Supporting Information

Green and efficient synthesis of pure β-sulfonyl aliphatic sulfonyl fluorides through a simple filtration in aqueous media

Kang Feng,[a] Jian-Bai Wang,[a,b] Wei-Dong Zhang[a] and Hua-Li Qin*[a]

[a]*School of Chemistry, Chemical Engineering and Life Science, Wuhan University of Technology, 205 Luoshi Road, Wuhan 430070, China.*

[b]*Changyi Tianyu Pharm. Co., Ltd., Weifang 261399, China.*

**Corresponding author: Hua-Li Qin*

E-mail: qinhuali@whut.edu.cn

Table of Contents

1.General Information

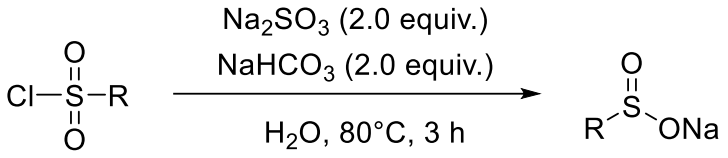
All reactions were carried out under an air atmosphere. Reagents used in the reactions were all purchased from commercial sources and used without further purification. Unless otherwise specified, NMR spectra were recorded in DMSO-d_6 or $CDCl_3$ on a 500 MHz (for ^1H), 126 MHz (for ^{13}C) and 471 MHz (for ^{19}F) spectrometer. All chemical shifts were reported in ppm relative to TMS (^1H NMR, 0 ppm) as internal standards. The HPLC experiments were carried out on a Waters e2695 instrument (column: J&K, RP-C18, 5 μm, 4.6 × 150 mm), and the yields of the products were determined by using the corresponding pure compounds as the external standards. Melting points of the products were measured on a micro melting point apparatus (SGW X-4) and uncorrected. HRMS experiments were performed on a TOF-Q ESI or CI/EI instrument. The coupling constants were reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

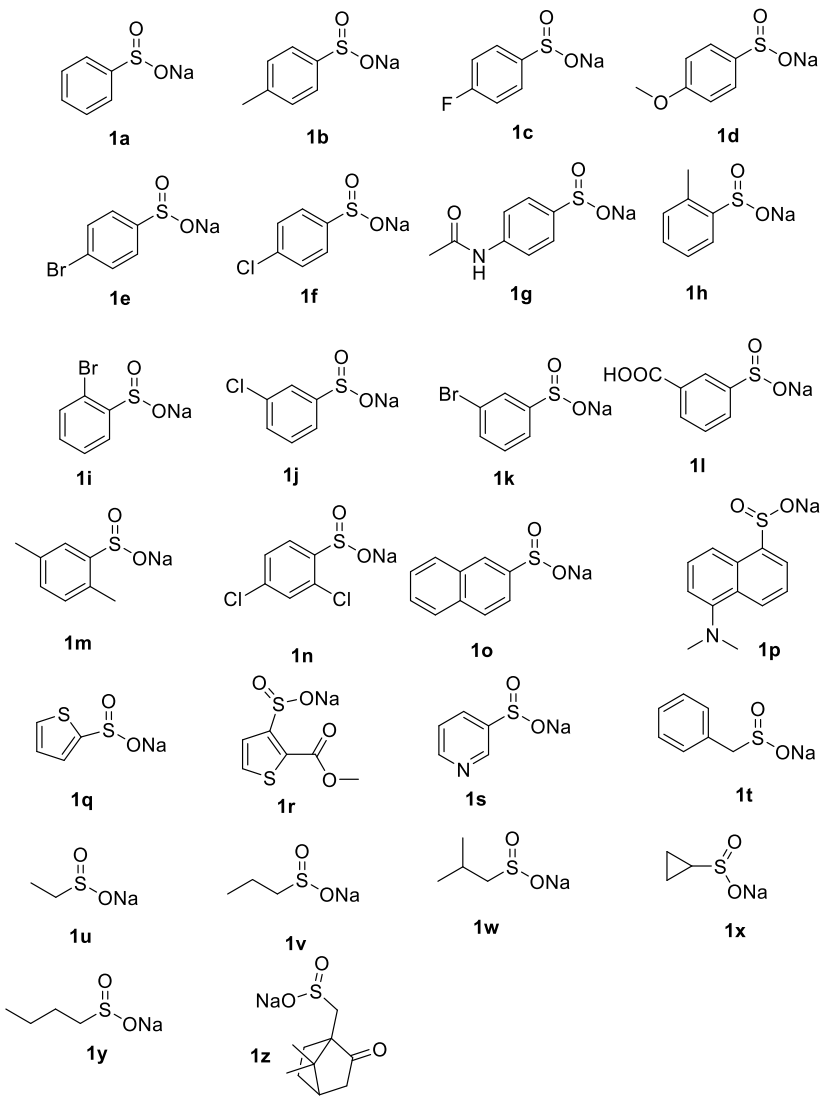
2. Raw material preparation

2.1 The ethene sulfonyl fluoride (ESF) were prepared according to literature[1].

2.2 General procedure for the preparation of sodium sulfinates[2].

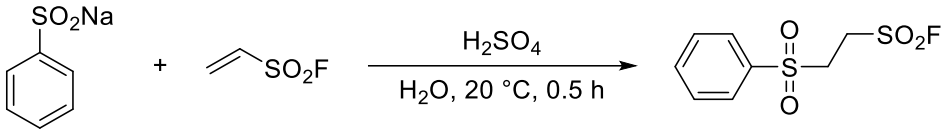
Sulfonyl chloride (5.0 mmol) was added to a solution of sodium sulfites (10.0 mmol) and sodium bicarbonate (840 mg, 10.0 mmol) in water (5 mL, 1 M). The mixture was heated at 80 °C for 3 h. After cooling to room temperature, the volatiles were removed in vacuo. The obtained solid were repeatedly washed with ethanol. The combined ethanol washes were evaporated under reduced pressure to yield the titled sulfinates as an amorphous solid.





3. Screening the optimized reaction conditions

3.1 Screening the equivalent of ESF [a]

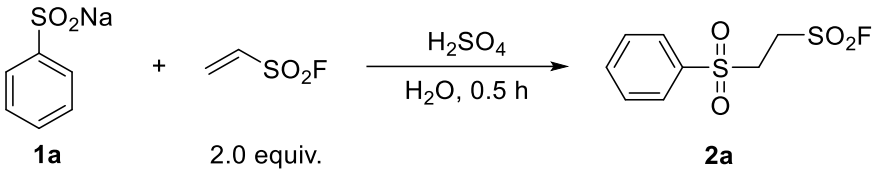


1a **2a**

Entry	**1a :ESF**	Yield (%)[b]
1	1:1	73.5
2	**1:2**	**83.2**
3	1:3	83.4

[a] Reaction conditions: a mixture of sodium benzene sulfinate (**1a**, 0.2 mmol), ethene sulfonyl fluoride and sulfuric acid (1.0 equiv.) in water (1 mL) was stirred for 0.5 h at 20 ℃. [b] HPLC yield ($t_{R,\mathbf{2a}}$ = 3.319 min, λmax, $_{\mathbf{2a}}$ = 218.1 nm; acetonitrile/water = 80: 20 (v/v)).

3.2 Screening the temperature[a]

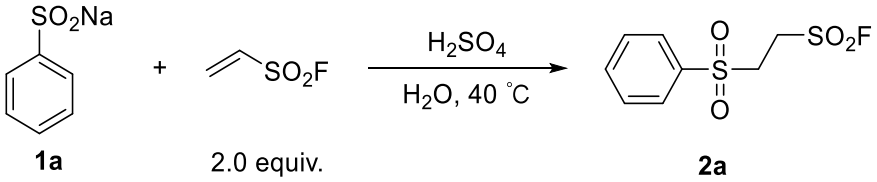


1a 2.0 equiv. **2a**

Entry	Temperature	Yield (%)[b]
1	20 ℃	83.2
2	**40 ℃**	**87.7**
3	60 ℃	75.5

[a] Reaction conditions: a mixture of sodium benzene sulfinate (**1a**, 0.2 mmol), ethene sulfonyl fluoride (2.0 equiv.) and sulfuric acid (1.0 equiv.) in water (1 mL) was stirred for 0.5 h at the corresponding temperature. [b] HPLC yield ($t_{R,\mathbf{2a}}$ = 3.319 min, λmax, $_{\mathbf{2a}}$ = 218.1 nm; acetonitrile/water = 80: 20 (v/v)).

3.3 Screening the reaction time[a]

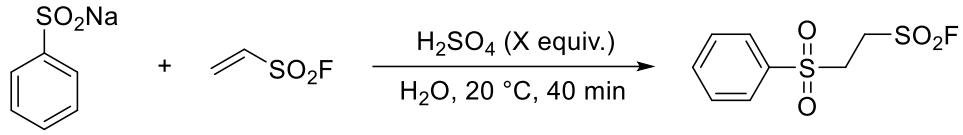


1a 2.0 equiv. **2a**

Entry	Time	Yield (%)[b]
1	20 min	69.6
2	30 min	87.7
3	**40 min**	**93.1**
4	1 h	88.3
5	3 h	89.3

[a] Reaction conditions: a mixture of sodium benzene sulfinate (**1a**, 0.2 mmol), ethene sulfonyl fluoride (2.0 equiv.) and sulfuric acid (1.0 equiv.) in water (1 mL) was stirred for the corresponding time at 40 ℃. [b] HPLC yield ($t_{R,\mathbf{2a}}$ = 3.319 min, λmax, $_{\mathbf{2a}}$ = 218.1 nm; acetonitrile/water = 80: 20 (v/v)).

3.4 Screening the equivalent of sulfuric acid [a]

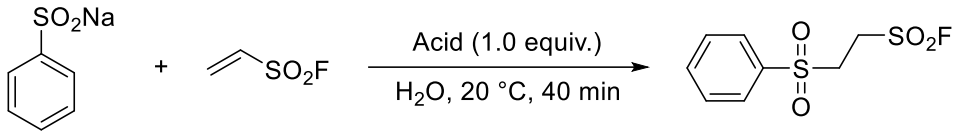


1a **2a**

Entry	H_2SO_4 (X equiv.)	Yield (%)[b]
1	0	30.0
2	**1**	**93.1**
3	2	83.4

[a] Reaction conditions: a mixture of sodium benzene sulfinate (**1a**, 0.2 mmol), ethene sulfonyl fluoride (2.0 equiv.) and sulfuric acid (X equiv.) in water (1 mL) was stirred for 40 min at 40 ℃. [b]HPLC yield ($t_{R,\mathbf{2a}}$ = 3.319 min, λmax, $_{\mathbf{2a}}$ = 218.1 nm; acetonitrile/water = 80: 20 (v/v)).

3.5 Screening the different acid [a]

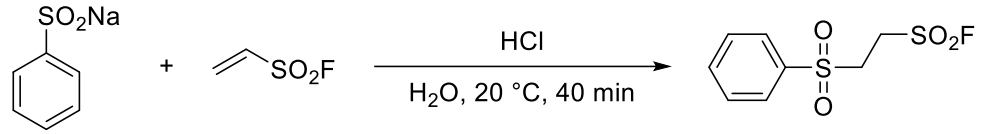


1a **2a**

Entry	Acid	Yield (%)[b]
1	acetic acid	11.3
2	formic acid	70.6
3	phosphoric acid	38.4
4	TFA	76.8
5	hydrochloric acid	86.4
6	**sulfuric acid**	**93.1**

[a] Reaction conditions: a mixture of sodium benzene sulfinate (**1a**, 0.2 mmol), ethene sulfonyl fluoride (2.0 equiv.) and acid (1.0 equiv.) in water (1 mL) was stirred for 40 min at 40 ℃. [b] HPLC yield ($t_{R,\mathbf{2a}}$ = 3.319 min, λmax, $_{\mathbf{2a}}$ = 218.1 nm; acetonitrile/water = 80: 20 (v/v)).

3.6 Reaction results under different pH conditions [a]



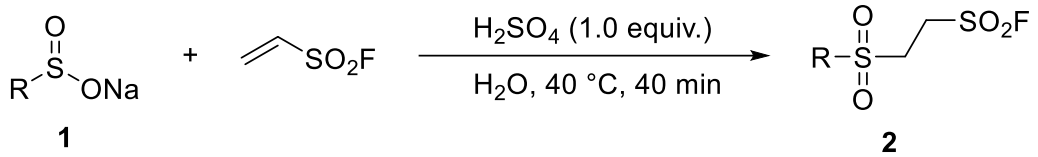
1a **2a**

Entry	pH in the solution	Yield (%)[b]
1	1	56.2
2	3	42.7
3	5	38.6
4	7	36.6
5	9	27.2
6	11	25.1

[a] Reaction conditions: a mixture of sodium benzene sulfinate (**1a**, 0.2 mmol), ethene sulfonyl fluoride (2.0 equiv.) and hydrochloric acid (used to adjust solution to a specific pH) in water (1 mL) was stirred for 40 min at 40 ℃. [b] HPLC yield ($t_{R,\mathbf{2a}}$ = 3.319 min, λmax, $_{\mathbf{2a}}$ = 218.1 nm; acetonitrile/water = 80: 20 (v/v)).

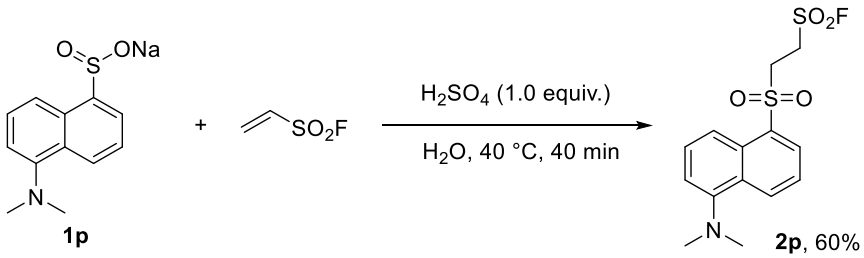
4. General Procedure

4.1 General Procedure for the Preparation of **2a-2o** and **2q-2y**.



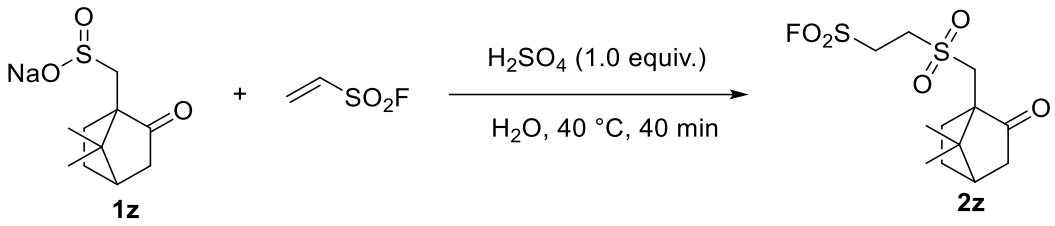
Sodium sulfinates (**1**, 1.0 mmol, 1.0 equiv.), ethene sulfonyl fluoride (2.0 mmol, 2.0 equiv.), sulphuric acid (1.0 mmol, 1.0 equiv.) and water (5 mL, 5 M) were added to a 25 mL reaction flask equipped with a stirring bar and covered with a rubber stopper. The reaction mixture was stirred at 40 °C for 40 minutes. The mixture was filtered under reduced pressure and the filter cake was washed with water. Dry the filter cake to obtain the product **2**.

4.2 General Procedure for the Preparation of **2p**.



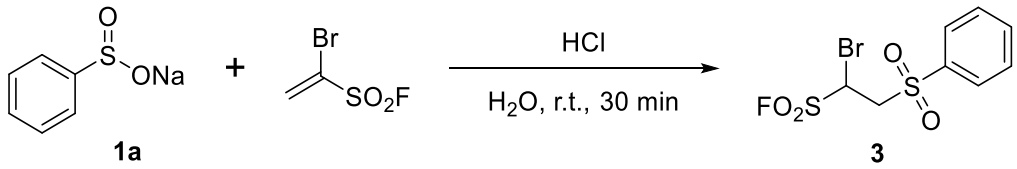
Sodium sulfinates (**1p**, 1.0 mmol, 1.0 equiv.), ethene sulfonyl fluoride (2.0 mmol, 2.0 equiv.), sulphuric acid (1.0 mmol, 1.0 equiv.) and water (5 mL, 5 M) were added to a 25 mL reaction flask equipped with a stirring bar and covered with a rubber stopper. The reaction mixture was stirred at 40 °C for 40 minutes. The mixture was filtered under reduced pressure and the filter cake was washed with water. The crude product was purified through silica gel chromatography using 30 % ethyl acetate / petroleum ether as eluents to afford the pure product **2p**.

4.3 General Procedure for the Preparation of **2z**



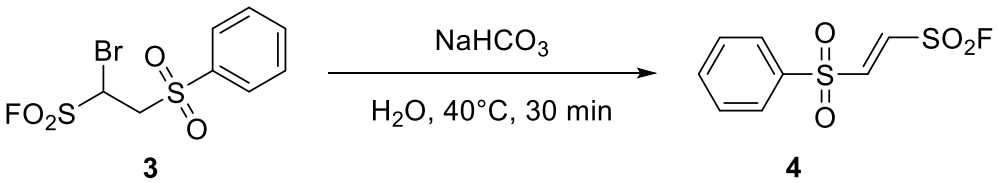
Sodium sulfinates (**1z**, 1.0 mmol, 1.0 equiv.), ethene sulfonyl fluoride (2.0 mmol, 2.0 equiv.), sulphuric acid (1.0 mmol, 1.0 equiv.) and water (5 mL, 5 M) were added to a 25 mL reaction flask equipped with a stirring bar and covered with a rubber stopper. The reaction mixture was stirred at 40 °C for 40 minutes. The solution was washed with water and extracted with EA (3 × 10 mL), the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to dryness to obtain product **2z**.

4.4 General Procedure for the Preparation of **3**.



Sodium sulfinates (**1a**, 1.0 mmol, 1.0 equiv.), 1-bromoethene-1-sulfonyl fluoride (2.0 mmol, 2.0 equiv.), hydrochloric acid (1.0 mmol, 1.0 equiv.) and water (5 mL, 5 M) were added to a 25 mL reaction flask equipped with a stirring bar and covered with a rubber stopper. The reaction mixture was stirred at room temperature for 30 minutes. The mixture was filtered under reduced pressure and the filter cake was washed with water. Dry the filter cake to obtain the product **3**.

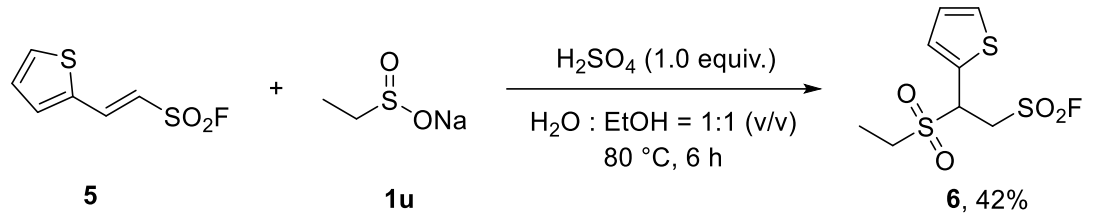
4.5 General Procedure for the Preparation of **4**



1-bromo-2-(phenylsulfonyl) ethane-1-sulfonyl fluoride (**3**, 1.0 mmol, 1.0 equiv.), sodium bicarbonate (1.0 mmol, 1.0 equiv.) and water (5 mL, 5 M) were added to a 25 mL reaction flask equipped with a stirring bar and covered with a rubber stopper. The reaction mixture was stirred at 40 °C for 30 minutes. The reaction mixture was extracted with dichloromethane (3 × 50 mL), dried over anhydrous Na_2SO_4 and concentrated to crude product. The pure product **4** was obtained by

column chromatography on silica gel using petroleum ether/ethyl acetate (5:1 v/v) as eluents.

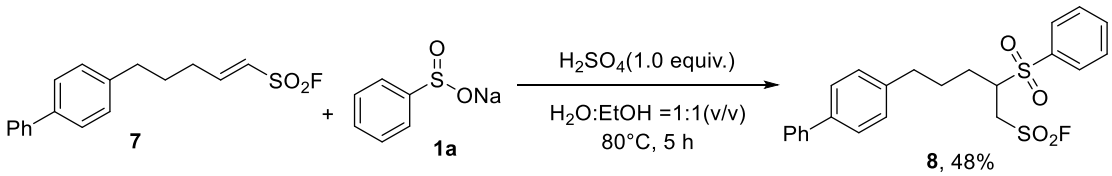
4.6 General Procedure for the Preparation of **6**.



5 **1u** **6**, 42%

(*E*)-2-(thiophen-2-yl)ethene-1-sulfonyl fluoride (**5**, 192 mg, 1.0 mmol), sodium sulfinates (**1u**, 232 mg, 2.0 mmol), H_2O (2.5 mL), EtOH (2.5 mL) and sulphuric acid (1.0 mmol, 1.0 equiv.) were added to an oven-dried reaction tube (30 mL) equipped with a magnetic stirring bar. The mixture was stirred at 80 ℃ for 6 h with monitoring by TLC. After the reaction was completed, cool the mixture to room temperature. The solvent was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel via gradient elution with petroleum ether/ dichloromethane (5:1 to 3:1, v/v) as eluent to afford pure product **6**.

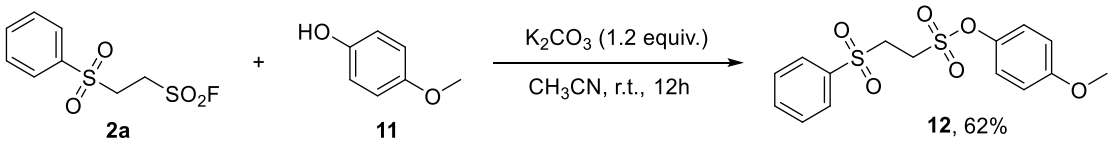
4.7 General Procedure for the Preparation of **8**.



8, 48%

(*E*)-5-([1,1'-biphenyl]-4-yl)pent-1-ene-1-sulfonyl fluoride (**7**, 304 mg, 1.0 mmol), sodium sulfinates (**1a**, 328g, 2.0 mmol), H_2O (2.5 mL), EtOH (2.5 mL) and sulphuric acid (1.0 mmol, 1.0 equiv.) were added to an oven-dried reaction tube (30 mL) equipped with a magnetic stirring bar. The mixture was stirred at 80℃ for 5 h with monitoring by TLC. After the reaction was completed, cool the mixture to room temperature. The solvent was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel using petroleum ether/ ethyl acetate (3:1, v/v) as eluent to afford pure product **8**.

4.8 General Procedure for the Preparation of **12**.

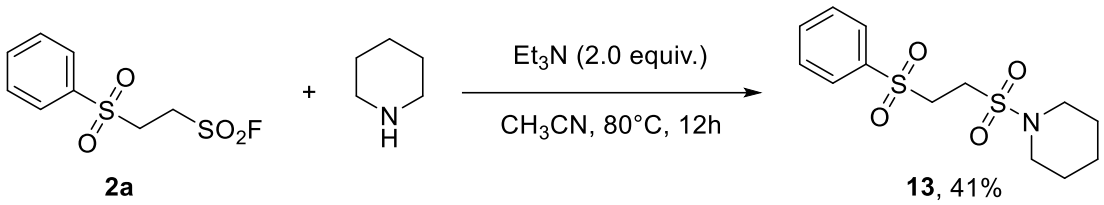


2a **11** **12**, 62%

2-(phenylsulfonyl)ethane-1-sulfonyl fluoride (**2a**, 252 mg, 1.0 mmol), 4- methoxyphenol (149 mg, 1.2 mmol), K_2CO_3 (166 mg, 1.2 mmol) were added in a solution of acetonitrile (5 mL) and reacted at room temperature for 12 h with monitoring by TLC. The solvent was evaporated under vacuum

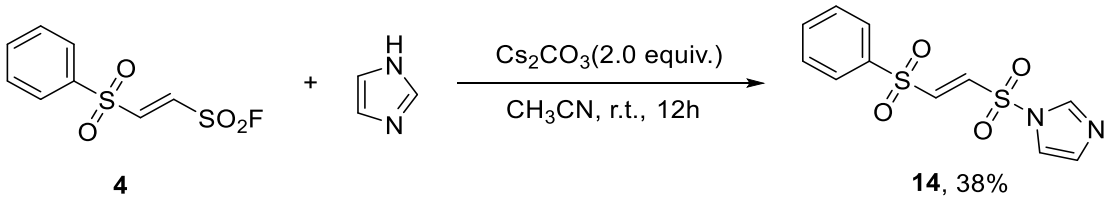
and the residue was purified through flash silica gel chromatography by gradient elution with petroleum ether/ethyl acetate (4:1 to 2:1, v/v) as eluent to obtain the desired product **12** as white solid.

4.9 General Procedure for the Preparation of **13**.

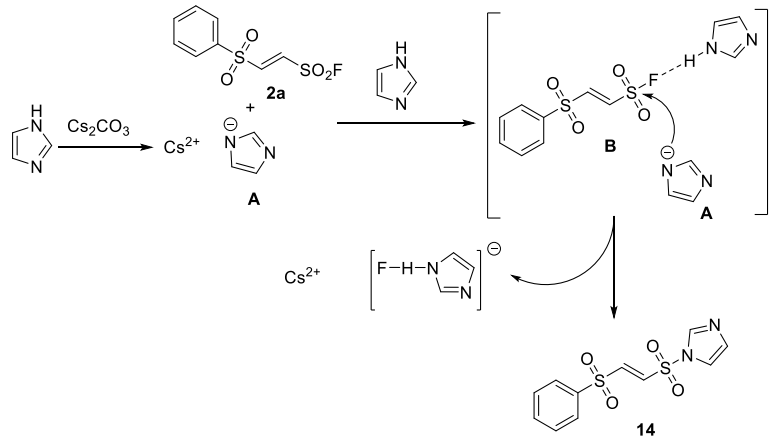


2-(phenylsulfonyl)ethane-1-sulfonyl fluoride (**2a**, 252 mg, 1.0 mmol), piperidine (120 mg, 1.5 mmol), Et_3N (202 mg, 2.0 mmol) were added in a solution of acetonitrile (5 mL) and reacted at 80℃ for 12 h with monitoring by TLC. The solvent was evaporated under vacuum and the residue was purified through flash silica gel chromatography using 5% methanol/ dichloromethane as eluent to obtain the desired product **13** as white solid.

4.10 General Procedure for the Preparation of **14** and the proposed mechanism.



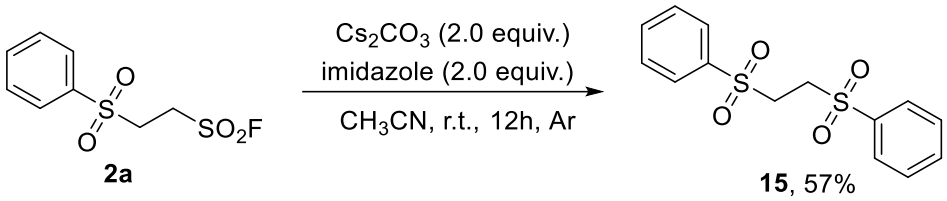
(*E*)-2-(phenylsulfonyl)ethene-1-sulfonyl fluoride (**4**, 250 mg, 1.0 mmol), imidazole (136 mg, 2.0 mmol), Cs_2CO_3 (650 mg, 2.0 mmol) were added in a solution of acetonitrile (5 mL) and reacted at room temperature for 12 h. After the reaction is completed, filter the mixture and wash the filter cake with ethyl acetate. The filtrate was evaporated under vacuum and the residue was purified through flash silica gel chromatography using EA as eluent to obtain the desired product **14** as white solid.



Scheme 1. The proposed mechanism for the formation of compound **14**

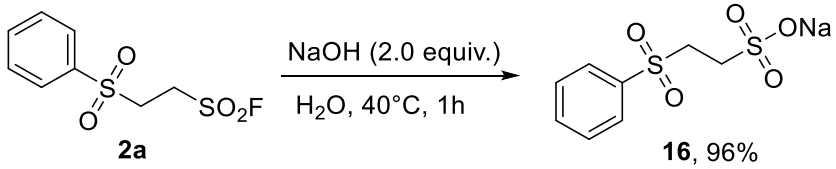
A putative mechanism of this reaction was proposed based on previous the literature [3]. As presented in Scheme 1, with the promotion of Cs_2CO_3, the hydrogen on the nitrogen atom in the imidazole ring departs as a proton to form a nucleophilic nitrogen anion intermediate **A**. At the same time, imidazole combines with sulfonyl fluoride **2a** through hydrogen bonding to form intermediate **B**, which accelerates reactions of -SO_2F electrophiles. Then, the nitrogen anion intermediate **A** attacks the sulfur atom of intermediate **B**, and a nucleophilic substitution occurs to generate the sulfur fluoride exchange product **14**.

4.11 General Procedure for the Preparation of **15**.



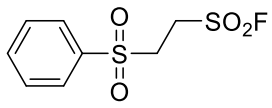
2-(phenylsulfonyl)ethane-1-sulfonyl fluoride (**2a**, 252 mg, 1.0 mmol), imidazole (**13**, 136 mg, 2.0 mmol), Cs_2CO_3 (650 mg, 2.0 mmol) were added in a solution of acetonitrile (5 mL) and reacted at room temperature for 12 h under argon atmosphere. After the reaction is completed, filter the mixture and wash the filter cake with ethyl acetate. The filtrate was evaporated under vacuum and the residue was purified through flash silica gel chromatography by gradient elution with petroleum ether/ethyl acetate (2:1 to 1:1, v/v) as eluent to obtain the product **15** as white solid.

4.12 General Procedure for the Preparation of **16**.



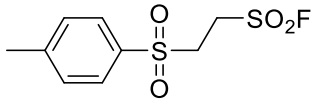
2-(phenylsulfonyl)ethane-1-sulfonyl fluoride (**2a**, 252 mg, 1.0 mmol), NaOH (80 mg, 2.0 mmol), H_2O (5 mL, 5 M) were added to an oven-dried reaction tube (30 mL) equipped with a magnetic stirring bar. The mixture was stirred at 40 °C for 1 h. After the reaction is completed, extract with ethyl acetate (10 mL × 2). Discard the organic phase and the aqueous phase was evaporated under vacuum. The resulting solid residue was dissolved in a warm mixture of H_2O (0.5 mL) and EtOH (2.5 mL). After filtration of some insoluble materials, the filtrate was cooled at −20 °C. The crystalline sodium salt was collected by filtration.

5.Characterization



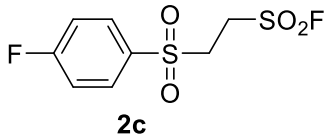
2a

2-(phenylsulfonyl)ethane-1-sulfonyl fluoride **(2a).** White solid. (229.20 mg, isolated yield 91%). M.p. 177-178 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.99 (d, J = 7.8 Hz, 2H), 7.82 (t, J = 7.6 Hz, 1H), 7.71 (t, J = 7.8 Hz, 2H), 4.30 (dt, J_1 = 10.8 Hz, J_2 =6.2 Hz, 2H), 3.97 – 3.94 (m, 2H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 137.9, 134.6, 129.6, 128.1, 48.5, 44.1 (d, J = 17.8 Hz). **^{19}F NMR** (471 MHz, DMSO-d_6) δ 56.31 (s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_8H_{10}FO_4S_2]^+$ ($[M+H]^+$): 252.9999, found: 253.0003.



2b

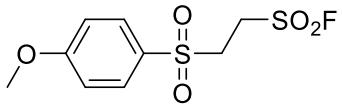
2-tosylethane-1-sulfonyl fluoride **(2b).** White solid. (213.04 mg, isolated yield 80%). M.p. 165-166 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.86 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 4.29 – 4.24 (m, 2H), 3.91 – 3.88 (m, 2H), 2.44 (s, 3H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 145.2, 135.0, 130.1, 128.2, 48.6, 44.1 (d, J = 17.7 Hz), 21.6. **^{19}F NMR** (471 MHz, DMSO-d_6) δ 56.29 (s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_9H_{12}FO_4S_2]^+$ ($[M+H]^+$): 267.0156, found:267.0159.



2c

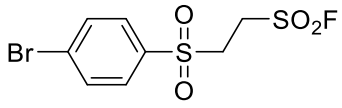
2-((4-fluorophenyl)sulfonyl)ethane-1-sulfonyl fluoride **(2c).** White solid. (210.80 mg, isolated yield 78%). M.p. 133-134 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.07 (dd, J_1 = 8.7 Hz, J_2=5.1 Hz, 2H), 7.55 (t, J = 8.7 Hz, 2H), 4.33 – 4.28 (m, 2H), 3.99 – 3.96 (m, 2H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 165.5 (d, J = 253.4 Hz), 134.1 (d, J = 3.8 Hz),

131.6 (d, *J* = 10.0 Hz), 116.8 (d, *J* = 22.8 Hz), 48.5, 44.1 (d, *J* = 17.4 Hz). **^{19}F NMR** (471 MHz, DMSO-d_6) δ 56.32 (s,1F), -103.84 (s,1F). **HRMS-ESI** (m/z) calcd. for $[C_8H_9F_2O_4S_2]^+$ ($[M+H]^+$): 270.9905, found: 270.9902.



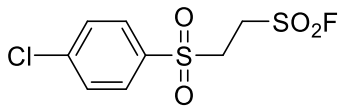
2d

2-((4-methoxyphenyl)sulfonyl)ethane-1-sulfonyl fluoride **(2d).** White solid. (157.92 mg, isolated yield 56%). M.p. 145-146 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.90 (d, *J* = 8.9 Hz, 2H), 7.21 (d, *J* = 9.0 Hz, 2H), 4.28 – 4.24 (m, 2H), 3.89 (s, 3H), 3.87 (dd, J_1 = 6.8 Hz, J_2 =4.0 Hz, 2H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 163.8, 130.5, 129.2, 114.8, 55.9, 48.8, 44.2 (d, *J* = 17.3 Hz). **^{19}F NMR** (471 MHz, DMSO-d_6) δ 56.20 (s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_9H_{12}FO_5S_2]^+$ ($[M+H]^+$): 283.0105, found: 283.0109.



2e

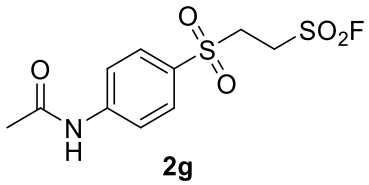
2-((4-bromophenyl)sulfonyl)ethane-1-sulfonyl fluoride **(2e).** White solid. (263.92 mg, isolated yield 80%). M.p. 190-191 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.94 – 7.88 (m, 4H), 4.34 – 4.29 (m, 2H), 4.01 – 3.98 (m, 2H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 137.0, 132.7, 130.3, 128.9, 48.4, 44.0 (d, *J* = 17.4 Hz). **^{19}F NMR** (471 MHz, DMSO-d_6) δ 56.32 (s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_8H_9BrFO_4S_2]^+$ ($[M+H]^+$): 330.9104, found: 330.9110.



2f

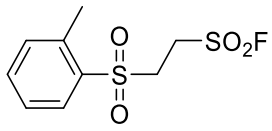
2-((4-chlorophenyl)sulfonyl)ethane-1-sulfonyl fluoride **(2f)**. White solid. (203.03 mg, isolated yield 71%). M.p. 162-163 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.00 (d, *J* =

8.6 Hz, 2H), 7.78 (d, *J* = 8.7 Hz, 2H), 4.34 – 4.29 (m, 2H), 4.01 – 3.98 (m, 2H).**^{13}C NMR** (126 MHz, DMSO-d_6) δ 139.7, 136.6, 130.3, 129.8, 48.4, 44.0 (d, *J* = 17.9 Hz). **^{19}F NMR** (471 MHz, DMSO-d_6) δ 56.33 (s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_8H_9ClFO_4S_2]^+$ ($[M+H]^+$): 286.9610, found: 286.9612.



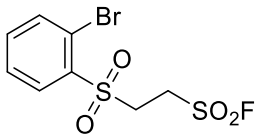
2g

2-((4-acetamidophenyl)sulfonyl)ethane-1-sulfonyl fluoride (**2g**). White solid. (259.83 mg, isolated yield 84%). M.p. 246-247 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 10.43 (s, 1H), 7.90 – 7.83 (m, 4H), 4.38 – 4.17 (m, 2H), 3.94 – 3.84 (m, 2H), 2.11 (s, 3H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 169.3, 144.7, 131.0, 129.5, 118.8, 48.7, 44.2 (d, *J* = 17.4 Hz), 24.2. **^{19}F NMR** (471 MHz, DMSO-d_6) δ 56.21 (s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_{10}H_{13}FNO_5S_2]^+$ ($[M+H]^+$): 310.0214, found: 310.0216.



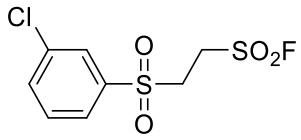
2h

2-(o-tolylsulfonyl)ethane-1-sulfonyl fluoride **(2h).** White solid. (221.03 mg, isolated yield 83%). M.p.118-119 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.92 (d, *J* = 6.8 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.52 – 7.49 (m, 2H), 4.34 – 4.30 (m, 2H), 3.90 – 3.86 (m, 2H), 2.65 (s, 3H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 138.2, 136.0, 134.6, 133.1, 130.0, 127.0, 48.3, 44.0 (d, *J* = 17.9 Hz), 19.9. **^{19}F NMR** (471 MHz, DMSO-d_6) δ 56.65 (s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_9H_{12}FO_4S_2]^+$ ($[M+H]^+$):267.0156, found: 267.0150.



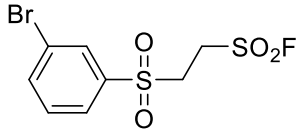
2i

2-((2-bromophenyl)sulfonyl)ethane-1-sulfonyl fluoride **(2i).** White solid. (228.51 mg, isolated yield 69%). M.p.156-157 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.10 – 8.08 (m, 1H), 7.98 – 7.96 (m, 1H), 7.72 – 7.70 (m, 2H), 4.42 – 4.38 (m, 2H), 4.15 – 4.11 (m, 2H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 136.8, 136.2, 135.8, 132.1, 128.8, 120.4, 47.0, 43.8 (d, J = 17.8 Hz). **^{19}F NMR** (471 MHz, DMSO-d_6) δ 56.45 (s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_8H_9BrFO_4S_2]^+$ ($[M+H]^+$): 330.9104, found: 330.9107.



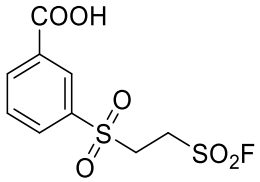
2j

2-((3-chlorophenyl)sulfonyl)ethane-1-sulfonyl fluoride **(2j).** White solid. (246.58 mg, isolated yield 86%). M.p.145-146 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.04 (t, J = 1.9 Hz, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.88 (dd, J_1 = 8.1, J_2 =1.1 Hz, 1H), 7.72 (t, J = 8.0 Hz, 1H), 4.37 – 4.29 (m, 2H), 4.08 – 4.02 (m, 2H).**^{13}C NMR** (126 MHz, DMSO-d_6) δ 139.7, 134.5, 134.2, 131.5, 128.0, 127.0, 48.3, 44.0 (d, J = 17.8 Hz). **^{19}F NMR** (471 MHz, DMSO-d_6) δ 56.30 (s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_8H_9ClFO_4S_2]^+$ ($[M+H]^+$): 286.9610, found: 286.9615.



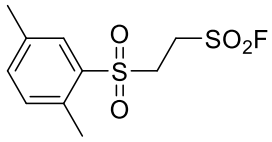
2k

2-((3-bromophenyl)sulfonyl)ethane-1-sulfonyl fluoride **(2k).** White solid. (298.05 mg, isolated yield 90%). M.p.127-128 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.16 (s, 1H), 8.02 (d, J = 6.1 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.66 (t, J = 7.9 Hz, 1H), 4.38 – 4.30 (m, 2H), 4.09 – 4.01 (m, 2H).**^{13}C NMR** (126 MHz, DMSO-d_6) δ 139.8, 137.4, 131.7, 130.7, 127.3, 122.5, 48.3, 44.0 (d, J = 17.4 Hz). **^{19}F NMR** (471 MHz, DMSO-d_6) δ 56.33 (s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_8H_9BrFO_4S_2]^+$ ($[M+H]^+$): 330.9104, found: 330.9103.



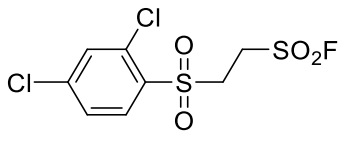
2l

3-((2-(fluorosulfonyl)ethyl)sulfonyl)benzoic acid **(2l).** White solid. (157.03 mg, isolated yield 53%). M.p.222-223 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 13.58 (s, 1H), δ 8.44 (s, 1H), 8.31 (d, J = 7.8 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H), 7.84 (t, J = 7.8 Hz, 1H), 4.38 – 4.30 (m, 2H), 4.10 – 4.00 (m, 2H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 165.9, 138.4, 135.0, 132.3, 132.2, 130.3, 129.0, 48.4, 44.0 (d, J = 17.4 Hz). **^{19}F NMR** (471 MHz, DMSO-d_6) δ 56.35(s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_9H_{10}FO_6S_2]^+$ ($[M+H]^+$): 296.9898, found: 296.9895.



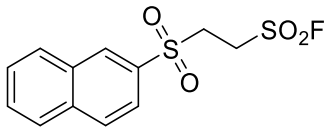
2m

2-((2,5-dimethylphenyl)sulfonyl)ethane-1-sulfonyl fluoride **(2m).** White solid. (232.67 mg, isolated yield 83%). M.p.121-122 °C. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.78 (s, 1H), 7.39 (d, J = 5.8 Hz, 1H), 7.28 (d, J = 7.8 Hz, 1H), 3.81 – 3.77 (m, 2H), 3.61 – 3.57 (m, 2H), 2.65 (s, 3H), 2.41 (s, 3H).**^{13}C NMR** (126 MHz, DMSO-d_6) δ 136.5, 135.6, 135.1, 134.9, 133.0, 130.2, 48.2, 44.0 (d, J = 17.6 Hz), 20.8, 19.9. **^{19}F NMR** (471 MHz, Chloroform-d) δ 55.44(s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_{10}H_{14}FO_4S_2]^+$ ($[M+H]^+$): 281.0312, found: 281.0317.



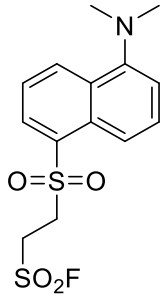
2n

2-((2,4-dichlorophenyl)sulfonyl)ethane-1-sulfonyl fluoride **(2n).** White solid. (279.41 mg, isolated yield 87%). M.p.150-151 °C. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.07 (d, J = 8.5 Hz, 1H), 7.65 (d, J = 2.0 Hz, 1H), 7.52 (dd, J_1 = 8.5 Hz, J_2 =2.0 Hz, 1H), 3.92 – 3.88 (m, 2H), 3.85 – 3.81 (m, 2H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 140.4, 134.0, 133.3, 133.2, 131.8, 128.5, 47.5, 43.8 (d, J = 17.3 Hz). **^{19}F NMR** (471 MHz, DMSO-d_6) δ 55.86 (s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_8H_8Cl_2FO_4S_2]^+$ ($[M+H]^+$): 320.9220, found: 320.9216.



2o

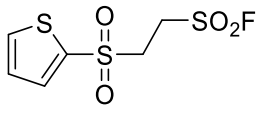
2-(naphthalen-2-ylsulfonyl)ethane-1-sulfonyl fluoride（**2o**）. White solid. (169.30 mg, isolated yield 56%). M.p.224-225 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.66 (s, 1H), 8.23 (d, J = 8.9 Hz, 2H), 8.12 (d, J = 8.2 Hz, 1H), 8.00 (d, J = 8.7 Hz, 1H), 7.76 (dt, J_1 = 27.4 Hz, J_2 =7.2 Hz, 2H), 4.38 – 4.33 (m, 2H), 4.05 – 4.02 (m, 2H).**^{13}C NMR** (126 MHz, DMSO-d_6) δ 135.2, 134.8, 131.7, 130.3, 129.8, 129.7, 129.6, 128.0, 127.8, 122.7, 48.5, 44.2 (d, J = 17.3 Hz). **^{19}F NMR** (471 MHz, DMSO-d_6) δ 56.23(s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_{12}H_{12}FO_4S_2]^+$ ($[M+H]^+$): 303.0156, found: 303.0160.



2p

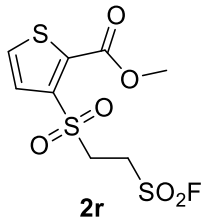
2-((5-(dimethylamino)naphthalen-1-yl)sulfonyl)ethane-1-sulfonyl fluoride（**2p**）. Chartreuse solid. (207.24 mg, isolated yield 60%). M.p.111-112 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.62 (d, J = 8.5 Hz, 1H), 8.27 – 8.24 (m, 2H), 7.76 – 7.68 (m, 2H), 7.32 (d, J = 7.6 Hz, 1H), 4.42 – 4.31 (m, 2H), 4.04 – 3.95 (m, 2H), 2.85 (s, 6H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 152.0, 133.0, 131.9, 131.0, 129.6, 129.2, 129.1, 123.9,

117.6, 115.5, 48.6, 45.0, 44.1 (d, J = 17.6 Hz). **^{19}F NMR** (471 MHz, DMSO-d_6) δ 56.58(s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_{14}H_{17}FNO_4S_2]^+$ ($[M+H]^+$): 346.0578, found: 346.0575.



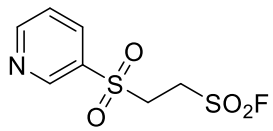
2q

2-(thiophen-2-ylsulfonyl)ethane-1-sulfonyl fluoride **(2q)**. White solid. (204.06 mg, isolated yield 79%). M.p.143-144 °C.**^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.20 (dd, J_1 = 5.0 Hz, J_2 =1.4 Hz, 1H), 7.94 (dd, J_1 = 3.8 Hz, J_2=1.4 Hz, 1H), 7.34 (dd, J_1 = 5.0 Hz, J_2 =3.9 Hz, 1H), 4.39 – 4.31 (m, 2H), 4.07 – 4.00 (m, 2H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 138.1, 136.5, 135.8, 128.8, 50.0, 44.3 (d, J = 17.3 Hz). **^{19}F NMR** (471 MHz, DMSO-d_6) δ 56.48 (s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_6H_8FO_4S_3]^+$ ($[M+H]^+$): 258.9563, found: 258.9561.



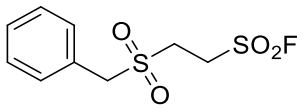
2r

methyl 3-((2-(fluorosulfonyl)ethyl)sulfonyl)thiophene-2-carboxylate (**2r**). White solid. (230.90 mg, isolated yield 73%). M.p.124-125 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.09 (d, J = 5.3 Hz, 1H), 7.57 (d, J = 5.2 Hz, 1H), 4.42 – 4.36 (m, 2H), 4.28 – 4.23 (m, 2H), 3.90 (s, 3H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 159.8, 141.1, 135.0, 132.6, 130.7, 53.3 (d, J = 7.4 Hz), 48.2, 44.0 (d, J = 17.7 Hz). **^{19}F NMR** (471 MHz, DMSO-d_6) δ 56.13 (s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_8H_{10}FO_6S_3]^+$ ($[M+H]^+$): 316.9618, found: 316.9622.



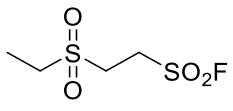
2s

2-(pyridin-3-ylsulfonyl)ethane-1-sulfonyl fluoride（**2s**）**.** White solid. (108.90 mg, isolated yield 43%). M.p.141-142 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 9.11 (d, J = 2.2 Hz, 1H), 8.96 (d, J = 4.7 Hz, 1H), 8.37 (d, J = 8.1 Hz, 1H), 7.73 (dd, J_1 = 8.0, J_2 =4.9 Hz, 1H), 4.41 – 4.33 (m, 2H), 4.13 – 4.06 (m, 2H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 154.9, 148.8, 136.6, 134.4, 124.4, 48.6, 44.0 (d, J = 17.4 Hz).**^{19}F NMR** (471 MHz, DMSO-d_6) δ 56.35(s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_7H_9FNO_4S_2]^+$ ($[M+H]^+$): 253.9952, found: 253.9955.



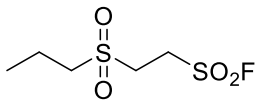
2t

2-(benzylsulfonyl)ethane-1-sulfonyl fluoride **(2t).** White solid. (237.01 mg, isolated yield 89%). M.p.122-123 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.42 (s, 5H), 4.70 (s, 2H), 4.51 – 4.40 (m, 2H), 3.71 – 3.65 (m, 2H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 176.3, 157.8, 114.0, 49.7, 43.8 (d, J = 17.8 Hz), 12.6, 10.4. **^{19}F NMR** (471 MHz, DMSO-d_6) δ 55.65 (s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_9H_{12}FO_4S_2]^+$ ($[M+H]^+$): 267.0156, found: 267.0154.



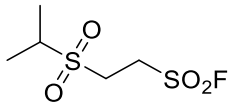
2u

2-(ethylsulfonyl)ethane-1-sulfonyl fluoride **(2u).** White solid. (152.21 mg, isolated yield 75%). M.p.122-123 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 4.43 – 4.39 (m, 2H), 3.75 – 3.68 (m, 2H), 3.28 (q, J = 7.4 Hz, 2H), 1.24 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 46.6, 44.9, 43.6 (d, J = 17.4 Hz), 5.7. **^{19}F NMR** (471 MHz, DMSO-d_6) δ 55.67(s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_4H_{10}FO_4S_2]^+$ ($[M+H]^+$): 204.9999, found: 205.0003.



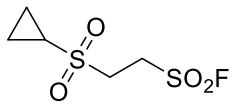
2v

2-(propylsulfonyl)ethane-1-sulfonyl fluoride **(2v)**. White solid. (178.64 mg, isolated yield 82%). M.p.113-114°C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 4.44 – 4.39 (m, 2H), 3.72 – 3.69 (m, 2H), 3.31 – 3.26 (m, 2H), 1.70 – 1.78 (m, 2H), 1.01 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 53.5, 45.6, 43.6 (d, J = 17.7 Hz), 14.8, 12.7. **^{19}F NMR** (471 MHz, DMSO-d_6) δ 55.67(s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_5H_{12}FO_4S_2]^+$ ($[M+H]^+$): 219.0156, found: 219.0159.



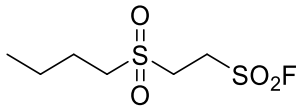
2w

2-(isopropylsulfonyl)ethane-1-sulfonyl fluoride **(2w)**. White solid. (164.70 mg, isolated yield 75%). M.p.128-129 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 4.42 – 4.38 (m, 2H), 3.71 – 3.67 (m, 2H), 3.52 – 3.45 (m, 1H), 1.29 (d, J = 6.9 Hz, 6H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 52.5, 43.4 (d, J = 17.8 Hz), 42.8, 14.6. **^{19}F NMR** (471 MHz, DMSO-d_6) δ 55.85(s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_5H_{12}FO_4S_2]^+$ ($[M+H]^+$): 219.0156, found: 219.0158.



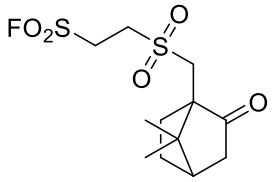
2x

2-(cyclopropylsulfonyl)ethane-1-sulfonyl fluoride **(2x).** White solid. (177.31 mg, isolated yield 82%). M.p.145-146 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 4.46 – 4.41 (m, 2H), 3.80 – 3.77 (m, 2H), 2.92 – 2.87 (m, 1H), 1.10 – 1.08 (m, 4H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 46.6, 43.9 (d, J = 17.5 Hz), 29.0, 4.5. **^{19}F NMR** (471 MHz, DMSO-d_6) δ 55.68(s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_5H_{10}FO_4S_2]^+$ ($[M+H]^+$): 216.9999, found: 216.9996.



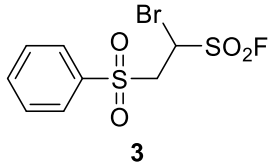
2y

2-(butylsulfonyl)ethane-1-sulfonyl fluoride **(2y)**. White solid. (195.12 mg, isolated yield 84%). M.p.112-113 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 4.42 (dt, J_1 = 11.2 Hz, J_2 =6.2 Hz, 2H), 3.73 – 3.70 (m, 2H), 3.31 – 3.28 (m, 2H), 1.72 – 1.66 (m, 2H), 1.46 – 1.38 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 51.6, 45.6, 43.6 (d, J = 17.3 Hz), 22.8, 21.0, 13.4. **^{19}F NMR** (471 MHz, DMSO-d_6) δ 55.68(s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_6H_{14}FO_4S_2]^+$ ($[M+H]^+$): 233.0312, found: 233.0317.



2z

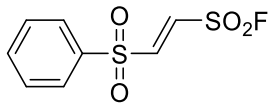
2-(((7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methyl)sulfonyl)ethane-1-sulfonyl fluoride **(2z)**. White solid. (146.88 mg, isolated yield 45%). M.p.74-75 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 4.55 – 4.40 (m, 2H), 3.98 – 3.77 (m, 2H), 3.70 (d, J = 15.0 Hz, 1H), 3.18 (d, J = 15.1 Hz, 1H), 2.43 – 2.32 (m, 1H), 2.31 – 2.22 (m, 1H), 2.07 (t, J = 4.5 Hz, 1H), 2.01 – 1.88 (m, 2H), 1.64 (m, 1H), 1.49 – 1.37 (m, 1H), 1.01 (s, 3H), 0.83 (s, 3H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 214.6, 58.5, 50.0, 48.3, 43.8 (d, J = 17.3 Hz), 42.0, 41.9, 26.4, 24.8, 19.4, 19.3. **^{19}F NMR** (471 MHz, DMSO-d_6) δ 55.77(s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_{12}H_{20}FO_5S_2]^+$ ($[M+H]^+$):327.4047, found: 327.4045.



3

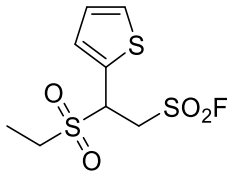
1-bromo-2-(phenylsulfonyl)ethane-1-sulfonyl fluoride **(3).** White solid. (317.93 mg, isolated yield 96%). M.p.99-100 °C. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.98 (d, J = 7.3 Hz, 2H), 7.76 (t, J = 7.6 Hz, 1H), 7.65 (t, J = 7.8 Hz, 2H), 5.50 (d, J = 10.4 Hz,

1H), 4.13 (dd, J_1 = 15.1 Hz, J_2 =2.1 Hz, 1H), 3.88 (dd, J_1 = 15.1 Hz, J_2 =10.4 Hz, 1H).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ 138.3, 135.2, 129.9, 128.5, 58.0, 48.9 (d, *J* = 25.4 Hz). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ 42.77(s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_8H_9BrFO_4S_2]^+$ ($[M+H]^+$): 330.9104, found: 330.9106.



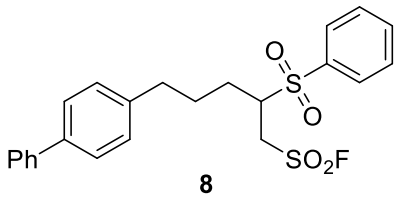
4

(E)-2-(phenylsulfonyl)ethene-1-sulfonyl fluoride **(4).** White solid. (135.14 mg, isolated yield 54%). M.p.145-146 °C. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 7.8 Hz, 2H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.67 (t, *J* = 7.7 Hz, 2H), 7.54 (d, *J* = 14.7 Hz, 1H), 7.39 (d, *J* = 14.8 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 147.5 (d, *J* = 3.1 Hz), 137.3, 136.0, 133.1 (d, *J* = 28.6 Hz), 130.5, 129.1. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ 62.00 (s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_8H_8FO_4S_2]^+$ ($[M+H]^+$): 250.9843, found: 250.9844.



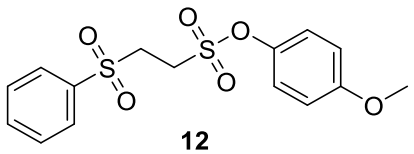
6

2-(ethylsulfonyl)-2-(thiophen-2-yl)ethane-1-sulfonyl fluoride (**6**). Yellowish brown solid. (120.26 mg, isolated yield 42%). M.p.88-89°C. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 5.2 Hz, 1H), 7.32 (d, *J* = 3.6 Hz, 1H), 7.19 – 6.99 (m, 1H), 4.94 (d, *J* = 11.6 Hz, 1H), 4.45 (dd, J_1 = 14.6, J_2 =7.3 Hz, 1H), 4.05 (dd, J_1 = 14.9, J_2 =11.5 Hz, 1H), 2.90 – 2.86 (m, 2H), 1.35 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 130.5, 130.4, 129.1, 127.9, 58.2, 50.3 (d, *J* = 18.0 Hz), 45.1, 6.4. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ 61.46 (s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_8H_{12}FO_4S_3]^+$ ($[M+H]^+$): 287.3577, found: 287.3579.



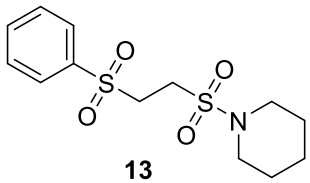
8

5-([1,1'-biphenyl]-4-yl)-2-(phenylsulfonyl)pentane-1-sulfonyl fluoride (**8**). White solid. (214.34 mg, isolated yield 48%) M.p.98-99 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.95 (dd, J_1 = 8.3, J_2 = 1.1 Hz, 2H), 7.79 (t, J = 7.5 Hz, 1H), 7.70 – 7.61 (m, 4H), 7.56 (d, J = 8.2 Hz, 2H), 7.46 (t, J = 7.7 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.22 (d, J = 8.2 Hz, 2H), 4.58 – 4.44 (m, 1H), 4.31 (dt, J_1 = 15.8, J_2 =3.6 Hz, 1H), 3.99 – 3.89 (m, 1H), 2.56 (t, J = 6.9 Hz, 2H), 1.93 – 1.67 (m, 4H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 140.5, 140.1, 137.8, 136.1, 134.7, 129.7, 129.0, 128.9, 128.8, 127.2, 126.6, 126.5, 58.4, 48.5 (d, J = 16.3 Hz), 34.3, 27.6, 26.9. **^{19}F NMR** (471 MHz, DMSO-d_6) δ 58.82 (s, 1F). **HRMS-ESI** (m/z) calcd. for $[C_{23}H_{24}FO_4S_2]^+$ ($[M+H]^+$): 447.5587, found:447.5590.



12

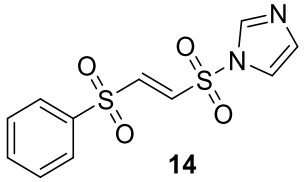
4-methoxyphenyl 2-(phenylsulfonyl)ethane-1-sulfonate (**12**). White solid. (220.94 mg, isolated yield 62%) M.p.105-106 °C. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.94 (d, J = 7.4 Hz, 2H), 7.75 (t, J = 7.5 Hz, 1H), 7.63 (t, J = 7.8 Hz, 2H), 7.12 (d, J = 9.1 Hz, 2H), 6.89 (d, J = 9.1 Hz, 2H), 3.80 (s, 3H), 3.65 – 3.59 (m, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 158.8, 142.1, 137.9, 134.8, 129.9, 128.2, 122.9, 115.1, 55.7, 50.3, 43.3. **HRMS-ESI** (m/z) calcd. for $[C_{15}H_{17}O_6S_2]^+$ ($[M+H]^+$):357.0461, found:357.0474.



13

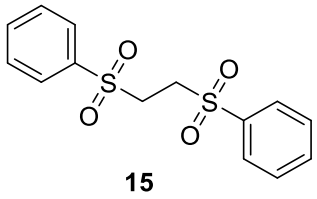
1-((2-(phenylsulfonyl)ethyl)sulfonyl)piperidine (**13**). White solid. (130.15 mg, isolated yield 41%) M.p.75-76 °C. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.90 (d, J = 7.0 Hz, 2H), 7.64 (t, J = 7.5 Hz, 1H), 7.55 (t, J = 7.8 Hz, 2H), 3.32 – 3.26 (m, 2H), 2.75 – 2.68 (m, 2H), 2.28 (t, J = 5.3 Hz, 4H), 1.42 (p, J = 5.5 Hz, 4H), 1.34 (q, J = 5.9 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 139.7, 133.6, 129.1, 128.0, 54.1, 53.6, 51.9, 25.7,

24.0. **HRMS-ESI** (m/z) calcd. for $[C_{13}H_{20}NO_4S_2]^+$ ($[M+H]^+$):318.0828, found:318.0833.



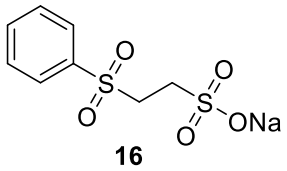
14

(E)-1-((2-(phenylsulfonyl)vinyl)sulfonyl)-1H-imidazole (**14**). White solid. (113.36 mg, isolated yield 38%) M.p.127-128 °C. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 13.8 Hz, 1H), 7.92 (d, *J* = 7.3 Hz, 2H), 7.78 (s, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.15 (d, *J* = 7.3 Hz, 2H), 6.57 (d, *J* = 13.7 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 140.4, 138.3, 134.9, 133.8, 132.3, 129.6, 127.5, 116.7, 116.4. **HRMS-ESI** (m/z) calcd. for $[C_{11}H_{11}N_2O_4S_2]^+$ ($[M+H]^+$):299.0155, found:299.0159.



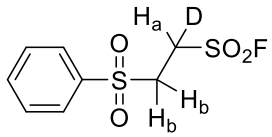
15

1,2-bis(phenylsulfonyl)ethane (**15**). White solid. (88.44 mg, isolated yield 57%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 7.8 Hz, 4H), 7.71 (t, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.8 Hz, 4H), 3.44 (s, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 138.1, 134.6, 129.8, 128.1, 49.5. **HRMS-ESI** (m/z) calcd. for $[C_{14}H_{15}O_4S_2]^+$ ($[M+H]^+$):311.0407, found:311.0405.



16

sodium 2-(phenylsulfonyl)ethane-1-sulfonate (**16**). White solid. (261.36 mg, isolated yield 96%). **^{1}H NMR** (500 MHz, Deuterium Oxide) δ 7.97 (d, *J* = 7.0 Hz, 2H), 7.83 (t, *J* = 7.2 Hz, 1H), 7.71 (t, *J* = 7.8 Hz, 2H), 3.78 – 3.70 (m, 2H), 3.24 – 3.17 (m, 2H). **^{13}C NMR** (126 MHz, Deuterium Oxide) δ 136.3, 135.2, 129.9, 128.0, 51.1, 44.0. **HRMS-ESI** (m/z) calcd. for $[C_8H_9NaO_5S_2]^+$ ($[M]^+$):271.9784, found: 271.9799.



18

2-(phenylsulfonyl)ethane-1-sulfonyl fluoride-1-d（**18**）. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.99 (dd, J_1 = 8.4 Hz, J_2 =1.3 Hz, 2H), 7.82 (t, J = 7.5 Hz, 1H), 7.71 (t, J = 7.8 Hz, 2H), 4.29 (q, J = 8.1 Hz, 1H), 3.95 (d, J = 7.9 Hz, 2H).

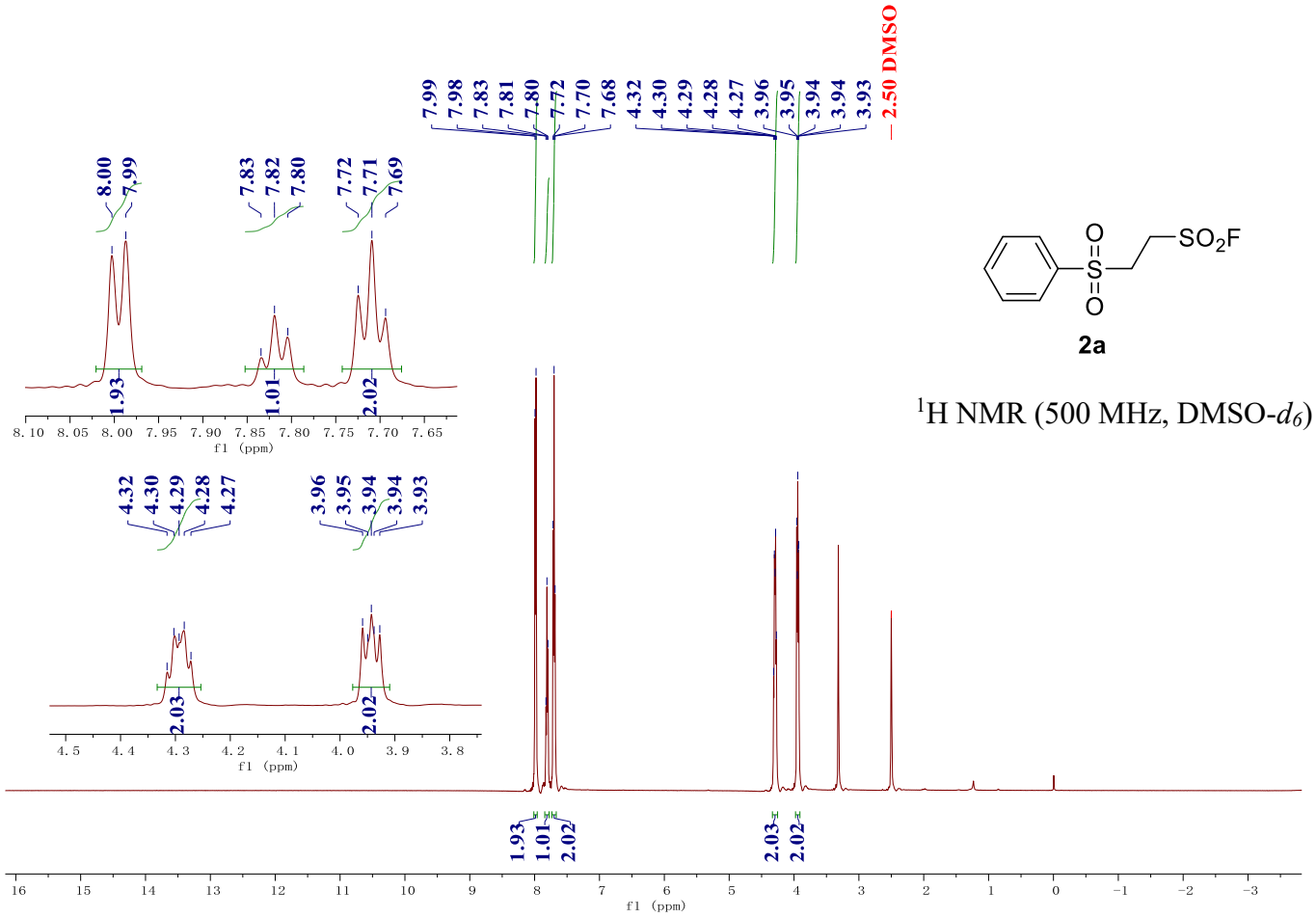
6. Reference

[1] Q.-H. Zheng, Jiajia Dong, and K. B. Sharpless. *J. Org. Chem.* 2016, **81**(22), 11360-11362.

[2] (a) B. Du, P. Qian, Y. Wang, H. Mei, J. Han, Y. Pan, *Org. Lett.* 2016, **18**, 4144-4147; (b) Y. Liu, P. Xie, Z. Sun, X. Wo, C. Gao, W. Fu, T. P. Loh, *Org. Lett*. 2018, **20**, 5353-5356

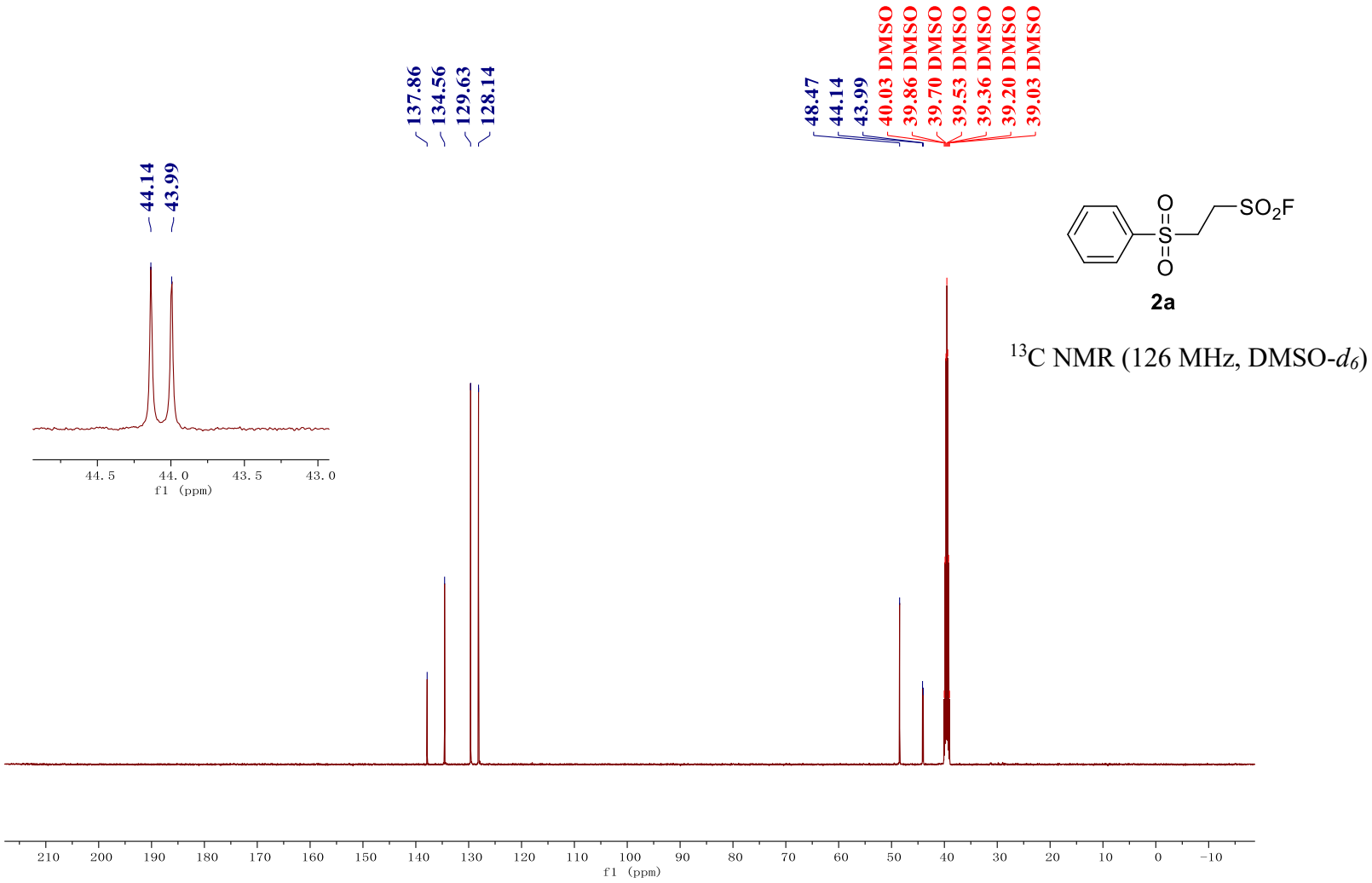
[3] Jiajia Dong, Larissa Krasnova, M. G. Finn, and K. B. Sharpless. *Angew. Chem. Int. Ed.* 2014, **53**, 9430 – 9448

7. NMR spectra



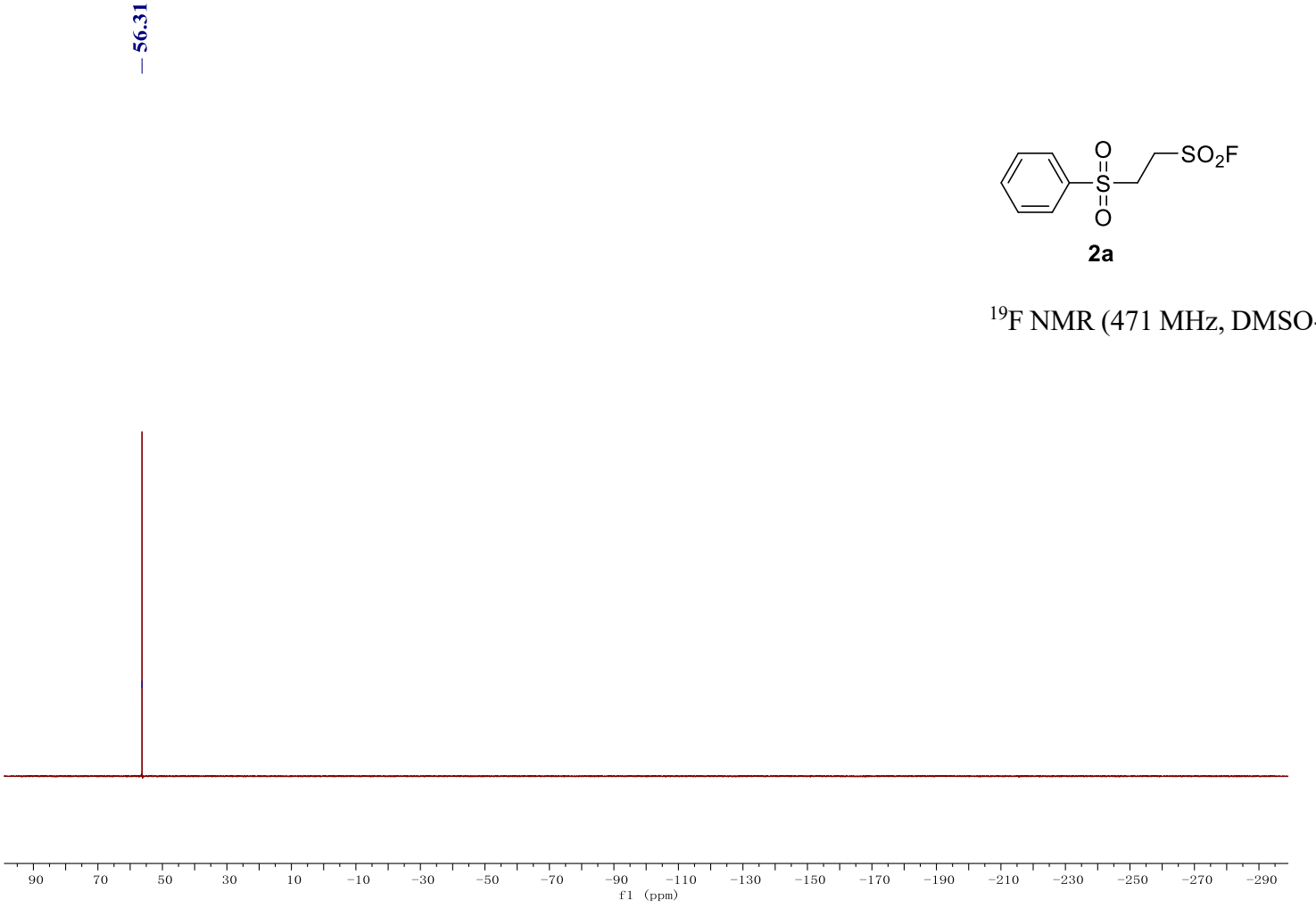
2a

^{1}H NMR (500 MHz, DMSO-d_6)



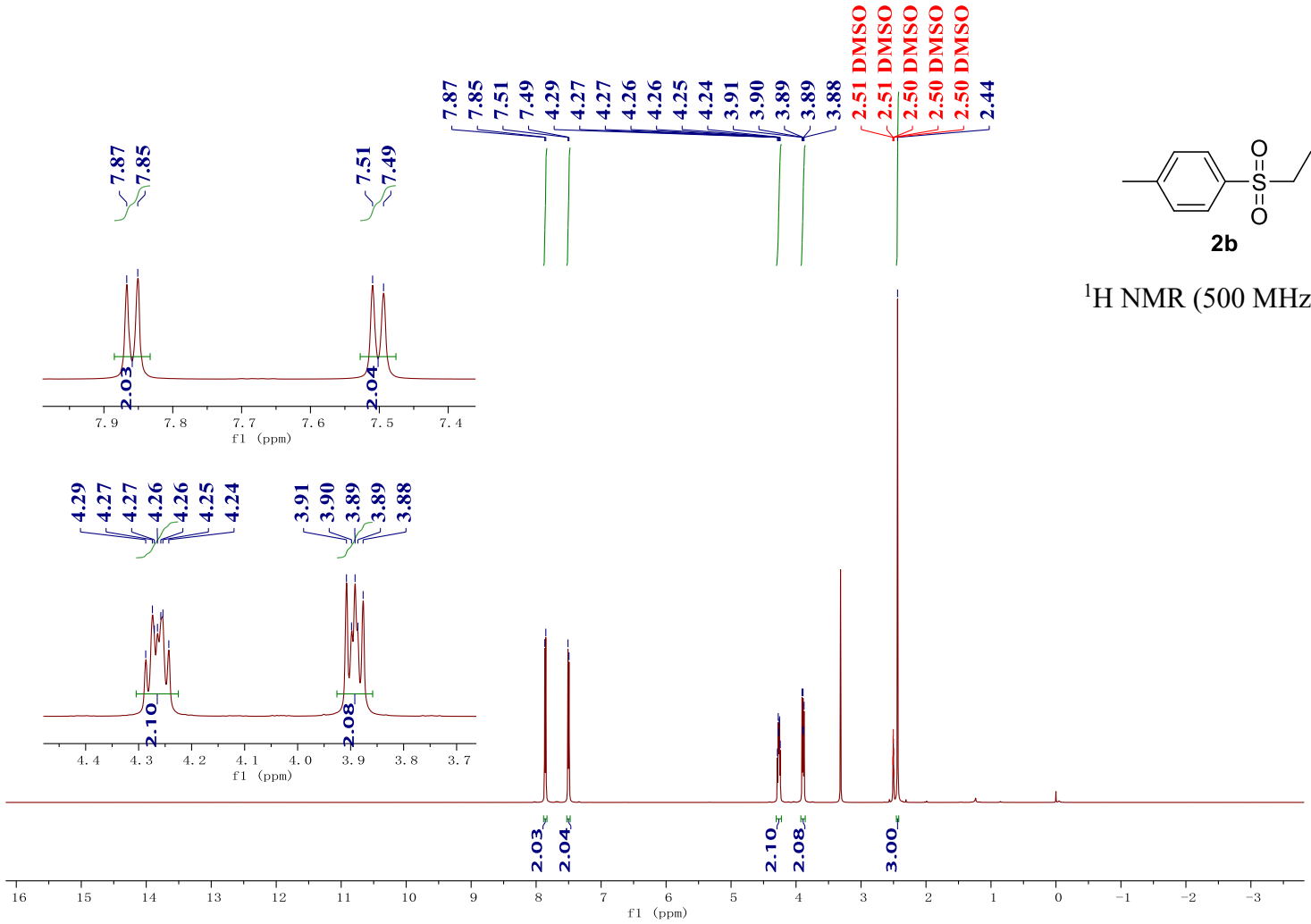
2a

^{13}C NMR (126 MHz, DMSO-d_6)



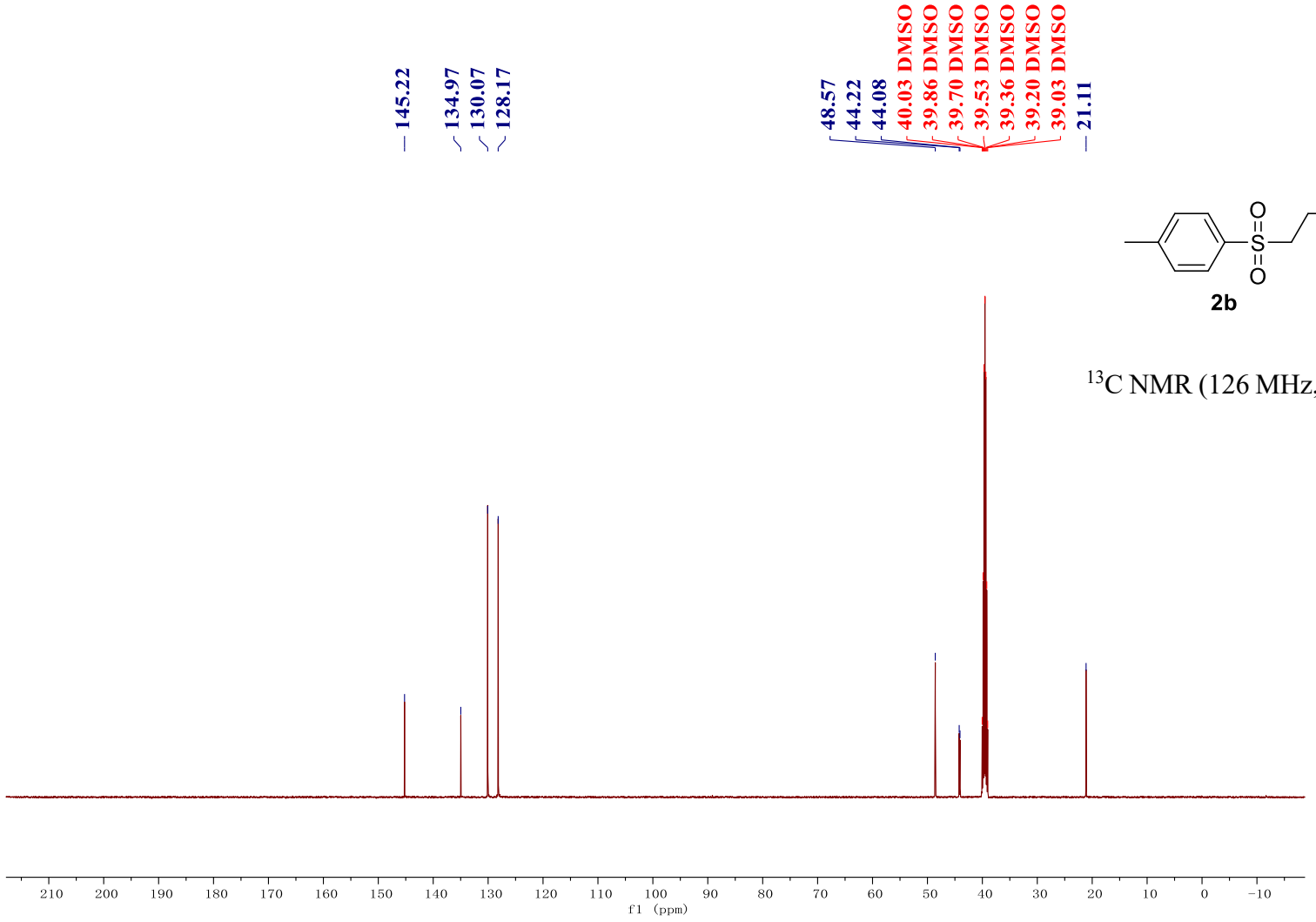
2a

^{19}F NMR (471 MHz, DMSO-d_6)

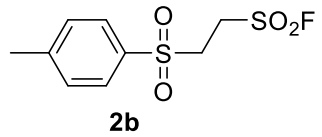


2b

^{1}H NMR (500 MHz, DMSO-d_6)

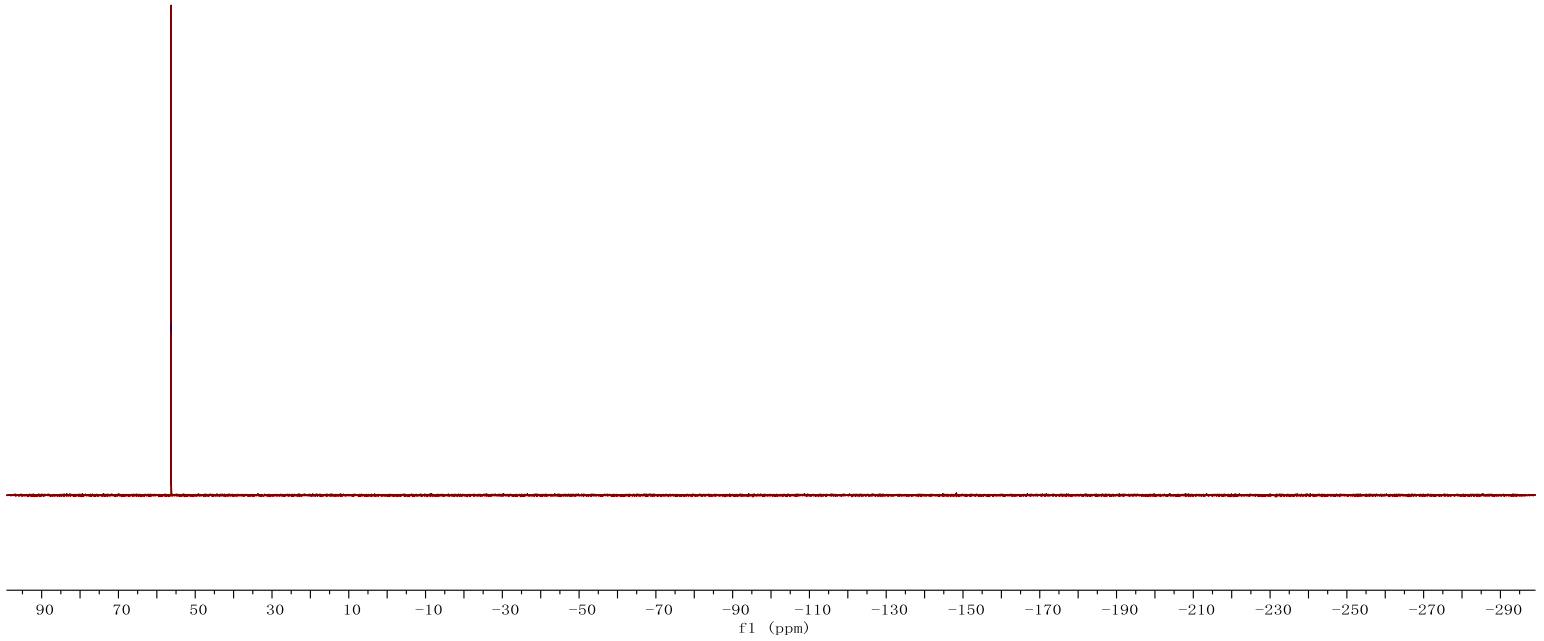


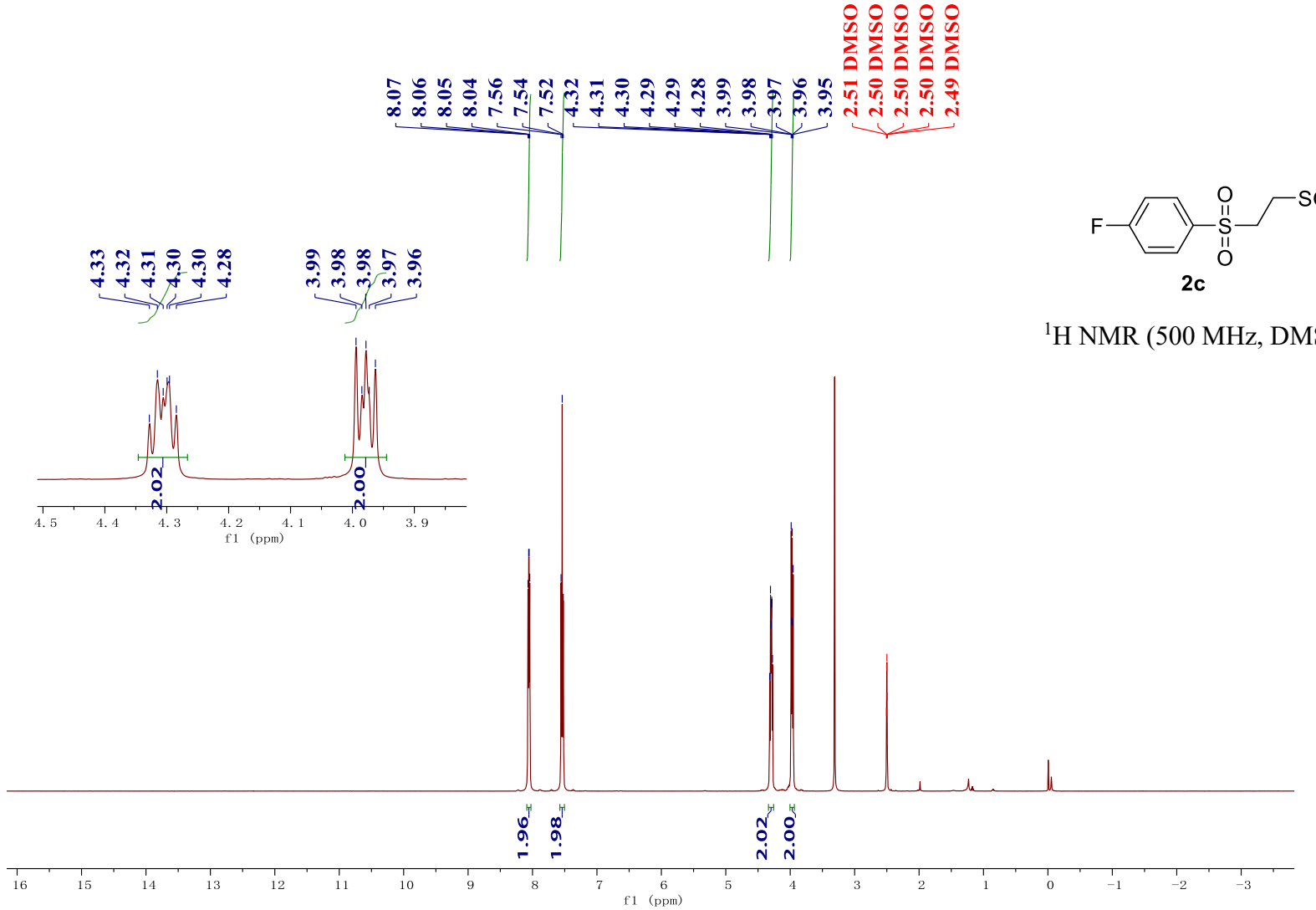
^{13}C NMR (126 MHz, DMSO-d_6)



2b

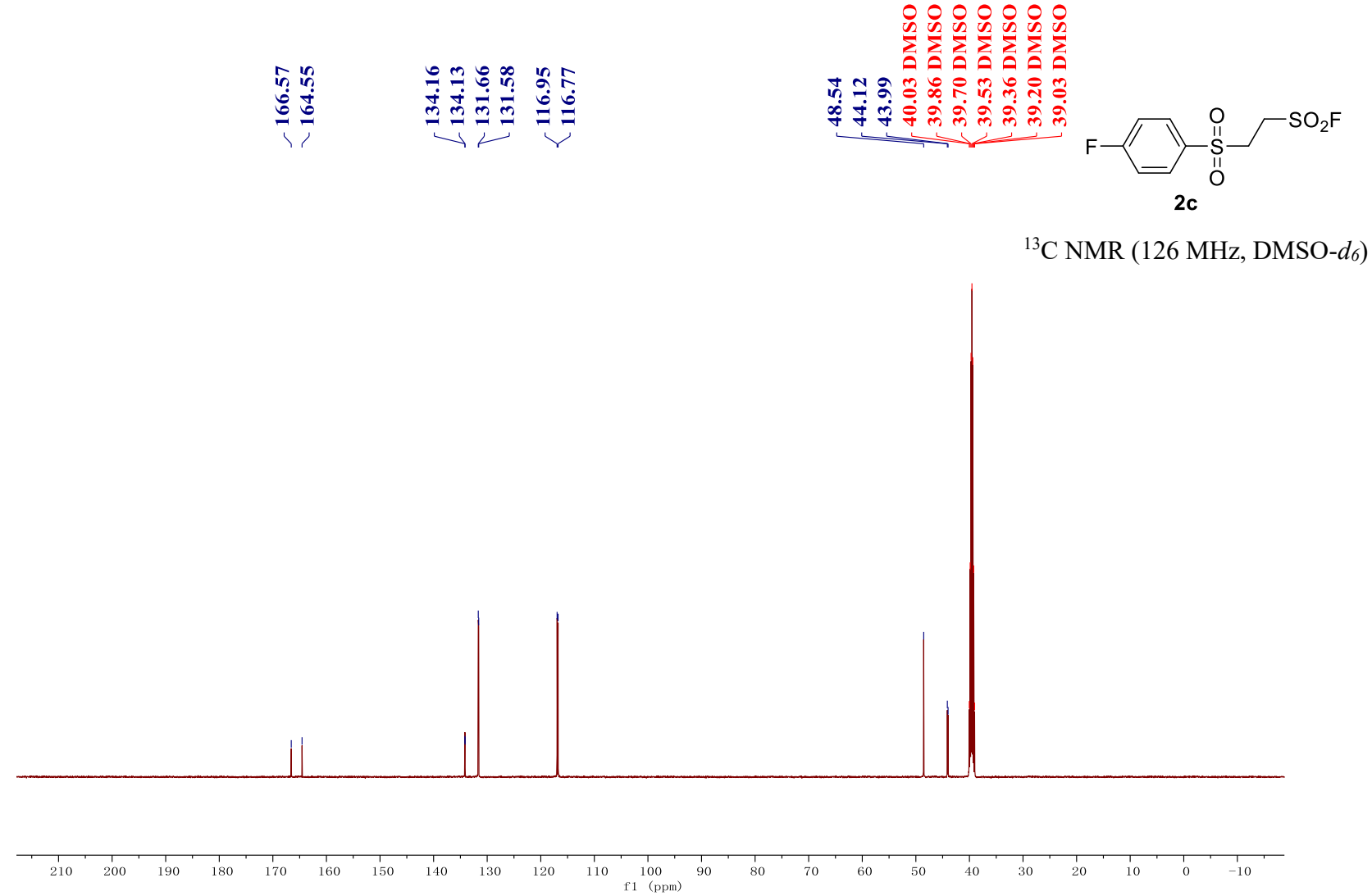
^{19}F NMR (471 MHz, DMSO-d_6)

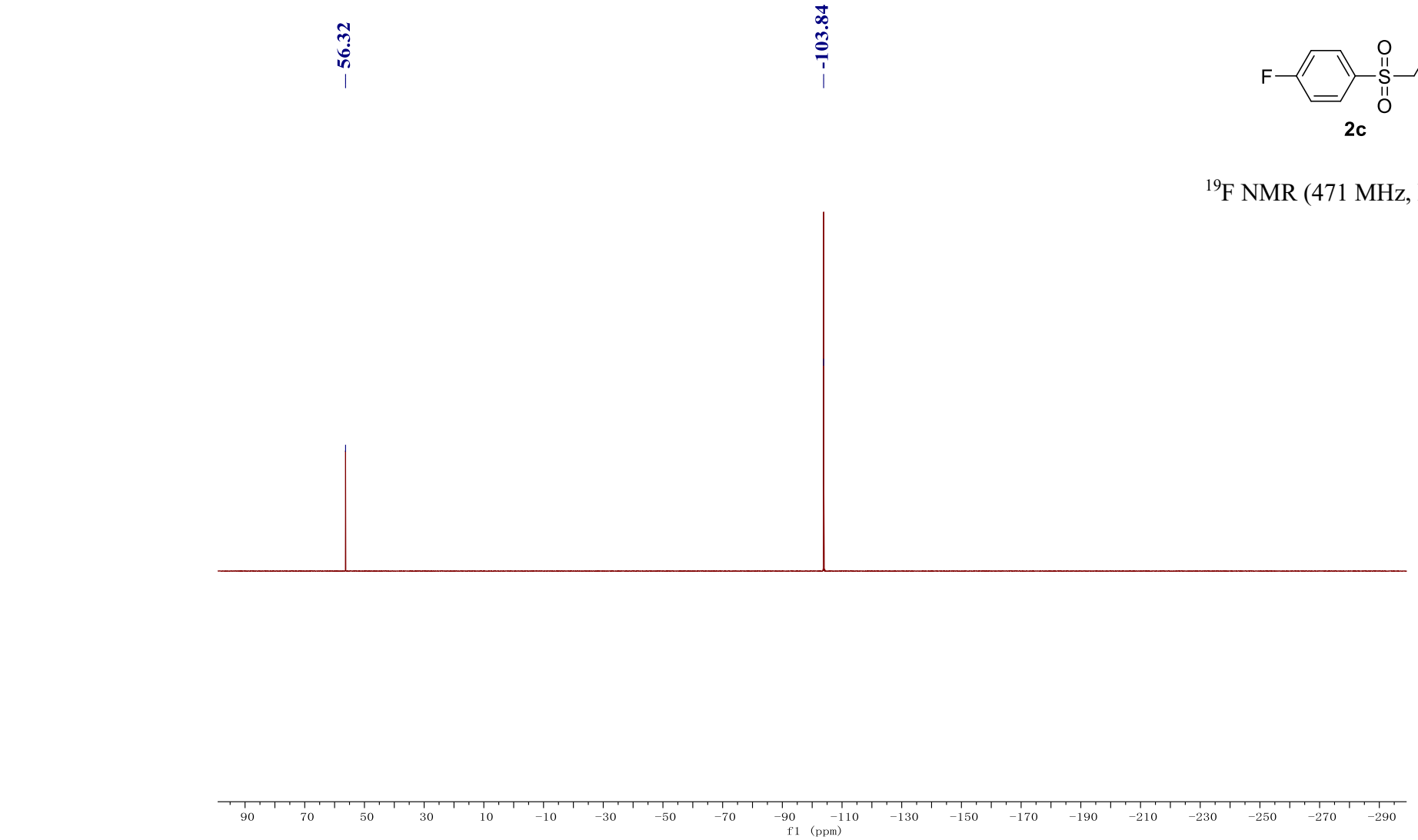




2c

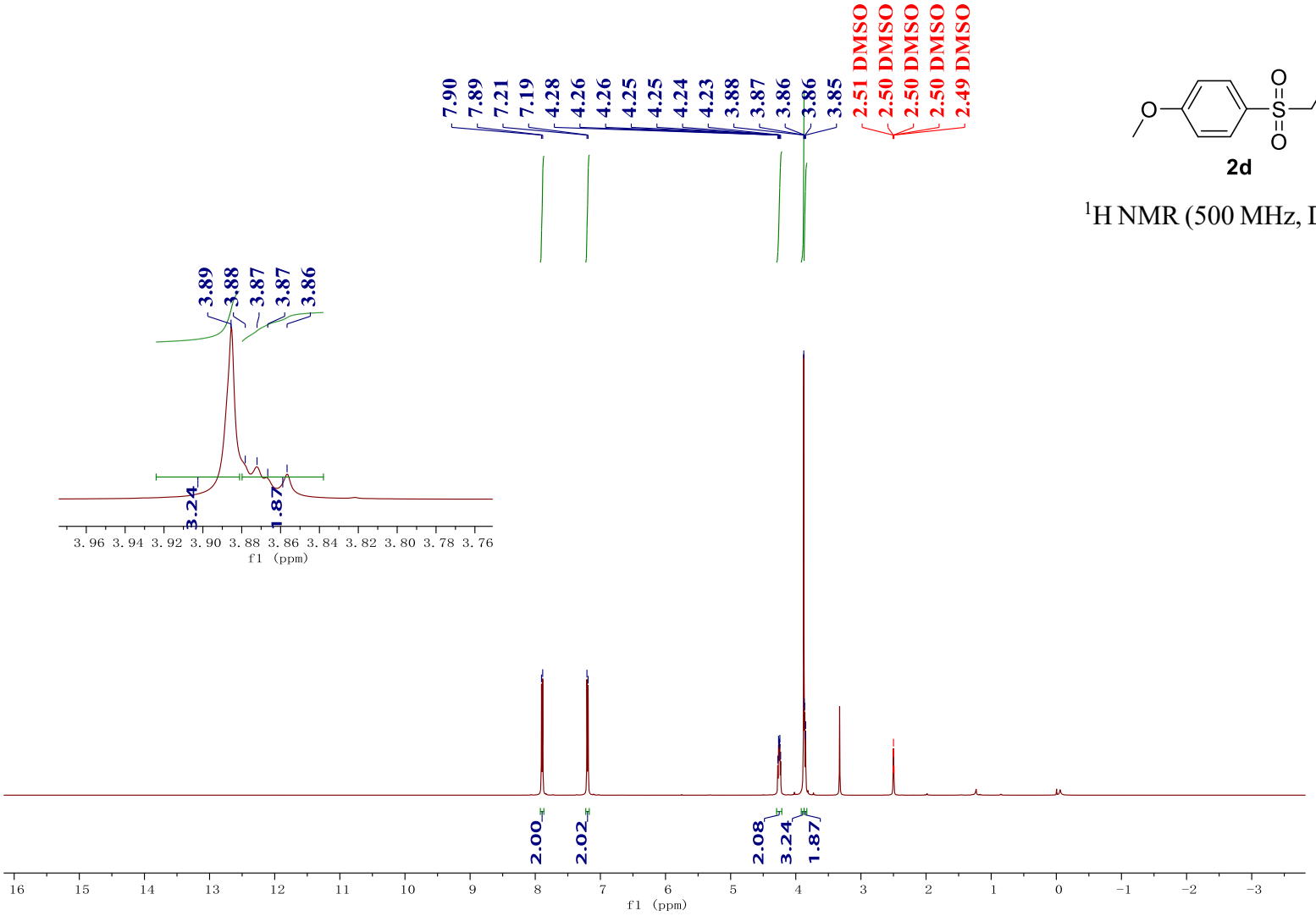
^{1}H NMR (500 MHz, DMSO-*d*$_6$)


166.57
164.55
134.16
134.13
131.66
131.58
116.95
116.77
48.54
44.12
43.99
40.03 DMSO
39.86 DMSO
39.70 DMSO
39.53 DMSO
39.36 DMSO
39.20 DMSO
39.03 DMSO
F
O
S
O
SO2F
2c
13C NMR (126 MHz, DMSO-d6)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



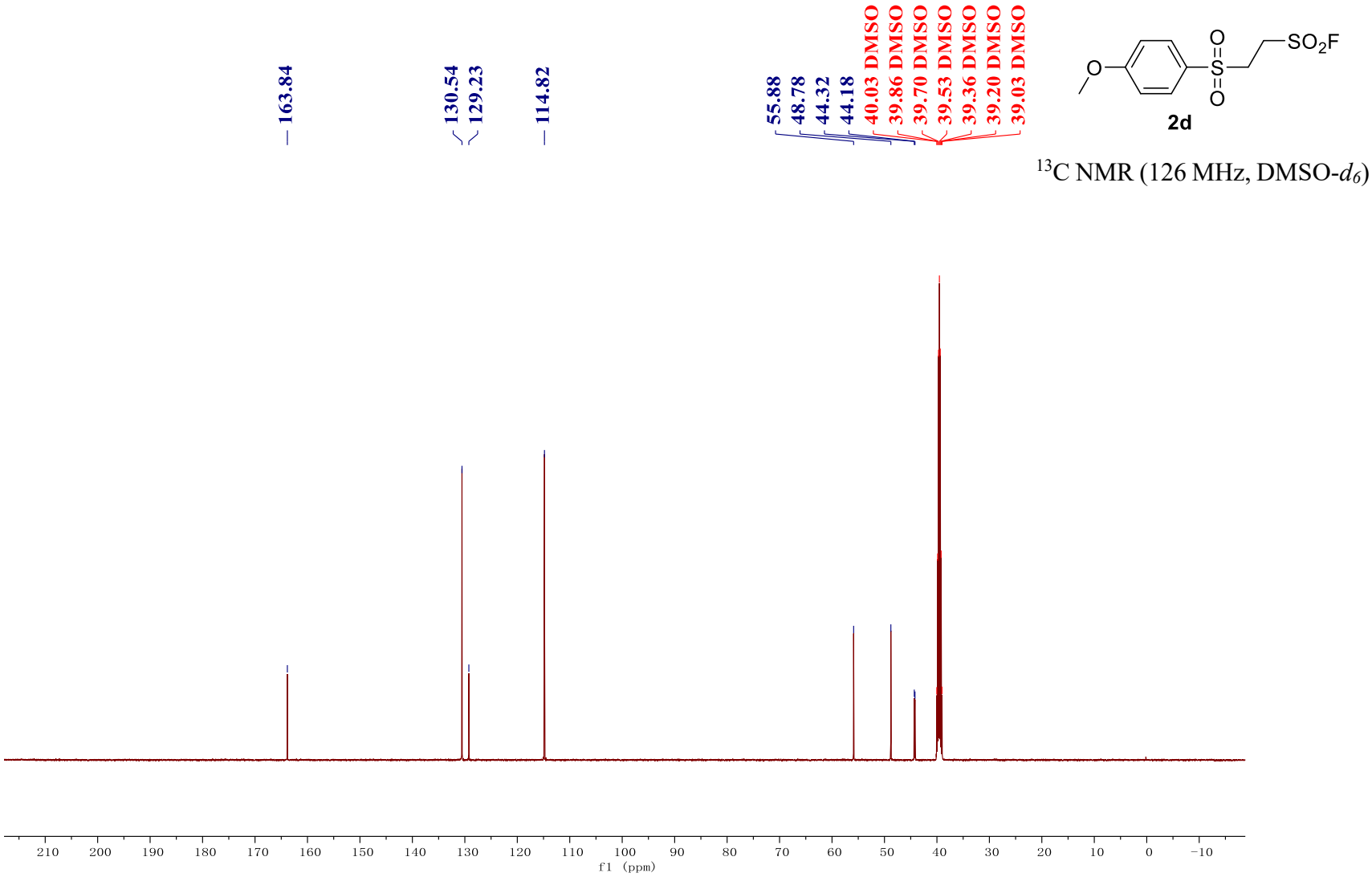
2c

^{19}F NMR (471 MHz, DMSO-*d*$_6$)

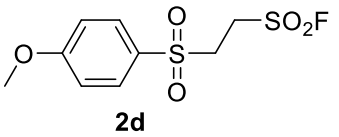


2d

^{1}H NMR (500 MHz, DMSO-d_6)

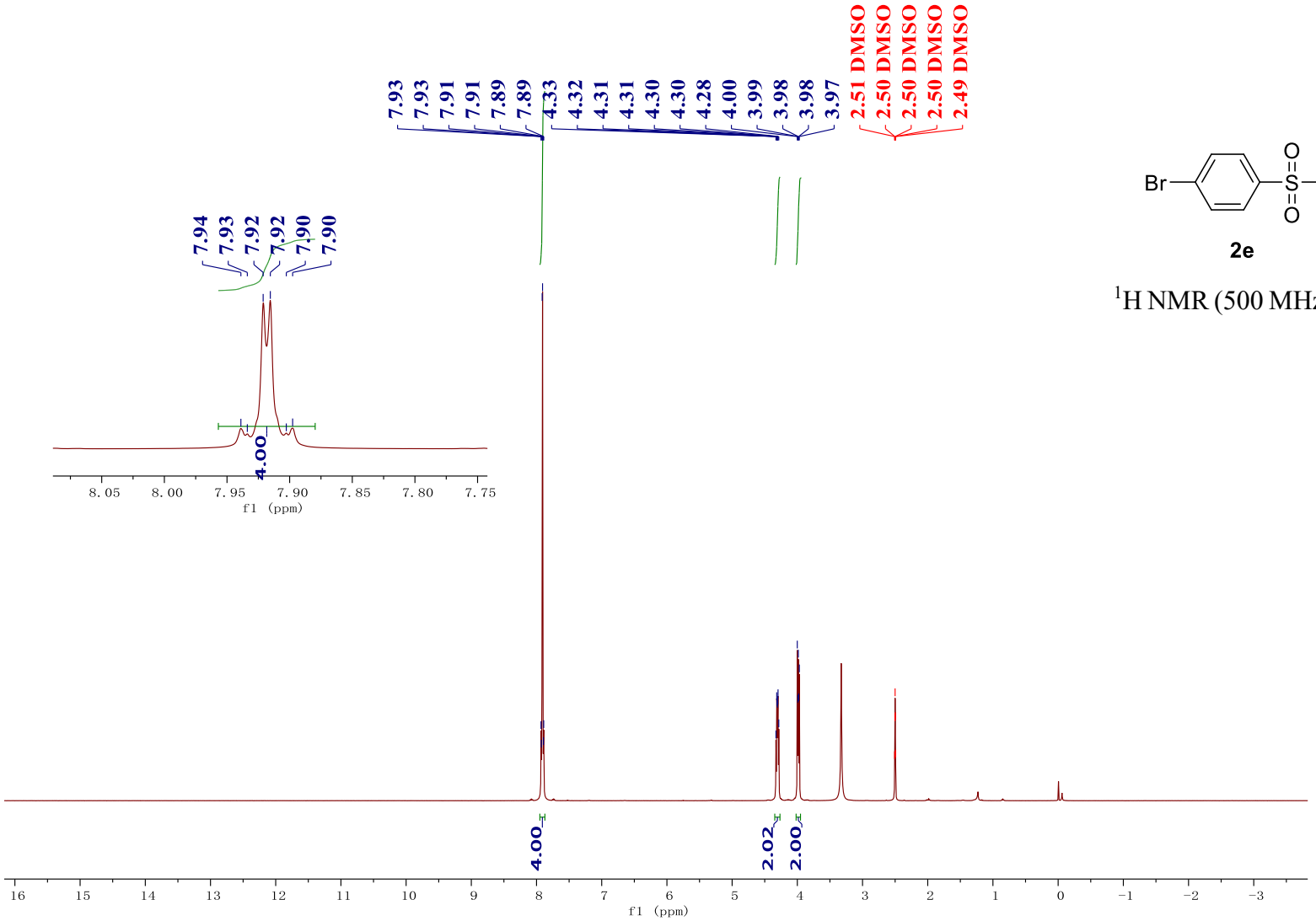


^{13}C NMR (126 MHz, DMSO-d_6)



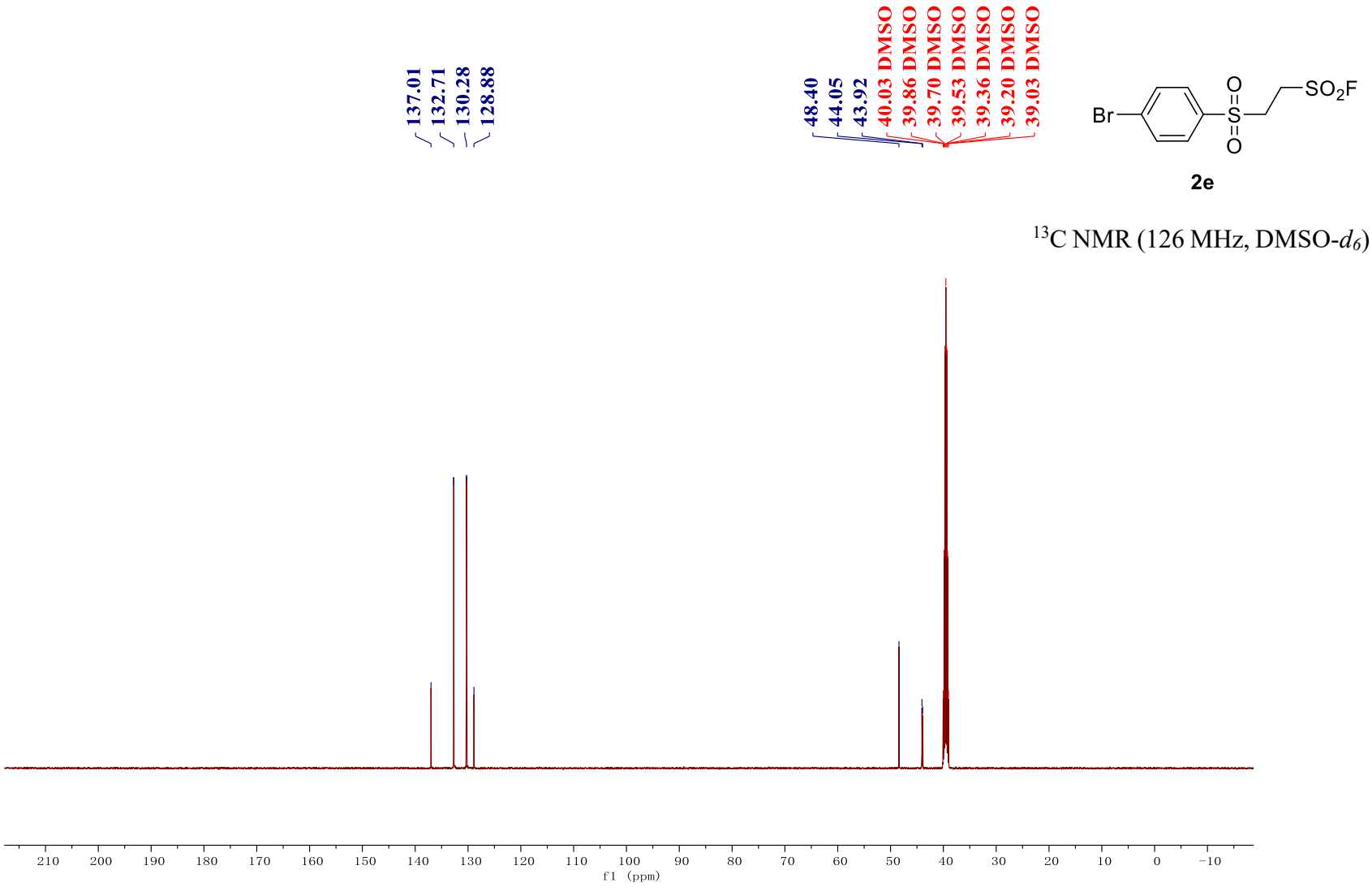
2d

^{19}F NMR (471 MHz, DMSO-d_6)



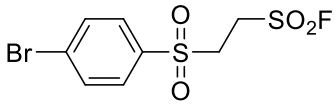
2e

^{1}H NMR (500 MHz, DMSO-d_6)



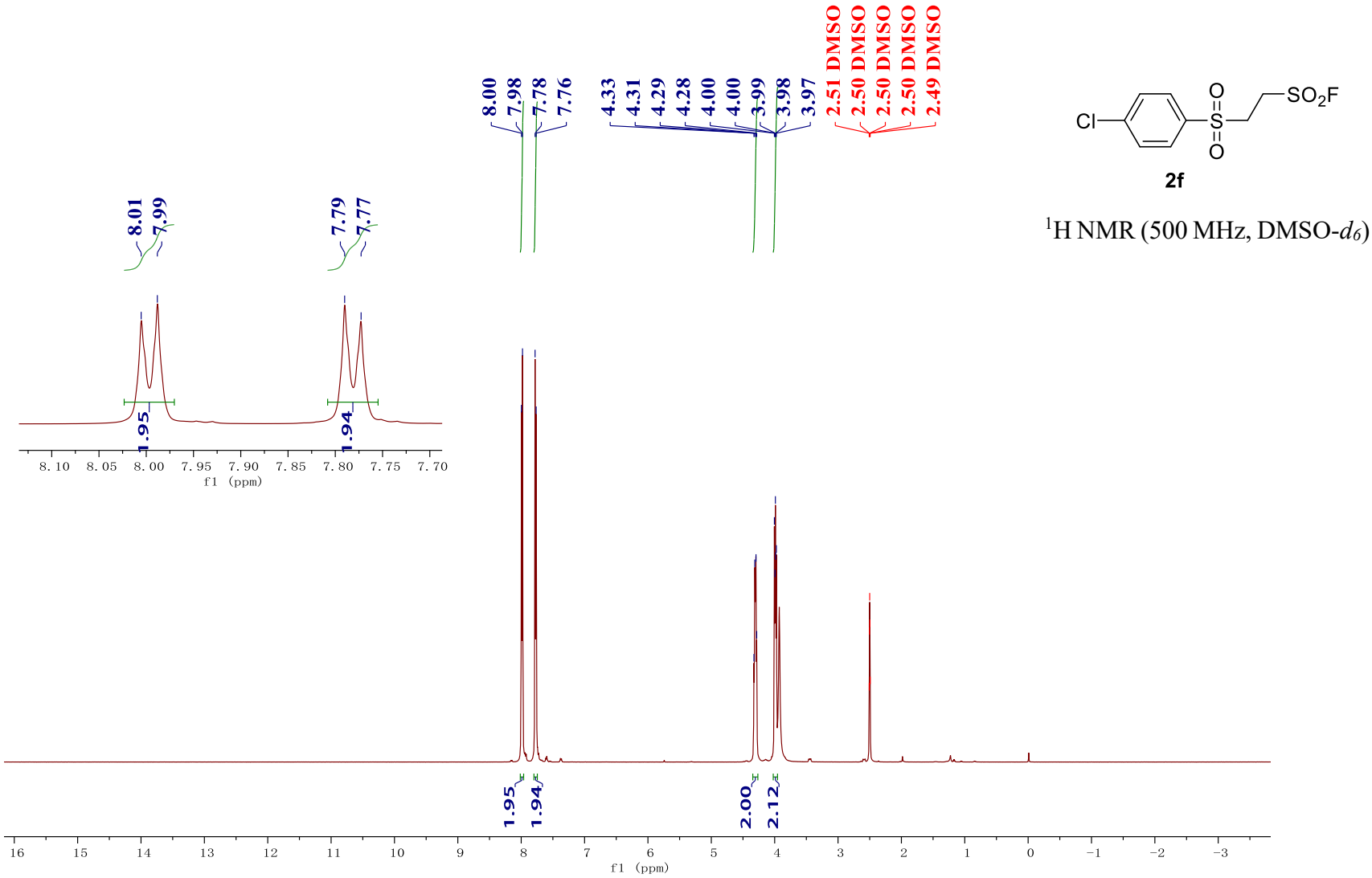
2e

^{13}C NMR (126 MHz, DMSO-d_6)



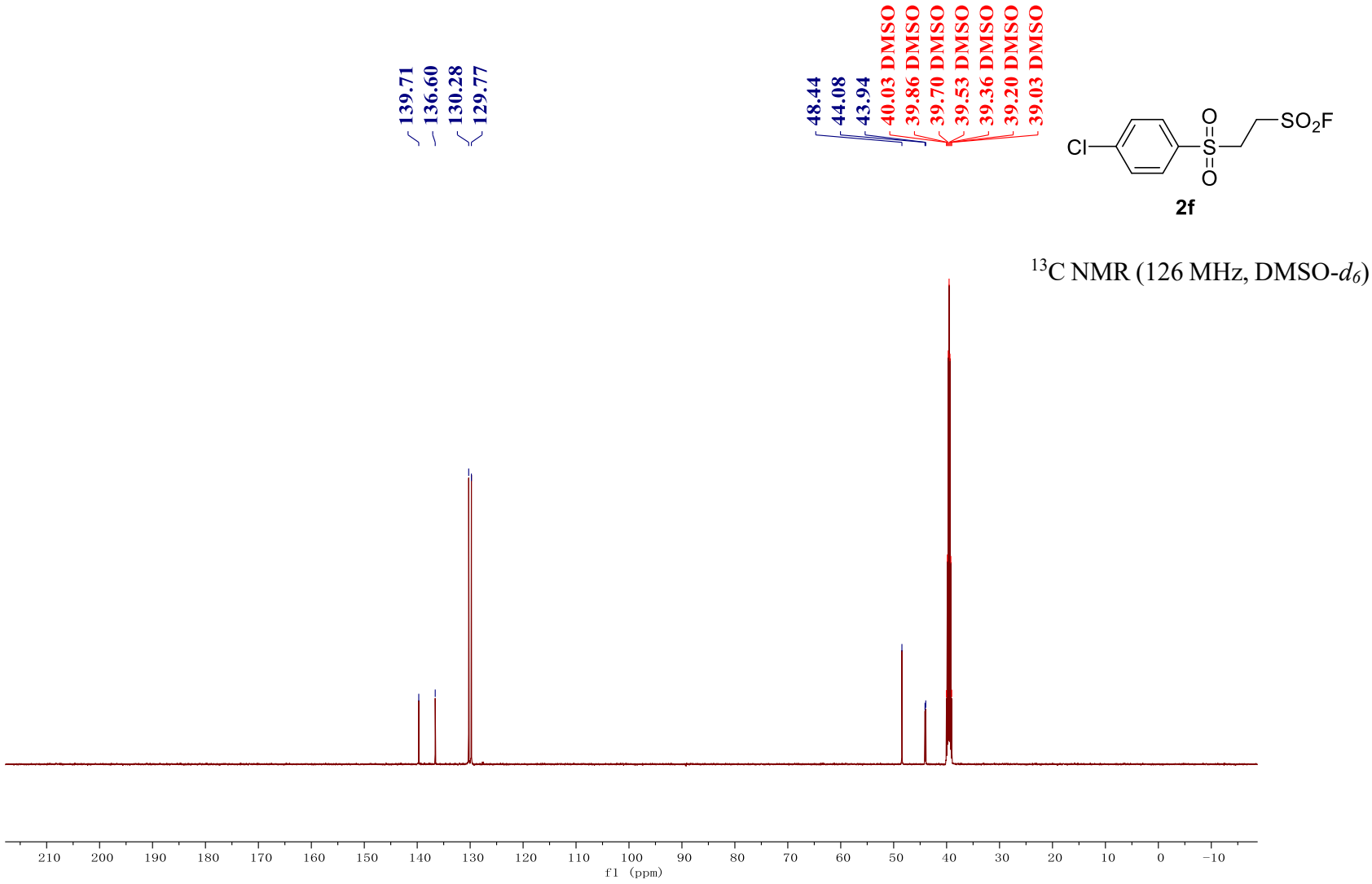
2e

^{19}F NMR (471 MHz, DMSO-d_6)

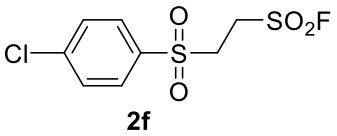


2f

^{1}H NMR (500 MHz, DMSO-d_6)

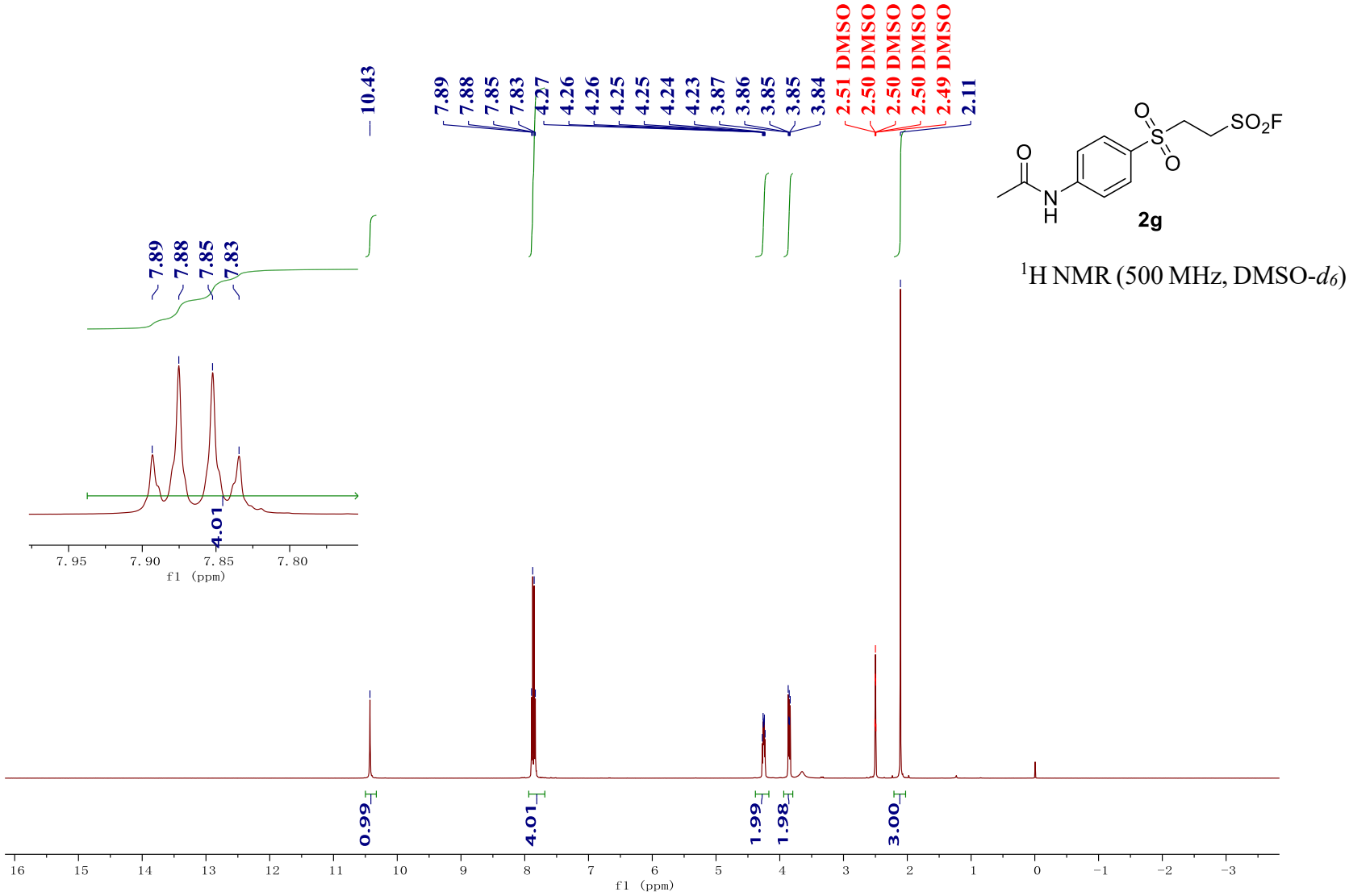


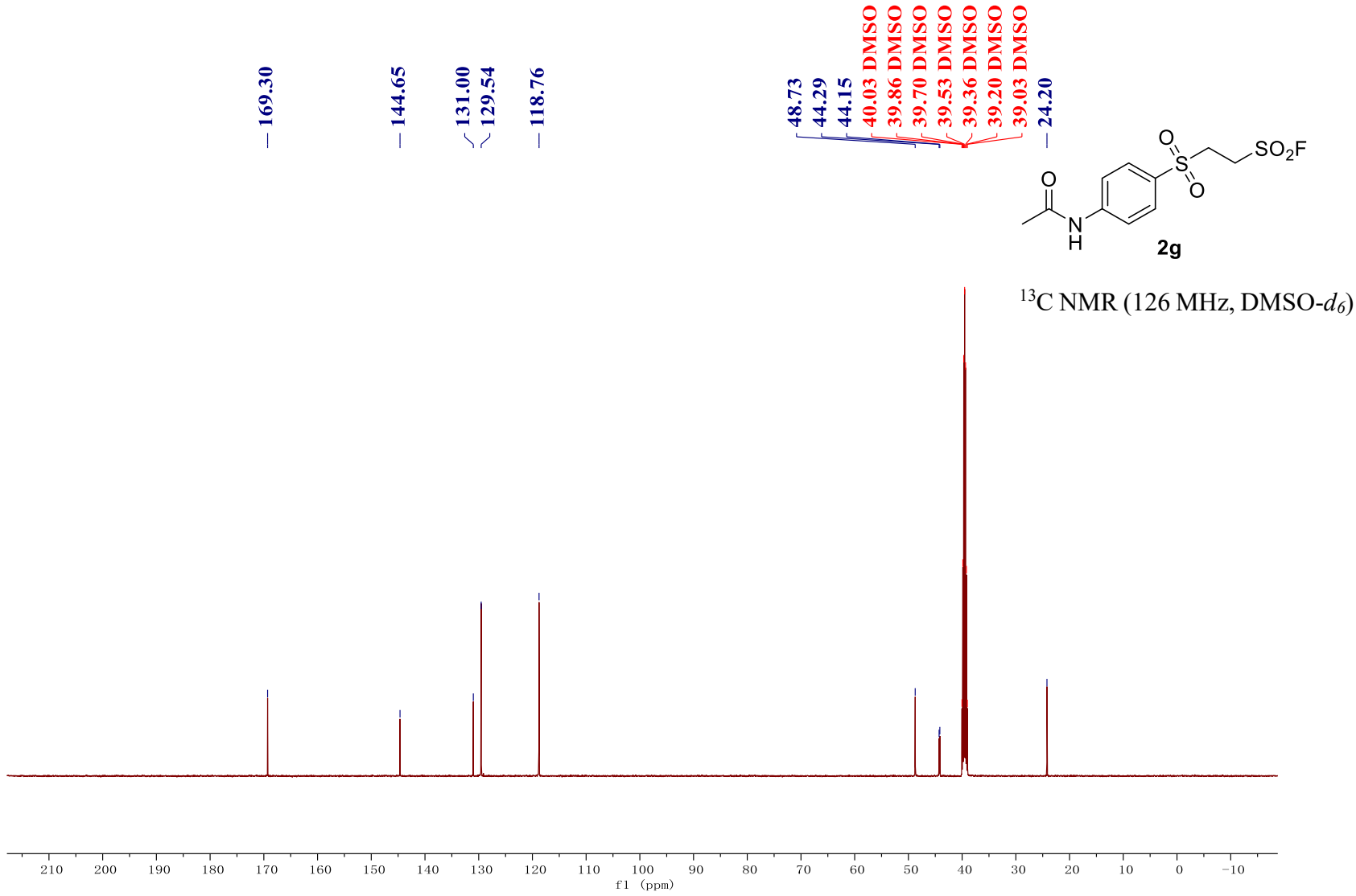
^{13}C NMR (126 MHz, DMSO-d_6)

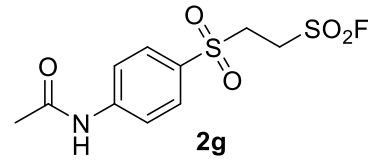


2f

^{19}F NMR (471 MHz, DMSO-d_6)

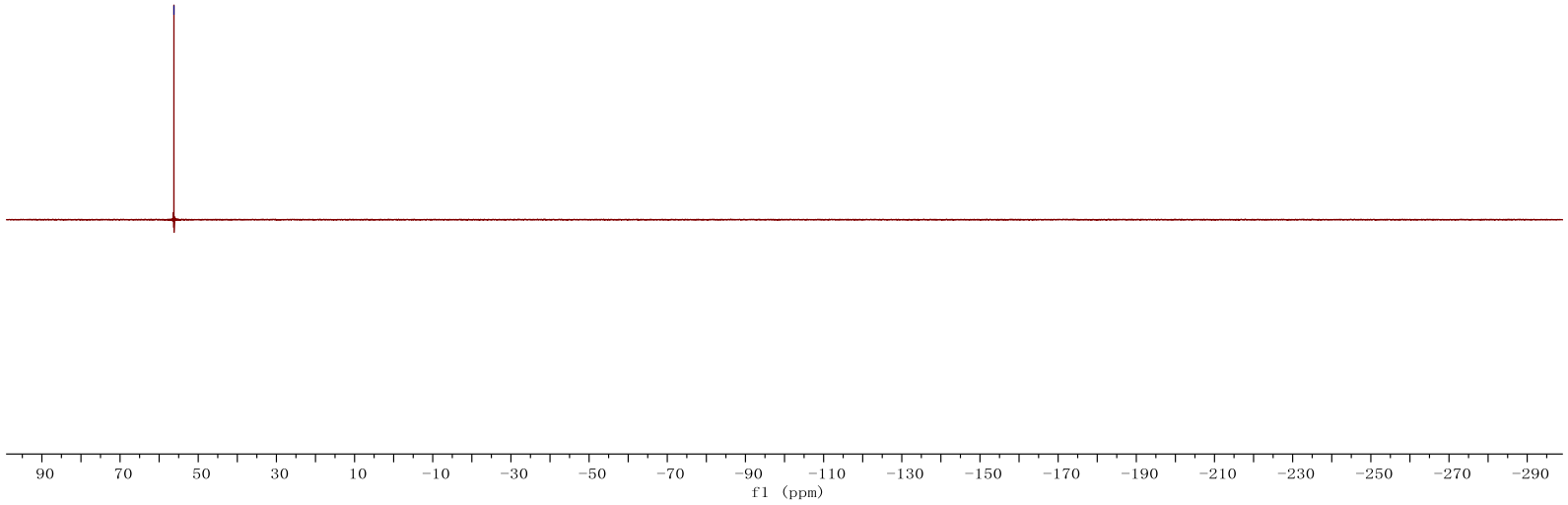

10.43
7.89
7.88
7.85
7.83
4.27
4.26
4.26
4.25
4.25
4.24
4.23
3.87
3.86
3.85
3.85
3.84
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
2.11
O
S
O
SO2F
O
N
H
2g
1H NMR (500 MHz, DMSO-d6)
4.01
7.95
7.90
7.85
7.80
f1 (ppm)
0.99
4.01
1.99
1.98
3.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
f1 (ppm)

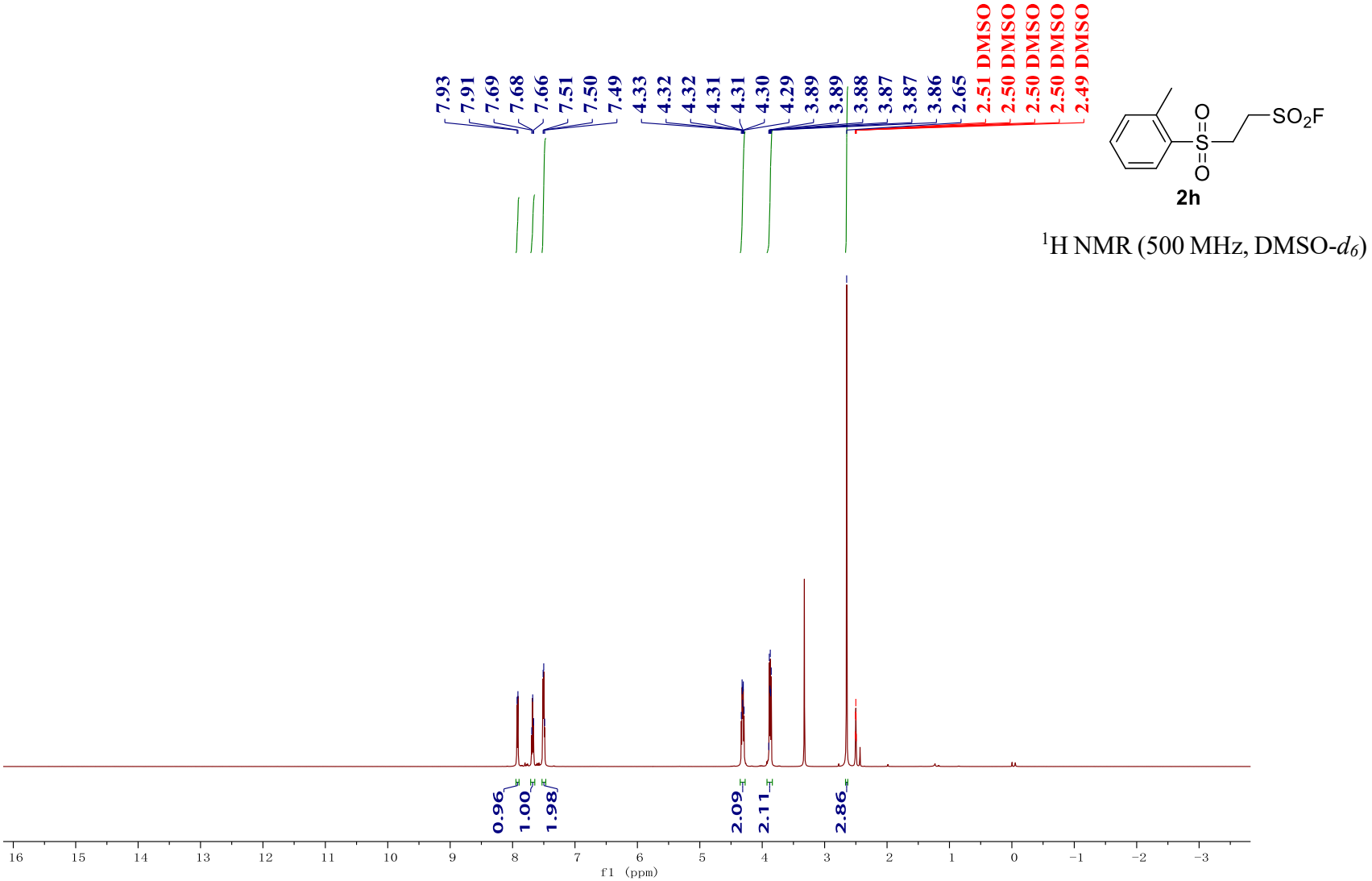

169.30
144.65
131.00
129.54
118.76
48.73
44.29
44.15
40.03 DMSO
39.86 DMSO
39.70 DMSO
39.53 DMSO
39.36 DMSO
39.20 DMSO
39.03 DMSO
24.20
O
S
O
SO2F
O
N
H
2g
13C NMR (126 MHz, DMSO-d6)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



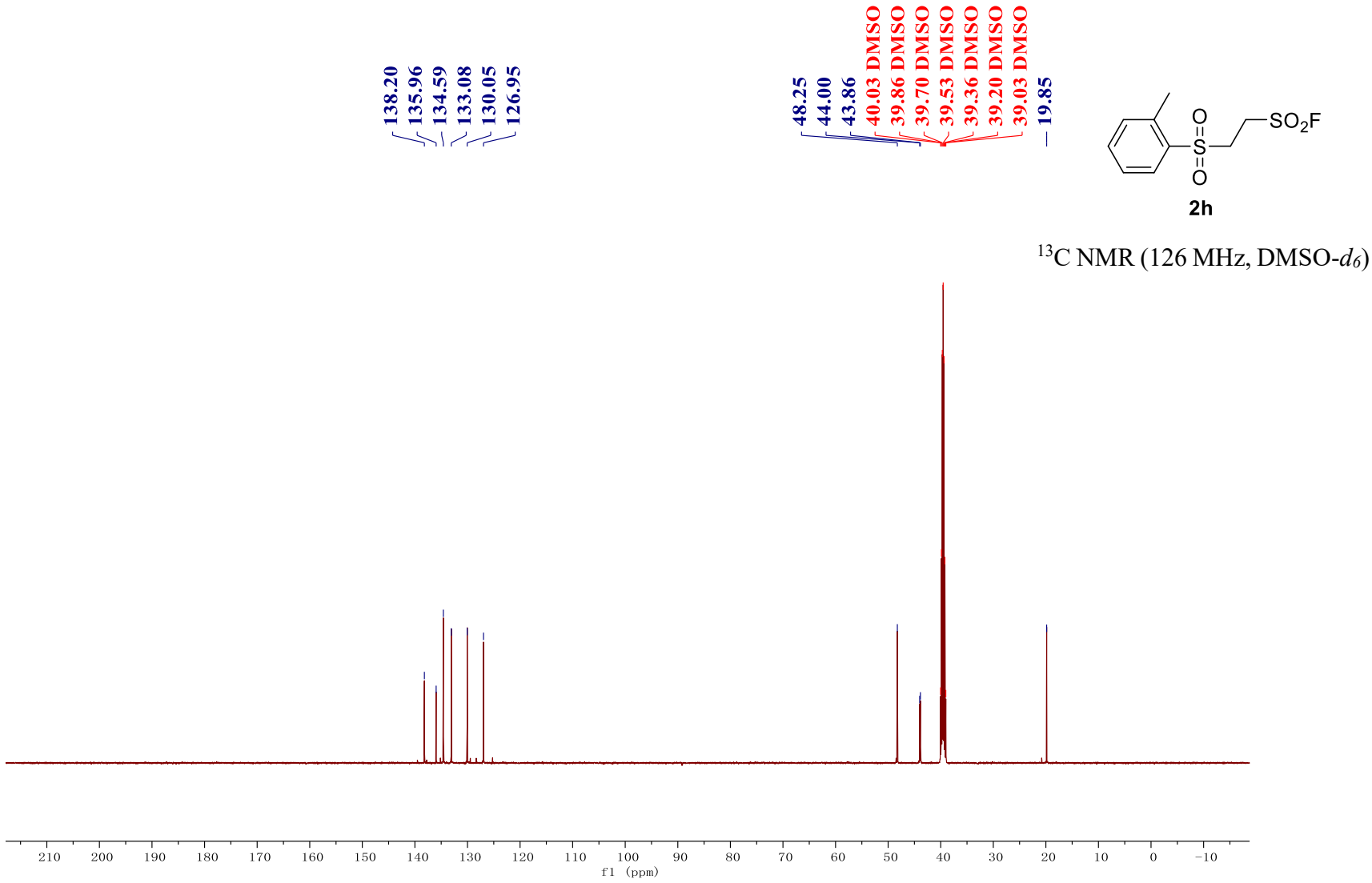
2g

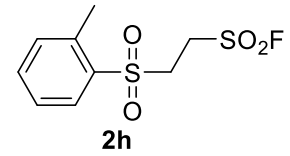
^{19}F NMR (471 MHz, DMSO-d_6)





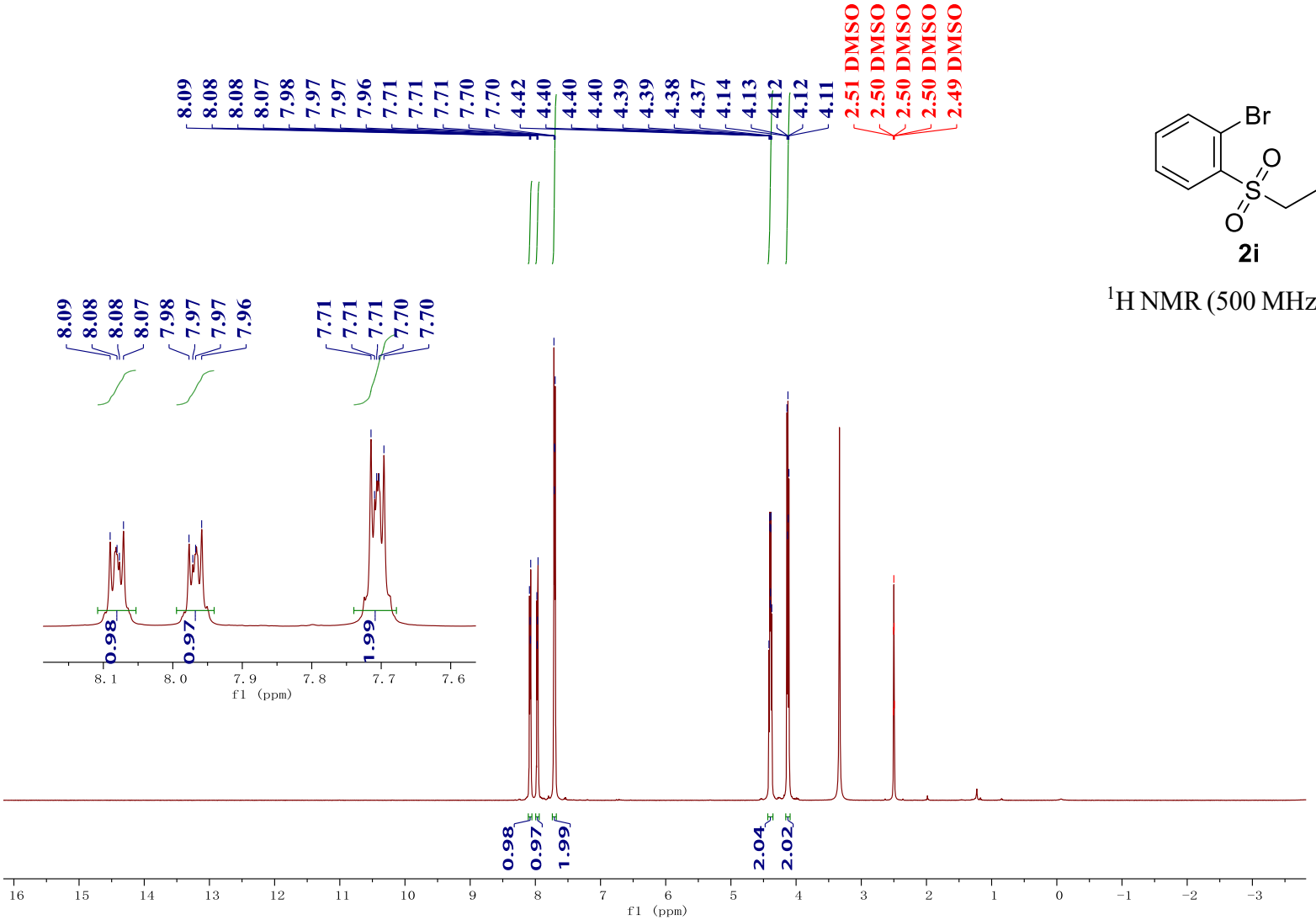
^{1}H NMR (500 MHz, DMSO-d_6)


138.20
135.96
134.59
133.08
130.05
126.95
48.25
44.00
43.86
40.03 DMSO
39.86 DMSO
39.70 DMSO
39.53 DMSO
39.36 DMSO
39.20 DMSO
39.03 DMSO
19.85
O
S
O
SO2F
2h
13C NMR (126 MHz, DMSO-d6)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



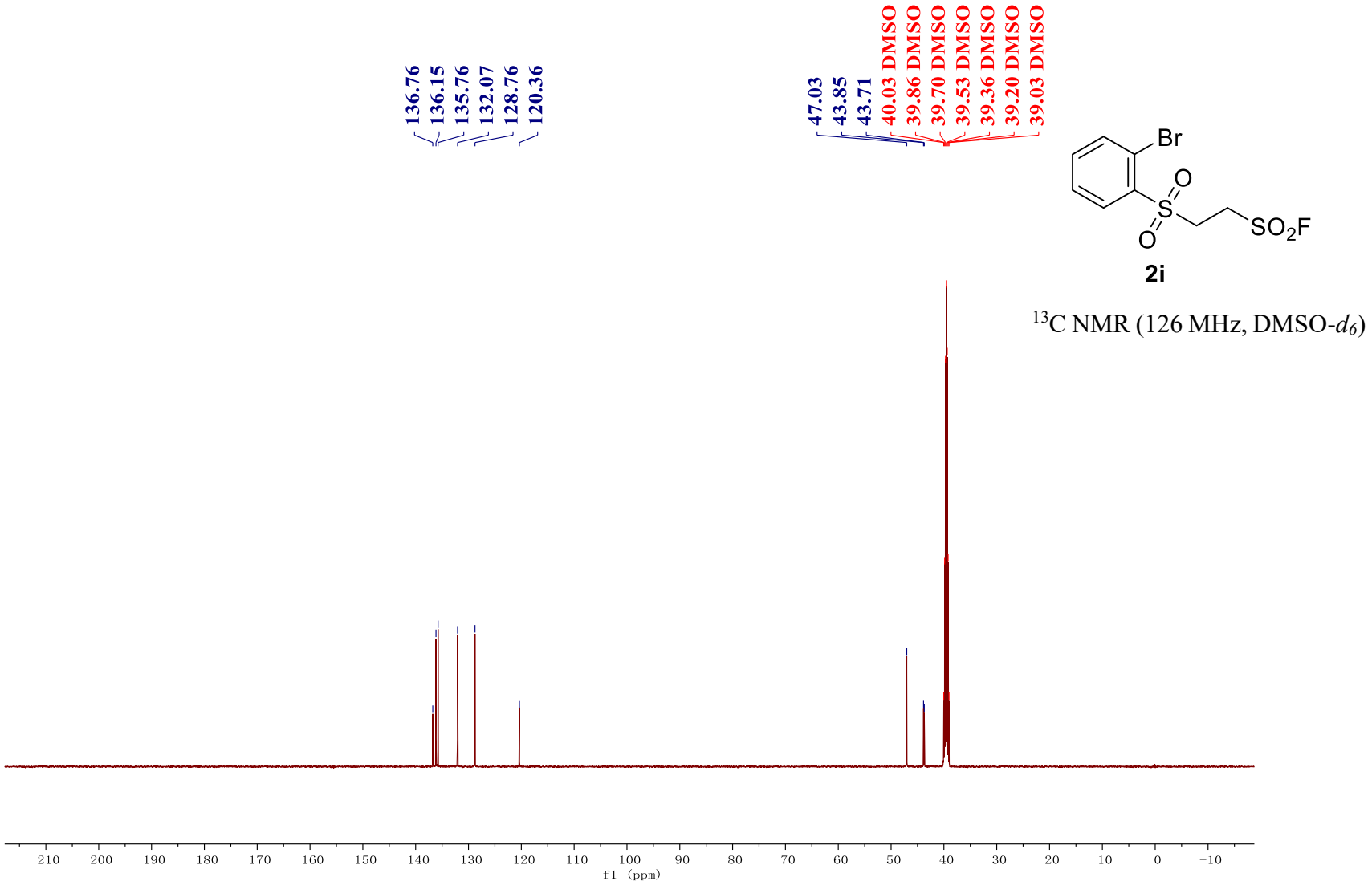
2h

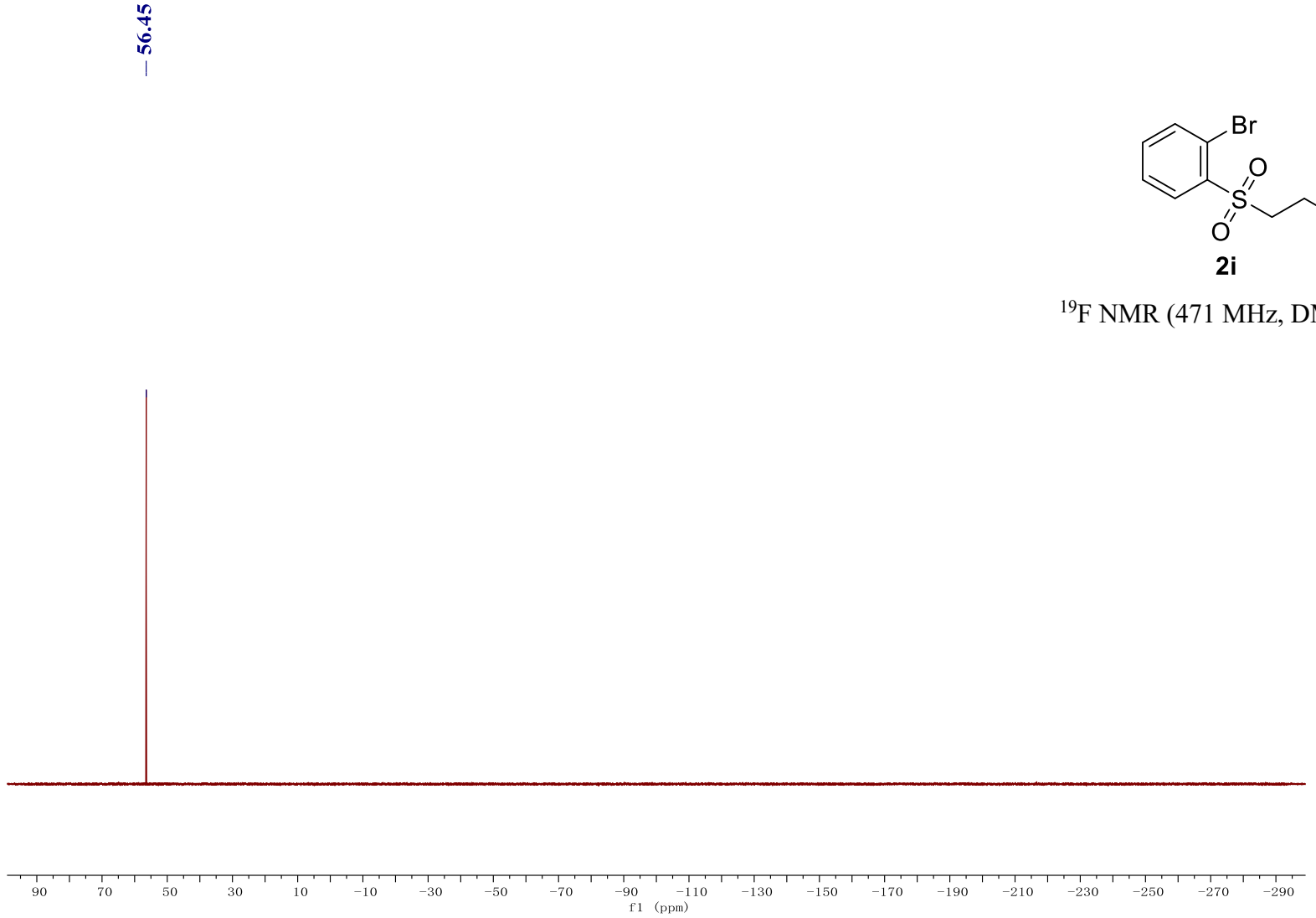
^{19}F NMR (471 MHz, DMSO-d_6)



2i

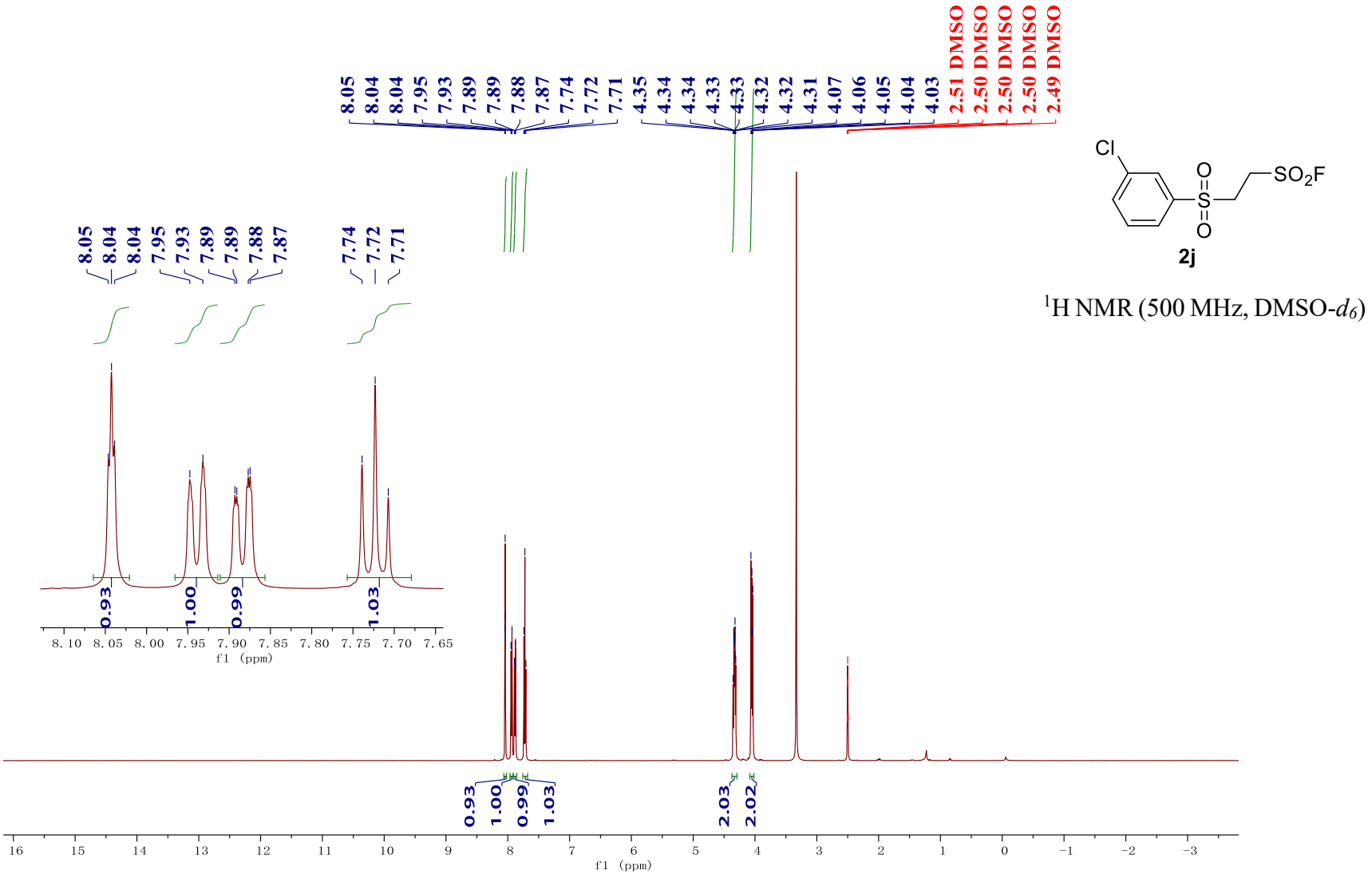
^{1}H NMR (500 MHz, DMSO-d_6)

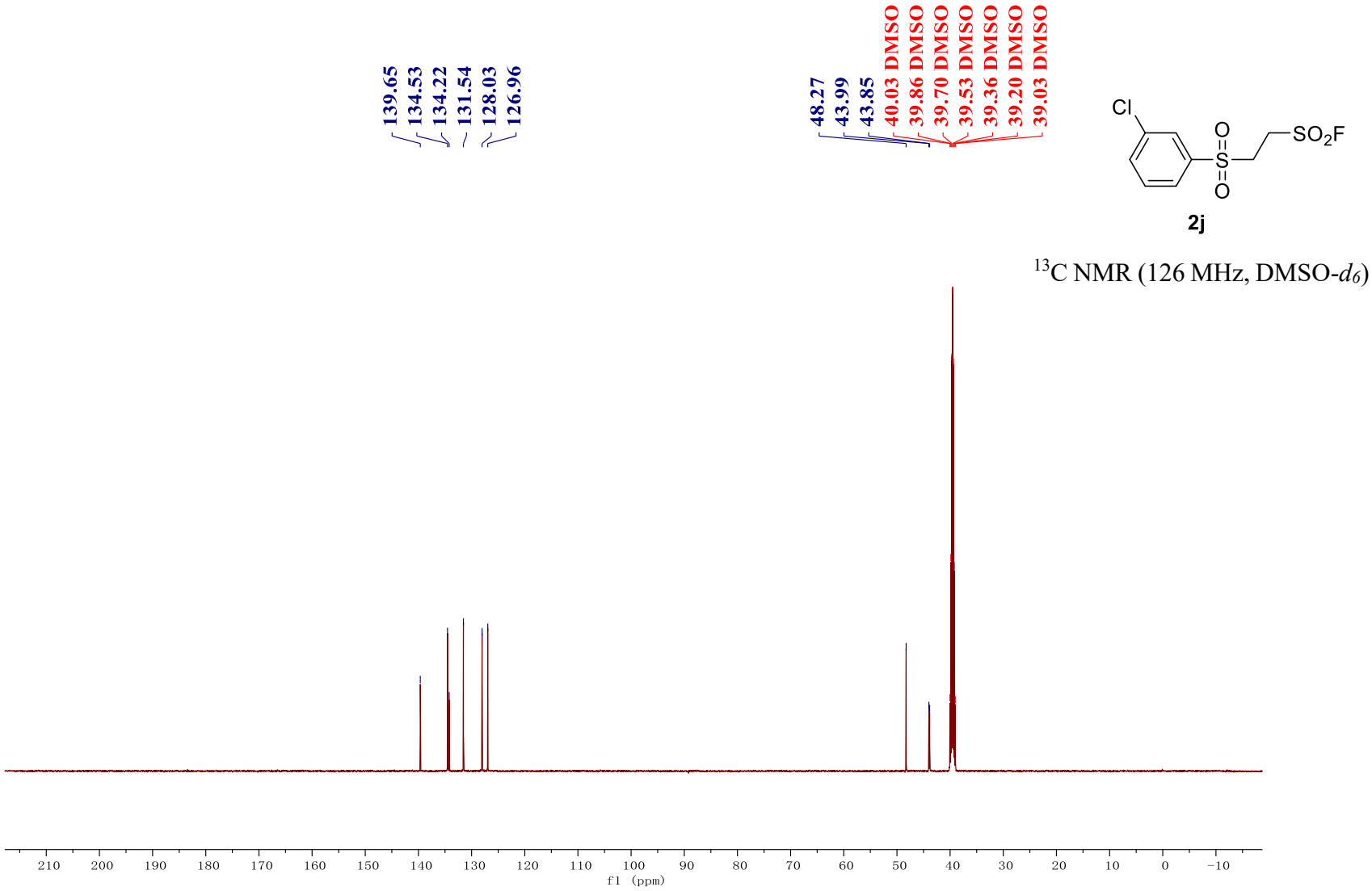

136.76
136.15
135.76
132.07
128.76
120.36
47.03
43.85
43.71
40.03 DMSO
39.86 DMSO
39.70 DMSO
39.53 DMSO
39.36 DMSO
39.20 DMSO
39.03 DMSO
Br
O
S
O
SO2F
2i
13C NMR (126 MHz, DMSO-d6)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

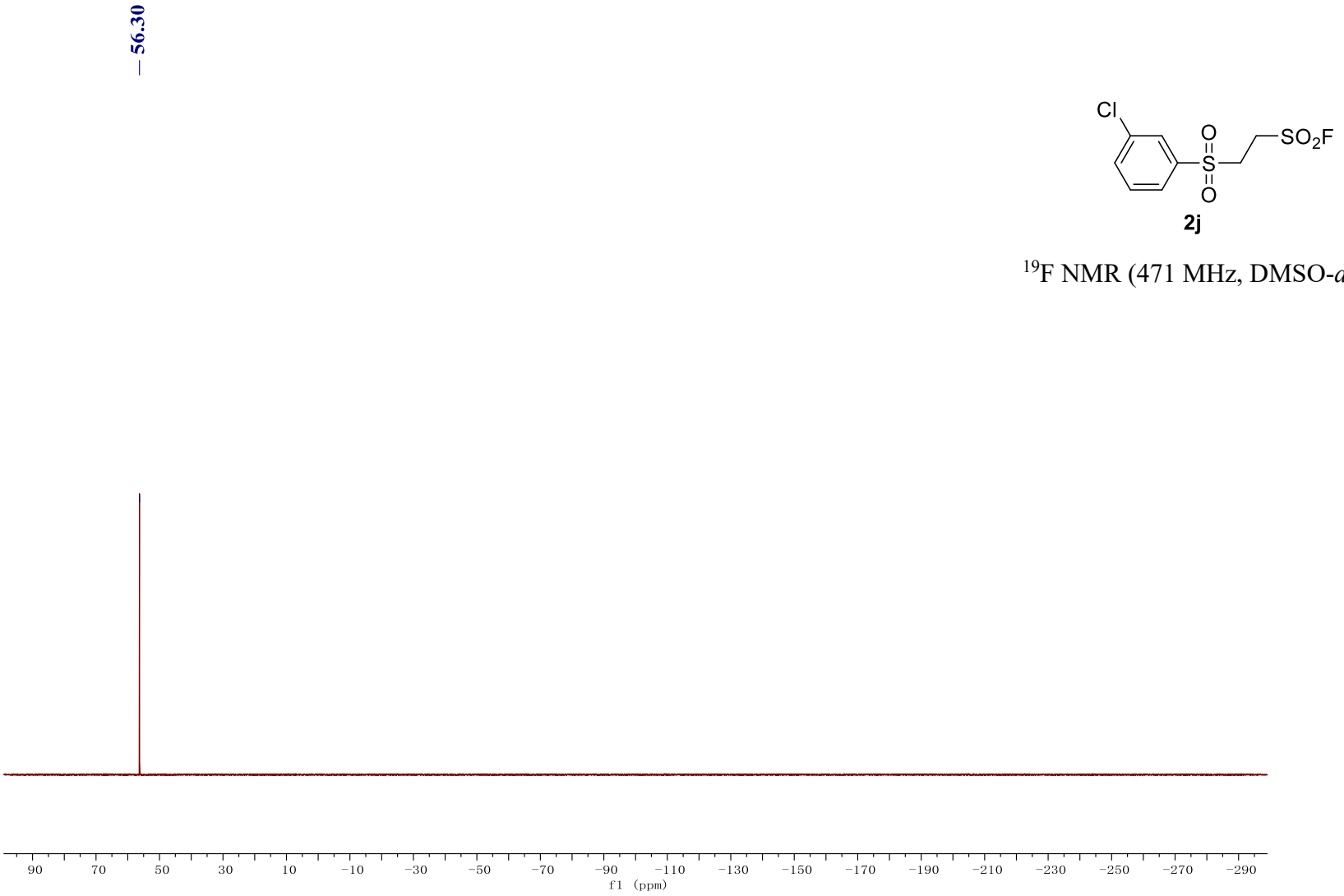


2i

^{19}F NMR (471 MHz, DMSO-d_6)

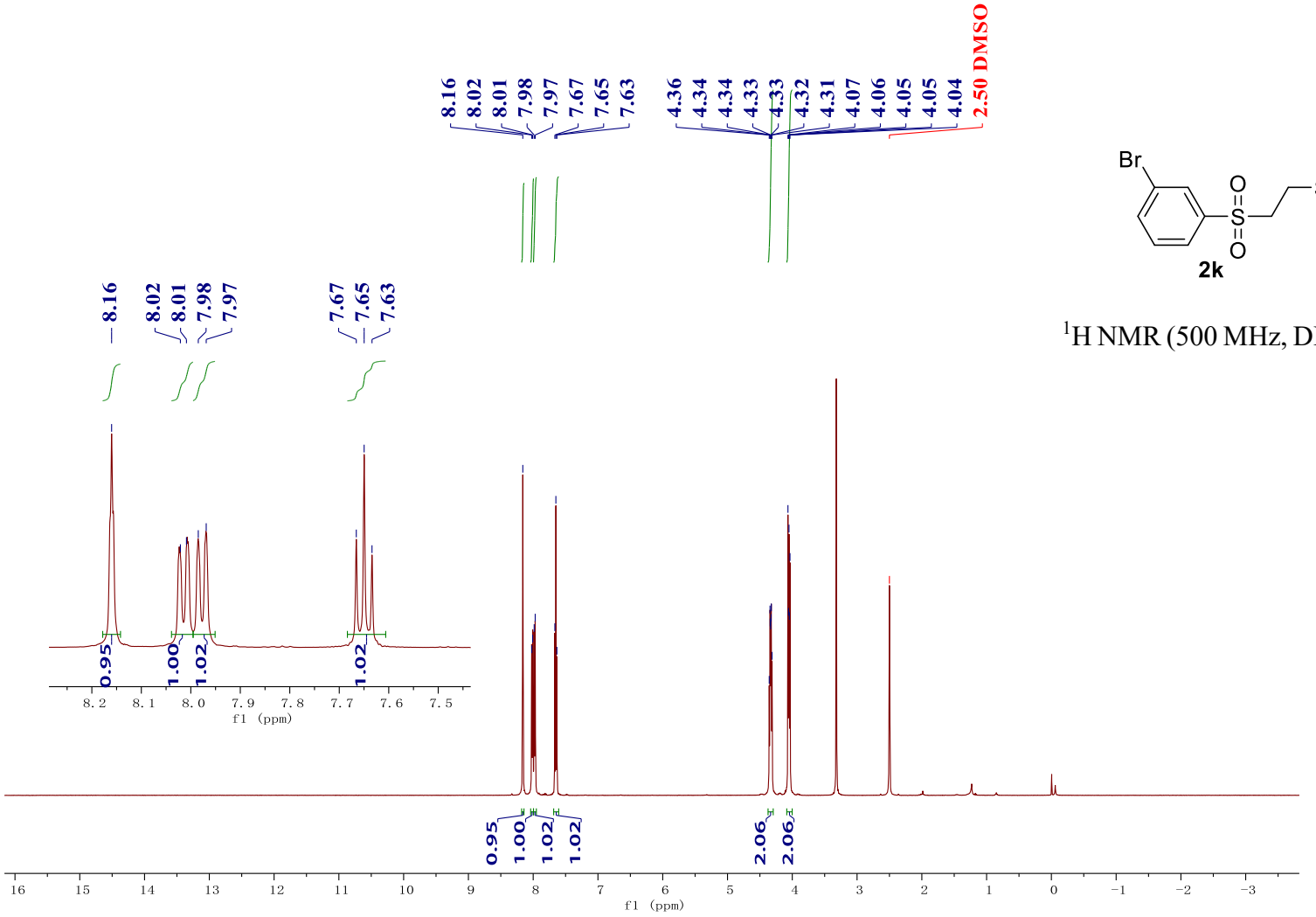

8.05 8.04 8.04 7.95 7.93 7.89 7.89 7.88 7.87 7.74 7.72 7.71 4.35 4.34 4.34 4.33 4.33 4.32 4.32 4.31 4.07 4.06 4.05 4.04 4.03 2.51 DMSO 2.50 DMSO 2.50 DMSO 2.50 DMSO 2.49 DMSO
0.93 1.00 0.99 1.03 2.03 2.02
f1 (ppm)
Cl
SO2F
2j
1H NMR (500 MHz, DMSO-d6)


139.65
134.53
134.22
131.54
128.03
126.96
48.27
43.99
43.85
40.03 DMSO
39.86 DMSO
39.70 DMSO
39.53 DMSO
39.36 DMSO
39.20 DMSO
39.03 DMSO
Cl
O
S
O
SO2F
2j
13C NMR (126 MHz, DMSO-d6)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

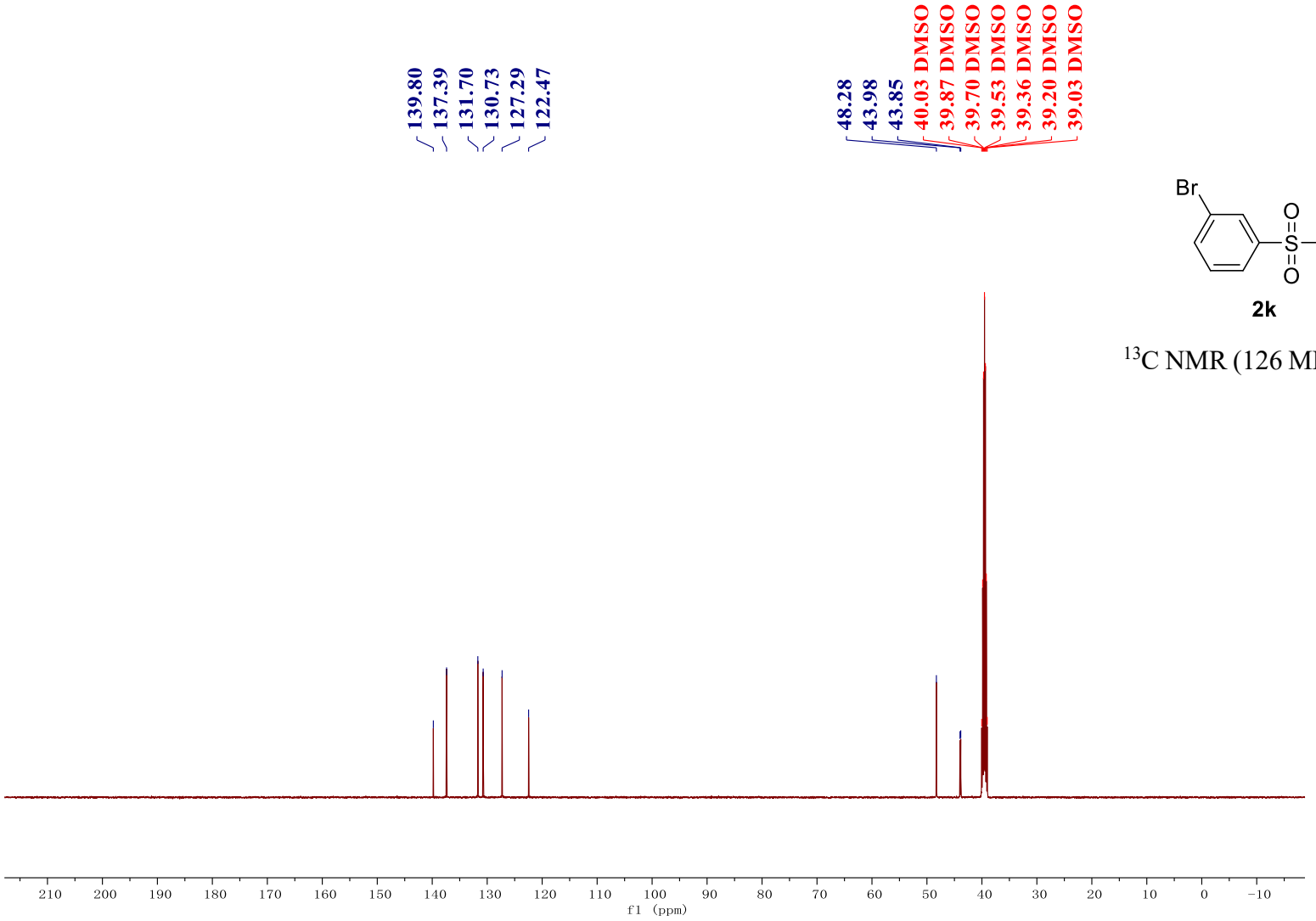


2j

^{19}F NMR (471 MHz, DMSO-d_6)

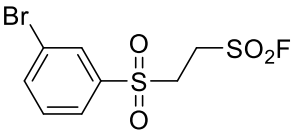


^{1}H NMR (500 MHz, DMSO-d_6)



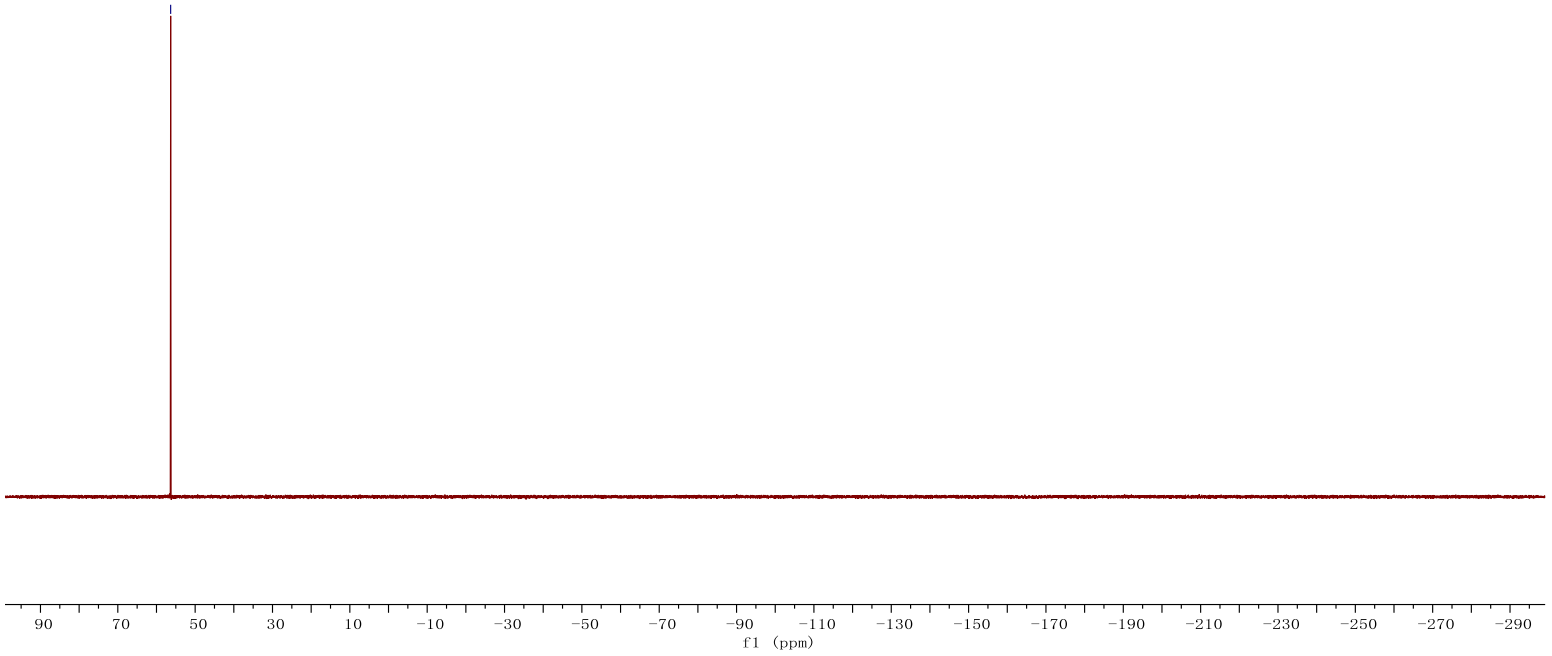
2k

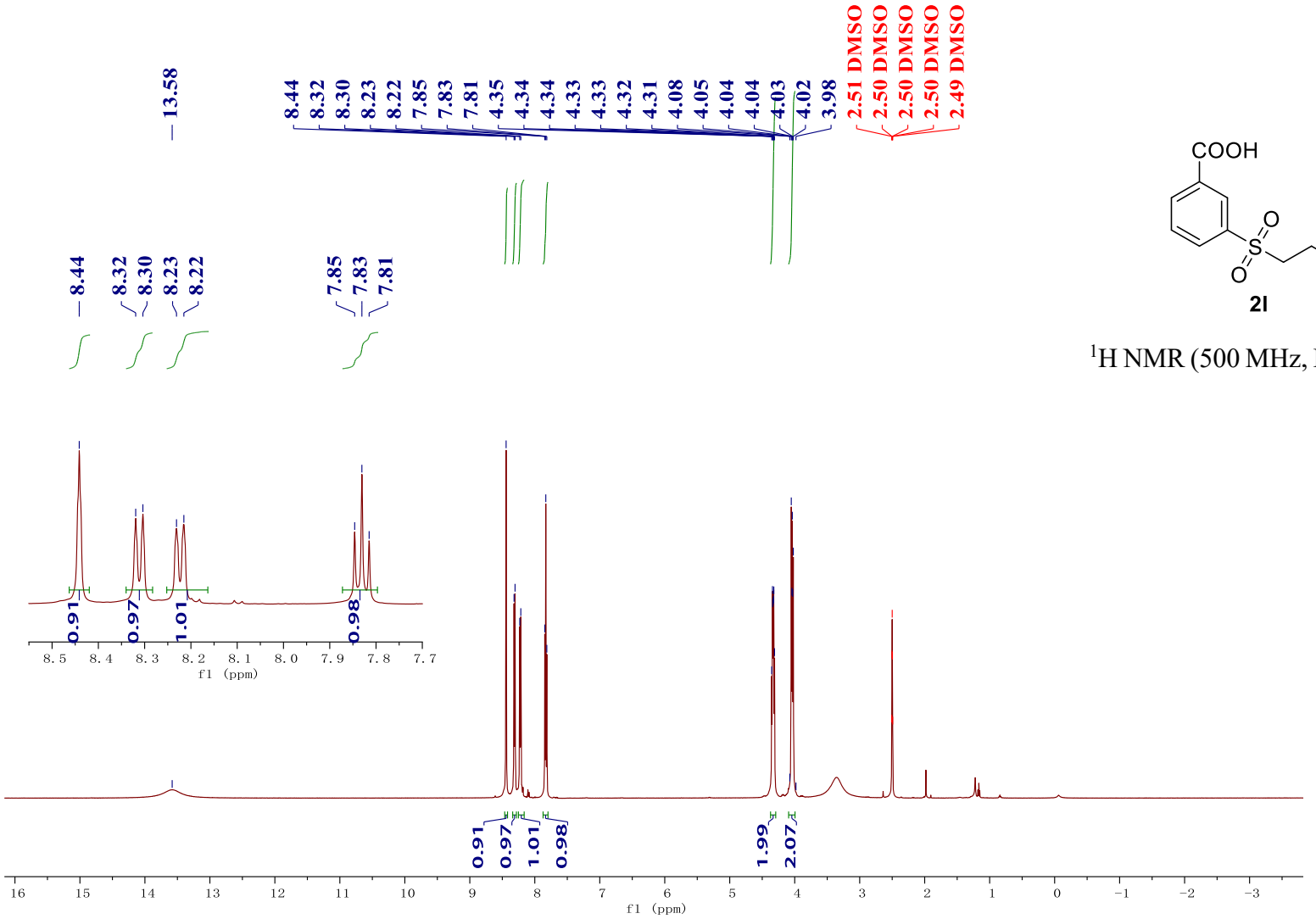
^{13}C NMR (126 MHz, DMSO-d_6)



2k

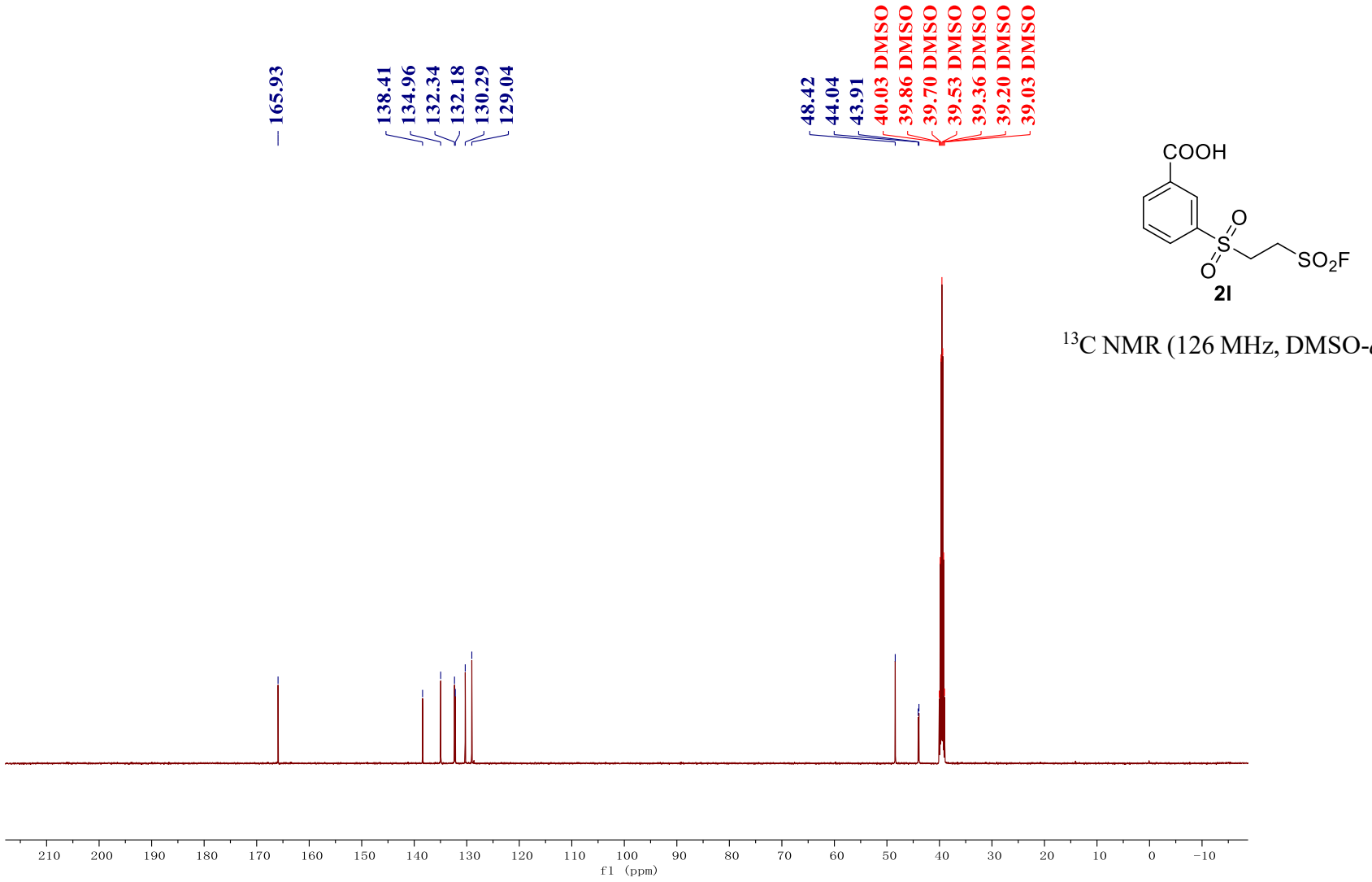
^{19}F NMR (471 MHz, DMSO-d_6)





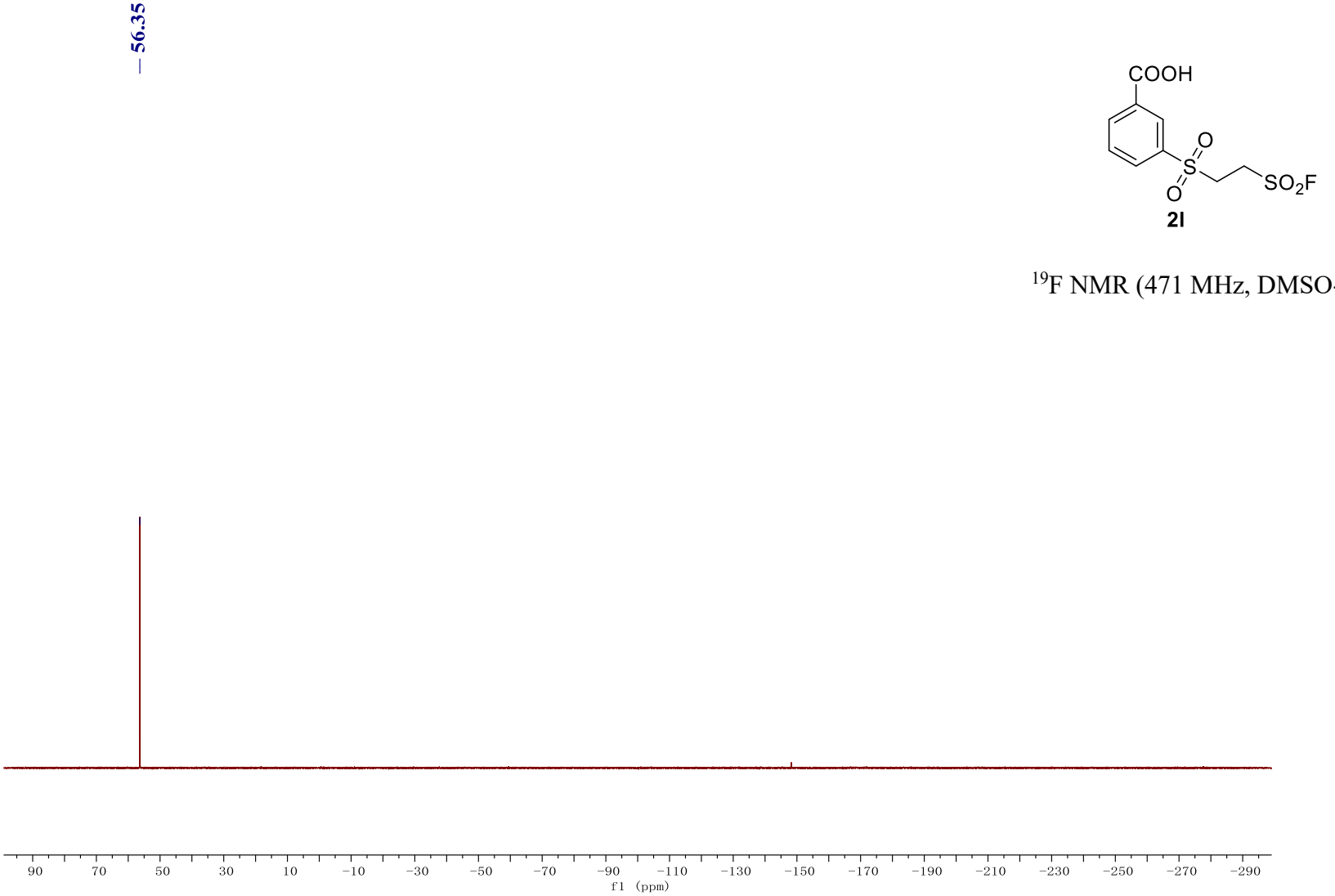
2l

^{1}H NMR (500 MHz, DMSO-d_6)



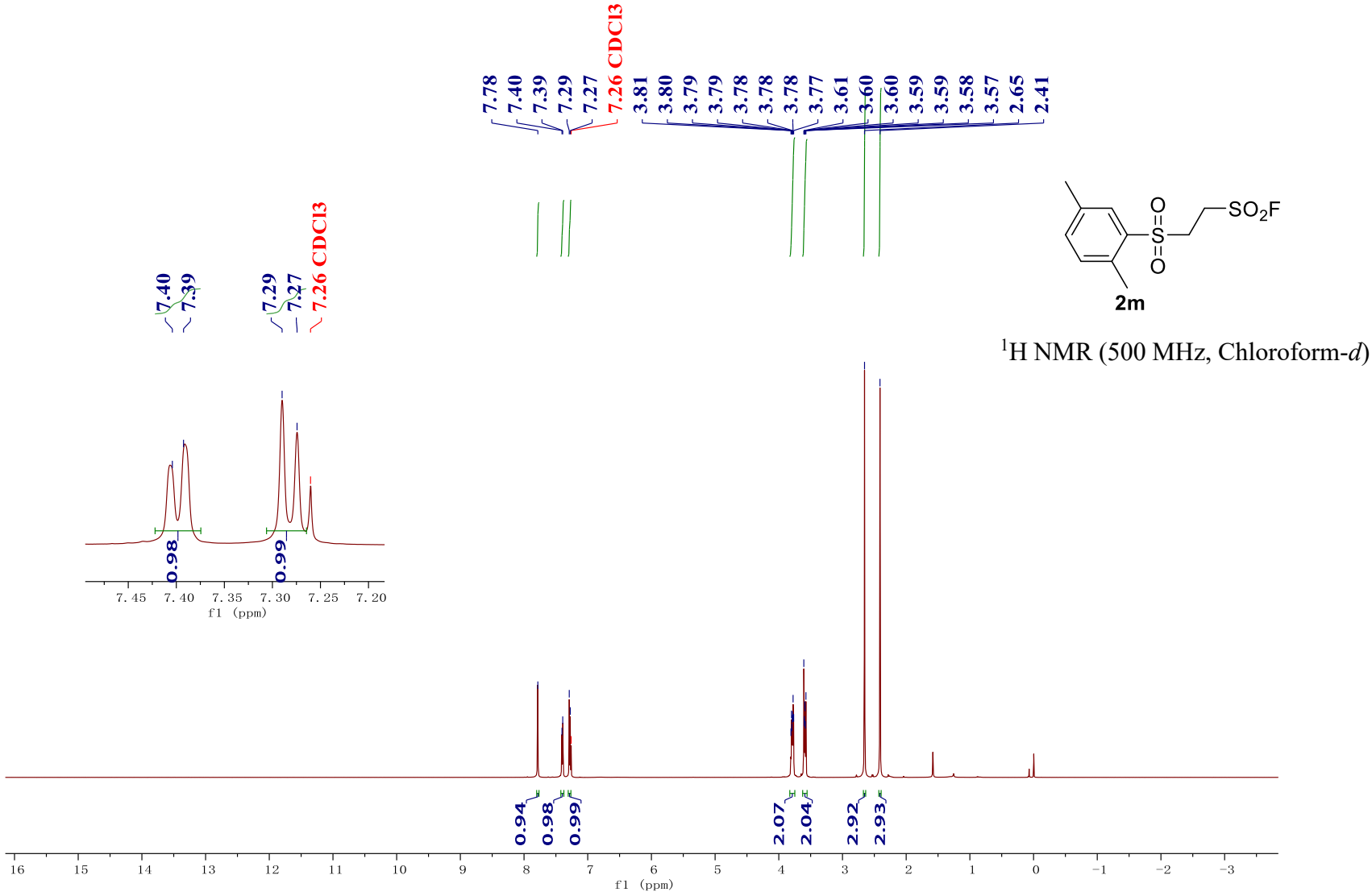
2l

^{13}C NMR (126 MHz, DMSO-d_6)

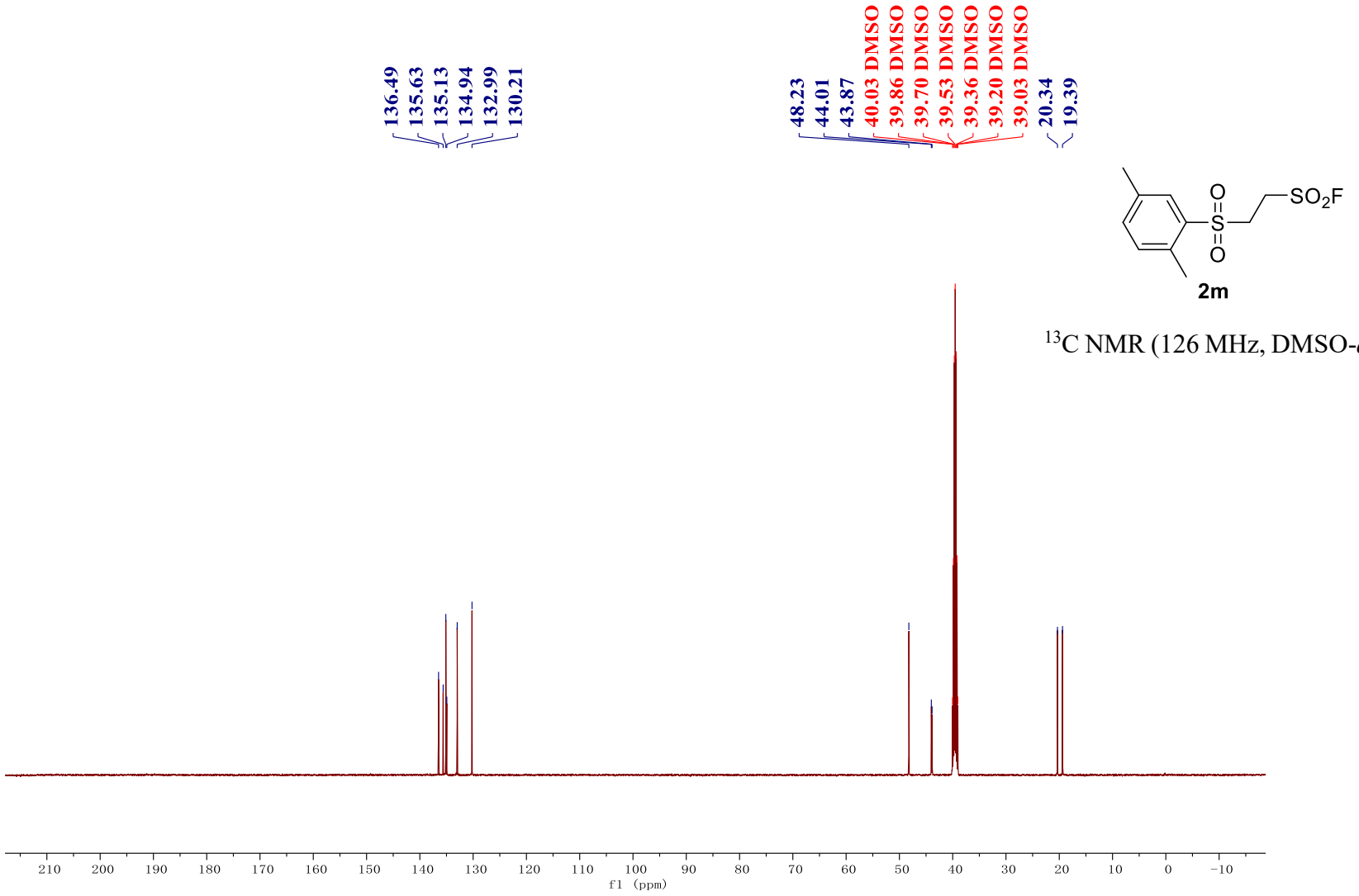


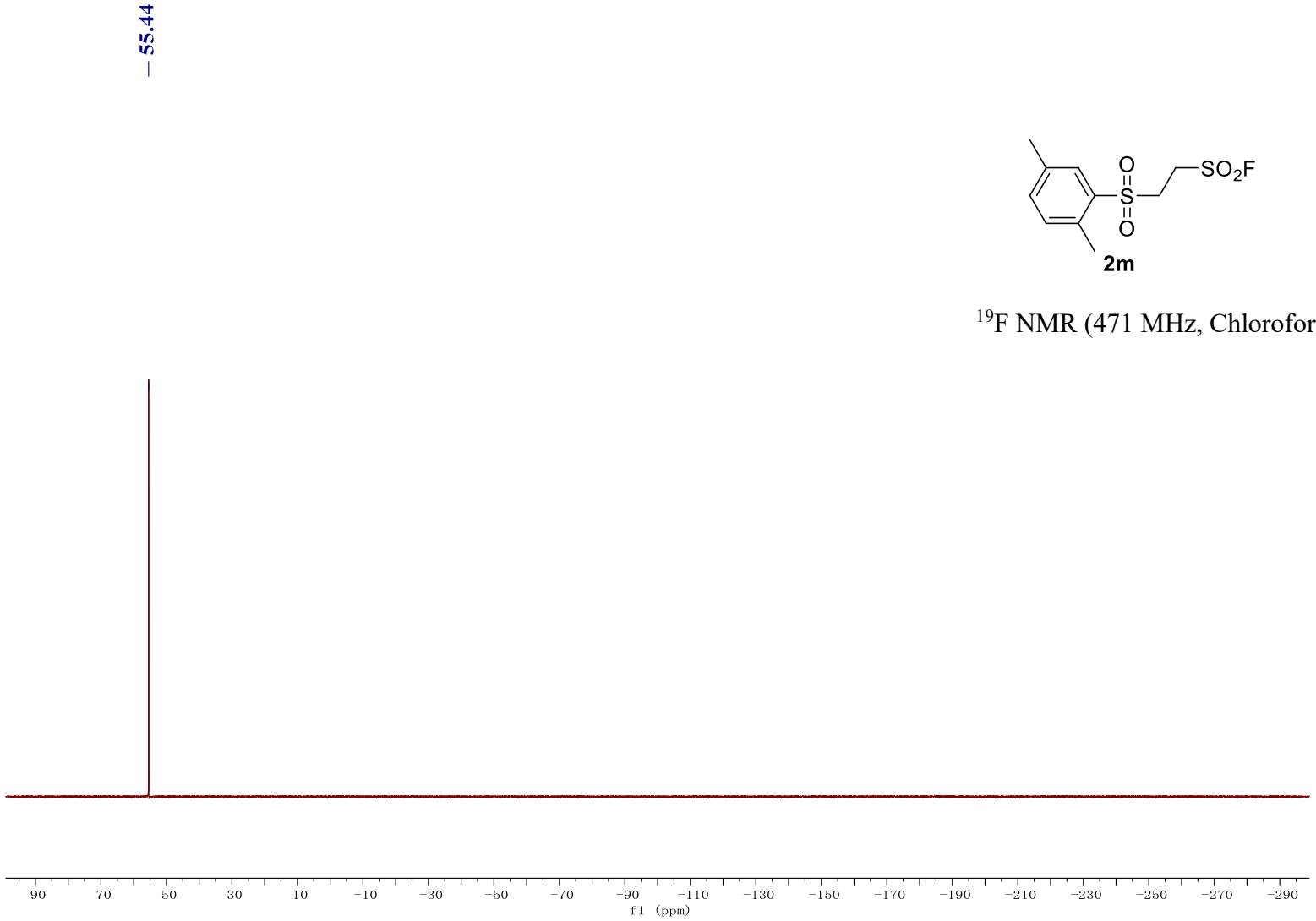
2l

^{19}F NMR (471 MHz, DMSO-d_6)



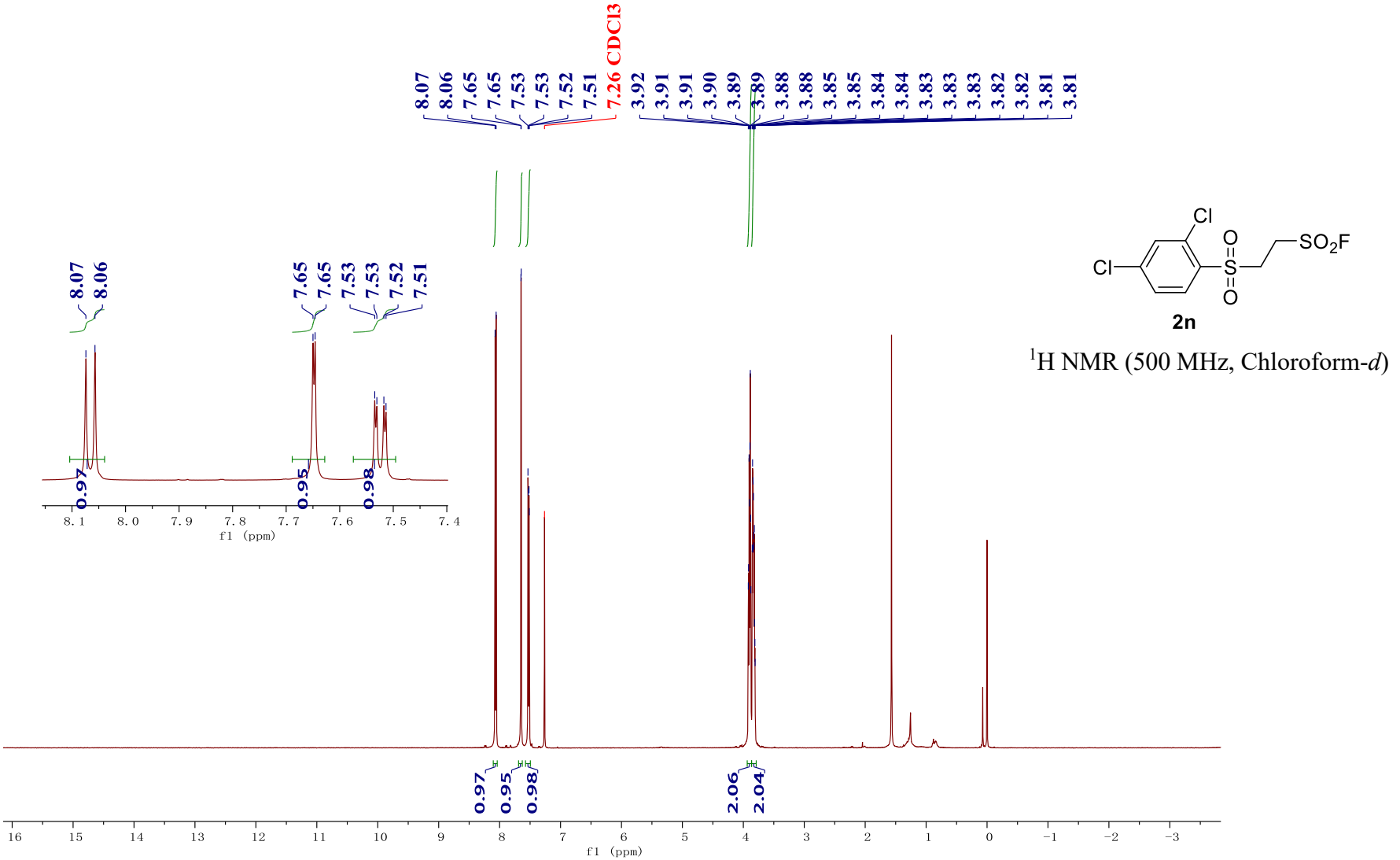
^{1}H NMR (500 MHz, Chloroform-*d*)


136.49
135.63
135.13
134.94
132.99
130.21
48.23
44.01
43.87
40.03 DMSO
39.86 DMSO
39.70 DMSO
39.53 DMSO
39.36 DMSO
39.20 DMSO
39.03 DMSO
20.34
19.39
O
S
O
SO2F
2m
13C NMR (126 MHz, DMSO-d6)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



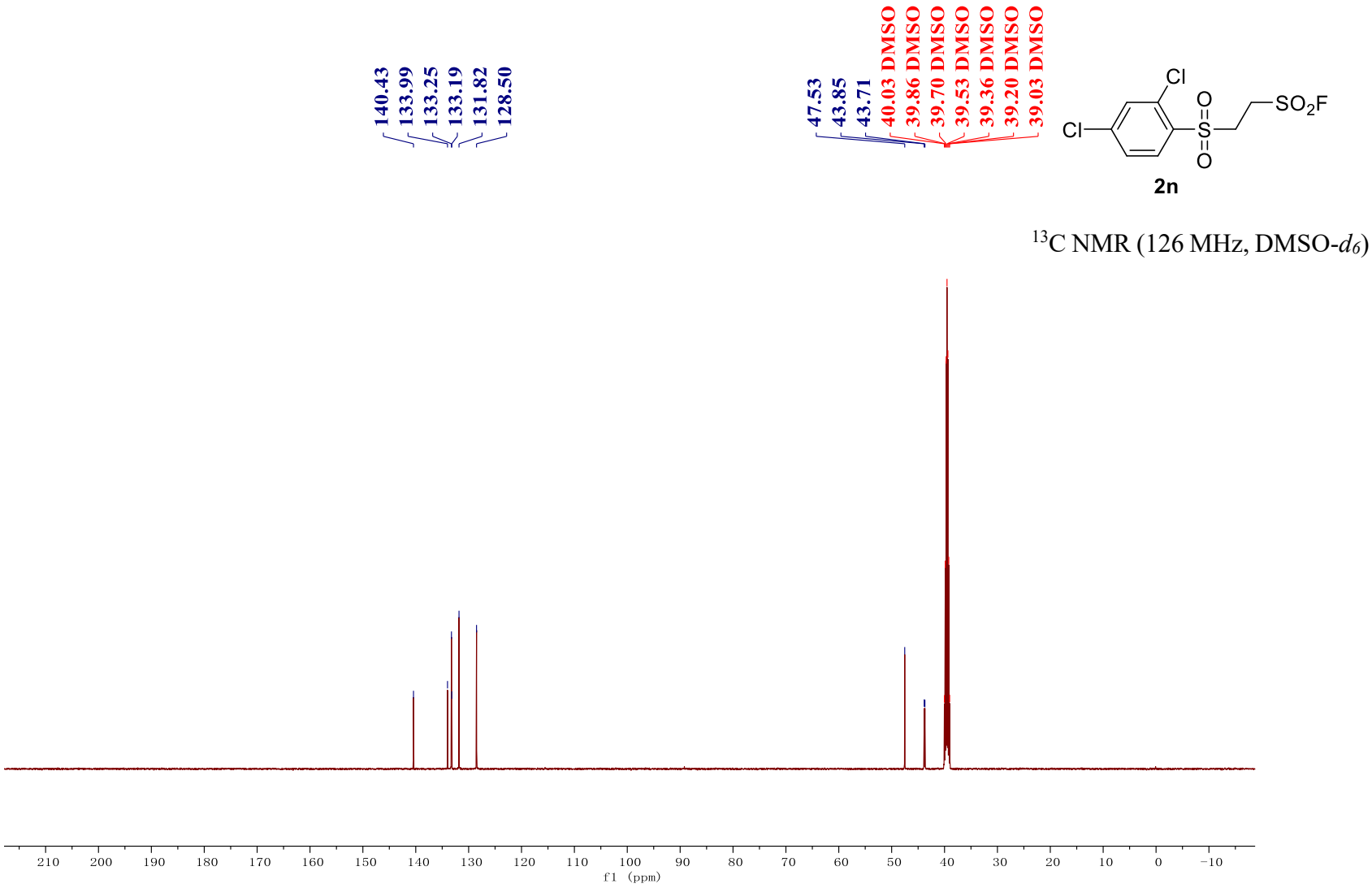
2m

^{19}F NMR (471 MHz, Chloroform-*d*)

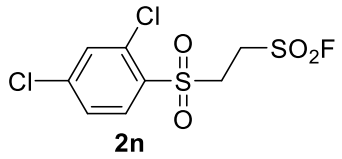


2n

^{1}H NMR (500 MHz, Chloroform-*d*)

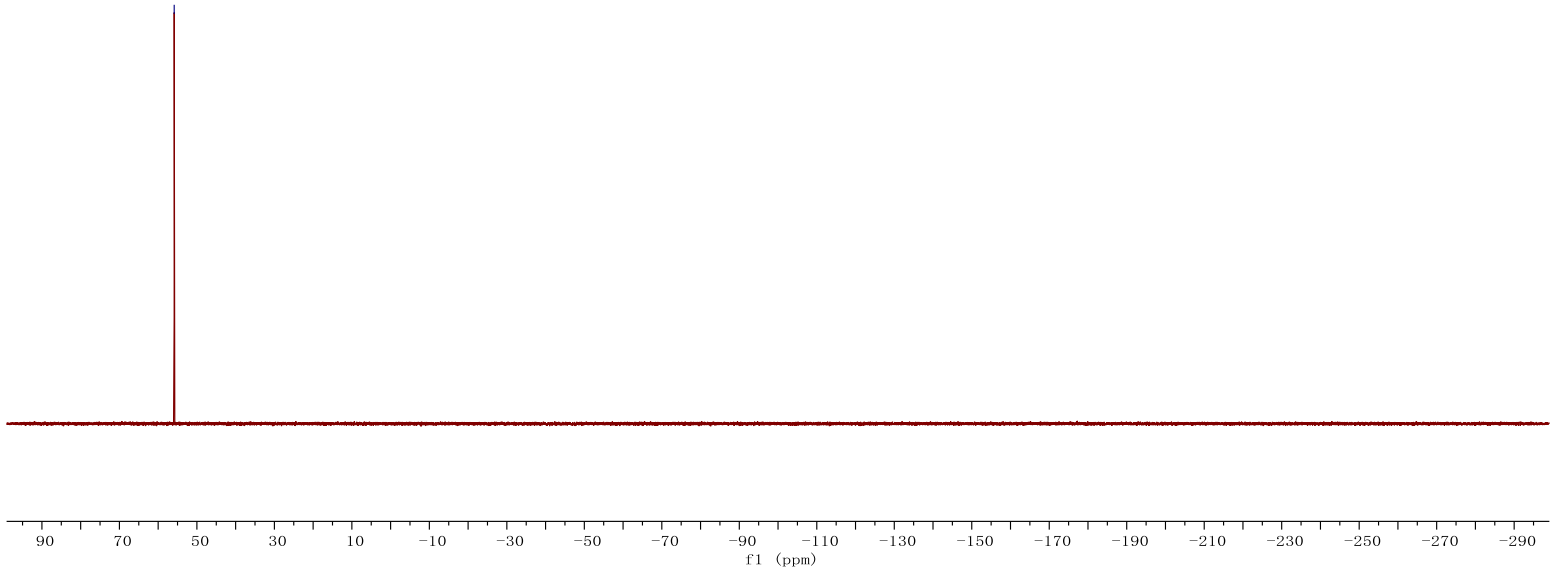


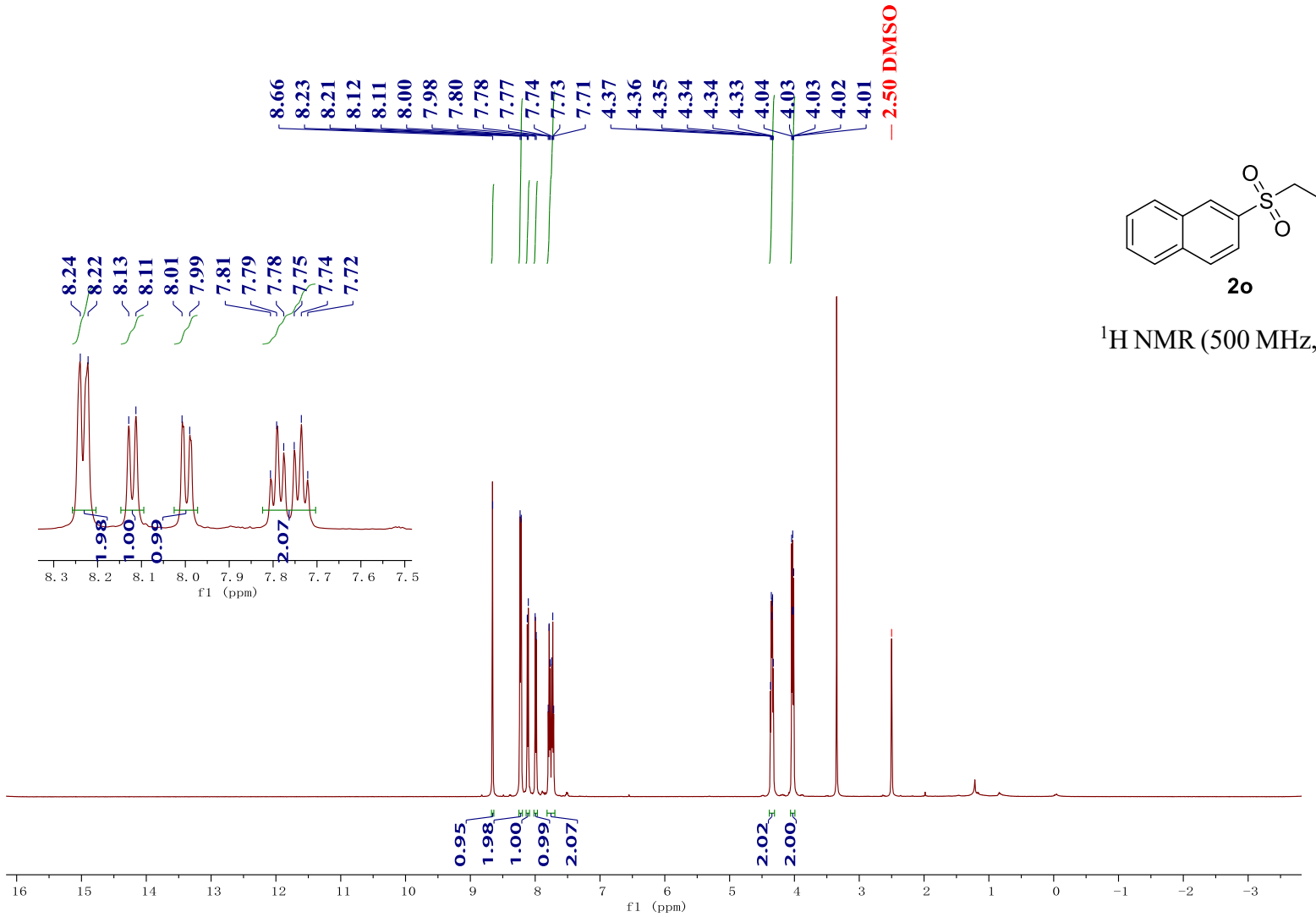
^{13}C NMR (126 MHz, DMSO-d_6)



2n

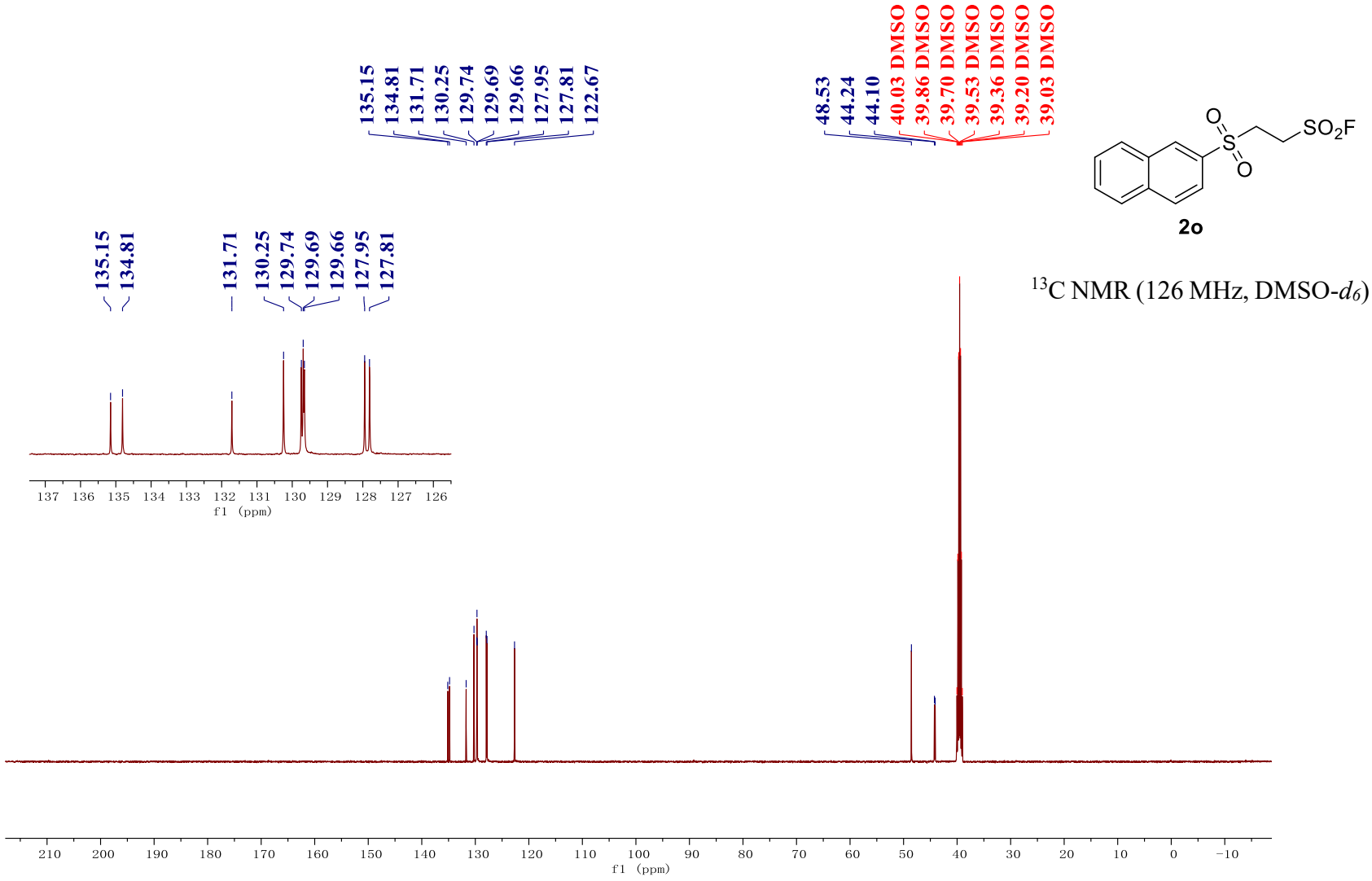
^{19}F NMR (471 MHz, Chloroform-*d*)

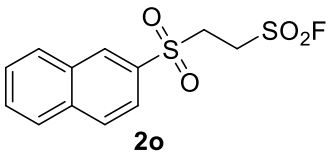




2o

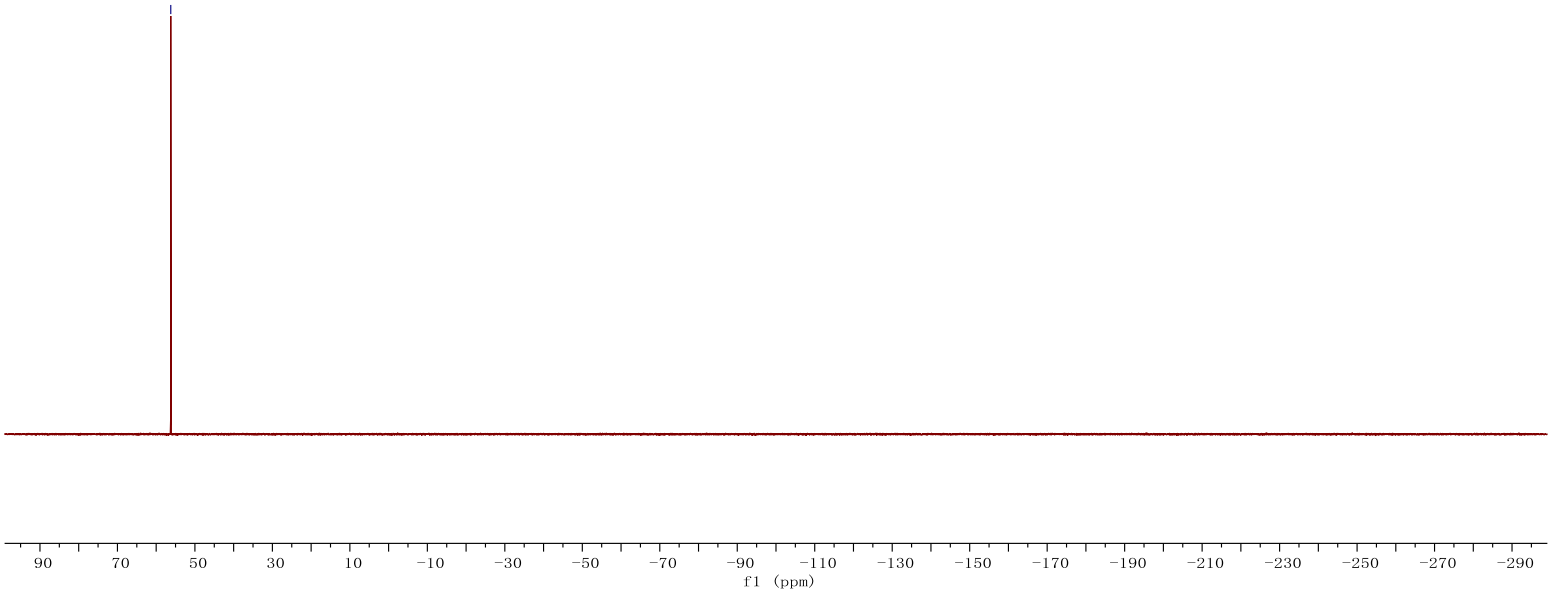
^{1}H NMR (500 MHz, DMSO-d_6)

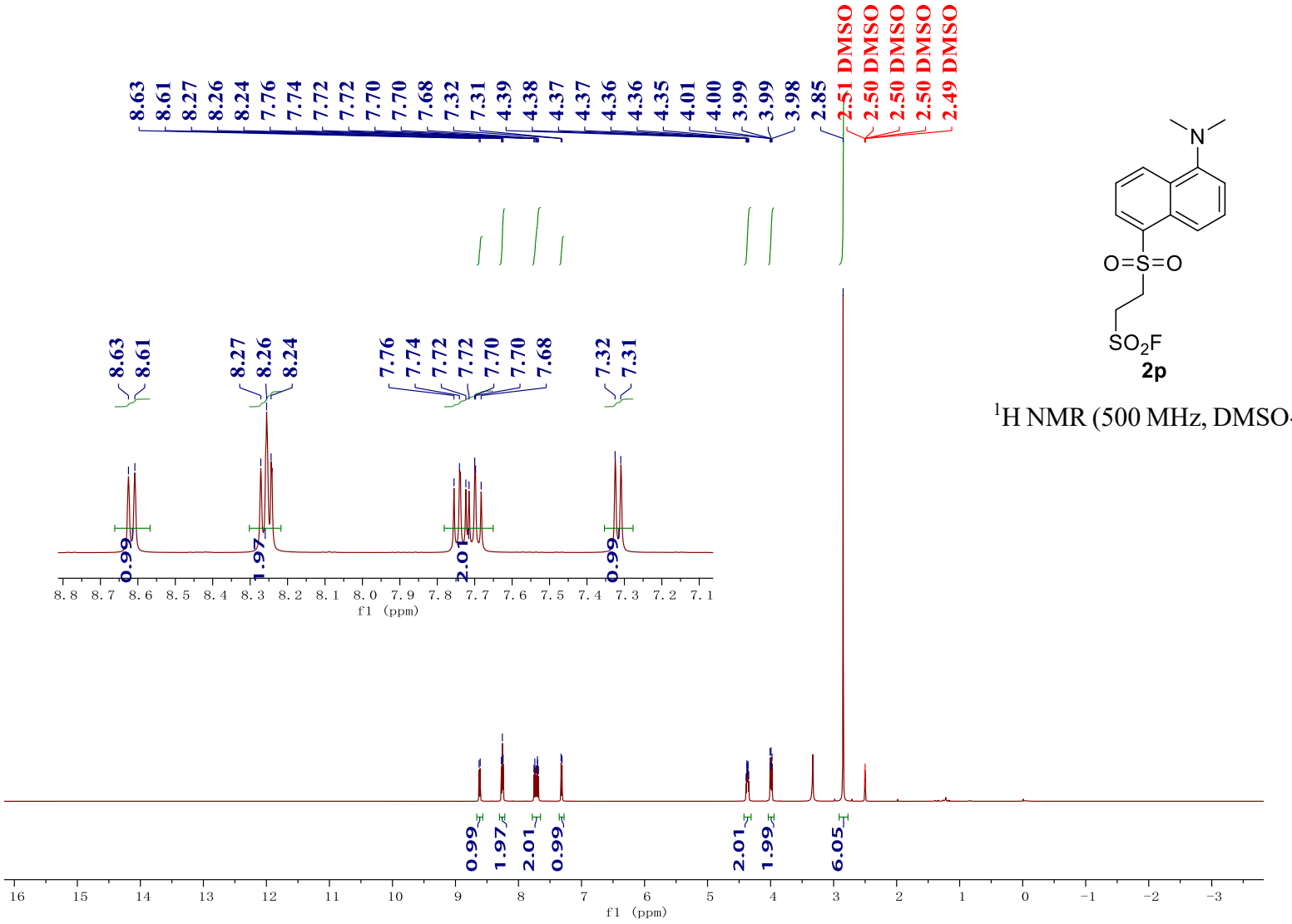

135.15
134.81
131.71
130.25
129.74
129.69
129.66
127.95
127.81
122.67
48.53
44.24
44.10
40.03 DMSO
39.86 DMSO
39.70 DMSO
39.53 DMSO
39.36 DMSO
39.20 DMSO
39.03 DMSO
O
S
O
SO2F
2o
13C NMR (126 MHz, DMSO-d6)
f1 (ppm)



2o

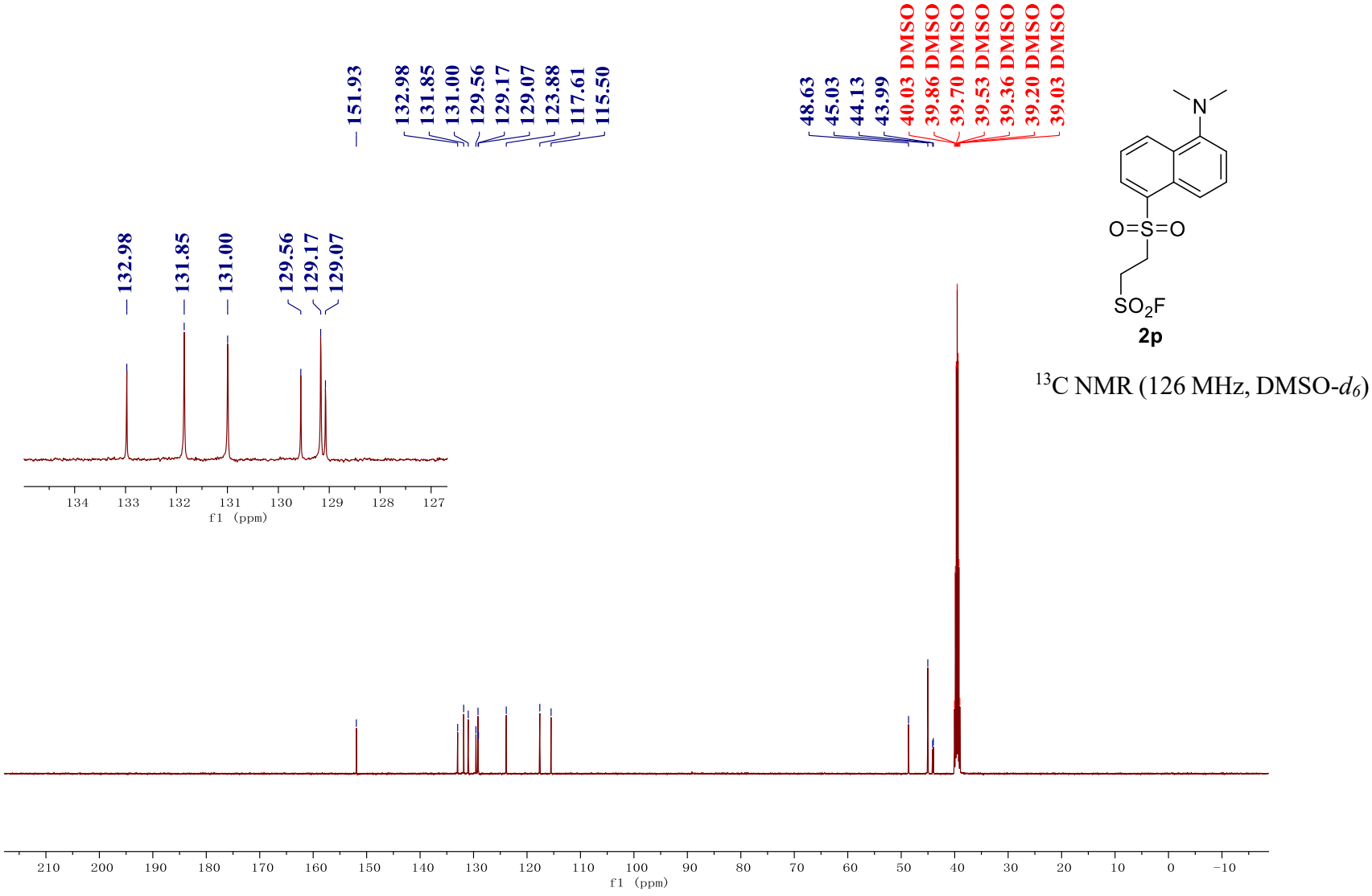
^{19}F NMR (471 MHz, DMSO-d_6)



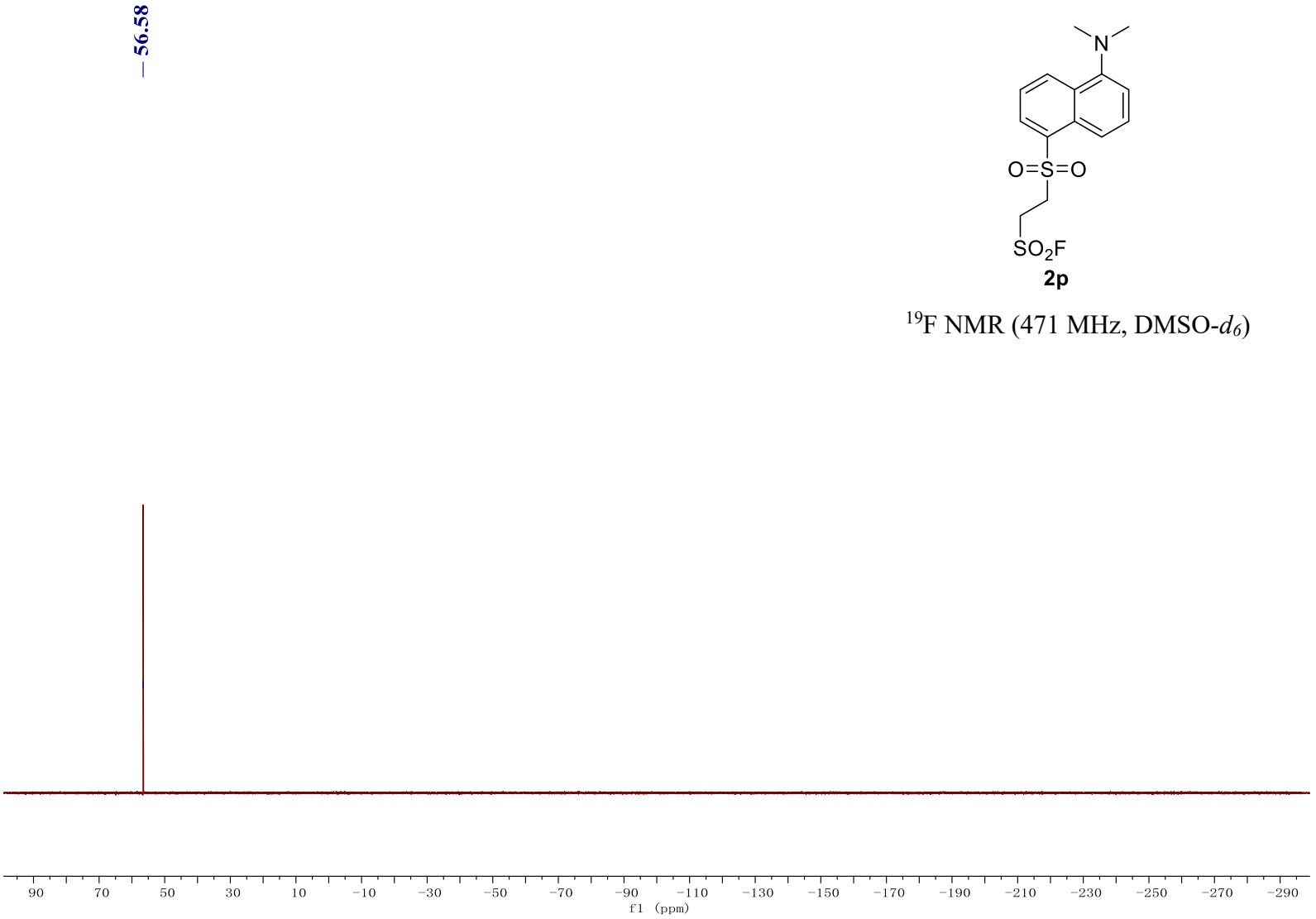


2p

^{1}H NMR (500 MHz, DMSO-d_6)

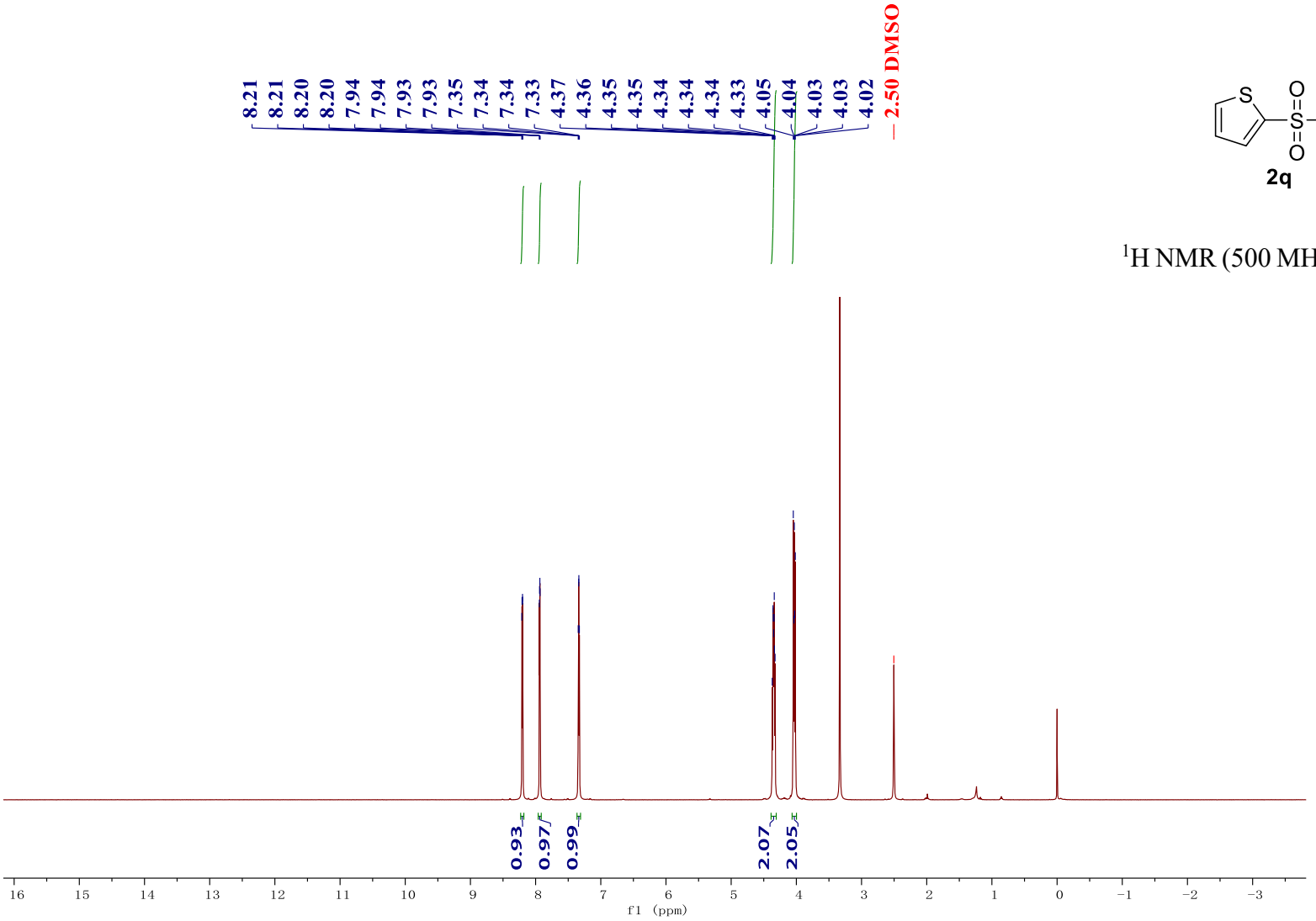


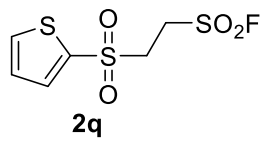
^{13}C NMR (126 MHz, DMSO-d_6)



2p

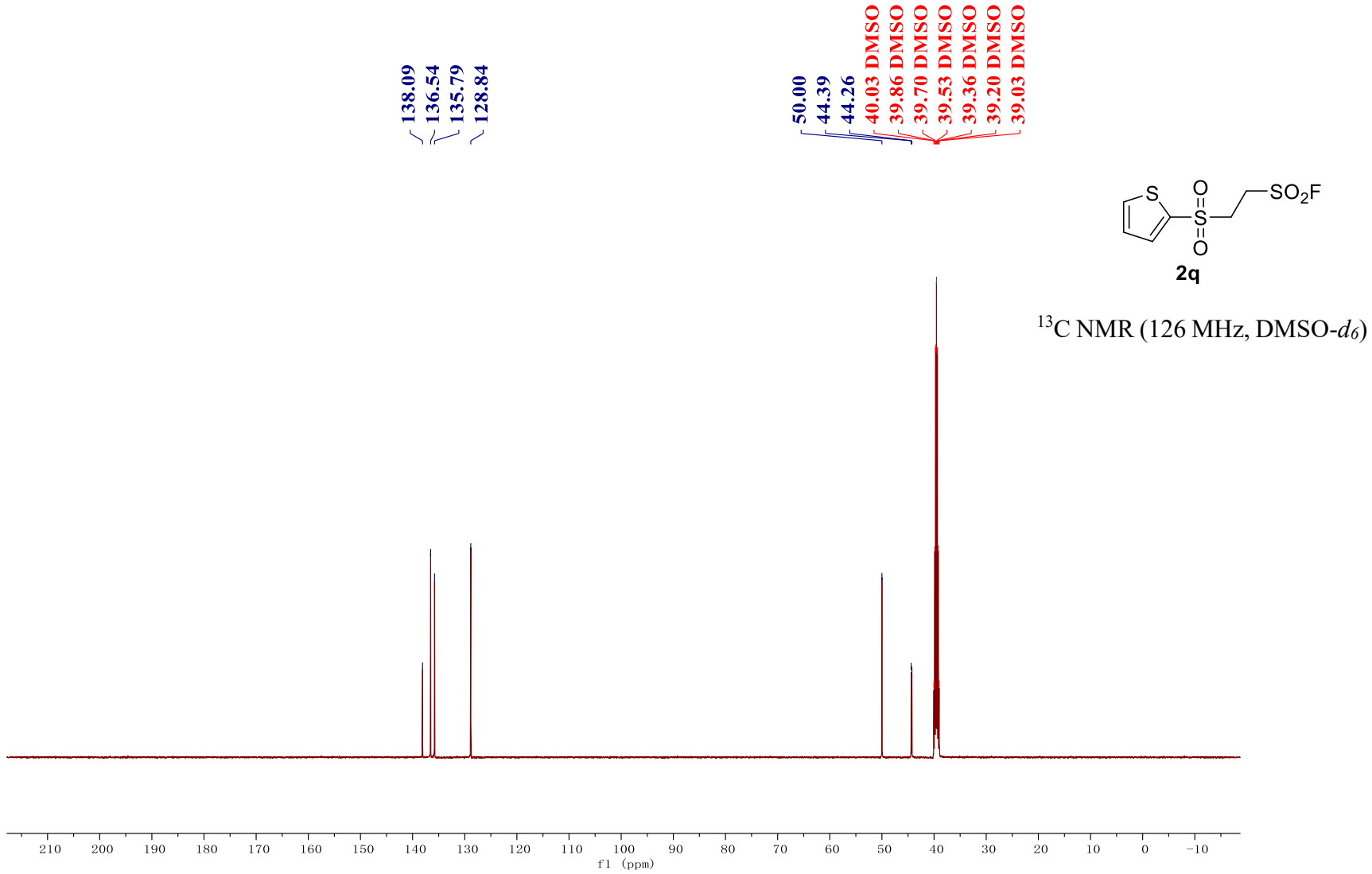
^{19}F NMR (471 MHz, DMSO-d_6)

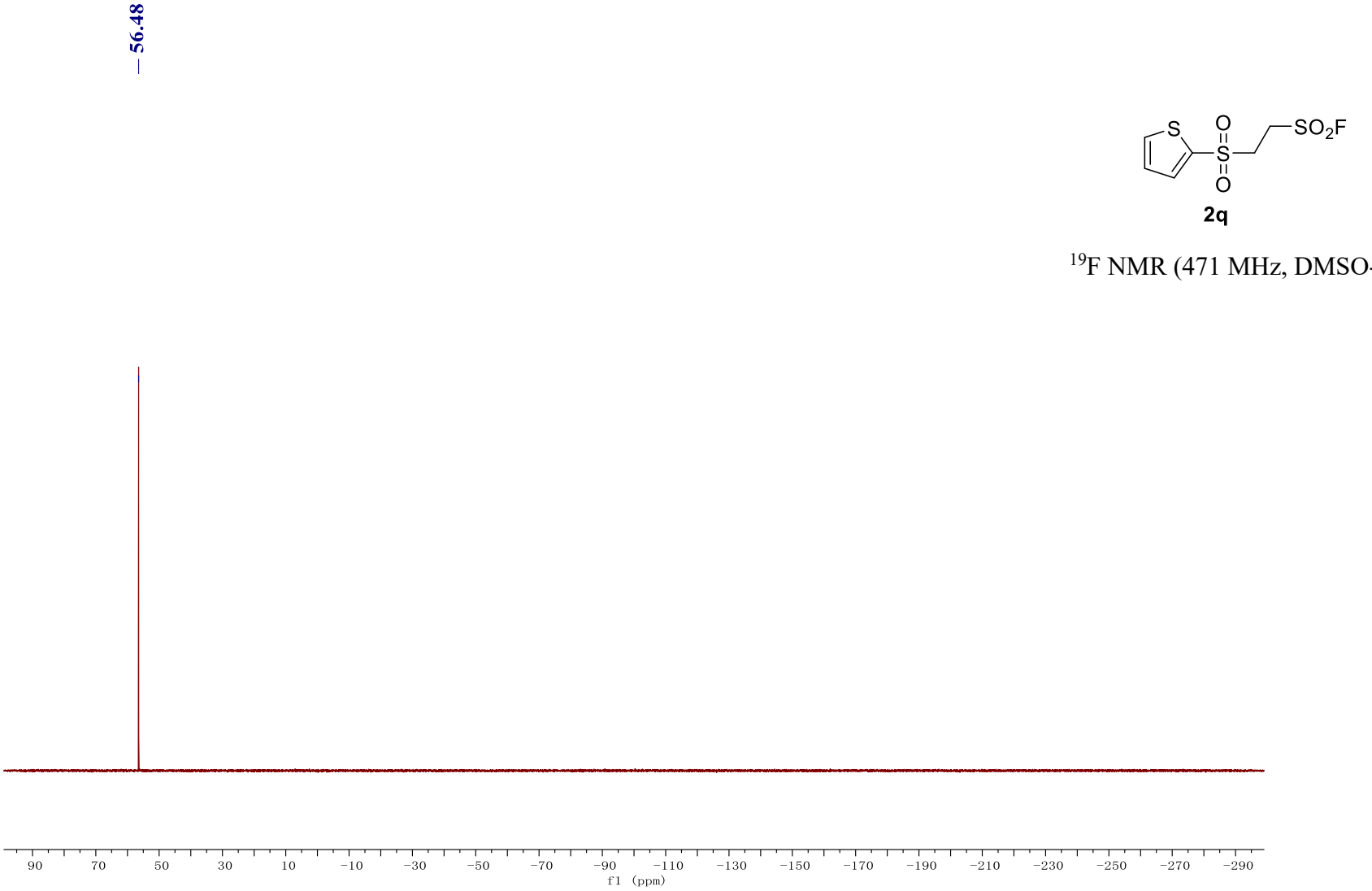




2q

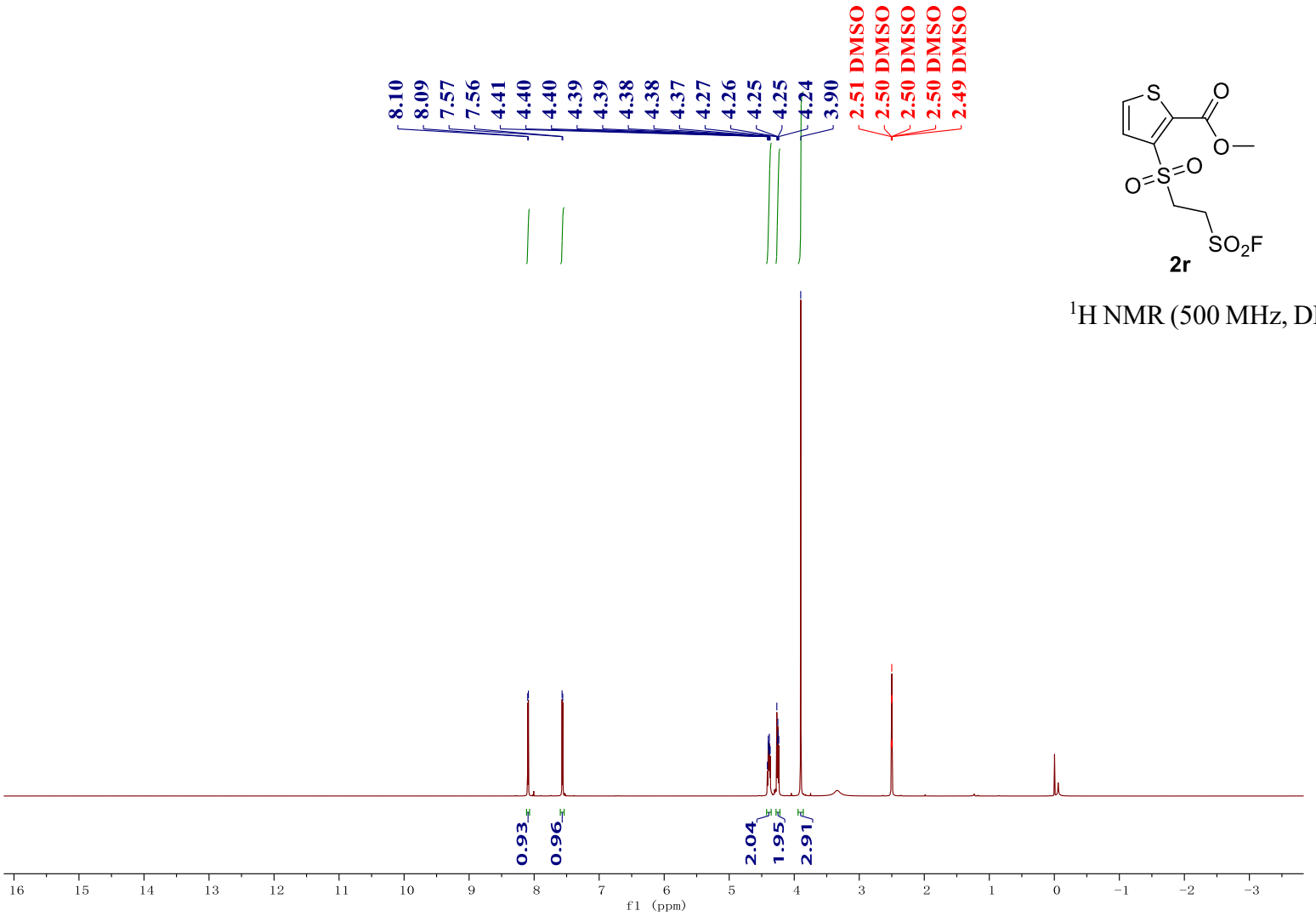
^{1}H NMR (500 MHz, DMSO-d_6)


138.09
136.54
135.79
128.84
50.00
44.39
44.26
40.03 DMSO
39.86 DMSO
39.70 DMSO
39.53 DMSO
39.36 DMSO
39.20 DMSO
39.03 DMSO
S
O
S
O
SO2F
2q
13C NMR (126 MHz, DMSO-d6)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



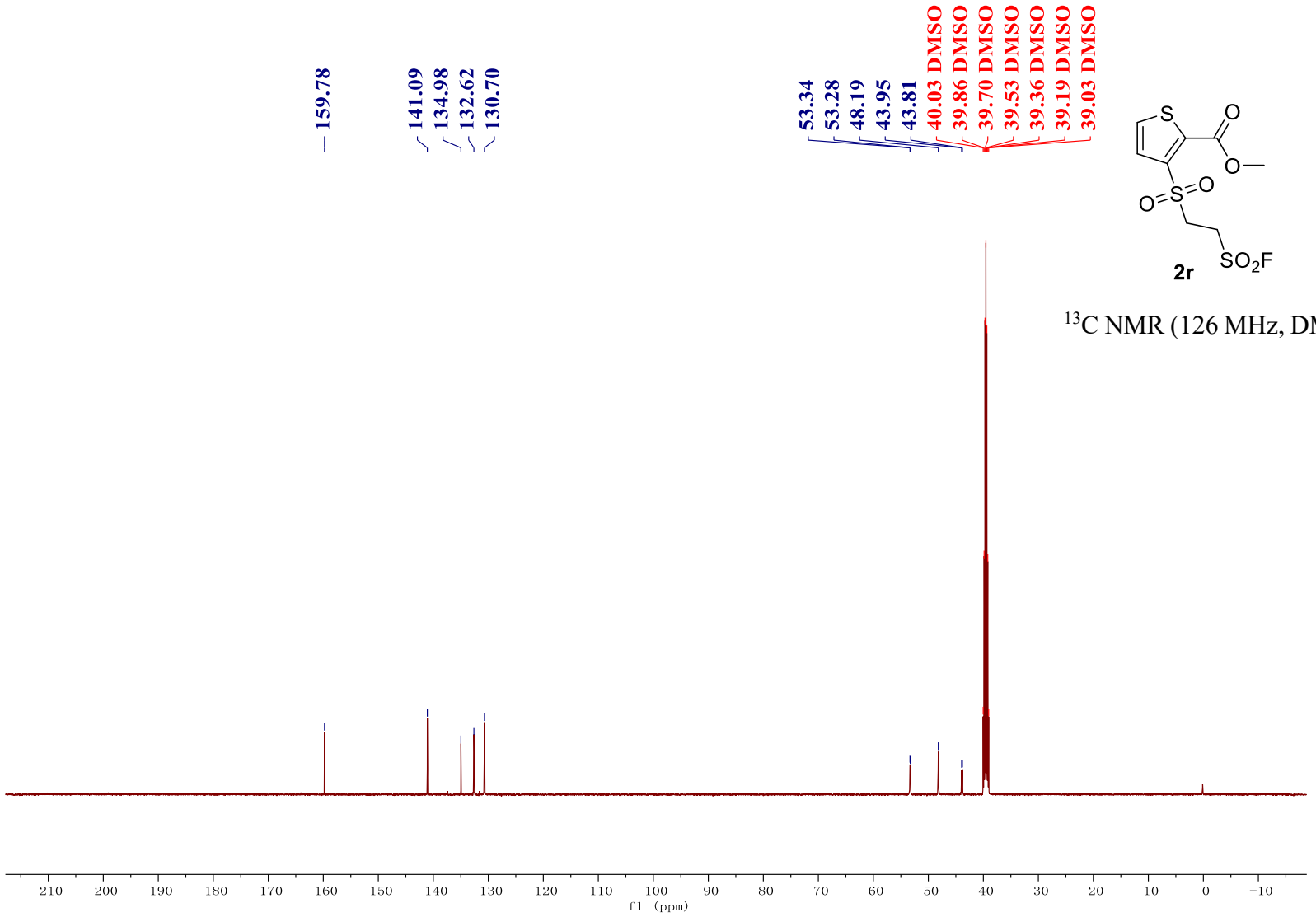
2q

^{19}F NMR (471 MHz, DMSO-*d*$_6$)

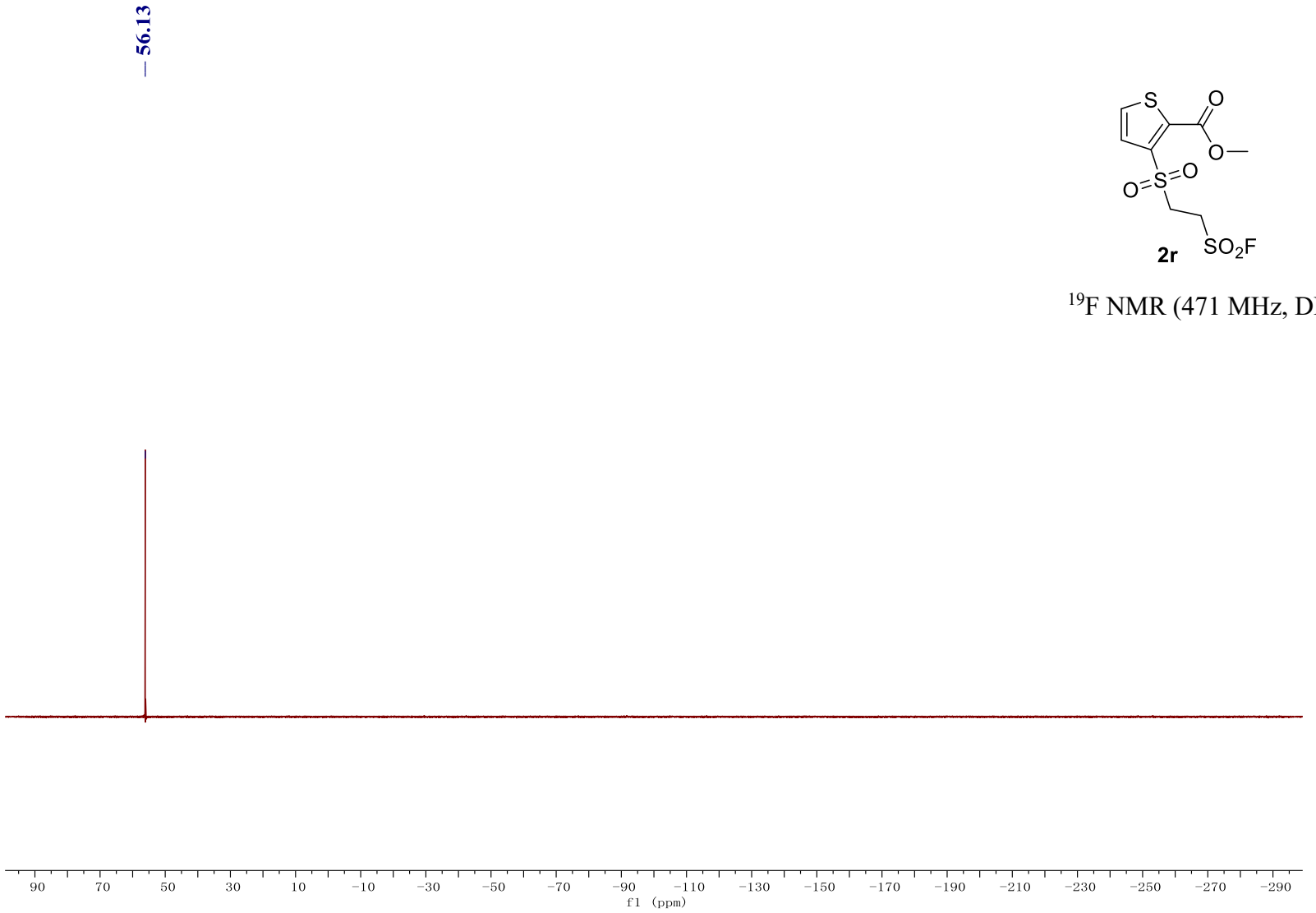


2r

^{1}H NMR (500 MHz, DMSO-d_6)

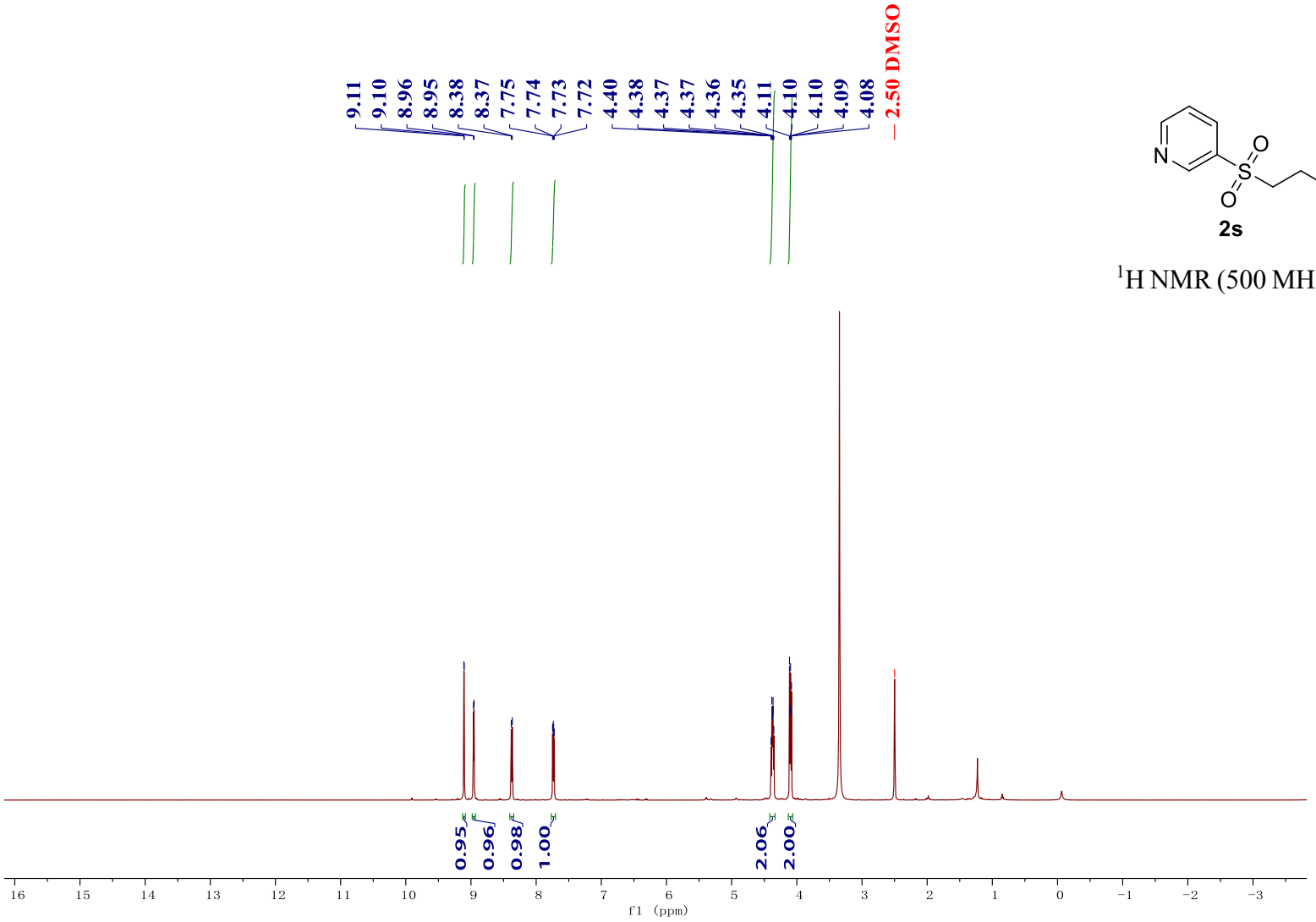


^{13}C NMR (126 MHz, DMSO-d_6)



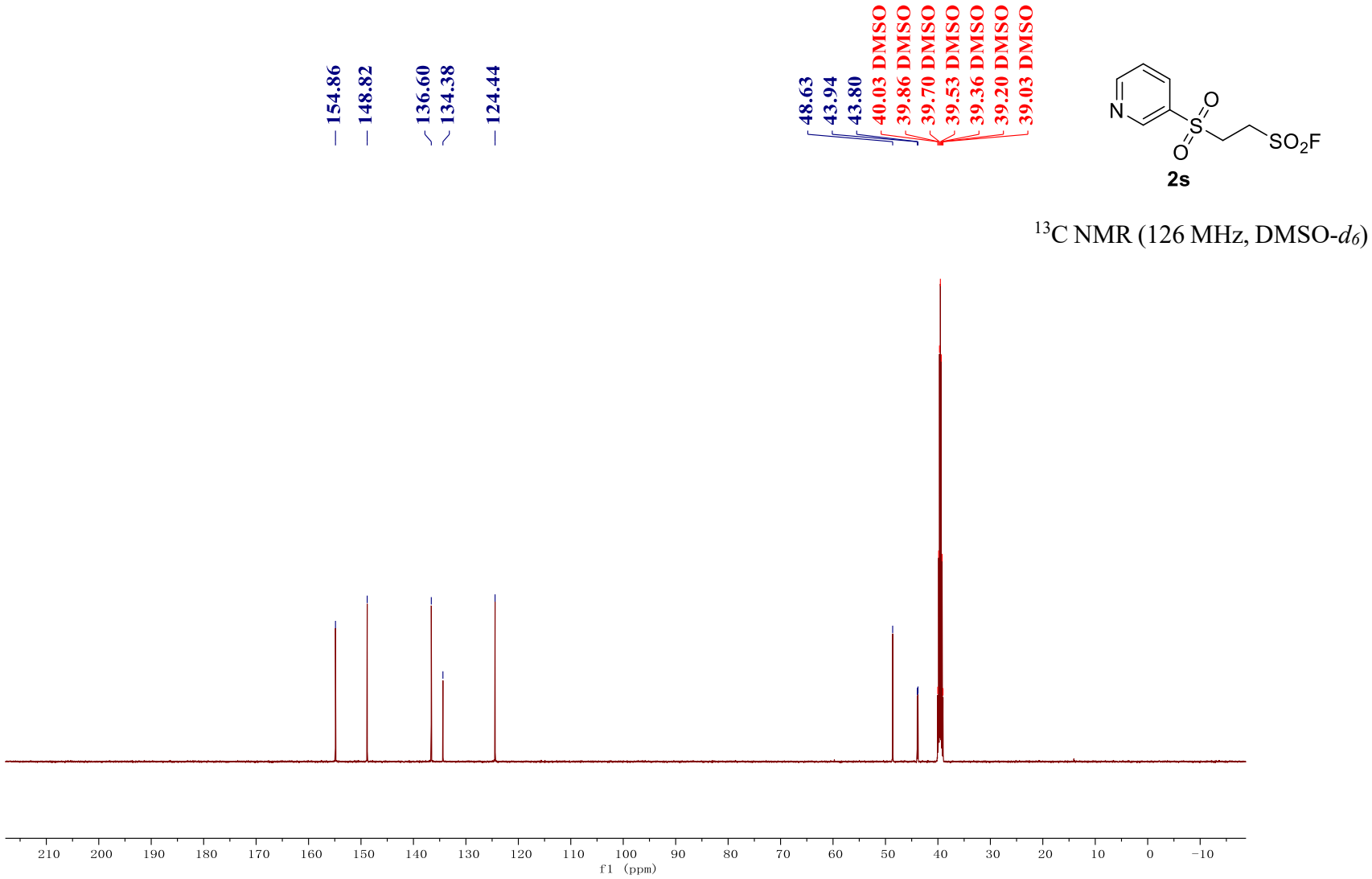
2r

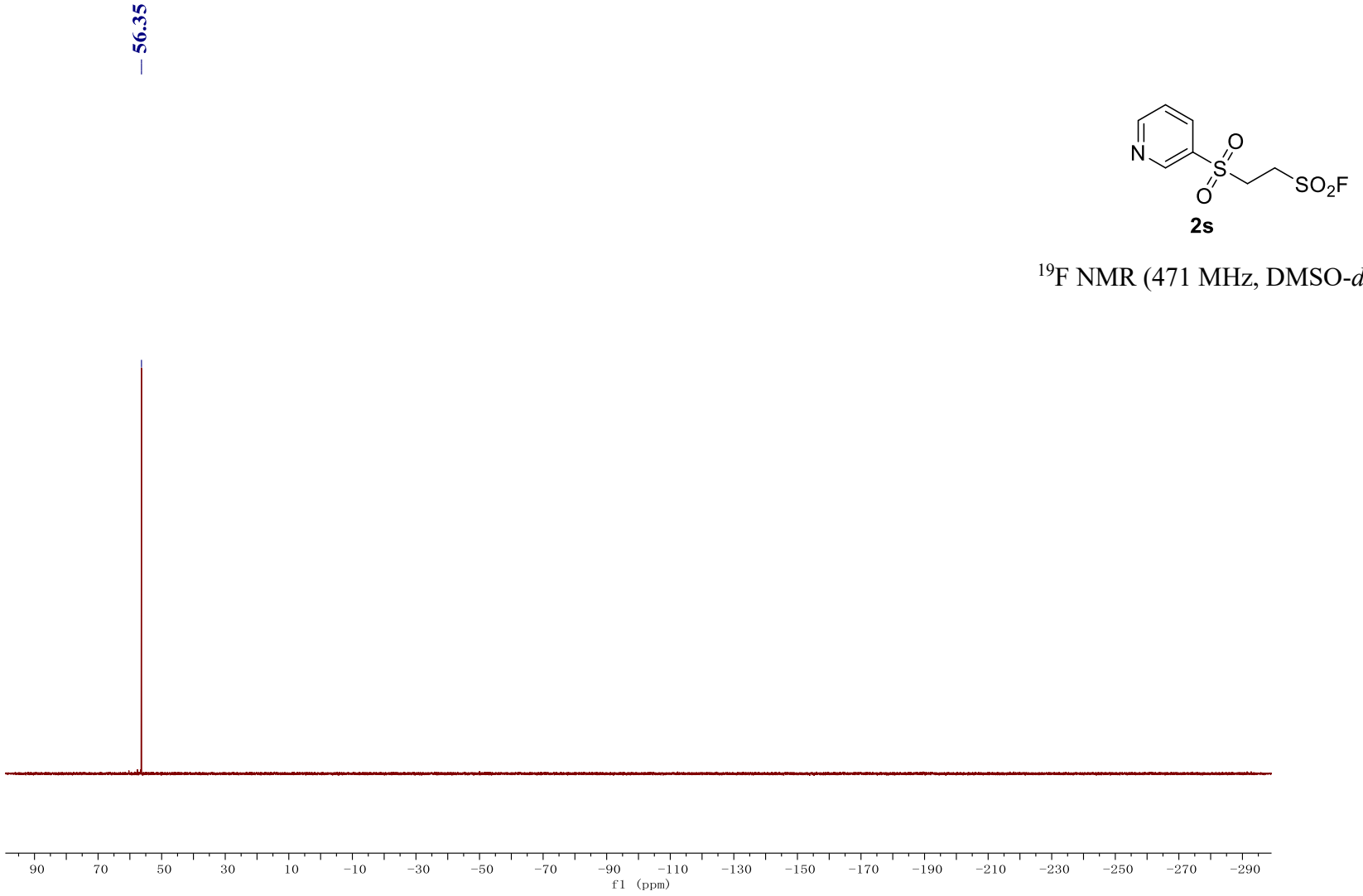
^{19}F NMR (471 MHz, DMSO-d_6)



2s

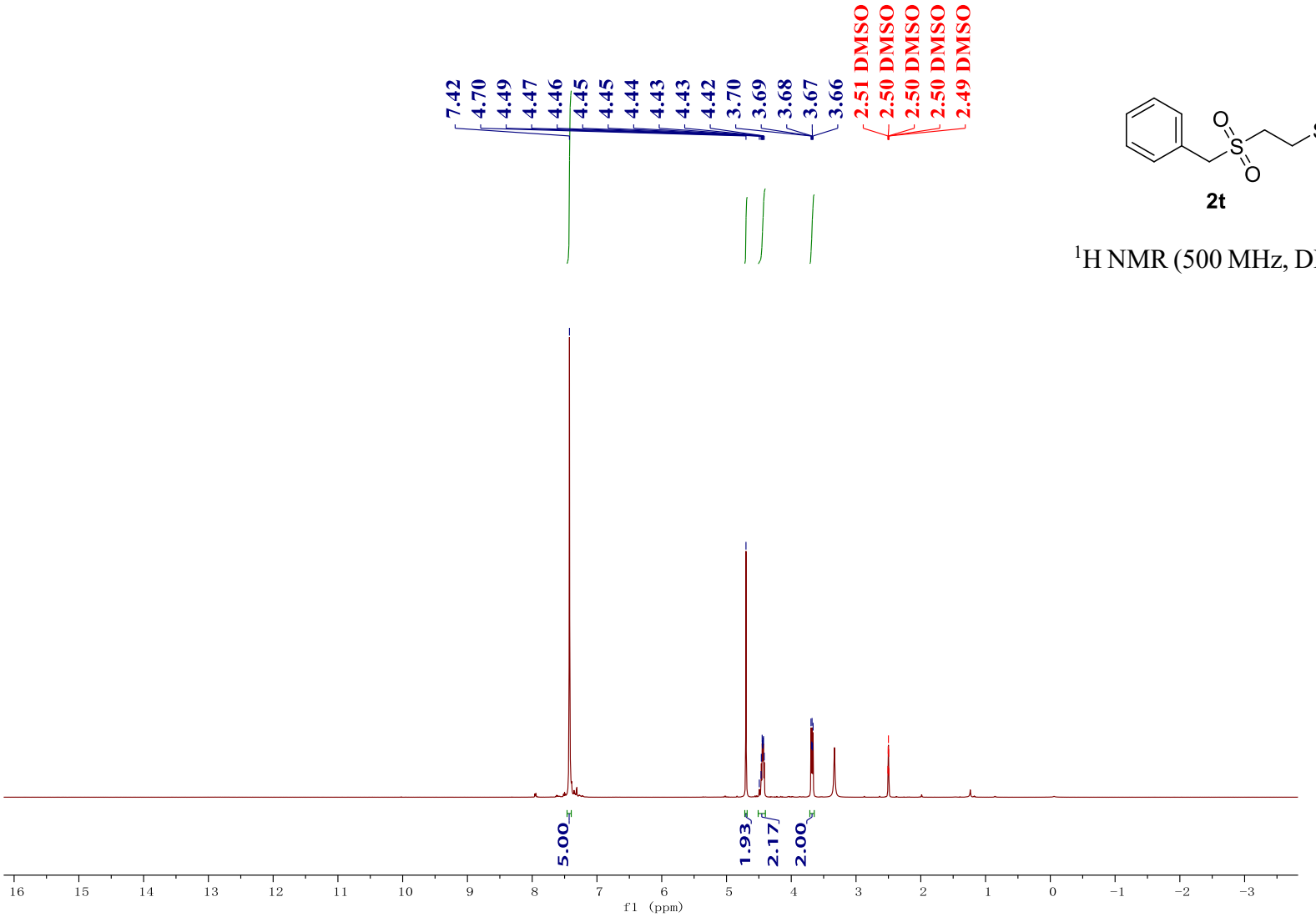
^{1}H NMR (500 MHz, DMSO-d_6)


154.86
148.82
136.60
134.38
124.44
48.63
43.94
43.80
40.03 DMSO
39.86 DMSO
39.70 DMSO
39.53 DMSO
39.36 DMSO
39.20 DMSO
39.03 DMSO
N
S
O
O
SO2F
2s
13C NMR (126 MHz, DMSO-d6)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



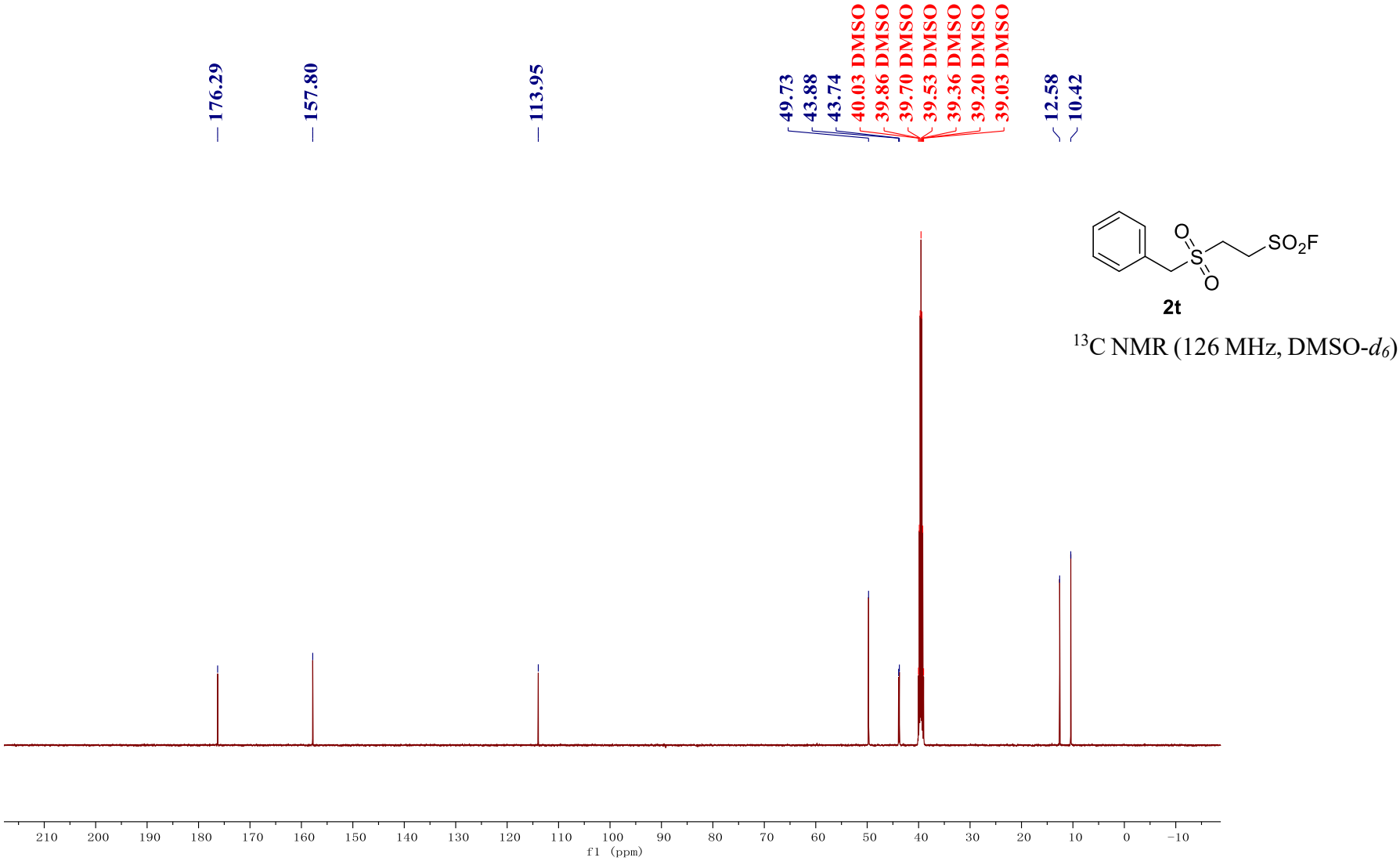
2s

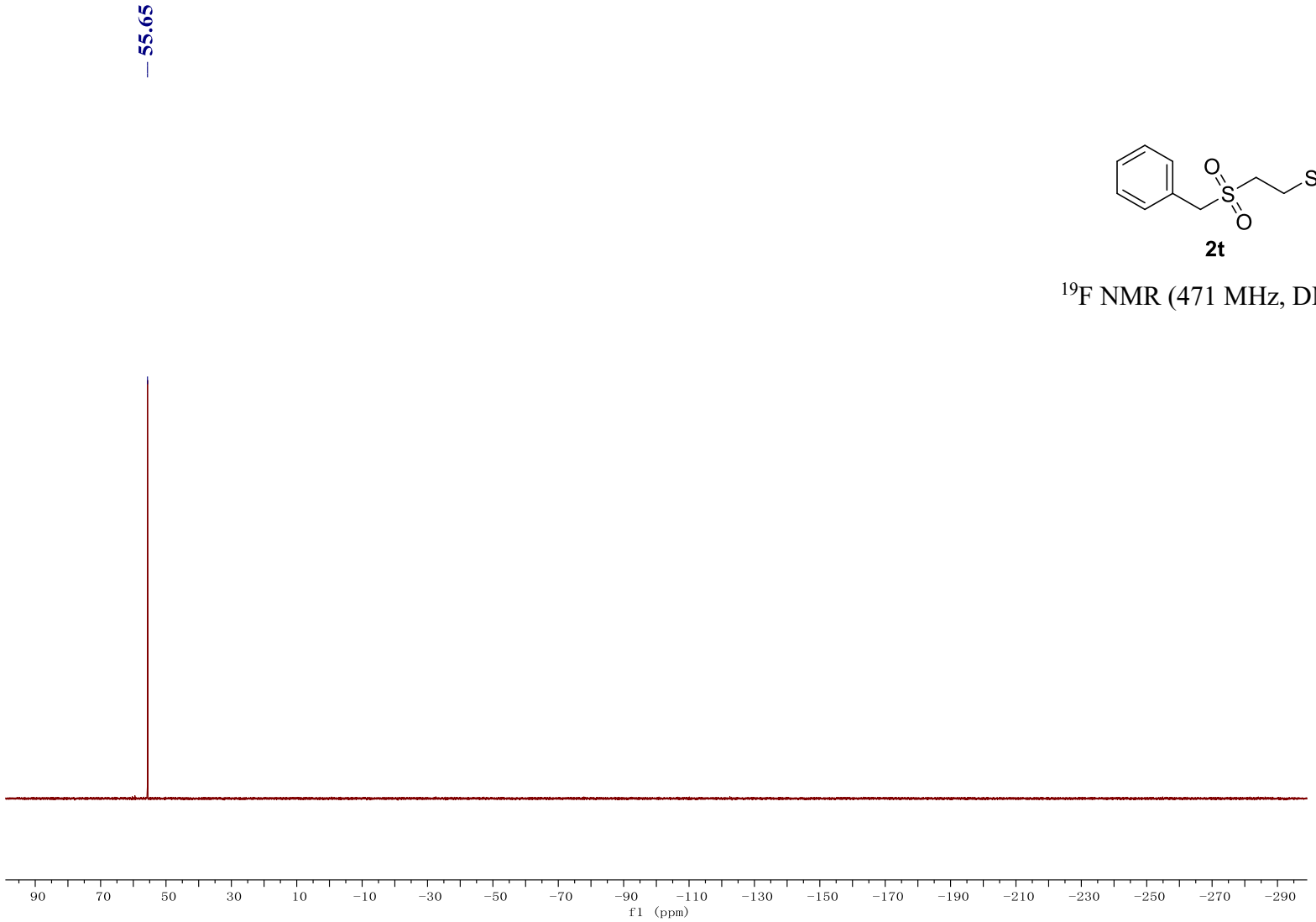
^{19}F NMR (471 MHz, DMSO-*d*$_6$)



2t

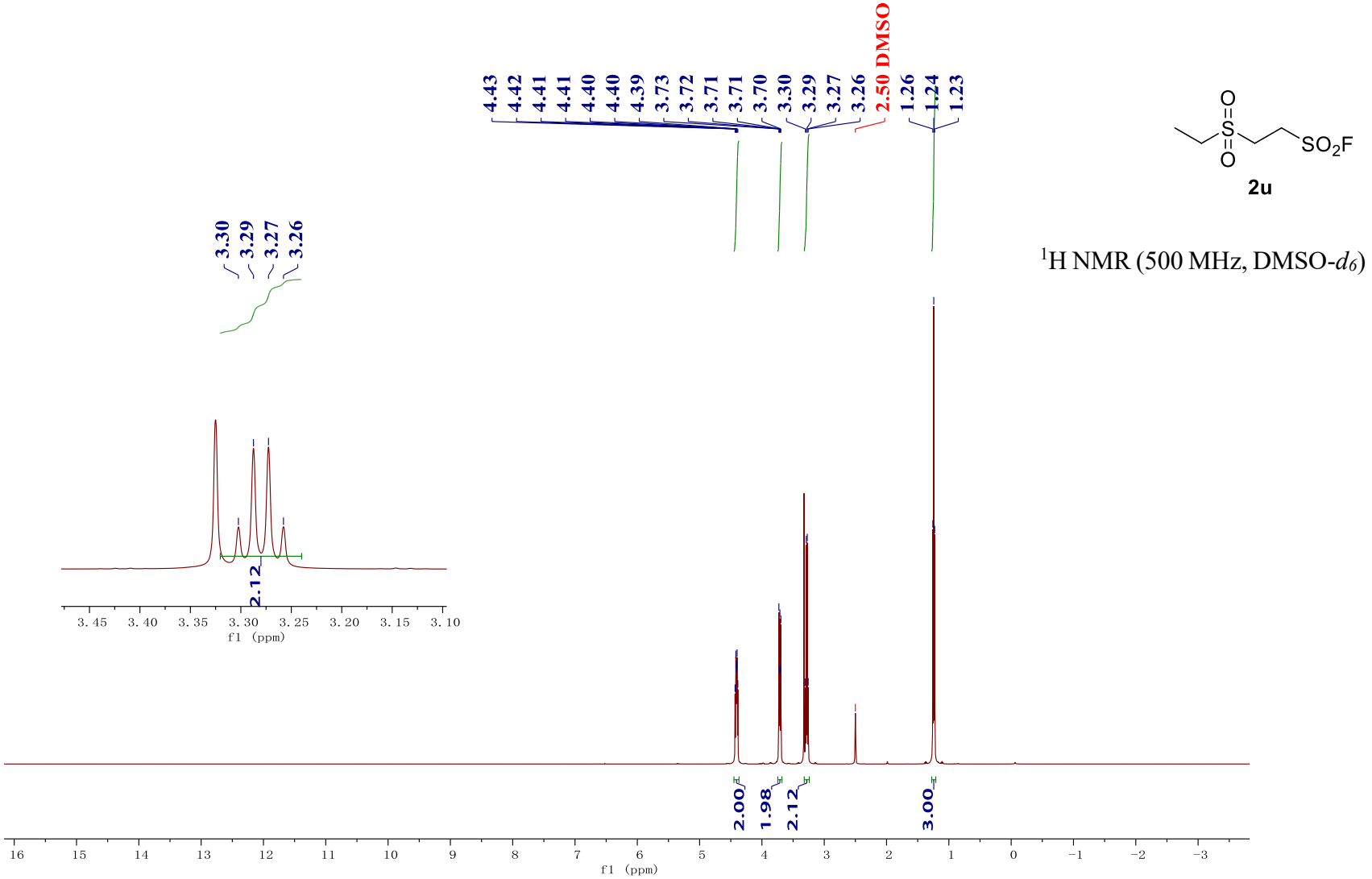
^{1}H NMR (500 MHz, DMSO-d_6)


176.29
157.80
113.95
49.73
43.88
43.74
40.03 DMSO
39.86 DMSO
39.70 DMSO
39.53 DMSO
39.36 DMSO
39.20 DMSO
39.03 DMSO
12.58
10.42
O
S
O
SO2F
2t
13C NMR (126 MHz, DMSO-d6)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



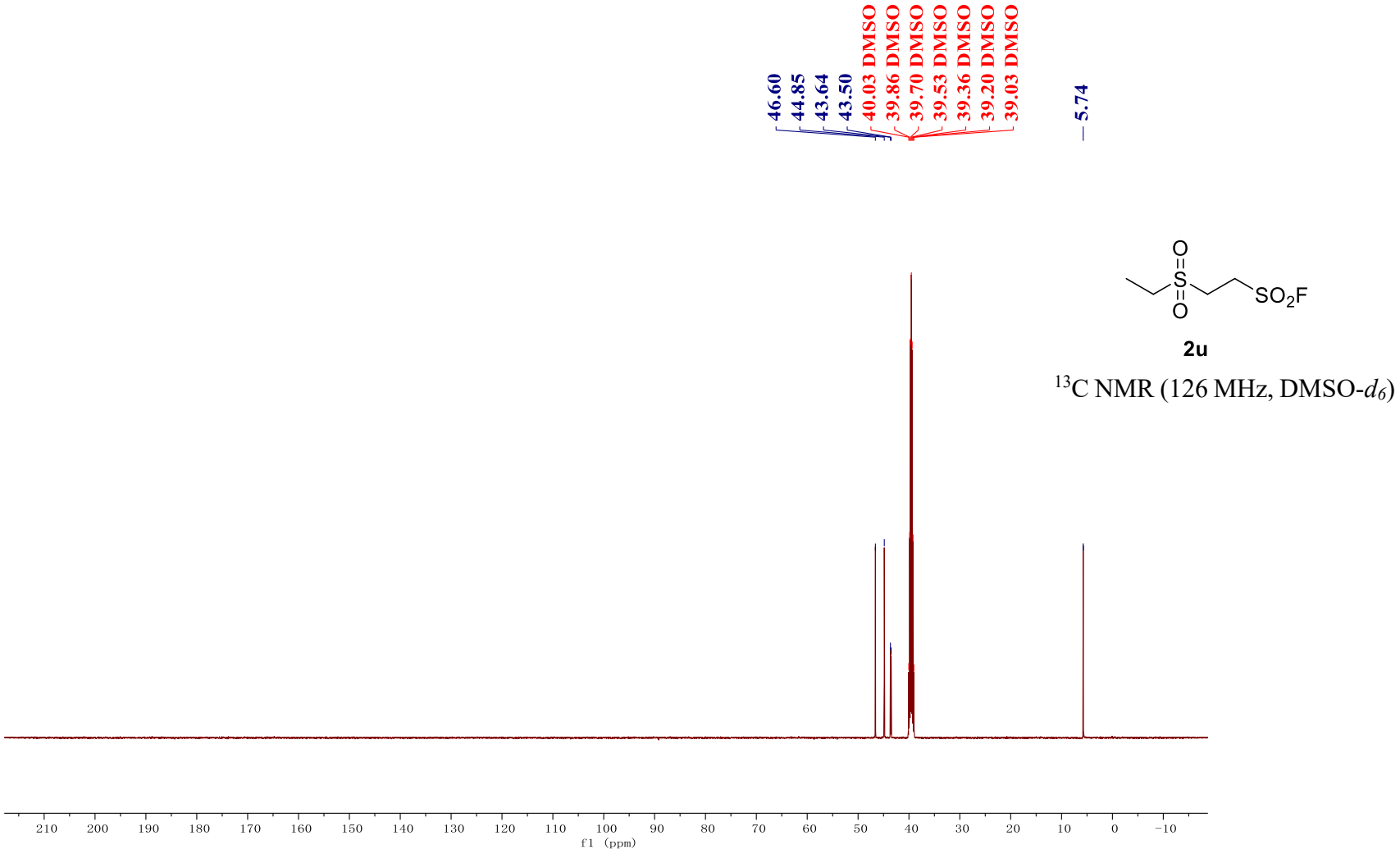
2t

^{19}F NMR (471 MHz, DMSO-d_6)



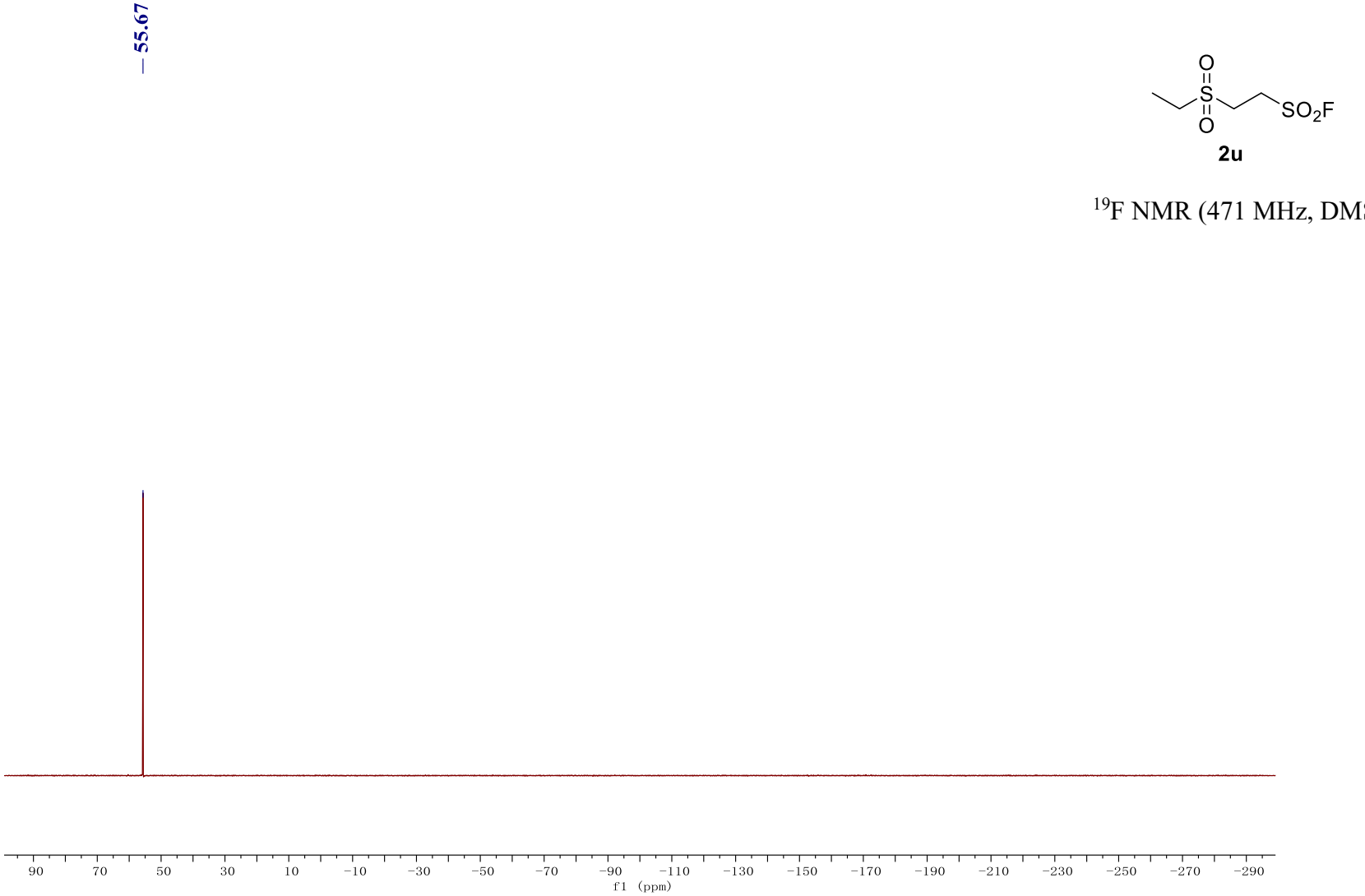
2u

^{1}H NMR (500 MHz, DMSO-d_6)



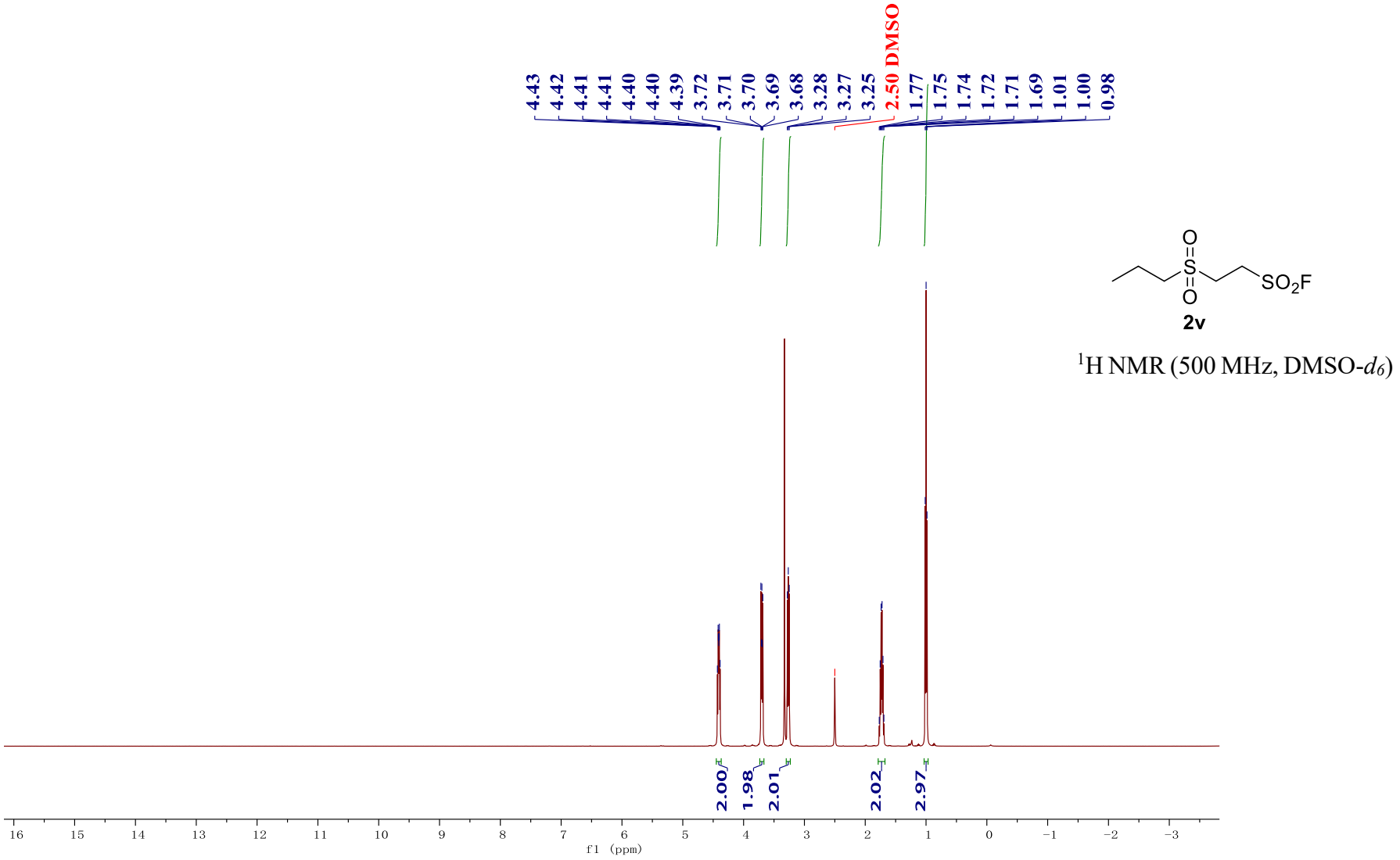
2u

^{13}C NMR (126 MHz, DMSO-d_6)

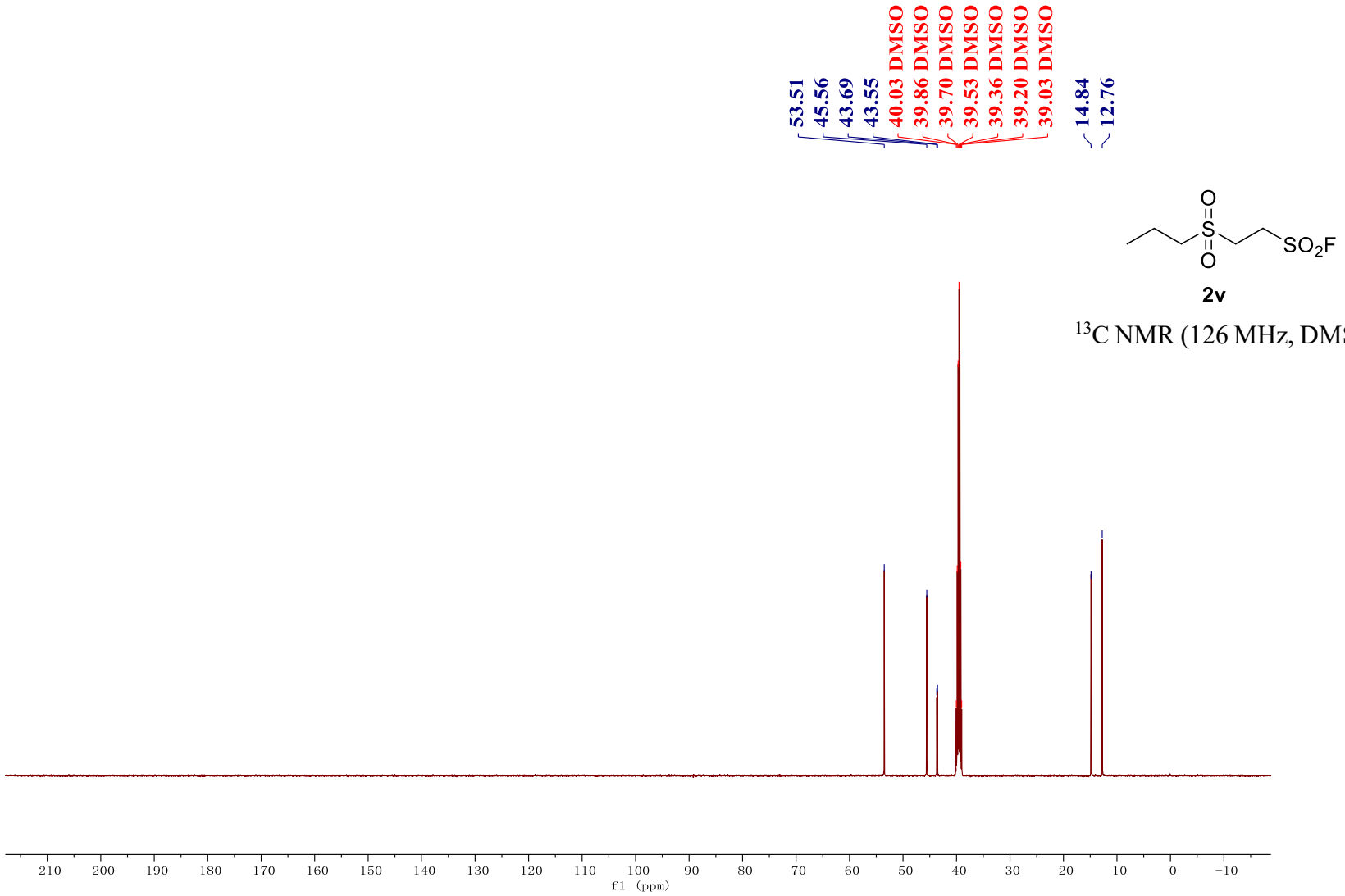


2u

^{19}F NMR (471 MHz, DMSO-d_6)

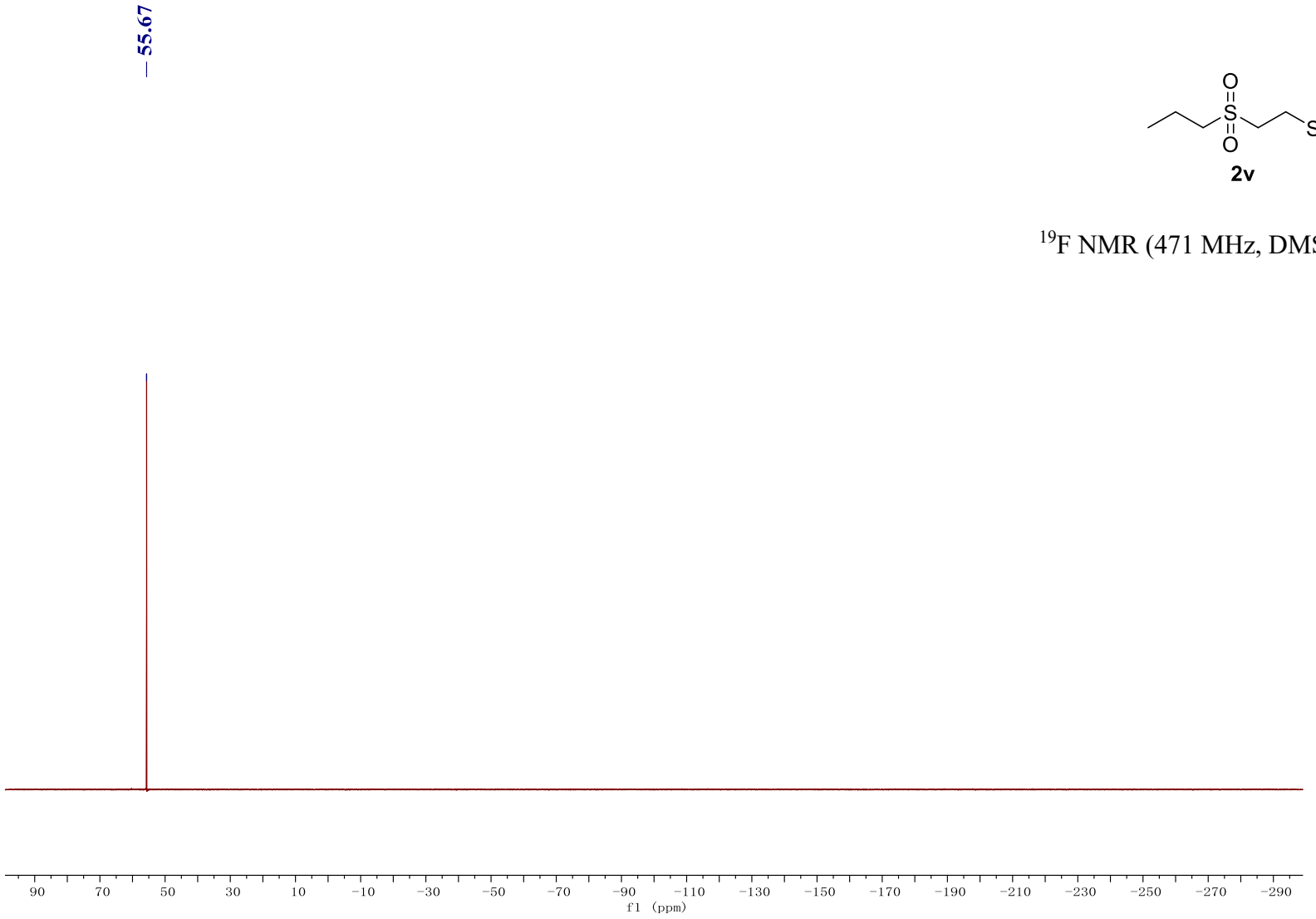


^{1}H NMR (500 MHz, DMSO-d_6)



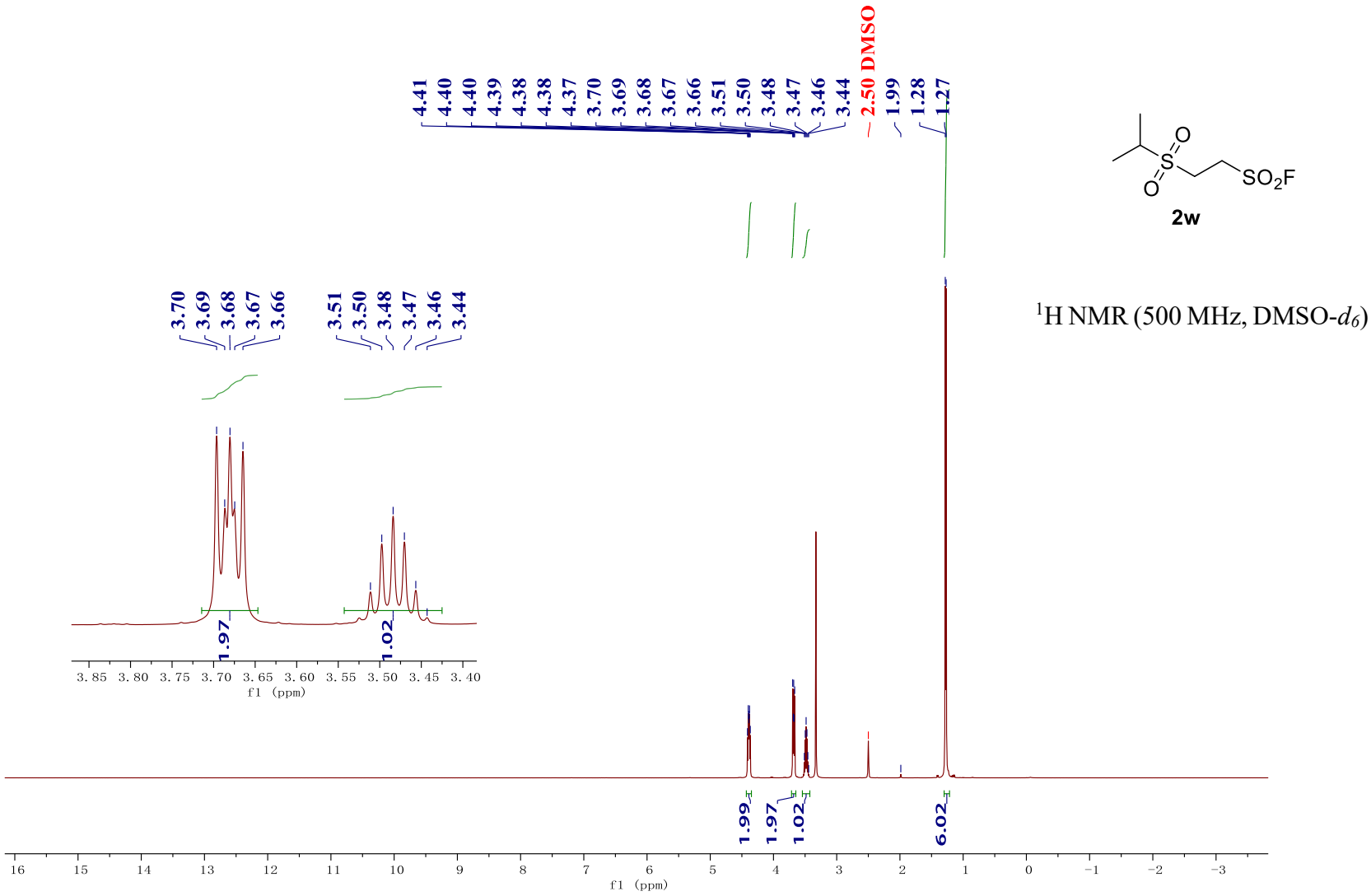
2v

^{13}C NMR (126 MHz, DMSO-d_6)



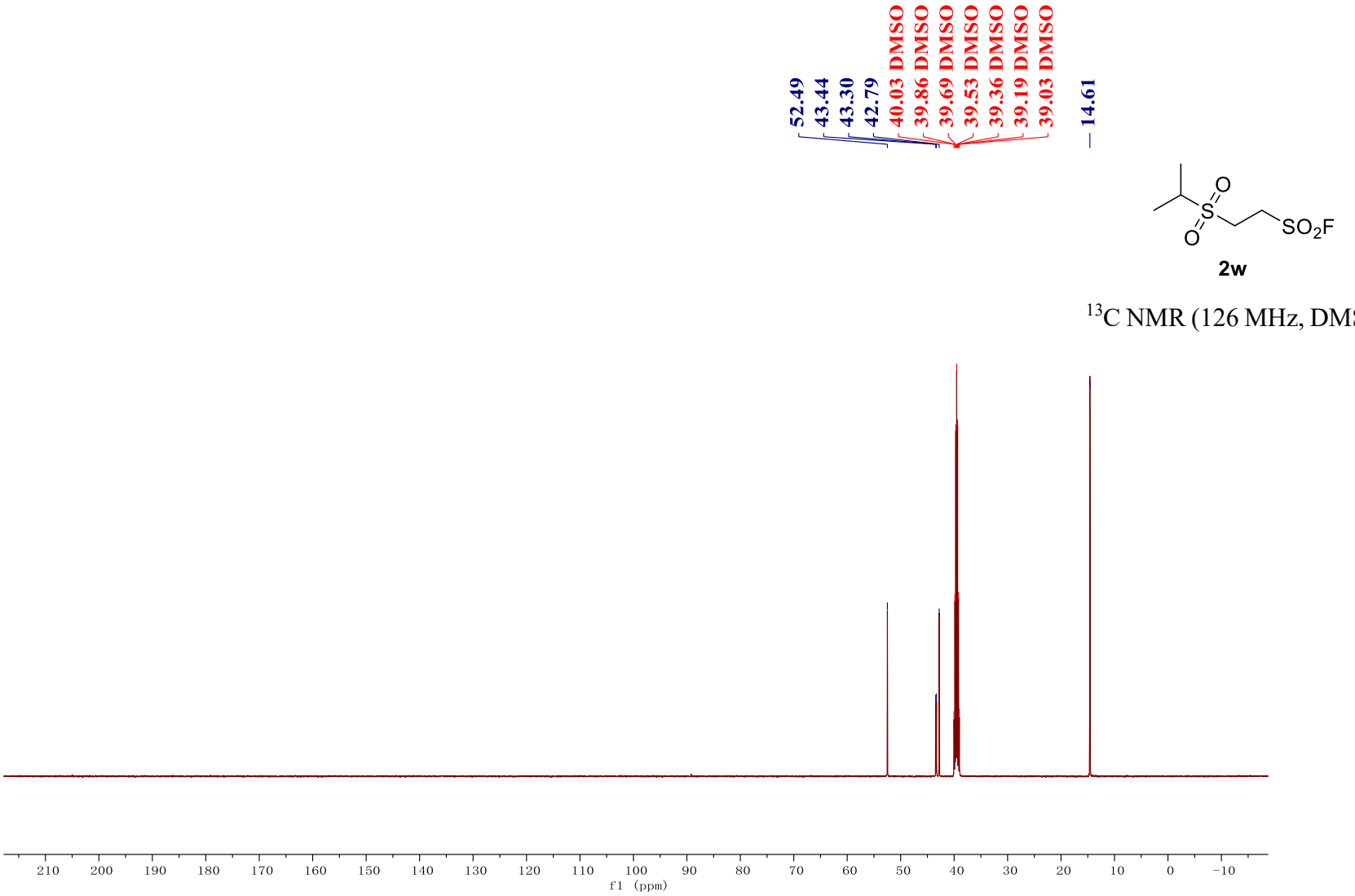
2v

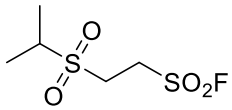
^{19}F NMR (471 MHz, DMSO-d_6)



2w

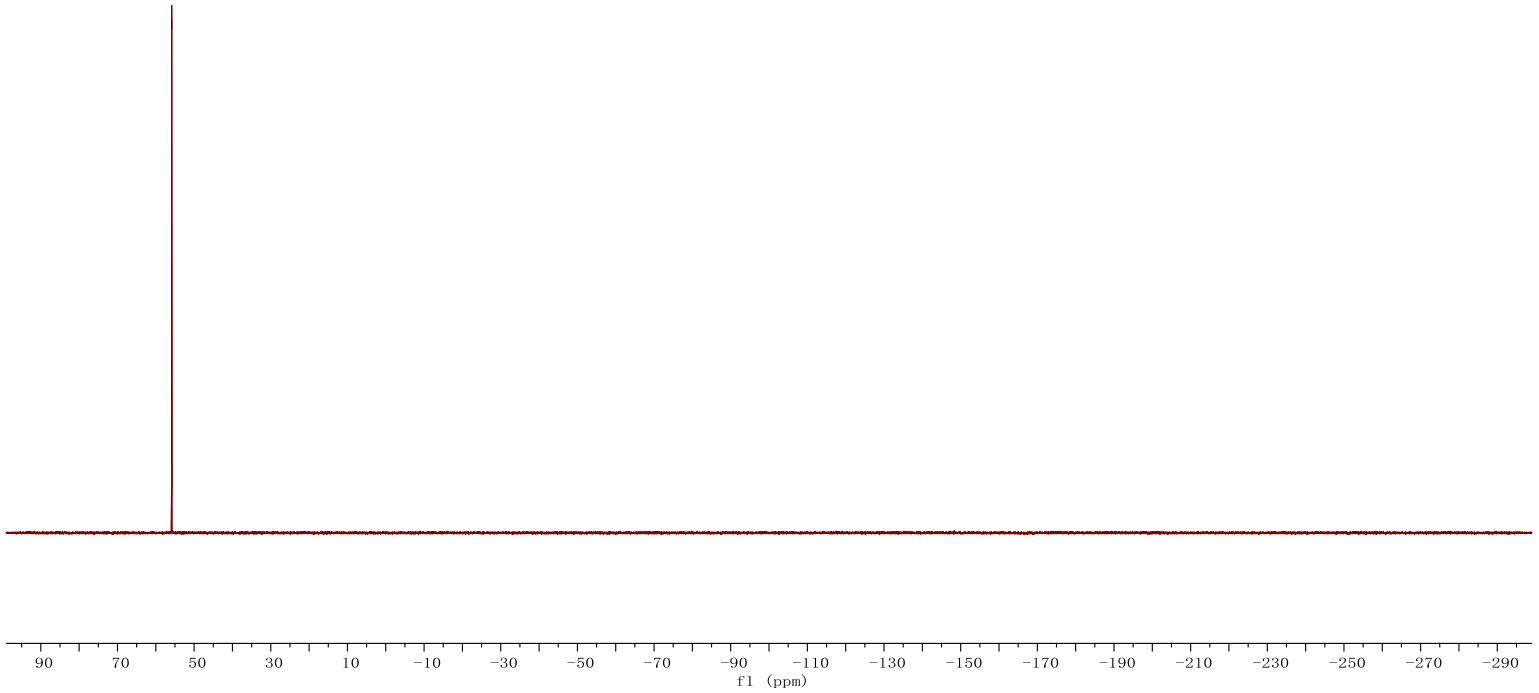
^{1}H NMR (500 MHz, DMSO-d_6)

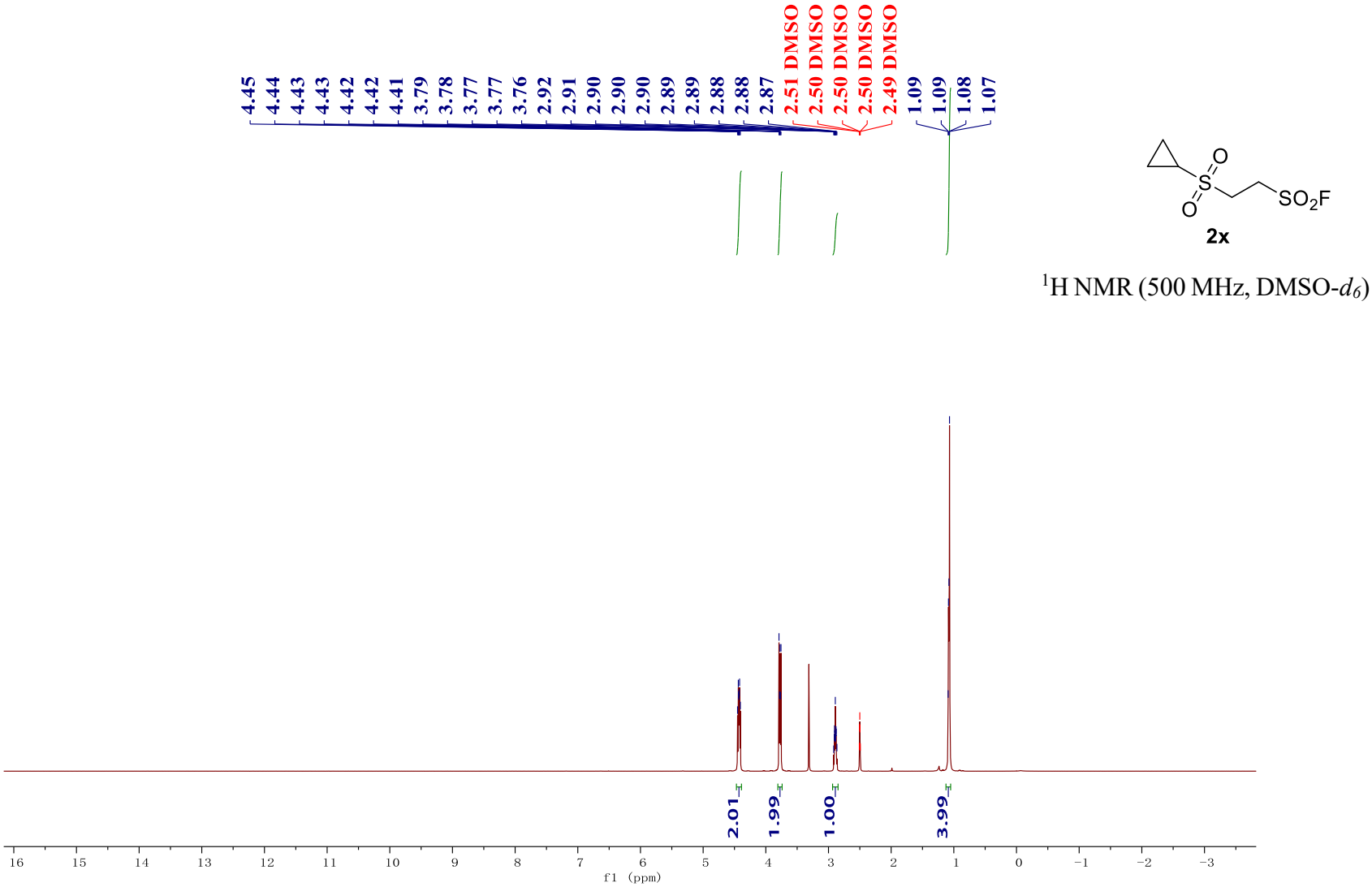

52.49
43.44
43.30
42.79
40.03 DMSO
39.86 DMSO
39.69 DMSO
39.53 DMSO
39.36 DMSO
39.19 DMSO
39.03 DMSO
14.61
O
S
O
SO2F
2w
13C NMR (126 MHz, DMSO-d6)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



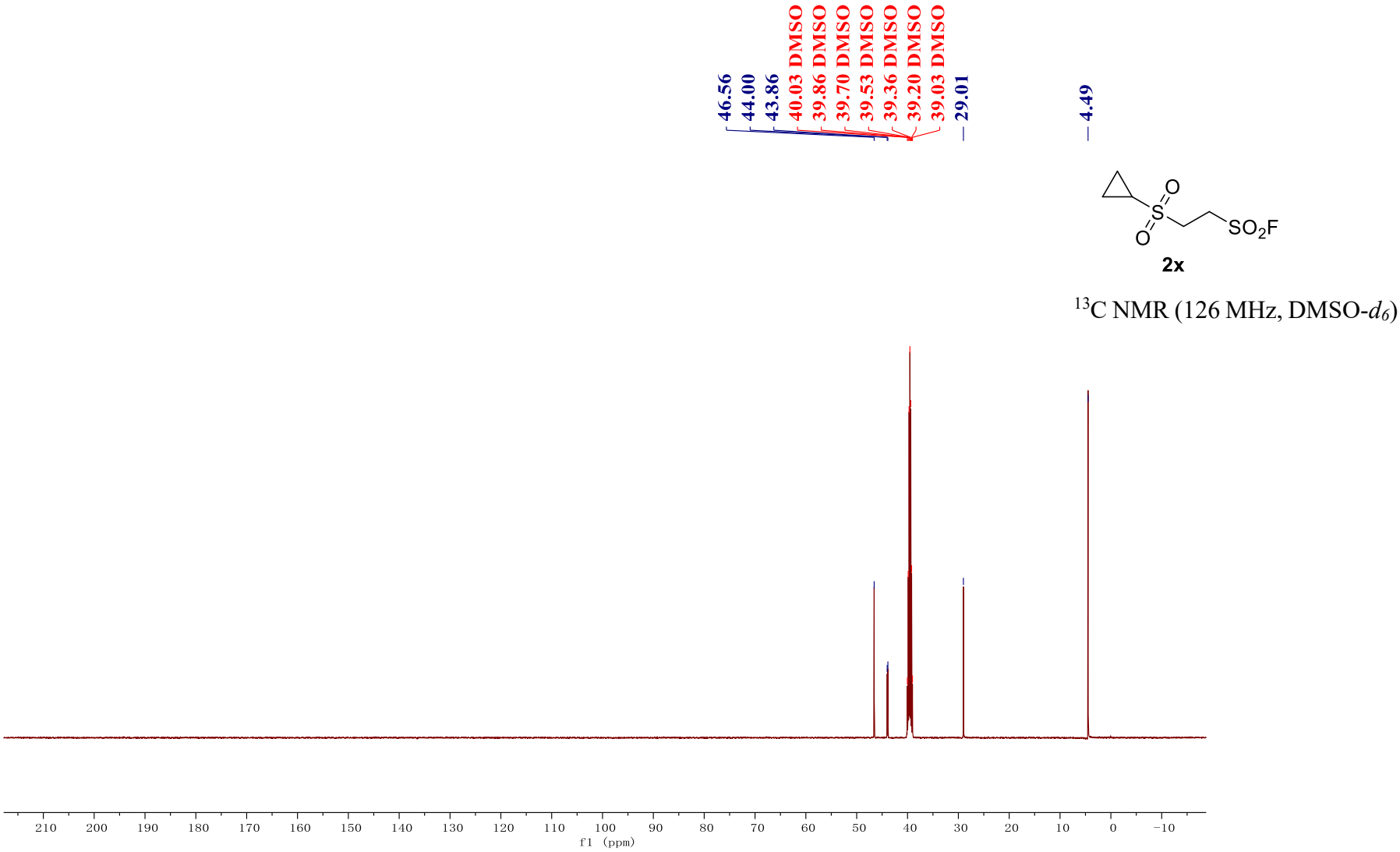
2w

^{19}F NMR (471 MHz, DMSO-d_6)

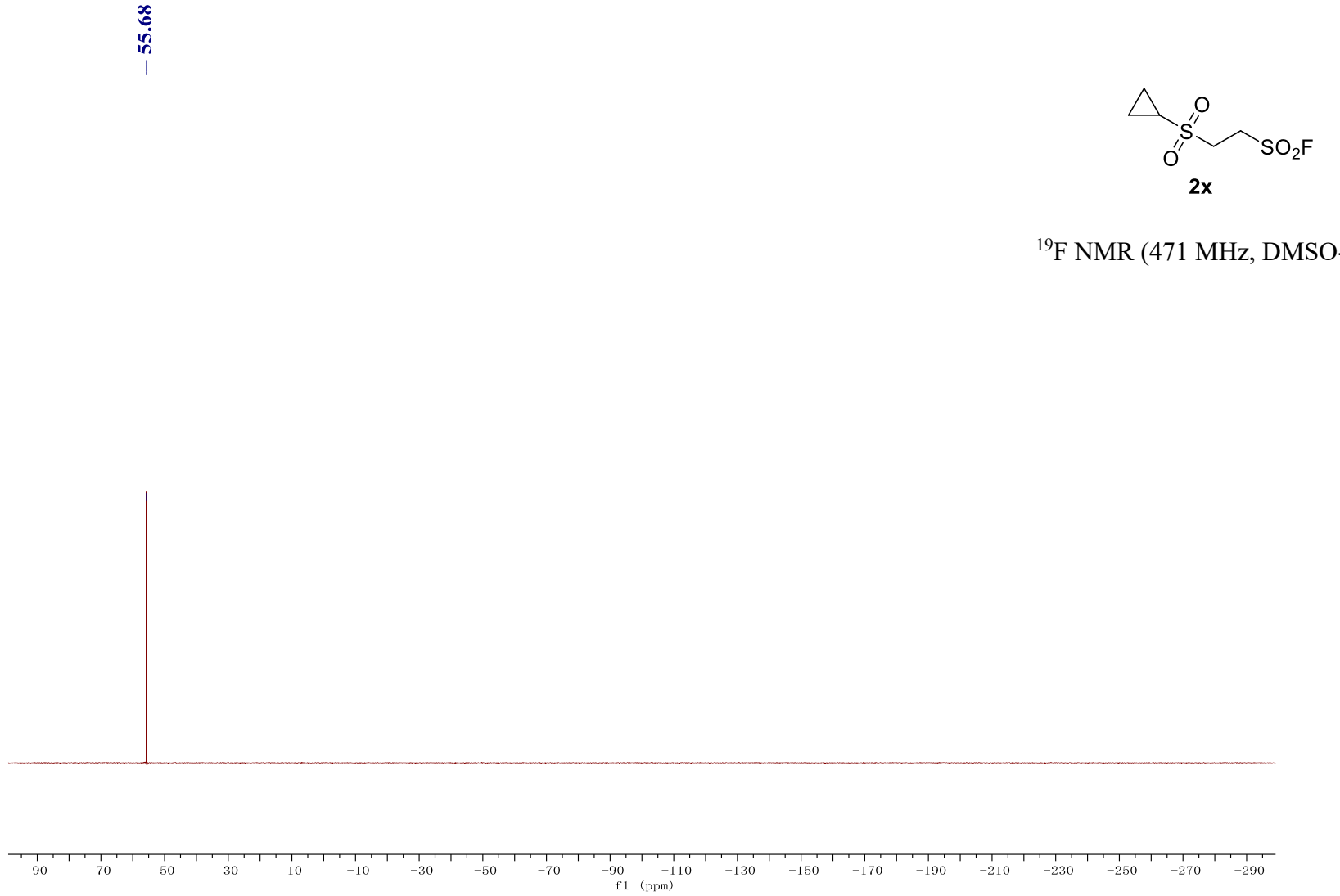




^{1}H NMR (500 MHz, DMSO-d_6)

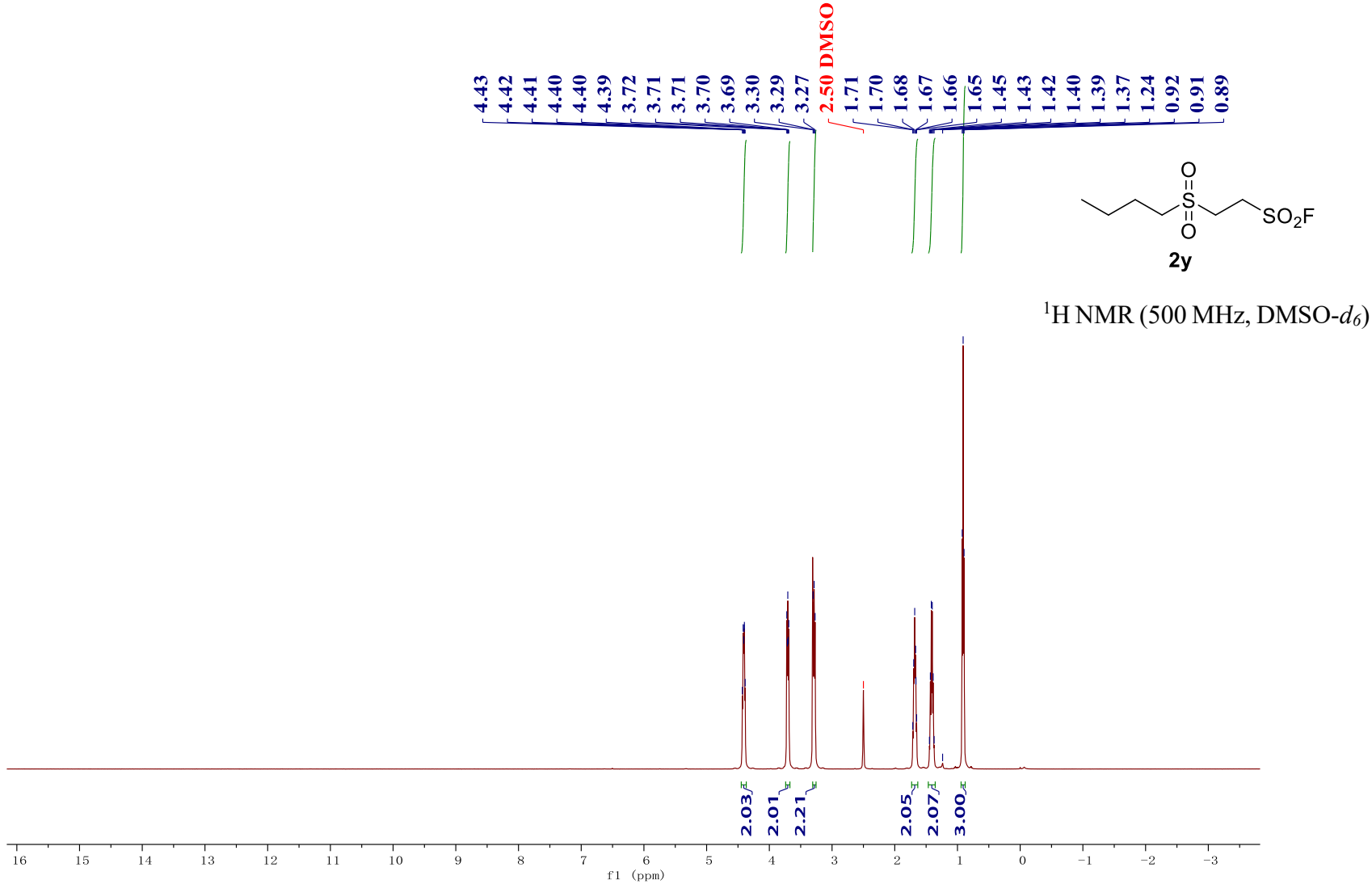


^{13}C NMR (126 MHz, DMSO-d_6)

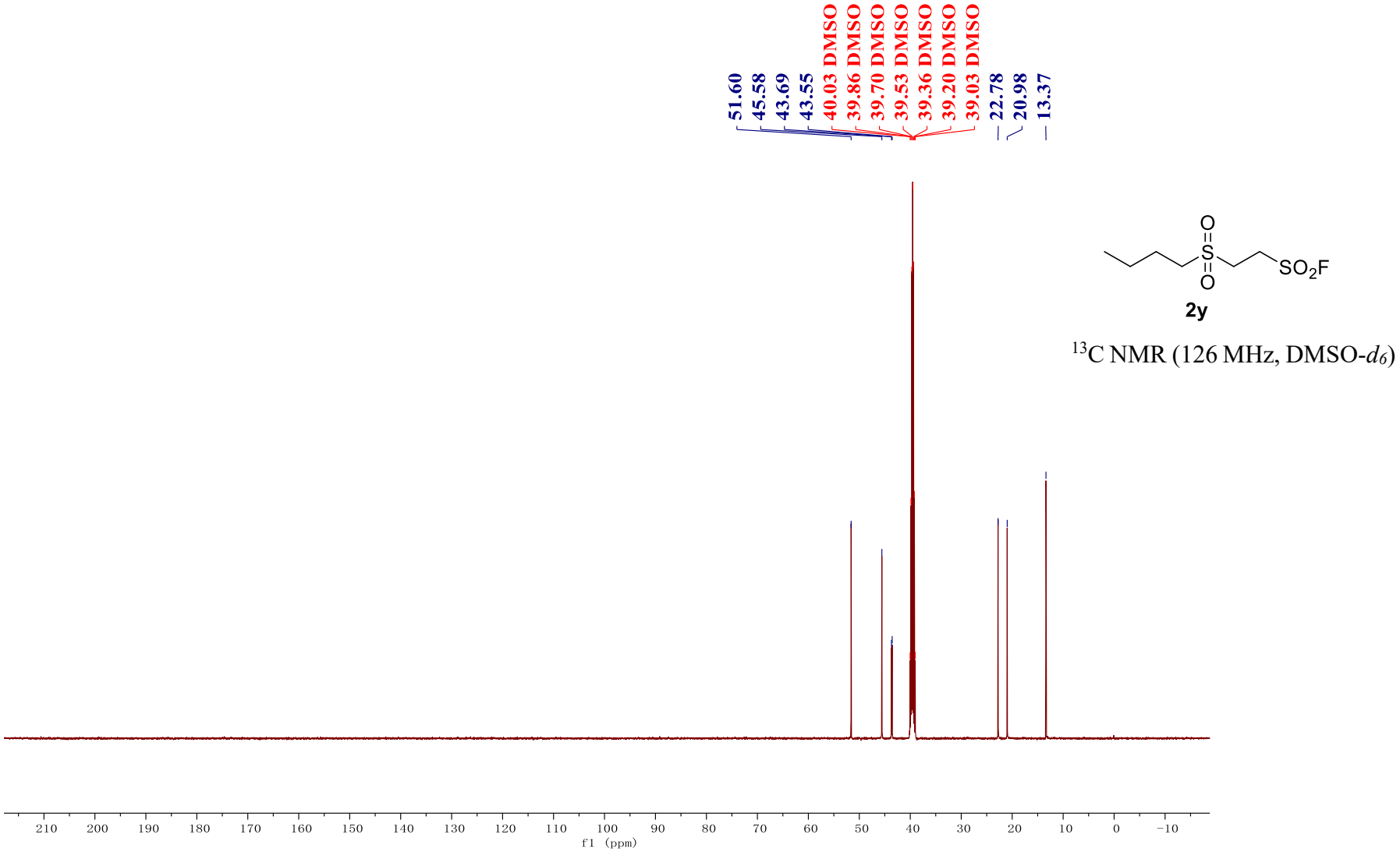


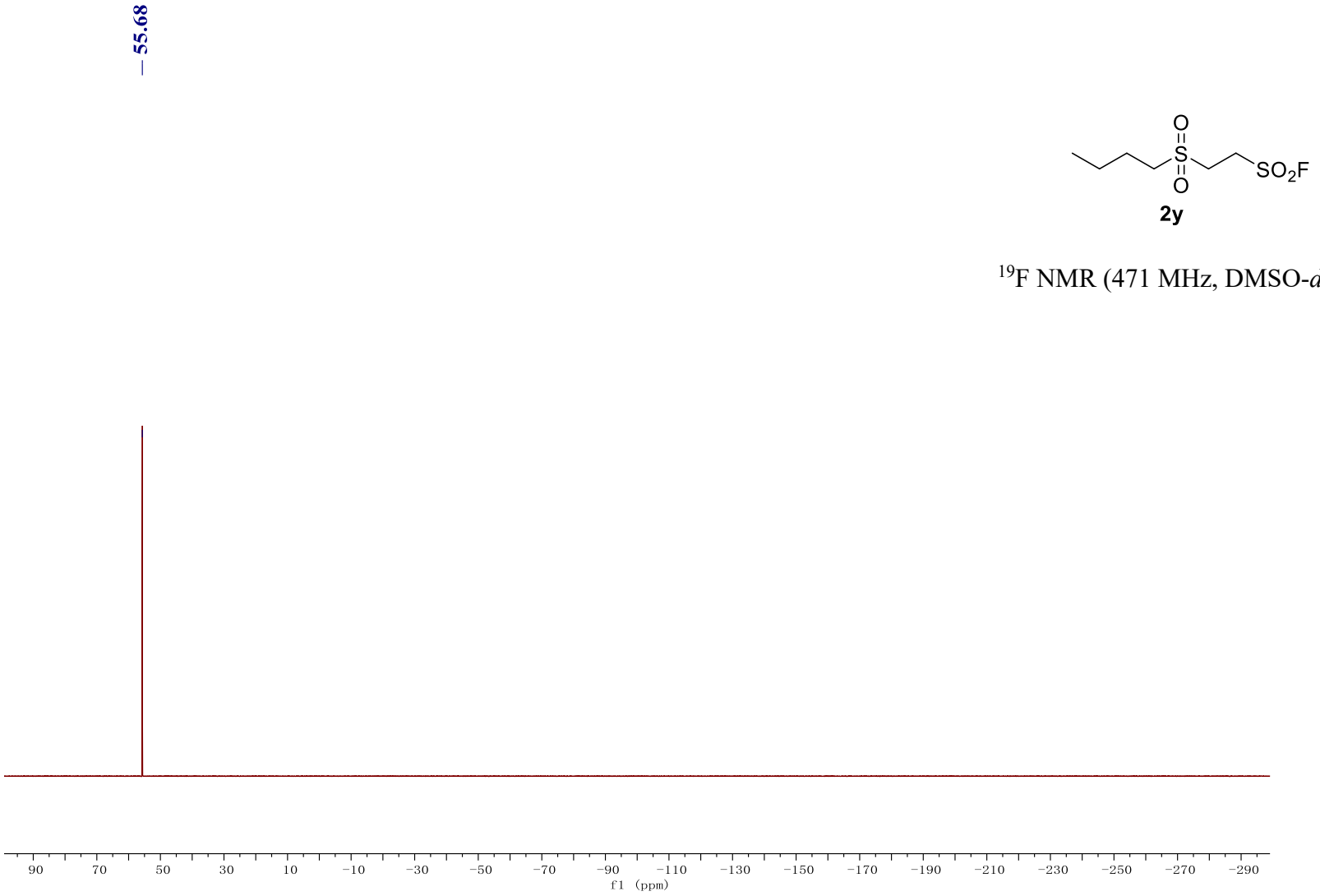
2x

^{19}F NMR (471 MHz, DMSO-d_6)



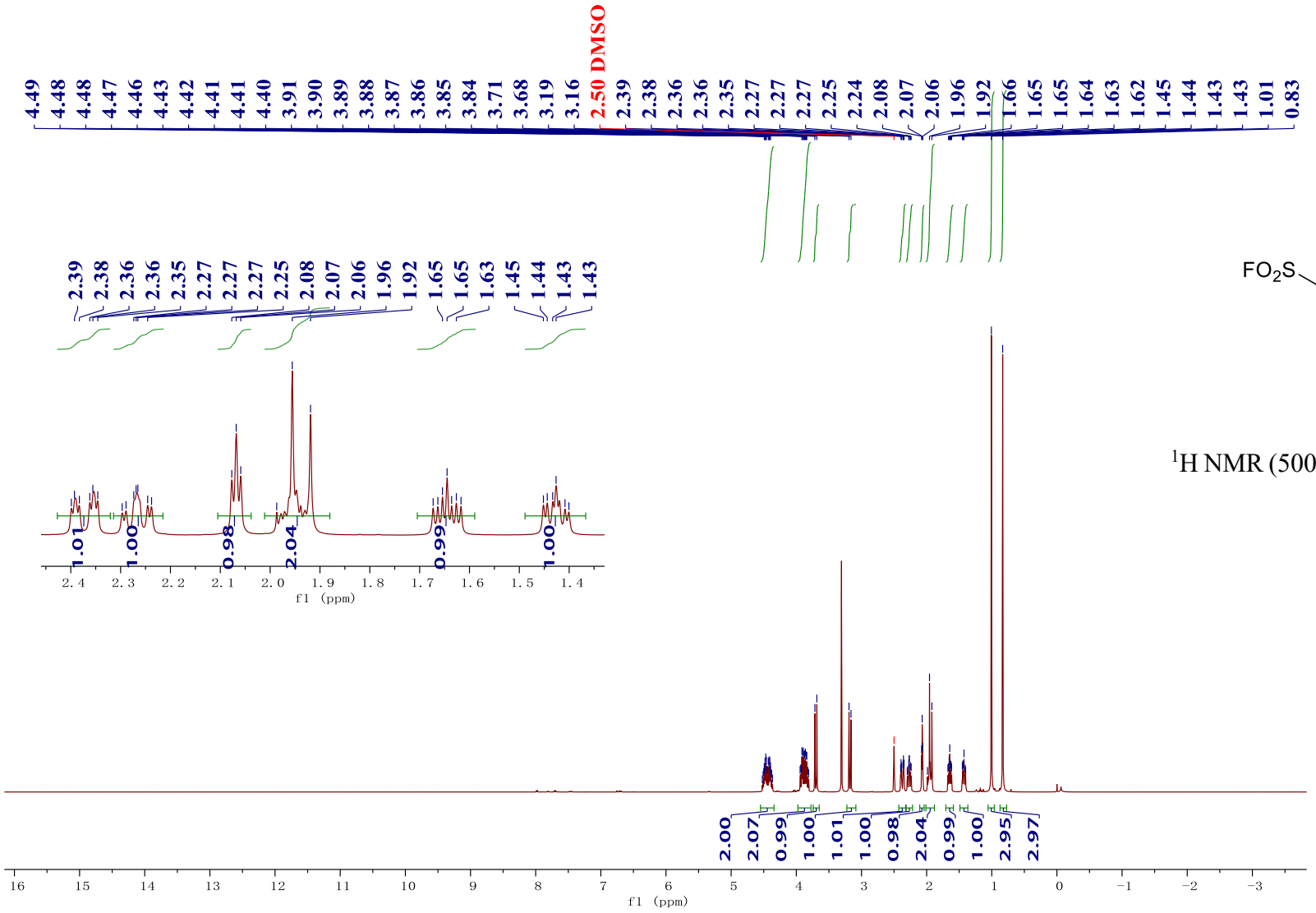
^{1}H NMR (500 MHz, DMSO-d_6)

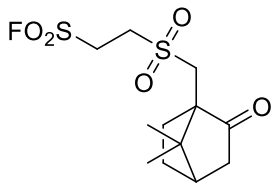

51.60
45.58
43.69
43.55
40.03 DMSO
39.86 DMSO
39.70 DMSO
39.53 DMSO
39.36 DMSO
39.20 DMSO
39.03 DMSO
22.78
20.98
13.37
O
S
O
SO2F
2y
13C NMR (126 MHz, DMSO-d6)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



2y

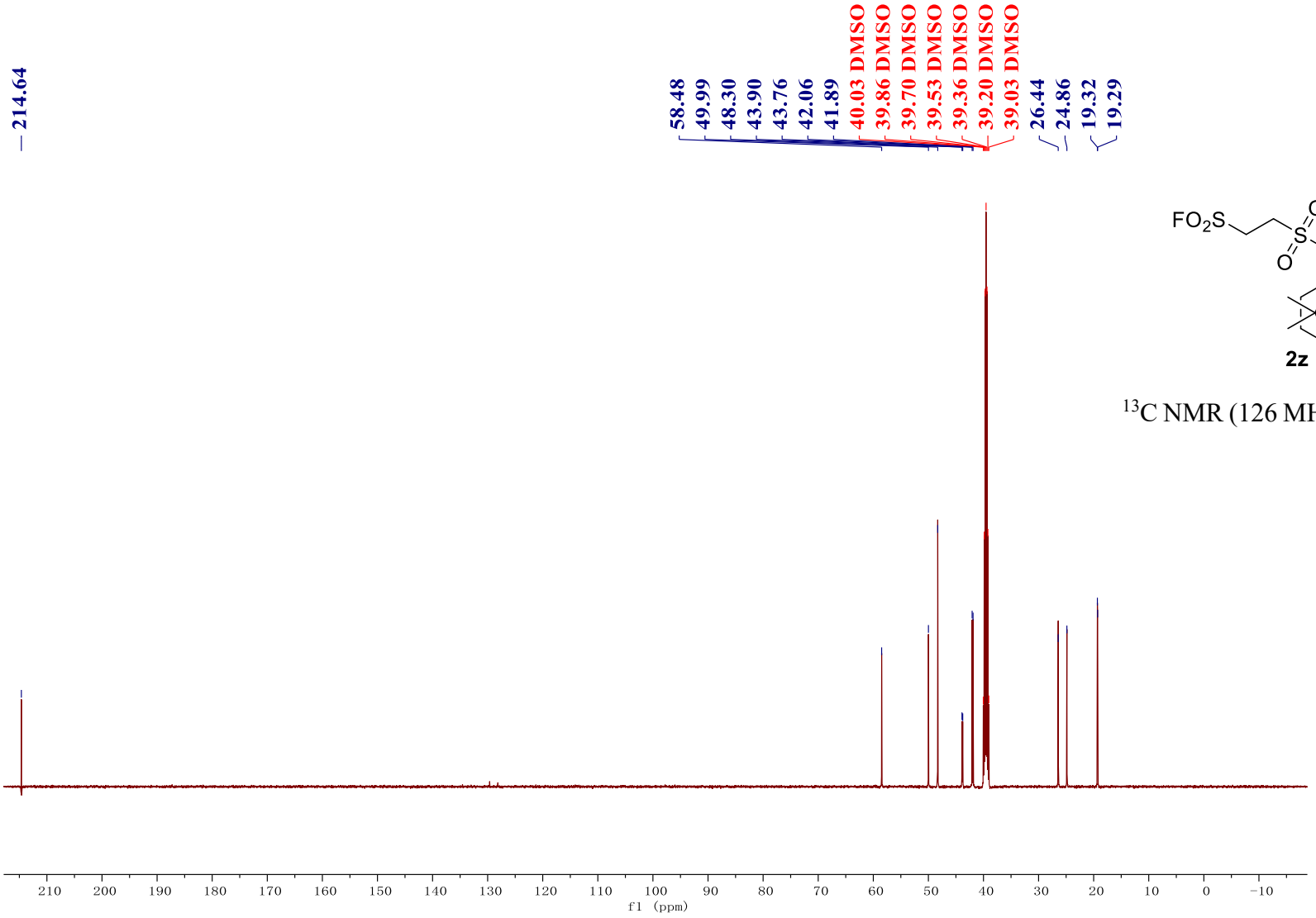
^{19}F NMR (471 MHz, DMSO-d_6)





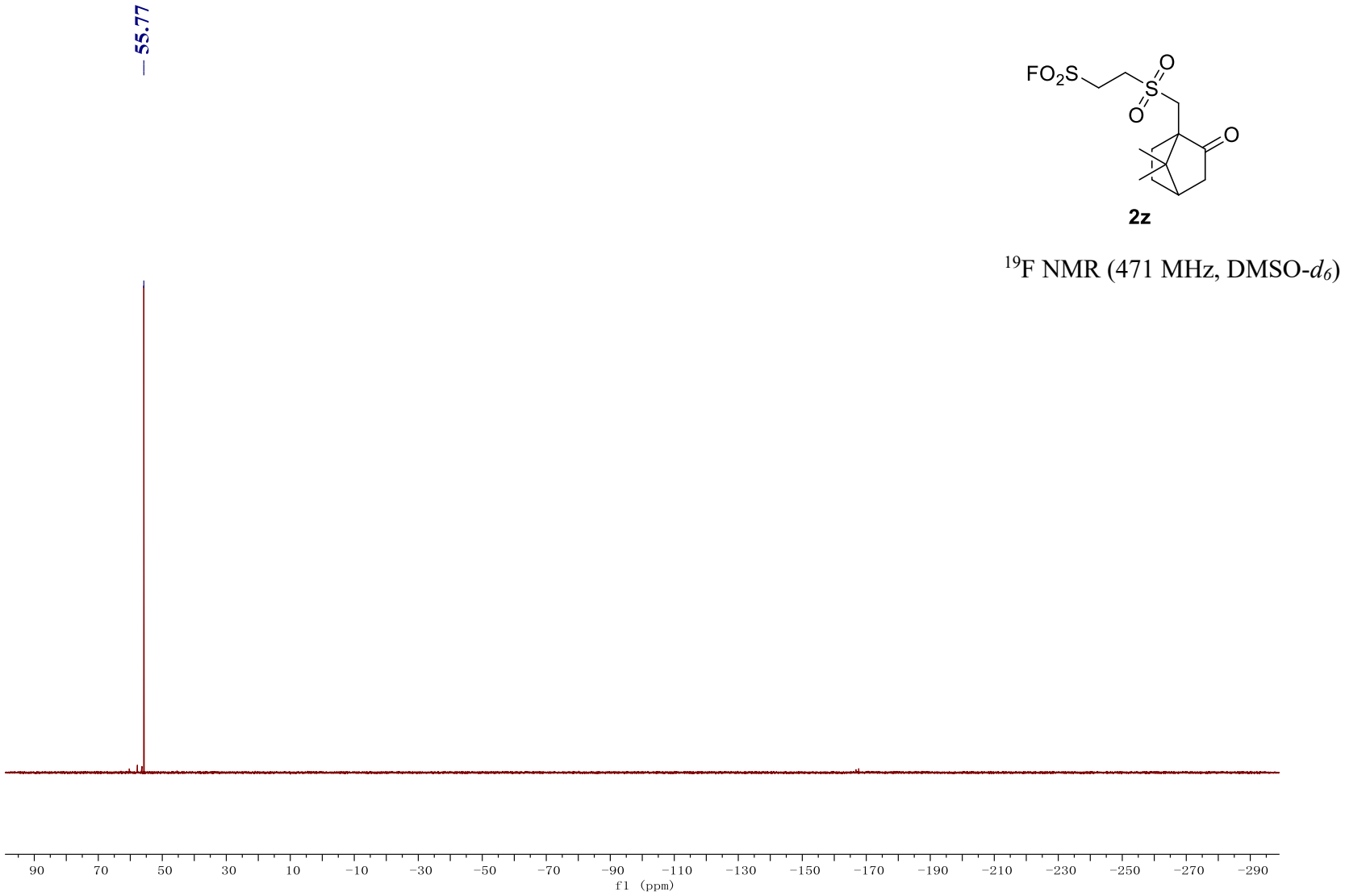
2z

^{1}H NMR (500 MHz, DMSO-d_6)



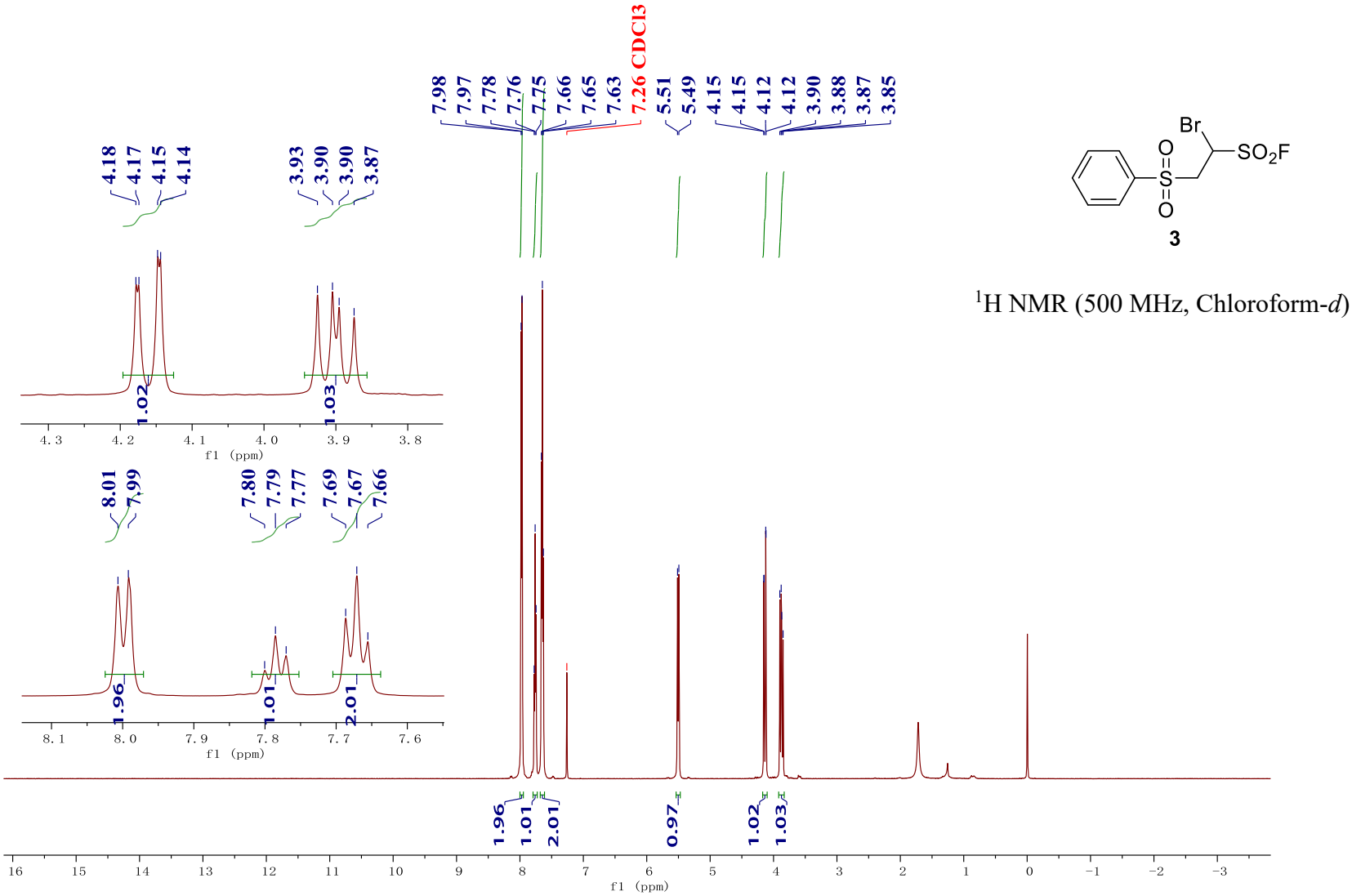
2z

^{13}C NMR (126 MHz, DMSO-d_6)



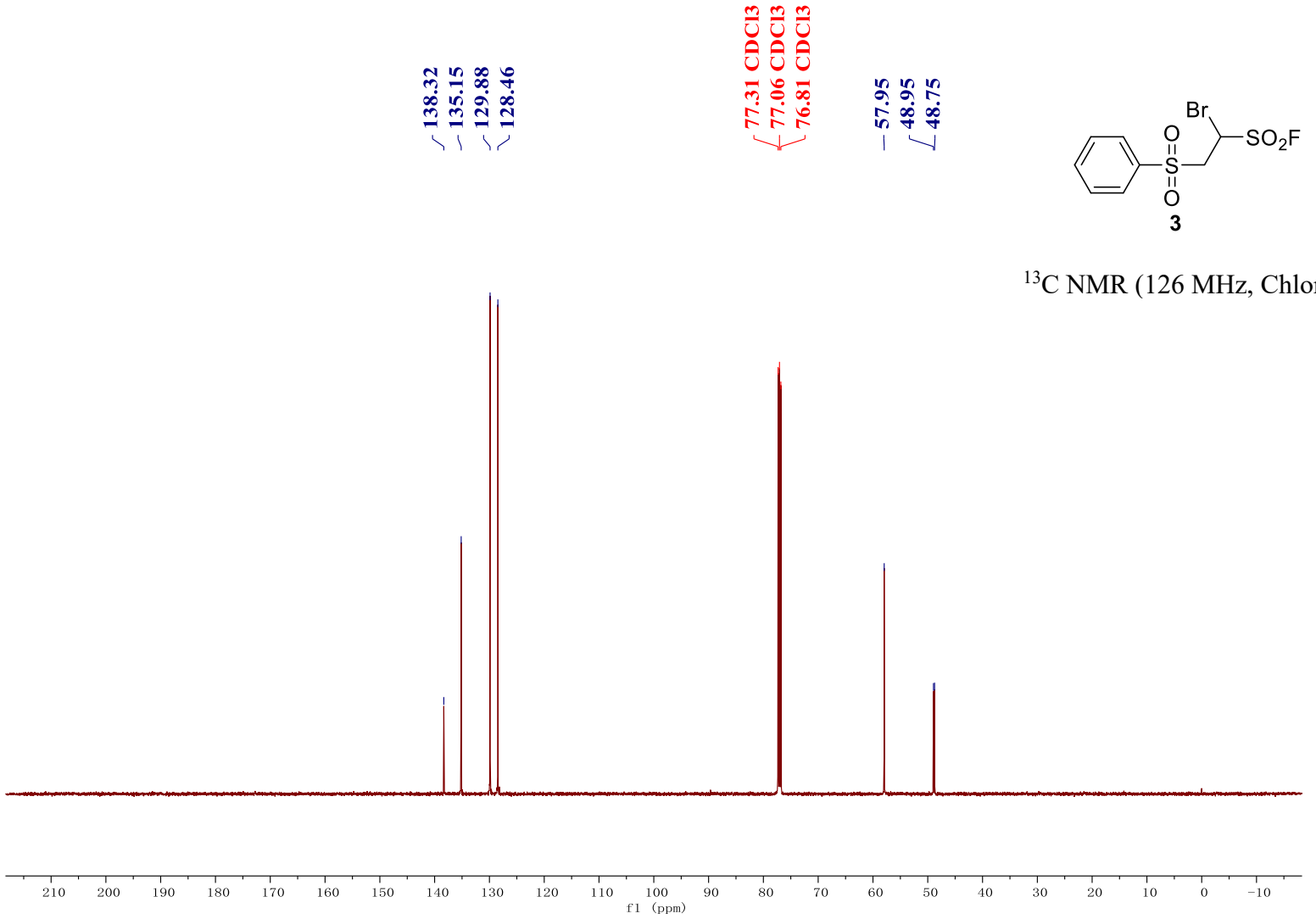
2z

^{19}F NMR (471 MHz, DMSO-d_6)

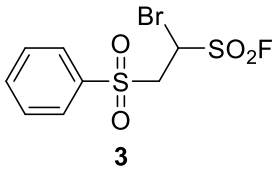


3

^{1}H NMR (500 MHz, Chloroform-*d*)

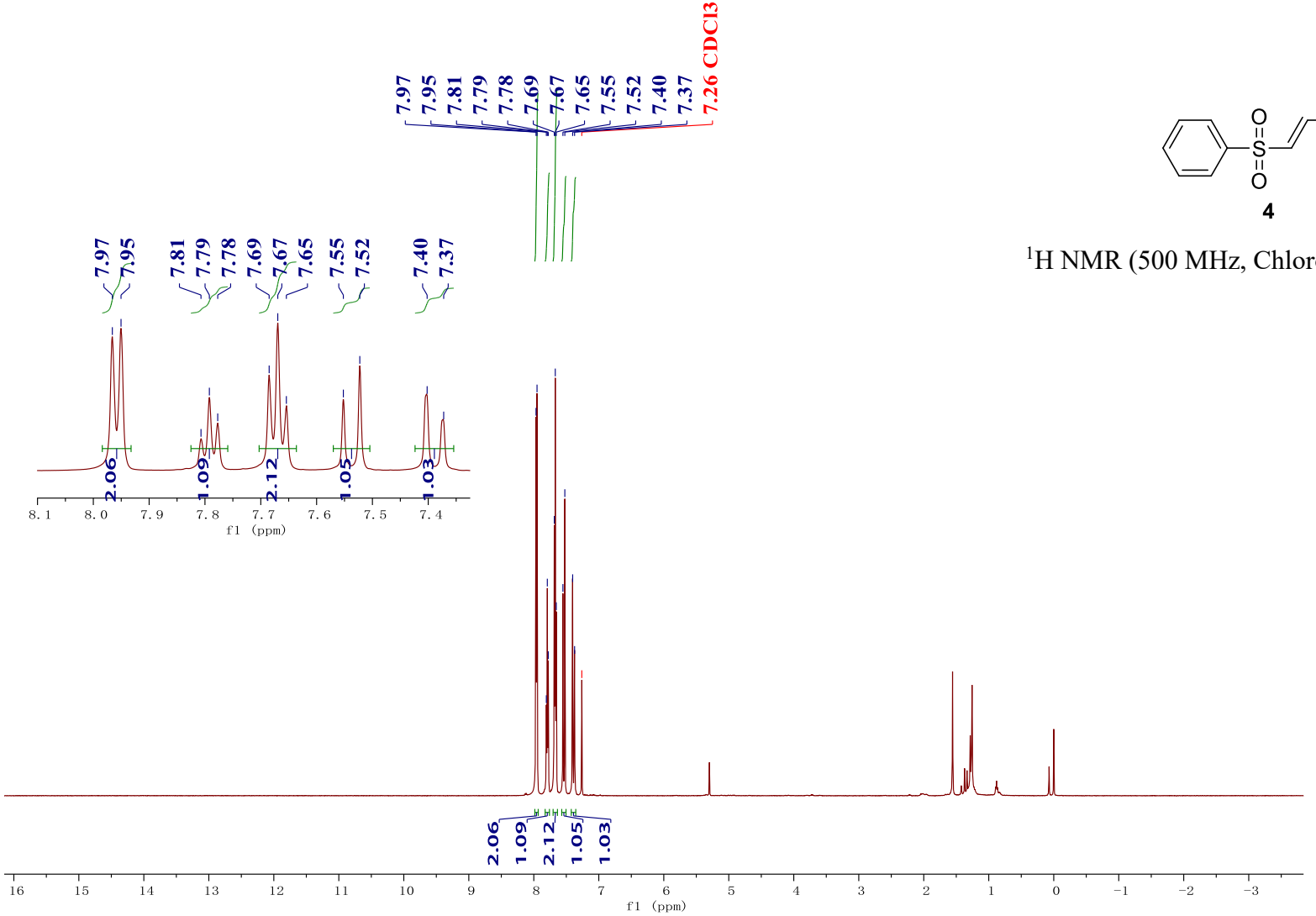


^{13}C NMR (126 MHz, Chloroform-*d*)



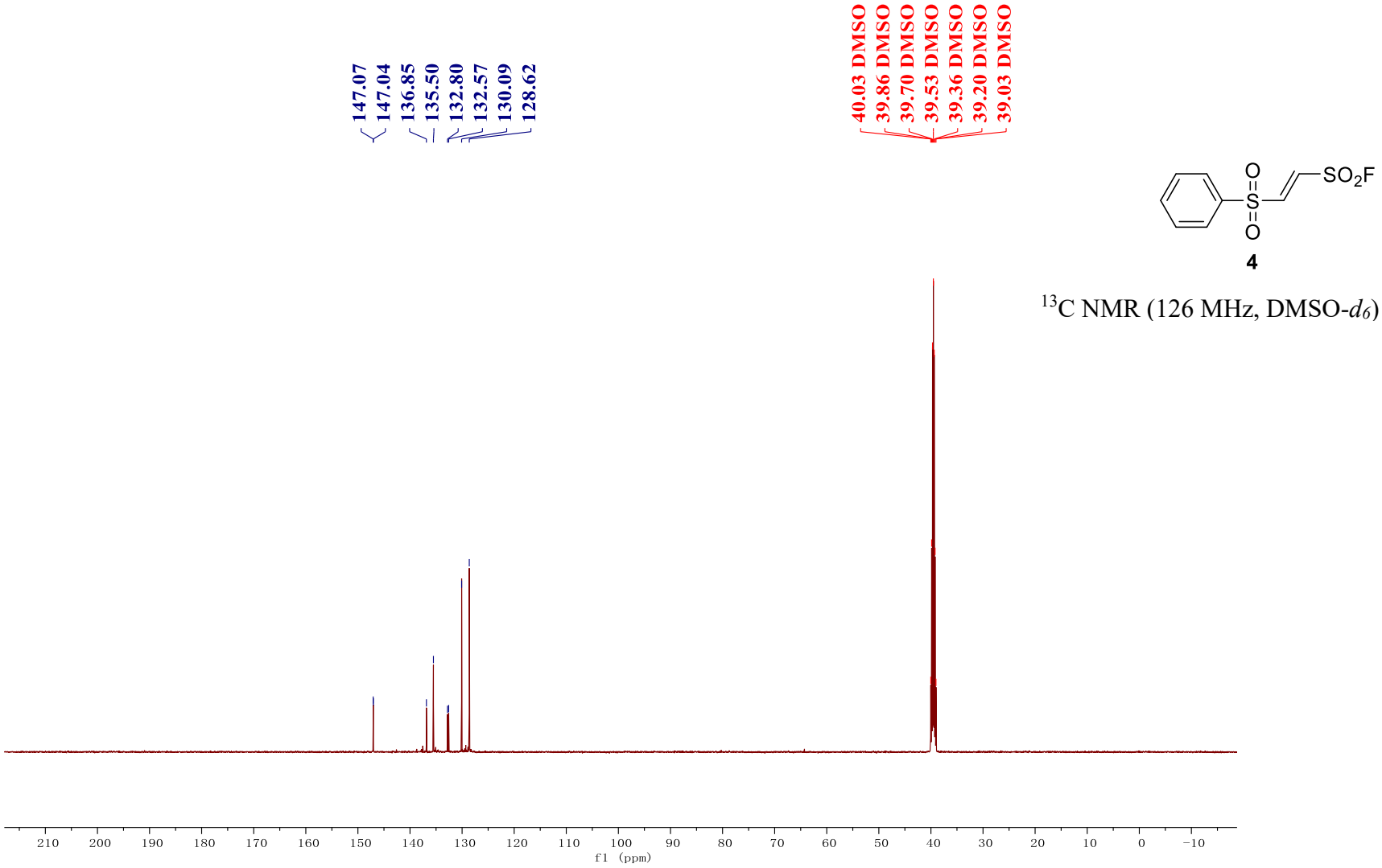
3

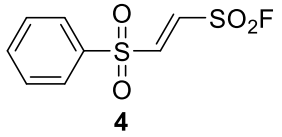
^{19}F NMR (471 MHz, Chloroform-*d*)



4

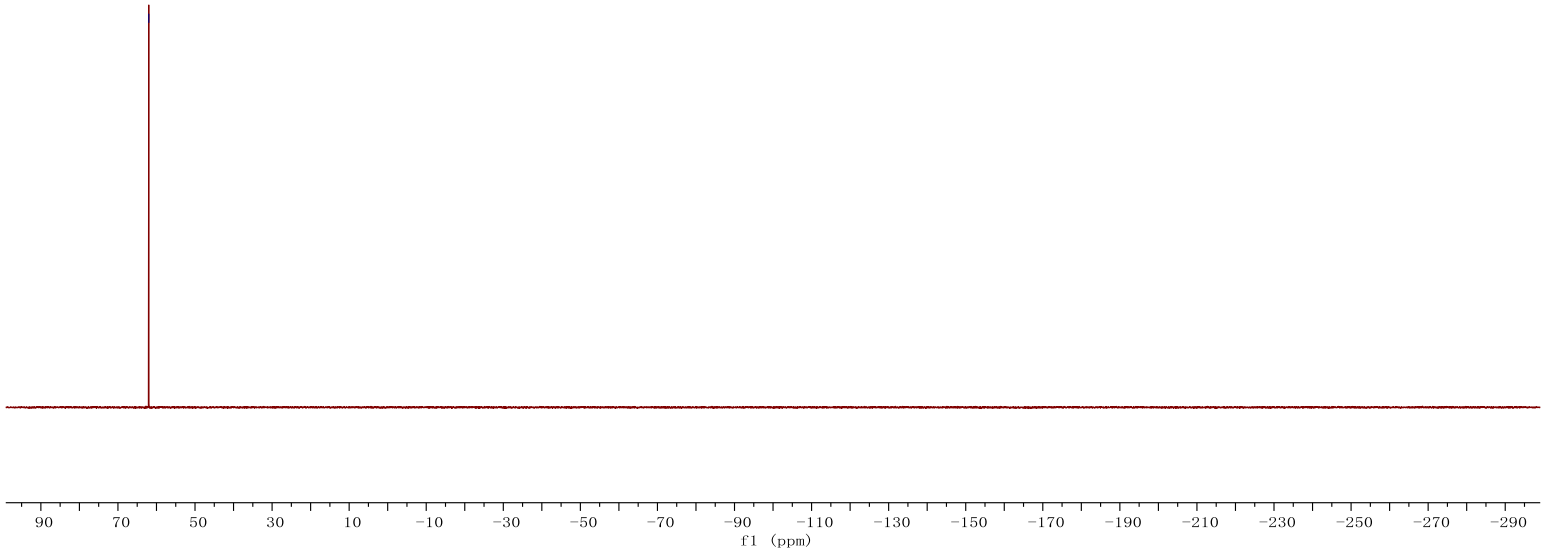
^{1}H NMR (500 MHz, Chloroform-*d*)

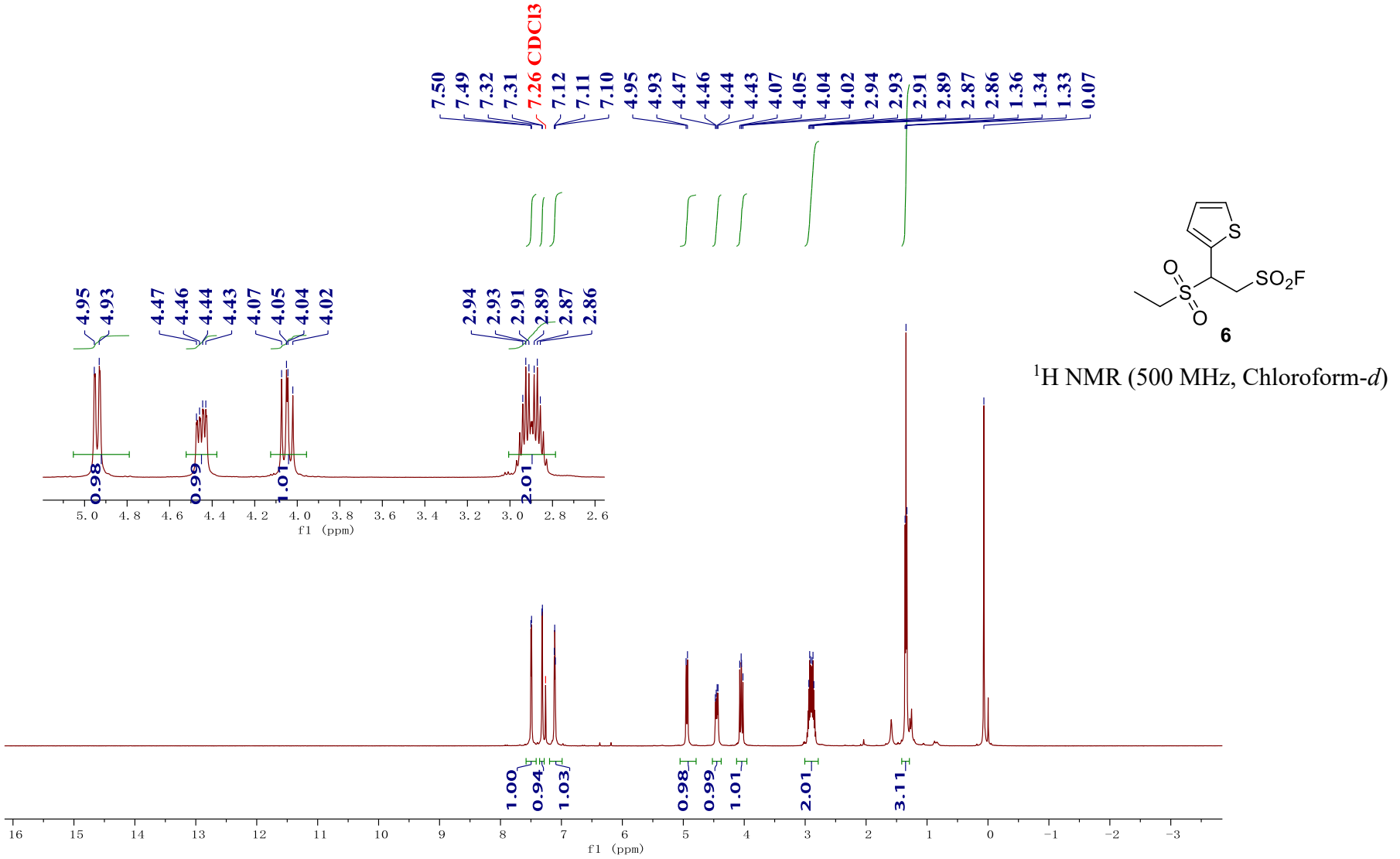

147.07
147.04
136.85
135.50
132.80
132.57
130.09
128.62
40.03 DMSO
39.86 DMSO
39.70 DMSO
39.53 DMSO
39.36 DMSO
39.20 DMSO
39.03 DMSO
O
S
O
SO2F
4
13C NMR (126 MHz, DMSO-d6)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



4

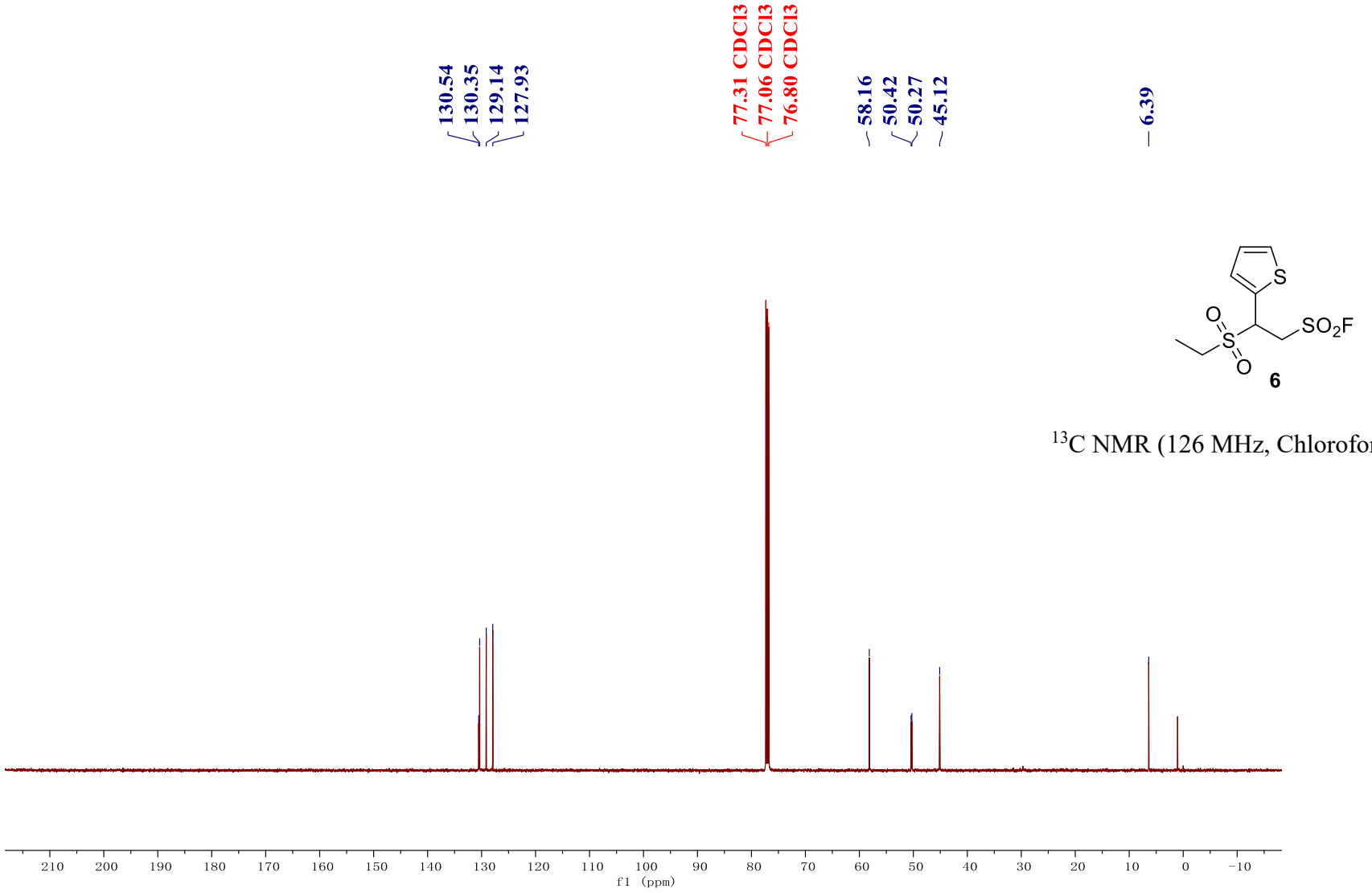
^{19}F NMR (471 MHz, Chloroform-*d*)



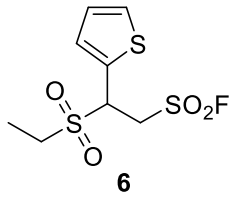


6

^{1}H NMR (500 MHz, Chloroform-*d*)

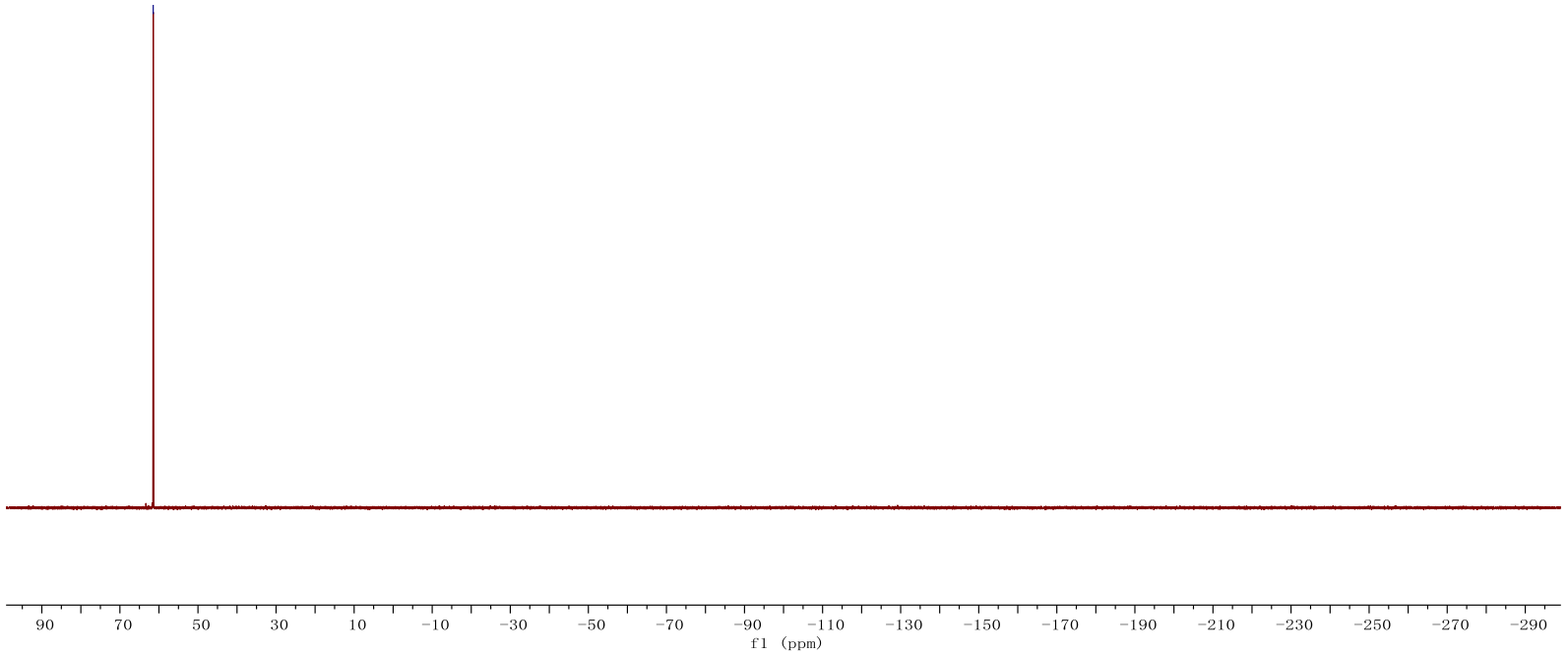


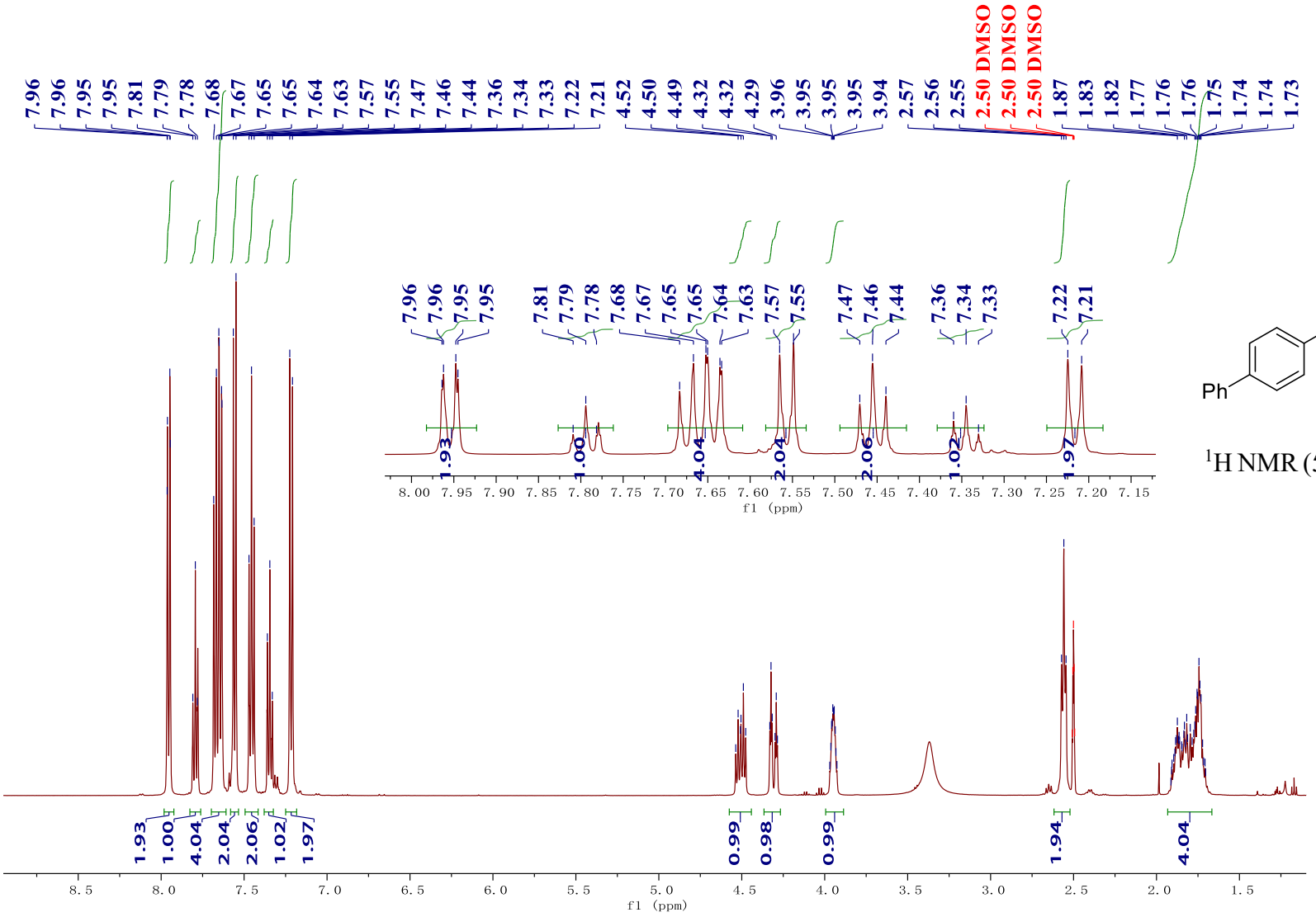
^{13}C NMR (126 MHz, Chloroform-*d*)

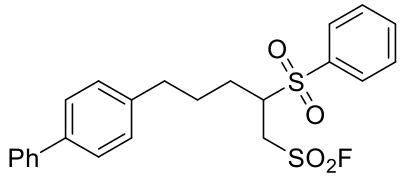


6

^{19}F NMR (471 MHz, Chloroform-*d*)

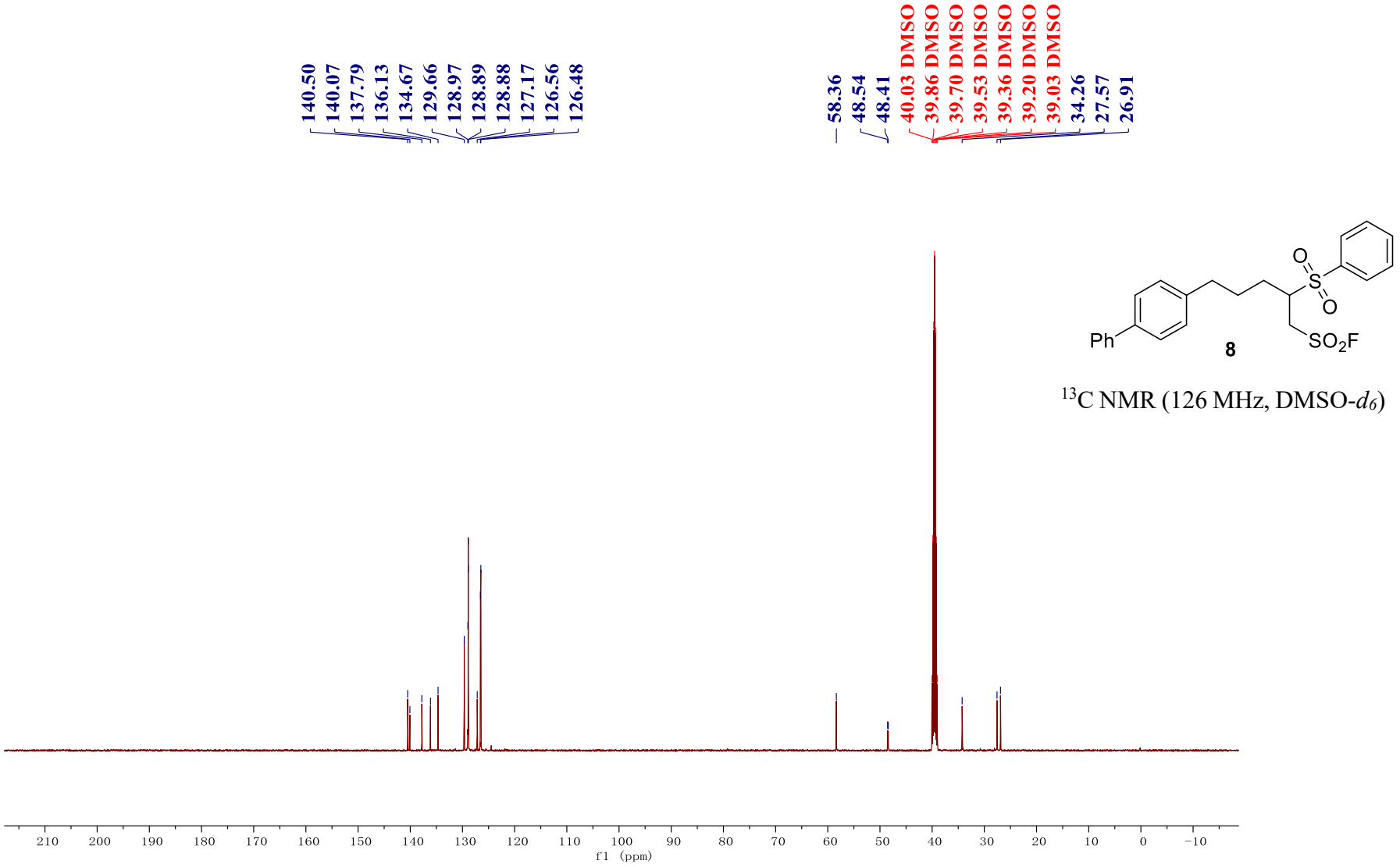




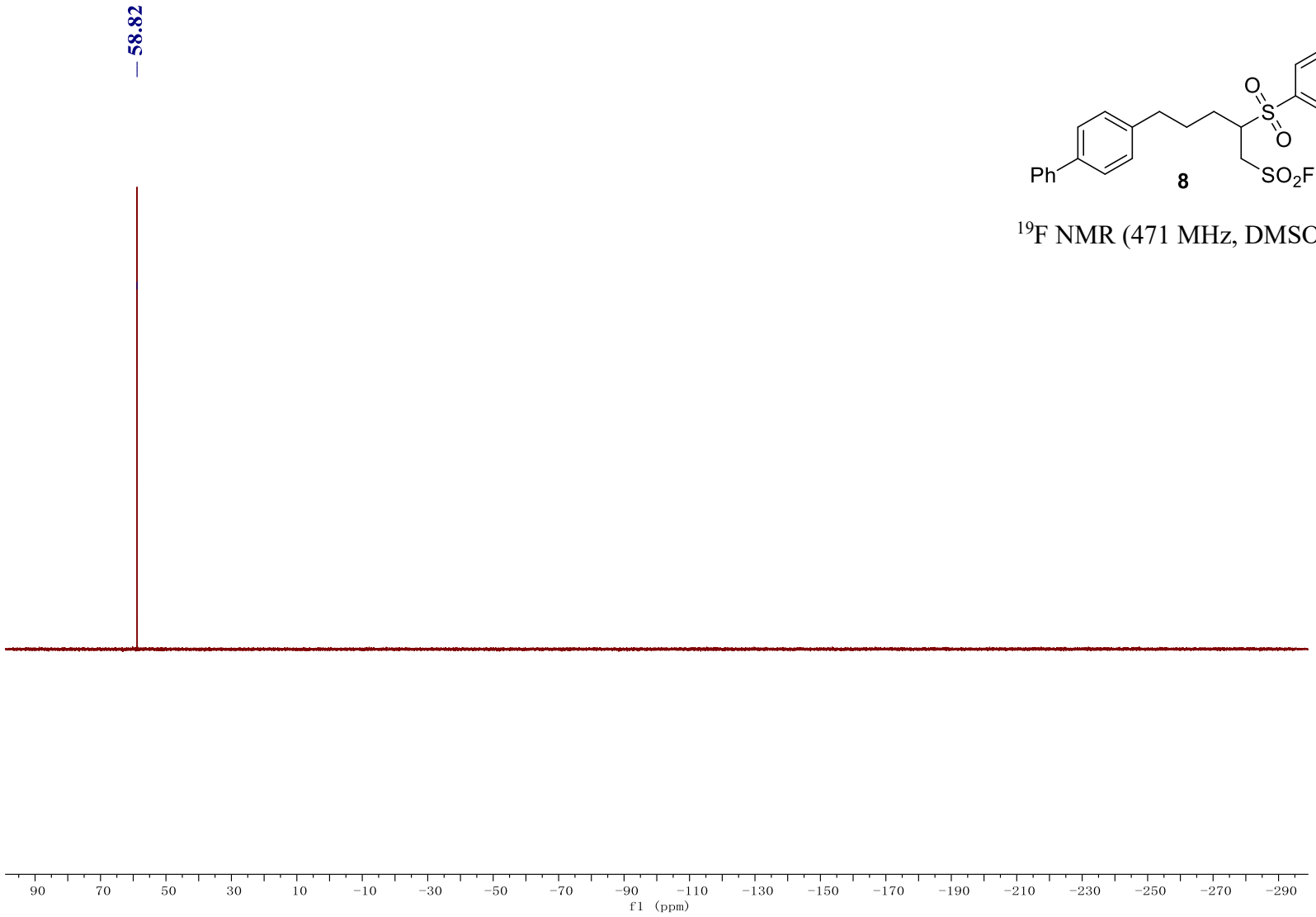


8

^{1}H NMR (500 MHz, DMSO-d_6)

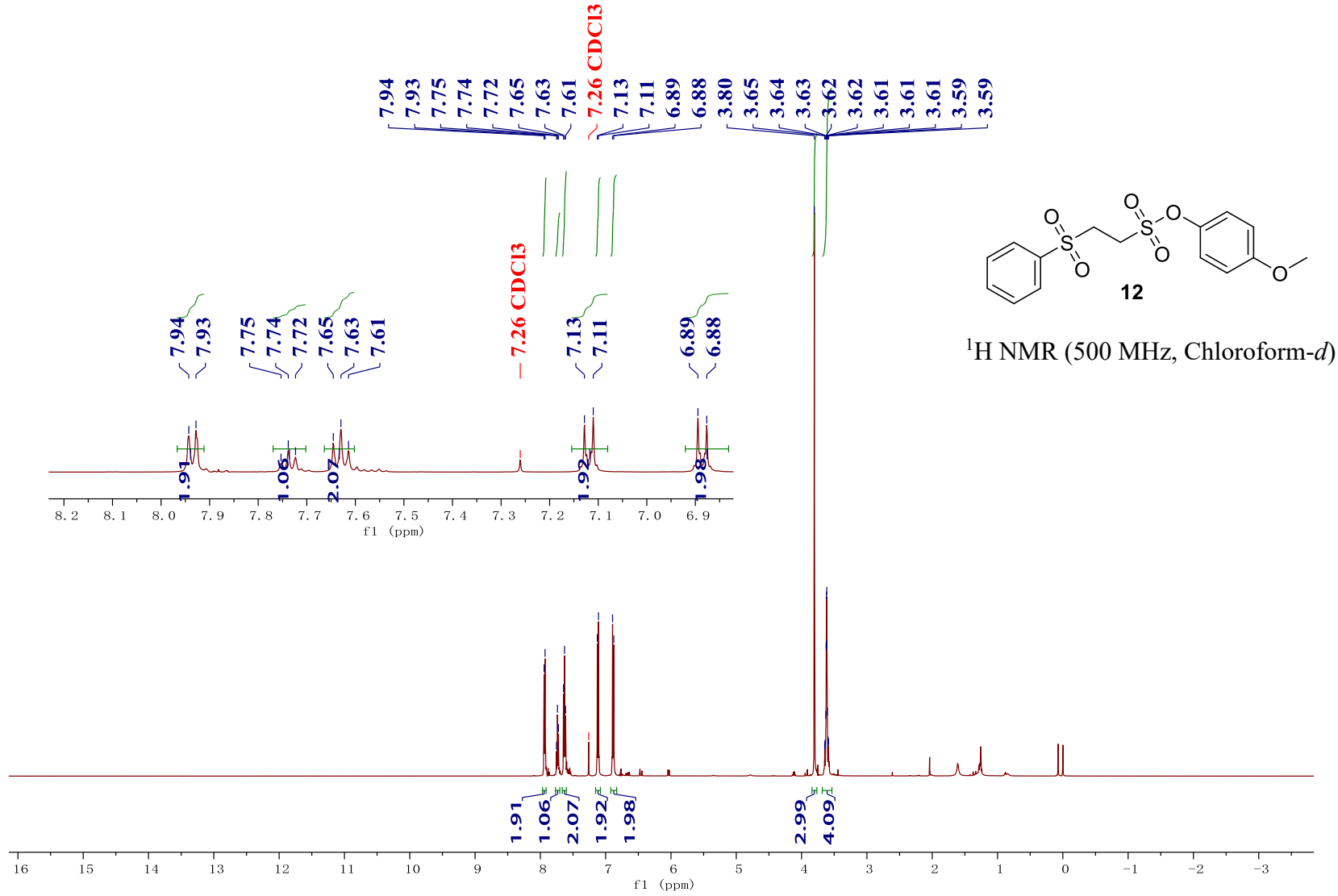


^{13}C NMR (126 MHz, DMSO-d_6)



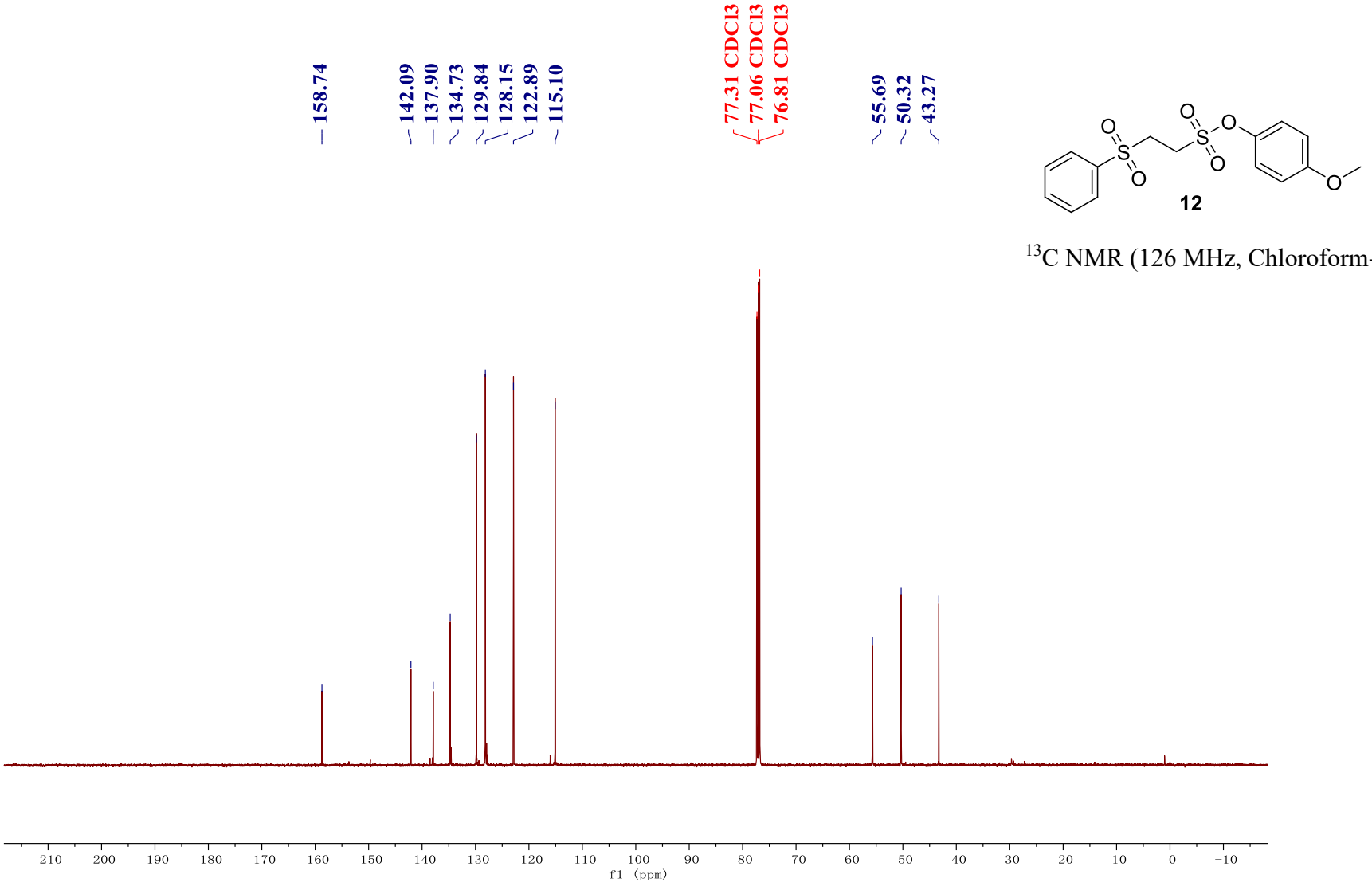
8

^{19}F NMR (471 MHz, DMSO-d_6)

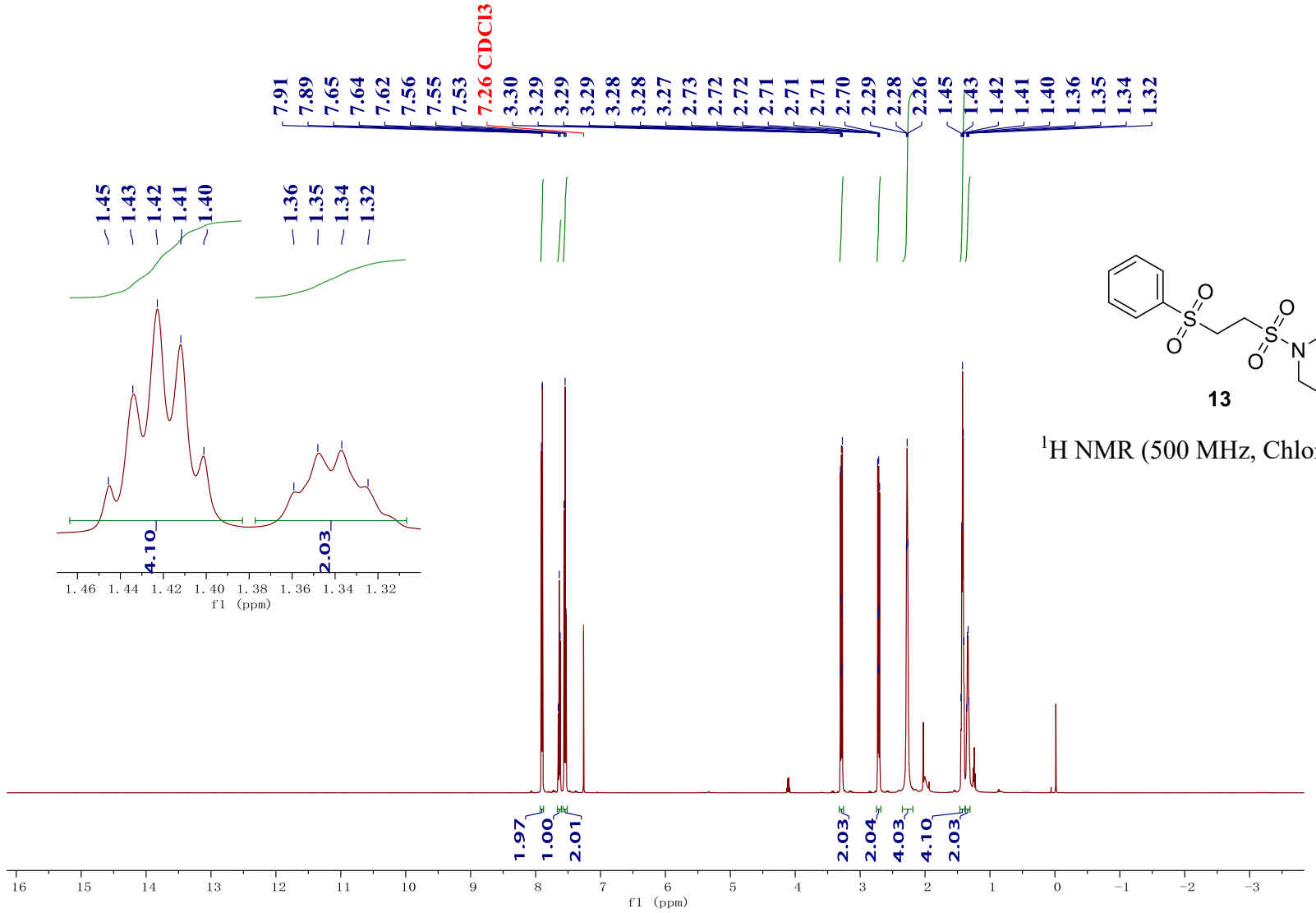


12

^{1}H NMR (500 MHz, Chloroform-*d*)

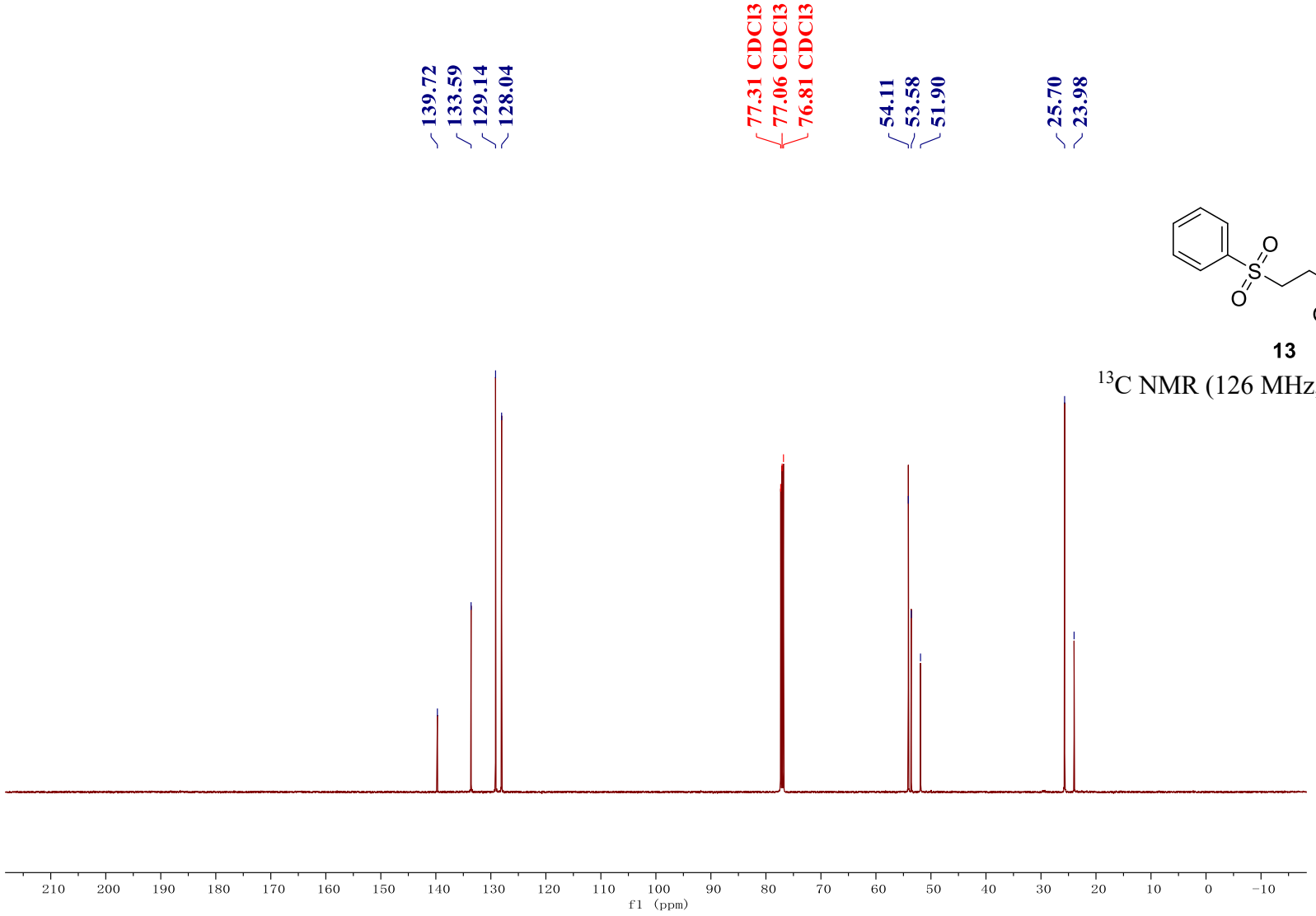


^{13}C NMR (126 MHz, Chloroform-*d*)



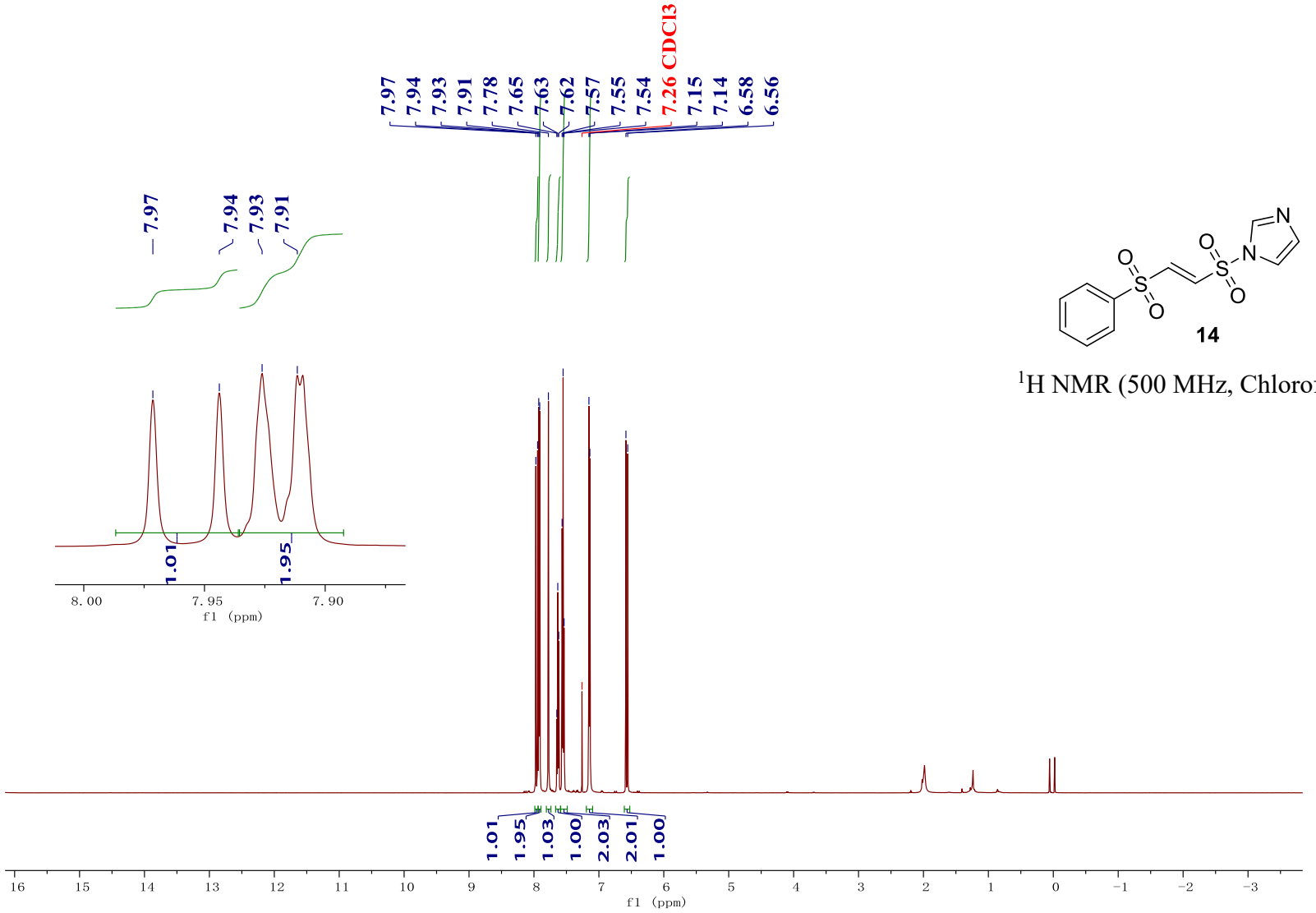
13

^{1}H NMR (500 MHz, Chloroform-*d*)



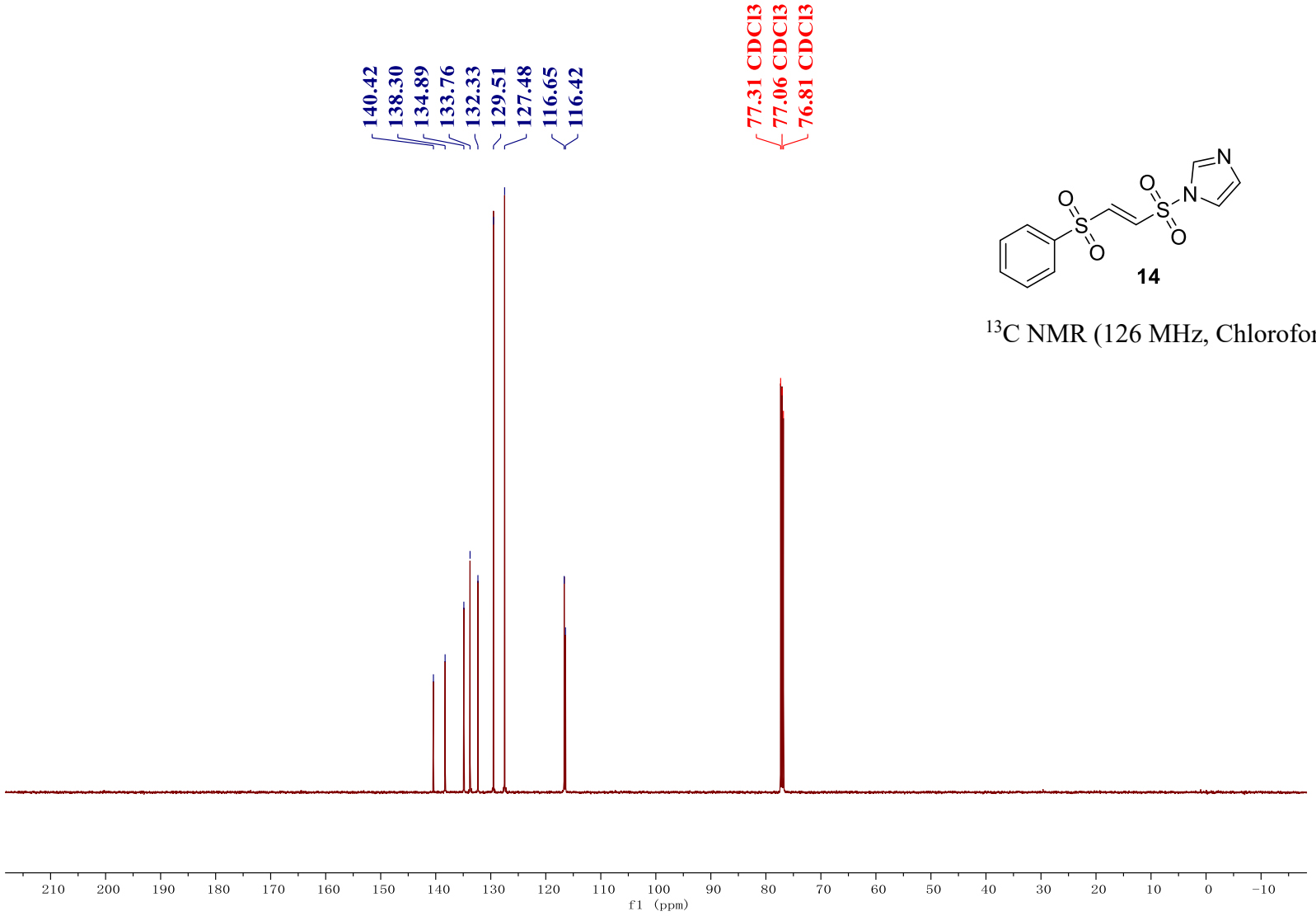
13

^{13}C NMR (126 MHz, Chloroform-*d*)



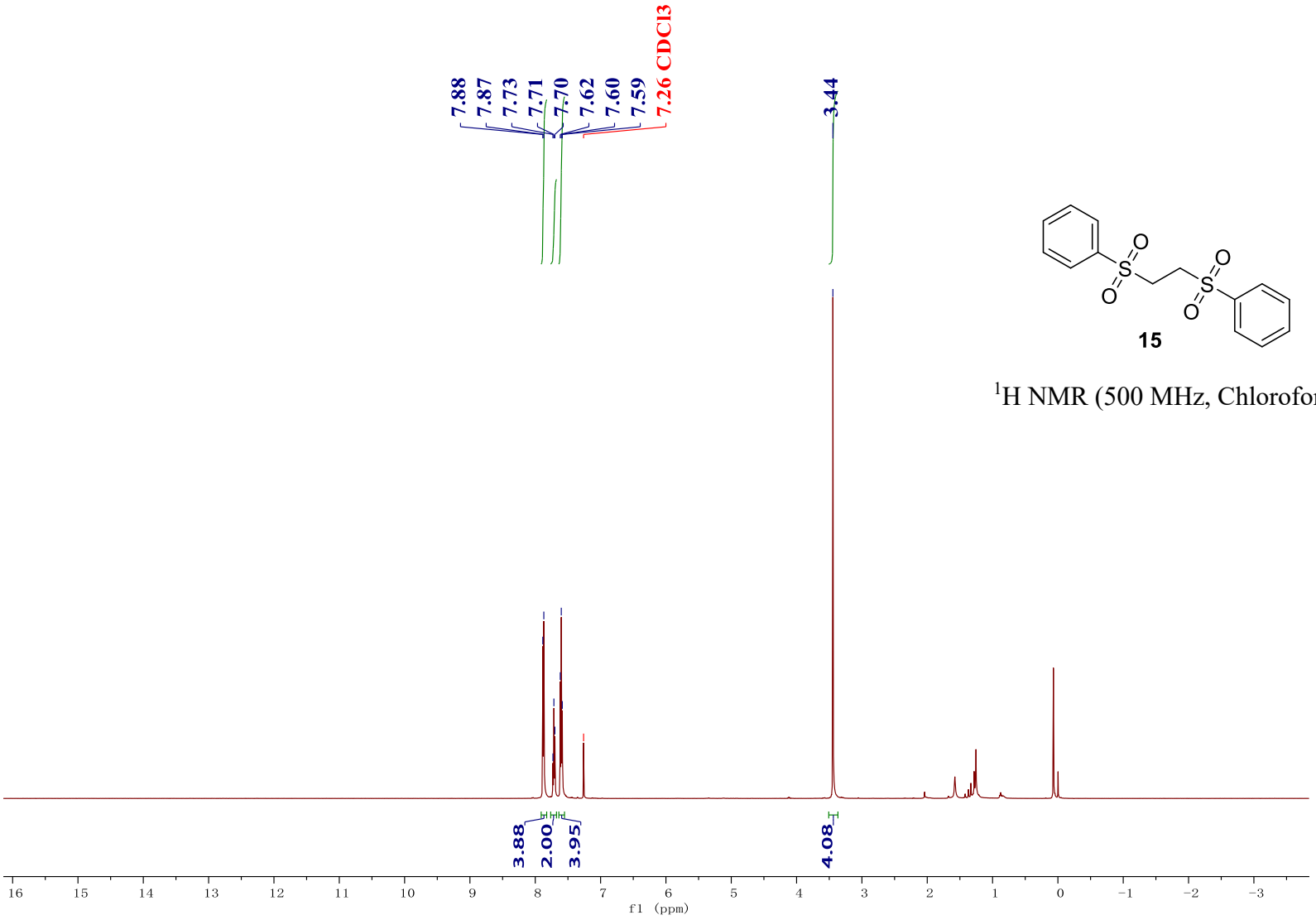
14

^{1}H NMR (500 MHz, Chloroform-*d*)



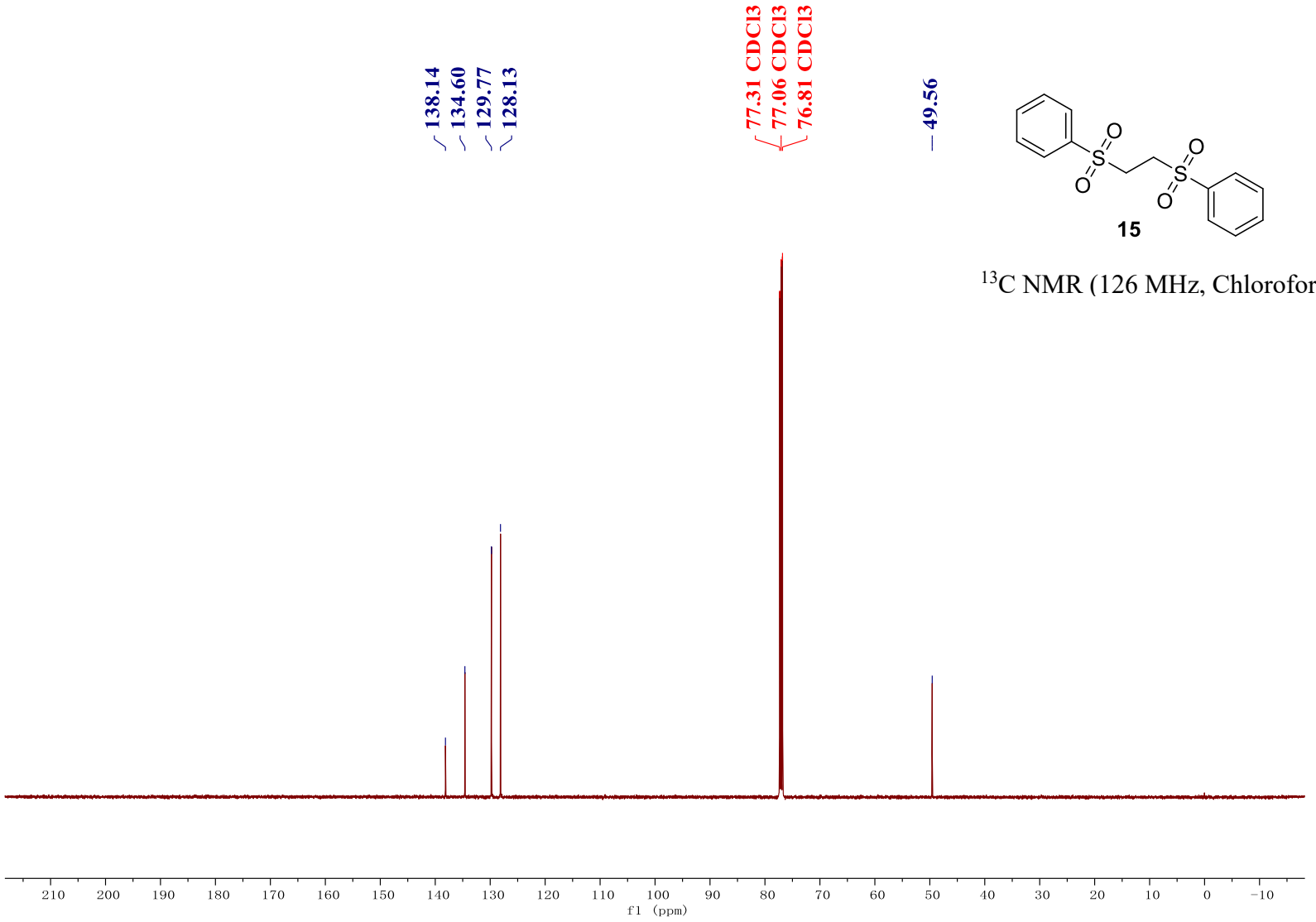
14

^{13}C NMR (126 MHz, Chloroform-*d*)

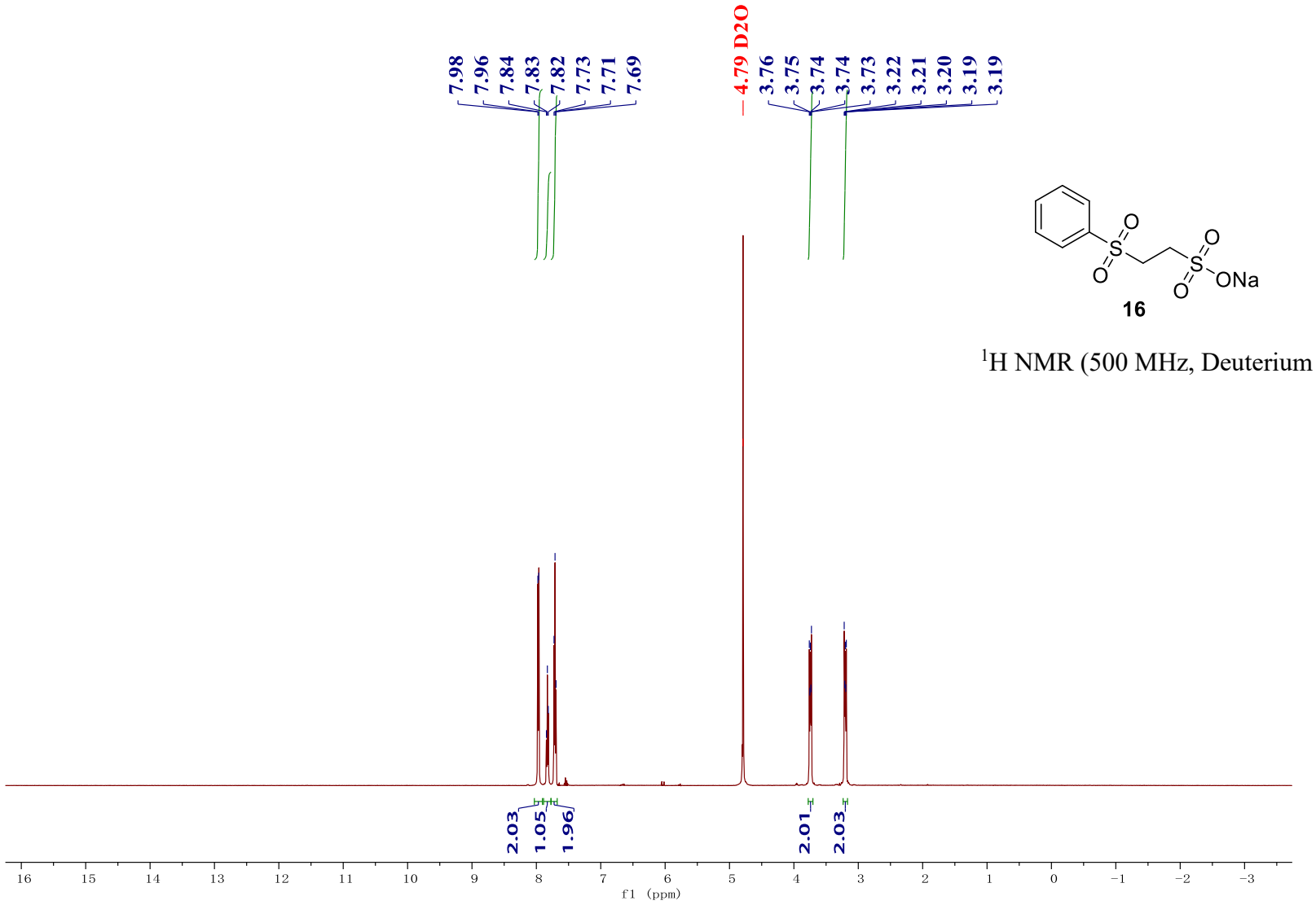


15

^{1}H NMR (500 MHz, Chloroform-*d*)

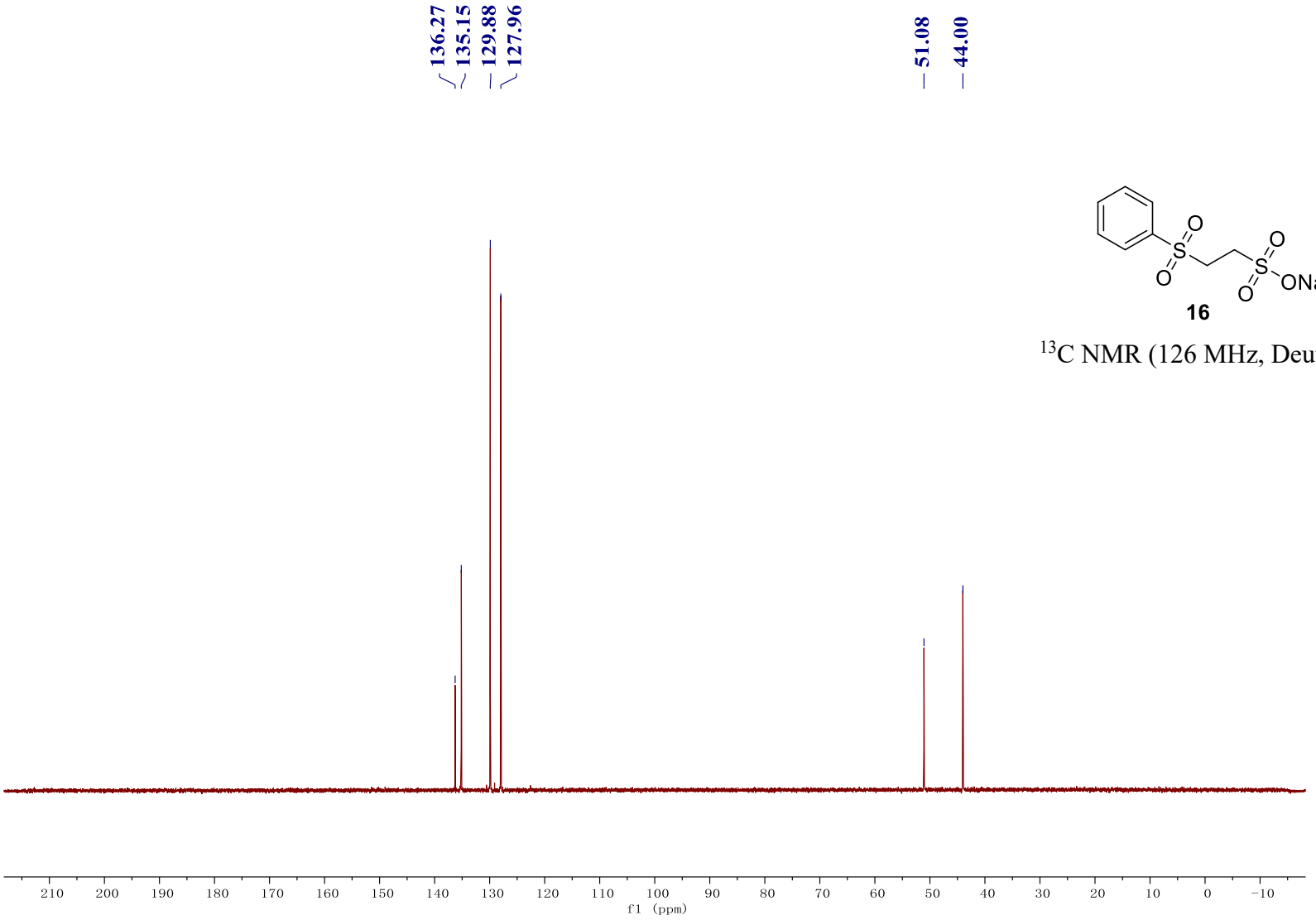


^{13}C NMR (126 MHz, Chloroform-*d*)



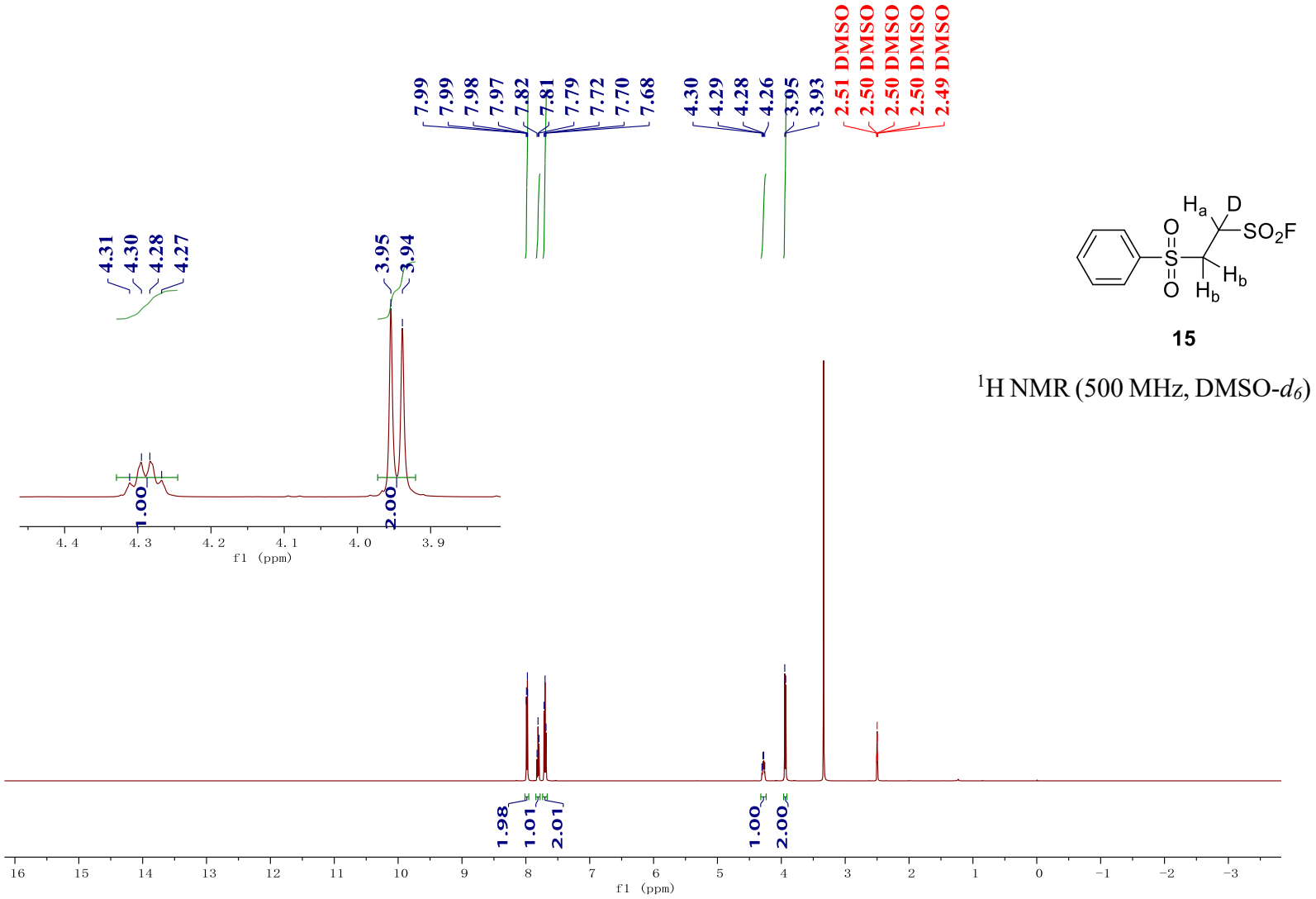
16

^{1}H NMR (500 MHz, Deuterium Oxide)



16

^{13}C NMR (126 MHz, Deuterium Oxide)



15

^{1}H NMR (500 MHz, DMSO-d_6)