DABCO-directed EDA-complex mediated regioselective C4-sulfonylation of quinoline *N*-oxide

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Contents:

1. General Information:

All the reagents were commercial grade and purified according to the established procedures. All the reagents were commercial grade and used without further purification unless otherwise stated. Thiosulfonates were prepared following the literature procedure from sodium salt of sulfinates and diphenyl disulfides and quinoline *N*-oxide were prepared from quinoline. All the reactions were carried out in an oven-dried 15 mL vial (see below). Reactions were monitored by thin layer chromatography (TLC) on a 0.25 mm silica gel plates ($60F_{254}$) and visualized under UV illumination at 254 nm. Organic extracts were dried over anhydrous sodium sulfate (Na_2SO_4). Column chromatography was performed to purify the crude product on silica gel 60–120 mesh using a mixture of hexane and ethyl acetate as eluent. The isolated compounds were characterized by spectroscopic [^1H, $^{13}C\{^1H\}$ NMR, and IR] techniques and HRMS analysis. NMR spectra were recorded in deuterochloroform ($CDCl_3$).^1H, $^{13}C\{^1H\}$ were recorded in 600 (151), 500 (126) or 400 (100) MHz spectrometer and were calibrated using tetramethylsilane or residual undeuterated solvent for ^1H NMR, deuterochloroform for ^{13}C NMR as an internal reference {$Si(CH_3)_4$: 0.00 ppm or $CHCl_3$: 7.260 ppm for ^1H NMR, 77.230 ppm for ^{13}C NMR}. ^{19}F NMR was calibrated without any internal standard in $CDCl_3$. The chemical shifts are quoted in δ units, parts per million (ppm). ^1H NMR data is represented as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets), integration and coupling constant(s) *J* in hertz (Hz). High-resolution mass spectra (HRMS) were recorded on a mass spectrometer using electrospray ionization-time of flight (ESI-TOF) reflection experiments. FT-IR spectra were recorded in neat and reported in the frequency of absorption (cm^{-1}). All UV experiments were performed in 1 mL quartz cuvettes of path length 1 cm at 25 ^oC on a UV-Vis spectrometer in HPLC-grade DMSO.

2. Light Information and Reaction Setup:

Philips 2 x 10 W white LEDs (flux 46 mW/cm^2) were used as the light source for this light-promoted reaction, and no filter was used. Borosilicate 15 mL vial was used as the reaction vessel. The distance from the light source to the irradiation vessel was ~6–8 cm. A Regular fan was used to ventilate the area to maintain the room temperature (27–30 ^oC). The reaction set-up for this photochemical reaction is shown below (Figure S1).

Figure S1. Photochemical reaction set-up.

3. Biologically Active Quinoline-Containing Sulfones and Sulfonamides:

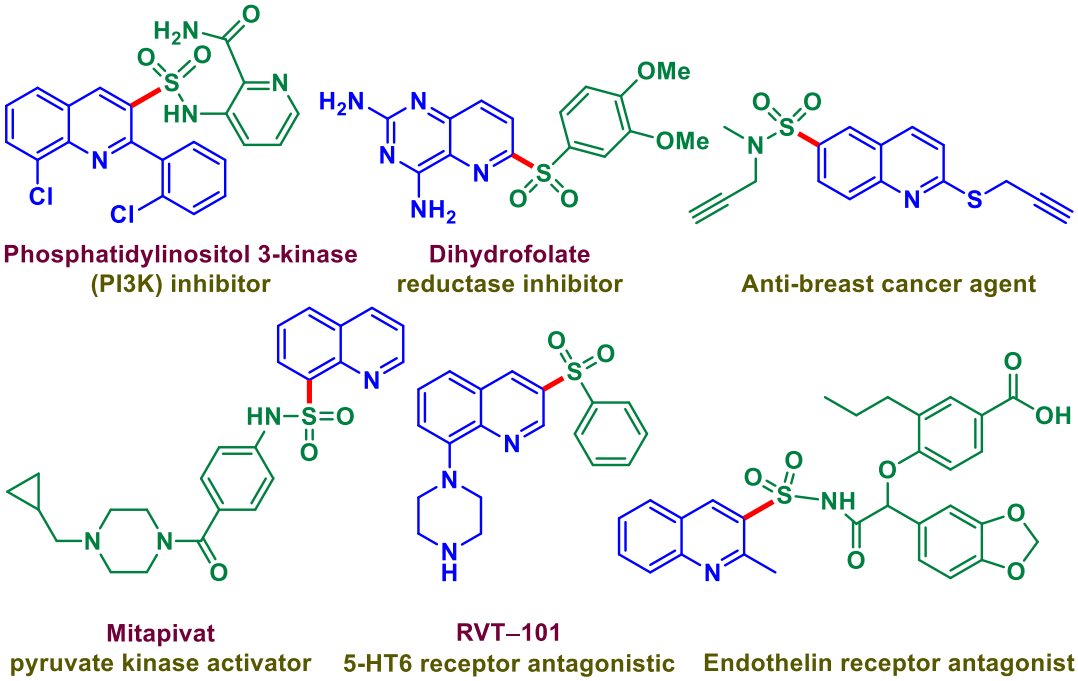


Figure S2. Biologically active quinoline-containing sulfones and sulfonamides.

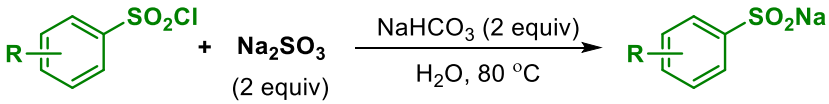
4. General Procedure:

(A) General Procedure for the Synthesis of Thiosulfonates (a–n):

Compounds (**a–n**) were synthesized by following the slightly modified literature procedures.[1]

(i) Procedure for the Synthesis of Sodium Sulfinates:

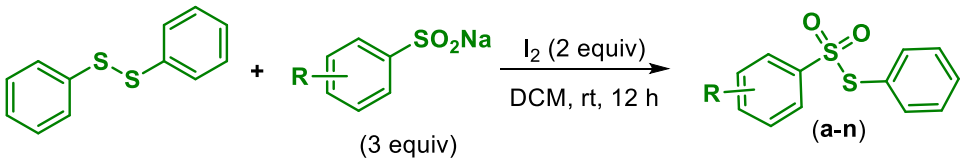
An oven-dried 50 mL round bottom flask containing a magnetic bead was added 4-methylbenzenesulphonyl chloride (1.90 g, 10 mmol), sodium sulfite (2.50g, 20 mmol), sodium bicarbonate (1.68 g, 20 mmol) in 10 mL H_2O and stirred at 80 ^oC for 4 h. After completion of the reaction (monitored by TLC analysis), water was removed by rotary evaporator. The remaining solid was then extracted using a vacuum pump and recrystallized in ethanol to obtain a white solid product (Scheme S1).



Scheme S1. Synthesis of sodium sulfinate.

(ii) Procedure for the Synthesis of Thiosulfonates (a–n):

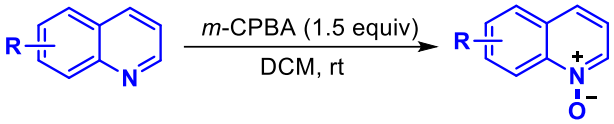
An oven-dried 50 mL round-bottom flask containing a magnetic bead was added diphenyldisulfide (0.44 g, 2 mmol), 4-methylbenzenesulfinate (1.06 g, 6 mmol), I_2 (1.01 g, 4 mmol) in DCM (10 mL). The reaction was stirred at room temperature for 12 h. After completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with DCM (25 mL) and washed with water (10 mL), followed by 5% sodium thiosulfate (10 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 5% ethyl acetate in hexane to give pure thiosulfonates (**k**) (0.470 g, 89%) (Scheme S2).



Scheme S2. Synthesis of thiosulfonates.

(iii) Procedure for the Synthesis of Quinoline *N*-Oxides:[1a]

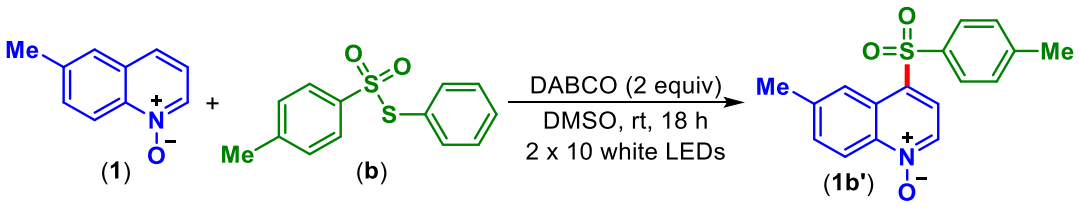
An oven-dried 25 mL round-bottom flask containing a magnetic bead was added quinoline (1 equiv, 5 mmol) in DCM and was stirred at 0 °C for 10 min. *m*-Chloroperbenzoic acid (*m*-CPBA, 1.5 equiv) was then added to the reaction mixture portion-wise. After the addition was complete, the reaction was allowed to come to room temperature (25 °C) and stirred for an additional 6 hours. After completion of the reaction, a saturated solution of $NaHCO_3$ (15 mL) was added to the reaction mixture to neutralize the excess acid and then it was extracted using DCM (20 mL × 3). It was dried with Na_2SO_4 and concentrated under reduced pressure. The crude was then purified by column chromatography on silica with ethyl acetate to afford the quinoline *N*-oxide as desired product (Scheme S3).



Scheme S3. Synthesis of quinoline *N*-oxides.

(B) Procedure for the Synthesis of 6-Methyl-4-tosylquinoline 1-oxide (1b′):

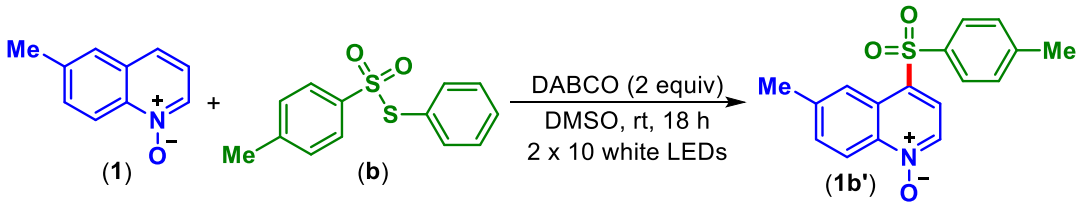
An oven-dried 15 mL vial containing a magnetic bead was added 6-methylquinoline 1-oxide (**1**) (0.032 g, 0.2 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (**b**) (0.105 g, 0.4 mmol), DABCO (0.044 g, 0.4 mmol), in DMSO (1 mL) under a nitrogen atmosphere. The reaction mixture was stirred at room temperature, maintaining an approximate distance of ~6–8 cm from two 10 W white LEDs for 18 h. After completion of the reaction (monitored by TLC analysis), the crude product so obtained was purified over a column of silica gel using 50% ethyl acetate in hexane to give pure 6-methyl-4-tosylquinoline 1-oxide (**1b′**) in 75% yield (47 mg) (Scheme S4). The identity and purity of the product were confirmed by spectroscopic analysis.



Scheme S4. Synthesis of 6-methyl-4-tosylquinoline 1-oxide (**1b′**).

(C) Large-Scale Synthesis of 6-Methyl-4-tosylquinoline 1-oxide (1b′):

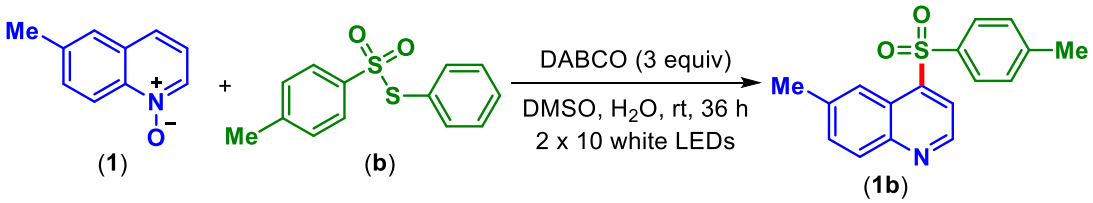
An oven-dried 25 mL vial was added 6-methylquinoline 1-oxide (**1**) (0.16 g, 1 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (**b**) (0.528 g, 2 mmol), DABCO (0.224 g, 2 mmol), in DMSO (3 mL) under a nitrogen atmosphere. The reaction mixture was stirred at room temperature, maintaining an approximate distance of ~6–8 cm from two 10 W white LEDs for 18 h. After completion of the reaction (monitored by TLC analysis), The crude product so obtained was purified over a column of silica gel using 50% ethyl acetate in hexane to give pure 6-methyl-4-tosylquinoline 1-oxide (**1b′**) in 62% yield (196 mg) (Scheme S5).



Scheme S5. Synthesis of 6-methyl-4-tosylquinoline 1-oxide (**1b′**).

(D) Procedure for the Synthesis of 6-Methyl-4-tosylquinoline (1b):

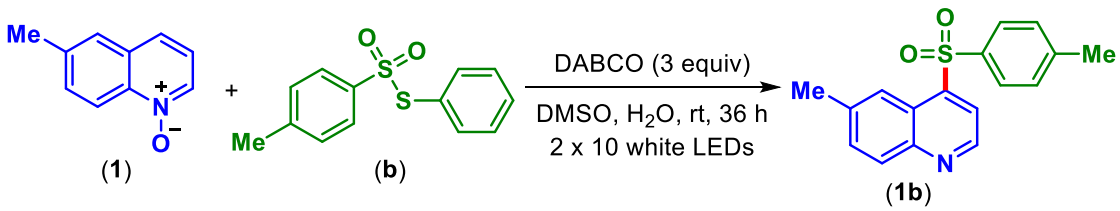
An oven-dried 15 mL vial was added 6-methylquinoline 1-oxide (**1**) (0.032 g, 0.2 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (**b**) (0.158 g, 0.6 mmol), DABCO (0.067 g, 0.6 mmol), in DMSO: H_2O (1 mL, 9:1) under a nitrogen atmosphere. The reaction mixture was stirred at room temperature, maintaining an approximate distance of ~6–8 cm from two 10 W white LEDs for 36 h. After completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with ethyl acetate (20 mL) and washed with ice-cooled water (10 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 30% ethyl acetate in hexane to give pure 6-methyl-4-tosylquinoline (**1b**) in 76% yield (45.5 mg) (Scheme S6). The identity and purity of the product were confirmed by spectroscopic analysis.



Scheme S6. Synthesis of 6-methyl-4-tosylquinoline (**1b**).

(E) Large-Scale Synthesis of 6-Methyl-4-tosylquinoline (1b):

An oven-dried 25 mL vial was added 6-methylquinoline 1-oxide (**1**) (0.16 g, 1 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (**b**) (0.79 g, 3 mmol), DABCO (0.34 g, 3 mmol), in DMSO: H_2O (3 mL, 9:1) under a nitrogen atmosphere. The reaction mixture was stirred at room temperature, maintaining an approximate distance of ~6–8 cm from two 10 W white LEDs for 36 h. After completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with ethyl acetate (30 mL) and washed with ice-cooled water (20 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 30% ethyl acetate in hexane to give pure 6-methyl-4-tosylquinoline (**1b**) in 66% yield (197 mg) (Scheme S7).



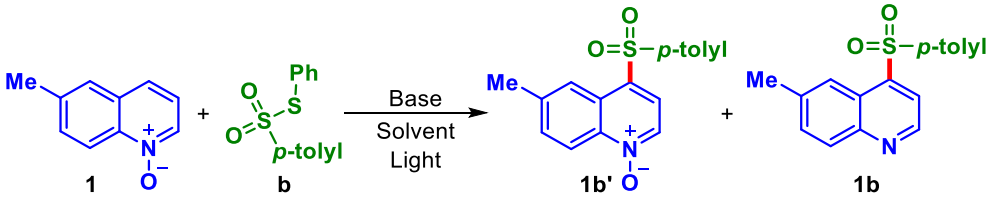
Scheme S7. Synthesis of 6-methyl-4-tosylquinoline (**1b**).

5. Optimization of Reaction Conditions:

6-methyl quinoline *N*-oxide (**1**) was reacted with *S*-phenyl 4-methylbenzenesulfonothioate (**b**) in the presence of Et_3N in DMSO under irradiation of 2 × 10 W blue LEDs (448 nm) under N_2 atmosphere. Gratifyingly, in addition to C4 sulfonylated quinoline *N*-oxide (**1b′**), a deoxygenated C4 sulfonylated quinoline (**1b**) were obtained in 21% and 9% yields, respectively (Table S1, entry 1) without giving any C2 sulfonylated product. With such a low yield of the products, we sought

to find the optimal reaction conditions for the exclusive formation of **1b′** and **1b**. For this purpose, various reaction parameters such as solvent, base, atmosphere, and light sources were systematically screened. Initially, a range of organic and inorganic bases were evaluated. Organic bases such as DIPEA, DBU, DBN, DABCO and DMAP afforded the C4 sulfonylated quinoline *N*-oxide product (**1b′**) in 18%, 47%, 45%, 53%, and 5% yield, respectively (Table S1, entries 2–6). Further, inorganic bases such as Cs_2CO_3 and KOH failed to give any of the C4 sulfonylated product (**1b′**) or (**1b**) (Table S1, entries 7 and 8). Accordingly, DABCO was found the most effective base for the formation of the C4 sulfonylated quinoline *N*-oxide product (**1b′**). Next, a series of solvents including DMF, MeCN, DCM, MeOH, 1,4-dioxane, DCE, and THF were screened, but none of them were effective in improving the yield of the C4 sulfonylated quinoline *N*-oxide (**1b′**) (Table S1, entries 9–15). Alternative light sources such as white and green were also examined, revealing that white LEDs improved the yield of **1b′** to 76%, whereas green LEDs was found less efficient (Table S1, entries 16 and 17). Increasing the loading of DABCO to 3 equiv had no significant effect on the yield of **1b′**; however, reducing it to 1 equiv curbed the yield to 42% (Table S1, entries 18 and 19). Next, we focused on improving the yield of C4 sulfonylated quinoline **1b**, assuming that a proton source would be required for the removal of the *N*-oxide. Accordingly, water was added as a proton source by employing a DMSO/H_2O (9:1) solvent system and interestingly, this resulted in an increment in the yield of the product **1b** to 29% (Table S1, entry 20). To further improve the yield of **1b**, the amounts of thiosulfonate and DABCO were increased up to 3 equivalents, and the reaction time was extended to 36 h, which enhanced the yield to 45% and 75%, respectively (Table S1, entries 21 and 22). Moreover, in the absence of base, light, and N_2, no product was formed at all (Table S1, entries 23–25). Thus, the optimized condition for the formation of C4 sulfonylated quinoline *N*-oxide (**1b′**) was the use of 6-methyl quinoline *N*-oxide (**1,** 0.2 mmol) with *S*-phenyl 4-methylbenzenesulfonothioate (**b,** 0.4 mmol) in the presence of DABCO (0.4 mmol) in DMSO under the irradiation of 20 W white LEDs under N_2 atmosphere for 18 h. On the other hand the optimized condition for the C4 sulfonylated quinoline (**1b**) formation was found to be the use of 6-methyl quinoline *N*-oxide (**1**, 0.2 mmol),*S*-phenyl 4-methylbenzenesulfonothioate (**b**, 0.6 mmol) in the presence of DABCO (0.6 mmol) in DMSO: H_2O (9:1) under the irradiation of 20W white LEDs in an atmosphere of N_2 for 36 h.

Table S1. Optimization of reaction conditions.



Entry	Base (equiv)	Solvent	Light	Yield (%) 1b′/1b
1	Et_3N (2)	DMSO	Blue	21/9
2	DIPEA (2)	DMSO	Blue	18/7
3	DBU (2)	DMSO	Blue	47/11
4	DBN (2)	DMSO	Blue	45/9
5	DABCO (2)	DMSO	Blue	53/15
6	DMAP (2)	DMSO	Blue	5/trace
7	Cs_2CO_3 (2)	DMSO	Blue	n.d/n.d
8	KOH (2)	DMSO	Blue	n.d/n.d
9	DABCO (2)	DMF	Blue	41/12
10	DABCO (2)	MeCN	Blue	14/trace
11	DABCO (2)	DCM	Blue	23/12
12	DABCO (2)	MeOH	Blue	18/13
13	DABCO (2)	1,4-Dioxane	Blue	n.d/n.d
14	DABCO (2)	DCE	Blue	n.d/n.d
15	DABCO (2)	THF	Blue	n.d/n.d
16	**DABCO (2)**	**DMSO**	**White**	**76/08**
17	DABCO (2)	DMSO	Green	45/09
18	DABCO (3)	DMSO	White	78/09
19	DABCO (1)	DMSO	White	42/trace
20	DABCO (2)	DMSO/H_2O	White	43/29
[c]21	DABCO (3)	DMSO/H_2O	White	27/45
[d]22	**DABCO (3)**	**DMSO/H_2O**	**White**	**09/75**
23	-	DMSO	White	n.d/n.d
[e]24	DABCO (2)	DMSO	-	n.d/n.d
[f]25	DABCO (2)	DMSO	White	n.d/n.d

[a]Reaction Conditions unless specified otherwise: **1** (0.2 mmol), **b** (0.4 mmol), base (2 equiv), solvent (1 mL) in 2 x 10 W LEDs for 18 h under N_2. [b]Isolated yield, [c]**b** (0.6 mmol), [d]**b** (0.6 mmol) and reaction time for 36 h, [e]reaction in dark, [f]open air, n.d. = not detected.

6. General Procedures of Mechanistic Investigation:

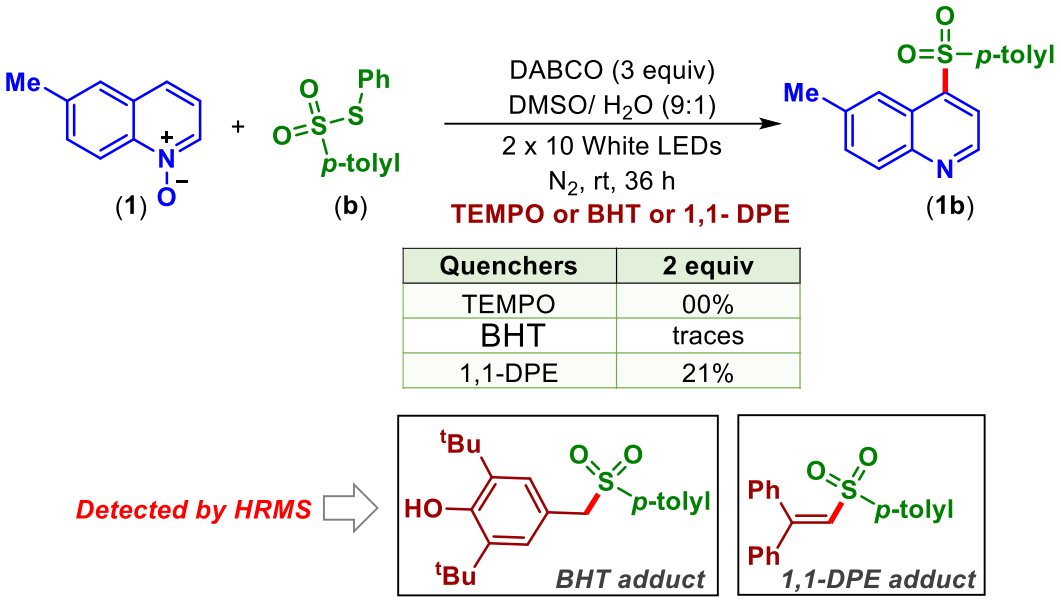
(A) Procedure for Radical-Trapping Experiments:

Three sets of oven-dried 15 mL vials containing a magnetic bead each were added 6-methylquinoline 1-oxide (**1**) (0.032 g, 0.2 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (**b**) (0.158 g, 0.6 mmol), DABCO (0.067 g, 0.6 mmol). To each of these three sets, a radical scavenger (i) (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (0.062 g, 2 equiv, 0.4 mmol), or (ii) BHT (0.088 g, 2 equiv, 0.4 mmol), or (iii) 1,1-diphenylethylene (DPE) (0.072 g, 2 equiv, 0.4 mmol) was added in DMSO:H_2O (1 mL, 9:1) under nitrogen atmosphere. The three reaction mixtures were stirred at room temperature, maintaining an approximate distance of ~6–8 cm from two 10 W white LEDs for 36 h.

In the case of TEMPO, the reaction failed to give the product (**1b**), which was monitored by TLC analysis. However, the reaction in the presence of BHT gave a trace amount of the product (**1b**), which was also monitored by TLC analysis. Whereas, in the presence of 1,1-DPE, after completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with ethyl acetate (20 mL) and ice-cooled water (10 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 30% ethyl acetate in hexane to give 21% (12.4 mg) of pure 6-methyl-4-tosylquinoline (**1b**). These results suggest that the reaction goes through a radical pathway (Scheme S8).

In another set of identical reaction in the presence of BHT, the formation of BHT-tosyl adduct (**P**) was monitored. Each time (10 μL) of reaction aliquot was taken at a time interval of 60 minutes and subjected to HRMS analysis. A BHT-tosyl adduct (**P**) was detected through HRMS after 6 h, which is given in Figure S3.

Again, in another set of identical reaction in the presence of 1,1-DPE, the formation of DPE-tosyl adduct (**Q**) was monitored. Each time (10 μL) of reaction aliquot was taken at a time interval of 60 minutes and subjected to HRMS analysis. A DPE-tosyl adduct (**Q**) was detected through HRMS after 5 h, which is given in Figure S4.



Quenchers	2 equiv
TEMPO	00%
BHT	traces
1,1-DPE	21%

Scheme S8. Reaction in the presence of radical scavengers

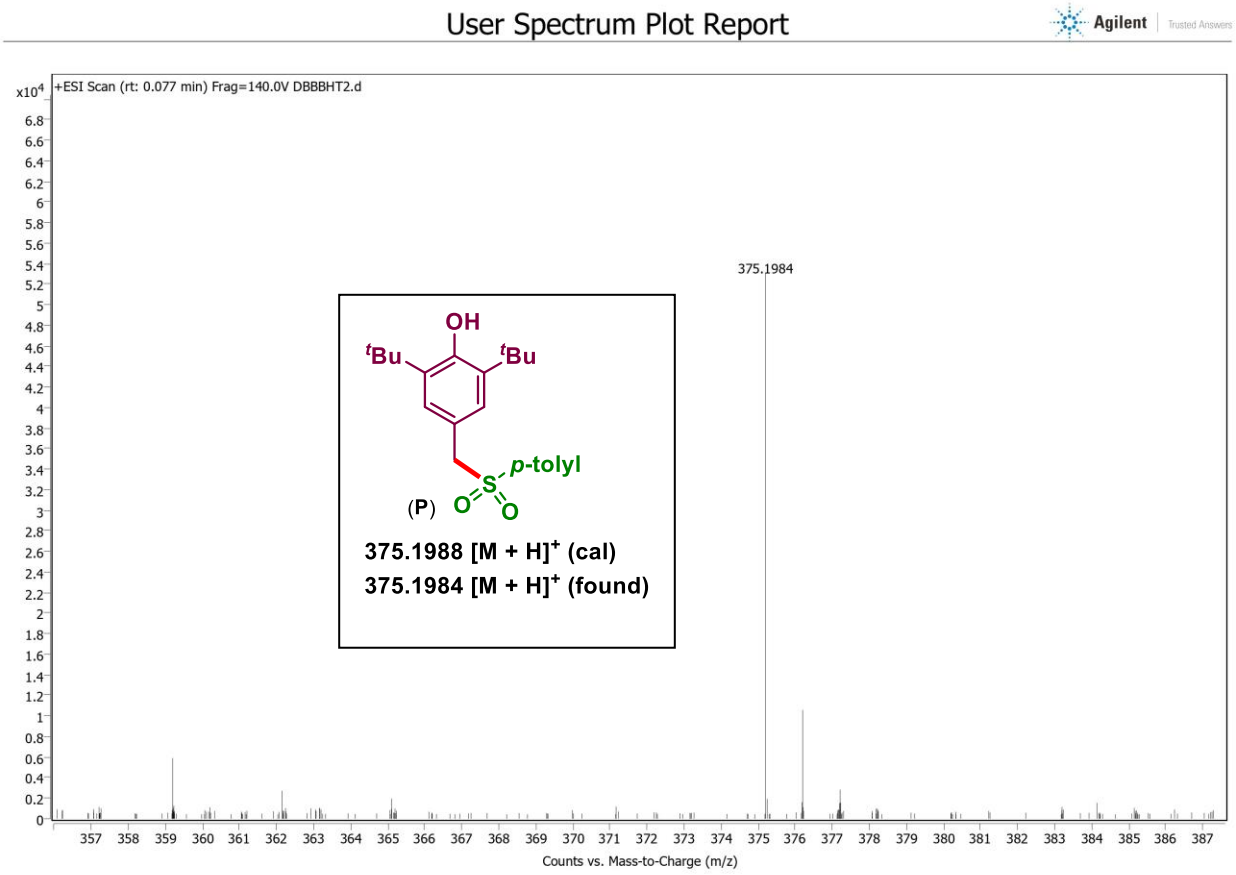


Figure S3. HRMS of BHT-tosyl adduct (**P**).

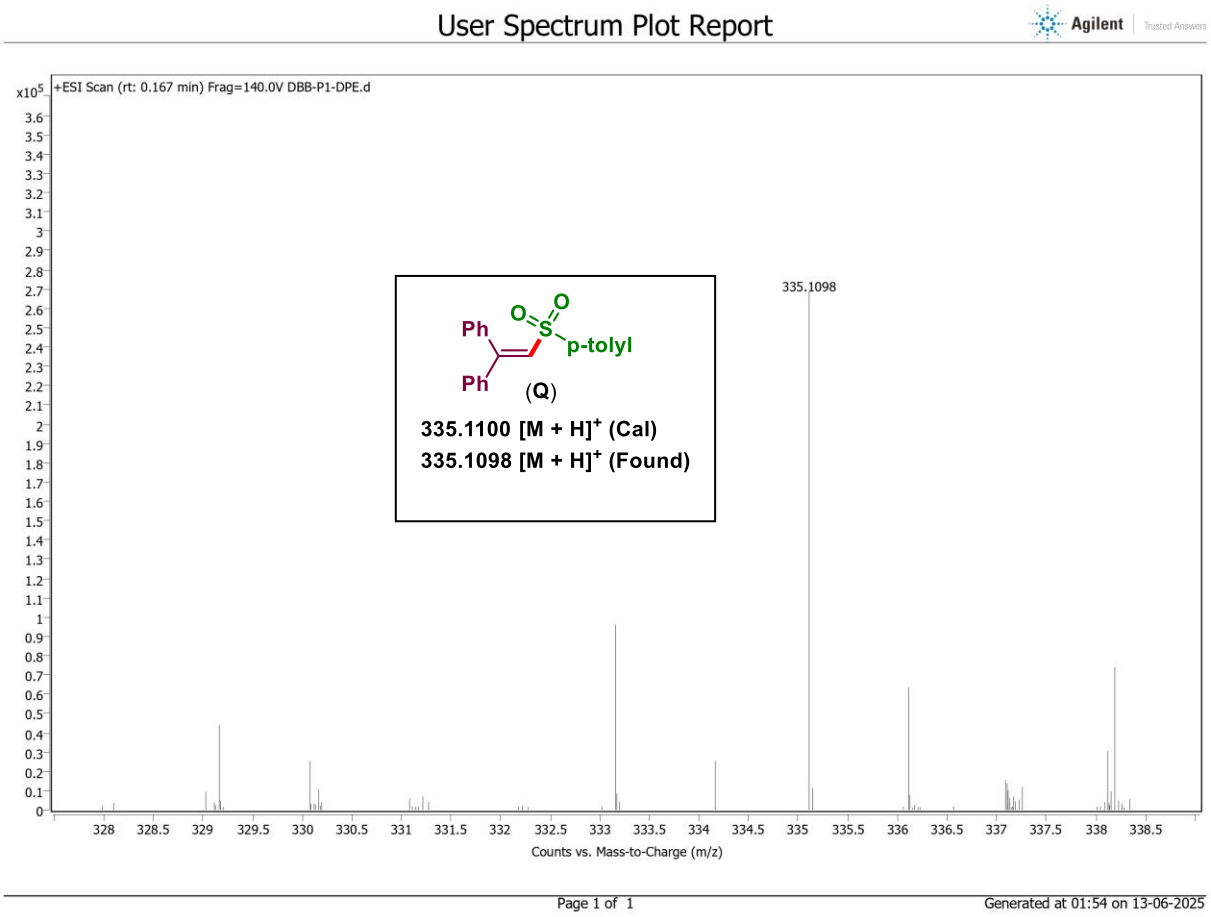
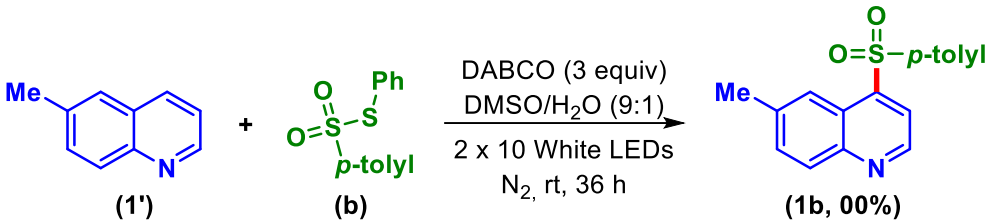


Figure S4. HRMS of 1,1–DPE-tosyl adduct (**Q**).

(B) Procedure for the Reaction with 6-Methylquinoline (1′):

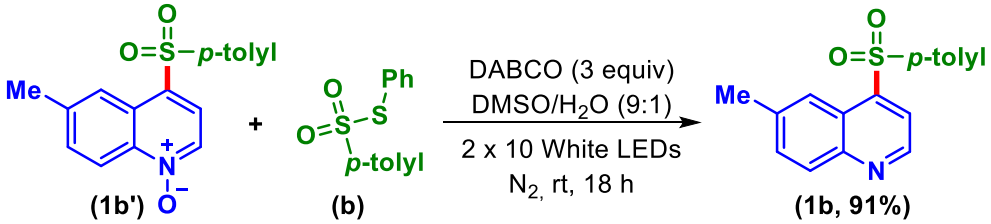
An oven-dried 15 mL vial containing a magnetic bead was added 6-methylquinoline (**1′**) (0.029 g, 0.2 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (**b**) (0.158 g, 0.6 mmol), DABCO (0.067 g, 0.6 mmol), in DMSO:H_2O (1 mL, 9:1) under nitrogen atmosphere. The reaction mixture was stirred at room temperature, maintaining an approximate distance of ~6–8 cm from two 10 W white LEDs for 36 h. After completion of the reaction (monitored by TLC analysis), it was found that no 6-methyl-4-tosylquinoline (**1b**) was formed, which suggests that the N–O group is necessary for the reaction (Scheme S9).



Scheme S9. Reaction with 6-methylquinoline (**1′**)

(C) Procedure for the Reaction with 6-Methyl-4-tosylquinoline 1-oxide (1b′):

An oven-dried 15 mL vial containing a magnetic bead was added 6-methyl-4-tosylquinoline 1-oxide (**1b′**) (0.062 g, 0.2 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (**b**) (0.158 g, 0.6 mmol), DABCO (0.067 g, 0.6 mmol), in DMSO:H_2O (1 mL, 9:1) under a nitrogen atmosphere. The reaction mixture was stirred at room temperature, maintaining an approximate distance of ~6–8 cm from two 10 W white LEDs for 18 h. After completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with ethyl acetate (20 mL) and washed with ice-cooled water (10 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 30% ethyl acetate in hexane to give pure 6-methyl-4-tosylquinoline (**1b**) in 91% yield (54 mg) (Scheme S10). The identity and purity of the product were confirmed by spectroscopic analysis.

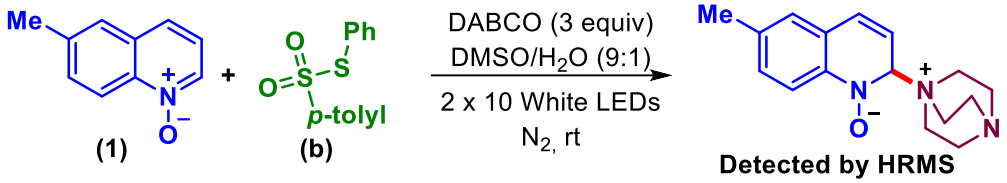


Scheme S10. Reaction with 6-methyl-4-tosylquinoline 1-oxide (**1b′**).

(D) Intermediate of the Reaction (C):

An oven-dried 15 mL vial containing a magnetic bead was added 6-methylquinoline 1-oxide (**1**) (0.032 g, 0.2 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (**b**) (0.158 g, 0.6 mmol), DABCO (0.067 g, 0.6 mmol), in DMSO:H_2O (1 mL, 9:1) under nitrogen atmosphere. The reaction mixture was stirred at room temperature, maintaining an approximate distance of ~6–8

cm from two 10 W white LEDs. The formation of intermediate (**C**) was monitored in HRMS (Scheme S11). Each time (10 µL) of reaction aliquot was taken at a time interval of 60 minutes and subjected to HRMS analysis. An intermediate (**C**) was detected through HRMS after 5 h, which is given in Figure S5.



Scheme S11. Reaction for the intermediate (**C**).

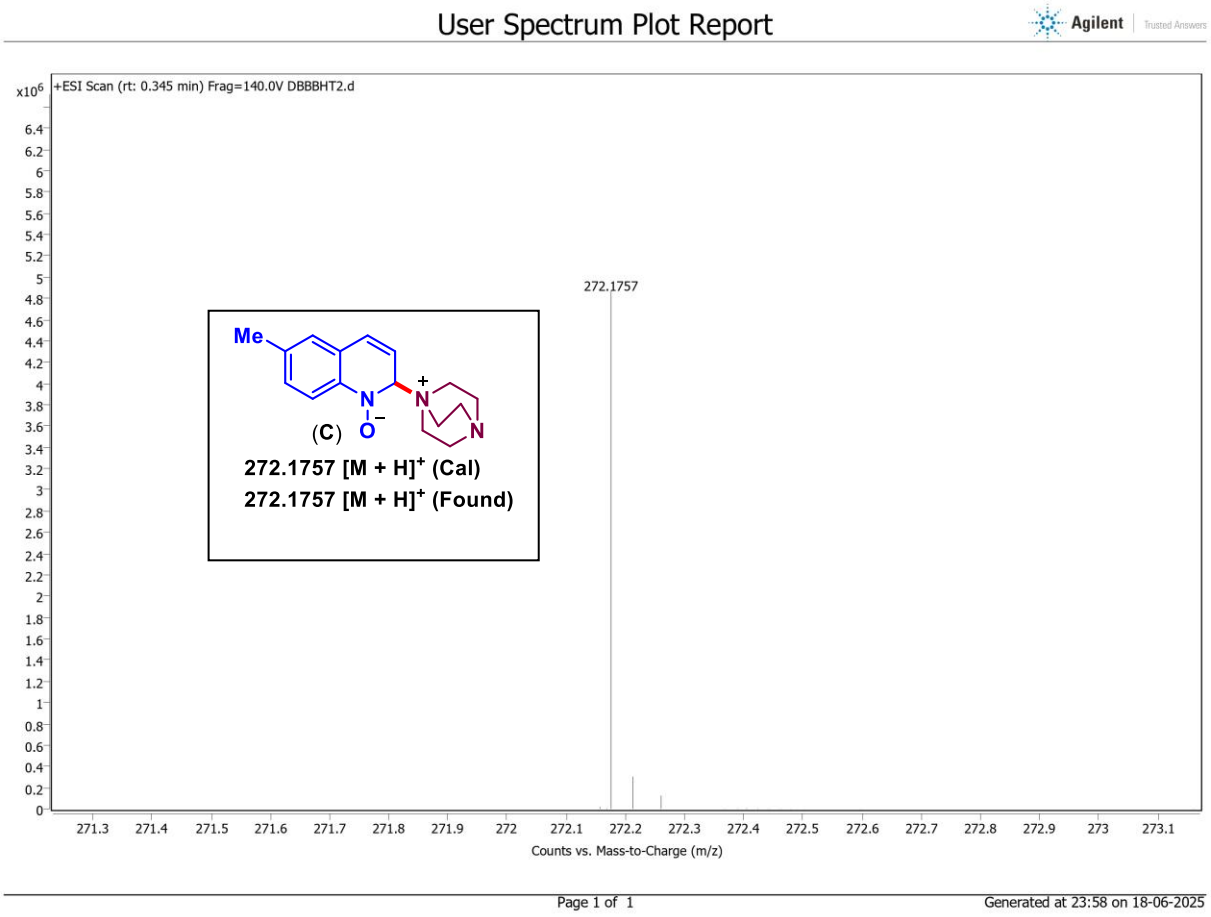


Figure S5. HRMS of Intermediate (**C**).

7. H_2O_2 Detection in the Reaction Mixture:

(A) H_2O_2 Detection by Mohr's Salt:

Three sets of oven-dried 15 mL vials containing a magnetic bead each were added 6-methylquinoline 1-oxide (**1**) (0.032 g, 0.2 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (**b**) (0.158 g, 0.6 mmol), DABCO (0.067 g, 0.6 mmol), in DMSO:H_2O (1 mL, 9:1) under a nitrogen atmosphere. The reaction mixture was stirred at room temperature, maintaining an approximate distance of ~6–8 cm from two 10 W white LEDs. After around 12 hours, a 100 μL solution of Mohr's Salt (10 mg in 100 μL H_2O) was added through a syringe to the reaction mixture. After 10 min, a rapid setting of $Fe(OH)_3$ floc was observed [Figure S6 (b)]. The floc observed was because of the rapid oxidation of Fe(II) to Fe(III) due to the presence of hydrogen peroxide (H_2O_2) in the medium (Figure S6).

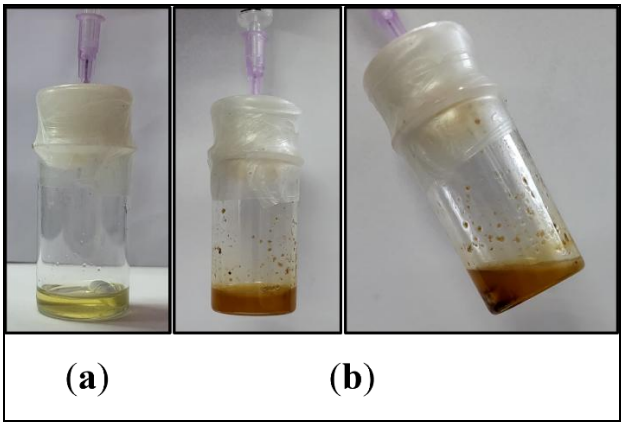


Figure S6. (a) Reaction mixture before addition of Fe(II) solution (Mohr's Salt) (b) Reaction mixture after addition of Fe(II) solution (Mohr's Salt).

(B) H_2O_2 Detection in Reaction with $KMnO_4$:

An oven-dried 15 mL vial containing a magnetic bead was added 6-methylquinoline 1-oxide (**1**) (0.032 g, 0.2 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (**b**) (0.158 g, 0.6 mmol), DABCO (0.067 g, 0.6 mmol), in DMSO:H_2O (1 mL, 9:1) under a nitrogen atmosphere. The reaction mixture was stirred at room temperature, maintaining an approximate distance of ~6–8 cm from two 10 W white LEDs. After around 12 hours, a small portion of the reaction mixture was taken out from the reaction vial using a syringe, which was added to a separately

prepared $KMnO_4$ solution (300 µM) in H_2O (10 mL). Instantly, the aqueous $KMnO_4$ solution turned colourless [Figure S7 (b)] indicating the presence of H_2O_2.

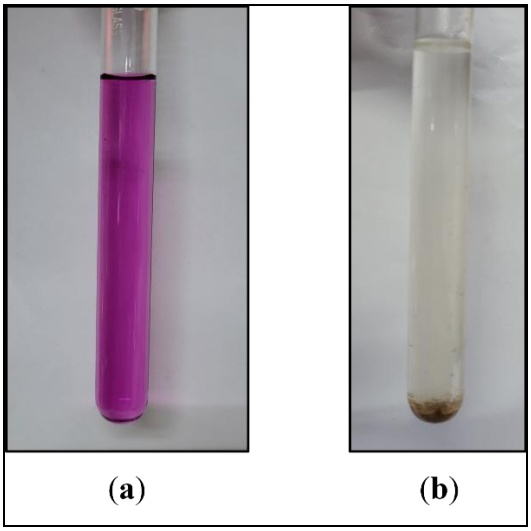
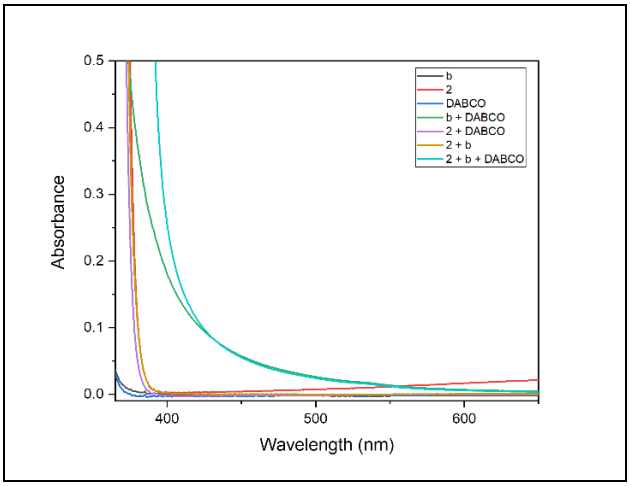


Figure S7. (a) $KMnO_4$ solution (b) $KMnO_4$ solution after adding a portion of the reaction mixture.

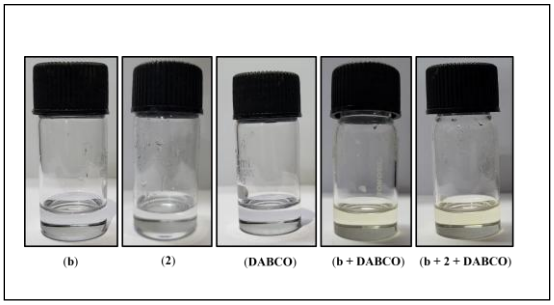
8. UV-Visible Experiments:

5 mL stock solutions of quinoline 1-oxide (**2**, 50 mM), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (**b**, 50 mM), and DABCO (50 mM) were prepared separately in DMSO. The UV absorption of all the individual and the combinations were recorded after the photoirradiation for 4 h. At first, the UV absorption of **2**, **b**, and DABCO each of 1 mL was taken individually, none of which showed any absorption in the visible region (Figure S7). Next, the combinations of (**2** + **b**), (**b** + DABCO), and (**2** + DABCO) were taken separately each ratio of 1:1 (0.5 mL : 0.5 mL) in 1 mL cuvette. The combination of (**2** + **b**) and (**2** + DABCO) showed no absorption in the visible region. However, in the combination of (**b** + DABCO), the solution turned to a light yellow colour after the irradiation and showed a bathochromic shift in the visible region, suggesting the formation of an EDA complex between **b** and DABCO. Next, a combination of **2**, **b**, and DABCO (0.33 mL each) was taken in a 1 mL UV cuvette. The solution turned light yellow colour after the irradiation and showed absorption in the visible region, suggesting the formation of an electron donor-acceptor complex (Figure S8). These results indicate that the combinations of (**b** + DABCO) and (**2** + **b** + DABCO) absorb light and show

absorption in the visible region, whereas (**2** + DABCO) does not. This confirms that an EDA complex is formed between **b** and DABCO (Figure S8).



(a)



(b)

Figure S8. (a) UV-vis spectra (b) Colour change for the formation of EDA complex.

9. ^{1}H NMR Experiments:

Further to confirm the formation of the EDA complex ^{1}H NMR experiment was performed by the preparation of $CDCl_3$ solutions containing *S*-phenyl 4-methoxybenzenesulfonothioate (**d**) and DABCO in different ratios, keeping the amount of *S*-phenyl 4-methoxybenzenesulfonothioate (**d**) constant (0.02 mmol) and increasing the amount of DABCO (**d** : DABCO = 1 : 0, 1 : 1, 1 : 2, 1 : 3, 1 : 4, 1 : 5 and 1 : 6). Each of the six ratios was prepared separately in 2 mL microcentrifuge tubes. Initially, 5.60 mg of compound (**d**) was added to each tube. Microcentrifuge tube 1 contained only compound (**d**), maintaining a 1:0 ratio. Varying amounts of DABCO were then added to other tubes to achieve the desired ratios: 2.24 mg for a 1:1 ratio, 4.48 mg for a 1:2 ratio, 6.72 mg for a 1:3 ratio, 8.96 mg for a 1:4 ratio, 11.20 mg for a 1:5 ratio, and 13.44 mg for a 1:6 ratio. Each ratio was prepared in $CDCl_3$, with the volume of each solution fixed at 400 μL. The solutions were then transferred to NMR tubes, and the data were recorded. Due to the interaction between (**d**) and DABCO, the chemical shift of the –OMe group of (**d**) progressively shifted upfield with increasing amounts of DABCO, as shown in Figures S9 and S10.

Table S2. ^{1}H NMR δ_{OMe} (ppm) value for the ratio of **d**, DABCO.

Entry	d (mmol)	DABCO (mmol)	d : DABCO	δ_{OMe} (ppm)
1	0.02	0	1: 0	3.860
2	0.02	0.02	1: 1	3.854
3	0.02	0.04	1: 2	3.844
4	0.02	0.06	1: 3	3.842
5	0.02	0.08	1: 4	3.833
6	0.02	0.10	1: 5	3.831
7	0.02	0.12	1:6	3.826

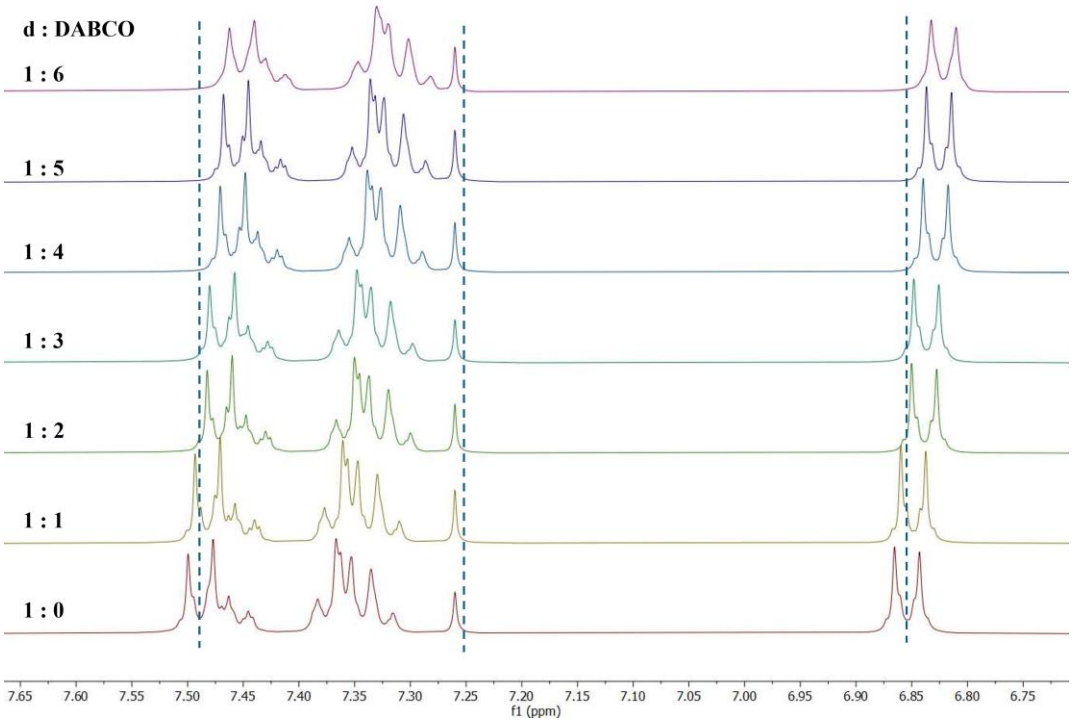


Figure S9. ^{1}H NMR spectra of the aromatic range of *S*-phenyl 4-methoxybenzenesulfonothioate (**d**) and DABCO in different ratios.

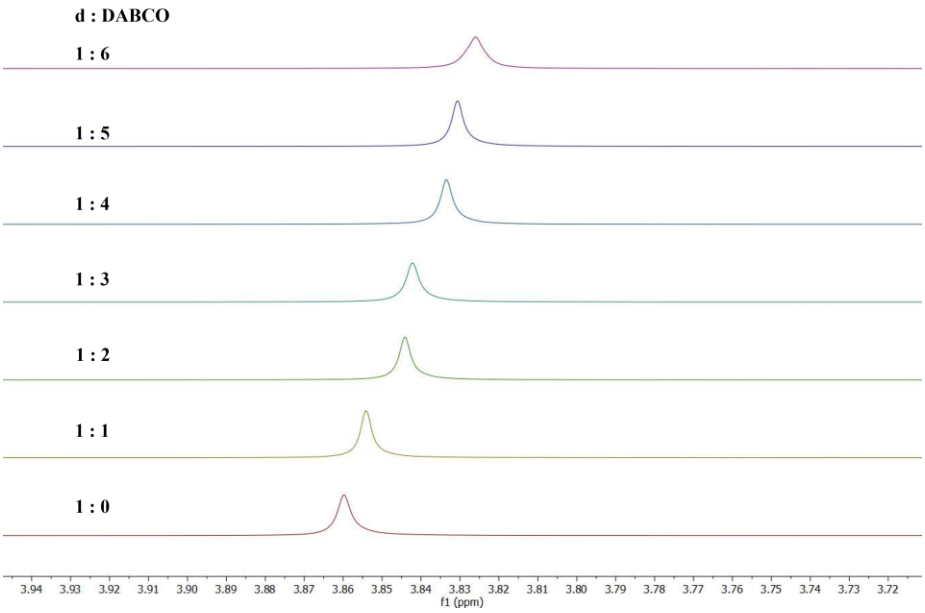


Figure S10. ^{1}H NMR spectra of the aliphatic range of *S*-phenyl 4-methoxybenzenesulfonothioate (**d**) and DABCO in different ratios.

10. Crystallographic Information:

Crystal data were collected with a Bruker Smart Apex-II CCD diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å) at 296 K. Cell parameters were retrieved using SMART [a] software and refined with SAINT[a] on all observed reflections. Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS[b]. The structure was solved by direct methods implemented in the SHELX-2014[c] program and refined by full-matrix least-squares methods on F2. All non-hydrogen atomic positions were located in different Fourier maps and refined anisotropically. The hydrogen atoms were placed in their geometrically generated positions. Yellow crystals of **1b′** were isolated from $CHCl_3$ solvent at 120 K temperature (Figure S11).

a. SMART V 4.043 Software for the CCD Detector System; Siemens Analytical Instruments Division: Madison, WI, 2008.

b. SAINT Plus (v 6.14) Bruker AXS Inc., Madison, WI, 2008.

c. Sheldrick, G. M. SHELXL-2014, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen (Germany), 1997.

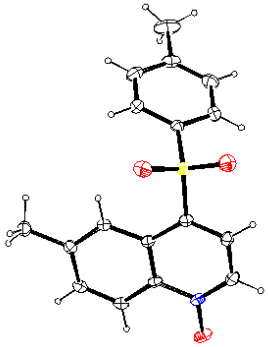


Figure S11. ORTEP diagram of **1b′** with the thermal ellipsoids set at 50% probability.

Table S3. Crystal data table for **1b′**.

Empirical formula	$C_{17}H_{15}NO_3S$
CCDC number	2504015
Formula weight	313.36
Temperature	298(2)
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C 1 2/c 1
Unit cell dimensions	a = 26.510(10) Å, b = 8.002(3) Å, c = 18.352(8) Å α= 90°, β= 126.765(17)°, γ= 90°
Volume	3119(2) $Å^3$
Z	8
Density (calculated)	1.335 g/cm^{-3}
Absorption coefficient	0.219
F (000)	1312
Theta range for data collection	3.450 to 24.732°
Index ranges	-31 < = h < = 31, -9 < = k < = 9, -21< = l < = 21
Reflections collected	33183
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	2584 / 0 / 201
Goodness-of-fit on F2	1.051
Final R indices [I>2sigma(I)]	0.0342, wR2 = 0.0879
R indices (all data)	0.0394, wR2 = 0.0952

Crystal data were collected with a Bruker Smart Apex-II CCD diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å) at 296 K. Cell parameters were retrieved using

SMART [a] software and refined with SAINT[a] on all observed reflections. Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS[b]. The structure was solved by direct methods implemented in the SHELX-2014[c] program and refined by full-matrix least-squares methods on F2. All non-hydrogen atomic positions were located in different Fourier maps and refined anisotropically. The hydrogen atoms were placed in their geometrically generated positions. yellow crystals of **5b** were isolated from $CHCl_3$ solvent at 120 K temperature (Figure S12).

a. SMART V 4.043 Software for the CCD Detector System; Siemens Analytical Instruments Division: Madison, WI, 2008.

b. SAINT Plus (v 6.14) Bruker AXS Inc., Madison, WI, 2008.

c. Sheldrick, G. M. SHELXL-2014, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen (Germany), 1997.

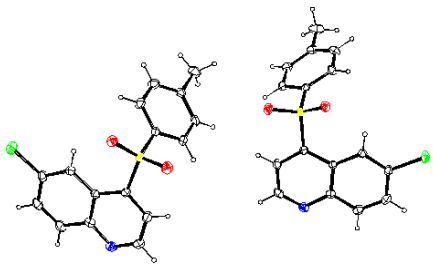


Figure S12. ORTEP diagram of **5b** with the thermal ellipsoids set at 50% probability.

Table S4. Crystal data table for **5b**.

Empirical formula	$C_{16}H_{12}ClNO_2S$
CCDC number	2504014
Formula weight	317.78
Temperature	299(2)
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 7.5367(4) Å, b = 10.6159(5) Å, c = 19.4914(9) Å α= 100.9080(10)°, β= 99.5550(10)°, γ= 102.9200(10)°
Volume	1456.76(12) $Å^3$

Z	4
Density (calculated)	1.449 g/cm^{-3}
Absorption coefficient	0.408
F (000)	656
Theta range for data collection	2.025 to 25.040^{o}
Index ranges	-8 < = h < = 8, -12 < = k < = 12, -23< = l < = 23
Reflections collected	33101
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	5129 / 0 / 381
Goodness-of-fit on F2	1.181
Final R indices [I>2sigma(I)]	0.0626, wR2 = 0.1648
R indices (all data)	0.0987, wR2 = 0.1925

11. References:

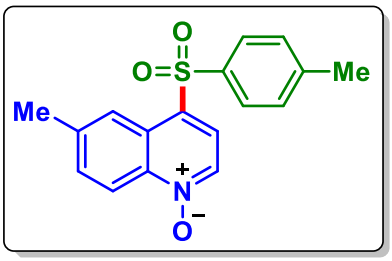
1. (a) B. Du, P. Qian, Y. Wang, H. Mei, J. Han and Y. Pan, *Org. Lett.*, 2016, **18**, 4144–4147.

(b) Z. Tan, F. Chen, G. Huang, Y. Li, H. Jiang, W. Zeng, *Org. Lett.*, 2023, **25**, 2846–2851.

2. R. H. Blessing, *Acta Crystallogr.*, 1995, **A51**, 33–38.
3. SMART and SAINT, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1996.
4. G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112–122.

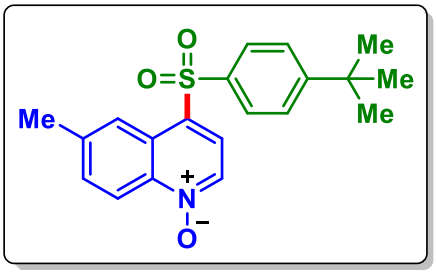
12. Spectral Data:

6-Methyl-4-tosylquinoline 1-oxide (1b'):



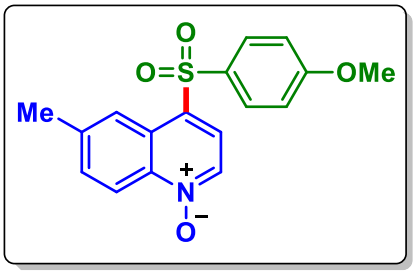
As yellow solid (47 mg, 75% yield); mp 129 – 132 °C; purified over a column of silica gel (50% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, J = 9.0 Hz, 1H), 8.49 – 8.47 (m, 1H), 8.38 (s, 1H), 8.11 – 8.10 (m, 1H), 7.85 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 8.5 Hz, 1H), 7.31 (d, J = 8.5 Hz, 2H), 2.53 (s, 3H), 2.38 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 145.3, 141.6, 141.2, 137.7, 133.7, 133.2, 132.5, 130.3, 127.9, 125.6, 124.4, 123.6, 120.4, 22.3, 21.8; IR (neat, cm^{-1}): 2918, 2852, 1579, 1499, 1356, 1311, 1211, 1157, 1141, 1084, 970; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{17}H_{16}NO_3S$, $[M + H]^+$: 314.0845, found: 314.0850.

4-((4-(Tert-butyl)phenyl)sulfonyl)-6-methylquinoline 1-oxide (1c'):



As yellow solid (50 mg, 70% yield); mp 184 – 187 °C; purified over a column of silica gel (50% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, J = 8.5 Hz, 1H), 8.48 (d, J = 6.5 Hz, 1H), 8.46 (s, 1H), 8.11 (d, J = 7.0 Hz, 1H), 7.89 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.5 Hz, 1H), 7.53 (d, J = 8.0 Hz, 2H), 2.56 (s, 3H), 1.30 (s, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.2, 141.6, 141.2, 137.6, 133.7, 133.3, 132.5, 127.7, 126.8, 125.8, 124.5, 123.7, 120.4, 35.5, 31.2, 22.3; IR (neat, cm^{-1}): 2956, 2873, 1502, 1355, 1296, 1318, 1156, 1108, 968; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{22}H_{22}NO_3S$, $[M + H]^+$: 356.1315, found: 356.1317.

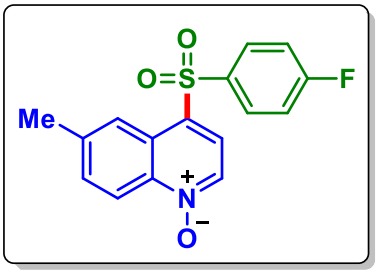
4-((4-Methoxyphenyl)sulfonyl)-6-methylquinoline 1-oxide (1d'):



As yellow solid (43.5 mg, 66% yield); mp 119 – 122 °C; purified over a column of silica gel (50% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl3) δ 8.60 (d, J = 9.0 Hz, 1H), 8.47 (d, J = 6.0 Hz, 1H), 8.40 (s, 1H), 8.07 (d, J = 7.0 Hz, 1H), 7.91 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.5 Hz, 1H), 6.98 (d, J = 8.5 Hz, 2H), 3.84 (s, 3H),

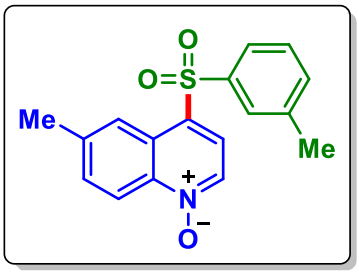
2.55 (s, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 164.1, 141.5, 141.2, 133.6, 133.2, 132.9, 132.0, 130.2, 125.6, 124.4, 123.4, 120.4, 114.9, 55.9, 22.3; IR (neat, cm^{-1}): 2947, 2842, 1572, 1497, 1356, 1309, 1154, 1138, 1085, 970; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{17}H_{16}NO_4S$, $[M + H]^+$: 330.0795, found: 330.0798.

4-((4-Fluorophenyl)sulfonyl)-6-methylquinoline 1-oxide (1e'):



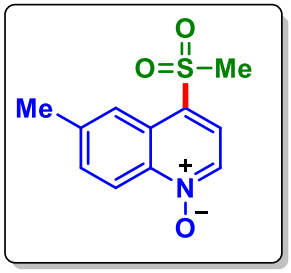
As yellow solid (34 mg, 53% yield); mp 132 – 135 °C; purified over a column of silica gel (50% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, J = 9.0 Hz, 1H), 8.49 (d, J = 6.5 Hz, 1H), 8.34 (s, 1H), 8.13 (d, J = 6.5 Hz, 1H), 8.01 – 7.98 (m, 2H), 7.59 (d, J = 9.0 Hz, 1H), 7.22 – 7.19 (m, 2H), 2.54 (s, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 165.9 (d, J = 258.0), 141.8, 141.3, 136.8 (d, J = 3.2 Hz), 133.7, 133.4, 131.6, 130.6 (d, J = 9.7 Hz), 125.5, 124.1, 123.9, 120.5, 117.1 (d, J = 22.8), 22.3; ^{19}F NMR (471 MHz, $CDCl_3$): δ –102.5 (s); IR (neat, cm^{-1}): 2920, 1589, 1493, 1356, 1312, 1151, 1013, 971; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{16}H_{13}FNO_3S$, $[M + H]^+$: 318.0595, found: 318.0594.

6-Methyl-4-(m-tolylsulfonyl)quinoline 1-oxide (1i'):



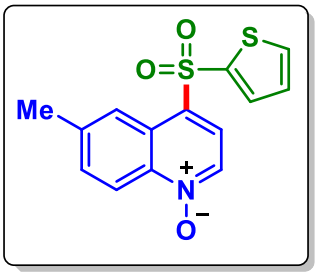
As yellow solid (39.5 mg, 63% yield); mp 125 – 128 °C; purified over a column of silica gel (50% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, J = 9.0 Hz, 1H), 8.49 (d, J = 6.5 Hz, 1H), 8.38 (s, 1H), 8.12 (d, J = 6.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.74 (s, 1H), 7.58 (d, J = 9.0 Hz, 1H), 7.43 – 7.38 (m, 2H), 2.53 (s, 3H), 2.39 (s, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 141.6, 141.2, 140.6, 140.1, 134.9, 133.7, 133.3, 132.1, 129.5, 128.1, 125.7, 124.9, 124.4, 123.8, 120.4, 22.3, 21.6; IR (neat, cm^{-1}): 2921, 2854, 1578, 1499, 1356, 1309, 1154, 1137, 1082, 969; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{17}H_{16}NO_3S$, $[M + H]^+$: 314.0845, found: 314.0850.

6-Methyl-4-(methylsulfonyl)quinoline 1-oxide (1l'):



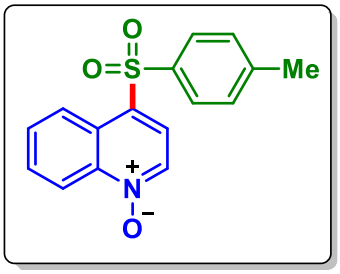
As pale yellow solid (23 mg, 48% yield); mp 181 – 184 °C; purified over a column of silica gel (50% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, J = 9.0 Hz, 1H), 8.50 (d, J = 6.0 Hz, 1H), 8.42 (s, 1H), 8.02 (d, J = 6.0 Hz, 1H), 7.69 (d, J = 9.0 Hz, 1H), 3.24 (s, 3H), 2.63 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 142.3, 141.3, 133.8, 133.5, 131.1, 126.0, 124.0, 123.8, 120.8, 44.7, 22.4; IR (neat, cm^{-1}): 2924, 1579, 1499, 1356, 1309, 1211, 1154, 1131, 979; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{11}H_{12}NO_3S$, $[M + H]^+$: 238.0532, found: 238.0531.

6-Methyl-4-(thiophen-2-ylsulfonyl)quinoline 1-oxide (1m'):



As yellow gummy (33 mg, 54% yield); purified over a column of silica gel (50% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, J = 9.0 Hz, 1H), 8.57 (s, 1H), 8.48 – 8.46 (m, 1H), 8.12 – 8.11 (m, 1H), 7.79 (s, 1H), 7.69 – 7.67 (m, 1H), 7.62 (d, J = 9.0 Hz, 1H), 7.10 (d, J = 4.5 Hz, 1H), 2.60 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 142.2, 141.8, 141.3, 134.8, 134.4, 133.8, 133.4, 132.6, 128.2, 125.5, 124.4, 123.5, 120.5, 22.3; IR (neat, cm^{-1}): 3103, 2922, 1579, 1498, 1310, 1275, 1157, 1017, 764; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{14}H_{12}NO_3S$, $[M + H]^+$: 306.0253, found: 306.0256.

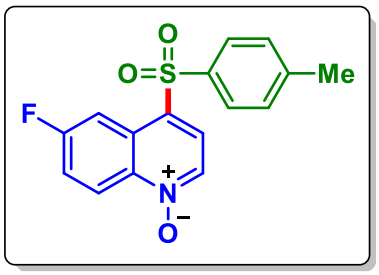
4-Tosylquinoline 1-oxide (2b'):



As pale yellow solid (41.5 mg, 69% yield); mp 148 – 151 °C; purified over a column of silica gel (50% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, J = 9.0 Hz, 1H), 8.65 (d, J = 8.5 Hz, 1H), 8.56 (d, J = 6.0 Hz, 1H), 8.17 (d, J = 6.5 Hz, 1H), 7.86 (d, J = 7.5 Hz, 2H), 7.78 – 7.71 (m, 2H), 7.31 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 145.4, 142.7, 137.7, 134.4, 133.1, 131.2, 130.8, 130.4, 127.9, 125.6, 125.5, 123.7, 120.7, 21.8; IR (neat, cm^{-1}): 2923, 2852, 1593, 1505,

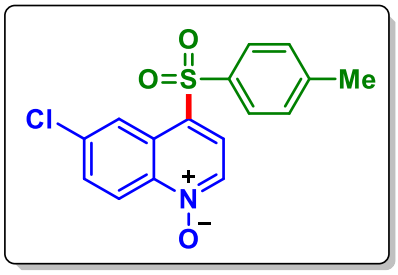
1377, 1313, 1151, 1143, 1084, 952; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{16}H_{14}NO_3S$, $[M + H]^+$: 300.0689, found: 300.0689.

6-Fluoro-4-tosylquinoline 1-oxide (4b'):



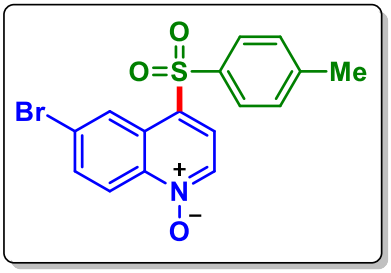
As pale yellow solid (39.5 mg, 62% yield); mp 165 – 168 °C; purified over a column of silica gel (50% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 – 8.73 (m, 1H), 8.50 (d, J = 6.5 Hz, 1H), 8.31 (dd, J = 10.0, 2.5 Hz, 1H), 8.19 (d, J = 6.5 Hz, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.53– 7.49 (m, 1H), 7.34 (d, J = 8.0 Hz, 2H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 162.9 (d, J = 255.2 Hz), 145.6, 139.8, 137.3, 133.9, 132.4 (d, J = 5.5 Hz), 130.5, 129.9, 127.9, 127.8, 127.1 (d, J = 11.1 Hz), 124.9, 123.8 (d, J = 9.7 Hz), 121.1 (d, J = 26.0 Hz), 110.2 (d, J = 26.2 Hz), 21.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ-104.6 (s); IR (neat, cm^{-1}): 2925, 1581, 1507, 1445, 1305, 1215, 1153, 1084, 985; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{16}H_{13}FNO_3S$, $[M + H]^+$: 318.0595, found: 318.0596.

6-Chloro-4-tosylquinoline 1-oxide (5b'):



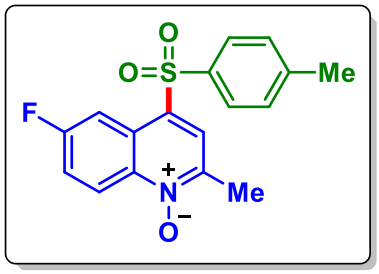
As white solid (41 mg, 61% yield); mp 160 – 163 °C; purified over a column of silica gel (50% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 – 8.63 (m, 2H), 8.50 (d, J = 6.4 Hz, 1H), 8.17 (d, J = 6.4 Hz, 1H), 7.85 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.8 Hz, 1H), 7.34 (d, J = 8.4 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.6, 141.2, 137.6, 137.3, 134.4, 132.1, 131.9, 130.5, 127.9, 126.3, 124.8, 124.6, 122.4, 21.8; IR (neat, cm^{-1}): 3109, 2922, 1573, 1492, 1350, 1305, 1147, 1082, 967; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{16}H_{13}NO_3SCl$, $[M + H]^+$: 334.0299, found: 334.0294.

6-Bromo-4-tosylquinoline 1-oxide (6b'):



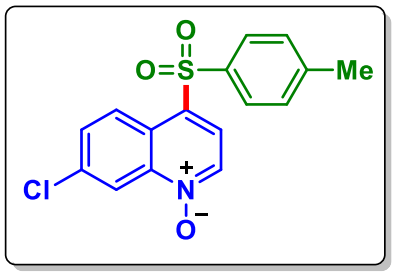
As white solid (45 mg, 60% yield); mp 159 – 162 °C; purified over a column of silica gel (50% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.57 (d, J = 9.0 Hz, 1H), 8.51 (d, J = 5.5 Hz, 1H), 8.16 (d, J = 7.0 Hz, 1H), 7.86 – 7.82 (m, 3H), 7.35 (d, J = 7.0 Hz, 2H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 145.7, 141.6, 137.4, 134.6, 134.5, 132.0, 130.6, 128.0, 127.9, 126.7, 126.1, 124.7, 122.4, 21.9; IR (neat, cm^{-1}): 2918, 2844, 1570, 1491, 1349, 1305, 1148, 1079, 961; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{16}H_{13}BrNO_3S$, $[M + H]^+$: 377.9794, found: 377.9765.

6-Fluoro-2-methyl-4-tosylquinoline 1-oxide (9b'):



As brown gummy (41.5 mg, 62% yield); purified over a column of silica gel (50% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (dd, J = 9.5, 5.5 Hz, 1H), 8.28 – 8.24 (m, 2H), 7.85 (d, J = 8.0 Hz, 2H), 7.49 – 7.45 (m, 1H), 7.32 (d, J = 8.0 Hz, 2H), 2.71 (s, 3H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 162.2 (d, J = 253.4 Hz), 145.4, 144.5 (d, J = 2.4 Hz), 139.8, 137.6, 131.3 (d, J = 5.4 Hz), 130.5, 129.8, 127.8, 127.7, 126.5, 125.6 (d, J = 11.0 Hz), 123.5 (d, J = 9.6 Hz), 120.8 (d, J = 25.8 Hz), 110.0 (d, J = 26.2 Hz), 21.8, 18.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -106.9 (s); IR (neat, cm^{-1}): 2924, 2853, 1561, 1457, 1319, 1222, 1154, 1084, 987; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{17}H_{15}FNO_3S$, $[M + H]^+$: 332.0751, found: 332.0758.

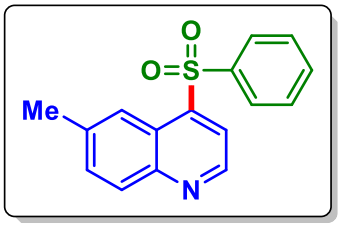
7-Chloro-4-tosylquinoline 1-oxide (10b'):



As yellow gummy (43 mg, 64% yield); purified over a column of silica gel (50% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (d, J = 2.0 Hz, 1H), 8.62 (d, J = 9.0 Hz, 1H), 8.54 (d, J = 6.5 Hz, 1H), 8.13 (d, J = 6.5 Hz, 1H), 7.84 (d, J = 8.5 Hz, 2H), 7.66 (dd, J = 9.3, 2.3 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 145.6, 143.1, 138.2, 137.5,

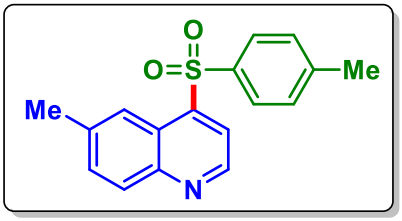
135.1, 133.1, 131.8, 130.5, 127.9, 127.0, 124.0, 123.7, 120.2, 21.9; IR (neat, cm^{-1}): 2918, 1548, 1497, 1366, 1296, 1150, 1082, 764; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{16}H_{13}ClNO_3S$, $[M + H]^+$: 334.0299, found: 334.0275.

6-Methyl-4-(phenylsulfonyl)quinoline (1a):



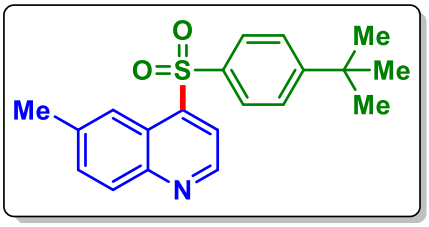
As white gummy (40 mg, 70% yield); purified over a column of silica gel (30% EtOAc in hexane); ^1H NMR (600 MHz, $CDCl_3$) δ 9.03 (d, J = 4.8 Hz, 1H), 8.39 (s, 1H), 8.09 (d, J = 4.8 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 7.8 Hz, 2H), 7.60 – 7.58 (m, 2H), 7.53 – 7.51 (m, 2H), 2.54 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 148.8, 148.4, 144.2, 140.5, 139.5, 134.0, 132.9, 130.4, 129.6, 128.0, 123.2, 122.4, 121.3, 22.5; IR (neat, cm^{-1}): 3064, 2920, 1501, 1446, 1317, 1213, 1165, 1142, 1084, 822; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{16}H_{14}NO_2S$, $[M + H]^+$: 284.0740, found: 284.0719.

6-Methyl-4-tosylquinoline (1b):



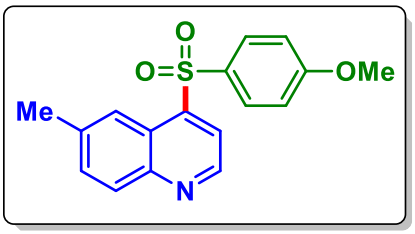
As pale yellow solid (45.5 mg, 76% yield); mp 87 – 90 °C; purified over a column of silica gel (30% EtOAc in hexane); ^1H NMR (600 MHz, $CDCl_3$) δ 9.02 (d, J = 4.8 Hz, 1H), 8.41 (s, 1H), 8.07 – 8.06 (m, 2H), 7.88 (d, J = 8.4 Hz, 2H), 7.60 (dd, J = 8.7, 2.1 Hz, 1H), 7.32 (d, J = 8.4 Hz, 2H), 2.56 (s, 3H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 148.8, 148.3, 145.3, 144.6, 139.5, 137.4, 132.9, 130.4, 130.3, 128.2, 123.3, 122.4, 121.2, 22.5, 21.9; IR (neat, cm^{-1}): 2921, 1501, 1446, 1320, 1277, 1164, 1141, 1085, 817; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{17}H_{16}NO_2S$, $[M + H]^+$: 298.0896, found: 298.0896.

4-((4-(Tert-butyl)phenyl)sulfonyl)-6-methylquinoline (1c):



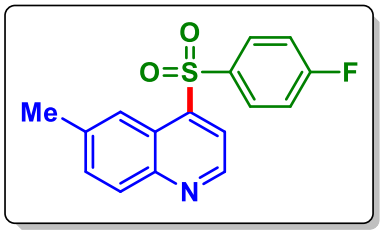
As white solid (48 mg, 71% yield); mp 135– 138 °C; purified over a column of silica gel (30% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.02 (d, J = 4.5 Hz, 1H), 8.47 (s, 1H), 8.08 – 8.07 (m, 2H), 7.92 (d, J = 8.5 Hz, 2H), 7.61 (d, J = 8.5 Hz, 1H), 7.53 (d, J = 8.5 Hz, 2H), 2.57 (s, 3H), 1.30 (s, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.2, 148.9, 148.4, 144.6, 139.5, 137.3, 132.9, 130.4, 128.1, 126.7, 123.4, 122.5, 121.3, 35.5, 31.2, 22.5; IR (neat, cm^{-1}): 2956, 2873, 1502, 1355, 1296, 1156, 1108, 968; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{20}H_{22}NO_2S$, $[M + H]^+$: 340.1366, found: 340.1366.

4-((4-Methoxyphenyl)sulfonyl)-6-methylquinoline (1d):



As pale brown solid (44 mg, 70% yield); mp 115– 118 °C; purified over a column of silica gel (30% EtOAc in hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.99 (d, J = 4.2 Hz, 1H), 8.43 (s, 1H), 8.06 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 4.2 Hz, 1H), 7.93 (d, J = 9.0 Hz, 2H), 7.59 (d, J = 8.4 Hz, 1H), 6.98 (d, J = 9.0 Hz, 2H), 3.83 (s, 3H), 2.56 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 164.1, 148.8, 148.4, 145.0, 139.4, 132.8, 131.7, 130.5, 130.4, 123.3, 122.4, 120.9, 114.9, 55.9, 22.5; IR (neat, cm^{-1}): 2925, 2845, 1592, 1497, 1320, 1261, 1138, 1085, 826; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{17}H_{16}NO_3S$, $[M + H]^+$: 314.0845, found: 314.0841.

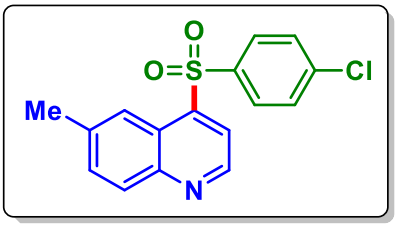
4-((4-Fluorophenyl)sulfonyl)-6-methylquinoline (1e):



As white solid (35.5 mg, 59% yield); mp 129– 132 °C; purified over a column of silica gel (30% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.04 (d, J = 4.5 Hz, 1H), 8.37 (s, 1H), 8.09 – 8.08 (m, 2H), 8.02 (dd, J = 9.0, 5.0 Hz, 2H), 7.61 (dd, J = 8.5, 2.0 Hz, 1H), 7.22 – 7.18 (m, 2H), 2.56 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.0 (d, J = 257.9 Hz), 148.8, 148.5, 144.0, 139.7, 136.5 (d, J = 3.4 Hz), 133.0, 131.0 (d, J = 9.7 Hz), 130.6, 129.6,

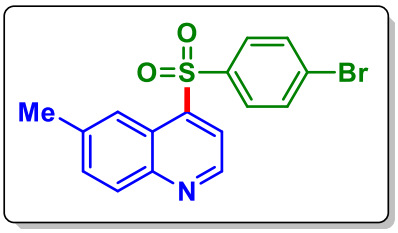
128.1, 123.0, 122.3, 121.3, 117.0 (d, J = 22.9 Hz), 22.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ -102.6 (s); IR (neat, cm^{-1}): 2922, 1589, 1493, 1323, 1293, 1142, 1083, 819; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{16}H_{13}FNO_2S$, $[M + H]^+$: 302.0646, found: 302.0647.

4-((4-Chlorophenyl)sulfonyl)-6-methylquinoline (1f):



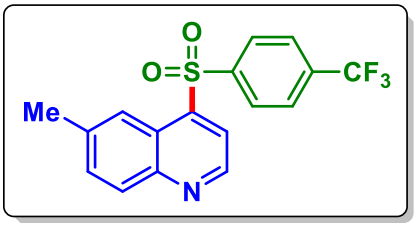
As pale yellow solid (40 mg, 63% yield); mp 78– 81 ^{o}C; purified over a column of silica gel (30% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.04 (d, J = 4.5 Hz, 1H), 8.35 (s, 1H), 8.11 – 8.08 (m, 2H), 7.93 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 8.5 Hz, 1H), 7.50 (d, J = 8.0 Hz, 2H), 2.56 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 148.8, 148.5, 143.7, 140.9, 139.8, 139.0, 133.0, 130.6, 130.0, 129.5, 123.0, 122.3, 121.4, 22.6; IR (neat, cm^{-1}): 2993, 2806, 1580, 1500, 1476, 1326, 1166, 1143, 1088, 980; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{16}H_{13}ClNO_2S$, $[M + H]^+$: 318.0350, found: 318.0356.

4-((4-Bromophenyl)sulfonyl)-6-methylquinoline (1g):



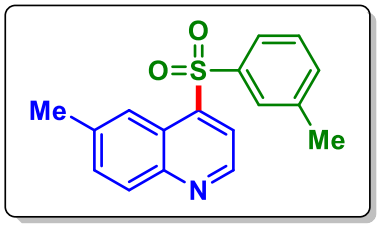
As brown solid (47 mg, 65% yield); mp 97 – 100 ^{o}C; purified over a column of silica gel (30% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.04 (d, J = 4.0 Hz, 1H), 8.34 (s, 1H), 8.11 – 8.08 (m, 2H), 7.85 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 8.5 Hz, 1H), 2.56 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 148.8, 148.4, 143.6, 139.8, 139.5, 133.04, 132.96, 130.6, 129.6, 129.5, 123.0, 122.3, 121.4, 22.6; IR (neat, cm^{-1}): 2993, 2853, 1572, 1501, 1470, 1388, 1323, 1165, 1141, 1087, 819; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{16}H_{13}BrNO_2S$, $[M + H]^+$: 361.9845, found: 361.9845.

6-Methyl-4-((4-(trifluoromethyl)phenyl)sulfonyl)quinoline (1h):



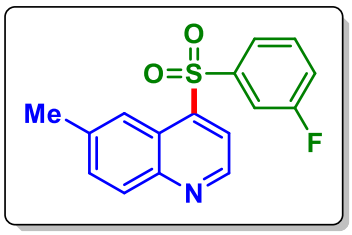
As white solid (44.5 mg, 63% yield); mp 155 – 158 °C; purified over a column of silica gel (30% EtOAc in hexane); ^{1}H NMR (400 MHz, CDCl3) δ 9.07 (d, J = 4.4 Hz, 1H), 8.35 (s, 1H), 8.16 (d, J = 4.4 Hz, 1H), 8.14 – 8.09 (m, 3H), 7.79 (d, J = 8.4 Hz, 2H), 7.63 (dd, J = 8.4, 2.0 Hz, 1H), 2.56 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, CDCl3) δ 148.8, 148.5, 144.2, 143.0, 140.1, 135.7 (q, J = 33.2 Hz), 133.2, 130.7, 128.6, 126.8 (q, J = 3.7 Hz), 123.1 (q, J = 273.8 Hz), 122.8, 122.3, 121.8, 22.6; ^{19}F NMR (471 MHz, $CDCl_3$): δ -63.3 (s); IR (neat, cm^{-1}): 2921, 1501, 1403, 1321, 1166, 1137, 1087, 843; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{17}H_{13}F_3NO_2S$, $[M + H]^+$: 352.0614, found: 352.0605.

6-Methyl-4-(m-tolylsulfonyl)quinoline (1i):



As yellow solid (40 mg, 67% yield); mp 97– 100 °C; purified over a column of silica gel (30% EtOAc in hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.03 (d, J = 4.2 Hz, 1H), 8.40 (s, 1H), 8.09 – 8.07 (m, 2H), 7.83 (d, J = 7.2 Hz, 1H), 7.77 (s, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.43 – 7.39 (m, 2H), 2.55 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.8, 148.4, 144.3, 140.3, 140.0, 139.5, 135.0, 132.9, 130.4, 129.4, 128.5, 125.3, 123.4, 122.4, 121.3, 22.5, 21.6; IR (neat, cm^{-1}): 3063, 2921, 1501, 1477, 1320, 1304, 1214, 1137, 1082, 984; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{17}H_{16}NO_2S$, $[M + H]^+$: 298.0896, found: 298.0897.

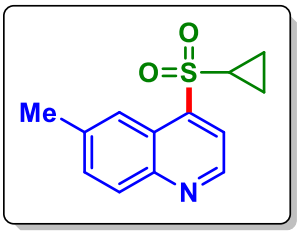
4-((3-Fluorophenyl)sulfonyl)-6-methylquinoline (1j):



As white solid (32.5 mg, 54% yield); mp 117 – 120 °C; purified over a column of silica gel (30% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.06 (d, J = 4.5 Hz, 1H), 8.36 (s, 1H), 8.12 – 8.09 (m, 2H), 7.79 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 7.5 Hz, 1H), 7.62 (d, J = 9.0 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.31 – 7.28 (m, 1H), 2.56 (s,

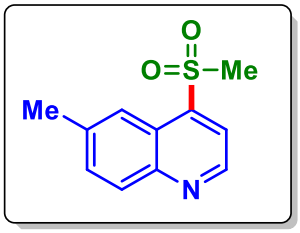
3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 162.6 (d, J = 253.5 Hz), 148.8, 148.5, 143.4, 142.7 (d, J = 6.6 Hz), 139.9, 133.1, 131.5 (d, J = 7.8 Hz), 130.6, 123.9 (d, J = 3.4 Hz), 123.0, 122.3, 121.6, 121.4 (d, J = 21.2 Hz), 115.4 (d, J = 24.6 Hz), 22.5; ^{19}F NMR (471 MHz, $CDCl_3$): δ -108.4 (s); IR (neat, cm^{-1}): 3072, 2921, 1474, 1432, 1326, 1225, 1165, 1082, 821; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{16}H_{13}FNO_2S$, $[M + H]^+$: 302.0646, found: 302.0638.

4-(Cyclopropylsulfonyl)-6-methylquinoline (1k):



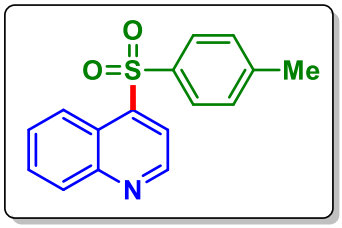
As white solid (24.5 mg, 49% yield); mp 129– 132 °C; purified over a column of silica gel (30% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.02 (d, J = 4.5 Hz, 1H), 8.52 (s, 1H), 8.14 (d, J = 8.5 Hz, 1H), 7.92 – 7.91 (m, 1H), 7.67 (d, J = 9.0 Hz, 1H), 2.78 – 2.73 (m, 1H), 2.62 (s, 3H), 1.41 – 1.40 (m, 2H), 1.07 – 1.05 (m, 2H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 148.9, 148.4, 143.5, 139.7, 132.9, 130.6, 123.2, 122.9, 121.0, 32.9, 22.5, 6.7; IR (neat, cm^{-1}): 3058, 2931, 1499, 1331, 1301, 1165, 1135, 1049, 885; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{13}H_{14}NO_2S$, $[M + H]^+$: 248.0740, found: 248.0742.

6-Methyl-4-(methylsulfonyl)quinoline (1l):



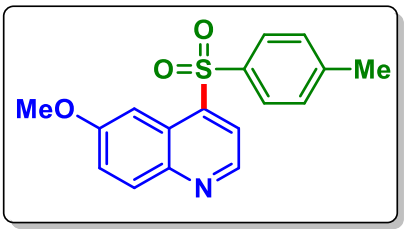
As white solid (23.5 mg, 53% yield); mp 125 – 128 °C; purified over a column of silica gel (30% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.03 (d, J = 4.5 Hz, 1H), 8.39 (s, 1H), 8.13 (d, J = 8.5 Hz, 1H), 8.03 – 8.02 (m, 1H), 7.67 (d, J = 8.5 Hz, 1H), 3.22 (s, 3H), 2.60 (s, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 148.9, 148.3, 143.1, 140.0, 133.0, 130.7, 122.6, 122.5, 121.4, 44.3, 22.5; IR (neat, cm^{-1}): 3005, 2922, 1502, 1308, 1227, 1165, 1130, 990, 824; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{11}H_{12}NO_2S$, $[M + H]^+$: 222.0583, found: 222.0561.

4-Tosylquinoline (2b):



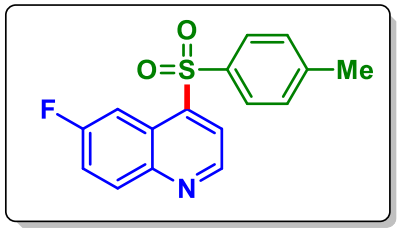
As white solid (41 mg, 72% yield); mp 102 – 105 °C; purified over a column of silica gel (30% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.10 (d, J = 4.5 Hz, 1H), 8.65 (d, J = 8.5 Hz, 1H), 8.18 (d, J = 8.5 Hz, 1H), 8.14 (d, J = 4.5 Hz, 1H), 7.88 (d, J = 8.0 Hz, 2H), 7.78 – 7.75 (m, 1H), 7.66 – 7.63 (m, 1H), 7.30 (d, J = 8.0 Hz, 2H), 2.37 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 149.9, 149.6, 145.4, 145.3, 137.3, 130.8, 130.6, 130.3, 129.0, 128.2, 124.4, 122.3, 121.2, 21.8; IR (neat, cm^{-1}): 2922, 2853, 1499, 1321, 1159, 1145, 1085, 975; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{16}H_{14}NO_2S$, $[M + H]^+$: 284.0740, found: 284.0739.

6-Methoxy-4-tosylquinoline (3b):



As pale yellow solid (50 mg, 80% yield); mp 147 – 150 °C; purified over a column of silica gel (30% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 – 8.93 (m, 1H), 8.14 – 8.13 (m, 1H), 8.06 (d, J = 9.0 Hz, 1H), 7.88 – 7.86 (m, 3H), 7.39 (d, J = 9.0 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 3.93 (s, 3H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.4, 147.0, 146.0, 145.3, 143.4, 137.5, 132.1, 130.2, 128.1, 123.8, 123.6, 121.5, 102.3, 55.9, 21.8; IR (neat, cm^{-1}): 2927, 1500, 1427, 1319, 1236, 1142, 1083, 852; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{17}H_{16}NO_3S$, $[M + H]^+$: 314.0845, found: 314.0845.

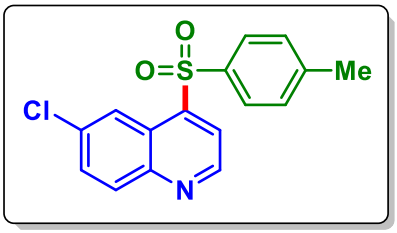
6-Fluoro-4-tosylquinoline (4b):



As yellow solid (38 mg, 63% yield); mp 70 – 73 °C; purified over a column of silica gel (30% EtOAc in hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.06 (d, J = 4.2 Hz, 1H), 8.31 (d, J = 9.6 Hz, 1H), 8.20 – 8.16 (m, 2H), 7.87 (d, J = 8.4 Hz, 2H), 7.55 – 7.52 (m, 1H), 7.32 (d, J = 7.8 Hz, 2H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 161.6 (d, J = 252.0 Hz), 149.1 (d, J = 3.0 Hz), 146.9, 145.6, 145.0 (d, J = 6.0 Hz), 137.1, 133.4 (d, J = 9.5 Hz), 130.4,

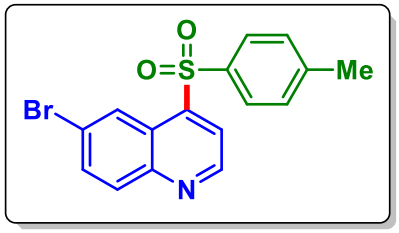
128.2, 123.4 (d, J = 11.0 Hz), 122.0, 121.1 (d, J = 26.0 Hz), 108.7 (d, J = 25.2 Hz), 21.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -107.0 (s); IR (neat, cm^{-1}): 3098, 2924, 1502, 1321, 1292, 1222, 1154, 1084, 863; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{16}H_{13}FNO_2S$, $[M + H]^+$: 302.0646, found: 302.0645.

6-Chloro-4-tosylquinoline (5b):



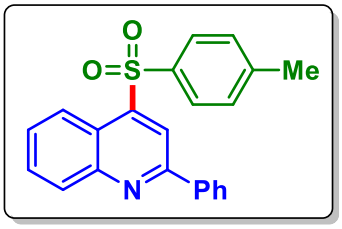
As white solid (42 mg, 66% yield); mp 163– 166 ^{o}C; purified over a column of silica gel (30% EtOAc in hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.07 (d, J = 4.2 Hz, 1H), 8.68 (s, 1H), 8.13 (d, J = 4.2 Hz, 1H), 8.11 (d, J = 9.0 Hz, 1H), 7.88 (d, J = 7.8 Hz, 2H), 7.70 (dd, J = 9.0, 2.1 Hz, 1H), 7.33 (d, J = 7.8 Hz, 2H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 150.0, 148.0, 145.6, 144.8, 137.0, 135.3, 132.2, 131.7, 130.4, 128.3, 123.6, 123.0, 122.0, 21.8; IR (neat, cm^{-1}): 2924, 2851, 1489, 1324, 1183, 1148, 1083, 861; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{16}H_{13}ClNO_2S$, $[M + H]^+$: 318.0350, found: 318.0320.

6-Bromo-4-tosylquinoline (6b):



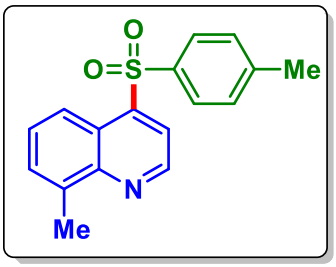
As white solid (46 mg, 64% yield); mp 180 – 183 ^{o}C; purified over a column of silica gel (30% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.10 – 9.08 (m, 1H), 8.86 (s, 1H), 8.14 – 8.12 (m, 1H), 8.04 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 7.5 Hz, 2H), 7.84 (d, J = 9.0 Hz, 1H), 7.34 (d, J = 7.5 Hz, 2H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.2, 148.3, 145.7, 144.7, 137.0, 134.3, 132.3, 130.5, 128.3, 126.9, 123.7, 123.4, 121.9, 21.9; IR (neat, cm^{-1}): 2921, 2853, 1488, 1321, 1183, 1149, 1084, 812; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{16}H_{13}BrNO_2S$, $[M + H]^+$: 361.9845, found: 361.9838.

2-Phenyl-4-tosylquinoline (7b):



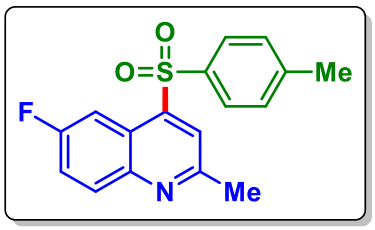
As white solid (45 mg, 62% yield); mp 178 – 181 °C; purified over a column of silica gel (30% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.63 (d, J = 8.5 Hz, 1H), 8.26 – 8.23 (m, 3H), 7.93 (d, J = 8.5 Hz, 2H), 7.76 – 7.73 (m, 1H), 7.62 – 7.50 (m, 4H), 7.30 (d, J = 8.5 Hz, 2H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 156.9, 149.7, 146.0, 145.2, 138.2, 137.6, 130.9, 130.6, 130.4, 130.2, 129.2, 128.4, 128.1, 127.7, 124.2, 121.2, 119.4, 21.7; IR (neat, cm^{-1}): 3007, 2926, 1578, 1441, 1321, 1263, 1133, 1085, 759; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{22}H_{18}NO_2S$, $[M + H]^+$: 360.1053, found: 360.1063.

8-Methyl-4-tosylquinoline (8b):



As pale yellow solid (43 mg, 72% yield); mp 106 – 109 °C; purified over a column of silica gel (20% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.12 (d, J = 4.0 Hz, 1H), 8.49 (d, J = 8.5 Hz, 1H), 8.16 (d, J = 3.0 Hz, 1H), 7.87 (d, J = 7.5 Hz, 2H), 7.61 – 7.60 (m, 1H), 7.54 – 7.51 (m, 1H), 7.29 (d, J = 7.5 Hz, 2H), 2.80 (s, 3H), 2.37 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, CDCl3) δ 148.8, 148.5, 145.4, 145.2, 138.7, 137.5, 130.8, 130.2, 128.7, 128.2, 122.4, 122.3, 121.0, 21.8, 18.9; IR (neat, cm^{-1}): 2922, 1493, 1463, 1318, 1197, 1151, 1103, 1072, 847; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{17}H_{16}NO_2S$, $[M + H]^+$: 298.0896, found: 298.0885.

6-Fluoro-2-methyl-4-tosylquinoline (9b):

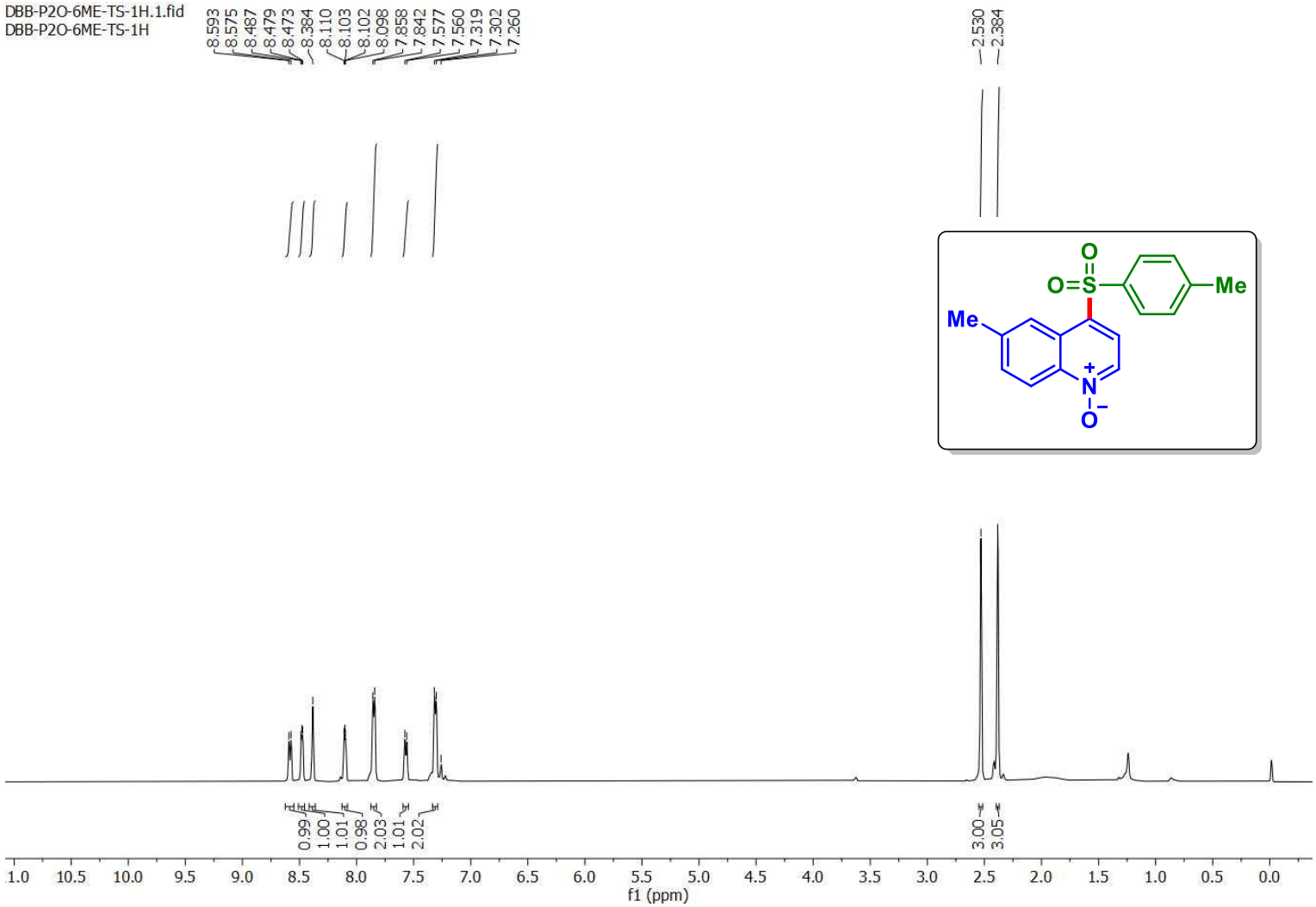


As white solid (42.5 mg, 67% yield); mp 179 – 182 °C; purified over a column of silica gel (30% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 – 8.21 (m, 1H), 8.10 – 8.05 (m, 2H), 7.87 (d, J = 8.0 Hz, 2H), 7.50 – 7.47 (m, 1H), 7.32 (d, J = 8.0 Hz, 2H), 2.83 (s, 3H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 161.0 (d, J = 250.5 Hz), 158.2 (d, J = 2.9 Hz), 146.6, 145.5, 145.0

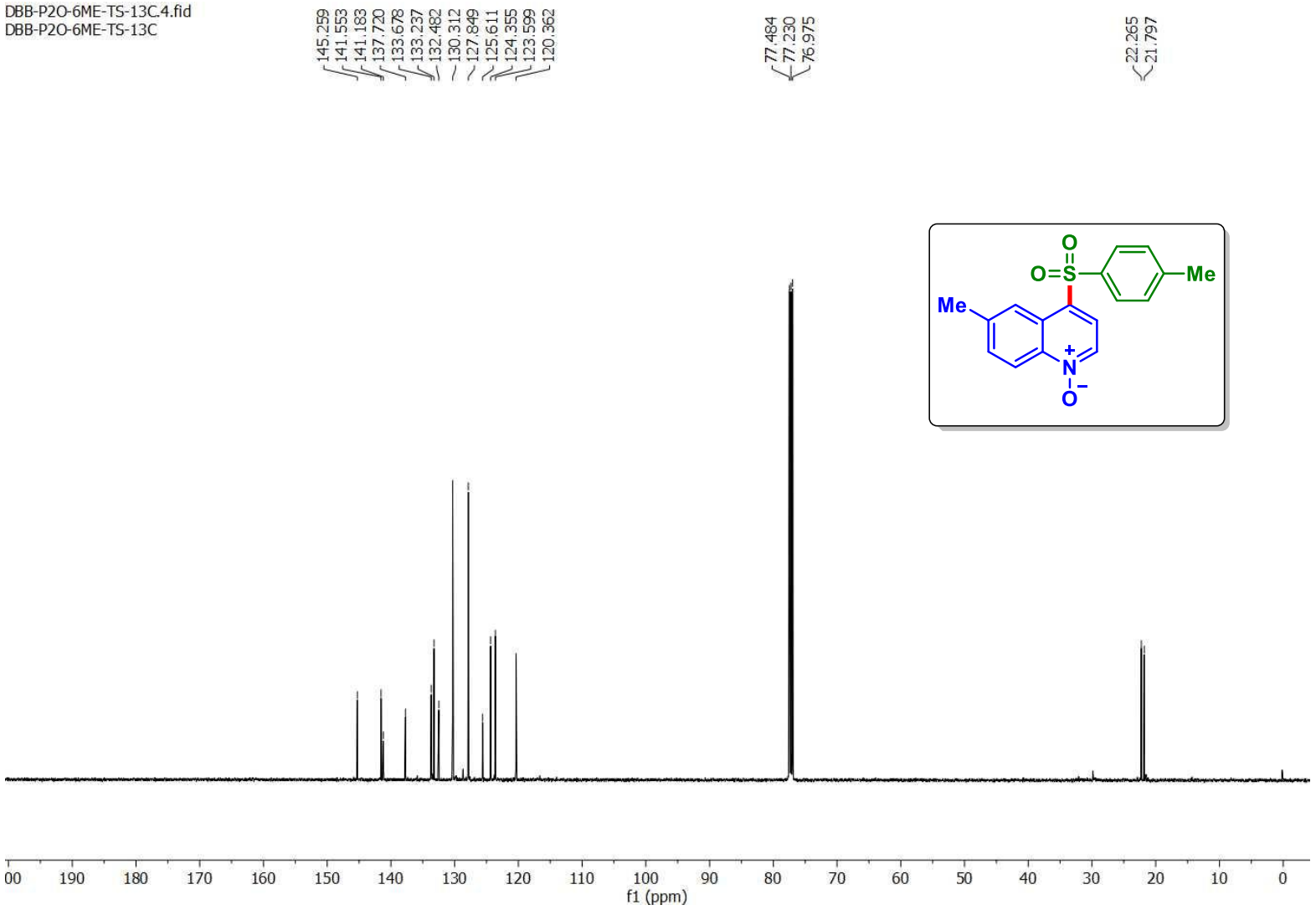
(d, J = 5.9 Hz), 137.2, 132.4 (d, J = 9.3 Hz), 130.4, 128.1, 123.1, 121.6 (d, J = 11.0 Hz), 120.8 (d, J = 25.8 Hz), 108.5 (d, J = 25.3 Hz), 25.5, 21.8; ^{19}F NMR (471 MHz, $CDCl_3$): δ -109.1 (s); IR (neat, cm^{-1}): 2922, 2852, 1494, 1326, 1228, 1158, 1083, 864; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{17}H_{15}FNO_2S$, $[M + H]^+$: 316.0802, found: 316.0792.

13. Spectra of all compounds:

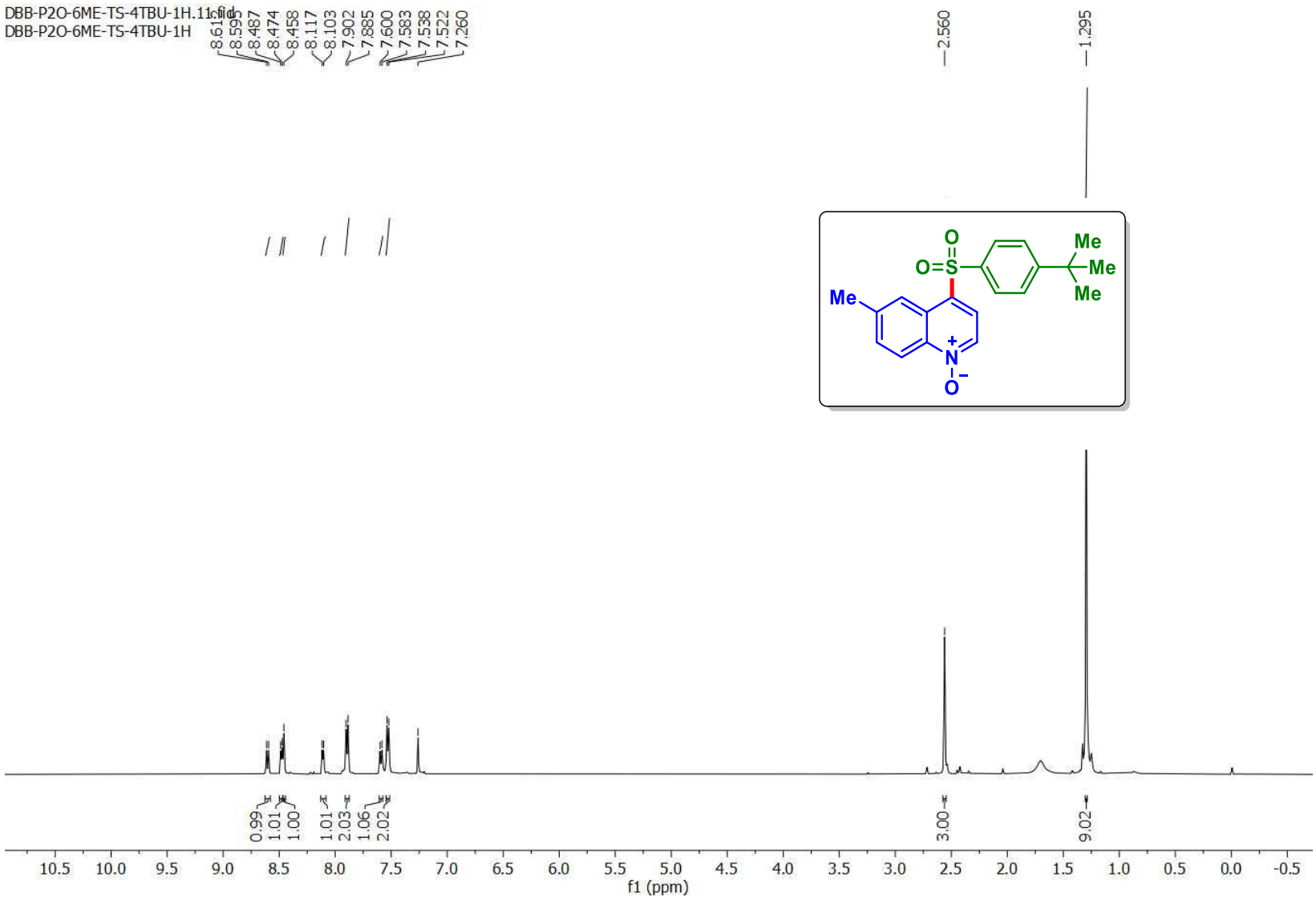
6-Methyl-4-tosylquinoline 1-oxide (1b'): ^{1}H NMR ($CDCl_3$, 500 MHz)



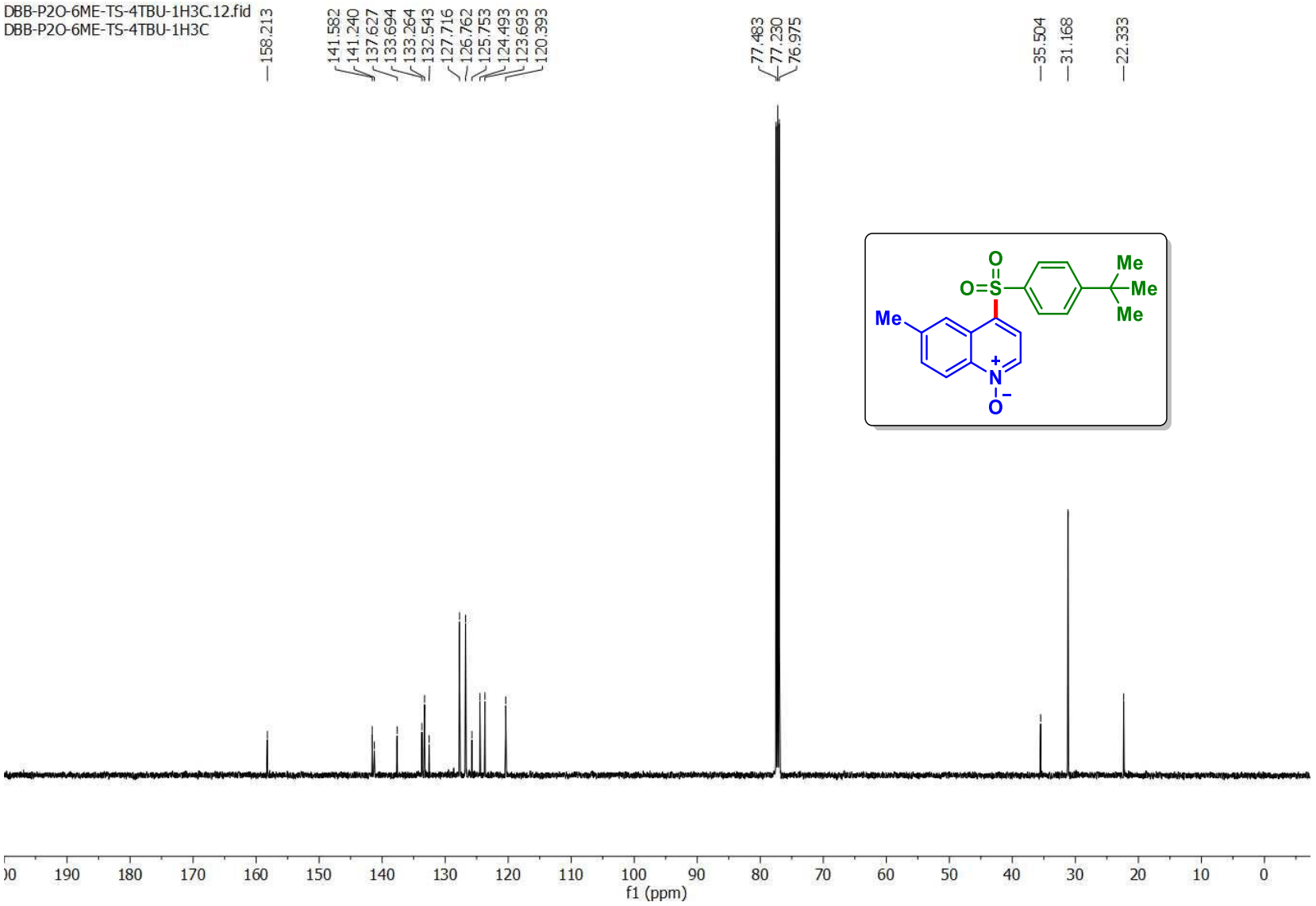
6-Methyl-4-tosylquinoline 1-oxide (1b'): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



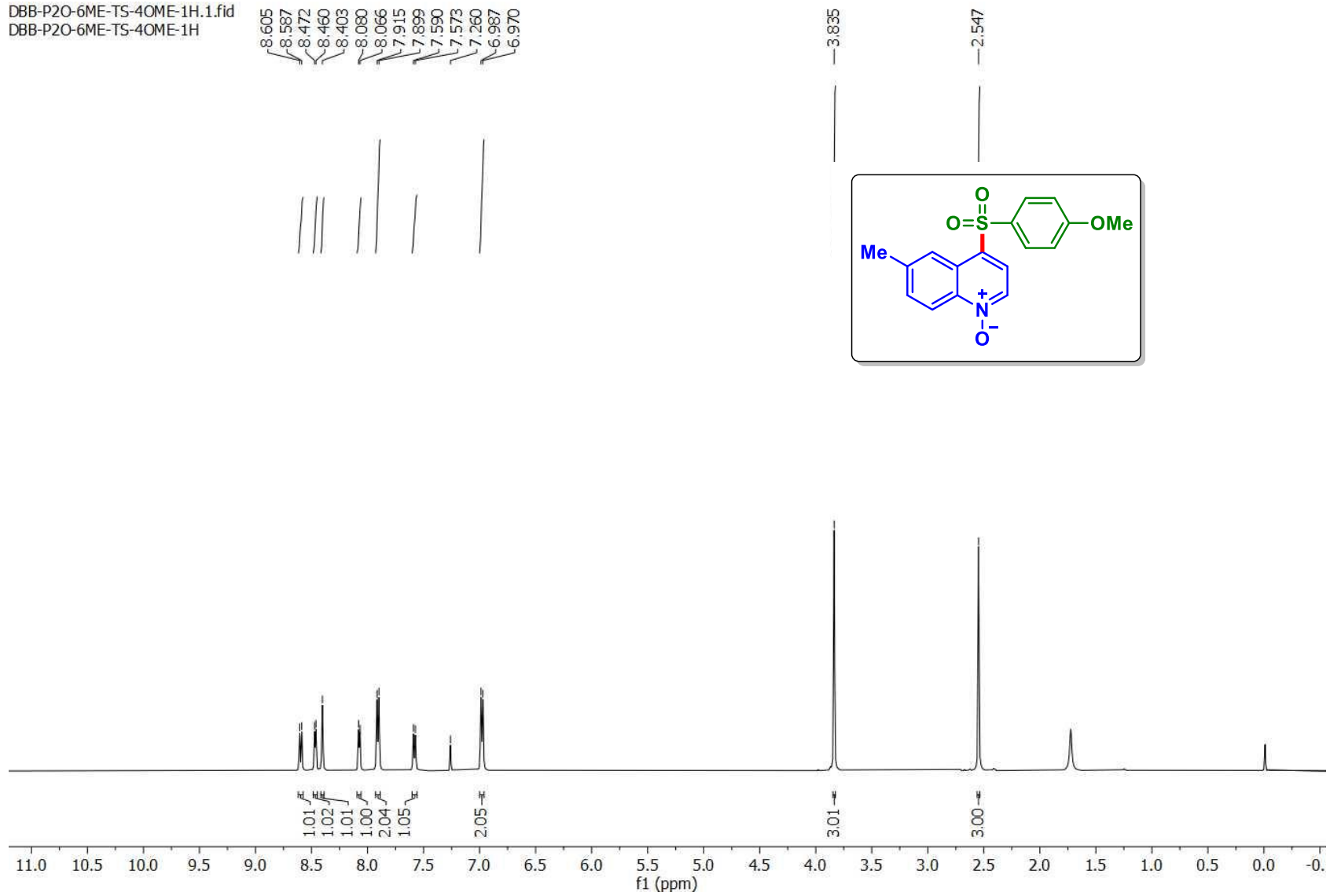
4-((4-(Tert-butyl)phenyl)sulfonyl)-6-methylquinoline 1-oxide (1c'): ^{1}H NMR ($CDCl_3$, 500 MHz)



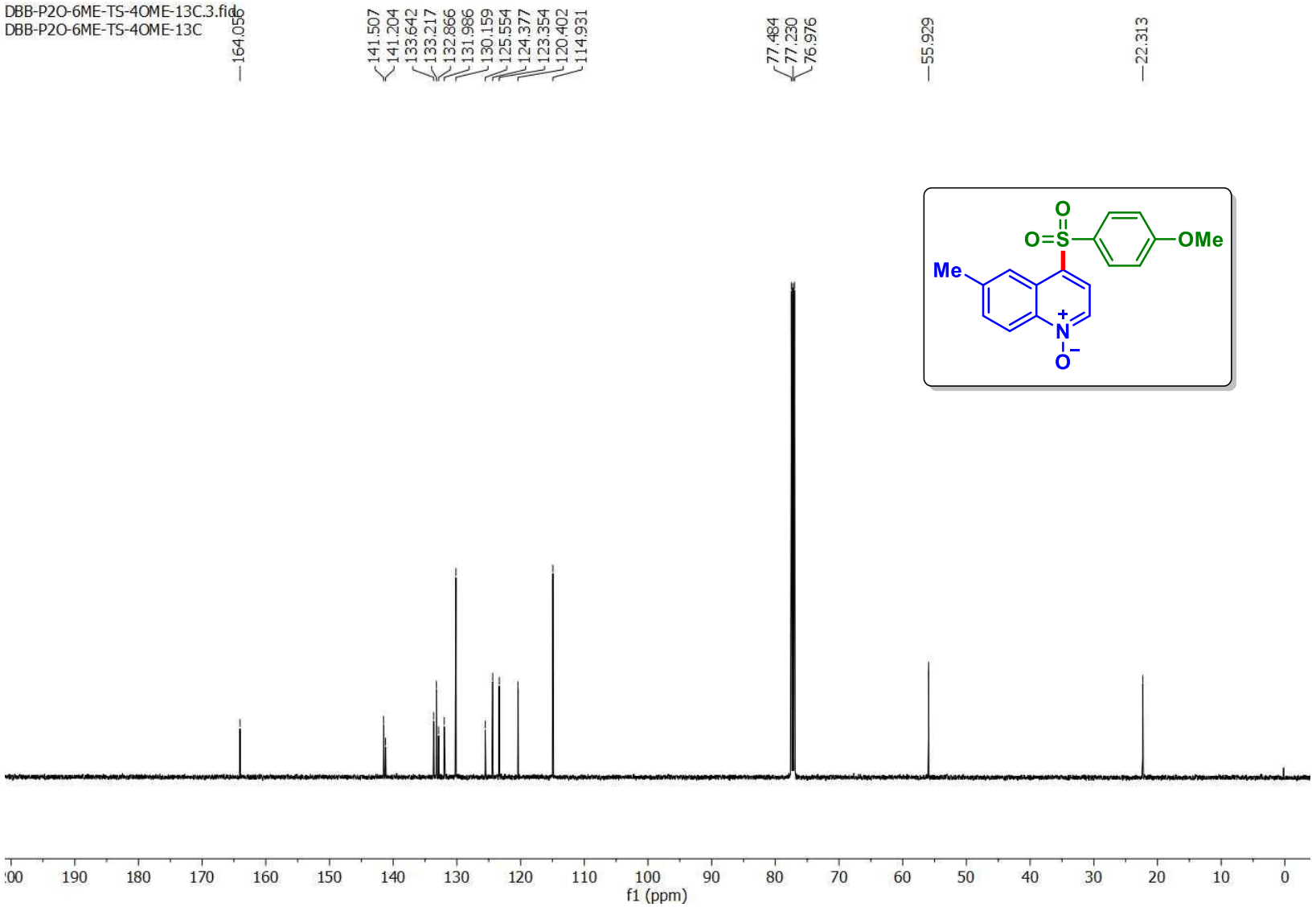
4-((4-(Tert-butyl)phenyl)sulfonyl)-6-methylquinoline 1-oxide (1c'): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



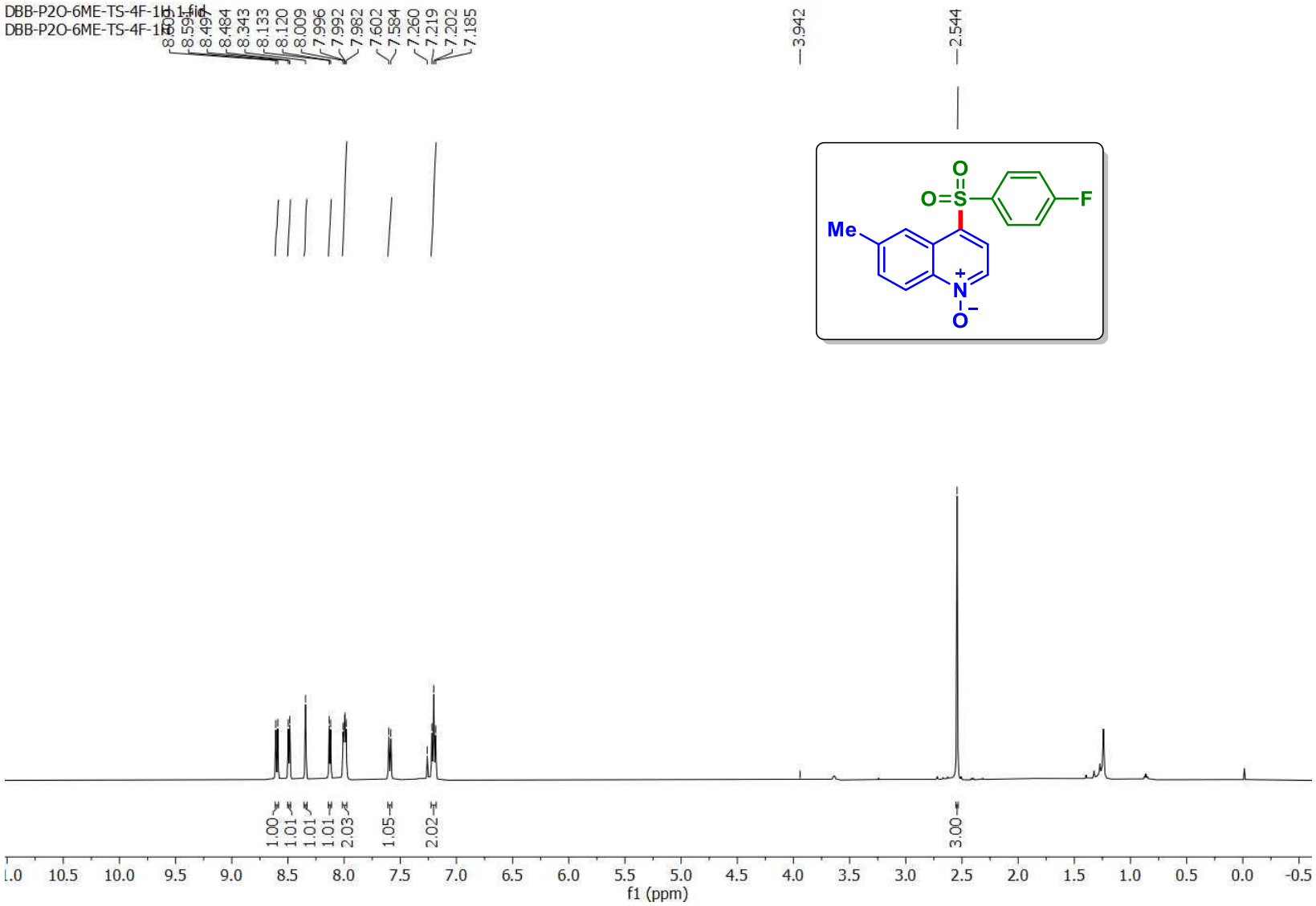
4-((4-Methoxyphenyl)sulfonyl)-6-methylquinoline 1-oxide (1d'): ^{1}H NMR ($CDCl_3$, 500 MHz)



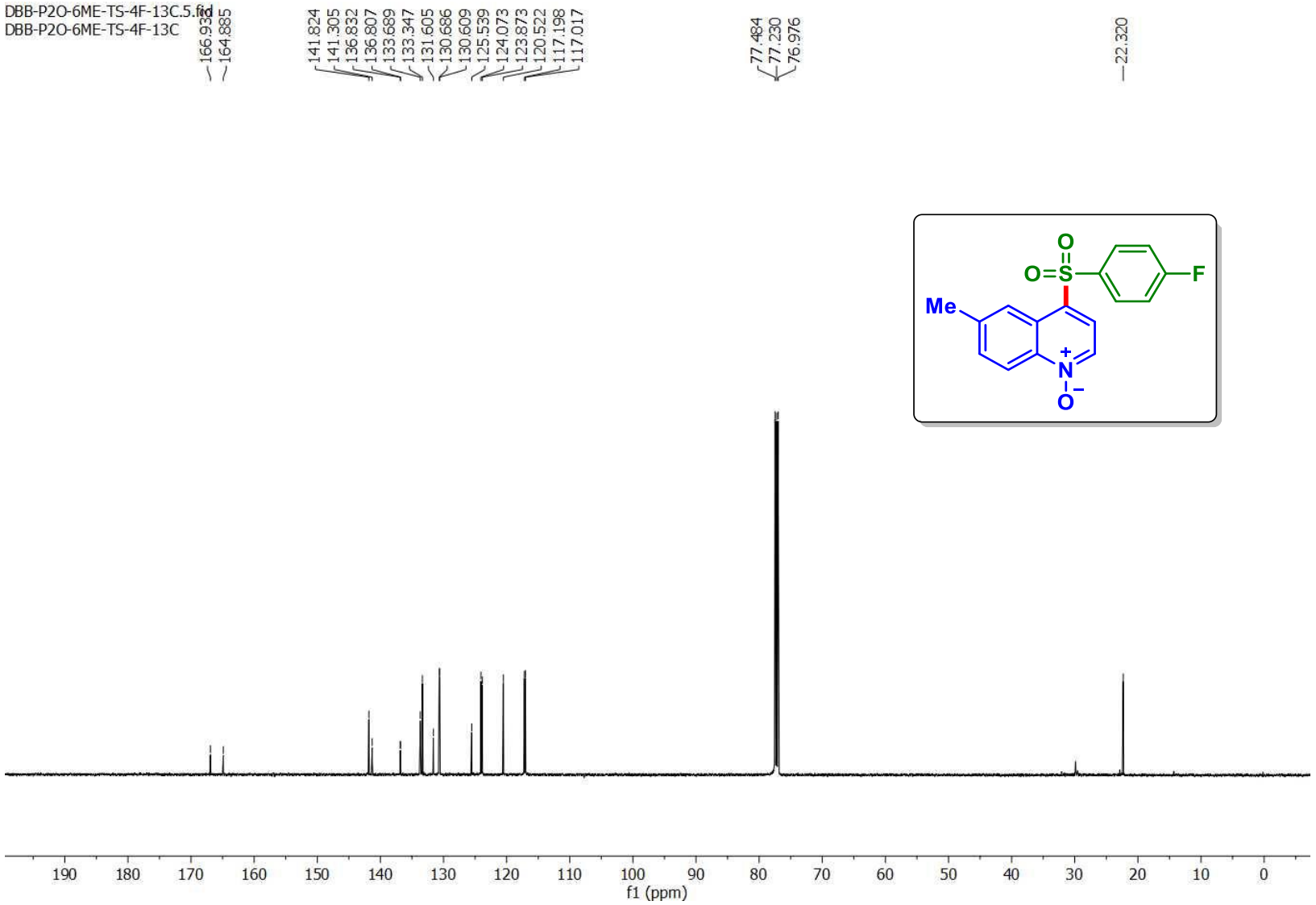
4-((4-Methoxyphenyl)sulfonyl)-6-methylquinoline 1-oxide (1d'): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



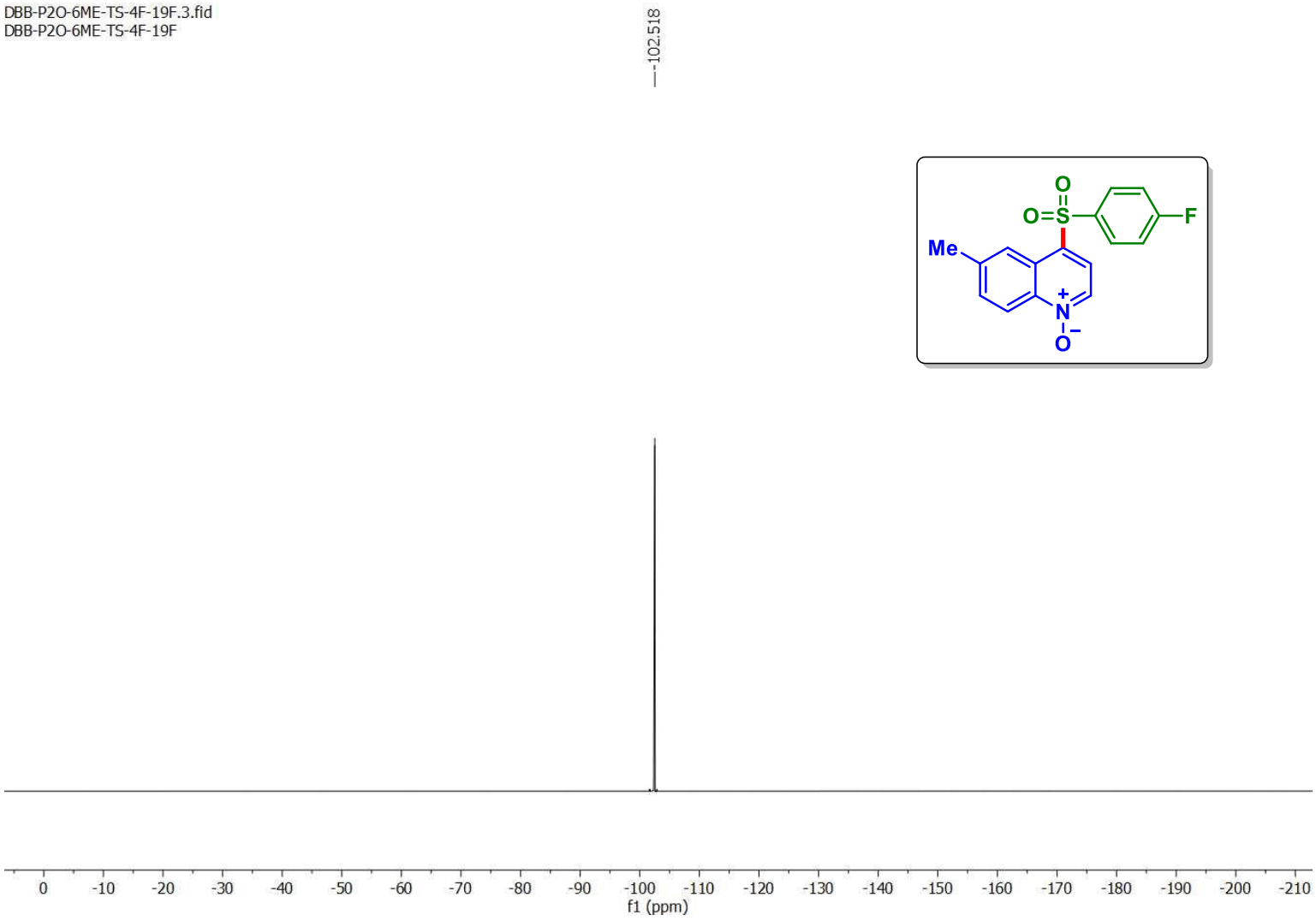
4-((4-Fluorophenyl)sulfonyl)-6-methylquinoline 1-oxide (1e'): ^{1}H NMR (CDCl$_3$, 500 MHz)



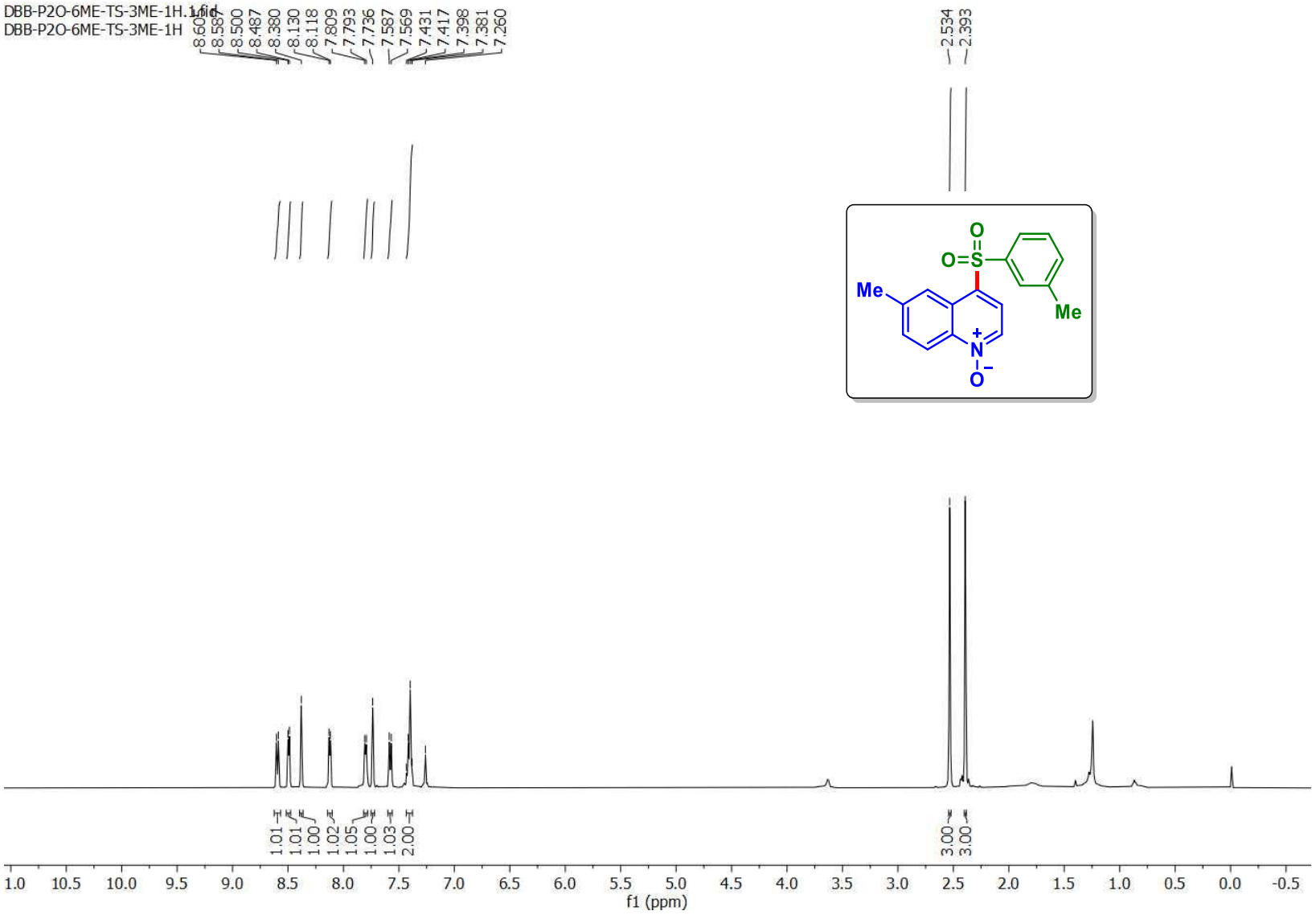
4-((4-Fluorophenyl)sulfonyl)-6-methylquinoline 1-oxide (1e'): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



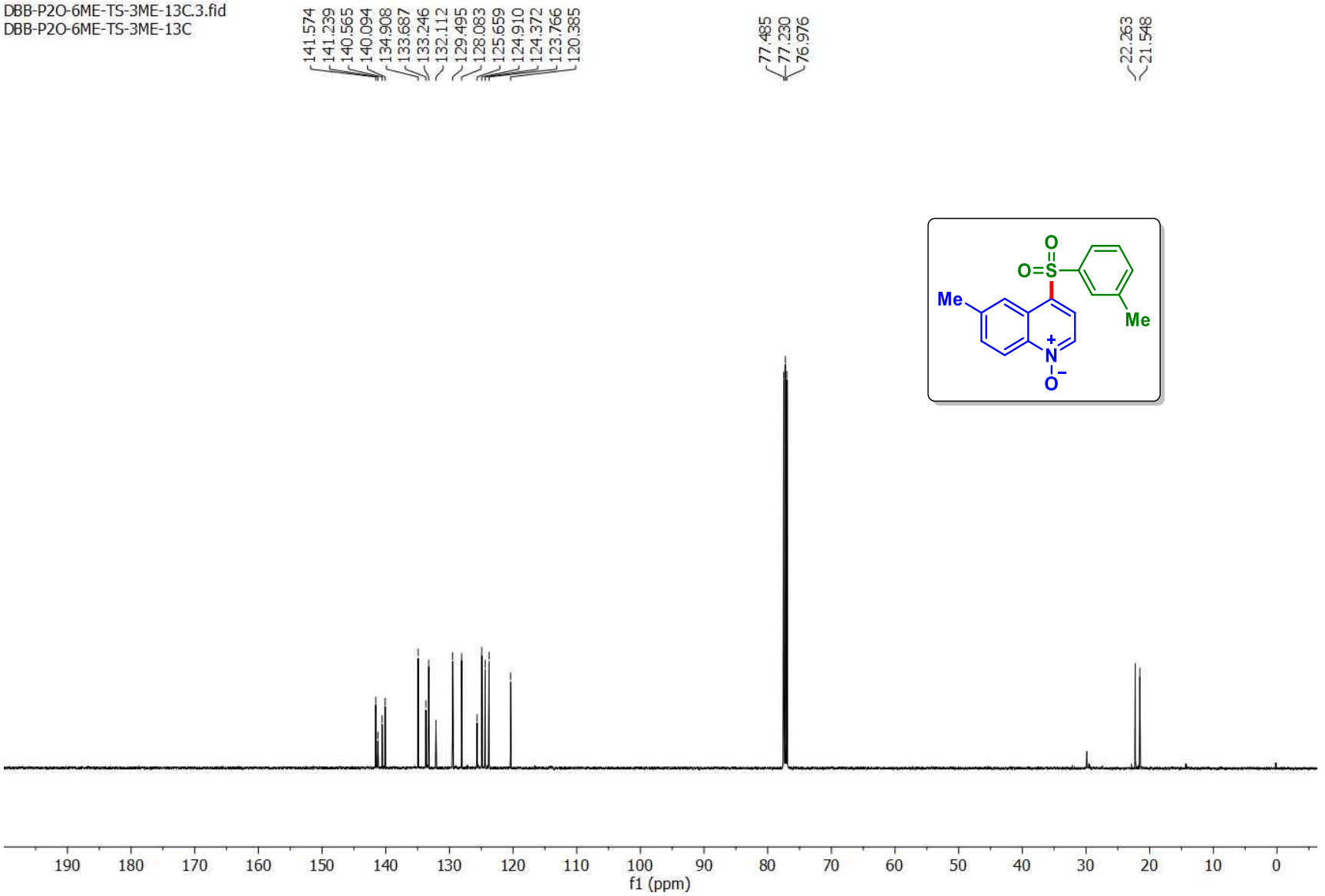
4-((4-Fluorophenyl)sulfonyl)-6-methylquinoline 1-oxide (1e'): ^{19}F NMR ($CDCl_3$, 471 MHz)



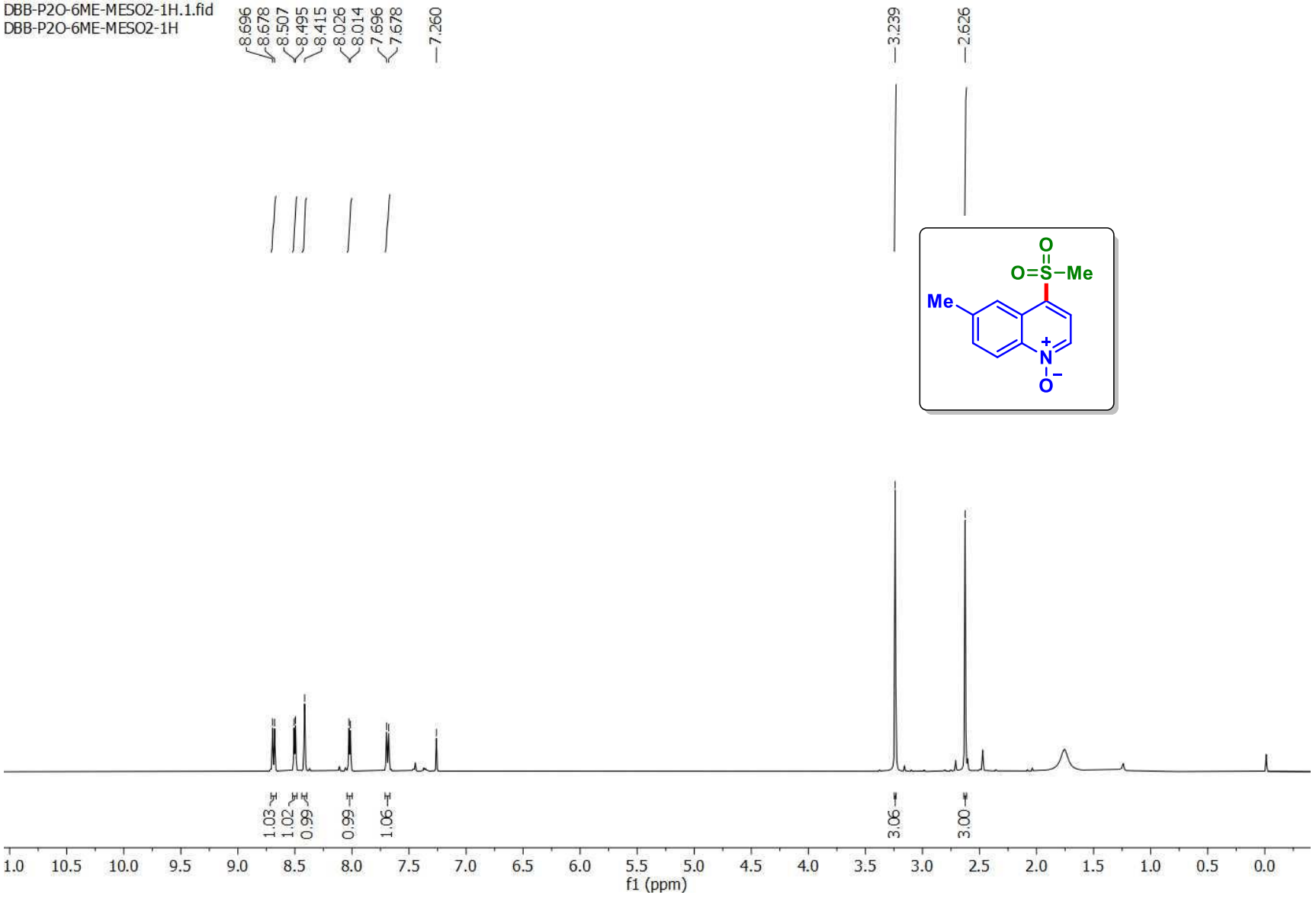
6-Methyl-4-(m-tolylsulfonyl)quinoline 1-oxide (1i'): ^{1}H NMR (CDCl$_3$, 500 MHz)



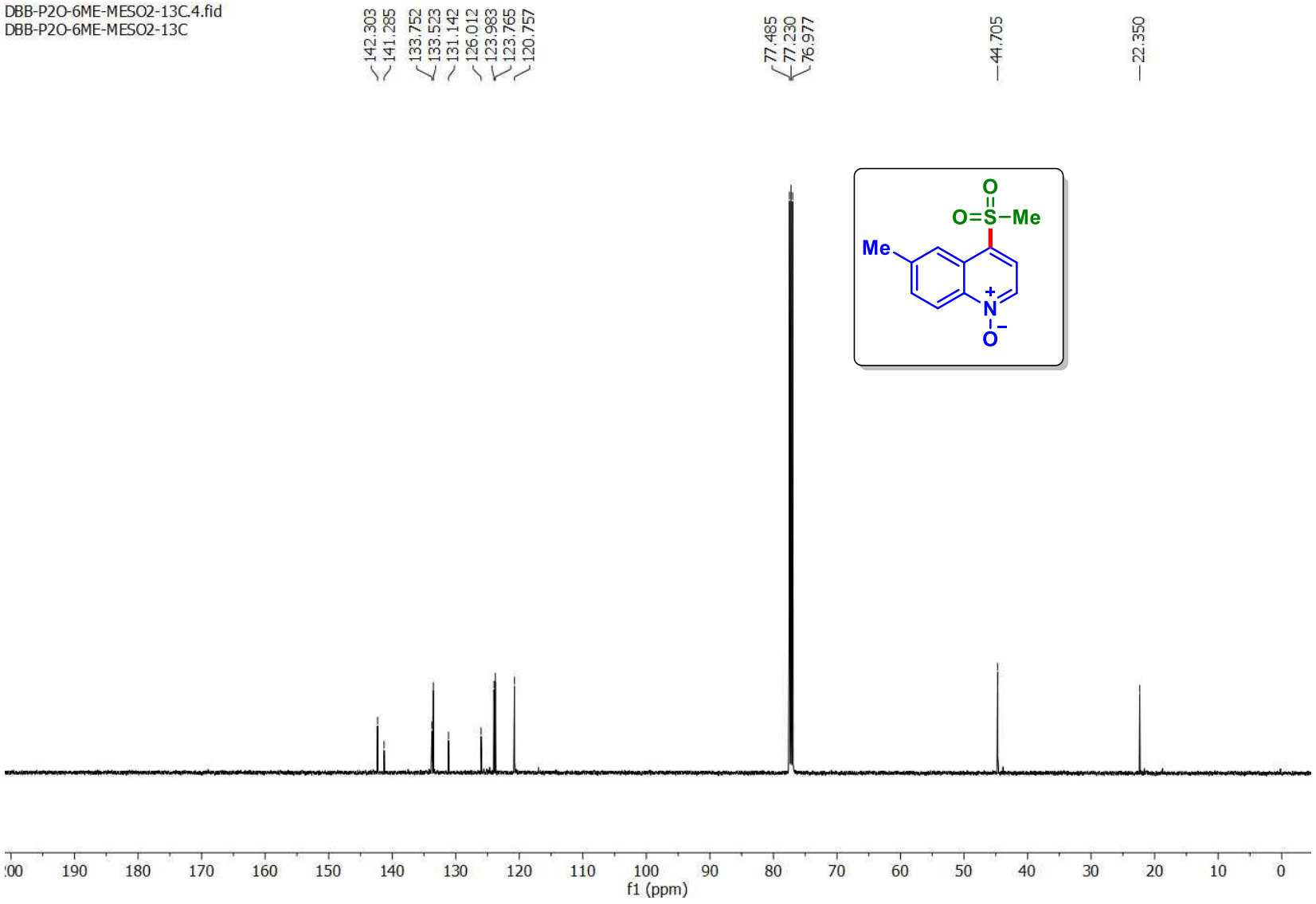
6-Methyl-4-(m-tolylsulfonyl)quinoline 1-oxide (1i'): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



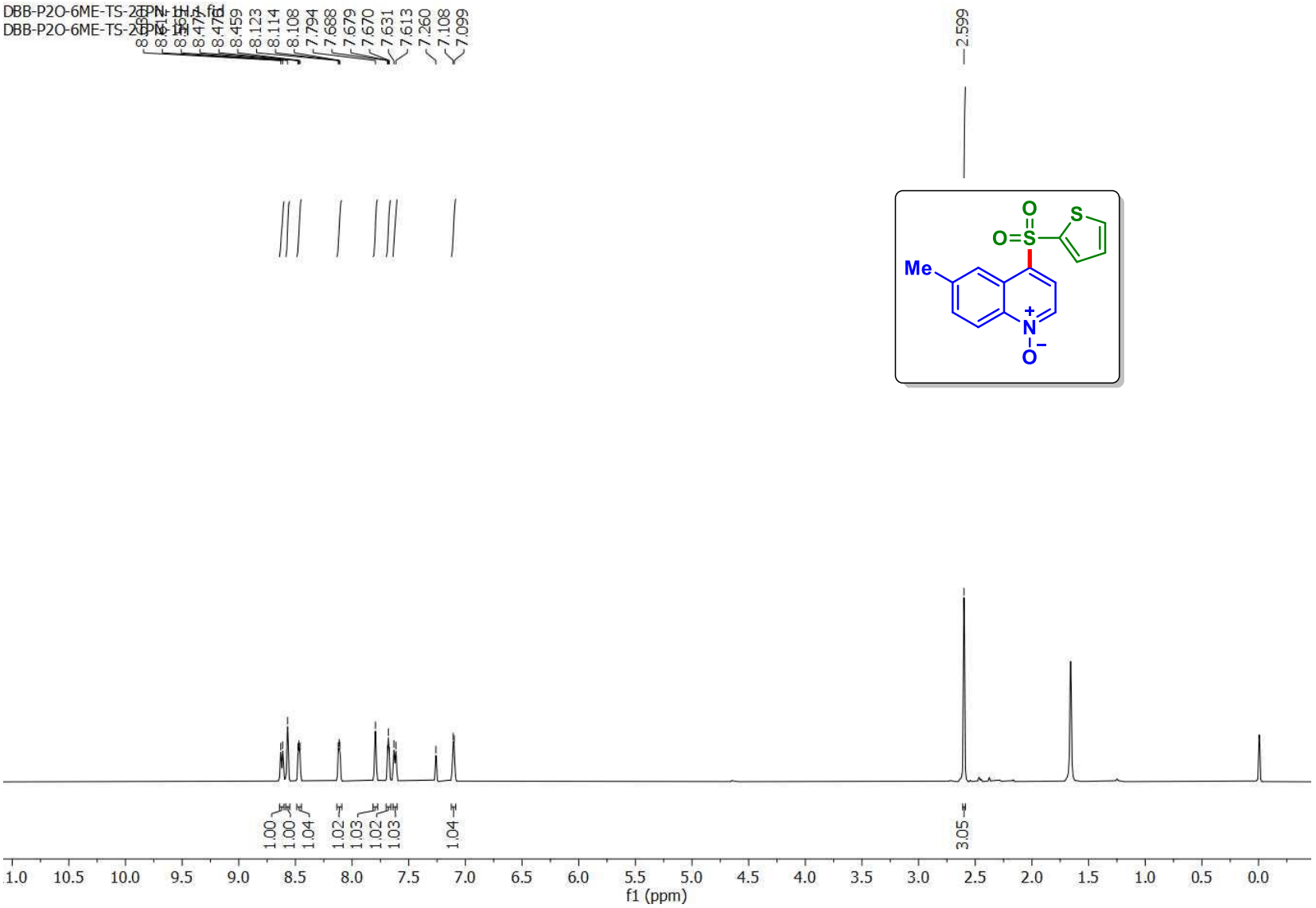
6-Methyl-4-(methylsulfonyl)quinoline 1-oxide (1l'): ^{1}H NMR ($CDCl_3$, 500 MHz)



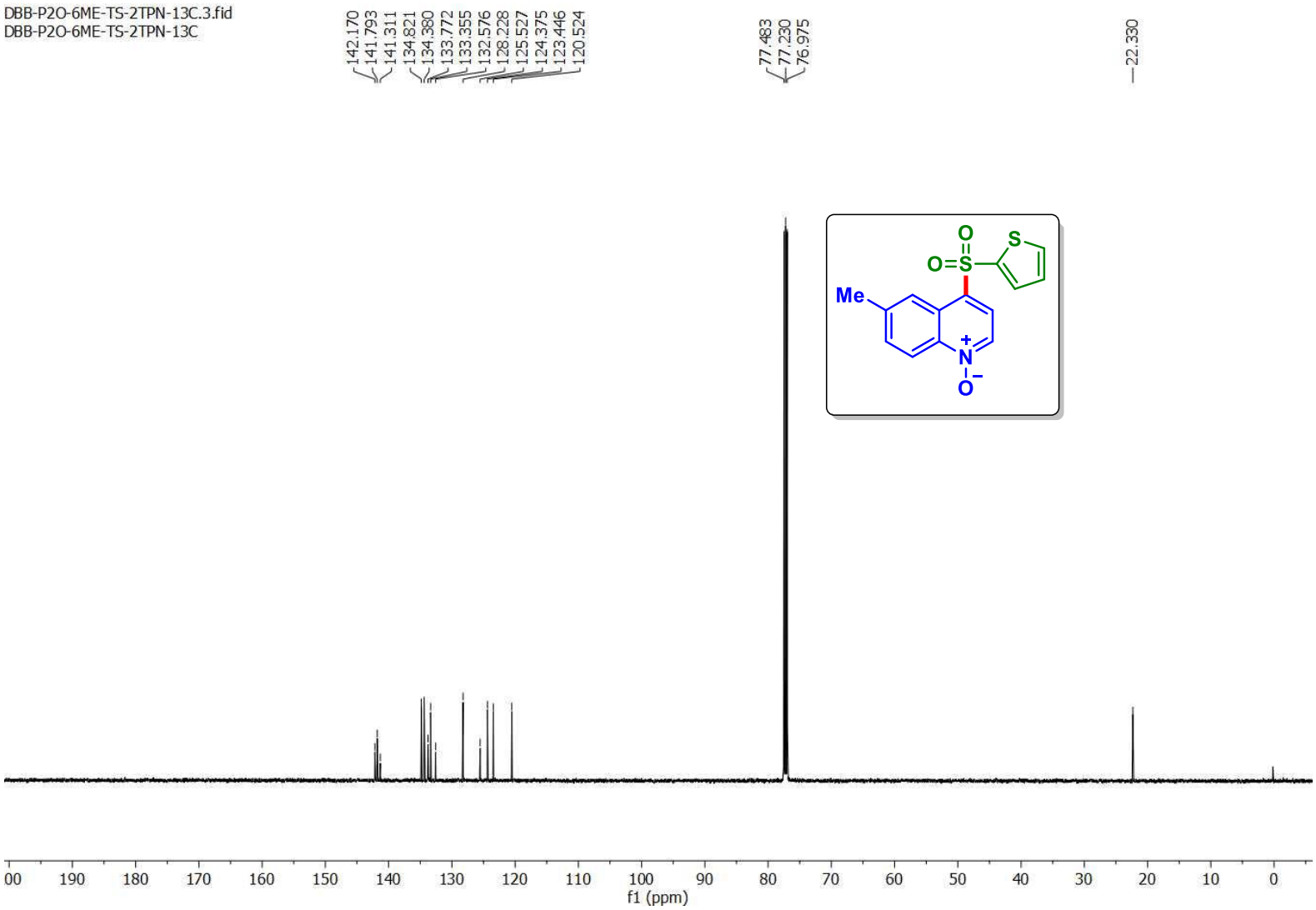
6-Methyl-4-(methylsulfonyl)quinoline 1-oxide (1l'): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



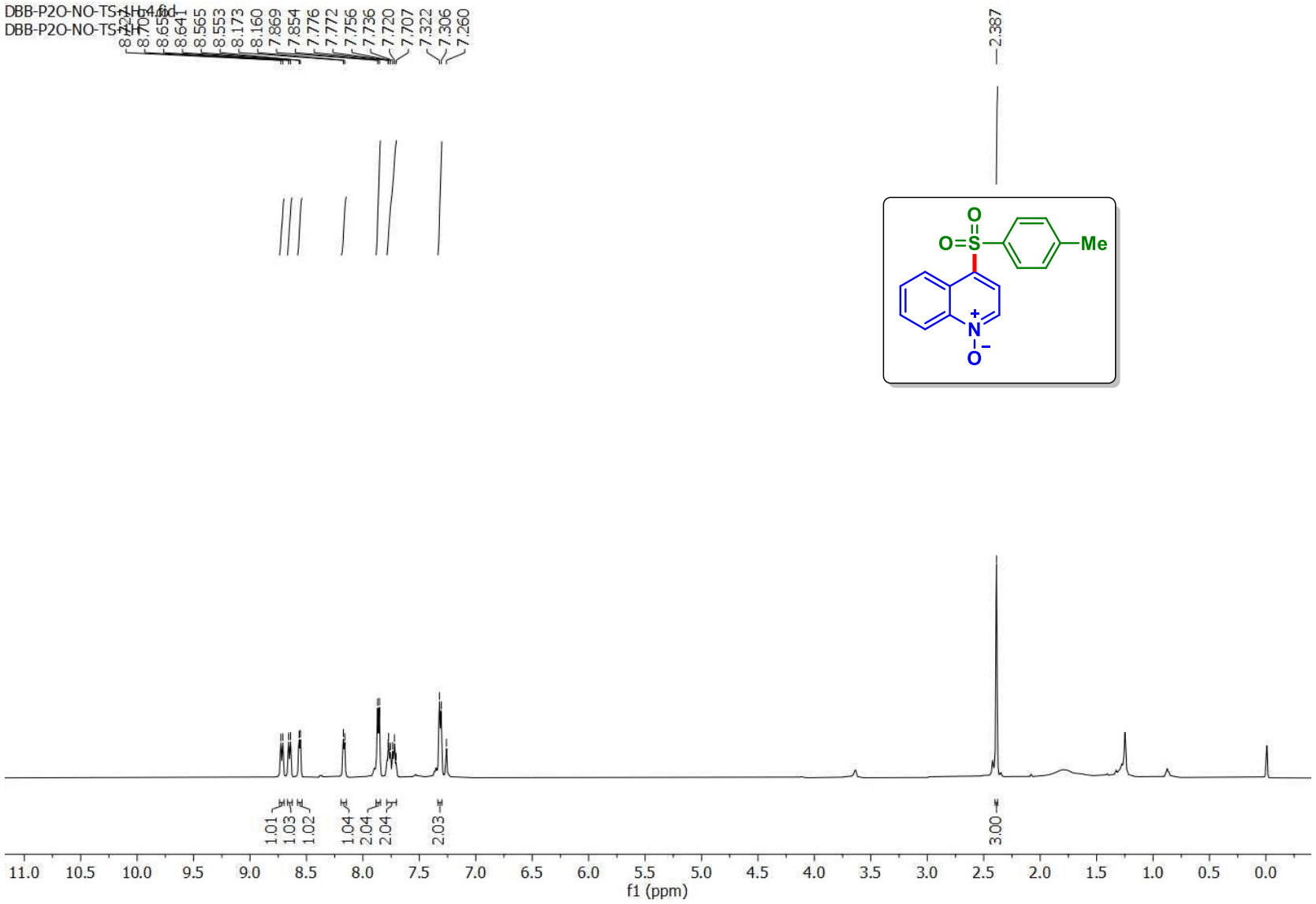
6-Methyl-4-(thiophen-2-ylsulfonyl)quinoline 1-oxide (1m'): ^{1}H NMR ($CDCl_3$, 500 MHz)



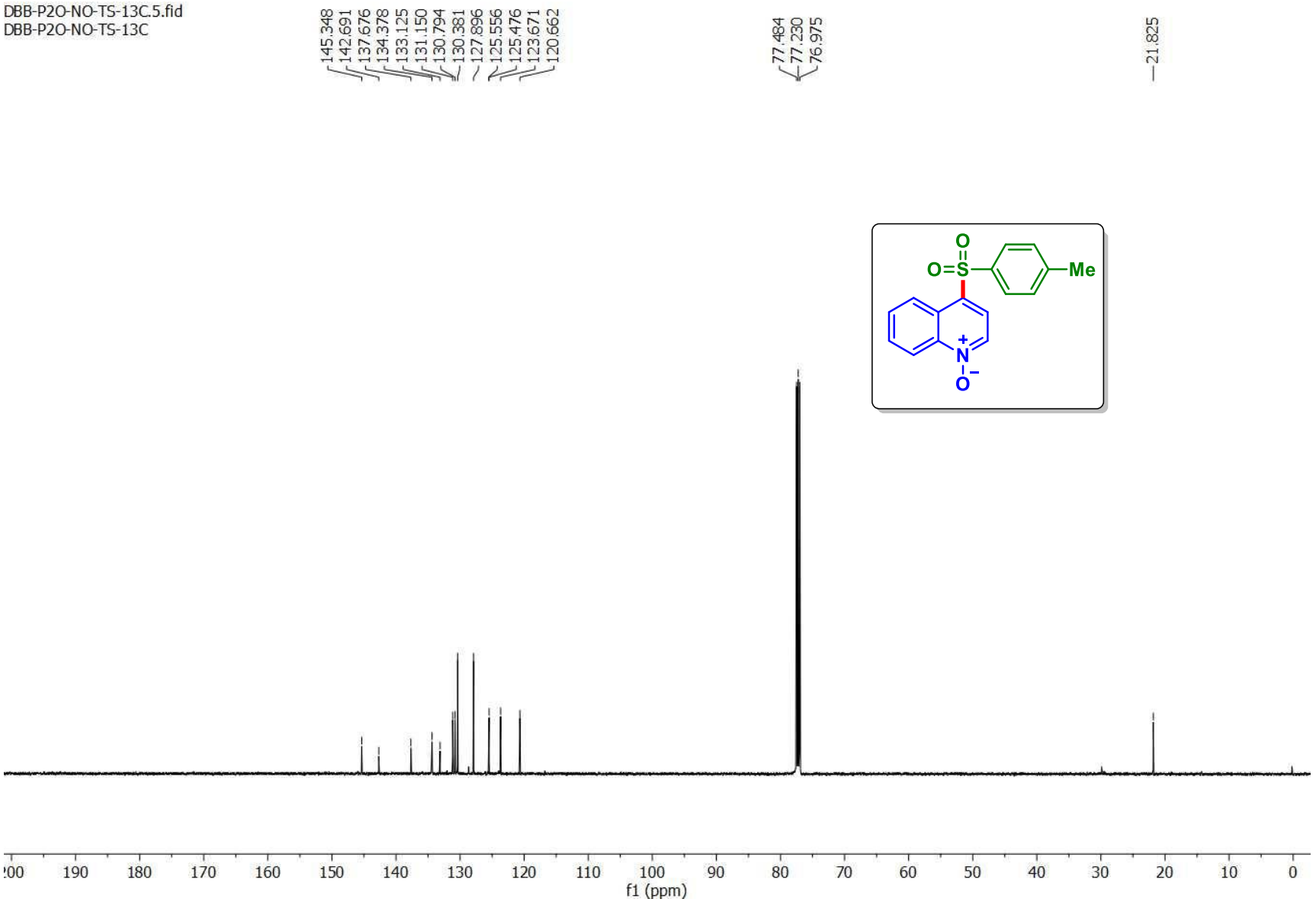
6-Methyl-4-(thiophen-2-ylsulfonyl)quinoline 1-oxide (1m'): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



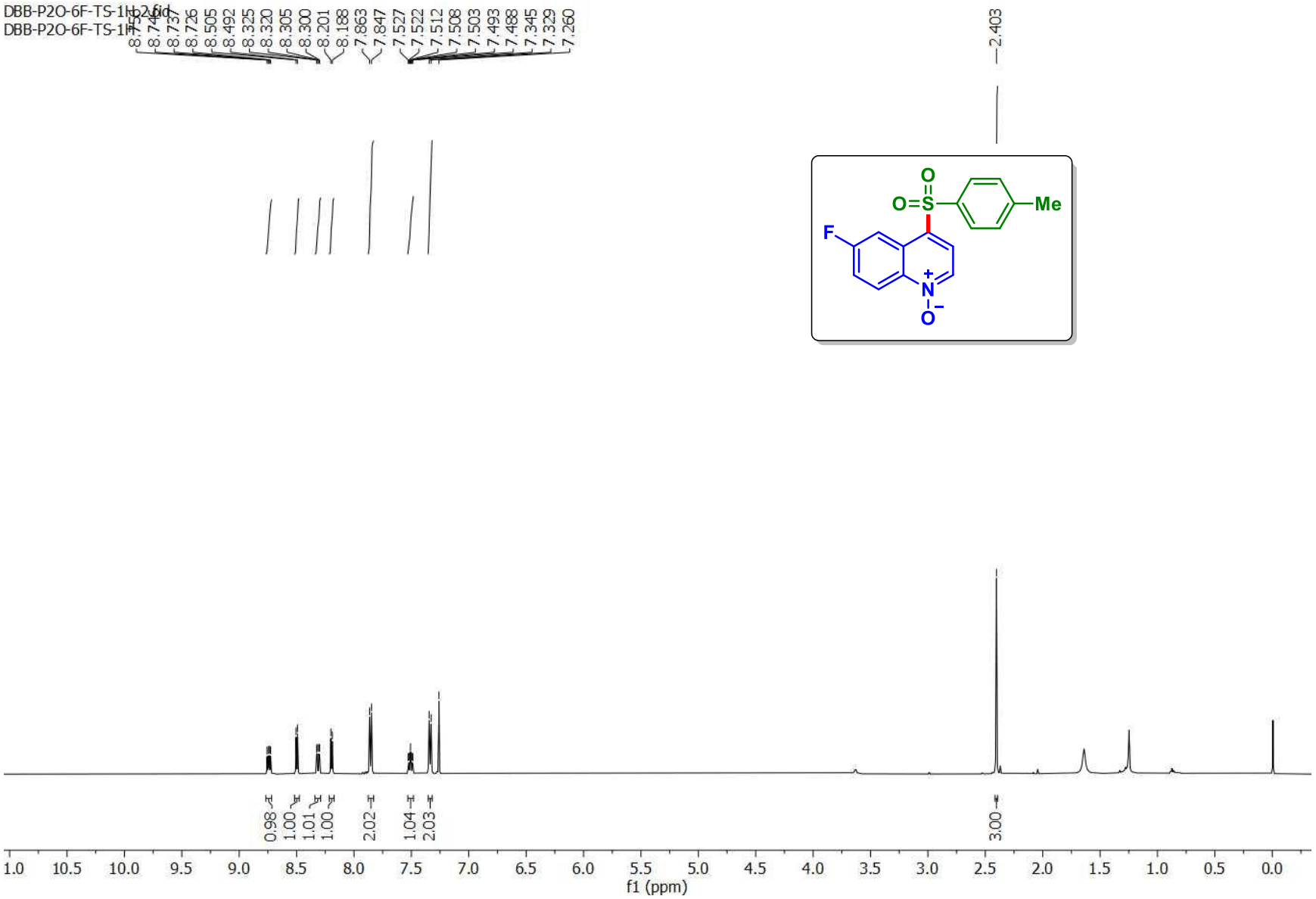
4-Tosylquinoline 1-oxide (2b'): ^{1}H NMR ($CDCl_3$, 500 MHz)



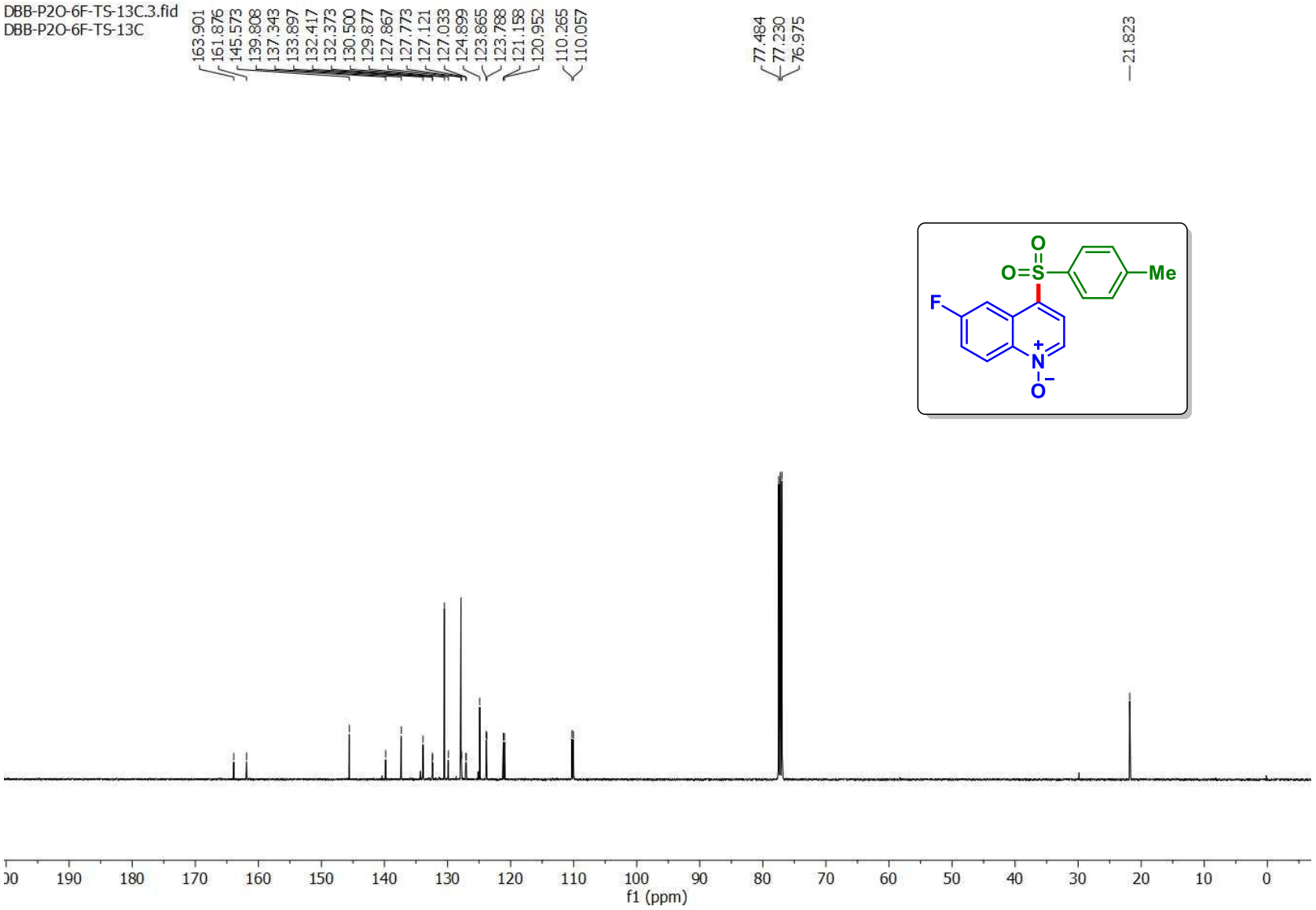
4-Tosylquinoline 1-oxide (2b'): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



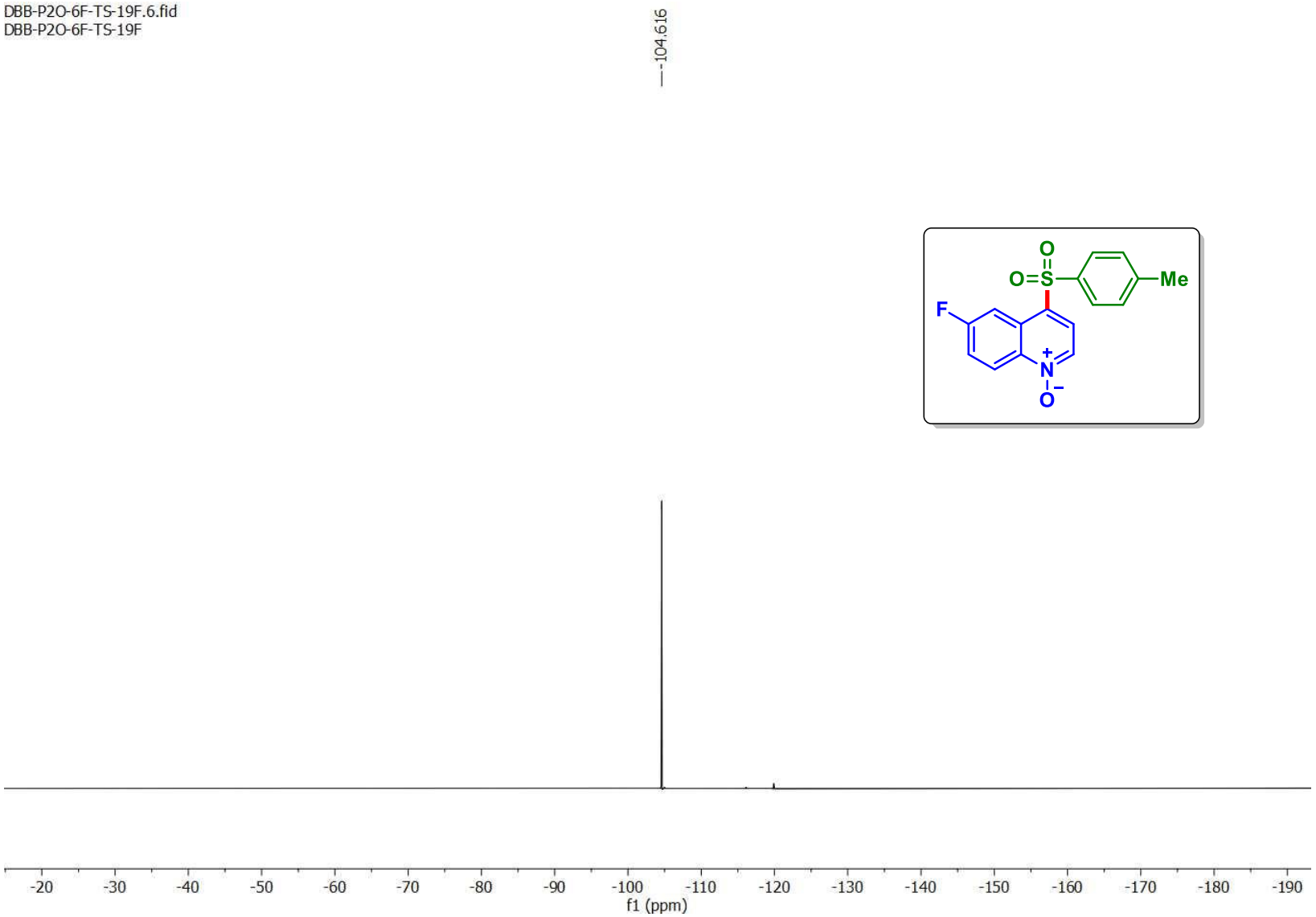
6-Fluoro-4-tosylquinoline 1-oxide (4b'): ^{1}H NMR ($CDCl_3$, 500 MHz)



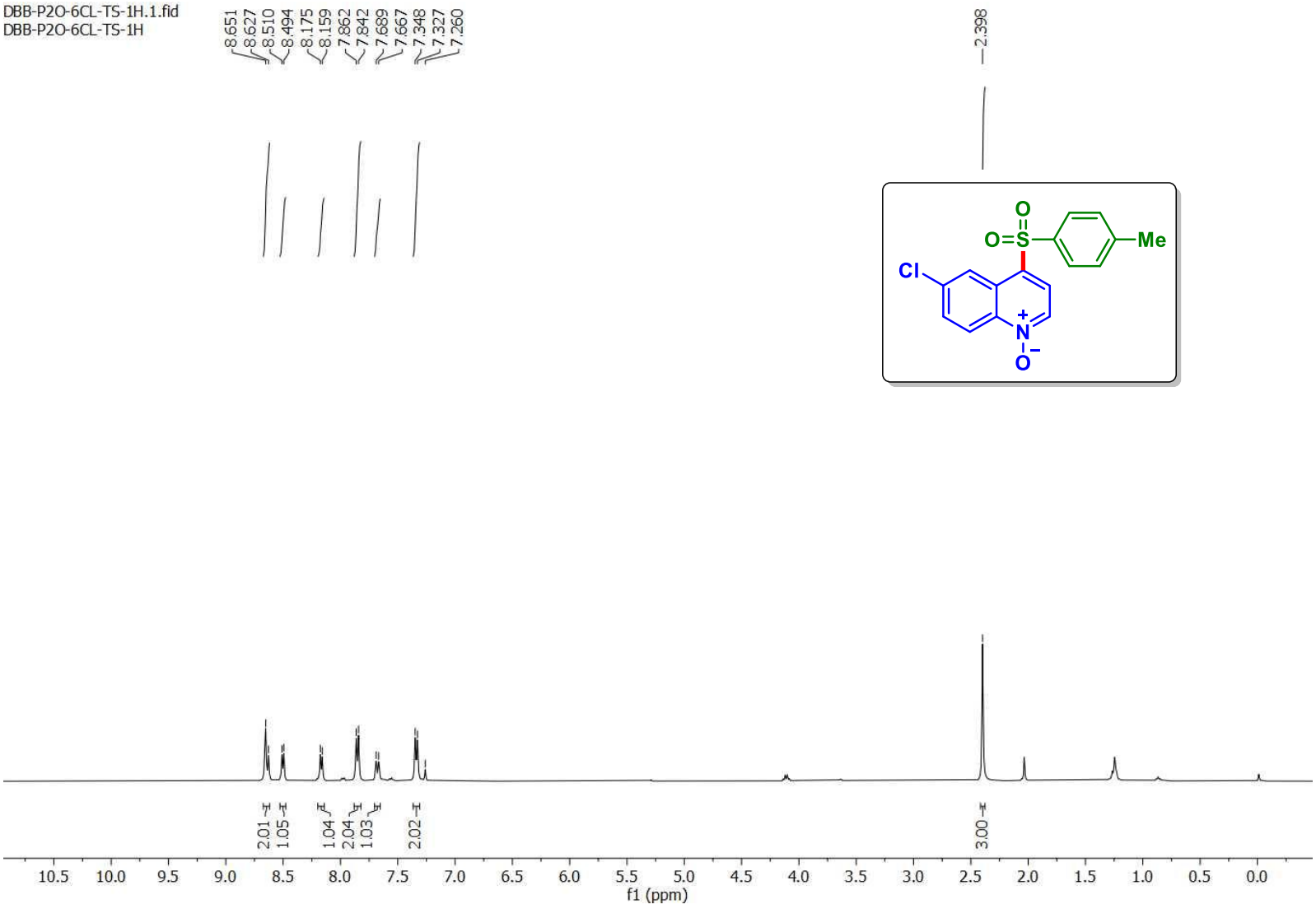
6-Fluoro-4-tosylquinoline 1-oxide (4b'): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



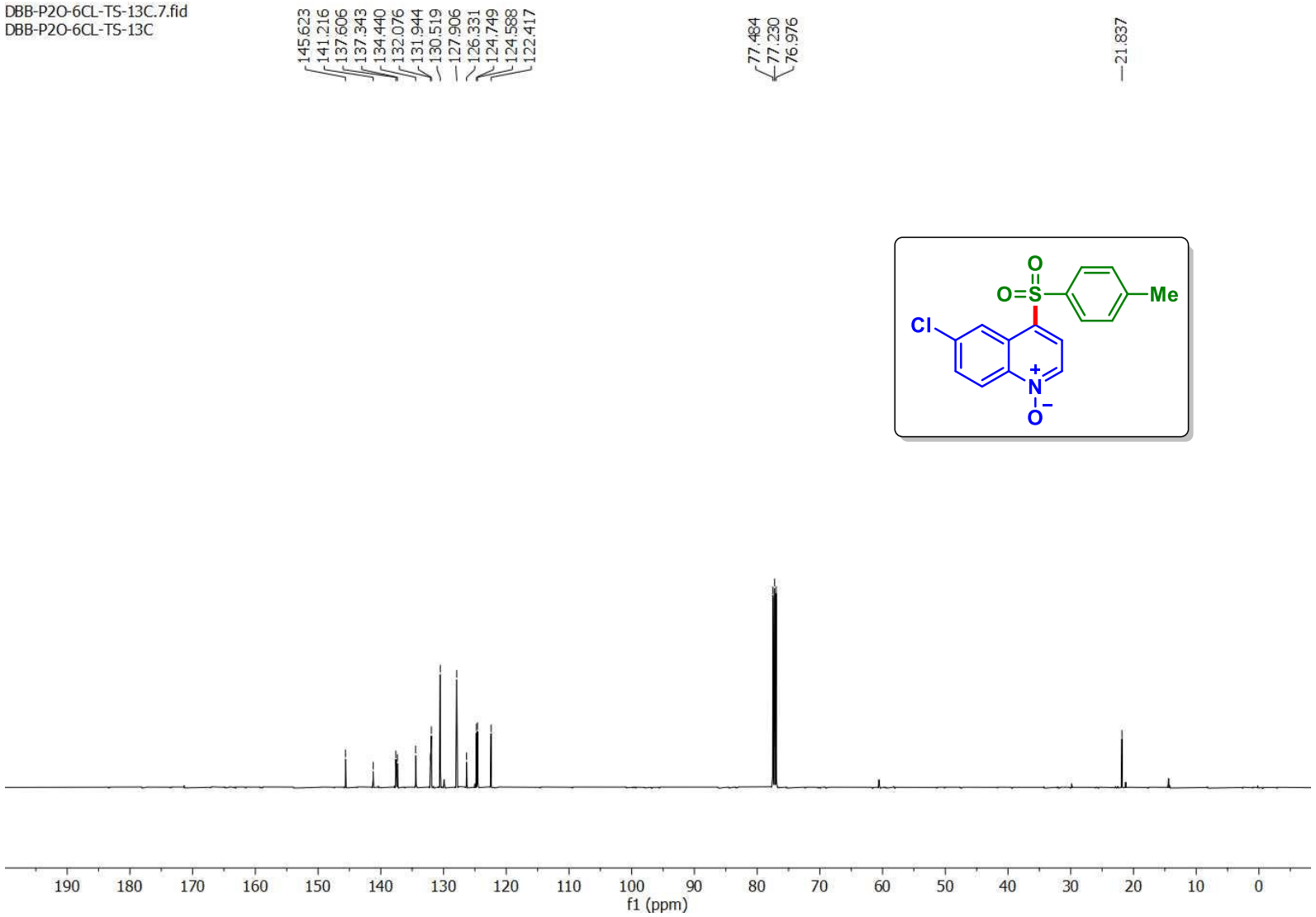
6-Fluoro-4-tosylquinoline 1-oxide (4b'): ^{19}F NMR ($CDCl_3$, 471 MHz)



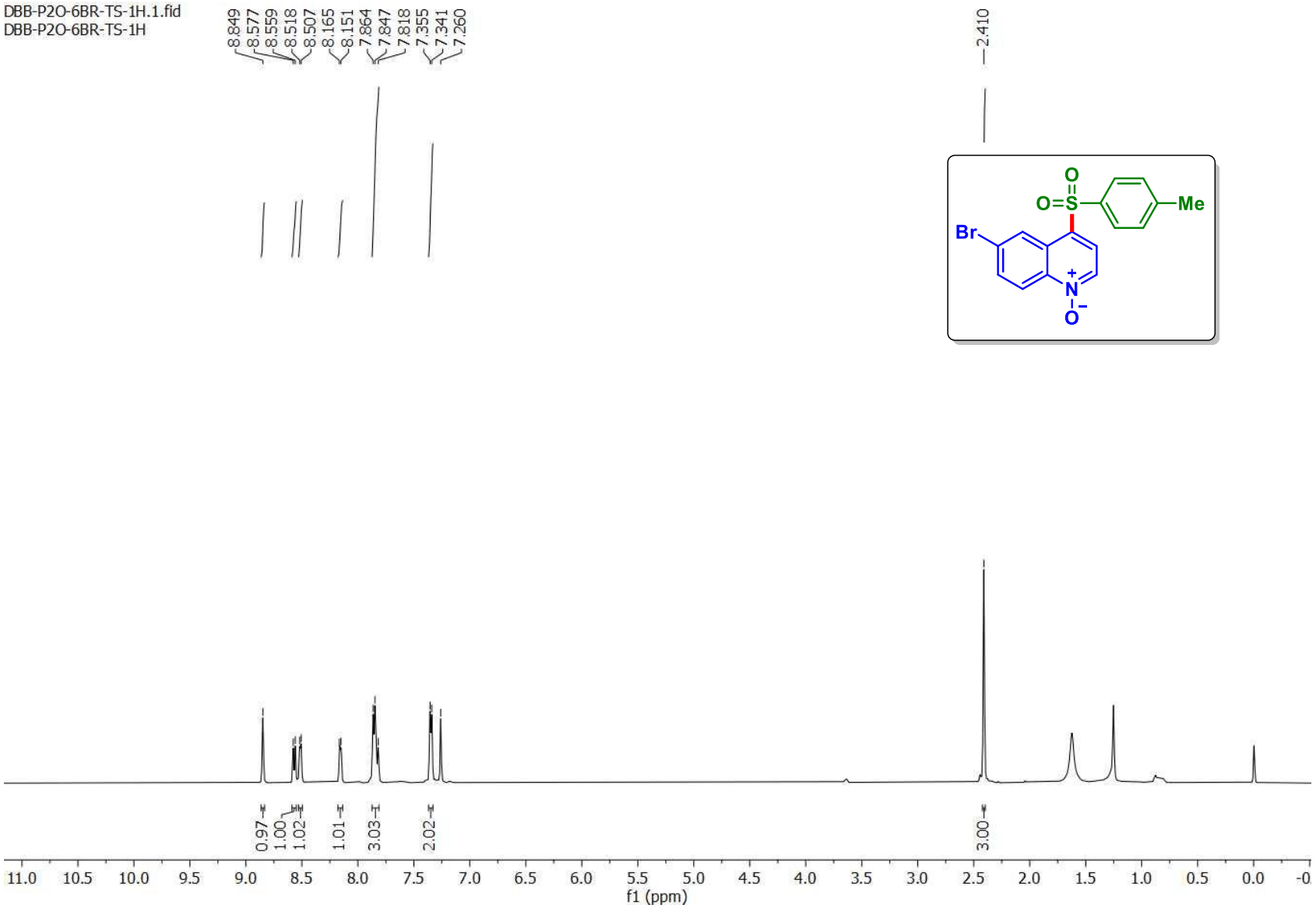
6-Chloro-4-tosylquinoline 1-oxide (5b'): ^{1}H NMR (CDCl3, 400 MHz)



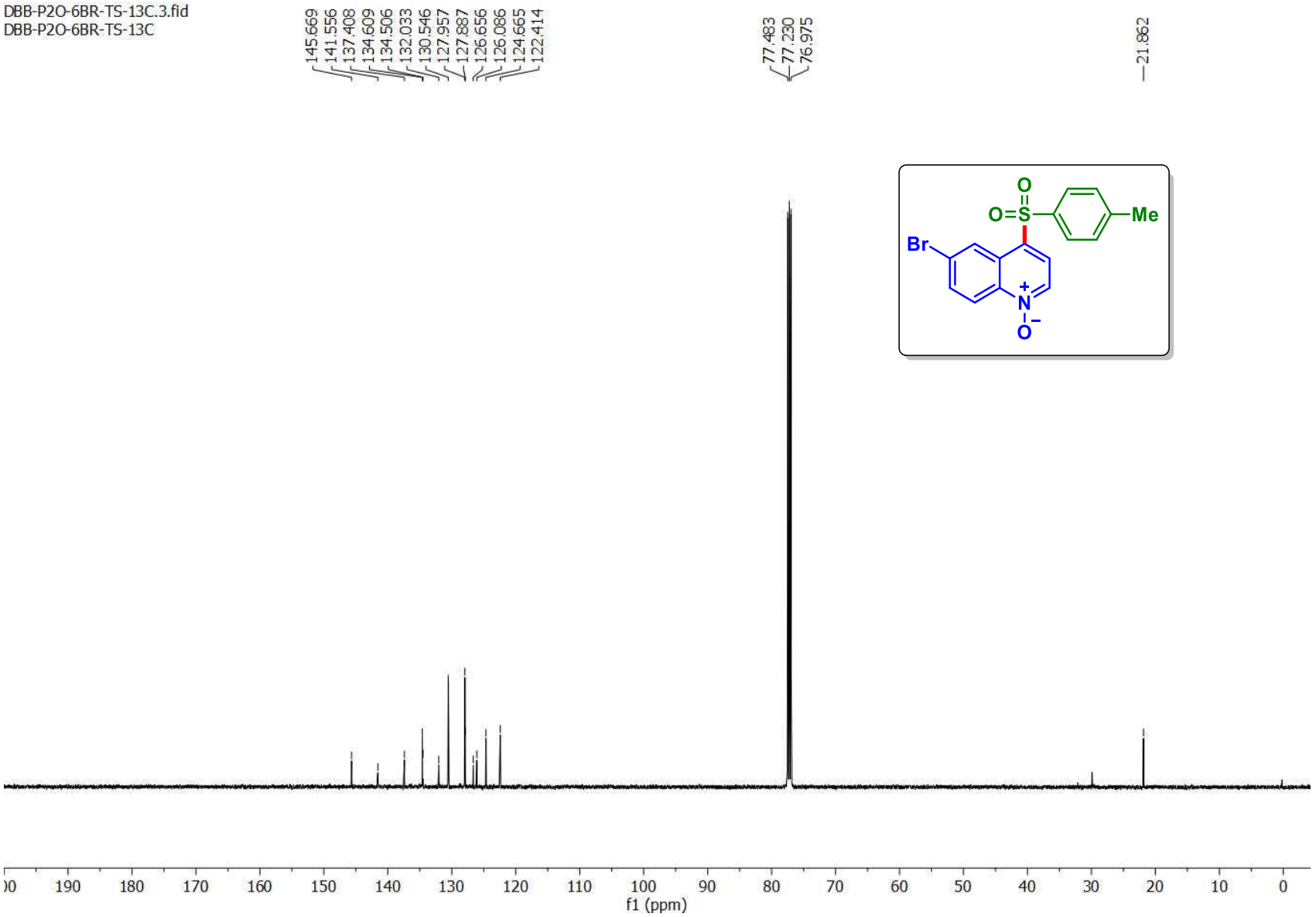
6-Chloro-4-tosylquinoline 1-oxide (5b'): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



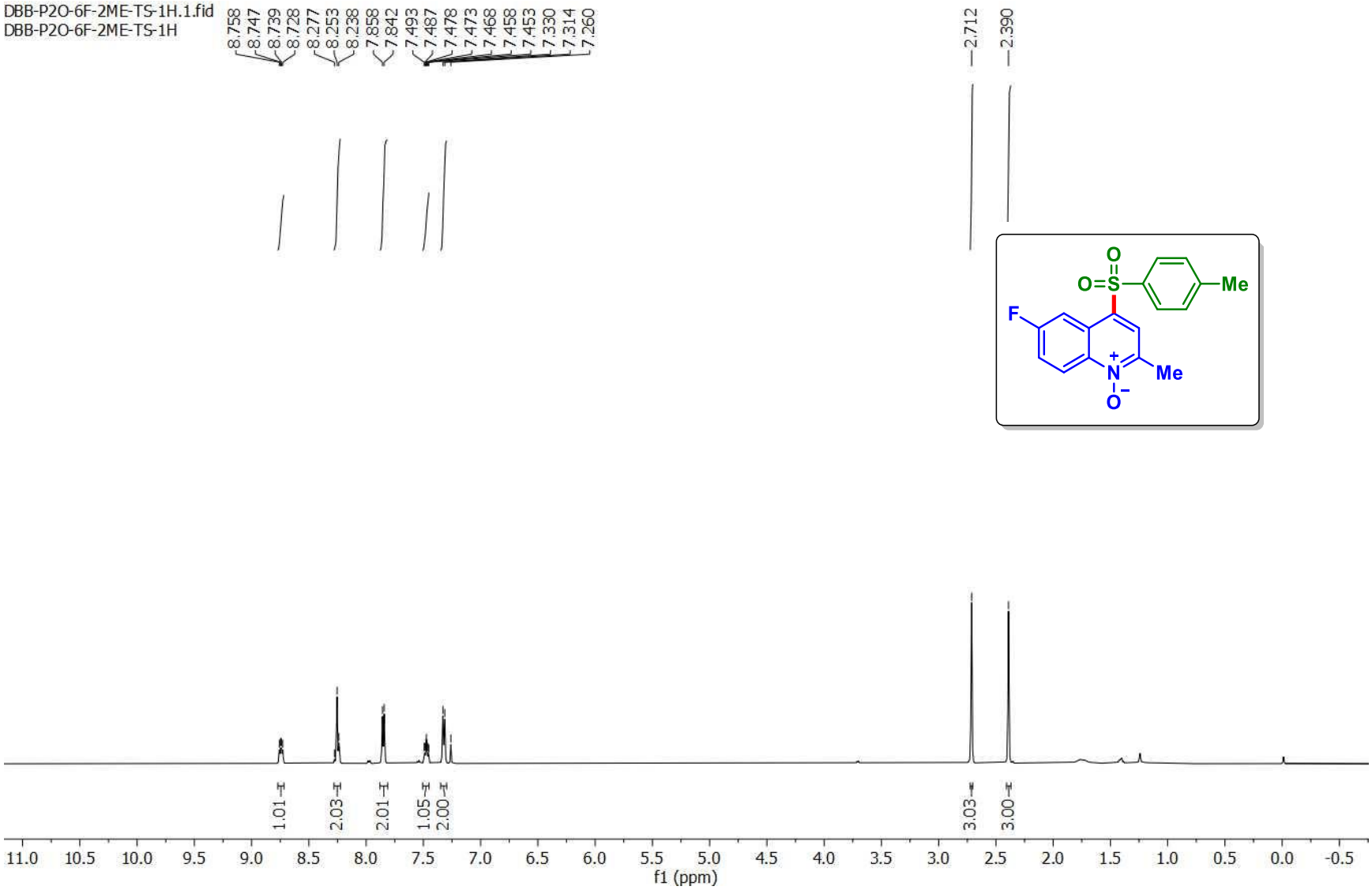
6-Bromo-4-tosylquinoline 1-oxide (6b'): ^{1}H NMR (CDCl3, 500 MHz)



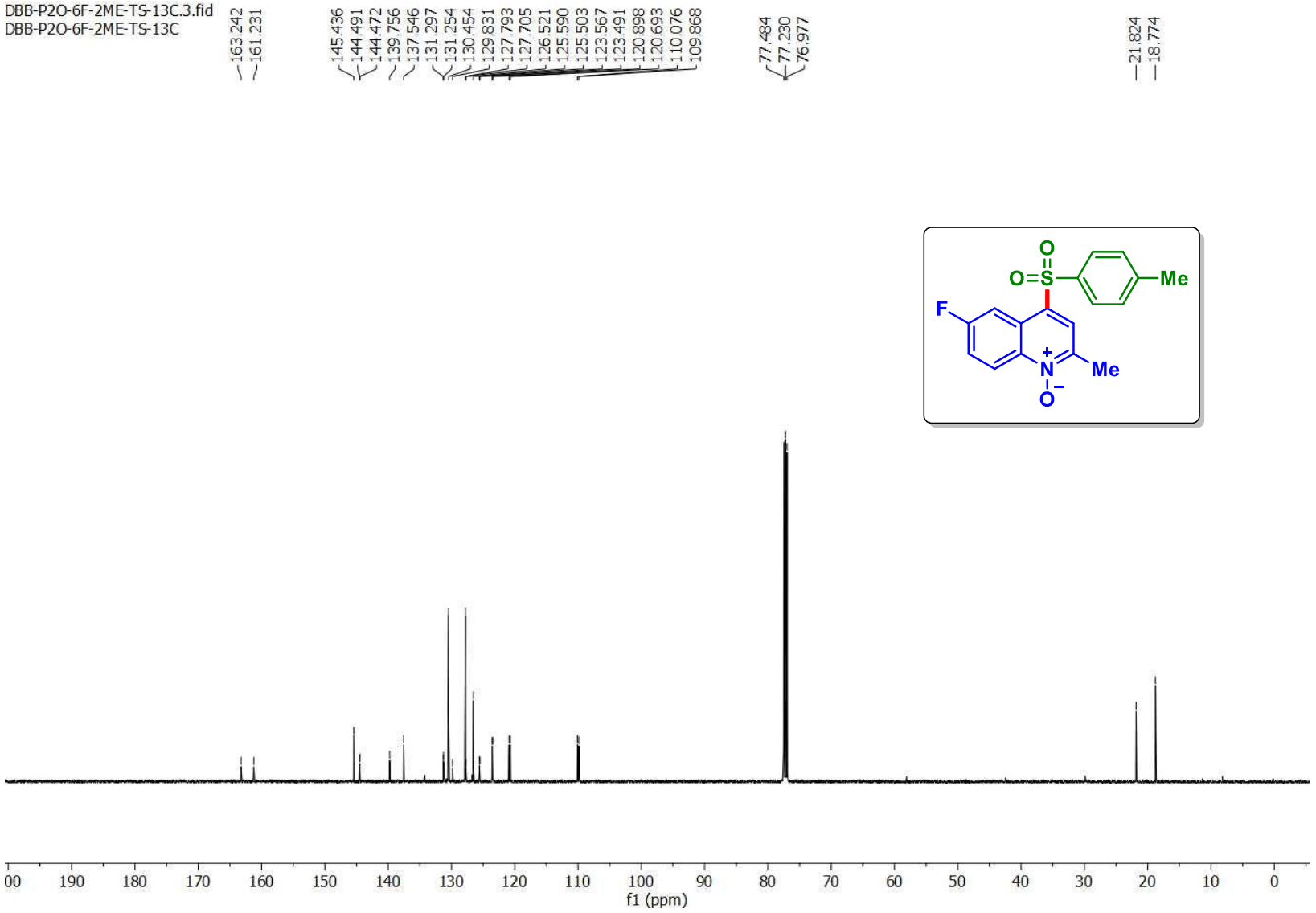
6-Bromo-4-tosylquinoline 1-oxide (6b'): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



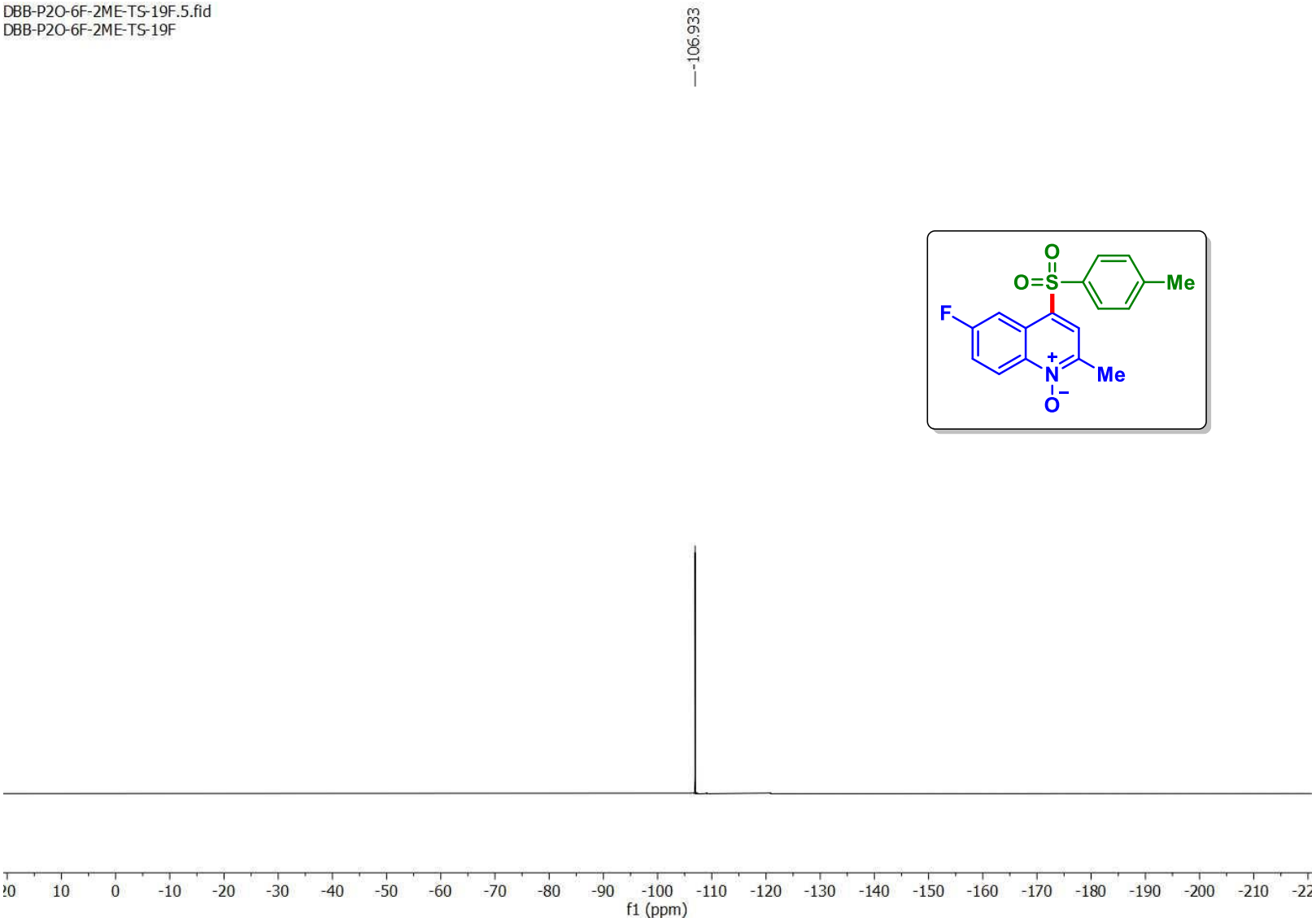
6-Fluoro-2-methyl-4-tosylquinoline 1-oxide (9b'): ^{1}H NMR ($CDCl_3$, 500 MHz)



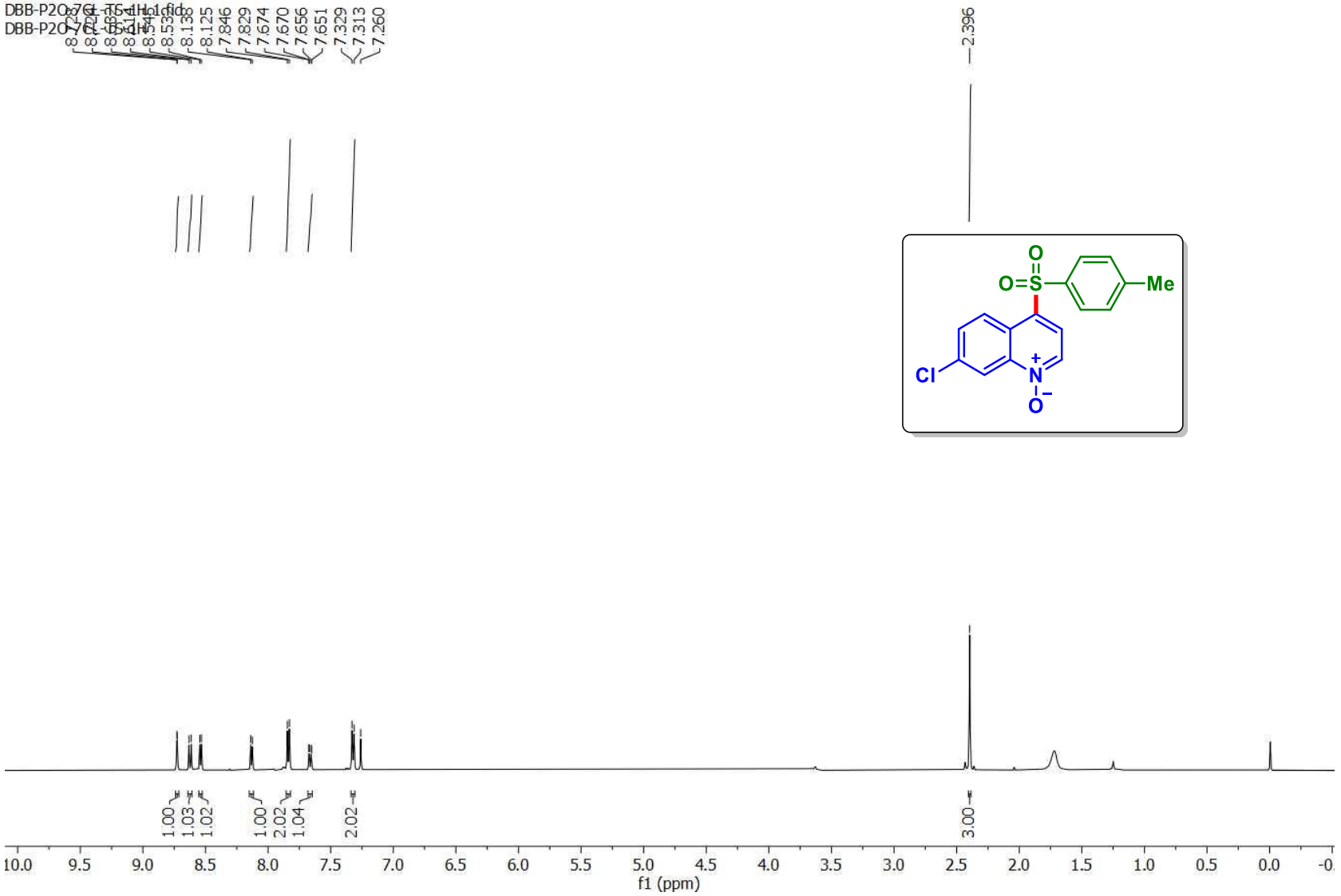
6-Fluoro-2-methyl-4-tosylquinoline 1-oxide (9b'): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



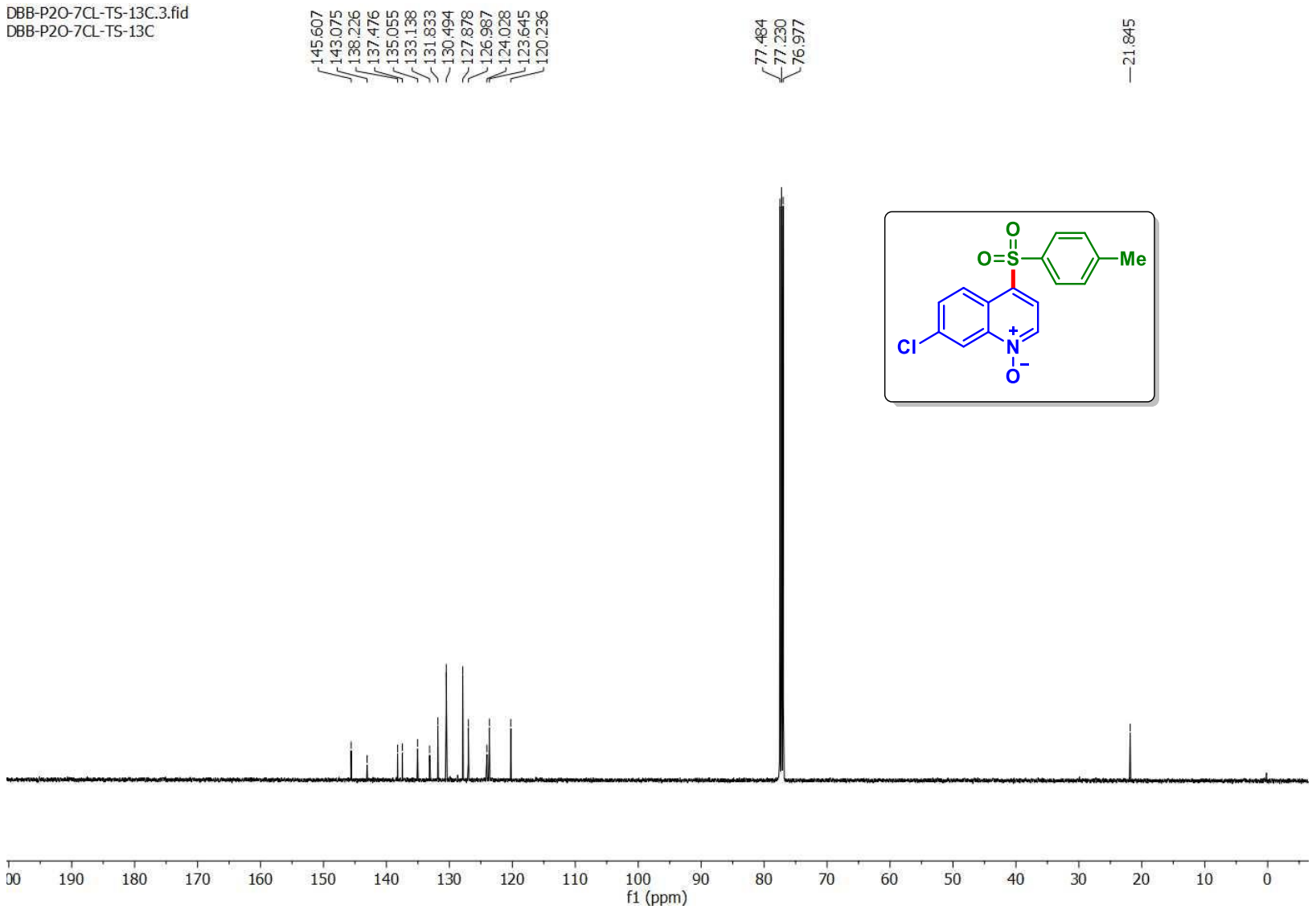
6-Fluoro-2-methyl-4-tosylquinoline 1-oxide (9b'): ^{19}F NMR ($CDCl_3$, 471 MHz)



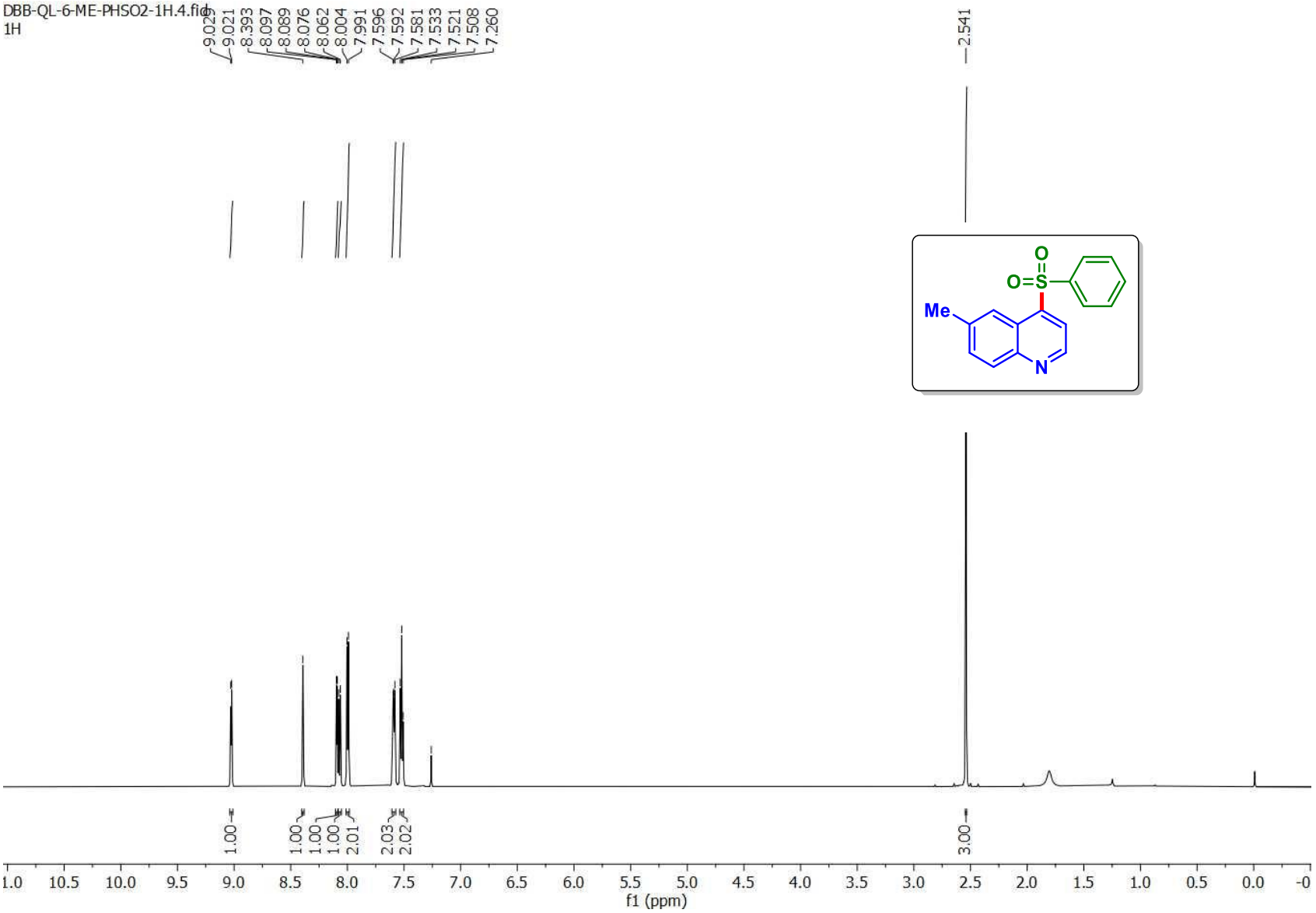
7-Chloro-4-tosylquinoline 1-oxide (10b'): ^{1}H NMR ($CDCl_3$, 500 MHz)



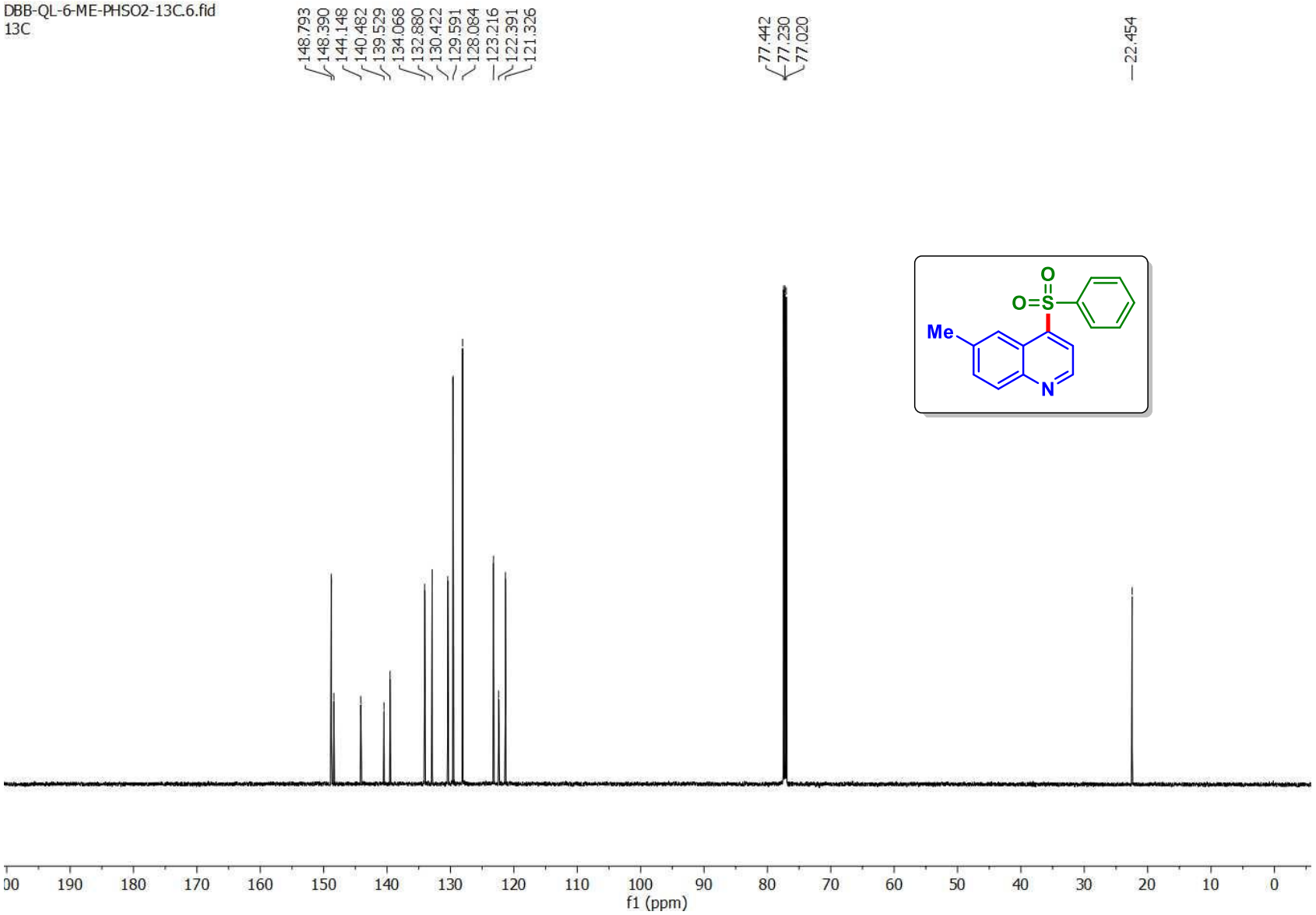
7-Chloro-4-tosylquinoline 1-oxide (10b'): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



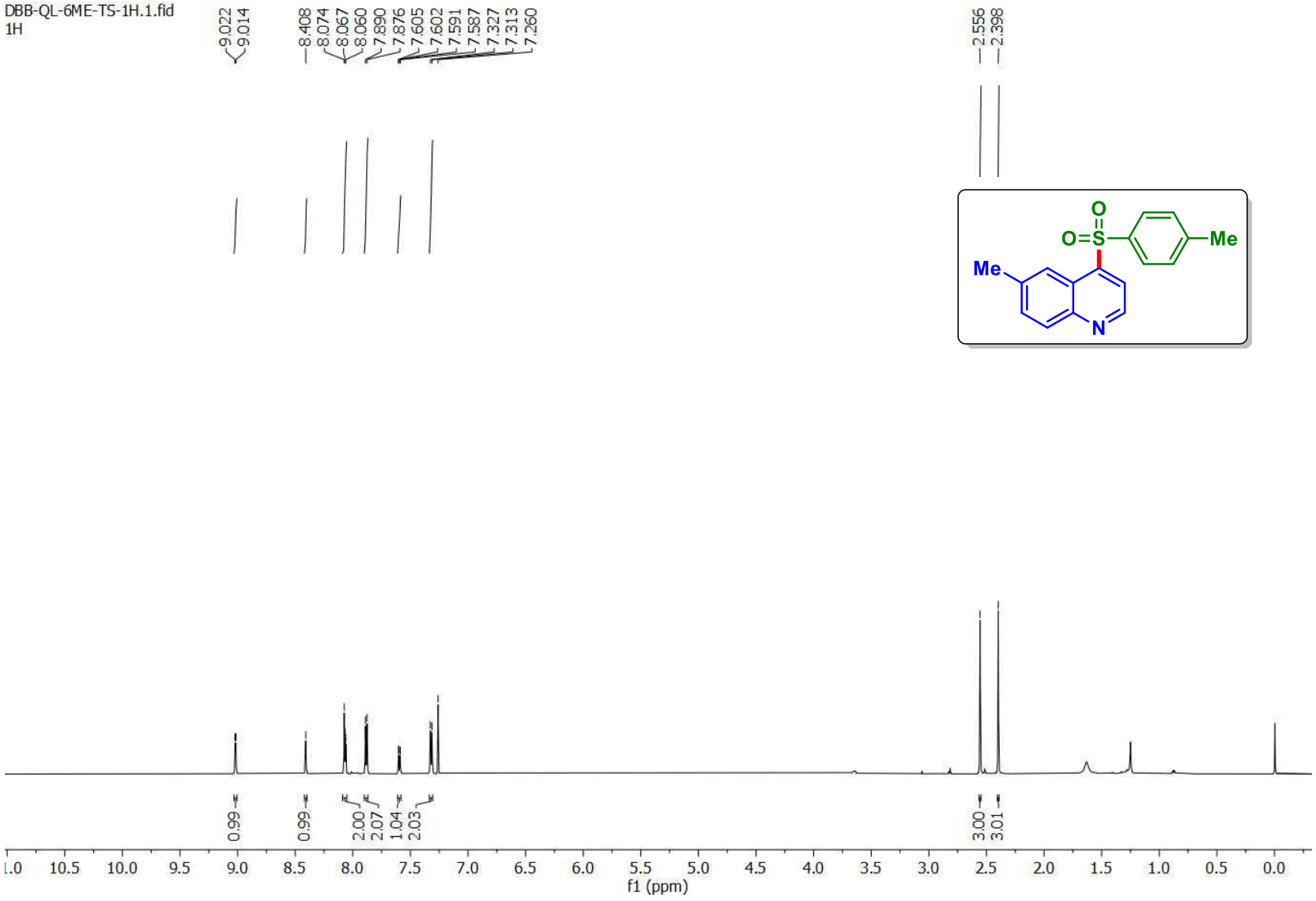
6-Methyl-4-(phenylsulfonyl)quinoline (1a): ^{1}H NMR (CDCl$_3$, 600 MHz)



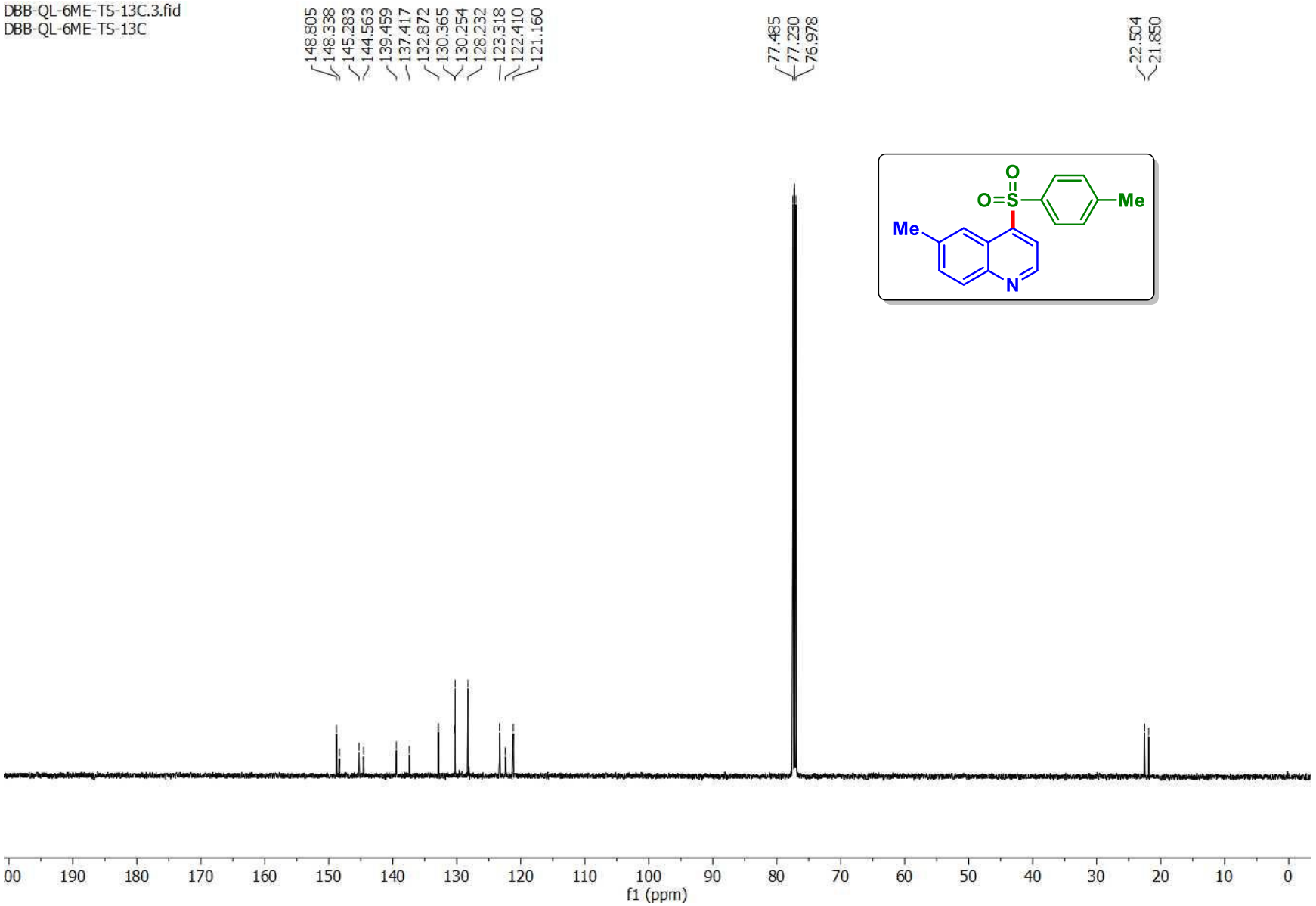
1-(6-Methyl-4-(phenylsulfonyl)quinoline (1a): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



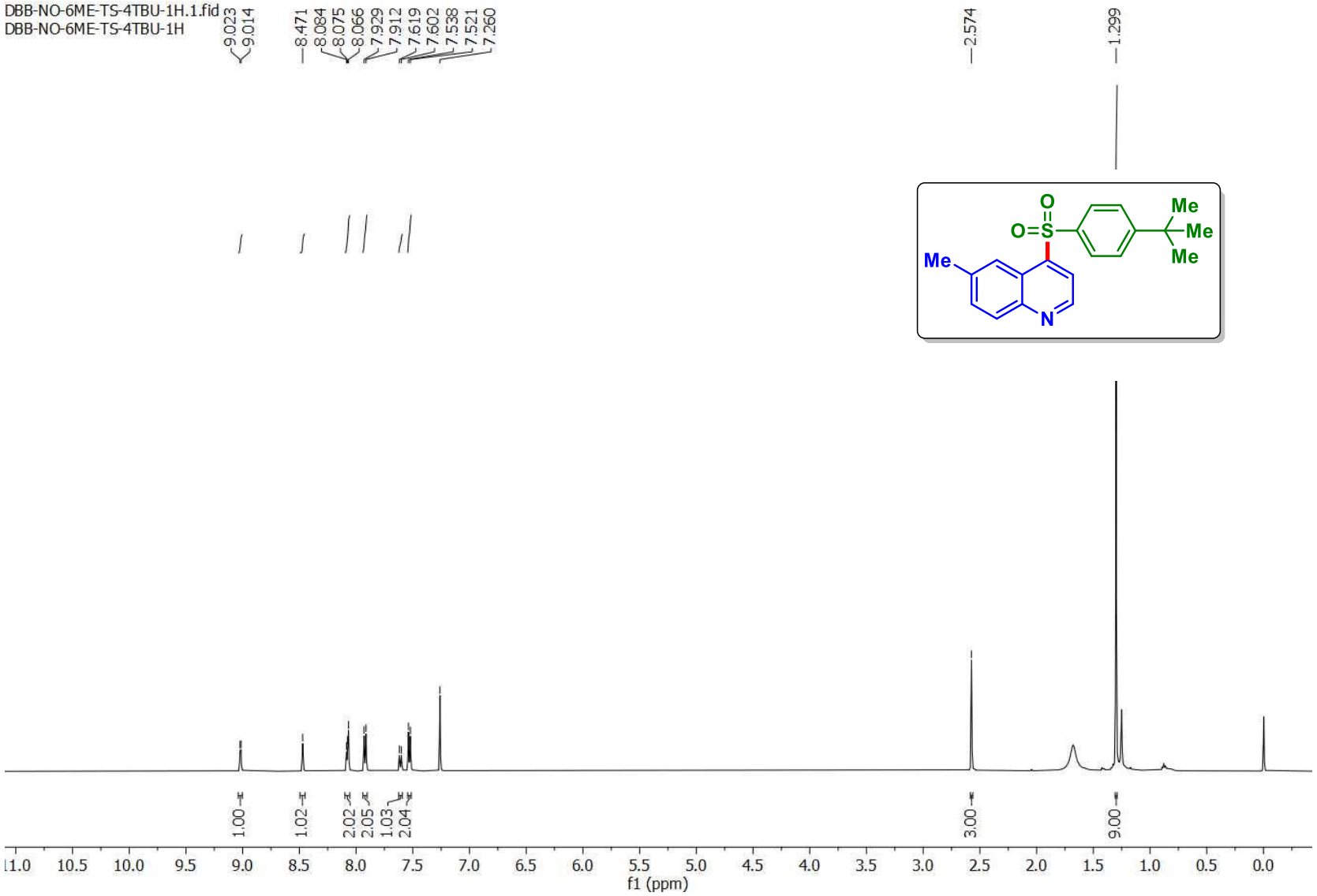
6-Methyl-4-tosylquinoline (1b): ^{1}H NMR ($CDCl_3$, 600 MHz)



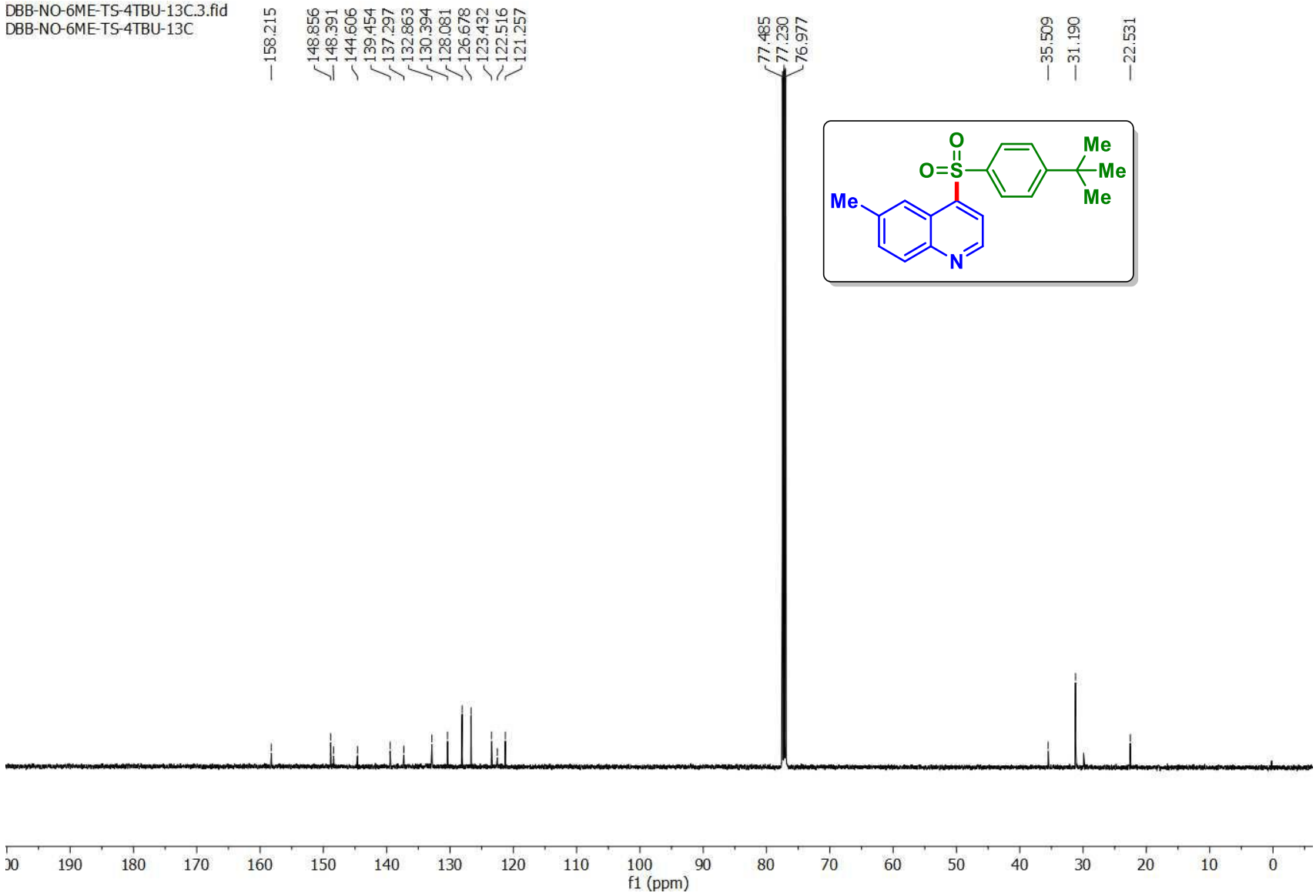
6-Methyl-4-tosylquinoline (1b): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz)



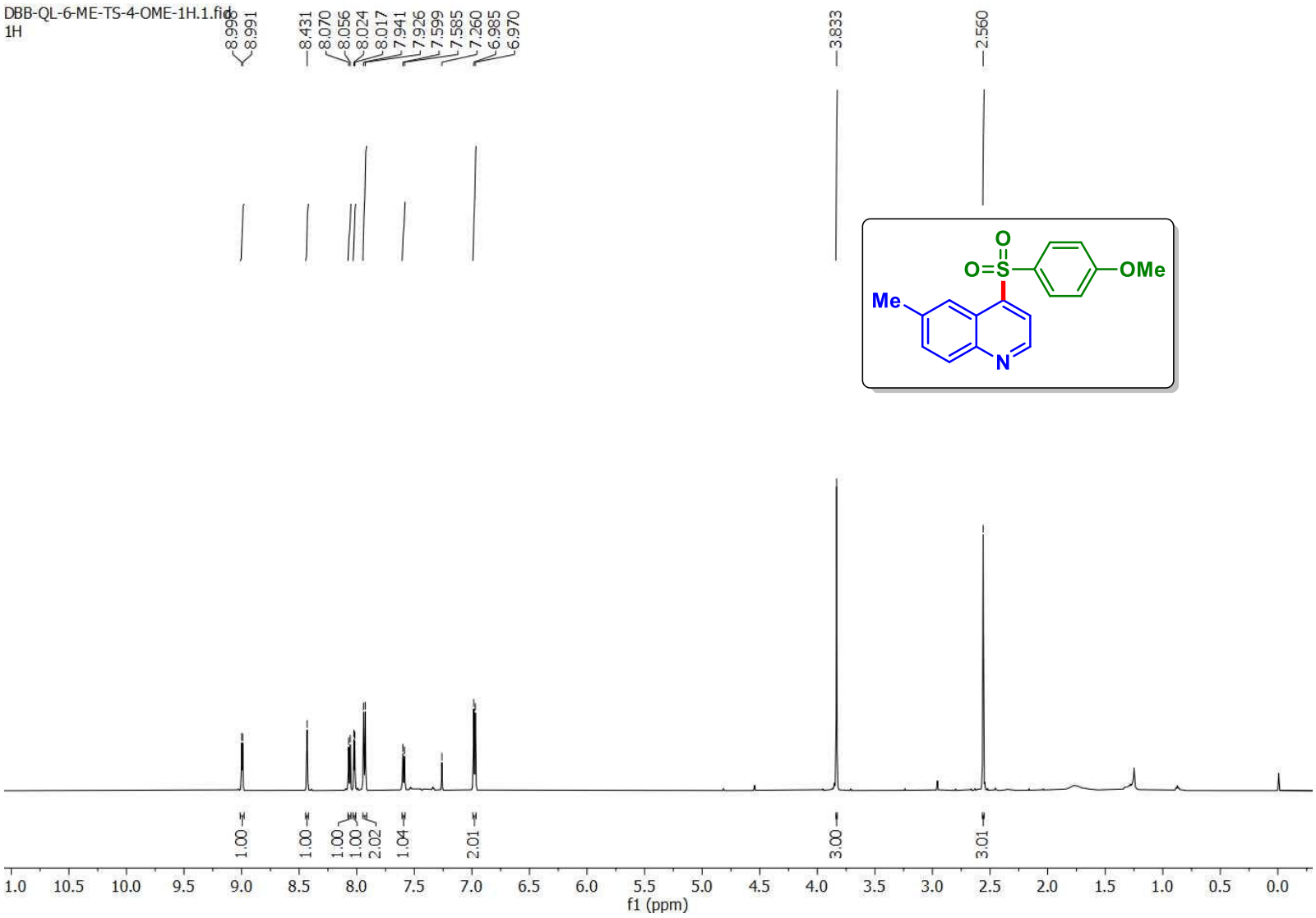
4-((4-(Tert-butyl)phenyl)sulfonyl)-6-methylquinoline (1c): ^{1}H NMR (CDCl$_3$, 500 MHz)



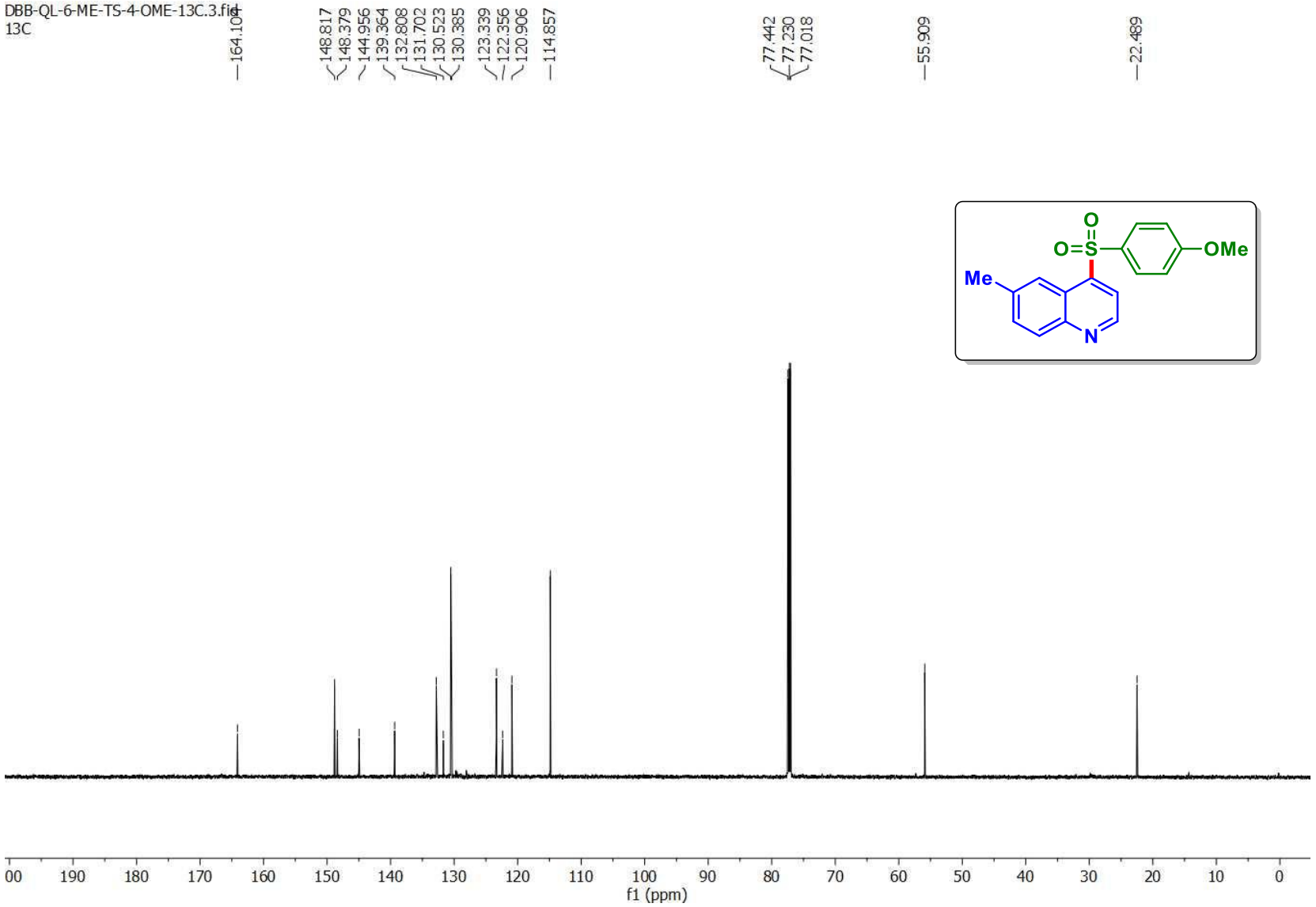
4-((4-(Tert-butyl)phenyl)sulfonyl)-6-methylquinoline (1c): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



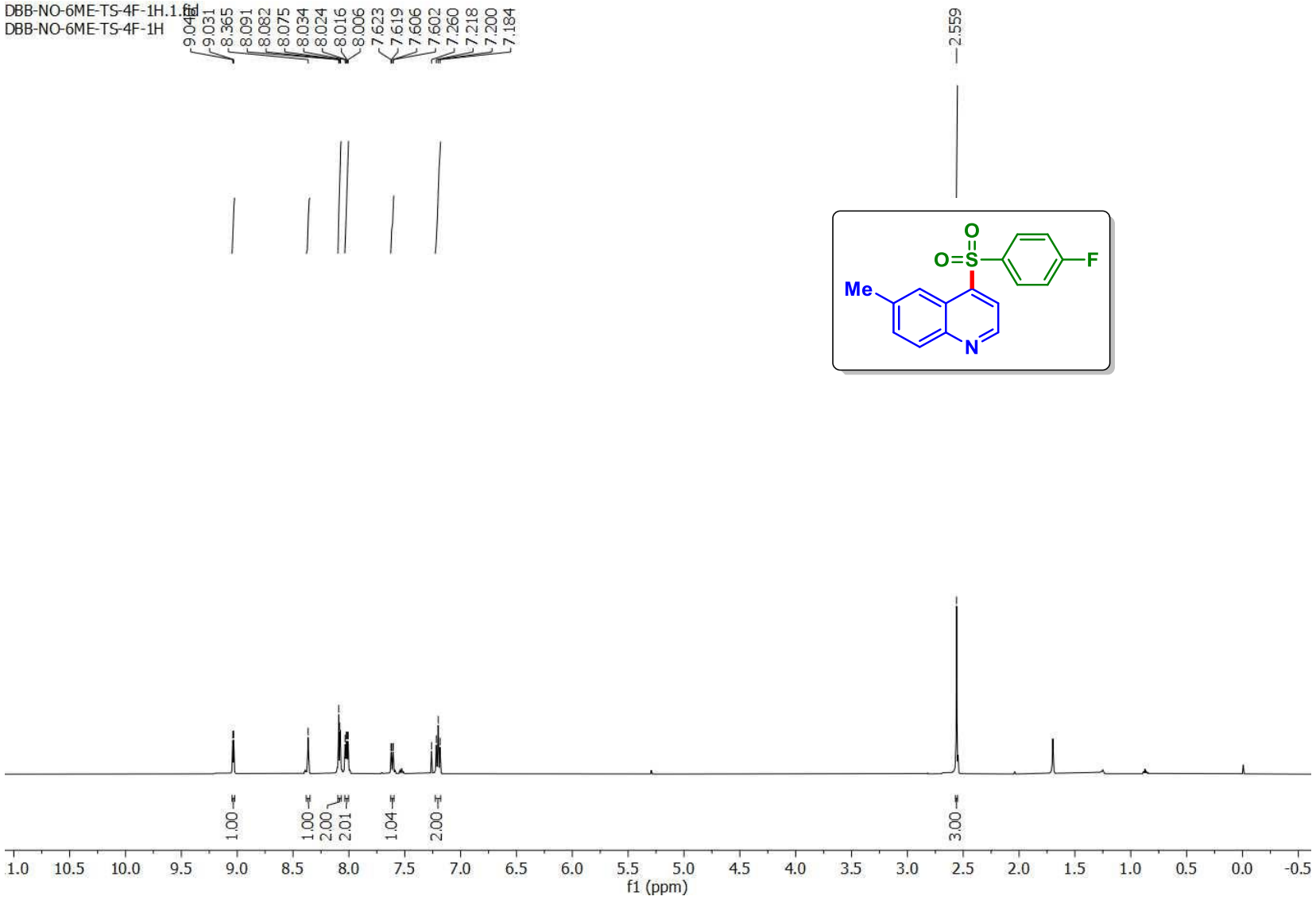
4-((4-Methoxyphenyl)sulfonyl)-6-methylquinoline (1d): ^{1}H NMR (CDCl$_3$, 600 MHz)



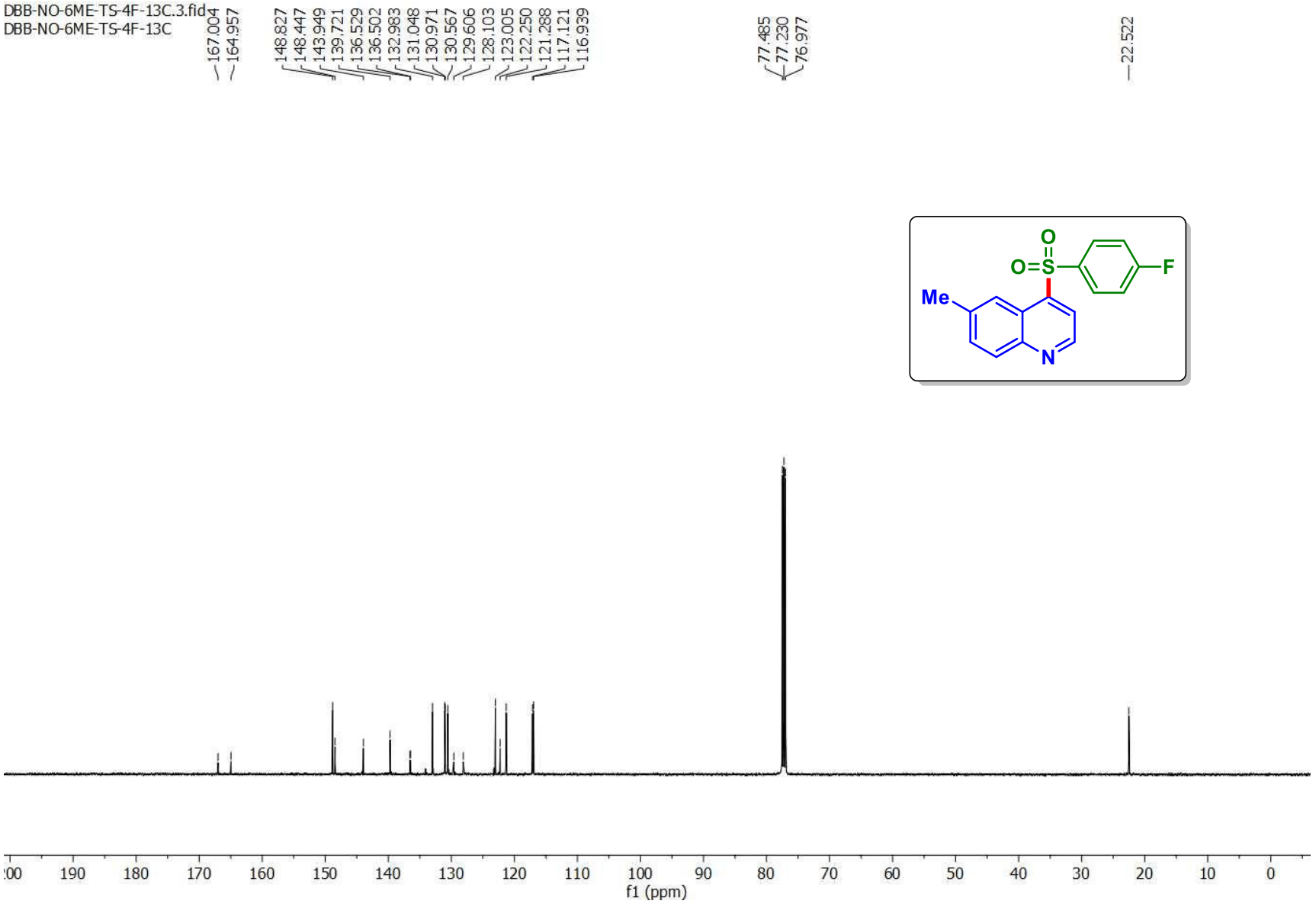
4-((4-Methoxyphenyl)sulfonyl)-6-methylquinoline (1d): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



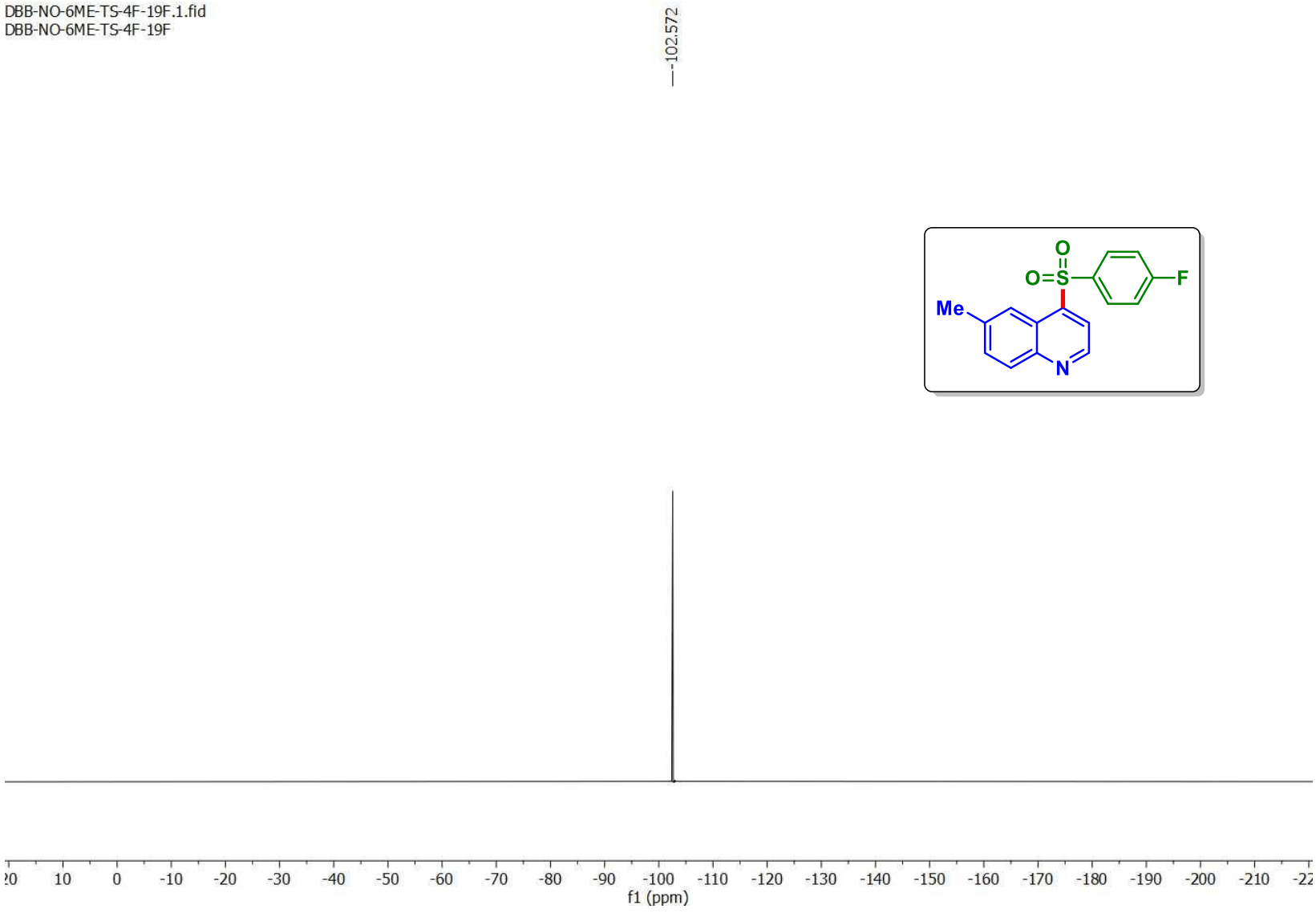
4-((4-Fluorophenyl)sulfonyl)-6-methylquinoline (1e): ^{1}H NMR ($CDCl_3$, 500 MHz)



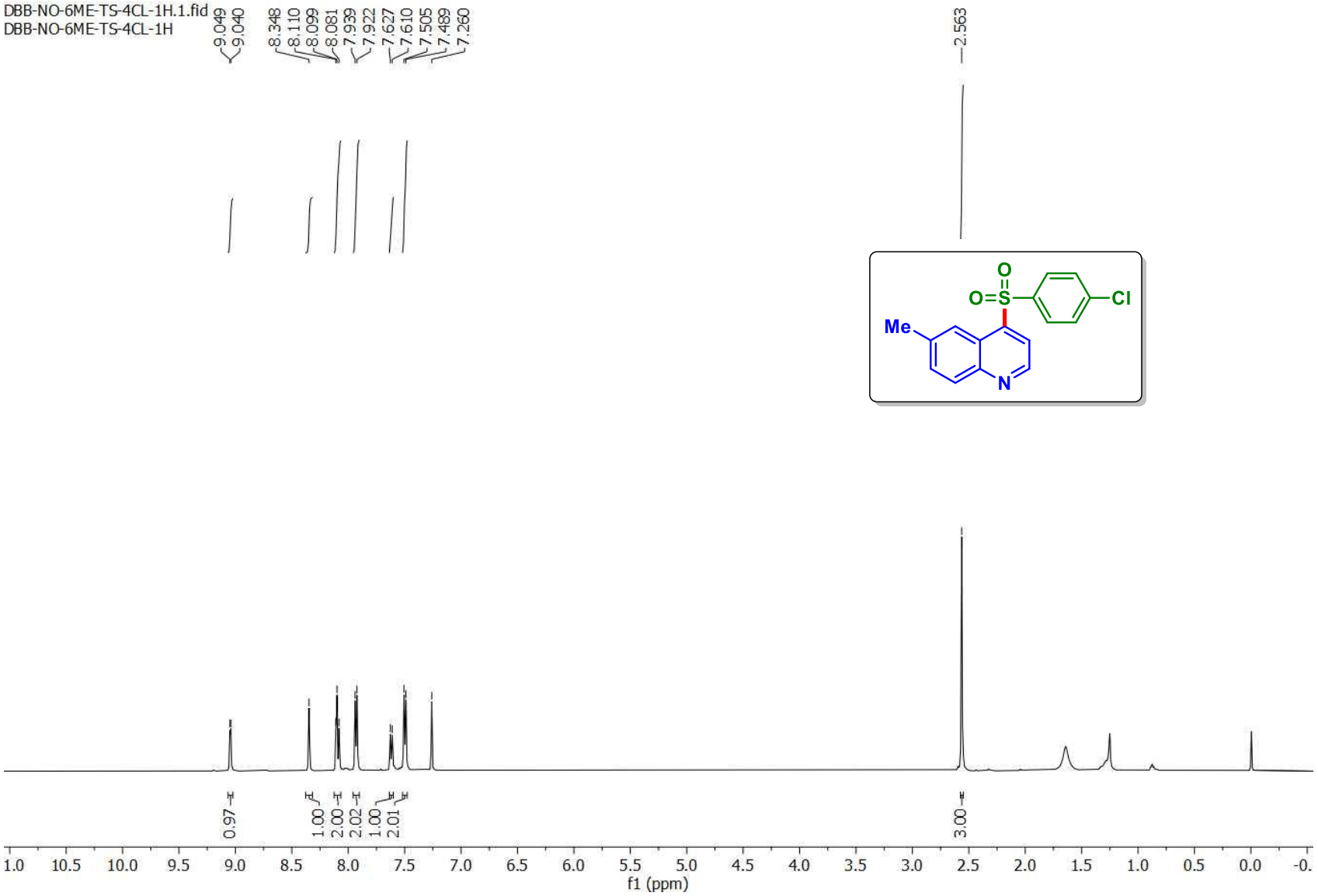
4-((4-Fluorophenyl)sulfonyl)-6-methylquinoline (1e): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



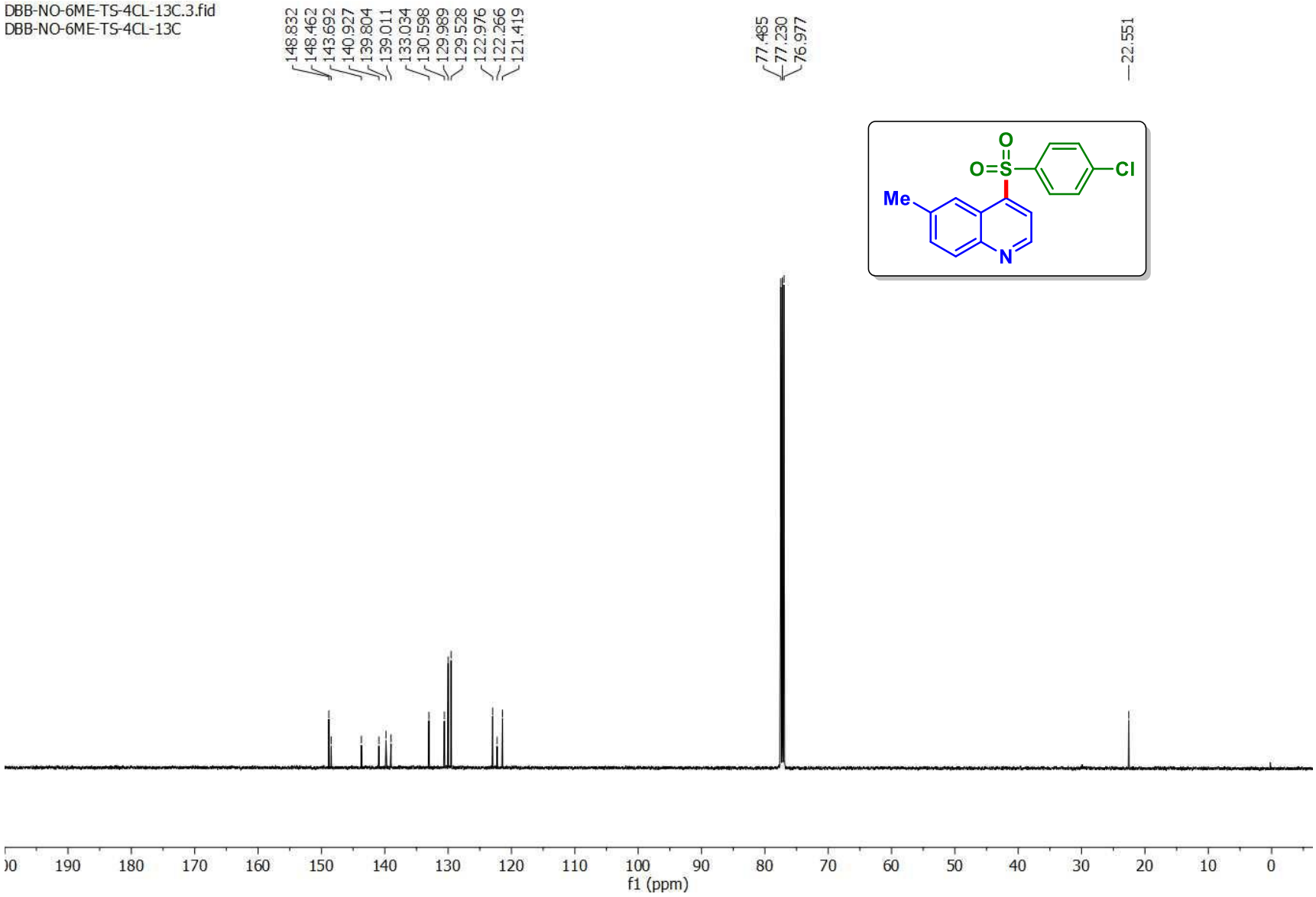
4-((4-Fluorophenyl)sulfonyl)-6-methylquinoline (1e): ^{19}F NMR ($CDCl_3$, 471 MHz)



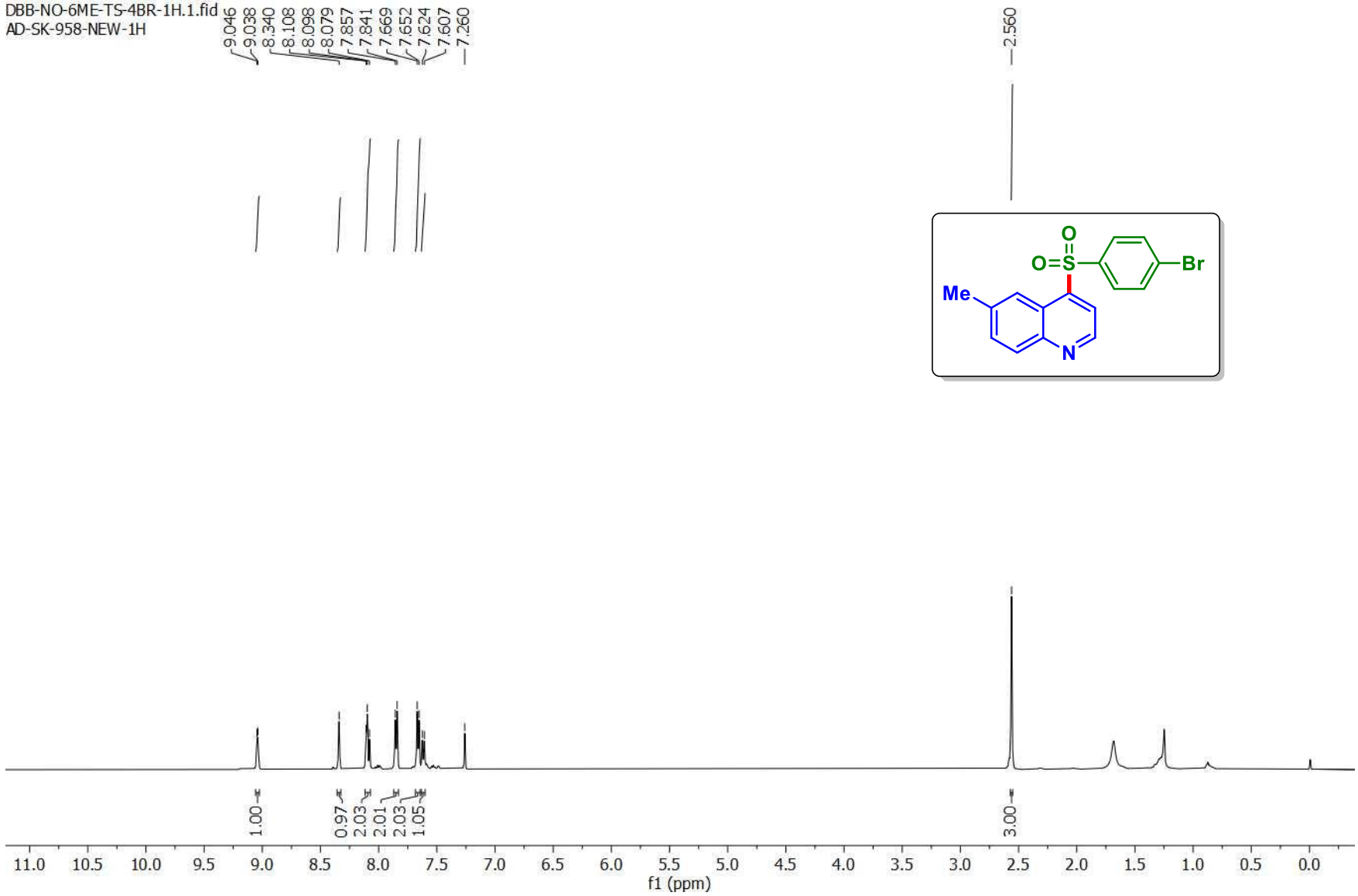
4-((4-Chlorophenyl)sulfonyl)-6-methylquinoline (1f): ^{1}H NMR ($CDCl_3$, 500 MHz)



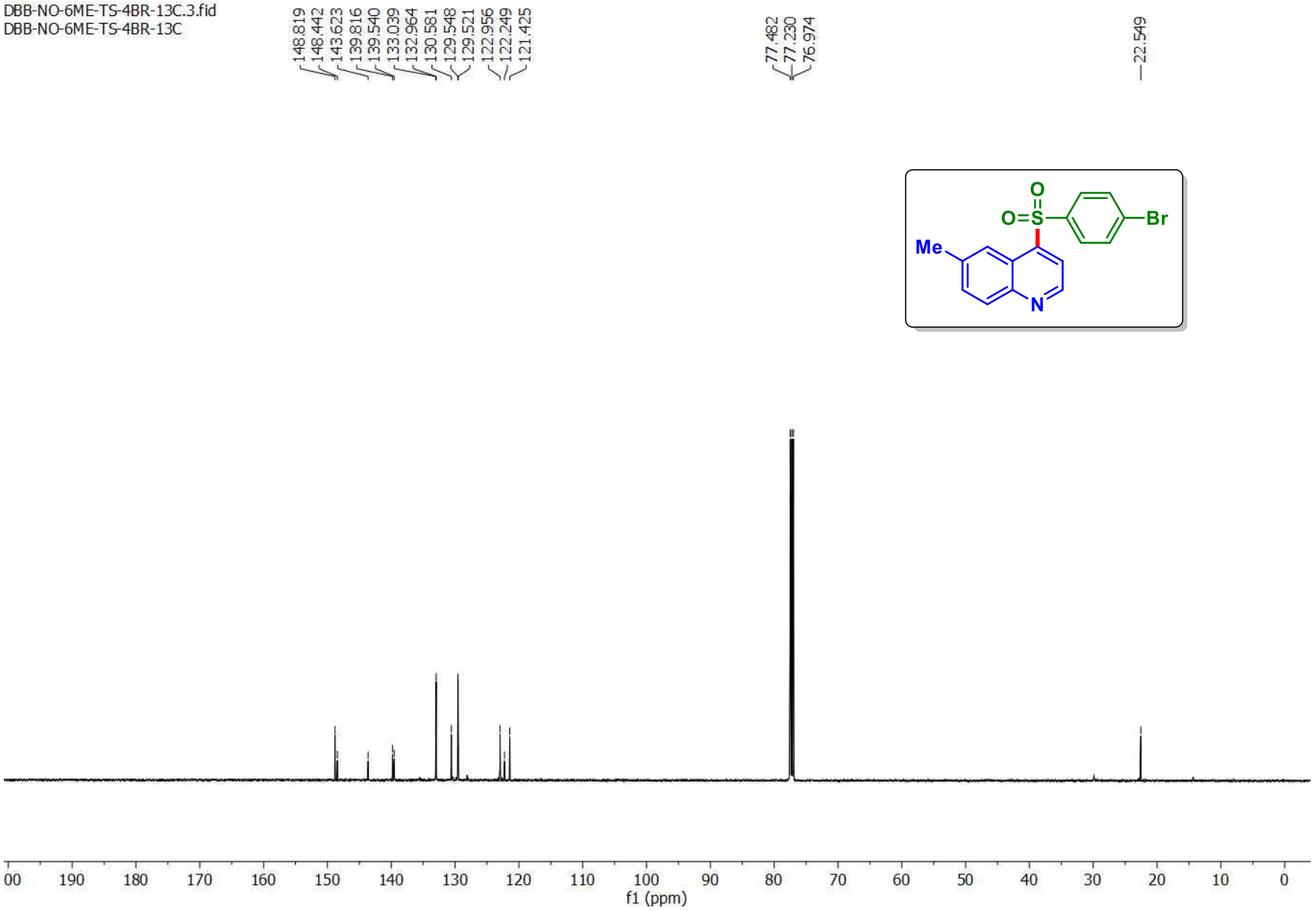
4-((4-Chlorophenyl)sulfonyl)-6-methylquinoline (1f): ^{13}C NMR ($CDCl_3$, 125 MHz)



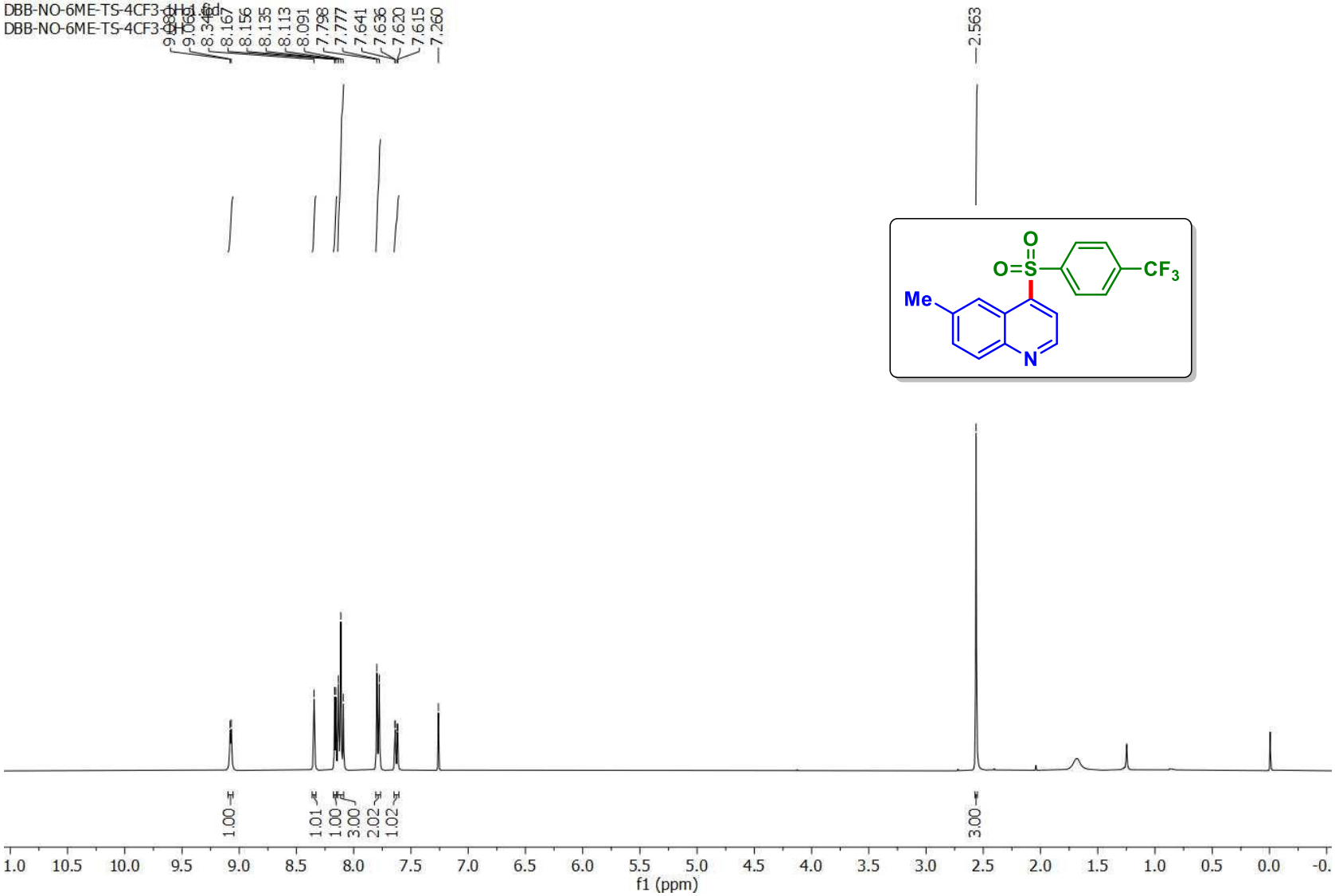
4-((4-Bromophenyl)sulfonyl)-6-methylquinoline (1g): ^{1}H NMR ($CDCl_3$, 500 MHz)



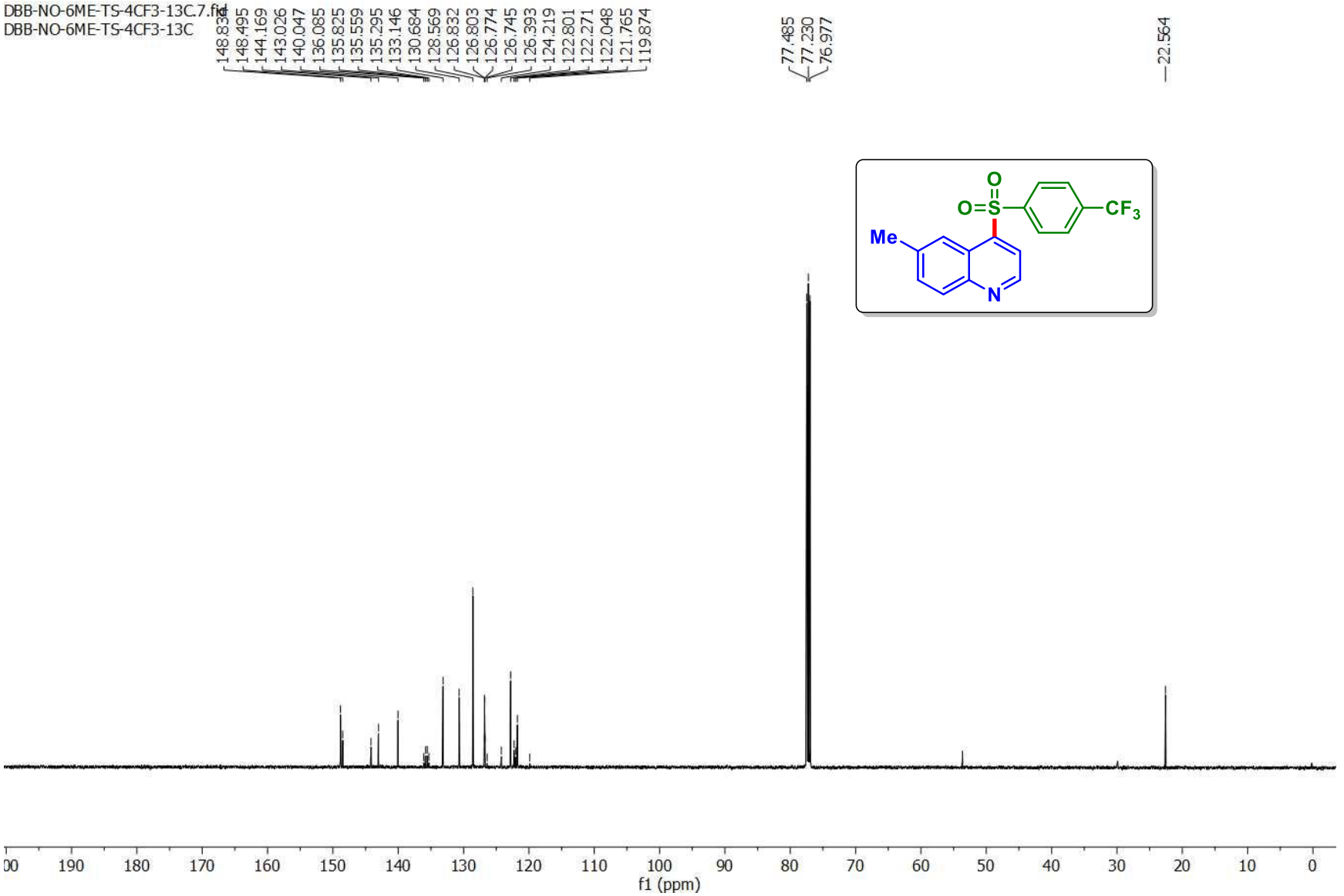
4-((4-Bromophenyl)sulfonyl)-6-methylquinoline (1g): ^{13}C NMR ($CDCl_3$, 125 MHz)



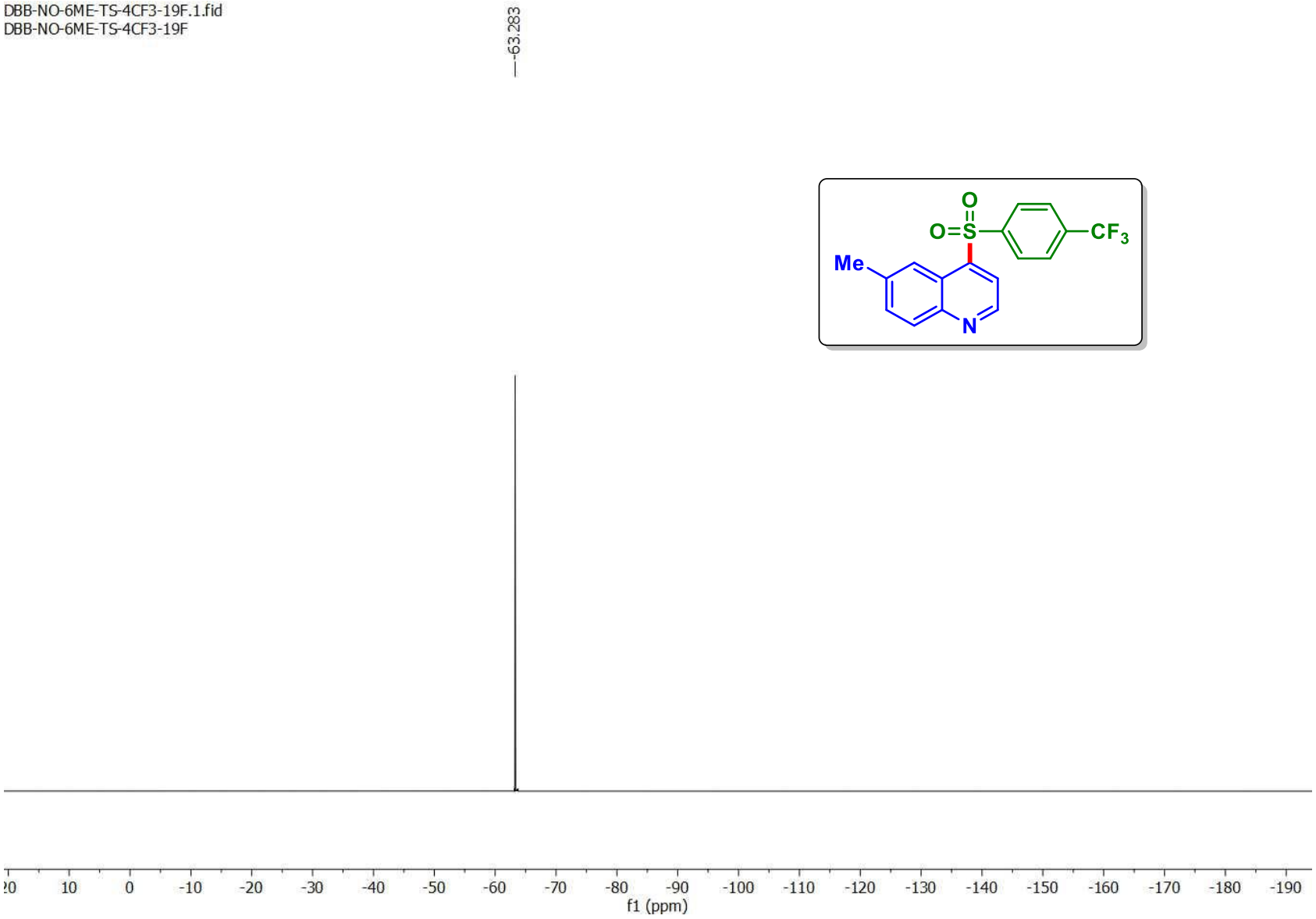
6-Methyl-4-((4-(trifluoromethyl)phenyl)sulfonyl)quinoline (1h): ^{1}H NMR ($CDCl_3$, 400 MHz)



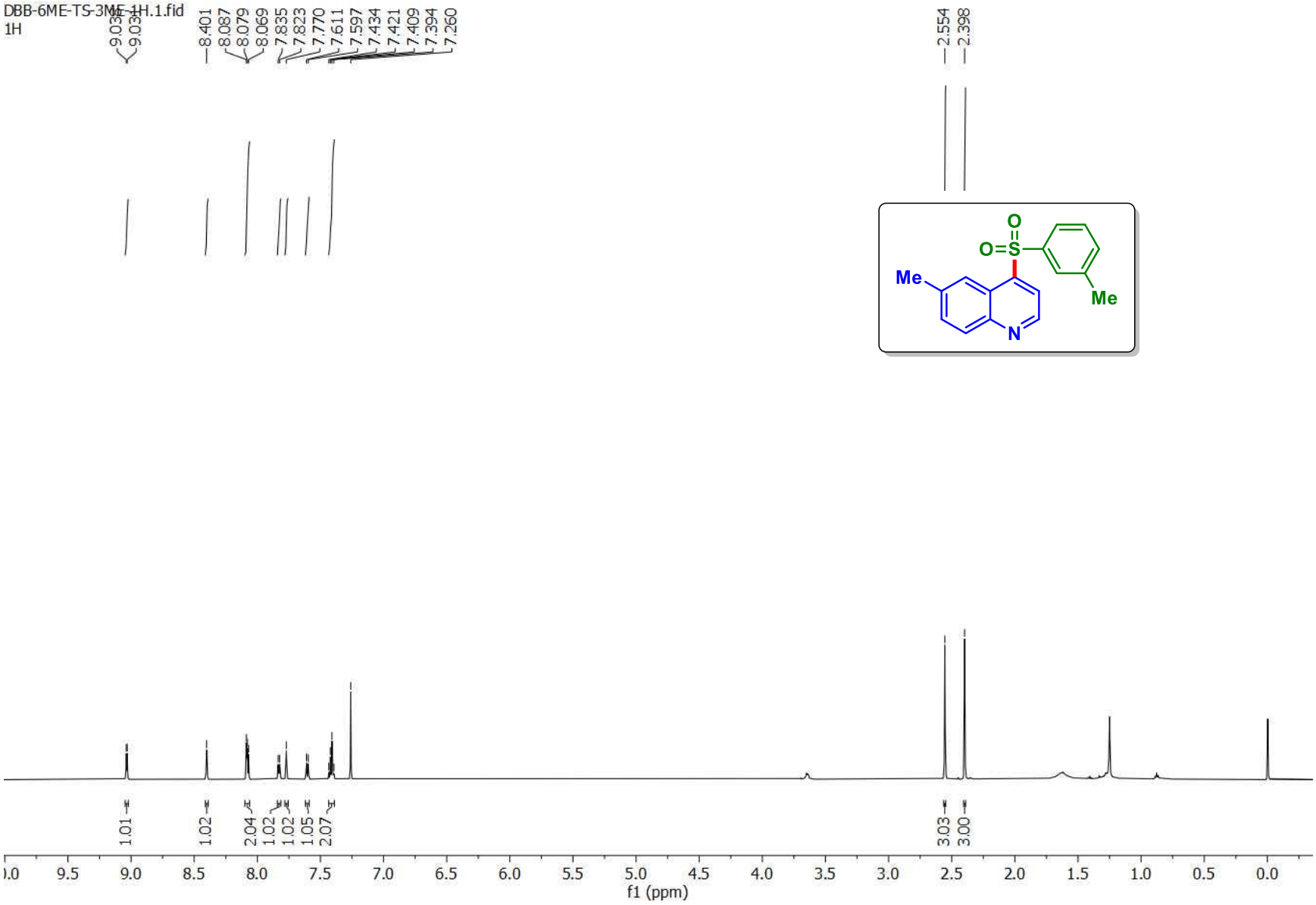
6-Methyl-4-((4-(trifluoromethyl)phenyl)sulfonyl)quinoline (1h): ^{13}C NMR ($CDCl_3$, 125 MHz)



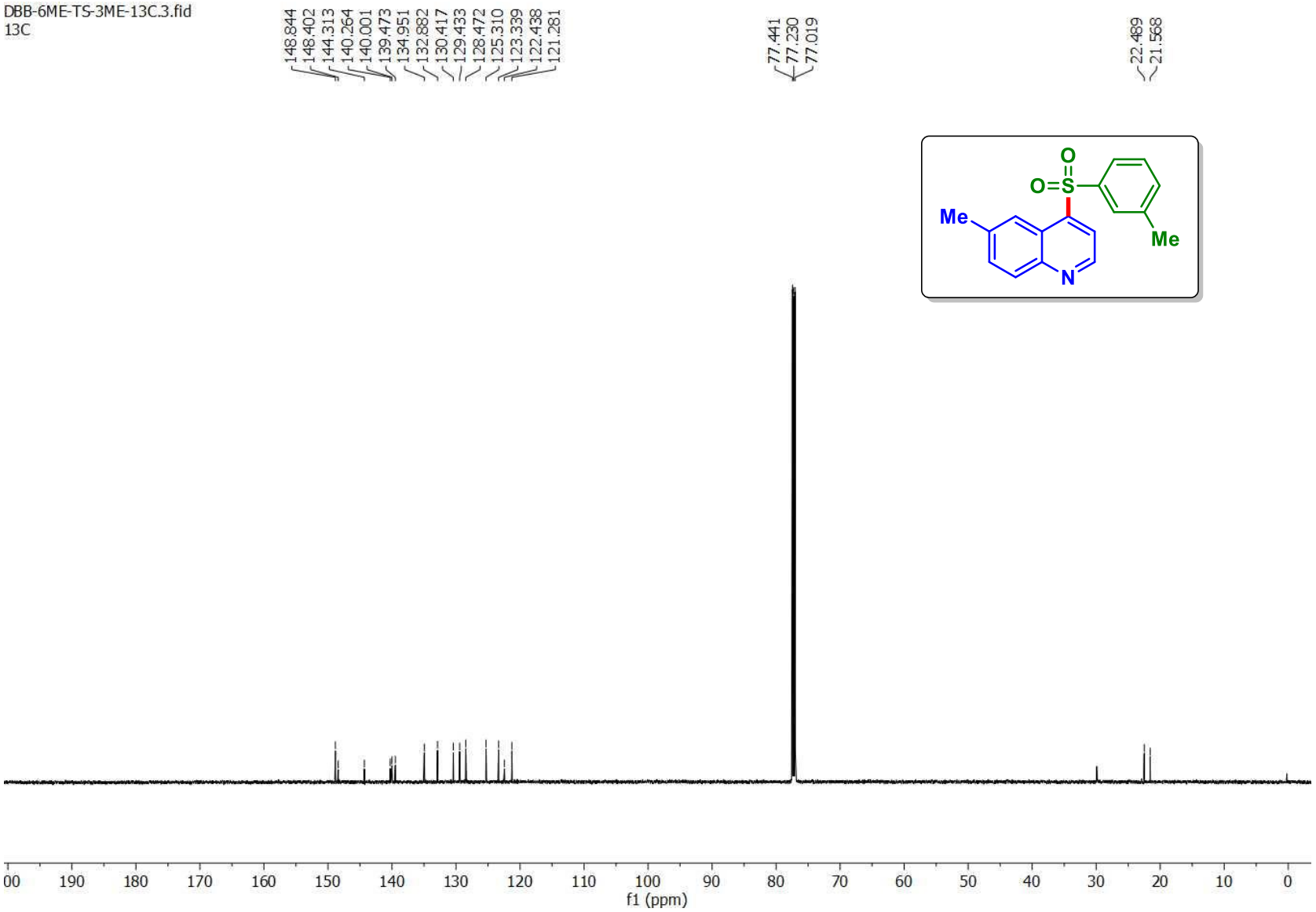
6-Methyl-4-((4-(trifluoromethyl)phenyl)sulfonyl)quinoline (1h): ^{19}F NMR ($CDCl_3$, 471 MHz)



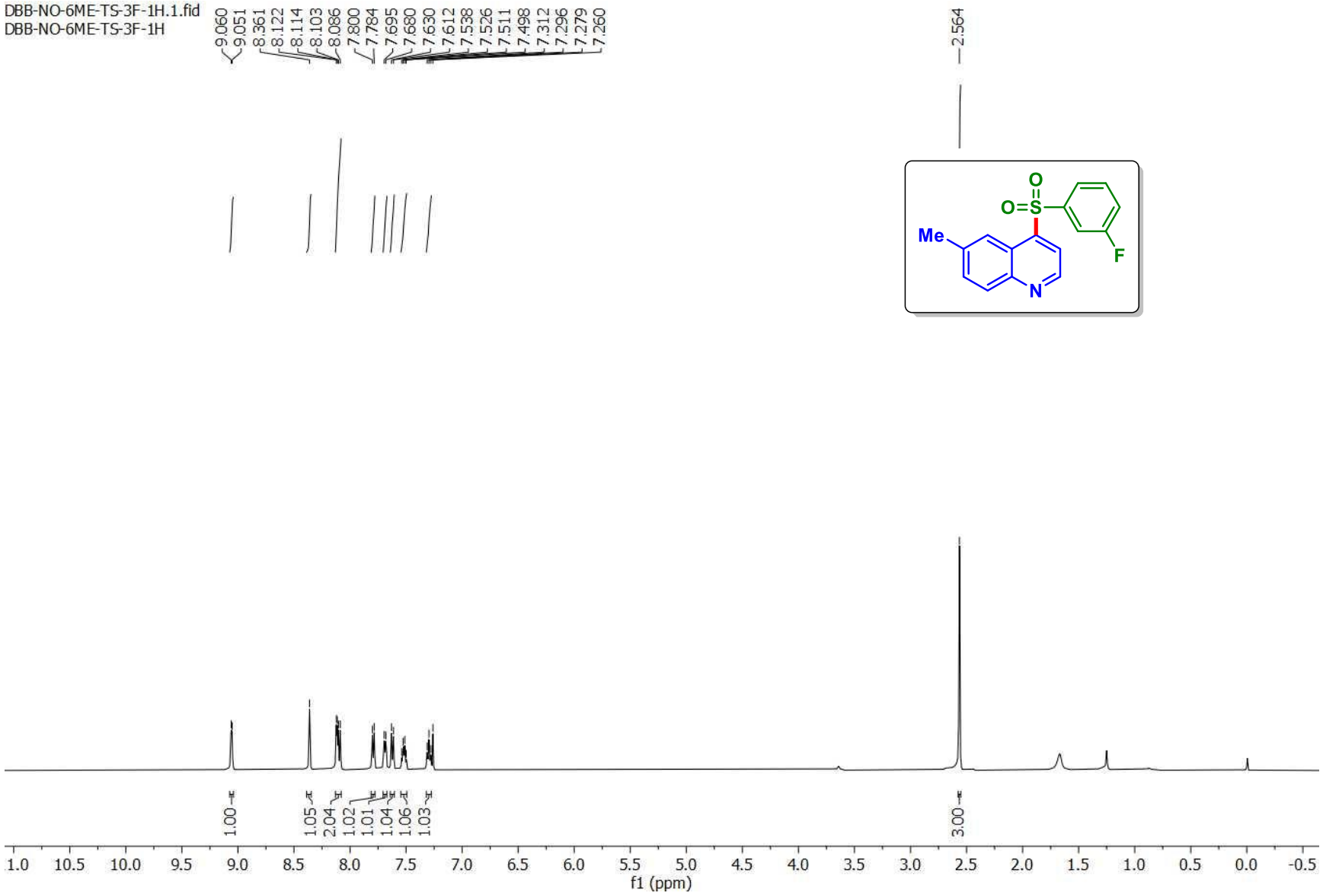
6-Methyl-4-(m-tolylsulfonyl)quinoline (1i): ^{1}H NMR ($CDCl_3$, 600 MHz)



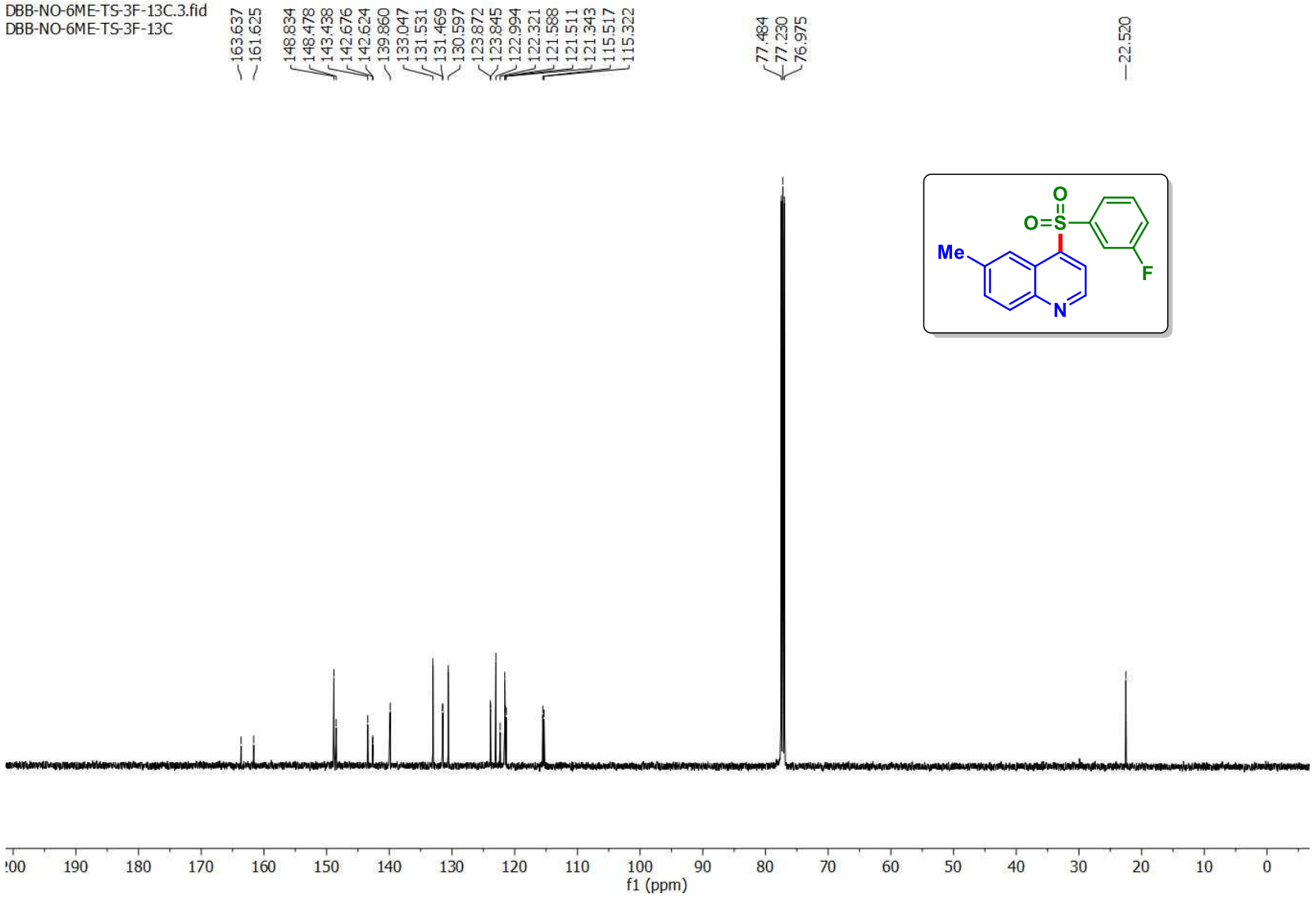
1-6-Methyl-4-(m-tolylsulfonyl)quinoline (1i): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



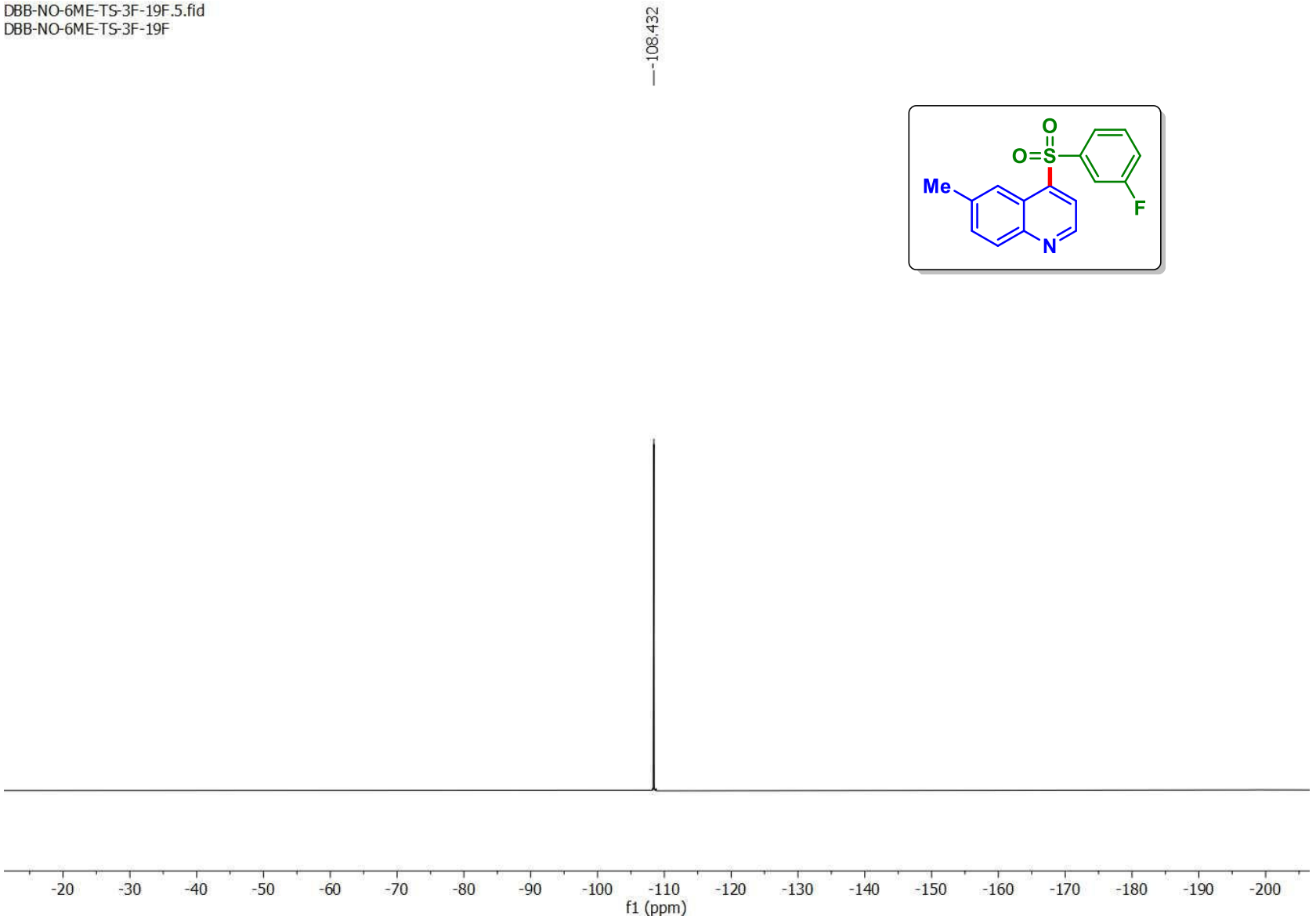
4-((3-Fluorophenyl)sulfonyl)-6-methylquinoline (1j): ^{1}H NMR ($CDCl_3$, 500 MHz)



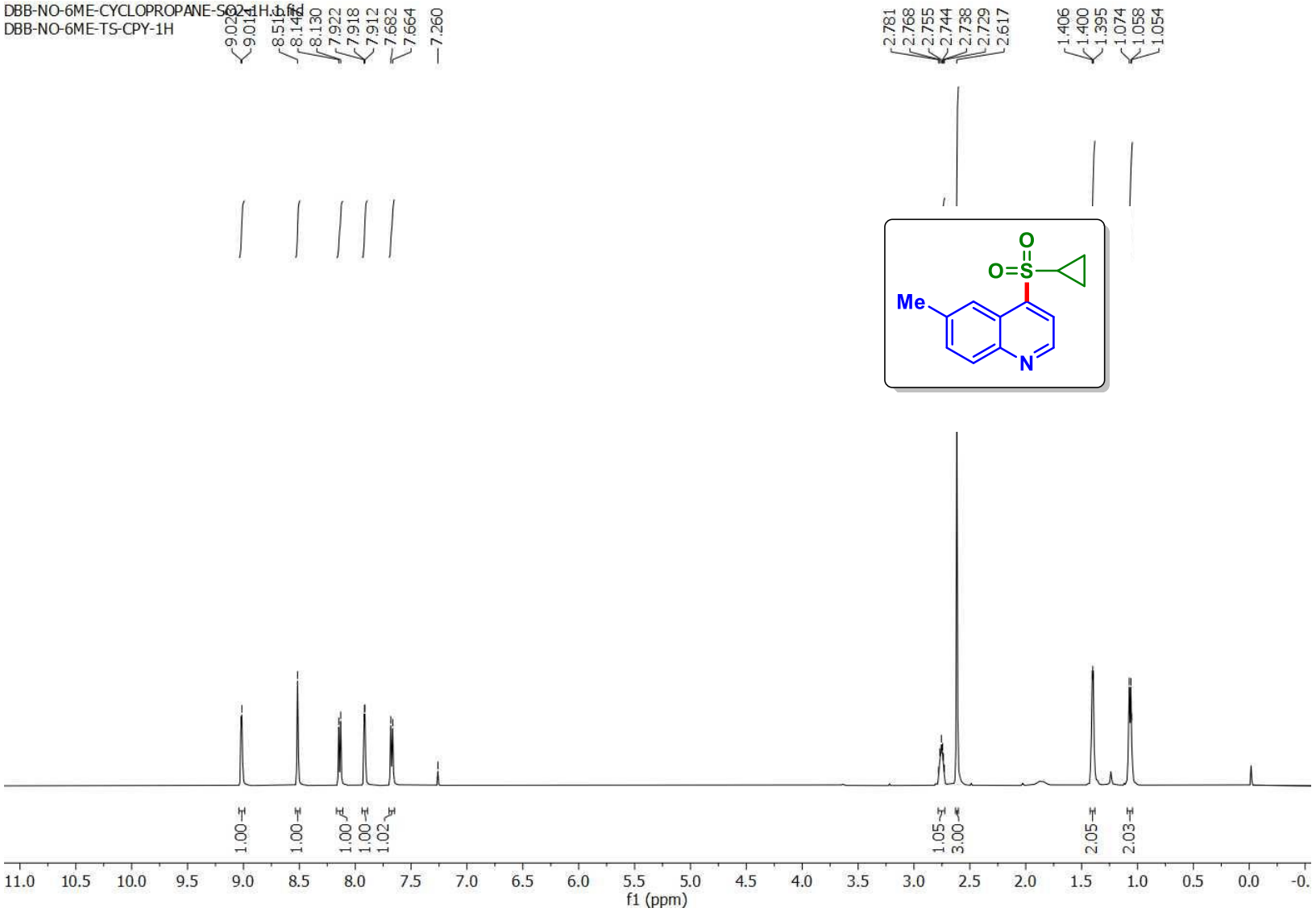
4-((3-Fluorophenyl)sulfonyl)-6-methylquinoline (1j): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



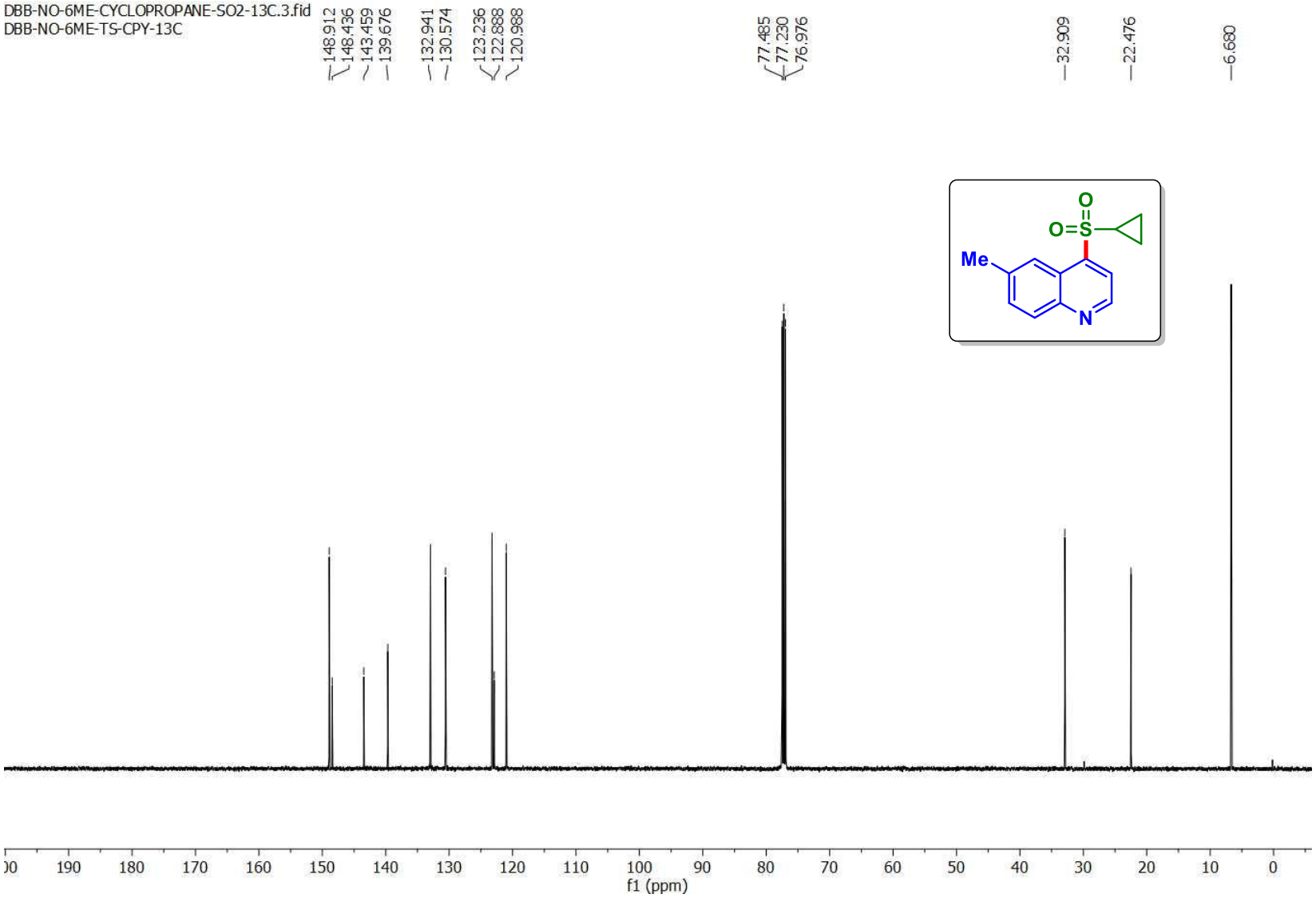
4-((3-Fluorophenyl)sulfonyl)-6-methylquinoline (1j): ^{19}F NMR ($CDCl_3$, 471 MHz)



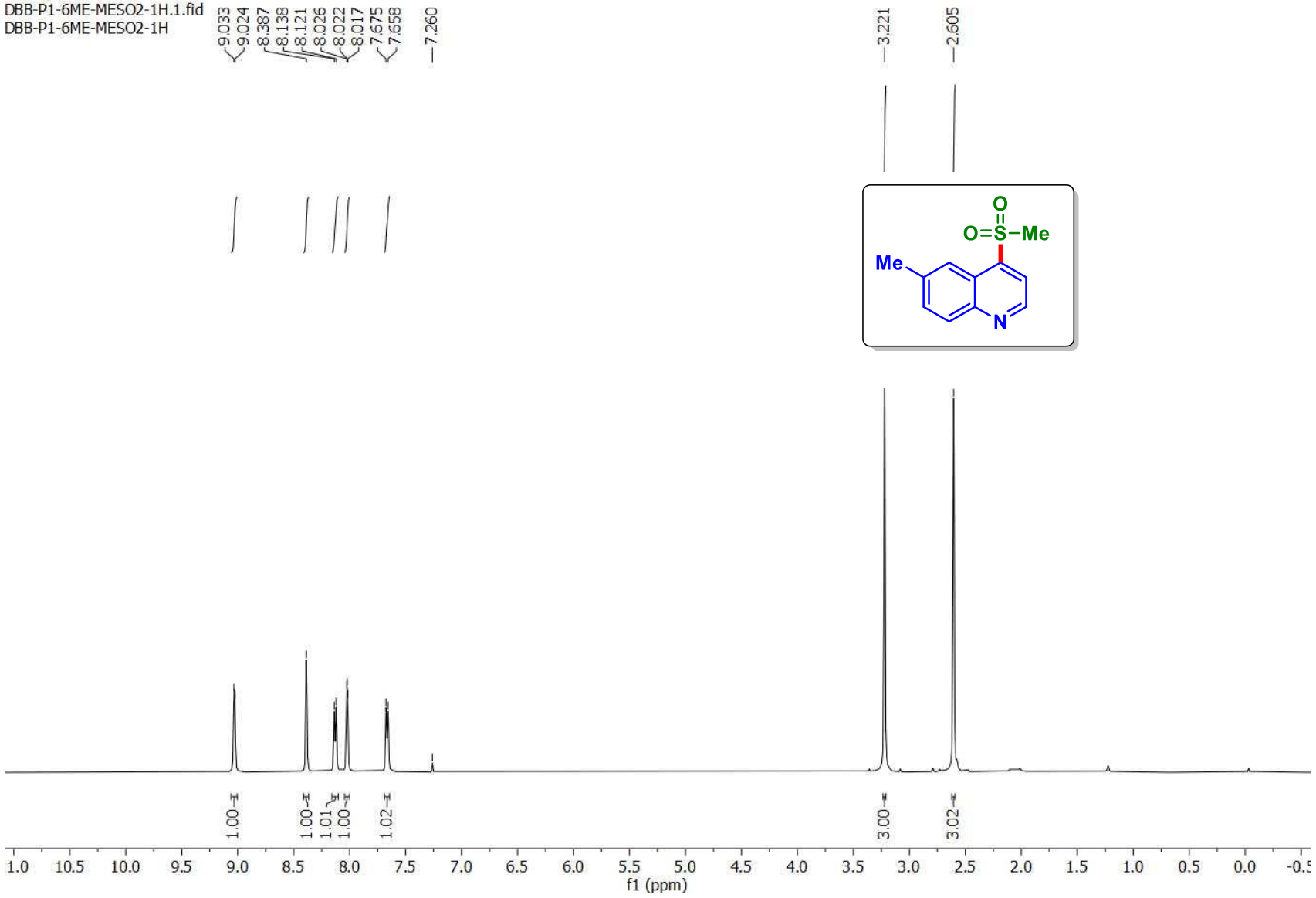
4-(Cyclopropylsulfonyl)-6-methylquinoline (1k): ^{1}H NMR (CDCl$_3$, 500 MHz)



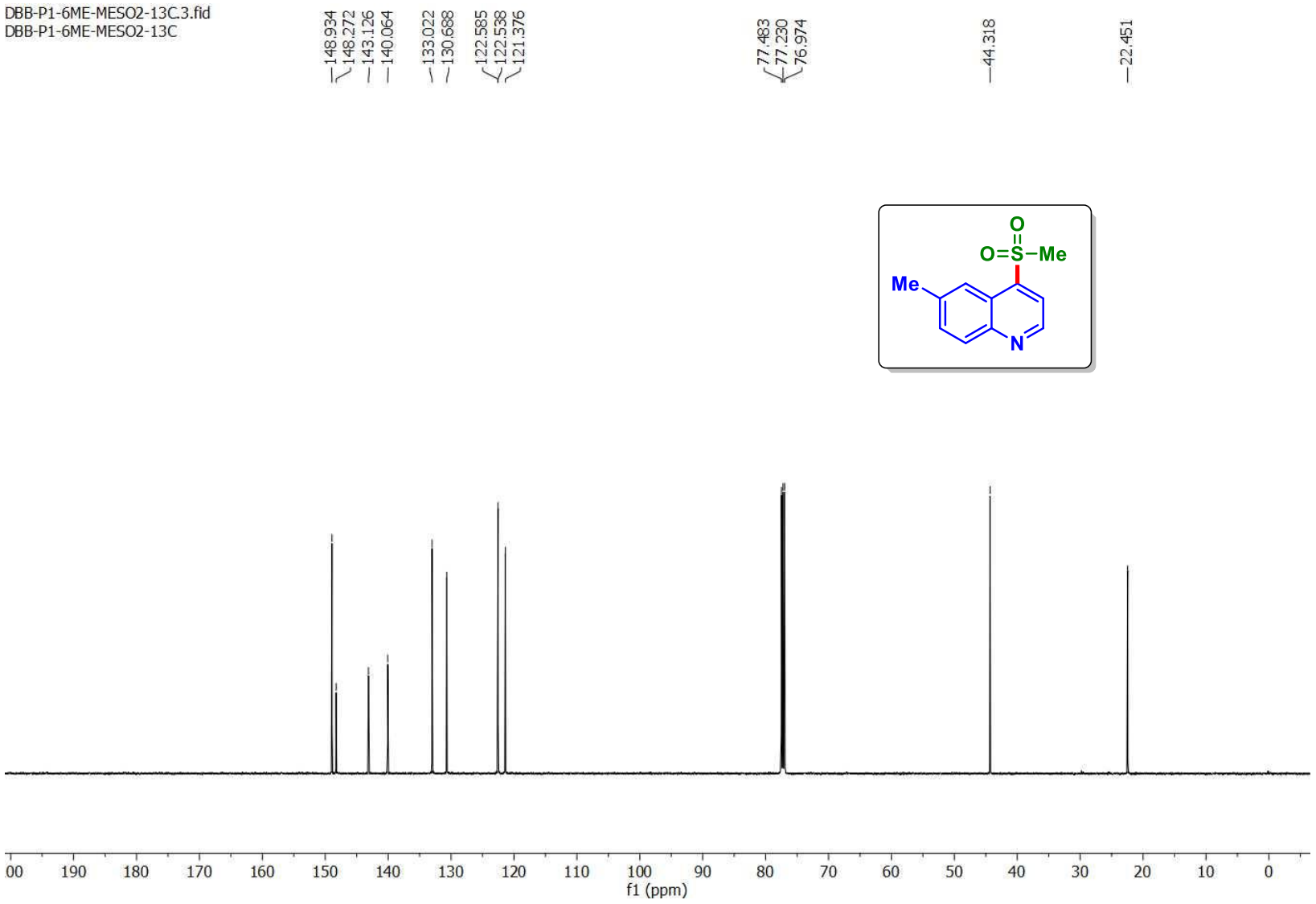
4-(Cyclopropylsulfonyl)-6-methylquinoline (1k): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



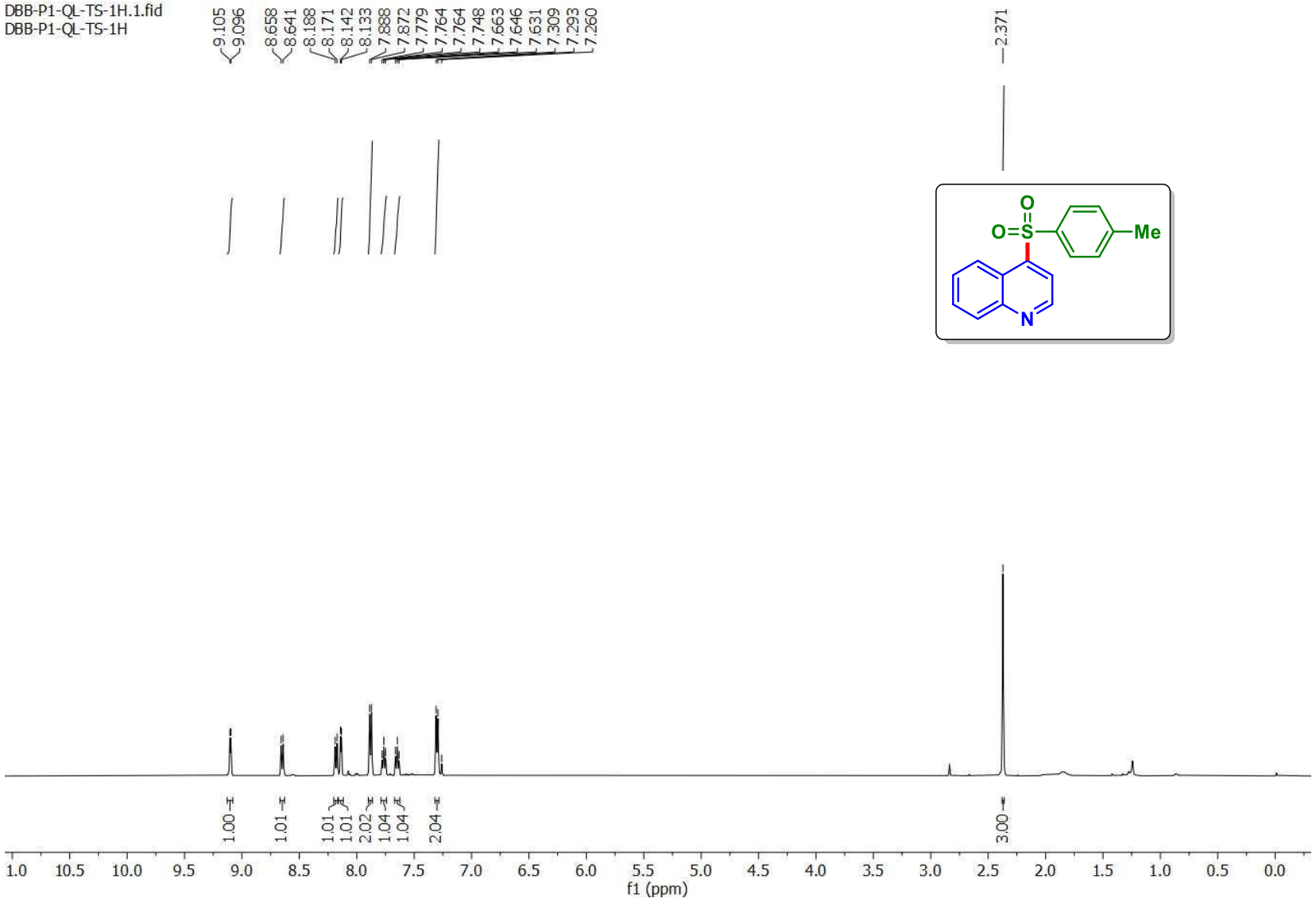
6-Methyl-4-(methylsulfonyl)quinoline (1l): ^{1}H NMR ($CDCl_3$, 500 MHz)



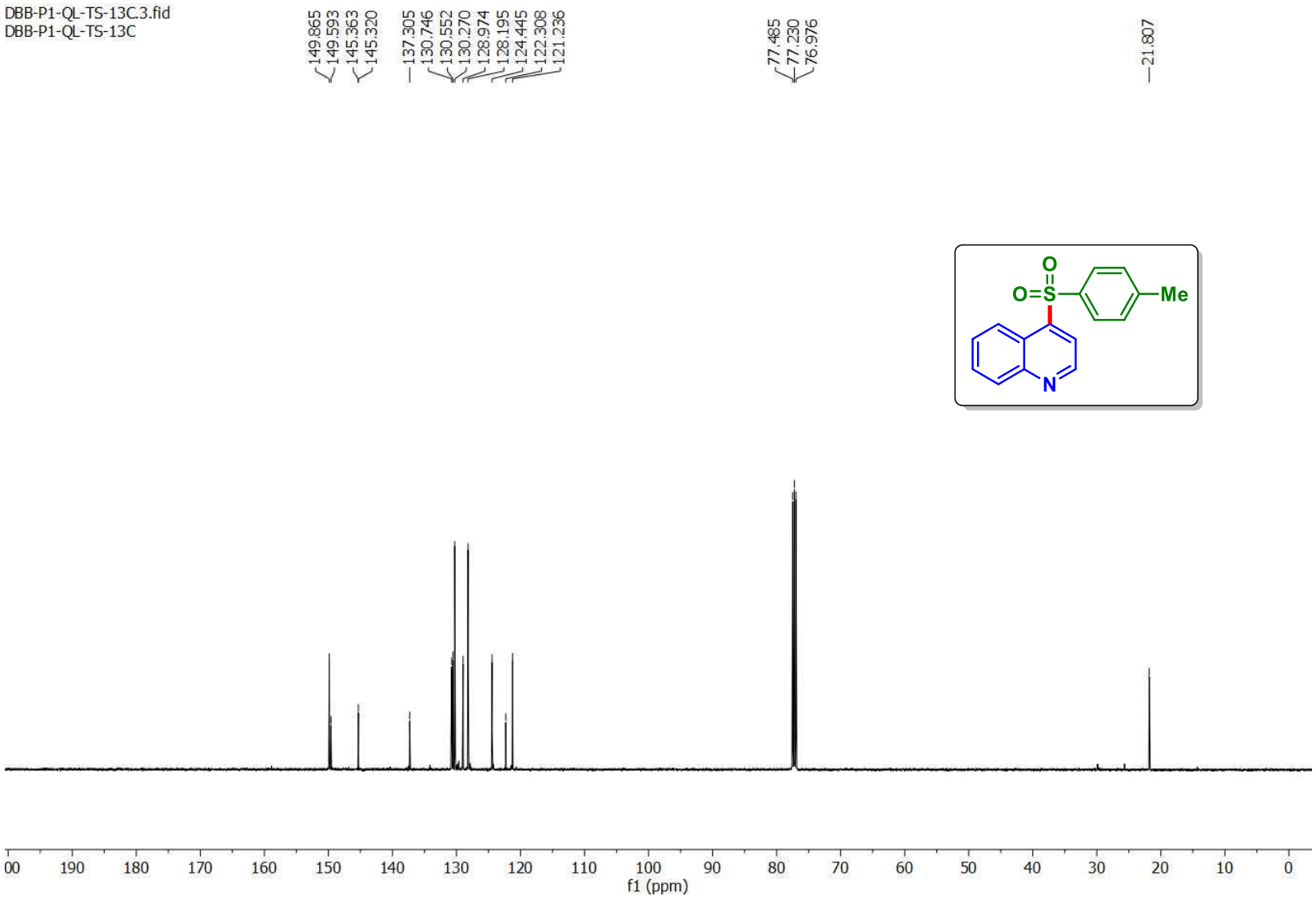
6-Methyl-4-(methylsulfonyl)quinoline (1l): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



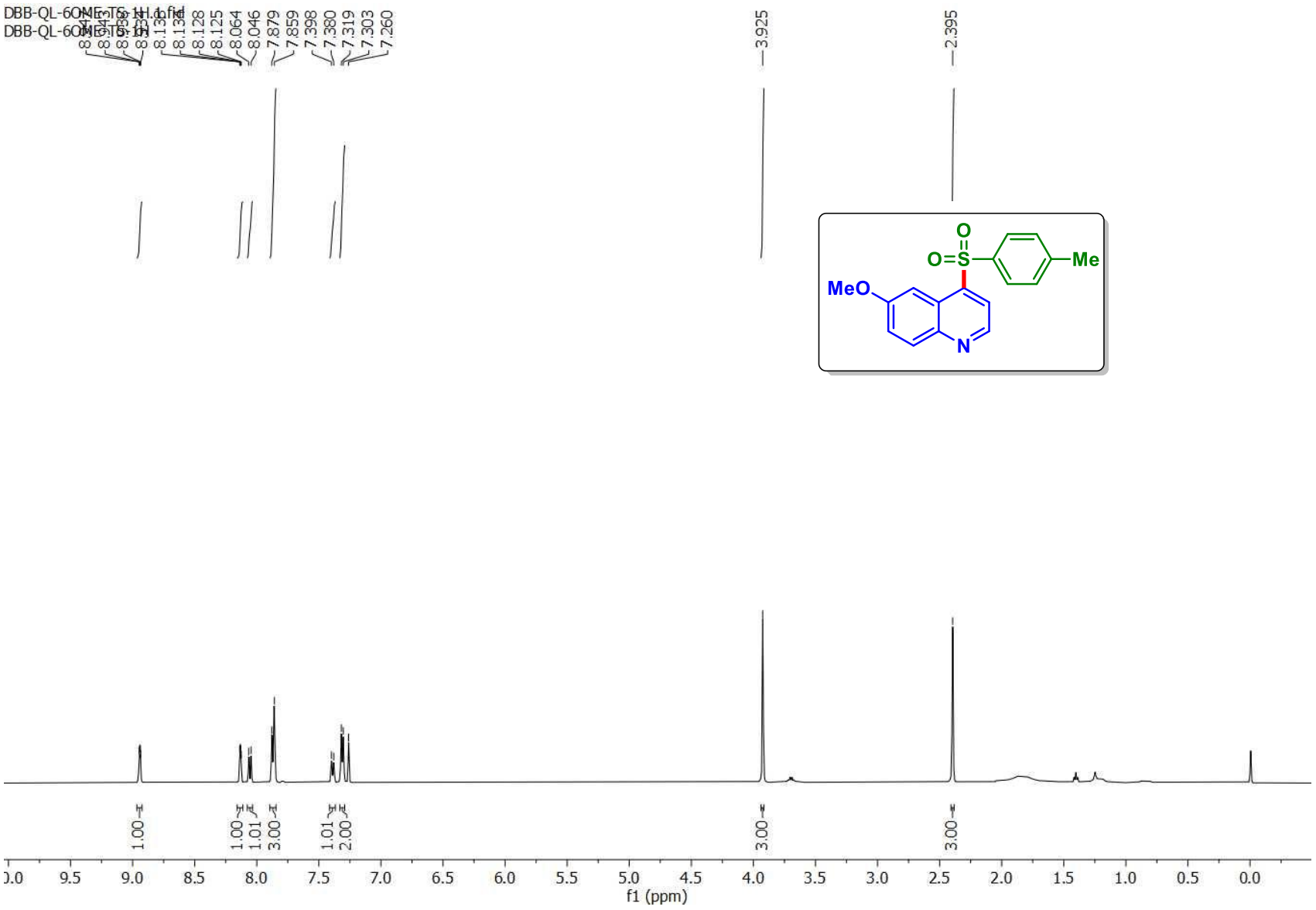
4-Tosylquinoline (2b): ^{1}H NMR ($CDCl_3$, 500 MHz)



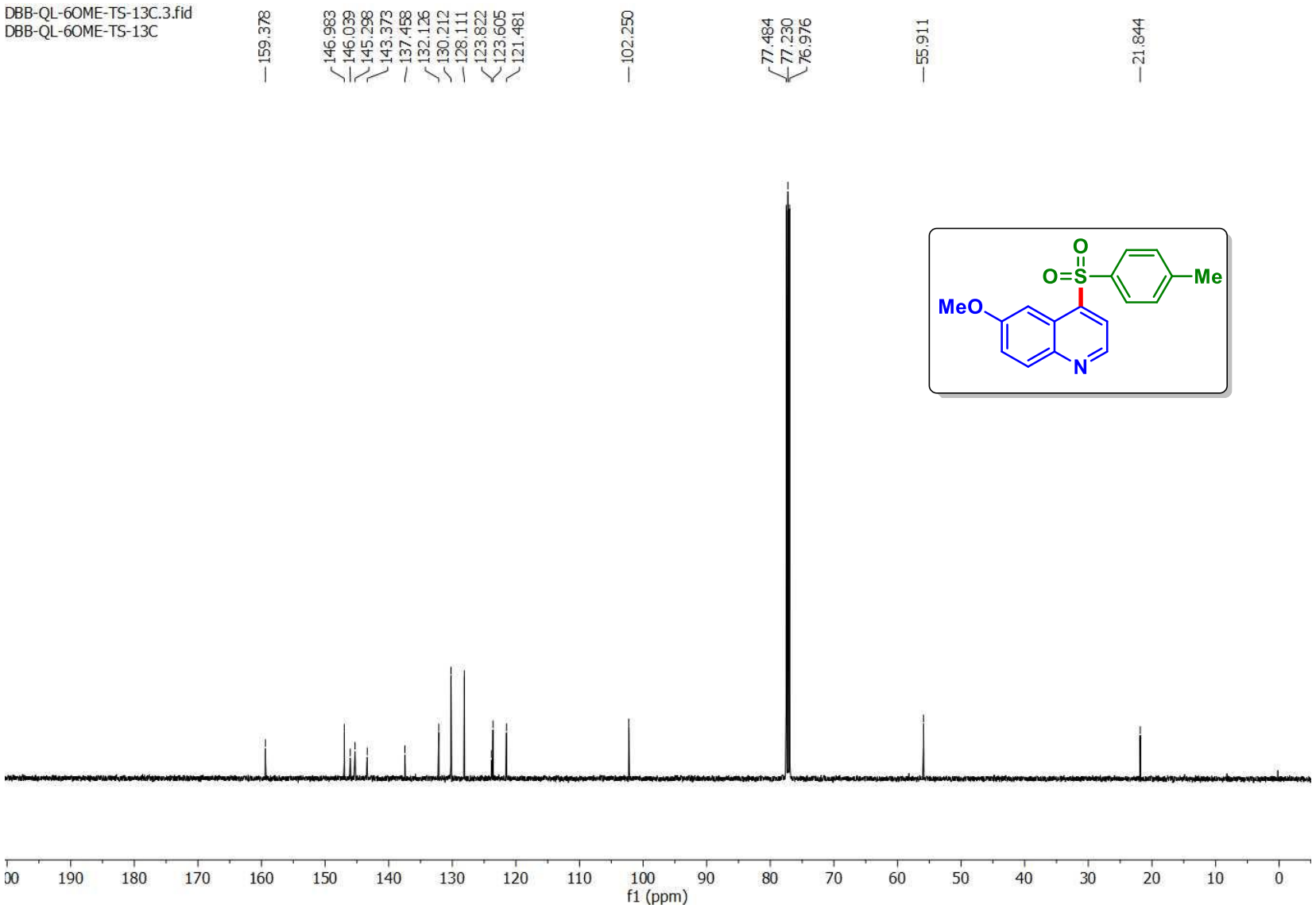
4-Tosylquinoline (2b): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



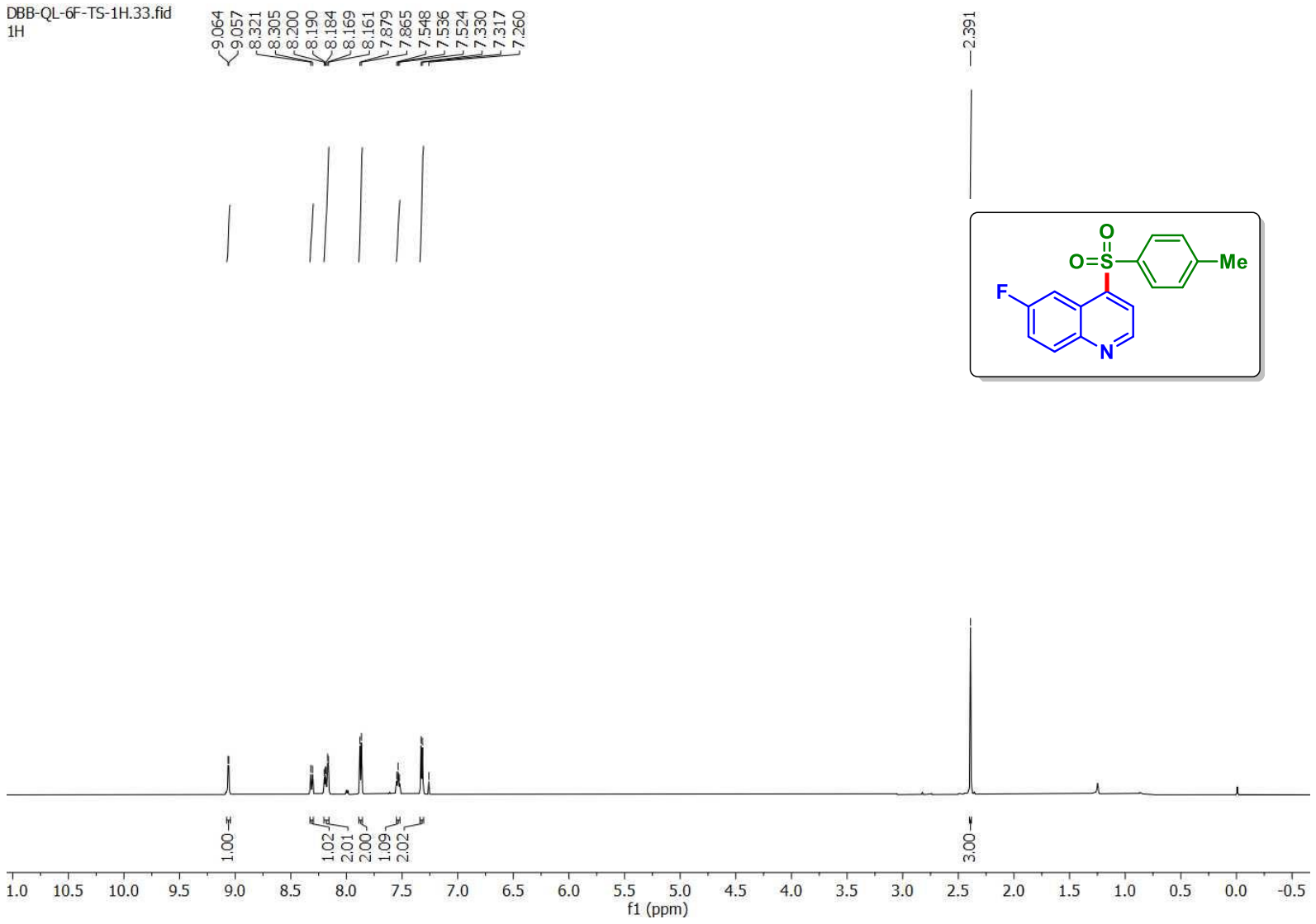
6-Methoxy-4-tosylquinoline (3b): ^{1}H NMR ($CDCl_3$, 500 MHz)



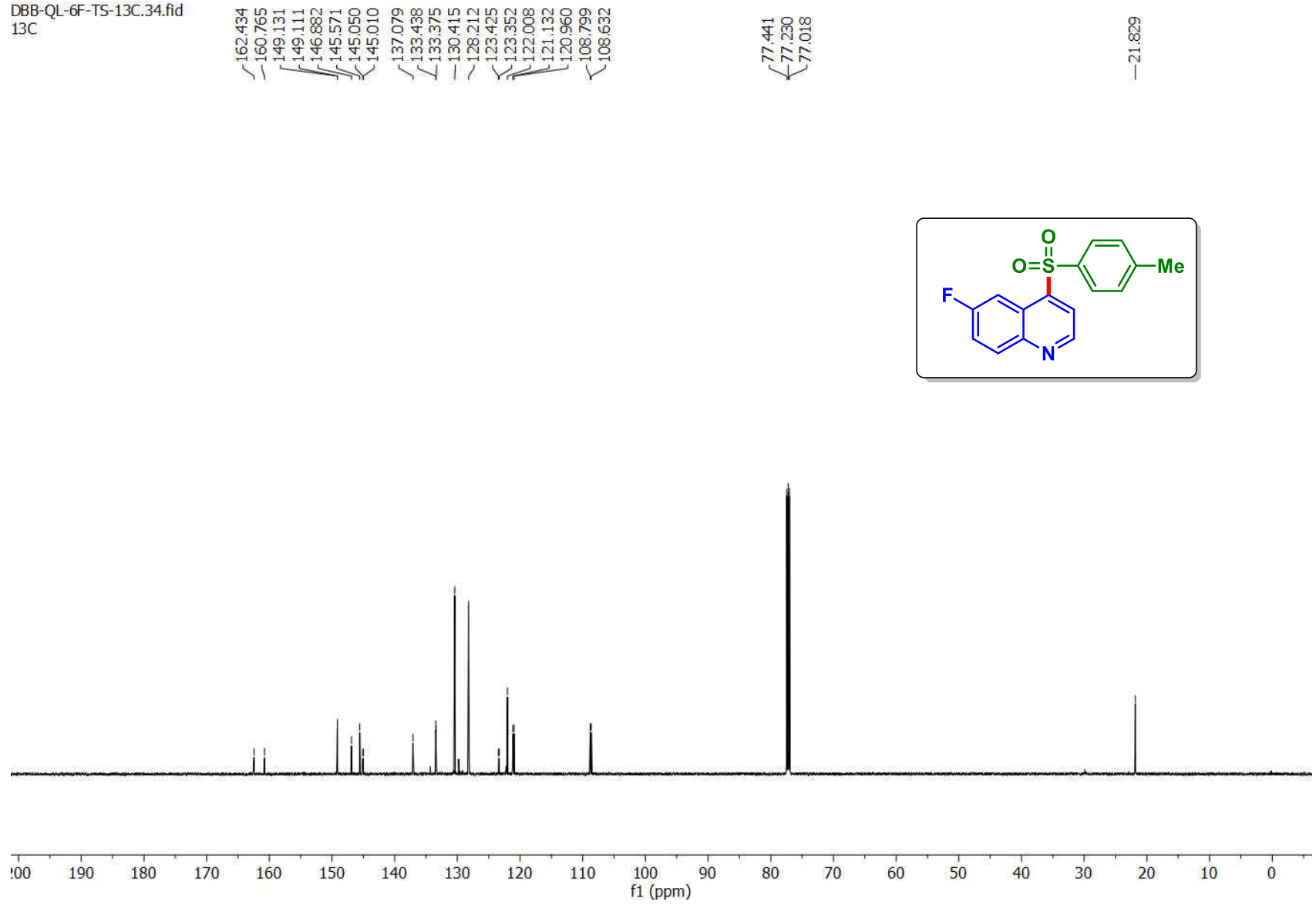
6-Methoxy-4-tosylquinoline (3b): ^{13}C NMR ($CDCl_3$, 125 MHz)



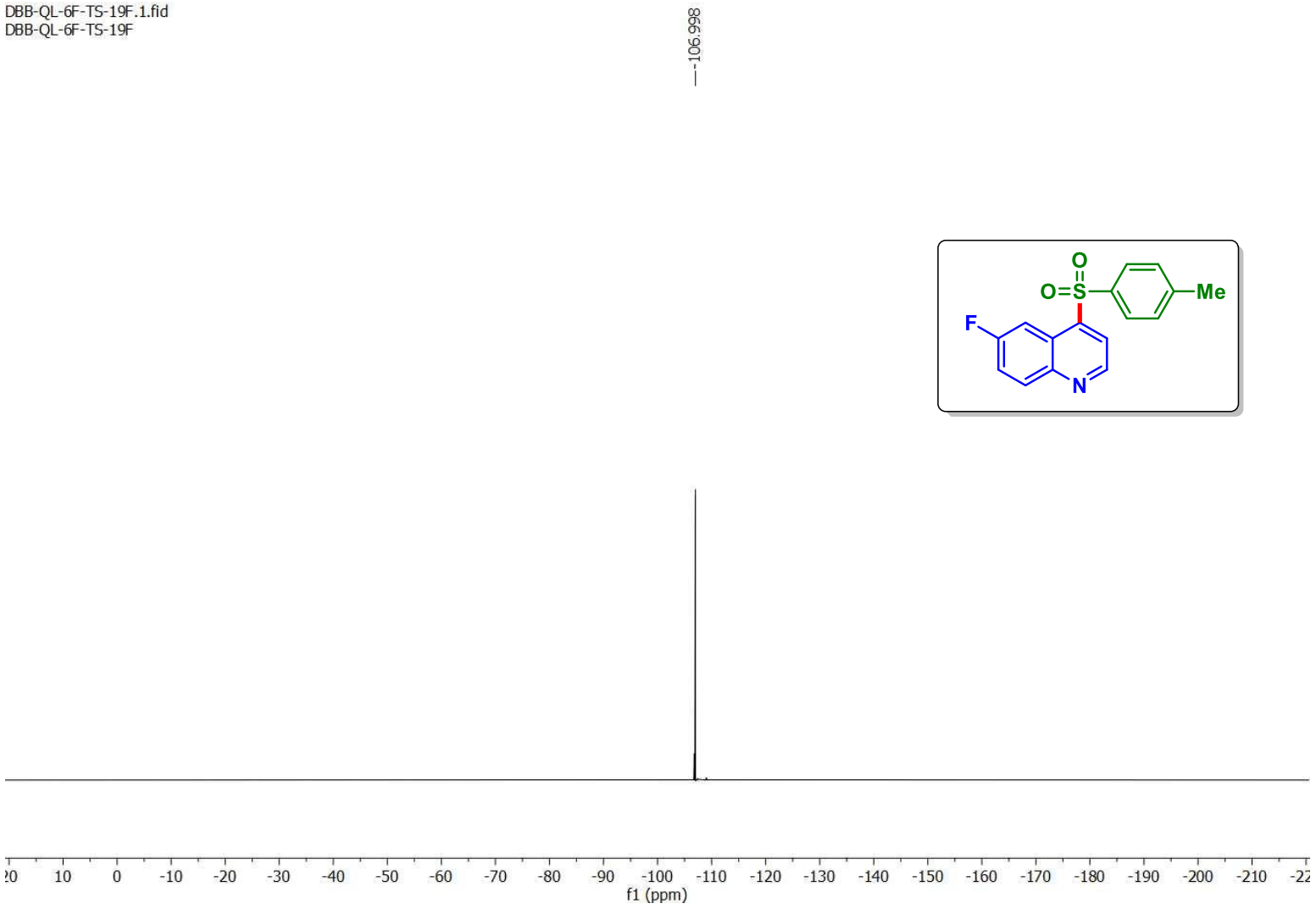
6-Fluoro-4-tosylquinoline (4b): ^{1}H NMR ($CDCl_3$, 600 MHz)



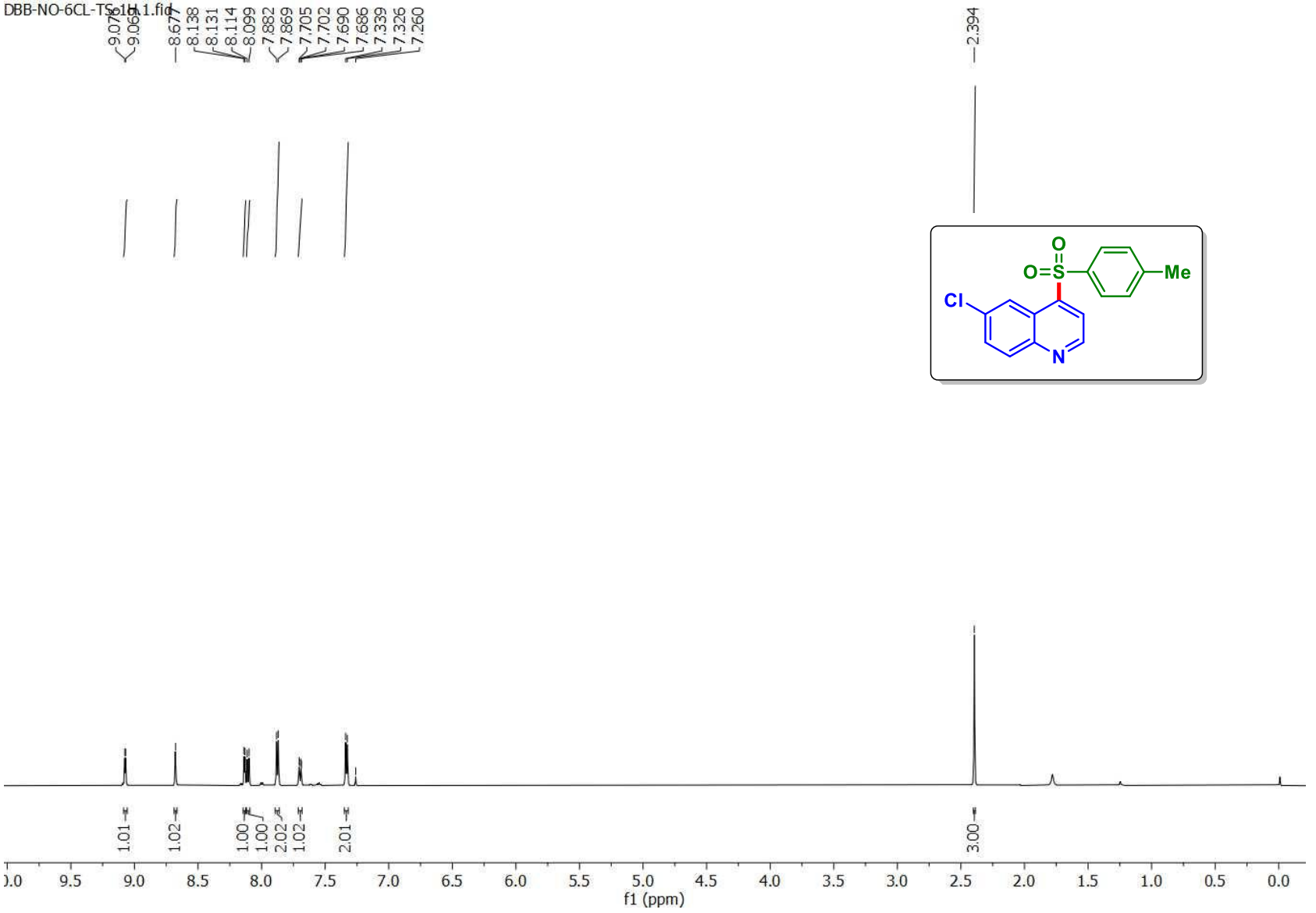
6-Fluoro-4-tosylquinoline (4b): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



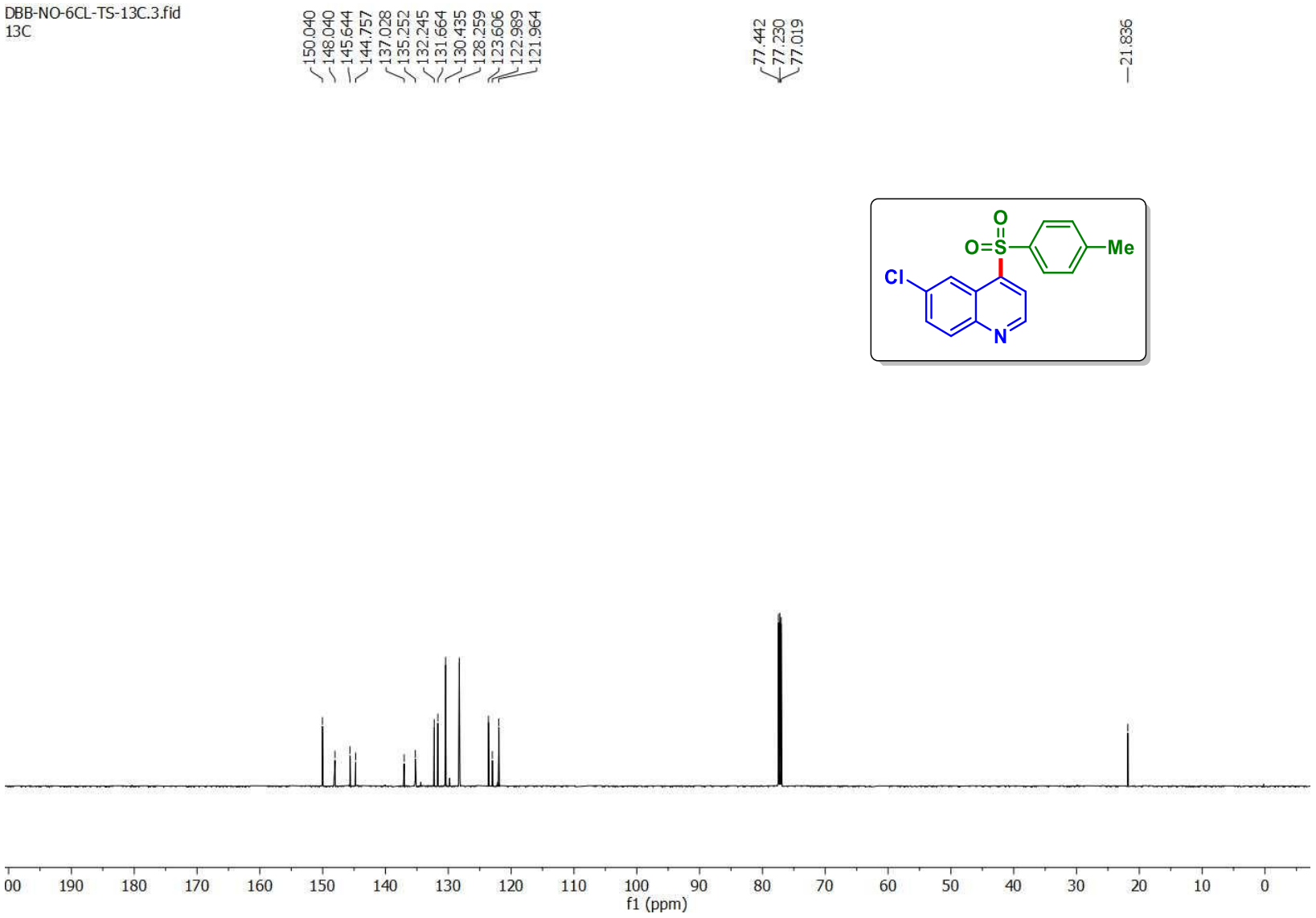
6-Fluoro-4-tosylquinoline (4b): ^{19}F NMR ($CDCl_3$, 471 MHz)



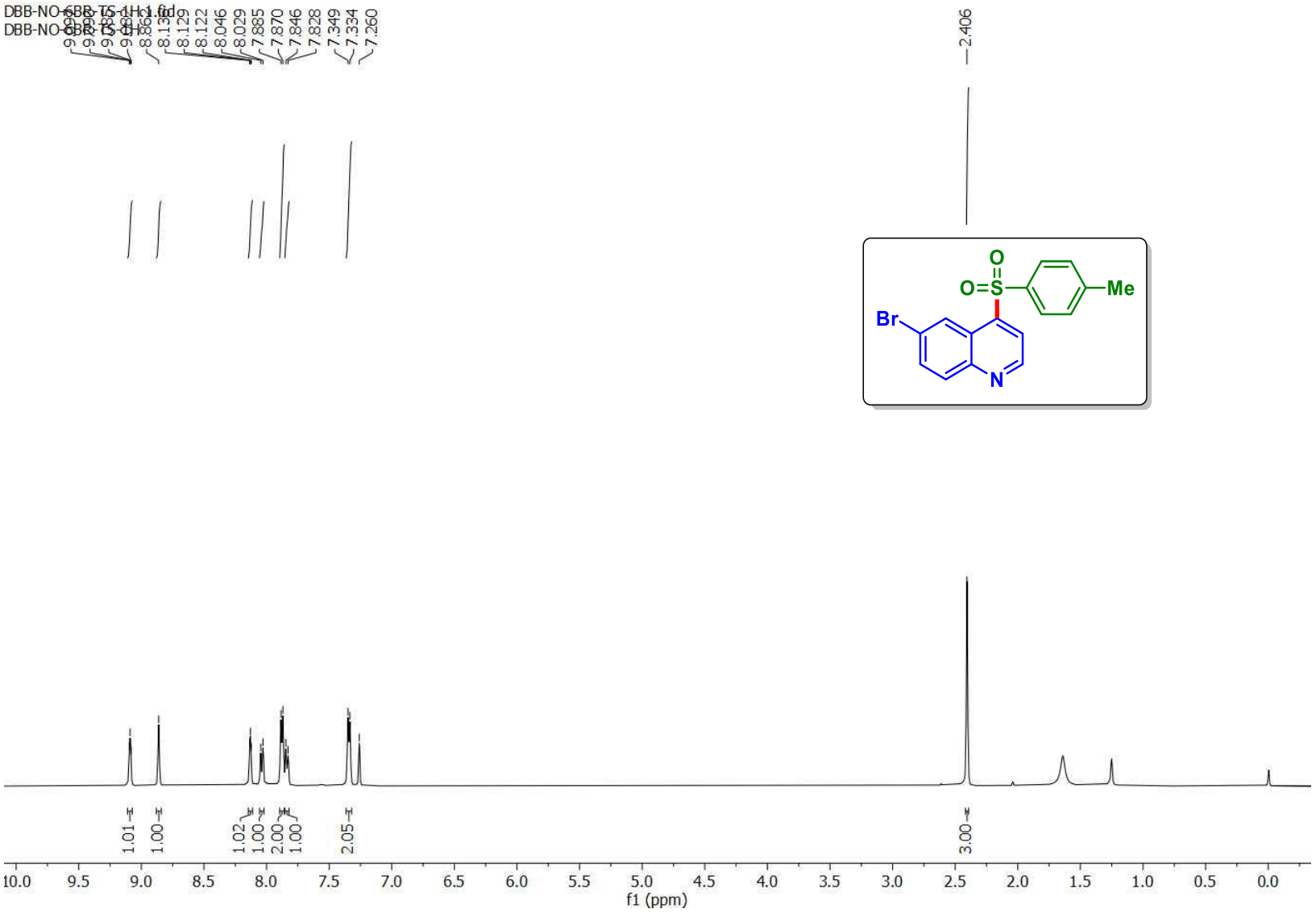
6-Chloro-4-tosylquinoline (5b): ^{1}H NMR ($CDCl_3$, 600 MHz)



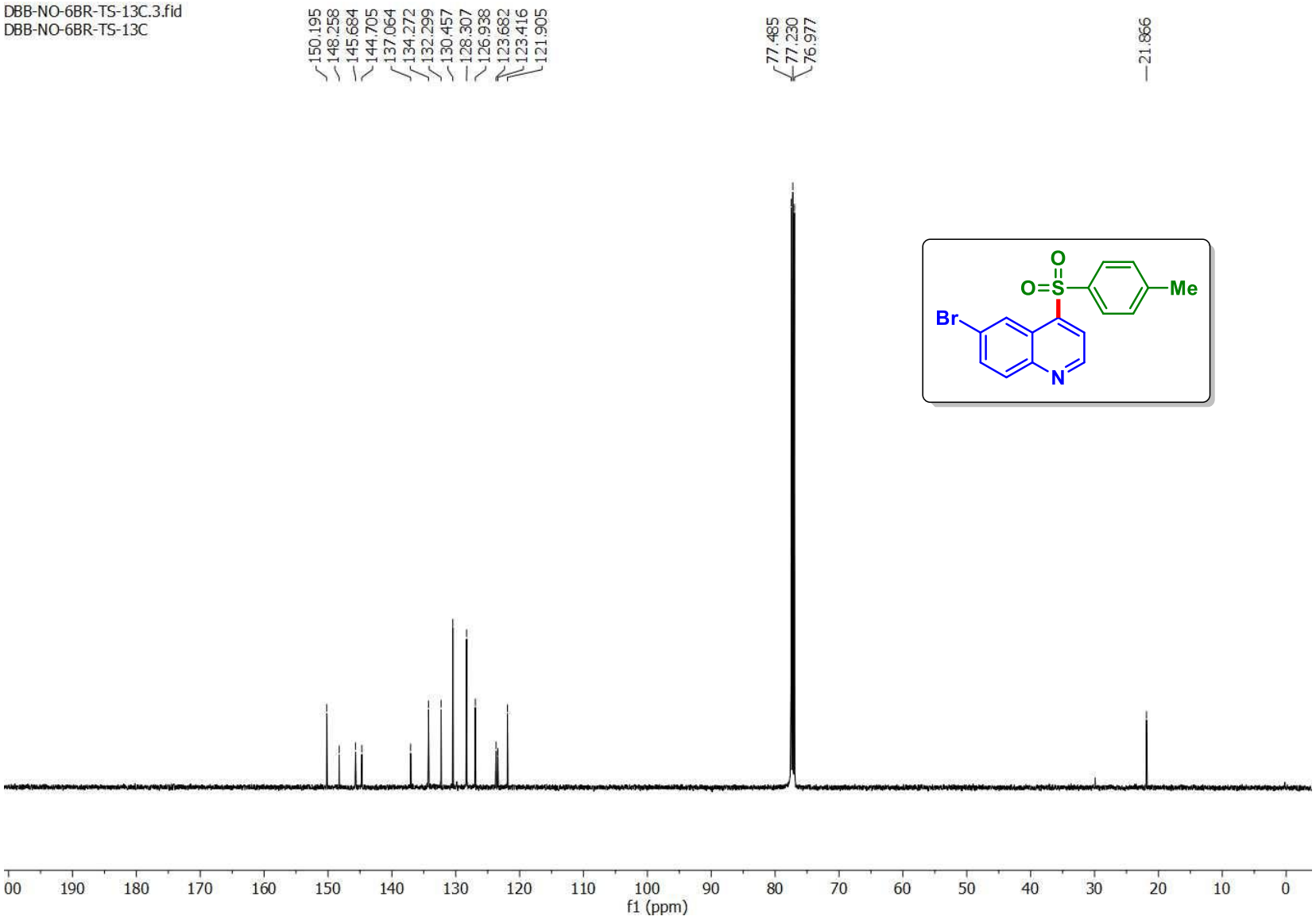
6-Chloro-4-tosylquinoline (5b): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



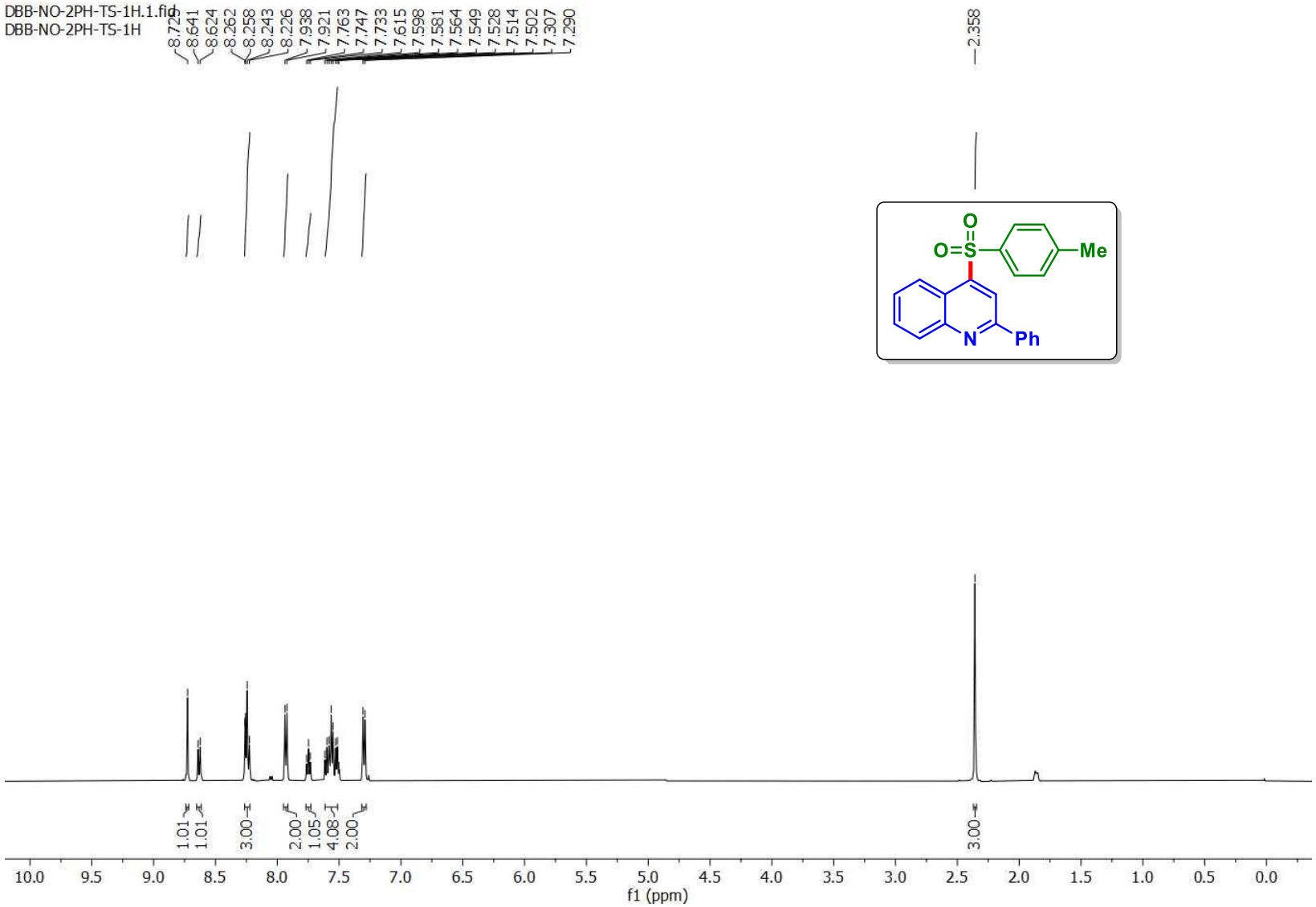
6-Bromo-4-tosylquinoline (6b): ^{1}H NMR ($CDCl_3$, 500 MHz)



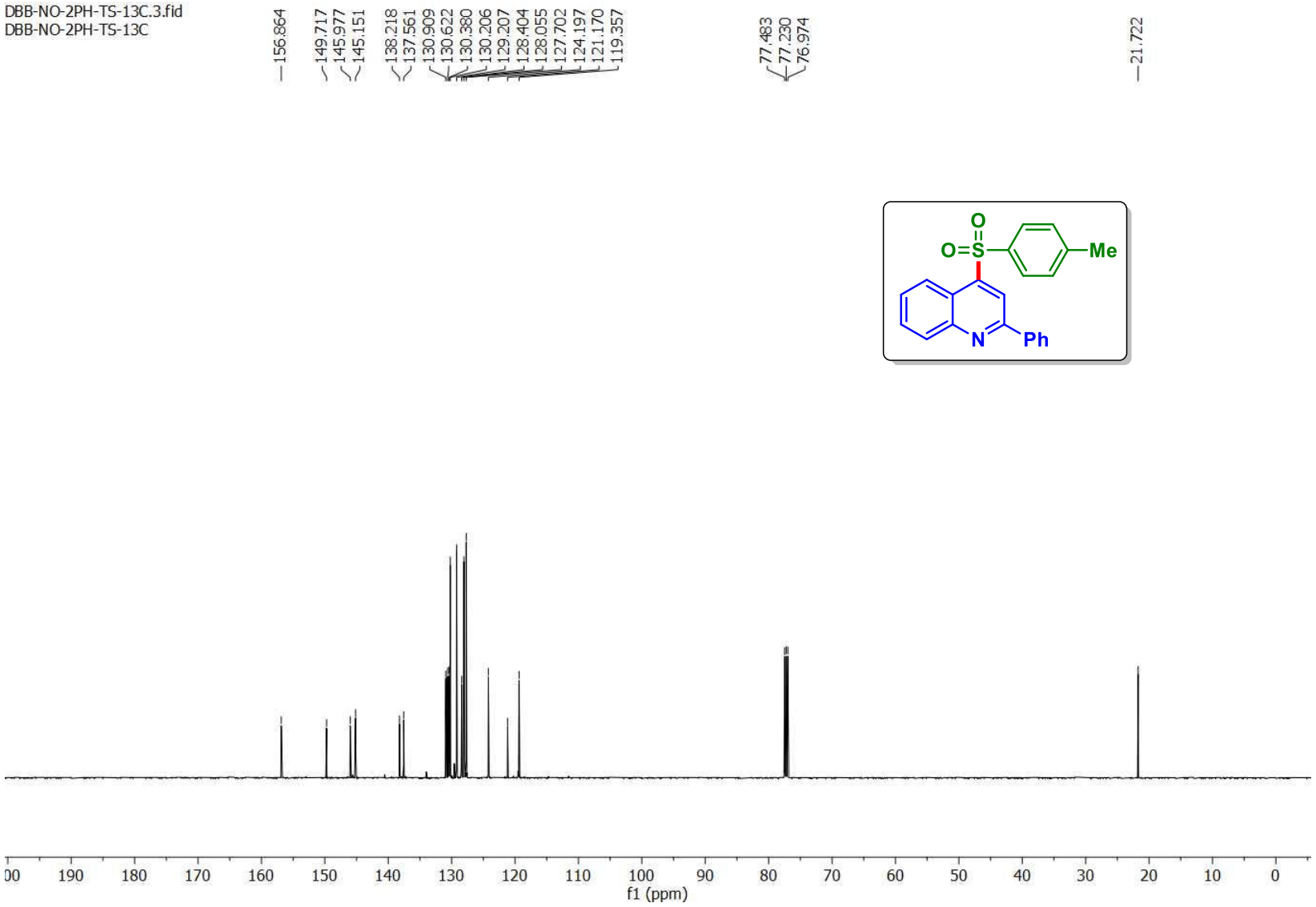
6-Bromo-4-tosylquinoline (6b): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



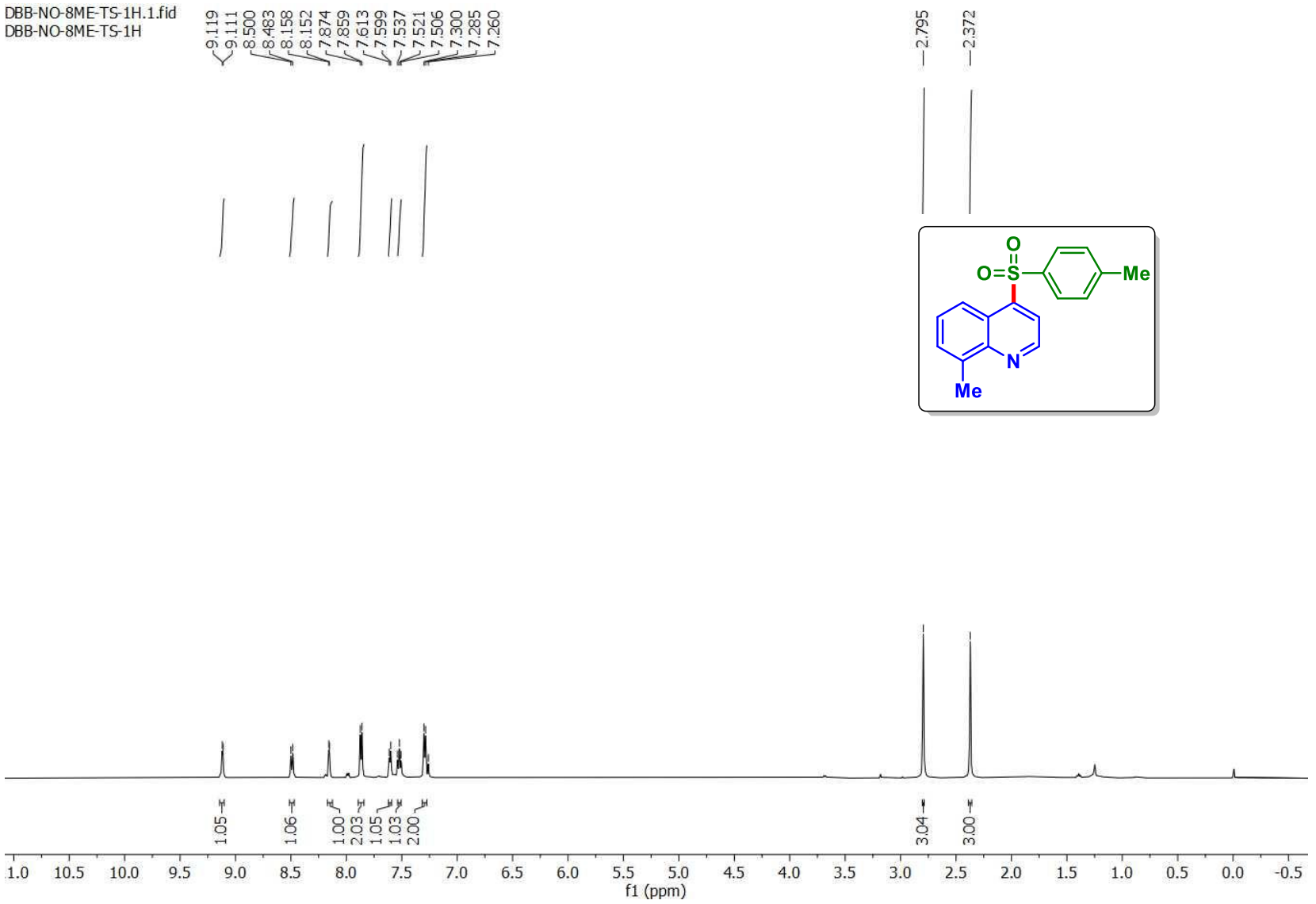
2-Phenyl-4-tosylquinoline (7b): ^{1}H NMR ($CDCl_3$, 500 MHz)



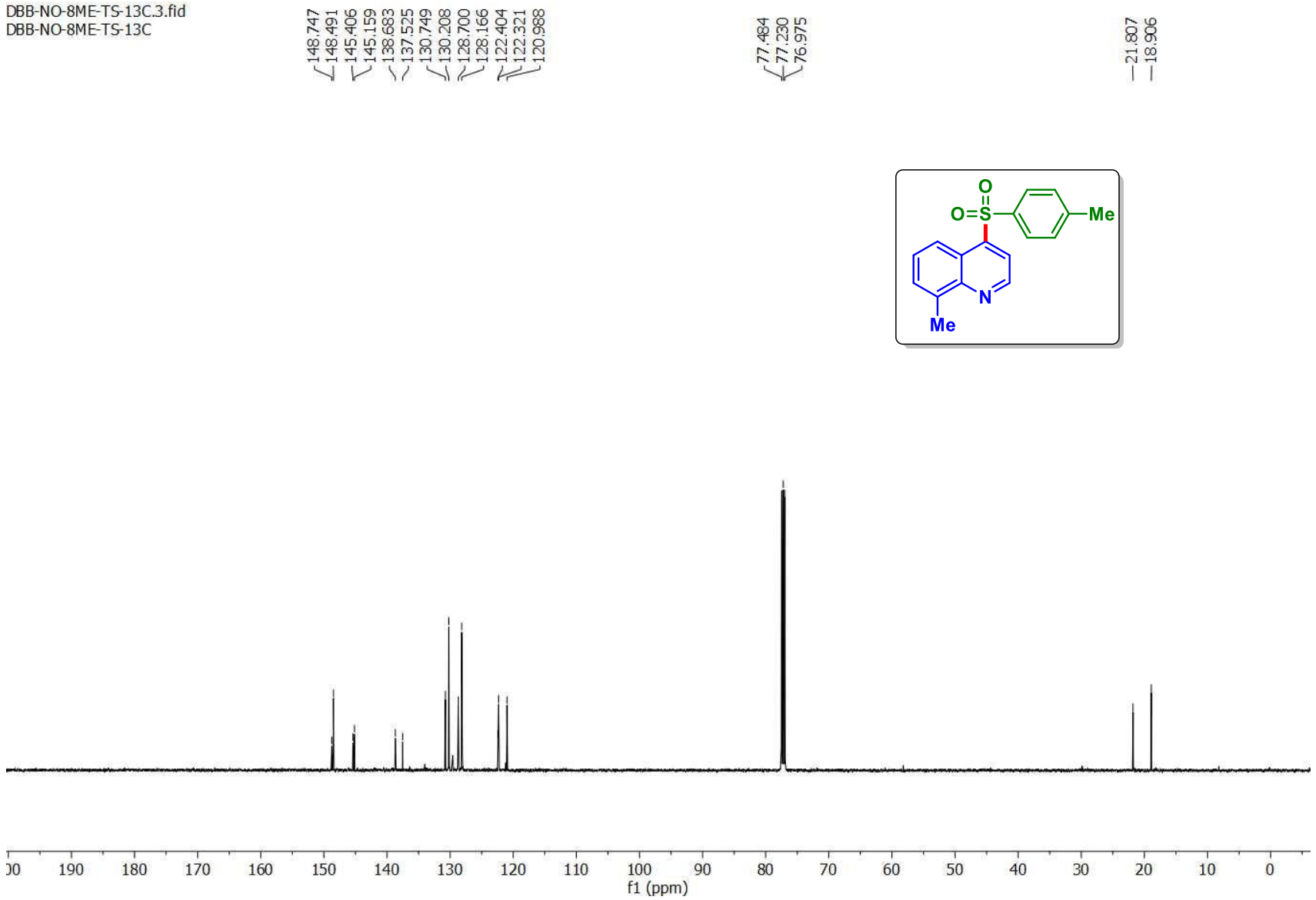
2-Phenyl-4-tosylquinoline (7b): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



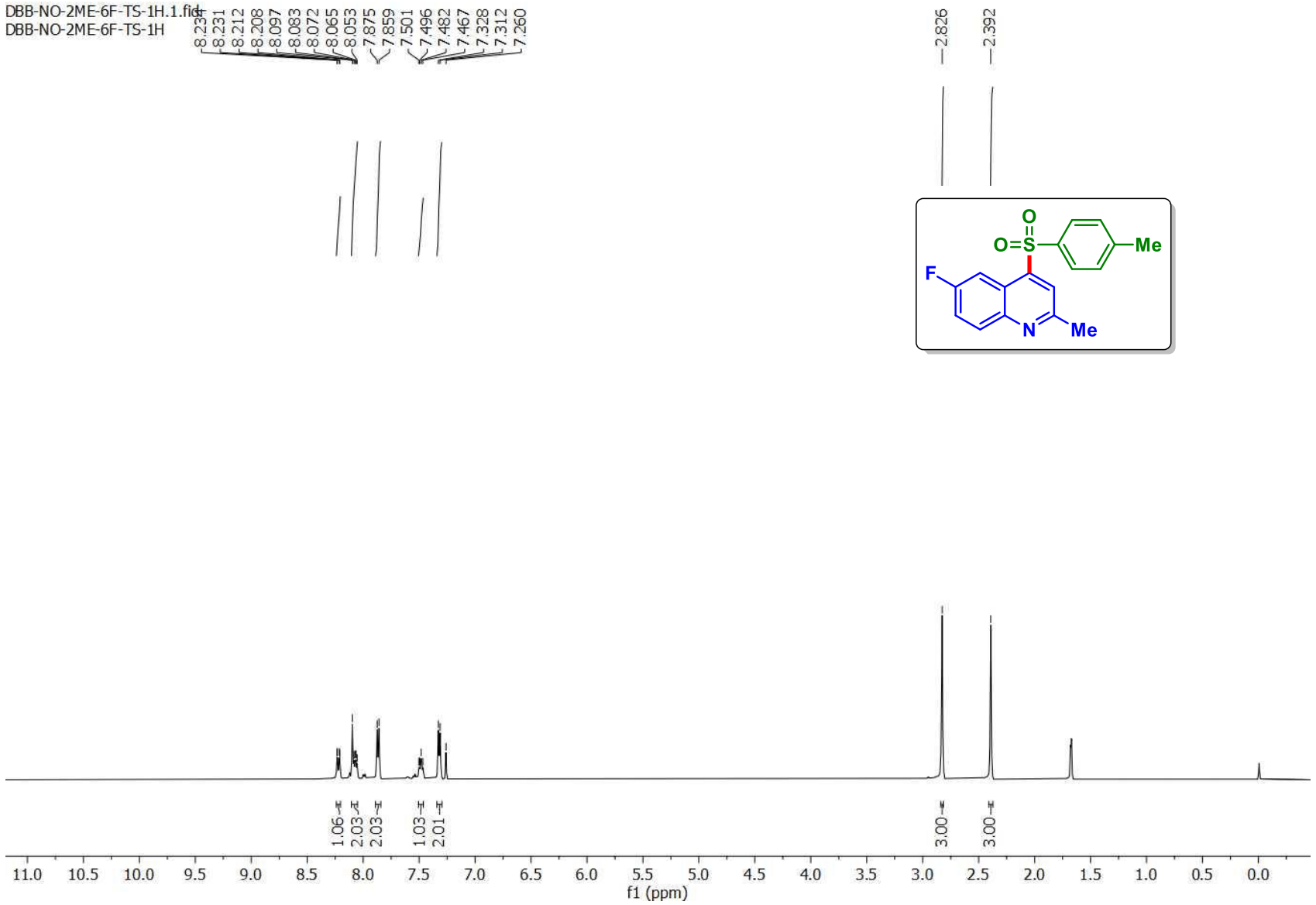
8-Methyl-4-tosylquinoline (8b): ^{1}H NMR ($CDCl_3$, 500 MHz)



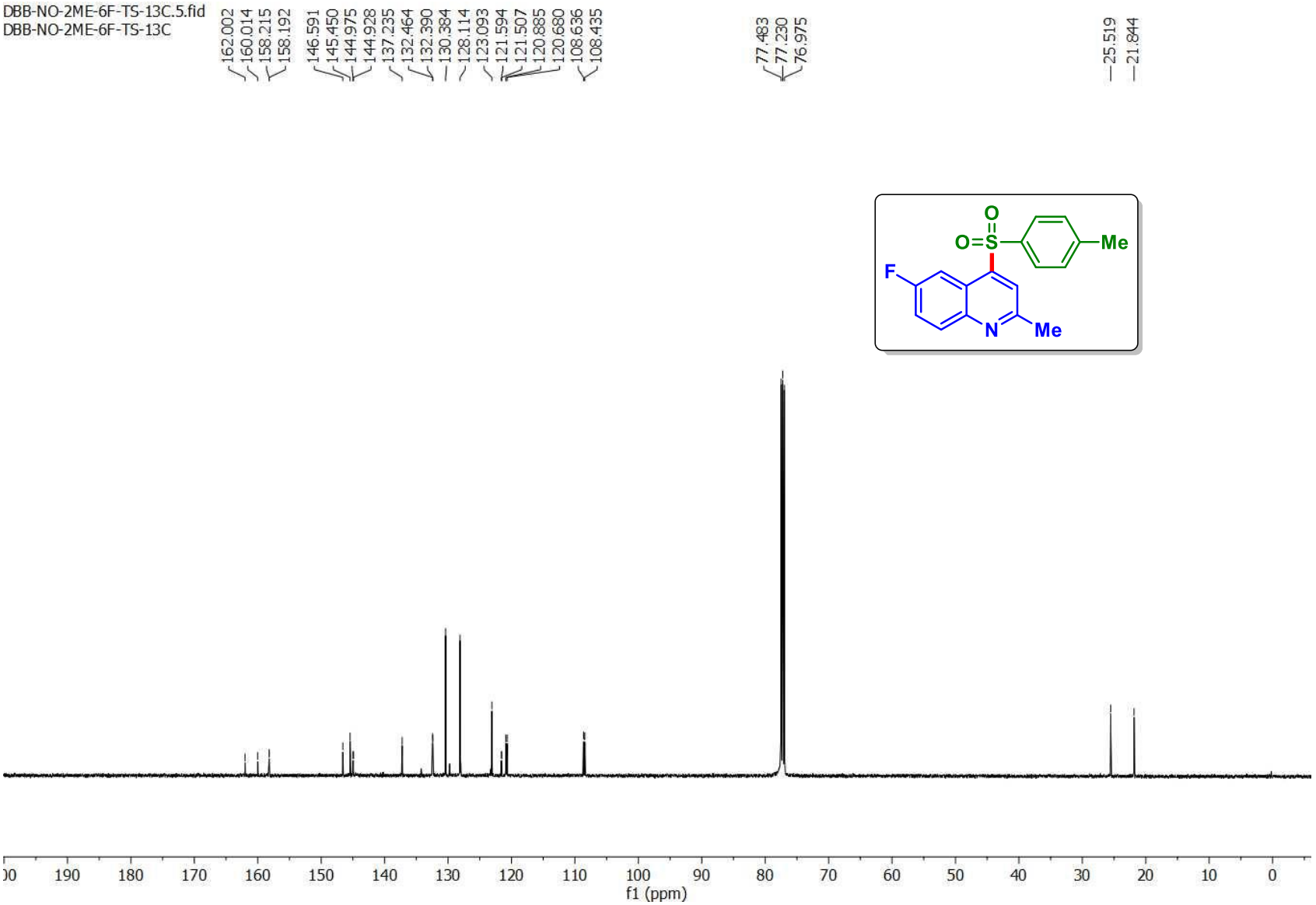
8-Methyl-4-tosylquinoline (8b): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



6-Fluoro-2-methyl-4-tosylquinoline (9b): ^{1}H NMR ($CDCl_3$, 500 MHz)



6-Fluoro-2-methyl-4-tosylquinoline (9b): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



6-Fluoro-2-methyl-4-tosylquinoline (9b): ^{19}F NMR ($CDCl_3$, 471 MHz)