.: 207.3-208.4 °C, 94.0 mg, 99% yield,$^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.46 (s, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.61 – 7.48 (m, 7H), 7.38 (s, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.80 (s, 1H), 2.39 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 152.67, 145.24, 144.44, 136.25, 135.87, 132.23, 131.69, 129.84, 129.31, 129.16, 128.61, 128.53, 128.41, 128.21, 127.71, 127.51, 127.47, 127.22, 127.06, 124.49, 122.84, 91.10, 88.56, 21.54. ESI-HRMS *m/z* calcd for $C_{30}H_{23}N_2O_2S^+$ $[M + H]^+$ 475.1475, found 475.1480.



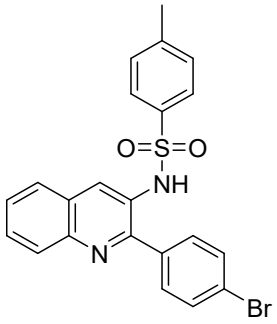
**3m**

***N*-(2-(4-fluorophenyl)quinolin-3-yl)-4-methylbenzenesulfonamide (3m)**: White solid, m.p.: 217.3-218.9 °C, 62 mg, 79% yield, $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.44 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.15 – 7.08 (m, 4H), 6.71 (s, 1H), 2.39 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 163.25 (d, *J* = 250.1 Hz), 152.29, 145.15, 144.50, 135.91, 132.72 (d, J = 3.3 Hz). 130.55, 130.47, 129.85, 129.31, 129.11, 128.27, 127.69, 127.48, 127.07, 126.92, 116.28 (d, *J* = 21.8 Hz)., 21.53. $^{19}$F NMR (376 MHz, Chloroform-*d*) δ -111.09. ESI-HRMS *m/z* calcd for $C_{22}H_{18}FN_2O_2S^+$ $[M + H]^+$ 393.1068, found 393.1076.



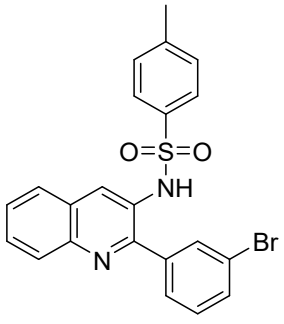
**3n**

***N*-(2-(4-chlorophenyl)quinolin-3-yl)-4-methylbenzenesulfonamide (3n)**: White solid, m.p.: 254.3-255.9 °C, 58.1 mg, 71% yield, $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.39 (s, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.59 (s, 1H), 2.32 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 152.15, 145.23, 144.56, 135.89, 135.66, 135.10, 129.93, 129.88, 129.41, 129.17, 128.19, 127.75, 127.57, 127.52, 127.16, 127.08, 21.56. ESI-HRMS *m/z* calcd for $C_{22}H_{18}ClN_2O_2S^+$ $[M + H]^+$ 409.0772, found 409.0776.



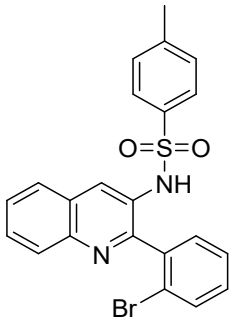

**3o**

***O*-(2-(4-bromophenyl)quinolin-3-yl)-4-methylbenzenesulfonamide (3o)**: White solid, m.p.: 278.3-279.5 °C, 90.0 mg, 99% yield, $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.46 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.68 (t, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.65 (s, 1H), 2.40 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 152.16, 145.22, 144.58, 135.84, 135.53, 132.36, 130.16, 129.89, 129.43, 129.15, 128.12, 127.74, 127.59, 127.54, 127.23, 127.07, 123.88, 21.58. ESI-HRMS *m/z* calcd for $C_{22}H_{18}BrN_2O_2S^+$ $[M + H]^+$ 453.0267, found 453.0270.



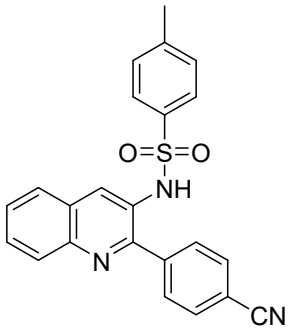

**3p**

***N*-(2-(3-bromophenyl)quinolin-3-yl)-4-methylbenzenesulfonamide (3p)**: White solid, m.p.: 221.3-222.5 °C, 86.1 mg, 95% yield, $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.51 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.59 (dd, *J* = 15.6, 7.9 Hz, 2H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.30 – 7.24 (m, 1H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.05 (s, 1H), 6.70 (s, 1H), 2.40 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 152.19, 145.28, 144.55, 138.63, 135.63, 132.36, 131.55, 130.50, 129.99, 129.56, 129.17, 128.31, 128.01, 127.80, 127.64, 127.59, 126.92, 126.75, 123.46, 21.63. ESI-HRMS *m/z* calcd for $C_{22}H_{18}BrN_2O_2S^+$ $[M + H]^+$ 453.0267, found 453.0267.



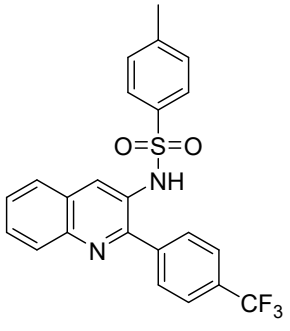
**3q**

***N*-(2-(2-bromophenyl)quinolin-3-yl)-4-methylbenzenesulfonamide (3q)**: White solid, m.p.: 104.6.3-106.5 °C, 68.9 mg, 76% yield,$^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.48 (s, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.68 (t, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 8.7 Hz, 1H), 6.45 (s, 1H), 2.38 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 152.63, 145.00, 144.31, 137.39, 135.84, 133.12, 130.96, 130.79, 129.77, 129.28, 129.21, 128.40, 128.07, 127.98, 127.66, 127.59, 127.27, 126.77, 122.29, 21.53. ESI-HRMS *m/z* calcd for $C_{22}H_{18}BrN_2O_2S^+$ $[M + H]^+$ 453.0267, found 453.0272.



**3r**

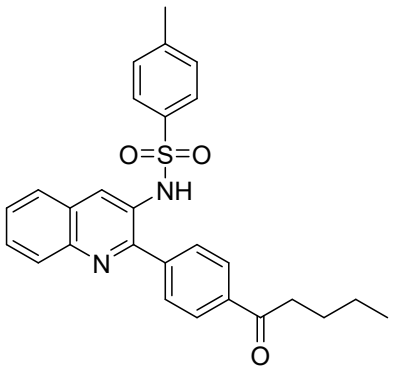
***N*-(2-(4-cyanophenyl)quinolin-3-yl)-4-methylbenzenesulfonamide (3r)**: Yellow solid, m.p.: 212.3-213.5 °C, 79.1 mg, 99% yield, $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 8.09 (s, 1H), 7.98 (dd, *J* = 17.6, 8.3 Hz, 2H), 7.84 (d, *J* = 7.9 Hz, 2H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 2.35 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 156.16, 146.45, 144.12, 143.80, 137.92, 135.05, 132.62, 131.15, 131.11, 130.52, 129.66, 129.19, 128.59, 128.20, 127.46, 119.76, 111.82, 21.92. ESI-HRMS *m/z* calcd for $C_{23}H_{18}N_3O_2S^+$ $[M + H]^+$ 400.1114, found 400.1111.



**3s**

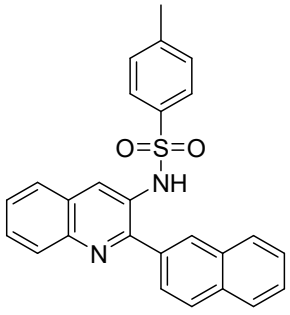
**4-methyl-*N*-(2-(4-(trifluoromethyl)phenyl)quinolin-3-yl)benzenesulfonamide (3s)**: White solid, m.p.: 243.4-244.6 °C, 72.5 mg, 82% yield, $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H),

7.70 (t, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.60 (t, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 2.9 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.64 (s, 1H), 2.40 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 152.10, 145.38, 144.59, 140.40, 135.87, 129.91, 129.64, 129.23, 128.20, 128.05 (q, *J* = 205.7 Hz), 127.98, 127.85, 127.79, 127.59, 126.03 (q, *J* = 3.9 Hz), 21.54. $^{19}$F NMR (376 MHz, Chloroform-*d*) δ -62.79. ESI-HRMS *m/z* calcd for $C_{23}H_{18}F_3N_2O_2S^+$ $[M + H]^+$ 443.1036, found 443.1037.



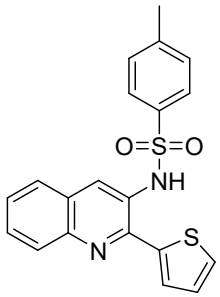
**3t**

**4-methyl-*N*-(2-(4-pentanoylphenyl)quinolin-3-yl)benzenesulfonamide (3t)**: White solid, m.p.: 196.8-197.5 °C, 90.0 mg, 98% yield, $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.48 (s, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 2H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.71 (t, *J* = 7.2 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 6.75 (s, 1H), 3.01 (t, *J* = 7.4 Hz, 2H), 2.42 (s, 3H), 1.85 – 1.74 (m, 2H), 1.51 – 1.41 (m, 2H), 1.01 (t, *J* = 7.3 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 199.81, 152.29, 145.15, 144.56, 140.88, 137.29, 135.80, 129.87, 129.43, 129.16, 128.84, 128.71, 128.11, 127.74, 127.65, 127.51, 127.32, 127.03, 38.49, 26.39, 22.42, 21.55, 13.93. ESI-HRMS *m/z* calcd for $C_{27}H_{27}N_2O_3S^+$ $[M + H]^+$ 459.1737, found 459.1746.



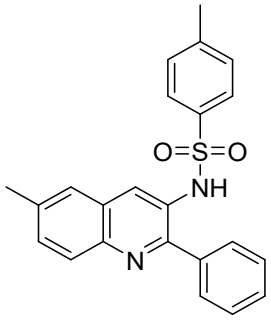
**3u**

**4-methyl-*N*-(2-(naphthalen-2-yl)quinolin-3-yl)benzenesulfonamide (3u)**: White solid, m.p.: 260.7-261.6 °C, 84.3 mg, 99% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.53 (s, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.94 – 7.87 (m, 3H), 7.76 (d, *J* = 8.9 Hz, 1H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.62 – 7.54 (m, 4H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.24 (dd, *J* = 1.7 Hz, 1H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.86 (s, 1H), 2.39 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 153.35, 145.29, 144.36, 135.89, 133.90, 133.31, 133.17, 129.81, 129.27, 129.26, 129.21, 128.50, 128.27, 128.11, 127.87, 127.75, 127.55, 127.40, 127.17, 127.09, 126.91, 125.42, 21.57. ESI-HRMS *m/z* calcd for $C_{26}H_{21}N_2O_2S^+$ $[M + H]^+$ 425.1318, found 425.1325.



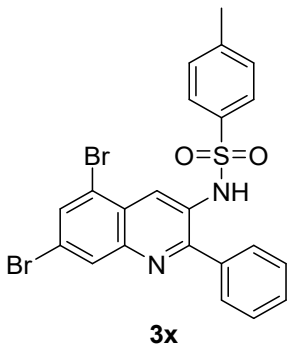
**3v**

**4-methyl-*N*-(2-(thiophen-2-yl)quinolin-3-yl)benzenesulfonamide (3v)**: White solid, m.p.: 184.7-185.3 °C, 60.0 mg, 77% yield, $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.40 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.61 – 7.52 (m, 3H), 7.46 (s, 1H), 7.30 (s, 1H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 4.9 Hz, 1H), 6.95 (s, 1H), 2.37 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 148.53, 145.13, 144.45, 137.61, 135.92, 129.86, 129.12, 129.07, 128.53, 127.72, 127.58, 127.40, 127.33, 127.05, 126.13, 125.67, 21.52. ESI-HRMS *m/z* calcd for $C_{20}H_{17}N_2O_2S_2^+$ $[M + H]^+$ 381.0726, found 381.0730.



**3w**

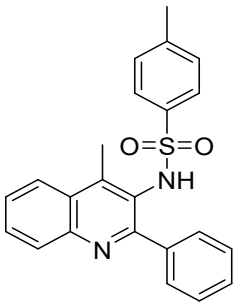
**4-methyl-*N*-(6-methyl-2-phenylquinolin-3-yl)benzenesulfonamide (3w)**: White solid, m.p.: 167.8-168.6 °C, 75.5 mg, 98% yield, $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.39 (s, 1H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.63 (s, 1H), 7.49 (d, *J* = 7.5 Hz, 3H), 7.43 (d, *J* = 7.8 Hz, 3H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.1 Hz, 2H), 6.76 (s, 1H), 2.56 (s, 3H), 2.38 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 152.24, 144.33, 143.72, 137.40, 136.67, 135.84, 131.51, 129.79, 129.26, 128.81, 128.42, 128.36, 127.76, 127.11, 126.27, 125.75, 21.63, 21.53. ESI-HRMS *m/z* calcd for $C_{23}H_{21}N_2O_2S^+$ $[M + H]^+$ 389.1318, found 389.1324.



**3x**

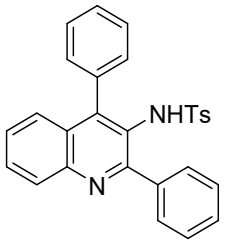
***N*-(5,7-dibromo-2-phenylquinolin-3-yl)-4-methylbenzenesulfonamide (3x)**: White solid, m.p.: 192.4-193.5°C, 76.6 mg, 72% yield, $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.30 (s, 1H), 8.04 (d, *J* = 2.0 Hz, 1H), 7.95 (d, *J* = 2.0 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 7.1 Hz, 3H), 7.30 (dd, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 6.98 (s, 1H), 2.38 (s, 3H). $^{13}$C NMR

(101 MHz, Chloroform-*d*) δ 153.31, 144.78, 140.63, 135.86, 135.55, 135.10, 130.08, 129.99, 129.83, 129.38, 129.08, 128.69, 127.08, 125.86, 123.80, 120.61, 21.56. ESI-HRMS *m/z* calcd for $C_{22}H_{17}Br_2N_2O_2S^+$ $[M + H]^+$ 530.9372, found 530.9382.



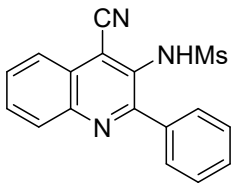

**3y**

**4-methyl-*N*-(4-methyl-2-phenylquinolin-3-yl)benzenesulfonamide (3y)**: White solid, m.p.: 167.8-168.6 °C, 75.5 mg, 97% yield, $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.08 (t, 2H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.27 (t, 1H), 7.21 (t, *J* = 7.4 Hz, 2H), 7.00 (t, 4H), 6.95 (d, *J* = 8.2 Hz, 2H), 6.84 (s, 1H), 2.95 (s, 3H), 2.38 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 157.45, 145.90, 145.56, 143.38, 138.36, 136.06, 129.93, 129.77, 129.57, 128.53, 128.21, 127.97, 126.88, 126.74, 125.20, 124.76, 21.48, 15.92. ESI-HRMS *m/z* calcd for $C_{23}H_{21}N_2O_2S^+$ $[M + H]^+$ 389.1318, found 389.1324.




**3z**

***N*-(2,4-diphenylquinolin-3-yl)-4-methylbenzenesulfonamide (3z)**: White solid, m.p.: 84.7-85.4 °C, 88.3 mg, 98% yield, $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.71 – 7.65 (m, 3H), 7.45 – 7.41 (m, 5H), 7.31 – 7.28 (m, 3H), 7.20 (dd, *J* = 7.2, 2.3 Hz, 2H), 7.03 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.36 (s, 1H), 2.35 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 157.94, 146.66, 146.47, 142.86, 139.61, 137.16, 133.88, 129.90, 129.71, 129.64, 129.29, 129.25, 128.62, 128.55, 128.29, 128.17, 127.00, 126.89, 126.64, 126.42, 125.16, 21.43. ESI-HRMS *m/z* calcd for $C_{28}H_{23}N_2O_2S^+$ $[M + H]^+$ 451.1475, found 451.1481.

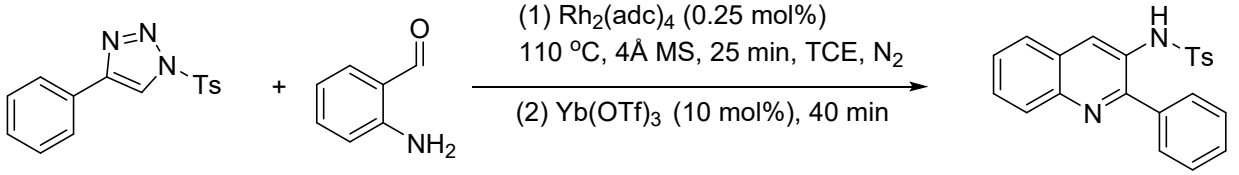



**3aa**

***O*-(4-cyano-2-phenylquinolin-3-yl)methanesulfonamide (3aa)**: Yellow solid, m.p.: 130.2-131.3, 49.2 mg, 76% yield, $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.21 (t, 2H), 7.86 (t, *J* = 7.8 Hz, 1H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 7.0 Hz, 2H), 7.56 (q, *J* = 11.1, 9.2 Hz, 3H), 6.79 (s, 1H), 3.17 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 156.38, 145.83, 136.16,

131.41, 131.21, 130.20, 129.98, 129.72, 129.42, 129.20, 125.82, 124.91, 115.78, 114.84, 43.83. ESI-HRMS *m/z* calcd for $C_{17}H_{14}N_3O_2S^+$ $[M + H]^+$ 324.0801, found 324.0809.

**4 Large scale reaction**




**1a**, 3 mmol
898 mg

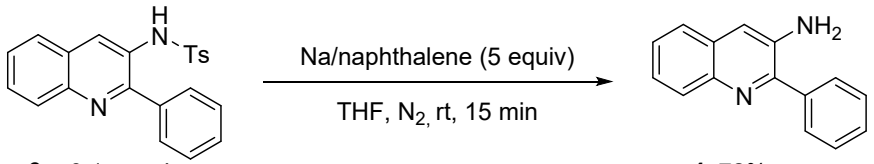
**2a**, 3.6 mmol
436 mg

**3a**, 1.11 g, 99% yield

Triazole **1a** (898 mg, 3 mmol), **2a** (436 mg, 3.6 mmol, 1.2 equiv), $Rh_2(adc)_4$ (69 mg, 0.0075 mmol, 0.25 mol%) and activated 4Å MS were successively added to the reaction tube containing a stirring bar under a nitrogen atmosphere. Then dried TCE (30 mL) was added as the solvent, and the mixture was heated at 110 °C. The reaction was monitored by TLC, and when triazole **1** was completely consumed, $Yb(OTf)_3$ (186 mg, 0.3 mmol, 10 mol%) was added as a Lewis acid to facilitate the conversion of the N-H inserted intermediate to the target product **3**. Upon completion, the mixture was filtered, the filtrate was concentrated, and the target product **3** was obtained by column chromatography in 99% yield (1.11 g).

**5 Further transformation**

**5.1 Synthesis of 4**

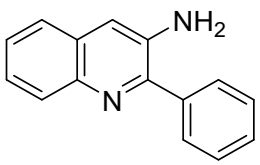



**3a,** 0.1 mmol

**4**, 72%

**Procedure:**

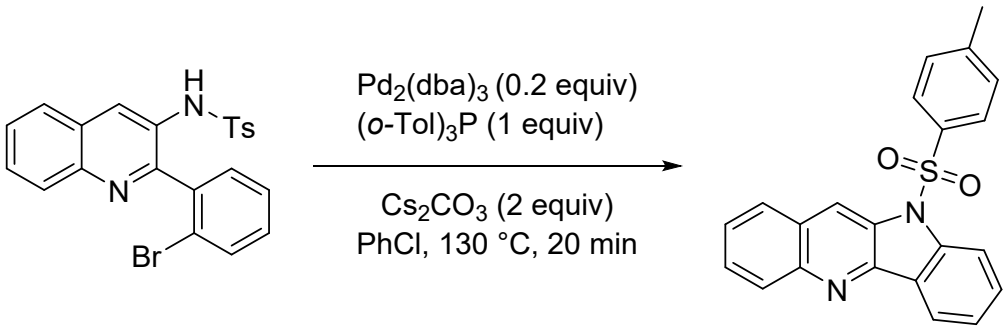
Under nitrogen atmosphere, **3a** (37.5 mg, 0.1 mmol) was added to a reaction tube containing a stirring bar. Then, the solvent THF (1 mL) was added to dissolve it, and a freshly prepared Na/naphthalene (5 equiv) mixed solution was slowly added into the reaction tube under ice-water bath conditions. The reaction was warmed to room temperature. TLC analysis monitored the reaction until **3a** was completely consumed. The reaction was then quenched with ethanol. Next, the mixture was filtered, concentrated and purified by column chromatography, affording the target product **4** in 72% yield.




**4**

**2-phenylquinolin-3-amine (4):** Yellow oil liquid, m.p.: 118.7-119.4 °C, 15.9 mg, 72% yield, $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 7.5 Hz, 1H), 7.73 (d, *J* = 7.0 Hz, 2H), 7.60 (t, 1H), 7.51 (t, *J* = 7.3 Hz, 2H), 7.45 (d, *J* = 7.3 Hz, 2H), 7.40 (d, *J* = 5.4 Hz, 1H), 7.30 (s, 1H), 3.96 (s, 2H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 150.58, 142.69, 138.34, 138.10, 129.17, 129.05, 128.90, 128.81, 128.64, 126.68, 125.67, 125.31, 116.11. ESI-HRMS *m/z* calcd for $C_{15}H_{13}N_2^+$ $[M + H]^+$ 221.1073, found 221.1061.

**5.2 Synthesis of 5**

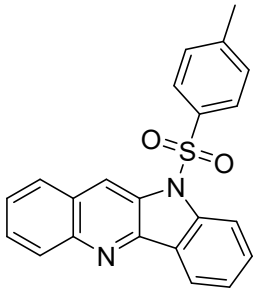



**3q,** 0.1 mmol

**5,** 84%

**Procedure:**

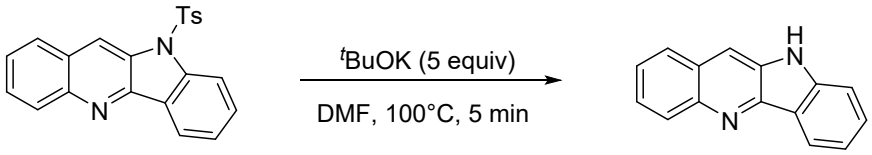
Under nitrogen atmosphere, **3q** (45.3 mg, 0.1 mmol), $Pd_2(dba)_3$ (18.3 mg, 0.02 mmol, 0.2 equiv), ($o$-Tol)$_3$P (30.4 mg, 0.1 mmol, 1 equiv) and $Cs_2CO_3$ (65.2 mg, 0.2 mmol, 2 equiv) were successively added to a reaction tube containing a stirring bar. PhCl (1 mL) was then added as the solvent. The reaction tube was heated at 130 °C. TLC analysis monitored the reaction until **3q** was completely consumed. The reaction mixture was then filtered and the filtrate was concentrated and purified by column chromatography to afford the target product **5** in 84% yield.




**5**

**10-tosyl-10*H*-indolo[3,2-b]quinoline (5)**: Yellow solid, m.p.: 188.3-189.4 °C, 29.8 mg, 80% yield, $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.96 (s, 1H), 8.37 (t, 2H), 8.23 (d, $J$ = 8.5 Hz, 1H), 8.05 (d, $J$ = 8.2 Hz, 1H), 7.77 – 7.72 (m, 1H), 7.69 (d, $J$ = 8.3 Hz, 2H), 7.66 (d, $J$ = 7.7 Hz, 1H), 7.61 (t, $J$ = 7.4 Hz, 1H), 7.48 (t, $J$ = 7.5 Hz, 1H), 7.08 (d, $J$ = 8.2 Hz, 2H), 2.23 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 147.42, 146.28, 145.34, 141.55, 134.28, 131.08, 130.80, 129.79, 129.00, 128.70, 128.40, 127.07, 126.57, 126.24, 125.65, 124.73, 121.89, 119.96, 115.23, 21.46. ESI-HRMS *m/z* calcd for $C_{22}H_{17}N_2O_2S^+$, $[M + H]^+$ 373.1005, found 373.1011.

**5.2 Synthesis of 6**



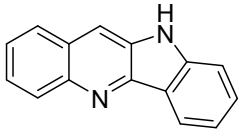

**5**, 0.1 mmol

**6**, 80%

**Procedure:**

Under nitrogen atmosphere, **5** (37.2 mg, 0.1 mmol) and $^t$BuOK (57.2 mg, 0.5 mmol, 5 equiv) were added to a reaction tube, followed by the addition of the solvent DMF (1 mL). The reaction was carried out at 100 °C. TLC analysis monitored the reaction until **5** was completely consumed, and then the reaction was quenched with $NH_4Cl$ saturated aqueous solution. The aqueous phase was extracted with ethyl acetate, and the combined organic phase was washed sequentially with water

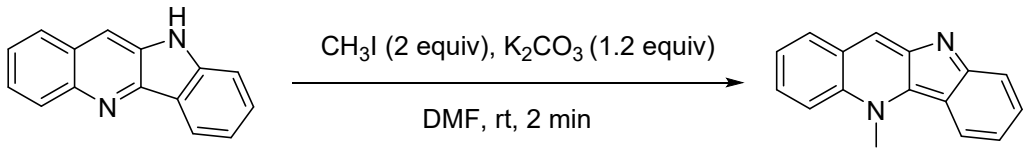
and brine and then dried over anhydrous sodium sulfate. After filtration, the filtrate was concentrated and purified by column chromatography, affording the target product **6** in 80% yield.



**6**

**10*H*-indolo[3,2-b]quinoline (6)**: Yellow solid, m.p.: 250.3-251.4°C, 17.5 mg, 80% yield, $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 11.43 (s, 1H), 8.37 (d, $J$ = 7.7 Hz, 1H), 8.29 (s, 1H), 8.21 (d, $J$ = 8.5 Hz, 1H), 8.11 (d, $J$ = 8.2 Hz, 1H), 7.67 – 7.53 (m, 4H), 7.29 (t, $J$ = 7.3 Hz, 1H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 146.68, 144.99, 144.35, 133.40, 130.61, 129.64, 128.42, 127.67, 126.95, 125.77, 122.30, 121.93, 120.27, 113.95, 112.44. ESI-HRMS *m/z* calcd for $C_{15}H_{11}N_2^+$, $[M + H]^+$ 219.0917, found 219.0927.

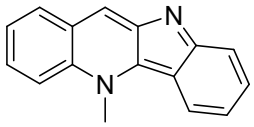
**5.3 Synthesis of 7**




**6**, 0.1 mmol **7**, 52%

**Procedure:**

Under atmosphere of nitrogen, **6** (21.9 mg, 0.1 mmol), $CH_3I$ (28.0 mg, 0.2 mmol, 2 equiv) and $K_2CO_3$ (32.0 mg, 0.12 mmol, 1.2 equiv) were successively added to a reaction tube equipped with a stirring bar. DMF (1 mL) was used as the solvent. The reaction tube was stirred at room temperature. TLC analysis monitored the reaction until **6** was completely consumed. The mixture was filtered. The filtrate was concentrated and then purified by column chromatography to afford **7** in 52% yield.



**7**

**5-methyl-5*H*-indeno[1,2-b]quinoline (7)**: Yellow solid, m.p.: 230.9-231.2 °C, 12.1 mg, 52% yield, $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.59 (d, $J$ = 7.8 Hz, 1H), 8.36 (d, $J$ = 8.6 Hz, 1H), 7.94 (d, $J$ = 8.2 Hz, 1H), 7.91 (s, 1H), 7.65 (q, $J$ = 7.1 Hz, 2H), 7.53 (t, $J$ = 7.5 Hz, 1H), 7.39 (d, $J$ = 8.2 Hz, 1H), 7.33 (t, $J$ = 7.5 Hz, 1H), 3.85 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 146.02, 144.98, 144.03, 134.13, 129.71, 129.24, 127.15, 126.86, 126.22, 125.26, 122.11, 121.60, 119.69, 110.70, 108.43, 29.12. ESI-HRMS m/z calcd for $C_{16}H_{13}N_2^+$, $[M + H]^+$ 233.1073, found 233.1078.

## 6 References

(1) W. Cheng, Y. Tang, Z.-F. Xu and C.-Y. Li, Synthesis of multifunctionalized 2-carbonylpyrrole by rhodium-catalyzed transannulation of 1-sulfonyl-1,2,3-triazole with *β*-diketone, *Org. Lett*., 2016, **18**, 6168-6171.

(2) Y.-J. Kwon, S.-g. Lee and W.-S. Kim, Continuous Flow Synthesis of *N*-Sulfonyl-1,2,3-triazoles for Tandem Relay Cu/Rh Dual Catalysis, *J. Org. Chem*., 2023, **88**, 1200-1214.

(3) G. Y. Kook, D. Kim, M. K. Chae and H. M. Ko, Rhodium(II)-Catalyzed Highly Selective 1,3-Insertion Reactions Using *N*-Sulfonyl-1,2,3-Triazoles with Heteroaryl Ethers or Heteroaryl Alcohols. *J. Org. Chem*., 2022, **87**, 7253-7263.

(4) J. Li, S.-R. Zhu, Y. Xu, X.-C. Lu, Z.-B. Wang, L. Liu and D.-F. Xu, Synthesis of 2,5-diaryloxazoles through rhodium-catalyzed annulation of triazoles and aldehydes, *RSC Adv.*, 2020, **10**, 24795-24799.

(5) S. Chuprakov, B. T. Worrell, N. Selander, R. K. Sit and V. V. Fokin, Stereoselective 1,3-Insertions of Rhodium(II) Azavinyl Carbenes, *J. Am. Chem. Soc.,* 2014, **136**, 195-202.

(6) Y. Shi, X. Yu and C.-Y. Li, Rhodium-catalyzed synthesis of 2,5-epoxybenzo[f][1,4] oxazepines by tandem reaction of 1-sulfonyl-1,2,3-triazoles and salicylaldehydes, *Eur. J. Org. Chem.,* 2015, **29**, 6429-6433.

## 7 Copies of NMR spectra

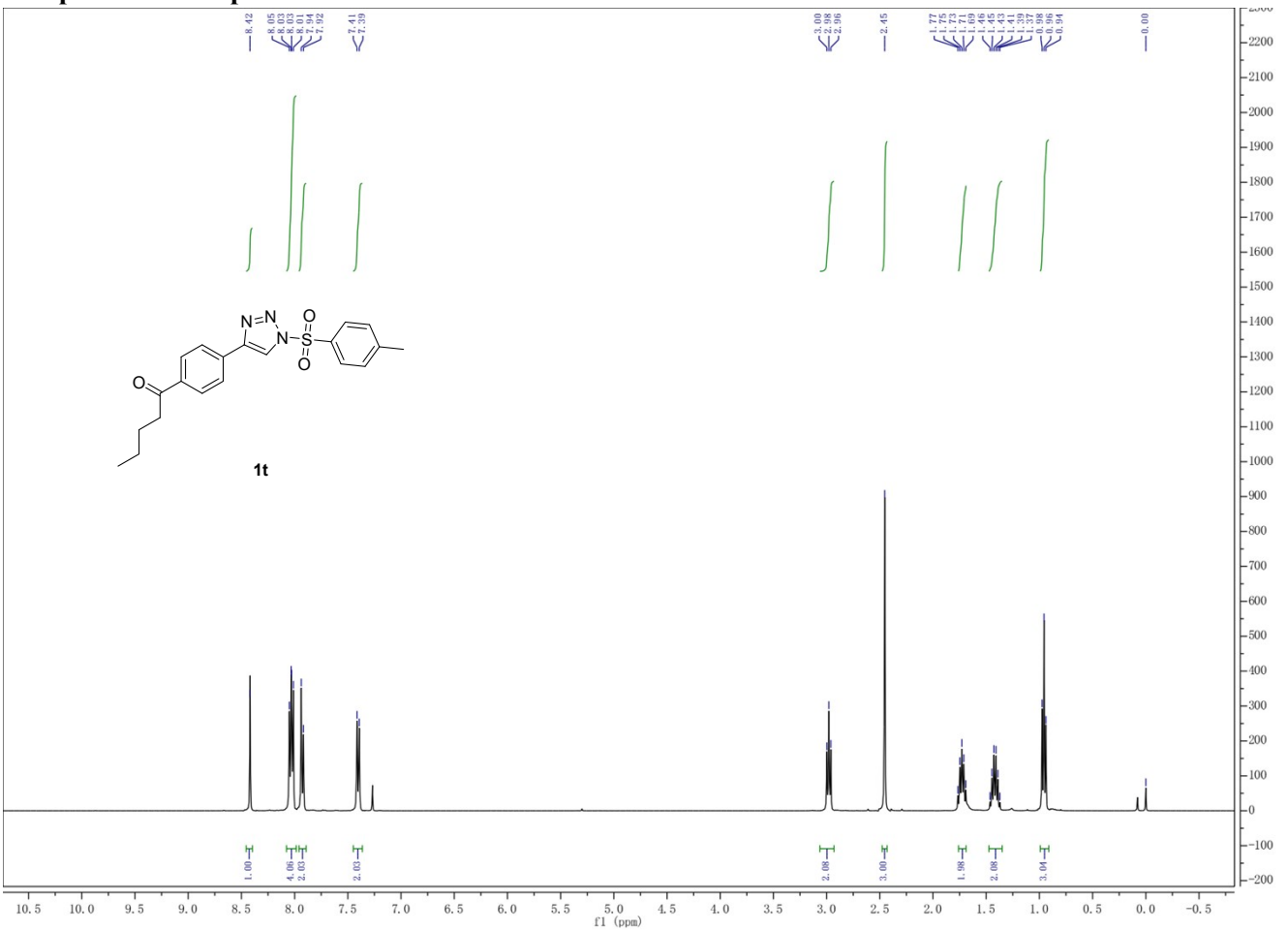



**Figure S1. $^{1}$H NMR of 1t ($CDCl_3$, 400 MHz)**

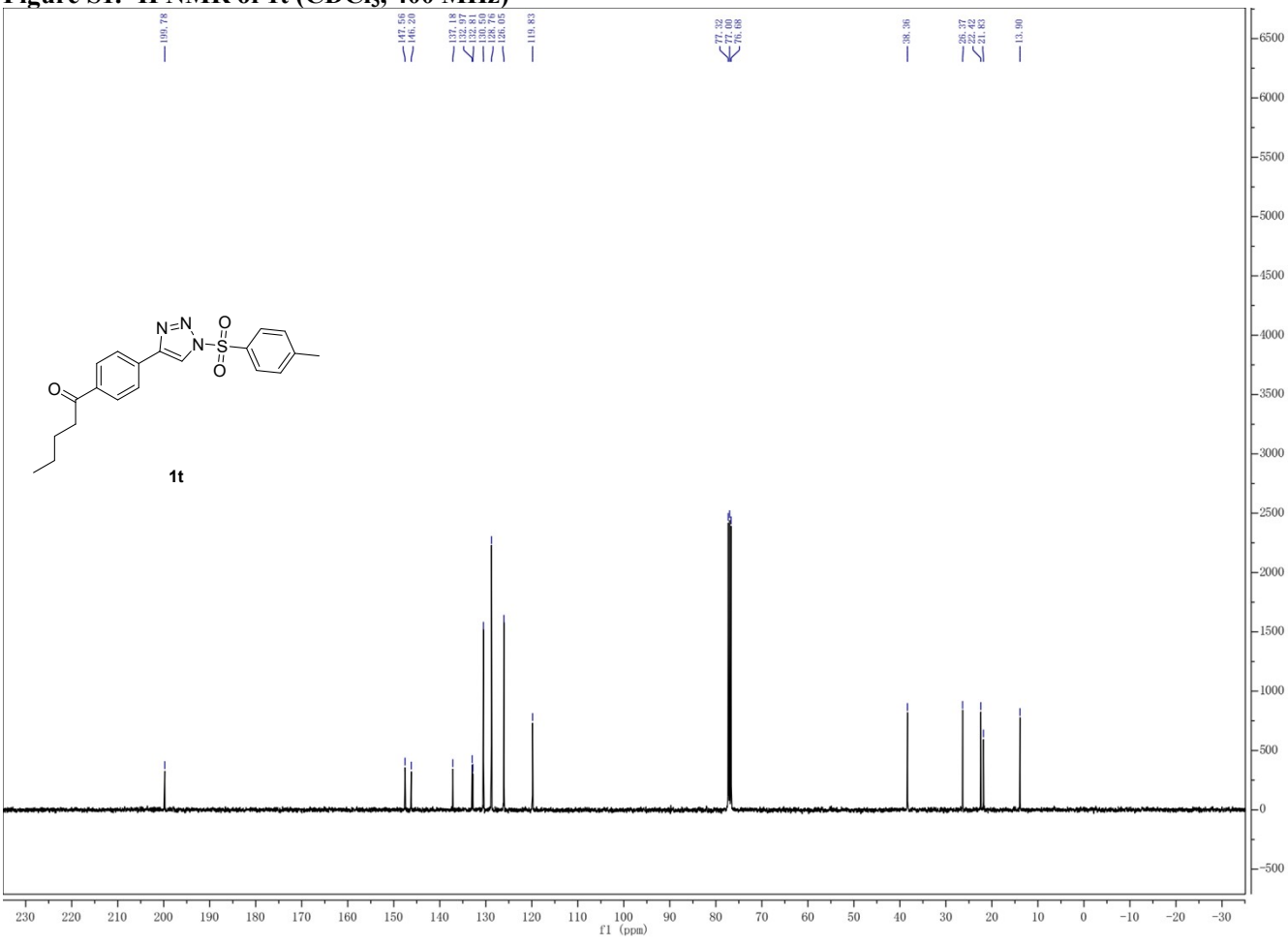


**Figure S2. $^{13}C$ NMR of 1t ($CDCl_3$, 101 MHz)**

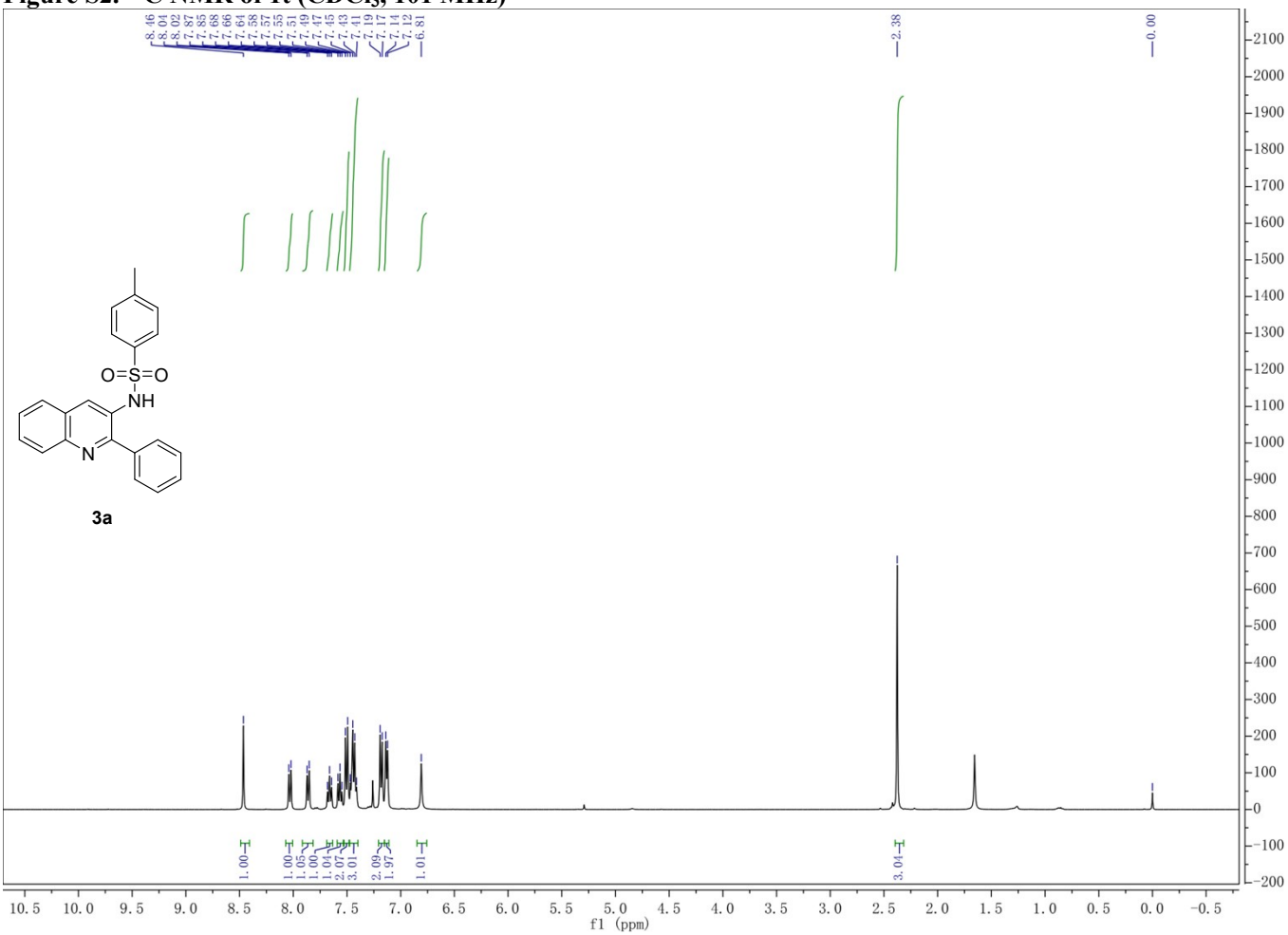



**Figure S3. $^{1}H$ NMR of 3a ($CDCl_3$, 400 MHz)**

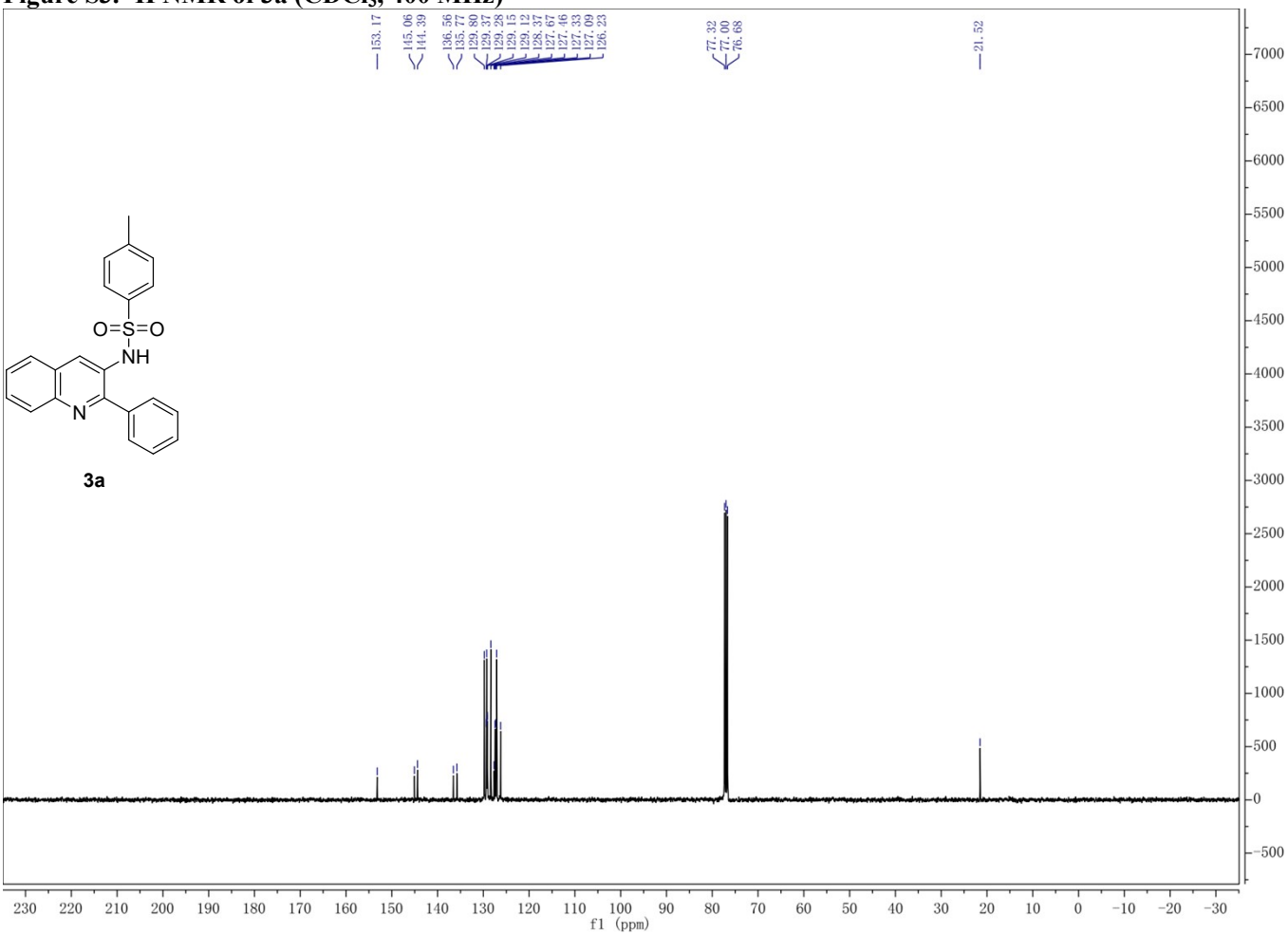



**Figure 4. $^{13}C$ NMR of 3a ($CDCl_3$, 101 MHz)**

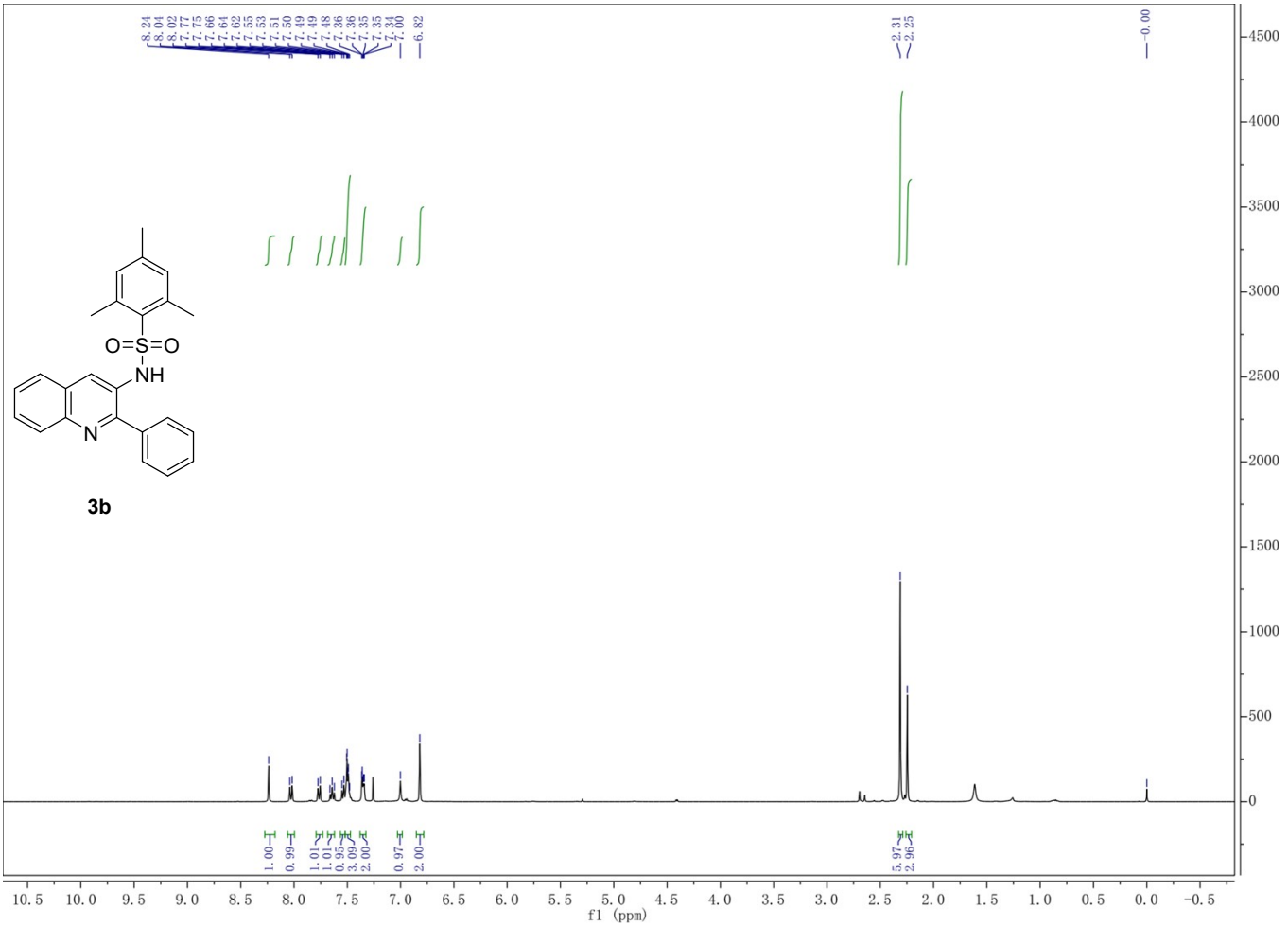



**Figure S5. $^{1}$H NMR of 3b ($CDCl_3$, 400 MHz)**

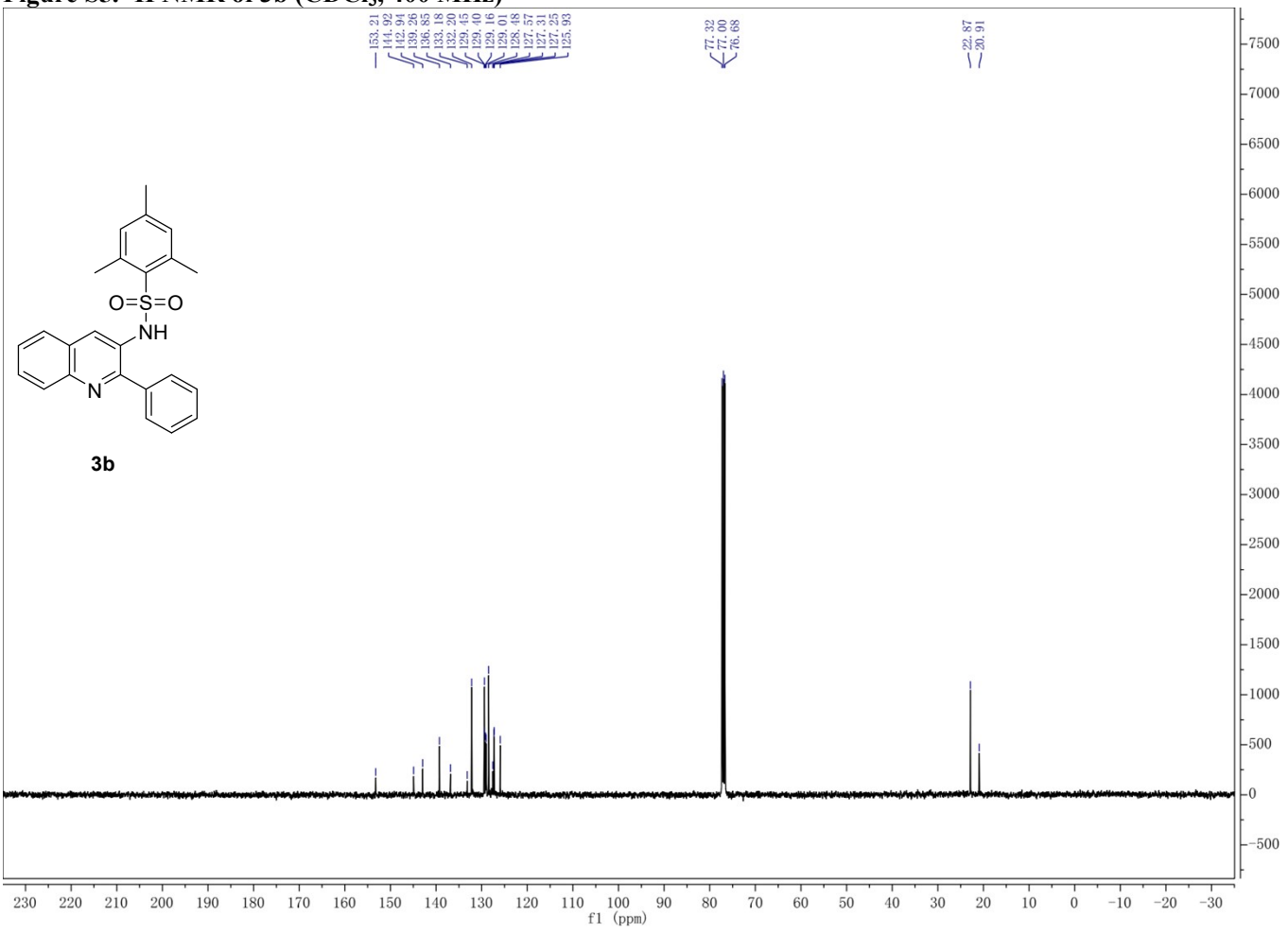



**Figure S6. $^{13}$C NMR of 3b ($CDCl_3$, 101 MHz)**

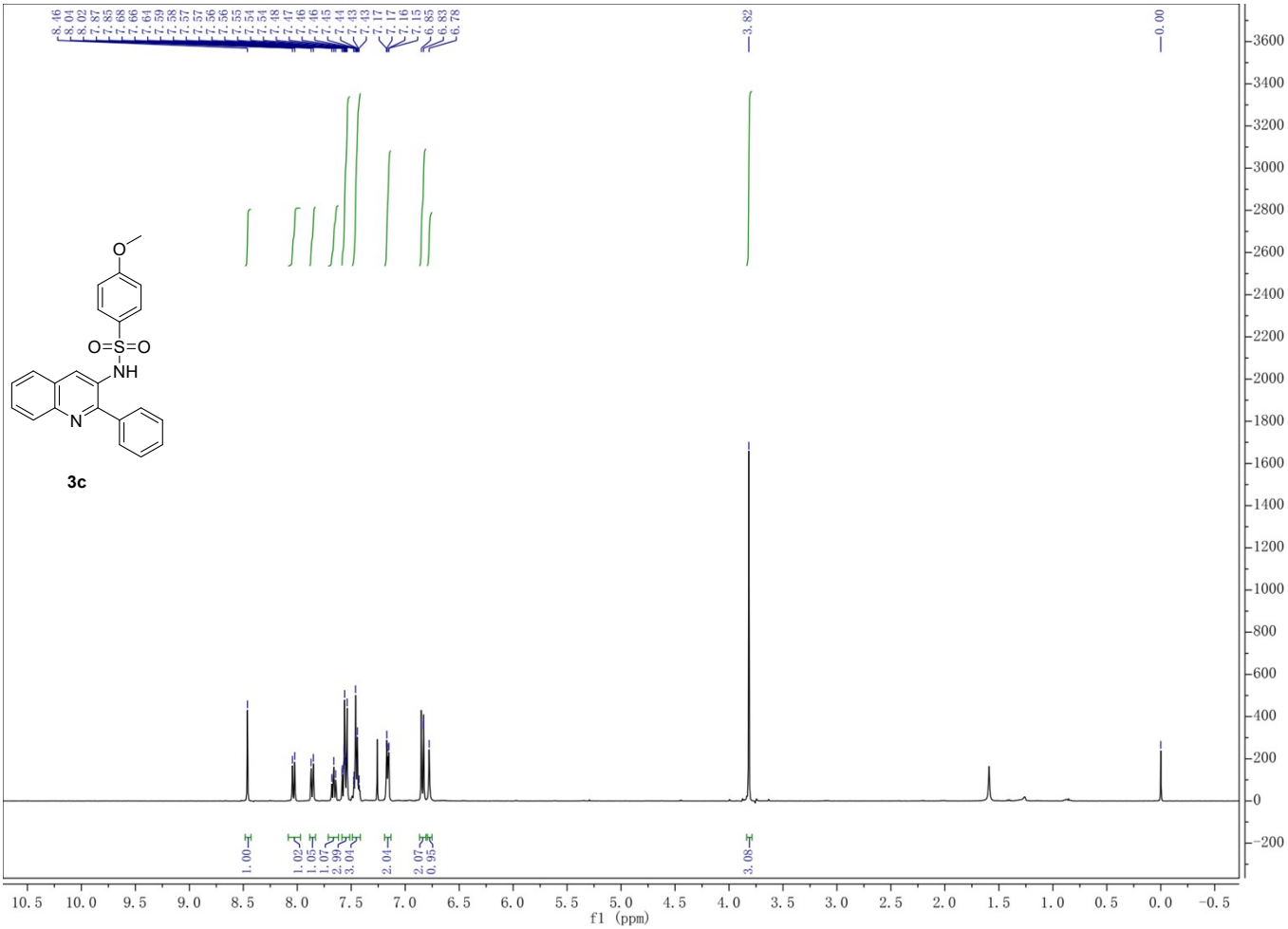



**Figure S7. $^{1}$H NMR of 3c ($CDCl_3$, 400 MHz)**

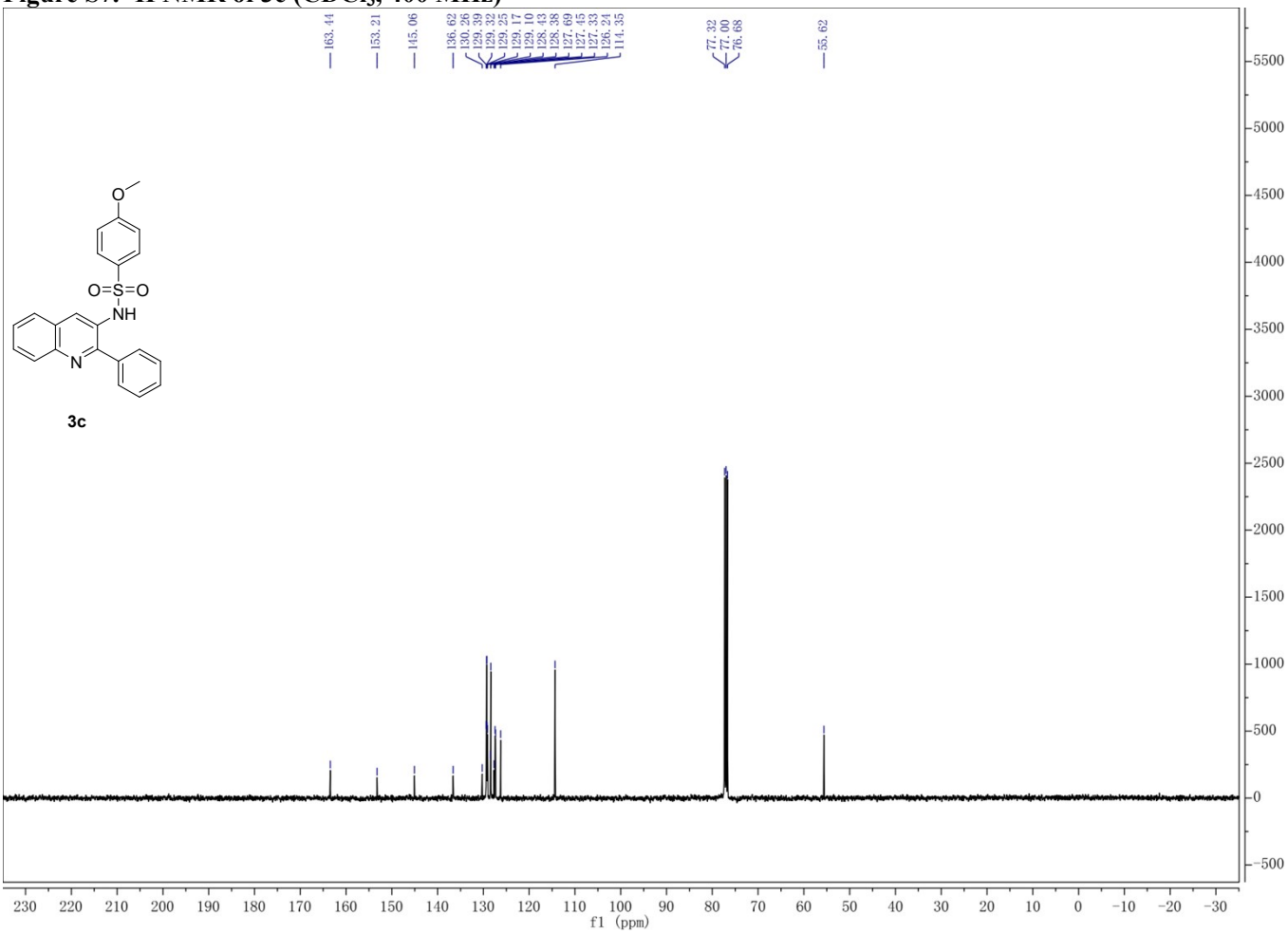



**Figure S8. $^{13}$C NMR of 3c ($CDCl_3$, 101 MHz)**

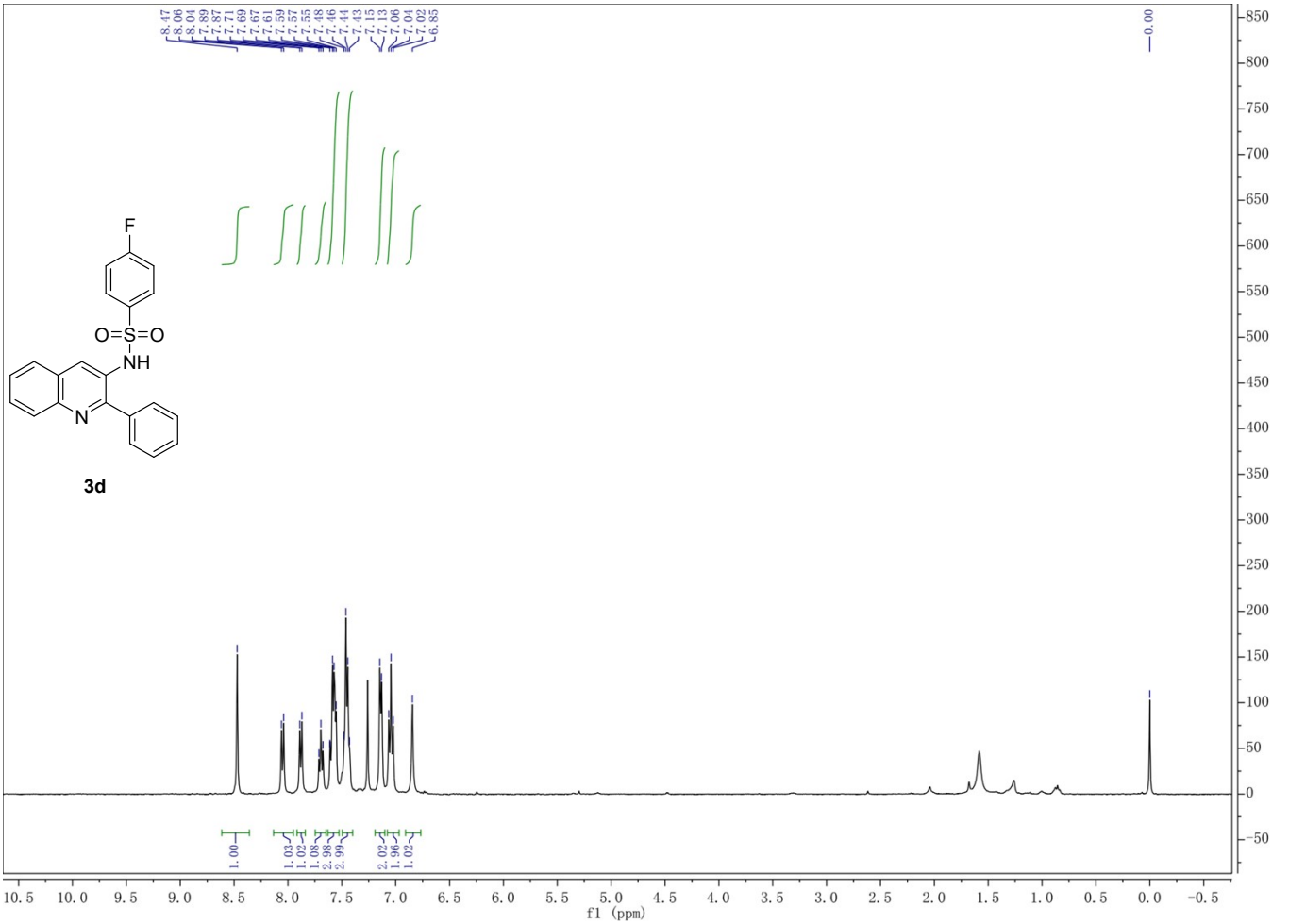



**Figure S9. $^{1}$H NMR of 3d ($CDCl_3$, 400 MHz)**

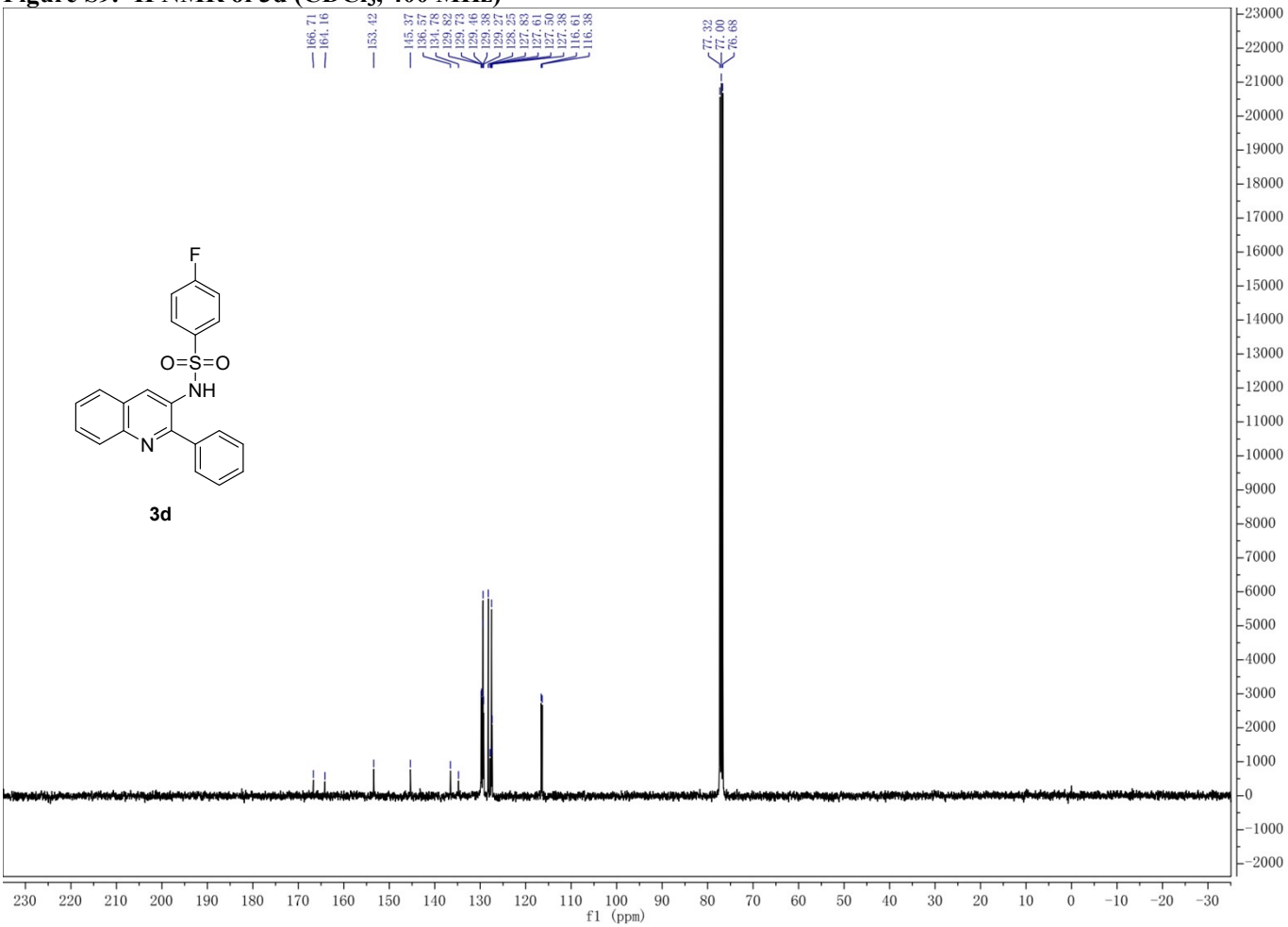



**Figure S10. $^{13}$C NMR of 3d ($CDCl_3$, 101 MHz)**

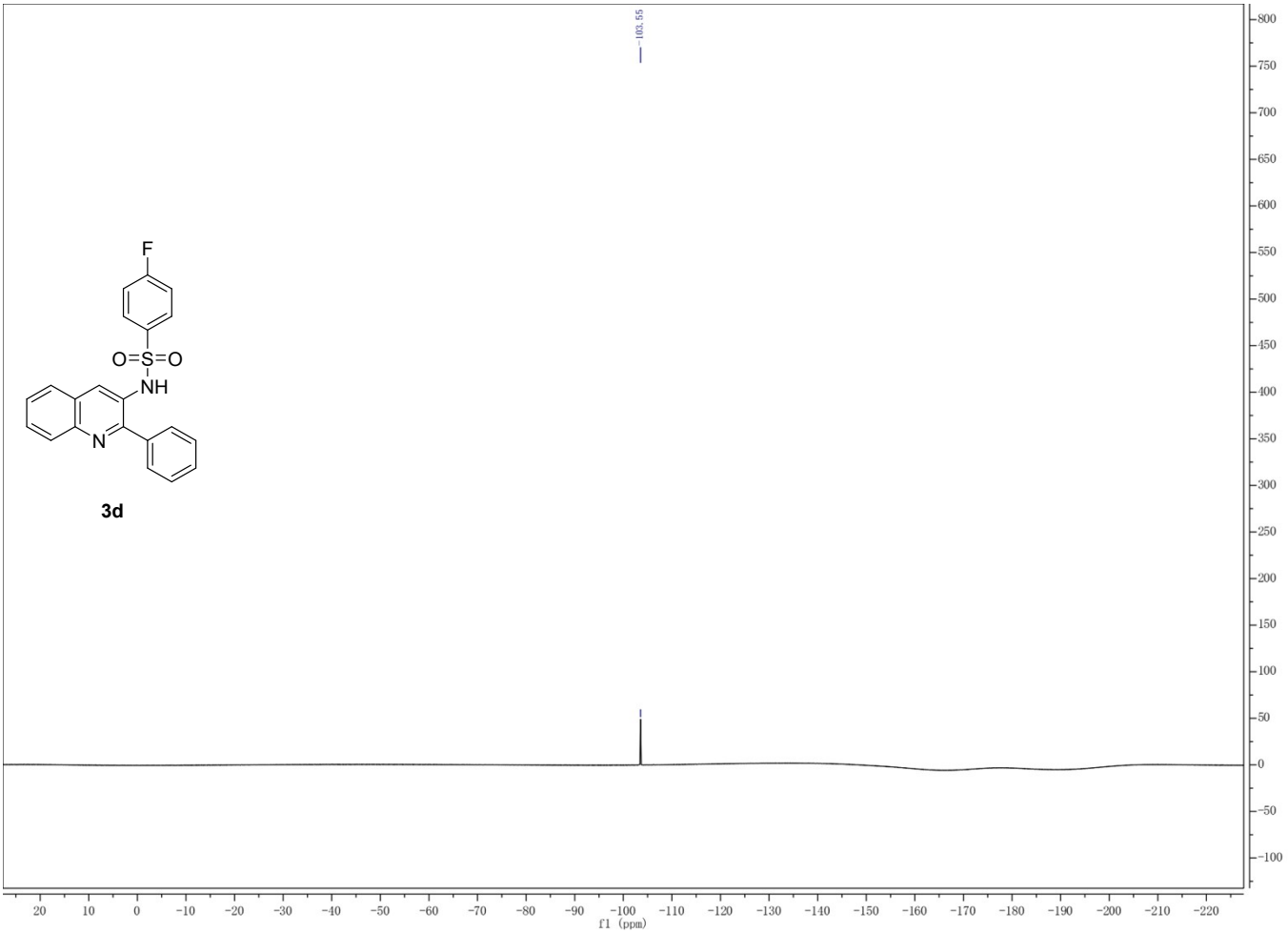



**Figure S11. $^{19}$F NMRof 3d ($CDCl_3$, 376 MHz)**

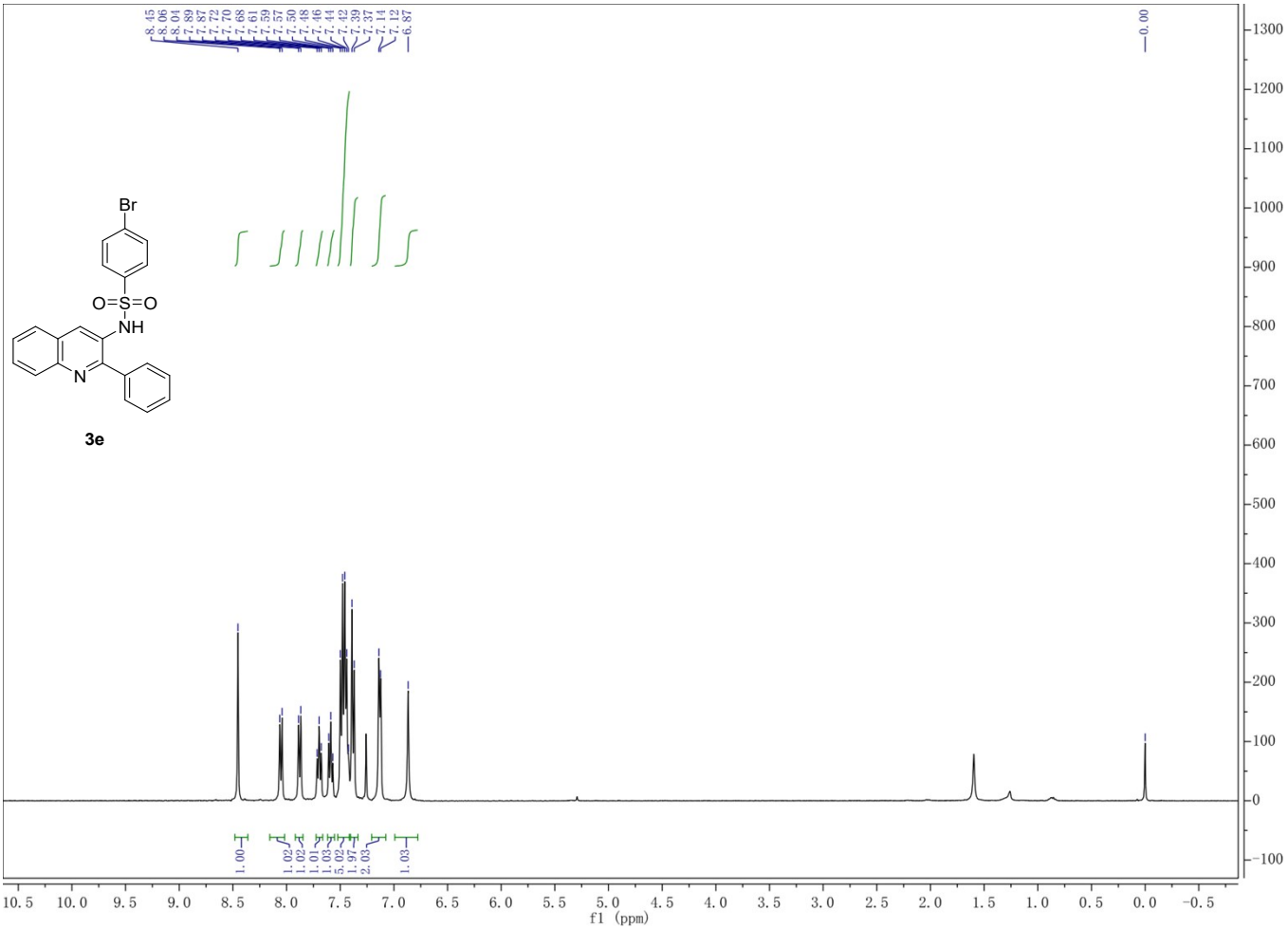



**Figure S12. $^{1}$H NMR of 3e ($CDCl_3$, 400 MHz)**

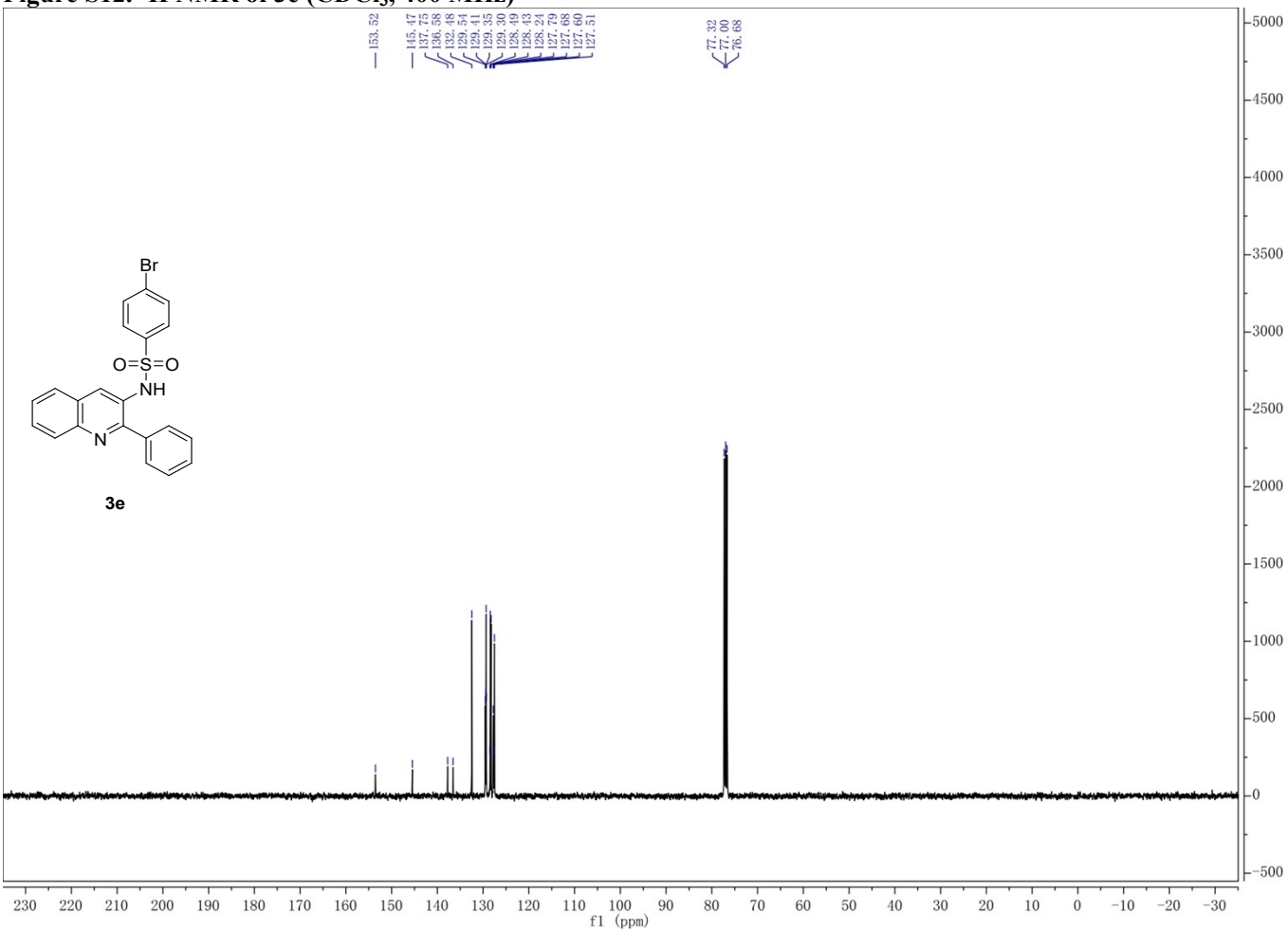



**Figure S13. $^{13}$C NMR of 3e ($CDCl_3$, 101 MHz)**

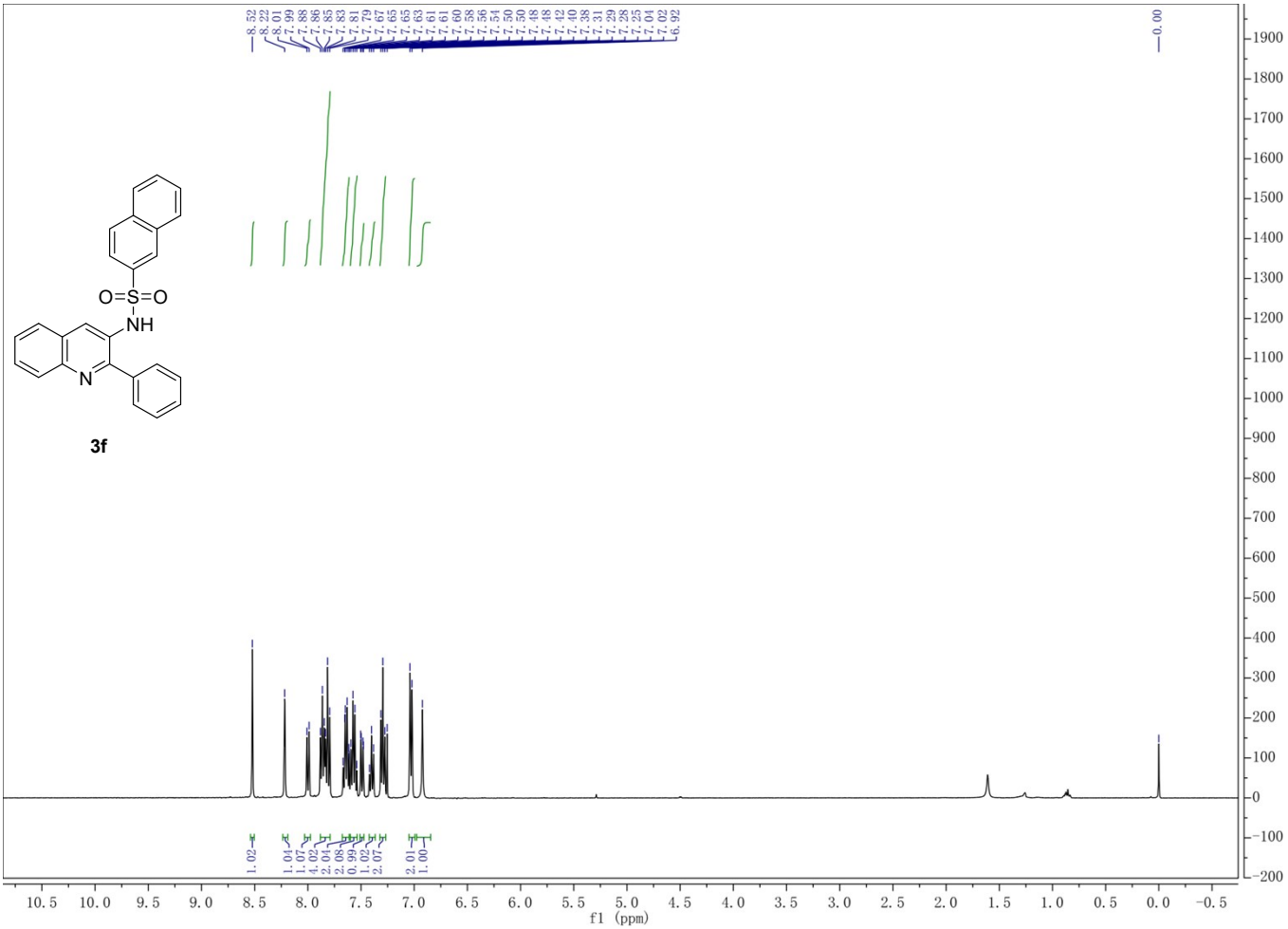



**Figure S14. $^{1}$H NMR of 3f ($CDCl_3$, 400 MHz)**

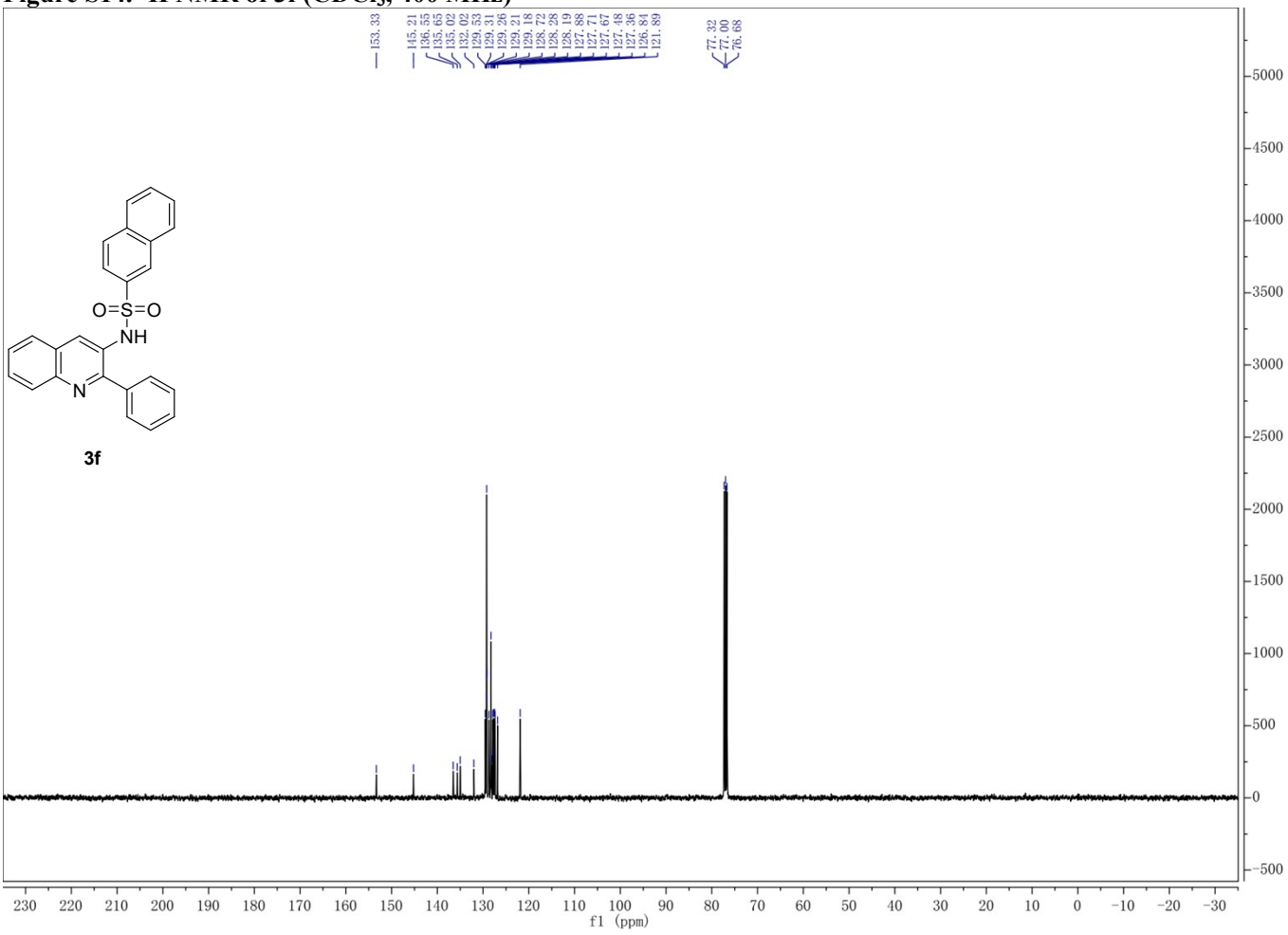



**Figure S15. $^{13}$C NMR of 3f ($CDCl_3$, 101 MHz)**

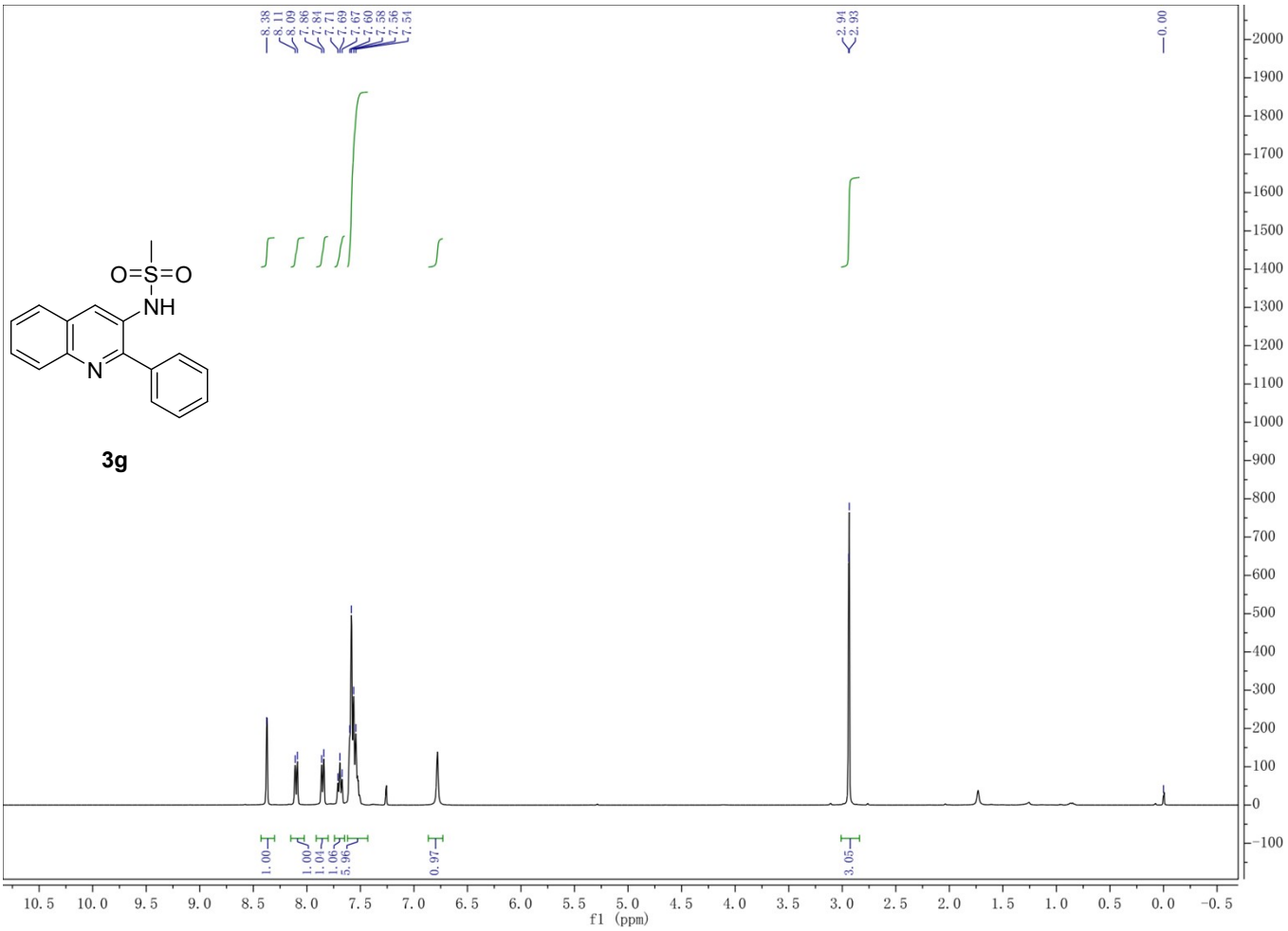



**Figure S16. $^{1}$H NMR of 3g ($CDCl_3$, 400 MHz)**

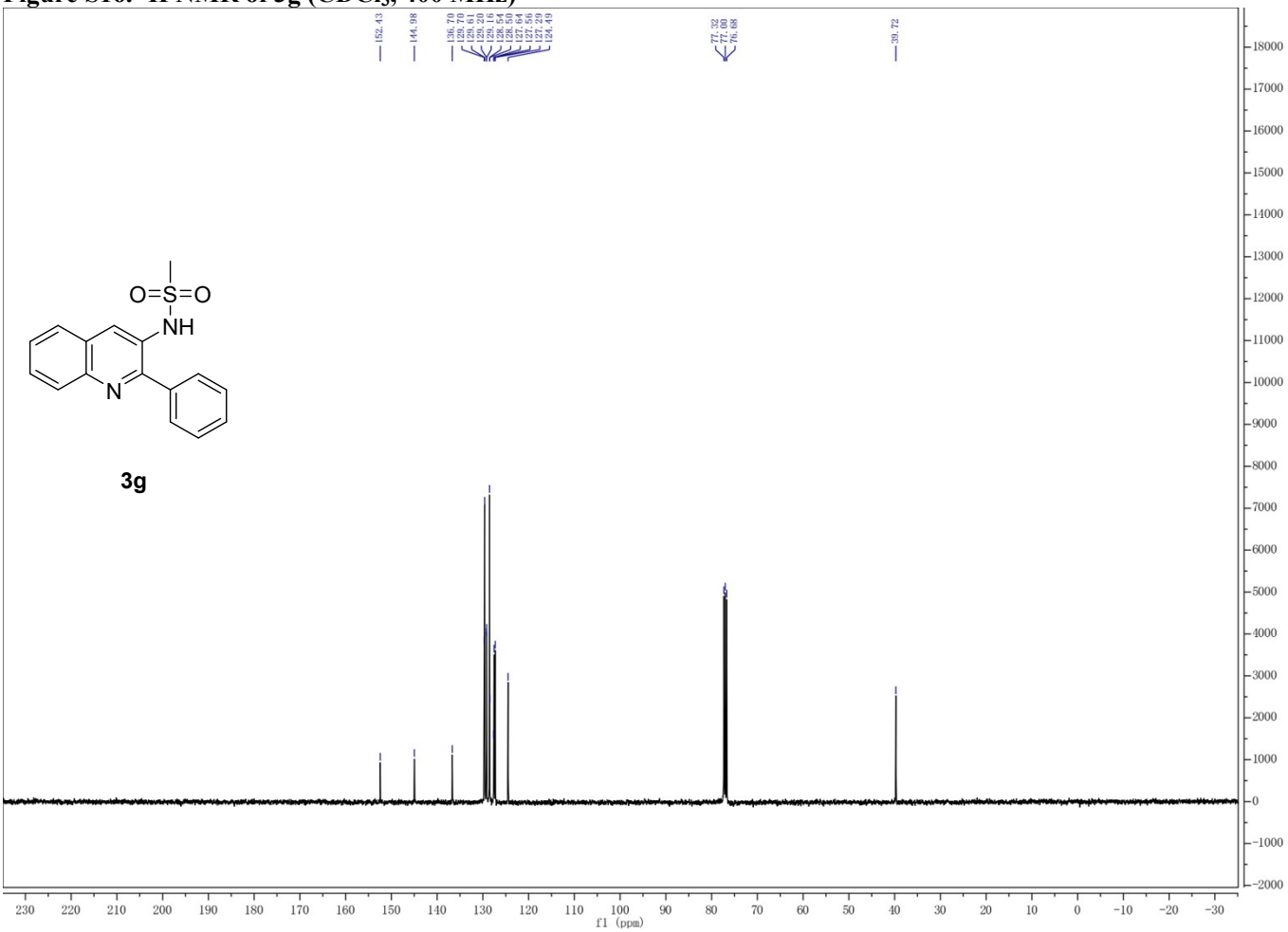



**Figure S17. $^{13}$C NMR of 3g ($CDCl_3$, 101 MHz)**

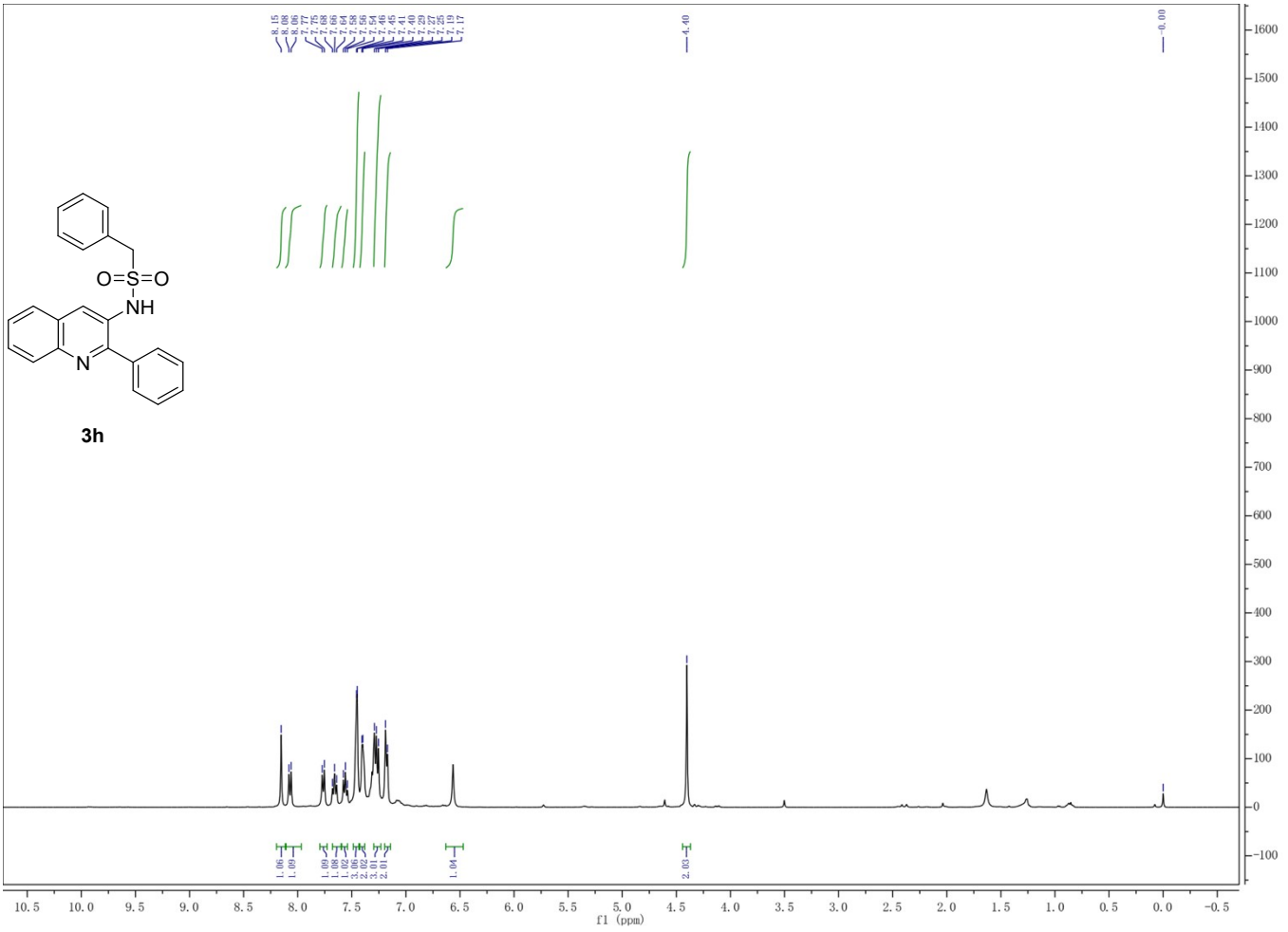



**Figure S18. $^{1}$H NMR of 3h ($CDCl_3$, 400 MHz)**

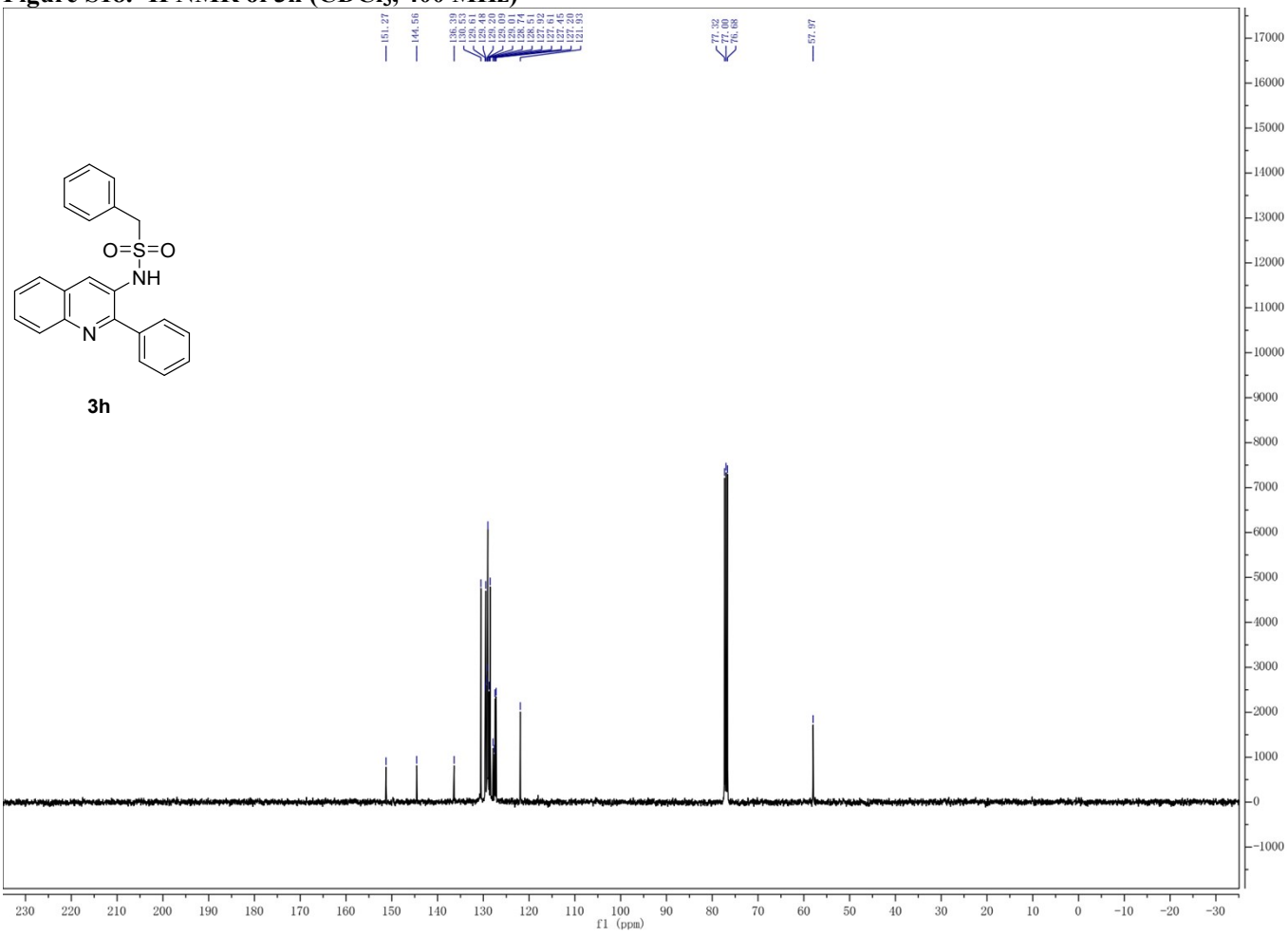



**Figure S19. $^{13}$C NMR of 3h ($CDCl_3$, 101 MHz)**

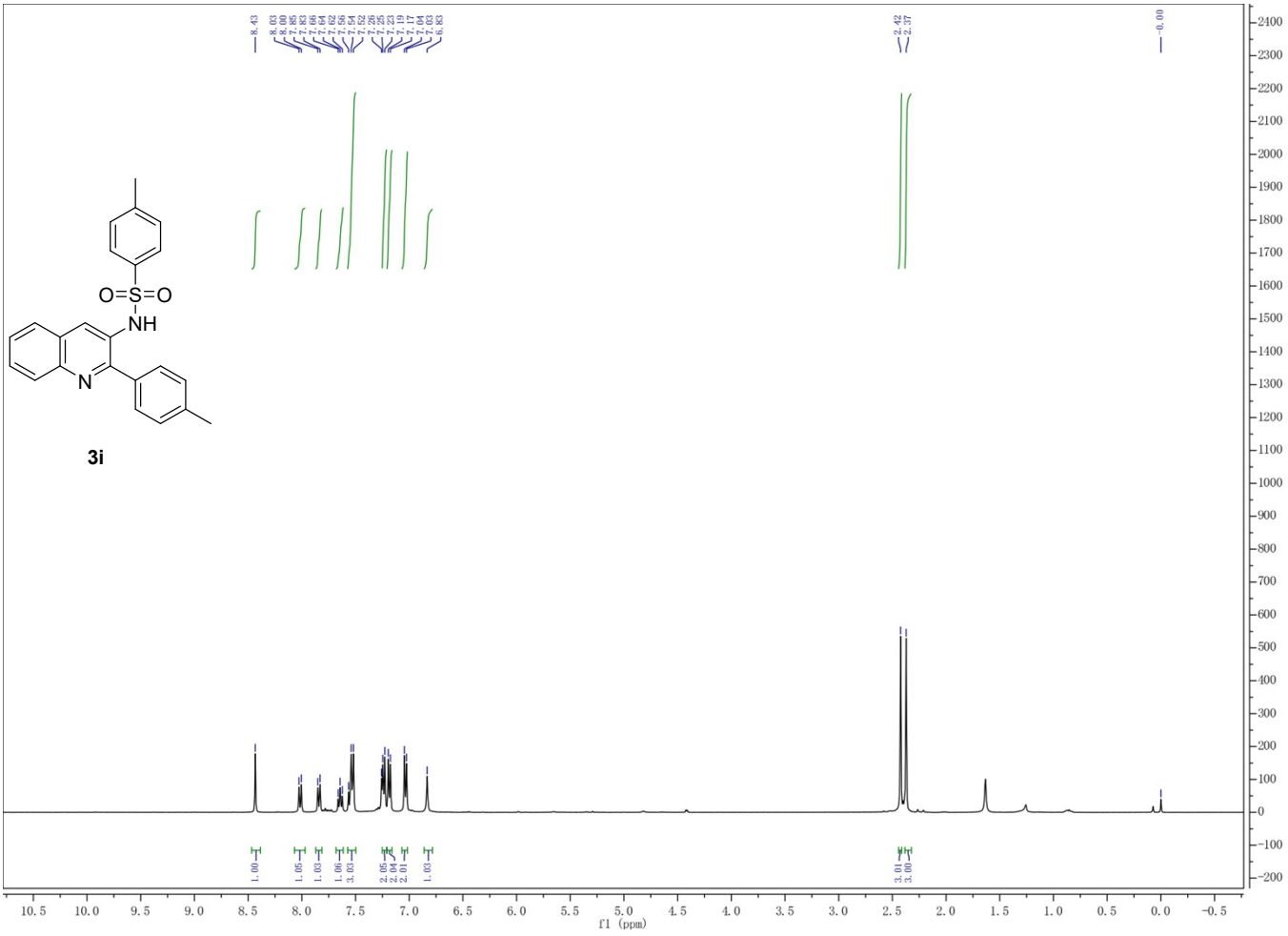



**Figure S20. $^{1}$H NMR of 3i ($CDCl_3$, 400 MHz)**

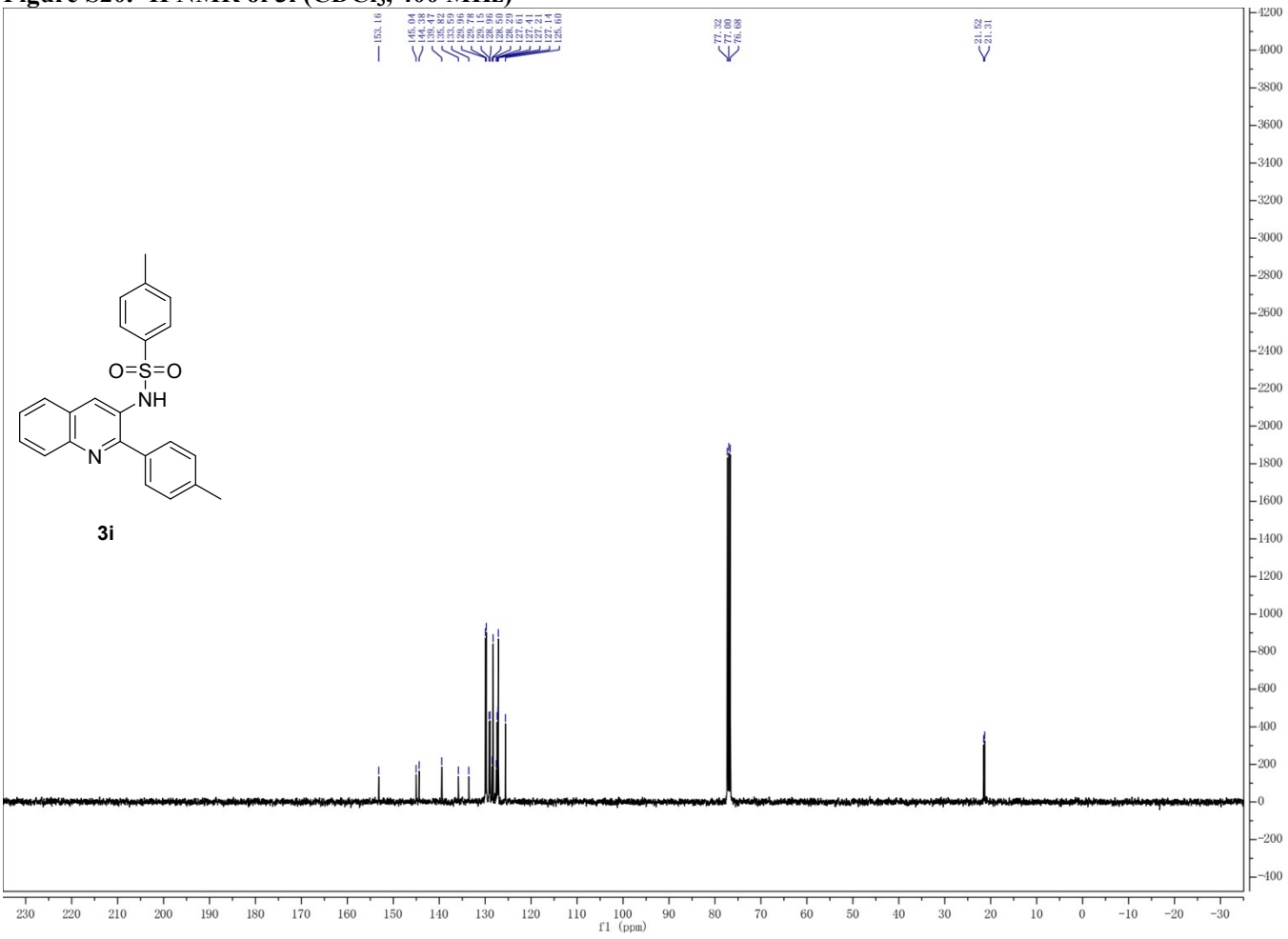



**Figure S21. $^{13}$C NMR of 3i ($CDCl_3$, 101 MHz)**

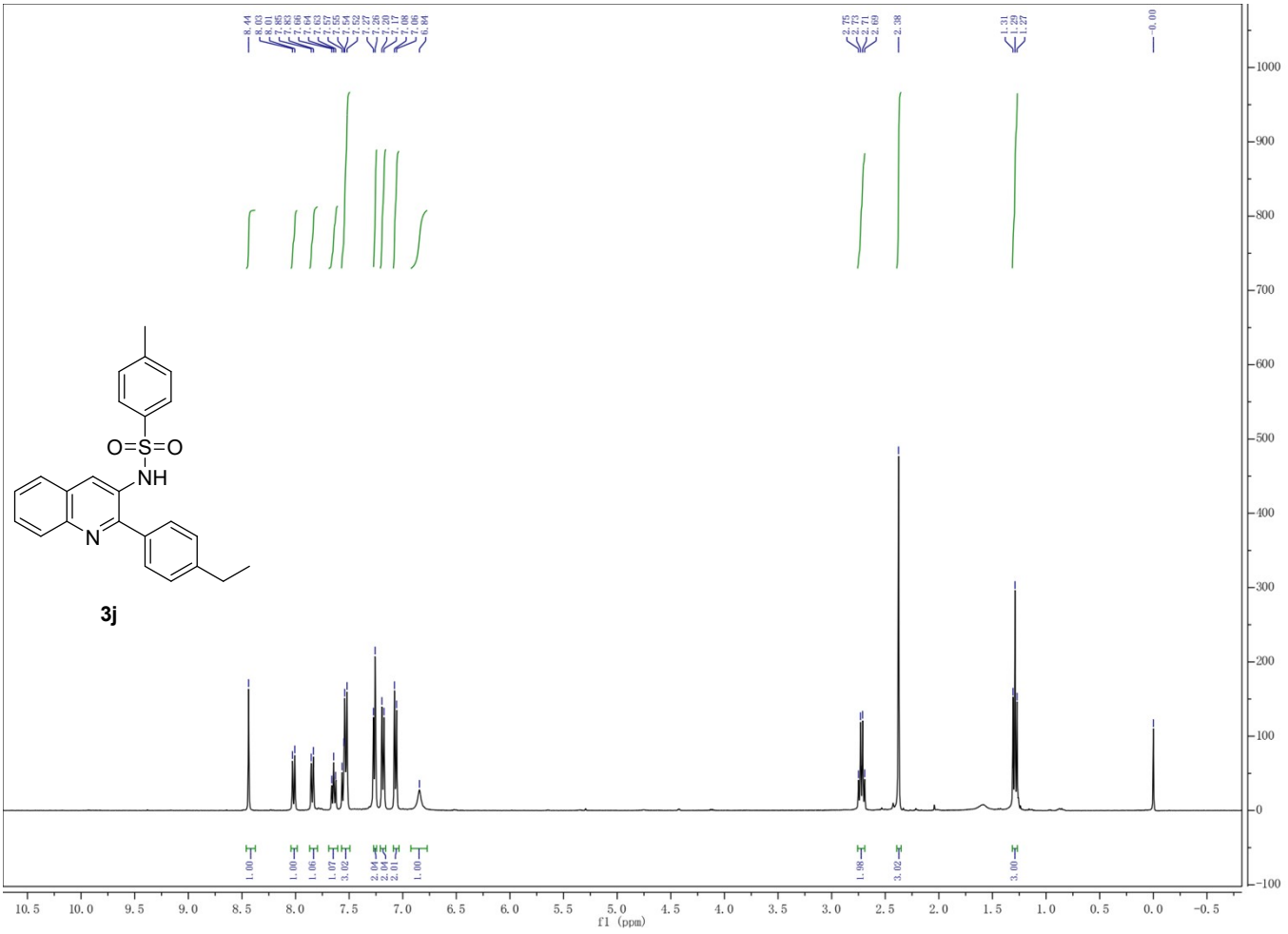



**Figure S22. $^{1}$H NMR of 3j ($CDCl_3$, 400 MHz)**

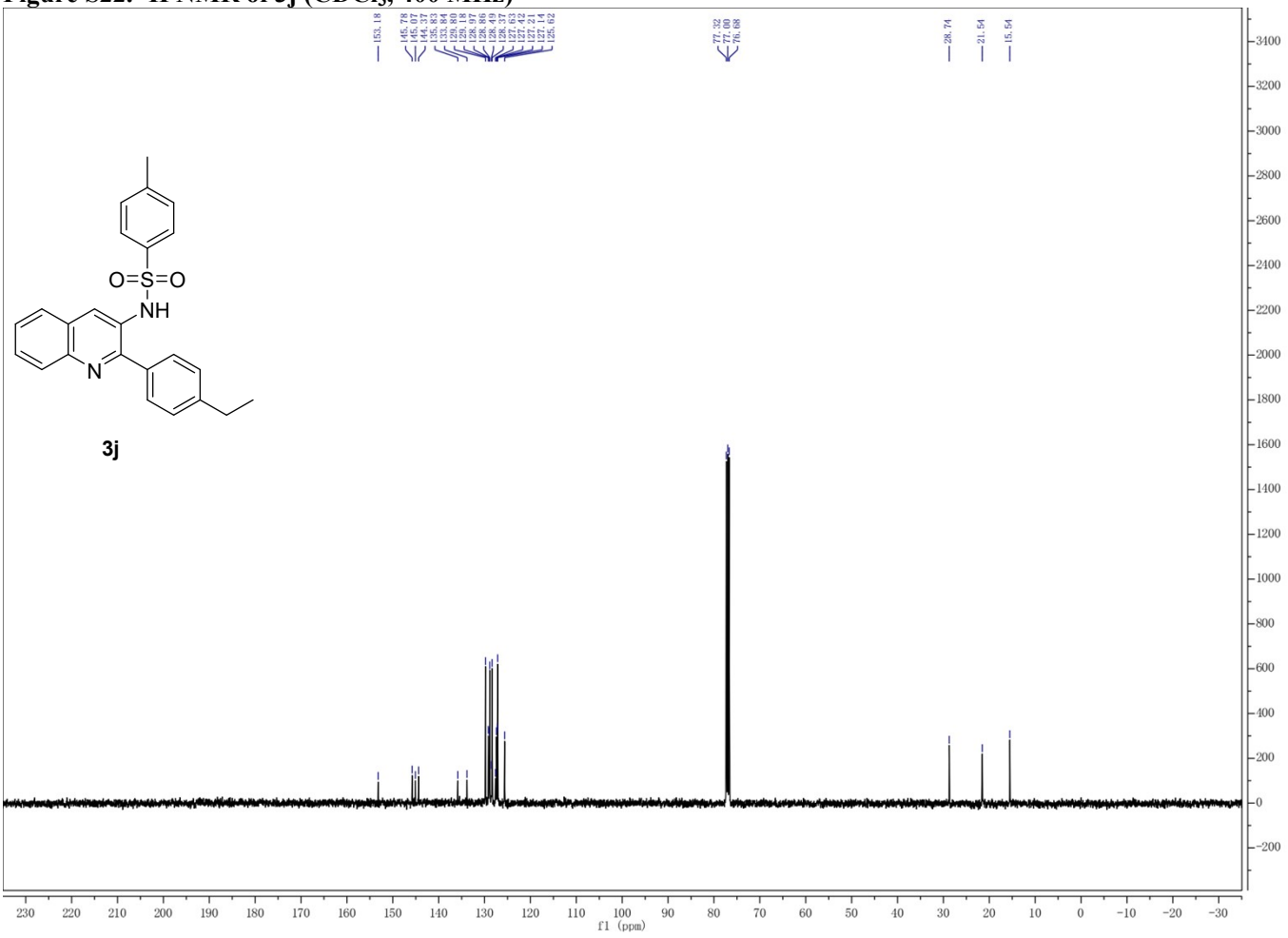



**Figure S23 $^{13}$C NMR of 3j ($CDCl_3$, 101 MHz)**

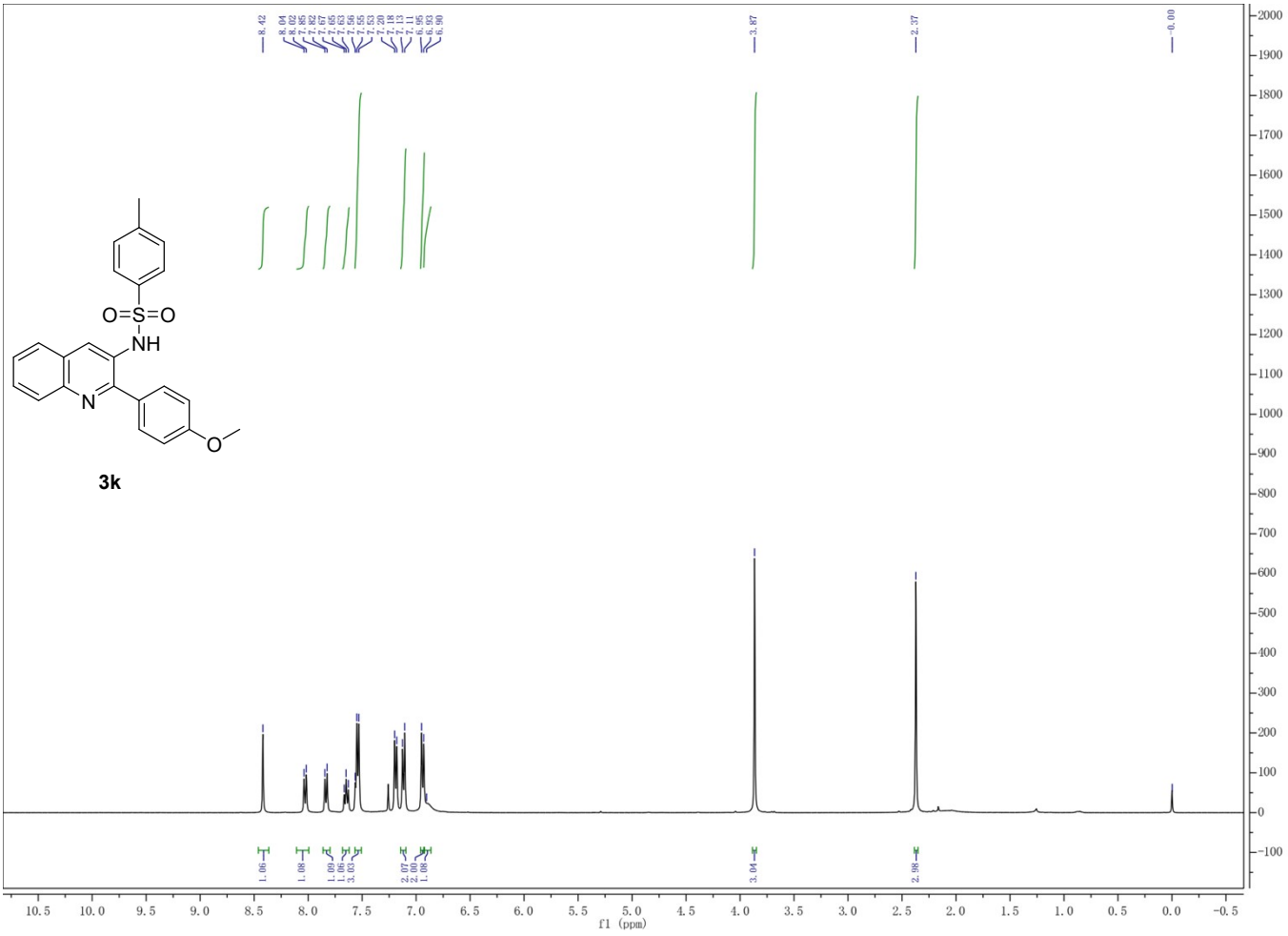



**Figure S24. $^{1}$H NMR of 3k ($CDCl_3$, 400 MHz)**

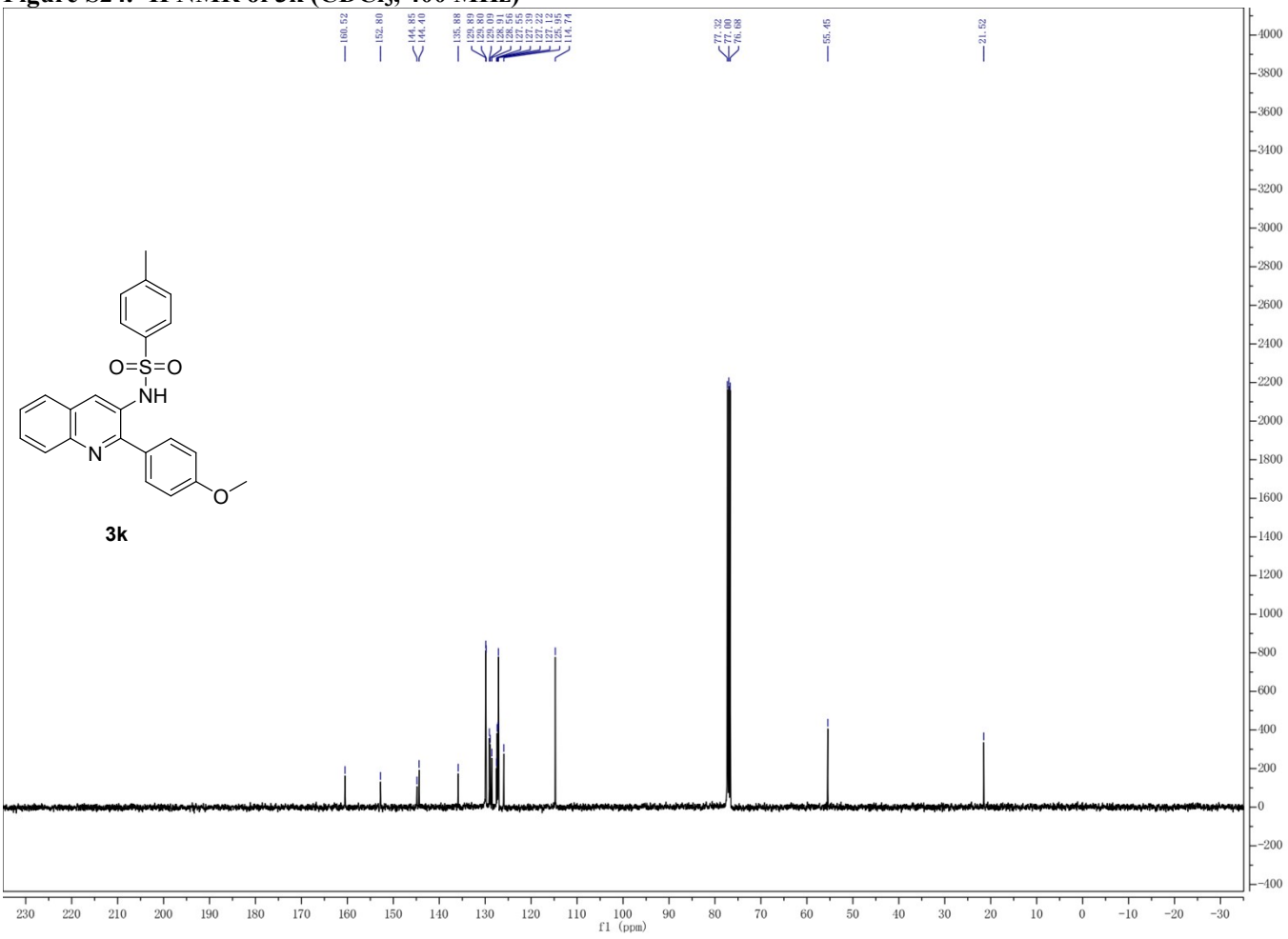



**Figure S25. $^{13}$C NMR of 3k ($CDCl_3$, 101 MHz)**

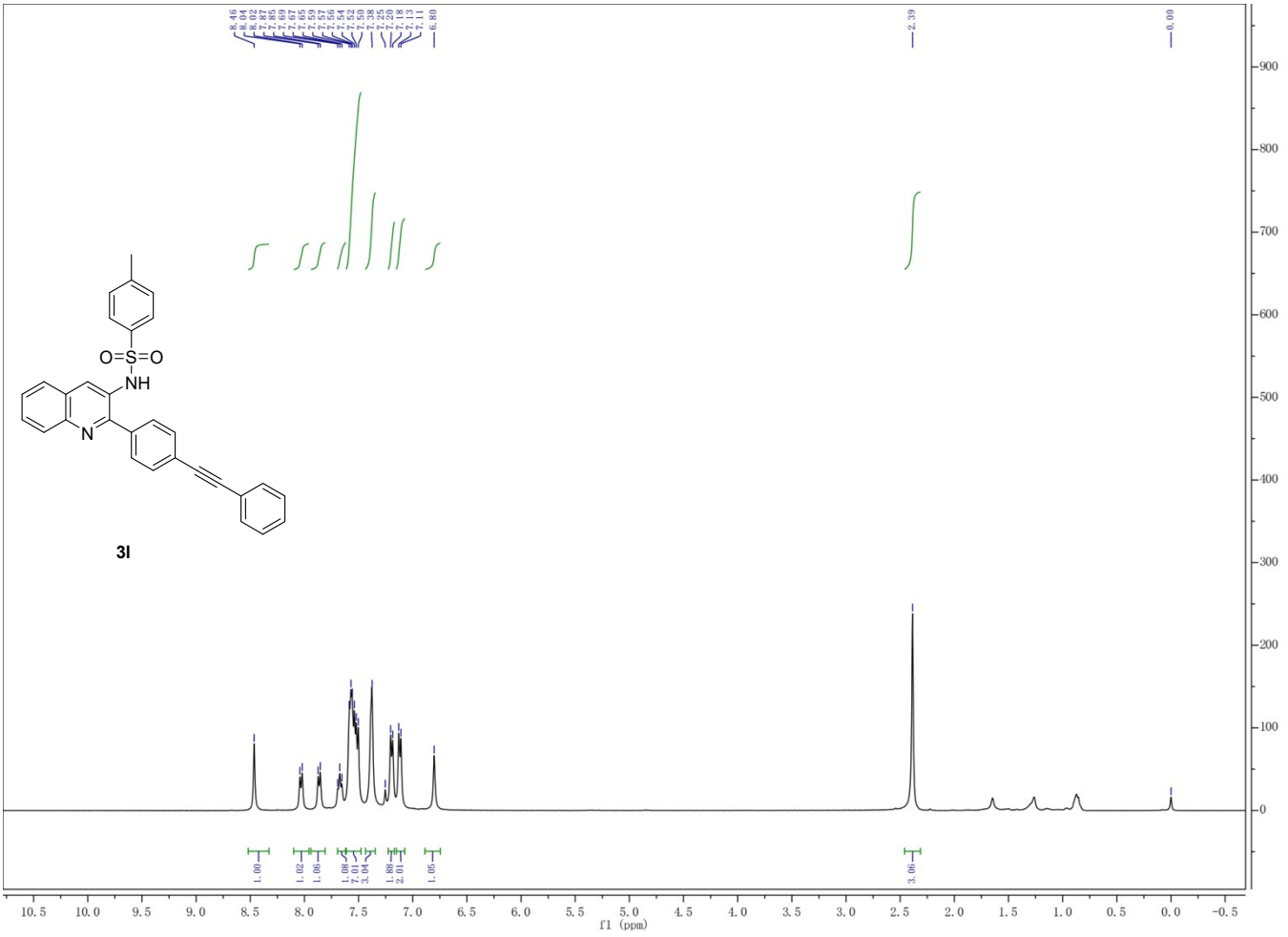



**Figure S26. $^{1}$H NMR of 3l ($CDCl_3$, 400 MHz)**

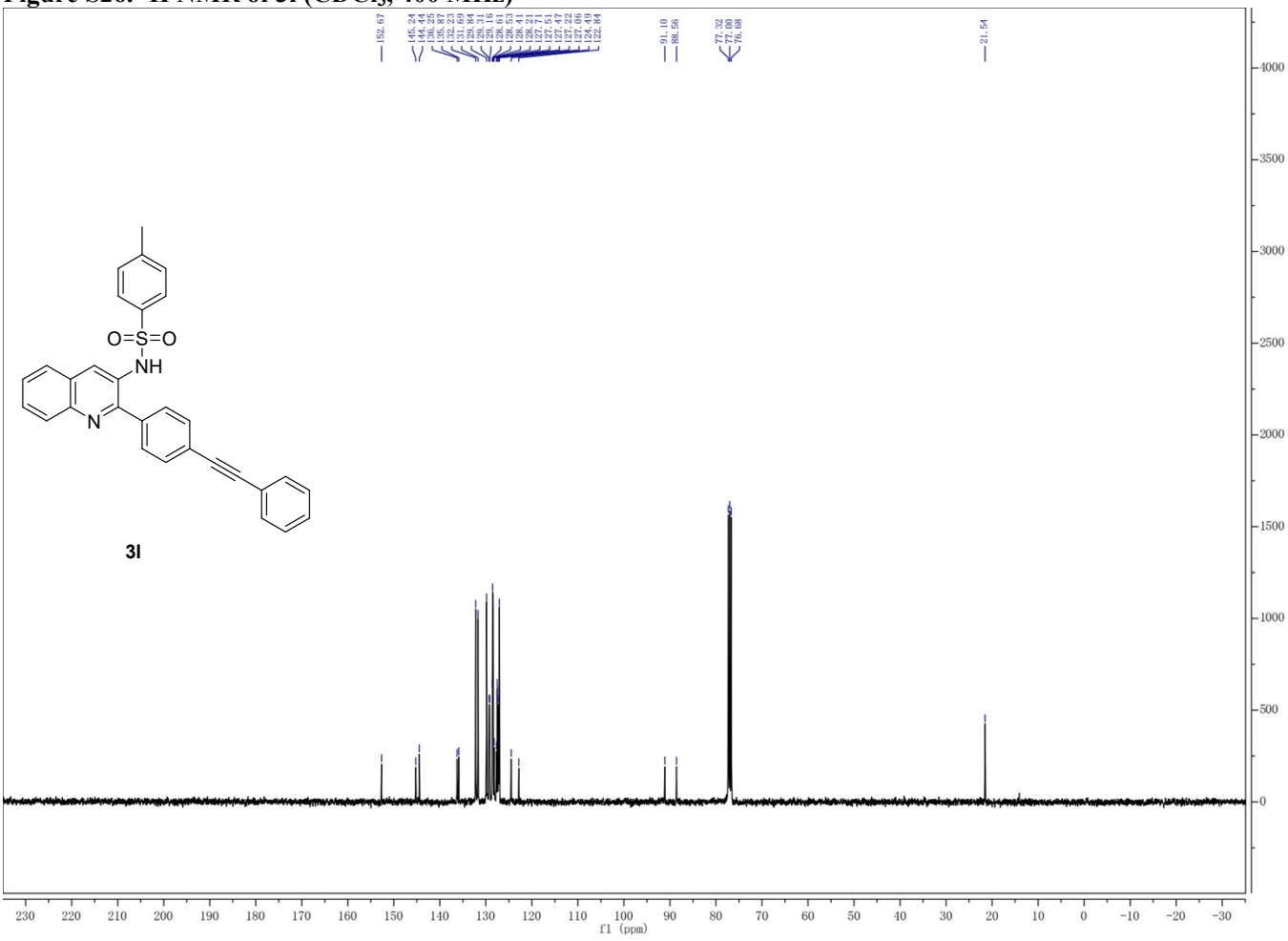



**Figure S27. $^{13}$C NMR of 3l ($CDCl_3$, 101 MHz)**

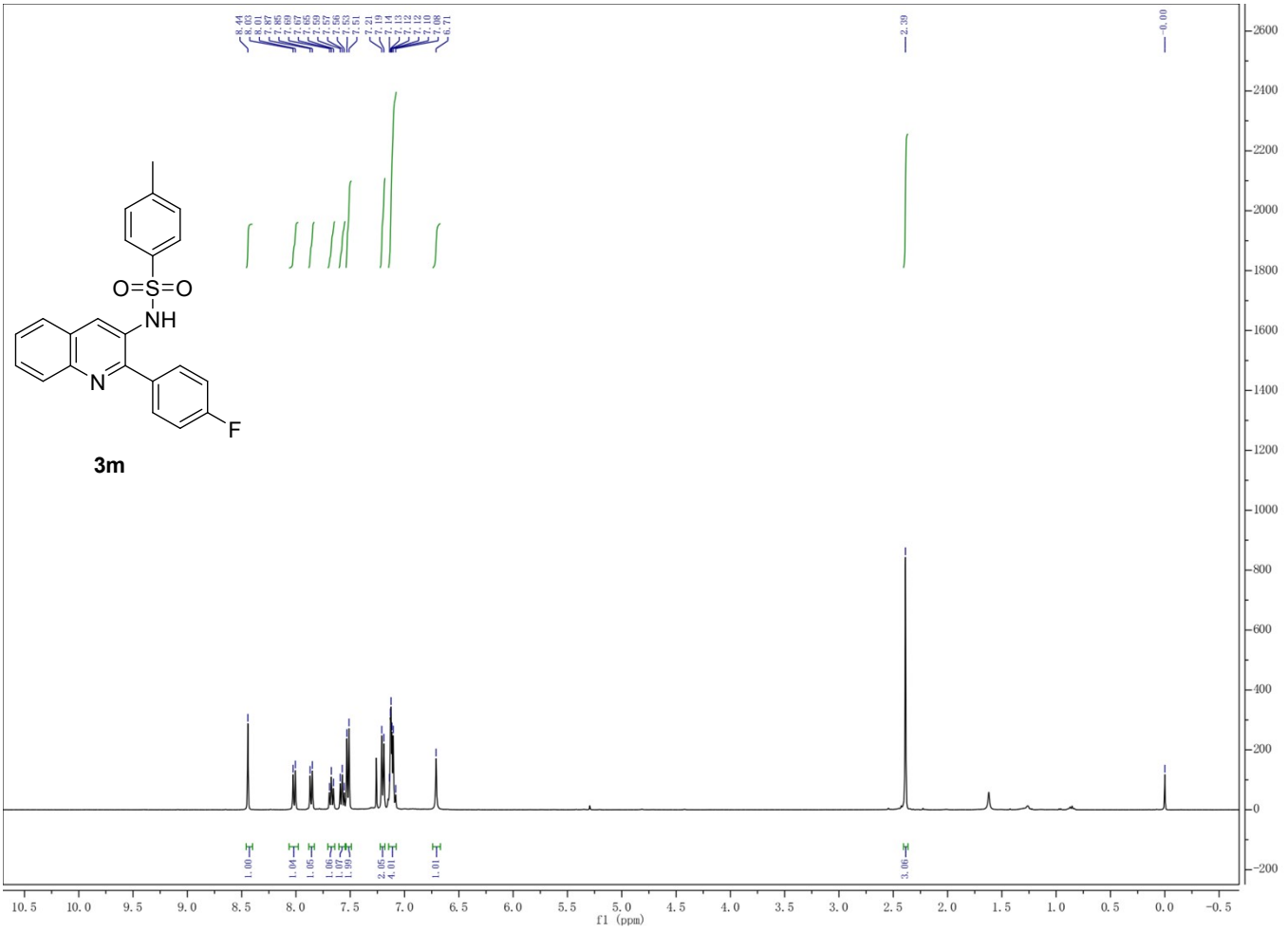



**Figure S28. $^{1}$H NMR of 3m ($CDCl_3$, 400 MHz)**

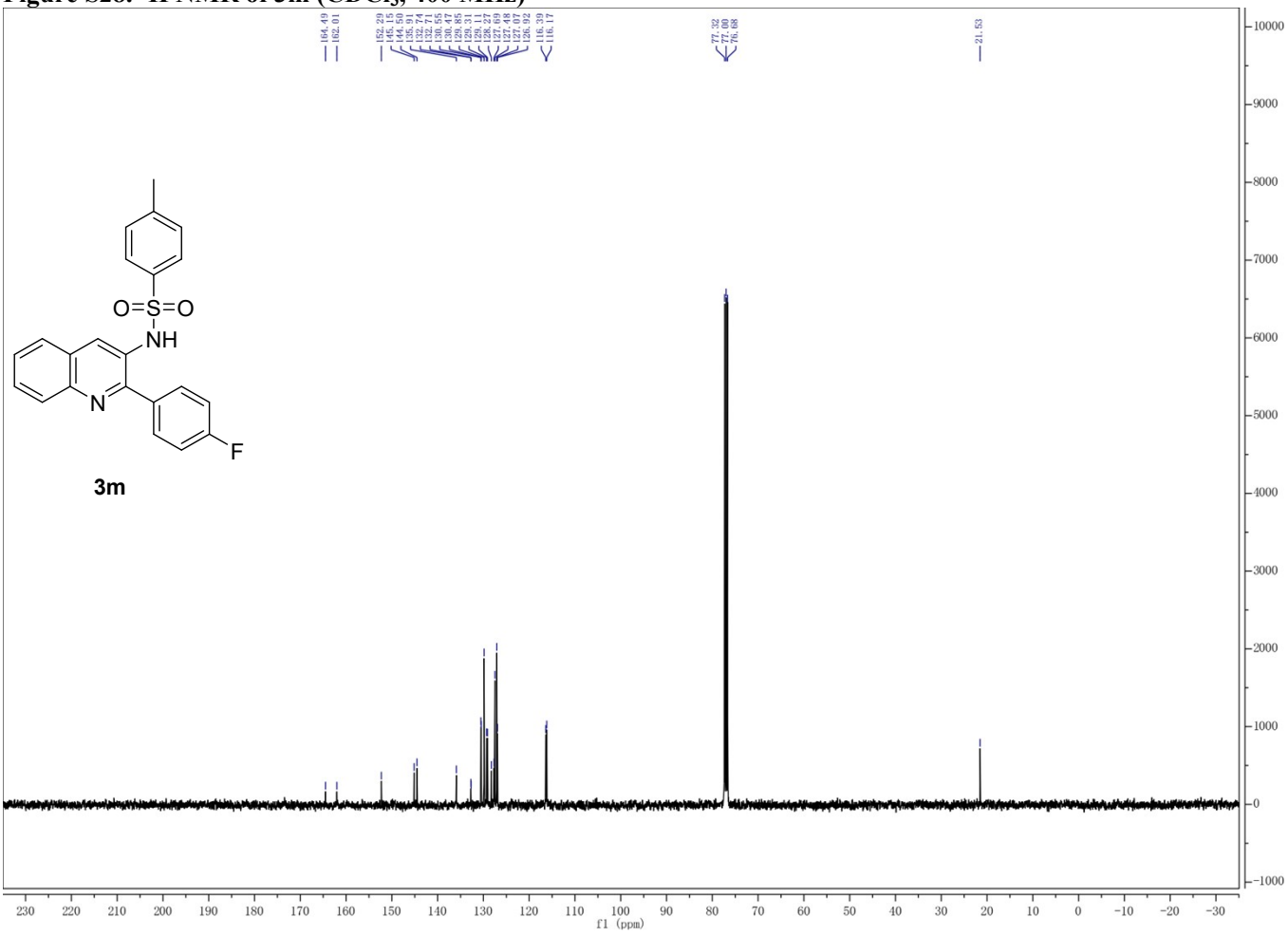



**Figure S29. $^{13}$C NMR of 3m ($CDCl_3$, 101 MHz)**

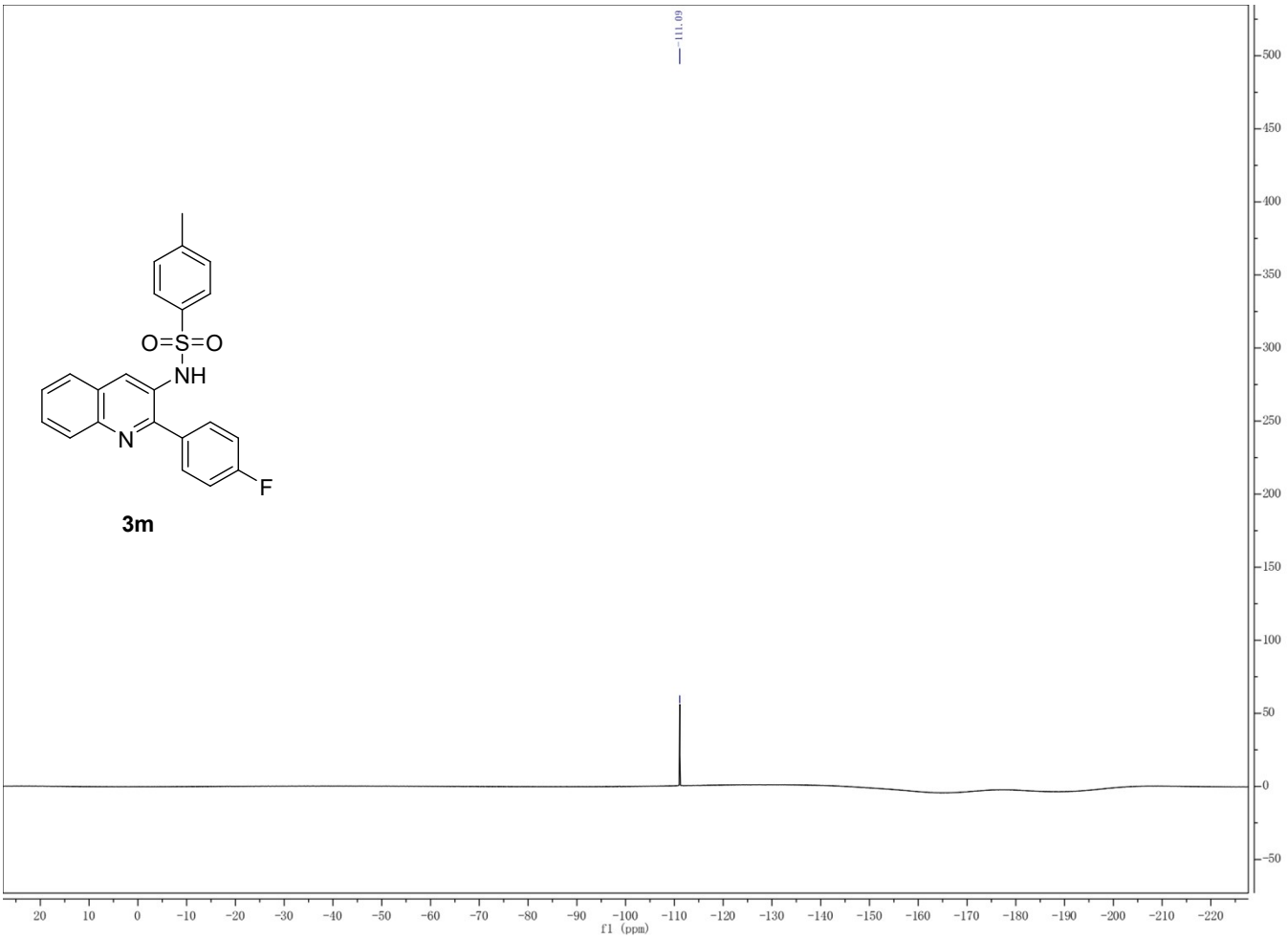



**Figure S30. $^{19}$F NMRof 3m ($CDCl_3$, 376 MHz)**

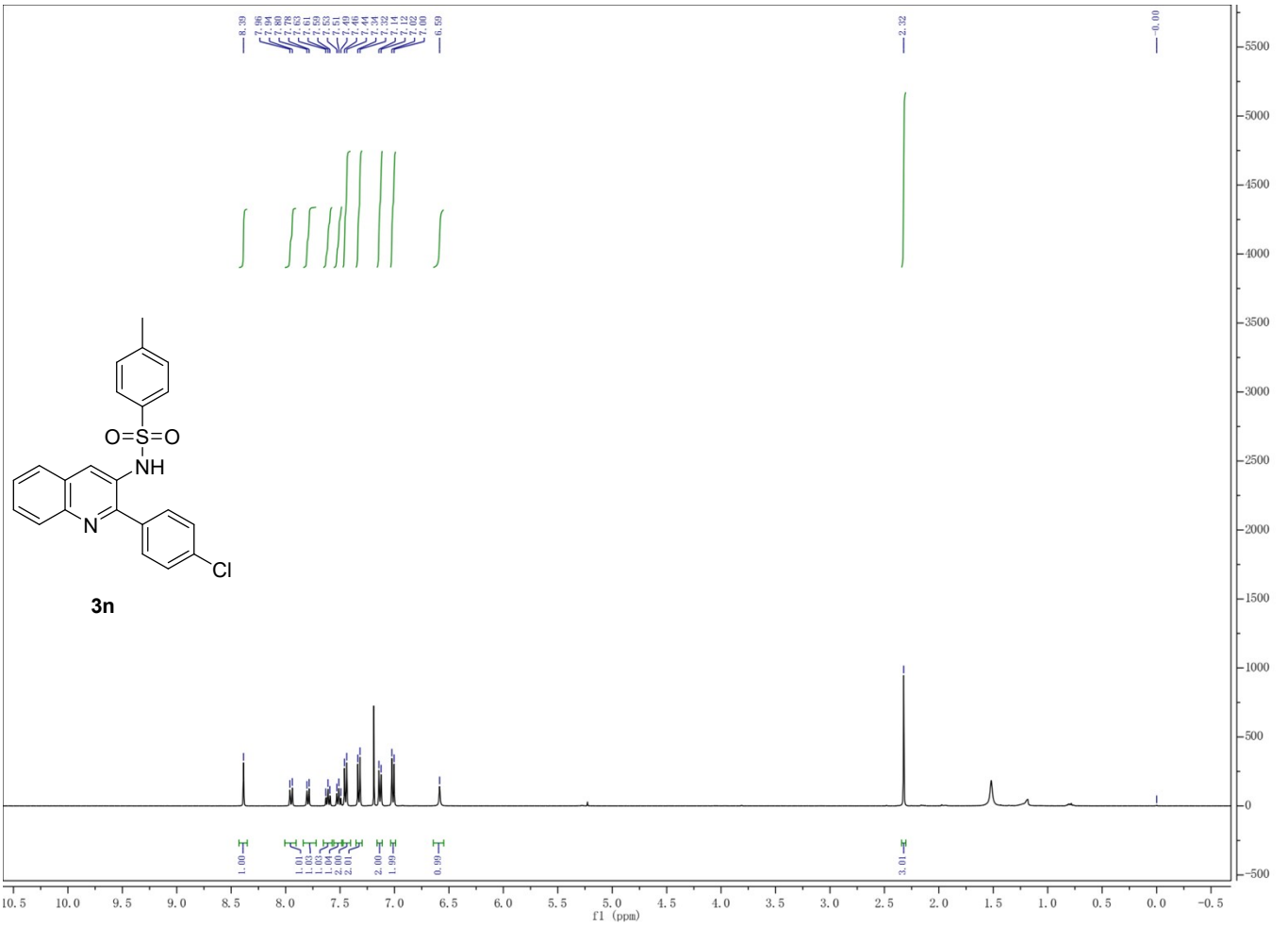



**Figure S31. $^{1}$H NMR of 3n ($CDCl_3$, 400 MHz)**

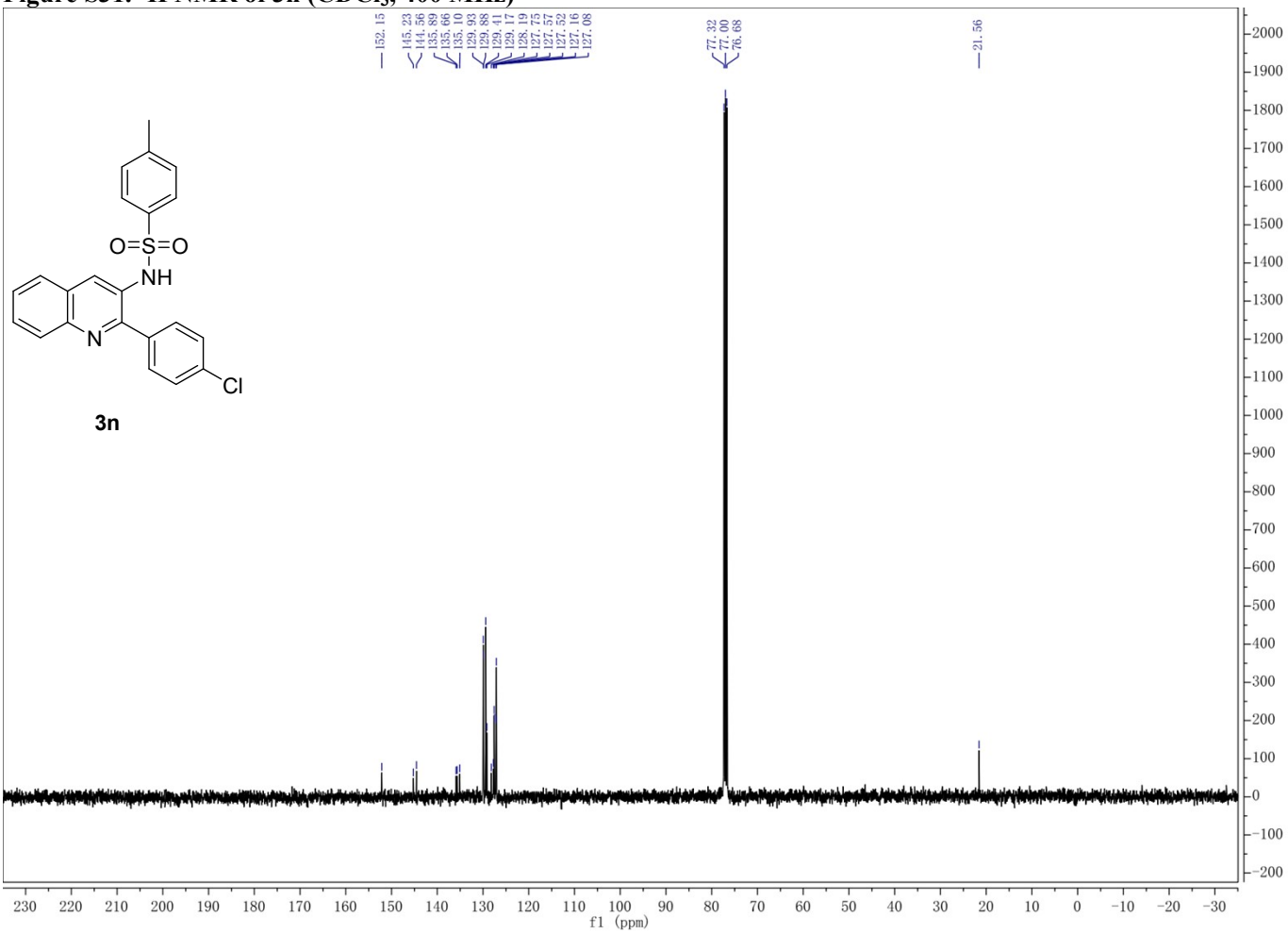



**Figure S32. $^{13}$C NMR of 3n ($CDCl_3$, 101 MHz)**

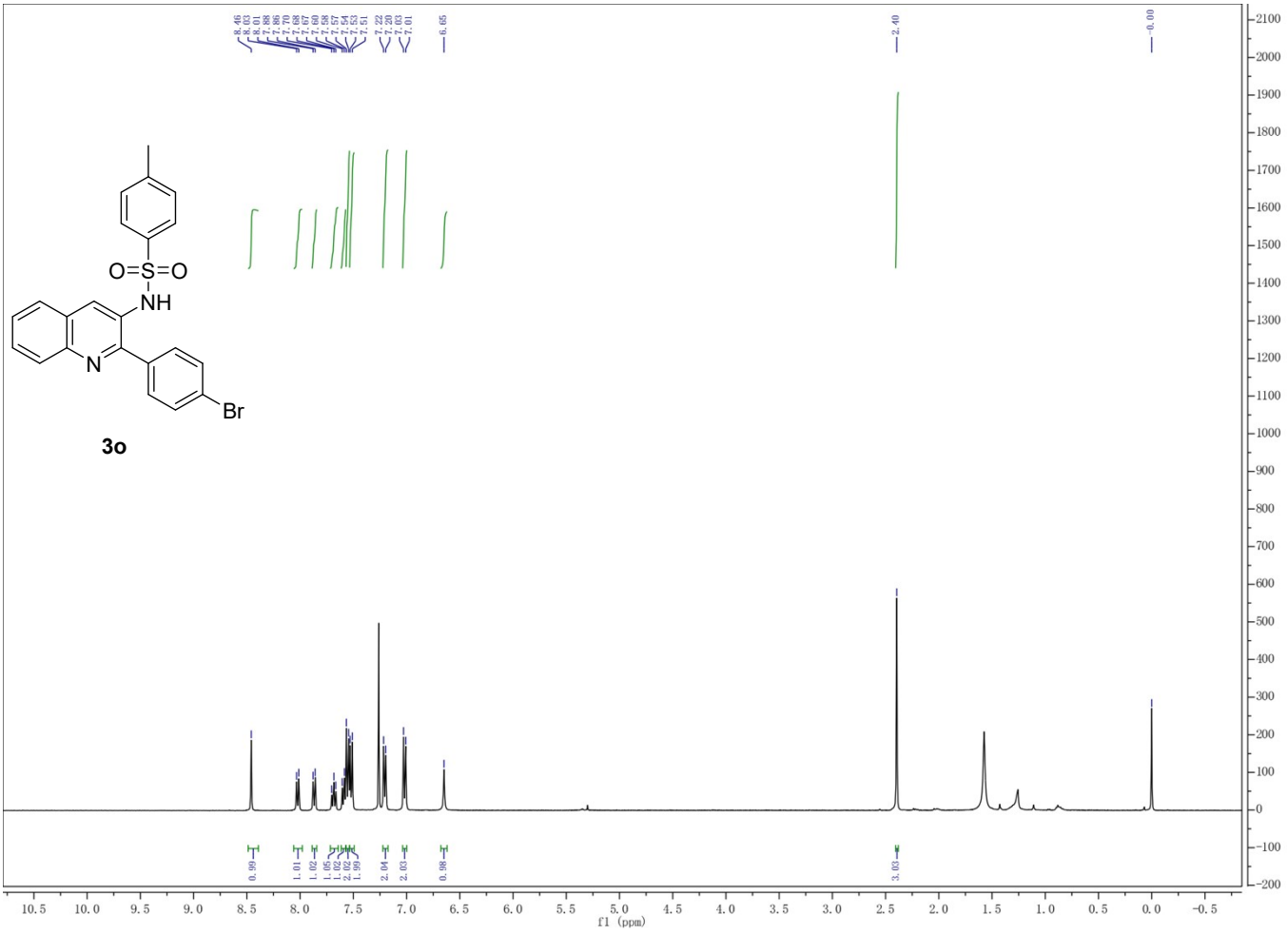



**Figure S33 $^{1}$H NMR of 3o ($CDCl_3$, 400 MHz)**

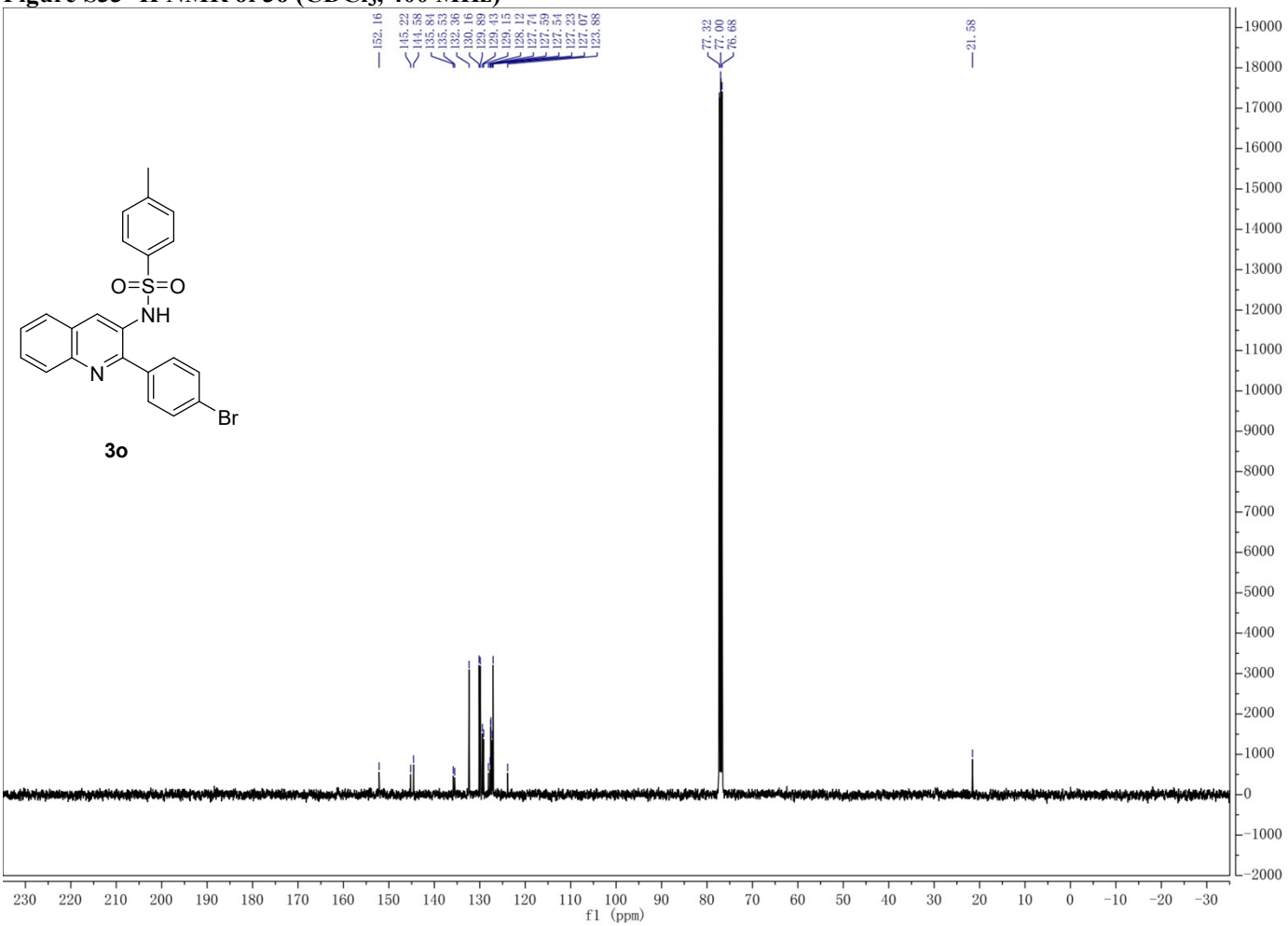



**Figure S34. $^{13}$C NMR of 3o ($CDCl_3$, 101 MHz)**

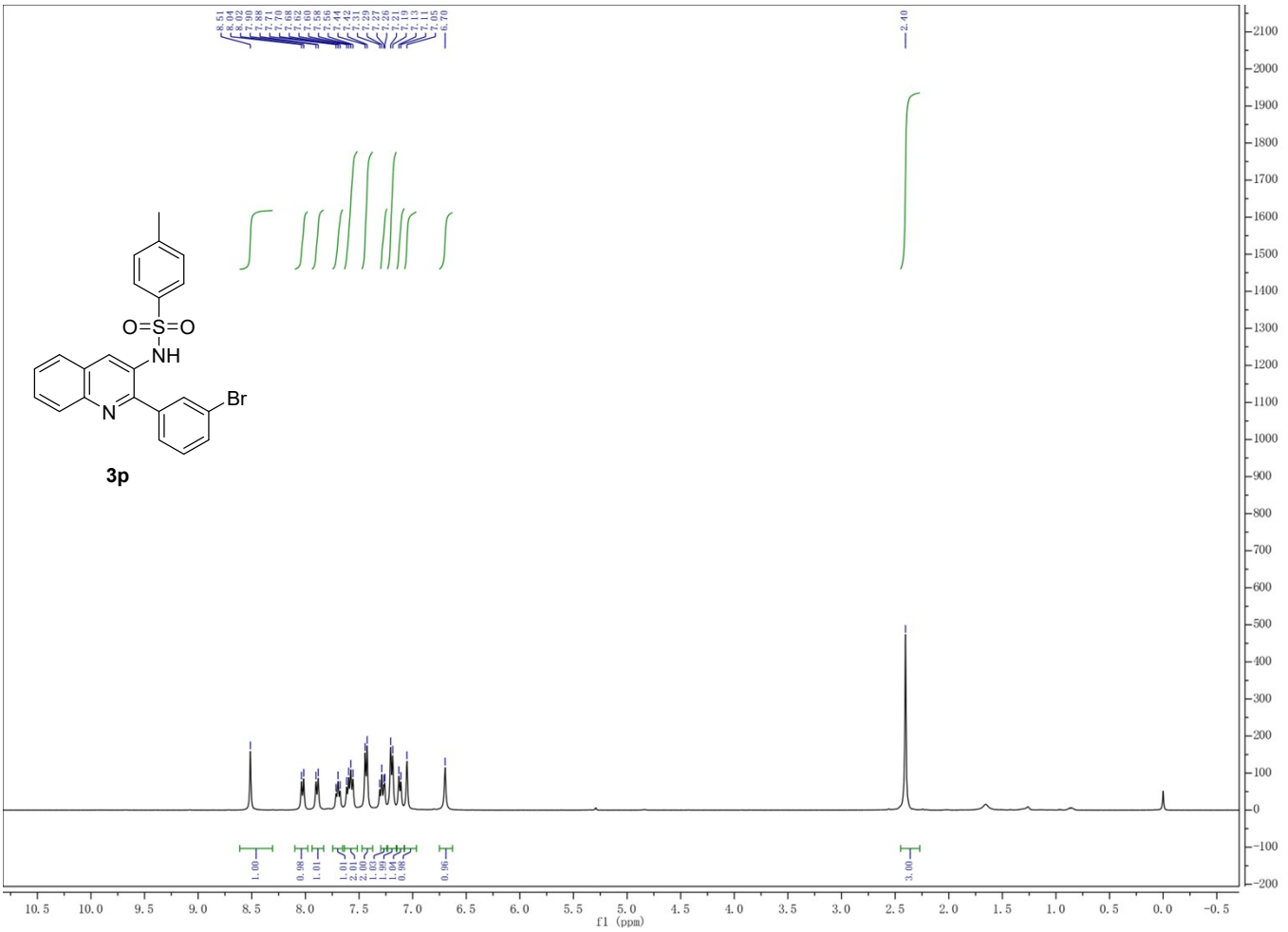



**Figure S35. $^{1}$H NMR of 3p ($CDCl_3$, 400 MHz)**

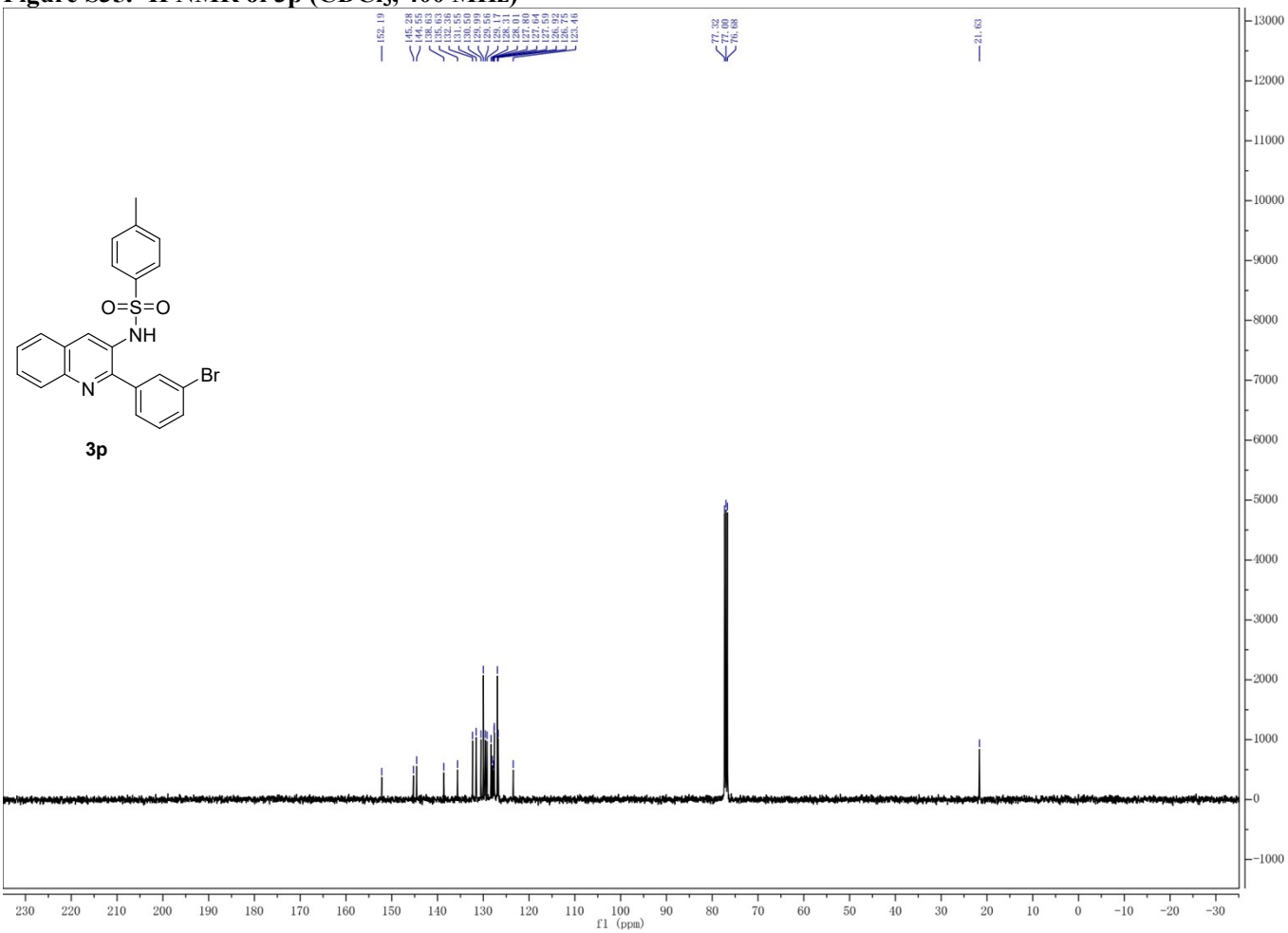



**Figure S36. $^{13}$C NMR of 3p ($CDCl_3$, 101 MHz)**

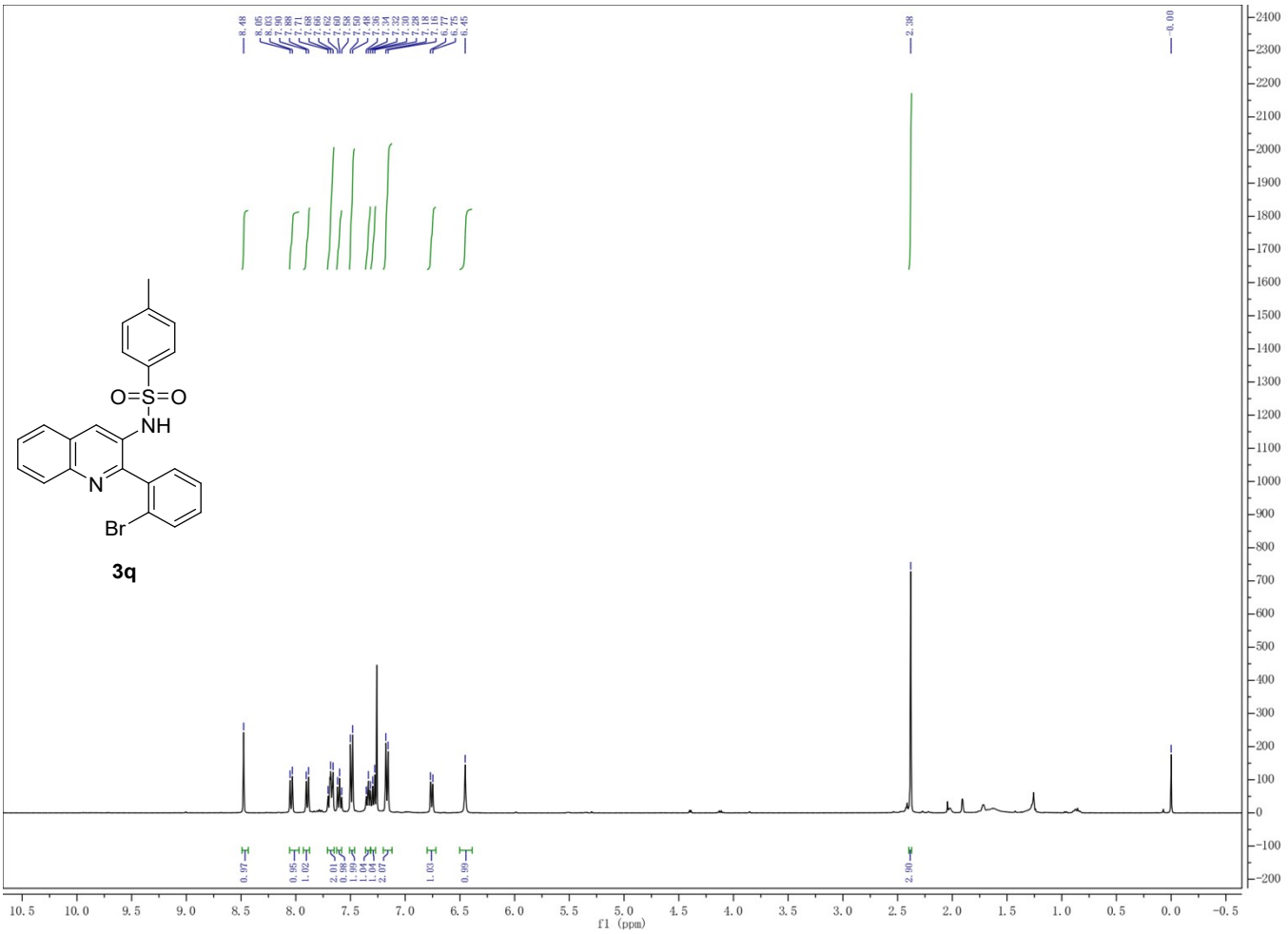



**Figure S37. $^{1}$H NMR of 3q ($CDCl_3$, 400 MHz)**

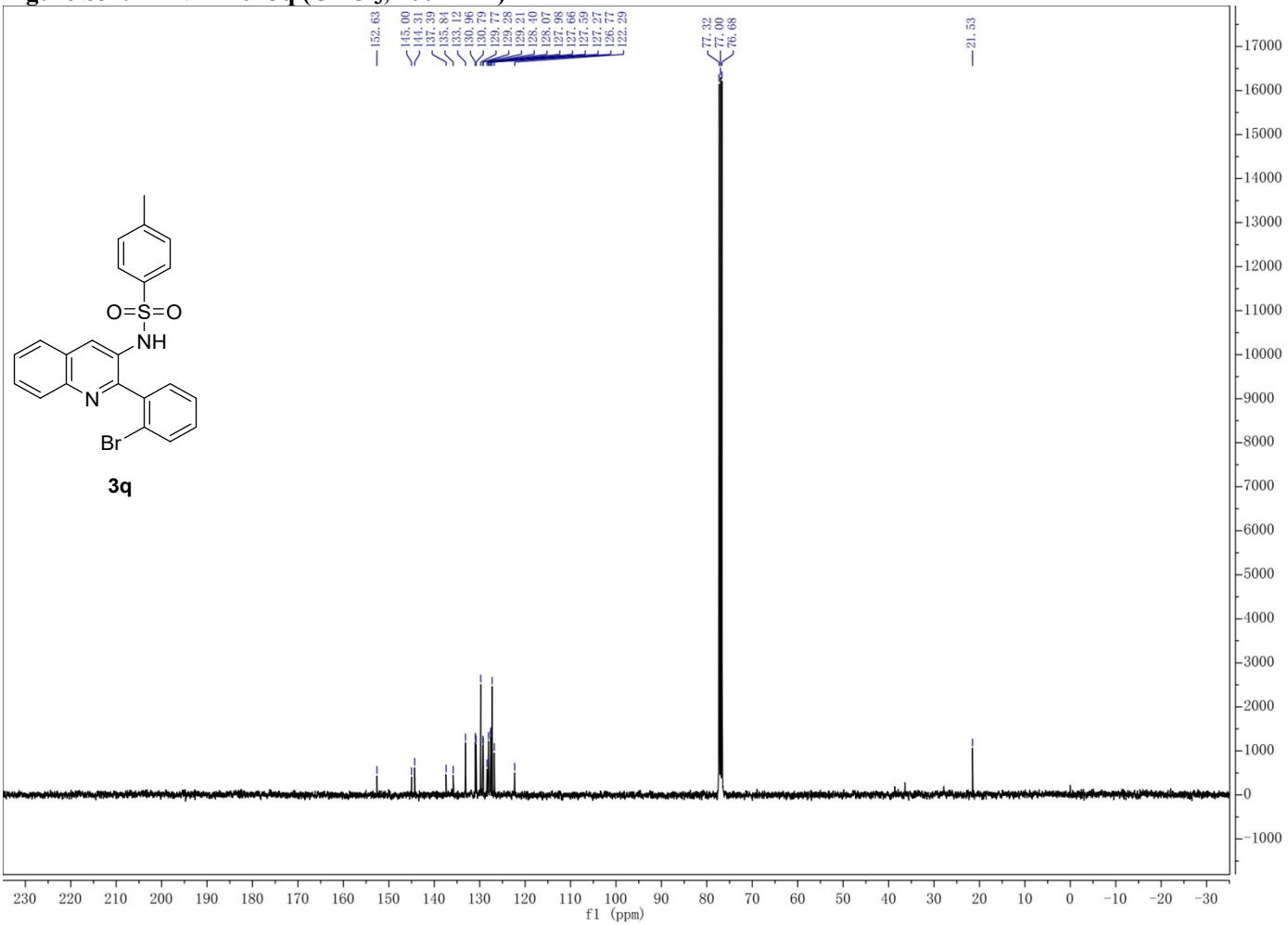



**Figure S38. $^{13}$C NMR of 3q ($CDCl_3$, 101 MHz)**

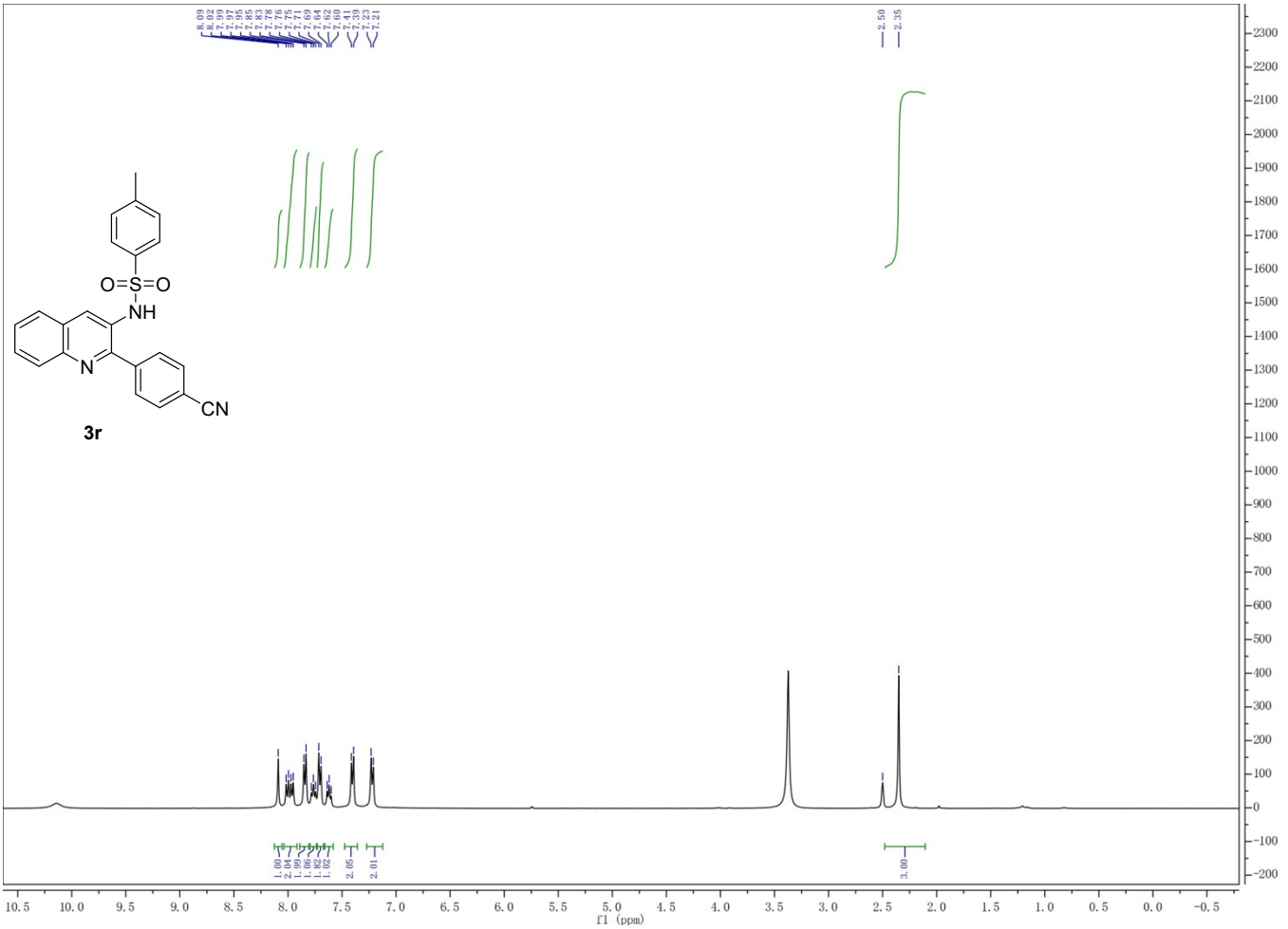



**Figure S39. $^{1}$H NMR of 3r (DMSO-d6, 400 MHz)**

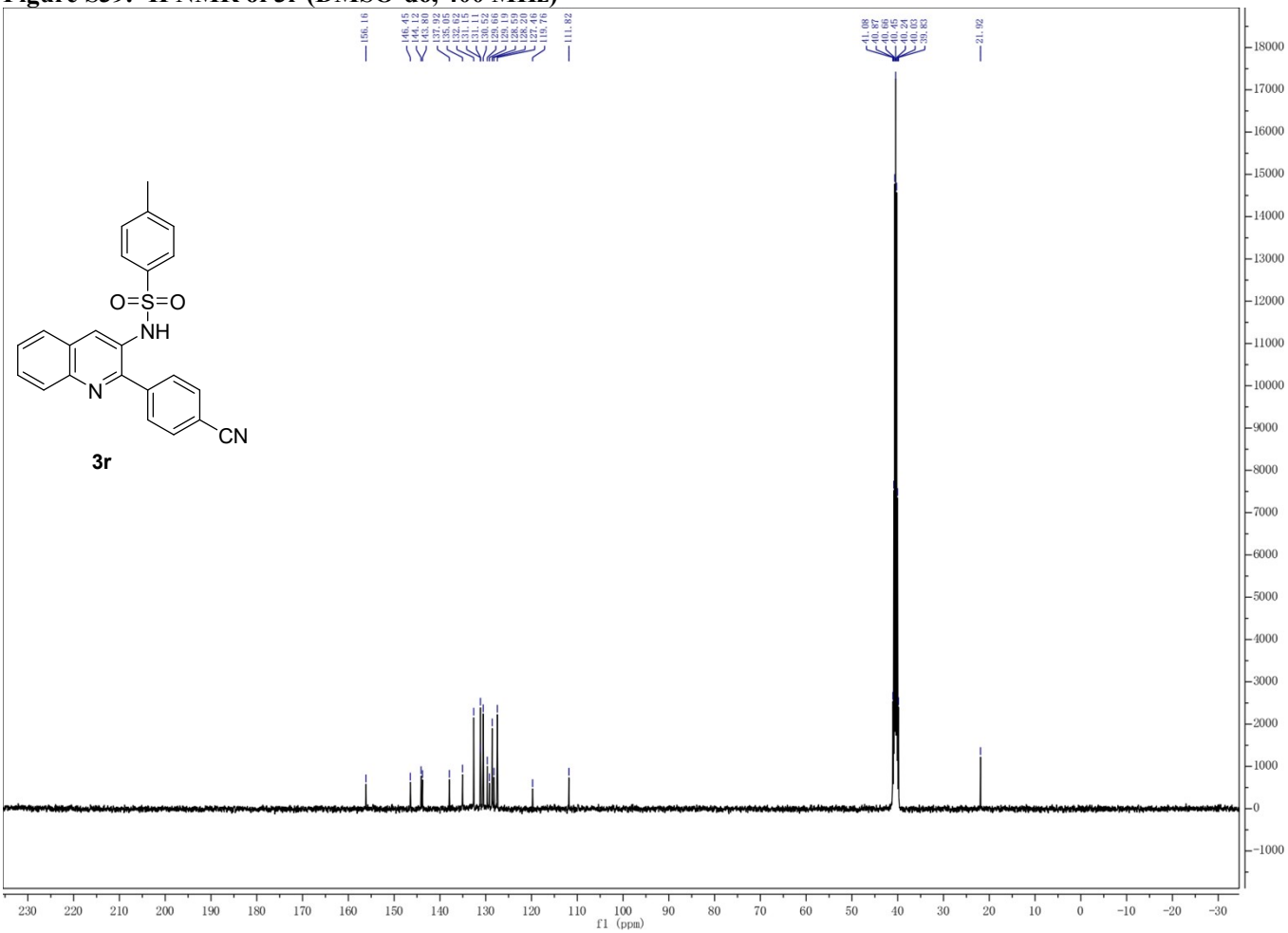



**Figure S40. $^{13}$C NMR of 3r (DMSO-d6, 101 MHz)**

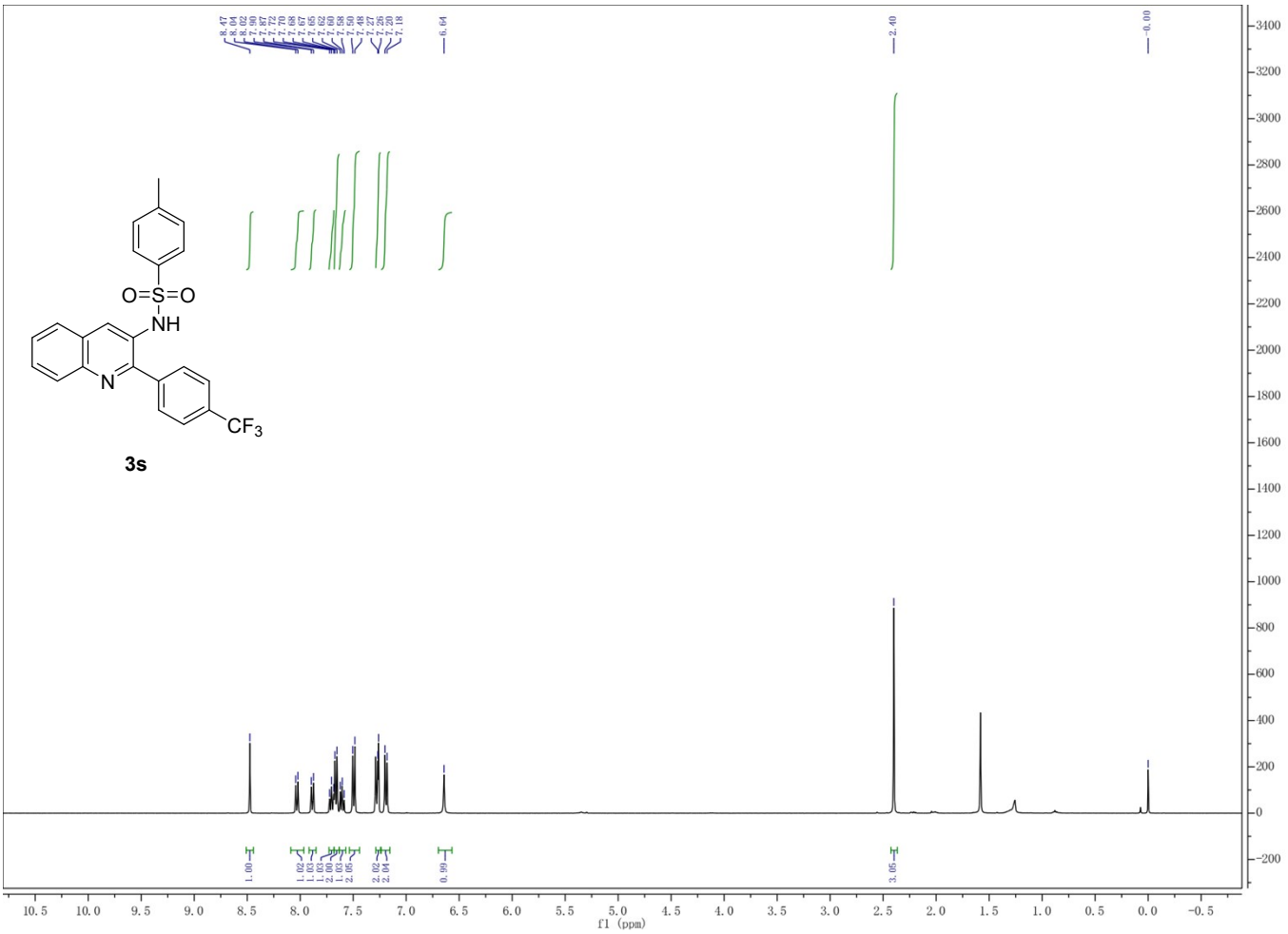



**Figure S41. $^{1}$H NMR of 3s ($CDCl_3$, 400 MHz)**

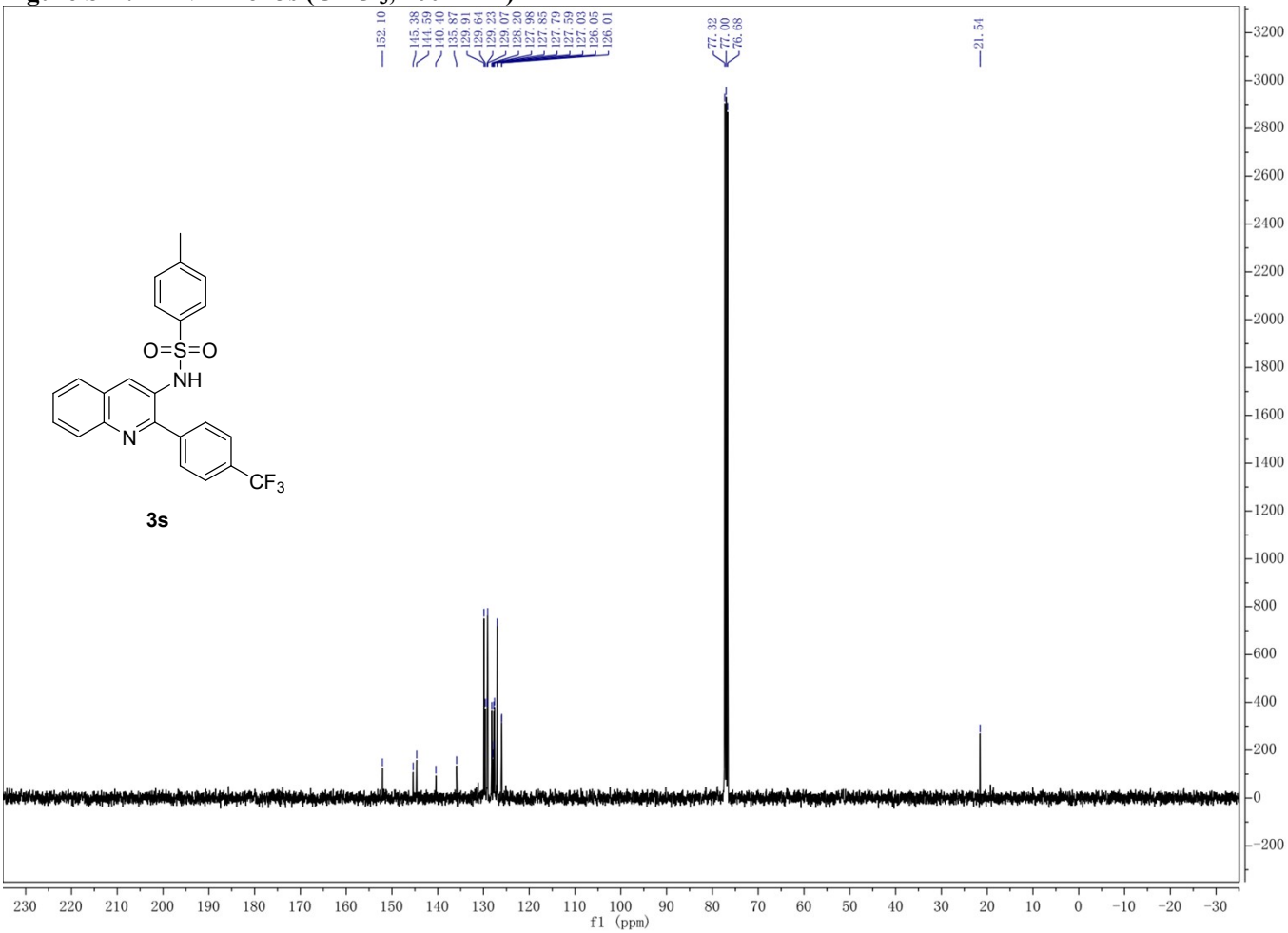



**Figure S42. $^{13}$C NMR of 3s ($CDCl_3$, 101 MHz)**

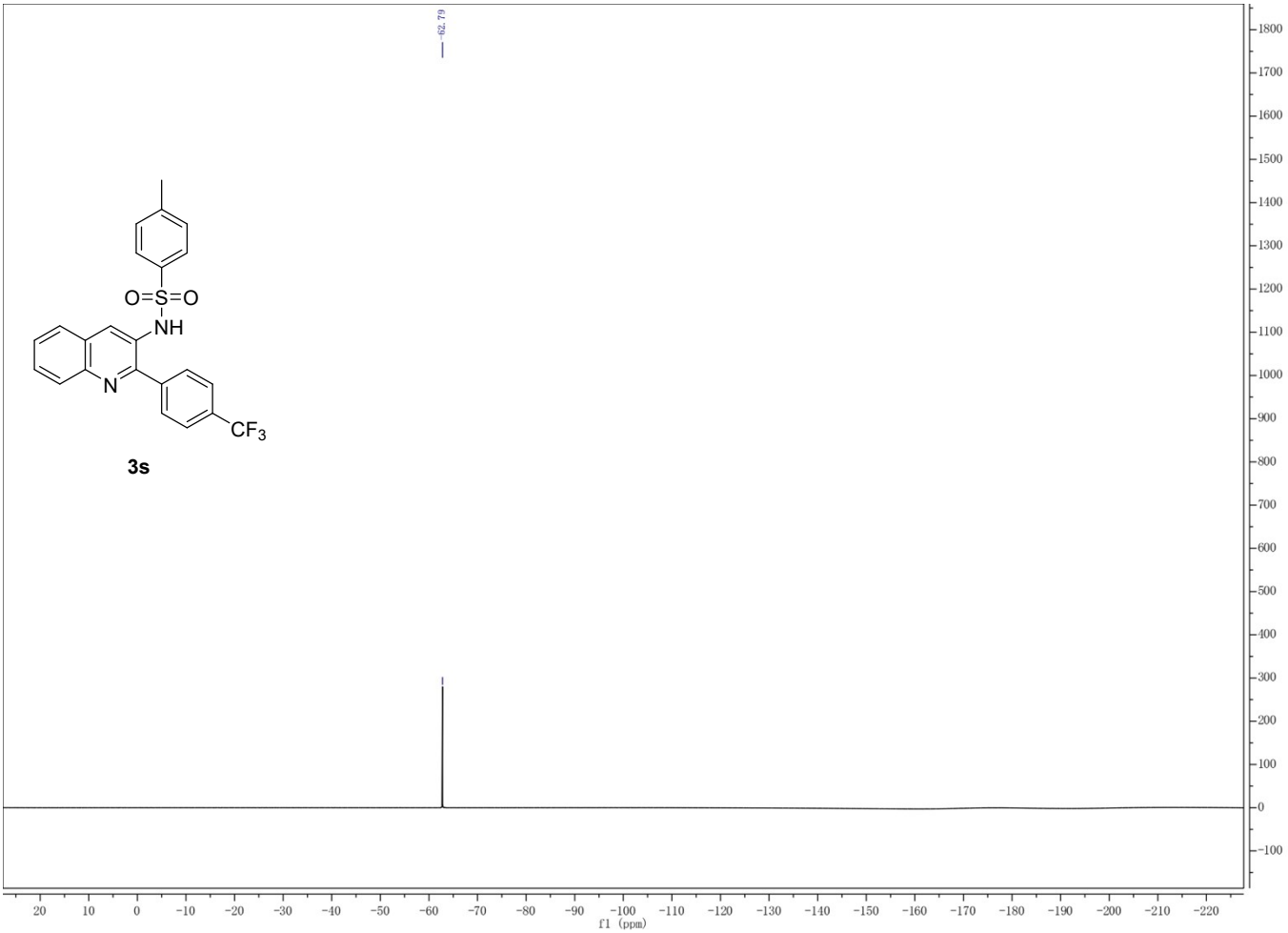



**Figure S43. $^{19}$F NMRof 3s ($CDCl_3$, 376 MHz)**

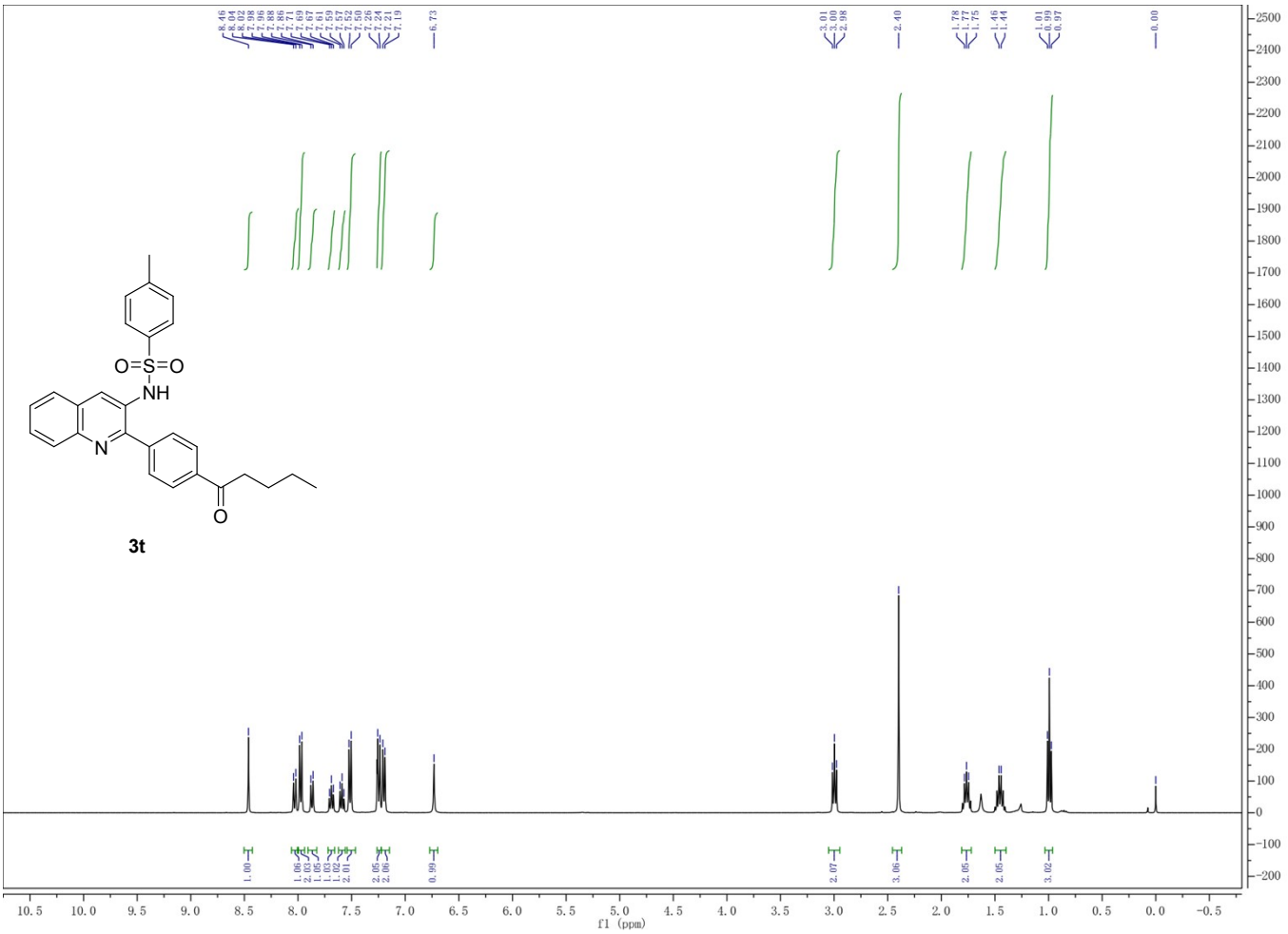



**Figure S44. $^{1}$H NMR of 3t ($CDCl_3$, 400 MHz)**

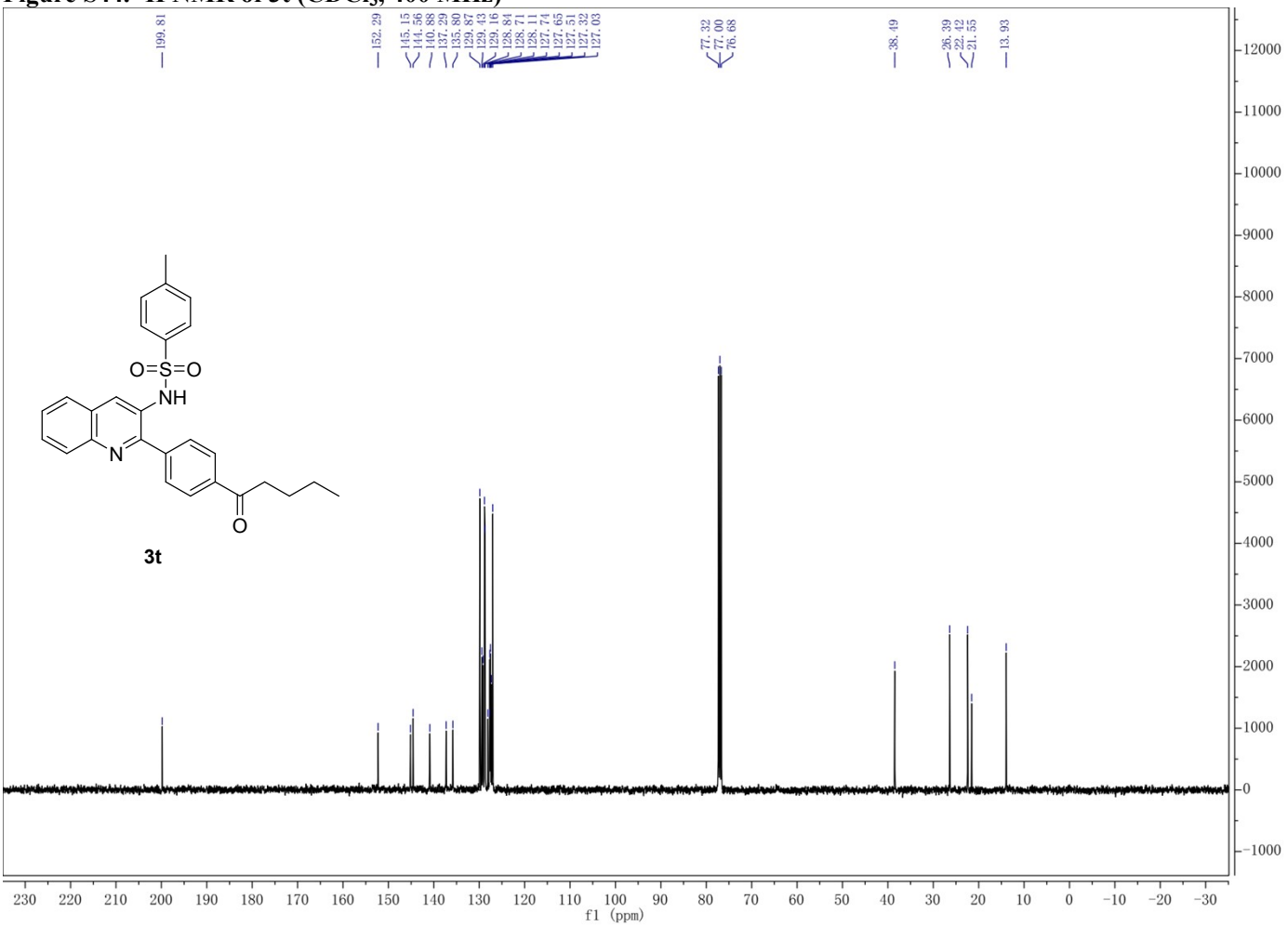



**Figure S45. $^{13}$C NMR of 3t ($CDCl_3$, 101 MHz)**

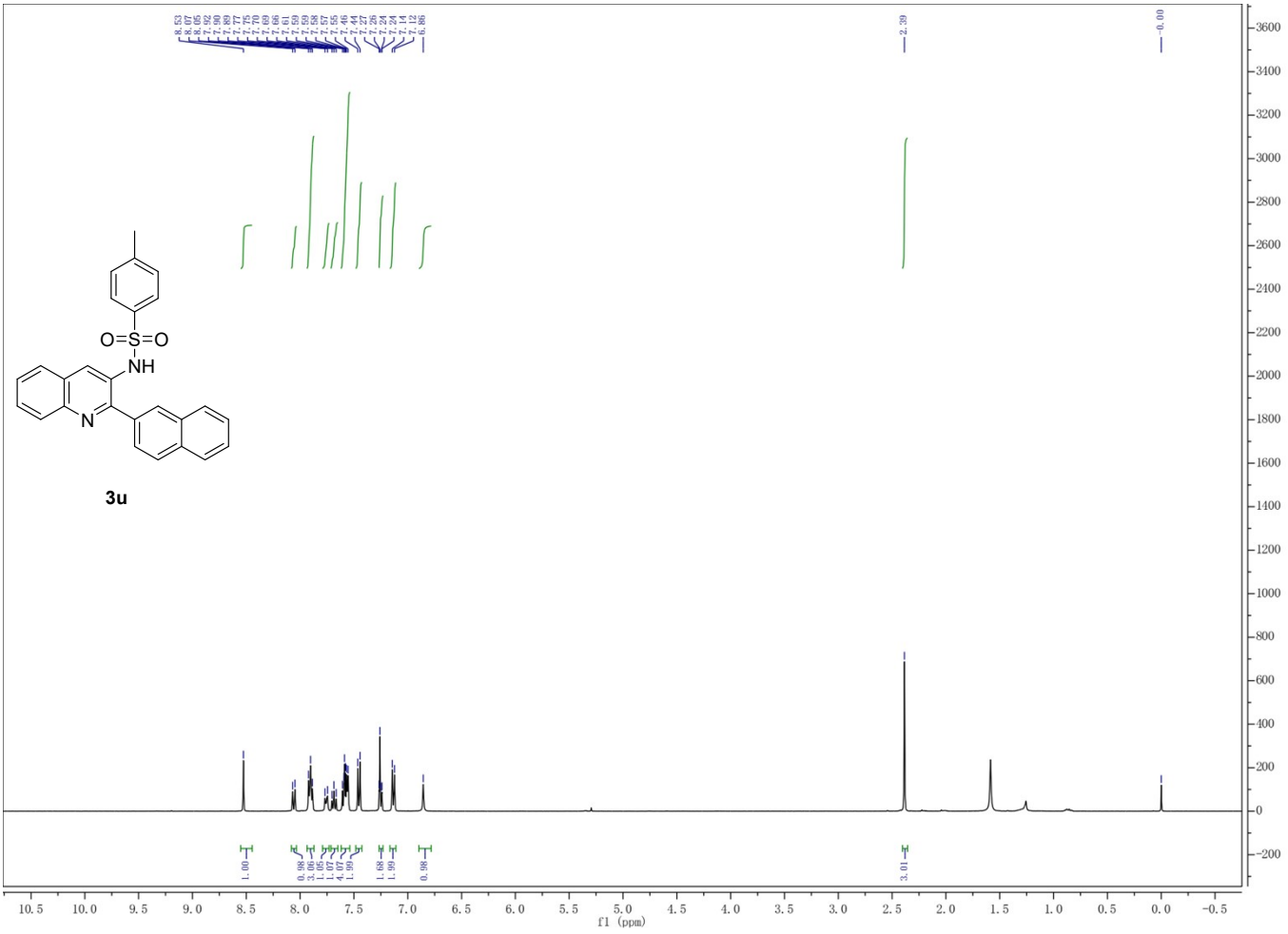



**Figure S46. $^{1}$H NMR of 3u ($CDCl_3$, 400 MHz)**

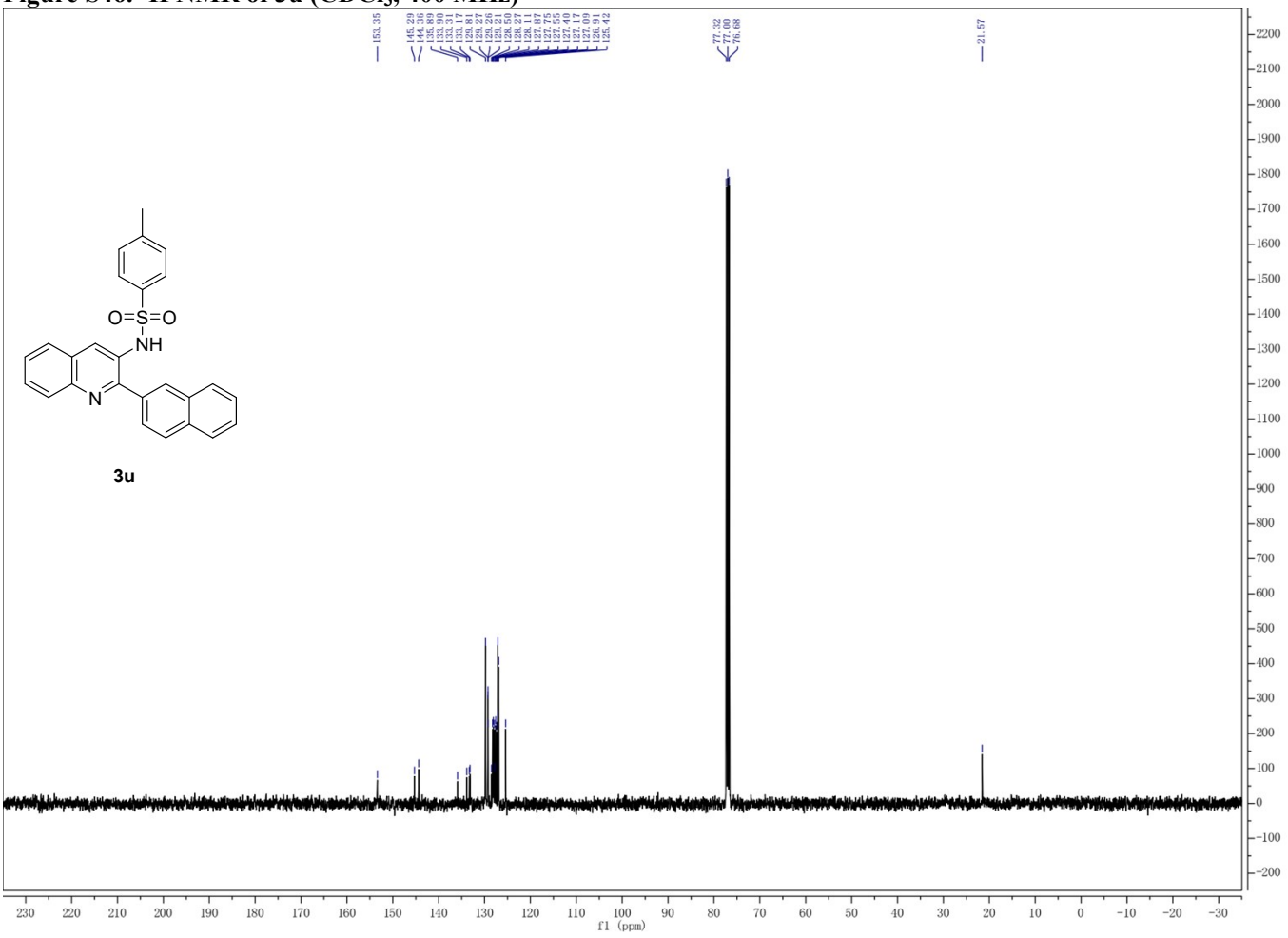



**Figure S47. $^{13}$C NMR of 3u ($CDCl_3$, 101 MHz)**

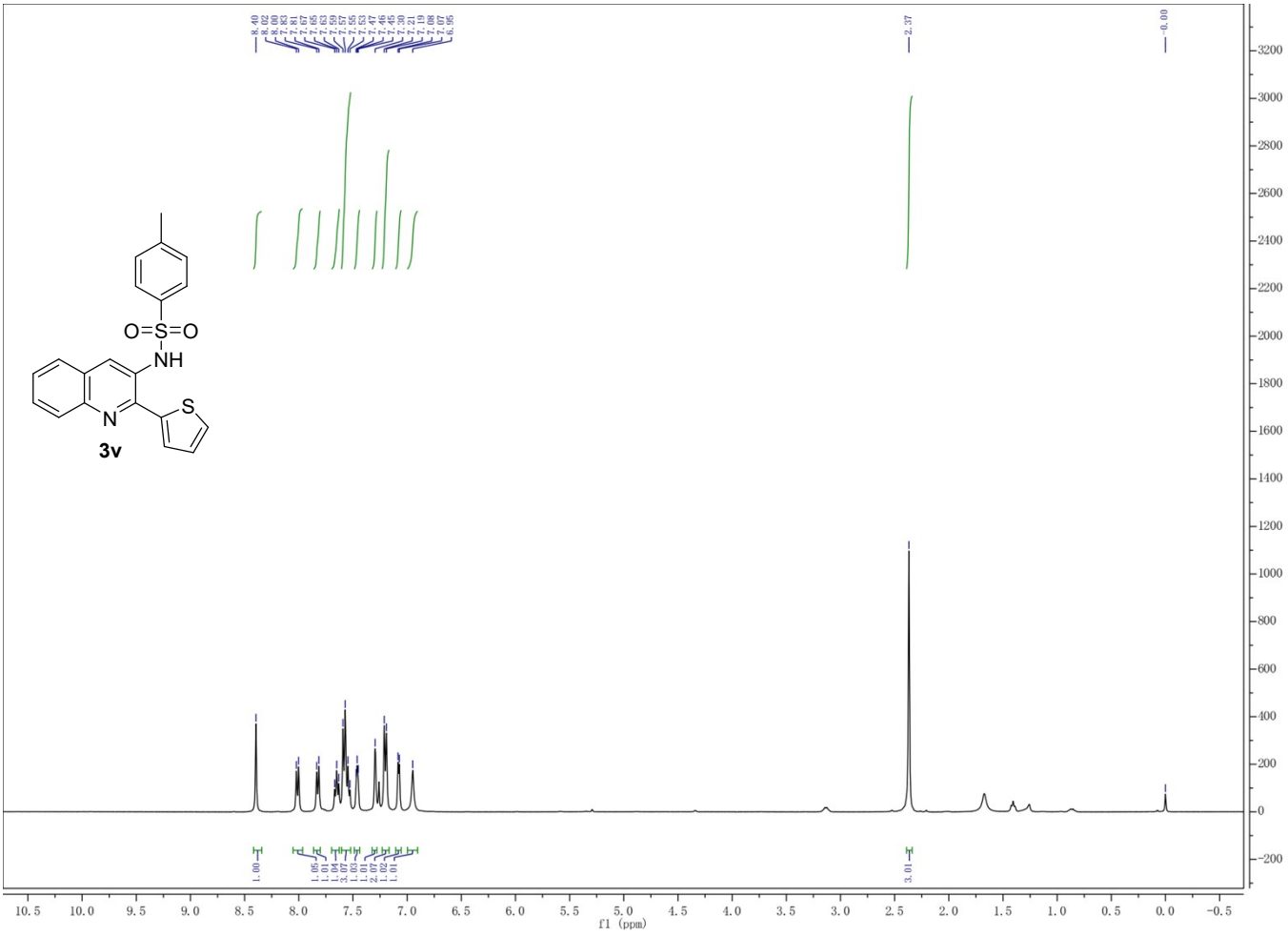



**Figure S48. $^{1}$H NMR of 3v ($CDCl_3$, 400 MHz)**

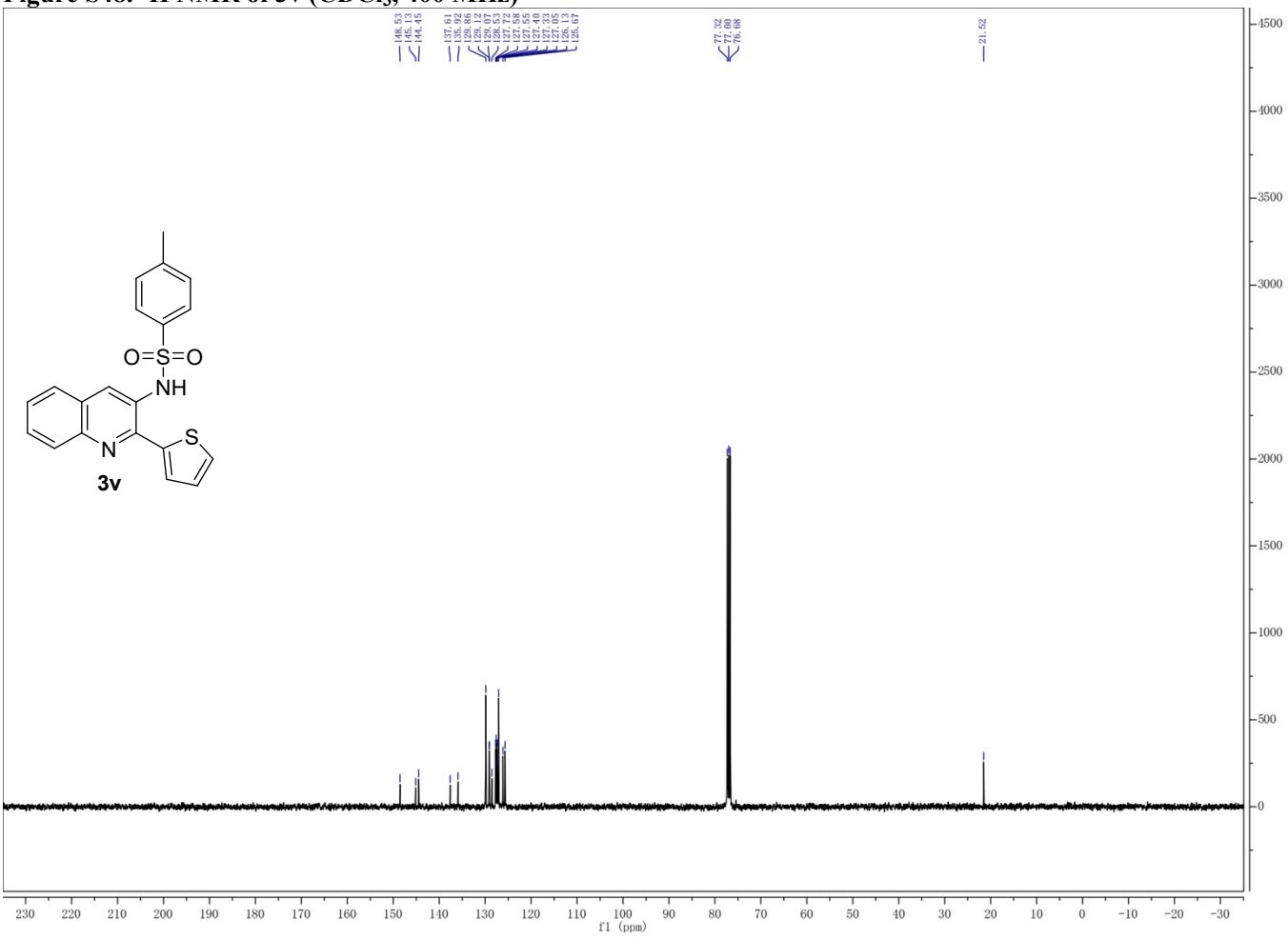



**Figure S49. $^{13}$C NMR of 3v ($CDCl_3$, 101 MHz)**

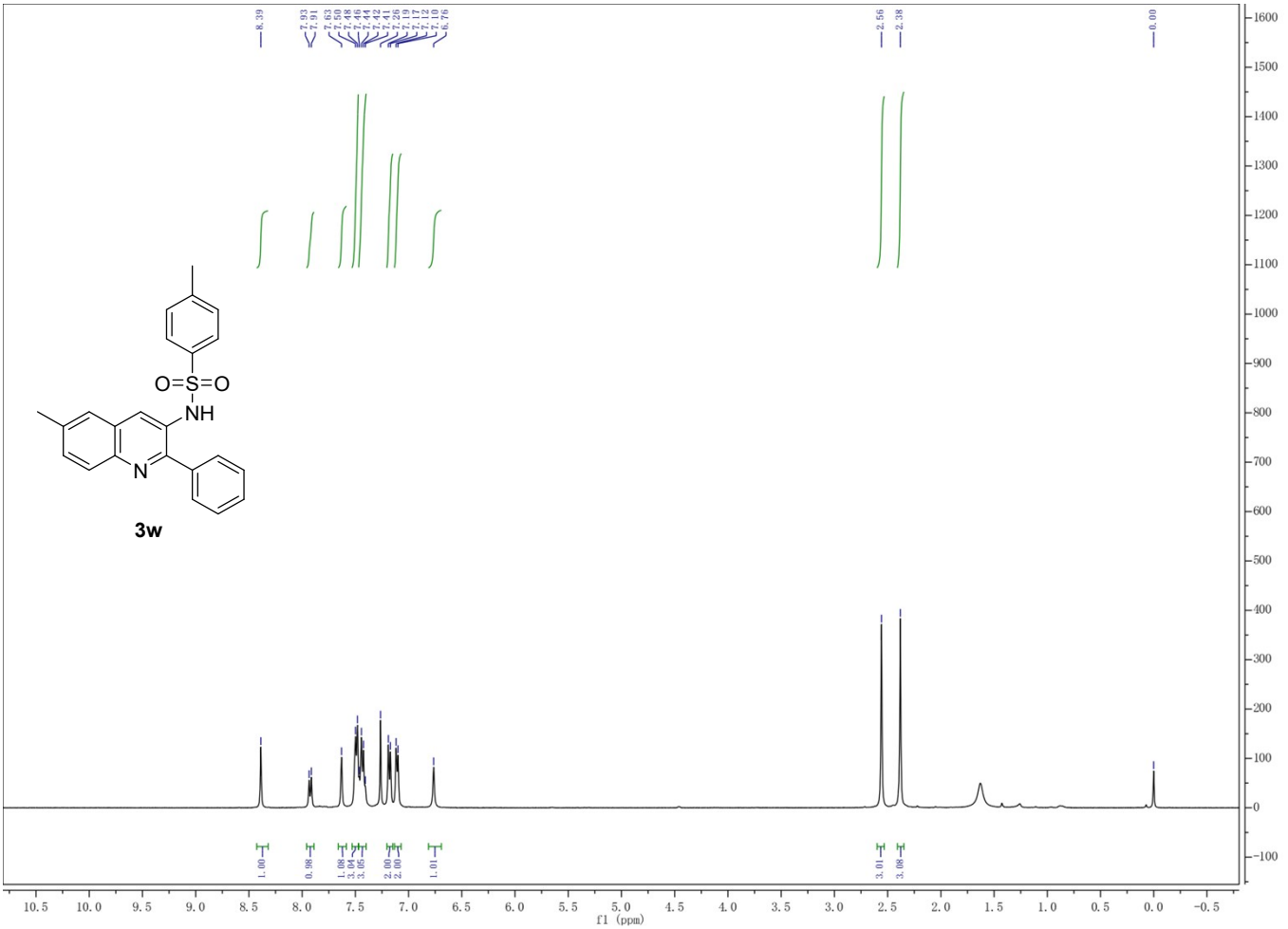



**Figure S50. $^{1}$H NMR of 3w ($CDCl_3$, 400 MHz)**

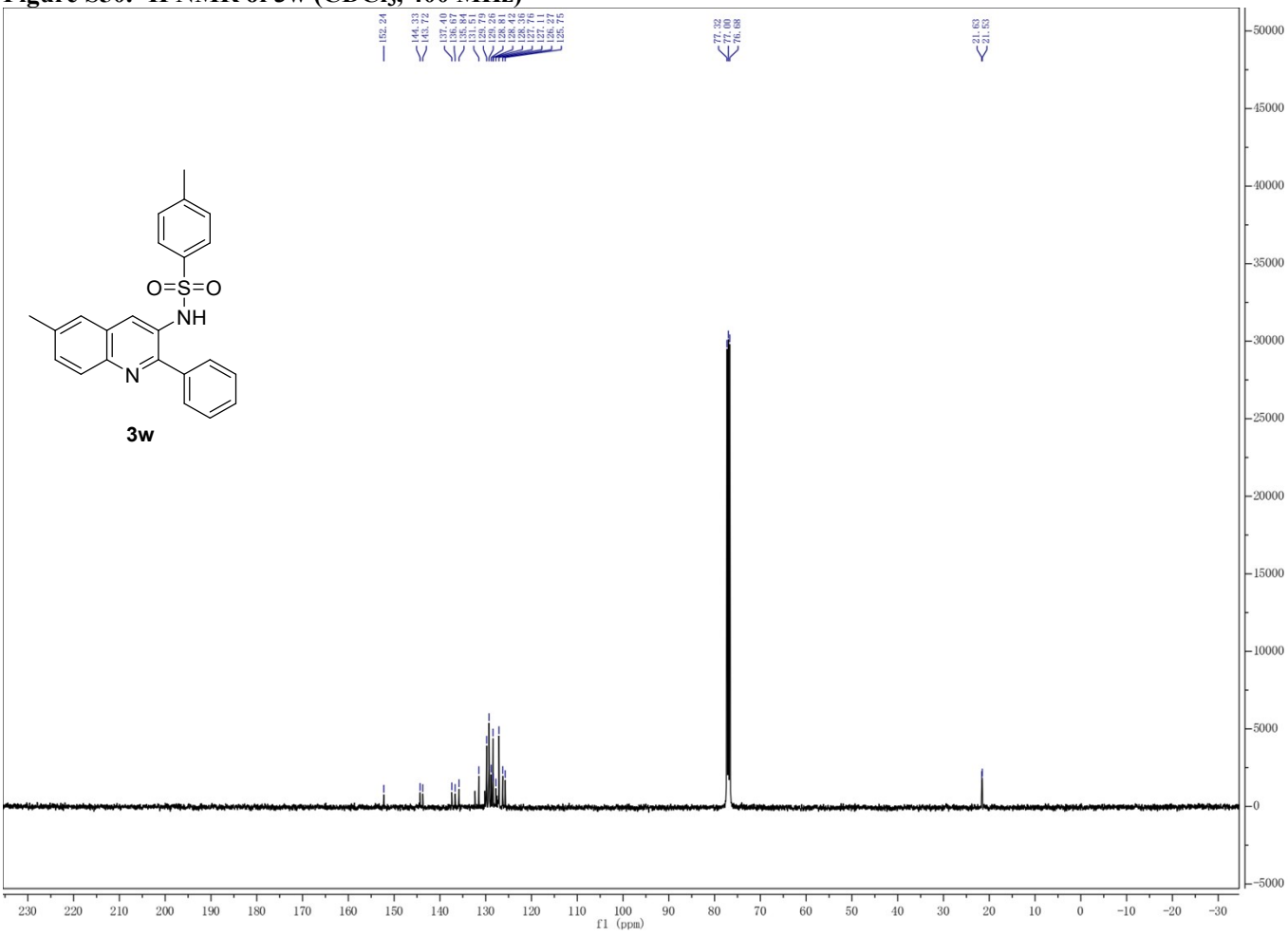



**Figure S51. $^{13}$C NMR of 3w ($CDCl_3$, 101 MHz)**

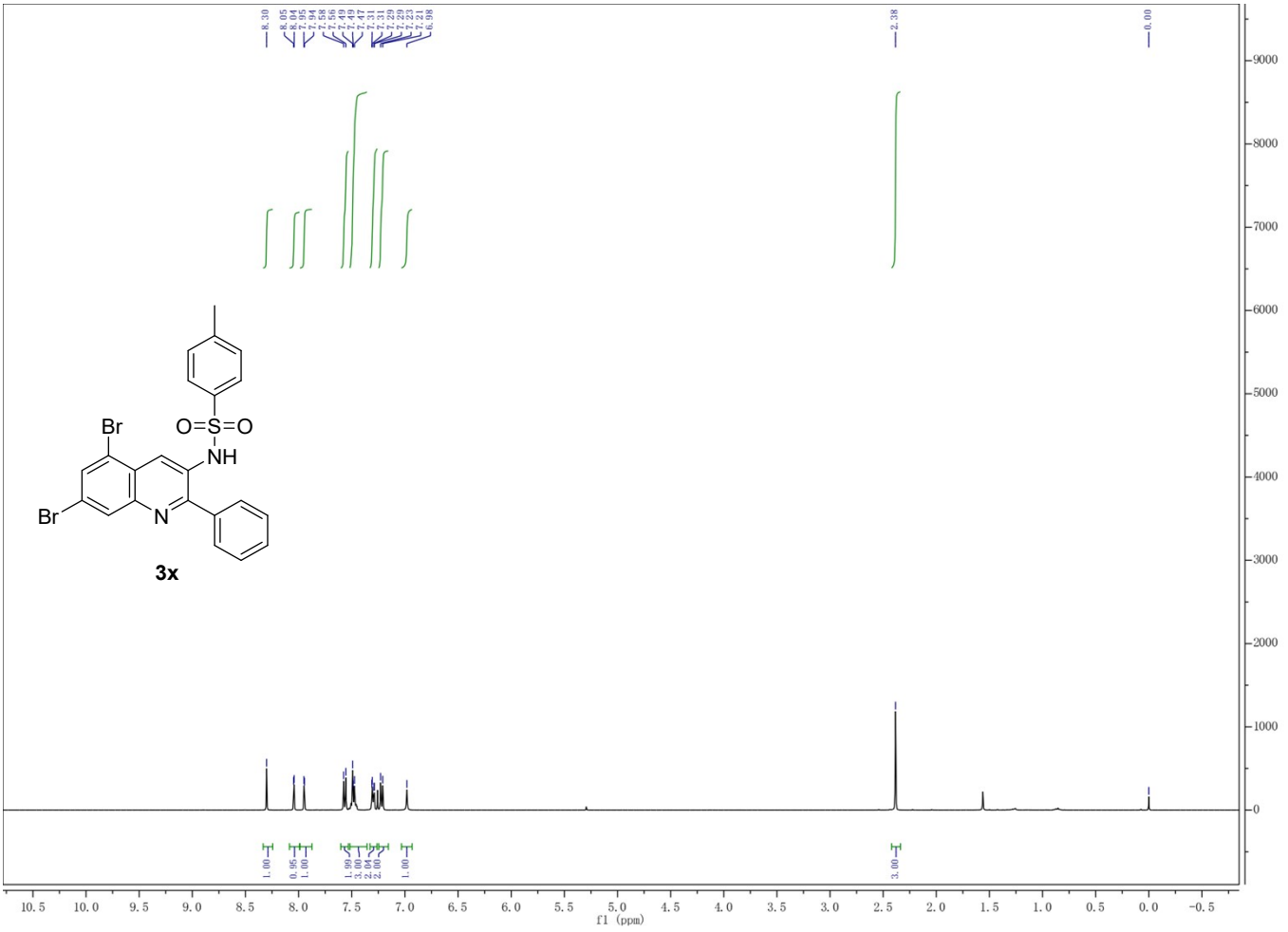



**Figure S52. $^{1}$H NMR of 3x ($CDCl_3$, 400 MHz)**

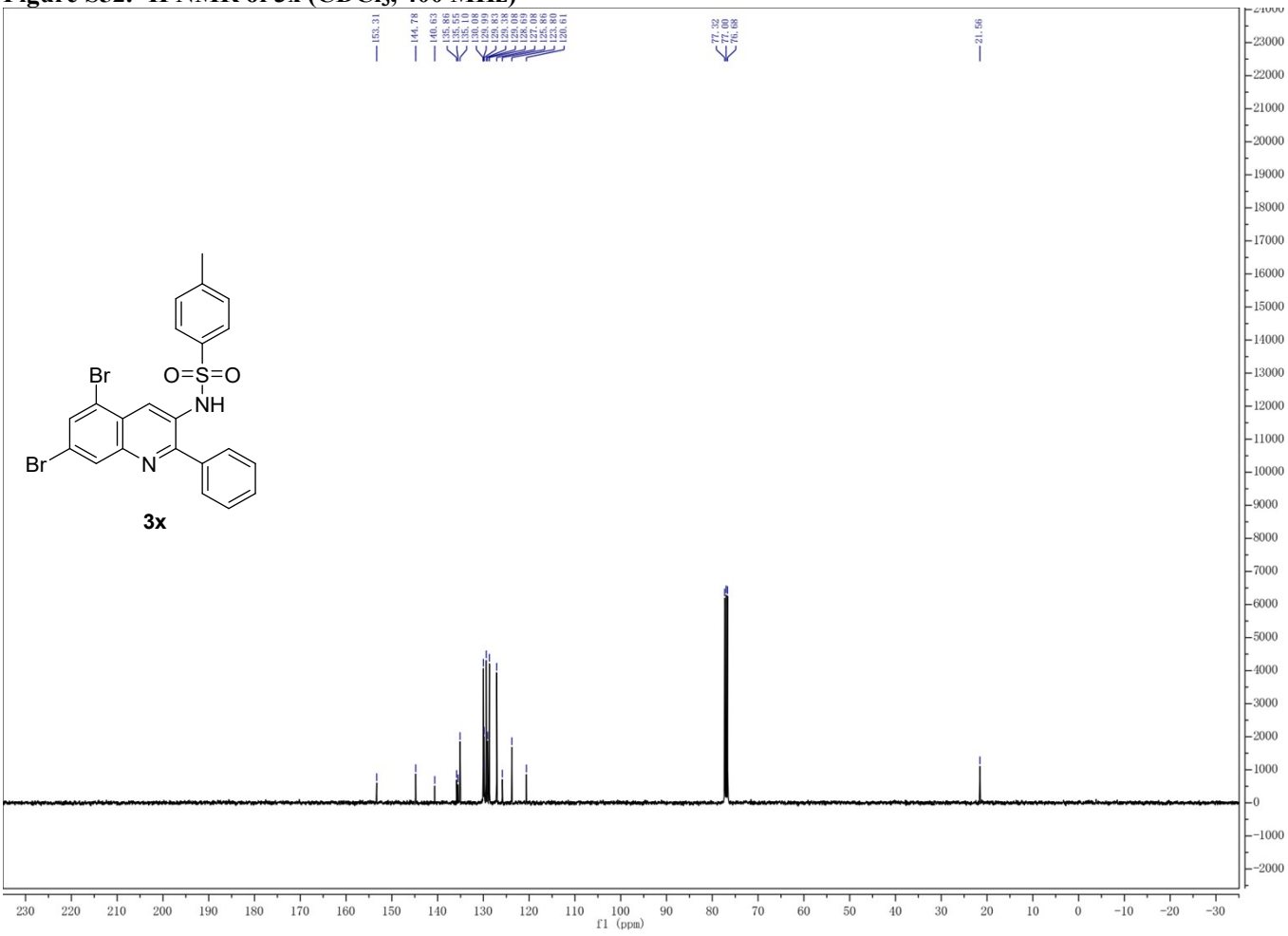



**Figure S53. $^{13}$C NMR of 3x ($CDCl_3$, 101 MHz)**

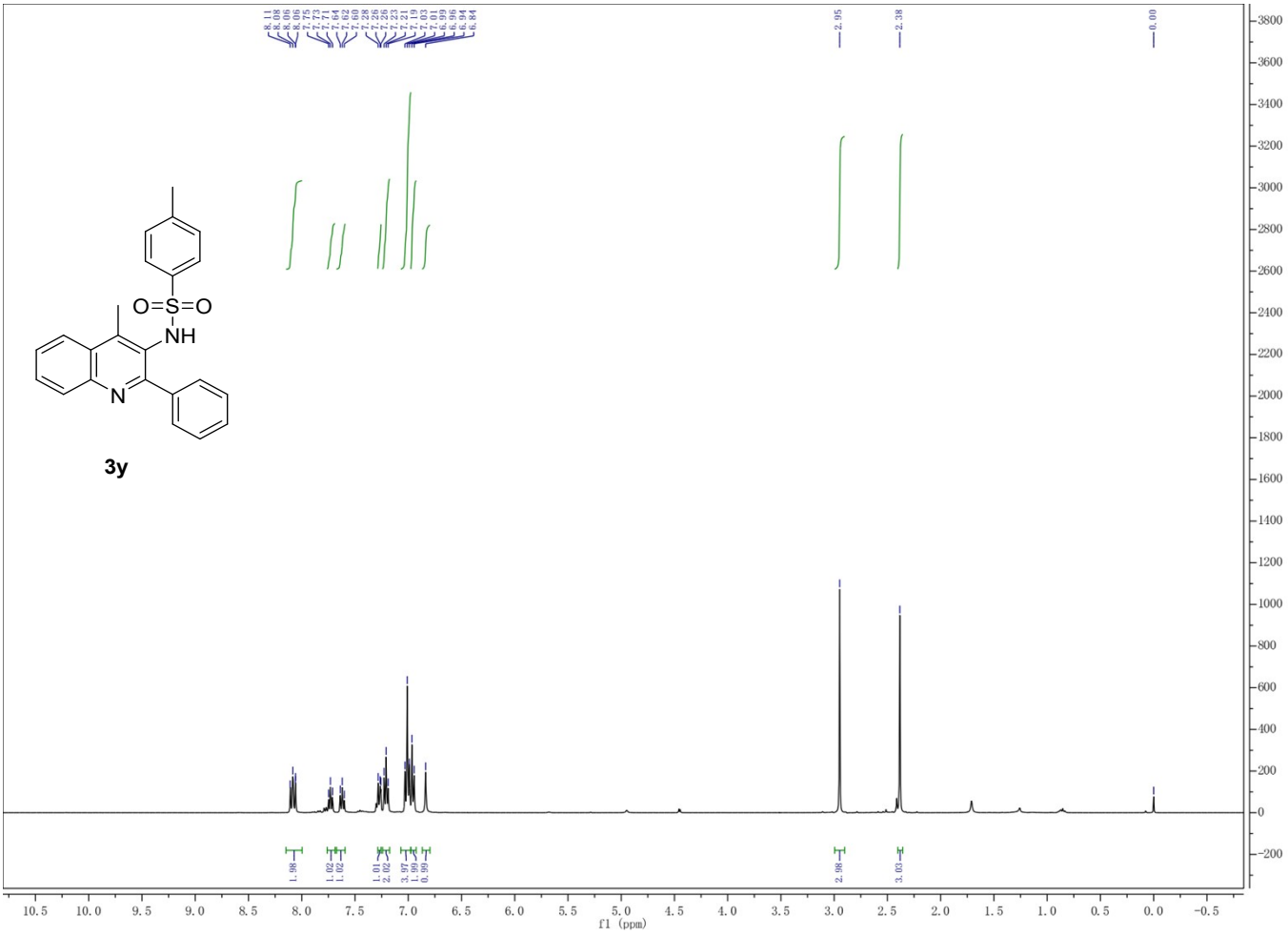



**Figure S54. $^{1}$H NMR of 3y ($CDCl_3$, 400 MHz)**

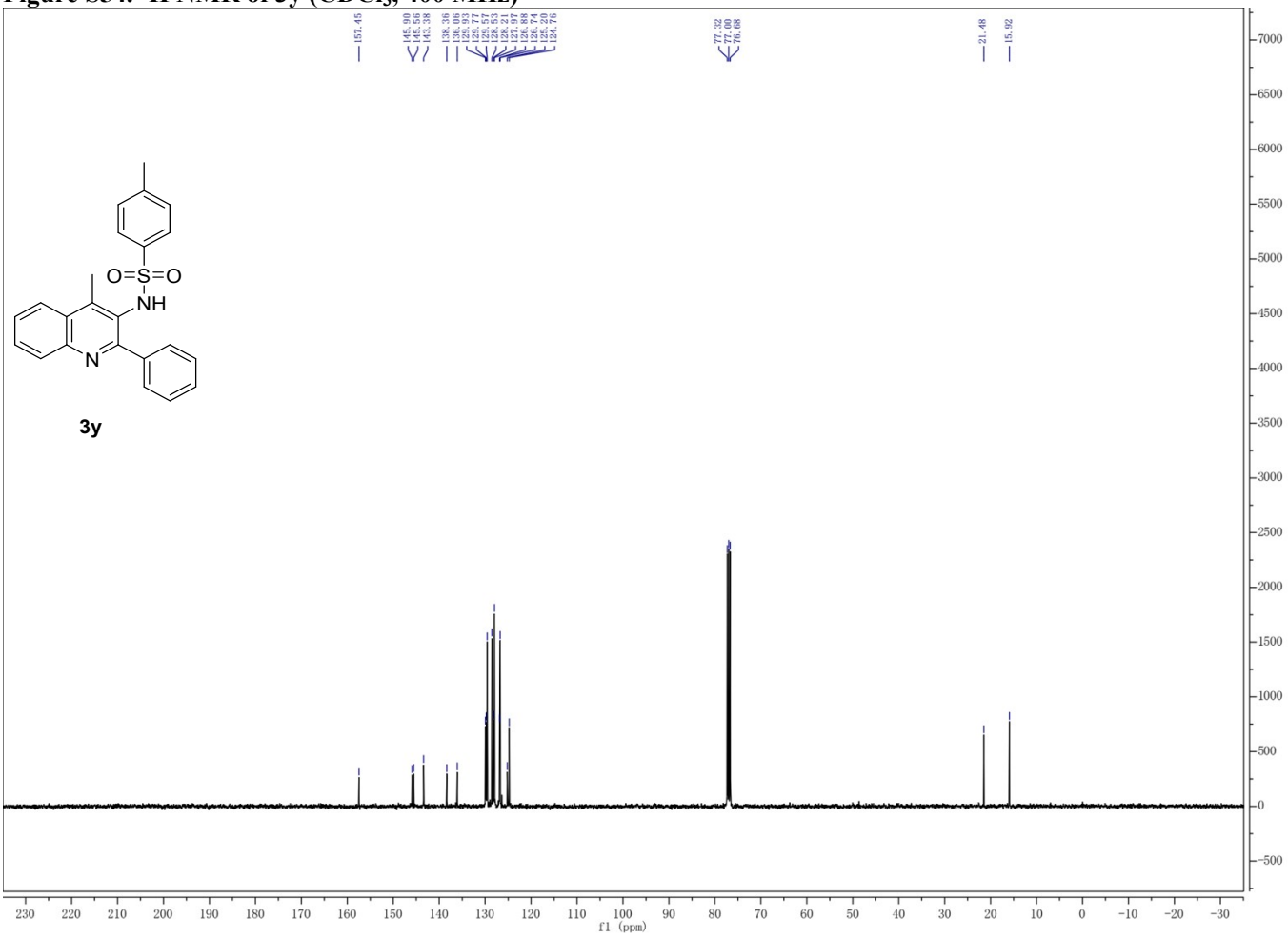



**Figure S55. $^{13}$C NMR of 3y ($CDCl_3$, 101 MHz)**

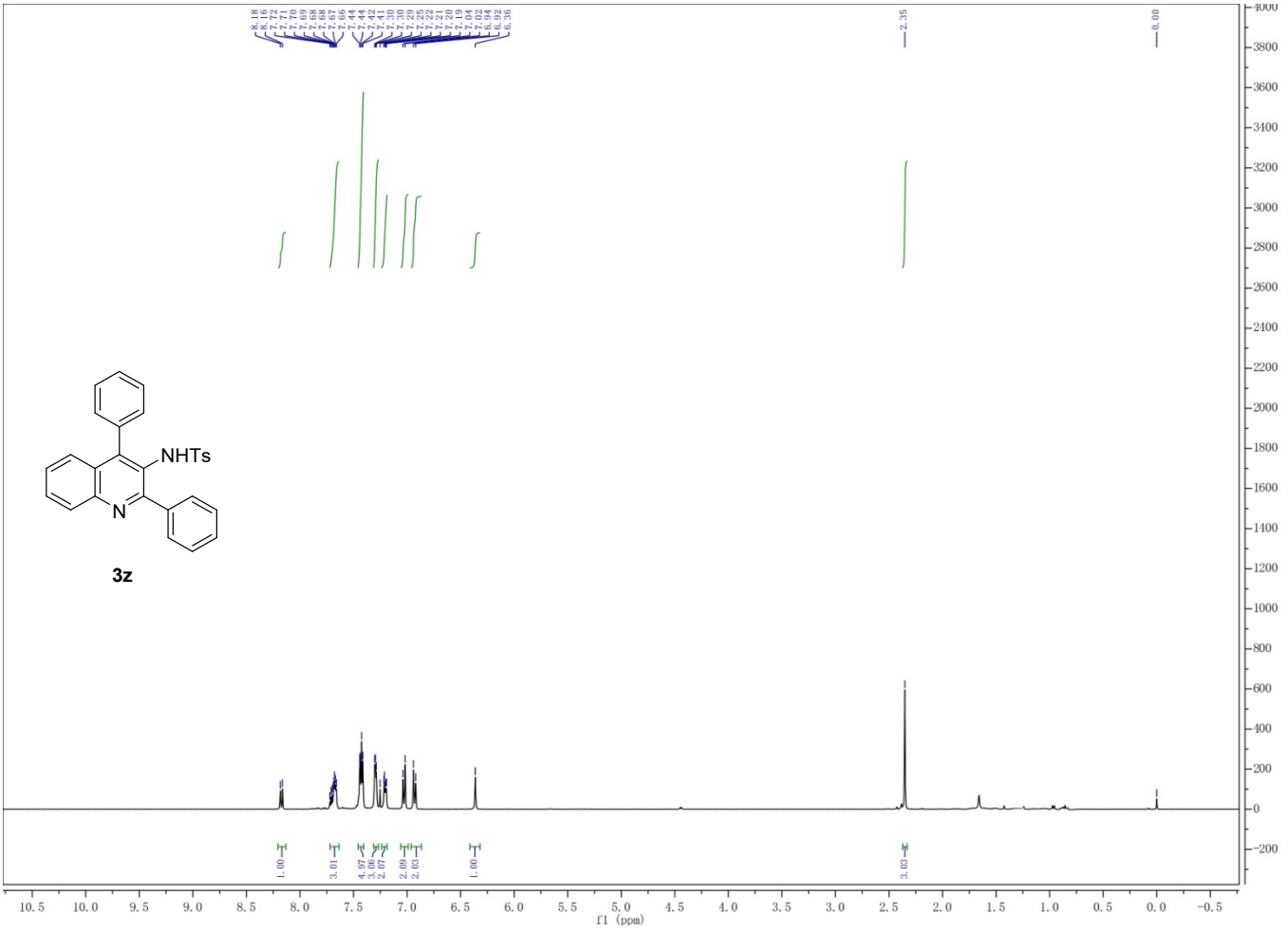



**Figure S56. $^{1}$H NMR of 3z ($CDCl_3$, 400 MHz)**

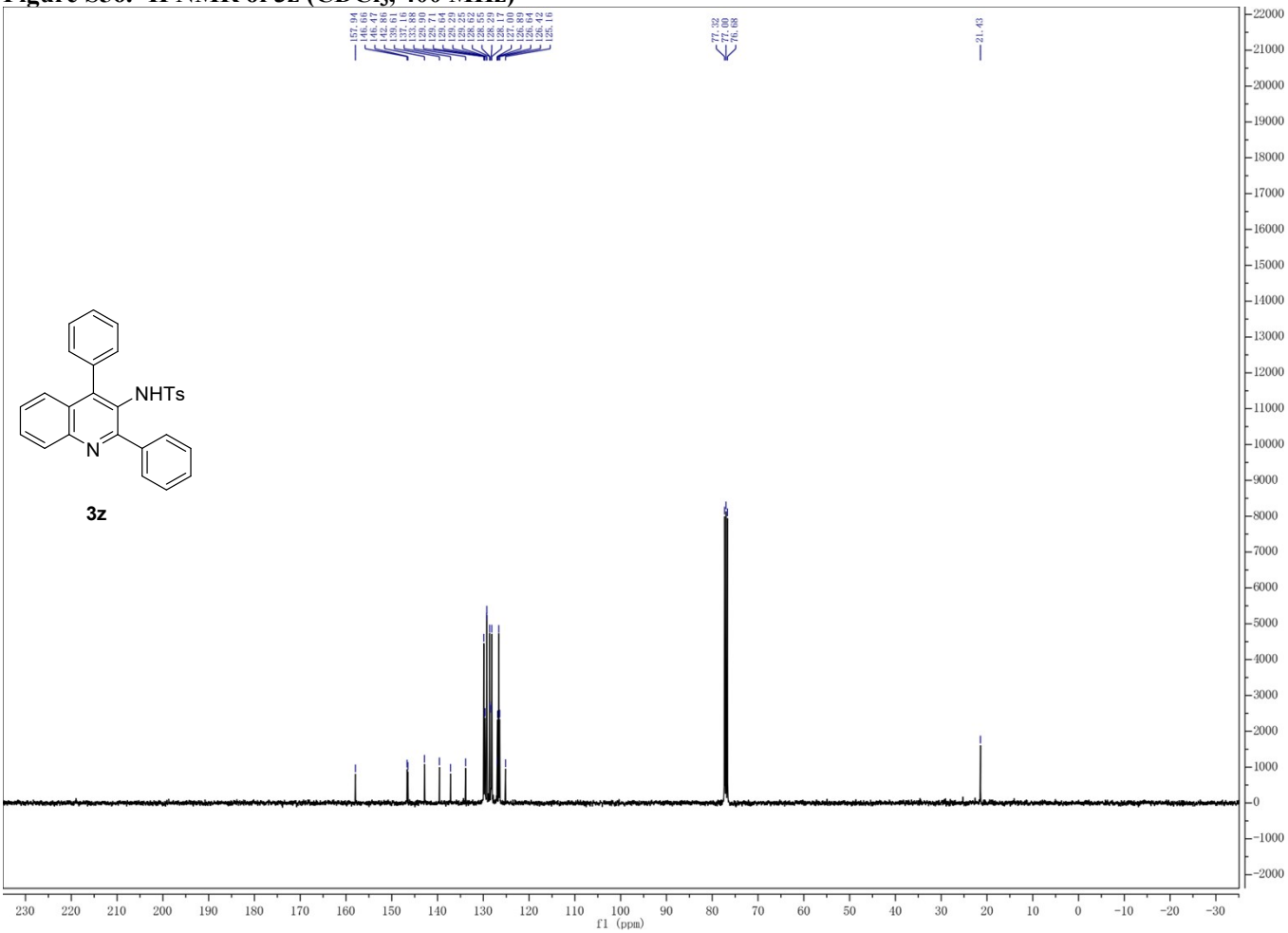



**Figure S57. $^{13}$C NMR of 3z ($CDCl_3$, 101 MHz)**

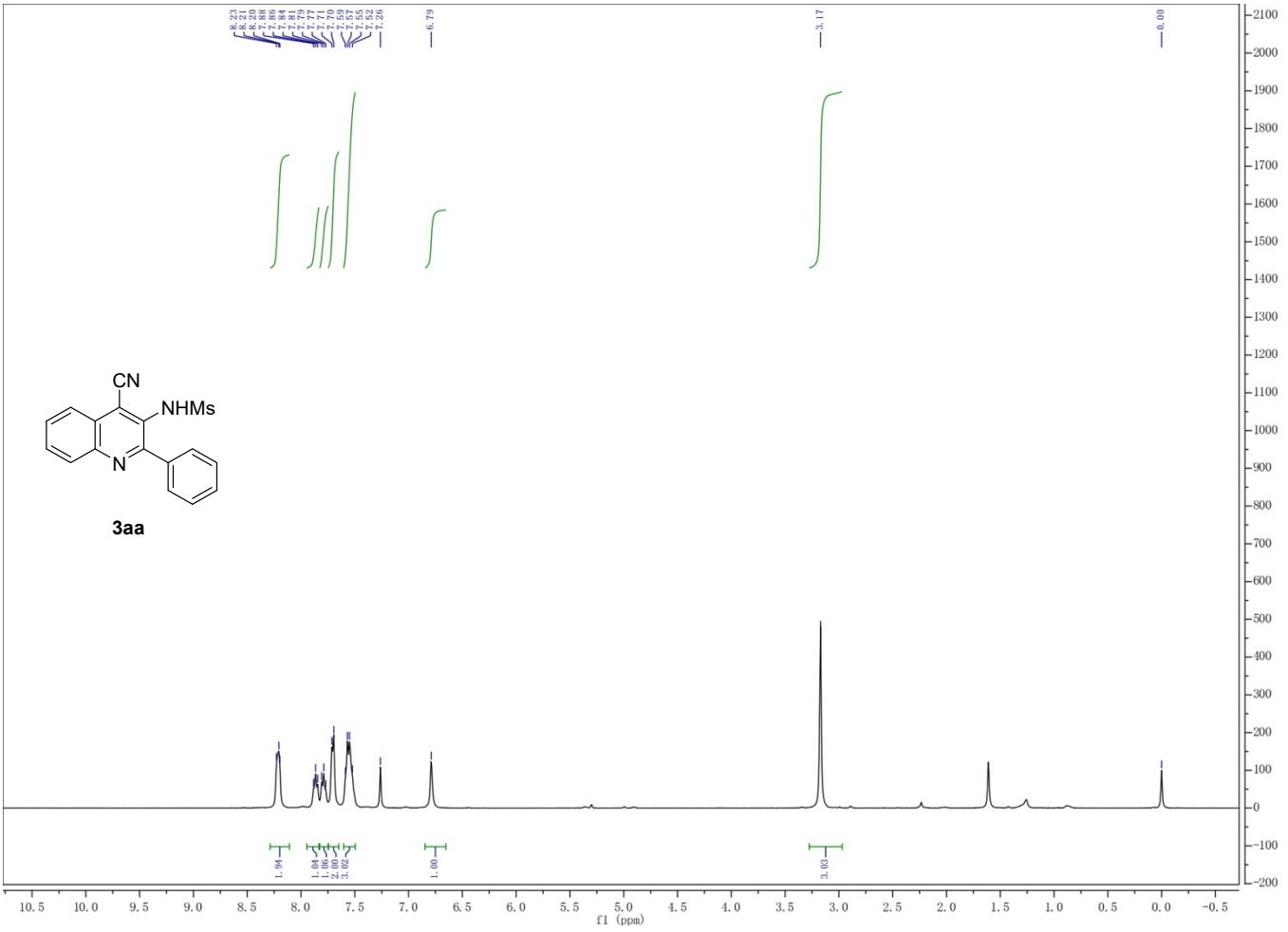



**Figure S58. $^{1}$H NMR of 3aa ($CDCl_3$, 400 MHz)**

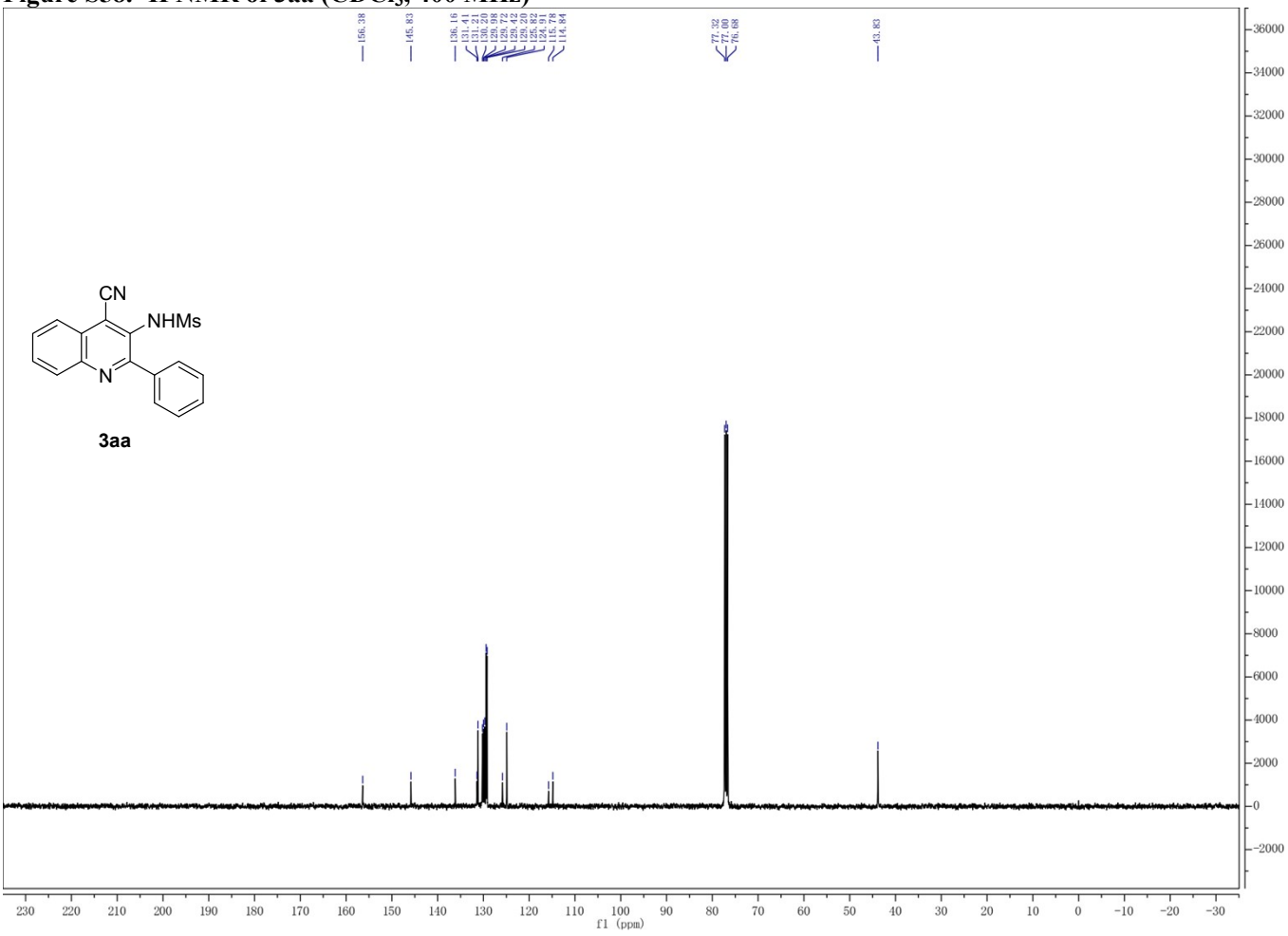



**Figure S59. $^{13}$C NMR of 3aa ($CDCl_3$, 101 MHz)**

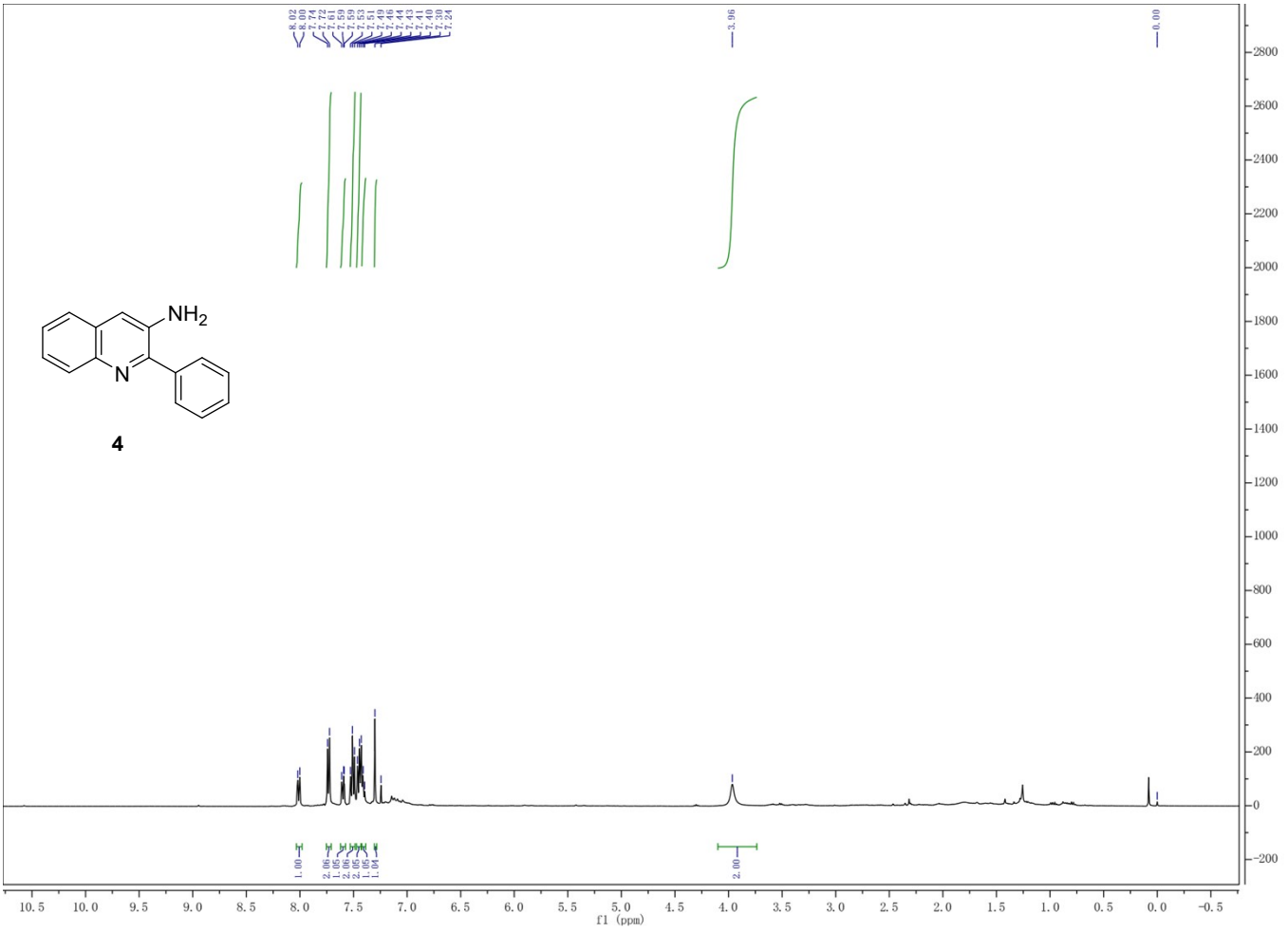



**Figure S60. $^{1}$H NMR of 4 ($CDCl_3$, 400 MHz)**

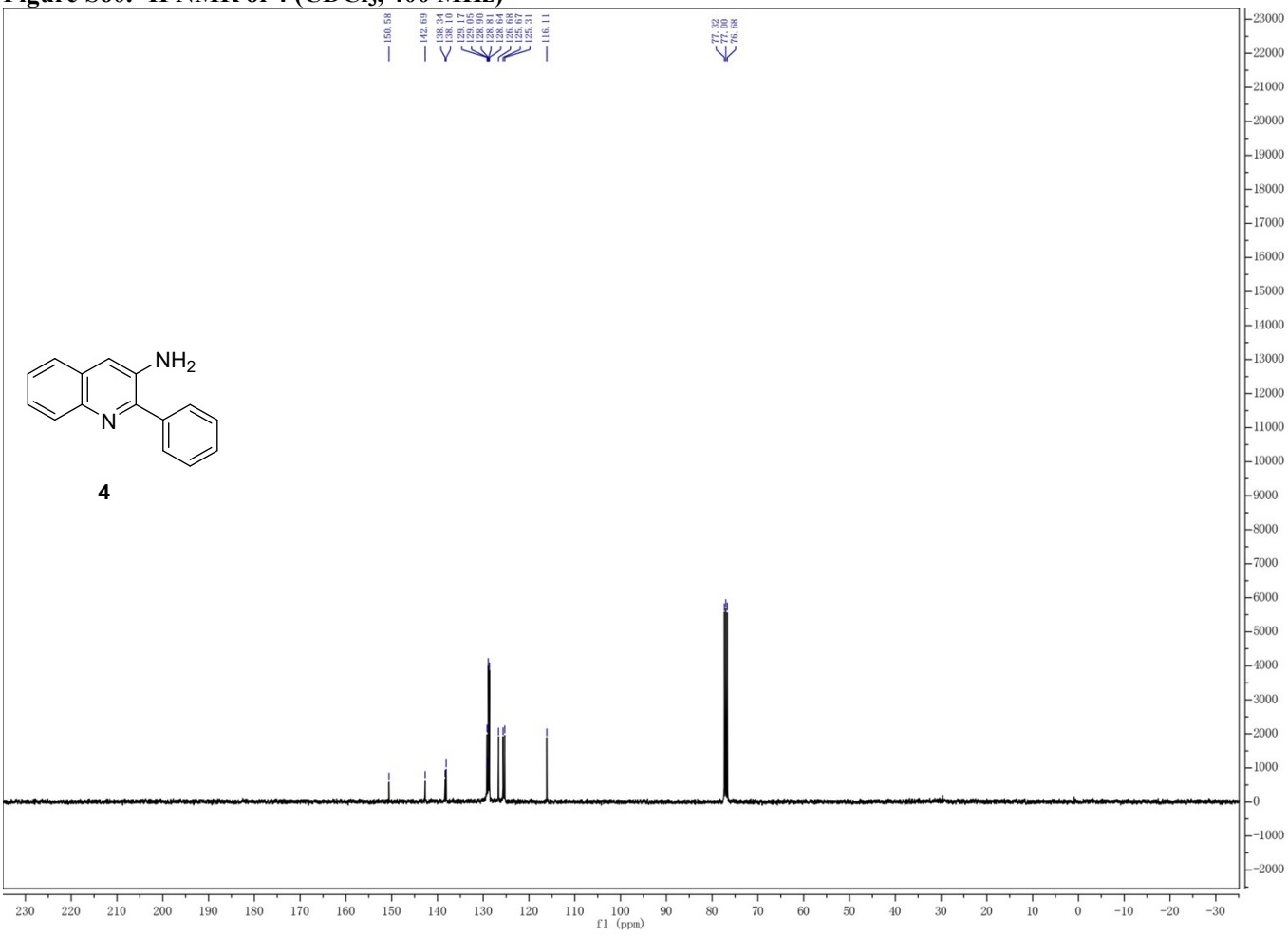



**Figure S61. $^{13}$C NMR of 4 (CDCl 101 MHz)**

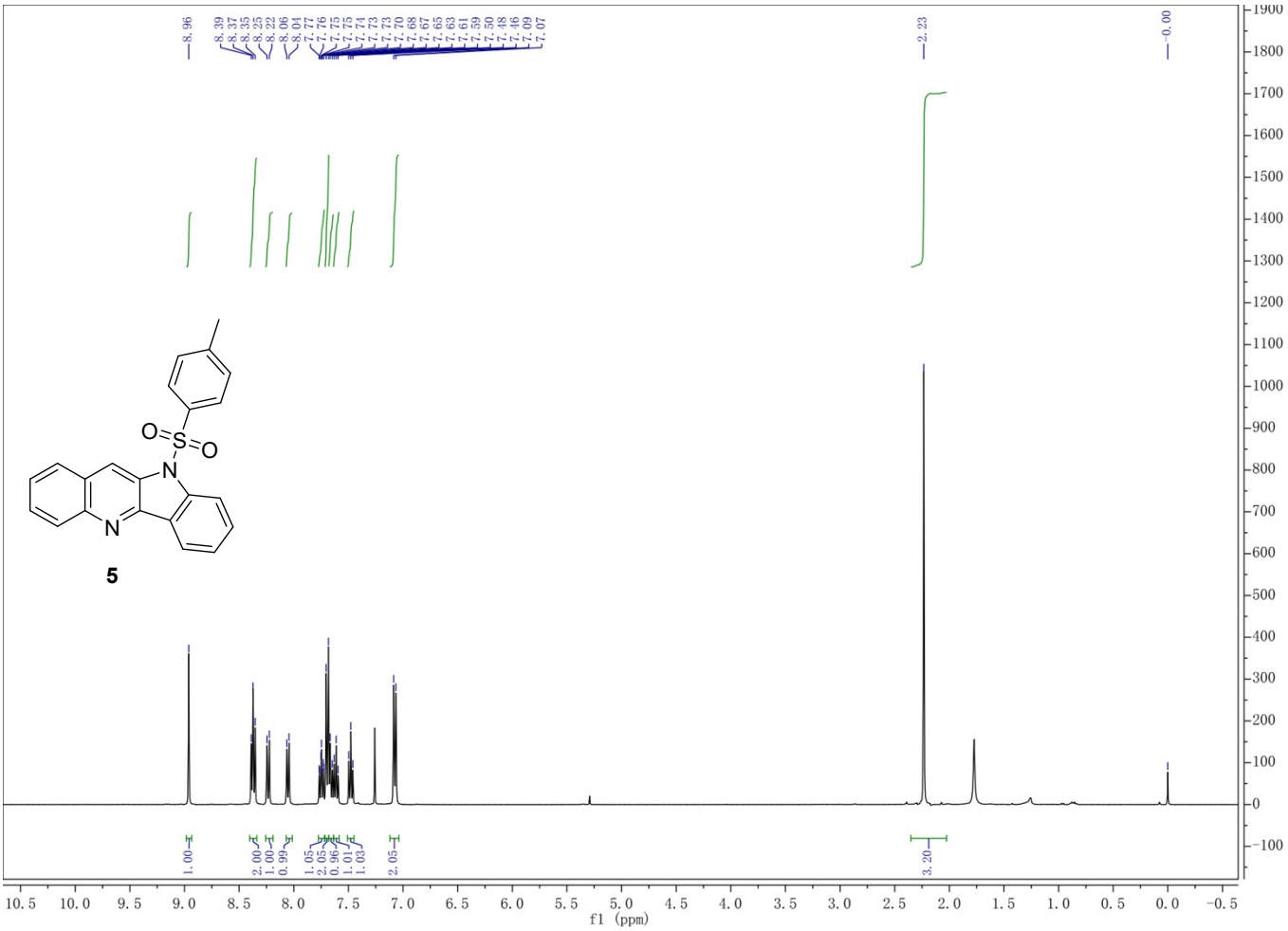



**Figure S62. $^{1}$H NMR of 5 ($CDCl_3$, 400 MHz)**

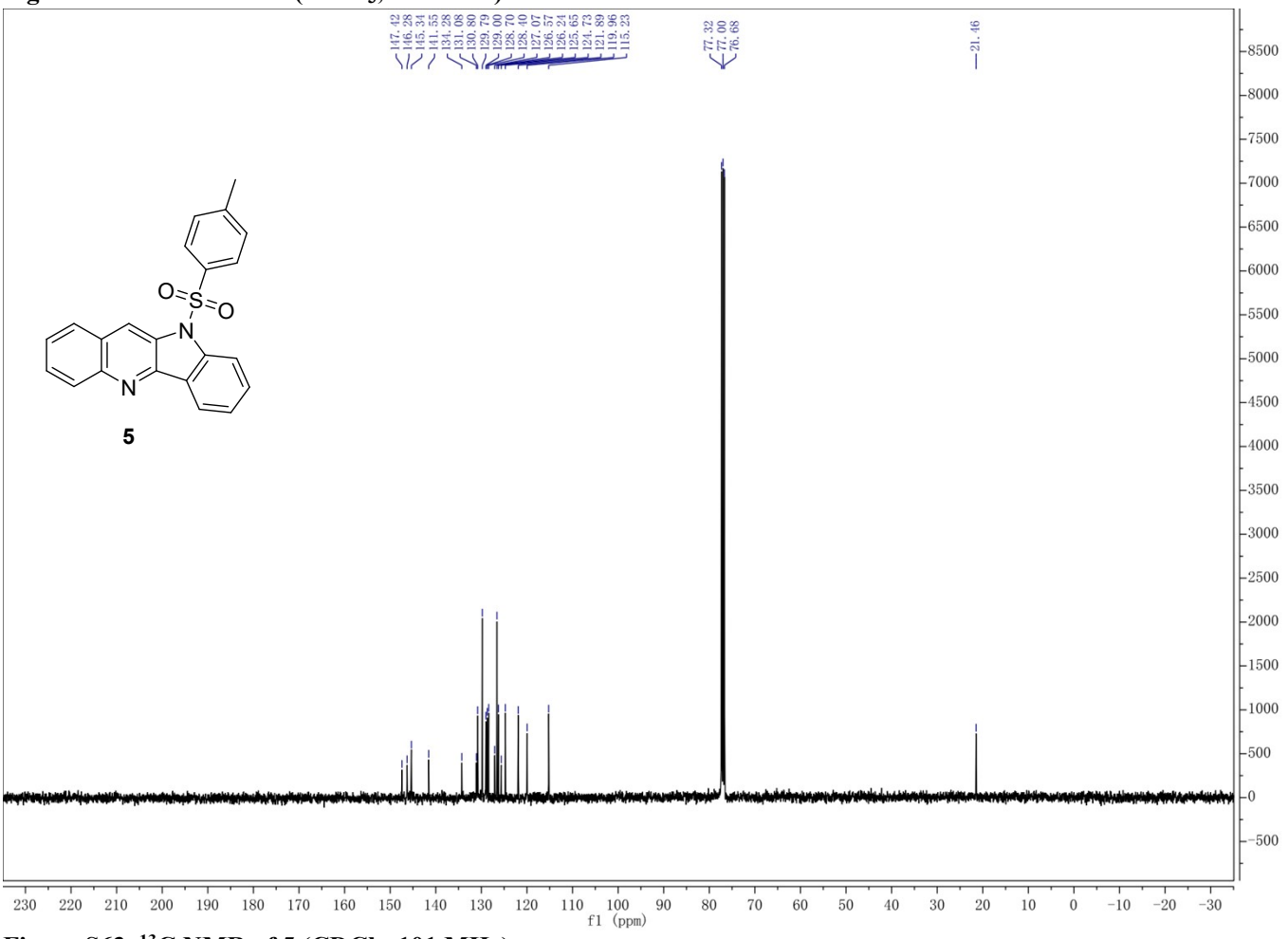



**Figure S63. $^{13}$C NMR of 5 ($CDCl_3$, 101 MHz)**

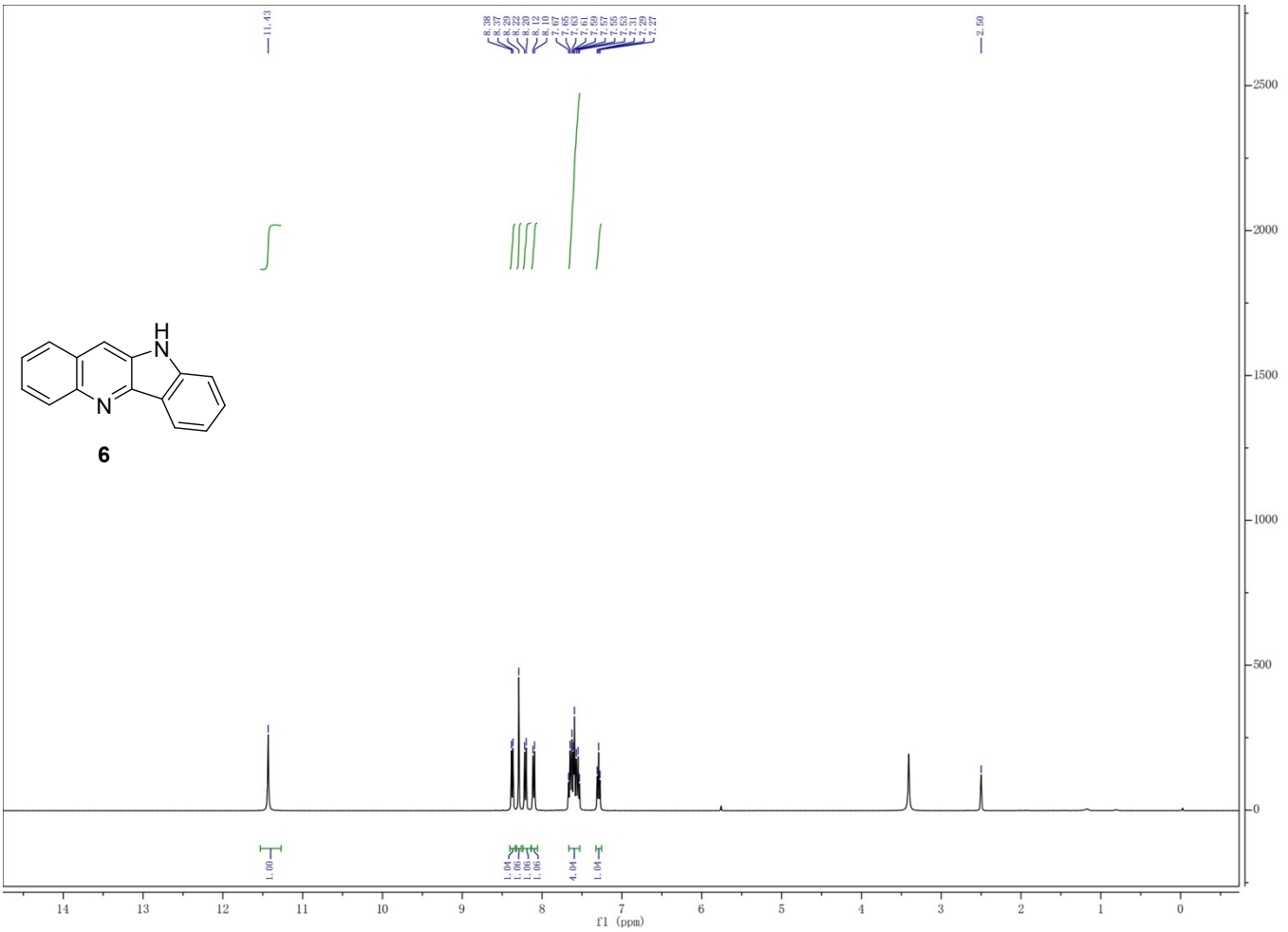



**Figure S64. $^{1}$H NMR of 6 (DMSO-d6, 400 MHz)**

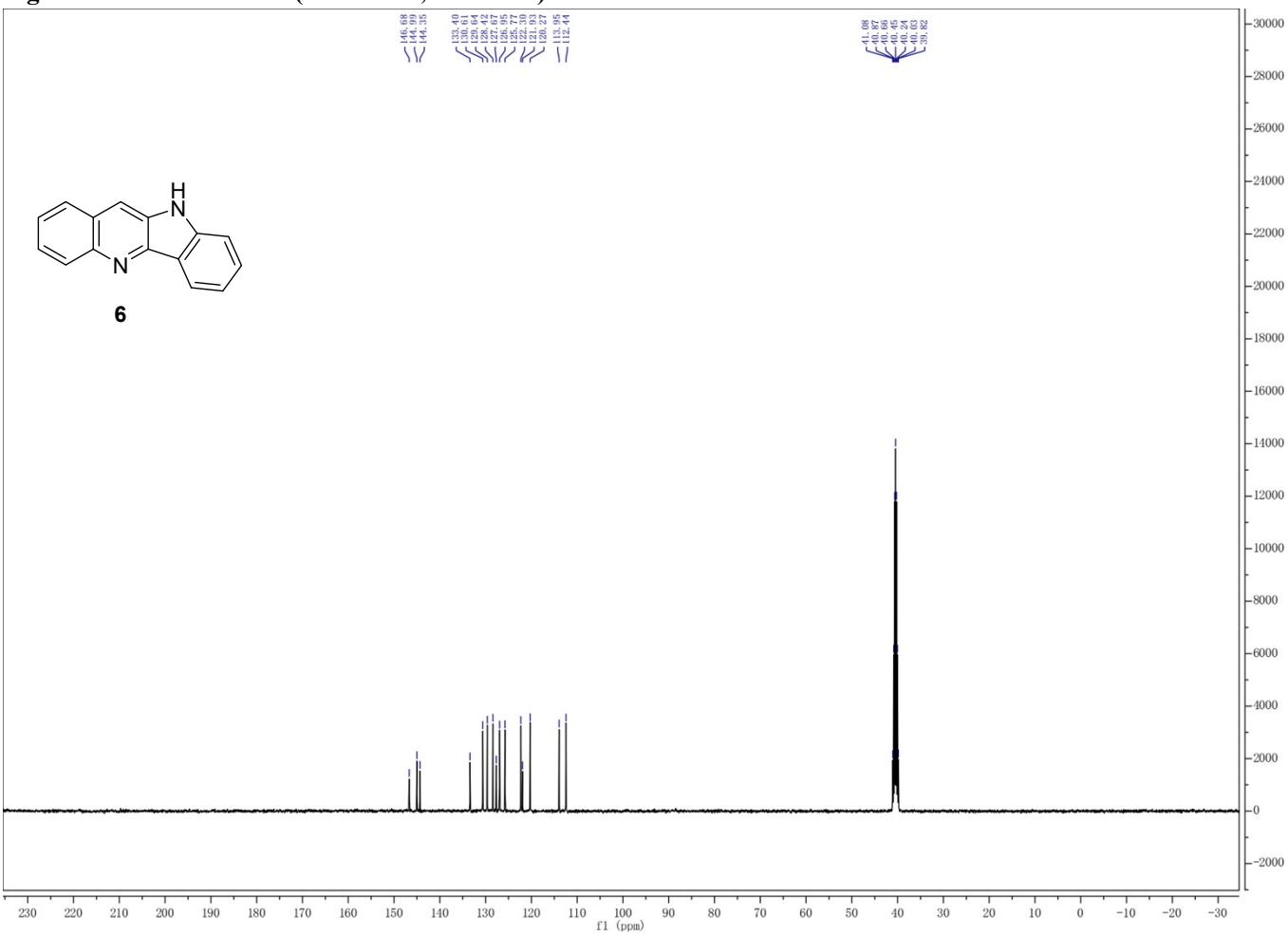



**Figure S65. $^{13}$C NMR of 6 (DMSO-d6, 101 MHz)**

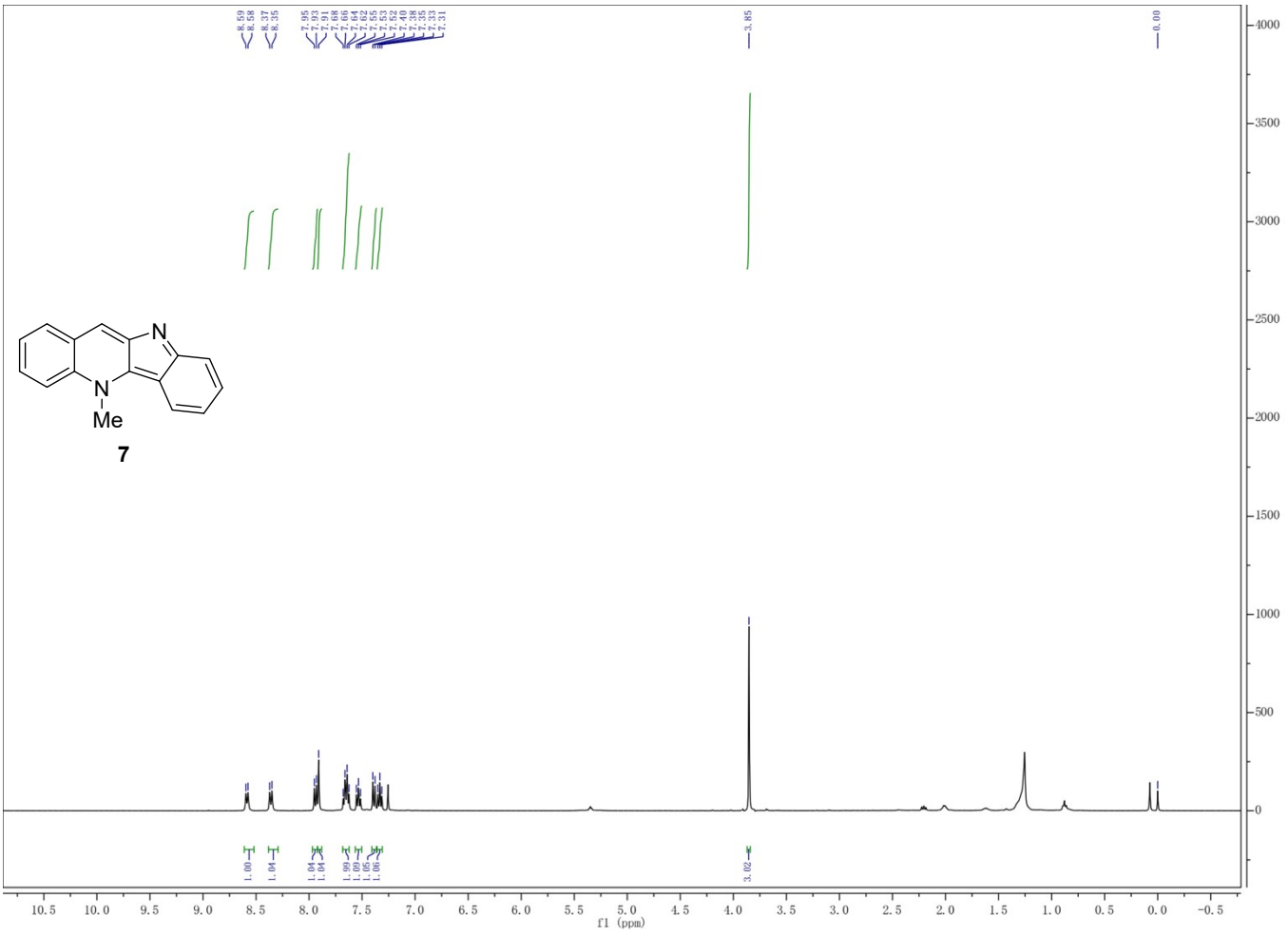



**Figure S66. $^{1}$H NMR of 7 ($CDCl_3$, 400 MHz)**

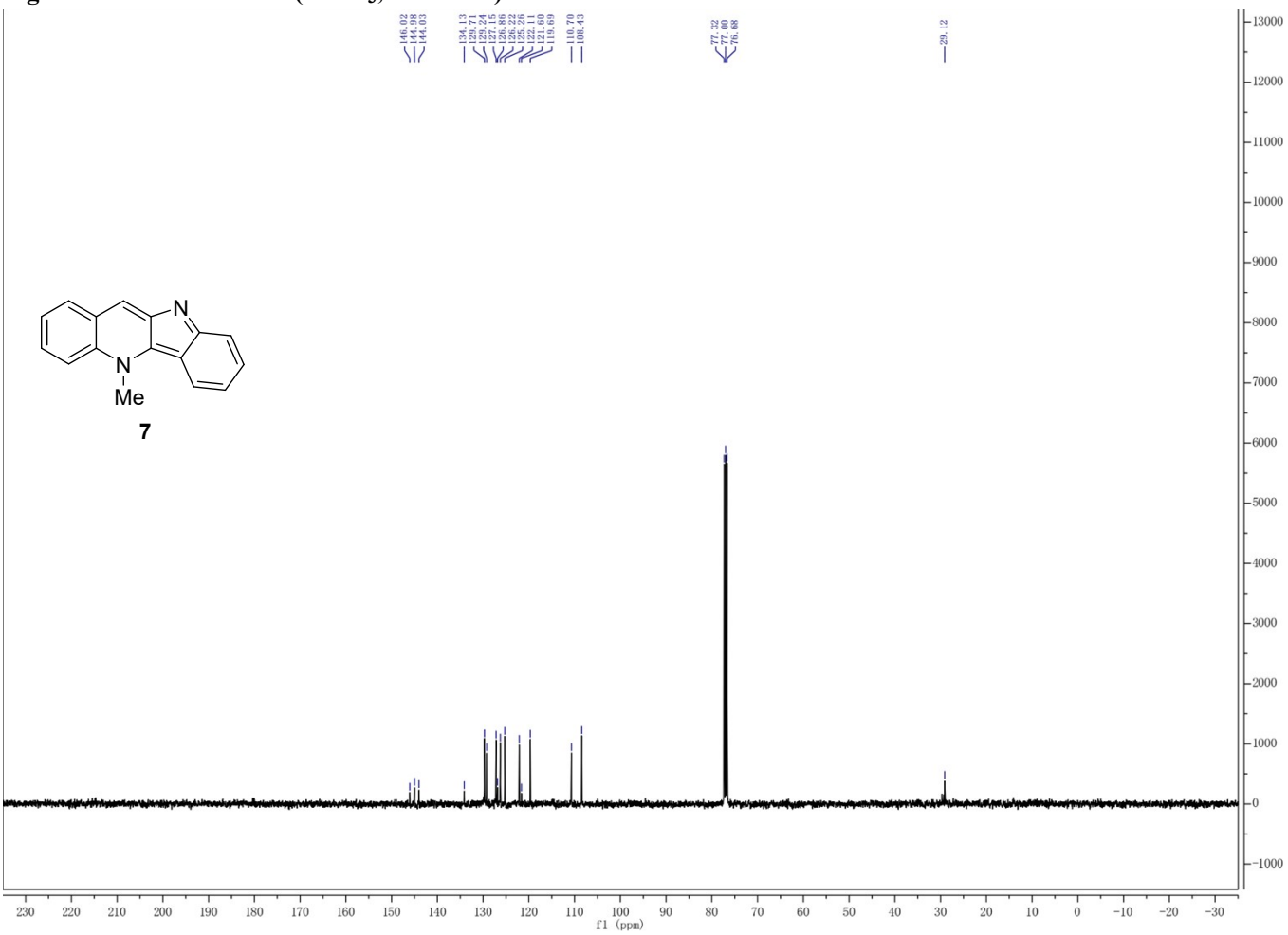
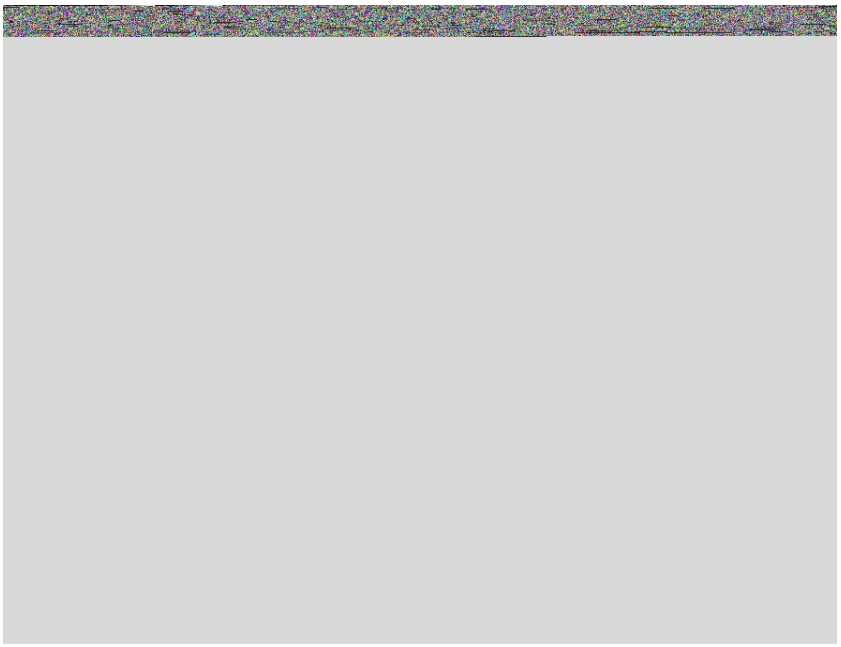



**Figure S67. $^{13}$C NMR of 7 ($CDCl_3$, 101 MHz)**

**8 X-ray data for compound 3a**



**CCDC 2256590**

## Datablock: 20220603_0m_a

Bond precision: C-C = 0.0039 A Wavelength=0.71073

Cell: a=7.817(3) b=12.371(5) c=19.295(7)
alpha=90 beta=90 gamma=90
Temperature: 296 K

| | Calculated | Reported |
|---|---|---|
| Volume | 1865.9(12) | 1865.8(12) |
| Space group | P 21 21 21 | P 21 21 21 |
| Hall group | P 2ac 2ab | P 2ac 2ab |
| Moiety formula | C22 H18 N2 O2 S | ? |
| Sum formula | C22 H18 N2 O2 S | C22 H18 N2 O2 S |
| Mr | 374.44 | 374.44 |
| Dx,g cm-3 | 1.333 | 1.333 |
| Z | 4 | 4 |
| Mu (mm-1) | 0.193 | 0.193 |
| F000 | 784.0 | 784.0 |
| F000' | 784.80 | |
| h,k,lmax | 10,16,25 | 10,16,25 |
| Nref | 4257[ 2436] | 4197 |
| Tmin,Tmax | 0.966,0.975 | |
| Tmin' | 0.966 | |

Correction method= Not given

Data completeness= 1.72/0.99 Theta(max)= 27.473

R(reflections)= 0.0373( 3703) wR2(reflections)= 0.0981( 4197)

S = 1.031 Npar= 249