Supporting Information

Photocatalytic Markovnikov-type addition and cyclization of terminal alkynes leading to 4-sulfonyl quinoline-2(1*H*)-ones

Yu-Lin Zhai,‡[a] Hui Zhou,‡[b] Qing-Quan Liu,[a] Bo-Rong Leng,[a] Zixian Zhang,[a] Jia-Zhuo Li,[a] De-Cai Wang,*[ab] Yi-Long Zhu*[ab]

[a] School of Pharmaceutical Sciences, Nanjing Tech University, Nanjing 211816, P. R. China.

[b] Institute of Materia Medica, Nanjing Tech University, Nanjing 211816, P. R. China.

E-mail: dcwang@njtech.edu.cn; zhuyilong_88@njtech.edu.cn

‡Yu-Lin Zhai and Hui Zhou contributed equally.

Content

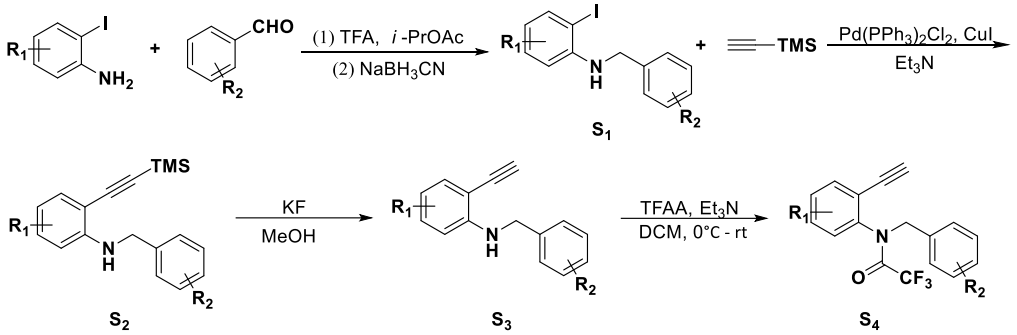
General Information

All glassware was thoroughly oven-dried and all reactions were carried out under nitrogen. Column chromatography was performed with silica gel (200-300 mesh) and used petroleum ether/ethyl acetate as eluents. Thin-layer chromatography (TLC) plates were visualized by exposure to ultraviolet light. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker DPX 400 MHz spectrometer in $CDCl_3$ with chemical shift (δ) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, m = multiplet), coupling constant (Hz)]. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.00 ppm)). HRMS (ESI) was performed on a Bruker Apex II mass instrument. X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer.

General procedure for the synthesis of substrates 1 and 4

General procedure for the synthesis of substrates 1:

N-alkyl-N-(2-ethynylphenyl)-2,2,2-trifluoroacetamide **1** were prepared from the corresponding 2-iodoaniline according to the known procedures reported in the literature.[1]



Using 1o as example:

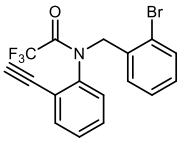
Product S_1: To a solution of 2-Iodoaniline (5 mmol, 1.0 equiv.) in isopropyl acetate (15.0 mL), *o*-Bromobenzaldehyde (5.5mmol, 1.1equiv) and TFA (10.0 mmol, 2.0 equiv.) was added sequentially. The mixture was stirred at room temperature for 3 h. After the formation of imine was detected, $NaBH_3CN$ (5.5 mmol, 1.1 equiv.) was added at 0°C and stirring at room temperature was continued for further 12 h. The aqueous phase was extracted three times with ethyl acetate and saturated $NaHCO_3$ aq. The combined organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford crude product S_1 as a yellow oil without f further purification.

Product S_2: In an oven-dried flask, S_1 (crude product, 1.0 equiv.), Pd $(PPh_3)_2Cl_2$ (0.01 equiv.) and CuI (0.02 equiv.) were added and charged with nitrogen more than three times. Et_3N(15mL) was injected into the flask via plastic syringes. After stirring for 5 minutes, trimethylsilylacetylene (1.2 equiv.) was added dropwise to the reaction mixture. The resulting suspension was stirred vigorously at room temperature for 12 h. After the reaction was completed, the reaction mixture was filtered through a pad of celite, eluting with EtOAc. Then the combined organics were sequentially washed with H_2O and brine, dried

over Na_2SO_4 and concentrated in vacuo. The product **S2** with brown oil properties was obtained by chromatography column on silica gel.

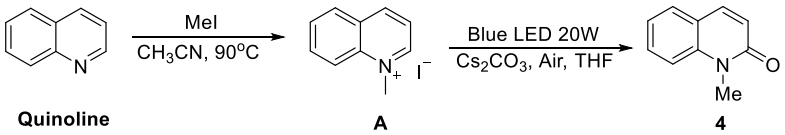
Product S3: The product **S2** of previous step was treated with KF (2.0 equiv.) in MeOH (20 mL) at room temperature for 3 h. Then MeOH was removed under reduced pressure. The residue was diluted with ethyl acetate (20 mL) and water (20 mL), and extracted twice with ethyl acetate. The combined organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford crude product. Then crude product **S3** was further purified by silica-gel column chromatography.

Product S4: To a solution of **S3** in CH_2Cl_2 (10 mL), Et_3N (2.0 equiv.) and trifluoroacetic anhydride (1.2 equiv.) was added sequentially. The reaction mixture was stirred at room temperature for 4h and then concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/Petroleum ether to give the final product **S4** as yellow oil.



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.56 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.35-7.25 (m, 2H), 7.24-7.16 (m, 2H), 7.15-7.08 (m, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 5.71 (d, *J* = 14.4 Hz, 1H), 4.66 (d, *J* = 14.4 Hz, 1H), 3.35 (s, 1H). (It's consistent with literature reports)

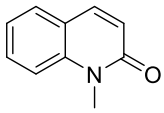
General procedure for the synthesis of substrate 4



1-methylquinolin-2(1H)-one 4 were prepared from quinoline according to the known procedures reported in the literature.[2]

Product A: Quinoline (5 mmol, 645.2 mg), CH_3I (10 mmol, 2.0 eq.) and CH_3CN (15 mL) were added to a round-bottom flask. The reaction mixture was stirred at 90 ºC with oil bath for 12 hours. After cooling to room temperature, ethyl acetate was added to precipitate the quinoline salt. Then through filtration, washing with ethyl acetate, and drying, pure product A was obtained.

Product 4: The product **A** of previous step was charged with Cs_2CO_3 (7.5 mmol, 244.4 mg, 1.5 eq) and THF (60 mL) in a 100 ml round-bottom flask with light irradiation by blue LEDs (20 W). The reaction mixture was stirred for 48h under air. When the reaction was complete, the reaction mixture was filtered and collected the filtrate. The pure product was obtained by column chromatography on silica gel (petroleum ether/ethyl acetate).



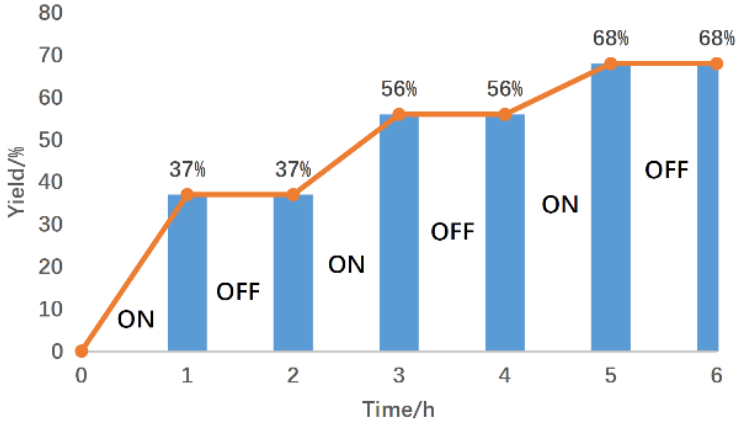
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.67 (d, *J* = 9.6 Hz, 1H), 7.60-7.55 (m, 2H), 7.38-7.36 (m, 1H), 7.26-7.22 (m, 1H), 6.72 (d, *J* = 9.6 Hz, 1H), 3.73 (s, 3H). (It's consistent with literature reports)

Reference

1. Xiong, P.; Xu, H.-H.; Song, J.; Xu, H.-C., Electrochemical Difluoromethylarylation of Alkynes. J. Am. Chem. Soc. 2018, 140, 2460-2464.
2. Zhou, Y.; Liu, W.; Xing, Z.; Guan, J.; Song Z.; Peng, Y., External-photocatalyst-free visible-light-mediated aerobic oxidation and 1,4-bisfunctionalization of *N*-alkyl isoquinolinium salts. Org. Chem. Front. 2020, 7, 2405–2413.

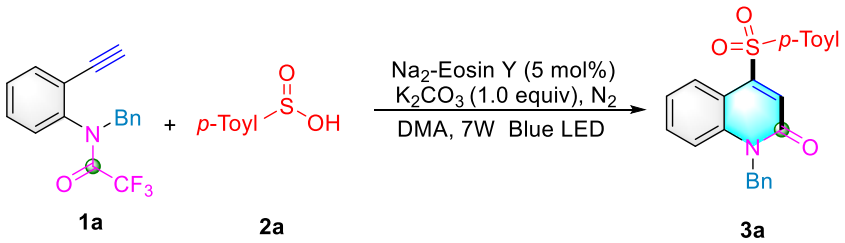
Light/Dark Experiment Procedure

p-toluenesulfinic acid **2a** (1.0 mmol, 2 equiv) was added to a mixture of potassium carbonate (0.5 mmol, 1 equiv), **1a** (0.5 mmol, 1 equiv) and Na_2-Eosin Y (0.025 mmol, 5 mol%) in dry DMA (5 mL) in 15 mL glass vial equipped with a magnetic stir bar and a nitrogen inlet. The mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with a 7 W blue LED. The light was turned off every one hour, and the reaction was allowed to stir in the dark for one hour before the LED was turned back on. 50 μL samples for analysis were removed via microsyringe immediately before the light was turned off/on. Yields were calculated by ^{1}H NMR using 1,3,5-trimethoxybenzene as the internal standard. An increase in yield was observed under irradiation, while no significant increase was observed when irradiation was stopped.



On/off experiments of **3a**

General Procedure for the Synthesis of 4-sulfonyl quinoline-2(1H)-ones



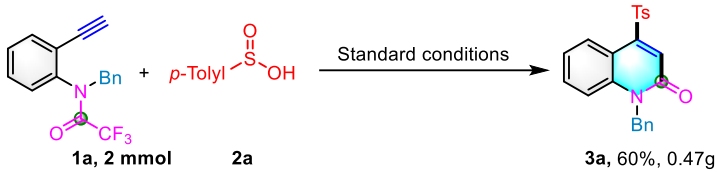
1a **2a** **3a**

To an oven-dried 10mL Schlenk tube under N_2 conditions, N-benzyl-N-(2-ethynylphenyl)-2,2,2-trifluoroacetamide **1a** (0.2 mmol, 60.6 mg, 1 equiv), *p*-toluenesulfinic acid **2a** (0.4 mmol, 62.5 mg, 2 equiv), K_2CO_3 (0.2 mmol, 27.7 mg, 1 equiv), Na_2-Eosin Y (6.9 mg, 5 mol%) and dry DMA (2 mL) were successively added. Then, the resulting mixture was stirred at 25°C for 9 h under 7W blue LEDs until complete consumption of **1a** as monitored by TLC analysis. The mixture was diluted with ethyl acetate (4 mL), which was followed by extraction with ethyl acetate (10 mL x 3 times). The combined organic

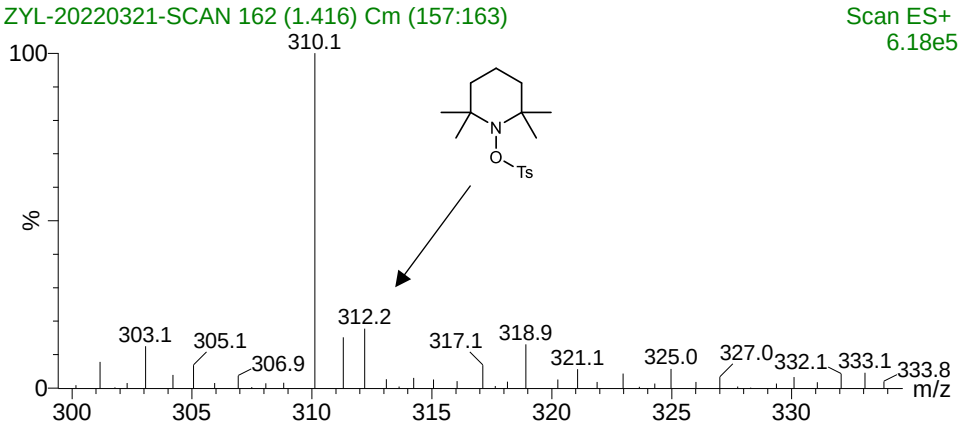
phase was washed with brine (10 mL), dried with dry Na_2SO_4 and the solvent was evaporated. The resulting residue was purified by column chromatography on silica gel to afford the desired product 3a.

Scale-Up Transformation of 3a

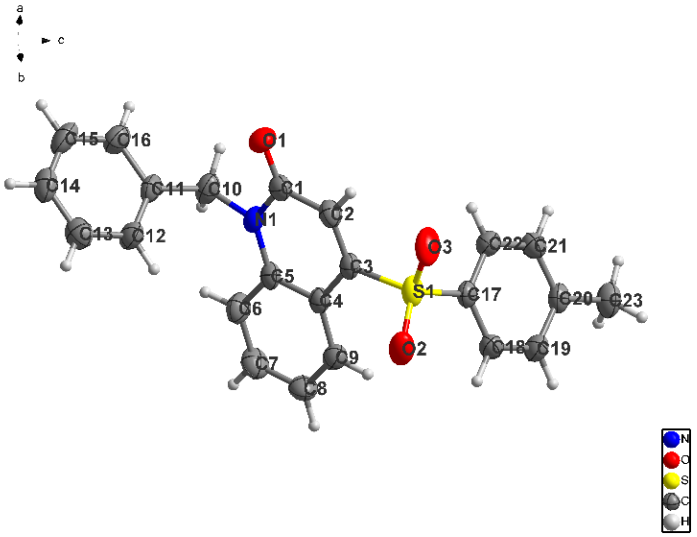
To expand the potential application of this method, an amplification reaction was conducted under the standard conditions. We were delighted to find that product 3a was isolated in 60% yield on a 2.0 mmol scale.



Copies of MS Data for Detecting Intermediate TEMPO



X-ray Crystallographic Data

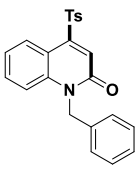


A single crystal 3a (CCDC 2145528) was obtained by slowly hexane 75% EtOAc solvent at room temperature under the air conditions. Its dimensions of 0.43 mm × 0.20 mm × 0.18 mm was mounted on a Siemens P1 diffractometer equipped with a graphite mono-chromated MoKa (λ = 0.71073 Å) radiation at 293(2) K. A total of 8513 reflections were collected in the 4.132° ≤ 2Θ ≤ 50.04°. Using Olex2, the structure was solved with the olex2.solve structure solution program using Charge Flipping and refined with the SHELXL refinement package using Least Squares minimisation. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were determined by theoretical calculations. The final cycle of refinement gave *R* was 0.0580 (I > 2σ(I)) and *wR* was 0.1562 (all data).

The crystal of compound 3a belongs to Monoclinic, space group P2(1)/n with a = 9.0023(9) Å, b = 12.4729(13) Å, c = 16.0823(15) Å, α = 90 deg, β = 90.973(2) deg, γ = 90 deg, V = 1805.5(3) $Å^3$, Mr = 389.45, Z = 4, Dc = 1.433 g/cm^3, μ(MoKα) = 0.205 mm^{-1}, F (000) = 816.0, the final R = 0.0580 and wR = 0.1562.

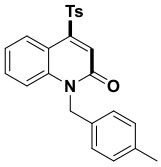
General Characterization Data of Products 3

1-benzyl-4-tosylquinolin-2(1*H*)-one (3a)



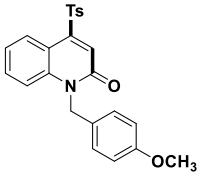
White solid; 55mg, 70% yield; m.p. 230-231℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.46 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.94-7.91 (m, 2H), 7.48-7.43 (m, 1H), 7.40-7.37 (m, 3H), 7.33-7.27 (m, 3H), 7.26-7.21 (m, 2H), 7.19-7.16 (m, 2H), 5.53 (s, 2H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.7, 148.74, 145.8, 140.1, 135.6, 135.3, 131.8, 130.3, 129.0, 128.7, 127.6, 126.6, 126.5, 123.7, 123.1, 115.9, 114.8, 46.6, 21.8. **IR** (KBr, *v*, cm^{-1}): 3044, 1654, 1588, 1313, 1145, 756. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{19}NO_3SNa$ 412.0983; Found 412.0979.

1-(4-methylbenzyl)-4-tosylquinolin-2(1*H*)-one (3e)



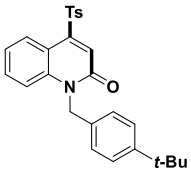
White solid; 69mg, 86% yield; m.p. 113-115℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.45 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.49-7.43 (m, 1H), 7.40-7.31 (m, 4H), 7.27-7.20 (m, 1H), 7.11-7.06 (m, 4H), 5.49 (s, 2H), 2.44 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.7, 148.6, 145.8, 140.2, 137.4, 135.6, 132.3, 131.8, 130.3, 129.6, 128.6, 126.6, 126.5, 123.7, 123.0, 115.9, 114.8, 46.4, 21.7, 21.1. **IR** (KBr, *v*, cm^{-1}): 3081, 2961, 1655, 1590, 1452, 1302, 1140, 756. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{21}NO_3SNa$ 426.1140; Found 426.1138.

1-(4-methoxybenzyl)-4-tosylquinolin-2(1*H*)-one (3f)



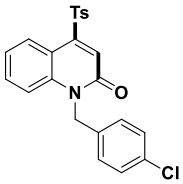
White solid; 68mg, 82% yield; m.p. 189-191℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.45 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.50-7.44 (m, 1H), 7.39-7.35 (m, 4H), 7.24 (dd, *J* = 11.2, 3.6 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 5.46 (s, 2H), 3.75 (s, 3H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.7, 159.0, 148.6, 145.8, 140.1, 135.6, 131.8, 130.3, 128.6, 128.0, 127.4, 126.6, 123.7, 123.0, 115.9, 114.8, 114.4, 55.3, 46.1, 21.7. **IR** (KBr, *v*, cm^{-1}): 1656, 1590, 1301, 1159, 818, 757, 674, 615. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{21}NO_4SNa$ 442.1089; Found 442.1084.

1-(4-(tert-butyl)benzyl)-4-tosylquinolin-2(1*H*)-one (3g)



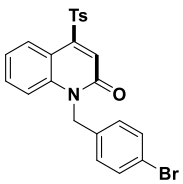
White solid; 45mg, 50% yield; m.p. 124-125℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.46 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.94-7.90 (m, 2H), 7.50-7.45 (m, 1H), 7.40-7.34 (m, 4H), 7.33-7.29 (m, 2H), 7.26-7.21 (m, 1H), 7.14-7.09 (m, 2H), 5.49 (s, 2H), 2.44 (s, 3H), 1.26 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.7, 150.6, 148.6, 145.8, 140.2, 135.6, 132.3, 131.8, 130.3, 128.6, 126.6, 126.3, 125.9, 123.8, 123.0, 116.0, 114.8, 46.3, 34.5, 31.3, 21.7. **IR** (KBr, *v*, cm^{-1}): 2962, 1659, 1588, 1449, 1302, 1147, 815, 753, 671. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{27}NO_3SNa$ 468.1609; Found 468.1603.

1-(4-chlorobenzyl)-4-tosylquinolin-2(1*H*)-one (3h)



White solid; 69mg, 82% yield; m.p. 171-172℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.48 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.93-7.91 (m, 2H), 7.50-7.46 (m, 1H), 7.38 (t, *J* = 8.0Hz, 3H), 7.28-7.24 (m, 4H), 7.12 (d, *J* = 8.4 Hz, 2H), 5.49 (s, 2H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.7, 148.9, 145.9, 139.9, 135.5, 133.9, 133.5, 131.9, 130.3, 129.2, 128.7, 128.0, 126.8, 123.6, 123.2, 115.7, 114.8, 46.0, 21.8. **IR** (KBr, *v*, cm^{-1}): 3062, 1659, 1588, 1303, 1153, 810, 757, 675. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{18}ClNO_3SNa$ 446.0594; Found 446.0590.

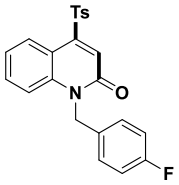
1-(4-bromobenzyl)-4-tosylquinolin-2(1*H*)-one (3i)



White solid; 75mg, 80% yield; m.p. 194-195℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.49-8.46 (m, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.50-7.45 (m, 1H), 7.43-7.36 (m, 5H), 7.28-7.23 (m, 2H), 7.06 (d, *J* = 8.4Hz, 2H), 5.47 (s, 2H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.7, 148.9, 145.9, 139.9, 137.6, 135.5, 134.4, 132.1, 131.9, 130.4, 128.7, 128.4, 126.8, 123.6, 123.2, 121.6, 115.7, 114.8, 46.1, 21.8. **IR**

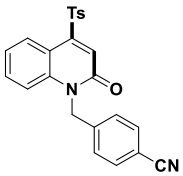
(KBr, *v*, cm^{-1}): 3064, 1657, 1587, 1448, 1153, 674, 612. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{18}BrNO_3SNa$ 490.0088; Found 490.0086.

1-(4-fluorobenzyl)-4-tosylquinolin-2(1*H*)-one (3j)



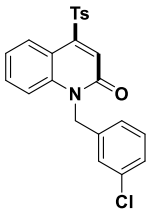
White solid; 64mg, 78% yield; m.p. 190-192℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.47 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.52-7.46 (m, 1H), 7.40-7.37 (m, 3H), 7.30-7.23 (m, 2H), 7.17 (dd, *J* = 8.4, 5.2Hz, 2H), 7.02-6.96 (m, 2H), 5.49 (s, 2H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 163.4(d, *J* = 244.9 Hz), 160.9, 160.7, 148.9, 145.9, 134.0, 135.5, 131.9, 131.1(1) (d, *J* = 3.4 Hz), 131.1(2), 130.3, 128.7, 128.4(d, *J* = 8.4 Hz), 128.3, 126.8, 123.6, 123.2, 116.0, 115.8, 115.7, 114.8, 46.0, 21.8. **IR** (KBr, *v*, cm^{-1}): 3044, 1654, 1588,1314, 1151, 757, 613. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{18}FNO_3SNa$ 430.0889; Found 430.0885.

4-((2-oxo-4-tosylquinolin-1(2*H*)-yl)methyl)benzonitrile (3k)



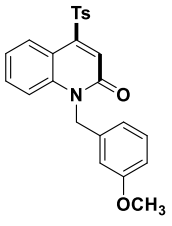
White solid; 54mg, 65% yield; m.p. 157-158℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.50 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.36 (s, 1H), 7.32-7.27 (m, 3H), 7.17 (d, *J* = 8.4 Hz, 1H), 5.57 (s, 2H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.6, 149.2, 146.0, 140.8, 139.7, 135.3, 132.8, 132.1, 130.4, 128.7, 127.3, 127.0, 123.5, 123.4, 118.4, 115.3, 114.9, 111.8, 46.3, 21.8. **IR** (KBr, *v*, cm^{-1}):3076, 2228, 1652, 1446, 1323, 1151, 815, 758, 616. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{18}N_2O_3SNa$ 437.0936; Found 437.0933.

1-(3-chlorobenzyl)-4-tosylquinolin-2(1*H*)-one (3l)



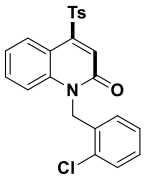
White solid; 50mg, 59% yield; m.p. 189-191℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.48 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 8.0Hz, 1H), 7.42-7.36 (m, 3H), 7.29-7.21 (m, 4H), 7.18 (s, 1H), 7.08-7.05 (m, 1H), 5.49 (s, 2H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.7, 149.0, 145.9, 139.9, 137.5, 135.5, 134.9, 132.0, 130.4, 130.3, 128.7, 128.0, 126.8, 126.7, 124.8, 123.6, 123.3, 115.7, 114.8, 46.2, 21.8. **IR** (KBr, *v*, cm^{-1}): 3089, 1660, 1588, 1444,1303, 1147, 767, 671. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{18}ClNO_3SNa$ 446.0594; Found 446.0591.

1-(3-methoxybenzyl)-4-tosylquinolin-2(1*H*)-one (3m)



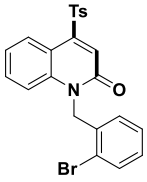
White solid; 75mg, 89% yield; m.p. 202-204℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.46 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.94-7.91 (m, 2H), 7.49-7.43 (m, 1H), 7.41-7.36 (m, 3H), 7.31 (dd, *J* = 8.8, 1.2 Hz, 1H), 7.27-7.19 (m, 2H), 6.80-6.70 (m, 3H), 5.50 (s, 2H), 3.75 (s, 3H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.7, 160.1, 148.8, 145.8, 140.2, 137.0, 135.6, 131.8, 130.3, 130.1, 128.7, 126.6, 123.6, 123.1, 118.7, 115.9, 114.8, 112.6, 55.3, 46.6, 21.8. **IR** (KBr, *v*, cm^{-1}): 3105, 2939, 1656, 1444, 1307, 1148, 1064, 756. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{21}ClNO_4SNa$ 442.1089; Found 442.1089.

1-(2-chlorobenzyl)-4-tosylquinolin-2(1*H*)-one (3n)



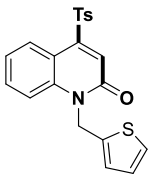
White solid; 36mg, 43% yield; m.p. 219-220℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.50 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.50-7.43 (m, 1H), 7.41-7.37 (m, 3H), 7.29-7.25 (m, 1H), 7.22-7.19(m, 1H), 7.11-7.07 (m, 2H), 6.69(d, *J* = 8.0 Hz ,1H), 5.59 (s, 2H), 2.46 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.7, 149.0, 145.9, 139.9, 135.5, 132.6, 132.3, 132.1, 130.4, 129.8, 128.8, 128.7, 127.4, 126.7, 123.4, 123.3, 115.8, 114.8, 44.4, 21.8. **IR** (KBr, *v*, cm^{-1}): 3072, 1651, 1587, 1446, 1304, 1158, 1088, 759, 673. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{18}ClNO_3SNa$ 446.0594; Found 446.0591.

1-(2-bromobenzyl)-4-tosylquinolin-2(1*H*)-one (3o)



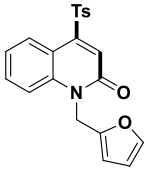
White solid; 49mg, 52% yield; m.p. 213-215℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.50 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.96-7.93 (m, 2H), 7.65-7.60 (m, 1H), 7.50-7.45 (m, 1H), 7.41 (d, *J* = 8.0, 2H), 7.37 (s, 1H), 7.29-7.25 (m, 1H), 7.15-7.11 (m, 2H), 7.07 (d, *J* = 8.8 Hz, 1H), 6.68-6.62 (m, 1H), 5.55 (s, 2H), 2.46 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.7, 149.1, 145.9, 139.8, 135.4, 133.8, 133.1, 132.1, 130.4, 129.1, 128.7, 128.0, 126.8, 126.7, 123.4, 123.3, 122.5, 115.9, 114.8, 47.1, 21.8. **IR** (KBr, *v*, cm^{-1}): 3072, 1661, 1594, 1316, 1154, 753. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{18}BrNO_3SNa$ 490.0088; Found 490.0086.

1-(thiophen-2-ylmethyl)-4-tosylquinolin-2(1*H*)-one (3p)



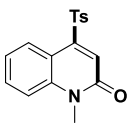
White solid; 30mg, 37% yield; m.p. 197-198℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.46 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.60-7.55 (m, 2H), 7.38-7.35 (m, 3H), 7.29-7.25 (m, 1H), 7.20 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.07 (d, *J* = 3.6 Hz, 1H), 6.92 (dd, *J* = 5.2, 3.6 Hz, 1H), 5.63 (s, 2H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 176.0, 160.2, 148.7, 145.8, 139.7, 137.6, 135.6, 131.8, 130.3, 128.6, 126.9, 126.8, 125.7, 123.7, 123.1, 115.3, 114.9, 41.8, 21.7. **IR** (KBr, *v*, cm^{-1}): 3108, 3049, 1655, 1585, 1443, 1307, 1149, 757, 609. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{17}NO_3S_2Na$ 418.0548; Found 418.0544.

1-(furan-2-ylmethyl)-4-tosylquinolin-2(1*H*)-one (3q)



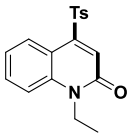
White solid; 26mg, 34% yield; m.p. 168-169℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.45 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.62-7.58 (m, 1H), 7.37-7.35 (m, 3H), 7.32-7.30 (m, 1H), 7.28-7.26 (m, 1H), 6.35 (d, *J* = 3.2Hz, 1H), 6.30 (t, *J* = 2.4 Hz, 1H), 5.47 (s, 2H), 2.43 (s, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.2, 149.0, 148.6, 145.7, 142.4, 140.0, 135.6, 131.8, 130.3, 128.6, 126.6, 123.8, 123.1, 115.6, 114.7, 110.7, 109.3, 39.6, 21.7. **IR** (KBr, *v*, cm^{-1}): 3120, 1656, 1590, 1446, 1340, 1147, 762, 673. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{17}NO_4SNa$ 402.0776; Found 402.0772.

1-methyl-4-tosylquinolin-2(1*H*)-one (3r)



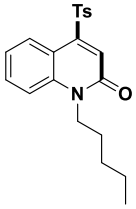
White solid; 44mg, 70% yield; m.p. 242-243℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.46-8.43 (m, 1H), 7.89-7.87 (m, 2H), 7.63-7.58 (m, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.37-7.34 (m, 3H), 7.30-7.25 (m, 1H), 3.71 (d, *J* = 2.0 Hz, 3H), 2.42 (d, *J* = 2.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.5, 148.1, 145.7, 140.6, 135.8, 131.9, 130.3, 128.5, 126.5, 123.9, 123.0, 115.0, 114.6, 30.1, 21.7. **IR** (KBr, *v*, cm^{-1})**:** 3100, 3049, 1663, 1585, 1456, 1304, 1147, 1085, 759, 674. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{15}NO_3SNa$ 336.0670; Found 336.0667.

1-ethyl-4-tosylquinolin-2(1*H*)-one (3s)



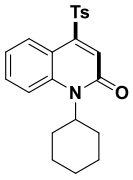
White solid; 38mg, 58% yield; m.p. 230-231℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.47 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.32 (s, 1H)., 7.30-7.26 (m, 1H), 4.38-4.33 (m, 2H), 2.43 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.1, 148.1, 145.7, 139.7, 135.8, 131.8, 130.2, 128.5, 126.8, 124.0, 122.8, 114.9, 114.8, 38.1, 21.7, 12.6. **IR** (KBr, *v*, cm^{-1})**:** 3098**,** 2980, 1653, 1584, 1450, 1304, 1147, 1085, 824, 760, 673. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{17}NO_3SNa$ 350.0827; Found 350.0823.

1-pentyl-4-tosylquinolin-2(1*H*)-one (3t)



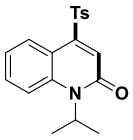
White solid; 36mg, 49% yield; m.p. 139-140℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.46 (dd, *J* = 8.4, 1.6Hz, 1H), 7.91-7.88(m, 2H), 7.60 (m, 1H), 7.38 (t, *J* = 9.6Hz, 3H), 7.32 (s, 1H), 7.30-7.24 (m, 1H), 4.29-4.23 (m, 2H), 2.43 (s, 3H), 1.75-1.68 (m, 2H), 1.47-1.34 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.2, 148.0, 145.6, 139.9, 135.8, 131.7, 130.2, 128.5, 126.7, 123.9, 122.7, 115.0, 114.80, 43.1, 29.0, 27.1, 22.4, 21.7, 14.0. **IR** (KBr, *v*, cm^{-1}): 2950, 2869, 1654, 1587, 1449, 1305, 1146, 1090, 750, 674. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{23}NO_3SNa$ 392.1296; Found 392.1294.

1-cyclohexyl-4-tosylquinolin-2(1*H*)-one (3u)



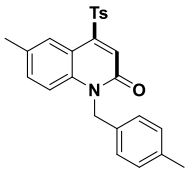
White solid; 38mg, 50% yield; m.p. 188-189℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.43 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.64-7.53 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.26-7.19 (m, 2H), 4.45 (s, 1H), 2.59 (s, 2H), 2.43 (s, 3H), 1.97-1.89 (m, 2H), 1.81-1.70 (m, 3H), 1.51-1,25 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 161.0, 147.5, 145.5, 140.5, 135.8, 131.0, 130.2, 128.5, 126.6, 125.2, 122.5, 115.3, 77.2, 28.6, 26.5, 25.3, 21.7. **IR** (KBr, *v*, cm^{-1}): 2921, 2853, 1590, 1307, 1148, 890, 754, 614. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{15}NO_3SNa$ 404.1296; Found 404.1292.

1-isopropyl-4-tosylquinolin-2(1*H*)-one (3v)



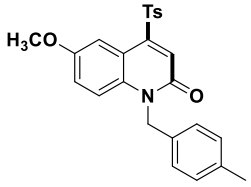
White solid; 22mg, 32% yield; m.p. 185-186℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.45 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.62-7.53 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.27-7.23 (m, 2H), 5.41 (s, 1H), 2.43 (s, 3H), 1.63 (d, *J* = 7.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.9, 147.6, 145.6, 139.9, 135.8, 131.0, 130.2, 128.5, 126.7, 124.8, 122.5, 115.7, 115.3, 77.2, 21.7, 19.6. **IR** (KBr, *v*, cm^{-1}): 3095, 2971, 1651, 1322, 1303, 1144, 761, 609. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{19}NO_3SNa$ 364.0983; Found 364.0981.

6-methyl-1-(4-methylbenzyl)-4-tosylquinolin-2(1*H*)-one（3w）



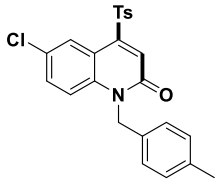
White solid; 58mg, 70% yield; m.p. 166-167℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.24 (d, *J* = 2.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 7.21 (d, 1H), 7.10-7.04 （m, 4H） 5.47 (s, 2H), 2.45 (s, 3H), 2.37 (s, 3H), 2.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.6, 148.4, 145.8, 138.2, 137.3, 135.5, 133.1, 132.7, 132.4, 130.3, 129.6, 128.7, 126.5, 126.3, 123.4, 115.8, 114.7, 46.3, 21.8, 21.1, 21.0. **IR** (KBr, *v*, cm^{-1}): 3092, 1660, 1447, 1328, 1147, 806, 670, 618. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{23}NO_3SNa$ 440.1296; Found 440.1292.

6-methoxy-1-(4-methylbenzyl)-4-tosylquinolin-2(1*H*)-one (3x)



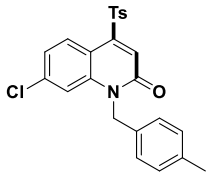
White solid; 43mg, 50% yield; m.p. 144-146℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 7.92 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 2.8 Hz, 1H), 7.45 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 10.0 Hz, 1H), 7.10-7.04 (m, 5H), 5.47 (s, 2H), 3.81 (s, 3H), 2.44 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.3, 154.9, 147.7, 145.8, 137.3, 135.8, 134.7, 132.4, 130.3, 129.6, 128.5, 126.5, 124.3, 120.9, 117.2, 115.5, 108.1, 55.7, 46.5, 21.8, 21.1. **IR** (KBr, *v*, cm^{-1}): 3092, 1656, 1445, 1303, 1153, 812, 673. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{23}NO_4SNa$ 456.1245; Found 456.1242.

6-chloro-1-(4-methylbenzyl)-4-tosylquinolin-2(1*H*)-one (3y)



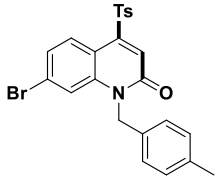
White solid; 49mg, 56% yield; m.p. 211-212℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.45 (d, *J* = 2.4 Hz, 1H), 7.92-7.90 (m, 2H), 7.41-7.38 (m, 4H), 7.25 (d, *J* = 8.8 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 5.46 (s, 2H), 2.46 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm):160.4, 147.8, 146.1, 138.7, 137.6, 135.3, 131.9, 130.4, 129.7, 128.8, 128.7, 126.5, 126.0, 124.8, 117.3, 115.8, 46.5, 21.8, 21.1. **IR** (KBr, *v*, cm^{-1}): 3093, 1662, 1418, 1325, 1147, 816, 616. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{20}ClNO_3SNa$ 460.0750; Found 460.0745.

7-chloro-1-(4-methylbenzyl)-4-tosylquinolin-2(1*H*)-one (3z)



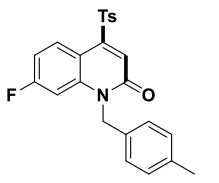
White solid; 46mg, 53% yield; m.p. 188-190℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.39 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.34-7.33 (m, 2H), 7.19 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.10 (q, *J* = 8.0 Hz, 4H), 5.43 (s, 2H), 2.45 (s, 3H), 2.31 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.6, 148.4, 146.0, 141.1, 138.3, 137.7, 135.3, 131.8, 130.4, 129.8, 128.6, 127.8, 126.6, 123.5, 123.5, 115.9, 113.3, 46.5, 21.8, 21.1. **IR** (KBr, *v*, cm^{-1}): 3089, 1664, 1591, 1420, 1310, 1151, 813. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{20}ClNO_3SNa$ 460.0750; Found 460.0746.

7-bromo-1-(4-methylbenzyl)-4-tosylquinolin-2(1*H*)-one (3aa)



White solid; 55mg, 57% yield; m.p. 217-218℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.31 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 2.0 Hz, 1H), 7.40-7.33 (m, 4H), 7.11 (m, 4H), 5.42(s, 2H), 2.45 (s, 3H), 2.31 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.5, 148.4, 146.0, 141.1, 137.7, 135.3, 131.8, 130.4, 129.8, 128.6, 127.8, 126.7, 126.6, 126.3, 123.8, 118.8, 113.6, 46.5, 21.8, 21.1. **IR** (KBr, *v*, cm^{-1}): 3090, 1662, 1587, 1308, 1150, 812, 676. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{20}BrNO_3SNa$ 504.0245; Found 504.0238.

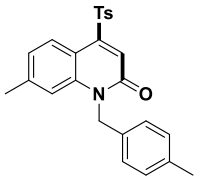
7-fluoro-1-(4-methylbenzyl)-4-tosylquinolin-2(1*H*)-one (3ab)



White solid; 66mg, 78% yield; m.p. 166-167℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.47 (dd, *J* = 9.2, 6.0 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 5.2 Hz, 1H), 7.13-7.06 (m, 4H), 7.02(dd, *J* =10.8, 2.4Hz, 1H), 6.98-6.93 (m, 1H), 5.42 (s, 2H), 2.45 (s, 3H), 2.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): δ 165.6(d, *J* = 252 Hz), 163.1, 160.9, 148.4, 146.0, 142.2(d, *J* = 11.5 Hz),

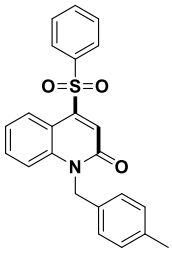
142.1, 137.6, 135.3, 131.7, 130.4, 129.8, 129.0(d, J = 10.2 Hz), 128.9, 128.6, 126.6, 122.5(d, J = 3.1 Hz), 122.4, 111.4(d, J = 22.6 Hz), 111.2, 103.2(d, J = 27.3 Hz), 102.9, 46.7, 21.8, 21.1. **IR** (KBr, v, cm^{-1}): 3089, 1658, 1449, 1309, 1148, 812, 675. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{20}FNO_3SNa$ 444.1046; Found 444.1039.

7-methyl-1-(4-methylbenzyl)-4-tosylquinolin-2(1*H*)-one（3ac）



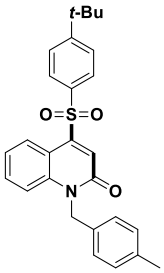
White solid; 47mg, 56% yield; m.p. 209-210℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.32 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.31 (s, 1H), 7.13-7.04 (m, 6H), 5.46 (s, 2H), 2.43 (s, 3H), 2.34 (s, 3H), 2.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.9, 148.5, 145.7, 142.7, 140.4, 137.3, 135.8, 132.5, 130.3, 129.6, 128.6, 126.6, 126.3, 124.4, 122.5, 116.0, 112.5, 46.3, 22.2, 21.7, 21.1. **IR** (KBr, v, cm^{-1}): 3089, 1658, 1449, 1309, 1148, 812, 675, 599. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{23}NO_3SNa$ 440.1296; Found 440.1290.

1-(4-methylbenzyl)-4-(phenylsulfonyl)quinolin-2(1*H*)-one (3ad)



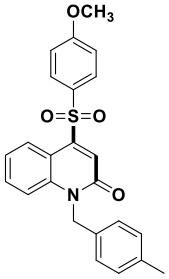
yellow solid; 49mg, 63% yield; m.p. 187-188℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.43 (dd, J = 8.4, 1.2 Hz, 1H), 8.04 (dd, J = 7.6, 2.0 Hz, 1H), 7.70-7.65 (m, 1H), 7.62-7.58 (m, 2H), 7.49-7.44 (m, 1H), 7.34 (d, J = 8.8 Hz, 1H), 7.23 (t, J = 7.6 Hz, 1H), 7.12-7.07 (m, 4H), 5.49 (s, 2H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.7, 148.3, 140.2, 138.8, 137.4, 134.5, 132.3, 131.9, 129.7, 129.7, 128.5, 126.6, 126.5, 124.1, 123.0, 116.0, 114.8, 46.4, 21.1. **IR** (KBr, v, cm^{-1}): 3086, 1650, 1580, 1446, 1309, 1154, 903, 751, 620. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{19}NO_3SNa$ 412.0983; Found 412.0978.

4-((4-(tert-butyl)phenyl)sulfonyl)-1-(4-methylbenzyl)quinolin-2(1*H*)-one (3ae)



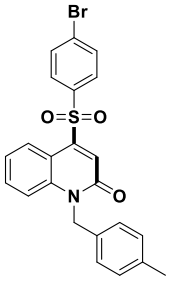
White solid; 46mg, 52% yield; m.p. 190-192℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.50 (dd, J = 8.4, 1.2 Hz, 1H), 7.96-7.95 (m, 2H), 7.60-7.58 (m, 2H), 7.49-7.45 (m, 1H), 7.37-7.33 (m, 2H), 7.27-7.23 (m, 1H), 7.09 (t, J = 9.2, 4H), 5.49 (s, 2H), 2.29 (s, 3H), 1.34 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.8, 158.7, 148.7, 140.2, 137.4, 135.4, 132.3, 131.8, 129.6, 128.5, 126.7, 126.7, 126.6, 123.7, 123.0, 115.9, 114.9, 46.4, 35.4, 31.0, 21.1. **IR** (KBr, v, cm^{-1}): 2964, 1660, 1449, 1308, 1153, 756, 617. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{27}NO_3SNa$ 468.1609; Found 468.1601.

4-((4-methoxyphenyl)sulfonyl)-1-(4-methylbenzyl)quinolin-2(1*H*)-one (3af)



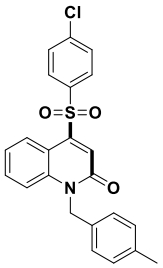
White solid; 59mg, 70% yield; m.p. 153-154℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.49 (d, J = 8.0 Hz, 1H), 7.89-7.96 (m, 2H), 7.49-7.44 (m, 1H), 7.34-7.30 (m, 2H), 7.25 (t, J = 7.6 Hz, 1H), 7.11-7.03 (m, 6H), 5.49 (s, 2H), 3.88 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 164.4, 160.8, 149.1, 140.2, 137.3, 132.3, 131.8, 131.0, 129.7, 129.6, 126.6, 126.5, 123.3, 123.0, 115.9, 114.9, 114.8, 55.8, 46.4, 21.1. **IR** (KBr, v, cm^{-1})： 3087, 1658, 1587, 1444, 1306, 1146, 765, 587. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{21}NO_4SNa$ 442.1089; Found 442.1089.

4-((4-bromophenyl)sulfonyl)-1-(4-methylbenzyl)quinolin-2(1*H*)-one (3ag)



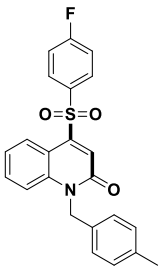
White solid; 73mg, 78% yield; m.p. 206-208℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.37 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 6.8 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.12-7.07 (m, 4H), 5.49 (s, 2H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.5, 147.8, 140.2, 137.9, 137.4, 133.0, 132.2, 132.0, 130.0, 129.9, 129.7, 126.6, 126.3, 124.4, 123.1, 116.1, 114.6, 46.5, 21.1. **IR** (KBr, *v*, cm^{-1}): 3090, 1658, 1584, 1443, 1332, 1159, 898, 762, 589. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{18}BrNO_3SNa$ 490.0088; Found 490.0080.

4-((4-chlorophenyl)sulfonyl)-1-(4-methylbenzyl)quinolin-2(1*H*)-one (3ah)



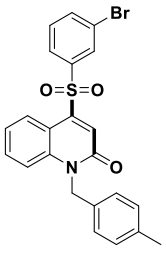
White solid; 72mg, 85% yield; m.p. 198-199℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.38 (d, *J* = 8.4 Hz, 1H), 7.99-7.64 (m, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.50-7.46 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.27-7.21 (m, 1H), 7.12-7.06 (m, 4H), 5.49 (s, 2H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.5, 147.9, 141.4, 140.2, 137.4, 137.3, 132.2, 132.0, 130.1, 129.9, 129.7, 126.6, 126.3, 124.4, 123.1, 116.1, 114.6, 46.5, 21.1. **IR** (KBr, *v*, cm^{-1}): 3093, 1660, 1446, 1329, 1153, 1086, 901, 759, 589. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{18}ClNO_3SNa$ 446.0594; Found 446.0590.

4-((4-fluorophenyl)sulfonyl)-1-(4-methylbenzyl)quinolin-2(1*H*)-one (3ai)



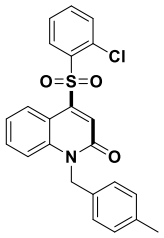
White solid; 59mg, 73% yield; m.p. 188-189℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.41 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.08-8.05 (m, 2H), 7.50-7.43 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.29-7.22 (m, 3H), 7.12-7.07 (m, 4H), 5.49 (s, 2H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 166.2 (d, *J* = 256.7 Hz), 160.6, 148.2, 140.2, 137.4, 134.8 (d, *J* = 3.2 Hz), 132.2, 132.0, 131.5 (d, *J* = 9.7 Hz), 129.7, 126.6, 126.3, 124.1, 123.1, 117.2, 117.0 (d, *J* = 15.9 Hz), 114.6, 46.5, 21.1. **IR** (KBr, *v*, cm^{-1}): 3096, 1661, 1588, 1449, 1306, 1154, 765, 674. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{18}FNO_3SNa$ 430.0889; Found 430.0880.

4-((3-bromophenyl)sulfonyl)-1-(4-methylbenzyl)quinolin-2(1*H*)-one (3aj)



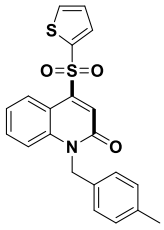
White solid; 42mg, 45% yield; m.p. 165-166℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.37 (dd, *J* = 8.4, 1.6 Hz, 1H), 8.15 (t, *J* = 2.0 Hz, 1H), 7.99-7.96 (m, 1H), 7.79 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.50 – 7.45 (m, 3H), 7.37 (d, *J* = 8.8 Hz, 1H), 7.27-7.23 (m, 1H), 7.12 – 7.08 (m, 4H), 5.50 (s, 2H), 2.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.5, 147.6, 140.8, 140.2, 137.5(1), 137.5(2), 132.2, 132.0, 131.2, 131.1, 129.7, 127.0, 126.6, 126.3, 124.6, 123.7, 123.2, 116.1, 114.6, 46.5, 21.1. **IR** (KBr, *v*, cm^{-1}): 3086, 1660, 1591, 1310, 1146, 751, 625. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{18}BrNO_3SNa$ 490.0088; Found 490.0080.

4-((2-chlorophenyl)sulfonyl)-1-(4-methylbenzyl)quinolin-2(1*H*)-one (3ak)



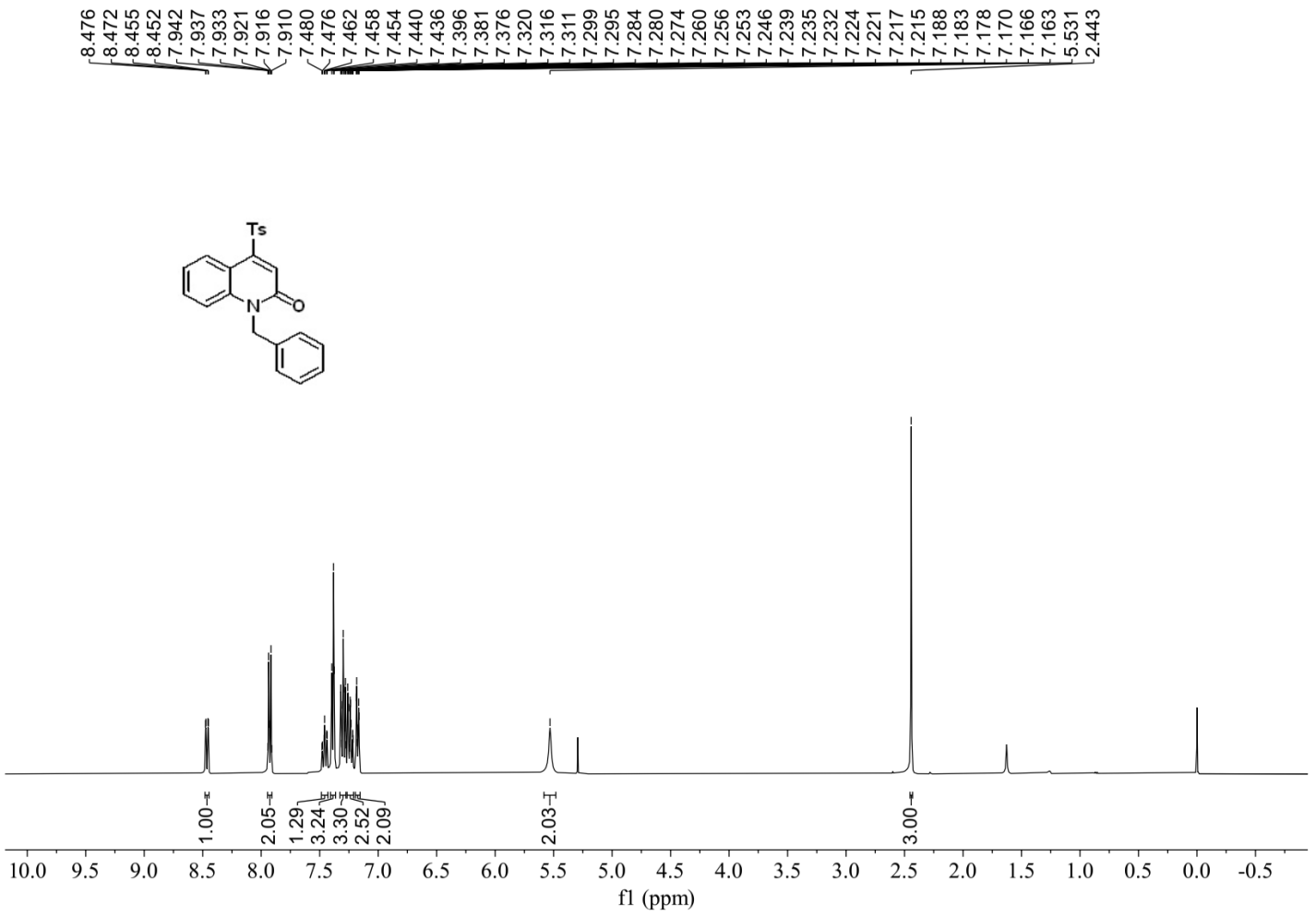
White solid; 38mg, 45% yield; m.p. 195-196℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.48-8.45 (m, 1H), 8.14 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.65-7.58 (m, 3H), 7.53 – 7.47 (m, 1H), 7.46-7.42 (m, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.16-7.07 (m, 5H), 5.53 (s, 2H), 2.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 160.5, 146.50, 140.1, 137.4, 136.7, 135.6, 133.8, 132.6, 132.3, 131.7, 131.5, 129.7, 127.8, 126.5, 126.1, 125.9, 122.9, 116.1, 114.6, 46.5, 21.1. **IR** (KBr, *v*, cm^{-1}): 3081, 1659, 1588, 1449, 1303, 1143, 763, 619. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{18}ClNO_3SNa$ 446.0594; Found 446.0587.

1-(4-methylbenzyl)-4-(thiophen-2-ylsulfonyl)quinolin-2(1*H*)-one (3al)

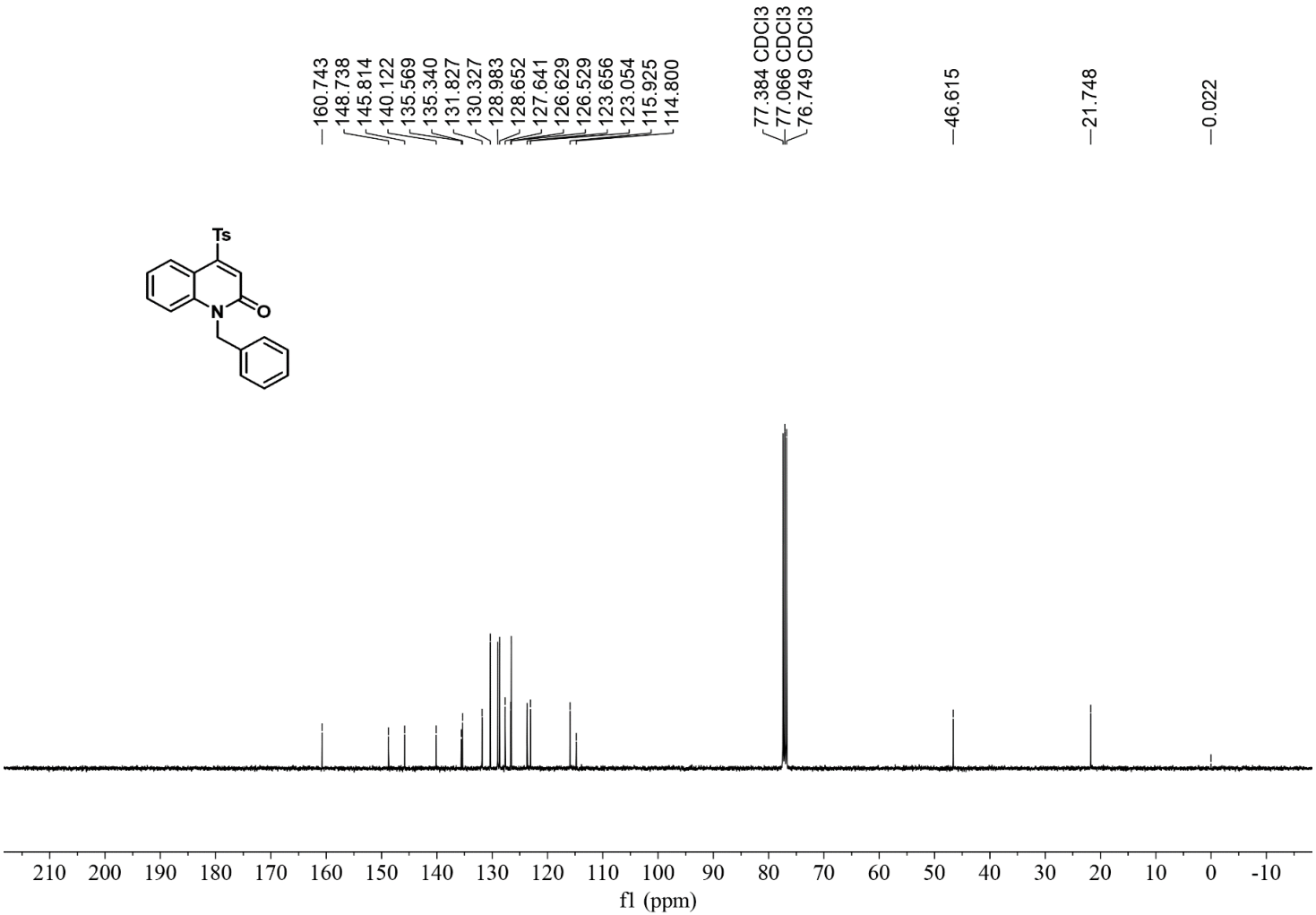


White solid; 38mg, 48% yield; m.p. 184-186℃; **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 8.58 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.88 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.78 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.52-7.46 (m, 2H), 7.36 (d, *J* = 8.8 Hz, 1H), 7.31-7.25 (m, 1H), 7.18 (dd, *J* = 5.2, 4.0 Hz, 1H), 7.13-7.07 (m, 4H), 5.50 (s, 2H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) (δ, ppm): 204.5, 160.7, 148.9, 140.2, 139.8, 137.4, 135.8, 132.3, 131.9, 129.7, 128.3, 126.6, 126.5, 123.7, 123.1, 116.0, 114.6, 46.5, 21.1. **IR** (KBr, *v*, cm^{-1}): 3098, 1656, 1316, 1144, 748, 623. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{17}NO_3S_2Na$ 418.0548; Found 418.0544.

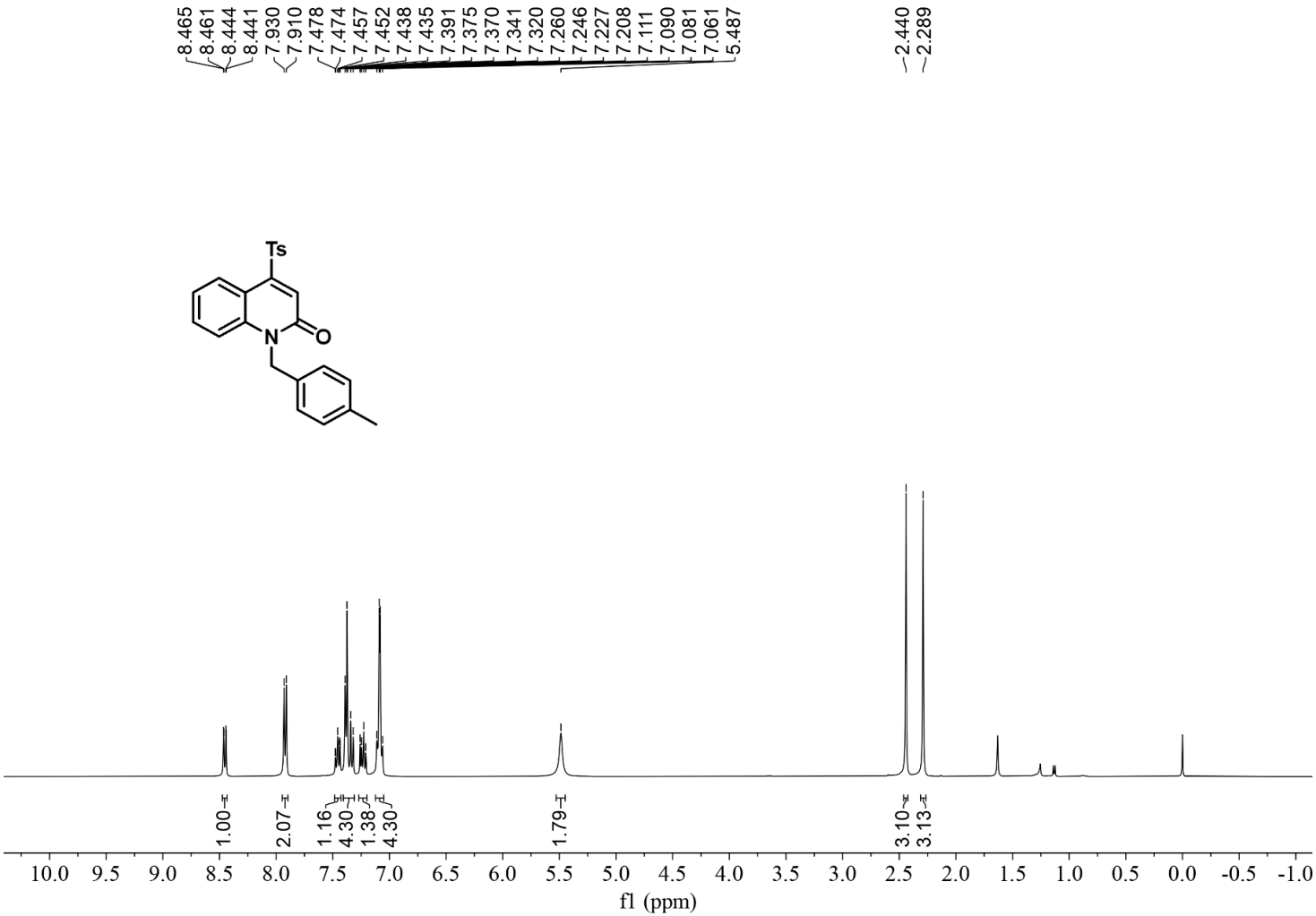
Copies of ^{1}H and ^{13}C NMR of Compounds 3, 4 and 1o



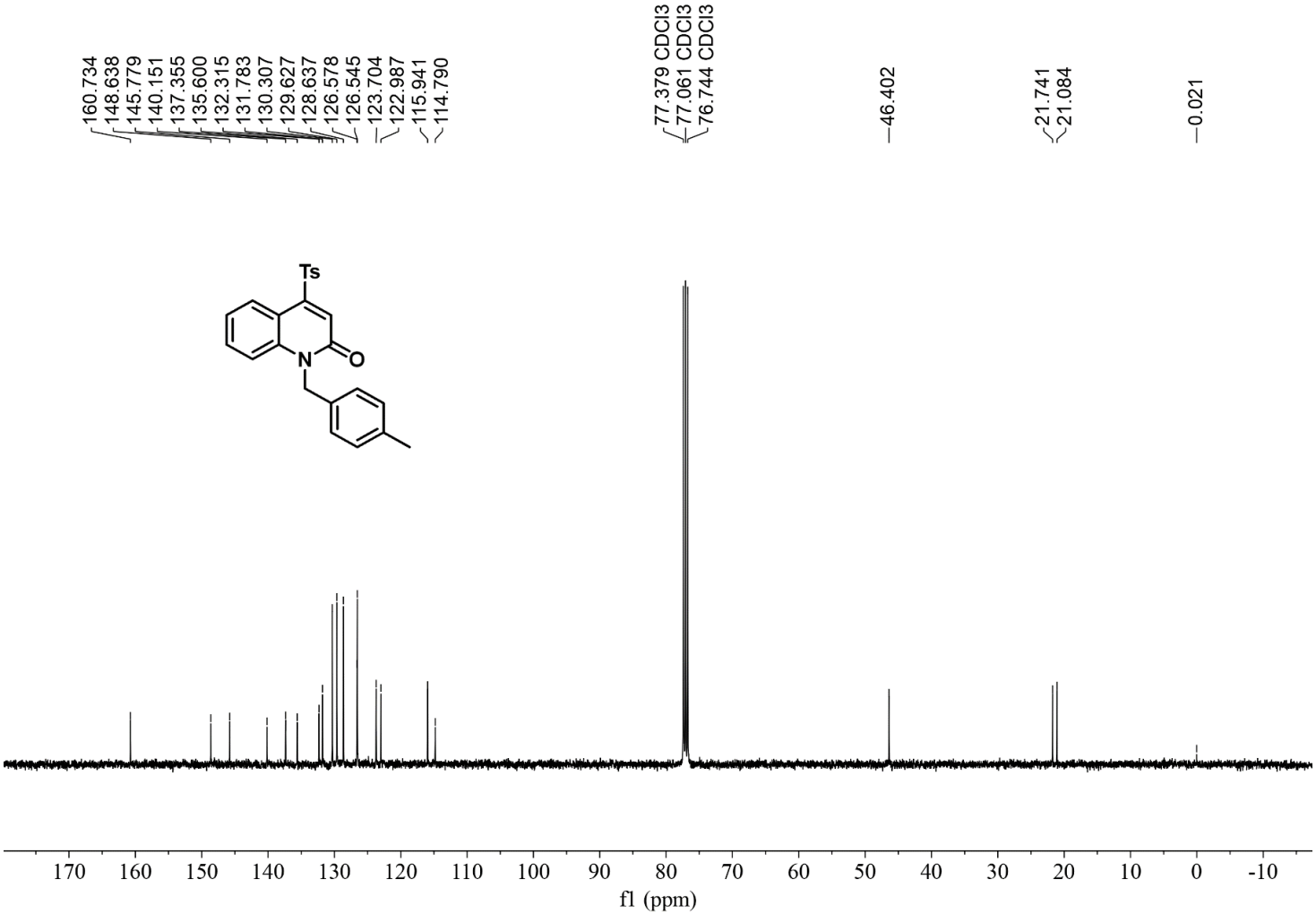
^{1}H NMR Spectrum of Compound 3a



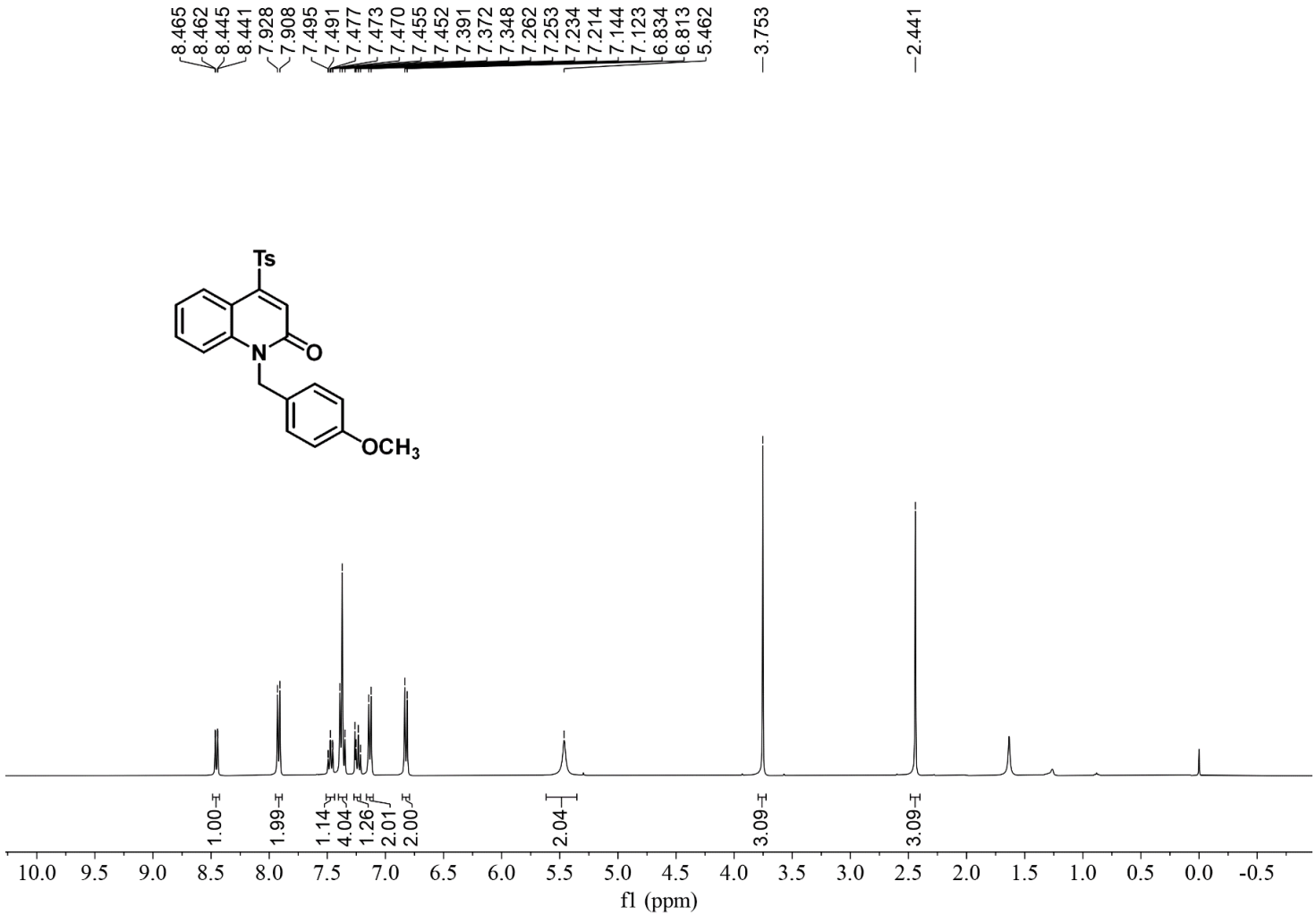
^{13}C NMR Spectrum of Compound 3a



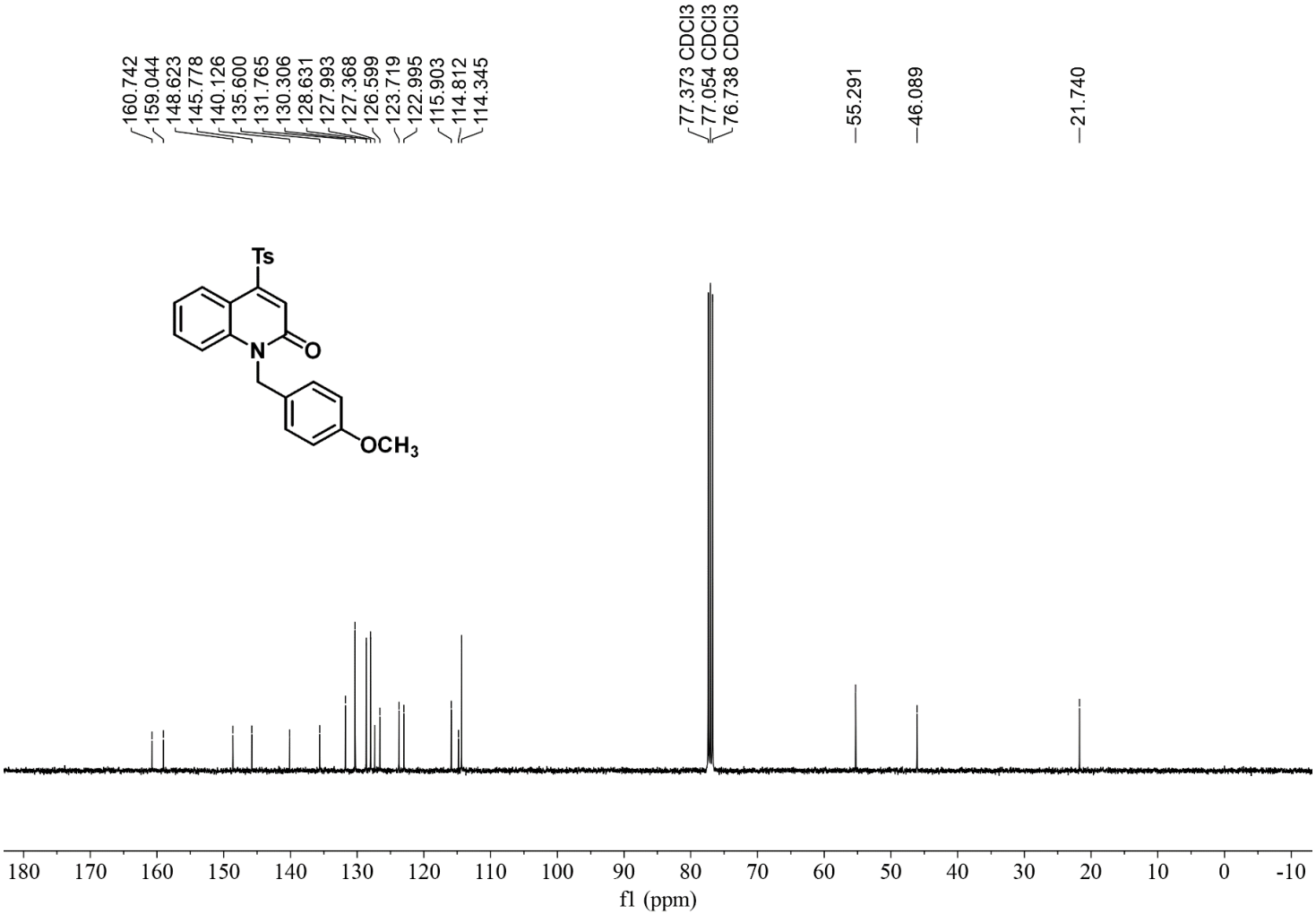
^{1}H NMR Spectrum of Compound 3e



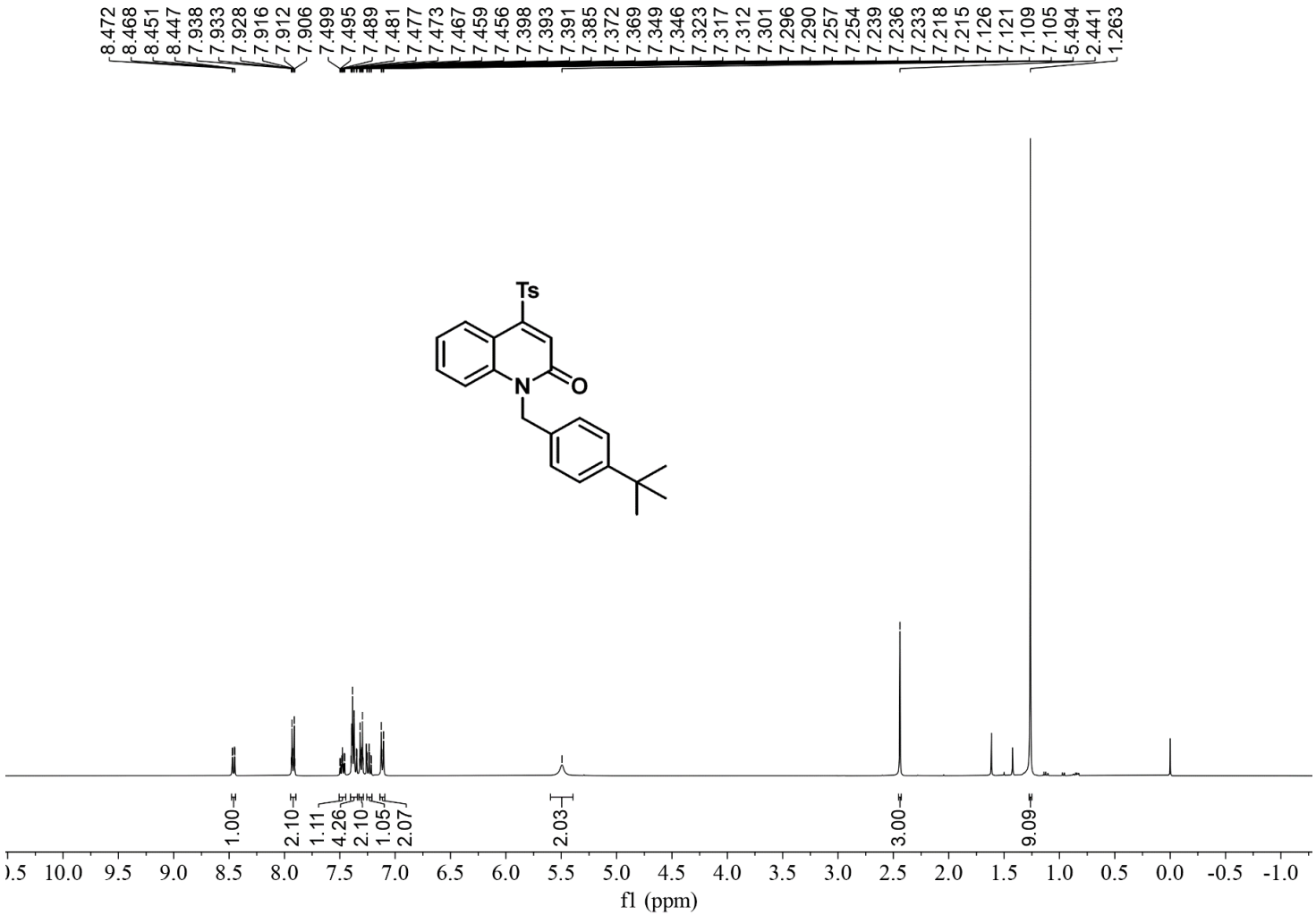
^{13}C NMR Spectrum of Compound 3e



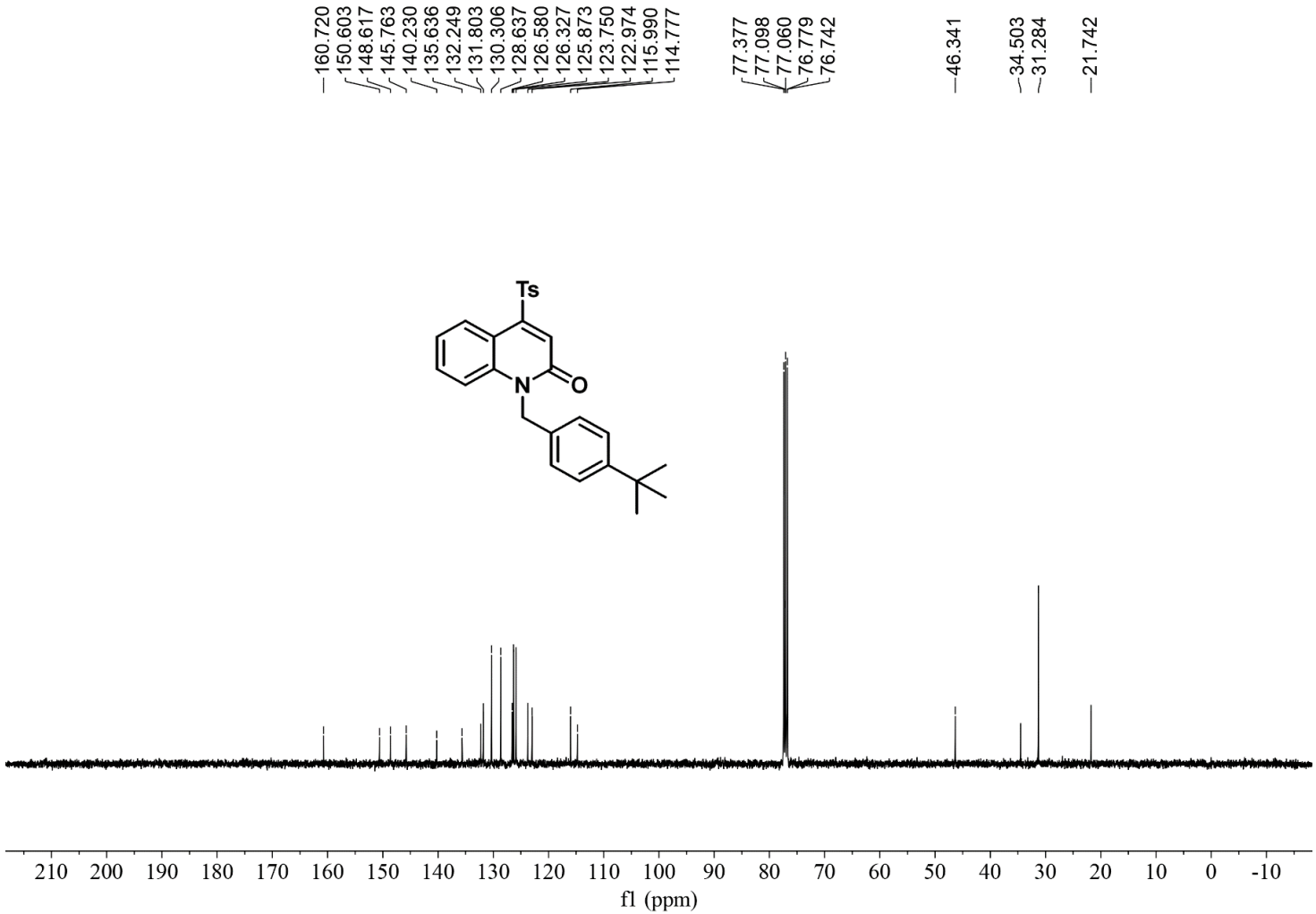
^{1}H NMR Spectrum of Compound 3f



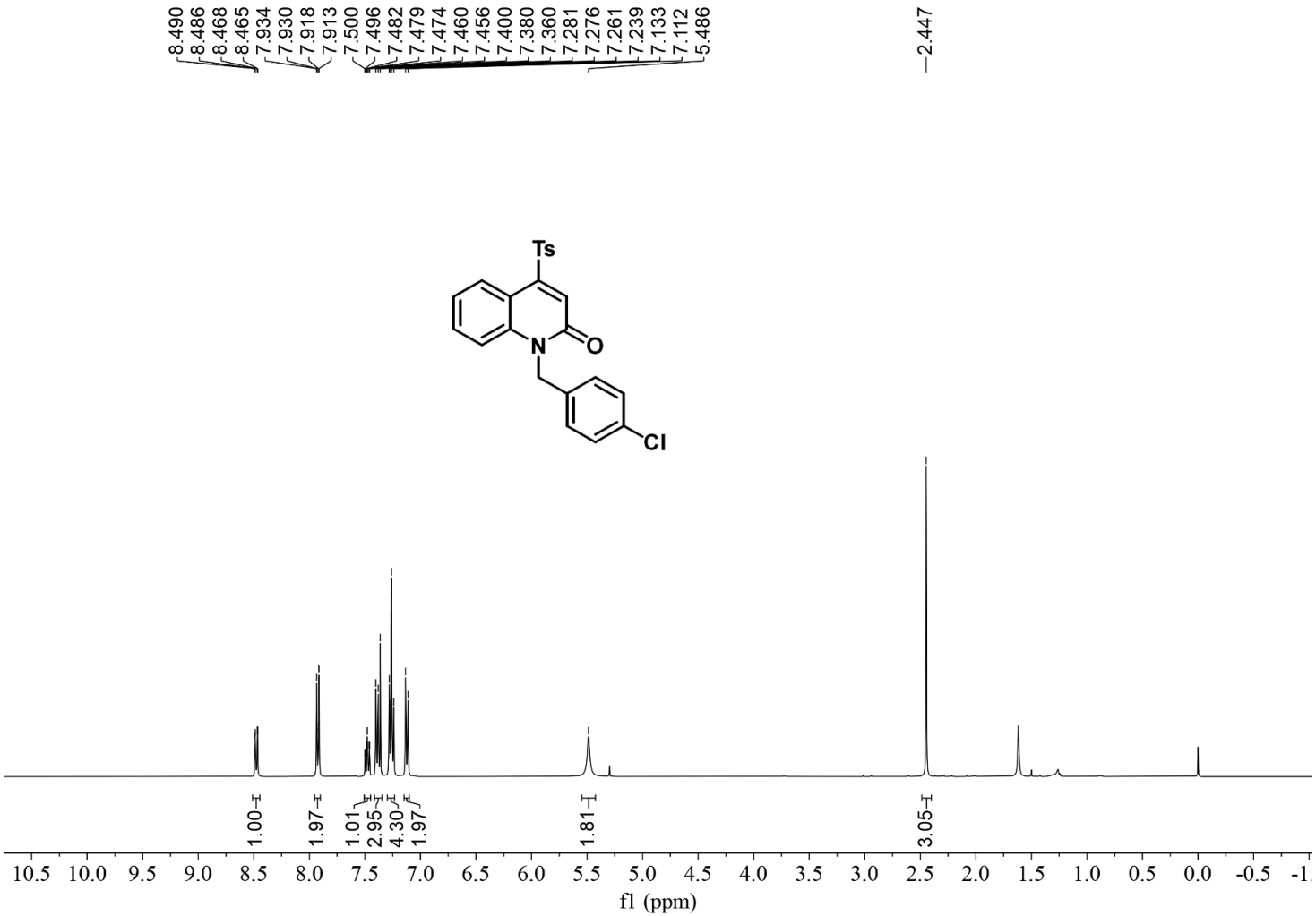
^{13}C NMR Spectrum of Compound 3f



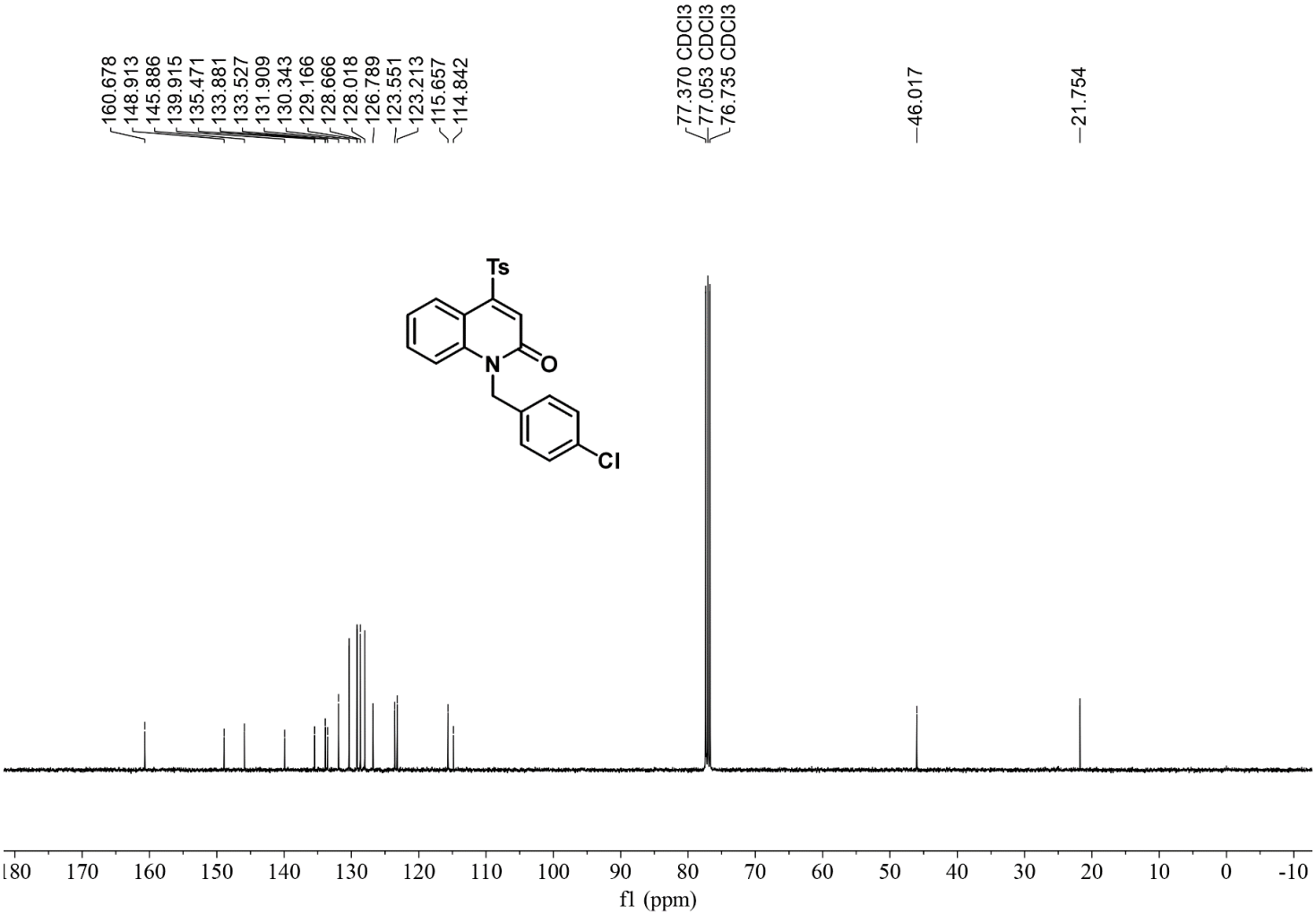
^{1}H NMR Spectrum of Compound 3g



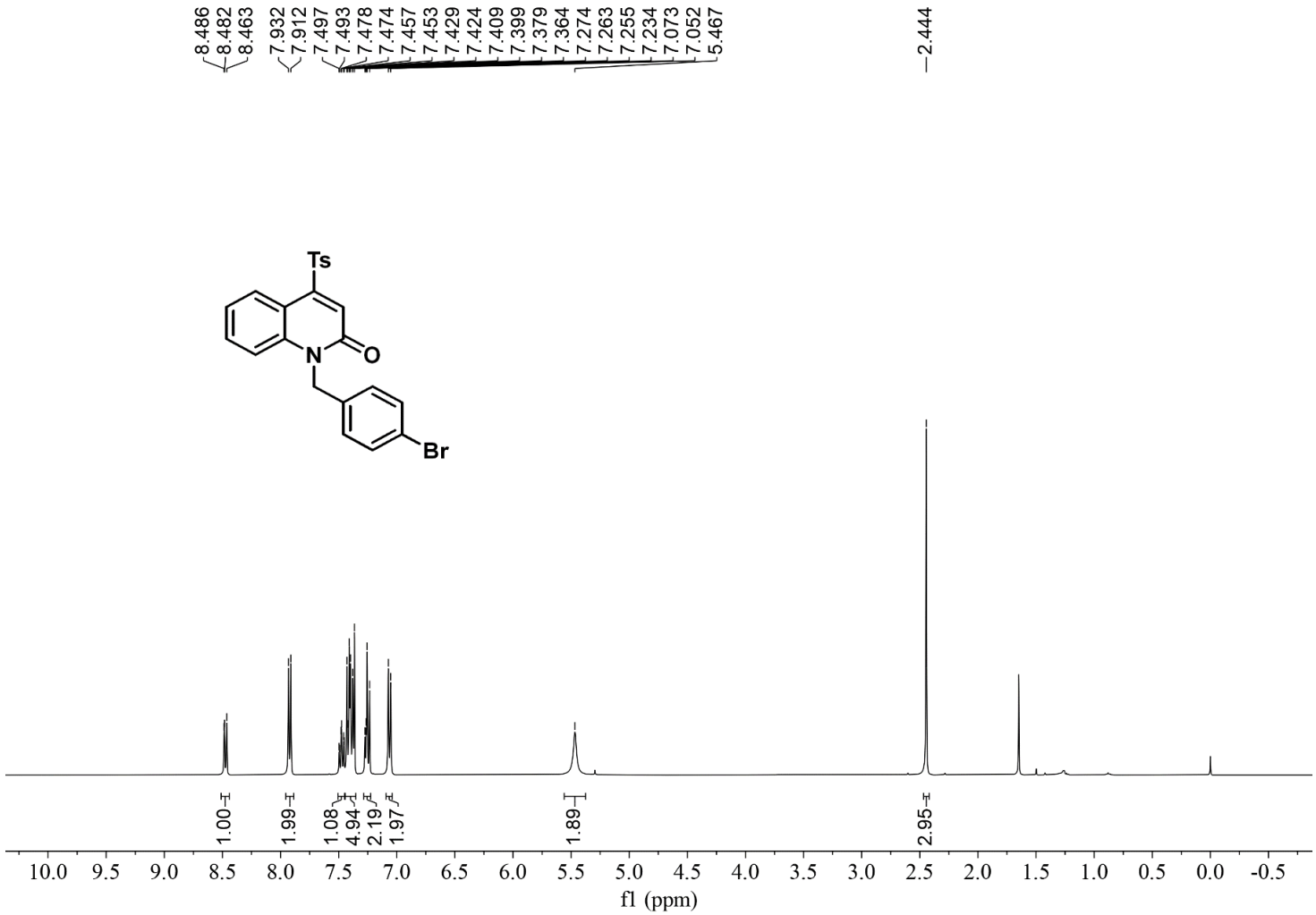
^{13}C NMR Spectrum of Compound 3g



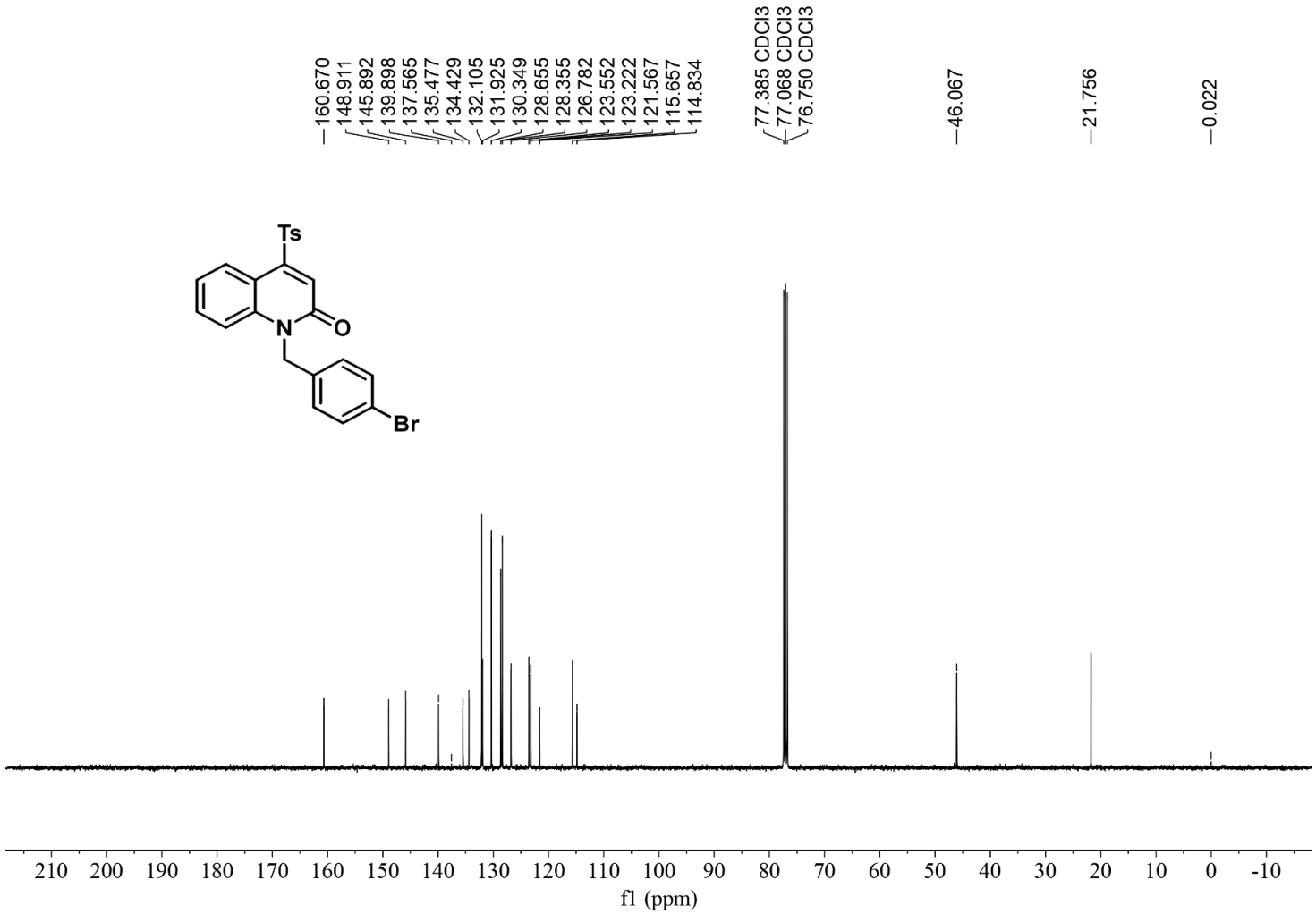
^{1}H NMR Spectrum of Compound 3h



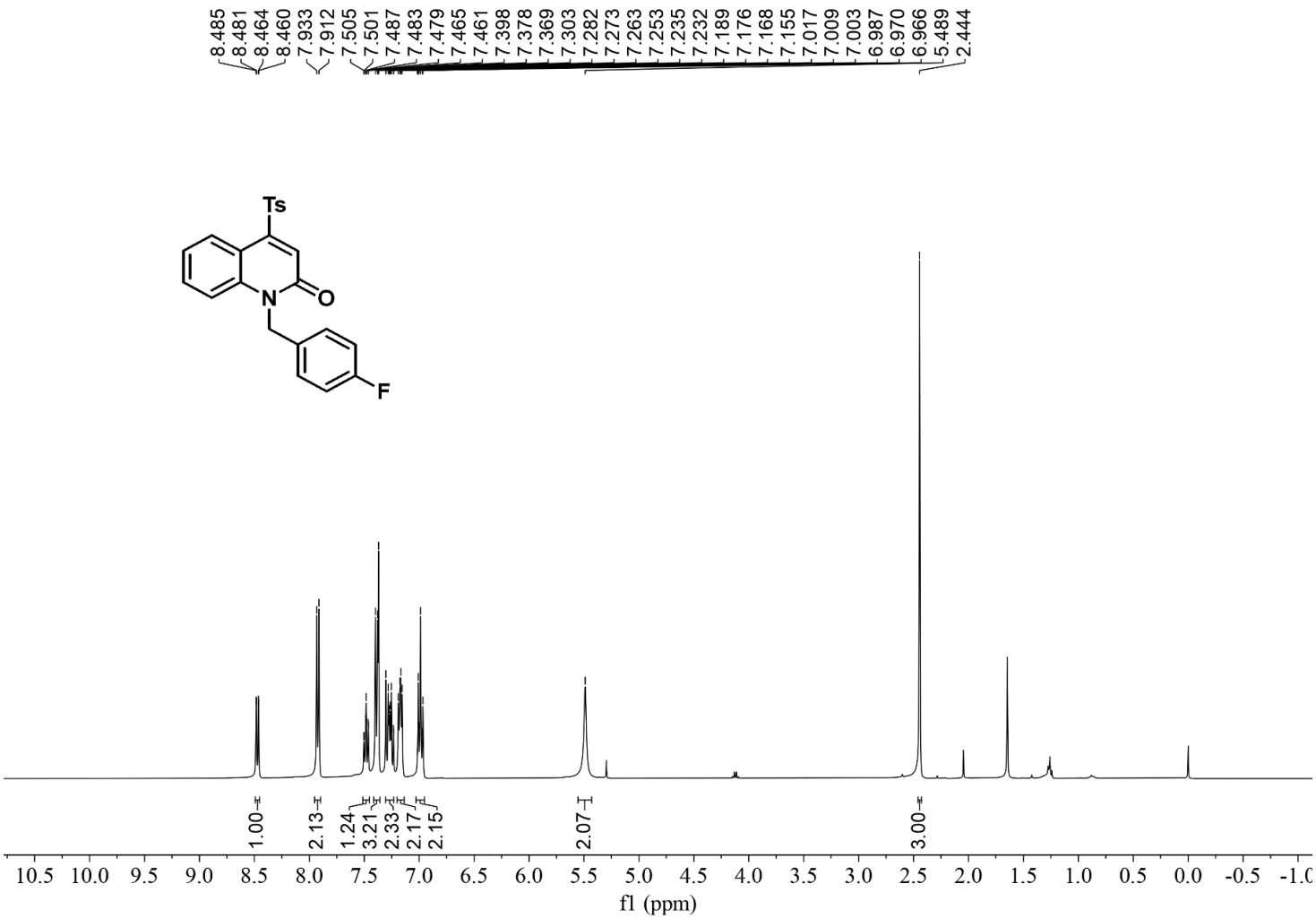
^{13}C NMR Spectrum of Compound 3h



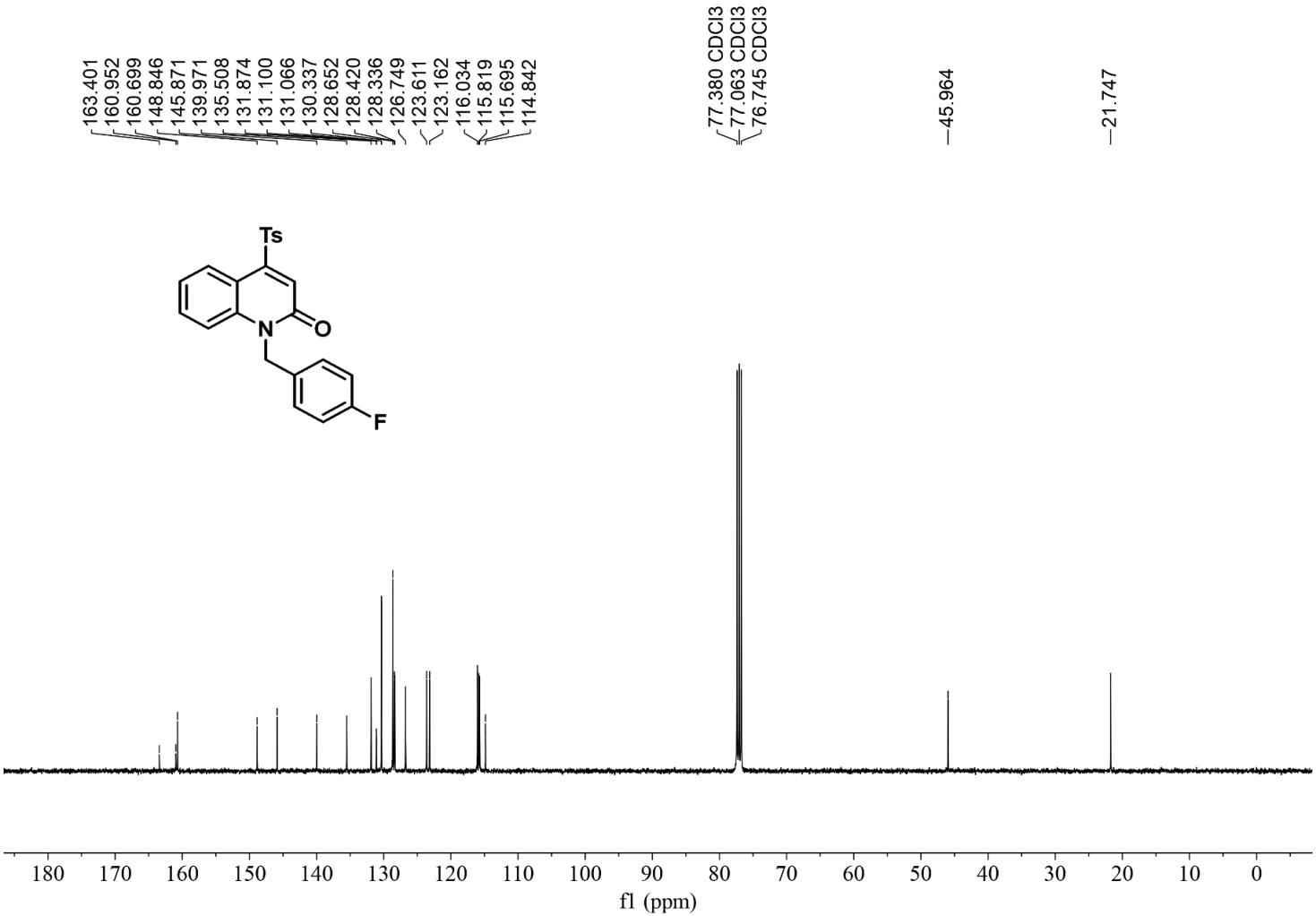
^{1}H NMR Spectrum of Compound 3i



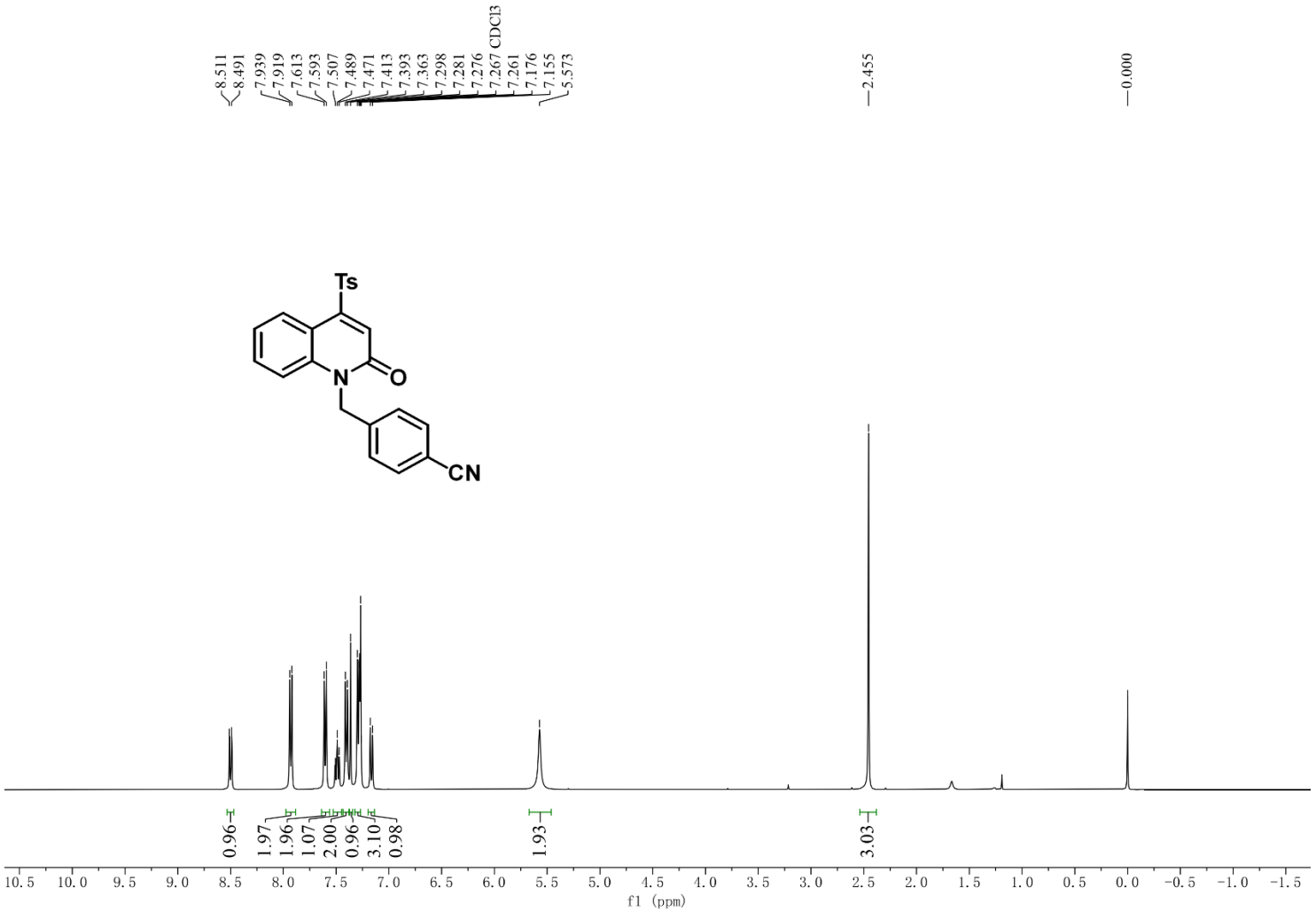
^{13}C NMR Spectrum of Compound 3i



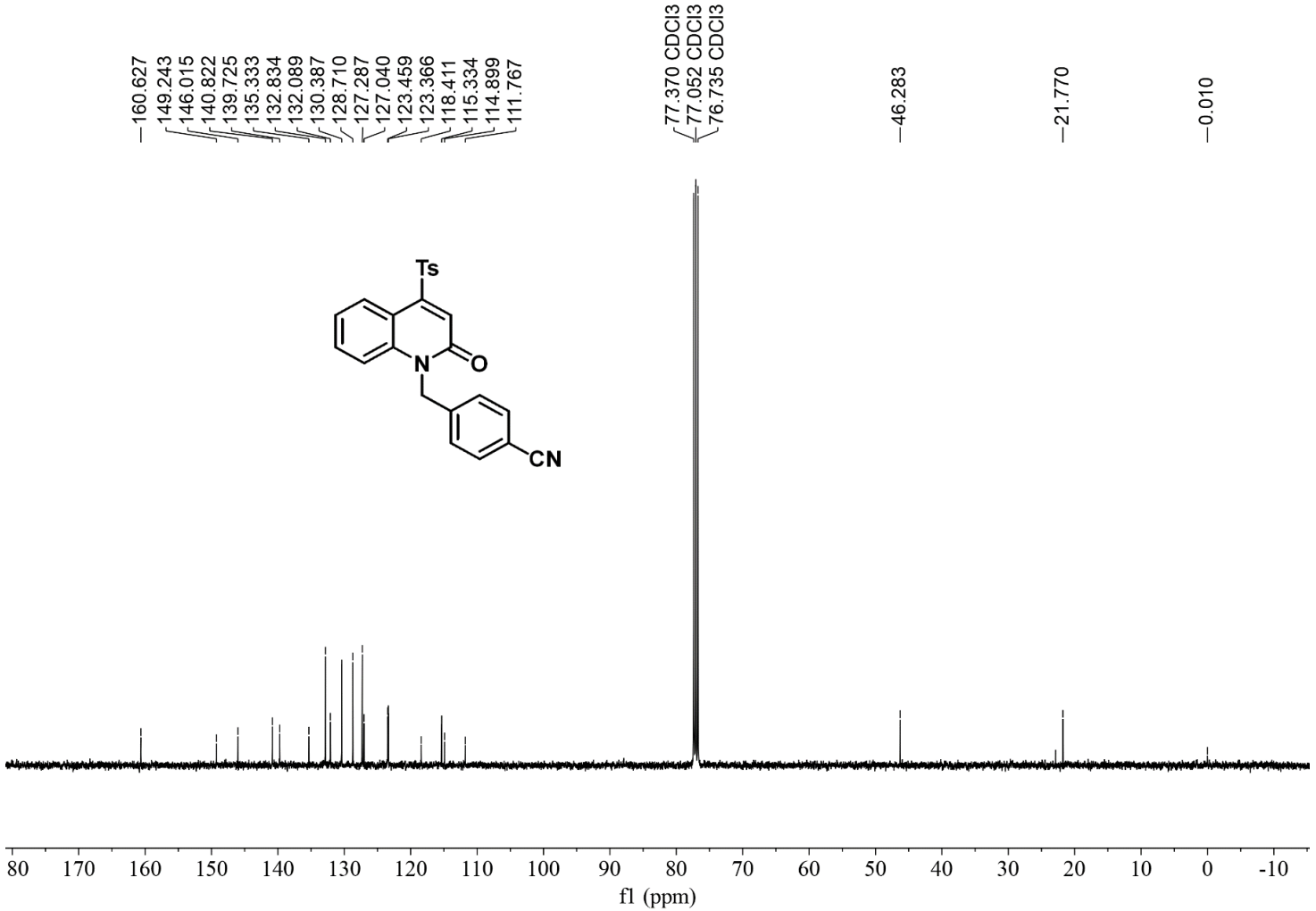
^{1}H NMR Spectrum of Compound 3j



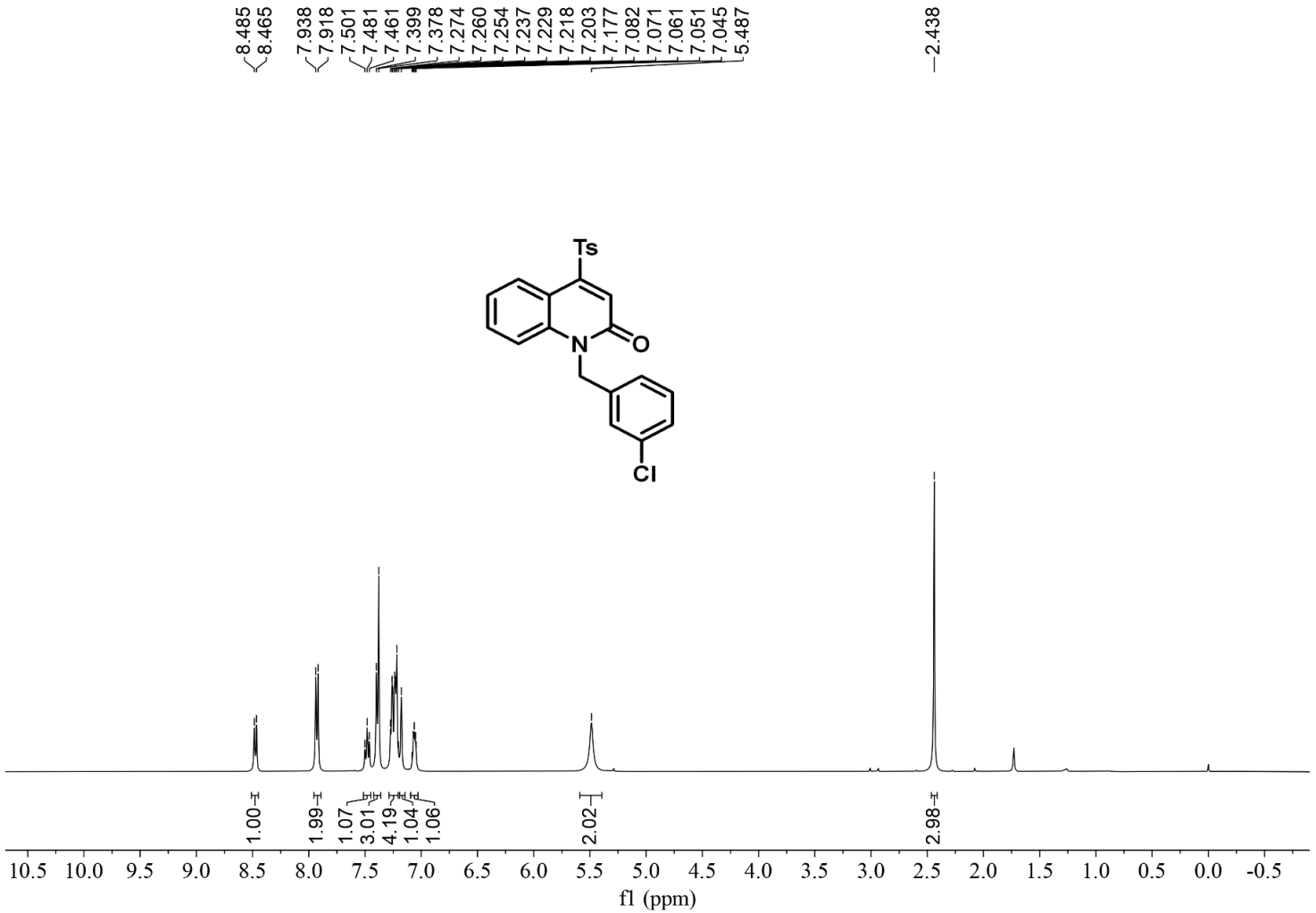
^{13}C NMR Spectrum of Compound 3j



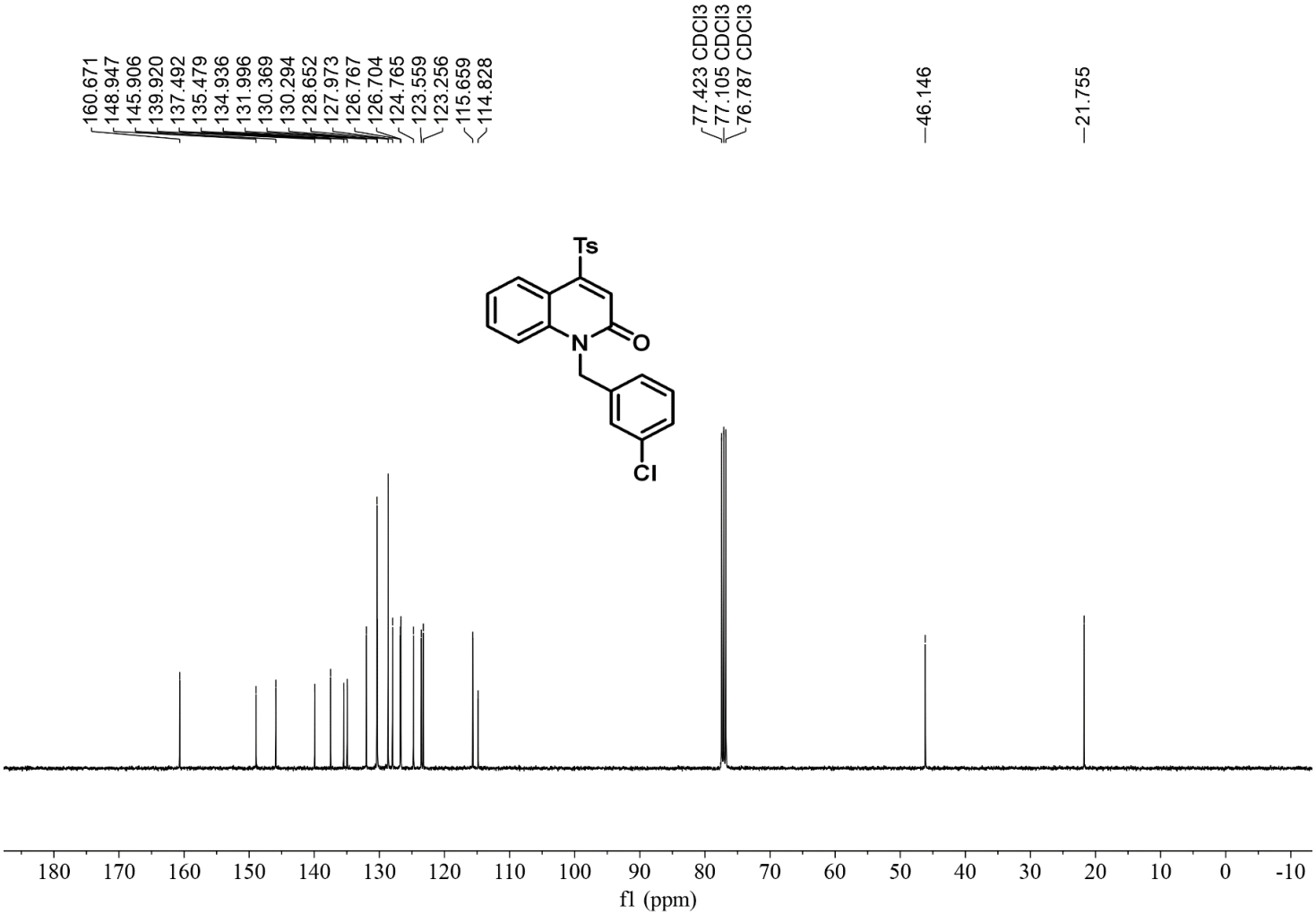
^{1}H NMR Spectrum of Compound 3k



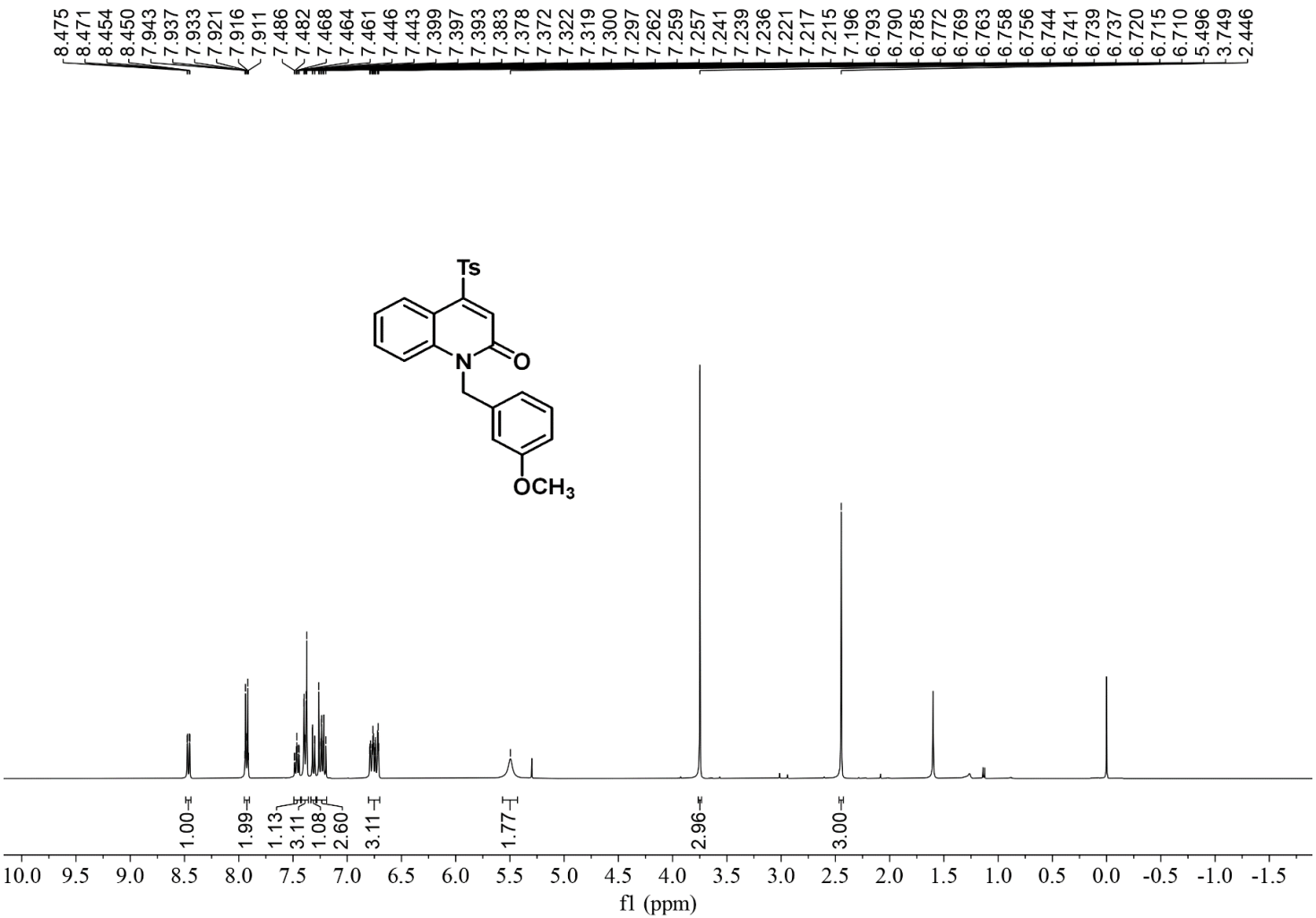
^{13}C NMR Spectrum of Compound 3k



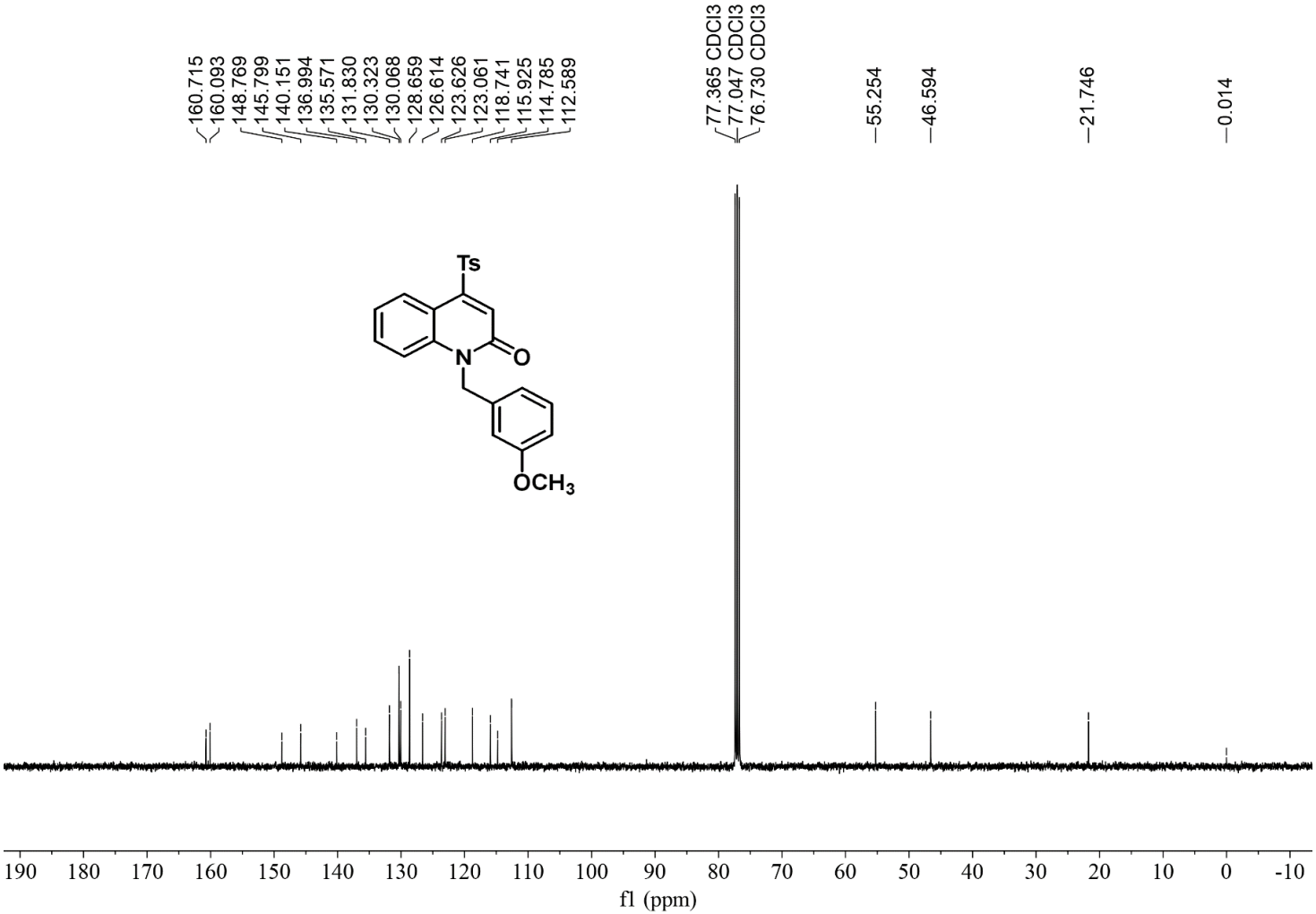
^{1}H NMR Spectrum of Compound 3l



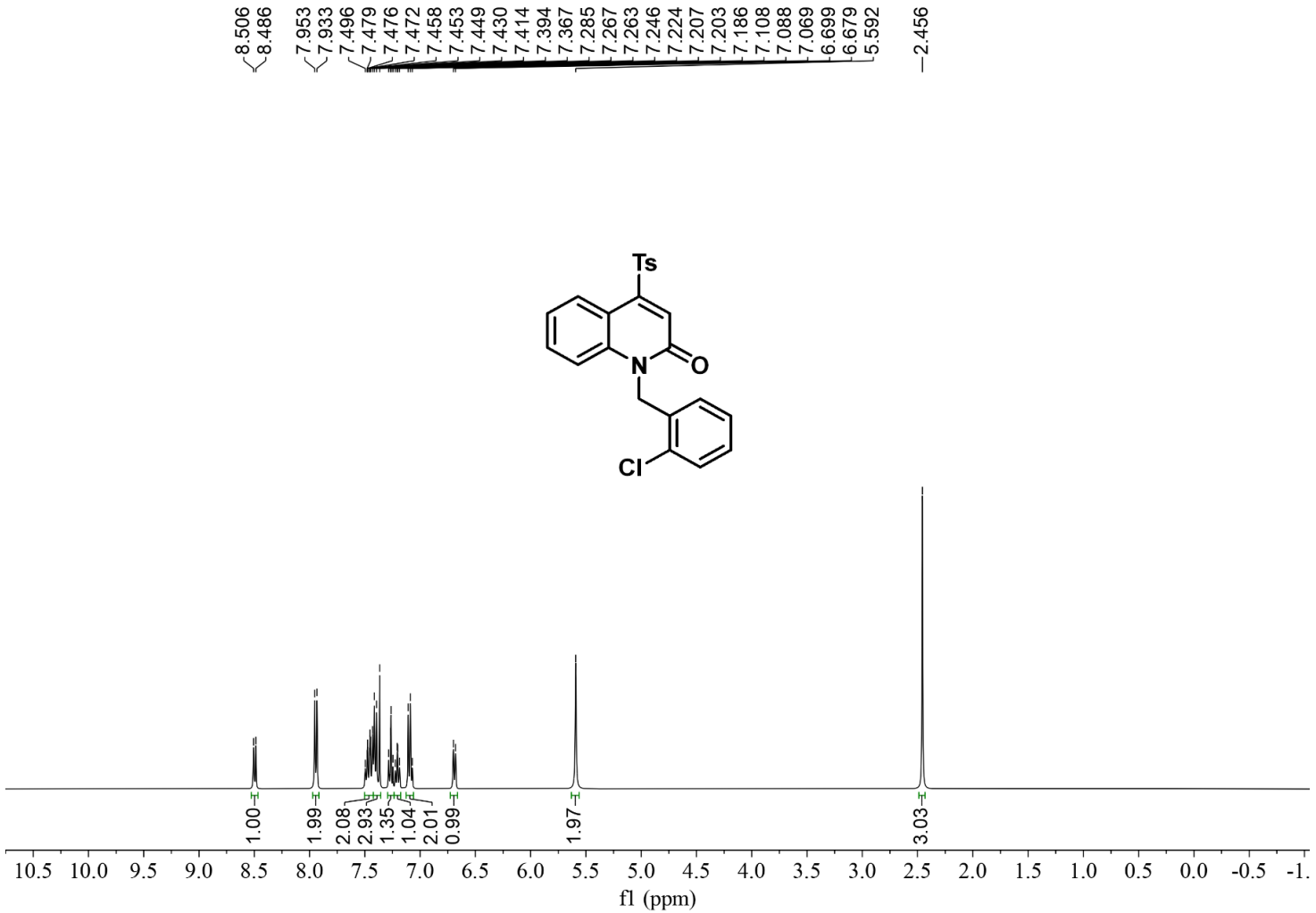
^{13}C NMR Spectrum of Compound 3l



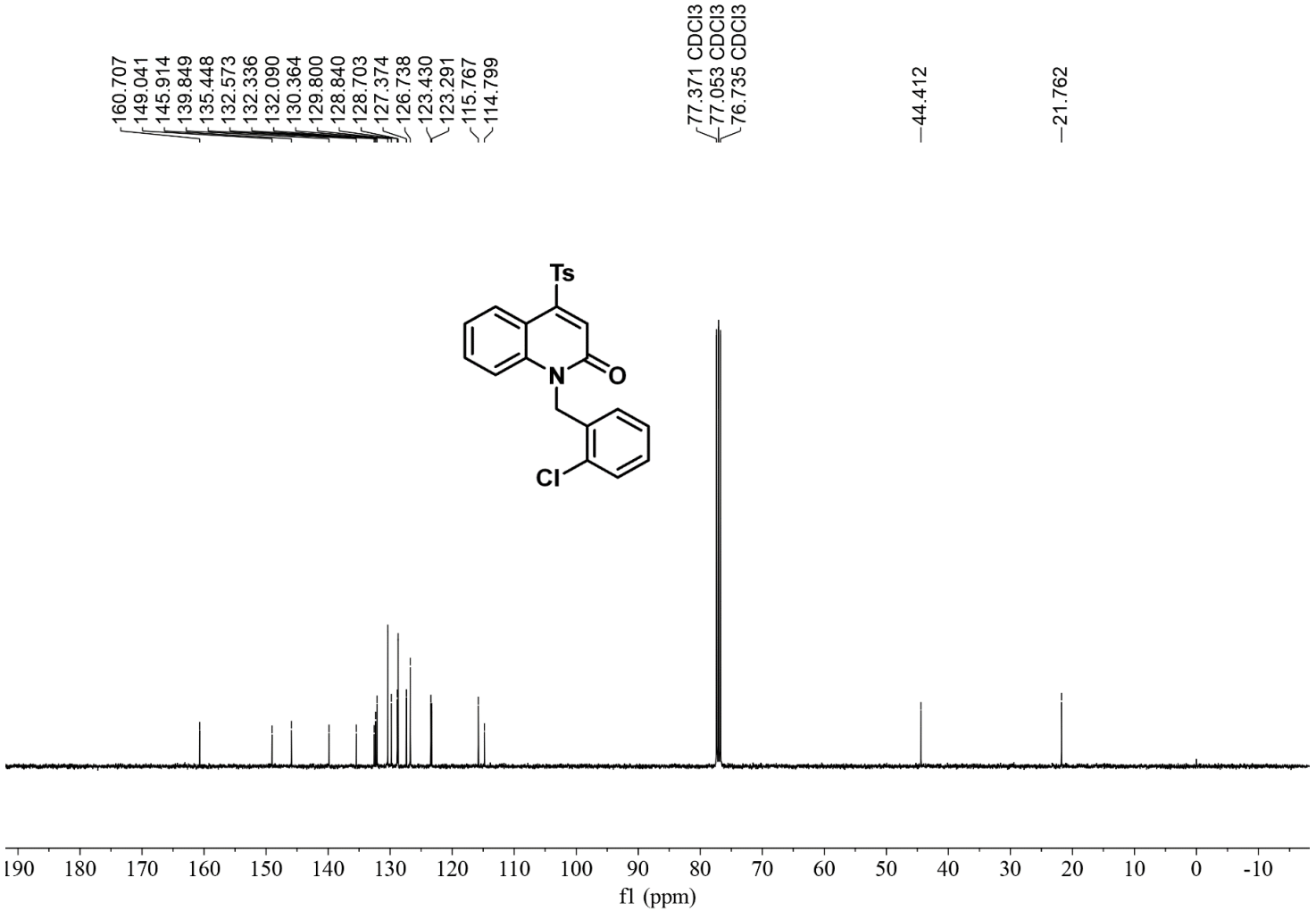
^{1}H NMR Spectrum of Compound 3m



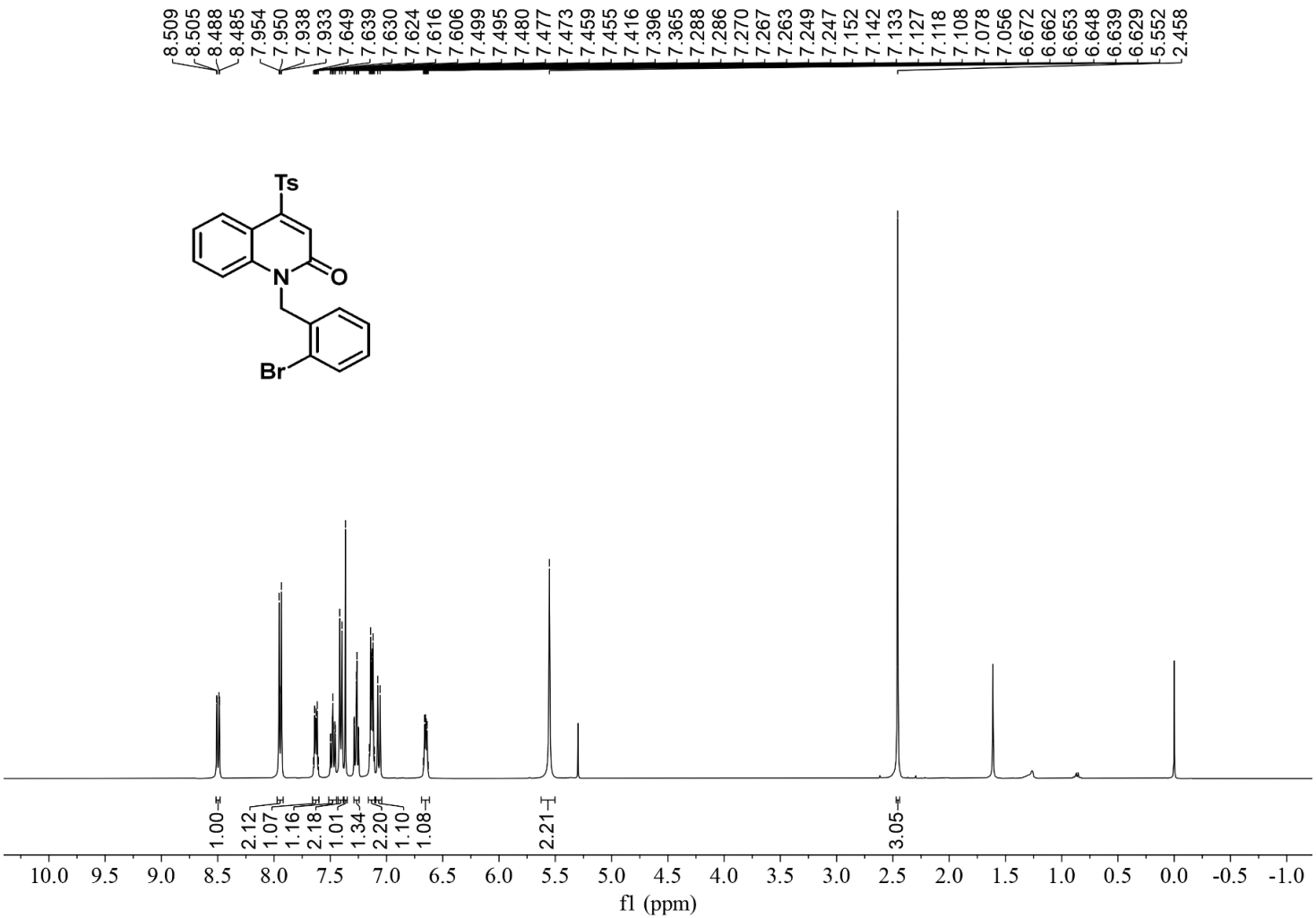
^{13}C NMR Spectrum of Compound 3m



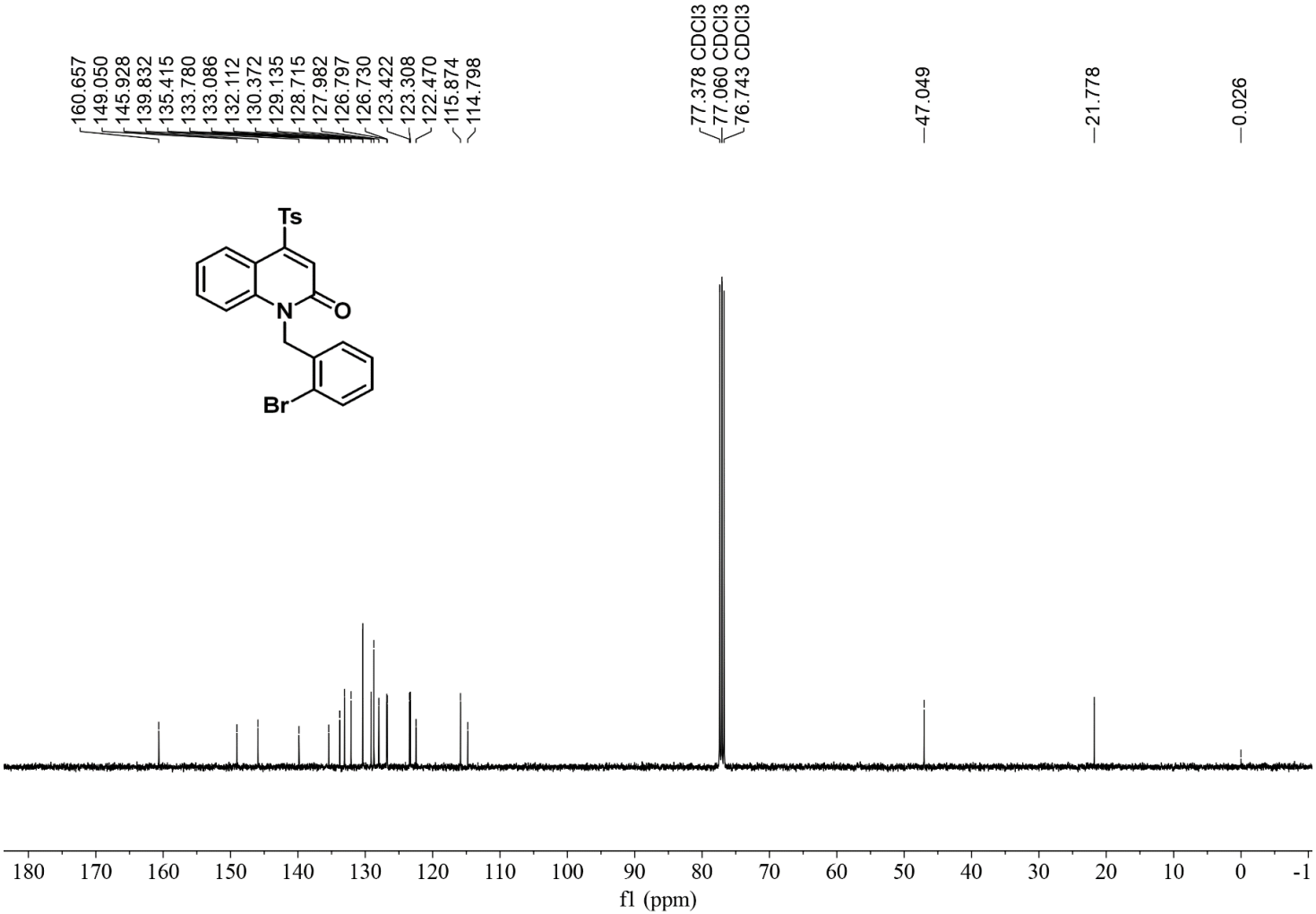
^{1}H NMR Spectrum of Compound 3n



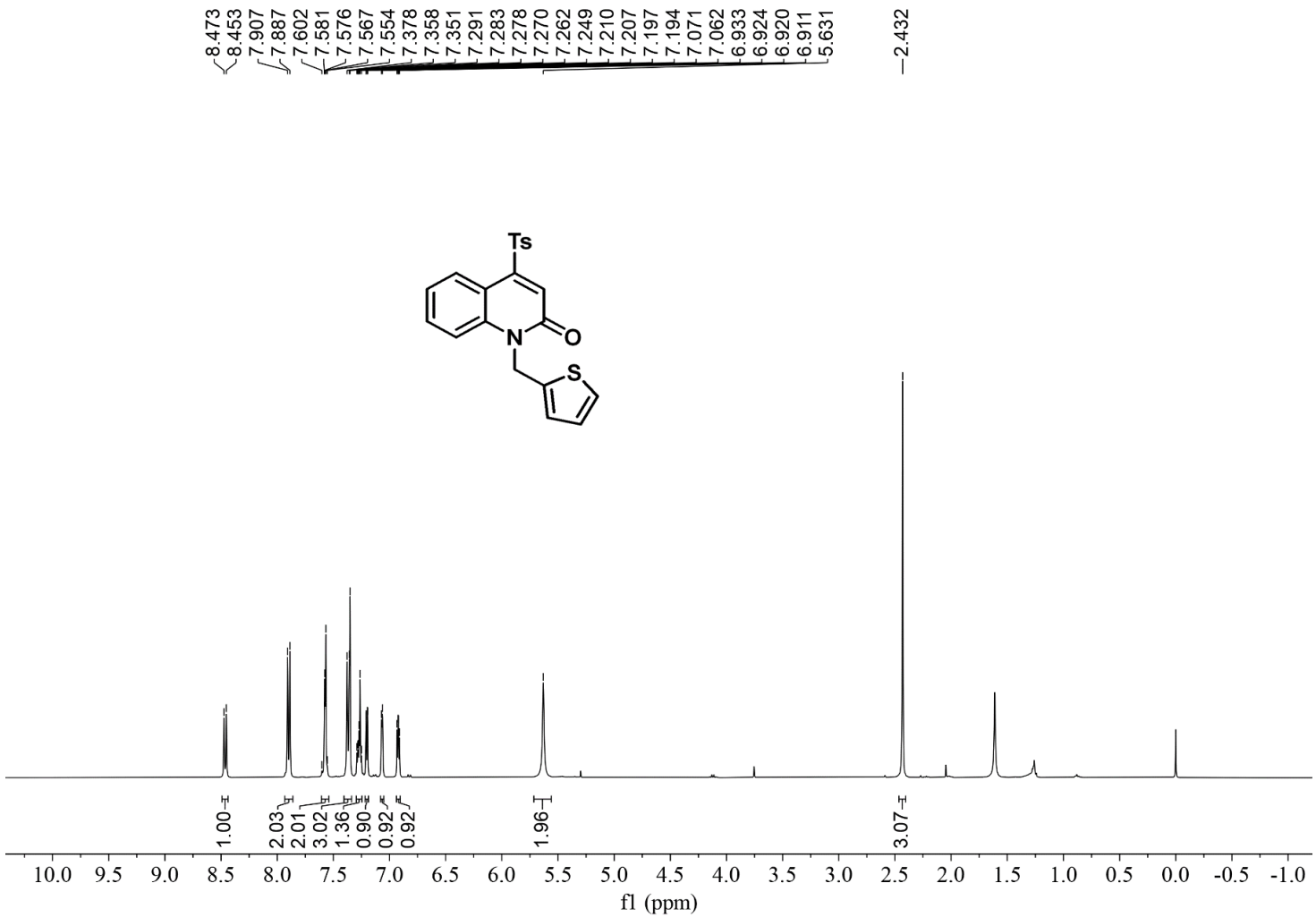
^{13}C NMR Spectrum of Compound 3n



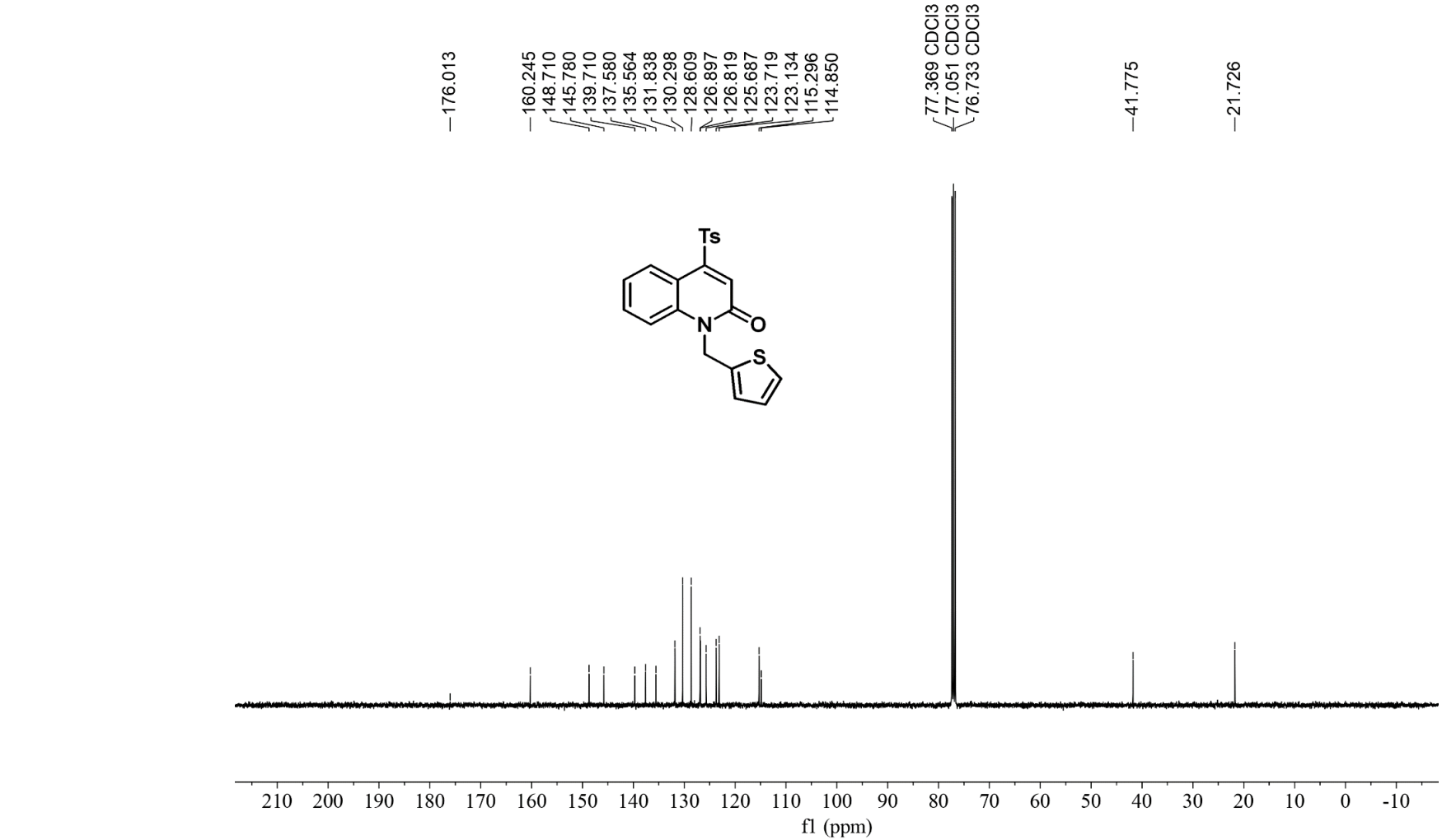
^{1}H NMR Spectrum of Compound 3o



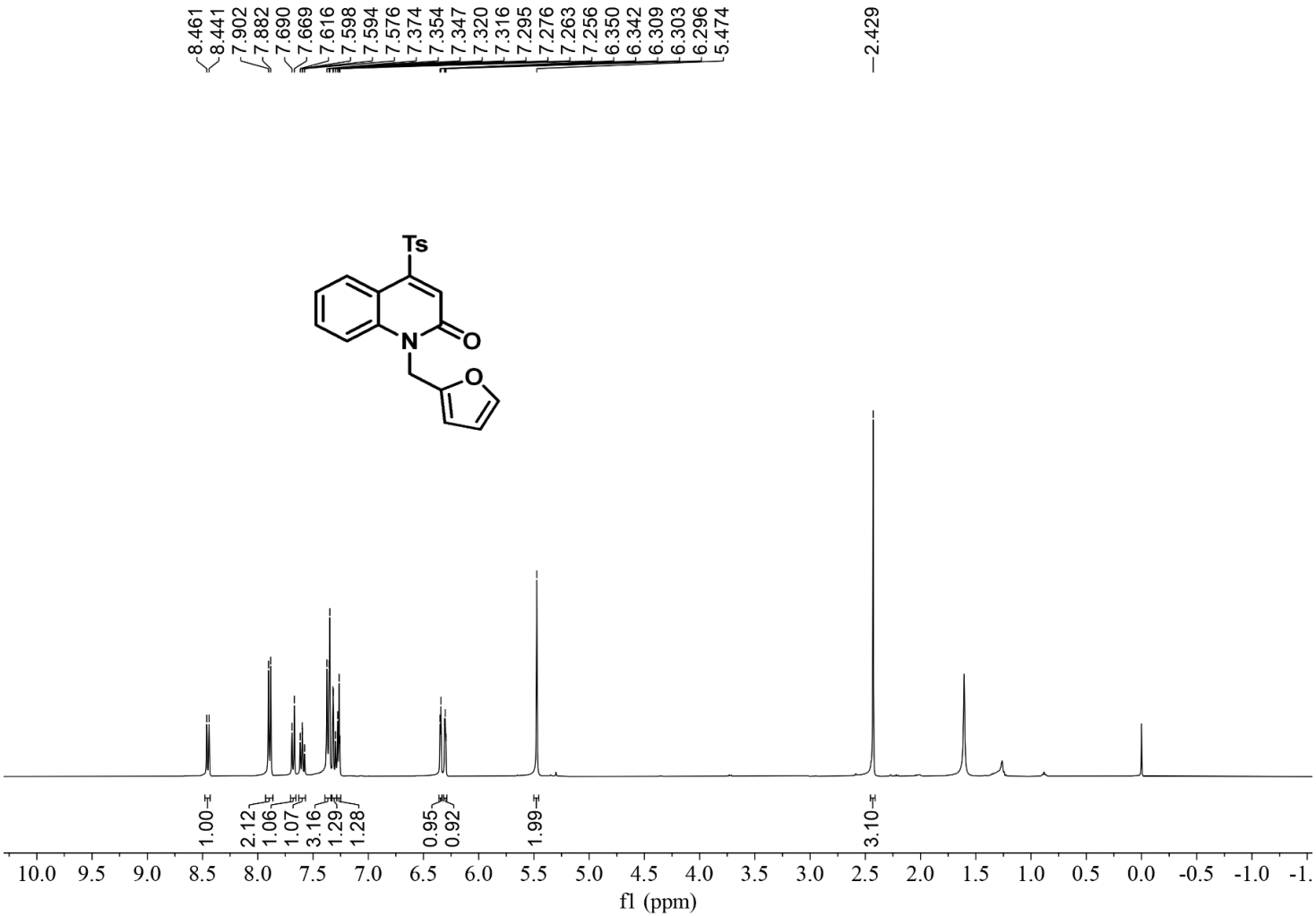
^{13}C NMR Spectrum of Compound 3o



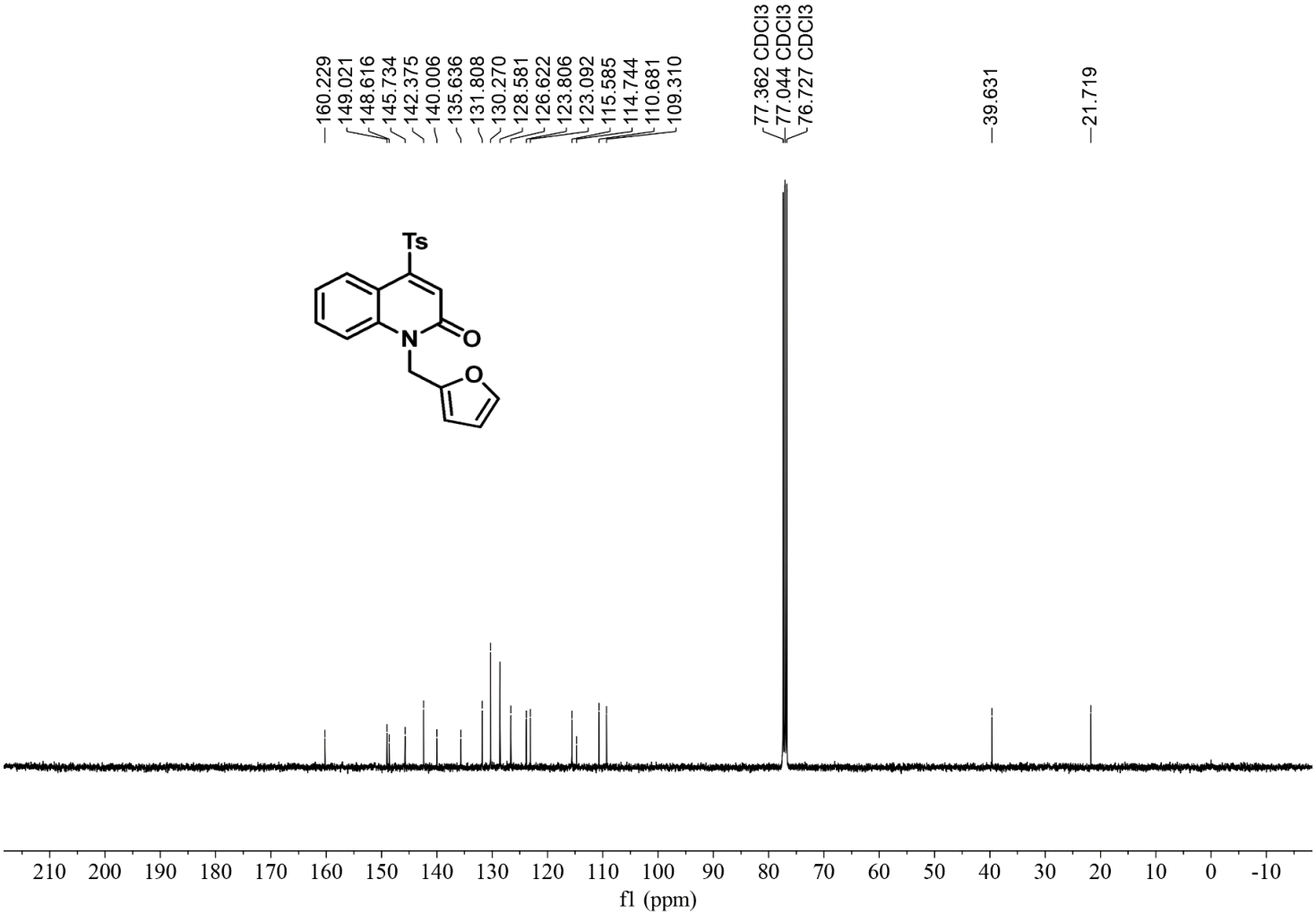
^{1}H NMR Spectrum of Compound 3p



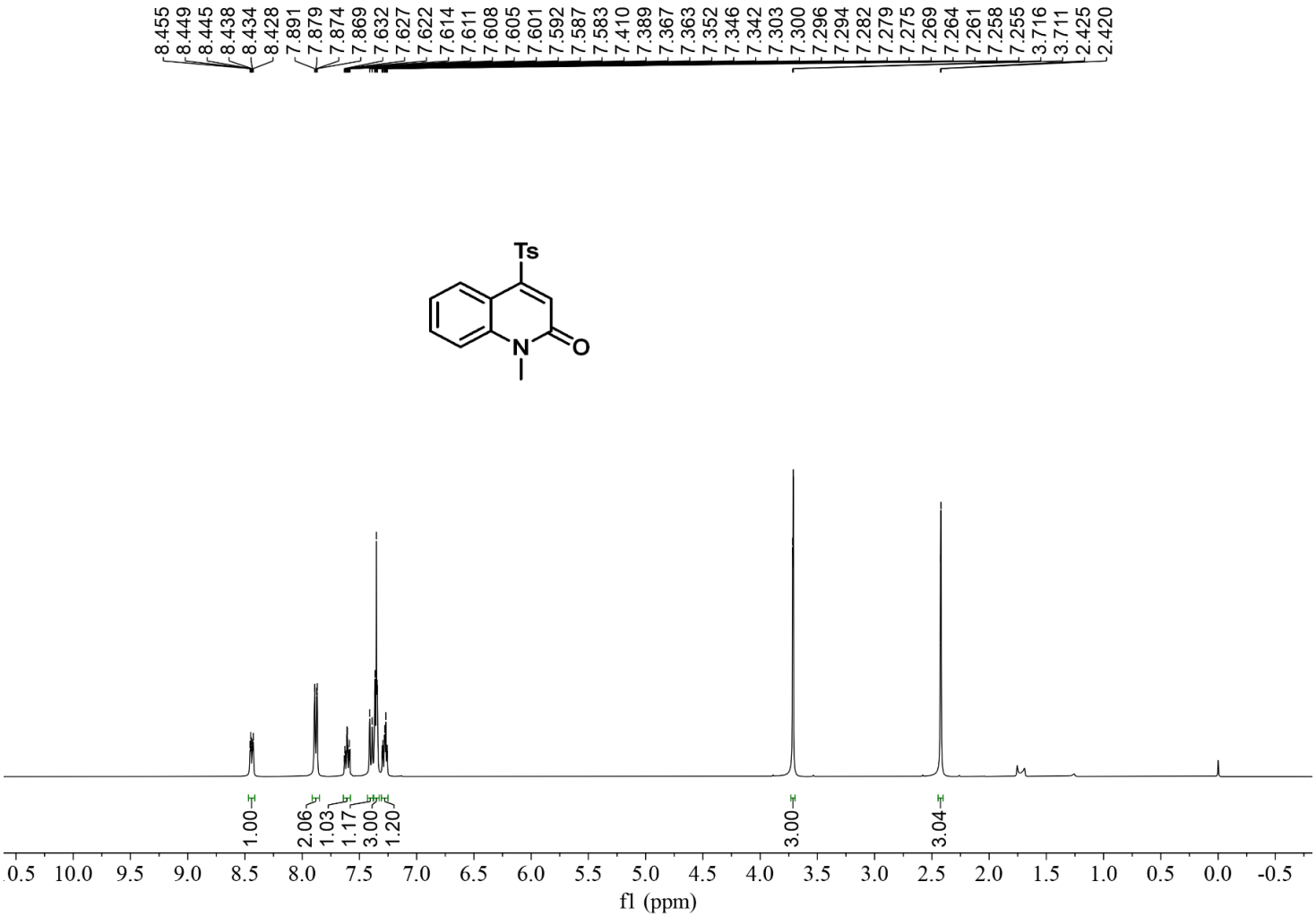
^{13}C NMR Spectrum of Compound 3p



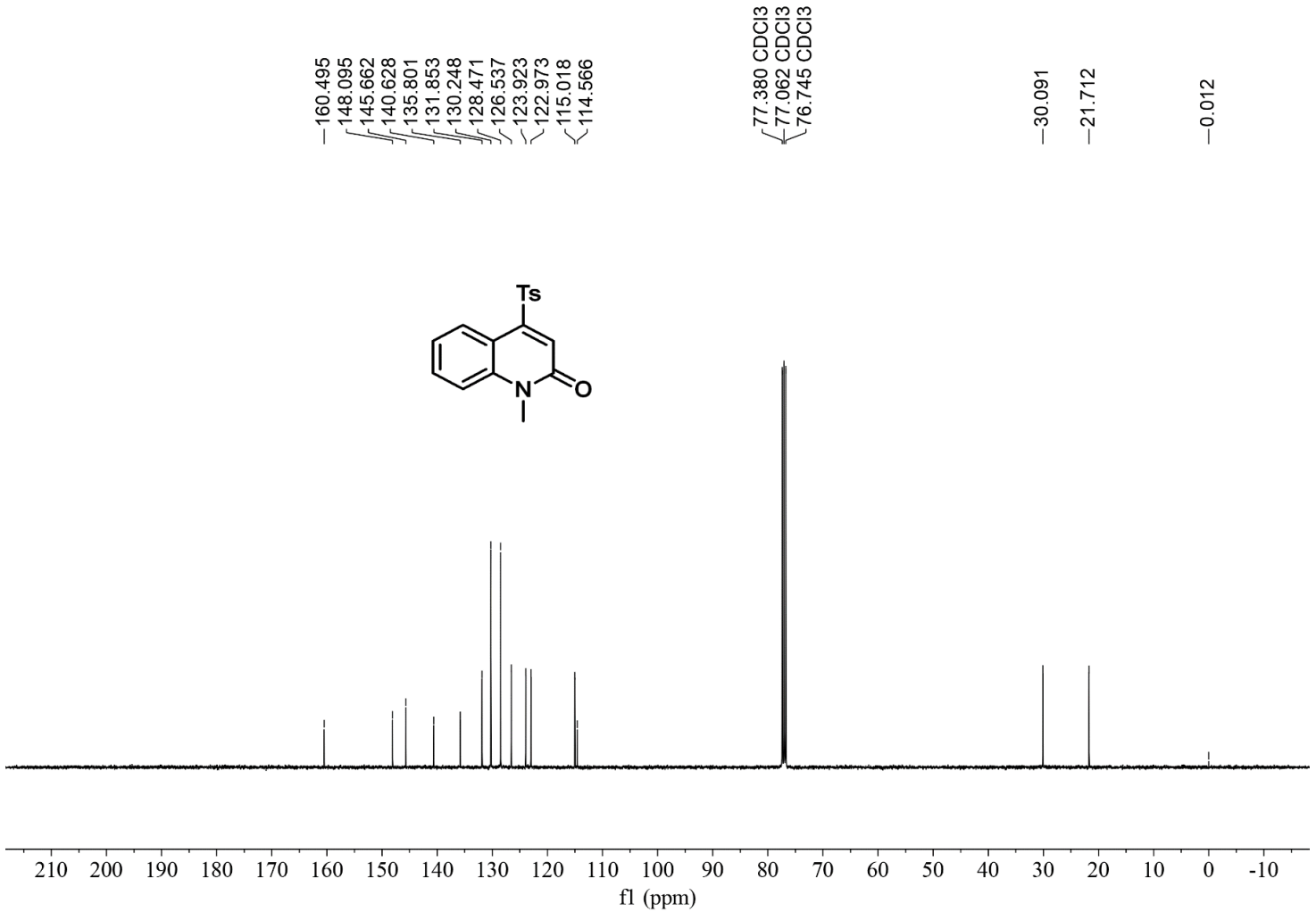
^{1}H NMR Spectrum of Compound 3q



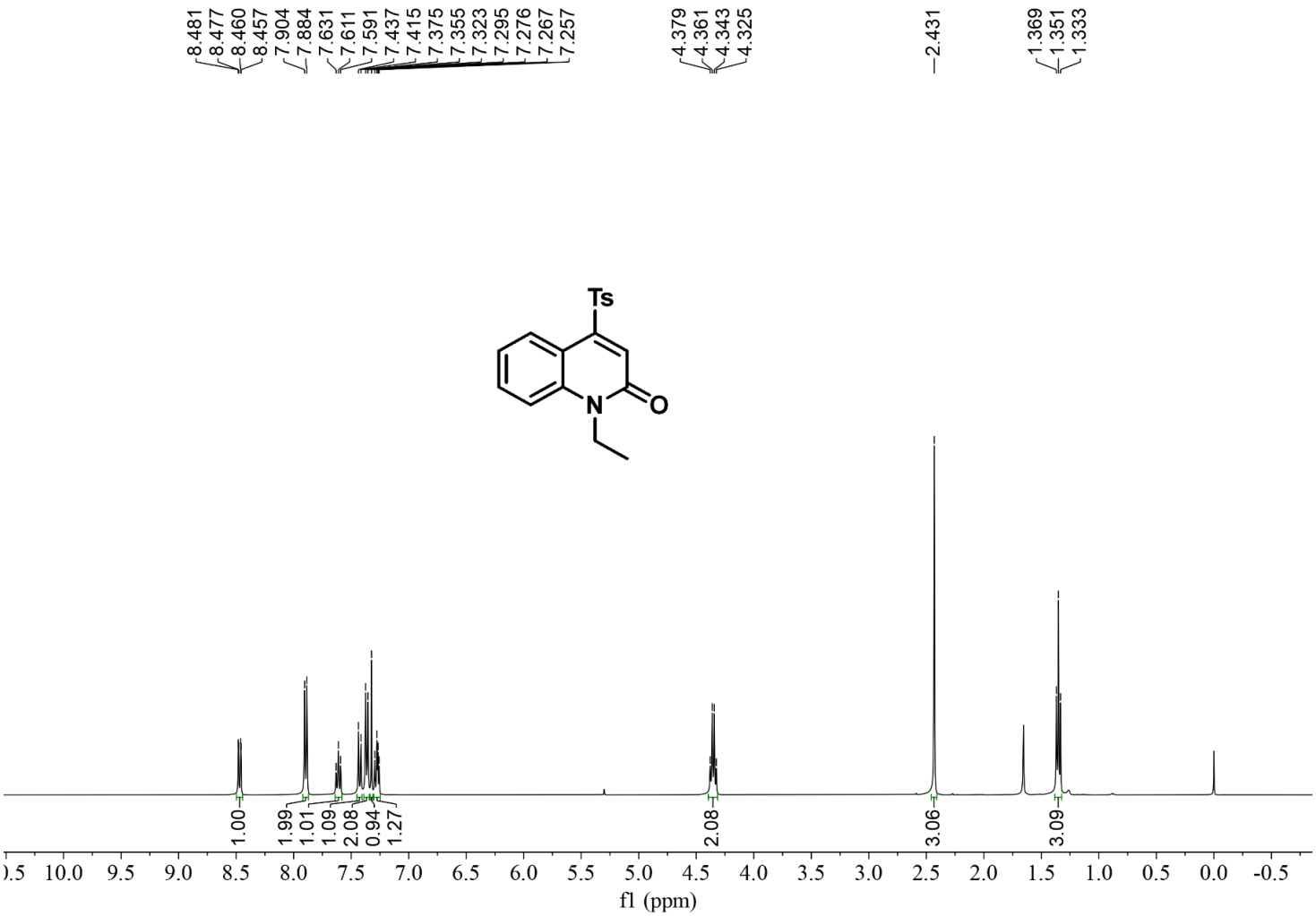
^{13}C NMR Spectrum of Compound 3q



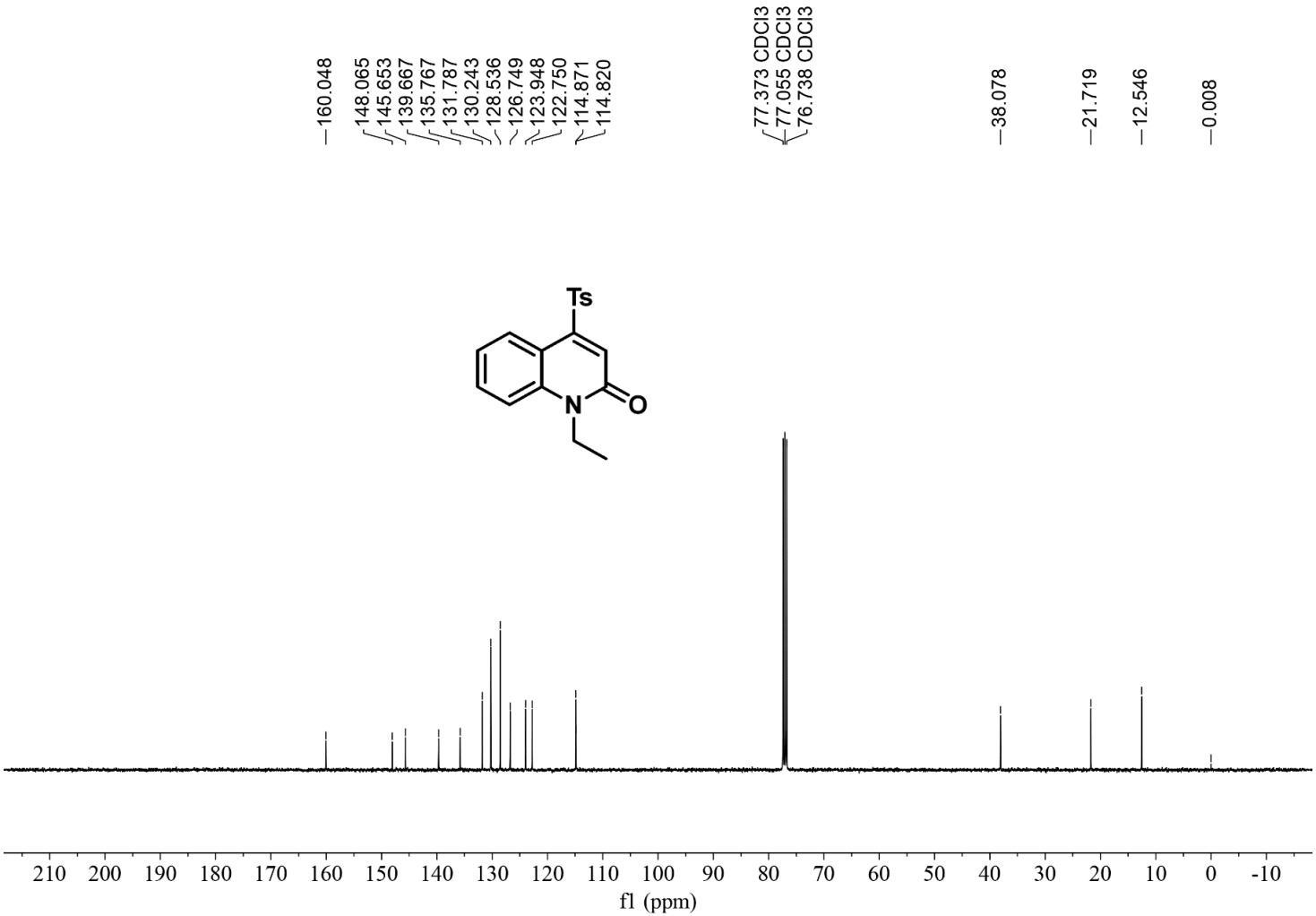
^{1}H NMR Spectrum of Compound 3r



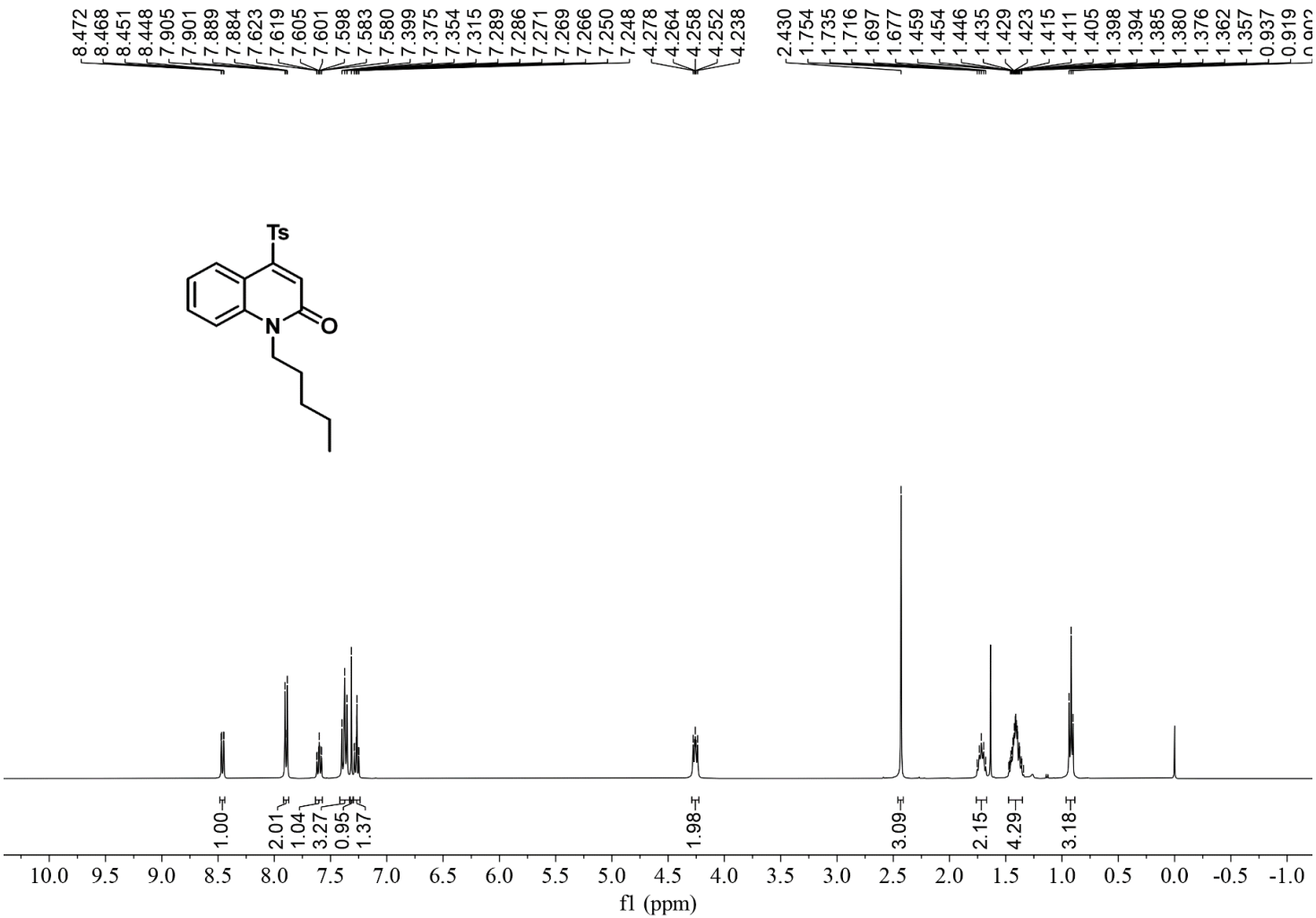
^{13}C NMR Spectrum of Compound 3r



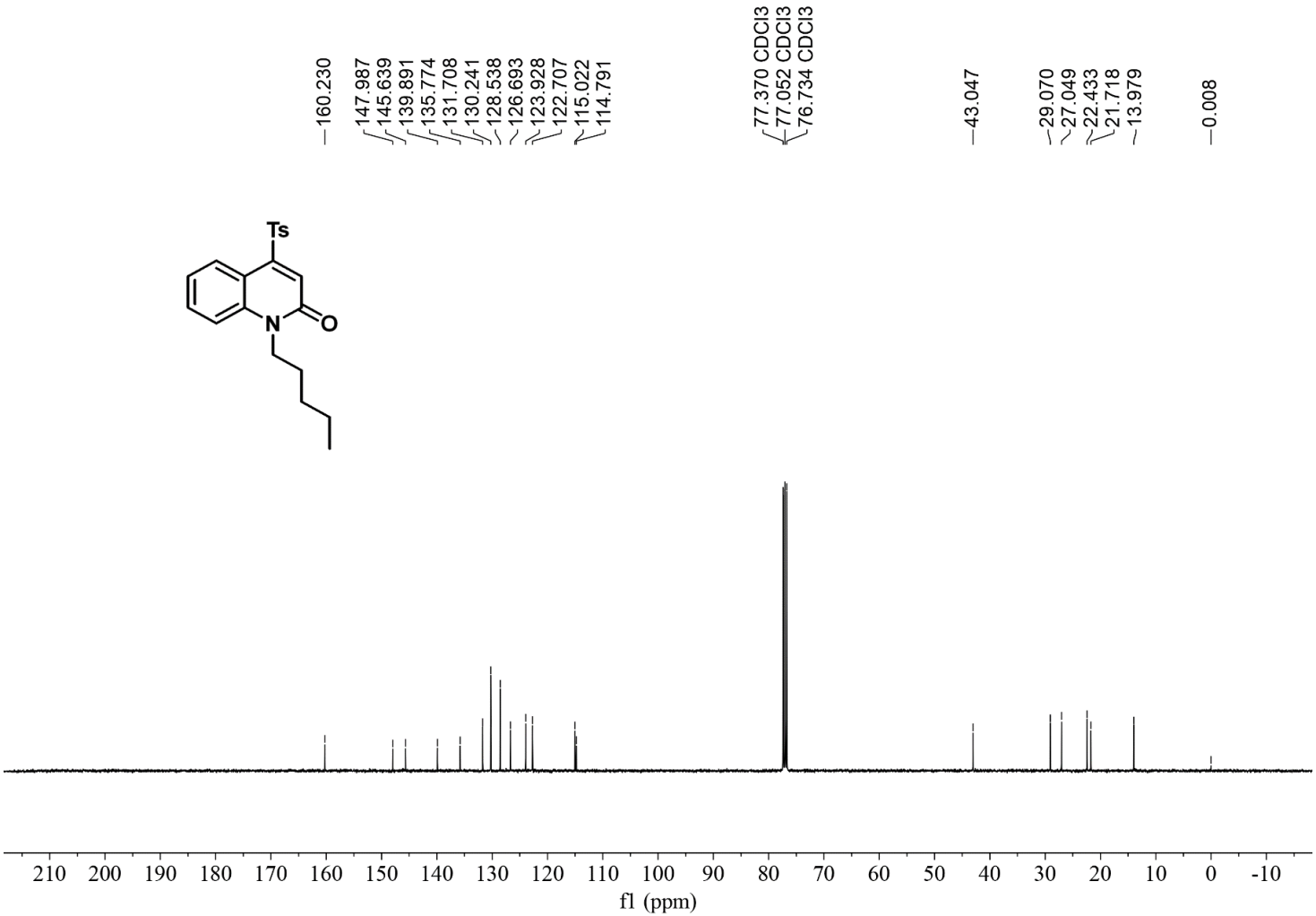
^{1}H NMR Spectrum of Compound 3s



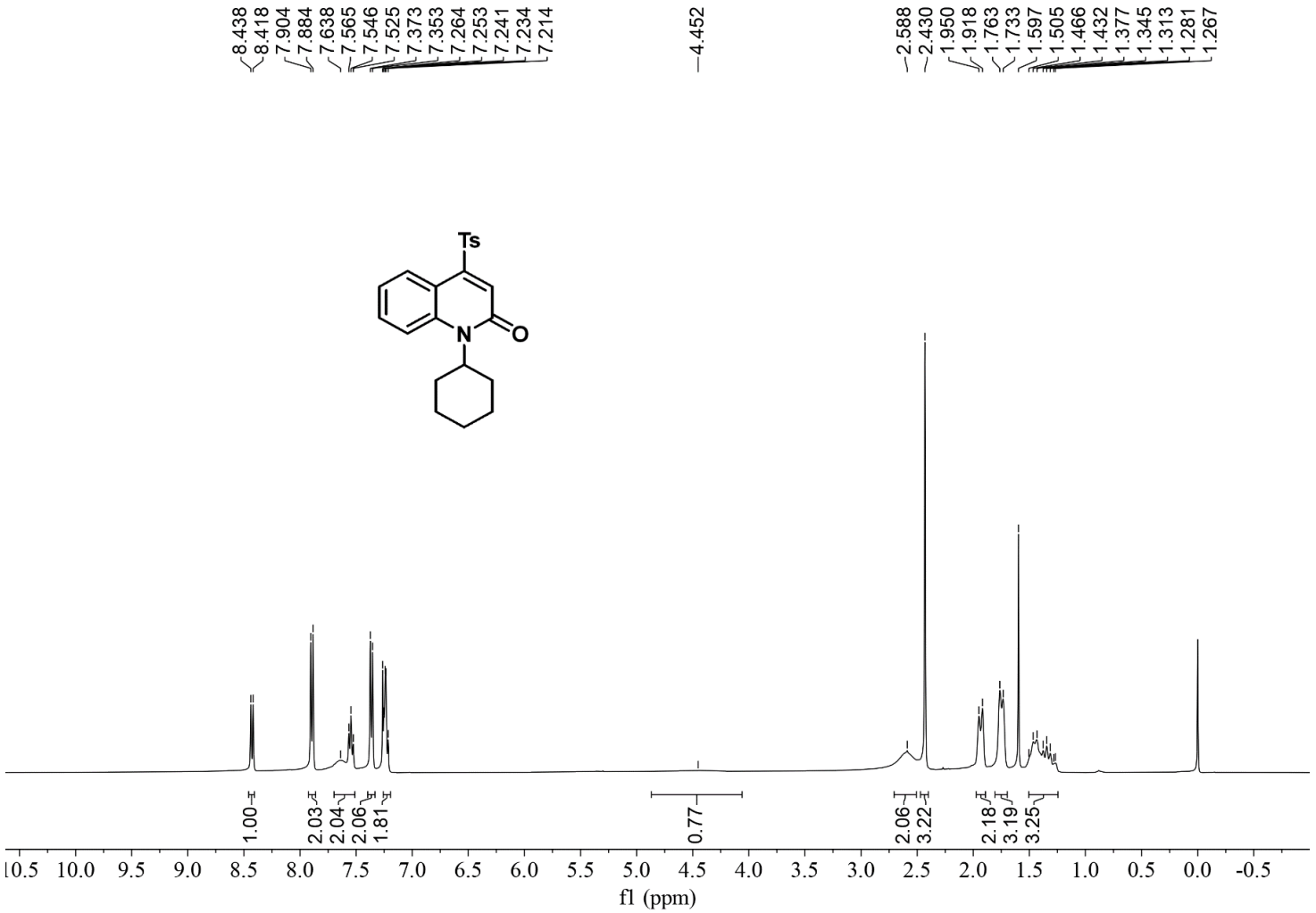
^{13}C NMR Spectrum of Compound 3s



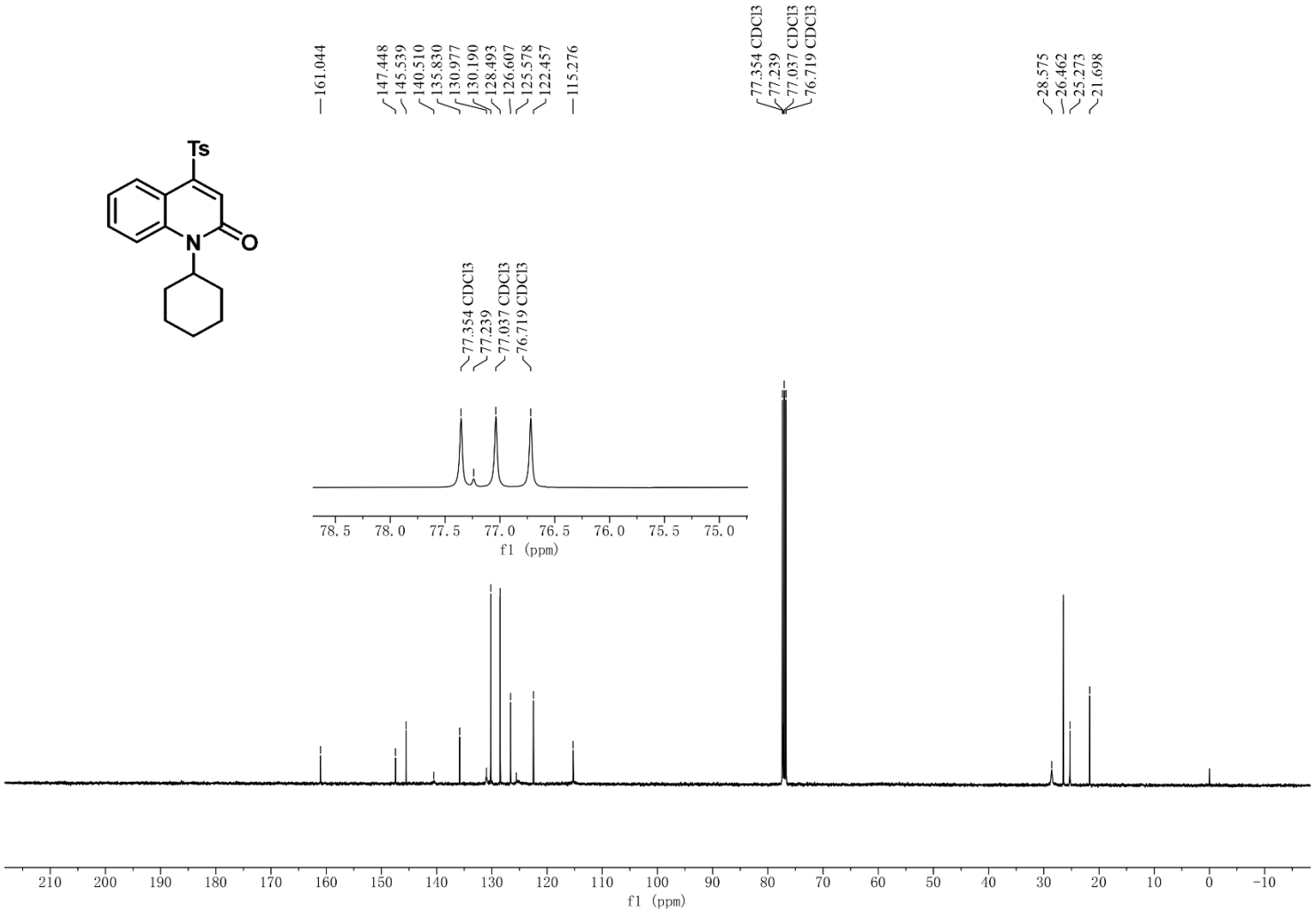
^{1}H NMR Spectrum of Compound 3t



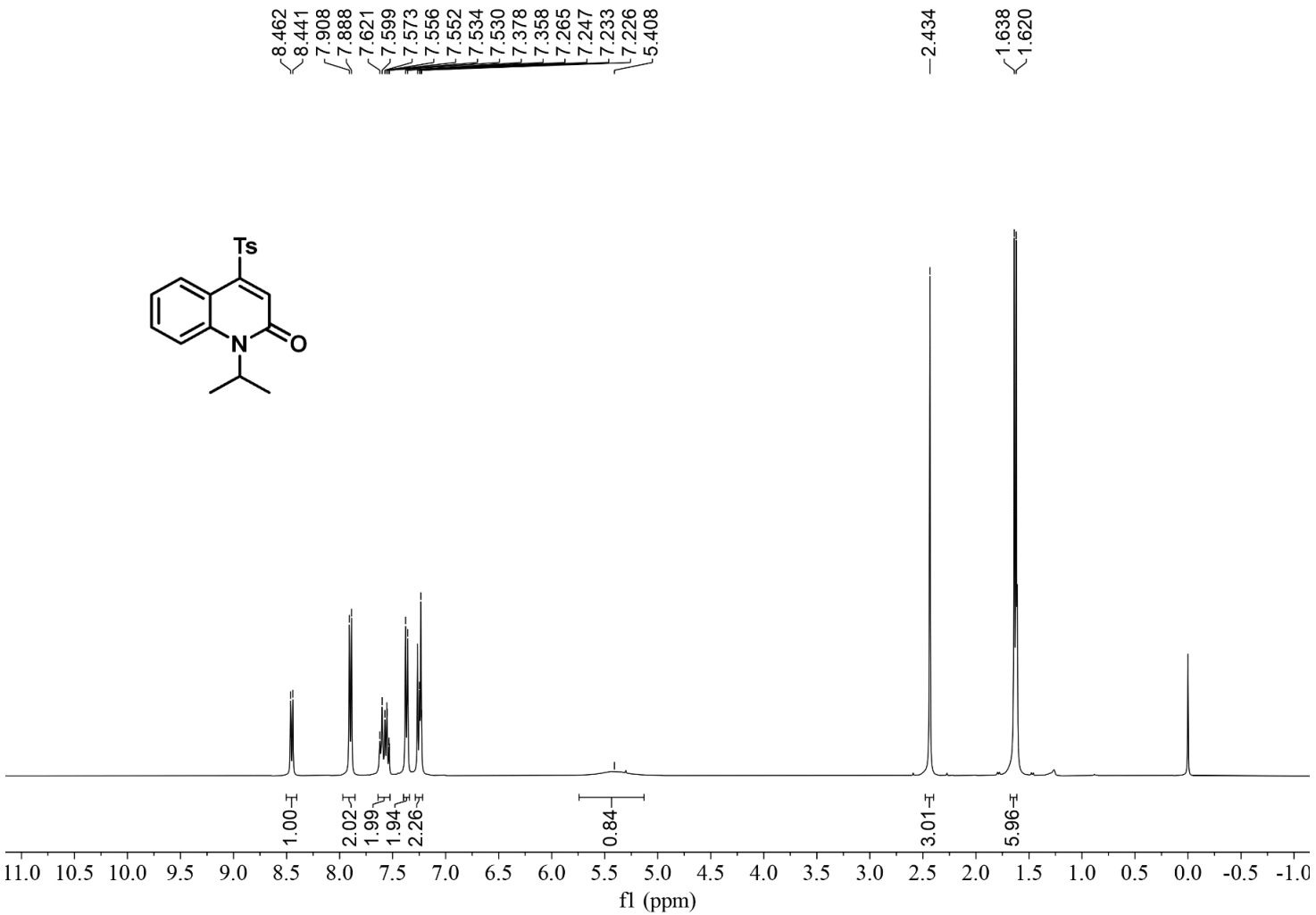
^{13}C NMR Spectrum of Compound 3t



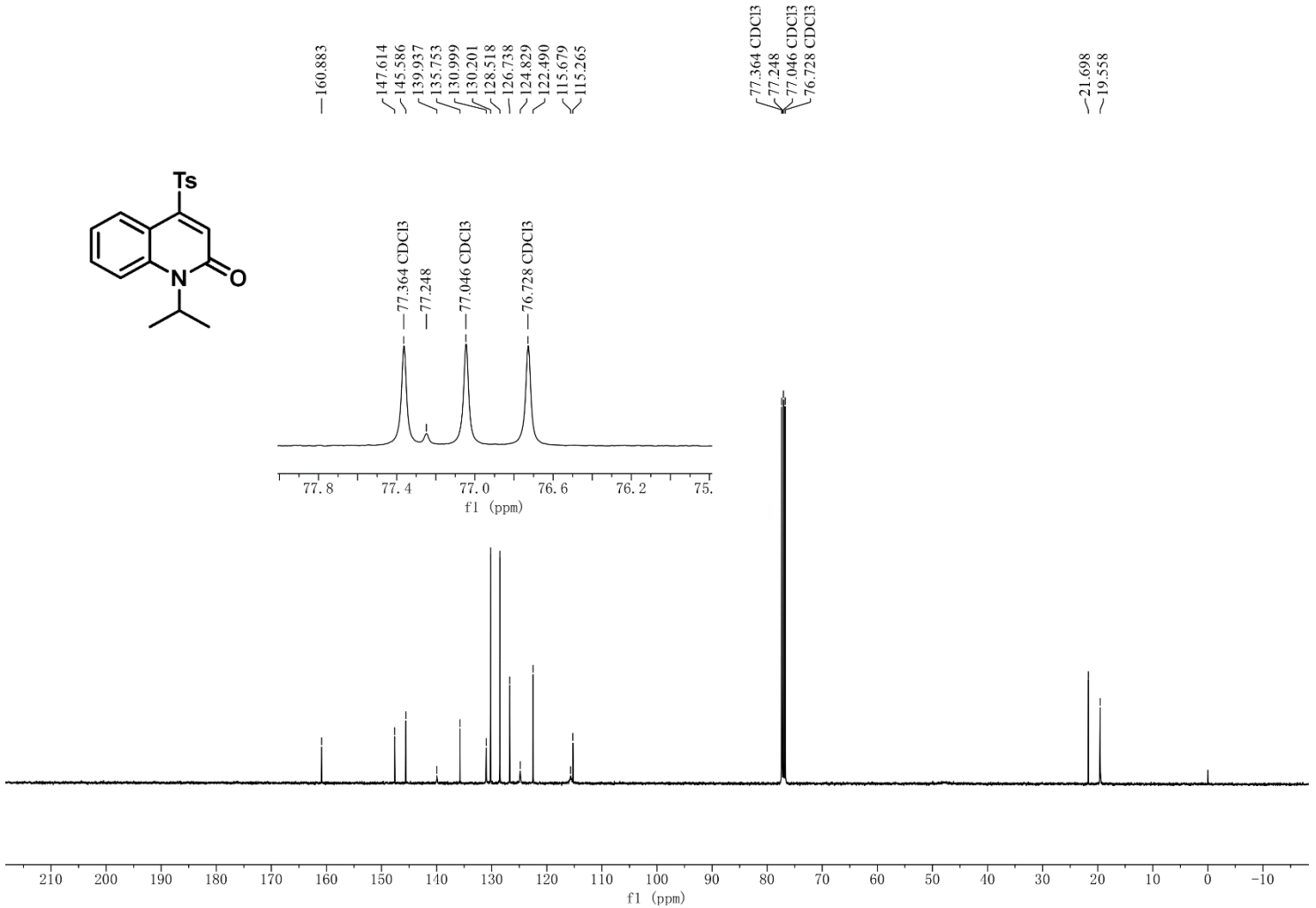
^{1}H NMR Spectrum of Compound 3u



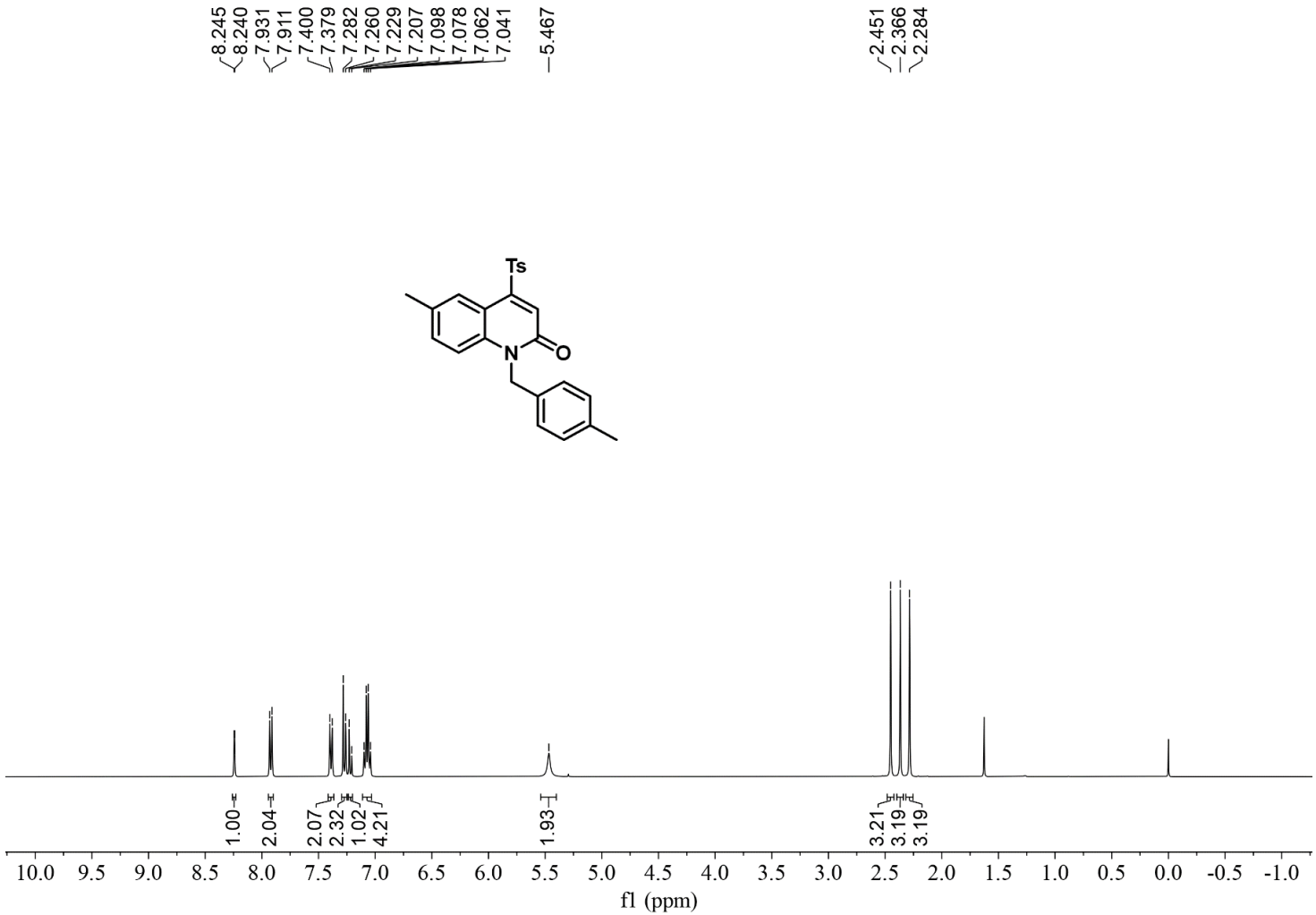
^{13}C NMR Spectrum of Compound 3u



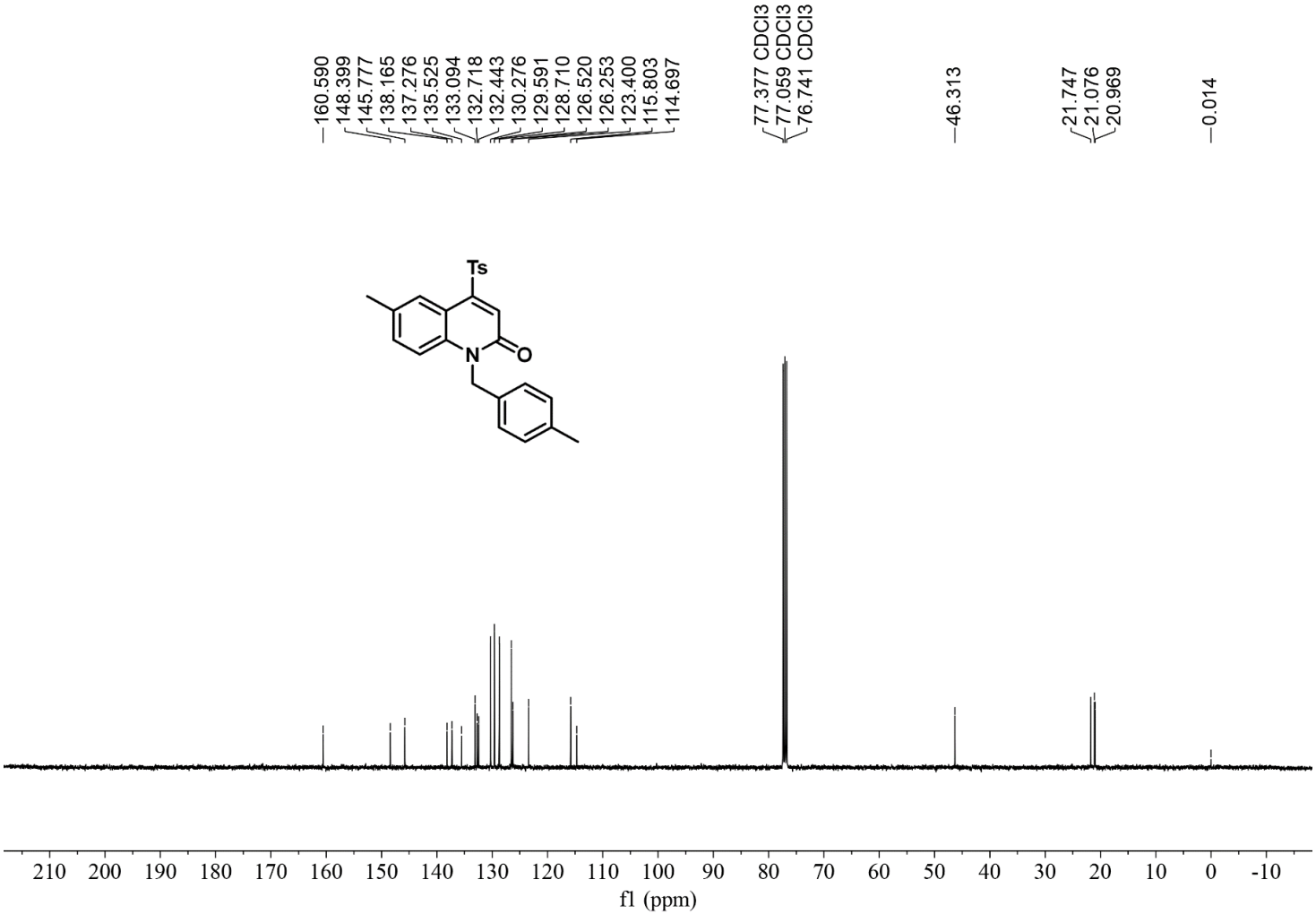
^{1}H NMR Spectrum of Compound 3v



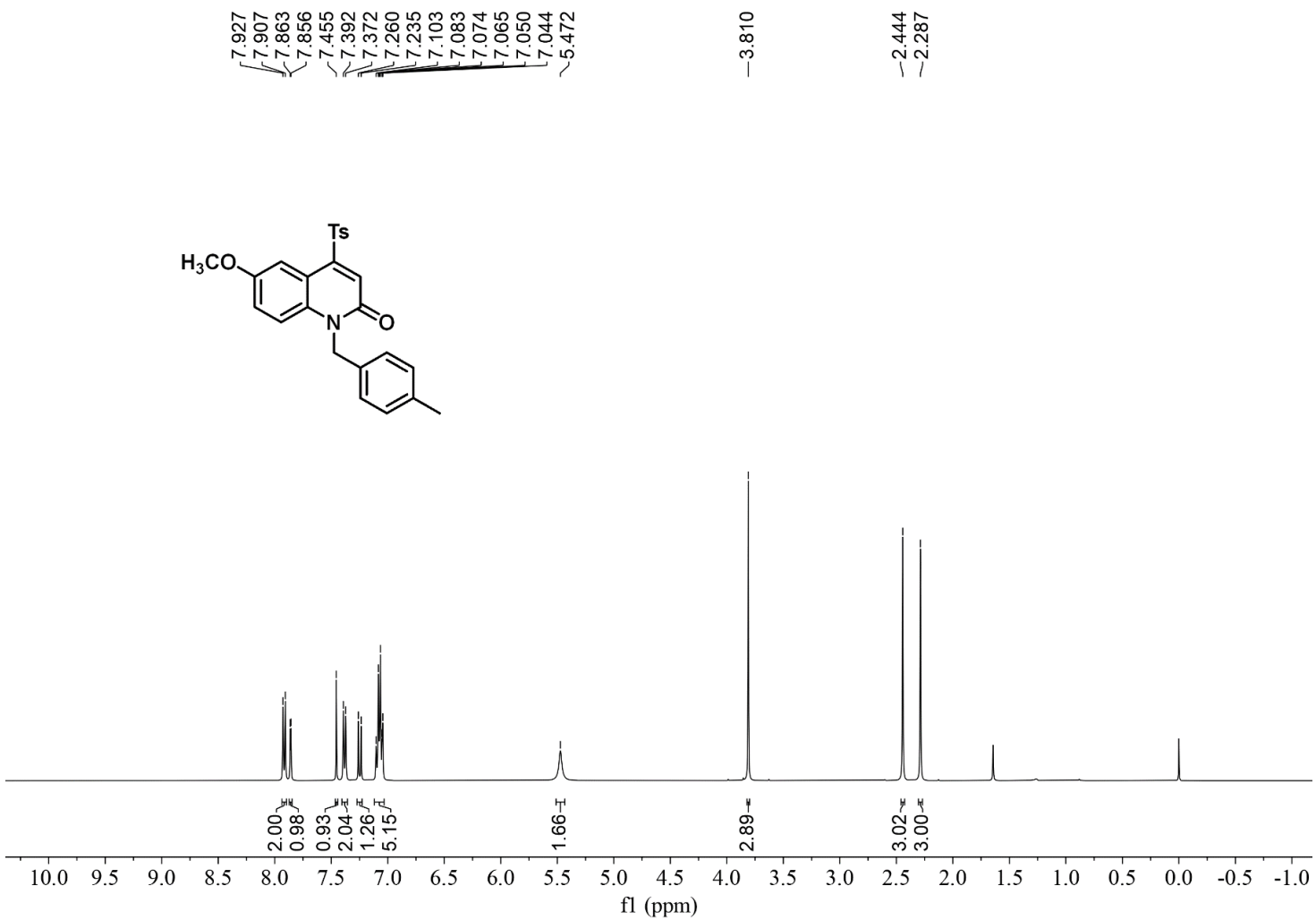
^{13}C NMR Spectrum of Compound 3v



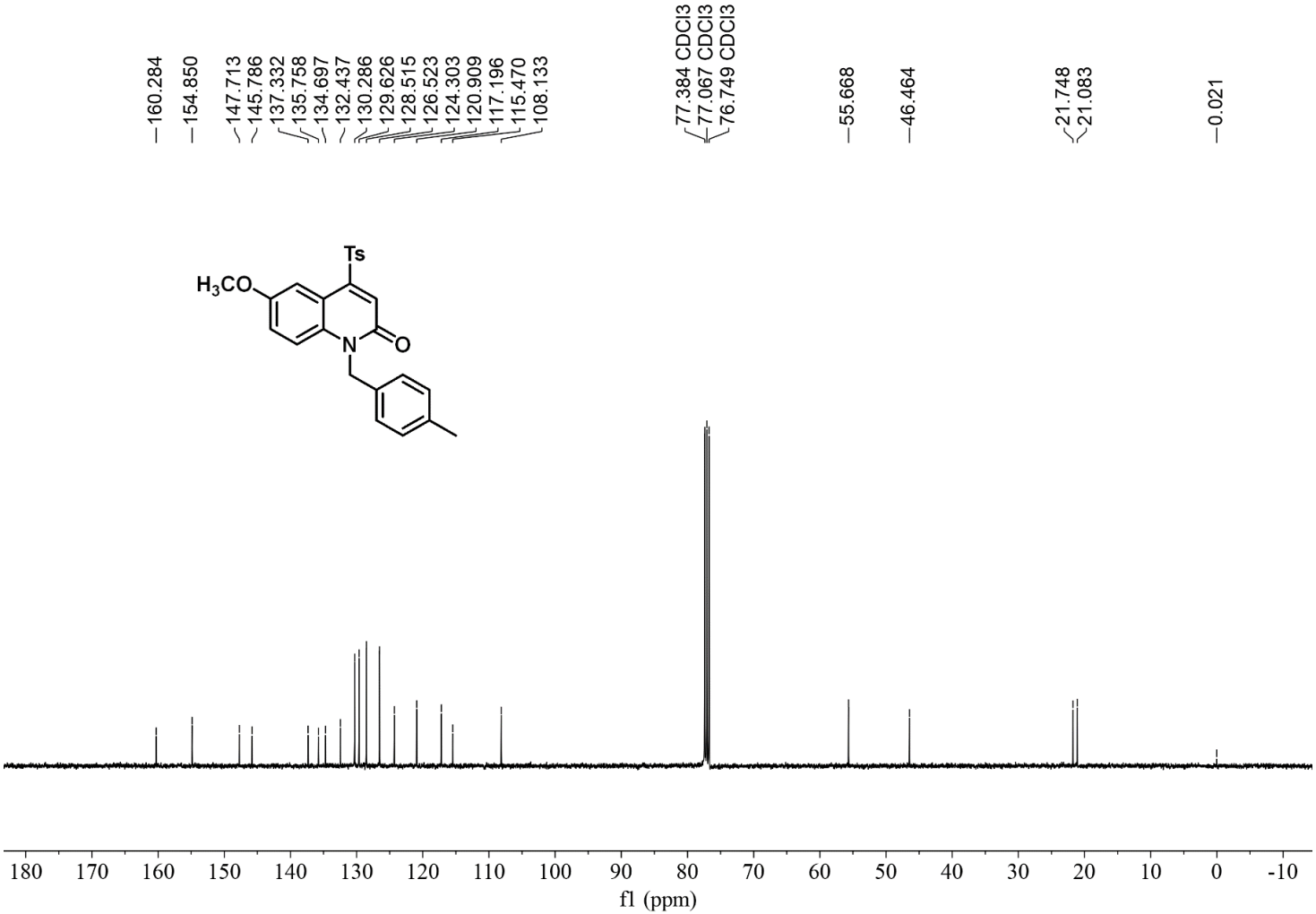
^{1}H NMR Spectrum of Compound 3w



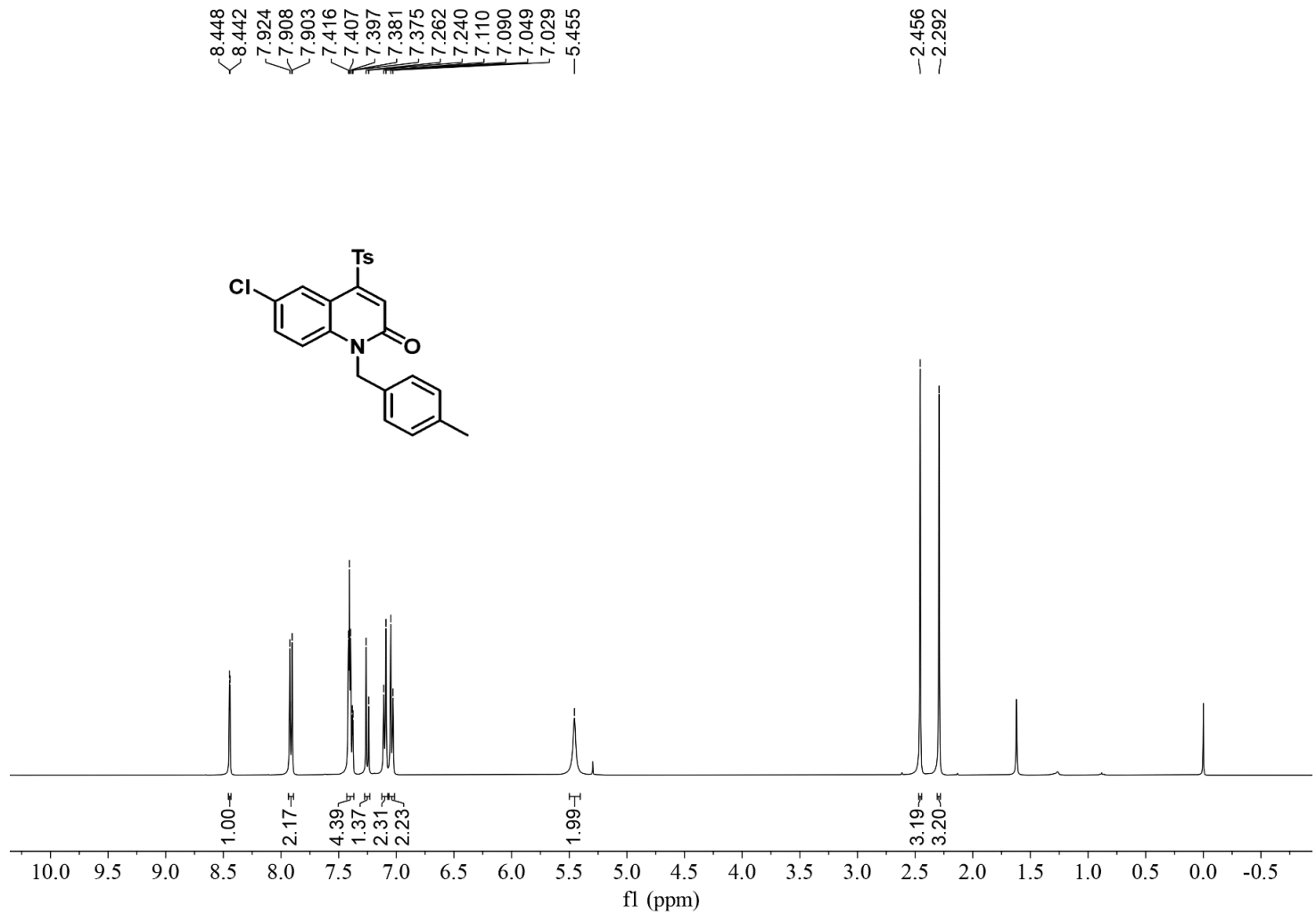
^{13}C NMR Spectrum of Compound 3w



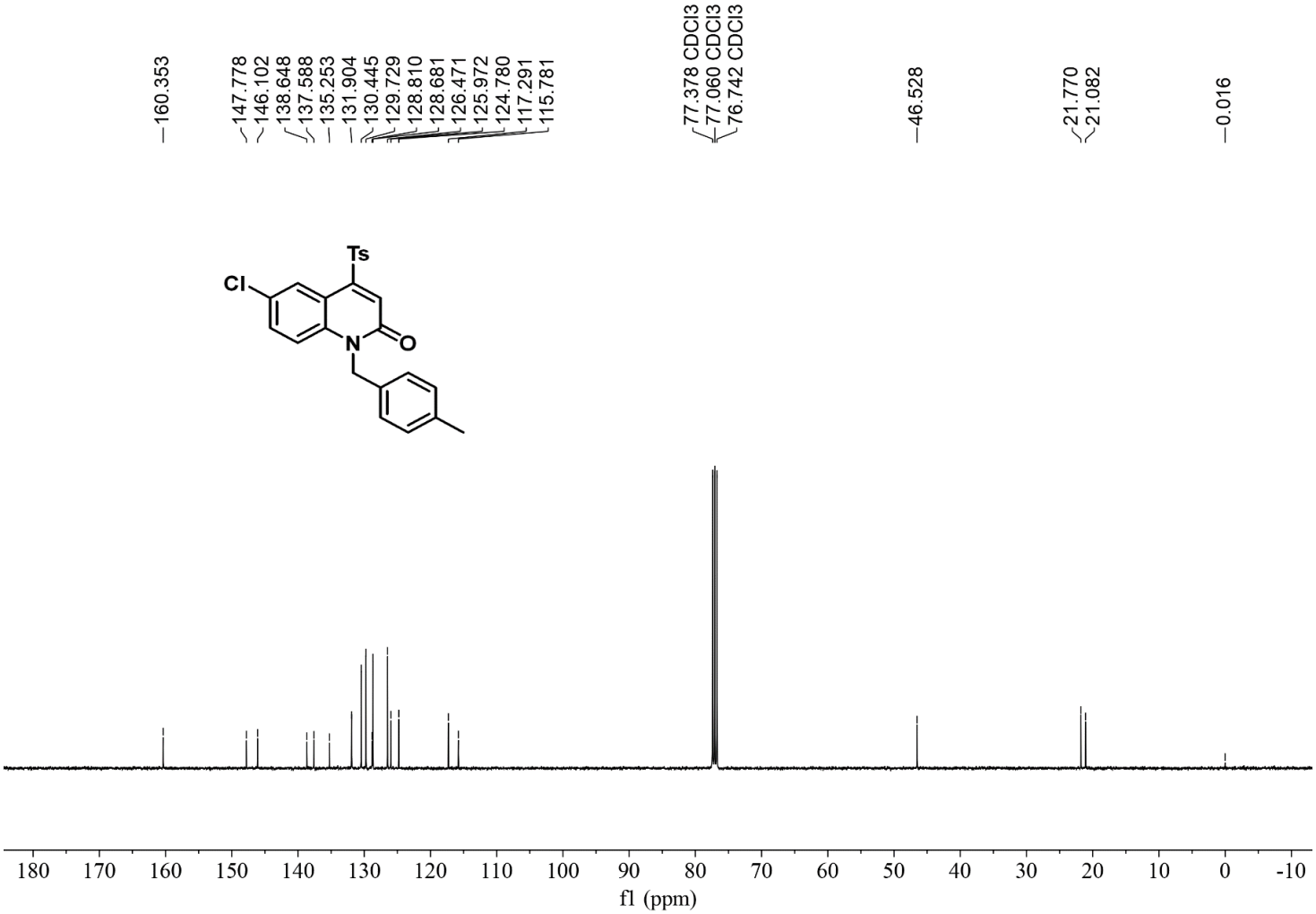
^{1}H NMR Spectrum of Compound 3x



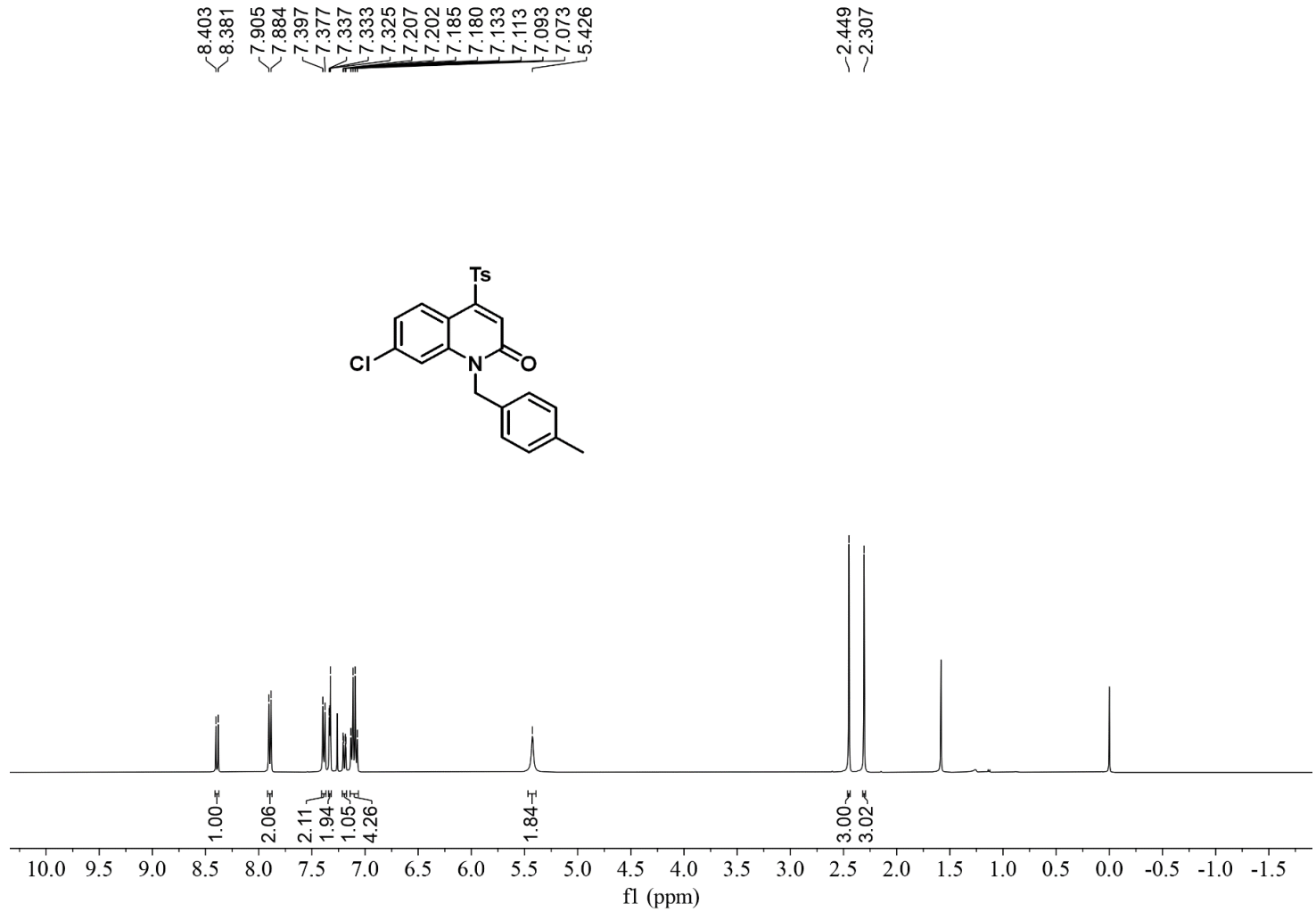
^{13}C NMR Spectrum of Compound 3x



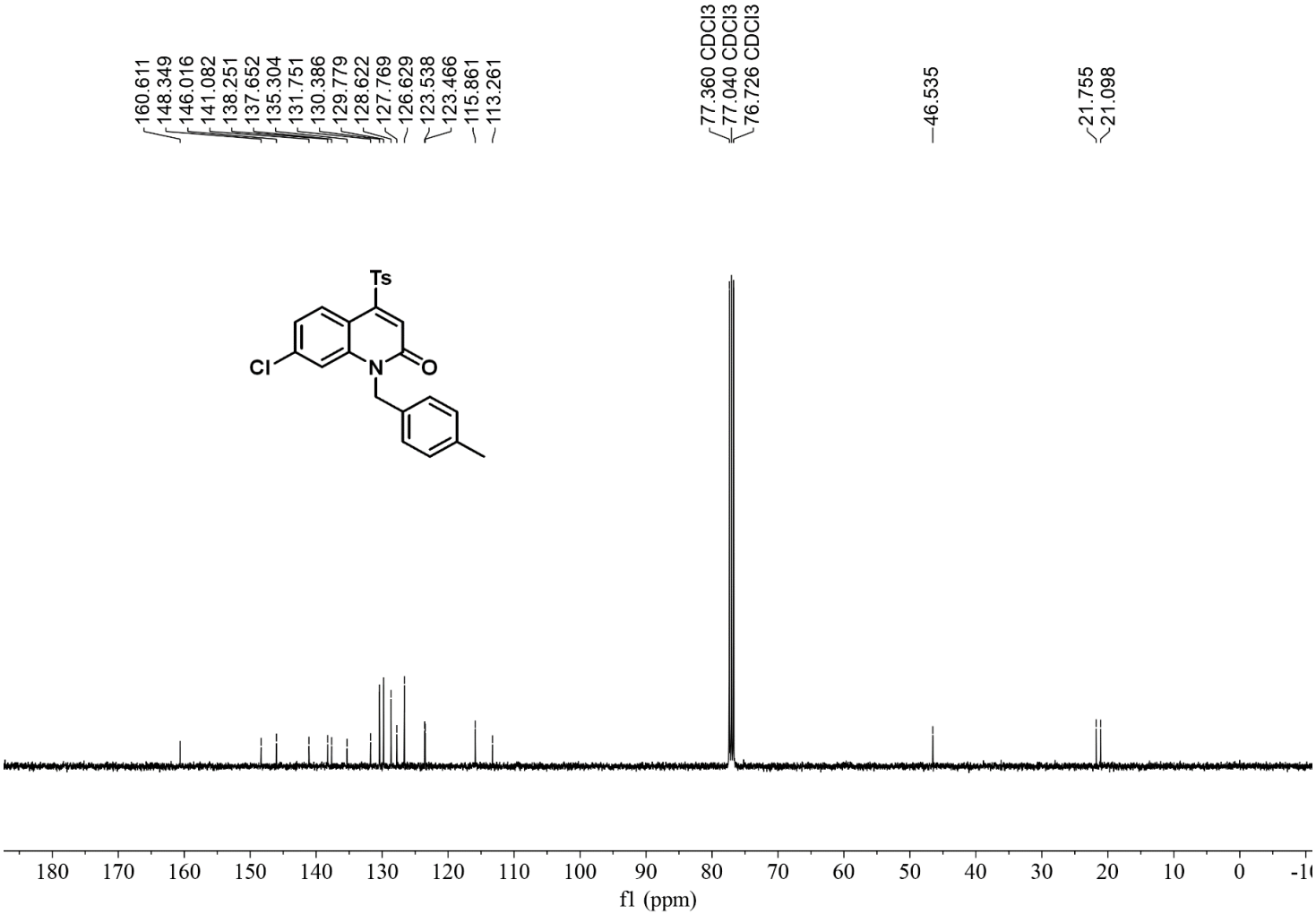
^{1}H NMR Spectrum of Compound 3y



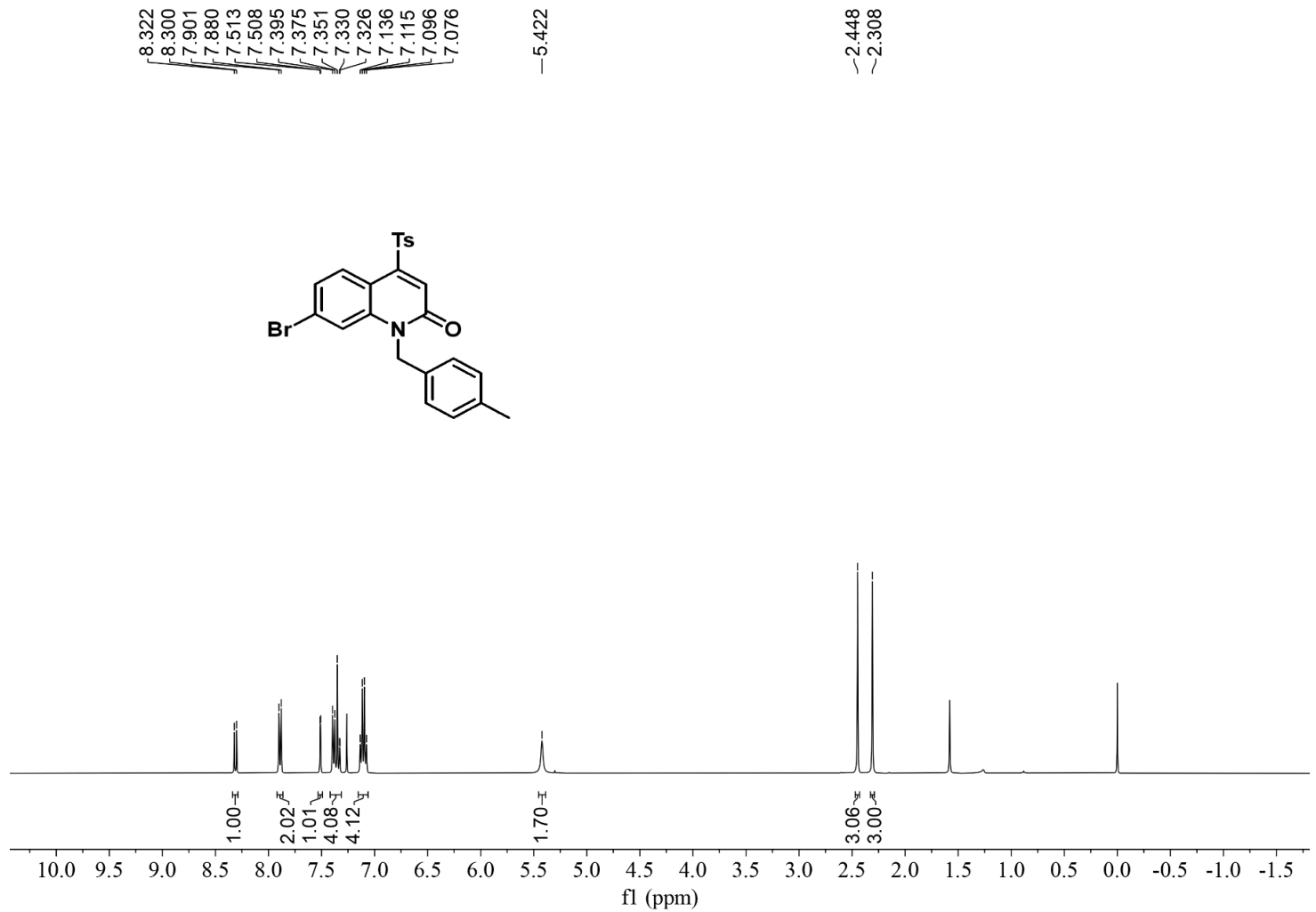
^{13}C NMR Spectrum of Compound 3y



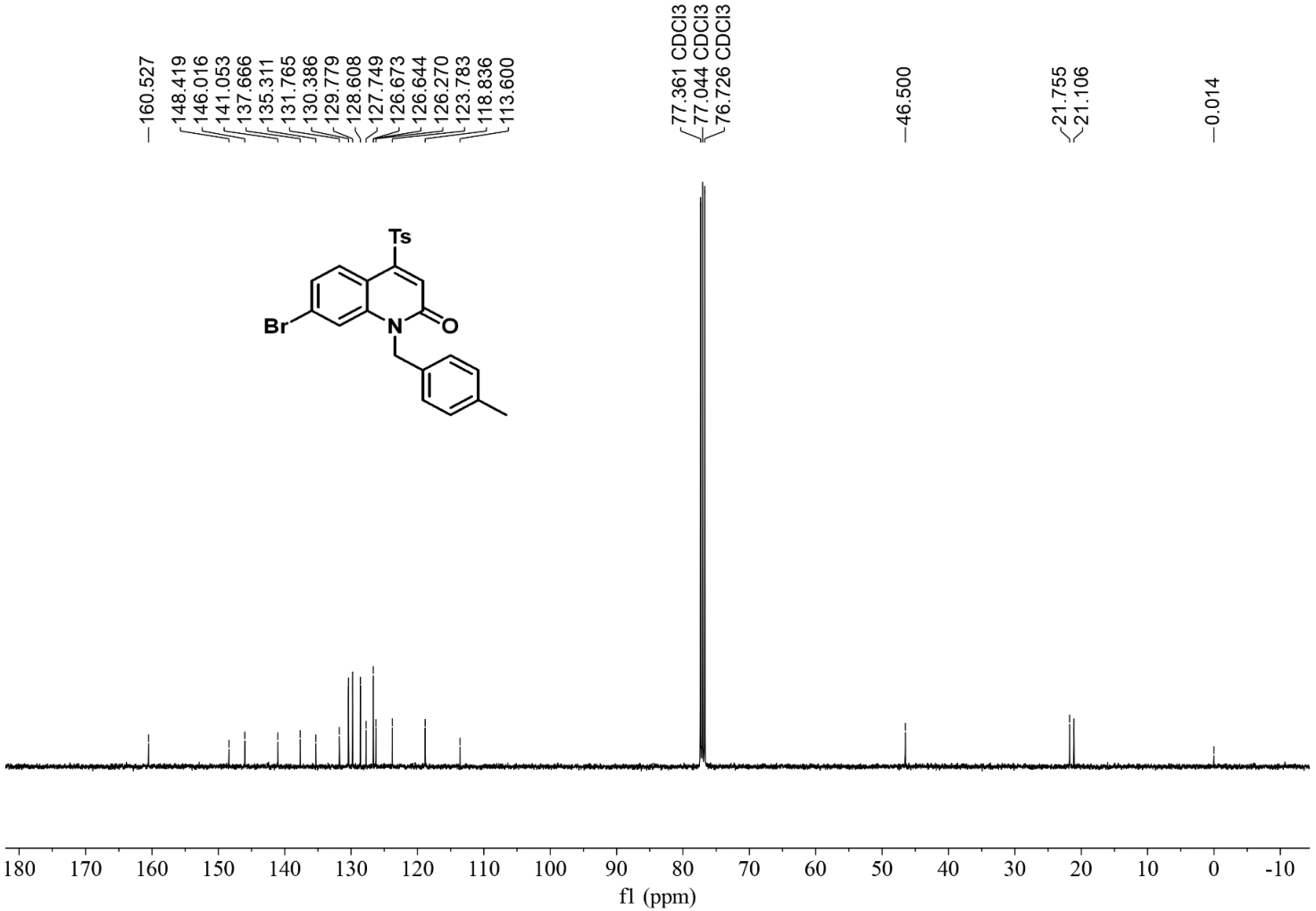
^{1}H NMR Spectrum of Compound 3z



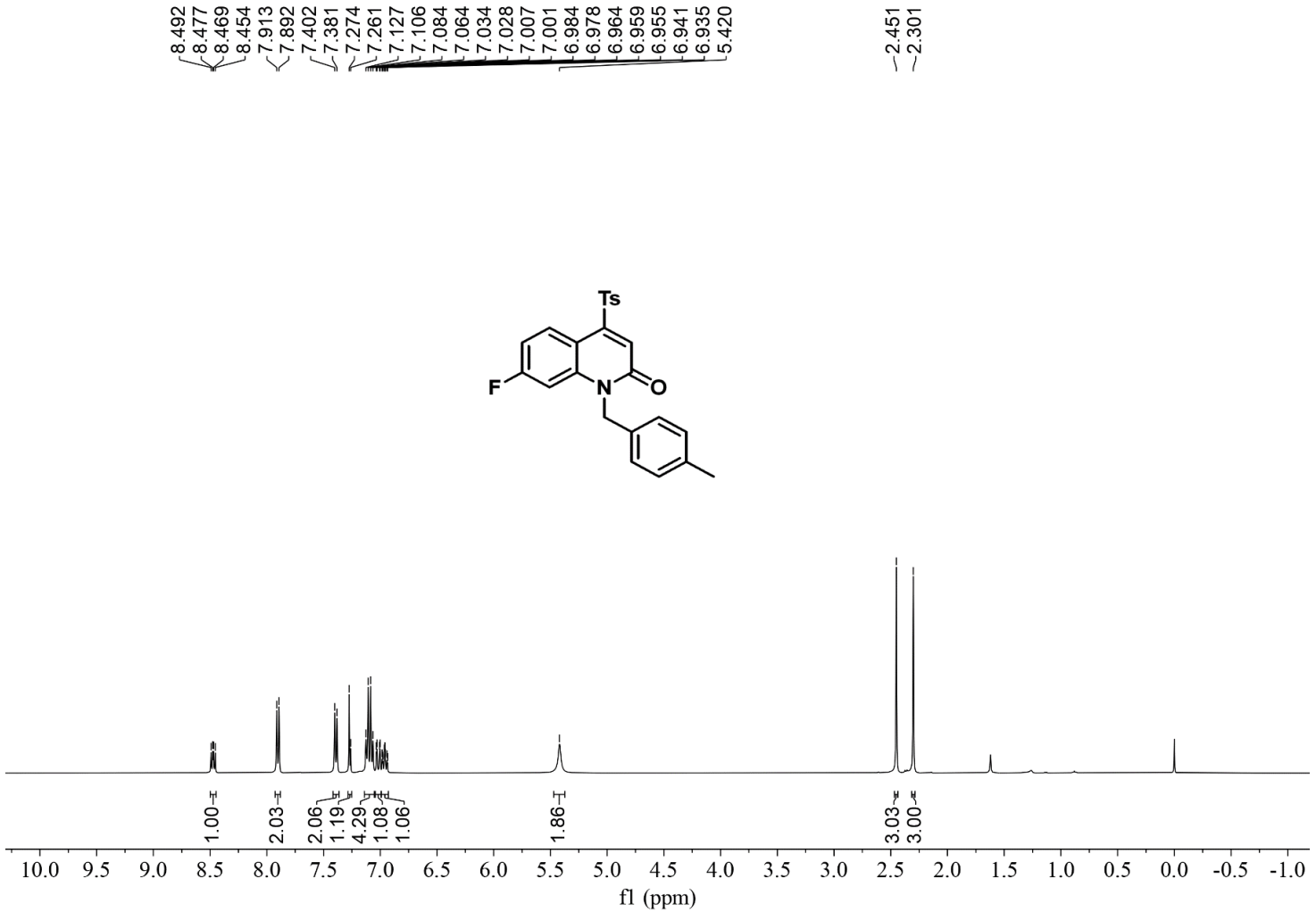
^{13}C NMR Spectrum of Compound 3z



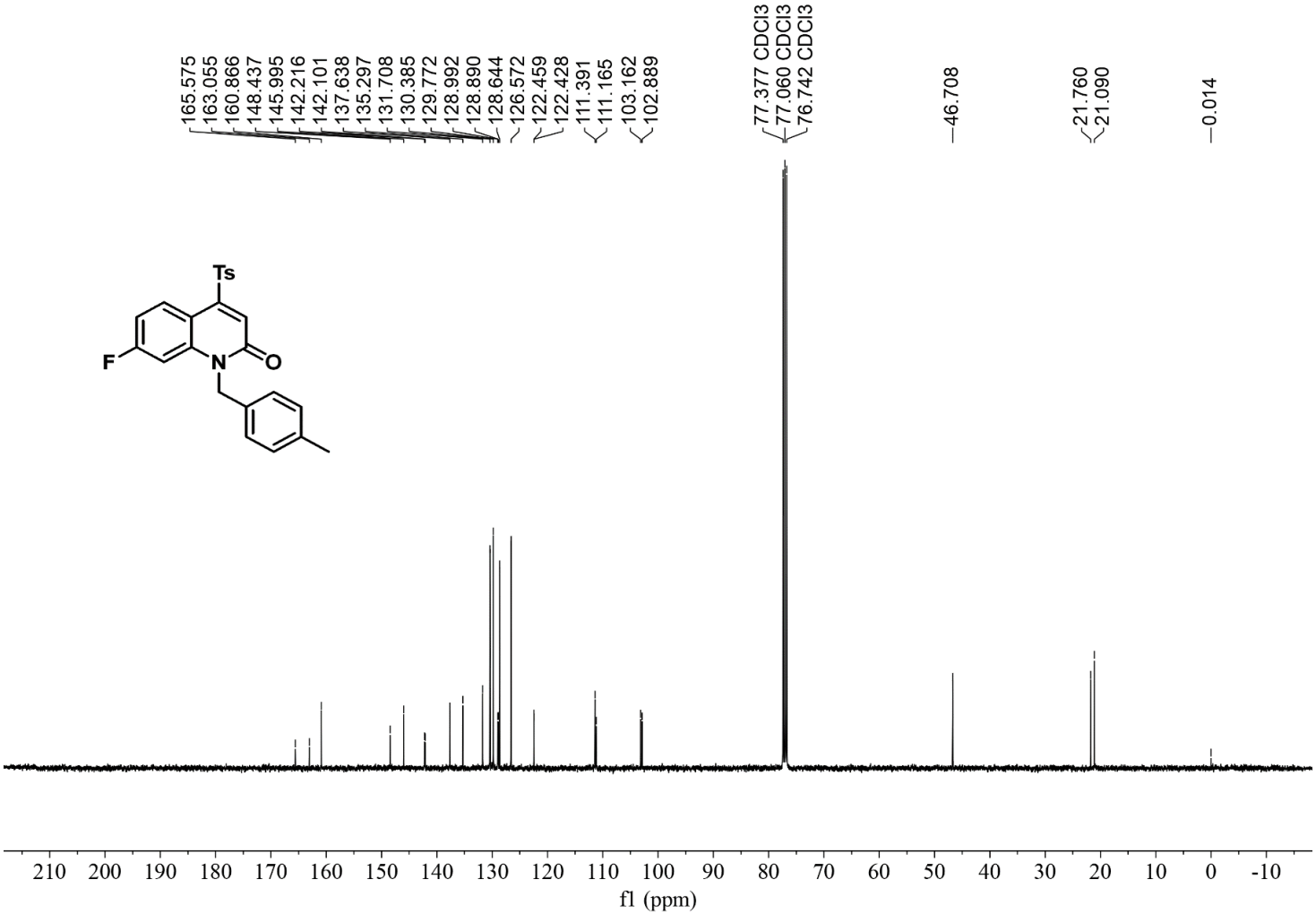
^{1}H NMR Spectrum of Compound 3aa



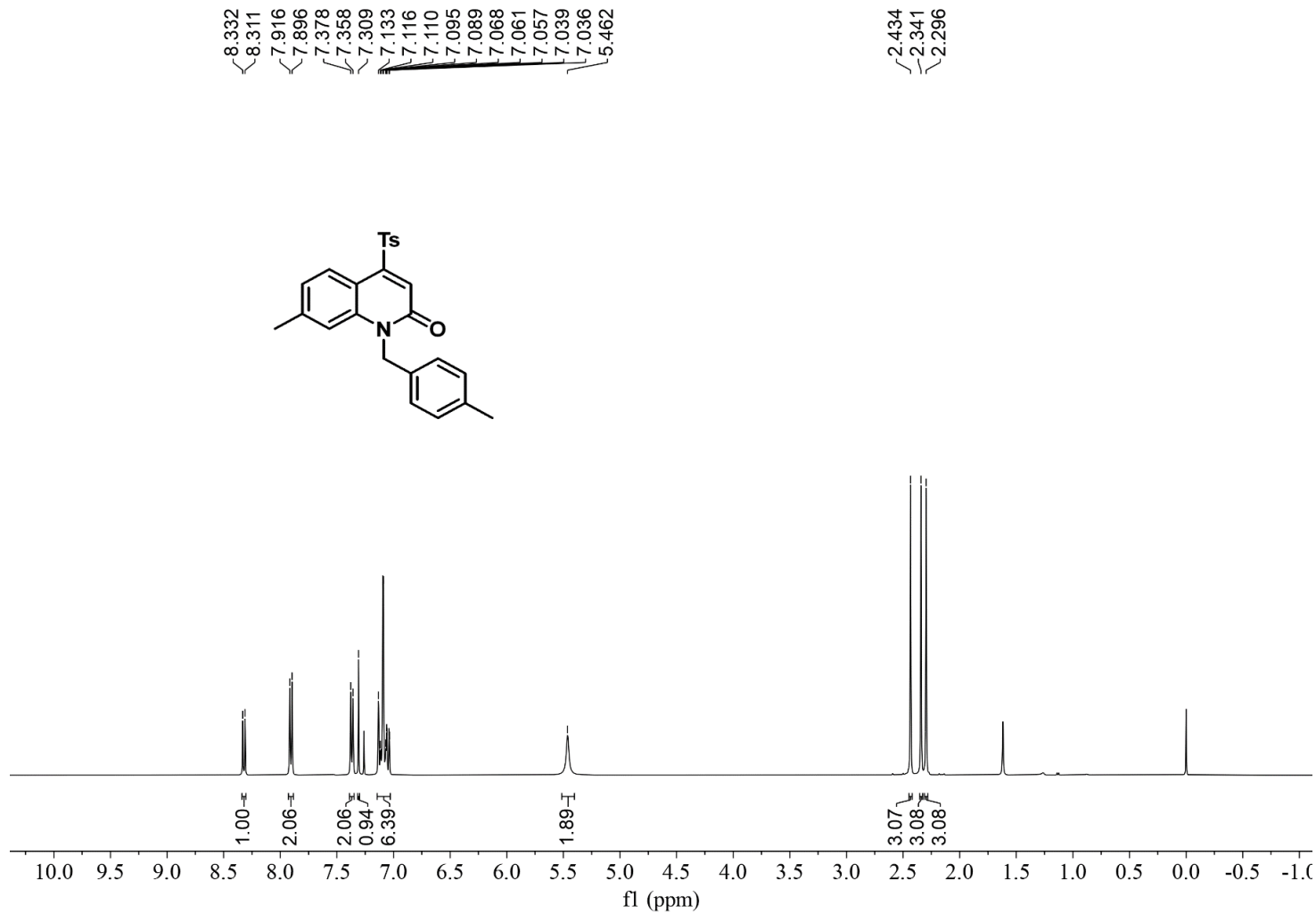
^{13}C NMR Spectrum of Compound 3aa



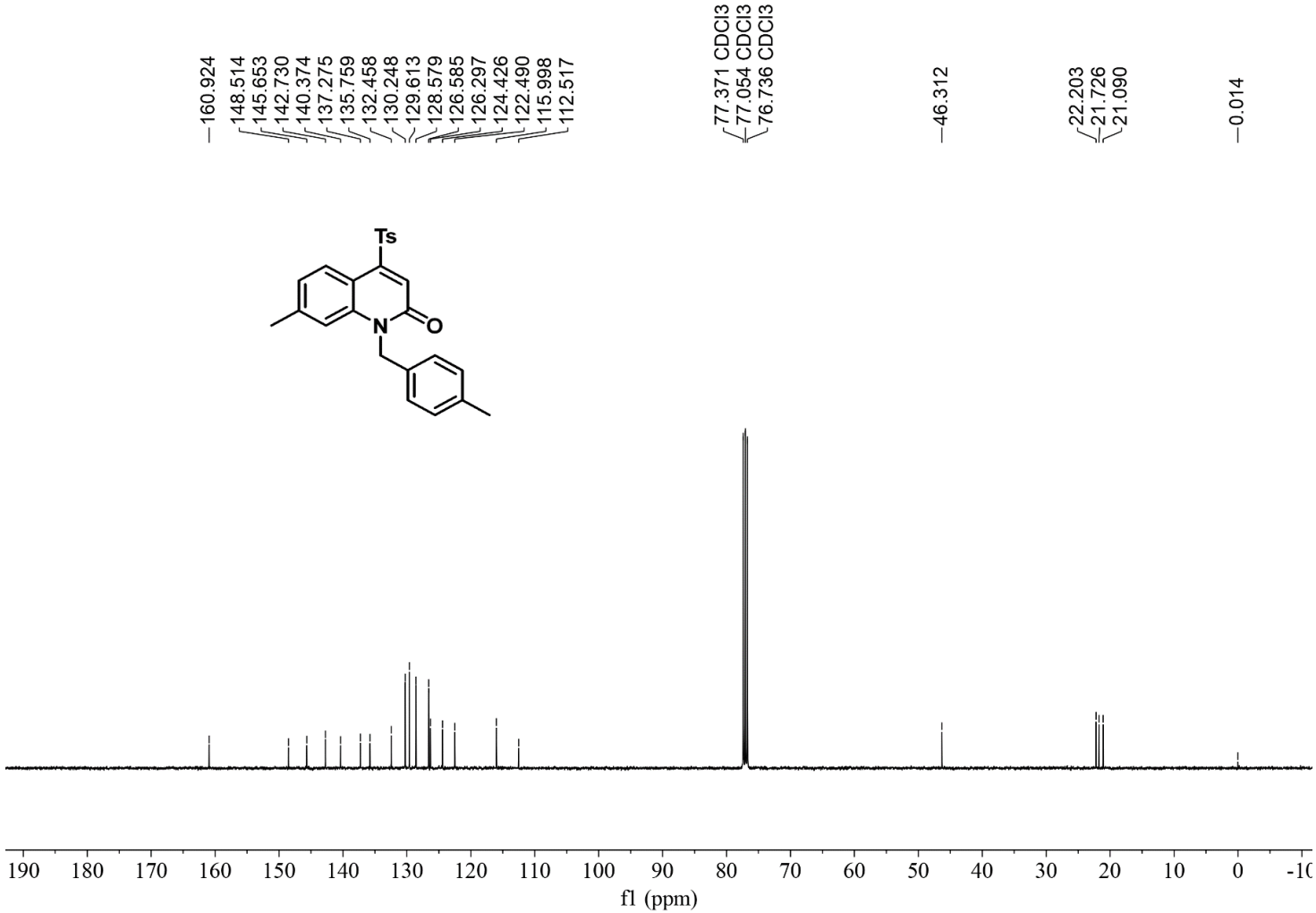
^{1}H NMR Spectrum of Compound 3ab



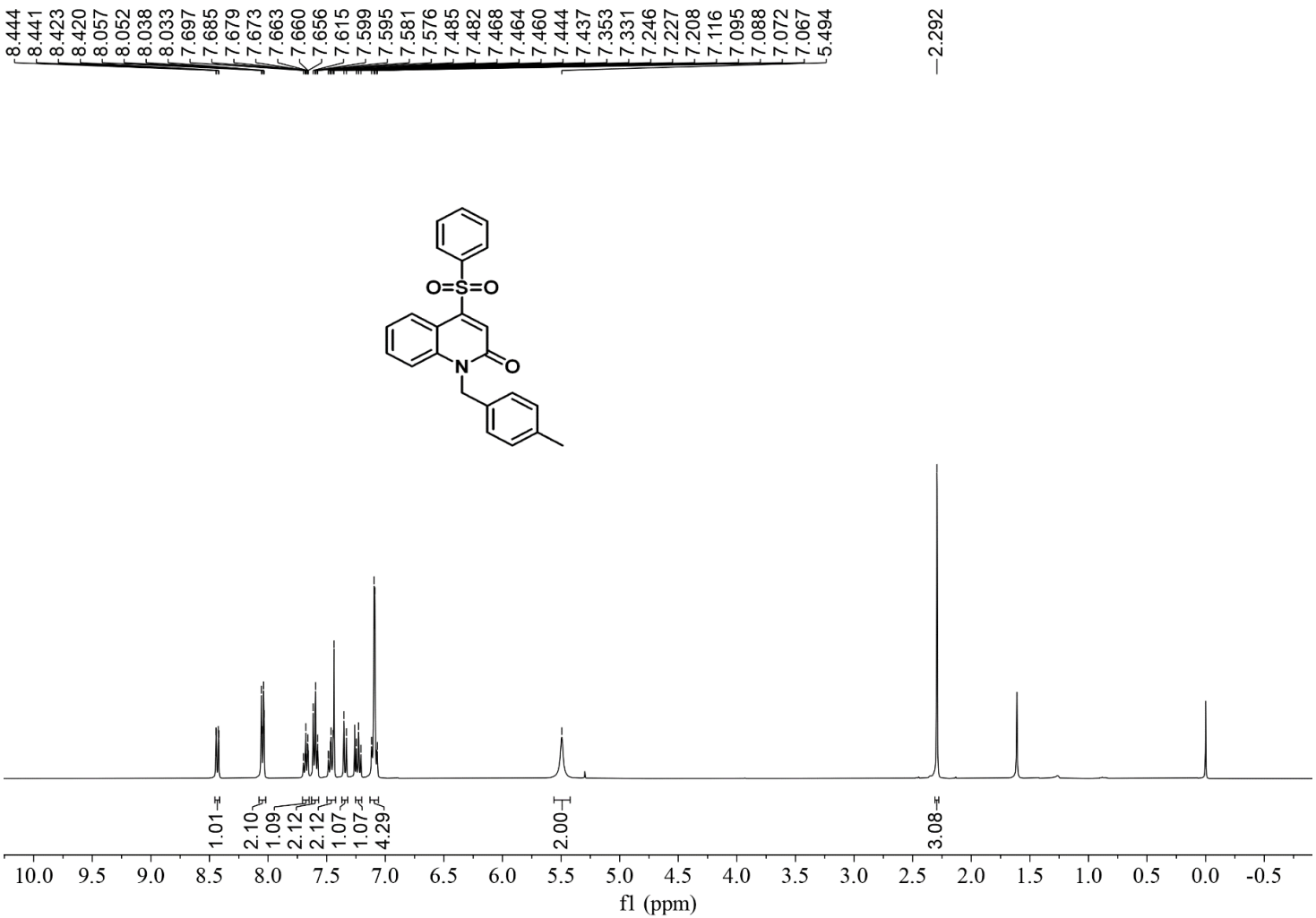
^{13}C NMR Spectrum of Compound 3ab



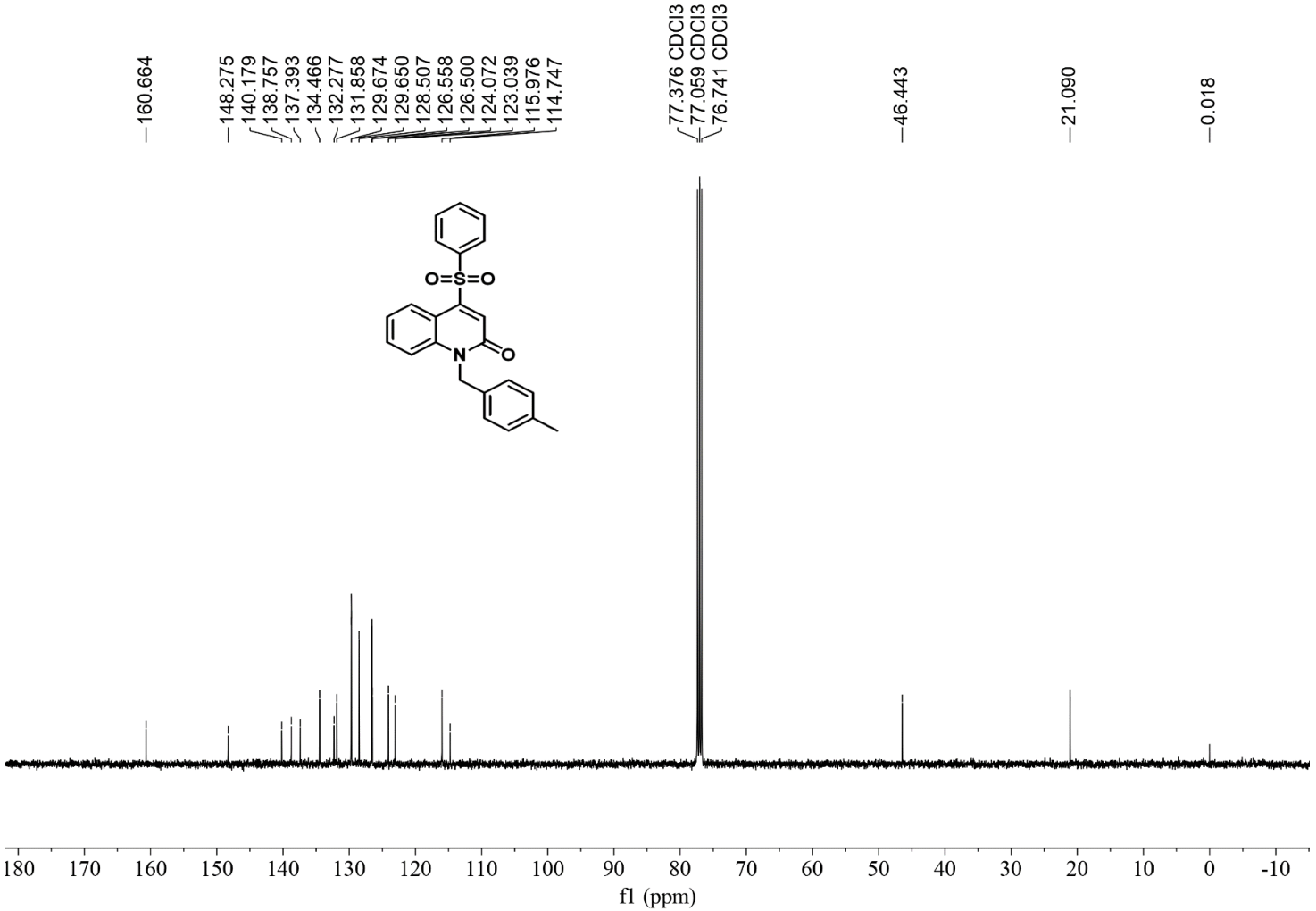
^{1}H NMR Spectrum of Compound 3ac



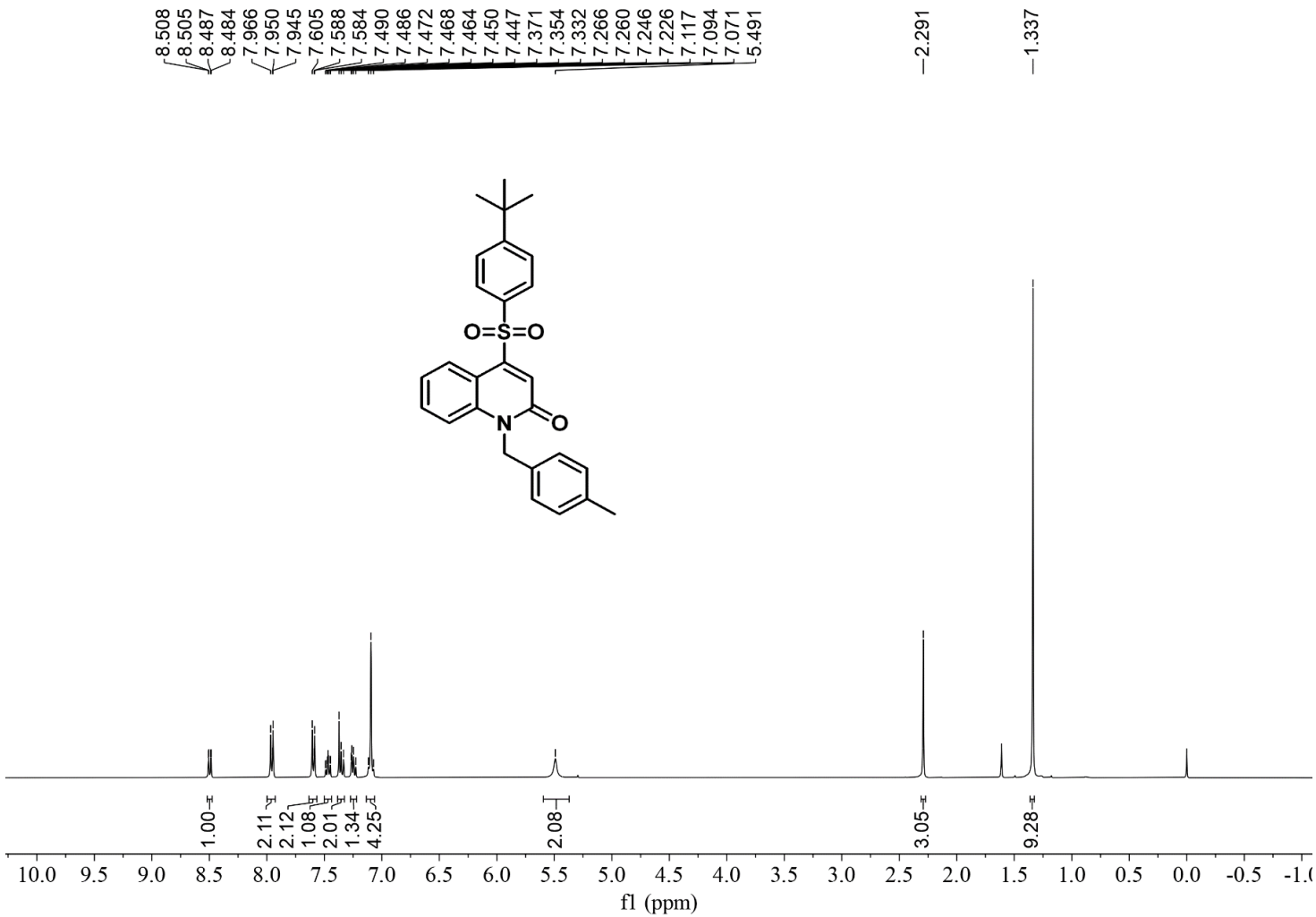
^{13}C NMR Spectrum of Compound 3ac



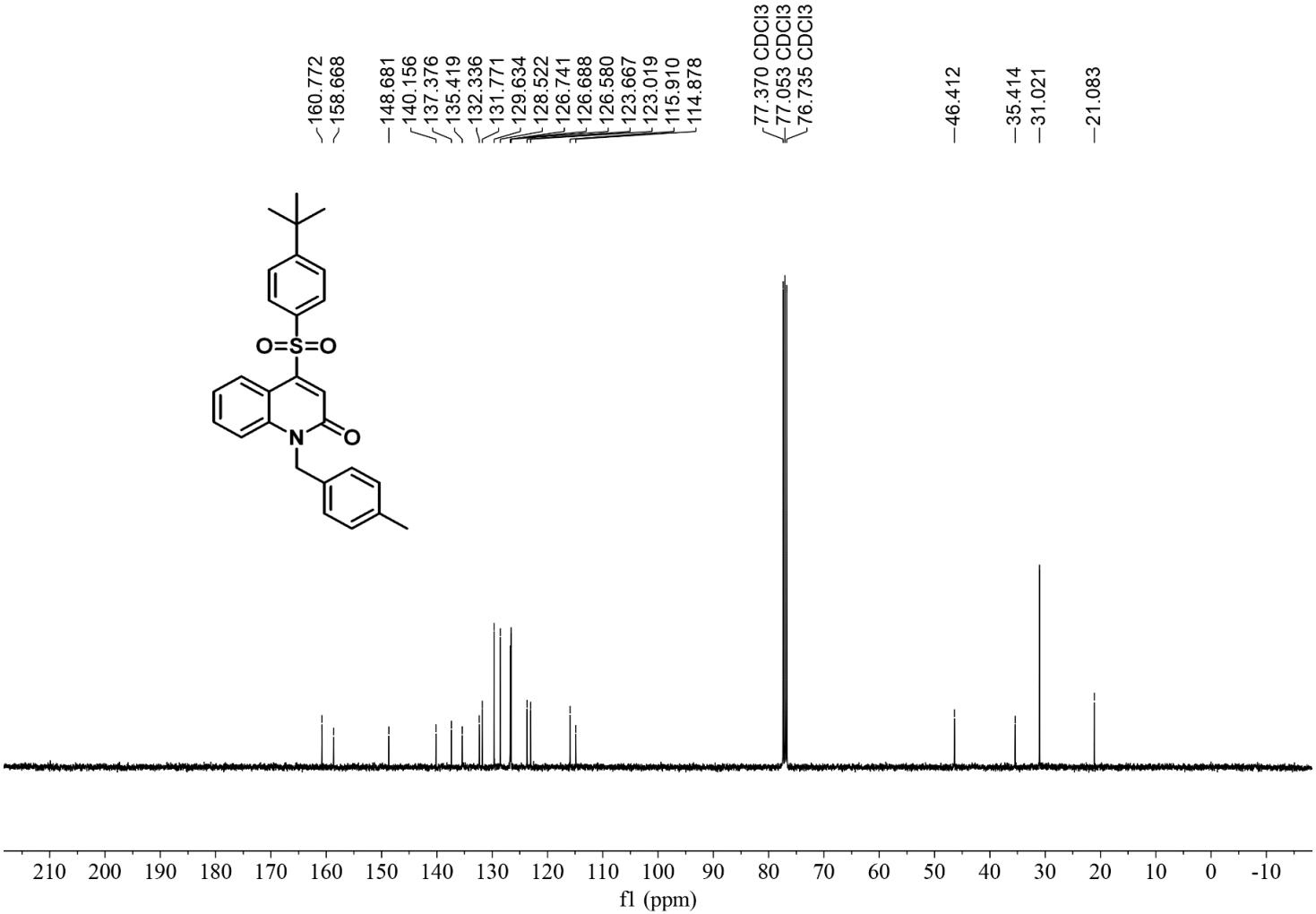
^{1}H NMR Spectrum of Compound 3ad



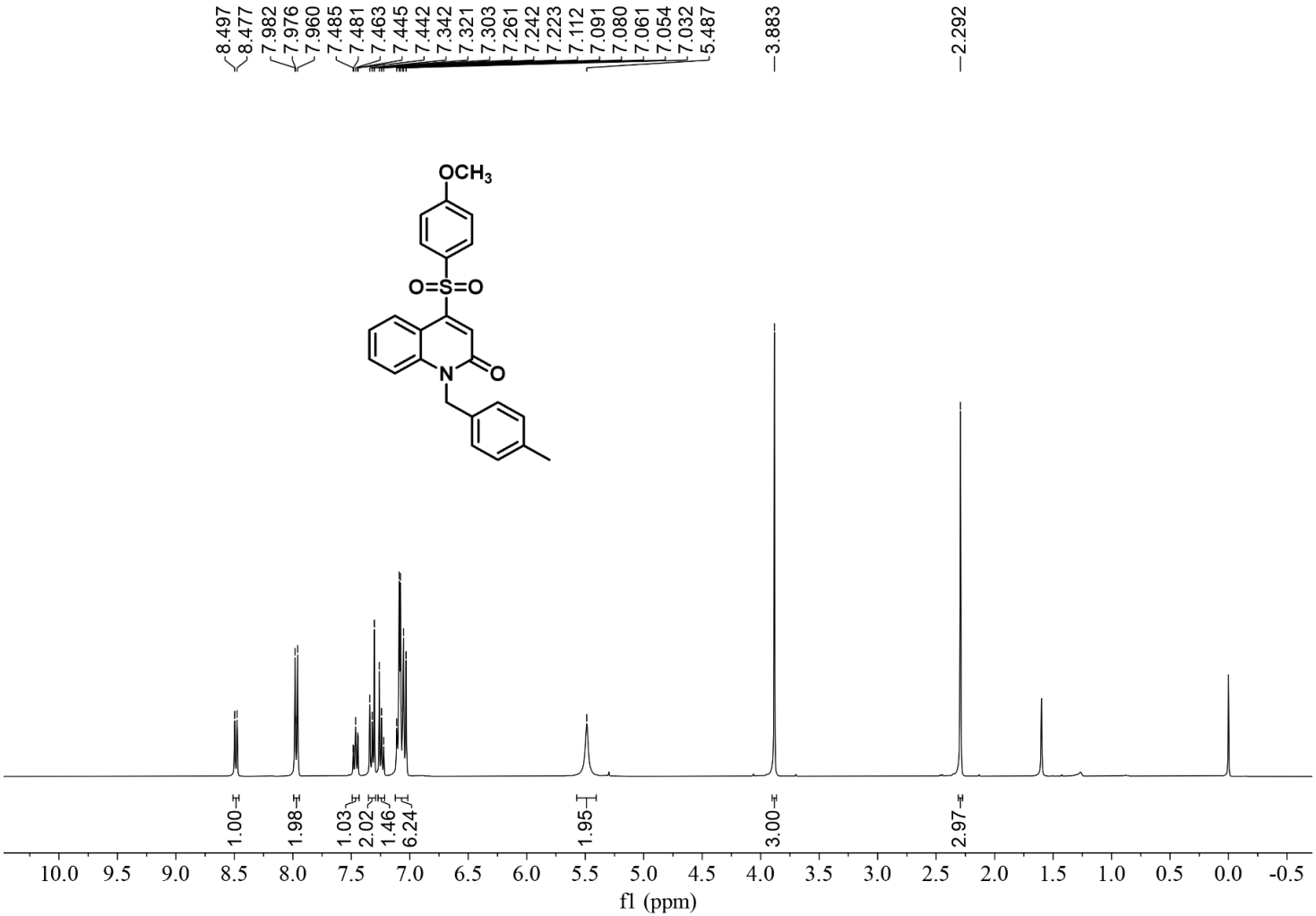
^{13}C NMR Spectrum of Compound 3ad



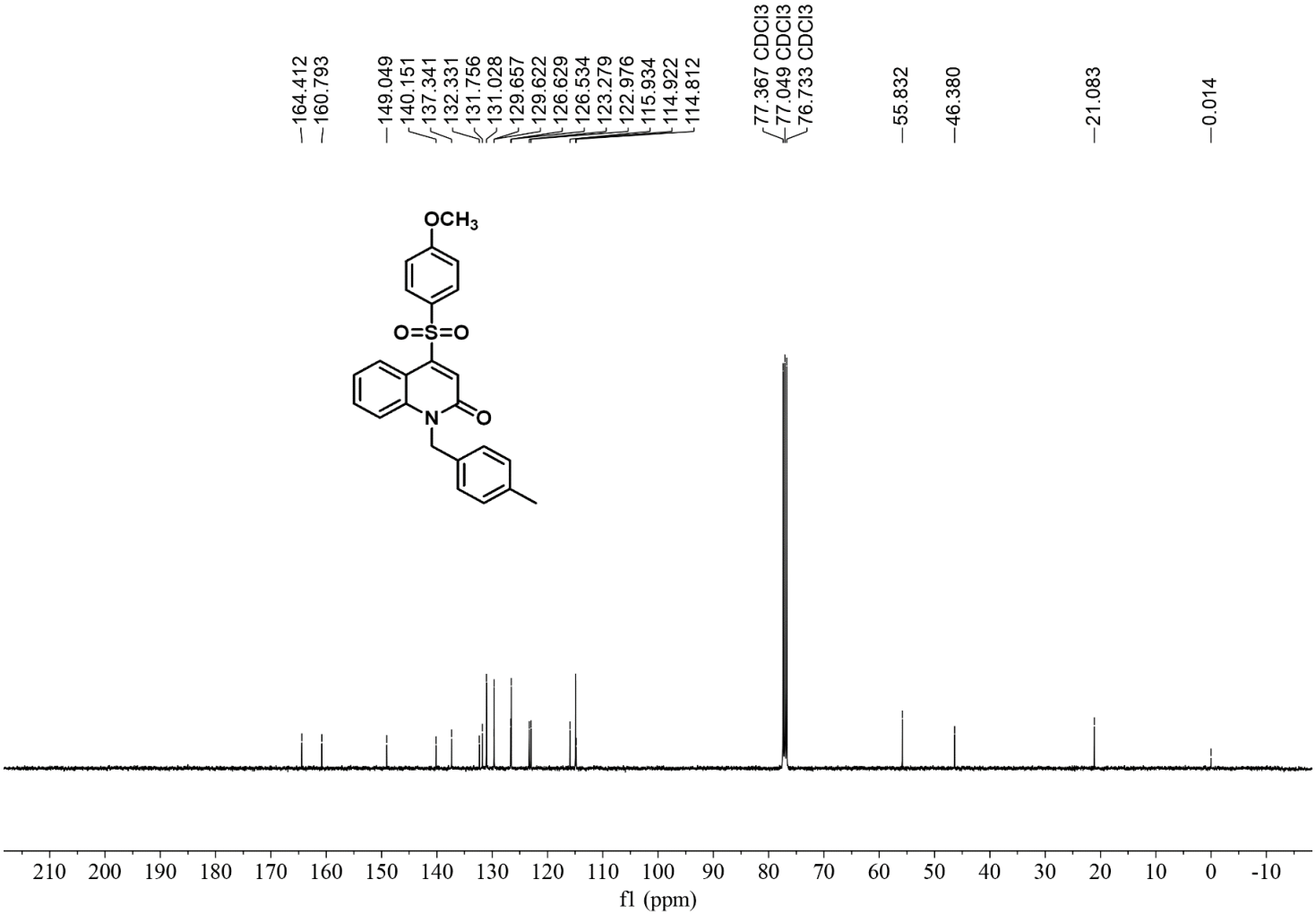
^{1}H NMR Spectrum of Compound 3ae



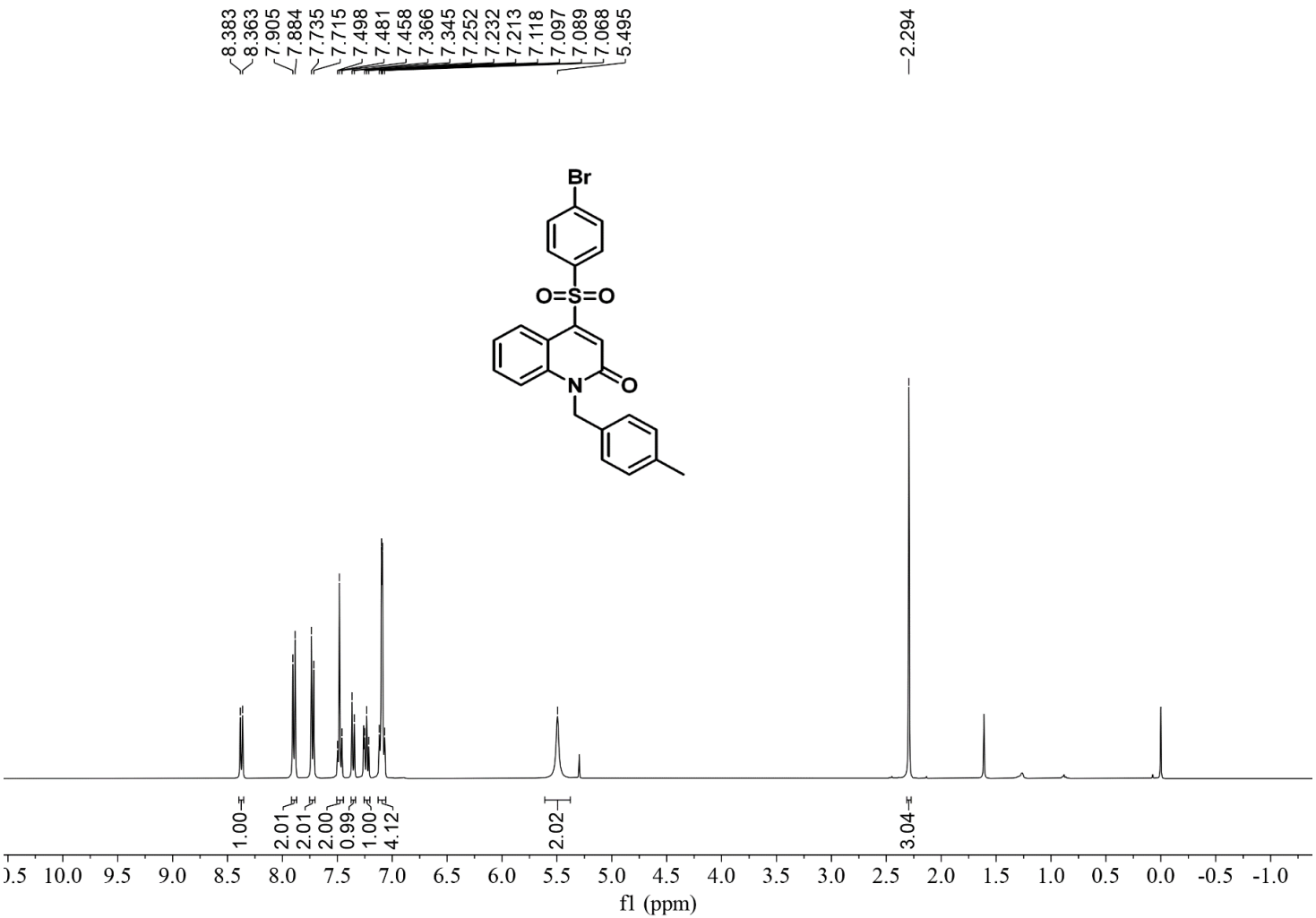
^{13}C NMR Spectrum of Compound 3ae



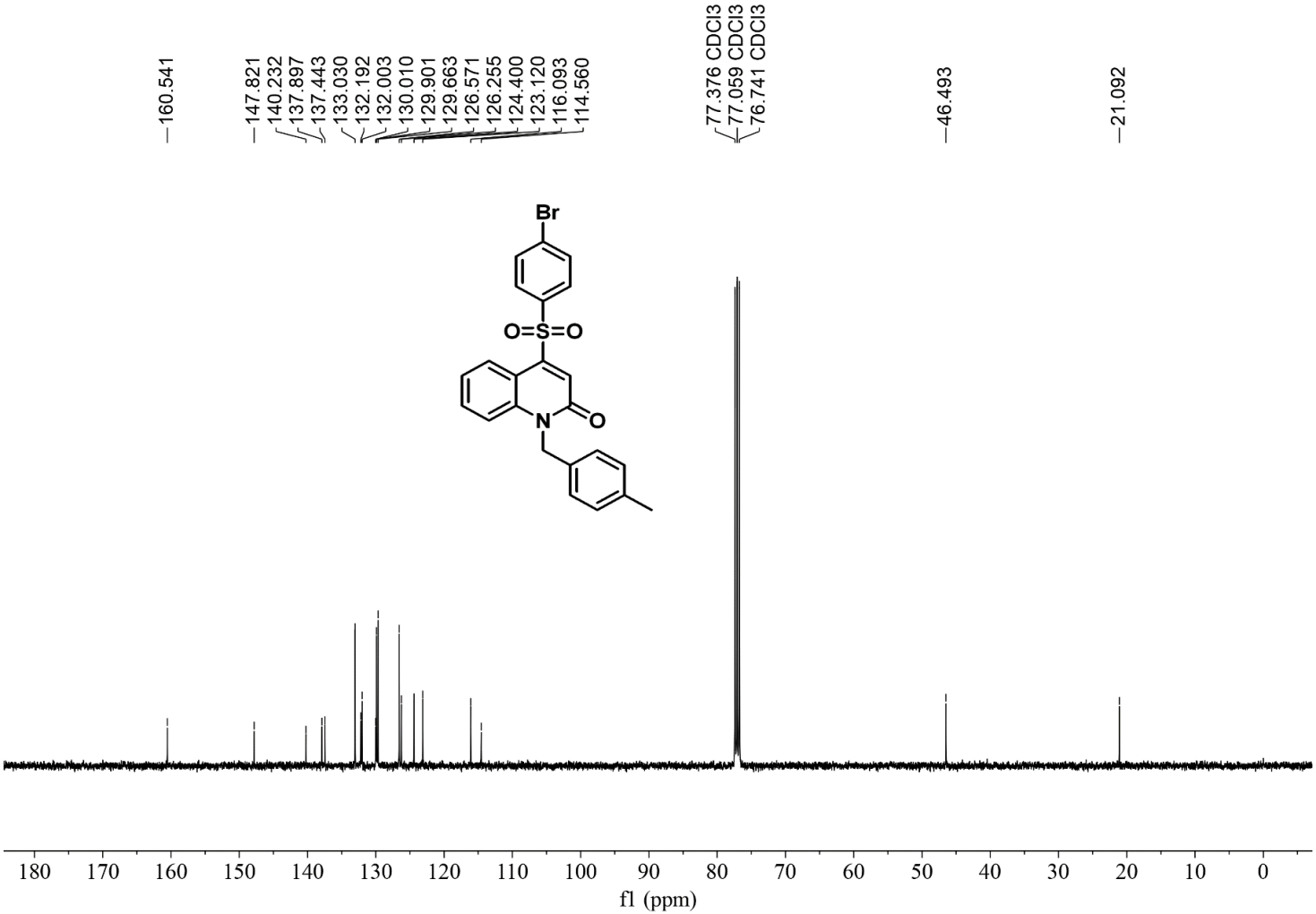
^{1}H NMR Spectrum of Compound 3af



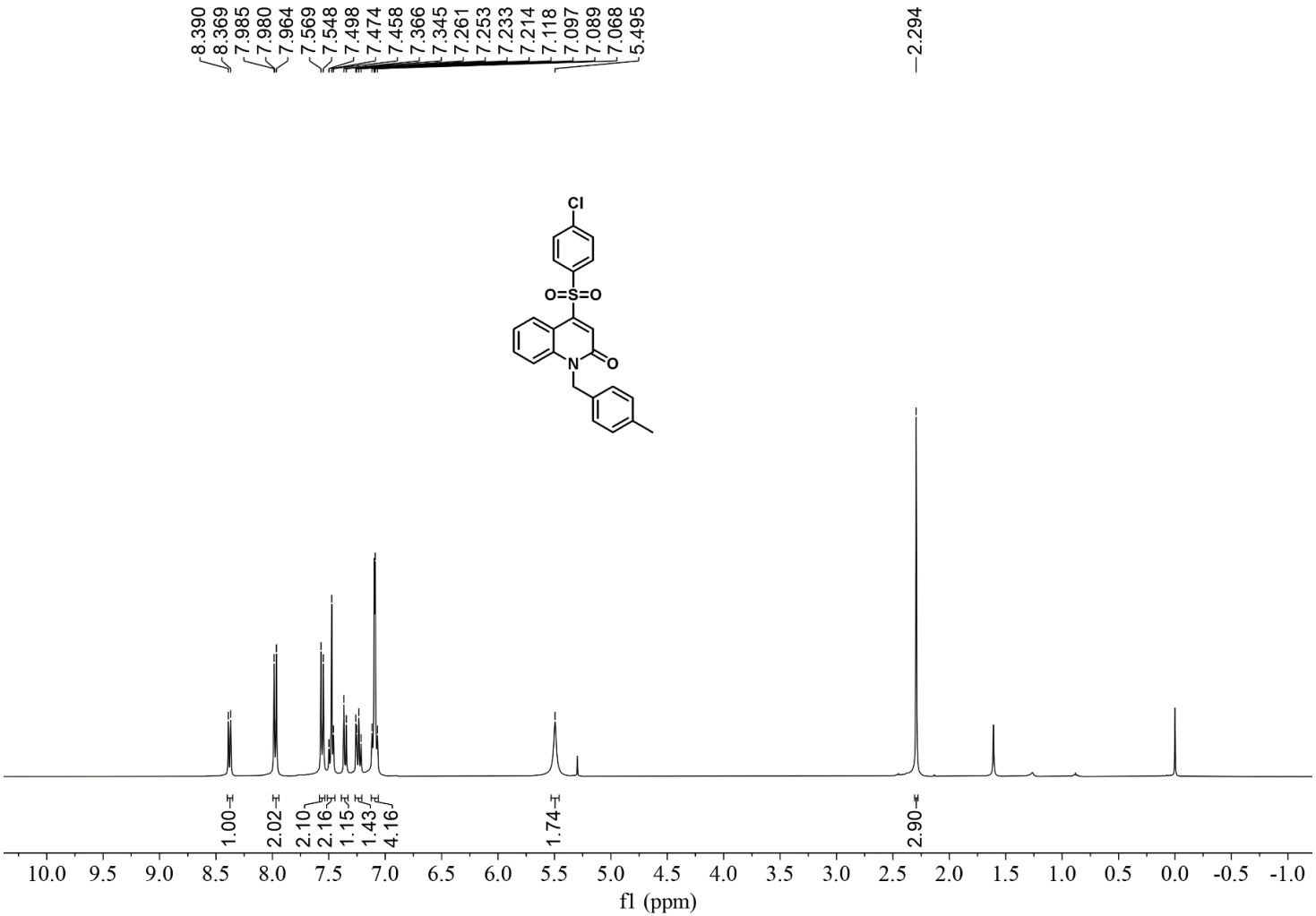
^{13}C NMR Spectrum of Compound 3af



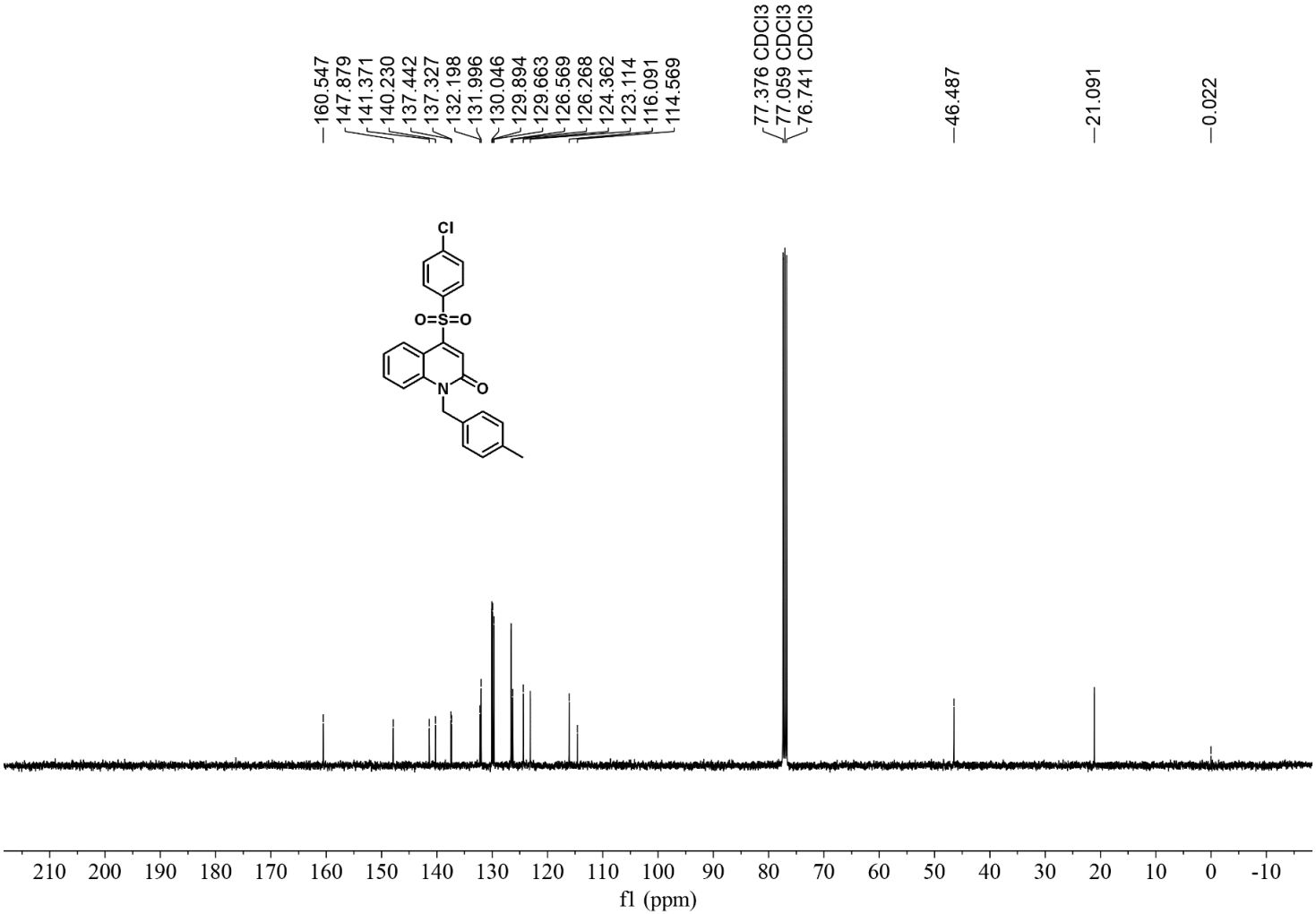
^{1}H NMR Spectrum of Compound 3ag



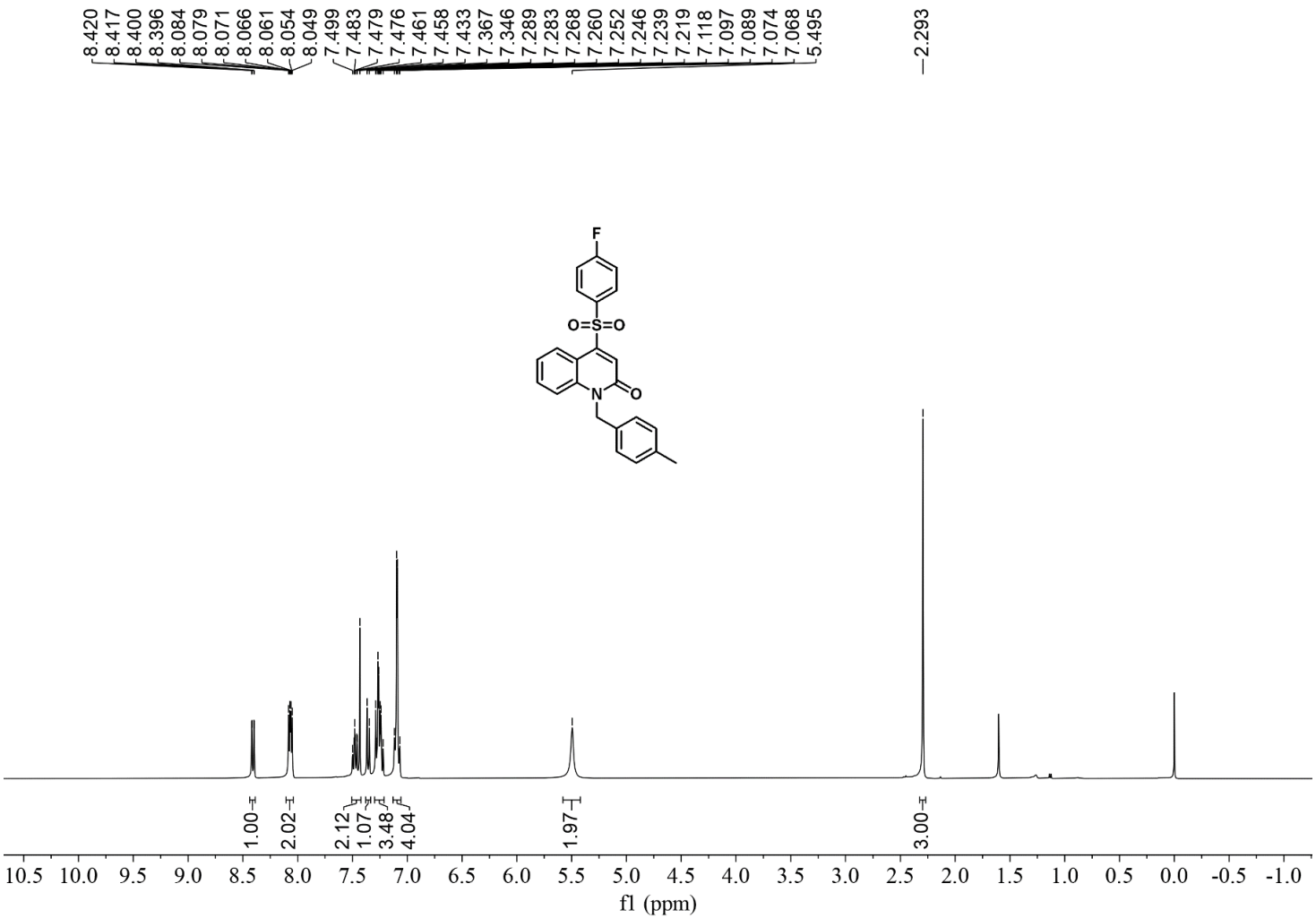
^{13}C NMR Spectrum of Compound 3ag



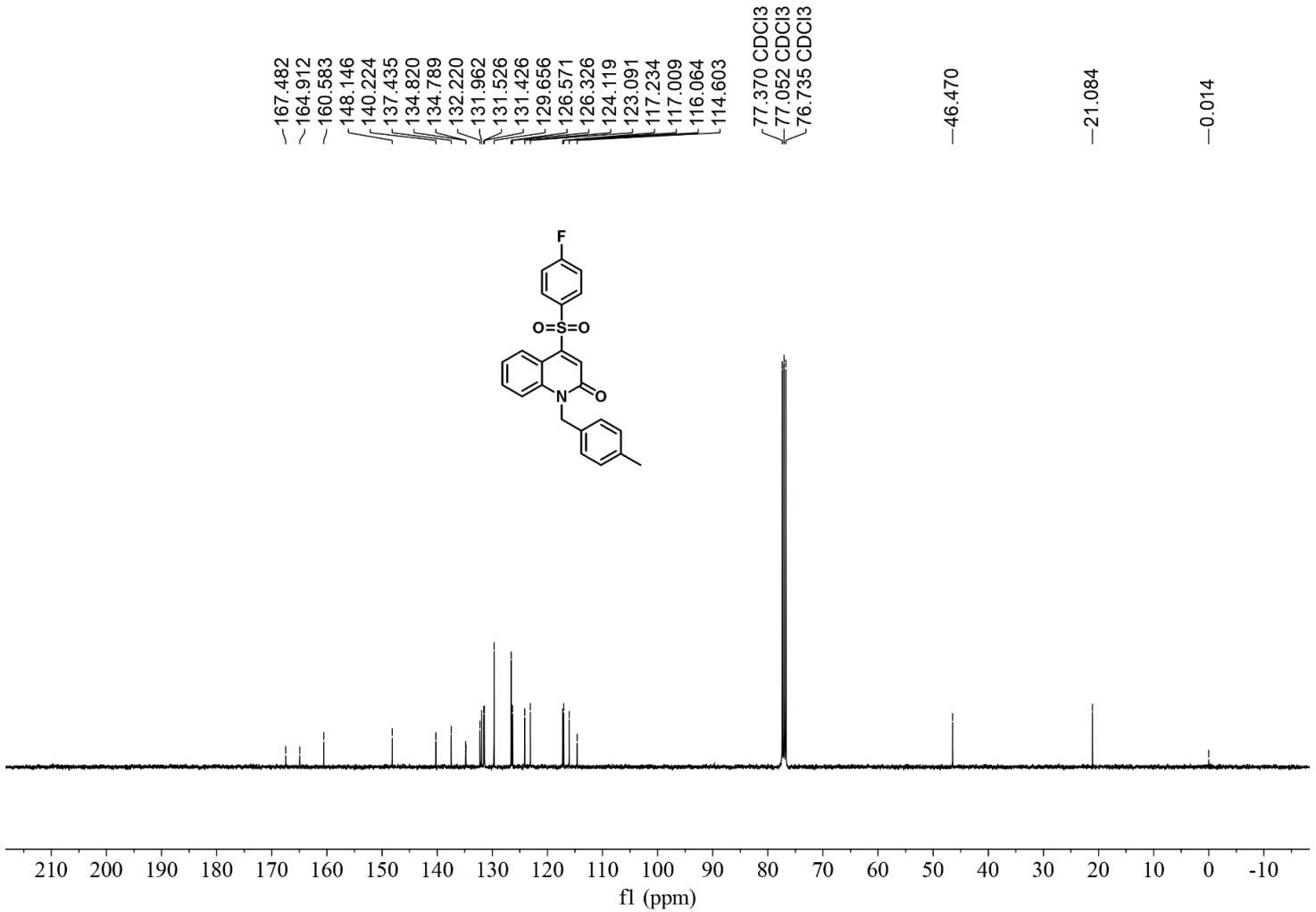
^{1}H NMR Spectrum of Compound 3ah



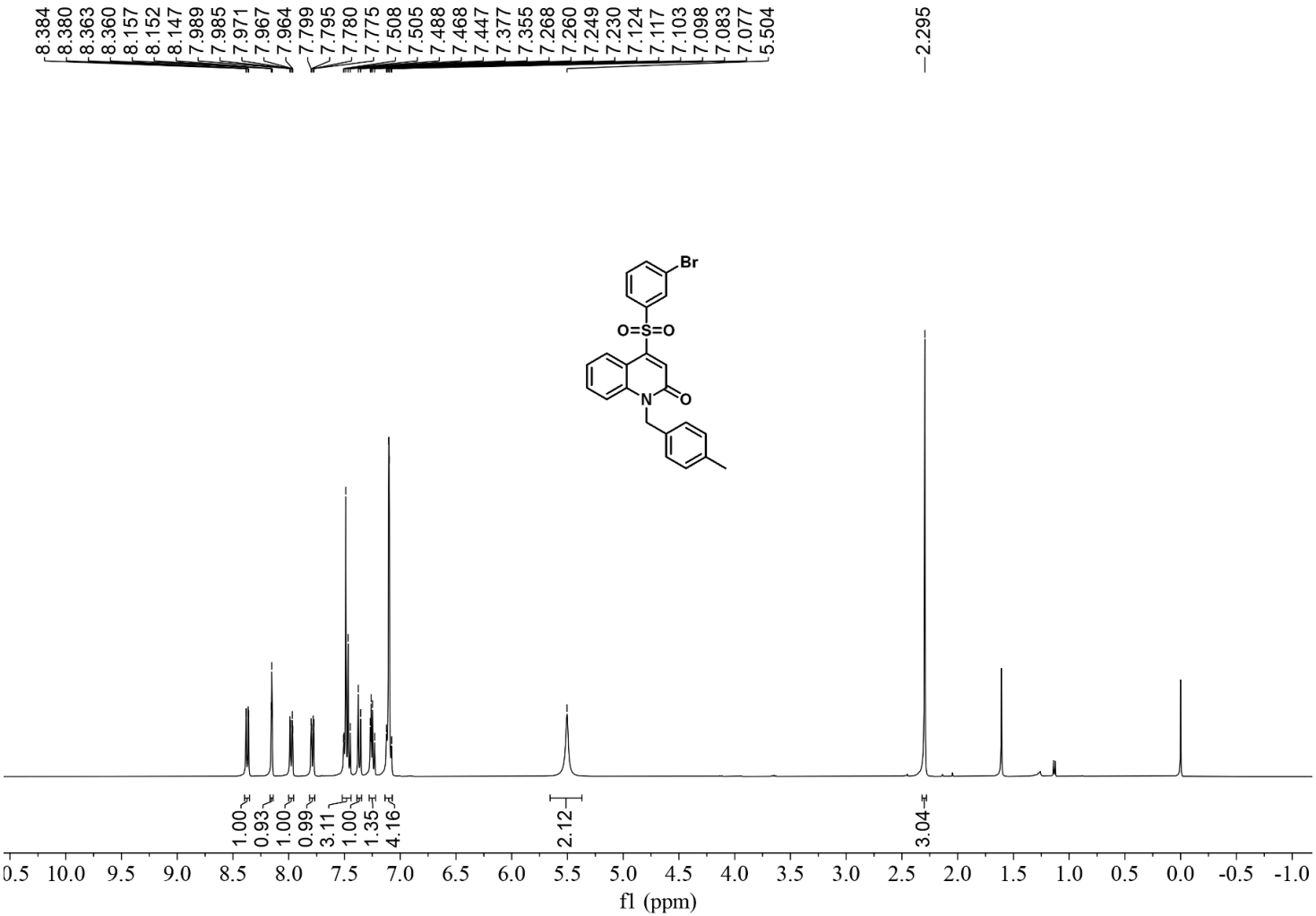
^{13}C NMR Spectrum of Compound 3ah



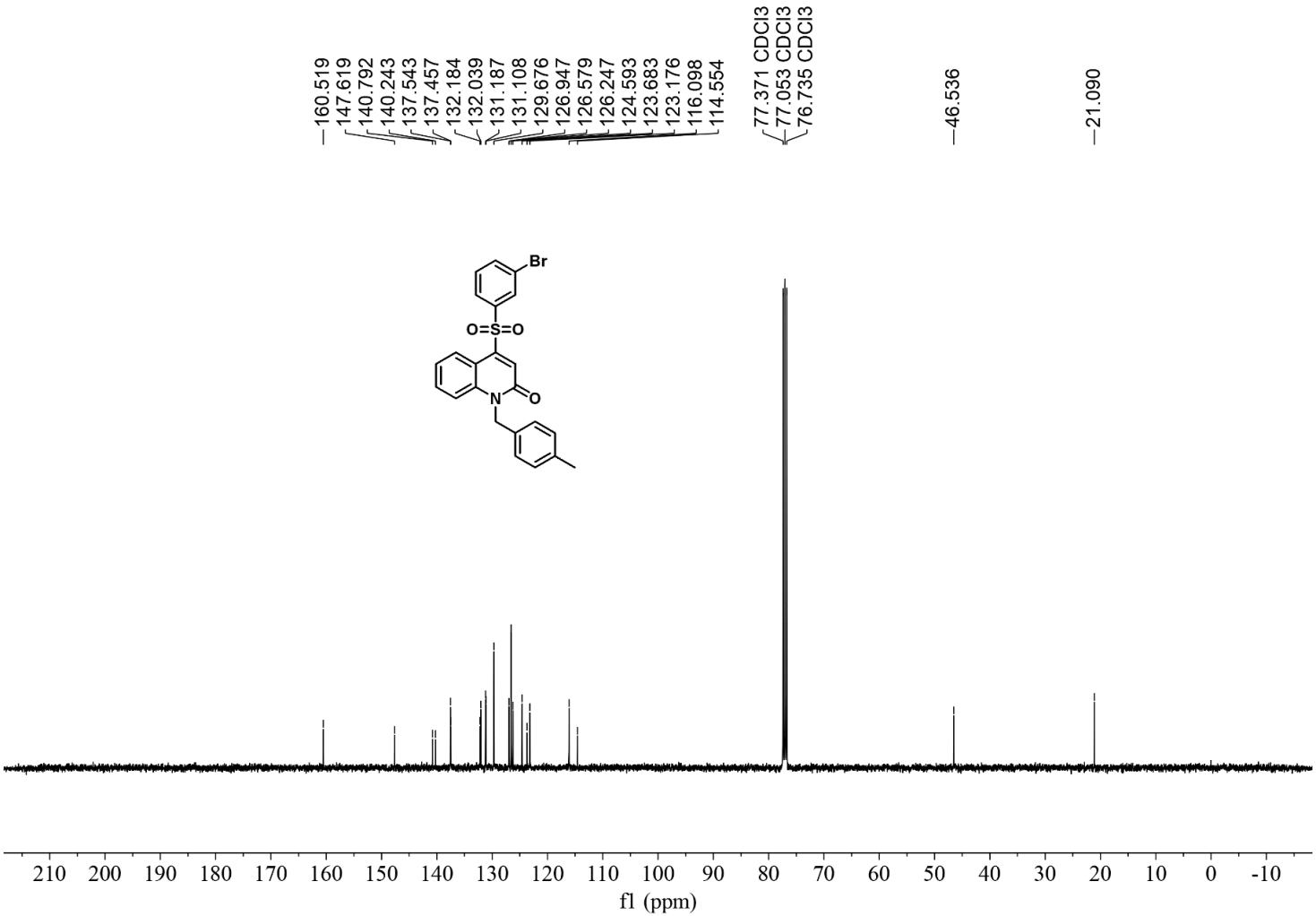
^{1}H NMR Spectrum of Compound 3ai



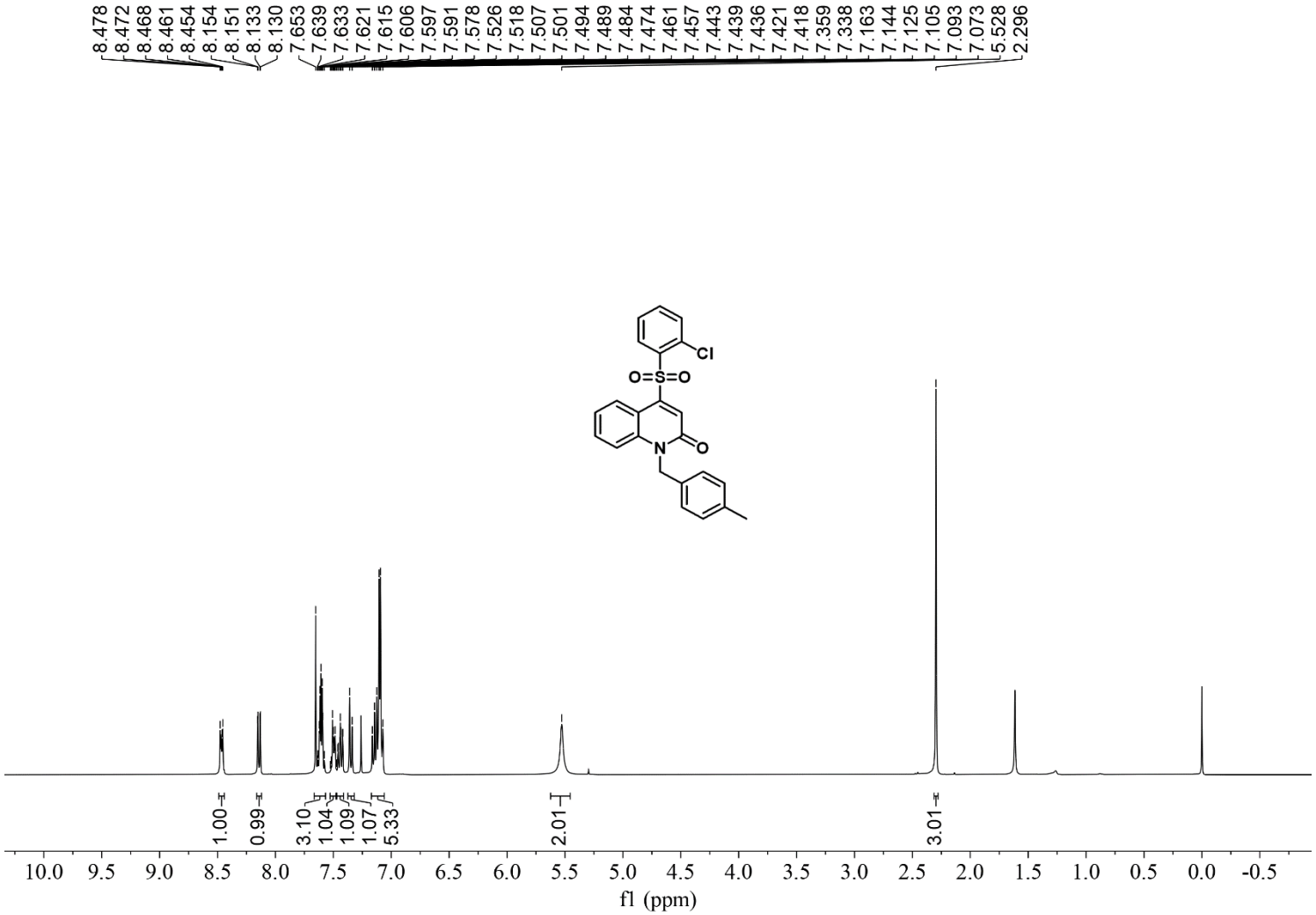
^{13}C NMR Spectrum of Compound 3ai



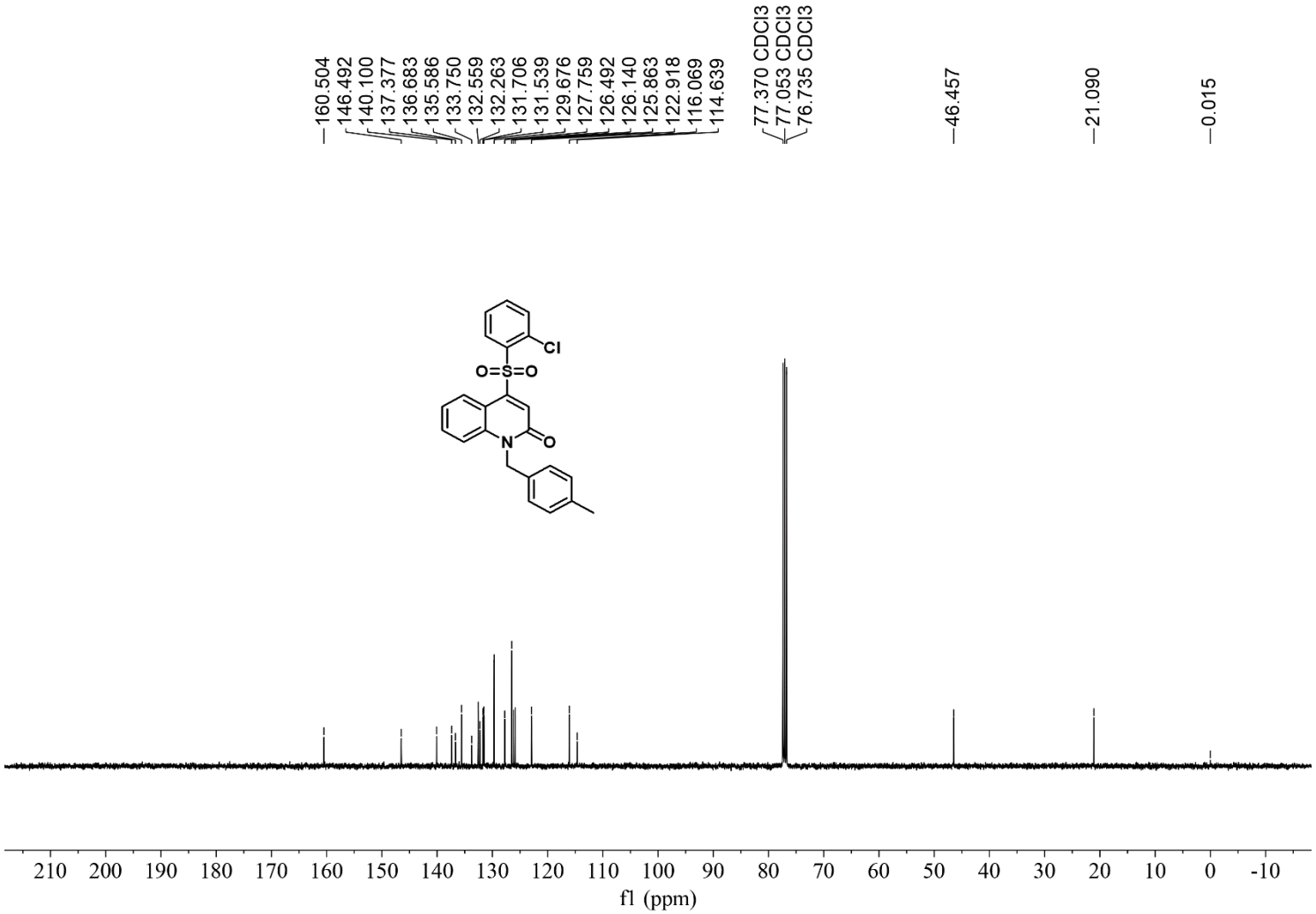
^{1}H NMR Spectrum of Compound 3aj



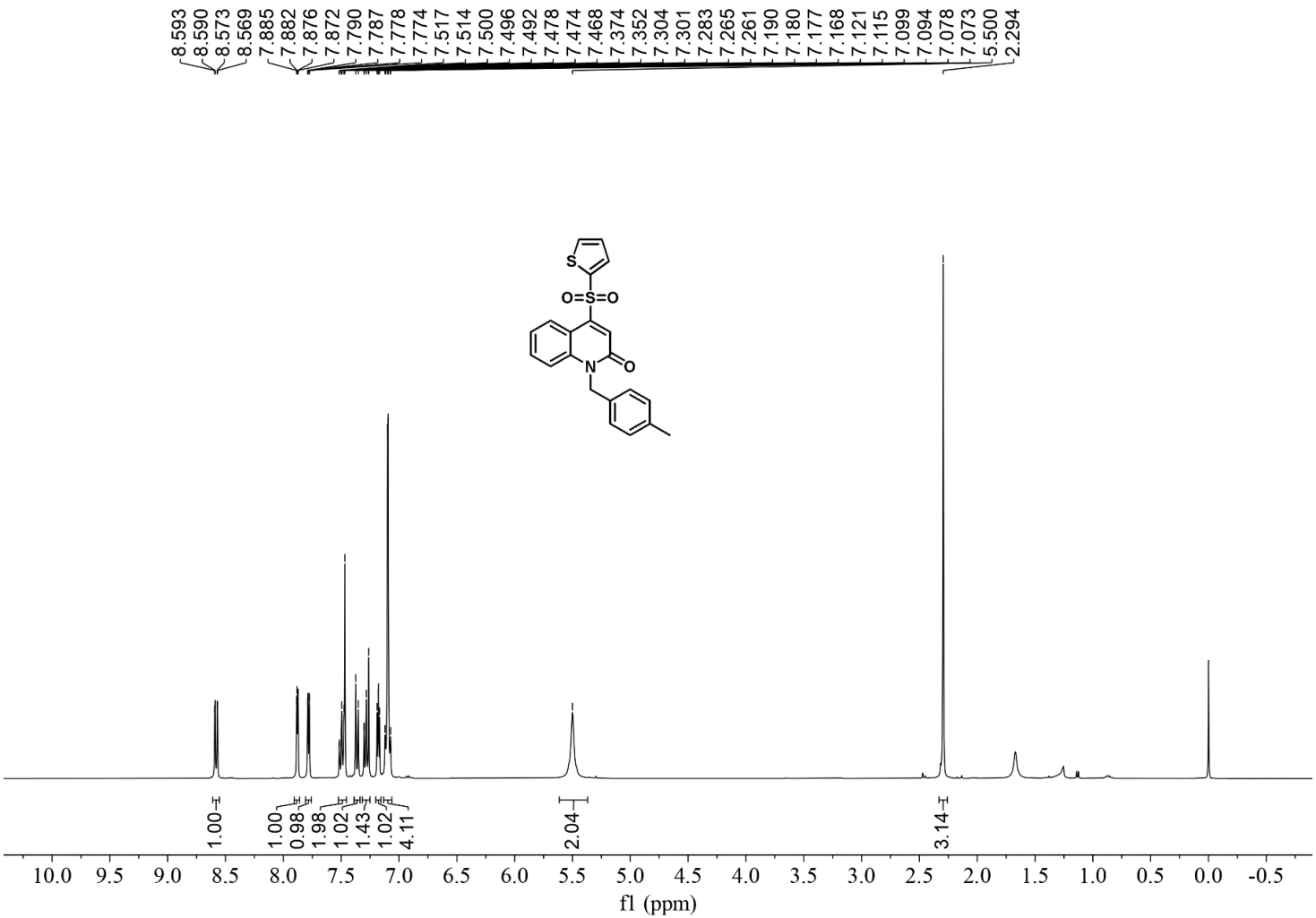
^{13}C NMR Spectrum of Compound 3aj



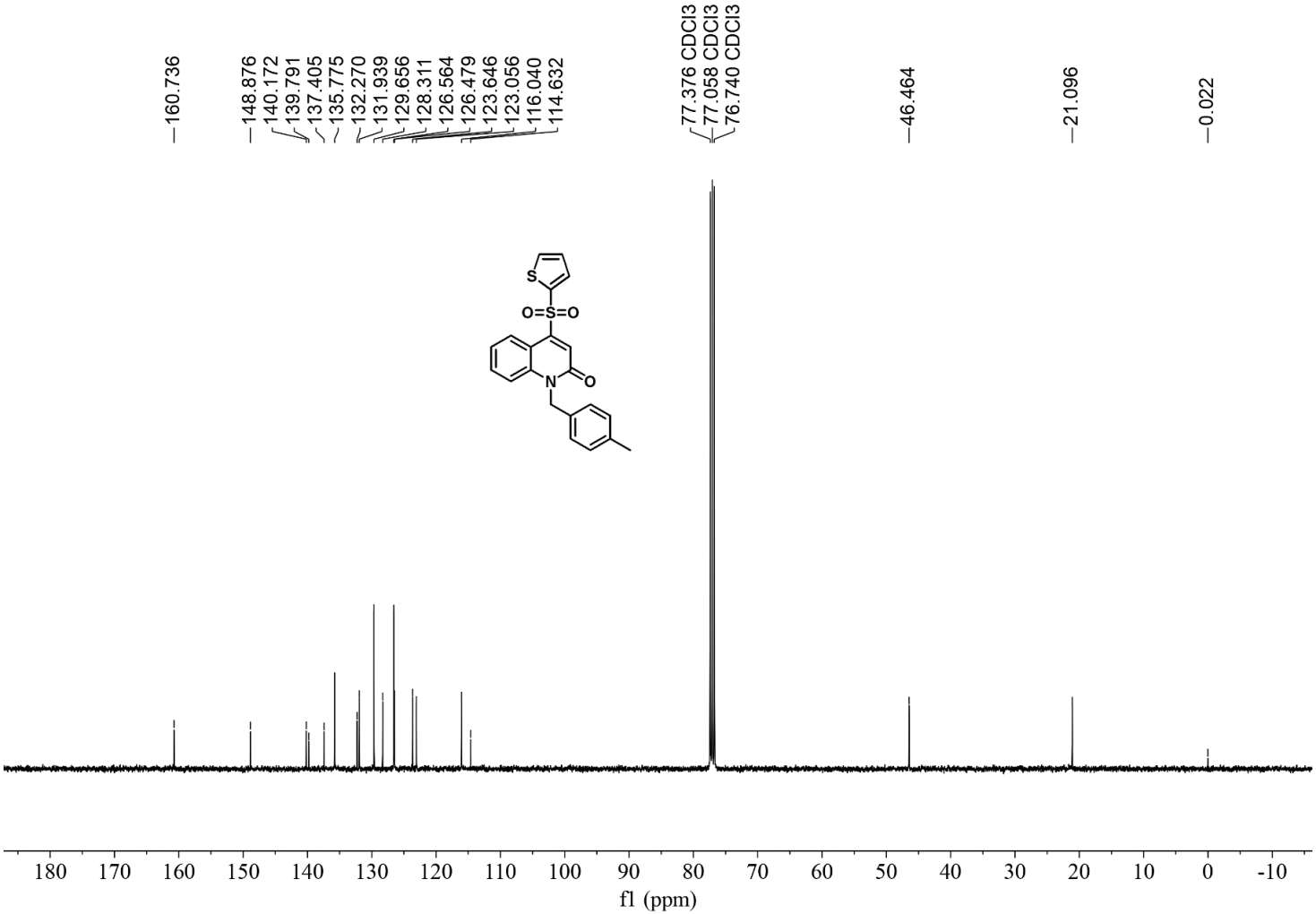
^{1}H NMR Spectrum of Compound 3ak



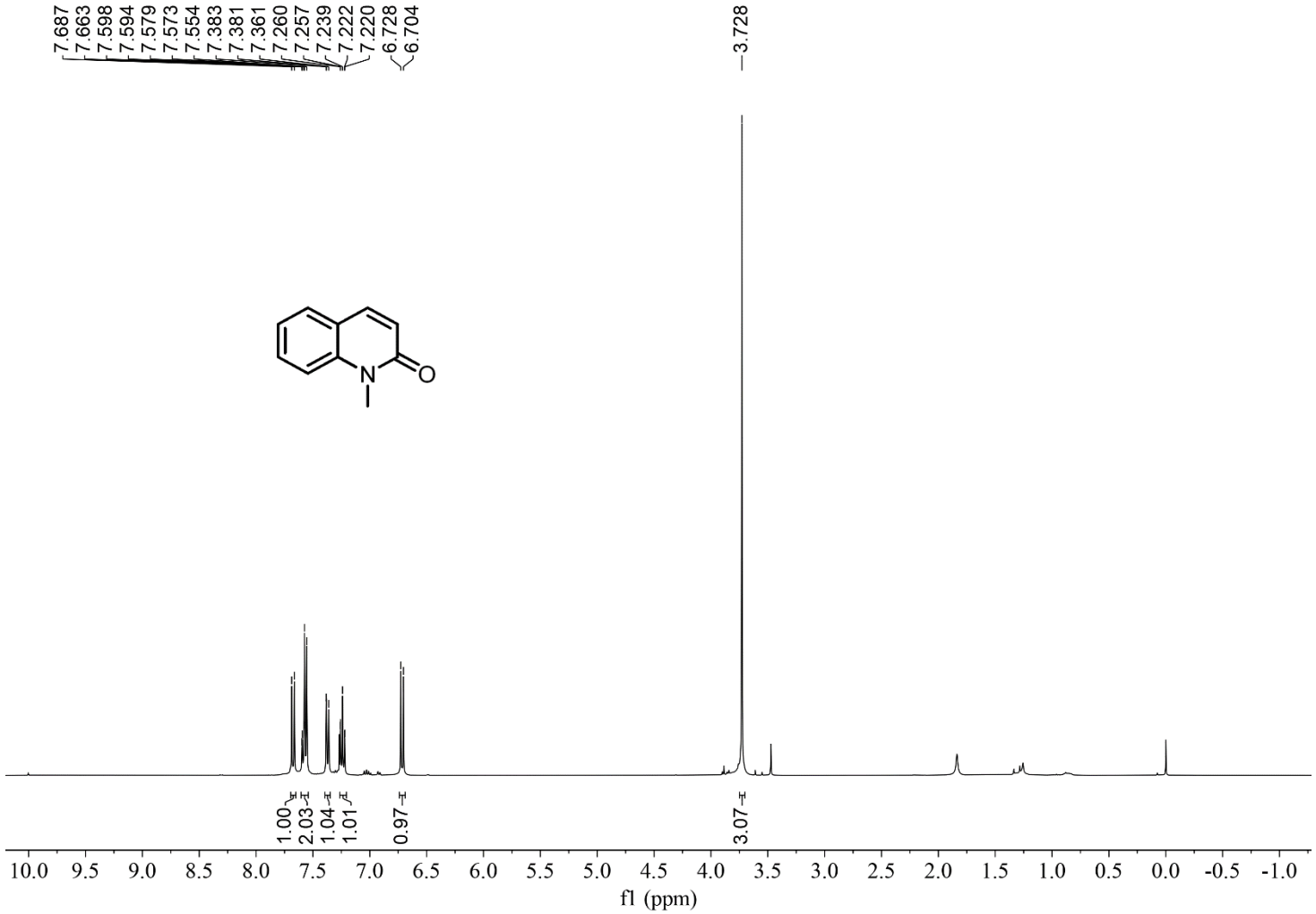
^{13}C NMR Spectrum of Compound 3ak



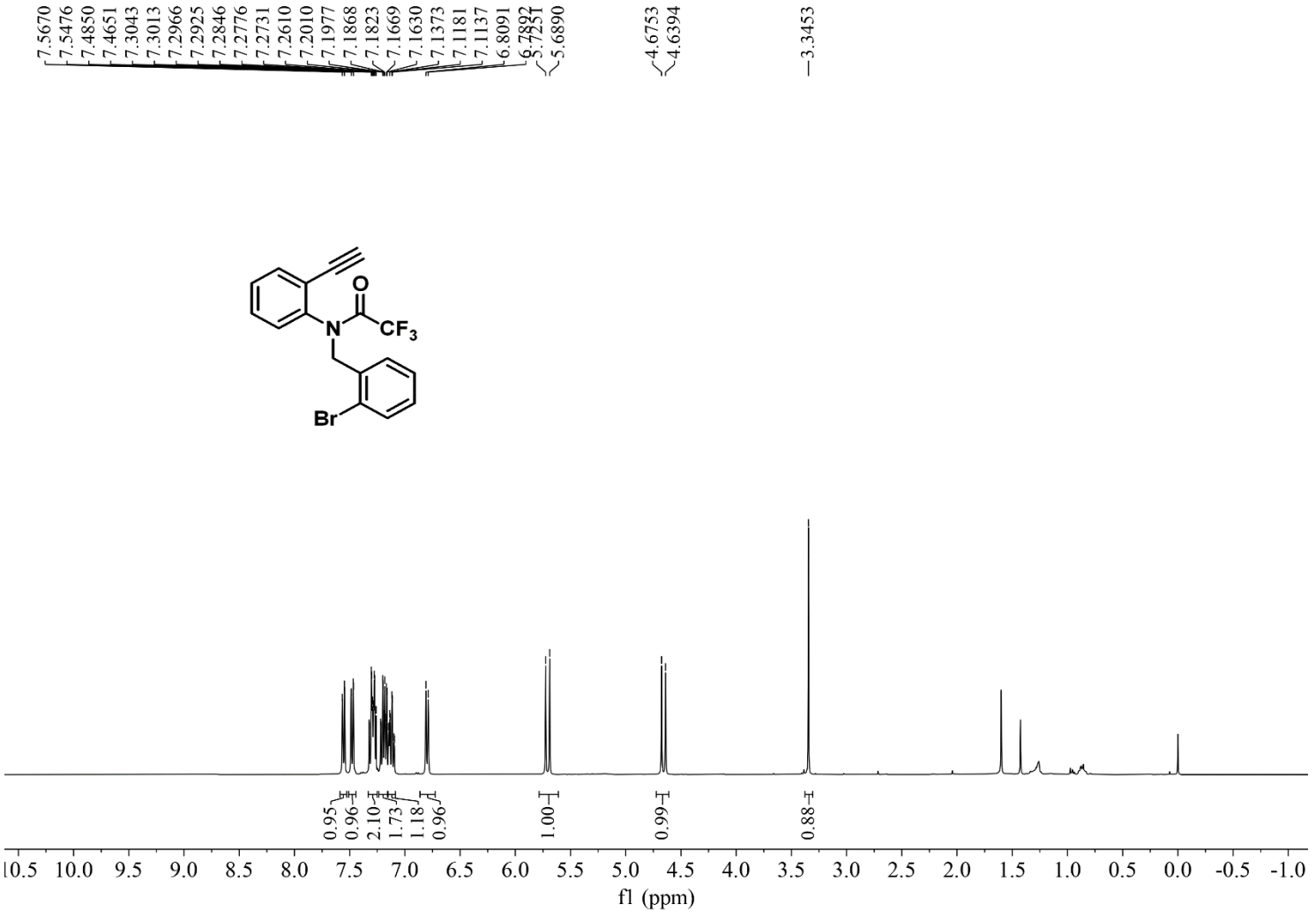
^{1}H NMR Spectrum of Compound 3al



^{13}C NMR Spectrum of Compound 3al



^{1}H NMR Spectrum of Compound 4



^{1}H NMR Spectrum of Compound 1o