Preparation of Pseudocyclic I(III) Reagents and Their Application in Selective Oxidations

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Supporting Information

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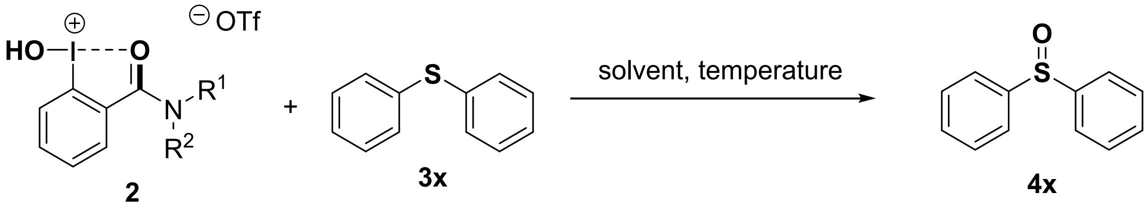
I. General Information and Materials.

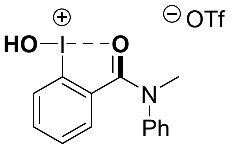
General Information: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer and are calibrated using residual undeuterated solvent ($CHCl_3$ at 7.26 ppm ^{1}H NMR; 77.0 ppm ^{13}C NMR). Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Melting points were measured with a Micromelting point apparatus. High resolution mass data were collected by the Thermo scientific Q Exactive HF. The infrared spectra of the samples were collected using a Tensor 27 FT-IR spectrophotometer (Bruker, Ettlingen, Germany). Thin layer chromatography (TLC) plates were visualized by exposures to the ultraviolet light (254 nm). Flash column chromatography was performed over silica gel (200-300 m) using a mixture of ethyl acetate (EtOAc) and petroleum ether (PE) as the eluent.

Materials: All reagents were used as received from commercial sources, unless otherwise specified, or prepared as described in the literature.

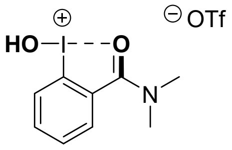
II. Optimization of Sulfinyldibenzene 4x Formation

Table S1 Optimization of 4x Formation[a]

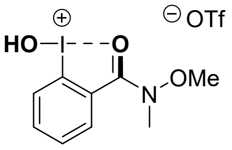




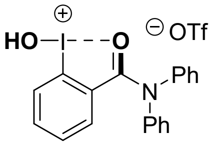
2a



2b



2c

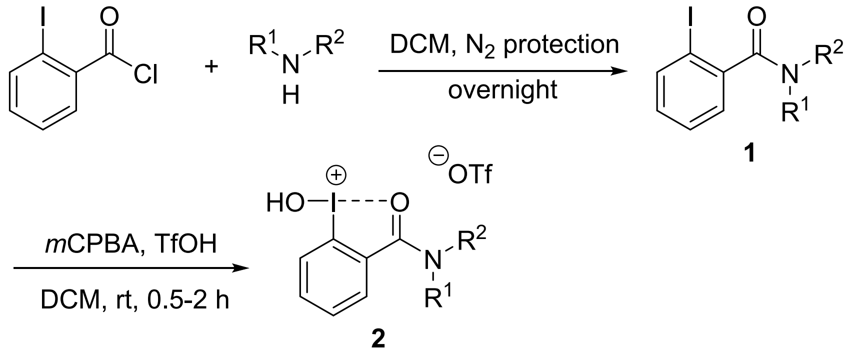


2d

Entry	Solvent	Oxidant **2** (Equiv.)	T (°C)	Time (h)	Yield[b] (%)
1	DCM	**2d** (1.1)	rt	24	N.R.[c]
2	MeCN	**2d** (1.1)	rt	24	N.R.
3	MeCN	**2a** (1.1)	rt	24	N.R.
4	MeCN	**2b** (1.1)	rt	24	N.R.
5	MeCN	**2c** (1.1)	rt	24	N.R.
6	MeCN	**2d** (1.1)	60	6	93
7	MeCN	**2a** (1.1)	60	24	70
8	MeCN	**2b** (1.1)	60	24	62
9	MeCN	**2c** (1.1)	60	24	53
10	MeCN	**2d** (1.1)	50	6	81
11	MeCN	**2d** (1.1)	70	6	88

[a]Reaction conditions: all reactions were carried out with **3x** (1.0 mmol) and **2d** (1.1 mmol) in solvent 5 mL. [b]Isolated yield. [c]N.R. = no reaction.

IV. Experimental Procedures and Spectroscopic Data

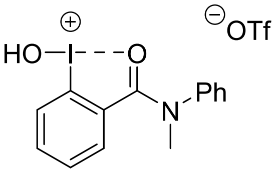


Preparation of ***o*-iodobenzamide derivatives 1**[1]:

In an oven-dried 250 mL round-bottom flask equipped with a magnetic stir bar, *o*-iodobenzoyl chloride (20.0 mmol, 1.0 equiv) was added to a stirred solution of amine or amine hydrochloride salt (24.0 mmol, 1.2 equiv), Et_3N (40.0 mmol, 2.0 equiv), and DMAP (1.0 mmol, 0.05 equiv) in DCM (40 mL) at room temperature under a nitrogen protection. The mixture was stirred at room temperature overnight. Upon completion, the reaction mixture was diluted with DCM (40 mL). The solution was extracted with 1 N HCl (50 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the corresponding *o*-iodobenzamide derivatives **1**.

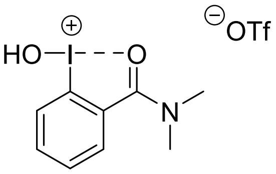
Preparation of **pseudocyclic hypervalent iodine triflates 2**: In an oven-dried 250 mL round-bottom flask equipped with a magnetic stir bar, *m*-CPBA (5.0 mmol, 2.0 equiv) was added to a stirred solution of *o*-iodobenzamide derivatives **1** (2.5 mmol, 1.0 equiv) in 25 mL DCM, followed by sequential addition of TfOH (3.75 mmol, 1.5 equiv). The reaction mixture was stirred at room temperature for 30 min to 2 h. Upon completion of the reaction, the solvent was removed under reduced pressure. Subsequently, diethyl ether (30 mL) was added to the residue. The resulting precipitate was filtered and air-dried to afford the desired products **2**.

1-Hydroxy-3-(methyl(phenyl)amino)-1*H*-λ³-benzo[*d*][1,2]iodaoxol-2-ium trifluoromethanesulfonate (2a)



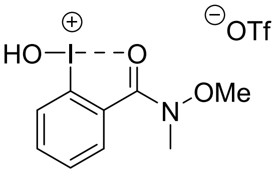
Following the general procedure, **2a** was obtained as a white powder (2.32 g, yield: 94%). ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 7.98 (d, *J* = 8.2 Hz, 1H), 7.91 (t, *J* = 7.7 Hz, 1H), 7.60 (s, 5H), 7.38 (t, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 8.2 Hz, 1H), 3.54 (s, 3H). ^{13}C NMR (151 MHz, DMSO-*d*$_6$) δ 168.2, 142.3, 135.1, 132.3, 130.6, 129.8, 129.7, 127.3, 127.0, 126.8, 123.3, 42.1. ^{19}F NMR (565 MHz, DMSO-*d*$_6$) δ -77.7. HRMS (ESI): Calcd. for $C_{14}H_{13}INO_2^+$ $[M\text{-}OTf]^+$ 353.9985, found 353.9990.

3-(Dimethylamino)-1-hydroxy-1*H*-λ³-benzo[*d*][1,2]iodaoxol-2-ium trifluoromethanesulfonate (2b)



Following the general procedure, **2b** was obtained as a white powder (2.10 g, yield: 95%). ^{1}H NMR (400 MHz, D_2O) δ 8.34 (d, *J* = 7.8 Hz, 1H), 8.07 – 7.98 (m, 2H), 7.82 (ddd, *J* = 8.3, 6.4, 2.0 Hz, 1H), 3.63 (s, 3H), 3.30 (s, 3H). ^{13}C NMR (101 MHz, D_2O) δ 169.4, 135.7, 133.0, 130.6, 126.9, 126.7, 121.7, 41.9, 39.8. ^{19}F NMR (376 MHz, D_2O) δ -78.8. HRMS (ESI): Calcd. for $C_{19}H_{15}INO_2^+$ $[M\text{-}OTf]^+$ 291.9829, found 291.9829.

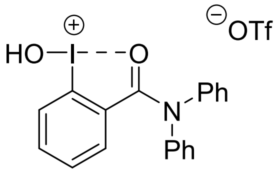
1-Hydroxy-3-(methoxy(methyl)amino)-1*H*-λ³-benzo[*d*][1,2]iodaoxol-2-ium trifluoromethanesulfonate (2c)



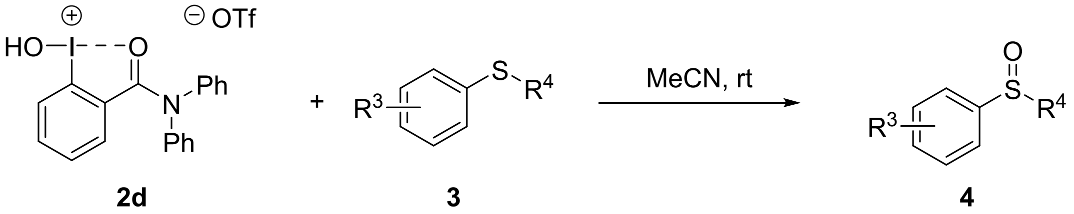
Following the general procedure, **2c** was obtained as a white powder (2.11 g, yield: 92%). ^{1}H

NMR (600 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.3 Hz, 1H), 8.22 – 8.16 (m, 1H), 801 (t *J* = 7.8 Hz, 1H), 7.81 – 7.75 (m, 1H), 3.96 (s, 3H), 3.58 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.9, 137.0, 133.5, 131.7, 127.9, 124.9, 122.4, 62.6, 36.3. ^{19}F NMR (565 MHz, CDC_{l3}) δ -78.2. HRMS (ESI): Calcd. for $C_9H_{11}INO_3^+$ [M-OTf]$^+$ 307.9778, found 307.9782.

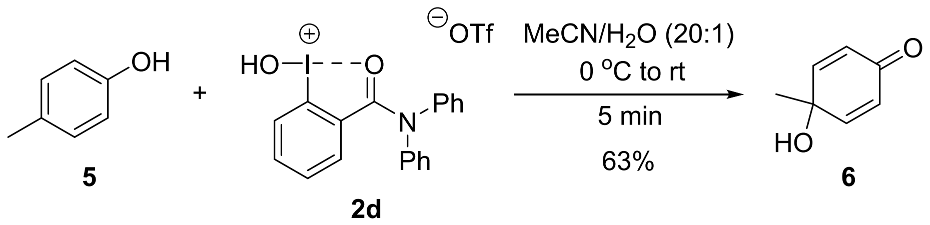
3-(Diphenylamino)-1-hydroxy-1*H*-λ^3-benzo[*d*][1,2]iodaoxol-2-ium trifluoromethanesulfonate (2d)



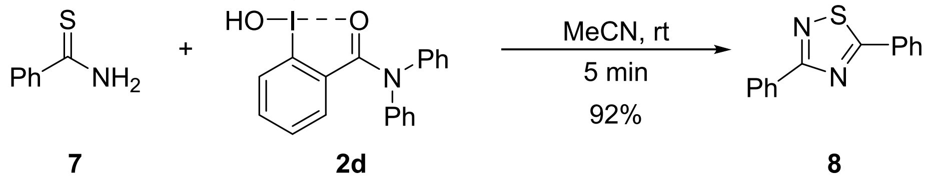
Following the general procedure, **2d** was obtained as a white solid (2.76 g, yield: 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.85 (ddd, *J* = 8.6, 7.2, 1.4 Hz, 1H), 7.58 – 7.37 (m, 8H), 7.35 – 7.27 (m, 3H), 6.95 (dd, *J* = 8.2, 1.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 136.5, 133.5, 131.2, 130.3, 130.1, 129.1, 127.9, 127.7, 126.4, 126.1, 123.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.2. HRMS (ESI): Calcd. for $C_{19}H_{15}INO_2^+$ [M-OTf]$^+$ 416.0142, found 416.0147.



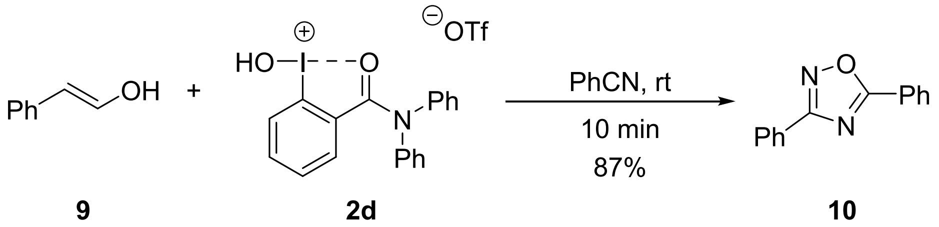
Preparation of **sulfoxides 4**: In an oven-dried 25 mL round-bottom flask equipped with a magnetic stir bar, substrate **2d** (1.1 mmol, 1.1 equiv) was added to a stirred solution of sulfide 3 in 5 mL MeCN. The mixture was stirred at room temperature for 5 min to 12 h. Upon completion, the solvent was removed under vacuum, and the resulting residue was purified by column chromatography on silica gel to afford the corresponding sulfoxides **4**.



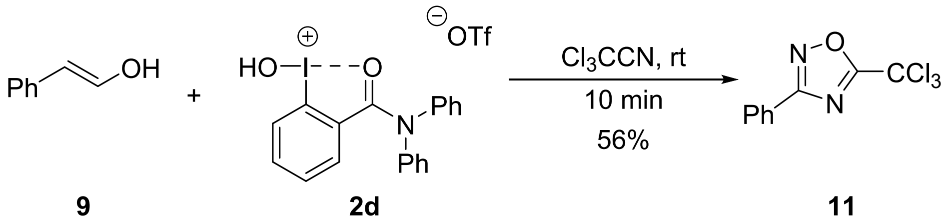
Preparation of **4-hydroxy-4-methyl-cyclohexa-2,5-dienone 6**: To a stirred solution of *p*-cresol **5** (0.5 mmol, 1.0 equiv) in 5 mL MeCN/H_2O (20:1 v/v), substrate **2d** (0.55 mmol, 1.1 equiv) was added. The mixture was stirred at room temperature for 5 min. Upon completion, the solvent was removed under vacuum, and the resulting residue was purified by column chromatography on silica gel to afford the corresponding dienone **6** as a red oil (39 mg, 63%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.87 (d, *J* = 10.1 Hz, 2H), 6.10 (d, *J* = 10.1 Hz, 2H), 1.47 (s, 3H). HRMS (ESI): Calcd. for $C_7H_8O_2$ $[M+H]^+$ 125.0597, found 125.0602. Characterization data matches with the literature values.[2]



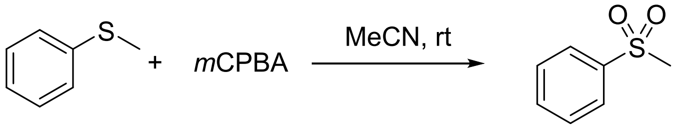
Preparation of **3,5-diphenyl-1,2,4-thiadiazole 8**: To a stirred solution of thiobenzamide **7** (0.3 mmol, 1.0 equiv) in 2 mL MeCN, substrate **2d** (0.48 mmol, 1.6 equiv) was added. The mixture was stirred at room temperature for 5 min. Upon completion, the solvent was removed under vacuum, and the resulting residue was purified by column chromatography on silica gel to afford 3,5-diphenyl-1,2,4-thiadiazole **8** as a white solid (33 mg, 92%); m.p. 88-89 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (d, *J* = 7.3 Hz, 2H), 8.06 (d, *J* = 7.1 Hz, 2H), 7.56 – 7.47 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 188.3, 174.0, 133.1, 132.0, 130.9, 130.5, 129.4, 128.8, 128.5, 127.6. HRMS (ESI): Calcd. for $C_{14}H_{10}N_2S$ $[M+H]^+$ 239.0637, found 239.0632. Characterization data matches with the literature values.[2]



Preparation of **3,5-diphenyl-1,2,4-oxadiazole 10**: To a stirred solution of α-benzaldehyde oxime **9** (0.3 mmol, 1.0 equiv) in 2 mL benzonitrile, substrate **2d** (0.36 mmol, 1.2 equiv) was added. The mixture was stirred at room temperature for 10 min. Upon completion, the solvent was removed under vacuum, and the resulting residue was purified by column chromatography on silica gel to afford 3,5-diphenyl-1,2,4-oxadiazole **10** as a yellow solid (29 mg, 87%); m.p. 105-106 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.2 Hz, 2H), 8.19 (dd, *J* = 7.5, 2.3 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.58 – 7.48 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.9, 169.1, 132.9, 131.3, 129.2, 129.0, 128.3, 127.7, 127.2, 124.5. HRMS (ESI): Calcd. for $C_{14}H_{10}N_2O$ $[M+H]^+$ 223.0866, found 223.0864. Characterization data matches with the literature values.[2]

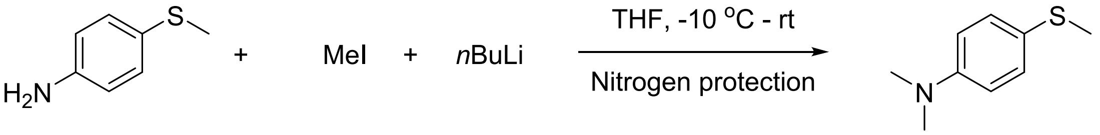


Preparation of **3-phenyl-5-(trichloromethyl)-1,2,4-oxadiazole 11**: To a stirred solution of α-benzaldehyde oxime **9** (0.3 mmol, 1.0 equiv) in 2 mL trichloroacetonitrile, substrate **2d** (0.36 mmol, 1.2 equiv) was added. The mixture was stirred at room temperature for 10 min. Upon completion, the solvent was removed under vacuum, and the resulting residue was purified by column chromatography on silica gel to afford 3-phenyl-5-(trichloromethyl)-1,2,4-oxadiazole **11** as a yellow oil (22 mg, yield: 56%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 – 8.10 (m, 3H), 7.59 – 7.54 (m, 1H), 7.56 – 7.49 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.6, 169.3, 132.2, 129.2, 127.8, 125.6, 83.7. HRMS (ESI): Calcd. for $C_9H_5{}^{35}Cl_3N_2O$ $[M+H]^+$ 262.9540, found 262.9538. Characterization data matches with the literature values.[2]



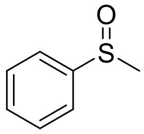
3a **16**

Preparation of **phenyl methyl sulfone 16**: To a stirred solution of phenyl methyl sulfide **3a** (0.4 mmol, 1.0 equiv) in 2 mL MeCN, *m*CPBA (0.64 mmol, 1.6 equiv) was added. The mixture was stirred at room temperature for 10 min. Upon completion, the reaction mixture was diluted with EtOAc (20 mL). The solution was washed by water (10 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford phenyl methyl sulfone **16** as a yellow oil (13 mg, yield: 22%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 2H), 3.06 (s, 3H). Characterization data matches with the literature values.[3]



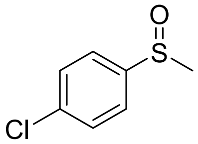
Preparation of ***N*,*N*-dimethyl-4-(methylthio)aniline**: A solution of 4-(methylthio)aniline (7.2 mmol, 1.0 equiv) in dry THF (10 mL) was blanketed with dry nitrogen. 1.2 M solution of butyllithium in hexane (7.9 mmol, 1.1 equiv) was added dropwise to the solution at -10 °C and the solution was stirred for 30 min at room temperature. Then the solution was cooled to -10 °C and treated with MeI (7.9 mmol, 1.1 equiv). The resulting solution was treated dropwise with 1.2 M butyllithium in hexane (7.9 mmol, 1.1 equiv) and MeI (7.9 mmol, 1.1 equiv). The mixture was stirred overnight. Upon completion, the reaction mixture was poured into water (25 mL) and the pH was adjusted to 5-6 with 1M HCl. The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford *N*,*N*-dimethyl-4-(methylthio)aniline as a yellow oil (862 mg, yield: 72%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 2.95 (s, 6H), 2.43 (s, 3H). Characterization data matches with the literature values.[4]

(Methylsulfinyl)benzene (4a)



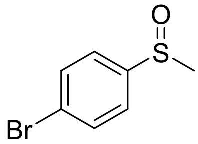
Following the general procedure, **4a** was obtained as a colorless oil (133 mg, yield: 95%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.64 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.55 – 7.48 (m, 3H), 2.71 (s, 3H). HRMS (ESI): Calcd. for C_7H_8OS [M+H]$^+$ 141.0369, found 141.0372. Characterization data matches with the literature values.[5]

1-Chloro-4-(methylsulfinyl)benzene (4b)



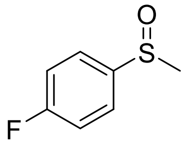
Following the general procedure, **4b** was obtained as a yellow oil (147 mg, yield: 84%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.59 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 2.71 (s, 3H). HRMS (ESI): Calcd. for $C_7H_7{}^{35}ClOS$ [M+H]$^+$ 174.9979, found 174.9986. Characterization data matches with the literature values.[5]

1-Bromo-4-(methylsulfinyl)benzene (4c)



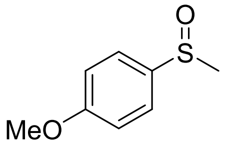
Following the general procedure, **4c** was obtained as a white solid (216 mg, yield: 99%); m.p. 84-85 °C. ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.67 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 2.71 (s, 3H). HRMS (ESI): Calcd. for $C_7H_7{}^{79}BrOS$ [M+H]$^+$ 218.9474, found 218.9480. Characterization data matches with the literature values.[6]

1-Fluoro-4-(methylsulfinyl)benzene (4d)



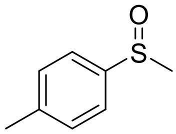
Following the general procedure, **4d** was obtained as a yellow oil (157 mg, yield: 99%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.67 – 7.62 (m, 2H), 7.24 – 7.18 (m, 2H), 2.70 (s, 3H). ^{19}F NMR (565 MHz, CDCl$_3$) δ -108.6. HRMS (ESI): Calcd. for $C_7H_7{}^{19}FOS$ [M+H]$^+$ 159.0274, found 159.0279. Characterization data matches with the literature values.[5]

1-Methoxy-4-(methylsulfinyl)benzene (4e)



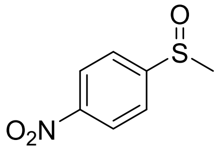
Following the general procedure, **4c** was obtained as a yellow oil (169 mg, yield: 99%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.58 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H), 2.69 (s, 3H). HRMS (ESI): Calcd. for $C_8H_{10}O_2S$ [M+H]$^+$ 171.0474, found 171.0479. Characterization data matches with the literature values.[5]

1-Methyl-4-(methylsulfinyl)benzene (4f)



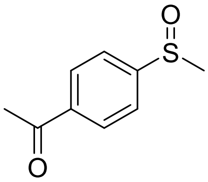
Following the general procedure, **4f** was obtained as a yellow oil (148 mg, yield: 96%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.50 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 2.66 (s, 3H), 2.37 (s, 3H). HRMS (ESI): Calcd. for $C_8H_{10}OS$ [M+H]$^+$ 155.0525, found 155.0530. Characterization data matches with the literature values.[7]

1-(Methylsulfinyl)-4-nitrobenzene (4g)



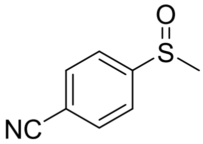
Following the general procedure, **4g** was obtained as a white solid (163 mg, yield: 88%); m.p. 151-152 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.36 (d, J = 8.9 Hz, 2H), 7.82 (d, J = 8.8 Hz, 2H), 2.77 (s, 3H). HRMS (ESI): Calcd. for $C_7H_7NO_3S$ [M+H]$^+$ 186.0219, found 186.0223. Characterization data matches with the literature values.[6]

1-(4-(Methylsulfinyl)phenyl)ethan-1-one (4h)



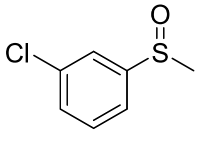
Following the general procedure, **4h** was obtained as a white solid (151 mg, yield: 83%); m.p. 107-108 ºC. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.98 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 8.1 Hz, 2H), 2.65 (s, 3H), 2.52 (s, 3H). HRMS (ESI): Calcd. for $C_9H_{10}O_2S$ $[M+H]^+$ 183.0474, found 183.0479. Characterization data matches with the literature values.[6]

4-(Methylsulfinyl)benzonitrile (4i)



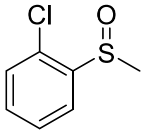
Following the general procedure, **4i** was obtained as a white solid (160 mg, yield: 97%); m.p. 91-93 ºC. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.82 (d, *J* = 8.7 Hz, 2H), 7.75 (d, *J* = 8.6 Hz, 2H), 2.75 (s, 3H). HRMS (ESI): Calcd. for C_8H_7NOS $[M+H]^+$ 166.0321, found 166.0325. Characterization data matches with the literature values.[5]

1-Chloro-3-(methylsulfinyl)benzene (4j)



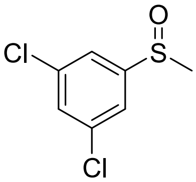
Following the general procedure, **4j** was obtained as a colorless oil (166 mg, yield: 95%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.61 (d, *J* = 1.2 Hz, 1H), 7.47 – 7.39 (m, 3H), 2.69 (s, 3H). HRMS (ESI): Calcd. for $C_7H_7{}^{35}ClOS$ $[M+H]^+$ 174.9979, found 174.9983. Characterization data matches with the literature values.[6]

1-Chloro-2-(methylsulfinyl)benzene (4k)



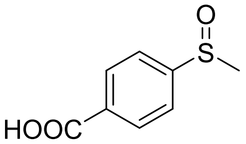
Following the general procedure, **4k** was obtained as a colorless oil (168 mg, yield: 96%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.93 (d, *J* = 7.9 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 2.80 (s, 3H). HRMS (ESI): Calcd. for $C_7H_7{}^{35}ClOS$ [M+H]$^+$ 174.9979, found 174.9983. Characterization data matches with the literature values.[6]

1,3-Dichloro-5-(methylsulfinyl)benzene (4l)



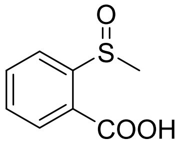
Following the general procedure, **4l** was obtained as a yellow solid (207 mg, yield: 99%); m.p. 68-70 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 1.8 Hz, 2H), 7.47 (t, *J* = 1.8 Hz, 1H), 2.75 (s, 3H). HRMS (ESI): Calcd. for $C_7H_6{}^{35}Cl_2OS$ [M+H]$^+$ 208.9589, found 208.9592. Characterization data matches with the literature values.[6]

4-(Methylsulfinyl)benzoic acid (4m)



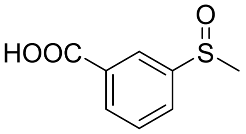
Following the general procedure, **4m** was obtained as a white solid (172 mg, yield: 93%); m.p. 207-208 °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.10 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H), 2.78 (s, 3H). HRMS (ESI): Calcd. for $C_8H_8O_3S$ [M+H]$^+$ 185.0267, found 185.0274. Characterization data matches with the literature values.[6]

2-(Methylsulfinyl)benzoic acid (4n)



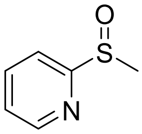
Following the general procedure, **4n** was obtained as a white solid (180 mg, yield: 98%); m.p. 156-158 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.14 (d, *J* = 7.9 Hz, 1H), 8.05 (d, *J* = 7.7 Hz, 1H), 7.91 (t, *J* = 7.6 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 2.74 (s, 3H). HRMS (ESI): Calcd. for $C_8H_8O_3S$ $[M+H]^+$ 185.0267, found 185.0276. Characterization data matches with the literature values.[5]

3-(Methylsulfinyl)benzoic acid (4o)



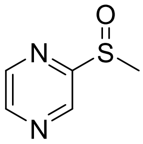
Following the general procedure, **4o** was obtained as a white solid (162 mg, yield: 88%); m.p. 171-173 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.23 (s, 1H), 8.08 (d, *J* = 7.7 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.71 (t, *J* = 7.7 Hz, 1H), 2.78 (s, 3H). HRMS (ESI): Calcd. for $C_8H_8O_3S$ $[M+H]^+$ 185.0267, found 185.0274. Characterization data matches with the literature values.[8]

2-(Methylsulfinyl)pyridine (4p)



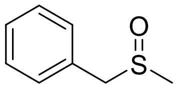
Following the general procedure, **4p** was obtained as a yellow oil (134 mg, yield: 95%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.63 (d, *J* = 4.8 Hz, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.94 (td, *J* = 7.7, 1.7 Hz, 1H), 7.38 (ddd, *J* = 7.5, 4.7, 1.3 Hz, 1H), 2.86 (s, 3H). HRMS (ESI): Calcd. for C_6H_7NOS $[M+H]^+$ 142.0321, found 142.0325. Characterization data matches with the literature values.[5]

2-(Methylsulfinyl)pyrazine (4q)



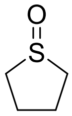
Following the general procedure, **4q** was obtained as a white solid (121 mg, yield: 85%); m.p. 63-64 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.19 (s, 1H), 8.70 (s, 1H), 8.58 (s, 1H), 2.90 (s, 3H). HRMS (ESI): Calcd. for $C_5H_6N_2OS$ $[M+H]^+$ 143.0274, found 143.0278. Characterization data matches with the literature values.[5]

((Methylsulfinyl)methyl)benzene (4r)



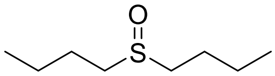
Following the general procedure, **4r** was obtained as a yellow oil (152 mg, yield: 99%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.41 – 7.28 (m, 5H), 4.12 (d, J = 12.7 Hz, 1H), 3.94 (d, J = 12.7 Hz, 1H), 2.46 (s, 3H). HRMS (ESI): Calcd. for $C_8H_{10}OS$ $[M+H]^+$ 155.0525, found 155.0528. Characterization data matches with the literature values.[5]

Tetrahydrothiophene 1-oxide (4s)



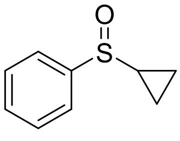
Following the general procedure, **4s** was obtained as a yellow oil (99 mg, yield: 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.93 – 2.73 (m, 4H), 2.47 – 2.32 (m, 2H), 2.05 – 1.90 (m, 2H). HRMS (ESI): Calcd. for C_4H_8OS $[M+H]^+$ 105.0369, found 105.0377. Characterization data matches with the literature values.[9]

1-(Butylsulfinyl)butane (4t)



Following the general procedure, **4t** was obtained as a yellow oil (151 mg, yield: 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.81 – 2.60 (m, 4H), 1.80 – 1.66 (m, 4H), 1.57 – 1.37 (m, 4H), 0.95 (t, J = 7.3 Hz, 6H). HRMS (ESI): Calcd. for $C_8H_{18}OS$ $[M+H]^+$ 163.1151, found 163.1155. Characterization data matches with the literature values.[5]

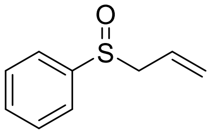
(Cyclopropylsulfinyl)benzene (4u)



Following the general procedure, **4u** was obtained as a colorless oil (125 mg, yield: 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.59 (m, 2H), 7.51 – 7.41 (m, 3H), 2.22 (ttd, J = 7.8, 4.8, 2.6

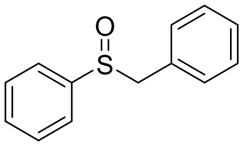
Hz, 1H), 1.24 – 1.14 (m, 1H), 1.03 – 0.83 (m, 3H). HRMS (ESI): Calcd. for $C_9H_{10}OS$ $[M+H]^+$ 167.0525, found 167.0530. Characterization data matches with the literature values.[5]

(Allylsulfinyl)benzene (4v)



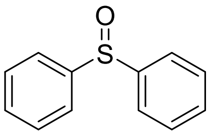
Following the general procedure, **4v** was obtained as a yellow oil (164 mg, yield: 99%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.50 – 7.41 (m, 3H), 5.60 (ddt, *J* = 17.5, 10.2, 7.5 Hz, 1H), 5.28 (d, *J* = 10.2 Hz, 1H), 5.15 (dd, *J* = 17.1, 1.3 Hz, 1H), 3.59 – 3.42 (m, 2H). HRMS (ESI): Calcd. for $C_9H_{10}OS$ $[M+H]^+$ 167.0525, found 167.0528. Characterization data matches with the literature values.[5]

(Benzylsulfinyl)benzene (4w)



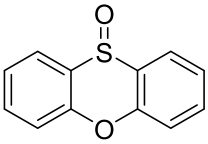
Following the general procedure, **4w** was obtained as a white solid (148 mg, yield: 68%); m.p. 121-122 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.44 (m, 1H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.39 – 7.36 (m, 2H), 7.31 – 7.27 (m, 1H), 7.26 – 7.23 (m, 2H), 6.98 (d, *J* = 6.7 Hz, 2H), 4.10 (d, *J* = 12.6 Hz, 1H), 4.00 (d, *J* = 12.6 Hz, 1H). HRMS (ESI): Calcd. for $C_{13}H_{12}OS$ $[M+H]^+$ 217.0682, found 217.0687. Characterization data matches with the literature values.[6]

Sulfinyldibenzene (4x)



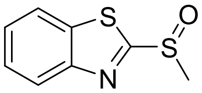
Following the general procedure, **4x** was obtained as a yellow solid (192 mg, yield: 93%); m.p. 69-70 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.5, 2.1 Hz, 4H), 7.51 – 7.42 (m, 6H). HRMS (ESI): Calcd. for $C_{12}H_{10}OS$ $[M+H]^+$ 203.0525, found 203.0529. Characterization data matches with the literature values.[6]

Phenoxathiine 10-oxide (4y)



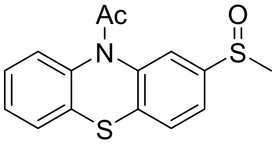
Following the general procedure, **4y** was obtained as a white solid (193 mg, yield: 89%); m.p. 154-155 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91 – 7.83 (m, 2H), 7.60 – 7.51 (m, 2H), 7.40 – 7.27 (m, 4H). HRMS (ESI): Calcd. for $C_{12}H_8O_2S$ [M+H]$^+$ 217.0318, found 217.0323. Characterization data matches with the literature values.[10]

2-(Methylsulfinyl)benzo[*d*]thiazole (4z)



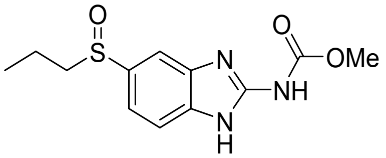
Following the general procedure, **4z** was obtained as a yellow solid (170 mg, yield: 86%); m.p. 66-68 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.06 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.56 (t, *J* = 8.1 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 3.07 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 178.5, 153.9, 136.1, 127.1, 126.4, 124.1, 122.5, 43.3. HRMS (ESI): Calcd. for $C_8H_7NOS_2$ [M+H]$^+$ 198.0042, found 198.0046. Characterization data matches with the literature values.[9]

1-(2-(methylsulfinyl)-10*H*-phenothiazin-10-yl)ethan-1-one (4aa)



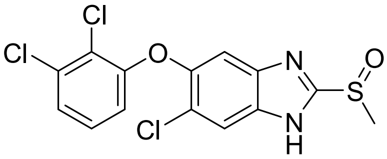
Following the general procedure, **4aa** was obtained as a red solid (168 mg, yield: 55%); m.p. 74-78 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.82 (d, *J* = 20.4 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.55 – 7.41 (m, 3H), 7.36 (td, *J* = 7.6, 1.5 Hz, 1H), 7.28 (dd, *J* = 7.6, 1.3 Hz, 1H), 2.76 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 169.3, 144.9, 138.6, 132.5, 128.7, 128.3, 127.7, 127.4, 127.2, 122.8, 44.3, 23.1. HRMS (ESI): Calcd. for $C_{15}H_{13}NO_2S_2$ [M+H]$^+$ 304.0460, found 304.0466. Characterization data matches with the literature values.[5]

Methyl (5-(propylsulfinyl)-1*H*-benzo[*d*]imidazol-2-yl)carbamate (4ab)



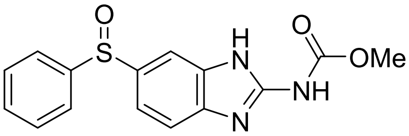
Following the general procedure, **4ab** was obtained as a white solid (249 mg, yield: 82%); m.p. 188-191 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.92 (s, 2H), 7.70 (s, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.32 (dd, *J* = 8.3, 1.7 Hz, 1H), 3.78 (s, 3H), 2.86 – 2.80 (m, 1H), 2.78 – 2.72 (m, 1H), 1.66 – 1.56 (m, 1H), 1.53 – 1.42 (m, 1H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 154.6, 148.6, 136.1, 116.7, 58.2, 52.5, 15.4, 12.9. HRMS (ESI): Calcd. for $C_{12}H_{15}N_3O_3S$ $[M+H]^+$ 282.0907, found 282.0915. Characterization data matches with the literature values.[11]

5-Chloro-6-(2,3-dichlorophenoxy)-2-(methylsulfinyl)-1*H*-benzo[*d*]imidazole (4ac)



Following the general procedure, **4ac** was obtained as a white solid (245 mg, yield: 65%); m.p. 175-177 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.28 (s, 1H), 7.21 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.08 (t, *J* = 8.2 Hz, 1H), 3.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 154.5, 148.3, 137.5, 134.5, 130.3, 127.6, 125.1, 123.6, 123.0, 116.1, 41.4. HRMS (ESI): Calcd. for $C_{14}H_9{}^{35}Cl_3N_2O_2S$ $[M+H]^+$ 374.9523, found 374.9552. Characterization data matches with the literature values.[12]

Oxfendazole (4ad)



Following the general procedure, **4ad** was obtained as a white solid (309 mg, yield: 65%); m.p. 246-255 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.75 (d, *J* = 1.7 Hz, 1H), 7.66 (d, *J* = 6.7 Hz, 2H), 7.55 – 7.43 (m, 4H), 7.38 (dd, *J* = 8.3, 1.7 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.30, 148.88, 146.69, 137.79, 130.70, 129.34, 124.04, 52.65. HRMS (ESI): Calcd. for $C_{15}H_{13}N_3O_3S$ $[M+H]^+$ 316.0750, found 316.0759. Characterization data matches with the literature values.[11]

V. X-ray Crystal Structure and Data of Product 2a

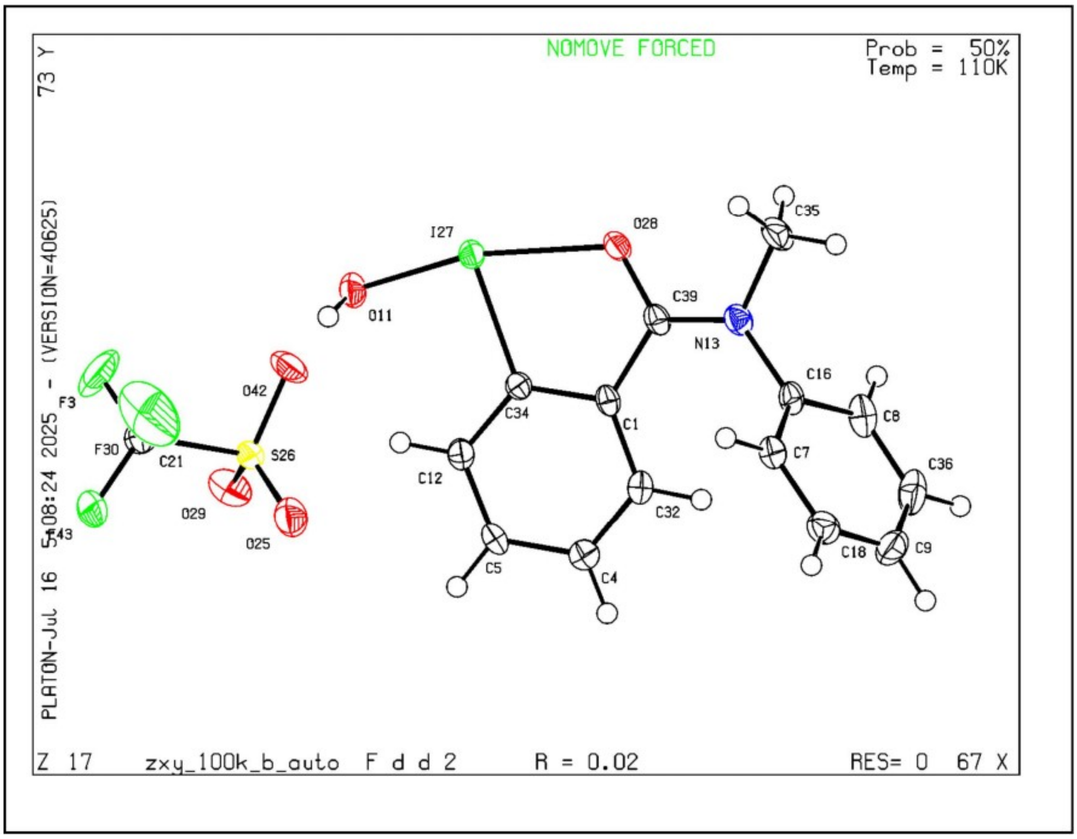


Figure S1 X-ray crystal structure of 2a with 50% ellipsoid probability X-ray structure determination of 2a. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a Diethyl ether/n-hexane solution of **2a**. Crystal data collection and refinement parameters of **2a** are summarized in Table S2. Intensity data were collected at 160 K on a ROD, Synergy Custom system, HyPix diffractometer using mirror-monochromated Cu Kα radiation, λ = 1.54184 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structure was solved by the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.

Table S2 Crystal data and structure refinement for 2a.

Identification code	ZXY_100K_B_auto
Empirical formula	$C_{15}H_{13}F_3INO_5S$
Formula weight	503.22
Temperature/K	110.4(8)
Crystal system	orthorhombic
Space group	Fdd2
a/Å	30.5483(10)
b/Å	19.5935(6)
c/Å	11.6668(3)
α/°	90

β/°	90
γ/°	90
Volume/Å^3	6983.1(4)
Z	16
ρ_{calc}g/cm^3	1.915
μ/mm^{-1}	2.012
F(000)	3936.0
Crystal size/mm^3	0.13 × 0.13 × 0.05
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.276 to 61.408
Index ranges	$-42 \leq h \leq 33$, $-26 \leq k \leq 22$, $-14 \leq l \leq 14$
Reflections collected	12909
Independent reflections	4128 [R_{int} = 0.0212, R_{sigma} = 0.0225]
Data/restraints/parameters	4128/193/240
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0194, wR_2 = 0.0440
Final R indexes [all data]	R_1 = 0.0233, wR_2 = 0.0457
Largest diff. peak/hole / e Å^{-3}	0.82/-0.38
Flack parameter	-0.016(8)

VI. Thermogravimetric and differential scanning calorimetry (TGA-DSC) profile of compound 2d

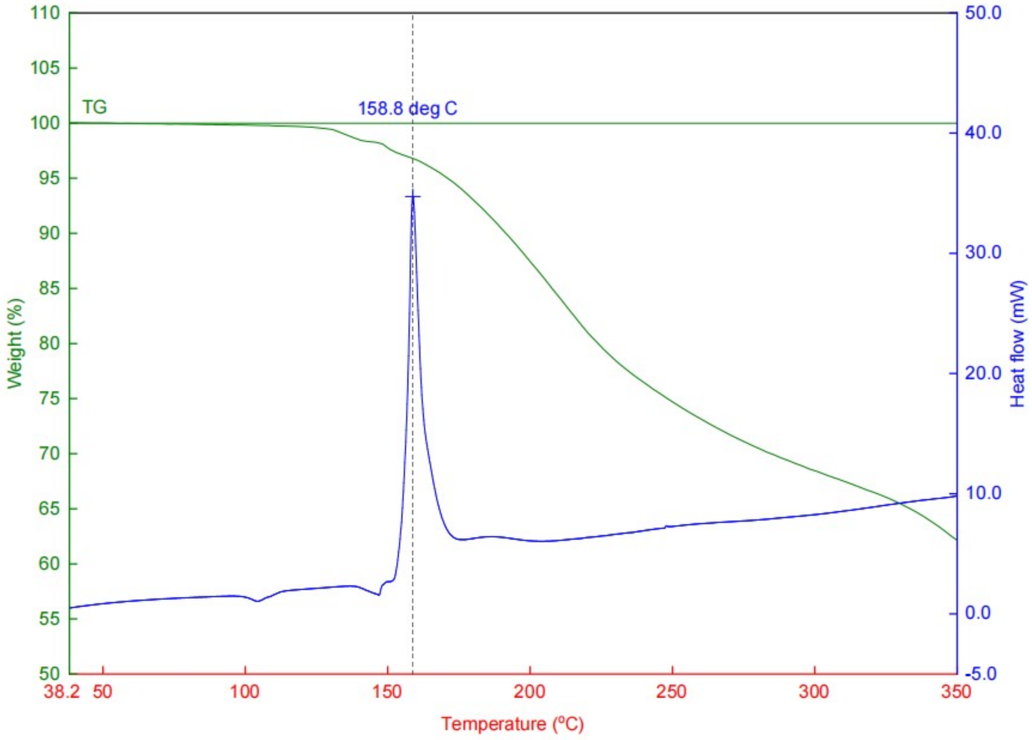


Figure S2. TGA-DSC profile of reagent 2d. Thermogravimetric and differential scanning calorimetry (TGA-DSC) measurements were performed in order to determine the melting point and decomposition temperature of **2d**. Reagent **2d** does not have a melting point, and shows an exothermic decomposition at 158.8 °C, accompanied with a mass change of 96.7%.

VII. Reference

(1) J. V. Suárez-Meneses; A. Oukhrib; M. Gouygou; M. Urrutigoïty; J. C. Daran; A. Cordero-Vargas; M. C. Ortega-Alfaro; J. G. López-Cortés. *Dalton Trans.* **2016**, *45*, 9621-9630.

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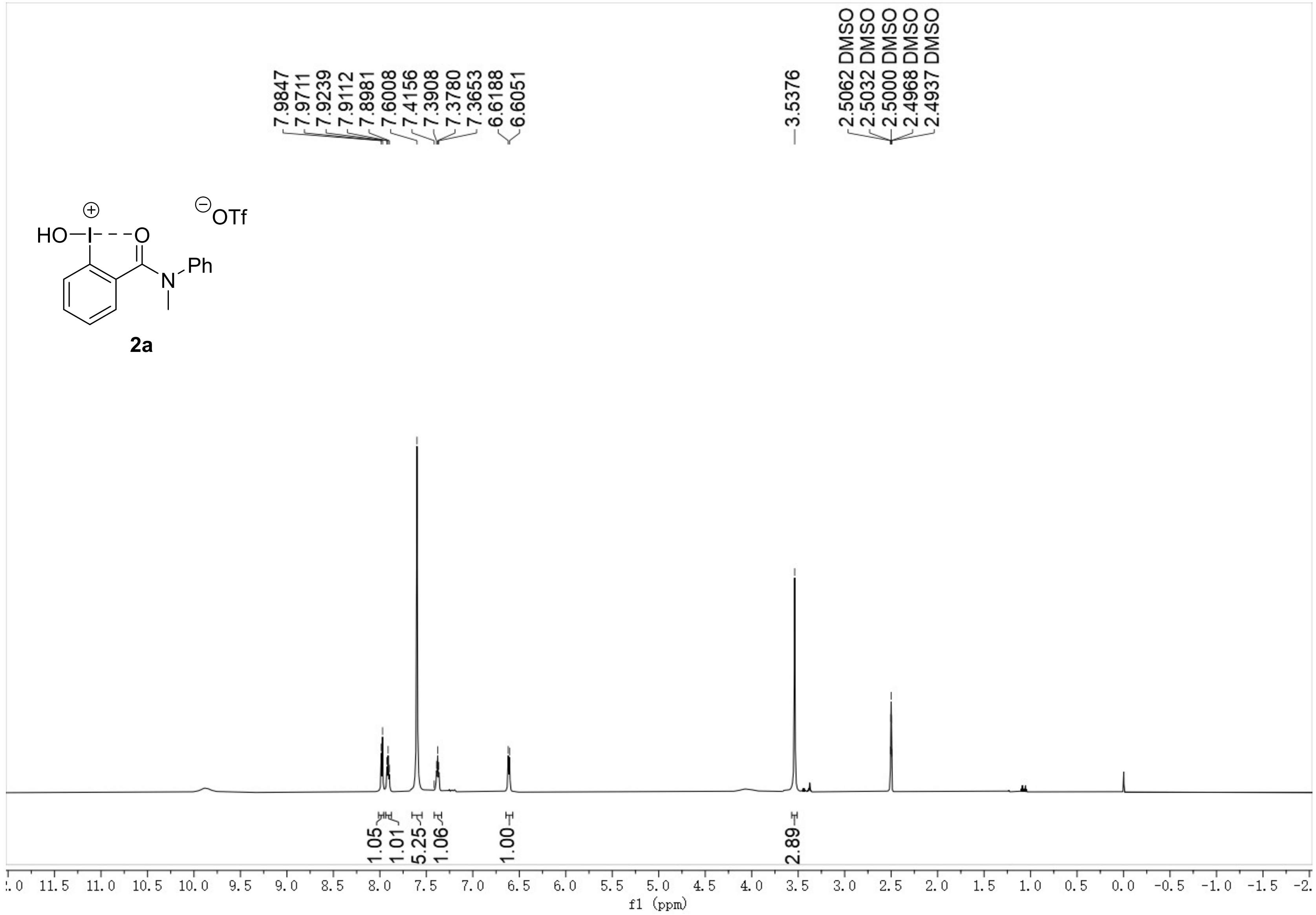
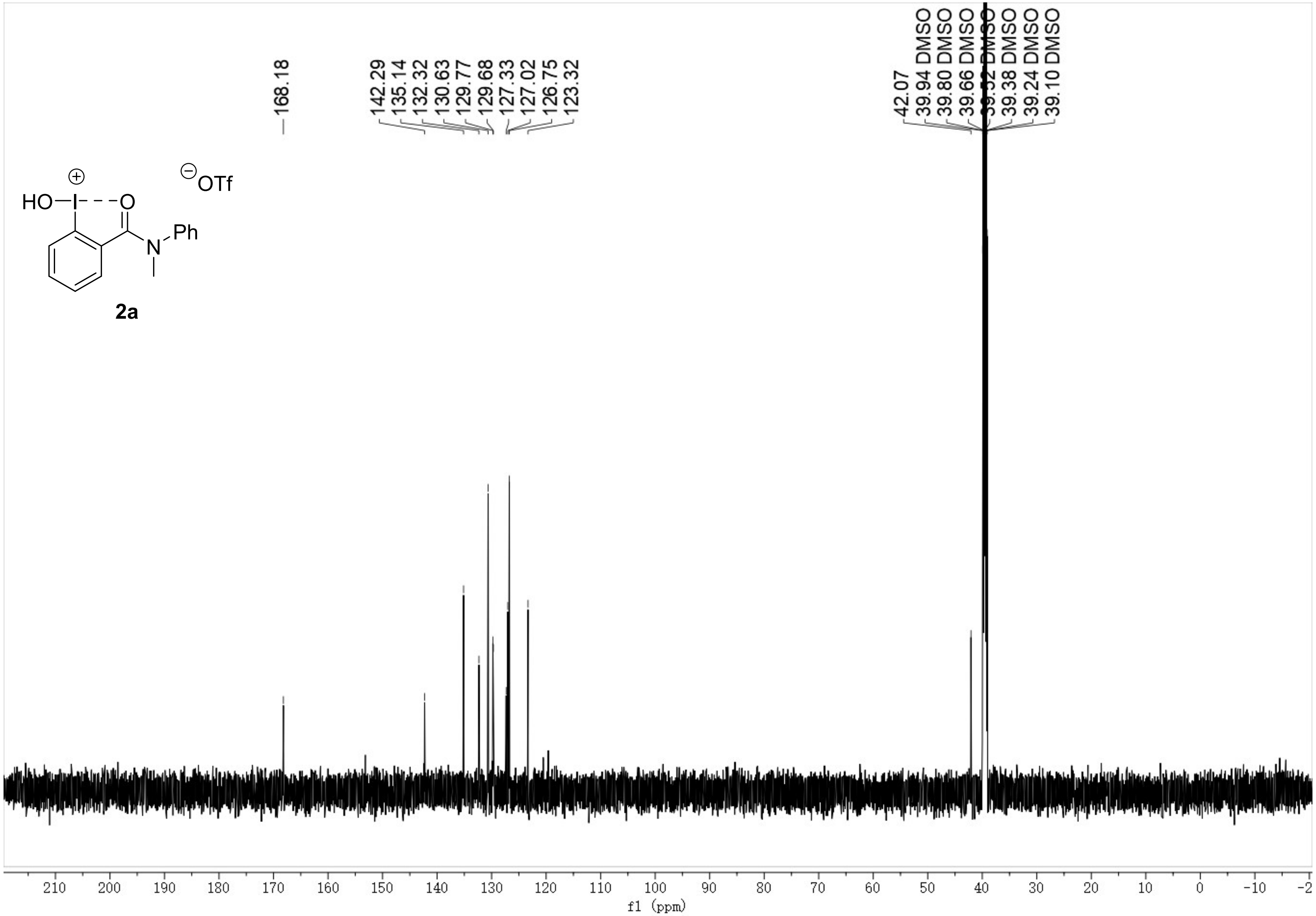
VIII. ^{1}H and ^{13}C NMR Spectra of Compounds 2a-11:

^{1}H NMR (600 MHz, DMSO-d_6)

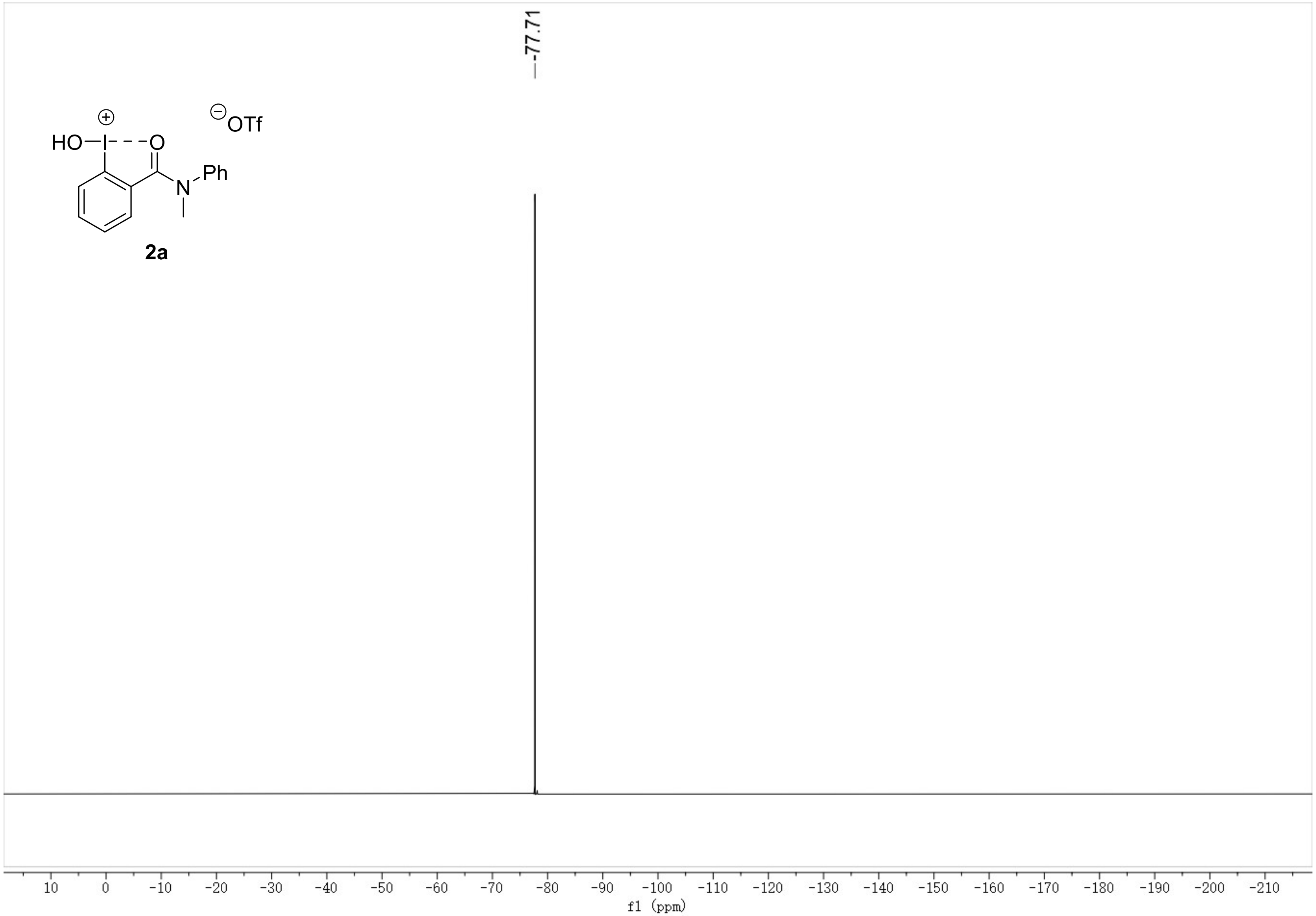


^{13}C NMR (151 MHz, DMSO-d_6)



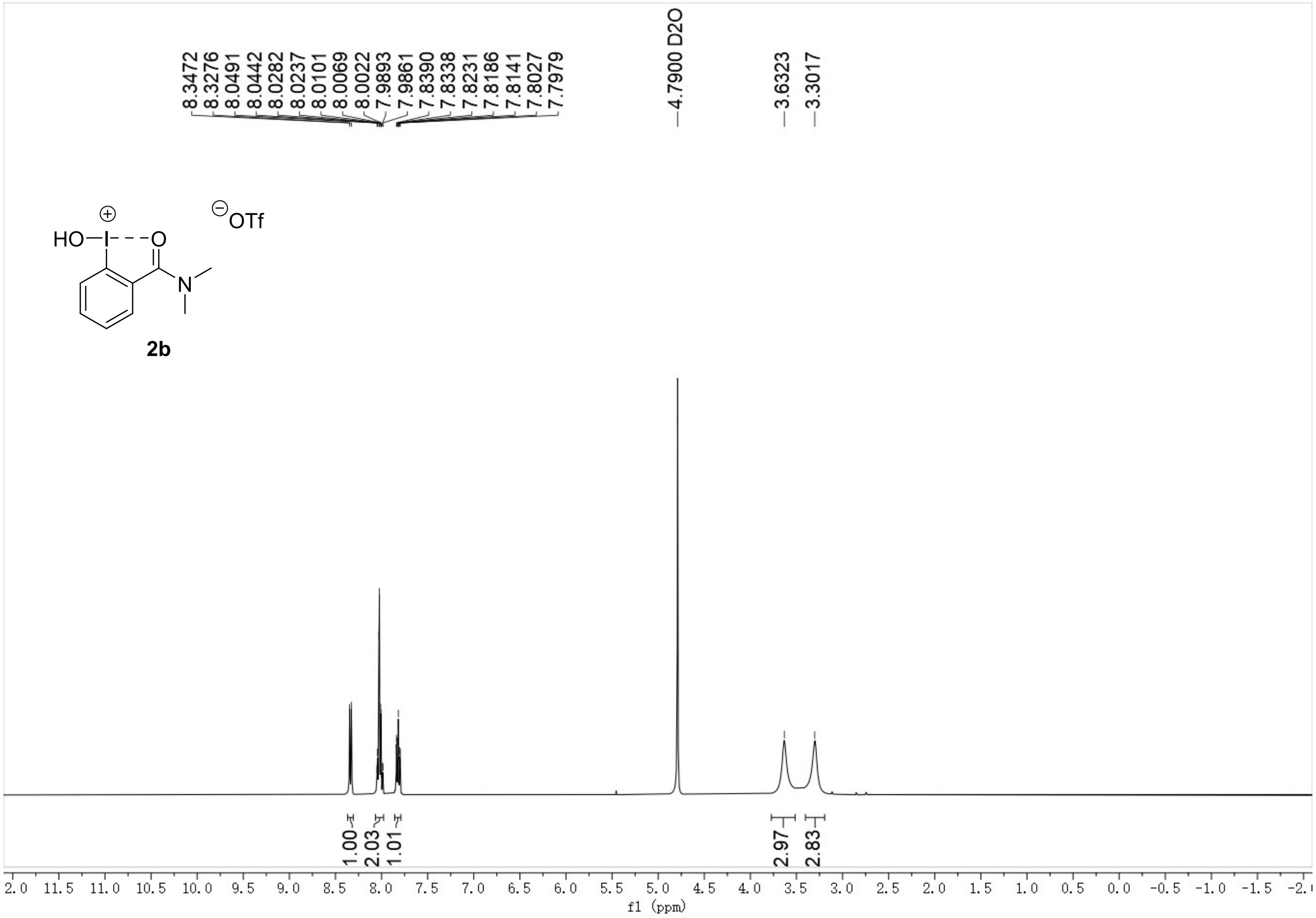
2a

^{19}F NMR (565 MHz, DMSO-d_6)

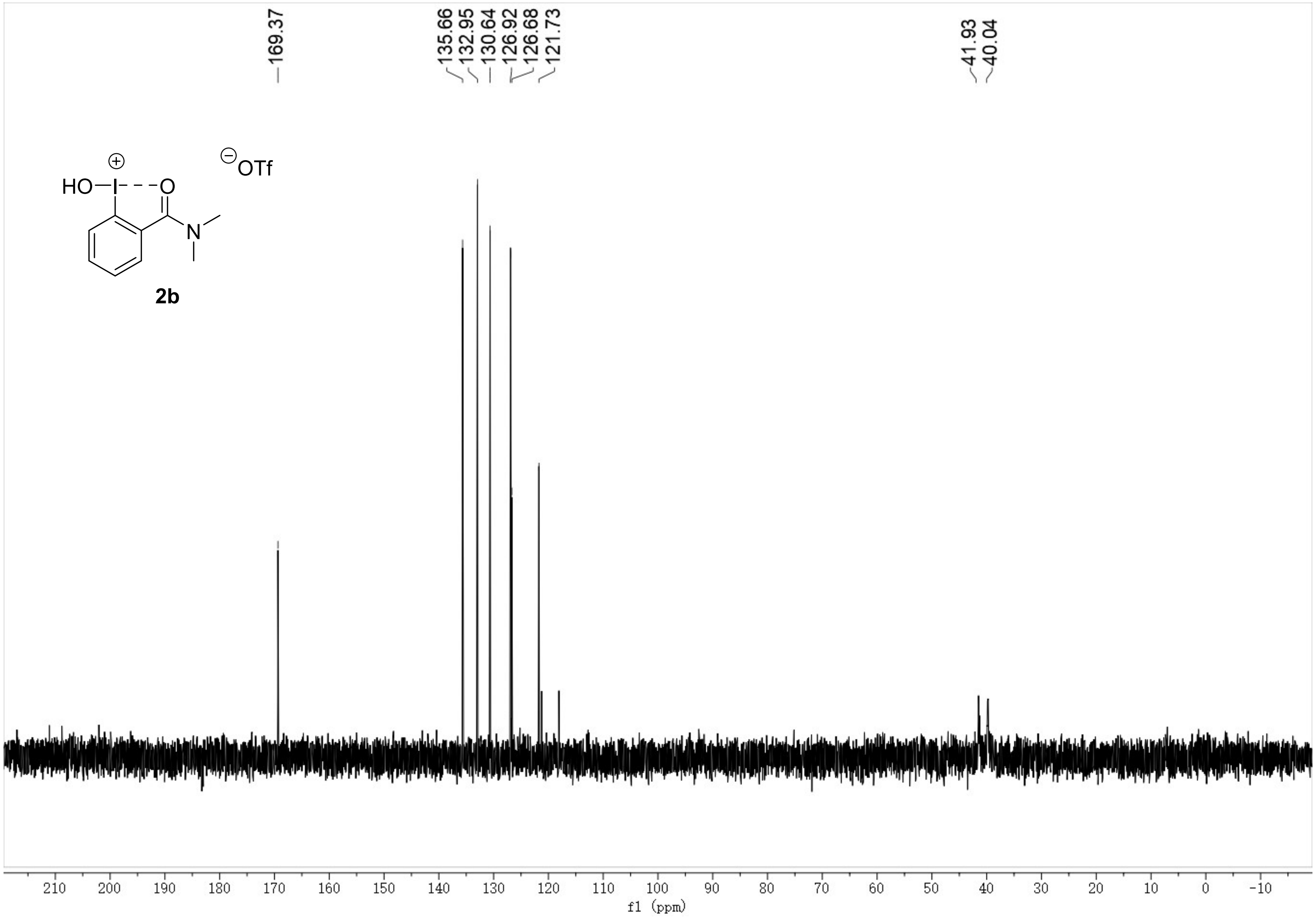


2a

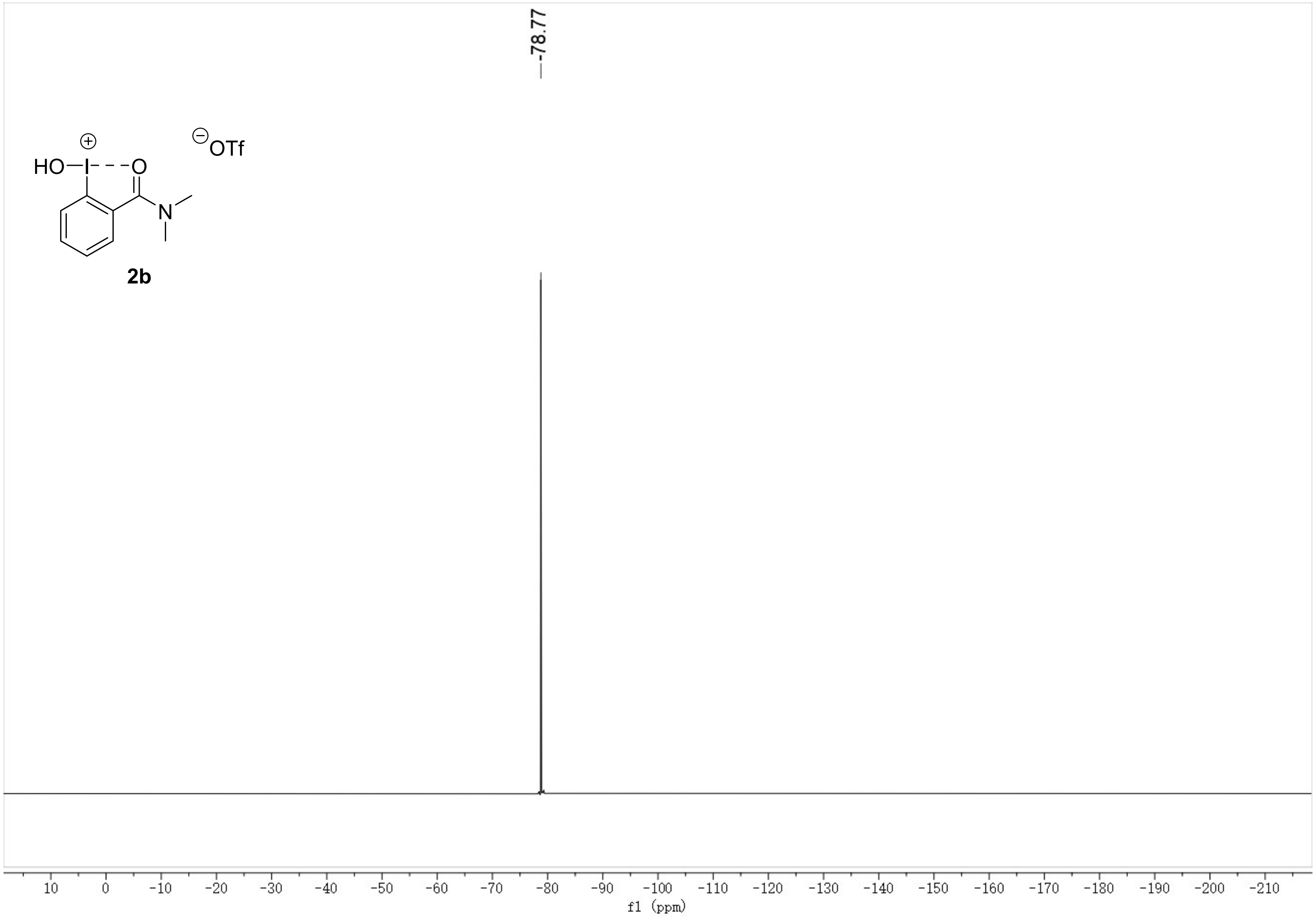
^{1}H NMR (400 MHz, D_2O)



^{13}C NMR (101 MHz, D_2O)

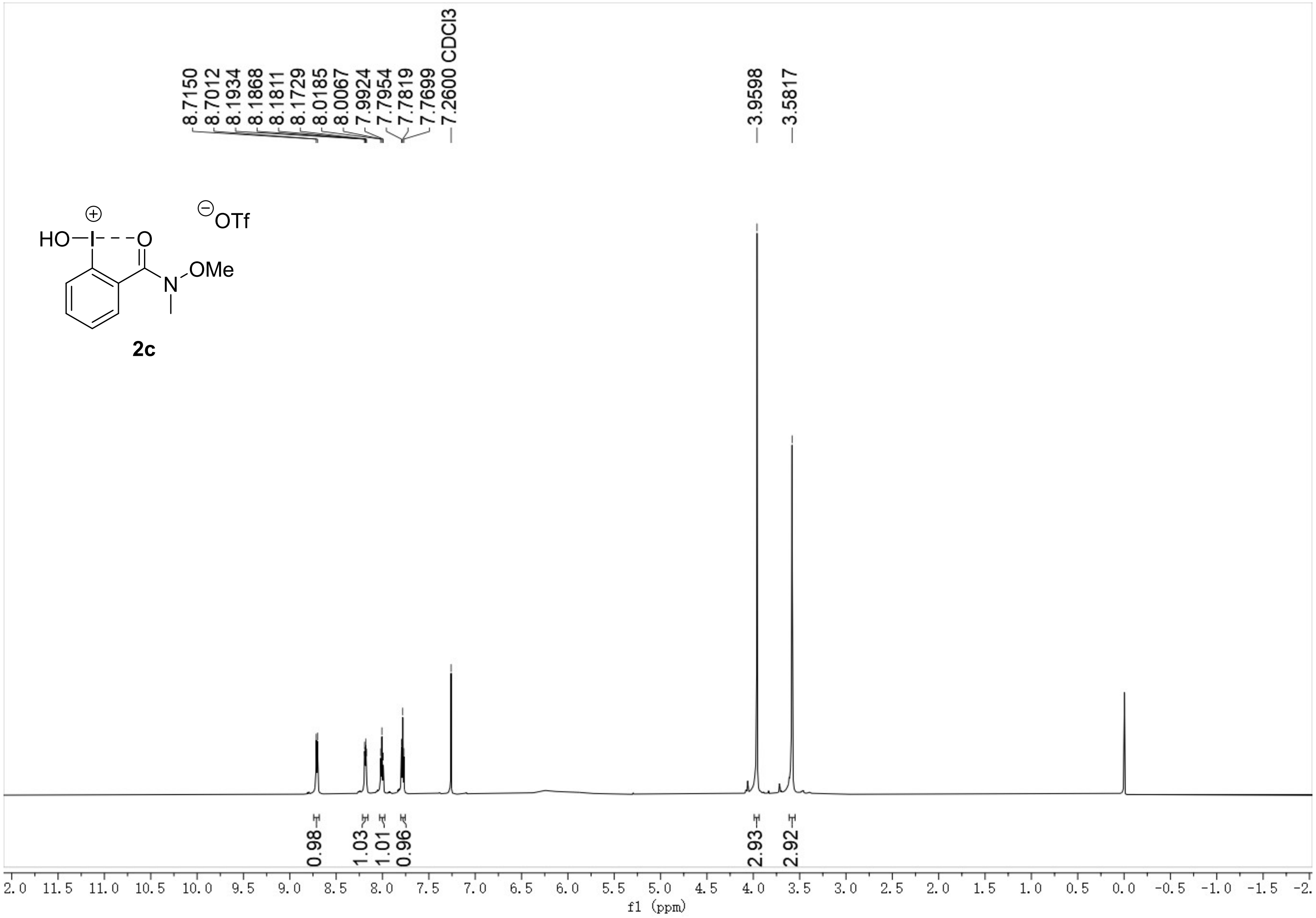


^{19}F NMR (376 MHz, D_2O)



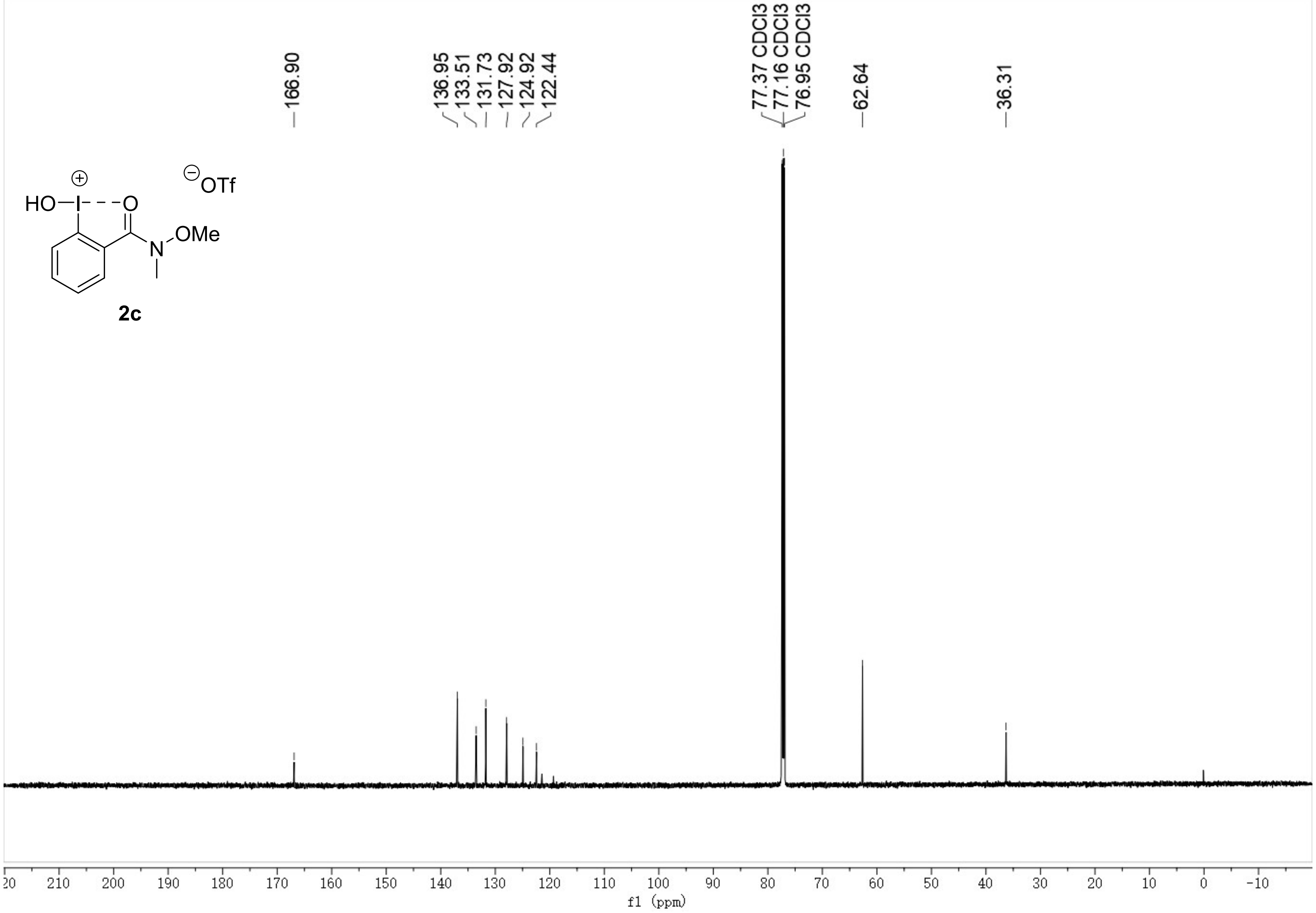
2b

^{1}H NMR (600 MHz, CDCl$_3$)

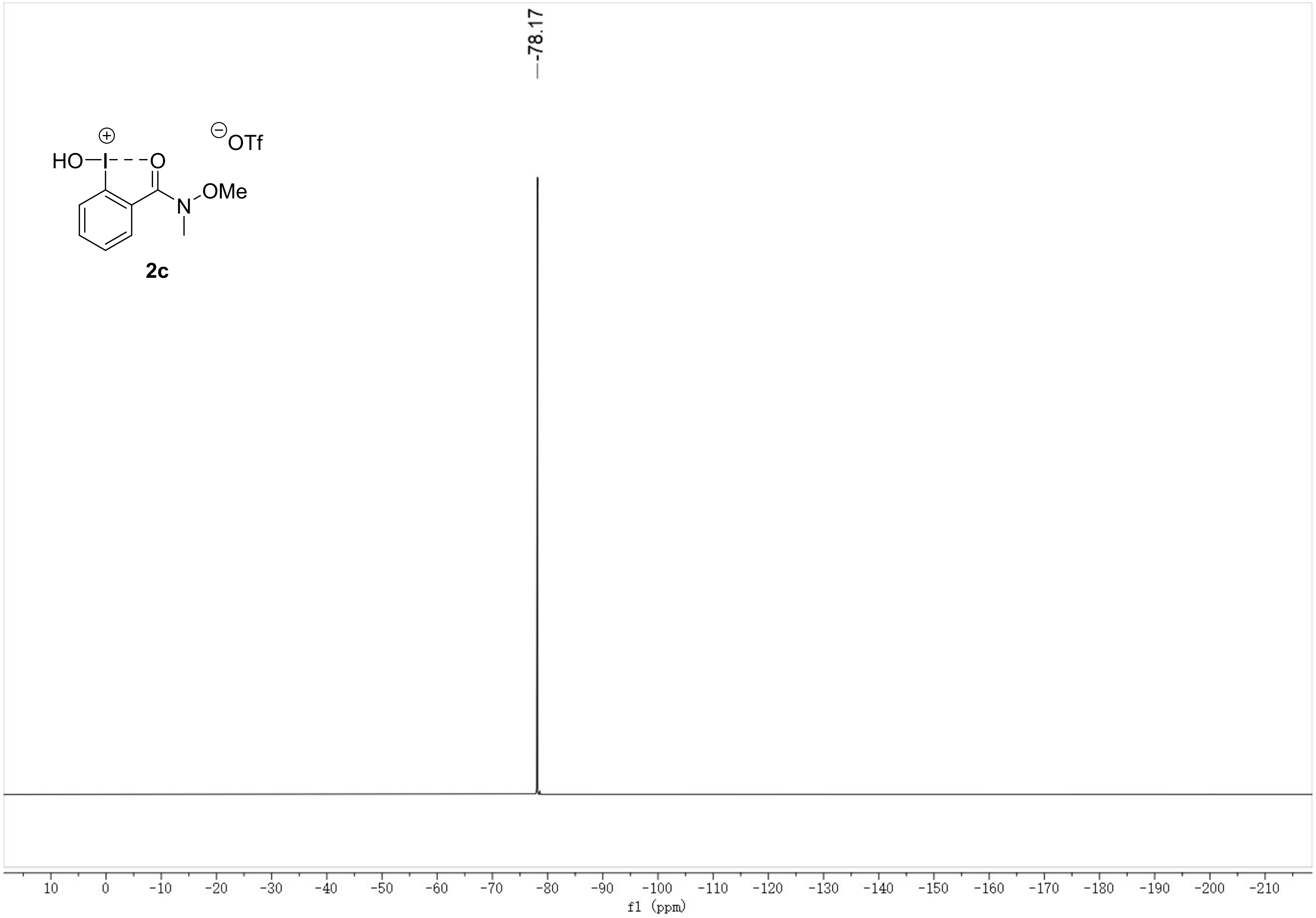


2c

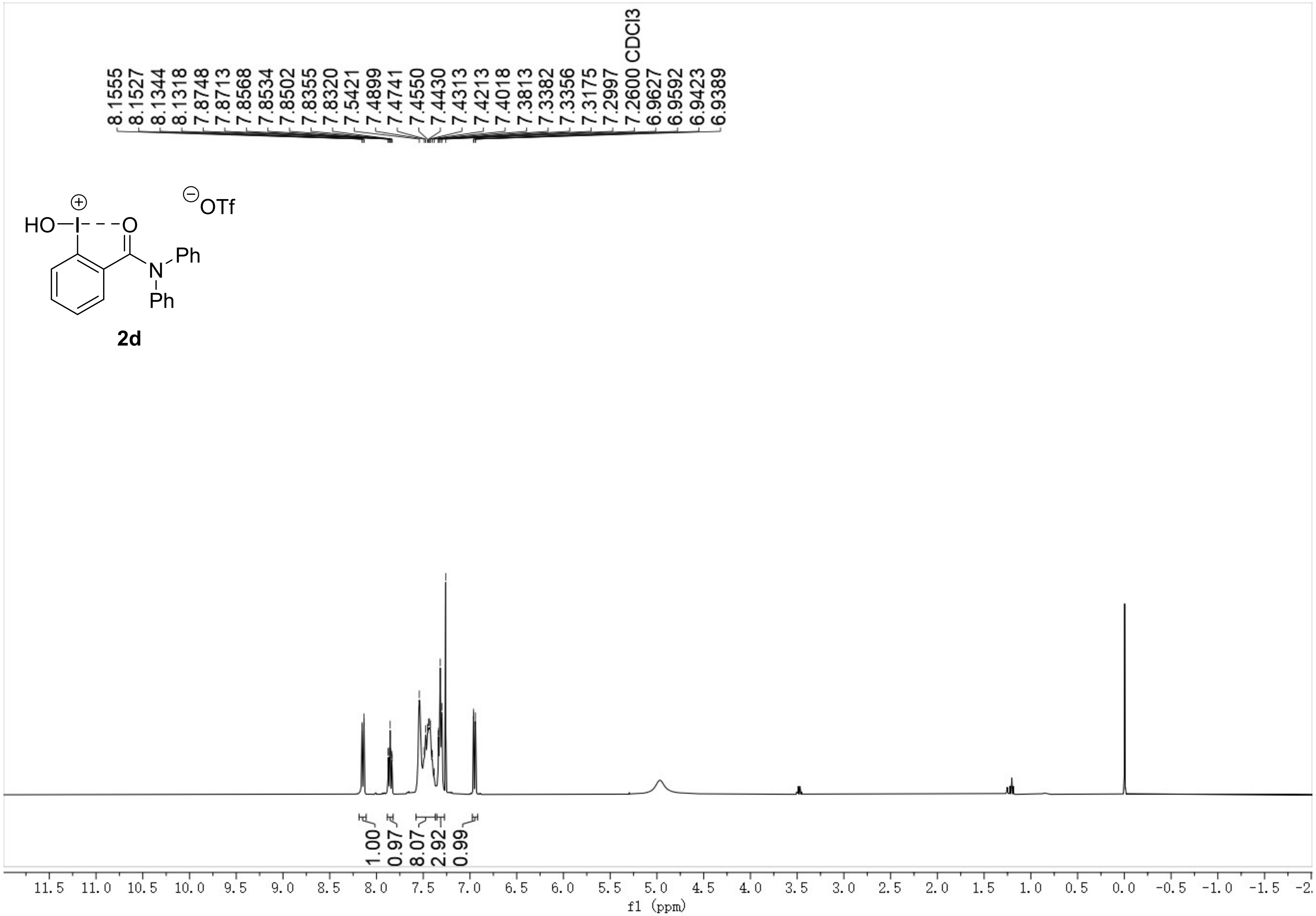
^{13}C NMR (151 MHz, $CDCl_3$)



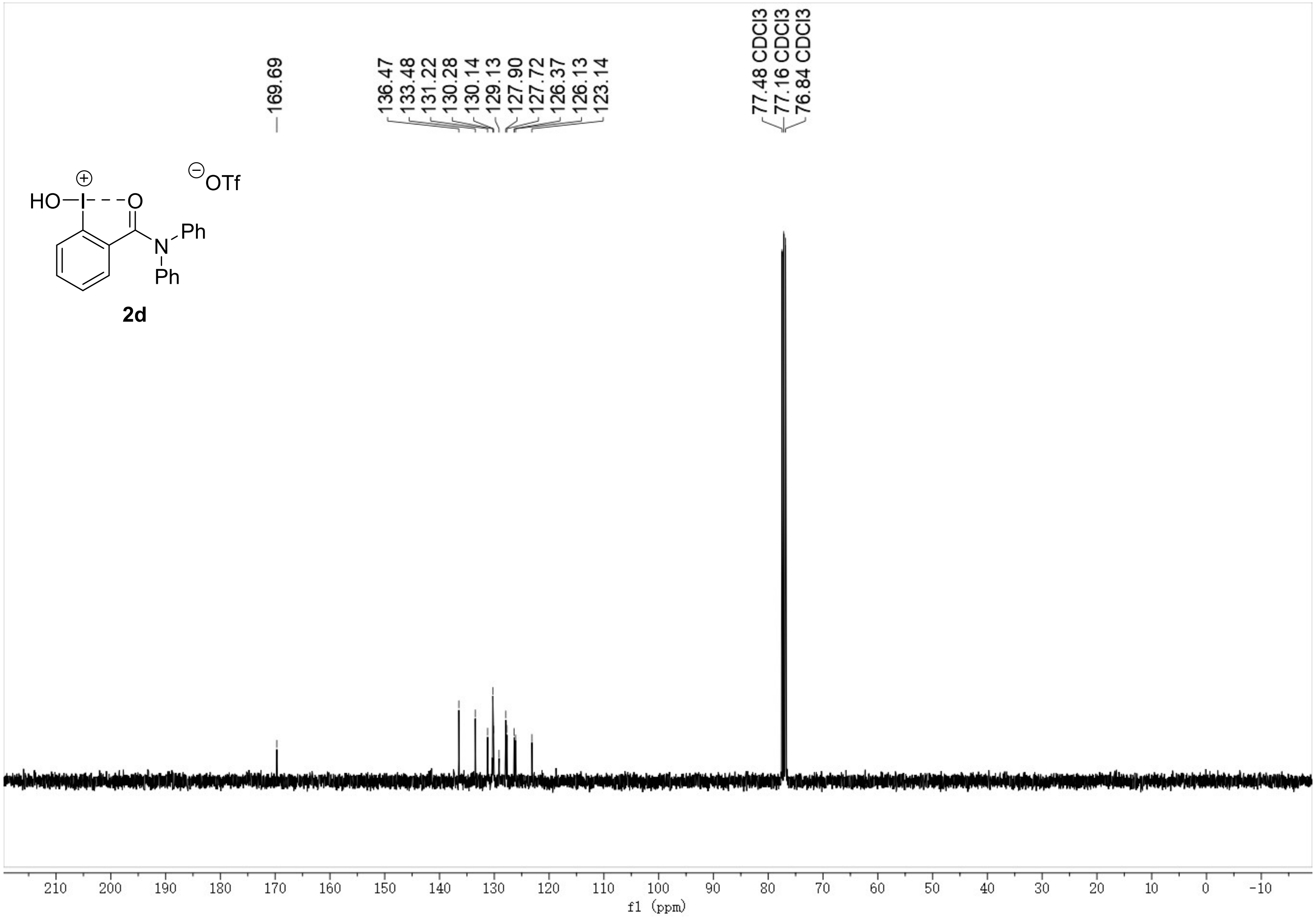
^{19}F NMR (565 MHz, CDC$_{l3}$)



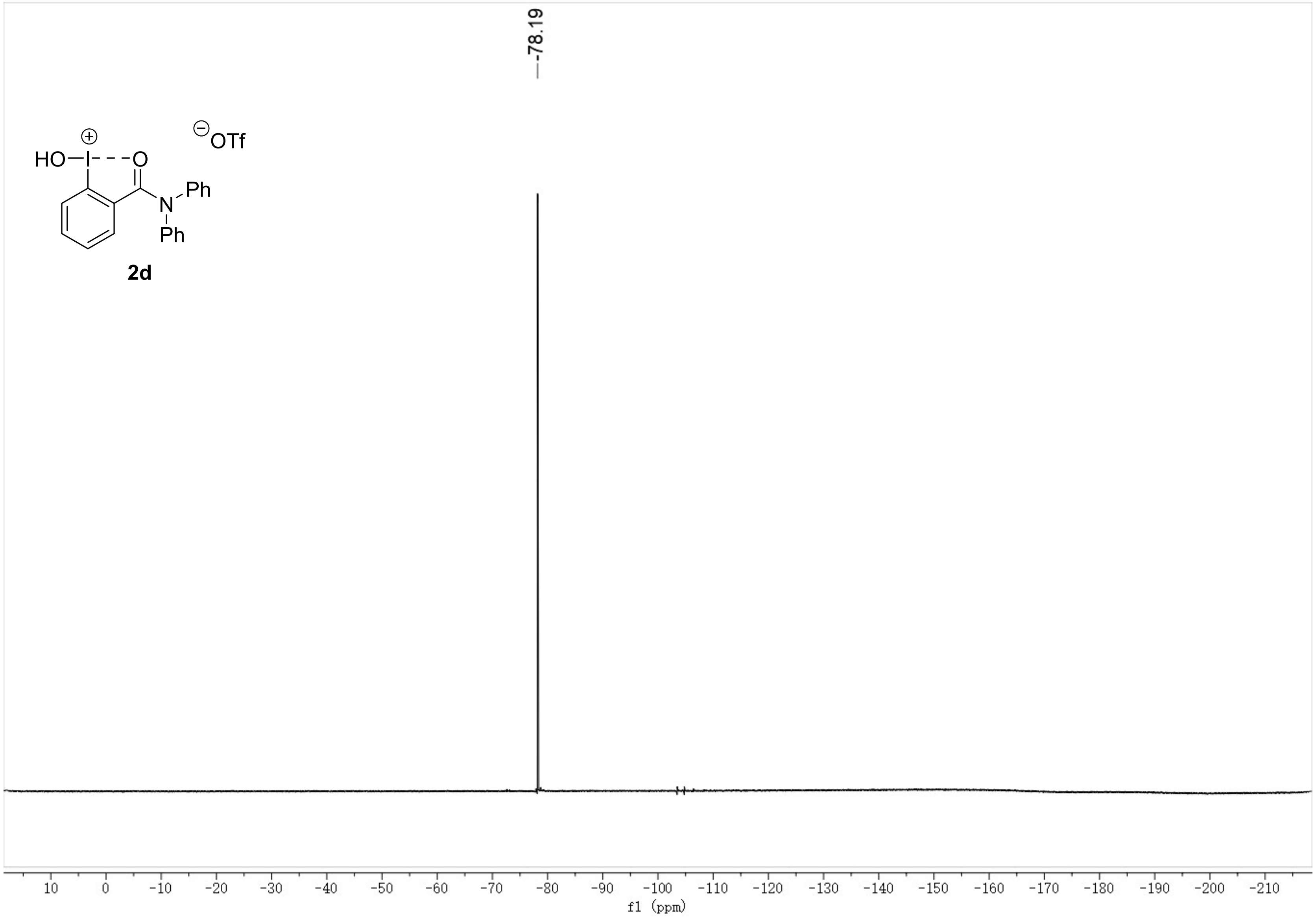
^{1}H NMR (400 MHz, CDCl$_3$)



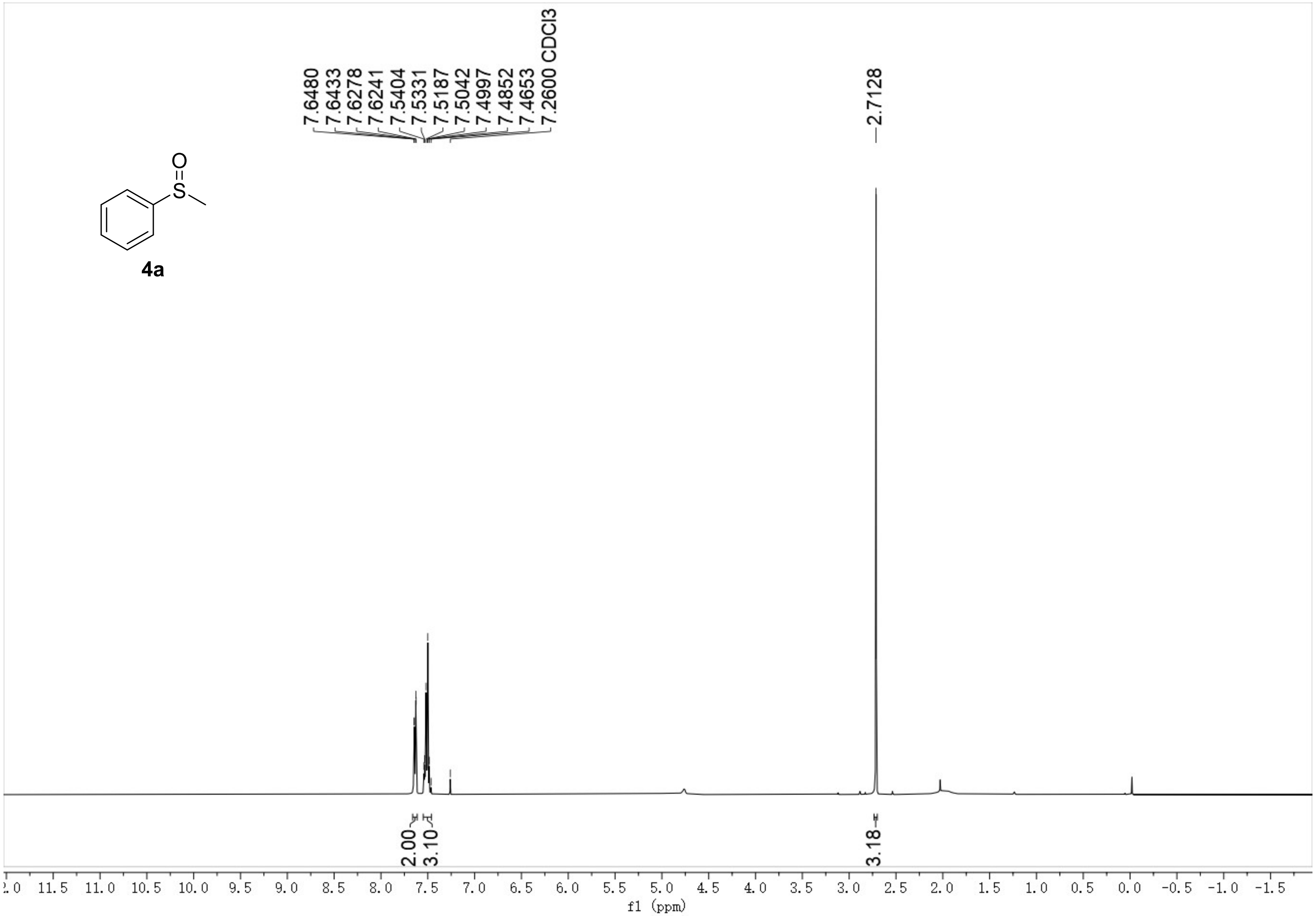
^{13}C NMR (101 MHz, CDCl$_3$)



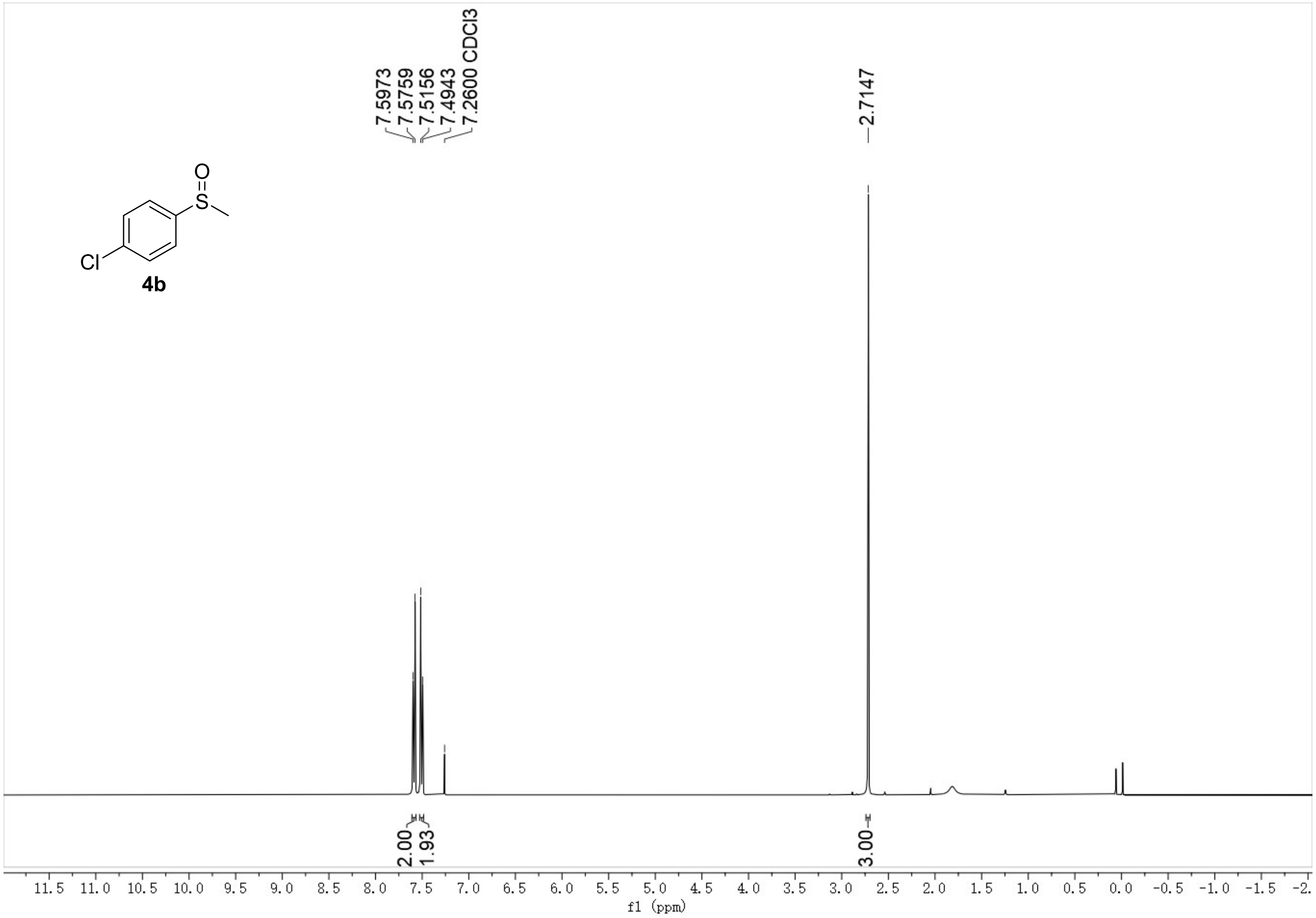
^{19}F NMR (376 MHz, $CDCl_3$)



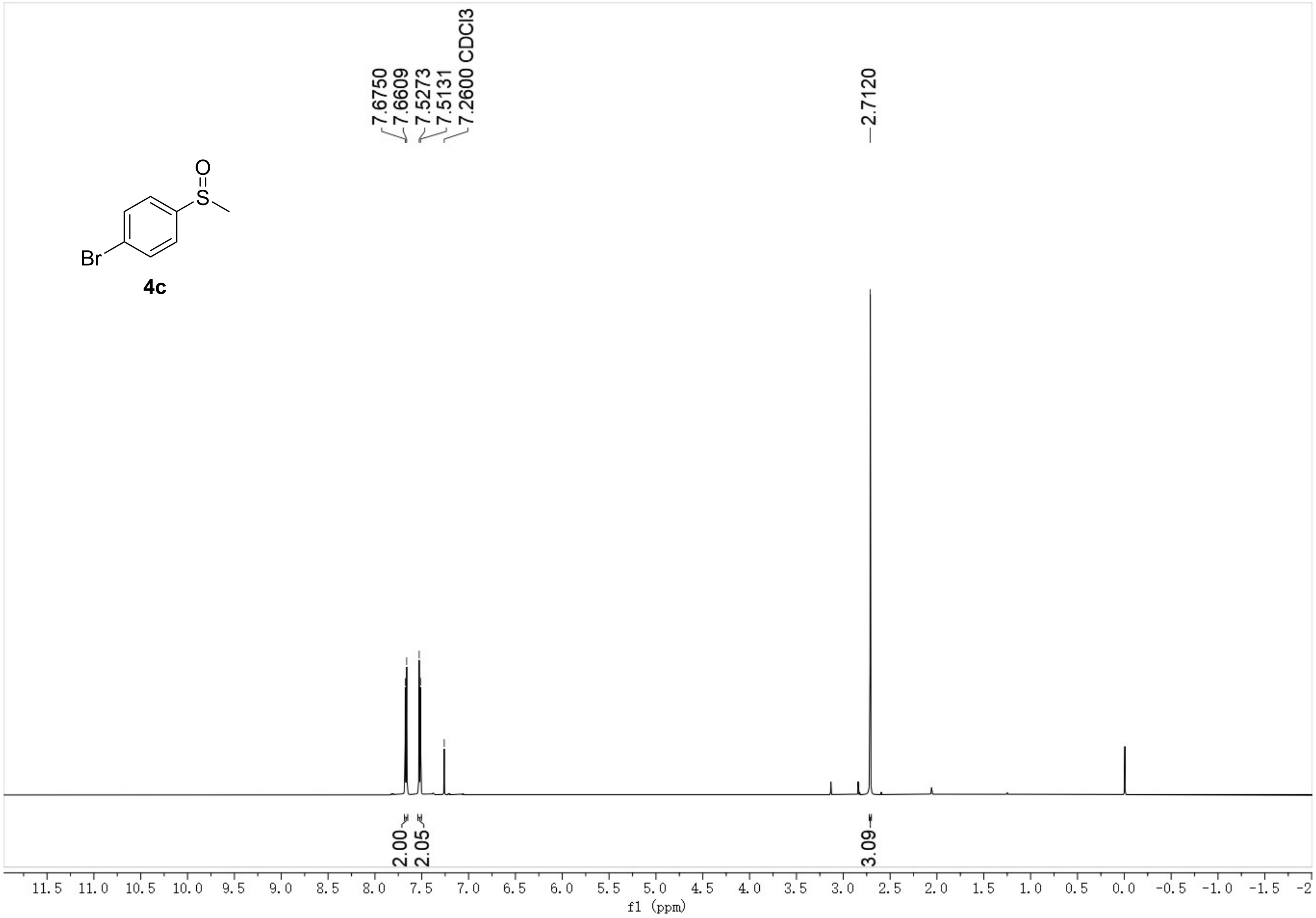
^{1}H NMR (400 MHz, $CDCl_3$)



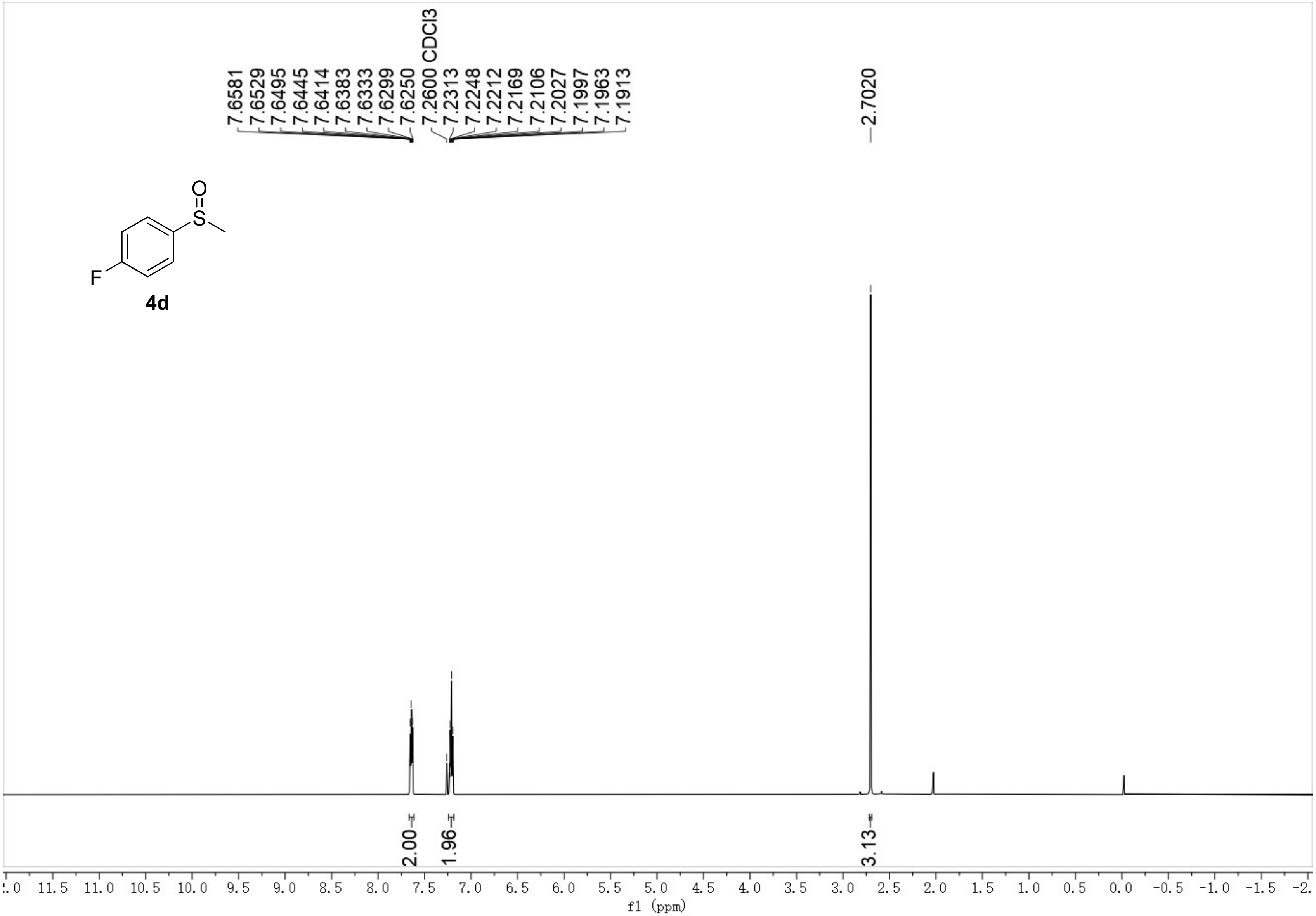
^{1}H NMR (400 MHz, $CDCl_3$)



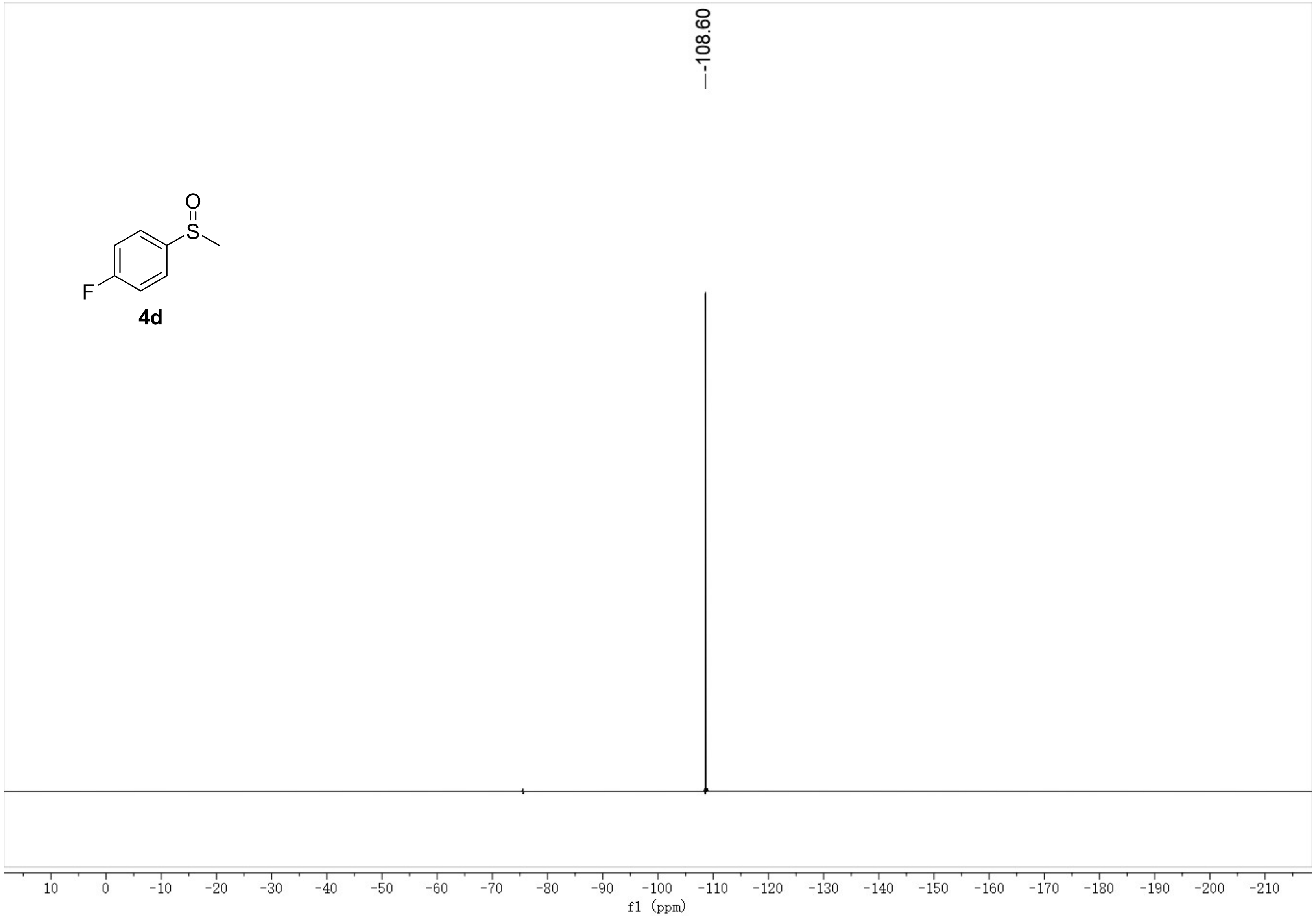
^{1}H NMR (600 MHz, $CDCl_3$)



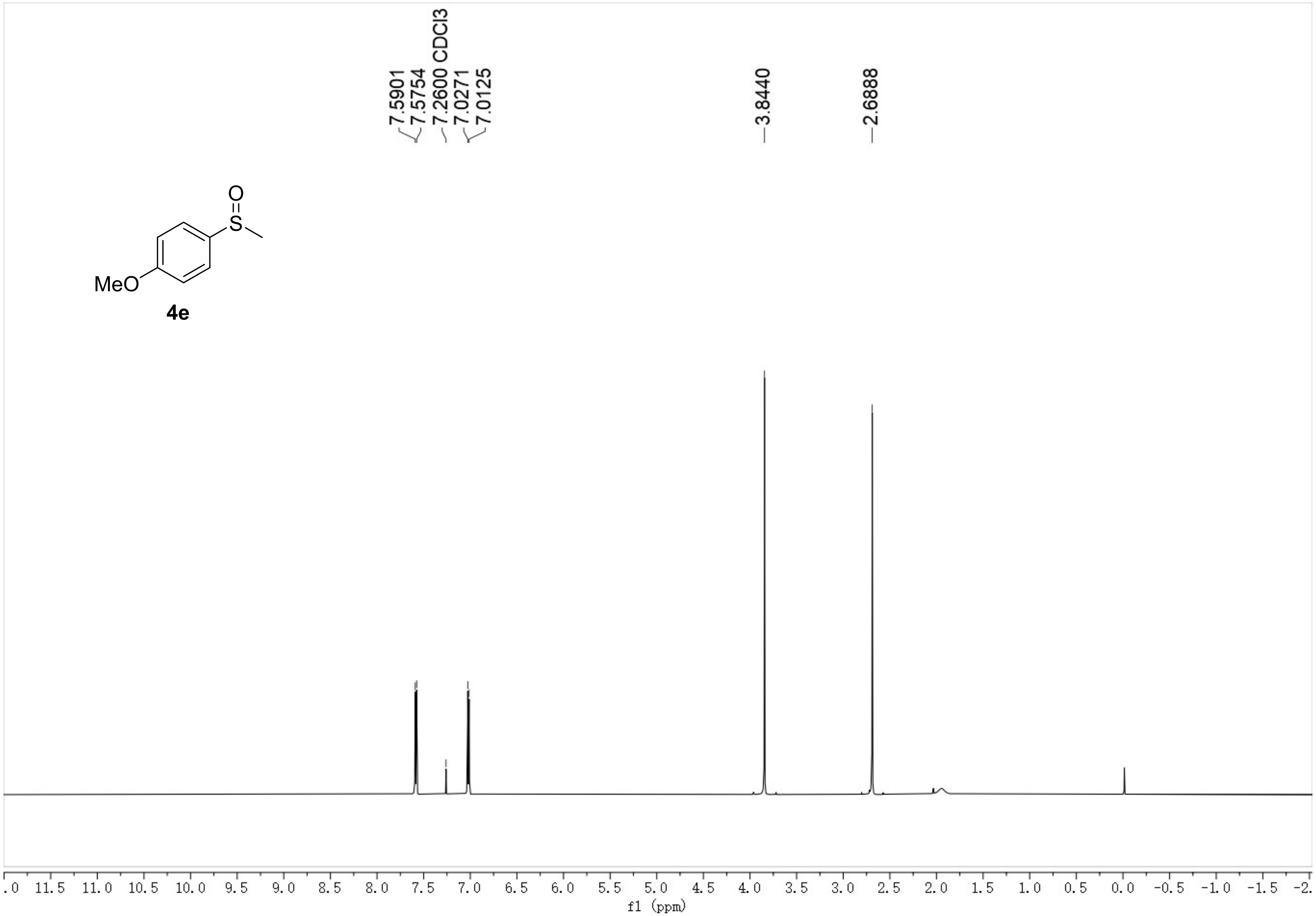
^{1}H NMR (600 MHz, $CDCl_3$)



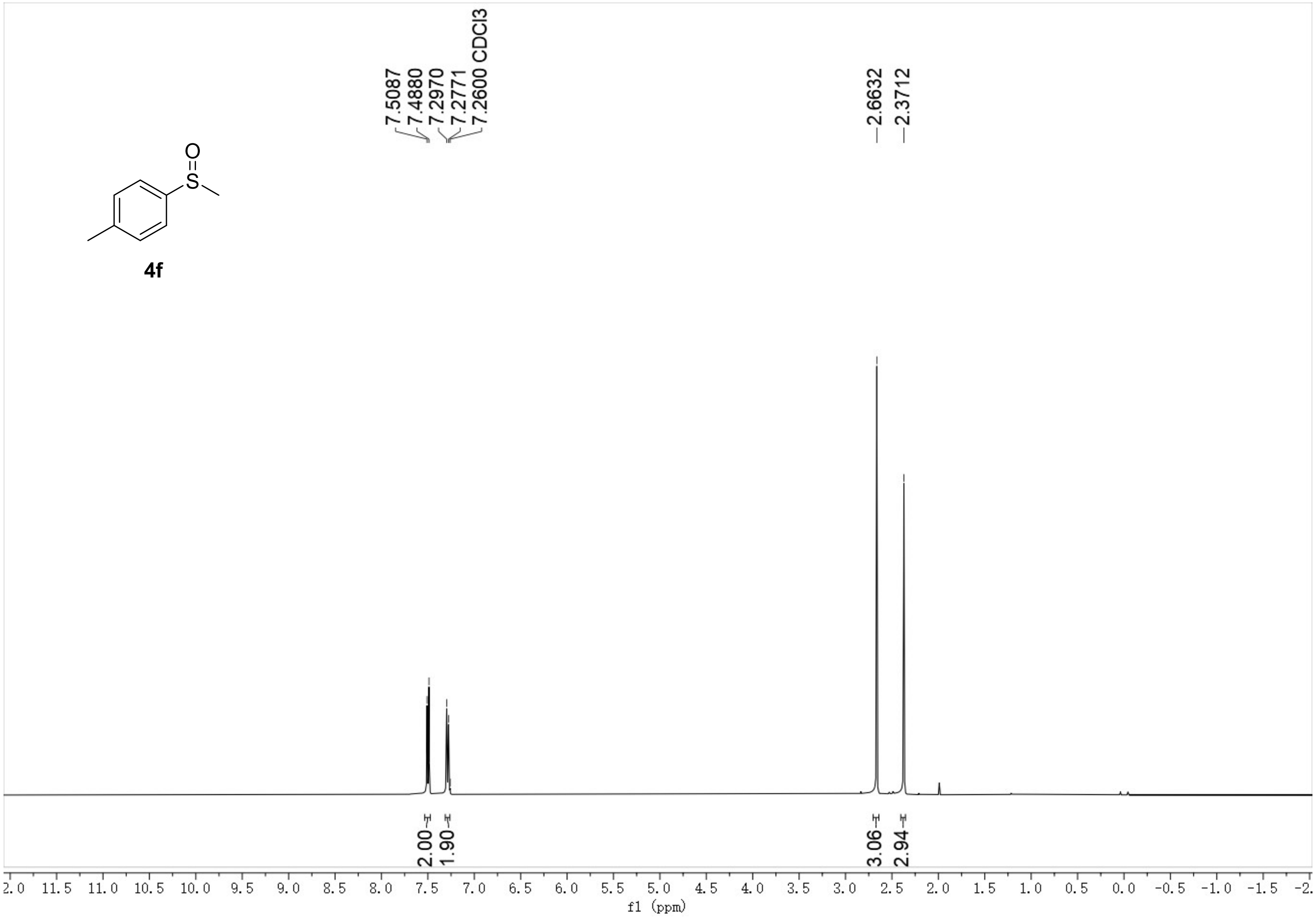
^{19}F NMR (565 MHz, $CDCl_3$)



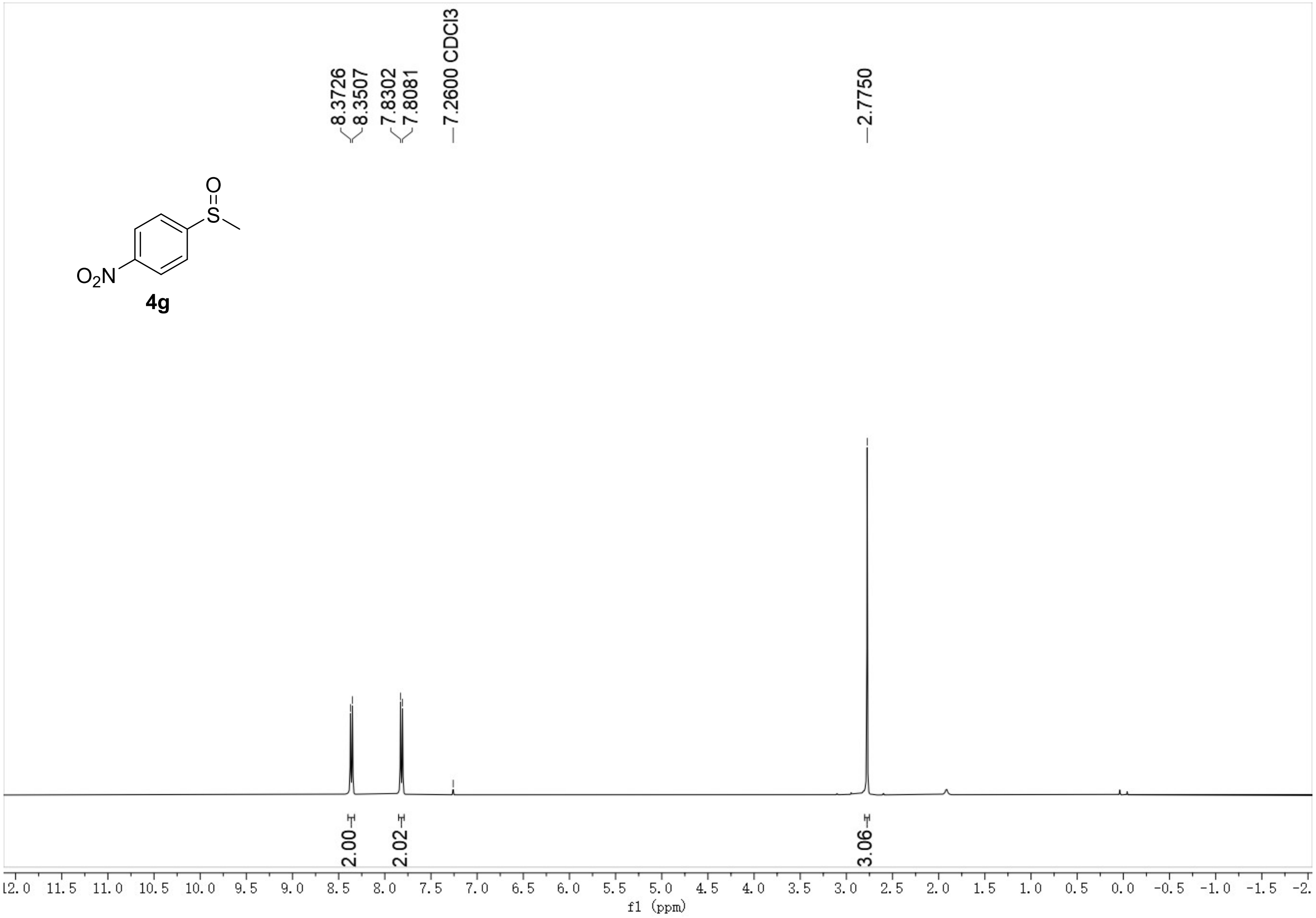
^1H NMR (600 MHz, $CDCl_3$)

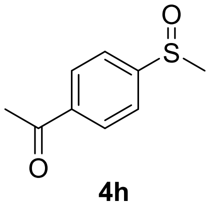


^{1}H NMR (400 MHz, CDCl$_3$)

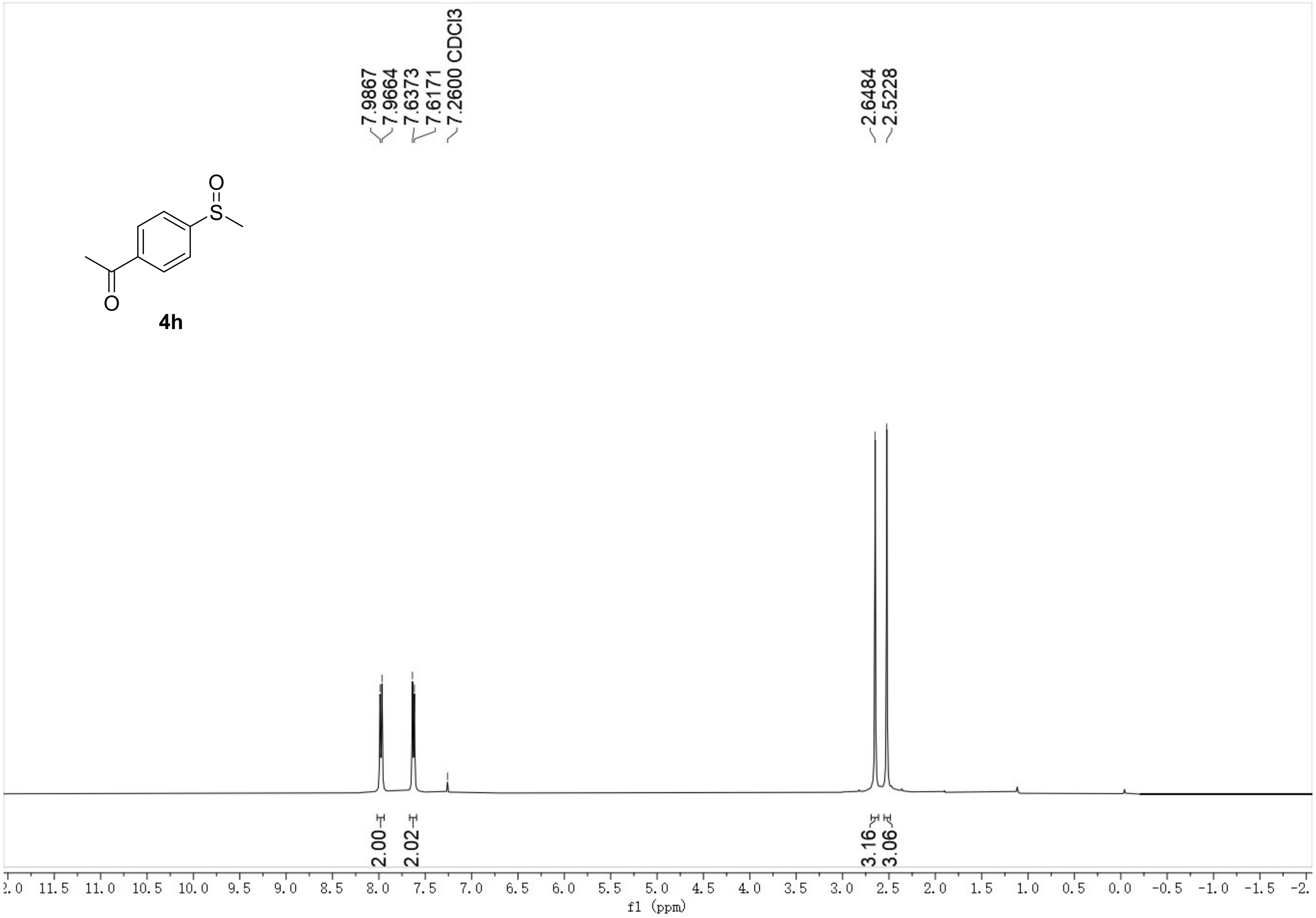


^{1}H NMR (400 MHz, $CDCl_3$)

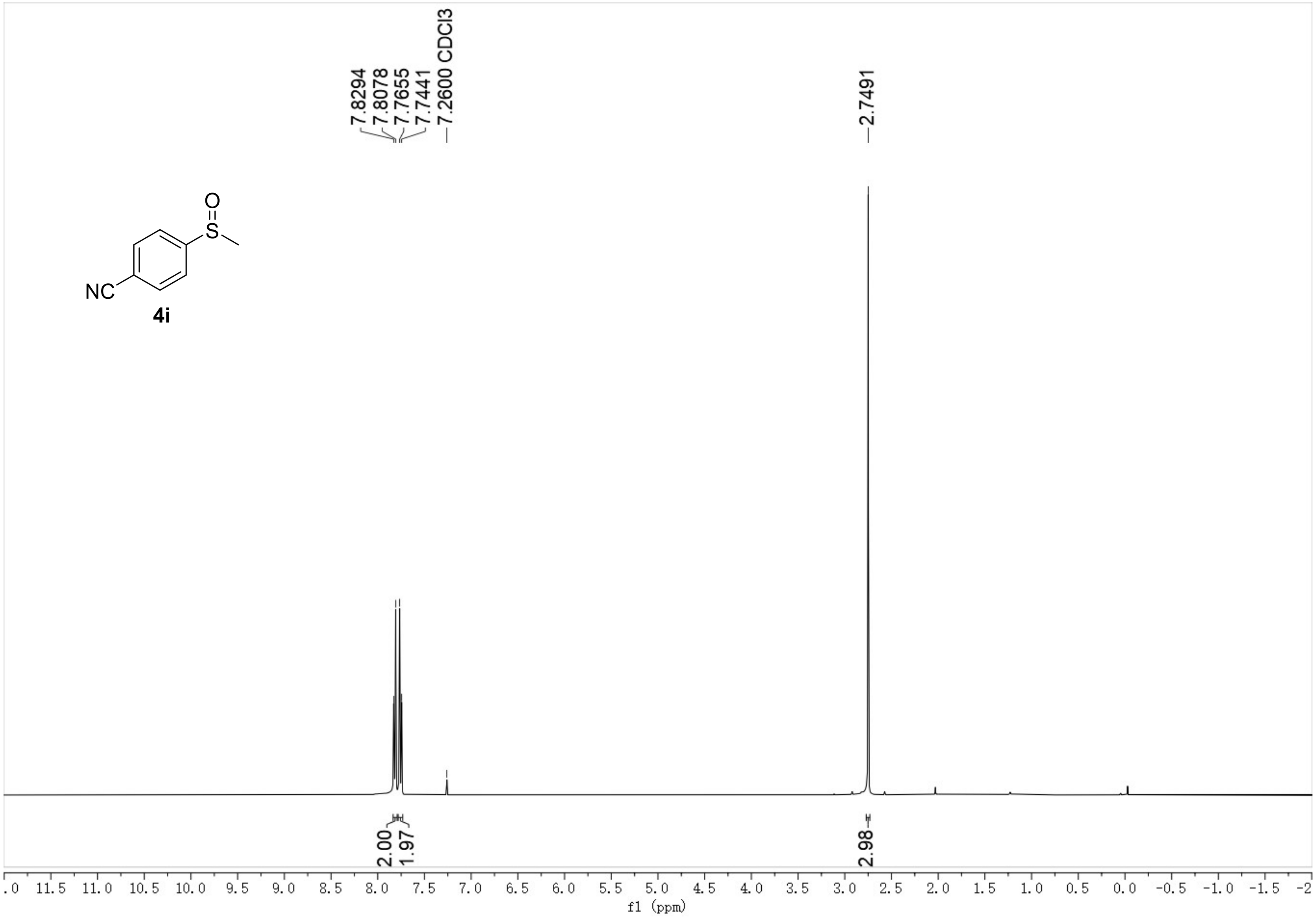




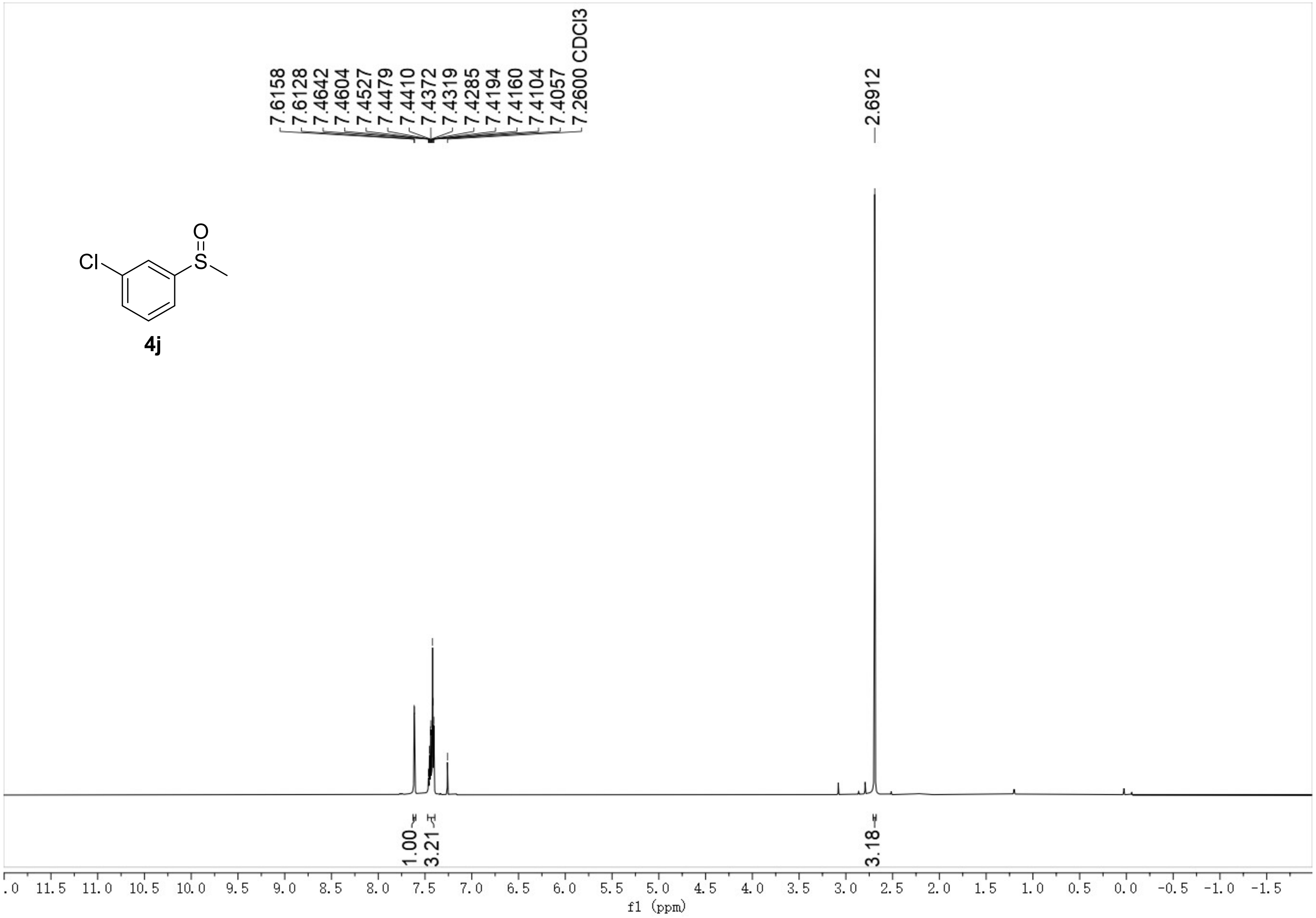
4h


^{1}H NMR (400 MHz, CDCl$_3$)
7.9867
7.9664
7.6373
7.6171
7.2600 CDCl3
2.6484
2.5228
2.00
2.02
3.16
3.06
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)

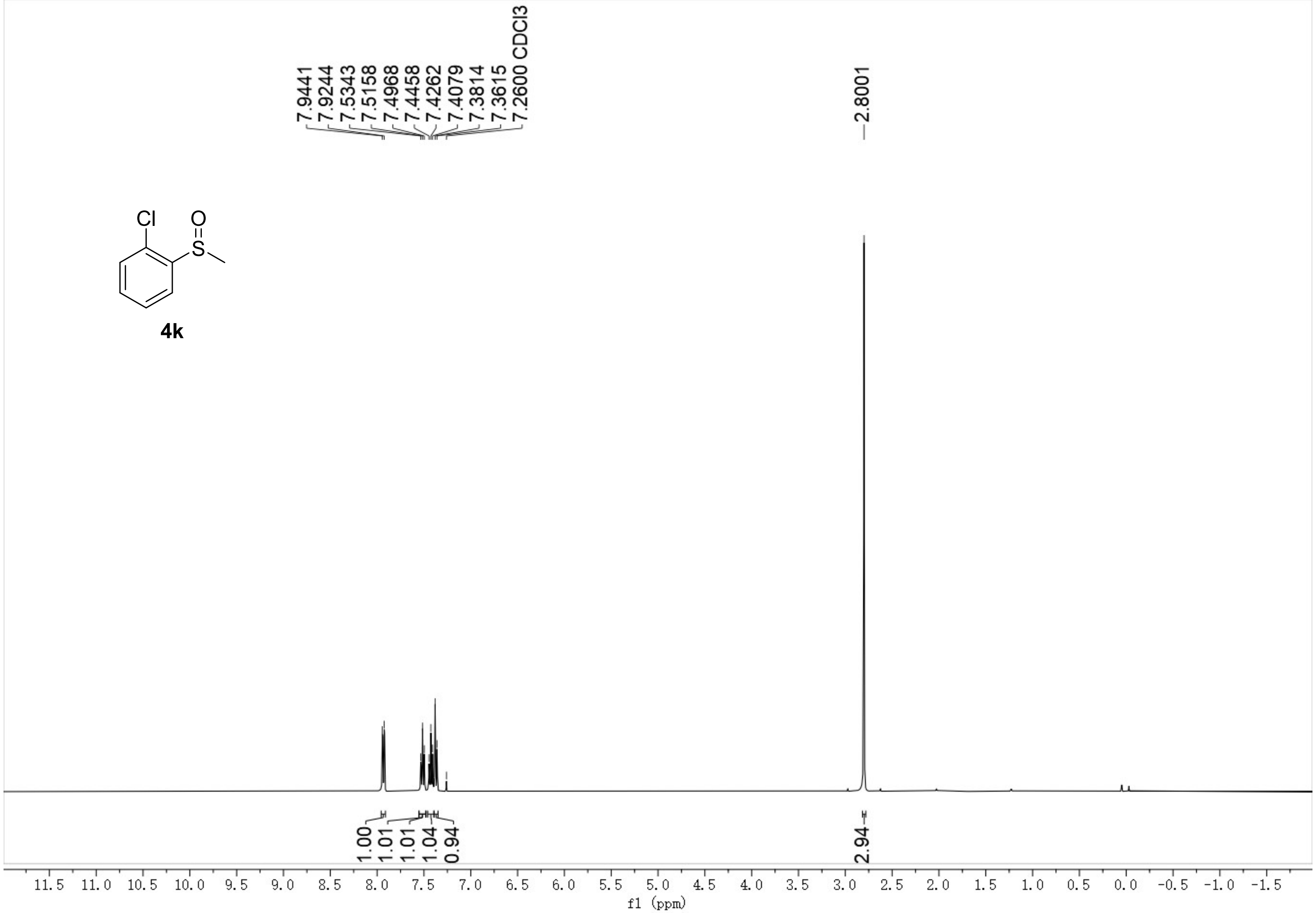
^{1}H NMR (400 MHz, $CDCl_3$)



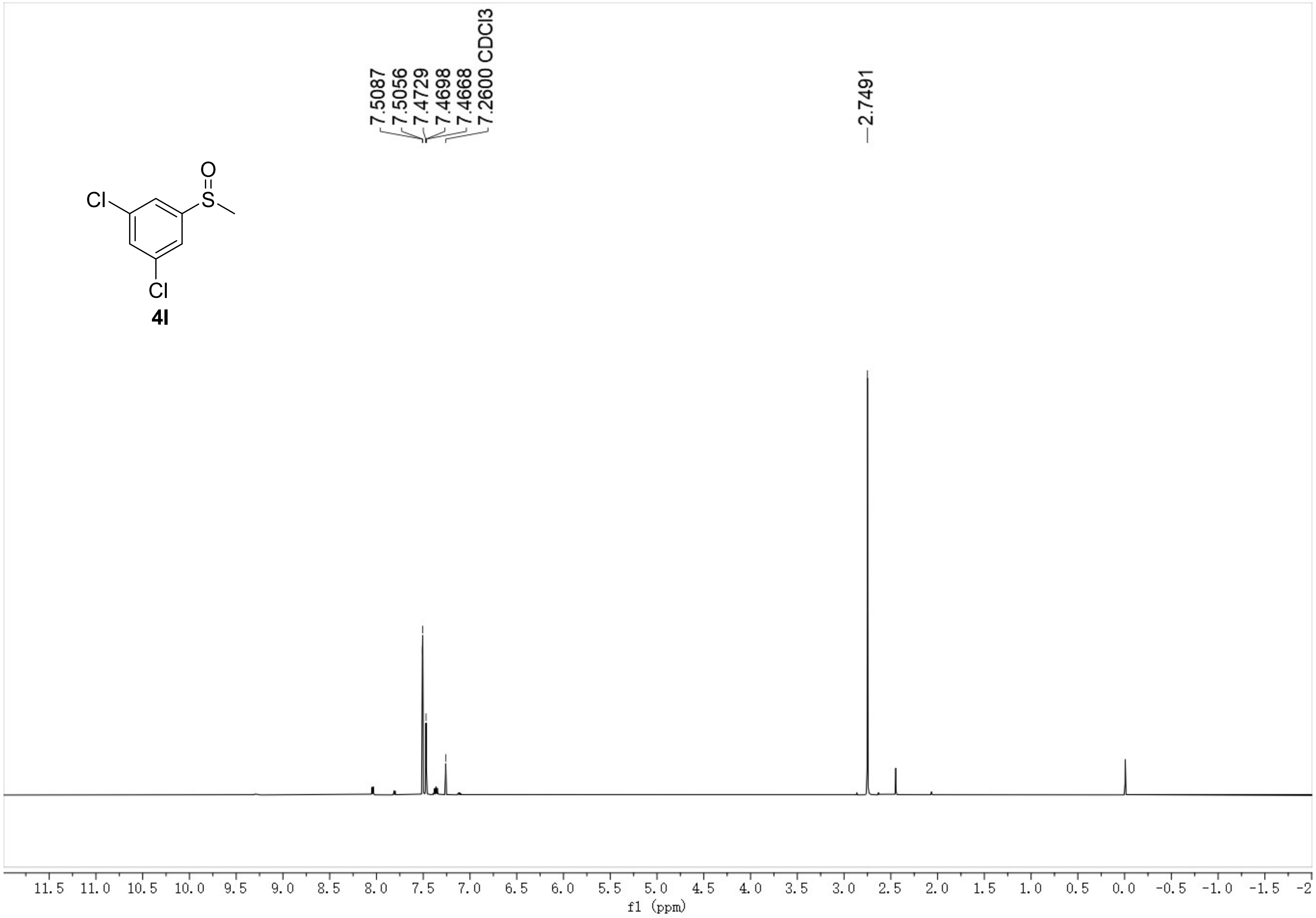
^1H NMR (400 MHz, $CDCl_3$)



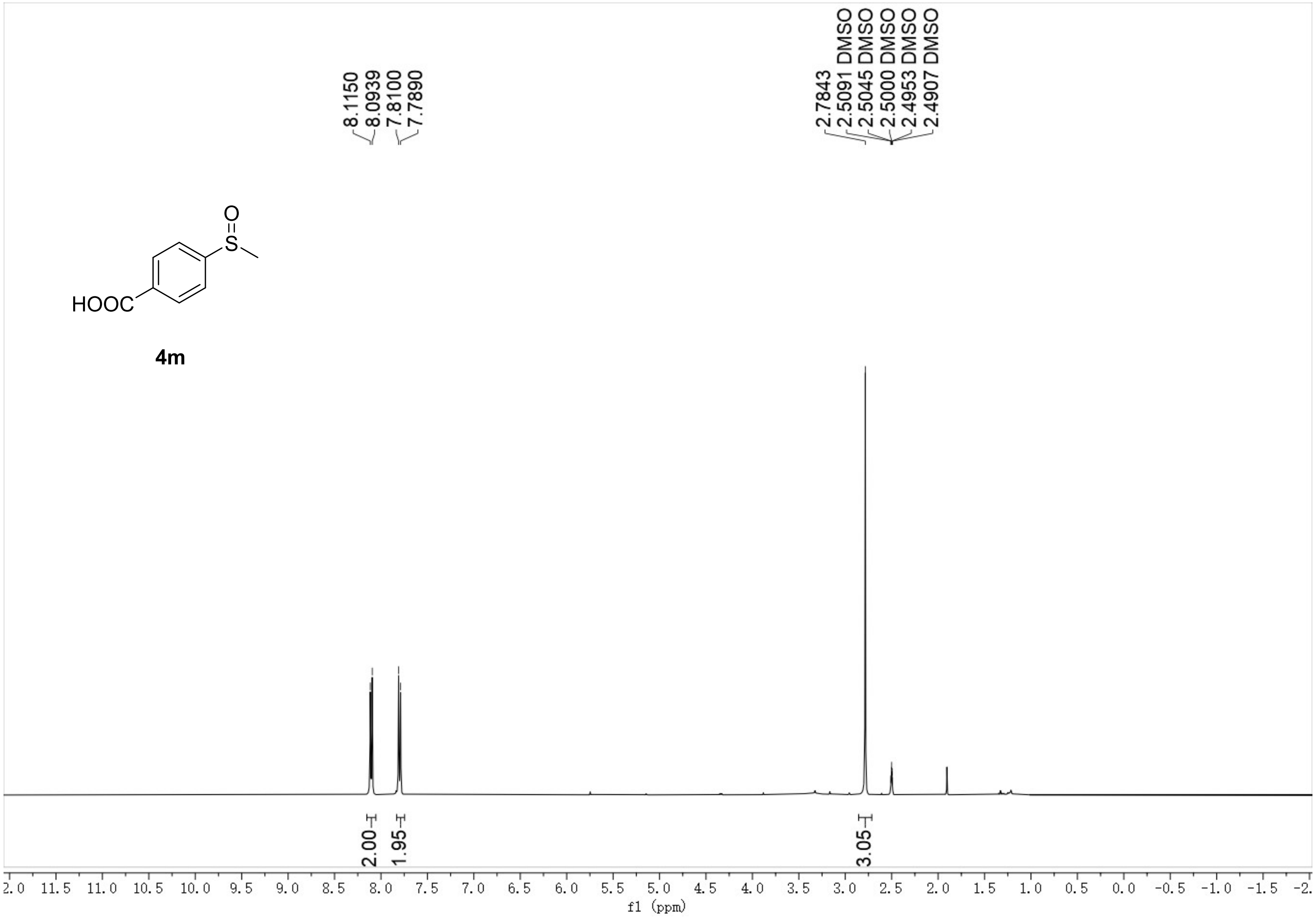
^{1}H NMR (400 MHz, $CDCl_3$)



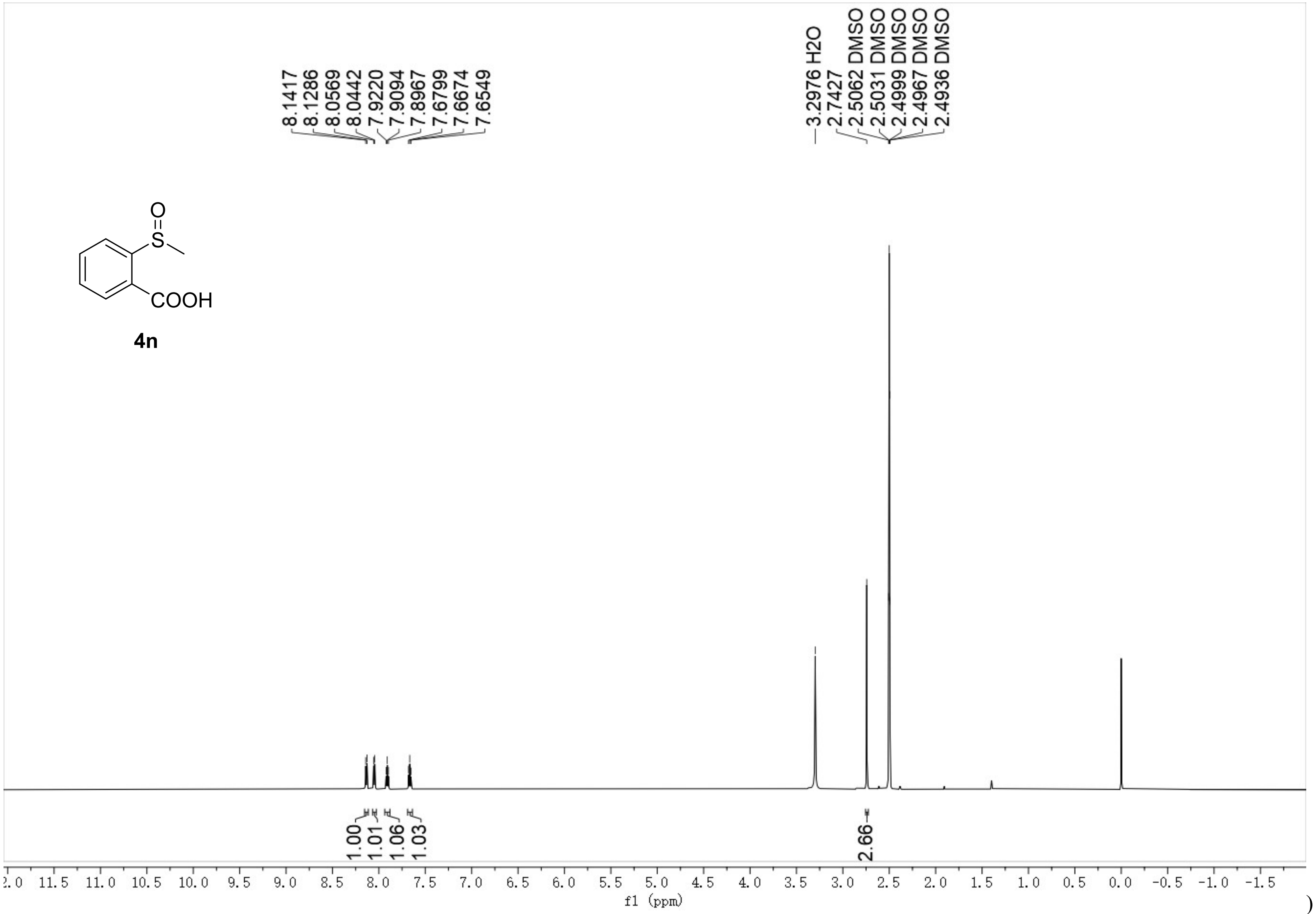
^{1}H NMR (600 MHz, CDCl$_3$)



^1H NMR (400 MHz, DMSO-d_6)

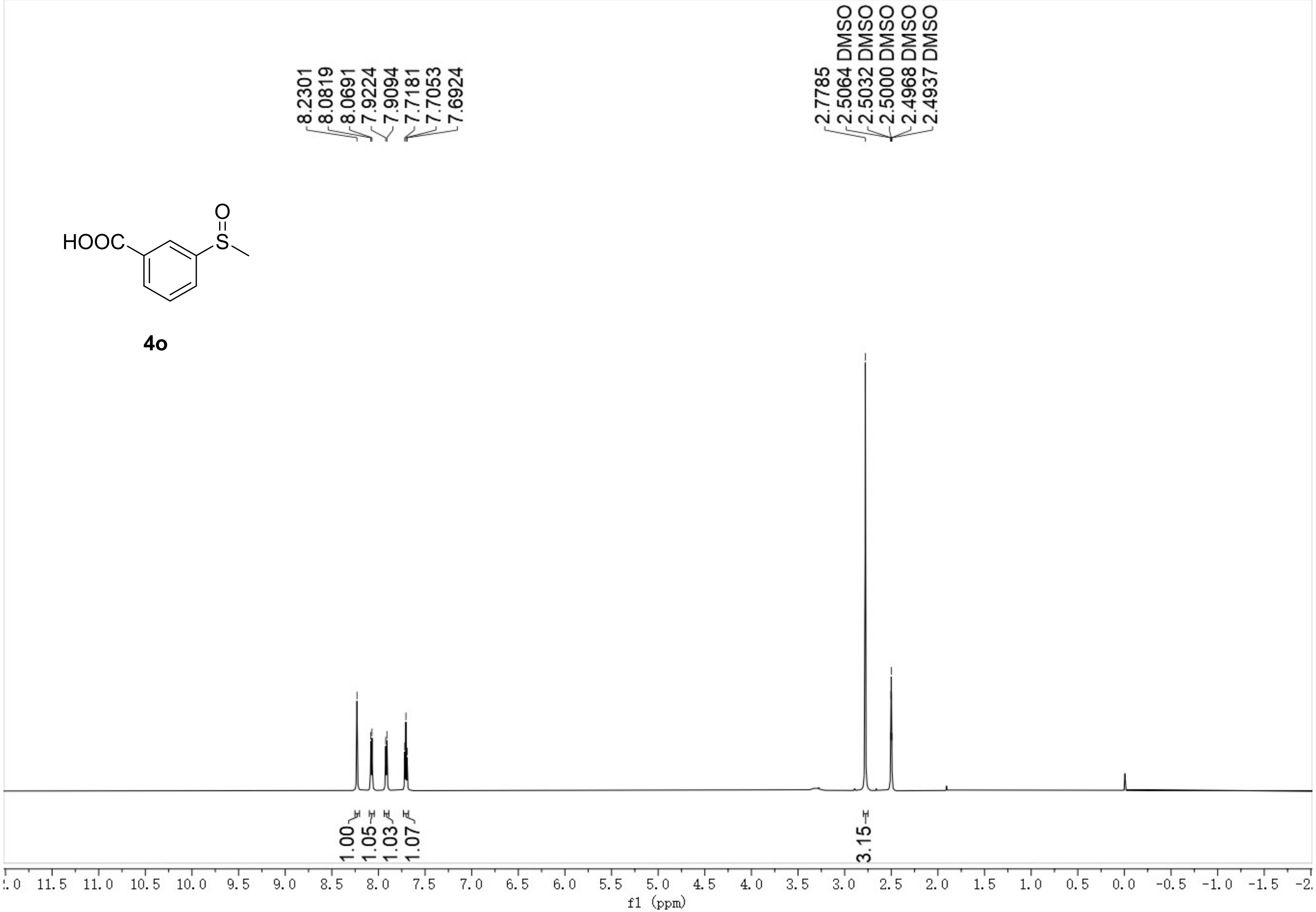


^{1}H NMR (600 MHz, DMSO-d_6）

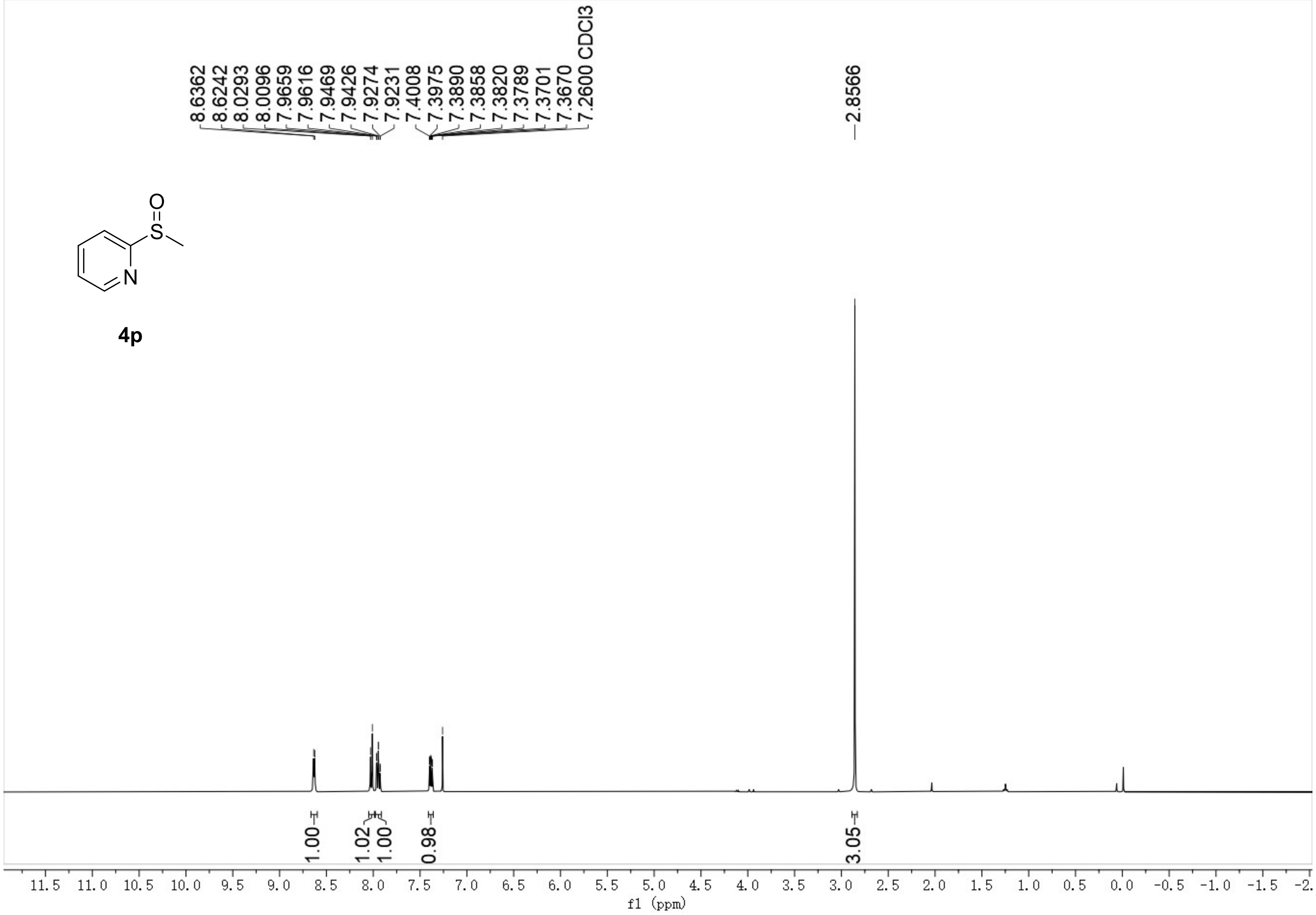


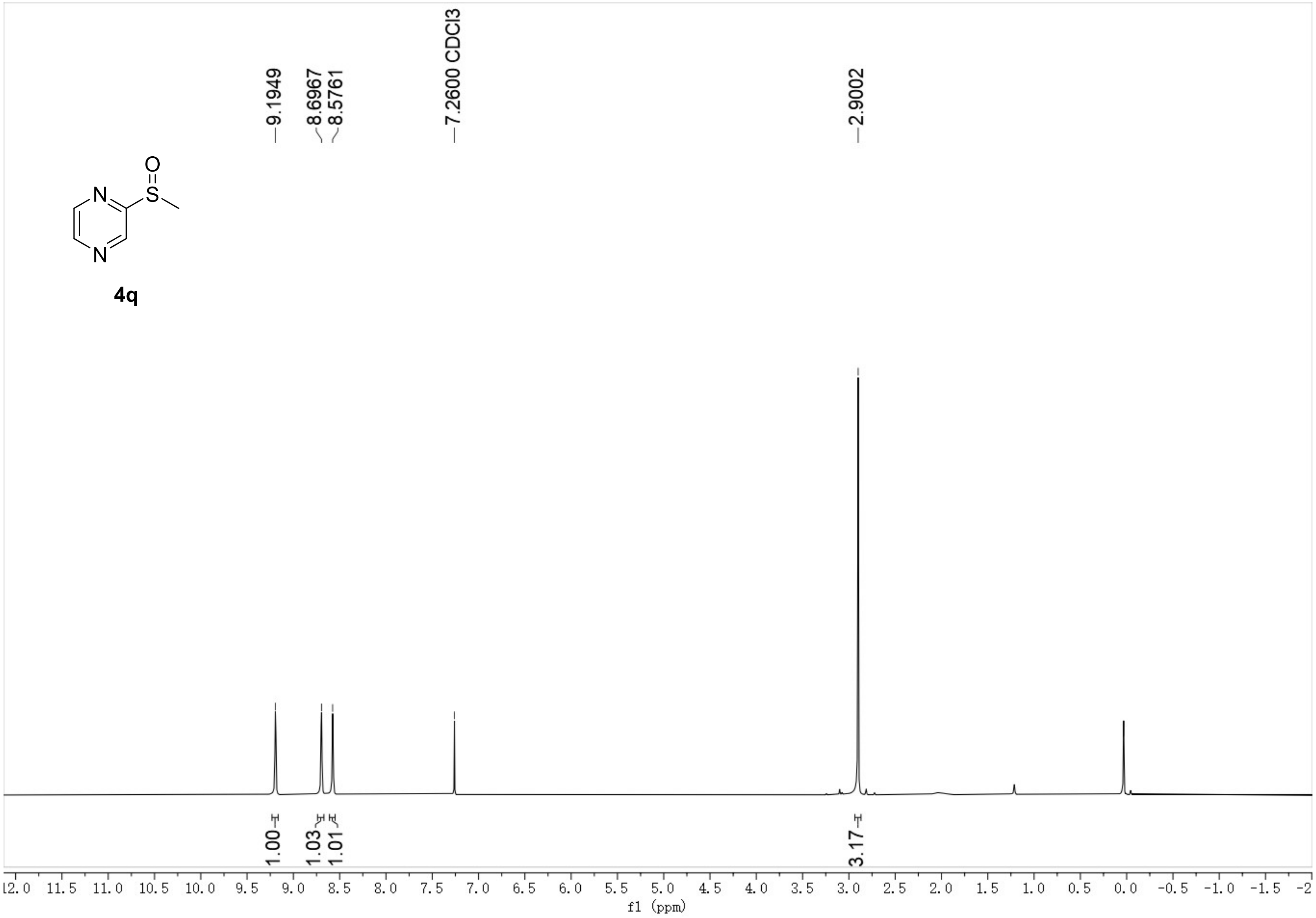
)

^{1}H NMR (600 MHz, DMSO-d_6）



^{1}H NMR (400 MHz, CDCl$_3$)



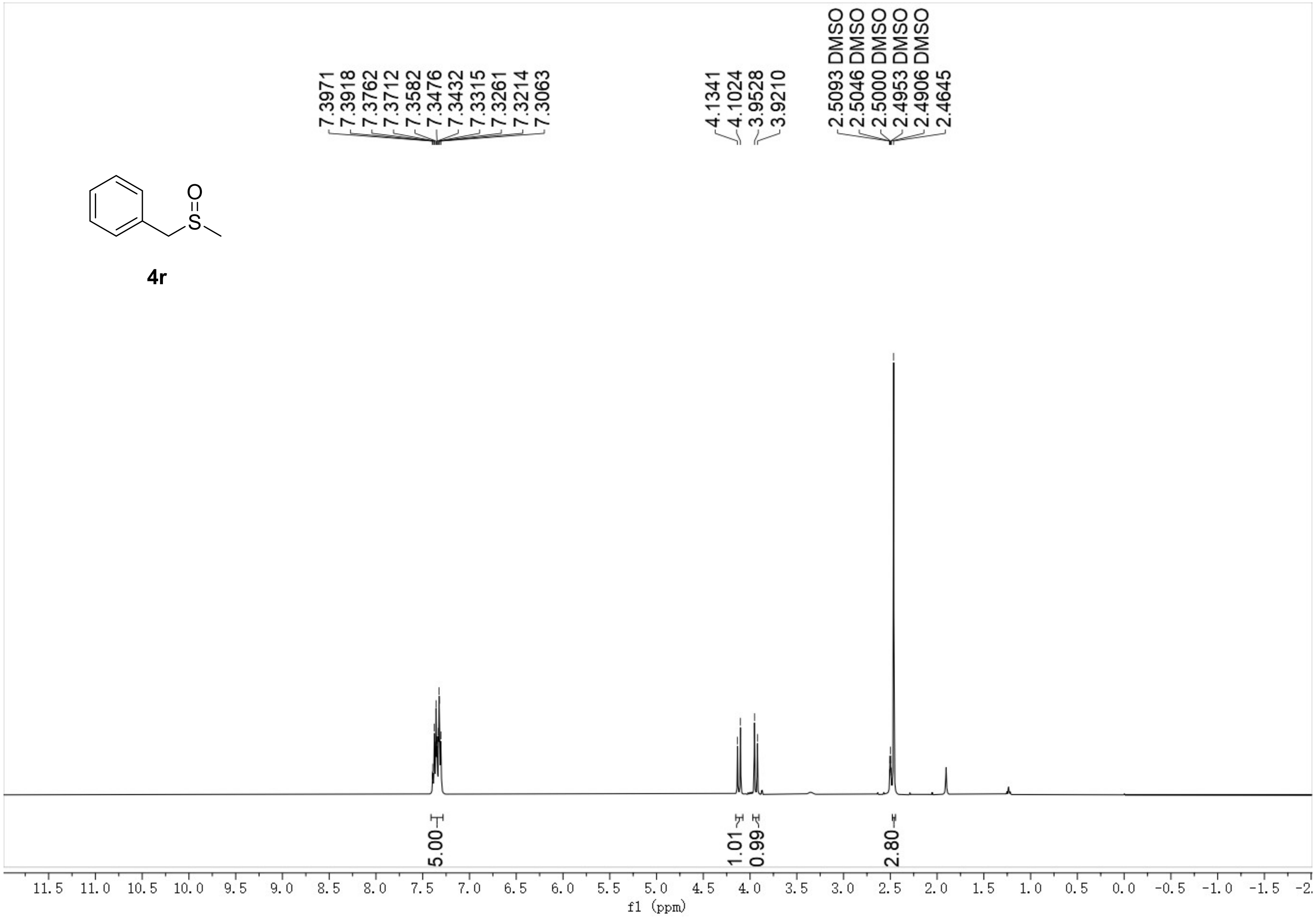


4q

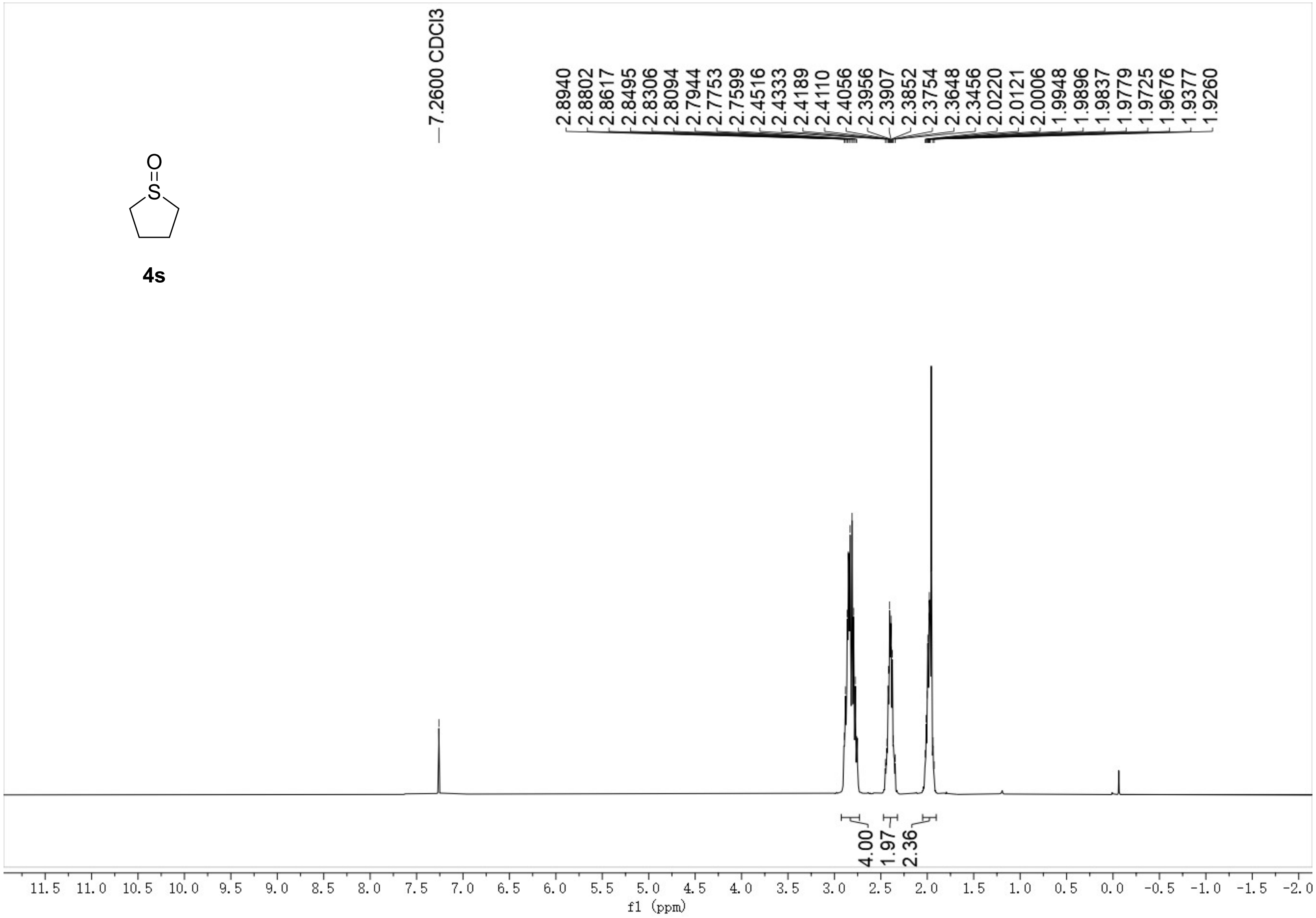
^{1}H NMR (400 MHz, CDCl$_3$)
9.1949
8.6967
8.5761
7.2600 CDCl3
2.9002
1.00
1.03
1.01
3.17
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$)

4r

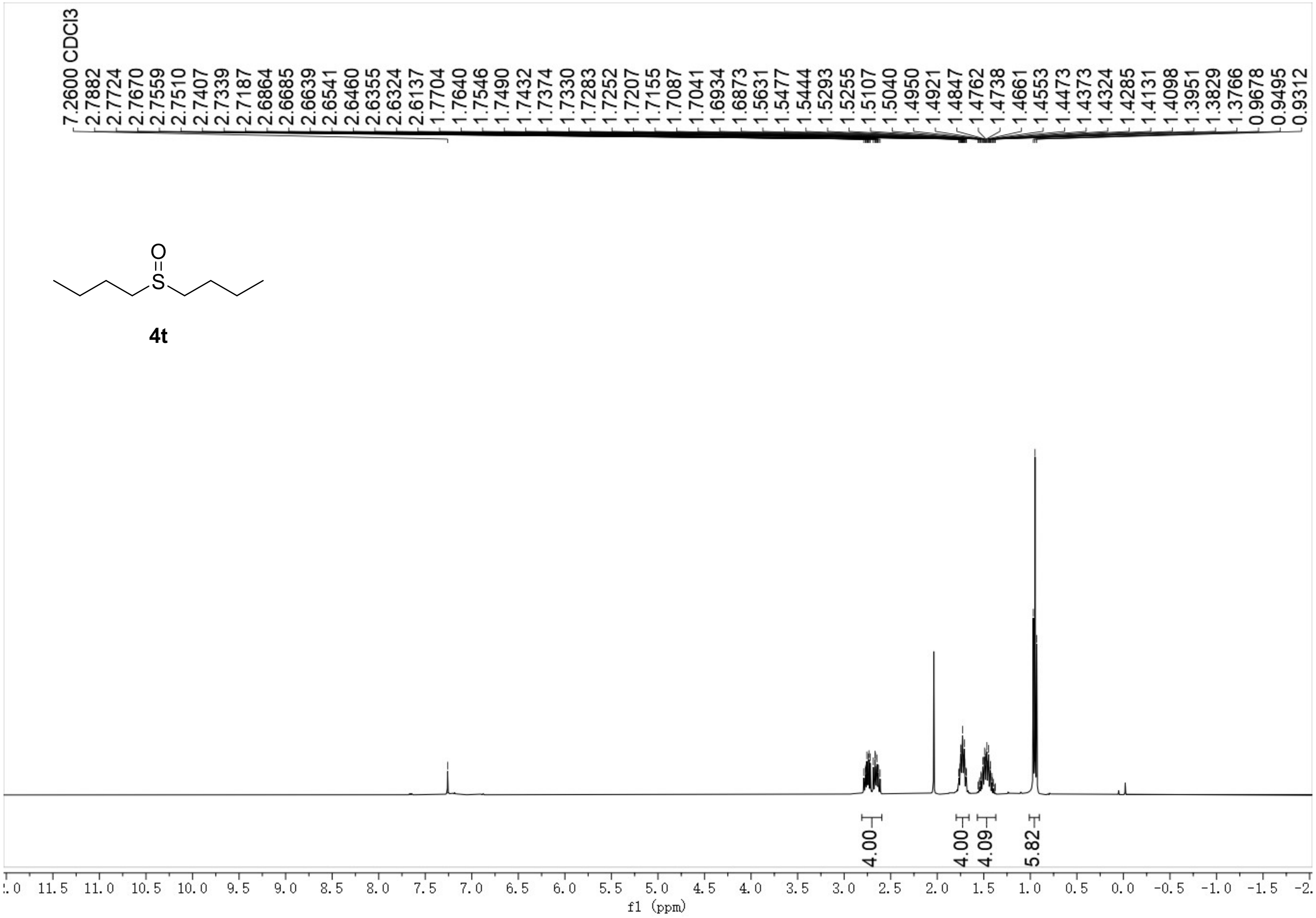


^{1}H NMR (400 MHz, $CDCl_3$)

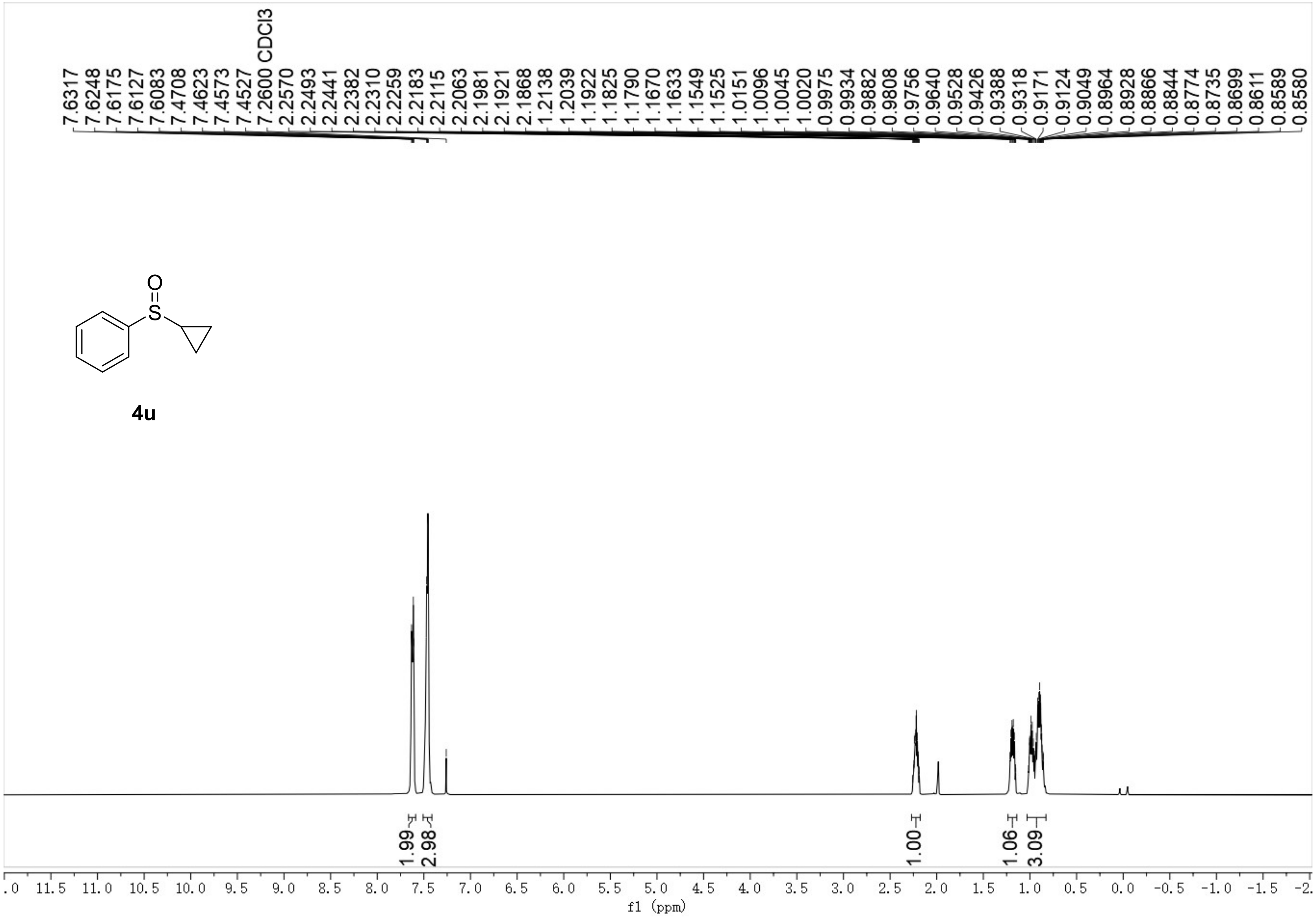


4s

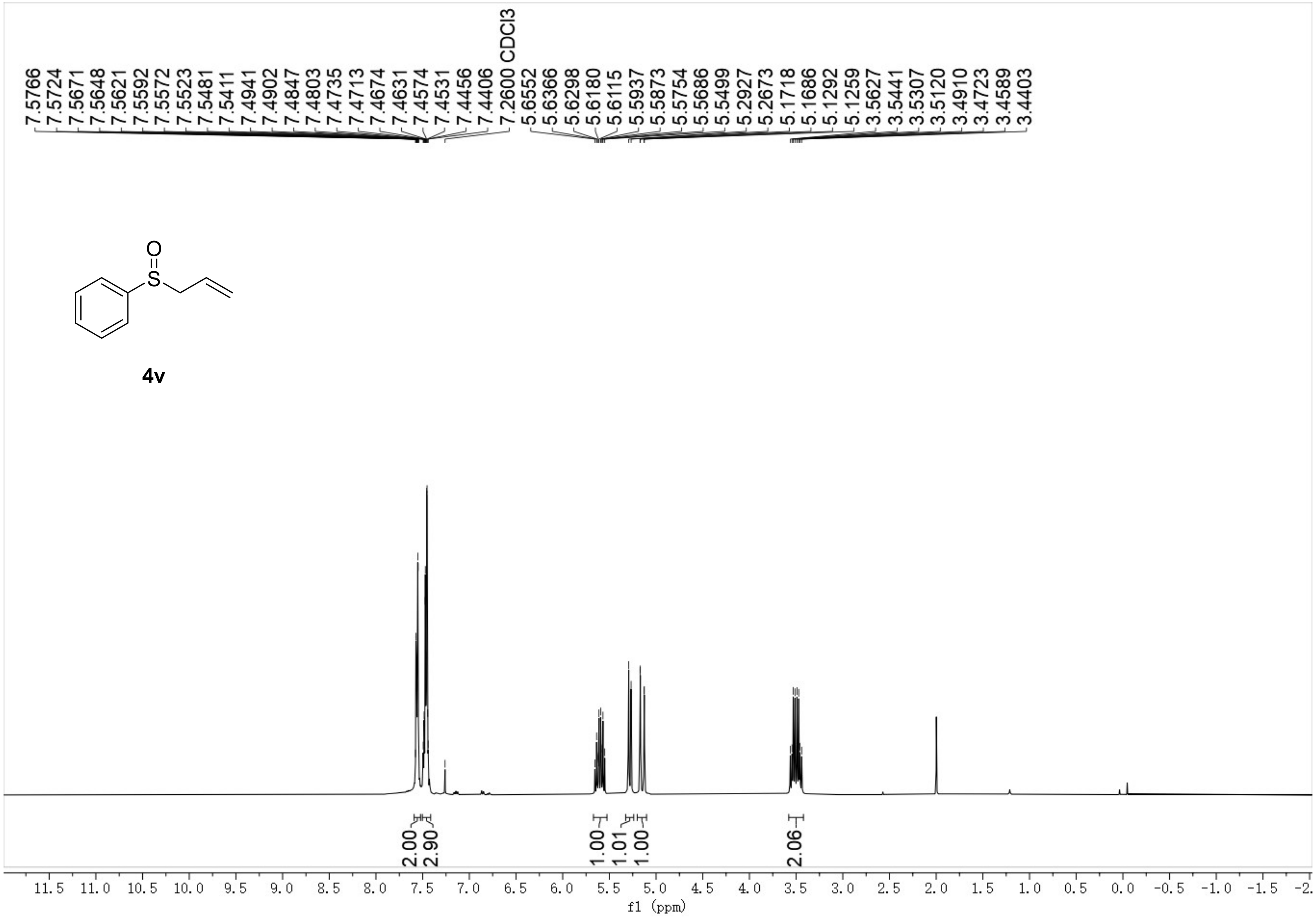
^{1}H NMR (400 MHz, $CDCl_3$)



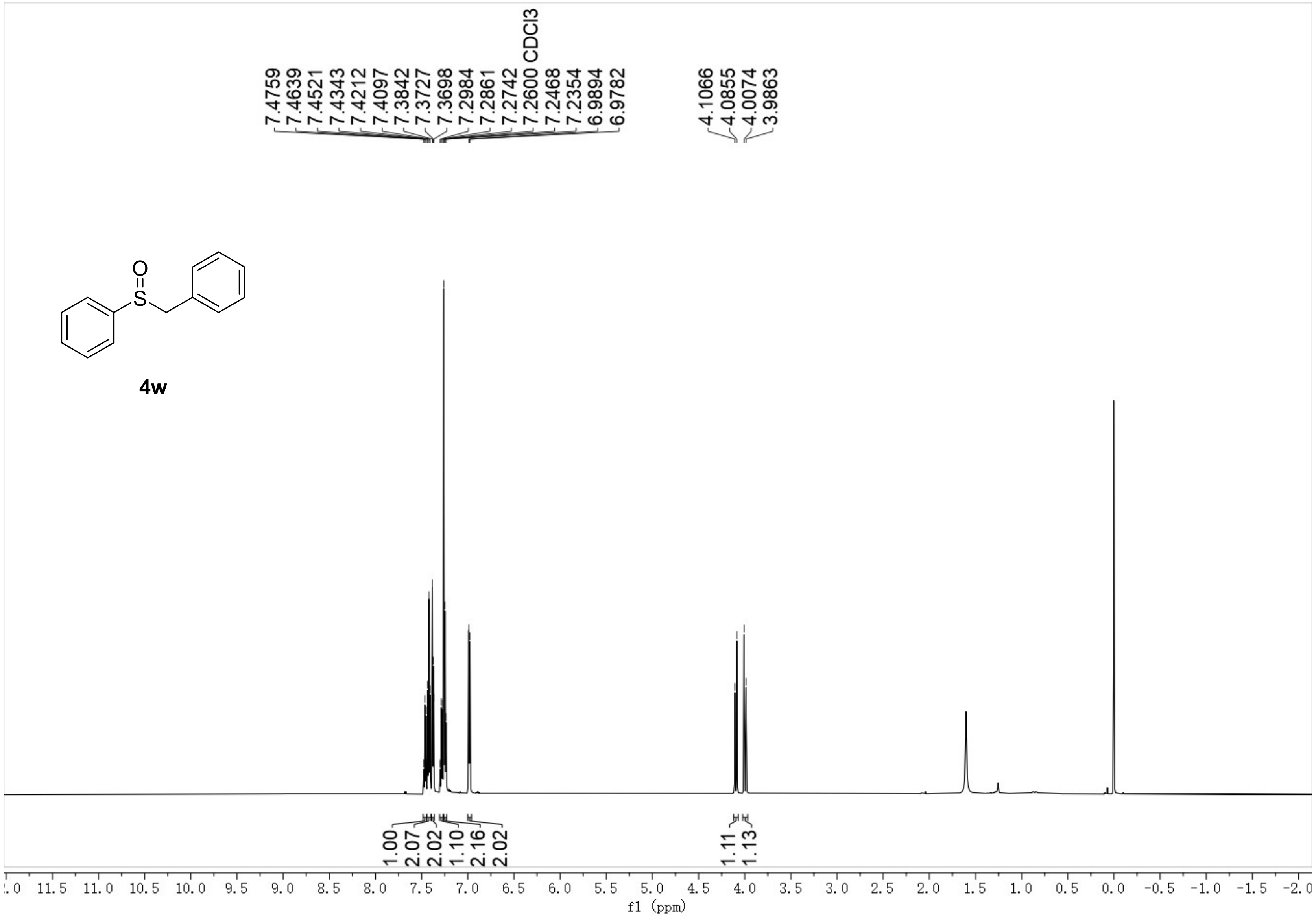
^1H NMR (400 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

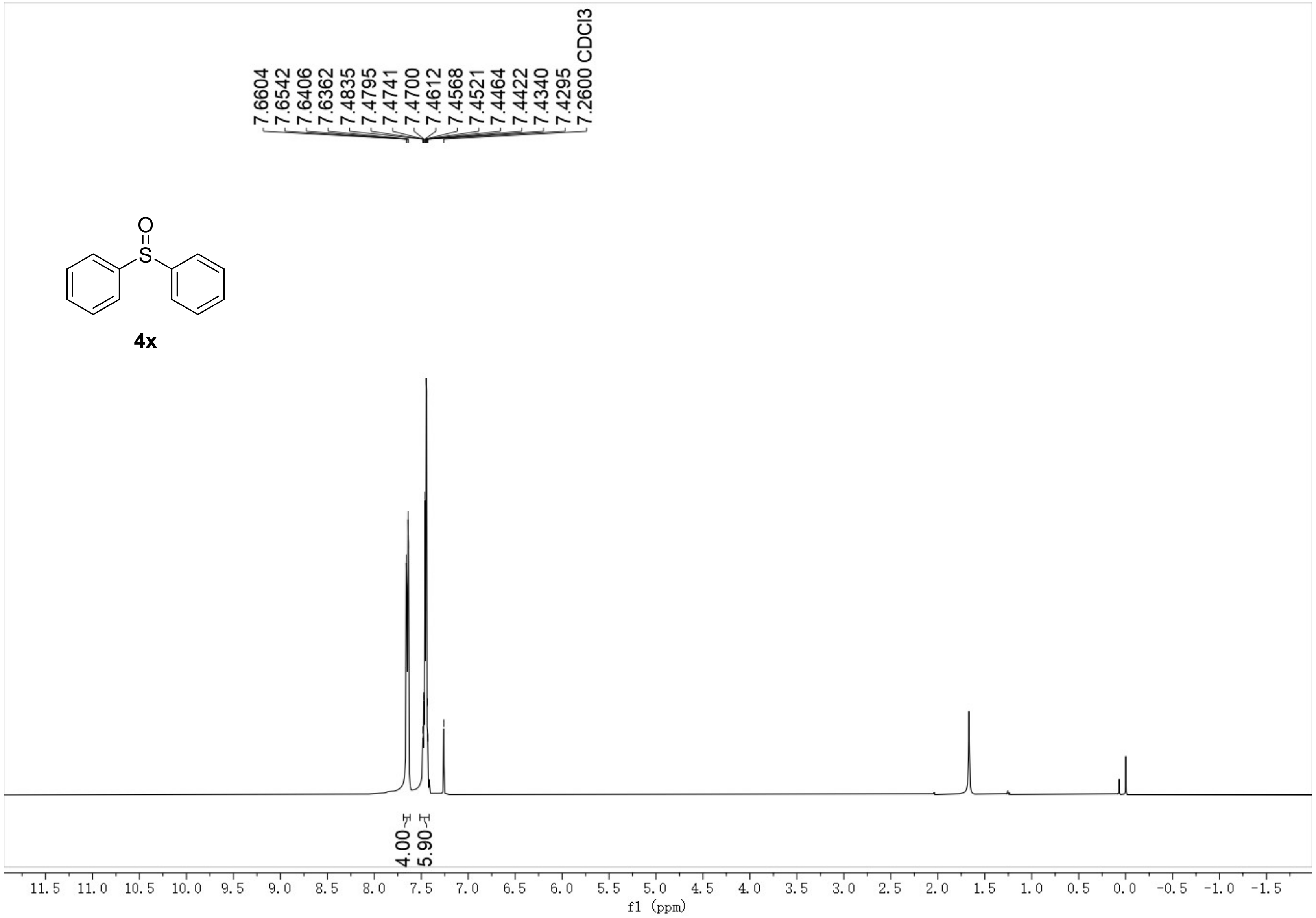


^{1}H NMR (400 MHz, CDCl$_3$)



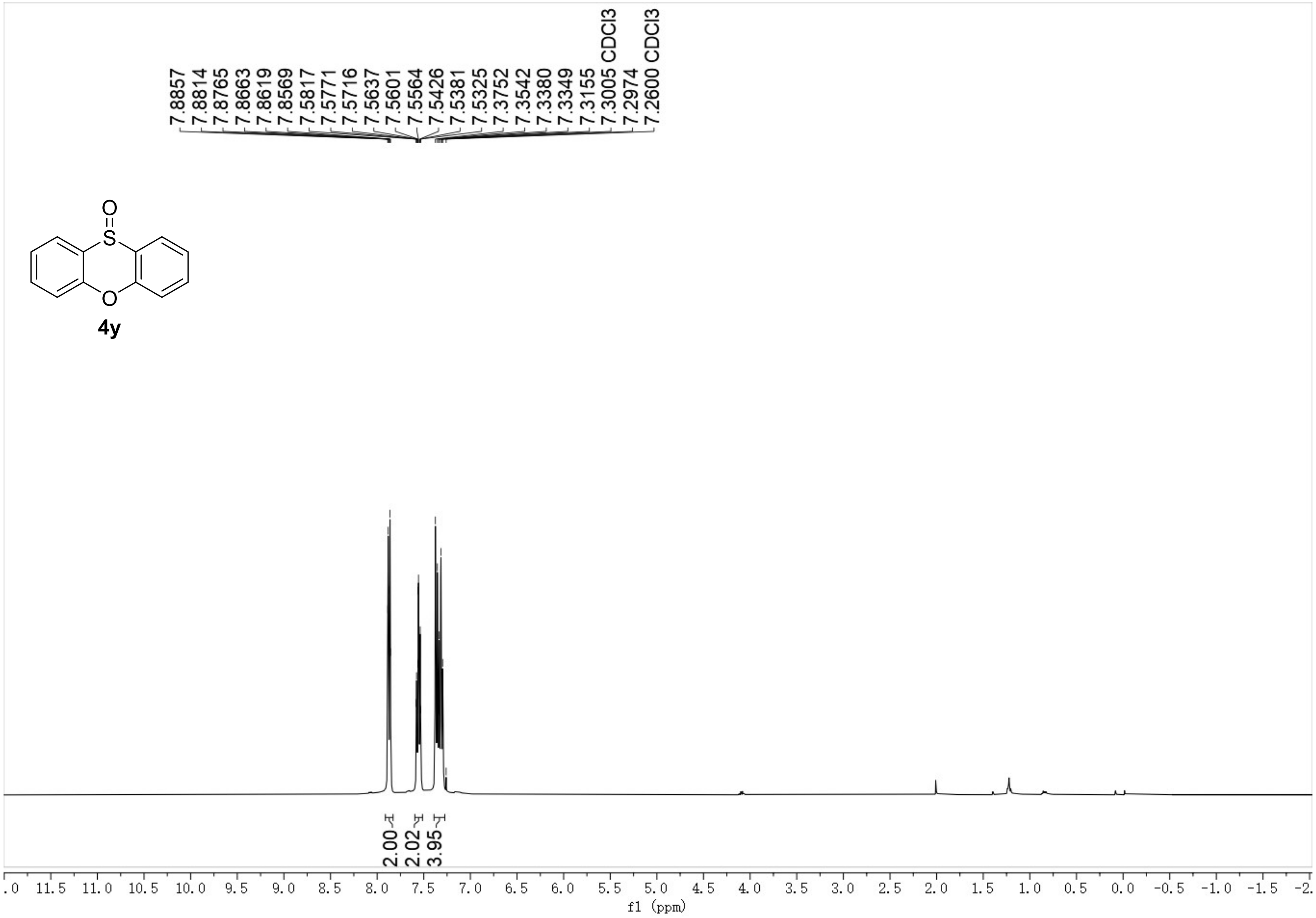
4w

^{1}H NMR (400 MHz, CDCl$_3$)



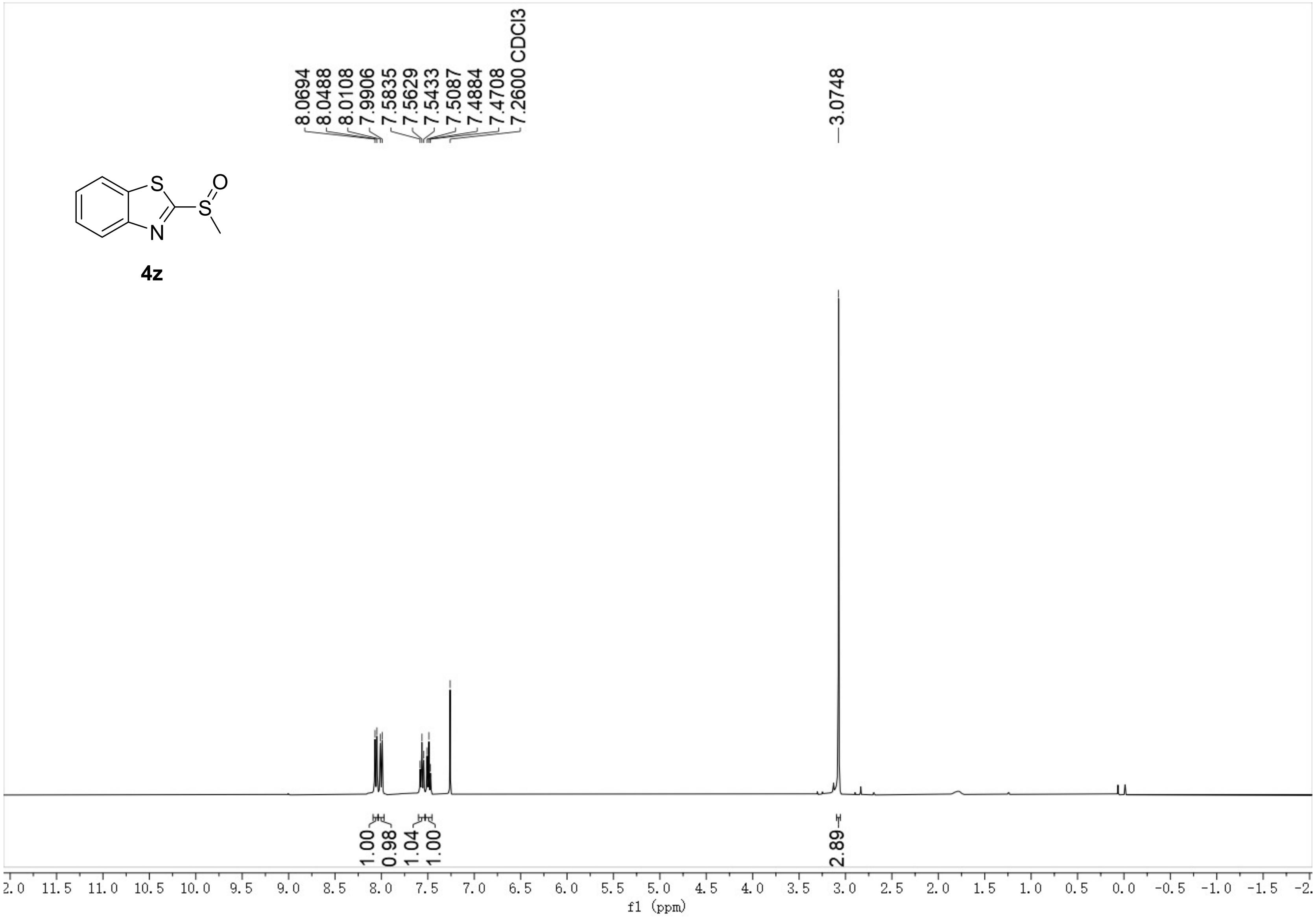
4x

^{1}H NMR (400 MHz, $CDCl_3$)



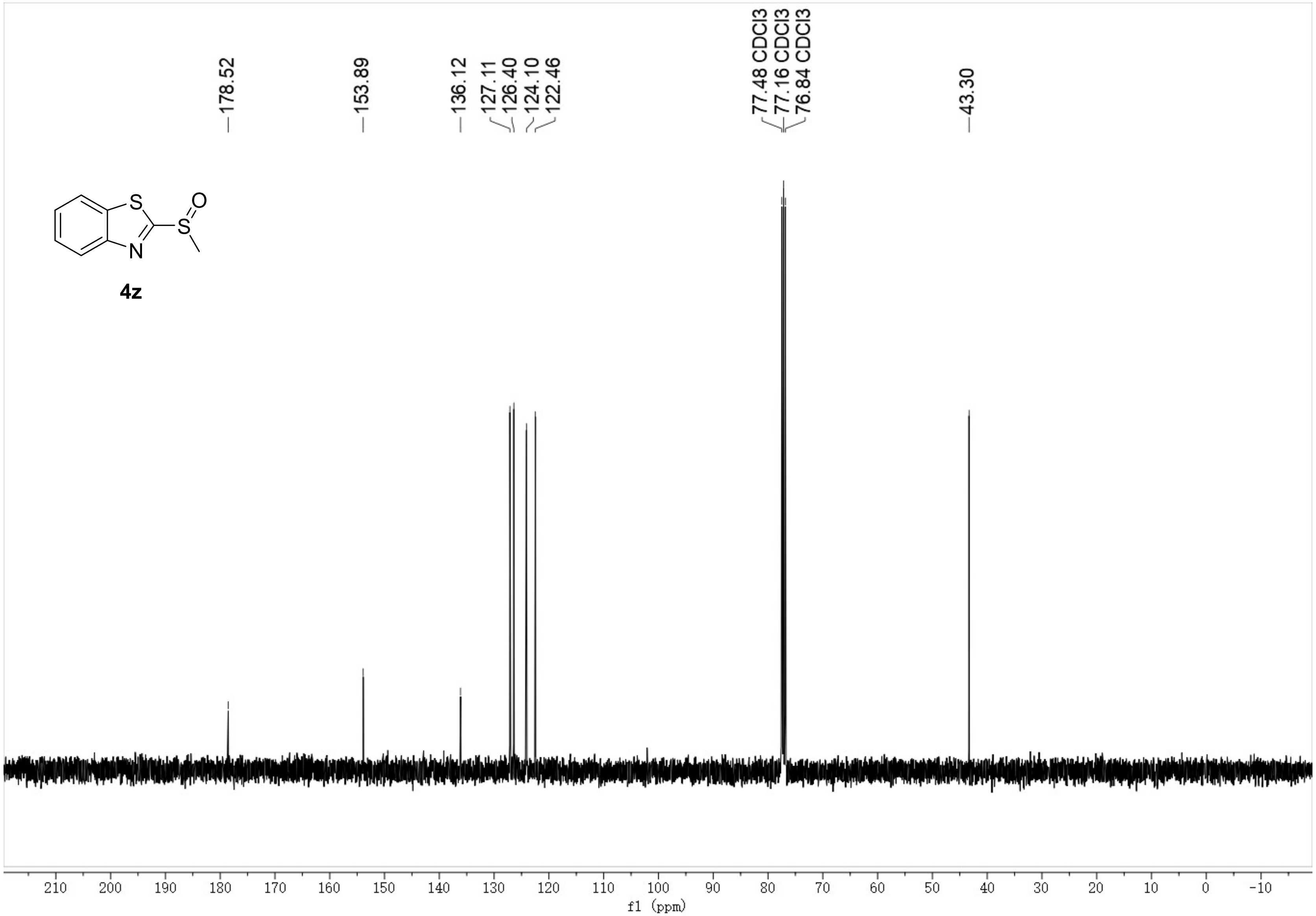
4y

^{1}H NMR (400 MHz, CDCl$_3$)

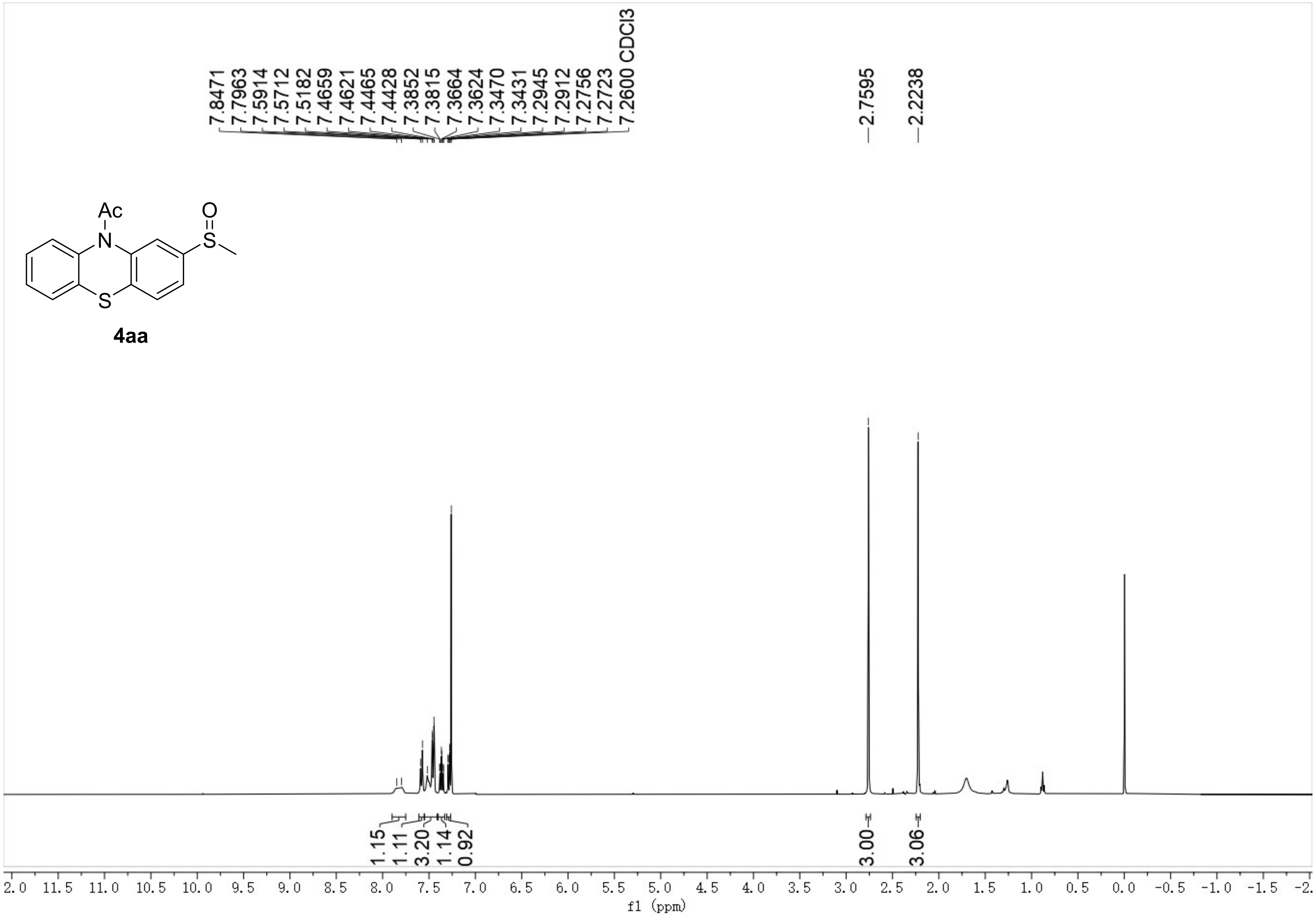


4z

^{13}C NMR (101 MHz, $CDCl_3$)

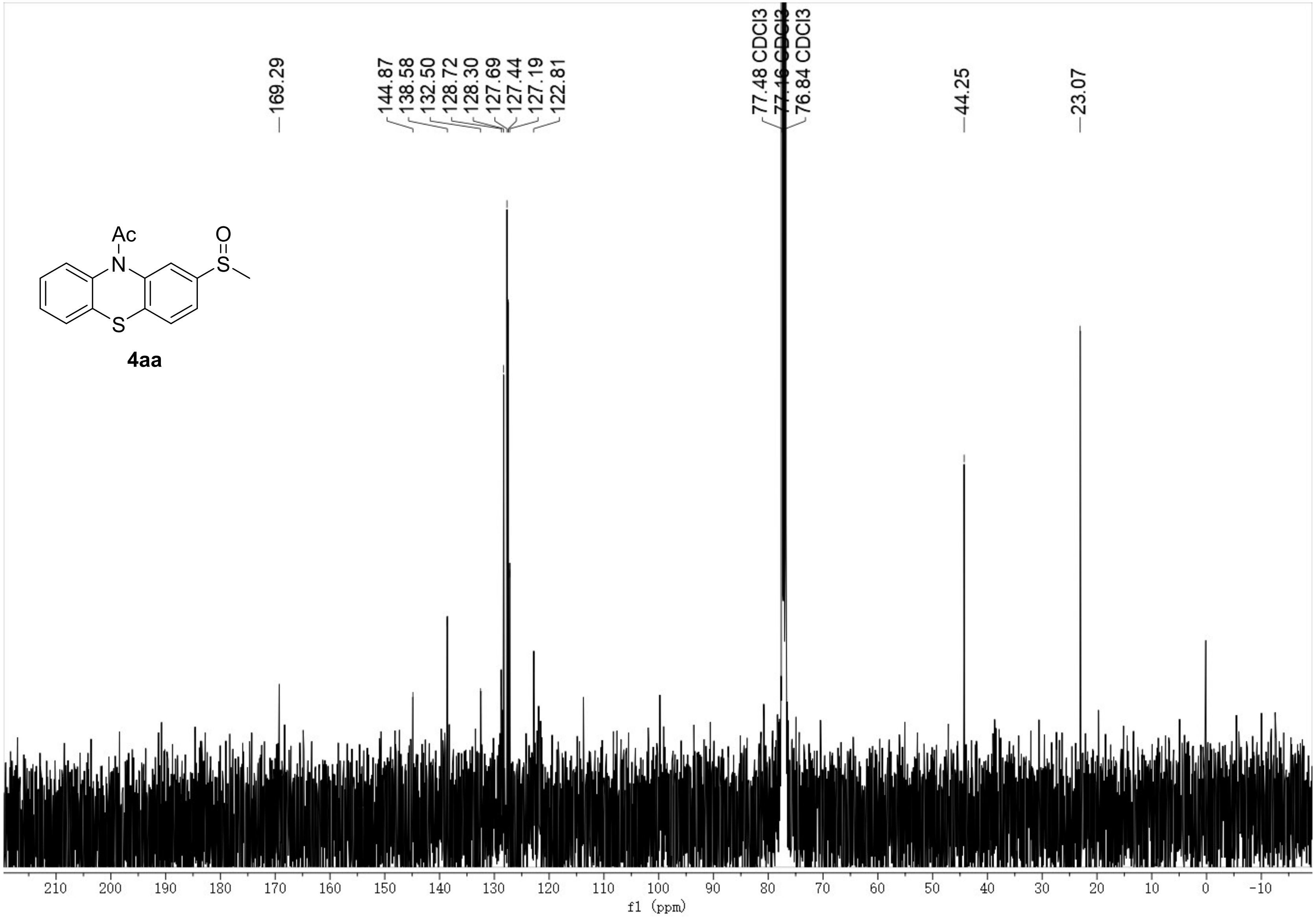


^1H NMR (400 MHz, $CDCl_3$)

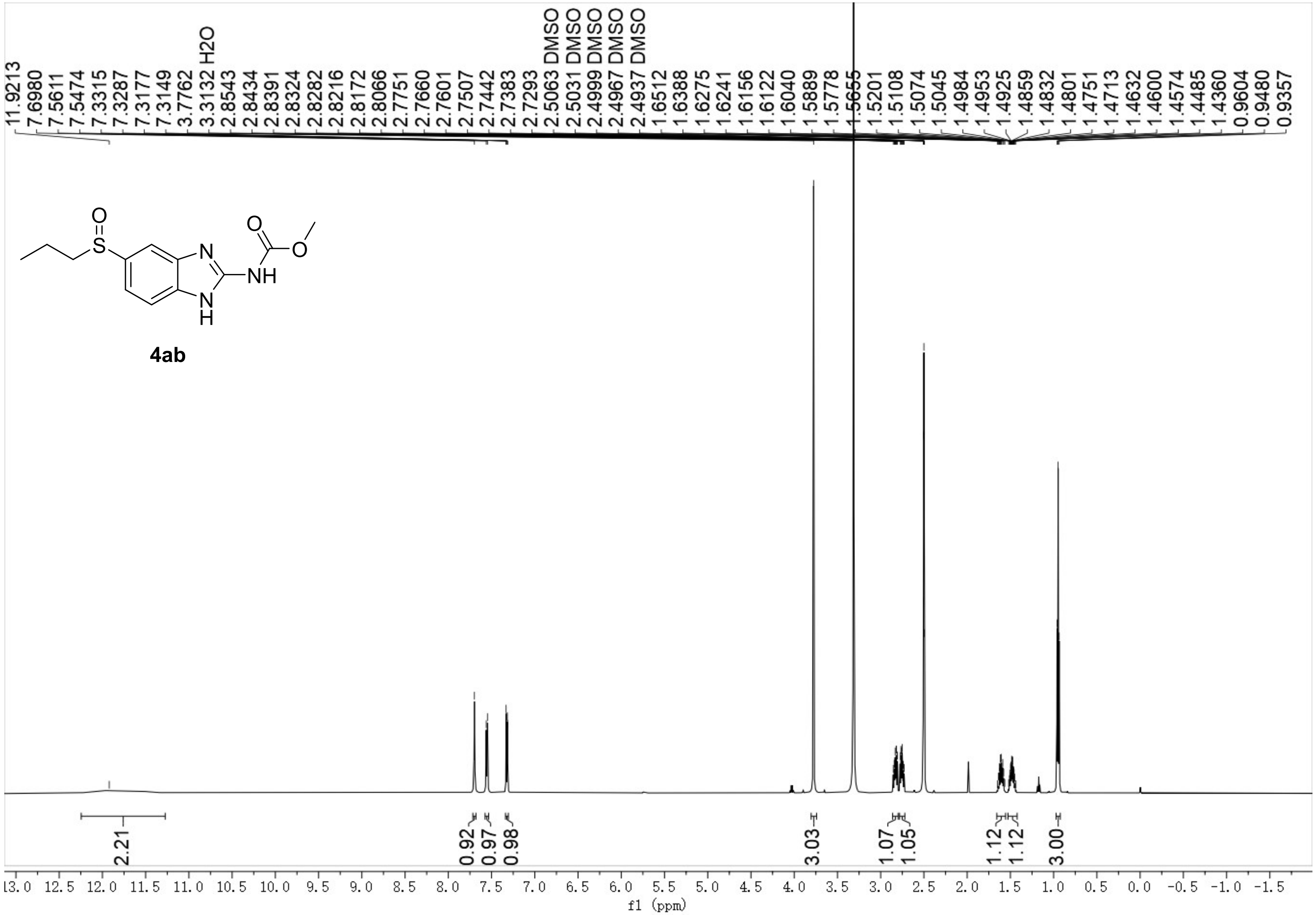

7.8471
7.7963
7.5914
7.5712
7.5182
7.4659
7.4621
7.4465
7.4428
7.3852
7.3815
7.3664
7.3624
7.3470
7.3431
7.2945
7.2912
7.2756
7.2723
7.2600 CDCl3
2.7595
2.2238
Ac
N
O
S
S
1.15
1.11
3.20
1.14
0.92
3.00
3.06
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.
f1 (ppm)

4aa

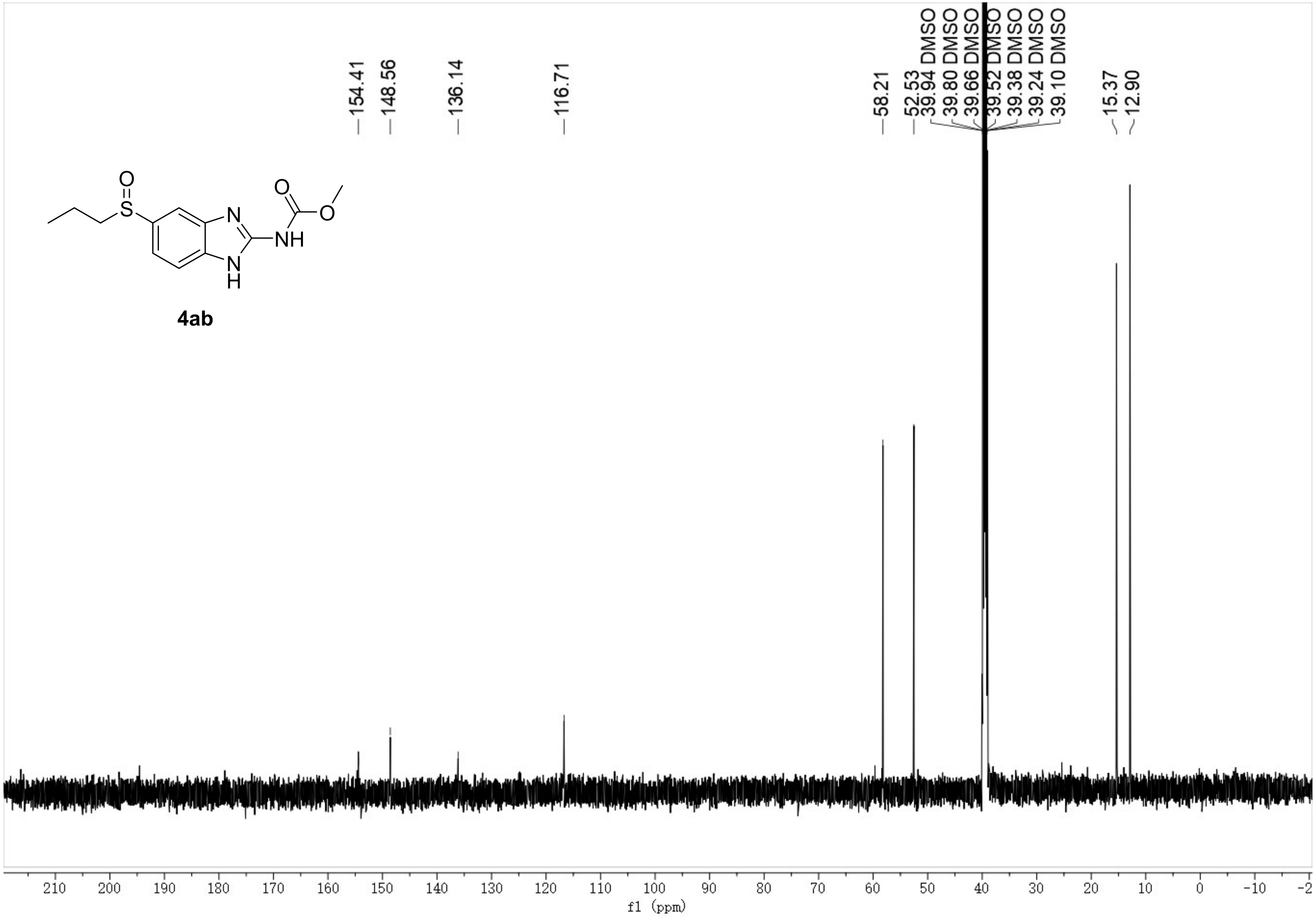
^{13}C NMR (101 MHz, $CDCl_3$)



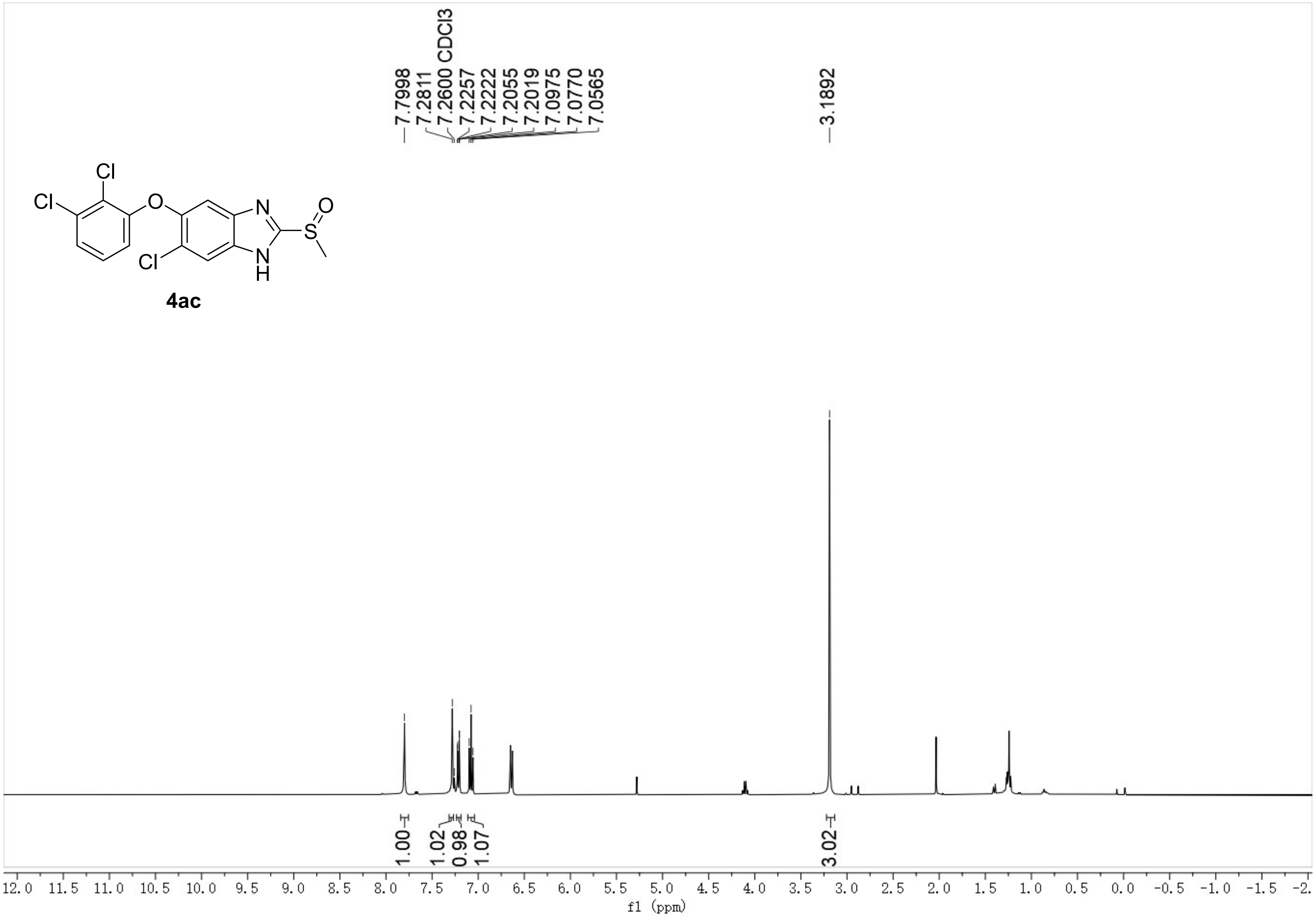
^{1}H NMR (600 MHz, DMSO-d_6)



^{13}C NMR (151 MHz, DMSO-d_6)

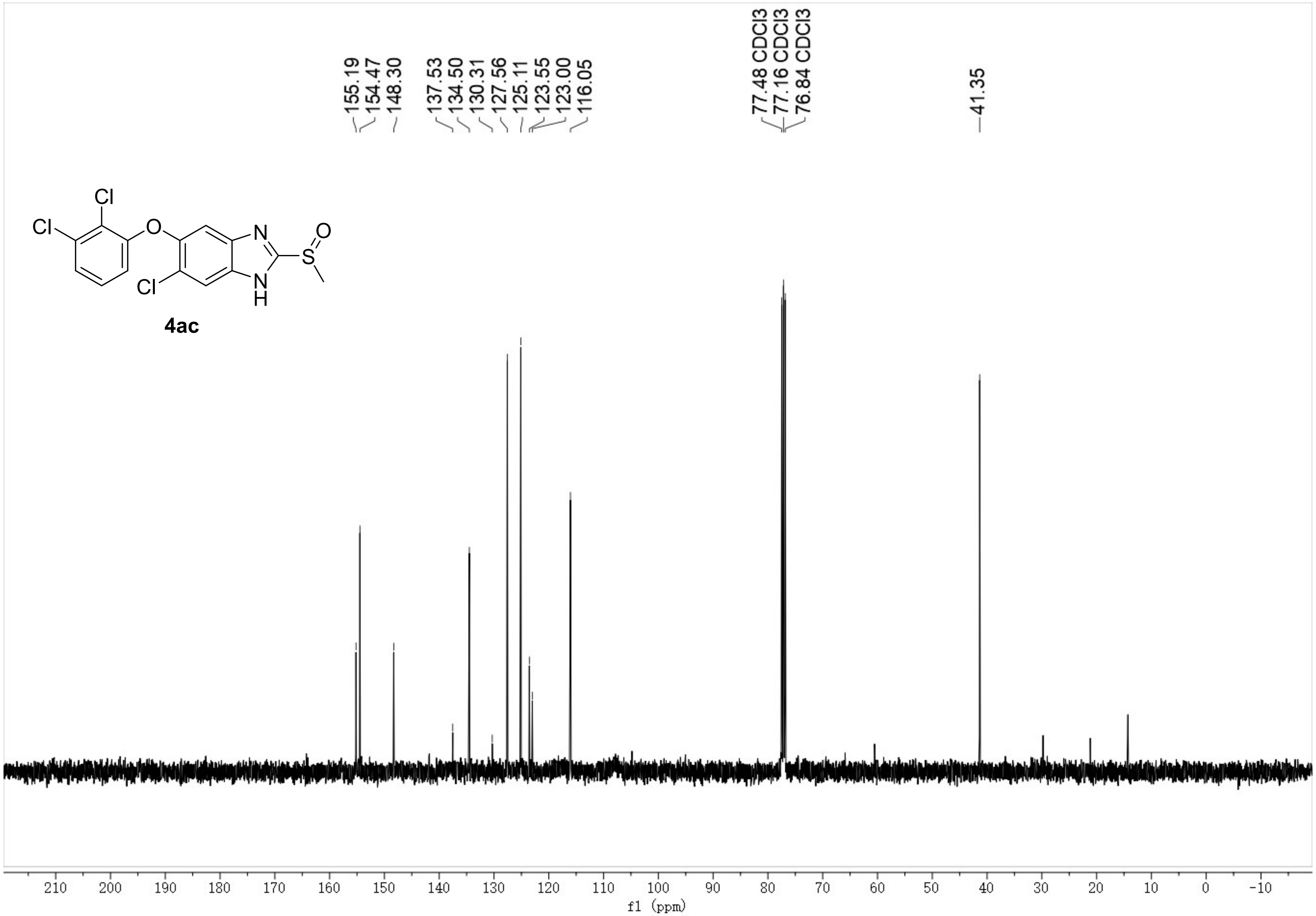


^{1}H NMR (400 MHz, CDCl$_3$)

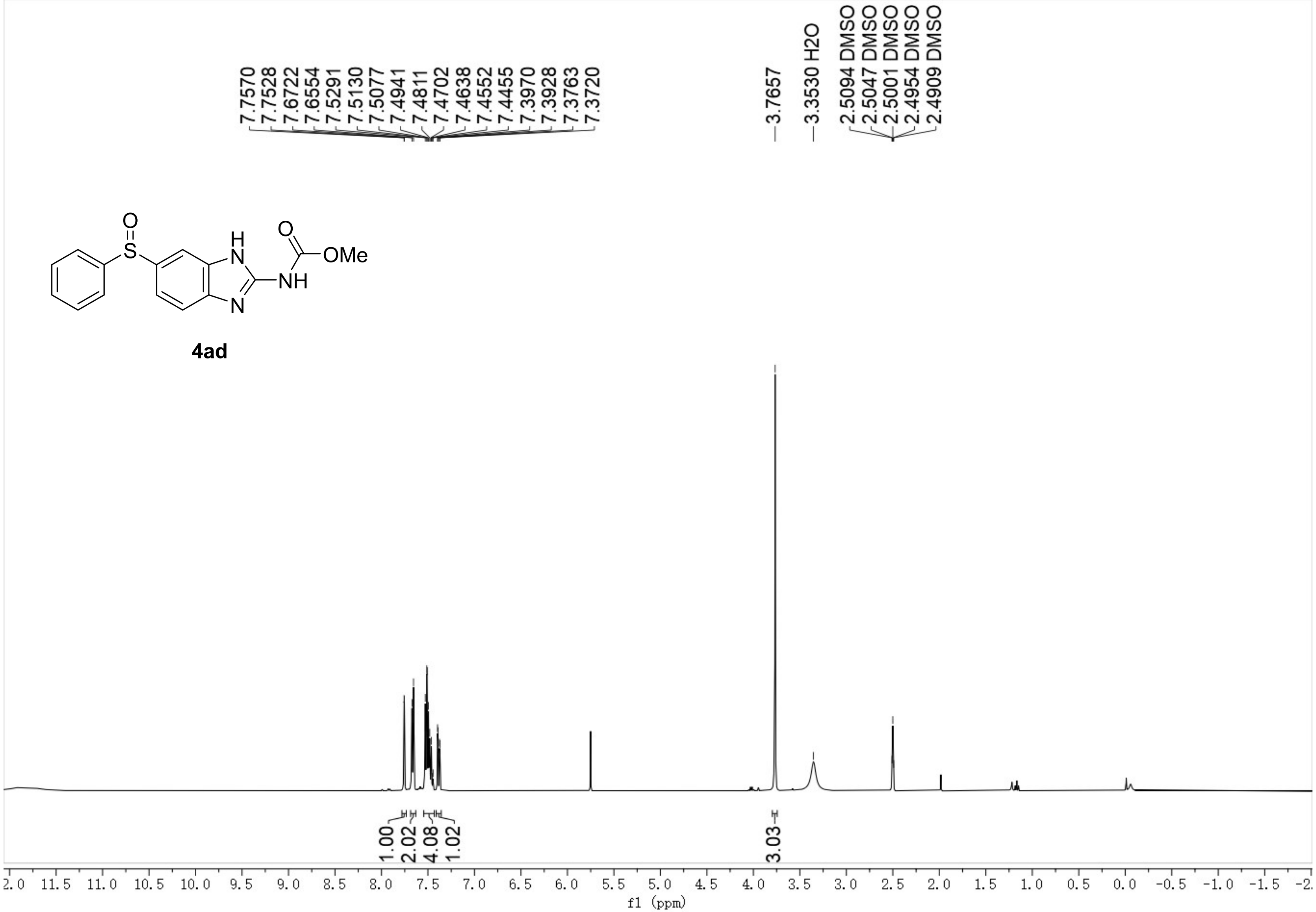


4ac

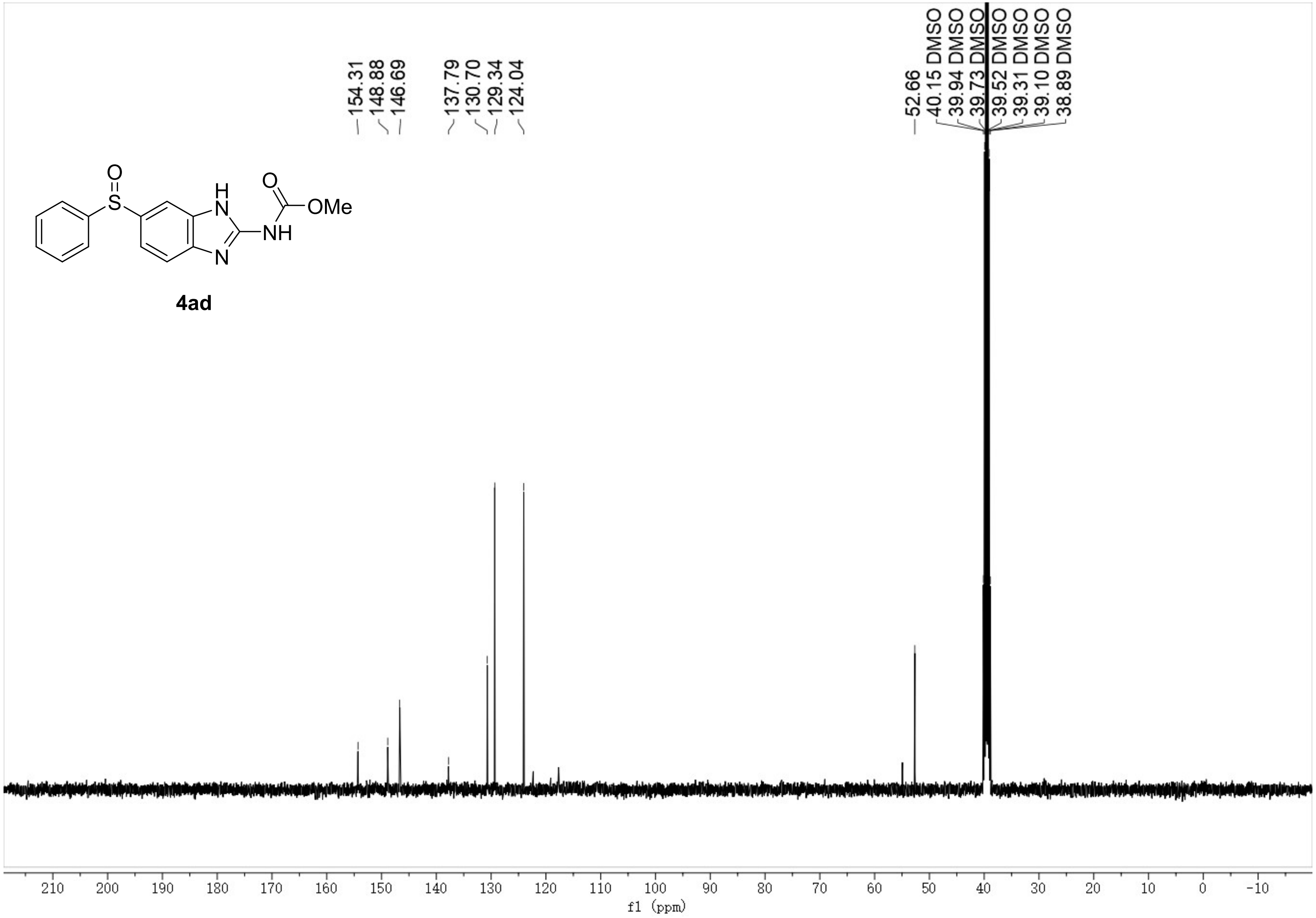
^{13}C NMR (101 MHz, $CDCl_3$)

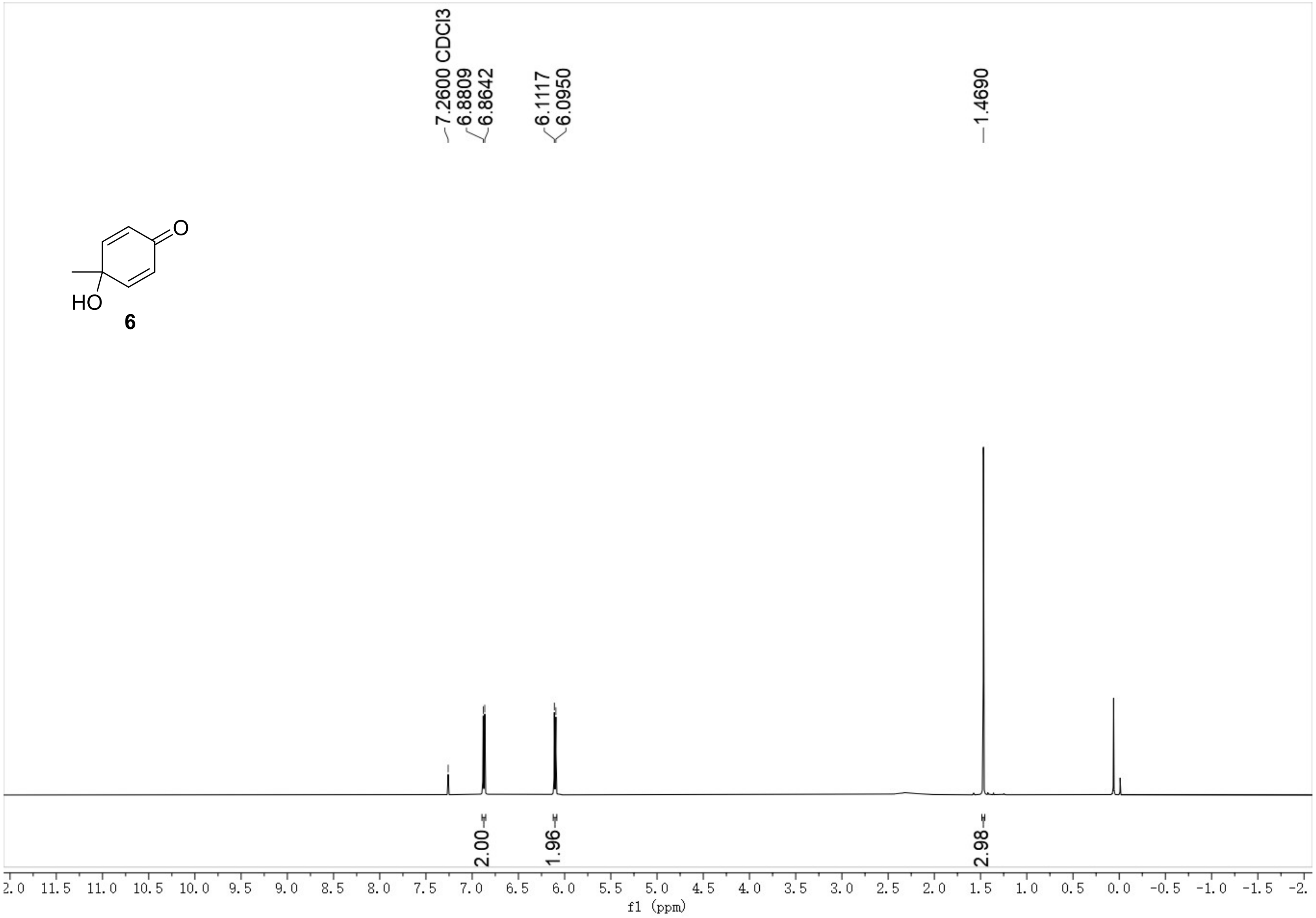


^{1}H NMR (400 MHz, DMSO-d_6)



^{13}C NMR (101 MHz, DMSO-d_6)



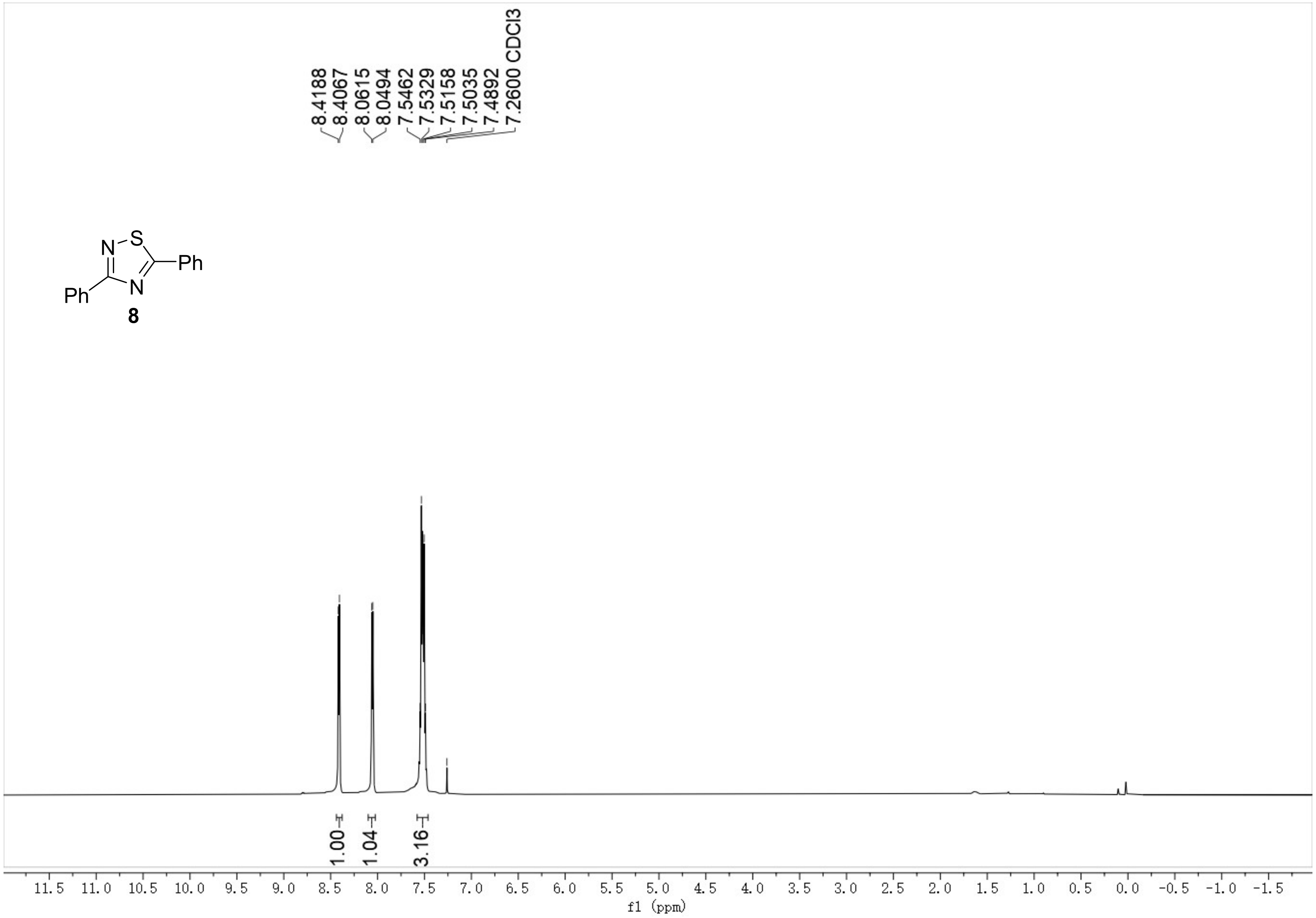


6

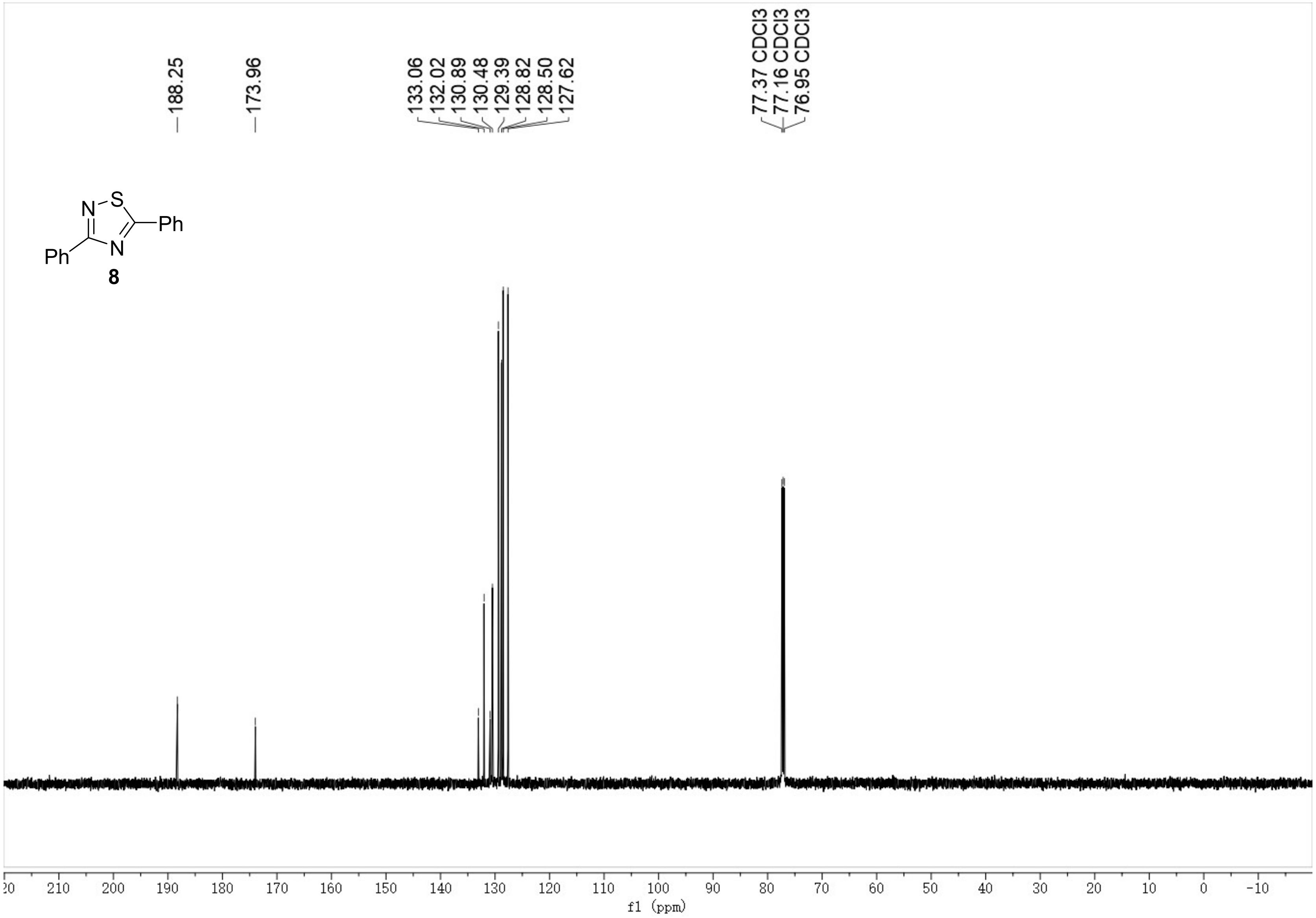
1H NMR (600 MHz, CDCl3)
7.2600 CDCl3
6.8809
6.8642
6.1117
6.0950
1.4690
2.00
1.96
2.98
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.
f1 (ppm)

^{1}H NMR (600 MHz, $CDCl_3$)

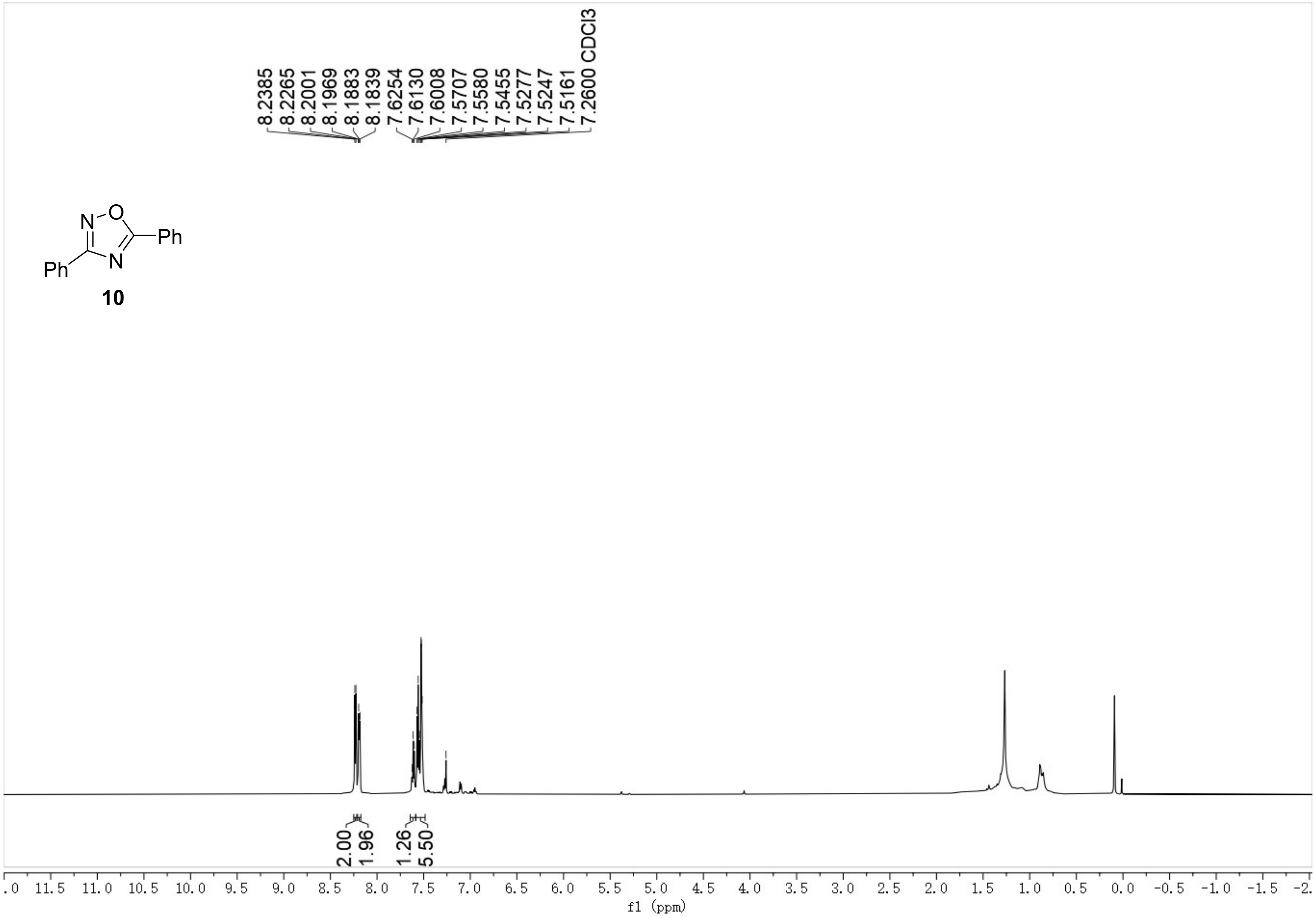
8



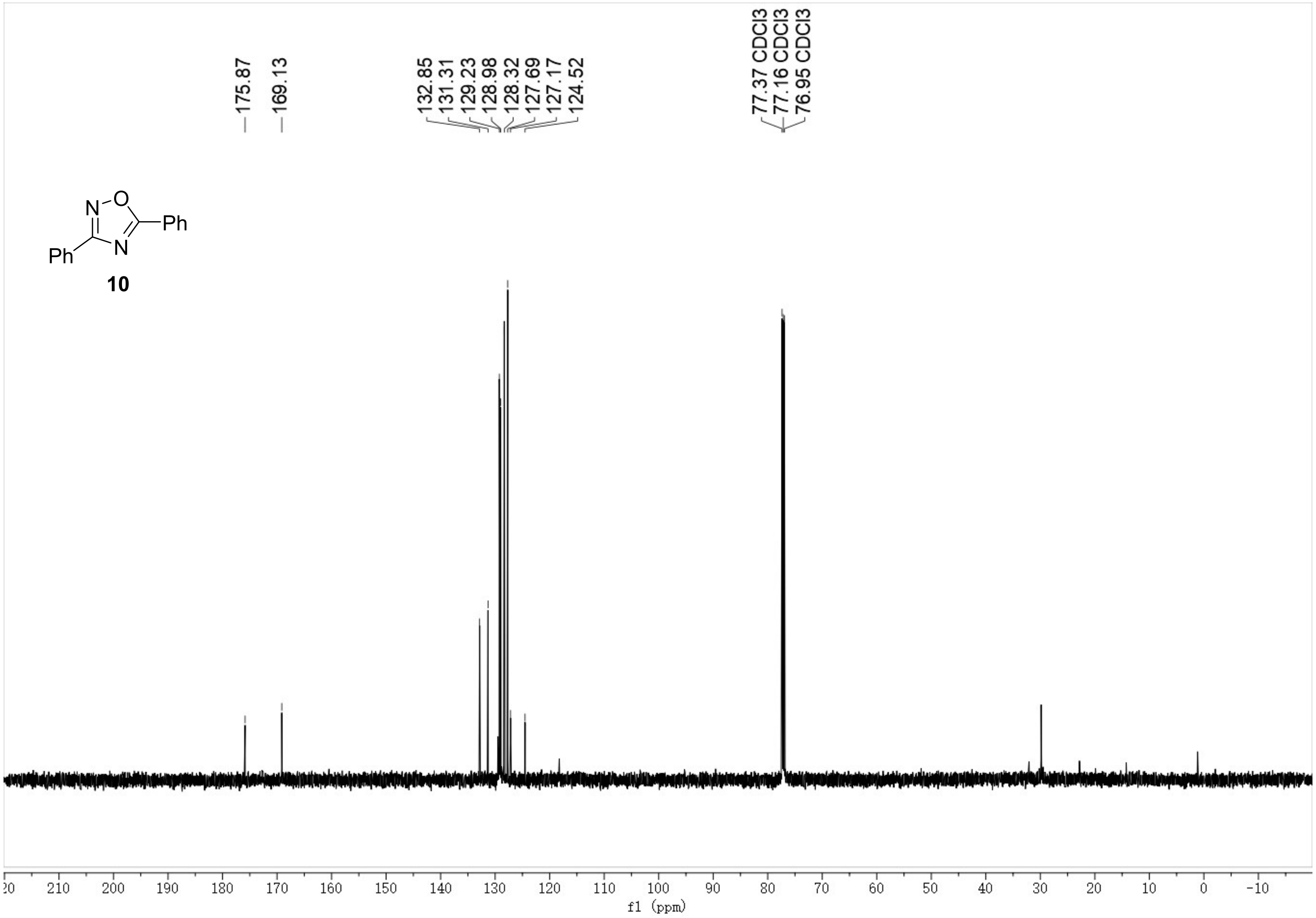
^{13}C NMR (151 MHz, $CDCl_3$)



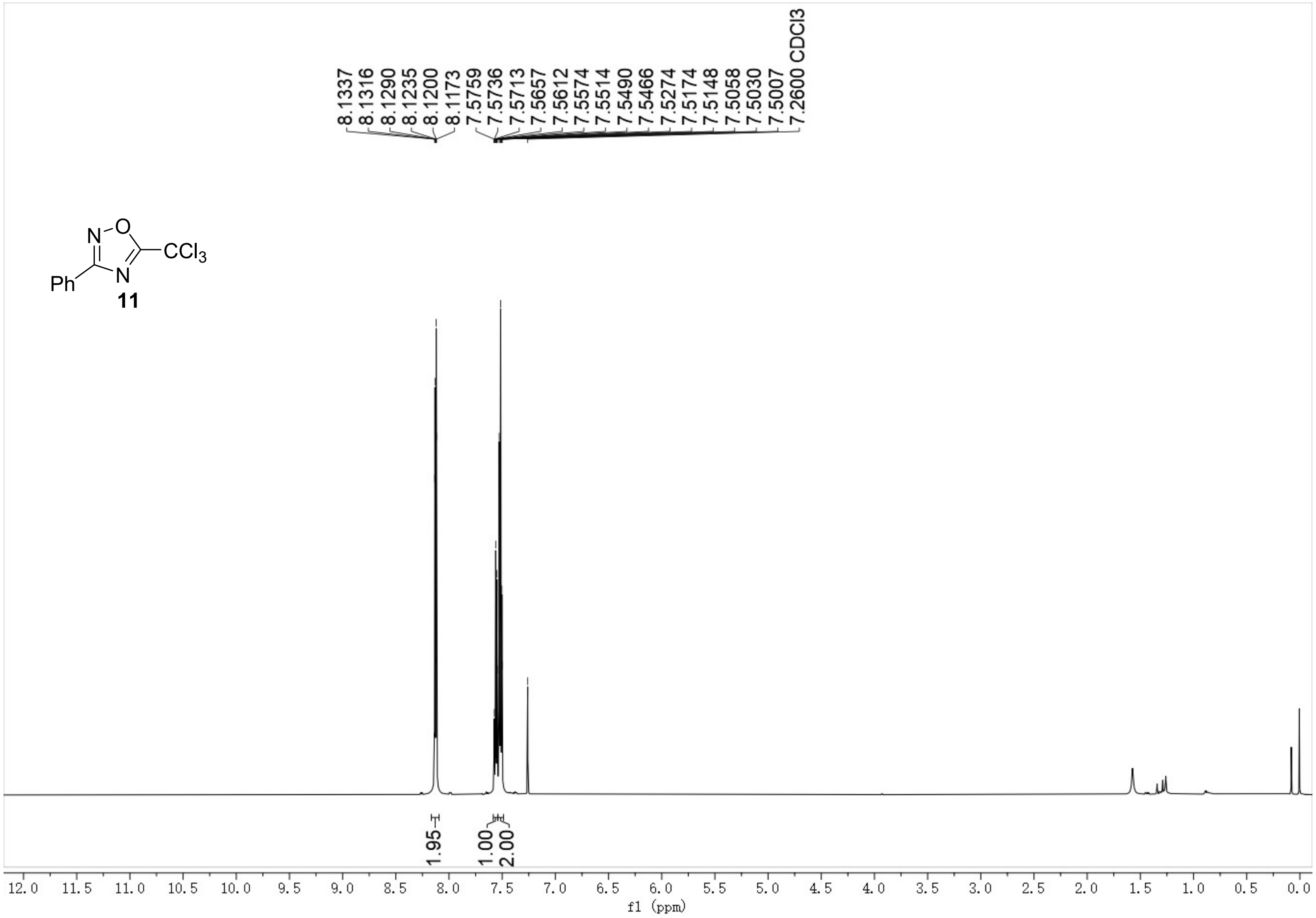
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



¹H NMR (600 MHz, $CDCl_3$)



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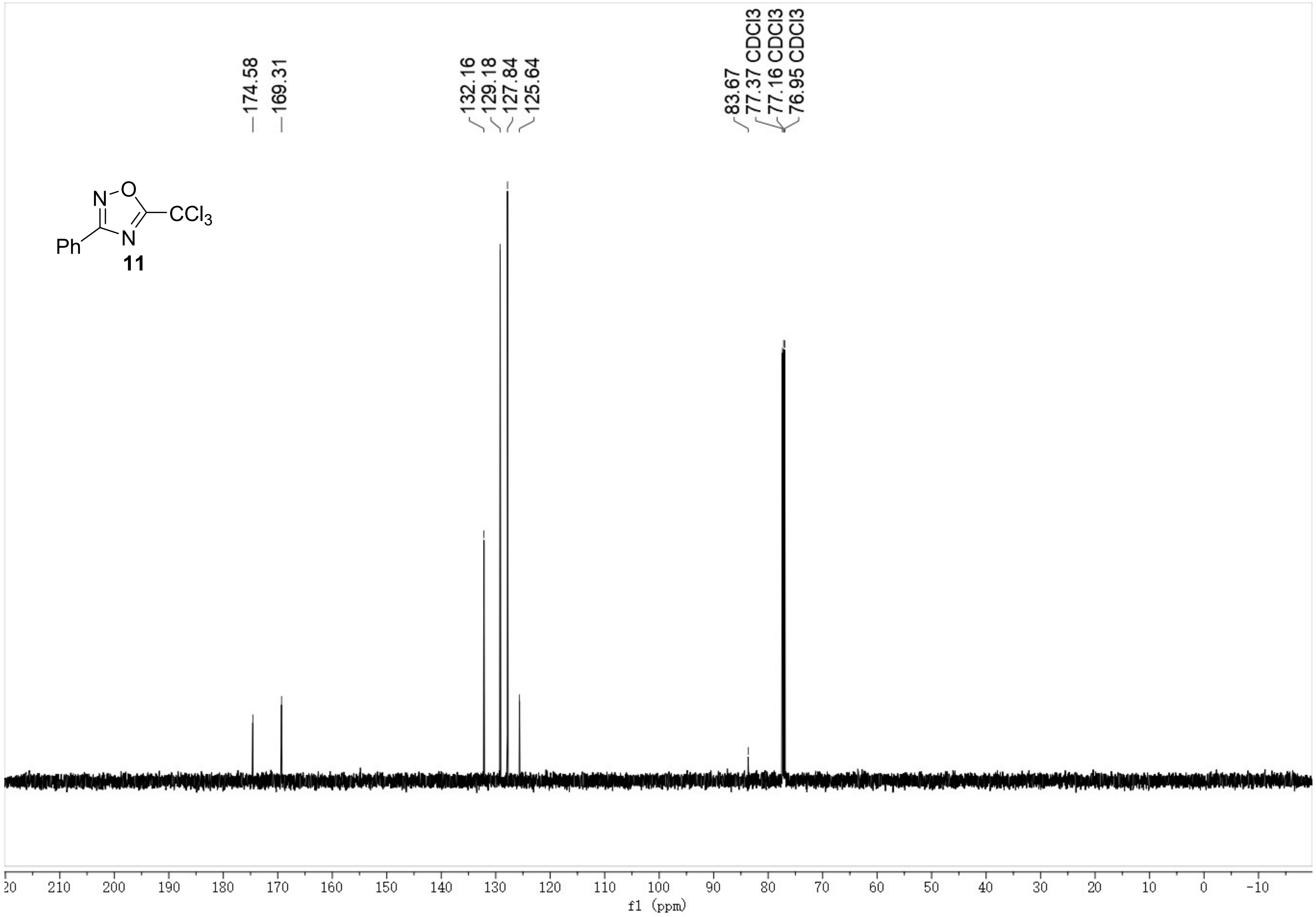
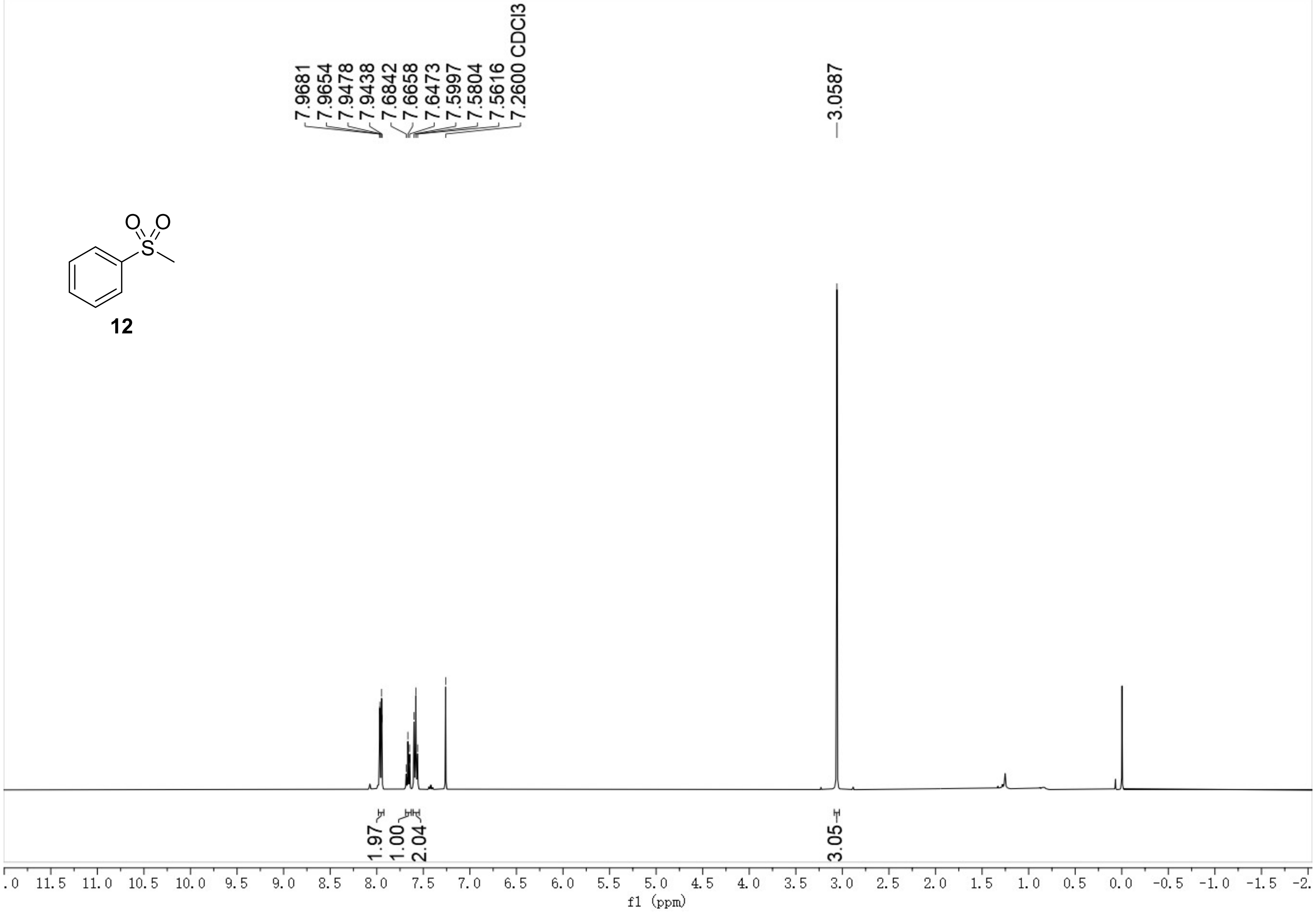
^{13}C NMR (151 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^1H NMR (400 MHz, $CDCl_3$)