Supporting Information

A Simple Protocol for the Stereoselective Construction of Enaminyl Sulfonyl Fluorides

Jing Leng,[a, †] Wenjian Tang, [b, †] Wan-Yin Fang, [a] Chuang Zhao, [a] and Hua-Li Qin *[a]

[a] State Key Laboratory of Silicate Materials for Architectures; and School of Chemistry, Chemical Engineering and Life Science, Wuhan University of Technology, 205 Luoshi Road, Wuhan, 430070, China. E-mail: qinhuali@whut.edu.cn

[b] School of Pharmacy, Anhui Medical University, Hefei, 230032, China

† These authors contributed equally

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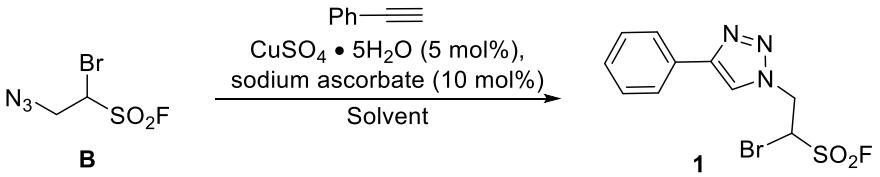
1. General considerations

All reactions were carried out under an air atmosphere. Unless otherwise specified, NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a 500 MHz (for ^1H), 471 MHz (for ^{19}F), or 126 MHz (for ^{13}C) spectrometer. The chemical shifts converted to the TMS scale ($CDCl_3$: δ H = 7.26 ppm, δ C = 77.16 ppm; DMSO-d_6: δ H = 2.50 ppm, δ C = 39.52 ppm). Data for ^{19}F NMR was reported in terms of chemical shift (ppm) relative to added internal standard ($CFCl_3$ at 0 ppm). All coupling constants (*J* values) were reported in Hertz (Hz). 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. The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Melting points are reported uncorrected. MS experiments were performed on a TOF-Q ESI or CI/EI instrument. Oil bath was used for the heating reaction. Reagents used in the reactions were all purchased from commercial sources and used without further purification.

2. Optimization of the reaction conditions

Table S1 Screening of solvents for the synthesis of BTESF [a,b]

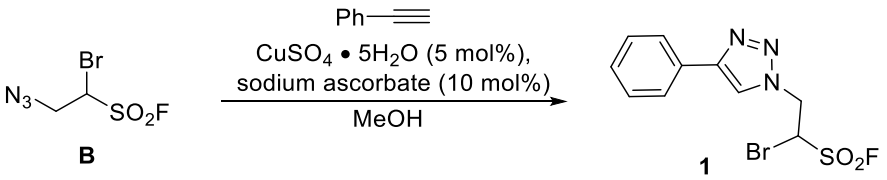


Entry	Solvent	Yield **1** [b] (%)
1	CH_3CN	n.d.
2	Toluene	55
3	THF	n.d.
4	1,4-Dioxane	21
5	DMSO	n.d.
6	DMF	n.d.
7	NMP	n.d.
8	**MeOH**	**63**
9	H_2O/*t*-BuOH = 2/1	39

[a] Reaction condition: $CuSO_4{\cdot}5H_2O$ (5 mol%, 12.5 mg), sodium ascorbate (10 mol% 19.8 mg) were dissolved in corresponding solvent (5 mL), phenylacetylene (1 mmol,

102 mg) and **B** (1 mmol, 232 mg) were added to the solvent and the mixture was stirred at room temperature for 12 hours. [b] Isolated yield.

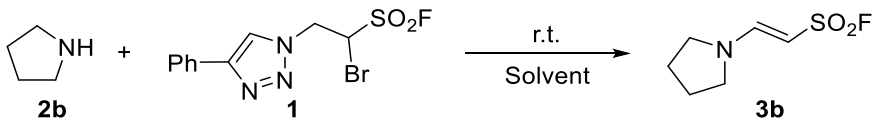
Table S2 Screening of ratio of B and alkyne for the synthesis of BTESF [a,b]

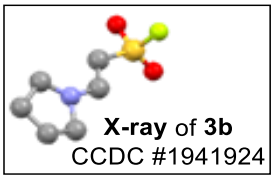


Entry	Ratio (**B** : **alkyne**)	Yield **1** [b] (%)
1	1 : 1	63
2	1 : 1.2	74
3	1 : 1.5	85
4	**1 : 2**	**99**
5	1.2 : 1	83
6	1.5 : 1	95

[a] Reaction condition: $CuSO_4 \cdot 5H_2O$ (5 mol%, 12.5 mg), sodium ascorbate (10 mol% 19.8 mg) were dissolved MeOH (5 mL), **B** and phenylacetylene were added to MeOH and the mixture was stirred at room temperature for 12 hours. [b] Isolated yield.

Table S3. Optimization for the synthesis of *N*-ESF [a,b]



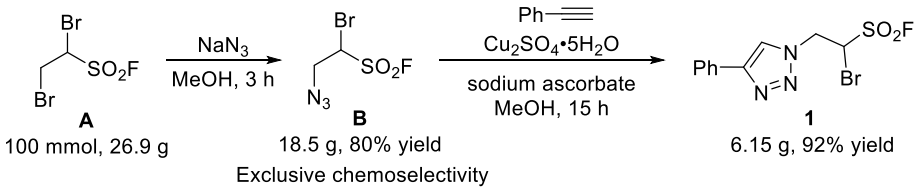


Entry	Solvent	**2b** (equiv)	Yield (%)[b]
1	CH_3CN	1.2	39
2	Acetone	1.2	2
3	THF	1.2	21
4	MeOH	1.2	6
5	**1,4-Dioxane**	**1.2**	**58**
6	DMSO	1.2	23
7	DMF	1.2	40
8	DCE	1.2	46
9	Toluene	1.2	51
10	NMP	1.2	37

11	1,4-Dioxane	1.0	54
12	1,4-Dioxane	1.5	74
13	**1,4-Dioxane**	**2.0**	**99**

[a] Reaction conditions: **1** (0.1 mmol, 33.4 mg) and **2b** were dissolved in the corresponding solvent (2 mL) and stirred for 12 h at room temperature. [b] The yield was determined by HPLC using pure **3b** as external standard. [$t_{\mathbf{3b}}$ = 5.100 min, λ_{max} = 240.5 nm, CH_3CN / water = 50 : 50 (v / v)].

3. General procedure for synthesis A, B, 1, 3, 5, I and 8



3.1 Procedure for synthesis of A

Ethenesulfonyl fluoride (ESF), 33 g (300 mmol) was dissolved in 300 mL CH_2Cl_2 and placed in a 500 mL round-bottom flask equipped with a stirred bar under the irradiation of 50 W white light. To the flask was added 96 g (600 mmol, 31 mL) bromine in three portions in 30 minutes, the reaction was stirred for about 12-16 hours. When the flask was swirled, the temperature rose rapidly to about 45 °C, the flask was cooled under ice-bath to maintain the temperature at near 25 °C. The reaction was monitored by TLC using $KMnO_4$ as chromogenic agent. After the ethenesulfonyl fluoride was completely consumed, the mixture turned dark organic, the solution was washed with sodium thiosulfate solution until the color turned light yellow. Then dried over anhydrous Na_2SO_4 and concentrated to dryness and used directly in the next step without further purification.

3.2 Procedure for synthesis of B

An oven-dried round-bottle flask (250 mL) was charged with 1, 2-dibromoethane-1-sulfonyl fluoride **A** (100 mmol, 26.7 g) and 100 mL MeOH. NaN_3 (100 mmol, 6.5 g) was then added to the solution slowly. The mixture was stirred at room temperature for

3h with monitoring by TLC using stained $KMnO_4$. After the reaction, the solution was concentrated to dryness and the residue was purified through silica gel chromatography using ethyl acetate / petroleum ether (EA / PE) = 1:10 (v / v) to afford 2-azido-1-bromoethane-1-sulfonyl fluoride **B** in 80% yield as a colorless liquid (18.5 g).

Caution: During the preparation and handling of organic azide **B**, safety precautions must be taken. And the azide **B** should be stored below 5 ^oC away from line-of-sight to reduce the risk of explosion.

3.3 Procedure for synthesis of 1

An oven-dried round-bottle flask (250 mL) was charged with $CuSO_4{\cdot}5H_2O$ (5 mol%, 250 mg), sodium ascorbate (10 mol%, 396 mg), alkyne (40 mmol, 4.08 g), 2-azido-1-bromoethane-1-sulfonyl fluoride **B** (20 mmol, 4.64 g) and 100 mL MeOH. The mixture was stirred at room temperature for 12-24 h with monitoring by TLC. After the reaction was completed, the solution was concentrated to dryness and the residue was purified through silica gel chromatography using EA / PE = 1:2 (v / v) to afford desired product **1** in 92% yield as white solid (6.15 g)

3.4 General procedure for synthesis of 3

Procedure A: An oven-dried reaction tube (20 mL) was charged with BTESF **1** (0.5 mmol, 167 mg), amine (1 mmol) and 5 mL 1, 4-dioxane. The mixture was stirred at room temperature for 3-12 h with monitoring by TLC. After the reaction was completed, the solution was concentrated to dryness and the residue was purified through silica gel chromatography using a mixture of DCM and PE to afford the desired 2-amino ethenesulfonyl fluorides **3a-3aj**.

When **2**·HCl or **2**·HBr were used (**2k**, **2s**, **2w**, **2ad** and **2af**), Et_3N (1 mmol, 101 mg) was added to the reaction mixture; for the substrates of **2k**, **2x**, **2z**, **2ad**, **2af**, **2ah**-**2aj**, Et_3N (1 mmol, 101 mg) was added to the reaction to improve the yields.

Procedure B: An oven-dried reaction tube (20 mL) was charged with BTESF **1** (0.6 mmol, 200.4 mg), amine (0.5 mmol), Et_3N (0.5 mmol, 50.5 mg) and 5 mL DCE. The mixture was stirred at room temperature for 12-18 h with monitoring by TLC. After the

reaction was completed, the solution was concentrated to dryness and the residue was purified through silica gel chromatography using pure EA followed by MeOH / DCM = 1:10 (v / v) as eluent to afford the desired 2-amino ethenesulfonyl fluorides **3ak-3aq**.

Large scale synthesis of **3b**

A round-bottom flask (100 mL) was charged with BTESF **1** (5 mmol, 1.67 g), pyrrolidine **2b** (10 mmol, 711 mg) and 50 mL 1, 4-dioxane. The mixture was stirred at room temperature for 12 h with monitoring by TLC. After the reaction was completed, the solution was concentrated to dryness and the residue was purified through silica gel chromatography using a mixture of DCM and PE from pure PE to DCM / PE = 1:1 (v / v) to afford the desired product **3b** in 92% yield as a white solid (895 mg).

3.5 General procedure for synthesis of 5

An oven-dried reaction tube (20 mL) was charged with 2-amino ethenesulfonyl fluoride **3** (0.5 mmol), corresponding phenol **4** (1 mmol), KOH (1 mmol, 56 mg) and 5 mL CH_3CN. The mixture was stirred at 50 ^oC under oil bath for 5-15 h with monitoring by TLC. After the reaction was completed, the solution was concentrated to dryness and the residue was purified through silica gel chromatography using a mixture of DCM and PE to afford the desired sulfonate products **5**.

3.6 Procedure for synthesis of I

An oven-dried reaction tube (20 mL) was charged with BTESF **1** (0.5 mmol, 167 mg), Et_3N (2 mmol, 202 mg) and 5 mL 1, 4-dioxane. The mixture was stirred at room temperature for 48 h with monitoring by TLC. After the reaction was completed, the solution was concentrated to dryness and the residue was purified through silica gel chromatography using a mixture of DCM and PE from DCM / PE = 1:5 to DCM / PE = 1:1 to afford the desired product **I** in 61% yield as a white solid (77 mg).

3.7 Procedure for synthesis of 8

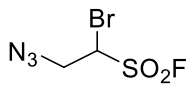
An oven-dried reaction tube (10 mL) was charged with **7**[1] (0.2 mmol, 51 mg), pyrrolidine **2b** (0.4 mmol, 28.5 mg) and 2 mL 1, 4-dioxane. The mixture was stirred at

room temperature for 12 h with monitoring by TLC. After the reaction was completed, the solution was concentrated to dryness and the residue was purified through silica gel chromatography using a mixture of EA and PE from EA / PE = 1:2 (v / v) to pure EA to afford the desired product **8** in 98% yield as a white solid (60 mg).

4. Determination of minimum inhibitory concentrations (MICs)

The antimicrobial potential of seven drugs and their fluorosulfonylvinylated products **3ak-3aq** were evaluated against a panel of bacteria and fungi in Mueller-Hinton (MH) broth, including two Gram-positive bacteria: *Staphylococcus aureus* ATCC 25923 and Methicillin Resistant *Staphylococcus aureus* isolated from clinical; two Gram-negative bacteria: *Pseudomonas aeruginosa* ATCC 9027 and *Escherichia coli* ATCC 8739; and one fungi: *Candida albicans* ATCC 10231, respectively. The MICs of title compounds were determined in Mueller-Hinton (MH) broth according to the methodology of the Clinical Laboratory Standards Institute (CLSI),[2] using the micro-broth dilution method in 96-well micro-test plates. The bacterial inoculation was prepared by growing colonies from MH agar in MH broth. The final test concentration of compounds ranged from 0.09-200 μM and bacterial inocula of 10^5 CFU/mL. The MICs were recorded as the lowest concentration of the test compound inhibiting visual growth, after incubation at 37°C for 18-20 hours. MICs were performed in at least duplicate and the mean MIC is reported. Each sample was tested in triplicate and each experiment was repeated three times.

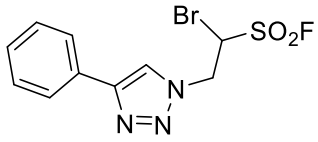
5. NMR spectra of B, 1, 3, 5-6, I and 8



B

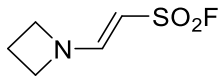
2-Azido-1-bromoethane-1-sulfonyl fluoride (**B**). Colorless liquid, 18.5 g, 80 %. EA / PE = 1:10 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.14-5.11 (m, 1H), 4.13 (dd, J = 13.9, 4.8 Hz, 1H), 4.02 (dd, J = 13.8, 6.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.8 (d, J = 20.6 Hz), 52.8 (s). ^{19}F NMR (471 MHz, $CDCl_3$)

δ 47.4 (s, 1F). EI-MS HRMS calculated for $C_2H_3FO_2SBr$ $[M]^+$ 230.9108, found 230.9105.



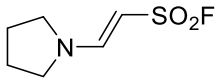
1

1-Bromo-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethane-1-sulfonyl fluoride (**1**). White solid, 6.15 g, 92%. M.p. 162-163 °C. EA / PE = 1:2 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 8.66 (s, 1H), 7.85 (d, J = 7.4 Hz, 2H), 7.47 (t, J = 7.7 Hz, 2H), 7.37 (t, J = 7.4 Hz, 1H), 7.00-6.97 (m, 1H), 5.47 (dd, J = 15.1, 5.2 Hz, 1H), 5.30 (dd, J = 15.1, 7.6 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ 146.5 (s), 130.2 (s), 129.1 (s), 128.2 (s), 125.3 (s), 122.6 (s), 55.4 (d, J = 18.9 Hz), 50.3 (s). ^{19}F NMR (471 MHz, DMSO) δ 47.1 (s, 1F). ESI-MS HRMS calculated for $C_{10}H_{10}BrFN_3O_2S$ $[M+H]^+$ 333.9656, found 333.9655.



3a

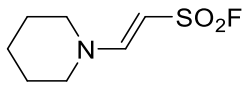
(*E*)-2-(azetidin-1-yl)ethene-1-sulfonyl fluoride (**3a**). Yellow liquid, 80 mg, 97%. A mixture of DCM and PE from pure PE to DCM / PE = 1:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, J = 12.2 Hz, 1H), 4.63 (dd, J = 12.2, 4.3 Hz, 1H), 4.14-4.13 (m, 2H), 4.06-3.87 (m, 2H), 2.49-2.43 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.9 (s), 81.2 (d, J = 25.9 Hz), 53.8 (s), 51.5 (s), 16.6 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.7 (s, 1F). EI-MS HRMS calculated for $C_5H_8FNO_2S$ $[M]^+$ 165.0254, found 165.0254.



3b

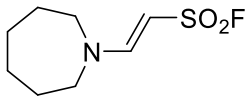
(*E*)-2-(pyrrolidin-1-yl)ethene-1-sulfonyl fluoride (**3b**). white solid, 89 mg, 99%. M.p.

105-107 °C. A mixture of DCM and PE from pure PE to DCM / PE = 1:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J = 12.3 Hz, 1H), 4.77 (dd, J = 12.3, 4.5 Hz, 1H), 3.53 (t, J = 6.4 Hz, 2H), 3.14 (t, J = 6.9 Hz, 2H), 2.08-2.03 (m, 2H), 1.99-1.93 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.5 (s), 81.9 (d, J = 25.5 Hz), 52.7 (s), 47.3 (s), 25.4 (s), 25.2 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.9 (s, 1F). EI-MS HRMS calculated for $C_6H_{10}FNO_2S$ $[M]^+$ 179.0411, found 179.0410.



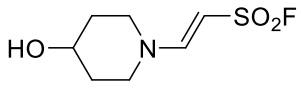
3c

(*E*)-2-(piperidin-1-yl)ethene-1-sulfonyl fluoride (**3c**). White solid, 96 mg, 99%. M.p. 74-75 °C. A mixture of DCM and PE from pure PE to DCM / PE = 1:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, J = 12.5 Hz, 1H), 4.89 (dd, J = 12.5, 4.7 Hz, 1H), 3.39-3.29 (m, 2H), 3.23-3.11 (m, 2H), 1.72-1.62 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.1 (s), 81.1 (d, J = 25.3 Hz), 55.1 (s), 46.5 (s), 26.3 (s), 24.6 (s), 23.6 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 71.1 (d, J = 4.1 Hz, 1F). EI-MS HRMS calculated for $C_7H_{12}FNO_2S$ $[M]^+$ 193.0567, found 193.0565.



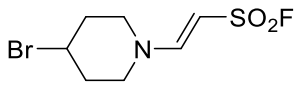
3d

(*E*)-2-(azepan-1-yl)ethene-1-sulfonyl fluoride (**3d**). White solid, 99 mg, 96%. M.p. 55-57 °C. A mixture of DCM and PE from pure PE to DCM / PE = 1:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 12.5 Hz, 1H), 4.82 (dd, J = 12.5, 4.6 Hz, 1H), 3.45 (t, J = 5.7 Hz, 2H), 3.20 (t, J = 6.0 Hz, 2H), 1.81-1.72 (m, 4H), 1.65-1.57 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.0 (s), 80.9 (d, J = 25.3 Hz), 56.3 (s), 49.3 (s), 30.2 (s), 28.1 (s), 27.0 (s), 25.3 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 71.0 (s, 1F). EI-MS HRMS calculated for $C_8H_{14}FNO_2S$ $[M]^+$ 207.0724, found 207.0722.



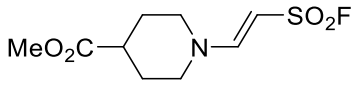
3e

(*E*)-2-(4-hydroxypiperidin-1-yl)ethene-1-sulfonyl fluoride (**3e**). Yellow liquid, 93 mg, 89%. A mixture of DCM and PE from pure PE to DCM / PE = 10:1 (v / v) as eluent for column chromatography.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, J = 12.6 Hz, 1H), 4.92 (dd, J = 12.6, 4.6 Hz, 1H), 4.02-3.99 (m, 1H), 3.67-3.53 (m, 1H), 3.49-3.36 (m, 1H), 3.30-3.20 (m, 1H), 3.13-3.00 (m, 1H), 2.09 (s, 1H), 1.97-1.87 (m, 2H), 1.70-1.60 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0 (s), 81.8 (d, J = 25.3 Hz), 65.5 (s), 50.9 (s), 42.4 (s), 34.1 (s), 32.4 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 71.0 (s, 1F). EI-MS HRMS calculated for $C_7H_{12}FNO_3S$ $[M]^+$ 209.0516, found 209.0514.



3f

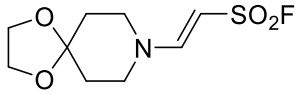
(*E*)-2-(4-bromopiperidin-1-yl)ethene-1-sulfonyl fluoride (**3f**). Yellow liquid, 134 mg, 99%. A mixture of DCM and PE from pure PE to DCM / PE = 1:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, J = 12.6 Hz, 1H), 4.99 (dd, J = 12.6, 4.5 Hz, 1H), 4.48-4.44 (m, 1H), 3.76-3.61 (m, 1H), 3.50-3.40 (m, 1H), 3.38-3.29 (m, 1H), 3.23-3.12 (m, 1H), 2.19-2.15 (m, 2H), 2.08-2.03 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.0 (s), 82.0 (d, J = 26.0 Hz), 50.3 (s), 46.1 (s), 42.1 (s), 34.3 (s), 32.7 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.5 (s, 1F). EI-MS HRMS calculated for $C_7H_{11}BrFNO_2S$ $[M]^+$ 270.9672, found 270.9671.



3g

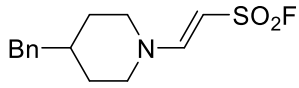
Methyl (*E*)-1-(2-(fluorosulfonyl)vinyl)piperidine-4-carboxylate (**3g**). White solid, 99 mg, 76%. M.p. 68-69 ^{o}C. A mixture of DCM and PE from pure PE to DCM / PE = 1:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, J = 12.6 Hz, 1H), 4.96 (dd, J = 12.6, 4.5 Hz, 1H), 3.71 (s, 3H), 3.56-3.41 (m, 2H), 3.36-

3.24 (m, 1H), 3.08-2.94 (m, 1H), 2.61-2.57 (m, 1H), 2.03-2.00 (m, 2H), 1.81-1.79 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9 (s), 153.0 (s), 82.6 (d, J = 25.8 Hz), 53.0 (s), 52.2 (s), 44.7 (s), 39.8 (s), 28.3 (s), 26.6 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.6 (s, 1F). EI-MS HRMS calculated for $C_9H_{14}FNO_4S$ $[M]^+$ 251.0622, found 251.0620.



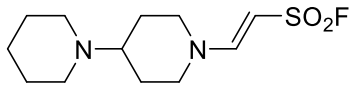
3h

(*E*)-2-(1,4-dioxa-8-azaspiro[4.5]decan-8-yl)ethene-1-sulfonyl fluoride (**3h**). White solid, 112 mg, 89%. M.p. 196-199 °C. A mixture of DCM and PE from pure PE to DCM / PE = 1:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, J = 12.6 Hz, 1H), 4.95 (dd, J = 12.6, 4.6 Hz, 1H), 3.99-3.96 (m, 4H), 3.54-3.44 (m, 2H), 3.35-3.26 (m, 2H), 1.80-1.74 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0 (s), 105.9 (s), 82.3 (d, J = 25.6 Hz), 64.7 (s), 52.2 (s), 43.6 (s), 35.4 (s), 33.7 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.7 (d, J = 4.2 Hz, 1F). EI-MS HRMS calculated for $C_9H_{14}FNO_4S$ $[M]^+$ 251.0622, found 251.0622.



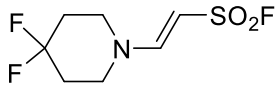
3i

(*E*)-2-(4-benzylpiperidin-1-yl)ethene-1-sulfonyl fluoride (**3i**). White solid, 109 mg, 77%. M.p. 94-95 °C. A mixture of DCM and PE from pure PE to DCM / PE = 1:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, J = 12.6 Hz, 1H), 7.30 (t, J = 7.4 Hz, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.14 (d, J = 7.1 Hz, 2H), 4.91 (dd, J = 12.5, 4.6 Hz, 1H), 3.47-3.44 (m, 2H), 3.25-3.21 (m, 1H), 2.88-2.84 (m, 1H), 2.58 (d, J = 6.9 Hz, 2H), 1.83-1.78 (m, 1H), 1.77-1.75 (m, 2H), 1.29-1.26 (d, J = 11.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0 (s), 139.4 (s), 129.1 (s), 128.5 (s), 126.4 (s), 81.5 (d, J = 25.4 Hz), 54.4 (s), 45.7 (s), 42.7 (s), 37.4 (s), 32.3 (s), 30.6 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 71.0 (s, 1F). EI-MS HRMS calculated for $C_{14}H_{18}FNO_2S$ $[M]^+$ 283.1037, found 283.1035.



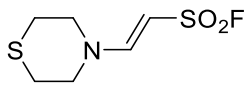
3j

(*E*)-2-([1,4'-bipiperidin]-1'-yl)ethene-1-sulfonyl fluoride (**3j**). Yellow solid, 115 mg, 83%. M.p. 89-91 ºC. A mixture of DCM and PE from pure PE to DCM / PE = 5:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, J = 12.6 Hz, 1H), 4.91 (dd, J = 12.5, 4.5 Hz, 1H), 3.58-3.48 (m, 2H), 3.31-3.22 (m, 1H), 2.96-2.84 (m, 1H), 2.55-2.46 (m, 5H), 1.91-1.89 (m, 2H), 1.60-1.56 (m, 6H), 1.47-1.41 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9 (s), 81.8 (d, J = 25.4 Hz), 61.3 (s), 53.6 (s), 50.2 (s), 45.0 (s), 28.4 (s), 26.7 (s), 26.2 (s), 24.6 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.9 (s, 1F). EI-MS HRMS calculated for $C_{12}H_{21}FN_2O_2S$ $[M]^+$ 276.1302, found 276.1301.



3k

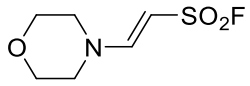
(*E*)-2-(4,4-difluoropiperidin-1-yl)ethene-1-sulfonyl fluoride (**3k**). Yellow solid, 60 mg, 52%. M.p. 75-77 ºC. A mixture of DCM and PE from pure PE to DCM / PE = 1:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, J = 12.7 Hz, 1H), 5.06 (dd, J = 12.7, 4.4 Hz, 1H), 3.51-3.37 (m, 4H), 2.14-2.06 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9 (s), 120.5 (t, J = 242.8 Hz), 84.6 (d, J = 26.4 Hz), 50.6 (s), 42.3 (s), 32.3 (s), 32.8 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.1 (d, J = 4.2 Hz, 1F), -99.1– -99.2 (m, 2F). EI-MS HRMS calculated for $C_7H_{10}F_3NO_2S$ $[M]^+$ 229.0379, found 229.0378.



3l

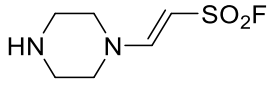
(*E*)-2-thiomorpholinoethene-1-sulfonyl fluoride (**3l**). White solid, 75 mg, 71%. M.p. 64-66 ºC. A mixture of DCM and PE from pure PE to DCM / PE = 1:1 (v / v) as eluent

for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, J = 12.7 Hz, 1H), 4.99 (dd, J = 12.7, 4.5 Hz, 1H), 3.73-3.61 (m, 2H), 3.58-3.47 (m, 2H), 2.74-2.66 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9 (s), 83.6 (d, J = 26.3 Hz), 56.5 (s), 48.3 (s), 28.2 (s), 26.2 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.3 (s, 1F). EI-MS HRMS calculated for $C_6H_{10}FNO_2S_2$ $[M]^+$ 211.0131, found 211.0131.



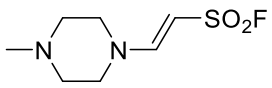
3m

(*E*)-2-morpholinoethene-1-sulfonyl fluoride (**3m**). White solid, 84 mg, 86%. M.p. 67-70 ºC. A mixture of DCM and PE from pure PE to DCM / PE = 1:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, J = 12.6 Hz, 1H), 4.99 (dd, J = 12.6, 4.5 Hz, 1H), 3.74 (t, J = 4.6 Hz, 4H), 3.47-3.31 (m, 2H), 3.29-3.12 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.2 (s), 83.2 (d, J = 26.1 Hz), 66.7 (s), 65.4 (s), 52.9 (s), 45.7 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.4 (d, J = 3.8 Hz, 1F). EI-MS HRMS calculated for $C_6H_{10}FNO_3S$ $[M]^+$ 195.0360, found 195.0357.



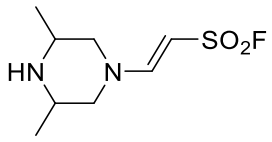
3n

(*E*)-2-(piperazin-1-yl)ethene-1-sulfonyl fluoride (**3n**). White solid, 95 mg, 98%. M.p. 79-80 ºC. A mixture of EA, MeOH and DCM from pure EA to MeOH / DCM = 1:20 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, J = 12.6 Hz, 1H), 4.93 (dd, J = 12.6, 4.5 Hz, 1H), 3.46 (s, 1H), 3.42-3.32 (m, 2H), 3.24-3.13 (m, 2H), 2.93-2.91 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.2 (s), 81.9 (d, J = 25.6 Hz), 54.5 (s), 46.6 (s), 46.2 (s), 44.7 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.7 (s, 1F). EI-MS HRMS calculated for $C_6H_{11}FN_2O_2S$ $[M]^+$ 194.0520, found 194.0520.



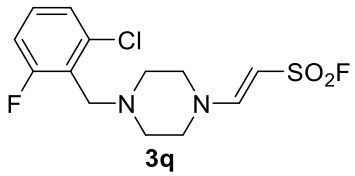
3o

(*E*)-2-(4-methylpiperazin-1-yl)ethene-1-sulfonyl fluoride (**3o**). White solid, 103 mg, 99%. M.p. 101-102 °C. A mixture of DCM and PE from pure PE to DCM / PE = 5:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 12.6 Hz, 1H), 4.93 (dd, J = 12.6, 4.5 Hz, 1H), 3.47-3.32 (m, 2H), 3.30-3.16 (m, 2H), 2.45-2.43 (m, 4H), 2.31 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0 (s), 82.4 (d, J = 25.8 Hz), 54.8 (s), 53.2 (s), 46.03 (s), 46.02 (s), 45.3 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.7 (s, 1F). EI-MS HRMS calculated for $C_7H_{13}FN_2O_2S$ $[M]^+$ 208.0676, found 208.0674.



3p

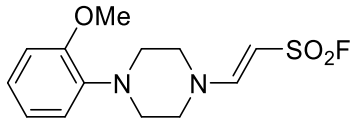
(*E*)-2-(3,5-dimethylpiperazin-1-yl)ethene-1-sulfonyl fluoride (**3p**). White solid, 107 mg, 96%. M.p. 86-87 °C. A mixture of EA, MeOH and DCM from pure EA to MeOH / DCM = 1:40 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 12.6 Hz, 1H), 4.92 (dd, J = 12.6, 4.5 Hz, 1H), 3.27-3.25 (m, 2H), 2.94-2.83 (m, 3H), 2.56-2.52 (m, 1H), 2.03 (s, 1H), 1.09-1.03 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.8 (s), 82.1 (d, J = 25.7 Hz), 60.0 (s), 52.1 (s), 51.3 (s), 49.9 (s), 19.3 (s), 19.0 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.7 (s, 1F). EI-MS HRMS calculated for $C_8H_{15}FN_2O_2S$ $[M]^+$ 233.0911, found 233.0910.



3q

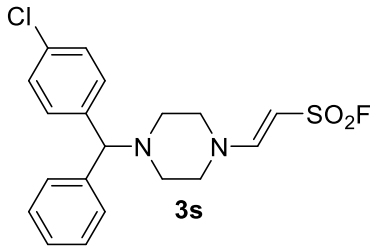
(*E*)-2-(4-(2-chloro-6-fluorobenzyl)piperazin-1-yl)ethene-1-sulfonyl fluoride (**3q**). Yellow solid, 144 mg, 86%. M.p. 97-99 °C. A mixture of DCM and PE from pure PE

to DCM / PE = 5:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 12.6 Hz, 1H), 7.25-7.20 (m, 2H), 7.02-6.98 (m, 1H), 4.92 (dd, J = 12.6, 4.5 Hz, 1H), 3.75-3.74 (m, 2H), 3.44-3.30 (m, 2H), 3.27-3.14 (m, 2H), 2.62-2.60 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.1 (d, J = 249.4 Hz), 152.9 (s), 136.7 (d, J = 5.6 Hz), 129.8 (d, J = 9.8 Hz), 125.7 (d, J = 3.4 Hz), 123.0 (d, J = 17.9 Hz), 114.2 (d, J = 23.3 Hz), 82.4 (d, J = 25.9 Hz), 53.4 (s), 52.5 (s), 52.2 (s), 51.1 (s), 45.5 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.6 (s, 1F), -112.7 (s, 1F). EI-MS HRMS calculated for $C_{13}H_{14}ClF_2N_2O_2S$ $[M]^+$ 335.0427, found 335.0425.



3r

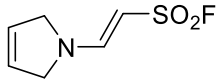
(*E*)-2-(4-(2-methoxyphenyl)piperazin-1-yl)ethene-1-sulfonyl fluoride (**3r**). White solid, 131 mg, 87%. M.p. 171-172 ºC. A mixture of DCM and PE from pure PE to DCM / PE = 5:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 12.5 Hz, 1H), 7.06 (t, J = 6.5 Hz, 1H), 6.95-6.90 (m, 3H), 5.01 (d, J = 12.5 Hz, 1H), 3.88-3.87 (m, 3H), 3.63-3.51 (m, 2H), 3.45-3.30 (m, 2H), 3.17-3.06 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.1 (s), 152.4 (s), 140.1 (s), 124.2 (s), 121.2 (s), 118.8 (s), 111.6 (s), 82.6 (d, J = 25.9 Hz), 55.6 (s), 53.6 (s), 50.9 (s), 49.4 (s), 45.8 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.7 (d, J = 12.1 Hz, 1F). EI-MS HRMS calculated for $C_{13}H_{17}FN_2O_3S$ $[M]^+$ 300.0938, found 300.0936.



3s

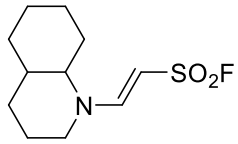
(*E*)-2-(4-((4-chlorophenyl)(phenyl)methyl)piperazin-1-yl)ethene-1-sulfonyl fluoride (**3s**). White solid, 150 mg, 80%. M.p. 68-69 ºC. A mixture of DCM and PE from pure PE to DCM / PE = 5:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz,

$CDCl_3$) δ 7.37-7.34 (m, 5H), 7.31 (d, J = 7.2 Hz, 2H), 7.29-7.26 (m, 2H), 7.23 (t, J = 7.3 Hz, 1H), 4.91 (dd, J = 12.6, 4.4 Hz, 1H), 4.28 (s, 1H), 3.47-3.32 (m, 2H), 3.28-3.11 (m, 2H), 2.46-2.44 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9 (s), 141.1 (s), 140.4 (s), 133.2 (s), 129.1 (s), 129.1 (s), 129.0(s), 127.78 (s), 127.75 (s), 82.4 (d, J = 25.6 Hz), 75.0 (s), 53.3 (s), 51.6 (s), 50.2 (s), 45.6 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.7 (s, 1F). EI-MS HRMS calculated for $C_{19}H_{20}ClFN_2O_2S$ $[M]^+$ 394.0913, found 394.0913.



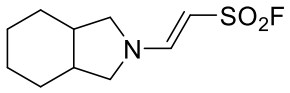
3t

(*E*)-2-(2,5-dihydro-1H-pyrrol-1-yl)ethene-1-sulfonyl fluoride (**3t**). Yellow solid, 75 mg, 85%. M.p. 88-89 ºC. A mixture of DCM and PE from pure PE to DCM / PE = 1:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 12.3 Hz, 1H), 5.92-5.83 (m, 2H), 4.82 (dd, J = 12.3, 4.4 Hz, 1H), 4.40-4.32 (m, 2H), 4.02-3.93 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.5 (s), 125.9 (s), 125.3 (s), 83.2 (d, J = 26.0 Hz), 58.4 (s), 54.5 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.5 (s, 1F). EI-MS HRMS calculated for $C_6H_8FNO_2S$ $[M]^+$ 177.0254, found 177.0253.



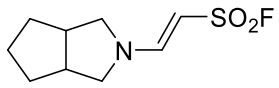
3u

(*E*)-2-(octahydroquinolin-1(2H)-yl)ethene-1-sulfonyl fluoride (**3u**). White solid, 122 mg, 99%. M.p. 95-96 ºC. A mixture of DCM and PE from pure PE to DCM / PE = 1:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, J = 12.4 Hz, 1H), 4.92 (dd, J = 12.4, 4.7 Hz, 1H), 3.60-3.57 (m, 1H), 2.92-2.87 (m, 1H), 2.82-2.78 (m, 1H), 2.00-1.95 (m, 2H), 1.82-1.70 (m, 4H), 1.63-1.59 (m, 1H), 1.52-1.44 (m, 1H), 1.33-1.19 (m, 4H), 1.11-1.03 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9 (s), 80.9 (d, J = 24.9 Hz), 66.0 (s), 48.5 (s), 43.2 (s), 32.9 (s), 32.1 (s), 29.1 (s), 25.4 (s), 25.3 (s), 24.7 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 71.2 (s, 1F). EI-MS HRMS calculated for $C_{11}H_{18}FNO_2S$ $[M]^+$ 247.1039, found 247.1030.



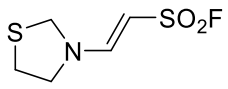
3v

(*E*)-2-(octahydro-2H-isoindol-2-yl)ethene-1-sulfonyl fluoride (**3v**). White solid, 91 mg, 78%. M.p. 64-66 ºC. A mixture of DCM and PE from pure PE to DCM / PE = 1:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 12.3 Hz, 1H), 4.75 (dd, J = 12.3, 4.6 Hz, 1H), 3.57-3.54 (m, 1H), 3.38-3.35 (m, 1H), 3.18-3.14 (m, 1H), 3.00-2.96 (m, 1H), 2.44-2.37 (m, 1H), 2.28-2.23 (m, 1H), 1.66-1.61 (m, 2H), 1.53-1.45 (m, 4H), 1.38-1.33 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.3 (s), 81.6 (d, J = 25.6 Hz), 56.9 (s), 51.0 (s), 37.2 (s), 37.1 (s), 25.7 (s), 25.6 (s), 22.9 (s), 22.2 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.9 (s, 1F). EI-MS HRMS calculated for $C_{10}H_{16}FNO_2S$ $[M]^+$ 233.0880, found 233.0876.



3w

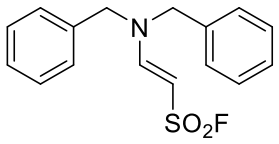
(*E*)-2-(hexahydrocyclopenta[c]pyrrol-2(1H)-yl)ethene-1-sulfonyl fluoride (**3w**). White solid, 65 mg, 59%. M.p. 80-81 ºC. A mixture of DCM and PE from pure PE to DCM / PE = 1:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, J = 12.3 Hz, 1H), 4.74 (dd, J = 12.3, 4.6 Hz, 1H), 3.73-3.70 (m, 1H), 3.37-3.33 (m, 1H), 3.30-3.27 (m, 1H), 2.89-2.86 (m, 1H), 2.82-2.77 (m, 1H), 2.74-2.69 (m, 1H), 1.91-1.82 (m, 2H), 1.77-1.69 (m, 1H), 1.68-1.60 (m, 1H), 1.51-1.39 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.3 (s), 81.7 (d, J = 25.3 Hz), 58.8 (s), 53.5 (s), 43.1 (s), 42.7 (s), 32.5 (s), 31.5 (s), 25.5 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.9 (s, 1F). EI-MS HRMS calculated for $C_9H_{14}FNO_2S$ $[M]^+$ 219.0724, found 219.0723.



3x

(*E*)-2-(thiazolidin-3-yl)ethene-1-sulfonyl fluoride (**3x**). White solid, 60 mg, 61%. M.p.

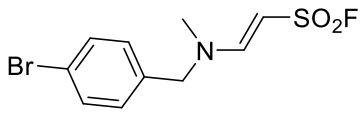
94-96 ºC. A mixture of DCM and PE from pure PE to DCM / PE = 1:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, J = 12.6 Hz, 1H), 4.95 (dd, J = 12.6, 4.3 Hz, 1H), 4.50-4.01 (m, 2H), 3.90-3.37 (m, 2H), 3.23-3.00 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6 (s), 85.0 (d, J = 26.7 Hz), 55.8(s), 48.9 (s), 30.4 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 69.9 (s, 1F). EI-MS HRMS calculated for $C_5H_8FNO_2S_2$ $[M]^+$ 196.9975, found 196.9973.



3y

(*E*)-2-(dibenzylamino)ethene-1-sulfonyl fluoride (**3y**). Yellow solid, 91 mg, 60%. M.p. 86-88 ºC. A mixture of DCM and PE from pure PE to DCM / PE = 1:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 12.6 Hz, 1H), 7.40-7.34 (m, 6H), 7.19-7.13 (m, 4H), 5.11 (dd, J = 12.6, 4.4 Hz, 1H), 4.44 (s, 2H), 4.24 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.2 (s), 134.7 (s), 133.6 (s), 129.3 (s), 128.9 (s), 128.4 (s), 128.0 (s), 127.3 (s), 84.2 (d, J = 26.1 Hz), 59.7 (s), 51.5 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.4 (s, 1F). EI-MS HRMS calculated for $C_{16}H_{16}FNO_2S$ $[M]^+$ 305.0880, found 305.0871.

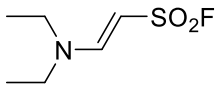
Note: In the ^{13}C NMR spectrum of **3y**, theoretically, there should be twelve peaks. Due to the compact overlaying, it is difficult to specify the overlaying peaks.



3z

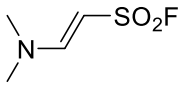
(*E*)-2-((4-bromobenzyl)(methyl)amino)ethene-1-sulfonyl fluoride (**3z**). White solid, 151 mg, 99%. M.p. 86-87 ºC. A mixture of DCM and PE from pure PE to DCM / PE = 1:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63-7.51 (m, 3H), 7.07 (d, J = 8.3 Hz, 2H), 4.96 (dd, J = 12.4, 4.3 Hz, 1H), 4.39-4.26 (m, 2H), 3.11-2.73 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.2 (s), 133.9 (s), 132.4 (s),

129.3 (s), 122.8 (s), 83.4 (d, J = 26.2 Hz), 61.2 (s), 35.5 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.2 (s, 1 F). EI-MS HRMS calculated for $C_{10}H_{11}BrFNO_2S$ $[M]^+$ 306.9672, found 306.9672.



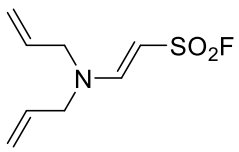
3aa

(*E*)-2-(diethylamino)ethene-1-sulfonyl fluoride (**3aa**). Colorless liquid, 80 mg, 89%. A mixture of DCM and PE from pure PE to DCM / PE = 1:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J = 12.6 Hz, 1H), 4.86 (dd, J = 12.6, 4.7 Hz, 1H), 3.31 (q, J = 7.1 Hz, 2H), 3.18 (q, J = 7.2 Hz, 2H), 1.24 (t, J = 7.2 Hz, 3H), 1.18 (t, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.6 (s), 81.1 (d, J = 25.4 Hz), 50.8 (s), 43.2 (s), 14.6 (s), 11.0 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 71.0 (s, 1H). EI-MS HRMS calculated for $C_6H_{12}FNO_2S$ $[M]^+$ 181.0567, found 181.0562.



3ab

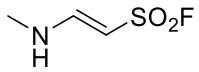
(*E*)-2-(dimethylamino)ethene-1-sulfonyl fluoride (**3ab**). Yellow liquid, 70 mg, 92%. A mixture of DCM and PE from pure PE to DCM / PE = 1:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, J = 12.4 Hz, 1H), 4.82 (dd, J = 12.4, 4.6 Hz, 1H), 3.13 (s, 3H), 2.83 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.7 (s), 81.8 (d, J = 25.6 Hz), 45.2 (s), 37.5 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.8 (s, 1F). EI-MS HRMS calculated for $C_4H_8FNO_2S$ $[M]^+$ 153.0254, found 153.0253.



3ac

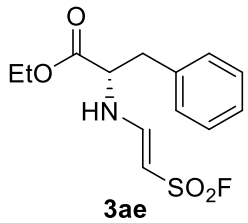
(*E*)-2-(diallylamino)ethene-1-sulfonyl fluoride (**3ac**). Yellow liquid, 69 mg, 67%. A mixture of DCM and PE from pure PE to DCM / PE = 1:1 (v / v) as eluent for column

chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, J = 12.6 Hz, 1H), 5.82-5.65 (m, 2H), 5.33-5.18 (m, 4H), 4.96 (dd, J = 12.6, 4.5 Hz, 1H), 3.86 (d, J = 5.5 Hz, 2H), 3.73 (d, J = 4.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.4 (s), 131.9 (s), 129.2 (s), 120.3 (s), 119.1 (s), 83.6 (d, J = 25.9 Hz), 58.6 (s), 51.0 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.4 (d, J = 3.4 Hz, 1F). EI-MS HRMS calculated for $C_8H_{12}FNO_2S$ $[M]^+$ 205.0567, found 205.0561.



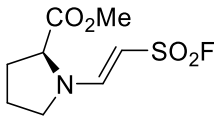
3ad

(*E*)-2-(methylamino)ethene-1-sulfonyl fluoride (**3ad**). Colorless liquid, 62 mg, 89%. A mixture of DCM and PE from pure PE to DCM / PE = 5:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, J = 12.6, 7.5 Hz, 1H), 5.39 (brs, 1H), 5.02 (dd, J = 12.6, 4.3 Hz, 1H), 2.82 (d, J = 5.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.4 (d, J = 6.8 Hz), 83.5 (dd, J = 26.3, 16.9 Hz), 30.4 (d, J = 3.4 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ 69.7 (s, 1F). EI-MS HRMS calculated for $C_3H_6FNO_2S$ $[M]^+$ 139.0098, found 139.0097.



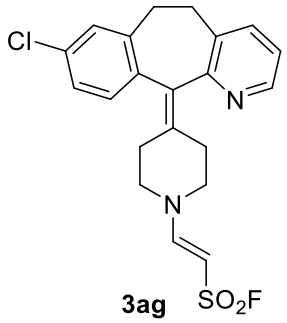
3ae

Ethyl (*E*)-(2-(fluorosulfonyl)vinyl)-L-phenylalaninate (**3ae**). Yellow liquid, 113 mg, 75%. A mixture of DCM and PE from pure PE to DCM / PE = 5:1 (v / v) as eluent for column chromatography. $[\alpha]_D^{25}$ = +35.2 (c = 1.0, MeOH). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53-7.38 (m, 1H), 7.33-7.28 (m, 3H), 7.10 (d, J = 6.9 Hz, 2H), 5.64 (s, 1H), 5.21-4.96 (m, 1H), 4.26-4.20 (m, 2H), 4.18-4.14 (m, 1H), 3.21-3.17 (m, 1H), 3.09-3.06 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1 (s), 149.5 (s), 134.6 (s), 129.4 (s), 129.0 (s), 127.9 (s), 81.2 (d, J = 23.9 Hz), 63.0 (s), 62.5 (s), 40.2 (s), 14.2 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 69.1 (s, 1F). EI-MS HRMS calculated for $C_{13}H_{16}FNO_4S$ $[M]^+$ 301.0779, found 301.0771.



3af

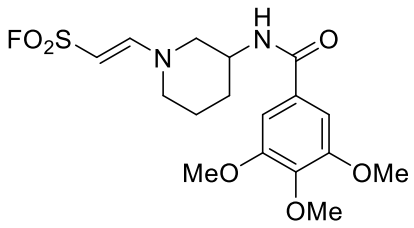
Methyl (*E*)-(2-(fluorosulfonyl)vinyl)-*L*-prolinate (**3af**). Yellow liquid, 107 mg, 90%. A mixture of DCM and PE from pure PE to DCM / PE = 1:1 (v / v) as eluent for column chromatography. $[\alpha]_D^{25}$ = -50.3 (c = 1.23, MeOH). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59-7.56 (m, 1H), 4.96-4.76 (m, 1H), 4.32-4.01 (m, 1H), 3.76 (s, 3H), 3.61-3.31 (m, 1H), 3.23-2.32 (m, 1H), 2.24-1.96 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5 (s), 150.7 (s), 84.9 (d, J = 26.3 Hz), 64.2 (s), 53.0 (s), 47.9 (s), 29.9 (s), 23.6 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 69.9 (s, 1F). EI-MS HRMS calculated for $C_8H_{12}FNO_4S$ $[M]^+$ 237.0466, found 237.0463.



3ag

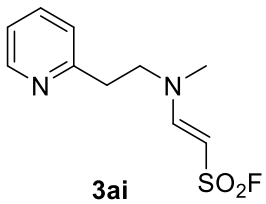
(*E*)-2-(4-(8-chloro-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidin-1-yl)ethene-1-sulfonyl fluoride (**3ag**). White solid, 196 mg, 94%. M.p. 110-113 ºC. A mixture of DCM and PE from pure PE to DCM / PE = 1:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, J = 4.2 Hz, 1H), 7.44 (d, J = 7.4 Hz, 1H), 7.39 (d, J = 12.5 Hz, 1H), 7.18-7.17 (m, 1H), 7.15-7.08 (m, 3H), 4.91 (dd, J = 12.5, 3.5 Hz, 1H), 3.57-5.50 (m, 1H), 3.38-3.28 (m, 4H), 3.15-3.01 (m, 1H), 2.89-2.76 (m, 2H), 2.69-2.64 (m, 1H), 2.55-2.45 (m, 1H), 2.45-2.35 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2 (s), 152.9 (s), 146.9 (s), 139.7 (s), 138.0 (s), 137.4 (s), 136.2 (s), 134.5 (s), 133.5 (s), 130.2 (s), 129.2 (s), 126.5 (s), 122.7 (s), 82.3 (d, J = 23.9 Hz), 54.2 (d, J = 12.2 Hz), 46.4 (s), 31.6 (s), 31.1 (d, J = 44.1 Hz), 28.9 (d, J = 24.6 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.7 (s, 1F). EI-MS HRMS

calculated for $C_{21}H_{20}ClFN_2O_2S$ $[M]^+$ 418.0913, found 418.0913.



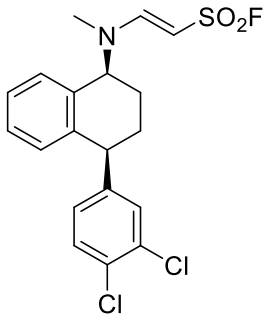
3ah

(*E*)-2-(3-(3,4,5-trimethoxybenzamido)piperidin-1-yl)ethene-1-sulfonyl fluoride (**3ah**). White solid, 195 mg, 97%. M.p. 126-127 ºC. A mixture of DCM and PE from pure PE to DCM / PE = 5:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, J = 12.5 Hz, 1H), 6.94 (s, 2H), 6.26 (s, 1H), 5.03-4.96 (m, 1H), 4.11 (s, 1H), 3.87 (s, 6H), 3.85 (s, 3H), 3.68-3.62 (m 1H), 3.39-3.09 (m, 3H), 2.09-2.05 (m, 1H), 1.91-1.83 (m, 1H), 1.75-1.66 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3 (s), 153.4 (s), 153.3 (s), 141.3 (s), 129.5 (s), 104.6 (s), 82.7 (d, J = 25.3 Hz), 61.0 (s), 58.0 (s), 56.4 (s), 49.8 (s), 45.7 (s), 29.2 (s), 23.8 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.9 (d, J = 46.3 Hz, 1F). EI-MS HRMS calculated for $C_{17}H_{23}FN_2O_6S$ $[M]^+$ 402.1255, found 402.1251.



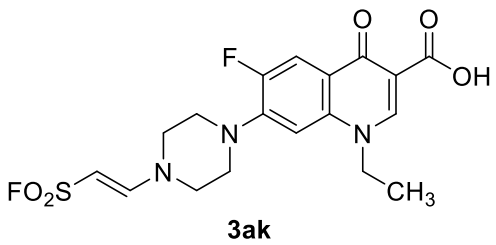
3ai

(*E*)-2-(methyl(2-(pyridin-2-yl)ethyl)amino)ethene-1-sulfonyl fluoride (**3ai**). White solid, 92 mg, 75%. M.p. 99-100 ºC. A mixture of DCM and PE from pure PE to DCM / PE = 5:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, J = 4.4 Hz, 1H), 7.63 (t, J = 7.5 Hz, 1H), 7.32-7.26 (m, 1H), 7.19-7.11 (m, 2H), 4.93-4.70 (m, 1H), 3.74-3.55 (t, J = 6.8 Hz, 2H), 3.06-2.79 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.1 (s), 154.2 (s), 149.9 (s), 137.0 (s), 123.7 (s), 122.3 (s), 82.2 (d, J = 25.9 Hz), 57.7 (s), 50.3 (s), 37.2 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.6 (s, 1F). EI-MS HRMS calculated for $C_{10}H_{13}FN_2O_2S$ $[M]^+$ 244.0676, found 244.0674.



3aj

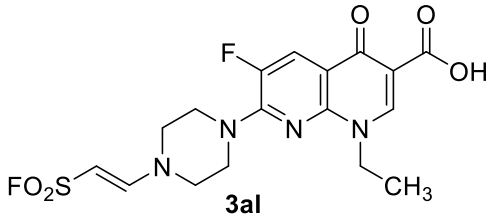
(*E*)-2-(((1S,4S)-4-(3,4-dichlorophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)(methyl)amino)ethene-1-sulfonyl fluoride (**3aj**). White solid, 112 mg, 54%. M.p. 77-79 ºC. A mixture of DCM and PE from pure PE to DCM / PE = 1:1 (v / v) as eluent for column chromatography. $[\alpha]_D^{25}$ = +39.4 (c = 0.97, MeOH). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, J = 12.4 Hz, 1H), 7.37 (d, J = 8.3 Hz, 1H), 7.32 (t, J = 7.3 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H), 7.17-7.13 (m, 2H), 6.99 (d, J = 7.6 Hz, 1H), 6.84 (dd, J = 8.3, 1.7 Hz, 1H), 4.99 (dd, J = 12.4, 4.3 Hz, 1H), 4.65 (t, J = 7.1 Hz, 1H), 4.17 (t, J = 5.1 Hz, 1H), 2.73 (s, 3H), 2.26-2.19 (m, 1H), 2.00-1.94 (m, 1H), 1.92-1.89 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.9 (s), 146.2 (s), 138.8 (s), 133.5 (s), 132.7 (s), 131.2 (s), 130.70 (s), 130.67 (s), 130.6 (s), 129.1 (s), 128.1 (s), 128.01 (s), 127.96 (s), 82.9 (d, J = 26.0 Hz), 65.9 (s), 43.4 (s), 33.6 (s), 29.2 (s), 24.5 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.3 (s, 1F). EI-MS HRMS calculated for $C_{19}H_{18}Cl_2FNO_2S$ $[M]^+$ 413.0414, found 413.0411.



3ak

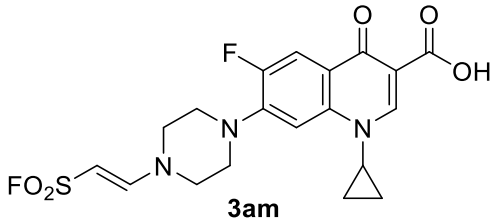
(*E*)-1-ethyl-6-fluoro-7-(4-(2-(fluorosulfonyl)vinyl)piperazin-1-yl)-4-oxo-1,4-dihydroquinoline-3-carboxylic acid (**3ak**). White solid, 176 mg, 82%. Decomposed at 190.1 ºC. A mixture of EA, MeOH and DCM from pure EA to MeOH / DCM = 1:10 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 15.28 (s, 1H),

8.96 (s, 1H), 7.95 (d, J = 13.1 Hz, 1H), 7.72 (d, J = 12.5 Hz, 1H), 7.23 (d, J = 7.1 Hz, 1H), 5.61 (dd, J = 12.5, 3.8 Hz, 1H), 4.60 (q, J = 6.8 Hz, 2H), 3.78-3.71 (m, 2H), 3.59-3.53 (m, 2H), 3.45-3.39 (m, 4H), 1.42 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 176.2 (s), 166.1 (s), 153.8 (s), 152.8 (d, J = 249.2 Hz), 148.6 (s), 144.8 (d, J = 10.4 Hz), 137.1 (s), 119.7 (d, J = 7.6 Hz), 111.3 (d, J = 22.7 Hz), 107.1 (s), 106.5 (d, J = 3.0 Hz), 80.9 (d, J = 23.1 Hz), 51.6 (s), 49.7 (s), 49.09 (s), 48.1 (s), 45.0 (s), 14.4 (s). ^{19}F NMR (471 MHz, DMSO) δ 74.0 (s, 1F), -121.8 (dd, J = 13.0, 7.2 Hz, 1F). EI-MS HRMS calculated for $C_{18}H_{19}F_2N_3O_5S$ $[M]^+$ 427.1008, found 427.1005.



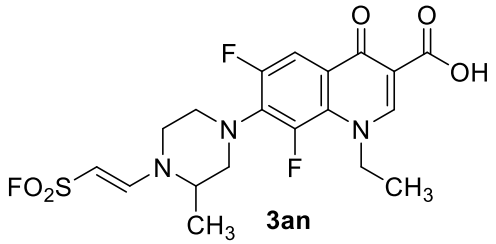
3al

(*E*)-1-ethyl-6-fluoro-7-(4-(2-(fluorosulfonyl)vinyl)piperazin-1-yl)-4-oxo-1,4-dihydro-1,8-naphthyridine-3-carboxylic acid (**3al**). White solid, 160 mg, 75%. Decomposed at 220.1 ºC. A mixture of EA, MeOH and DCM from pure EA to MeOH / DCM = 1:10 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 15.23 (s, 1H), 8.96 (s, 1H), 8.09 (d, J = 13.3 Hz, 1H), 7.71 (d, J = 12.5 Hz, 1H), 5.53 (dd, J = 12.4, 3.9 Hz, 1H), 4.49 (q, 7.0 Hz, 2H), 3.96-3.90 (m, 4H), 3.79-3.73 (m, 2H), 3.57-3.51 (m, 2H), 1.39 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.4 (s), 165.8 (s), 154.0 (s), 153.9 (s), 149.9 (s), 140.0 (d, J = 248.9 Hz), 145.9 (s), 144.8 (s), 113.0 (d, J = 3.6 Hz), 108.2 (s), 80.9 (d, J = 23.1 Hz), 51.1 (s), 47.2 (s), 46.9 (d, J = 7.8 Hz), 45.0 (s), 44.8 (d, J = 7.8 Hz), 14.7 (s).^{19}F NMR (471 MHz, DMSO) δ 73.9 (s, 1F), -127.9 (d, J = 13.3 Hz, 1F). EI-MS HRMS calculated for $C_{17}H_{18}F_2N_4O_5S$ $[M]^+$ 428.0960, found 428.0959.



3am

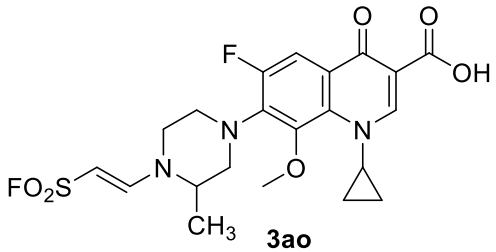
(*E*)-1-cyclopropyl-6-fluoro-7-(4-(2-(fluorosulfonyl)vinyl)piperazin-1-yl)-4-oxo-1,4-dihydroquinoline-3-carboxylic acid (**3am**). White solid, 251 mg, 95%. Decomposed at 199.0 °C. A mixture of EA, MeOH and DCM from pure EA to MeOH / DCM = 1:10 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 14.80 (s, 1H), 8.71 (s, 1H), 7.77 (d, J = 12.0 Hz, 1H), 7.67-7.61 (m, 1H), 5.63-5.54 (m, 1H), 4.19-4.15 (m, 1H), 4.05-3.99 (d, J = 6.4 Hz, 1H), 3.93-3.86 (m, 1H), 3.77-3.71 (m, 4H), 3.59-3.41 (m, 4H), 1.40-1.30 (m, 3H), 1.15-1.10 (m, 2H), 1.06-1.02 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.3 (s), 165.7 (s), 153.9 (s), 152.8 (d, J = 238.7 Hz), 148.0 (d, J = 42.5 Hz), 144.5 (d, J = 10.2 Hz), 139.0 (s), 119.0 (d, J = 7.7 Hz), 111.0 (dd, J = 23.0, 14.1 Hz), 106.9 (s), 106.8 (s), 81.0 (d, J = 23.8 Hz), 51.5 (s), 49.5 (s), 48.0 (s), 44.9 (s), 35.9 (s), 7.6 (s). ^{19}F NMR (471 MHz, DMSO) δ 74.0 (s, 1F), -121.9 (dd, J = 12.9, 7.4 Hz, 1F). EI-MS HRMS calculated for $C_{19}H_{19}F_2N_3O_5S$ $[M]^+$ 439.1008, found 439.1008.



3an

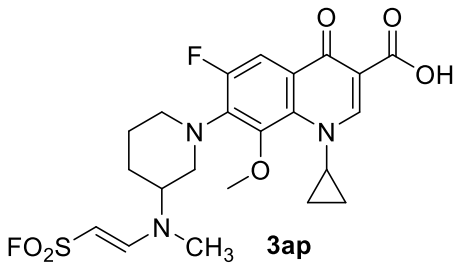
(*E*)-1-ethyl-6,8-difluoro-7-(4-(2-(fluorosulfonyl)vinyl)-3-methylpiperazin-1-yl)-4-oxo-1,4-dihydroquinoline-3-carboxylic acid (**3an**). White solid, 190 mg, 69%. Decomposed at 190.2 °C. A mixture of EA, MeOH and DCM from pure EA to MeOH / DCM = 1:10 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 14.78 (s, 1H), 8.92 (s, 1H), 7.87 (d, J = 11.5 Hz, 1H), 7.66-7.59 (m, 1H), 5.58 (d, J = 11.9 Hz, 1H), 4.62-4.56 (m, 2H), 4.05-4.97 (m, 1H), 3.75-3.65 (m, 1H), 3.58-3.37 (m, 4H), 1.45 (t, J = 6.7 Hz, 3H), 1.38-1.30 (m, 3H), 1.24-1.21 (m, 1H). ^{13}C NMR (126 MHz, DMSO) δ 175.50 (s), 165.45 (s), 159.7 (d, J = 249.5 Hz), 153.2 (d, J = 127.8 Hz), 151.2 (s), 146.5 (d, J = 248.9 Hz), 133.5 (s), 127.2(d, J = 6.6 Hz), 121.1 (d, J = 8.2 Hz),

107.1 (s), 106.9 (s), 81.0 (dd, J = 76.4, 23.0 Hz), 56.7 (s), 53.7 (d, J = 15.8 Hz), 50.4 (s), 49.3 (d, J = 36.9 Hz), 48.2 (s), 16.1 (s), 15.9 (d, J = 5.3 Hz). ^{19}F NMR (471 MHz, DMSO) δ 74.0 (s), 73.8 (s), -119.4 (s), -128.8 (s). EI-MS HRMS calculated for $C_{19}H_{20}F_3N_3O_5S$ $[M]^+$ 459.1070, found 459.1069.



3ao

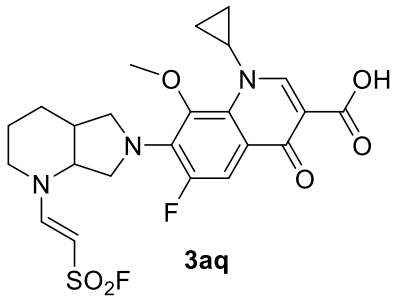
(*E*)-1-cyclopropyl-6-fluoro-7-(4-(2-(fluorosulfonyl)vinyl)-3-methylpiperazin-1-yl)-8-methoxy-4-oxo-1,4-dihydroquinoline-3-carboxylic acid (**3ao**). White solid, 226 mg, 78%. Decomposed at 181.6 ^{o}C. A mixture of EA, MeOH and DCM from pure EA to MeOH / DCM = 1:10 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 14.78 (s, 1H), 8.71 (s, 1H), 7.77 (d, J = 12.0 Hz, 1H), 7.67-7.61 (m, 1H), 5.60-5.53 (m, 1H), 4.17 (hept, J = 3.5 Hz, 1H), 4.02-4.01 (m, 1H), 3.79-3.69 (m, 4H), 3.57-3.46 (m, 4H), 1.37-1.32 (m, 3H), 1.26-1.19 (m, 1H), 1.15-1.10 (m, 2H), 1.06-1.01 (m, 2H). ^{13}C NMR (126 MHz, DMSO) δ 176.4 (s), 165.6 (s), 155.5 (d, J = 249.6 Hz), 153.7 (s), 152.5 (d, J = 2.2 Hz), 150.8 (s), 146.3 (s), 134.2 (s), 121.5 (d, J = 8.4 Hz), 106.7 (d, J = 2.3 Hz), 106.6 (s), 81.1 (d, J = 24.7 Hz), 63.7 (d, J = 27.3 Hz), 56.7 (s), 55.3 (s), 49.3 (s), 45.1 (s), 40.7 (s), 16.3 (s), 9.0 (s). ^{19}F NMR (471 MHz, DMSO) δ 73.9 (s, 1F), -119.9 (d, J = 11.5 Hz, 1F). EI-MS HRMS calculated for $C_{21}H_{23}F_2N_3O_6S$ $[M]^+$ 483.1270, found 483.1270.



3ap

(*E*)-1-cyclopropyl-6-fluoro-7-(3-((2-(fluorosulfonyl)vinyl)(methyl)amino)piperidin-1-

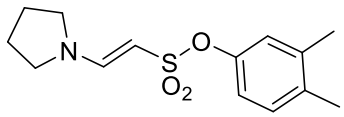
yl)-8-methoxy-4-oxo-1,4-dihydroquinoline-3-carboxylic acid (**3ap**). White solid, 265 mg, 89%. Decomposed at 170.8 °C. A mixture of EA, MeOH and DCM from pure EA to MeOH / DCM = 1:10 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.64 (s, 1H), 8.81 (s, 1H), 7.87 (d, J = 11.9 Hz, 1H), 7.58 (d, J = 12.3 Hz, 1H), 4.94 (dd, J = 12.2, 3.3 Hz, 1H), 4.03 (hept, J = 3.5 Hz, 1H), 3.79 (s, 3H), 3.61-3.58 (m, 1H), 3.50-3.48 (m, 2H), 3.19-3.10 (m, 2H), 2.91 (s, 3H), 2.15-2.13 (m, 1H), 1.99-1.96 (m, 1H), 1.86-1.75 (m, 2H), 1.25-1.24 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.1 (s), 166.7 (s), 156.3 (d, J = 251.2 Hz), 151.8 (s), 150.2 (s), 145.9 (d, J = 5.4 Hz), 139.1 (d, J = 12.2 Hz), 134.0 (s), 122.7 (d, J = 9.1 Hz), 108.5 (d, J = 23.0 Hz), 108.1 (s), 83.7 (d, J = 26.7 Hz), 63.3 (s), 62.92 (s), 55.3 (s), 51.0 (s), 40.7 (s), 34.9 (s), 29.1 (s), 25.5 (s). 9.74 (s), 9.65 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 70.0 (s, 1F), -120.36 (d, J = 11.5 Hz, 1F). EI-MS HRMS calculated for $C_{22}H_{25}F_2N_3O_6S$ $[M]^+$ 497.1427, found 497.1426.



3aq

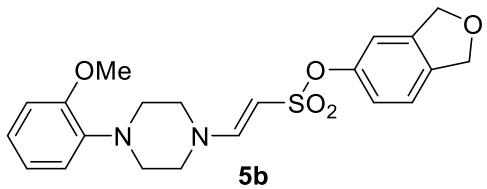
(*E*)-1-cyclopropyl-6-fluoro-7-(1-(2-(fluorosulfonyl)vinyl)octahydro-6H-pyrrolo[3,4-b]pyridin-6-yl)-8-methoxy-4-oxo-1,4-dihydroquinoline-3-carboxylic acid (**3aq**). White solid, 213 mg, 70%. Decomposed at 185.9 °C. A mixture of EA, MeOH and DCM from pure EA to MeOH / DCM = 1:10 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.82 (s, 1H), 8.78 (s, 1H), 7.79 (d, J = 13.7 Hz, 1H), 7.46 (d, J = 12.6 Hz, 1H), 5.12-5.10 (m, 1H), 4.20-4.15 (m, 1H), 4.12-4.06 (m, 1H), 4.02-3.97 (m, 2H), 3.61 (s, 3H), 3.36-3.34 (m, 1H), 2.51-2.43 (m, 1H), 1.97-1.91 (m, 2H), 1.71-1.61 (m, 3H), 1.31-1.25 (m, 4H), 1.14-1.11 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.9 (s), 166.9 (s), 153.9 (d, J = 251.0 Hz), 152.1 (s), 150.0 (s), 141.9 (d, J = 6.7 Hz), 136.6 (d, J = 10.7 Hz), 134.4 (s), 119.8 (d, J = 8.8 Hz), 108.3 (d,

J = 23.9 Hz), 107.9 (s), 84.4 (d, *J* = 22.6 Hz), 62.7 (s), 61.5 (s), 56.1 (s), 56.0 (s), 50.3 (s), 40.6 (s), 36.2 (s), 31.8 (s), 24.8 (s), 10.5 (s), 8.8 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 69.9 (s, 1F), -121.5 (s, 1F). EI-MS HRMS calculated for $C_{23}H_{25}F_2N_3O_6S$ $[M]^+$ 509.1427, found 509.1425.



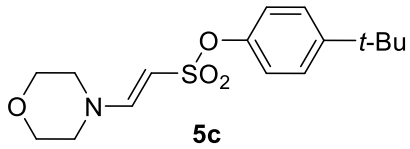
5a

3,4-dimethylphenyl (*E*)-2-(pyrrolidin-1-yl)ethene-1-sulfonate (**5a**). White solid, 139 mg, 99%. M.p. 81-82 ºC. DCM / PE = 1:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 12.4 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 7.03 (d, *J* = 1.8 Hz, 1H), 6.96 (dd, *J* = 8.1, 2.2 Hz, 1H), 4.72 (d, *J* = 12.4 Hz, 1H), 3.45-3.35 (m, 2H), 3.10-3.02 (m, 2H), 2.23 (s, 3H), 2.22 (s, 3H), 2.04-1.96 (m, 2H), 1.92-1.84 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.9 (s), 148.4 (s), 137.9 (s), 134.7 (s), 130.3 (s), 123.8 (s), 119.8 (s), 84.9 (s), 52.2 (s), 47.0 (s), 25.3 (s), 25.2 (s), 19.9 (s), 19.3 (s). EI-MS HRMS calculated for $C_{14}H_{19}NO_3S$ $[M]^+$ 281.1080, found 281.1077.



5b

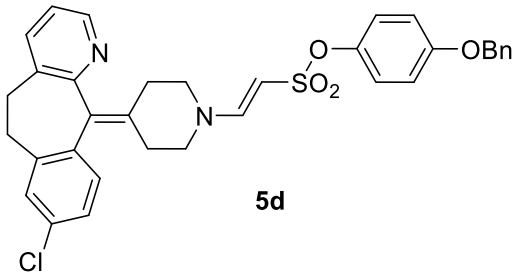
Benzo[*d*][1,3]dioxol-5-yl (*E*)-2-(4-(2-methoxyphenyl)piperazin-1-yl)ethene-1-sulfonate (**5b**). Yellow liquid, 145 mg, 69%. DCM / PE = 1:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 12.7 Hz, 1H), 7.06 (td, *J* = 7.7, 1.6 Hz, 1H), 6.94 (td, *J* = 7.6, 1.2 Hz, 1H), 6.89 (dd, *J* = 7.9, 1.3 Hz, 2H), 6.79 (d, *J* = 2.2 Hz, 1H), 6.75-6.70 (m, 2H), 5.97 (s, 2H), 4.95 (d, *J* = 12.7 Hz, 1H), 3.87 (s, 3H), 3.45-3.32 (m, 4H), 3.06 (t, *J* = 5.1 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.4 (s), 152.0 (s), 148.0 (s), 146.1 (s), 144.6 (s), 140.3 (s), 124.1 (s), 121.2 (s), 118.7 (s), 115.8 (s), 111.6 (s), 107.9 (s), 105.1 (s), 101.9 (s), 85.6 (s), 55.6 (s), 52.7 (s), 50.5 (s). EI-MS HRMS calculated for $C_{20}H_{22}N_2O_6S$ $[M]^+$ 418.1193, found 418.1193.



5c

4-(*Tert*-butyl)phenyl (*E*)-2-morpholinoethene-1-sulfonate (**5c**). White solid, 143 mg, 88%. M.p. 116-118 °C. DCM / PE = 1:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, J = 8.8 Hz, 2H), 7.15 (d, J = 8.7 Hz, 2H), 7.05 (d, J = 12.8 Hz, 1H), 4.98 (d, J = 12.8 Hz, 1H), 3.66 (t, J = 4.8 Hz, 4H), 3.21-3.15 (m, 4H), 1.30 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.8 (s), 149.6 (s), 147.9 (s), 126.5 (s), 122.2 (s), 86.9 (s), 66.1 (s), 34.6 (s), 31.5 (s). EI-MS HRMS calculated for $C_{16}H_{23}NO_4S$ $[M]^+$ 325.1342, found 325.1333.

Note: In the ^{13}C NMR spectrum of **5c**, theoretically, there should be ten peaks. Due to the compact overlaying, it is difficult to specify the overlaying peaks.

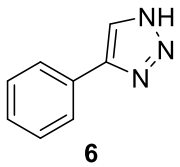


5d

4-(Benzyloxy)phenyl (E)-2-(4-(8-chloro-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidin-1-yl)ethene-1-sulfonate (**5d**). Yellow liquid, 296 mg, 99%. DCM / PE = 1:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, J = 3.7 Hz, 1H), 7.45-7.36 (m, 5H), 7.32 (t, J = 7.1 Hz, 1H), 7.19-7.09 (m, 6H), 7.05 (d, J = 12.7 Hz, 1H), 6.94-6.91 (m, 2H), 5.04 (s, 2H), 4.88 (d, J = 12.7 Hz, 1H), 3.39-3.29 (m, 4H), 3.20-2.95 (m, 2H), 2.90-2.77 (m, 2H), 2.62-2.57 (m, 1H), 2.45-2.36 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2 (s), 156.4 (s), 151.6 (s), 146.9 (s), 144.0 (s), 139.7 (s), 138.0 (s), 137.5 (s), 136.8 (s), 135.8 (s), 135.1 (s), 133.5 (s), 133.4 (s), 130.3 (s), 129.2 (s), 128.7 (s), 128.2(s), 127.6 (s), 126.5 (s), 124.0 (s), 122.7 (s), 115.5 (s), 85.3 (s), 70.5 (s), 31.7 (s), 31.6 (s). EI-MS HRMS calculated for $C_{34}H_{31}ClN_2O_4S$ $[M]^+$ 598.1688, found 598.1687.

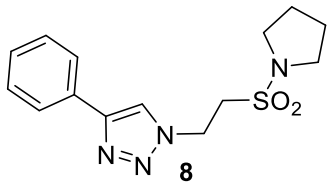
Note: In the ^{13}C NMR spectrum of **5d**, theoretically, there should be twenty-eight peaks.

Due to the compact overlaying, it is difficult to specify the overlaying peaks.



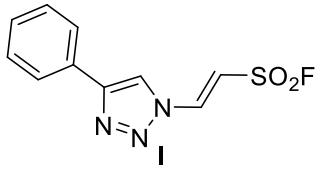
6

4-Phenyl-1H-1,2,3-triazole (**6**).[3] White solid, 72 mg, 99%. A mixture of DCM, PE and EA from pure DCM to PE / EA = 1:2 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 14.98 (s, 1H), 8.24 (s, 1H), 7.86 (d, J = 7.3 Hz, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.0 Hz, 1H).



8

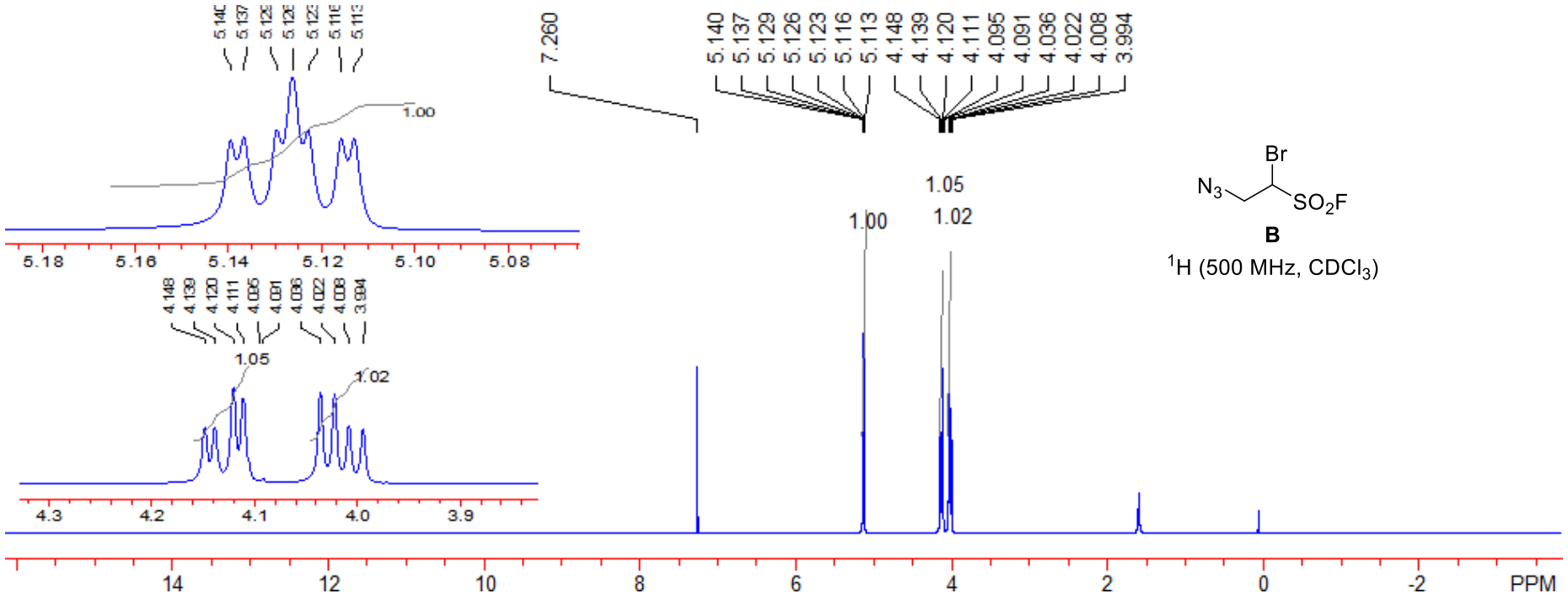
4-Phenyl-1-(2-(pyrrolidin-1-ylsulfonyl)ethyl)-1H-1,2,3-triazole (**8**). White solid, 60 mg, 98%. M.p. 196-197 °C. A mixture of EA and PE from EA / PE = 1:2 (v / v) to pure EA as eluent for column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 8.65 (s, 1H), 7.82 (d, J = 7.8 Hz, 2H), 7.46 (t, J = 7.7 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 4.79 (t, J = 6.9 Hz, 2H), 3.79 (t, J = 6.9 Hz, 2H), 3.22 (t, J = 6.7 Hz, 4H), 1.79-1.76 (m, 4H). ^{13}C NMR (126 MHz, DMSO) δ 146.4 (s), 130.7 (s), 129.0 (s), 128.0 (s), 125.1 (s), 121.9 (s), 47.3 (s), 47.0 (s), 44.3 (s), 25.2 (s). ESI-MS HRMS calculated for $C_{14}H_{19}N_4O_2S$ $[M+H]^+$ 307.1223, found 307.1222.



I

(*E*)-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethene-1-sulfonyl fluoride (**I**). White solid, 77 mg, 61%. M.p. 119-120 °C. A mixture of DCM and PE from DCM / PE= 1:5 to DCM / PE = 1:1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, J = 13.5 Hz, 1H), 8.20 (s, 1H), 7.86 (d, J = 7.5 Hz, 2H), 7.53-7.47 (m, 3H),

7.15 (dd, J = 13.5, 2.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9 (s), 142.0 (d, J = 3.0 Hz), 137.3 (s), 130.7 (s), 129.4 (s), 128.0 (s), 126.8 (s), 108.8 (d, J = 31.9 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ 65.2 (s, 1F). EI-MS HRMS calculated for $C_{10}H_8FN_3O_2S$ $[M]^+$ 253.0316, found 253.0314.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5.126
5.123
5.116
5.113
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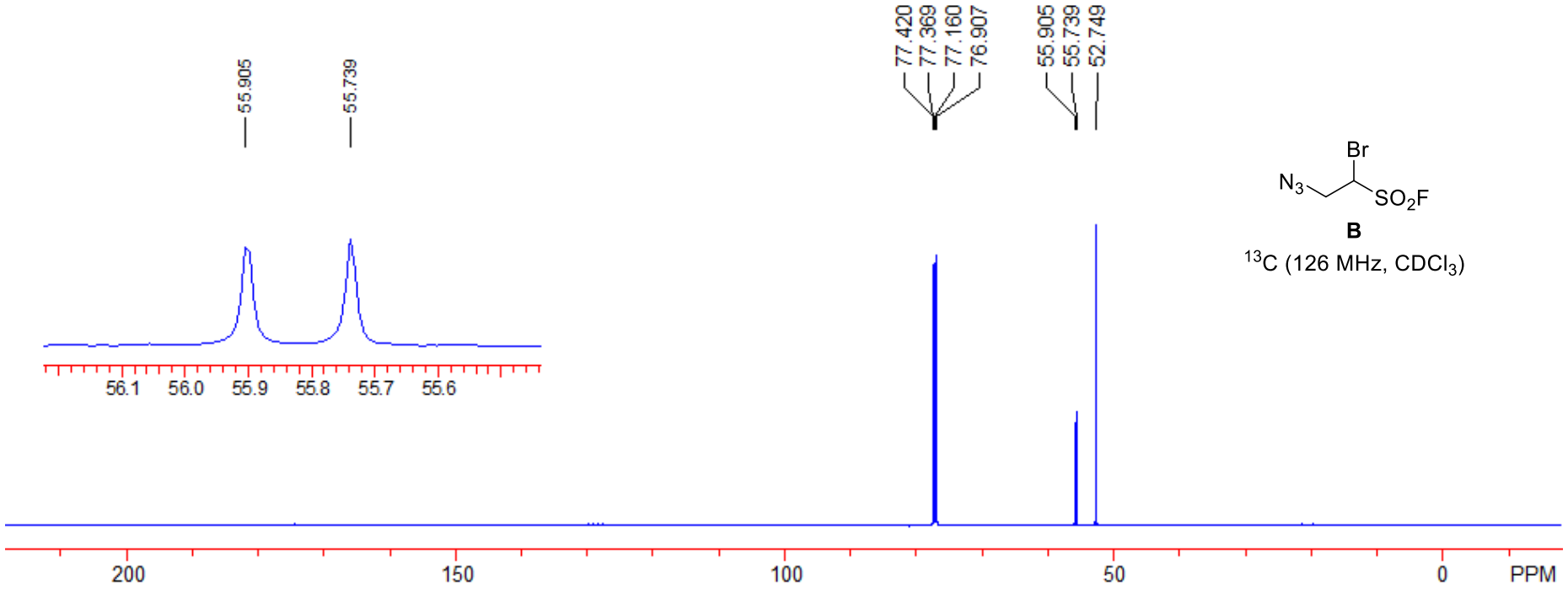
4.139
4.120
4.111
4.095
4.091
4.036
4.022
4.008
3.994
1.00
1.05
1.02
Br
N3
SO2F
B
1H (500 MHz, CDCl3)
PPM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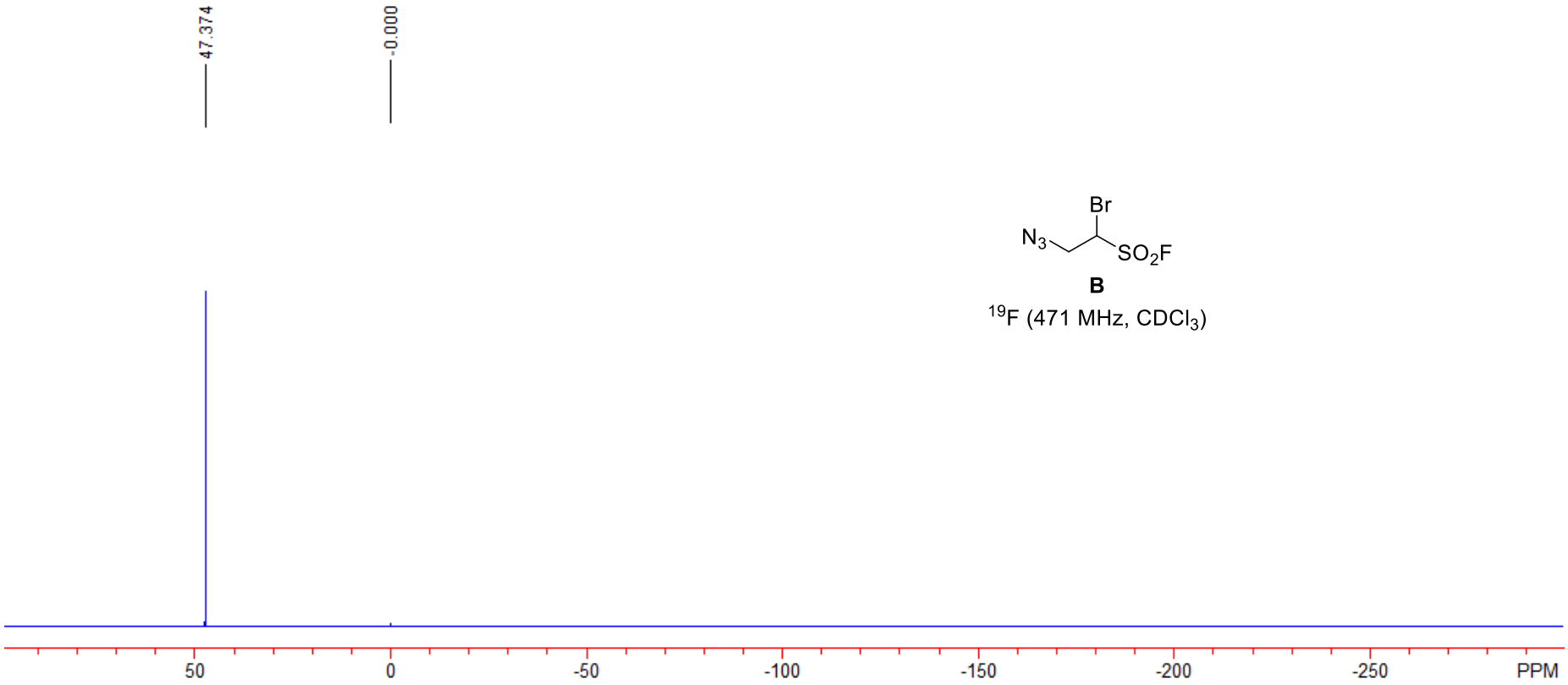
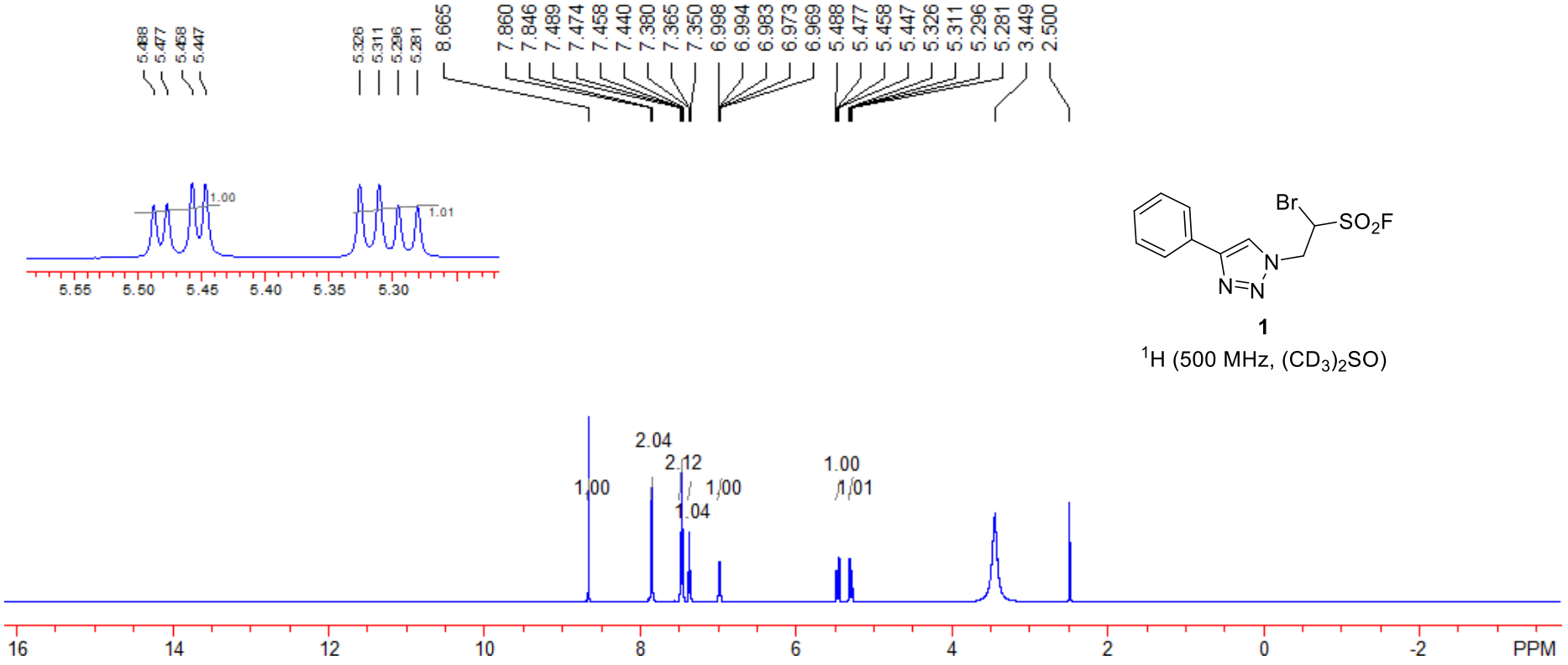
55.739
52.749
56.1
56.0
55.9
55.8
55.7
55.6
200
150
100
50
0
PPM
Br
N3
SO2F
B
13C (126 MHz, CDCl3)



B

^{19}F (471 MHz, $CDCl_3$)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7.846
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5.458
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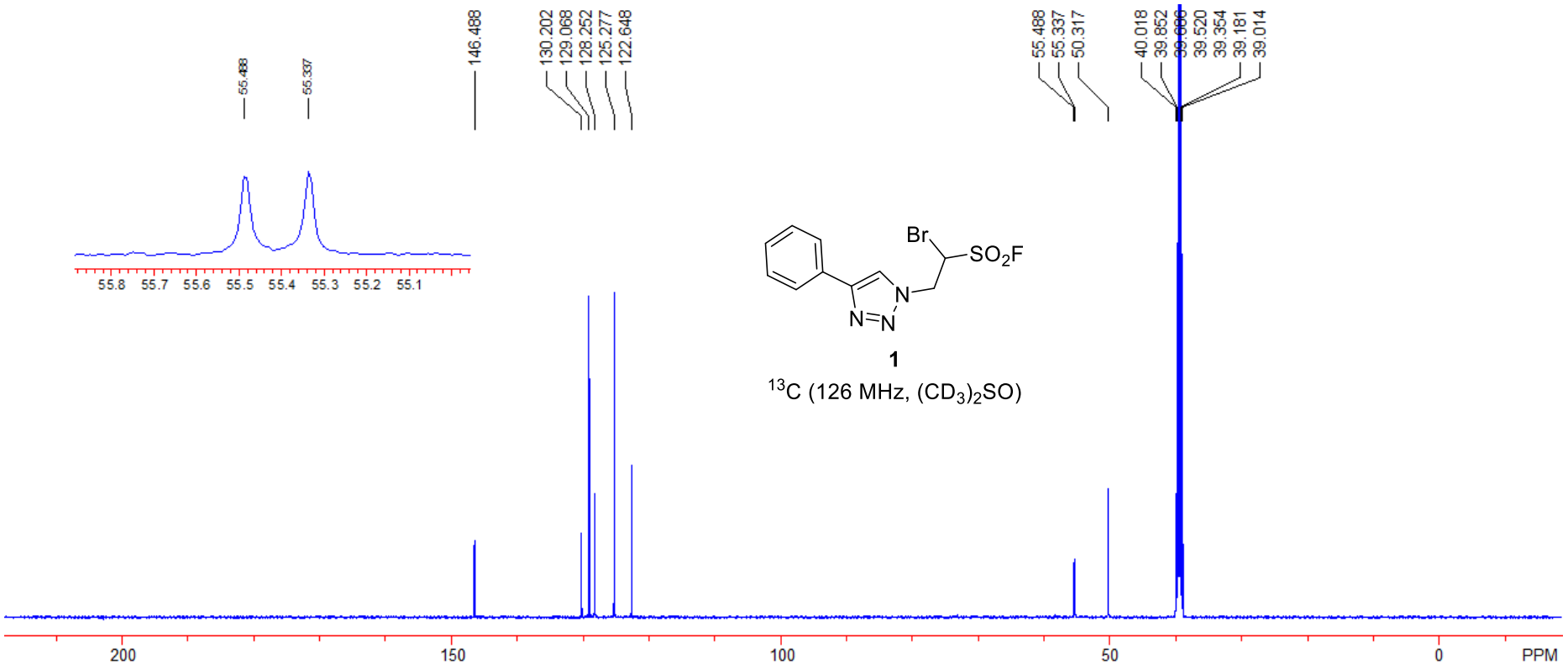
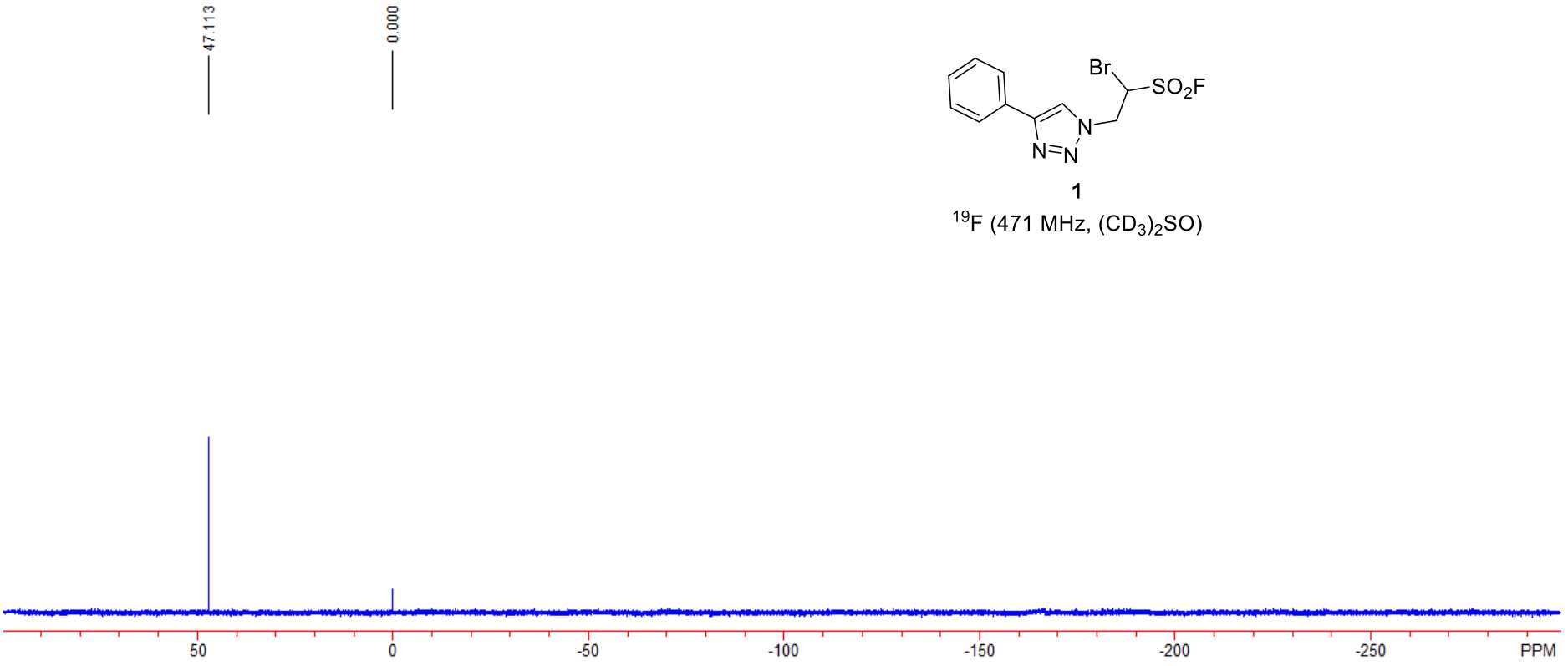
5.281
3.449
2.500
1.00
1.01
5.55
5.50
5.45
5.40
5.35
5.30
Br
SO2F
N
N=N
1
1H (500 MHz, (CD3)2SO)
2.04
2.12
1.00
1.00
1.04
1.00
1.01
16
14
12
10
8
6
4
2
0
-2
PPM



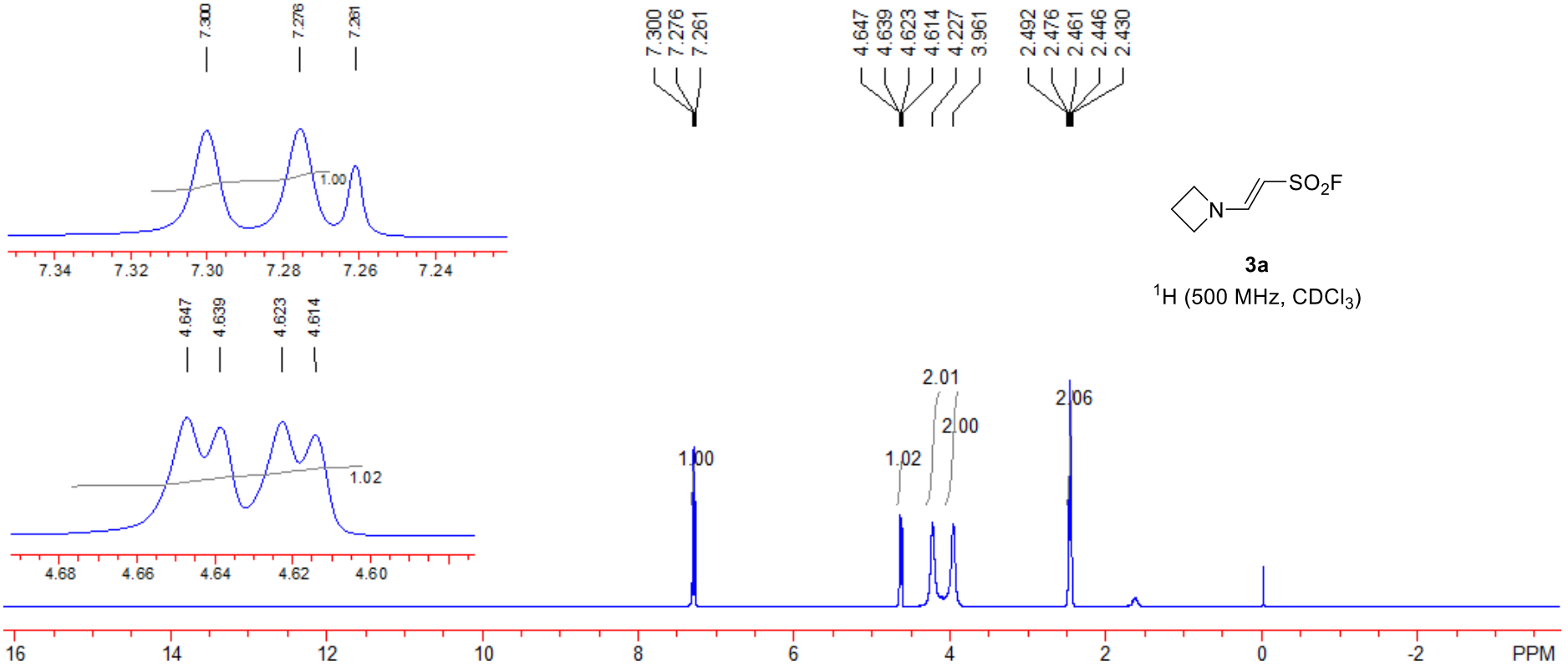
1

^{13}C (126 MHz, $(CD_3)_2SO$)



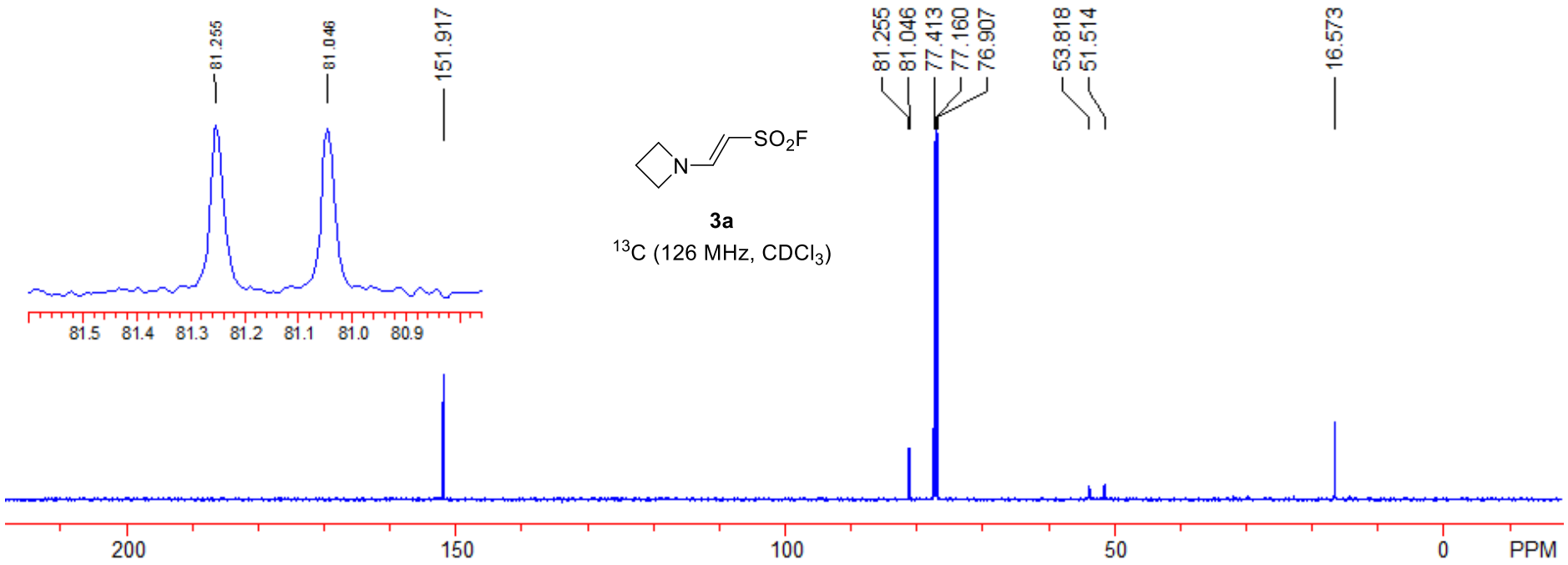
1

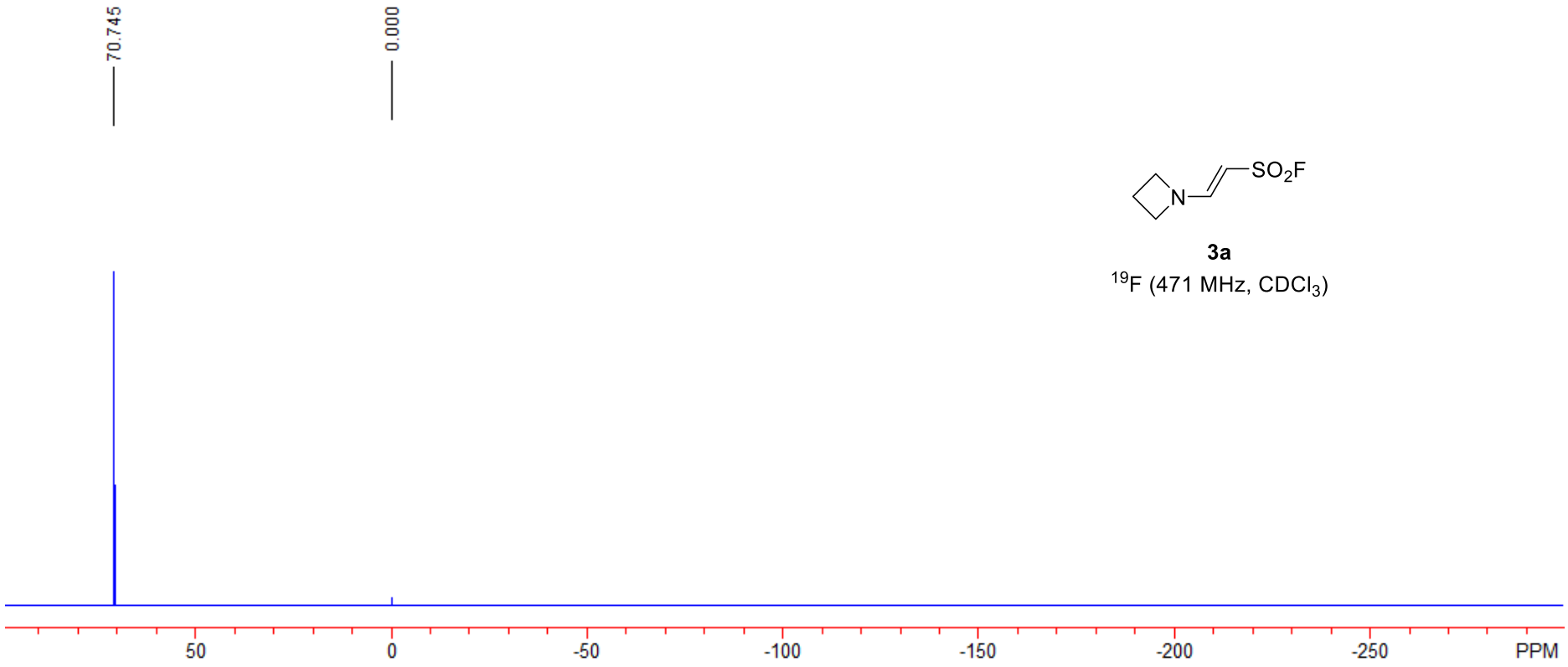
^{19}F (471 MHz, $(CD_3)_2SO$)



3a

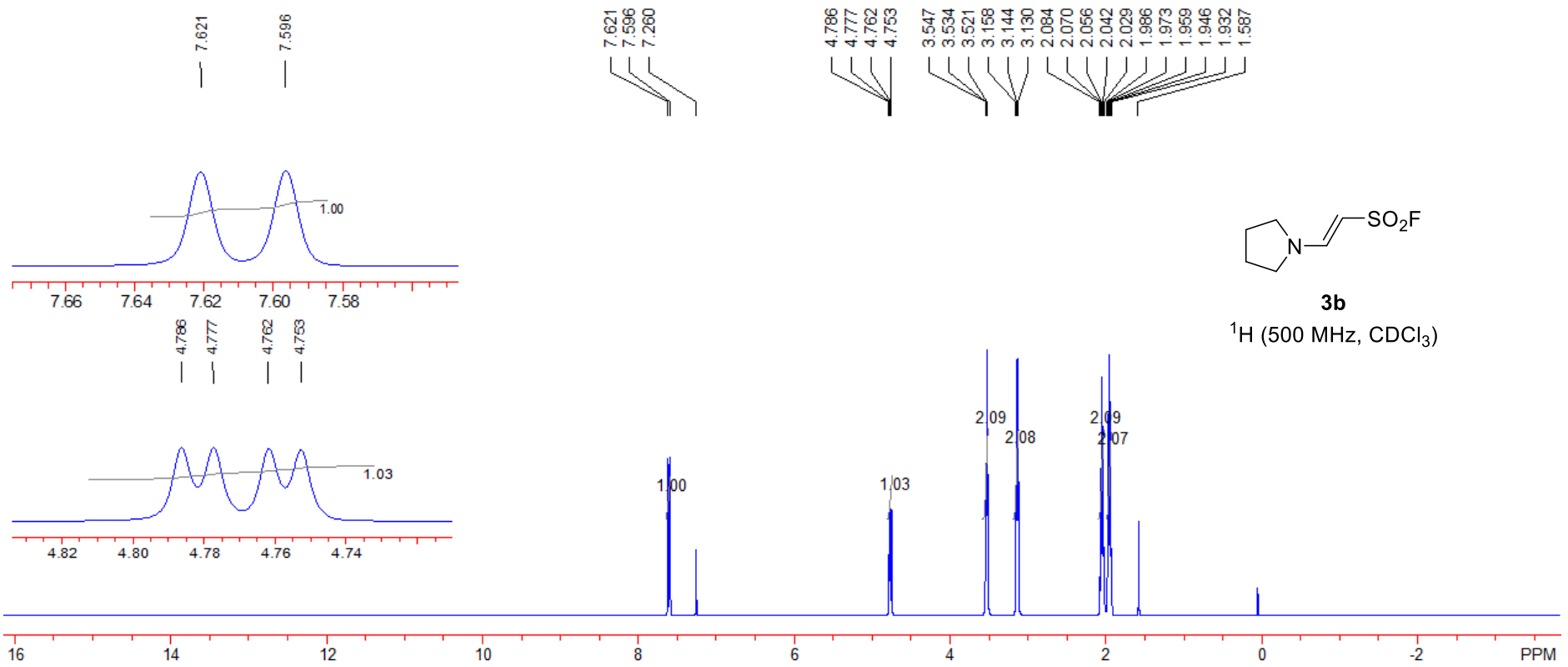
^{1}H (500 MHz, $CDCl_3$)

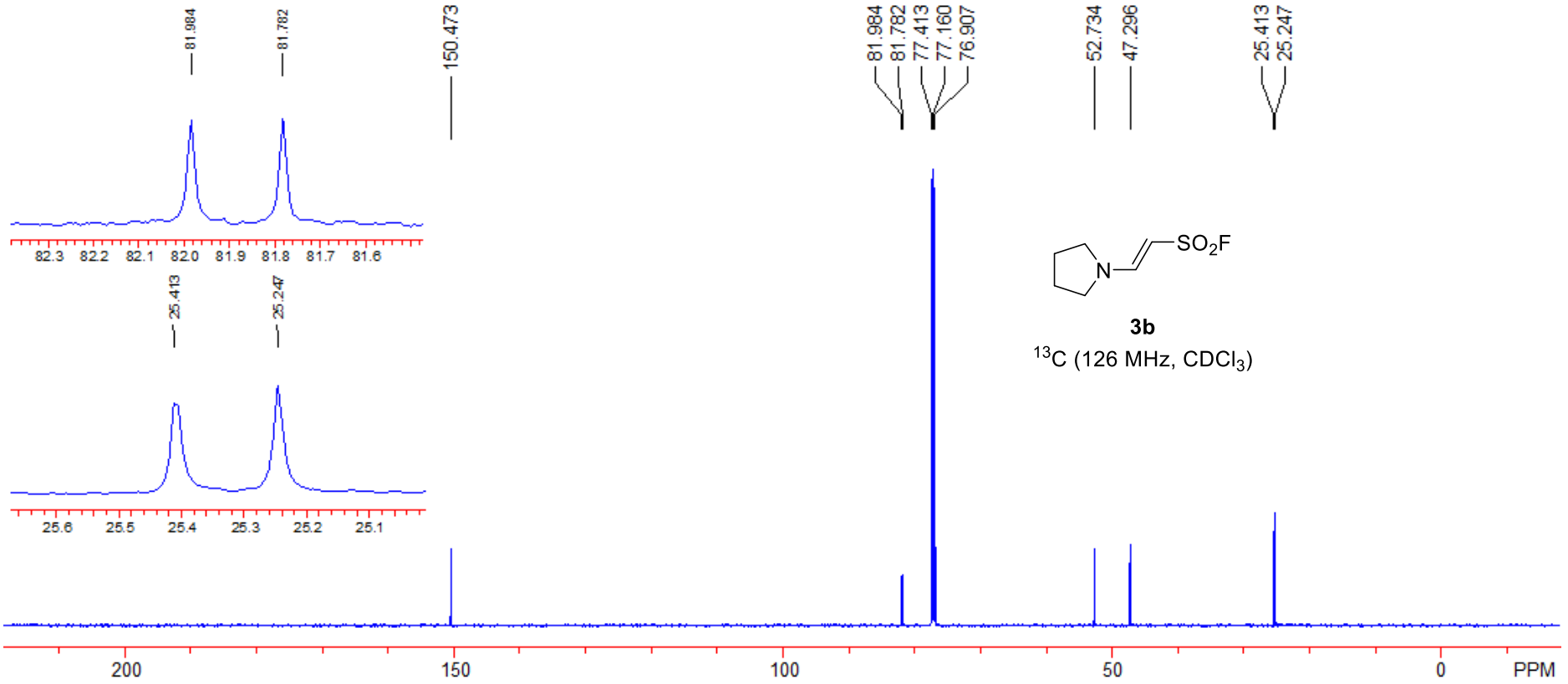

81.255
81.046
151.917
81.255
81.046
77.413
77.160
76.907
53.818
51.514
16.573
SO2F
N
3a
13C (126 MHz, CDCl3)
81.5
81.4
81.3
81.2
81.1
81.0
80.9
200
150
100
50
0
PPM

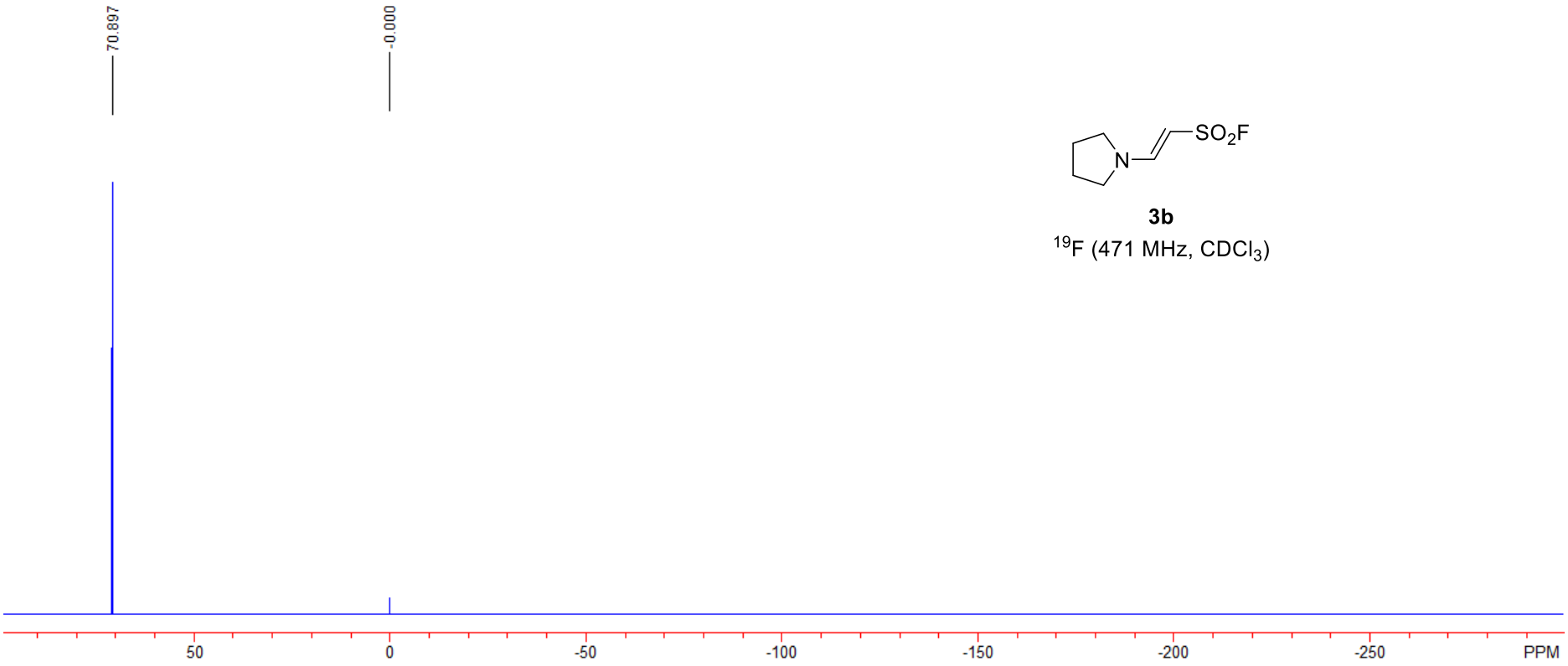


3a

^{19}F (471 MHz, $CDCl_3$)

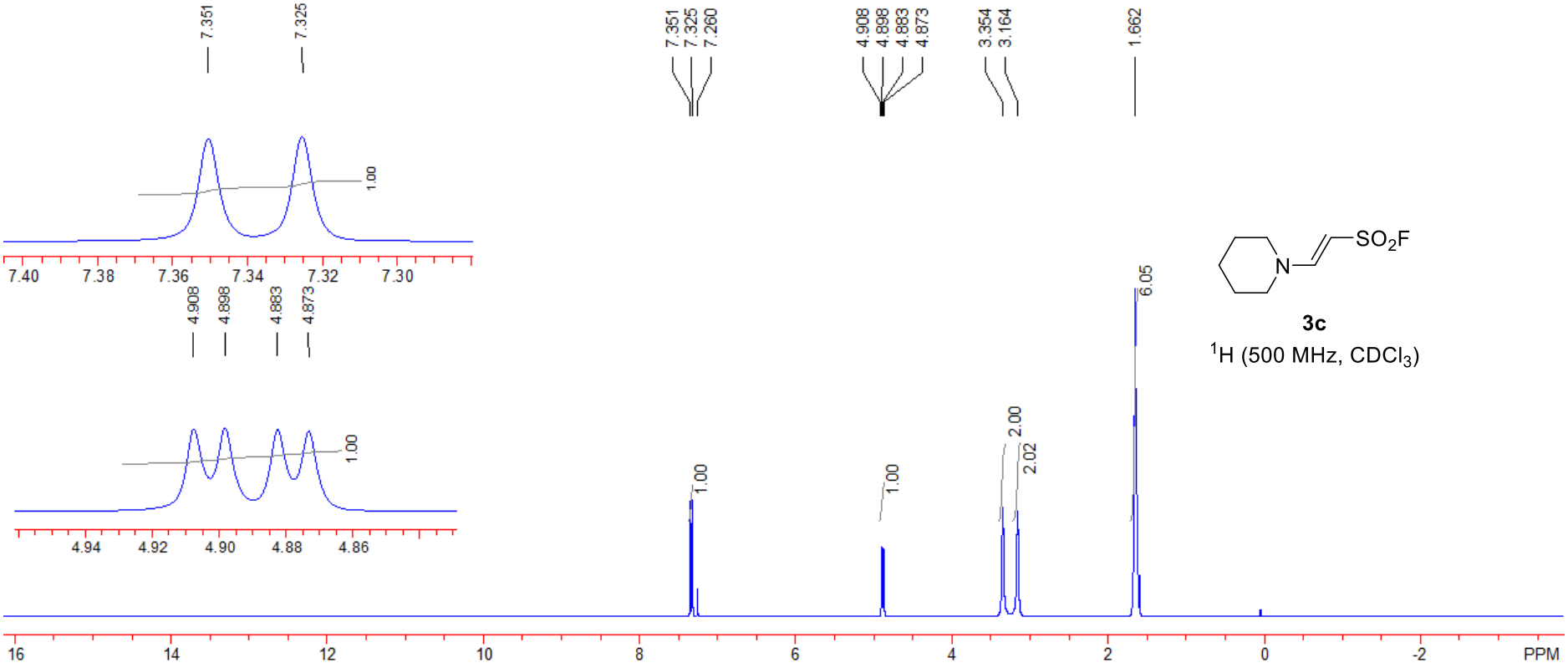

7.621
7.596
7.260
4.786
4.777
4.762
4.753
3.547
3.534
3.521
3.158
3.144
3.130
2.084
2.070
2.056
2.042
2.029
1.986
1.973
1.959
1.946
1.932
1.587
1.00
7.66
7.64
7.62
7.60
7.58
4.786
4.777
4.762
4.753
1.03
4.82
4.80
4.78
4.76
4.74
1.00
1.03
2.09
2.08
2.09
2.07
16
14
12
10
8
6
4
2
0
-2
PPM
SO2F
N
3b
1H (500 MHz, CDCl3)

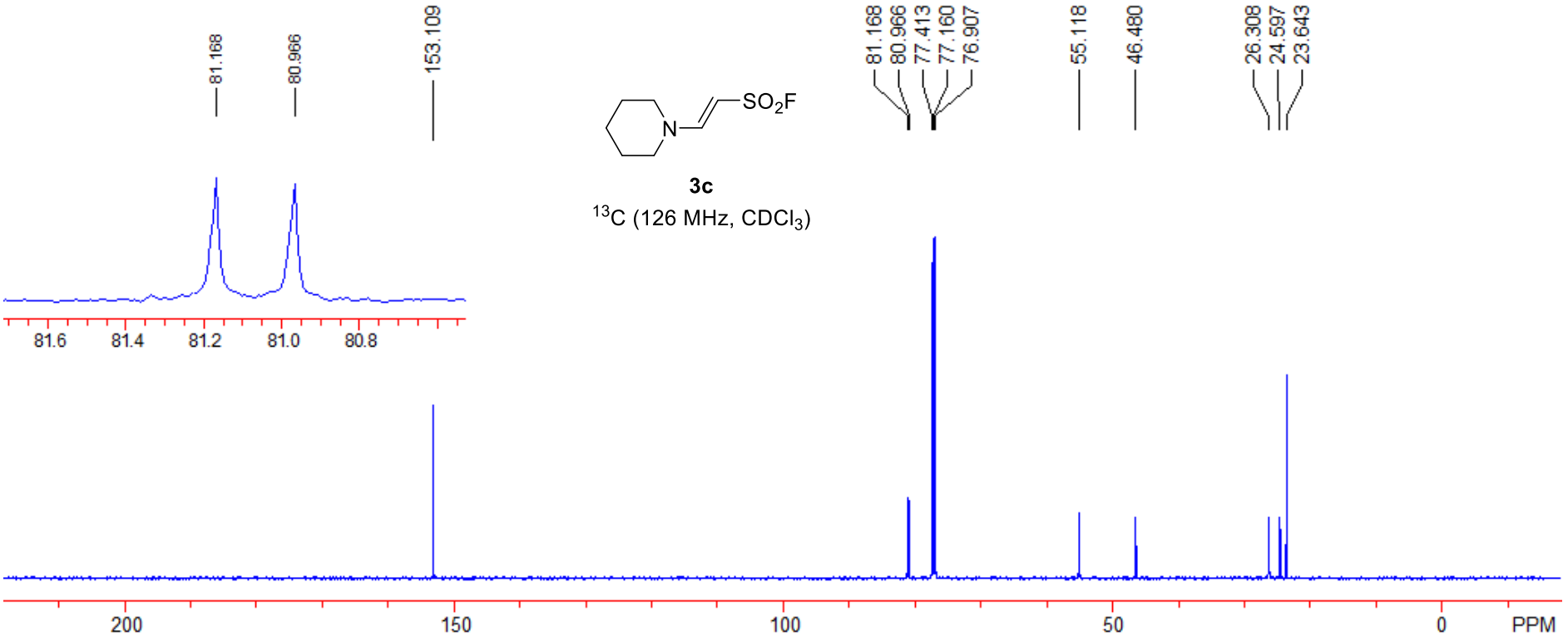

81.984
81.782
150.473
81.984
81.782
77.413
77.160
76.907
52.734
47.296
25.413
25.247
82.3 82.2 82.1 82.0 81.9 81.8 81.7 81.6
25.413
25.247
25.6 25.5 25.4 25.3 25.2 25.1
200 150 100 50 0 PPM
N
SO2F
3b
13C (126 MHz, CDCl3)

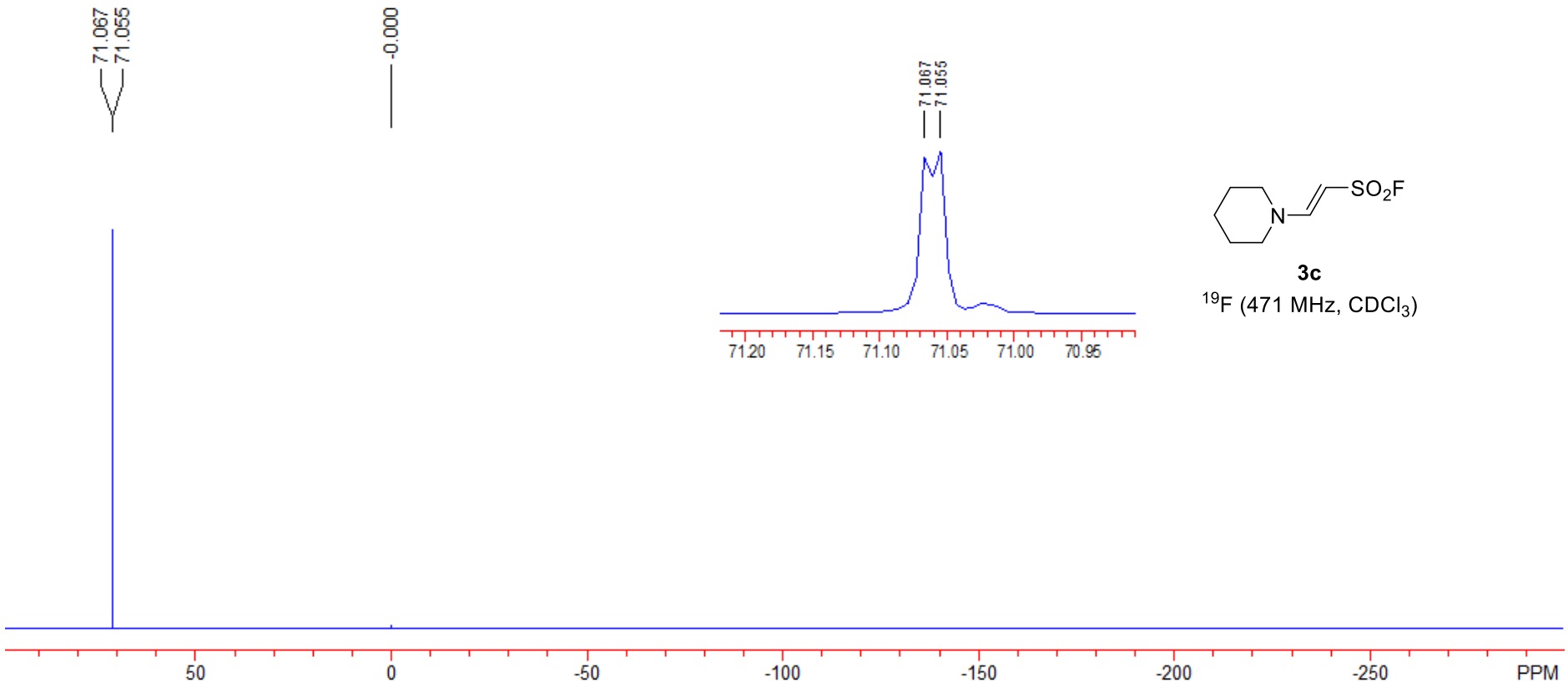


3b

^{19}F (471 MHz, $CDCl_3$)

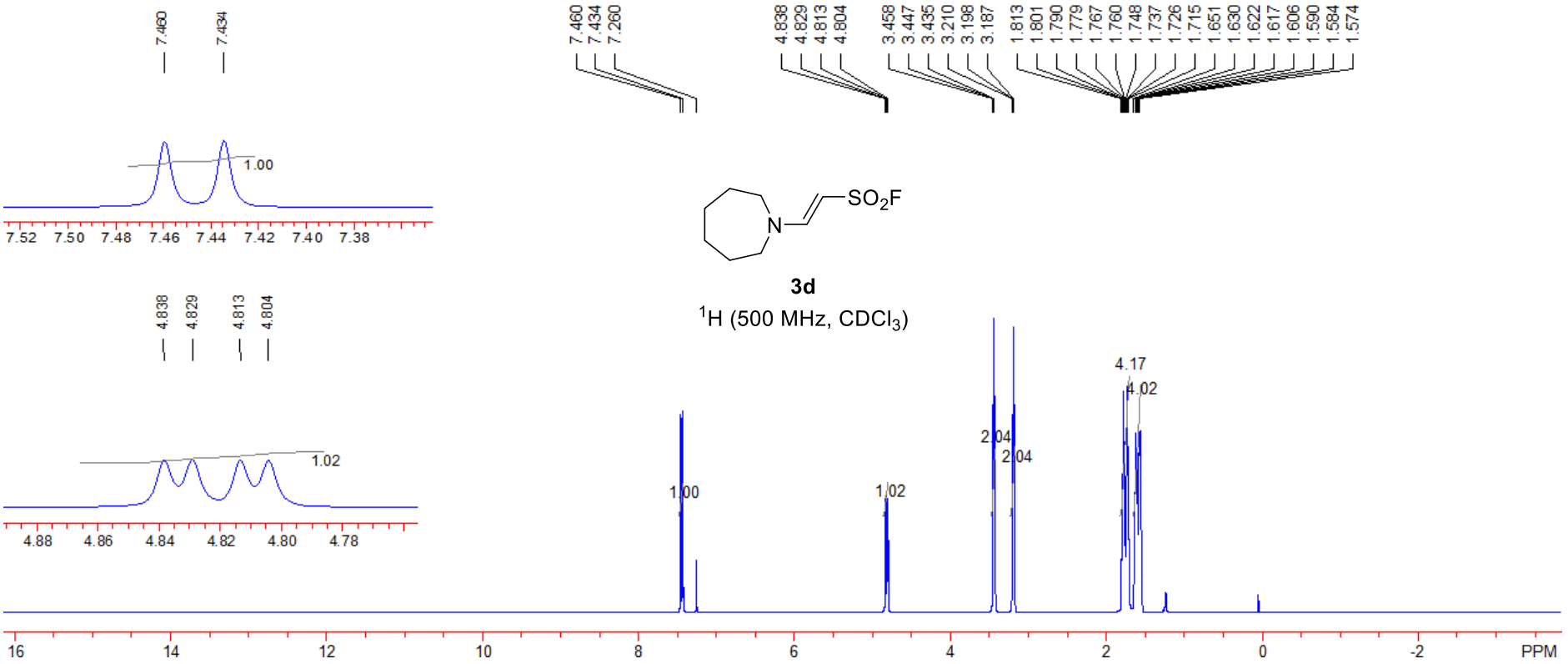

7.351
7.325
7.260
4.908
4.898
4.883
4.873
3.354
3.164
1.662
1.00
1.00
2.00
2.02
6.05
7.40
7.38
7.36
7.34
7.32
7.30
4.94
4.92
4.90
4.88
4.86
16
14
12
10
8
6
4
2
0
-2
PPM
N
SO2F
3c
1H (500 MHz, CDCl3)

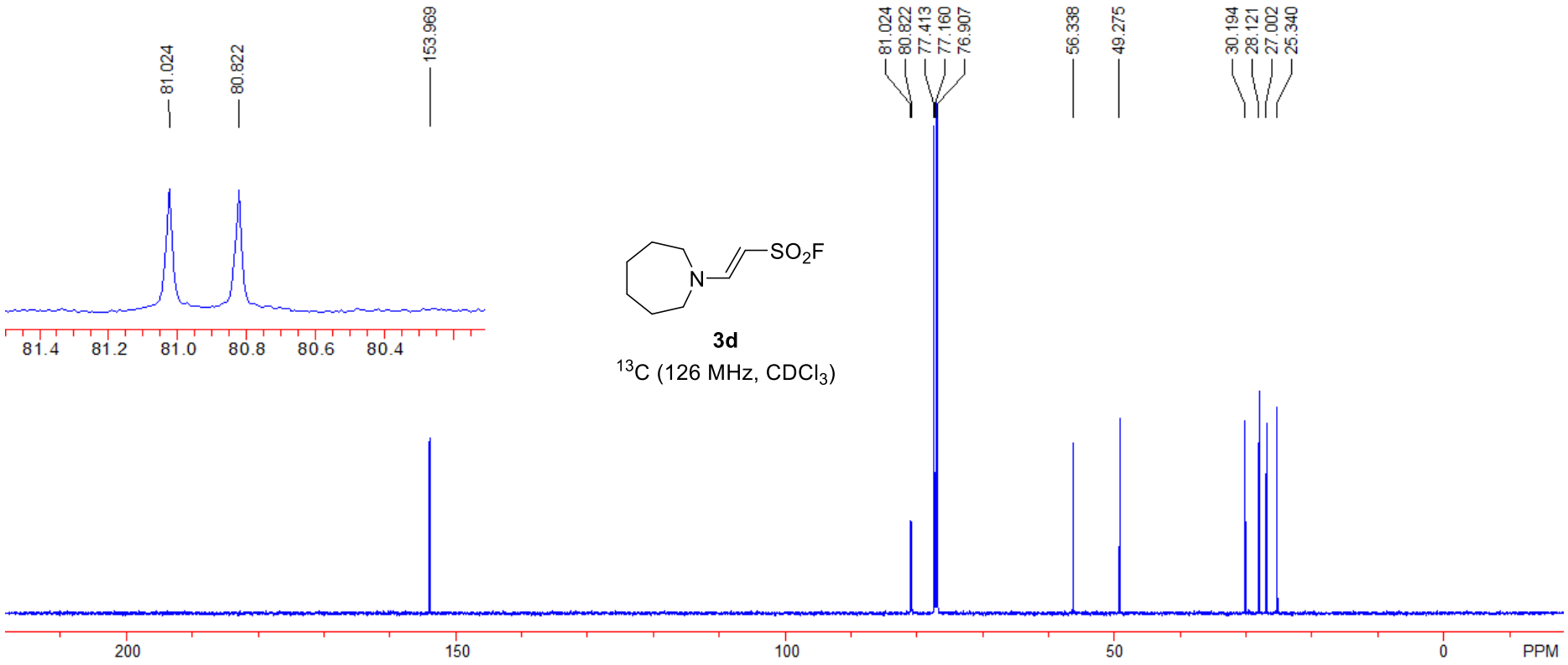

81.168
80.966
153.109
81.168
80.966
77.413
77.160
76.907
55.118
46.480
26.308
24.597
23.643
SO2F
N
3c
13C (126 MHz, CDCl3)
81.6
81.4
81.2
81.0
80.8
200
150
100
50
0
PPM

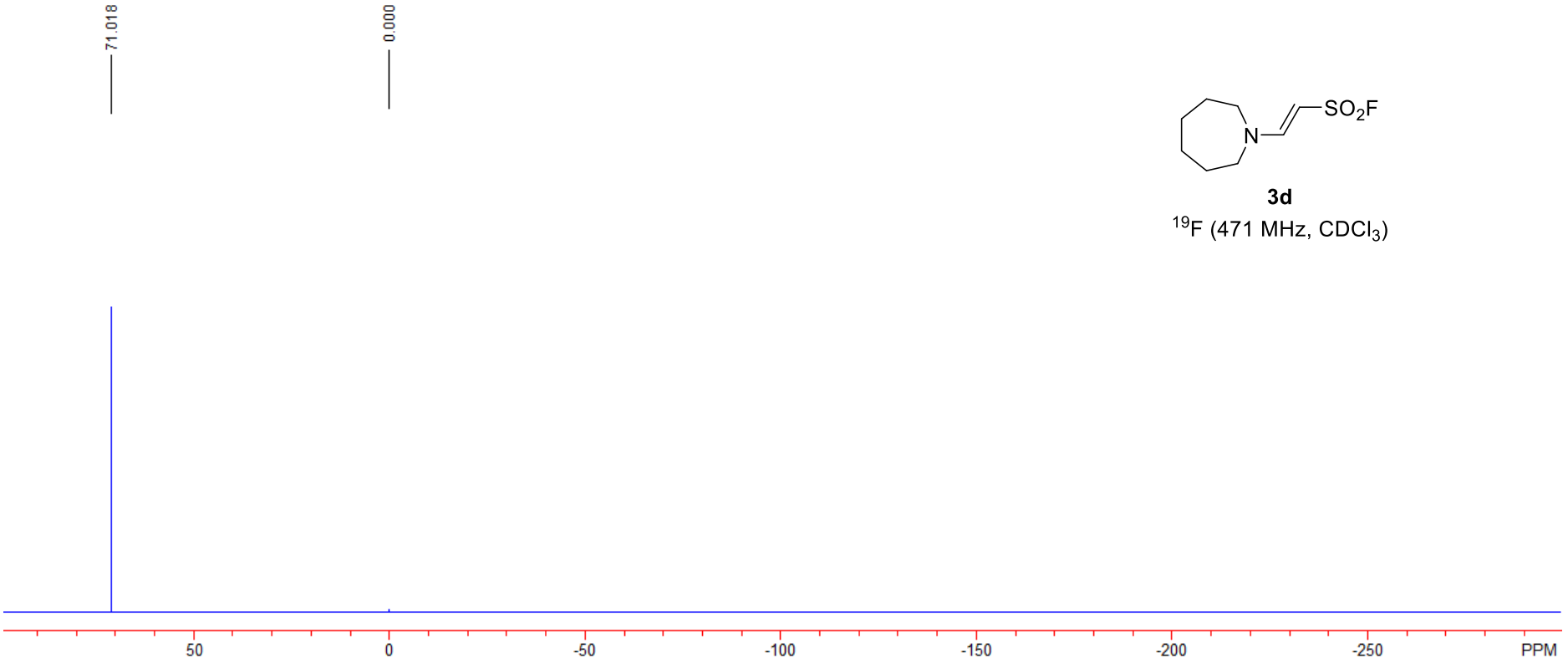


3c

^{19}F (471 MHz, $CDCl_3$)

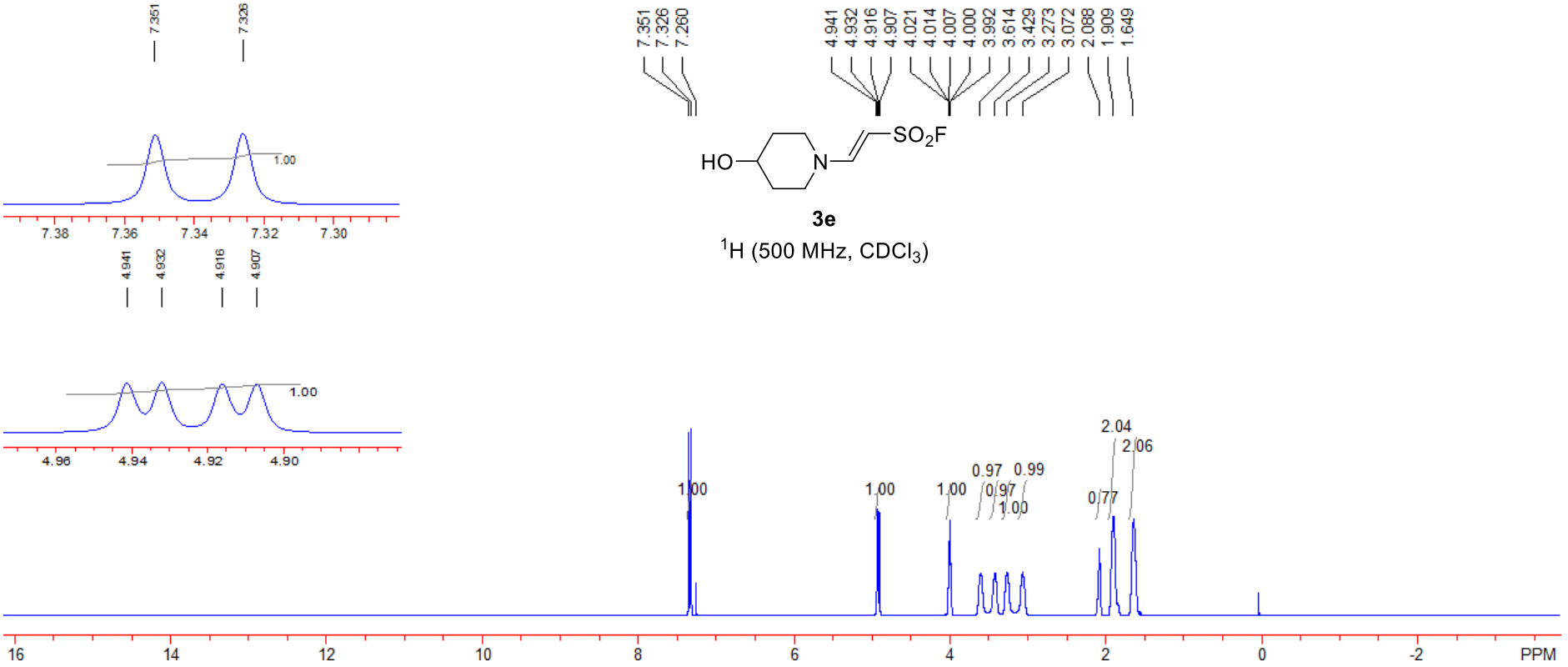

7.460
7.434
7.260
4.838
4.829
4.813
4.804
3.458
3.447
3.435
3.210
3.198
3.187
1.813
1.801
1.790
1.779
1.767
1.760
1.748
1.737
1.726
1.715
1.651
1.630
1.622
1.617
1.606
1.590
1.584
1.574
1.00
7.52 7.50 7.48 7.46 7.44 7.42 7.40 7.38
SO2F
N
3d
1H (500 MHz, CDCl3)
4.838
4.829
4.813
4.804
1.02
4.88 4.86 4.84 4.82 4.80 4.78
1.00
1.02
2.04
2.04
4.17
4.02
16 14 12 10 8 6 4 2 0 -2 PPM

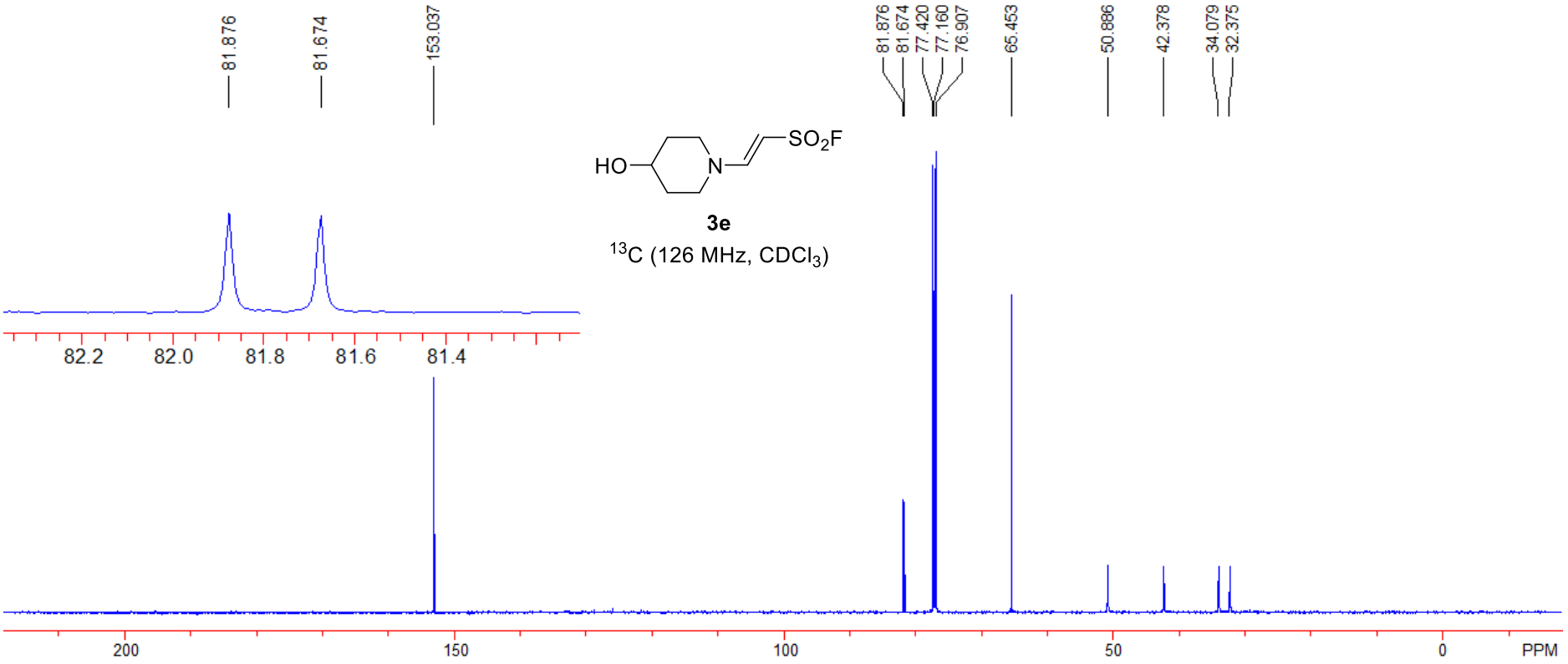

81.024
80.822
153.969
81.024
80.822
77.413
77.160
76.907
56.338
49.275
30.194
28.121
27.002
25.340
81.4
81.2
81.0
80.8
80.6
80.4
N
SO2F
3d
13C (126 MHz, CDCl3)
200
150
100
50
0
PPM

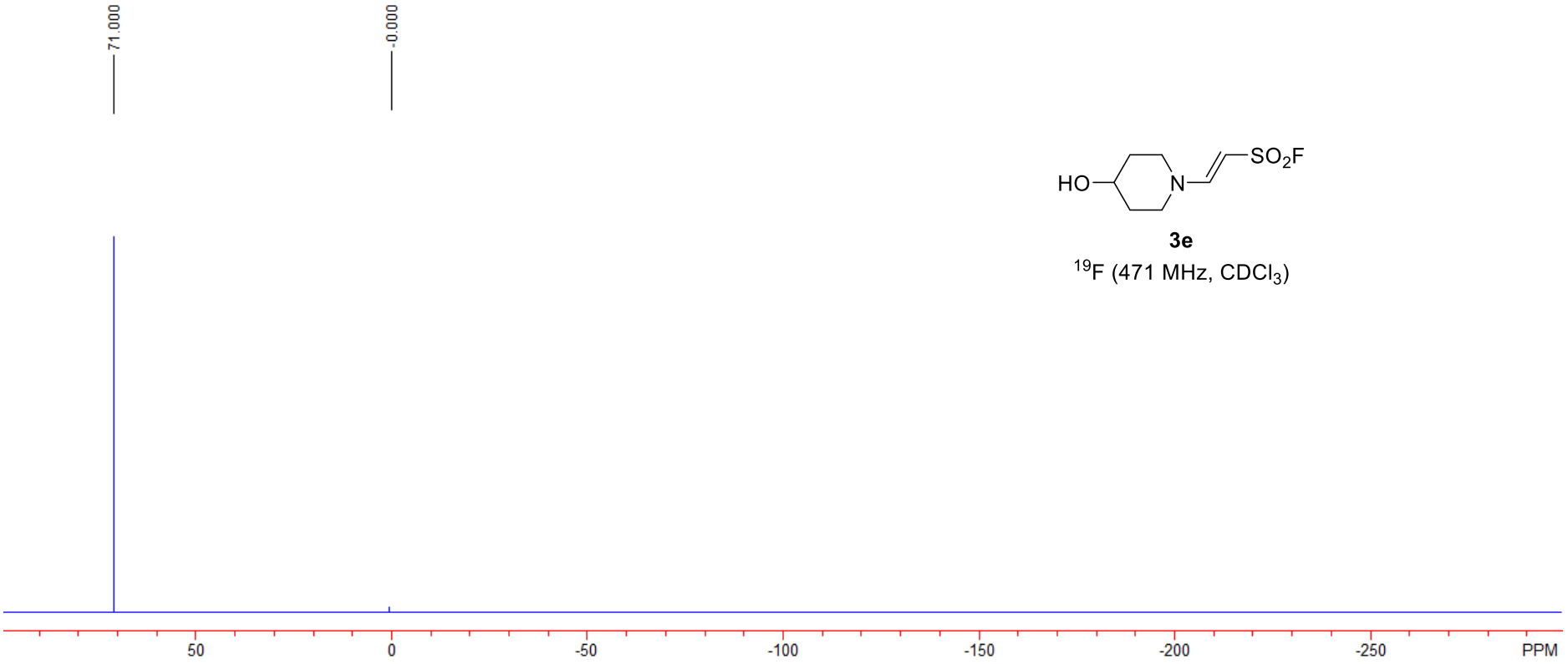


3d

^{19}F (471 MHz, $CDCl_3$)

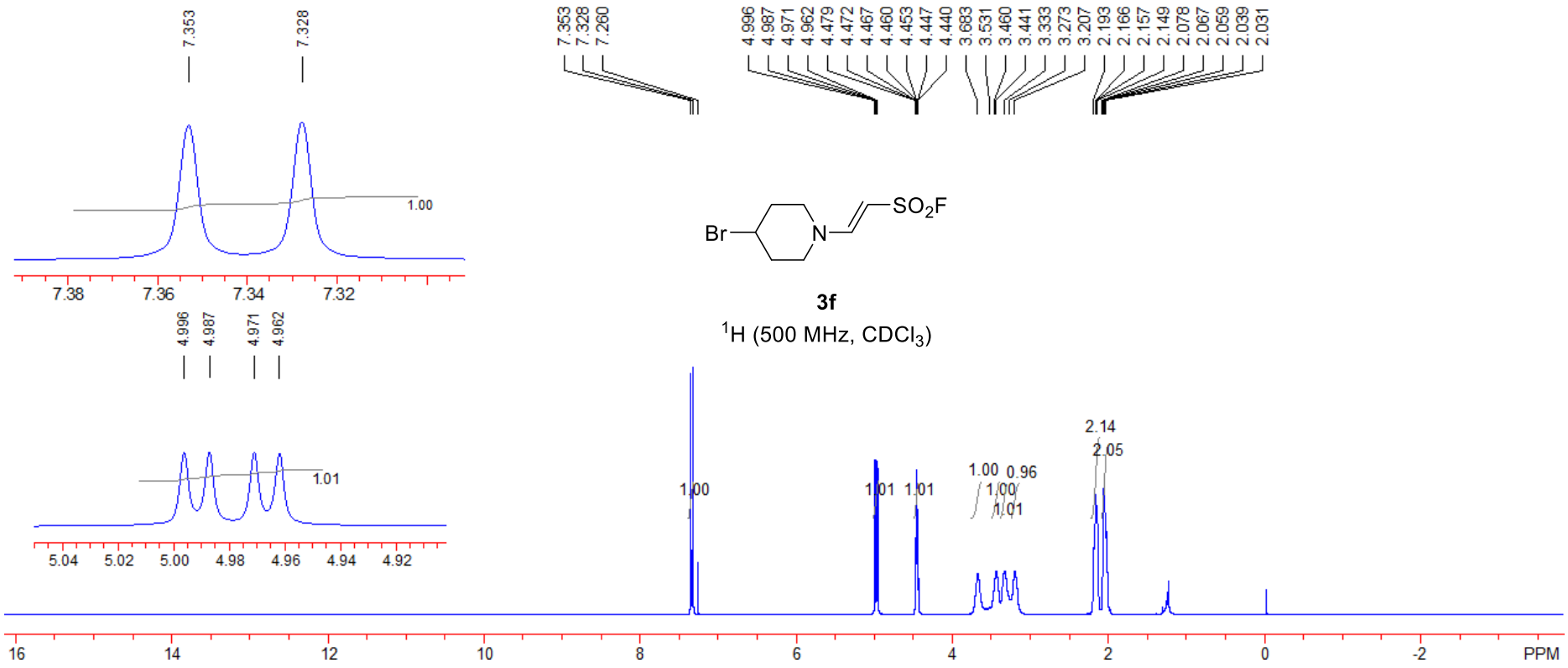

7.351
7.326
7.260
4.941
4.932
4.916
4.907
4.021
4.014
4.007
4.000
3.992
3.614
3.429
3.273
3.072
2.088
1.909
1.649
HO
N
SO2F
3e
1H (500 MHz, CDCl3)
1.00
7.38
7.36
7.34
7.32
7.30
4.96
4.94
4.92
4.90
1.00
1.00
1.00
0.97
0.97
1.00
0.99
0.77
2.04
2.06
16
14
12
10
8
6
4
2
0
-2
PPM

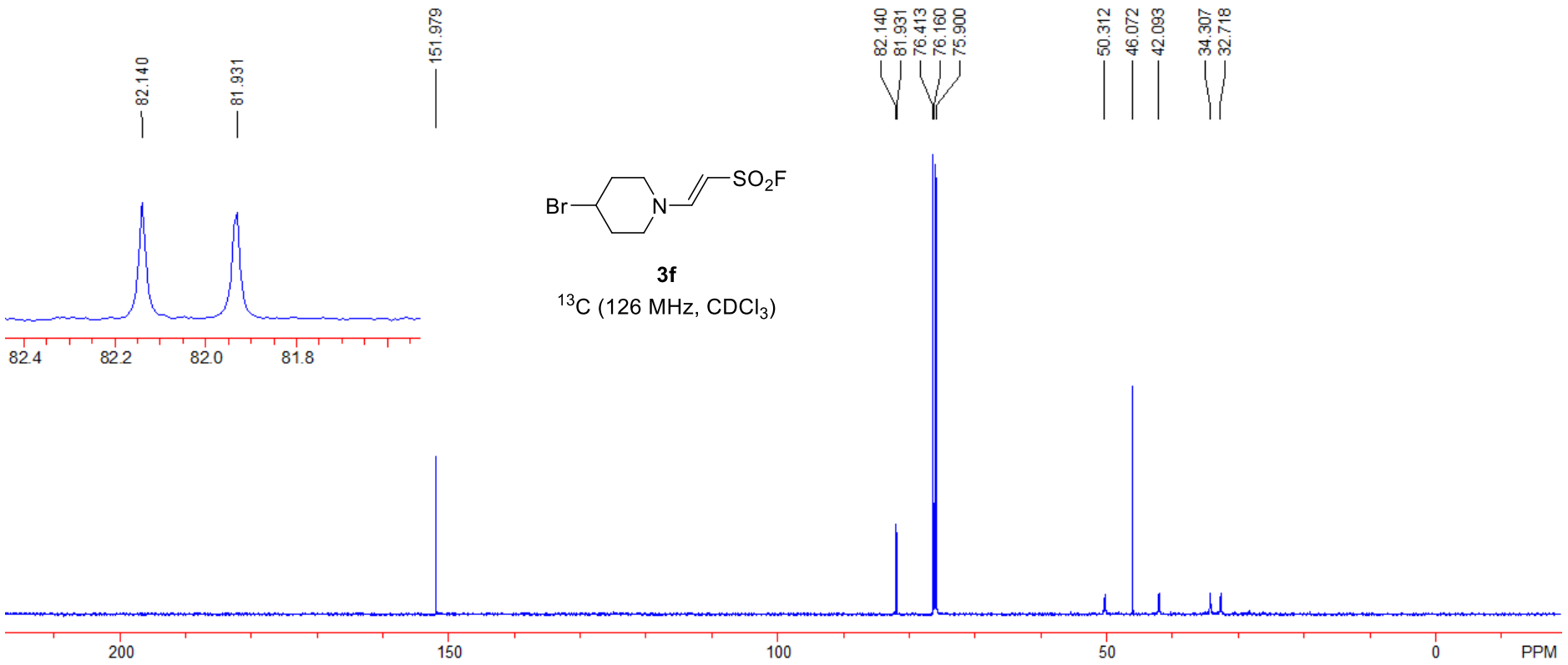

81.876
81.674
153.037
81.876
81.674
77.420
77.160
76.907
65.453
50.886
42.378
34.079
32.375
HO
N
SO2F
3e
13C (126 MHz, CDCl3)
82.2
82.0
81.8
81.6
81.4
200
150
100
50
0
PPM

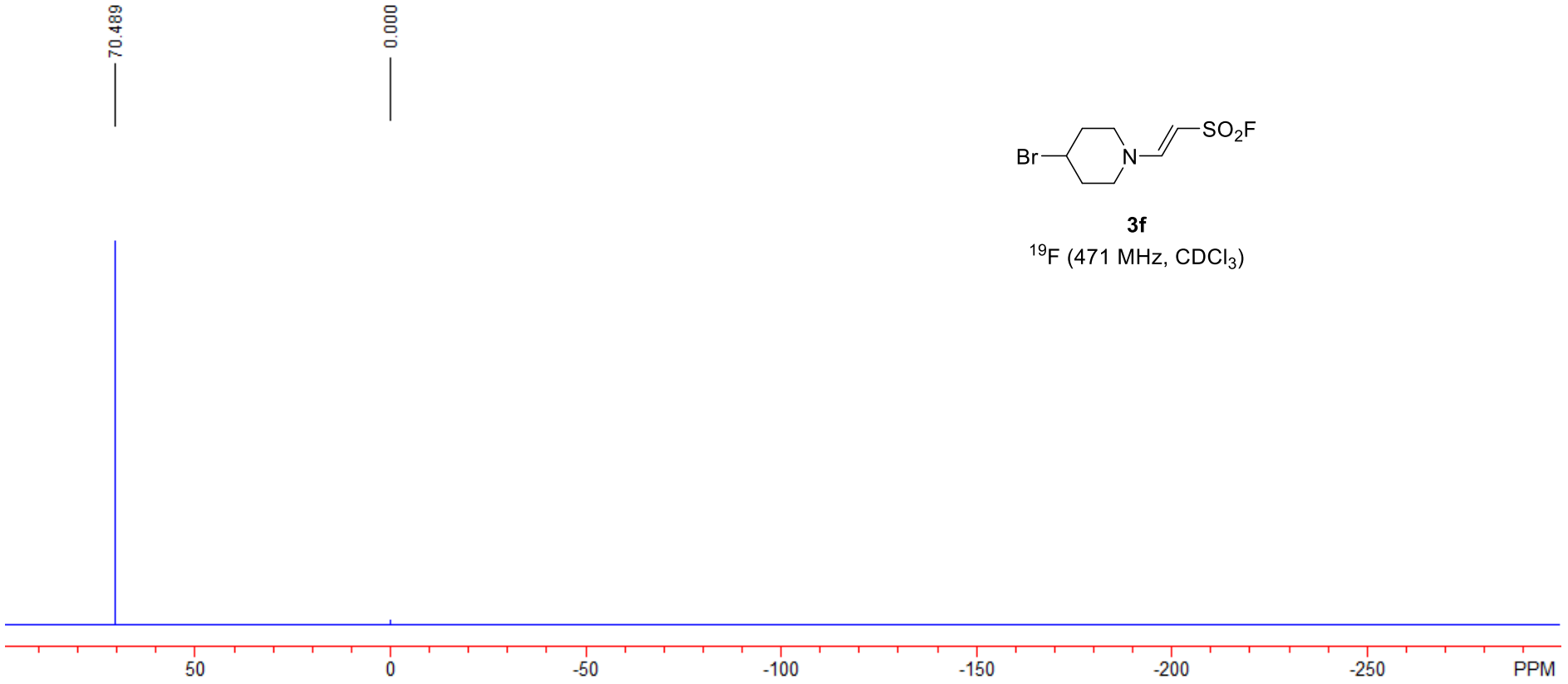


3e

^{19}F (471 MHz, $CDCl_3$)

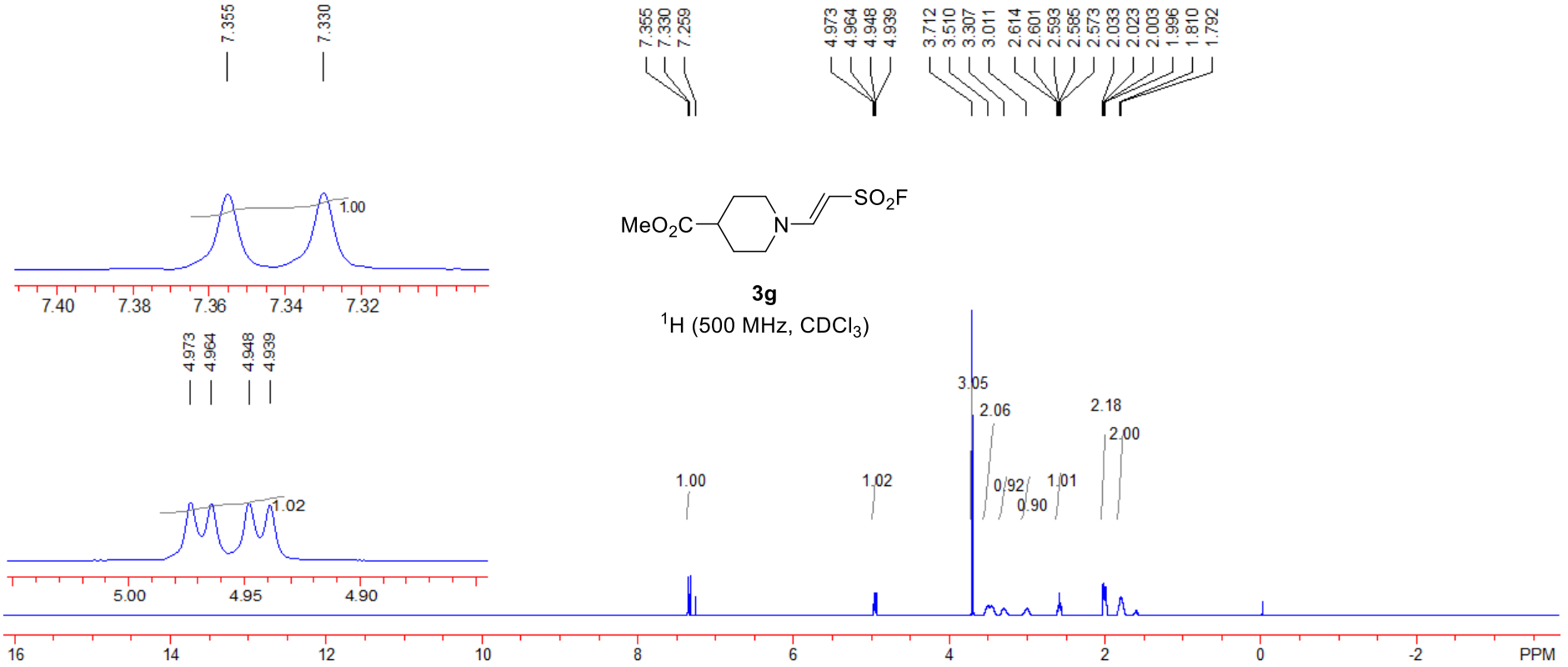

7.353
7.328
7.260
4.996
4.987
4.971
4.962
4.479
4.472
4.467
4.460
4.453
4.447
4.440
3.683
3.531
3.460
3.441
3.333
3.273
3.207
2.193
2.166
2.157
2.149
2.078
2.067
2.059
2.039
2.031
1.00
7.38
7.36
7.34
7.32
Br
N
SO2F
3f
1H (500 MHz, CDCl3)
4.996
4.987
4.971
4.962
1.01
5.04
5.02
5.00
4.98
4.96
4.94
4.92
1.00
1.01
1.01
1.00
0.96
1.00
1.01
2.14
2.05
16
14
12
10
8
6
4
2
0
-2
PPM

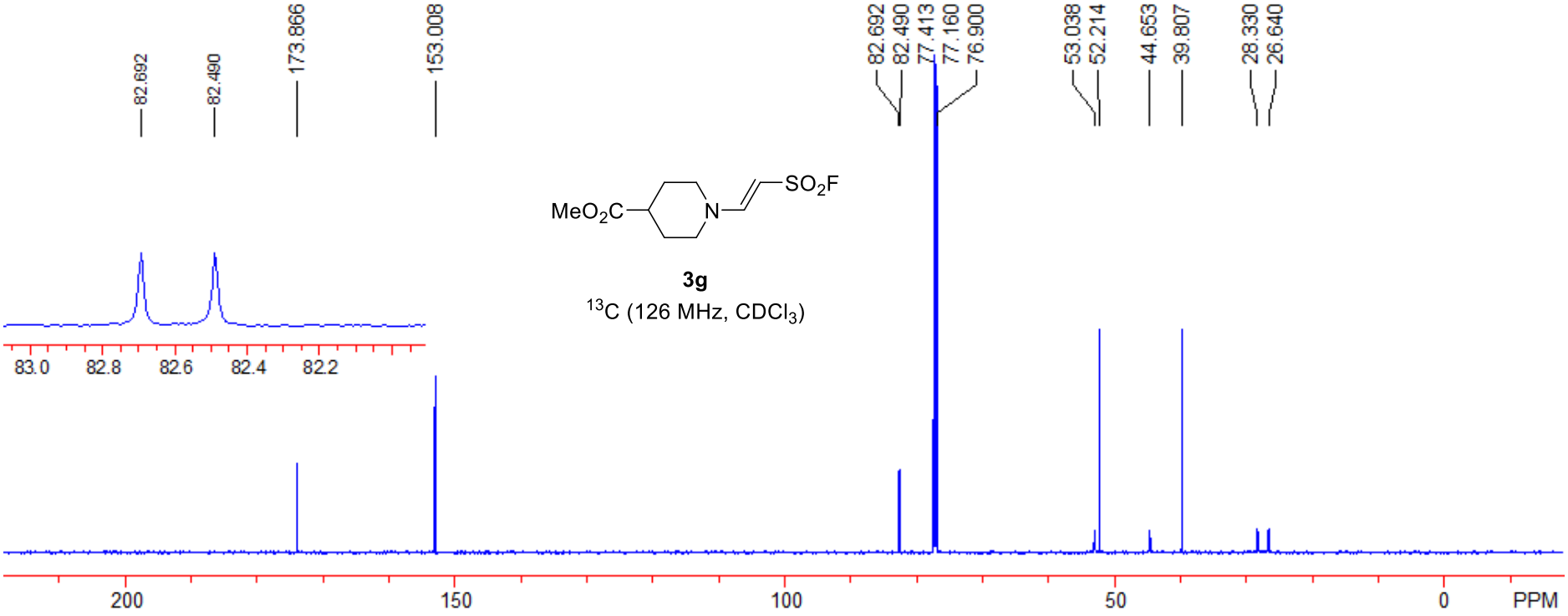

82.140
81.931
151.979
82.140
81.931
76.413
76.160
75.900
50.312
46.072
42.093
34.307
32.718
82.4
82.2
82.0
81.8
Br
N
SO2F
3f
13C (126 MHz, CDCl3)
200
150
100
50
0
PPM

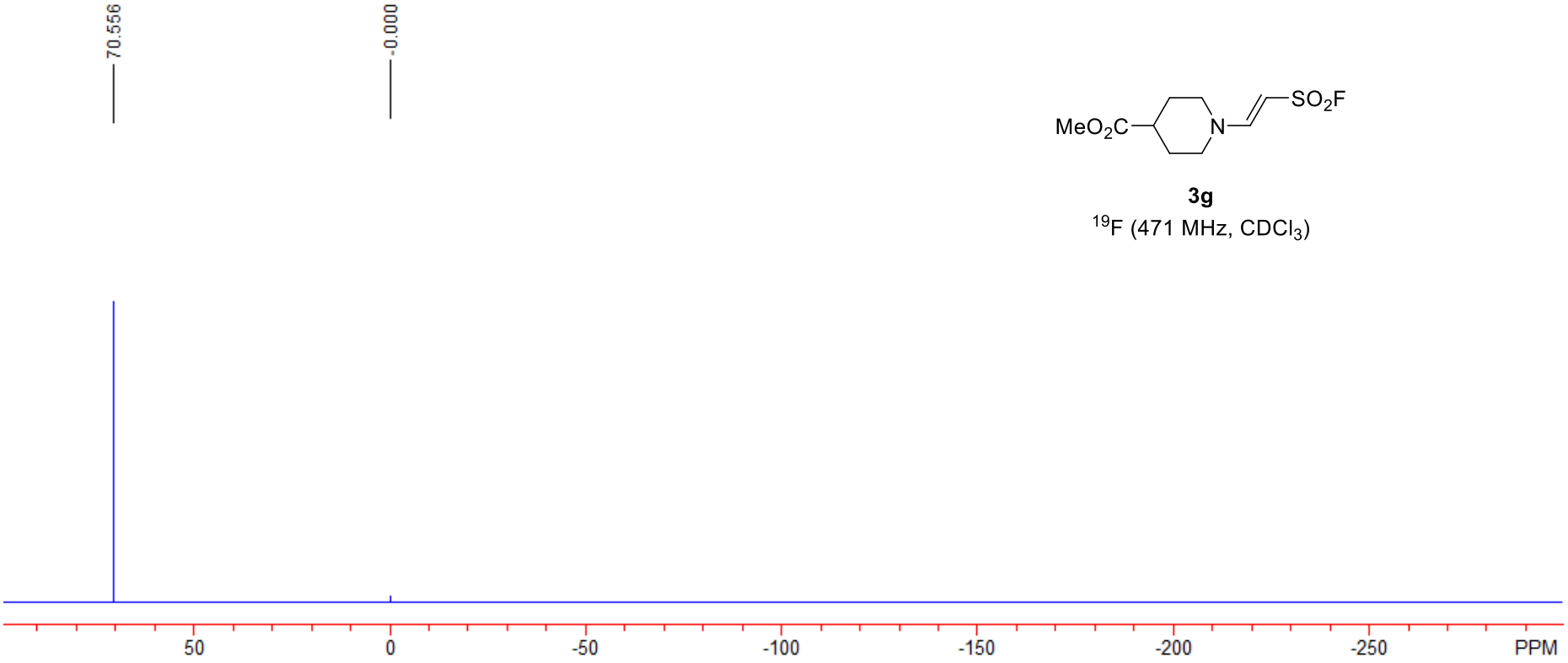


3f

^{19}F (471 MHz, $CDCl_3$)

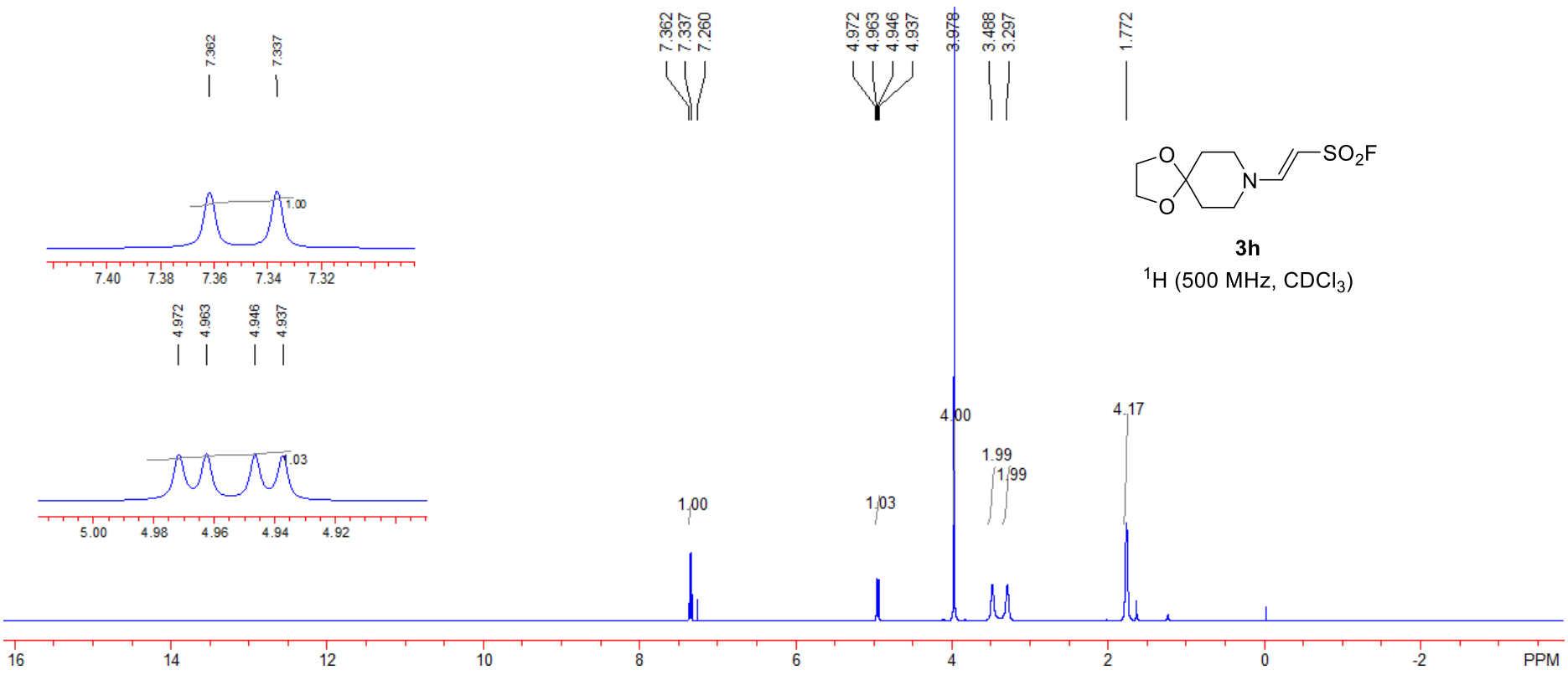

7.355
7.330
7.259
4.973
4.964
4.948
4.939
3.712
3.510
3.307
3.011
2.614
2.601
2.593
2.585
2.573
2.033
2.023
2.003
1.996
1.810
1.792
MeO2C
N
SO2F
3g
1H (500 MHz, CDCl3)
1.00
7.40
7.38
7.36
7.34
7.32
1.02
5.00
4.95
4.90
3.05
2.06
2.18
2.00
1.00
1.02
0.92
0.90
1.01
16
14
12
10
8
6
4
2
0
-2
PPM

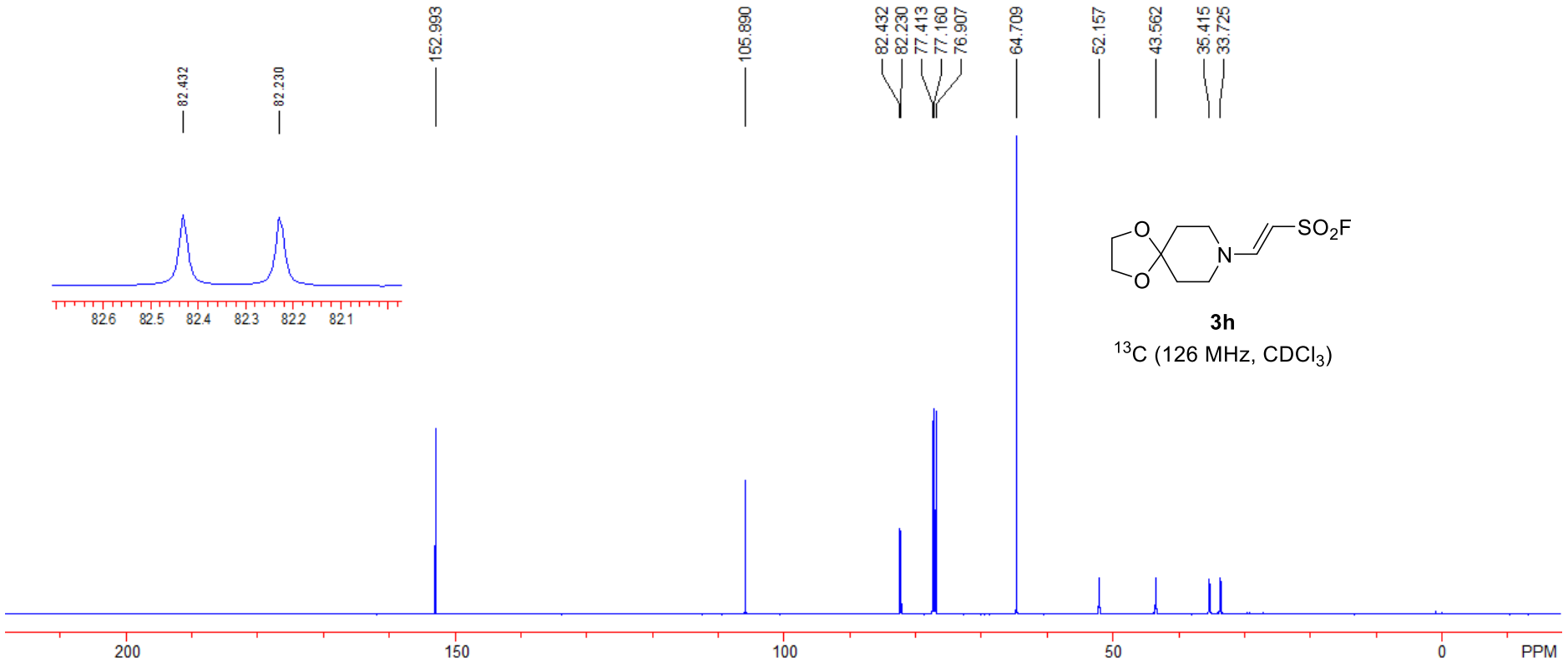

82.692
82.490
173.866
153.008
82.692
82.490
77.413
77.160
76.900
53.038
52.214
44.653
39.807
28.330
26.640
MeO2C
N
SO2F
3g
13C (126 MHz, CDCl3)
83.0
82.8
82.6
82.4
82.2
200
150
100
50
0
PPM



3g

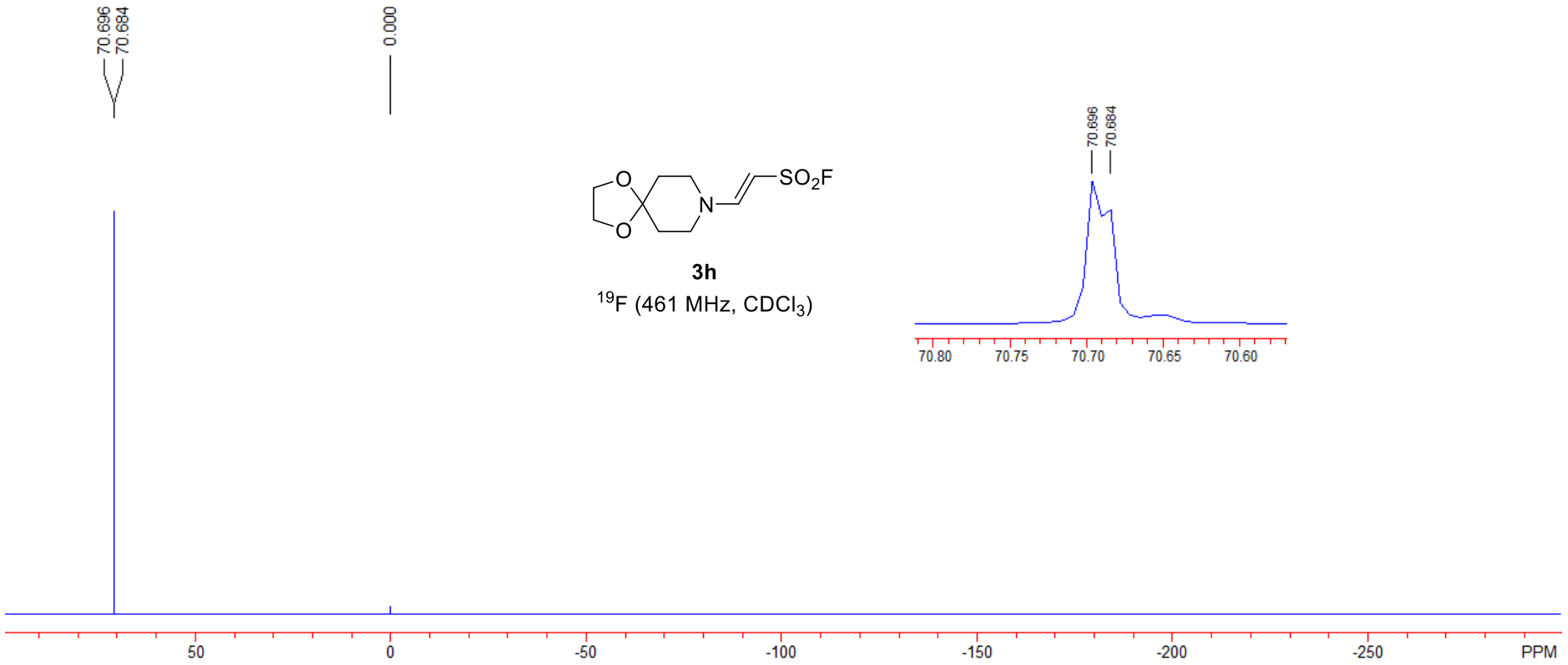
^{19}F (471 MHz, $CDCl_3$)

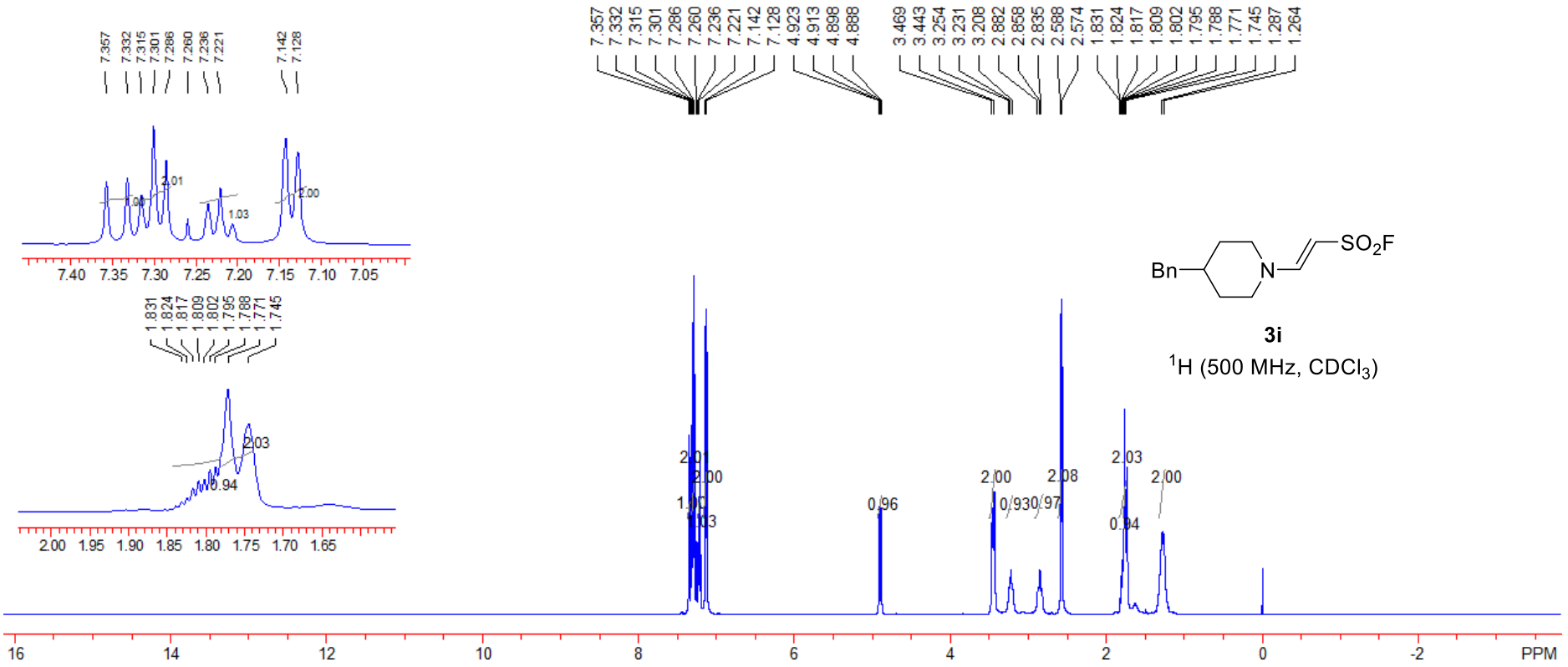

7.362
7.337
7.260
4.972
4.963
4.946
4.937
3.978
3.488
3.297
1.772
1.00
1.03
4.00
1.99
1.99
4.17
7.40
7.38
7.36
7.34
7.32
5.00
4.98
4.96
4.94
4.92
16
14
12
10
8
6
4
2
0
-2
PPM
O
O
N
SO2F
3h
1H (500 MHz, CDCl3)

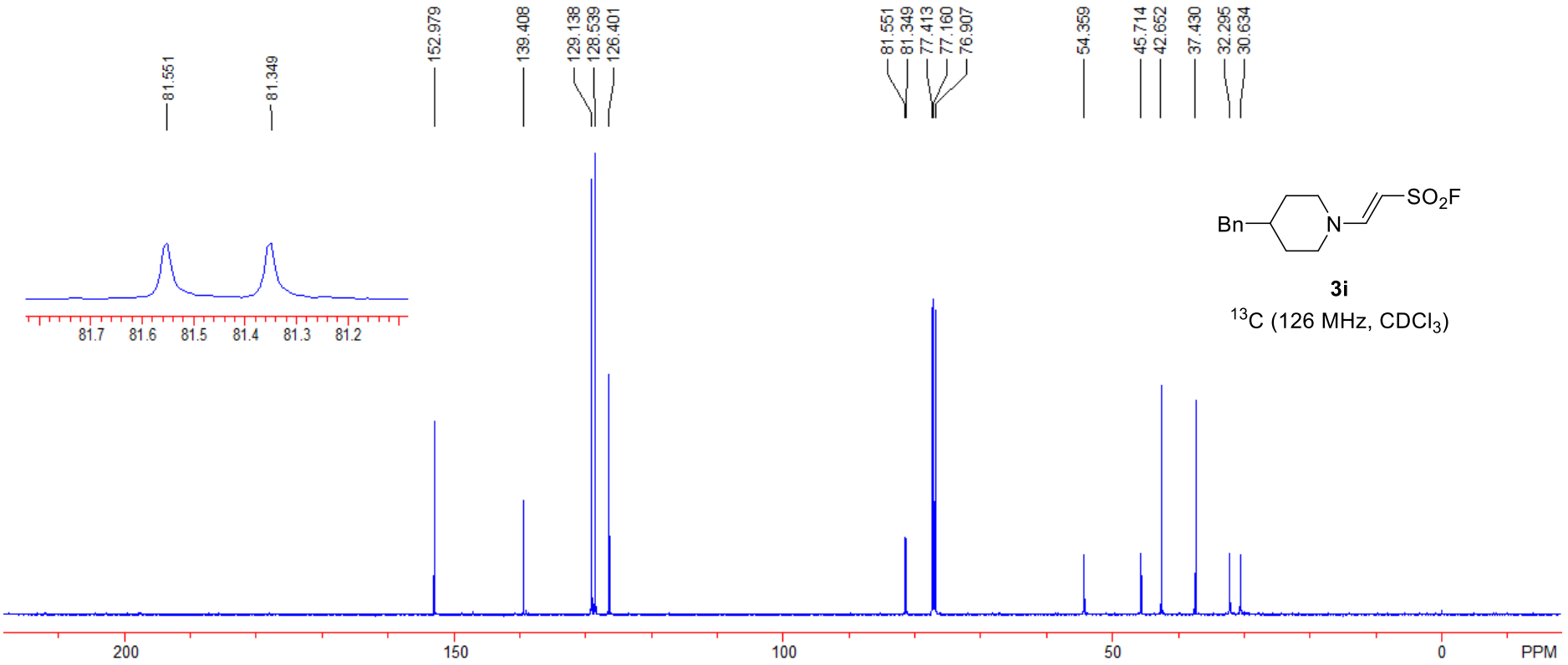


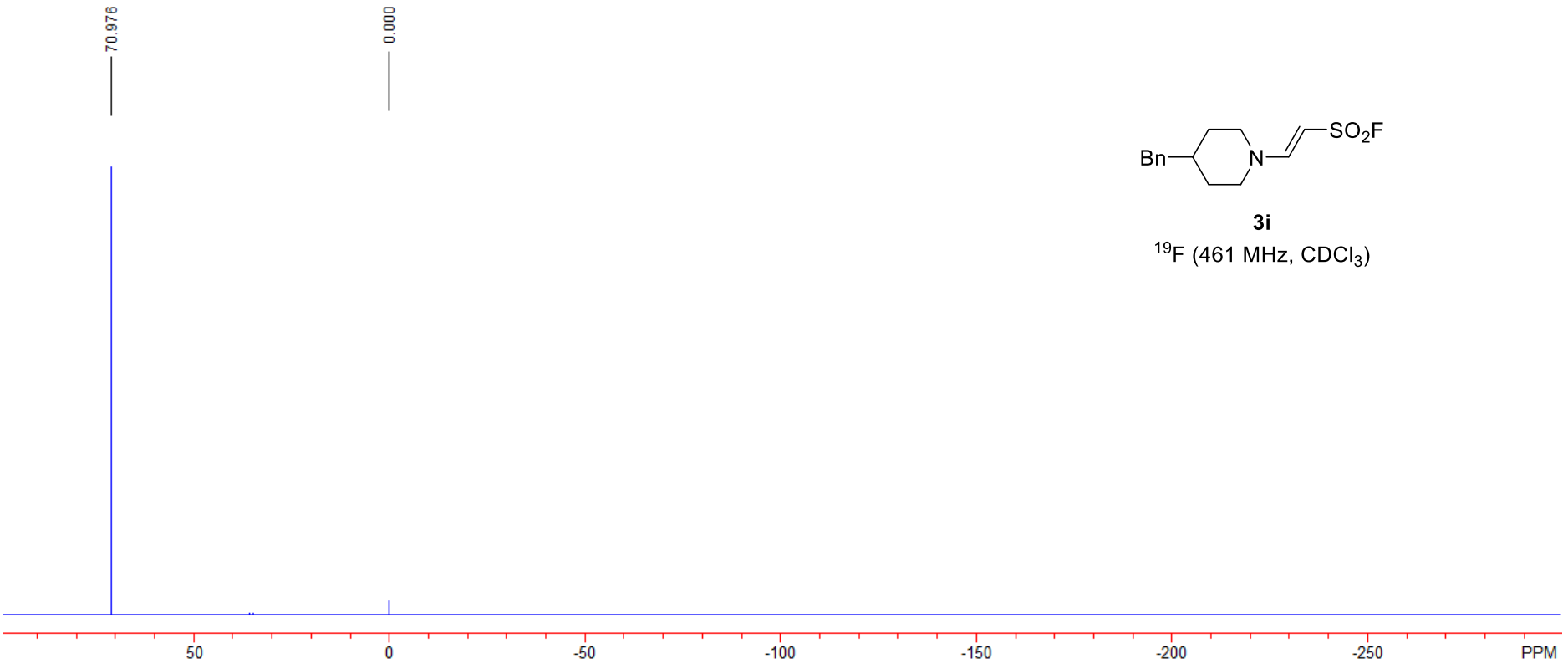
3h

^{13}C (126 MHz, $CDCl_3$)


70.696
70.684
0.000
O
O
N
SO2F
3h
19F (461 MHz, CDCl3)
70.696
70.684
70.80
70.75
70.70
70.65
70.60
50
0
-50
-100
-150
-200
-250
PPM

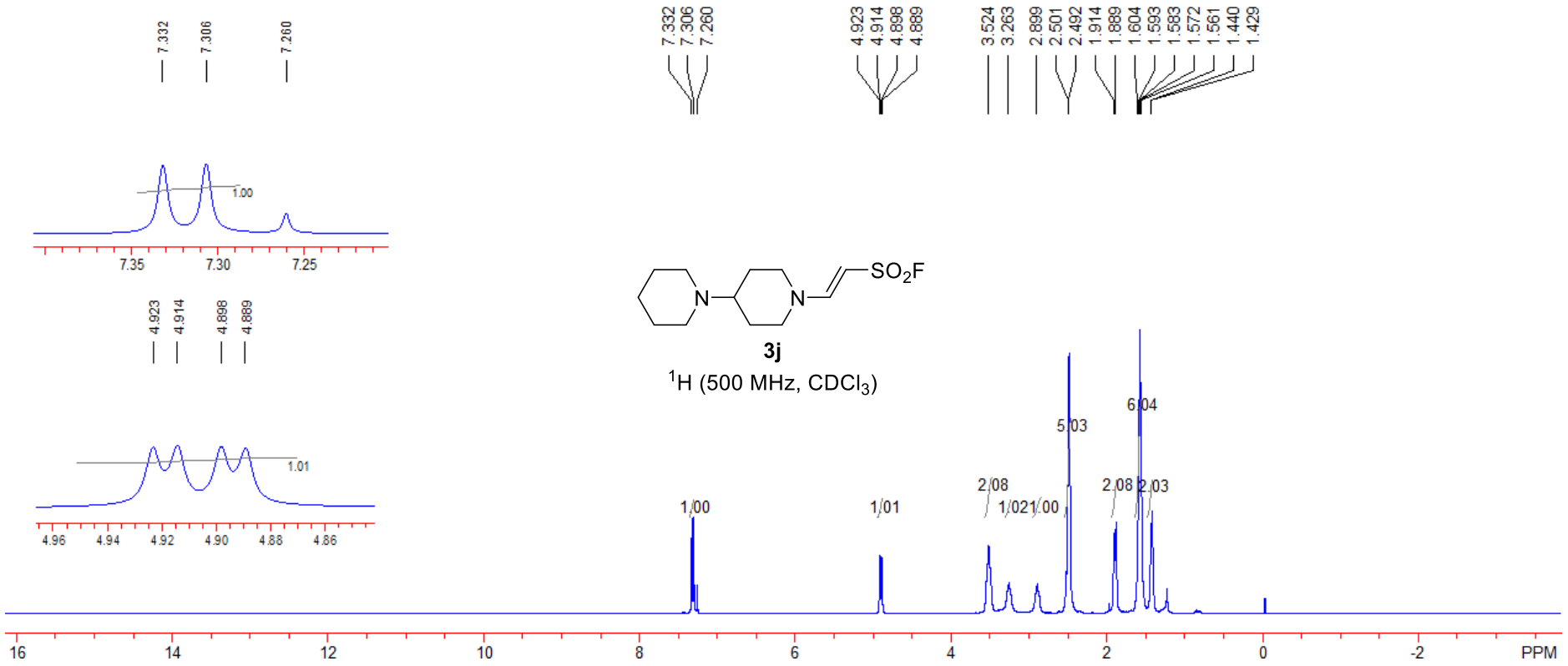

7.357
7.332
7.315
7.301
7.286
7.260
7.236
7.221
7.142
7.128
4.923
4.913
4.898
4.888
3.469
3.443
3.254
3.231
3.208
2.882
2.858
2.835
2.588
2.574
1.831
1.824
1.817
1.809
1.802
1.795
1.788
1.771
1.745
1.287
1.264
2.01
1.00
1.03
2.00
7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05
2.03
0.94
2.00 1.95 1.90 1.85 1.80 1.75 1.70 1.65
Bn
N
SO2F
3i
1H (500 MHz, CDCl3)
2.00
2.00
1.00
1.03
0.96
2.00
0.93
0.97
2.08
2.03
0.94
2.00
16 14 12 10 8 6 4 2 0 -2 PPM

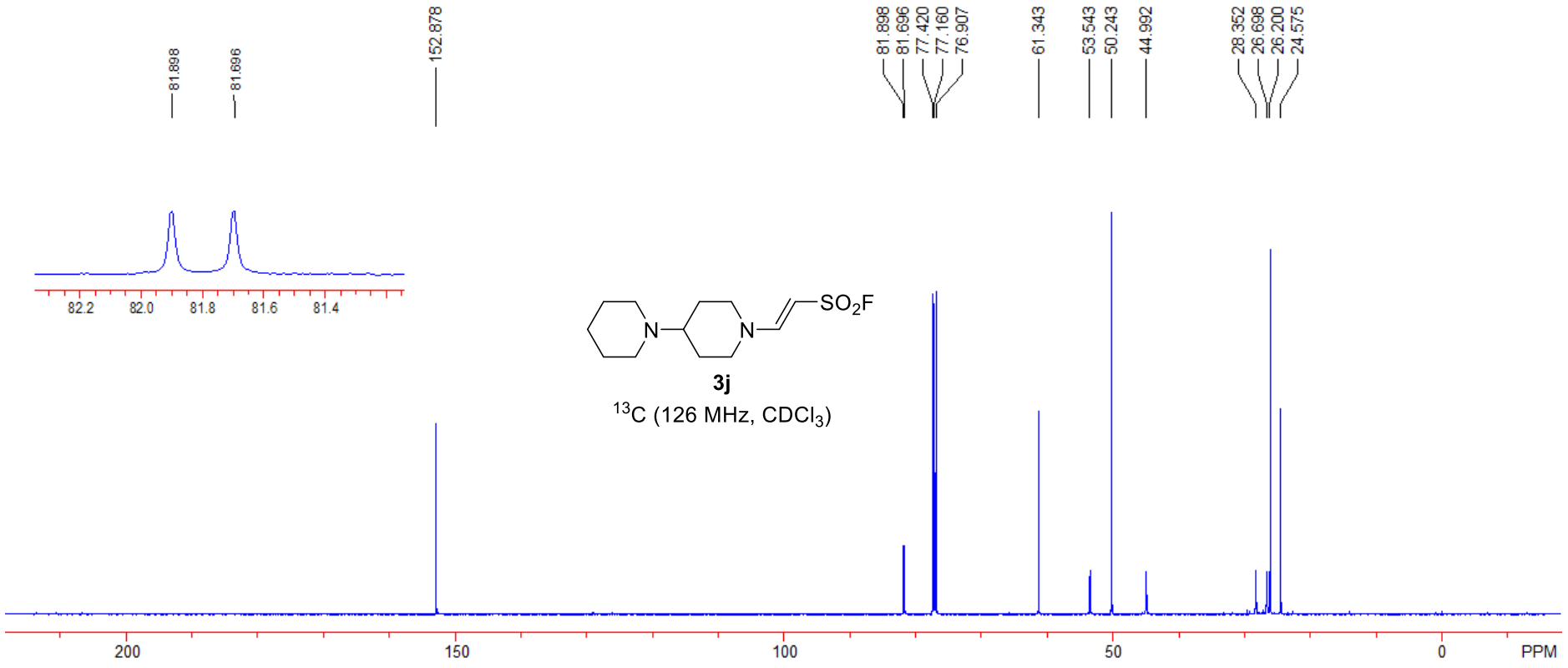

81.551
81.349
152.979
139.408
129.138
128.539
126.401
81.551
81.349
77.413
77.160
76.907
54.359
45.714
42.652
37.430
32.295
30.634
81.7
81.6
81.5
81.4
81.3
81.2
Bn
N
SO2F
3i
13C (126 MHz, CDCl3)
200
150
100
50
0
PPM



3i

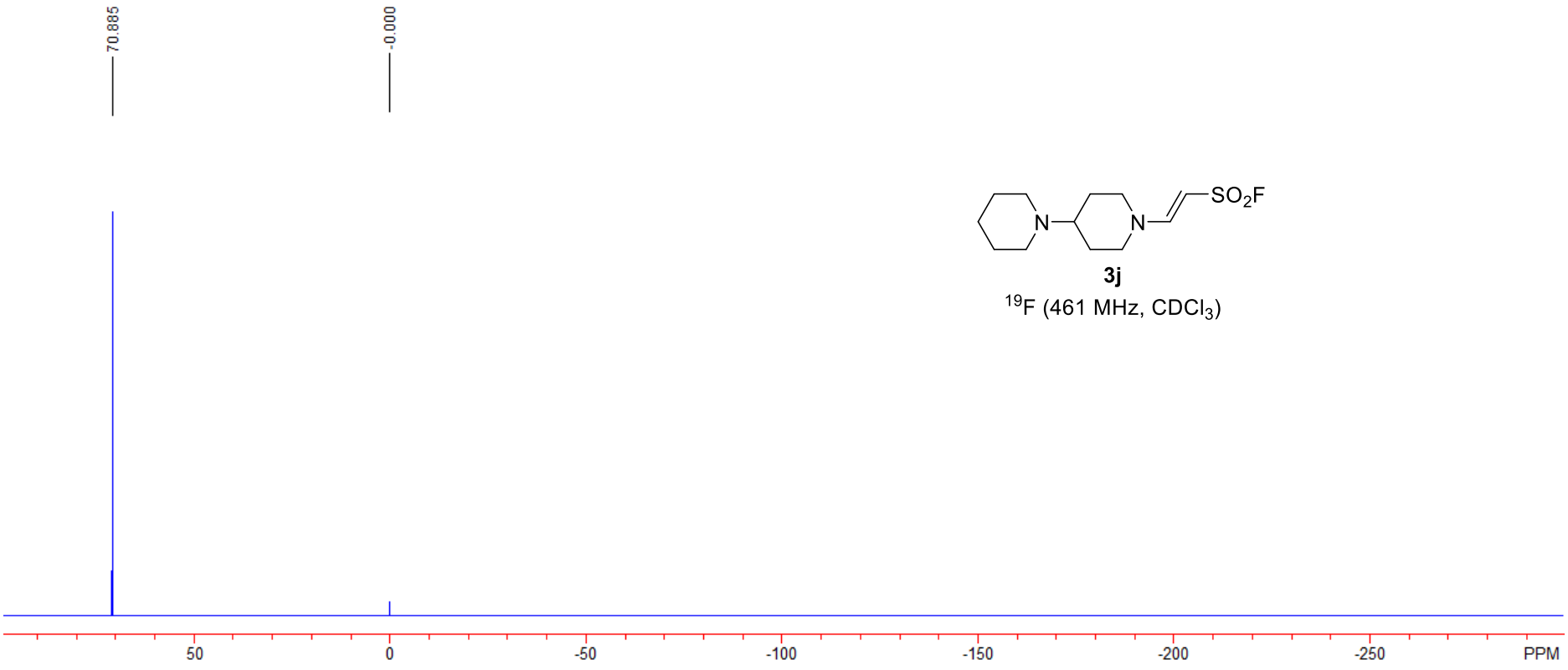
^{19}F (461 MHz, $CDCl_3$)


7.332
7.306
7.260
4.923
4.914
4.898
4.889
3.524
3.263
2.899
2.501
2.492
1.914
1.889
1.604
1.593
1.583
1.572
1.561
1.440
1.429
1.00
7.35
7.30
7.25
1.01
4.96
4.94
4.92
4.90
4.88
4.86
N
N
SO2F
3j
1H (500 MHz, CDCl3)
1.00
1.01
2.08
1.02
1.00
5.03
2.08
6.04
2.03
16
14
12
10
8
6
4
2
0
-2
PPM



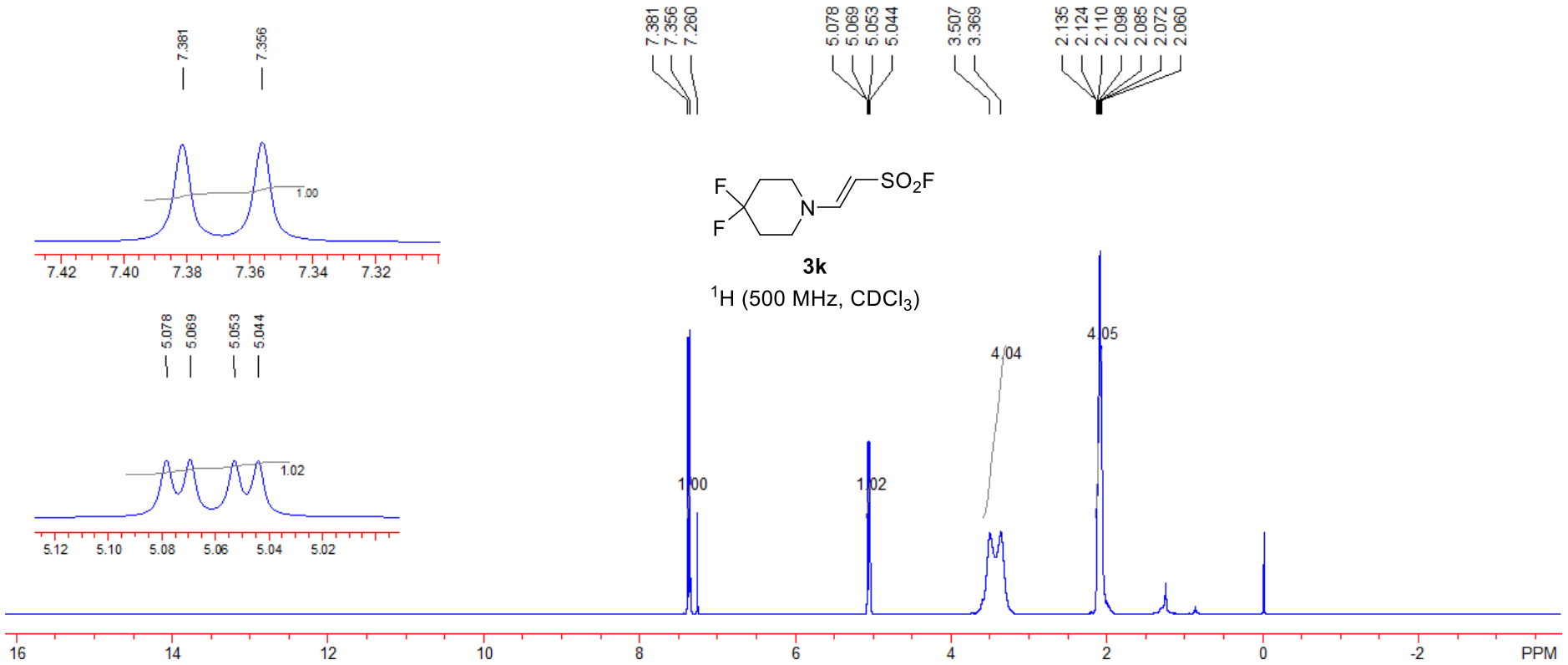
3j

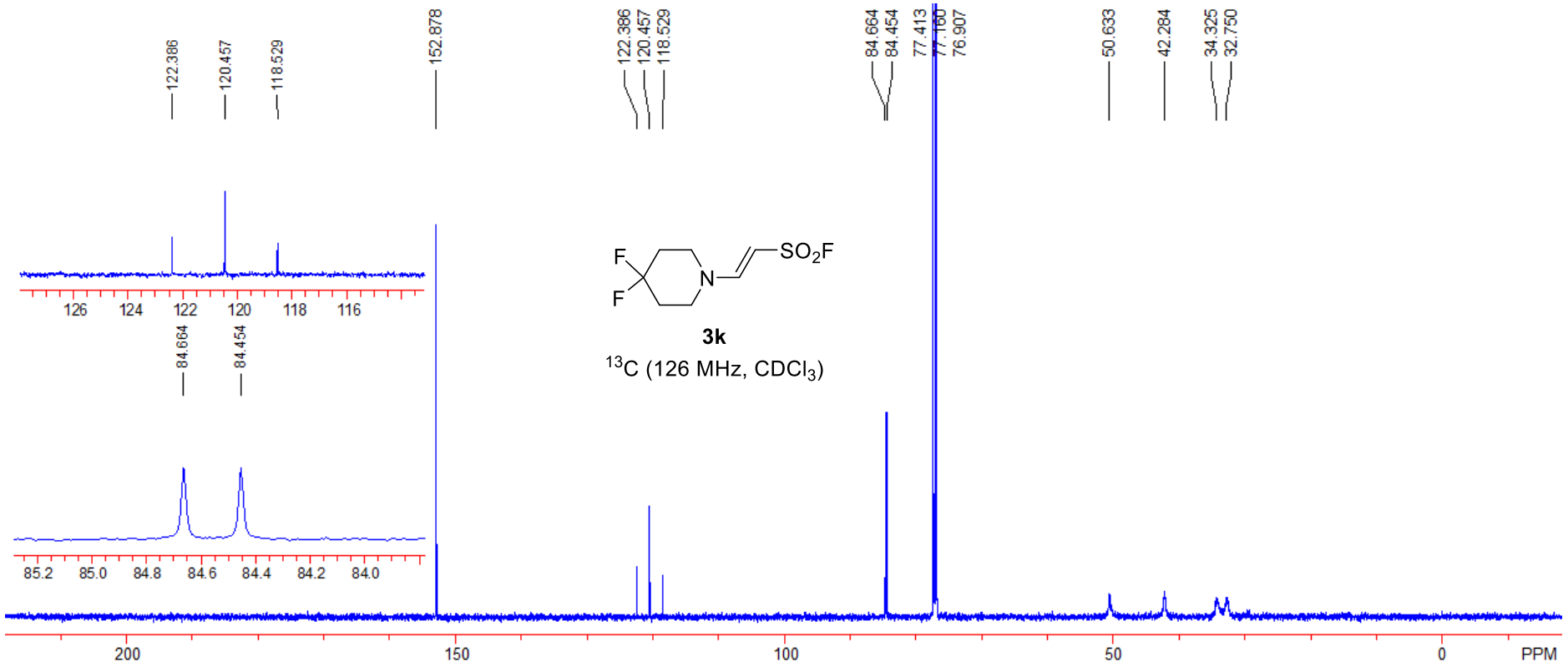
^{13}C (126 MHz, $CDCl_3$)



3j

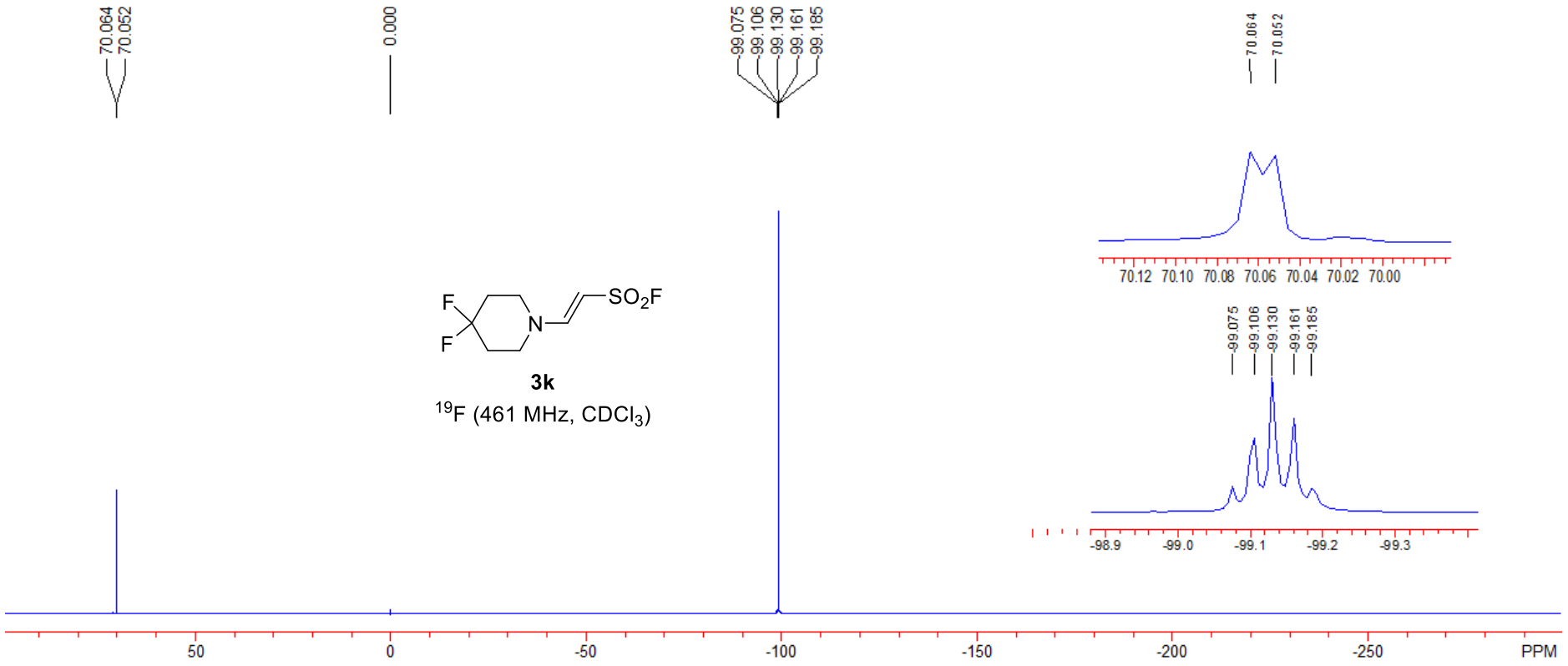
^{19}F (461 MHz, $CDCl_3$)

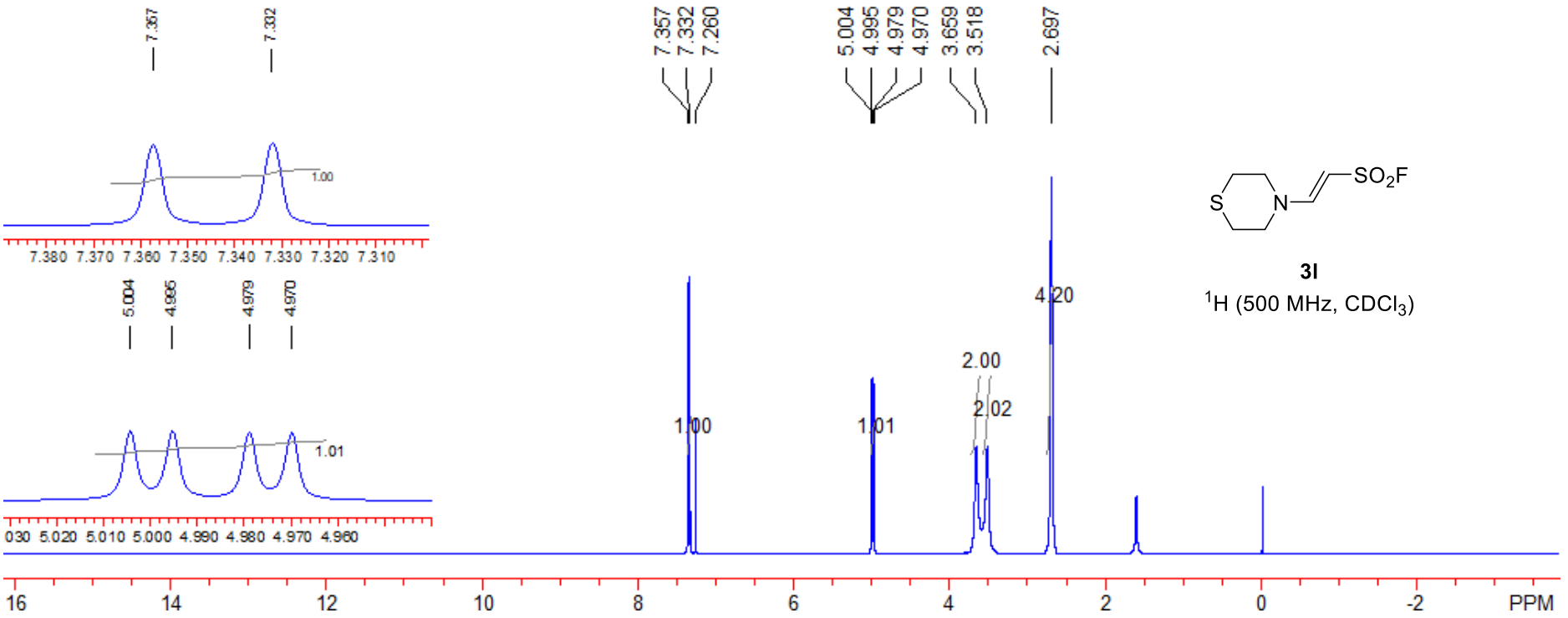

7.381
7.356
7.260
5.078
5.069
5.053
5.044
3.507
3.369
2.135
2.124
2.110
2.098
2.085
2.072
2.060
F
F
N
SO2F
3k
1H (500 MHz, CDCl3)
1.00
1.02
4.04
4.05
PPM

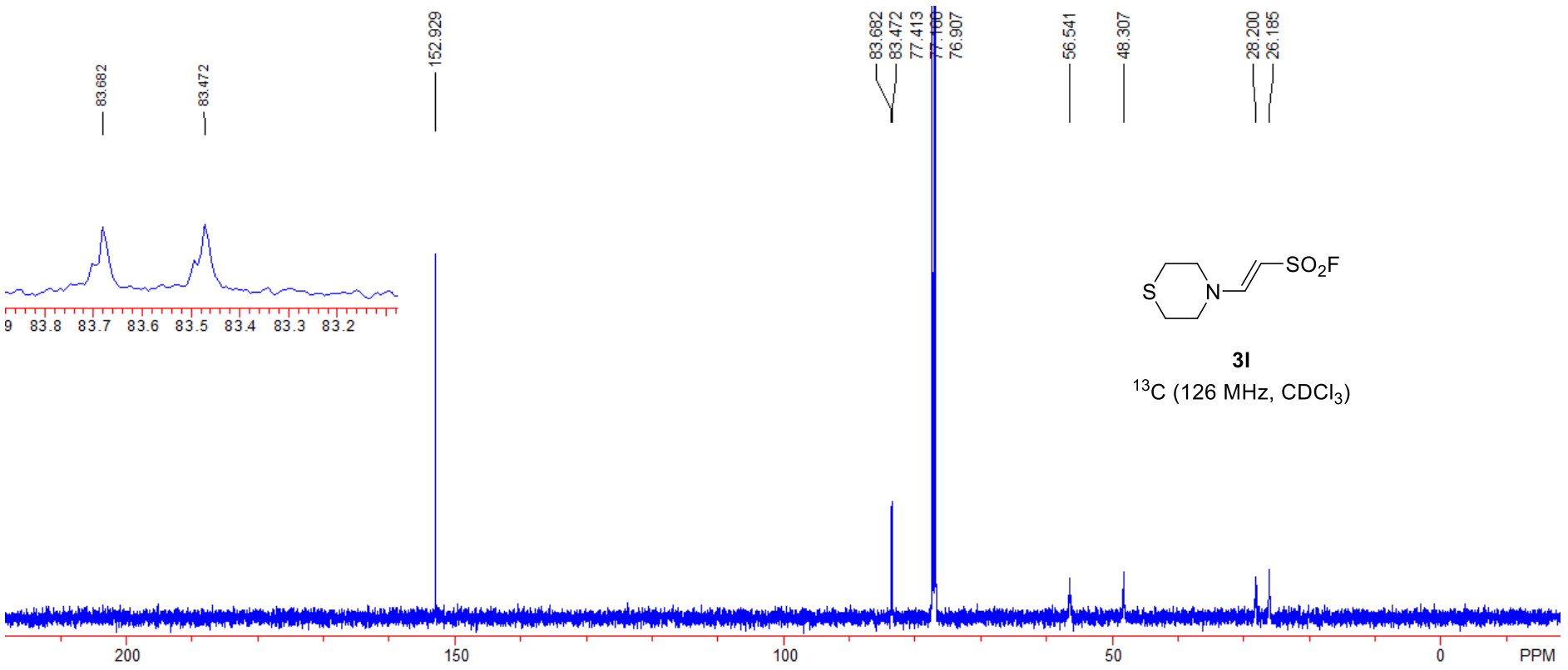


3k

^{13}C (126 MHz, $CDCl_3$)

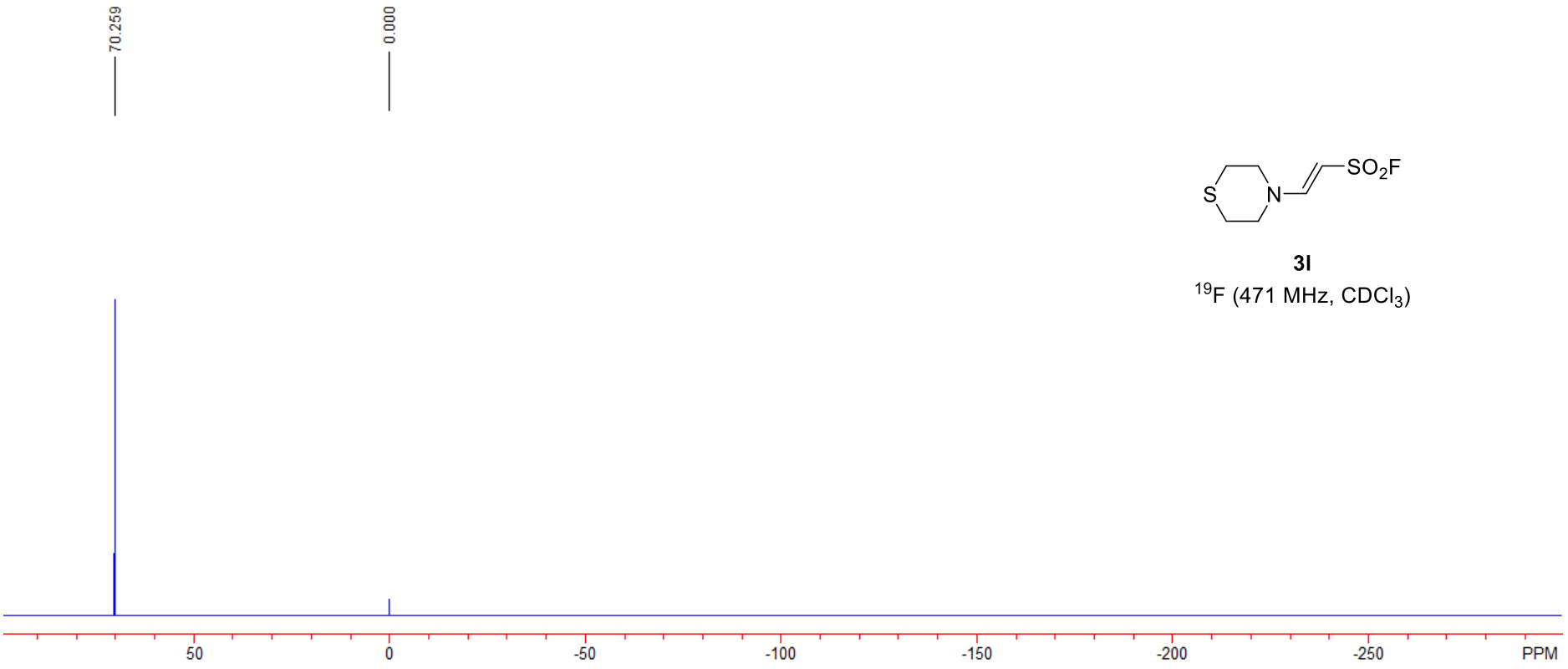

70.064
70.052
0.000
-99.075
-99.106
-99.130
-99.161
-99.185
F
F
N
SO2F
3k
19F (461 MHz, CDCl3)
70.12 70.10 70.08 70.06 70.04 70.02 70.00
-98.9 -99.0 -99.1 -99.2 -99.3
50 0 -50 -100 -150 -200 -250 PPM


7.357
7.332
7.260
5.004
4.995
4.979
4.970
3.659
3.518
2.697
1.00
1.01
2.00
2.02
4.20
SO2F
S
N
3l
1H (500 MHz, CDCl3)
PPM



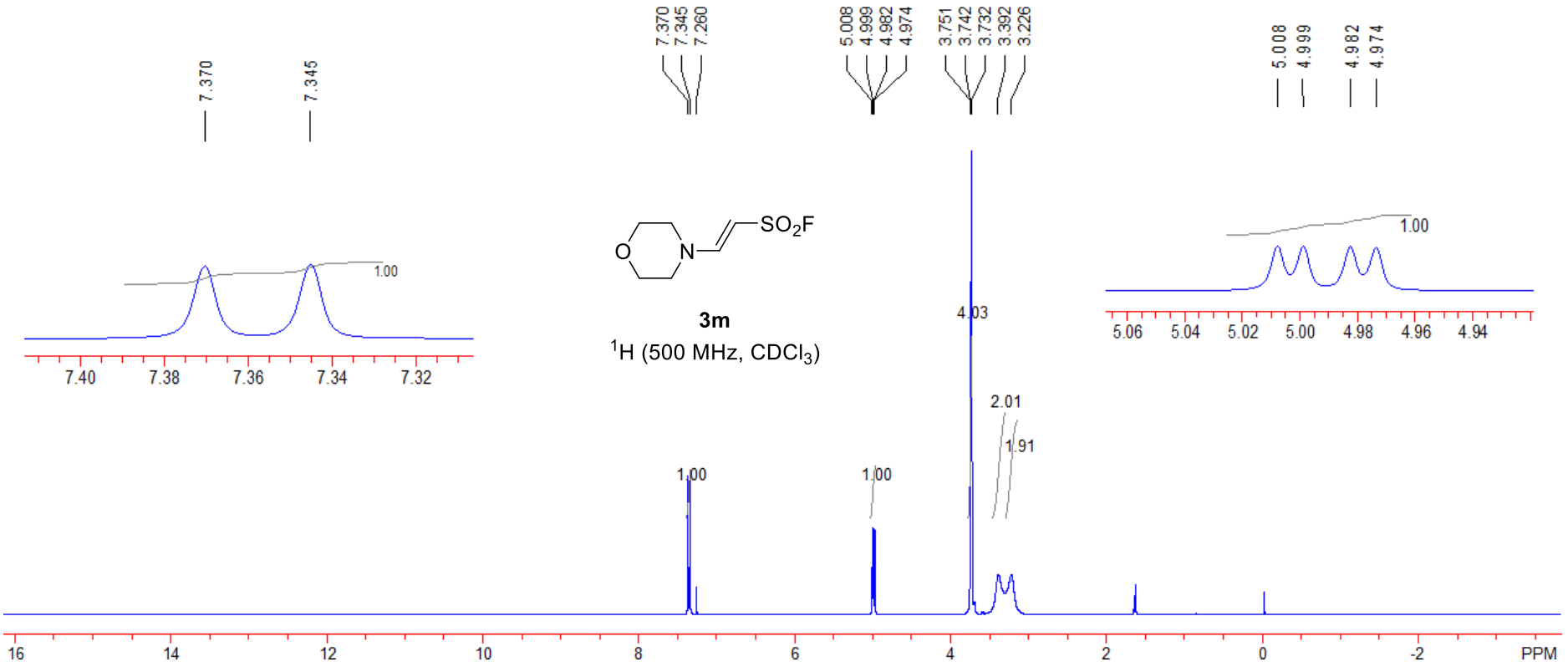
3l

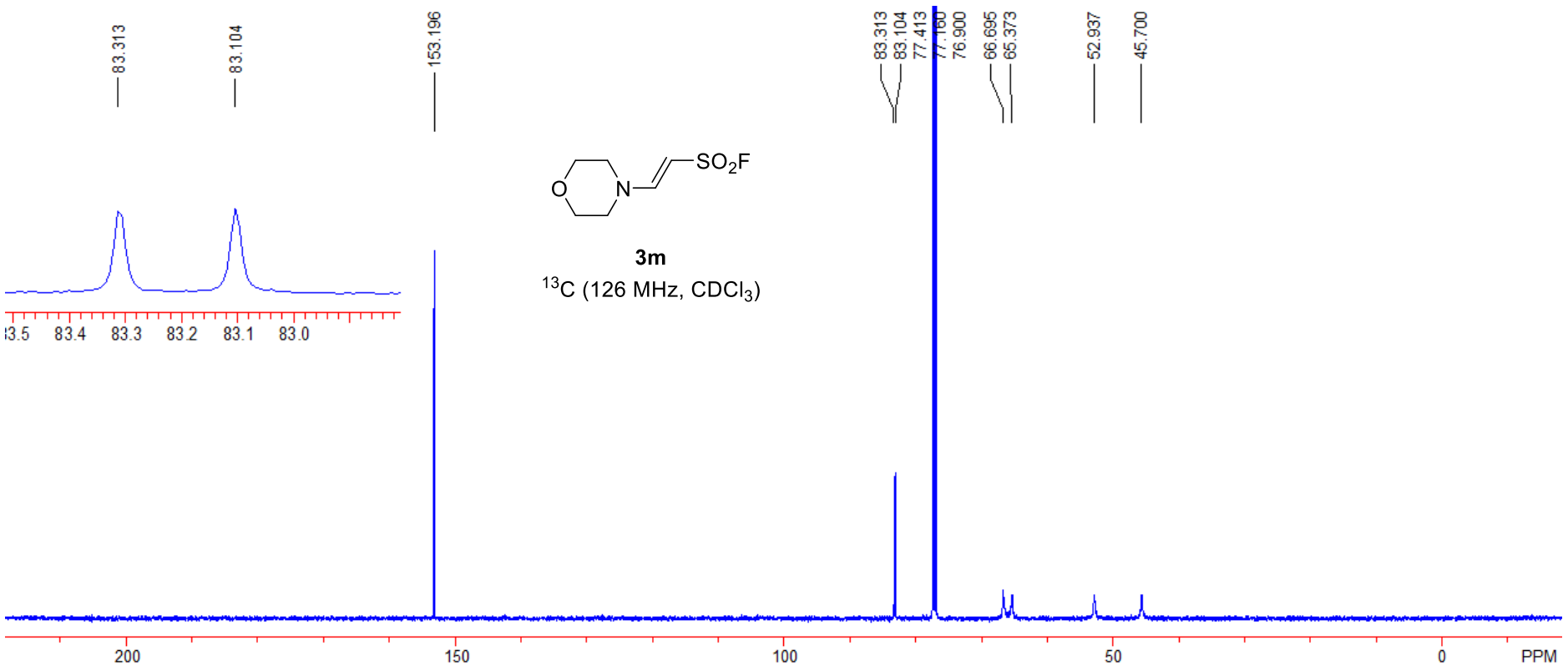
^{13}C (126 MHz, $CDCl_3$)

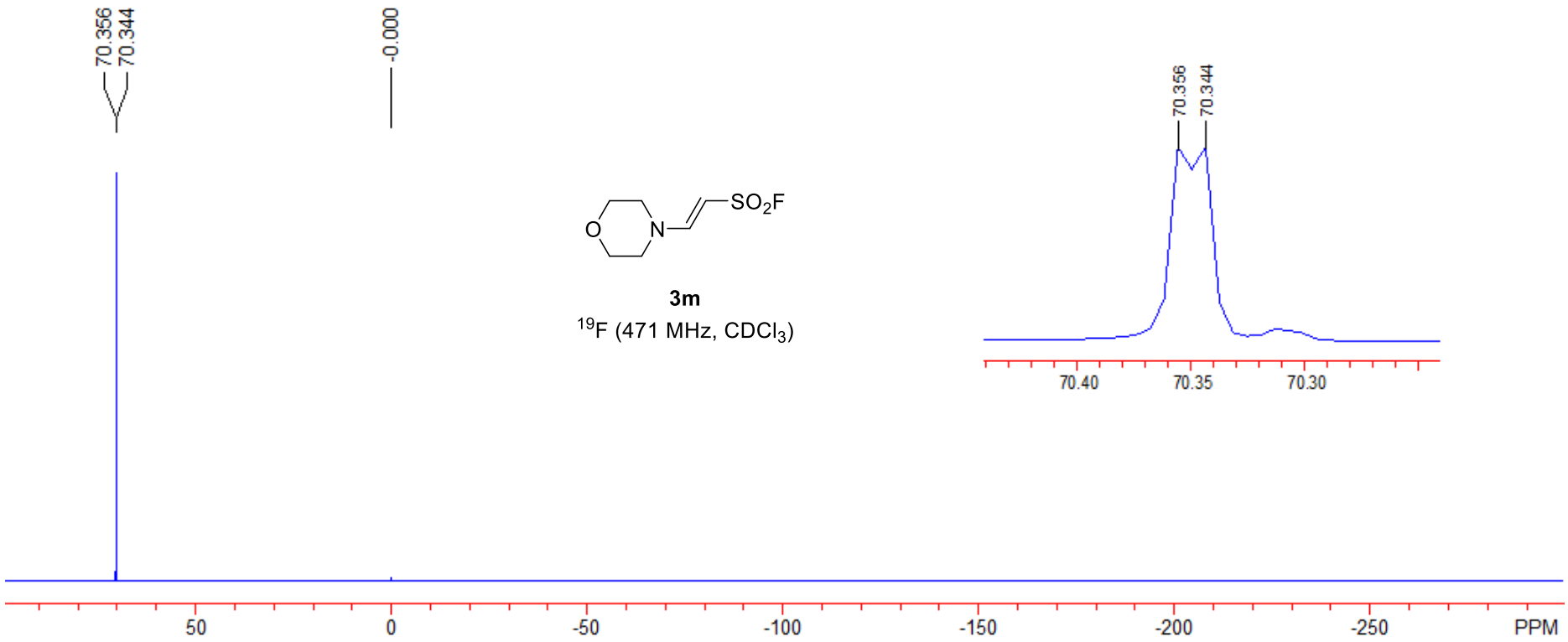


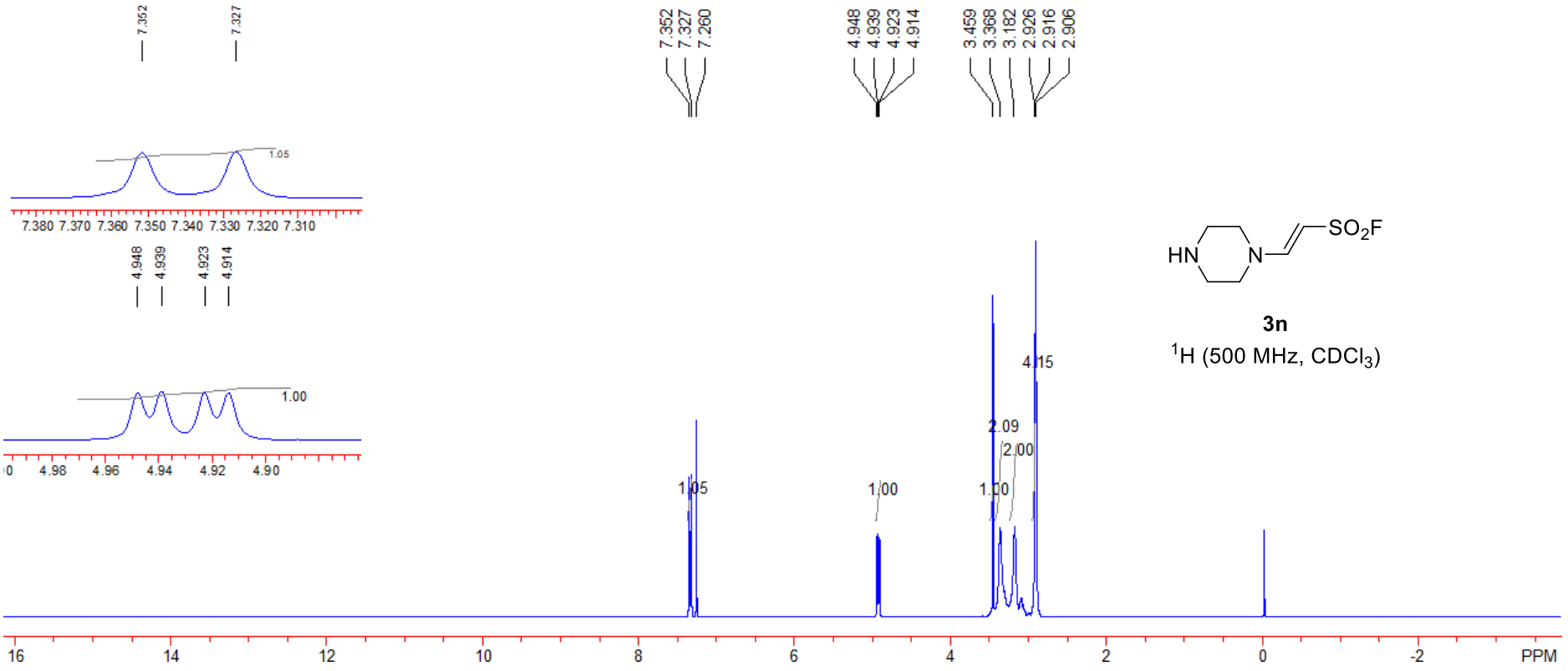
3l

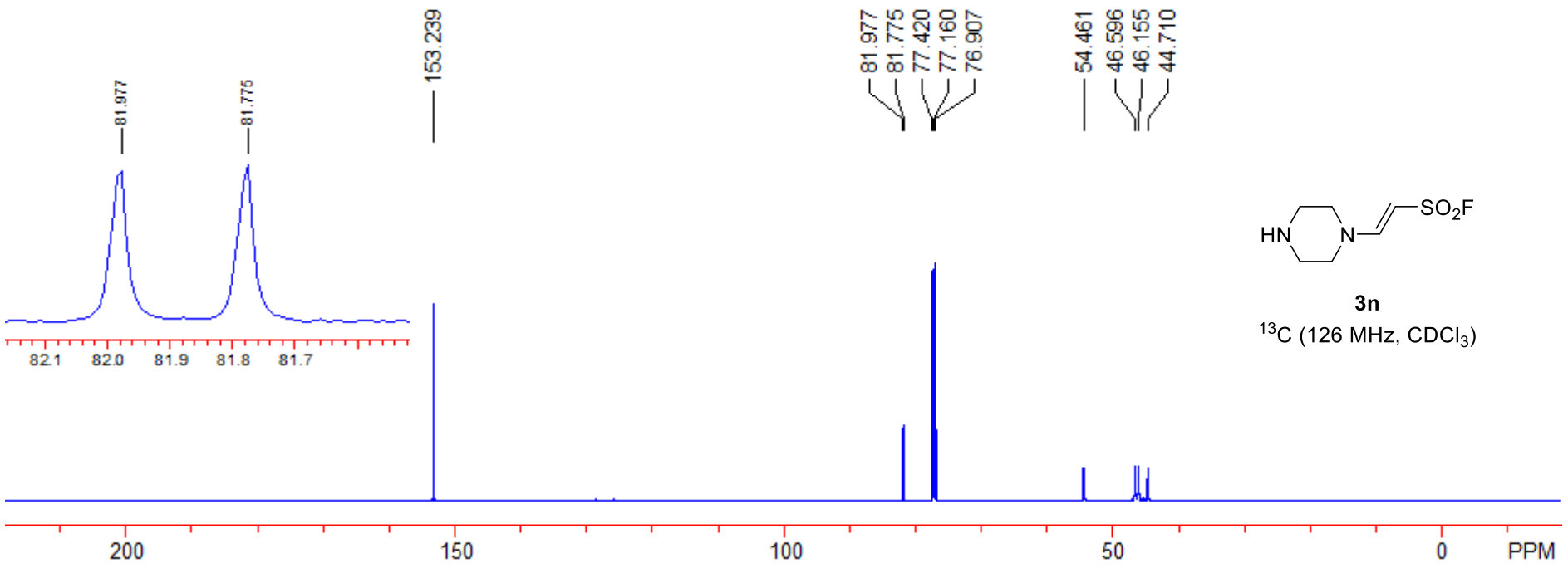
^{19}F (471 MHz, $CDCl_3$)

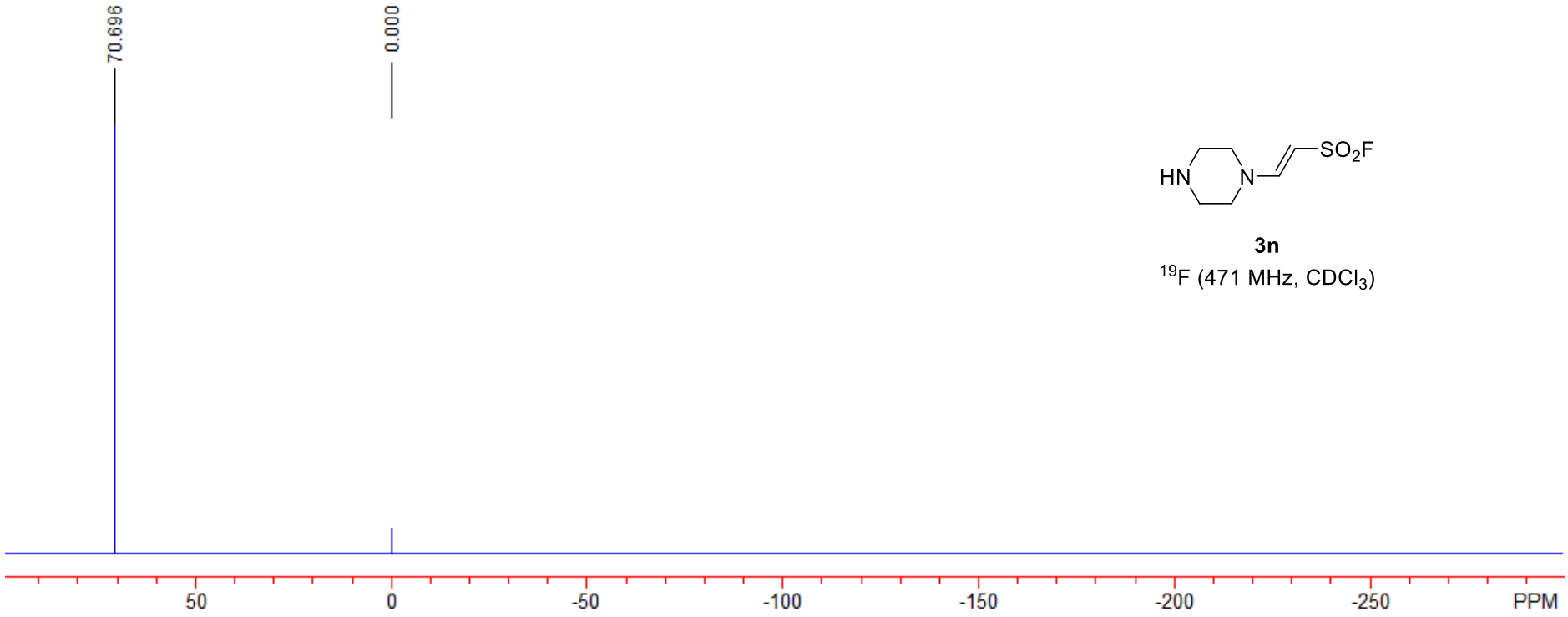

7.370
7.345
7.260
5.008
4.999
4.982
4.974
3.751
3.742
3.732
3.392
3.226
5.008
4.999
4.982
4.974
7.370
7.345
1.00
7.40
7.38
7.36
7.34
7.32
SO2F
O
N
3m
1H (500 MHz, CDCl3)
1.00
5.06
5.04
5.02
5.00
4.98
4.96
4.94
4.03
2.01
1.91
1.00
1.00
16
14
12
10
8
6
4
2
0
-2
PPM


83.313
83.104
153.196
83.313
83.104
77.413
77.160
76.900
66.695
65.373
52.937
45.700
O
N
SO2F
3m
13C (126 MHz, CDCl3)
83.5
83.4
83.3
83.2
83.1
83.0
200
150
100
50
0
PPM


70.356
70.344
-0.000
O
N
SO2F
3m
19F (471 MHz, CDCl3)
70.356
70.344
70.40
70.35
70.30
50
0
-50
-100
-150
-200
-250
PPM

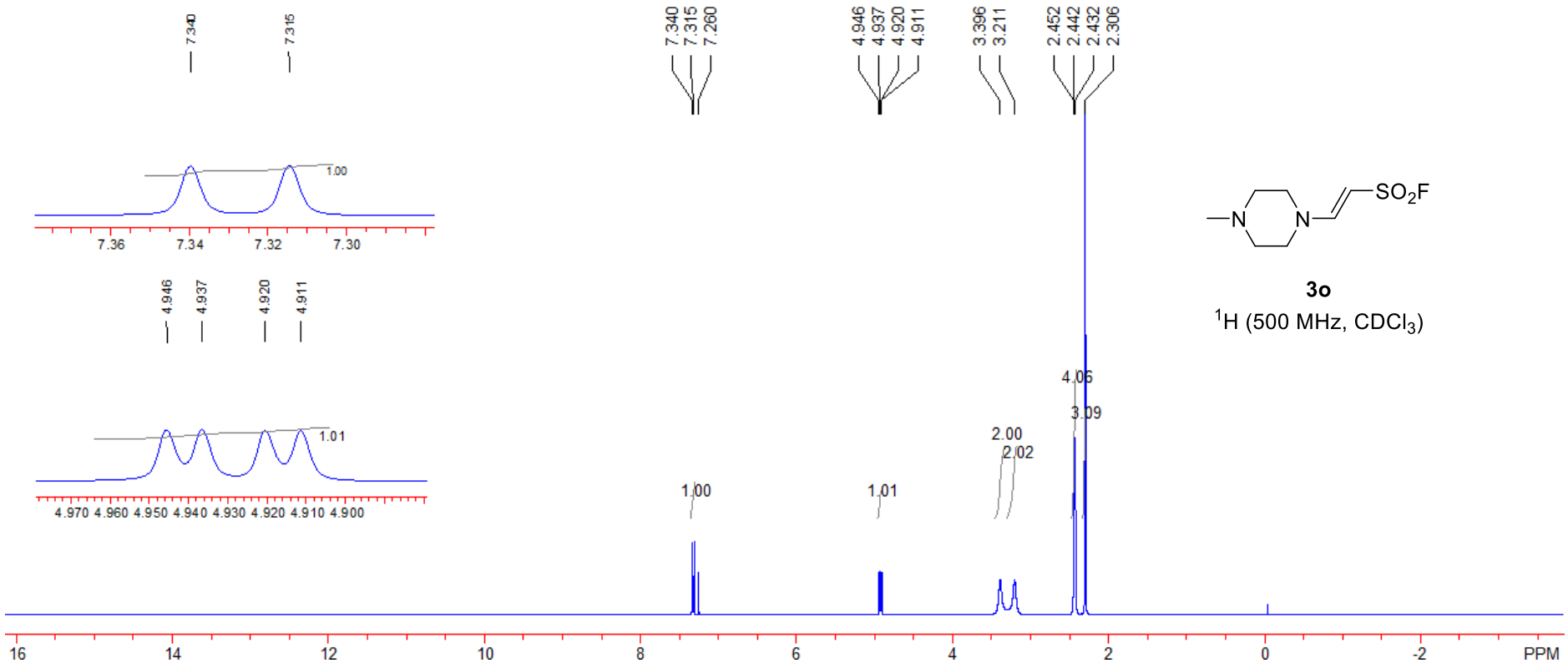

7.352
7.327
7.260
4.948
4.939
4.923
4.914
3.459
3.368
3.182
2.926
2.916
2.906
1.05
7.380 7.370 7.360 7.350 7.340 7.330 7.320 7.310
1.00
4.98 4.96 4.94 4.92 4.90
4.15
2.09
2.00
1.05
1.00
1.00
HN
N
SO2F
3n
1H (500 MHz, CDCl3)
16 14 12 10 8 6 4 2 0 -2 PPM

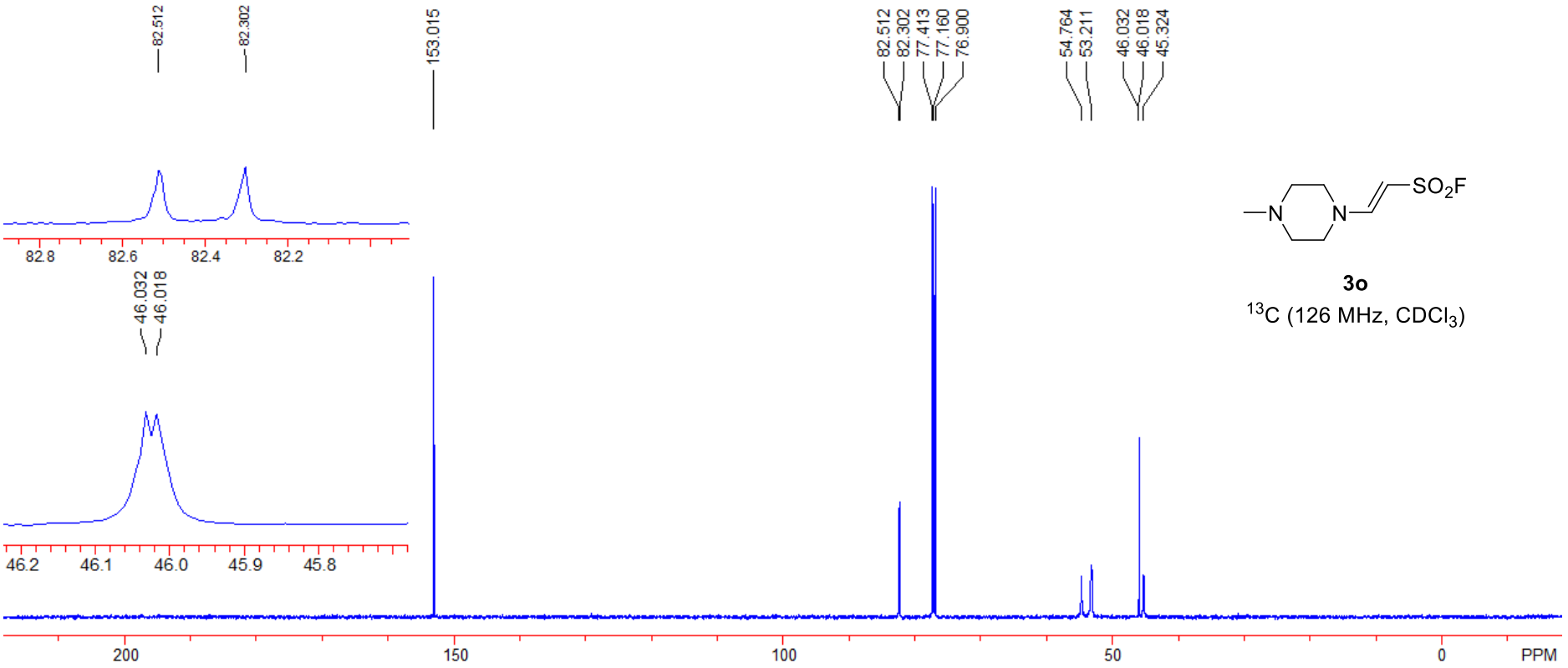

153.239
81.977
81.775
77.420
77.160
76.907
54.461
46.596
46.155
44.710
82.1
82.0
81.9
81.8
81.7
200
150
100
50
0
PPM
HN
N
SO2F
3n
13C (126 MHz, CDCl3)

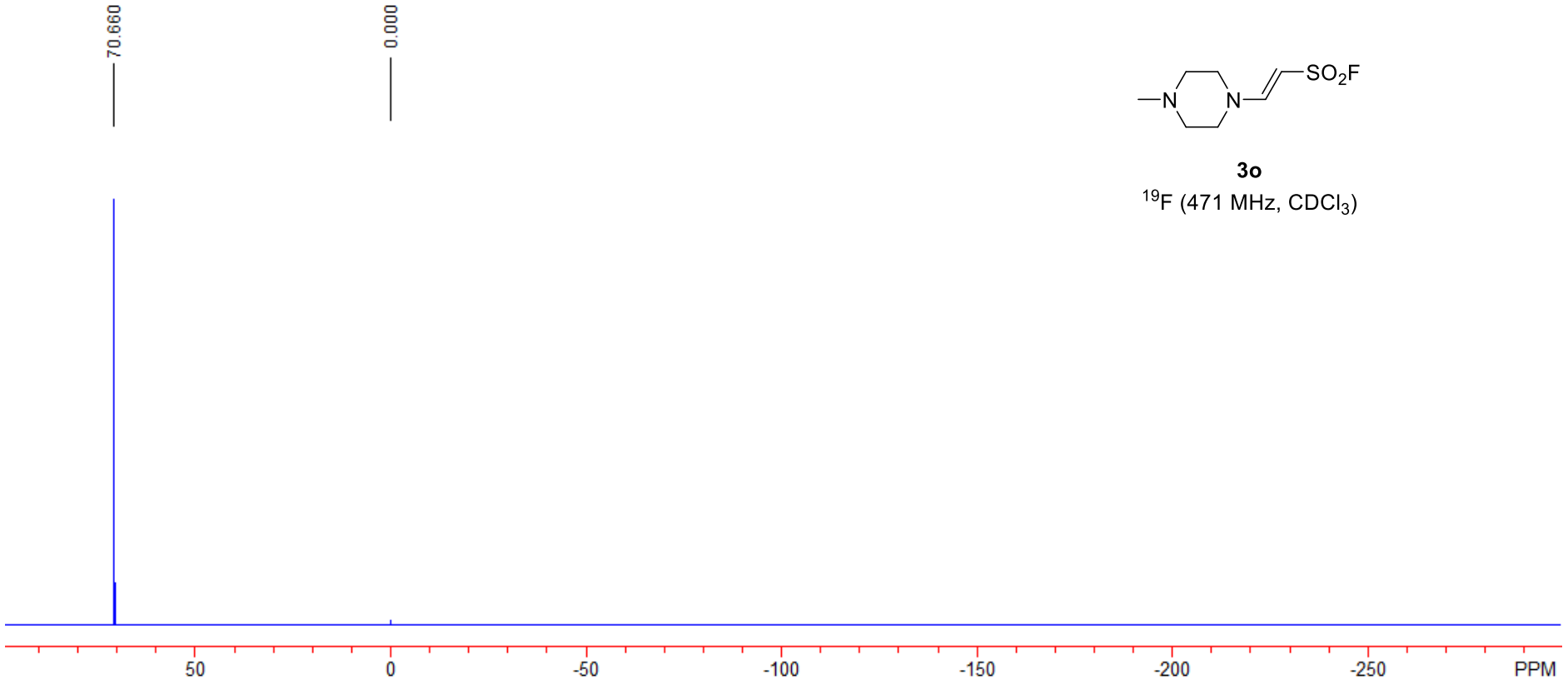


3n

^{19}F (471 MHz, $CDCl_3$)

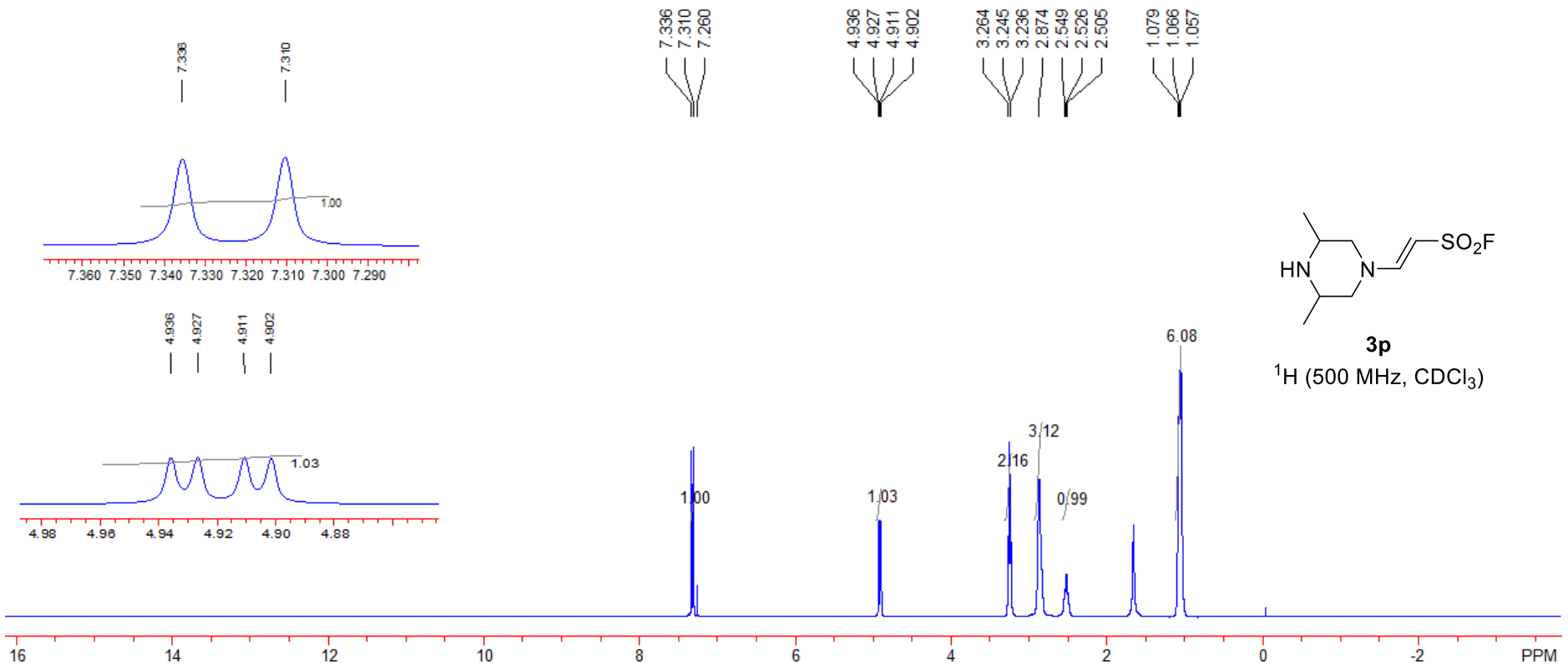

7.340
7.315
7.260
4.946
4.937
4.920
4.911
3.396
3.211
2.452
2.442
2.432
2.306
1.00
1.01
2.00
2.02
4.06
3.09
7.36
7.34
7.32
7.30
4.970 4.960 4.950 4.940 4.930 4.920 4.910 4.900
16
14
12
10
8
6
4
2
0
-2
PPM
SO2F
3o
1H (500 MHz, CDCl3)

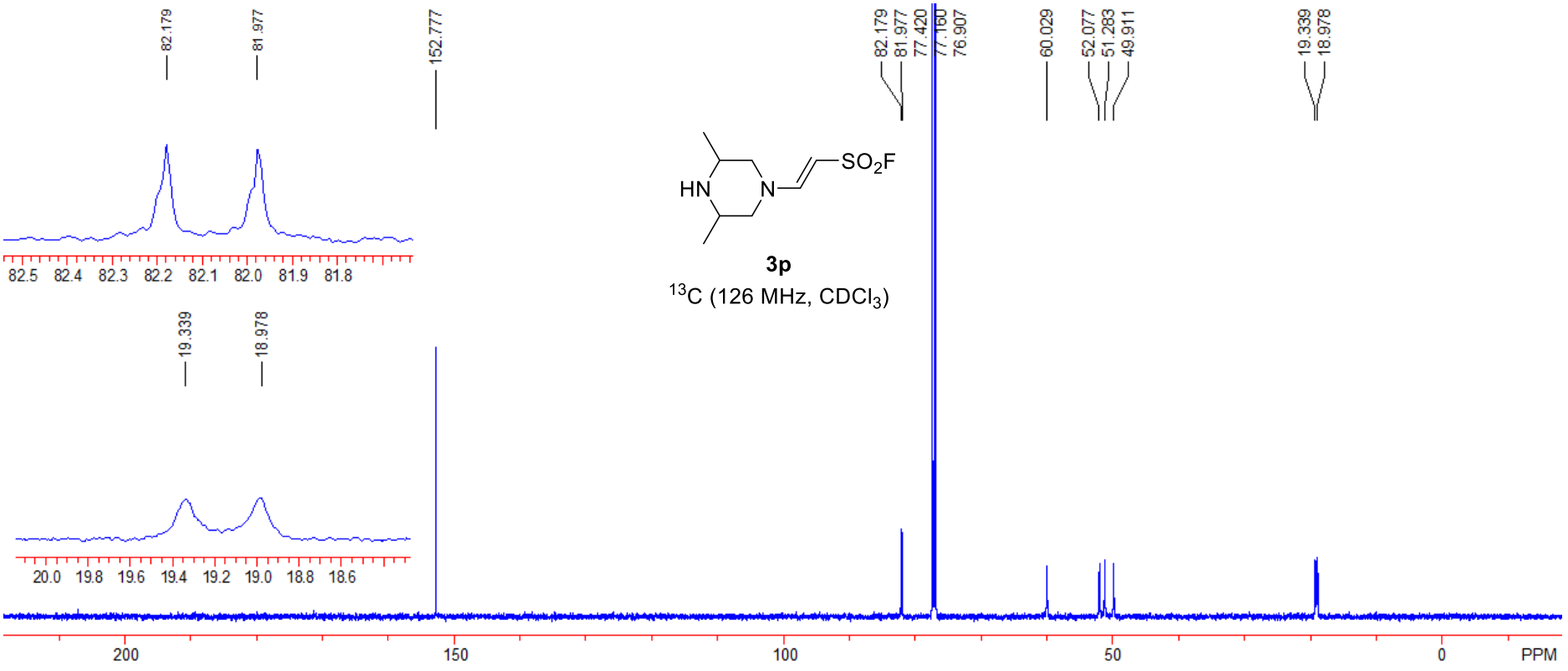

82.512
82.302
153.015
82.512
82.302
77.413
77.160
76.900
54.764
53.211
46.032
46.018
45.324
82.8
82.6
82.4
82.2
46.032
46.018
46.2
46.1
46.0
45.9
45.8
200
150
100
50
0
PPM
N
N
SO2F
3o
13C (126 MHz, CDCl3)

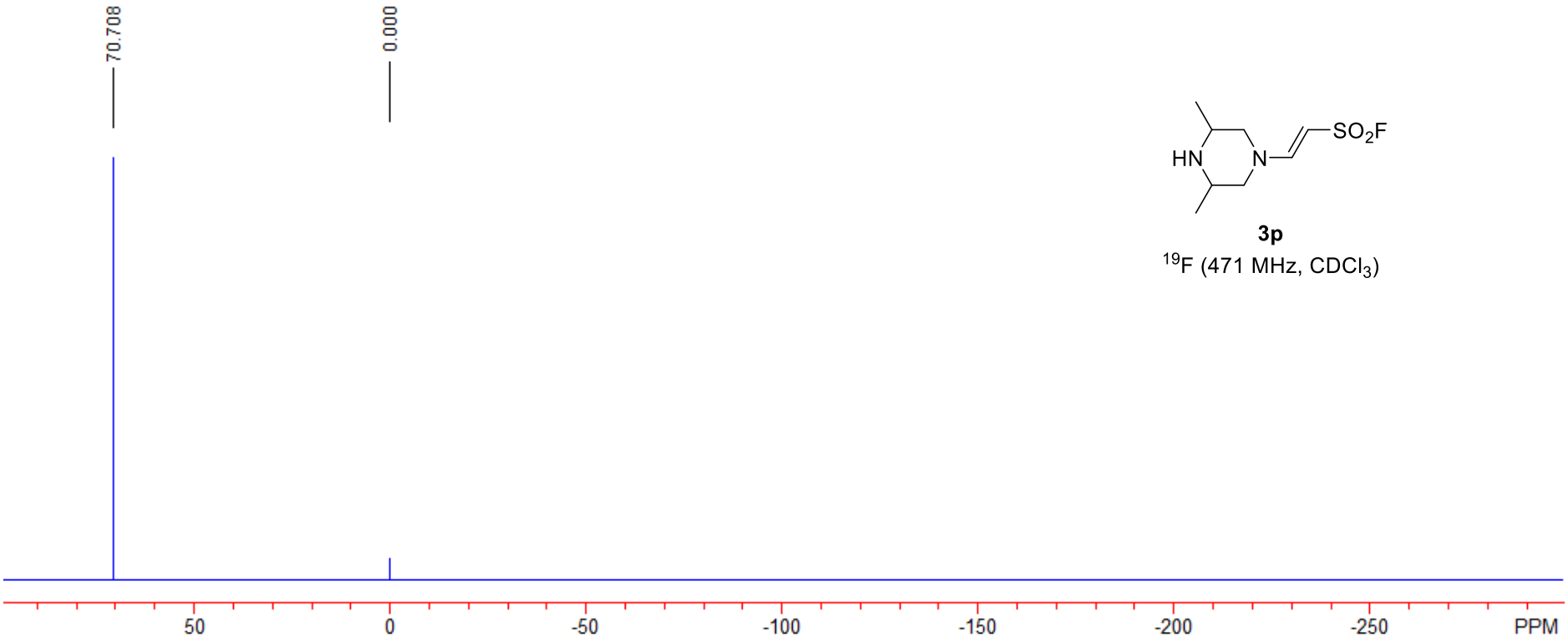


3o

^{19}F (471 MHz, $CDCl_3$)

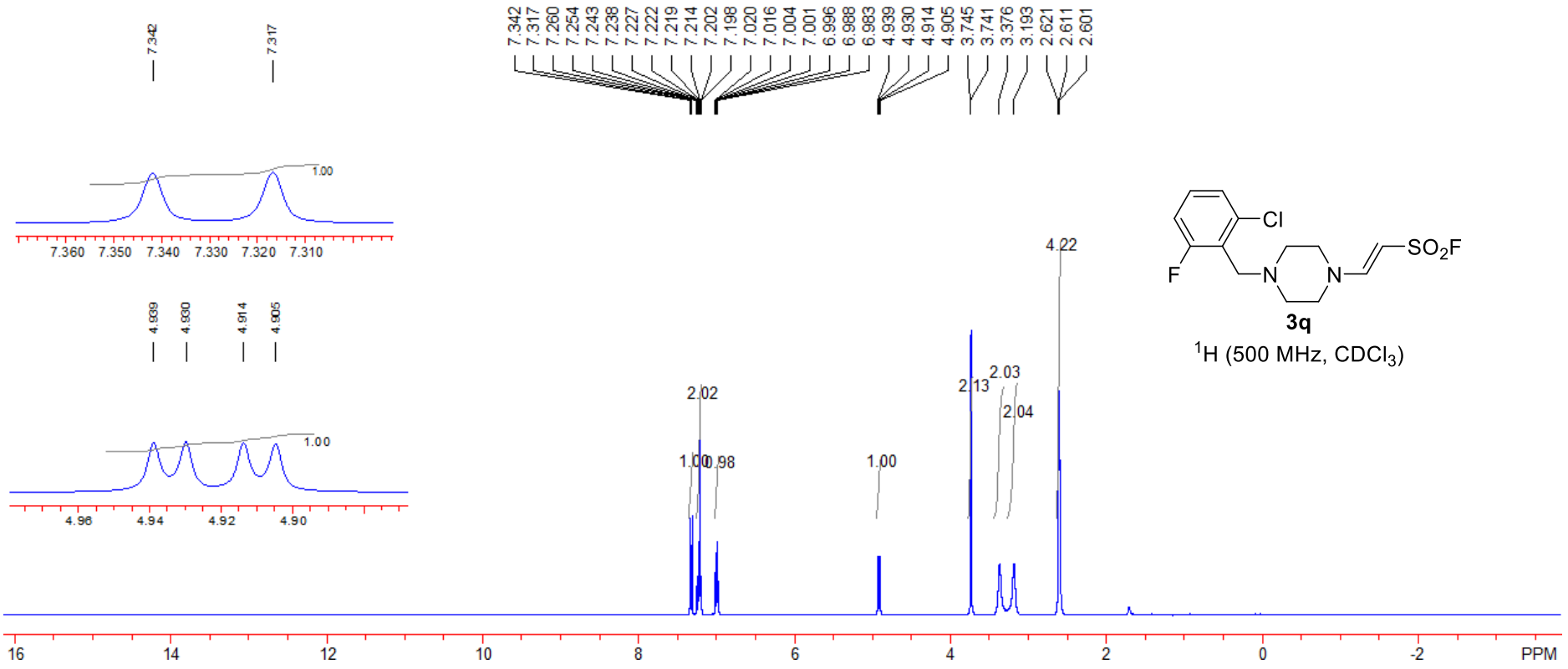

7.336
7.310
7.260
4.936
4.927
4.911
4.902
3.264
3.245
3.236
2.874
2.549
2.526
2.505
1.079
1.066
1.057
1.00
1.03
2.16
3.12
0.99
6.08
HN
N
SO2F
3p
1H (500 MHz, CDCl3)
PPM

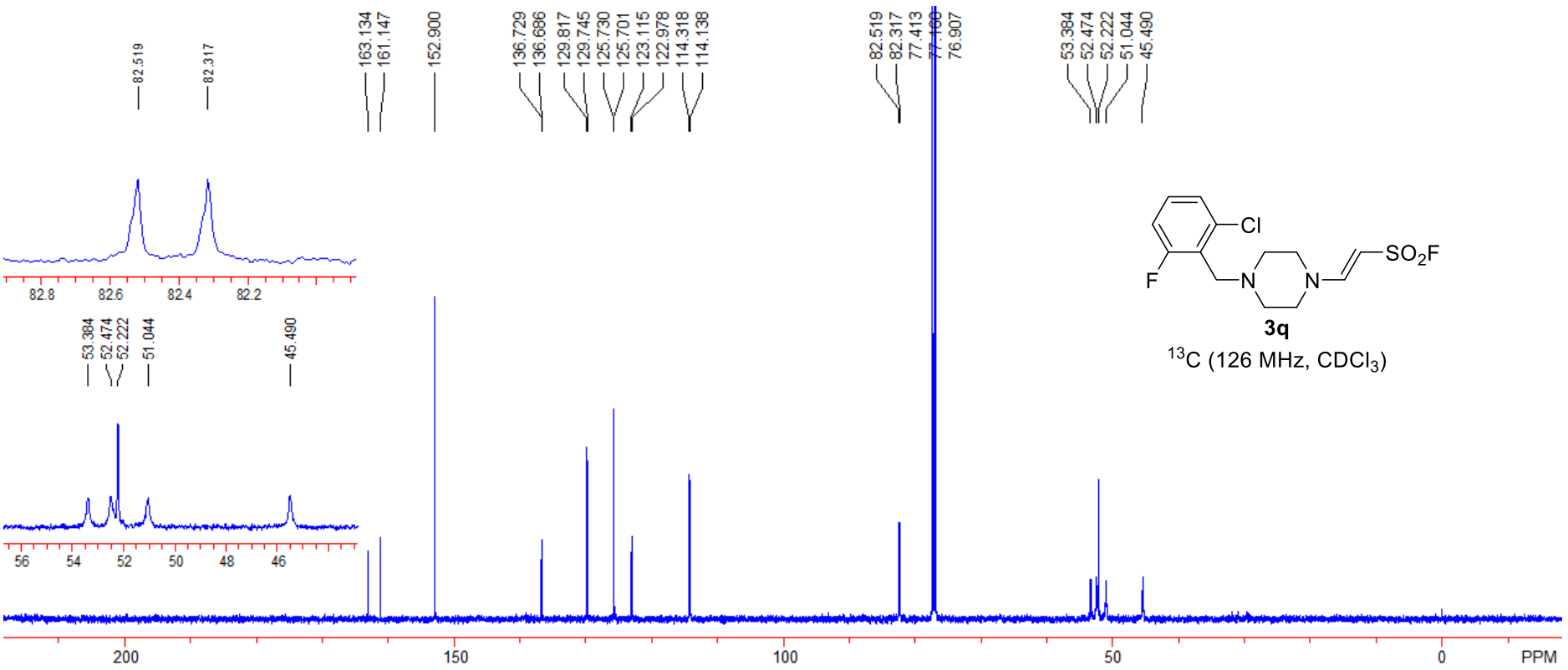

82.179
81.977
152.777
82.179
81.977
77.420
77.160
76.907
60.029
52.077
51.283
49.911
19.339
18.978
HN
N
SO2F
3p
13C (126 MHz, CDCl3)
82.5 82.4 82.3 82.2 82.1 82.0 81.9 81.8
19.339
18.978
20.0 19.8 19.6 19.4 19.2 19.0 18.8 18.6
200
150
100
50
0
PPM

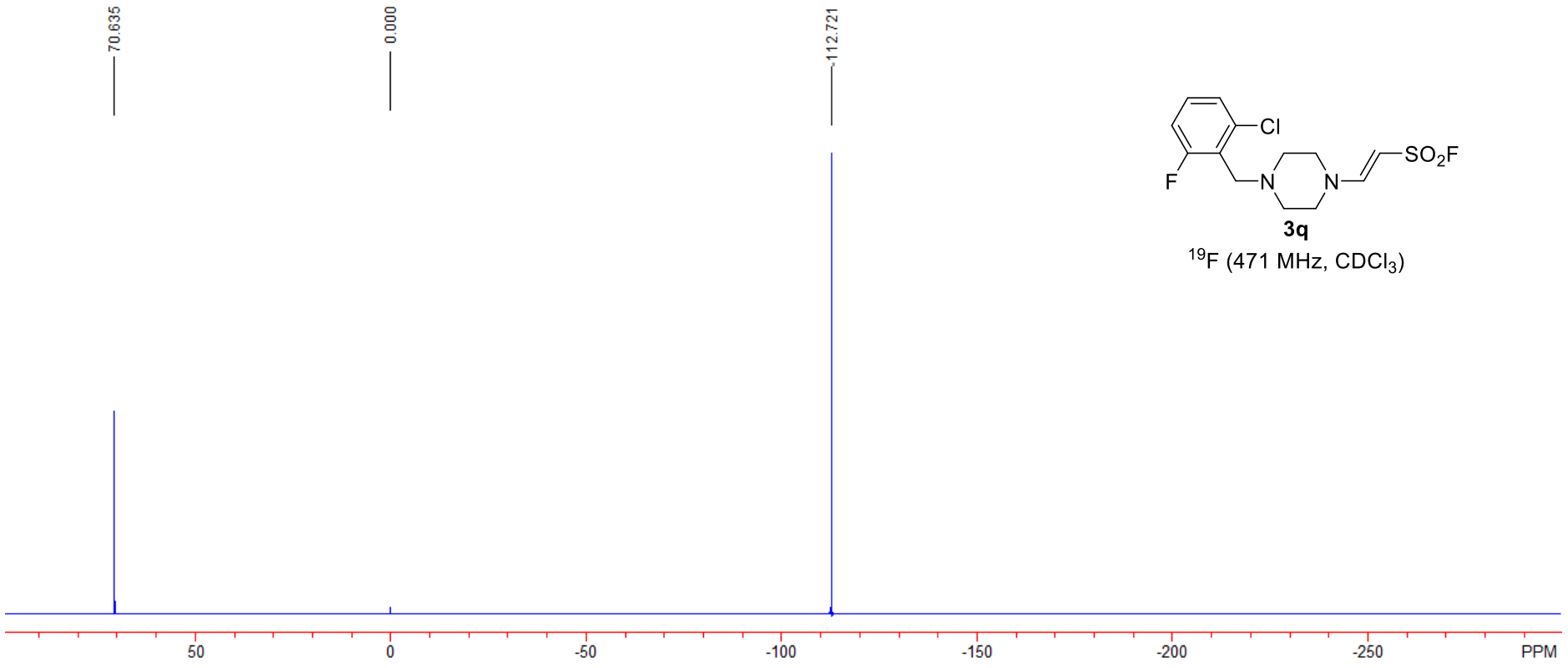


3p

^{19}F (471 MHz, $CDCl_3$)

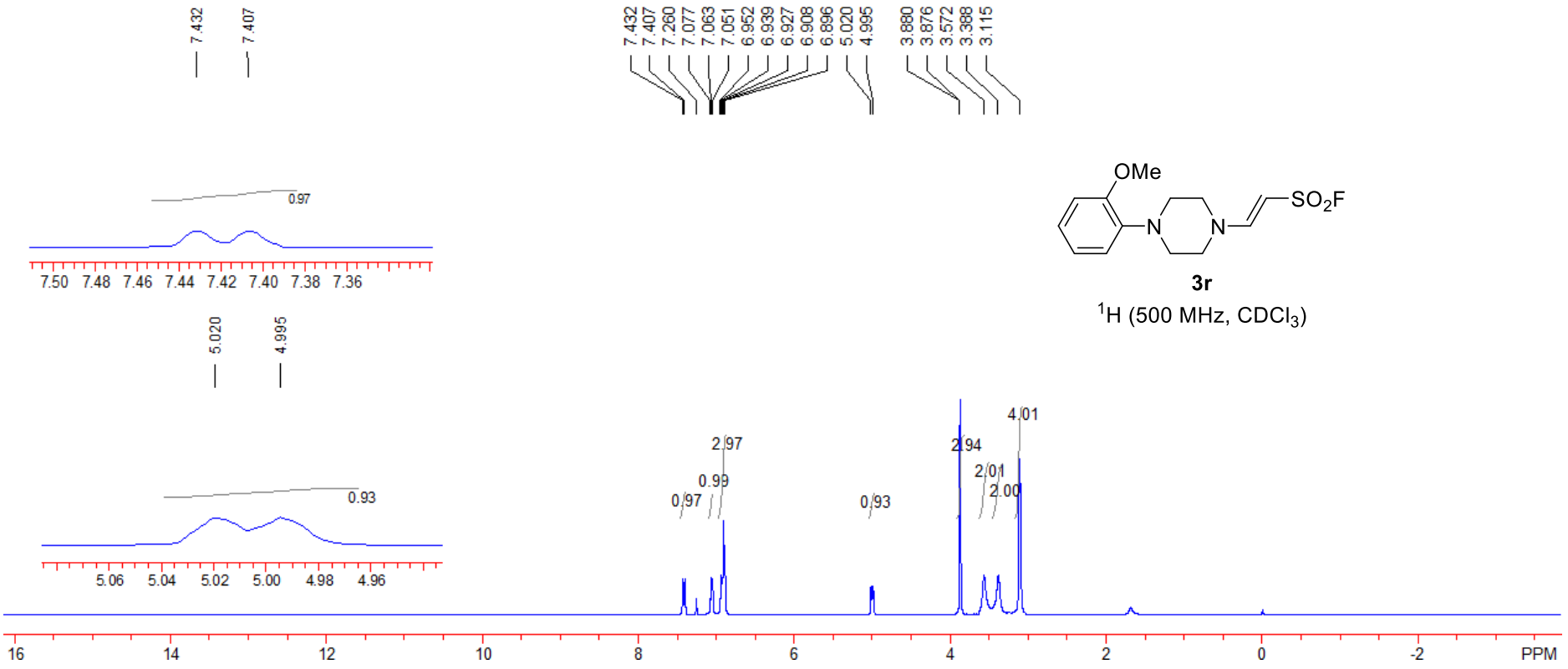

7.342
7.317
7.260
7.254
7.243
7.238
7.227
7.222
7.219
7.214
7.202
7.198
7.020
7.016
7.004
7.001
6.996
6.988
6.983
4.939
4.930
4.914
4.905
3.745
3.741
3.376
3.193
2.621
2.611
2.601
1.00
7.360 7.350 7.340 7.330 7.320 7.310
4.939
4.930
4.914
4.905
1.00
4.96 4.94 4.92 4.90
2.02
1.00
0.98
1.00
2.13
2.03
2.04
4.22
16 14 12 10 8 6 4 2 0 -2 PPM
Cl
F
N
N
SO2F
3q
1H (500 MHz, CDCl3)

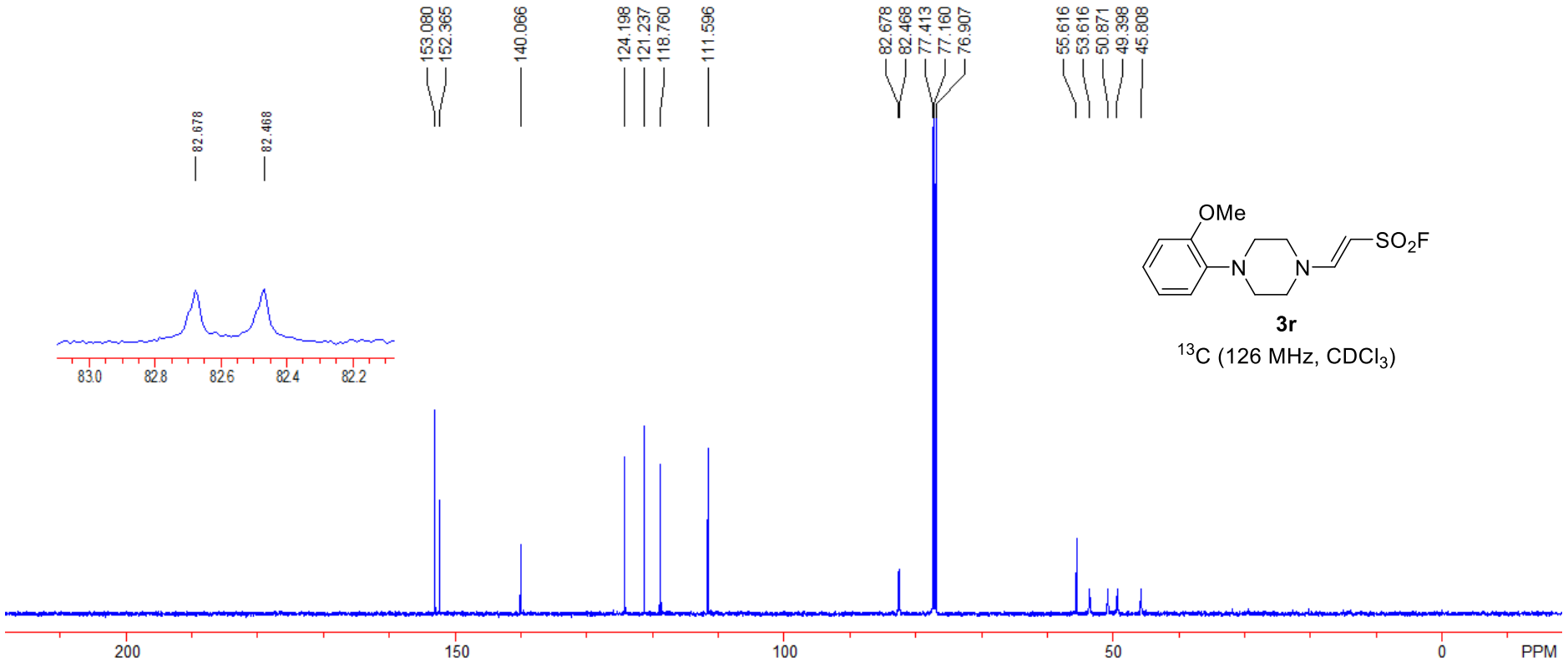

82.519
82.317
163.134
161.147
152.900
136.729
136.686
129.817
129.745
125.730
125.701
123.115
122.978
114.318
114.138
82.519
82.317
77.413
77.160
76.907
53.384
52.474
52.222
51.044
45.490
82.8
82.6
82.4
82.2
53.384
52.474
52.222
51.044
45.490
56
54
52
50
48
46
200
150
100
50
0
PPM
Cl
F
N
N
SO2F
3q
13C (126 MHz, CDCl3)

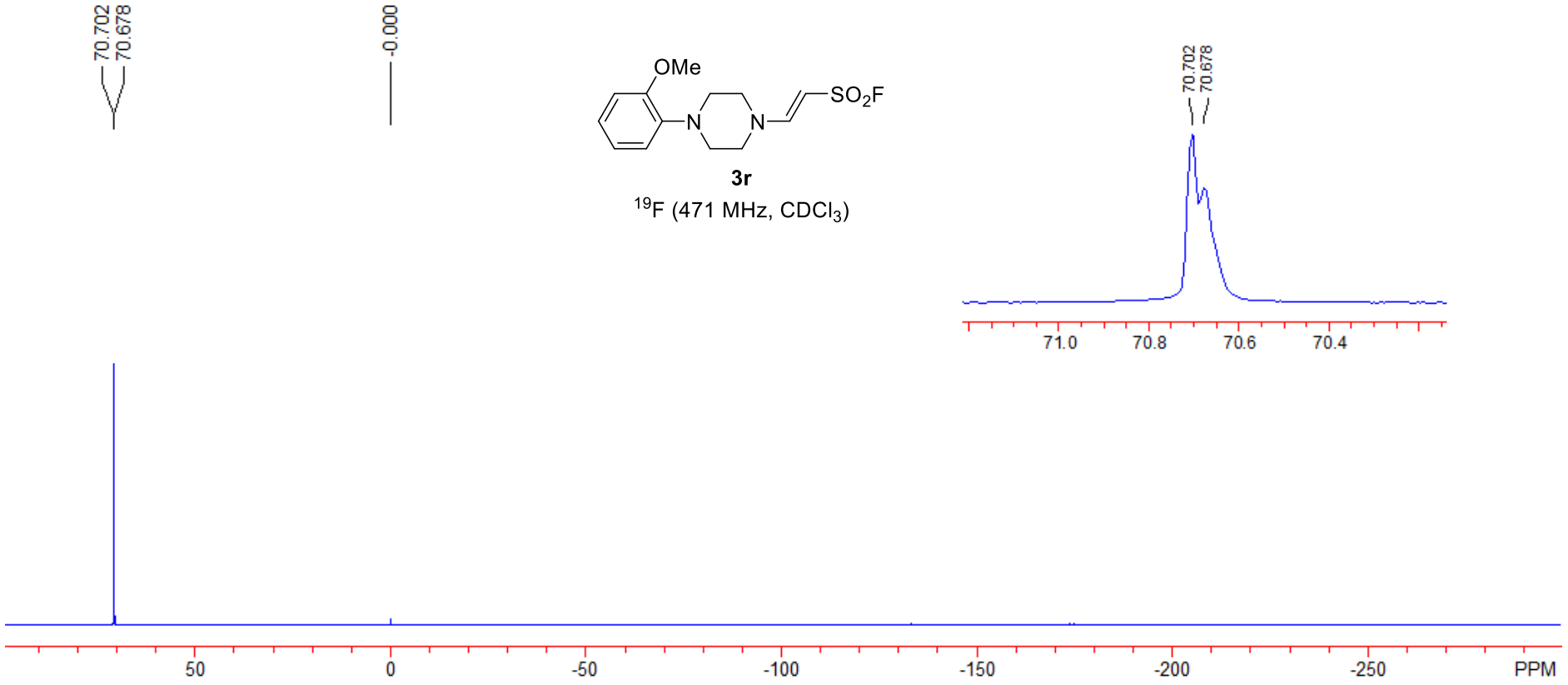


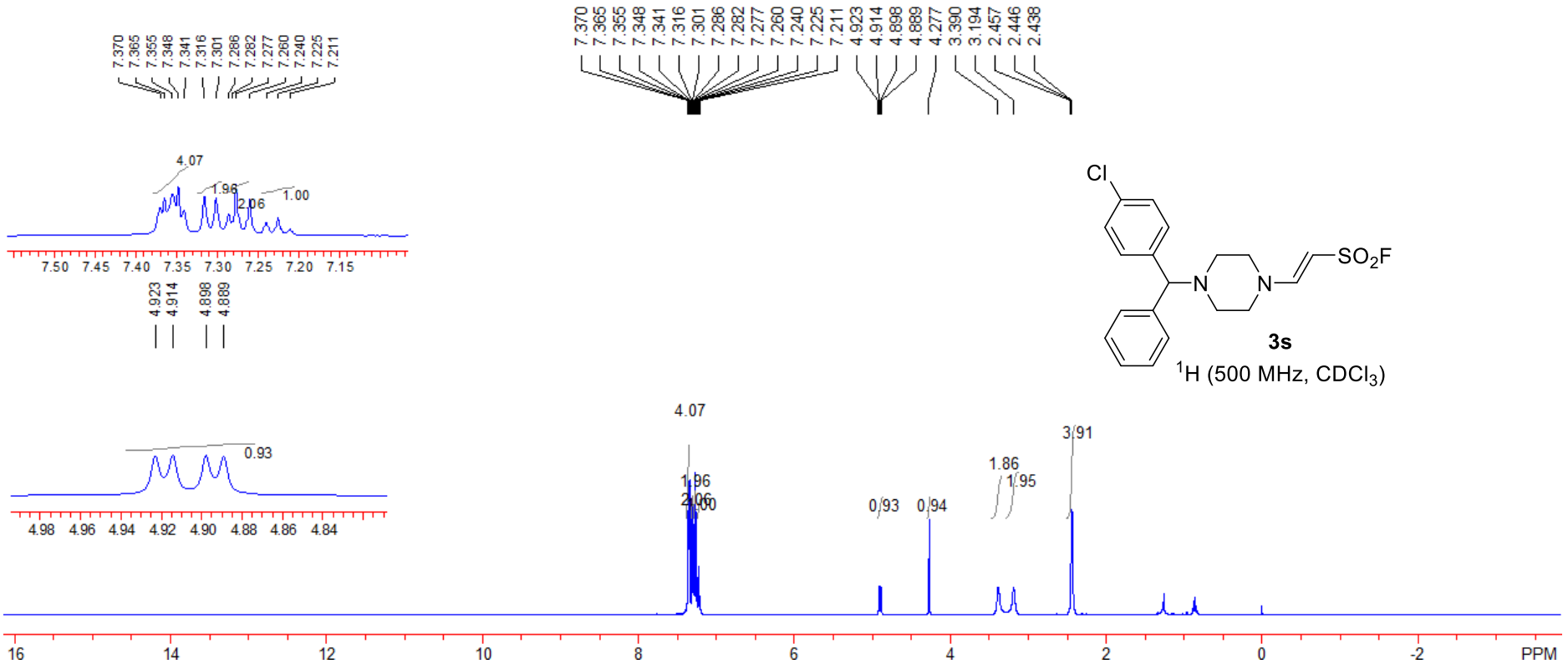
3q

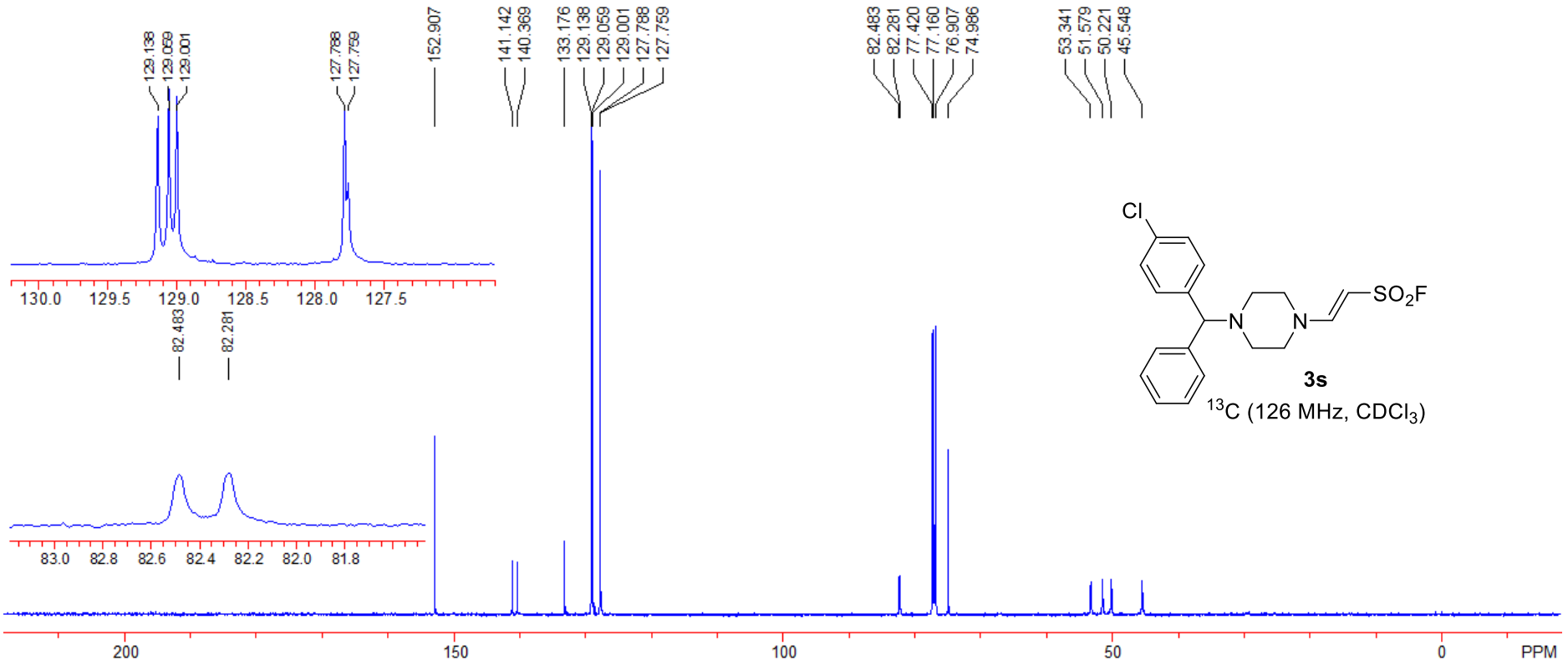
^{19}F (471 MHz, $CDCl_3$)

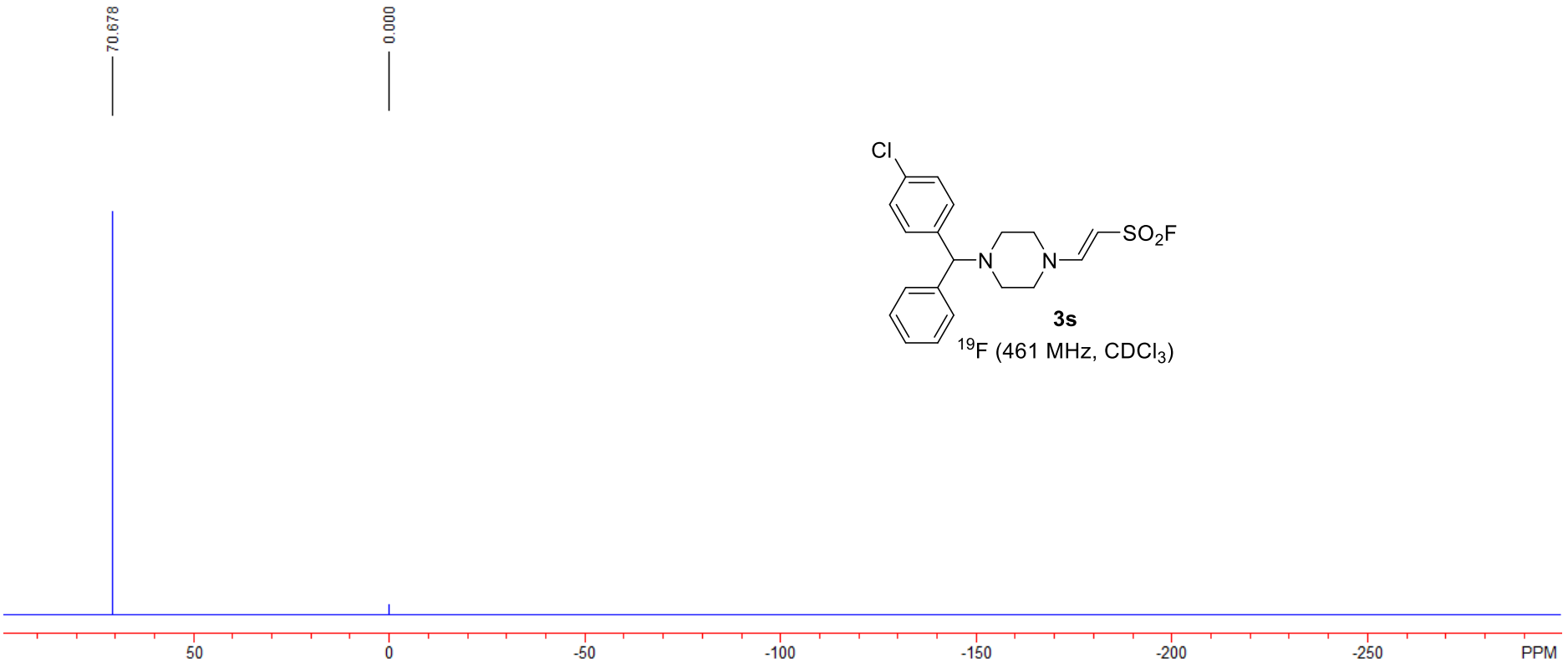

7.432
7.407
7.260
7.077
7.063
7.051
6.952
6.939
6.927
6.908
6.896
5.020
4.995
3.880
3.876
3.572
3.388
3.115
OMe
SO2F
N
N
3r
1H (500 MHz, CDCl3)
0.97
7.50 7.48 7.46 7.44 7.42 7.40 7.38 7.36
5.020
4.995
0.93
5.06 5.04 5.02 5.00 4.98 4.96
0.97
2.97
0.99
0.93
2.94
2.01
2.00
4.01
16 14 12 10 8 6 4 2 0 -2 PPM


153.080
152.365
140.066
124.198
121.237
118.760
111.596
82.678
82.468
77.413
77.160
76.907
55.616
53.616
50.871
49.398
45.808
82.678
82.468
83.0
82.8
82.6
82.4
82.2
OMe
N
N
SO2F
3r
13C (126 MHz, CDCl3)
200
150
100
50
0
PPM


70.702
70.678
-0.000
OMe
N
N
SO2F
3r
19F (471 MHz, CDCl3)
70.702
70.678
71.0
70.8
70.6
70.4
50
0
-50
-100
-150
-200
-250
PPM

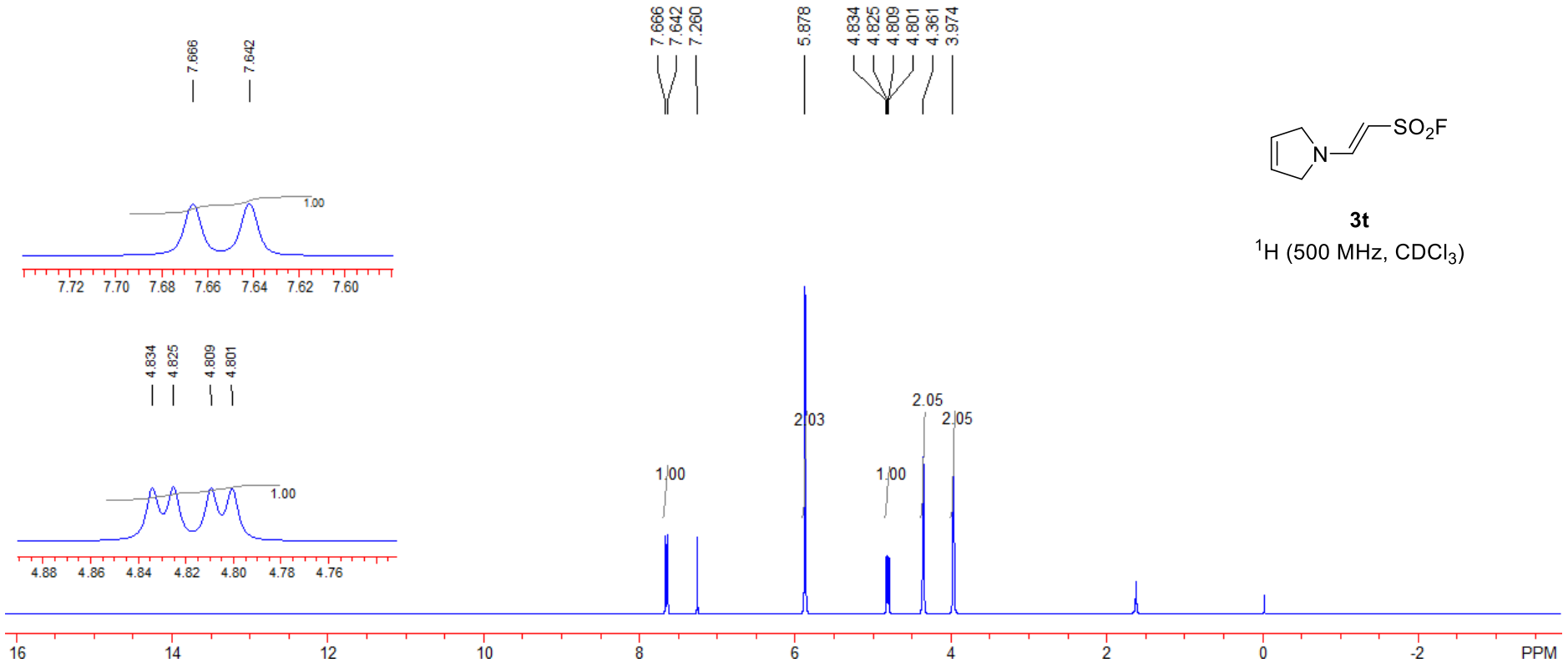

7.370
7.365
7.355
7.348
7.341
7.316
7.301
7.286
7.282
7.277
7.260
7.240
7.225
7.211
4.923
4.914
4.898
4.889
4.277
3.390
3.194
2.457
2.446
2.438
4.07
1.96
2.06
1.00
7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15
0.93
4.98 4.96 4.94 4.92 4.90 4.88 4.86 4.84
Cl
N
N
SO2F
3s
1H (500 MHz, CDCl3)
4.07
1.96
2.06
1.00
0.93
0.94
1.86
1.95
3.91
16 14 12 10 8 6 4 2 0 -2 PPM

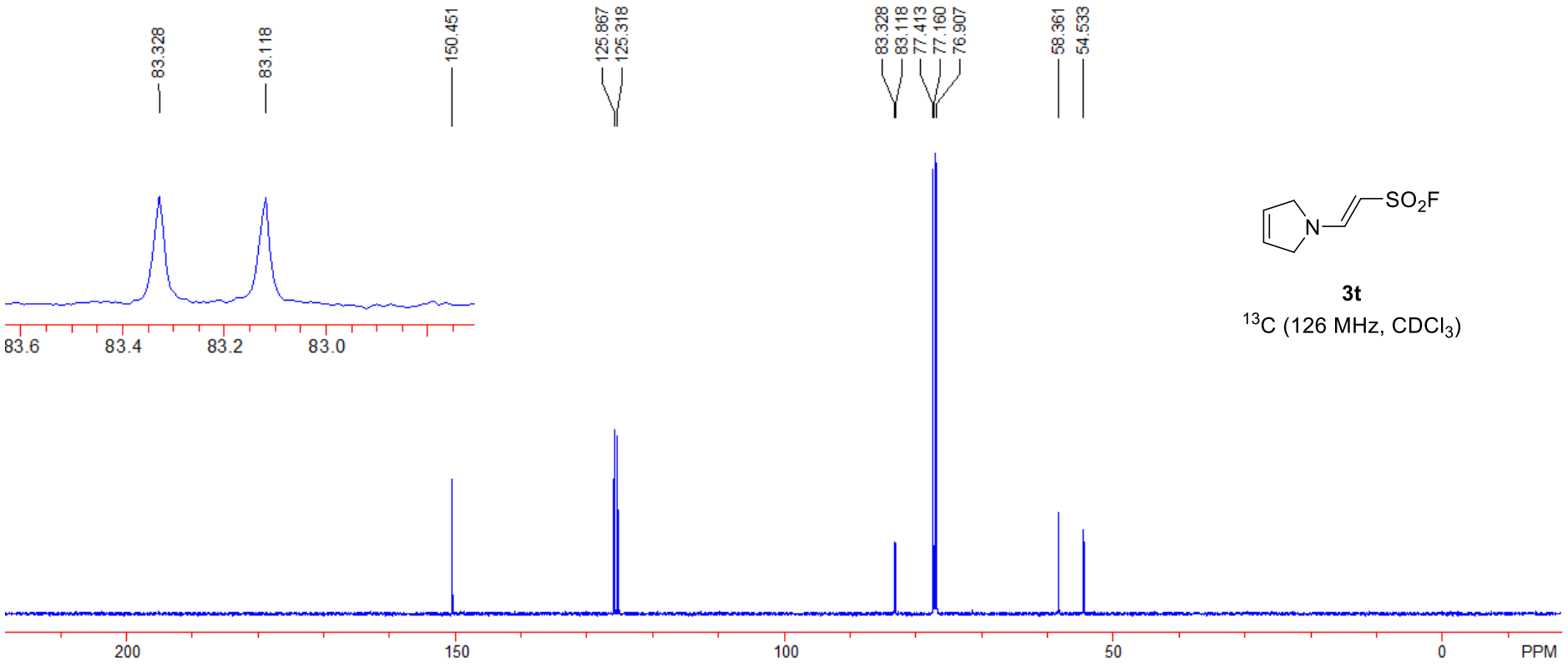

129.138
129.059
129.001
127.788
127.759
152.907
141.142
140.369
133.176
129.138
129.059
129.001
127.788
127.759
82.483
82.281
77.420
77.160
76.907
74.986
53.341
51.579
50.221
45.548
130.0
129.5
129.0
128.5
128.0
127.5
82.483
82.281
83.0
82.8
82.6
82.4
82.2
82.0
81.8
200
150
100
50
0
PPM
Cl
N
N
SO2F
3s
13C (126 MHz, CDCl3)



3s

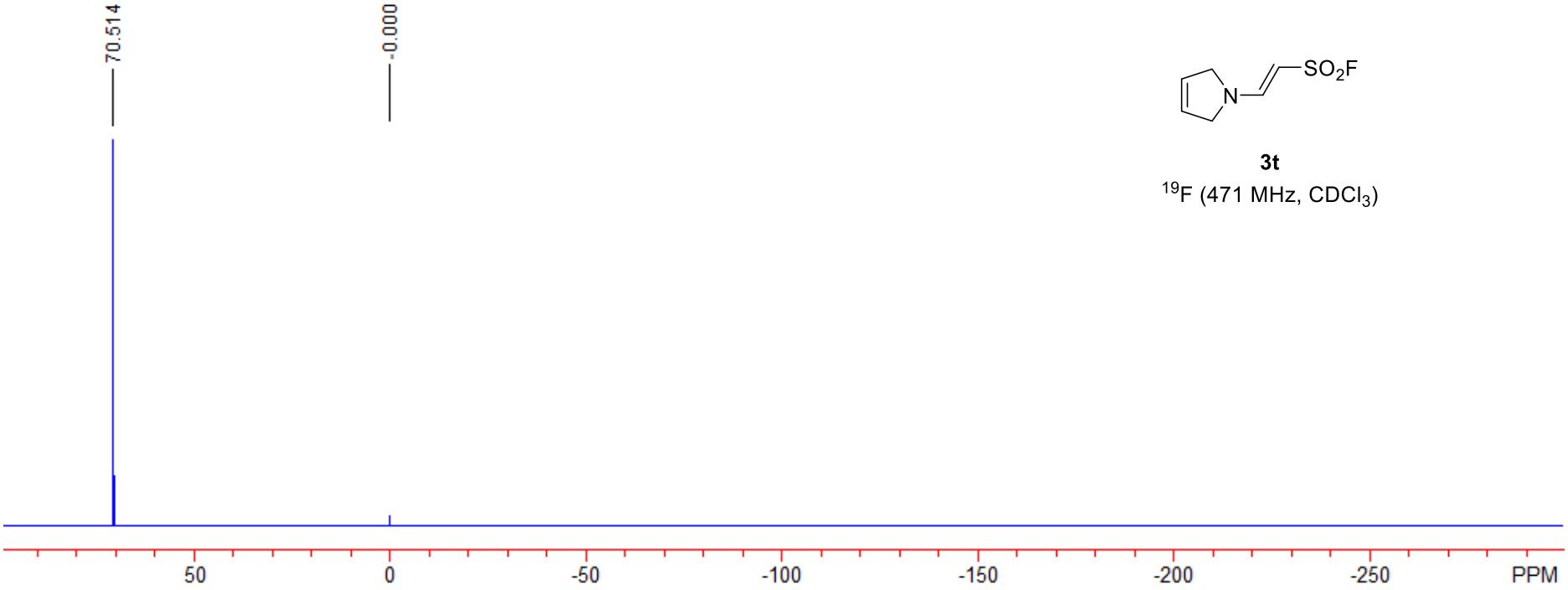
^{19}F (461 MHz, $CDCl_3$)


7.666
7.642
7.260
5.878
4.834
4.825
4.809
4.801
4.361
3.974
1.00
7.72 7.70 7.68 7.66 7.64 7.62 7.60
4.834
4.825
4.809
4.801
1.00
4.88 4.86 4.84 4.82 4.80 4.78 4.76
1.00
2.03
1.00
2.05
2.05
16 14 12 10 8 6 4 2 0 -2 PPM
N
SO2F
3t
1H (500 MHz, CDCl3)



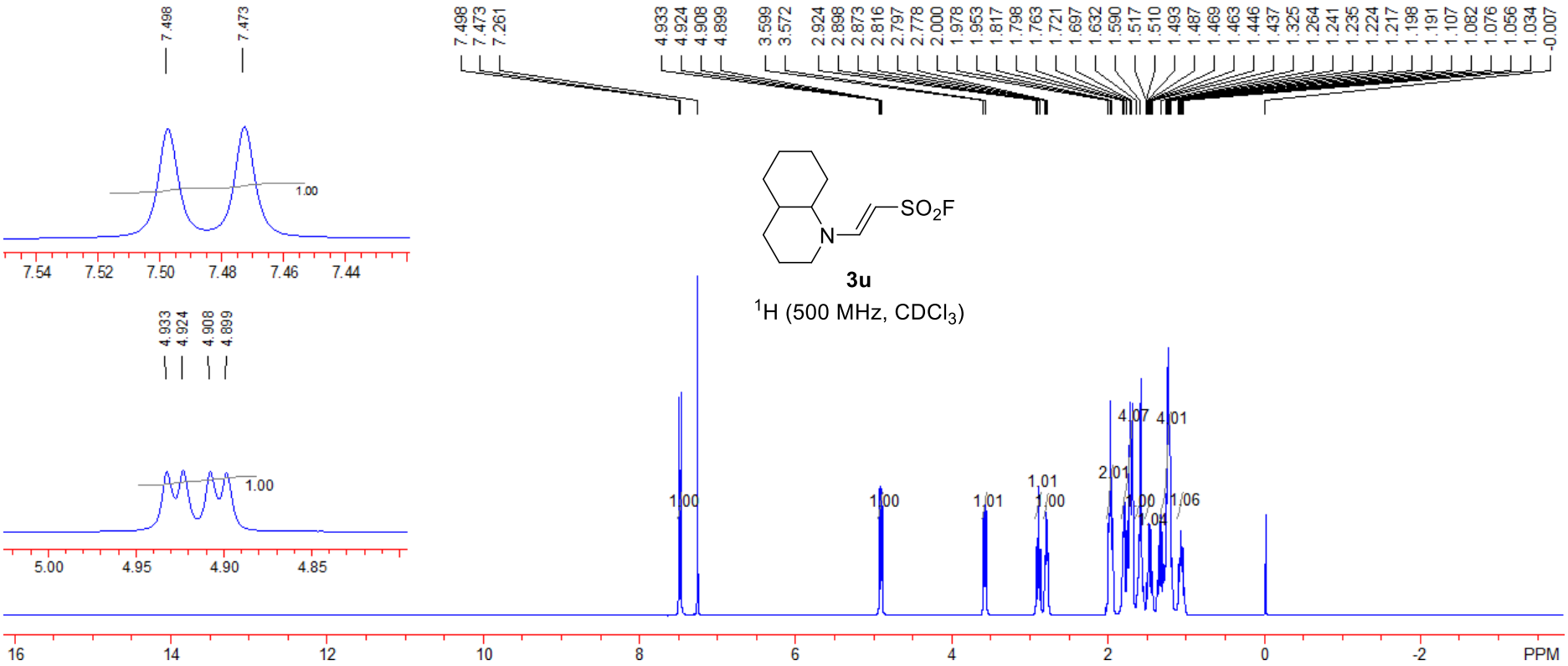
3t

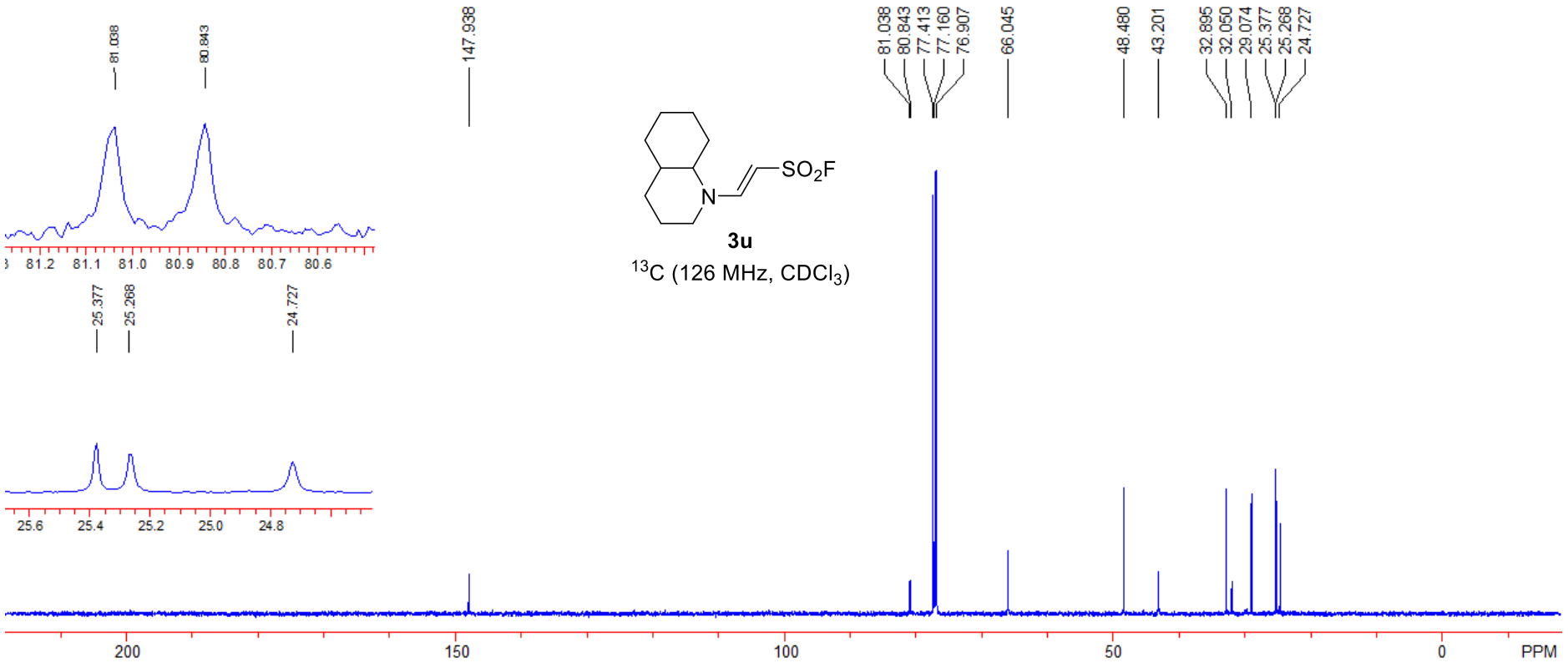
^{13}C (126 MHz, $CDCl_3$)

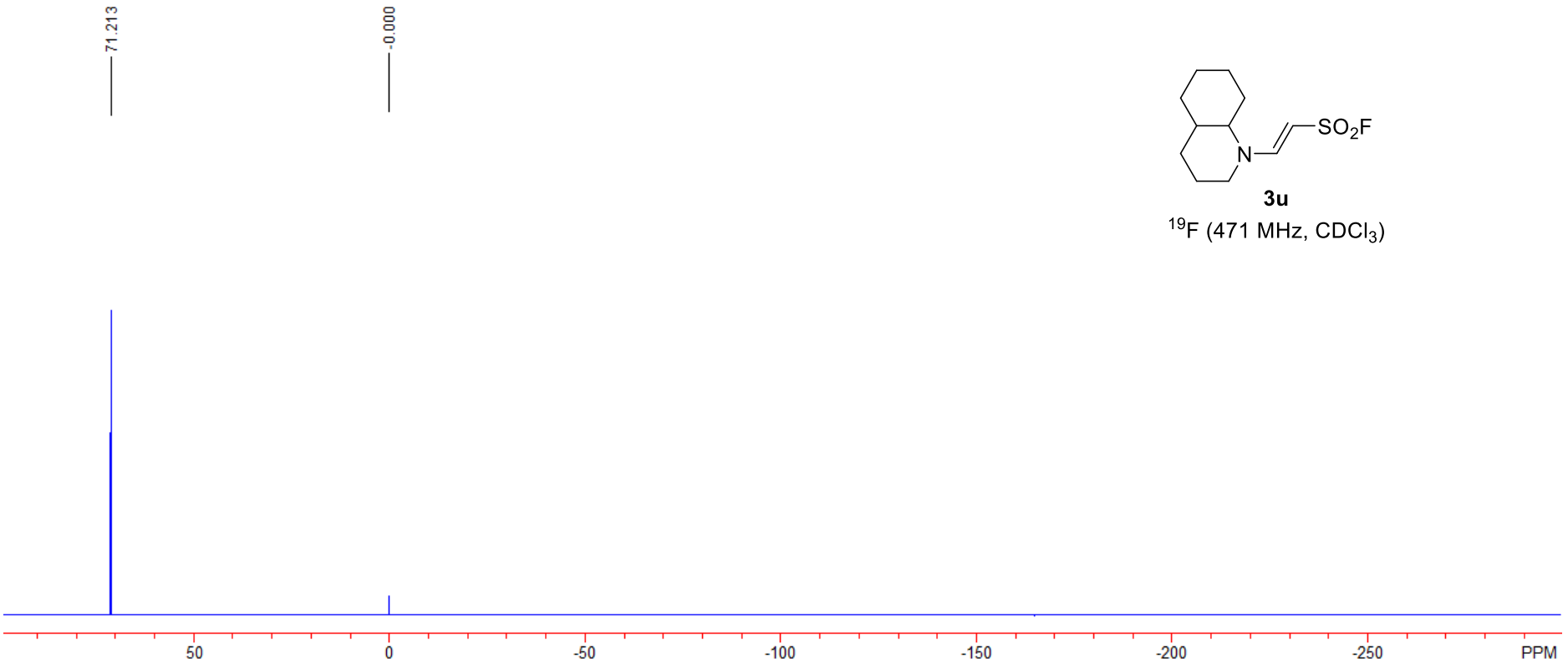


3t

^{19}F (471 MHz, $CDCl_3$)

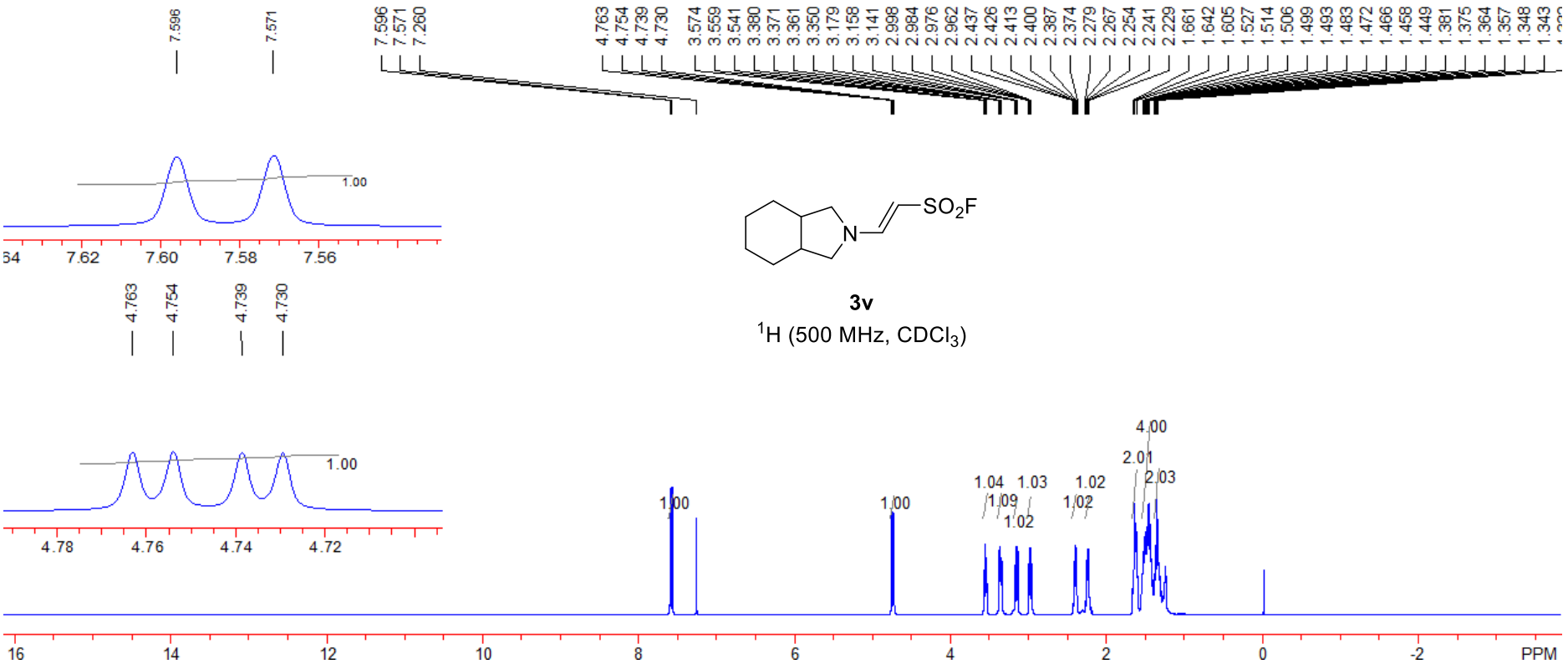

7.498
7.473
7.261
4.933
4.924
4.908
4.899
3.599
3.572
2.924
2.898
2.873
2.816
2.797
2.778
2.000
1.978
1.953
1.817
1.798
1.763
1.721
1.697
1.632
1.590
1.517
1.510
1.493
1.487
1.469
1.463
1.446
1.437
1.325
1.264
1.241
1.235
1.224
1.217
1.198
1.191
1.107
1.082
1.076
1.056
1.034
-0.007
SO2F
N
3u
1H (500 MHz, CDCl3)
1.00
1.00
1.01
1.00
1.01
1.00
2.01
4.07
4.01
1.00
1.06
0.94
16
14
12
10
8
6
4
2
0
-2
PPM


147.938
81.038
80.843
77.413
77.160
76.907
66.045
48.480
43.201
32.895
32.050
29.074
25.377
25.268
24.727
SO2F
N
3u
13C (126 MHz, CDCl3)
200
150
100
50
0
PPM



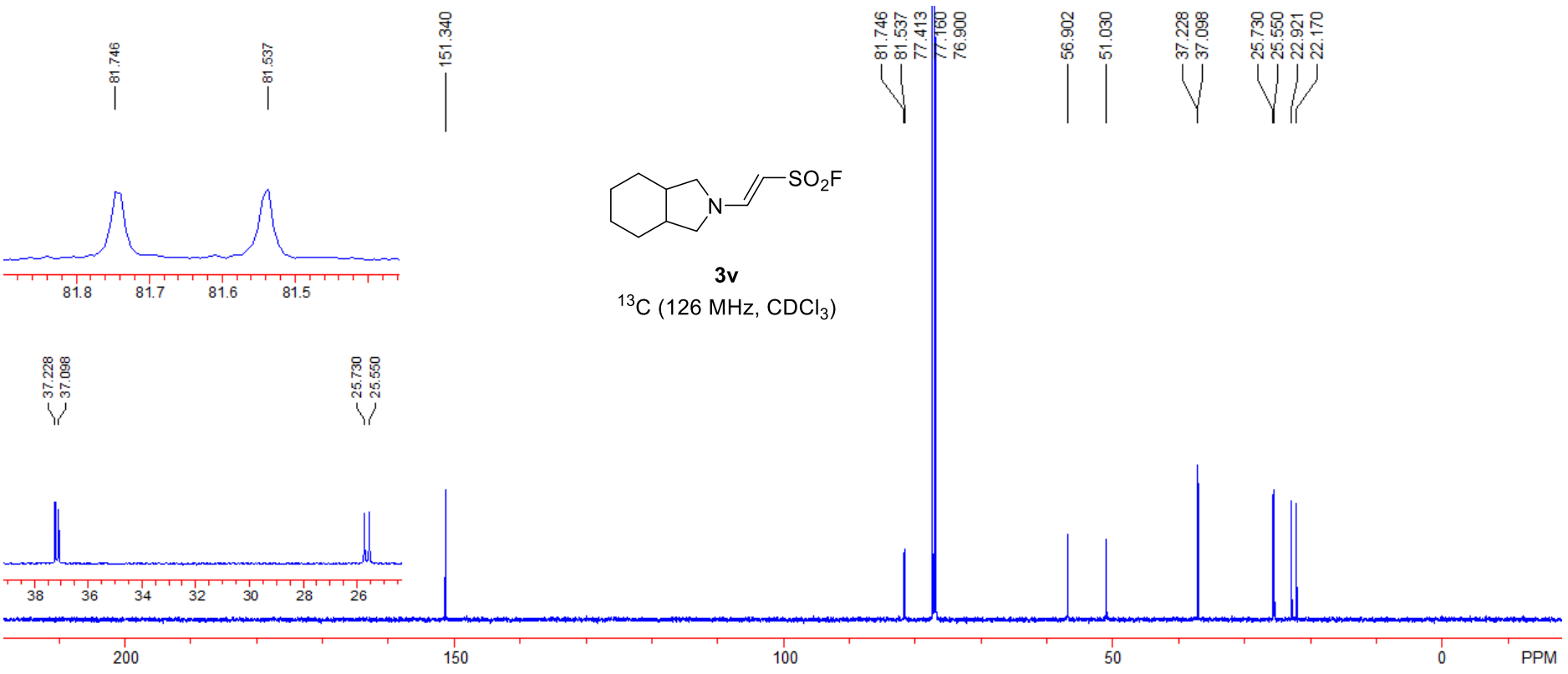
3u

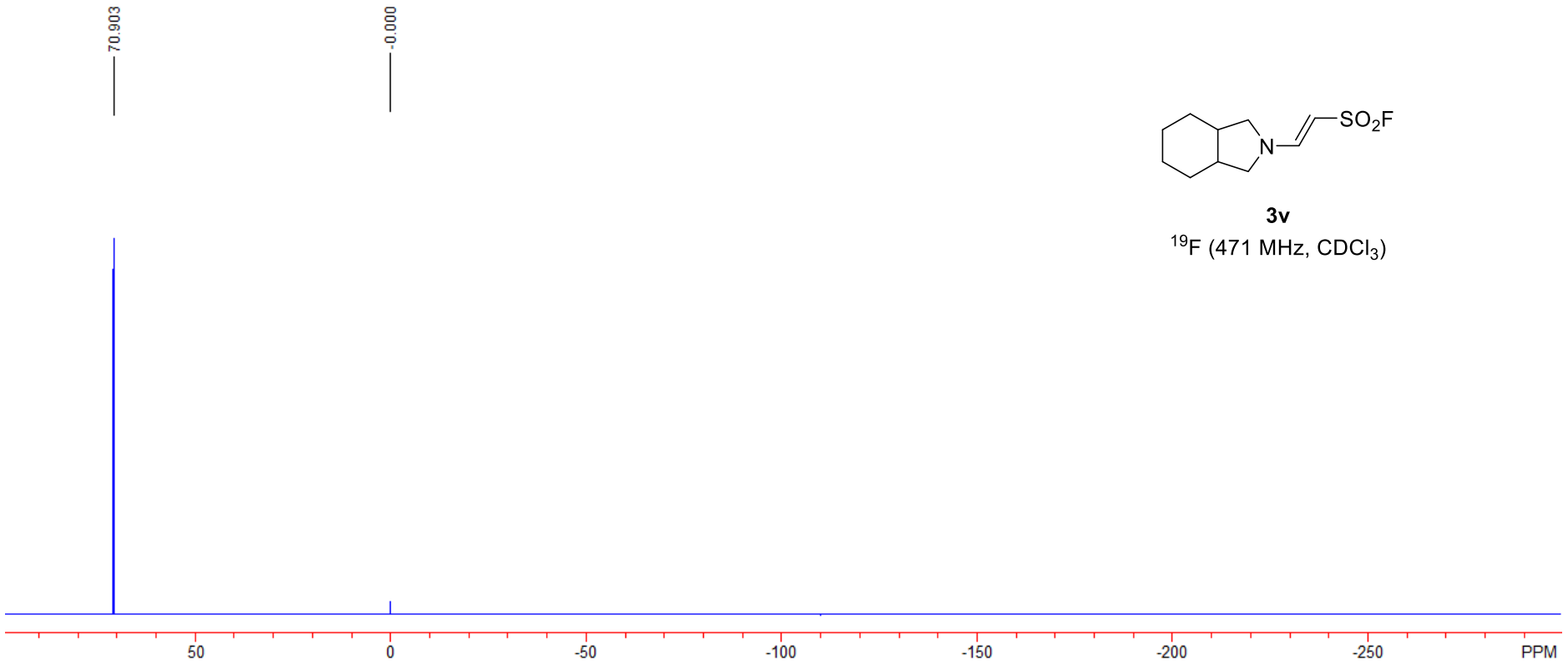
^{19}F (471 MHz, $CDCl_3$)



3v

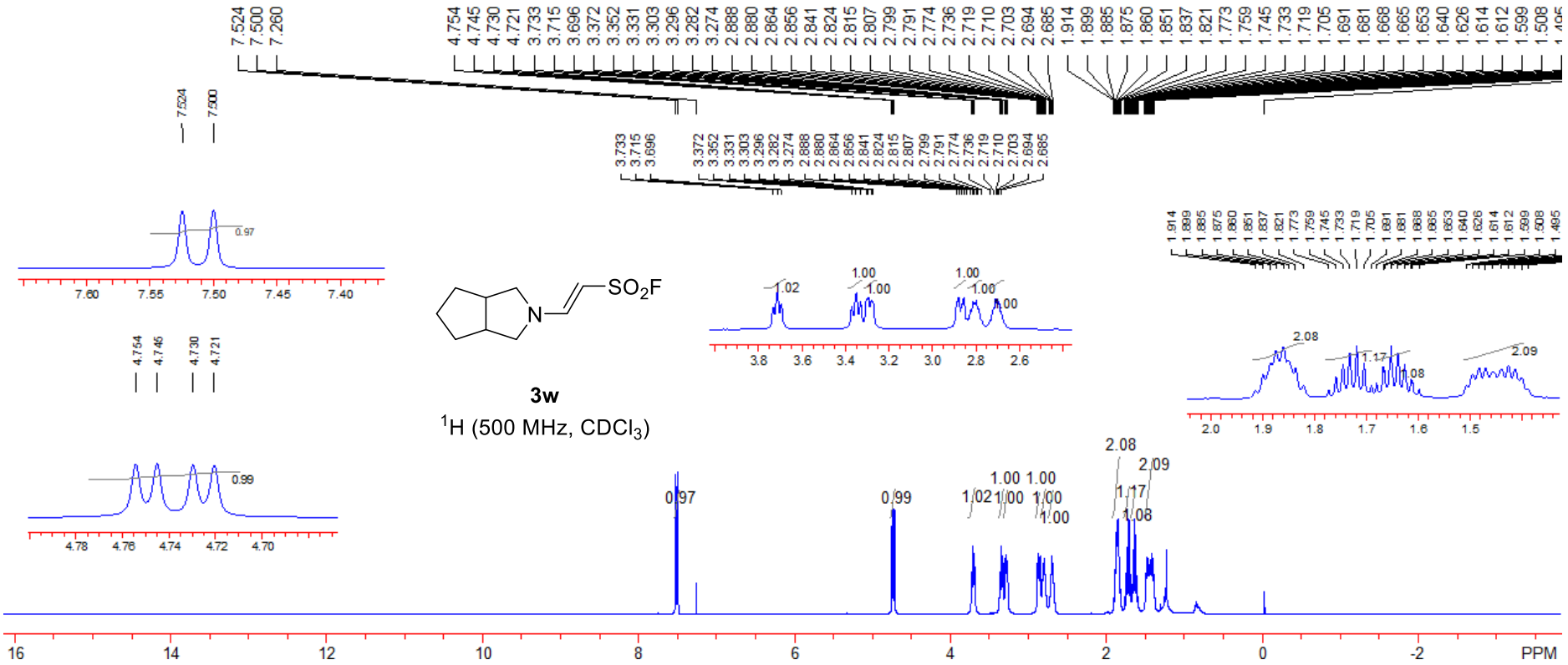
^{1}H (500 MHz, $CDCl_3$)

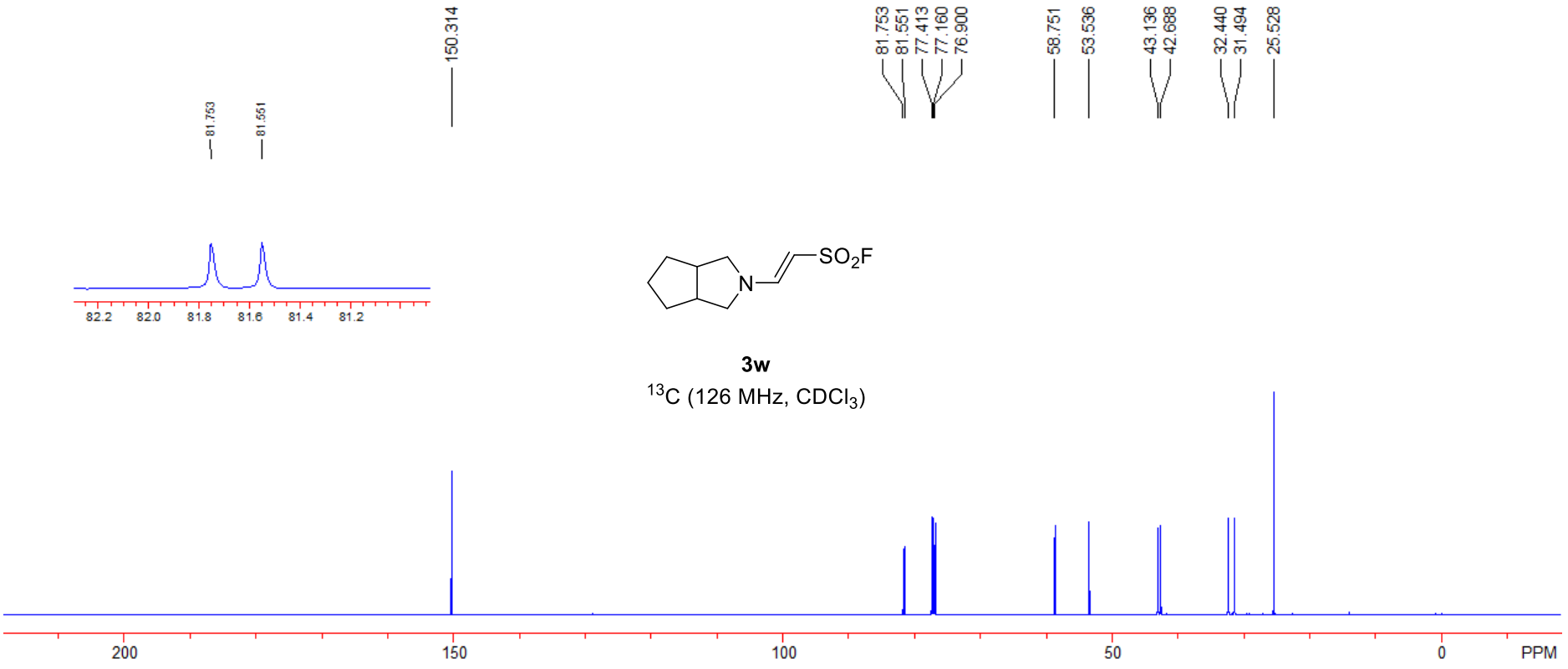

81.746
81.537
151.340
81.746
81.537
77.413
77.160
76.900
56.902
51.030
37.228
37.098
25.730
25.550
22.921
22.170
SO2F
N
3v
13C (126 MHz, CDCl3)
81.8
81.7
81.6
81.5
37.228
37.098
25.730
25.550
38
36
34
32
30
28
26
200
150
100
50
0
PPM



3v

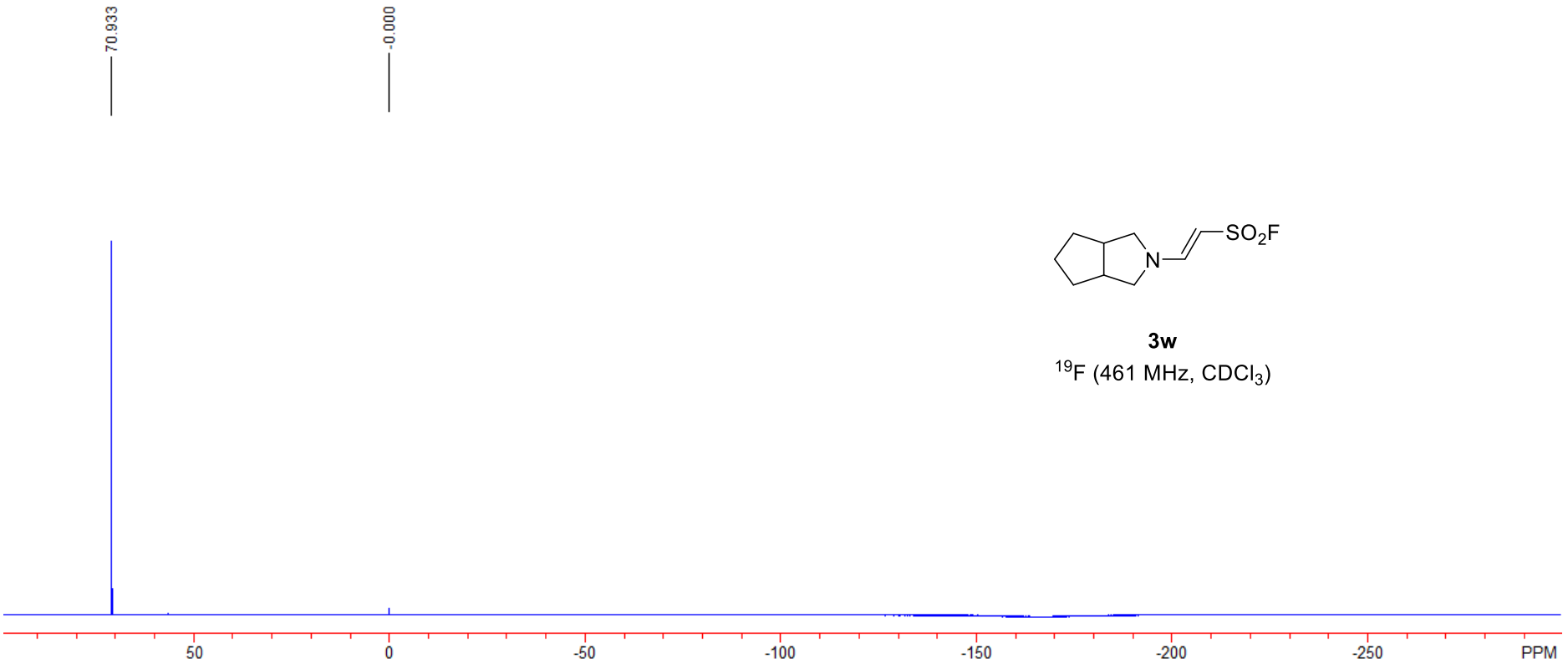
^{19}F (471 MHz, $CDCl_3$)


3w
1H (500 MHz, CDCl3)
SO2F
N
PPM



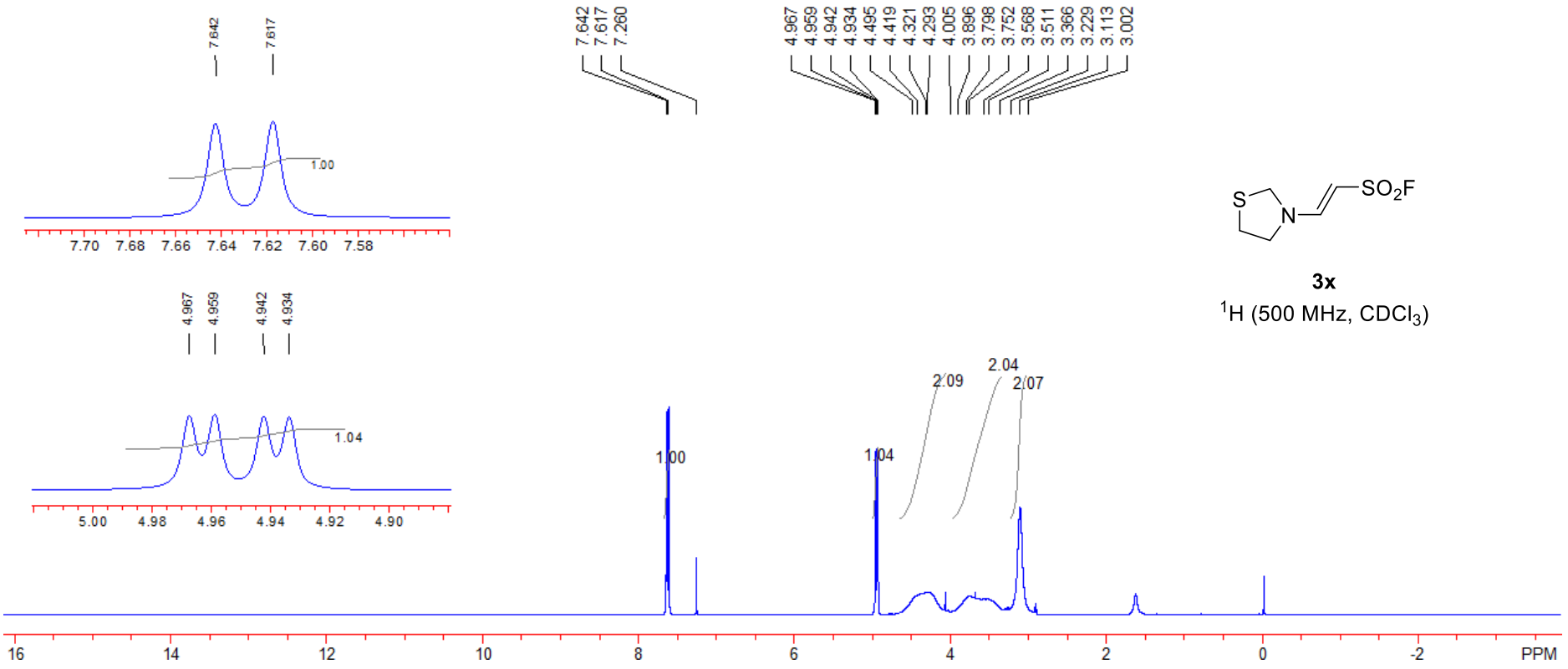
3w

^{13}C (126 MHz, $CDCl_3$)



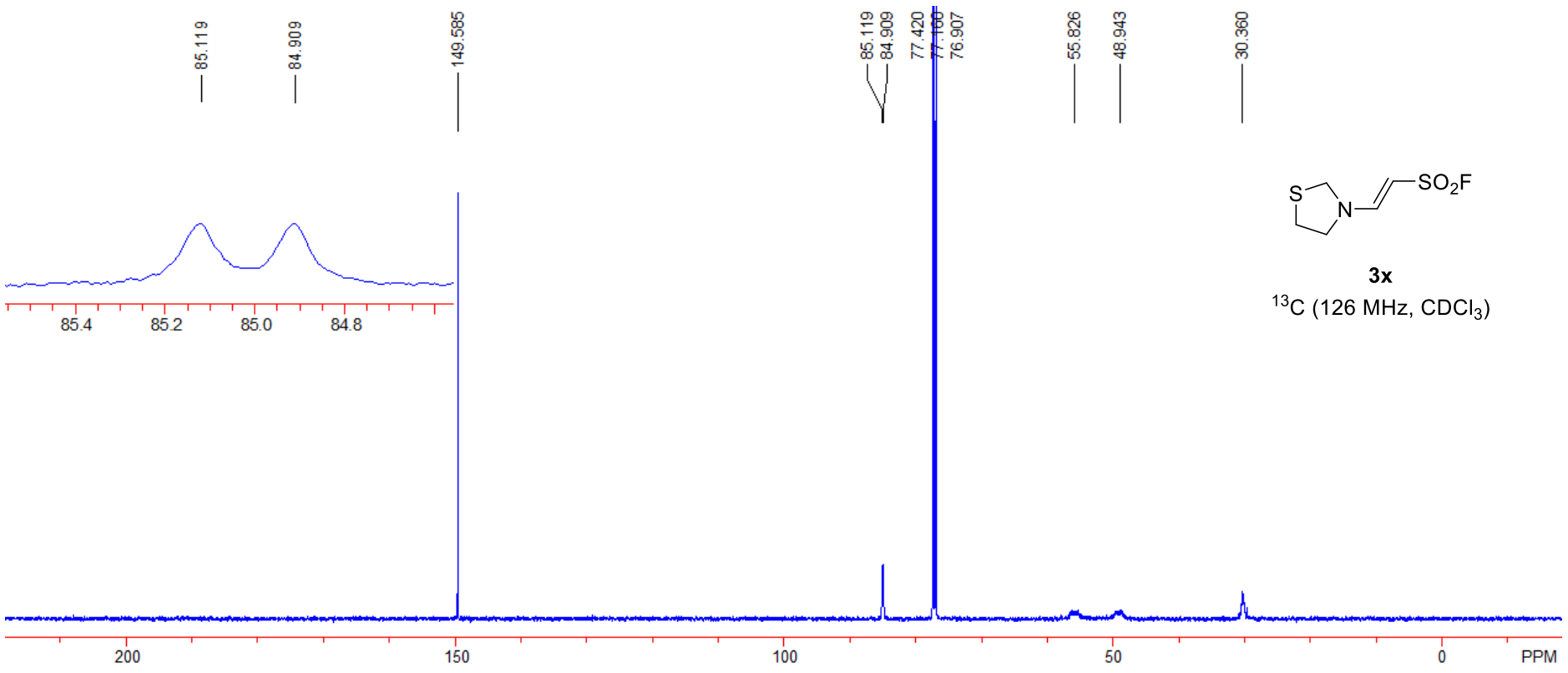
3w

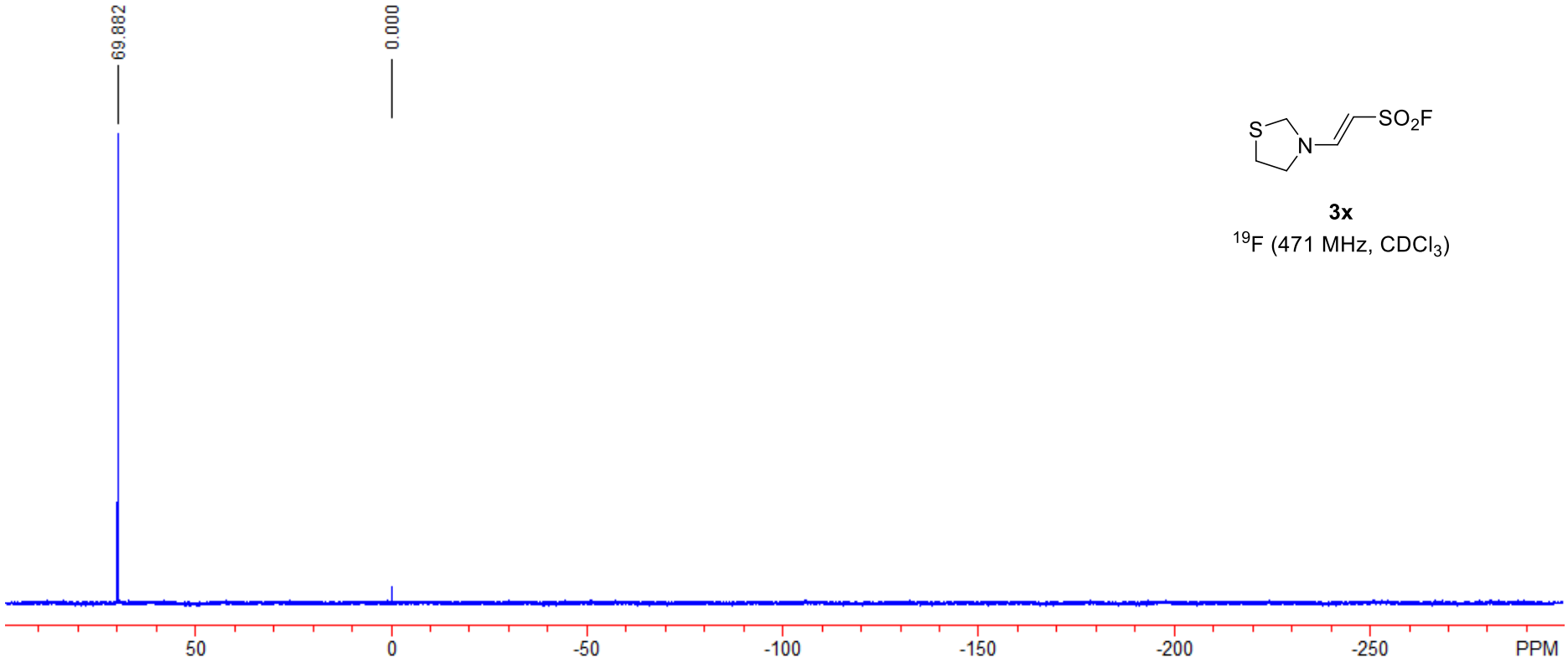
^{19}F (461 MHz, $CDCl_3$)



3x

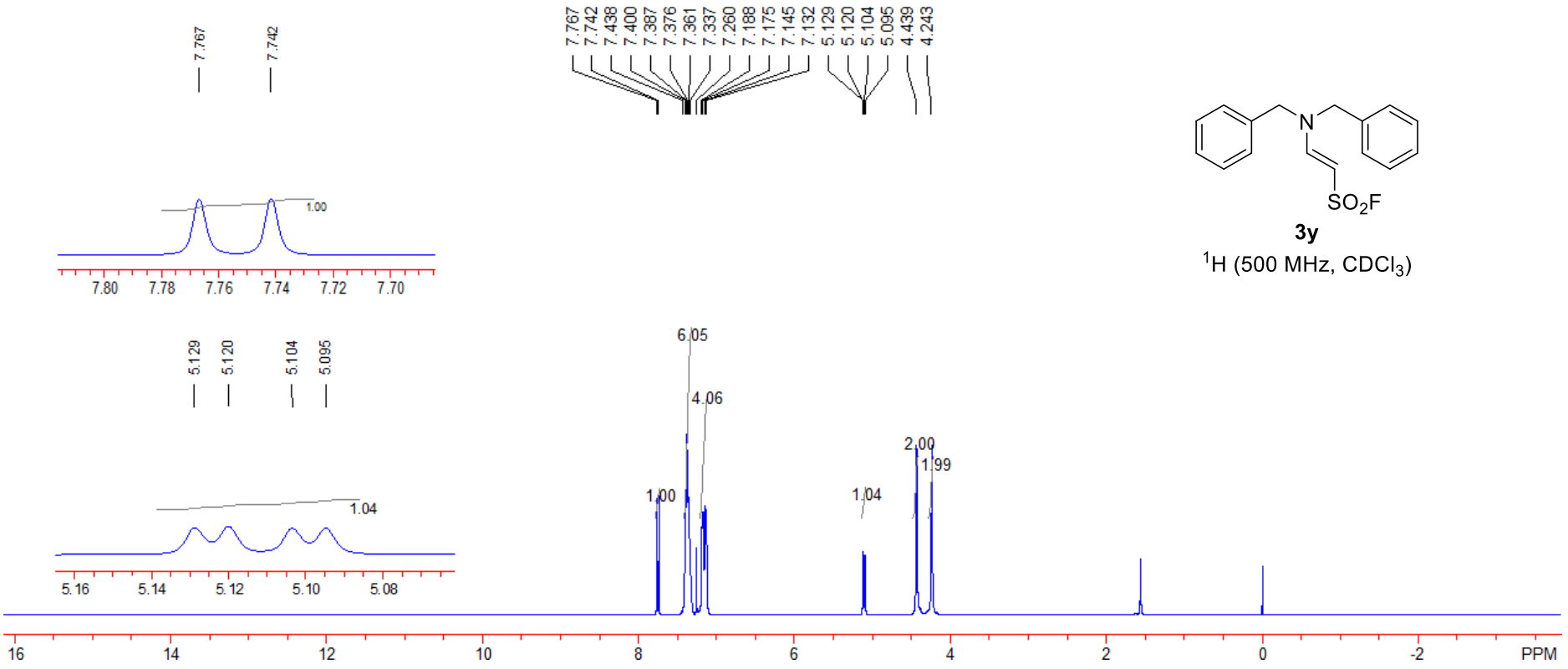
^{1}H (500 MHz, $CDCl_3$)

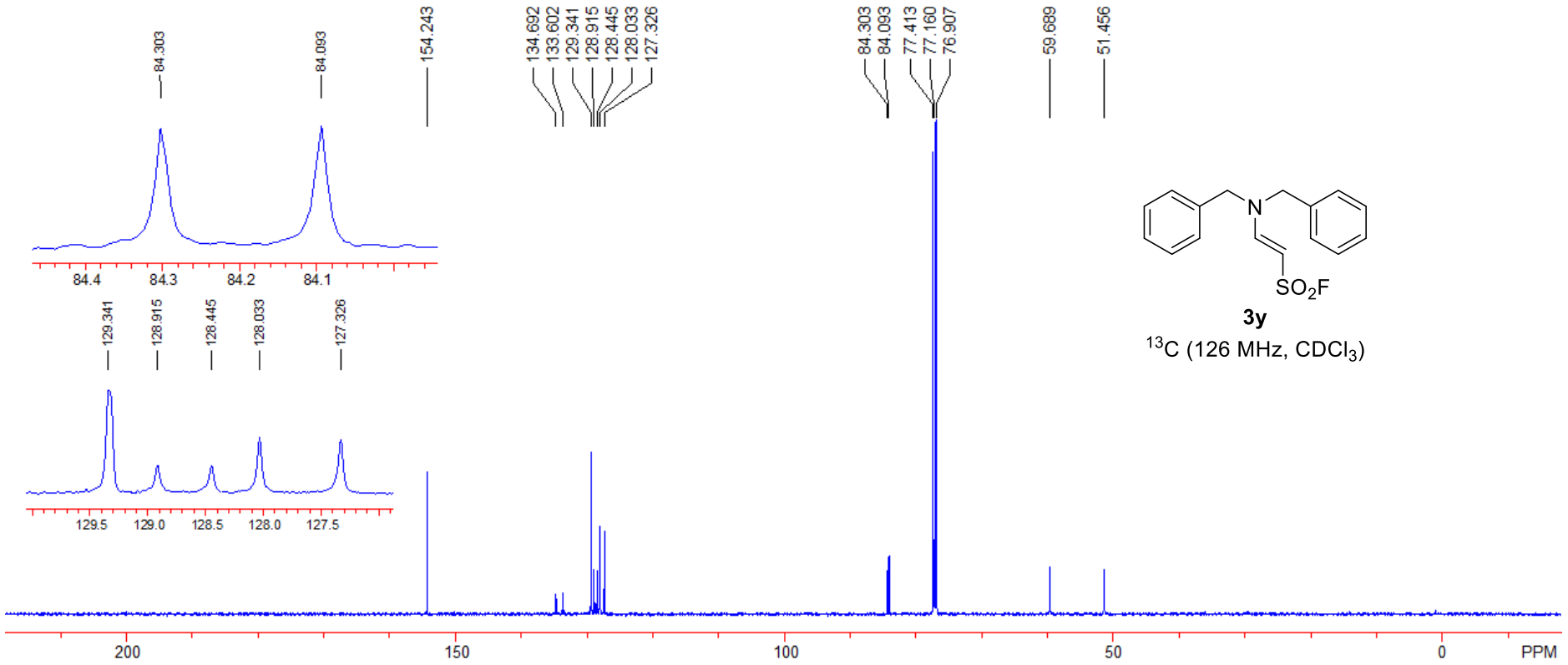

85.119
84.909
149.585
85.119
84.909
77.420
77.166
76.907
55.826
48.943
30.360
85.4
85.2
85.0
84.8
200
150
100
50
0
PPM
S
N
SO2F
3x
13C (126 MHz, CDCl3)

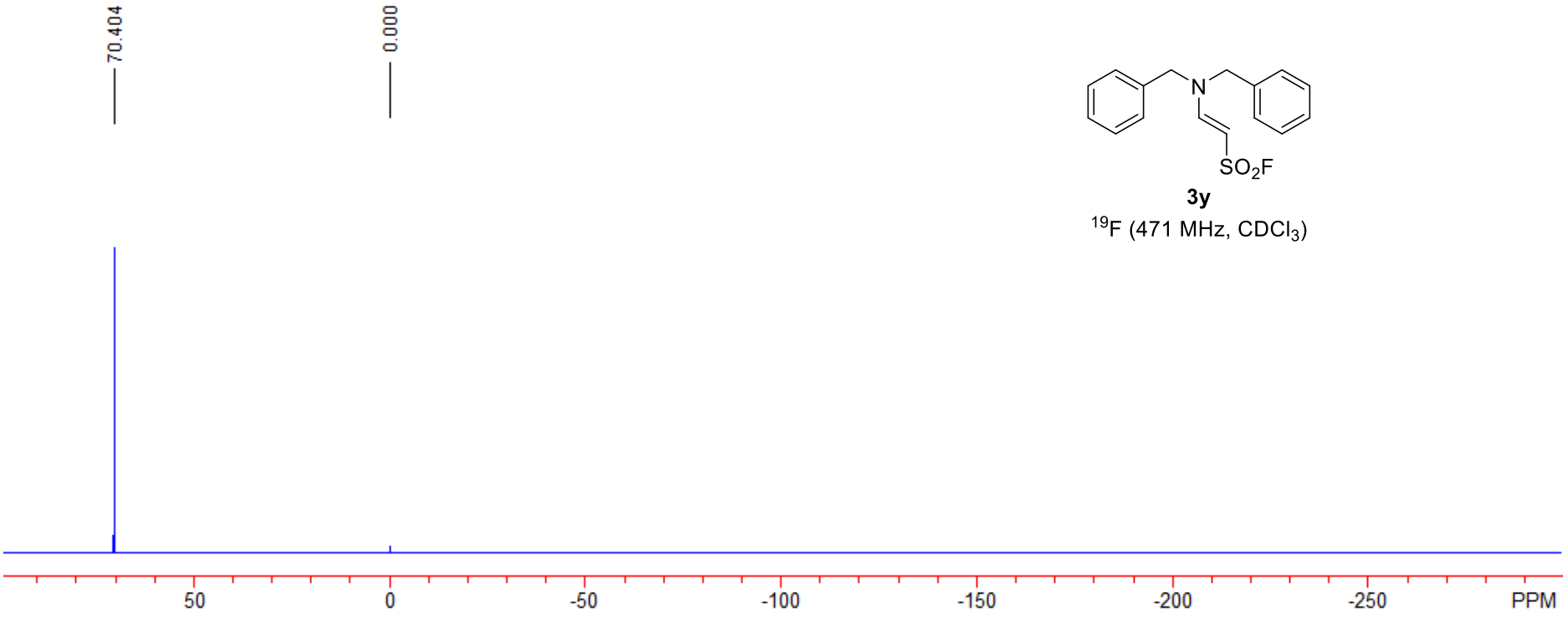


3x

^{19}F (471 MHz, $CDCl_3$)

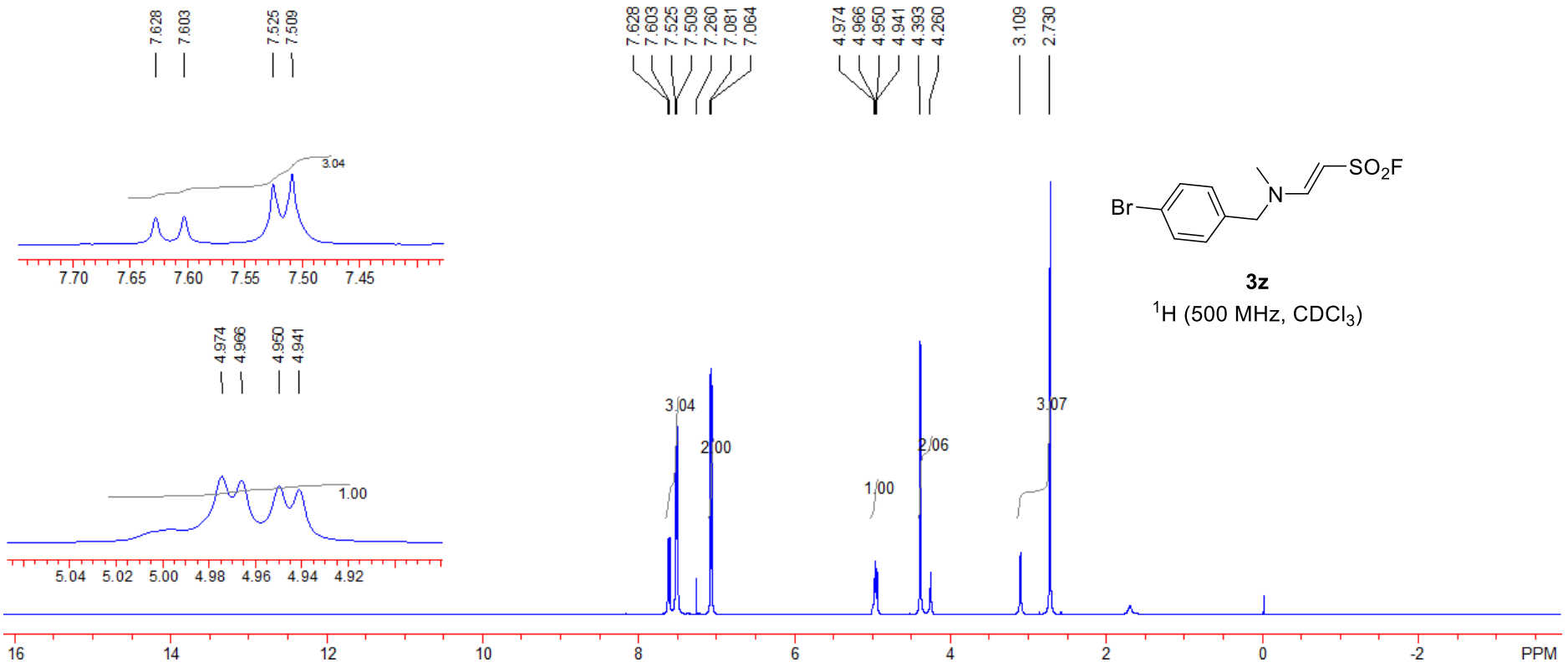

7.767
7.742
7.438
7.400
7.387
7.376
7.361
7.337
7.260
7.188
7.175
7.145
7.132
5.129
5.120
5.104
5.095
4.439
4.243
N
SO2F
3y
1H (500 MHz, CDCl3)
1.00
7.80
7.78
7.76
7.74
7.72
7.70
5.129
5.120
5.104
5.095
1.04
5.16
5.14
5.12
5.10
5.08
6.05
4.06
1.00
1.04
2.00
1.99
16
14
12
10
8
6
4
2
0
-2
PPM

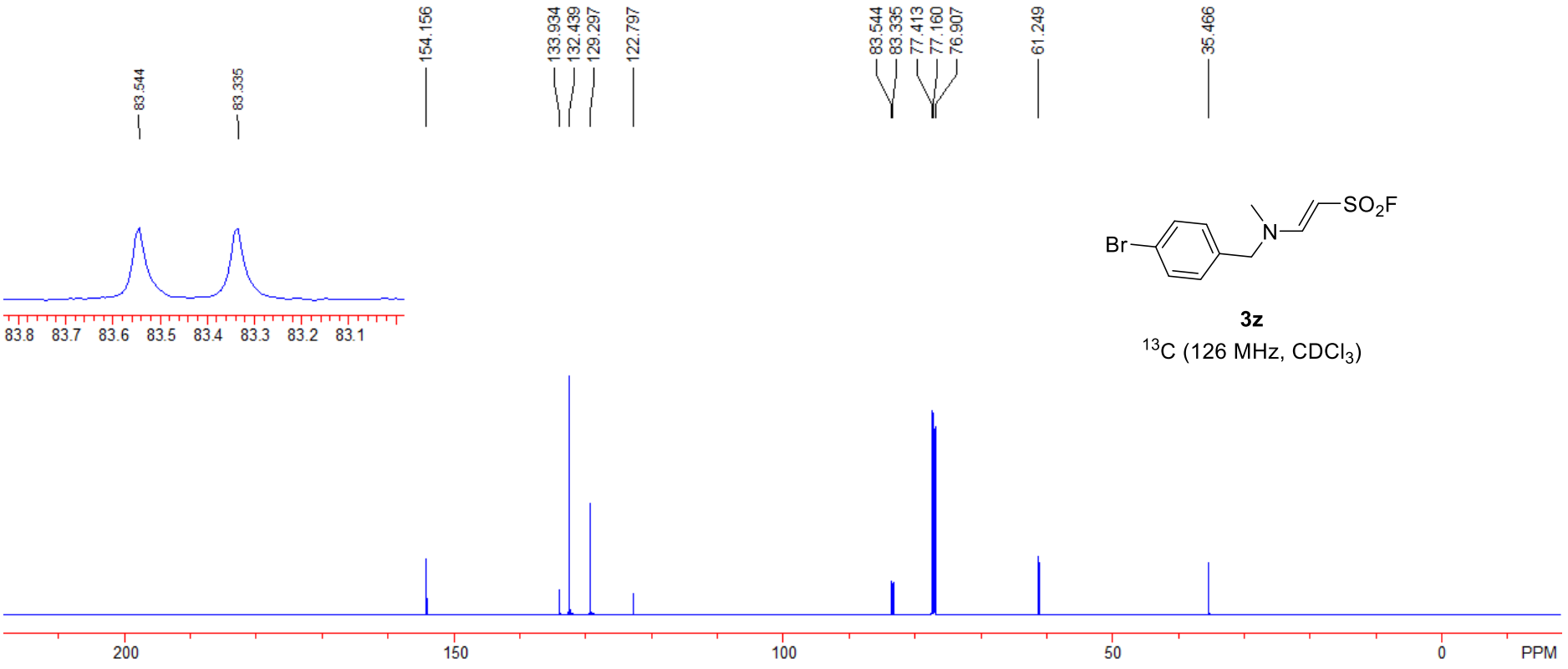

84.303
84.093
154.243
134.692
133.602
129.341
128.915
128.445
128.033
127.326
84.303
84.093
77.413
77.160
76.907
59.689
51.456
84.4
84.3
84.2
84.1
129.341
128.915
128.445
128.033
127.326
129.5
129.0
128.5
128.0
127.5
200
150
100
50
0
PPM
N
SO2F
3y
13C (126 MHz, CDCl3)

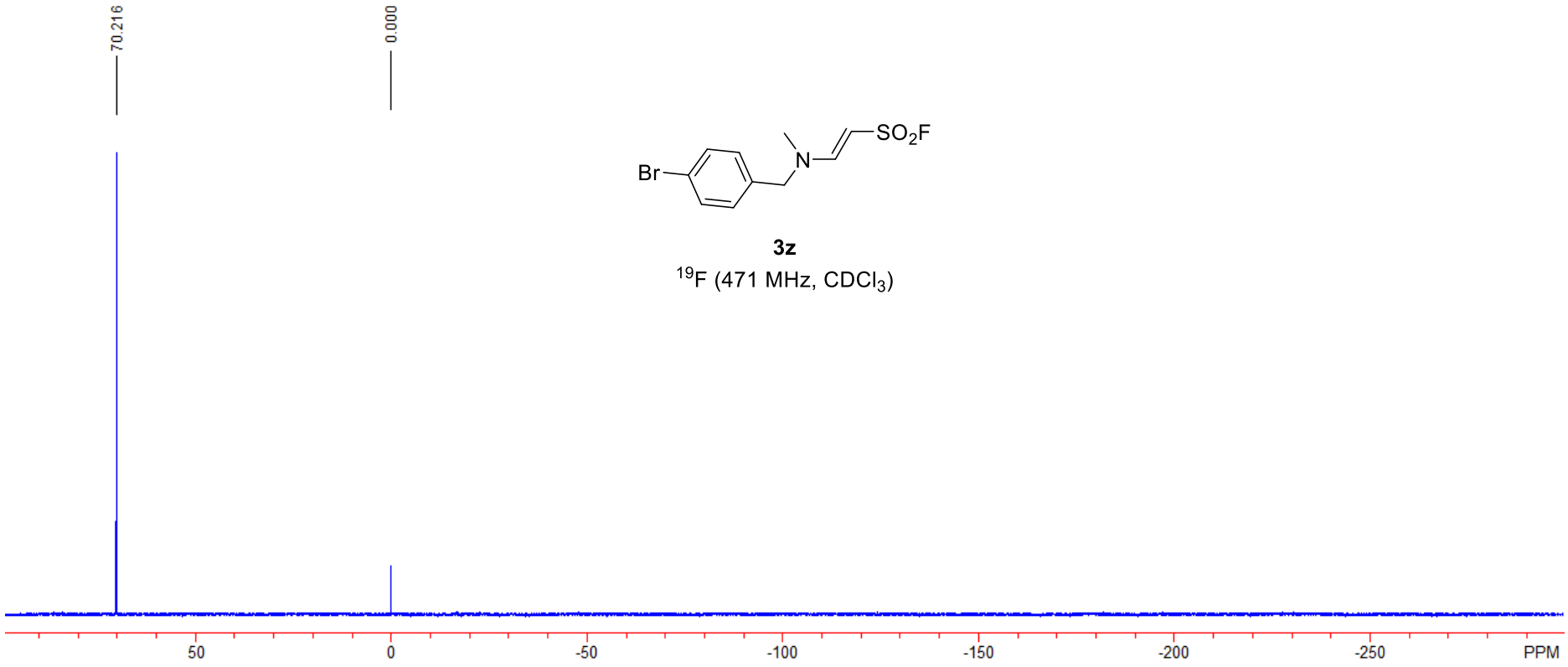


3y

^{19}F (471 MHz, $CDCl_3$)

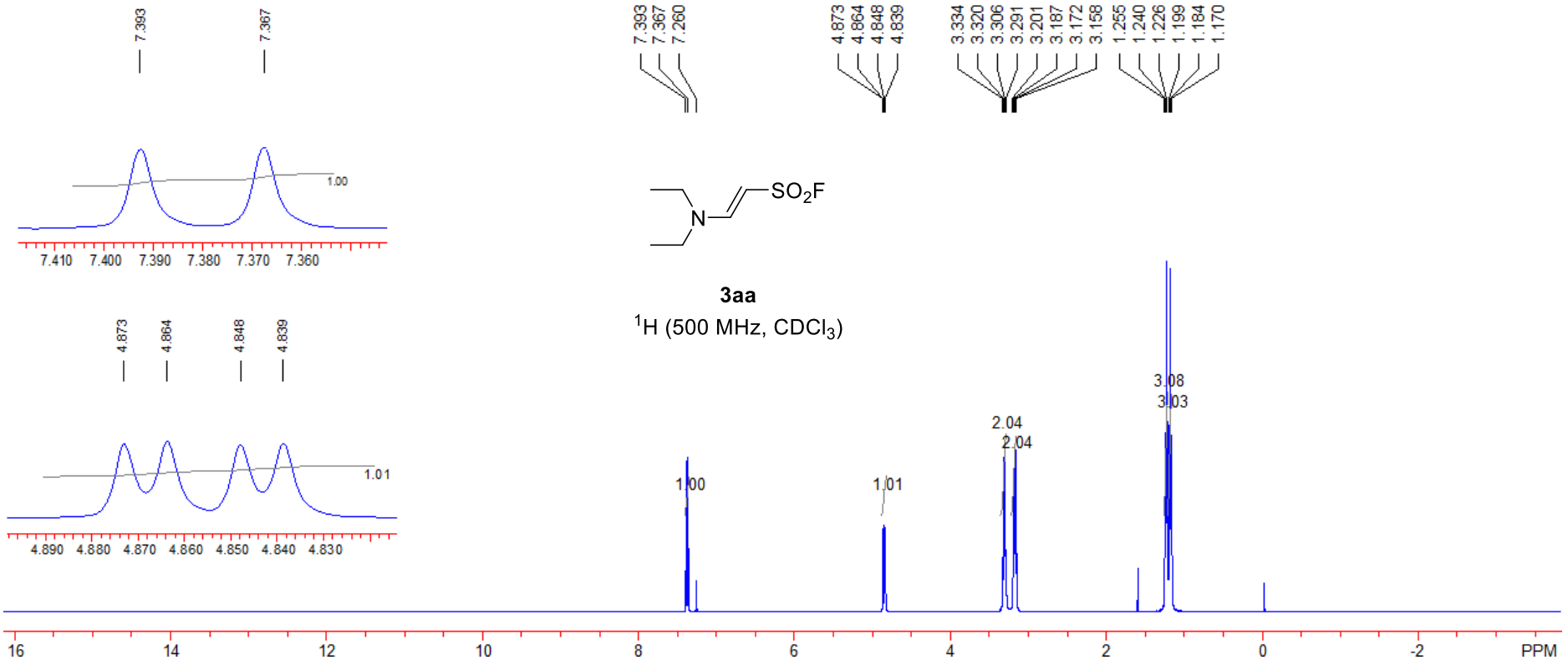

7.628
7.603
7.525
7.509
7.260
7.081
7.064
4.974
4.966
4.950
4.941
4.393
4.260
3.109
2.730
3.04
7.70 7.65 7.60 7.55 7.50 7.45
4.974
4.966
4.950
4.941
1.00
5.04 5.02 5.00 4.98 4.96 4.94 4.92
3.04
2.00
1.00
2.06
3.07
16 14 12 10 8 6 4 2 0 -2 PPM
Br
N
SO2F
3z
1H (500 MHz, CDCl3)

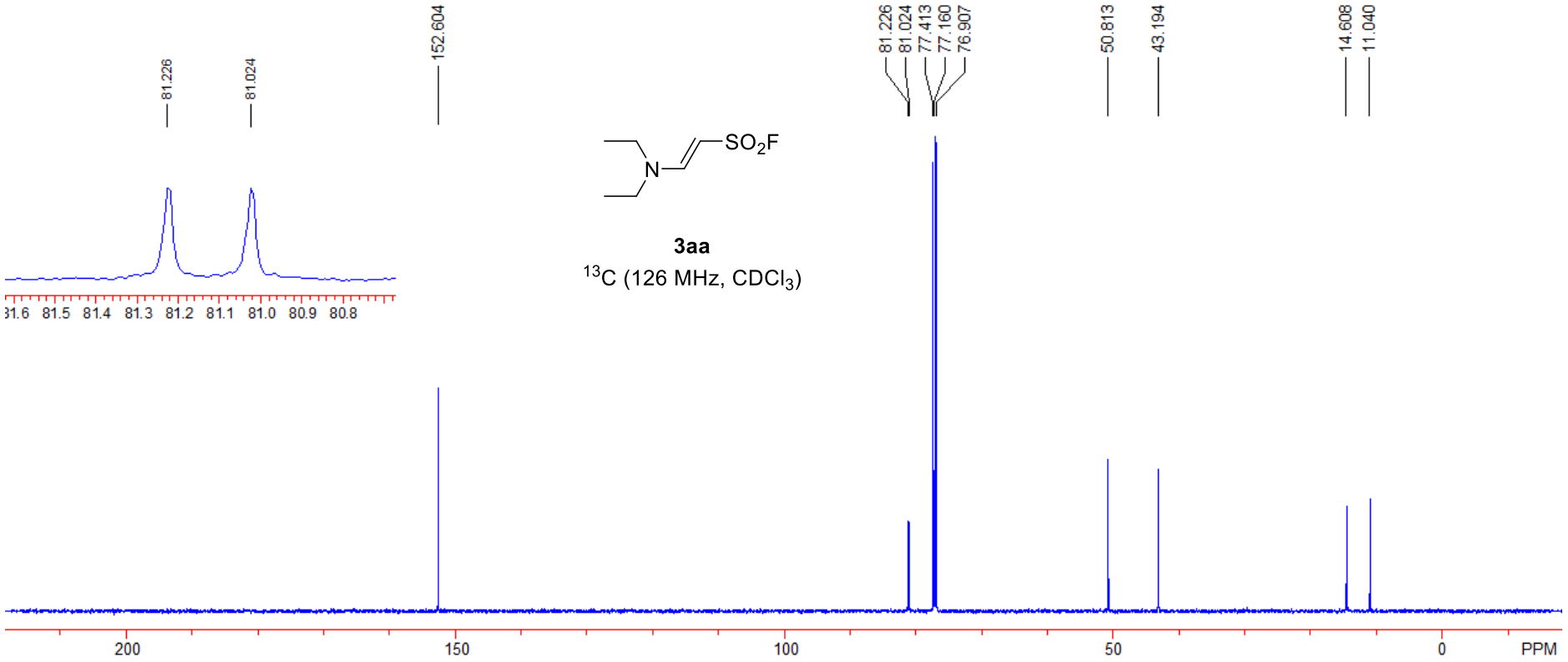

83.544
83.335
154.156
133.934
132.439
129.297
122.797
83.544
83.335
77.413
77.160
76.907
61.249
35.466
83.8 83.7 83.6 83.5 83.4 83.3 83.2 83.1
Br
N
SO2F
3z
13C (126 MHz, CDCl3)
200 150 100 50 0 PPM

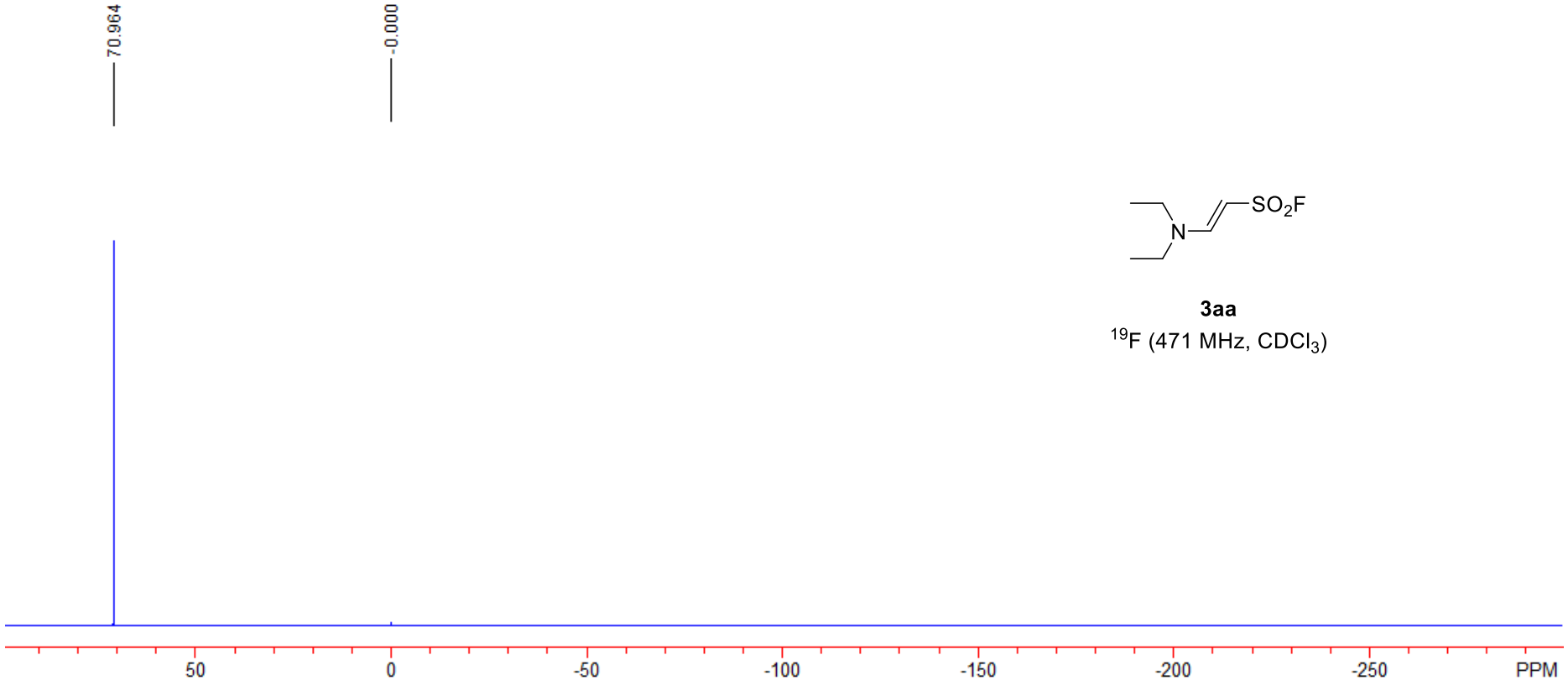


3z

^{19}F (471 MHz, $CDCl_3$)

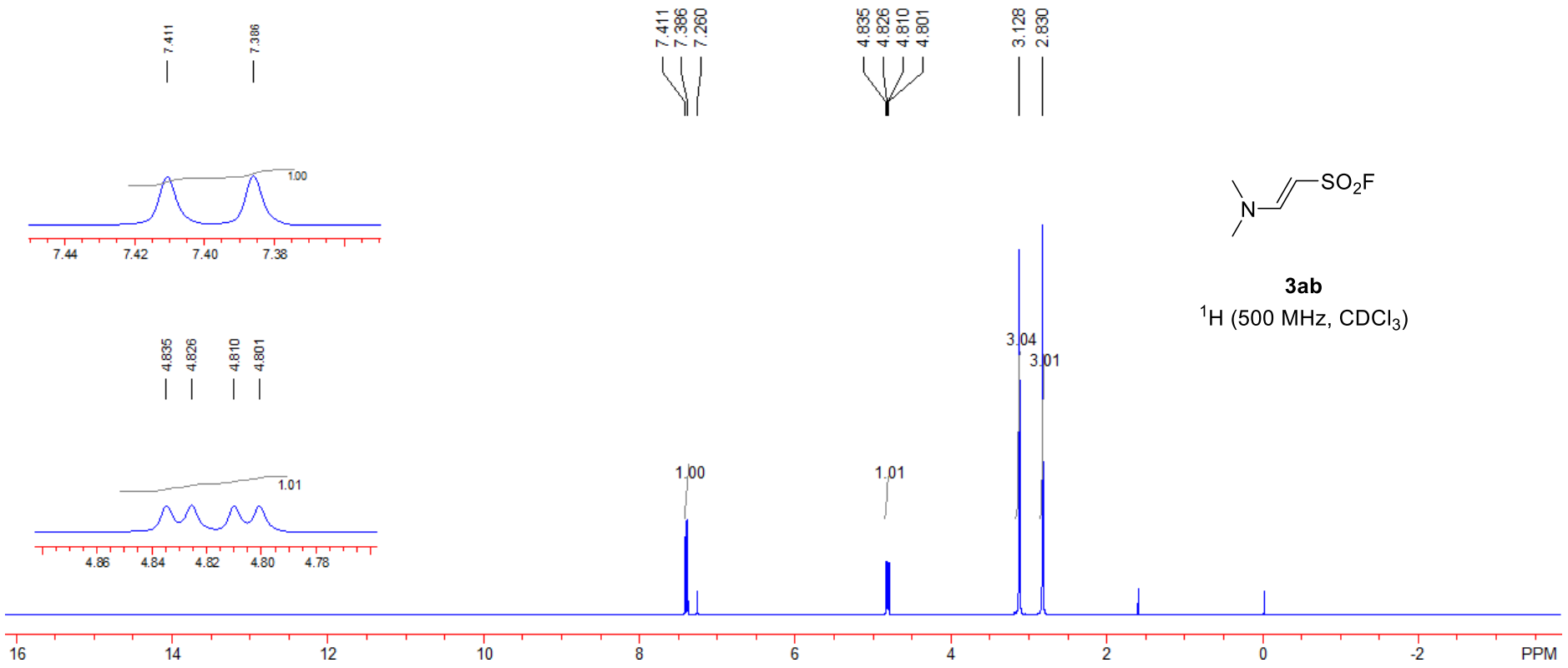

7.393
7.367
7.260
4.873
4.864
4.848
4.839
3.334
3.320
3.306
3.291
3.201
3.187
3.172
3.158
1.255
1.240
1.226
1.199
1.184
1.170
SO2F
N
3aa
1H (500 MHz, CDCl3)
1.00
1.01
2.04
2.04
3.08
3.03
PPM

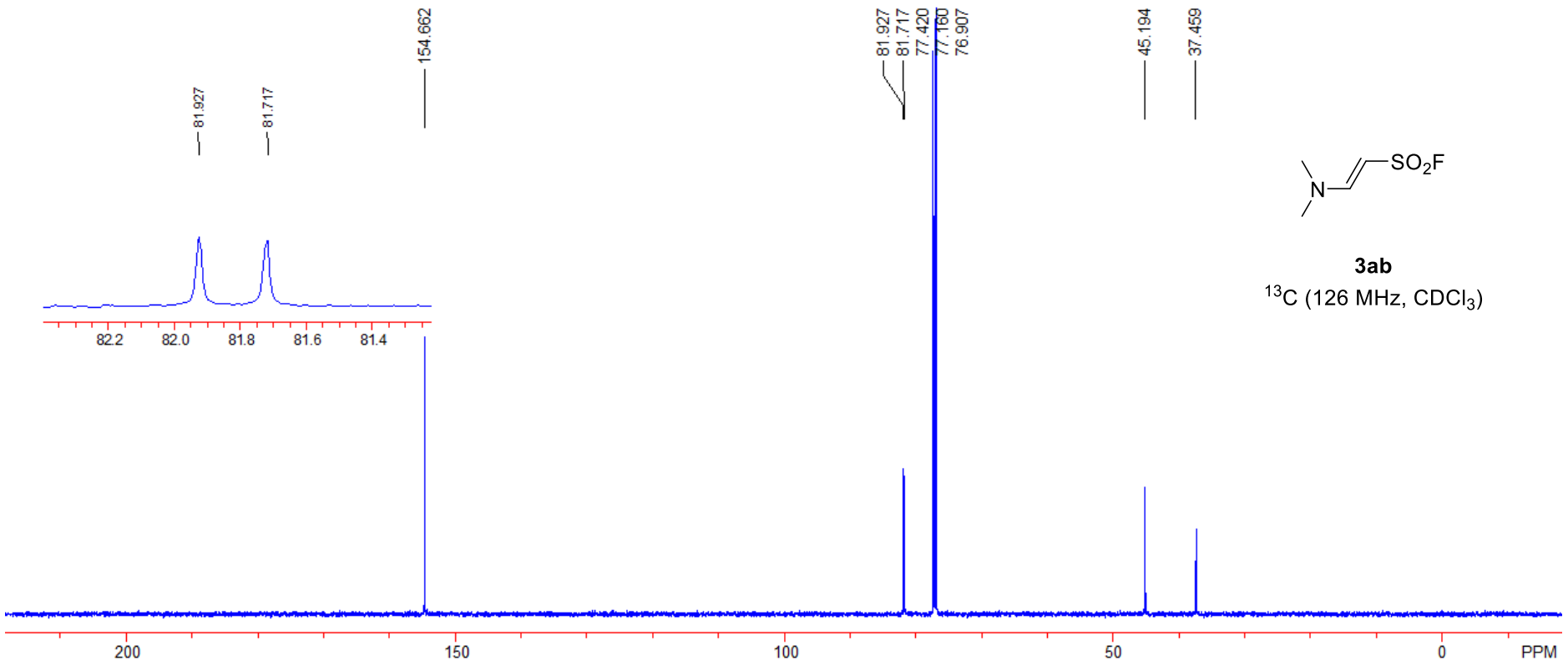

81.226
81.024
152.604
81.226
81.024
77.413
77.160
76.907
50.813
43.194
14.608
11.040
SO2F
N
3aa
13C (126 MHz, CDCl3)
81.6 81.5 81.4 81.3 81.2 81.1 81.0 80.9 80.8
200
150
100
50
0
PPM

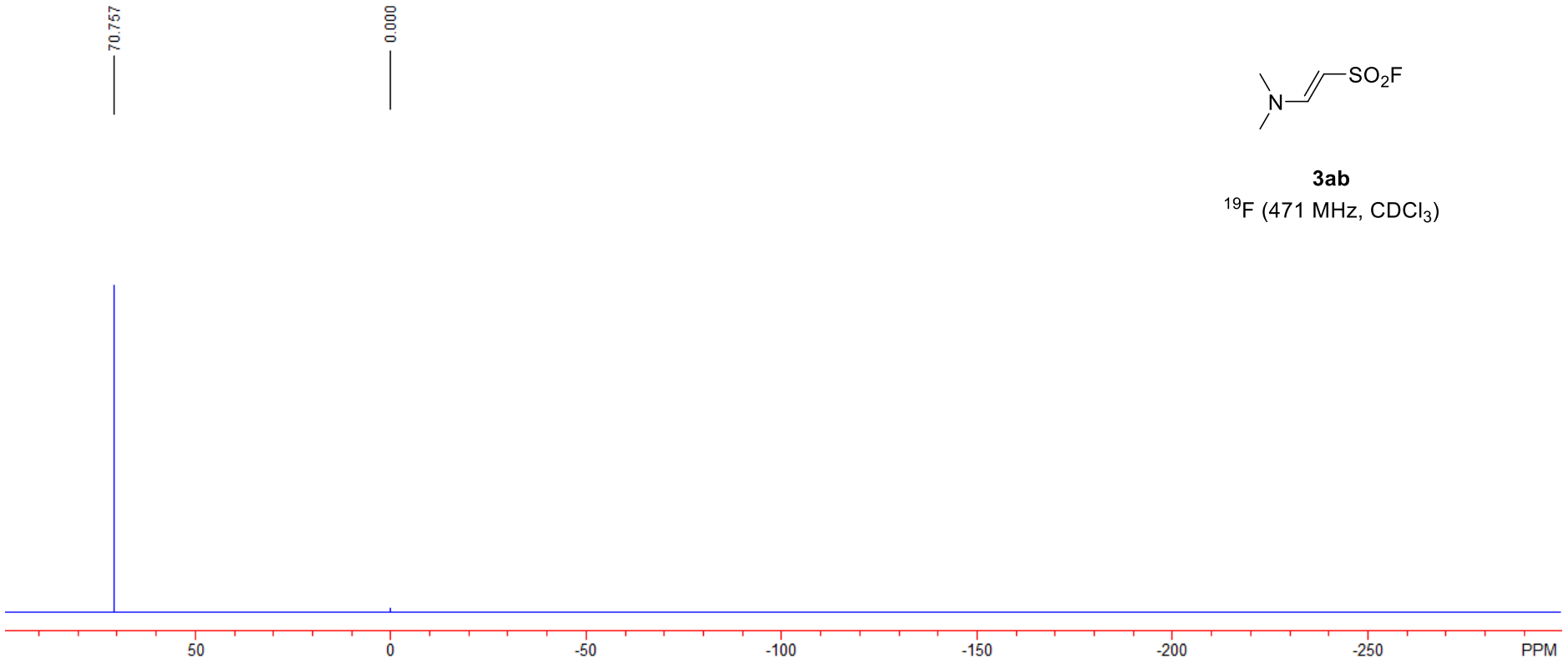


3aa

^{19}F (471 MHz, $CDCl_3$)

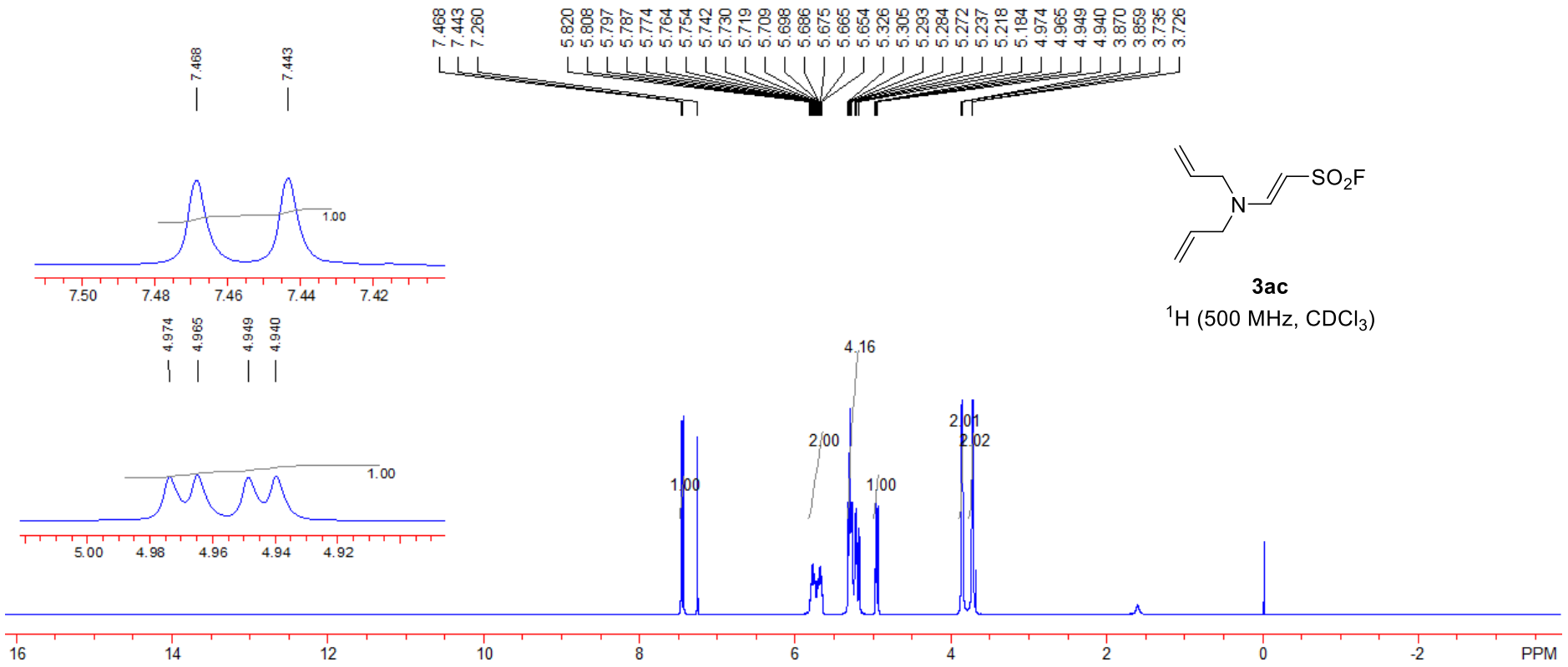

7.411
7.386
7.260
4.835
4.826
4.810
4.801
3.128
2.830
1.00
1.01
3.04
3.01
SO2F
N
3ab
1H (500 MHz, CDCl3)
PPM


154.662
81.927
81.717
77.420
77.160
76.907
45.194
37.459
81.927
81.717
82.2
82.0
81.8
81.6
81.4
200
150
100
50
0
PPM
SO2F
N
3ab
13C (126 MHz, CDCl3)



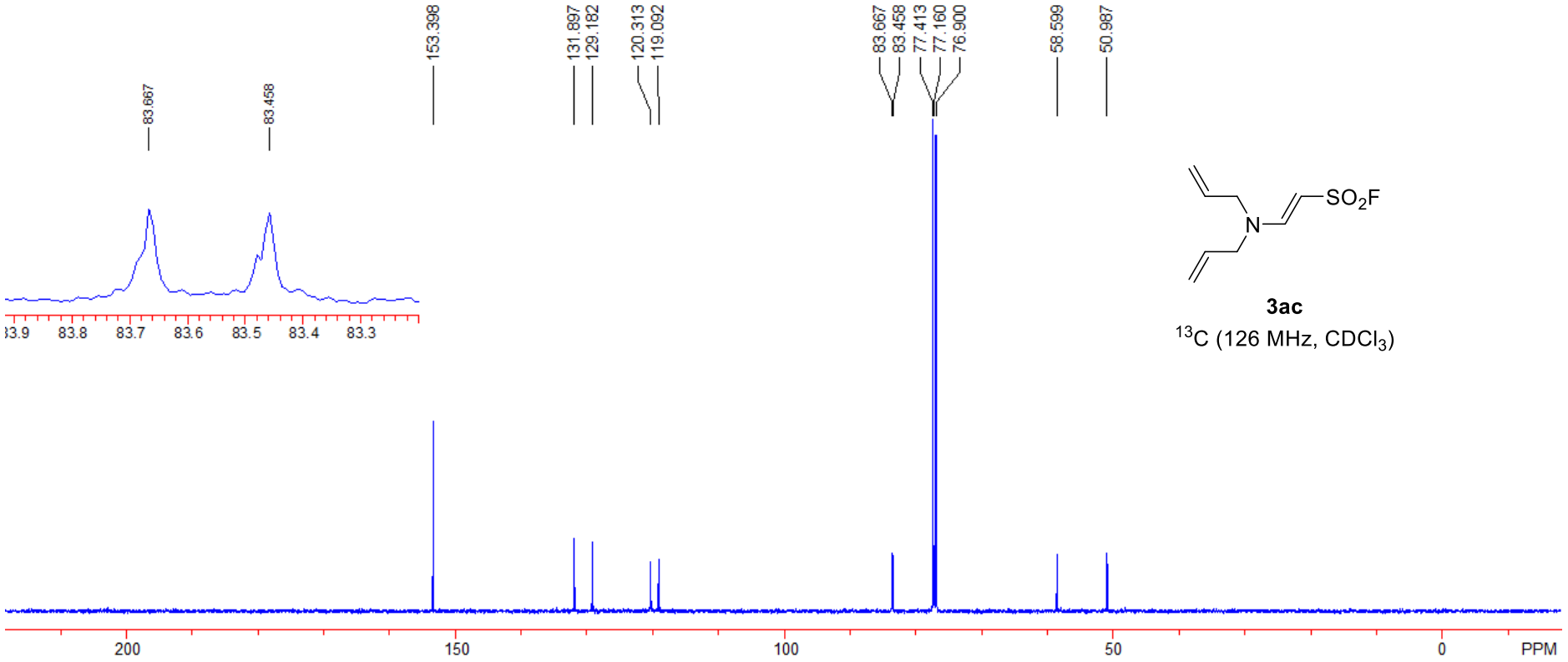
3ab

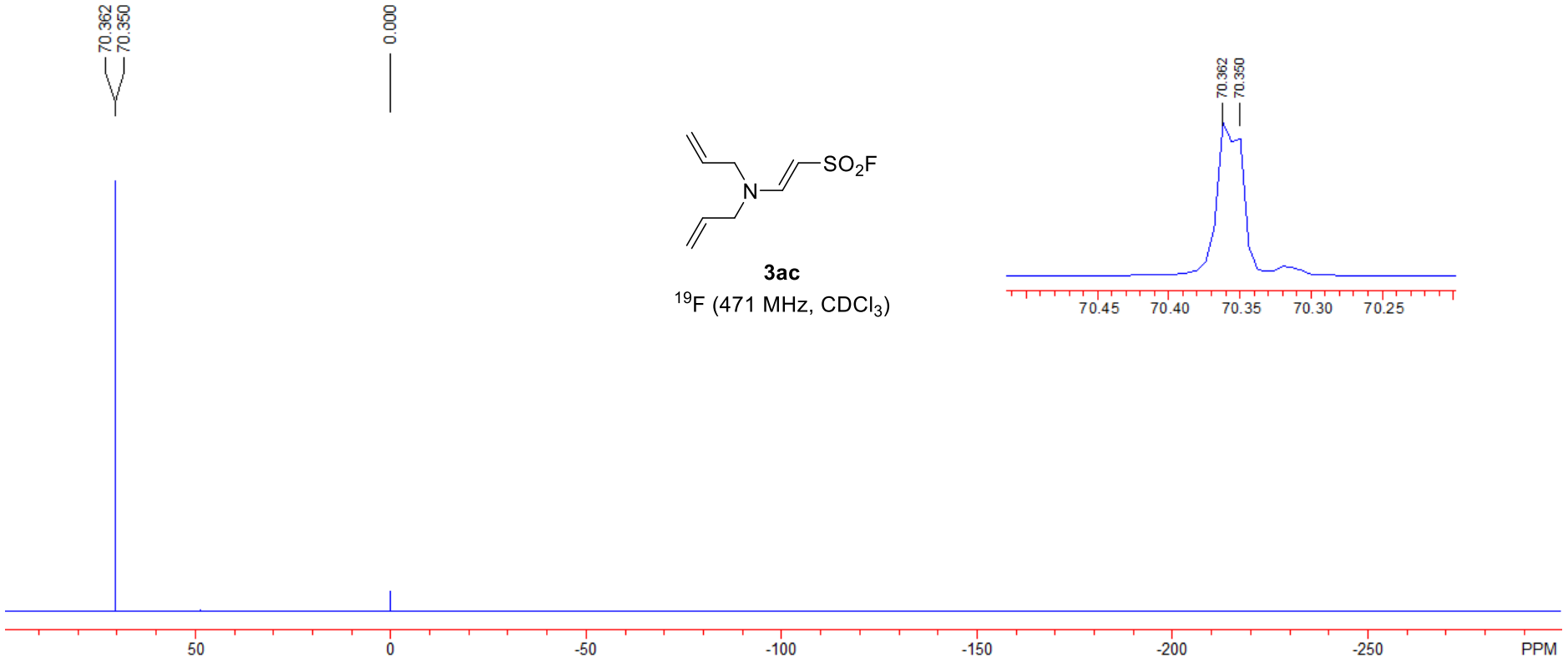
^{19}F (471 MHz, $CDCl_3$)



3ac

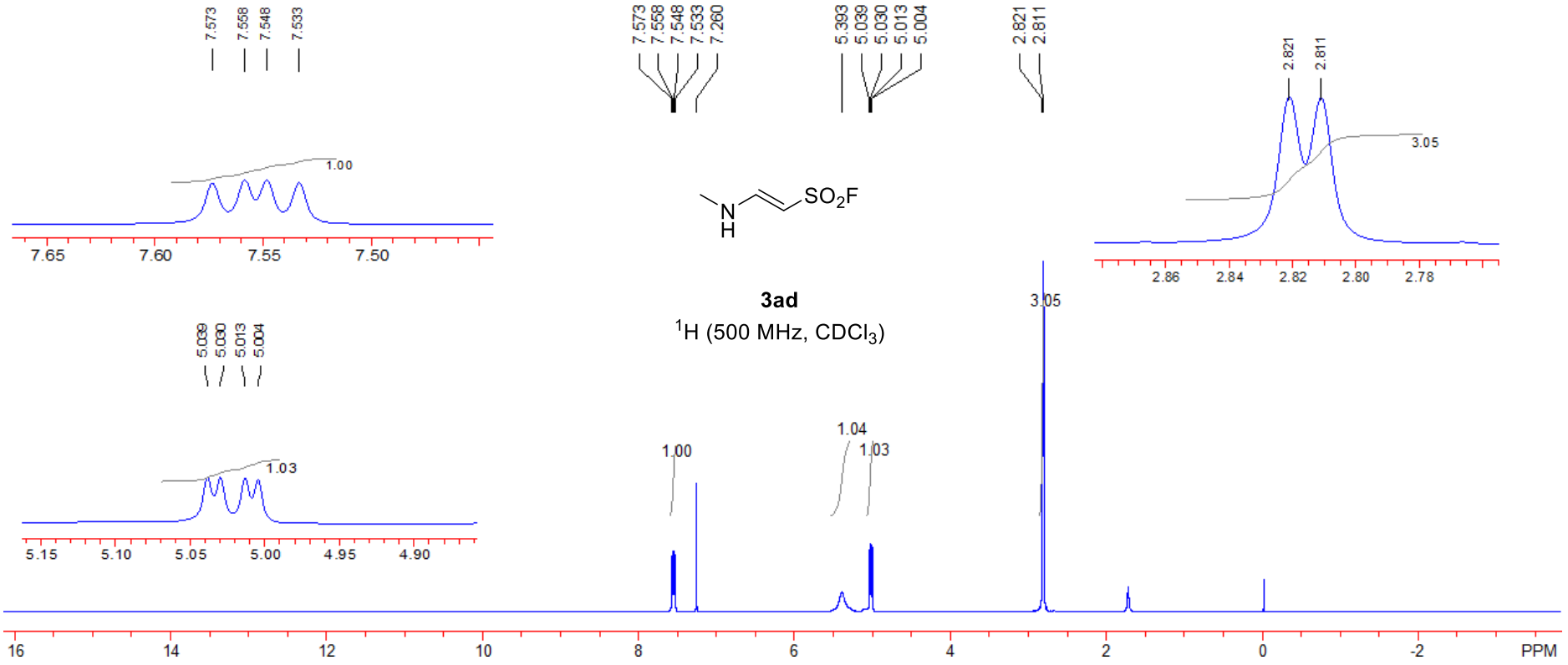
^{1}H (500 MHz, $CDCl_3$)

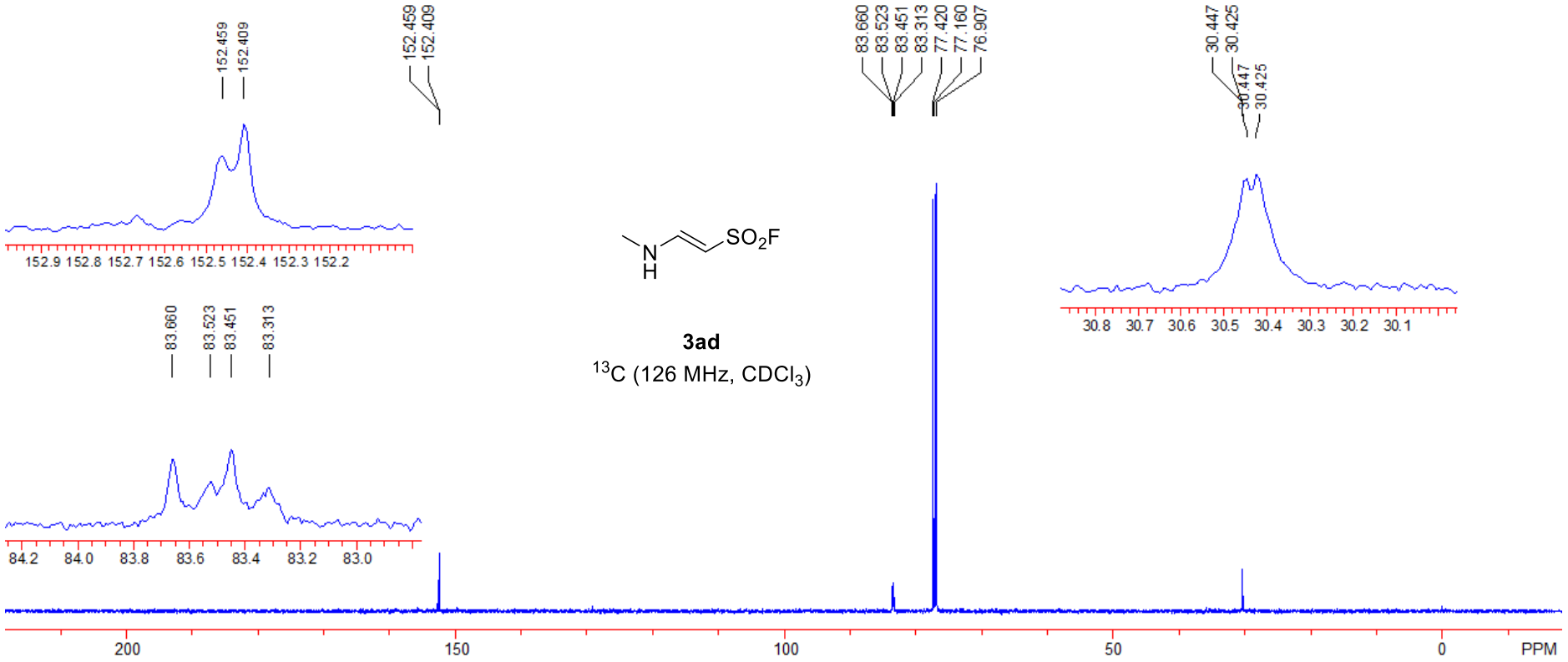

153.398
131.897
129.182
120.313
119.092
83.667
83.458
77.413
77.160
76.900
58.599
50.987
83.667
83.458
83.9
83.8
83.7
83.6
83.5
83.4
83.3
200
150
100
50
0
PPM
SO2F
N
3ac
13C (126 MHz, CDCl3)

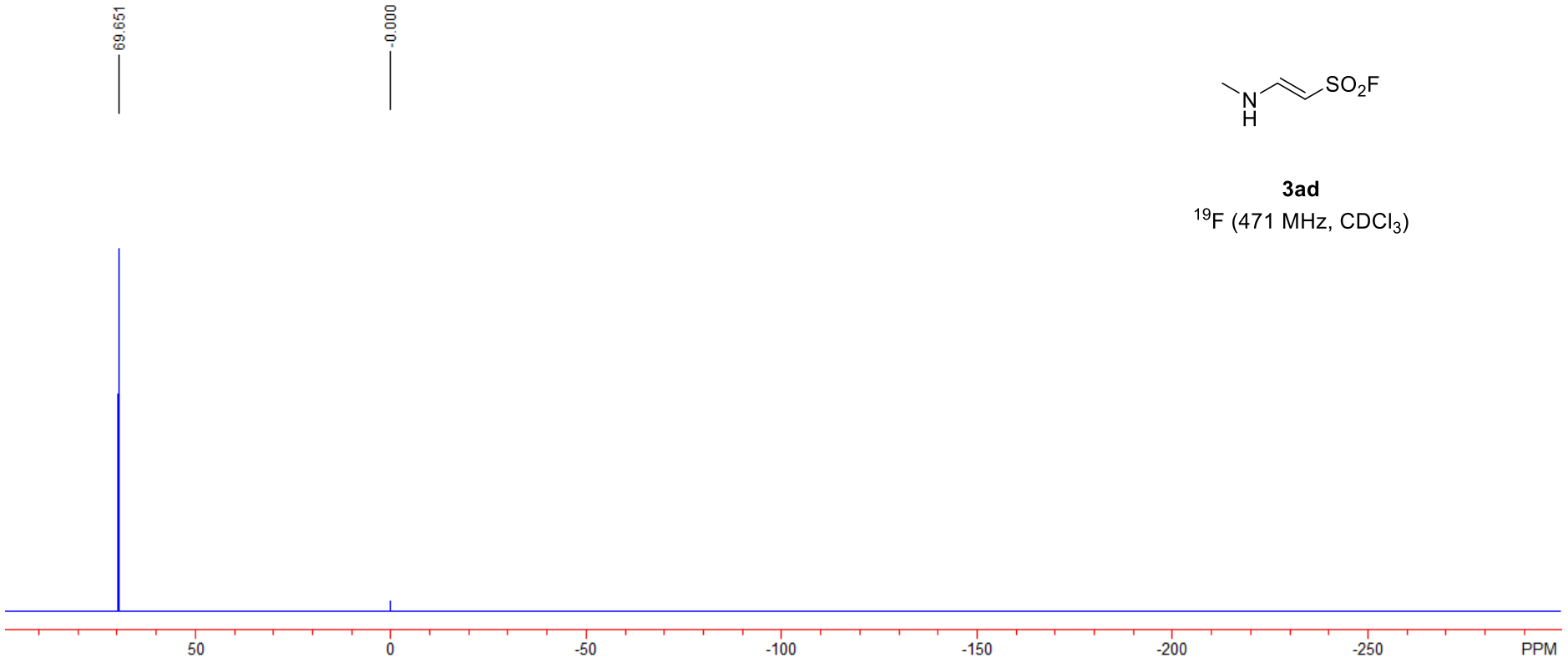


3ac

^{19}F (471 MHz, $CDCl_3$)

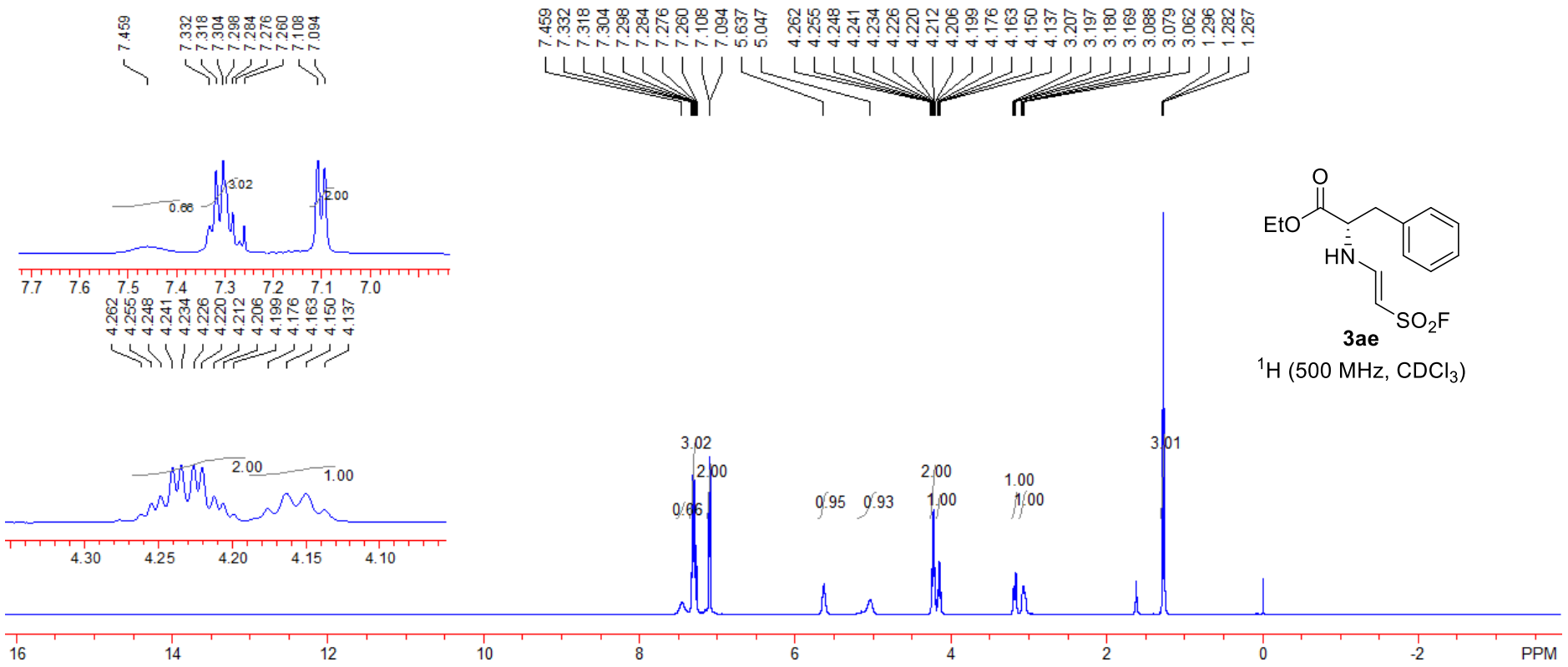

7.573
7.558
7.548
7.533
7.260
5.393
5.039
5.030
5.013
5.004
2.821
2.811
1.00
3.05
SO_2F
N
H
3ad
^{1}H (500 MHz, $CDCl_3$)
1.03
1.04
16
14
12
10
8
6
4
2
0
-2
PPM

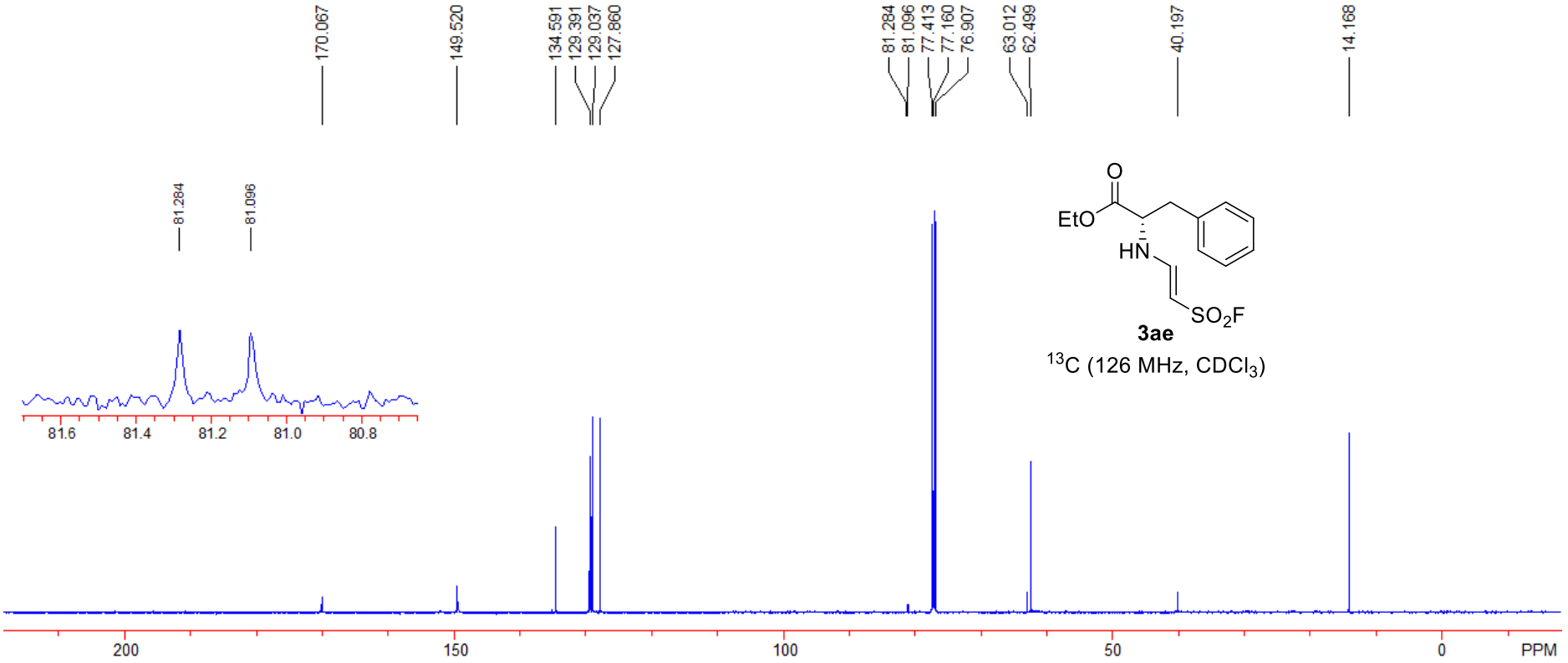

152.459
152.409
83.660
83.523
83.451
83.313
77.420
77.160
76.907
30.447
30.425
30.447
30.425
152.9 152.8 152.7 152.6 152.5 152.4 152.3 152.2
83.660
83.523
83.451
83.313
84.2 84.0 83.8 83.6 83.4 83.2 83.0
30.8 30.7 30.6 30.5 30.4 30.3 30.2 30.1
N
H
SO2F
3ad
13C (126 MHz, CDCl3)
200
150
100
50
0
PPM

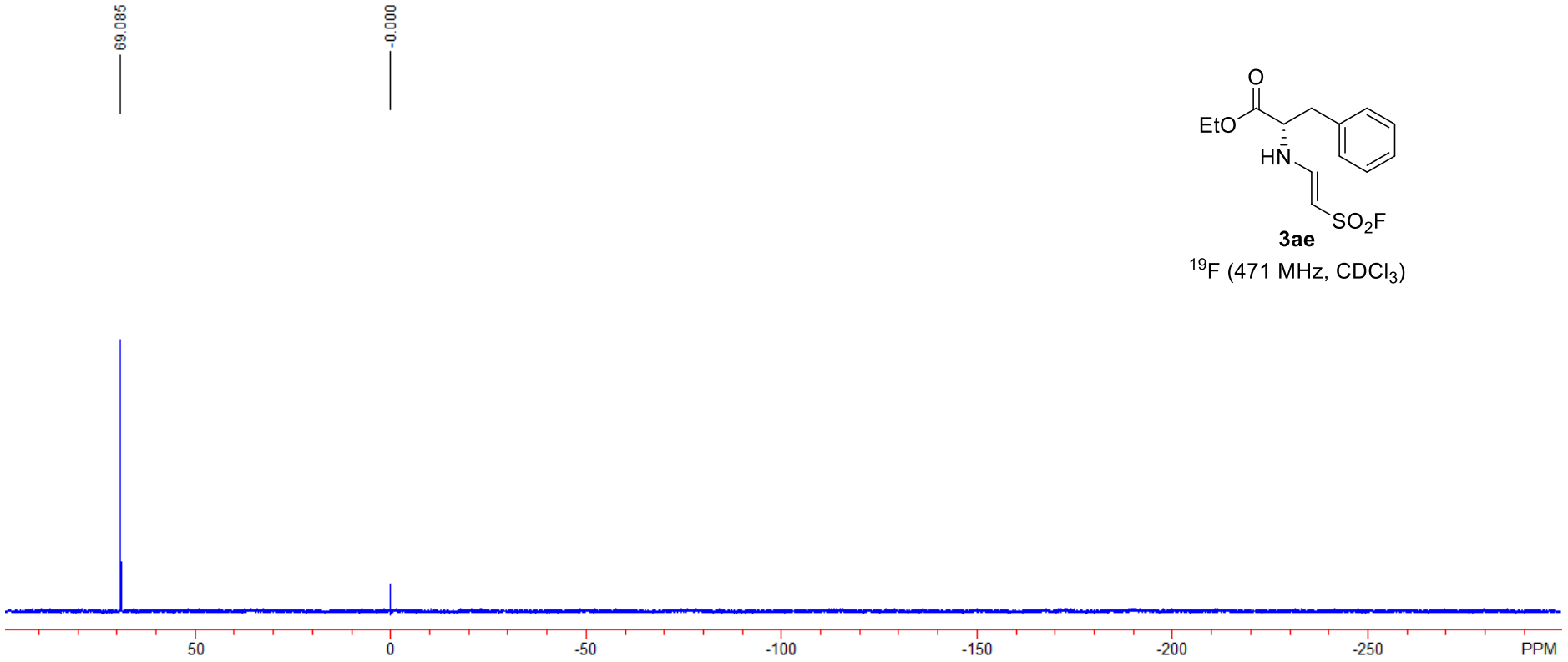


3ad

^{19}F (471 MHz, $CDCl_3$)

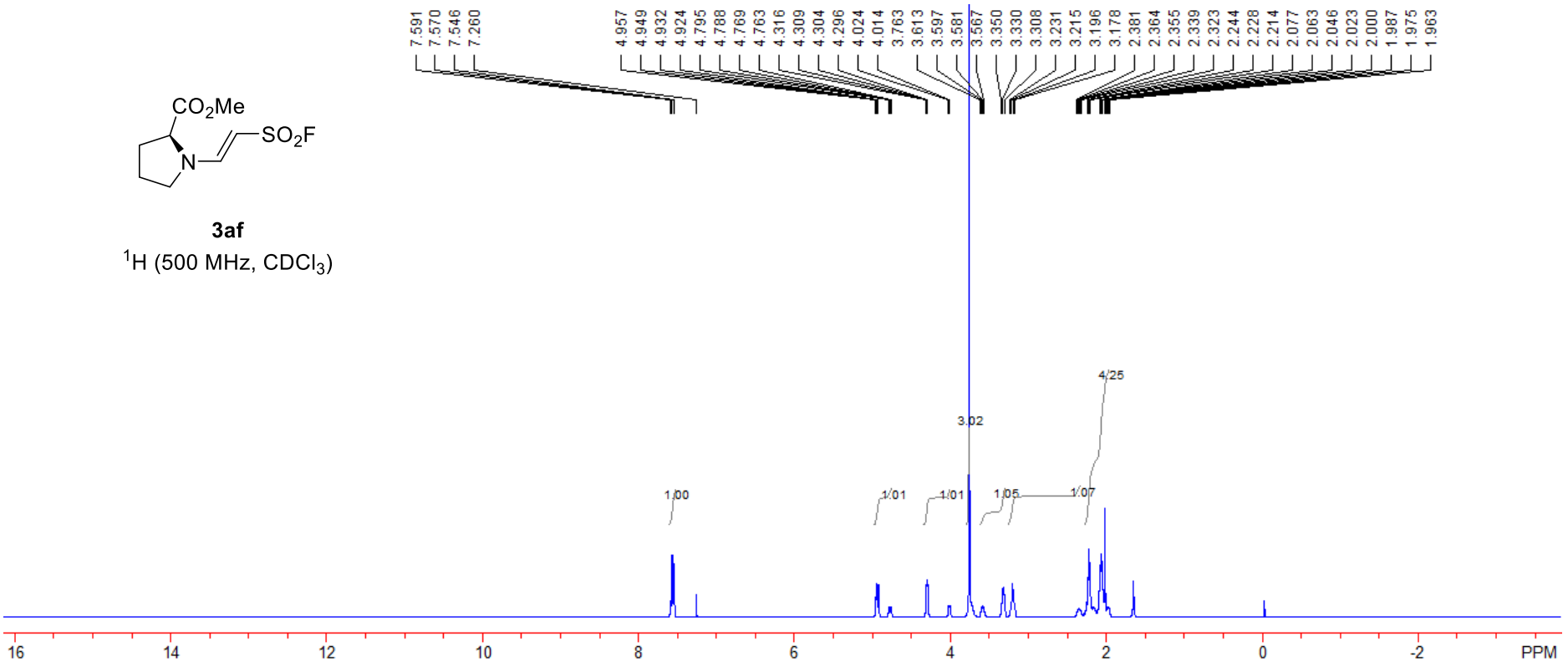

7.459
7.332
7.318
7.304
7.298
7.284
7.276
7.260
7.108
7.094
5.637
5.047
4.262
4.255
4.248
4.241
4.234
4.226
4.220
4.212
4.206
4.199
4.176
4.163
4.150
4.137
3.207
3.197
3.180
3.169
3.088
3.079
3.062
1.296
1.282
1.267
3.02
0.66
2.00
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
2.00
1.00
4.30
4.25
4.20
4.15
4.10
3.02
2.00
0.66
0.95
0.93
2.00
1.00
1.00
1.00
3.01
16
14
12
10
8
6
4
2
0
-2
PPM
EtO
O
HN
SO2F
3ae
1H (500 MHz, CDCl3)

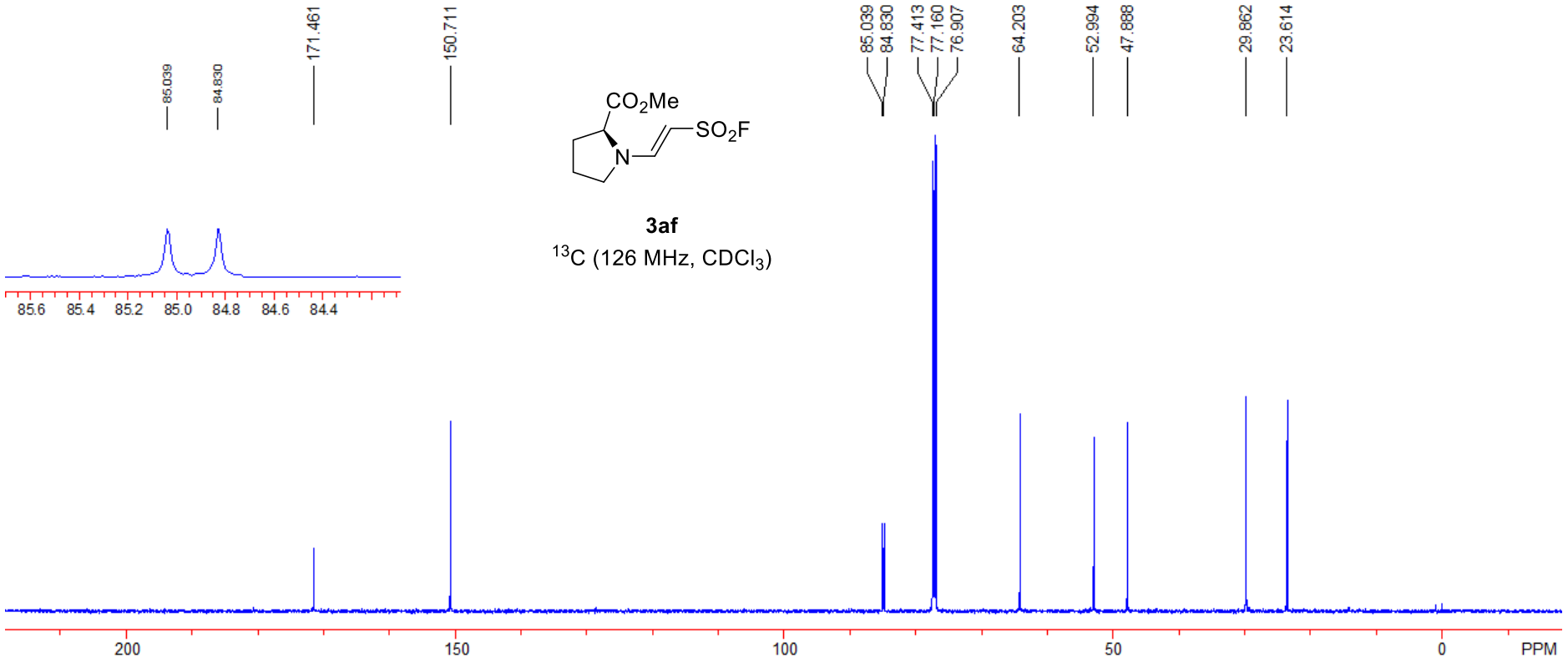

170.067
149.520
134.591
129.391
129.037
127.860
81.284
81.096
77.413
77.160
76.907
63.012
62.499
40.197
14.168
81.284
81.096
81.6
81.4
81.2
81.0
80.8
O
EtO
HN
SO2F
3ae
13C (126 MHz, CDCl3)
200
150
100
50
0
PPM

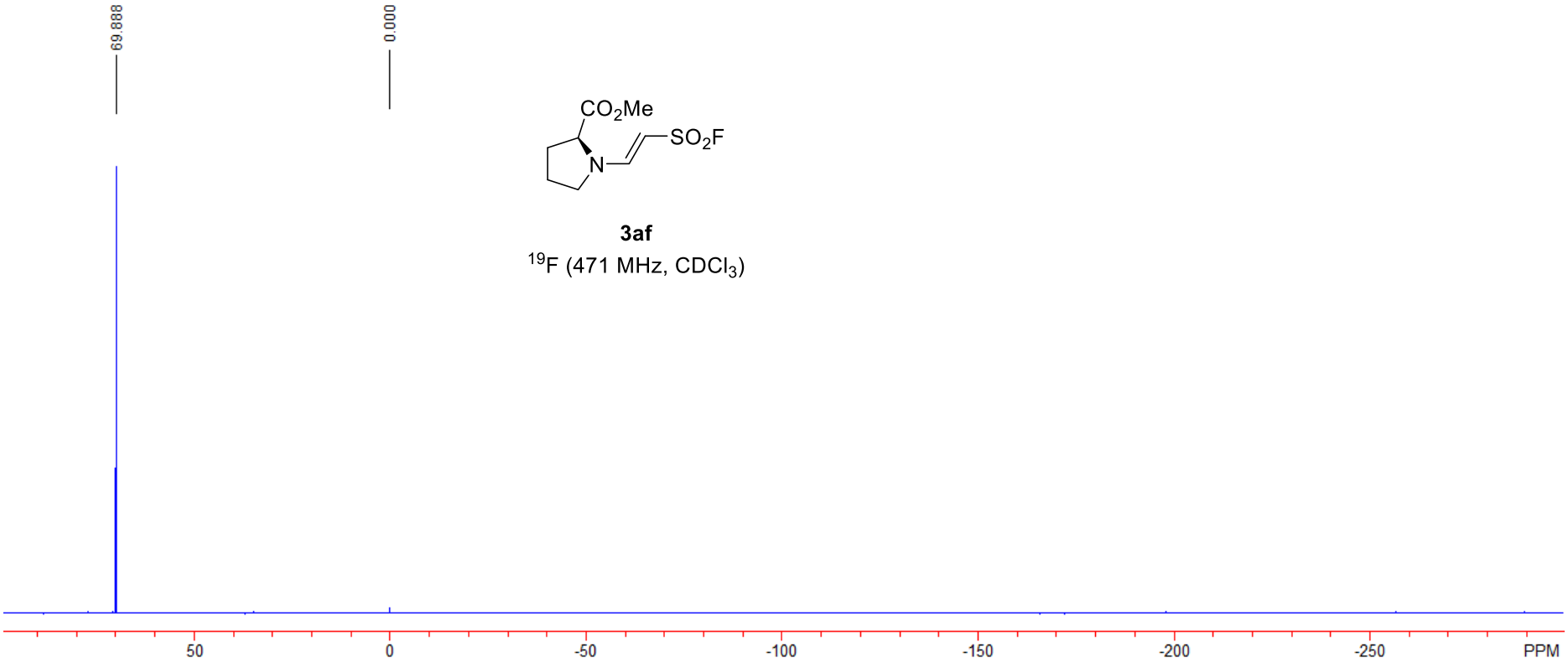


3ae

^{19}F (471 MHz, $CDCl_3$)

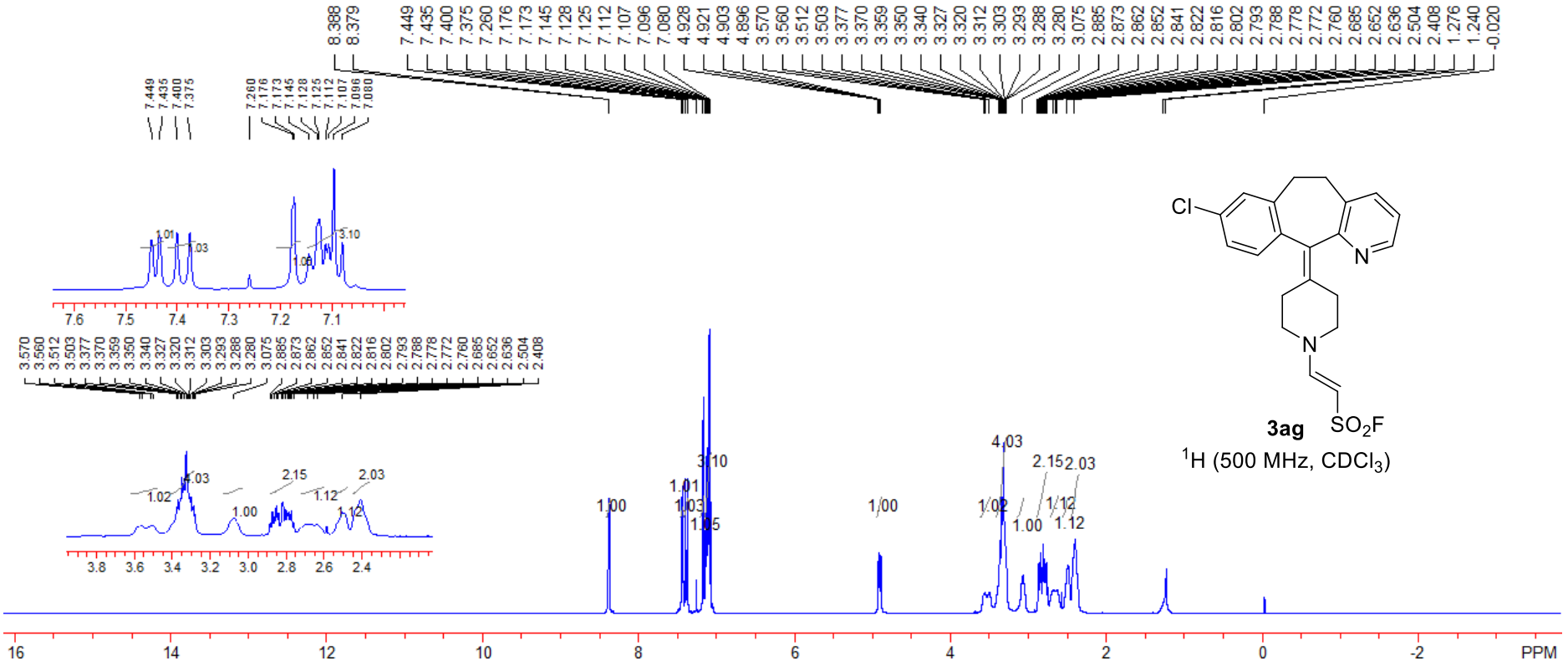

CO2Me
SO2F
N
3af
1H (500 MHz, CDCl3)
7.591
7.570
7.546
7.260
4.957
4.949
4.932
4.924
4.795
4.788
4.769
4.763
4.316
4.309
4.304
4.296
4.024
4.014
3.763
3.613
3.597
3.581
3.567
3.350
3.330
3.308
3.231
3.215
3.196
3.178
2.381
2.364
2.355
2.339
2.323
2.244
2.228
2.214
2.077
2.063
2.046
2.023
2.000
1.987
1.975
1.963
4.25
3.02
1.00
1.01
1.01
1.05
1.07
16
14
12
10
8
6
4
2
0
-2
PPM

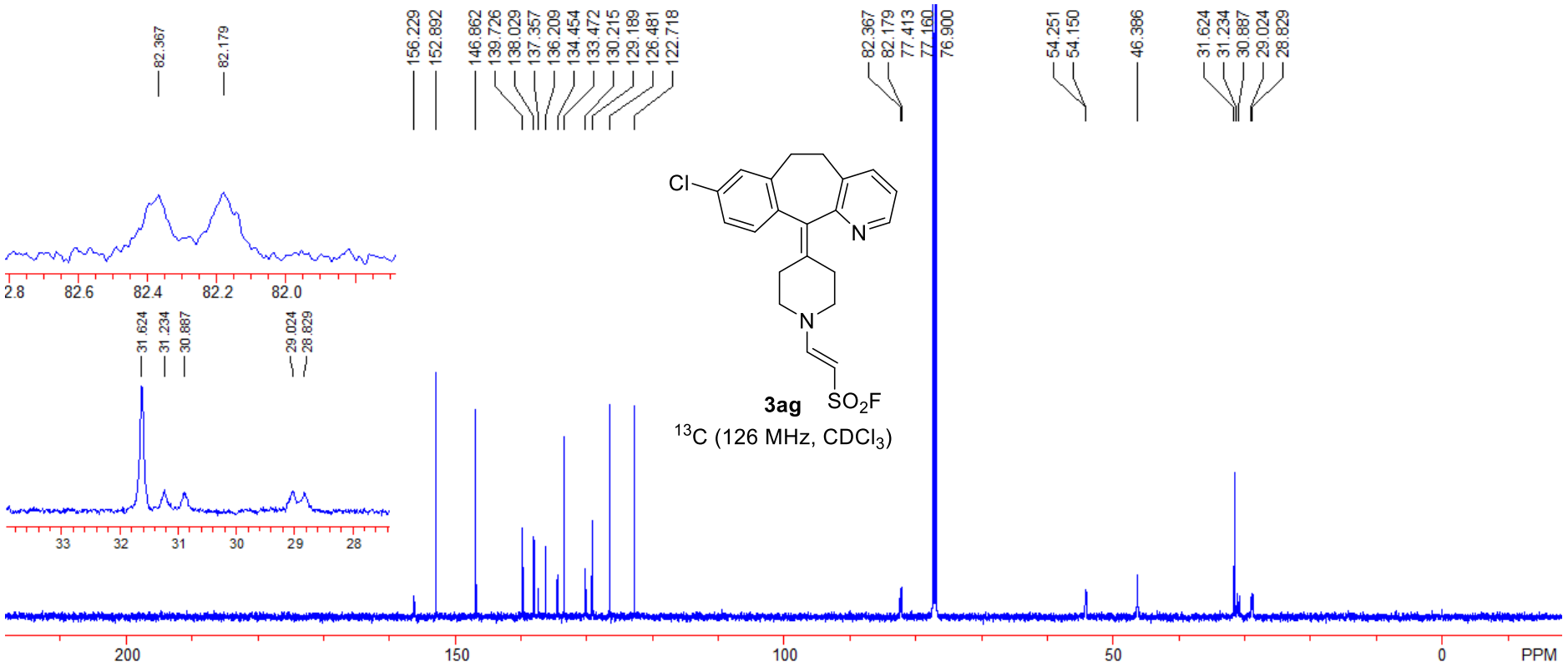

85.039
84.830
171.461
150.711
85.039
84.830
77.413
77.160
76.907
64.203
52.994
47.888
29.862
23.614
CO2Me
SO2F
N
3af
13C (126 MHz, CDCl3)
85.6
85.4
85.2
85.0
84.8
84.6
84.4
200
150
100
50
0
PPM

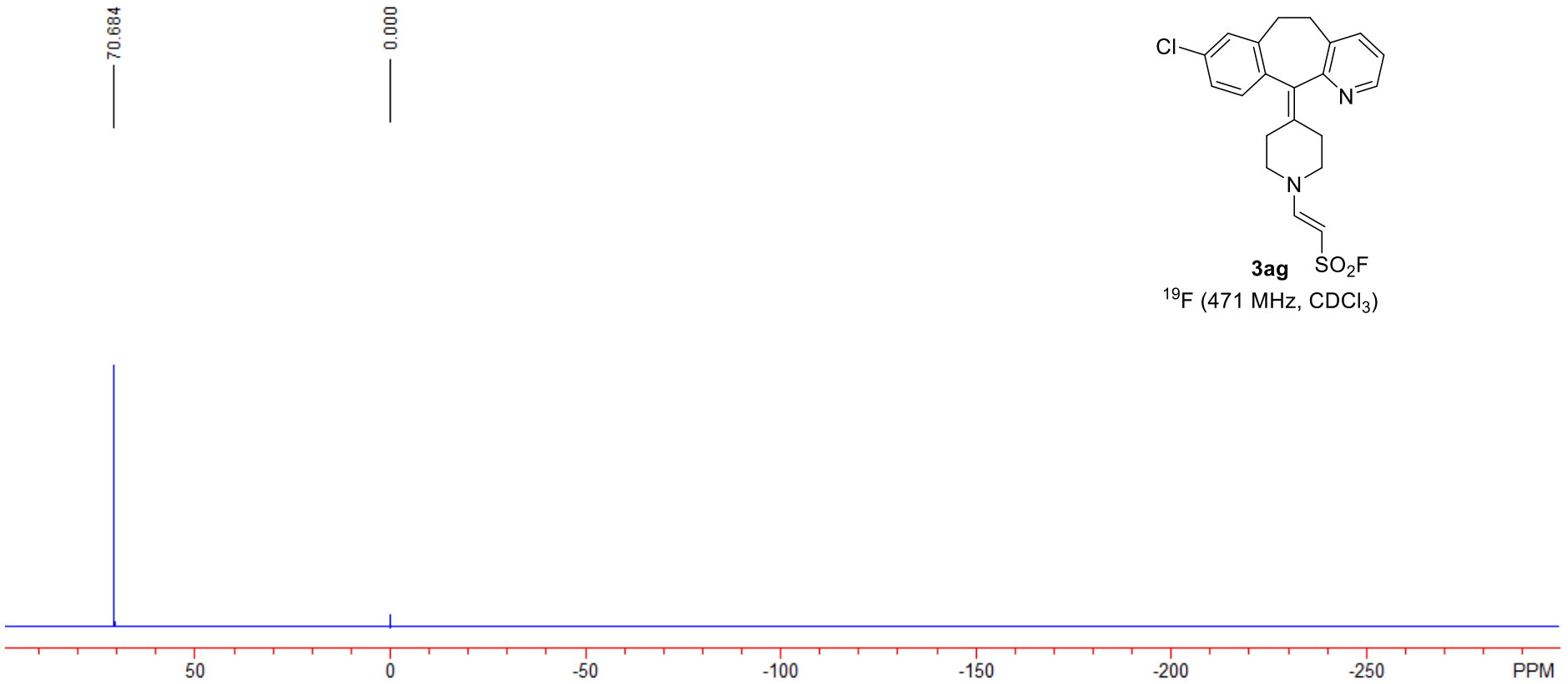


3af

^{19}F (471 MHz, $CDCl_3$)

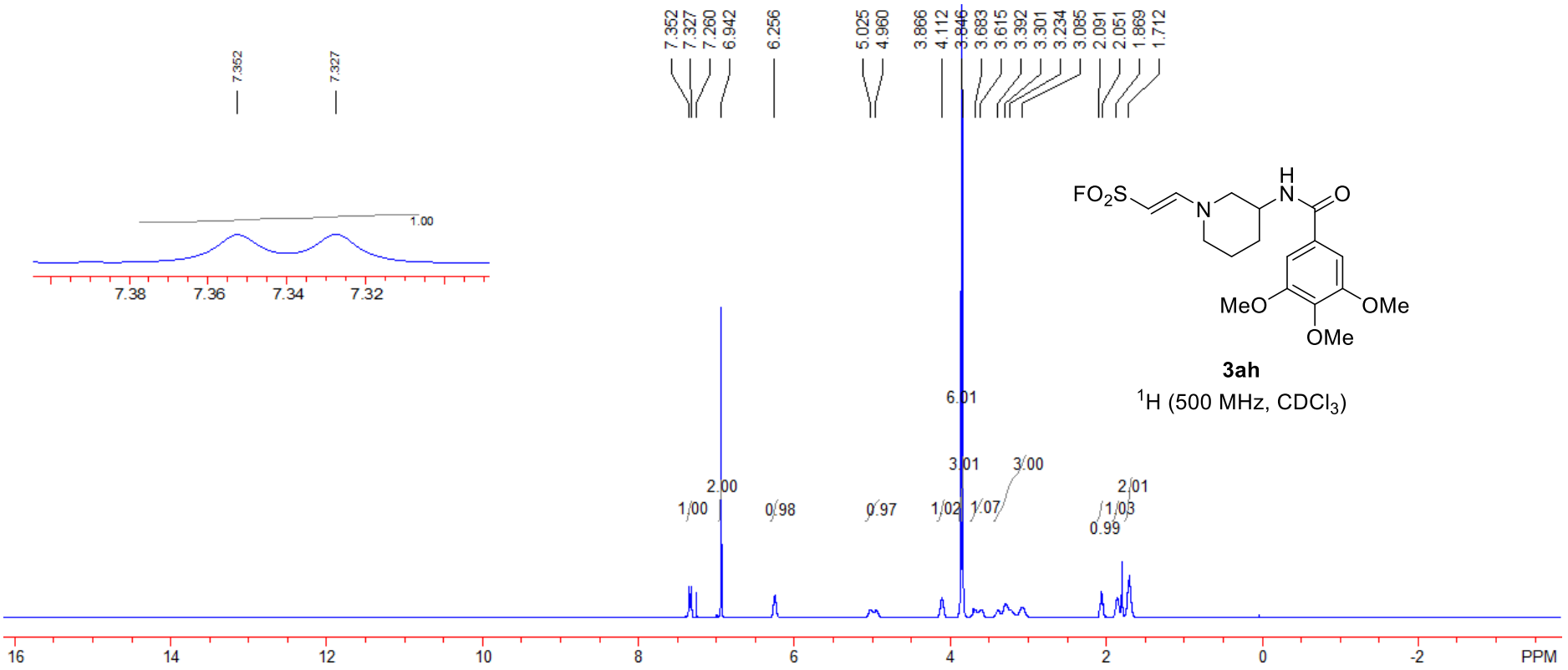

Cl
N
N
SO2F
3ag
1H (500 MHz, CDCl3)
PPM

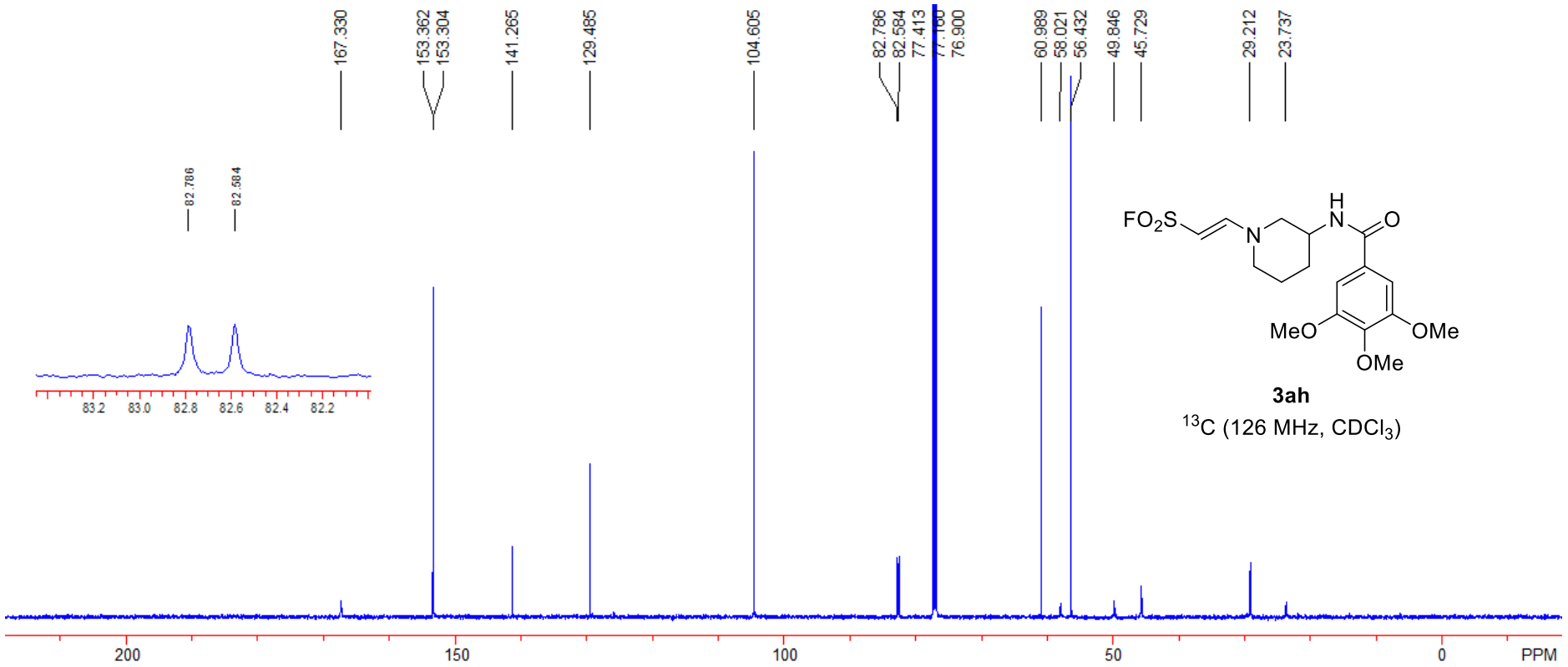

156.229
152.892
146.862
139.726
138.029
137.357
136.209
134.454
133.472
130.215
129.189
126.481
122.718
82.367
82.179
77.413
77.160
76.900
54.251
54.150
46.386
31.624
31.234
30.887
29.024
28.829
Cl
N
N
SO2F
3ag
13C (126 MHz, CDCl3)
PPM

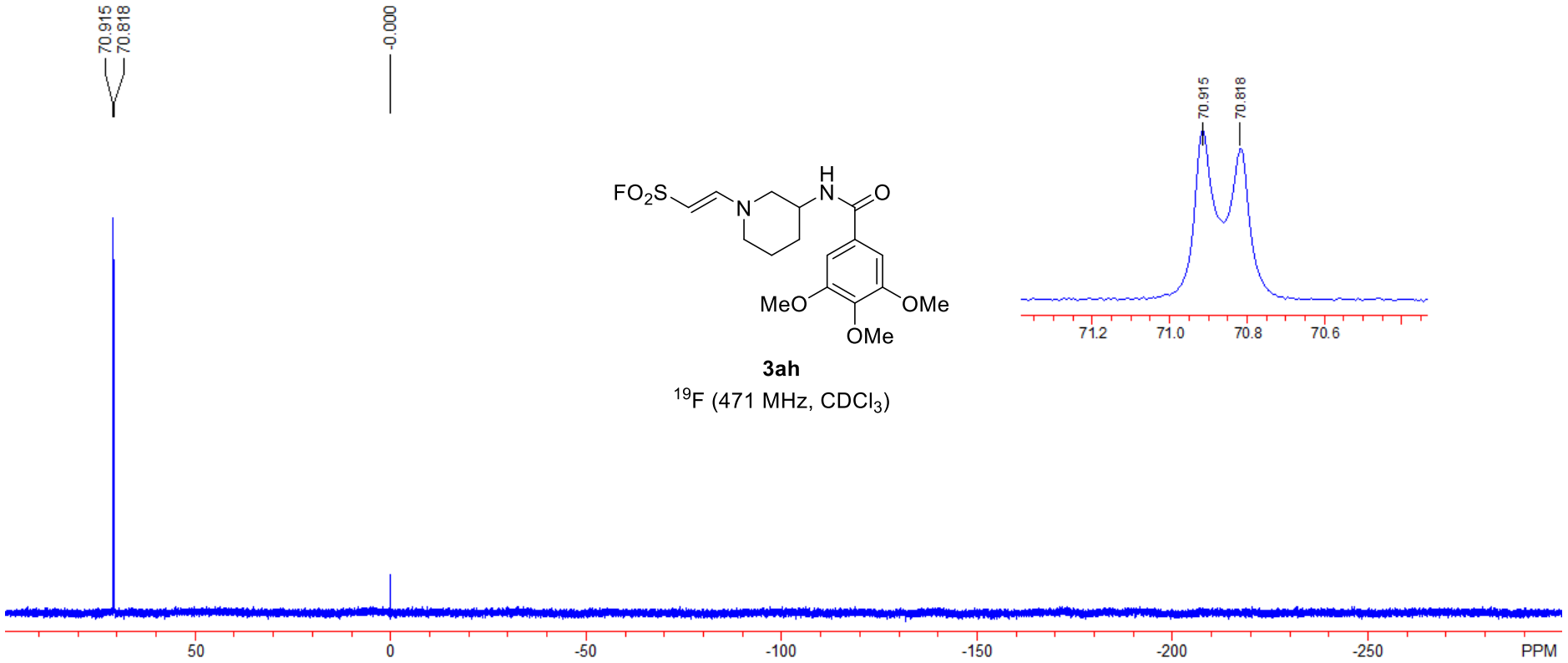


3ag

^{19}F (471 MHz, $CDCl_3$)

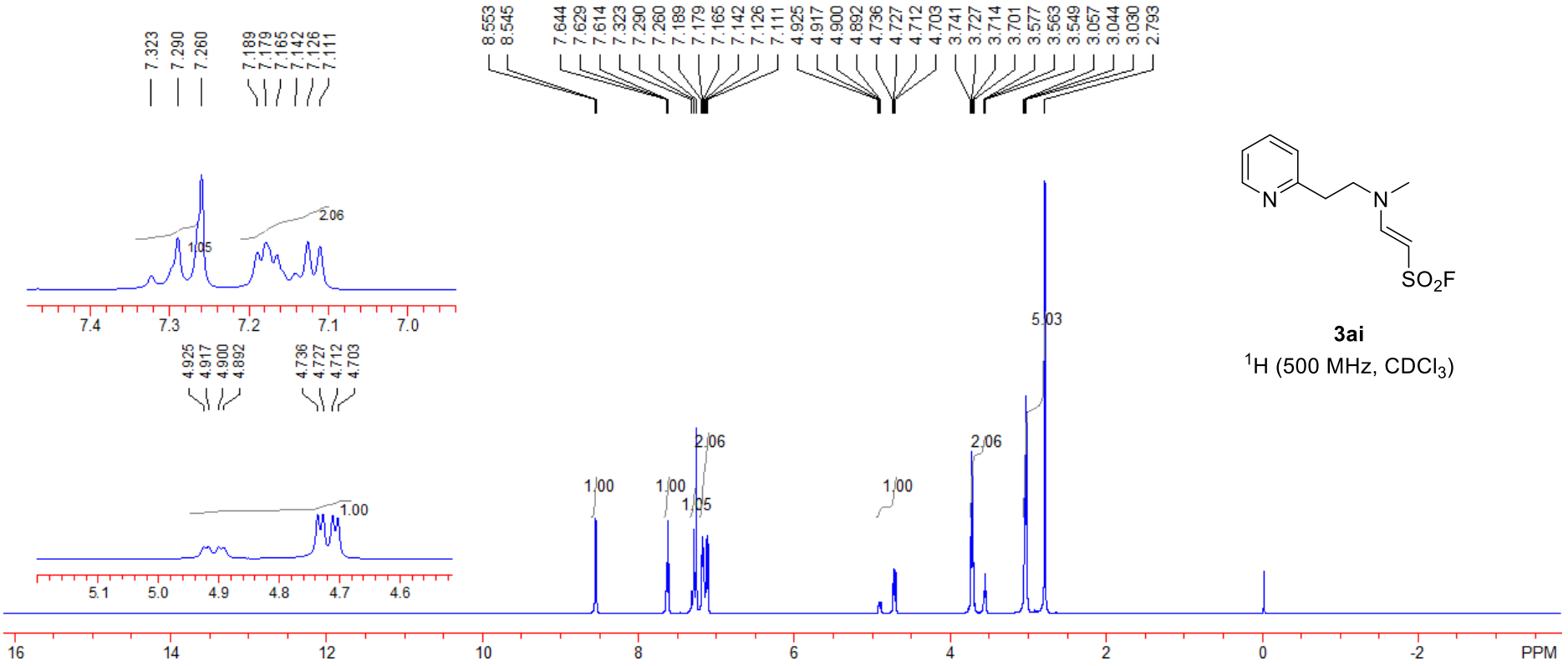

7.352
7.327
7.260
6.942
6.256
5.025
4.960
3.866
4.112
3.846
3.683
3.615
3.392
3.301
3.234
3.085
2.091
2.051
1.869
1.712
1.00
7.38
7.36
7.34
7.32
FO2S
N
H
N
O
MeO
OMe
OMe
3ah
1H (500 MHz, CDCl3)
6.01
3.01
3.00
2.00
2.01
1.00
0.98
0.97
1.02
1.07
1.03
0.99
16
14
12
10
8
6
4
2
0
-2
PPM

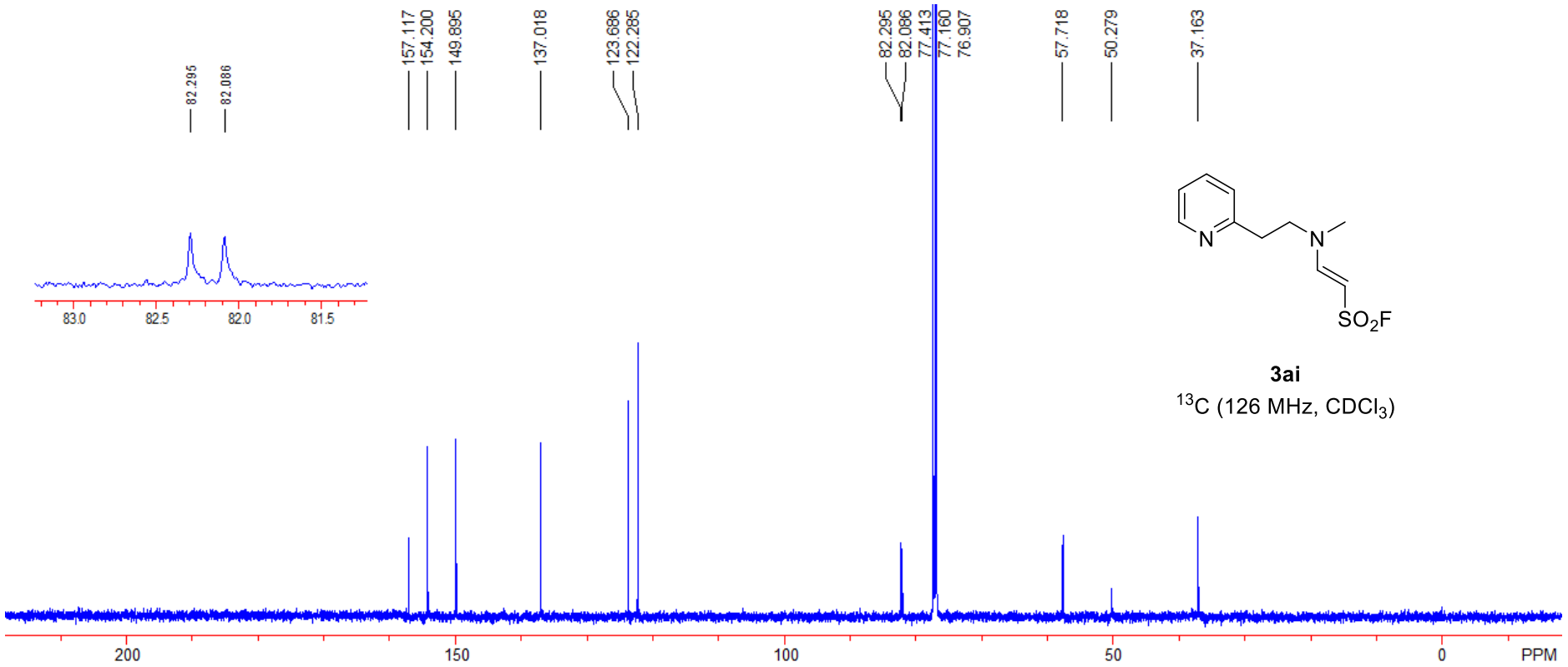

167.330
153.362
153.304
141.265
129.485
104.605
82.786
82.584
77.413
77.160
76.900
60.989
58.021
56.432
49.846
45.729
29.212
23.737
82.786
82.584
83.2
83.0
82.8
82.6
82.4
82.2
200
150
100
50
0
PPM
FO2S
N
H
N
O
MeO
OMe
OMe
3ah
13C (126 MHz, CDCl3)

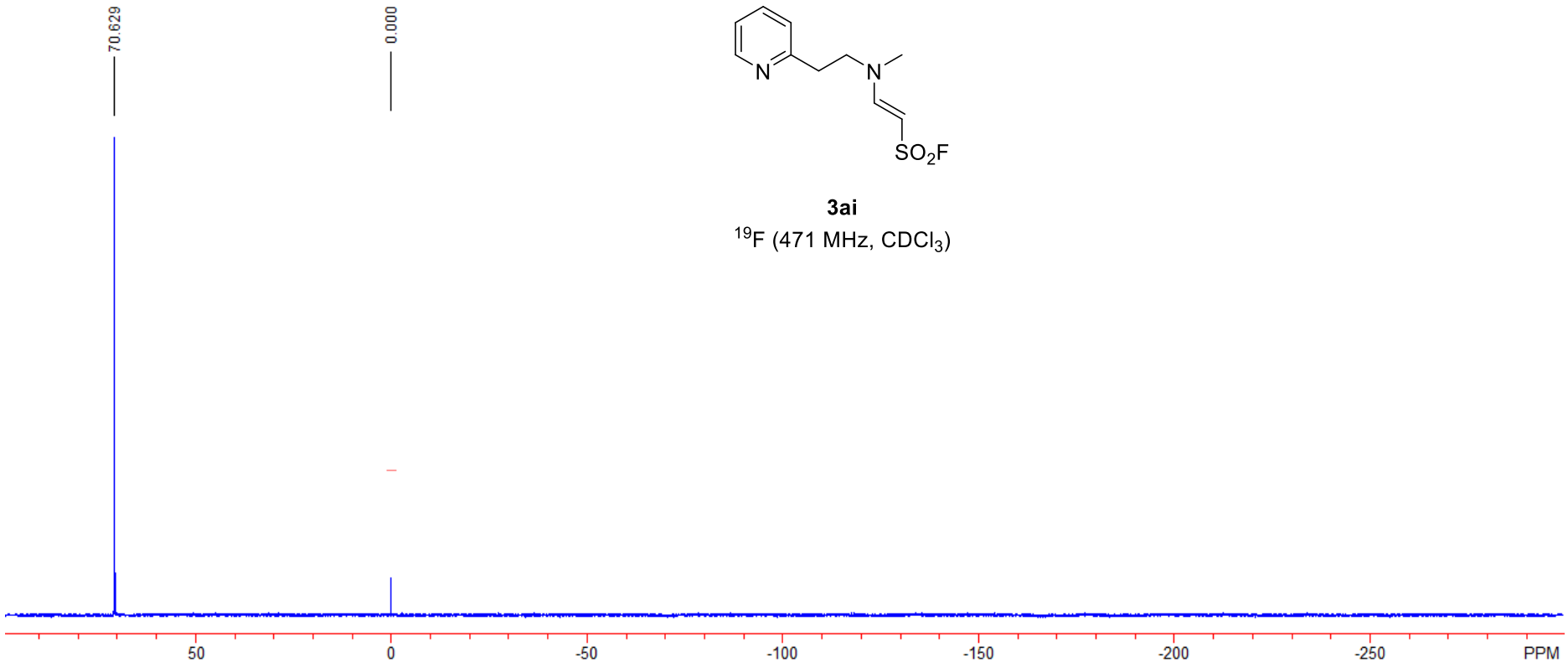


3ah

^{19}F (471 MHz, $CDCl_3$)

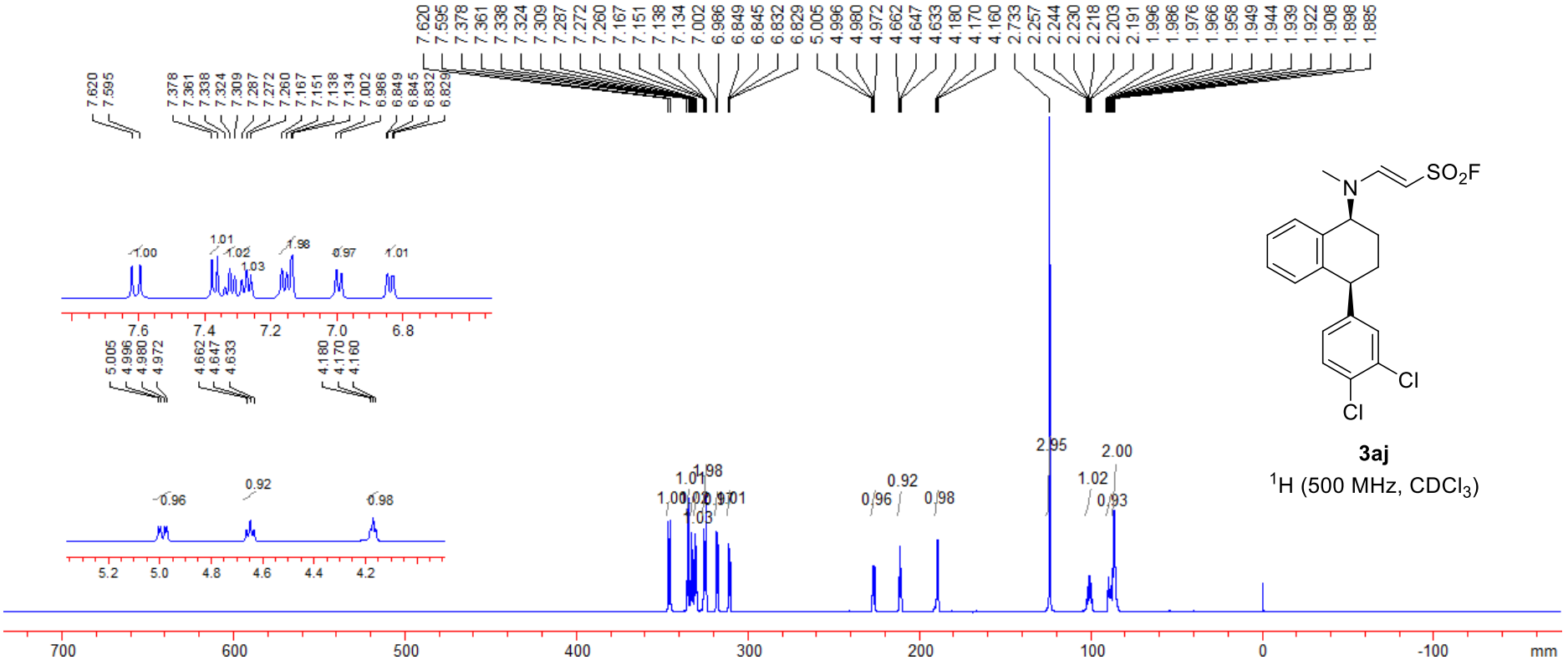

8.553
8.545
7.644
7.629
7.614
7.323
7.290
7.260
7.189
7.179
7.165
7.142
7.126
7.111
4.925
4.917
4.900
4.892
4.736
4.727
4.712
4.703
3.741
3.727
3.714
3.701
3.577
3.563
3.549
3.057
3.044
3.030
2.793
1.00
1.00
2.06
1.05
1.00
2.06
5.03
PPM
3ai
^{1}H (500 MHz, $CDCl_3$)

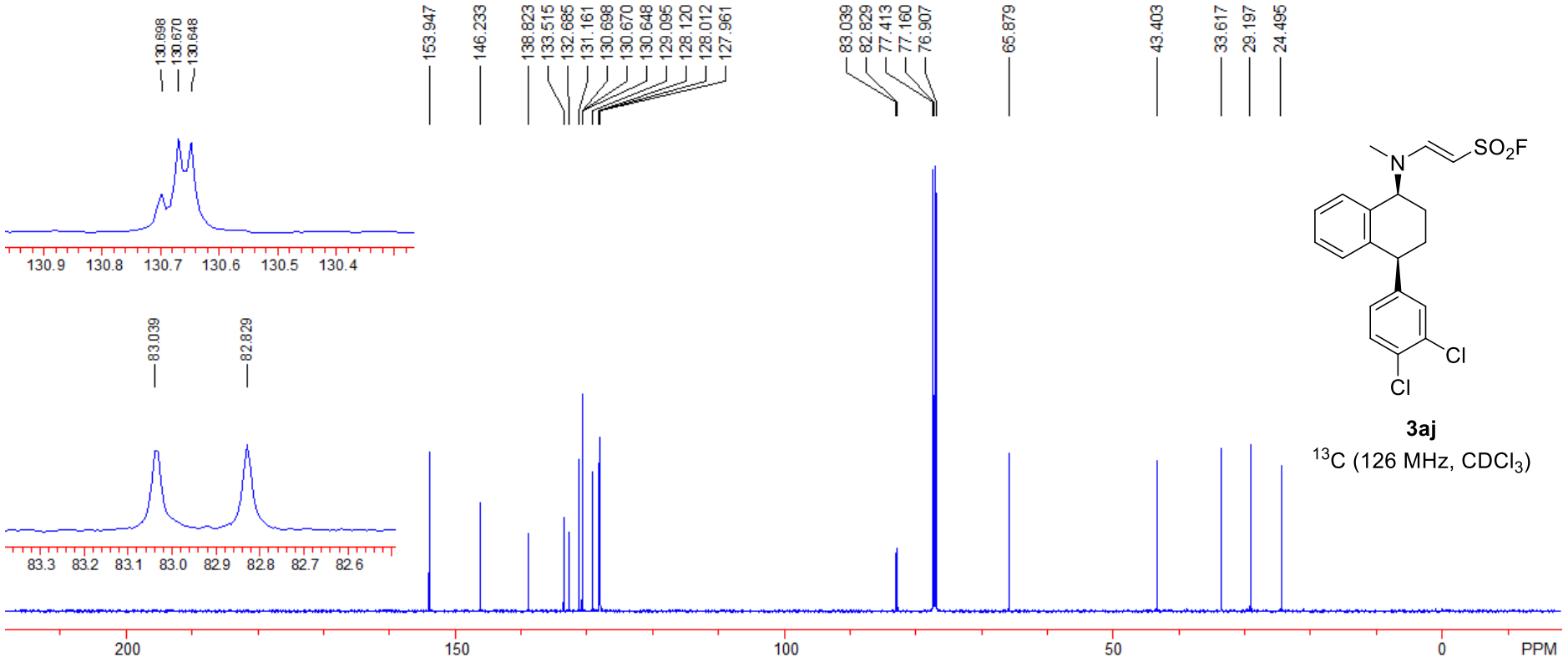

82.295
82.086
157.117
154.200
149.895
137.018
123.686
122.285
82.295
82.086
77.413
77.160
76.907
57.718
50.279
37.163
83.0
82.5
82.0
81.5
N
N
SO2F
3ai
13C (126 MHz, CDCl3)
200
150
100
50
0
PPM



3ai

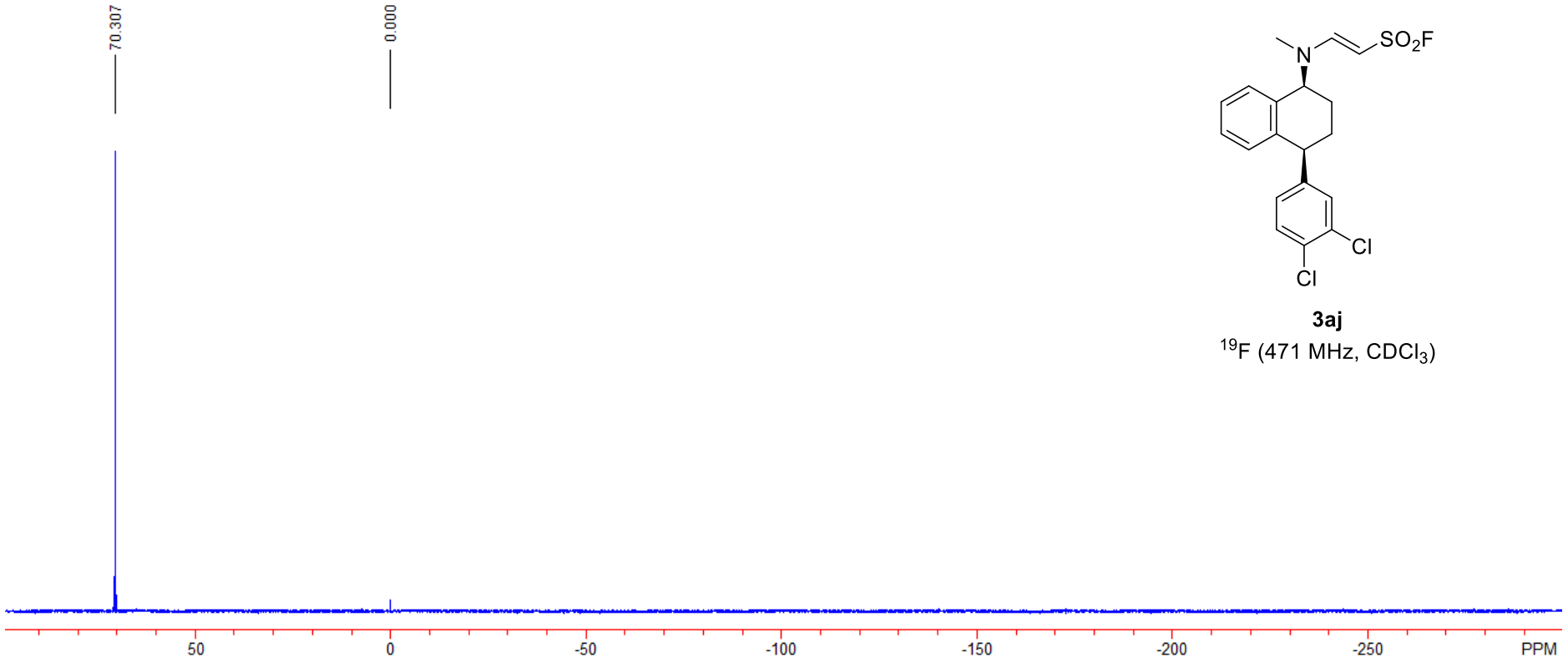
^{19}F (471 MHz, $CDCl_3$)


7.620
7.595
7.378
7.361
7.338
7.324
7.309
7.287
7.272
7.260
7.167
7.151
7.138
7.134
7.002
6.986
6.849
6.845
6.832
6.829
5.005
4.996
4.980
4.972
4.662
4.647
4.633
4.180
4.170
4.160
2.733
2.257
2.244
2.230
2.218
2.203
2.191
1.996
1.986
1.976
1.966
1.958
1.949
1.944
1.939
1.922
1.908
1.898
1.885
1.00
1.01
1.02
1.03
1.98
0.97
1.01
0.96
0.92
0.98
2.95
2.00
1.02
0.93
SO2F
N
Cl
Cl
3aj
1H (500 MHz, CDCl3)
700
600
500
400
300
200
100
0
-100
mm



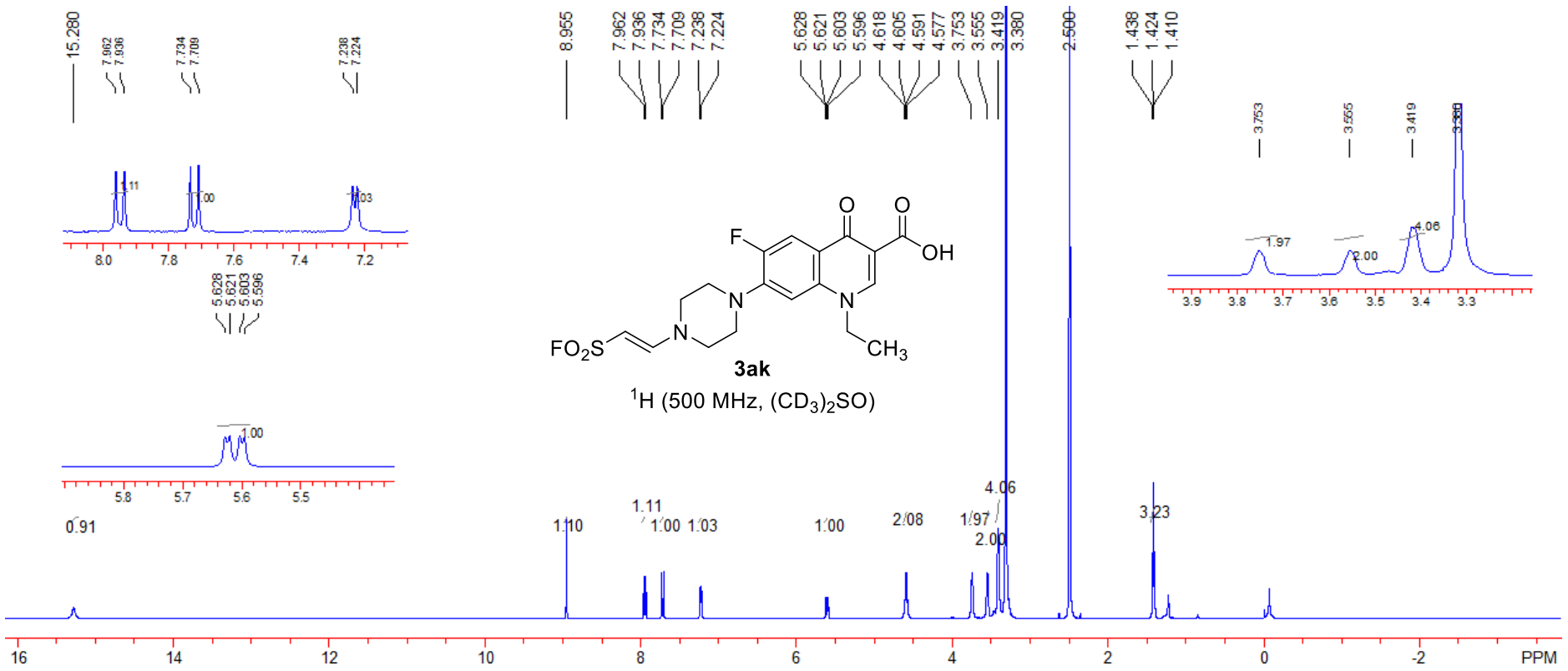
3aj

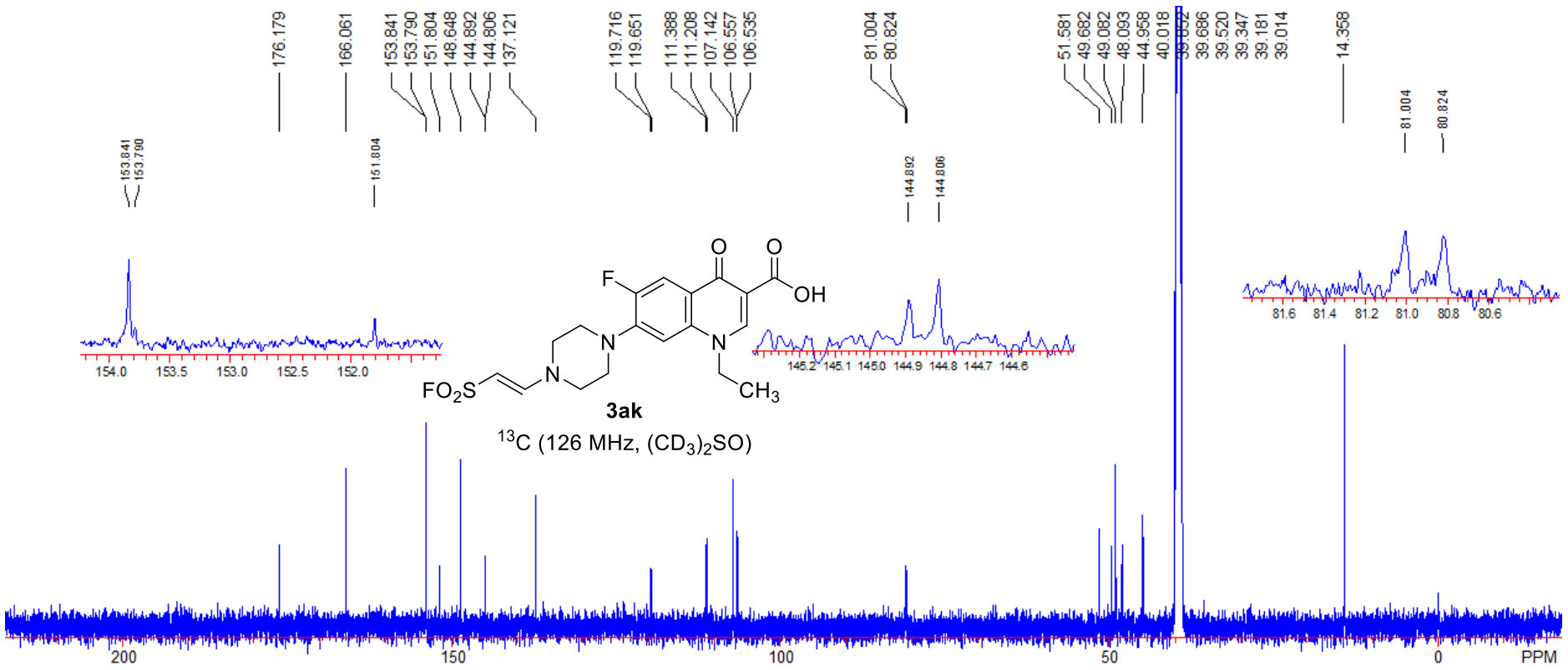
^{13}C (126 MHz, $CDCl_3$)

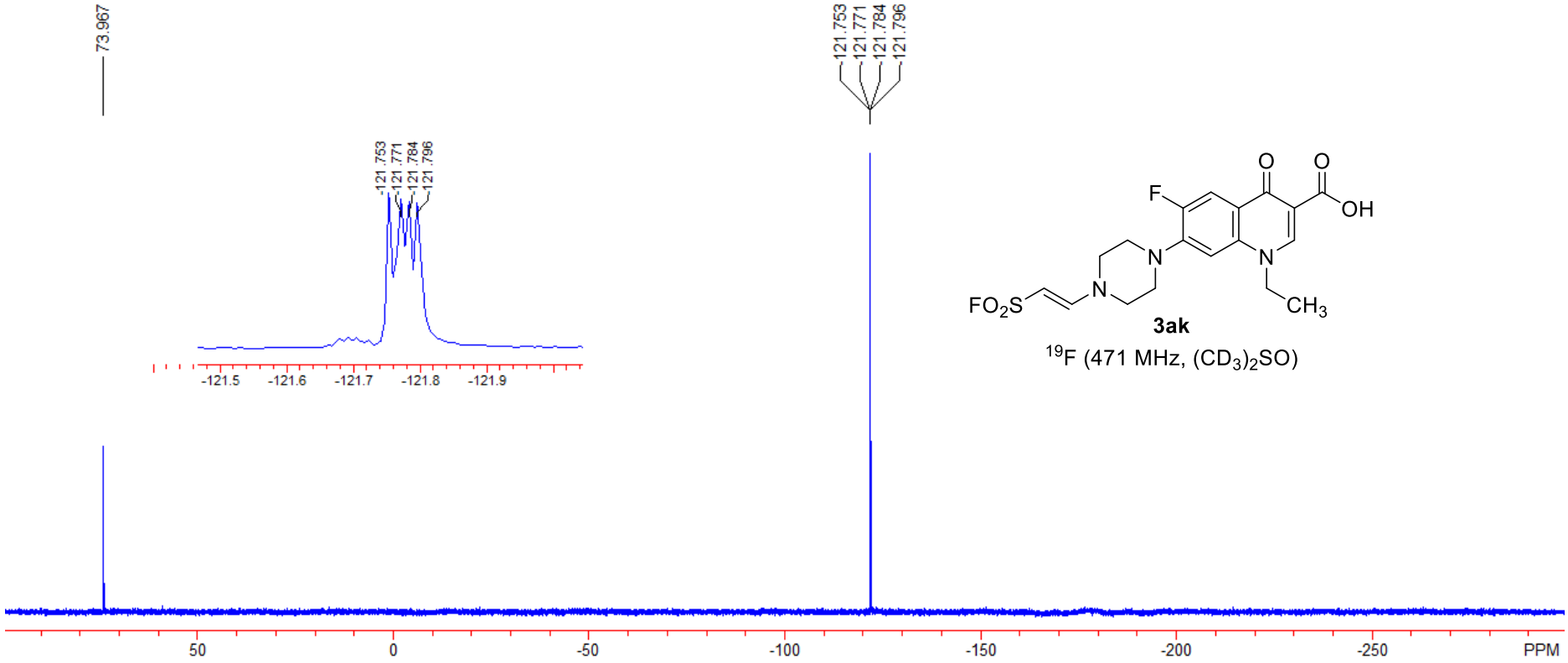


3aj

^{19}F (471 MHz, $CDCl_3$)

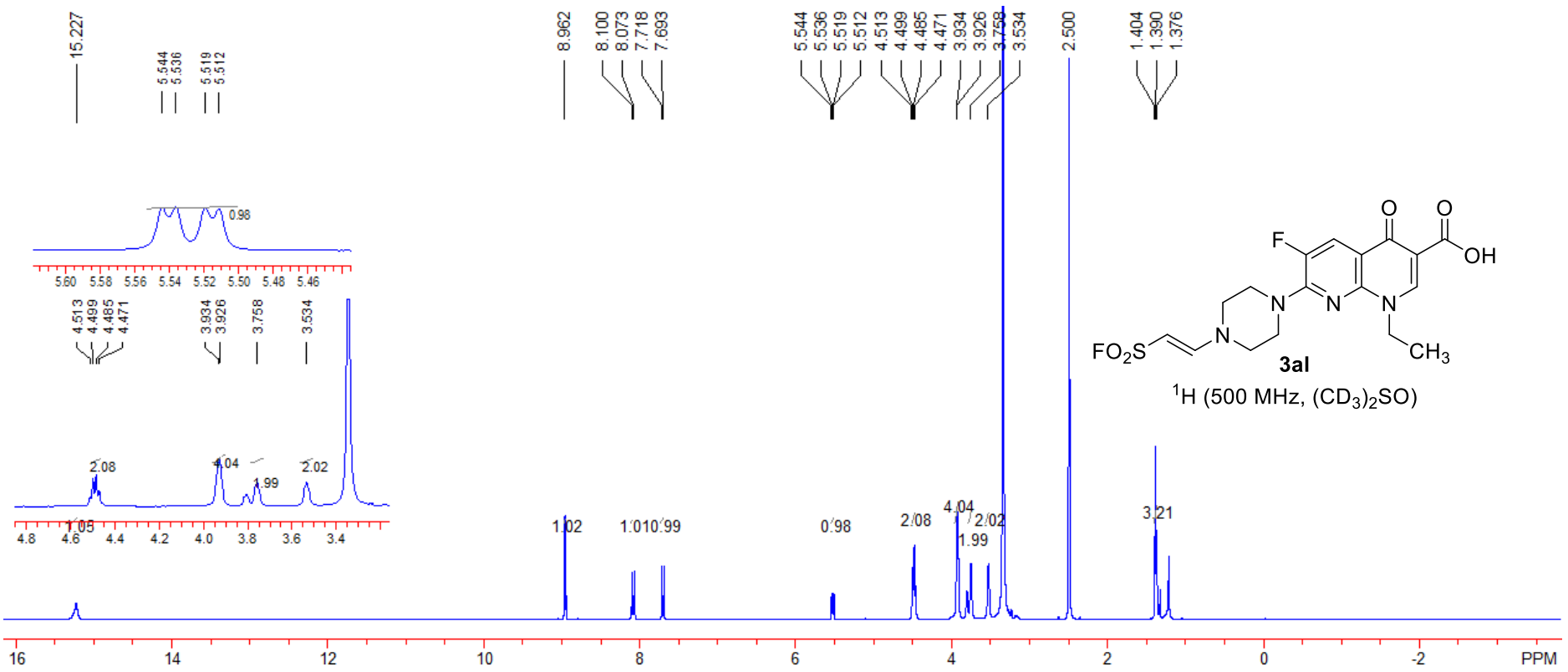

15.280
7.962
7.936
7.734
7.709
7.238
7.224
8.955
5.628
5.621
5.603
5.596
4.618
4.605
4.591
4.577
3.753
3.555
3.419
3.380
2.500
1.438
1.424
1.410
F
O
O
OH
N
N
N
FO2S
CH3
3ak
1H (500 MHz, (CD3)2SO)
0.91
1.10
1.11
1.00
1.03
1.00
2.08
1.97
4.06
2.00
3.23
PPM

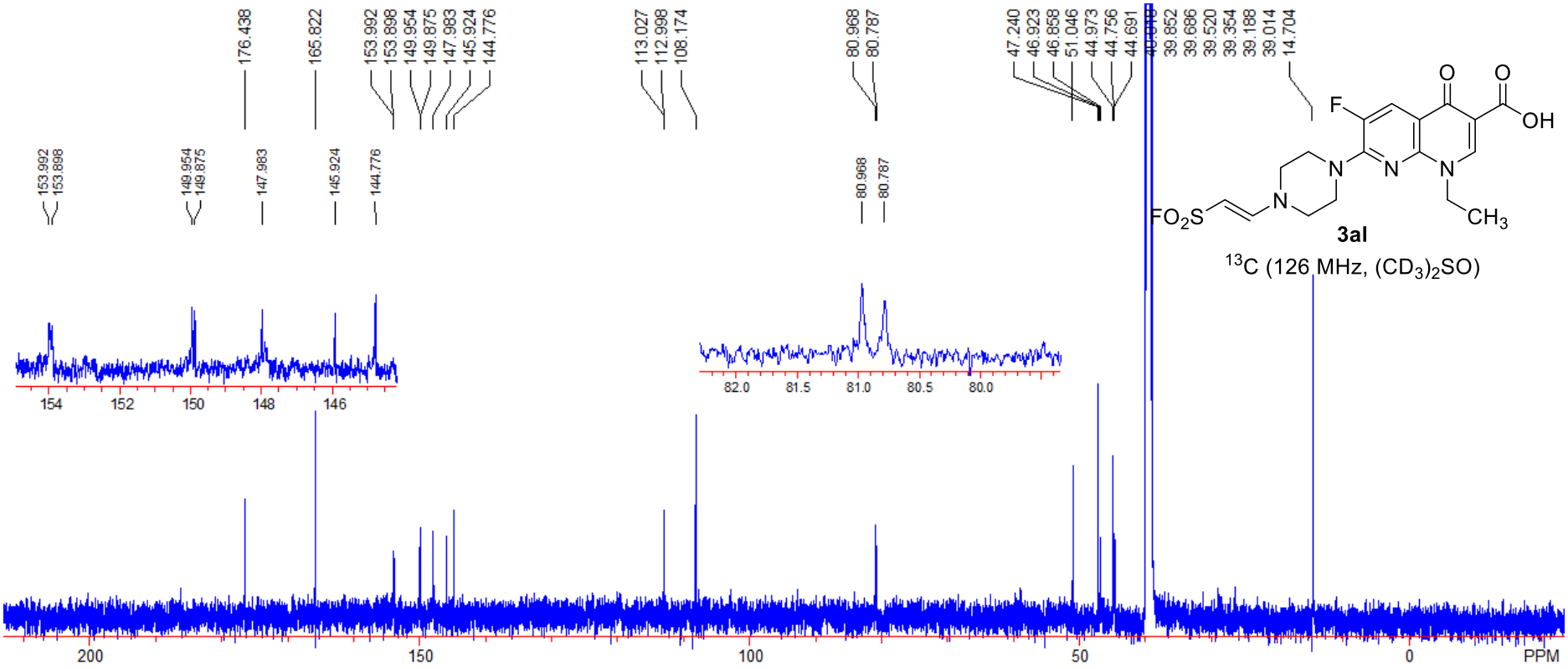

176.179
166.061
153.841
153.790
151.804
148.648
144.892
144.806
137.121
119.716
119.651
111.388
111.208
107.142
106.557
106.535
81.004
80.824
51.581
49.682
49.082
48.093
44.958
40.018
39.852
39.686
39.520
39.347
39.181
39.014
14.358
F
O
O
OH
N
N
N
FO2S
CH3
3ak
13C (126 MHz, (CD3)2SO)
200
150
100
50
0
PPM

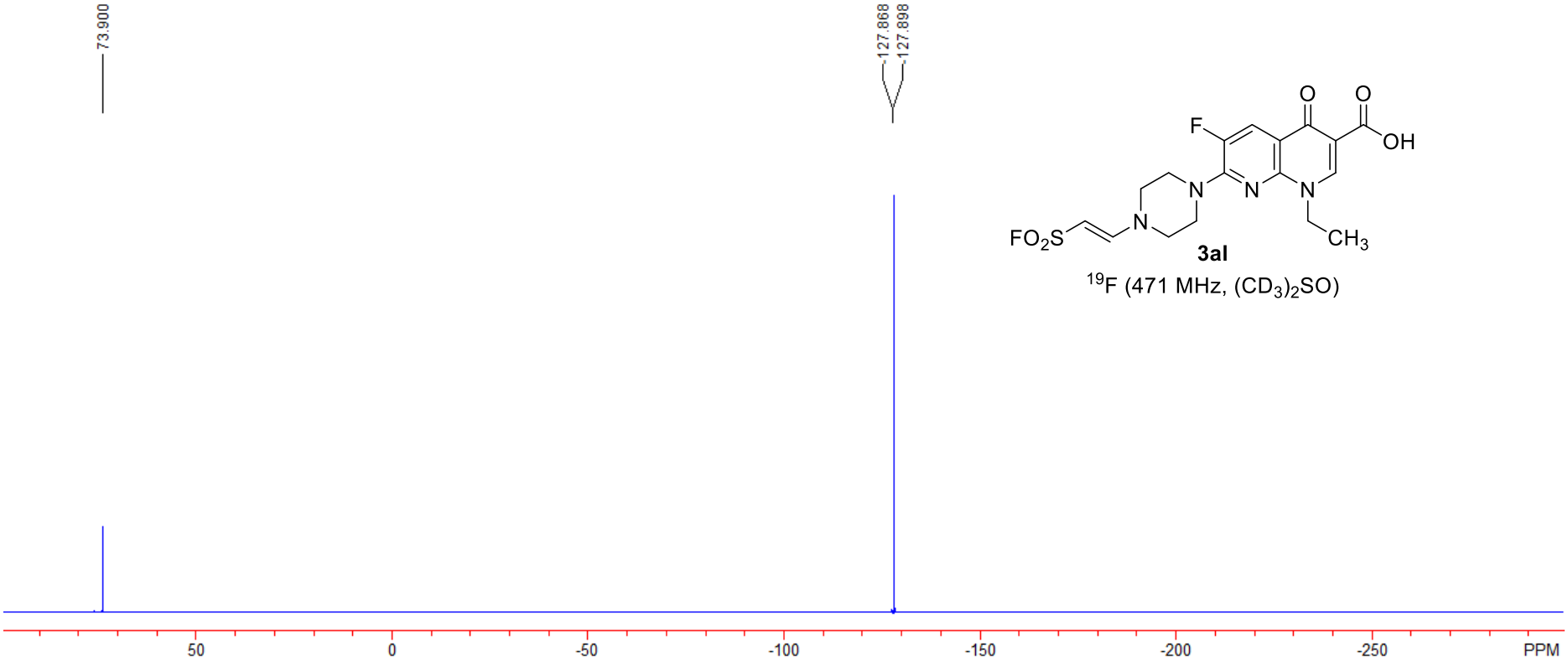


3ak

^{19}F (471 MHz, $(CD_3)_2SO$)

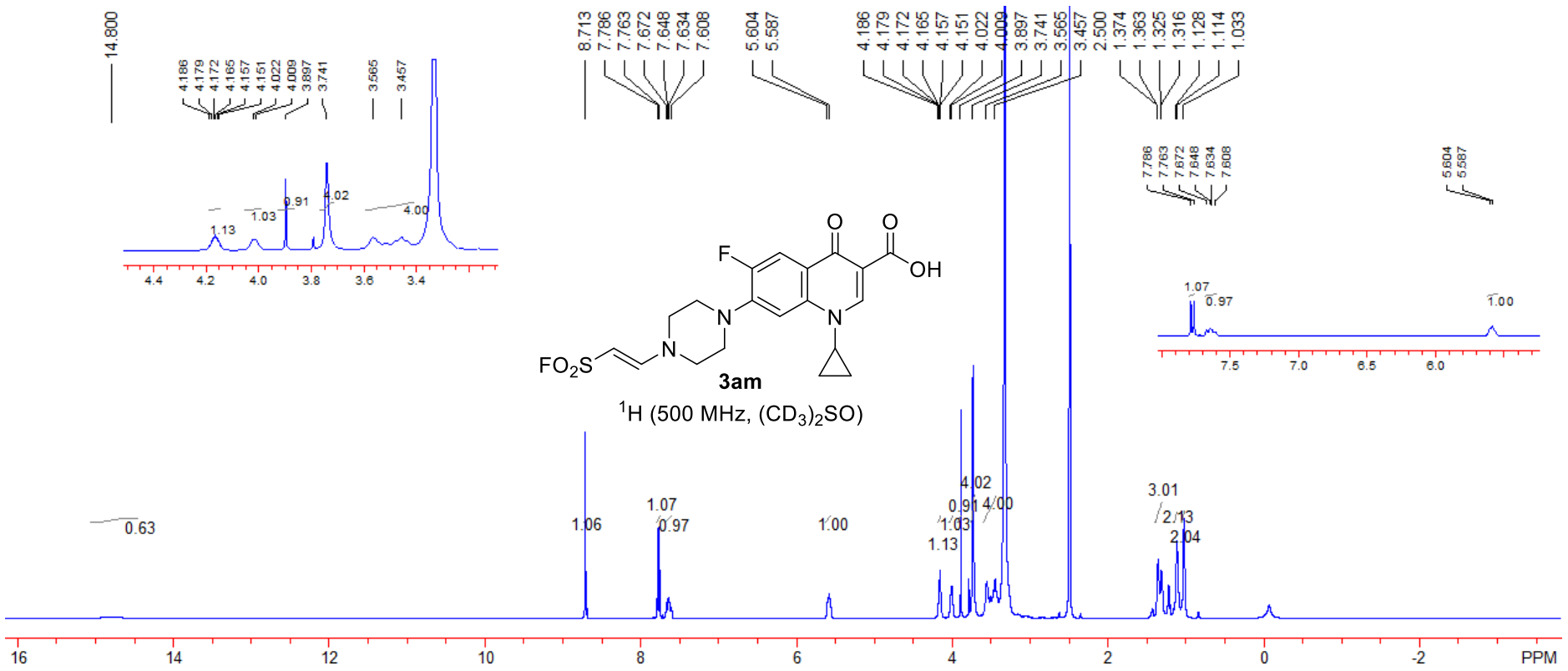

15.227
5.544
5.536
5.519
5.512
8.962
8.100
8.073
7.718
7.693
5.544
5.536
5.519
5.512
4.513
4.499
4.485
4.471
3.934
3.926
3.758
3.534
2.500
1.404
1.390
1.376
0.98
4.513
4.499
4.485
4.471
3.934
3.926
3.758
3.534
2.08
4.04
1.99
2.02
1.05
1.02
1.01
0.99
0.98
2.08
4.04
1.99
2.02
3.21
16
14
12
10
8
6
4
2
0
-2
PPM
F
O
O
OH
N
N
N
N
FO2S
CH3
3aI
1H (500 MHz, (CD3)2SO)

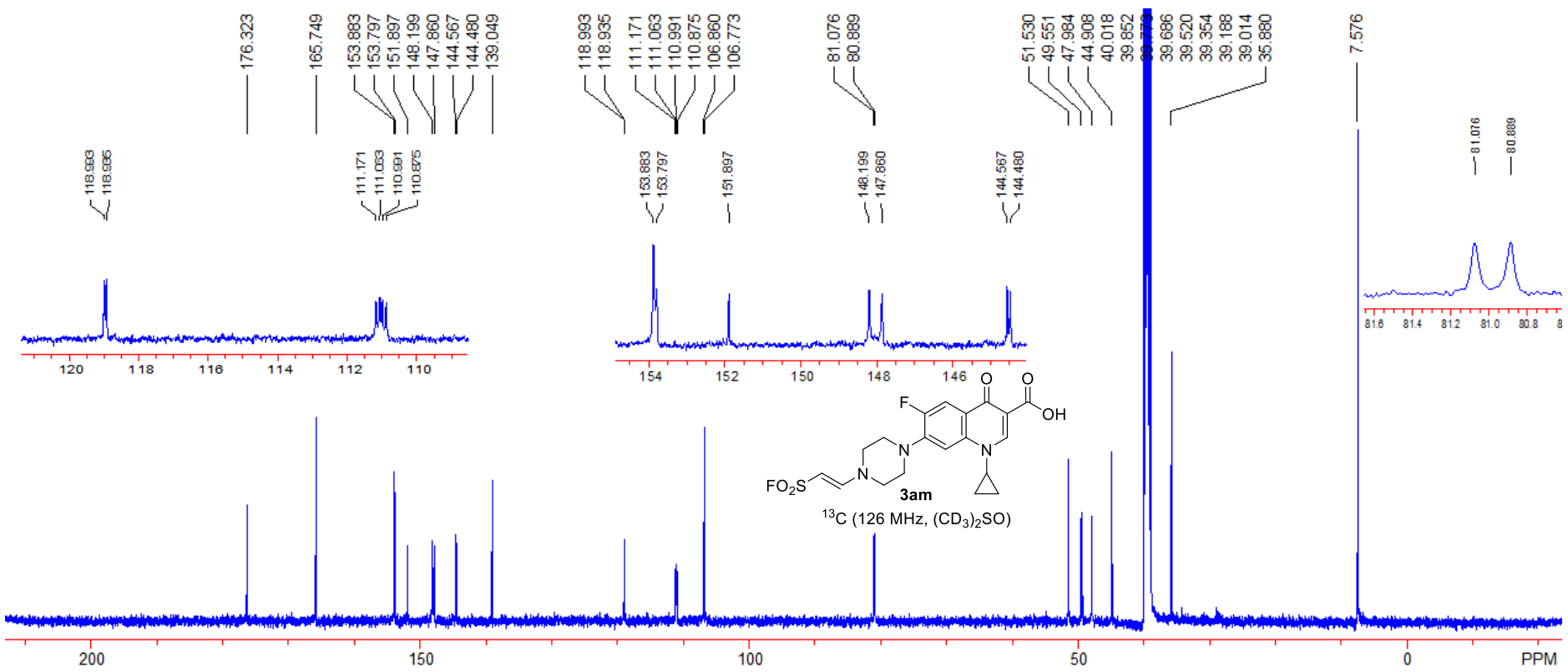

176.438
165.822
153.992
153.898
149.954
149.875
147.983
145.924
144.776
113.027
112.998
108.174
80.968
80.787
47.240
46.923
46.858
51.046
44.973
44.756
44.691
39.852
39.686
39.520
39.354
39.188
39.014
14.704
F
O
O
OH
N
N
N
N
FO2S
CH3
3al
13C (126 MHz, (CD3)2SO)
154
152
150
148
146
82.0
81.5
81.0
80.5
80.0
200
150
100
50
0
PPM

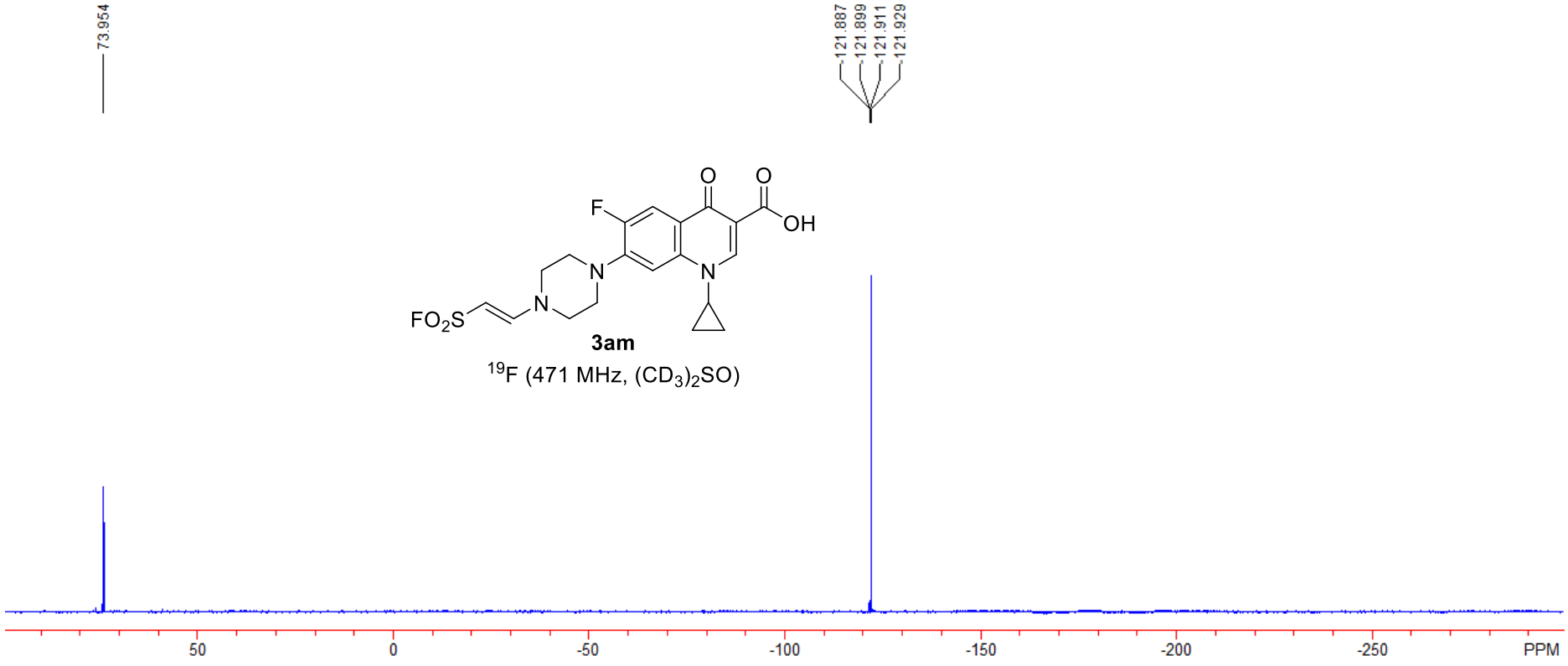


3al

^{19}F (471 MHz, $(CD_3)_2SO$)

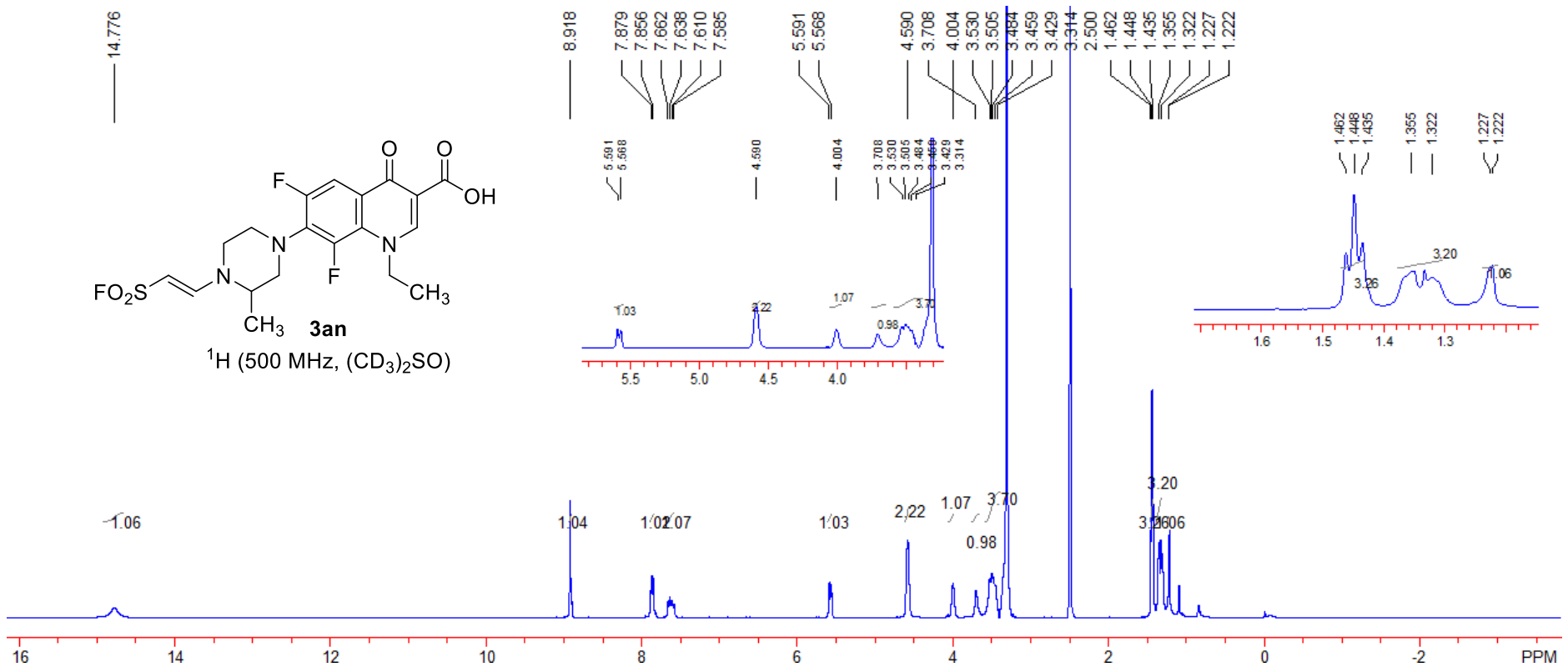

3am
^{1}H (500 MHz, $(CD_3)_2SO$)
F
O
O
OH
N
N
N
FO_2S
14.800
8.713
7.786
7.763
7.672
7.648
7.634
7.608
5.604
5.587
4.186
4.179
4.172
4.165
4.157
4.151
4.022
4.009
3.897
3.741
3.565
3.457
2.500
1.374
1.363
1.325
1.316
1.128
1.114
1.033
0.63
1.06
1.07
0.97
1.00
4.02
0.91
4.00
1.03
1.13
3.01
2.13
2.04
PPM

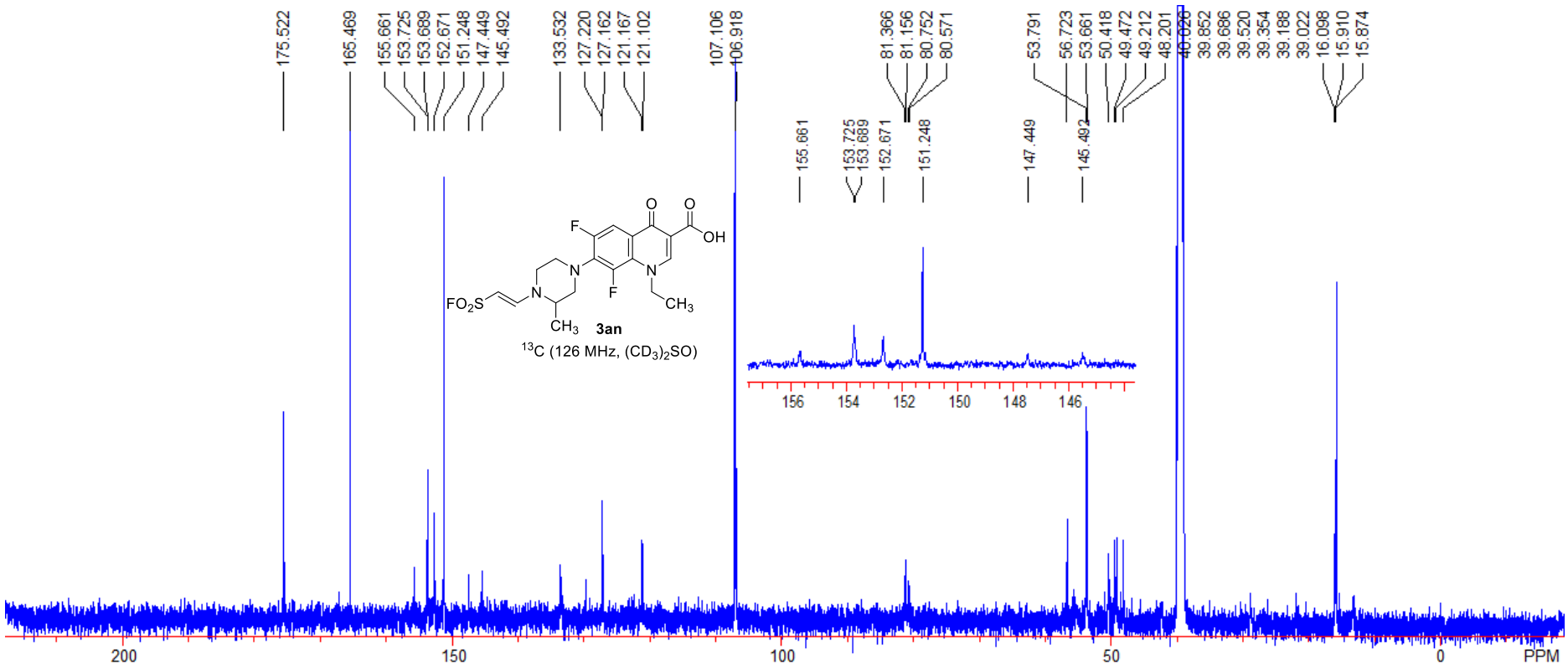

176.323
165.749
153.883
153.797
151.897
148.199
147.860
144.567
144.480
139.049
118.993
118.935
111.171
111.063
110.991
110.875
106.860
106.773
81.076
80.889
51.530
49.551
47.984
44.908
40.018
39.852
39.686
39.520
39.354
39.188
39.014
35.880
7.576
F
O
O
OH
N
N
N
FO2S
3am
13C (126 MHz, (CD3)2SO)
200
150
100
50
0
PPM

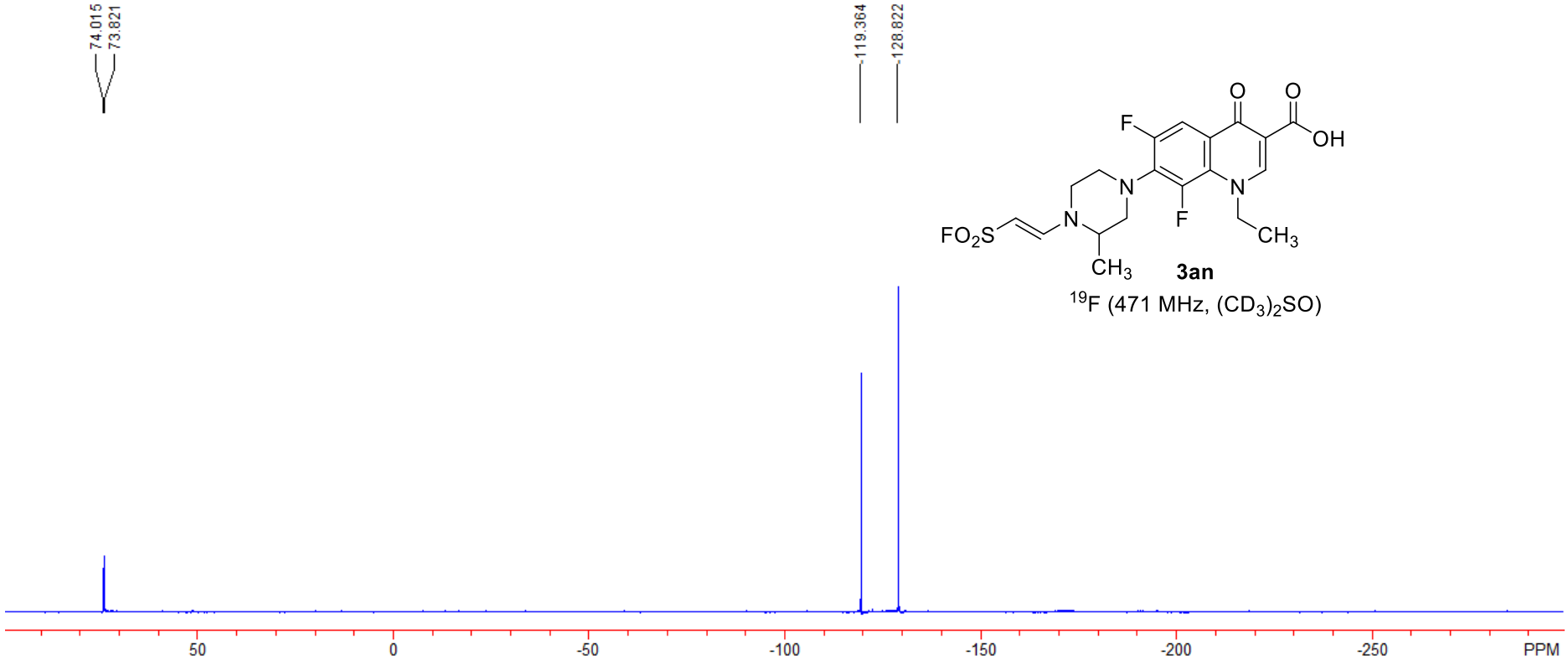


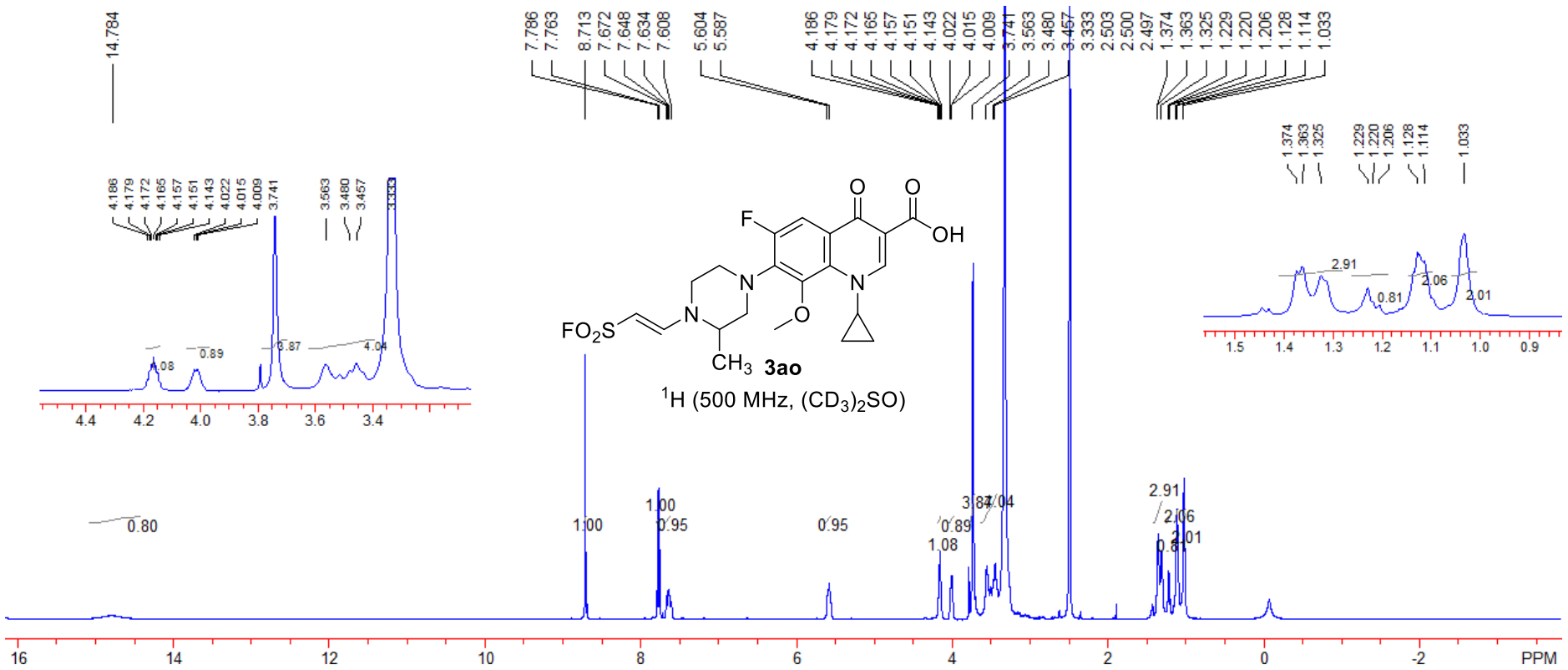
3am

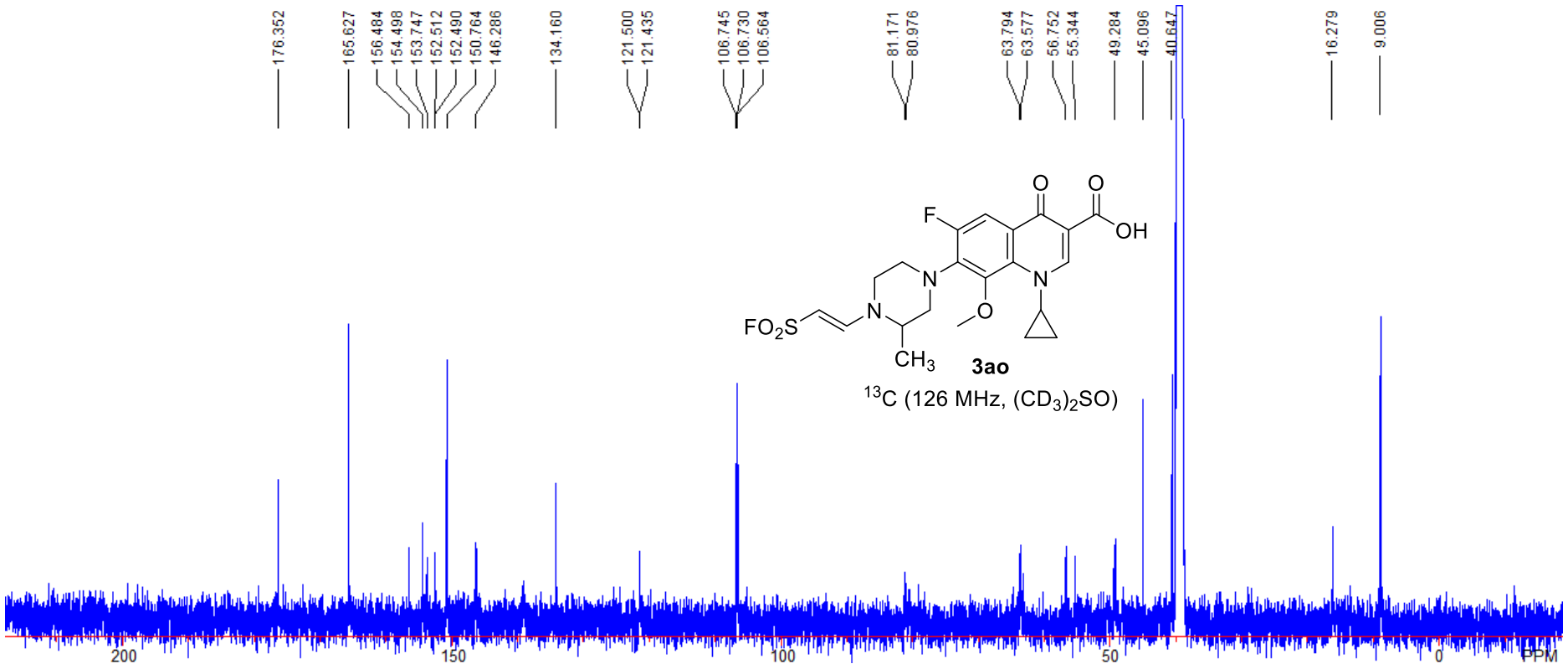
^{19}F (471 MHz, $(CD_3)_2SO$)

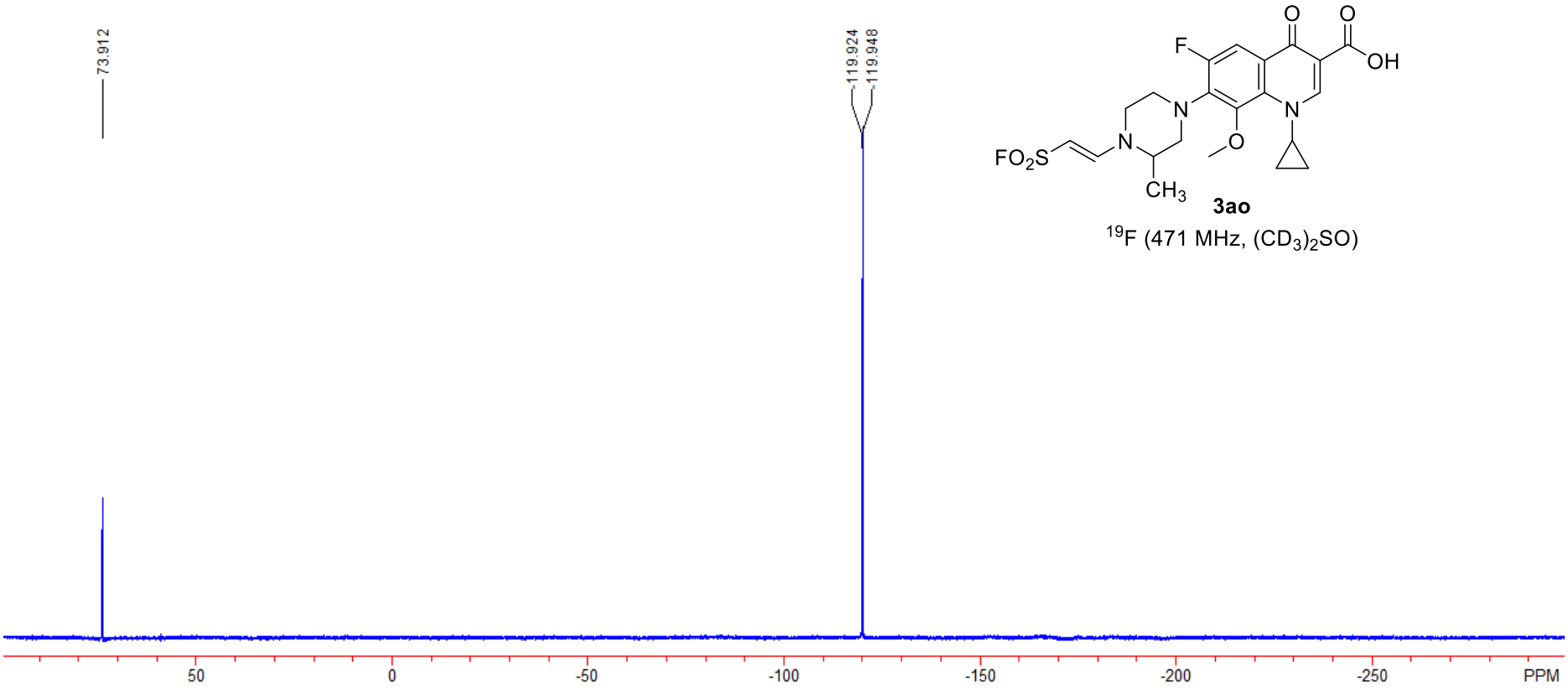

3an
^{1}H (500 MHz, $(CD_3)_2SO$)
14.776
8.918
7.879
7.856
7.662
7.638
7.610
7.585
5.591
5.568
4.590
3.708
4.004
3.530
3.505
3.484
3.459
3.429
3.314
2.500
1.462
1.448
1.435
1.355
1.322
1.227
1.222
1.06
1.04
1.02
1.07
1.03
2.22
1.07
3.70
0.98
3.20
3.06
PPM


175.522
165.469
155.661
153.725
153.689
152.671
151.248
147.449
145.492
133.532
127.220
127.162
121.167
121.102
107.106
106.918
81.366
81.156
80.752
80.571
53.791
56.723
53.661
50.418
49.472
49.212
48.201
40.026
39.852
39.686
39.520
39.354
39.188
39.022
16.098
15.910
15.874
F
O
O
OH
N
N
F
N
FO2S
CH3
CH3
3an
13C (126 MHz, (CD3)2SO)
200
150
100
50
0
PPM
156
154
152
150
148
146


74.015
73.821
119.364
128.822
O
O
F
OH
N
N
N
F
FO2S
CH3
CH3
3an
19F (471 MHz, (CD3)2SO)
50
0
-50
-100
-150
-200
-250
PPM

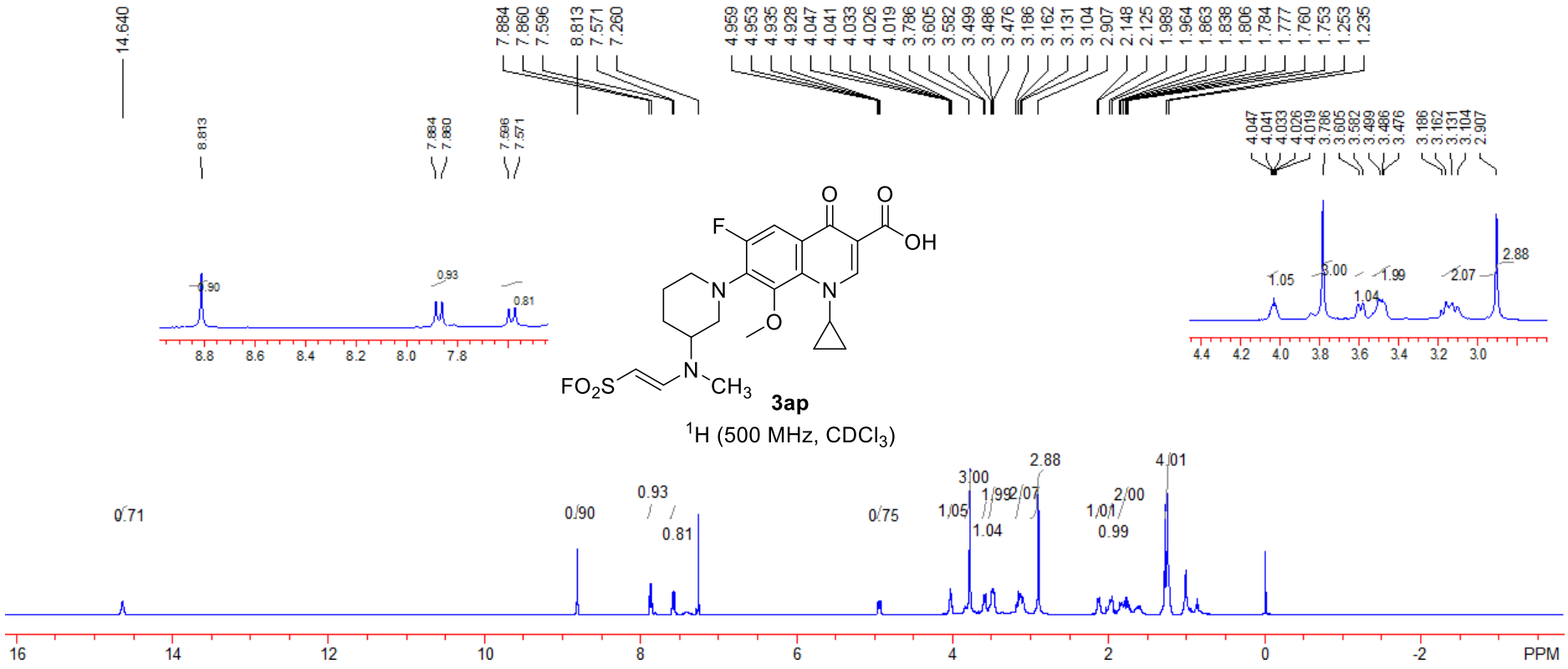

14.784
7.786
7.763
8.713
7.672
7.648
7.634
7.608
5.604
5.587
4.186
4.179
4.172
4.165
4.157
4.151
4.143
4.022
4.015
4.009
3.741
3.563
3.480
3.457
3.333
2.503
2.500
2.497
1.374
1.363
1.325
1.229
1.220
1.206
1.128
1.114
1.033
F
O
O
OH
N
N
N
O
FO2S
CH3
3ao
1H (500 MHz, (CD3)2SO)
0.80
1.00
1.00
0.95
0.95
0.89
1.08
3.87
4.04
2.91
2.06
2.01
0.81
PPM

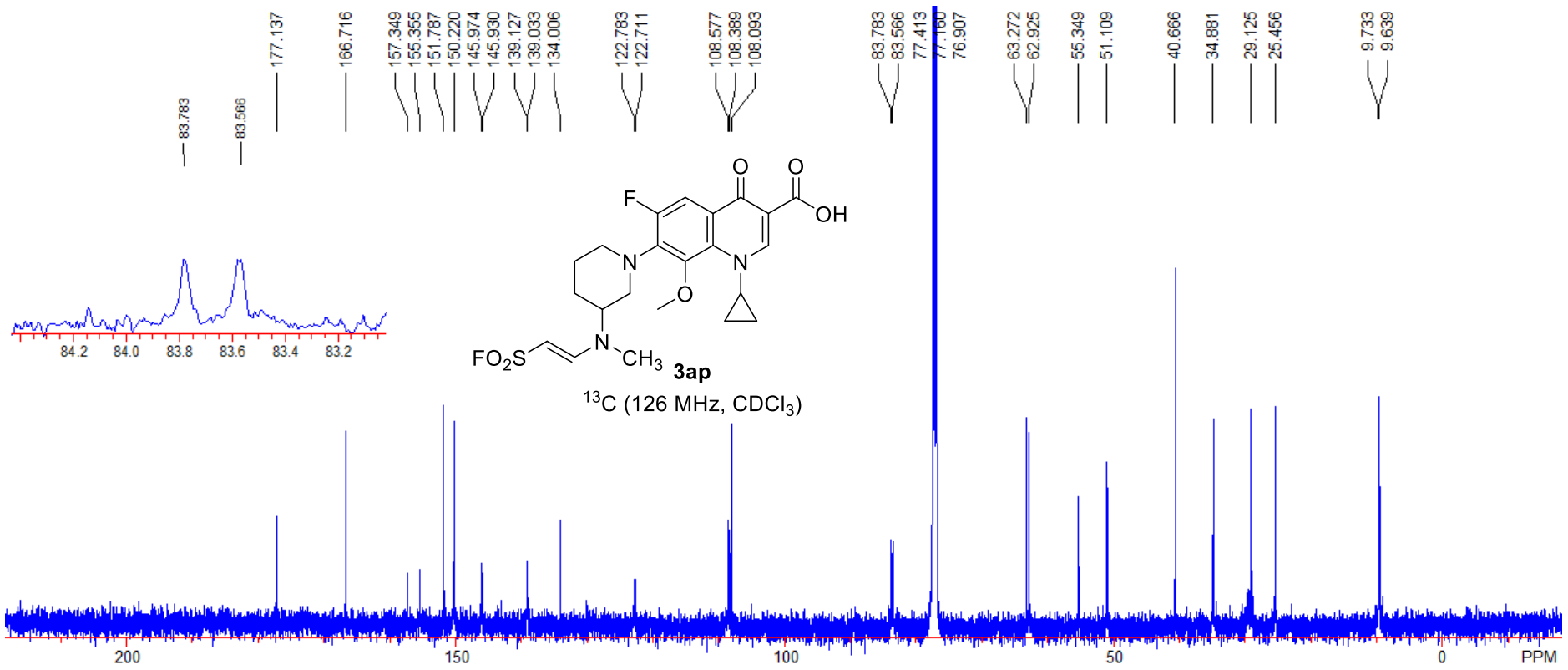

176.352
165.627
156.484
154.498
153.747
152.512
152.490
150.764
146.286
134.160
121.500
121.435
106.745
106.730
106.564
81.171
80.976
63.794
63.577
56.752
55.344
49.284
45.096
40.647
16.279
9.006
F
O
O
OH
N
N
N
O
FO2S
CH3
3ao
13C (126 MHz, (CD3)2SO)
200
150
100
50
0
PPM

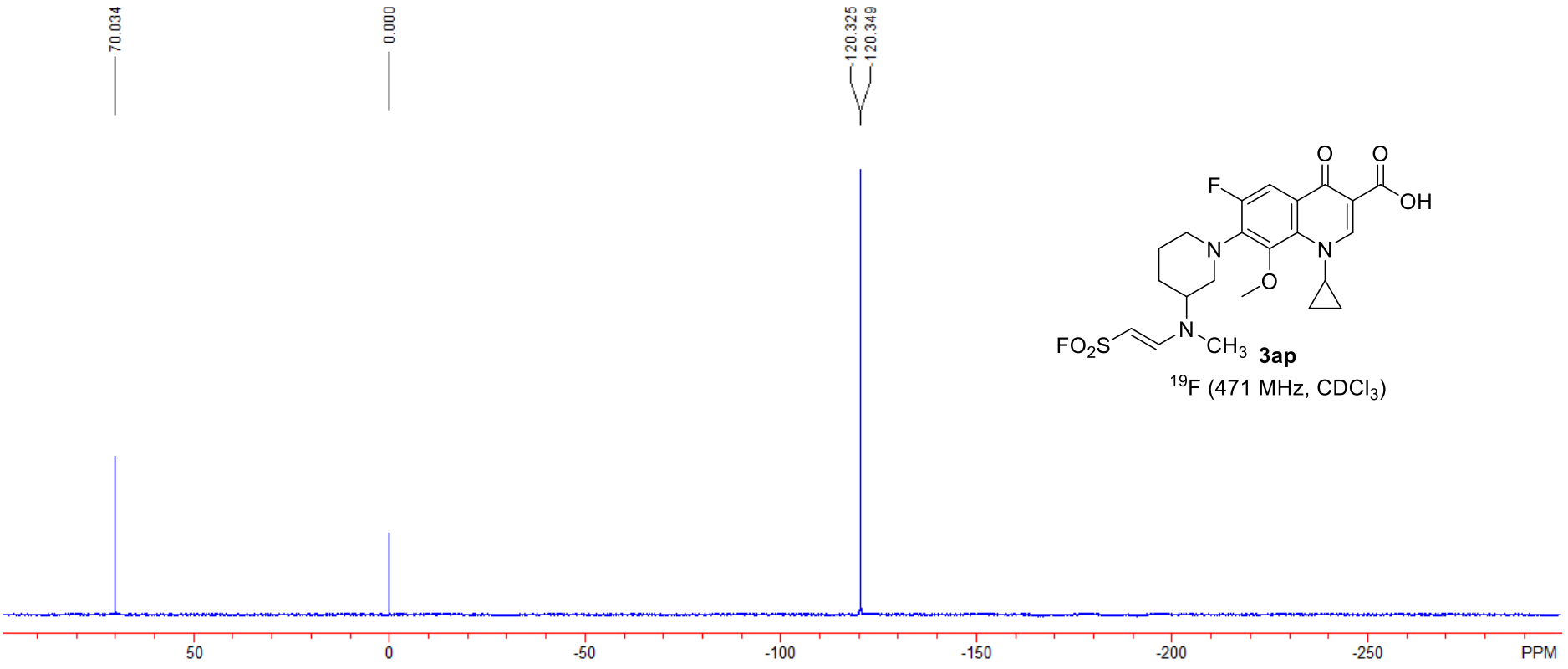


3ao

^{19}F (471 MHz, $(CD_3)_2SO$)

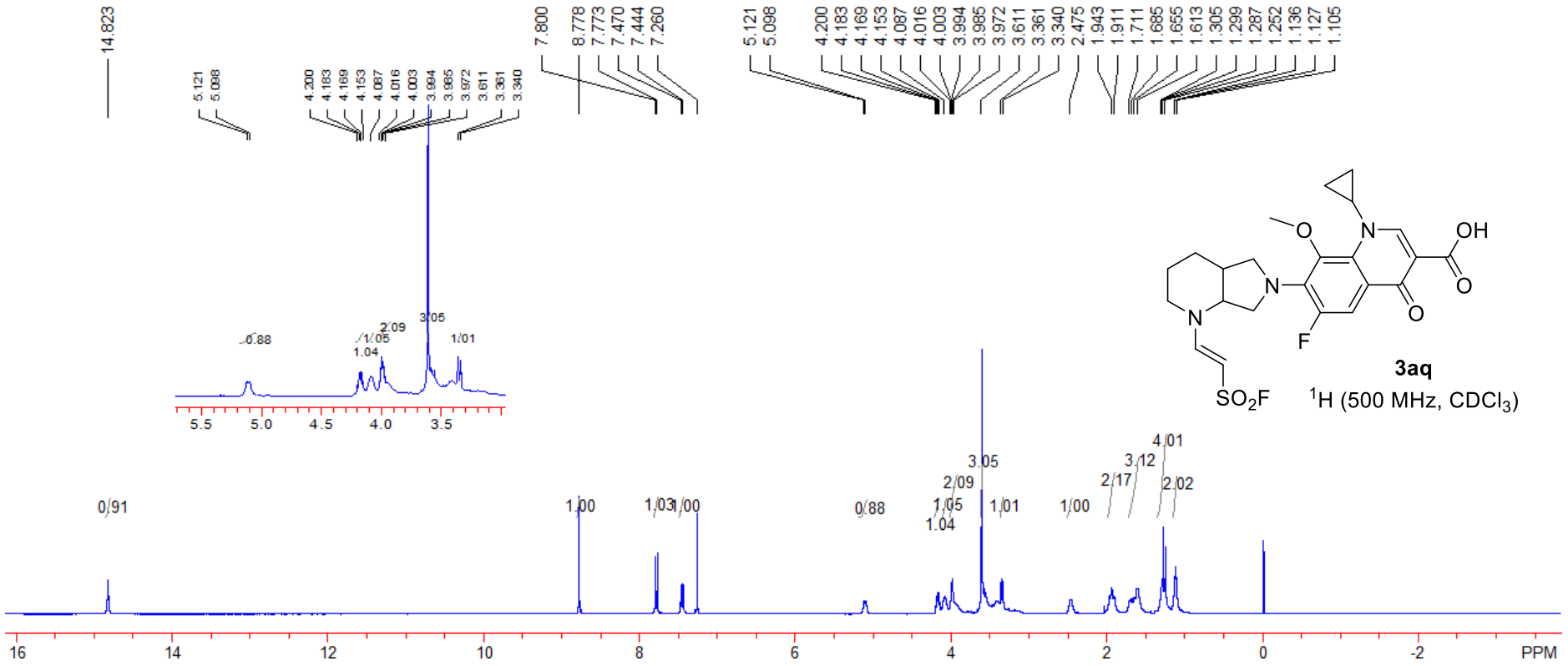

14.640
7.884
7.860
7.596
8.813
7.571
7.260
4.959
4.953
4.935
4.928
4.047
4.041
4.033
4.026
4.019
3.786
3.605
3.582
3.499
3.486
3.476
3.186
3.162
3.131
3.104
2.907
2.148
2.125
1.989
1.964
1.863
1.838
1.806
1.784
1.777
1.760
1.753
1.253
1.235
F
O
O
OH
N
N
O
N
CH3
FO2S
3ap
1H (500 MHz, CDCl3)
0.71
0.90
0.93
0.81
0.75
3.00
1.05
1.99
1.04
2.07
2.88
1.01
2.00
0.99
4.01
16
14
12
10
8
6
4
2
0
-2
PPM

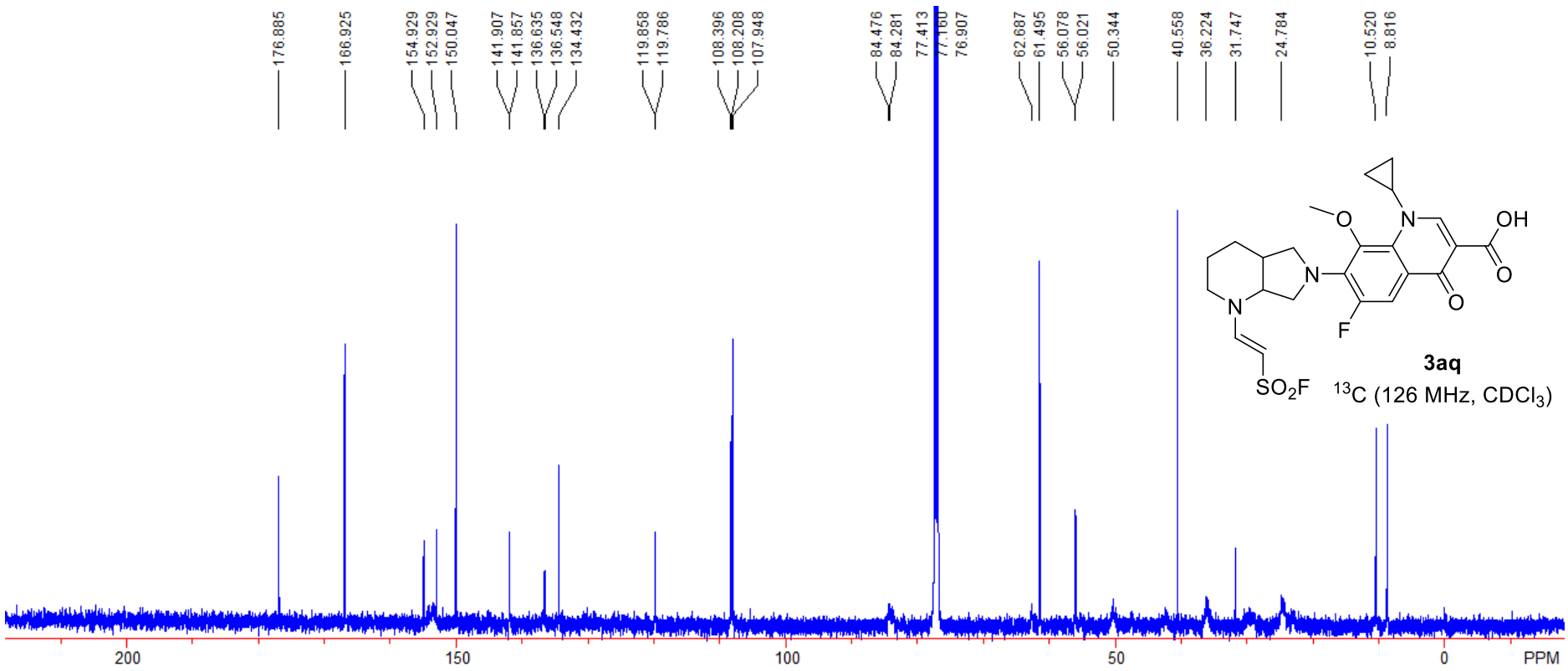

177.137
166.716
157.349
155.355
151.787
150.220
145.974
145.930
139.127
139.033
134.006
122.783
122.711
108.577
108.389
108.093
83.783
83.566
77.413
77.160
76.907
63.272
62.925
55.349
51.109
40.666
34.881
29.125
25.456
9.733
9.639
84.2
84.0
83.8
83.6
83.4
83.2
F
O
O
OH
N
N
O
N
CH3
FO2S
3ap
13C (126 MHz, CDCl3)
200
150
100
50
0
PPM

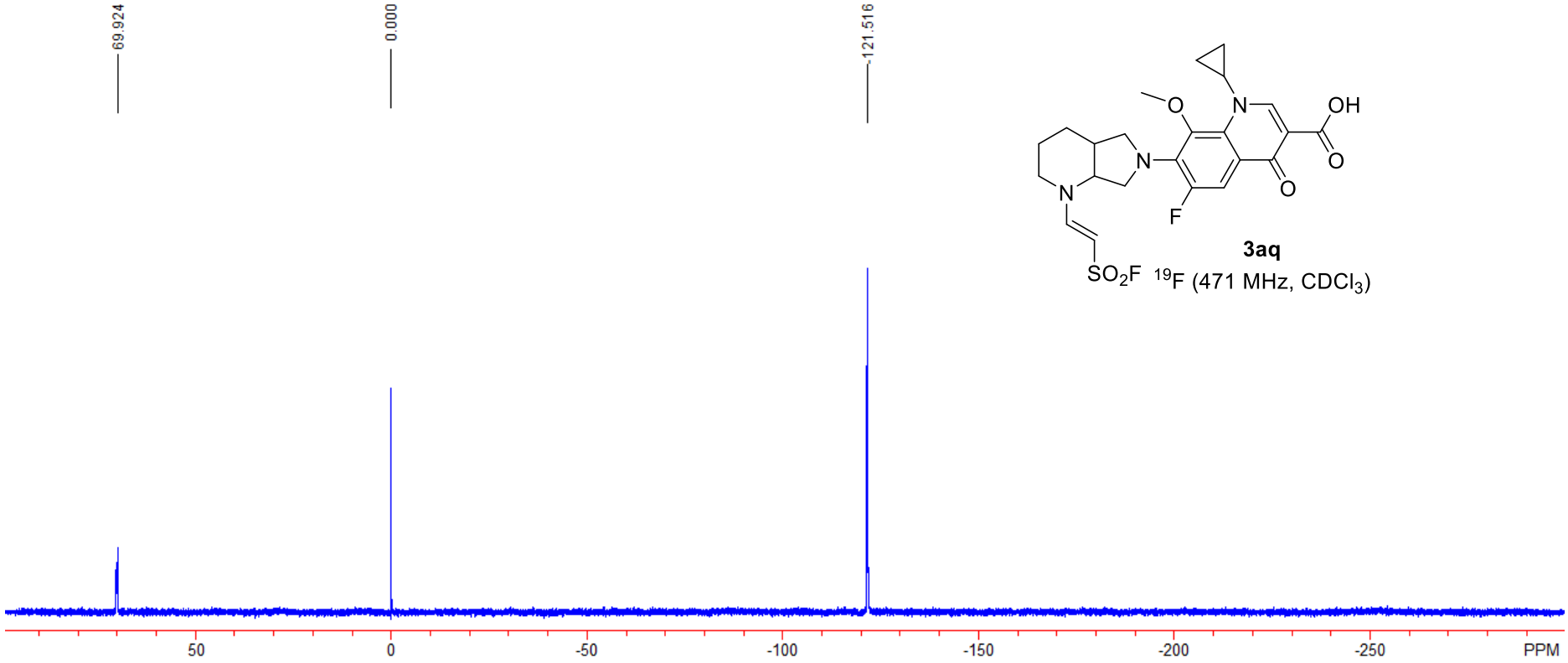


3ap

^{19}F (471 MHz, $CDCl_3$)

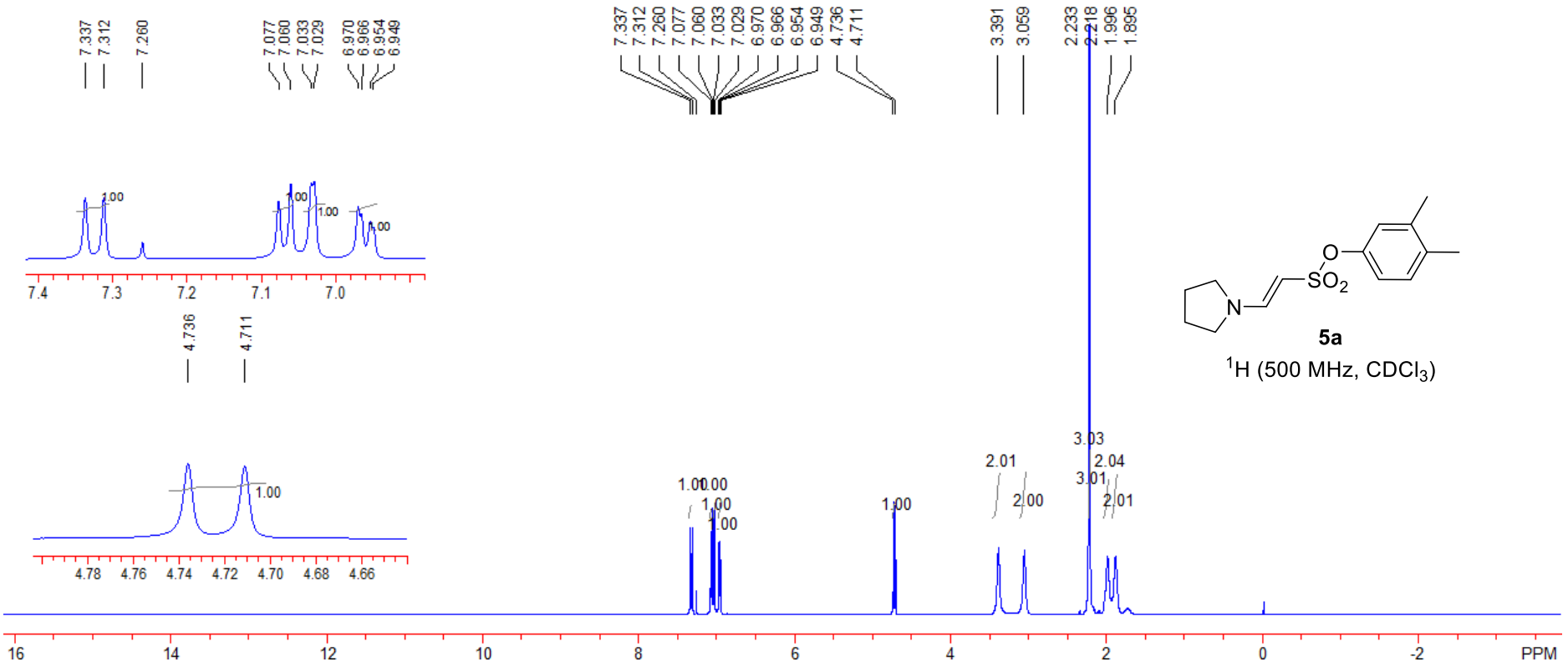

14.823
5.121
5.098
4.200
4.183
4.169
4.153
4.087
4.016
4.003
3.994
3.985
3.972
3.611
3.361
3.340
7.800
8.778
7.773
7.470
7.444
7.260
2.475
1.943
1.911
1.711
1.685
1.655
1.613
1.305
1.299
1.287
1.252
1.136
1.127
1.105
0.88
1.05
1.04
2.09
3.05
1.01
5.5
5.0
4.5
4.0
3.5
0.91
1.00
1.03
1.00
0.88
1.04
1.05
3.05
2.09
1.01
1.00
2.17
3.12
4.01
2.02
16
14
12
10
8
6
4
2
0
-2
PPM
OH
O
O
N
N
O
F
N
SO2F
3aq
1H (500 MHz, CDCl3)

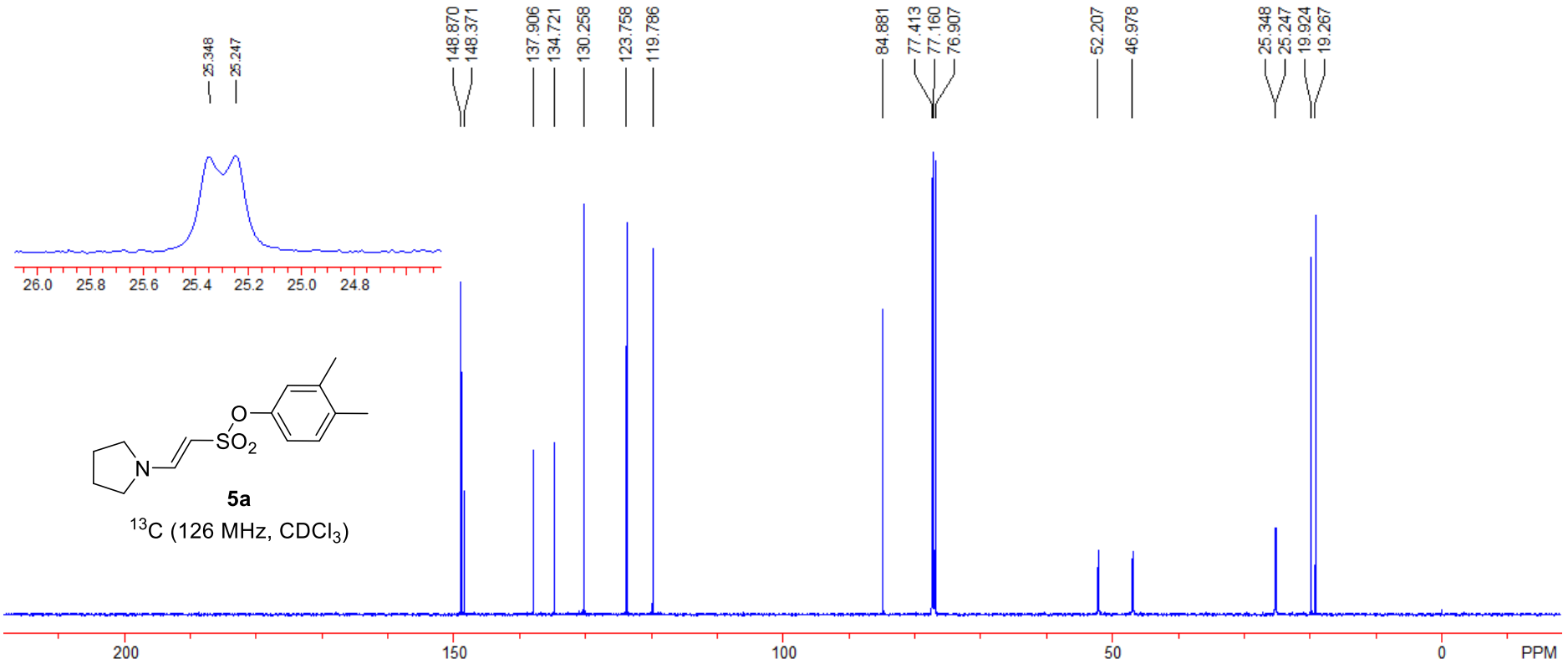

176.885
166.925
154.929
152.929
150.047
141.907
141.857
136.635
136.548
134.432
119.858
119.786
108.396
108.208
107.948
84.476
84.281
77.413
77.160
76.907
62.687
61.495
56.078
56.021
50.344
40.558
36.224
31.747
24.784
10.520
8.816
200
150
100
50
0
PPM
O
N
OH
O
N
O
N
F
SO2F
3aq
13C (126 MHz, CDCl3)



3aq

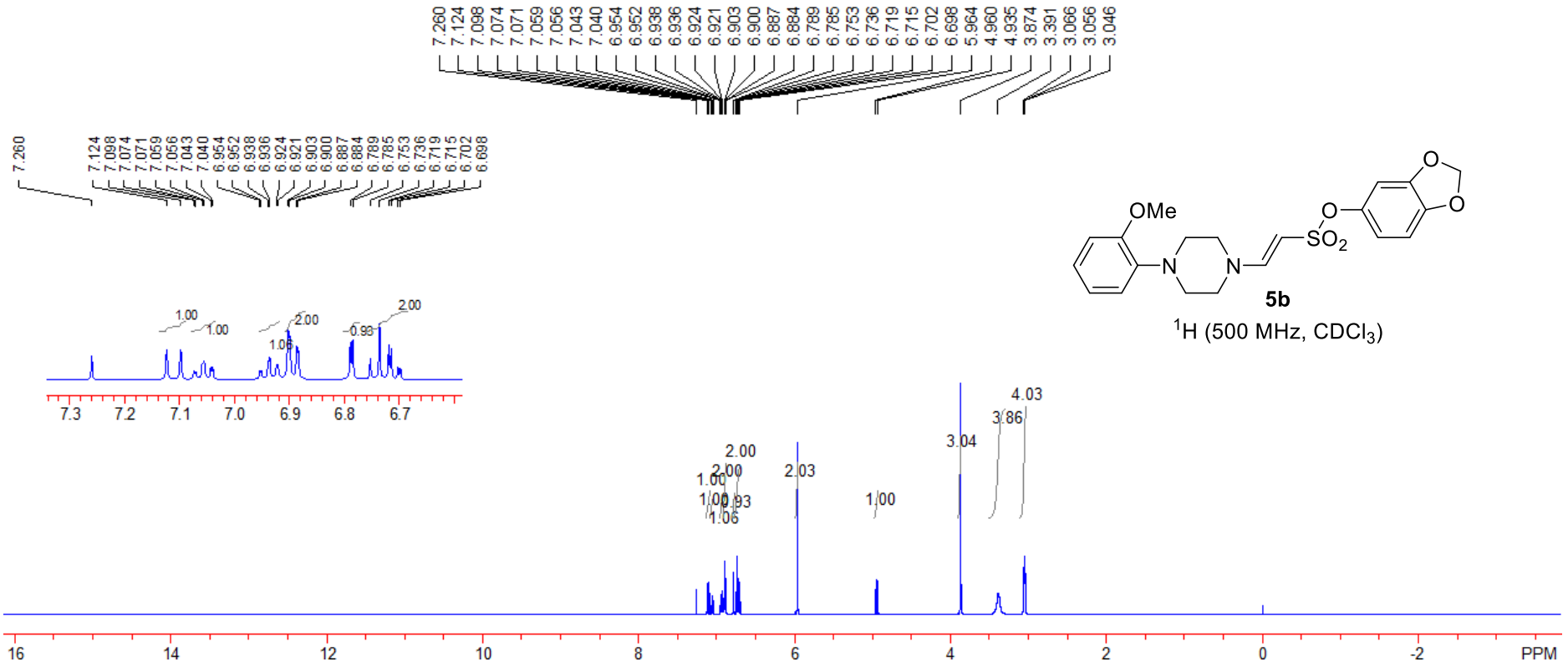
^{19}F (471 MHz, $CDCl_3$)

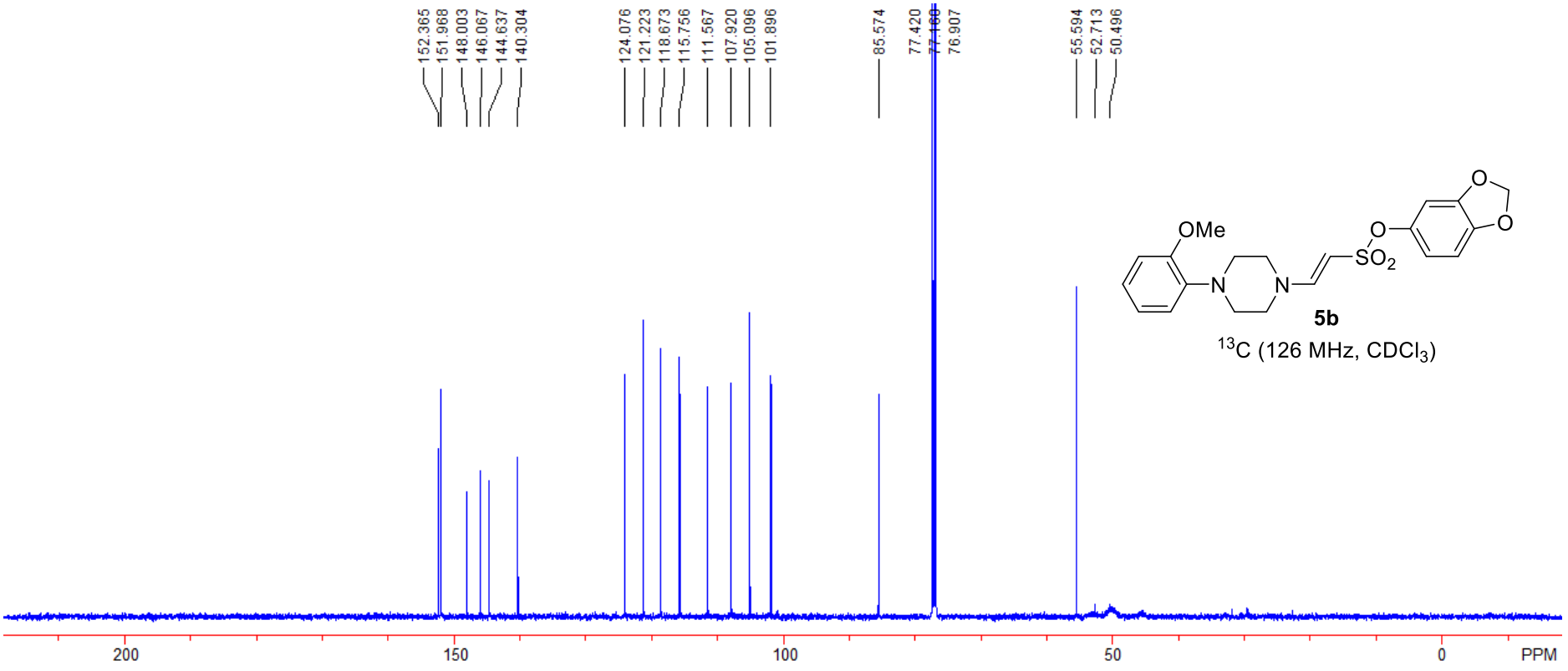

7.337
7.312
7.260
7.077
7.060
7.033
7.029
6.970
6.966
6.954
6.949
4.736
4.711
3.391
3.059
2.233
2.218
1.996
1.895
1.00
1.00
1.00
1.00
7.4
7.3
7.2
7.1
7.0
4.736
4.711
1.00
4.78
4.76
4.74
4.72
4.70
4.68
4.66
1.00
1.00
1.00
1.00
1.00
2.01
2.00
3.03
2.04
3.01
2.01
16
14
12
10
8
6
4
2
0
-2
PPM
O
SO2
N
5a
1H (500 MHz, CDCl3)



5a

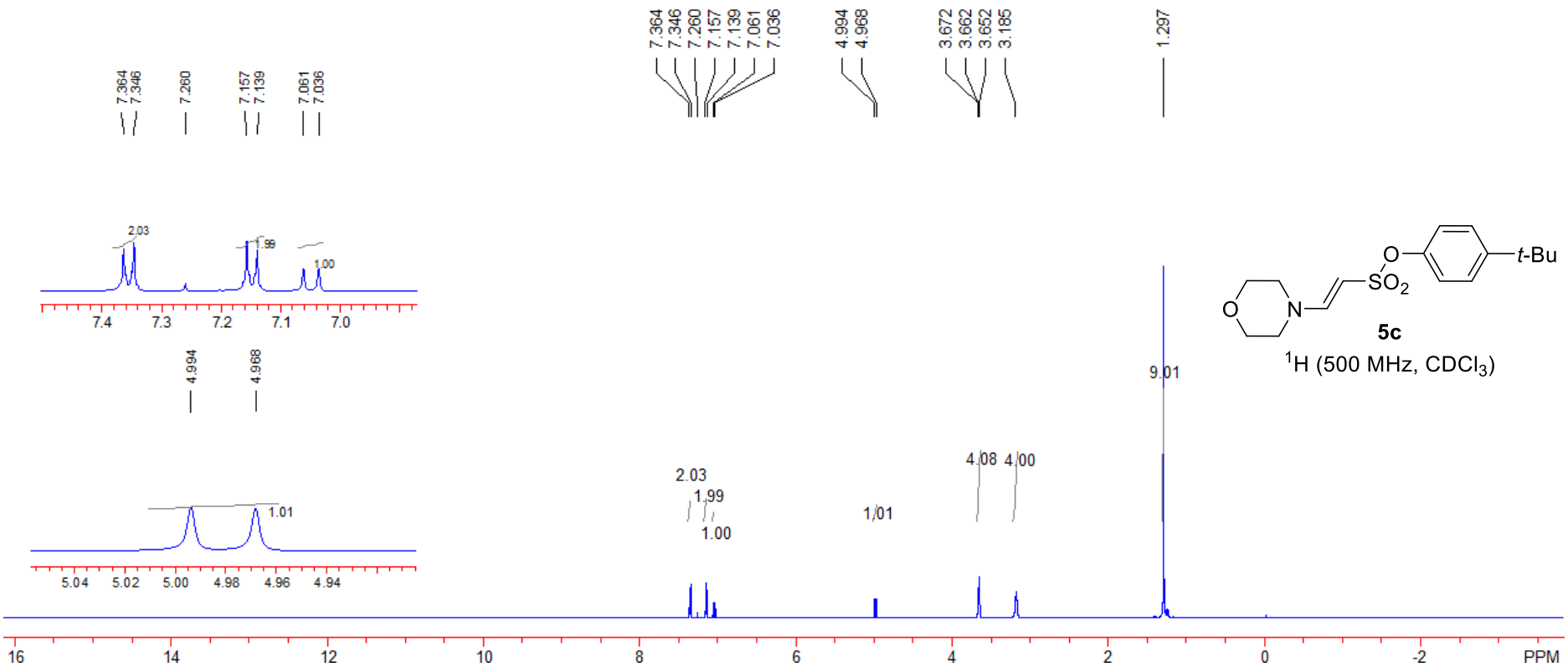
^{13}C (126 MHz, $CDCl_3$)

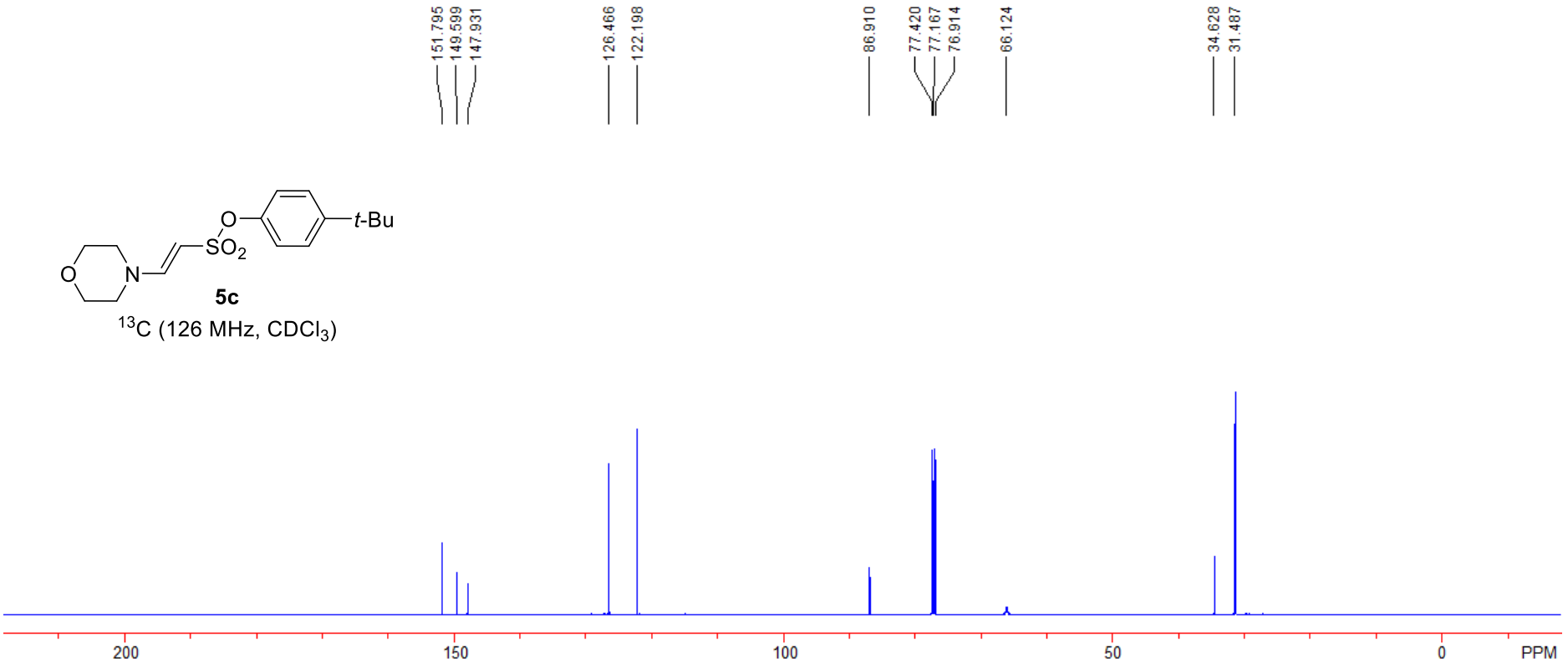

7.260
7.124
7.098
7.074
7.071
7.059
7.056
7.043
7.040
6.954
6.952
6.938
6.936
6.924
6.921
6.903
6.900
6.887
6.884
6.789
6.785
6.753
6.736
6.719
6.715
6.702
6.698
5.964
4.960
4.935
3.874
3.391
3.066
3.056
3.046
OMe
O
O
O
SO2
N
N
5b
1H (500 MHz, CDCl3)
1.00
1.00
2.00
1.06
0.93
2.00
7.3
7.2
7.1
7.0
6.9
6.8
6.7
2.00
2.00
1.00
1.00
1.06
2.03
1.00
3.04
3.86
4.03
16
14
12
10
8
6
4
2
0
-2
PPM

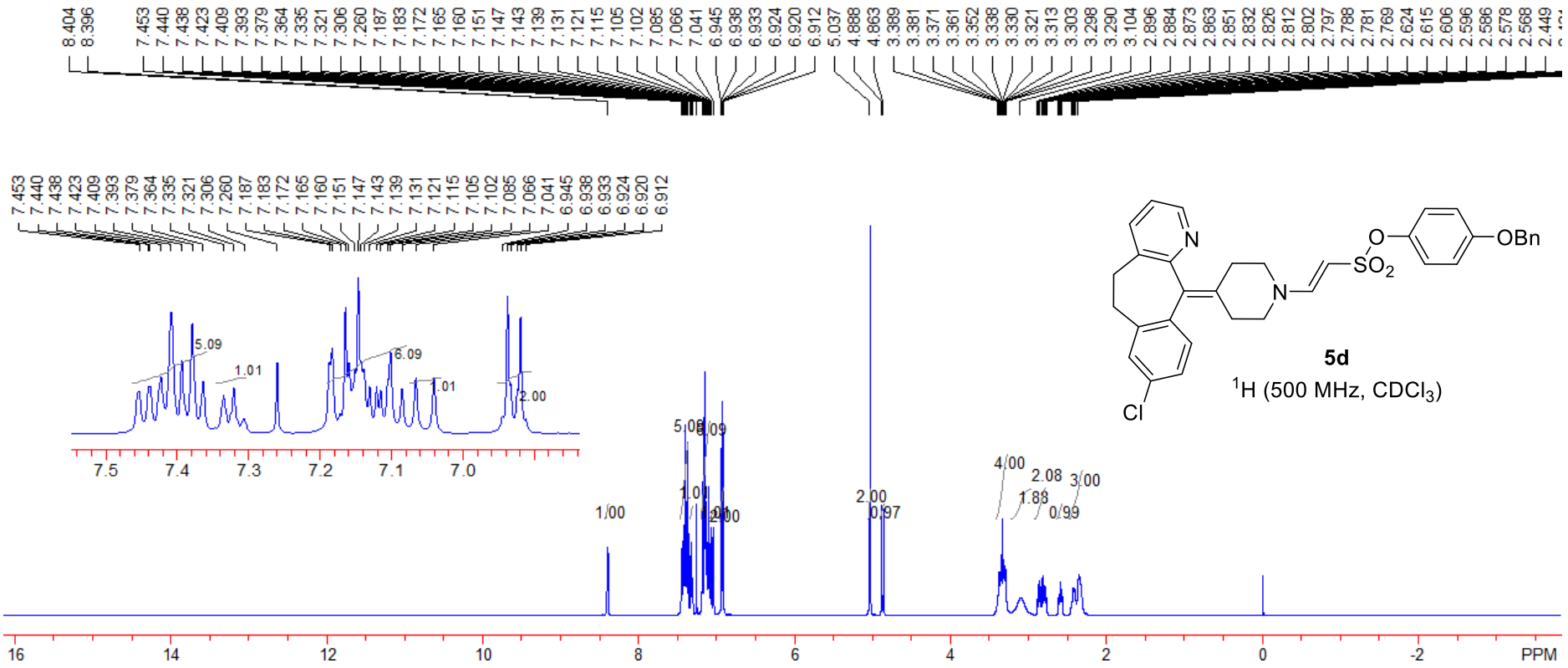


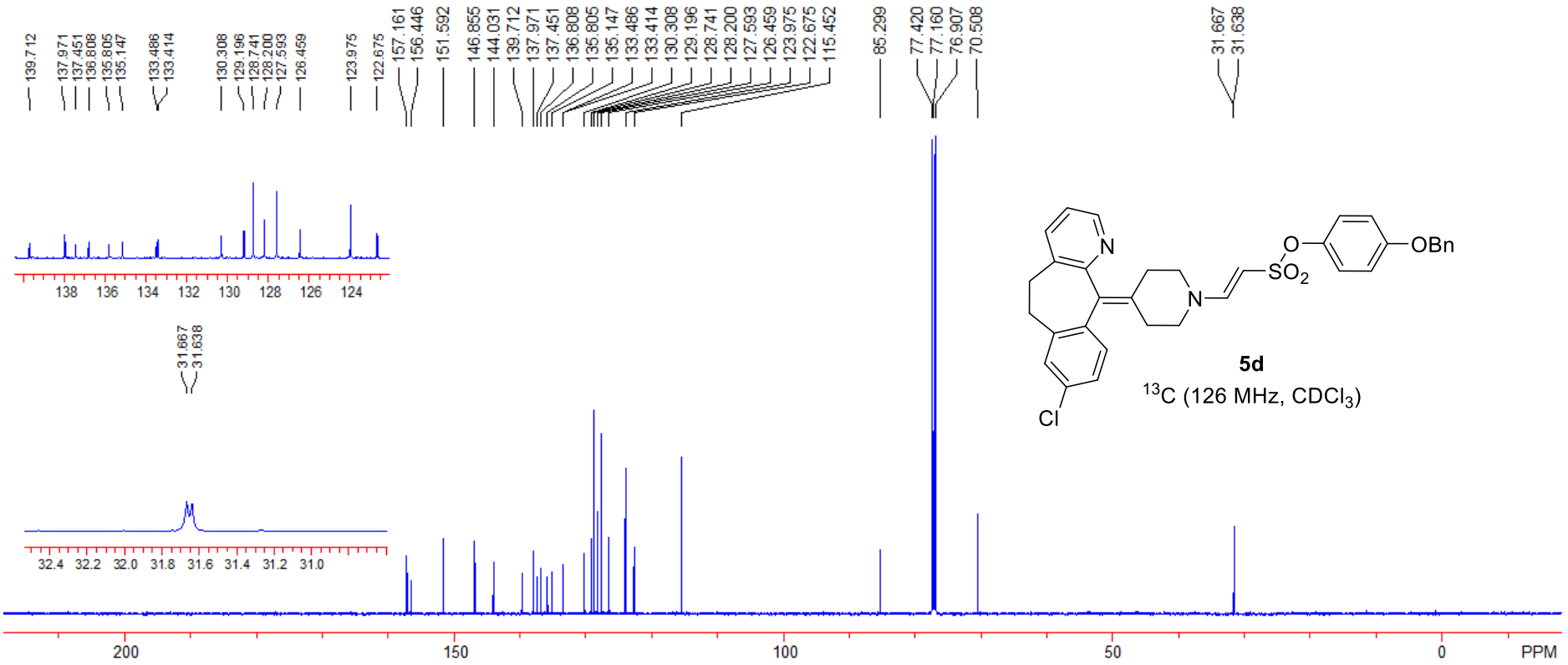
5b

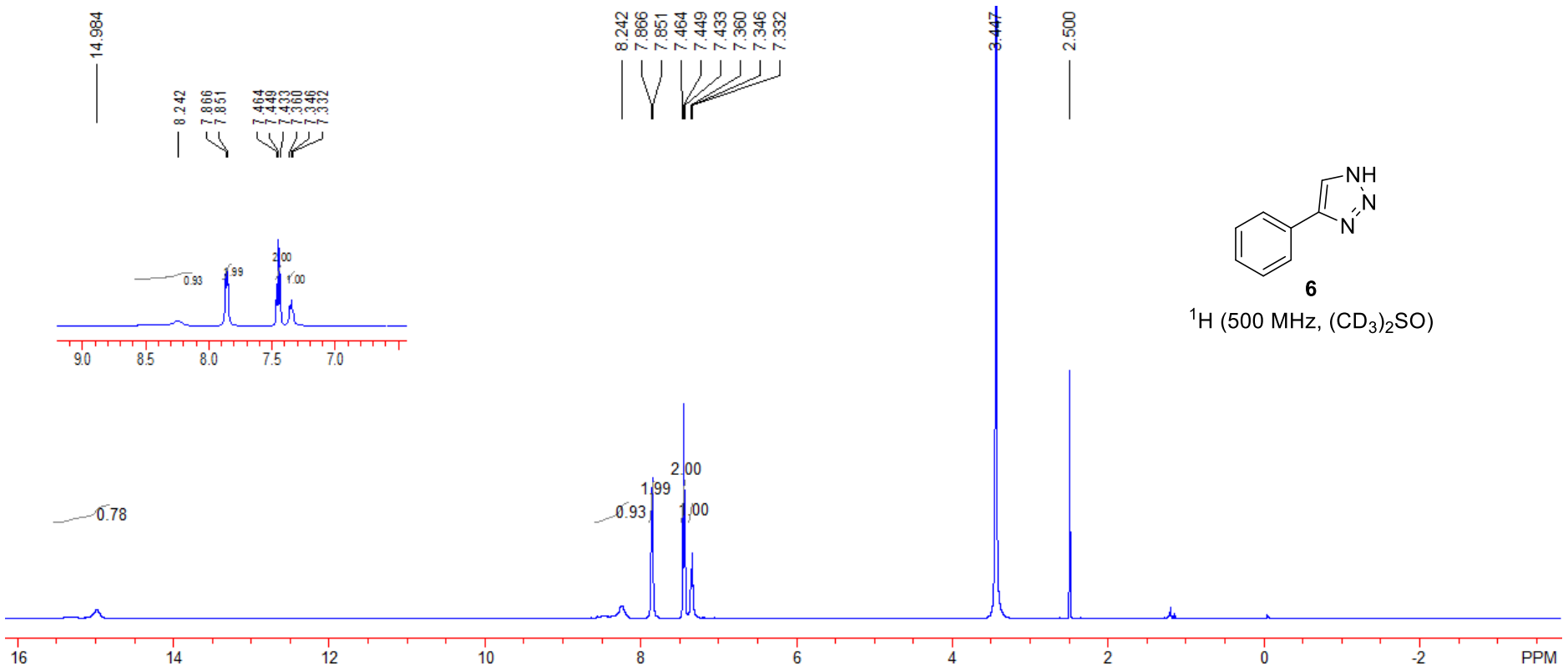
^{13}C (126 MHz, $CDCl_3$)

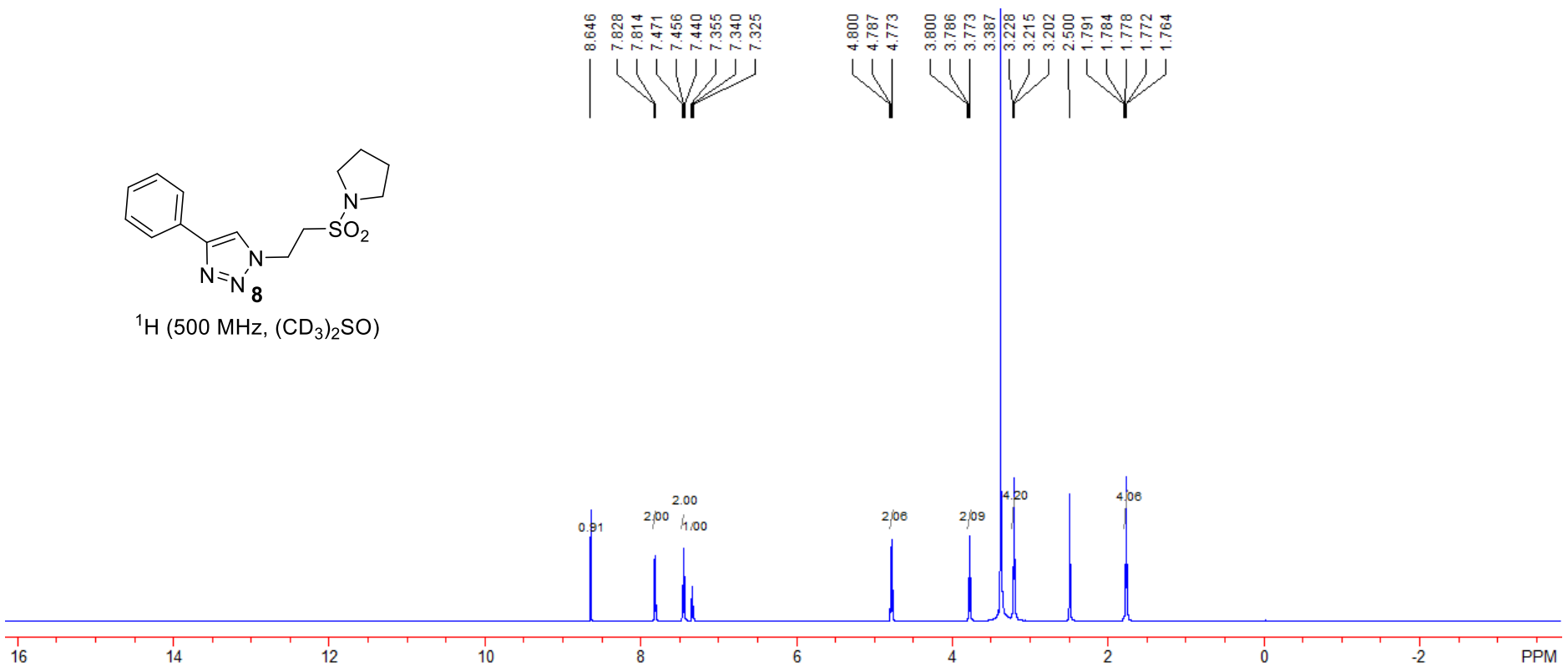

7.364
7.346
7.260
7.157
7.139
7.061
7.036
4.994
4.968
3.672
3.662
3.652
3.185
1.297
2.03
1.99
1.00
1.01
4.08
4.00
9.01
O
SO2
t-Bu
O
N
5c
1H (500 MHz, CDCl3)
PPM


151.795
149.599
147.931
126.466
122.198
86.910
77.420
77.167
76.914
66.124
34.628
31.487
O
SO2
t-Bu
O
N
5c
13C (126 MHz, CDCl3)
200
150
100
50
0
PPM


8.404
8.396
7.453
7.440
7.438
7.423
7.409
7.393
7.379
7.364
7.335
7.321
7.306
7.260
7.187
7.183
7.172
7.165
7.160
7.151
7.147
7.143
7.139
7.131
7.121
7.115
7.105
7.102
7.085
7.066
7.041
6.945
6.938
6.933
6.924
6.920
6.912
5.037
4.888
4.863
3.389
3.381
3.371
3.361
3.352
3.338
3.330
3.321
3.313
3.303
3.298
3.290
3.104
2.896
2.884
2.873
2.863
2.851
2.832
2.826
2.812
2.802
2.797
2.788
2.781
2.769
2.624
2.615
2.606
2.596
2.586
2.578
2.568
2.449
5.09
1.01
6.09
1.01
2.00
7.5
7.4
7.3
7.2
7.1
7.0
1.00
5.08
6.09
1.01
2.00
2.00
0.97
4.00
2.08
1.88
3.00
0.99
16
14
12
10
8
6
4
2
0
-2
PPM
N
O
SO2
OBn
N
Cl
5d
1H (500 MHz, CDCl3)

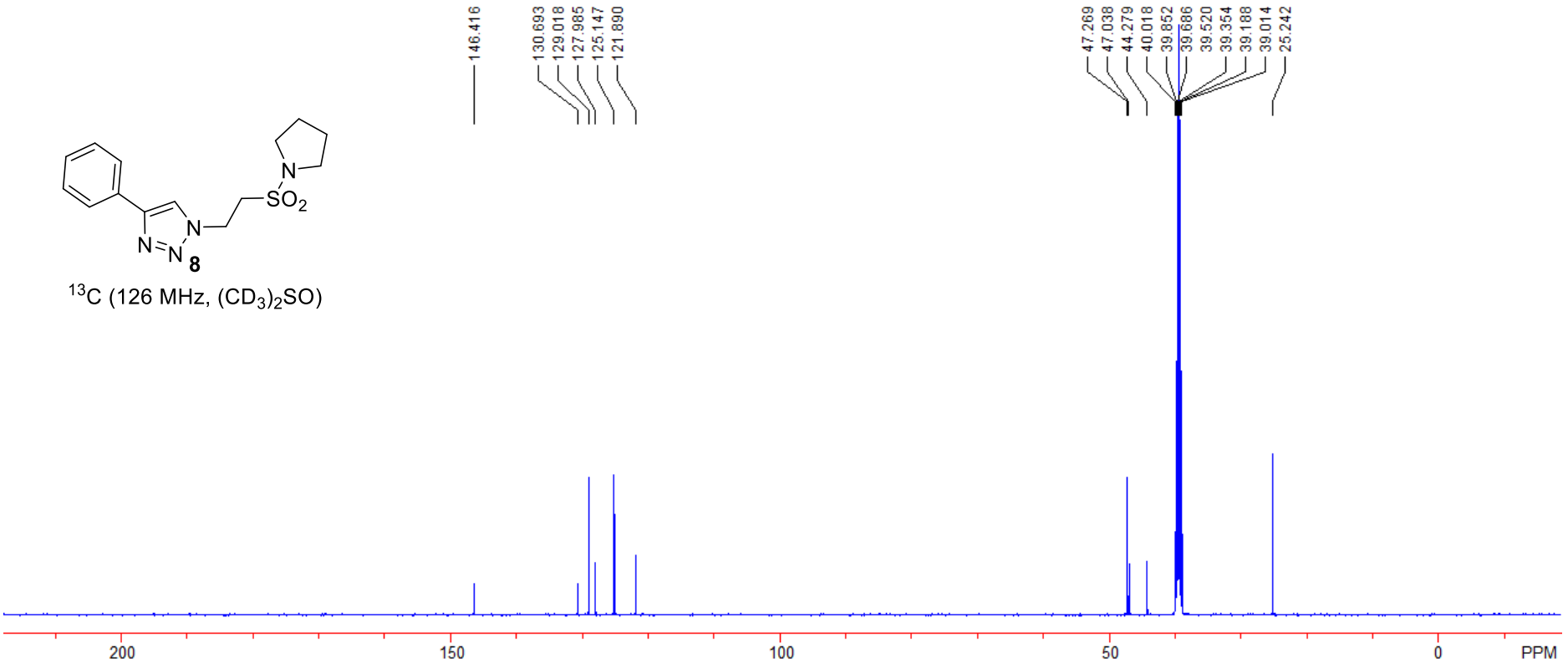

139.712
137.971
137.451
136.808
135.805
135.147
133.486
133.414
130.308
129.196
128.741
128.200
127.593
126.459
123.975
122.675
157.161
156.446
151.592
146.855
144.031
139.712
137.971
137.451
136.808
135.805
135.147
133.486
133.414
130.308
129.196
128.741
128.200
127.593
126.459
123.975
122.675
115.452
85.299
77.420
77.160
76.907
70.508
31.667
31.638
138 136 134 132 130 128 126 124
31.667
31.638
32.4 32.2 32.0 31.8 31.6 31.4 31.2 31.0
200 150 100 50 0 PPM
N
O
SO2
OBn
N
Cl
5d
13C (126 MHz, CDCl3)


14.984
8.242
7.866
7.851
7.464
7.449
7.433
7.360
7.346
7.332
3.447
2.500
0.78
0.93
1.99
2.00
1.00
NH
N
N
6
1H (500 MHz, (CD3)2SO)
16
14
12
10
8
6
4
2
0
-2
PPM

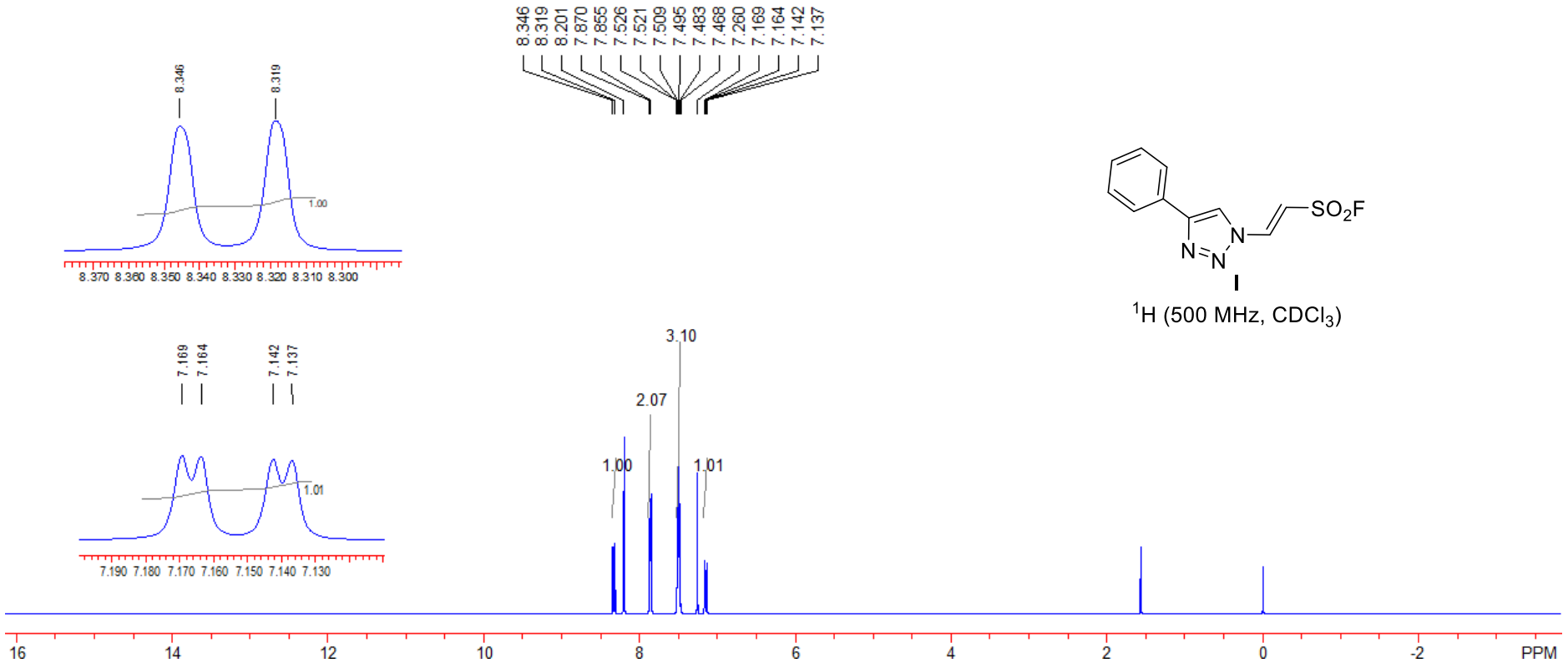


8

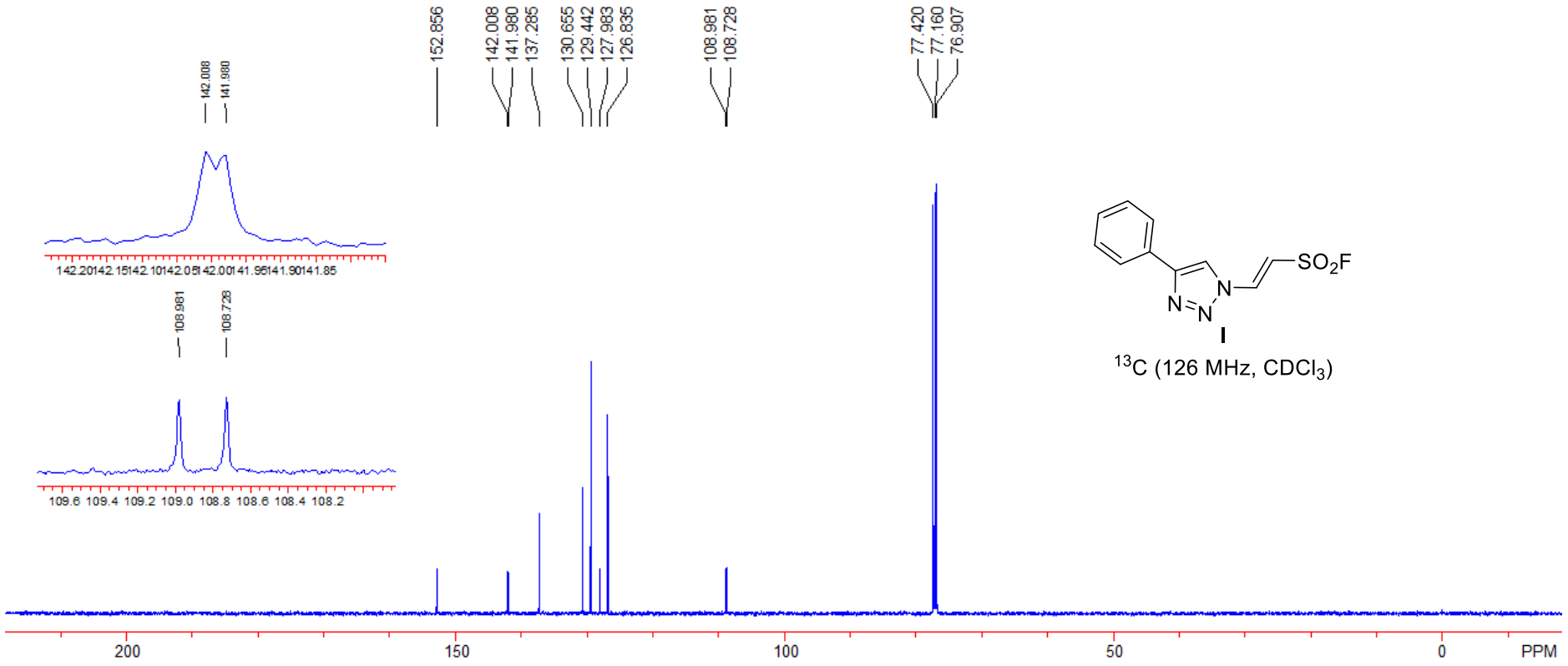
^{1}H (500 MHz, $(CD_3)_2SO$)

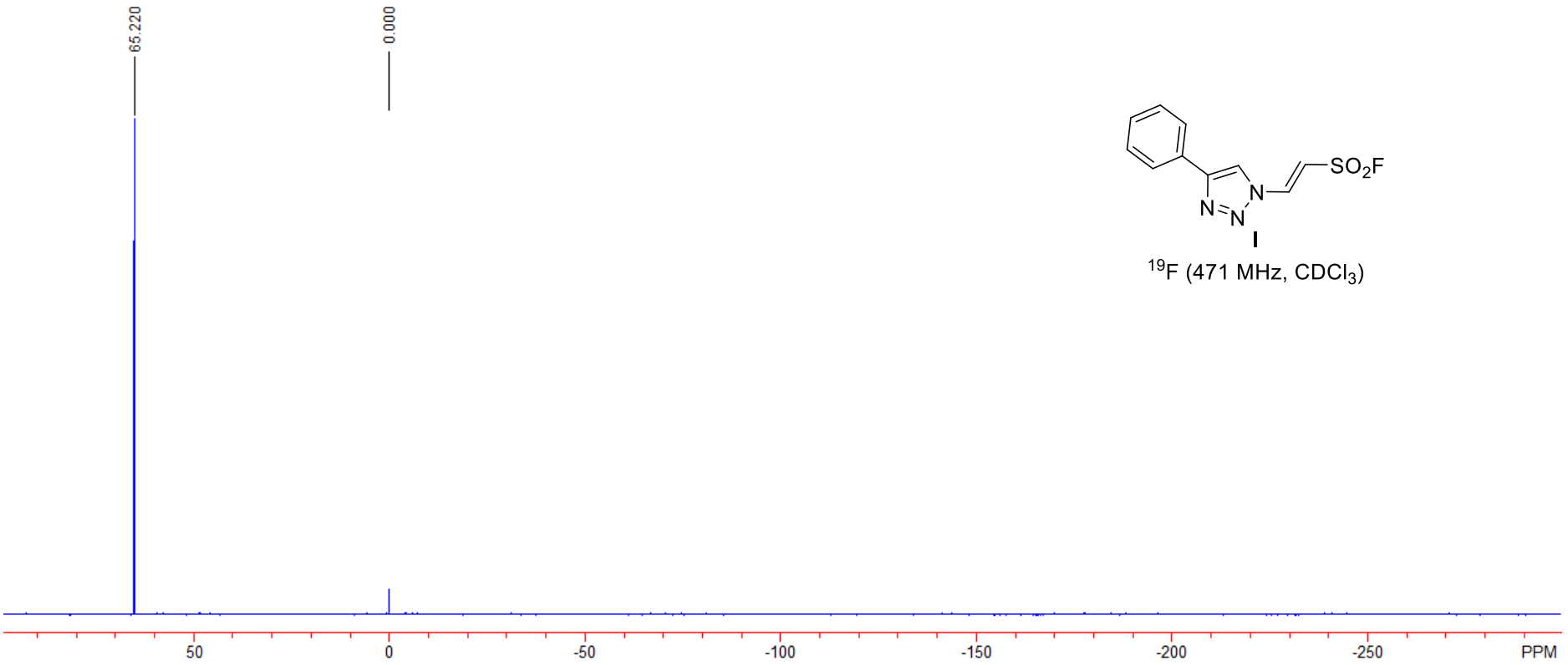


^{13}C (126 MHz, $(CD_3)_2SO$)



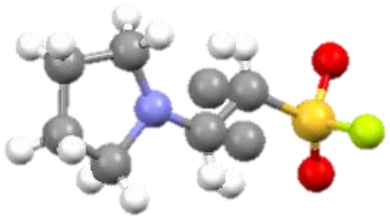
^{1}H (500 MHz, $CDCl_3$)


152.856
142.008
141.980
137.285
130.655
129.442
127.983
126.835
108.981
108.728
77.420
77.160
76.907
142.008
141.980
142.20142.15142.10142.05142.00141.95141.90141.85
108.981
108.728
109.6 109.4 109.2 109.0 108.8 108.6 108.4 108.2
SO2F
N
N
N
13C (126 MHz, CDCl3)
200
150
100
50
0
PPM



^{19}F (471 MHz, $CDCl_3$)

6. Data of Crystal Structure of 3b



The purified compound **3b** about 100 mg is dissolved in diethyl ether and placed in a dark cabinet to slowly evaporate. After several days, a colorless bulk crystal is obtained. The X-ray crystal-structure determinations were obtained on a Bruker Smart-1000 CDCC diffractometer (graphite-monochromated Mo Kα radiation, λ=0.71073 nm) at 298(2) K. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 1941924).

The ellipsoid contour probability level in the caption is 50 %.

Table S4. Crystal data and structure refinement for 190328e.

Identification code	190328e
Empirical formula	C6 H10 F N O2 S
Formula weight	179.21
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 5.1313(4) A alpha = 90 deg.
	b = 9.5990(8) A beta = 91.1720(10) deg.
	c = 8.4892(7) A gamma = 90 deg.
Volume	418.05(6) A^3
Z, Calculated density	2, 1.424 Mg/m^3
Absorption coefficient	0.356 mm^-1
F(000)	188
Crystal size	0.45 x 0.40 x 0.30 mm
Theta range for data collection	2.40 to 25.02 deg.
Limiting indices	-6<=h<=6, -9<=k<=11, -7<=l<=10

Reflections collected / unique	2085 / 1338 [R(int) = 0.0202]
Completeness to theta = 25.02	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9008 and 0.8564
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1338 / 1 / 120
Goodness-of-fit on F^2	1.081
Final R indices [I>2sigma(I)]	R1 = 0.0515, wR2 = 0.1424
R indices (all data)	R1 = 0.0656, wR2 = 0.1608
Absolute structure parameter	0.4(3)
Extinction coefficient	0.25(3)
Largest diff. peak and hole	0.210 and -0.249 e.A^-3

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic

displacement parameters (A^2 x 10^3) for 190328e.

U(eq) is defined as one third of the trace of the orthogonalized

Uij tensor.

	x	y	z	U(eq)
F(1)	8054(6)	6076(14)	2046(3)	137(1)
N(1)	5294(7)	6093(17)	7083(4)	93(1)
O(1)	11160(20)	4795(6)	3401(12)	136(3)
O(2)	11295(19)	7249(7)	3409(11)	127(3)
S(1)	9873(2)	6065(5)	3521(1)	69(1)
C(1)	7870(40)	5543(16)	5050(30)	58(6)
C(2)	6800(40)	6500(30)	5850(20)	57(7)
C(3)	4460(20)	7352(13)	7871(19)	128(5)
C(4)	2510(30)	6800(12)	8973(15)	103(4)
C(5)	2770(30)	5277(13)	9174(13)	106(4)
C(6)	4240(20)	4873(10)	7750(13)	102(4)
C(1')	8030(50)	6624(17)	4990(30)	58(8)
C(2')	6890(40)	5560(30)	5920(30)	57(7)

Table S6. Bond lengths [A] and angles [deg] for 190328e.

F(1)-S(1)	1.547(3)
N(1)-C(2)	1.37(2)
N(1)-C(2')	1.39(3)
N(1)-C(6)	1.414(15)
N(1)-C(3)	1.451(16)
O(1)-S(1)	1.391(8)
O(2)-S(1)	1.355(8)
S(1)-C(1')	1.67(2)
S(1)-C(1)	1.75(2)
C(1)-C(2)	1.27(4)
C(1)-H(1)	0.9300
C(2)-H(2)	0.9300
C(3)-C(4)	1.481(16)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(5)	1.478(8)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5)-C(6)	1.489(15)
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(1')-C(2')	1.43(4)
C(1')-H(1')	0.9300
C(2')-H(2')	0.9300
C(2)-N(1)-C(2')	38.3(5)
C(2)-N(1)-C(6)	140.3(15)

C(2')-N(1)-C(6)	102.4(15)
C(2)-N(1)-C(3)	106.9(15)
C(2')-N(1)-C(3)	144.8(15)
C(6)-N(1)-C(3)	112.7(4)
O(2)-S(1)-O(1)	118.2(3)
O(2)-S(1)-F(1)	104.7(6)
O(1)-S(1)-F(1)	103.1(6)
O(2)-S(1)-C(1')	95.5(8)
O(1)-S(1)-C(1')	127.9(8)
F(1)-S(1)-C(1')	105.1(7)
O(2)-S(1)-C(1)	128.2(7)
O(1)-S(1)-C(1)	95.2(8)
F(1)-S(1)-C(1)	104.5(6)
C(1')-S(1)-C(1)	35.5(4)
C(2)-C(1)-S(1)	117.0(18)
C(2)-C(1)-H(1)	121.5
S(1)-C(1)-H(1)	121.5
C(1)-C(2)-N(1)	117(3)
C(1)-C(2)-H(2)	121.5
N(1)-C(2)-H(2)	121.5
N(1)-C(3)-C(4)	101.8(9)
N(1)-C(3)-H(3A)	111.4
C(4)-C(3)-H(3A)	111.4
N(1)-C(3)-H(3B)	111.4
C(4)-C(3)-H(3B)	111.4
H(3A)-C(3)-H(3B)	109.3
C(5)-C(4)-C(3)	111.4(12)
C(5)-C(4)-H(4A)	109.3
C(3)-C(4)-H(4A)	109.3
C(5)-C(4)-H(4B)	109.3

C(3)-C(4)-H(4B)	109.3
H(4A)-C(4)-H(4B)	108.0
C(4)-C(5)-C(6)	102.2(11)
C(4)-C(5)-H(5A)	111.3
C(6)-C(5)-H(5A)	111.3
C(4)-C(5)-H(5B)	111.3
C(6)-C(5)-H(5B)	111.3
H(5A)-C(5)-H(5B)	109.2
N(1)-C(6)-C(5)	108.3(8)
N(1)-C(6)-H(6A)	110.0
C(5)-C(6)-H(6A)	110.0
N(1)-C(6)-H(6B)	110.0
C(5)-C(6)-H(6B)	110.0
H(6A)-C(6)-H(6B)	108.4
C(2')-C(1')-S(1)	115.4(16)
C(2')-C(1')-H(1')	122.3
S(1)-C(1')-H(1')	122.3
N(1)-C(2')-C(1')	113(2)
N(1)-C(2')-H(2')	123.6
C(1')-C(2')-H(2')	123.6

Symmetry transformations used to generate equivalent atoms:

Table S7. Anisotropic displacement parameters (A^2 x 10^3) for 190328e.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
F(1)	107(2)	243(4)	62(1)	-6(6)	-2(1)	-2(9)
N(1)	75(2)	142(4)	63(2)	-12(7)	19(2)	-3(8)
O(1)	217(9)	51(4)	139(7)	-13(3)	23(7)	12(5)
O(2)	167(7)	76(5)	137(7)	-20(4)	2(6)	-40(5)
S(1)	70(1)	77(1)	59(1)	0(1)	16(1)	3(1)
C(1)	72(11)	42(12)	60(11)	6(7)	10(9)	-12(7)
C(2)	69(12)	43(12)	59(12)	1(7)	12(10)	-6(7)
C(3)	107(7)	105(9)	175(11)	26(8)	61(7)	10(6)
C(4)	118(9)	101(7)	92(6)	-21(5)	42(5)	17(5)
C(5)	140(10)	95(8)	84(6)	0(5)	40(5)	-8(6)
C(6)	131(8)	85(7)	90(6)	-16(5)	13(5)	39(6)
C(1')	72(12)	42(13)	60(12)	6(7)	9(9)	-12(6)
C(2')	69(13)	43(13)	59(13)	1(8)	12(10)	-6(8)

Table S8. Hydrogen coordinates (x 10^4) and isotropic

displacement parameters (A^2 x 10^3) for 190328e.

	x	y	z	U(eq)
H(1)	7599	4606	5279	70
H(2)	7029	7439	5605	68
H(3A)	3673	8008	7132	154
H(3B)	5893	7799	8432	154
H(4A)	2733	7253	9989	124
H(4B)	768	7014	8573	124
H(5A)	1080	4825	9191	127
H(5B)	3738	5049	10133	127
H(6A)	5630	4231	8038	122
H(6B)	3086	4416	6993	122
H(1')	7772	7567	5183	70
H(2')	7175	4614	5764	68

Table S9. Torsion angles [deg] for 190328e.

O(2)-S(1)-C(1)-C(2)	29.2(18)
O(1)-S(1)-C(1)-C(2)	161.6(14)
F(1)-S(1)-C(1)-C(2)	-93.4(15)
C(1')-S(1)-C(1)-C(2)	2.4(14)
S(1)-C(1)-C(2)-N(1)	-178.0(12)
C(2')-N(1)-C(2)-C(1)	2.6(13)
C(6)-N(1)-C(2)-C(1)	-8(3)
C(3)-N(1)-C(2)-C(1)	175.9(15)
C(2)-N(1)-C(3)-C(4)	170.4(12)
C(2')-N(1)-C(3)-C(4)	177.7(16)
C(6)-N(1)-C(3)-C(4)	-6.8(9)
N(1)-C(3)-C(4)-C(5)	16.8(15)
C(3)-C(4)-C(5)-C(6)	-19.8(17)
C(2)-N(1)-C(6)-C(5)	179.0(15)
C(2')-N(1)-C(6)-C(5)	172.1(11)
C(3)-N(1)-C(6)-C(5)	-5.3(9)
C(4)-C(5)-C(6)-N(1)	14.8(14)
O(2)-S(1)-C(1')-C(2')	-156.9(15)
O(1)-S(1)-C(1')-C(2')	-24(2)
F(1)-S(1)-C(1')-C(2')	96.2(16)
C(1)-S(1)-C(1')-C(2')	2.2(12)
C(2)-N(1)-C(2')-C(1')	2.6(15)
C(6)-N(1)-C(2')-C(1')	175.5(14)
C(3)-N(1)-C(2')-C(1')	-9(3)
S(1)-C(1')-C(2')-N(1)	-177.6(12)

Symmetry transformations used to generate equivalent atoms:

Table S10. Hydrogen bonds for 190328e [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

7. References

[1] Zhang, X.; Moku, B.; Leng, J.; Rakesh, K. P.; Qin, H.-L. *Eur. J. Org. Chem.* **2019**, 1763.

[2] Fothergill, A. W. Antifungal susceptibility testing: clinical laboratory and standards institute (CLSI) methods[M]. Interactions of Yeasts, Moulds, and Antifungal Agents. Humana Press, 2012, 65-74.

[3] Shu, W.-M.; Zhang, X.-F.; Zhang, X.-X.; Li, M.; Wang, A.-J.; Wu, A.-X. *J. Org. Chem.* **2019**, *84*, 14919.