

Supporting Information

Organoboron/Iodide-Catalyzed Photoredox N-Functionalization of NH-Sulfoximines/Sulfonimidamides

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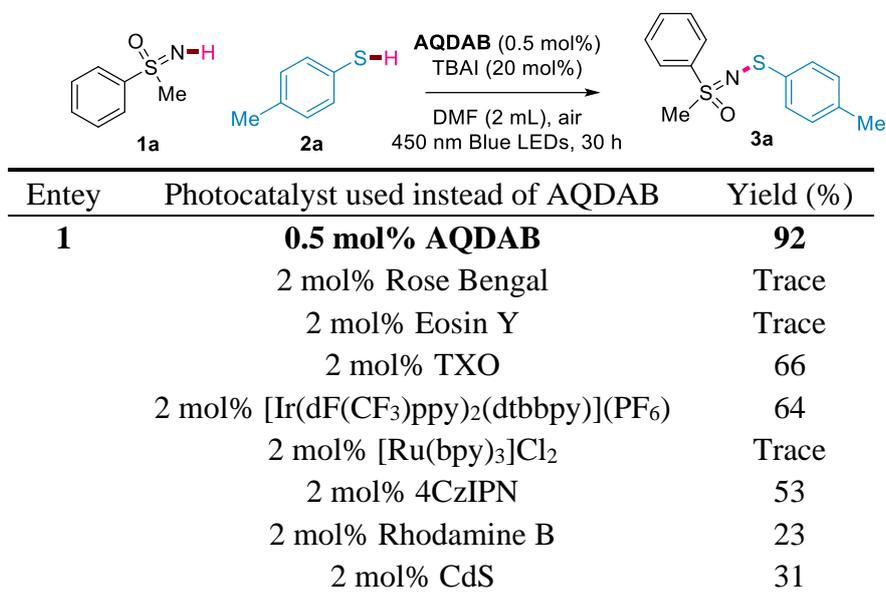
1. General considerations

General. Unless otherwise noted, all reactions were carried out under an air atmosphere. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator. Visualization was accomplished by exposure to a UV lamp. All the products in this article are compatible with standard silica gel chromatography. Column chromatography was performed on silica gel (200–300 mesh) using standard methods.

Structural analysis. NMR spectra were measured on a Bruker Ascend 400 spectrometer and chemical shifts (δ) are reported in parts per million (ppm). ^1H NMR spectra were recorded at 400 MHz in NMR solvents and referenced internally to corresponding solvent resonance, and ^{13}C NMR spectra were recorded at 101 MHz and referenced to corresponding solvent resonance. Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Infrared spectra were collected on a Thermo Fisher Nicolet 6700 FT-IR spectrometer using ATR (Attenuated Total Reflectance) method. Absorption maxima (ν max) are reported in wavenumbers (cm^{-1}). High resolution mass spectra (HRMS) were acquired on Thermo Scientific LTQ Orbitrap XL with an APCI source.

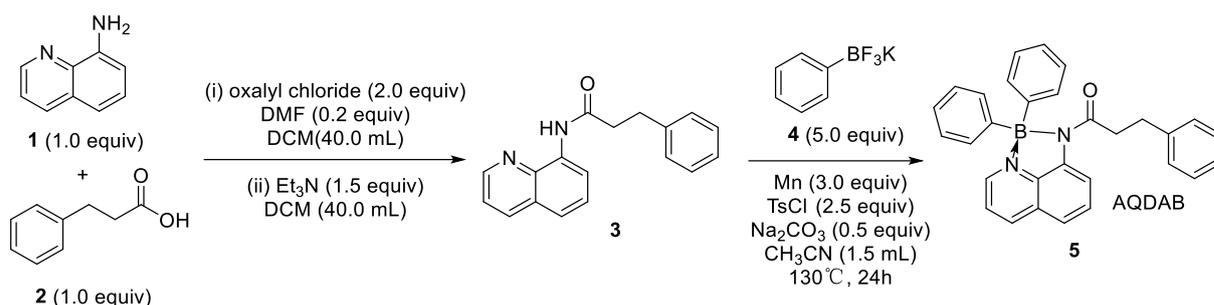
Materials. Commercial reagents and solvent were purchased from Adamas, J&K, Energy, Sigma-Aldrich, Alfa Aesar, Acros Organics, TCI and used as received unless otherwise stated.

2. Optimizing the selection of photocatalysts for the synthesis of N-sulfenylated products



Scheme S1. Optimizing the selection of photocatalysts for the synthesis of N-sulfenylated products.

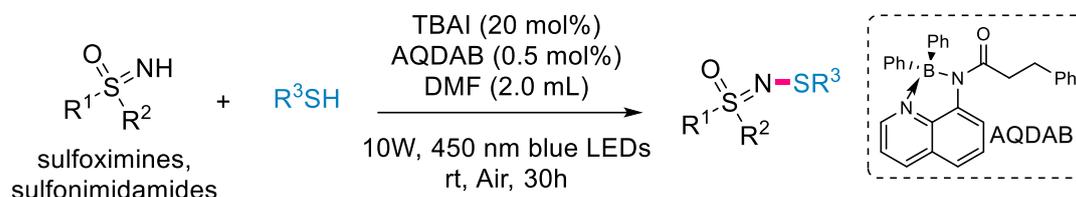
3. The synthesis of the photocatalyst used



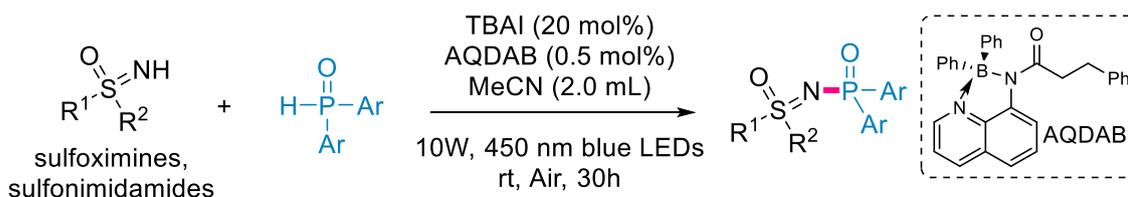
A mixture of hydrocinnamic acid **2** (3.0 g, 20 mmol), oxalyl chloride (5.1 g, 40 mmol, 2.0 equiv), DMF (0.3 mL, 4 mmol, 0.2 equiv) in anhydrous DCM (40.0 mL) was stirred at room temperature overnight. The reaction mixture was then concentrated in vacuo to give the crude hydrocinnamoyl chloride. A mixture of hydrocinnamoyl chloride, 8-aminoquinoline **1** (2.9 g, 20 mmol, 1.0 equiv), and triethylamine (4.2 mL, 30 mmol, 1.5 equiv) in anhydrous DCM (40 mL) was stirred at room temperature overnight. The reaction mixture was then washed with water and brine, dried over anhydrous Na₂SO₄ and concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography to give 4.1 g of the 3-phenyl-N-(quinolin-8-yl)propanamide **3** in 75% yield.

A flame-dried 25 mL reaction tube was placed with a stirring bar. Then, 3-phenyl-N-(quinolin-8-yl)propanamide **3** (41.4 mg, 0.15 mmol, 1.0 equiv), phenyl trifluoroborate **4** (138 mg, 0.75 mmol, 5.0 equiv), Mn (24.7 mg, 0.45 mmol, 3.0 equiv), 4-toluenesulfonyl chloride (71.5 mg, 0.375 mmol, 2.5 equiv), Na₂CO₃ (7.9 mg, 0.075 mmol, 0.5 equiv) and CH₃CN (1.5 mL) were added. The resulting mixture was stirred at 130 °C for 24 hours. Then, the reaction mixture was filtered, concentrated and purified by column chromatography (silica gel) to give 62.7 mg of the target product **AQDAB** in 95% yield.

4. General procedure for the N-functionalization of sulfoximines and sulfonimidamides



General Procedure A: sulfoximines or sulfonimidamides (0.20 mmol, 1.0 equiv), thiol (0.40 mmol, 2.0 equiv), TBAI (0.04 mmol, 20 mol%), AQDAB (0.001 mmol, 0.5 mol%), and DMF (2.0 mL) were added to a dried 25 mL reaction tube. The reaction tube was placed on a photocatalytic parallel reactor with a 450 nm blue LEDs light source (10 W) at the bottom (**Figure S1**). Then the reaction mixture was irradiated with the 450 nm blue LEDs (at approximately 0.3 cm away from the light source). After stirring for 30 hours at 25 °C, the reaction mixture was added 10 mL H₂O and then extracted with ethyl acetate (3 × 10 mL). The combined organic phase was dried over Na₂SO₄, and concentrated under vacuum to afford the crude product, which was purified by column chromatography on silica gel using PE/EA (3: 1) as eluent to give the target products.



General Procedure B: sulfoximines or sulfonimidamides (0.20 mmol, 1.0 equiv), diphenylphosphine oxide (0.40 mmol, 2.0 equiv), TBAI (0.04 mmol, 20 mol%), AQDAB (0.001 mmol, 0.5 mol%), and MeCN (2.0 mL) were added to a dried 25 mL reaction tube. The reaction tube was placed on a photocatalytic parallel reactor with a 450 nm blue LEDs light source (10 W) at the bottom (**Figure S1**). Then the reaction mixture was irradiated with the 450 nm blue LEDs (at approximately 0.3 cm away from the light source). After stirring for 30 hours at 25 °C, the reaction mixture was added 10 mL H₂O and then extracted with ethyl acetate (3 × 10 mL). The combined organic phase was dried over Na₂SO₄, and concentrated under vacuum to afford the crude product, which was purified by column chromatography on silica gel using PE/EA (3: 1) as eluent to give the target products.

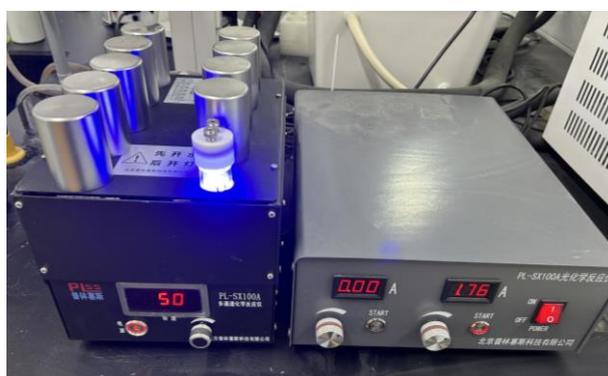
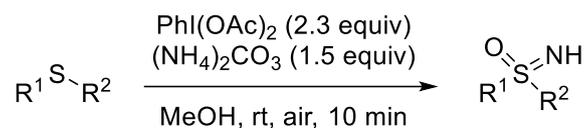


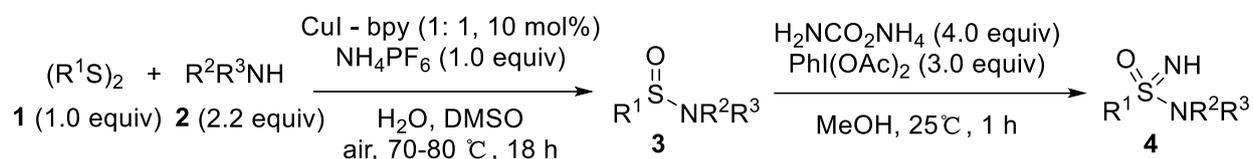
Figure S1. Picture of the reactor

5. General Procedure for the Synthesis of NH-Sulfoximines ^[1]



General Procedure for the Synthesis of NH-Sulfoximines. In a dried 50 mL pear-shaped flask equipped with a stirring bar, sulfide (1.0 mmol), PhI(OAc)₂ (2.3 mmol, 2.3 equiv), and (NH₄)₂CO₃ (1.5 mmol, 1.5 equiv) were added. Then, MeOH (10.0 mL) was added, and the reaction mixture was stirred at 25 °C for 10 min. The reaction was then quenched by the addition of saturated sodium bicarbonate (10.0 mL). The aqueous phase was extracted with ethyl acetate (10 mL × 3). The combined organic phase was dried over anhydrous MgSO₄, filtered, and concentrated. The resulting residual was purified by flash silica gel column chromatography using a mixture of PE and EA as the eluent to afford the NH-sulfoximines.

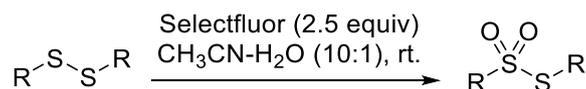
6. General Procedure for the Synthesis of NH- Sulfonimidamides ^[2,3]



To a mixture of disulfides **1** (1.0 mmol), diethylamine **2** (2.2 mmol, 2.2 equiv), and NH₄PF₆ (1.0 mmol, 1.0 equiv), in DMSO (0.6 mL) and H₂O (0.15 mL) were added CuI (0.1 mmol, 10 mmol%) and bpy (0.1 mmol, 10 mmol%), and the mixture was stirred at 80 °C for 18 h in the presence of air provided by a balloon. After the residue was dissolved in Et₂O, the solution was washed with H₂O and saturated sodium chloride and dried with anhydrous magnesium sulfate. The resulting residual was purified by flash silica gel column chromatography using a mixture of diethyl ether and hexane as the eluent to afford the Sulfinamides **3**.

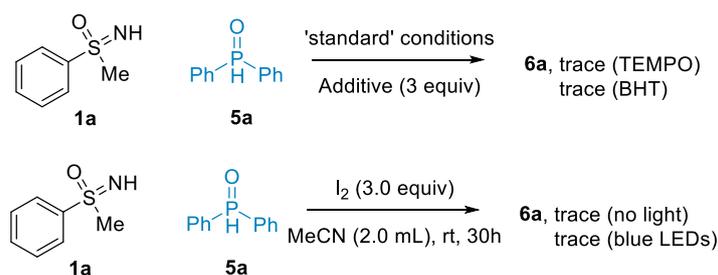
To the sulfinamide **3** (1.0 mmol) were added PhI(OAc)₂ (3.0 mmol, 3.0 equiv), H₂NCO₂NH₄ (4.0 mmol, 4.0 equiv) and finally MeOH (2.0 mL, 0.5 M). The mixture was stirred in an open flask at 25°C for 1 h. The reaction was then quenched by the addition of saturated sodium bicarbonate (10.0 mL). The aqueous phase was extracted with ethyl acetate (10 mL × 3). The combined organic phase was dried over anhydrous MgSO₄, filtered, and concentrated. The resulting residual was purified by flash silica gel column chromatography using a mixture of PE and EA as the eluent to afford the NH-sulfonimidamides **4**.

7. General Procedure for the Synthesis of Thiosulfonate ^[4]



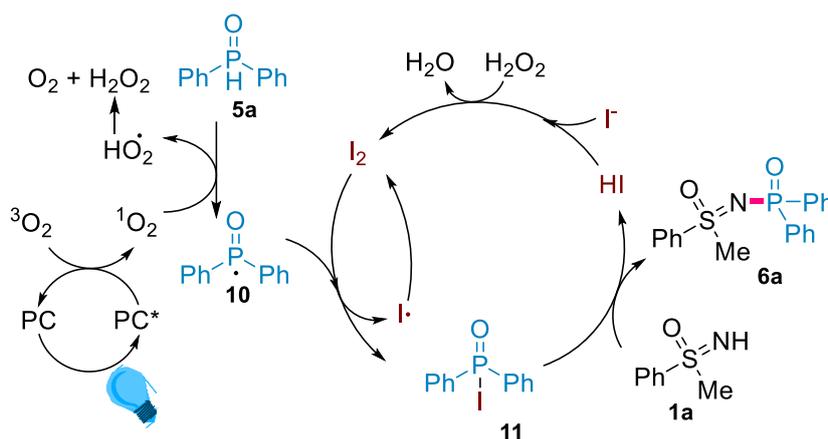
To a mixture of p-tolyl disulfide (1.0 mmol, 1.0 equiv), in acetonitrile (2.0 ml) and water (0.2 mL) were added Selectfluor (2.5 mmol, 2.5 equiv), and the mixture was stirred at room temperature for 20 min. The reaction was monitored by thin layer chromatography (TLC). After the disulfide disappeared from the TLC, water (5 mL) was added and the resulting mixture was extracted with ethyl acetate (15 mL × 3). The extract was washed with brine, dried over anhydrous magnesium sulfate, and evaporated. Chromatography on silica gel gave thiosulfonate as colorless crystals.

8. A possible mechanism of N-phosphonylation of NH-sulfoximines



Scheme S2. Mechanistic studies for N-phosphonylation of NH-sulfoximines.

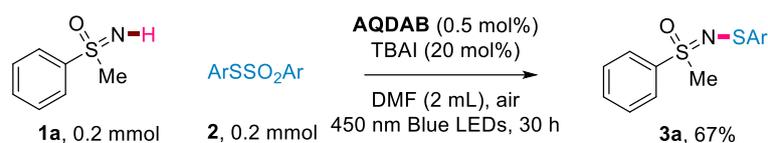
To further investigate the reaction mechanism for N-phosphonylation of NH-sulfoximines, a series of control experiments were conducted (**Scheme S2**). When a radical scavenger (TEMPO, BHT) was introduced into the reaction mixture, a significant suppression of the reaction process was observed. This indicates that radical species might be involved in the reaction mechanism. To confirm the role of iodine in the reaction, we attempted to carry out the reaction between diphenylphosphine oxide **5a** and sulfoximine **1a** using stoichiometric iodine. However, the desired compound could not be generated.



Scheme S3. A proposed mechanism for the N-phosphonylation of NH-sulfoximines.

A possible reaction mechanism has been proposed (**Scheme S3**). Initially, the photocatalyst PC was excited by visible light. The excited state PC* was then quenched by triplet oxygen to generate singlet oxygen $^1\text{O}_2$. Subsequently, the hydrogen atom transfer (HAT) of the diphenylphosphine oxide **5a** by singlet oxygen $^1\text{O}_2$ produced the P-centered radical **10** and hydroperoxide radical species. The disproportionation of the hydroperoxide radical would generate O_2 and H_2O_2 . At the same time, iodides were oxidized to I_2 in the presence of H_2O_2 . P-centered radical **10** reacted with I_2 to generate active electrophilic species **11**. Subsequently, intermediate **11** and sulfoxide imine **1a** undergo nucleophilic substitution to obtain the final product **6a**.

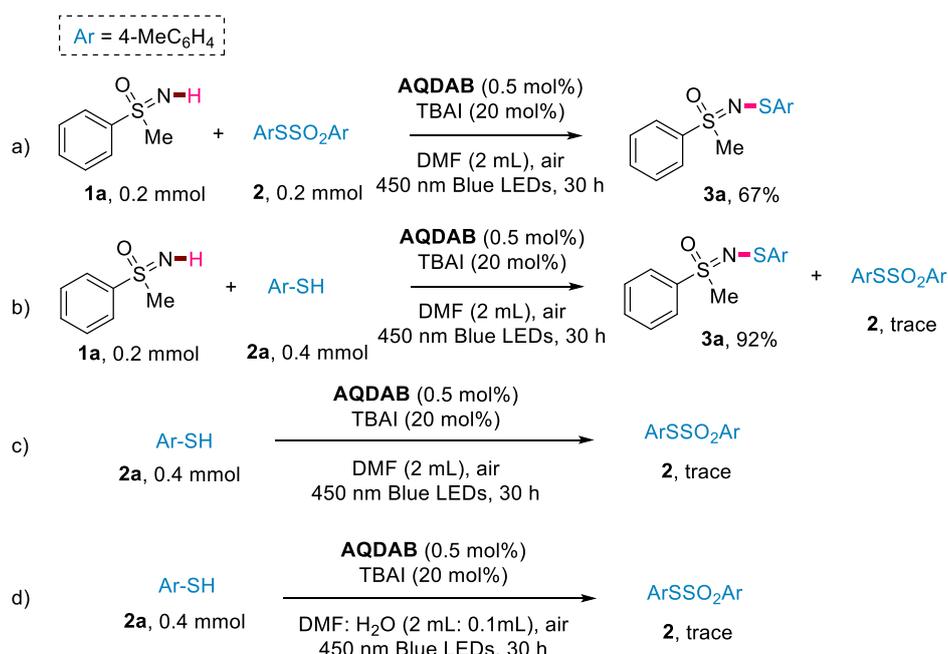
9. Mechanism Study on N-sulfonylation of NH-sulfoximines using thiosulfonate



Entry	Deviation from 'standard' conditions	Yield (%)
1	None	67%
2	Without AQDAB	N.R.
3	Without TBAI	N.R.
4	Without light	N.R.

Scheme S4. Control Experiment for N-sulfonylation of NH-sulfoximines using thiosulfonate.

When thiosulfonate was used instead of thiol, the reaction proceeded smoothly and achieved a yield of 67%. In the absence of photocatalyst, iodine source or blue LEDs, no desired product was obtained (**Scheme S4** entries 2-4), indicating their essential role in N-sulfonylation during this transformation.

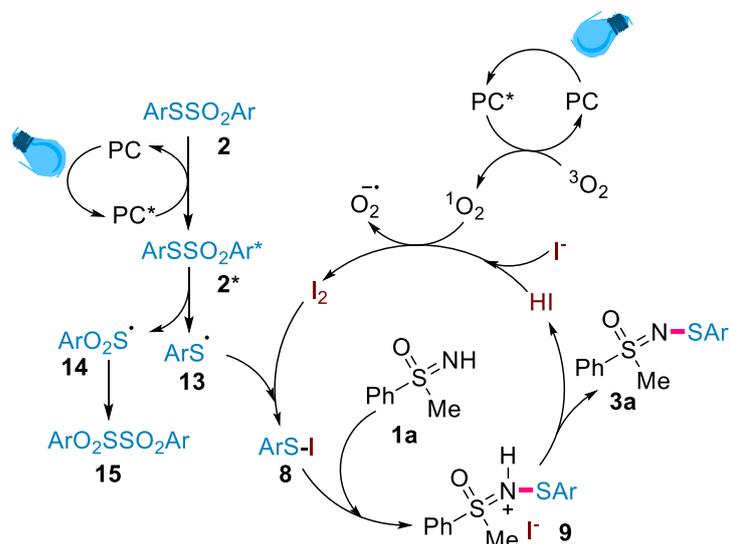


Scheme S5. Mechanistic studies for N-sulfonylation of NH-sulfoximines using thiosulfonate.

In order to further investigate the mechanism of thiosulfonate conversion in this reaction, we conducted control experiments (**Scheme S5**). Firstly, we substituted thiol with thiosulfonate under standard conditions and achieved a 67% yield of the desired product (**Scheme S5a**). However, we did not observe the formation of thiosulfonate in the reaction using thiol and sulfoximines (**Scheme S5b**). Similarly, when the reaction involved only thiol, we were unable to detect the formation of the oxidized product, thiosulfonate (**Scheme S5cd**). Based on these results, we propose a possible mechanism for this transformation.

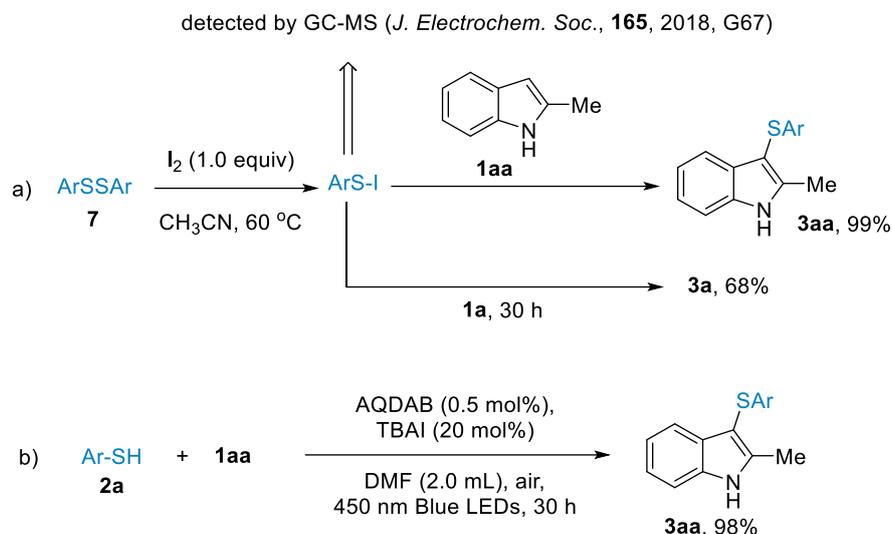
A possible reaction mechanism has been proposed (**Scheme S6**). Initially, the photocatalyst PC was excited by visible light. The excited state PC* was then quenched by triplet oxygen to generate singlet oxygen ¹O₂. Subsequently, singlet oxygen ¹O₂ oxidizes I⁻ to I₂ via a process of single electron transfer

(SET), resulting in the formation of the superoxide radical anion, $O_2^{\cdot-}$. In addition, PC was activated to excited state under the irradiation of blue LEDs and underwent energy transfer to thiosulfonate **2**. This process resulted in an excited **2***. The excited **2*** underwent homolytic cleavage to give thiol radicals **13** and sulfonyl radicals **14**. Thiol radicals **13** reacted with I_2 to generate active electrophilic species ArS-I **8**. Then, **1a** functioned as the nucleophile to attack ArS-I **8**, affording **9**, which underwent deprotonation to generate the desired product **3a**.



Scheme S6. A proposed mechanism for the N-sulfonylation of NH-sulfoximines using thiosulfonate.

10. Trapping experiment of ArS-I

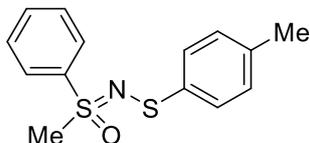


Scheme S7. Trapping experiment of ArS-I

In order to further confirm the existence of ArS-I intermediates, we designed and conducted several trapping experiments. According to the literature^[6-8] by Chen group (*J. Electrochem. Soc.*, **165**, 2018, G67), ArS-I could be generated *in situ* from ArSSAr and I₂, which was detected by GC-MS analysis, when they explored the mechanism of sulfonylation of 2-methylindole **1aa** (Scheme S7a). Using the same method, to the mixture of **7** and I₂ at 60°C, 2-methylindole **1aa** and sulfoximine **1a** were added separately. 2-Methylindole was then sulfonylated to afford **3aa** in 99% yield, in line with the result reported by Chen group. In the meanwhile, **3a** was isolated in 68% yield. This implied these two reactions might involve the same ArS-I intermediate during the reaction process. Furthermore, **3aa** could also be successfully generated in 98% yield under the AQDAB/TBAI-catalyzed system (Scheme S7b). This also provided an indirect evidence for the involvement of ArS-I in the photoinduced transformation.

11. Characterization data of products

(3a) methyl(phenyl)((p-tolylthio)imino)- λ^6 -sulfanone (CAS: 2247600-31-1)^[9]



methyl(phenyl)((p-tolylthio)imino)- λ^6 -sulfanone

Chemical Formula: C₁₄H₁₅NOS₂

Exact Mass: 277.0595

Molecular Weight: 277.4000

2.29 (s, 3H).

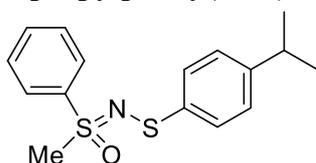
¹³C NMR (101 MHz, CDCl₃) δ 138.8, 138.2, 135.2, 133.6, 129.4, 129.3, 128.4, 125.0, 43.7, 21.0.

Following the General Procedure A with sulfoximine (31.0 mg, 0.2 mmol) and 4-toluenethiol (49.7 mg, 0.4 mmol), **3a** was obtained as a colorless oil (51.1 mg, 92%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.64 (d, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.25 (s, 3H),

(3b) (((4-isopropylphenyl)thio)imino)(methyl)(phenyl)- λ^6 -sulfanone



(((4-isopropylphenyl)thio)imino)(methyl)(phenyl)- λ^6 -sulfanone

Chemical Formula: C₁₆H₁₉NOS₂

Exact Mass: 305.0908

Molecular Weight: 305.4540

¹³C NMR (101 MHz, CDCl₃) δ 146.4, 138.9, 138.6, 133.6, 129.5, 128.5, 126.7, 125.0, 43.8, 33.7, 24.0, 24.0.

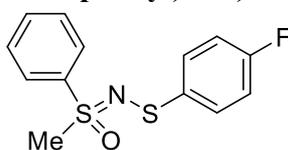
IR (cm⁻¹): 3060, 3018, 2961, 2926, 2870, 1595, 1493, 1447, 1406, 1213, 1092, 982, 822, 743, 687, 525
HRMS (APCI) *m/z* calcd for C₁₆H₂₀NOS₂⁺ (M+H)⁺ 306.0981, found 306.0980.

Following the General Procedure A with sulfoximine (31.0 mg, 0.2 mmol) and 4-isopropylbenzenethiol (60.9 mg, 0.4 mmol), **3b** was obtained as a colorless oil (47.0 mg, 78%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 6.4 Hz, 1H), 7.54 (t, *J* = 6.8 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 2H), 7.12 (d, *J* = 7.6 Hz, 2H), 3.24 (s, 3H), 2.89 – 2.80 (m, 1H), 1.22 (s, 3H), 1.20 (s, 3H).

(3c) (((4-fluorophenyl)thio)imino)(methyl)(phenyl)- λ^6 -sulfanone (CAS: 2247600-33-3)^[10]



(((4-fluorophenyl)thio)imino)(methyl)(phenyl)- λ^6 -sulfanone

Chemical Formula: C₁₃H₁₂FNOS₂

Exact Mass: 281.0344

Molecular Weight: 281.3634

¹³C NMR (101 MHz, CDCl₃) δ 161.3 (d, *J* = 244.4 Hz), 138.6, 136.9 (d, *J* = 3.0 Hz), 133.8, 129.6, 128.4, 127.0 (d, *J* = 7.9 Hz), 115.6 (d, *J* = 22.1 Hz), 43.9.

¹⁹F NMR (376 MHz, CDCl₃) δ -117.31.

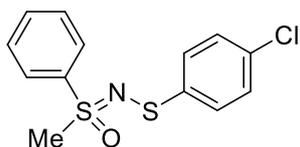
Following the General Procedure A with sulfoximine (31.0 mg, 0.2 mmol) and 4-fluorobenzenethiol (50.5 mg, 0.4 mmol), **3c** was obtained as a colorless oil (50.6 mg, 90%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 2H), 7.43 – 7.34 (m, 2H), 6.96 (t, *J* = 8.8 Hz, 2H), 3.26 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 161.3 (d, *J* = 244.4 Hz),

(3d) (((4-chlorophenyl)thio)imino)(methyl)(phenyl)- λ^6 -sulfanone (CAS: 2247600-32-2)^[10]



((4-chlorophenylthio)imino)(methyl)(phenyl)- λ^6 -sulfanone

Chemical Formula: $C_{13}H_{12}ClNOS_2$

Exact Mass: 297.0049

Molecular Weight: 297.8150

129.6, 128.5, 128.4, 125.1, 43.8.

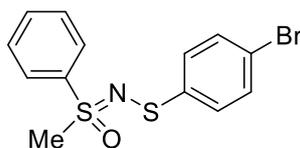
Following the General Procedure A with sulfoximine (31.0 mg, 0.2 mmol) and 4-chlorobenzenethiol (57.8 mg, 0.4 mmol), **3d** was obtained as a colorless oil (53.4 mg, 90%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.6 Hz, 2H), 7.66 (t, J = 7.2 Hz, 1H), 7.57 (t, J = 7.6 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 3.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 138.5, 133.9, 130.6,

(3e) (((4-bromophenyl)thio)imino)(methyl)(phenyl)- λ^6 -sulfanone (CAS: 2762998-29-6)^[9]



((4-bromophenylthio)imino)(methyl)(phenyl)- λ^6 -sulfanone

Chemical Formula: $C_{13}H_{12}BrNOS_2$

Exact Mass: 340.9544

Molecular Weight: 342.2690

129.6, 128.4, 125.3, 118.4, 43.9.

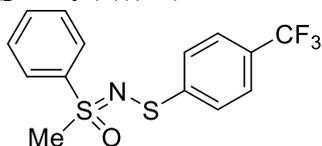
Following the General Procedure A with sulfoximine (31.0 mg, 0.2 mmol) and 4-bromobenzenethiol (74.8 mg, 0.4 mmol), **3e** was obtained as a colorless oil (65.6 mg, 96%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.2 Hz, 2H), 7.66 (t, J = 7.6 Hz, 1H), 7.57 (t, J = 8.0 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 3.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 138.5, 133.9, 131.4,

(3f) methyl(phenyl)((4-(trifluoromethyl)phenyl)thio)imino)- λ^6 -sulfanone (CAS: 2762998-27-4)^[9]



methyl(phenyl)((4-(trifluoromethyl)phenyl)thio)imino)- λ^6 -sulfanone

Chemical Formula: $C_{14}H_{12}F_3NOS_2$

Exact Mass: 331.0312

Molecular Weight: 331.3712

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 138.3, 134.0, 129.7, 128.4, 126.6 (q, J = 32.4 Hz), 125.3 (q, J = 3.8 Hz), 124.4 (q, J = 271.3 Hz), 122.5, 44.0.

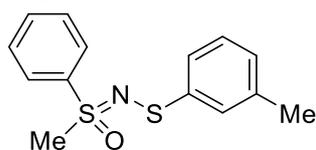
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.10.

Following the General Procedure A with sulfoximine (31.0 mg, 0.2 mmol) and 4-(trifluoromethyl)benzenethiol (71.3 mg, 0.4 mmol), **3f** was obtained as a colorless oil (55.6 mg, 84%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.0 Hz, 2H), 7.68 (t, J = 7.6 Hz, 1H), 7.60 (t, J = 7.6 Hz, 2H), 7.47 (q, J = 8.8 Hz, 4H), 3.31 (s, 3H).

(3g) methyl(phenyl)((*m*-tolylthio)imino)- λ^6 -sulfanone (CAS: 2247600-37-7)^[10]



methyl(phenyl)((*m*-tolylthio)imino)- λ^6 -sulfanone

Chemical Formula: $C_{14}H_{15}NOS_2$

Exact Mass: 277.0595

Molecular Weight: 277.4000

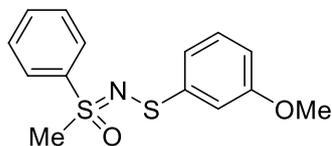
Following the General Procedure A with sulfoximine (31.0 mg, 0.2 mmol) and 3-methylbenzenethiol (49.7 mg, 0.4 mmol), **3g** was obtained as a colorless oil (46.7 mg, 84%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 7.6$ Hz, 2H), 7.64 (t, $J = 7.6$ Hz, 1H), 7.56 (t, $J = 7.6$ Hz, 2H), 7.23 – 7.11 (m, 3H), 6.89 (d, $J = 7.2$ Hz, 1H), 3.26 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 141.9, 138.8, 138.2, 133.7, 129.5, 128.4, 128.4, 126.1, 124.4, 121.1, 43.8, 21.5.

(3h) (((3-methoxyphenyl)thio)imino)(methyl)(phenyl)- λ^6 -sulfanone



(((3-methoxyphenyl)thio)imino)(methyl)(phenyl)- λ^6 -sulfanone

Chemical Formula: $\text{C}_{14}\text{H}_{15}\text{NO}_2\text{S}_2$

Exact Mass: 293.0544

Molecular Weight: 293.3990

Following the General Procedure A with sulfoximine (31.0 mg, 0.2 mmol) and 3-methoxybenzenethiol (56.1 mg, 0.4 mmol), **3h** was obtained as a colorless oil (43.4 mg, 74%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, $J = 8.0$ Hz, 2H), 7.68 – 7.62 (m, 1H), 7.61 – 7.53 (m, 2H), 7.22 – 7.13 (m, 1H), 7.00 (s, 1H), 6.94 (d, $J = 8.0$ Hz, 1H), 6.63 (d,

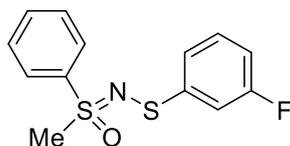
$J = 8.0$ Hz, 1H), 3.78 (s, 3H), 3.27 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 159.9, 143.8, 138.7, 133.8, 129.5, 129.4, 128.4, 115.9, 111.1, 108.9, 55.2, 43.7.

IR (cm^{-1}): 3298, 3063, 3005, 2928, 2835, 1576, 1474, 1281, 1217, 1092, 984, 858, 744, 685, 525.

HRMS (APCI) m/z calcd for $\text{C}_{14}\text{H}_{16}\text{NO}_2\text{S}_2^+$ ($\text{M}+\text{H}$) $^+$ 294.0617, found 294.0611.

(3i) (((3-fluorophenyl)thio)imino)(methyl)(phenyl)- λ^6 -sulfanone



(((3-fluorophenyl)thio)imino)(methyl)(phenyl)- λ^6 -sulfanone

Chemical Formula: $\text{C}_{13}\text{H}_{12}\text{FNOS}_2$

Exact Mass: 281.0344

Molecular Weight: 281.3634

Following the General Procedure A with sulfoximine (31.0 mg, 0.2 mmol) and 3-fluorobenzenethiol (51.3 mg, 0.4 mmol), **3i** was obtained as a colorless oil (47.3 mg, 84%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, $J = 8.4$ Hz, 2H), 7.67 (t, $J = 6.4$ Hz, 1H), 7.59 (t, $J = 7.2$ Hz, 2H), 7.21 – 7.12 (m, 2H), 7.08 (d, $J = 8.0$ Hz, 1H), 6.76 – 6.67 (m, 1H), 3.30 (s, 3H).

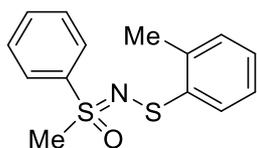
^{13}C NMR (101 MHz, CDCl_3) δ 163.1 (d, $J = 247.1$ Hz), 145.3 (d, $J = 7.5$ Hz), 138.5, 133.9, 129.7 (d, $J = 8.5$ Hz), 129.6, 128.4, 118.6 (d, $J = 2.8$ Hz), 111.7 (d, $J = 21.6$ Hz), 110.3 (d, $J = 24.6$ Hz), 43.9.

^{19}F NMR (376 MHz, CDCl_3) δ -112.66.

IR (cm^{-1}): 3065, 3017, 2926, 1597, 1470, 1207, 1092, 983, 879, 777, 743, 679, 525.

HRMS (APCI) m/z calcd for $\text{C}_{13}\text{H}_{13}\text{FNOS}_2^+$ ($\text{M}+\text{H}$) $^+$ 282.0417, found 282.0413.

(3j) methyl(phenyl)((o-tolylthio)imino)- λ^6 -sulfanone (CAS: 2247600-34-4)^[10]



methyl(phenyl)((o-tolylthio)imino)- λ^6 -sulfanone

Chemical Formula: $\text{C}_{14}\text{H}_{15}\text{NOS}_2$

Exact Mass: 277.0595

Molecular Weight: 277.4000

Following the General Procedure A with sulfoximine (31.0 mg, 0.2 mmol) and 2-methylbenzenethiol (49.7 mg, 0.4 mmol), **3j** was obtained as a colorless oil (37.2 mg, 67%).

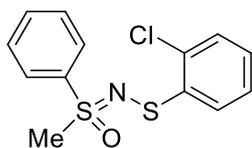
This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 7.6$ Hz, 2H), 7.64 (t, $J = 8.0$ Hz, 2H), 7.56 (t, $J = 8.0$ Hz, 2H), 7.23 –

7.16 (m, 1H), 7.04 – 6.91 (m, 2H), 3.27 (s, 3H), 2.15 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 140.8, 138.9, 133.7, 132.2, 129.5, 129.5, 128.4, 126.3, 124.5, 123.3, 43.8, 18.8.

(3k) (((2-chlorophenyl)thio)imino)(methyl)(phenyl)- λ^6 -sulfanone (CAS: 2762998-28-5)^[9]



(((2-chlorophenyl)thio)imino)(methyl)(phenyl)- λ^6 -sulfanone

Chemical Formula: $\text{C}_{13}\text{H}_{12}\text{ClNOS}_2$

Exact Mass: 297.0049

Molecular Weight: 297.8150

Following the General Procedure A with sulfoximine (31.0 mg, 0.2 mmol) and 2-chlorobenzenethiol (57.8 mg, 0.4 mmol), **3k** was obtained as a colorless oil (44.4 mg, 75%).

This target product was purified by column

chromatography on silica gel (PE/EA = 3:1).

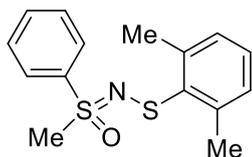
^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, J = 8.6 Hz, 2H),

7.68 (dd, J = 16.3, 7.7 Hz, 2H), 7.59 (t, J = 7.6 Hz, 2H),

7.26 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 7.9 Hz, 1H), 7.00 (t, J = 7.6 Hz, 1H), 3.31 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 141.4, 138.6, 133.9, 129.7, 128.7, 128.4, 127.0, 126.9, 125.2, 124.1, 44.0.

(3l) (((2,6-dimethylphenyl)thio)imino)(methyl)(phenyl)- λ^6 -sulfanone



(((2,6-dimethylphenyl)thio)imino)(methyl)(phenyl)- λ^6 -sulfanone

Chemical Formula: $\text{C}_{15}\text{H}_{17}\text{NOS}_2$

Exact Mass: 291.0752

Molecular Weight: 291.4270

Following the General Procedure A with sulfoximine (31.0 mg, 0.2 mmol) and 2,6-dimethylbenzenethiol (55.3 mg, 0.4 mmol), **3l** was obtained as a colorless oil (37.3 mg, 64%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, J = 7.6 Hz, 2H),

7.54 (t, J = 7.6 Hz, 1H), 7.39 (t, J = 8.0 Hz, 2H), 7.06 –

7.00 (m, 1H), 6.94 (d, J = 7.6 Hz, 2H), 3.09 (s, 3H),

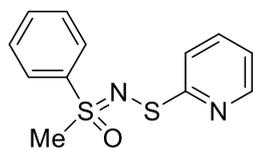
2.43 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 141.8, 139.1, 137.6, 133.2, 129.1, 128.7, 128.6, 127.8, 44.2, 21.6.

IR (cm^{-1}): 3057, 3011, 2928, 1580, 1447, 1202, 1090, 989, 771, 746, 689, 523.

HRMS (APCI) m/z calcd for $\text{C}_{15}\text{H}_{18}\text{NOS}_2^+$ ($\text{M}+\text{H}$) $^+$ 292.0824, found 292.0816.

(3m) methyl(phenyl)((pyridin-2-ylthio)imino)- λ^6 -sulfanone (CAS: 2762998-30-9)^[9]



methyl(phenyl)((pyridin-2-ylthio)imino)- λ^6 -sulfanone

Chemical Formula: $\text{C}_{12}\text{H}_{12}\text{N}_2\text{OS}_2$

Exact Mass: 264.0391

Molecular Weight: 264.3610

Following the General Procedure A with sulfoximine (31.0 mg, 0.2 mmol) and 2-pyridinethione (44.5 mg, 0.4 mmol), **3m** was obtained as a colorless oil (33.8 mg, 64%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

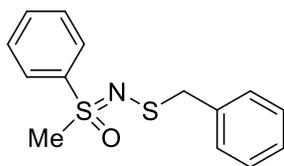
^1H NMR (400 MHz, CDCl_3) δ 8.39 – 8.31 (m, 1H),

8.04 – 7.94 (m, 2H), 7.70 – 7.56 (m, 5H), 6.98 – 6.89

(m, 1H), 3.35 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 165.8, 148.6, 138.4, 136.6, 133.9, 129.6, 128.5, 119.1, 117.9, 43.8.

(3n) ((benzylthio)imino)(methyl)(phenyl)- λ^6 -sulfanone (CAS: 2762998-33-2)^[9]



((benzylthio)imino)(methyl)(phenyl)- λ^6 -sulfanone

Chemical Formula: C₁₄H₁₅NOS₂

Exact Mass: 277.0595

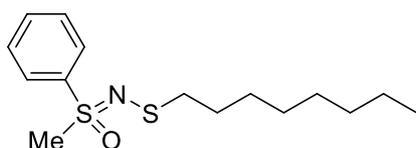
Molecular Weight: 277.4000

Following the General Procedure A with sulfoximine (31.0 mg, 0.2 mmol) and benzyl mercaptan (49.7 mg, 0.4 mmol), **3n** was obtained as a colorless oil (22.7 mg, 41%). This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.85 (m, 2H), 7.67 – 7.61 (m, 1H), 7.59 – 7.53 (m, 2H), 7.37 – 7.32 (m, 2H), 7.31 – 7.25 (m, 2H), 7.24 – 7.19 (m, 1H), 4.16 – 4.02 (m, 2H), 3.09 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 139.2, 136.8, 133.5, 129.5, 129.4, 128.5, 128.4, 127.1, 45.9, 43.4.

(3o) methyl((octylthio)imino)(phenyl)- λ^6 -sulfanone



methyl((octylthio)imino)(phenyl)- λ^6 -sulfanone

Chemical Formula: C₁₅H₂₅NOS₂

Exact Mass: 299.1378

Molecular Weight: 299.4910

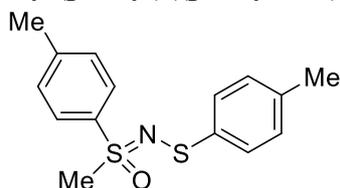
Following the General Procedure A with sulfoximine (31.0 mg, 0.2 mmol) and 1-mercaptooctane (58.5 mg, 0.4 mmol), **3o** was obtained as a colorless oil (18.5 mg, 31%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

¹H NMR (400 MHz, CDCl₃) δ 7.99 – 7.85 (m, 2H), 7.68 – 7.62 (m, 1H), 7.62 – 7.54 (m, 2H), 3.19 (s, 3H), 2.91 – 2.72 (m, 2H), 1.68 (t, *J* = 7.6 Hz, 2H), 1.41 – 1.34 (m, 2H), 1.31 – 1.23 (m, 8H), 0.89 – 0.85 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 139.3, 133.4, 129.4, 128.5, 43.9, 41.1, 31.8, 29.2, 29.2, 28.8, 27.8, 22.7, 14.1.

(3p) methyl(*p*-tolyl)((*p*-tolylthio)imino)- λ^6 -sulfanone



methyl(*p*-tolyl)((*p*-tolylthio)imino)- λ^6 -sulfanone

Chemical Formula: C₁₅H₁₇NOS₂

Exact Mass: 291.0752

Molecular Weight: 291.4270

Following the General Procedure A with imino(methyl)(*p*-tolyl)- λ^6 -sulfanone (33.8 mg, 0.2 mmol) and 4-toluenethiol (49.7 mg, 0.4 mmol), **3p** was obtained as a colorless oil (50.7 mg, 87%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

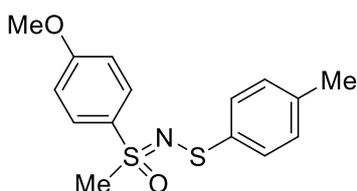
¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 3.22 (s, 3H), 2.44 (s, 3H), 2.29 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 144.7, 138.5, 135.7, 135.1, 130.2, 129.3, 128.5, 124.8, 43.9, 21.6, 21.0.

IR (cm⁻¹): 3306, 3020, 2922, 1917, 1597, 1489, 1448, 1398, 1315, 1204, 1090, 980, 806, 752, 528.

HRMS (APCI) *m/z* calcd for C₁₅H₁₇NOS₂Na⁺ (M+Na)⁺ 314.0644, found 314.0635.

(3q) (4-methoxyphenyl)(methyl)((*p*-tolylthio)imino)- λ^6 -sulfanone



(4-methoxyphenyl)(methyl)((*p*-tolylthio)imino)- λ^6 -sulfanone

Chemical Formula: C₁₅H₁₇NO₂S₂

Exact Mass: 307.0701

Molecular Weight: 307.4260

129.7, 129.2, 124.7, 114.6, 55.7, 44.0, 20.9.

IR (cm⁻¹): 3308, 3013, 2924, 2575, 1900, 1593, 1491, 1406, 1310, 1258, 1094, 831, 764, 704, 522.

HRMS (APCI) *m/z* calcd for C₁₅H₁₇NO₂S₂Na⁺ (M+Na)⁺ 330.0593, found 330.0582.

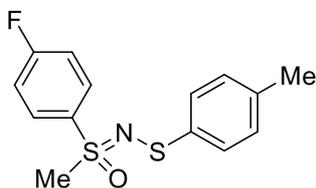
Following the General Procedure A with imino(4-methoxyphenyl)(methyl)- λ^6 -sulfanone (37.0 mg, 0.2 mmol) and 4-toluenethiol (49.7 mg, 0.4 mmol), **3q** was obtained as a colorless oil (48.3 mg, 79%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 6.8 Hz, 2H), 7.31 (d, *J* = 6.4 Hz, 2H), 7.07 (d, *J* = 7.2 Hz, 2H), 7.05 – 6.96 (m, 2H), 3.87 (s, 3H), 3.23 (s, 3H), 2.29 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 163.7, 138.5, 135.0, 130.5,

(3r) (4-fluorophenyl)(methyl)((*p*-tolylthio)imino)- λ^6 -sulfanone



(4-fluorophenyl)(methyl)((*p*-tolylthio)imino)- λ^6 -sulfanone

Chemical Formula: C₁₄H₁₄FNOS₂

Exact Mass: 295.0501

Molecular Weight: 295.3904

138.0, 135.5, 134.6 (d, *J* = 3.1 Hz), 131.3 (d, *J* = 9.6 Hz), 129.4, 125.2, 116.8 (d, *J* = 22.7 Hz), 43.9, 21.0.

¹⁹F NMR (376 MHz, CDCl₃) δ -103.77.

IR (cm⁻¹): 3099, 3057, 3018, 2928, 1587, 1489, 1402, 1207, 1094, 991, 962, 847, 800, 714, 532, 482.

HRMS (APCI) *m/z* calcd for C₁₄H₁₅FNOS₂⁺ (M+H)⁺ 296.0574, found 296.0568.

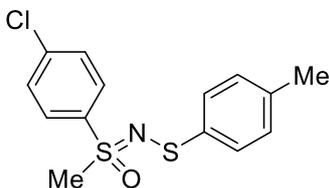
Following the General Procedure A with (4-fluorophenyl)(imino)(methyl)- λ^6 -sulfanone (34.6 mg, 0.2 mmol) and 4-toluenethiol (49.7 mg, 0.4 mmol), **3r** was obtained as a colorless oil (53.9 mg, 91%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

¹H NMR (400 MHz, CDCl₃) δ 7.97 – 7.89 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 8.8 Hz, 2H), 7.08 (d, *J* = 7.6 Hz, 2H), 3.25 (s, 3H), 2.29 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 165.8 (d, *J* = 256.4 Hz),

(3s) (4-chlorophenyl)(methyl)((*p*-tolylthio)imino)- λ^6 -sulfanone



(4-chlorophenyl)(methyl)((*p*-tolylthio)imino)- λ^6 -sulfanone

Chemical Formula: C₁₄H₁₄ClNOS₂

Exact Mass: 311.0205

Molecular Weight: 311.8420

130.0, 129.8, 129.4, 125.3, 43.8, 21.0.

IR (cm⁻¹): 3076, 3017, 2920, 1572, 1489, 1396, 1215, 1086, 945, 802, 775, 525.

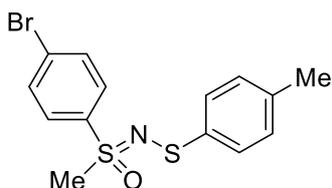
HRMS (APCI) *m/z* calcd for C₁₄H₁₅ClNOS₂⁺ (M+H)⁺ 312.0278, found 312.0283.

Following the General Procedure A with (4-chlorophenyl)(imino)(methyl)- λ^6 -sulfanone (37.9 mg, 0.2 mmol) and 4-toluenethiol (49.7 mg, 0.4 mmol), **3s** was obtained as a colorless oil (53.7 mg, 86%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.24 (s, 3H), 2.29 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 140.5, 137.9, 137.3, 135.6,

(3t) (4-bromophenyl)(methyl)((p-tolylthio)imino)- λ^6 -sulfanone

(4-bromophenyl)(methyl)((p-tolylthio)imino)- λ^6 -sulfanone

Chemical Formula: C₁₄H₁₄BrNOS₂

Exact Mass: 354.9700

Molecular Weight: 356.2960

129.4, 129.0, 125.3, 43.8, 21.1.

IR (cm⁻¹): 3298, 3082, 3015, 2922, 2864, 1570, 1489, 1387, 1209, 1090, 982, 804, 766, 519.

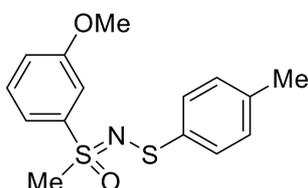
HRMS (APCI) m/z calcd for C₁₄H₁₅BrNOS₂⁺ (M+H)⁺ 355.9773, found 355.9766.

Following the General Procedure A with (4-bromophenyl)(imino)(methyl)- λ^6 -sulfanone (46.8 mg, 0.2 mmol) and 4-toluenethiol (49.7 mg, 0.4 mmol), **3t** was obtained as a colorless oil (64.2 mg, 90%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.24 (s, 3H), 2.29 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 137.9, 135.6, 132.8, 130.1,

(3u) (3-methoxyphenyl)(methyl)((p-tolylthio)imino)- λ^6 -sulfanone

(3-methoxyphenyl)(methyl)((p-tolylthio)imino)- λ^6 -sulfanone

Chemical Formula: C₁₅H₁₇NO₂S₂

Exact Mass: 307.0701

Molecular Weight: 307.4260

¹³C NMR (101 MHz, CDCl₃) δ 160.1, 139.9, 138.2, 135.2, 130.4, 129.2, 125.0, 120.5, 120.2, 112.7, 55.6, 43.8, 20.9.

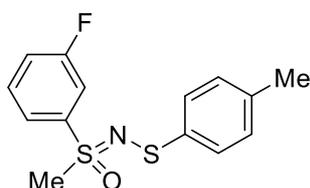
IR (cm⁻¹): 3437, 3308, 3013, 2922, 1894, 1597, 1483, 1321, 1086, 852, 710, 530.

HRMS (APCI) m/z calcd for C₁₅H₁₇NO₂S₂Na⁺ (M+Na)⁺ 330.0593, found 330.0582.

Following the General Procedure A with imino(3-methoxyphenyl)(methyl)- λ^6 -sulfanone (37.0 mg, 0.2 mmol) and 4-toluenethiol (49.7 mg, 0.4 mmol), **3u** was obtained as a colorless oil (51.1 mg, 83%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

¹H NMR (400 MHz, CDCl₃) δ 7.52 – 7.44 (m, 2H), 7.40 (s, 1H), 7.31 (d, *J* = 6.8 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 2H), 3.82 (s, 3H), 3.24 (s, 3H), 2.29 (s, 3H).

(3v) (3-fluorophenyl)(methyl)((p-tolylthio)imino)- λ^6 -sulfanone

(3-fluorophenyl)(methyl)((p-tolylthio)imino)- λ^6 -sulfanone

Chemical Formula: C₁₄H₁₄FNOS₂

Exact Mass: 295.0501

Molecular Weight: 295.3904

¹³C NMR (101 MHz, CDCl₃) δ 162.7 (d, *J* = 252.8 Hz), 141.1 (d, *J* = 6.5 Hz), 137.8, 135.7, 131.2 (d, *J* = 7.6 Hz), 129.4, 125.4, 124.2 (d, *J* = 3.4 Hz), 116.0 (d, *J* = 24.5 Hz), 43.8, 21.0.

¹⁹F NMR (376 MHz, CDCl₃) δ -108.83.

IR (cm⁻¹): 3298, 3072, 3018, 2924, 1593, 1477, 1431, 1223, 1082, 991, 878, 804, 766, 677, 527.

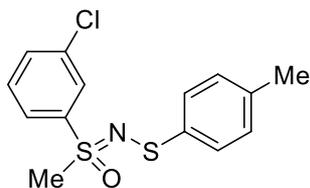
Following the General Procedure A with (3-fluorophenyl)(imino)(methyl)- λ^6 -sulfanone (34.6 mg, 0.2 mmol) and 4-toluenethiol (49.7 mg, 0.4 mmol), **3v** was obtained as a colorless oil (49.7 mg, 84%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.58 – 7.50 (m, 1H), 7.37 – 7.33 (m, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 3.26 (s, 3H), 2.30 (s, 3H).

HRMS (APCI) m/z calcd for $C^{14}H^{15}FNOS_2^+$ ($M+H$) $^+$ 296.0574, found 296.0566.

(3w) (3-chlorophenyl)(methyl)((p-tolylthio)imino)- λ^6 -sulfanone



(3-chlorophenyl)(methyl)((p-tolylthio)imino)- λ^6 -sulfanone

Chemical Formula: $C_{14}H_{14}ClNOS_2$

Exact Mass: 311.0205

Molecular Weight: 311.8420

Following the General Procedure A with (3-chlorophenyl)(imino)(methyl)- λ^6 -sulfanone (37.9 mg, 0.2 mmol) and 4-toluenethiol (49.7 mg, 0.4 mmol), **3w** was obtained as a colorless oil (51.1 mg, 82%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

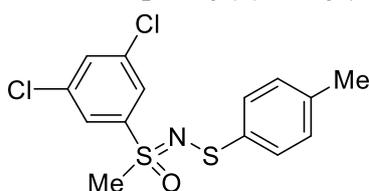
1H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.60 (d, J = 6.8 Hz, 1H), 7.49 (t, J = 8.0 Hz, 1H), 7.29 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 3.25 (s, 3H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 137.7, 135.7, 135.7, 133.8, 130.7, 129.4, 128.6, 126.6, 125.6, 43.8, 21.1.

IR (cm^{-1}): 3298, 3065, 3017, 2922, 2864, 1701, 1576, 1489, 1466, 1406, 1317, 1217, 1119, 986, 783, 675, 517.

HRMS (APCI) m/z calcd for $C_{14}H_{15}ClNOS_2^+$ ($M+H$) $^+$ 312.0278, found 312.0270.

(3x) (3,5-dichlorophenyl)(methyl)((p-tolylthio)imino)- λ^6 -sulfanone



(3,5-dichlorophenyl)(methyl)((p-tolylthio)imino)- λ^6 -sulfanone

Chemical Formula: $C_{14}H_{13}Cl_2NOS_2$

Exact Mass: 344.9816

Molecular Weight: 346.2840

Following the General Procedure A with (3,5-dichlorophenyl)(imino)(methyl)- λ^6 -sulfanone (44.8 mg, 0.2 mmol) and 4-toluenethiol (49.7 mg, 0.4 mmol), **3x** was obtained as a colorless oil (53.4 mg, 77%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

1H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 2H), 7.58 (s, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 3.25 (s, 3H), 2.30 (s, 3H).

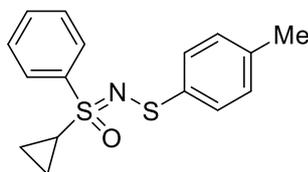
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 137.1, 136.4,

136.2, 133.6, 129.4, 127.0, 126.2, 43.8, 21.1.

IR (cm^{-1}): 3300, 3074, 3018, 2922, 1568, 1491, 1416, 1217, 1142, 1096, 1003, 868, 802, 702, 665, 513.

HRMS (APCI) m/z calcd for $C_{14}H_{14}Cl_2NOS_2^+$ ($M+H$) $^+$ 345.9888, found 345.9889.

(3y) cyclopropyl(phenyl)((p-tolylthio)imino)- λ^6 -sulfanone



cyclopropyl(phenyl)((p-tolylthio)imino)- λ^6 -sulfanone

Chemical Formula: $C_{16}H_{17}NOS_2$

Exact Mass: 303.0752

Molecular Weight: 303.4380

Following the General Procedure A with cyclopropyl(imino)(phenyl)- λ^6 -sulfanone (36.3 mg, 0.2 mmol) and 4-toluenethiol (49.7 mg, 0.4 mmol), **3y** was obtained as a colorless oil (47.8 mg, 79%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

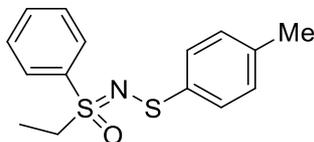
1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 1H), 7.54 (t, J = 7.2 Hz, 2H), 7.28 (d, J = 6.8 Hz, 2H), 7.06 (d, J = 7.6 Hz, 2H), 2.71 – 2.59 (m, 1H), 2.28 (s, 3H), 1.70 – 1.60 (m, 1H), 1.23 – 1.09 (m, 2H), 0.97 – 0.85 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 139.2, 138.8, 135.0, 1333, 129.3, 129.2, 128.5, 124.8, 33.0, 21.0, 7.0, 5.6.

IR (cm^{-1}): 3057, 30315, 2920, 1489, 1445, 1215, 1186, 1094, 982, 885, 806, 735, 689, 533.

HRMS (APCI) m/z calcd for $\text{C}_{16}\text{H}_{18}\text{NOS}_2^+$ ($\text{M}+\text{H}$) $^+$ 304.0824, found 304.0819.

(3z) ethyl(phenyl)((p-tolylthio)imino)- λ^6 -sulfanone



ethyl(phenyl)((p-tolylthio)imino)- λ^6 -sulfanone

Chemical Formula: $\text{C}_{15}\text{H}_{17}\text{NOS}_2$

Exact Mass: 291.0752

Molecular Weight: 291.4270

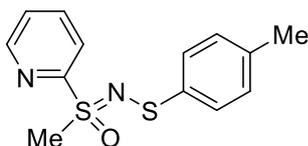
This target product was purified by column chromatography on silica gel (PE/EA = 3:1). ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, $J = 7.2$ Hz, 2H), 7.64 (t, $J = 7.6$ Hz, 1H), 7.55 (t, $J = 8.0$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.07 (d, $J = 8.0$ Hz, 2H), 3.52 – 3.40 (m, 1H), 3.39 – 3.27 (m, 1H), 2.28 (s, 3H), 1.27 (t, $J = 7.6$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 138.7, 136.8, 135.1, 133.6, 129.4, 129.3, 128.6, 124.9, 50.2, 21.0, 7.8.

IR (cm^{-1}): 3059, 2976, 2937, 2872, 1491, 1447, 1204, 1094, 970, 804, 731, 689, 544.

HRMS (APCI) m/z calcd for $\text{C}_{15}\text{H}_{17}\text{NOS}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 314.0644, found 314.0635.

(3za) methyl(pyridin-2-yl)((p-tolylthio)imino)- λ^6 -sulfanone



methyl(pyridin-2-yl)((p-tolylthio)imino)- λ^6 -sulfanone

Chemical Formula: $\text{C}_{13}\text{H}_{14}\text{N}_2\text{OS}_2$

Exact Mass: 278.0548

Molecular Weight: 278.3880

Following the General Procedure A with imino(methyl)(pyridin-2-yl)- λ^6 -sulfanone (31.2 mg, 0.2 mmol) and 4-toluenethiol (49.7 mg, 0.4 mmol), **3za** was obtained as a colorless oil (34.3 mg, 62%).

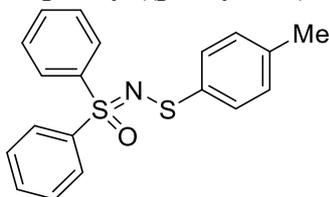
This target product was purified by column chromatography on silica gel (PE/EA = 3:1). ^1H NMR (400 MHz, CDCl_3) δ 8.67 (d, $J = 4.4$ Hz, 1H), 8.15 (d, $J = 7.6$ Hz, 1H), 7.90 (t, $J = 7.6$ Hz, 1H), 7.51 – 7.43 (m, 1H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.02 (d, $J = 8.0$ Hz, 2H), 3.45 (s, 3H), 2.26 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 156.9, 150.1, 138.0, 137.8, 135.0, 129.2, 127.1, 124.5, 123.7, 39.5, 21.0.

IR (cm^{-1}): 3294, 3015, 2924, 2866, 1578, 1489, 1425, 1312, 1213, 1084, 989, 804, 758, 689, 615, 523.

HRMS (APCI) m/z calcd for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{OS}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 301.0440, found 301.0430.

(3zb) diphenyl((p-tolylthio)imino)- λ^6 -sulfanone (CAS: 91378-34-6)^[11]



diphenyl((p-tolylthio)imino)- λ^6 -sulfanone

Chemical Formula: $\text{C}_{19}\text{H}_{17}\text{NOS}_2$

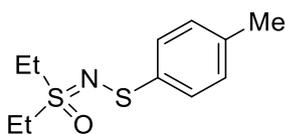
Exact Mass: 339.0752

Molecular Weight: 339.4710

Following the General Procedure A with iminodiphenyl- λ^6 -sulfanone (43.5 mg, 0.2 mmol) and 4-toluenethiol (49.7 mg, 0.4 mmol), **3zb** was obtained as a colorless oil (52.7 mg, 78%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1). ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 7.6$ Hz, 4H), 7.53 (d, $J = 7.2$ Hz, 2H), 7.48 (t, $J = 7.6$ Hz, 4H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.06 (d, $J = 8.0$ Hz, 2H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 140.1, 138.3, 135.2, 133.2,

(3zc) diethyl((p-tolylthio)imino)-λ⁶-sulfanonediethyl((p-tolylthio)imino)-λ⁶-sulfanoneChemical Formula: C₁₁H₁₇NOS₂

Exact Mass: 243.0752

Molecular Weight: 243.3830

Following the General Procedure A with diethyl(imino)-λ⁶-sulfanone (24.2 mg, 0.2 mmol) and 4-toluenethiol (49.7 mg, 0.4 mmol), **3zc** was obtained as a colorless oil (36.5 mg, 75%).

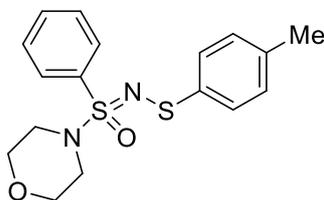
This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.24 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 3.36 – 3.09 (m, 4H), 2.29 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 141.0, 138.5, 133.9, 130.6, 129.6, 128.5, 128.4, 125.1, 43.8.

IR (cm⁻¹): 3275, 2974, 2937, 1491, 1454, 1408, 1248, 1198, 1013, 806, 714, 490.

HRMS (APCI) *m/z* calcd for C₁₁H₁₇NOS₂Na⁺ (M+Na)⁺ 266.0644, found 266.0637.

(3zd) N-(morpholino(oxo)(phenyl)-λ⁶-sulfaneylidene)-S-(p-tolyl)thiohydroxylamineN-(morpholino(oxo)(phenyl)-λ⁶-sulfaneylidene)-

S-(p-tolyl)thiohydroxylamine

Chemical Formula: C₁₇H₂₀N₂O₂S₂

Exact Mass: 348.0966

Molecular Weight: 348.4790

Following the General Procedure A with 4-(phenylsulfonimidoyl)morpholine (45.2 mg, 0.2 mmol) and 4-toluenethiol (49.7 mg, 0.4 mmol), **3zd** was obtained as a colorless oil (55.4 mg, 80%).

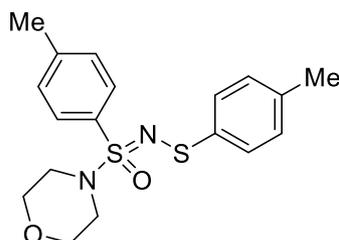
This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 7.2 Hz, 2H), 7.65 – 7.58 (m, 1H), 7.57 – 7.50 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.15 – 7.02 (m, 3H), 3.73 – 3.63 (m, 4H), 3.06 – 2.94 (m, 4H), 2.29 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 137.7, 135.4, 134.7, 133.1, 129.4, 129.1, 128.1, 125.4, 66.1, 46.7, 21.1.

IR (cm⁻¹): 2963, 2916, 2854, 1489, 1445, 1242, 1111, 993, 926, 806, 739, 690, 577, 523.

HRMS (APCI) *m/z* calcd for C₁₇H₂₁N₂O₂S₂⁺ (M+H)⁺ 349.1039, found 349.1031.

(3ze) N-(morpholino(oxo)(p-tolyl)-λ⁶-sulfaneylidene)-S-(p-tolyl)thiohydroxylamineN-(morpholino(oxo)(p-tolyl)-λ⁶-sulfaneylidene)-

S-(p-tolyl)thiohydroxylamine

Chemical Formula: C₁₈H₂₂N₂O₂S₂

Exact Mass: 362.1123

Molecular Weight: 362.5060

Following the General Procedure A with 4-(4-methylphenylsulfonimidoyl)morpholine (48.1 mg, 0.2 mmol) and 4-toluenethiol (49.7 mg, 0.4 mmol), **3ze** was obtained as a colorless oil (59.4 mg, 82%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

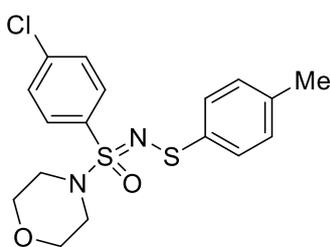
¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 8.8 Hz, 4H), 7.13 – 7.03 (m, 2H), 3.74 – 3.63 (m, 4H), 3.07 – 2.91 (m, 4H), 2.44 (s, 3H), 2.29 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 144.0, 137.8, 135.3, 131.5, 129.7, 129.3, 128.2, 125.3, 66.1, 46.7, 21.6, 21.0.

IR (cm⁻¹): 2966, 2918, 2856, 1491, 1452, 1240, 1113, 989, 935, 810, 737, 521.

HRMS (APCI) *m/z* calcd for C₁₈H₂₂N₂O₂S₂⁺ (M+H)⁺ 363.1195, found 363.1187.

(3zf) N-((4-chlorophenyl)(morpholino)(oxo)-λ⁶-sulfaneylidene)-S-(p-tolyl)thiohydroxylamine



N-((4-chlorophenyl)(morpholino)(oxo)- λ^6 -sulfaneylidene)-*S*-(*p*-tolyl)thiohydroxylamine

Chemical Formula: $C_{17}H_{19}ClN_2O_2S_2$

Exact Mass: 382.0576

Molecular Weight: 382.9210

129.5, 129.4, 129.4, 125.4, 66.1, 46.7, 21.1.

IR (cm^{-1}): 2968, 2918, 2858, 1568, 1493, 1452, 1393, 1244, 1113, 1084, 989, 937, 810, 768, 717, 530.

HRMS (APCI) m/z calcd for $C_{17}H_{20}ClN_2O_2S_2^+$ ($M+H$) $^+$ 383.0649, found 383.0640.

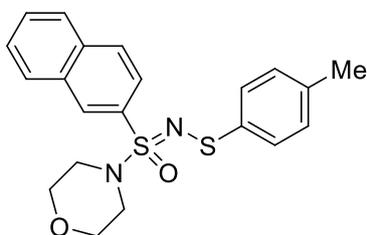
Following the General Procedure A with 4-(4-chlorophenylsulfonimidoyl)morpholine (52.1 mg, 0.2 mmol) and 4-toluenethiol (49.7 mg, 0.4 mmol), **3zf** was obtained as a colorless oil (53.3 mg, 70%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 3.74 – 3.67 (m, 4H), 3.07 – 2.93 (m, 4H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 137.3, 135.7, 133.,

(3zg) *N*-(morpholino(naphthalen-2-yl)(oxo)- λ^6 -sulfaneylidene)-*S*-(*p*-tolyl)thiohydroxylamine



N-(morpholino(naphthalen-2-yl)(oxo)- λ^6 -sulfaneylidene)-*S*-(*p*-tolyl)thiohydroxylamine

Chemical Formula: $C_{21}H_{22}N_2O_2S_2$

Exact Mass: 398.1123

Molecular Weight: 398.5390

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7, 135.5, 135.0, 132.2, 131.8, 129.6, 129.4, 129.4, 129.2, 129.1, 128.0, 127.7, 125.5, 123.3, 66.2, 46.8, 21.1.

IR (cm^{-1}): 2966, 2916, 2856, 1489, 1452, 1248, 1113, 1074, 1007, 932, 804, 731, 636, 480.

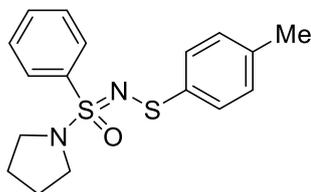
HRMS (APCI) m/z calcd for $C_{21}H_{22}N_2O_2S_2^+$ ($M+H$) $^+$ 399.1195, found 399.1188.

Following the General Procedure A with 4-(naphthalene-2-sulfonimidoyl)morpholine (55.3 mg, 0.2 mmol) and 4-toluenethiol (49.7 mg, 0.4 mmol), **3zg** was obtained as a colorless oil (59.7 mg, 75%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

1H NMR (400 MHz, $CDCl_3$) δ 8.53 – 8.45 (m, 1H), 7.98 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.70 – 7.57 (m, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.14 – 7.07 (m, 2H), 3.75 – 3.64 (m, 4H), 3.16 – 3.00 (m, 4H), 2.29 (s, 3H).

(3zh) *N*-(oxo(phenyl)(pyrrolidin-1-yl)- λ^6 -sulfaneylidene)-*S*-(*p*-tolyl)thiohydroxylamine



N-(oxo(phenyl)(pyrrolidin-1-yl)- λ^6 -sulfaneylidene)-*S*-(*p*-tolyl)thiohydroxylamine

Chemical Formula: $C_{17}H_{20}N_2OS_2$

Exact Mass: 332.1017

Molecular Weight: 332.4800

4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 136.5, 134.9, 132.7, 129.3, 129.0, 128.0, 124.8, 48.6, 25.4, 21.0.

IR (cm^{-1}): 3061, 2974, 2874, 1489, 1445, 1240, 1099, 1013, 804, 748, 690, 581.

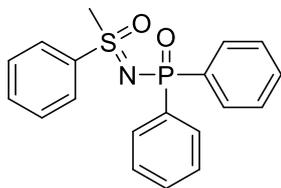
Following the General Procedure A with 1-(phenylsulfonimidoyl)pyrrolidine (42.1 mg, 0.2 mmol) and 4-toluenethiol (49.7 mg, 0.4 mmol), **3zh** was obtained as a colorless oil (47.3 mg, 71%).

This target product was purified by column chromatography on silica gel (PE/EA = 3:1).

1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 7.2 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.35 (d, J = 8.0 Hz, 1H), 7.14 – 7.10 (m, 1H), 7.09 – 7.00 (m, 2H), 3.33 – 3.18 (m, 4H), 2.28 (s, 3H), 1.81 – 1.69 (m,

HRMS (APCI) m/z calcd for $C_{17}H_{21}N_2OS_2^+$ ($M+H$)⁺ 333.1090, found 333.1082.

(6a) N-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-P,P-diphenylphosphinic amide (CAS: 2384177-23-3)^[12]



N-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-*P,P*-diphenylphosphinic amide

Chemical Formula: $C_{19}H_{18}NO_2PS$

Exact Mass: 355.0796

Molecular Weight: 355.3918

131.0, 129.4, 128.3, 128.2, 127.2, 48.02, 48.00.

³¹P NMR (162 MHz, $CDCl_3$) δ 18.21.

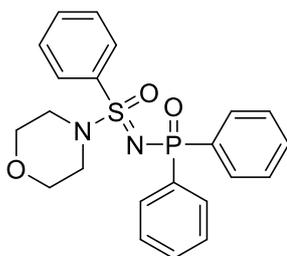
Following the General Procedure B with sulfoximine (31.0 mg, 0.2 mmol) and diphenylphosphine oxide (80.9 mg, 0.4 mmol), **6a** was obtained as a yellow oil (57.5 mg, 81%).

This target product was purified by column chromatography on silica gel (PE/EA = 1:1).

¹H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.0 Hz, 2H), 7.98 – 7.84 (m, 4H), 7.66 – 7.60 (m, 1H), 7.58 – 7.51 (m, 2H), 7.49 – 7.32 (m, 6H), 3.40 (s, 3H).

¹³C NMR (101 MHz, $CDCl_3$) δ 141.3, 141.2, 136.9, 136.6, 135.6, 135.2, 133.6, 131.3, 131.21, 131.16, 131.1,

(6b) N-(morpholino(oxo)(phenyl)- λ^6 -sulfaneylidene)-P,P-diphenylphosphinic amide



N-(morpholino(oxo)(phenyl)- λ^6 -sulfaneylidene)-*P,P*-diphenylphosphinic amide

Chemical Formula: $C_{22}H_{23}N_2O_3PS$

Exact Mass: 426.1167

Molecular Weight: 426.4708

129.1, 128.3, 128.2, 128.1, 128.0, 127.7, 66.0, 46.6.

³¹P NMR (162 MHz, $CDCl_3$) δ 14.48.

IR (cm^{-1}): 3058, 2966, 2858, 1645, 1439, 1288, 1259, 1171, 1111, 937, 737, 694, 598, 542.

HRMS (APCI) m/z calcd for $C_{22}H_{24}N_2O_3PS$ ($M+H$)⁺ 427.1240, found 427.1235.

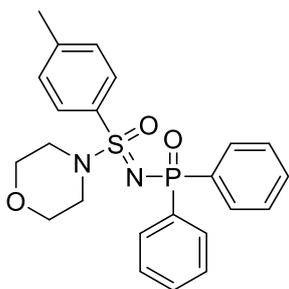
Following the General Procedure B with 4-(phenylsulfonimidoyl)morpholine (45.2 mg, 0.2 mmol) and diphenylphosphine oxide (80.9 mg, 0.4 mmol), **6b** was obtained as a yellow oil (67.7 mg, 76%).

This target product was purified by column chromatography on silica gel (PE/EA = 1:1).

¹H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.80 (m, 6H), 7.64 – 7.58 (m, 1H), 7.54 (t, J = 7.6 Hz, 2H), 7.48 – 7.33 (m, 6H), 3.67 – 3.55 (m, 4H), 3.19 – 3.06 (m, 2H), 2.98 – 2.82 (m, 2H).

¹³C NMR (101 MHz, $CDCl_3$) δ 136.2, 135.8, 135.7, 134.8, 134.8, 133.2, 131.5, 131.4, 131.3, 131.2,

(6c) N-(morpholino(oxo)(p-tolyl)- λ^6 -sulfaneylidene)-P,P-diphenylphosphinic amide



N-(morpholino(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)-*P,P*-diphenylphosphinic amide
 Chemical Formula: C₂₃H₂₅N₂O₃PS
 Exact Mass: 440.13
 Molecular Weight: 440.50

128.1, 128.1, 128.0, 127.8, 66.0, 46.5, 21.5.

³¹P NMR (162 MHz, CDCl₃) δ 14.42.

IR (cm⁻¹): 3057, 2966, 2922, 2585, 1593, 1439, 1292, 1169, 1111, 937, 725, 696, 526.

HRMS (APCI) *m/z* calcd for C₂₃H₂₆N₂O₃PS (M+H)⁺ 441.1396, found 441.1391.

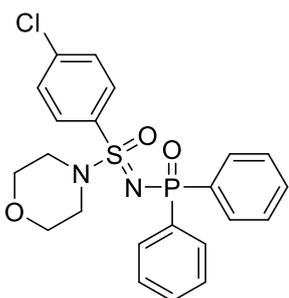
Following the General Procedure B with 4-(4-methylphenylsulfonimidoyl)morpholine (48.0 mg, 0.2 mmol) and diphenylphosphine oxide (80.9 mg, 0.4 mmol), **6c** was obtained as a yellow oil (63.4 mg, 72%).

This target product was purified by column chromatography on silica gel (PE/EA = 1:1).

¹H NMR (400 MHz, CDCl₃) δ 7.96 – 7.82 (m, 4H), 7.74 (d, *J* = 7.6 Hz, 2H), 7.48 – 7.29 (m, 8H), 3.65 – 3.53 (m, 4H), 3.18 – 3.03 (m, 2H), 2.94 – 2.80 (m, 2H), 2.42 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 144.1, 136.2, 136.1, 134.8, 132.7, 132.7, 131.5, 131.4, 131.3, 131.2, 129.8, 128.3,

(6d) N-((4-chlorophenyl)(morpholino)(oxo)- λ^6 -sulfaneylidene)-P,P-diphenylphosphinic amide



N-((4-chlorophenyl)(morpholino)(oxo)- λ^6 -sulfaneylidene)-*P,P*-diphenylphosphinic amide
 Chemical Formula: C₂₂H₂₂ClN₂O₃PS
 Exact Mass: 460.0777
 Molecular Weight: 460.9128

³¹P NMR (162 MHz, CDCl₃) δ 14.71.

IR (cm⁻¹): 3429, 3057, 2966, 2918, 2858, 1577, 1436, 1288, 1178, 1109, 930, 723, 696, 527.

HRMS (APCI) *m/z* calcd for C₂₂H₂₃ClN₂O₃PS (M+H)⁺ 461.0850, found 461.0843.

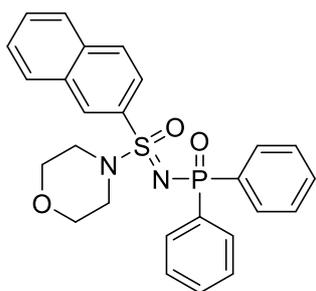
Following the General Procedure B with 4-(4-chlorophenylsulfonimidoyl)morpholine (52.0 mg, 0.2 mmol) and diphenylphosphine oxide (80.9 mg, 0.4 mmol), **6d** was obtained as a yellow oil (60.7 mg, 66%).

This target product was purified by column chromatography on silica gel (PE/EA = 1:1).

¹H NMR (400 MHz, CDCl₃) δ 7.94 – 7.84 (m, 4H), 7.81 – 7.75 (m, 2H), 7.51 – 7.47 (m, 2H), 7.46 – 7.33 (m, 6H), 3.67 – 3.54 (m, 4H), 3.16 – 3.05 (m, 2H), 2.95 – 2.86 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 139.9, 135.8, 134.4, 134.3, 131.5, 131.4, 131.4, 131.3, 131.2, 129.4, 129.2, 128.3, 128.2, 128.1, 127.7, 127.6, 66.0, 46.5.

(6e) N-(morpholino(naphthalen-2-yl)(oxo)- λ^6 -sulfaneylidene)-P,P-diphenylphosphinic amide



N-(morpholino(naphthalen-2-yl)(oxo)- λ^6 -sulfaneylidene)-*P,P*-diphenylphosphinic amide

Chemical Formula: $C_{26}H_{25}N_2O_3PS$

Exact Mass: 476.1323

Molecular Weight: 476.5308

Following the General Procedure B with 4-(naphthalene-2-sulfonimidoyl)morpholine (55.2 mg, 0.2 mmol) and diphenylphosphine oxide (80.9 mg, 0.4 mmol), **6e** was obtained as a yellow oil (61.9 mg, 65%).

This target product was purified by column chromatography on silica gel (PE/EA = 1:1).

1H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.00 – 7.82 (m, 8H), 7.68 – 7.56 (m, 2H), 7.49 – 7.33 (m, 6H), 3.68 – 3.54 (m, 4H), 3.26 – 3.13 (m, 2H), 3.03 – 2.92 (m, 2H).

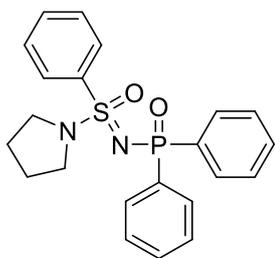
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1, 135.0, 134.8, 134.7, 133.0, 132.9, 132.1, 131.6, 131.5, 131.3, 131.2, 129.4, 129.4, 129.2, 129.2, 128.3, 128.2, 128.0, 128.0, 127.7, 122.8, 66.1, 46.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 14.56.

IR (cm^{-1}): 3057, 2964, 2858, 2220, 1715, 1589, 1439, 1292, 1174, 1113, 1074, 935, 723, 696, 636, 538.

HRMS (APCI) m/z calcd for $C_{26}H_{26}N_2O_3PS$ ($M+H$)⁺ 477.1396, found 477.1391.

(6f) *N*-(oxo(phenyl)(pyrrolidin-1-yl)- λ^6 -sulfaneylidene)-*P,P*-diphenylphosphinic amide



N-(oxo(phenyl)(pyrrolidin-1-yl)- λ^6 -sulfaneylidene)-*P,P*-diphenylphosphinic amide

Chemical Formula: $C_{22}H_{23}N_2O_2PS$

Exact Mass: 410.1218

Molecular Weight: 410.4718

Following the General Procedure B with 1-(phenylsulfonimidoyl)pyrrolidine (42.0 mg, 0.2 mmol) and diphenylphosphine oxide (80.9 mg, 0.4 mmol), **6f** was obtained as a yellow oil (50.8 mg, 62%).

This target product was purified by column chromatography on silica gel (PE/EA = 1:1).

1H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.82 (m, 6H), 7.59 – 7.53 (m, 1H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.45 – 7.31 (m, 6H), 3.38 – 3.26 (m, 2H), 3.24 – 3.11 (m, 2H), 1.68 (s, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 138.0, 136.5, 135.2, 135.1, 132.7, 131.4, 131.3, 131.3, 131.2, 131.1,

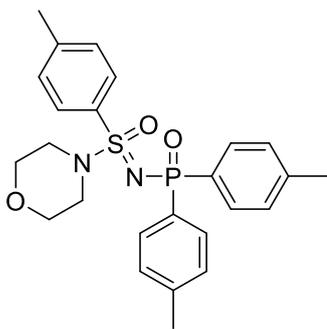
129.0, 128.2, 128.1, 128.0, 127.4, 48.5, 25.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ 14.19.

IR (cm^{-1}): 3057, 2976, 2876, 2216, 1717, 1591, 1483, 1439, 1271, 1165, 997, 914, 721, 690, 517.

HRMS (APCI) m/z calcd for $C_{22}H_{24}N_2O_2PS$ ($M+H$)⁺ 411.1291, found 411.1285.

(6g) *N*-(morpholino(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)-*P,P*-di-*p*-tolylphosphinic amide



N-(morpholino(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)-*P,P*-*di-p*-tolylphosphinic amide
 Chemical Formula: C₂₅H₂₉N₂O₃PS
 Exact Mass: 468.1637
 Molecular Weight: 468.5518

Following the General Procedure B with 4-(4-methylphenylsulfonimidoyl)morpholine (48.0 mg, 0.2 mmol) and di-*p*-tolylphosphine oxide (92.0 mg, 0.4 mmol), **6g** was obtained as a yellow oil (65.5 mg, 70%). This target product was purified by column chromatography on silica gel (PE/EA = 1:1).

¹H NMR (400 MHz, CDCl₃) δ 7.81 – 7.71 (m, 6H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.22 – 7.15 (m, 4H), 3.69 – 3.57 (m, 4H), 3.18 – 3.07 (m, 2H), 2.94 – 2.83 (m, 2H), 2.43 (s, 3H), 2.34 (d, *J* = 2.8 Hz, 6H).

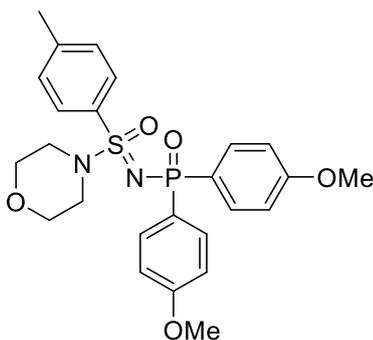
¹³C NMR (101 MHz, CDCl₃) δ 144.0, 141.4, 133.4, 133.3, 132.9, 132.9, 132.0, 131.5, 131.4, 131.3, 131.2, 129.7, 129.0, 128.8, 128.7, 127.8, 66.1, 46.6, 21.6, 21.5.

³¹P NMR (162 MHz, CDCl₃) δ 14.93.

IR (cm⁻¹): 3022, 2966, 2920, 2860, 1601, 1452, 1288, 1259, 1169, 1111, 937, 810, 727, 663, 530.

HRMS (APCI) *m/z* calcd for C₂₅H₃₀N₂O₃PS (M+H)⁺ 469.1709, found 469.1700.

(6h) P,P-bis(4-methoxyphenyl)-N-(morpholino(oxo)(p-tolyl)- λ^6 -sulfaneylidene)phosphinic amide



P,P-bis(4-methoxyphenyl)-*N*-(morpholino(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)phosphinic amide
 Chemical Formula: C₂₅H₂₉N₂O₅PS
 Exact Mass: 500.15
 Molecular Weight: 500.55

Following the General Procedure B with 4-(4-methylphenylsulfonimidoyl)morpholine (48.0 mg, 0.2 mmol) and bis(4-methoxyphenyl)phosphine oxide (104.8 mg, 0.4 mmol), **6h** was obtained as a yellow oil (70.0 mg, 70%).

This target product was purified by column chromatography on silica gel (PE/EA = 1:1).

¹H NMR (400 MHz, CDCl₃) δ 7.88 – 7.71 (m, 6H), 7.32 (d, *J* = 7.6 Hz, 2H), 6.90 (t, *J* = 8.8 Hz, 4H), 3.80 (d, *J* = 4.4 Hz, 6H), 3.70 – 3.56 (m, 4H), 3.19 – 3.07 (m, 2H), 2.98 – 2.84 (m, 2H), 2.43 (s, 3H).

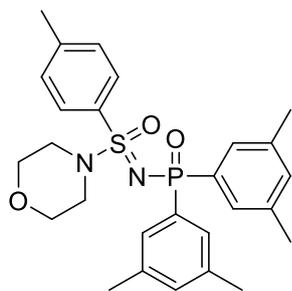
¹³C NMR (101 MHz, CDCl₃) δ 161.9, 144.0, 133.3, 133.2, 133.0, 132.9, 132.8, 129.7, 128.3, 128.2, 127.8, 126.8, 113.7, 113.6, 113.4, 66.1, 55.2, 55.2, 46.6, 21.5.

³¹P NMR (162 MHz, CDCl₃) δ 14.59.

IR (cm⁻¹): 2964, 2916, 2858, 1597, 1500, 1452, 1283, 1254, 1165, 1123, 1026, 937, 802, 723, 667, 530.

HRMS (APCI) *m/z* calcd for C₂₅H₃₀N₂O₅PS (M+H)⁺ 501.1608, found 501.1603.

(6i) P,P-bis(3,5-dimethylphenyl)-N-(morpholino(oxo)(p-tolyl)- λ^6 -sulfaneylidene)phosphinic amide



P,P-bis(3,5-dimethylphenyl)-*N*-(morpholino(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)phosphinic amide
 Chemical Formula: C₂₇H₃₃N₂O₃PS
 Exact Mass: 496.19
 Molecular Weight: 496.61

Following the General Procedure B with 4-(4-methylphenylsulfonimidoyl)morpholine (48.0 mg, 0.2 mmol) and bis(3,5-dimethylphenyl)phosphine oxide (103.2 mg, 0.4 mmol), **6i** was obtained as a yellow oil (67.5 mg, 68%).

This target product was purified by column chromatography on silica gel (PE/EA = 1:1).

¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 14.4 Hz, 4H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 3.70 – 3.55 (m, 4H), 3.15 – 3.04 (m, 2H), 2.95 – 2.86 (m, 2H), 2.43 (s, 4H), 2.30 (d, *J* = 7.6 Hz, 12H).

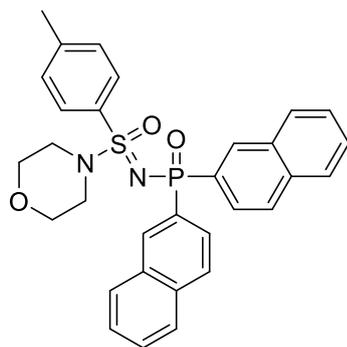
¹³C NMR (101 MHz, CDCl₃) δ 144.0, 137.8, 137.6, 137.6, 137.4, 132.97, 132.95, 132.90, 132.88, 129.7, 129.1, 129.0, 128.9, 128.78, 127.8, 66.1, 46.5, 21.5, 21.3, 21.3.

³¹P NMR (162 MHz, CDCl₃) δ 15.49.

IR (cm⁻¹): 2964, 2918, 2856, 2214, 1599, 1452, 1277, 1169, 1113, 937, 852, 725, 692, 588, 528.

HRMS (APCI) *m/z* calcd for C₂₇H₃₄N₂O₃PS (M+H)⁺ 497.2022, found 497.2015.

(6j) *N*-(morpholino(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)-*P,P*-di(naphthalen-2-yl)phosphinic amide



N-(morpholino(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)-*P,P*-di(naphthalen-2-yl)phosphinic amide
 Chemical Formula: C₃₁H₂₉N₂O₃PS
 Exact Mass: 540.16
 Molecular Weight: 540.62

Following the General Procedure B with 4-(4-methylphenylsulfonimidoyl)morpholine (48.0 mg, 0.2 mmol) and di(naphthalen-2-yl)phosphine oxide (120.8 mg, 0.4 mmol), **6j** was obtained as a yellow oil (75.6 mg, 70%).

This target product was purified by column chromatography on silica gel (PE/EA = 1:1).

¹H NMR (400 MHz, CDCl₃) δ 8.59 (d, *J* = 14.4 Hz, 1H), 8.51 (d, *J* = 14.4 Hz, 1H), 7.94 – 7.87 (m, 4H), 7.87 – 7.74 (m, 6H), 7.55 – 7.46 (m, 4H), 7.31 (d, *J* = 7.6 Hz, 2H), 3.69 – 3.54 (m, 4H), 3.22 – 3.12 (m, 2H), 2.98 – 2.87 (m, 2H), 2.41 (s, 3H).

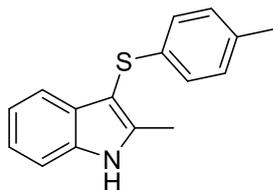
¹³C NMR (101 MHz, CDCl₃) δ 144.2, 134.6, 134.5, 132.8, 132.6, 132.4, 129.8, 129.0, 128.1, 128.0, 127.9, 127.8, 127.7, 127.7, 127.1, 127.0, 126.8, 126.7, 126.5, 66.1, 46.6, 21.5.

³¹P NMR (162 MHz, CDCl₃) δ 14.20.

IR (cm⁻¹): 3057, 2964, 2918, 2858, 2220, 1593, 1501, 1452, 1275, 1165, 1111, 1088, 933, 858, 818, 725, 662, 528.

HRMS (APCI) *m/z* calcd for C₃₁H₃₀N₂O₃PS (M+H)⁺ 541.1709, found 541.1703.

(3aa) 2-methyl-3-(*p*-tolylthio)-1*H*-indole (CAS: 955125-54-9)^[13]



2-methyl-3-(*p*-tolylthio)-1*H*-indole
 Chemical Formula: C₁₆H₁₅NS
 Exact Mass: 253.0925
 Molecular Weight: 253.3630

¹H NMR (400 MHz, CDCl₃) δ 8.18 (s, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.22 – 7.15 (m, 1H), 7.14 – 7.08 (m, 1H), 6.95 (s, 4H), 2.50 (s, 3H), 2.24 (s, 3H).

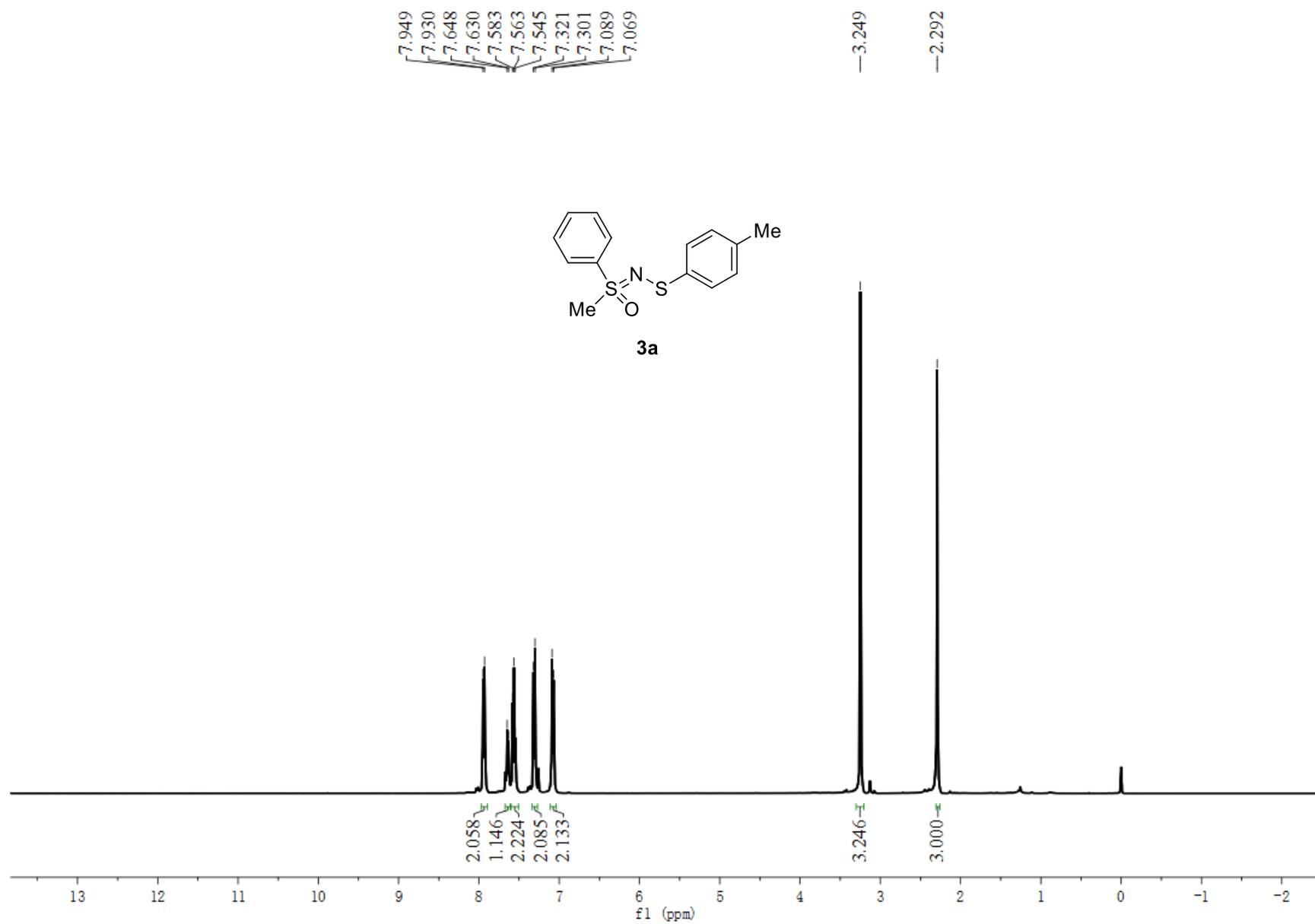
¹³C NMR (101 MHz, CDCl₃) δ 140.9, 135.7, 135.4, 134.3, 130.4, 129.5, 125.78, 122.2, 120.7, 119.4, 110.6, 99.9, 20.9, 12.2.

12. References

- [1]. Xie, Y.; Zhou, B.; Zhou, S., *ChemistrySelect*. 2 (2017), 1620-1624.
- [2]. Taniguchi, N., *Eur. J. Org. Chem.* 2016 (2016), 2157-2162.
- [3]. Izzo, F.; Schafer, M.; Stockman, R.; Lucking, U., *Chem. – A Eur. J.* 23 (2017), 15189-15193.
- [4]. Kiriwara, M. , Naito, S. , Ishizuka, Y. , Hanai, H. , Noguchi, T., *Tetrahedron Letters*, 52 (2011), 3086-3089.
- [5]. Dhineshkumar, J., Prabhu, K., *Org. Lett.*, 15 (2013), 6062–6065.
- [6]. Chen, C., Niu, P., Shen, Z., Li, M., *J. Electrochem. Soc.* 165 (2018), G67.
- [7]. Mampuy, P., Zhu, Y., Sergeyev, S., Ruijter, E., V.A.Orru, R., V. Doorslaer, S., U.W.Maes, B., *Org. Lett.*, 18 (2016), 2808–2811.
- [8]. Du, H., Tang, R., Deng, C., Liu, Y., Li, J., Zhang, X., *Adv. Synth. Catal.*, 353 (2011), 2739–2748.
- [9]. Kong, D., Ma, D., Wu, P., Bolm, C., *ACS Sustain. Chem. Eng.* 10 (2022), 2863–2867.
- [10]. Wang, H.; Zhang, D.; Cao, M.; Bolm, C., *Synthesis* 51 (2018), 271-275.
- [11]. Yang, L.; Feng, J.; Qiao, M.; Zeng, Q., *Org. Chem. Front.* 5 (2018), 24-28.
- [12]. Tan, M. , Zheng, W. , Yang, L., *Asian J. Org. Chem.* 8 (2019), 2027-2031.
- [13]. Huang, Q.; Peng, X.; Li, H.; He, H.; Liu, L. *Molecules*, 27 (2022), 772.

13. Copies of NMR spectra

¹H NMR spectra of compound **3a** (400 MHz, CDCl₃)

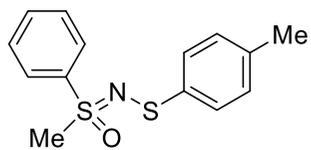


¹³C NMR spectra of compound **3a** (101 MHz, CDCl₃)

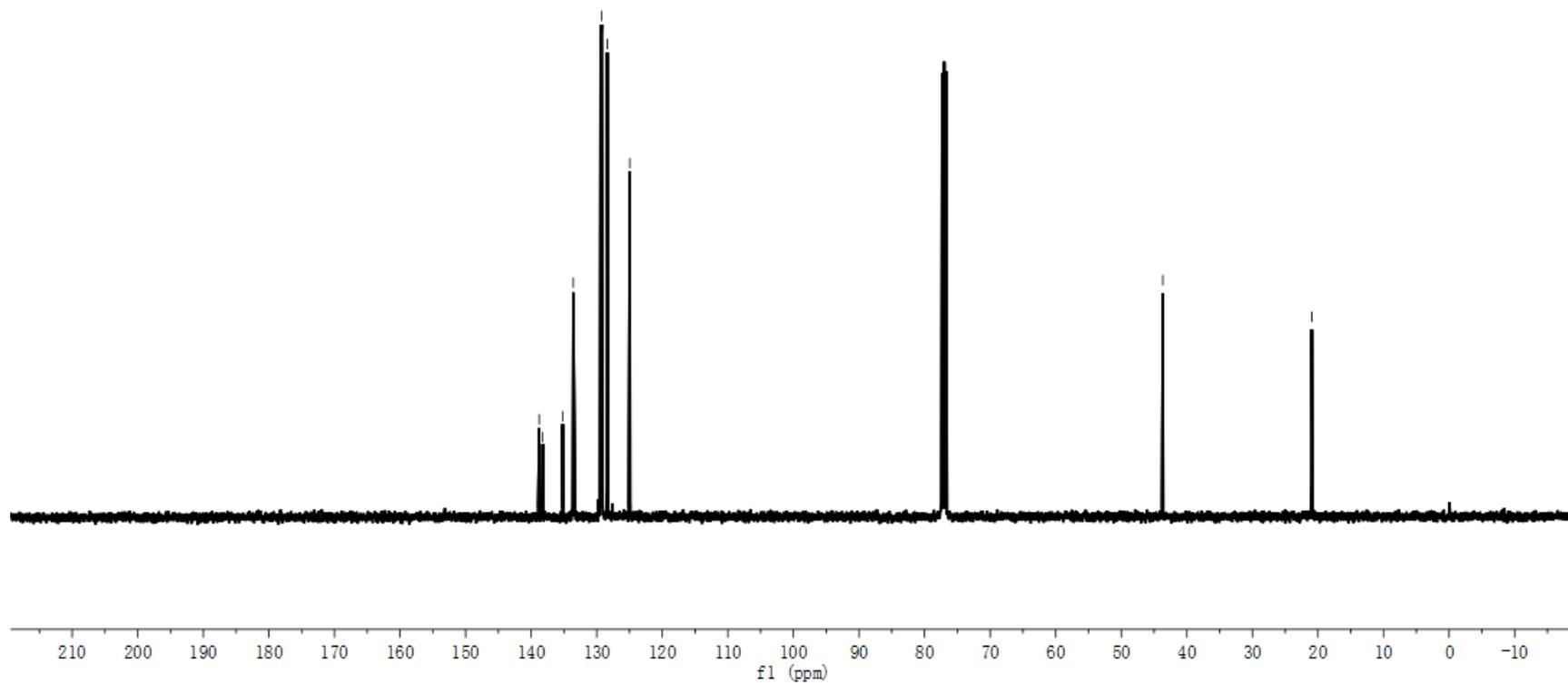
138.780
138.244
135.194
133.574
129.402
129.254
128.385
124.954

—43.666

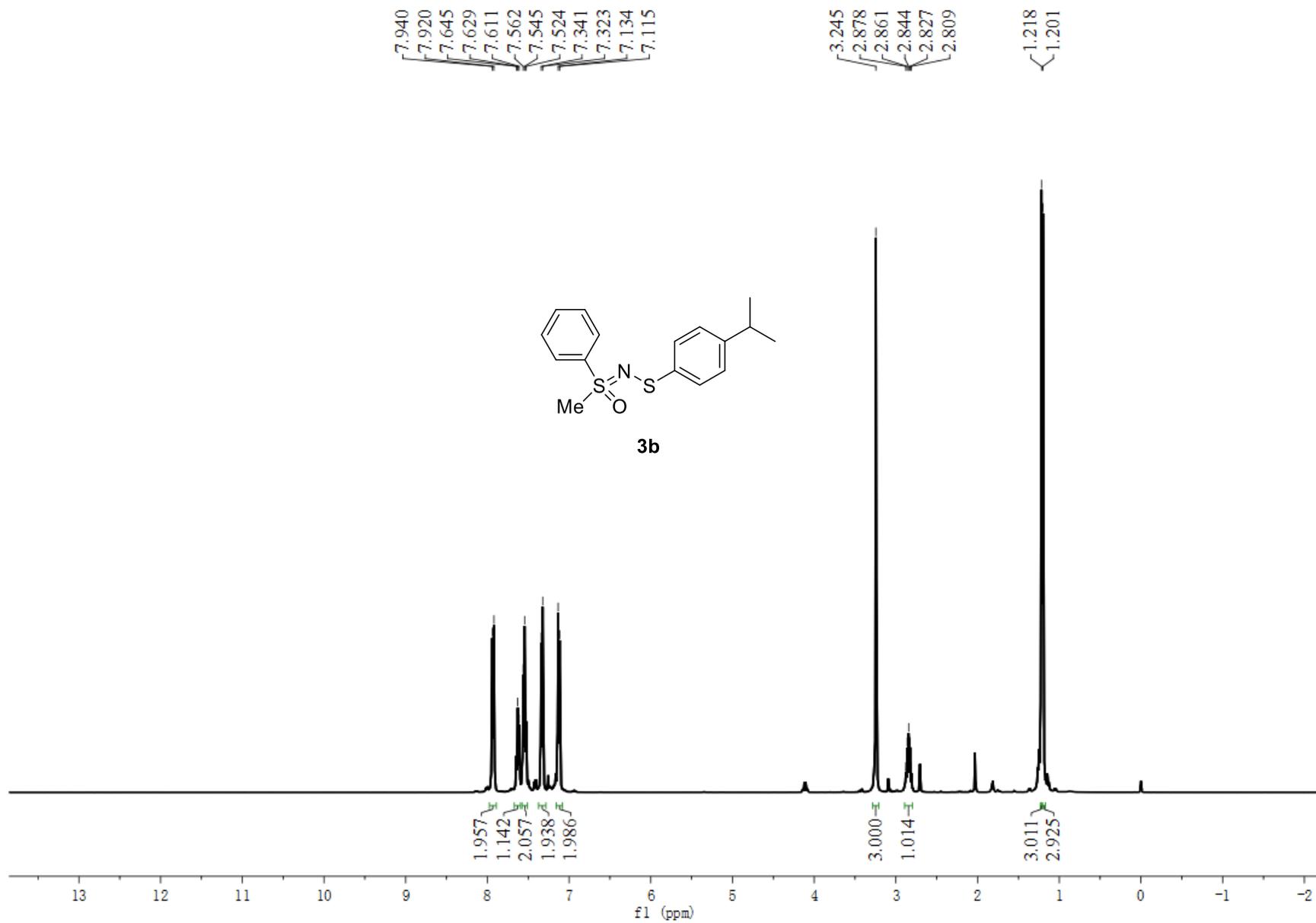
—20.958



3a



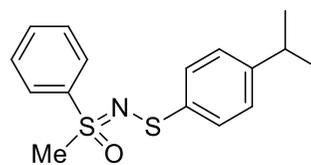
¹H NMR spectra of compound **3b** (400 MHz, CDCl₃)



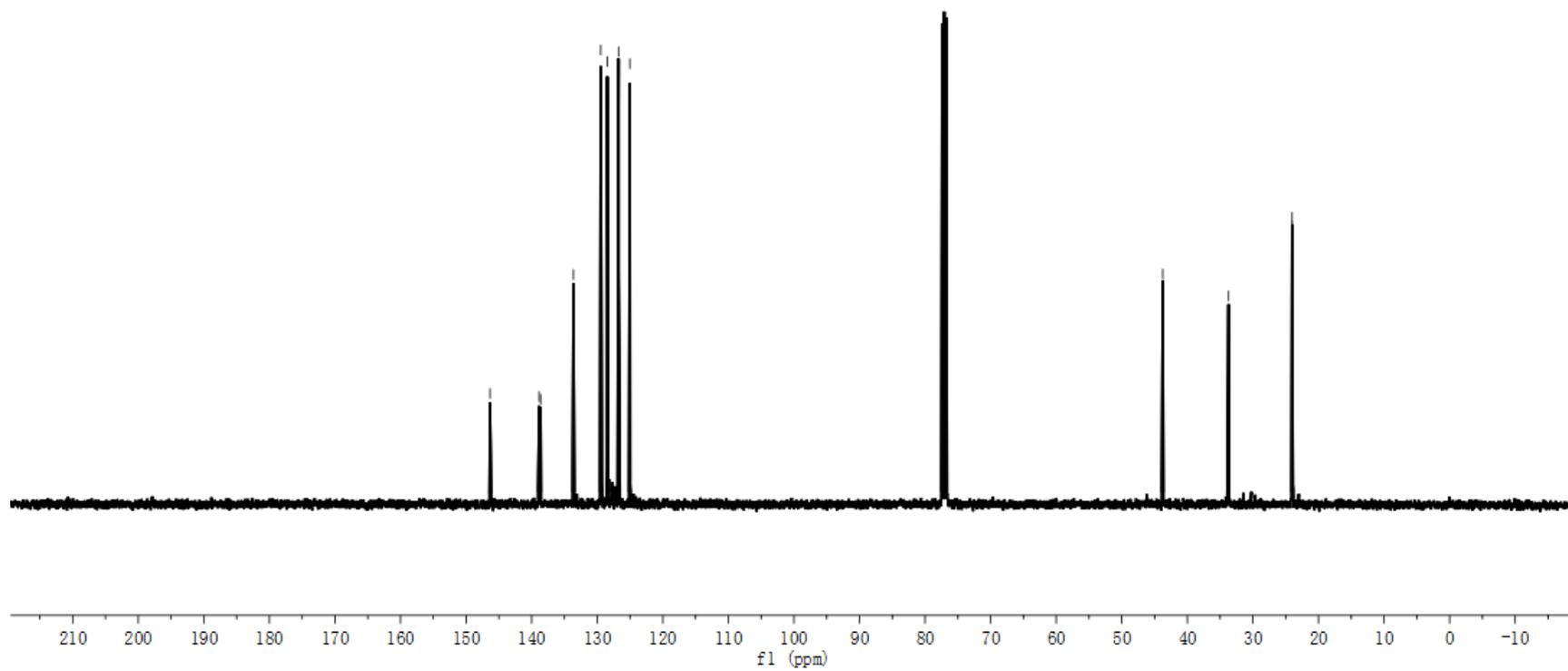
$^{13}\text{C}\{^1\text{H}\}$ spectra of compound **3b** (101 MHz, CDCl_3)

146.353
138.876
138.636
133.632
129.458
128.466
126.744
125.018

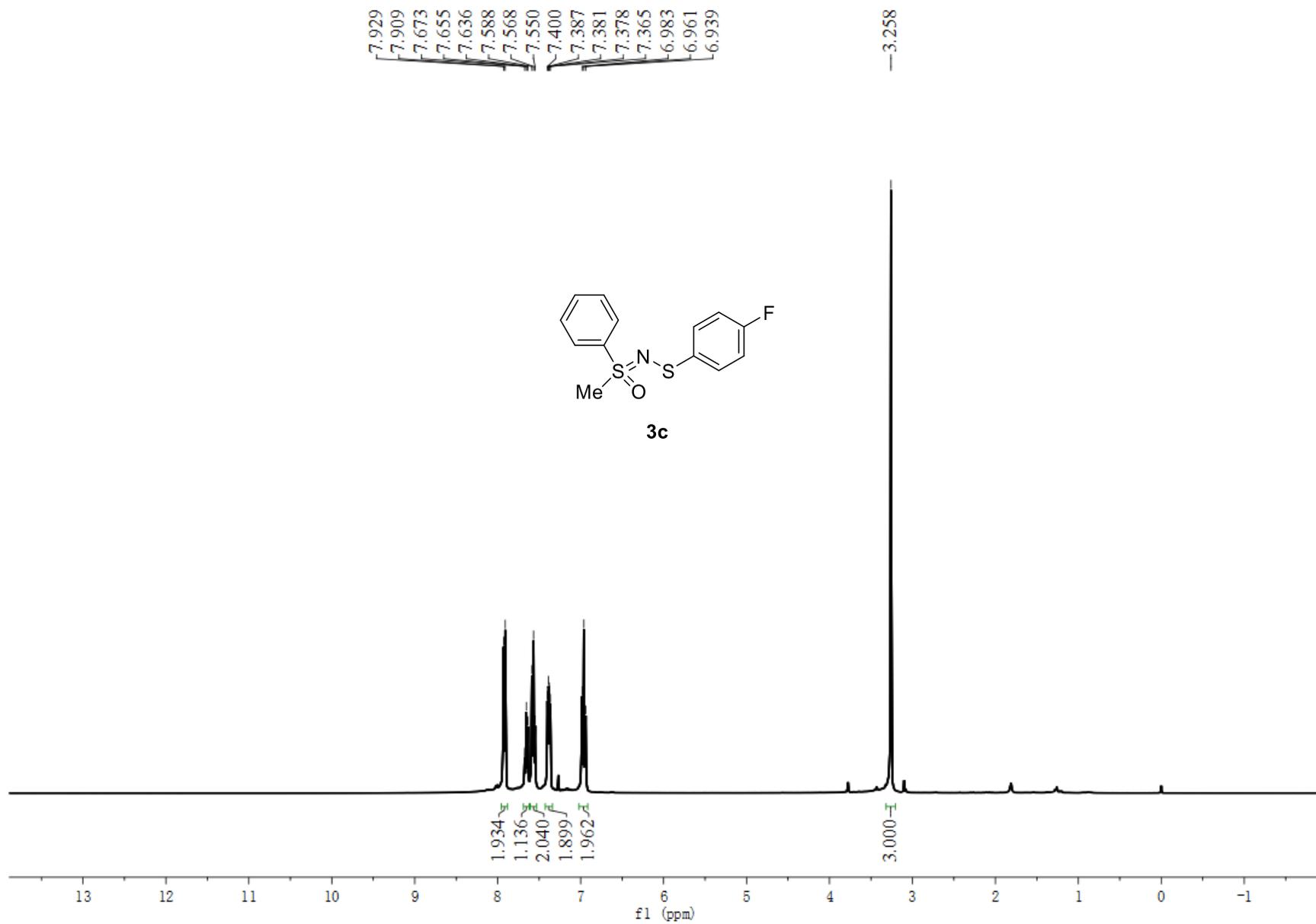
43.752
33.714
24.022
24.010



3b



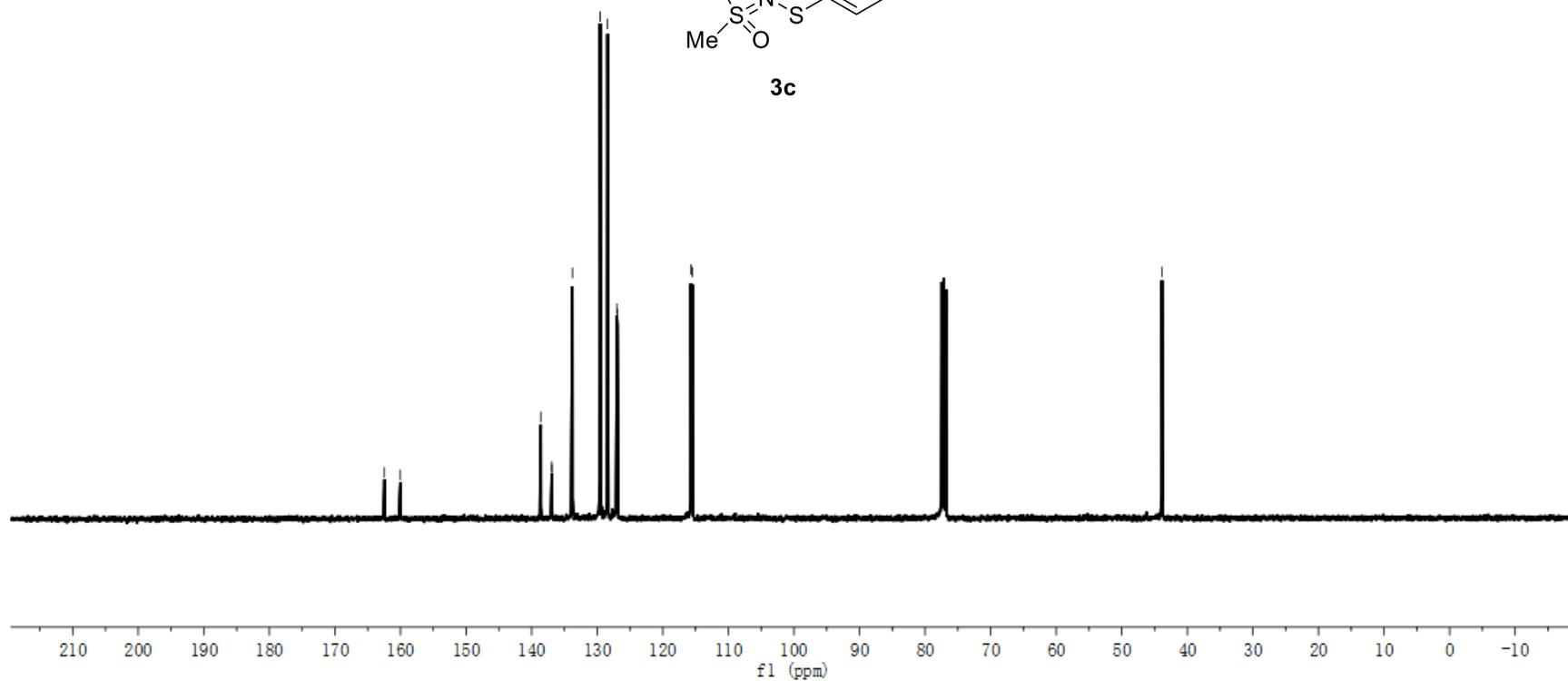
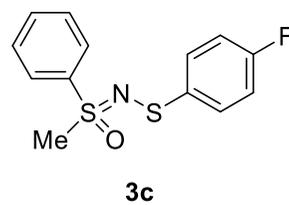
¹H NMR spectra of compound **3c** (400 MHz, CDCl₃)



¹³C NMR spectra of compound **3c** (101 MHz, CDCl₃)

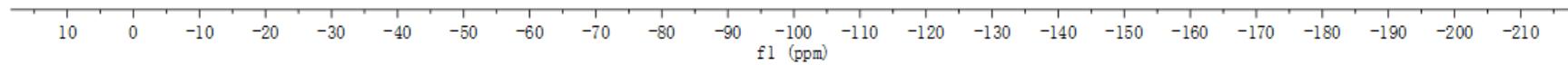
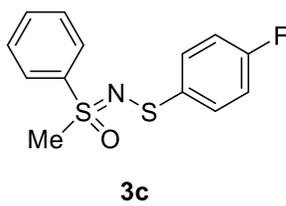
162.460
160.031
138.619
136.937
136.907
133.793
129.555
128.417
127.000
126.921
115.704
115.484

43.871

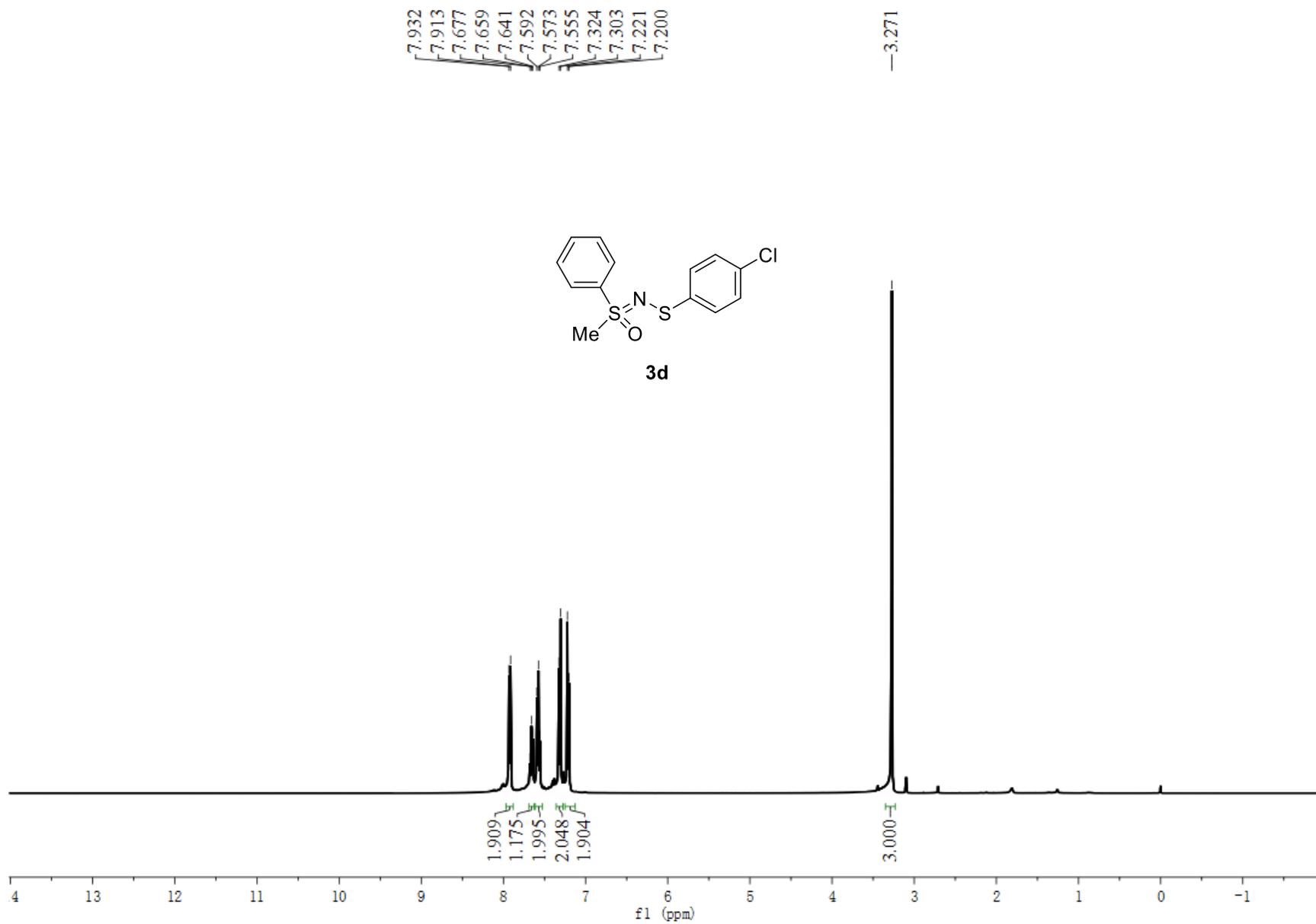


^{19}F NMR spectra of compound **3c** (376 MHz, CDCl_3)

-117.314



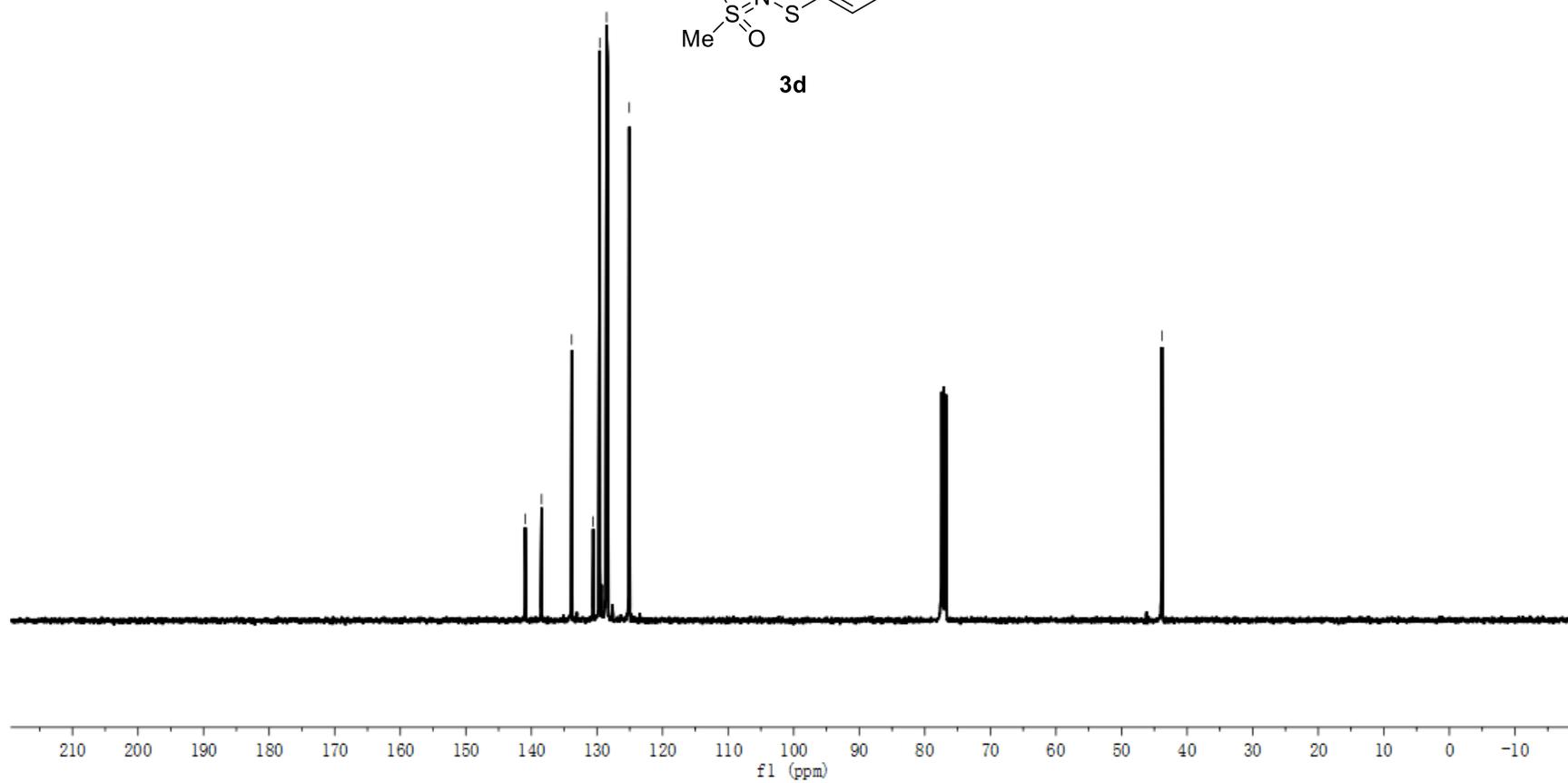
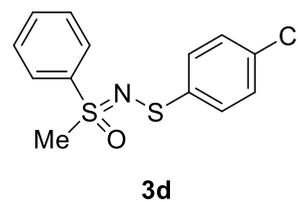
¹H NMR spectra of compound **3d** (400 MHz, CDCl₃)



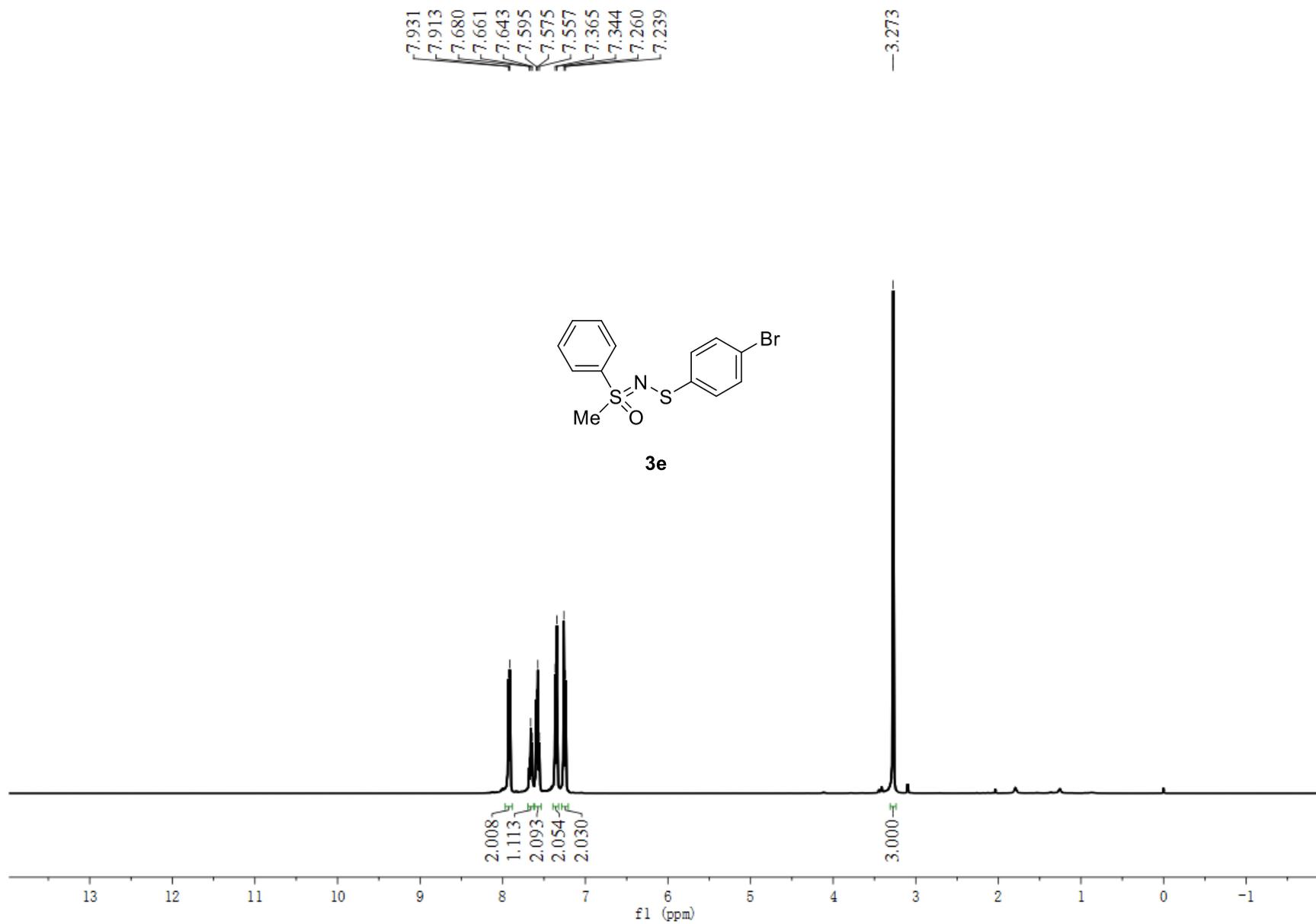
¹³C NMR spectra of compound **3d** (400 MHz, CDCl₃)

140.948
138.448
133.853
130.579
129.576
128.536
128.352
125.075

—43.839



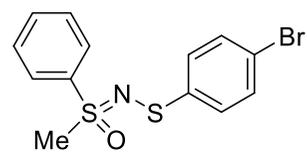
¹H NMR spectra of compound **3e** (400 MHz, CDCl₃)



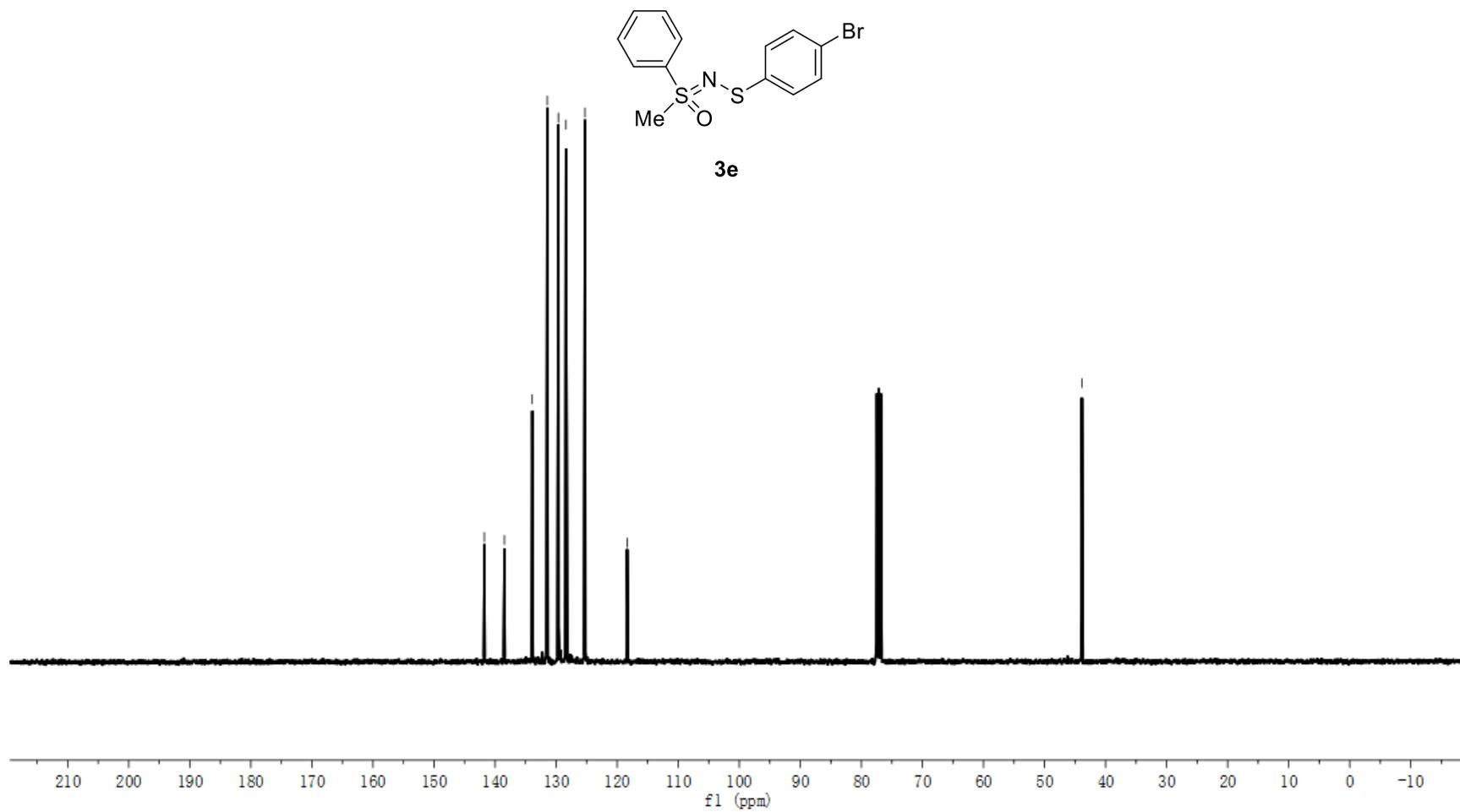
¹³C NMR spectra of compound **3e** (101 MHz, CDCl₃)

141.746
138.460
133.907
131.440
129.625
128.387
125.268
118.363

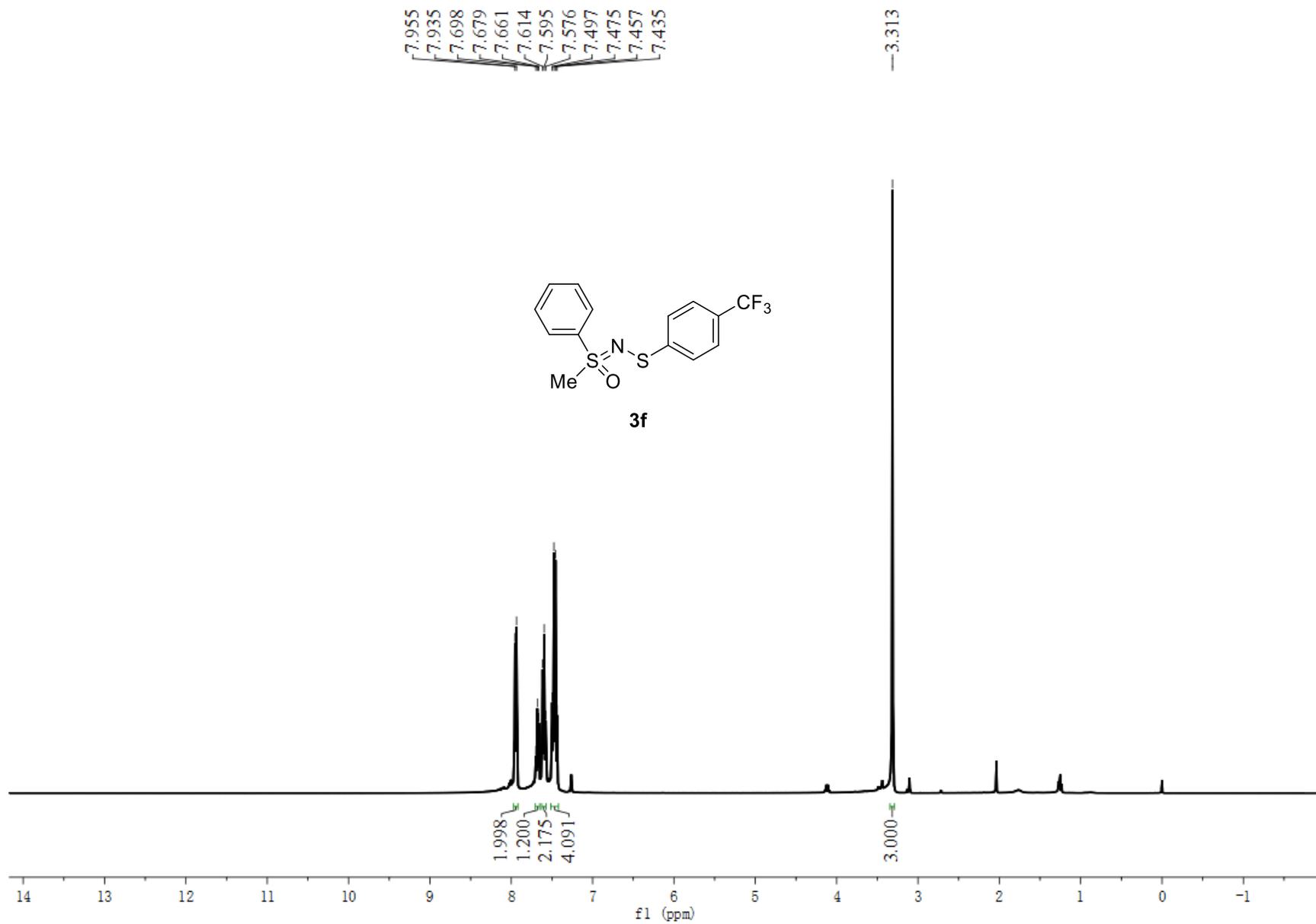
—43.881



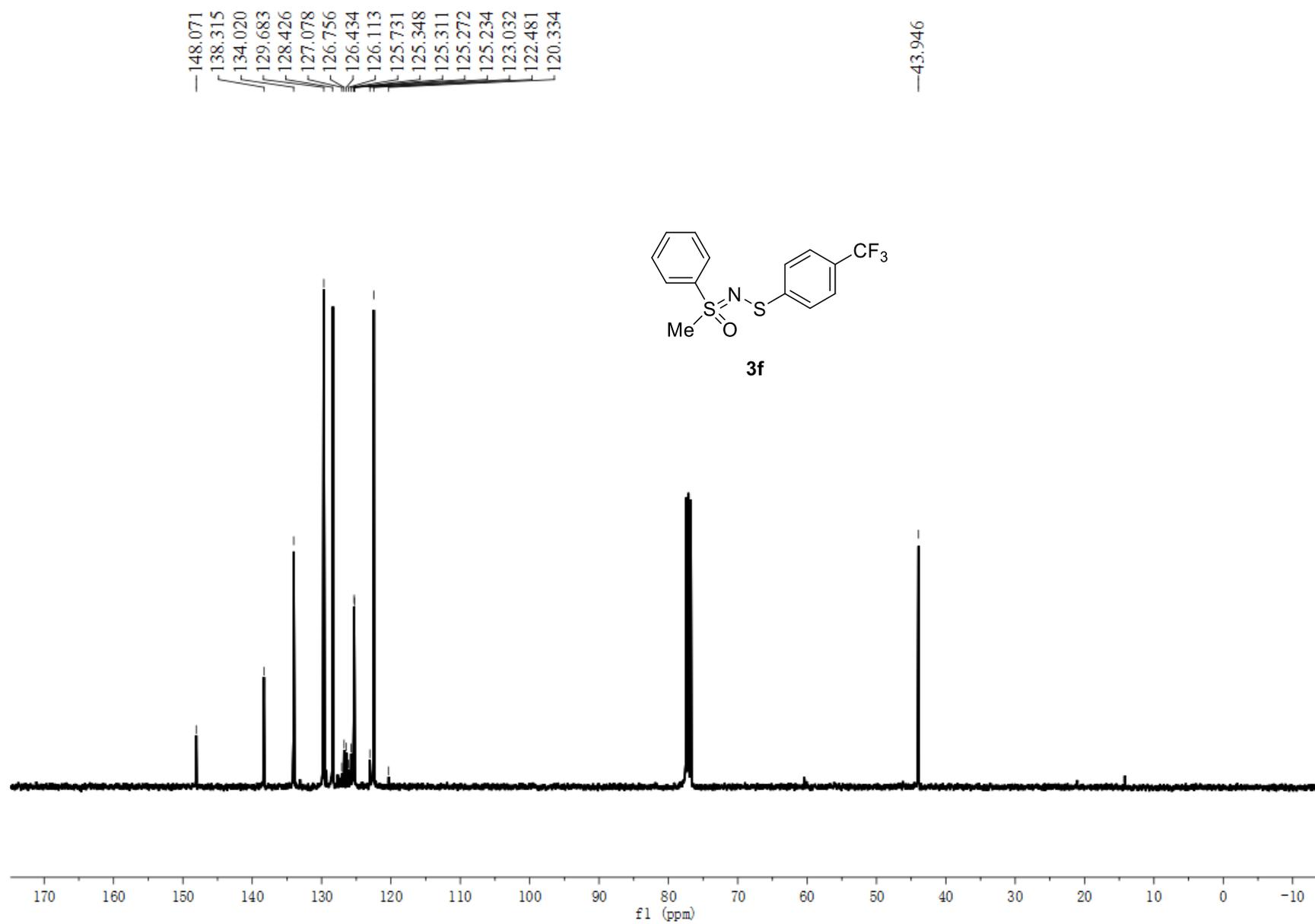
3e



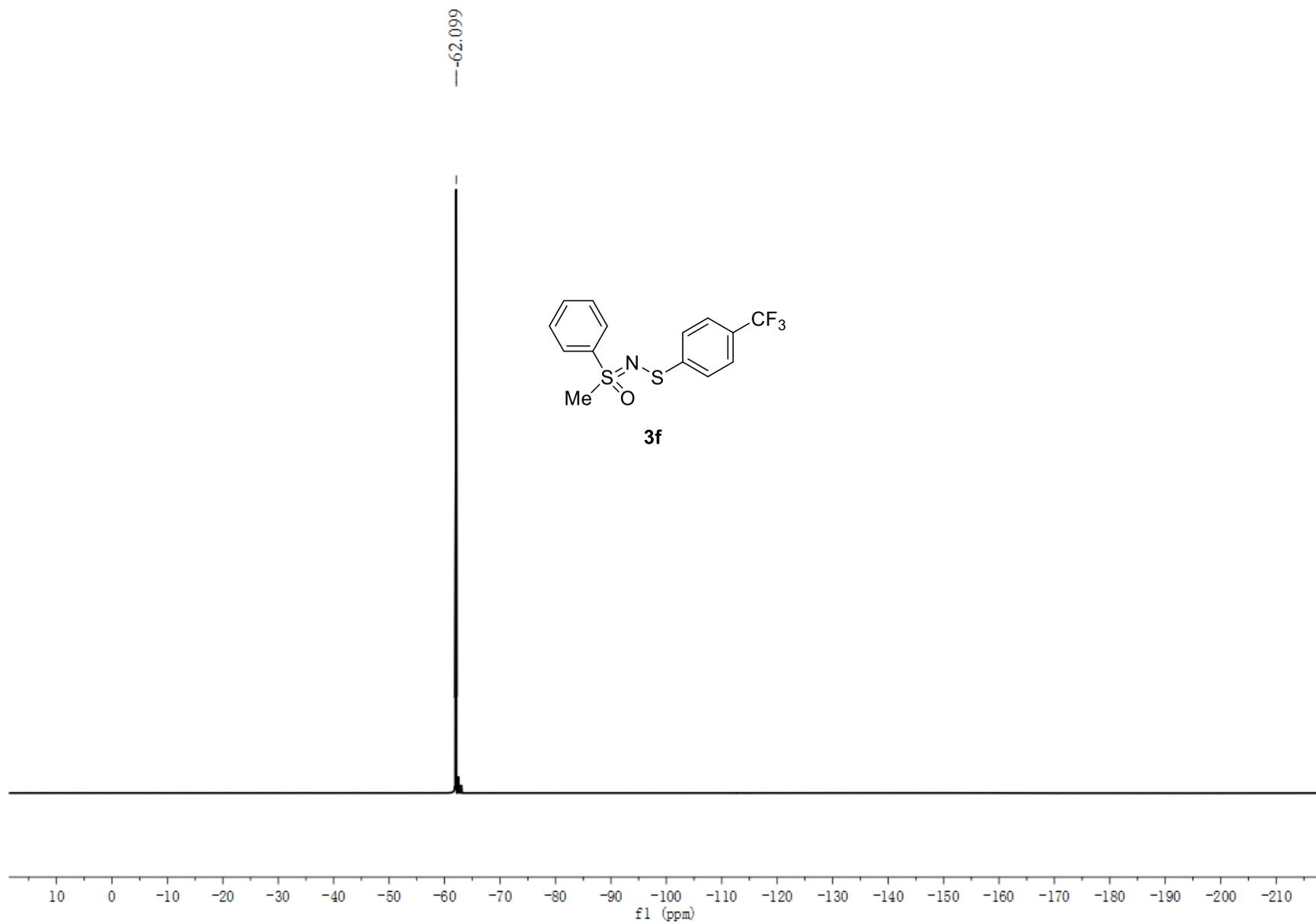
¹H NMR spectra of compound **3f** (400 MHz, CDCl₃)



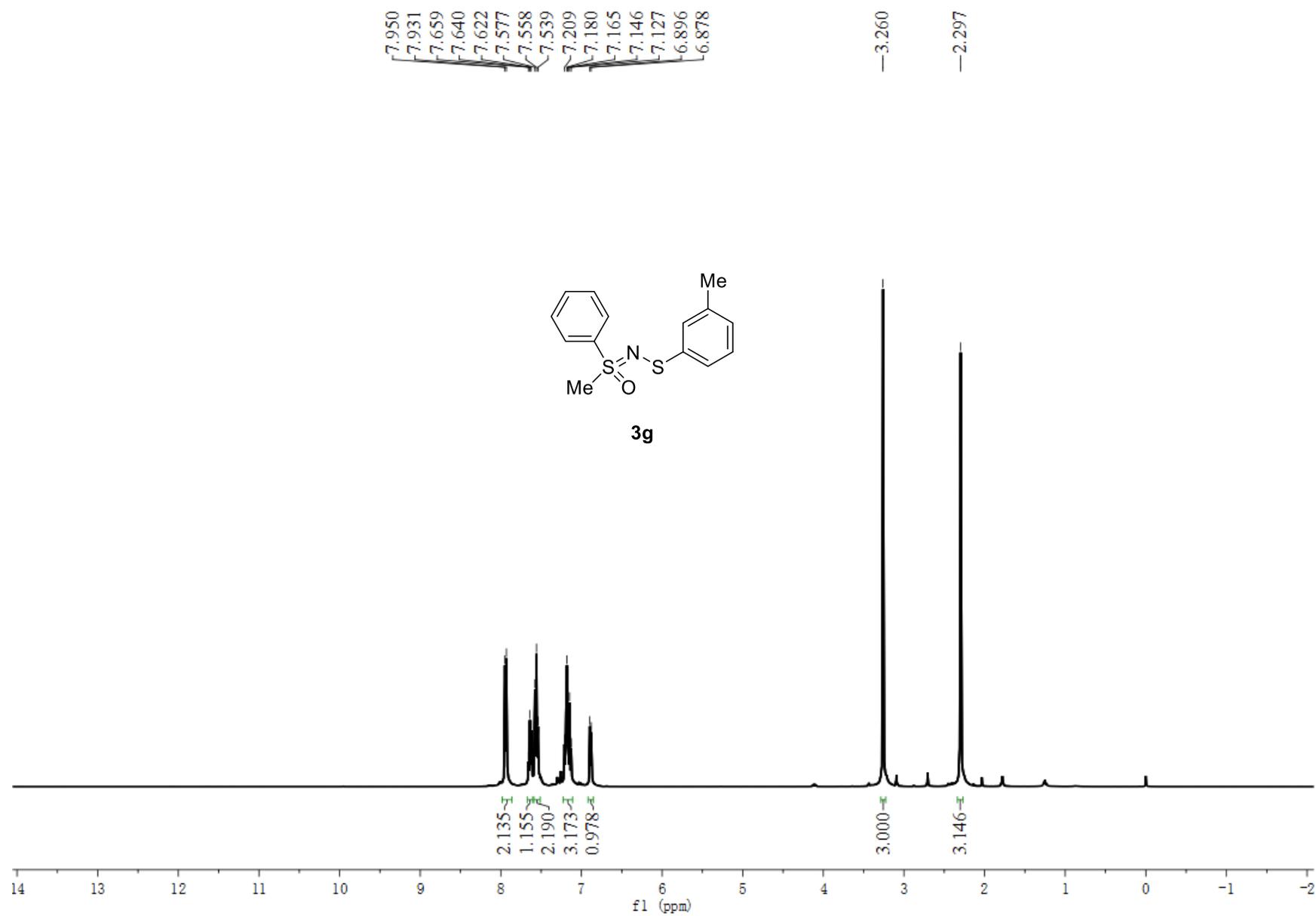
¹³C NMR spectra of compound **3f** (101 MHz, CDCl₃)



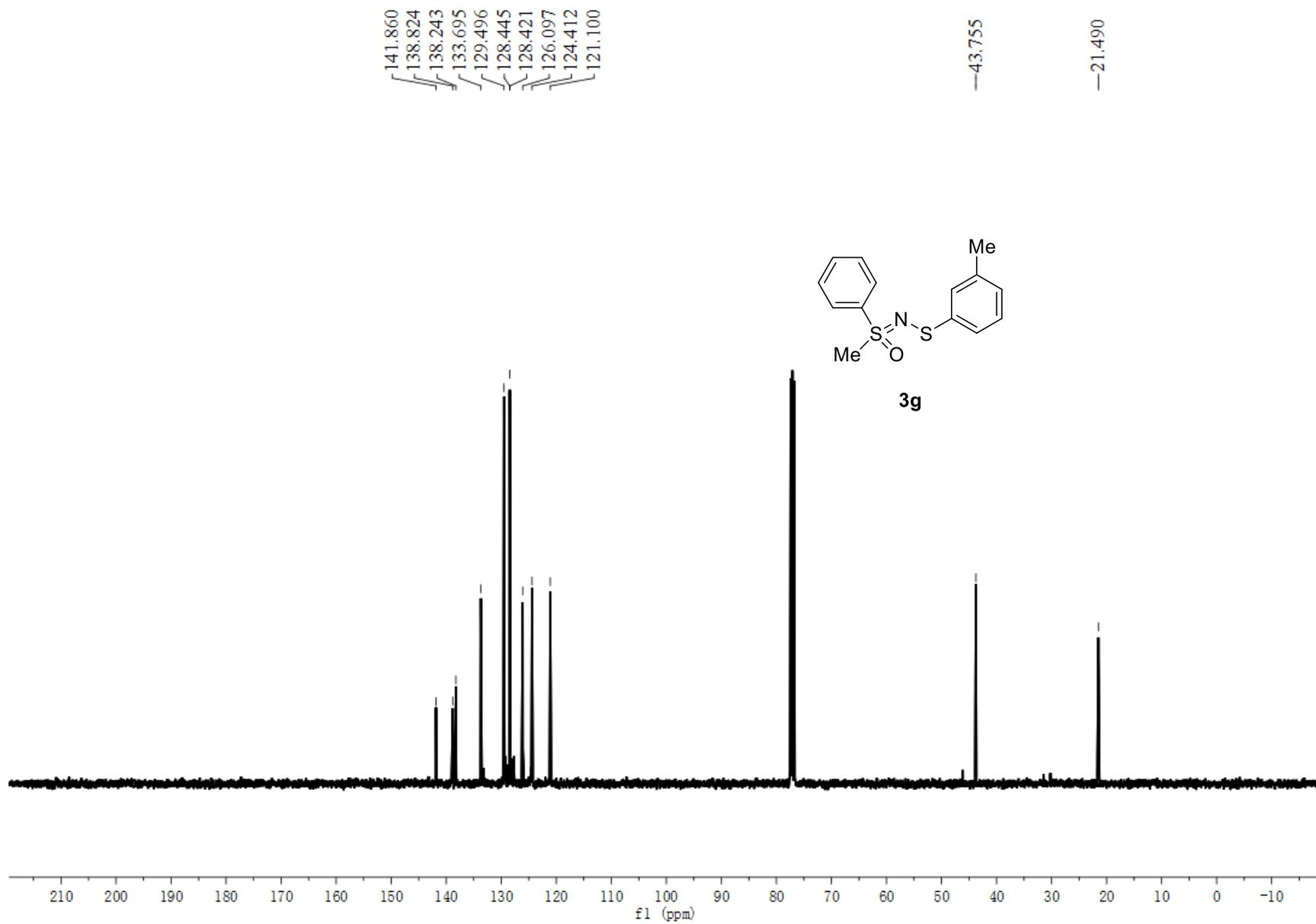
^{19}F NMR spectra of compound **3f** (376 MHz, CDCl_3)



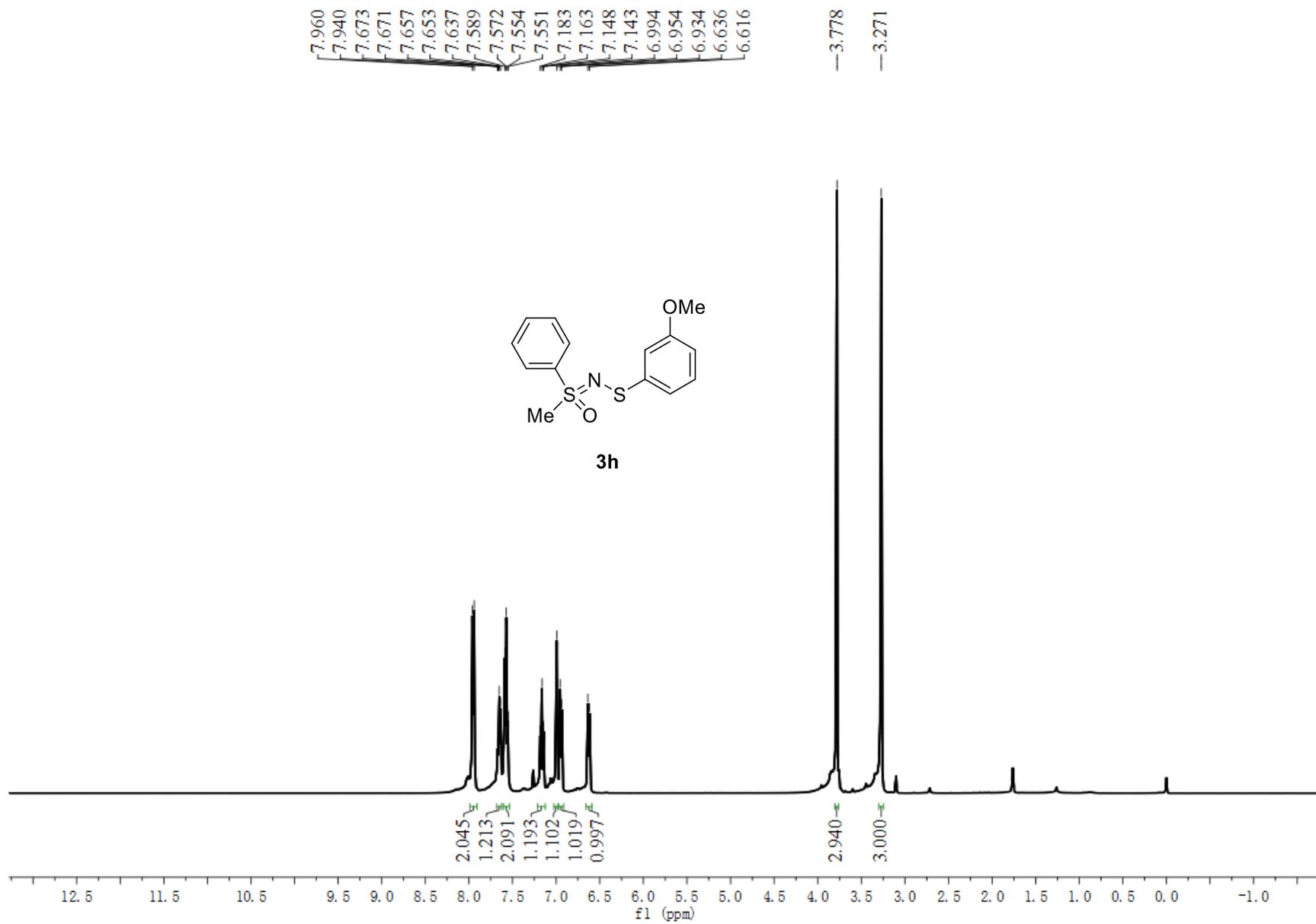
¹H NMR spectra of compound **3g** (400 MHz, CDCl₃)



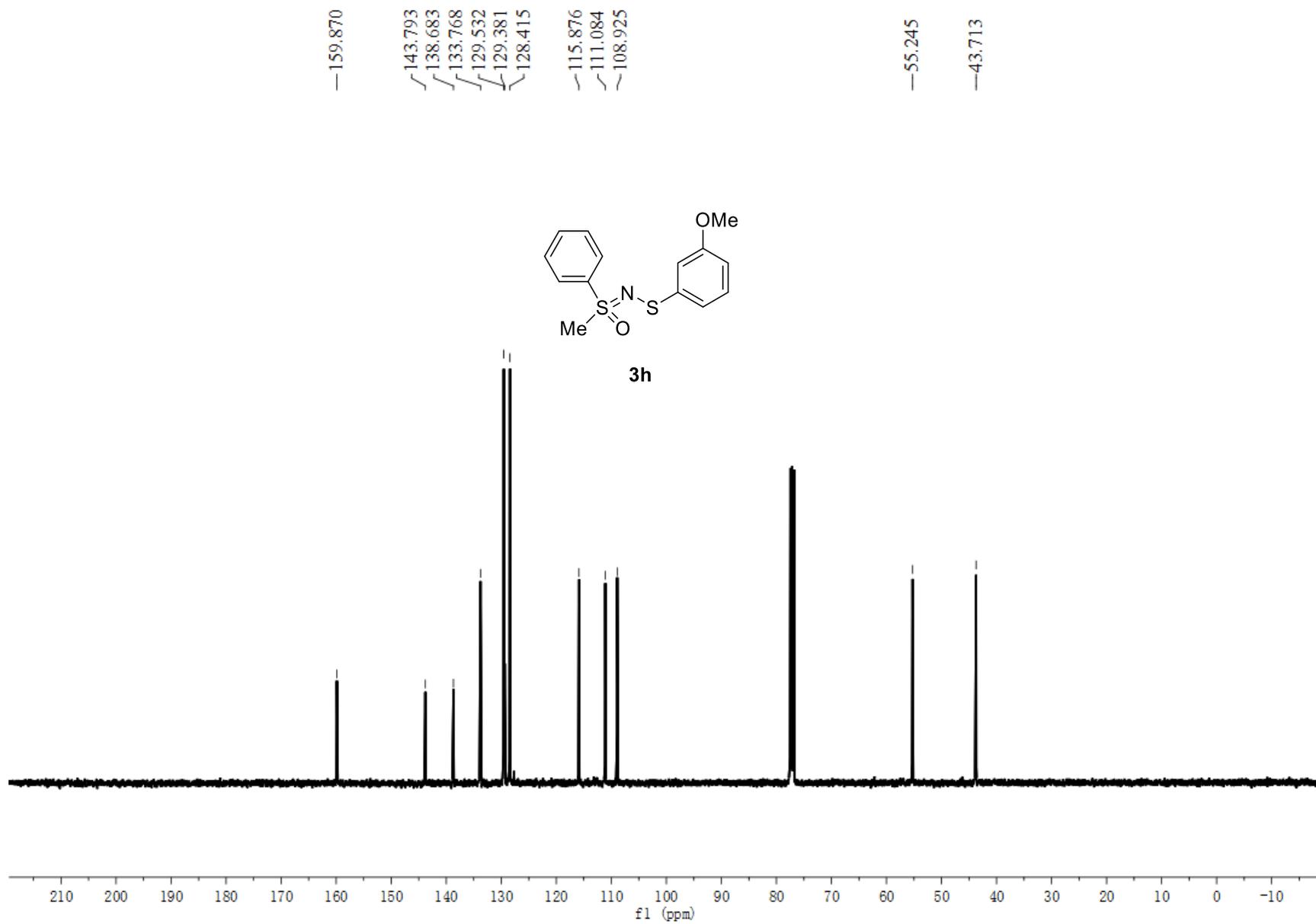
¹³C NMR spectra of compound **3g** (101 MHz, CDCl₃)



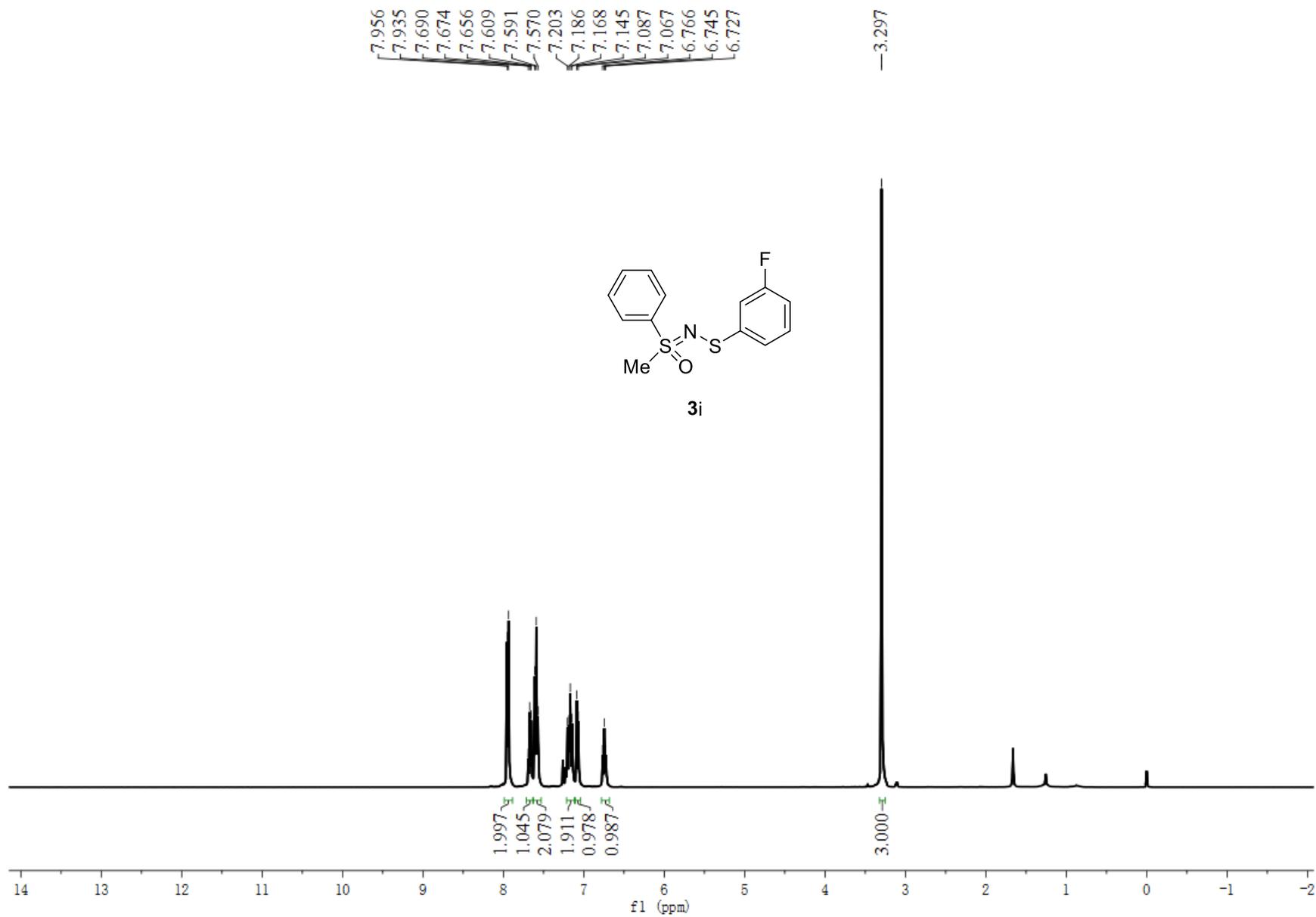
¹H NMR spectra of compound **3h** (400 MHz, CDCl₃)



^{13}C NMR spectra of compound **3h** (101 MHz, CDCl_3)



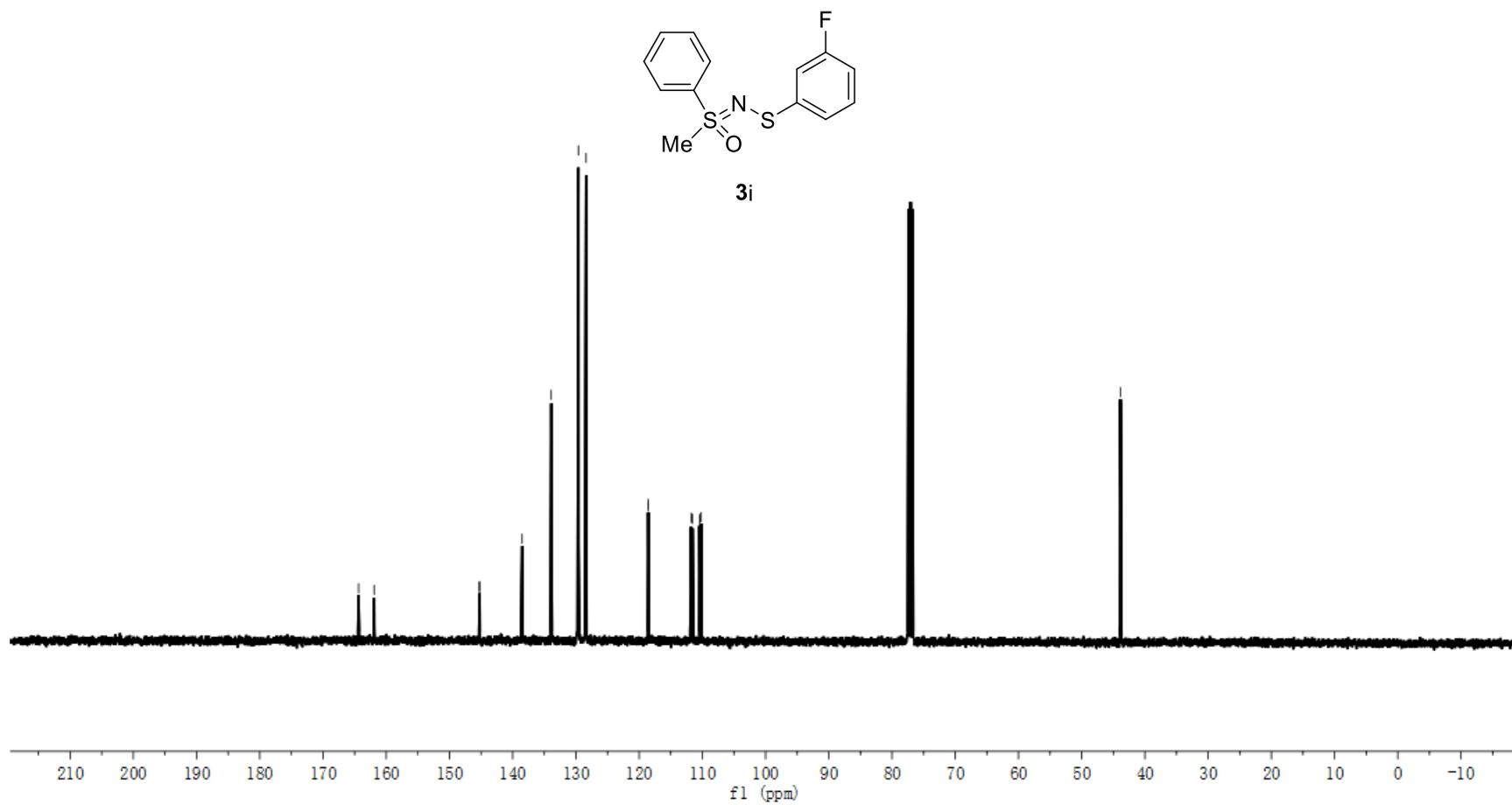
¹H NMR spectra of compound **3i** (400 MHz, CDCl₃)



¹³C NMR spectra of compound **3i** (101 MHz, CDCl₃)

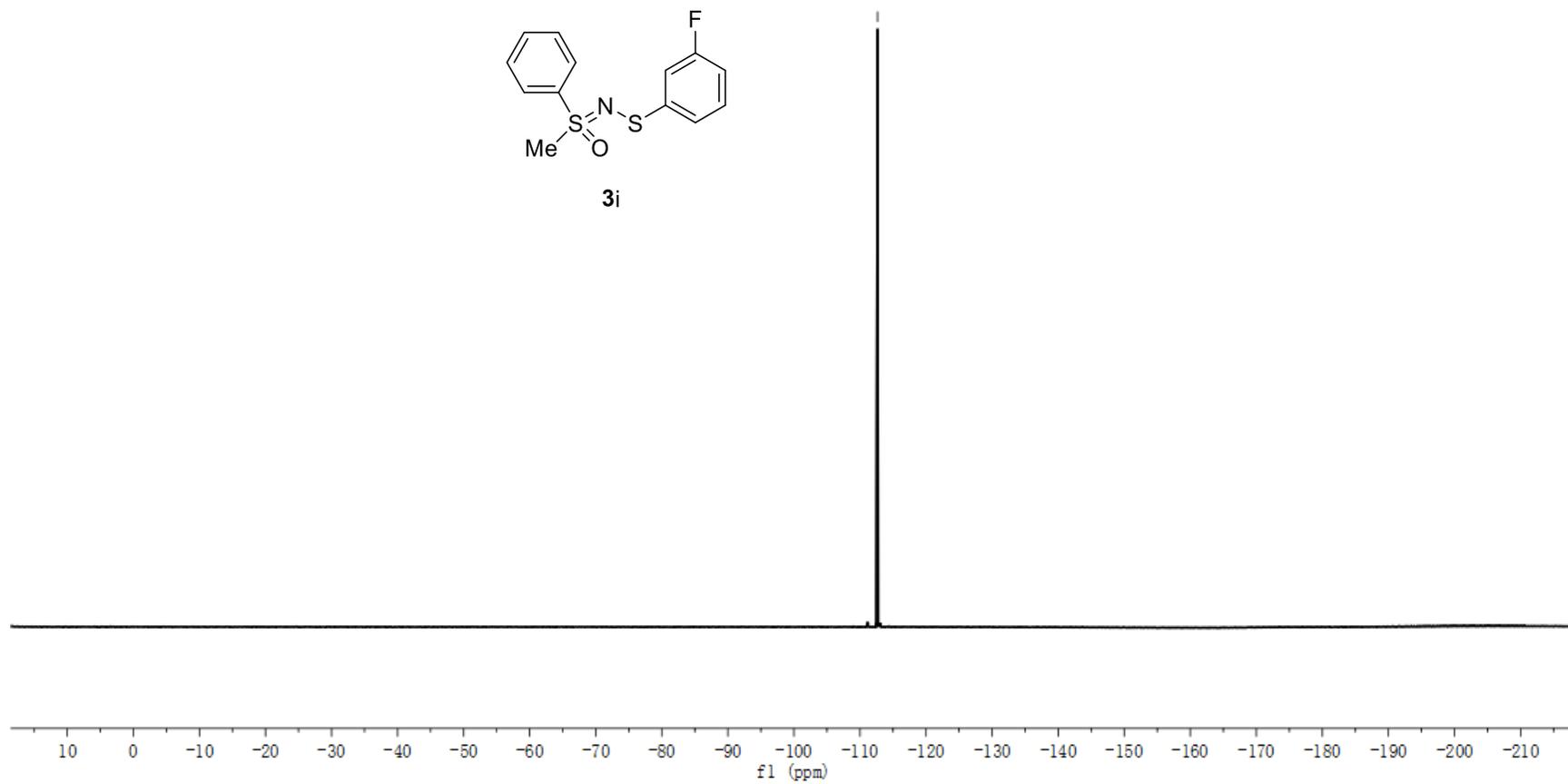
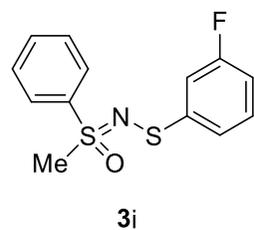
164.368
161.912
145.299
145.224
138.510
133.902
129.784
129.699
129.611
128.387
118.571
118.543
111.788
111.573
110.427
110.182

43.872

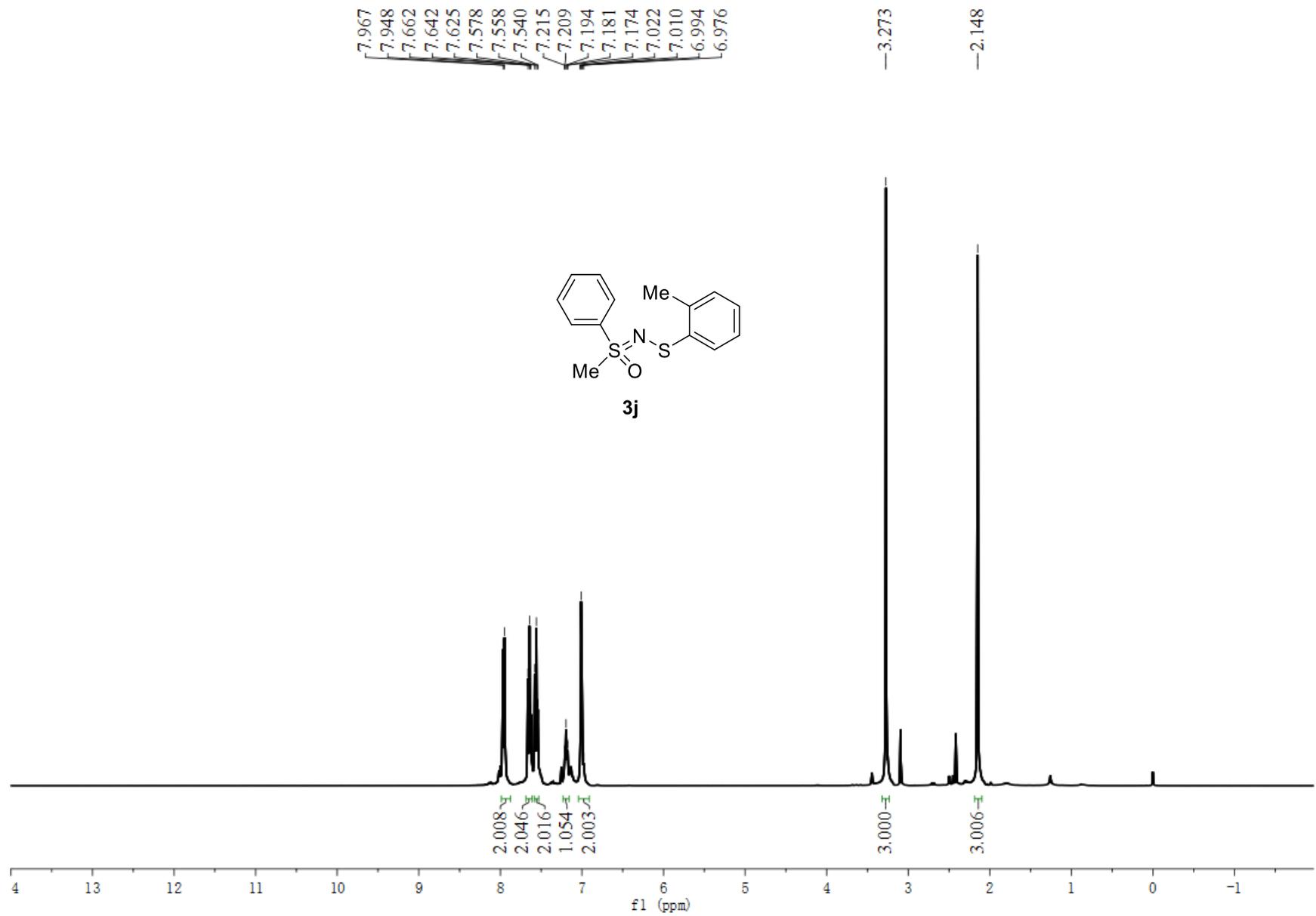


^{19}F NMR spectra of compound **3i** (376 MHz, CDCl_3)

---112.656



¹H NMR spectra of compound **3j** (400 MHz, CDCl₃)

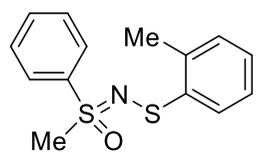


¹³C NMR spectra of compound **3j** (101 MHz, CDCl₃)

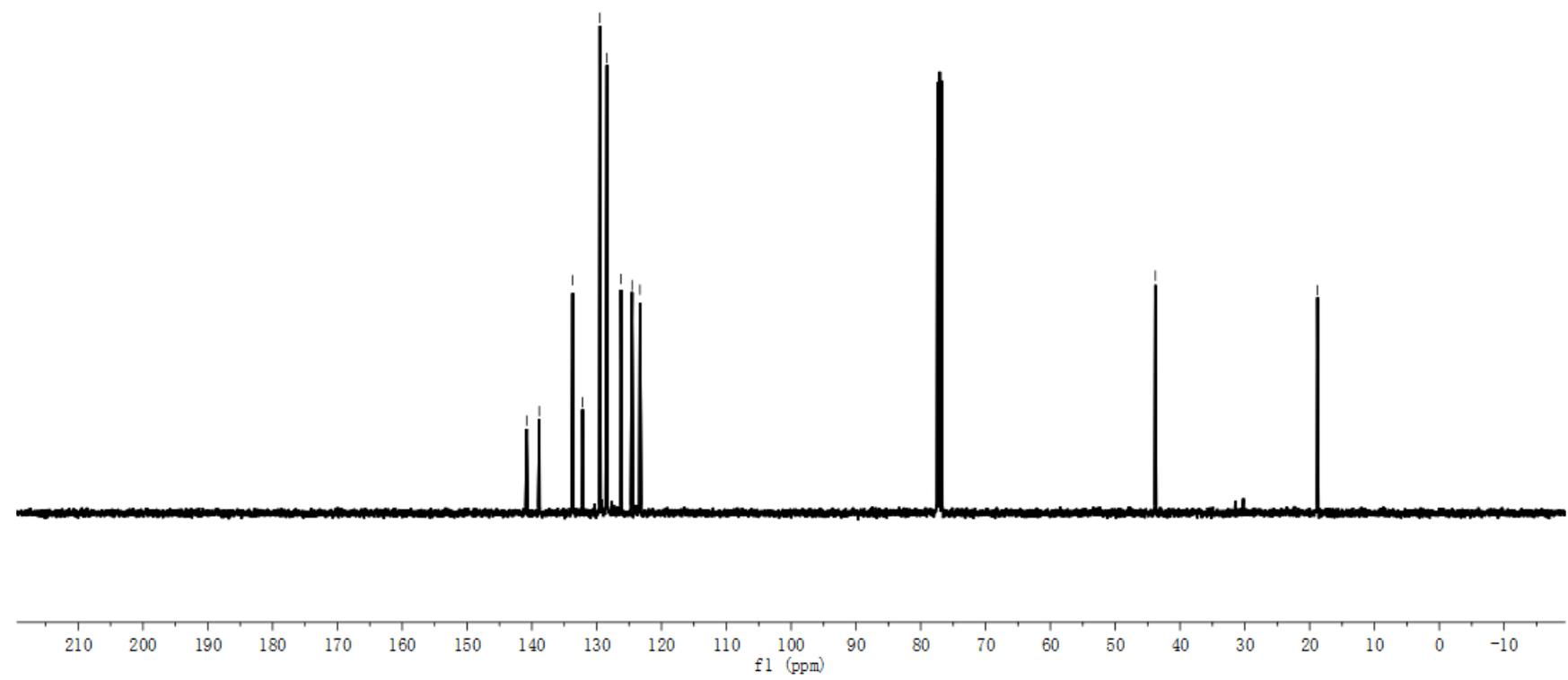
140.801
138.858
133.702
132.181
129.504
129.483
128.414
126.247
124.542
123.323

—43.801

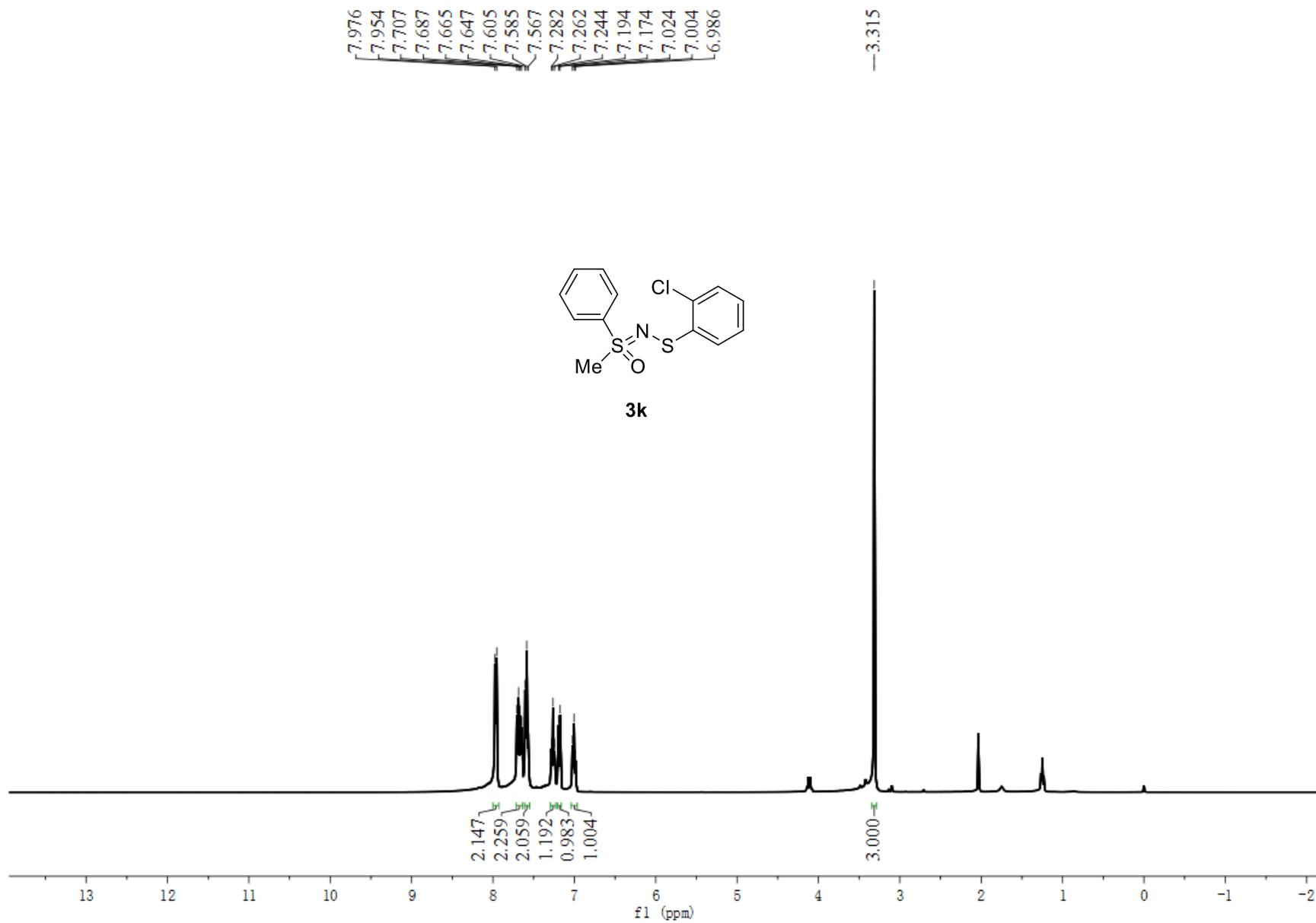
—18.782



3j



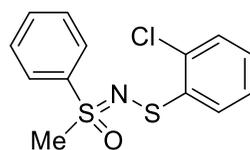
¹H NMR spectra of compound **3k** (400 MHz, CDCl₃)



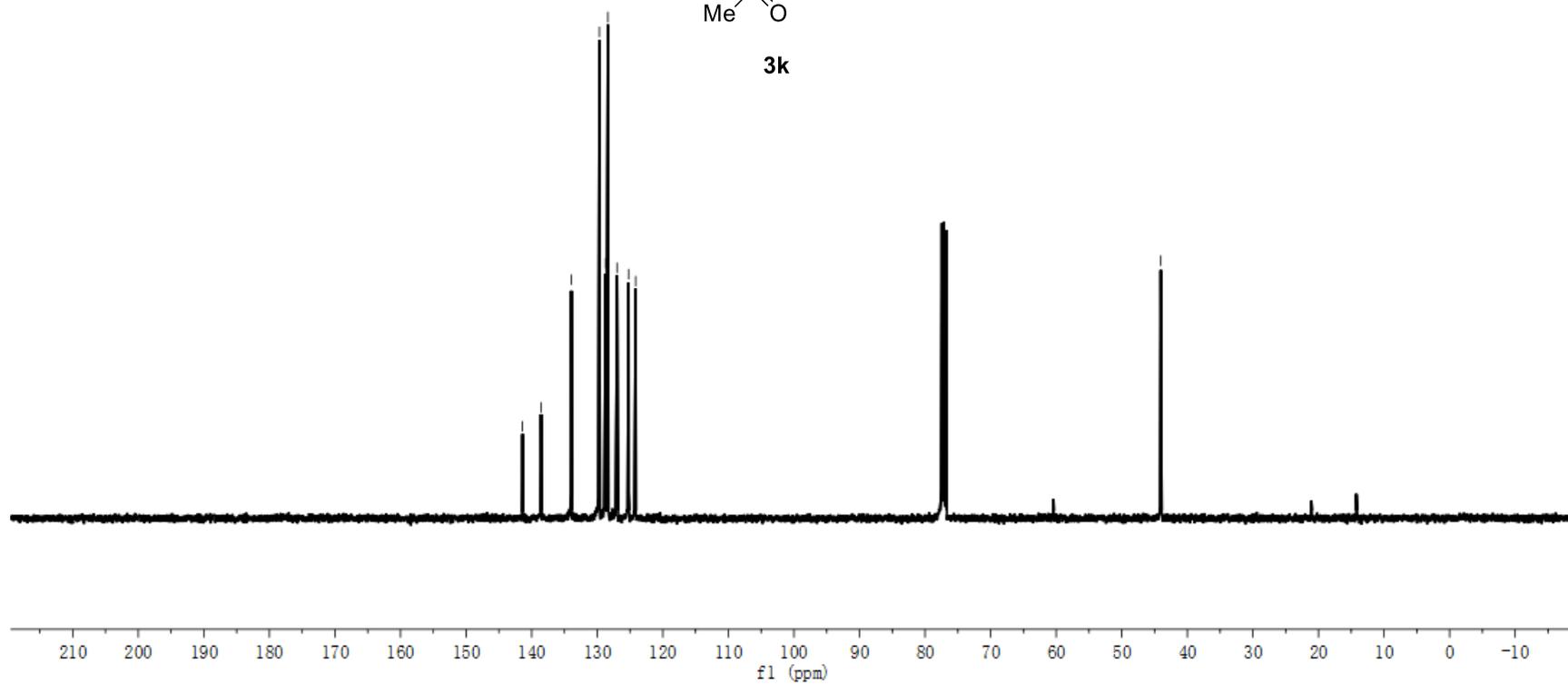
¹³C NMR spectra of compound **3k** (101 MHz, CDCl₃)

141.394
138.557
133.943
129.673
128.737
128.363
126.977
126.896
125.223
124.145

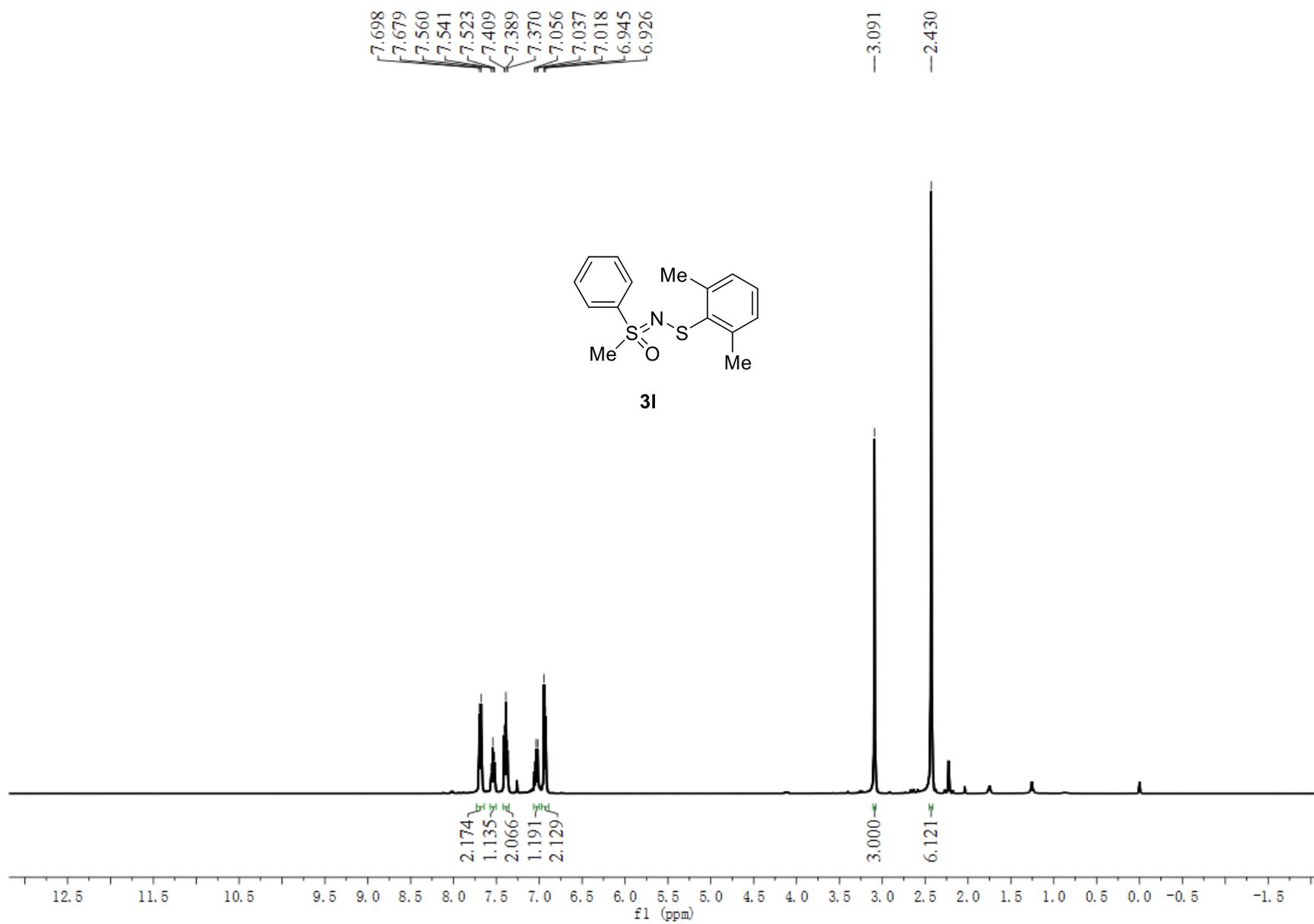
—44.044



3k



¹H NMR spectra of compound **31** (400 MHz, CDCl₃)

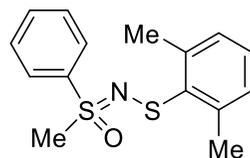


¹³C NMR spectra of compound **31** (101 MHz, CDCl₃)

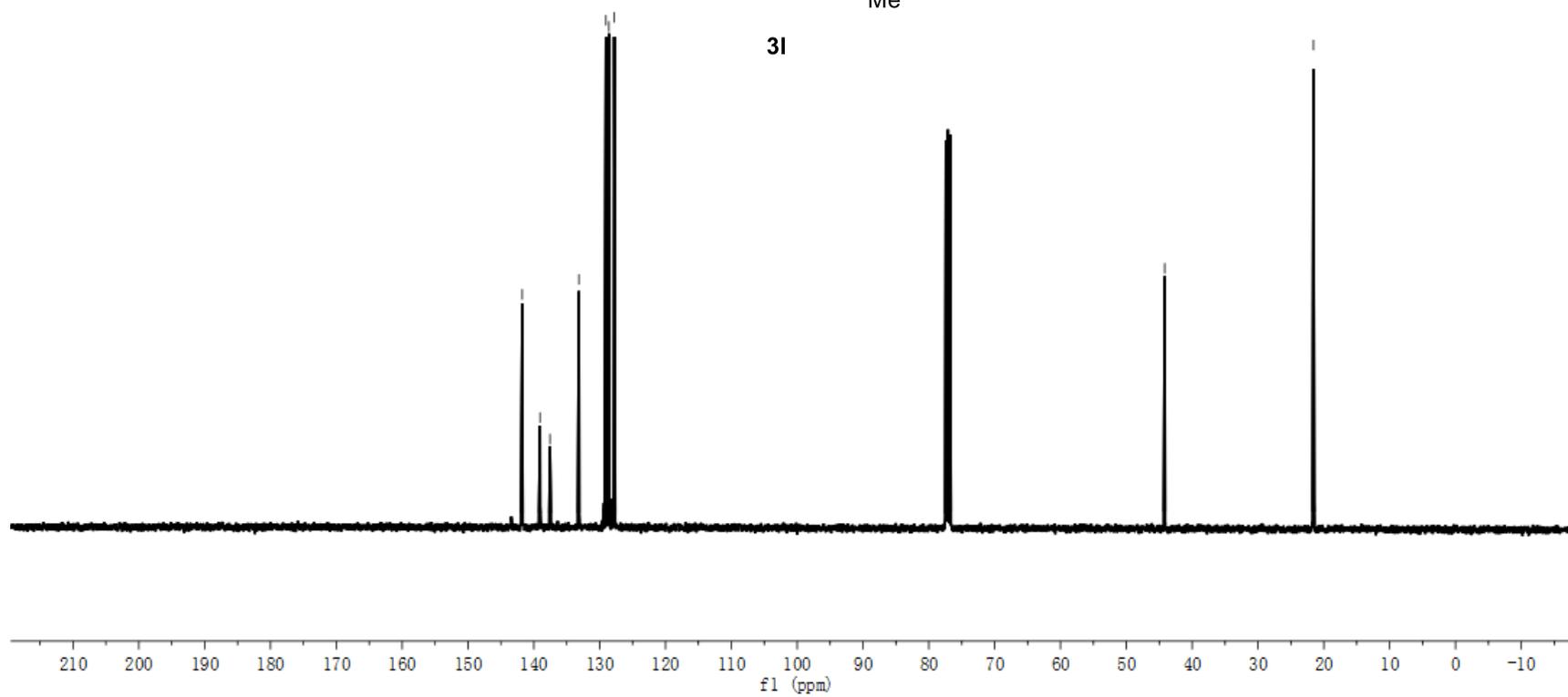
141.762
139.062
137.547
133.148
129.047
128.717
128.597
127.770

—44.174

—21.573

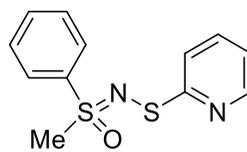


31

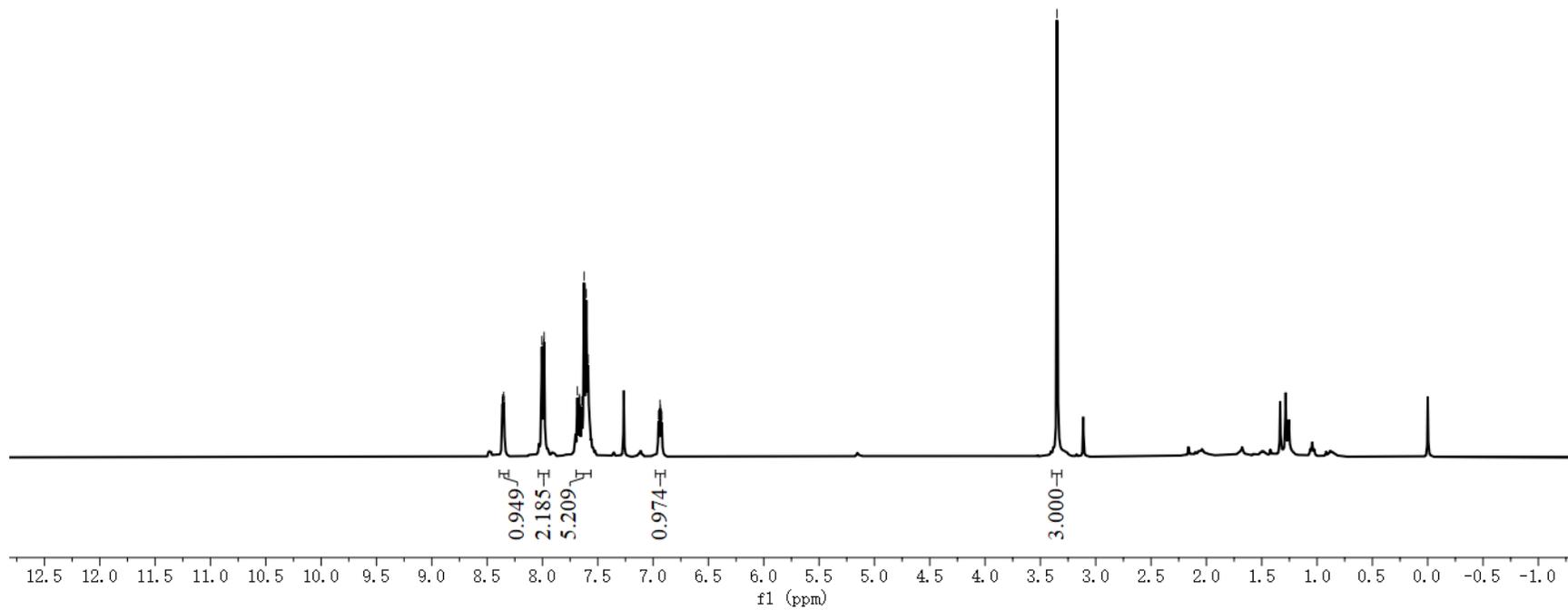


¹H NMR spectra of compound **3m** (400 MHz, CDCl₃)

8.362
8.358
8.350
8.346
8.005
7.987
7.985
7.982
7.684
7.667
7.664
7.646
7.624
7.605
7.591
7.587
7.584
7.573
6.954
6.951
6.938
6.933
6.924
6.921
— 3.350



3m



¹³C NMR spectra of compound **3m** (101 MHz, CDCl₃)

—165.829

—148.590

—138.373

—136.606

—133.925

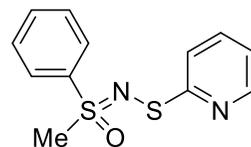
—129.610

—128.464

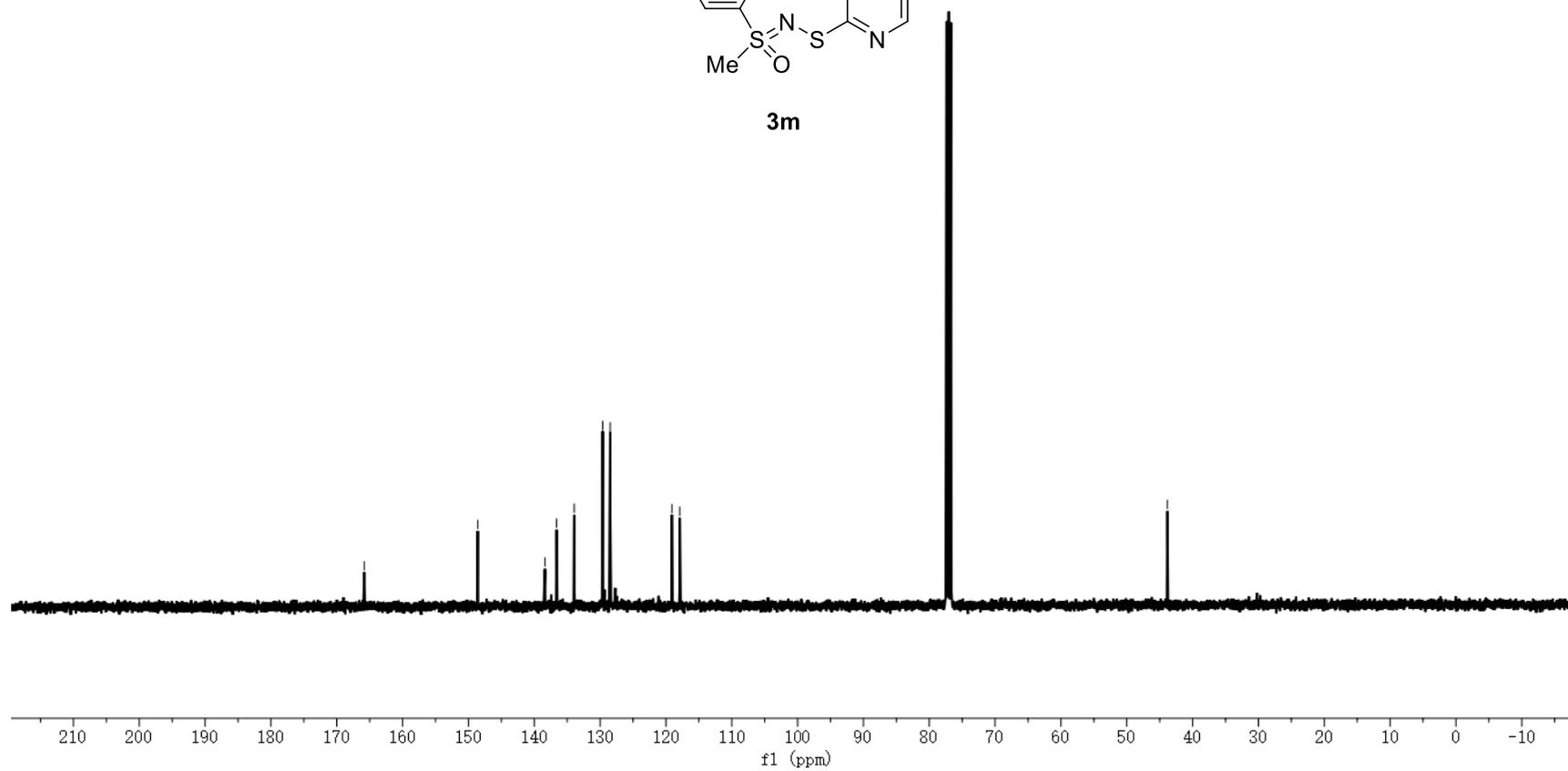
—119.101

—117.902

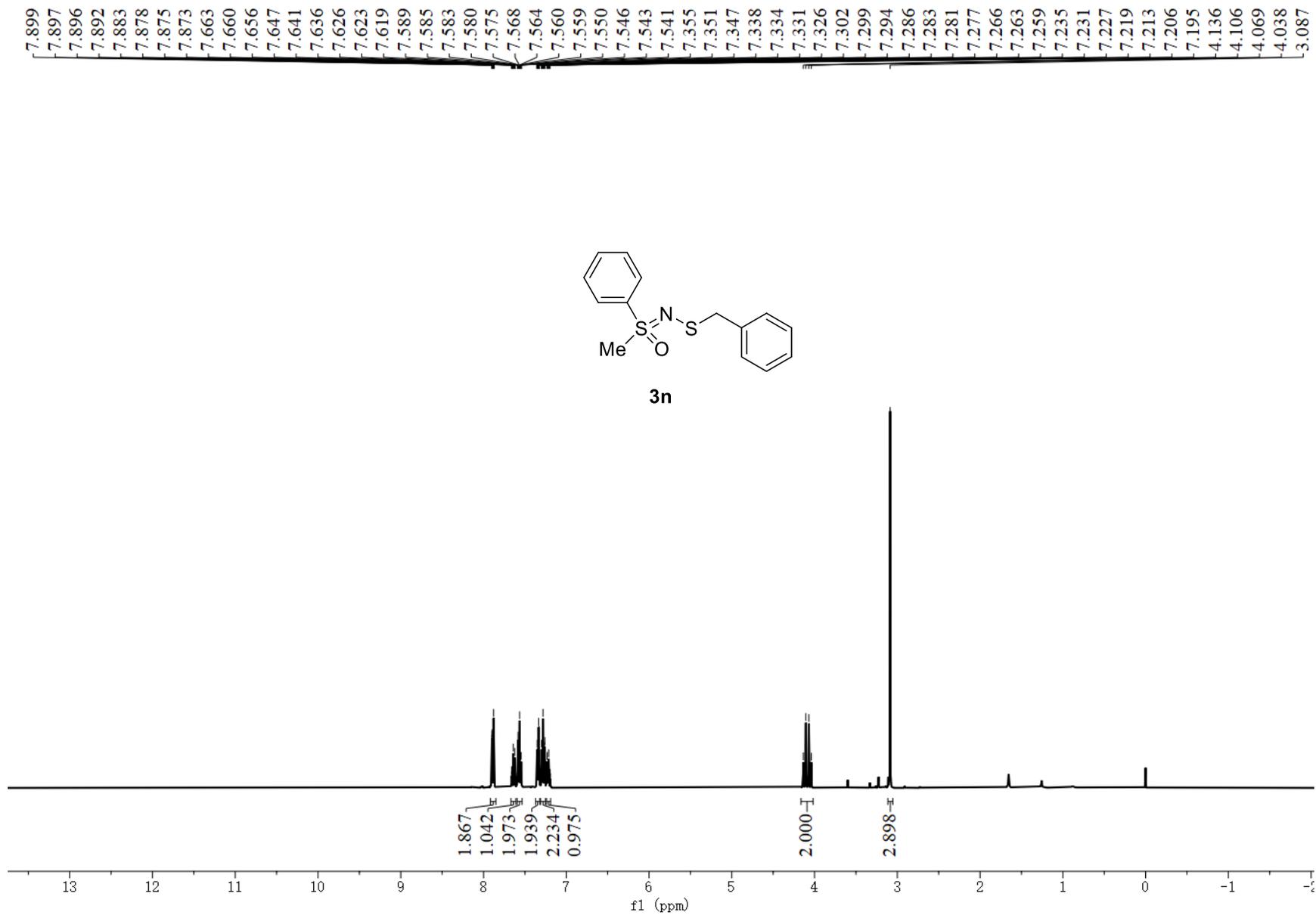
—43.832



3m



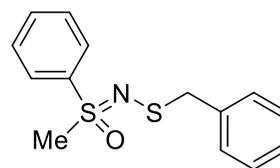
¹H NMR spectra of compound **3n** (400 MHz, CDCl₃)



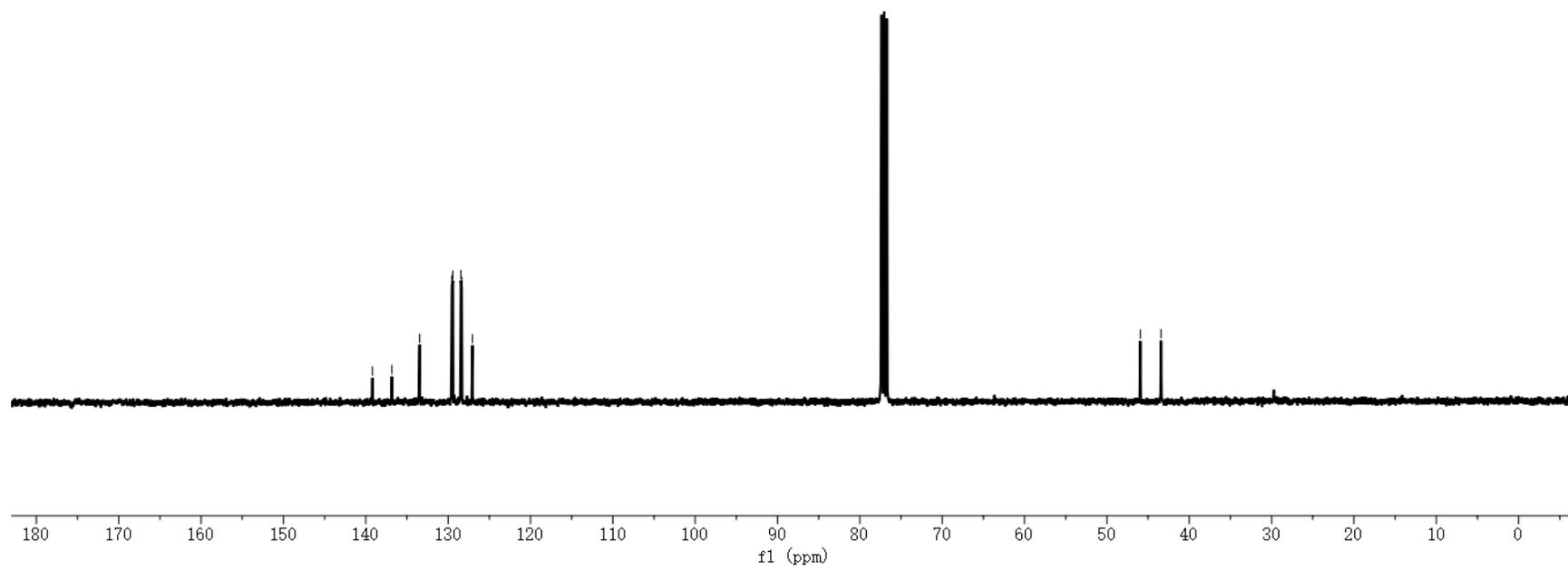
¹³C NMR spectra of compound **3n** (101 MHz, CDCl₃)

139.190
136.834
133.459
129.545
129.423
128.451
128.356
127.051

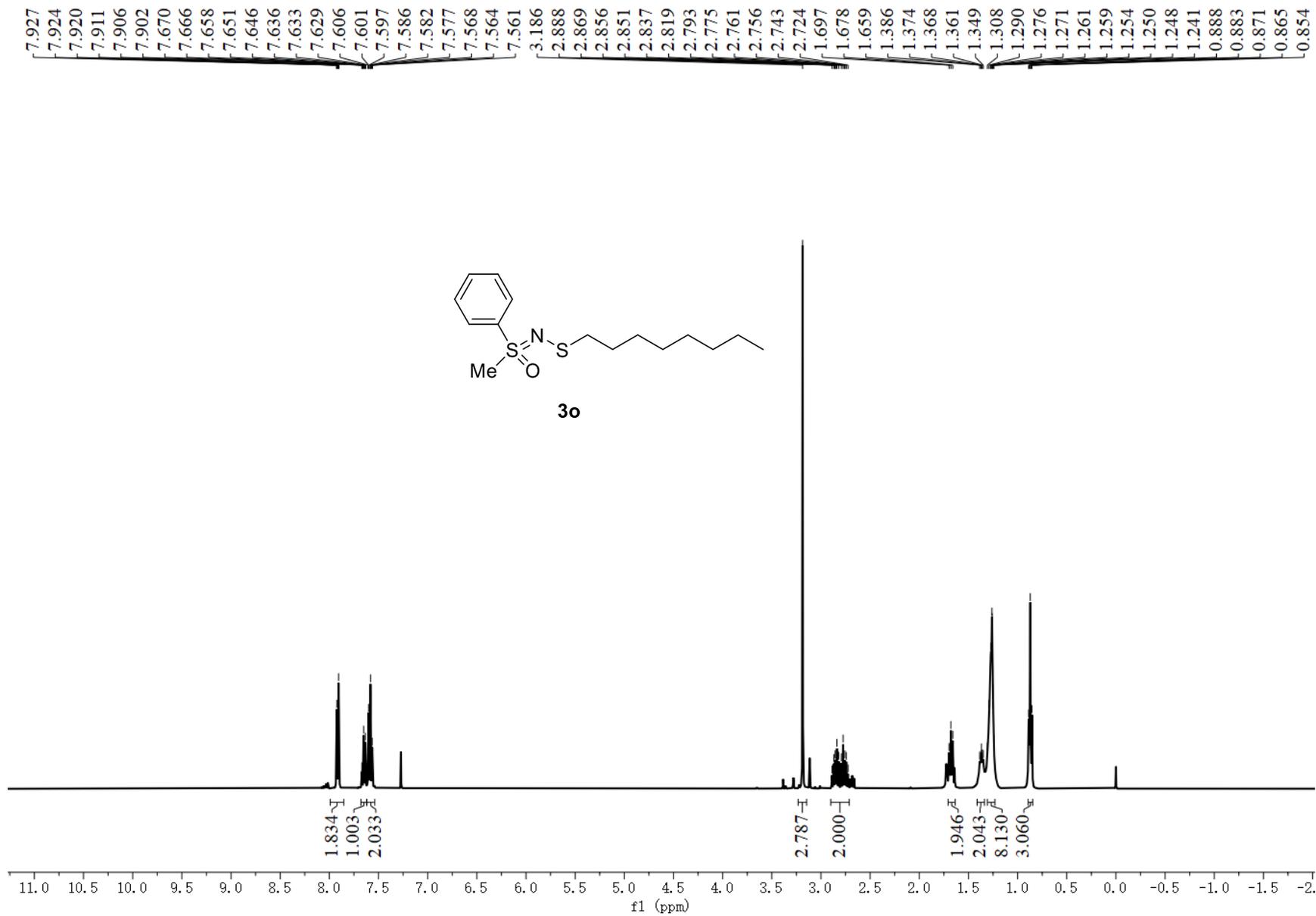
45.943
43.435



3n



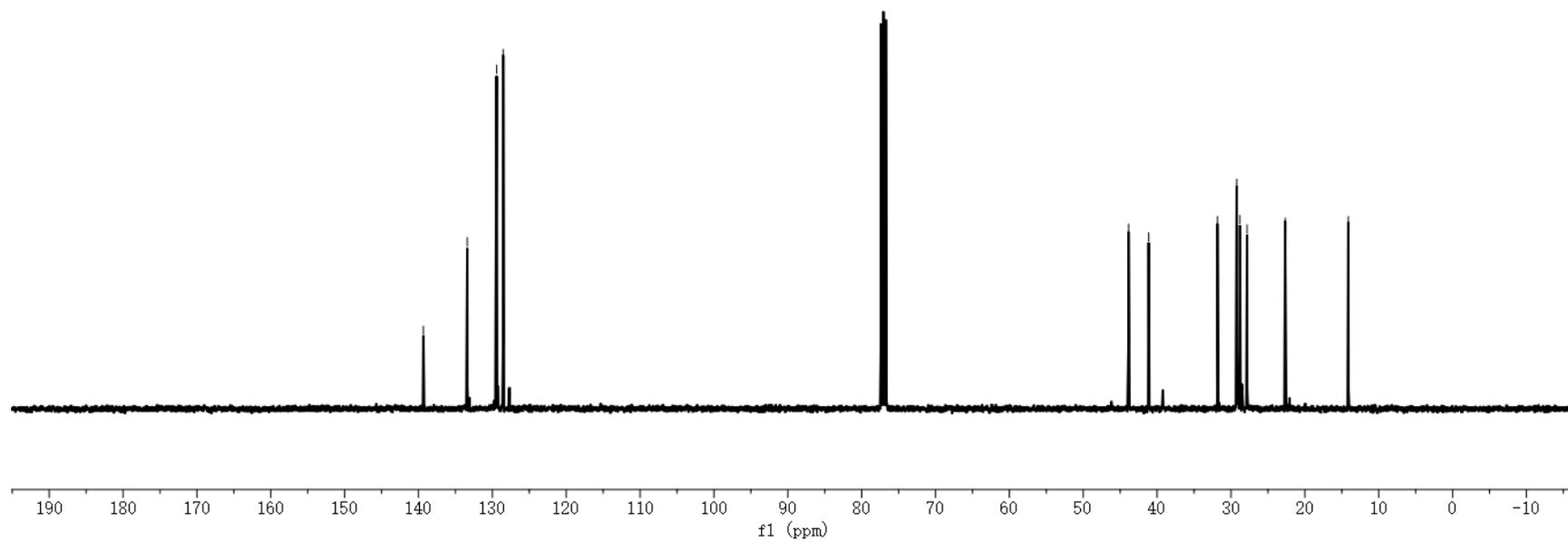
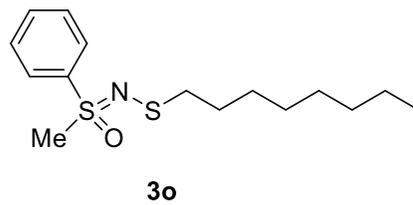
¹H NMR spectra of compound **3o** (400 MHz, CDCl₃)



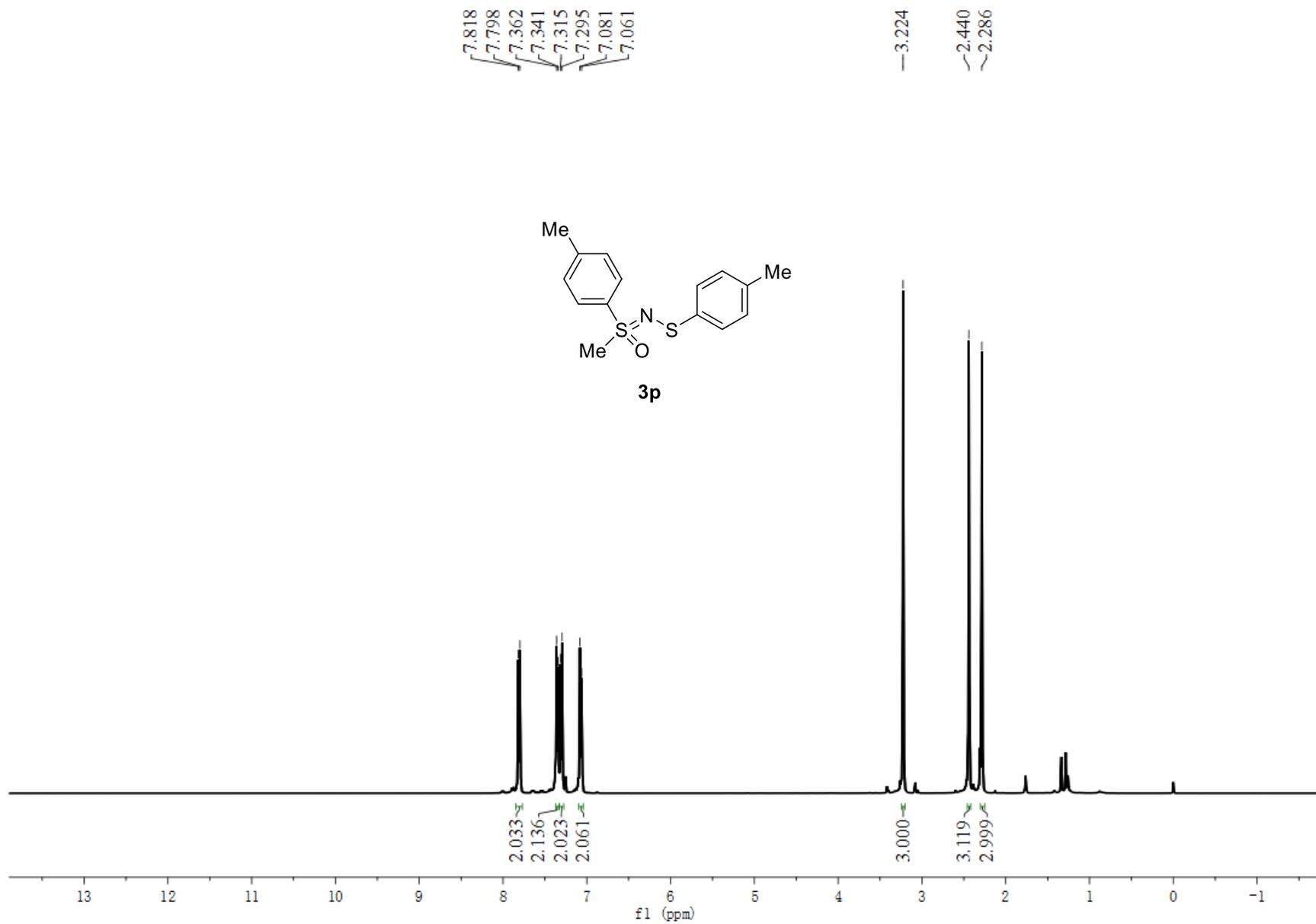
NMR spectra of compound **3o** (101 MHz, CDCl₃)

139.340
133.395
129.422
128.533

43.861
41.137
31.838
29.243
29.224
28.794
27.825
22.657
14.112



¹H NMR spectra of compound **3p** (400 MHz, CDCl₃)

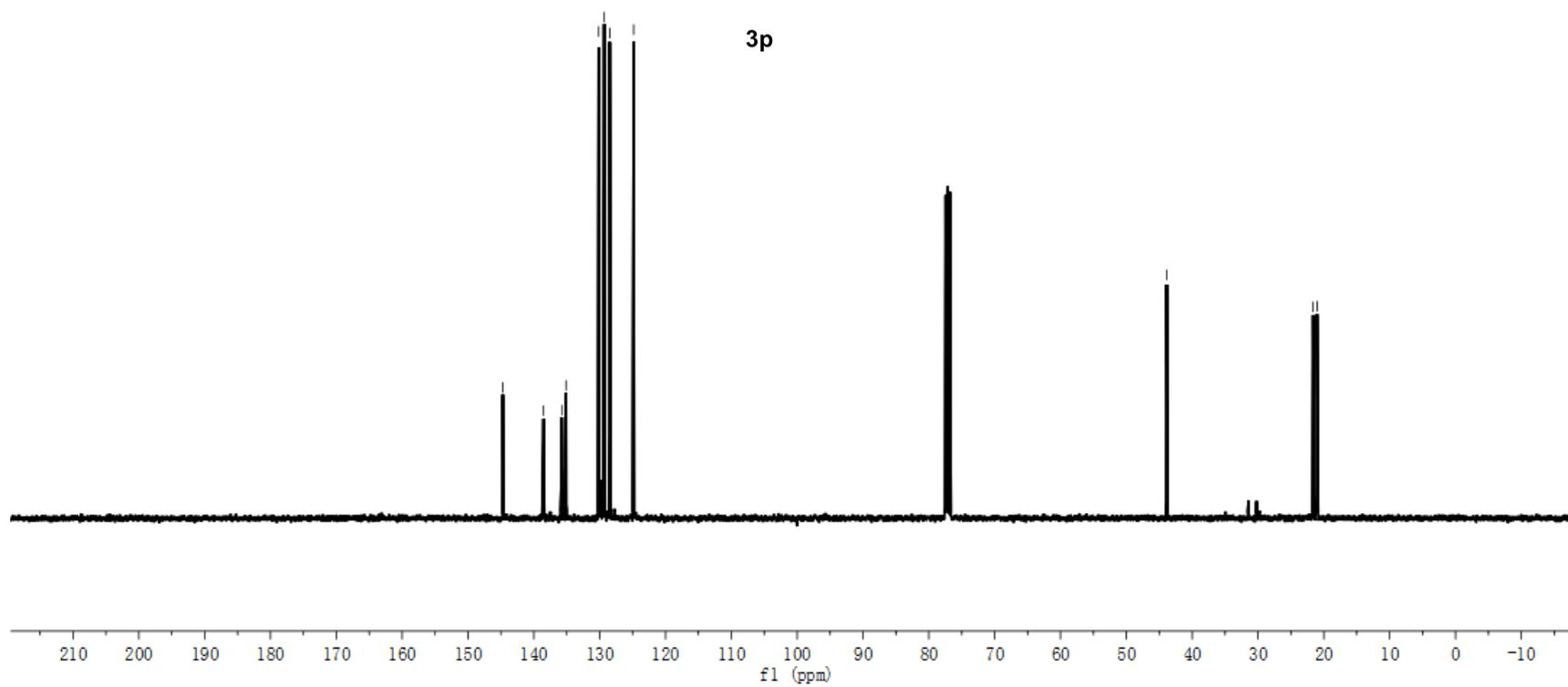
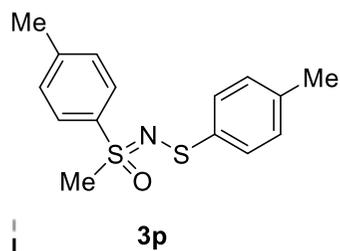


^{13}C NMR spectra of compound **3p** (101 MHz, CDCl_3)

144.717
138.524
135.742
135.107
130.148
129.300
128.480
124.835

—43.869

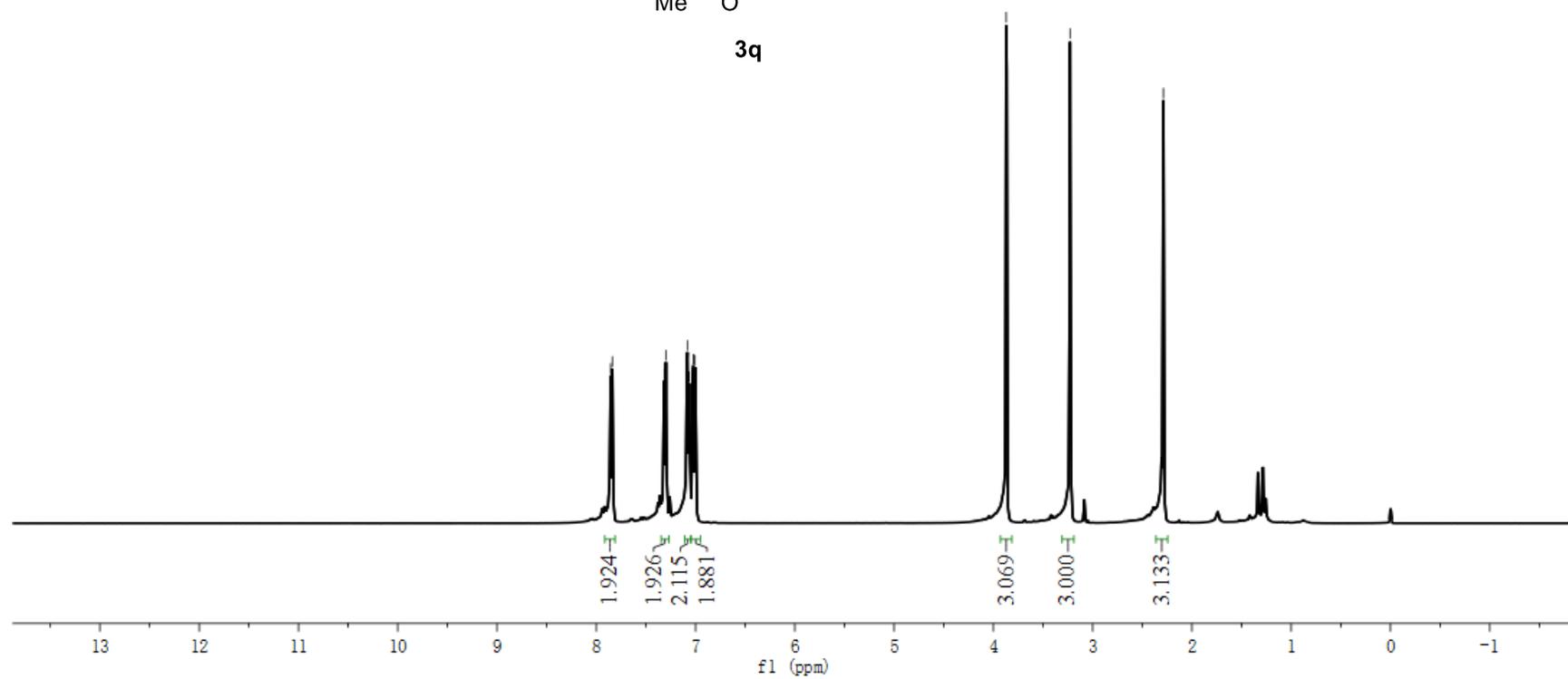
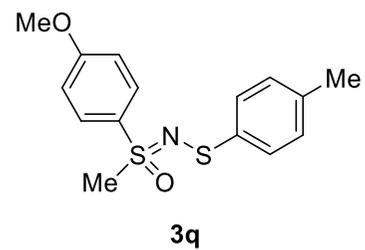
21.629
21.029



¹H NMR spectra of compound **3q** (400 MHz, CDCl₃)

7.855
7.838
7.314
7.298
7.082
7.064
7.027
7.022
7.005
7.000

— 3.870
— 3.227
— 2.288



¹³C NMR spectra of compound **3q** (101 MHz, CDCl₃)

—163.719

138.458

135.009

130.534

129.741

129.211

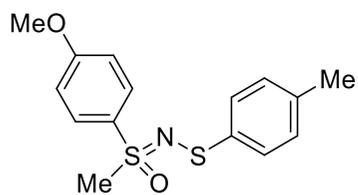
124.719

—114.636

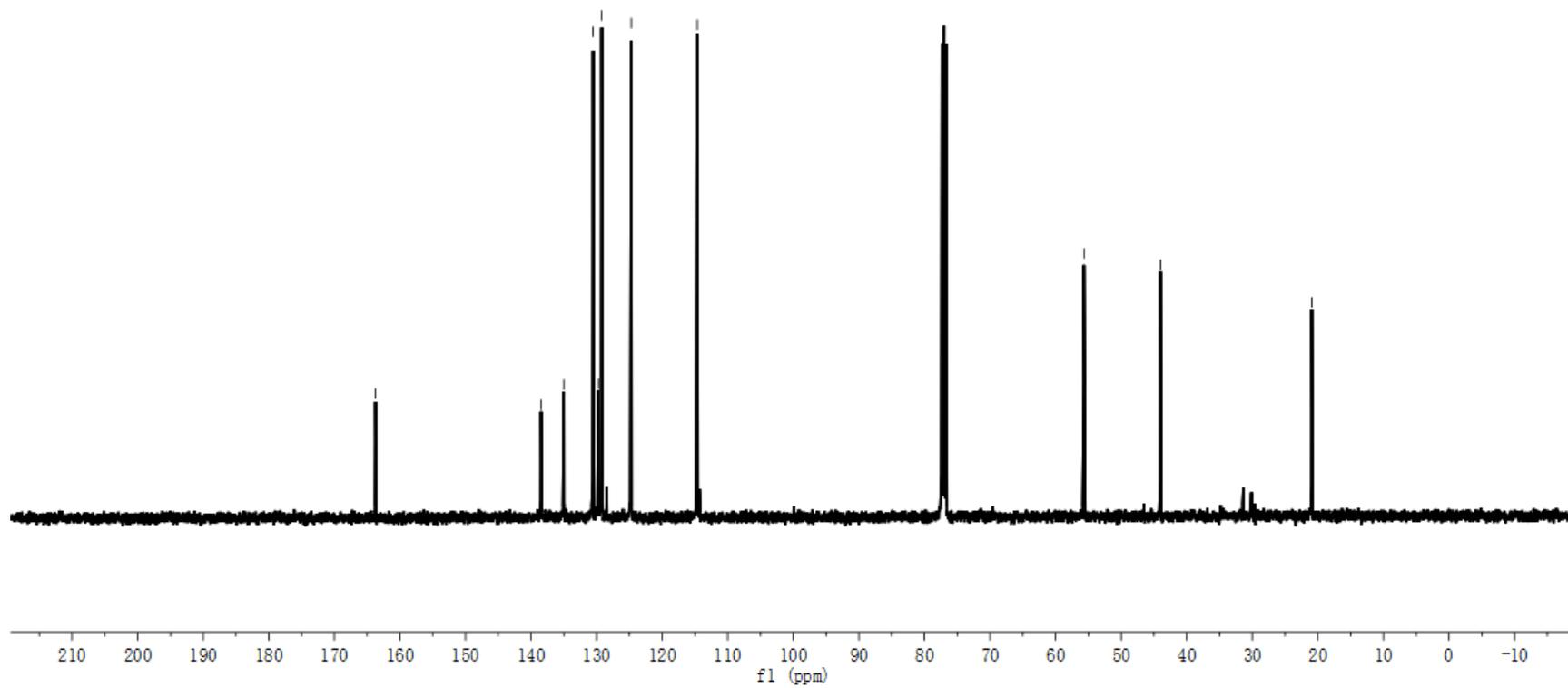
—55.667

—43.996

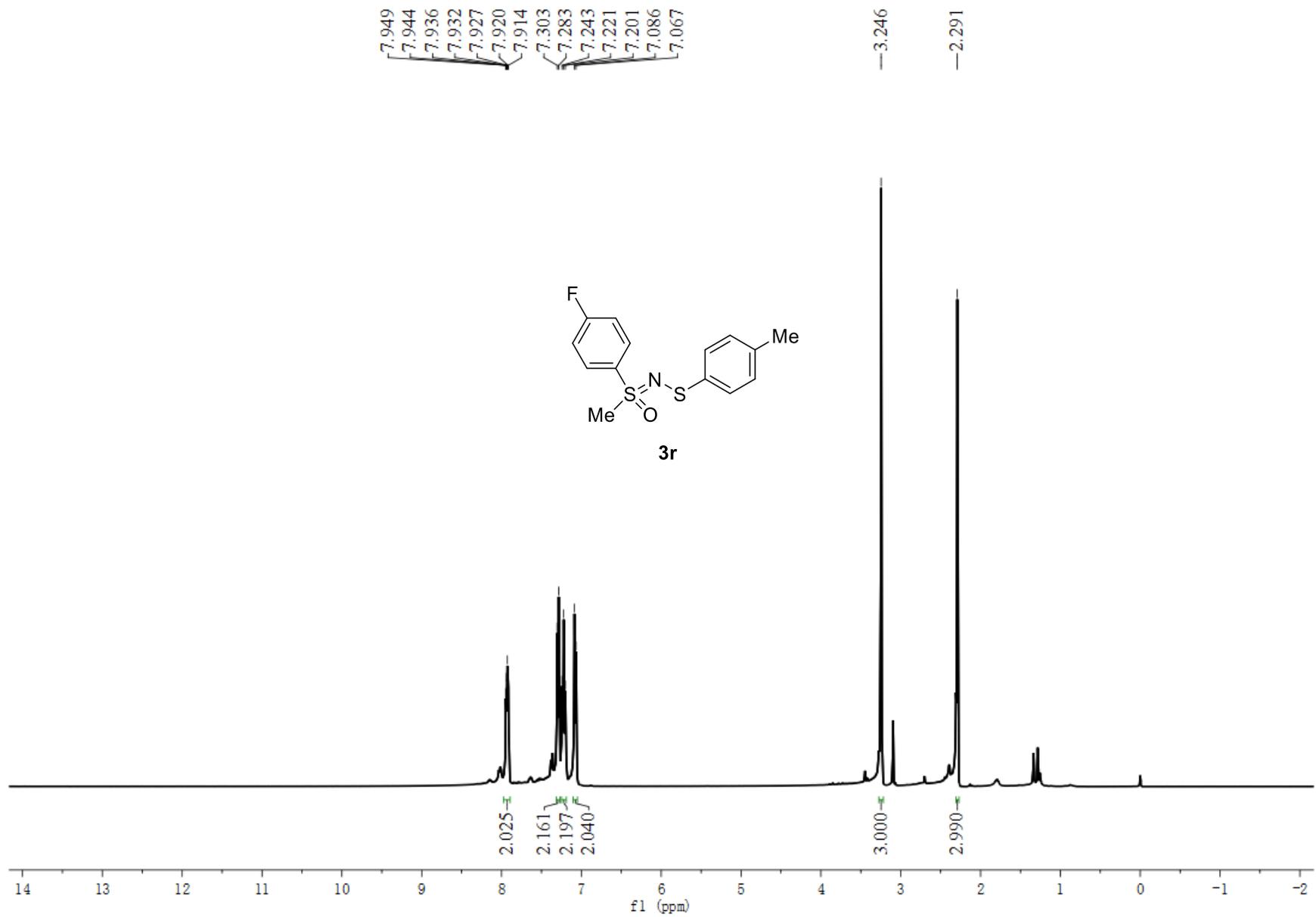
—20.930



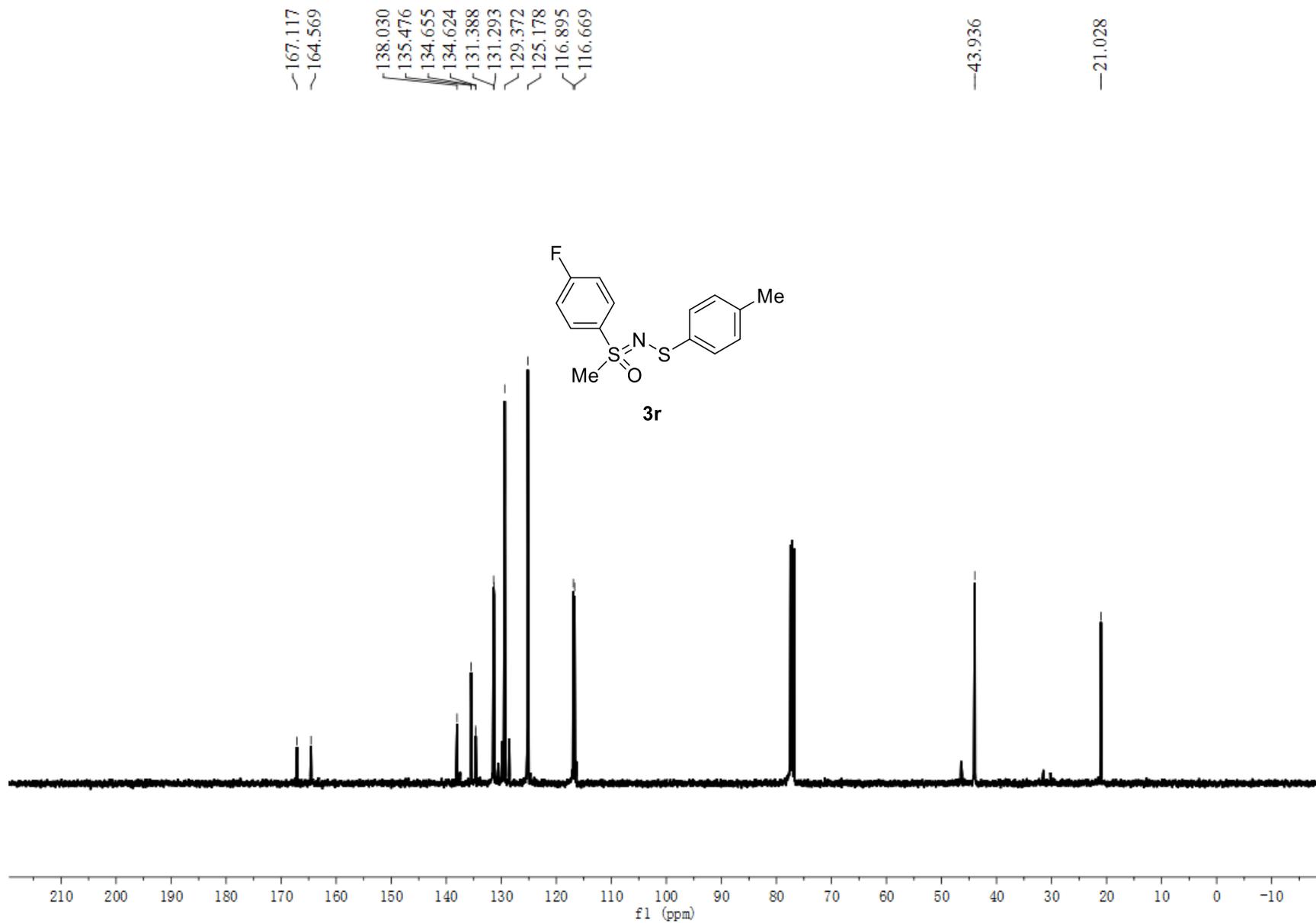
3q



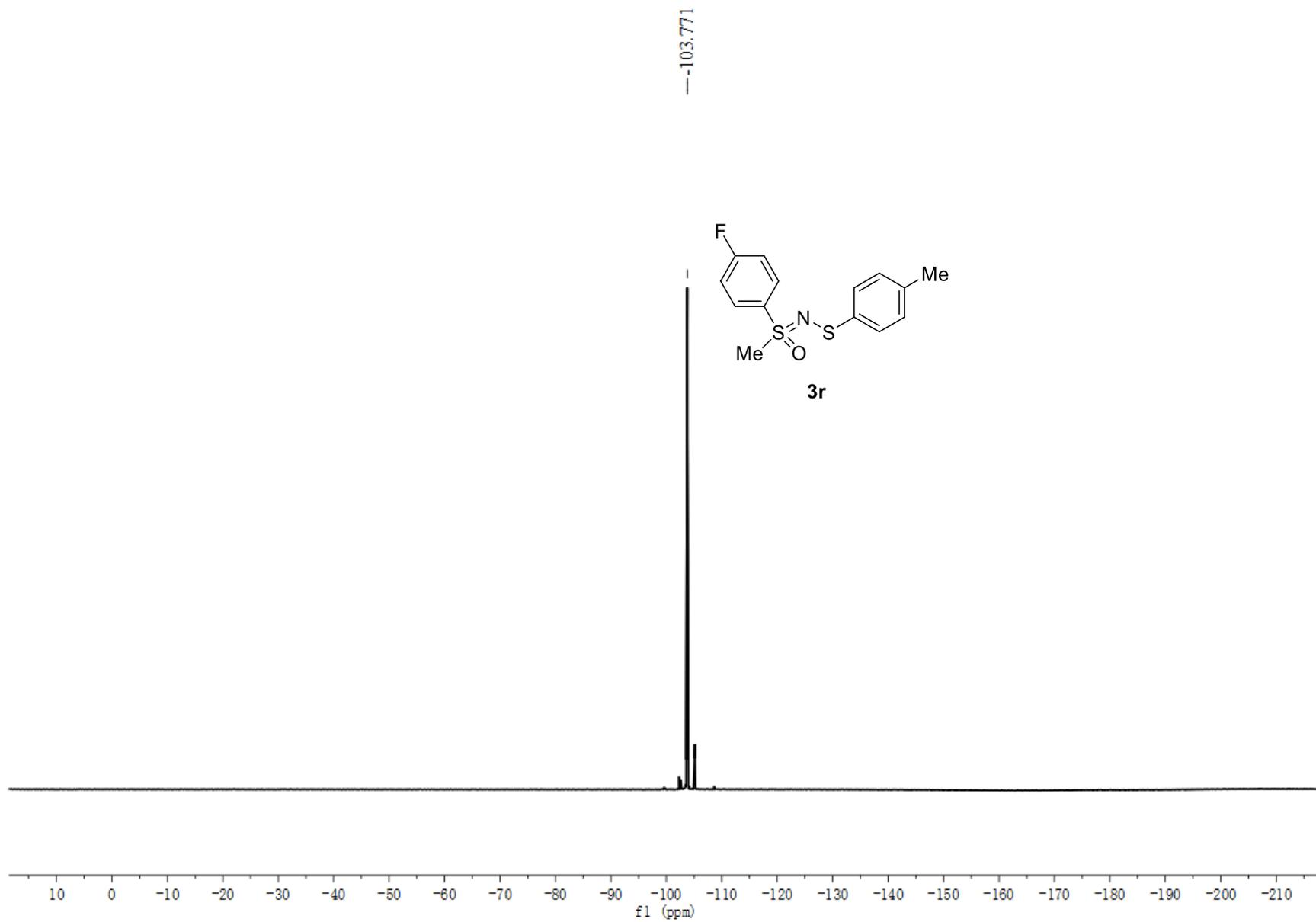
¹H NMR spectra of compound **3r** (400 MHz, CDCl₃)



¹³C NMR spectra of compound **3r** (101 MHz, CDCl₃)

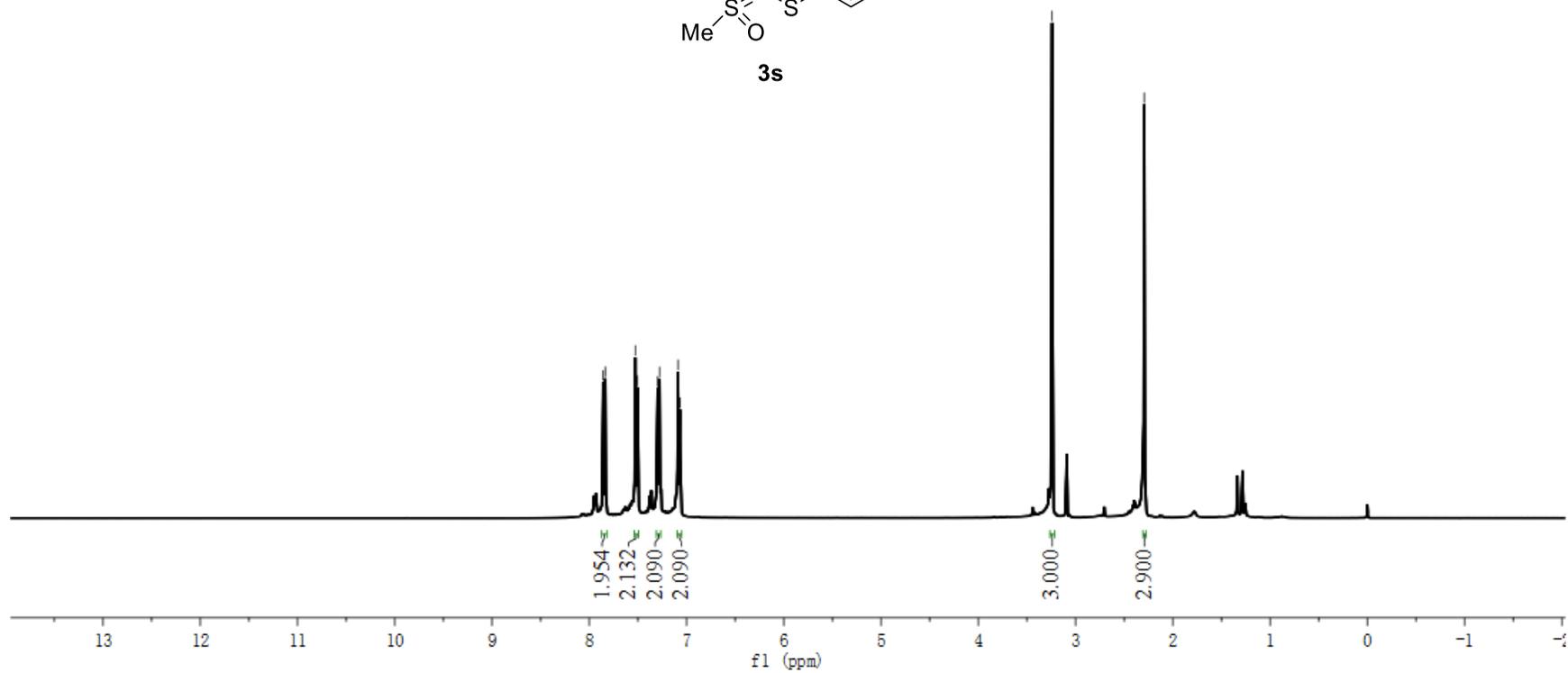
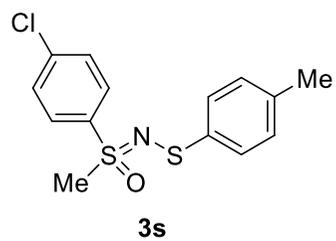


^{19}F NMR spectra of compound **3r** (376 MHz, CDCl_3)



¹H NMR spectra of compound **3s** (400 MHz, CDCl₃)

7.857
7.835
7.526
7.504
7.297
7.277
7.087
7.067
— 3.242
— 2.294

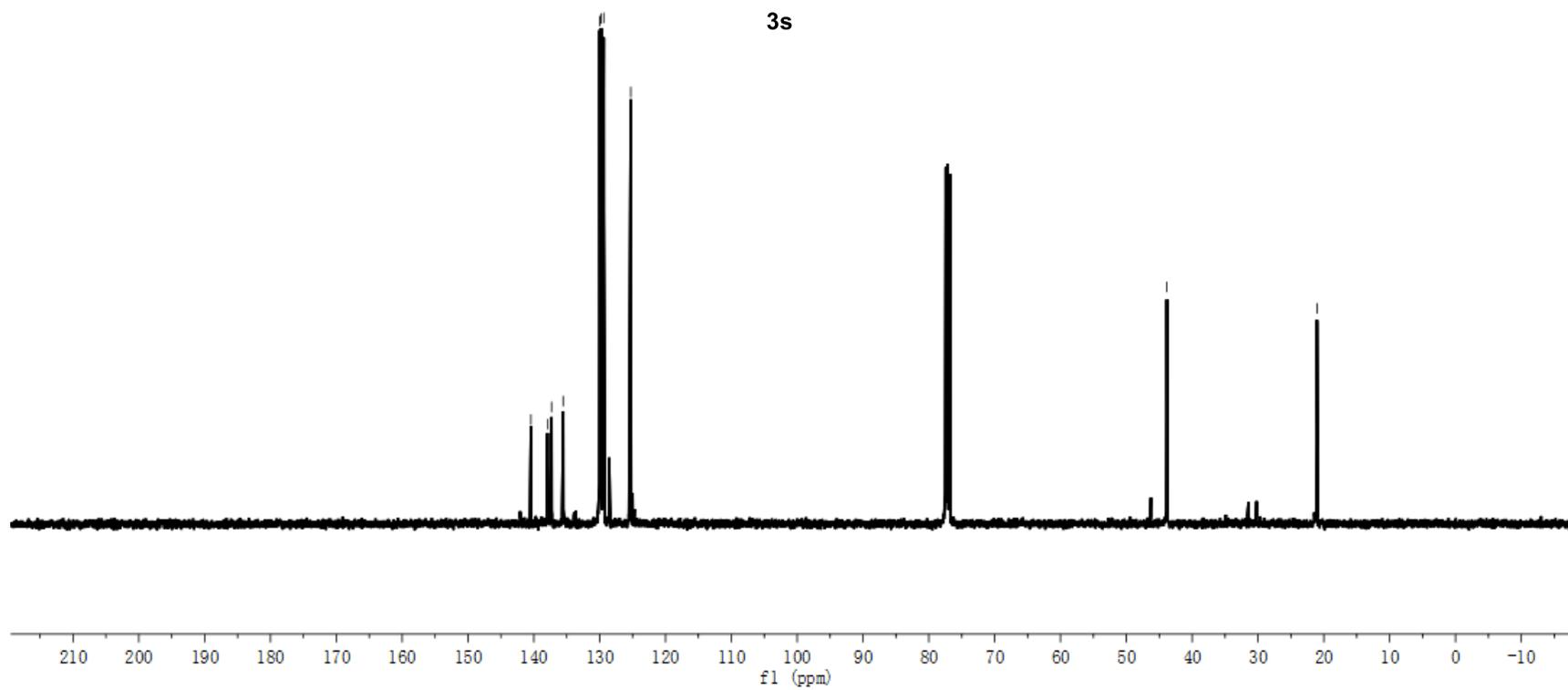
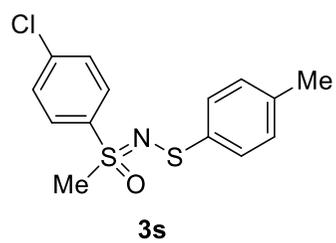


¹³C NMR spectra of compound **3s** (101 MHz, CDCl₃)

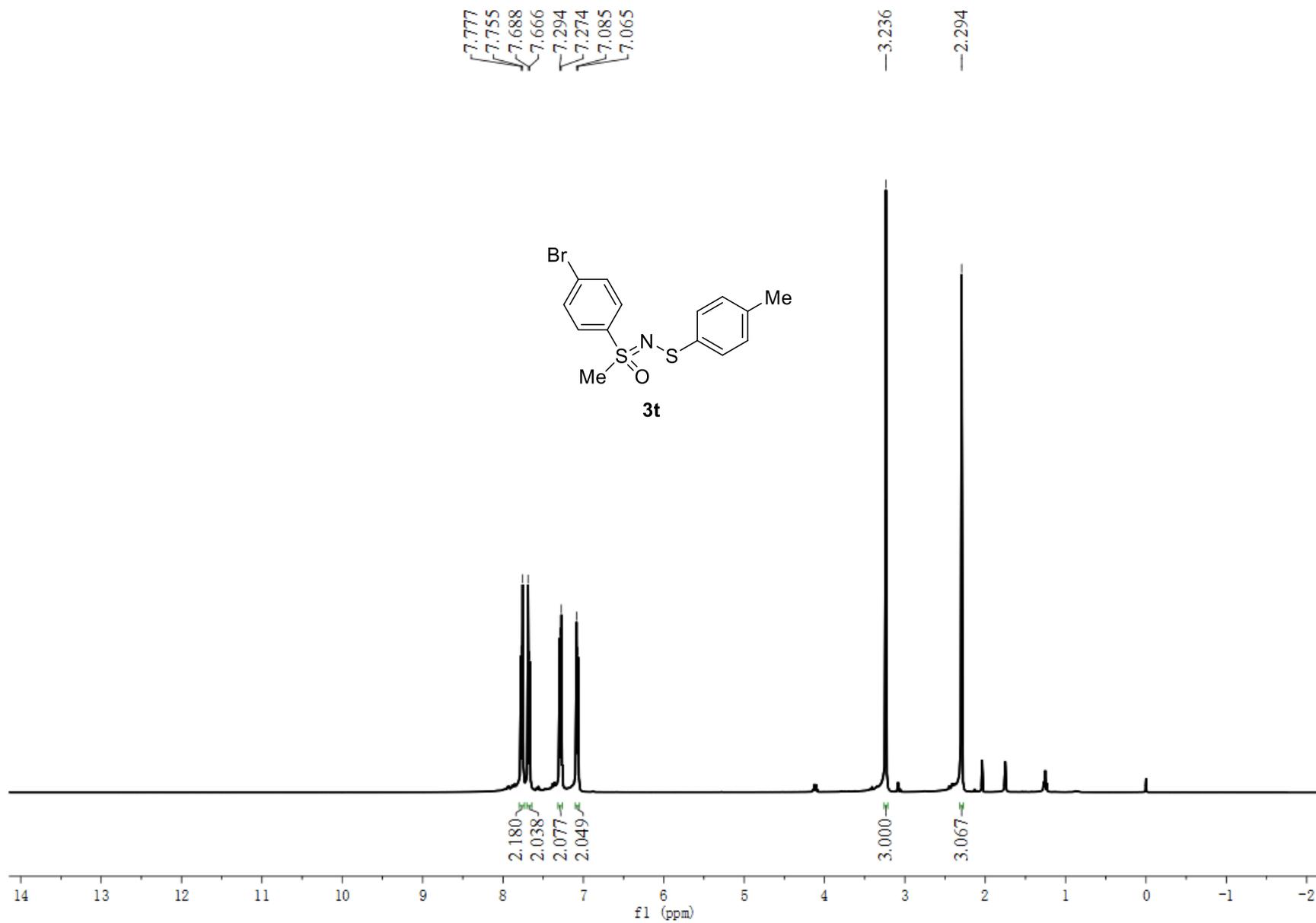
140.452
137.917
137.304
135.547
129.985
129.770
129.379
125.271

—43.844

—21.044



¹H NMR spectra of compound **3t** (400 MHz, CDCl₃)

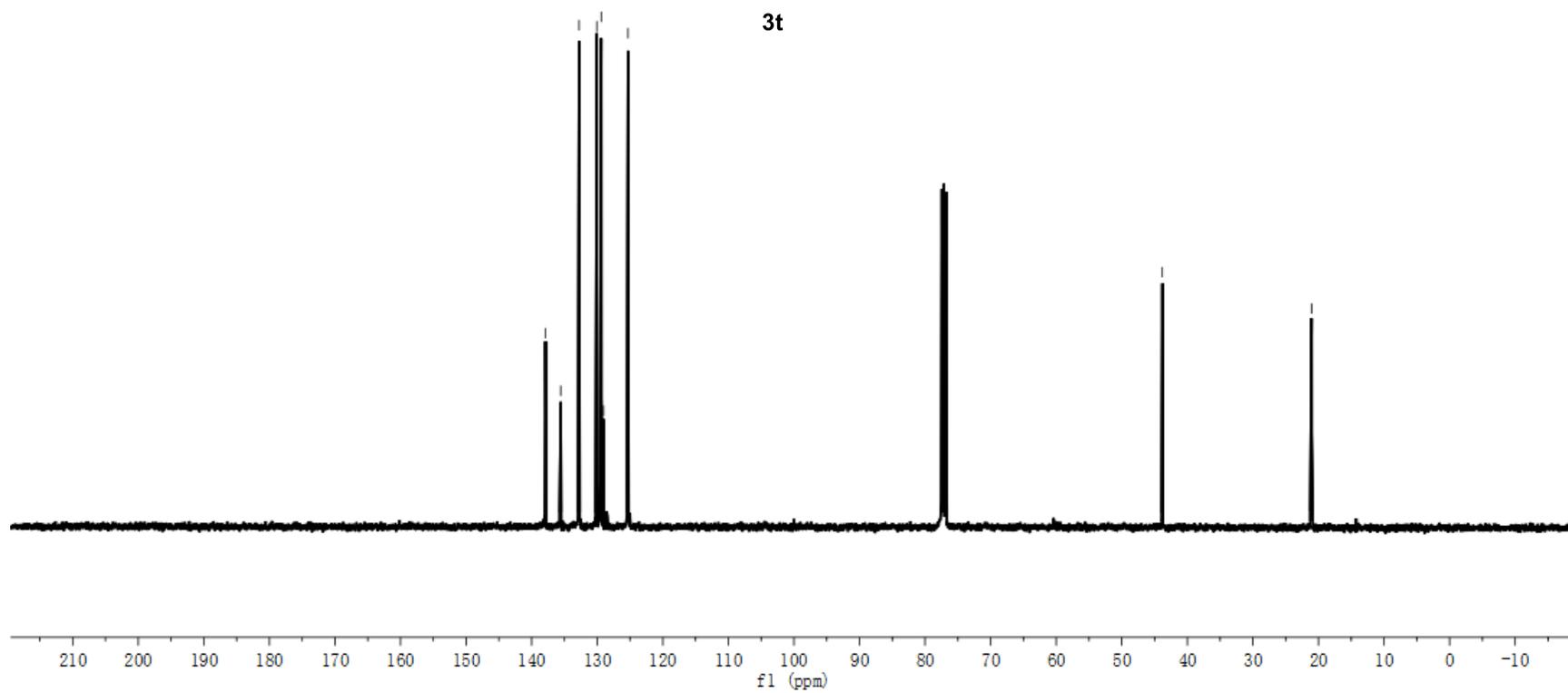
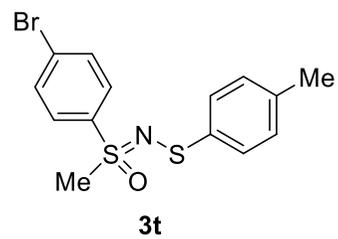


^{13}C NMR spectra of compound **3t** (101 MHz, CDCl_3)

137.887
135.568
132.761
130.058
129.386
129.036
125.302

—43.815

—21.058



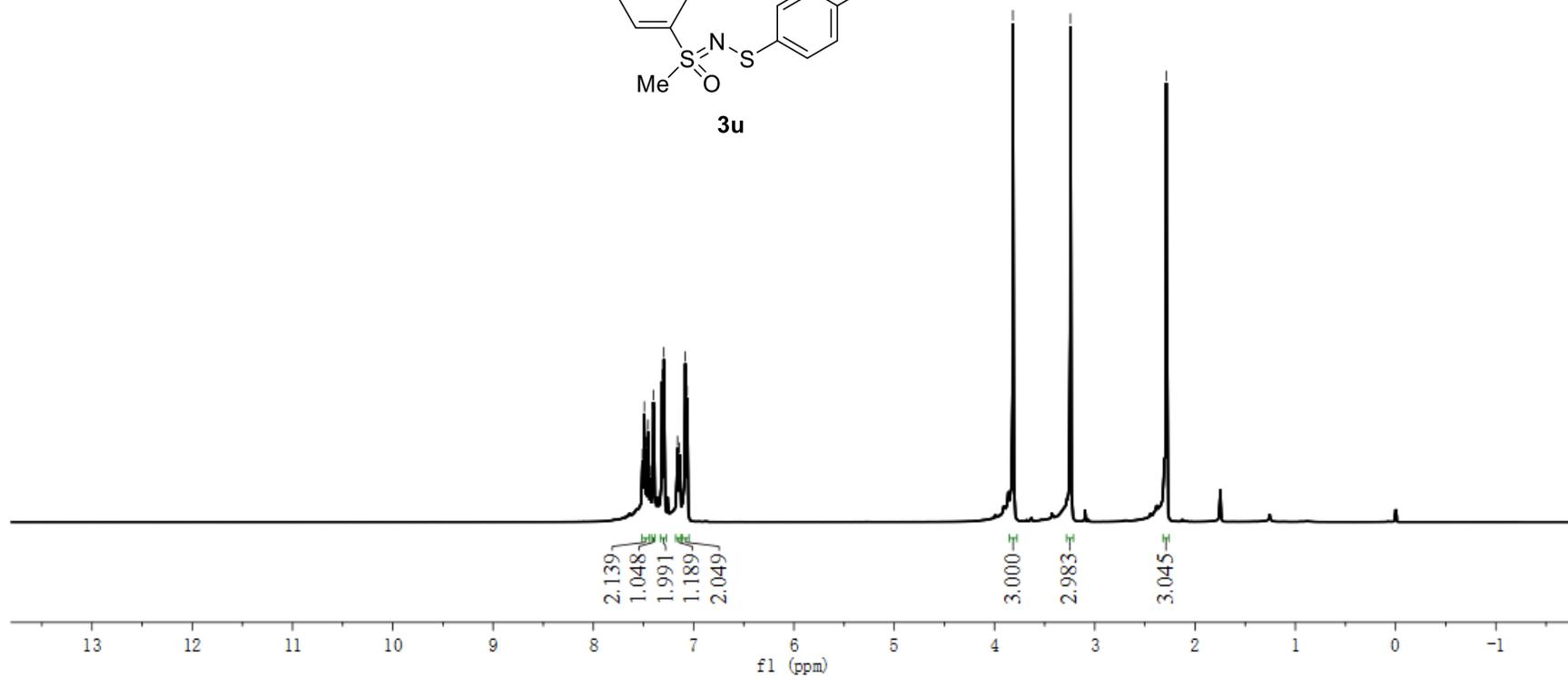
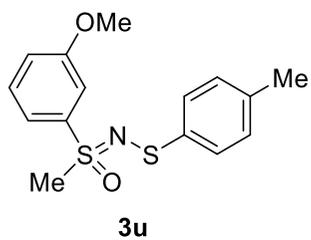
¹H NMR spectra of compound **3u** (400 MHz, CDCl₃)

7.509
7.491
7.474
7.454
7.434
7.401
7.314
7.297
7.161
7.141
7.083
7.065

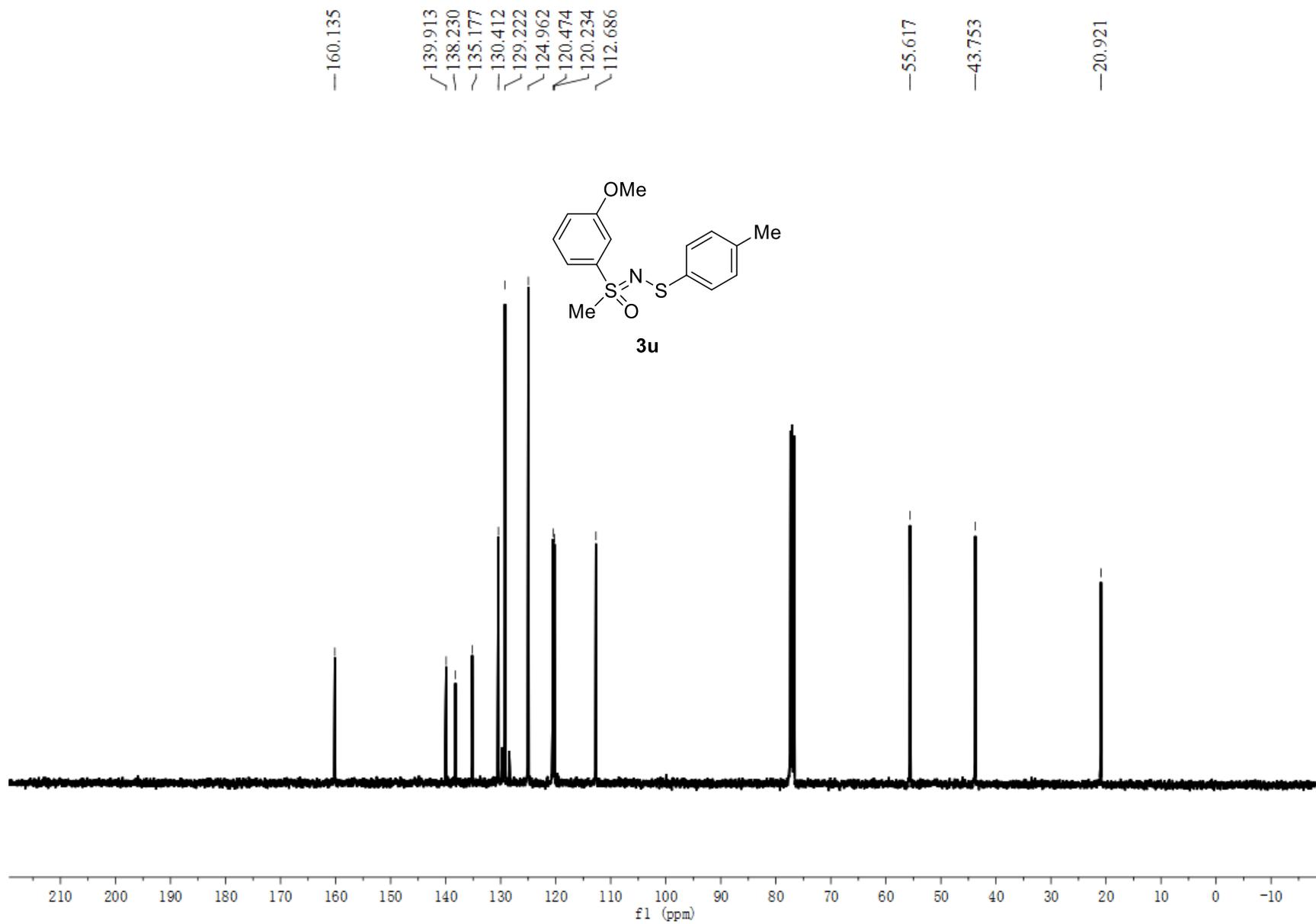
3.816

3.243

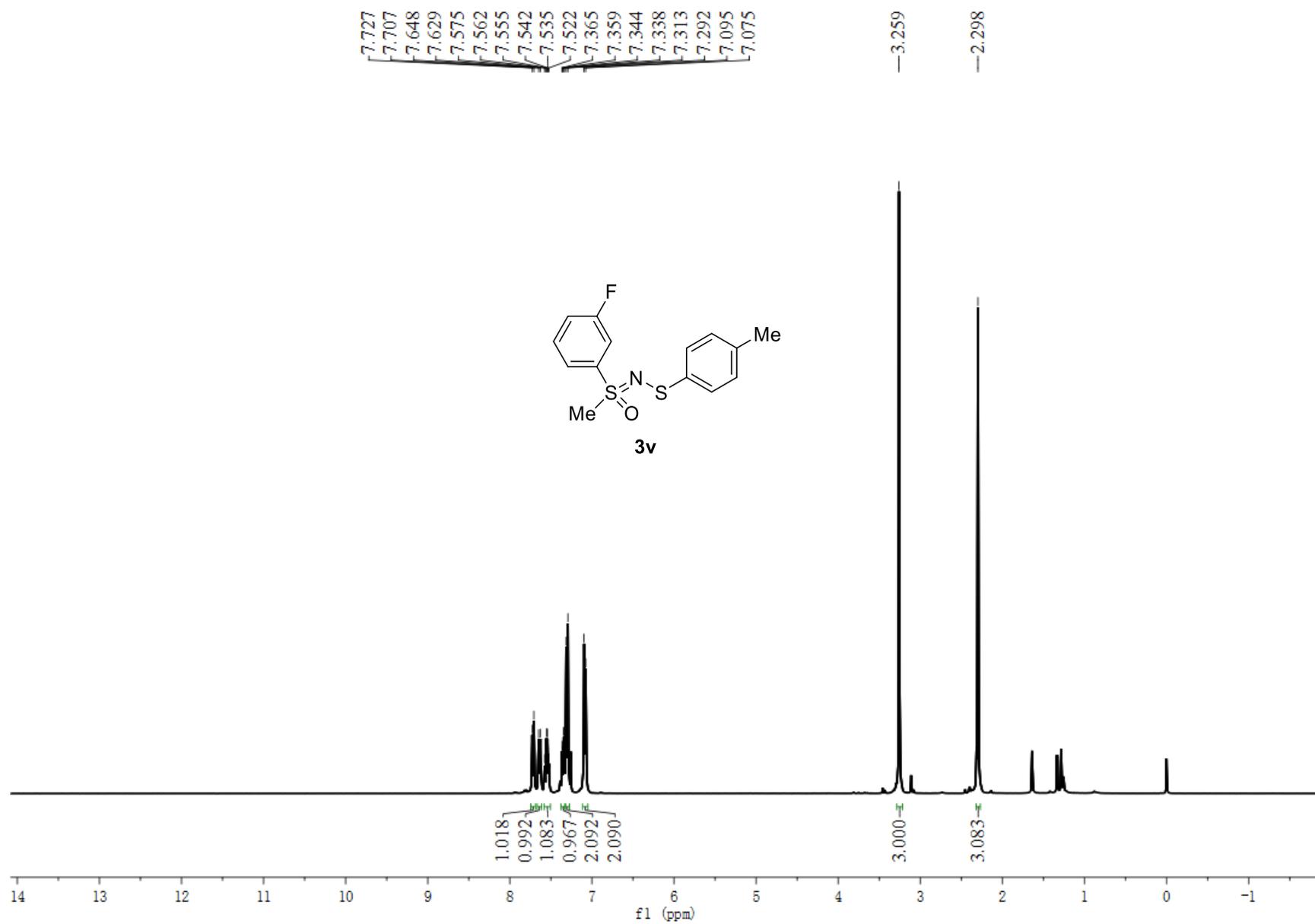
2.288



^{13}C NMR spectra of compound **3u** (101 MHz, CDCl_3)

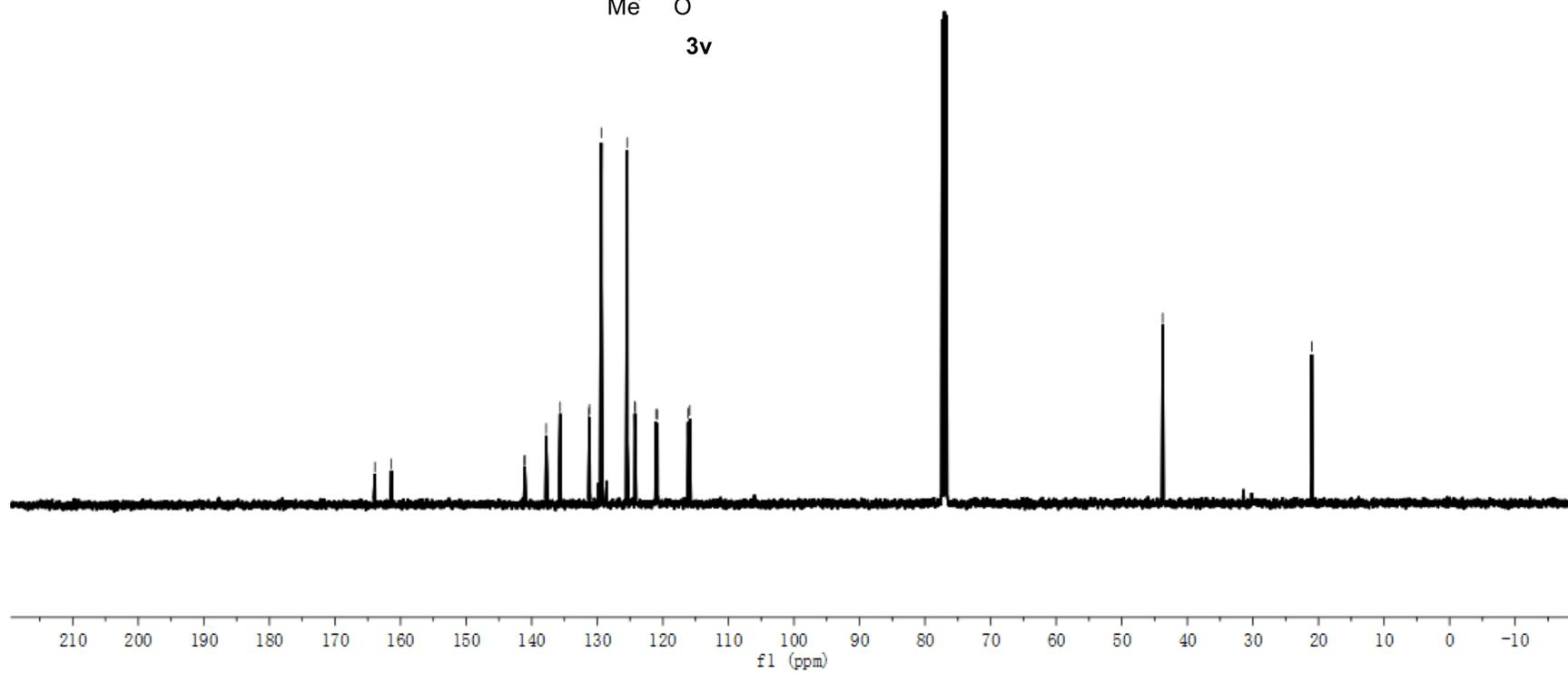
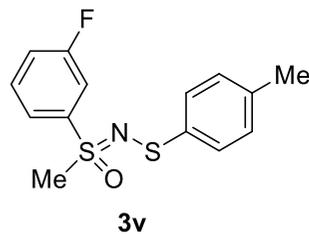


¹H NMR spectra of compound **3v** (400 MHz, CDCl₃)



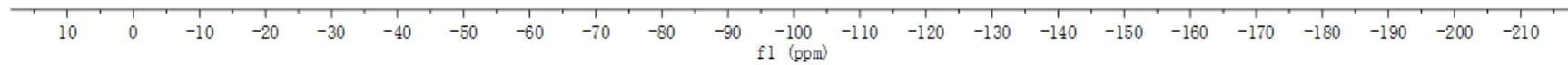
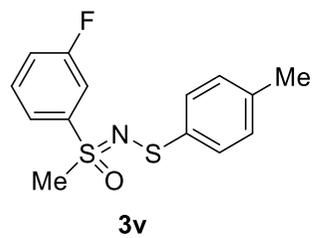
¹³C NMR spectra of compound **3v** (101 MHz, CDCl₃)

163.901
161.389
141.122
141.057
137.797
135.651
131.263
131.188
129.379
125.436
124.244
124.211
121.040
120.829
116.115
115.872
43.752
21.035



^{19}F NMR spectra of compound **3v** (376 MHz, CDCl_3)

-108.828

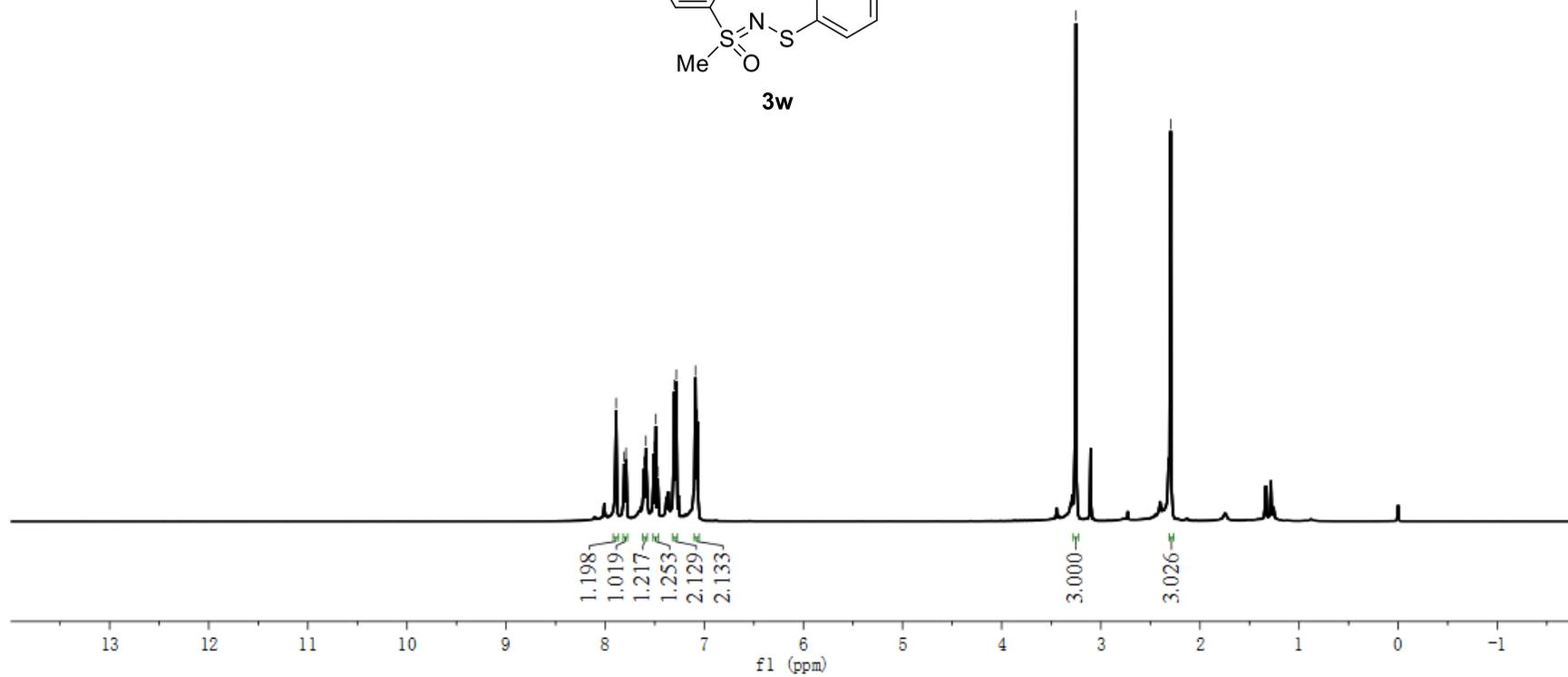
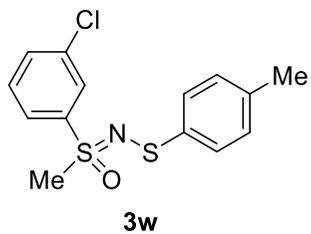


¹H NMR spectra of compound **3w** (400 MHz, CDCl₃)

7.895
7.890
7.886
7.808
7.789
7.607
7.590
7.509
7.489
7.469
7.303
7.282
7.089
7.069

3.251

2.295

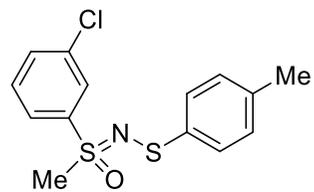


¹³C NMR spectra of compound **3w** (101 MHz, CDCl₃)

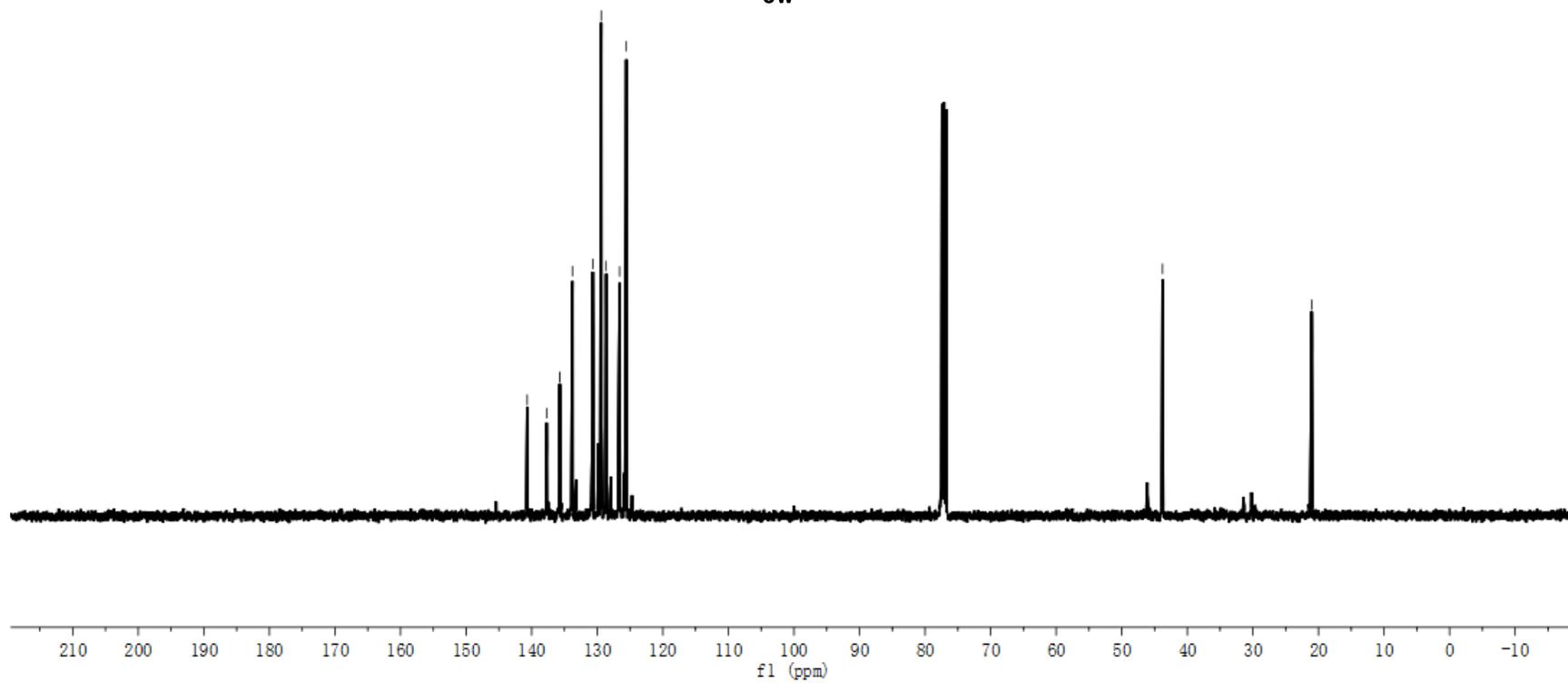
140.682
137.720
135.728
135.713
133.785
130.686
129.388
128.639
126.585
125.564

—43.789

—21.050

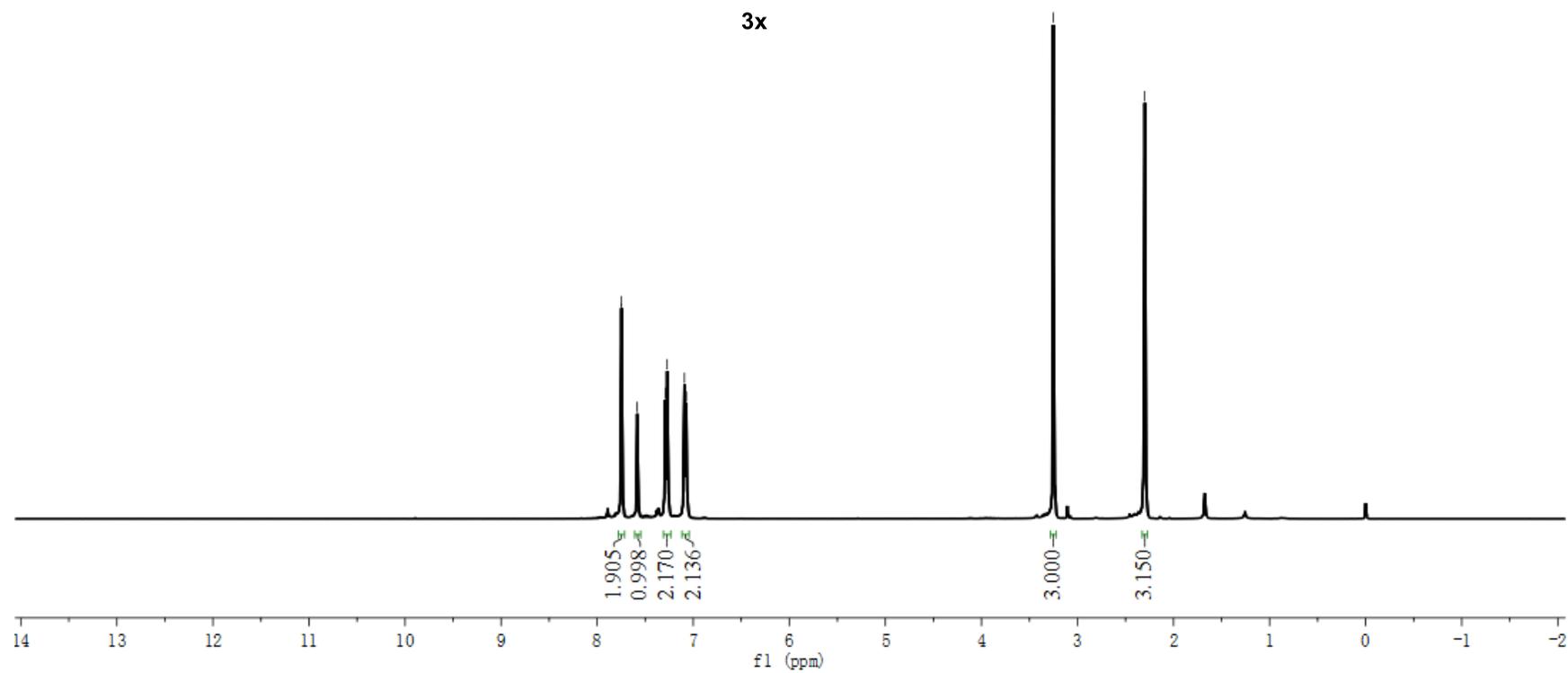
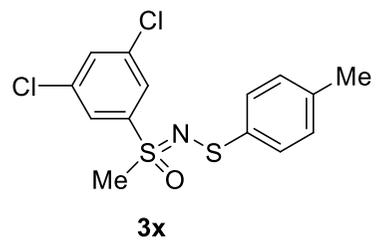


3w



¹H NMR spectra of compound **3x** (400 MHz, CDCl₃)

7.751
7.747
7.583
7.292
7.272
7.092
7.072
3.252
2.300

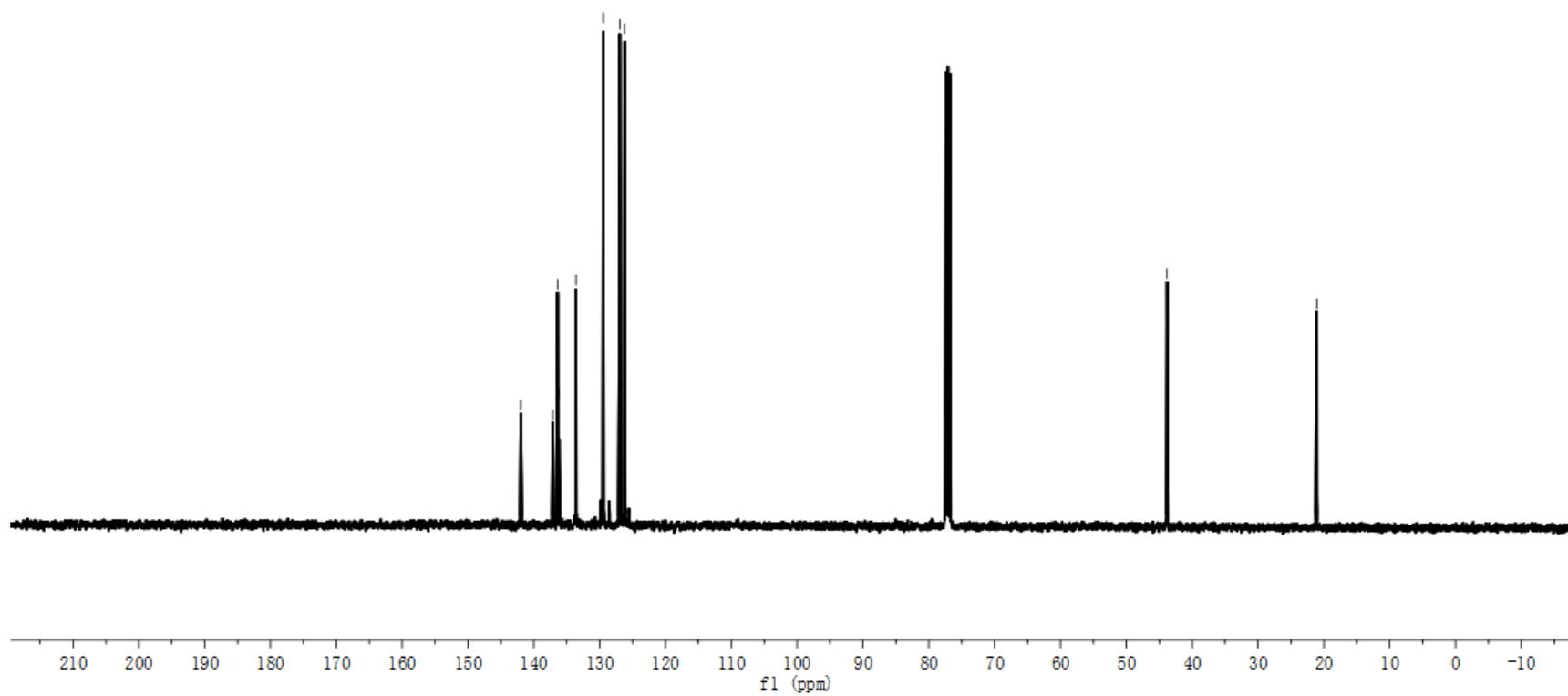
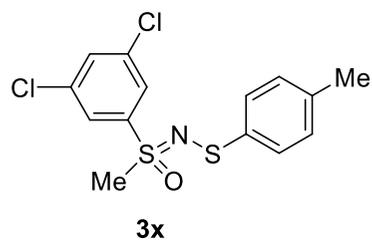


¹³C NMR spectra of compound **3x** (101 MHz, CDCl₃)

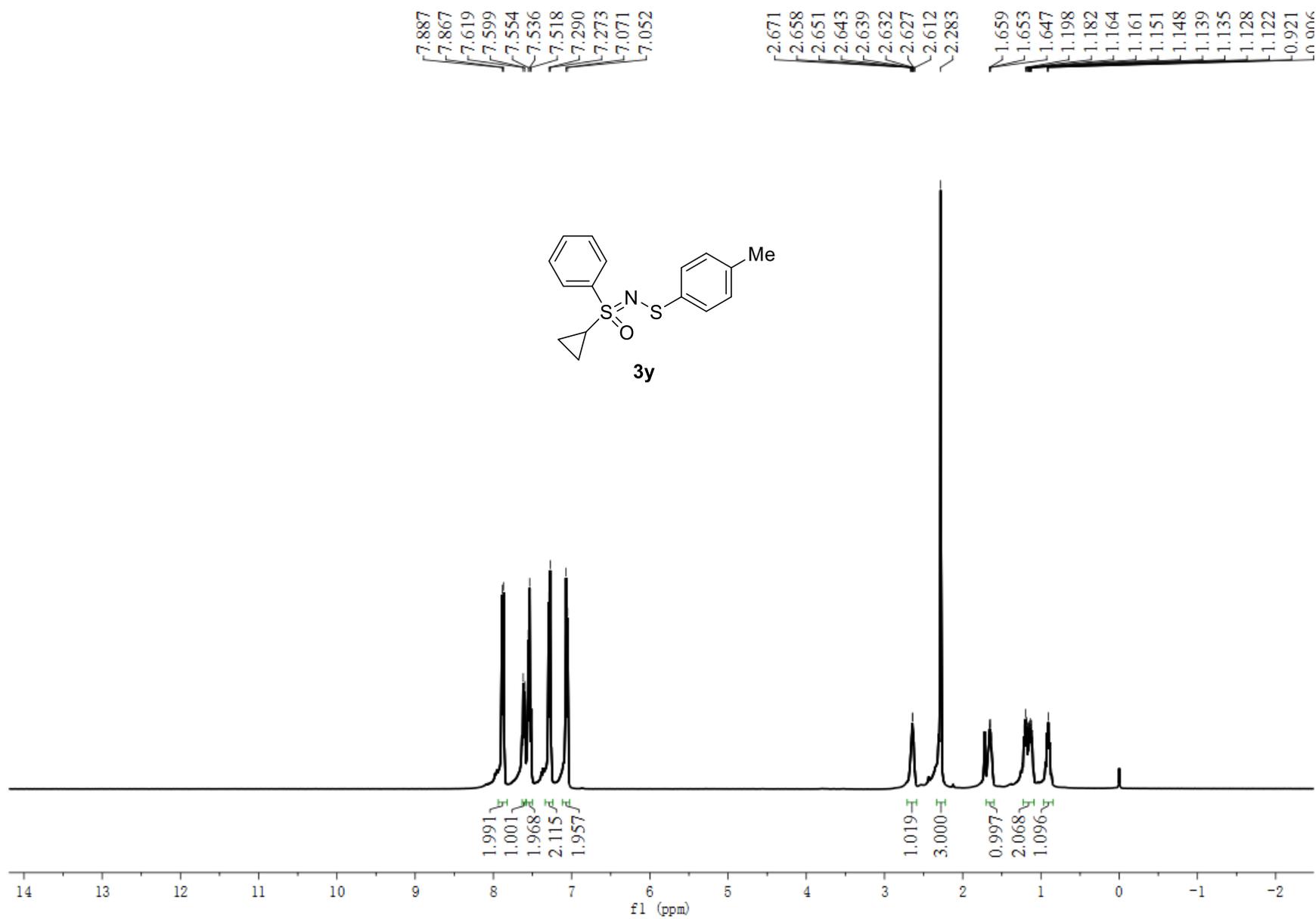
141.986
137.123
136.394
136.188
133.592
129.441
126.953
126.204

—43.820

—21.072



¹H NMR spectra of compound **3y** (400 MHz, CDCl₃)



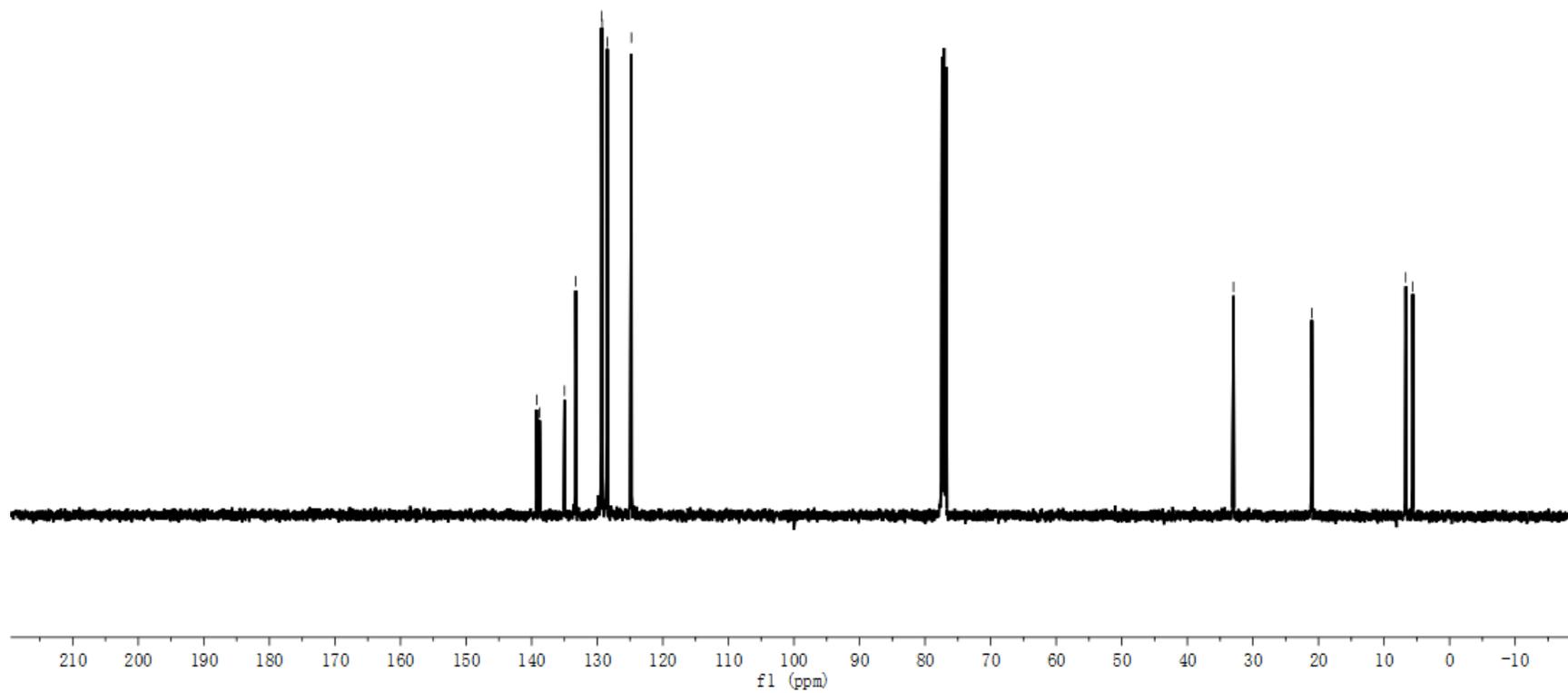
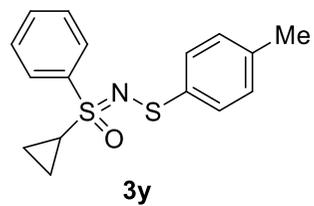
¹³C NMR spectra of compound **3y** (101 MHz, CDCl₃)

139.240
138.800
134.985
133.273
129.328
129.242
128.469
124.796

— 32.965

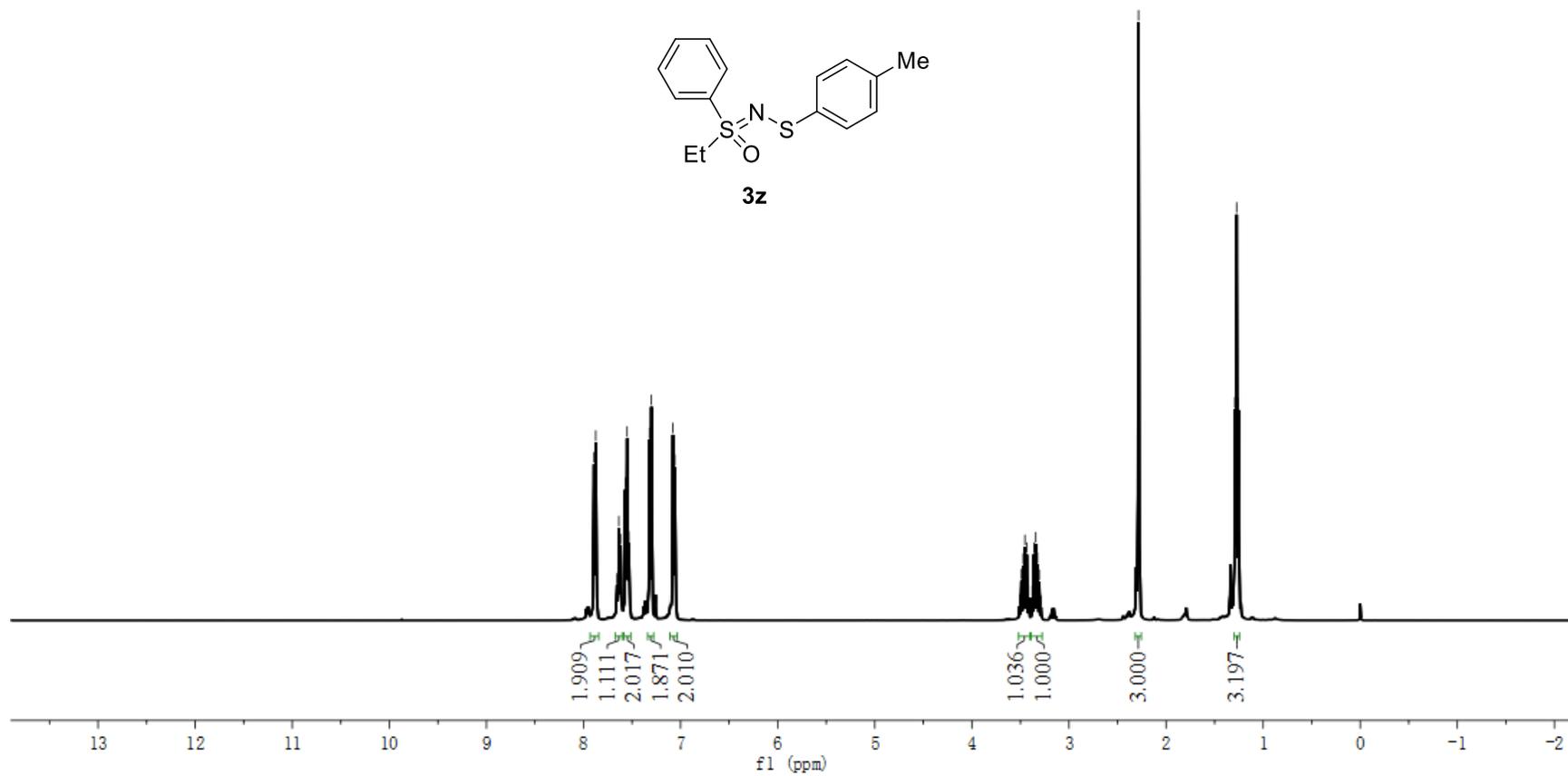
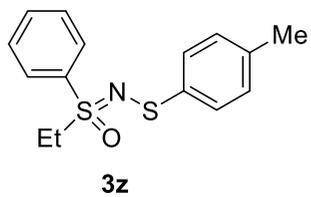
— 21.028

— 6.687
— 5.619

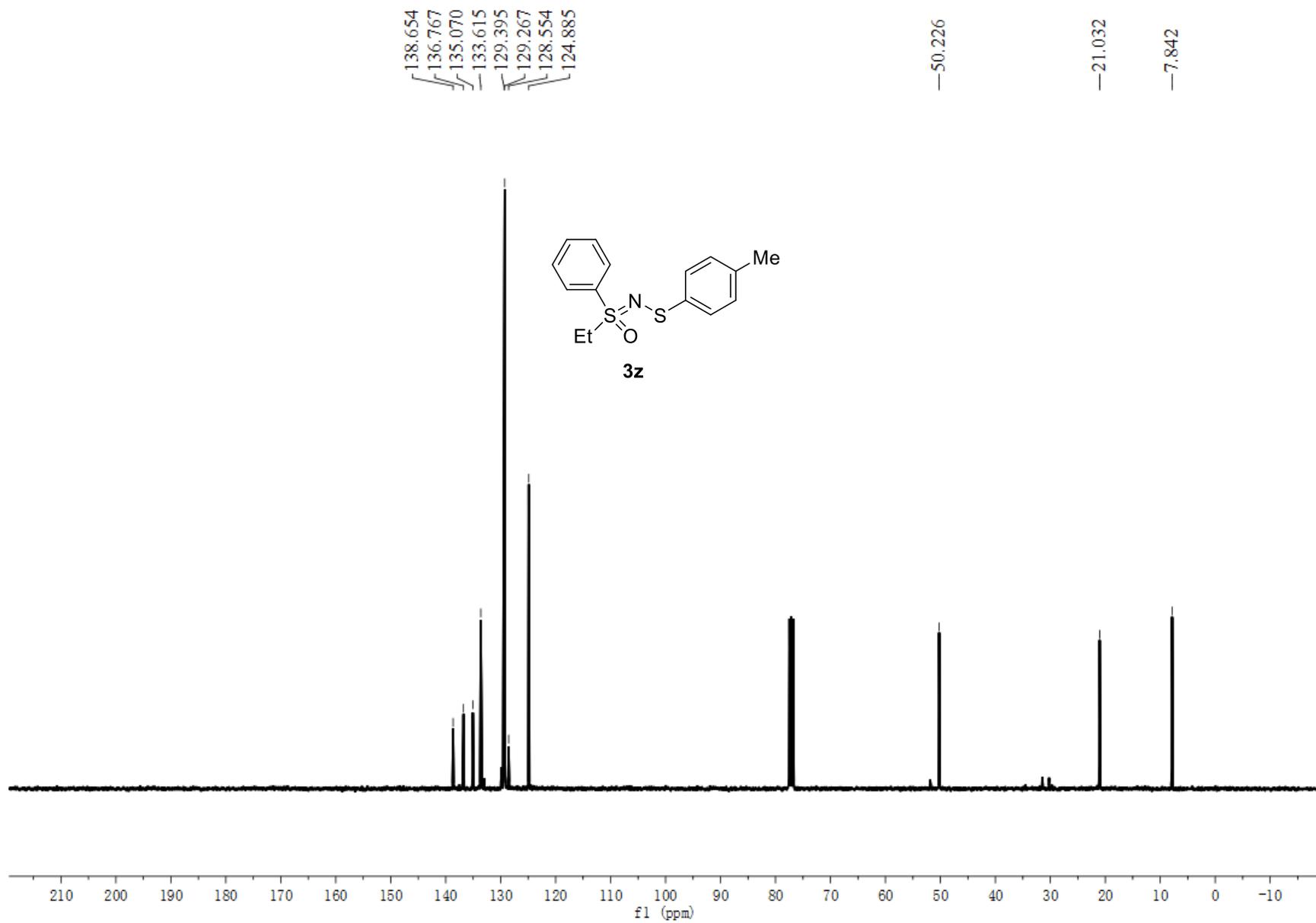


¹H NMR spectra of compound **3z** (400 MHz, CDCl₃)

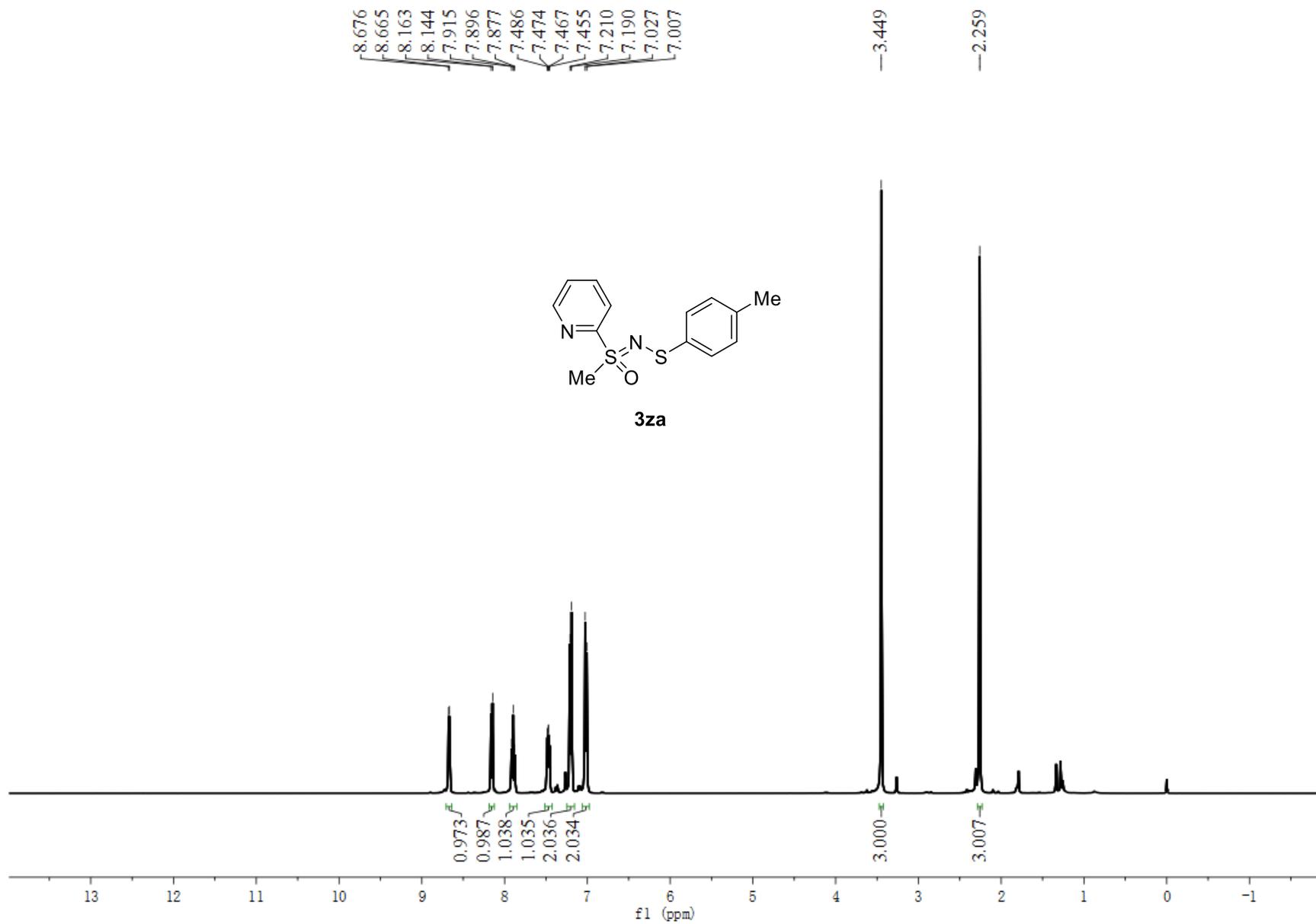
7.892
7.874
7.655
7.636
7.618
7.571
7.551
7.533
7.321
7.301
7.079
7.059
3.508
3.490
3.471
3.454
3.435
3.417
3.379
3.361
3.342
3.325
3.307
3.288
-2.284
1.292
1.273
1.255



¹³C NMR spectra of compound **3z** (101 MHz, CDCl₃)



¹H NMR spectra of compound **3za** (400 MHz, CDCl₃)

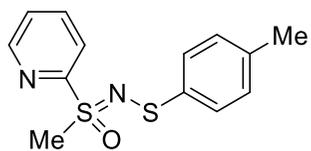


¹³C NMR spectra of compound **3za** (101 MHz, CDCl₃)

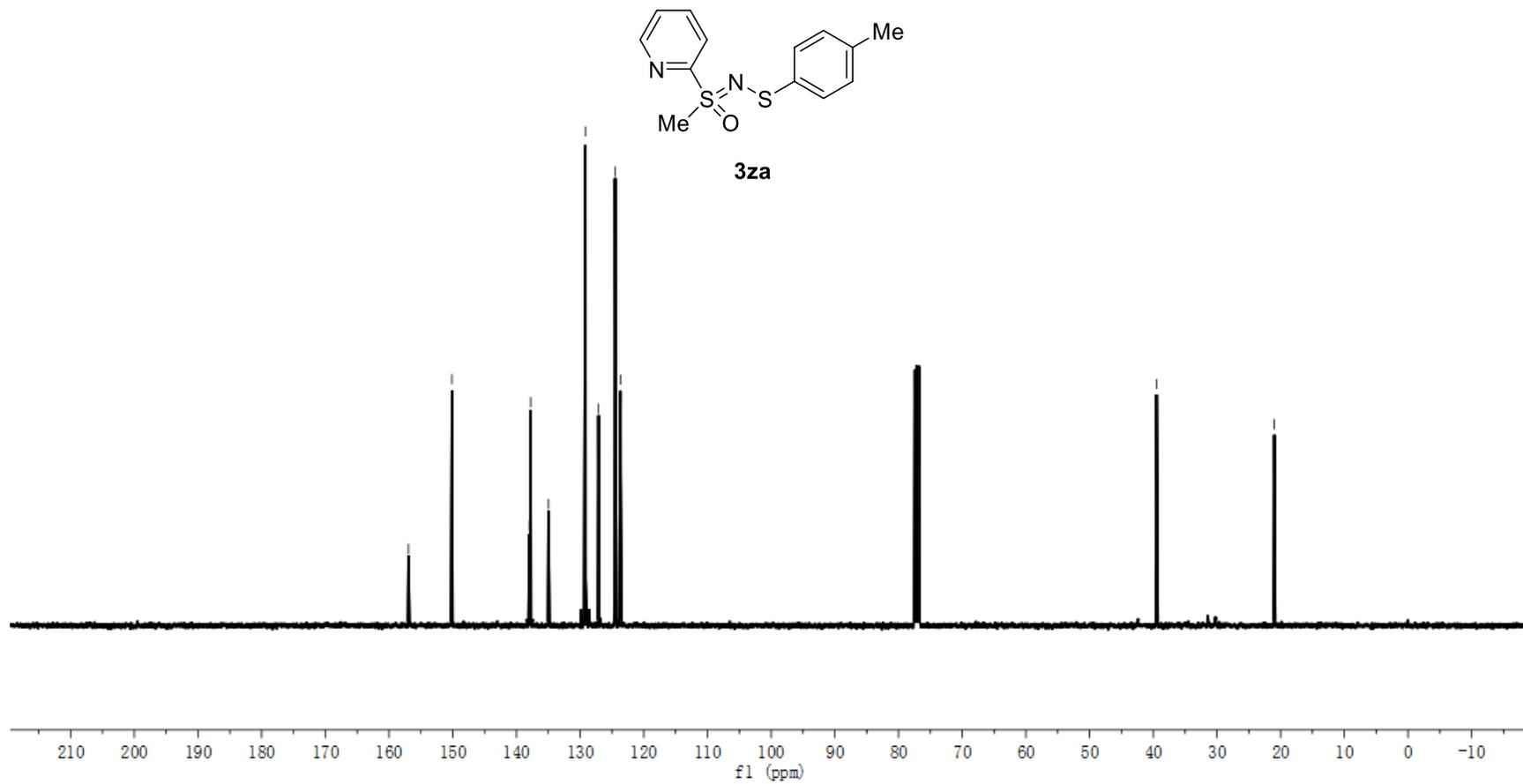
— 156.938
— 150.119
↙ 137.971
↘ 137.770
— 134.966
↙ 129.177
↘ 127.102
↙ 124.488
↘ 123.666

— 39.498

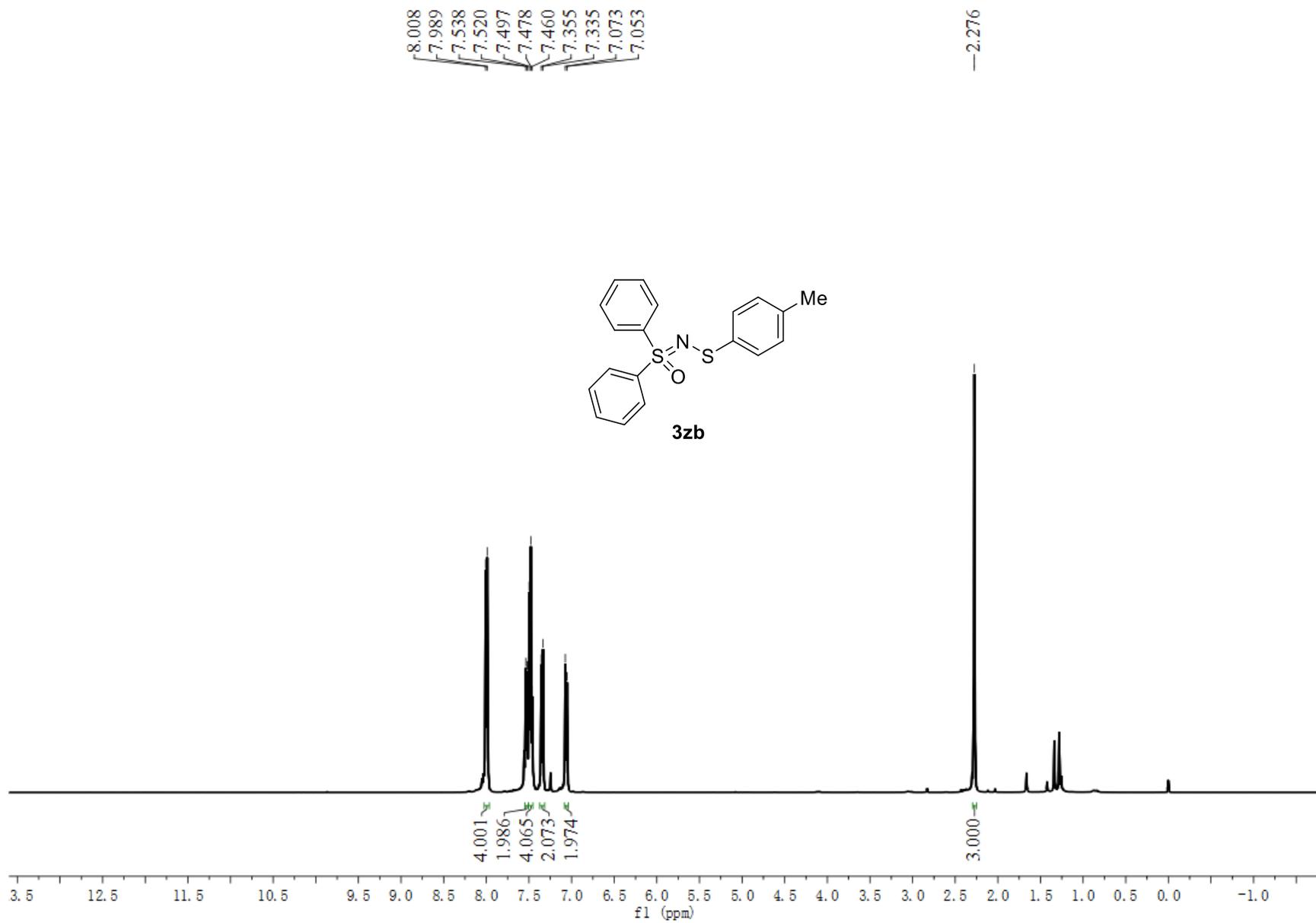
— 20.986



3za



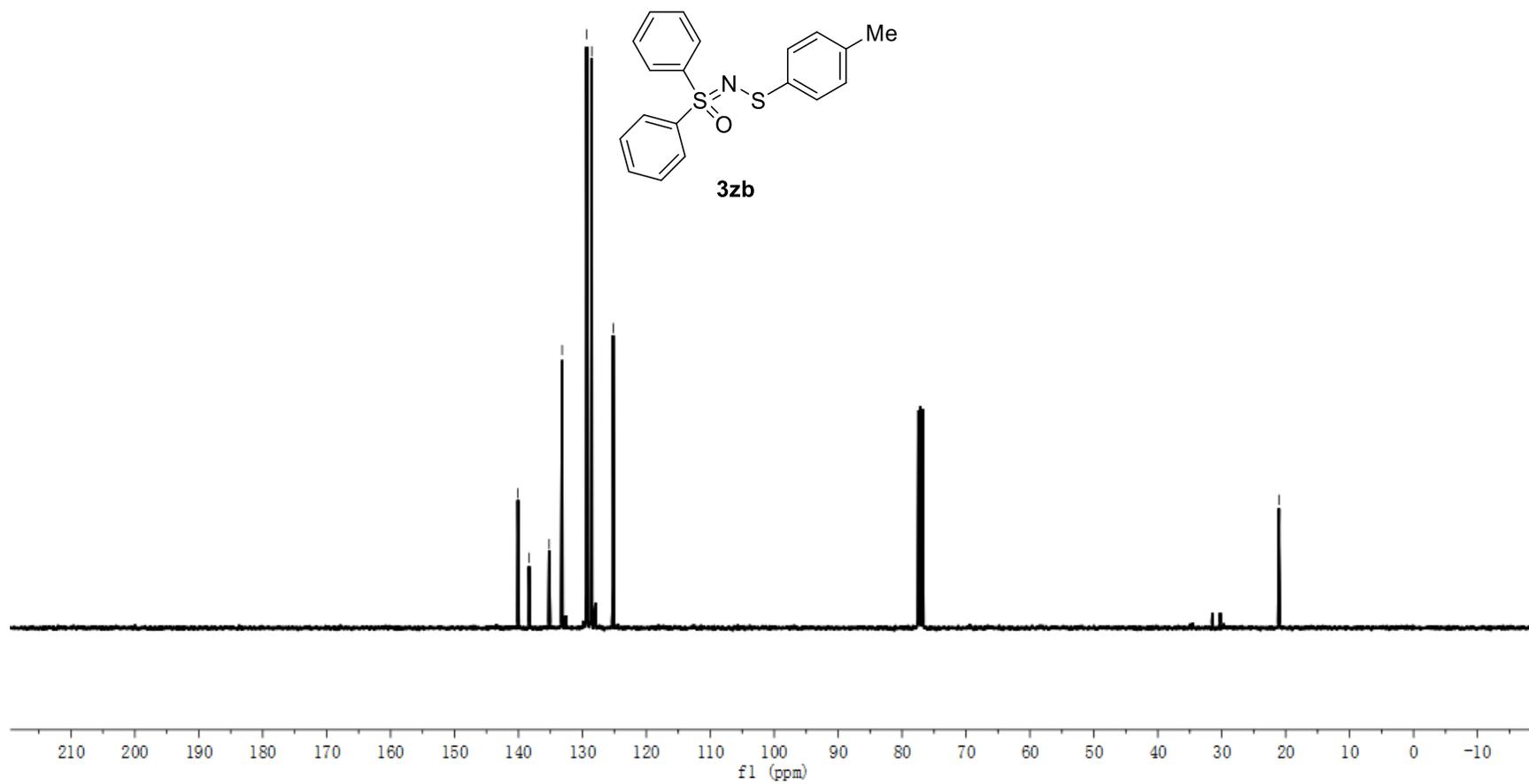
¹H NMR spectra of compound **3zb** (400 MHz, CDCl₃)



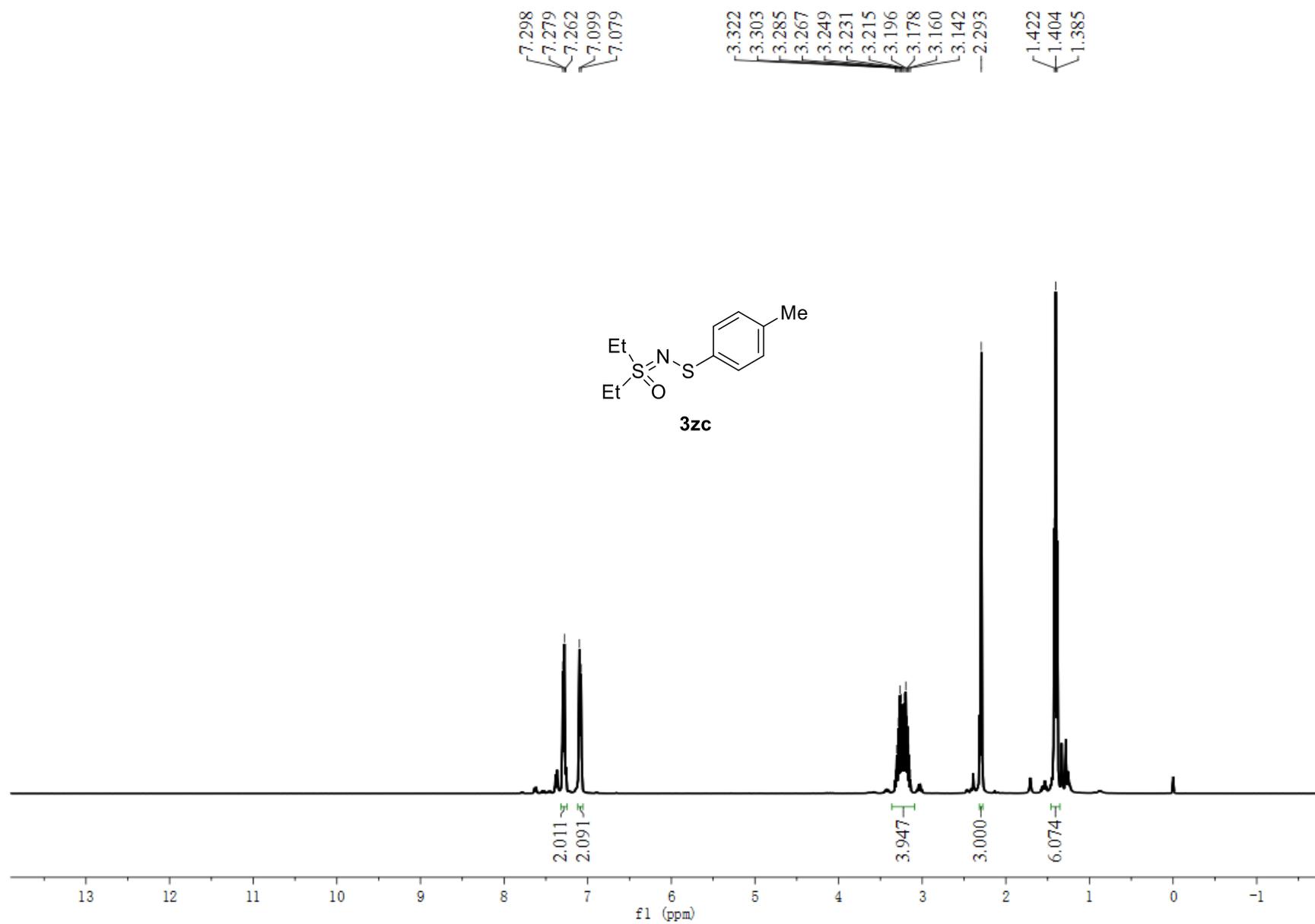
^{13}C NMR spectra of compound **3zb** (101 MHz, CDCl_3)

140.076
138.339
135.202
133.162
129.330
129.289
128.535
125.180

—21.055



¹H NMR spectra of compound **3zc** (400 MHz, CDCl₃)



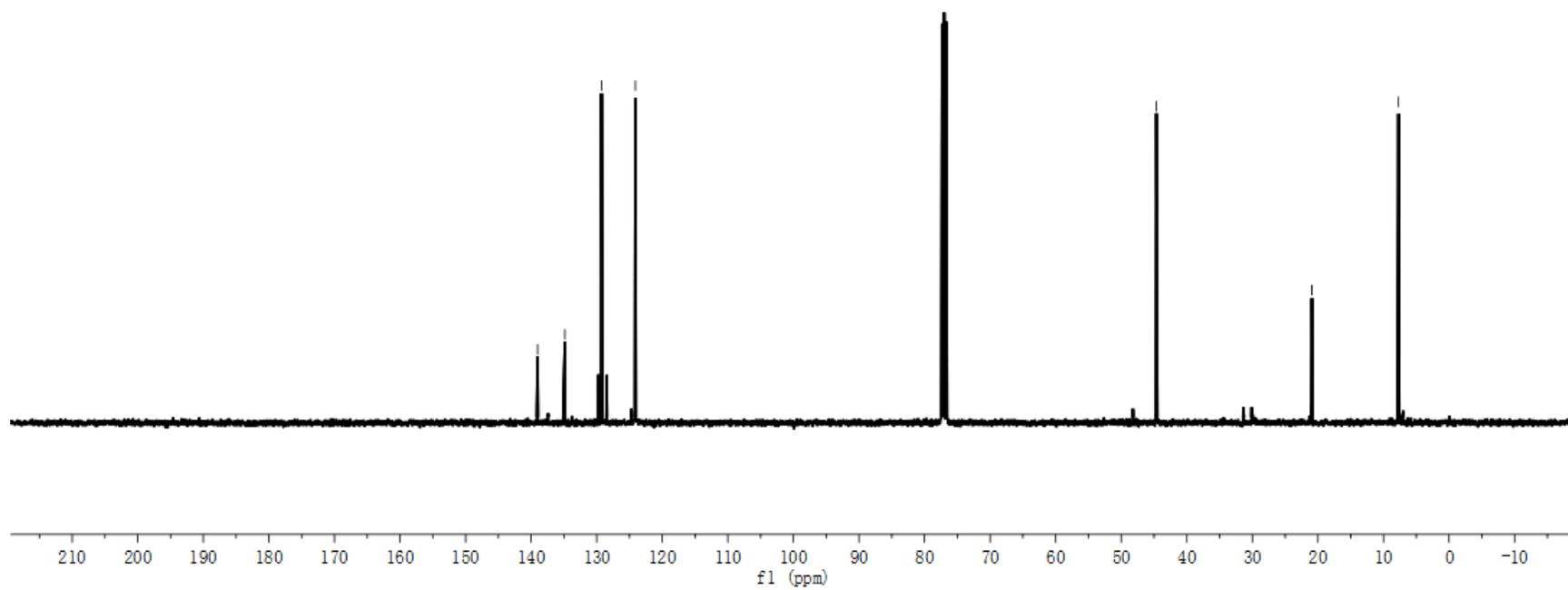
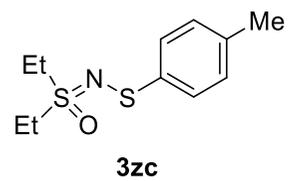
^{13}C NMR spectra of compound **3zc** (101 MHz, CDCl_3)

139.014
134.862
129.269
124.098

44.638

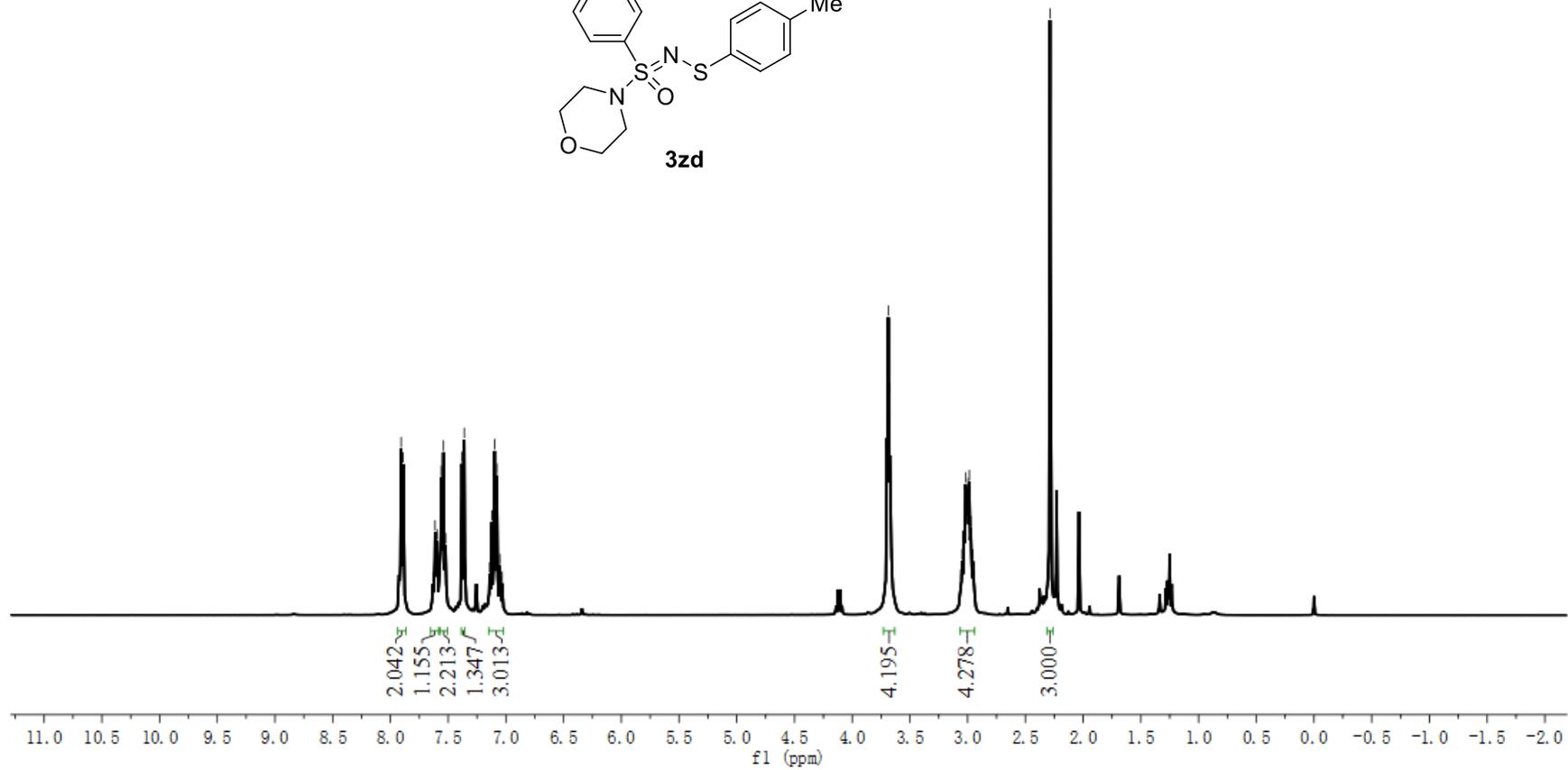
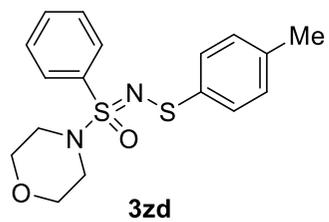
20.921

7.713



¹H NMR spectra of compound **3zd** (400 MHz, CDCl₃)

7.907
7.889
7.632
7.620
7.613
7.595
7.560
7.541
7.523
7.381
7.361
7.141
7.122
7.098
7.078
7.052
7.032
3.699
3.687
3.676
3.656
3.018
3.007
2.997
2.989
2.287



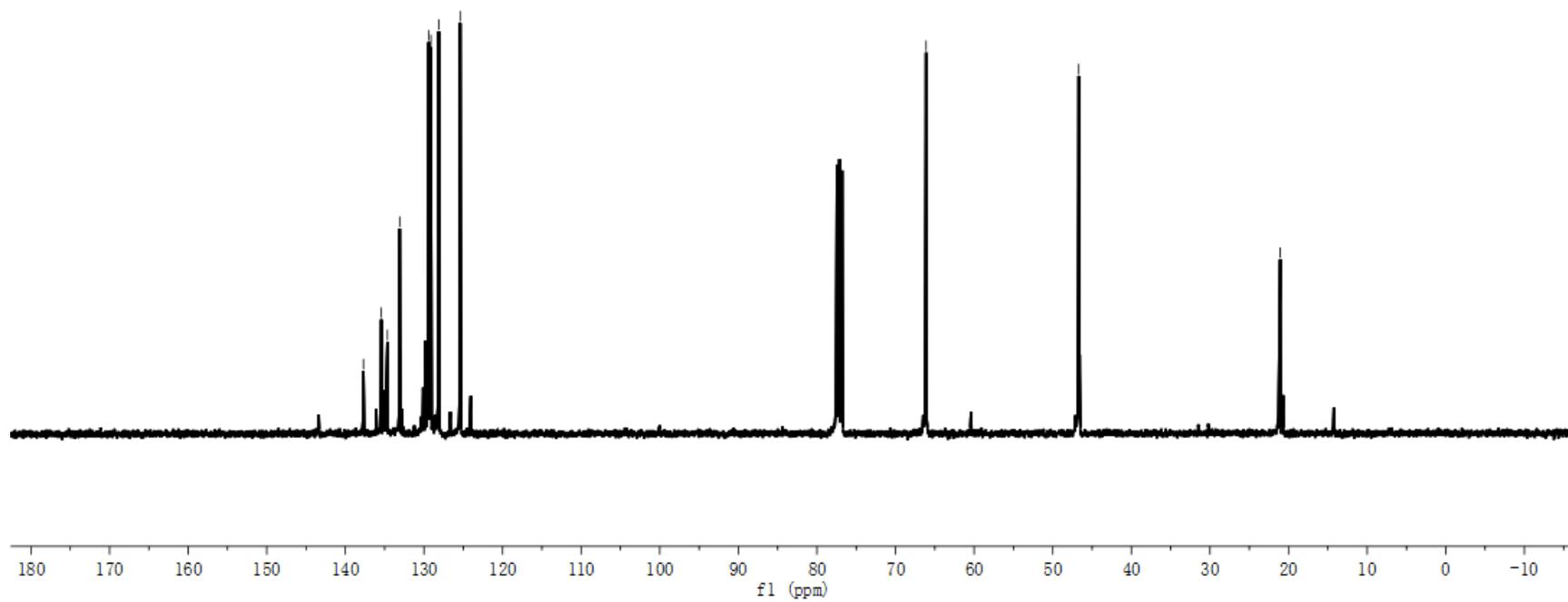
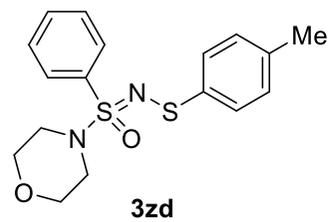
$^{13}\text{C}\{^1\text{H}\}$ NMR spectra of compound **3zd** (101 MHz, CDCl_3)

137.699
135.425
134.653
133.088
129.388
129.107
128.115
125.393

—66.118

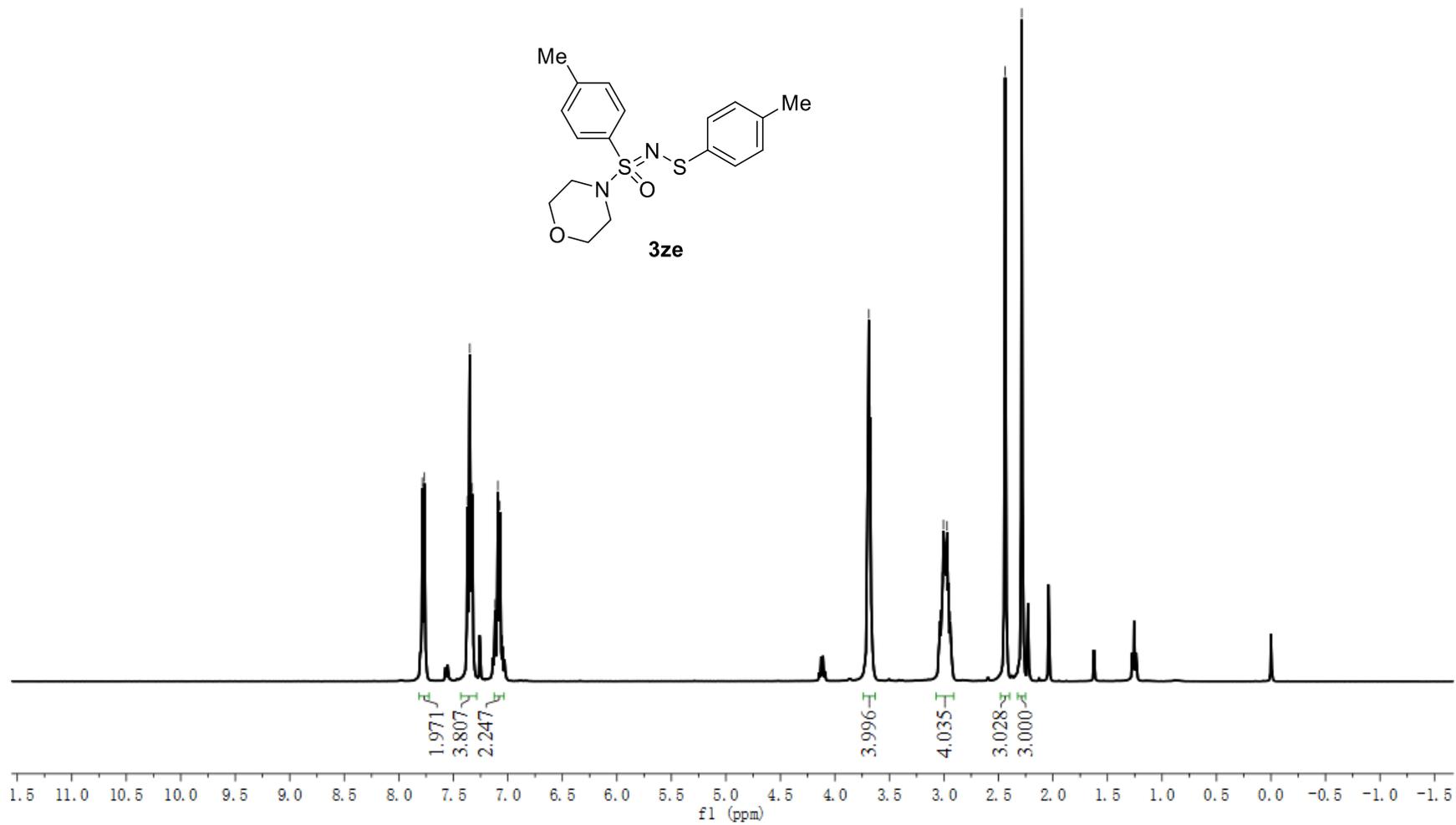
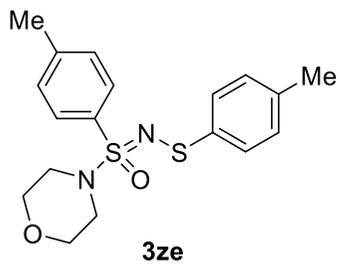
—46.695

—21.059



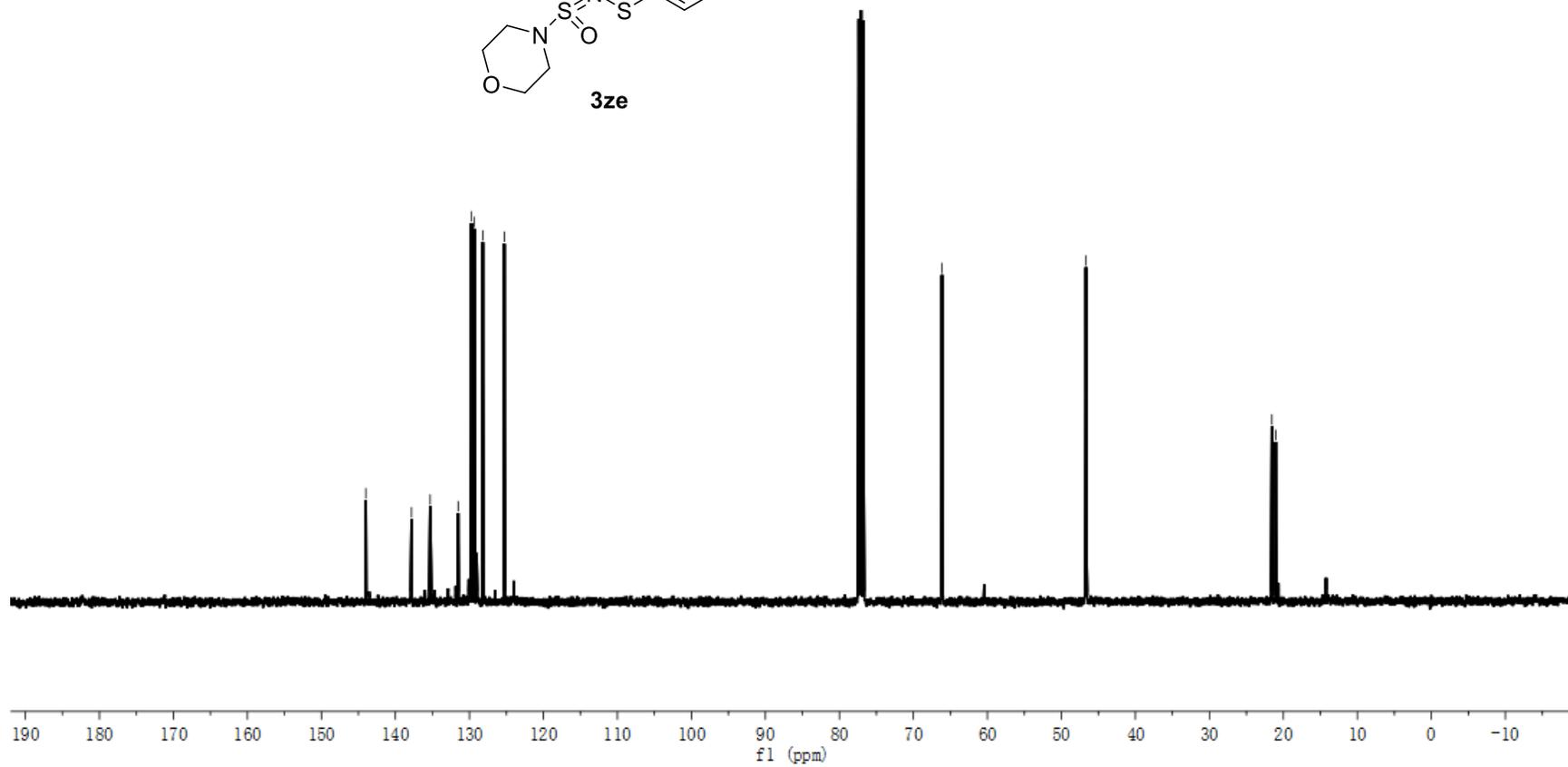
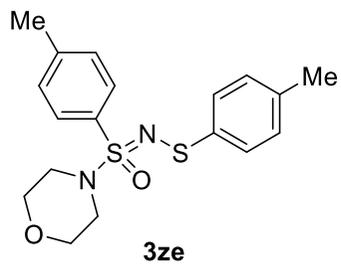
¹H NMR spectra of compound **3ze** (400 MHz, CDCl₃)

7.784
7.765
7.371
7.349
7.326
7.118
7.092
7.072
7.050
3.700
3.688
3.677
3.004
2.983
2.971
2.438
2.286



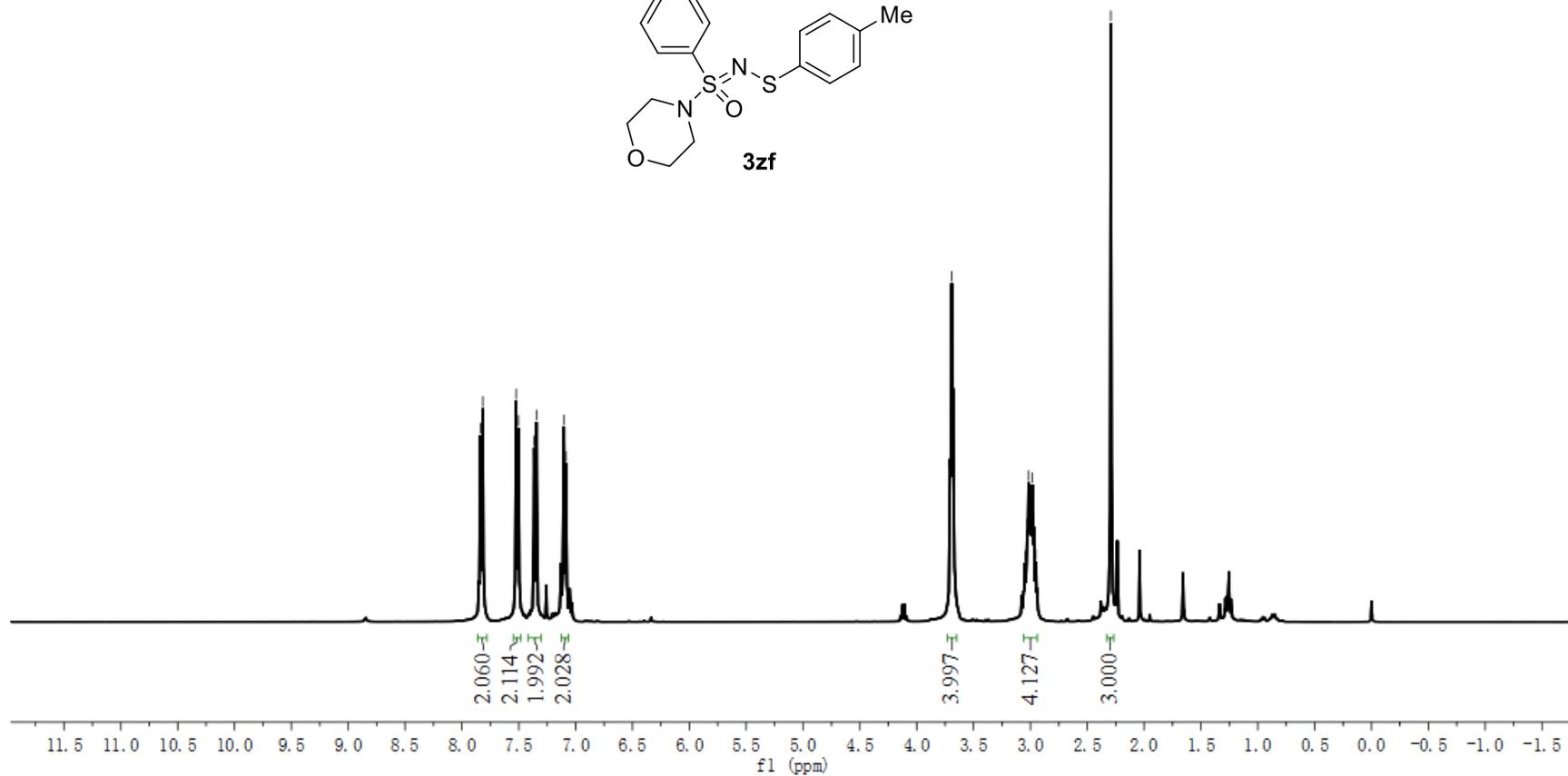
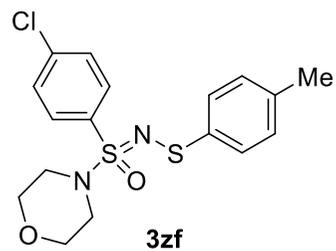
¹³C NMR spectra of compound **3ze** (101 MHz, CDCl₃)

143.989
137.828
135.303
131.519
129.722
129.343
128.193
125.284
—66.130
—46.683
21.553
21.037



¹H NMR spectra of compound **3zf** (400 MHz, CDCl₃)

7.838
7.816
7.524
7.502
7.365
7.344
7.104
7.084
3.704
3.692
3.680
3.016
3.005
2.995
2.983
2.983



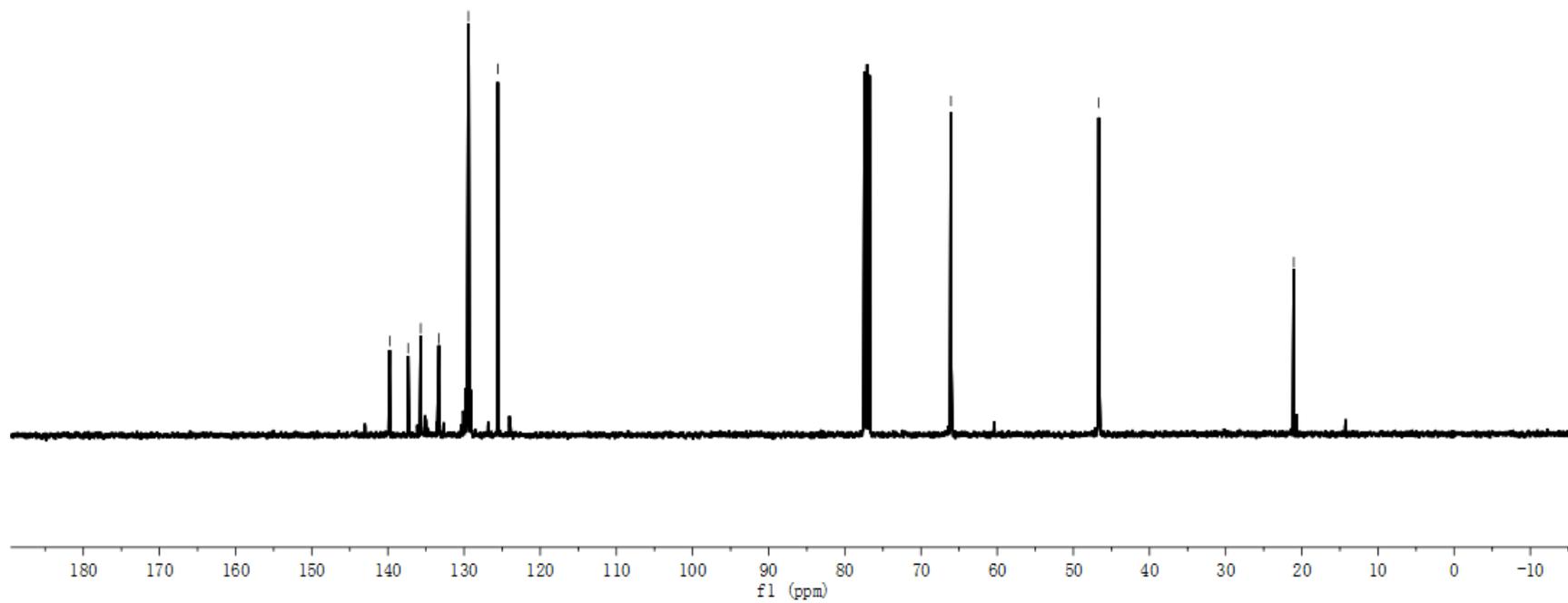
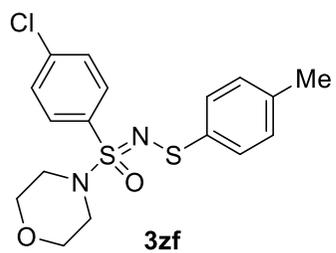
¹³C NMR spectra of compound **3zf** (101 MHz, CDCl₃)

139.765
137.339
135.686
133.303
129.535
129.438
129.396
125.577

—66.076

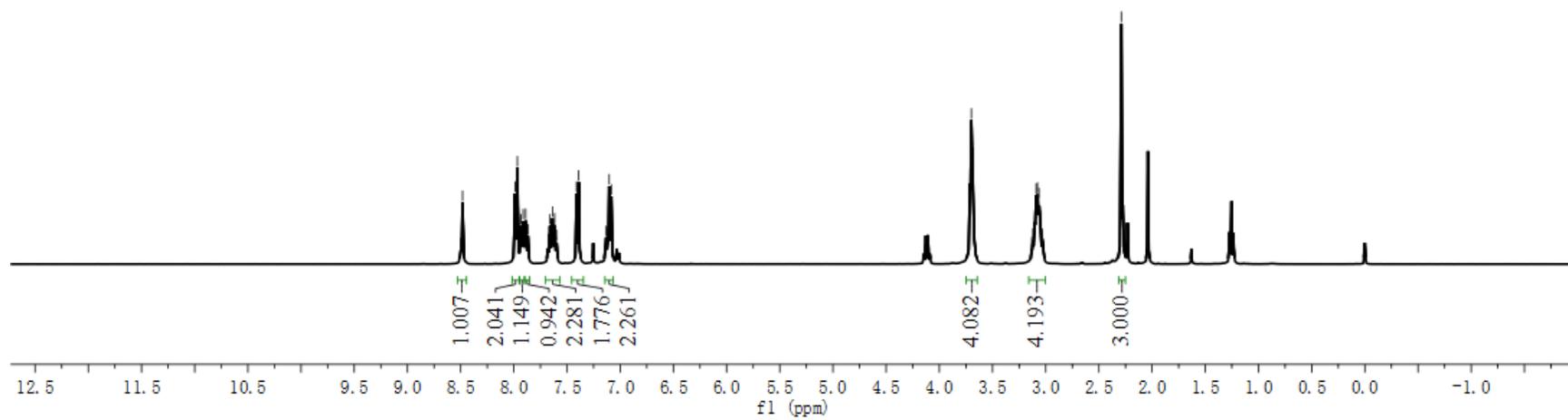
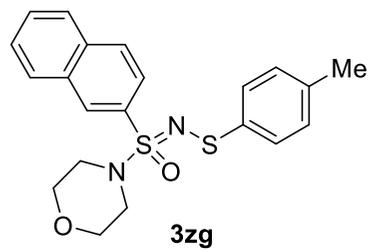
—46.659

—21.058

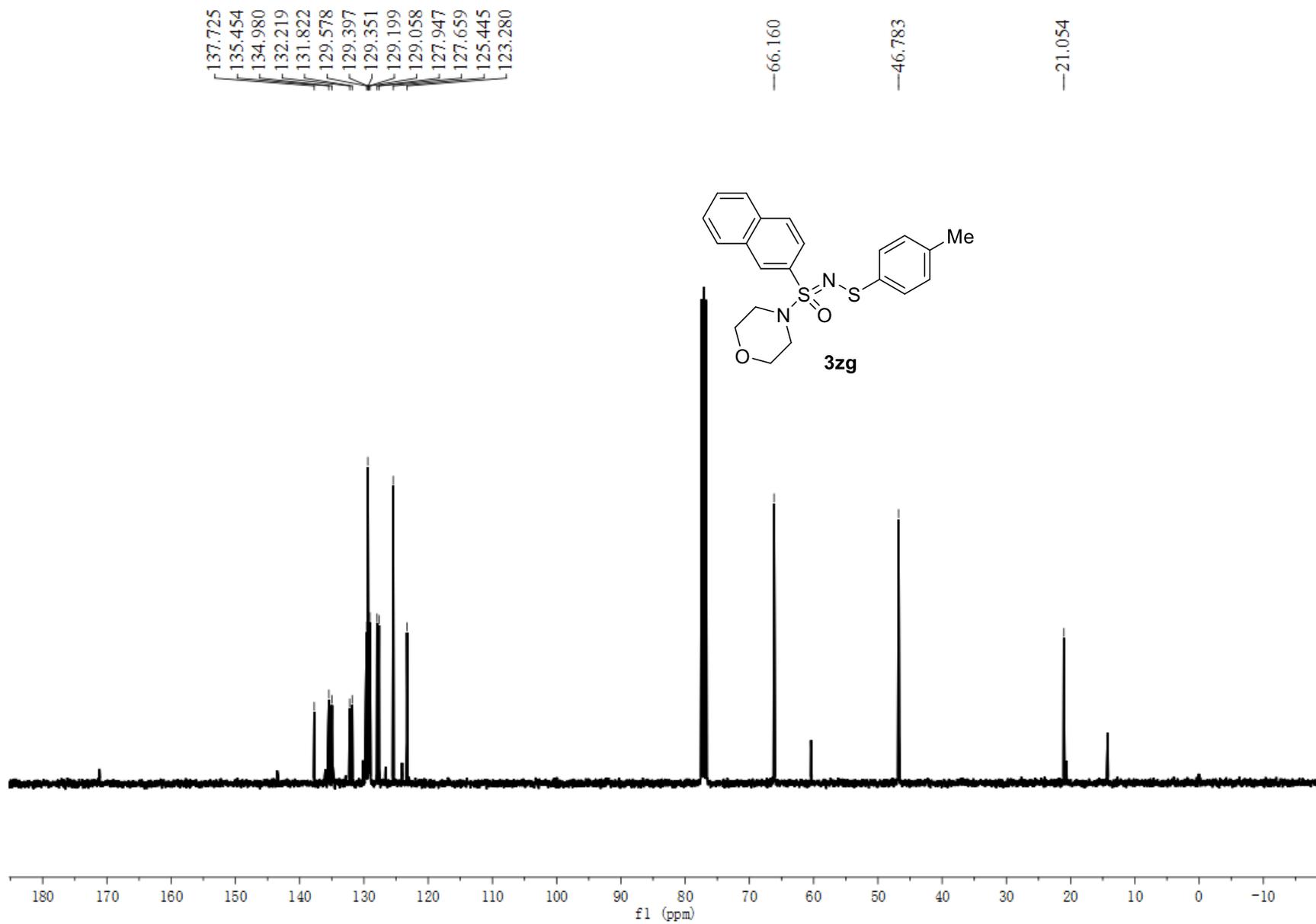


¹H NMR spectra of compound **3zg** (400 MHz, CDCl₃)

8.499
8.482
7.988
7.967
7.932
7.912
7.888
7.867
7.677
7.660
7.637
7.616
7.599
7.410
7.390
7.132
7.118
7.104
7.084
3.710
3.699
3.687
3.090
3.077
3.063

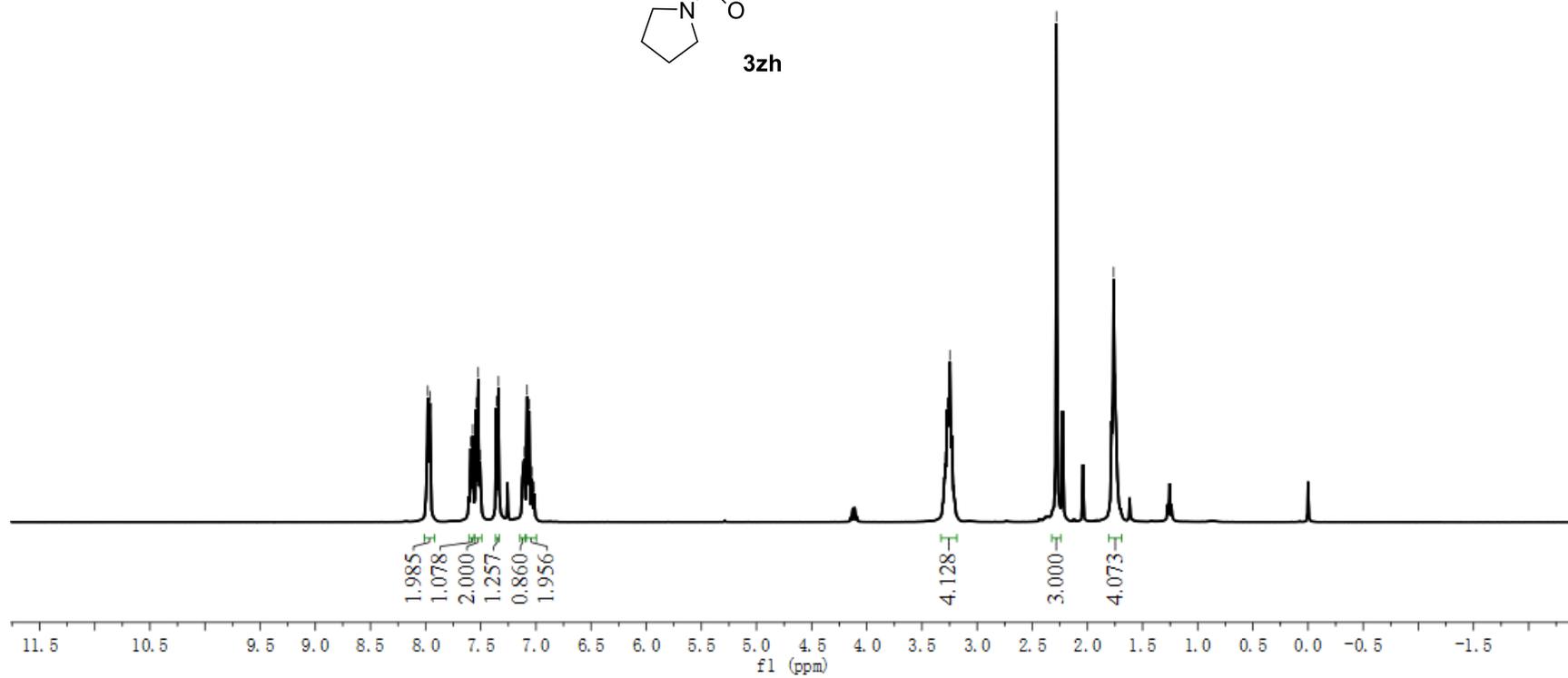
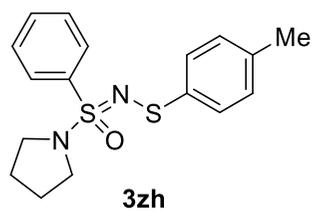


¹³C NMR spectra of compound **3zg** (101 MHz, CDCl₃)



¹H NMR spectra of compound **3zh** (400 MHz, CDCl₃)

7.981
7.961
7.591
7.573
7.543
7.524
7.506
7.360
7.340
7.118
7.111
7.105
7.081
7.061
7.036
7.016
3.312
3.295
3.289
3.271
3.264
3.255
3.247
3.231
3.207
-2.281
1.779
1.771
1.763
1.756
1.747

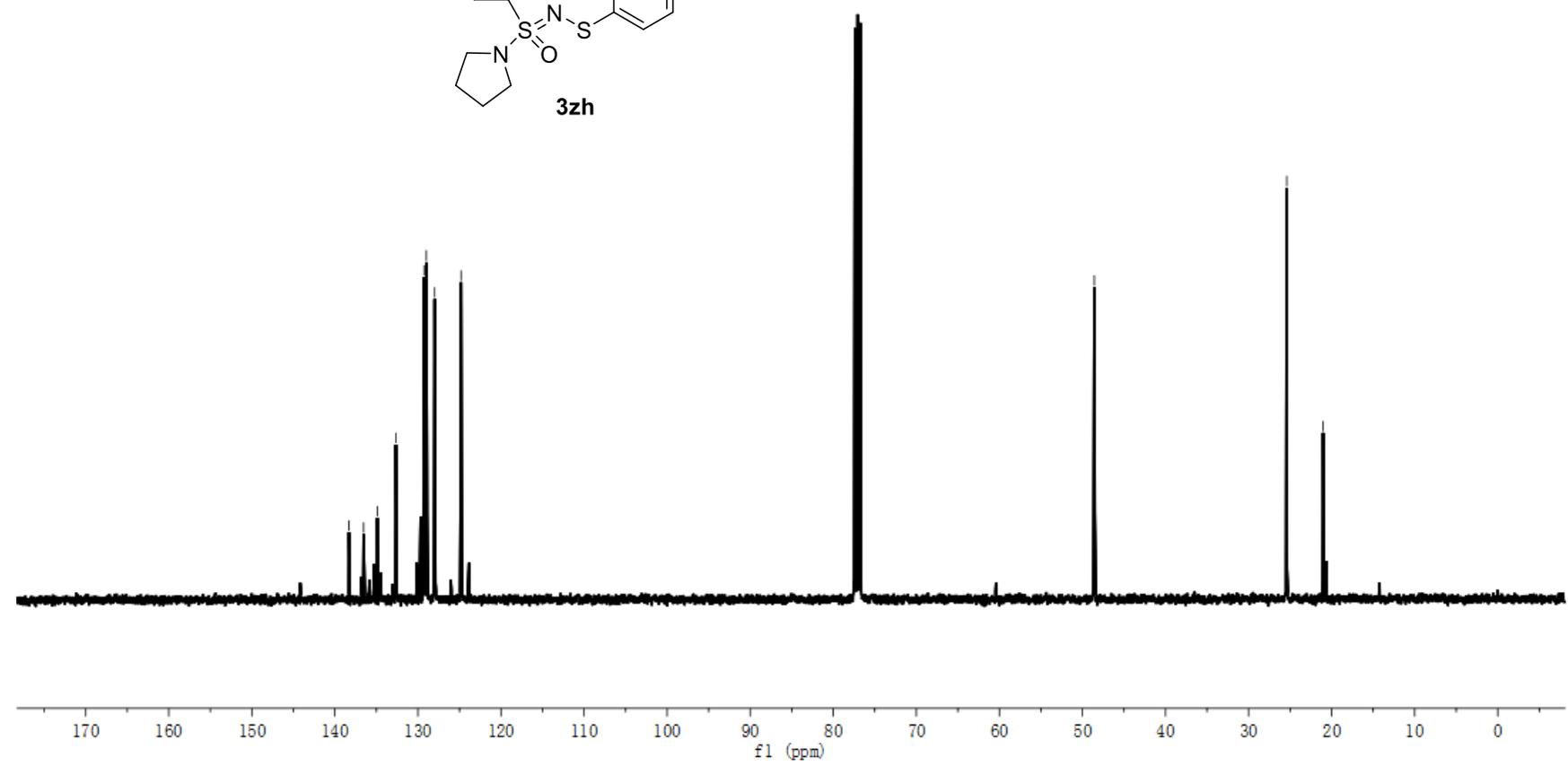
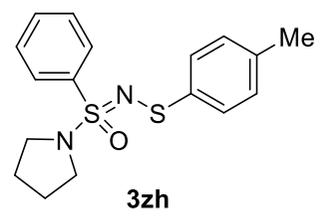


¹³C NMR spectra of compound **3zh** (101 MHz, CDCl₃)

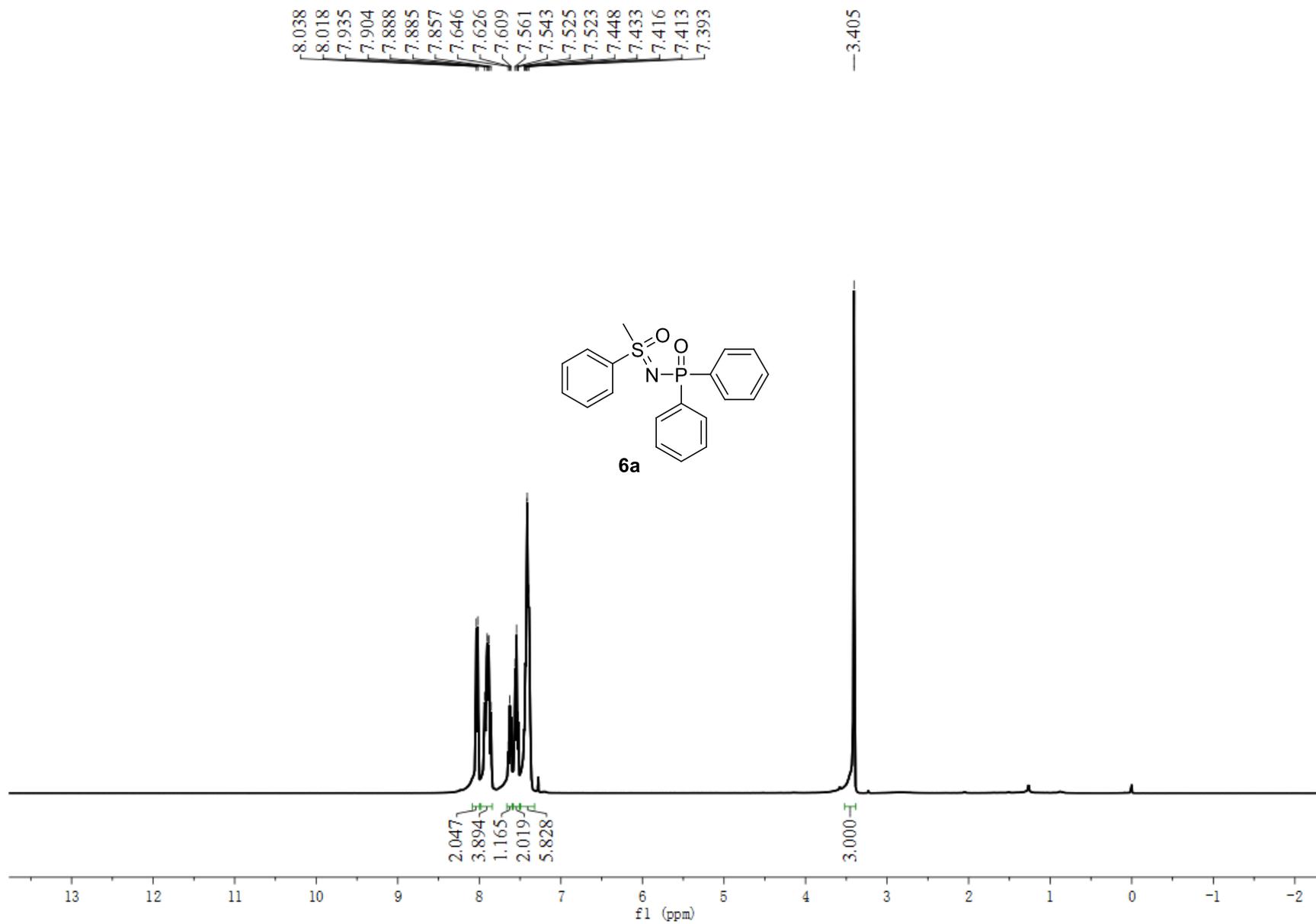
138.309
136.540
134.886
132.658
129.264
128.991
127.989
124.809

—48.564

—25.395
—21.024



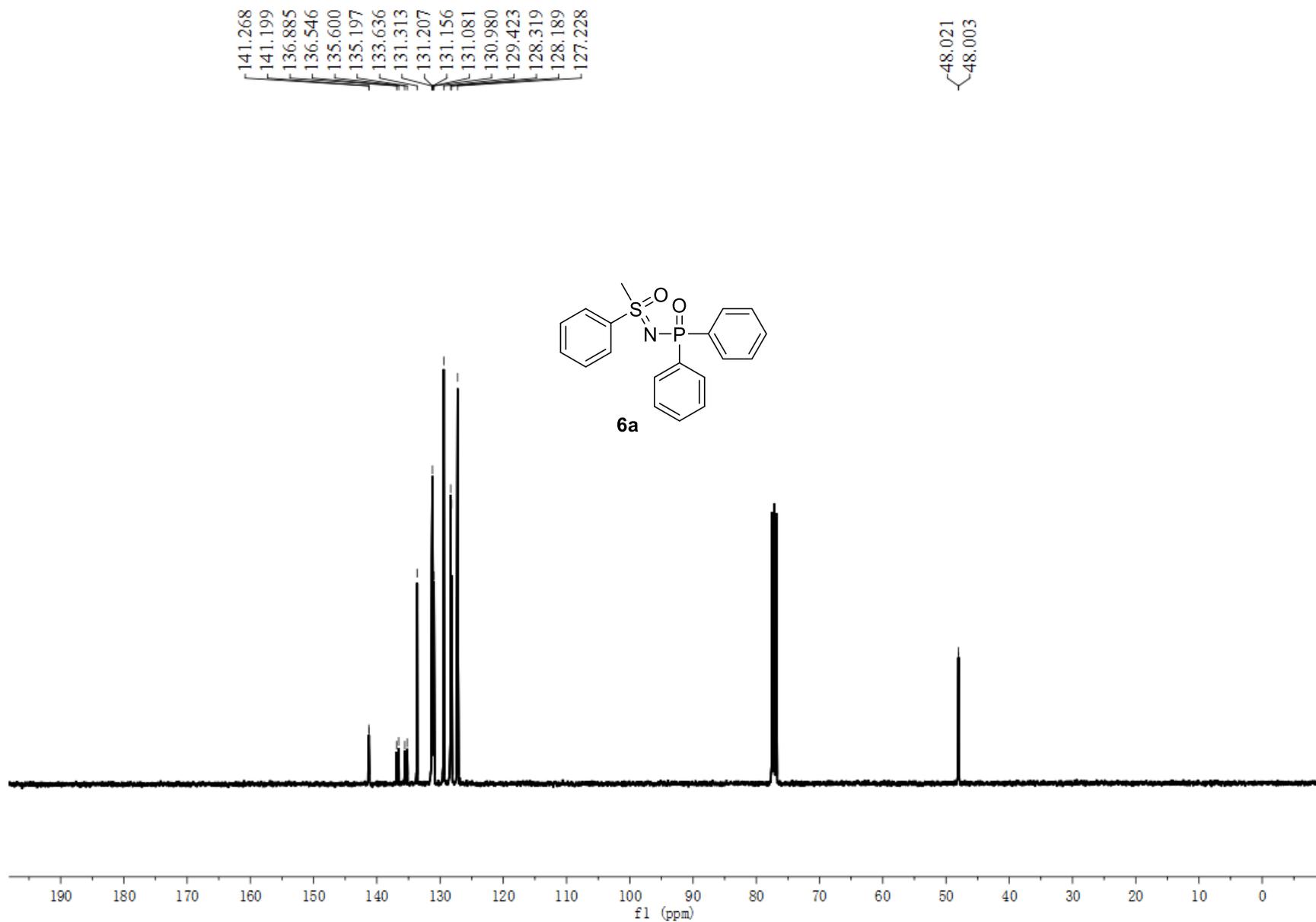
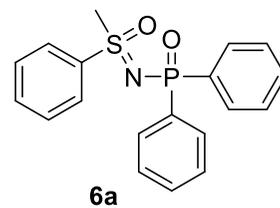
¹H NMR spectra of compound **6a** (400 MHz, CDCl₃)



¹³C NMR spectra of compound **6a** (101 MHz, CDCl₃)

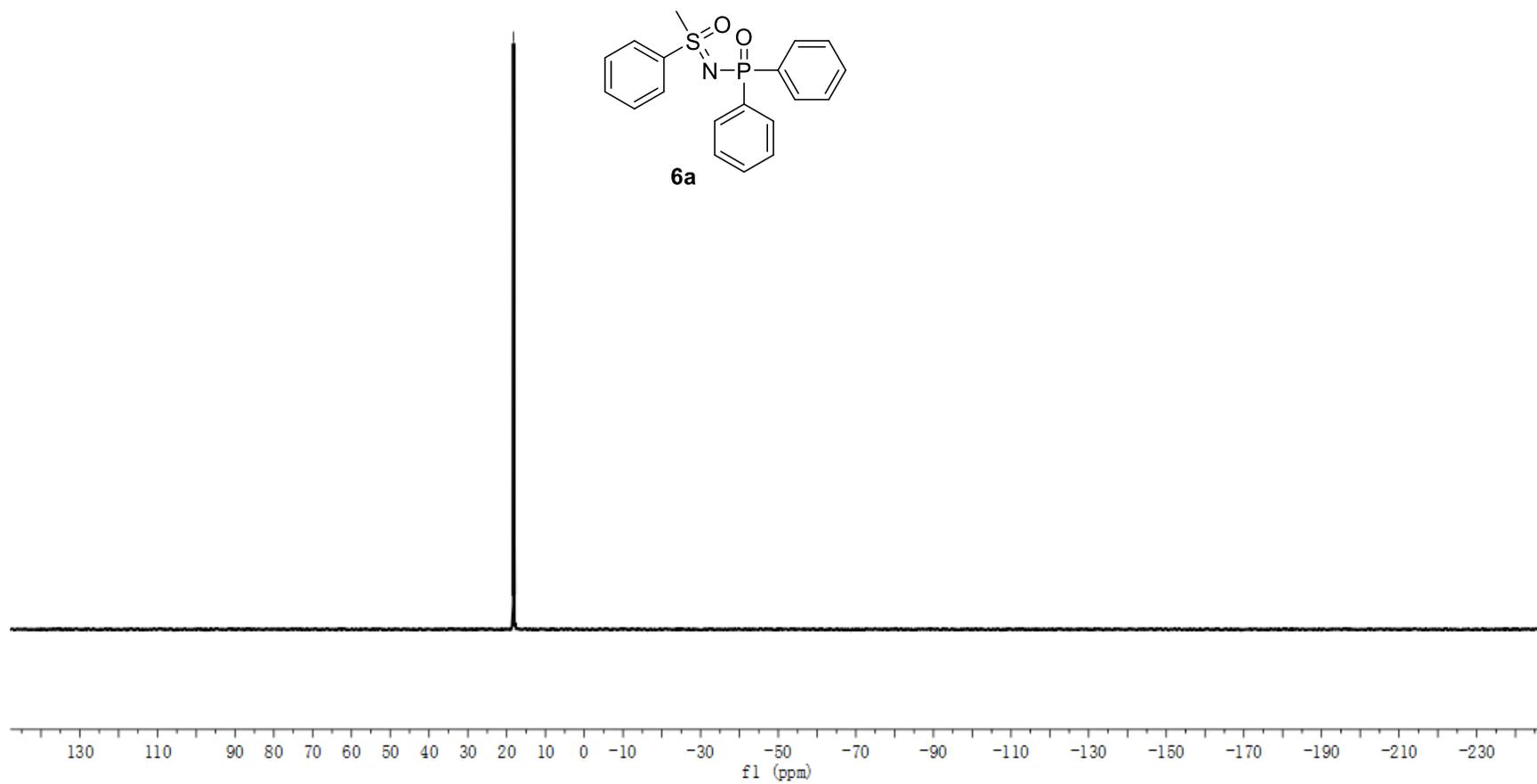
141.268
141.199
136.885
136.546
135.600
135.197
133.636
131.313
131.207
131.156
131.081
130.980
129.423
128.319
128.189
127.228

48.021
48.003



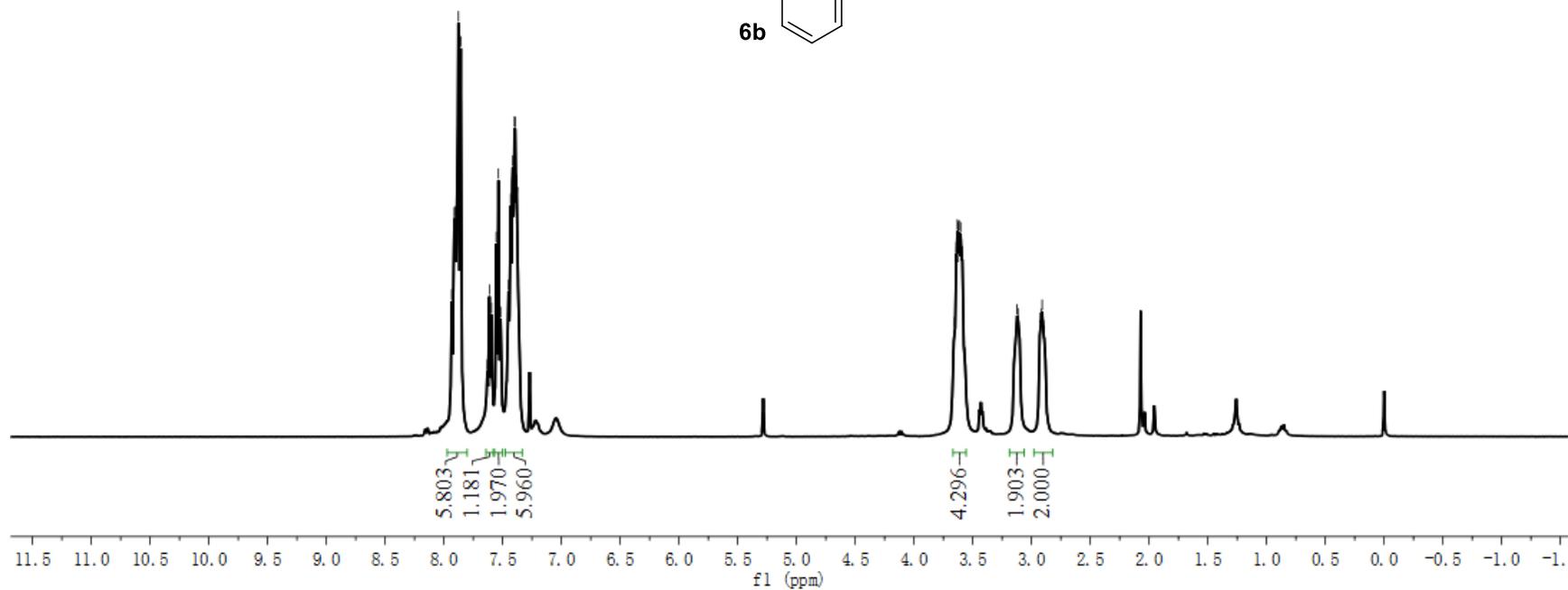
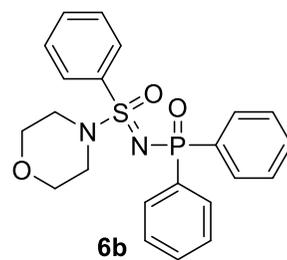
^{31}P NMR spectra of compound **6a** (162 MHz, CDCl_3)

—18.205



¹H NMR spectra of compound **6b** (400 MHz, CDCl₃)

7.934, 7.911, 7.905, 7.876, 7.857, 7.631, 7.613, 7.595, 7.555, 7.536, 7.517, 7.450, 7.432, 7.413, 7.400, 7.393, 7.381, 3.668, 3.654, 3.640, 3.631, 3.625, 3.615, 3.603, 3.596, 3.589, 3.568, 3.134, 3.134, 3.122, 3.115, 2.926, 2.918, 2.909, 2.898, 2.892

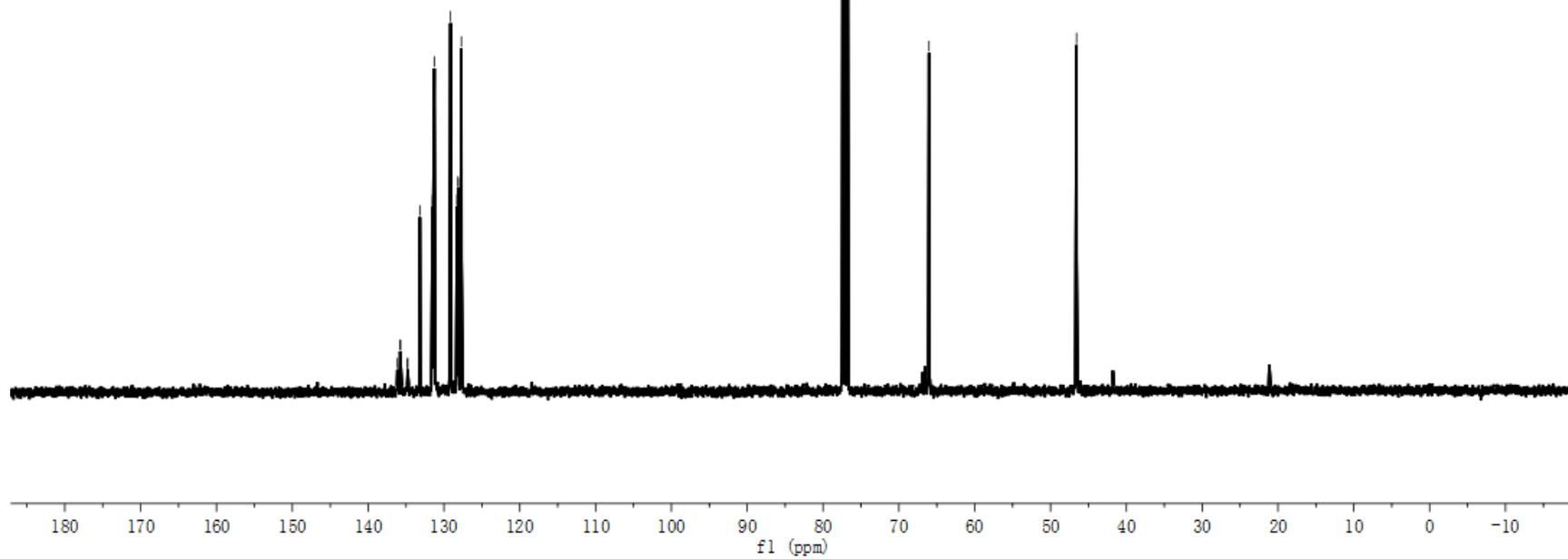
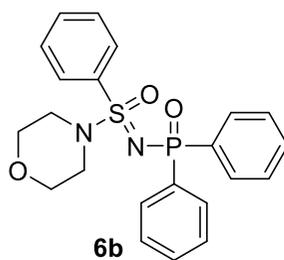


¹³C NMR spectra of compound **6b** (101 MHz, CDCl₃)

136.145
135.779
135.720
134.825
134.780
133.179
131.512
131.406
131.277
131.174
129.136
128.287
128.155
128.125
127.994
127.700

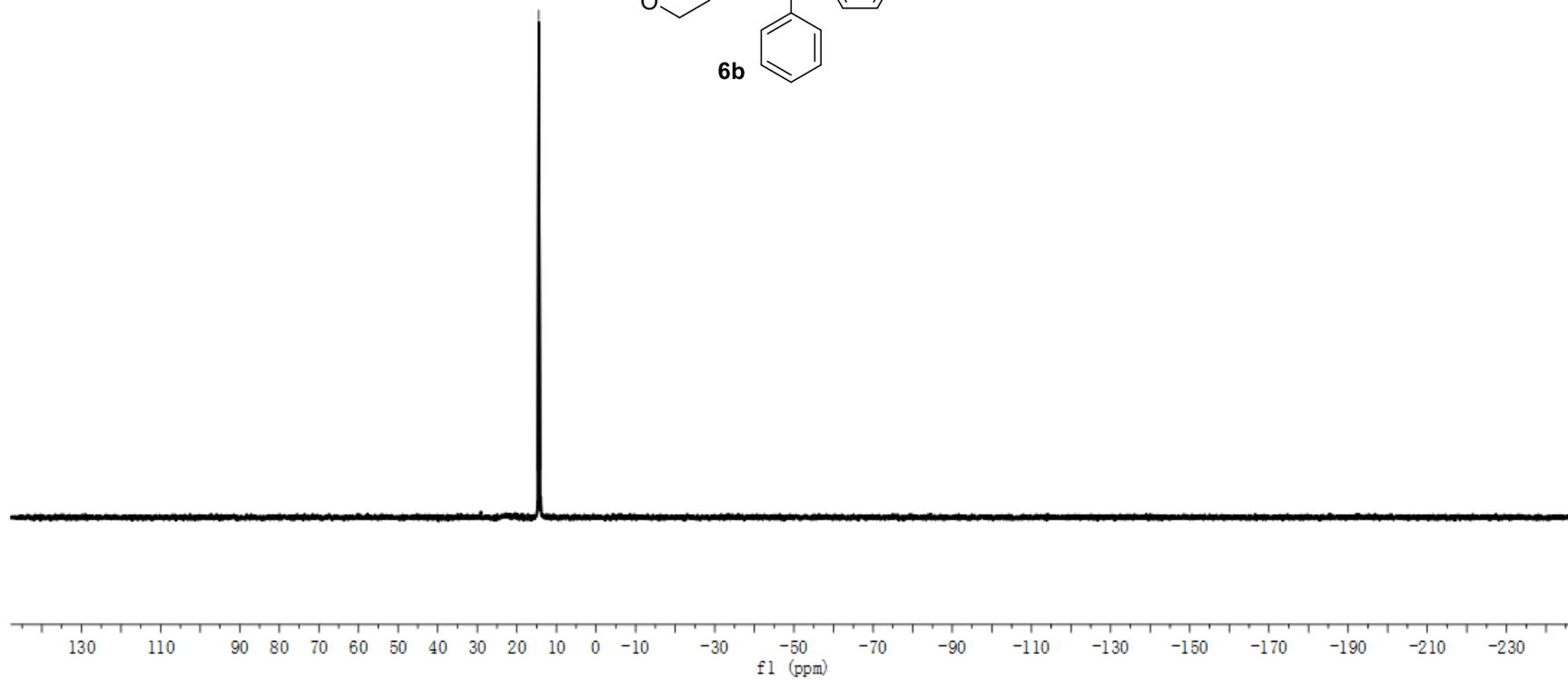
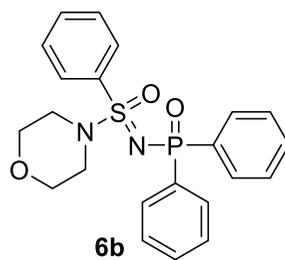
—66.034

—46.569

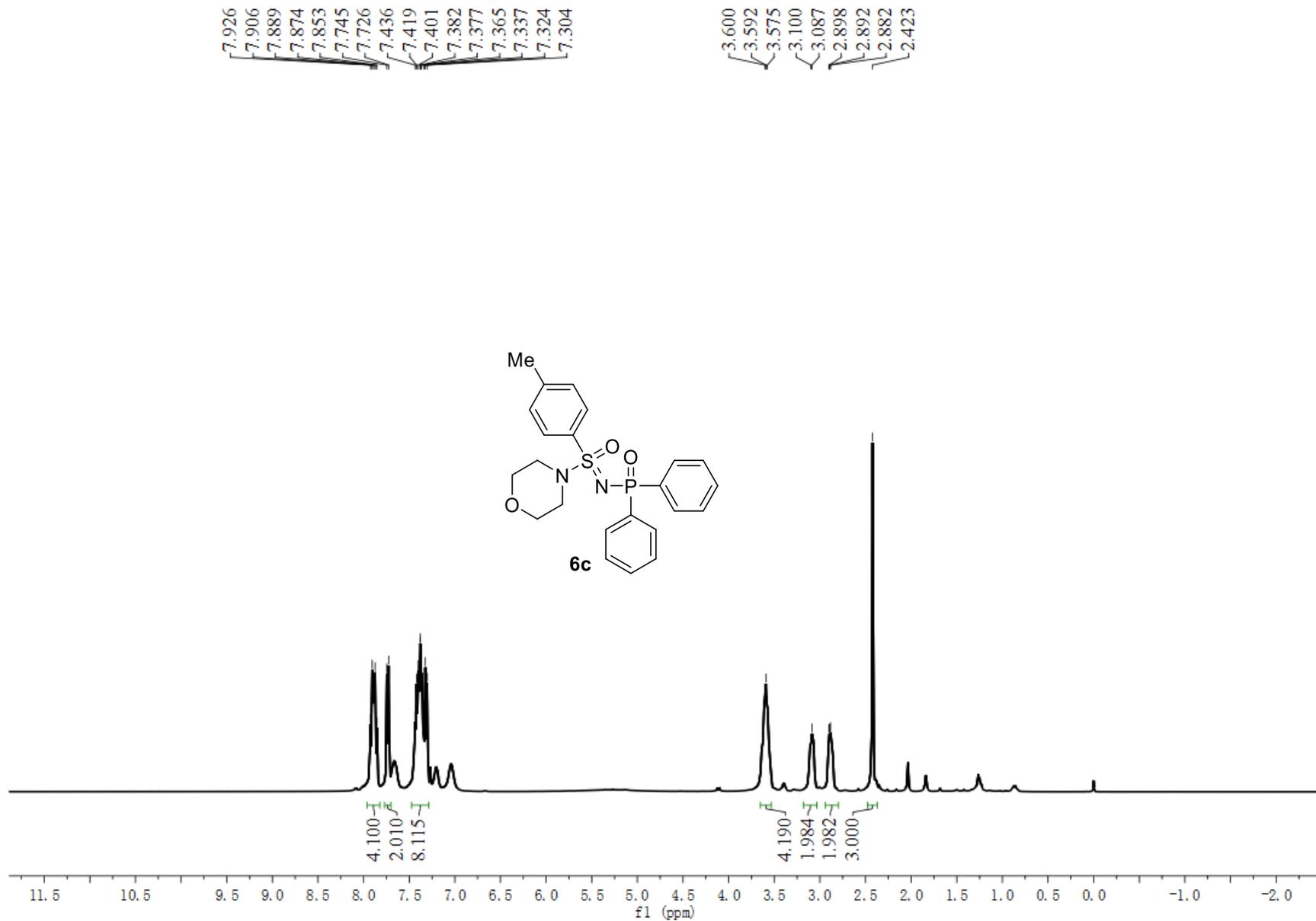


^{31}P NMR spectra of compound **6b** (162 MHz, CDCl_3)

-14.477

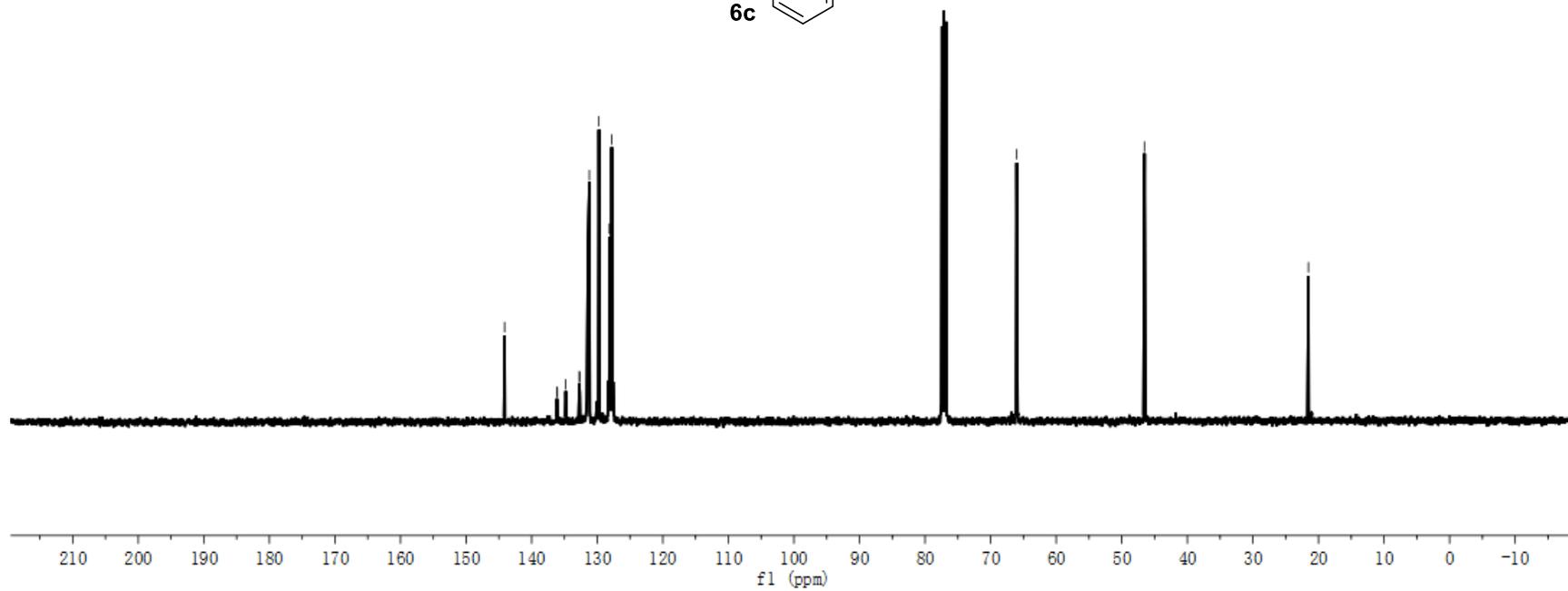
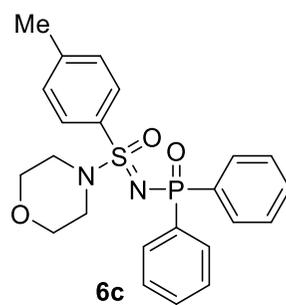


¹H NMR spectra of compound **6c** (400 MHz, CDCl₃)



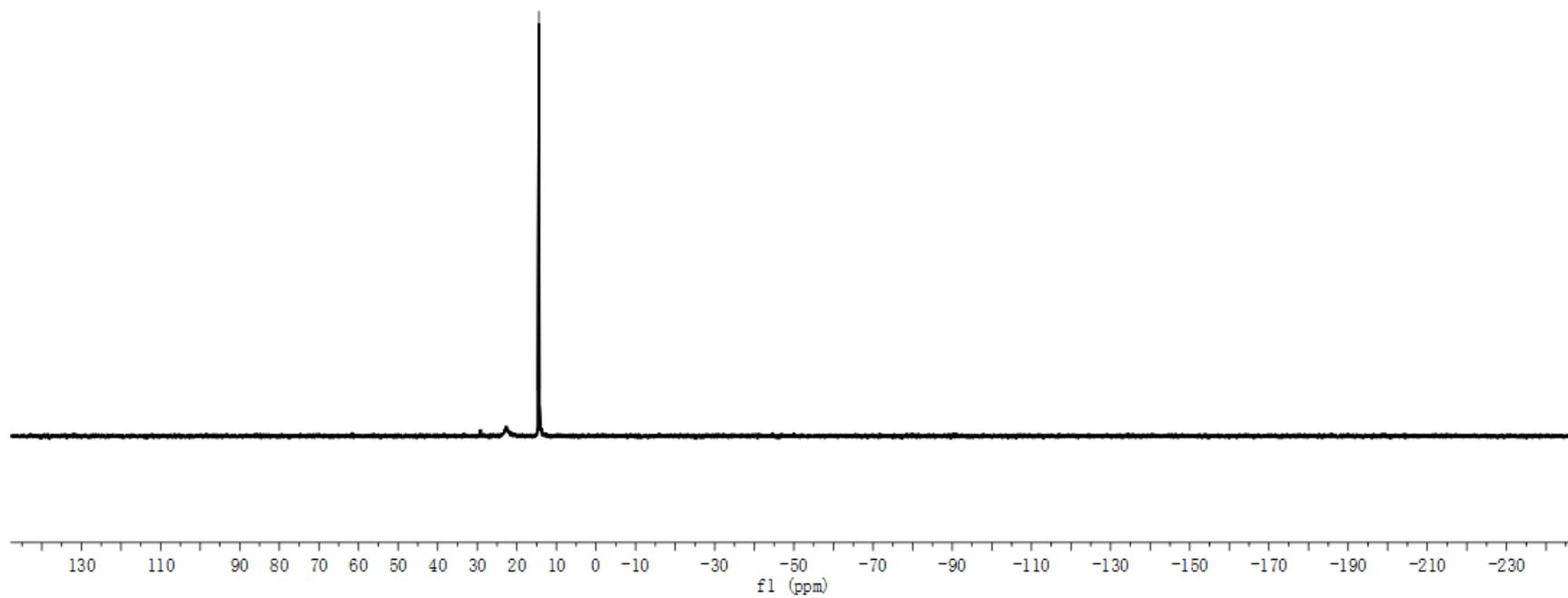
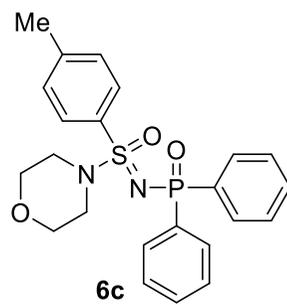
¹³C NMR spectra of compound **6c** (101 MHz, CDCl₃)

144.136
136.151
136.081
134.802
132.734
132.675
131.530
131.424
131.305
131.203
129.746
128.257
128.124
128.103
127.970
127.792
—66.020
—46.540
—21.533



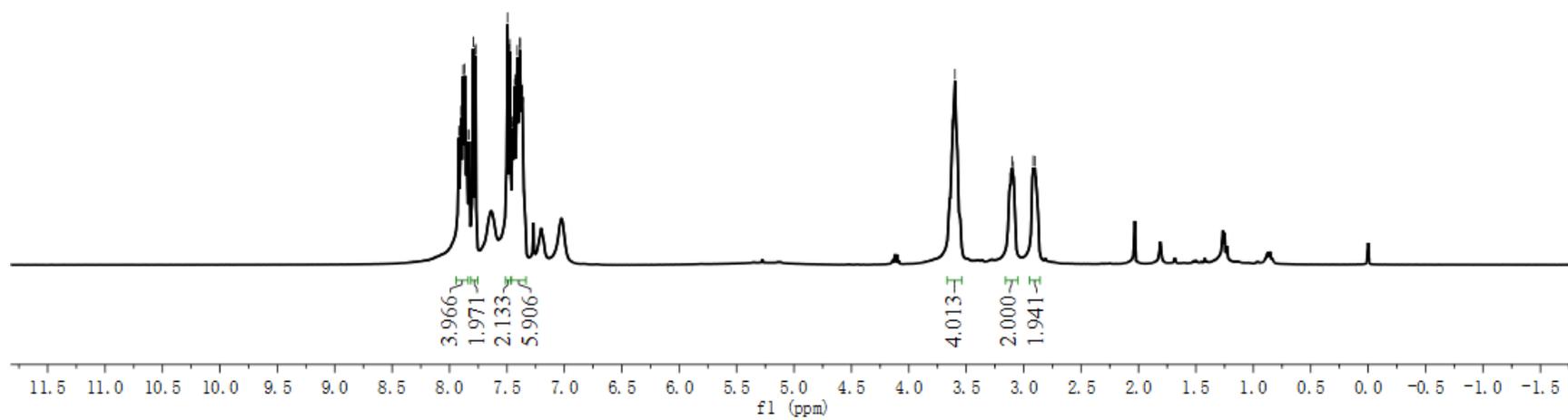
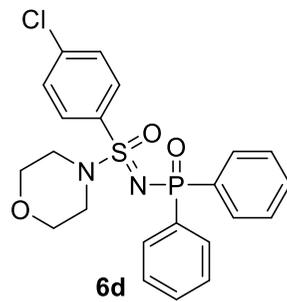
^{31}P NMR spectra of compound **6c** (162 MHz, CDCl_3)

-14.424



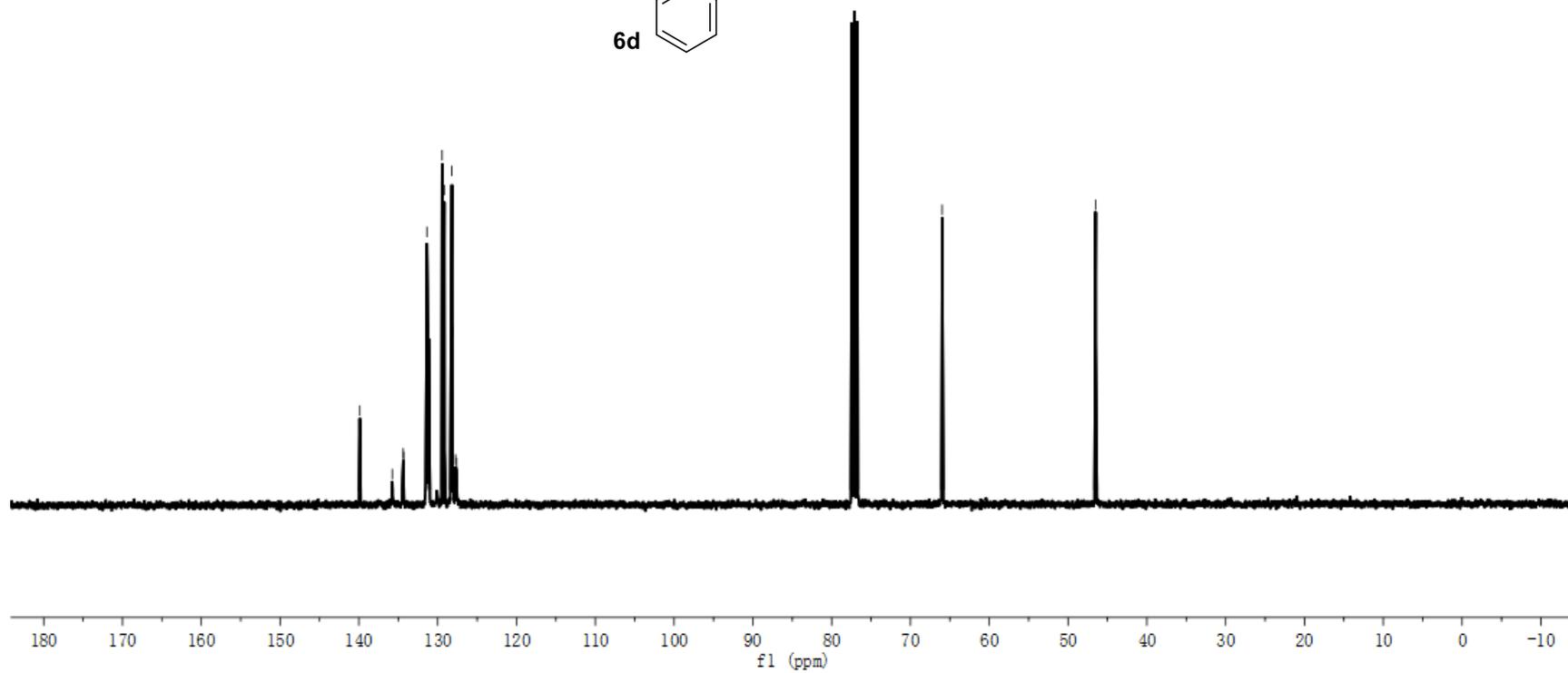
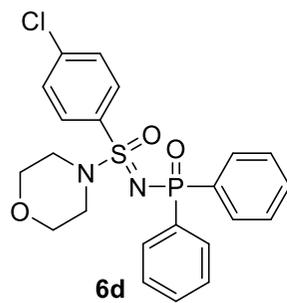
¹H NMR spectra of compound **6d** (400 MHz, CDCl₃)

7.920
7.900
7.884
7.867
7.850
7.830
7.794
7.775
7.772
7.495
7.476
7.474
7.451
7.448
7.433
7.430
7.411
7.387
7.385
7.376
7.369
7.367
7.348
3.641
3.620
3.598
3.118
3.102
3.093
2.917
2.902
2.889



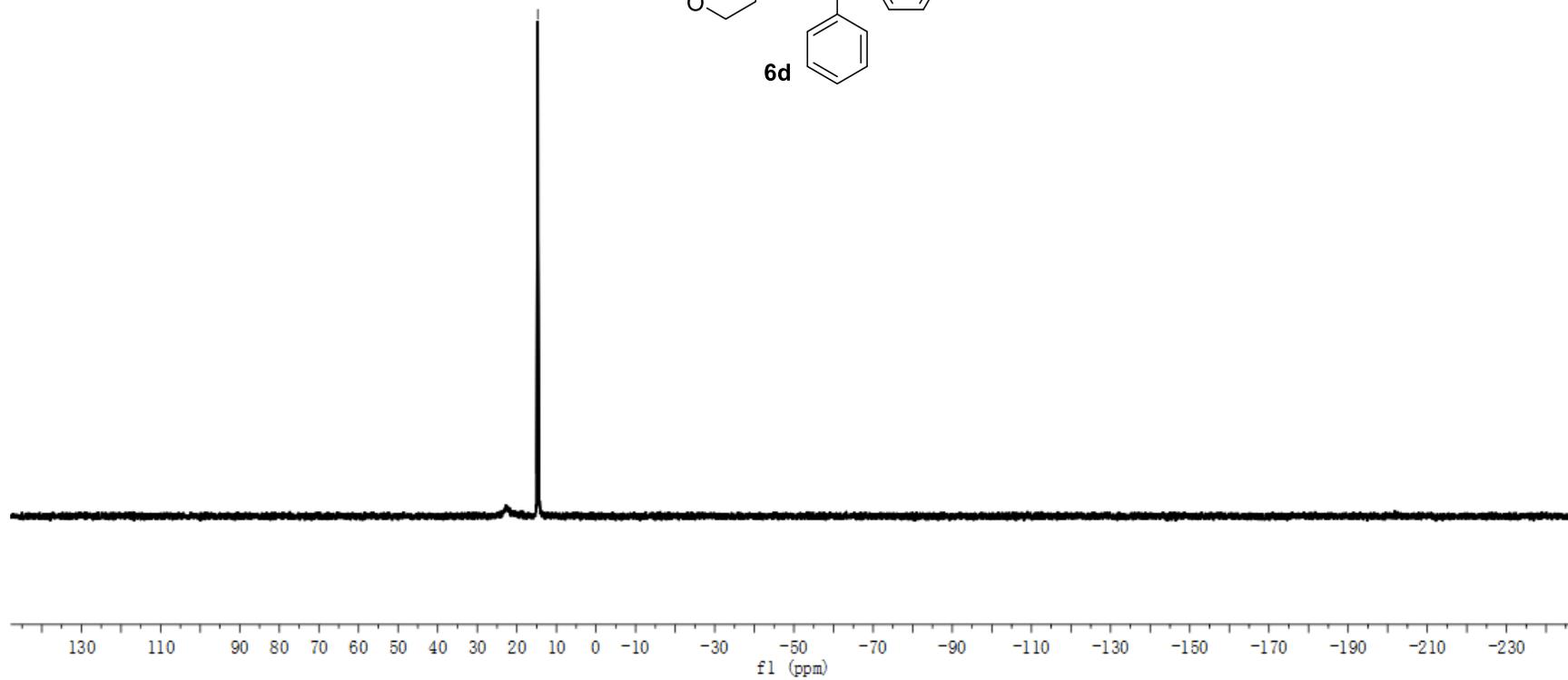
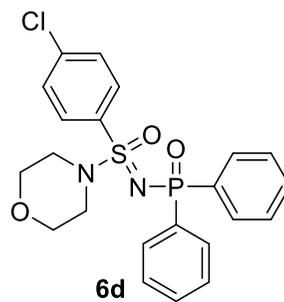
¹³C NMR spectra of compound **6d** (101 MHz, CDCl₃)

139.879
135.769
134.372
134.314
131.475
131.412
131.369
131.254
131.150
129.439
129.167
128.330
128.197
128.065
127.734
127.607
—65.972
—46.512



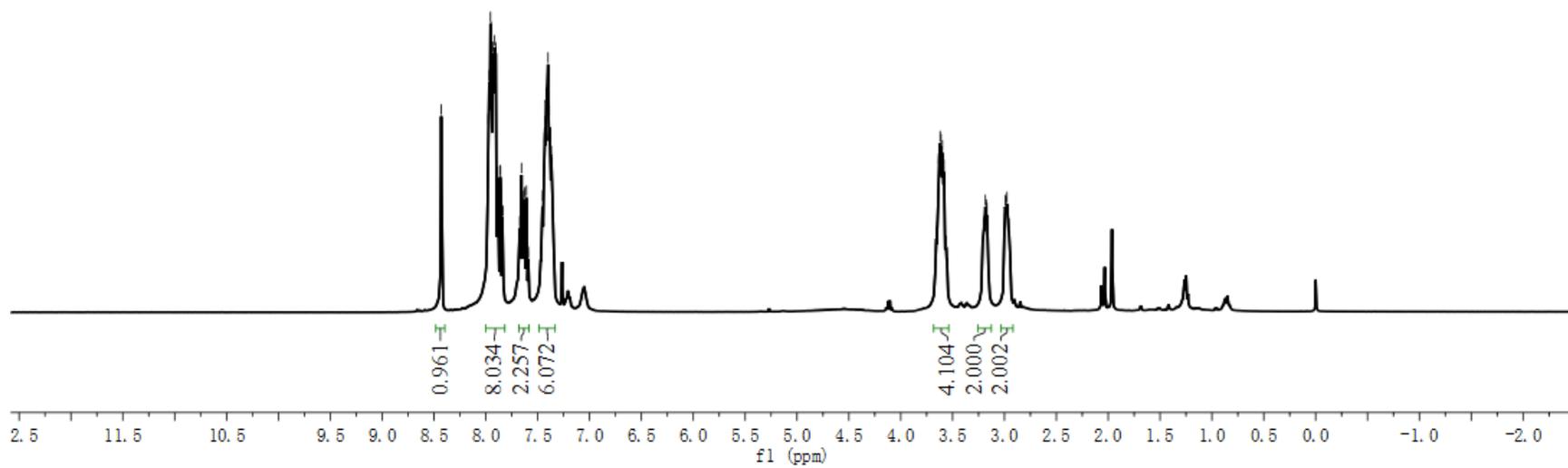
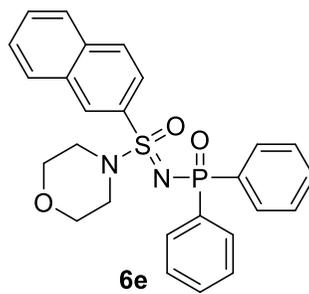
^{31}P NMR spectra of compound **6d** (162 MHz, CDCl_3)

-14.713



¹H NMR spectra of compound **6e** (400 MHz, CDCl₃)

8.430
7.977
7.968
7.955
7.949
7.933
7.915
7.904
7.886
7.862
7.858
7.840
7.656
7.636
7.627
7.608
7.453
7.435
7.428
7.418
7.414
7.410
7.401
7.388
7.380
7.369
7.361
3.663
3.656
3.649
3.635
3.627
3.620
3.611
3.599
3.591
3.583
3.570
3.562
3.555
3.203
3.197
3.184
3.176
3.169
2.992
2.984
2.975
2.964
2.957

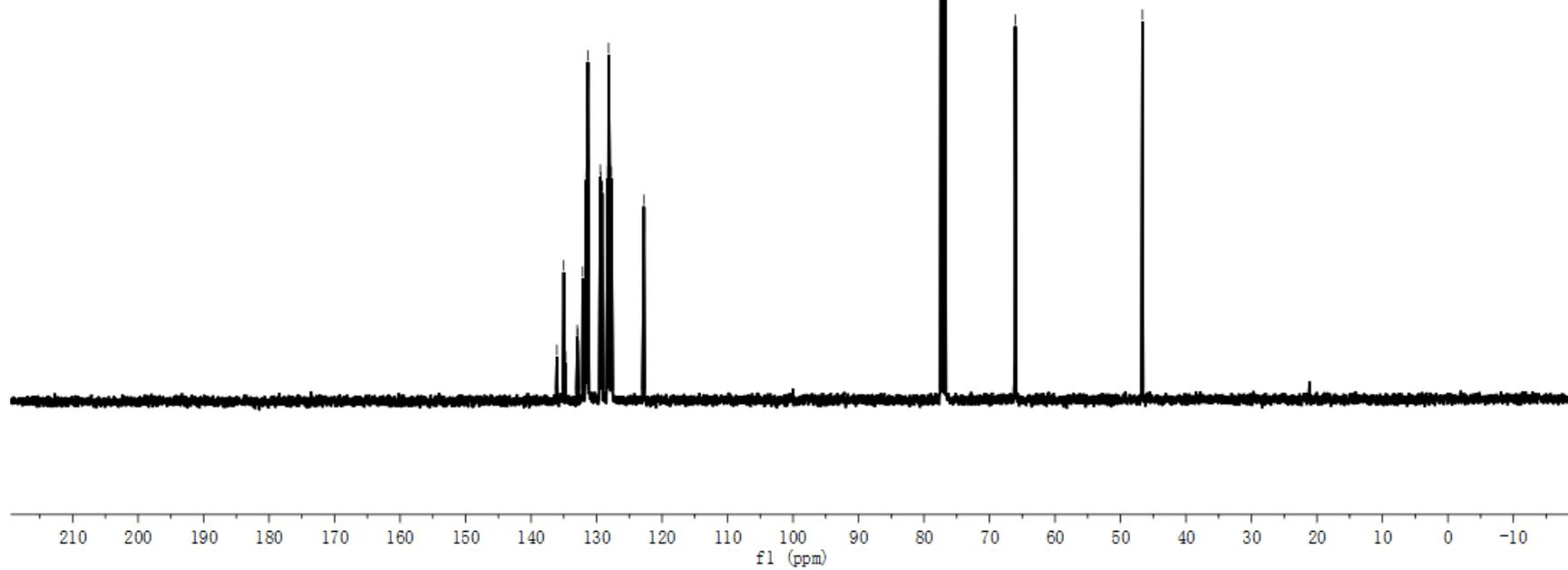
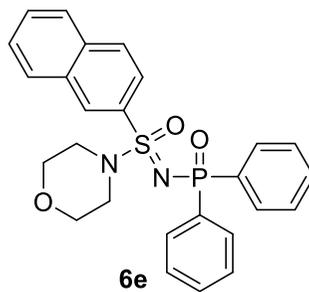


¹³C NMR spectra of compound **6e** (101 MHz, CDCl₃)

136.059
135.009
134.790
134.723
132.948
132.889
132.115
131.577
131.470
131.325
131.223
129.420
129.351
129.227
129.145
128.291
128.154
128.018
127.930
127.726
122.781

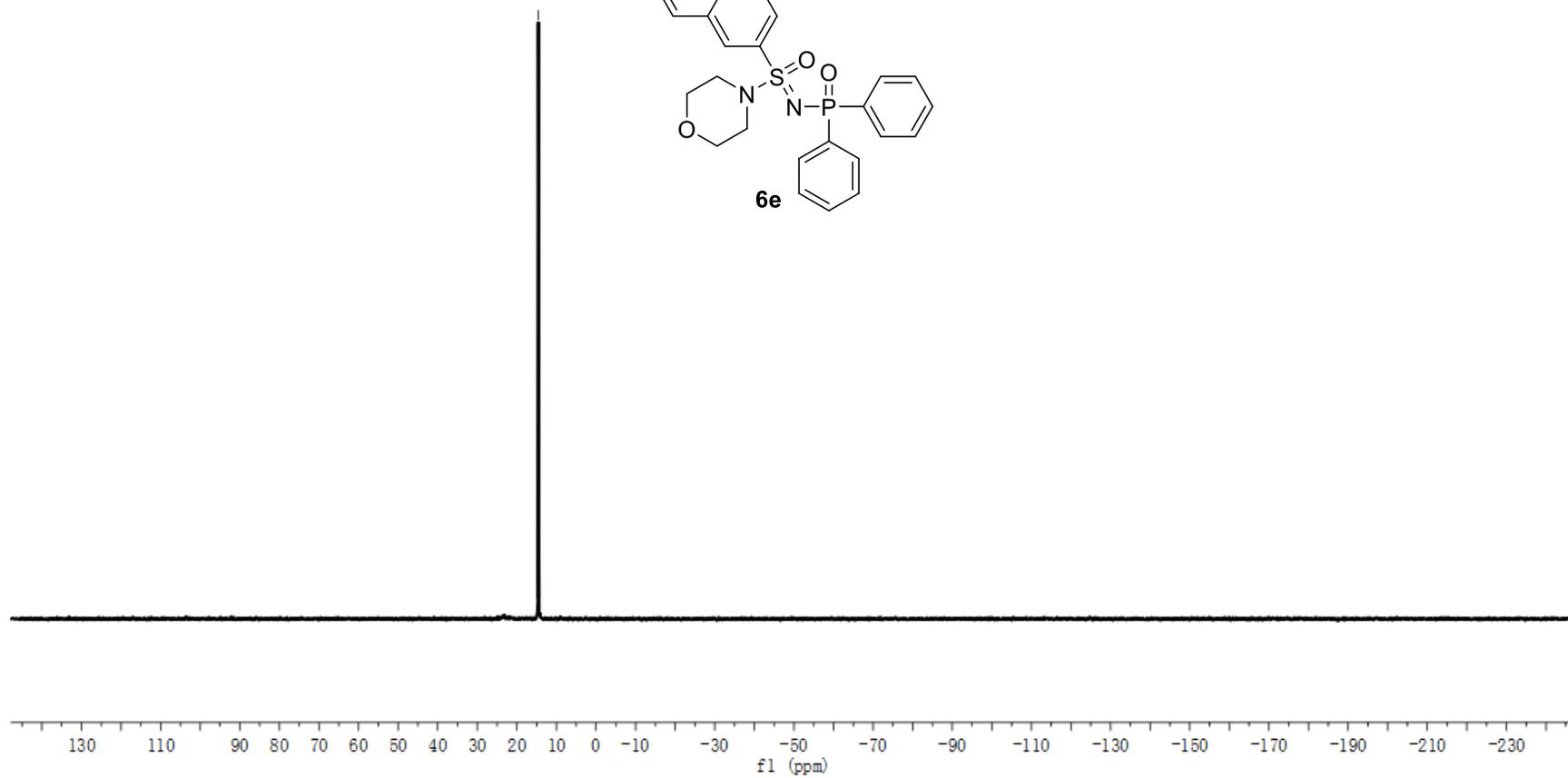
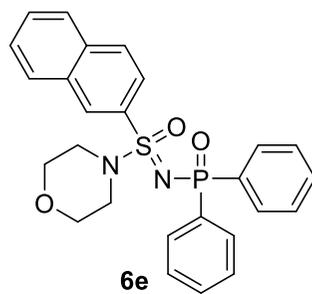
—66.063

—46.641



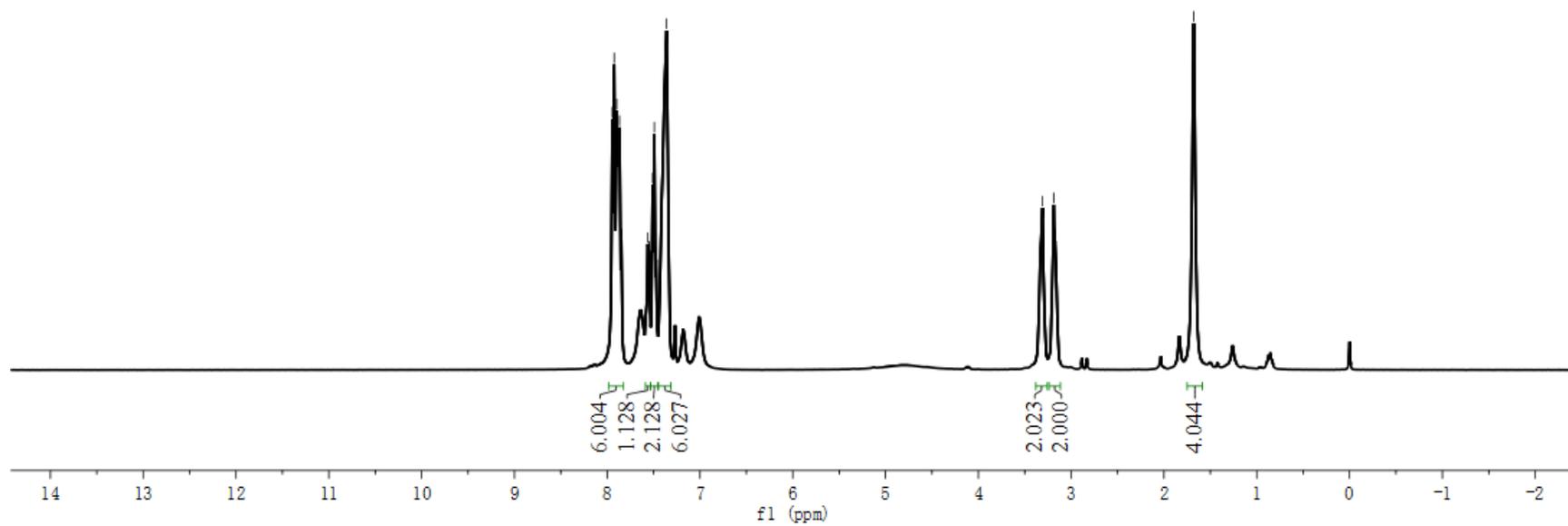
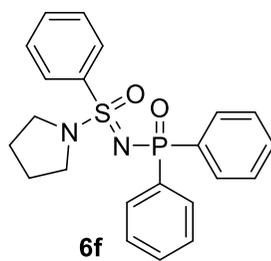
^{31}P NMR spectra of compound **6e** (162 MHz, CDCl_3)

— 14,560

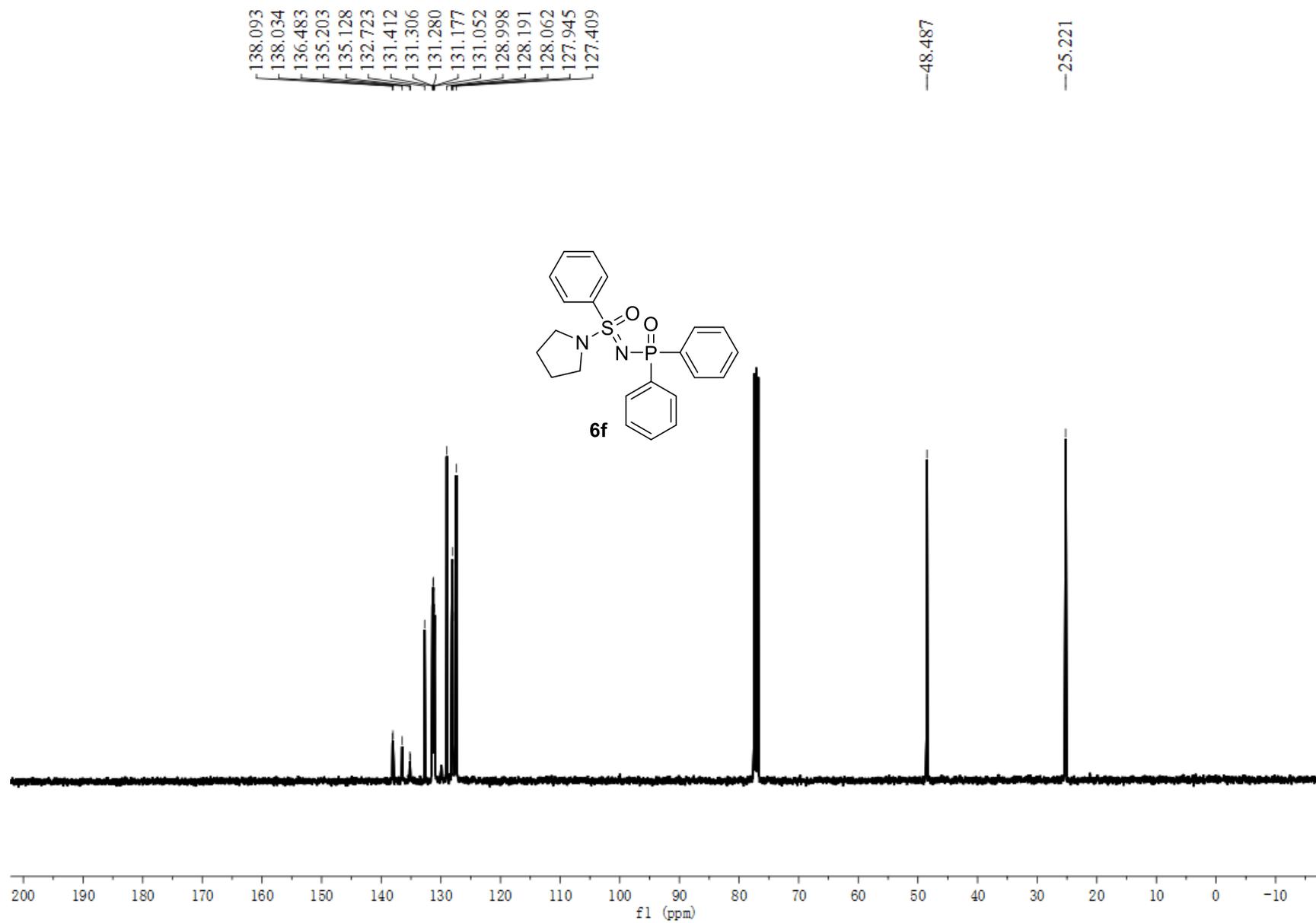


¹H NMR spectra of compound **6f** (400 MHz, CDCl₃)

7.945
7.925
7.898
7.882
7.867
7.847
7.581
7.563
7.546
7.510
7.492
7.473
7.409
7.392
7.376
7.360
3.324
3.308
3.188
3.173
-1.679

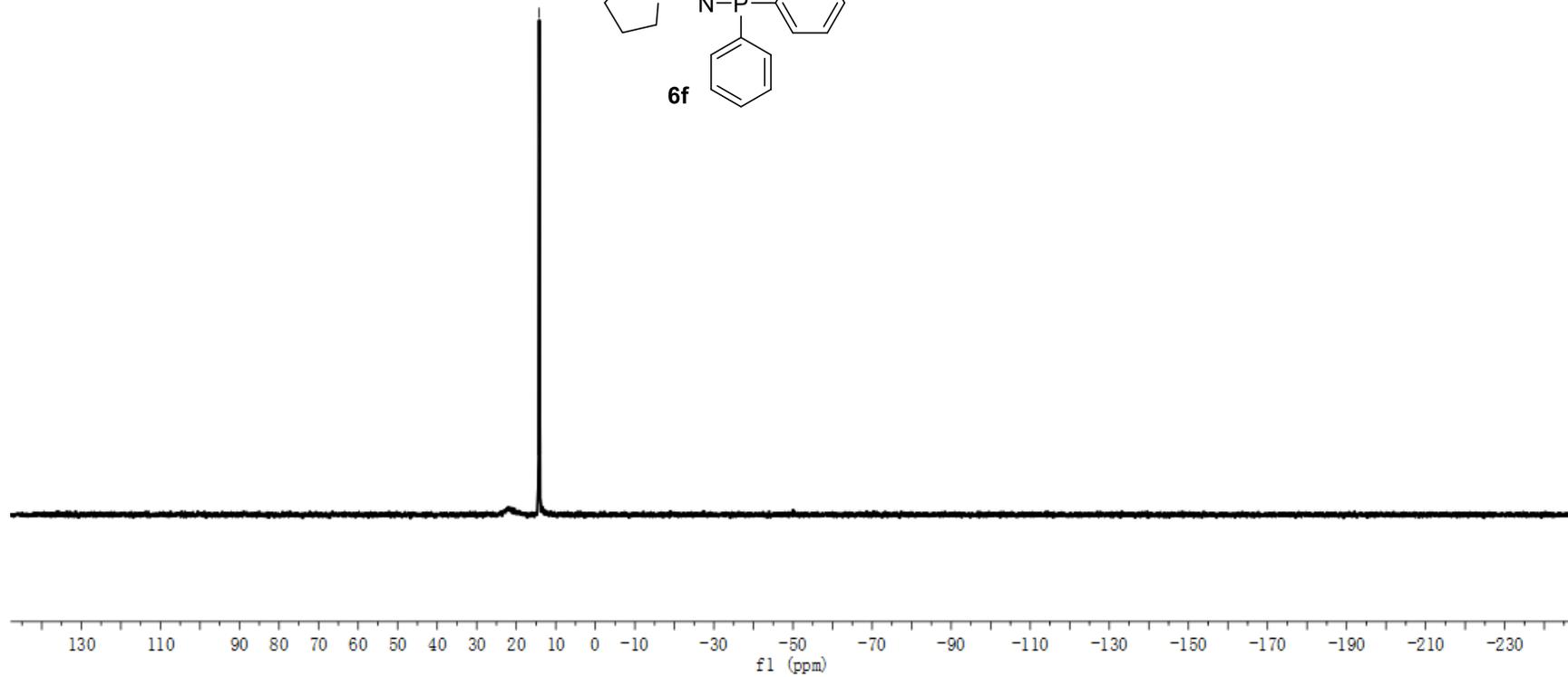
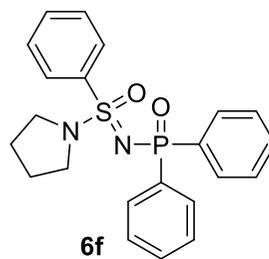


¹³C NMR spectra of compound **6f** (101 MHz, CDCl₃)



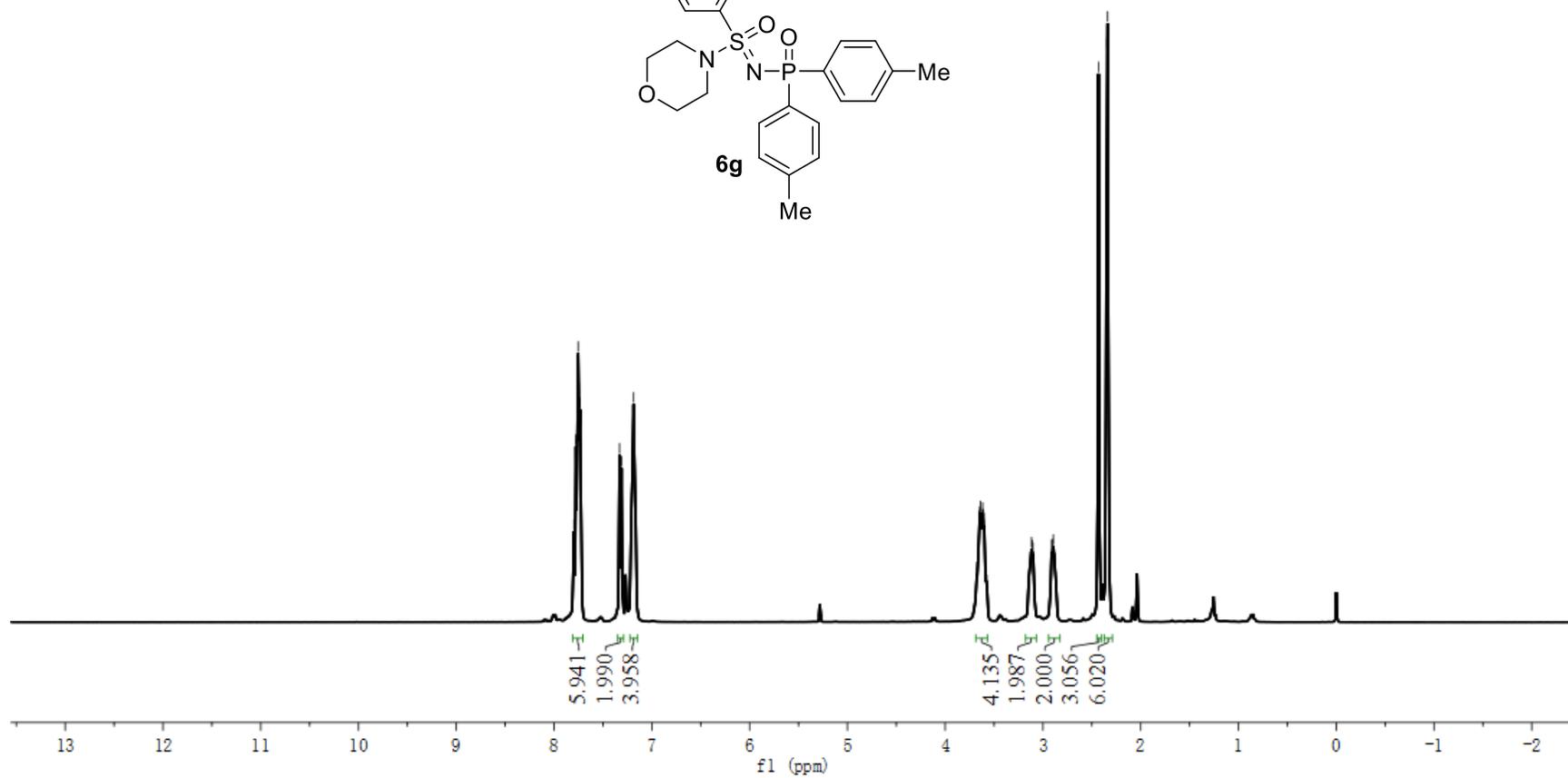
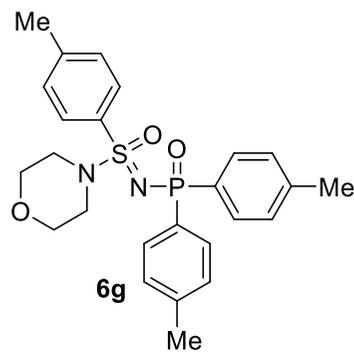
^{31}P NMR spectra of compound **6f** (162 MHz, CDCl_3)

-14.193

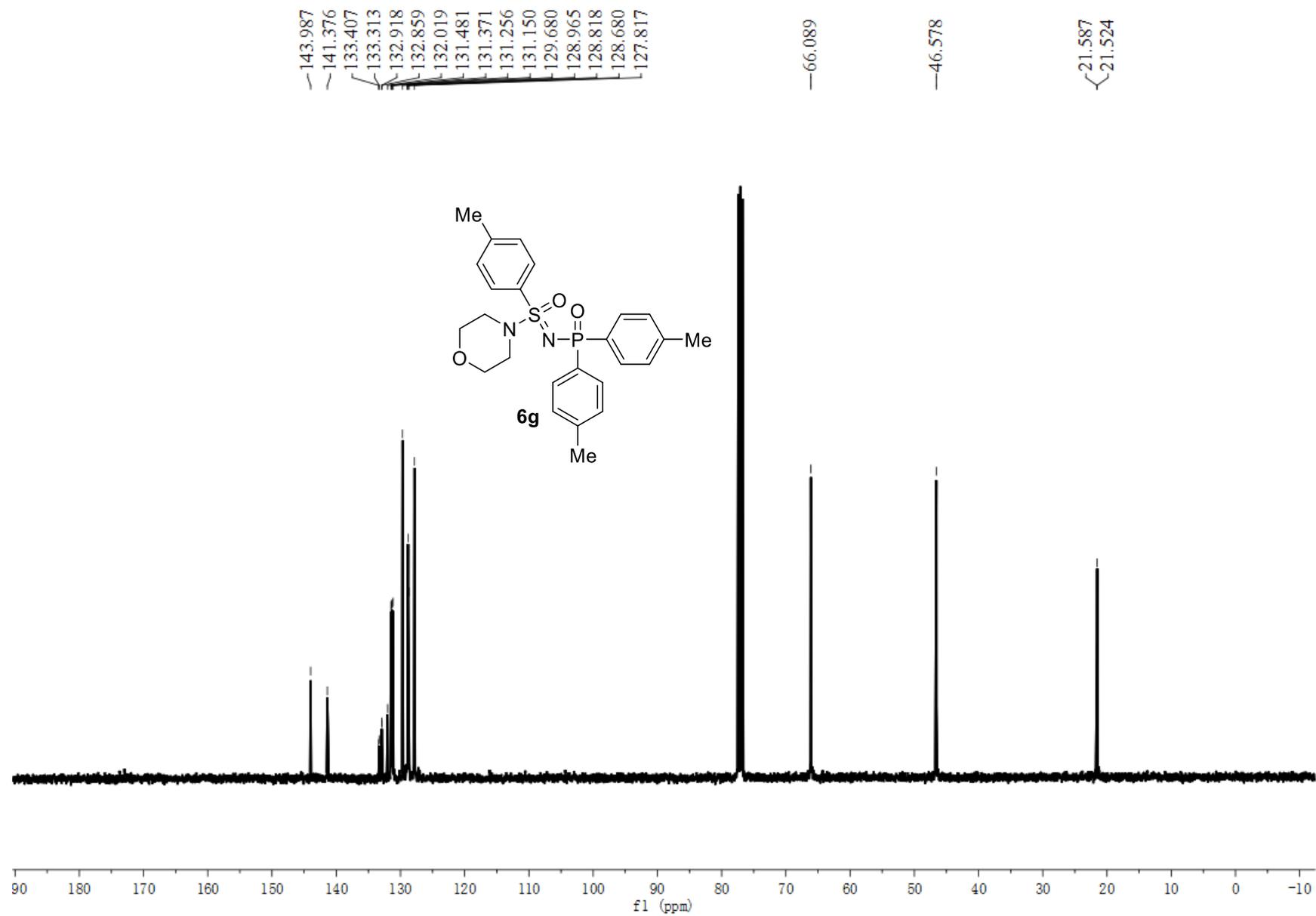


¹H NMR spectra of compound **6g** (400 MHz, CDCl₃)

7.797
7.776
7.754
7.746
7.734
7.726
7.330
7.310
7.202
7.186
3.675
3.667
3.654
3.647
3.640
3.631
3.624
3.616
3.609
3.601
3.580
3.573
3.128
3.116
3.110
3.102
2.911
2.903
2.894
2.883
2.876
2.431
2.345
2.338

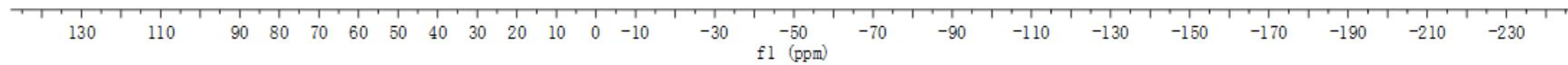
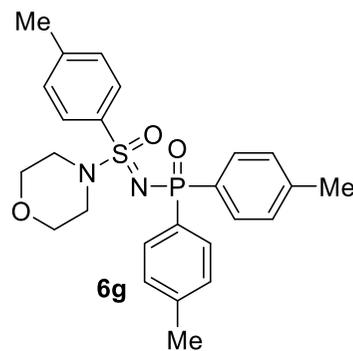


¹³C NMR spectra of compound **6g** (101 MHz, CDCl₃)



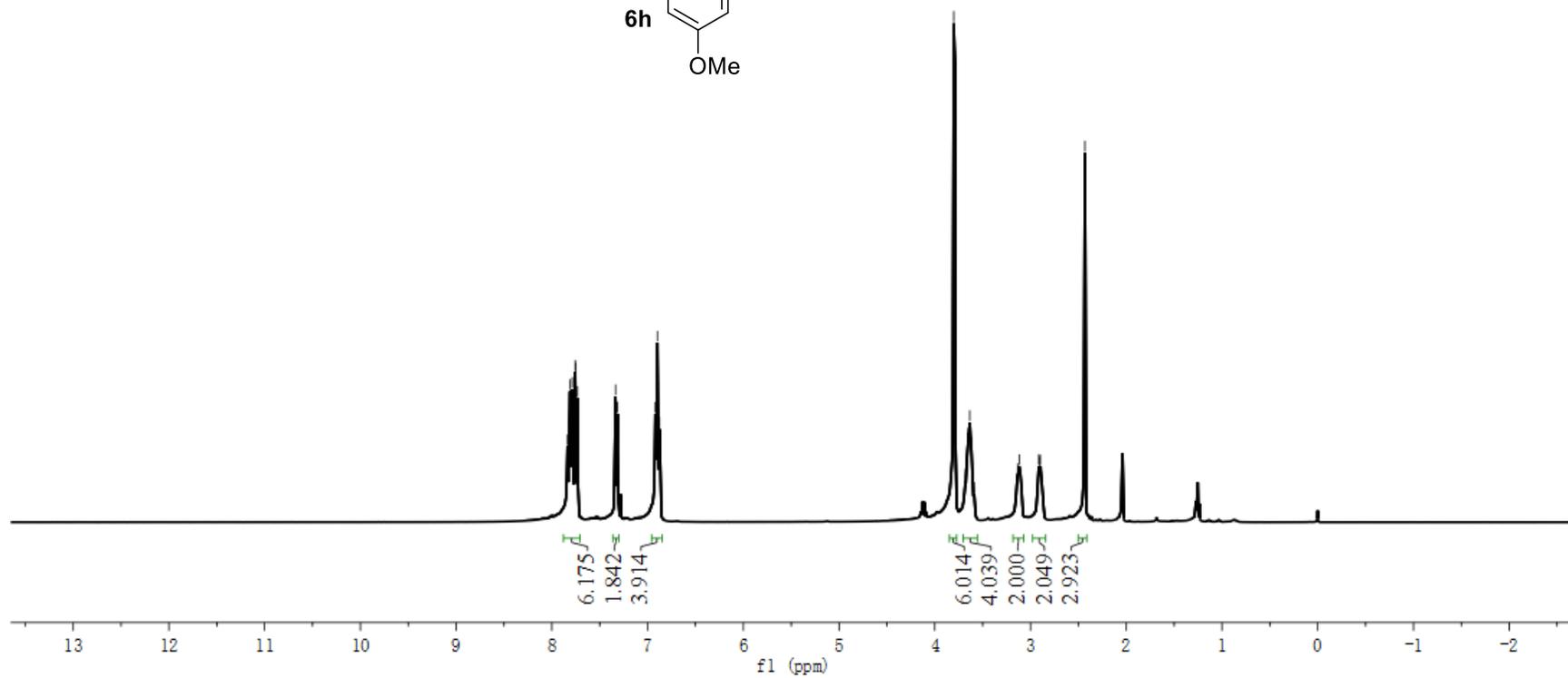
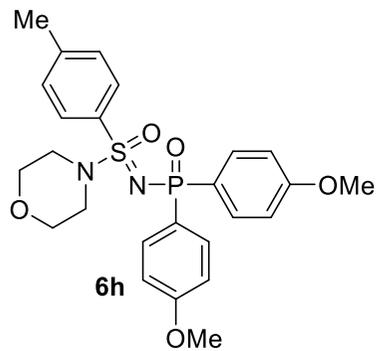
^{31}P NMR spectra of compound **6g** (162 MHz, CDCl_3)

— 14.933

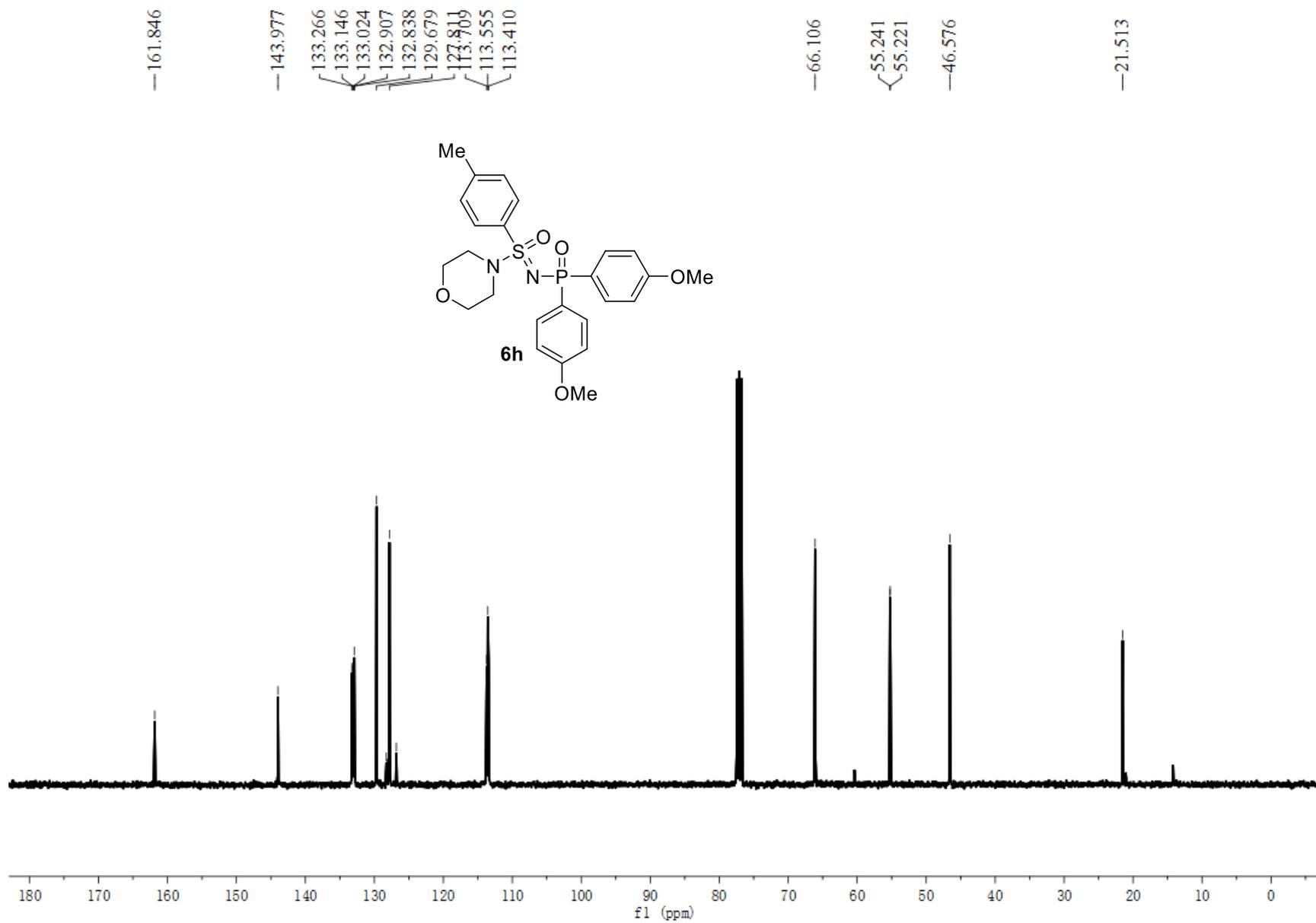


¹H NMR spectra of compound **6h** (400 MHz, CDCl₃)

7.837
7.809
7.787
7.756
7.753
7.732
7.334
7.315
6.919
6.897
6.875
3.801
3.790
3.680
3.659
3.651
3.643
3.635
3.624
3.617
3.595
3.588
3.135
3.118
2.914
2.907
2.898
2.886
2.432

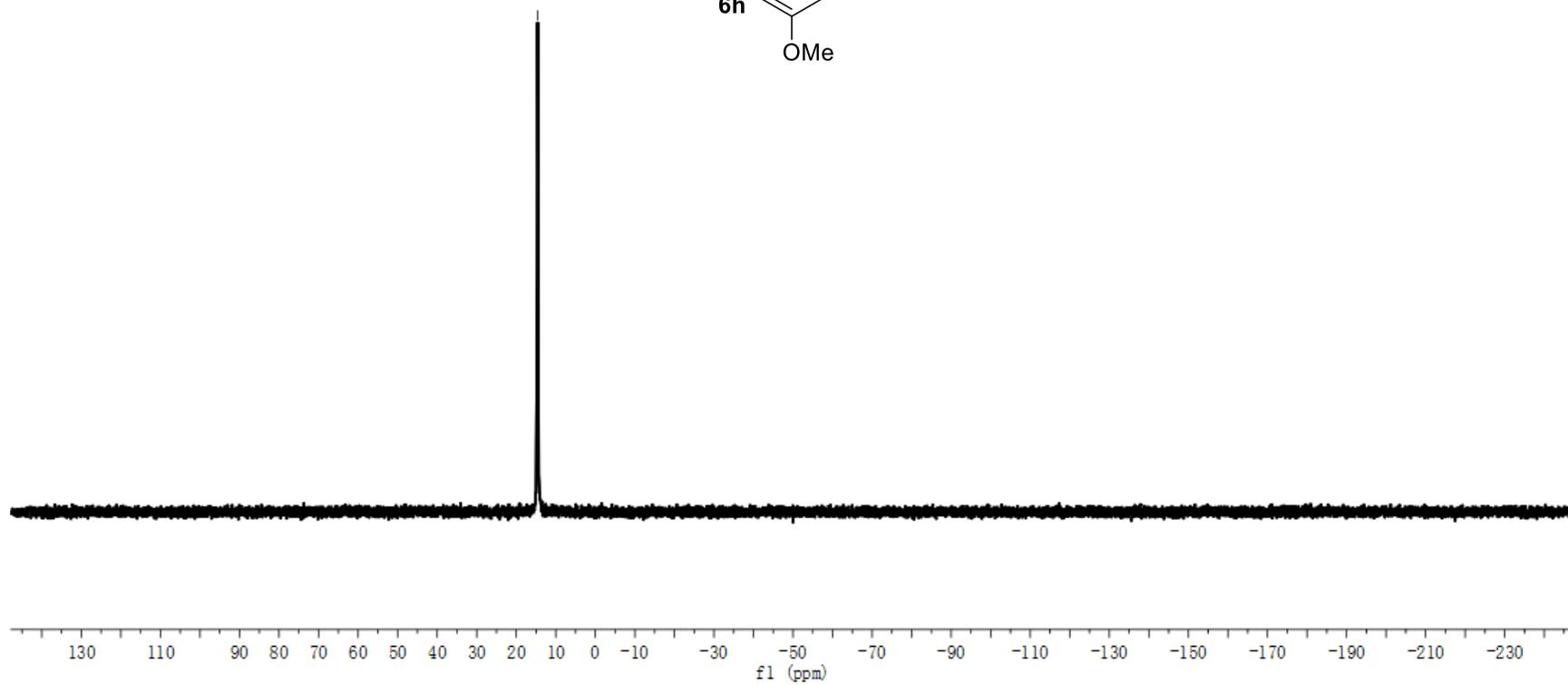
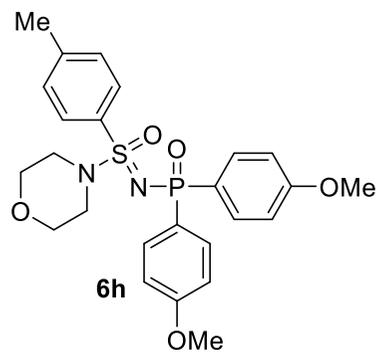


¹³C NMR spectra of compound **6h** (101 MHz, CDCl₃)



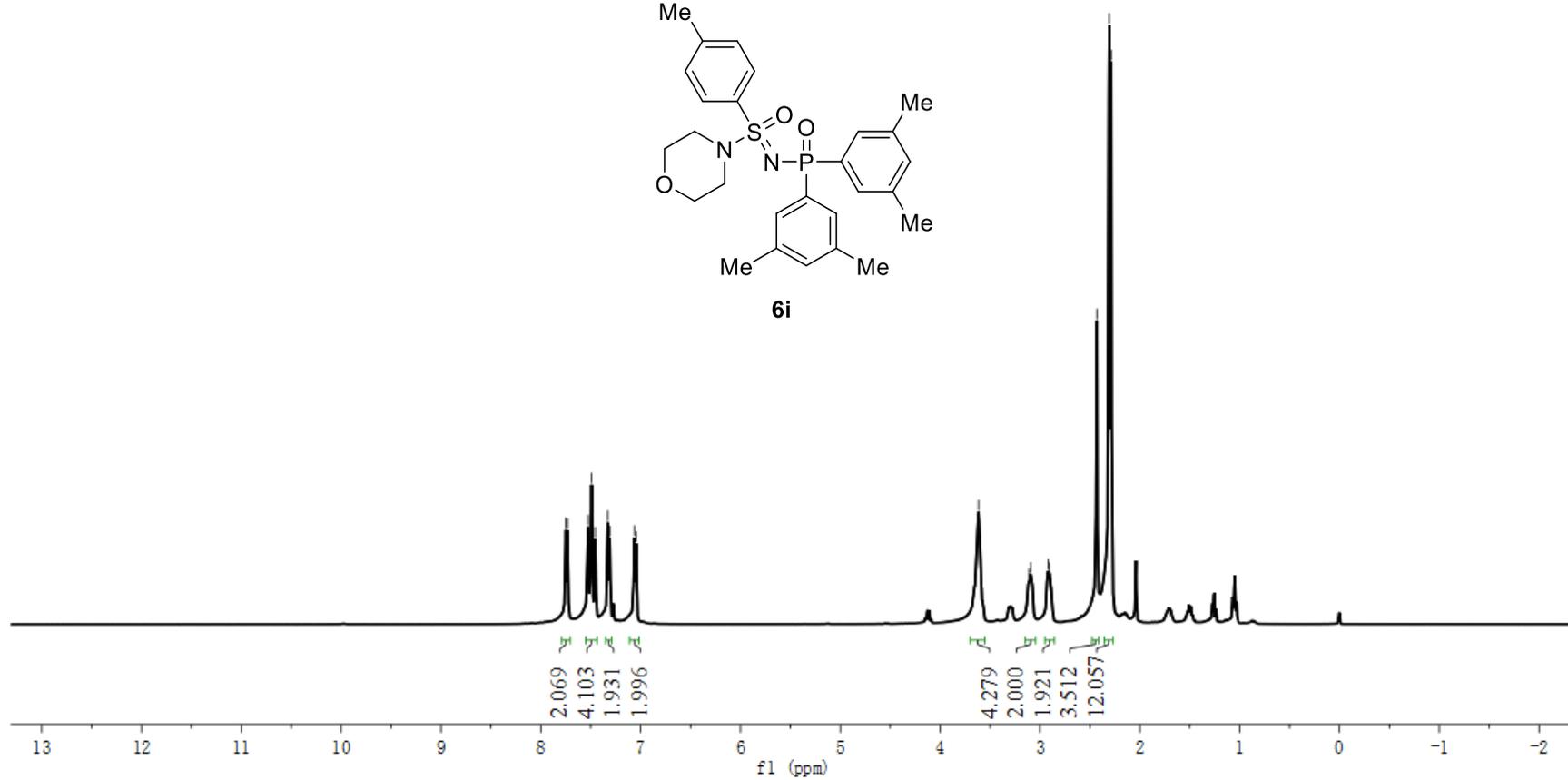
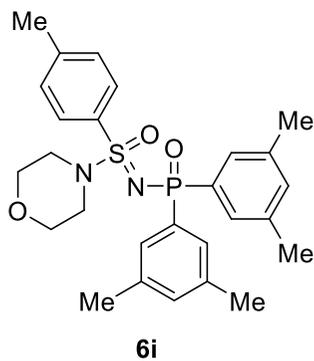
^{31}P NMR spectra of compound **6h** (162 MHz, CDCl_3)

— 14.592



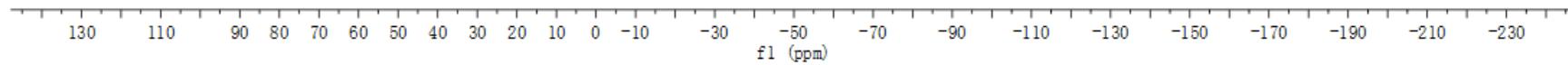
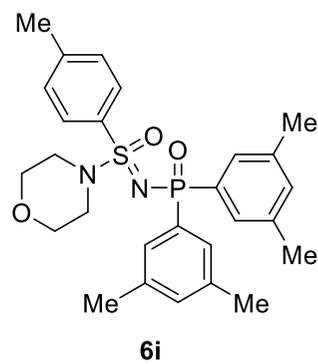
¹H NMR spectra of compound **6i** (400 MHz, CDCl₃)

7.750
7.732
7.528
7.492
7.456
7.328
7.309
7.063
7.043
3.653
3.616
3.577
3.111
3.094
2.920
2.906
2.892
2.431
2.306
2.287



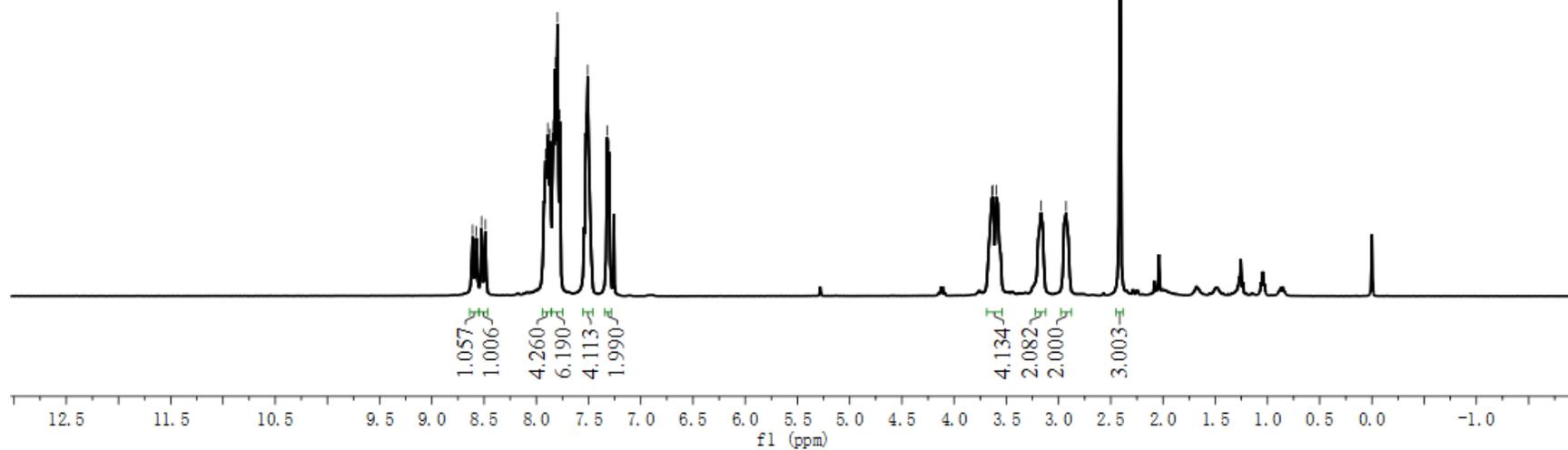
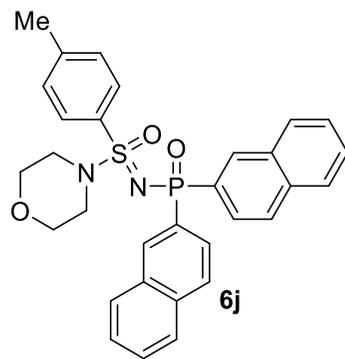
^{31}P NMR spectra of compound **6i** (162 MHz, CDCl_3)

-15.487

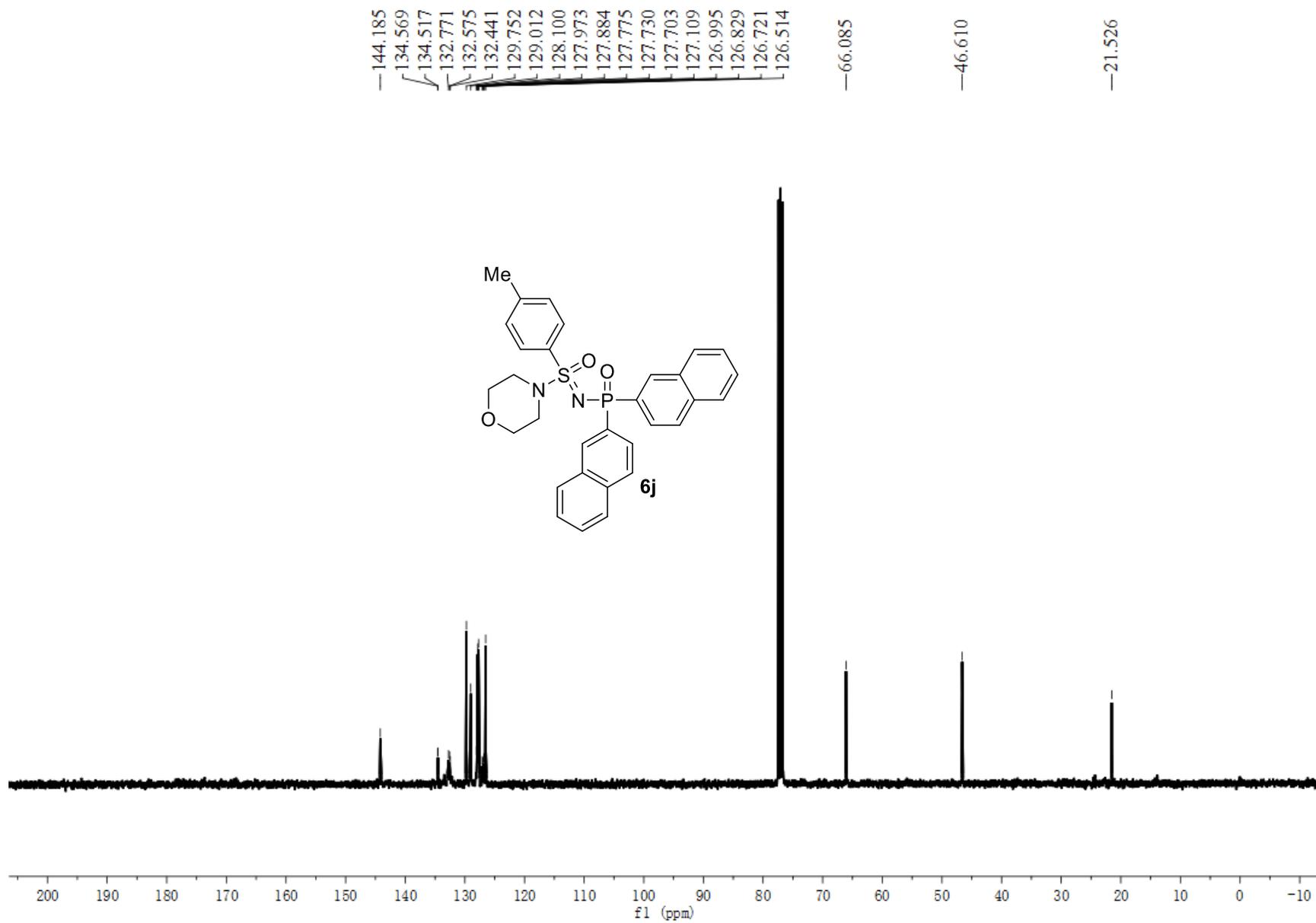


¹H NMR spectra of compound **6j** (400 MHz, CDCl₃)

8.610
8.574
8.524
8.488
7.927
7.911
7.890
7.868
7.837
7.820
7.797
7.776
7.541
7.524
7.508
7.322
7.303
3.639
3.630
3.595
3.169
2.929
-2.412

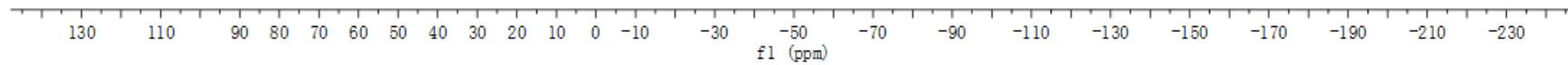
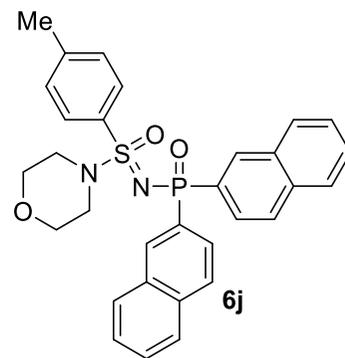


¹³C NMR spectra of compound **6j** (101 MHz, CDCl₃)



^{31}P NMR spectra of compound **6j** (162 MHz, CDCl_3)

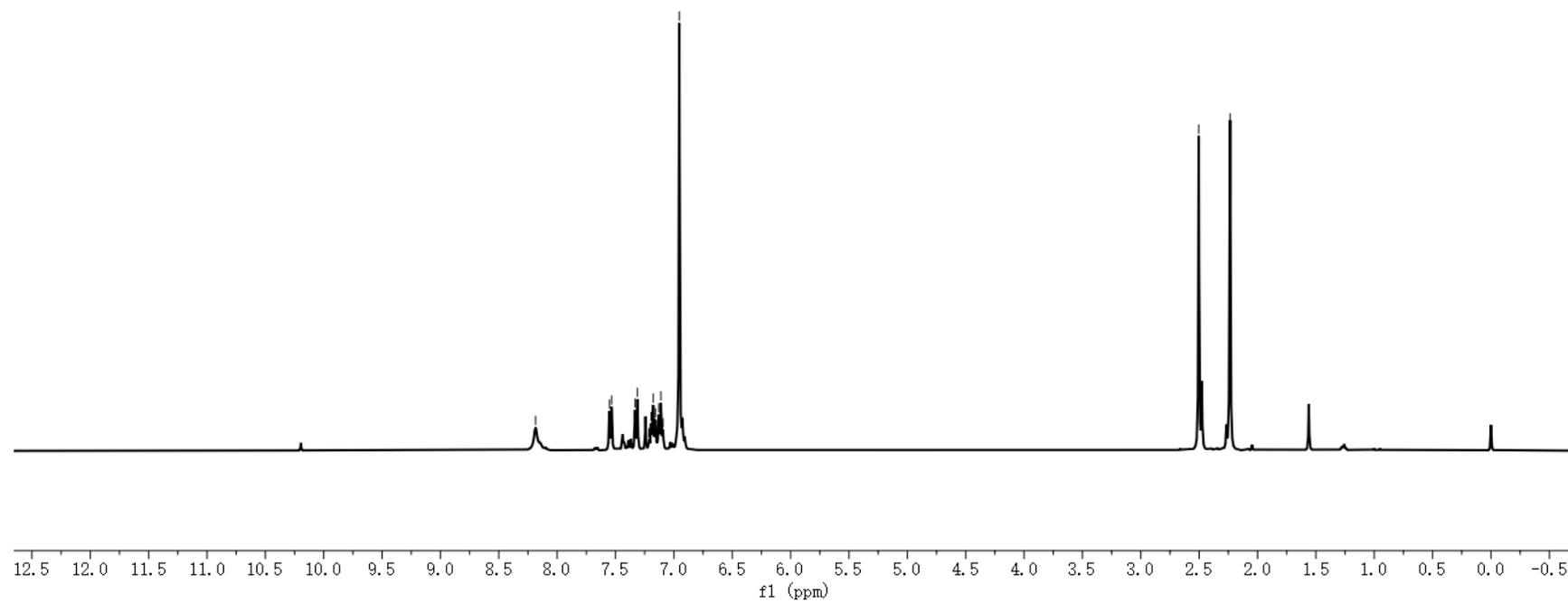
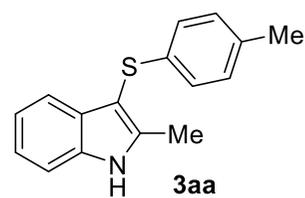
—14.203



¹H NMR spectra of compound **3aa** (400 MHz, CDCl₃)

8.185
7.553
7.534
7.332
7.312
7.214
7.210
7.195
7.178
7.159
7.130
7.111
7.102
7.093
6.954

2.504
2.235



¹³C NMR spectra of compound **3aa** (101 MHz, CDCl₃)

140.922
135.689
135.422
134.311
130.354
129.487
125.780
122.138
120.664
119.039
110.593

— 99.926

— 20.856

— 12.184

