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Supporting Information

Photoredox-Catalyzed Radical Fluorosulfonylation of Allyl Sulfones

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Table of Contents

1 General Information 1
2 Preparation of the Starting Materials 2
3 General Procedure 5
4 Products Characterization 6
5 References 11
6 NMR Spectra 12

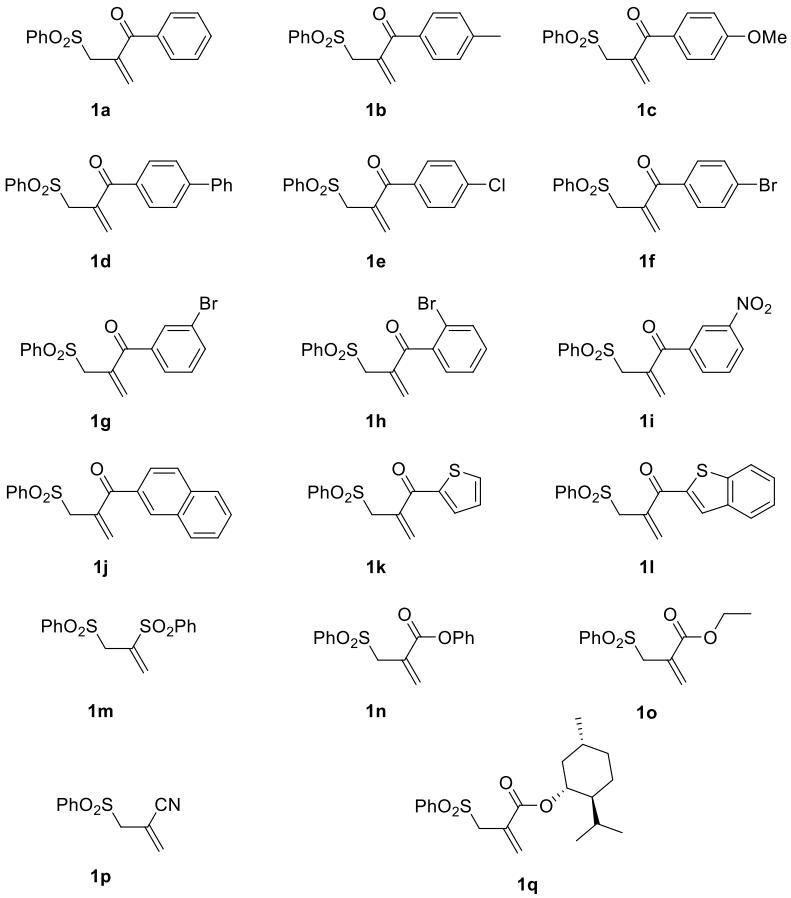
1 General Information

Unless otherwise stated, all glassware was oven dried. All solvents were distilled from appropriate drying agents prior to use. All reagents were used as received from commercial suppliers unless otherwise indicated. Reactions were monitored using Thin Layer Chromatography (TLC) carried out on Merck silica gel plates (60F-254), using short-wave UV light and $KMnO_4$ stain as the visualizing agent. Flash column chromatography was performed using silica gel 60 (200-300 mesh). High-resolution mass spectra (HRMS) were recorded on a Bruker MTQ III q-TOF instrument. All ^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra were recorded on Bruker DRX-600 and AMX-400 instruments. Chemical shifts were given in parts per million (ppm, δ), referenced to the solvent peak of $CDCl_3$, defined at δ = 7.26 (^{1}H NMR), defined at δ = 77.16 (^{13}C NMR). or ^{d}Acetone, defined at δ = 2.05 (^{1}H NMR), defined at δ = 206.26 (^{13}C NMR). Coupling constants were quoted in Hz (*J*). ^{1}H NMR spectroscopy splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad singlet (bs).

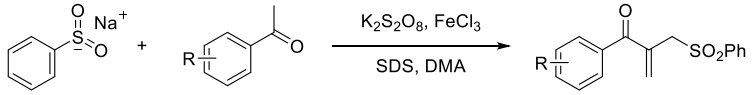
FSO_2Cl was prepared according to the literature procedure.[1]

2 Preparation of the Starting Materials

1a-q are known compounds and were synthesized according to the literature[2-6].



Procedure A: Synthesis of allyl sulfones **1a-1l**.

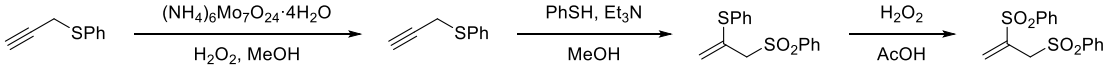


s1 **s2**

A 10 mL oven-dried reaction vessel was charged with $K_2S_2O_8$ (35.0 equiv.), sodium dodecyl (0.1 equiv.), FeCl3 (0.1 equiv.), **s1** (1.0 equiv), sulfatesodium benzenesulfinate (2.5 equiv.), and DMA under air. The sealed reaction vessel was stirred at 110 ºC for 14 h. After cooling to room temperature, the reaction was diluted with ethyl acetate (5 mL) and washed with saturated sodium chloride solution. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate for three times. The combined organic layer was dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **s2**.

These allyl sulfones **1a-l** have been reported previously[2].

Procedure B: Synthesis of allyl sulfones **1m**.



s3 **s4** **1m**

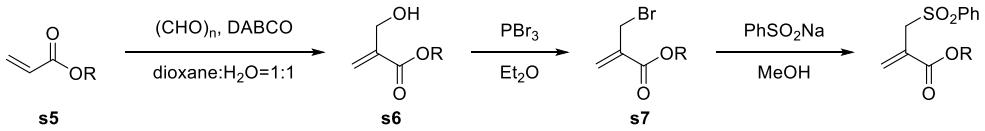
To a MeOH solution (100 mL) of phenyl propargyl sulfide (10.1 g, 68 mmol) and $(NH_4)_6Mo_7O_{24}$•$4H_2O$ (0.84 g, 0.68 mmol) was dropwisely added 30% aq H_2O_2 (34 mL, 333 mmol;) at 0 ºC under an argon atmosphere. The reaction mixture was stirred at room temperature for 15 h. The mixture was extracted with $CHCl_3$ and the combined organic layers were washed with water and brine, dried over Na_2SO_4, and concentrated. Phenyl propargyl sulfone **s3** was obtained in 99% yield (12.1 g) as a colorless solid, and used without further purification.

To a MeOH solution (80 mL) of phenyl propargyl sulfone **s3** (5.00 g, 27.7 mmol) were added benzenethiol (2.83 mL, 27.7mmol) and Et_3N (0.39 mL, 2.77 mmol) under an argon atmosphere. The reaction mixture was stirred at room temperature for 0.5 h. The mixture was concentrated, and the residue was purified to provide the vinyl sulfide **s4** in 99% yield (7.94 g) as a colorless oil. The vinyl sulfide **s4** can be stored in a freezer (–30 ºC).

To an AcOH solution (22 mL) of the vinyl sulfide **s4** (9.52 g, 32.8 mmol) was dropwisely added 30% aq H_2O_2 (26 mL, 252 mmol) at rt under an argon atmosphere. The reaction mixture was stirred at 80 ºC for 1 h and at rt for 15 h. After addition of water (120 mL), the reaction mixture was filtered to collect the colorless precipitate. The precipitate was recrystallized from CH_2Cl_2/hexane to provide the allyl sulfone **1m** in 86% yield (9.12 g) as a colorless solid.

These allyl sulfones **1m** have been reported previously[3].

Procedure C: Synthesis of allyl sulfones **1n, 1o, 1q**.



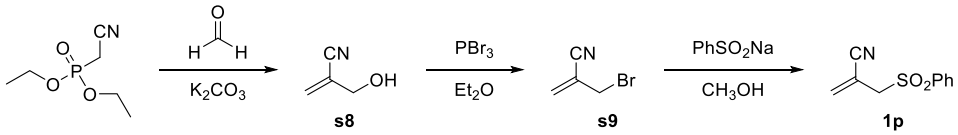
To a solution of paraformaldehyde (1.3 equiv.) and **s5** (1.0 equiv.) in dioxane-water (6 M, 1:1, v/v) was added DABCO (1.3 equiv.) and the reaction progress was monitored by TLC. Upon completion, the reaction mixture was partitioned with EtOAc and water. The organic layer was separated and washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford corresponding **s6**.

To a solution of **s6** was added phosphorus (III) bromide (1.88 mmol, 0.33 equiv.) in dry Et_2O (20 mL) at 0°C. The temperature was allowed to rise to 25°C and stirring was continued for 3 h. Water (10 mL) was then added and the mixture was extracted with petroleum ether (3 × 10 mL). The organic phase was washed with saturated aq. NaCl (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give corresponding **s7**.

To a solution of **s7** (1.0 equiv.) in dry methanol was added sodium phenylsulfinate (1.5 equiv.). After 2.5 h of reflux with a heating mantle, the mixture was concentrated under reduced pressure, the crude residue was dissolved in EtOAc and the mixture was washed with water, brine, dried with Na_2SO_4, filtered and the filtrate was evaporated and purified by column chromatography to afford **1n**, **1o** and **1q** .

These allyl sulfones **1n**, **1o**, **1q** have been reported previously[4-5].

Procedure D: Synthesis of allyl sulfones **1p**[6].



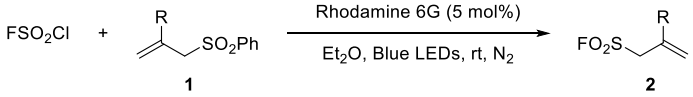
To a mixture of diethyl (cyanomethyl)phosphonate (20 mmol) and a 37% aqueous solution of formaldehyde (80 mmol), a saturated aqueous solution of potassium carbonate (37.5 mmol) was added at room temperature dropwise over 30 min. After stirring for an additional 2 h, the reaction was quenched with saturated aqueous ammonium chloride (20 mL). Afterwards, the reaction mixture was extracted with diethyl ether (3 × 12.5 mL). The organic layers were combined and dried over sodium sulfate. The solvent was evaporated using a rotary evaporator, and the remaining colorless oil was purified by flash chromatography using pentane/CH_2Cl_2 (2/1) giving the pure product **s8** as a colorless oil (70% yeild).

To a solution of **s8** (14 mmol) in dry ether (20 mL) was added phosphorus(III) bromide (5 mmol) at −10 °C. The temperature was allowed to rise to 20 °C and stirring was continued for 3 h. Water (10 mL) was then added and the mixture was extracted with diethyl ether (3 × 30 mL). The organic phase was washed with brine (20 mL), dried with sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (pentane/ CH_2Cl_2, 1/1) to give **s9** as a colorless oil (89% yield).

To a solution of **s9** (2.0 mmol) in methanol (5 mL) was added corresponding sodium aryl sulfinate (3.0 mmol). After 2.5 h of reflux, the mixture was concentrated under reduced pressure, the thereby obtained residue was dissolved in EtOAc and the mixture was washed with water, brine, dried with Na_2SO_4, filtered and the filtrate was evaporated and purified by chromatography (EtOAc/n-hexane, 1/1) to give corresponding products **1p**.

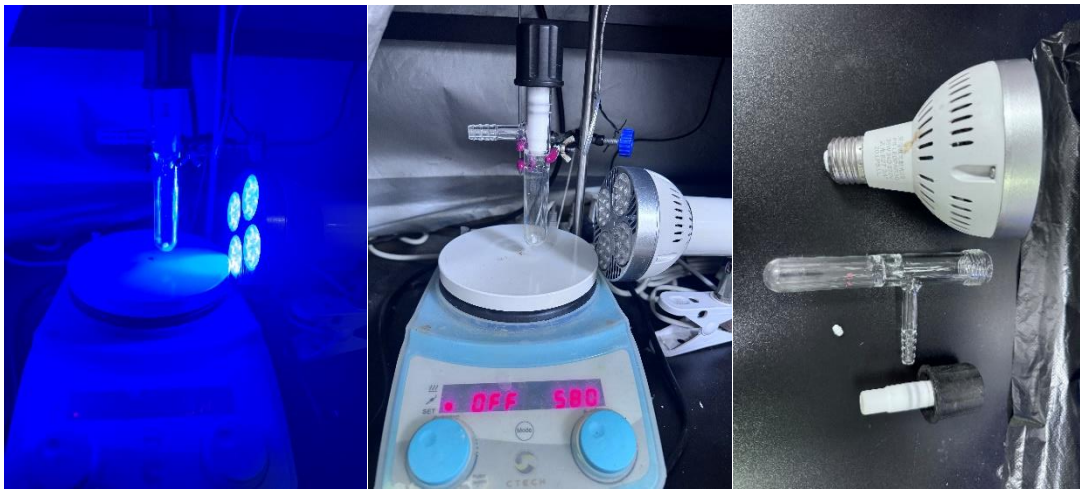
These allyl sulfones **1p** have been reported previously[6].

3 General Procedure

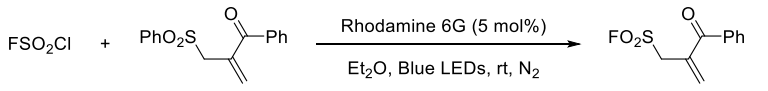


General Procedure:

A mixture of allyl sulfones **1** (0.1 mmol), FSO_2Cl (0.2 mmol, 2.0 equiv., 1 M in $PhCF_3$) Rhodamine 6G (5 mol%) and Et_2O (0.05 M) in a 10 mL Schlenk flask under N_2 atmosphere. The reaction mixture was stirred under the irradiation of 35 W Blue LED at room temperature for 24 h. The reaction mixture was quenched by EtOAc and concentrated in vacuo. The crude was purified by flash chromatography (petroleumether/ethyl acetate = 10/1 to 4/1) on silica gel to provide the corresponding products.



Large-Scale Synthesis：



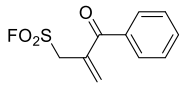
1 mmol, 286.3 mg

65 %,148.4 mg

A mixture of allyl sulfones **1** (1.0 mmol), FSO_2Cl (2.0 mmol, 2.0 equiv., 1 M in $PhCF_3$) Rhodamine 6G (5 mol%) and Et_2O (0.05 M) in a 50 mL Schlenk flask under N_2 atmosphere. The reaction mixture was stirred under the irradiation of 35 W Blue LED at room temperature for 24 h. The reaction mixture was quenched by EtOAc and concentrated in vacuo. The crude was purified by flash chromatography (petroleumether/ethyl acetate = 10/1 to 4/1) on silica gel to provide the corresponding products.

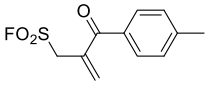
4 Products Characterization

2-Benzoylprop-2-ene-1-sulfonyl fluoride (2a)



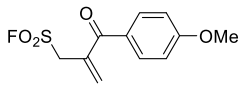
Yellow oil; 20h; 20.6 mg, 90% yield; R_f = 0.6, petroleum ether/ethyl acetate = 4/1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 6.45 (s, 1H), 6.20 (s, 1H), 4.62 (d, *J* = 4.6 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 194.1, 136.0, 134.9, 134.4, 133.3, 129.8, 128.7, 52.3 (d, *J* = 18.7 Hz).
^{19}F NMR (565 MHz, $CDCl_3$) δ 54.3.
HRMS-ESI *m/z*: $[M+H]^+$ calculated for $C_{10}H_{10}FO_3S$ 229.0329; found 229.0334.

2-(4-Methylbenzoyl)prop-2-ene-1-sulfonyl fluoride (2b)



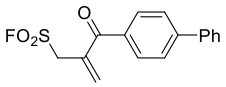
Yellow oil; 24 h; 16.0 mg, 66% yield; R_f = 0.6, petroleum ether/ethyl acetate = 4/1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.40 (s, 1H), 6.17 (s, 1H), 4.61 (d, *J* = 4.6 Hz, 2H), 2.43 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 193.8, 144.4, 134.4, 134.1, 133.3, 130.0, 129.4, 52.5 (d, *J* = 18.6 Hz), 21.8.
^{19}F NMR (565 MHz, $CDCl_3$) δ 54.3.
HRMS-ESI *m/z*: $[M+Na]^+$ calculated for $C_{11}H_{11}FNaO_3S$ 265.0305; found 265.0307.

2-(4-Methoxybenzoyl)prop-2-ene-1-sulfonyl fluoride (2c)



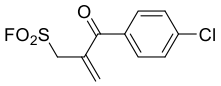
Yellow oil; 24 h; 18.6 mg, 73% yield; R_f = 0.6, petroleum ether/ethyl acetate = 4/1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.34 (s, 1H), 6.13 (s, 1H), 4.60 (d, *J* = 4.6 Hz, 2H), 3.88 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 192.7, 164.1, 134.4, 133.1, 132.4, 128.5, 114.1, 55.7, 52.9 (d, *J* = 18.4 Hz).
^{19}F NMR (377 MHz, $CDCl_3$) δ 54.2.
HRMS-ESI *m/z*: $[M+Na]^+$ calculated for $C_{11}H_{11}FNaO_4S$ 281.0254; found 281.0258.

2-([1,1'-Biphenyl]-4-carbonyl)prop-2-ene-1-sulfonyl fluoride (2d)



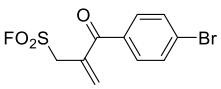
Yellow oil; 24 h; 28.3 mg, 93% yield. R_f = 0.5, petroleum ether/ethyl acetate = 4/1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 – 7.86 (m, 2H), 7.74 – 7.69 (m, 2H), 7.64 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.49 (dd, *J* = 10.3, 4.8 Hz, 2H), 7.45 – 7.40 (m, 1H), 6.46 (s, 1H), 6.25 (s, 1H), 4.65 (d, *J* = 4.5 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 193.7, 146.2, 139.8, 134.6, 134.5, 134.4, 130.5, 129.2, 128.5, 127.4, 127.4, 52.5 (d, *J* = 18.6 Hz).
^{19}F NMR (565 MHz, $CDCl_3$) δ 54.3.
HRMS-ESI *m/z*: $[M+H]^+$ calculated for $C_{16}H_{14}FO_3S$ 305.0642; found 305.0640.

2-(4-Chlorobenzoyl)prop-2-ene-1-sulfonyl fluoride (2e)



Yellow oil; 22 h; 21.3 mg, 81% yield; R_f = 0.6, petroleum ether/ethyl acetate = 4/1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 – 7.72 (m, 2H), 7.50 – 7.45 (m, 2H), 6.44 (s, 1H), 6.17 (s, 1H), 4.61 (d, *J* = 4.4 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 192.9, 140.0, 134.6, 134.3, 134.2, 131.2, 129.2, 52.4 (d, *J* = 18.8 Hz).
^{19}F NMR (377 MHz, $CDCl_3$) δ 54.4.
HRMS-ESI *m/z*: $[M+Na]^+$ calculated for $C_{10}H_8ClFNaO_3S$ 284.9759; found 284.9761.

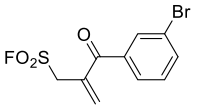
2-(4-Bromobenzoyl)prop-2-ene-1-sulfonyl fluoride (2f)



Yellow oil; 24 h; 20.9 mg, 68% yield. R_f = 0.6, petroleum ether/ethyl acetate = 4/1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 – 7.61 (m, 4H), 6.44 (s, 1H), 6.16 (s, 1H), 4.61 (d, *J* = 4.5 Hz, 2H).

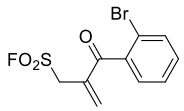
^{13}C NMR (150 MHz, $CDCl_3$) δ 193.1, 134.7, 134.7, 134.3, 132.1, 131.3, 128.6, 52.3 (d, *J* = 18.9 Hz).
^{19}F NMR (377 MHz, $CDCl_3$) δ 54.4.
HRMS-ESI *m/z*: $[M+Na]^+$ calculated for $C_{10}H_8BrFNaO_3S$ 328.9254; found 328.9257.

2-(3-Bromobenzoyl)prop-2-ene-1-sulfonyl fluoride (2g)



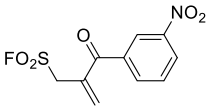
Yellow oil; 22 h;15.1 mg, 49% yield; R_f = 0.7, petroleum ether/ethyl acetate = 4/1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 5.1 Hz, 1H), 7.72 (ddd, *J* = 30.8, 9.6, 6.2 Hz, 1H), 7.37 (dd, *J* = 9.7, 5.7 Hz, 1H), 6.49 (d, *J* = 6.5 Hz, 1H), 6.21 (d, *J* = 3.7 Hz, 1H), 4.61 (t, *J* = 5.5 Hz, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 192.6, 137.8, 136.2, 135.4, 134.2, 132.5, 130.3, 128.3, 123.0, 52.2 (d, *J* = 18.8 Hz).
^{19}F NMR (565 MHz, $CDCl_3$) δ 54.4.
HRMS-ESI *m/z*: $[M+NH_4]^+$ calculated for $C_{10}H_{12}BrFNO_3S$ 323.9700; found 323.9699.

2-(2-Bromobenzoyl)prop-2-ene-1-sulfonyl fluoride (2h)



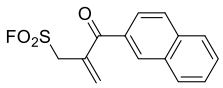
Yellow oil; 24 h; 19.7 mg, 32% yield. R_f = 0.6, petroleum ether/ethyl acetate = 4/1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.41 (td, *J* = 7.5, 1.0 Hz, 1H), 7.36 (td, *J* = 7.7, 1.8 Hz, 1H), 7.30 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.61 (s, 1H), 6.18 (s, 1H), 4.61 (d, *J* = 4.3 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 193.8, 138.6, 138.5, 134.7, 133.6, 131.9, 129.1, 127.4, 119.6, 50.0 (d, *J* = 19.3 Hz).
^{19}F NMR (565 MHz, $CDCl_3$) δ 54.8.
HRMS-ESI *m/z*: $[M+NH_4^+]^+$ calculated for $C_{10}H_{12}BrFNO_3S$: 323.9700; found 323.9706.

2-(3-Nitrobenzoyl)prop-2-ene-1-sulfonyl fluoride (2i)



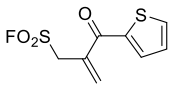
Yellow oil; 18 h; 8.8 mg, 32% yield； R_f = 0.4, petroleum ether/ethyl acetate = 4/1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.60 (t, *J* = 1.9 Hz, 1H), 8.47 (ddd, *J* = 8.2, 2.1, 0.9 Hz, 1H), 8.10 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.72 (t, *J* = 7.9 Hz, 1H), 6.55 (s, 1H), 6.22 (s, 1H), 4.65 (d, *J* = 4.6 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 191.8, 148.5, 137.4, 135.7, 135.2, 134.1, 130.2, 127.6, 124.5, 52.2 (d, *J* = 19.2 Hz).
^{19}F NMR (565 MHz, $CDCl_3$) δ 54.6.
HRMS-ESI *m/z*: $[M+NH_4]^+$ calculated for $C_{10}H_{12}FN_2O_5S$ 291.0445; found 291.0447.

2-(2-Naphthoyl)prop-2-ene-1-sulfonyl fluoride (2j)



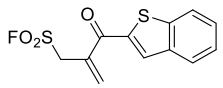
Yellow oil; 24 h; 17.6 mg,63% yield; R_f = 0.6, petroleum ether/ethyl acetate = 4/1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.95 (dd, *J* = 16.7, 8.3 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.86 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.60 – 7.56 (m, 1H), 6.49 (s, 1H), 6.27 (s, 1H), 4.68 (d, *J* = 4.4 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 194.1, 135.7, 134.7, 134.5, 133.2, 132.3, 131.7, 129.7, 128.9, 128.9, 128.0, 127.2, 125.2, 52.5 (d, *J* = 18.6 Hz).
^{19}F NMR (565 MHz, $CDCl_3$) δ 54.5.
HRMS-ESI *m/z*: $[M+H]^+$ calculated for $C_{14}H_{12}FO_3S$ 279.0486; found 279.0482.

2-(Thiophene-2-carbonyl)prop-2-ene-1-sulfonyl fluoride (2k)



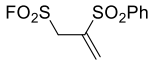
Yellow oil; 18 h; 16.0 mg, 68% yield; R_f = 0.7, petroleum ether/ethyl acetate = 4/1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 11.8, 4.3 Hz, 2H), 7.18 (dd, *J* = 4.6, 4.1 Hz, 1H), 6.41 (s, 1H), 6.35 (s, 1H), 4.58 (d, *J* = 4.5 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 185.3, 141.4, 135.5, 135.1, 134.5, 132.7, 128.4, 52.7 (d, *J* = 18.9 Hz).
^{19}F NMR (565 MHz, $CDCl_3$) δ 54.2.
HRMS-ESI *m/z*: $[M+H]^+$ calculated for $C_8H_8FO_3S_2$ 234.9894; found 234.9893.

2-(3a,7a-Dihydrobenzo[b]thiophene-2-carbonyl)prop-2-ene-1-sulfonyl fluoride (2l)



Yellow oil; 22 h;10.3 mg, 36% yield; R_f = 0.4, petroleum ether/ethyl acetate = 4/1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.95 – 7.88 (m, 2H), 7.54 – 7.49 (m, 1H), 7.46 – 7.42 (m, 1H), 6.50 (s, 1H), 6.42 (s, 1H), 4.61 (d, *J* = 4.3 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 186.8, 143.2, 140.9, 138.8, 134.4, 133.2, 132.6, 128.2, 126.5, 125.5, 123.1, 52.7 (d, *J* = 18.9 Hz).
^{19}F NMR (565 MHz, $CDCl_3$) δ 54.41 (t, *J* = 4.6 Hz).
HRMS-ESI *m/z*: $[M+H]^+$ calculated for $C_{12}H_{10}FO_3S_2$ 285.0050; found 285.0046.

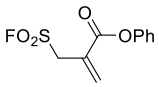
2-(Phenylsulfonyl)prop-2-ene-1-sulfonyl fluoride (2m)



Yellow oil; 20 h; 7.7 mg,29% yield; R_f = 0.4, petroleum ether/ethyl acetate = 4/1.

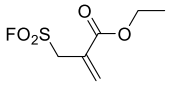
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.70 (dd, *J* = 10.6, 4.2 Hz, 1H), 7.60 (dd, *J* = 11.0, 4.6 Hz, 2H), 6.87 (s, 1H), 6.49 (s, 1H), 4.37 (d, *J* = 3.4 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 138.1, 137.4, 134.8, 132.7, 129.9, 128.7, 49.4 (d, *J* = 21.3 Hz).
^{19}F NMR (565 MHz, $CDCl_3$) δ 56.1.
HRMS-ESI *m/z*: $[M+NH_4^+]^+$ calculated for $C_9H_{13}FNO_4S_2$:282.0265; found 282.0269.

Phenyl 2-((fluorosulfonyl)methyl)acrylate (2n)



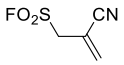
Yellow oil; 20 h; 13.0 mg, 53% yield; R_f = 0.4, petroleum ether/ethyl acetate = 4/1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 2H), 7.31 – 7.23 (m, 1H), 7.15 (dt, *J* = 8.9, 1.8 Hz, 2H), 6.96 (s, 1H), 6.36 (s, 1H), 4.54 (d, *J* = 4.3 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 162.9, 150.5, 136.5, 129.8, 127.2, 126.6, 121.5, 52.2 (d, *J* = 19.5 Hz).
^{19}F NMR (565 MHz, $CDCl_3$) δ 53.8.
HRMS-ESI *m/z*: $[M+NH_4]^+$ calculated for $C_{10}H_{13}FNO_4S$ 262.0544; found 262.0541.

Ethyl 2-((fluorosulfonyl)methyl)acrylate (2o)



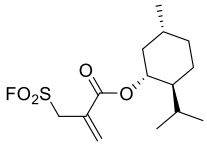
Yellow oil; 20 h;16.7 mg, 85% yield; R_f = 0.7, petroleum ether/ethyl acetate = 4/1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.72 (s, 1H), 6.18 (s, 1H), 4.44 (d, *J* = 4.4 Hz, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 164.1, 134.6, 127.4, 62.2, 52.0 (d, *J* = 19.1 Hz), 14.1.
HRMS-ESI *m/z*: $[M+Na]^+$ calculated for $C_6H_9FNaO_4S$ 219.0098; found 219.0099.

2-Cyanoprop-2-ene-1-sulfonyl fluoride (2p)



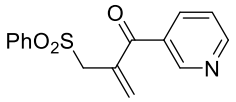
Yellow oil; 16 h; 7.6 mg, 51% yield; R_f = 0.5, petroleum ether/ethyl acetate = 4/1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.47 (s, 1H), 6.32 (s, 1H), 4.24 (d, *J* = 4.0 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 141.2, 115.7, 109.7, 54.3, 54.1.
^{19}F NMR (565 MHz, $CDCl_3$) δ 55.3.
HRMS-ESI *m/z*: $[M-H]^-$ calculated for $C_4H_3FNO_2S$ 147.9869; found 147.9868

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 2-((fluorosulfonyl)methyl)acrylate (2q)

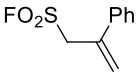


Yellow oil; 24 h; 20.8 mg, 68% yield; R_f = 0.6, petroleum ether/ethyl acetate = 4/1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.68 (s, 1H), 6.15 (s, 1H), 4.83 (td, *J* = 10.9, 4.4 Hz, 1H), 4.43 (d, *J* = 3.7 Hz, 2H), 2.05 – 2.00 (m, 1H), 1.84 (tt, *J* = 9.7, 3.5 Hz, 1H), 1.74 – 1.66 (m, 2H), 1.54 – 1.42 (m, 2H), 1.11 – 1.01 (m, 2H), 0.91 (dd, *J* = 12.2, 6.8 Hz, 7H), 0.76 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 163.8, 134.3, 127.9, 52.2 (d, *J* = 19.1 Hz), 47.2, 40.7, 34.3, 31.6, 26.5, 23.6, 22.1, 20.8, 16.4.
^{19}F NMR (565 MHz, $CDCl_3$) δ 53.6.
HRMS-ESI *m/z*: $[M+NH_4]^+$ calculated for $C_{14}H_{27}FNO_4S$: 324.1639; found 324.1636.

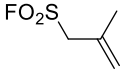
Unsuccessful substrates



not observed



13%



<10%

5 References

1. Prakash Reddy, V.; Bellew, D. R.; Prakash, G. K. S. A convenient preparation of sulfuryl chloride fluoride. J. Fluorine Chem. 1992, 56, 195-197.
2 F. Xiao, C. Liu, D. Wang, H. Huang and G.-J. Deng, Concise synthesis of ketoallyl sulfones through an iron-catalyzed sequential four-component assembly, *Green Chem.*, 2018, **20**, 973-977.
3. S. Kamijo, K. Kamijo, K. Maruoka and T. Murafuji, Aryl Ketone Catalyzed Radical Allylation of C(sp3)–H Bonds under Photoirradiation, *Org. Lett.*, 2016, **18**, 6516-6519.
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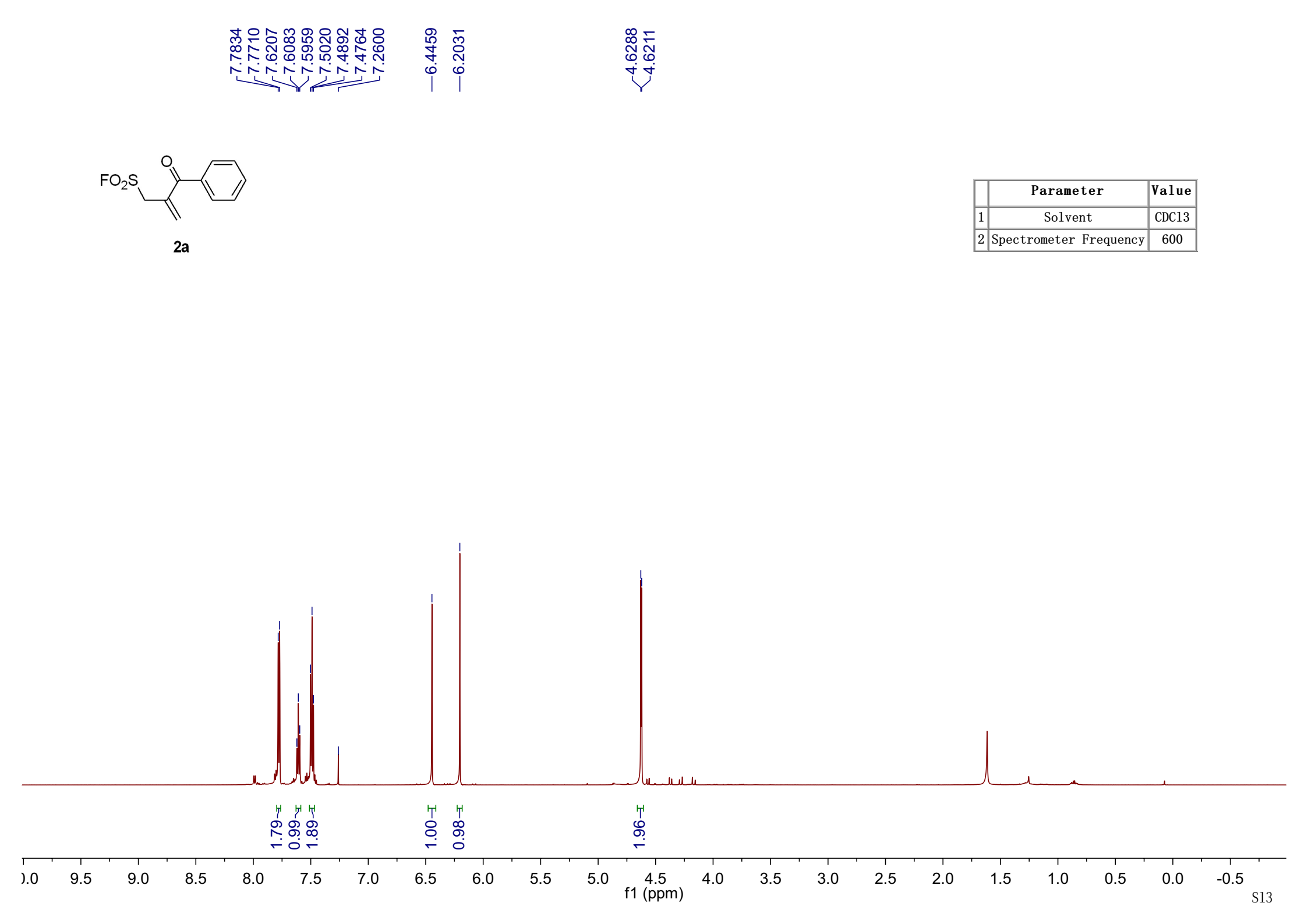
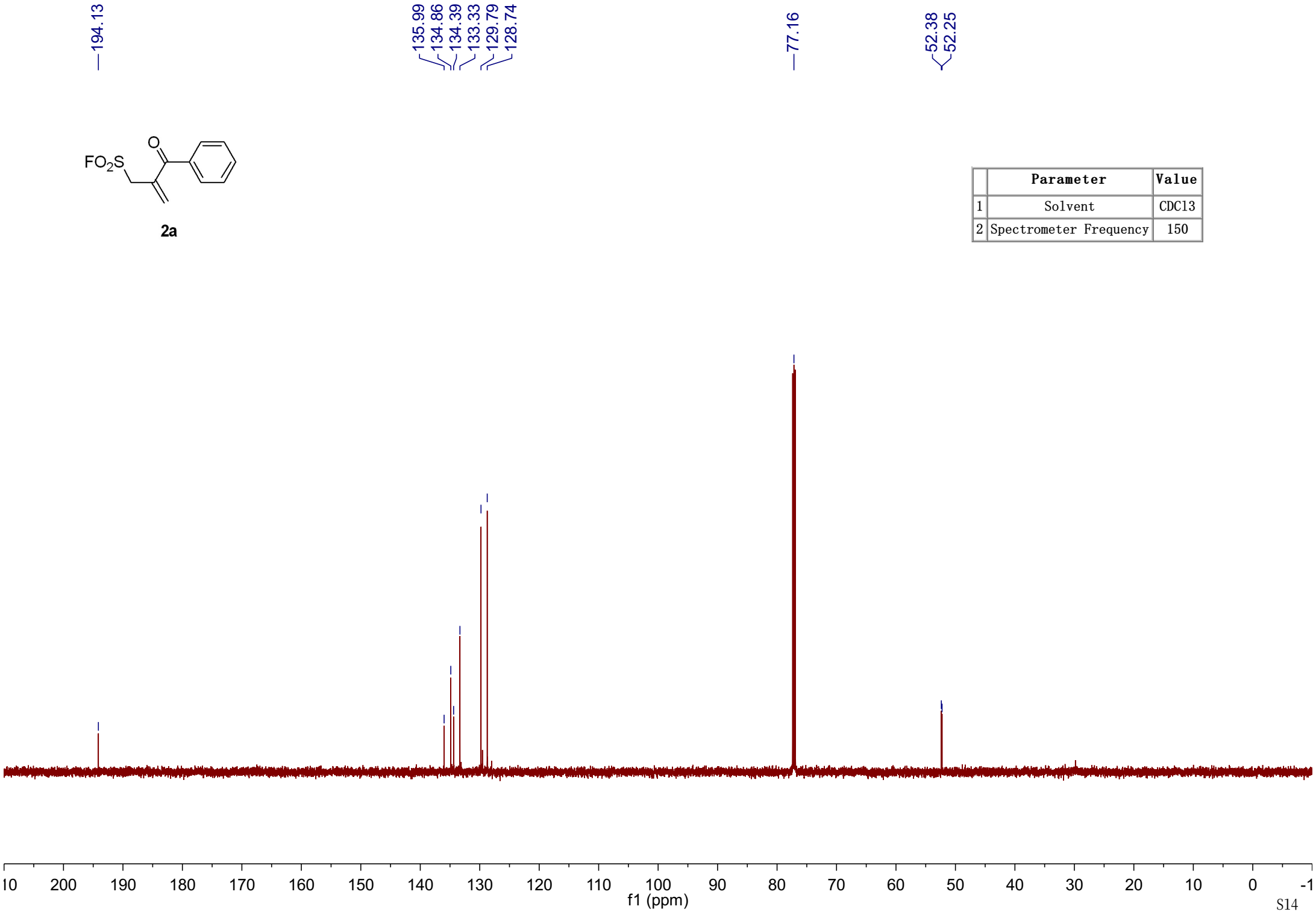
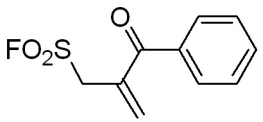
5. F. Wang, Y. Tang, X. Li, J. Chen and J. Yang, Visible Light-Induced Deoxygenation and Allylation/Vinylation of Pyridyl Ethers, *Org. Lett.*, 2022, **24**, 7309-7314.
6. X. Huang, S. Luo, O. Burghaus, R. D. Webster, K. Harms and E. Meggers, Combining the catalytic enantioselective reaction of visible-light-generated radicals with a by-product utilization system, *Chem. Sci.*, 2017, **8**, 7126-7131.

6 NMR Spectra

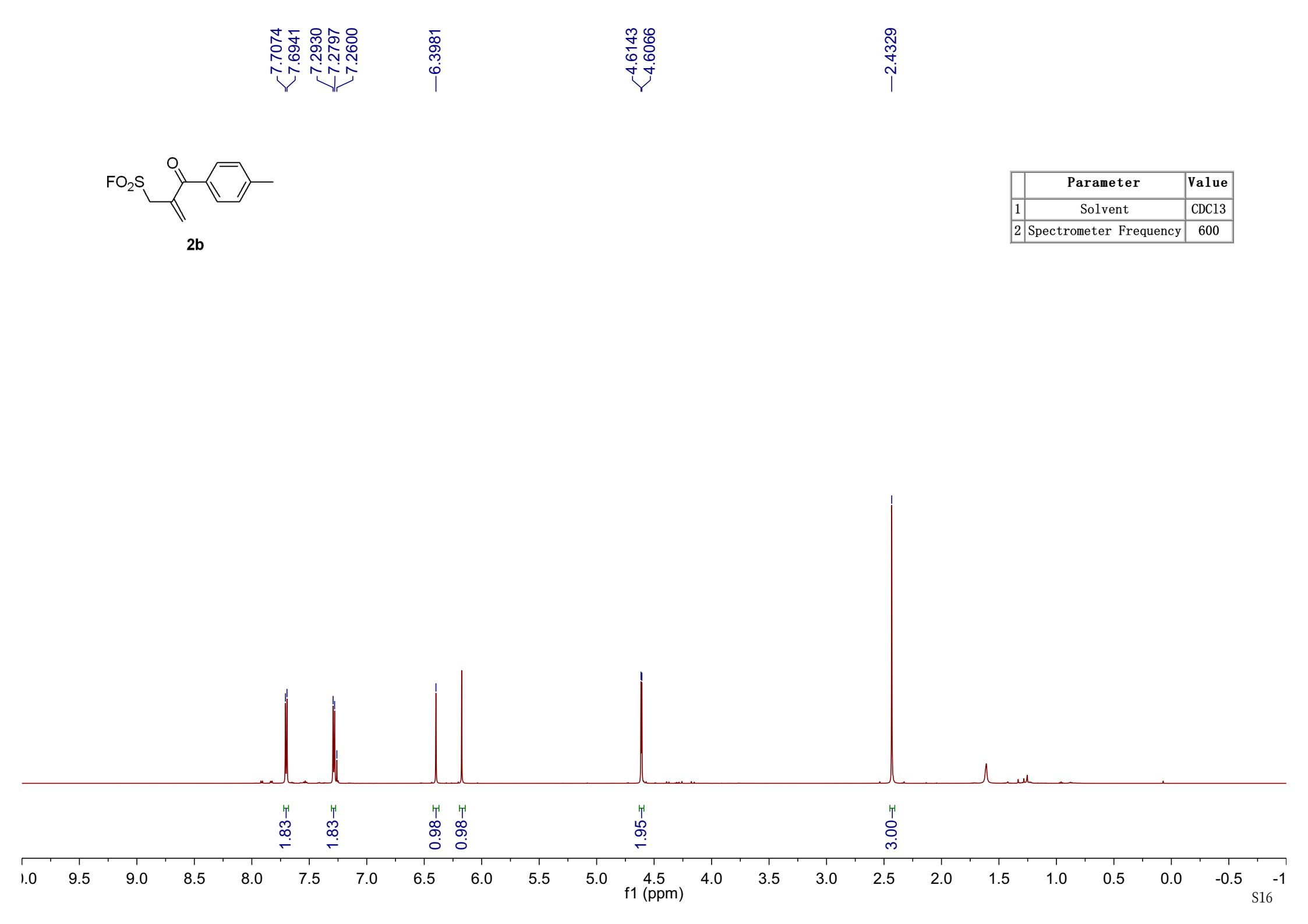

7.7834
7.7710
7.6207
7.6083
7.5959
7.5020
7.4892
7.4764
7.2600
6.4459
6.2031
4.6288
4.6211
FO2S
O
2a
Parameter
Value
1
Solvent
CDCl3
2
Spectrometer Frequency
600
1.79
0.99
1.89
1.00
0.98
1.96
f1 (ppm)

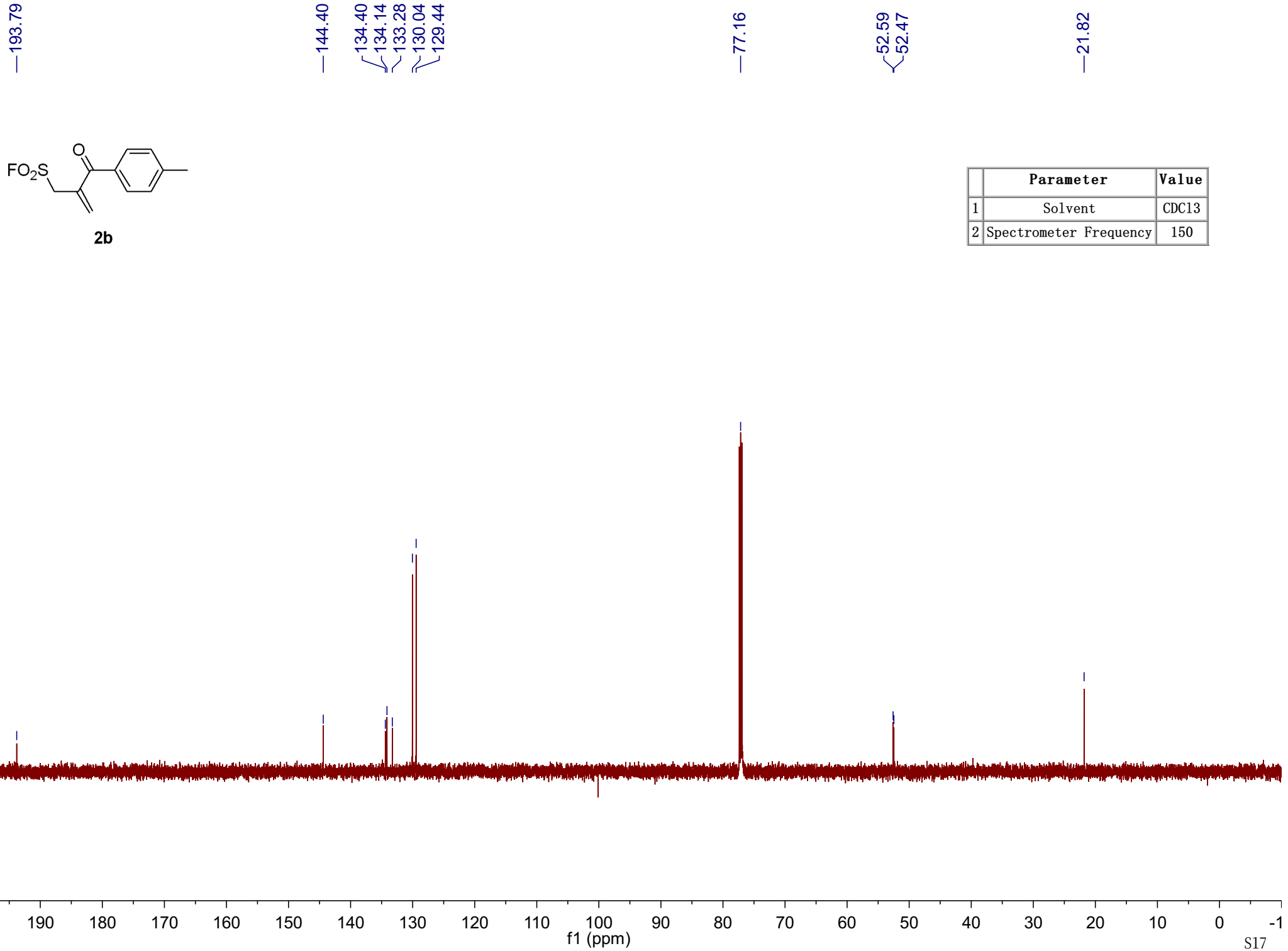

194.13
135.99
134.86
134.39
133.33
129.79
128.74
77.16
52.38
52.25
O
FO2S
2a
Parameter
Value
1
Solvent
CDCl3
2
Spectrometer Frequency
150
f1 (ppm)

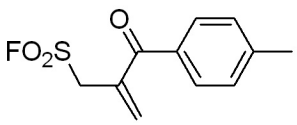


2a

	Parameter	Value
1	Solvent	CDC13
2	Spectrometer Frequency	565


7.7074
7.6941
7.2930
7.2797
7.2600
6.3981
4.6143
4.6066
2.4329
FO2S
O
2b
Parameter
Value
1
Solvent
CDCl3
2
Spectrometer Frequency
600
1.83
1.83
0.98
0.98
1.95
3.00
f1 (ppm)

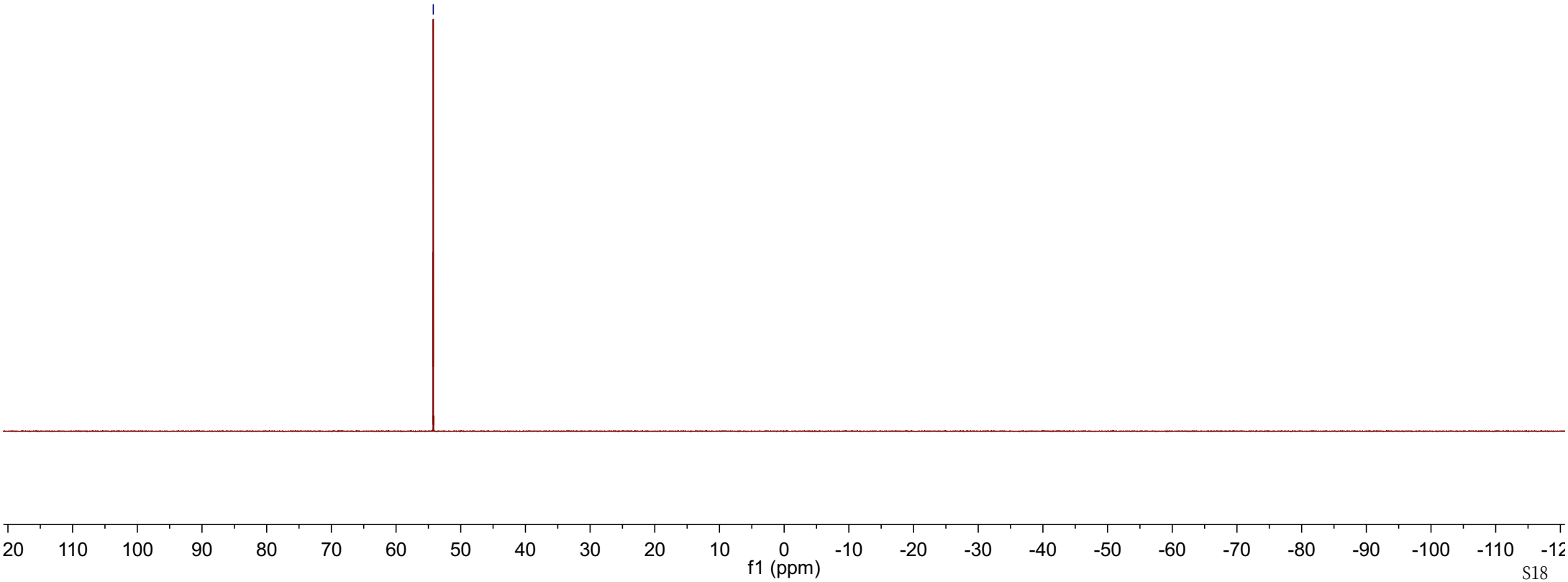

193.79
144.40
134.40
134.14
133.28
130.04
129.44
77.16
52.59
52.47
21.82
FO2S
O
2b
Parameter
Value
1
Solvent
CDCl3
2
Spectrometer Frequency
150
f1 (ppm)

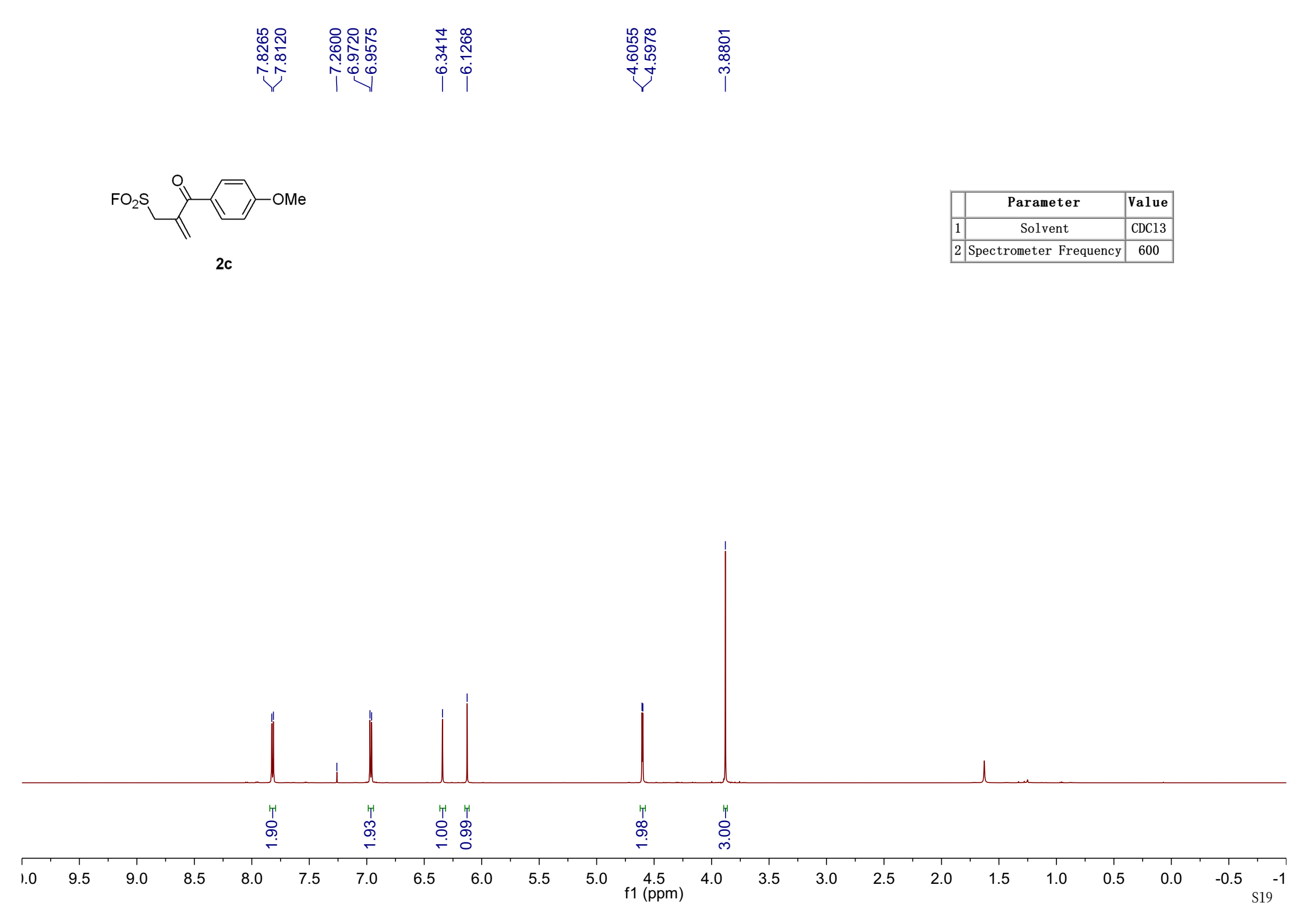


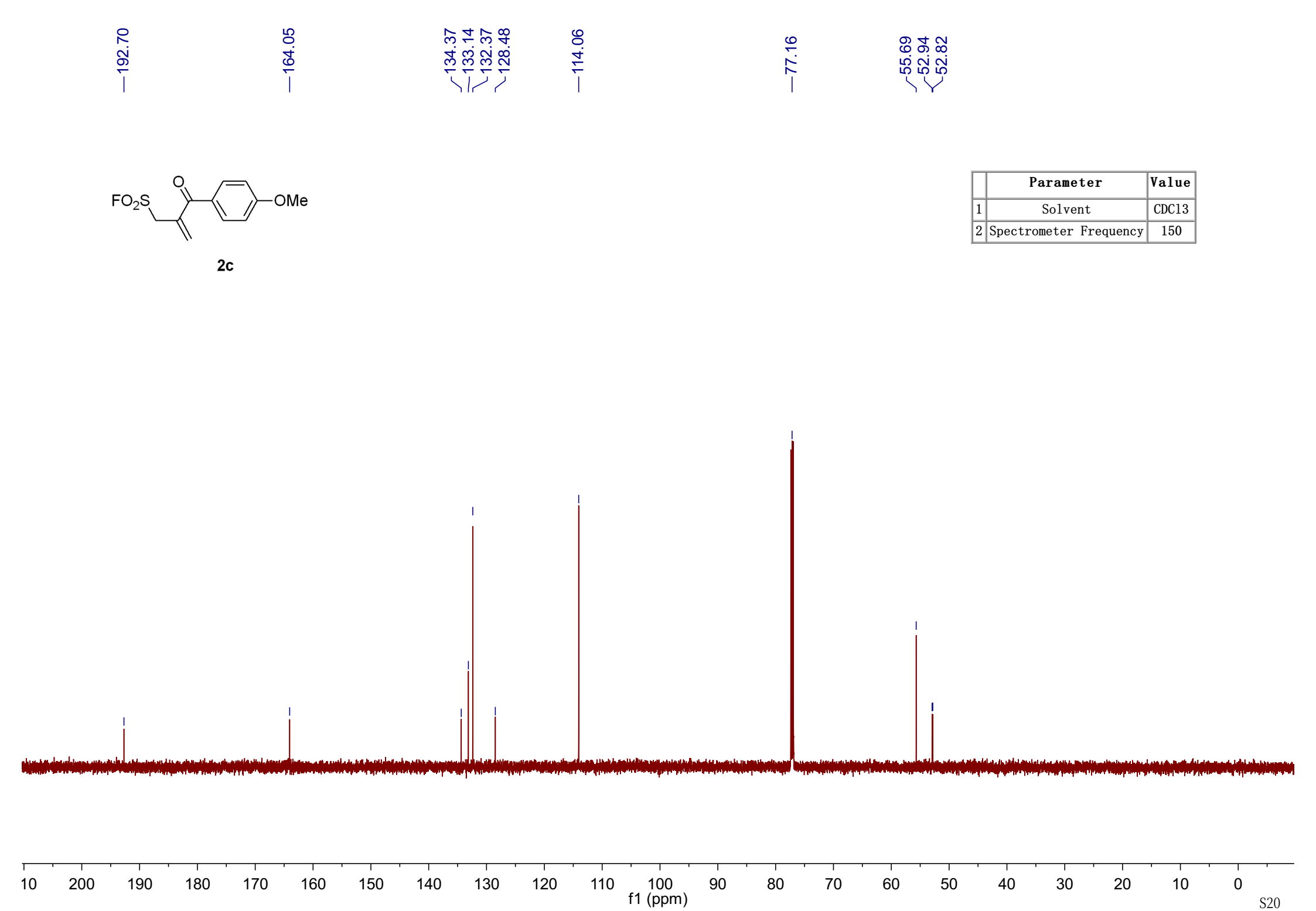
2b

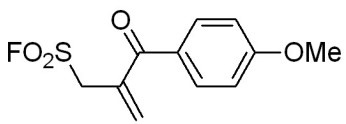
54.25

	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	377



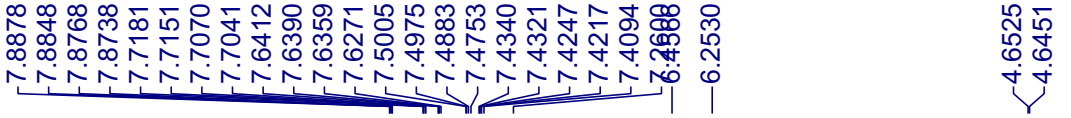

7.8265
7.8120
7.2600
6.9720
6.9575
6.3414
6.1268
4.6055
4.5978
3.8801
O
FO2S
OMe
2c
Parameter
Value
1
Solvent
CDCl3
2
Spectrometer Frequency
600
1.90
1.93
1.00
0.99
1.98
3.00
f1 (ppm)

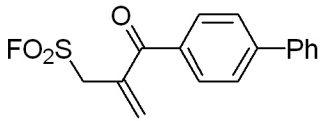

192.70
164.05
134.37
133.14
132.37
128.48
114.06
77.16
55.69
52.94
52.82
FO2S
O
OMe
2c
Parameter
Value
1
Solvent
CDCl3
2
Spectrometer Frequency
150
f1 (ppm)



2c

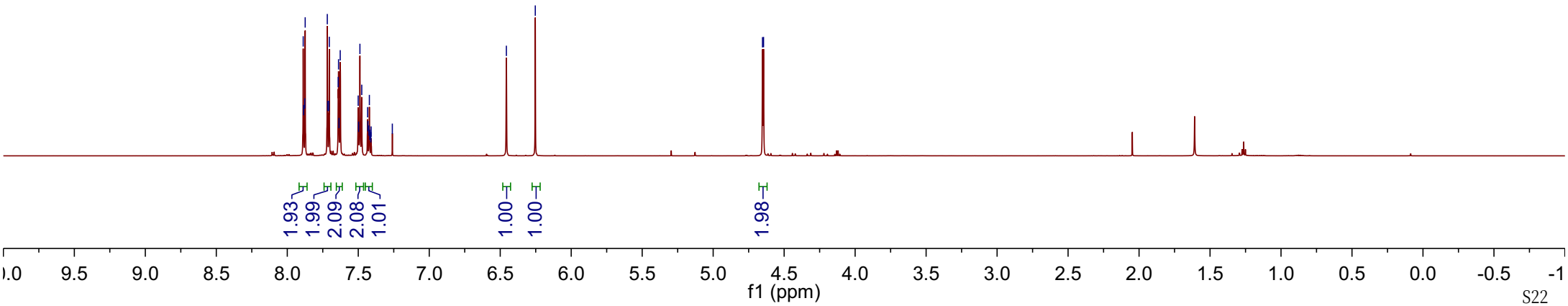
	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	377

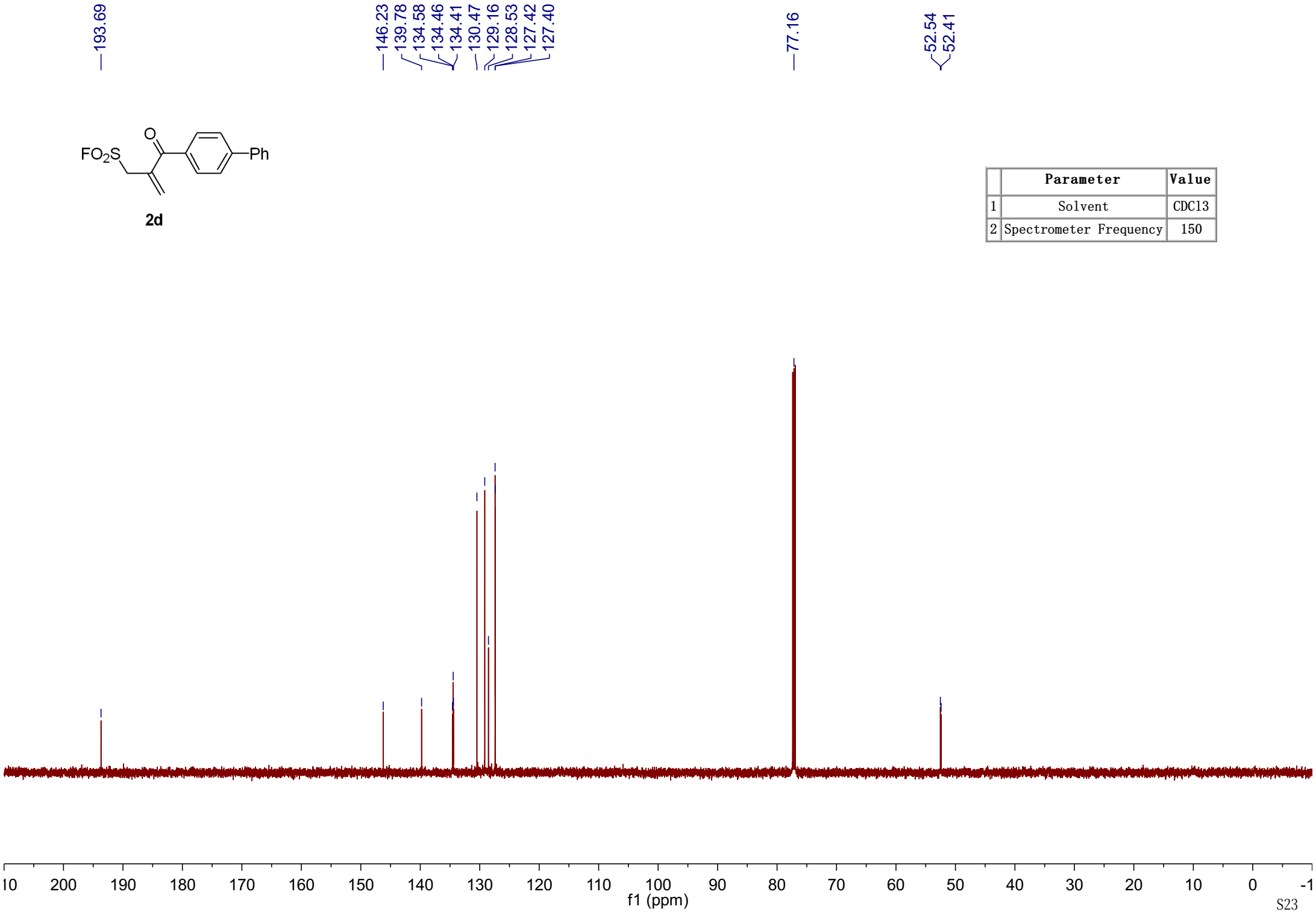




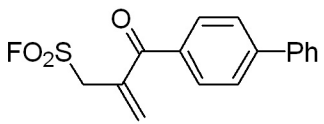
2d

	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	600





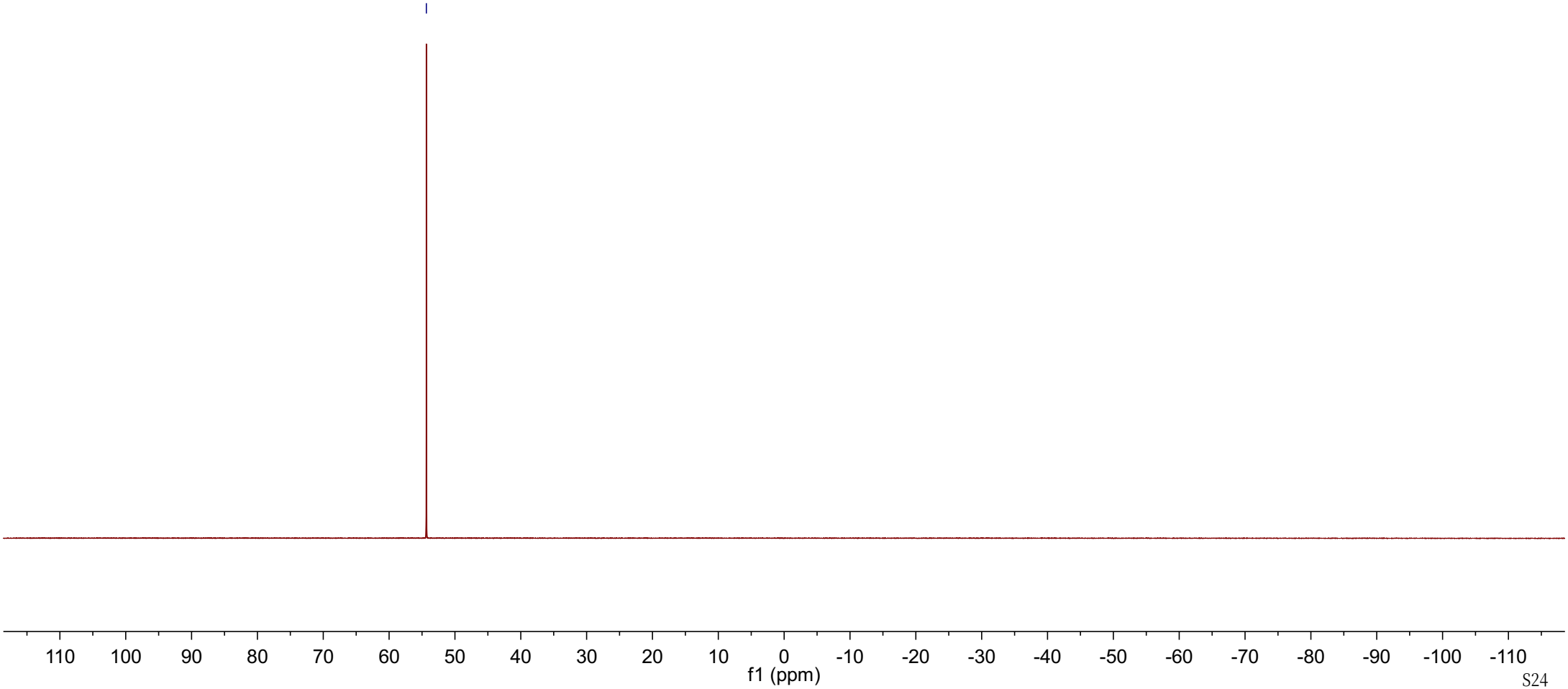
	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	150

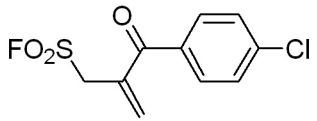


2d

54.34

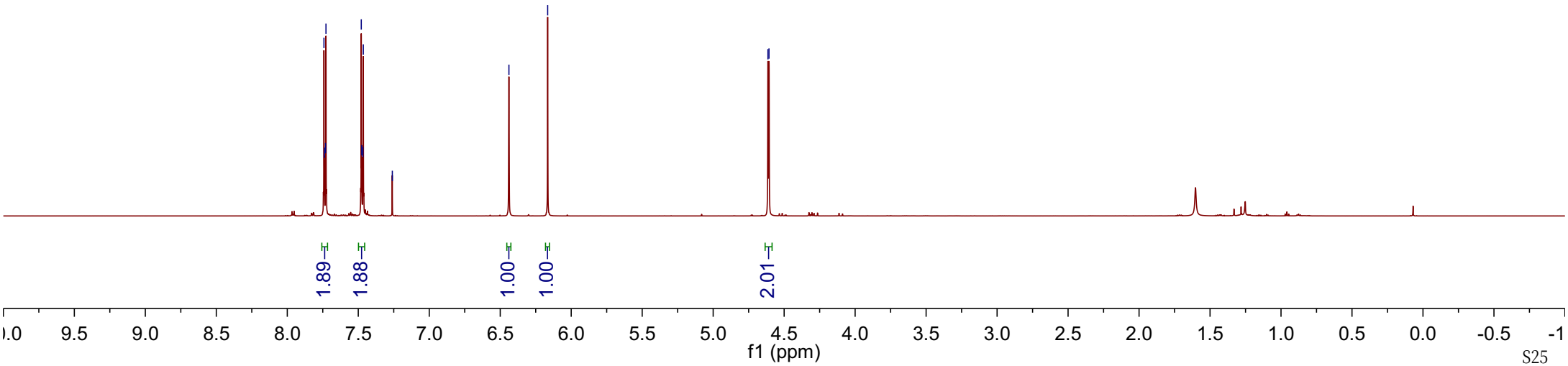
	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	565



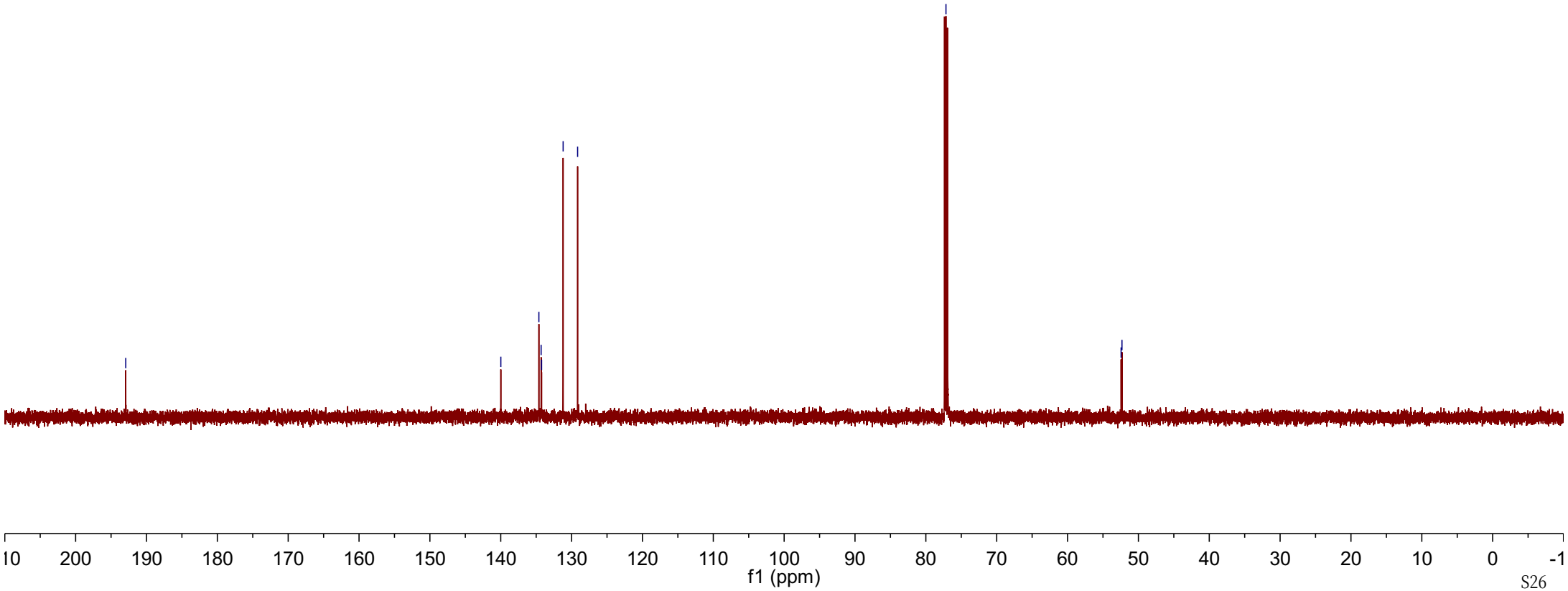


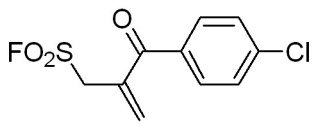
2e

	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	600



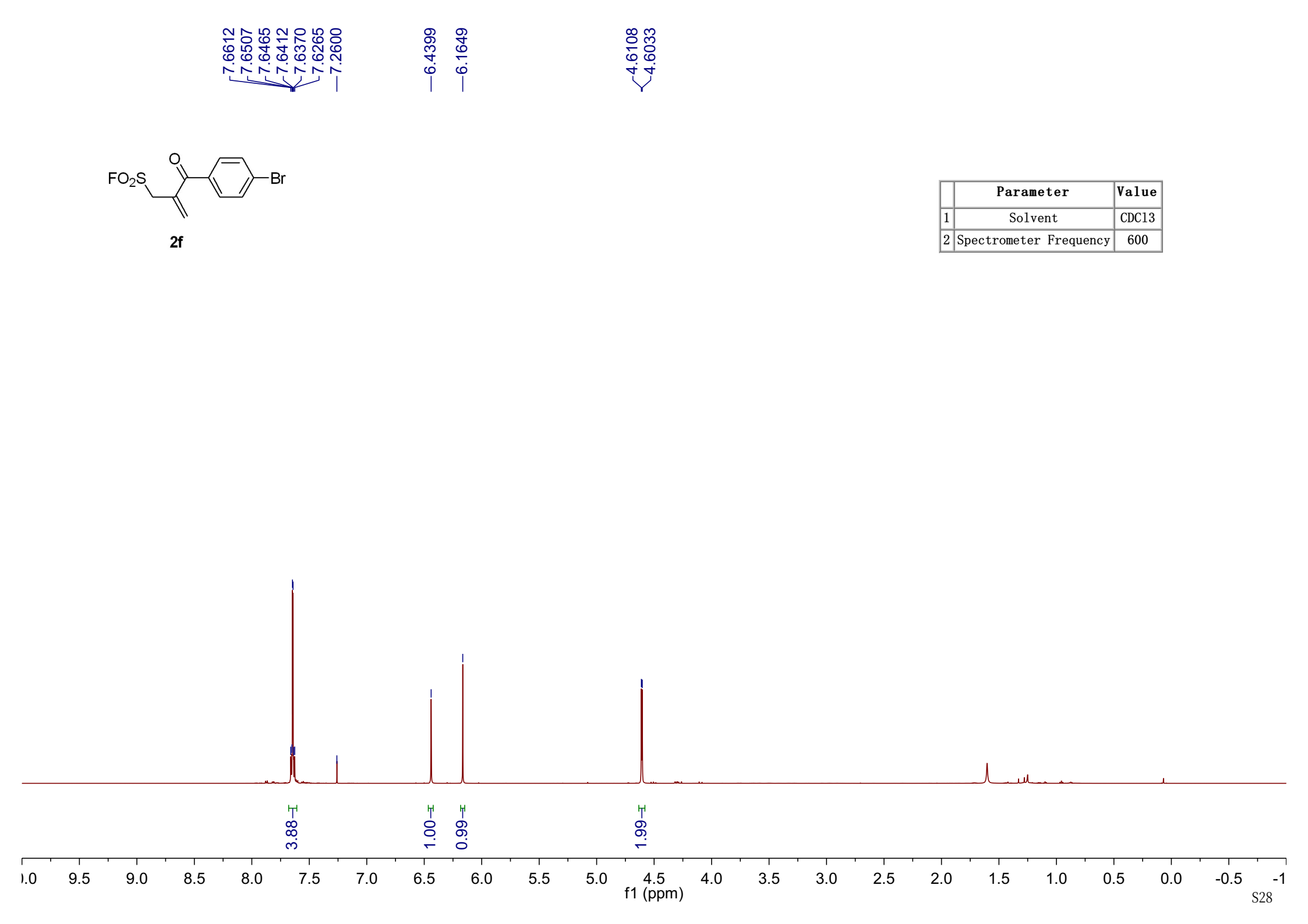
	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	150

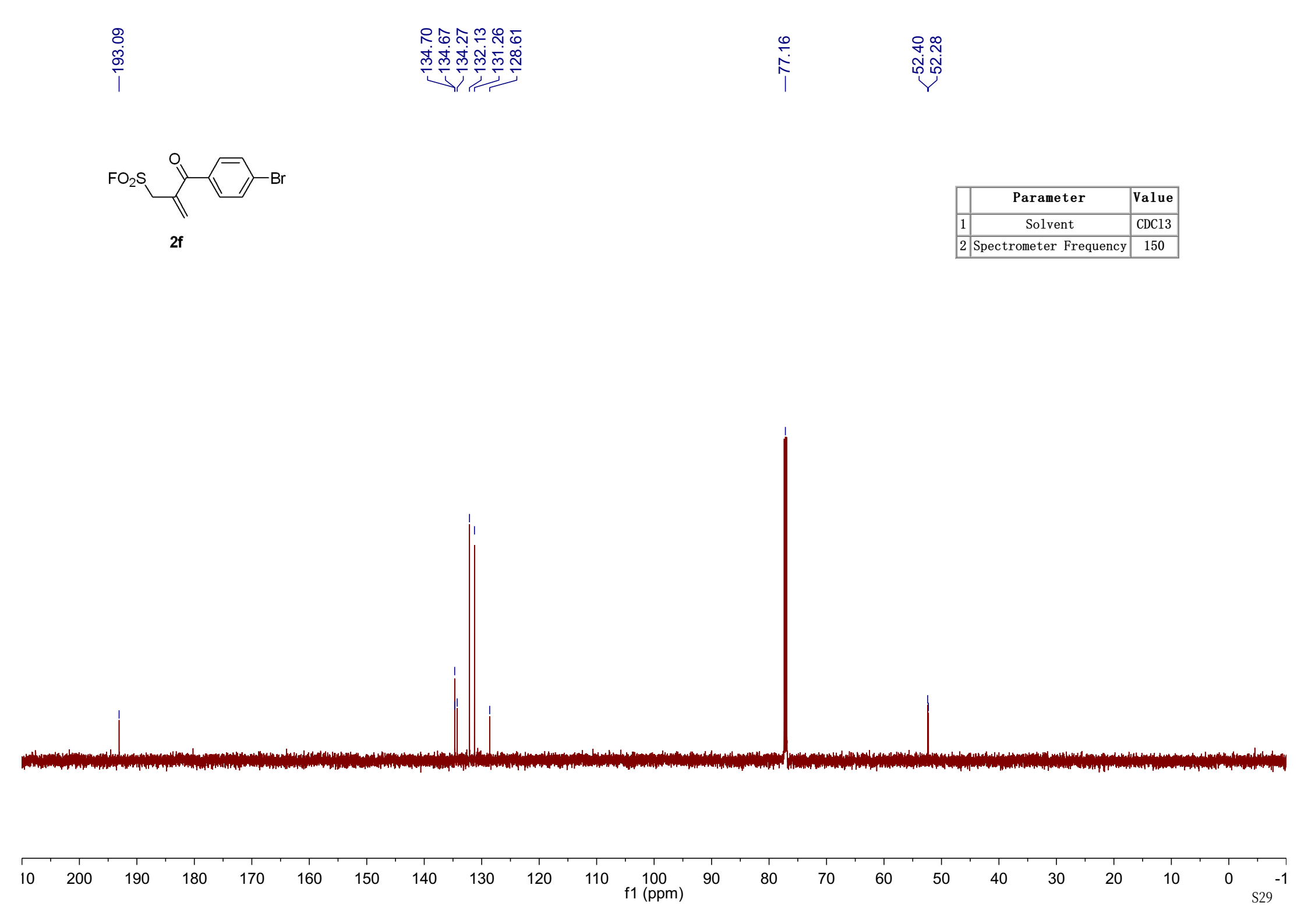


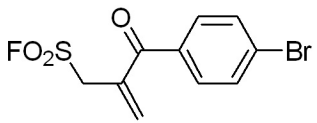


2e

	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	377

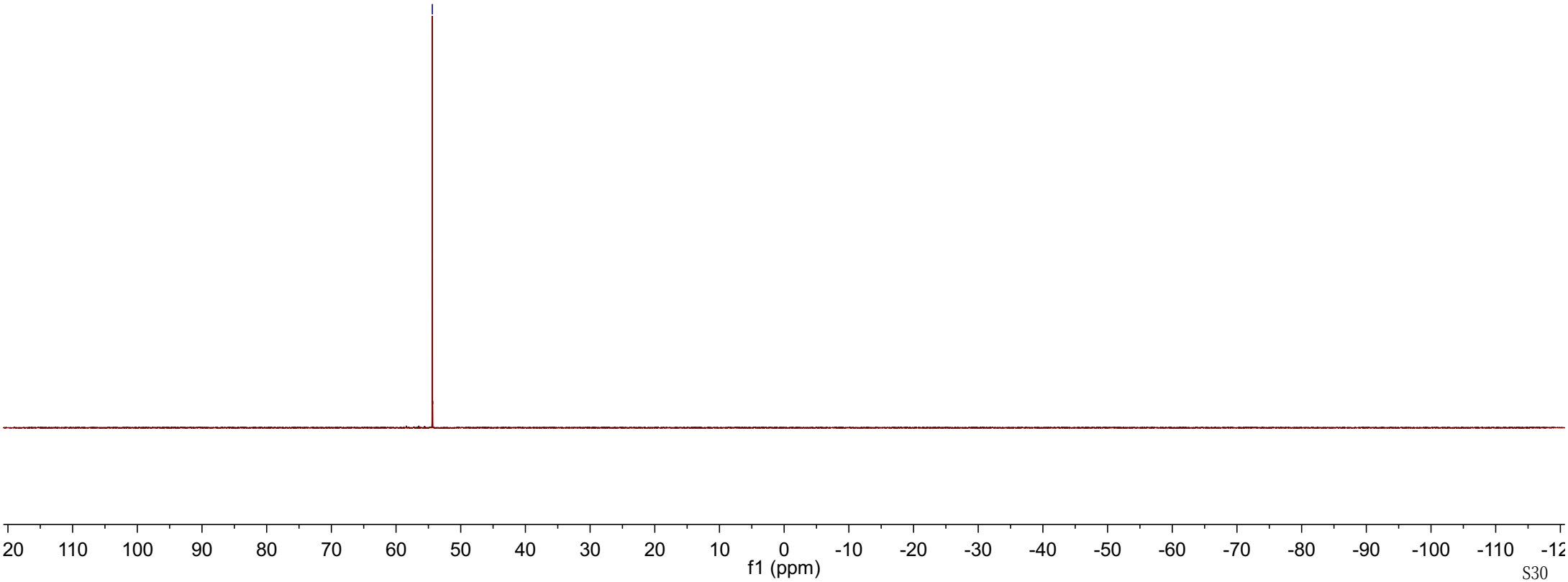

7.6612
7.6507
7.6465
7.6412
7.6370
7.6265
7.2600
6.4399
6.1649
4.6108
4.6033
O
FO2S
Br
2f
Parameter
Value
1
Solvent
CDCl3
2
Spectrometer Frequency
600
3.88
1.00
0.99
1.99
f1 (ppm)

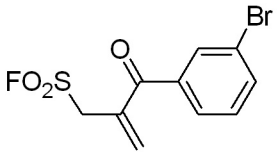

193.09
134.70
134.67
134.27
132.13
131.26
128.61
77.16
52.40
52.28
FO2S
O
Br
2f
Parameter
Value
1
Solvent
CDCl3
2
Spectrometer Frequency
150
f1 (ppm)



2f

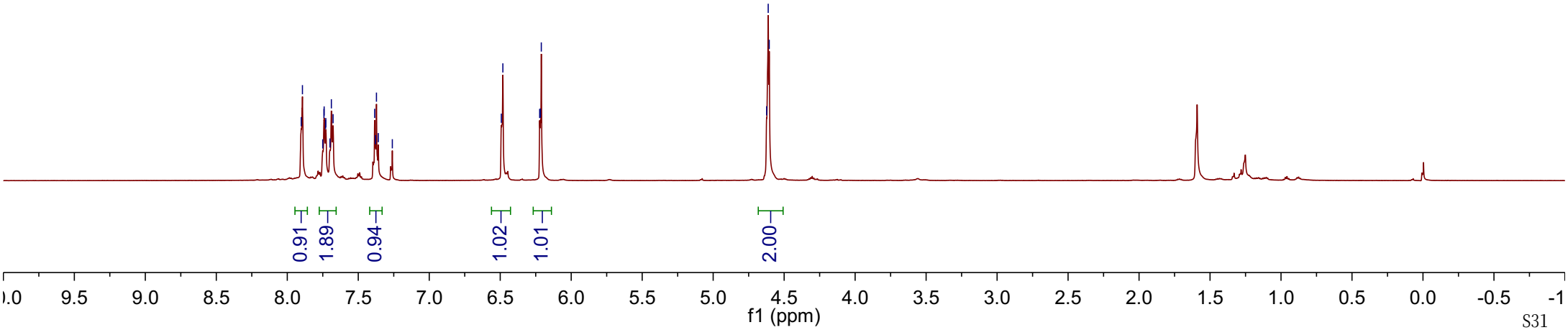
	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	377

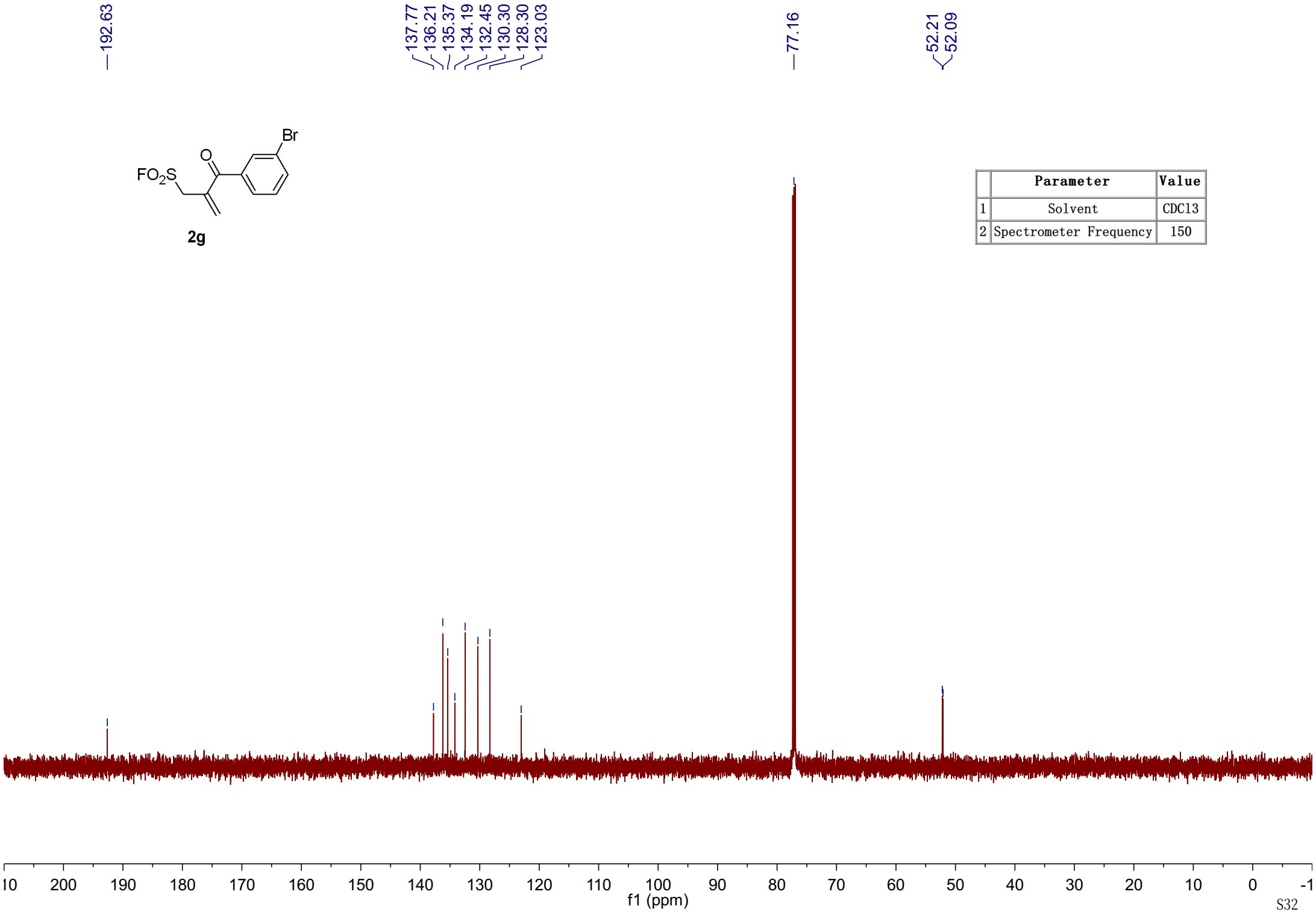


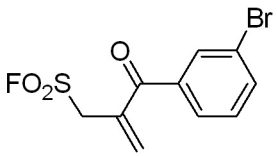


2g

	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	600

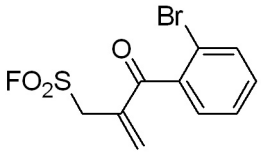



192.63
137.77
136.21
135.37
134.19
132.45
130.30
128.30
123.03
77.16
52.21
52.09
Br
O
FO2S
2g
Parameter
Value
1
Solvent
CDCl3
2
Spectrometer Frequency
150
f1 (ppm)



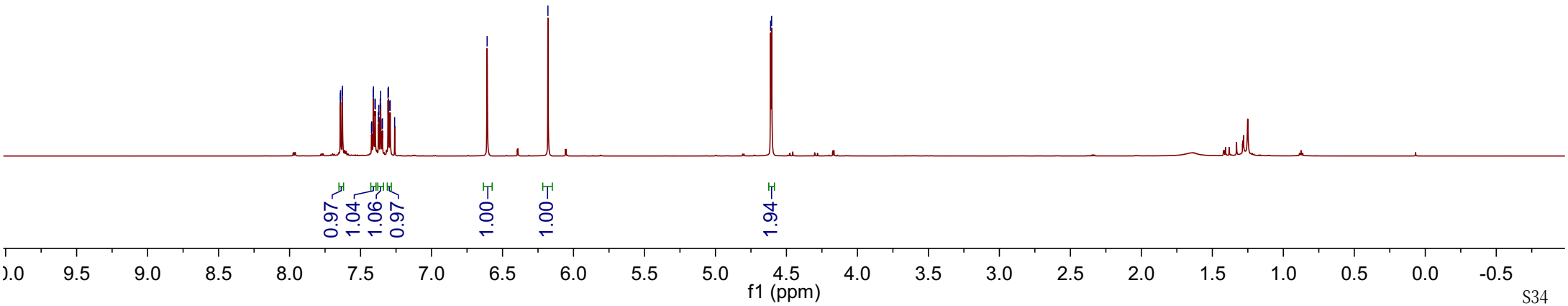
2g

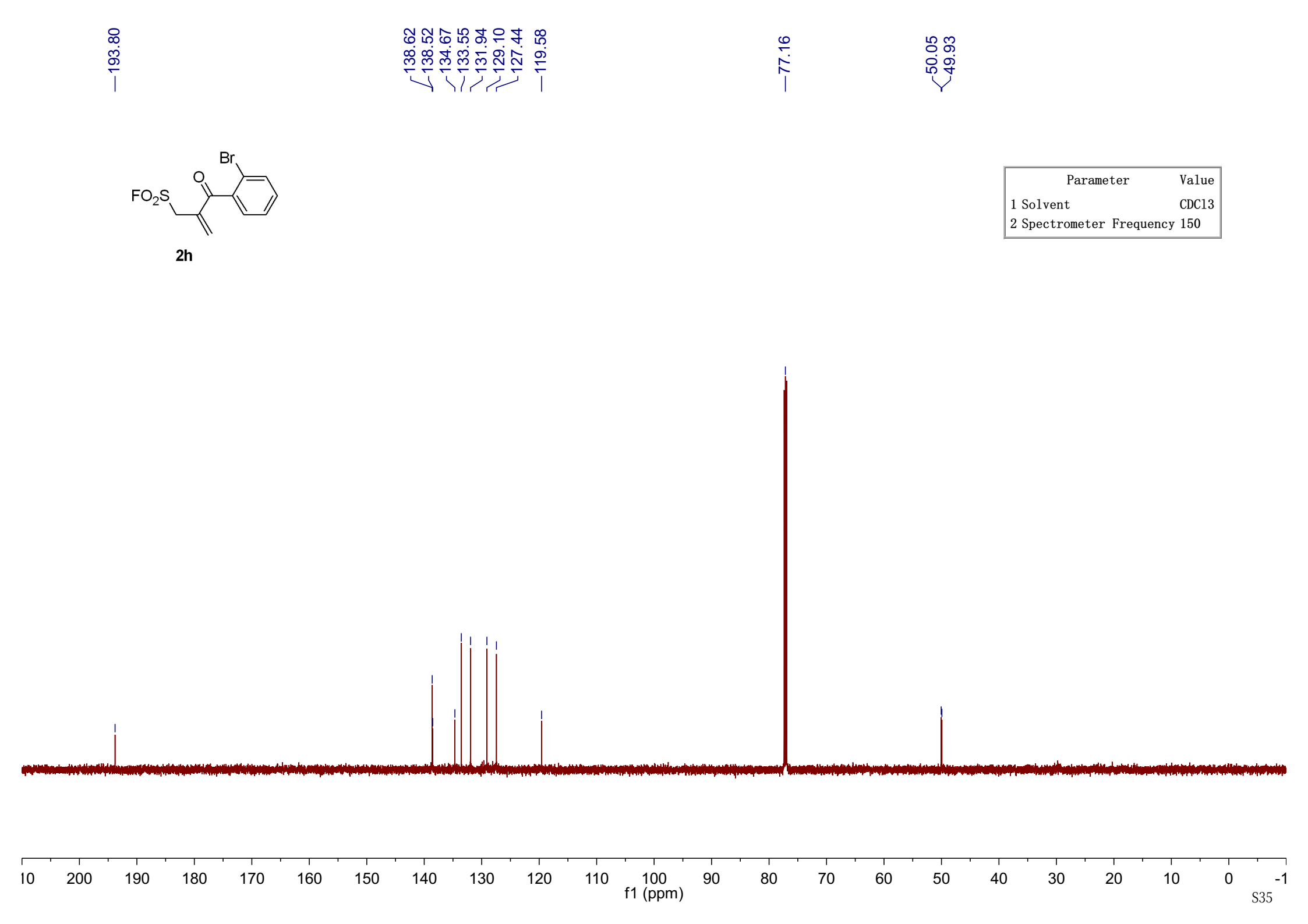
	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	565

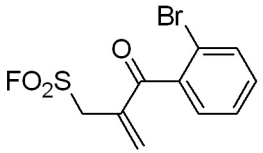


2h

Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	600



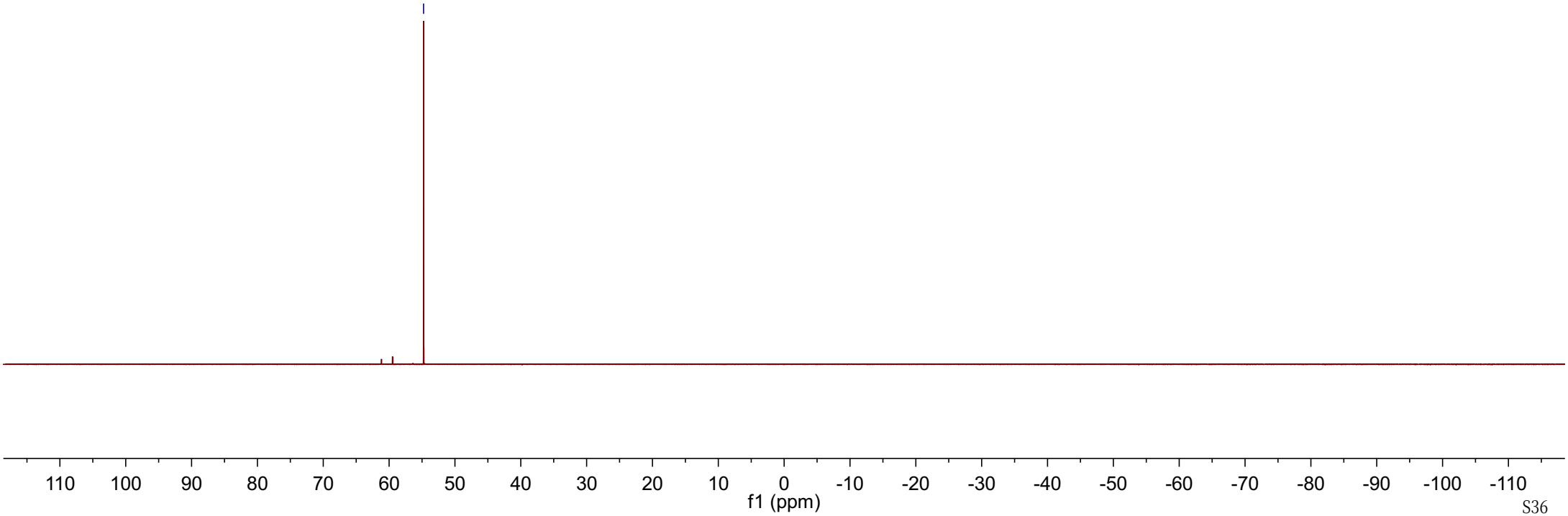

193.80
138.62
138.52
134.67
133.55
131.94
129.10
127.44
119.58
77.16
50.05
49.93
Br
O
FO2S
2h
Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 150
f1 (ppm)

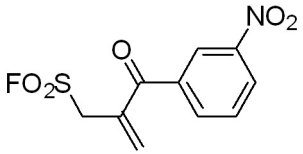


2h

—54.7657

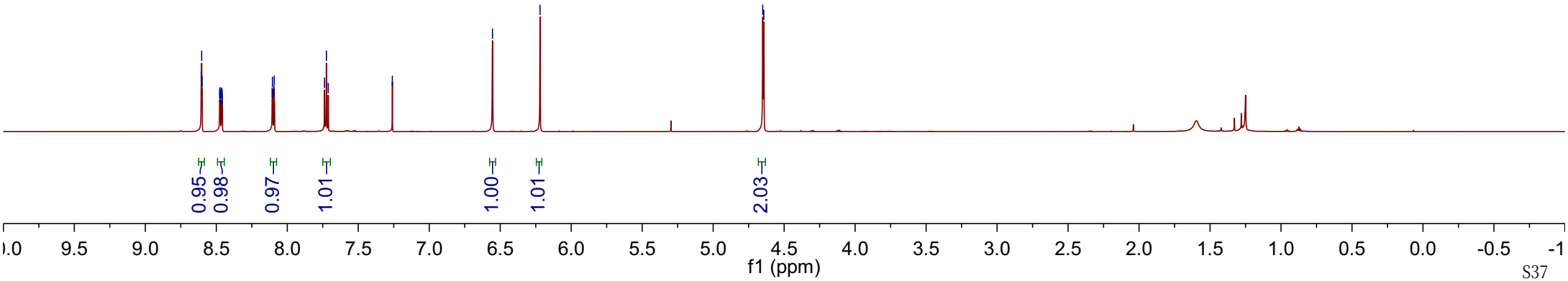
Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	565

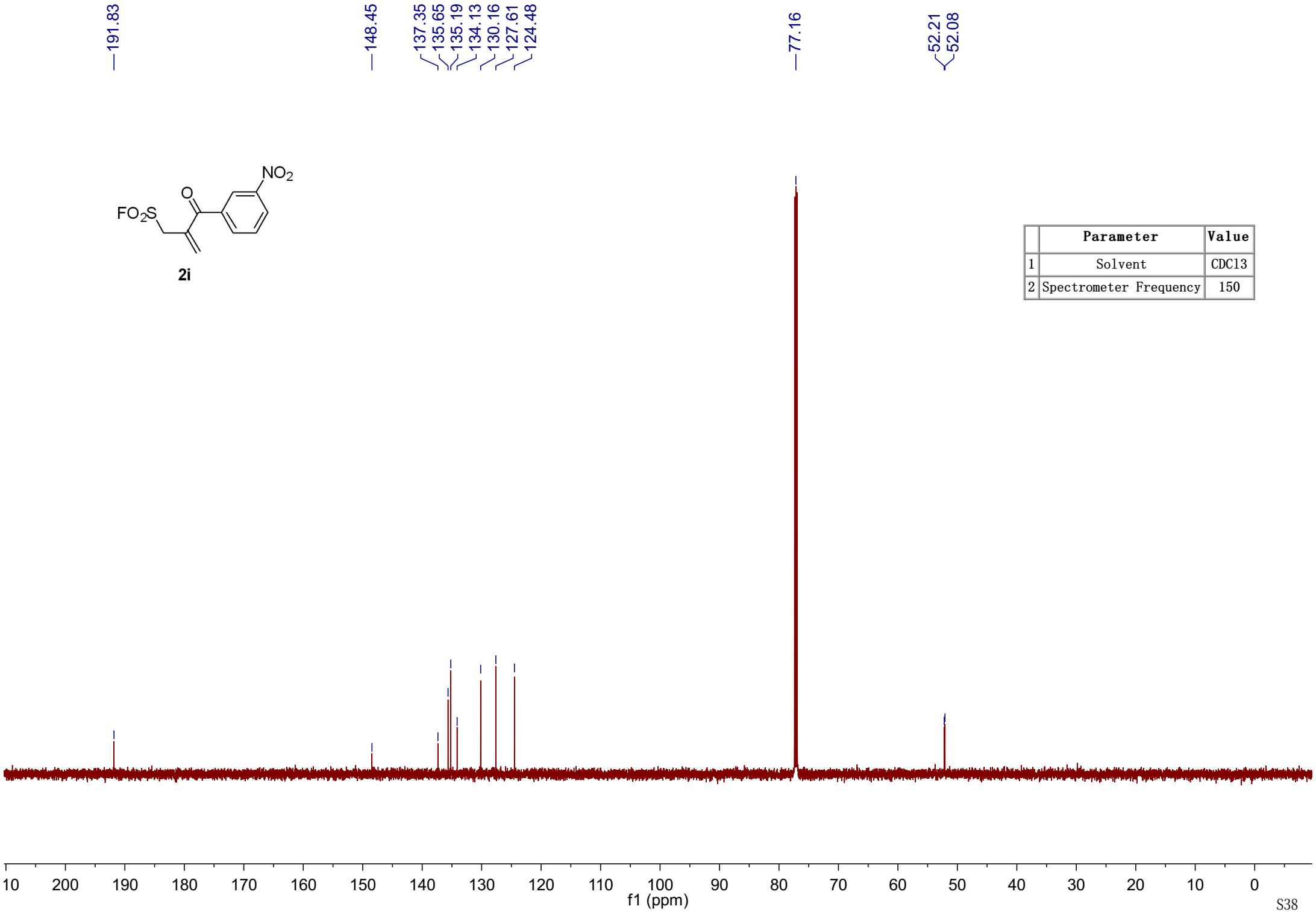


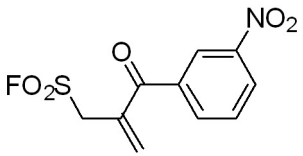


2i

	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	600

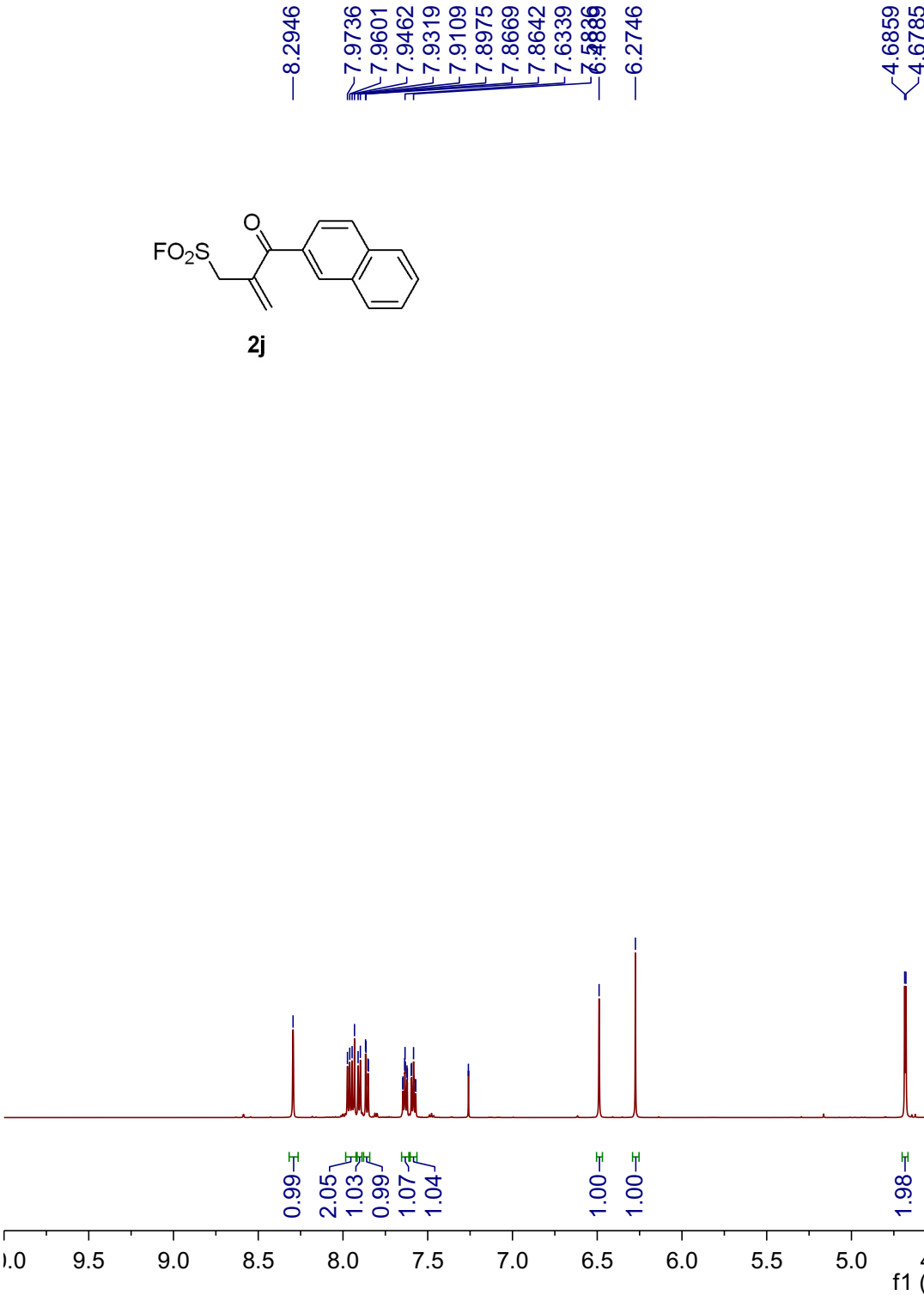



191.83
148.45
137.35
135.65
135.19
134.13
130.16
127.61
124.48
77.16
52.21
52.08
NO2
O
FO2S
2i
Parameter
Value
1
Solvent
CDCl3
2
Spectrometer Frequency
150
f1 (ppm)

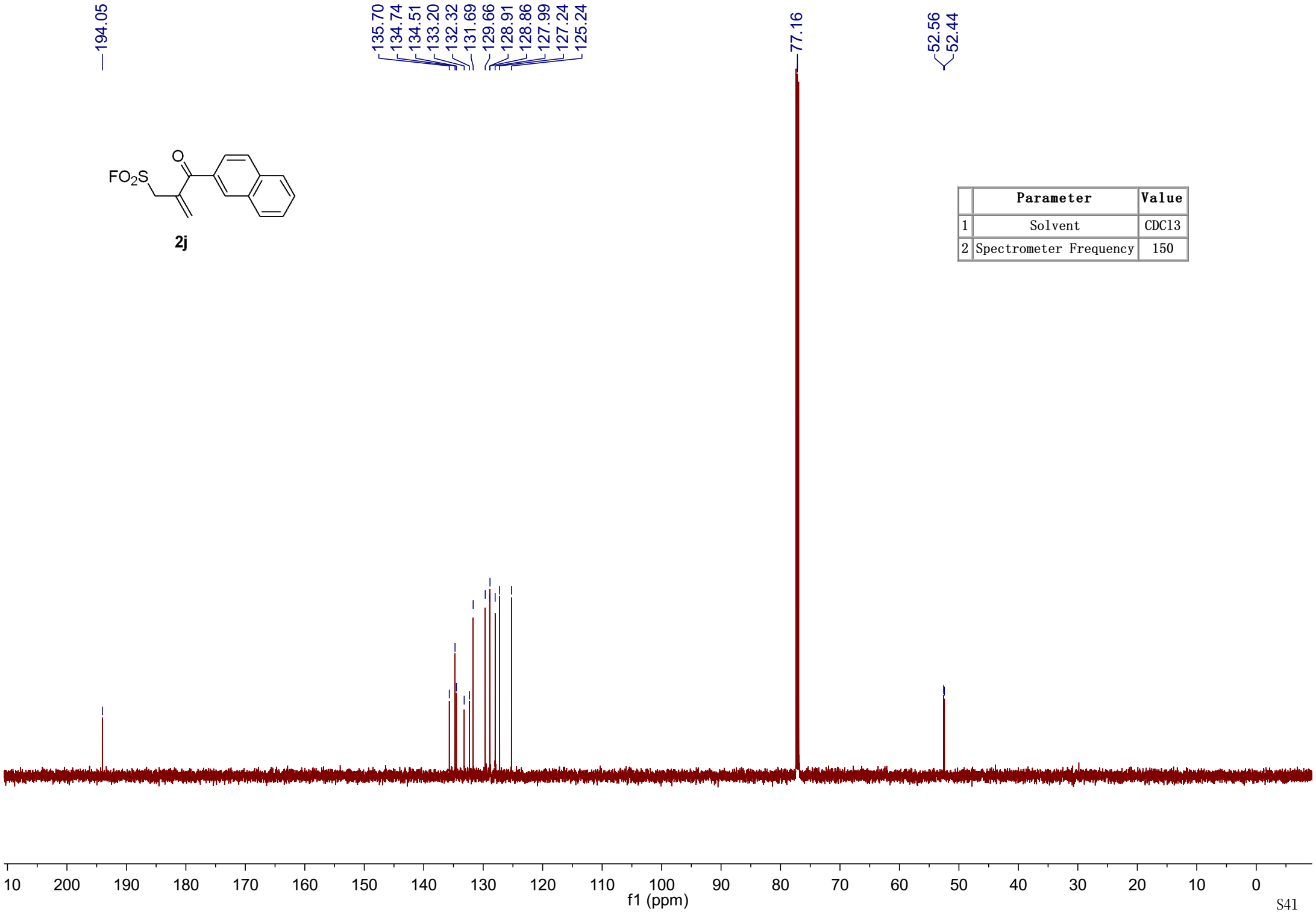


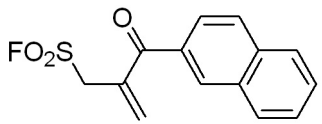
2i

	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	565



	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	600

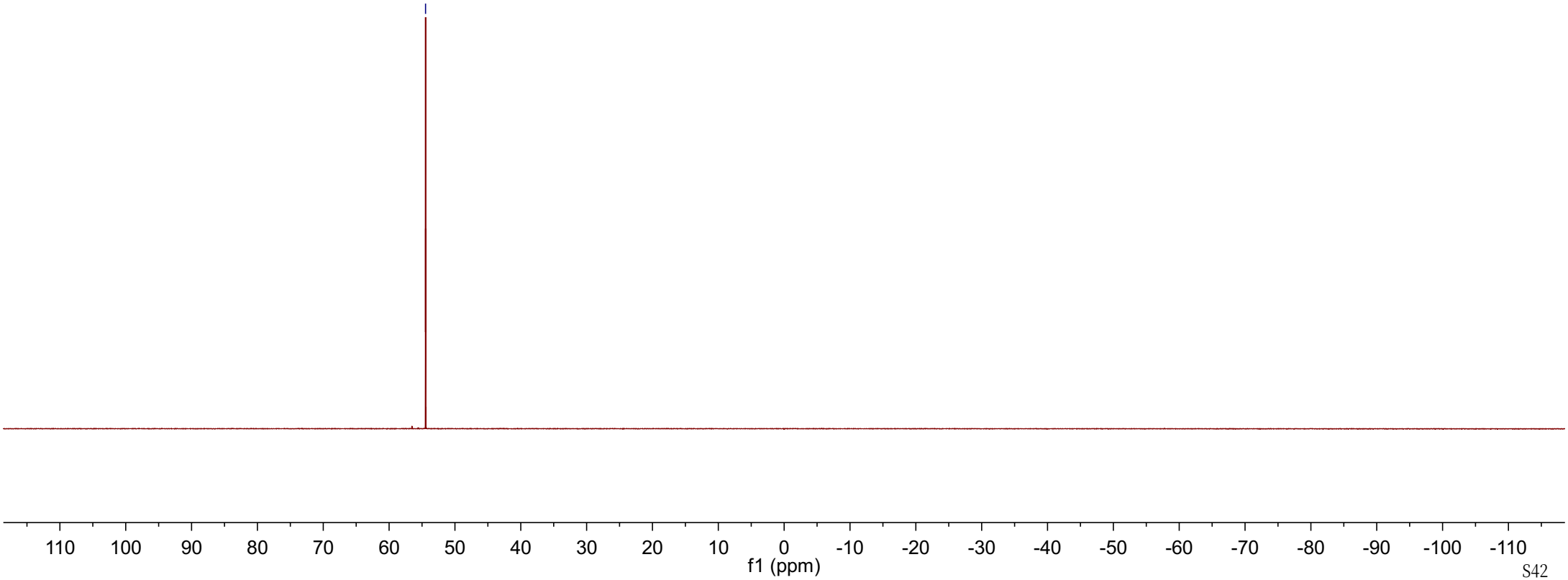

194.05
135.70
134.74
134.51
133.20
132.32
131.69
129.66
128.91
128.86
127.99
127.24
125.24
77.16
52.56
52.44
O
FO2S
2j
Parameter
Value
1
Solvent
CDCl3
2
Spectrometer Frequency
150
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

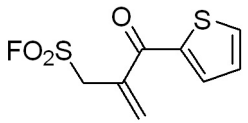


2j

54.46

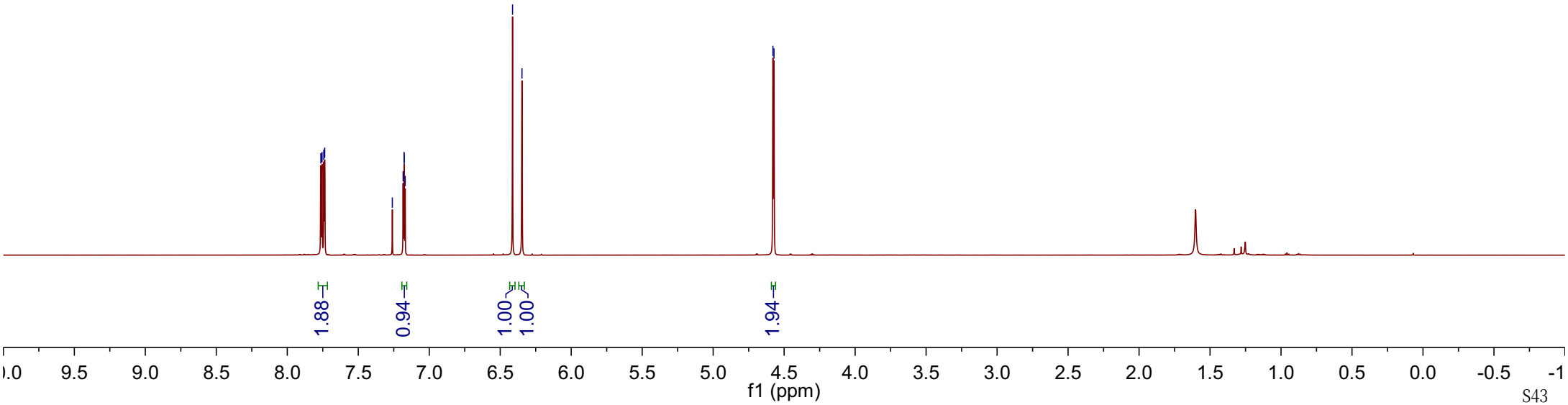
	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	565

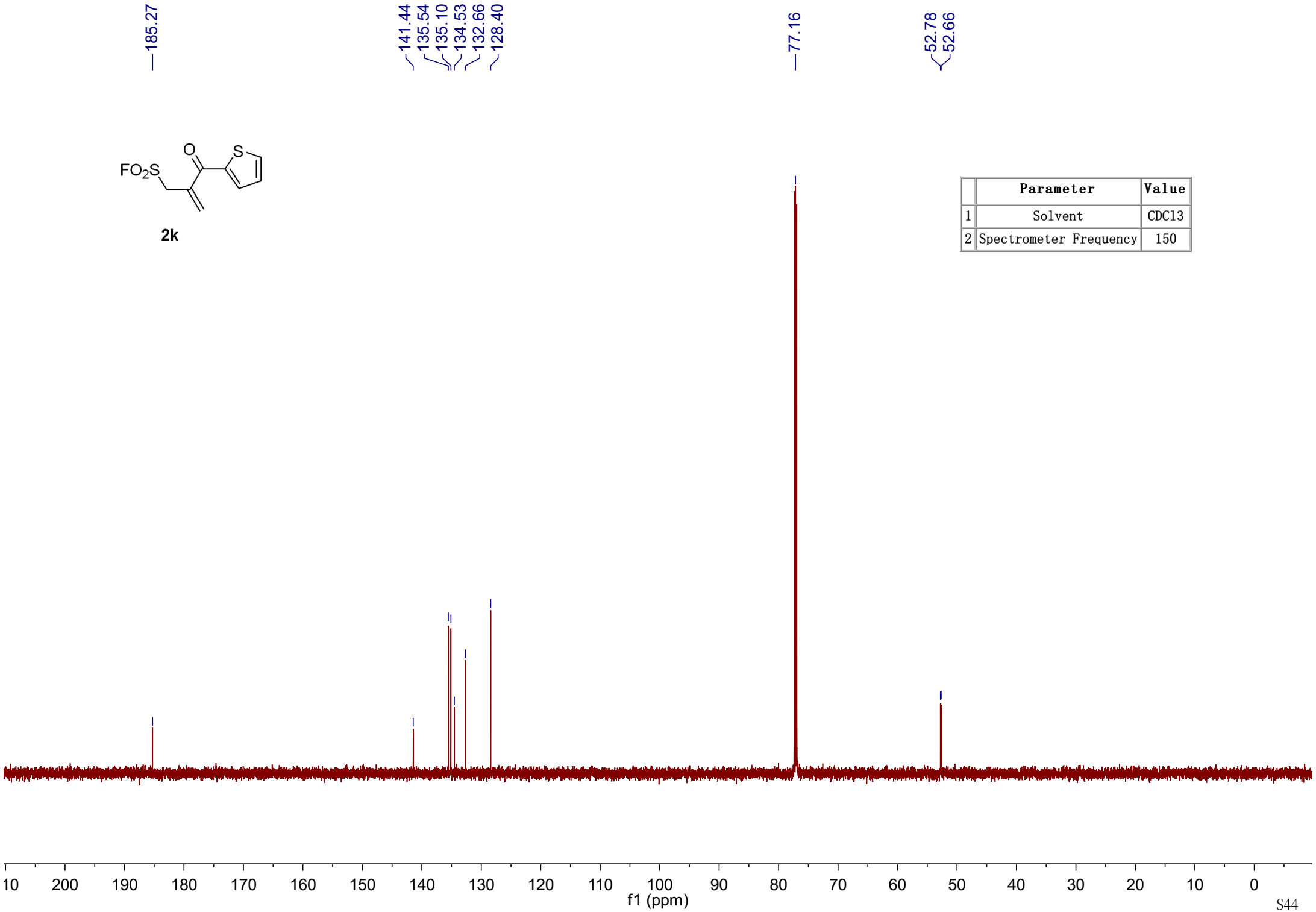


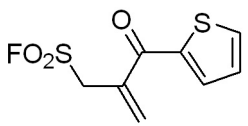


2k

	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	600



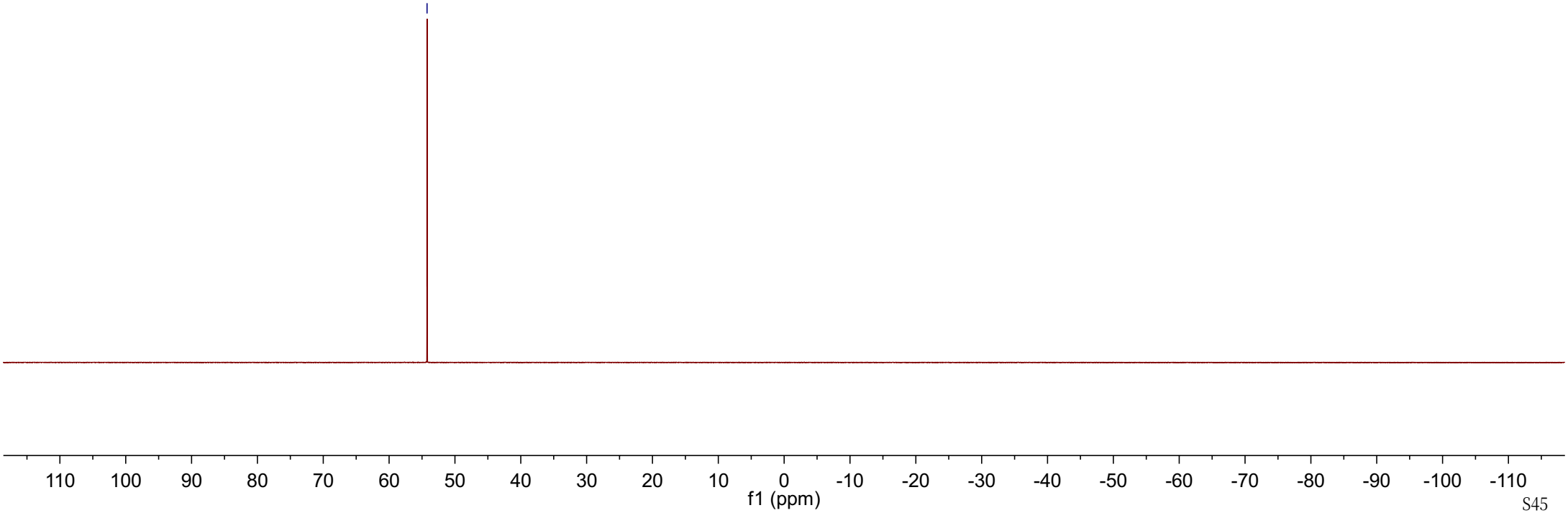

185.27
141.44
135.54
135.10
134.53
132.66
128.40
77.16
52.78
52.66
FO2S
O
S
2k
Parameter
Value
1
Solvent
CDCl3
2
Spectrometer Frequency
150
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

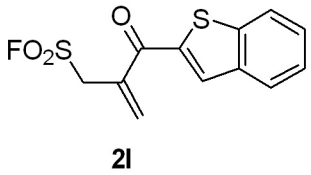


2k

54.24

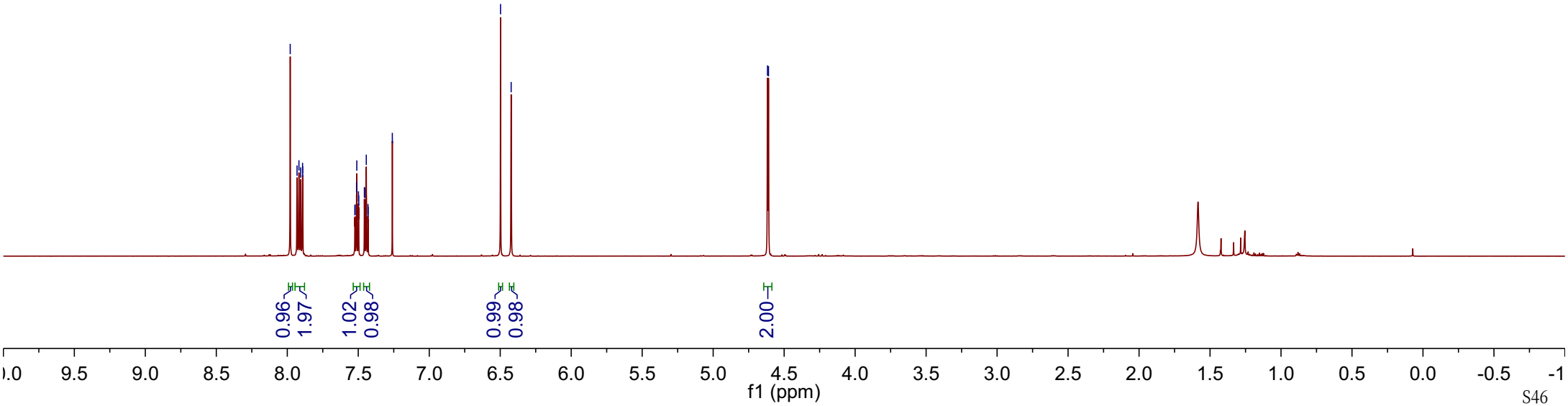
	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	565

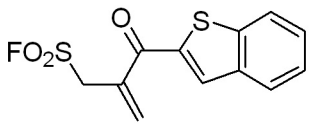




2l

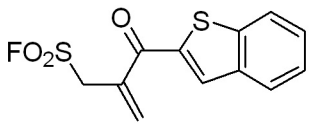
	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	600





2l

	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	150



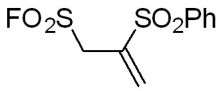
2l

54.42
54.41
54.40

	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	565

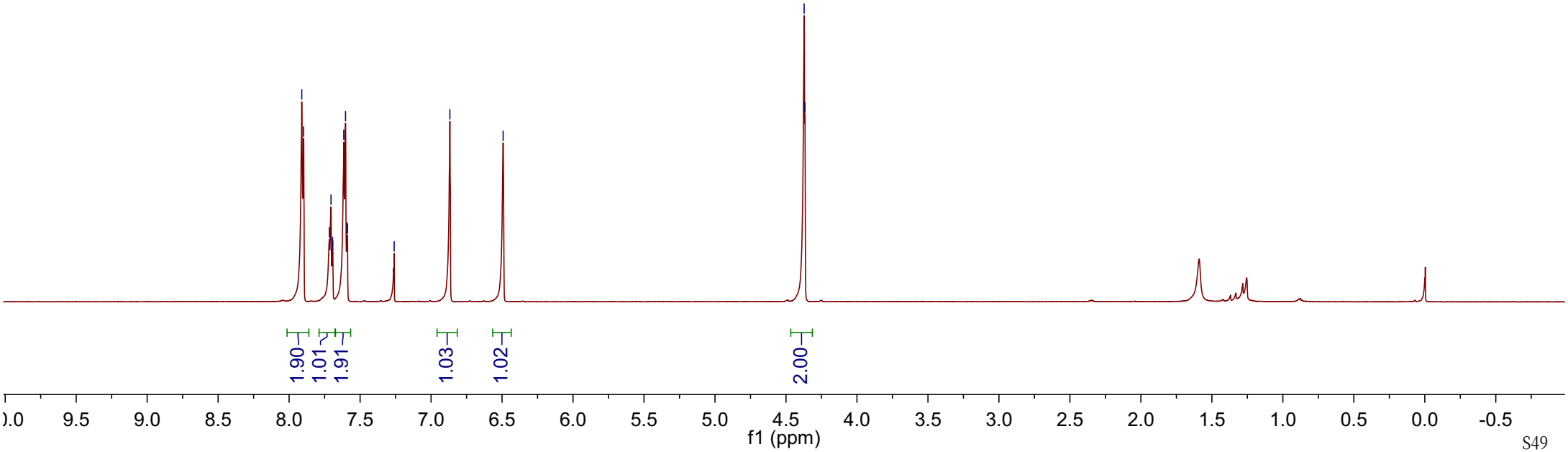
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110

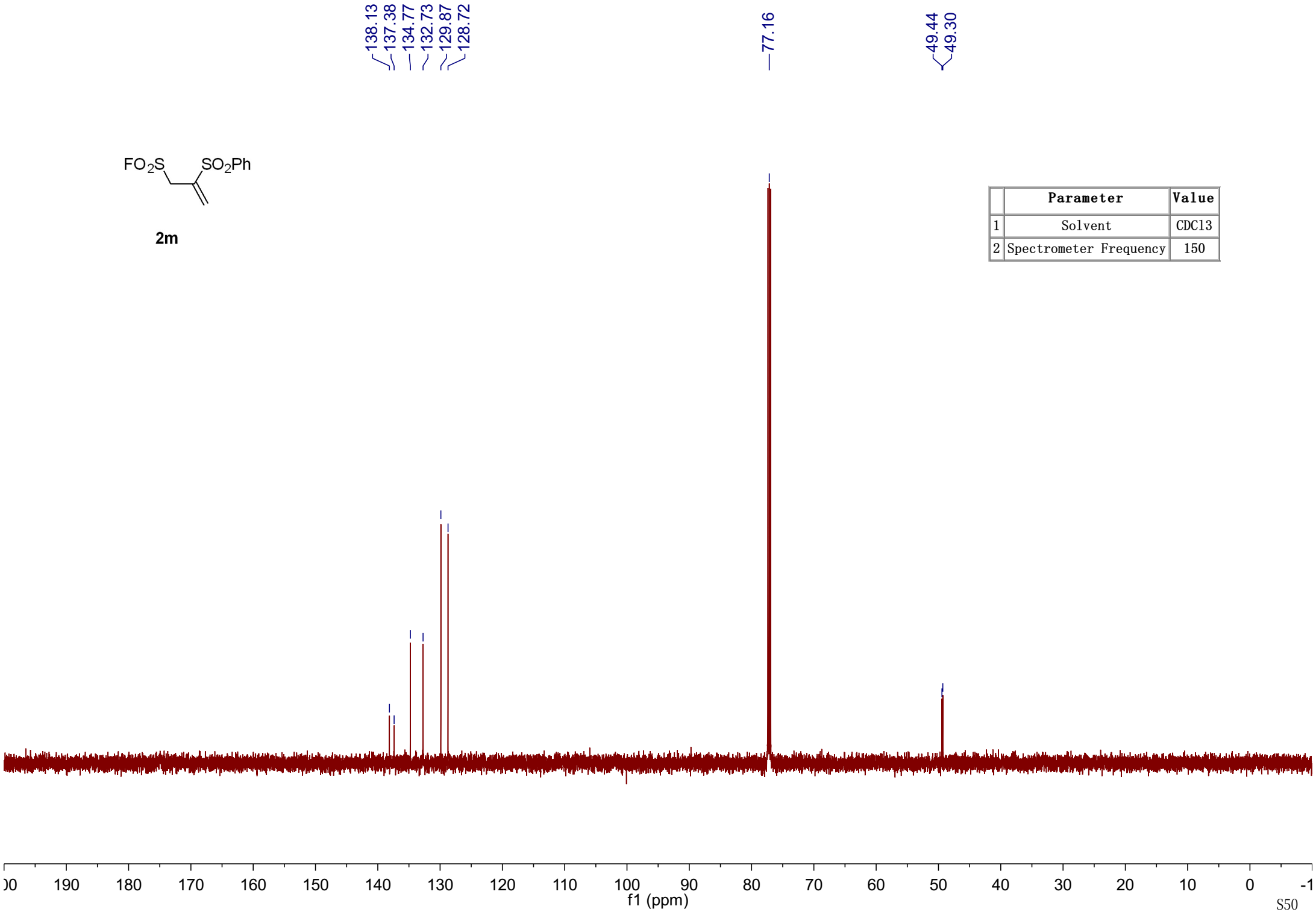
f1 (ppm)

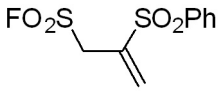


2m

	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	600

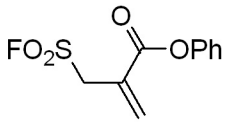



138.13
137.38
134.77
132.73
129.87
128.72
77.16
49.44
49.30
FO2S
SO2Ph
2m
Parameter
Value
1
Solvent
CDCl3
2
Spectrometer Frequency
150
f1 (ppm)



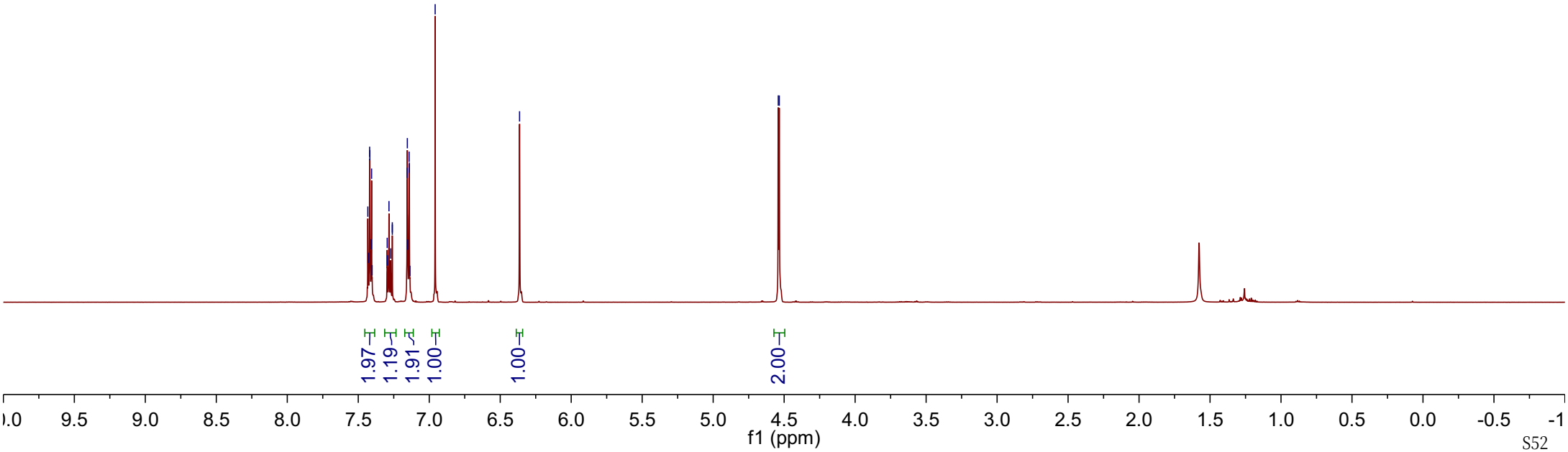
2m

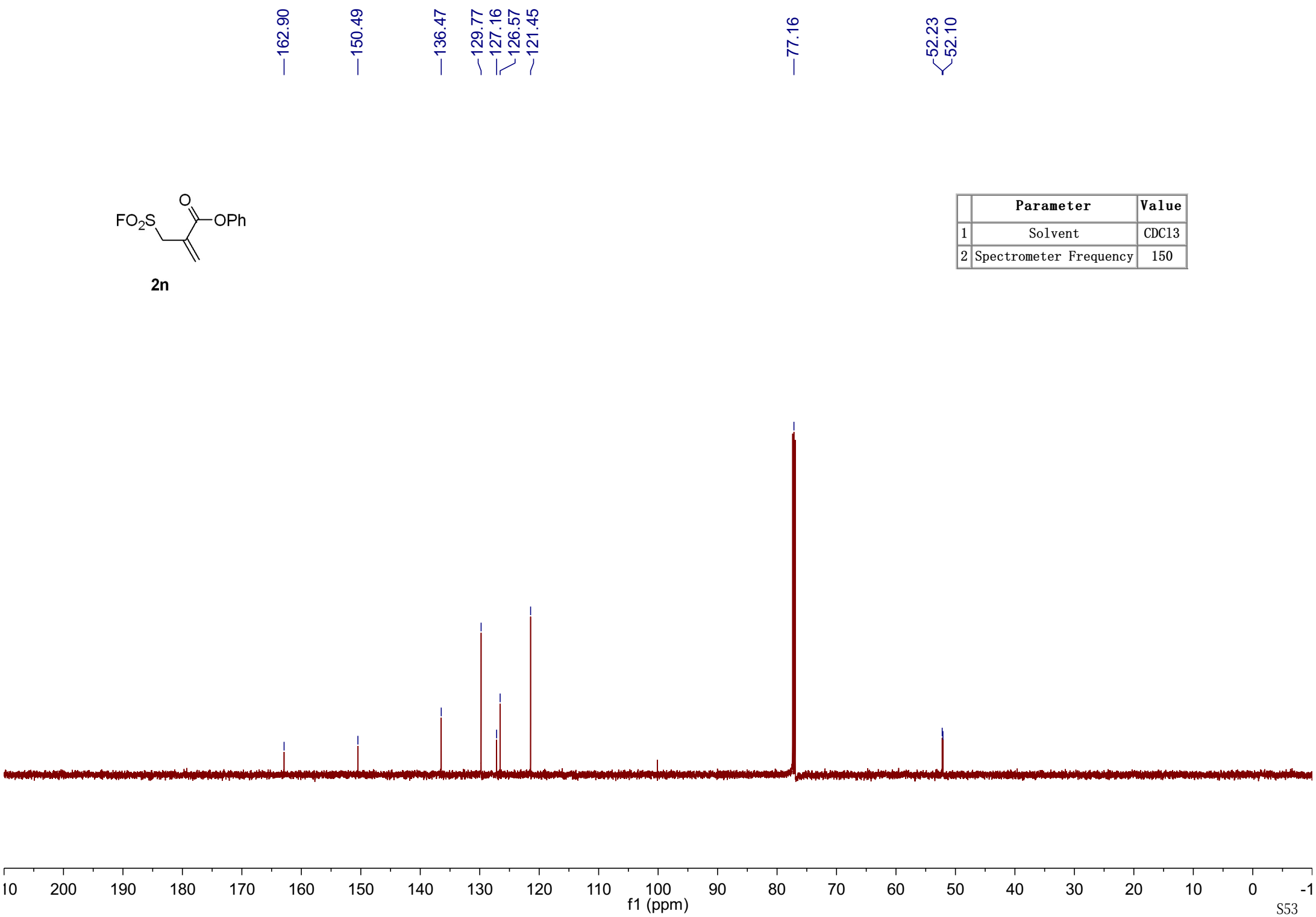
	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	565

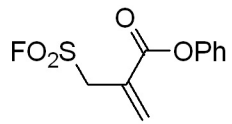


2n

	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	600

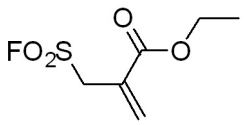



162.90
150.49
136.47
129.77
127.16
126.57
121.45
77.16
52.23
52.10
O
FO2S
OPh
2n
Parameter
Value
1
Solvent
CDCl3
2
Spectrometer Frequency
150
f1 (ppm)



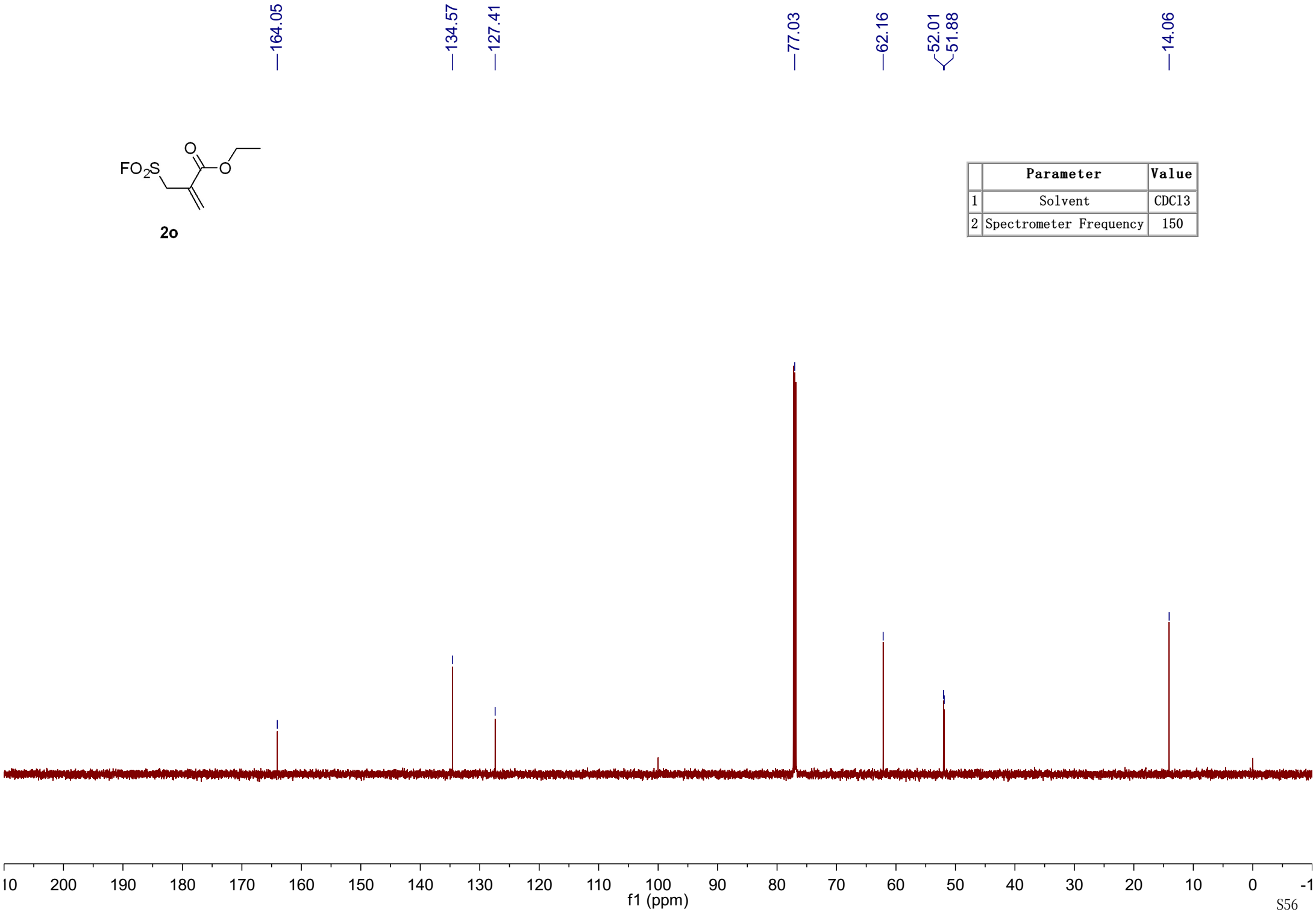
2n

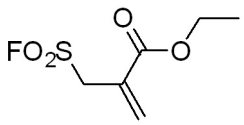
	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	565



2o

	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	600

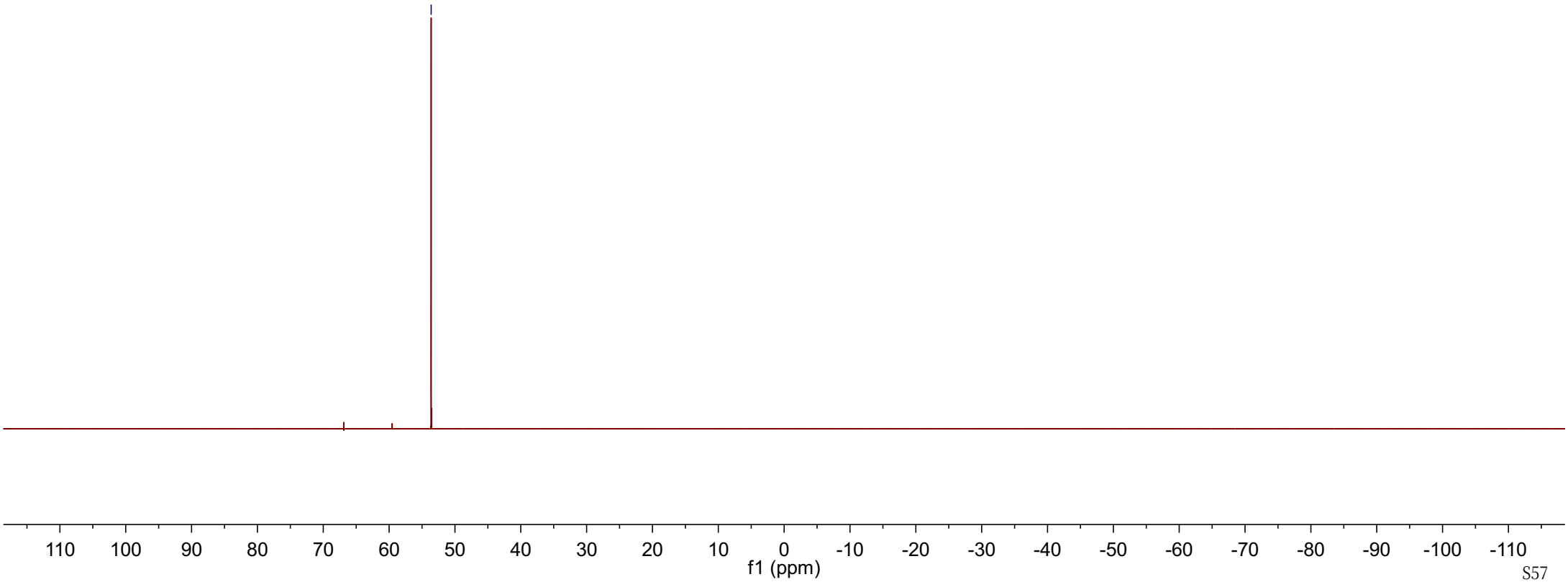

164.05
134.57
127.41
77.03
62.16
52.01
51.88
14.06
FO2S
O
O
2o
Parameter
Value
1
Solvent
CDCl3
2
Spectrometer Frequency
150
f1 (ppm)

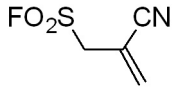


2o

53.61

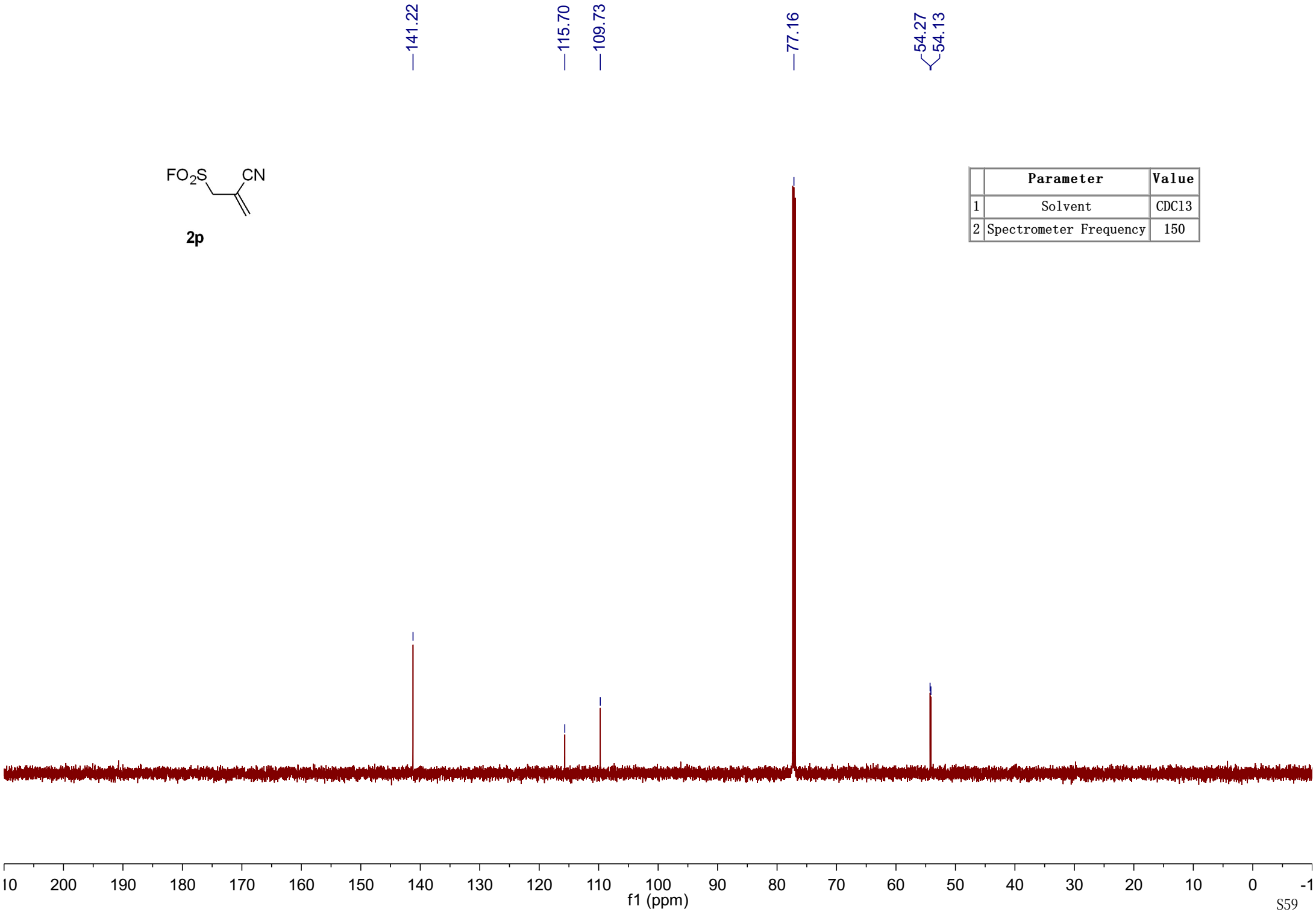
	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	565

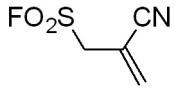




2p

	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	600

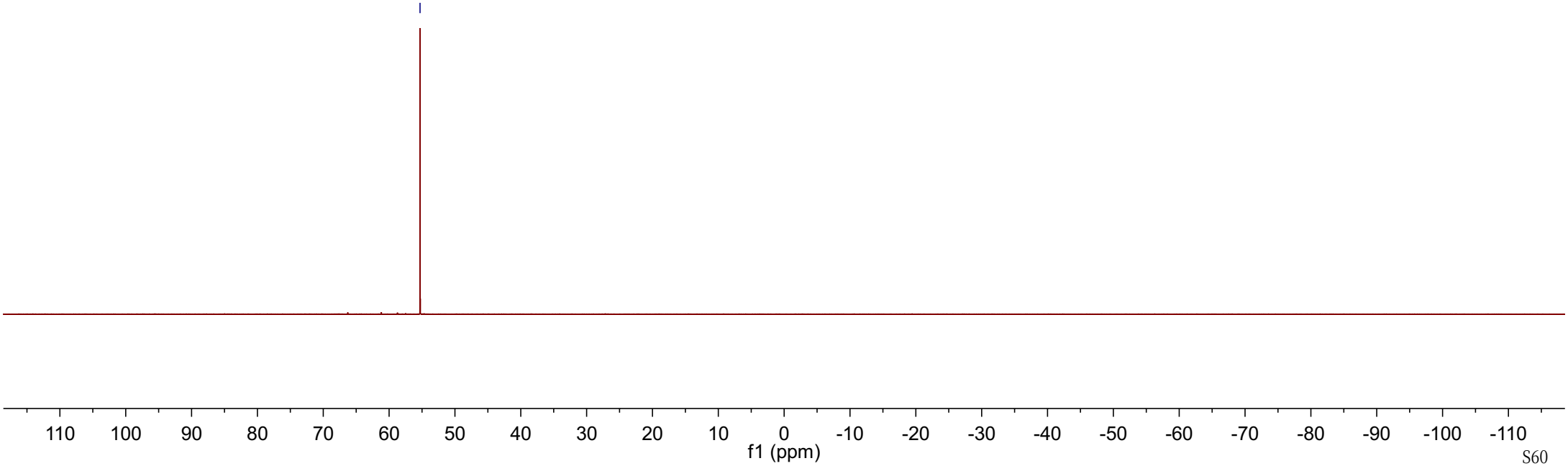

141.22
115.70
109.73
77.16
54.27
54.13
FO2S
CN
2p
Parameter
Value
1
Solvent
CDCl3
2
Spectrometer Frequency
150
f1 (ppm)

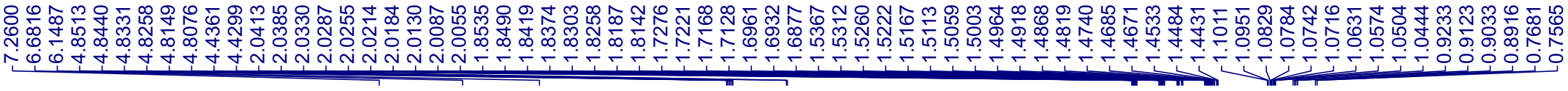


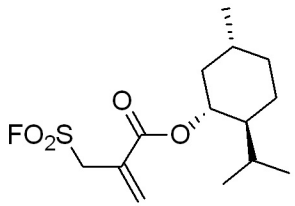
2p

55.30

	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	565

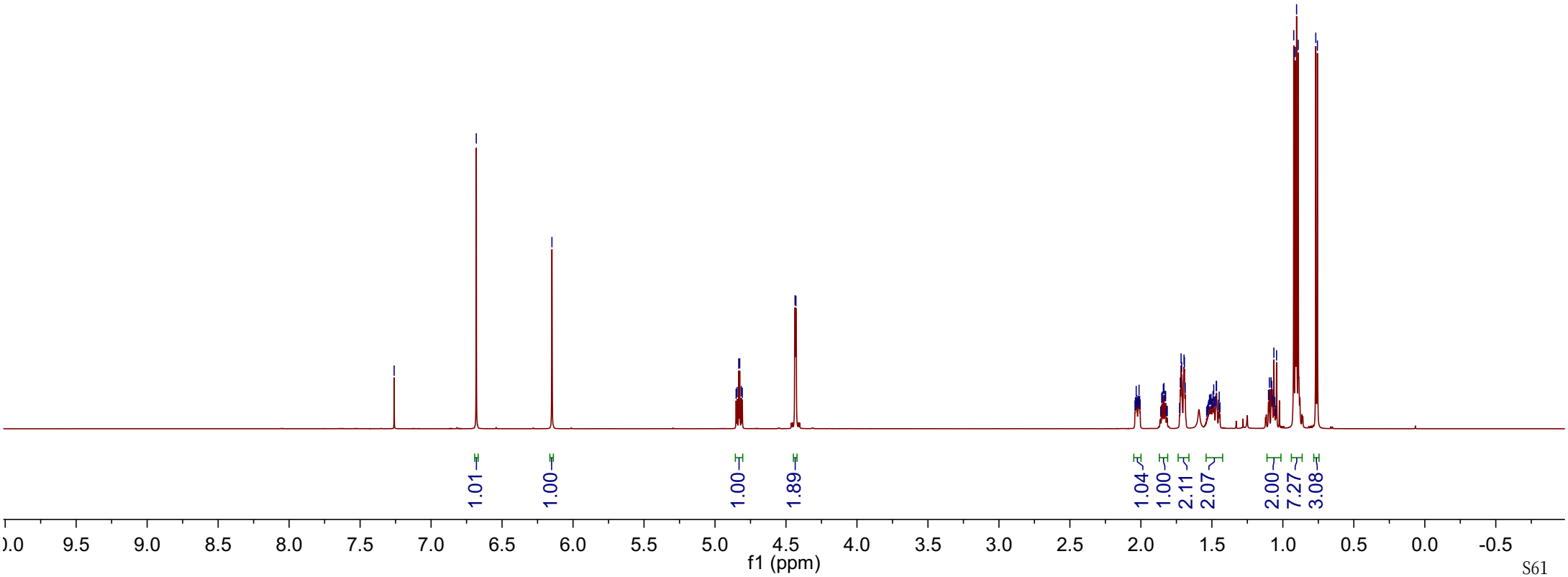


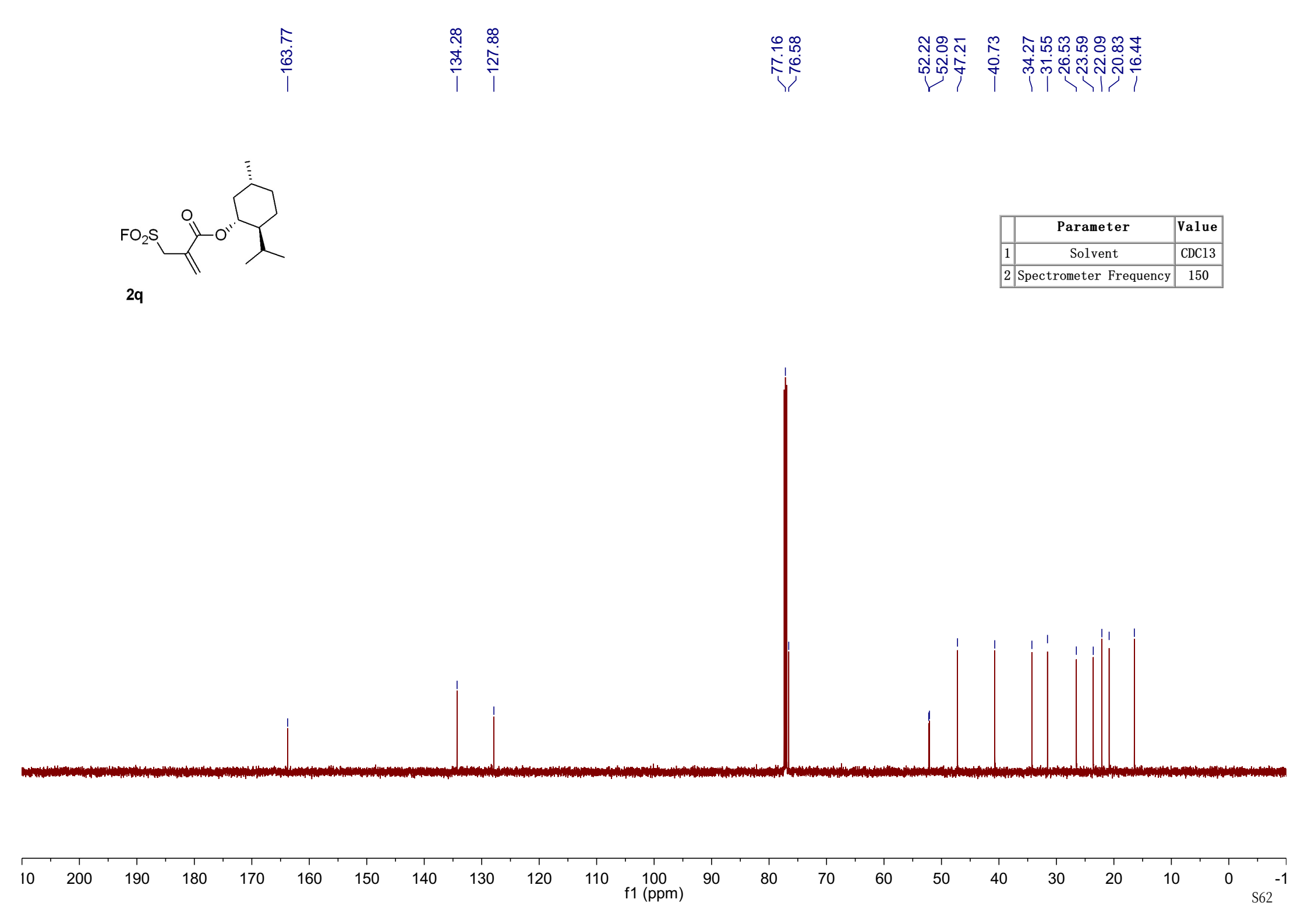


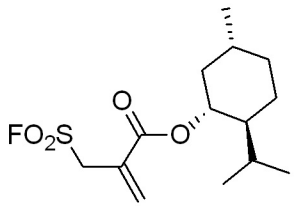


2q

	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	600




163.77
134.28
127.88
77.16
76.58
52.22
52.09
47.21
40.73
34.27
31.55
26.53
23.59
22.09
20.83
16.44
FO2S
O
O
2q
Parameter
Value
1
Solvent
CDCl3
2
Spectrometer Frequency
150
f1 (ppm)



2q

53.60

	Parameter	Value
1	Solvent	CDC13
2	Spectrometer Frequency	565