Ex Situ Generation of Sulfuryl Fluoride for the Synthesis of Aryl Fluorosulfates

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Supporting Information

Contents

1. General Information

^{1}H NMR spectra

^{1}H NMR spectra were recorded on Bruker Avance 400 (400 MHz) and Bruker Avance II^{+} 600 (600 MHz) spectrometers. Samples were dissolved in $CDCl_3$ (7.26 ppm, singlet) or DMSO-d_6 (2.50 ppm, quintet) and tetramethylsilane was used as an internal standard. The δ-values are expressed in ppm.

^{13}C NMR spectra

^{13}C-NMR spectra were recorded on Bruker Avance 400 (working at 101 MHz) and Bruker Avance II^{+} 600 (working at 151 MHz) spectrometers. The deuterated solvents were used as internal standard ($CDCl_3$: 77.16 ppm, triplet; DMSO-d_6: 39.52 ppm, quintet). The δ-values are expressed in ppm.

^{19}F NMR spectra

^{19}F NMR spectra were recorded on Bruker Avance 400 (working at 376 MHz) and Bruker Avance II^{+} 600 (working at 565 MHz) spectrometers. Samples were dissolved in $CDCl_3$ or DMSO-d_6 and trichlorofluoromethane was used as an internal standard. The δ-values are expressed in ppm

IR spectra

Bruker Alpha-T FT-IR spectrometer with universal sampling module. Data processing using Opus software.

Melting points

Melting points were determined on a Mettler-Toledo DSC1 instrument, using a heating rate of 10 °C min^{-1} under helium atmosphere.

CHN analysis

CHN (carbon, hydrogen, nitrogen) elemental analyses were obtained with the aid of a Thermo Scientific Interscience Flash 2000 Elemental analyser.

Chromatography

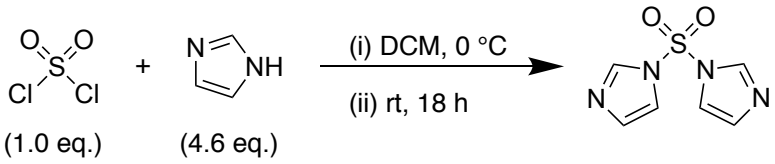
- TLC plates: pre-coated silica gel 60 F254 (250 µm) glass-supported TLC plates.
- Silica gel for column chromatography: MP Silica 32-63, average pore diameter 60 A, Ecochron
- MPLC apparatus: Buchi Sepacore^{TM} flash apparatus, consisting of a C-660 Buchi fraction collector, C-615 Pump manager, C-635 UV-photometer, two C-605 pump modules and a Linseis D120S plotter.

Materials

All reagents were obtained from commercially available sources and were used as purchased without further purification. 1,1'-Sulfonyldiimidazole (SDI) was obtained from Fluorochem. Chromatography solvents were distilled prior to use. Reactions were magnetically stirred. Compounds were visualized by UV irradiation (254 nm). Flash column chromatography was performed using an MPLC apparatus. Solvents were evaporated with a rotavapor at a temperature of 50 °C. Yields refer to isolated compounds after chromatography.

2. Synthesis of 1,1'-sulfonyldiimidazole

Scheme S1. Synthesis of 1,1'-sulfonyldiimidazole from sulfuryl chloride and imidazole.



To a suspension of imidazole (15.82 g, 99 wt%, 230 mmol, 4.6 eq.) in DCM (100 mL) at 0 °C, a solution of sulfuryl chloride (4.13 mL, 98.5 wt%, 50 mmol, 1.0 eq.) in DCM (25 mL) was added dropwise. The reaction mixture was allowed to gradually warm to room temperature while stirring for 18 hours. Next, the straw colored solution was filtered and washed excessively with DCM. The resulting filtrate was evaporated under reduced pressure. The crystalline material was recrystallized from boiling isopropyl alcohol (75 mL). After washing with cold isopropyl alcohol and drying under reduced pressure, 8.53 g (86%) of analytically pure 1,1'-sulfonyldiimidazole was obtained in the form of thick colorless needles (Figure S1).

This procedure is based on reference[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.30 (s, 1H), 7.14 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 136.65, 132.54, 117.49.

Figure S1. Crystalline 1,1'-sulfonyldiimidazole.

3. Synthesis of Aryl Fluorosulfates

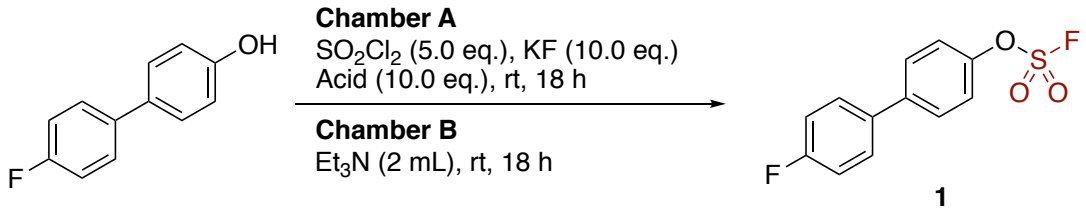
3.1. Optimization Study

3.1.1. Sulfuryl Chloride as Precursor

A. Acid screen in chamber A

Chamber A of a flame-dried small two-chamber reactor (Figure S2) was filled with sulfuryl chloride (SO_2Cl_2, 337 mg, 2.5 mmol, 5.0 eq.) and potassium fluoride (KF, 290 mg, 5.0 mmol, 10.0 eq.). Next, chamber B was charged with 96 mg of 4-fluoro-4'-hydroxybiphenyl (98 wt%, 0.5 mmol, 1.0 eq.).and triethylamine (Et_3N, 2 mL). Finally, 10 eq. of the appropriate acid were added by injection through the septum in chamber A. The reaction was stirred for 18 hours at room temperature. Trifluorotoluene was added as an internal standard and the reaction mixture was analyzed by ^{19}F NMR. (Table S1)

Table S1. Acid screen for the fluorosulfation of 4-fluoro-4'-hydroxybiphenyl with sulfuryl chloride as precursor.



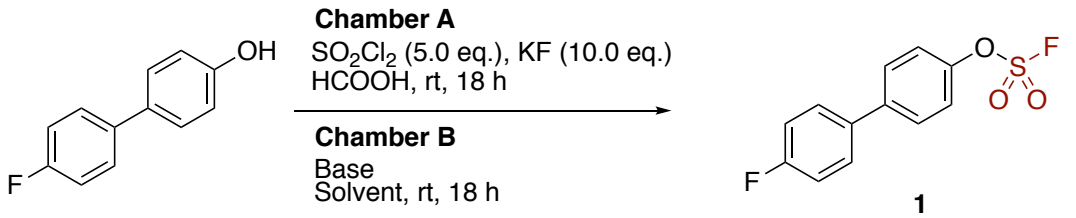
entry	acid	yield[a] [%]
1	acetic acid	16
2	lactic acid	6
3	**formic acid**	**34**
4	pyruvic acid	4
5	trifluoroacetic acid	7

[a]Determined by ^{19}F NMR using trifluorotoluene as an internal standard.

B. Base and solvent screen in chamber B

Chamber A of a flame-dried small two-chamber reactor (Figure S2) was filled with sulfuryl chloride (SO_2Cl_2, 337 mg, 2.5 mmol, 5.0 eq.) and potassium fluoride (KF, 290 mg, 5.0 mmol, 10.0 eq.). Next, chamber B was charged with 96 mg of 4-fluoro-4'-hydroxybiphenyl (98 wt%, 0.5 mmol, 1.0 eq.), the appropiate base and solvent. Finally, 0.2 mL (= 10 eq.) or 1 mL formic acid was added by injection through the septum in chamber A. The reaction was stirred for 18 hours at room temperature. Trifluorotoluene was added as an internal standard and the reaction mixture was analyzed by ^{19}F NMR. (Table S2)

Table S2. Base and solvent screen for the fluorosulfation of 4-fluoro-4'-hydroxybiphenyl with sulfuryl chloride as precursor.



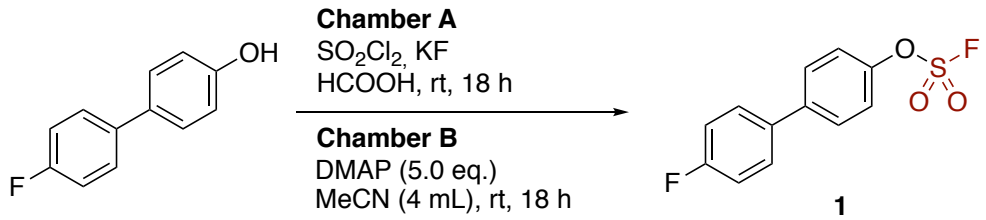
entry	HCOOH [mL]	base (eq).	solvent (mL)	yield[a] [%]
1	0.2	Et_3N (15.0)	MeCN, 1	75
2	0.2	Et_3N (15.0)	DCM, 1	75
3	0.2	DMAP (5.0)	MeCN, 4	77
4	**1.0**	**DMAP (5.0)**	**MeCN, 4**	**>99**
5	1.0	DMAP (3.0)	MeCN, 4	82
6	1.0	DABCO (3.0)	MeCN, 4	51
7	1.0	TMG (3.0)	MeCN, 4	48
8	1.0	TMEDA (3.0)	MeCN, 4	47

[a]Determined by ^{19}F NMR using trifluorotoluene as an internal standard. DMAP = 4-dimethylamino pyridine, DABCO = 1,4-diazabicyclo[2.2.2]octane, TMG = 1,1,3,3-tetramethylguanidine, TMEDA = *N,N,N',N'*-tetramethylethylenediamine, MeCN = acetonitrile, DCM = dichloromethane.

C. Optimization of the amount of SO_2Cl_2, KF and HCOOH in chamber A

Chamber A of a flame-dried small two-chamber reactor (Figure S2) was filled with sulfuryl chloride (SO_2Cl_2) and potassium fluoride (KF). Next, chamber B was charged with 96 mg of 4-fluoro-4'-hydroxybiphenyl (98 wt%, 0.5 mmol, 1.0 eq.), 4-dimethylaminopyridine (DMAP, 305 mg, 2.5 mmol, 5.0 eq.) and acetonitrile (4 mL). Finally, formic acid was added by injection through the septum in chamber A. The reaction was stirred for 18 hours at room temperature. Trifluorotoluene was added as an internal standard and the reaction mixture was analyzed by ^{19}F NMR. (Table S3)

Table S3. Optimization of the amount of SO_2Cl_2, KF and HCOOH for the fluorosulfation of 4-fluoro-4'-hydroxybiphenyl with sulfuryl chloride as precursor.



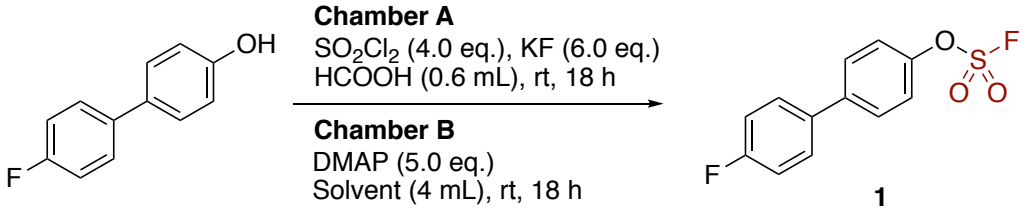
entry	SO_2Cl_2 [eq.]	KF [eq.]	HCOOH [mL]	yield[a] [%]
1	5.0	10.0	1.0	>99
2	4.0	8.0	0.8	>99
3	**4.0**	**6.0**	**0.6**	**95**
4	3.0	6.0	0.6	93
5	3.2	2.0	0.4	87
6	2.0	4.0	0.4	84

[a]Determined by ^{19}F NMR using trifluorotoluene as an internal standard.

D. Solvent screen in chamber B

Chamber A of a flame-dried small two-chamber reactor (Figure S2) was filled with sulfuryl chloride (SO_2Cl_2, 270 mg, 2.0 mmol, 4.0 eq.) and potassium fluoride (KF, 174 mg, 3.0 mmol, 6.0 eq.). Next, chamber B was charged with 96 mg of 4-fluoro-4'-hydroxybiphenyl (98 wt%, 0.5 mmol, 1.0 eq.), 4-dimethylaminopyridine (DMAP, 305 mg, 2.5 mmol, 5.0 eq.) and solvent (4 mL). Finally, 0.6 mL formic acid was added by injection through the septum in chamber A. The reaction was stirred for 18 hours at room temperature. Trifluorotoluene was added as an internal standard and the reaction mixture was analyzed by ^{19}F NMR. (Table S4)

Table S4. Solvent screen for the fluorosulfation of 4-fluoro-4'-hydroxybiphenyl with sulfuryl chloride as precursor.



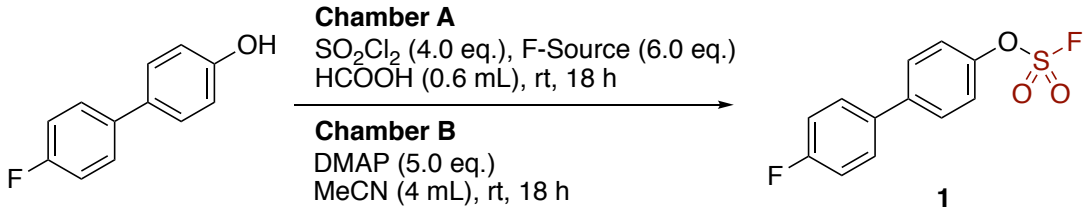
entry	solvent	yield[a] [%]
1	DMSO	Traces
2	MEK	11
3	EtOAc	10
4	DMC	38
5	**MeCN**	**95**

[a]Determined by ^{19}F NMR using trifluorotoluene as an internal standard. DMSO = dimethylsulfoxide, MEK = methyl ethyl ketone, EtOAc = ethyl acetate, DMC = dimethyl carbonate, MeCN = acetonitrile.

E. Fluoride source screen in chamber A

Chamber A of a flame-dried small two-chamber reactor (Figure S2) was filled with sulfuryl chloride (SO_2Cl_2, 270 mg, 2.0 mmol, 4.0 eq.) and the appropriate fluoride source (3.0 mmol, 6.0 eq.). Next, chamber B was charged with 96 mg of 4-fluoro-4'-hydroxybiphenyl (98 wt%, 0.5 mmol, 1.0 eq.), 4-dimethylaminopyridine (DMAP, 305 mg, 2.5 mmol, 5.0 eq.) and acetonitrile (4 mL). Finally, 0.6 mL formic acid was added by injection through the septum in chamber A. The reaction was stirred for 18 hours at room temperature. Trifluorotoluene was added as an internal standard and the reaction mixture was analyzed by ^{19}F NMR. (Table S5)

Table S5. Fluoride source screen for the fluorosulfation of 4-fluoro-4'-hydroxybiphenyl with sulfuryl chloride as precursor.



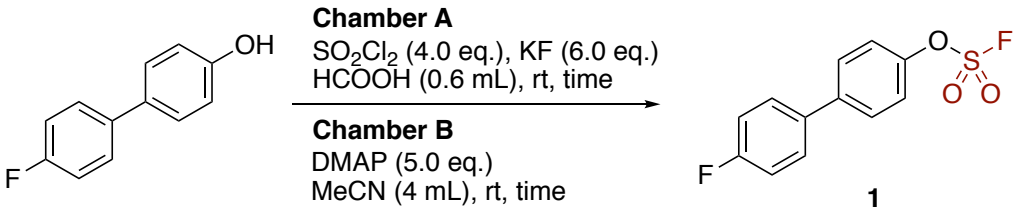
entry	F-source	yield[a] [%]
1	**KF**	**95**
2	NaF	86
3	NH_4F	84
4	ZnF_2	Traces

[a]Determined by ^{19}F NMR using trifluorotoluene as an internal standard.

F. Reaction time

Chamber A of a flame-dried small two-chamber reactor (Figure S2) was filled with sulfuryl chloride (SO_2Cl_2, 270 mg, 2.0 mmol, 4.0 eq.) and potassium fluoride (KF, 174 mg, 3.0 mmol, 6.0 eq.). Next, chamber B was charged with 96 mg of 4-fluoro-4'-hydroxybiphenyl (98 wt%, 0.5 mmol, 1.0 eq.), 4-dimethylaminopyridine (DMAP, 305 mg, 2.5 mmol, 5.0 eq.) and acetonitrile (4 mL). Finally, 0.6 mL formic acid was added by injection through the septum in chamber A. The reaction was stirred for the appropriate amount of time at room temperature. Trifluorotoluene was added as an internal standard and the reaction mixture was analyzed by ^{19}F NMR. (Table S6)

Table S6. Reaction time for the fluorosulfation of 4-fluoro-4'-hydroxybiphenyl with sulfuryl chloride as precursor.



entry	time [h]	yield[a] [%]
1	1	55
2	2	86
3	5	92
4	**18**	**95**

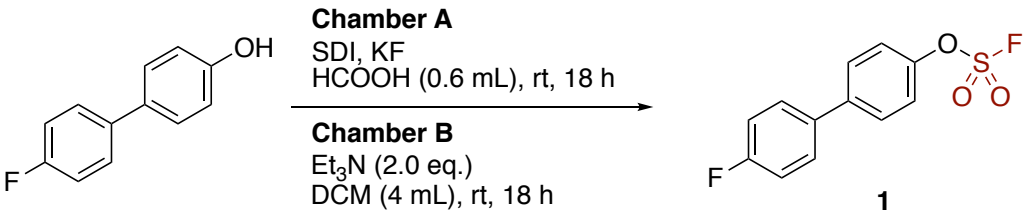
[a]Determined by ^{19}F NMR using trifluorotoluene as an internal standard.

3.1.2. 1,1'-Sulfonyldiimidazole as Precursor

A. Optimization of the amount of SDI and KF in chamber A

Chamber A of a flame-dried small two-chamber reactor (Figure S2) was filled with 1,1'-sulfonyldiimidazole (SDI) and potassium fluoride (KF). Next, chamber B was charged with 96 mg of 4-fluoro-4'-hydroxybiphenyl (98 wt%, 0.5 mmol, 1.0 eq.), triethylamine (139 µL, 1.0 mmol, 2.0 eq.) and dichloromethane (DCM, 4 mL). Finally, 0.6 mL formic acid was added by injection through the septum in chamber A. The reaction was stirred for 18 hours at room temperature. Trifluorotoluene was added as an internal standard and the reaction mixture was analyzed by ^{19}F NMR. (Table S7)

Table S7. Optimization of the amount of SDI and KF for the fluorosulfation of 4-fluoro-4'-hydroxybiphenyl with 1,1'-sulfonyldiimidazole as precursor.



entry	SDI [eq.]	KF [eq.]	yield[a] [%]
1	4.0	6.0	>99
2	**3.0**	**6.0**	**>99**
3	2.0	6.0	81
4	2.0	4.0	73
5	1.5	6.0	76
6	1.5	3.0	61

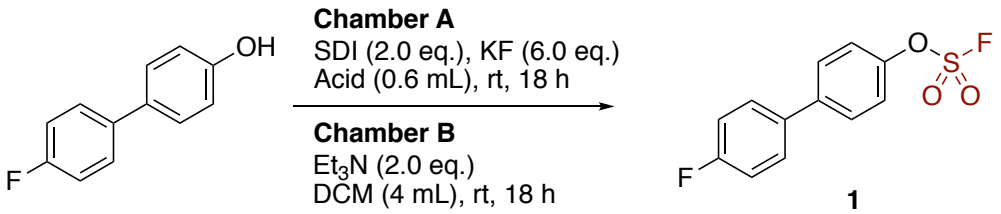
[a]Determined by ^{19}F NMR using trifluorotoluene as an internal standard.

B. Acid screen in chamber A

Chamber A of a flame-dried small two-chamber reactor (Figure S2) was filled with 1,1'-sulfonyldiimidazole (SDI, 198 mg, 1.0 mmol, 2.0 eq.) and potassium fluoride (KF, 174 mg, 3.0 mmol, 6.0 eq.). Next, chamber B was charged with 96 mg of 4-fluoro-4'-hydroxybiphenyl (98 wt%, 0.5 mmol, 1.0

eq.), triethylamine (139 µL, 1.0 mmol, 2.0 eq.) and dichloromethane (DCM, 4 mL). Finally, 0.6 mL of the appropriate acid was added by injection through the septum in chamber A. The reaction was stirred for 18 hours at room temperature. Trifluorotoluene was added as an internal standard and the reaction mixture was analyzed by ^{19}F NMR. (Table S8)

Table S8. Acid screen for the fluorosulfation of 4-fluoro-4'-hydroxybiphenyl with 1,1'-sulfonyldiimidazole as precursor.



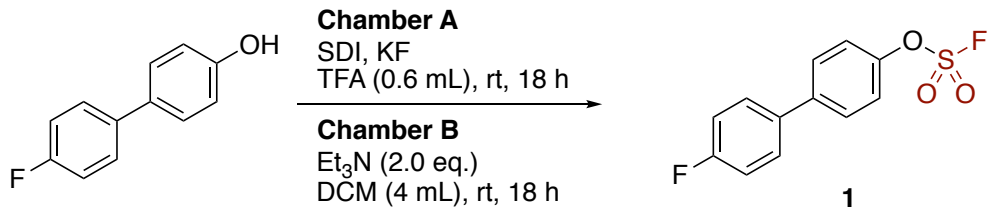
entry	acid	yield[a] [%]
1	formic acid	81
2	formic acid	82[b]
3	formic acid	89[c]
4	methanesulfonic acid	35
5	**trifluoroacetic acid**	**>99**

[a]Determined by ^{19}F NMR using trifluorotoluene as an internal standard.
[b]The reaction was performed at 40 °C. [c]8 eq. of KF were used.

C. Optimization of the amount of SDI and KF in chamber A and screening of the reaction time

Chamber A of a flame-dried small two-chamber reactor (Figure S2) was filled with the appropriate amount of 1,1'-sulfonyldiimidazole (SDI) and potassium fluoride (KF). Next, chamber B was charged with 96 mg of 4-fluoro-4'-hydroxybiphenyl (98 wt%, 0.5 mmol, 1.0 eq.), triethylamine (139 µL, 1.0 mmol, 2.0 eq.) and dichloromethane (DCM, 4 mL). Finally, 0.6 mL the trifluoroacetic acid was added by injection through the septum in chamber A. The reaction was stirred for 18 hours at room temperature. Trifluorotoluene was added as an internal standard and the reaction mixture was analyzed by ^{19}F NMR. (Table S9)

Table S9. Optimization of the amount of SDI and KF and screening of the reaction time for the fluorosulfation of 4-fluoro-4'-hydroxybiphenyl with 1,1'-sulfonyldiimidazole as precursor.

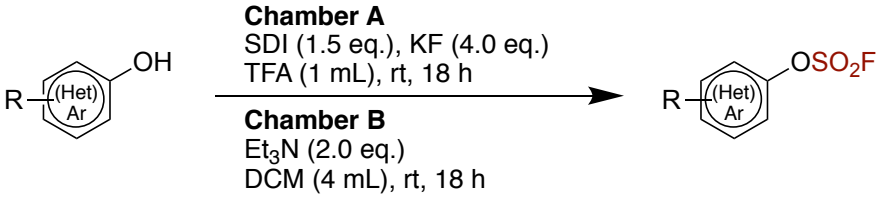


entry	SDI [eq.]	KF [eq.]	time [h]	yield[a] [%]
1	2.0	6.0	18	>99
2	2.0	4.0	18	>99
3	1.5	4.5	18	>99
4	**1.5**	**4.0**	**18**	**>99 (96)[b]**
5	1.5	3.0	18	93
6	1.3	6.0	18	89
8	1.5	4.0	2	84
9	1.5	4.0	6	94

[a]Determined by ^{19}F NMR using trifluorotoluene as an internal standard. [b]Isolated yield.

3.2. General Procedures

Scheme S2 Synthesis of aryl fluorosulfates through ex situ generation of sulfuryl fluoride in a two-chamber reactor.



Procedure A

Chamber A of a flame-dried small two-chamber reactor (Figure S2) was filled with 1,1'-sulfonyldiimidazole (SDI, 297 mg, 1.5 mmol, 1.5 eq.) and potassium fluoride (KF, 232 mg, 4.0 mmol, 4.0 eq.). Next, chamber B was charged with the appropriate (hetero)aryl alcohol (1.0 mmol), triethylamine (279 µL, 2.0 mmol, 2.0 eq.) and dichloromethane (DCM, 4 mL). Finally, 1 mL trifluoroacetic acid (TFA) was added by injection through the septum in chamber A and instant gas formation was observed.

After 18 hours stirring at room temperature, one of the caps was carefully removed to release the residual pressure. The reaction was stirred for another 15 minutes to ensure that all sulfuryl fluoride was extracted out of the fume hood. Next, the content of chamber B was transferred to a 100 mL round-bottomed flask. Chamber B was rinsed five times with 2 mL of dichloromethane and these fractions were added to the same flask. After the addition of 1 gram Celite®545, the solvent was removed under reduced pressure. The crude product was purified by solid-phase flash column chromatography on silica gel.

An instructional video is available: General_Procedure.mp4

Figure S2. Small two-chamber reactor. Inner volume = 20 mL.
Invented by the Skrydstrup group.[2]

Procedure B

Identical to procedure A, except that *N,N*-diisopropylethylamine (DIPEA, 524 µL, 3.0 mmol, 3.0 eq.) was used as base and acetonitrile (MeCN, 4 mL) as solvent in chamber B.

Large scale synthesis of 2-bromophenyl fluorosulfate

Chamber A of a flame-dried large two-chamber reactor (Figure S3) was filled with 1,1'-sulfonyldiimidazole (5.95 g, 30.0 mmol, 1.5 eq.) and potassium fluoride (4.65 g, 80.0 mmol, 4.0 eq.). Next, chamber B was charged with 2-bromophenol (98 wt%, 3.53 g, 20.0 mmol, 1.0 eq.), triethylamine (5.58 mL, 40.0 mmol, 2.0 eq.) and dichloromethane (80 mL). Finally, 20 mL trifluoroacetic acid was added by injection through the septum in chamber A and instant gas formation was observed.

After 18 hours stirring at room temperature, one of the caps was carefully removed to release the residual pressure. The reaction was stirred for another 15 minutes to ensure that all sulfuryl fluoride was extracted out of the fume hood. Next, the content of chamber B was transferred to a 250 mL round-bottomed flask. Chamber B was rinsed five times with 10 mL of dichloromethane and these fractions were added to the same flask. The solvent was removed under reduced pressure. The residue was dissolved in 50 mL of ethyl acetate and washed successively with 1M HCl (3 x 50 mL), saturated $NaHCO_3$ (3 x 50 mL), and brine (1 x 50 mL). The organic layer was dried over magnesium sulfate and concentrated *in vacuo* to give analytically pure 2-bromophenyl fluorosulfate (4.92 g, 96%).

Figure S3. Large two-chamber reactor. Inner volume = 400 mL. Invented by the Skrydstrup group.[2]

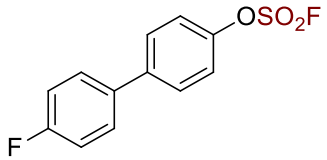
Caution!

1) After reaction, chamber A was quenched with NaOH (1M) to neutralize trifluoroacetic acid and the *in situ* formed HF. The alkaline solution was discarded in basic waste. Etching of the glassware was seen after multiple experiments.

2) The maximally allowed pressure in the two-chamber vessel is 5 bar. In order not to exceed this pressure in the small two-chamber vessel, the amount of generated gas was limited to 2.5 mmol at room temperature. This was calculated based on an inner volume of 15 mL (20 mL total minus 5 mL solvent). For the large two-chamber vessel, the amount of generated gas was limited to 50 mmol at room temperature. This was calculated based on an inner volume of 300 mL (400 mL total minus 100 mL solvent). Pressure measurements revealed that the internal pressure never exceeded 2.8 bar when the general procedure was followed (*vide infra*).

3.3. The Synthesized Aryl Fluorosulfates

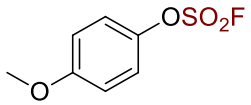
4-fluoro-[1,1'-biphenyl]-4-yl sulfurofluoridate (compound 1)



General procedure A was followed using 192 mg of 4-fluoro-4'-hydroxybiphenyl (98 wt%, 1.0 mmol, 1.0 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (heptane, 100%). The title compound was obtained as a white solid (258 mg, 96%).

R_f = 0.39 (heptane/ethyl acetate, 9/1). **Melting point** = 47 – 49 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.62 (d, *J* = 8.5 Hz, 1H), 7.52 (dd, *J* = 8.1, 5.5 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.16 (t, *J* = 8.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 163.05 (d, *J* = 247.9 Hz), 149.51, 141.17, 135.55 (d, *J* = 3.3 Hz), 129.06, 128.98, 121.42, 116.13 (d, *J* = 21.6 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 37.18, -114.68 (m). **IR** (neat) cm^{-1}: 1437, 1232, 921, 815. **CHN**: calculated for $C_{12}H_8F_2O_3S$: C 53.33%, H 2.98%, N 0.00%; found: C 53.43%, H 3.26%, N 0.00%.

4-methoxyphenyl sulfurofluoridate (compound 2)

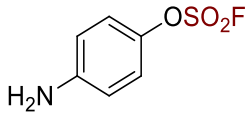


General procedure A was followed using 125 mg of 4-methoxyphenol (99 wt%, 1.0 mmol, 1.0 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (petroleum ether, 100%). The title compound was obtained as a colorless oil (188 mg, 91%).

R_f = 0.57 (petroleum ether/diethyl ether, 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.26 (d, *J* = 9.2 Hz, 2H), 6.94 (d, *J* = 9.2 Hz, 2H), 3.83 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 159.43, 143.71, 122.10, 115.29, 55.87. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 35.85.

These data are in agreement with literature data.[3]

4-aminophenyl sulfurofluoridate (compound 3)

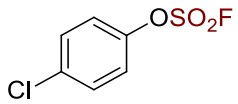


General procedure A was followed using 110 mg of 4-aminophenol (99 wt%, 1.0 mmol, 1.0 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (heptane/ethyl acetate, 7/3). The title compound was obtained as a brown solid (171 mg, 89%).

R_f = 0.48 (heptane/ethyl acetate, 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.09 (d, *J* = 8.7 Hz, 2H), 6.65 (d, *J* = 8.7 Hz, 2H), 3.84 (brd, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$): δ 146.88, 142.18, 121.83, 115.59. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 35.48.

These data are in agreement with literature data.[4]

4-chlorophenyl sulfurofluoridate (compound 4)

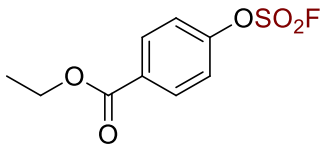


General procedure A was followed using 130 mg of 4-chlorophenol (99 wt%, 1.0 mmol, 1.0 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (petroleum ether, 100%). The title compound was obtained as a colorless oil (183 mg, 87%).

R_f = 0.81 (petroleum ether/diethyl ether, 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 148.47, 134.75, 130.69, 122.50. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 37.17.

These data are in agreement with literature data.[5]

ethyl 4-((fluorosulfonyl)oxy)benzoate (compound 5)

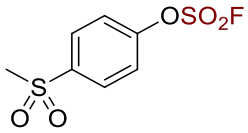


General procedure A was followed using 168 mg of ethyl 4-hydroxybenzoate (99 wt%, 1.0 mmol, 1.0 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (heptane/ethyl acetate, 99/1). The title compound was obtained as a colorless oil (236 mg, 95%).

R_f = 0.37 (heptane/ethyl acetate, 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 164.98, 152.88, 132.10, 131.10, 121.00, 61.71, 14.34. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 38.16.

These data are in agreement with literature data.[3]

4-(methylsulfonyl)phenyl sulfurofluoridate (compound 6)

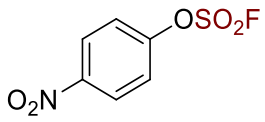


General procedure A was followed using 178 mg of 4-(methylsulfonyl)phenol (97 wt%, 1.0 mmol, 1.0 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (petroleum ether/diethyl ether, 5/5). The title compound was obtained as a white solid (238 mg, 94%).

R_f = 0.39 (petroleum ether/diethyl ether, 3/7). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 3.09 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 153.12, 141.21, 130.40, 122.32, 44.58. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 38.73.

These data are in agreement with literature data.[3]

4-nitrophenyl sulfurofluoridate (compound 7)

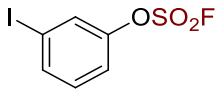


General procedure A was followed using 141 mg of 4-nitrophenol (99 wt%, 1.0 mmol, 1.0 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (petroleum ether/diethyl ether, 95/5). The title compound was obtained as a yellowish oil (188 mg, 85%).

R_f = 0.45 (petroleum ether/diethyl ether, 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.39 (d, *J* = 8.9 Hz, 2H), 7.56 (d, *J* = 8.9 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 153.50, 147.47, 126.32, 122.27. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 39.00.

These data are in agreement with literature data.[4]

3-iodophenyl sulfurofluoridate (compound 8)

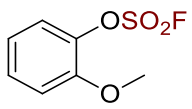


General procedure A was followed using 222 mg of 3-iodophenol (99 wt%, 1.0 mmol, 1.0 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (petroleum ether, 100%). The title compound was obtained as a colorless oil (281 mg, 93%).

R_f = 0.74 (petroleum ether/ethyl acetate, 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81 – 7.74 (m, 1H), 7.73 – 7.68 (m, 1H), 7.38 – 7.31 (m, 1H), 7.25 – 7.18 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 149.82, 138.09, 131.74, 130.18, 120.52, 94.07. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 37.73.

These data are in agreement with literature data.[5]

2-methoxyphenyl sulfurofluoridate (compound 9)

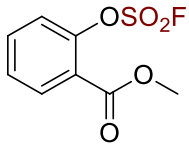


General procedure A was followed using 125 mg of 2-methoxyphenol (99 wt%, 1.0 mmol, 1.0 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (petroleum ether/ethyl acetate, 95/5). The title compound was obtained as a light yellowish oil (190 mg, 92%).

R_f = 0.47 (petroleum ether/ethyl acetate, 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39 – 7.29 (m, 2H), 7.09 – 7.03 (m, 1H), 7.03 – 6.96 (m, 1H), 3.92 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 151.36, 139.18, 129.74, 122.53, 121.01, 113.61, 56.29. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 39.09.

These data are in agreement with literature data.[3]

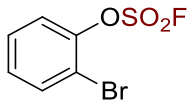
methyl 2-((fluorosulfonyl)oxy)benzoate (compound 10)



General procedure B was followed using 154 mg of methyl 2-hydroxybenzoate (99 wt%, 1.0 mmol, 1.0 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (heptane/ethyl acetate, 95/5). The title compound was obtained as a light yellowish oil (220 mg, 94%).

R_f = 0.22 (heptane/ethyl acetate, 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.14 – 8.07 (m, 1H), 7.70 – 7.62 (m, 1H), 7.54 – 7.47 (m, 1H), 7.44 – 7.39 (m, 1H), 3.97 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 163.97, 148.65, 134.51, 133.10, 128.93, 124.01, 122.60, 52.93. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 41.11. **IR** (neat) cm^{-1}: 2957, 1727, 1447, 1231, 1139, 911, 806. **CHN**: calculated for $C_8H_7FO_5S$: C 41.04%, H 3.01%, N 0.00%; found: C 41.21%, H 3.10%, N 0.00%.

2-bromophenyl sulfurofluoridate (compound 11)

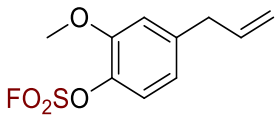


General procedure A was followed using 177 mg of 2-bromophenol (98 wt%, 1.0 mmol, 1.0 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (petroleum ether, 100%). The title compound was obtained as a light yellowish oil (237 mg, 93%).

Large scale procedure was followed using 3.53 g of 2-bromophenol (98 wt%, 1.0 mmol, 1.0 eq.). The crude reaction mixture was purified by aqueous workup. The title compound was obtained as a light yellowish oil (4.92 g, 96%).

R_f = 0.72 (petroleum ether/ethyl acetate, 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 – 7.66 (m, 1H), 7.50 – 7.39 (m, 2H), 7.34 – 7.27 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 147.40, 134.76, 129.99, 129.33, 122.76, 115.69. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 40.90. **IR** (neat) cm^{-1}: 1449, 1233, 908, 812. **CHN**: calculated for $C_6H_4BrFO_3S$: C 28.25%, H 1.58%, N 0.00%; found: C 28.72%, H 1.72%, N 0.00%.

4-allyl-2-methoxyphenyl sulfurofluoridate (compound 12)

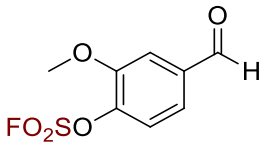


General procedure A was followed using 166 mg of eugenol (99 wt%, 1.0 mmol, 1.0 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (petroleum ether/diethyl ether, 98/2). The title compound was obtained as a colorless oil (235 mg, 95%).

R_f = 0.60 (petroleum ether/diethyl ether, 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.3 Hz, 1H), 6.88 (s, 1H), 6.82 (d, *J* = 8.3 Hz, 1H), 6.02 – 5.88 (m, 1H), 5.18 – 5.14 (m, 1H), 5.14 – 5.07 (m, 1H), 3.90 (s, 3H), 3.41 (d, *J* = 6.7 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 151.07, 142.34, 137.47, 136.35, 122.18, 120.90, 116.96, 113.74, 56.20, 40.13. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 38.86.

These data are in agreement with literature data.[4]

4-formyl-2-methoxyphenyl sulfurofluoridate (compound 13)

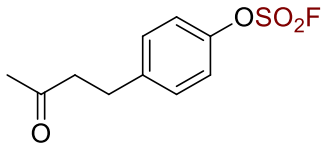


General procedure A was followed using 154 mg of vanillin (99 wt%, 1.0 mmol, 1.0 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (petroleum ether/diethyl ether, 7/3). The title compound was obtained as a white solid (230 mg, 98%).

R_f = 0.13 (petroleum ether/diethyl ether, 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 7.57 (s, 1H), 7.54 – 7.48 (m, 2H), 3.99 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 190.46, 152.14, 142.88, 137.19, 124.06, 123.24, 112.25, 56.62. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 40.52.

These data are in agreement with literature data.[4]

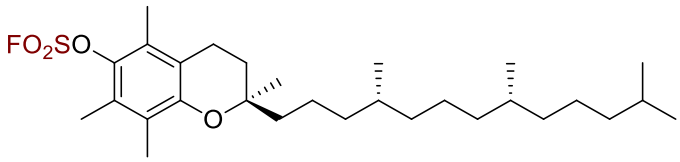
4-(3-oxobutyl)phenyl sulfurofluoridate (compound 14)



General procedure A was followed using 166 mg of raspberry ketone (99 wt%, 1.0 mmol, 1.0 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (petroleum ether/diethyl ether, 7/3). The title compound was obtained as a colorless oil (238 mg, 97%).

R_f = 0.13 (petroleum ether/diethyl ether, 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 2.94 (t, *J* = 7.3 Hz, 2H), 2.79 (t, *J* = 7.3 Hz, 2H), 2.16 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 207.17, 148.51, 142.16, 130.38, 120.91, 44.71, 30.12, 28.93. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 36.76. **IR** (neat) cm^{-1}: 2935, 1716, 1445, 1232, 1138, 912, 815. **CHN**: calculated for $C_{10}H_{11}FO_4S$: C 48.78%, H 4.50%, N 0.00%; found: C 48.83%, H 4.68%, N 0.00%.

(*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl sulfurofluoridate (compound 15)



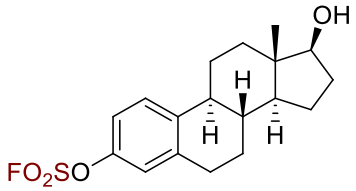
General procedure B was followed using 444 mg of D-α-tocopherol (97 wt%, 1.0 mmol, 1.0 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (petroleum ether/diethyl ether, 98/2). The title compound was obtained as a colorless oil (507 mg, 99%).

R_f = 0.70 (petroleum ether/diethyl ether, 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.61 (t, *J* = 6.7 Hz, 2H), 2.24 (s, 3H), 2.21 (s, 3H), 2.11 (s, 3H), 1.91 – 1.73 (m, 2H), 1.60 – 1.03 (m, 24H), 0.91 – 0.82 (m, 12H). **^{13}C**

NMR (101 MHz, $CDCl_3$): δ 151.16, 142.05, 127.64, 126.21, 124.51, 118.55, 75.86, 40.08, 39.53, 37.60, 37.54, 37.44, 32.95, 32.83, 30.98, 28.14, 24.96, 24.59, 24.00, 22.87, 22.77, 21.12, 20.76, 19.90, 19.80, 13.67 (d, *J* = 2.7 Hz), 12.84 (d, *J* = 2.6 Hz), 12.05. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 40.81.

These data are in agreement with literature data.[4]

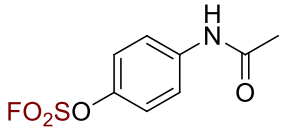
(8*R*,9*S*,13*S*,14*S*,17*S*)-17-hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl sulfurofluoridate (compound 16)



General procedure B was followed using 281 mg of β-estradiol (97 wt%, 1.0 mmol, 1.0 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (petroleum ether/diethyl ether, 5/5). The title compound was obtained as a white solid (342 mg, 96%).

R_f = 0.29 (petroleum ether/diethyl ether, 5/5). **Melting point** = 103 – 105 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.7 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 1H), 7.03 (s, 1H), 3.74 (t, *J* = 8.3 Hz, 1H), 2.95 – 2.77 (m, 2H), 2.39 – 2.29 (m, 1H), 2.29 – 2.20 (m, 1H), 2.17 – 2.07 (m, 1H), 2.01 – 1.89 (m, 2H), 1.77 – 1.67 (m, 1H), 1.55 – 1.18 (m, 8H), 1.03 – 0.87 (m, 1H), 0.79 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 148.14, 141.29, 139.81, 127.42, 120.73, 117.74, 81.86, 50.15, 44.22, 43.28, 38.35, 36.70, 30.67, 29.65, 26.88, 26.23, 23.22, 11.13. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 36.79. **IR** (neat) cm^{-1}: 3599, 3287, 2920, 1444, 1231, 909, 797. **CHN**: calculated for $C_{18}H_{23}FO_4S$: C 61.00%, H 6.54%, N 0.00%; found: C 60.10%, H 6.55%, N 0.00%.

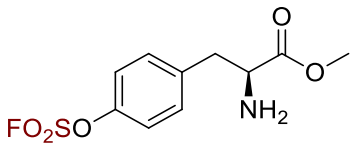
4-acetamidophenyl sulfurofluoridate (compound 17)



General procedure B was followed using 154 mg of paracetamol (98 wt%, 1.0 mmol, 1.0 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (petroleum ether/diethyl ether, 2/8). The title compound was obtained as a white solid (229 mg, 98%).

R_f = 0.56 (diethyl ether, 100%). **Melting point** = 152 – 154 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.7 Hz, 2H), 7.45 (brd, 1H), 7.29 (d, *J* = 8.7 Hz, 2H), 2.20 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 168.59, 145.92, 138.29, 121.72, 121.27, 24.71. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 36.65. **IR** (neat) cm^{-1}: 3268, 3092, 1666, 1435, 1233, 1138, 906, 799. **CHN**: calculated for $C_8H_8FNO_4S$: C 41.20%, H 3.46%, N 6.01%; found: C 41.42%, H 3.57%, N 5.78%.

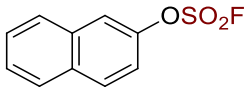
methyl (*S*)-2-amino-3-(4-((fluorosulfonyl)oxy)phenyl)propanoate (compound 18)



General procedure B was followed using 236 mg of L-tyrosine methyl ester hydrochloride (98 wt%, 1.0 mmol, 1.0 eq.) and 699 µL of *N,N*-diisopropylethylamine (4.0 mmol, 4.0 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (ethyl acetate, 100%). The title compound was obtained as a yellow oil (274 mg, 99%).

R_f = 0.49 (ethyl acetate, 100%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36 – 7.23 (m, 4H), 3.76 – 3.67 (m, 4H), 3.10 (dd, *J* = 13.7, 5.3 Hz, 1H), 2.89 (dd, *J* = 13.7, 7.9 Hz, 1H), 1.58 (brd, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 175.11, 148.98, 138.50, 131.27, 120.92, 55.62, 52.15, 40.25. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 36.94. **IR** (neat) cm^{-1}: 2956, 1739, 1443, 1230, 1139, 912, 804. **CHN**: calculated for $C_{10}H_{12}FNO_5S$: C 43.32%, H 4.36%, N 5.05%; found: C 42.86%, H 4.42%, N 4.84%.

naphthalen-2-yl sulfurofluoridate (compound 19)

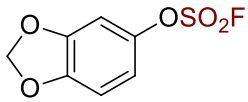


General procedure A was followed using 146 mg of 2-naphthol (99 wt%, 1.0 mmol, 1.0 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (petroleum ether/diethyl ether, 9/1). The title compound was obtained as a white solid (219 mg, 97%).

R_f = 0.54 (petroleum ether/diethyl ether, 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.00 – 7.93 (m, 1H), 7.93 – 7.86 (m, 2H), 7.82 (m, 1H), 7.64 – 7.55 (m, 2H), 7.48 – 7.40 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 147.72, 133.46, 132.63, 130.98, 128.22, 128.11, 127.79, 127.47, 119.13, 118.98. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 37.18.

These data are in agreement with literature data.[4]

benzo[*d*][1,3]dioxol-5-yl sulfurofluoridate (compound 20)

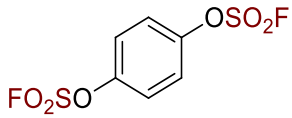


General procedure A was followed using 141 mg of sesamol (98 wt%, 1.0 mmol, 1.0 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (petroleum ether/diethyl ether, 98/2). The title compound was obtained as a colorless oil (210 mg, 95%).

R_f = 0.50 (petroleum ether/diethyl ether, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.88 – 6.76 (m, 3H), 6.05 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 148.75, 147.80, 144.21, 114.14, 108.41, 103.09, 102.66. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 36.04.

These data are in agreement with literature data.[4]

1,4-phenylene bis(sulfurofluoridate) (compound 21)

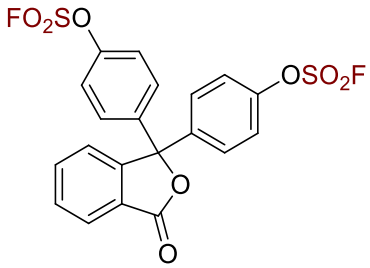


General procedure A was followed using 55.6 mg of hydroquinone (99 wt%, 0.5 mmol, 0.5 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (petroleum ether/diethyl ether, 95/5). The title compound was obtained as a white (126 mg, 92%).

R_f = 0.52 (petroleum ether/diethyl ether, 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.50 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 149.12, 123.47. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 37.78.

These data are in agreement with literature data.[4]

(3-oxo-1,3-dihydroisobenzofuran-1,1-diyl)bis(4,1-phenylene) bis(sulfurofluoridate) (compound 22)



General procedure A was followed using 161 mg of phenolphthalein (99 wt%, 0.5 mmol, 0.5 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (petroleum ether/diethyl ether, 5/5). The title compound was obtained as a white solid (237 mg, 98%).

R_f = 0.40 (petroleum ether/diethyl ether, 5/5). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.05 – 7.95 (m, 1H), 7.84 – 7.75 (m, 1H), 7.68 – 7.62 (m, 1H), 7.60 – 7.55 (m, 1H), 7.50 – 7.42 (m, 4H), 7.39 – 7.31 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 168.71, 150.43, 150.15, 141.13, 135.00, 130.44, 129.36, 126.82, 125.41, 123.99, 121.50, 89.67. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 37.71.

These data are in agreement with literature data.[4]

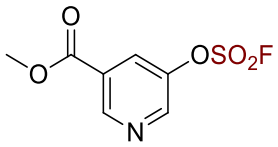
methyl 3-((fluorosulfonyl)oxy)thiophene-2-carboxylate (compound 23)

General procedure A was followed using 163 mg of methyl 3-hydroxythiophene-2-carboxylate (97 wt%, 1.0 mmol, 1.0 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (petroleum ether/diethyl ether, 95/5). The title compound was obtained as a colorless oil (226 mg, 94%).

R_f = 0.30 (petroleum ether/diethyl ether, 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 5.5 Hz, 1H), 7.11 (d, *J* = 5.5 Hz, 1H), 3.92 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 159.85, 145.66, 130.86, 122.52, 121.98, 52.77. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 39.56.

These data are in agreement with literature data.[6]

methyl 5-((fluorosulfonyl)oxy)nicotinate (compound 24)



General procedure A was followed using 156 mg of methyl 5-hydroxynicotinate (98 wt%, 1.0 mmol, 1.0 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (petroleum ether/diethyl ether, 9/1). The title compound was obtained as a white solid (207 mg, 88%).

R_f = 0.70 (petroleum ether/diethyl ether, 5/5). **Melting point** = 54 – 56 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.27 (s, 1H), 8.84 (s, 1H), 8.29 (s, 1H), 4.00 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 163.93, 150.76, 146.81, 146.40, 129.67, 127.89, 53.21. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 38.78. **IR** (neat) cm^{-1}: 3064, 1723, 1447, 1229, 917, 809. **CHN:** calculated for $C_7H_6FNO_5S$: C 35.75%, H 2.57%, N 5.96%; found: C 35.72%, H 2.60%, N 5.74%.

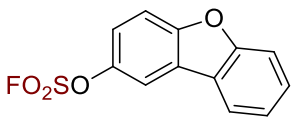
quinolin-8-yl sulfurofluoridate (compound 25)

General procedure A was followed using 147 mg of 8-hydroxyquinoline (99 wt%, 1.0 mmol, 1.0 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (heptane/ethyl acetate, 98/2). The title compound was obtained as a white solid (220 mg, 97%).

R_f = 0.09 (heptane/ethyl acetate, 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.09 – 8.99 (m, 1H), 8.26 – 8.17 (m, 1H), 7.92 – 7.83 (m, 1H), 7.78 – 7.70 (m, 1H), 7.63 – 7.48 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 151.93, 145.94, 140.48, 136.04, 130.05, 128.82, 125.96, 122.80, 121.39. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 40.12.

These data are in agreement with literature data.[6]

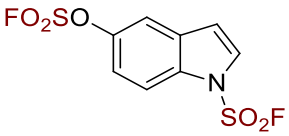
dibenzo[*b*,*d*]furan-2-yl sulfurofluoridate (compound 26)



General procedure A was followed using 188 mg of 2-hydroxydibenzofuran (98 wt%, 1.0 mmol, 1.0 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (petroleum ether/diethyl ether, 98/2). The title compound was obtained as a white solid (260 mg, 98%).

R_f = 0.69 (petroleum ether/diethyl ether, 9/1). **Melting point** = 94 – 95 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.00 – 7.88 (m, 2H), 7.67 – 7.58 (m, 2H), 7.57 – 7.50 (m, 1H), 7.46 – 7.36 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 157.44, 154.99, 145.72, 128.75, 125.88, 123.53, 123.35, 121.25, 119.77, 113.53, 113.15, 112.25. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 36.22. **IR** (neat) cm^{-1}: 1443, 1228, 923, 801. **CHN**: calculated for $C_{12}H_7FO_4S$: C 54.14%, H 2.65%, N 0.00%; found: C 54.27%, H 2.70%, N 0.00%.

1-(fluorosulfonyl)-1*H*-indol-5-yl sulfurofluoridate (compound 27)



General procedure B was followed using 68.6 mg of 5-hydroxyindole (97 wt%, 0.5 mmol, 0.5 eq.). The crude reaction mixture was purified by solid-phase flash column chromatography on silicagel (petroleum ether/diethyl ether, 95/5). The title compound was obtained as a colorless oil (145 mg, 97%).

R_f = 0.68 (petroleum ether/diethyl ether, 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06 – 7.95 (m, 1H), 7.72 – 7.63 (m, 1H), 7.62 – 7.55 (m, 1H), 7.48 – 7.38 (m, 1H), 6.93 – 6.83 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 147.23, 133.91, 131.62, 128.71 (d, *J* = 1.6 Hz), 118.76, 115.34, 114.57, 110.79 (d, *J* = 1.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 55.29, 36.80.

These data are in agreement with literature data.[6]

4. Decomposition Study of 1,1'-Sulfonyldiimidazole

To gain insight into the decomposition of 1,1'-sulfonyldiimidazole (SDI), a ^{13}C NMR study was conducted at room temperature (Figure S4 andFigure S5). For this study, the following five samples were prepared:

- Sample A: SDI (150 mg, 0.75 mmol, 1.0 eq.) in 0.5 mL (6.49 mmol, 8.7 eq.) of TFA. After 2 minutes, the reaction was quenched with Et_3N (1.8 mL, 12.98 mmol, 17.3 eq.).
- Sample B: SDI (150 mg) and KF (116 mg, 2.0 mmol, 2.7 eq.) in 0.5 mL of TFA. After 5 seconds, the reaction was quenched with Et_3N (1.8 mL).
- Sample C: SDI (150 mg) and KF (116 mg) in 0.5 mL of TFA. After 30 seconds, the reaction was quenched with Et_3N (1.8 mL).
- Sample D: SDI (150 mg) and KF (116 mg) in 0.5 mL of TFA. After 1 minute, the reaction was quenched with Et_3N (1.8 mL).
- Sample E: Imidazole (102 mg, 1.5 mmol, 2.0 eq.) and KF (29 mg, 0.5 mmol, 0.67 eq.) in 0.5 mL of TFA. After 2 minutes, the reaction was quenched with Et_3N (1.8 mL).

Then, 100 µL of each sample was dissolved in 1 mL DMSO-d_6 and immediately measured on the Bruker Avance II$^+$ 600 spectrometer.

We hypothesized that 1,1'-sulfonyldiimidazole could generate pure SO_2F_2 gas from a fluoride source in acidic conditions. Under these conditions, the imidazole groups of SDI should be protonated and thus act as an excellent leaving group. After a twofold displacement by fluoride, the desired gas should be released together with an imidazolium salt as byproduct.

In order to confirm this hypothesis, two control samples were first measured. Spectrum A shows the reference ppm-values of 1,1'-sulfonyldiimidazole (118.56, 131.84 and 137.73 ppm) in trifluoroacetic acid (TFA, 117.12 (q, J = 297.7 Hz), 159.29 (q, J = 32.1 Hz)) and spectrum E shows the reference ppm-values of imidazole (121.61 and 135.21 ppm) in TFA. Next, TFA was added to a mixture of 1,1'-sulfonyldiimidazole and KF which resulted in gas formation for several seconds. This experiment was performed three times and quenched with triethylamine after 5, 30 and 60 seconds (spectrum B, C and D, respectively). In spectrum B, two new intense peaks appeared at 121.6 and 135.2 ppm and were identified as imidazole as they matched spectrum E. Also, three small peaks were observed at 119.4, 132.2 and 138.5 ppm. We speculate that these peaks originate from the *in situ* formed intermediate Im-SO_2-F. After 30 seconds, the SDI peaks completely disappeared and only imidazole peaks were observed (spectrum C). This indicates that SDI completely decomposes in less than half a minute under the applied reaction conditions. The same observations were true when the reaction was quenched after one minute (spectrum D).

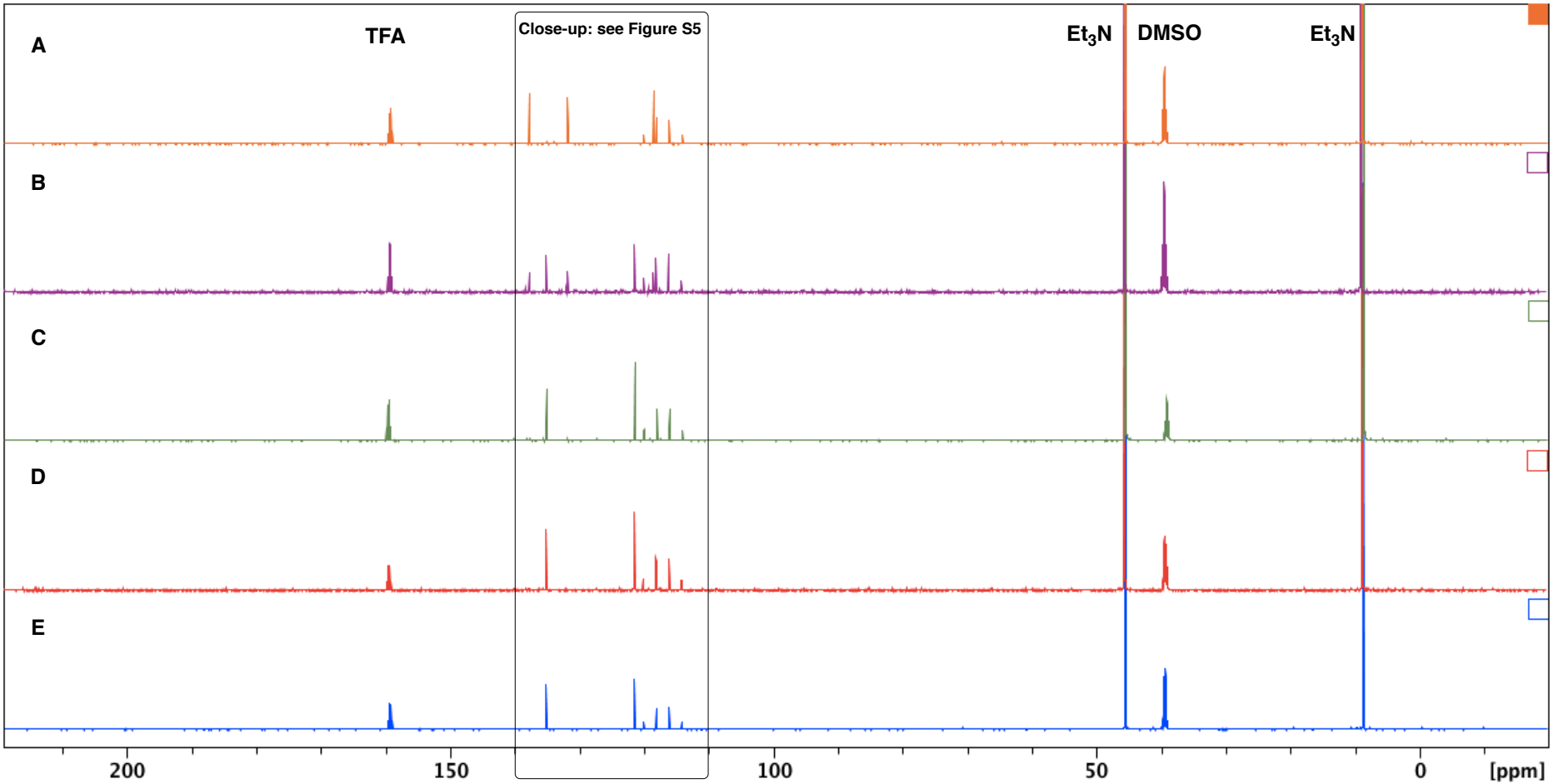


Figure S4. ^{13}*C-NMR decomposition study of 1,1'-sulfonyldiimidazole (SDI). All spectra were recorded in DMSO-*d_6*. A: SDI in TFA quenched by* Et_3N *after 2 minutes. B: SDI and KF in TFA quenched by* Et_3N *after 5 seconds. C: SDI and KF in TFA quenched by* Et_3N *after 30 seconds. D: SDI and KF in TFA quenched by* Et_3N *after 1 minute. E: Imidazole and KF in TFA quenched by* Et_3N *after 2 minutes.*

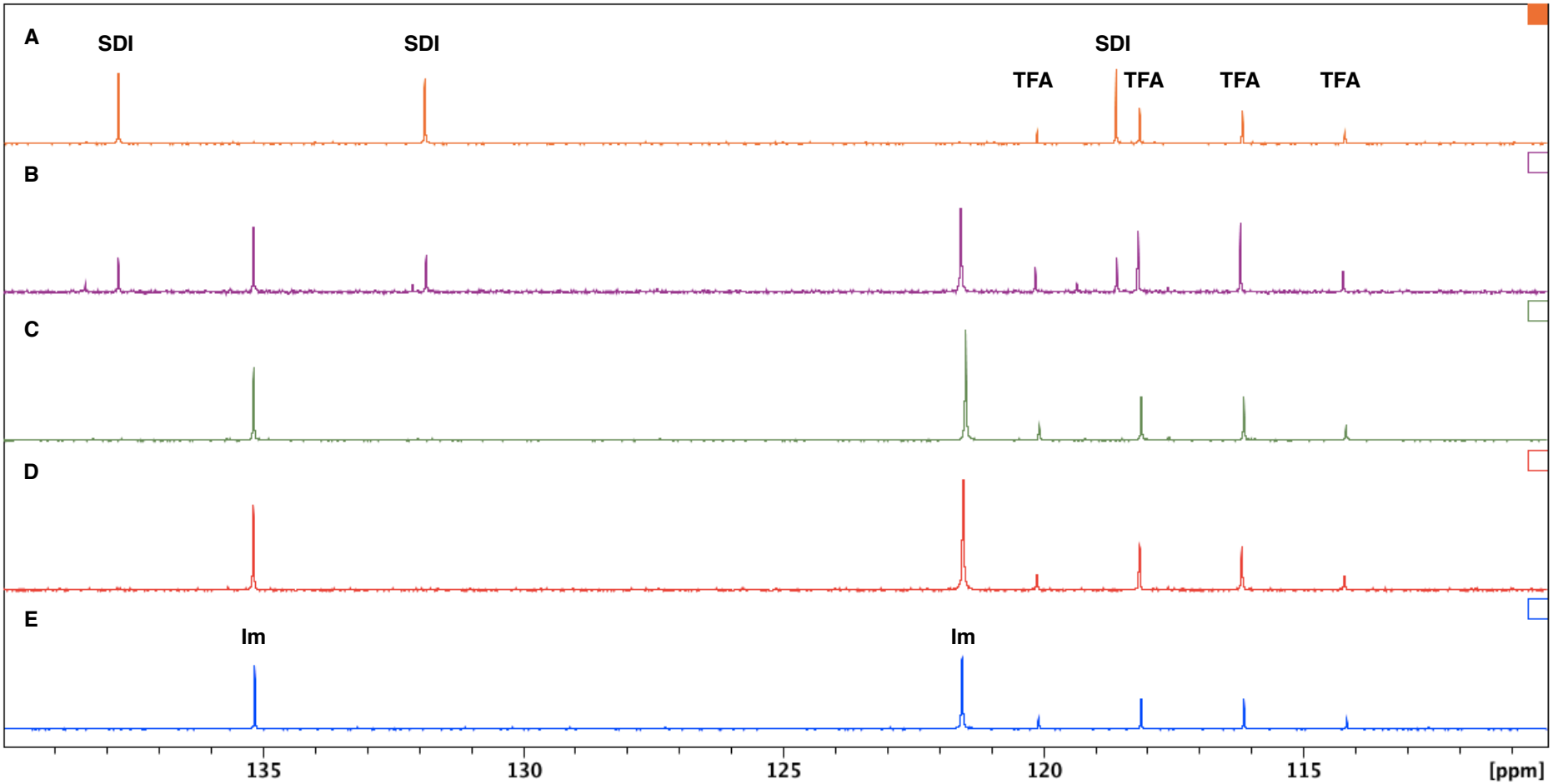
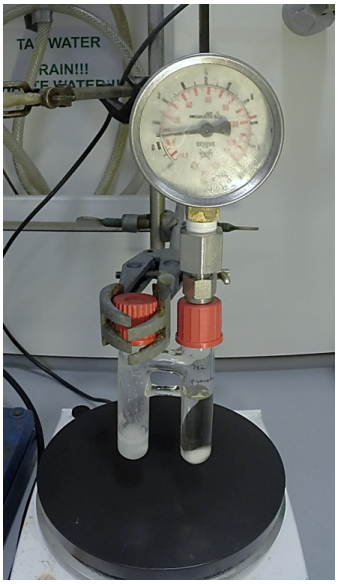


Figure S5. Close-up of the ^{13}C-NMR decomposition study of 1,1'-sulfonyldiimidazole (SDI). All spectra were recorded in DMSO-d_6. A: SDI in TFA quenched by Et_3N after 2 minutes. B: SDI and KF in TFA quenched by Et_3N after 5 seconds. C: SDI and KF in TFA quenched by Et_3N after 30 seconds. D: SDI and KF in TFA quenched by Et_3N after 1 minute. E: Imidazole and KF in TFA quenched by Et_3N after 2 minutes.

5. Pressure Profile in a Typical Reaction



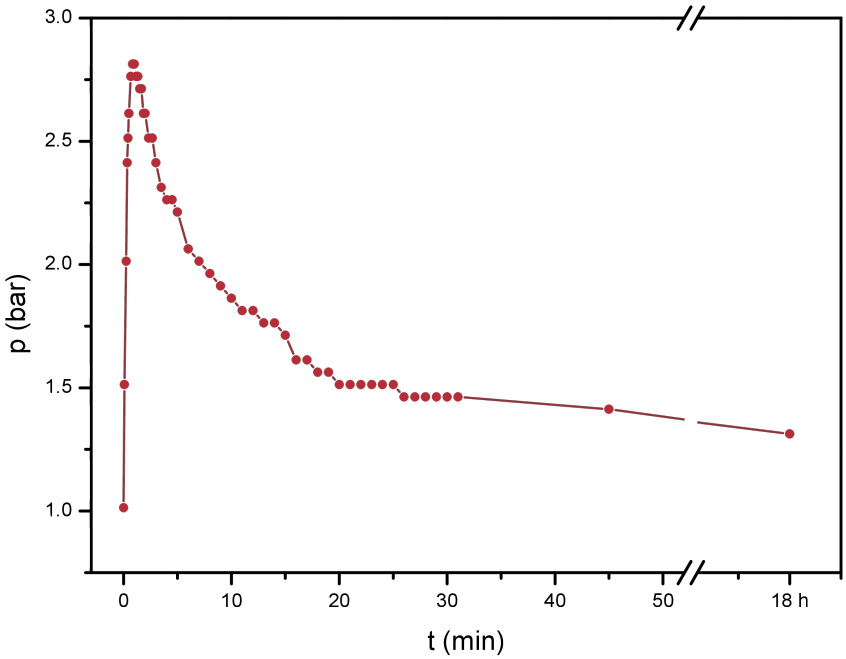


Figure S6. Left: Set-up with manometer attached to the two-chamber vessel. Right: Pressure profile inside the vessel over time.

A study of the pressure was then conducted in order to verify that safety measures concerning the glassware were met. It has been described that the two chamber vessels can minimally resist 5 bar, hence we ensure that we never surpass this limit.

A calculation was done to determine the theoretical pressure generated inside. The ideal gas law was first used to know the amount of air already inside the vessel. The remaining volume amounts to 15 mL, since 5 mL solvent is already present.

$$n = \frac{pV}{RT} = \frac{1\ atm \times 0.015\ L}{0.082\ \frac{L \times atm}{K \times mol} \times 298\ K} = 0.61 \times 10^{-3} mol$$

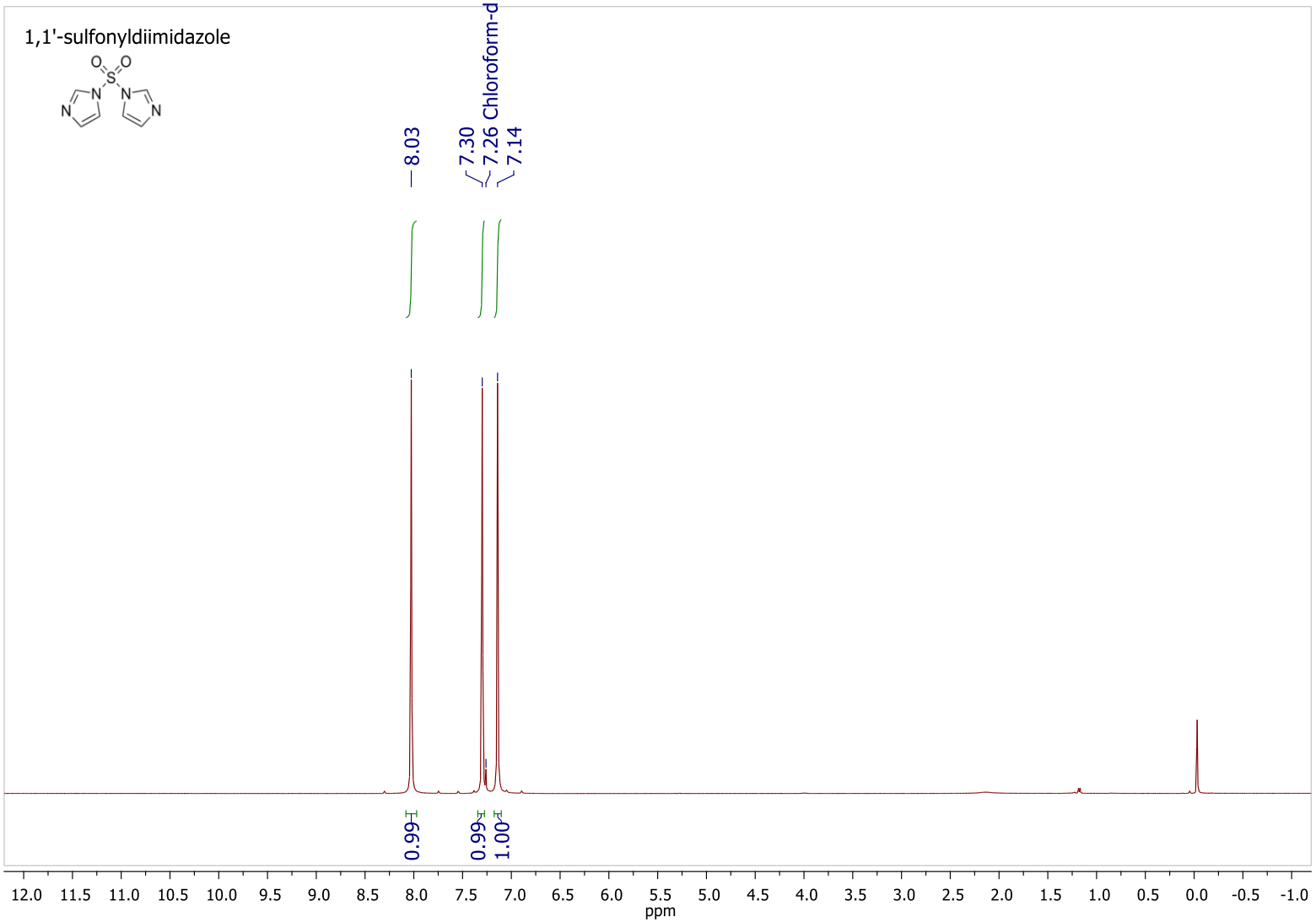
The amount of air is 0.61 mmol. Next, we know the amount of generated SO_2F_2 gas since it is equal to the amount of SDI added, 1.50 mmol. The total amount of gas after generation is then 2.11 mmol. The pressure can then be calculated as follows:

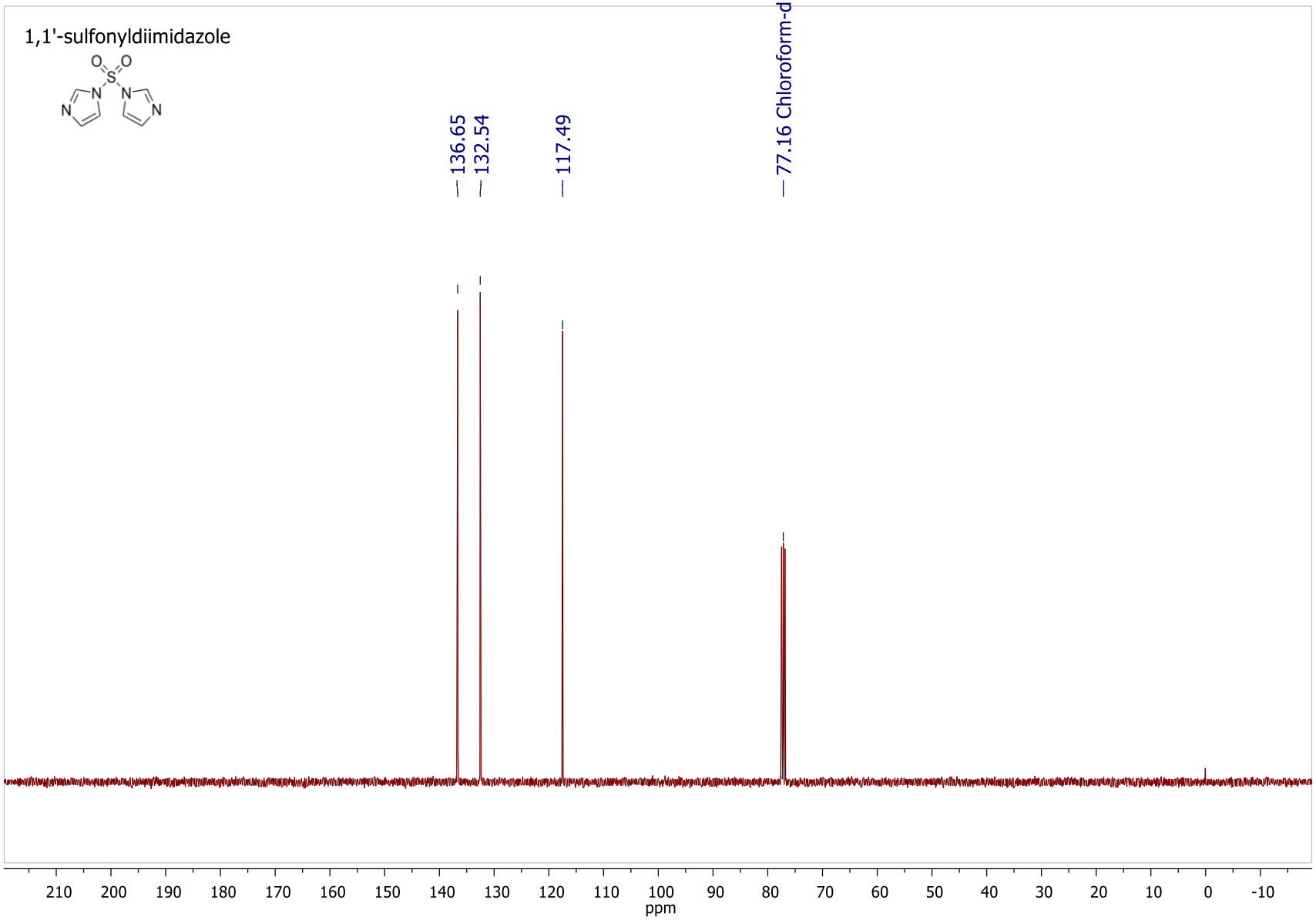
$$p = \frac{nRT}{V} = \frac{0.00211\ mol \times 0.082\ \frac{L \times atm}{K \times mol} \times 298\ K}{0.015\ L} = 3.44\ atm = 3.49\ bar$$

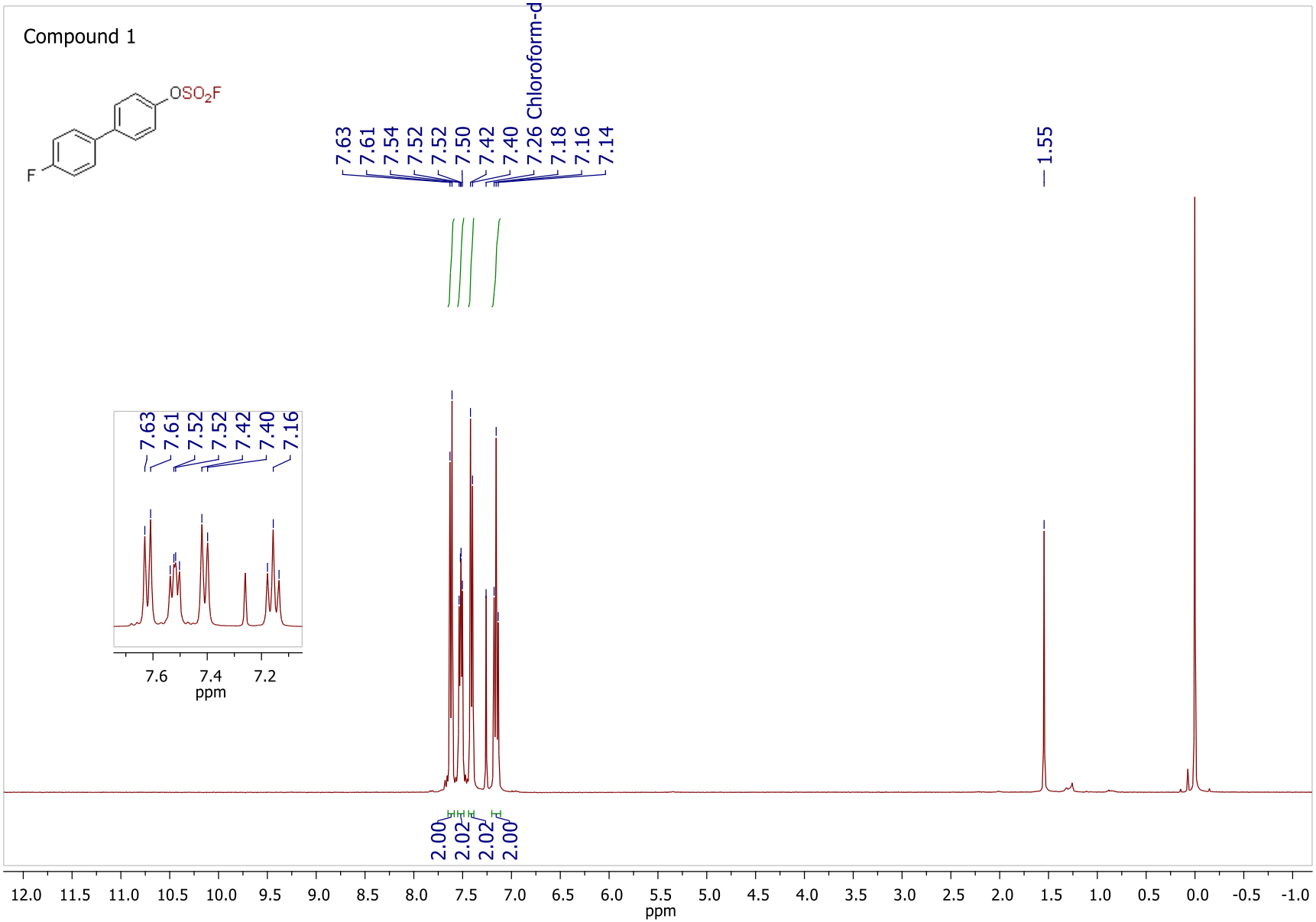
The theoretical pressure is thus 3.49 bar. When we measure this using a manometer (range: 1-10 bar), we notice a rapid increase of the pressure from the moment of addition to 60 s thereafter (Figure S6). At this point, we measure the maximum pressure of 2.8 bar.

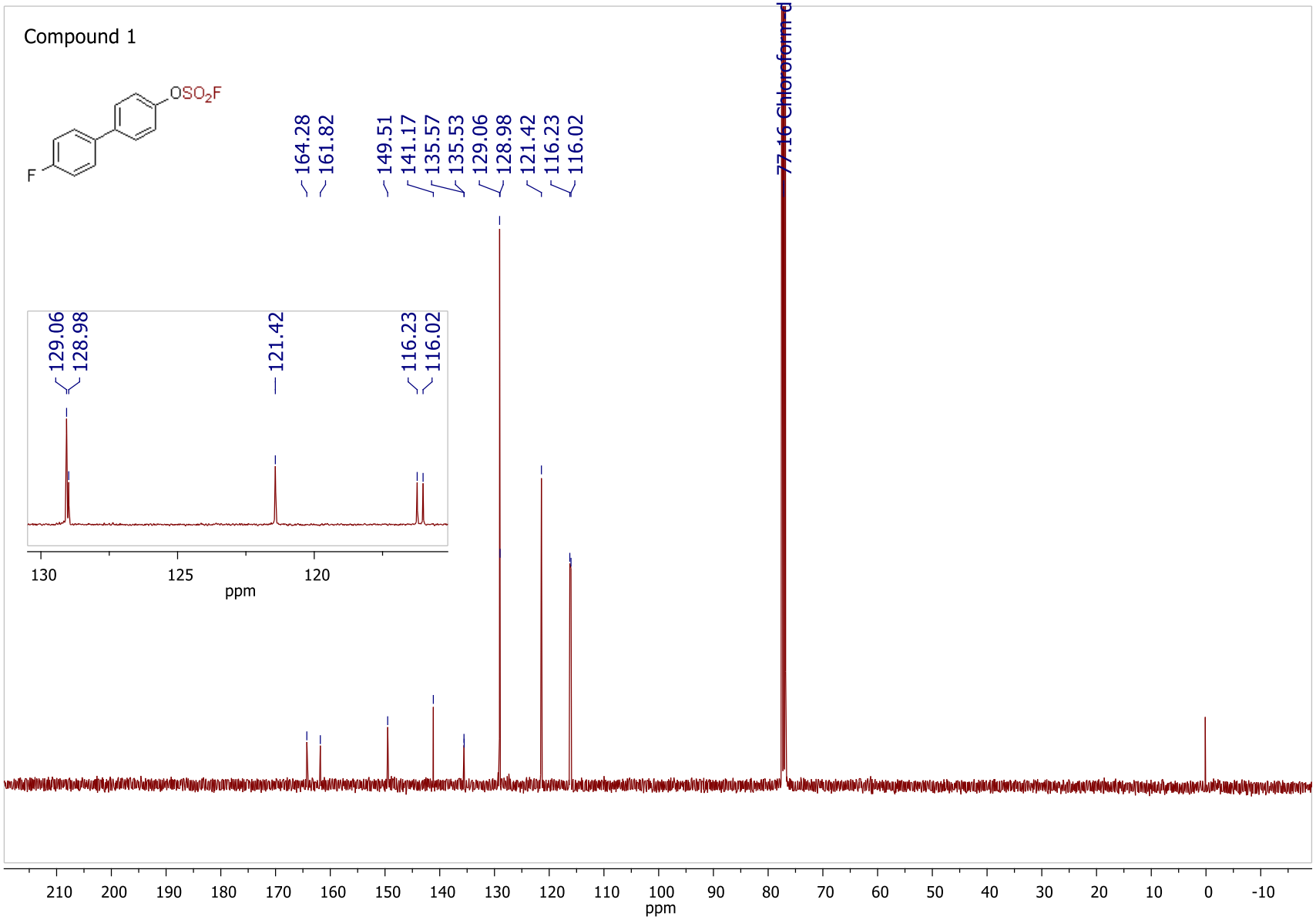
In this way, we are certain that all the applicable safety measures are met and no danger of explosion is present.

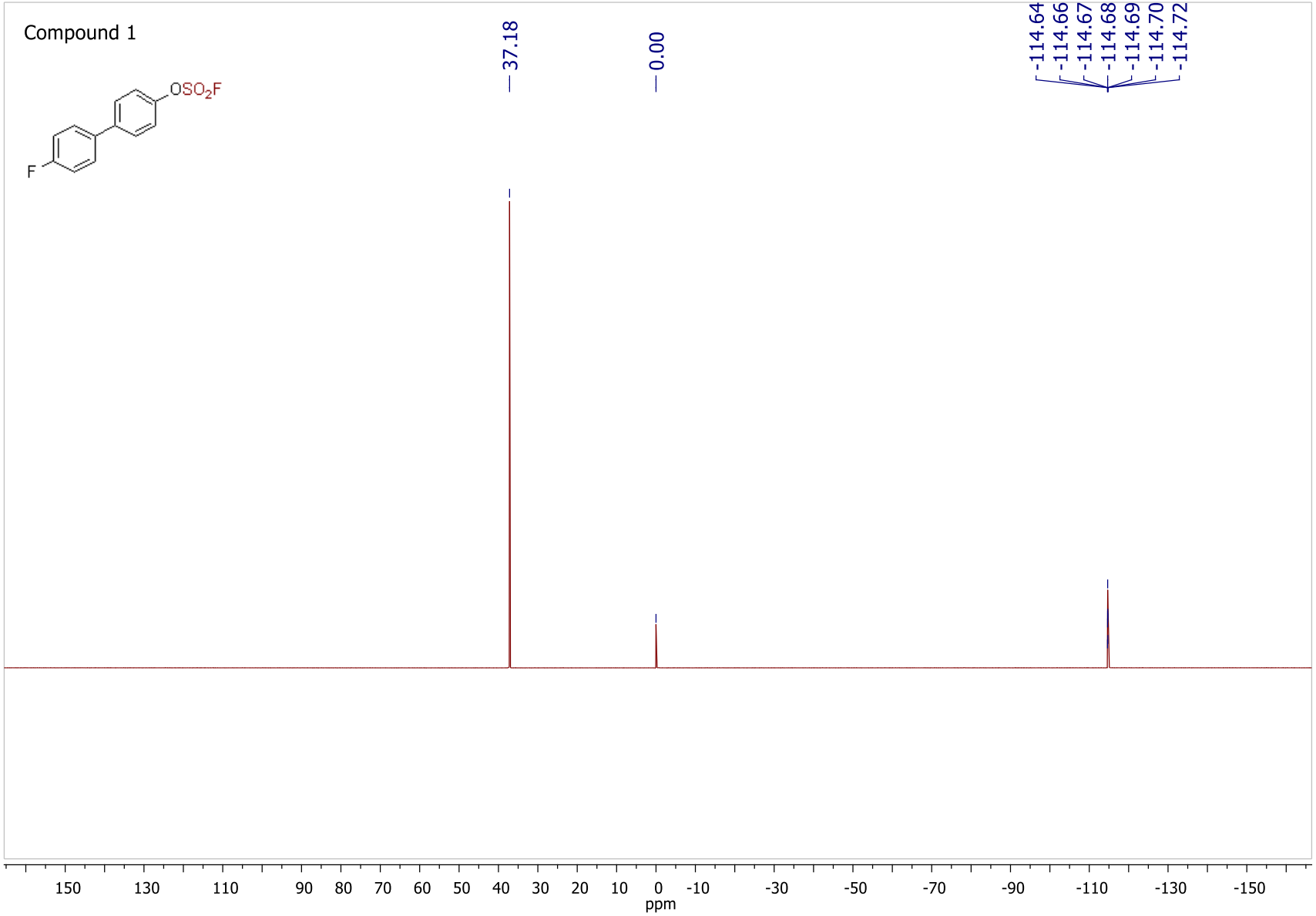
6. NMR Spectra of the Synthesized Compounds

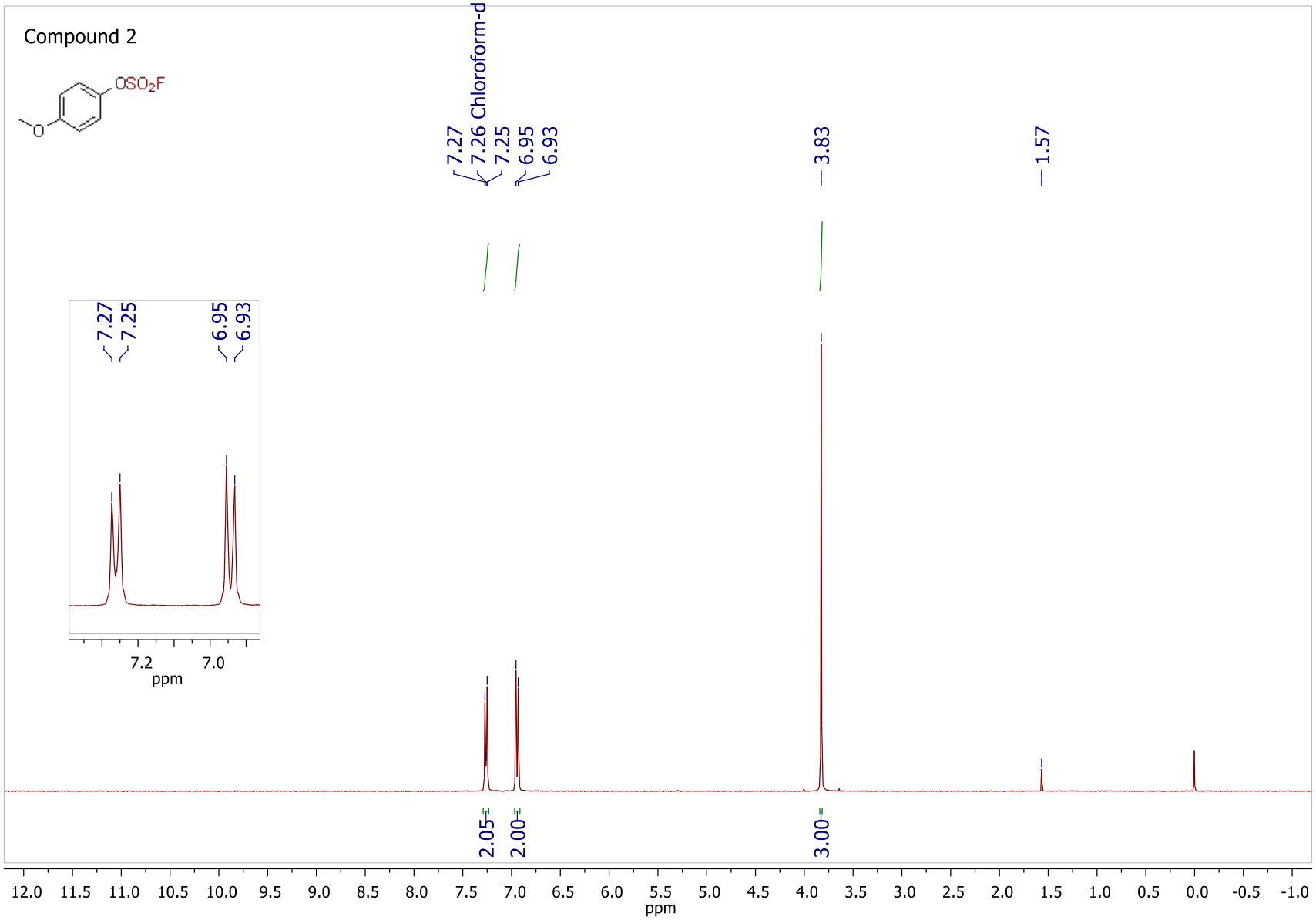


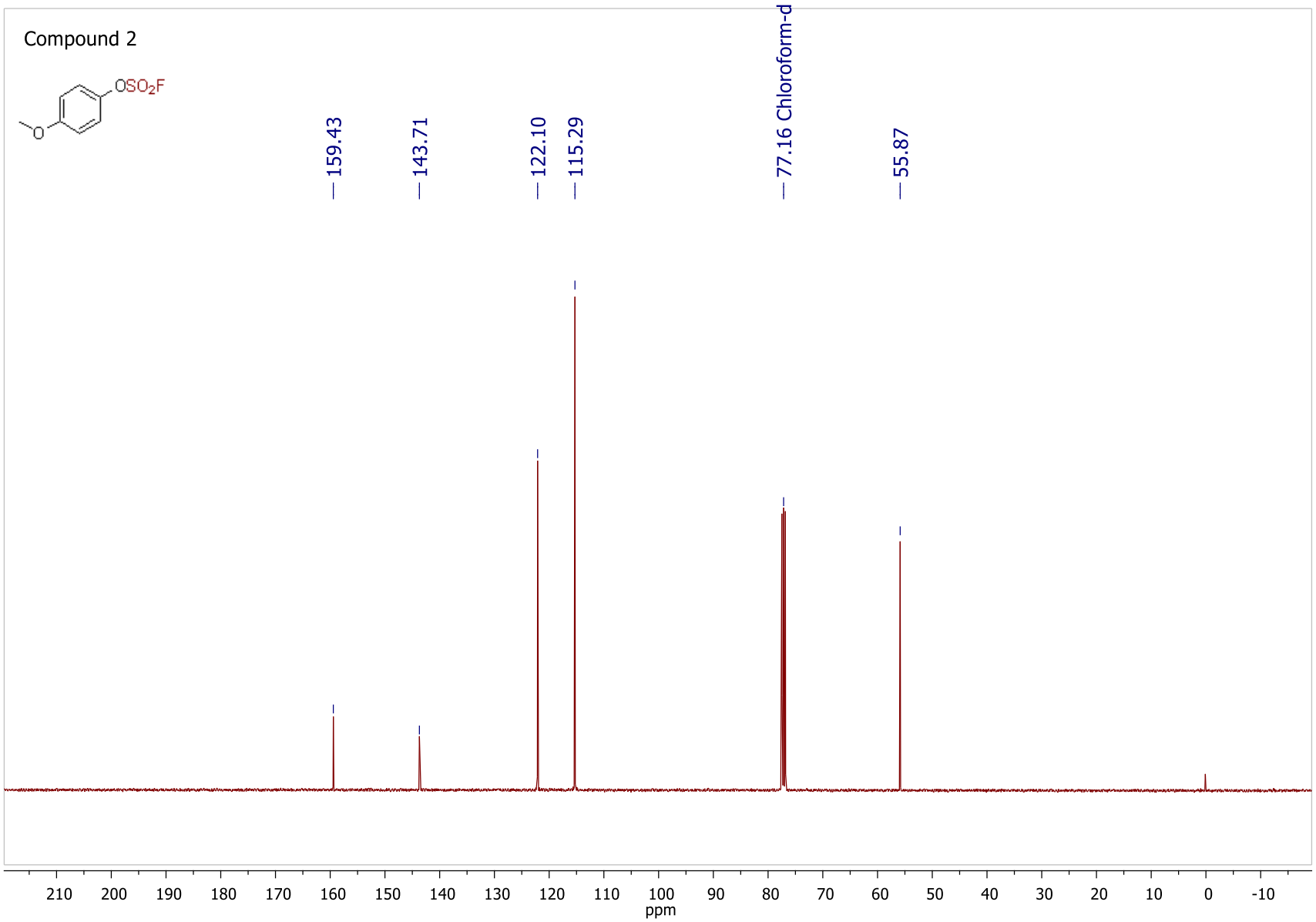

1,1'-sulfonyldiimidazole
136.65
132.54
117.49
77.16 Chloroform-d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

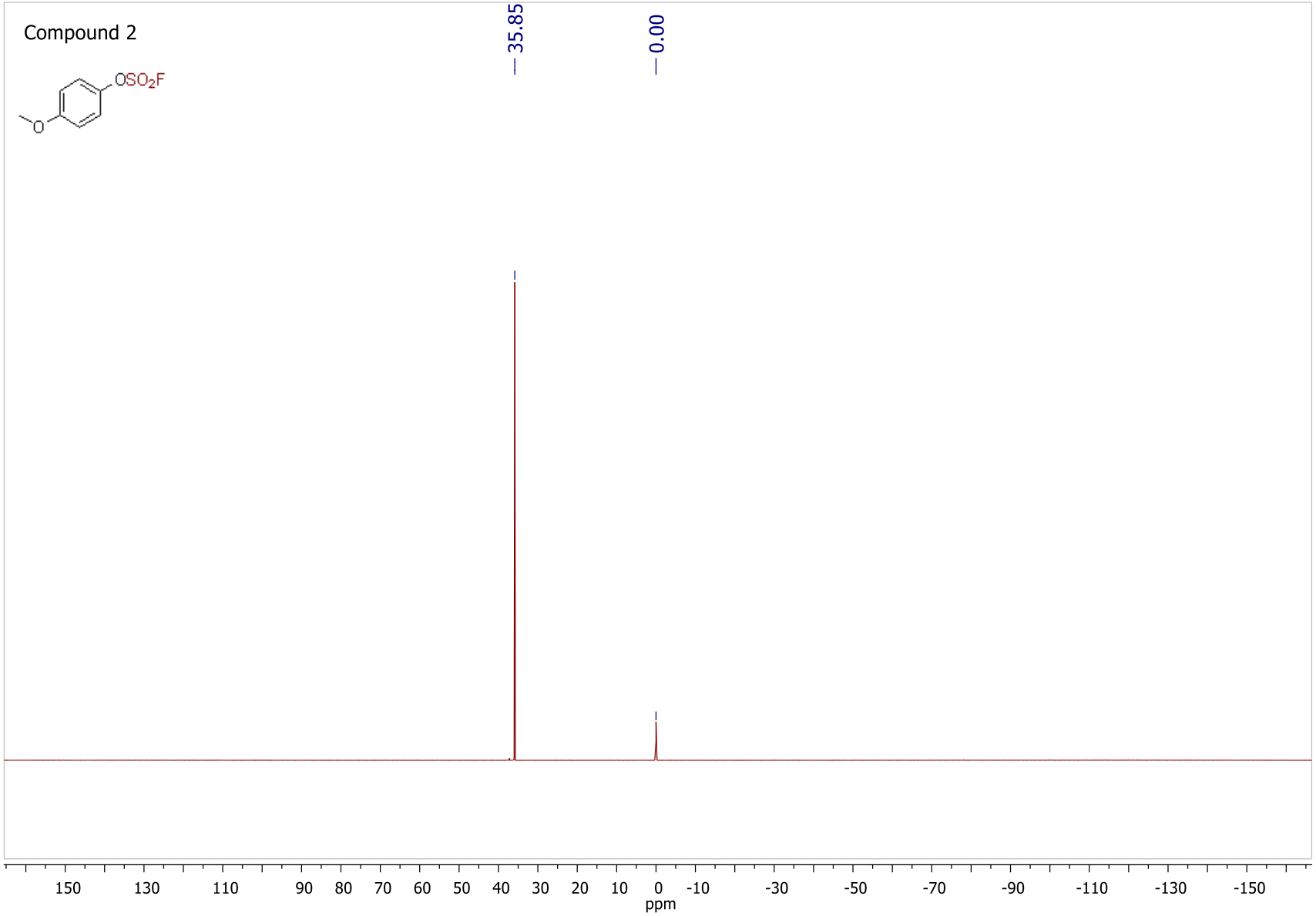

Compound 1
OSO2F
F
7.63
7.61
7.54
7.52
7.52
7.50
7.42
7.40
7.26 Chloroform-d
7.18
7.16
7.14
1.55
7.63
7.61
7.52
7.52
7.42
7.40
7.16
7.6
7.4
7.2
ppm
2.00
2.02
2.02
2.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

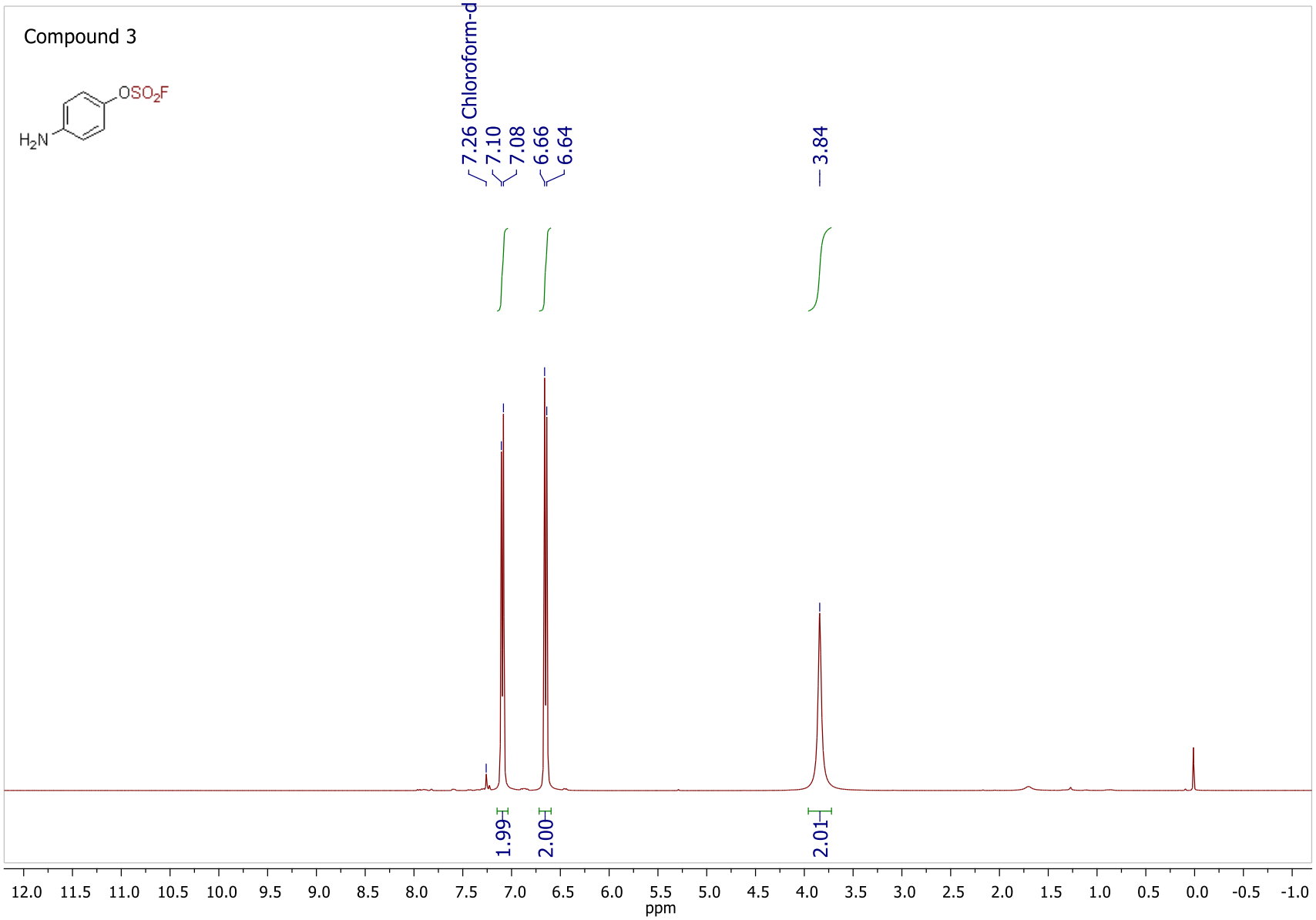

Compound 1
OSO2F
F
164.28
161.82
149.51
141.17
135.57
135.53
129.06
128.98
121.42
116.23
116.02
77.16 Chloroform-d
129.06
128.98
121.42
116.23
116.02
130
125
120
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

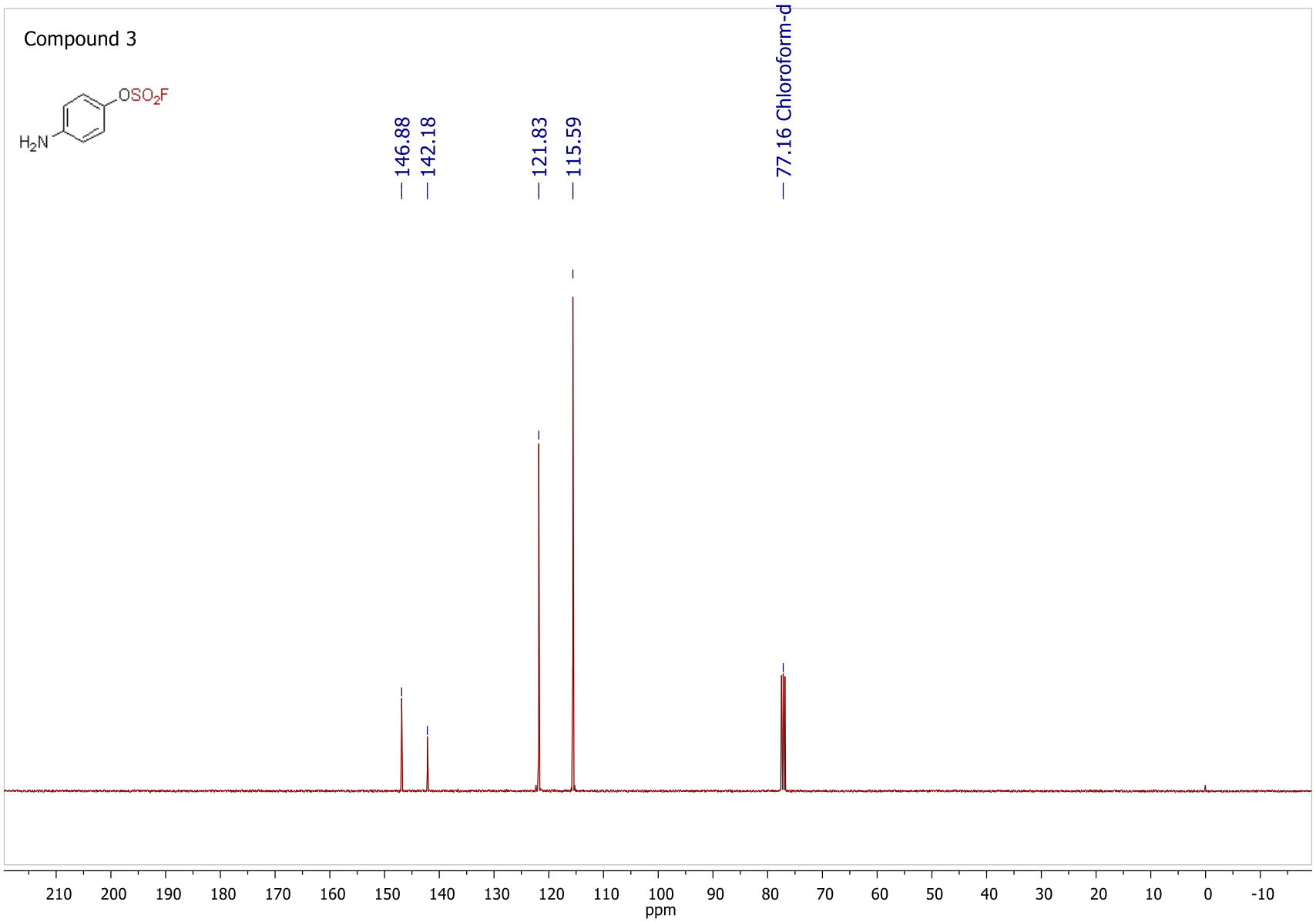

Compound 1
OSO2F
F
37.18
0.00
-114.64
-114.66
-114.67
-114.68
-114.69
-114.70
-114.72
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm

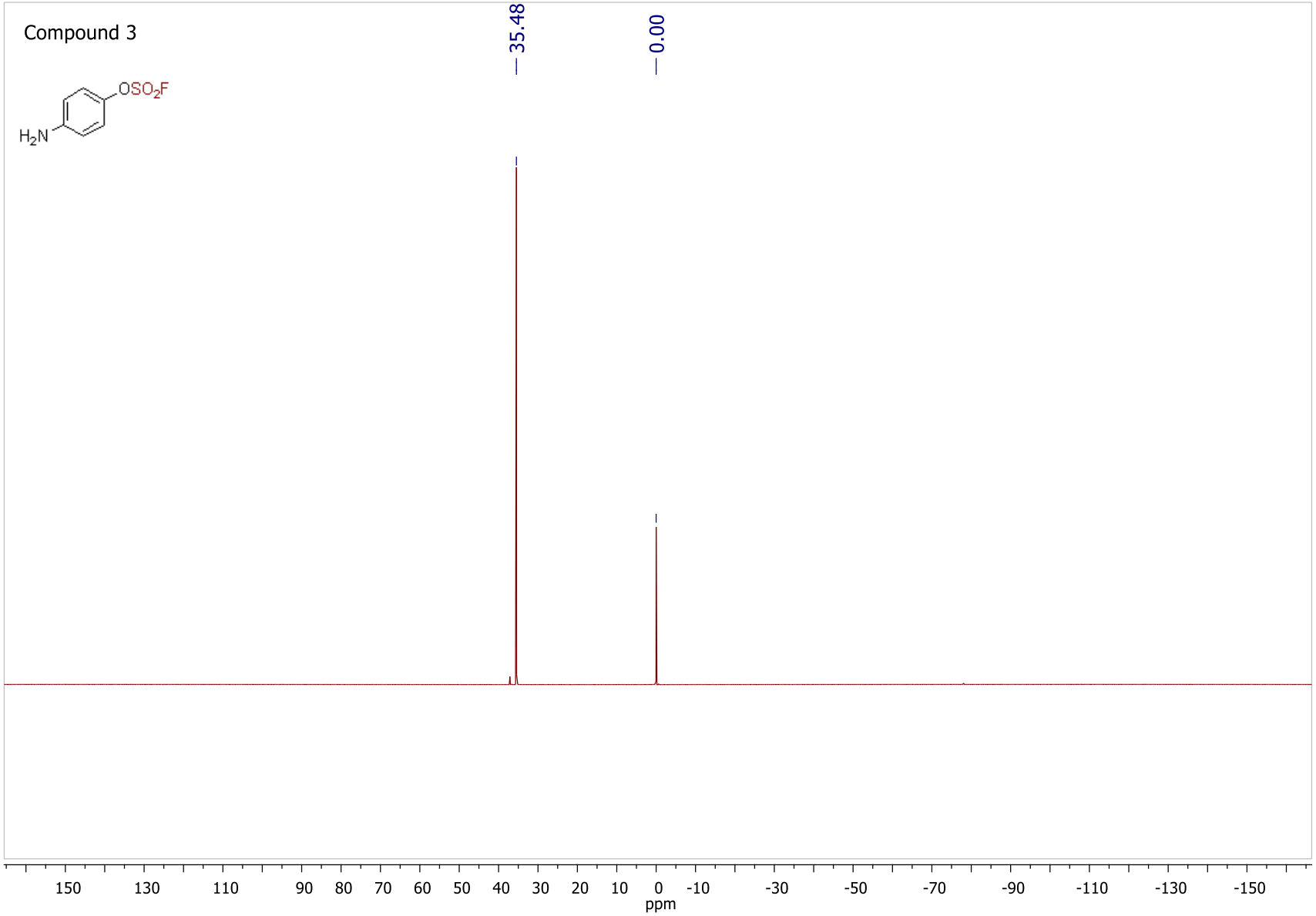

Compound 2
OSO2F
O
7.27
7.26 Chloroform-d
7.25
6.95
6.93
3.83
1.57
7.27
7.25
6.95
6.93
7.2
7.0
ppm
2.05
2.00
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

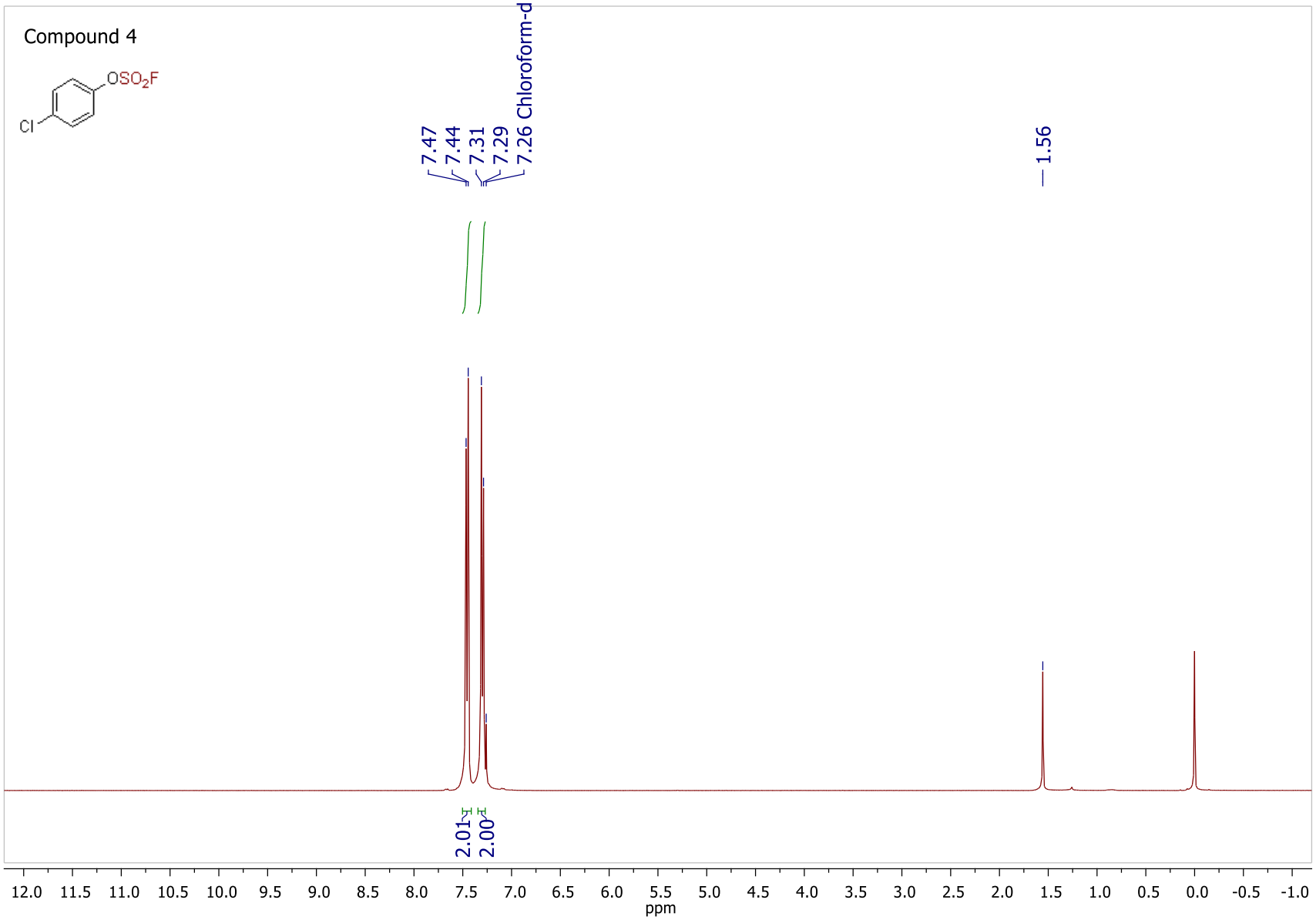

Compound 2
OSO2F
O
159.43
143.71
122.10
115.29
77.16 Chloroform-d
55.87
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

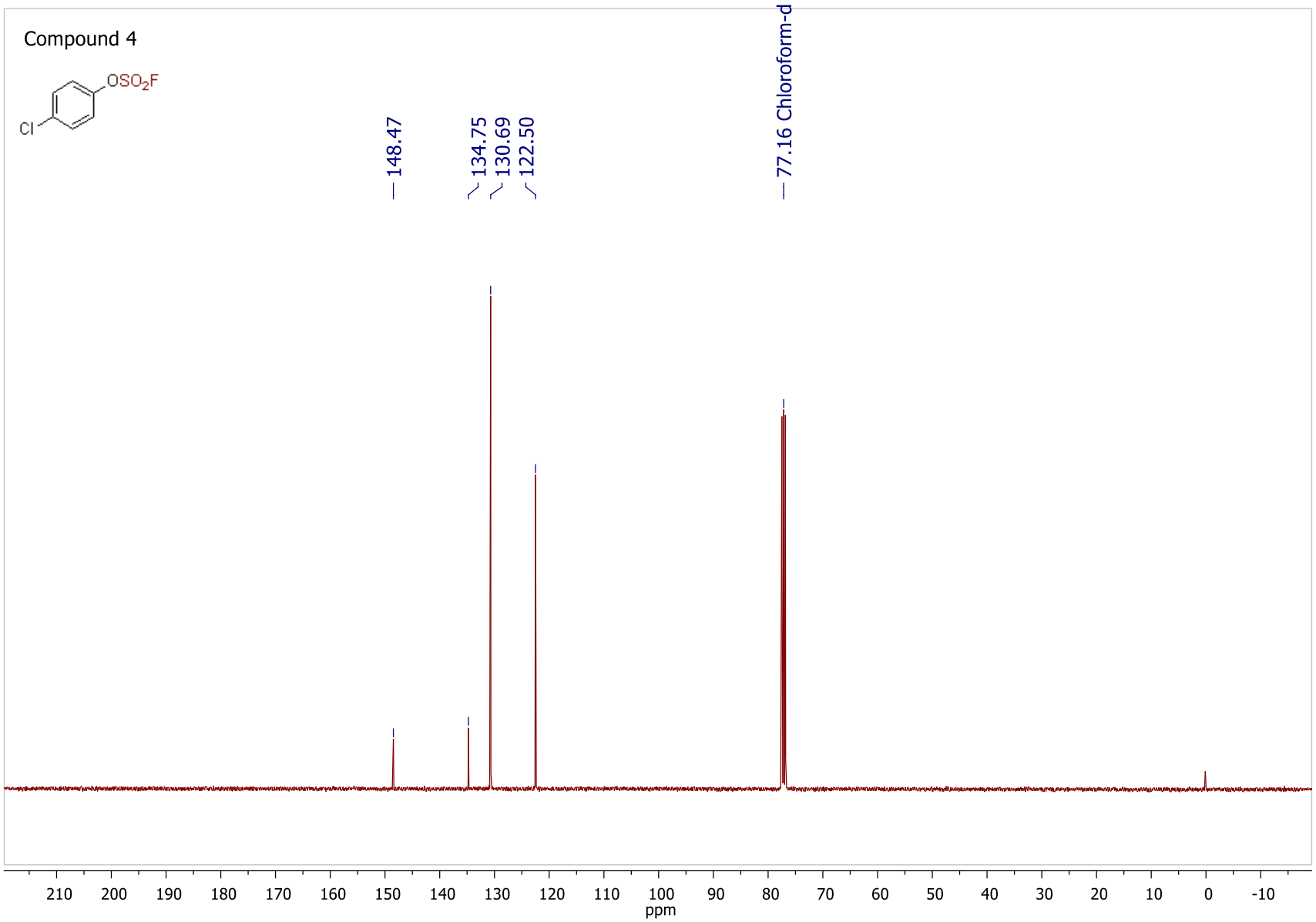

Compound 2
OSO2F
O
35.85
0.00
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm

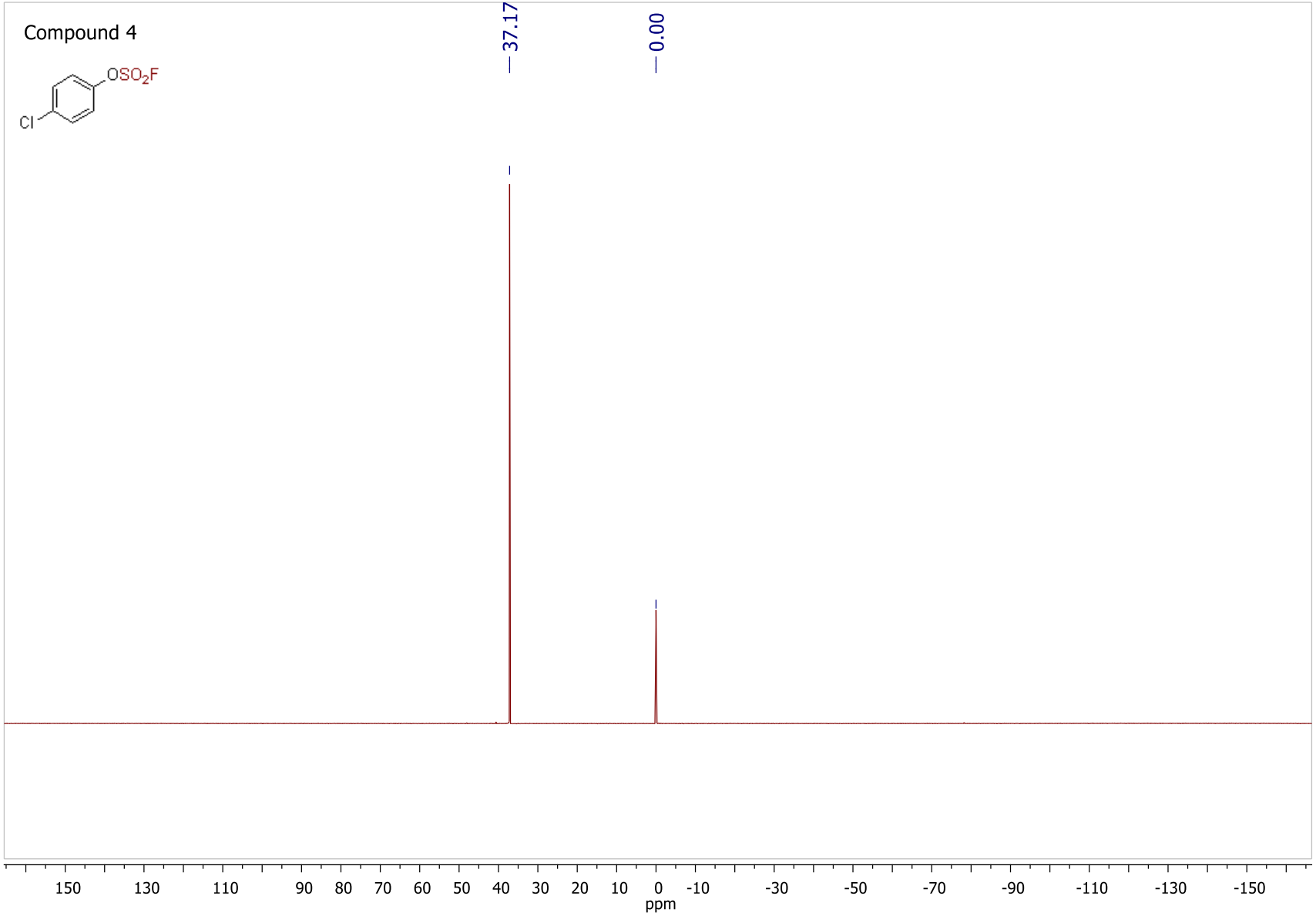

Compound 3
OSO2F
H2N
7.26 Chloroform-d
7.10
7.08
6.66
6.64
3.84
1.99
2.00
2.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

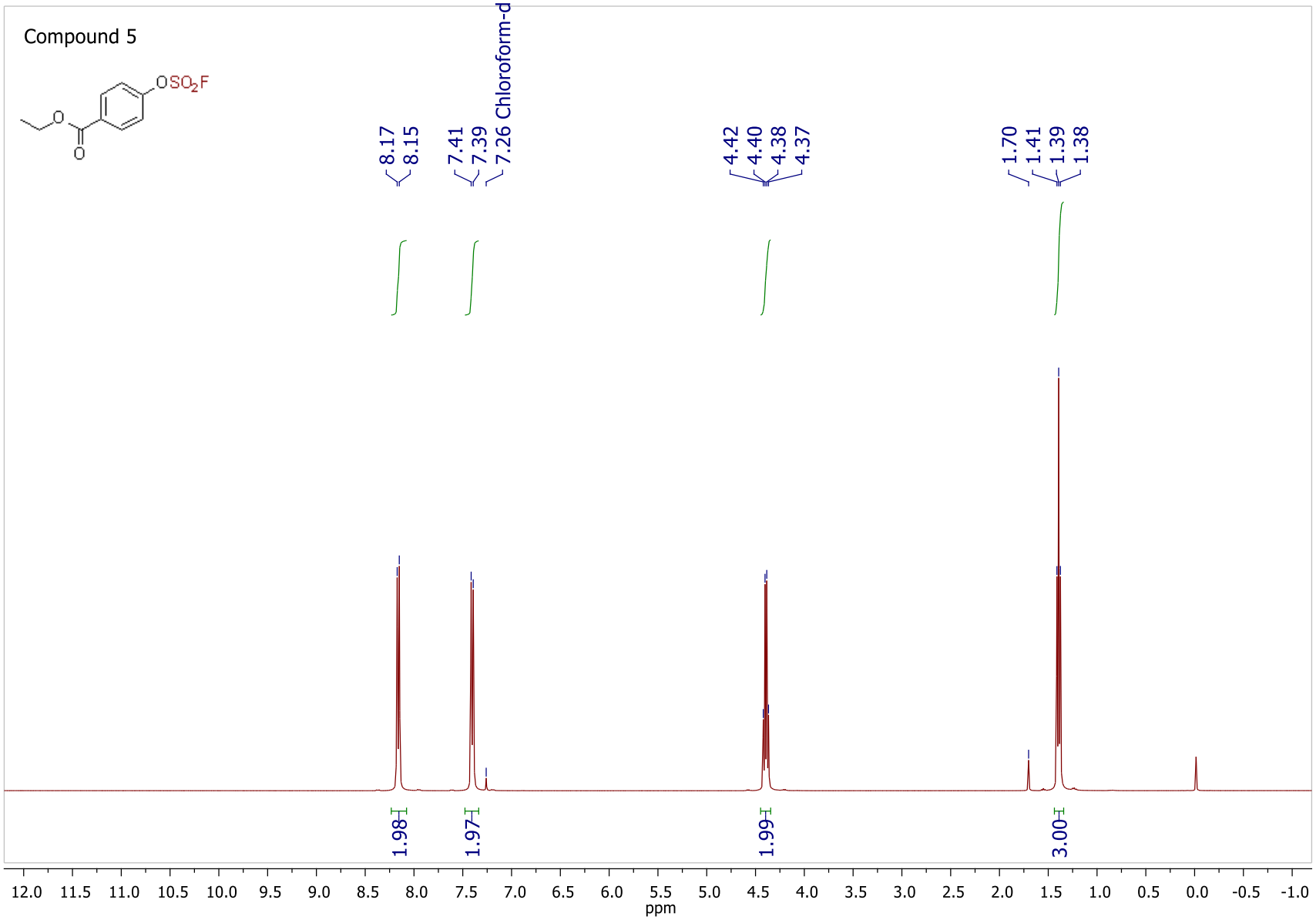

Compound 3
OSO2F
H2N
146.88
142.18
121.83
115.59
77.16 Chloroform-d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

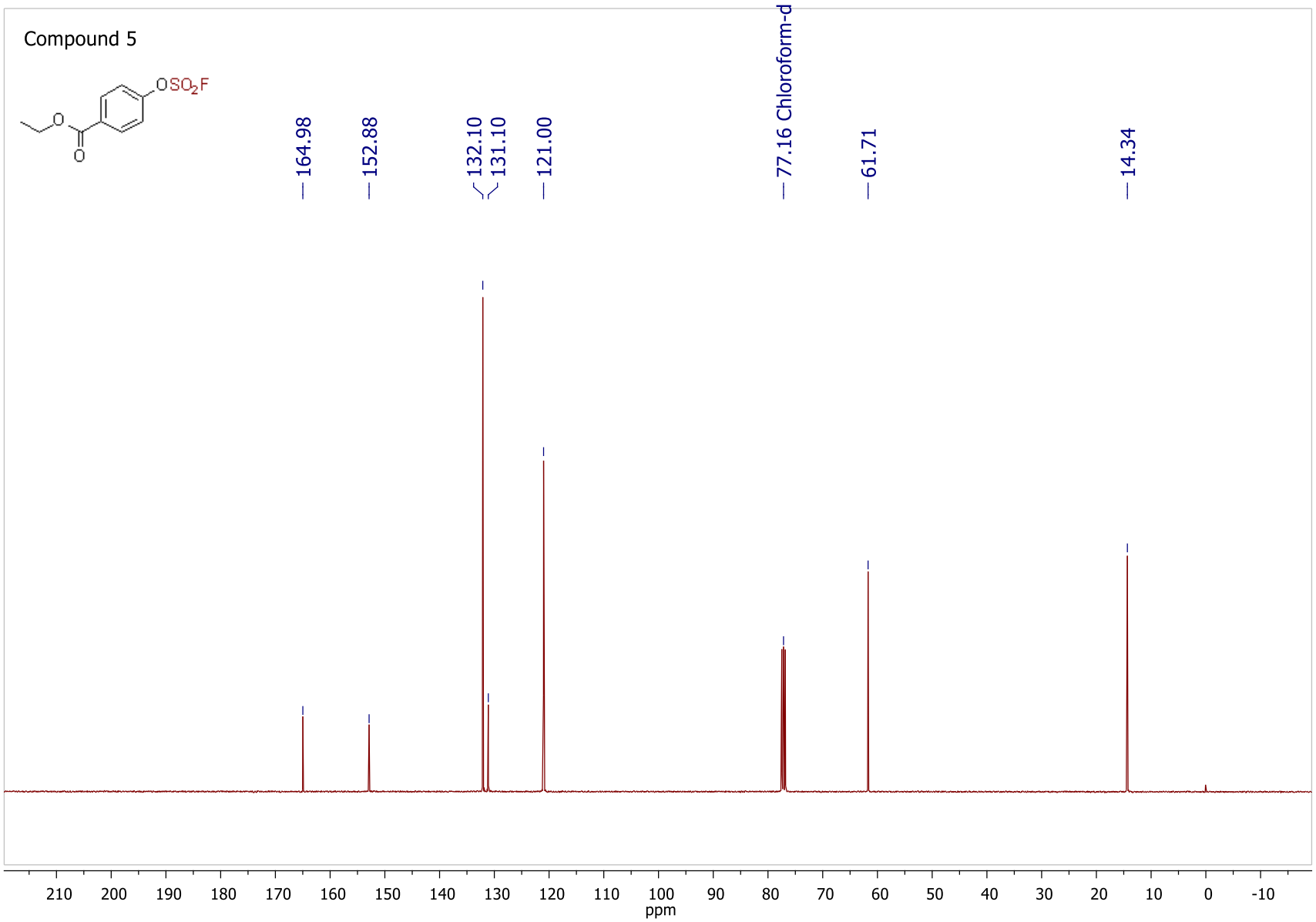

Compound 3
OSO2F
H2N
35.48
0.00
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm

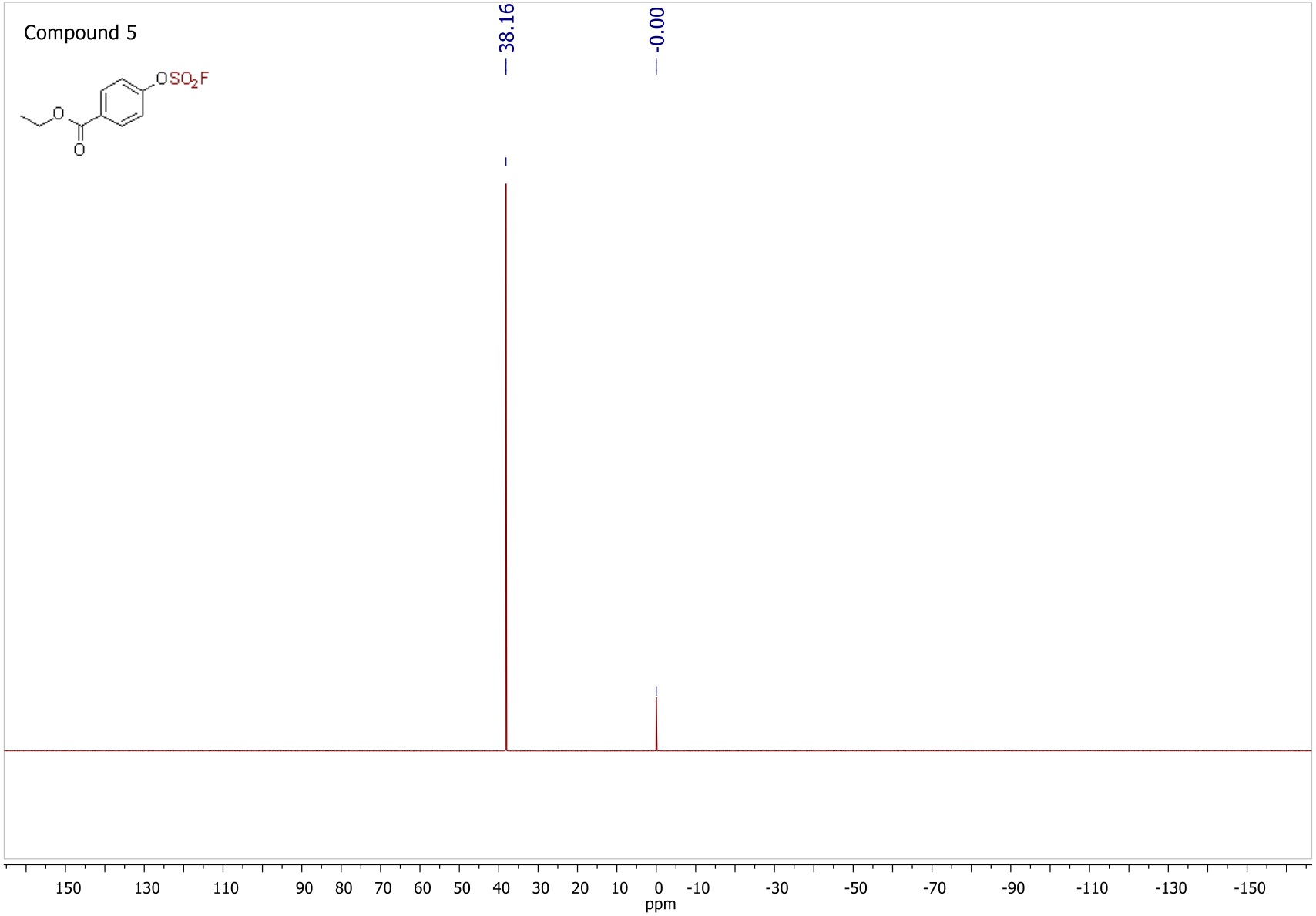

Compound 4
OSO2F
Cl
7.47
7.44
7.31
7.29
7.26 Chloroform-d
1.56
2.01
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

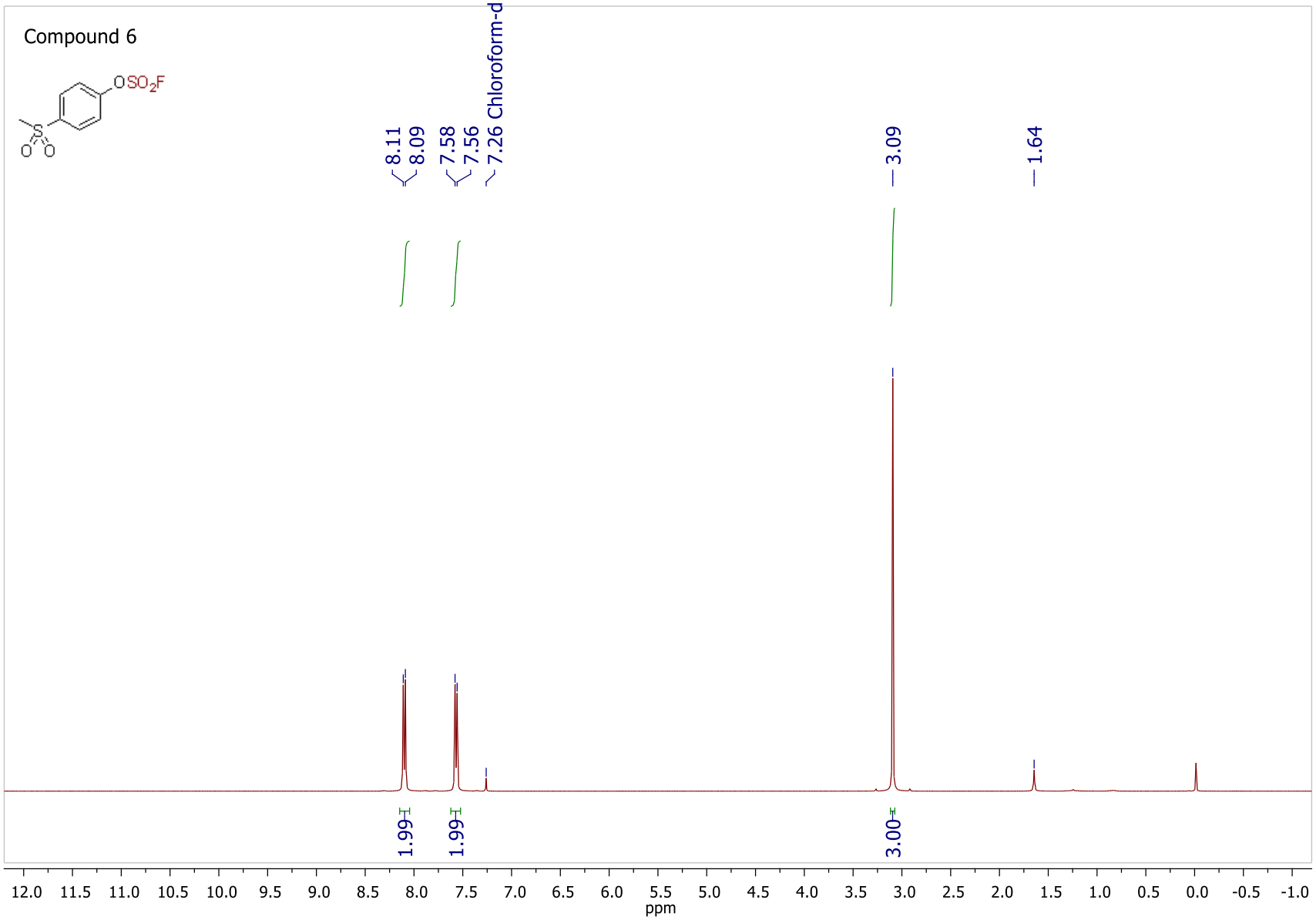

Compound 4
OSO2F
Cl
148.47
134.75
130.69
122.50
77.16 Chloroform-d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

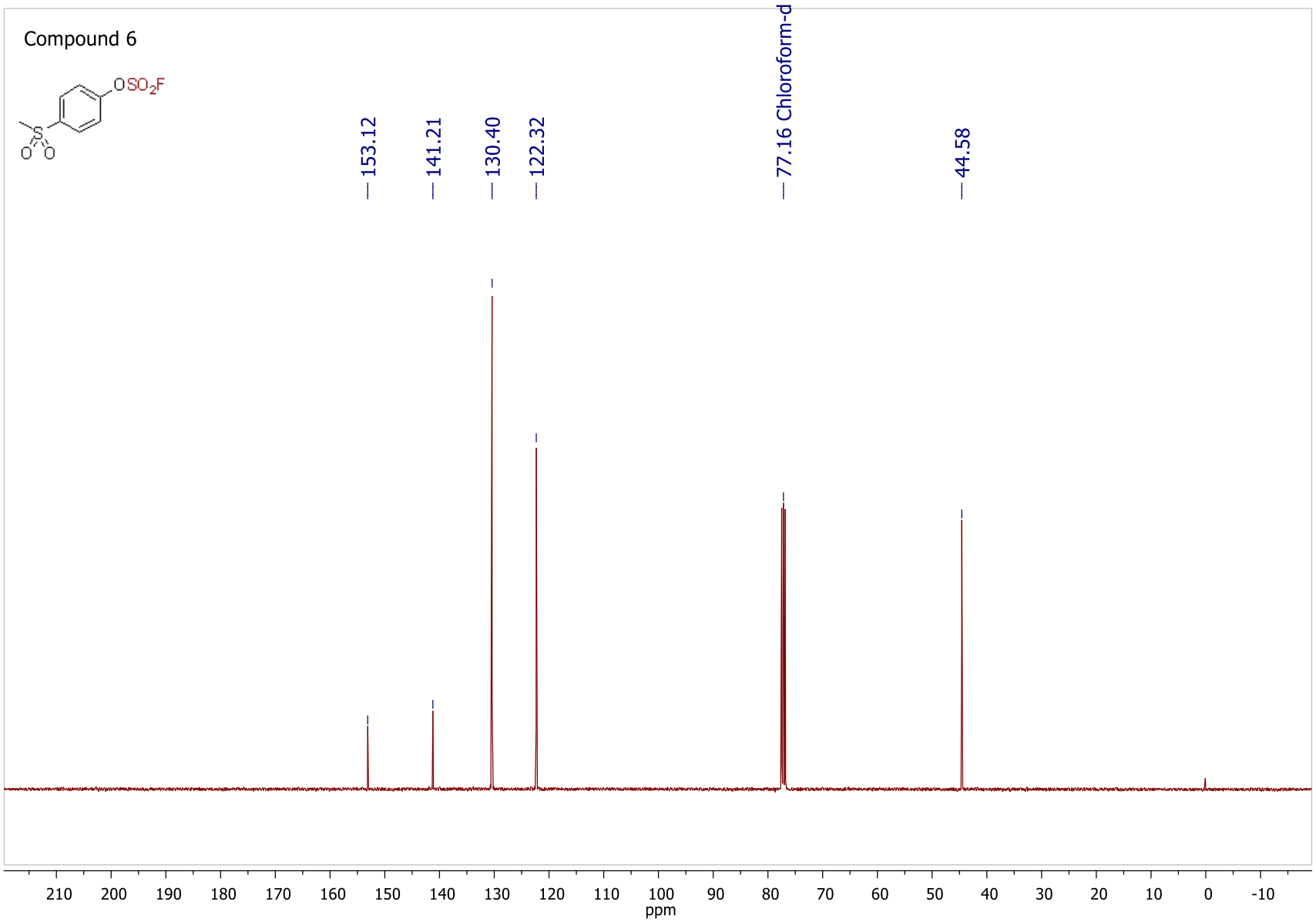

Compound 4
OSO2F
Cl
37.17
0.00
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm

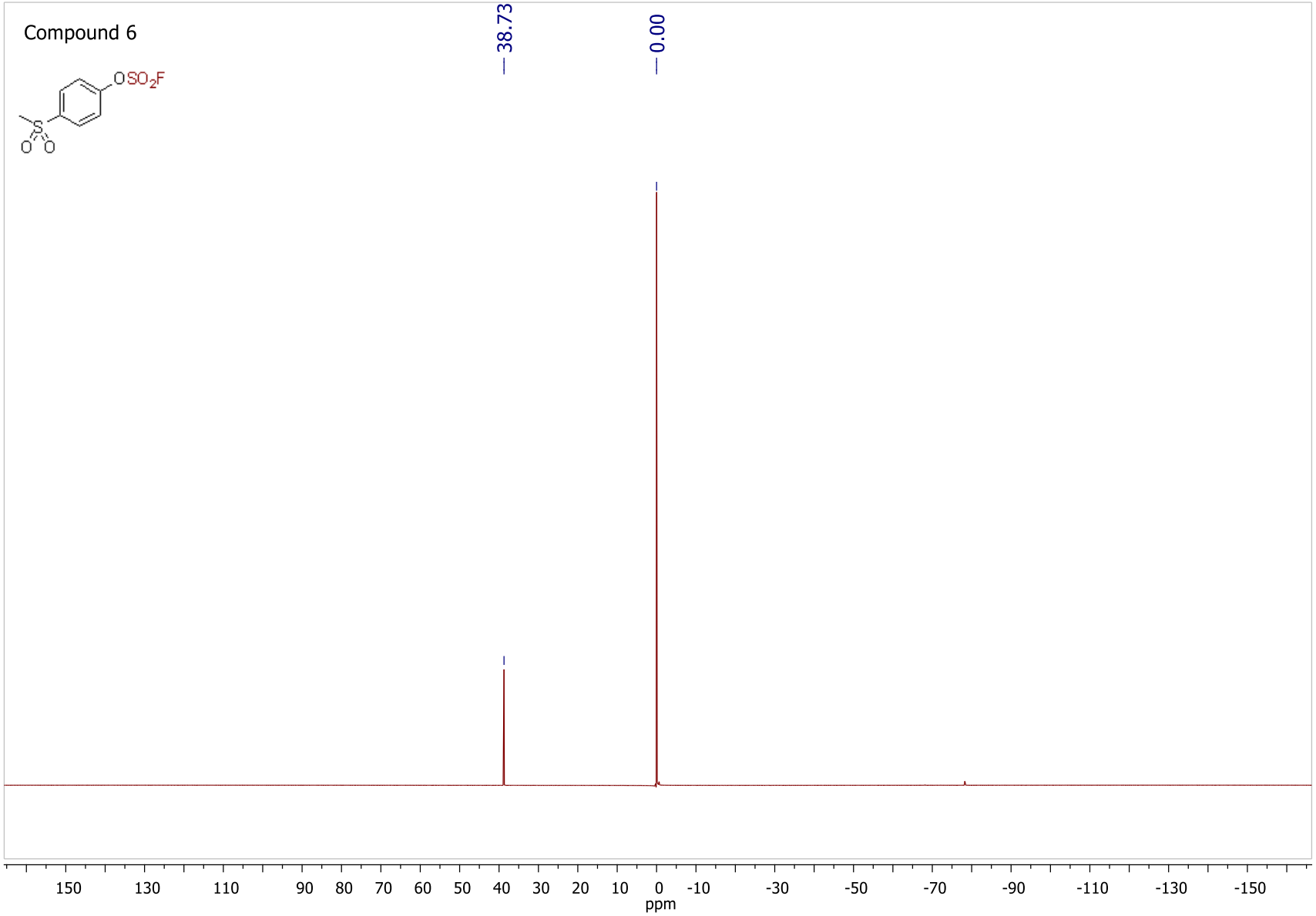

Compound 5
OSO2F
O
O
8.17
8.15
7.41
7.39
7.26 Chloroform-d
4.42
4.40
4.38
4.37
1.70
1.41
1.39
1.38
1.98
1.97
1.99
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

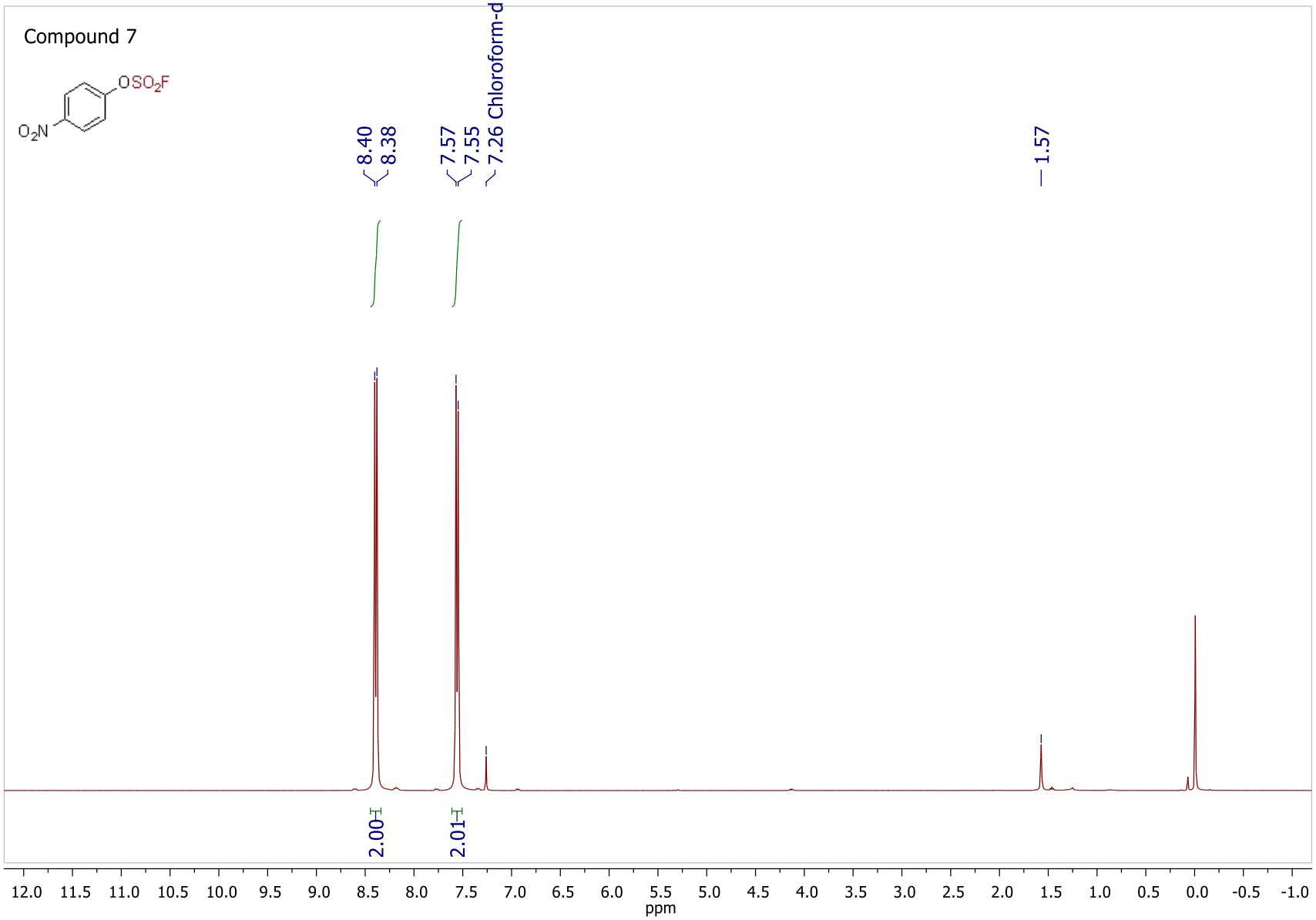

Compound 5
OSO2F
O
O
164.98
152.88
132.10
131.10
121.00
77.16 Chloroform-d
61.71
14.34
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

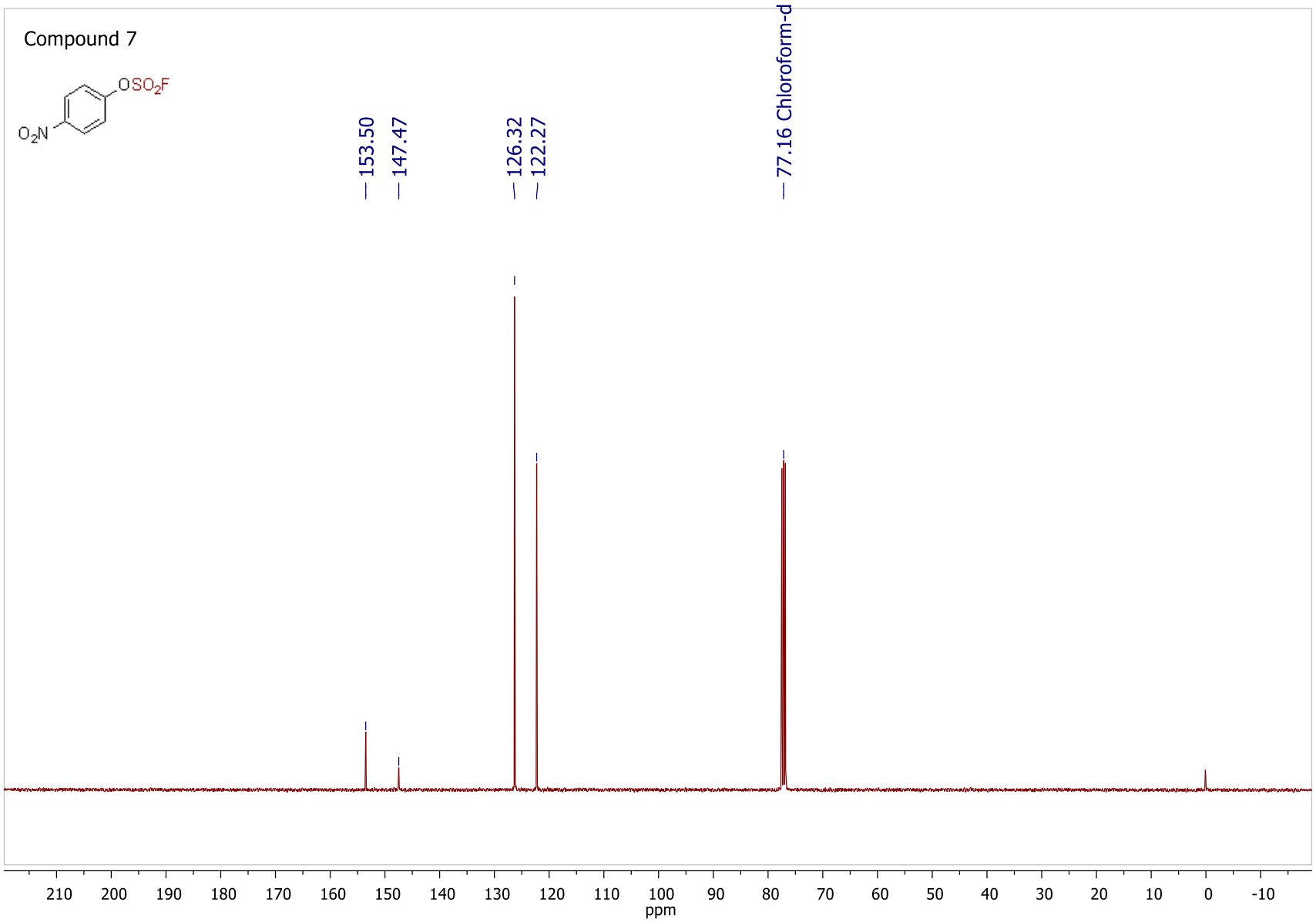

Compound 5
OSO2F
O
O
38.16
-0.00
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm

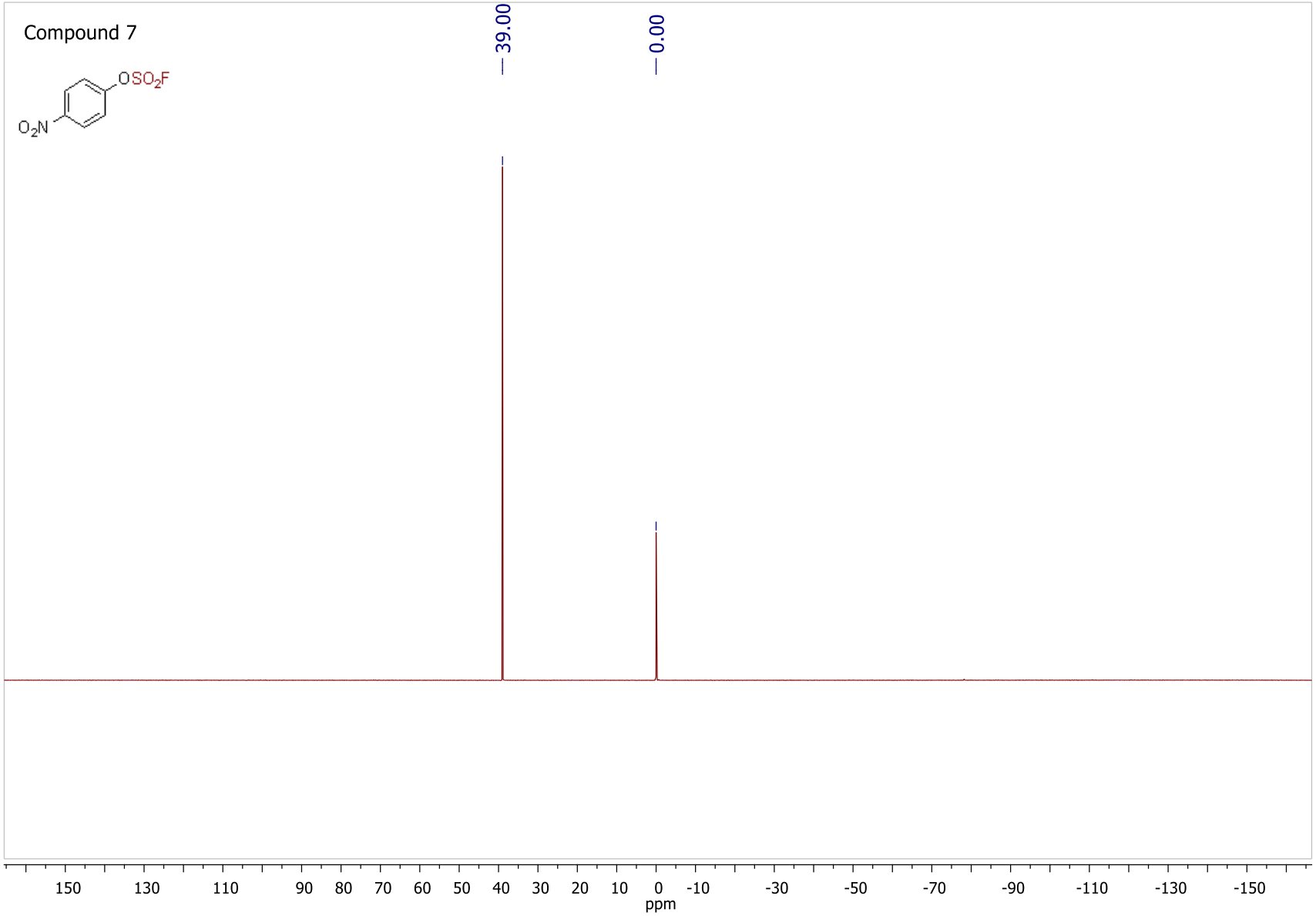

Compound 6
OSO2F
8.11
8.09
7.58
7.56
7.26 Chloroform-d
3.09
1.64
1.99
1.99
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

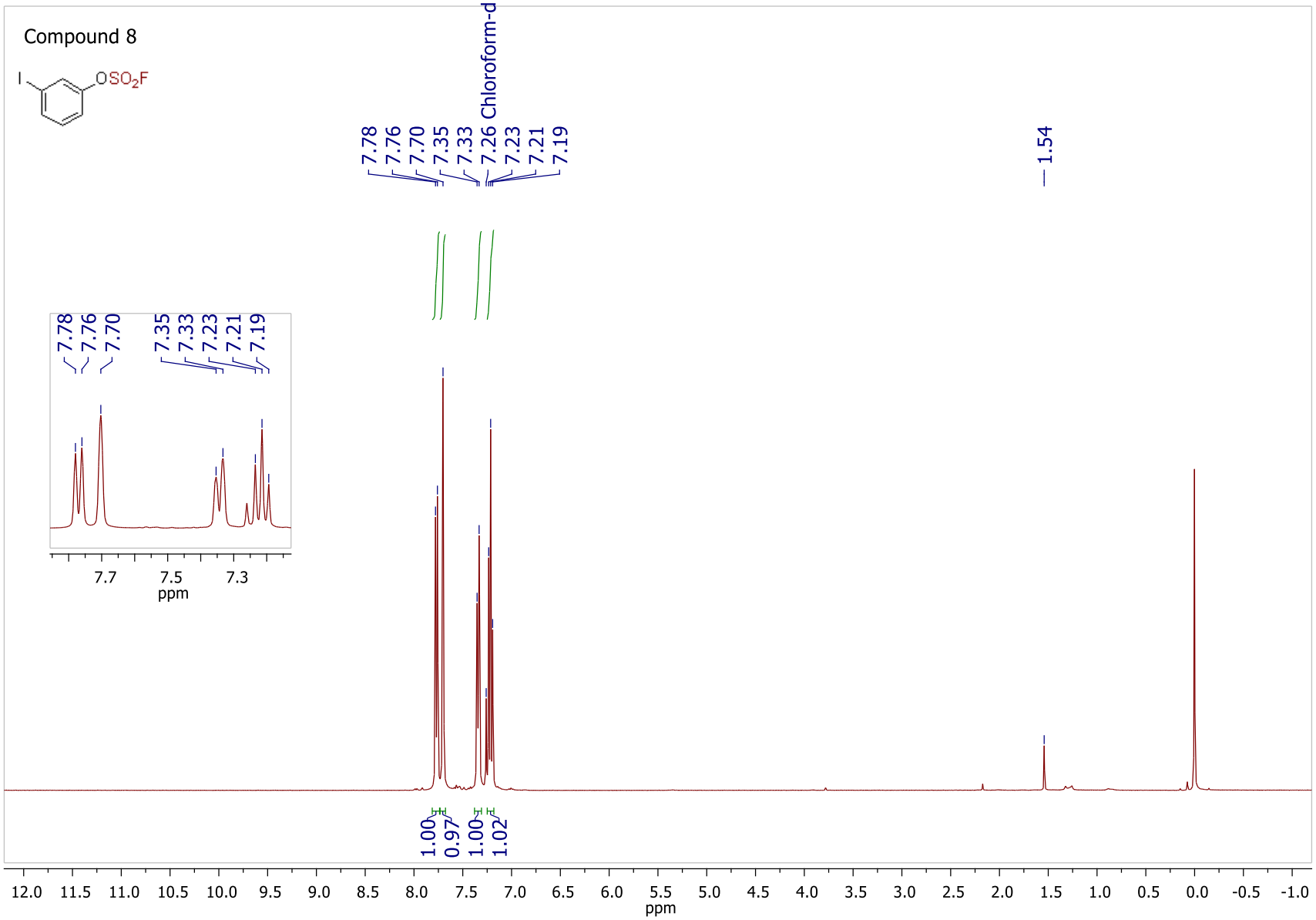

Compound 6
OSO2F
153.12
141.21
130.40
122.32
77.16 Chloroform-d
44.58
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

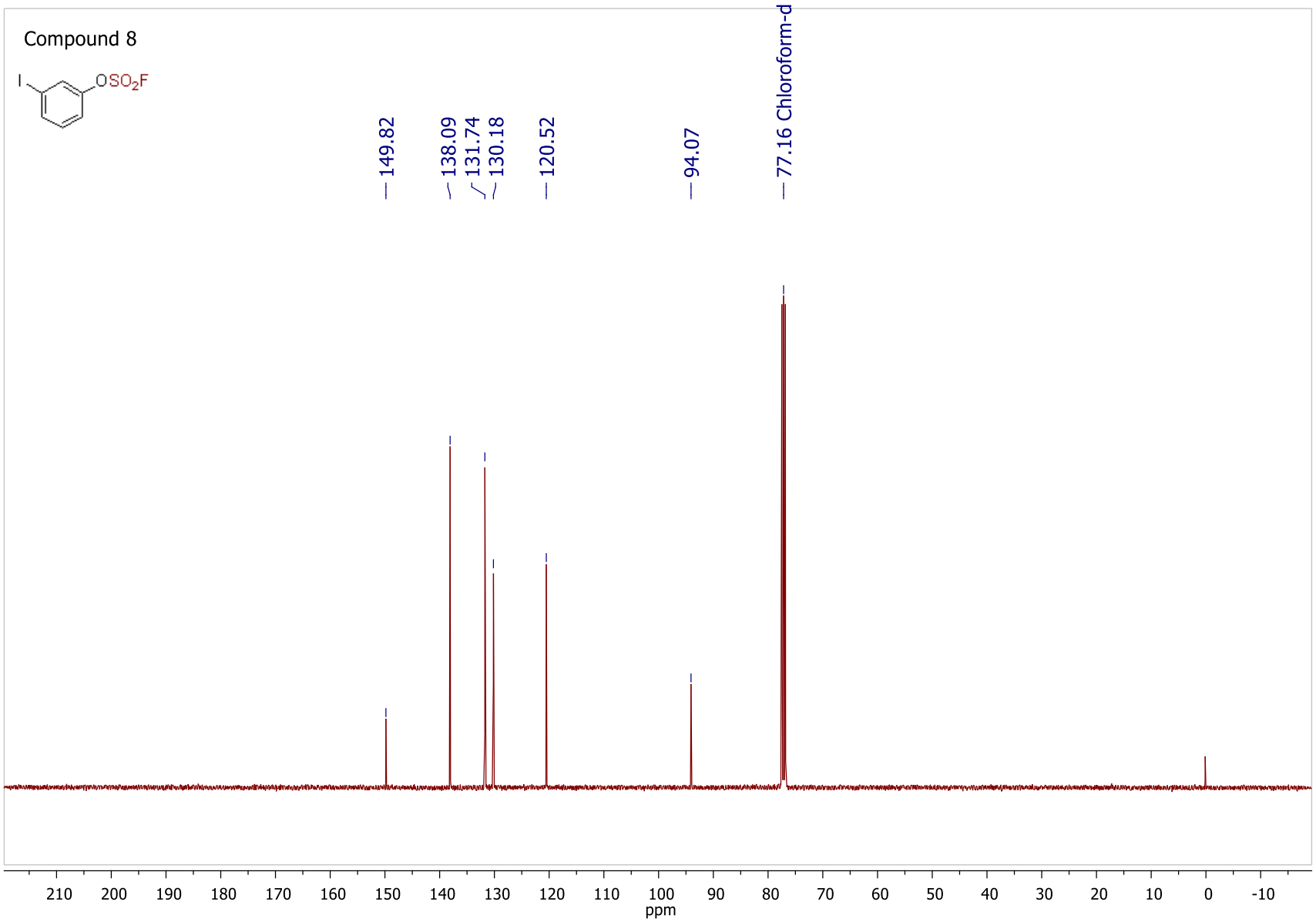

Compound 6
OSO2F
38.73
0.00
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm

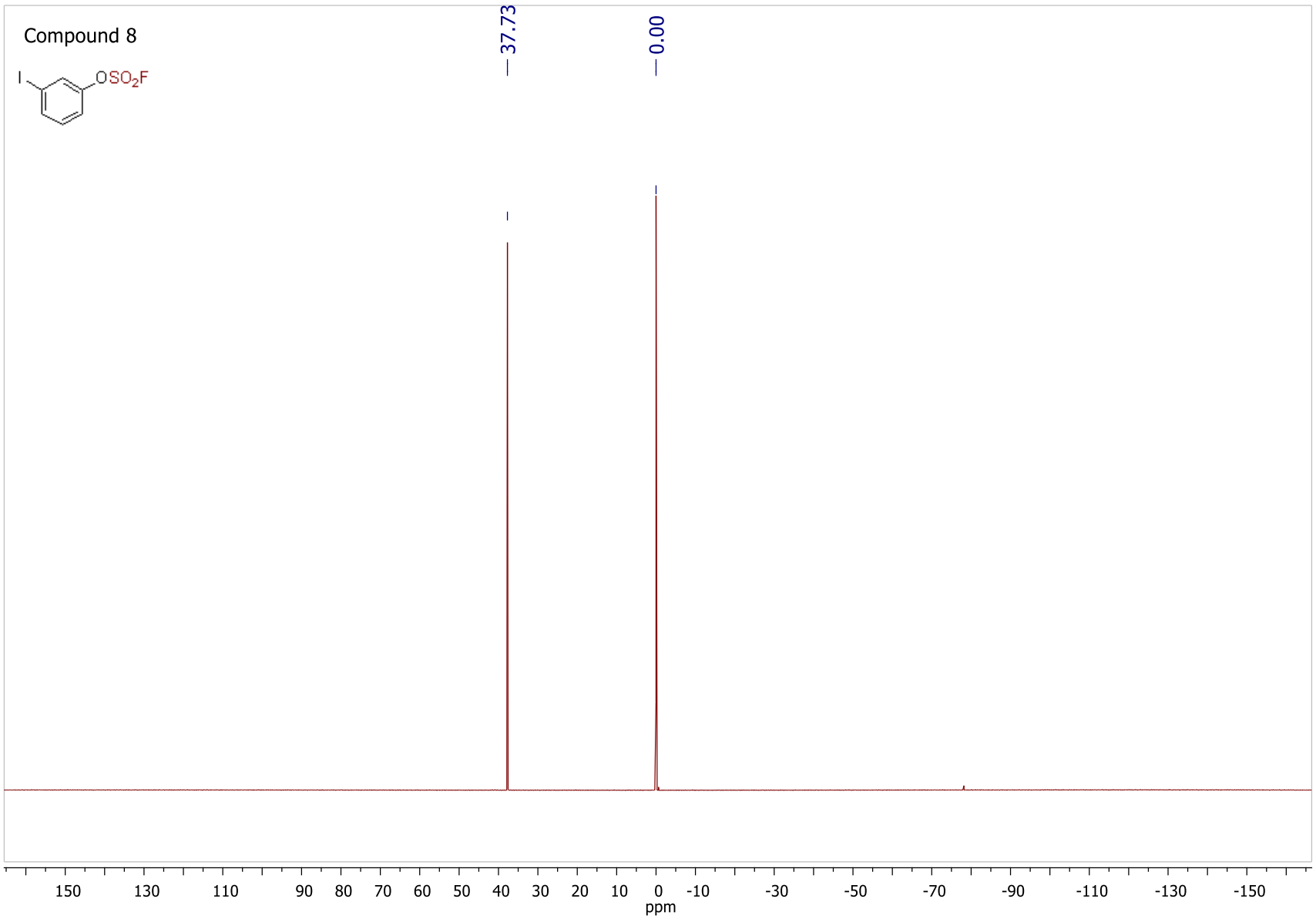

Compound 7
OSO2F
O2N
8.40
8.38
7.57
7.55
7.26 Chloroform-d
1.57
2.00
2.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

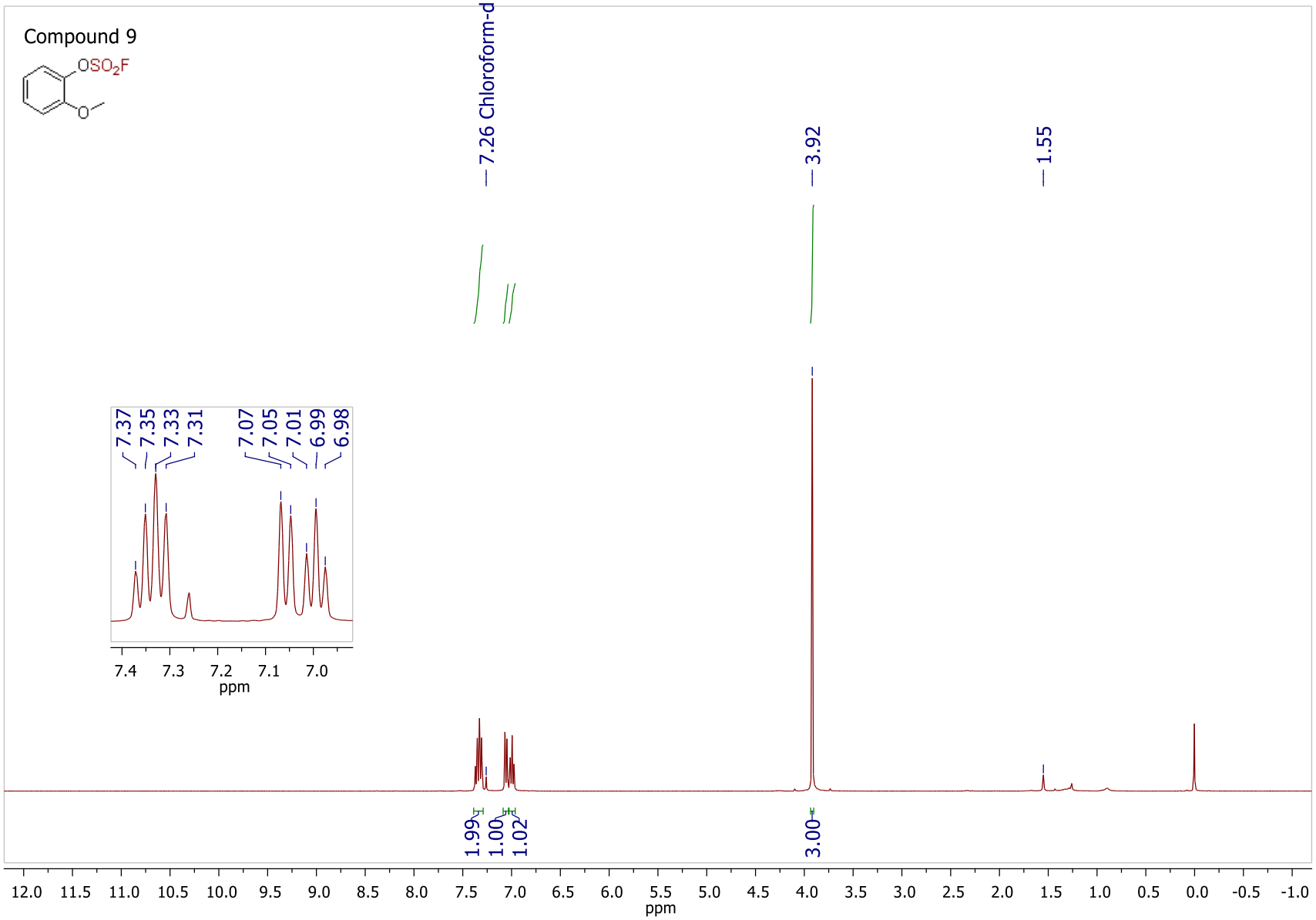

Compound 7
OSO2F
O2N
153.50
147.47
126.32
122.27
77.16 Chloroform-d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

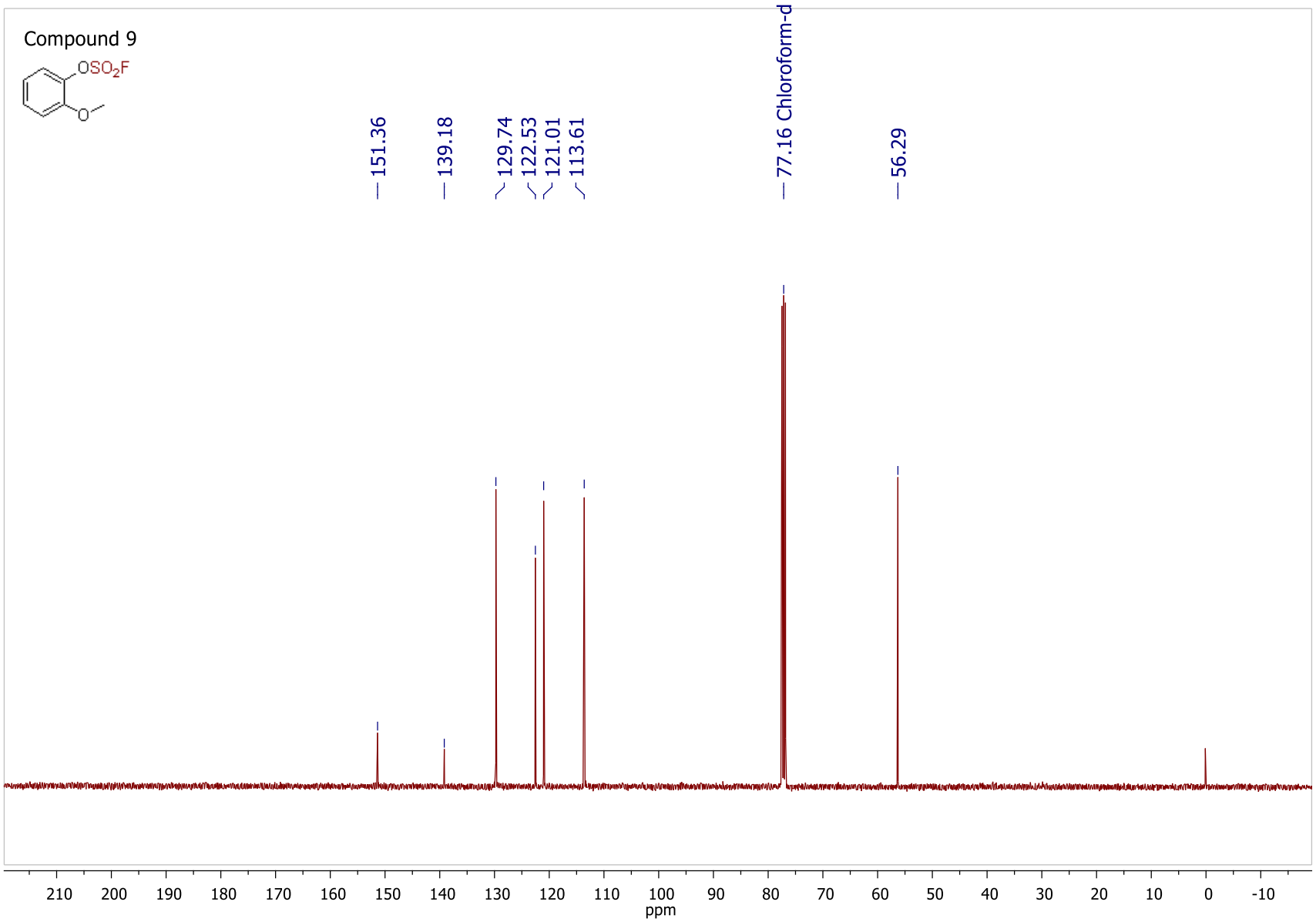

Compound 7
OSO2F
O2N
39.00
0.00
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm

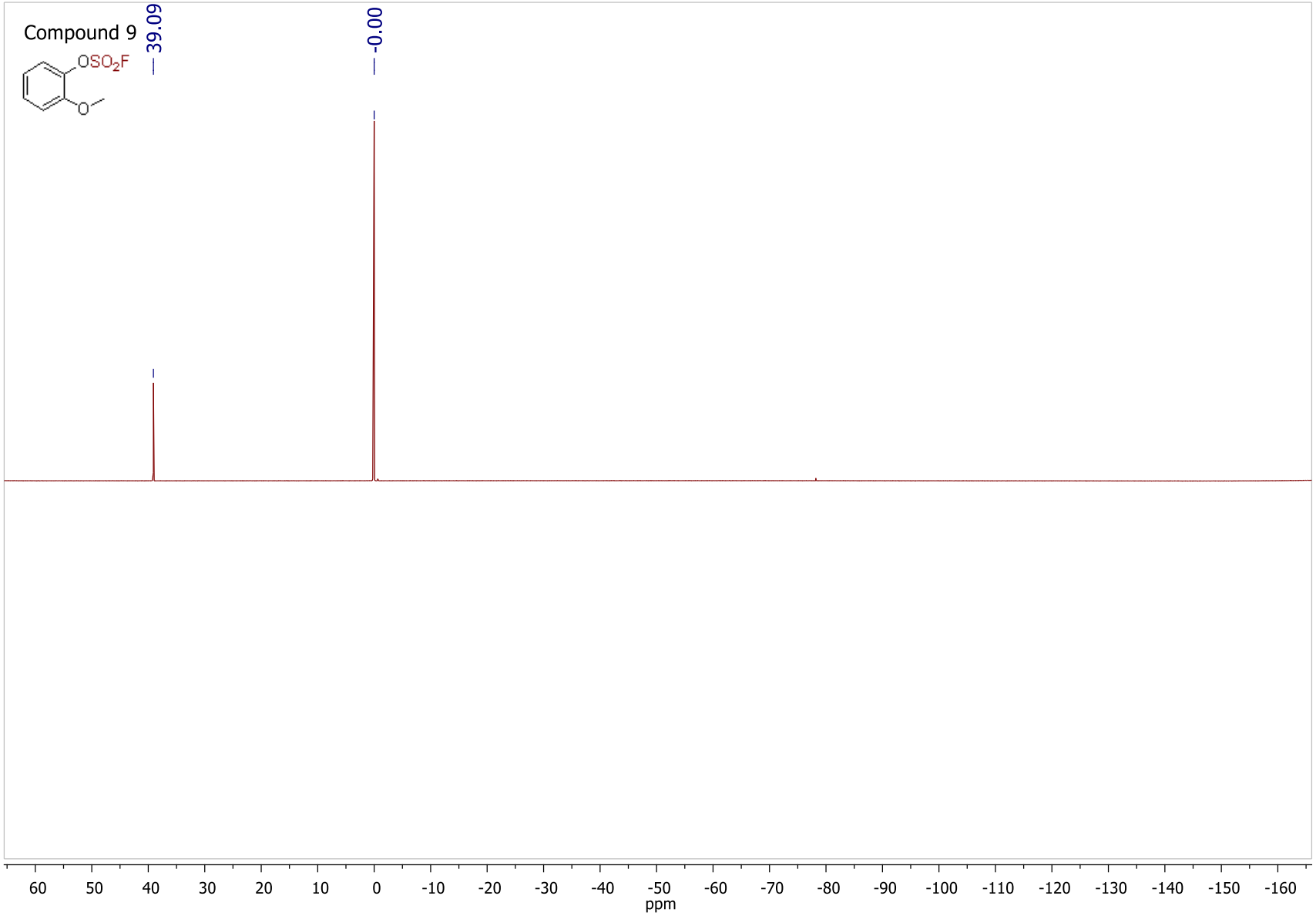

Compound 8
I
OSO2F
7.78
7.76
7.70
7.35
7.33
7.26 Chloroform-d
7.23
7.21
7.19
1.54
7.78
7.76
7.70
7.35
7.33
7.23
7.21
7.19
7.7
7.5
7.3
ppm
1.00
0.97
1.00
1.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

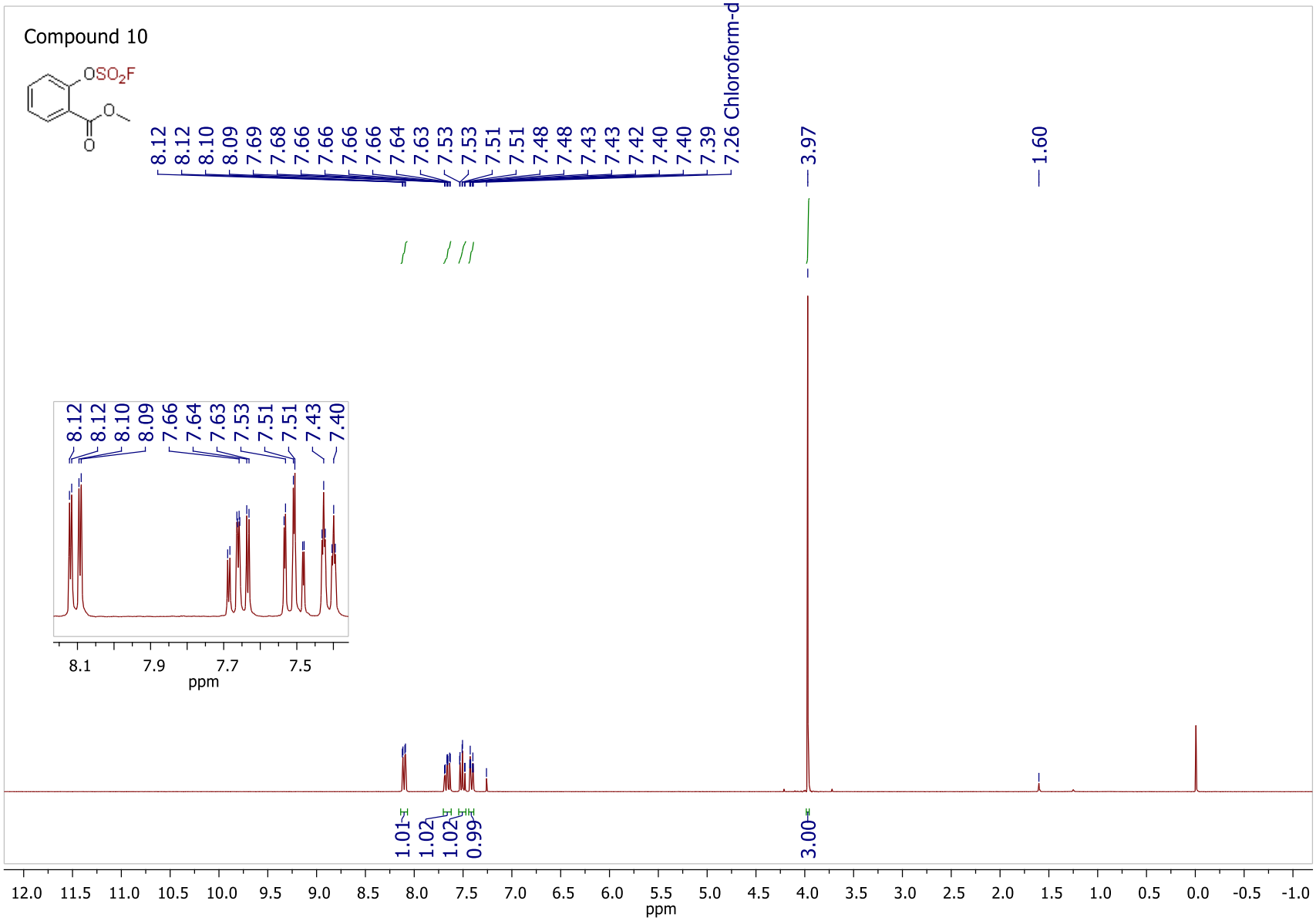

Compound 8
I
OSO2F
149.82
138.09
131.74
130.18
120.52
94.07
77.16 Chloroform-d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

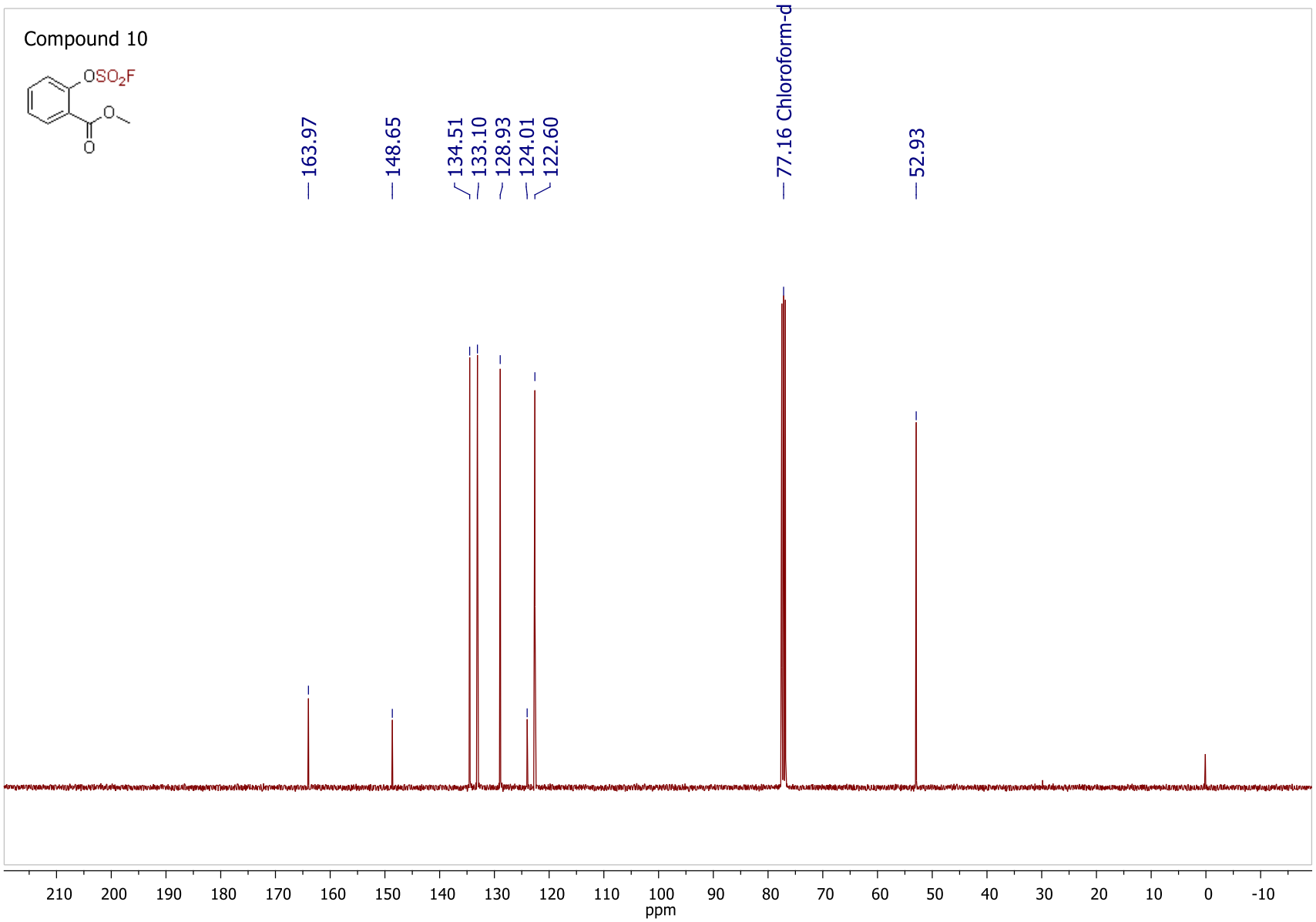

Compound 8
I
OSO2F
37.73
0.00
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm

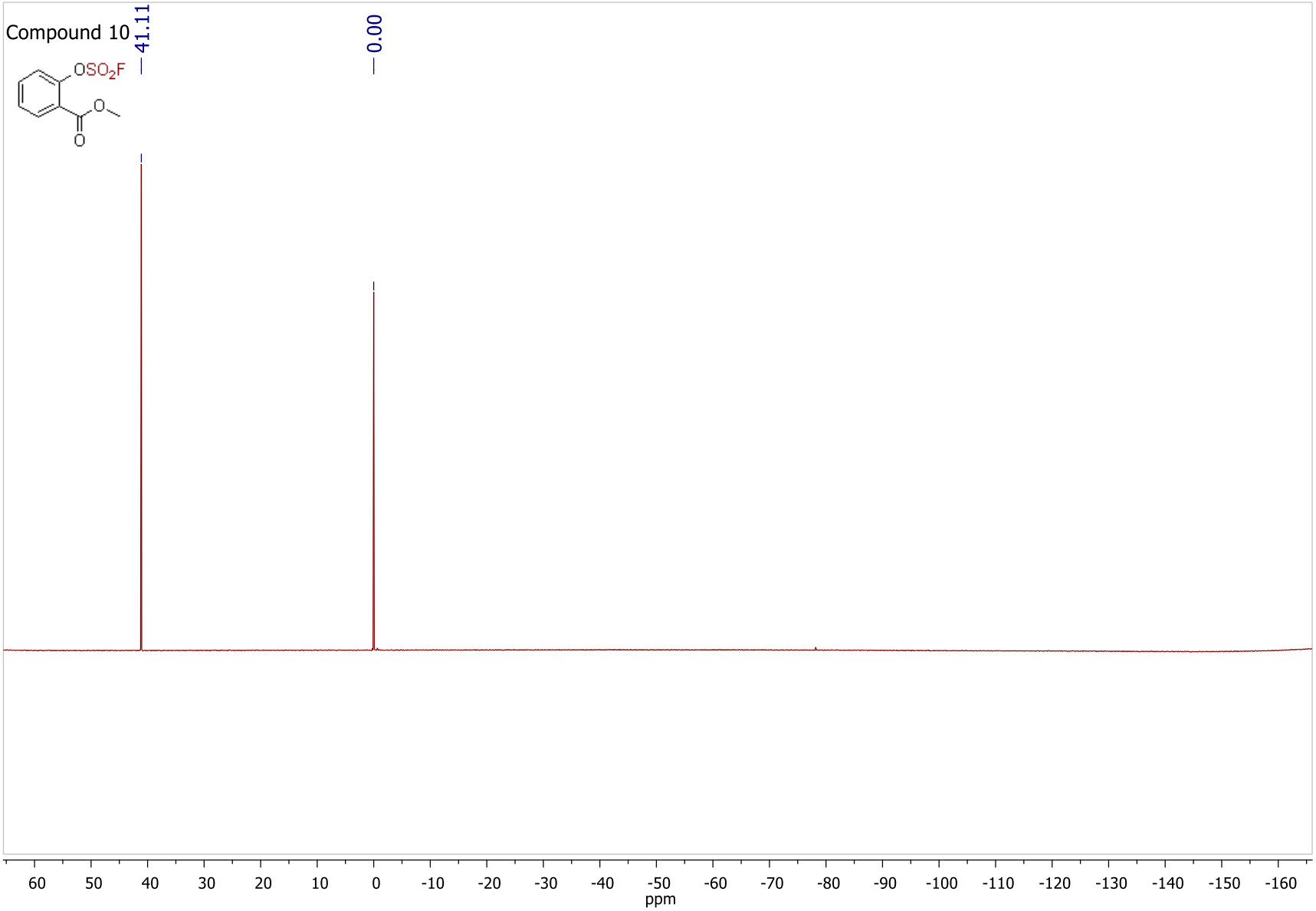

Compound 9
OSO2F
O
7.26 Chloroform-d
3.92
1.55
7.37
7.35
7.33
7.31
7.07
7.05
7.01
6.99
6.98
7.4
7.3
7.2
7.1
7.0
ppm
1.99
1.00
1.02
3.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

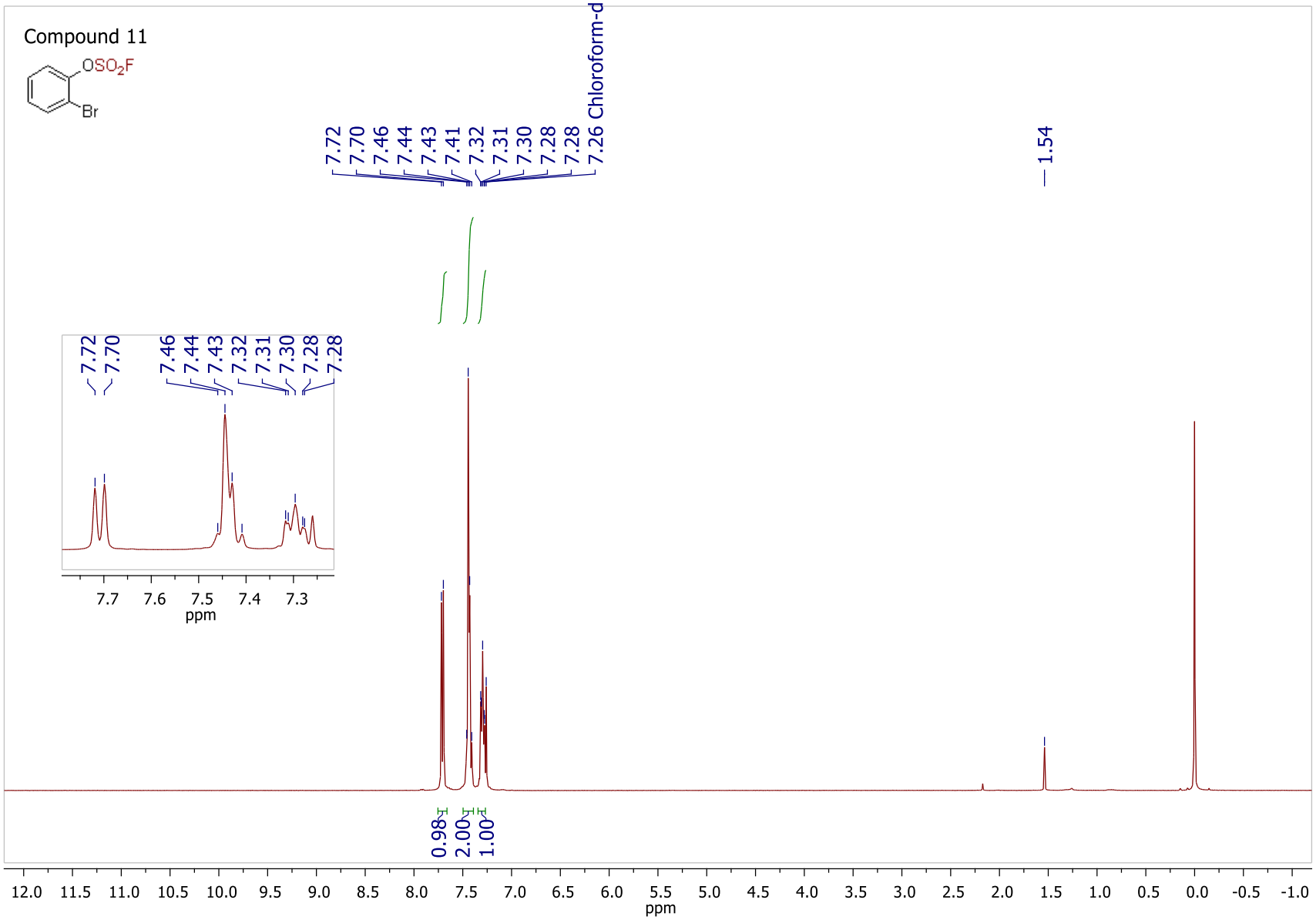

Compound 9
OSO2F
O
151.36
139.18
129.74
122.53
121.01
113.61
77.16 Chloroform-d
56.29
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

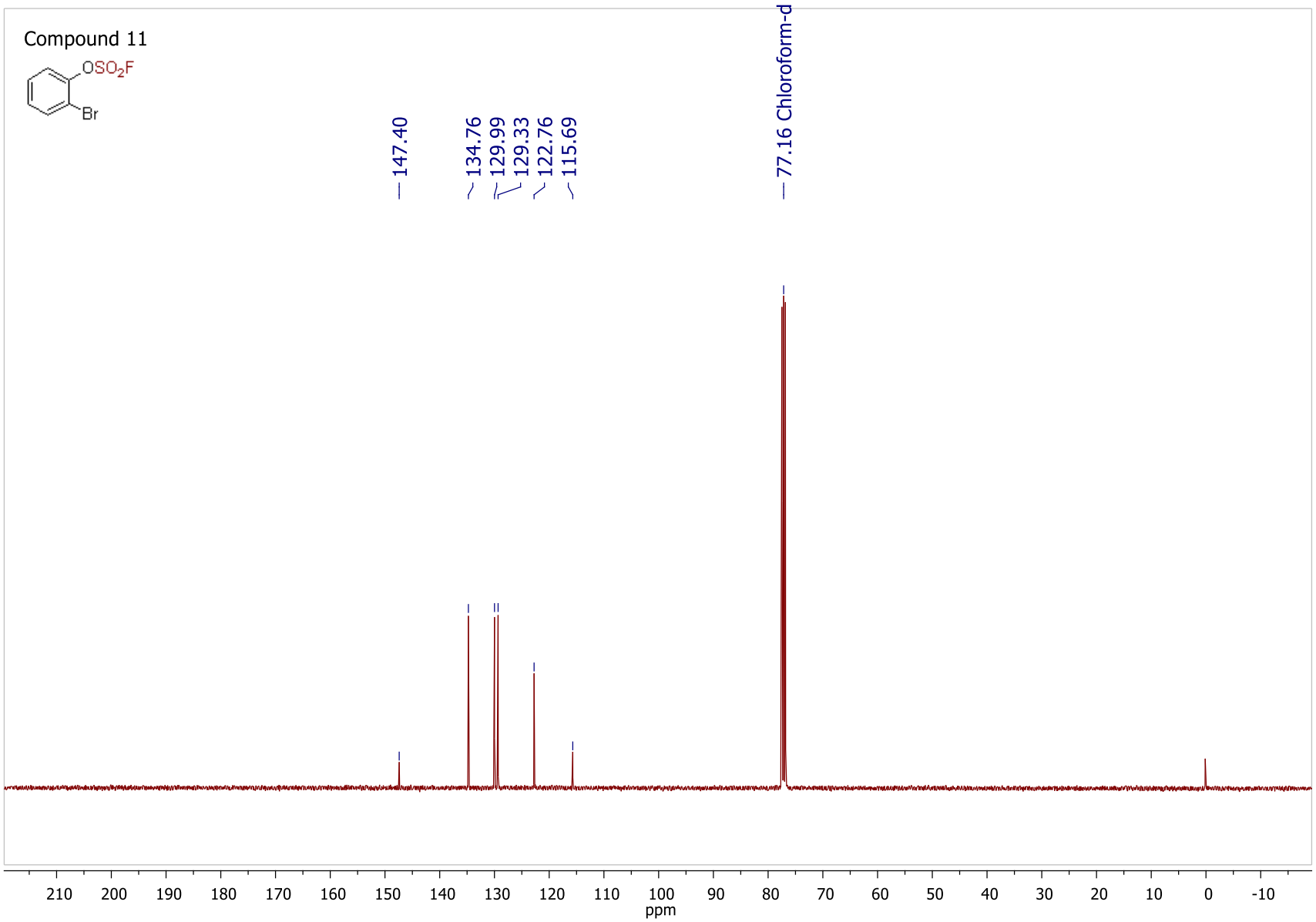

Compound 9
OSO2F
O
39.09
-0.00
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
ppm

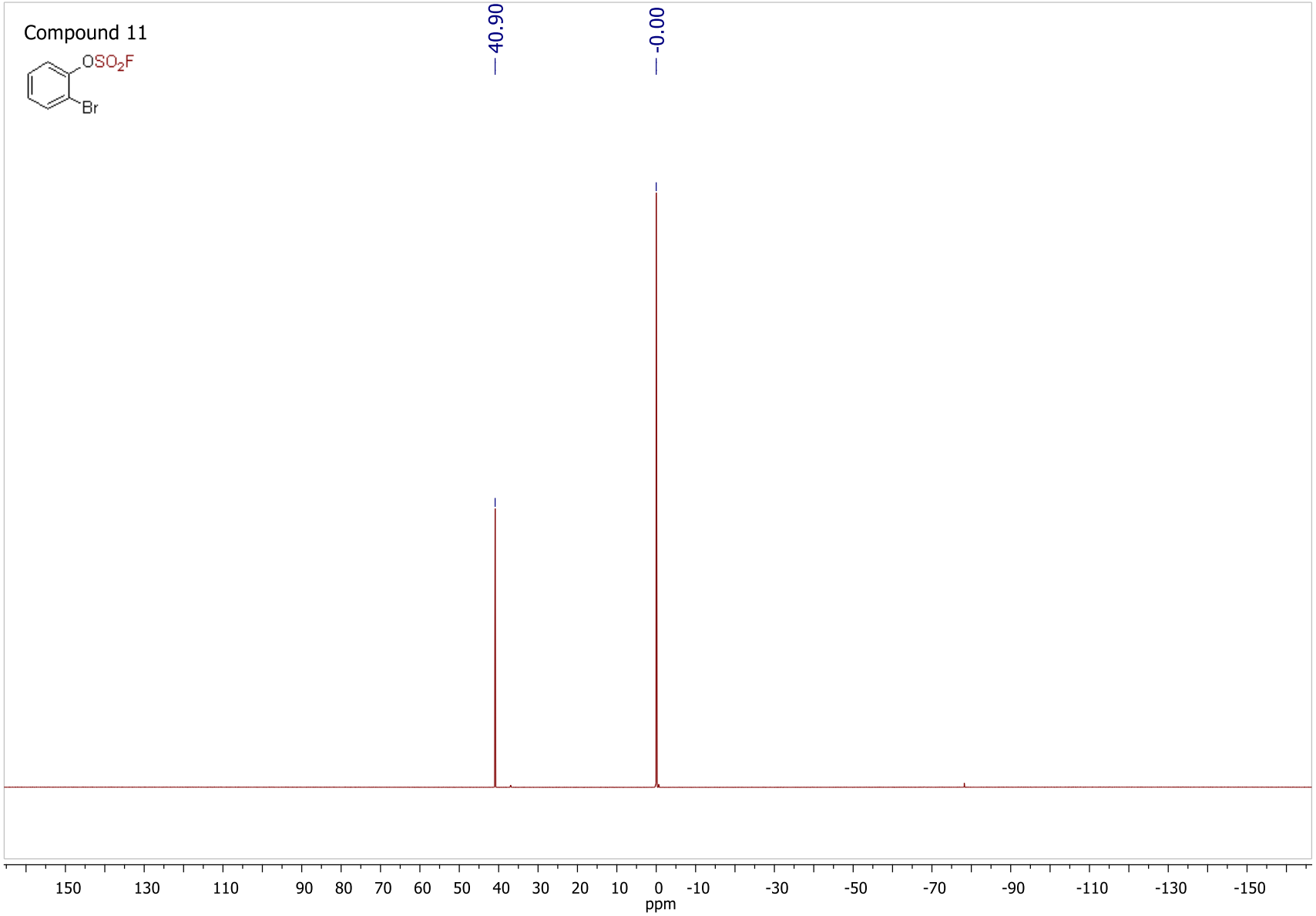

Compound 10
OSO2F
O
O
8.12
8.12
8.10
8.09
7.69
7.68
7.66
7.66
7.66
7.66
7.64
7.63
7.53
7.53
7.51
7.51
7.48
7.48
7.43
7.43
7.42
7.40
7.40
7.39
7.26 Chloroform-d
3.97
1.60
8.12
8.12
8.10
8.09
7.66
7.64
7.63
7.53
7.51
7.51
7.43
7.40
8.1
7.9
7.7
7.5
ppm
1.01
1.02
1.02
0.99
3.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

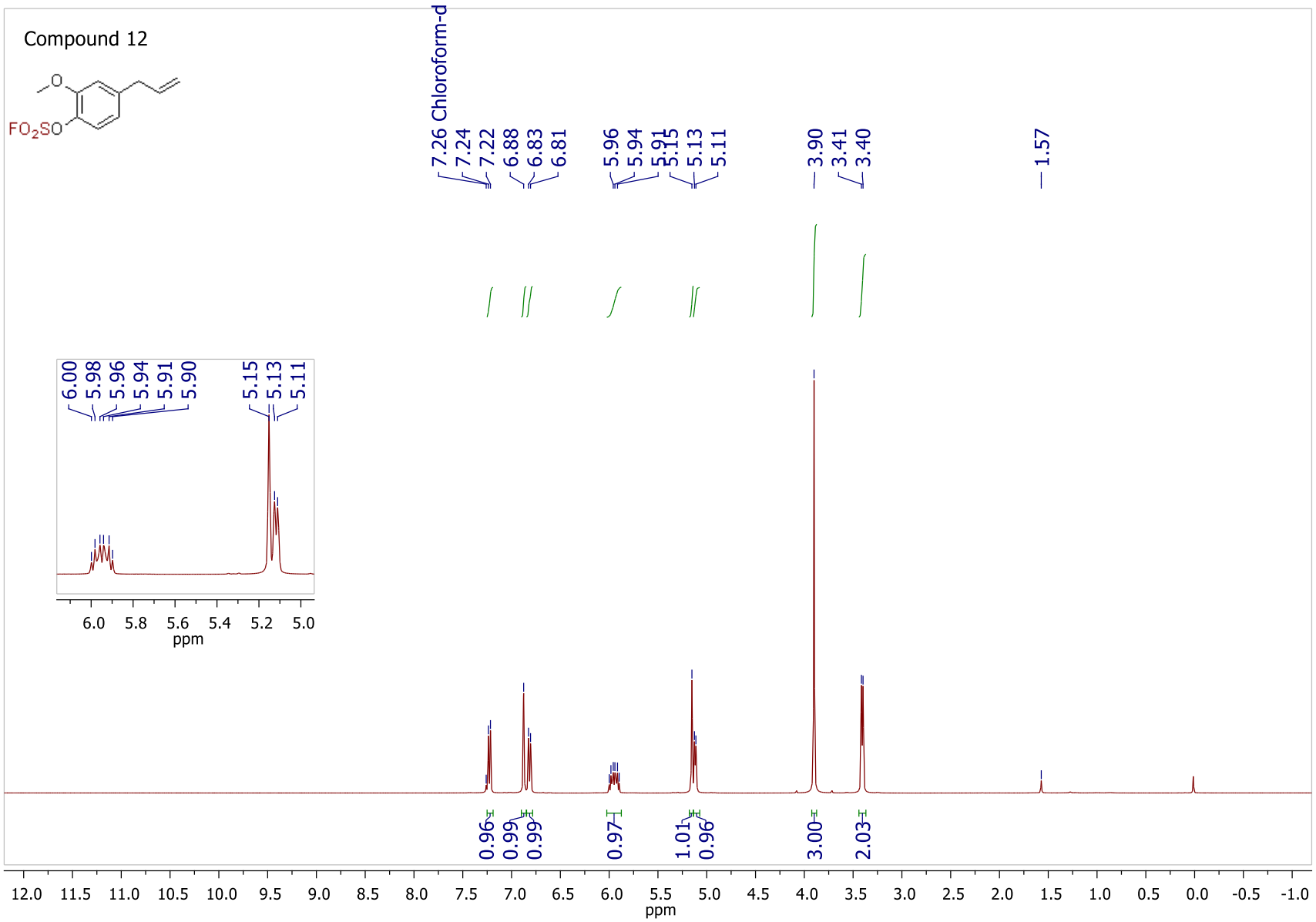

Compound 10
OSO2F
O
O
163.97
148.65
134.51
133.10
128.93
124.01
122.60
77.16 Chloroform-d
52.93
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

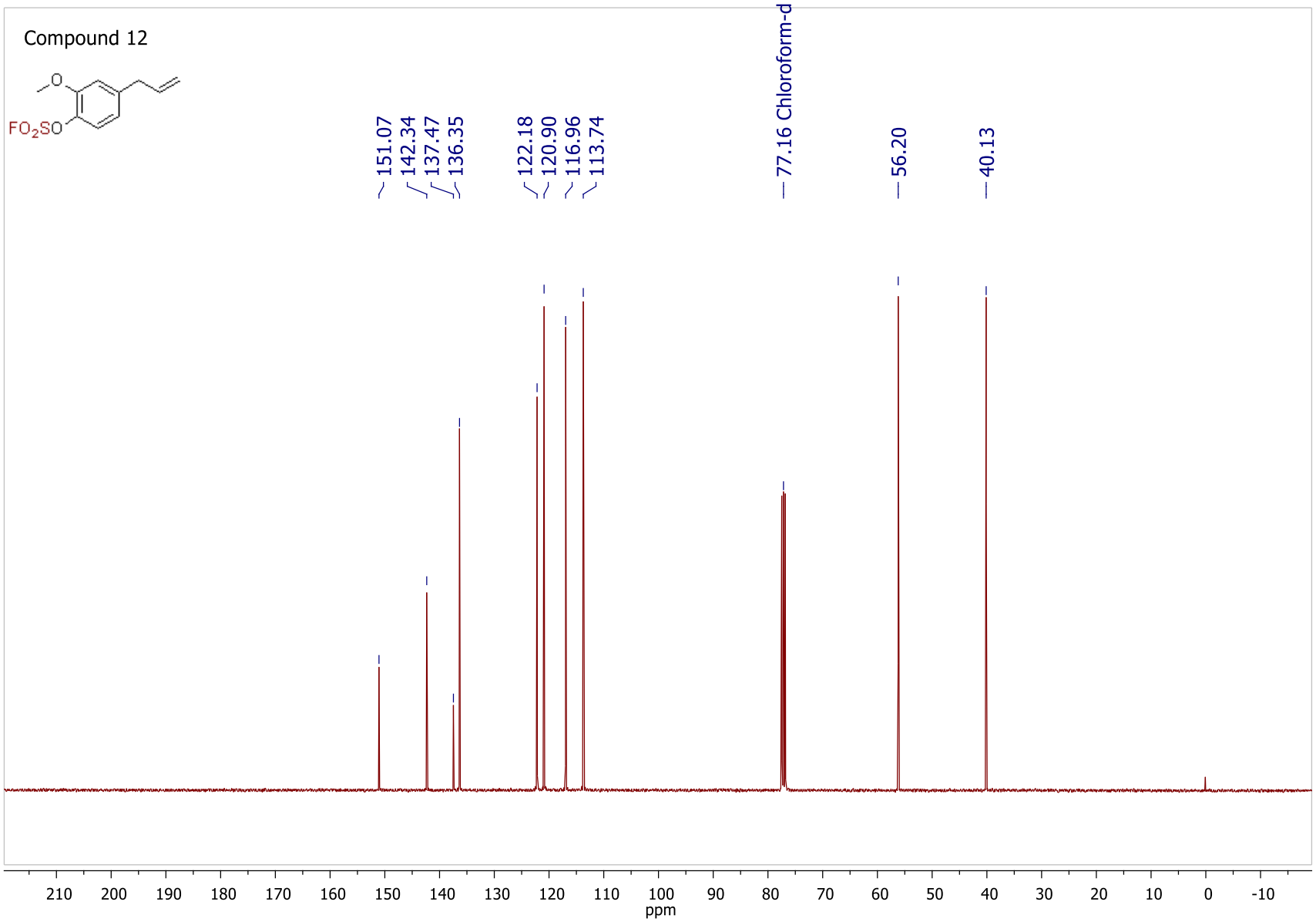

Compound 10
OSO2F
O
O
41.11
0.00
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
ppm

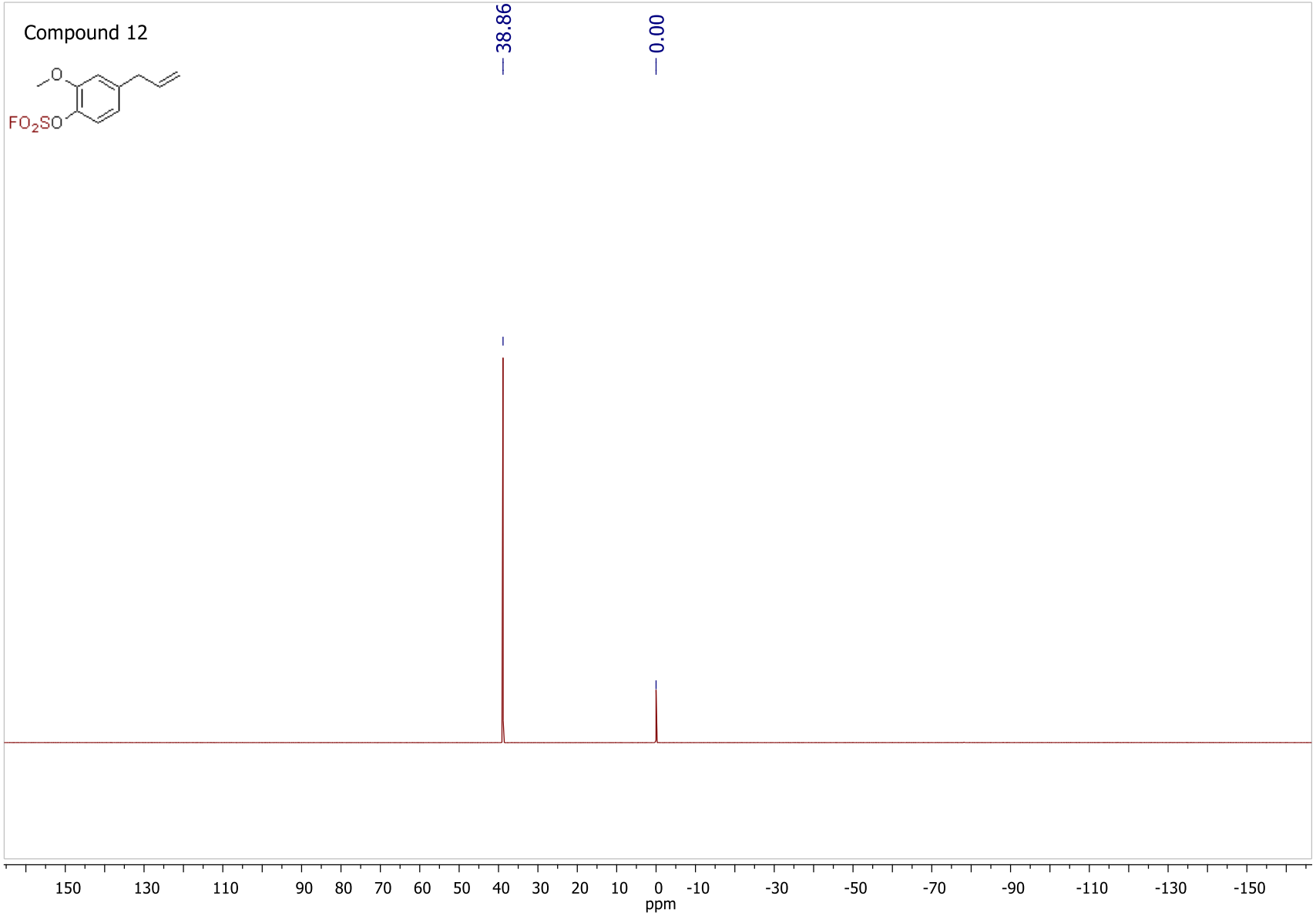

Compound 11
OSO2F
Br
7.72
7.70
7.46
7.44
7.43
7.41
7.32
7.31
7.30
7.28
7.28
7.26 Chloroform-d
1.54
0.98
2.00
1.00
7.7
7.6
7.5
7.4
7.3
ppm
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

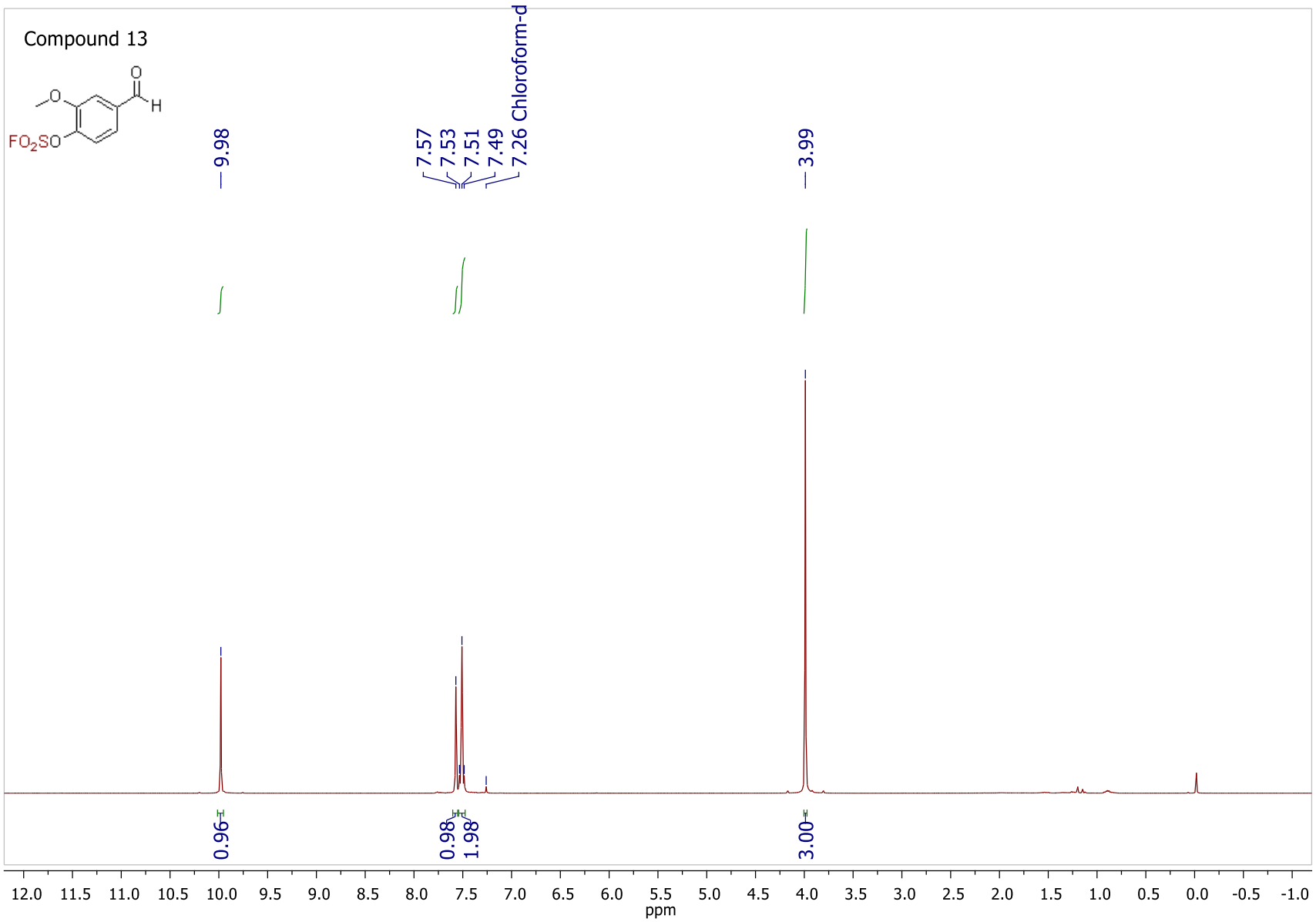

Compound 11
OSO2F
Br
147.40
134.76
129.99
129.33
122.76
115.69
77.16 Chloroform-d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

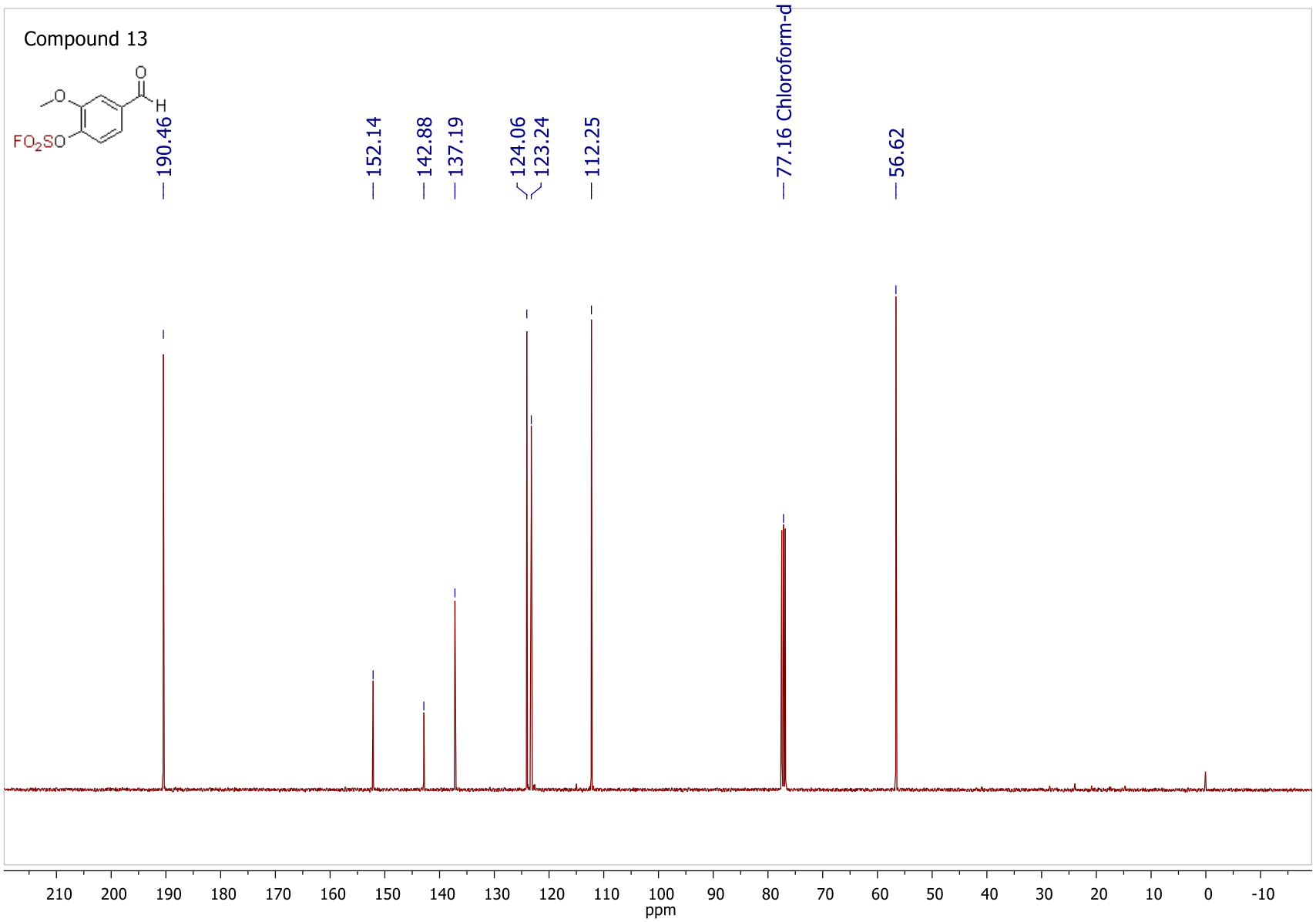

Compound 11
OSO2F
Br
40.90
-0.00
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm

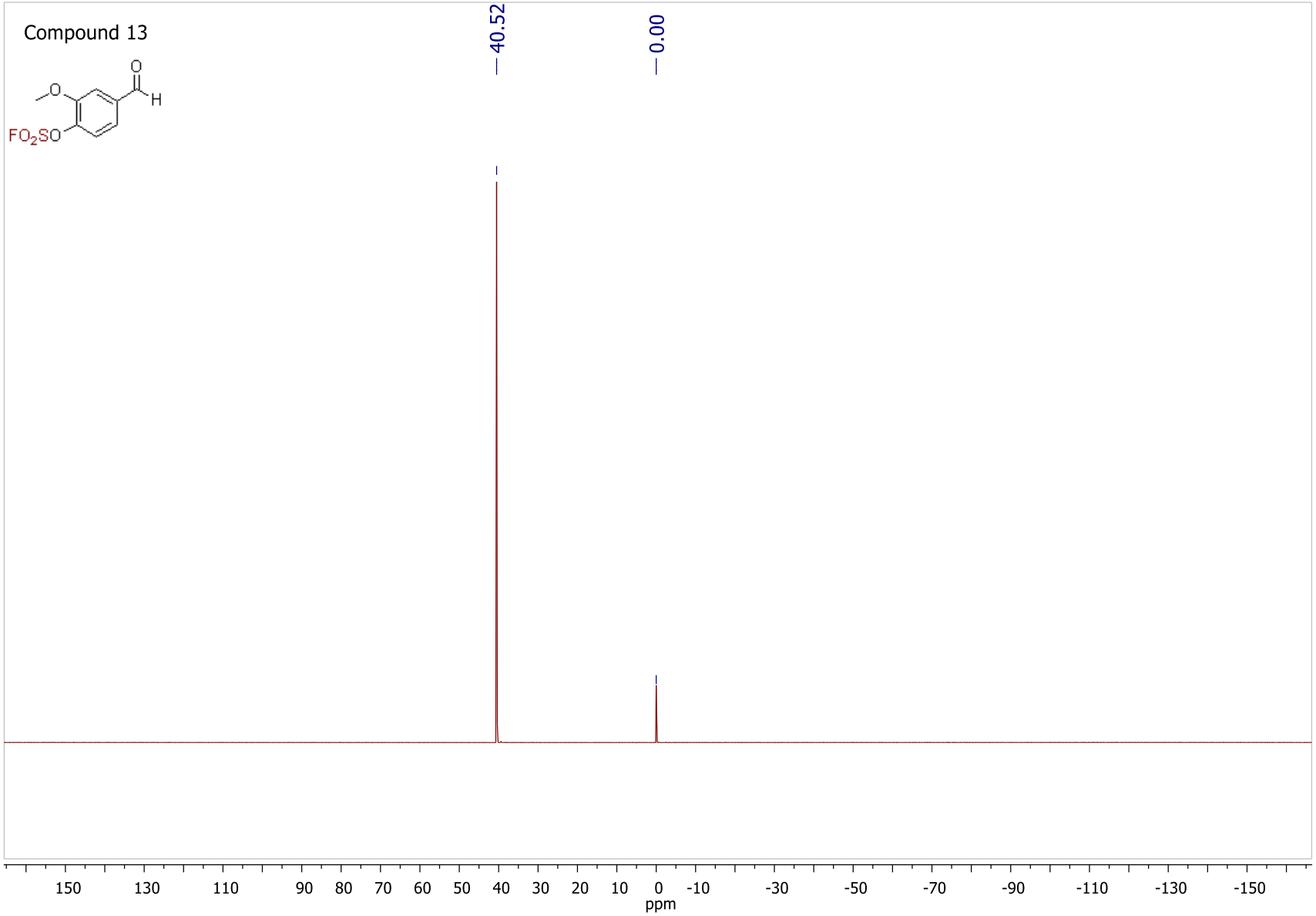

Compound 12
FO2SO
Chloroform-d
7.26
7.24
7.22
6.88
6.83
6.81
5.96
5.94
5.91
5.15
5.13
5.11
3.90
3.41
3.40
1.57
6.00
5.98
5.96
5.94
5.91
5.90
5.15
5.13
5.11
6.0 5.8 5.6 5.4 5.2 5.0
ppm
0.96
0.99
0.99
0.97
1.01
0.96
3.00
2.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

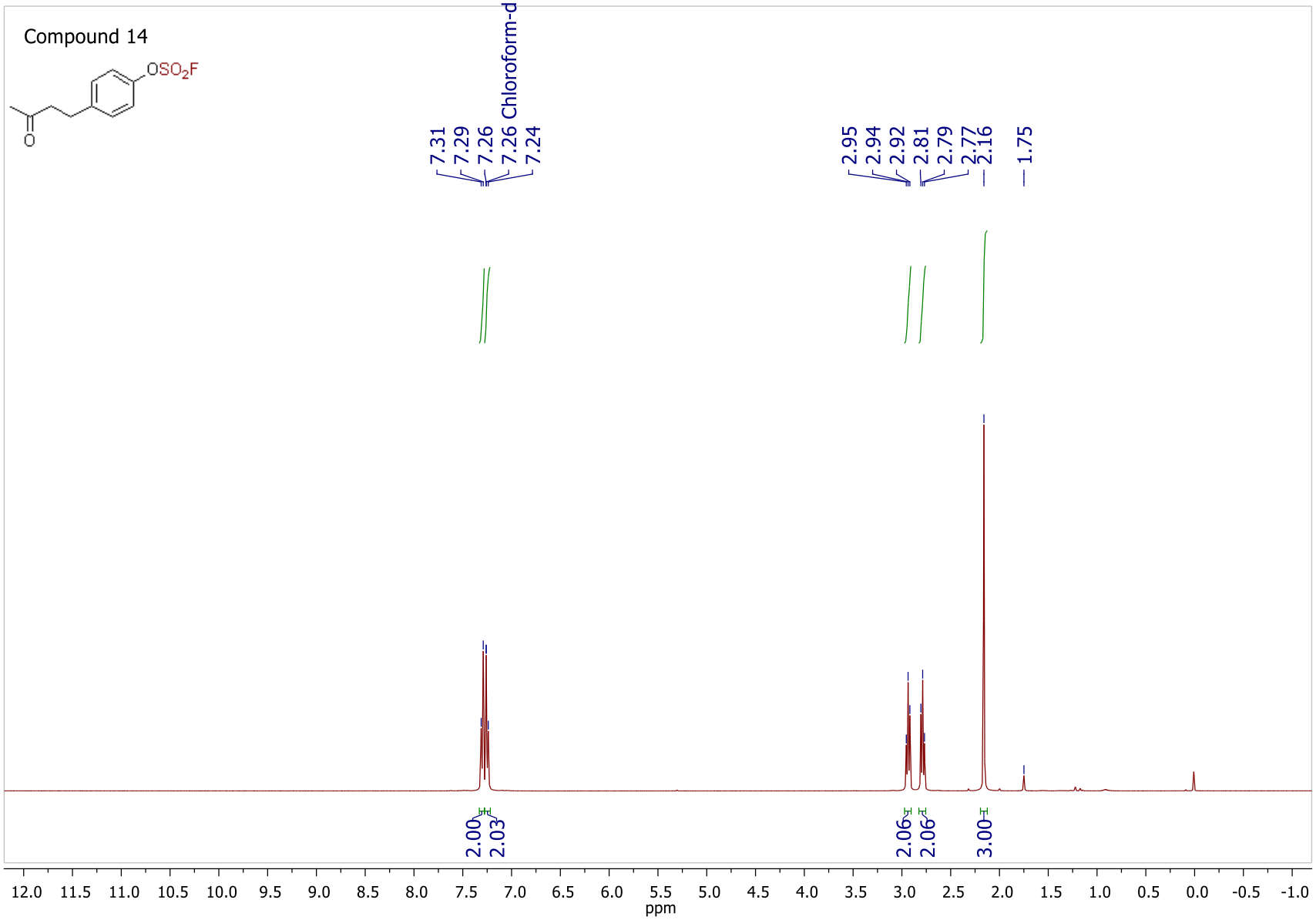

Compound 12
FO2SO
151.07
142.34
137.47
136.35
122.18
120.90
116.96
113.74
77.16 Chloroform-d
56.20
40.13
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

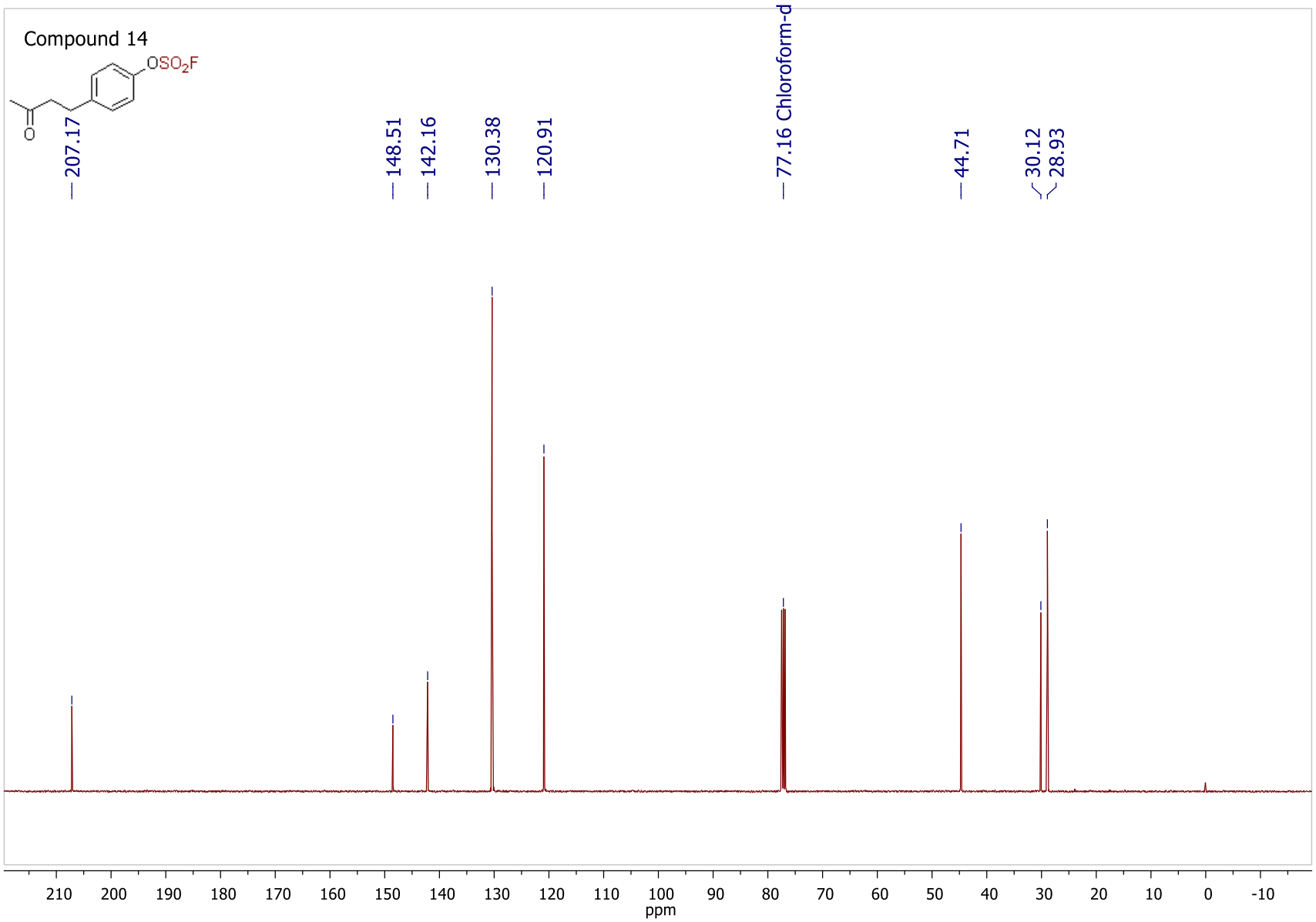

Compound 12
O
FO2SO
38.86
0.00
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm

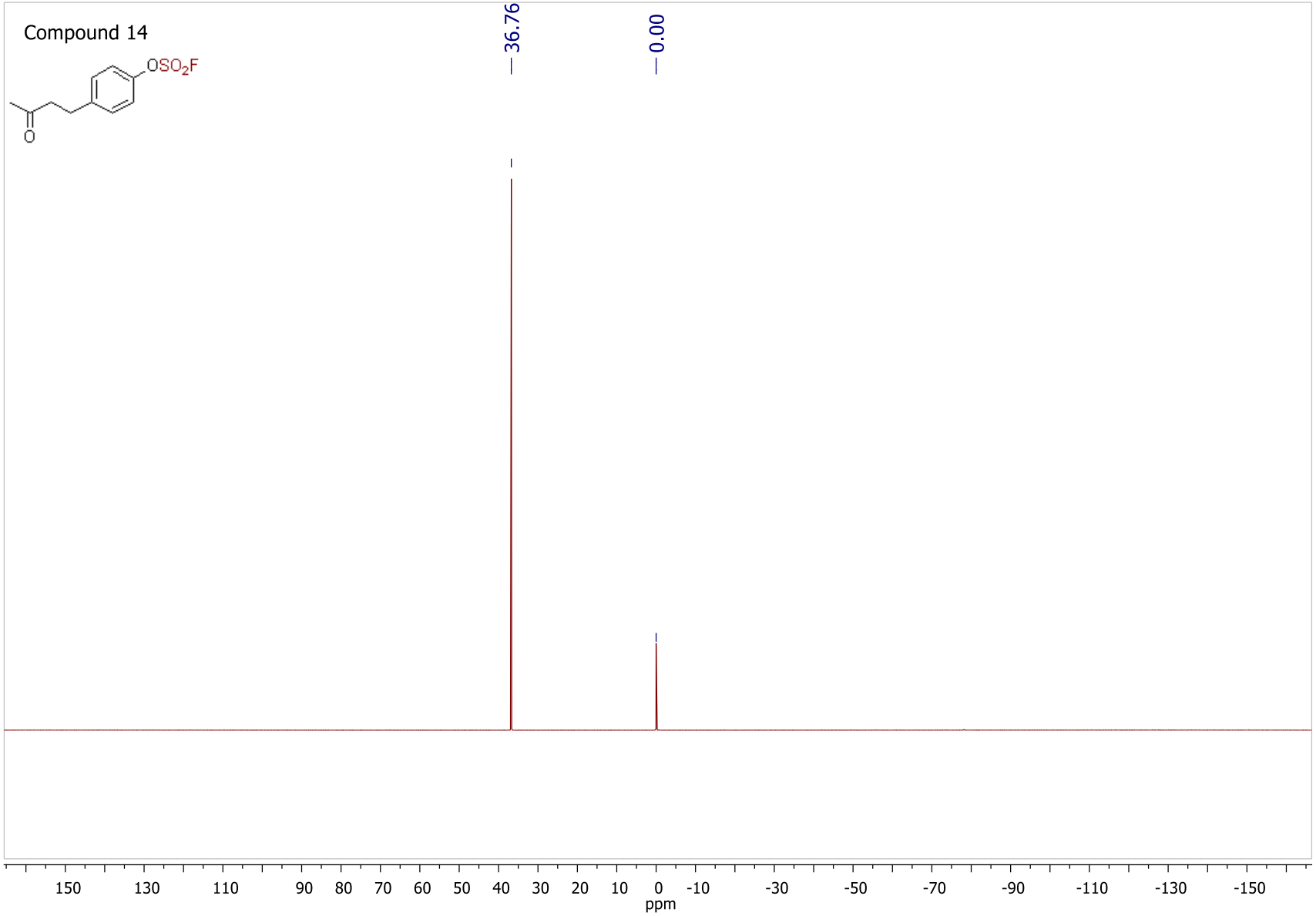

Compound 13
O
H
O
FO2SO
9.98
7.57
7.53
7.51
7.49
7.26 Chloroform-d
3.99
0.96
0.98
1.98
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

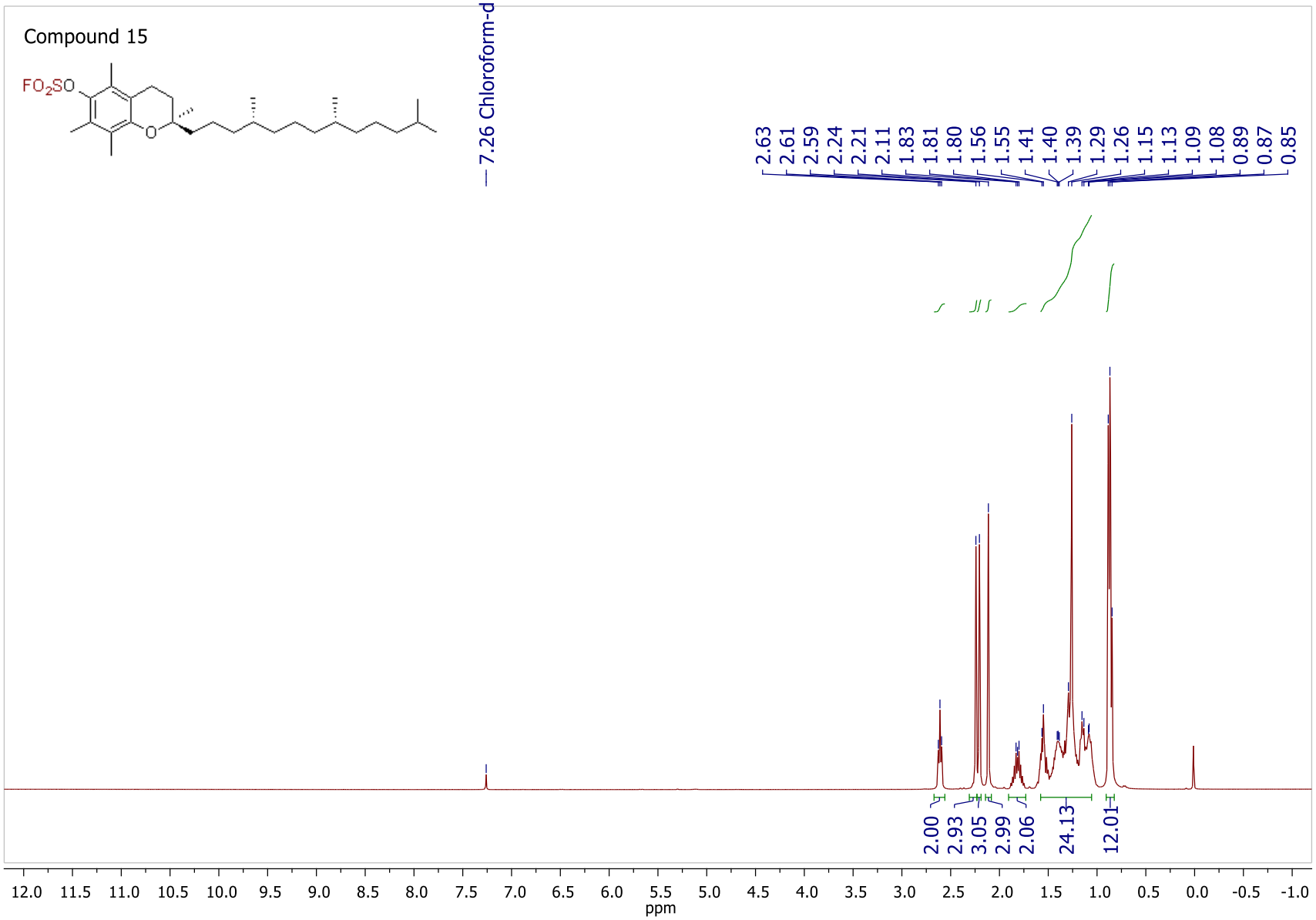

Compound 13
O
H
O
FO2SO
190.46
152.14
142.88
137.19
124.06
123.24
112.25
77.16 Chloroform-d
56.62
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

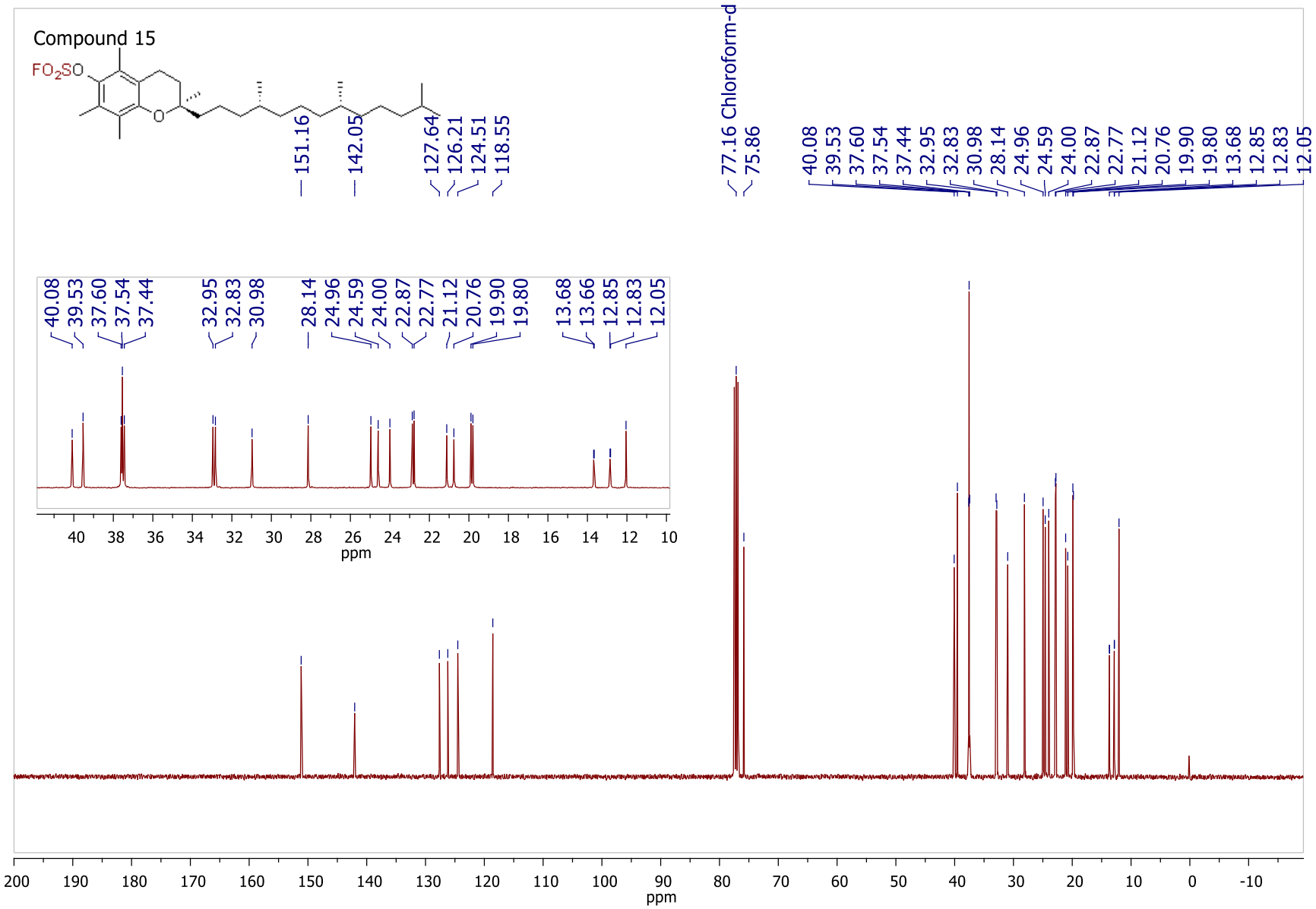

Compound 13
O
H
O
FO2SO
40.52
0.00
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm

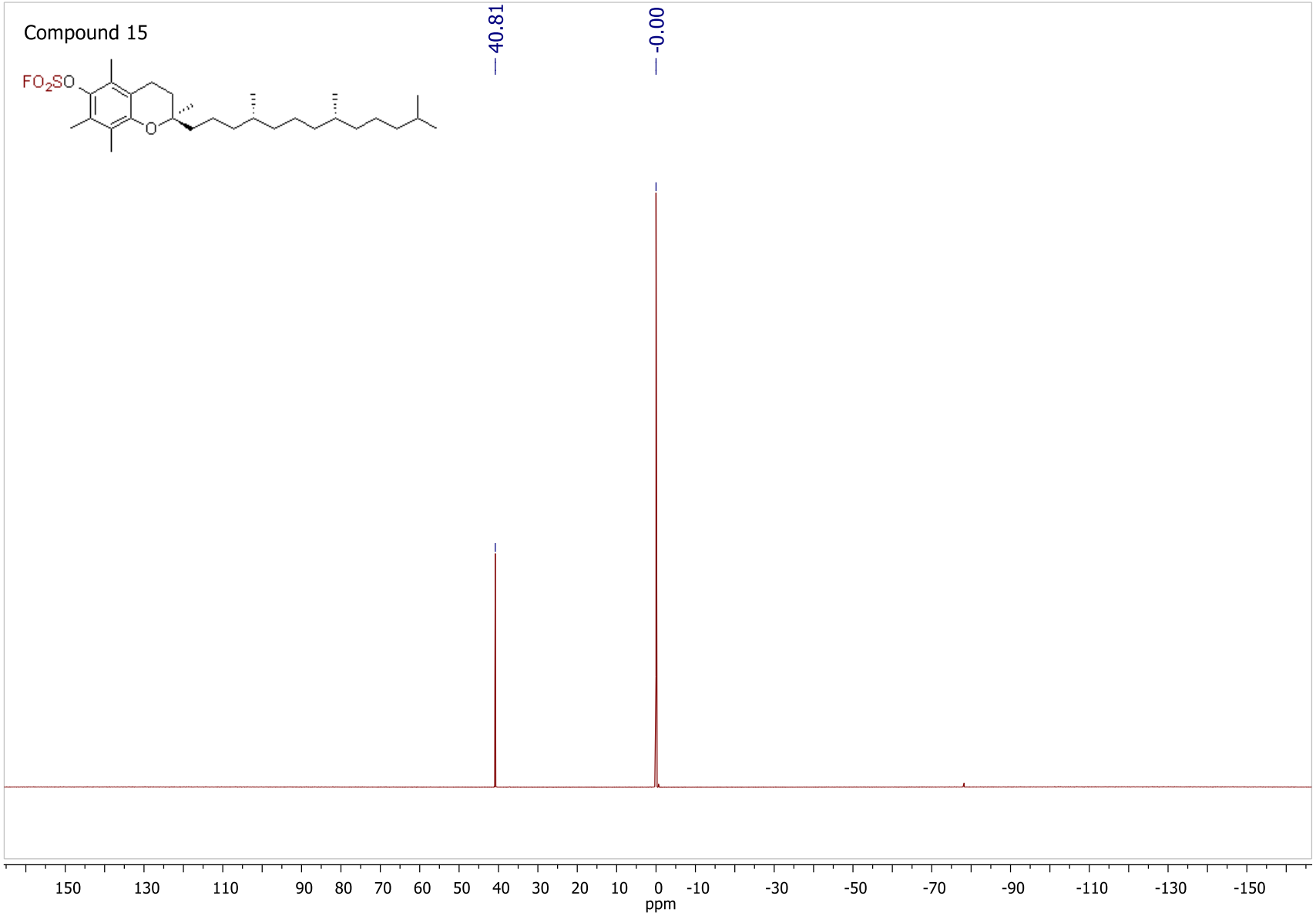

Compound 14
OSO2F
O
7.31
7.29
7.26
7.26 Chloroform-d
7.24
2.95
2.94
2.92
2.81
2.79
2.77
2.16
1.75
2.00
2.03
2.06
2.06
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

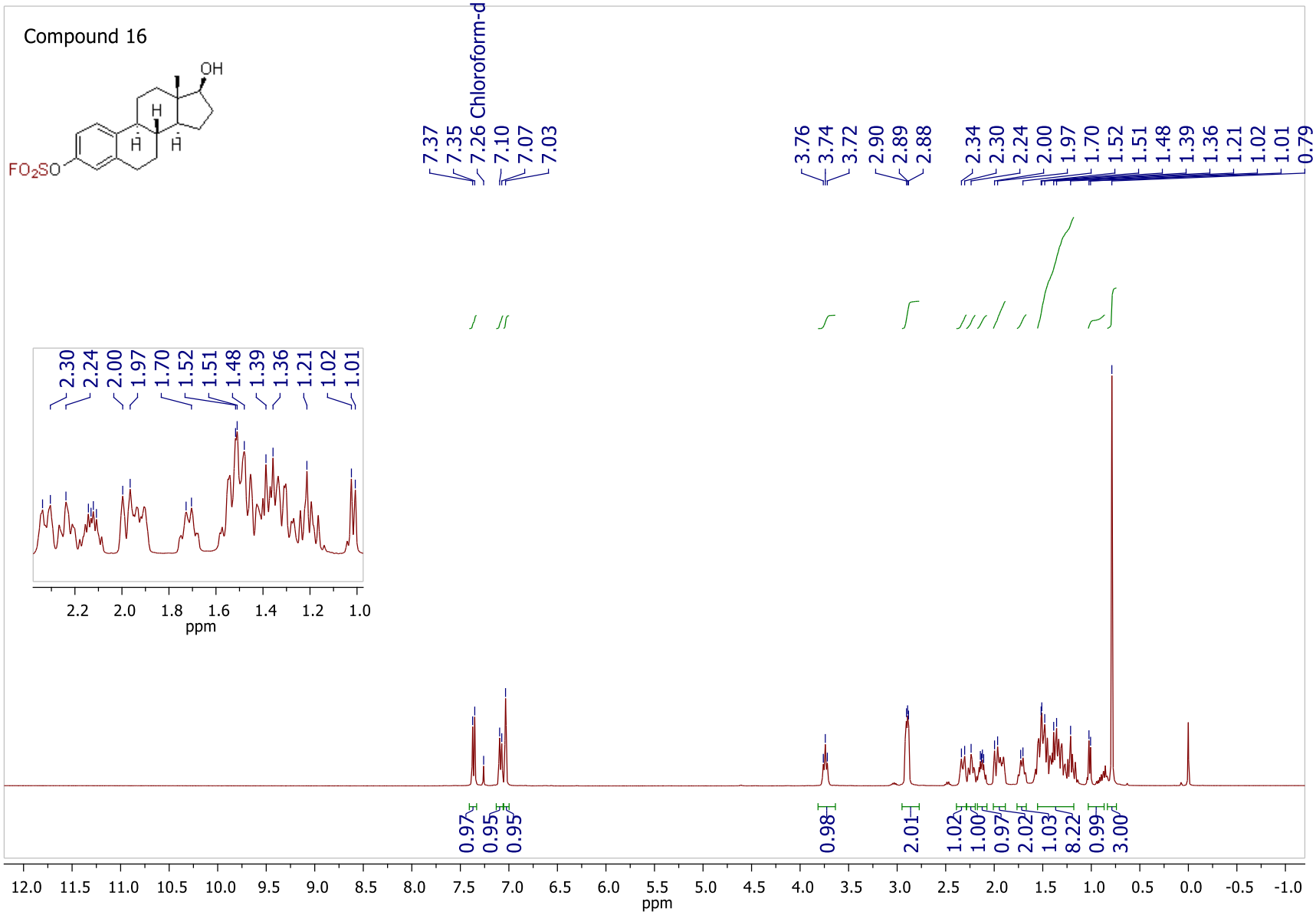

Compound 14
OSO2F
O
207.17
148.51
142.16
130.38
120.91
77.16 Chloroform-d
44.71
30.12
28.93
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

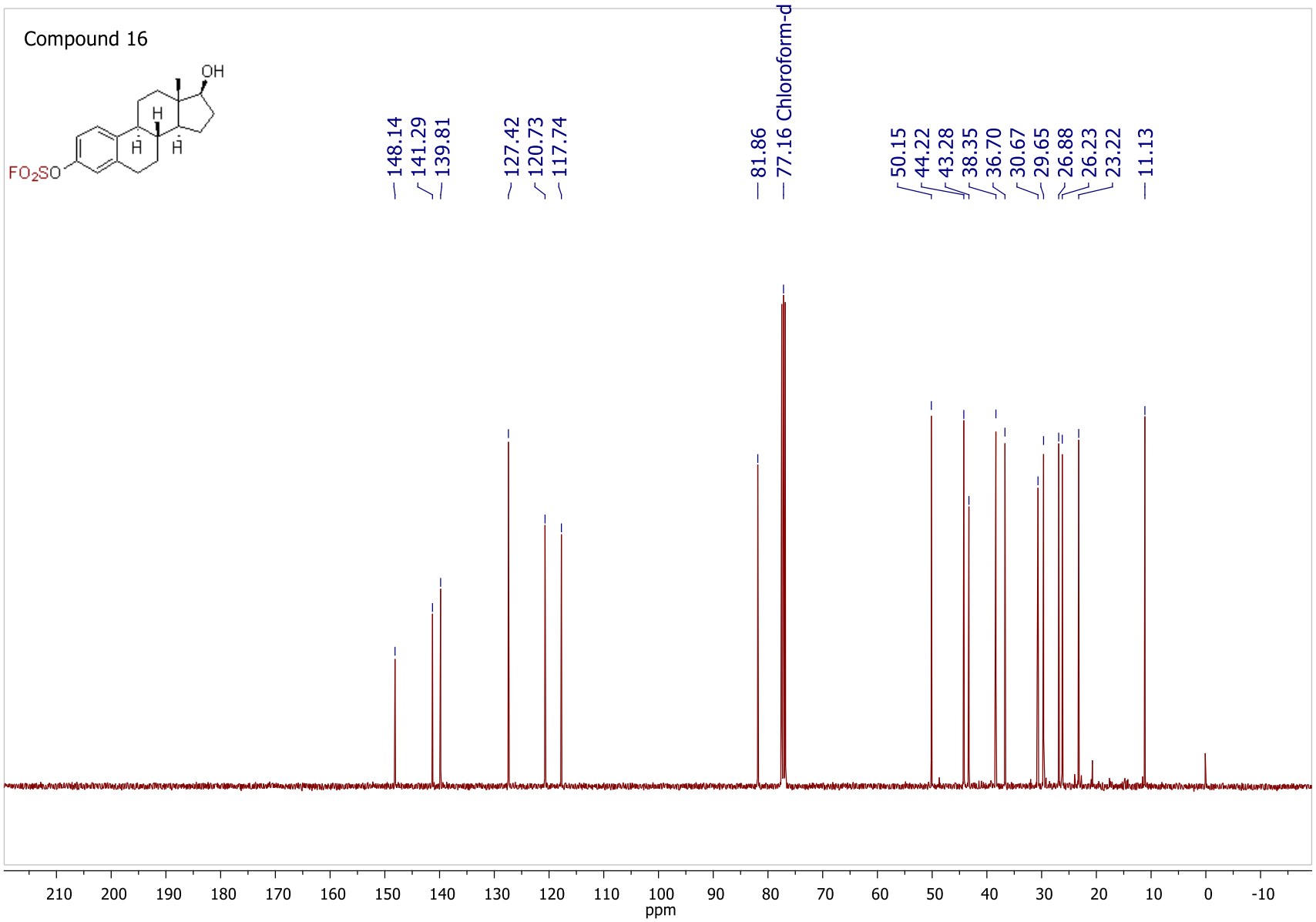

Compound 14
OSO2F
O
36.76
0.00
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm

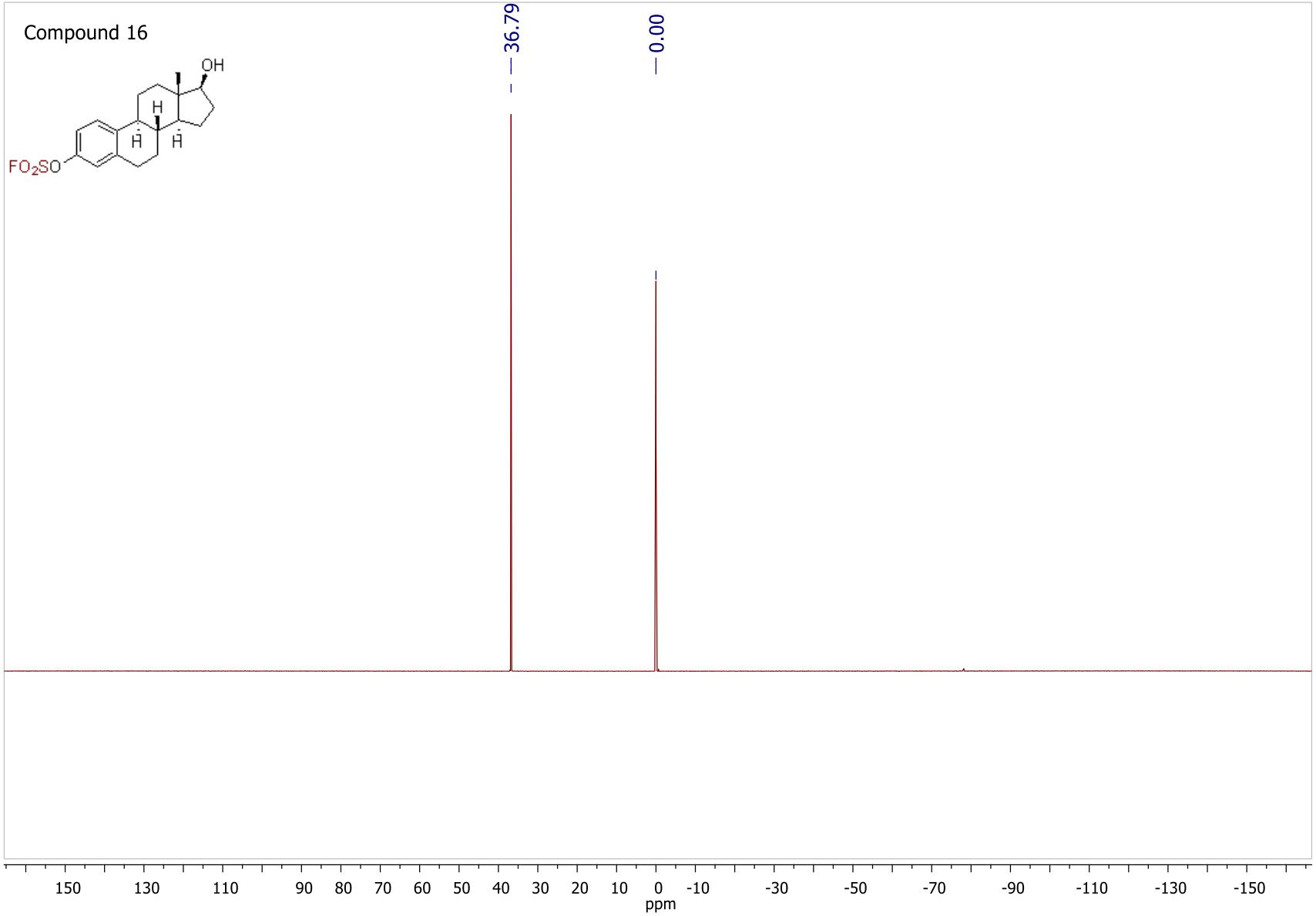

Compound 15
FO2SO
O
7.26 Chloroform-d
2.63
2.61
2.59
2.24
2.21
2.11
1.83
1.81
1.80
1.56
1.55
1.41
1.40
1.39
1.29
1.26
1.15
1.13
1.09
1.08
0.89
0.87
0.85
2.00
2.93
3.05
2.99
2.06
24.13
12.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

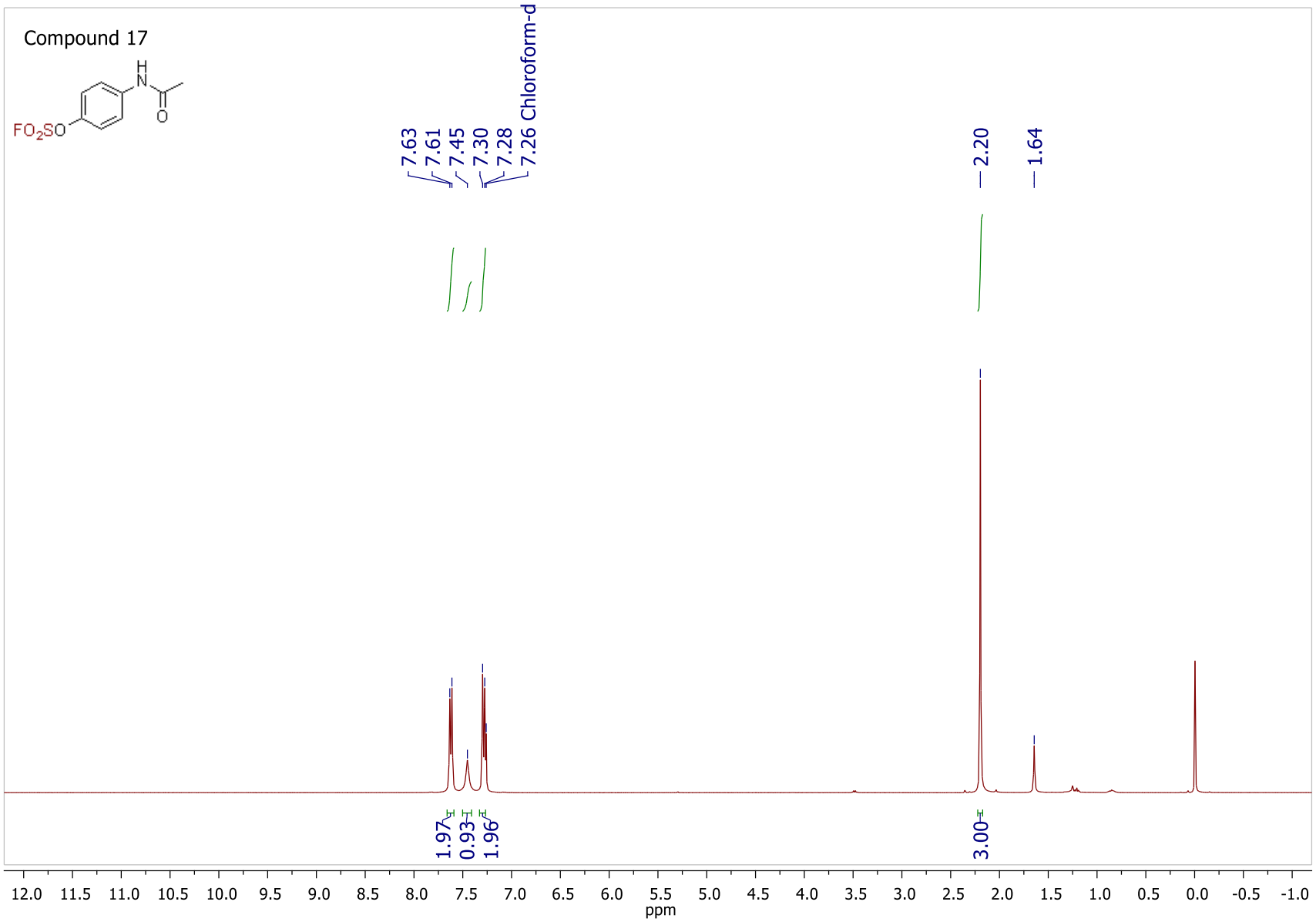

Compound 15
FO2SO
O
151.16
142.05
127.64
126.21
124.51
118.55
77.16 Chloroform-d
75.86
40.08
39.53
37.60
37.54
37.44
32.95
32.83
30.98
28.14
24.96
24.59
24.00
22.87
22.77
21.12
20.76
19.90
19.80
13.68
13.66
12.85
12.83
12.05
ppm

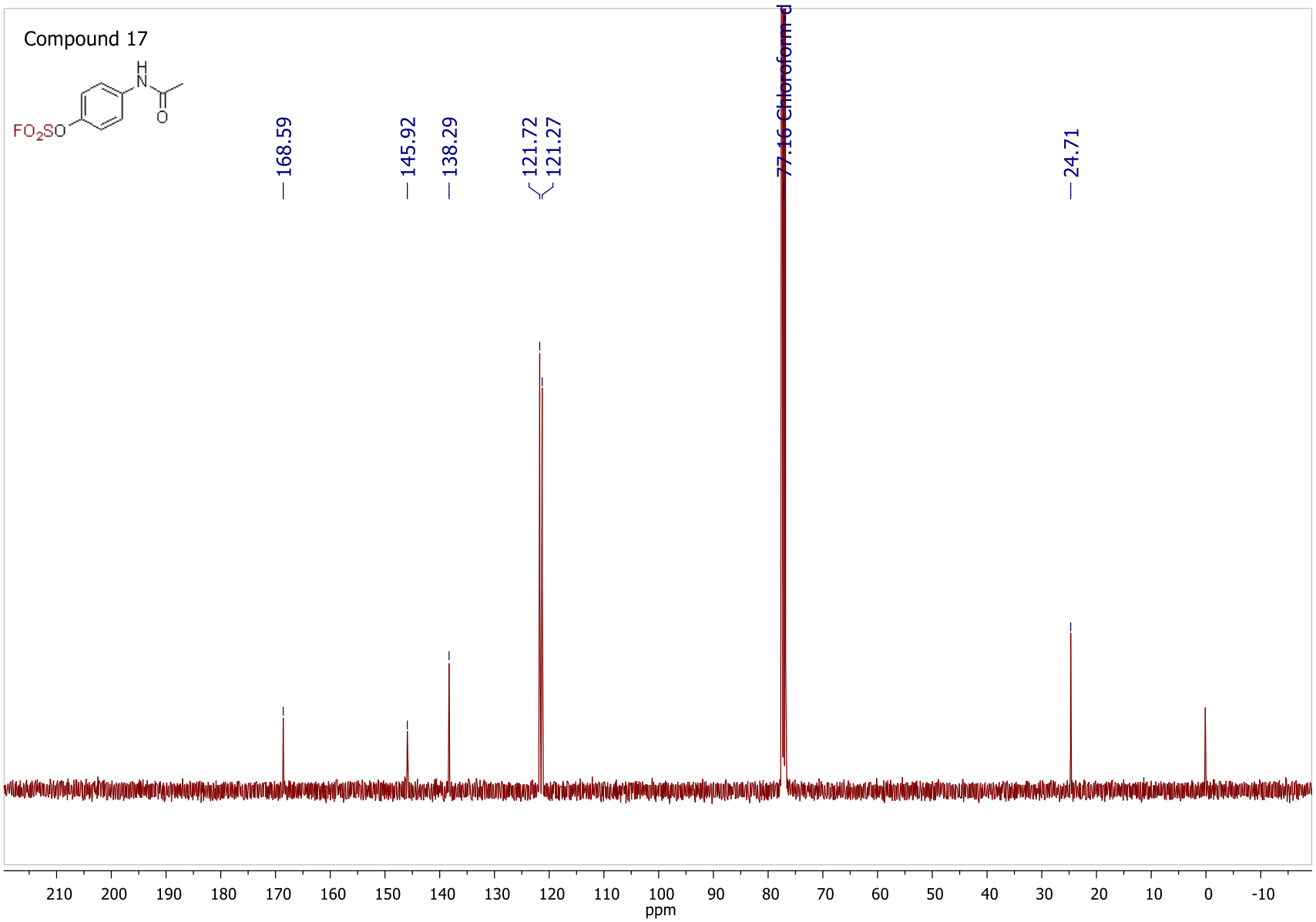

Compound 15
FO2SO
O
40.81
-0.00
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm

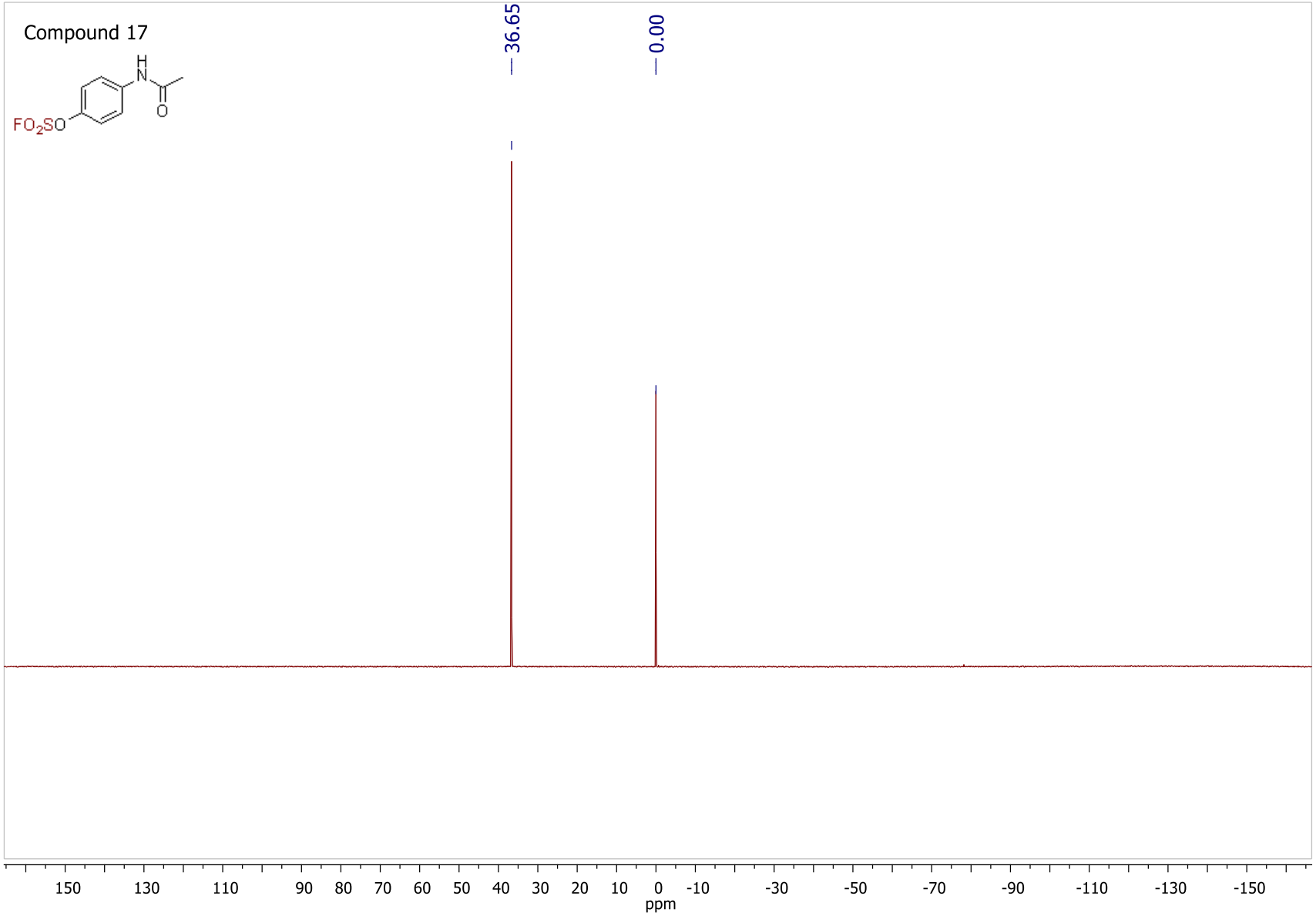

Compound 16
OH
H
H
H
FO2SO
Chloroform-d
7.37
7.35
7.26
7.10
7.07
7.03
3.76
3.74
3.72
2.90
2.89
2.88
2.34
2.30
2.24
2.00
1.97
1.70
1.52
1.51
1.48
1.39
1.36
1.21
1.02
1.01
0.79
0.97
0.95
0.95
0.98
2.01
1.02
1.00
0.97
2.02
1.03
8.22
0.99
3.00
ppm

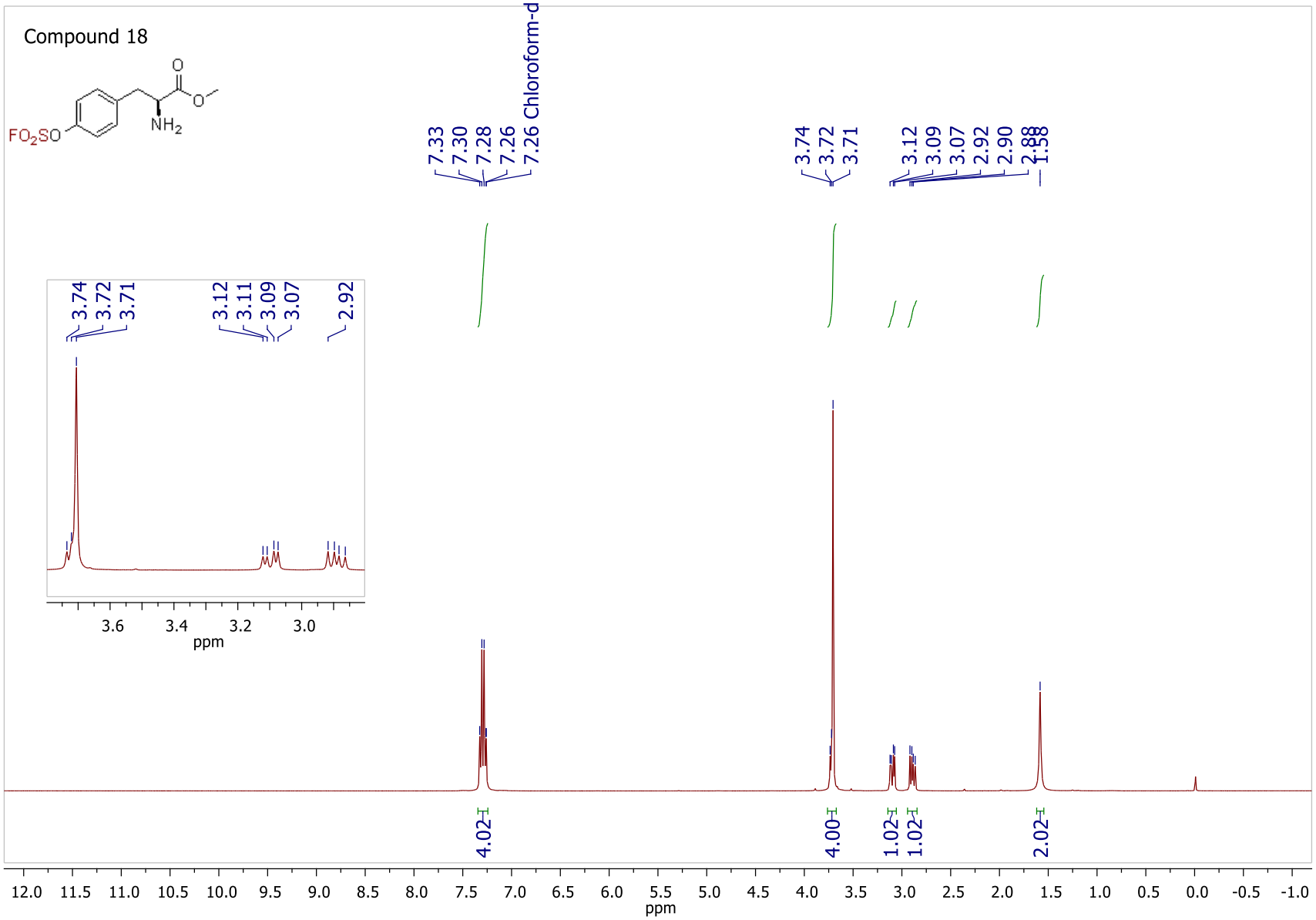

Compound 16
OH
H
H
H
FO2SO
148.14
141.29
139.81
127.42
120.73
117.74
81.86
77.16 Chloroform-d
50.15
44.22
43.28
38.35
36.70
30.67
29.65
26.88
26.23
23.22
11.13
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

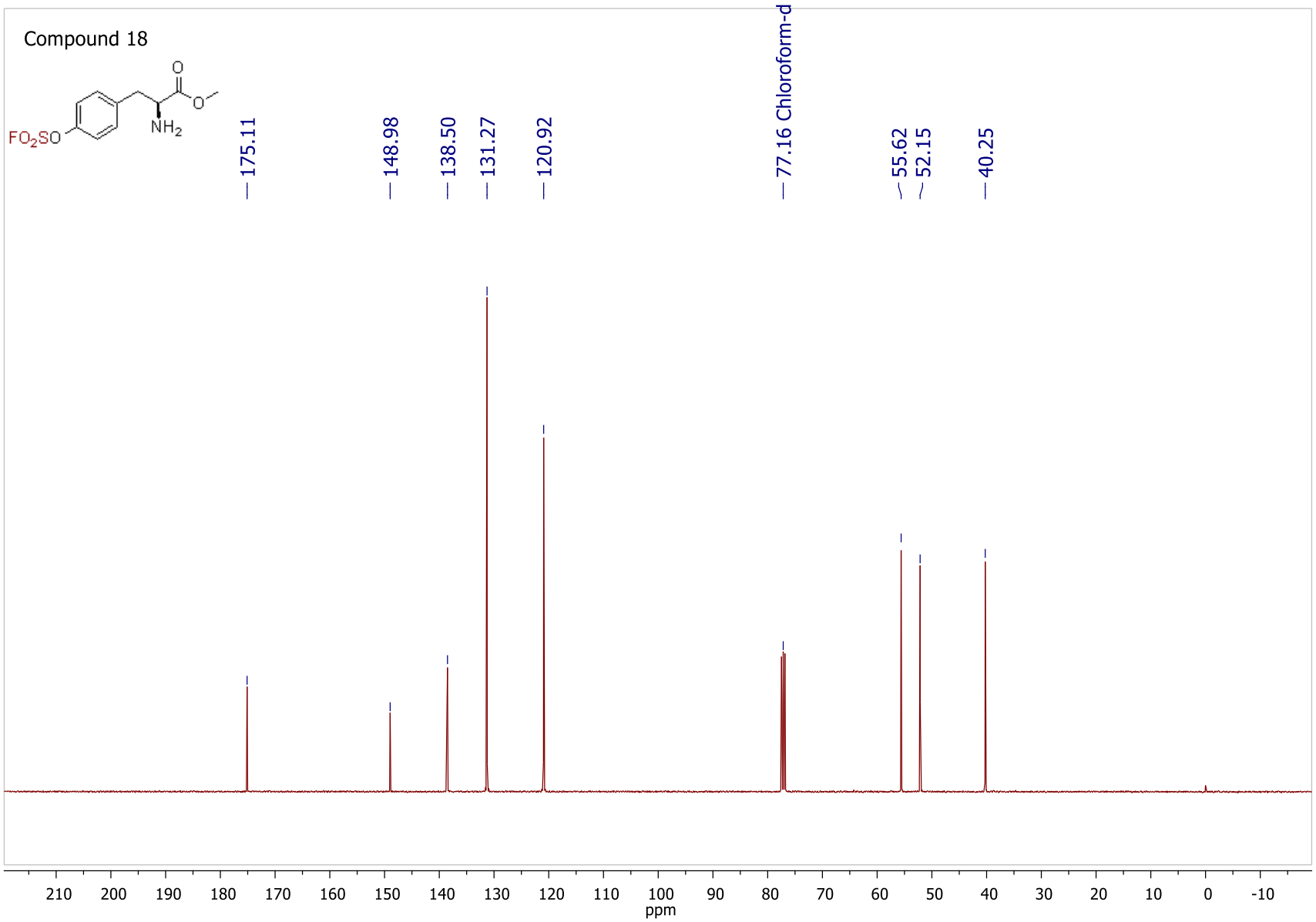

Compound 16
OH
H
H
H
FO2SO
36.79
0.00
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm

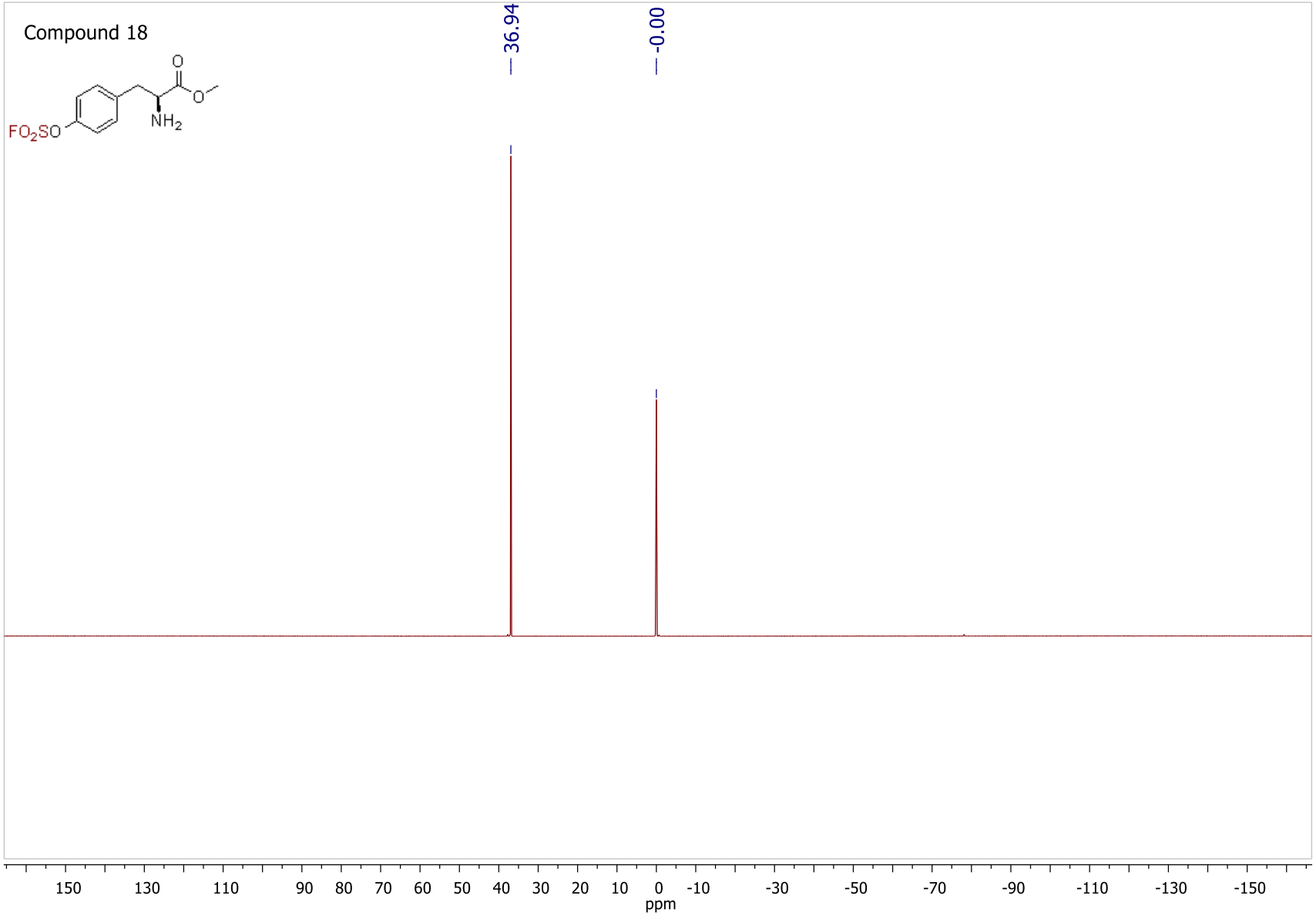

Compound 17
FO2SO
H
N
O
7.63
7.61
7.45
7.30
7.28
7.26 Chloroform-d
2.20
1.64
1.97
0.93
1.96
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

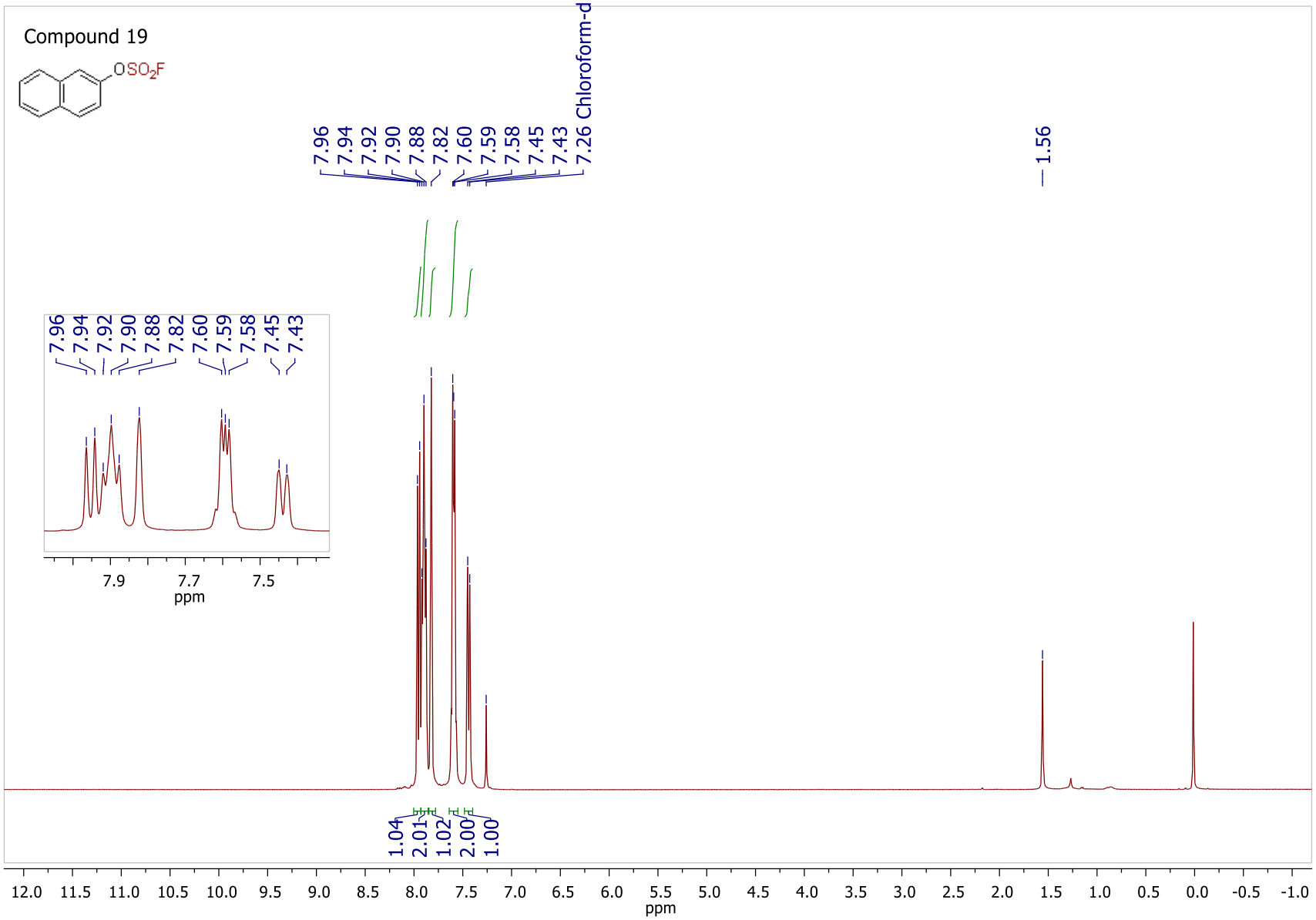

Compound 17
FO2SO
H
N
O
168.59
145.92
138.29
121.72
121.27
77.16 Chloroform-d
24.71
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

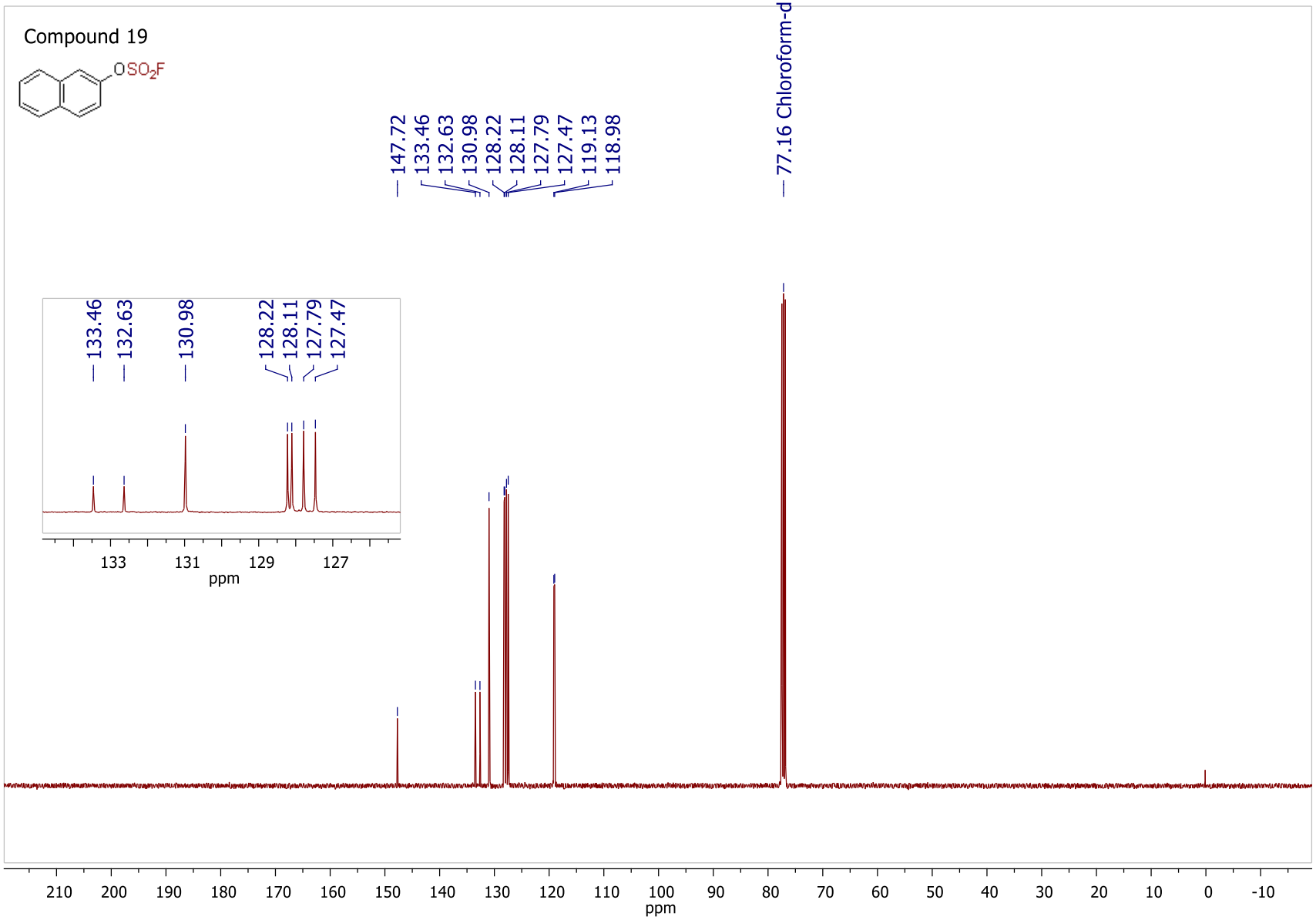

Compound 17
FO2SO
H
N
O
36.65
0.00
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm

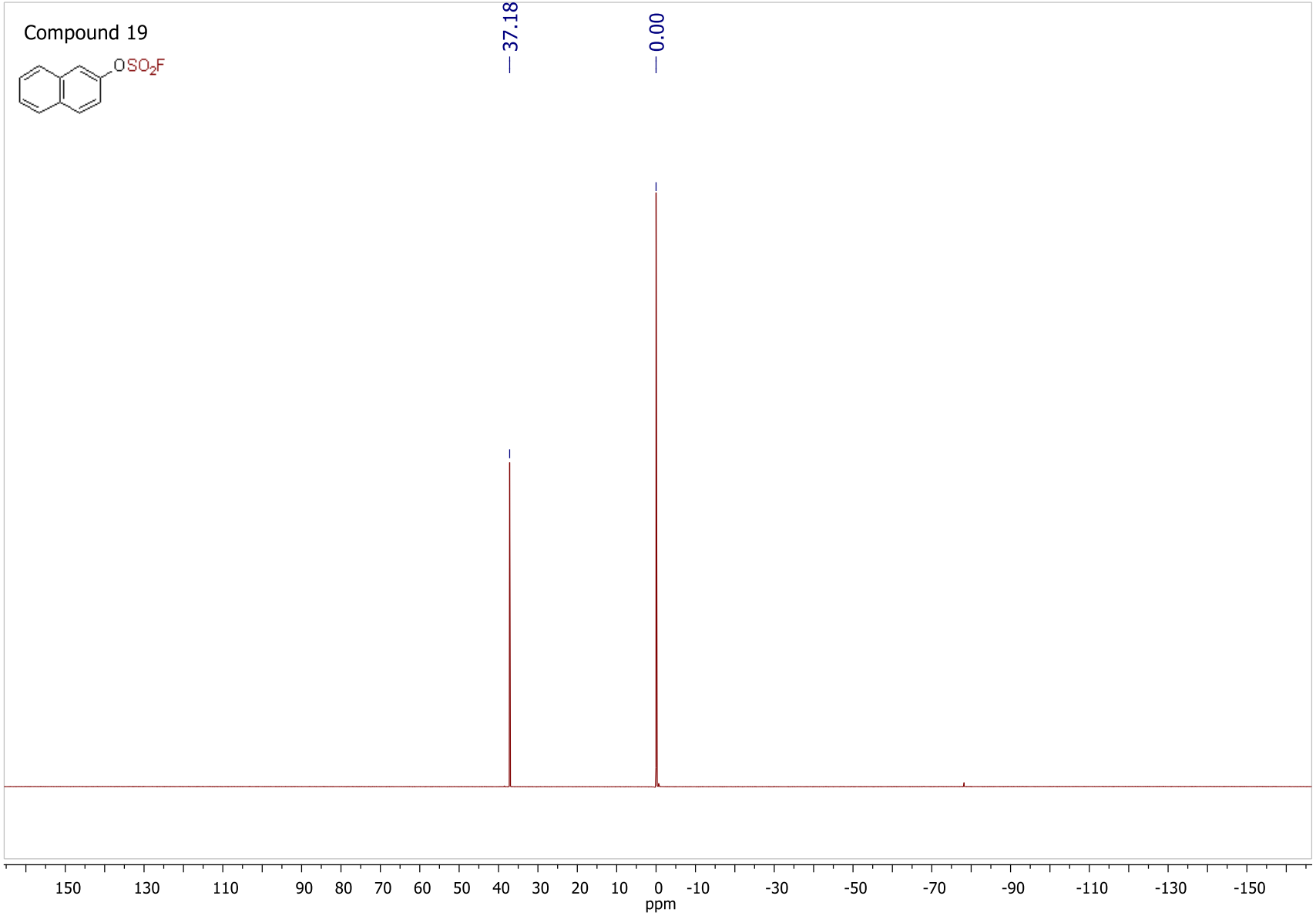

Compound 18
FO2SO
NH2
O
O
7.33
7.30
7.28
7.26
7.26 Chloroform-d
3.74
3.72
3.71
3.12
3.09
3.07
2.92
2.90
2.88
1.58
3.74
3.72
3.71
3.12
3.11
3.09
3.07
2.92
3.6
3.4
3.2
3.0
ppm
4.02
4.00
1.02
1.02
2.02
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

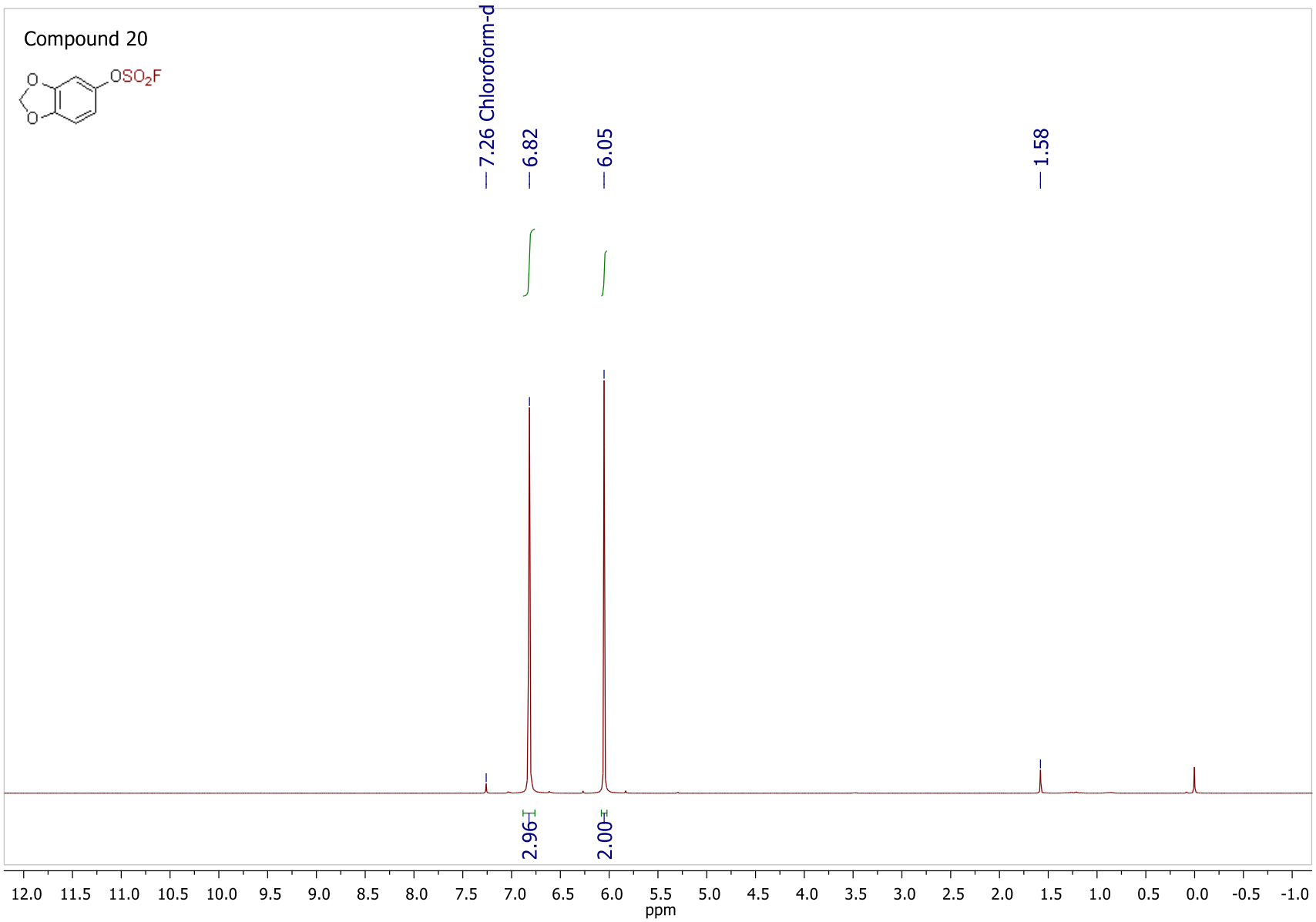

Compound 18
FO2SO
NH2
O
O
175.11
148.98
138.50
131.27
120.92
77.16 Chloroform-d
55.62
52.15
40.25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm


Compound 18
FO2SO
NH2
O
O
36.94
-0.00
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm


Compound 19
OSO2F
7.96
7.94
7.92
7.90
7.88
7.82
7.60
7.59
7.58
7.45
7.43
7.26 Chloroform-d
1.56
7.9
7.7
7.5
ppm
1.04
2.01
1.02
2.00
1.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

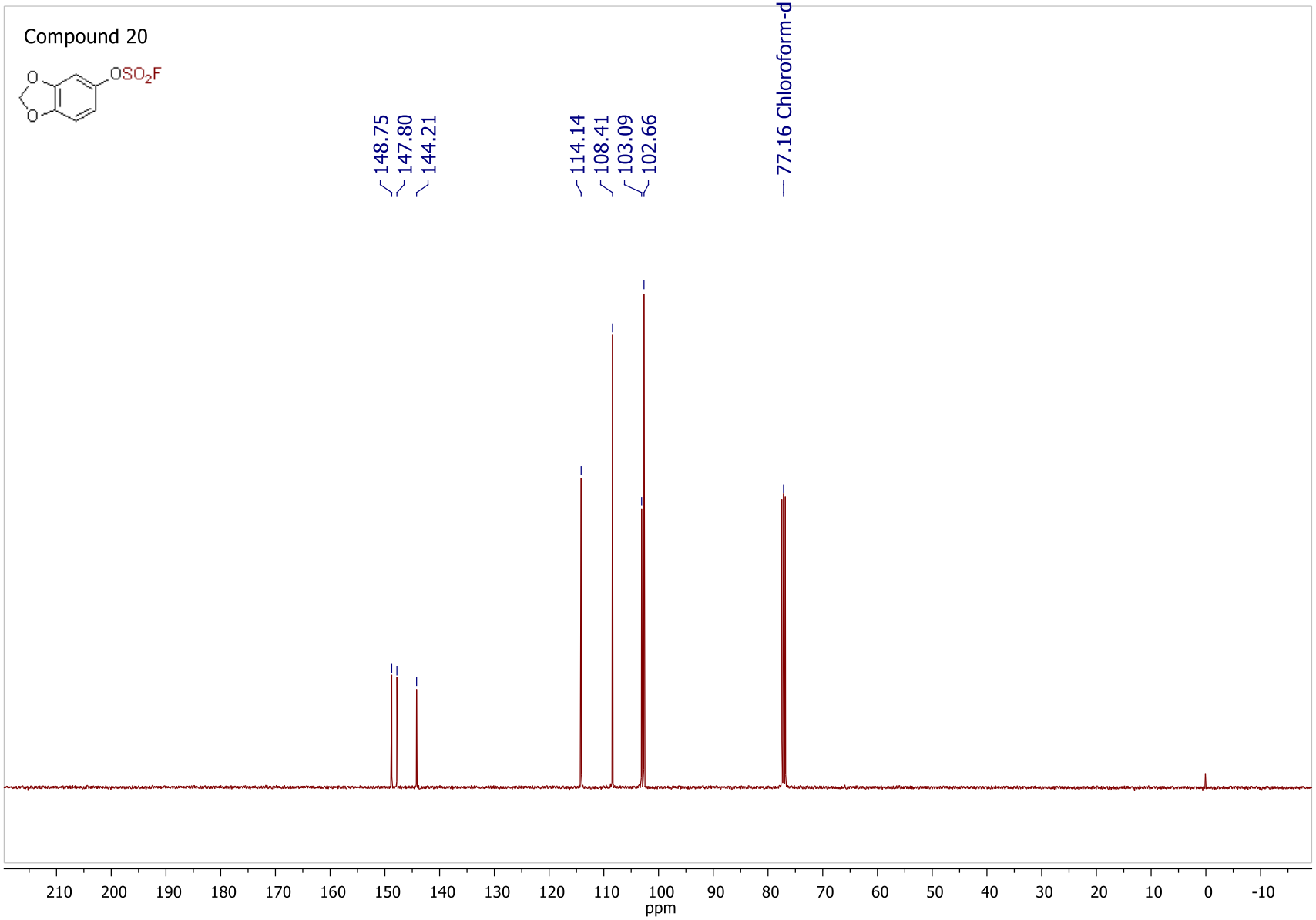

Compound 19
OSO2F
147.72
133.46
132.63
130.98
128.22
128.11
127.79
127.47
119.13
118.98
77.16 Chloroform-d
133.46
132.63
130.98
128.22
128.11
127.79
127.47
133
131
129
127
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

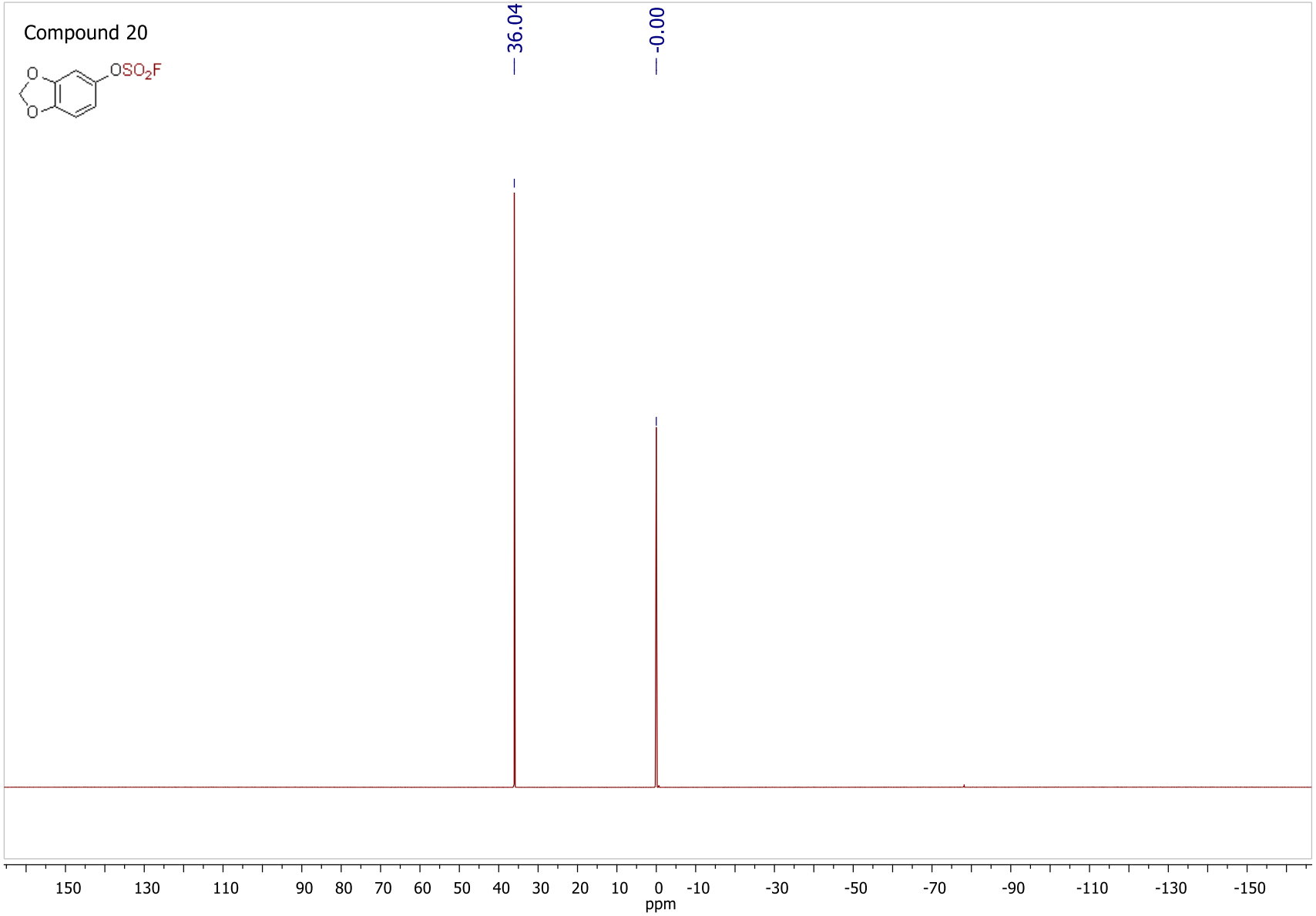

Compound 19
OSO2F
37.18
0.00
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm

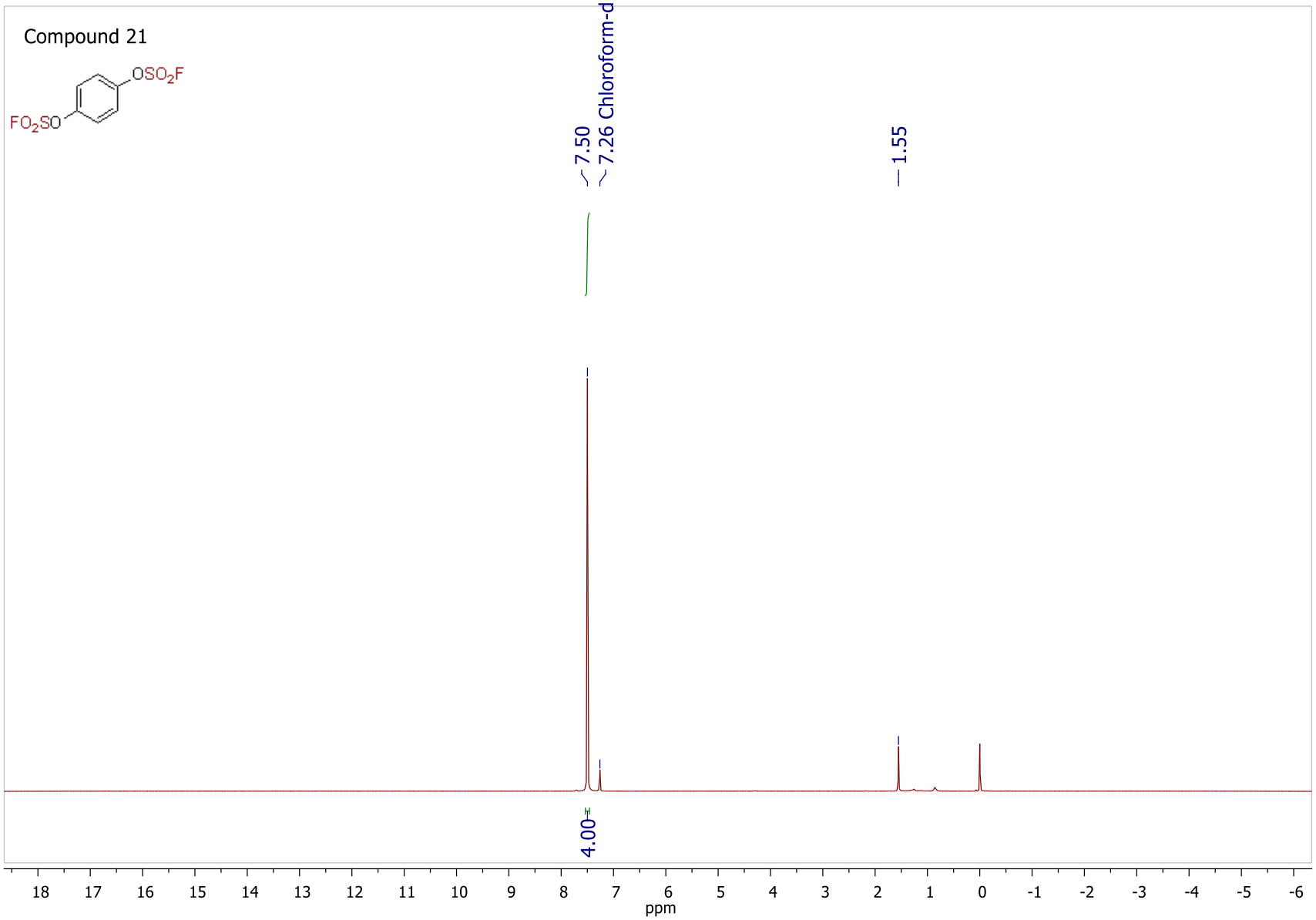

Compound 20
OSO2F
7.26 Chloroform-d
6.82
6.05
1.58
2.96
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

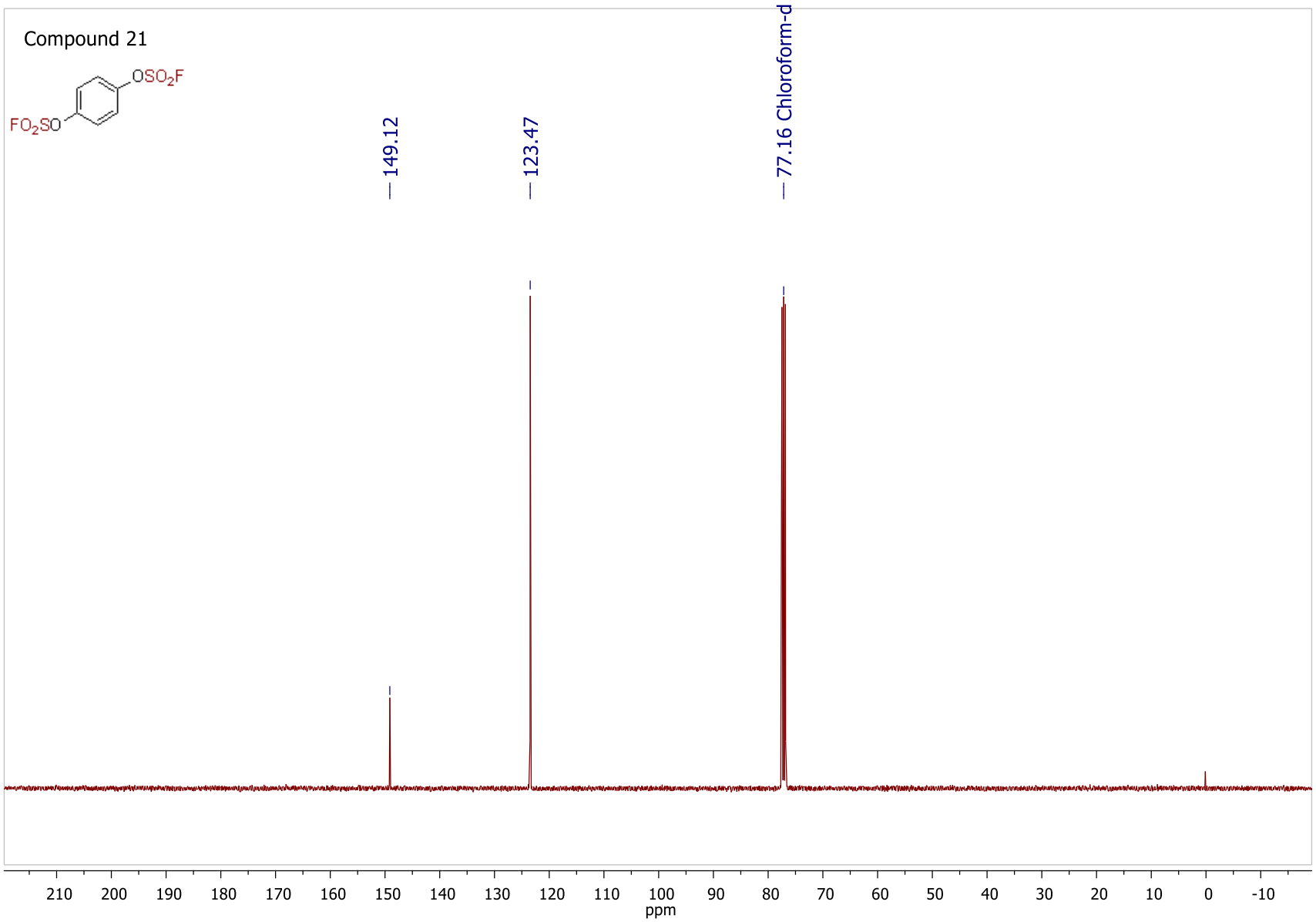
Compound 20

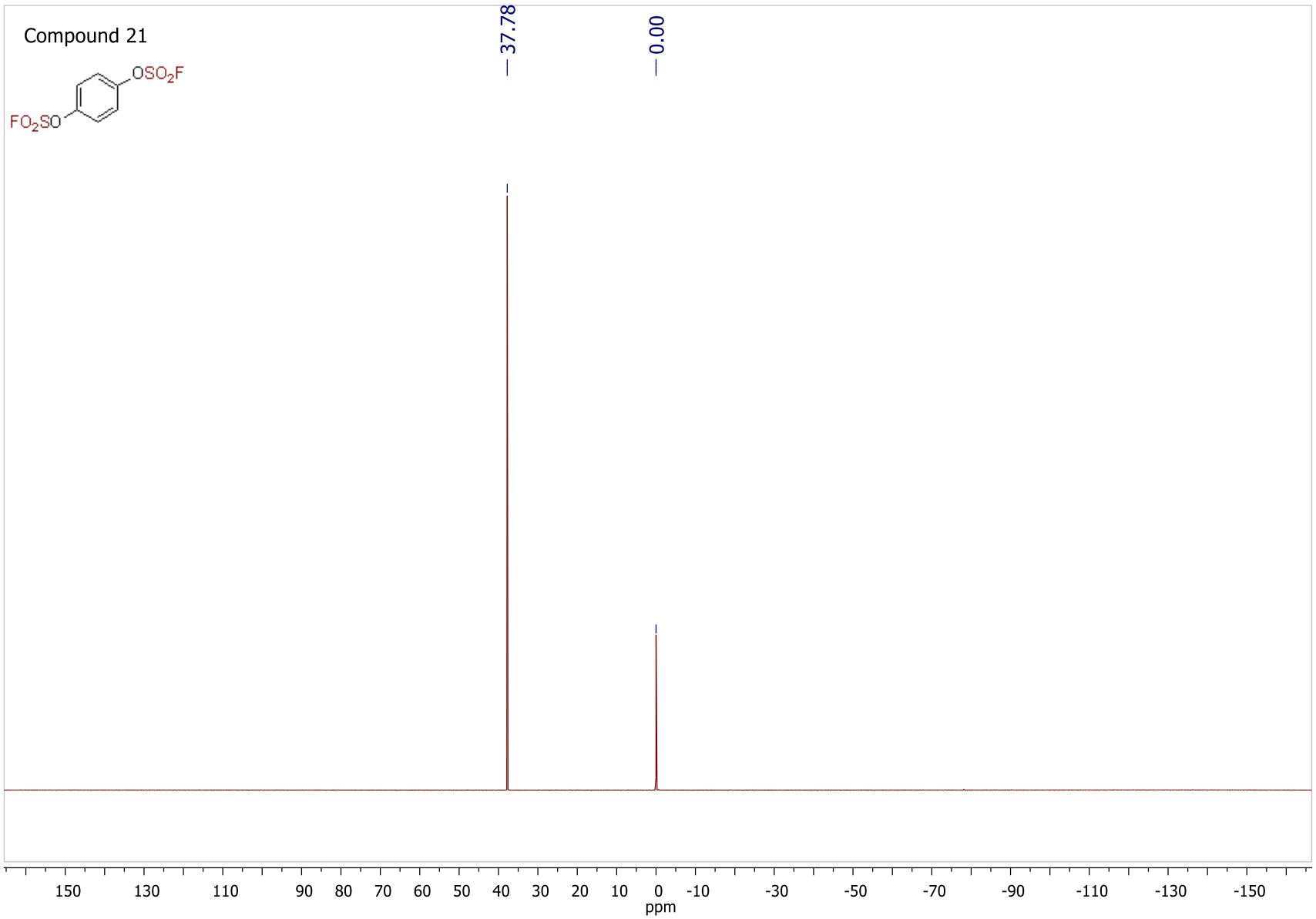
O
O
OSO2F

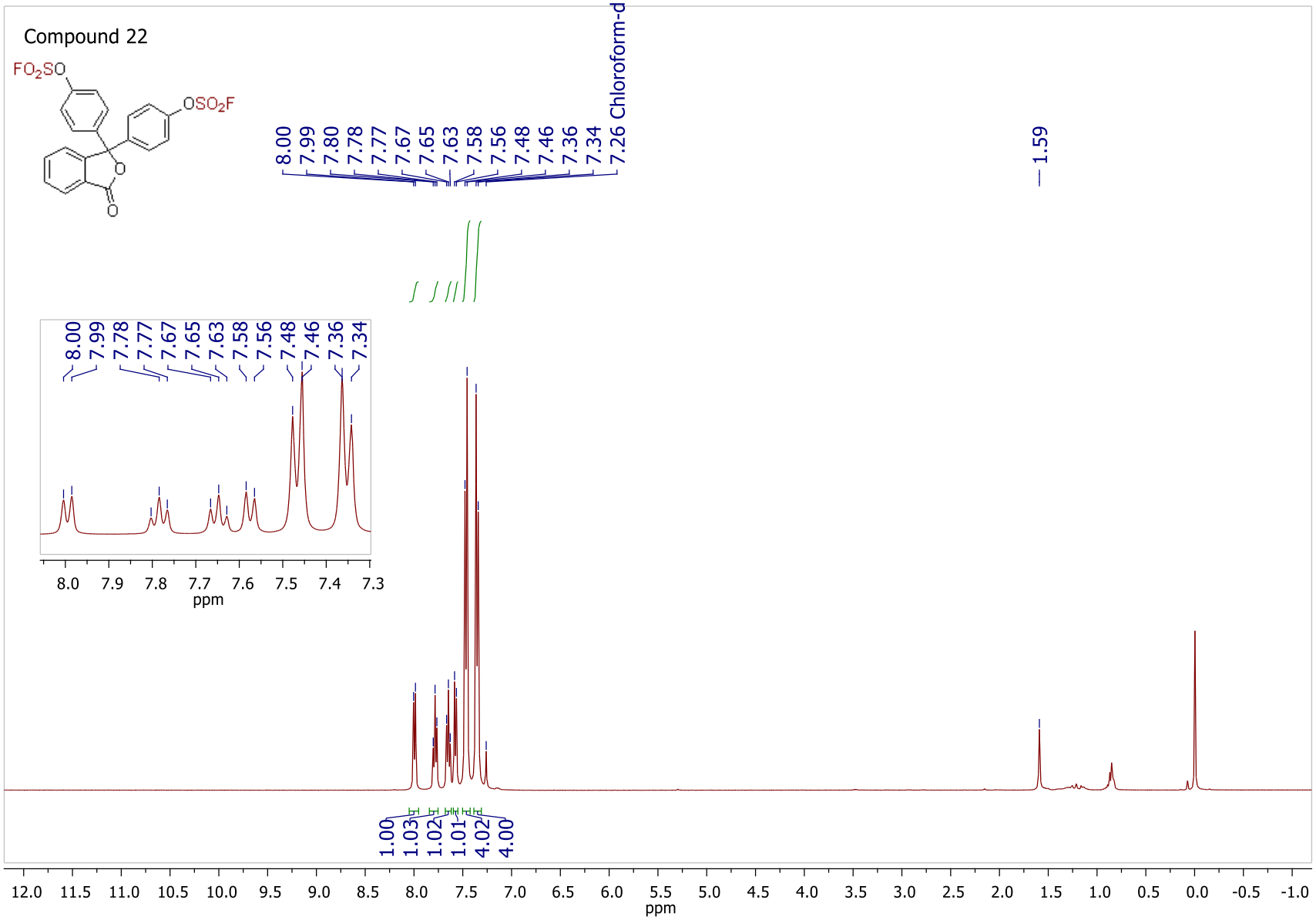

148.75
147.80
144.21
114.14
108.41
103.09
102.66
77.16 Chloroform-d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

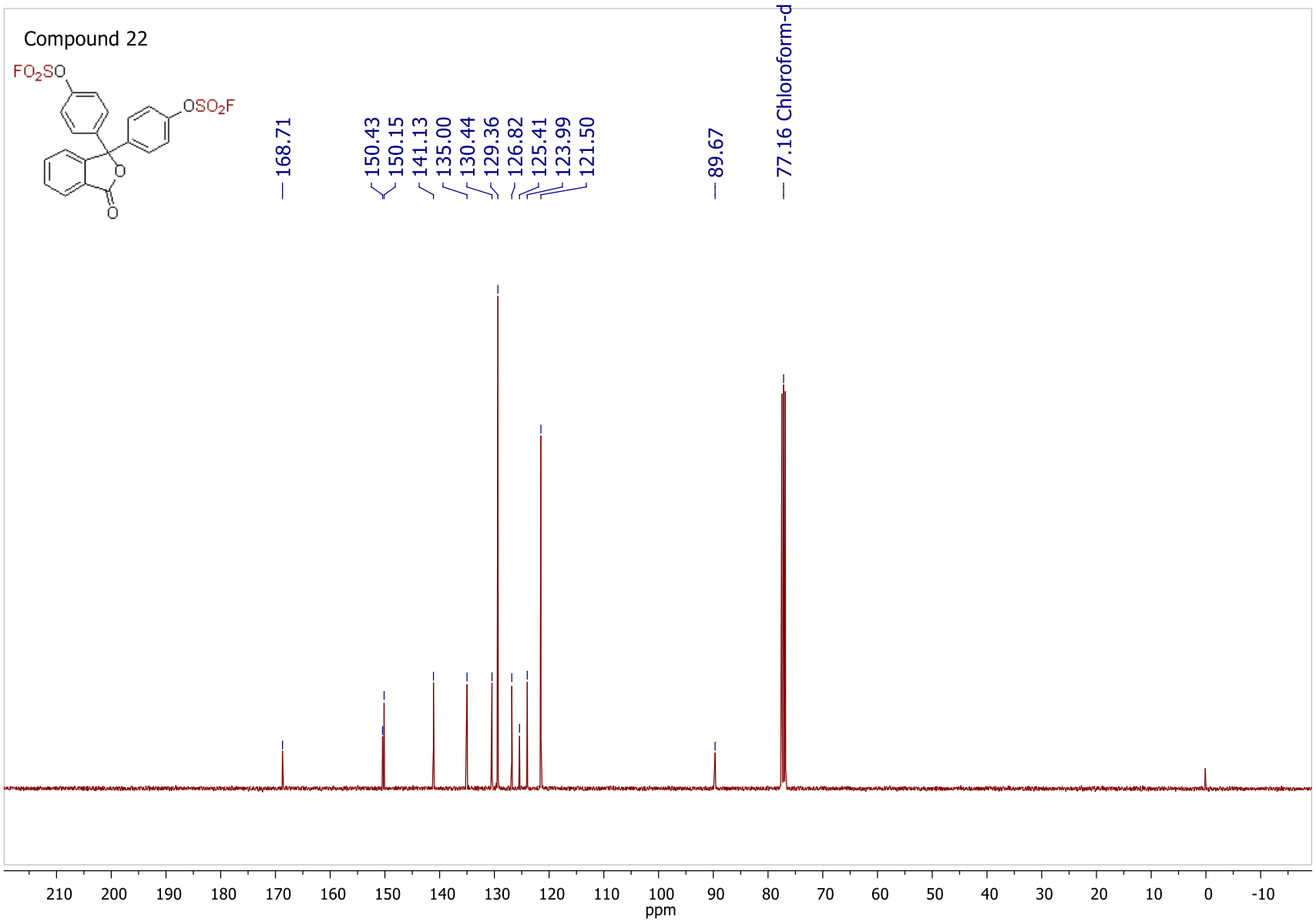

Compound 20
OSO2F
O
O
36.04
-0.00
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm

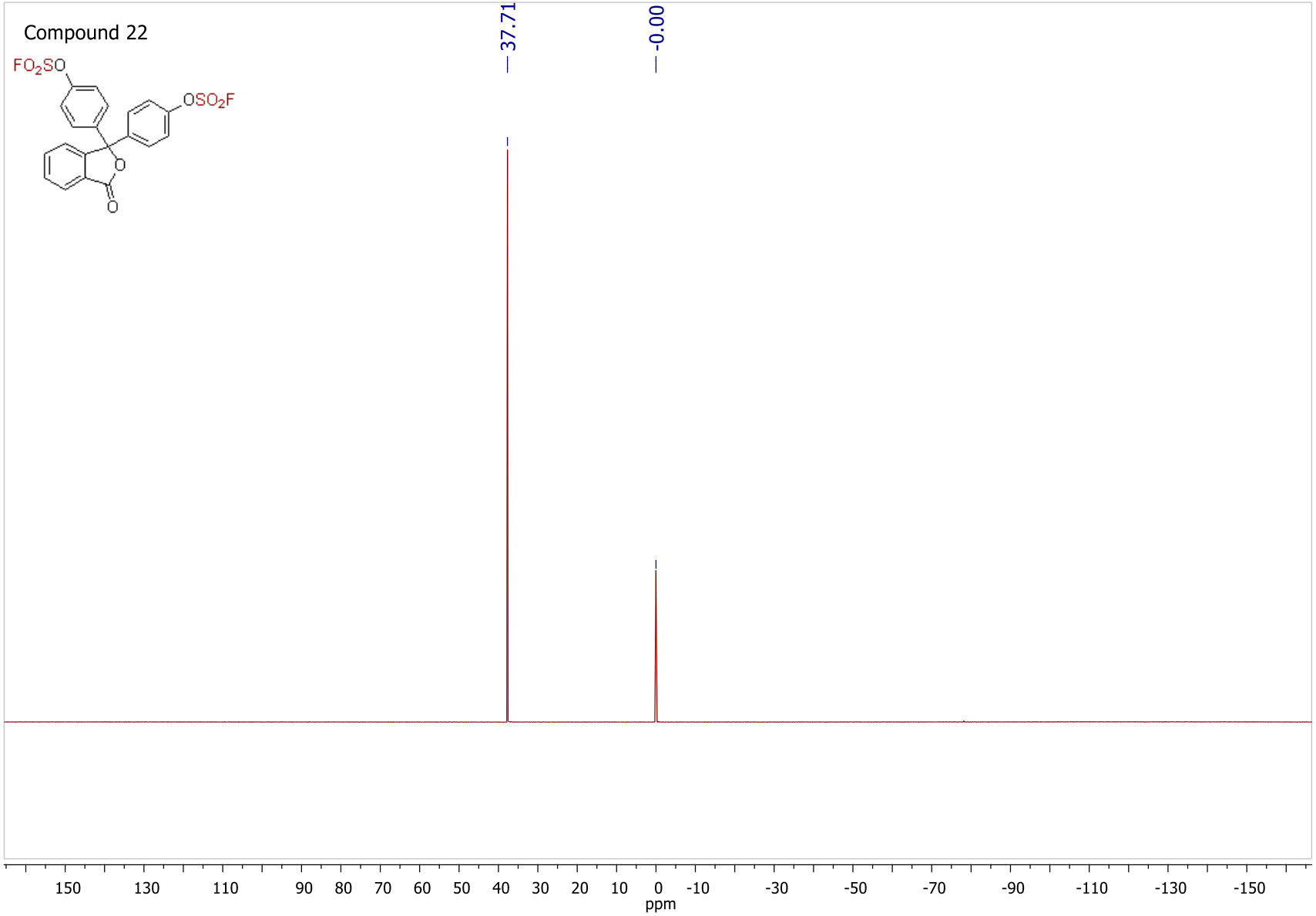

Compound 21
OSO2F
FO2SO
7.50
7.26 Chloroform-d
1.55
4.00
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6
ppm

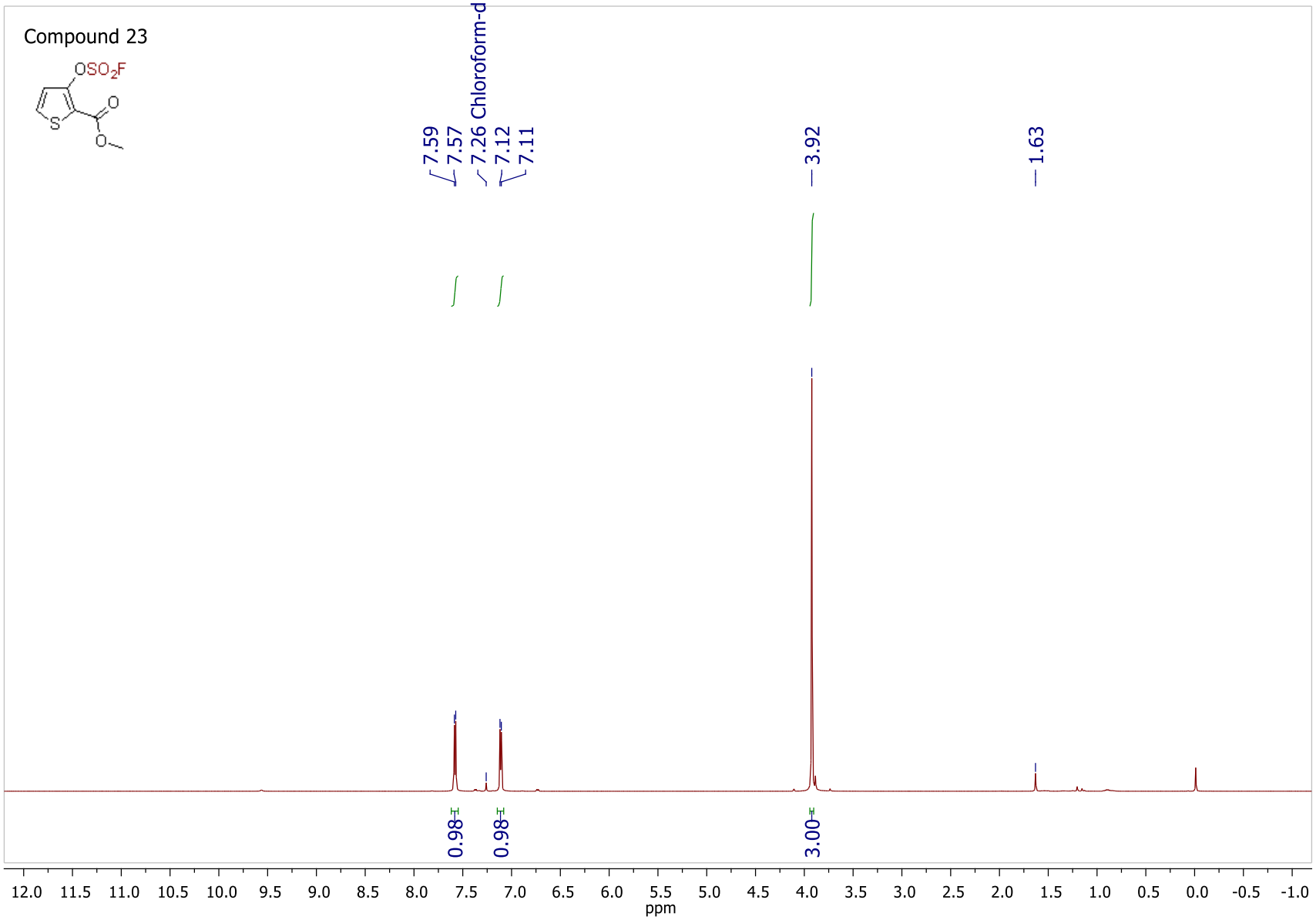

Compound 21
OSO2F
FO2SO
149.12
123.47
77.16 Chloroform-d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

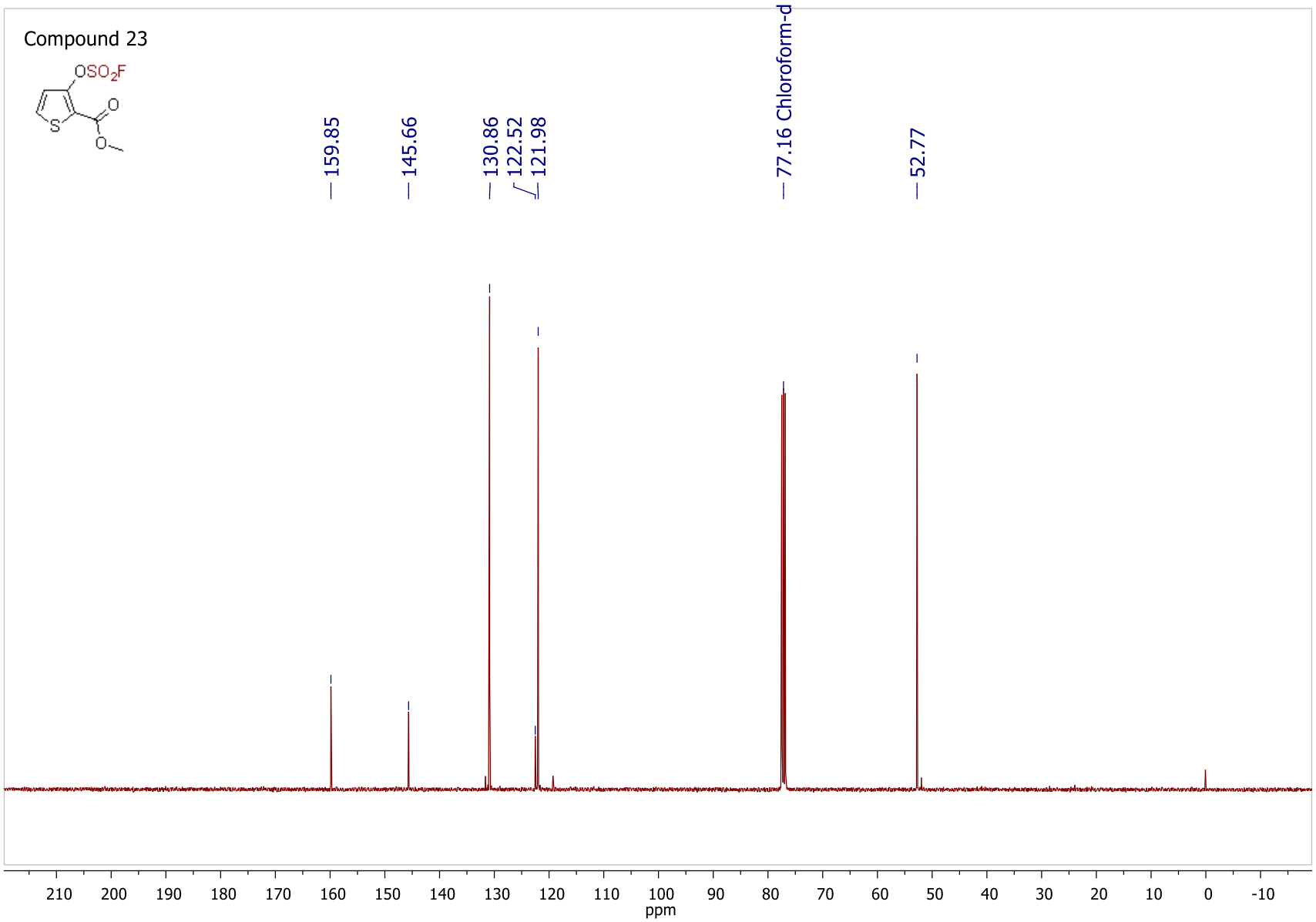

Compound 21
OSO2F
FO2SO
37.78
0.00
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm

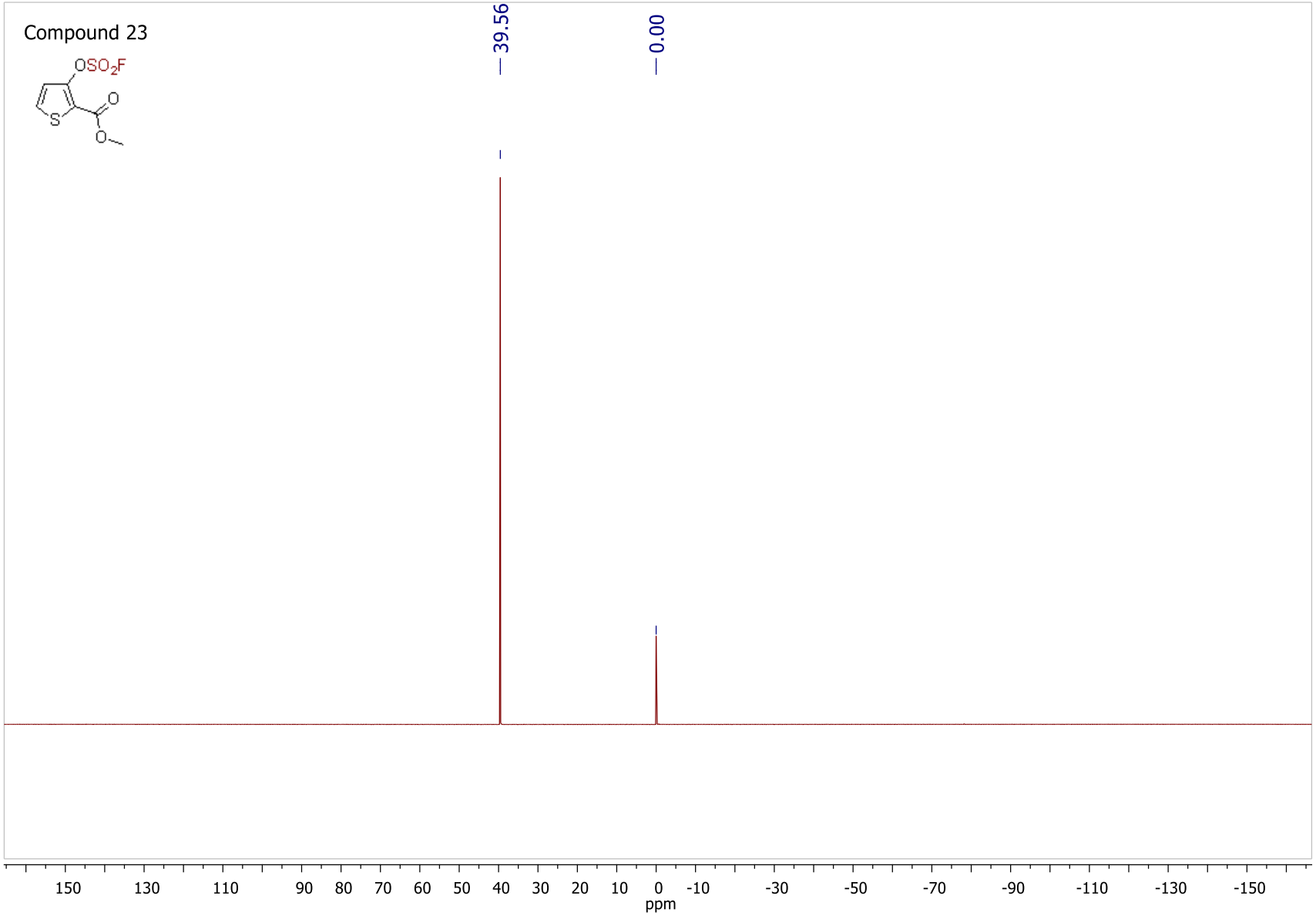

Compound 22
FO2SO
OSO2F
O
O
8.00
7.99
7.80
7.78
7.77
7.67
7.65
7.63
7.58
7.56
7.48
7.46
7.36
7.34
7.26 Chloroform-d
1.59
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3
ppm
1.00
1.03
1.02
1.01
4.02
4.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

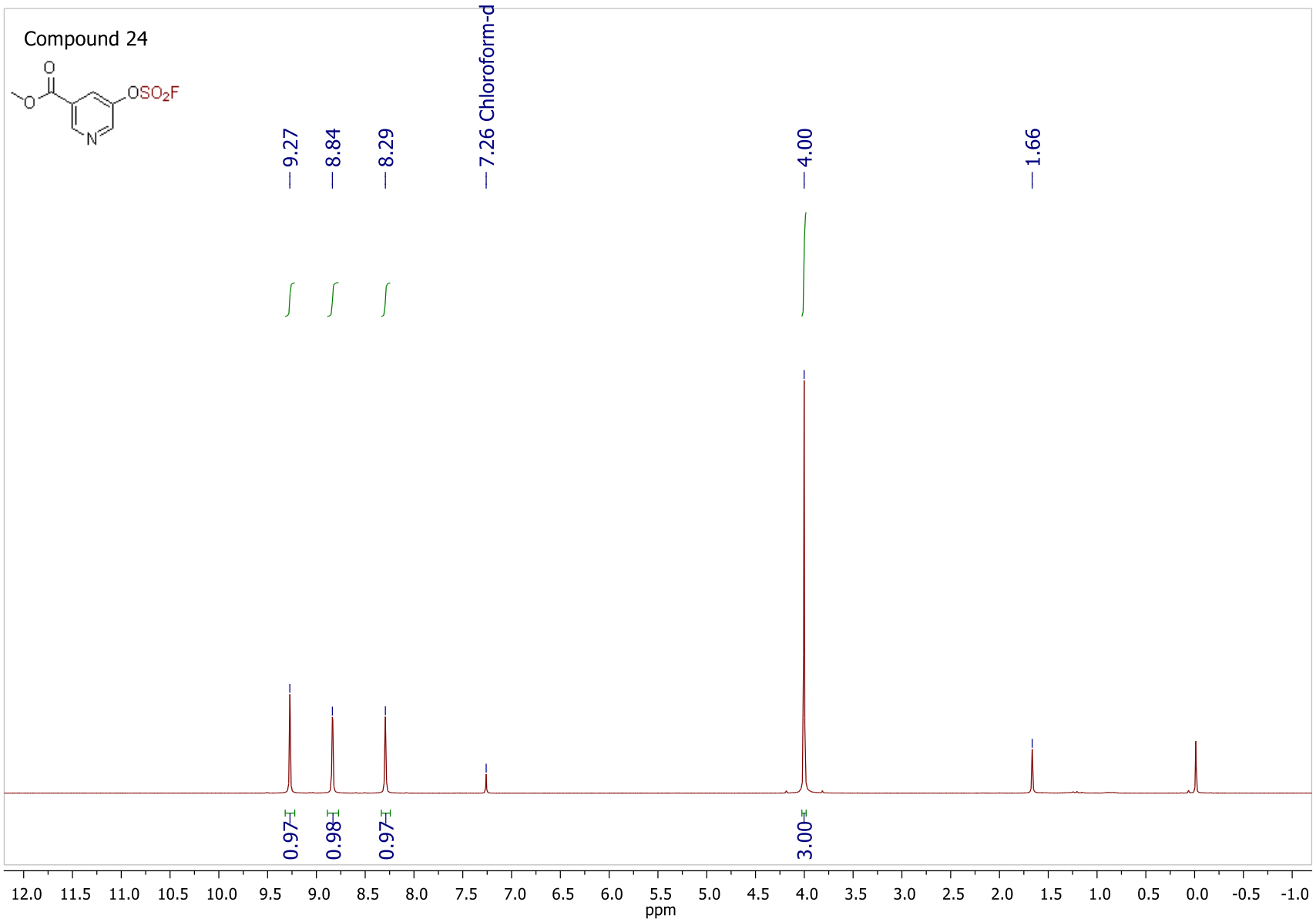

Compound 22
FO2SO
OSO2F
O
O
168.71
150.43
150.15
141.13
135.00
130.44
129.36
126.82
125.41
123.99
121.50
89.67
77.16 Chloroform-d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

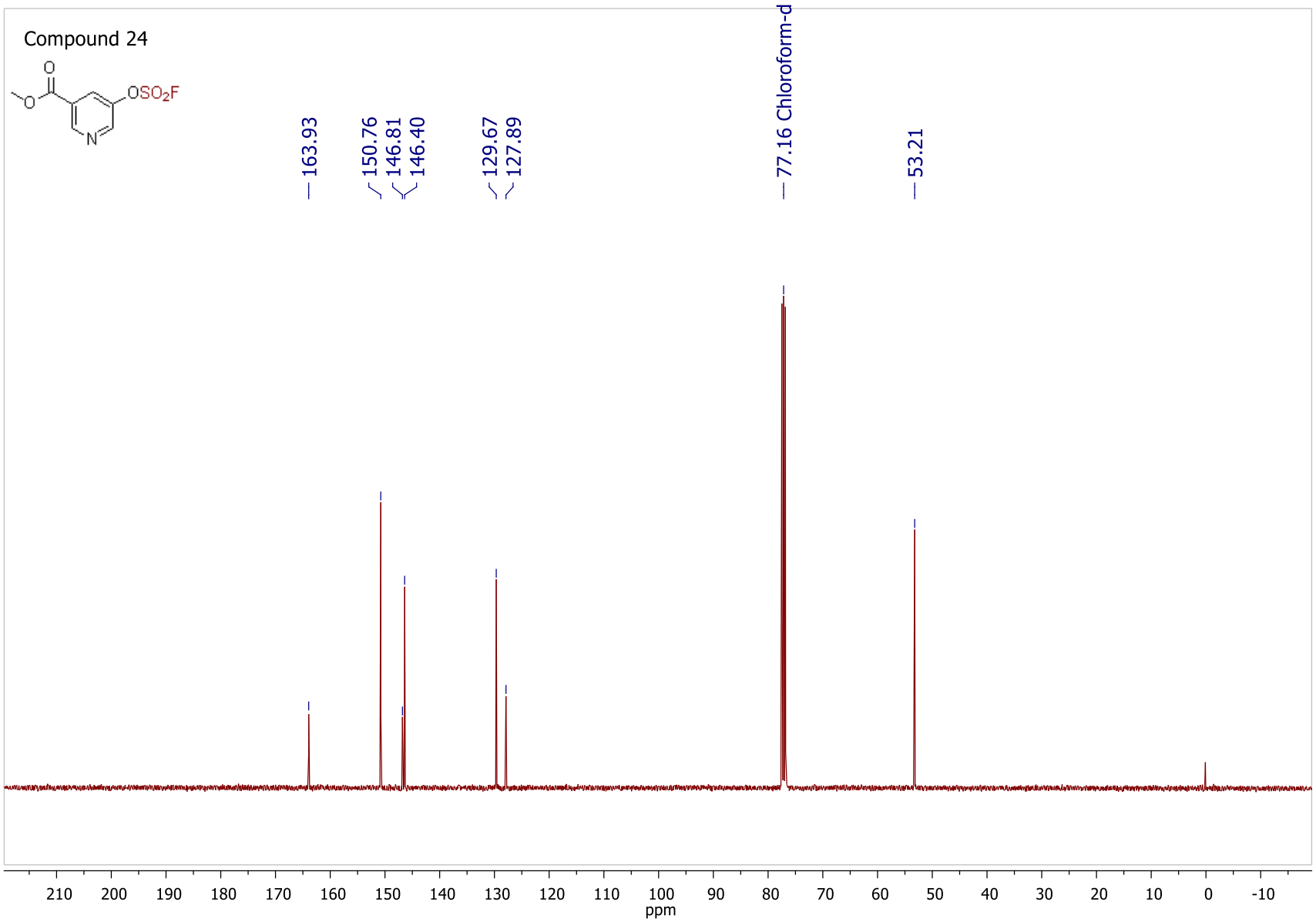

Compound 22
FO2SO
OSO2F
O
O
37.71
-0.00
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm

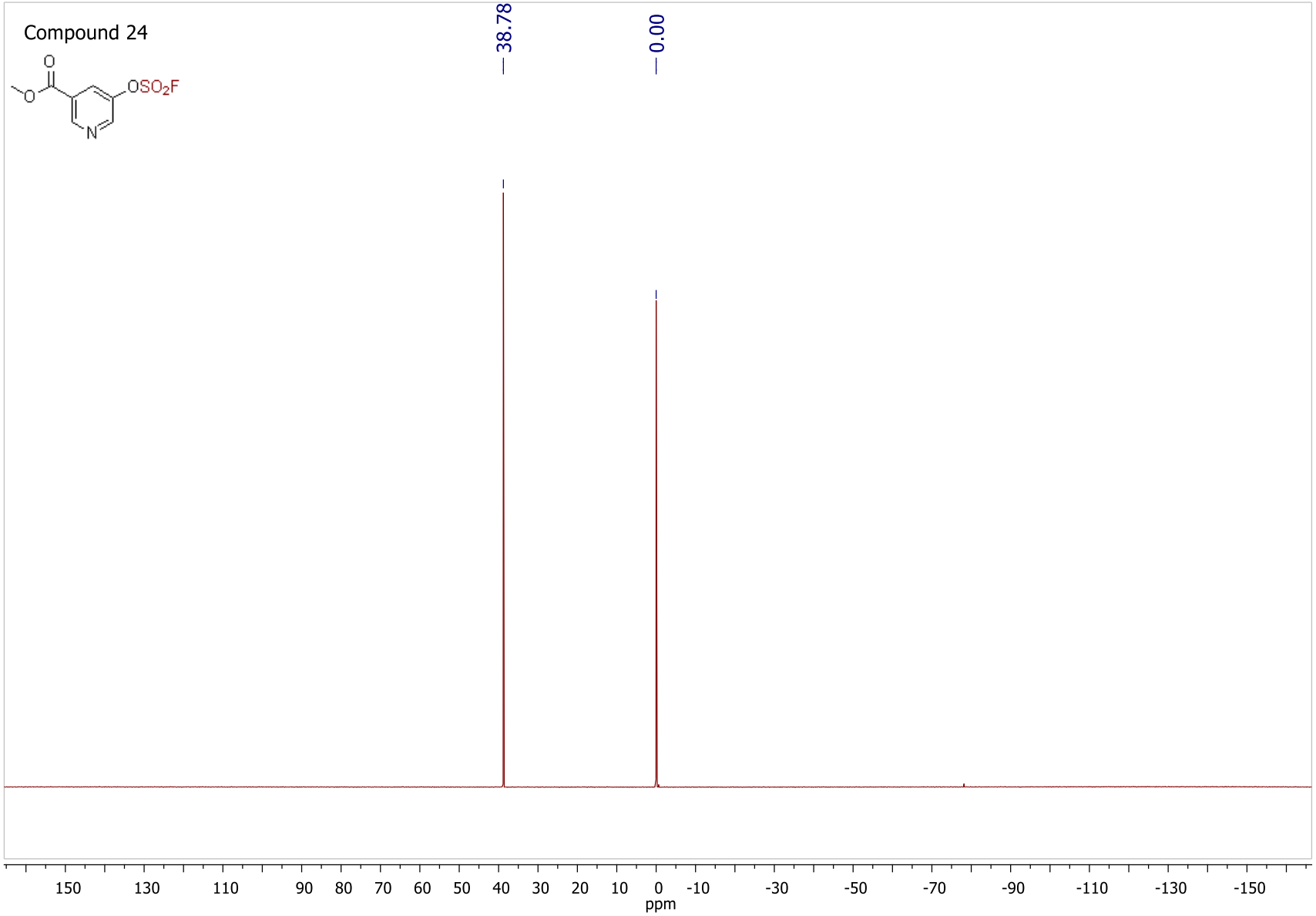

Compound 23
OSO2F
O
S
O
7.59
7.57
7.26 Chloroform-d
7.12
7.11
3.92
1.63
0.98
0.98
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

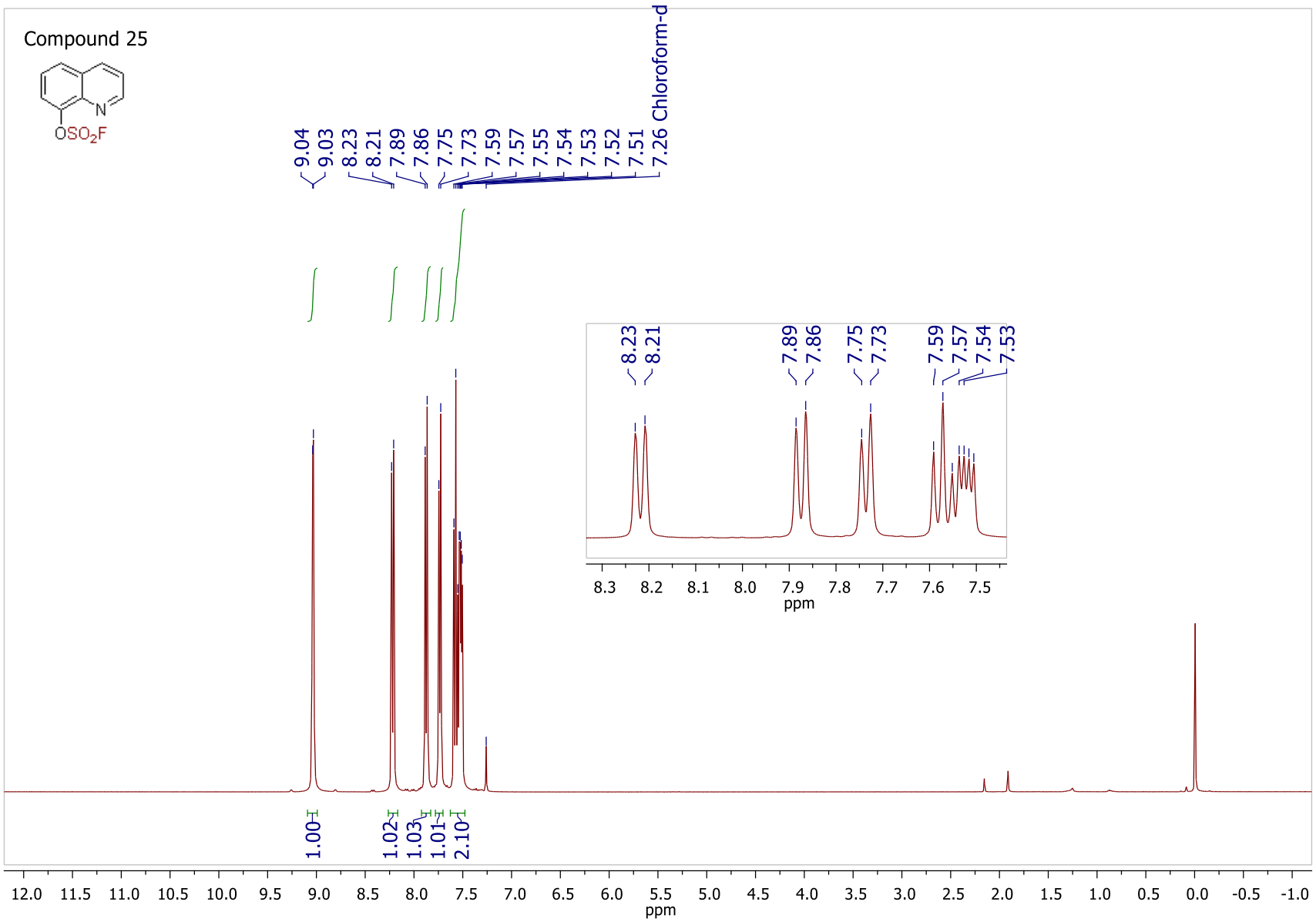

Compound 23
OSO2F
O
S
O
159.85
145.66
130.86
122.52
121.98
77.16 Chloroform-d
52.77
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

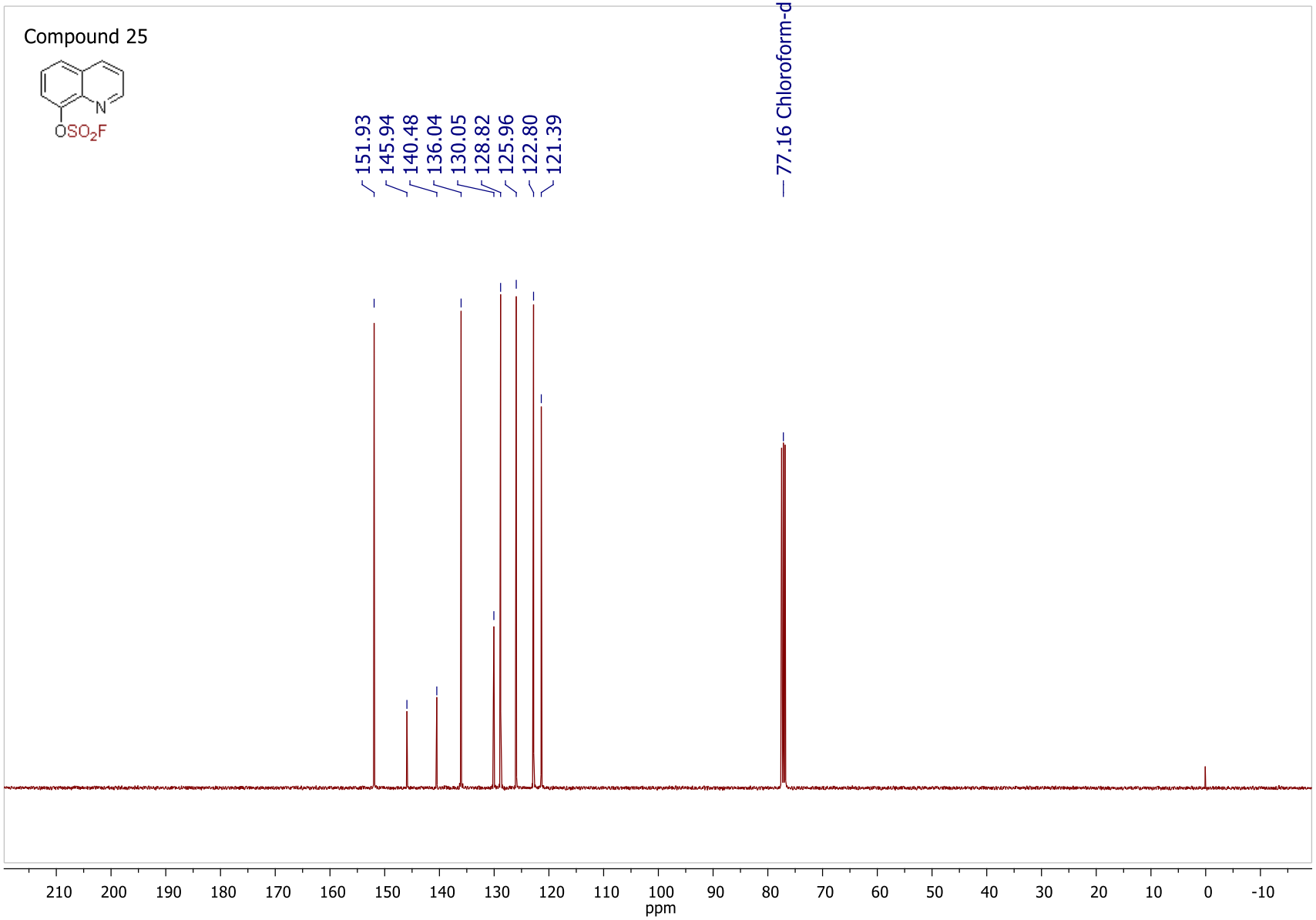

Compound 23
OSO2F
O
S
O
39.56
0.00
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm

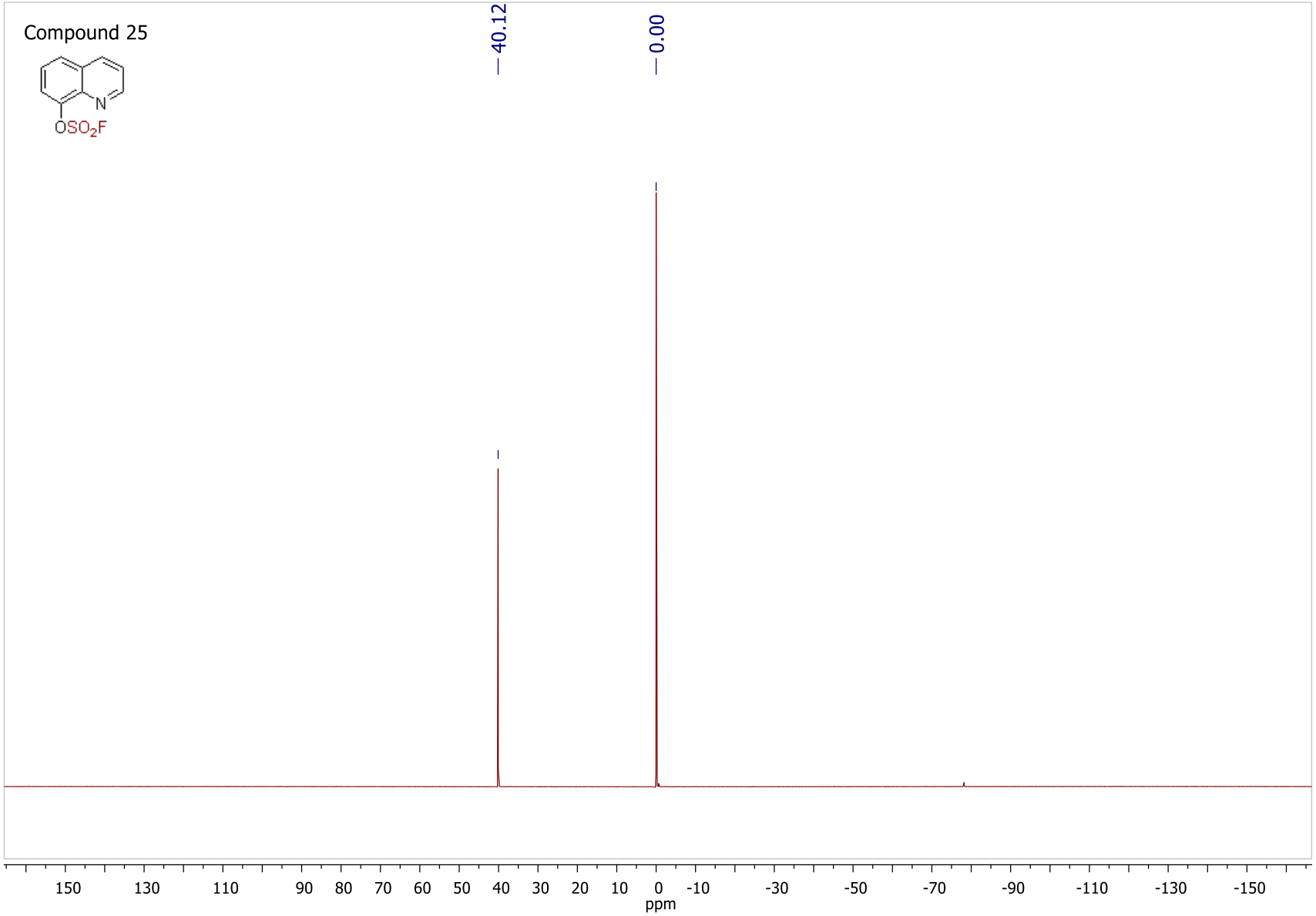

Compound 24
O
O
OSO2F
N
9.27
8.84
8.29
7.26 Chloroform-d
4.00
1.66
0.97
0.98
0.97
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

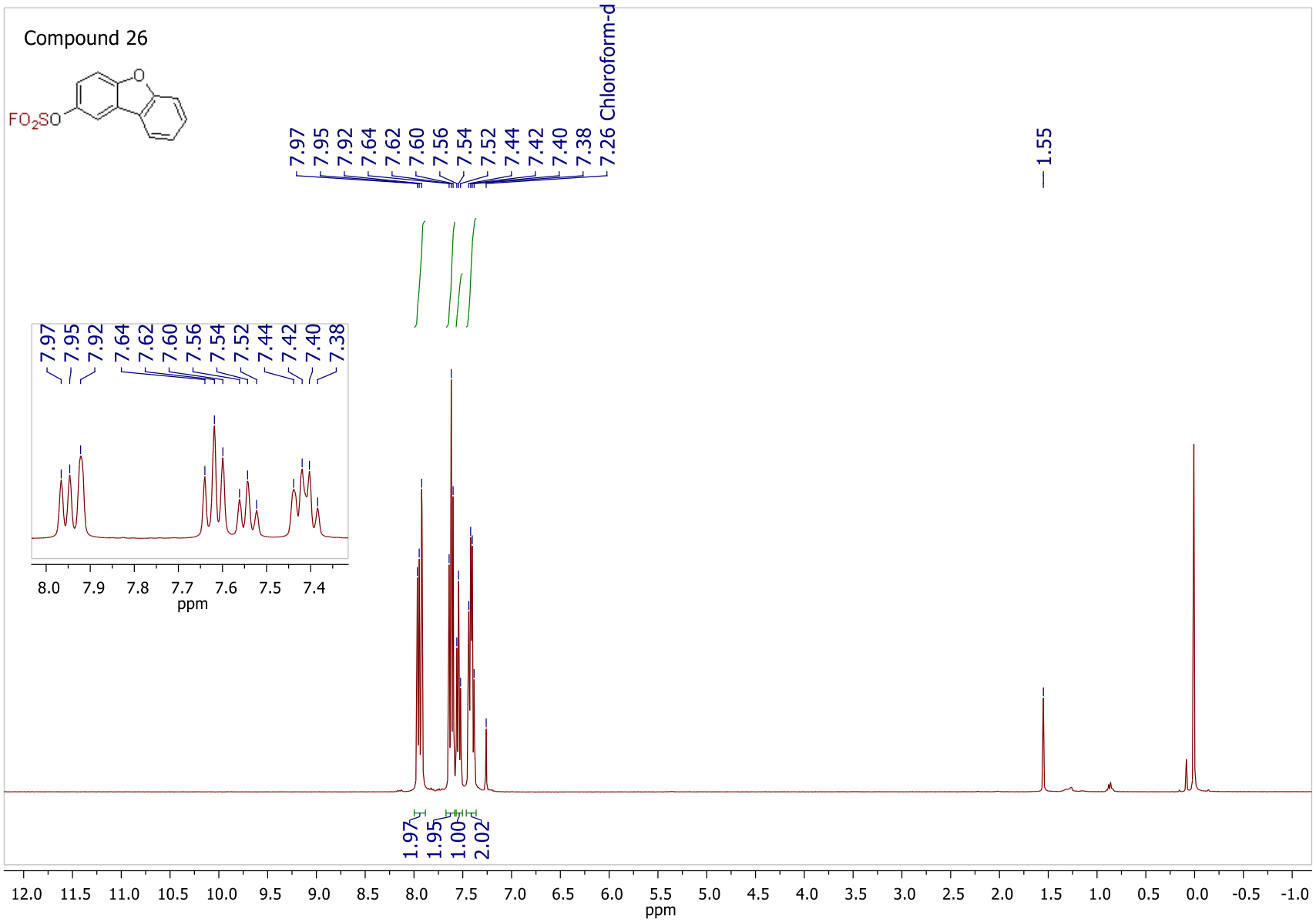

Compound 24
O
O
OSO2F
N
163.93
150.76
146.81
146.40
129.67
127.89
77.16 Chloroform-d
53.21
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

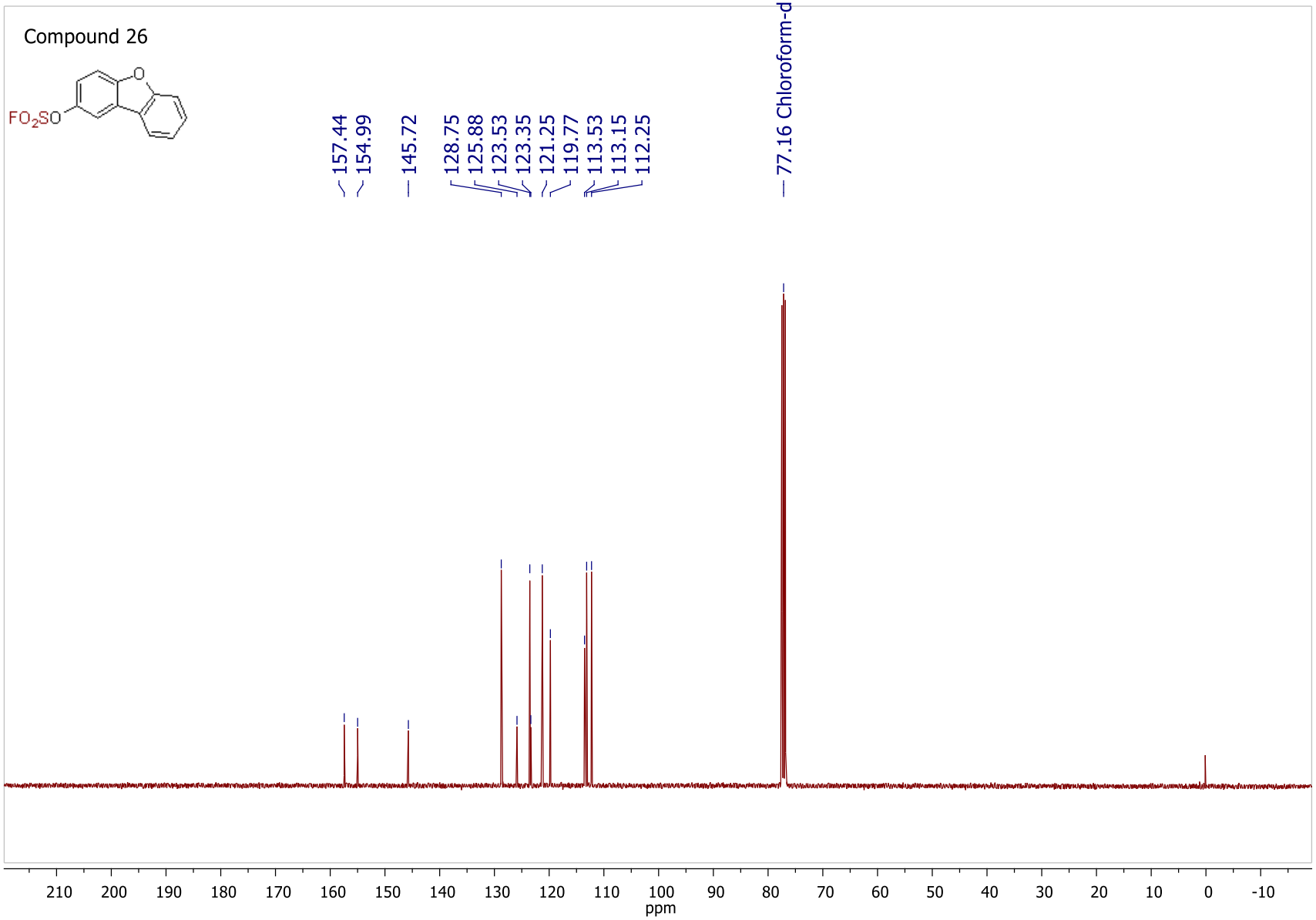

Compound 24
O
O
OSO2F
N
38.78
0.00
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm

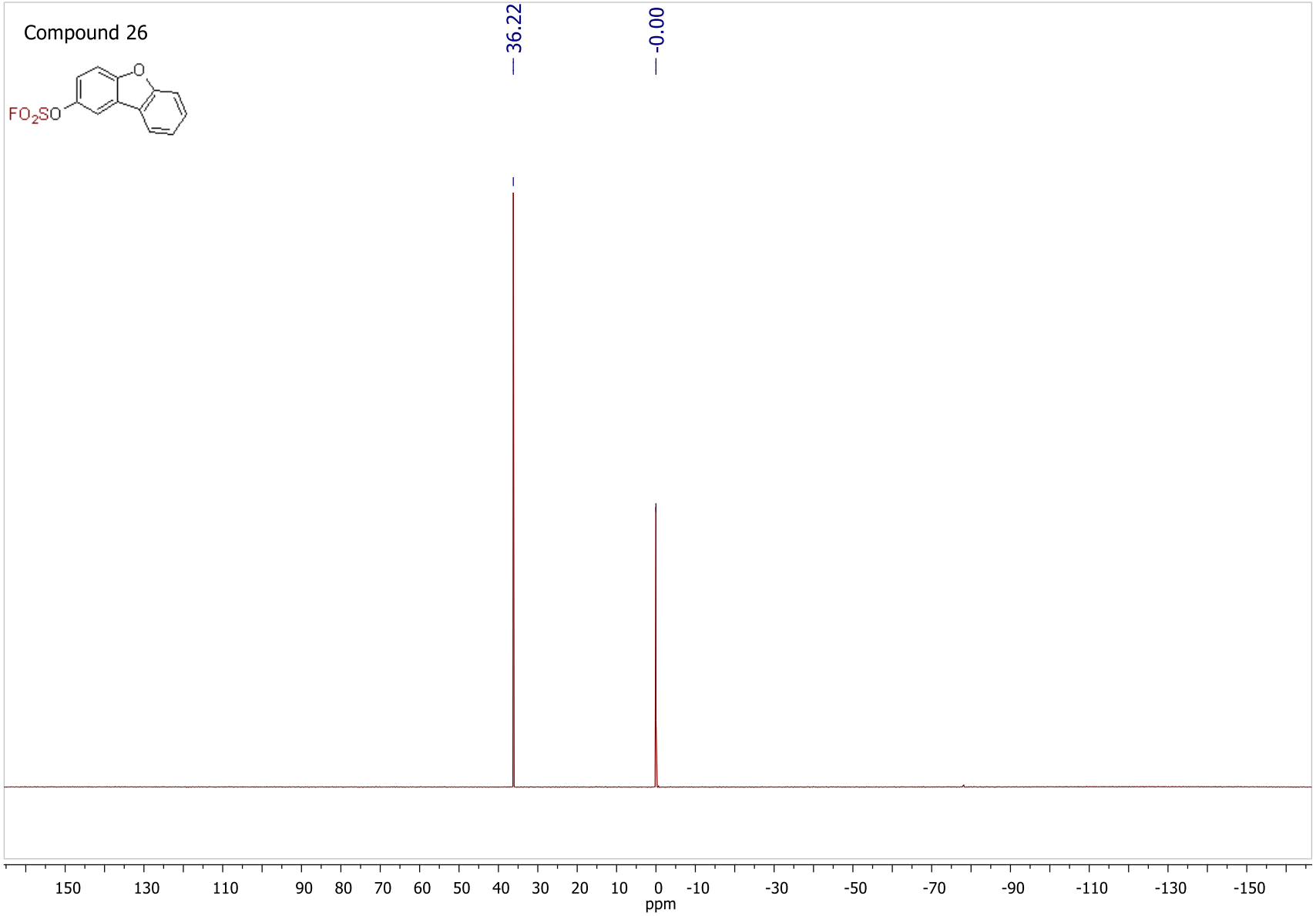

Compound 25
OSO2F
N
9.04
9.03
8.23
8.21
7.89
7.86
7.75
7.73
7.59
7.57
7.55
7.54
7.53
7.52
7.51
7.26 Chloroform-d
1.00
1.02
1.03
1.01
2.10
ppm

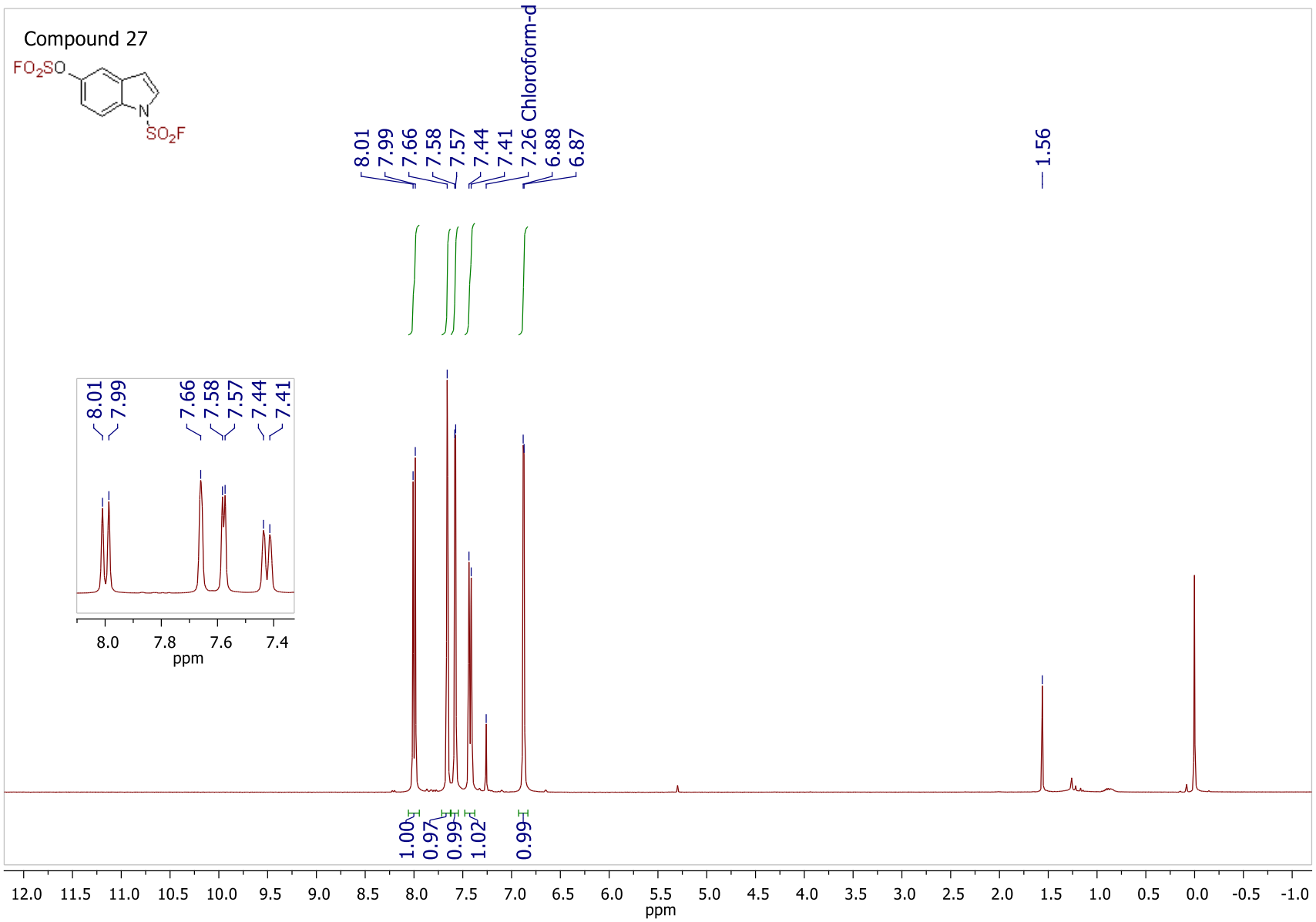

Compound 25
N
OSO2F
151.93
145.94
140.48
136.04
130.05
128.82
125.96
122.80
121.39
77.16 Chloroform-d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

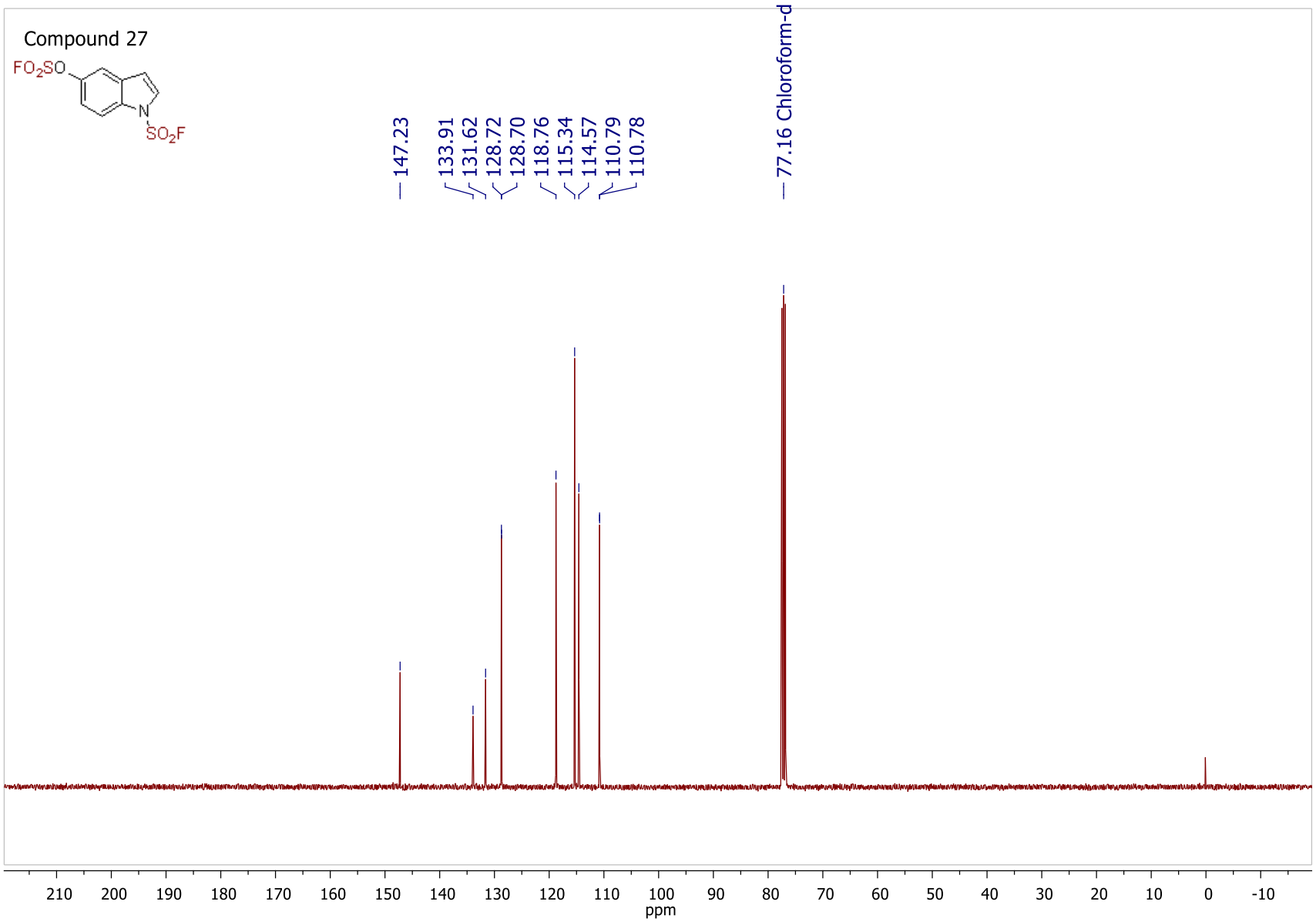

Compound 25
N
OSO2F
40.12
0.00
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm

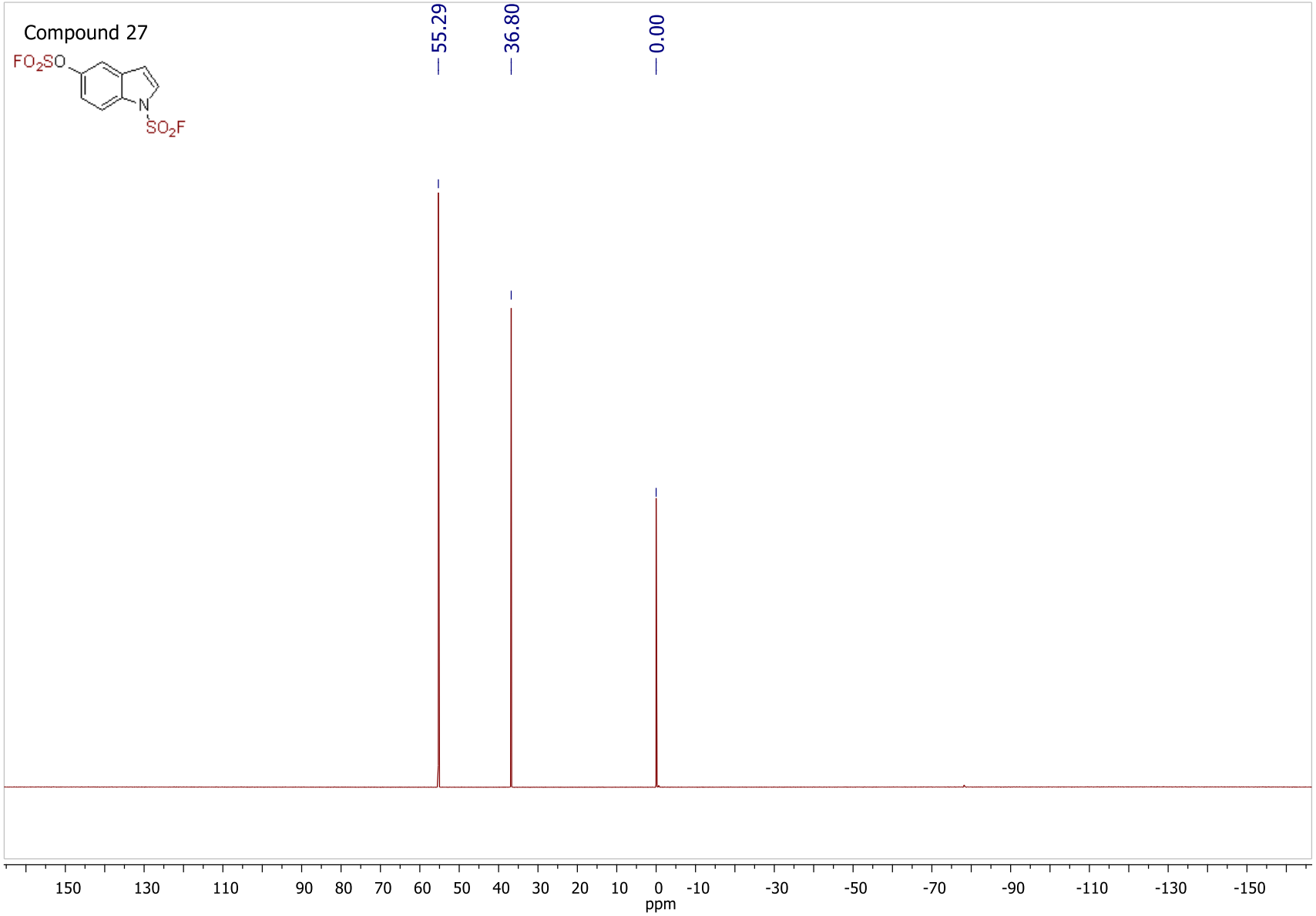

Compound 26
FO2SO
7.97
7.95
7.92
7.64
7.62
7.60
7.56
7.54
7.52
7.44
7.42
7.40
7.38
7.26 Chloroform-d
1.55
1.97
1.95
1.00
2.02
ppm


Compound 26
FO2SO
157.44
154.99
145.72
128.75
125.88
123.53
123.35
121.25
119.77
113.53
113.15
112.25
77.16 Chloroform-d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm


Compound 26
FO2SO
36.22
-0.00
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm


Compound 27
FO2SO
N
SO2F
8.01
7.99
7.66
7.58
7.57
7.44
7.41
7.26 Chloroform-d
6.88
6.87
1.56
1.00
0.97
0.99
1.02
0.99
ppm


Compound 27
FO2SO
N
SO2F
147.23
133.91
131.62
128.72
128.70
118.76
115.34
114.57
110.79
110.78
77.16 Chloroform-d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm


Compound 27
FO2SO
N
SO2F
55.29
36.80
0.00
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm

7. References

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